Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2022

***Supporting Information for：***

# Radical Modulated Regioselective Difunctionalization of Vinyl Enynes: Tunable Access to Naphthalen-1(2H)-ones and Tetra-substituted Allenes

Xiao-Yu Xie,[a] Yun-Fang Xu, [a] Yang Li, [a] Xiao-Dong Wang, [a] Jie Zhu,*[a] and Lei Wu, * [a,b]

[a] *Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210095, P. R. China. E-mail: zhujie@njau.edu.cn; rickywu@njau.edu.cn.*

[b] *College of Chemistry and Chemical Engineering, Xinjiang Agricultural University, Urumqi 830052, P. R. China*

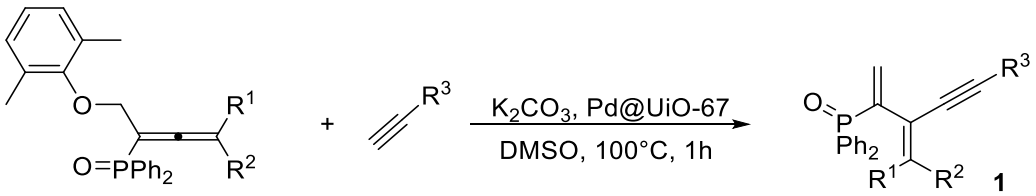
## ---*Table of Contents*---

## 1. General Information

Solvents and reagents were reagent grade and used without purification unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). All $^{1}$H-NMR (400 MHz or 600 MHz) spectra were recorded on a Bruker-DMX 400 or 600 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 Substrates Preparation

### 2.1 Synthesis of Vinyl Enynes

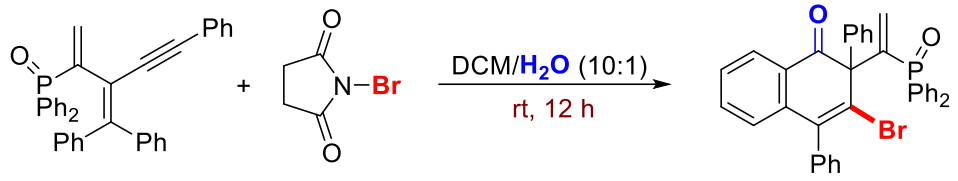



The vinyl enyne substrates (**1**) were prepared according to a procedure reported in our previous work, please see more details in: X.-D. Wang, J.-J. Wu, X. Sun, W.-C. Yang, J. Zhu, L. Wu, *Adv. Synth. Catal*. **2018**, *360*, 3518-3525.

To a 10 mL vial was added allenylphosphine oxides (0.3 mmol), alkynes (0.6 mmol), potassium carbonate (0.6 mmol), DMSO (3 mL) and Pd@UIO-67 (1 mol%, 30 mg), respectively. The reaction was then allowed to react at 100 $^{o}$C for a certain time until the complete consuming of starting materials monitored by TLC. The reaction mixture was extracted with EtOAc (1 mL×3). The combined organic extract was washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1) as the eluent to afford the vinyl enynes (**1**). After being finished, the purity and structure of compounds were confirmed by NMR.

## 3. General Procedures for the Radical Cascade Reactions

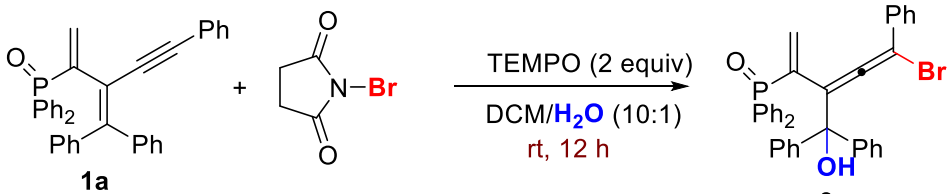
### 3.1 General Procedures for the Radical Reactions Accessing Naphthalen-1(2H)-ones




**1a** **2a**

To a 10 mL vial was added vinyl enyne (0.1 mmol, 1.0 equiv), NBS (0.4 mmol, 4.0 equiv), Then 2 mL solvent ($CH_2Cl_2$/water) (v:v=10:1) was injected into the vial. The reaction mixture was stirred at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (3:1) to afford the target product (**2a**).

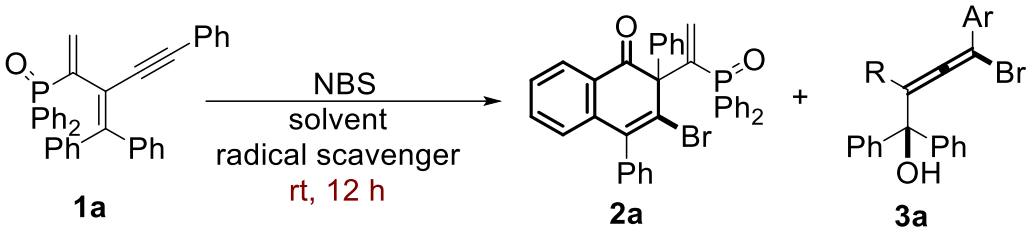
### 3.2 General Procedures for the Radical Reactions Accessing *Tetra*-substituted Allenes




**1a** **3a**

To a 10 mL vial was added vinyl enyne (0.1 mmol, 1.0 equiv), NBS (0.2 mmol, 2.0 equiv), TEMPO (0.2 mmol, 2.0 equiv). Then 2 mL solvent ($CH_2Cl_2$/water) (v:v=10:1) was injected into the vial. The reaction mixture was stirred at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (5:1) to afford the target product (**3a**).

## 4. Optimization of the Reaction Conditions[a]



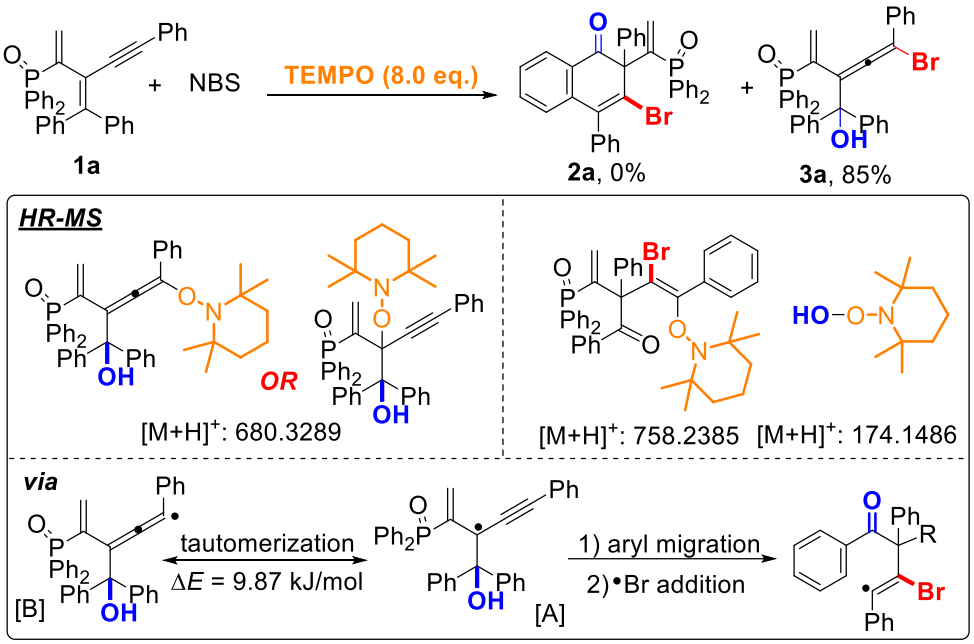

| entry | solvent | Radical Scavenger (2 equiv.) | yield (**2a**, %) | yield (**3a**, %) |
|---|---|---|---|---|
| 1[b] | DCM:$H_2O$ (10:1) | / | 31 | <5 |
| 2[c] | DCM:$H_2O$ (10:1) | / | 47 | <5 |
| **3** | **DCM:$H_2O$ (10:1)** | **/** | **84** | **0** |
| 4 | DCE:$H_2O$ (10:1) | / | 69 | 0 |
| 5 | $CH_3CN$:$H_2O$(10:1) | / | 10 | 0 |
| 6 | EtOAc:$H_2O$ (10:1) | / | 57 | 0 |
| 7 | MeOH:$H_2O$ (10:1) | / | 13 | 0 |
| 8 | THF:$H_2O$ (10:1) | / | 21 | 0 |
| 9 | DMF:$H_2O$ (10:1) | / | 0 | 0 |
| 10 | anhydrous DCM | / | 0 | 0 |
| 11 | DCM:$H_2O$ (20:1) | / | 65 | 0 |
| 12 | DCM:$H_2O$ (5:1) | / | 78 | 0 |
| 13[d] | DCM:$H_2O$ (10:1) | / | <5 | 0 |
| 14[e] | DCM:$H_2O$ (10:1) | / | 0 | 0 |
| 15 | DCM:$H_2O$ (10:1) | TEMPO | 59 | <5 |
| 16[b] | DCM:$H_2O$ (10:1) | TEMPO [f] | 12 | 64 |
| **17[b]** | **DCM:$H_2O$ (10:1)** | **TEMPO** | **0** | **93** |
| 18[b] | DCM:$H_2O$ (10:1) | 4-OH-TEMPO | 0 | 27 |
| 19[b] | DCM:$H_2O$ (10:1) | 4-oxo-TEMPO | 60 | <5 |
| 20[b] | DCM:$H_2O$ (10:1) | BHT | <5 | 48 |
| 21[b] | DCM:$H_2O$ (10:1) | AIBN | 48 | <5 |
| 22[g] | DCM:$H_2O$ (10:1) | / | 84 | 0 |
| 23[h] | DCM:$H_2O$ (10:1) | / | 57 | 0 |

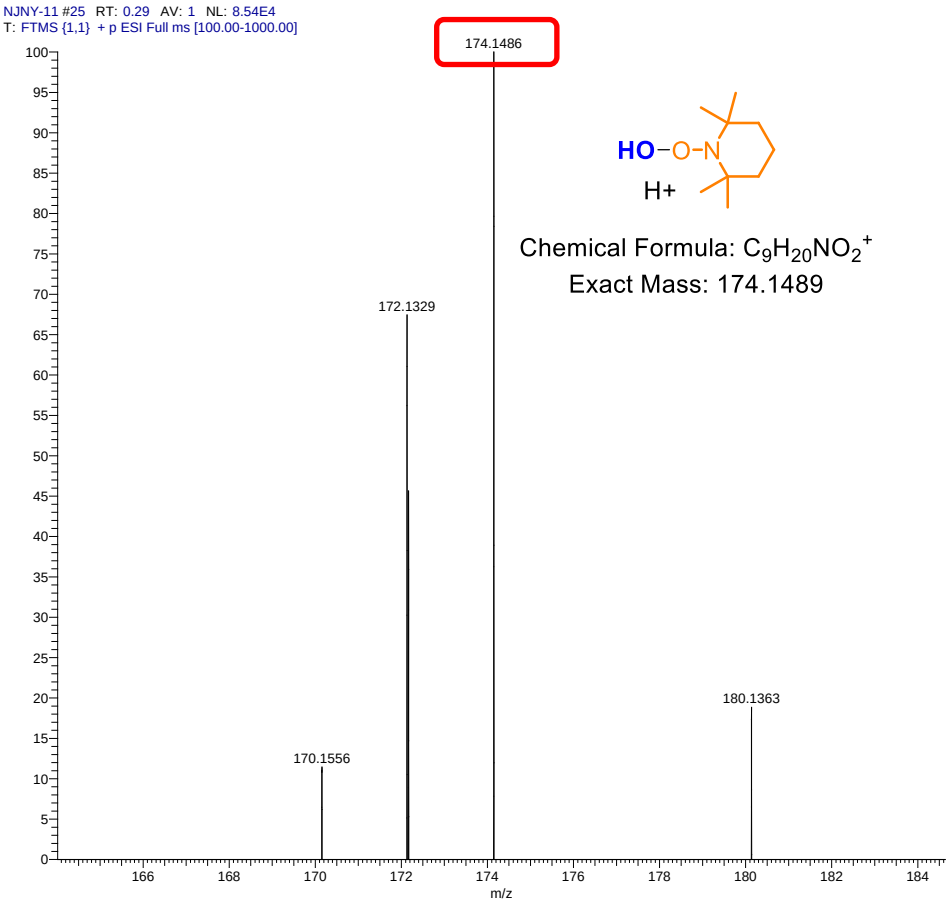
[a] Reaction conditions: 1,3-enyne (**1a**, 0.10 mmol), NBS (4 equiv.), solvent (2.0 mL), rt, 12 h, isolated yield. [b] 2 equiv. of NBS was used. [c] 3 equiv. of NBS was used. [d] DBNPA (4 equiv.) instead of NBS. [e] KBr (4 equiv.) instead of NBS. [f] 1 equiv. of TEMPO was used. [g] under $N_2$ atmosphere. [h] 8 h.

# 5. Mechanistic Studies

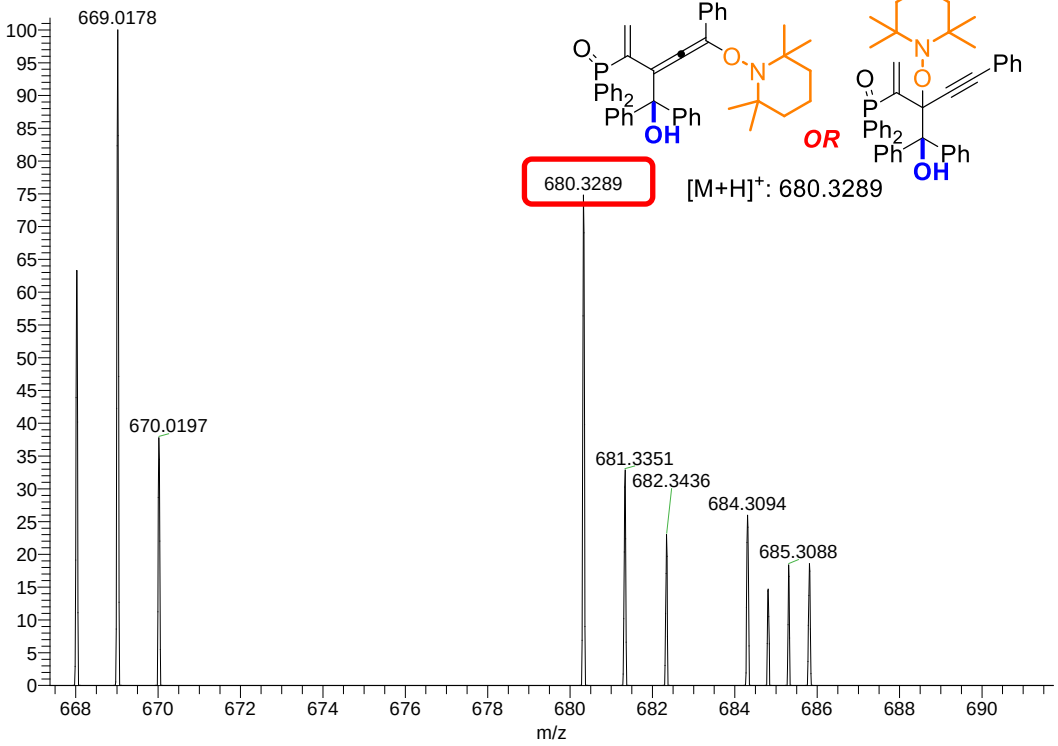
## 5.1 Radical Intermediates Capture

**eq.a: Radical Intermediates Capture by TEMPO**

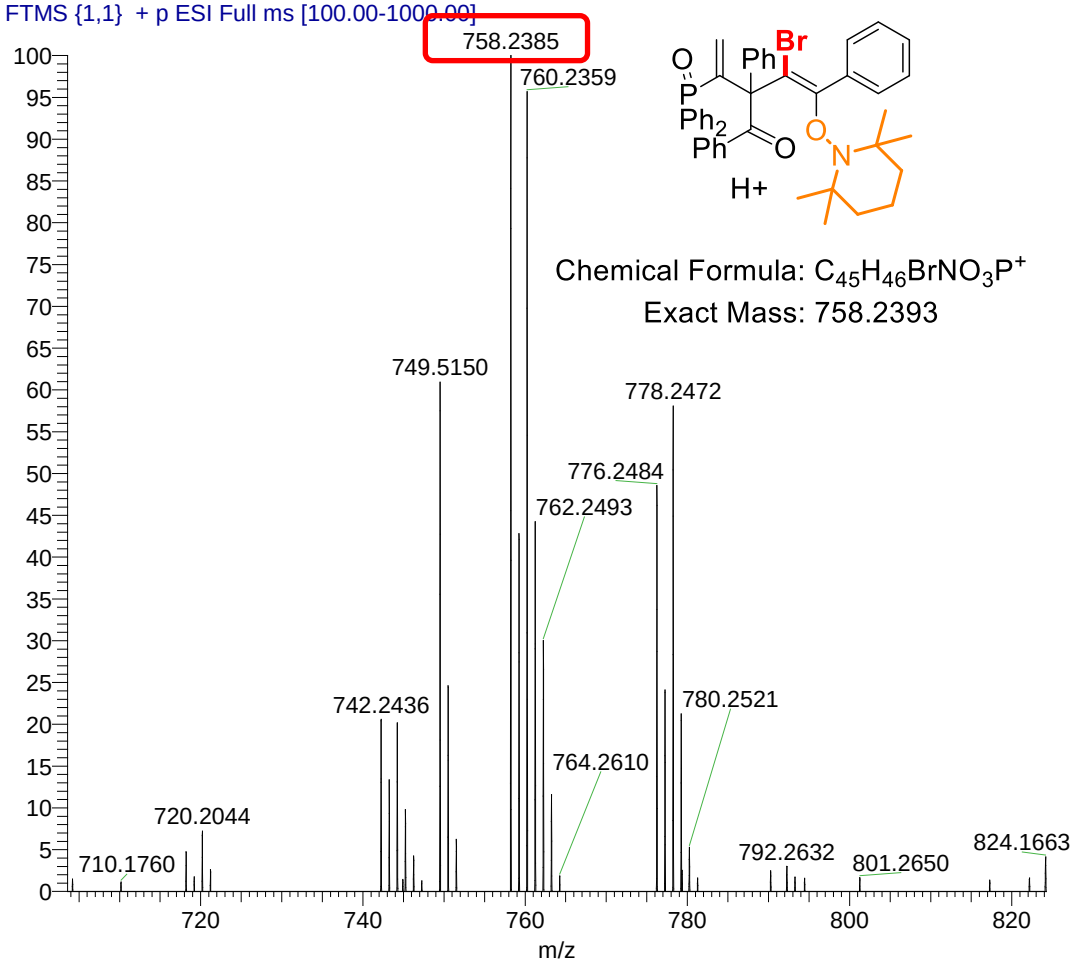


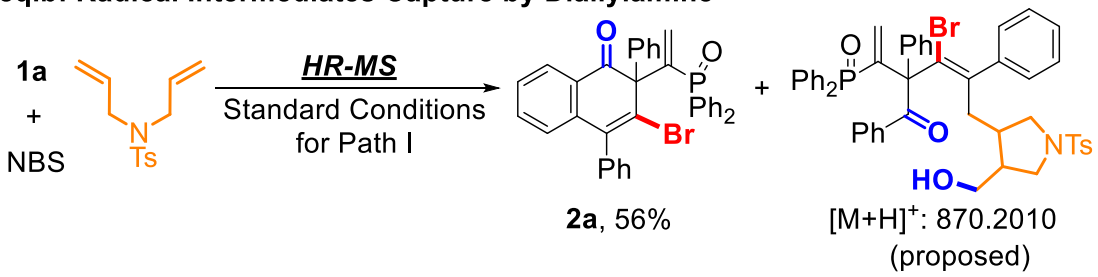
NJNY-11 #23 RT: 0.27 AV: 1 NL: 9.64E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]




NJNY-11 #45 RT: 0.51 AV: 1 NL: 3.86E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

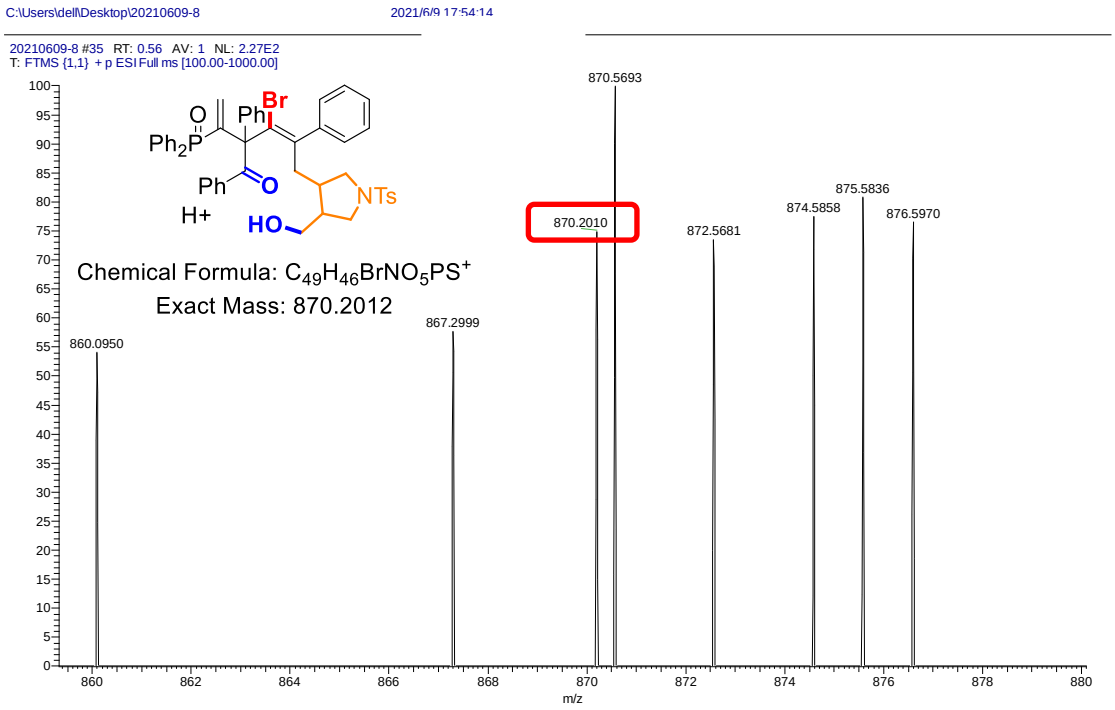


**eq.b: Radical Intermediates Capture by Diallylamine**

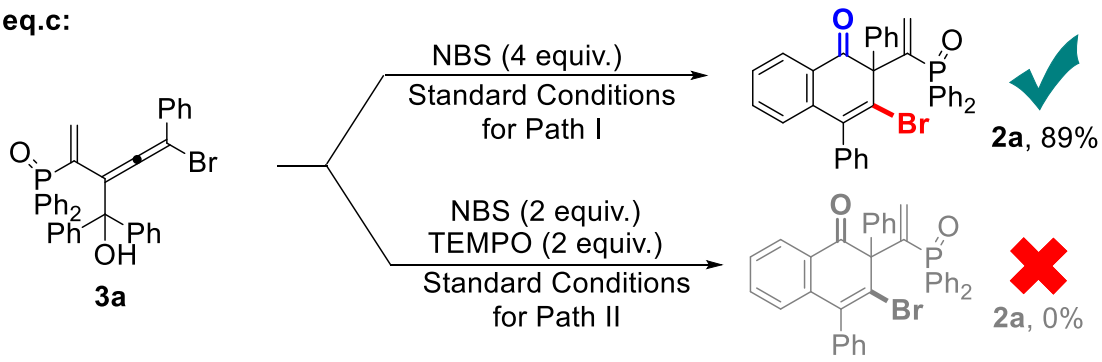


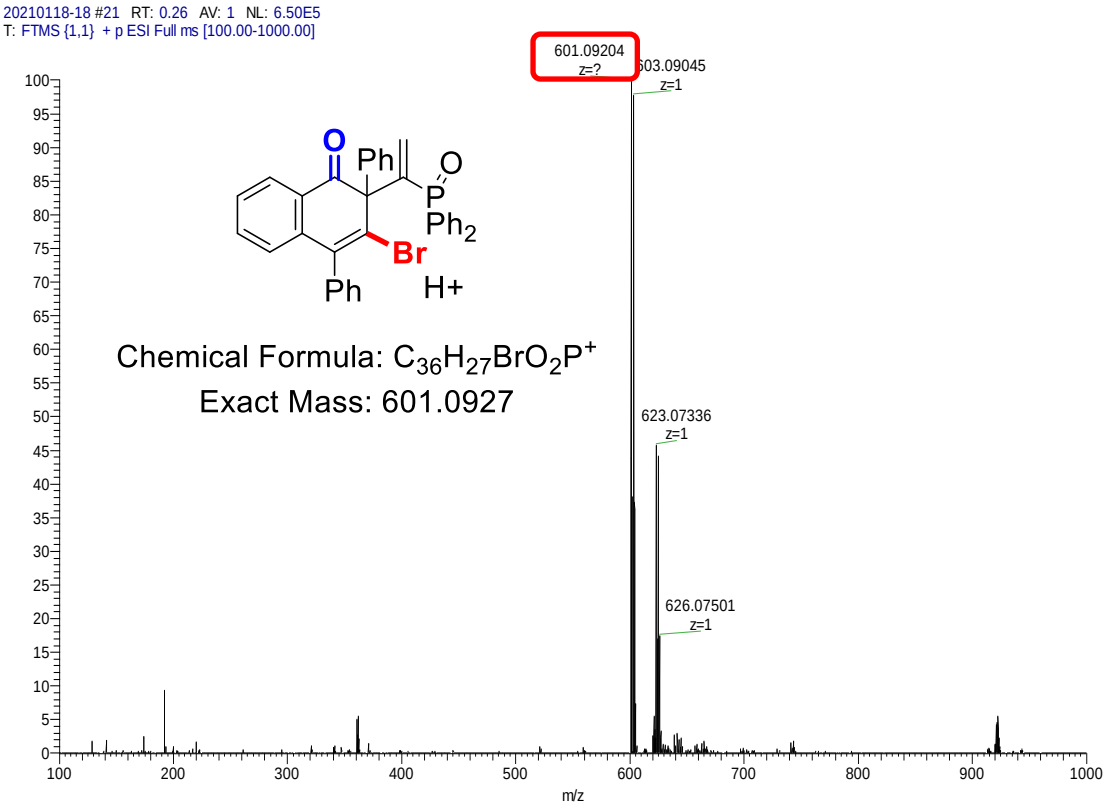

**2a**, 56%

$[M+H]^+$: 870.2010
(proposed)

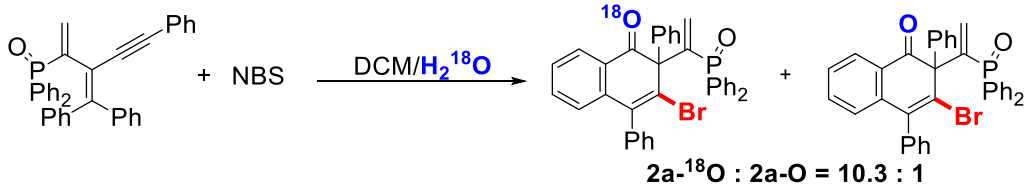



**eq.c:**

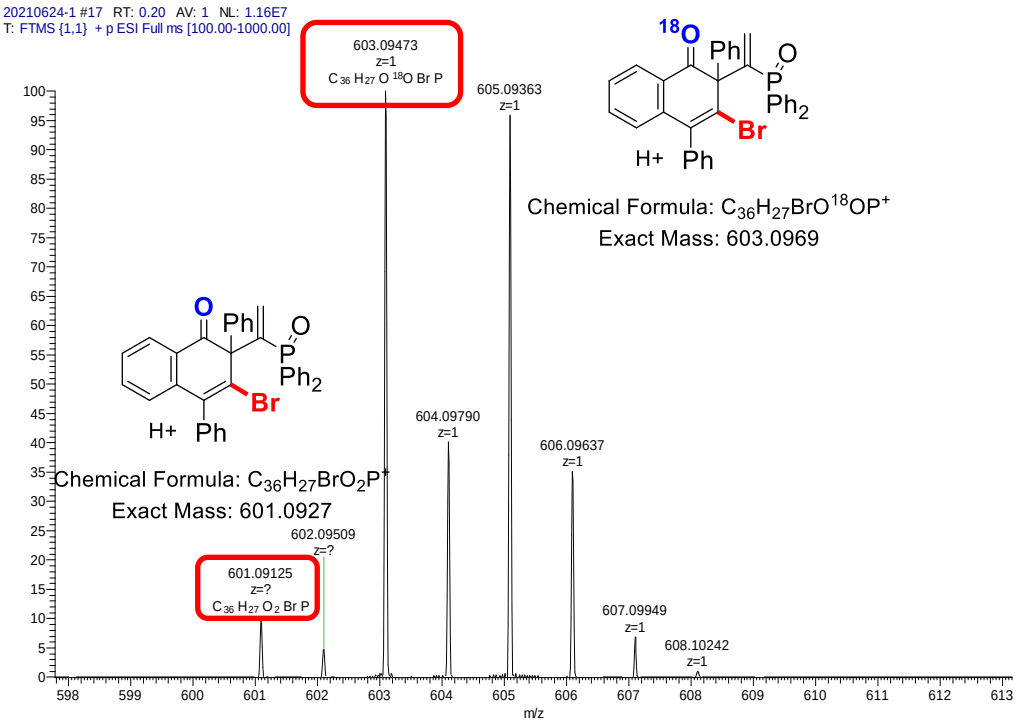





**eq.d: Oxygen Isotopic Labelling**

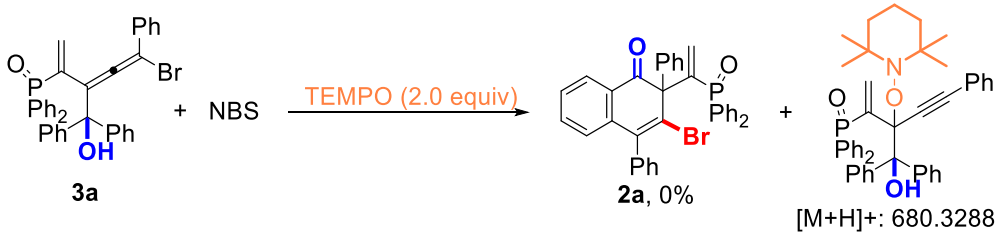


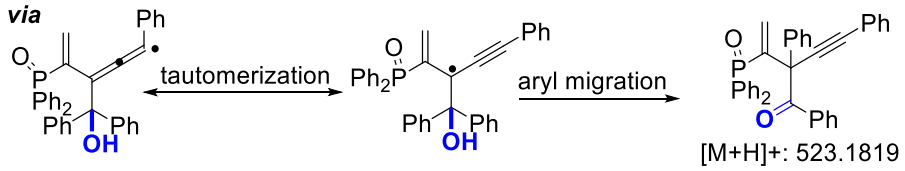

*Detected by HR-MS*

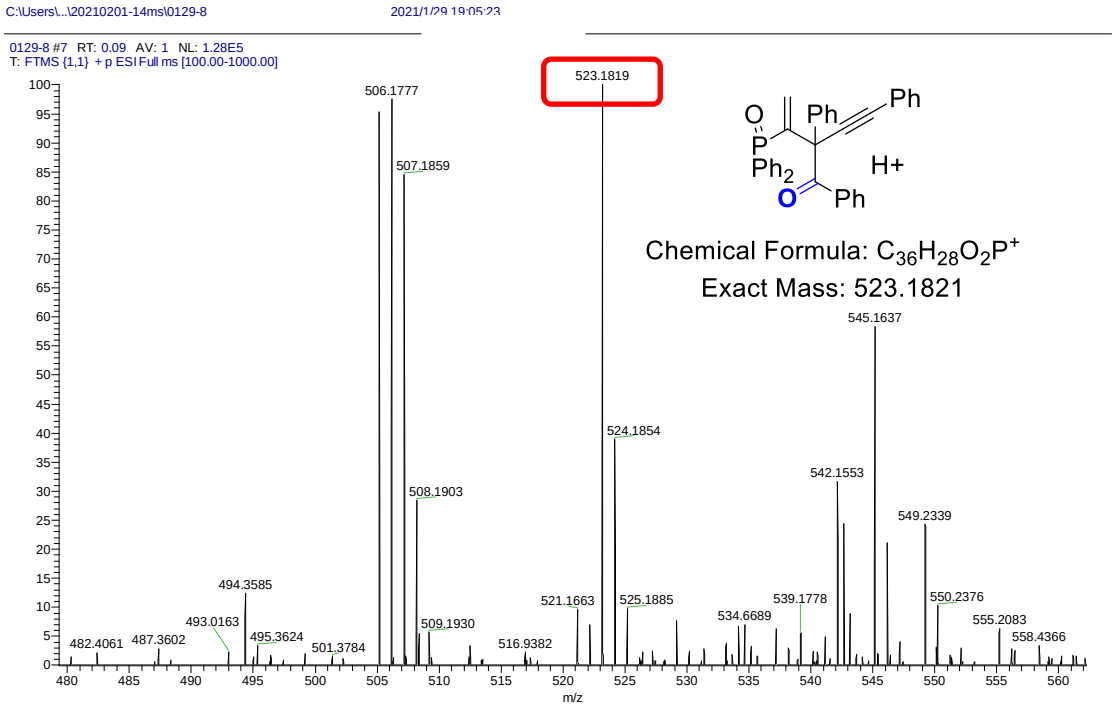


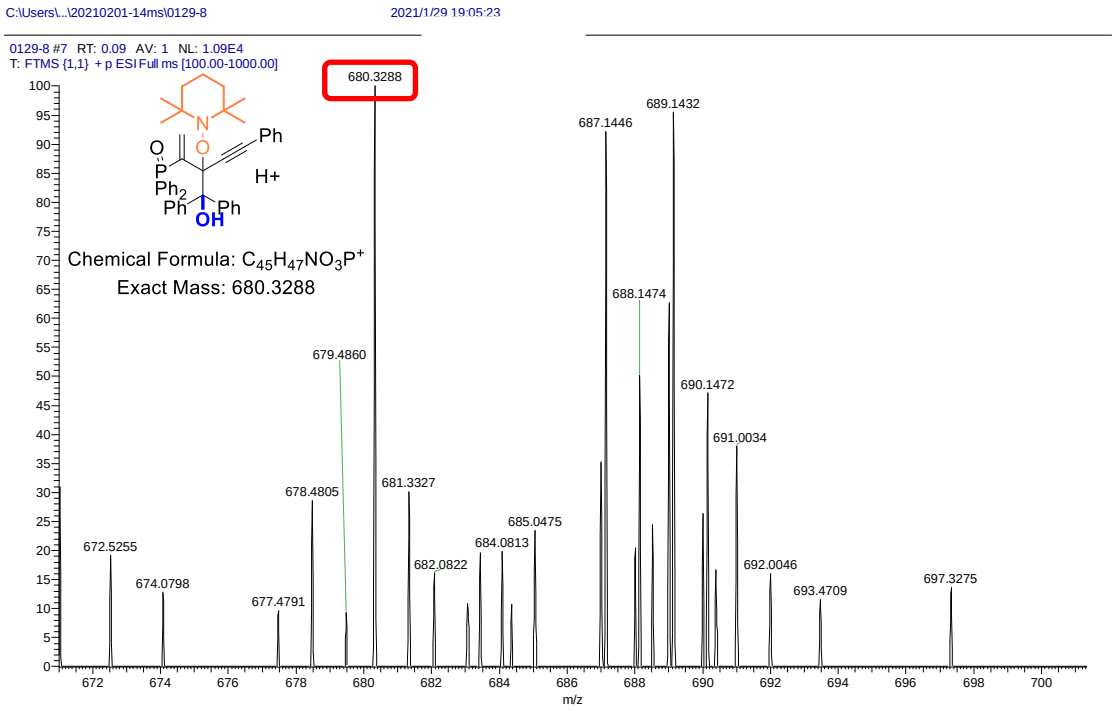
| m/z | Intensity | Relative | Charge | Composition |
|---|---|---|---|---|
| 524.17645 | 554913.1 | 4.66 | 1.00 | |
| 601.09125 | 1153936.8 | 9.68 | 0.00 | $C_{36}H_{27}O_2BrP$ |
| 602.09509 | 564638.8 | 4.74 | 0.00 | |
| 603.09473 | 11920732.0 | 100.00 | 1.00 | $C_{36}H_{27}O\,^{[18]}OBrP$ |
| 604.09790 | 4715449.0 | 39.56 | 1.00 | |
| 605.09363 | 11170870.0 | 93.71 | 1.00 | |
| 606.09637 | 4184530.0 | 35.10 | 1.00 | |
| 607.09949 | 834745.1 | 7.00 | 1.00 | |
| 622.06744 | 421121.2 | 3.53 | 0.00 | $C_{38}H_{24}O_2BrP$ |
| 623.06757 | 808321.2 | 6.78 | 0.00 | $C_{38}H_{23}O\,^{[18]}OBrP$ |
| 623.56873 | 568198.1 | 4.77 | 0.00 | |
| 624.06787 | 447473.8 | 3.75 | 2.00 | |
| 625.07581 | 457593.3 | 3.84 | 2.00 | |
| 923.11090 | 392496.2 | 3.29 | 0.00 | |
| 923.61267 | 445367.7 | 3.74 | 2.00 | |
| 924.11169 | 947320.6 | 7.95 | 2.00 | |
| 924.61279 | 926225.4 | 7.77 | 2.00 | |
| 925.11206 | 1044060.2 | 8.76 | 2.00 | |
| 925.61249 | 831069.7 | 6.97 | 2.00 | |
| 926.11237 | 651229.6 | 5.46 | 2.00 | |

**eq.e: Radical Intermediates Capture by TEMPO**

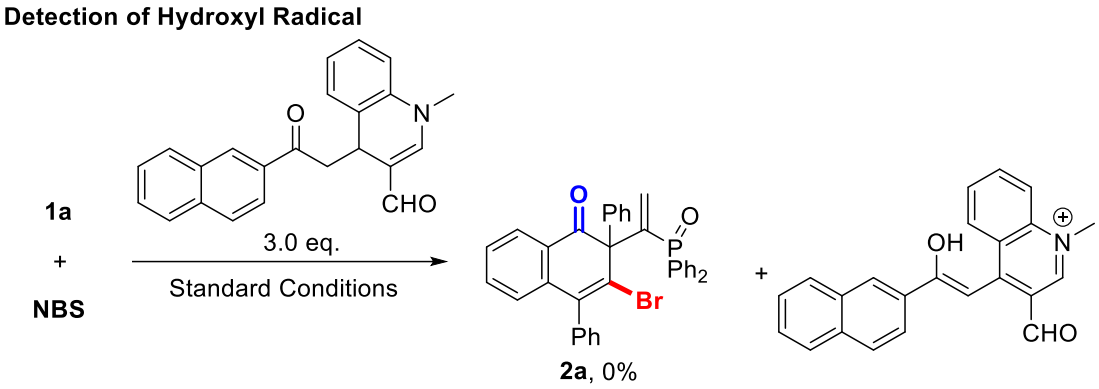


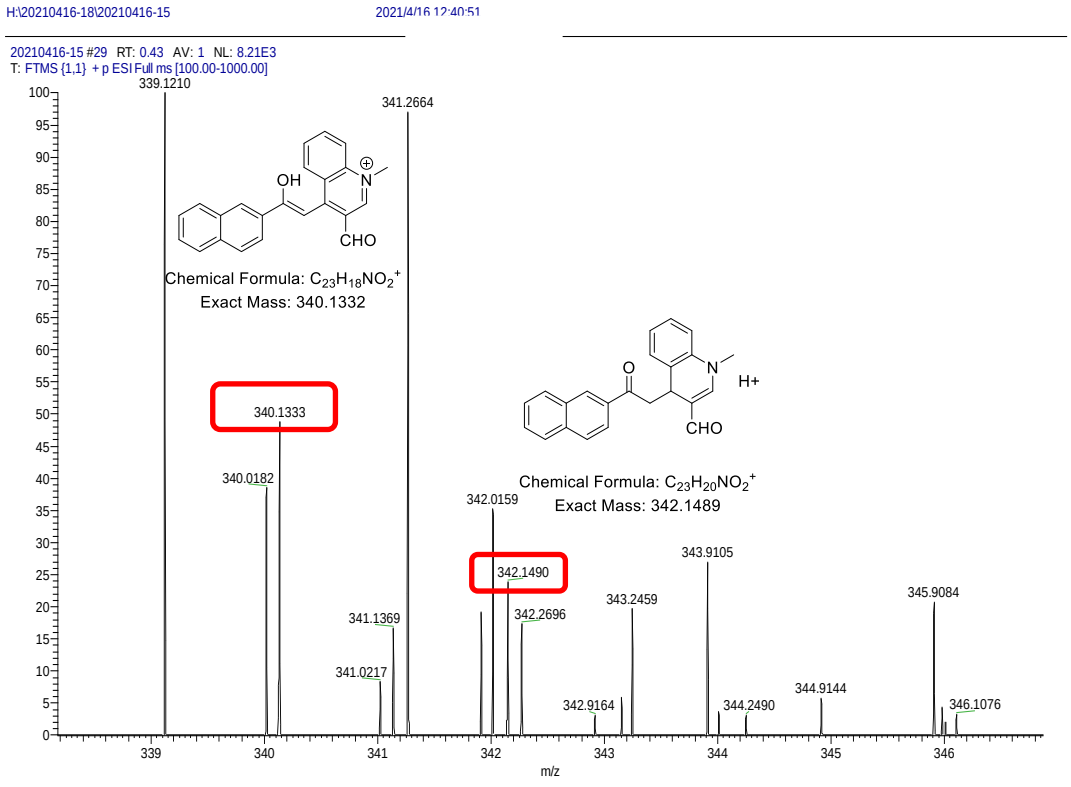

C:\Users\...\20210201-14ms\0129-8
2021/1/29 19:05:23
0129-8 #7 RT: 0.09 AV: 1 NL: 1.28E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
523.1819
506.1777
507.1859
508.1903
524.1854
545.1637
542.1553
549.2339
550.2376
555.2083
558.4366
539.1778
534.6689
525.1885
521.1663
509.1930
516.9382
501.3784
495.3624
494.3585
493.0163
487.3602
482.4061
O
Ph
Ph
P
Ph2
H+
O
Ph
Chemical Formula: C36H28O2P+
Exact Mass: 523.1821
m/z

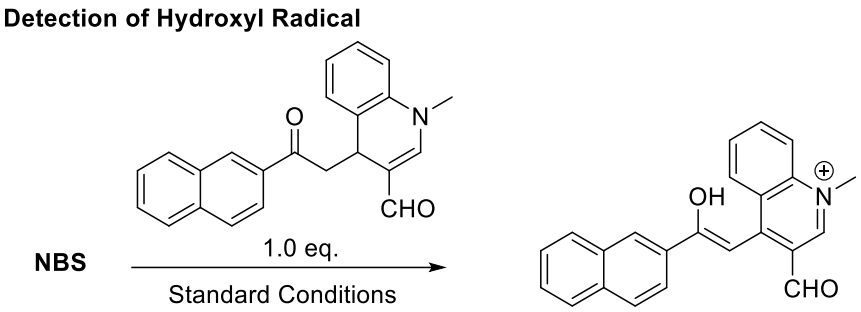

C:\Users\...\20210201-14ms\0129-8
2021/1/29 19:05:23
0129-8 #7 RT: 0.09 AV: 1 NL: 1.09E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
680.3288
689.1432
687.1446
688.1474
679.4860
690.1472
691.0034
681.3327
678.4805
685.0475
684.0813
682.0822
672.5255
674.0798
677.4791
692.0046
693.4709
697.3275
N
O
O
Ph
P
Ph2
H+
Ph
Ph
OH
Chemical Formula: C45H47NO3P+
Exact Mass: 680.3288
m/z

## 5.2 Fluorescence Sensing for the Detection of •OH




According to the Liu's work, dihydroquinoline was used as probe to detect the hydroxyl radicals. And no desired product of **2a** was detected. The HR-MS showed that the product caused by the hydroxyl radicals was detected. Standard condition: **1a** (0.1 mmol), NBS (0.4 mmol), DCM/$H_2O$ (10:1, 2 mL). Reference: Wu, Y.; Huang, W.; Peng, D.; Huang, X.; Gu, S.; Wu, S.; Deng, T.; Liu, F. Synthesis of Dihydroquinolines as Scaffolds for Fluorescence Sensing of Hydroxyl Radical. *Org. Lett*. **2021**, *23*, 135-139.






According to the Liu's work, dihydroquinoline was used as probe to detect the hydroxyl radicals. The fluorescence image demonstrated obvious color change due to the generation of •OH, the HR-MS showed that the product caused by the hydroxyl radicals was detected.

Standard condition: **NBS** (0.8 mmol), DCM/$H_2O$ (10:1, 2 mL).

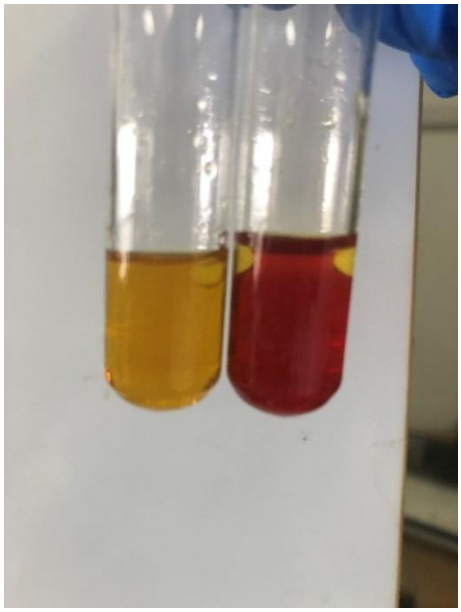
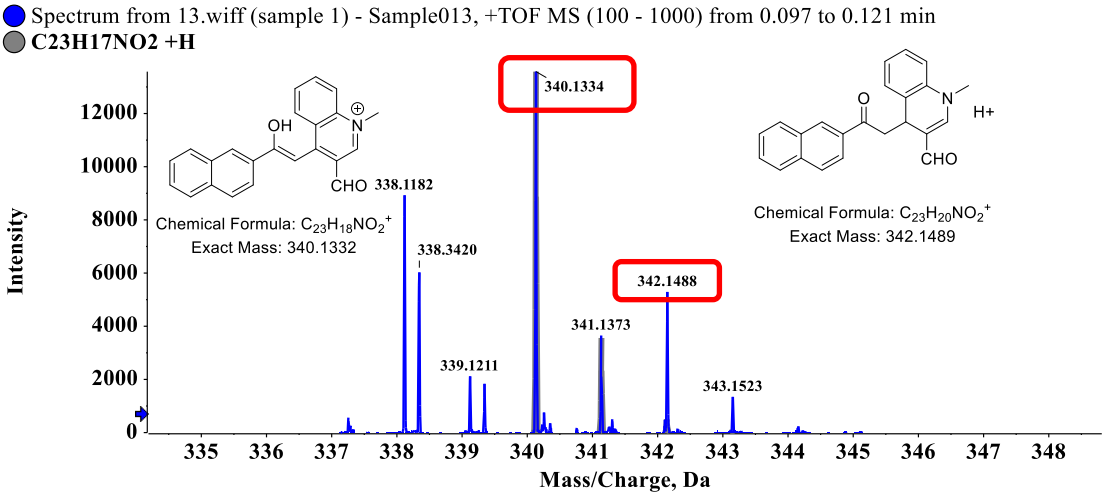
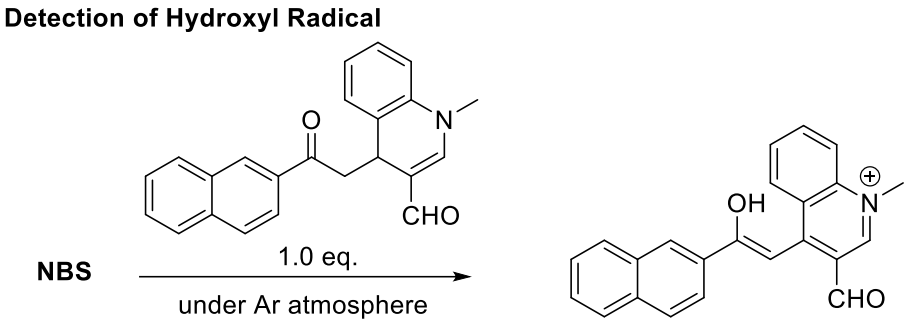


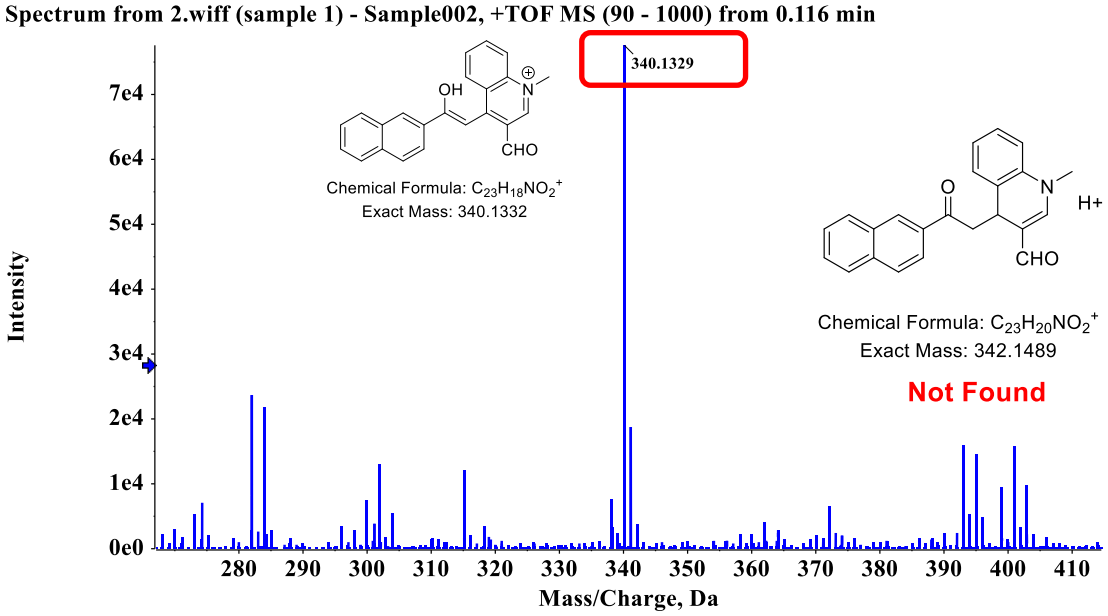
**Figure S1.** The fluorescence image of dihydroquinoline probe added after the completion of the reaction (left) and the standard condition with dihydroquinoline probe added (right).



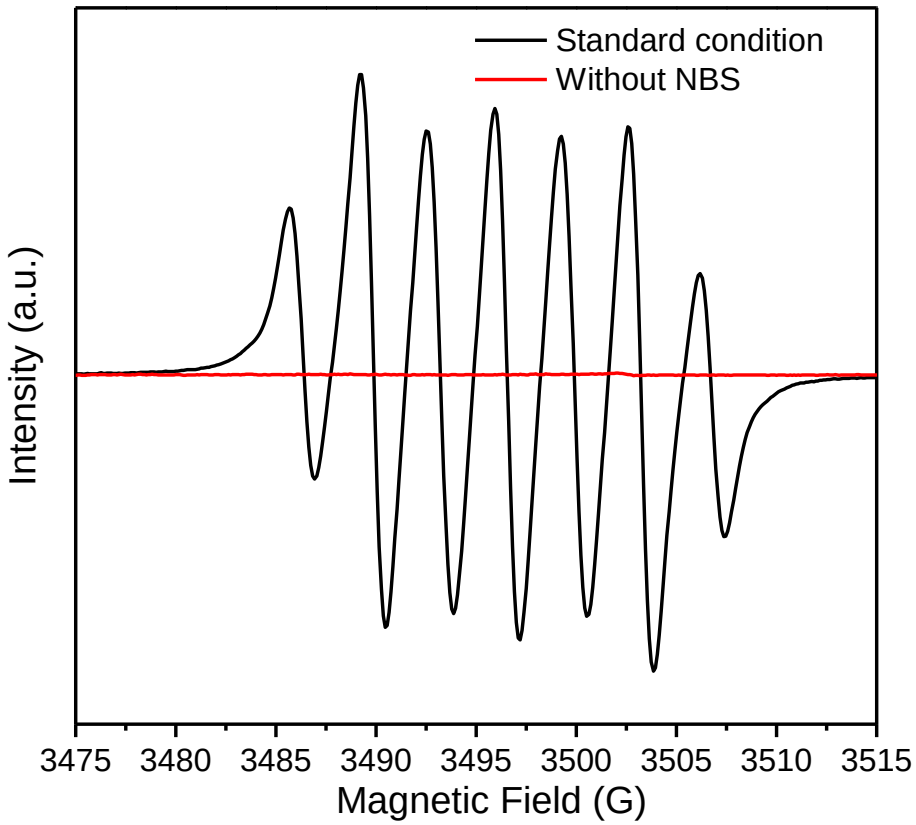

The fluorescence sensing under Ar atmosphere was further performed to rule out the influence of $O_2$. The HR-MS showed that the product caused by the hydroxyl radicals was detected which confirmed that the •OH radical was produced from water.

Standard condition: **NBS** (0.4 mmol), DCM/$H_2O$ (10:1, 2 mL) at room temperature under argon atmosphere.



### 5.3 EPR Analysis

The EPR signals were acquired at 60 seconds after mixing the reactants and the radical trapping agents. When using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as capture agents, the DMPO trapped radicals were detected, while no signal was observed without NBS. Standard condition: DMPO (0.5 mmol), NBS (0.8 mmol), DCM/$H_2O$ (10:1, 2 mL) at room temperature. This signal may be caused by the co-existence of hydroxyl radical, bromine radical and amide radical.

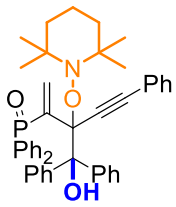


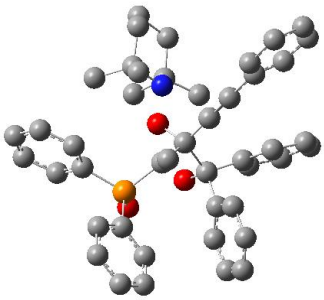
## 5.4 Structure Simulation for [A]-TEMPO and [B]-TEMPO

Structure Simulation were carried out on Gaussian 09 package with opt b3lyp method at 6-31G(d) basis set.

Reference: 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

**[A]-TEMPO**:



Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.451476 | 0.186357 | -0.796780 |
| 2 | 6 | 0 | -1.022554 | 0.195561 | -0.647261 |
| 3 | 6 | 0 | -1.085797 | 0.416820 | -1.965799 |
| 4 | 1 | 0 | -0.188443 | 0.548790 | -2.562463 |
| 5 | 1 | 0 | -2.032381 | 0.498613 | -2.491143 |
| 6 | 6 | 0 | 0.405301 | 1.370708 | 1.268426 |
| 7 | 6 | 0 | -0.351608 | 2.647852 | 0.802564 |
| 8 | 6 | 0 | -0.215723 | 3.213131 | -0.474104 |
| 9 | 6 | 0 | -1.077908 | 3.364163 | 1.764860 |
| 10 | 6 | 0 | -0.794423 | 4.444737 | -0.780693 |

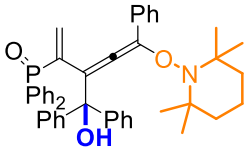
| | | | | | |
|---|---|---|---|---|---|
| 11 | 1 | 0 | 0.349814 | 2.696065 | -1.241223 |
| 12 | 6 | 0 | -1.650914 | 4.601065 | 1.462889 |
| 13 | 1 | 0 | -1.176484 | 2.946898 | 2.759888 |
| 14 | 6 | 0 | -1.513161 | 5.148891 | 0.186955 |
| 15 | 1 | 0 | -0.675694 | 4.856805 | -1.779683 |
| 16 | 1 | 0 | -2.201210 | 5.137502 | 2.232031 |
| 17 | 1 | 0 | -1.953815 | 6.113846 | -0.050142 |
| 18 | 6 | 0 | 1.812975 | 1.924472 | 1.643097 |
| 19 | 6 | 0 | 2.153472 | 2.028118 | 3.000936 |
| 20 | 6 | 0 | 2.692237 | 2.499799 | 0.713569 |
| 21 | 6 | 0 | 3.348613 | 2.622023 | 3.407513 |
| 22 | 1 | 0 | 1.469824 | 1.638029 | 3.743366 |
| 23 | 6 | 0 | 3.892300 | 3.087925 | 1.116912 |
| 24 | 1 | 0 | 2.443885 | 2.516605 | -0.337820 |
| 25 | 6 | 0 | 4.234486 | 3.145973 | 2.467563 |
| 26 | 1 | 0 | 3.580857 | 2.677329 | 4.468253 |
| 27 | 1 | 0 | 4.549731 | 3.519037 | 0.365750 |
| 28 | 1 | 0 | 5.165849 | 3.609725 | 2.782253 |
| 29 | 8 | 0 | -0.141269 | 0.872793 | 2.453905 |
| 30 | 1 | 0 | -1.078190 | 0.593982 | 2.282727 |
| 31 | 15 | 0 | -2.642205 | -0.068749 | 0.218696 |
| 32 | 6 | 0 | -3.874983 | 0.963054 | -0.668291 |
| 33 | 6 | 0 | -3.960274 | 2.313374 | -0.294532 |
| 34 | 6 | 0 | -4.753570 | 0.467977 | -1.643849 |
| 35 | 6 | 0 | -4.892011 | 3.153783 | -0.901385 |
| 36 | 1 | 0 | -3.304700 | 2.703158 | 0.475473 |
| 37 | 6 | 0 | -5.684309 | 1.313883 | -2.249839 |
| 38 | 1 | 0 | -4.730176 | -0.579597 | -1.924146 |
| 39 | 6 | 0 | -5.753312 | 2.657985 | -1.882127 |
| 40 | 1 | 0 | -4.943248 | 4.197434 | -0.604001 |
| 41 | 1 | 0 | -6.360646 | 0.917169 | -3.002316 |
| 42 | 1 | 0 | -6.480555 | 3.314519 | -2.352661 |
| 43 | 6 | 0 | -3.194296 | -1.793209 | -0.038183 |
| 44 | 6 | 0 | -3.775524 | -2.426172 | 1.069782 |
| 45 | 6 | 0 | -3.140861 | -2.466295 | -1.267137 |
| 46 | 6 | 0 | -4.299387 | -3.713919 | 0.946371 |
| 47 | 1 | 0 | -3.802205 | -1.903001 | 2.020544 |
| 48 | 6 | 0 | -3.672673 | -3.750174 | -1.388615 |
| 49 | 1 | 0 | -2.674631 | -1.997392 | -2.128709 |
| 50 | 6 | 0 | -4.253016 | -4.374722 | -0.282107 |
| 51 | 1 | 0 | -4.743380 | -4.200163 | 1.810705 |
| 52 | 1 | 0 | -3.626777 | -4.265117 | -2.344433 |
| 53 | 1 | 0 | -4.663473 | -5.376418 | -0.377556 |
| 54 | 8 | 0 | -2.607540 | 0.275382 | 1.693245 |

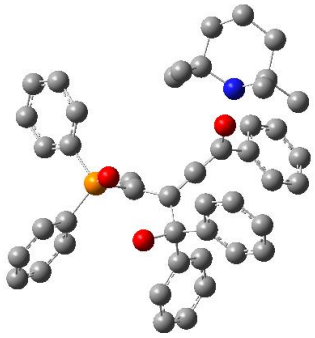
| | | | | | |
|---|---|---|---|---|---|
| 55 | 6 | 0 | 2.367020 | 0.242142 | -1.591057 |
| 56 | 6 | 0 | 3.485842 | 0.321627 | -2.475792 |
| 57 | 6 | 0 | 3.336498 | 0.072030 | -3.853863 |
| 58 | 6 | 0 | 4.761723 | 0.649744 | -1.975405 |
| 59 | 6 | 0 | 4.434643 | 0.150702 | -4.706564 |
| 60 | 1 | 0 | 2.355953 | -0.184618 | -4.243782 |
| 61 | 6 | 0 | 5.854172 | 0.724572 | -2.835703 |
| 62 | 1 | 0 | 4.877248 | 0.845258 | -0.914079 |
| 63 | 6 | 0 | 5.695624 | 0.476586 | -4.201521 |
| 64 | 1 | 0 | 4.306533 | -0.044270 | -5.767900 |
| 65 | 1 | 0 | 6.833547 | 0.977457 | -2.438569 |
| 66 | 1 | 0 | 6.550821 | 0.536336 | -4.869174 |
| 67 | 6 | 0 | 0.332420 | 0.123333 | 0.132961 |
| 68 | 8 | 0 | 0.263937 | -1.173986 | 0.823369 |
| 69 | 6 | 0 | 1.953091 | -2.415643 | 1.994549 |
| 70 | 6 | 0 | 0.895235 | -3.287479 | -0.175727 |
| 71 | 6 | 0 | 3.097870 | -3.438570 | 1.793417 |
| 72 | 6 | 0 | 2.093770 | -4.260183 | -0.315035 |
| 73 | 6 | 0 | 2.696383 | -4.689202 | 1.018673 |
| 74 | 1 | 0 | 3.487926 | -3.696237 | 2.786027 |
| 75 | 1 | 0 | 3.910975 | -2.935232 | 1.253091 |
| 76 | 1 | 0 | 1.750139 | -5.128805 | -0.891443 |
| 77 | 1 | 0 | 2.871523 | -3.766622 | -0.912847 |
| 78 | 1 | 0 | 3.572686 | -5.328118 | 0.849547 |
| 79 | 1 | 0 | 1.983765 | -5.292694 | 1.594351 |
| 80 | 6 | 0 | 2.590397 | -1.134669 | 2.535795 |
| 81 | 1 | 0 | 3.208852 | -0.650137 | 1.775226 |
| 82 | 1 | 0 | 1.821272 | -0.441877 | 2.864613 |
| 83 | 1 | 0 | 3.225235 | -1.373739 | 3.397615 |
| 84 | 6 | 0 | 0.936131 | -2.902358 | 3.053927 |
| 85 | 1 | 0 | 0.057384 | -2.252596 | 3.055910 |
| 86 | 1 | 0 | 0.610613 | -3.934472 | 2.912234 |
| 87 | 1 | 0 | 1.398956 | -2.840723 | 4.045985 |
| 88 | 6 | 0 | -0.335437 | -4.031087 | 0.393632 |
| 89 | 1 | 0 | -0.080302 | -4.721867 | 1.199421 |
| 90 | 1 | 0 | -1.076254 | -3.325458 | 0.769606 |
| 91 | 1 | 0 | -0.808069 | -4.621245 | -0.398912 |
| 92 | 6 | 0 | 0.559138 | -2.816266 | -1.600179 |
| 93 | 1 | 0 | 0.334961 | -3.692087 | -2.220594 |
| 94 | 1 | 0 | -0.313024 | -2.163647 | -1.616629 |
| 95 | 1 | 0 | 1.401231 | -2.282526 | -2.045354 |
| 96 | 7 | 0 | 1.375954 | -2.111256 | 0.635617 |

---

Rotational constants (GHZ): 0.0725495 0.0565059 0.0456624

**[B]-TEMPO**:



Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.631471 | -0.550030 | 0.319495 |
| 2 | 6 | 0 | -2.640718 | -1.179594 | 1.573454 |
| 3 | 6 | 0 | -3.216390 | -0.529488 | 2.674813 |
| 4 | 6 | 0 | -2.702545 | -2.580885 | 1.506277 |
| 5 | 6 | 0 | -3.841118 | -1.265141 | 3.681998 |
| 6 | 1 | 0 | -3.176568 | 0.551000 | 2.737914 |
| 7 | 6 | 0 | -3.327283 | -3.315198 | 2.515472 |
| 8 | 1 | 0 | -2.264276 | -3.088325 | 0.651365 |
| 9 | 6 | 0 | -3.899146 | -2.658680 | 3.606049 |
| 10 | 1 | 0 | -4.280885 | -0.747989 | 4.530994 |
| 11 | 1 | 0 | -3.368241 | -4.399100 | 2.446564 |
| 12 | 1 | 0 | -4.385781 | -3.228322 | 4.393477 |
| 13 | 6 | 0 | 0.659994 | -0.671413 | 0.105159 |
| 14 | 6 | 0 | 1.590321 | 0.316689 | 0.747434 |
| 15 | 6 | 0 | 1.621030 | 0.499564 | 2.074412 |
| 16 | 1 | 0 | 1.033395 | -0.130297 | 2.737366 |
| 17 | 1 | 0 | 2.209217 | 1.284711 | 2.541699 |
| 18 | 6 | 0 | 1.262241 | -1.816447 | -0.756367 |
| 19 | 6 | 0 | 0.200127 | -2.412524 | -1.704744 |
| 20 | 6 | 0 | -0.393652 | -1.565251 | -2.655165 |
| 21 | 6 | 0 | -0.148982 | -3.766553 | -1.710995 |
| 22 | 6 | 0 | -1.312365 | -2.058502 | -3.578136 |
| 23 | 1 | 0 | -0.137712 | -0.509281 | -2.669403 |
| 24 | 6 | 0 | -1.075490 | -4.262297 | -2.634782 |
| 25 | 1 | 0 | 0.305500 | -4.446202 | -0.998624 |
| 26 | 6 | 0 | -1.660611 | -3.412241 | -3.570362 |
| 27 | 1 | 0 | -1.757235 | -1.384306 | -4.305633 |
| 28 | 1 | 0 | -1.330830 | -5.319004 | -2.621487 |
| 29 | 1 | 0 | -2.378745 | -3.797654 | -4.289540 |
| 30 | 6 | 0 | 1.882345 | -2.863376 | 0.186695 |
| 31 | 6 | 0 | 3.150813 | -3.389696 | -0.087550 |

| | | | | | |
|---|---|---|---|---|---|
| 32 | 6 | 0 | 1.193844 | -3.324473 | 1.317256 |
| 33 | 6 | 0 | 3.715150 | -4.354484 | 0.749524 |
| 34 | 1 | 0 | 3.690681 | -3.032466 | -0.955832 |
| 35 | 6 | 0 | 1.757414 | -4.290437 | 2.151819 |
| 36 | 1 | 0 | 0.211613 | -2.926084 | 1.551449 |
| 37 | 6 | 0 | 3.022626 | -4.809538 | 1.871954 |
| 38 | 1 | 0 | 4.701700 | -4.750067 | 0.520657 |
| 39 | 1 | 0 | 1.205946 | -4.633208 | 3.023769 |
| 40 | 1 | 0 | 3.463804 | -5.559970 | 2.523038 |
| 41 | 8 | 0 | 2.341709 | -1.307735 | -1.538073 |
| 42 | 1 | 0 | 2.049663 | -0.489998 | -1.997933 |
| 43 | 15 | 0 | 2.539959 | 1.403743 | -0.403965 |
| 44 | 6 | 0 | 2.474461 | 3.091076 | 0.300507 |
| 45 | 6 | 0 | 1.504021 | 3.964765 | -0.211559 |
| 46 | 6 | 0 | 3.345220 | 3.539288 | 1.304423 |
| 47 | 6 | 0 | 1.394824 | 5.262013 | 0.289712 |
| 48 | 1 | 0 | 0.855849 | 3.623977 | -1.013007 |
| 49 | 6 | 0 | 3.229225 | 4.836051 | 1.806760 |
| 50 | 1 | 0 | 4.127364 | 2.885818 | 1.681214 |
| 51 | 6 | 0 | 2.252387 | 5.696984 | 1.302484 |
| 52 | 1 | 0 | 0.644877 | 5.935993 | -0.115771 |
| 53 | 1 | 0 | 3.908796 | 5.176899 | 2.583253 |
| 54 | 1 | 0 | 2.167138 | 6.708472 | 1.690766 |
| 55 | 6 | 0 | 4.302998 | 0.925360 | -0.360082 |
| 56 | 6 | 0 | 5.084073 | 1.298043 | -1.464447 |
| 57 | 6 | 0 | 4.897739 | 0.240138 | 0.706931 |
| 58 | 6 | 0 | 6.446175 | 1.001955 | -1.491080 |
| 59 | 1 | 0 | 4.616277 | 1.802756 | -2.304843 |
| 60 | 6 | 0 | 6.262548 | -0.051822 | 0.677303 |
| 61 | 1 | 0 | 4.295280 | -0.086861 | 1.548768 |
| 62 | 6 | 0 | 7.037792 | 0.330840 | -0.418485 |
| 63 | 1 | 0 | 7.044408 | 1.289774 | -2.351376 |
| 64 | 1 | 0 | 6.716180 | -0.588644 | 1.506111 |
| 65 | 1 | 0 | 8.099279 | 0.098618 | -0.440993 |
| 66 | 8 | 0 | 1.943734 | 1.382236 | -1.797896 |
| 67 | 6 | 0 | -1.933055 | -0.443088 | 0.481476 |
| 68 | 8 | 0 | -2.634685 | 0.237366 | -0.515557 |
| 69 | 6 | 0 | -3.227985 | 2.524076 | -0.164443 |
| 70 | 6 | 0 | -4.933417 | 0.686141 | -0.821026 |
| 71 | 6 | 0 | -4.426922 | 3.441166 | 0.175847 |
| 72 | 6 | 0 | -6.064752 | 1.673328 | -0.452656 |
| 73 | 6 | 0 | -5.681753 | 3.140828 | -0.642828 |
| 74 | 1 | 0 | -4.106181 | 4.481917 | 0.041238 |
| 75 | 1 | 0 | -4.665198 | 3.317718 | 1.241040 |

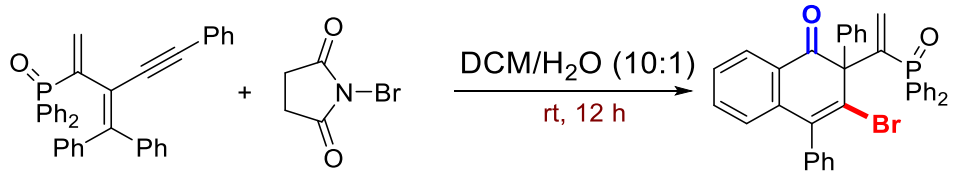
| | | | | | |
|---|---|---|---|---|---|
| 76 | 1 | 0 | -6.947571 | 1.415367 | -1.050787 |
| 77 | 1 | 0 | -6.335491 | 1.512276 | 0.599601 |
| 78 | 1 | 0 | -6.505244 | 3.789350 | -0.318186 |
| 79 | 1 | 0 | -5.515632 | 3.364523 | -1.703785 |
| 80 | 7 | 0 | -3.712545 | 1.103545 | -0.048287 |
| 81 | 6 | 0 | -2.153159 | 2.745433 | 0.917736 |
| 82 | 1 | 0 | -2.529927 | 2.465600 | 1.906687 |
| 83 | 1 | 0 | -1.244330 | 2.173433 | 0.718774 |
| 84 | 1 | 0 | -1.879113 | 3.806217 | 0.950176 |
| 85 | 6 | 0 | -2.605343 | 2.900992 | -1.528248 |
| 86 | 1 | 0 | -2.096547 | 3.867920 | -1.436807 |
| 87 | 1 | 0 | -1.865165 | 2.155666 | -1.829178 |
| 88 | 1 | 0 | -3.341833 | 2.997802 | -2.327950 |
| 89 | 6 | 0 | -5.345639 | -0.712053 | -0.325997 |
| 90 | 1 | 0 | -4.617409 | -1.471368 | -0.621362 |
| 91 | 1 | 0 | -5.441481 | -0.729577 | 0.762761 |
| 92 | 1 | 0 | -6.312705 | -0.982464 | -0.765866 |
| 93 | 6 | 0 | -4.742828 | 0.604723 | -2.354656 |
| 94 | 1 | 0 | -5.595120 | 0.073432 | -2.793840 |
| 95 | 1 | 0 | -4.686293 | 1.582488 | -2.837469 |
| 96 | 1 | 0 | -3.835558 | 0.046104 | -2.597599 |

---

Rotational constants (GHZ): 0.0753917 0.0514120 0.0394871

## 6. Synthetic Applications

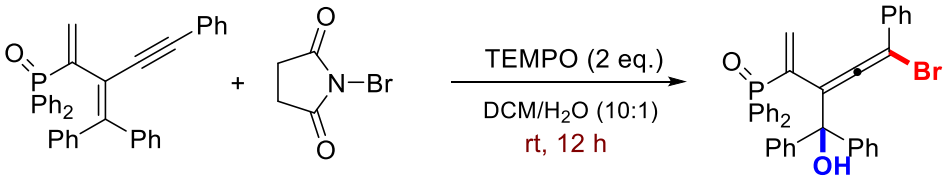
### 6.1 Scale-up Experiments




**1a**, 1.0 mmol

**2a**, 69%

To a 50 mL vial was added vinyl enyne (1.0 mmol, 1.0 equiv), NBS (4.0 mmol, 4.0 equiv), Then 10 mL solvent ($CH_2Cl_2$/water) (v:v=10:1) was injected into the vial. The reaction mixture was stirred at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (3:1) to afford the target product (**2a**) in 69% yield.




**1a**, 1mmol

**3a**, 82%

To a 10 mL vial was added vinyl enyne (1.0 mmol, 1.0 equiv), NBS (2.0 mmol, 2.0 equiv), TEMPO (2.0 mmol, 2.0 equiv). Then 10 mL solvent ($CH_2Cl_2$/water) (v:v=10:1) was injected into the vial. The reaction mixture was stirred at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (5:1) to afford the target product (**3a**) in 82% yield.

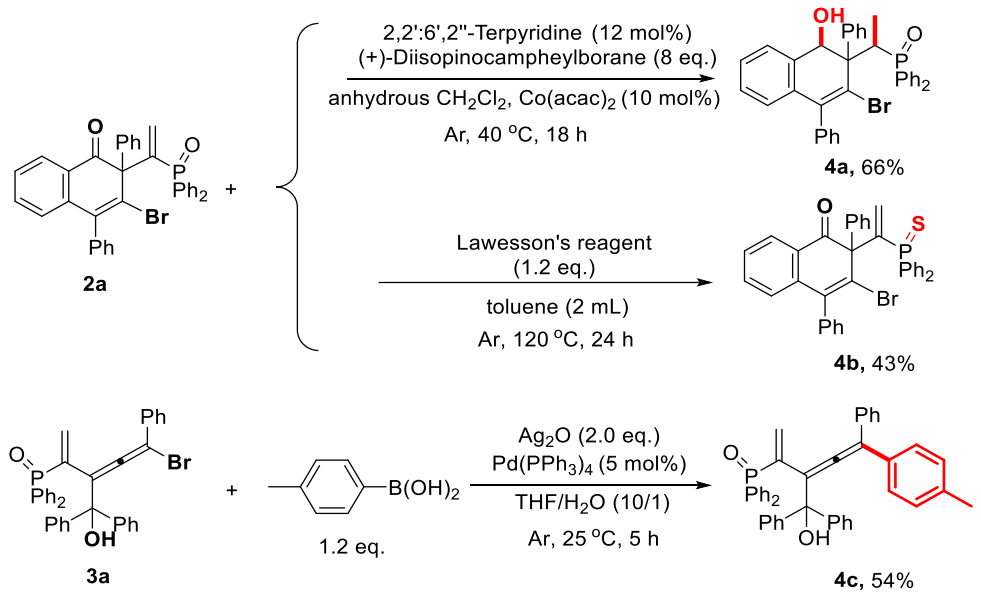
### 6.2 Further Transformations

Synthetic application of **2a** was then explored. To a 10 mL flask equipped with **2a** (0.2 mmol), 2,2':6',2''-Terpyridine (12 mol%), (+)-Diisopinocampheylborane (8 eq.), $Co(acac)_2$ (10 mol%) and 2 mL anhydrous $CH_2Cl_2$. The reaction mixture was then heated to 40 °C in an oil bath for 18 hours under argon atmosphere. After all the volatiles were removed under vacuum, the crude product was purified on flash

chromatography (eluent: 1:4 (v/v) of ethyl acetate/petroleum ether) to afford **4a** in 66% yield, and the compounds were characterized by NMR and MS, see details as follows.

To a 10 mL flask equipped with **2a** (0.2 mmol), Lawesson's reagent (1.2 equiv) and 2 mL anhydrous toluene. The reaction mixture was then heated to 120 °C in an oil bath for 24 hours under argon atmosphere. After all 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 **4b** in 43% yield, and the compounds were characterized by NMR and MS, see details as follows.

Synthetic application of the product **3a** was explored as well. To a 10 mL flask equipped with **3a** (0.2 mmol), $PhB(OH)_2$ (0.24 mmol, 1.2 equiv), $Ag_2O$ ( 0.4 mmol, 2.0 equiv), $Pd(PPh_3)_4$ ( 0.01 mmol, 0.05 equiv), THF (2.4 mL) and distillated water (0.24 mL). The reaction mixture was stirred at RT for 5 hours under argon atmosphere. After all the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:5 (v/v) of ethyl acetate/petroleum ether) to afford **4c** in 54% yield, and the compounds were characterized by NMR and MS, see details as follows.



## 7. X-Ray Crystallography Data of 2a

Crystal **2a** (the ellipsoid contour percent probability level is 50%) was obtained in solvent $CH_2Cl_2$/*n*-hexane=1:5 through natural volatilization at room temperature.

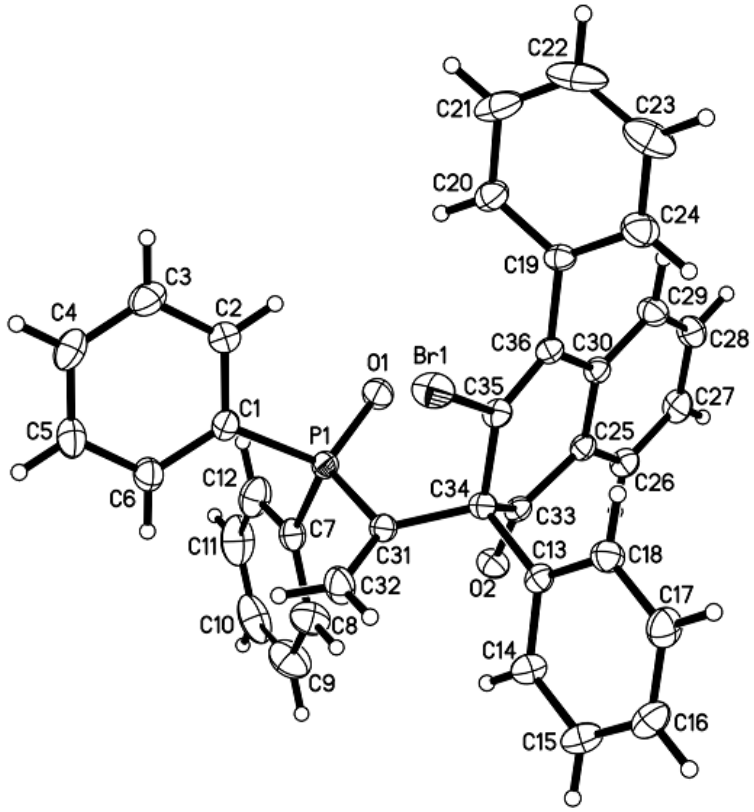



**Table 1 Crystal data and structure refinement for 2a.**

| | |
|---|---|
| Identification code | **2a** |
| Empirical formula | $C_{36}H_{26}BrO_2P$ |
| Formula weight | 601.44 |
| Temperature/K | 295(2) |
| Crystal system | monoclinic |
| Space group | I2/a |
| a/Å | 19.891(4) |
| b/Å | 9.6242(19) |
| c/Å | 29.836(12) |
| α/° | 90 |
| β/° | 95.97(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 5681(3) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.406 |

| | |
|---|---|
| μ/mm$^{-1}$ | 1.536 |
| F(000) | 2464.0 |
| Crystal size/mm$^3$ | 0.110 × 0.090 × 0.070 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.34 to 54.88 |
| Index ranges | -24 ≤ h ≤ 25, -12 ≤ k ≤ 12, -38 ≤ l ≤ 38 |
| Reflections collected | 65371 |
| Independent reflections | 6418 [$R_{int}$ = 0.0542, $R_{sigma}$ = 0.0289] |
| Data/restraints/parameters | 6418/0/361 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0429, $wR_2$ = 0.0930 |
| Final R indexes [all data] | $R_1$ = 0.0623, $wR_2$ = 0.1007 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.39/-0.41 |

**Table 2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3aa. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Br1 | 426.0(2) | 4363.5(2) | 1105.6(2) | 50.38(10) |
| P1 | -1396.9(3) | 6224.1(6) | 1227.8(2) | 32.10(14) |
| O1 | -1052.5(9) | 6732.7(19) | 1664.3(5) | 43.7(4) |
| O2 | -835.4(8) | 9137.1(16) | 915.1(6) | 39.1(4) |
| C1 | -1657.8(12) | 4424(2) | 1271.2(8) | 34.8(5) |
| C2 | -1322.1(13) | 3634(3) | 1616.8(8) | 43.7(6) |
| C3 | -1486.9(14) | 2243(3) | 1672(1) | 51.6(7) |
| C4 | -1980.1(14) | 1622(3) | 1380.5(10) | 52.0(7) |
| C5 | -2322.4(13) | 2393(3) | 1040.1(10) | 50.2(7) |
| C6 | -2170.9(13) | 3790(3) | 985.5(9) | 44.2(6) |
| C7 | -2160.4(11) | 7192(2) | 1045.5(8) | 37.1(5) |
| C8 | -2276.6(14) | 7922(3) | 644.1(10) | 56.0(7) |
| C9 | -2853.7(17) | 8744(4) | 559.1(12) | 70.8(9) |
| C10 | -3308.9(15) | 8840(4) | 871.1(15) | 73.6(11) |
| C11 | -3200.8(16) | 8125(4) | 1268.3(15) | 74.8(10) |
| C12 | -2628.4(15) | 7295(3) | 1357.0(11) | 58.5(8) |
| C13 | 215.6(11) | 7428(2) | 493.0(7) | 30.7(5) |
| C14 | -130.6(13) | 8038(3) | 111.8(8) | 40.7(6) |
| C15 | 201.5(14) | 8396(3) | -256.5(9) | 49.0(6) |
| C16 | 884.0(14) | 8181(3) | -253.7(9) | 49.1(6) |
| C17 | 1234.0(13) | 7604(3) | 120.8(9) | 49.6(6) |
| C18 | 906.2(12) | 7227(3) | 495.2(8) | 40.5(6) |
| C19 | 1063.5(11) | 5919(2) | 1963.1(7) | 31.2(5) |

| | | | | |
|---|---|---|---|---|
| C20 | 767.4(14) | 5031(3) | 2250.9(8) | 42.1(6) |
| C21 | 1162(2) | 4206(3) | 2557.5(9) | 62.6(9) |
| C22 | 1851(2) | 4282(3) | 2578.9(11) | 74.5(11) |
| C23 | 2153.8(17) | 5174(4) | 2301.7(11) | 71.4(10) |
| C24 | 1762.5(13) | 5999(3) | 1992.8(9) | 50.7(7) |
| C25 | 103.3(11) | 9138(2) | 1468.1(7) | 29.1(4) |
| C26 | 32.2(12) | 10556(2) | 1566.0(8) | 35.8(5) |
| C27 | 403.6(13) | 11139(3) | 1935.3(8) | 42.7(6) |
| C28 | 842.2(13) | 10317(3) | 2210.9(8) | 43.5(6) |
| C29 | 920.3(12) | 8915(3) | 2116.4(8) | 39.5(5) |
| C30 | 557.4(11) | 8297(2) | 1739.2(7) | 29.4(4) |
| C31 | -828.7(11) | 6280(2) | 784.5(7) | 30.2(5) |
| C32 | -977.3(14) | 5583(3) | 405.8(9) | 47.7(6) |
| C33 | -345.8(11) | 8525(2) | 1093.0(7) | 28.3(4) |
| C34 | -160.7(10) | 7077(2) | 909.3(7) | 28.2(4) |
| C35 | 297.3(11) | 6277(2) | 1258.6(7) | 29.7(4) |
| C36 | 627.2(10) | 6798(2) | 1633.9(7) | 28.8(4) |

**Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Br1 | 74.1(2) | 23.68(13) | 50.42(16) | -5.59(11) | -7.44(13) | 12.08(11) |
| P1 | 37.6(3) | 30.0(3) | 28.7(3) | -2.7(2) | 3.7(2) | -4.5(2) |
| O1 | 52.9(10) | 46.3(10) | 31.9(8) | -7.3(7) | 4.0(7) | -9.5(8) |
| O2 | 42.6(9) | 29.9(9) | 43.0(9) | -1.1(7) | -4.4(7) | 7.7(7) |
| C1 | 36.6(12) | 32.2(12) | 36.4(12) | -0.5(10) | 8.0(9) | -4.4(10) |
| C2 | 45.6(14) | 43.9(15) | 40.8(13) | 4.7(11) | 1.1(11) | -4.0(11) |
| C3 | 53.5(16) | 44.1(15) | 57.5(16) | 14.5(13) | 7.1(13) | 5.4(12) |
| C4 | 55.5(17) | 31.1(13) | 71.4(18) | 4.8(13) | 16.6(14) | -1.4(12) |
| C5 | 45.7(15) | 39.1(14) | 65.2(17) | -6.3(13) | 2.1(13) | -8.6(12) |
| C6 | 43.2(14) | 37.0(13) | 50.9(15) | 0.9(12) | -1.7(11) | -3.8(11) |
| C7 | 35.9(12) | 31.0(12) | 44.7(13) | -8.2(10) | 5.6(10) | -2.2(9) |
| C8 | 50.5(16) | 65.4(19) | 51.4(16) | -1.4(14) | 2.0(13) | 16.0(14) |
| C9 | 61(2) | 70(2) | 78(2) | -5.6(18) | -13.6(17) | 21.0(17) |
| C10 | 37.5(16) | 62(2) | 118(3) | -33(2) | -6.3(18) | 9.5(14) |
| C11 | 45.1(17) | 71(2) | 113(3) | -27(2) | 30.9(19) | -1.8(16) |
| C12 | 57.1(17) | 53.1(18) | 69.2(19) | -7.1(15) | 25.6(15) | -6.6(14) |
| C13 | 36.9(12) | 23.1(10) | 32.6(11) | -0.8(9) | 5.6(9) | -0.1(9) |
| C14 | 44.4(14) | 41.6(14) | 36.8(12) | 5.2(10) | 7.3(10) | 6.8(11) |
| C15 | 64.5(17) | 43.8(15) | 39.5(13) | 10.9(12) | 9.4(12) | 9.0(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 63.7(18) | 43.3(15) | 43.6(14) | 1.7(12) | 21.4(13) | -2.2(13) |
| C17 | 41.2(14) | 57.8(17) | 52.2(15) | -2.8(13) | 15.7(12) | -1.9(13) |
| C18 | 38.6(13) | 46.6(15) | 36.1(12) | 0.4(11) | 3.4(10) | 0.4(11) |
| C19 | 39.5(12) | 25.7(11) | 27.7(10) | 0.0(8) | 0.2(9) | 4.6(9) |
| C20 | 58.7(16) | 32.6(13) | 35.0(12) | 2(1) | 4.9(11) | -4.8(11) |
| C21 | 120(3) | 31.0(14) | 34.6(14) | 6.1(11) | -1.7(16) | 1.4(16) |
| C22 | 114(3) | 56(2) | 45.8(17) | -3.5(15) | -25.9(18) | 42(2) |
| C23 | 55.3(19) | 89(3) | 66(2) | -7(2) | -14.3(15) | 31.7(18) |
| C24 | 40.6(14) | 64.3(18) | 47.0(15) | 4.7(13) | 3.6(11) | 6.5(13) |
| C25 | 34.4(11) | 24.4(11) | 29(1) | -0.6(8) | 6.3(9) | -1.9(8) |
| C26 | 42.8(13) | 25.5(11) | 39.5(12) | -0.1(10) | 6(1) | 2.2(10) |
| C27 | 54.1(15) | 25.4(11) | 49.2(14) | -8.3(11) | 8.6(12) | -4.4(11) |
| C28 | 51.7(15) | 37.8(14) | 39.6(13) | -9.9(11) | -2.9(11) | -9.8(11) |
| C29 | 44.0(13) | 35.6(12) | 37.0(12) | -1.8(10) | -4.2(10) | -0.5(10) |
| C30 | 32.3(11) | 25.9(11) | 30.3(10) | 1.4(9) | 3.6(8) | -0.6(9) |
| C31 | 34.5(11) | 25.2(11) | 30.4(11) | -1.2(9) | 1.3(9) | -0.7(9) |
| C32 | 47.7(15) | 54.9(16) | 41.6(14) | -15.2(12) | 9.3(11) | -14.5(12) |
| C33 | 34.9(11) | 21.4(10) | 28.8(10) | 2.8(8) | 5.0(9) | 1.6(9) |
| C34 | 34.1(11) | 22.9(10) | 27.3(10) | -1.9(8) | 1.6(8) | 1.7(8) |
| C35 | 38.4(12) | 15.8(10) | 34.6(11) | -0.7(8) | 2.4(9) | 3.5(8) |
| C36 | 32.4(11) | 25.3(11) | 29.1(10) | 2.4(9) | 4.2(8) | 1.4(9) |

**Table 4 Bond Lengths for 2a.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Br1 | C35 | 1.921(2) | C16 | C17 | 1.371(4) |
| P1 | O1 | 1.4897(17) | C17 | C18 | 1.398(3) |
| P1 | C1 | 1.817(2) | C19 | C20 | 1.386(3) |
| P1 | C7 | 1.816(2) | C19 | C24 | 1.386(3) |
| P1 | C31 | 1.828(2) | C19 | C36 | 1.502(3) |
| O2 | C33 | 1.212(3) | C20 | C21 | 1.390(4) |
| C1 | C2 | 1.394(3) | C21 | C22 | 1.369(5) |
| C1 | C6 | 1.400(3) | C22 | C23 | 1.373(5) |
| C2 | C3 | 1.392(4) | C23 | C24 | 1.392(4) |
| C3 | C4 | 1.378(4) | C25 | C30 | 1.405(3) |
| C4 | C5 | 1.379(4) | C25 | C26 | 1.406(3) |
| C5 | C6 | 1.392(4) | C25 | C33 | 1.480(3) |
| C7 | C12 | 1.386(4) | C26 | C27 | 1.380(3) |
| C7 | C8 | 1.387(4) | C27 | C28 | 1.383(4) |
| C8 | C9 | 1.395(4) | C28 | C29 | 1.391(3) |
| C9 | C10 | 1.368(5) | C29 | C30 | 1.404(3) |

| | | | | | |
|---|---|---|---|---|---|
| C10 | C11 | 1.368(5) | C30 | C36 | 1.486(3) |
| C11 | C12 | 1.393(5) | C31 | C32 | 1.321(3) |
| C13 | C18 | 1.386(3) | C31 | C34 | 1.546(3) |
| C13 | C14 | 1.396(3) | C33 | C34 | 1.556(3) |
| C13 | C34 | 1.553(3) | C34 | C35 | 1.520(3) |
| C14 | C15 | 1.383(3) | C35 | C36 | 1.335(3) |
| C15 | C16 | 1.372(4) | | | |

**Table 5 Bond Angles for 2a.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | P1 | C1 | 111.09(11) | C21 | C20 | C19 | 120.9(3) |
| O1 | P1 | C7 | 112.79(11) | C22 | C21 | C20 | 119.6(3) |
| C1 | P1 | C7 | 105.93(11) | C21 | C22 | C23 | 120.3(3) |
| O1 | P1 | C31 | 111.11(10) | C22 | C23 | C24 | 120.4(3) |
| C1 | P1 | C31 | 106.40(10) | C19 | C24 | C23 | 119.9(3) |
| C7 | P1 | C31 | 109.21(11) | C30 | C25 | C26 | 120.8(2) |
| C2 | C1 | C6 | 118.4(2) | C30 | C25 | C33 | 120.50(19) |
| C2 | C1 | P1 | 117.02(18) | C26 | C25 | C33 | 118.5(2) |
| C6 | C1 | P1 | 124.58(19) | C27 | C26 | C25 | 120.2(2) |
| C3 | C2 | C1 | 120.8(2) | C26 | C27 | C28 | 119.6(2) |
| C4 | C3 | C2 | 120.2(3) | C27 | C28 | C29 | 120.7(2) |
| C3 | C4 | C5 | 119.7(3) | C28 | C29 | C30 | 121.0(2) |
| C4 | C5 | C6 | 120.7(3) | C25 | C30 | C29 | 117.6(2) |
| C5 | C6 | C1 | 120.2(2) | C25 | C30 | C36 | 120.41(19) |
| C12 | C7 | C8 | 118.7(2) | C29 | C30 | C36 | 121.9(2) |
| C12 | C7 | P1 | 115.8(2) | C32 | C31 | C34 | 124.6(2) |
| C8 | C7 | P1 | 125.27(19) | C32 | C31 | P1 | 120.24(18) |
| C7 | C8 | C9 | 120.3(3) | C34 | C31 | P1 | 114.90(14) |
| C10 | C9 | C8 | 120.3(3) | O2 | C33 | C25 | 122.14(19) |
| C9 | C10 | C11 | 120.0(3) | O2 | C33 | C34 | 119.32(19) |
| C10 | C11 | C12 | 120.3(3) | C25 | C33 | C34 | 118.47(18) |
| C7 | C12 | C11 | 120.4(3) | C35 | C34 | C31 | 110.64(17) |
| C18 | C13 | C14 | 117.8(2) | C35 | C34 | C13 | 110.75(17) |
| C18 | C13 | C34 | 121.70(19) | C31 | C34 | C13 | 112.89(17) |
| C14 | C13 | C34 | 120.34(19) | C35 | C34 | C33 | 111.05(17) |
| C15 | C14 | C13 | 121.1(2) | C31 | C34 | C33 | 107.48(17) |
| C16 | C15 | C14 | 120.8(2) | C13 | C34 | C33 | 103.80(16) |
| C15 | C16 | C17 | 118.9(2) | C36 | C35 | C34 | 126.32(19) |
| C16 | C17 | C18 | 121.1(2) | C36 | C35 | Br1 | 119.53(16) |
| C13 | C18 | C17 | 120.3(2) | C34 | C35 | Br1 | 114.07(14) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C20 | C19 | C24 | 118.9(2) | C35 | C36 | C30 | 119.53(19) |
| C20 | C19 | C36 | 119.9(2) | C35 | C36 | C19 | 122.51(19) |
| C24 | C19 | C36 | 121.2(2) | C30 | C36 | C19 | 117.96(18) |

**Table 6 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$× 10$^3$) for 2a.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H2A | -984 | 4041 | 1813 | 52 |
| H3A | -1263 | 1731 | 1906 | 62 |
| H4A | -2082 | 686 | 1413 | 62 |
| H5A | -2658 | 1975 | 845 | 60 |
| H6A | -2411 | 4305 | 759 | 53 |
| H8A | -1969 | 7864 | 431 | 67 |
| H9A | -2929 | 9229 | 289 | 85 |
| H10A | -3692 | 9392 | 813 | 88 |
| H11A | -3511 | 8193 | 1480 | 90 |
| H12A | -2560 | 6807 | 1627 | 70 |
| H14A | -592 | 8207 | 105 | 49 |
| H15A | -41 | 8787 | -509 | 59 |
| H16A | 1106 | 8424 | -502 | 59 |
| H17A | 1697 | 7459 | 126 | 60 |
| H18A | 1152 | 6841 | 747 | 49 |
| H20A | 299 | 4986 | 2239 | 51 |
| H21A | 958 | 3606 | 2747 | 75 |
| H22A | 2117 | 3727 | 2782 | 89 |
| H23A | 2623 | 5226 | 2320 | 86 |
| H24A | 1970 | 6604 | 1807 | 61 |
| H26A | -266 | 11104 | 1381 | 43 |
| H27A | 359 | 12079 | 1998 | 51 |
| H28A | 1088 | 10707 | 2462 | 52 |
| H29A | 1217 | 8379 | 2306 | 47 |
| H32A | -669 | 5548 | 192 | 57 |
| H32B | -1390 | 5126 | 353 | 57 |

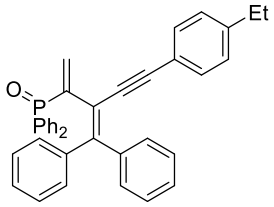
## 8. Characterizations of Substrates and Products

### 8.1 Substrates

All the vinyl enyne substrates were prepared according to the procedures reported by our previous works: L. Wu et. al., *Adv. Synth. Catal*. **2018**, *360*, 3518-3525; L. Wu et. al., *Org. Lett*. **2019**, *21*, 6383-6387.

For new compounds, please see characterizations as follows:

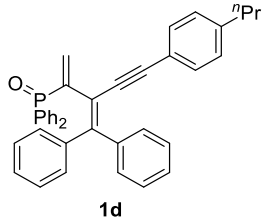
**(3-(diphenylmethylene)-5-(4-ethylphenyl)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1c)**




**1c**

White solids, *m.p.*: 173.5-175.3 ℃ (136.0 mg, 85% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.39 (m, 6H), 7.29-7.24 (m, 3H), 7.21-7.19 (m, 3H), 7.05-7.04 (m, 2H), 6.96 (d, *J* = 5.0 Hz, 2H), 6.60 (d, *J* = 35.0 Hz, 2H), 6.08 (d, *J* = 15.0 Hz, 1H), 6.00 (d, *J* = 20.0 Hz, 1H), 2.56 (q, *J* = 10.0 Hz, 2H), 1.17 (t, *J* = 5.0 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.0 (d, *J* = 7.0 Hz), 144.6, 142.9, 142.1, 141.7, 140.7, 136.1 (d, *J* = 7.9 Hz), 132.6, 132.3 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8, 131.3, 130.3 (d, *J* = 22.9 Hz), 128.4 (d, *J* = 12.2 Hz), 128.0, 128.0, 127.6 (d, *J* = 6.3 Hz), 127.5, 120.3, 118.1 (d, *J* = 8.9 Hz), 96.4, 89.4, 28.9, 15.5. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 28.4 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{32}OP^+$: 535.2185, Found: 535.2160.

**(3-(diphenylmethylene)-5-(4-propylphenyl)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1d)**

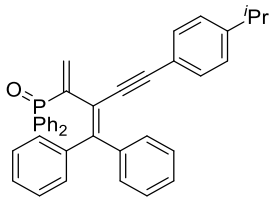



**1d**

White solids, *m.p.*: 136.7-138.4 ℃ (136.5 mg, 83% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.80-7.77 (m, 4H), 7.52-7.49 (m, 2H), 7.44-7.41 (m, 4H), 7.39-7.38 (m, 2H), 7.29-7.24 (m, 3H), 7.20-7.18 (m, 3H),

7.03-7.02 (m, 2H), 6.93 (d, *J* = 12.0 Hz, 2H), 6.59 (d, *J* = 6.0 Hz, 2H), 6.07 (d, *J* = 36.0 Hz, 1H), 6.01 (d, *J* = 18.0 Hz, 1H), 2.50 (t, *J* = 6.0 Hz, 2H), 1.60-1.54 (m, 2H), 0.89 (t, *J* = 6.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 151.8 (d, *J* = 6.9 Hz), 143.0, 142.9, 142.2, 141.6, 140.6, 135.9 (d, *J* = 7.8 Hz), 132.6, 132.2 (d, *J* = 9.8 Hz), 131.9, 131.8 (d, *J* = 2.8 Hz), 131.1, 130.2 (d, *J* = 32.2 Hz), 128.3 (d, *J* = 12.1 Hz), 127.9 (d, *J* = 32.4 Hz), 127.6 (d, *J* = 70.9 Hz), 127.5, 120.2, 118.0 (d, *J* = 9.0 Hz), 96.3, 89.4, 37.9, 24.3, 13.7. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 27.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{34}OP^+$: 549.2342, Found: 549.2314.

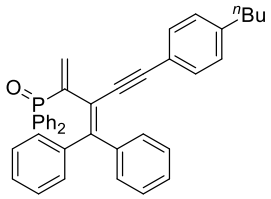
**(3-(diphenylmethylene)-5-(4-isopropylphenyl)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1e)**




**1e**

White solids, *m.p.*: 163.8-165.5 ℃ (123.3 mg, 75% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 4H), 7.57-7.52 (m, 2H), 7.49-7.42 (m, 6H), 7.34-7.28 (m, 3H), 7.24-7.22 (m, 3H), 7.08-7.06 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.12 (d, *J* = 32.0 Hz, 1H), 6.05 (d, *J* = 16.0 Hz, 1H), 2.89-2.80 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H) . **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.9 (d, *J* = 6.9 Hz), 149.1, 142.9, 142.0, 141.6, 140.6, 136.0 (d, *J* = 7.4 Hz), 132.7, 132.2 (d, *J* = 9.9 Hz), 131.8 (d, *J* = 2.8 Hz), 131.7, 131.2, 130.2 (d, *J* = 19.3 Hz), 128.3 (d, *J* = 12.2 Hz), 127.9, 127.7 (d, *J* = 32.7 Hz), 127.4, 126.1, 120.4, 118.0 (d, *J* = 9.1 Hz), 96.3, 89.3 (d, *J* = 2.4 Hz), 34.1, 23.8. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 27.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{34}OP^+$: 549.2342, Found: 549.2316.

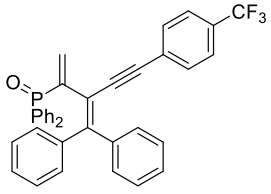
**(5-(4-butylphenyl)-3-(diphenylmethylene)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1f)**




**1f**

White solids, *m.p.*: 121.3-124.2 ℃ (118.0 mg, 70% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.80-7.77 (m, 4H), 7.51-7.49 (m, 2H), 7.44-7.38 (m, 6H), 7.28-7.23 (m, 3H), 7.19-7.18 (m, 3H), 7.03-7.02 (m, 2H), 6.94 (d, *J* = 6.0 Hz, 2H), 6.59 (d, *J* = 6.0 Hz, 2H), 6.07 (d, *J* = 36.0 Hz, 1H), 6.01 (d, *J* = 18.0 Hz, 1H), 2.52 (t, *J* = 6.0 Hz, 2H), 1.55-1.50 (m, 2H), 1.33-1.27 (m, 2H), 0.90 (t, *J* = 6.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 151.8 (d, *J* = 6.8 Hz), 143.2, 142.9, 142.3, 141.6, 140.6, 135.9 (d, *J* = 8.0 Hz), 132.6, 132.2 (d, *J* = 9.8 Hz), 131.9, 131.8 (d, *J* = 2.7 Hz), 131.1, 130.2 (d, *J* = 32.6 Hz), 128.3 (d, *J* = 12.2 Hz), 128.0, 127.9, 127.7 (d, *J* = 47.4 Hz), 127.4, 120.2, 118.0 (d, *J* = 8.8 Hz), 96.3, 89.4 (d, *J* = 2.3 Hz), 35.6, 33.3, 22.3, 13.9. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 27.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{36}OP^+$: 563.2498, Found: 563.2470.

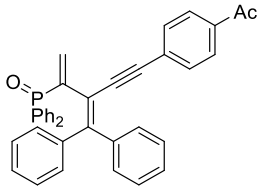
**(3-(diphenylmethylene)-5-(4-(trifluoromethyl)phenyl)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1l)**




**1l**

White solids, *m.p.*: 173.1-174.8 ℃ (130.9 mg, 76% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 4H), 7.57-7.53 (m, 2H), 7.49-7.42 (m, 6H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 3H), 7.28-7.26 (m, 3H), 7.20-7.19 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 40.0 Hz, 1H), 5.90 (d, *J* = 16.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.0 (d, *J* = 7.0 Hz), 142.3 (d, *J* = 94.1 Hz), 140.9 (d, *J* = 98.3 Hz), 136.1 (d, *J* = 8.4 Hz), 132.5, 132.1 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 2.7 Hz), 131.5, 131.3, 130.2 (d, *J* = 17.1 Hz), 129.5 (d, *J* = 32.5 Hz), 128.4 (d, *J* = 12.2 Hz), 128.3, 127.9, 127.7, 127.6, 126.7, 125.2, 124.8 (q, *J* = 3.7 Hz), 122.5, 117.4 (d, *J* = 8.7 Hz), 94.2, 92.1. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 28.0 (s). **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{27}F_3OP^+$: 575.1746, Found: 575.1743.

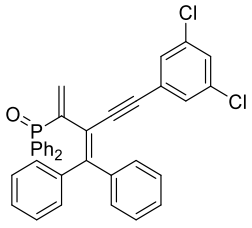
**1-(4-(3-(diphenylmethylene)-4-(diphenylphosphoryl)pent-4-en-1-yn-1-yl)phenyl)ethan-1-one (1m)**




**1m**

White solids, *m.p.*: 167.8-169.3 ℃ (90.4 mg, 55% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.55-7.51 (m, 2H), 7.47-7.41 (m, 6H), 7.30-7.28 (m, 3H), 7.26-7.23 (m, 3H), 7.18-7.16 (m, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 40.0 Hz, 1H), 5.88 (d, *J* = 16.0 Hz, 1H), 2.52 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.3, 153.9 (d, *J* = 6.9 Hz), 142.7, 141.8, 141.4, 140.4, 136.1 (d, *J* = 8.5 Hz), 135.8, 132.5, 132.1 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 2.8 Hz), 131.5, 131.2, 130.3 (d, *J* = 16.1 Hz), 128.4 (d, *J* = 12.2 Hz), 128.3, 127.9, 127.9, 127.8 (d, *J* = 4.0 Hz), 127.6, 117.5 (d, *J* = 8.7 Hz), 94.9, 93.2 (d, *J* = 2.3 Hz), 26.6. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 28.0 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{30}O_2P^+$: 549.1978, Found: 549.1973.

**(5-(3,5-dichlorophenyl)-3-(diphenylmethylene)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1p)**

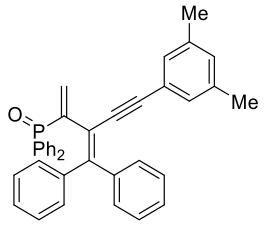



**1p**

White solids, *m.p.*: 191.5-192.9 ℃ (117.1 mg, 68% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 4H), 7.60-7.56 (m, 2H), 7.51-7.46 (m, 4H), 7.42-7.40 (m, 2H), 7.34-7.32 (m, 3H), 7.28-7.26 (m, 3H), 7.21-7.16 (m, 3H), 6.42 (d, *J* = 4.0 Hz, 2H), 6.01 (d, *J* = 40.0 Hz, 1H), 5.85 (d, *J* = 20.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.3 (d, *J* = 6.9 Hz), 142.6, 141.7, 141.2, 140.4, 136.1 (d, *J* = 8.6 Hz), 134.3, 132.4, 132.1, 132.0, 131.4, 130.2 (d, *J* = 17.6 Hz), 129.1, 128.5 (d, *J* = 12.2 Hz), 128.1 (d, *J* = 17.5 Hz), 127.8, 127.7, 125.6,

117.2 (d, *J* = 8.7 Hz), 93.0, 91.9. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 27.9 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{26}Cl_2OP^+$: 575.1093, Found: 575.1055.

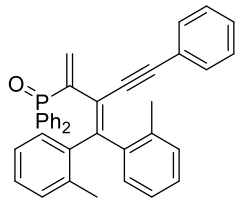
**(5-(3,5-dimethylphenyl)-3-(diphenylmethylene)pent-1-en-4-yn-2-yl)diphenylphosphine oxide (1q)**




**1q**

White solids, *m.p.*: 197.1-198.8 ℃ (104 mg, 65% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H), 7.52-7.49 (m, 2H), 7.44-7.39 (m, 6H), 7.29-7.24 (m, 3H), 7.19-7.18 (m, 3H), 7.03-7.02 (m, 2H), 6.80 (s, 1H), 6.27 (s, 2H), 6.05 (d, *J* = 36.0 Hz, 1H), 6.00 (d, *J* = 18.0 Hz, 1H), 2.16 (s, 6H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 151.9 (d, *J* = 7.1 Hz), 142.9, 142.2, 141.6, 140.6, 137.3, 135.9 (d, *J* = 7.7 Hz), 132.6, 132.2 (d, *J* = 9.8 Hz), 132.0, 131.8 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 27.6 Hz), 130.0, 128.8, 128.3 (d, *J* = 12.0 Hz), 127.7 (d, *J* = 48.6 Hz), 127.6 (d, *J* = 73.7 Hz), 122.6, 118.0 (d, *J* = 8.9 Hz), 96.6, 89.2 (d, *J* = 2.5 Hz), 21.0. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 27.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{32}OP^+$: 535.2185, Found: 535.2166.

**(3-(di-o-tolylmethylene)-5-phenylpent-1-en-4-yn-2-yl)diphenylphosphine oxide (1r)**

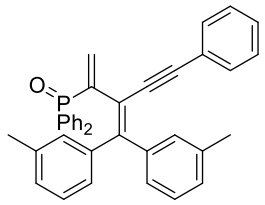



**1r**

White solids, *m.p.*: 193.2-194.7 ℃ (104.1 mg, 65% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.58-7.54 (m, 2H), 7.50-7.46 (m, 4 H), 7.24-7.13 (m, 7H), 7.11-7.05 (m, 4H), 6.51 (d, *J* = 4.0 Hz, 2H), 5.98 (d, *J* = 40.0 Hz, 1H), 5.84 (d, *J* = 12.0 Hz, 1H), 2.38 (s, 3H), 2.11 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.0 (d, *J* = 7.5 Hz), 142.4, 141.5, 140.1, 139.9, 137.0, 136.7, 135.0 (d, *J* = 8.2 Hz), 132.2 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 2.8 Hz), 131.1, 131.0, 130.7, 130.4, 130.3, 128.4 (d, *J* = 12.3 Hz), 128.0, 127.8, 127.7 (d, *J* = 9.8 Hz),

125.5, 124.9, 122.9, 121.3 (d, *J* = 8.6 Hz), 96.7, 89.3 (d, *J* = 2.0 Hz), 20.7, 20.6. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 28.1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{32}OP^+$ : 535.2185, Found: 535.2183.

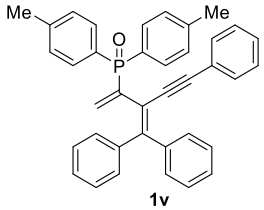
**(3-(di-m-tolylmethylene)-5-phenylpent-1-en-4-yn-2-yl)diphenylphosphine oxide (1s)**




**1s**

White solids, *m.p.*: 184.2-185.7 ℃ (88.1 mg, 55% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 4H), 7.53-7.49 (m, 2H), 7.45-7.42 (m, 4 H), 7.25 (s, 1H), 7.18-7.17 (m, 2H), 7.16-7.15 (m, 1H), 7.13-7.11 (m, 2H), 7.10-7.07 (m, 2H), 7.01 (d, *J* = 5.0 Hz, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.75 (s, 1H), 6.66-6.64 (m, 2H), 6.10-5.99 (m, 2H), 2.29 (s, 3 H), 2.25 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.9 (d, *J* = 7.1 Hz), 142.8, 142.0, 141.6, 140.7, 137.4, 137.0, 136.1 (d, *J* = 7.8 Hz), 132.7, 132.3 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 2.8 Hz), 131.2, 130.7 (d, *J* = 7.2 Hz), 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 123.2, 117.6 (d, *J* = 8.9 Hz), 95.9, 90.1 (d, *J* = 2.4 Hz), 21.6, 21.5. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 28.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{32}OP^+$: 535.2185, Found: 535.2187.

**(3-(diphenylmethylene)-5-phenylpent-1-en-4-yn-2-yl)di-p-tolylphosphine oxide (1v)**

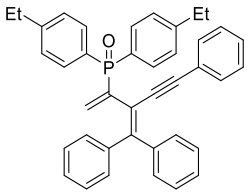



**1v**

White solids, *m.p.*: 173.5-175.5 ℃ (125.0 mg, 78% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 4H), 7.45-7.44 (m, 2H), 7.32-7.24 (m, 10 H), 7.20-7.14 (m, 5H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.07-5.93 (m, 2H), 2.40 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.2 (d, *J* = 6.9 Hz), 143.4, 142.5, 142.2 (d, *J* = 2.8 Hz), 141.6, 140.7, 135.5 (d, *J* = 8.0 Hz), 132.2 (d, *J* = 10.2 Hz), 131.2, 130.3 (d, *J* = 15.6 Hz), 129.4, 129.1 (d, *J* = 12.6 Hz), 128.4, 127.9, 127.8 (d, *J* = 3.1 Hz), 127.5, 127.4, 123.1, 118.1 (d, *J* = 8.9 Hz), 95.8, 89.9 (d, *J* = 2.2 Hz),

21.6. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 27.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{32}OP^+$: 535.2185, Found: 535.2161.

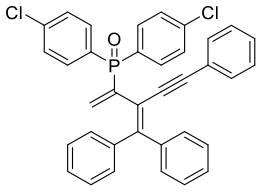
**(3-(diphenylmethylene)-5-phenylpent-1-en-4-yn-2-yl)bis(4-ethylphenyl)phosphine oxide (1w)**




1w

White solids, *m.p.*: 144.3-146.1 ℃ (139.9 mg, 83% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4H), 7.41 (d, *J* = 6.0 Hz, 2H), 7.28-7.24 (m, 7H), 7.21-7.20 (m, 3H), 7.15 (t, *J* = 6.0 Hz,1H), 7.10-7.07 (m, 4H), 6.65 (d, *J* = 6.0 Hz, 2H), 6.01(d, *J* = 42.0 Hz, 1H), 5.93 (d, *J* = 18.0 Hz, 1H), 2.66 (q, *J* = 6.0 Hz, 4H), 1.22 (t, *J* = 6.0 Hz, 6H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 152.2 (d, *J* = 7.0 Hz), 148.4 (d, *J* = 2.7 Hz), 143.1, 142.5, 141.7, 140.7, 135.6 (d, *J* = 7.9 Hz), 132.3 (d, *J* = 10.2 Hz), 131.1, 130.3 (d, *J* = 27.6 Hz), 129.5, 128.8, 127.9, 127.8, 127.8, 127.5, 127.4, 123.1, 118.2 (d, *J* = 8.8 Hz), 95.8, 89.9 (d, *J* = 2.2 Hz), 28.9, 15.3. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 28.1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{36}OP^+$: 563.2498, Found: 563.2462.

**bis(4-chlorophenyl)(3-(diphenylmethylene)-5-phenylpent-1-en-4-yn-2-yl)phosphine oxide (1x)**

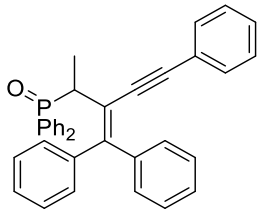



1x

White solids, *m.p.*: 147.8-149.5 ℃ (130.9 mg, 76% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 4H), 7.45-7.42 (m, 6H), 7.35-7.31 (m, 3H), 7.26-7.18 (m, 6H), 7.11-7.09 (m, 2H), 6.77-6.74 (m, 2H), 6.15 (d, *J* = 40.0 Hz, 1H), 6.04 (d, *J* = 16.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.6 (d, *J* = 7.0 Hz), 142.6, 141.7, 141.3, 140.4 (d, *J* = 1.7 Hz), 138.8 (d, *J* = 3.4 Hz), 136.5 (d, *J* = 7.9 Hz), 133.5 (d, *J* = 10.9 Hz), 131.0, 130.8, 130.2 (d, *J* = 20.0 Hz), 129.7, 128.8 (d, *J* = 12.9 Hz), 128.3 (d, *J* = 11.1 Hz), 128.1, 127.9, 127.7, 127.6, 122.7, 117.0 (d, *J* = 9.1 Hz), 96.1, 89.8 (d, *J* = 2.7 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$)

δ 26.1 (s). **HRMS (ESI):** ([M+Na]$^+$) Calcd for $C_{36}H_{25}Cl_2NaOP^+$: 597.0912, Found: 597.0905.

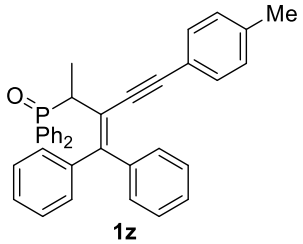
**(3-(diphenylmethylene)-5-phenylpent-4-yn-2-yl)diphenylphosphine oxide (1y)**




**1y**

White solids, *m.p.*: 145.3-147.2 ℃ (118.9 mg, 78% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.61-7.58 (m, 2H), 7.48-7.44 (m, 2 H), 7.41-7.33 (m, 9H), 7.26-7.25 (m, 3H), 7.21-7.20 (m, 3H), 7.12-7.10 (m, 2H), 6.86-6.85 (m, 2H), 3.76-3.71 (m, 1H), 1.65 (dd, *J* = 6.0 Hz, 12.0 Hz, 3H), **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 149.6 (d, *J* = 10.5 Hz), 141.3 (d, *J* = 2.4 Hz), 140.8 (d, *J* = 2.2 Hz), 132.7, 132.1, 131.7, 131.6 (d, *J* = 9.3 Hz), 131.3 (d, *J* = 8.2 Hz), 130.0, 129.3, 128.6 (d, *J* = 11.0 Hz), 128.5, 128.2, 128.1 (d, *J* = 5.9 Hz), 127.8 (d, *J* = 15.3 Hz), 127.5, 123.5, 119.0 (d, *J* = 6.9 Hz), 96.4, 88.7 (d, *J* = 4.1 Hz), 39.2 (d, *J* = 67.8 Hz), 13.6 (d, *J* = 3.3 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 33.6 (s). **HRMS (ESI):** ([M+H]$^+$) Calcd for $C_{36}H_{30}OP^+$: 509.2029, Found: 509.2019.

**(3-(diphenylmethylene)-5-(p-tolyl)pent-4-yn-2-yl)diphenylphosphine oxide (1z)**

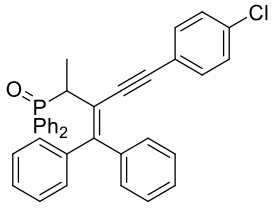



**1z**

White solids, *m.p.*: 162.2-163.8 ℃ (117.5 mg, 75% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.61-7.58 (m, 2H), 7.48-7.44 (m, 2H), 7.41-7.36 (m, 4H), 7.33-7.32 (m, 3H), 7.25-7.24 (m, 2H), 7.21-7.19 (m, 3H), 7.12-7.10 (m, 2H), 7.08 (d, *J* = 6.0 Hz, 2H), 6.85-6.84 (m, 2H), 3.75-3.70 (m, 1H), 2.32 (s, 3H), 1.64 (dd, *J* = 6.0 Hz, 12.0 Hz, 3H), **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 149.1 (d, *J* = 10.5 Hz), 141.4 (d, *J* = 2.2 Hz), 140.9 (d, *J* = 2.2 Hz), 138.3, 132.7, 132.1, 131.6, 131.3 (d, *J* = 8.3 Hz), 130.0, 129.3, 129.0, 128.6 (d, *J* = 11.1 Hz), 128.5, 128.1 (d, *J* = 11.5 Hz), 127.7 (d, *J* = 17.9 Hz), 127.4, 120.5, 119.1 (d,

*J* = 6.9 Hz), 96.7, 88.1 (d, *J* = 4.0 Hz), 39.3 (d, *J* = 67.8 Hz), 21.6, 13.6 (d, *J* = 3.2 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 33.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{32}OP^+$: 523.2185, Found: 523.2183.

**(5-(4-chlorophenyl)-3-(diphenylmethylene)pent-4-yn-2-yl)diphenylphosphine oxide (1aa)**

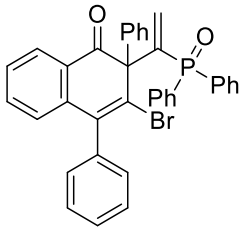



**1aa**

White solids, *m.p.*: 137.8-139.6 ℃ (99.2 mg, 61% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.62-7.59 (m, 2H), 7.47-7.43 (m, 2H), 7.41-7.36 (m, 4H), 7.35-7.33 (m, 3H), 7.30-7.29 (m, 2H), 7.24-7.22 (m, 2H), 7.21-7.19 (m, 3H), 7.09-7.07 (m, 2H), 6.87-6.86 (m, 2H), 3.75-3.70 (m, 1H), 1.64 (dd, *J* = 6.0 Hz, 12.0 Hz, 3H), **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 149.9 (d, *J* = 10.3 Hz), 141.3, 140.7, 134.1, 132.9, 131.7 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 9.2 Hz), 131.3 (d, *J* = 8.2 Hz), 129.9, 129.3, 128.6 (d, *J* = 11.2 Hz), 128.5, 128.2 (d, *J* = 11.5 Hz), 127.9 (d, *J* = 17.4 Hz), 127.5, 122.1, 118.9 (d, *J* = 6.7 Hz), 95.2, 89.8, 39.1 (d, *J* = 68.1 Hz), 13.6 (d, *J* = 3.2 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 33.1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{29}ClOP^+$: 543.1639, Found: 543.1633.

## 8.2 Products

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-2,4-diphenylnaphthalen-1(2H)-one (2a)**

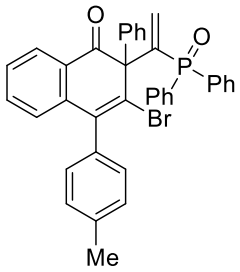



**2a**

White solids, *m.p.*: 191.7-193.5 ℃ (50.4 mg, 84% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94-7.90 (m, 3H), 7.79-7.76 (m, 2H), 7.73 (d, *J* = 6.0 Hz, 2H), 7.56-7.50 (m, 5H), 7.46-7.43 (m, 3H), 7.40-7.37 (m,

3H), 7.35-7.31 (m, 2H), 7.30-7.26 (m, 2H), 7.24-7.22 (m, 1H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.07 (d, *J* = 12.0 Hz, 1H), 6.02 (d, *J* = 30.0 Hz, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.0, 148.0 (d, *J* = 94.5 Hz), 140.6 (d, *J* = 91.4 Hz), 138.2, 135.6 (d, *J* = 9.7 Hz), 135.3 (d, *J* = 7.4 Hz), 134.3, 133.9, 133.4 (d, *J* = 56.7 Hz), 132.4 (d, *J* = 9.6 Hz), 132.1 (d, *J* = 10.4 Hz), 131.7 (d, *J* = 2.2 Hz), 131.6 (d, *J* = 2.1 Hz), 129.8 (d, *J* = 90.9 Hz), 129.2 (d, *J* = 32.9 Hz), 128.8 (d, *J* = 25.7 Hz), 128.6, 128.5, 128.3 (d, *J* = 1.8 Hz), 128.2, 128.1 (d, *J* = 12.0 Hz), 127.9 (d, *J* = 5.1 Hz), 127.7, 69.7 (d, *J* = 9.4 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{26}BrNaO_2P^+$: 623.0746, Found: 623.0745.

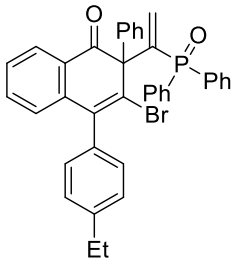
**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-2-phenyl-4-(p-tolyl)naphthalen-1(2H)-one (2b)**




**2b**

White solids, *m.p.*: 267.3-269.1 ℃ (47.9 mg, 78% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.93-7.89 (m, 3H), 7.79-7.76 (m, 2H), 7.72 (d, *J* = 12.0 Hz, 2H), 7.56-7.54 (m, 1H), 7.52-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.37 (m, 2H), 7.36-7.32 (m, 5H), 7.30-7.28 (m, 1H), 7.27-7.25 (m, 2H), 7.24-7.22 (m, 1H), 6.80 (d, *J* = 6.0 Hz, 1H), 6.07 (d, *J* = 6.0 Hz, 1H), 6.02 (d, J = 30.0 Hz, 1H), 2.45 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.1, 148.0 (d, *J* = 94.3 Hz), 140.9, 137.8 (d, *J* = 155.2 Hz), 137.6, 135.6 (d, *J* = 9.7 Hz), 135.4 (d, *J* = 7.6 Hz), 134.1 (d, *J* = 58.6 Hz), 133.9, 133.4 (d, *J* = 57.2 Hz), 132.4 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 10.0 Hz), 131.7 (d, *J* = 2.1 Hz), 131.6 (d, *J* = 2.8 Hz), 130.0 (d, *J* = 56.8 Hz), 129.3 (d, *J* = 21.7 Hz), 129.1, 128.7 (d, *J* = 18.3 Hz), 128.5, 128.3 (d, *J* = 16.1 Hz), 128.2, 128.1 (d, *J* = 12.0 Hz), 127.8 (d, *J* = 17.7 Hz), 69.7 (d, *J* = 9.4 Hz), 21.5. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{29}BrO_2P^+$: 615.1083, Found: 615.1077.

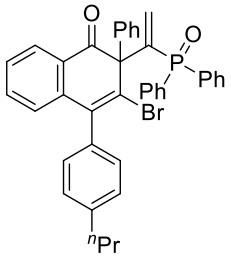
**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-4-(4-ethylphenyl)-2-phenylnaphthalen-1(2H)-one (2c)**



**2c**

White solids, *m.p.*: 266.7-268.5 ℃ (51.5 mg, 82% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 3H), 7.83-7.79 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.61-7.52 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45-7.35 (m, 7H), 7.33-7.25 (m, 4H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 6.04 (d, *J* = 28.0 Hz, 1H), 2.80 (q, *J* = 8.0 Hz, 2H), 1.37 (t, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.1, 147.9 (d, *J* = 94.5 Hz), 143.7, 140.9, 137.9 (d, *J* = 90.4 Hz), 135.7 (d, *J* = 9.8 Hz), 135.4 (d, *J* = 7.5 Hz), 134.2 (d, *J* = 36.9 Hz), 133.9, 133.2 (d, *J* = 36.0 Hz), 132.3 (d, *J* = 9.5 Hz), 132.1 (d, *J* = 10.2 Hz), 131.7 (d, *J* = 7.9 Hz), 130.1, 129.2 (d, *J* = 22.4 Hz), 128.8, 128.6, 128.5, 128.4 (d, *J* = 15.6 Hz), 128.2, 128.1, 128.0 (d, *J* = 13.2 Hz), 127.8 (d, *J* = 6.8 Hz), 69.7 (d, *J* = 9.2 Hz), 28.7, 15.4. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{31}BrO_2P^+$: 629.1240, Found: 629.1242.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-2-phenyl-4-(4-propylphenyl)naphthalen-1(2H)-one (2d)**

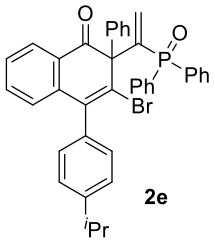


**2d**

White solids, *m.p.*: 258.6-260.3 ℃ (57.1 mg, 89% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 3H), 7.86-7.81 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.62-7.55 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 2H), 7.40-7.31 (m, 7H), 7.28-7.25 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 6.06 (d, *J* = 28.0 Hz, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.84-1.75 (m, 2H), 1.07 (t, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.2, 148.0 (d, *J* = 94.2 Hz), 142.3, 140.9, 137.9 (d, *J* = 85.6 Hz), 135.6 (d, *J* = 9.7 Hz), 135.4 (d, *J* = 7.6 Hz), 134.4 (d, *J* = 35.8 Hz), 133.9, 133.3 (d, *J* = 34.6 Hz), 132.4 (d, *J* = 9.3 Hz), 132.2

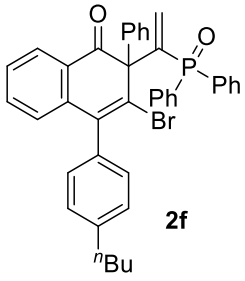
(d, *J* = 10.2 Hz), 131.7 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 2.8 Hz), 130.2, 129.3, 129.1, 128.8 (d, *J* = 16.1 Hz), 128.5, 128.3, 128.2, 128.1 (d, *J* = 12.0 Hz), 127.8 (d, *J* = 7.7 Hz), 69.8 (d, *J* = 9.2 Hz), 38.0, 24.5, 14.1. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{33}BrO_2P^+$: 643.1396, Found: 643.1391.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-4-(4-isopropylphenyl)-2-phenylnaphthalen-1(2H)-one (2e)**




White solids, *m.p.*: 228.2-230.0 ℃ (53.3 mg, 83% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.95 (m, 3H), 7.88-7.79 (m, 4H), 7.60-7.51 (m, 3H), 7.50-7.43 (m, 6H), 7.40-7.30 (m, 5H), 7.27-7.23 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 28.0 Hz, 1H), 3.12-3.02 (m, 1H), 1.41 (s, 3H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.1, 148.4, 148.1 (d, *J* = 94.3 Hz), 140.9, 138.0 (d, *J* = 81.4 Hz), 135.6 (d, *J* = 9.6 Hz), 135.5 (d, *J* = 7.6 Hz), 134.4 (d, *J* = 34.9 Hz), 133.9, 133.4 (d, *J* = 33.9 Hz), 132.4 (d, *J* = 9.4 Hz), 132.2 (d, *J* = 10.2 Hz), 131.7 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 2.6 Hz), 130.2, 129.3 (d, *J* = 18.6 Hz), 128.9, 128.6, 128.3, 128.2 (d, *J* = 2.3 Hz), 128.1, 127.8, 126.8 (d, *J* = 59.0 Hz), 69.8 (d, *J* = 9.2 Hz), 34.0, 24.1 (d, *J* = 11.8 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{33}BrO_2P^+$: 643.1396, Found: 643.1390.

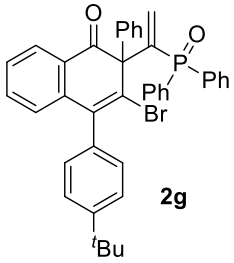
**3-bromo-4-(4-butylphenyl)-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2f)**




White solids, *m.p.*: 247.5-249.3 ℃ (55.8 mg, 85% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94-7.89 (m, 3H), 7.79-7.76

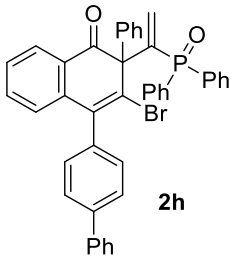
(m, 2H), 7.72 (d, *J* = 12.0 Hz, 2H), 7.55-7.53 (m, 1H), 7.51-7.49 (m, 2H), 7.46-7.44 (m, 1H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 5H), 7.29-7.25 (m, 3H), 7.23-7.20 (m, 1H), 6.79 (d, *J* = 12.0 Hz, 1H), 6.06 (d, *J* = 12.0 Hz, 1H), 6.01 (d, *J* = 36.0 Hz, 1H), 2.71 (t, *J* = 12.0 Hz, 2H), 1.73-1.68 (m, 2H), 1.47-1.41 (m, 2H), 0.98 (t, *J* = 12.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.0, 148.1 (d, *J* = 94.4 Hz), 142.5, 140.9, 138.4, 137.5, 135.5, 134.2 (d, *J* = 51.4 Hz), 133.8, 133.5 (d, *J* = 50.7 Hz), 132.4 (d, *J* = 9.5 Hz), 132.2 (d, *J* = 10.0 Hz), 131.6 (d, *J* = 10.2 Hz), 130.2, 129.3, 129.1 (d, *J* = 20.4 Hz), 128.8 (d, *J* = 16.6 Hz), 128.5, 128.4, 128.3, 128.2, 128.1 (d, *J* = 12.0 Hz), 127.8 (d, *J* = 9.7 Hz), 69.8 (d, *J* = 9.1 Hz), 35.6, 33.6, 22.6, 14.1. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{35}BrO_2P^+$: 657.1553, Found: 657.1556.

**3-bromo-4-(4-(tert-butyl)phenyl)-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2g)**




White solids, *m.p.*: 250.8-252.7 ℃ (48.5 mg, 74% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 3H), 7.84-7.79 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.59-7.49 (m, 6H), 7.46-7.42 (m, 2H), 7.39-7.35 (m, 3H), 7.33-7.24 (m, 4H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 32.0 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.1, 150.6, 148.5, 140.9, 137.7 (d, *J* = 125.1 Hz), 135.6, 135.4, 134.3 (d, *J* = 29.3 Hz), 133.8, 133.5, 132.4 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 10.2 Hz), 131.6 (d, *J* = 7.4 Hz), 130.1, 128.9 (d, *J* = 13.9 Hz), 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 125.5 (d, *J* = 47.1 Hz), 69.8 (d, *J* = 9.2 Hz), 34.8, 31.5. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{35}BrO_2P^+$: 657.1553, Found: 657.1555.

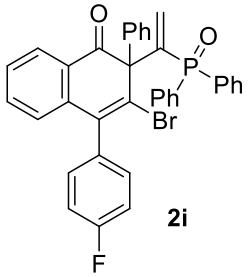
**4-([1,1'-biphenyl]-4-yl)-3-bromo-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2h)**




**2h**

White solids, *m.p.*: 157.7-159.6 ℃ (42.6 mg, 63% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94-7.91 (m, 3H), 7.81-7.78 (m, 3H), 7.76-7.73 (m, 3H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.58-7.55 (m, 1H), 7.53-7.46 (m, 6H), 7.44-7.39 (m, 4H), 7.37-7.33 (m, 3H), 7.30-7.25 (m, 2H), 6.86 (d, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 12.0 Hz, 1H), 6.03 (d, *J* = 36.0 Hz, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 195.9, 148.0 (d, *J* = 94.0 Hz), 140.7, 140.6 (d, *J* = 4.6 Hz), 139.2, 138.1, 135.5, 135.4, 134.4, 133.9, 132.4 (d, *J* = 9.5 Hz), 132.1 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 9.3 Hz), 130.1, 129.9 (d, *J* = 33.2 Hz), 128.9, 128.8 (d, *J* = 26.8 Hz), 128.5, 128.3 (d, *J* = 2.9 Hz), 128.2, 128.1 (d, *J* = 12.0 Hz), 127.9, 127.7 (d, *J* = 4.6 Hz), 127.5, 127.2, 127.1, 69.7 (d, *J* = 8.8 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 30.4 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{42}H_{31}BrO_2P^+$: 677.1240, Found: 677.1241.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-4-(4-fluorophenyl)-2-phenylnaphthalen-1(2H)-one (2i)**

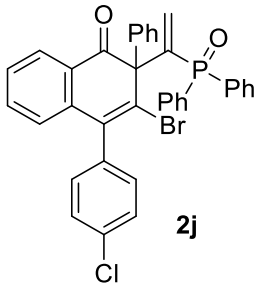



**2i**

White solids, *m.p.*: 229.5-231.3 ℃ (43.3 mg, 70% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 3H), 7.82-7.77 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.60-7.52 (m, 3H), 7.51-7.49 (m, 1H), 7.47-7.41 (m, 3H), 7.40-7.31 (m, 5H), 7.30-7.21 (m, 3H), 6.80 (d, *J* = 4.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 6.04 (d, *J* = 24.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.9, 162.3 (d, *J* = 246.9 Hz), 147.8 (d, *J* = 94.5 Hz), 139.0 (d, *J* = 196.8 Hz), 136.1, 135.6 (d, *J* = 9.7 Hz), 135.1 (d, *J* = 7.6 Hz), 134.2 (d, *J* = 38.2 Hz), 133.9, 133.2 (d, *J* = 36.9 Hz), 132.2 (dd, *J* = 21.8, 9.8 Hz), 131.7 (dd, *J* = 5.9, 2.9 Hz), 131.2 (dd, *J* = 13.1, 8.1 Hz), 130.1, 129.5, 128.7, 128.6, 128.4 (d, *J* = 7.5 Hz), 128.3 (d, *J* = 5.8 Hz), 128.1 (d, *J* = 12.0 Hz), 127.7 (d, *J* = 51.8 Hz), 116.2 (d, *J* = 21.4 Hz), 115.6 (d, *J* = 21.7 Hz), 69.70 (d, *J*

= 9.2 Hz). **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -116.2 (s). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{26}BrFO_2P^+$: 619.0832, Found: 619.0836.

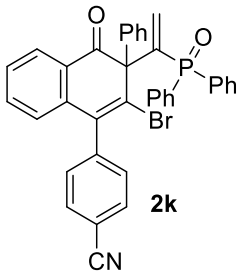
**3-bromo-4-(4-chlorophenyl)-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2j)**



**2j**

White solids, *m.p.*: 260.7-262.6 ℃ (41.2 mg, 65% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 3H), 7.82-7.77 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.62-7.49 (m, 6H), 7.46-7.41 (m, 3H), 7.39-7.34 (m, 4H), 7.33-7.27 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 4.0 Hz, 1H), 6.05 (d, *J* = 28.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.8, 147.8 (d, *J* = 94.3 Hz), 139.8, 138.2 (d, *J* = 81.4 Hz), 135.7 (d, *J* = 9.7 Hz), 135.1 (d, *J* = 7.6 Hz), 134.4, 133.9 (d, *J* = 9.8 Hz), 133.2 (d, *J* = 38.8 Hz), 132.3 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 10.2 Hz), 131.7 (d, *J* = 7.4 Hz), 130.9 (d, *J* = 19.1 Hz), 130.0, 129.4, 129.3, 128.8, 128.6, 128.5 (d, *J* = 18.3 Hz), 128.3 (d, *J* = 5.4 Hz), 128.2 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 7.0 Hz), 127.4, 69.7 (d, *J* = 9.1 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{26}BrClO_2P^+$: 635.0537, Found: 635.0540.

**4-(2-bromo-3-(1-(diphenylphosphoryl)vinyl)-4-oxo-3-phenyl-3,4-dihydronaphthalen-1-yl)benzonitrile (2k)**

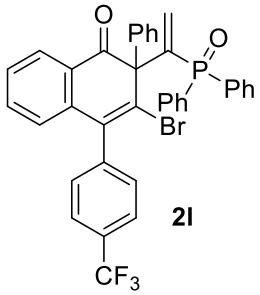


**2k**

White solids, *m.p.*: 146.3-148.3 ℃ (38.8 mg, 62% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 3H), 7.89-7.83 (m, 2H), 7.79-7.74 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.62-7.49 (m, 6H), 7.45-7.34 (m,

5H), 7.32-7.28 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 6.04 (d, *J* = 28.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.4, 147.5 (d, *J* = 94.2 Hz), 145.0, 138.2 (d, *J* = 223.3 Hz), 135.8 (d, *J* = 9.7 Hz), 134.8 (d, *J* = 7.5 Hz), 134.1 (d, *J* = 33.0 Hz), 133.5 (d, *J* = 100.0 Hz), 133.1 (d, *J* = 31.5 Hz), 132.4, 132.2 (d, *J* = 9.4 Hz), 132.0 (d, *J* = 10.3 Hz), 131.8, 130.5 (d, *J* = 18.3 Hz), 129.9, 129.4, 128.8, 128.6, 128.4 (d, *J* = 3.5 Hz), 128.2 (d, *J* = 1.8 Hz), 128.1, 127.0, 118.7, 112.0, 69.6 (d, *J* = 9.1 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{26}BrNO_2P^+$: 626.0879, Found: 626.0867.

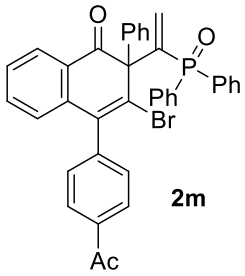
**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-2-phenyl-4-(4-(trifluoromethyl)phenyl) naphthalen-1(2H)-one (2l)**




**2l**

White solids, *m.p.*: 257.6-259.4 ℃ (43.4 mg, 65% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.95-7.91 (m, 3H), 7.84-7.75 (m, 4H), 7.73-7.71 (m, 2H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.57-7.51 (m, 4H), 7.49-7.46 (m, 1H), 7.43-7.39 (m, 2H), 7.37-7.32 (m, 3H), 7.31-7.24 (m, 2H), 6.69 (d, *J* = 10.0 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 6.04 (d, *J* = 35.0 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 195.7, 147.8 (d, *J* = 94.1 Hz), 144.0, 139.8, 137.6, 135.8 (d, *J* = 9.6 Hz), 135.1 (d, *J* = 7.6 Hz), 134.2 (d, *J* = 43.9 Hz), 134.1, 133.4 (d, *J* = 42.5 Hz), 132.3 (d, *J* = 9.3 Hz), 132.1 (d, *J* = 10.2 Hz), 131.8 (t, *J* = 3.6 Hz), 130.3, 130.1 (t, *J* = 11.9 Hz), 129.4, 128.6 (d, *J* = 34.4 Hz), 128.3 (d, *J* = 5.5 Hz), 128.2, 127.3, 126.2 (d, *J* = 3.9 Hz), 125.7 (d, *J* = 4.0 Hz), 125.4, 123.2, 69.7 (d, *J* = 9.0 Hz). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -62.2 (s). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{26}BrF_3O_2P^+$: 669.0800, Found: 669.0788.

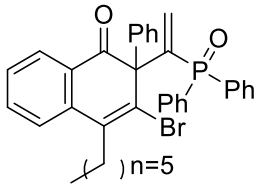
**4-(4-acetylphenyl)-3-br**om**o-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen -1(2H)-one (2m)**




**2m**

White solids, *m.p.*:185.4-187.2 ℃ (36.6 mg, 57% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate = 3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.16-8.14 (m, 1H), 8.11-8.09 (m, 1H), 7.93-7.88 (m, 3H), 7.77-7.73 (m, 2H), 7.71-7.69 (m, 2H), 7.57-7.54 (m, 2H), 7.53-7.49 (m, 3H), 7.47-7.45 (m, 1H), 7.41-7.37 (m, 2H), 7.36-7.33 (m, 2H), 7.31-7.24 (m, 3H), 6.70-6.68 (m, 1H), 6.08 (d, *J* = 5 Hz, 1H), 6.01 (d, *J* = 30 Hz, 1H), 2.68 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 197.9, 195.7, 147.8 (d, *J* = 94.5 Hz), 145.2, 140.1, 137.1 (d, *J* = 119.6 Hz), 135.8 (d, *J* = 9.6 Hz), 135.1 (d, *J* = 7.3 Hz), 134.1 (d, *J* = 48.6 Hz), 134.0, 133.3 (d, *J* = 47.7 Hz), 132.3 (d, *J* = 9.2 Hz), 132.1 (d, *J* = 10.2 Hz), 131.8 (d, *J* = 6.1 Hz), 130.1 (d, *J* = 3.9 Hz), 129.6 (d, *J* = 58.0 Hz), 129.0, 128.7, 128.6 (d, *J* = 4.8 Hz), 128.4, 128.3 (d, *J* = 6.5 Hz), 128.2 (d, *J* = 4.3 Hz), 127.3, 69.7 (d, *J* = 9.2 Hz), 26.8. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{29}BrO_3P^+$: 643.1032, Found: 643.1020.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-4-hexyl-2-phenylnaphthalen-1(2H)-one (2o)**

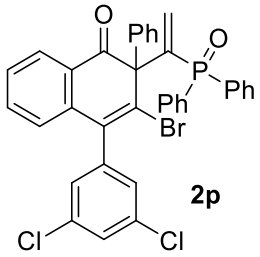



**2o**

White solids, *m.p.*:102.7-103.8 ℃ (18.2 mg, 30% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate = 3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.88-7.83 (m, 3H), 7.78-7.74 (m, 2H), 7.55-7.53 (m, 2H), 7.52-7.48 (m, 3H), 7.46-7.40 (m, 4H), 7.28-7.22 (m, 5H), 6.08 (d, *J* = 20 Hz, 1H), 6.00 (d, *J* = 40 Hz, 1H), 2.91-2.88 (m, 2H), 1.82-1.73 (m, 1H), 1.67-1.64 (m, 1H), 1.56-1.50 (m, 2H), 1.41-1.35 (m, 4H), 0.93 (t, *J* = 5 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 196.4, 147.8, 138.1, 136.7, 135.6 (d, *J* = 8.7 Hz), 134.2, 132.4 (dd, *J* = 13.4, 9.8 Hz), 132.0, 131.6 (d, *J* = 10.8 Hz), 130.2, 129.6, 129.1, 128.4, 128.3 (d, *J* = 5.7 Hz), 128.1, 128.1, 127.9, 127.5, 124.9, 69.9, 34.2, 31.8, 29.8, 27.7, 22.8, 14.3. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.0 (s).

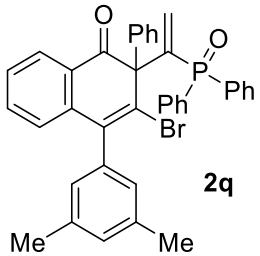
**HRMS (ESI):** ([M+H]$^+$) Calcd for $C_{36}H_{35}BrO_2P^+$: 609.1553, Found: 609.1544.

**3-bromo-4-(3,5-dichlorophenyl)-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2p)**




White solids, *m.p.*: 209.3-210.7 ℃ (46.8 mg, 70% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.91 (m, 3H), 7.86-7.81 (m, 2H), 7.72-7.70 (m, 2H), 7.60-7.52 (m, 4H), 7.50-7.47 (m, 3H), 7.41-7.37 (m, 4H), 7.34-7.30 (m, 3H), 6.80 (d, *J* = 8 Hz, 1H), 6.14 (s, 1H), 6.07 (d, *J* = 20 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.4 (d, *J* = 1.9 Hz), 147.9 (d, *J* = 94.2 Hz), 142.8, 137.9 (d, *J* = 180.8 Hz), 135.5 (d, *J* = 9.7 Hz), 135.4 (d, *J* = 70.7 Hz), 134.8 (d, *J* = 7.5 Hz), 134.4, 134.0, 133.4 (d, *J* = 3.8 Hz), 132.3 (d, *J* = 9.3 Hz), 132.2 (d, *J* = 10.4 Hz), 131.9 (d, *J* = 2.8 Hz), 130.0, 129.7, 128.8 (d, *J* = 9.1 Hz), 128.7, 128.4 (d, *J* = 4.9 Hz), 128.3, 128.2, 128.1 (d, *J* = 2.9 Hz), 128.0 (d, *J* = 6.8 Hz), 127.1, 69.5 (d, *J* = 9.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.3 (s). **HRMS (ESI):** ([M+H]$^+$) Calcd for $C_{36}H_{25}BrCl_2O_2P^+$: 669.0147, Found: 669.0132.

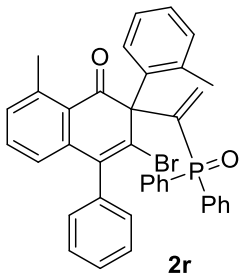
**3-bromo-4-(3,5-dimethylphenyl)-2-(1-(diphenylphosphoryl)vinyl)-2-phenylnaphthalen-1(2H)-one (2q)**




White solids, *m.p.*: 222.3-223.7 ℃ (50.2 mg, 80% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.93-7.90 (m, 3H), 7.83-7.79 (m, 2H), 7.73 (d, *J* = 6.0 Hz, 2H), 7.55-7.44 (m, 4H), 7.40-7.38 (m, 2H), 7.35-7.32 (m, 2H), 7.31-7.25 (m, 2H), 7.23-7.21 (m, 1H), 7.05 (d, *J* = 18.0 Hz, 2H), 6.95 (s, 1H), 6.80 (d, *J* = 12.0 Hz, 1H), 6.08 (d, *J* = 6.0 Hz, 1H), 6.03 (d, *J* = 18.0 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.0, 148.2 (d, *J* = 94.5 Hz), 141.2,

140.1, 138.4 (d, *J* = 35.4 Hz), 137.9, 135.4 (d, *J* = 4.4 Hz), 134.5, 133.8, 133.1, 132.4 (d, *J* = 9.4 Hz), 132.2 (d, *J* = 10.2 Hz), 131.6 (d, *J* = 10.6 Hz), 130.2, 129.4, 128.7, 128.5, 128.3 (d, *J* = 12.5 Hz), 128.2 (d, *J* = 4.2 Hz), 128.1 (d, *J* = 12.0 Hz), 127.8 (d, *J* = 8.1 Hz), 126.9 (d, *J* = 25.2 Hz), 69.7 (d, *J* = 9.3 Hz), 21.5 (d, *J* = 19.2 Hz). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{31}BrO_2P^+$: 629.1240, Found: 629.1238.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-8-methyl-4-phenyl-2-(o-tolyl)naphthalen-1(2H)-one (2r)**

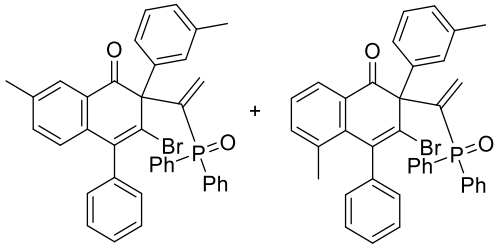



**2r**

Yellow oil, (35.2 mg, 56% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.74-7.68 (m, 3H), 7.56-7.51 (m, 3H), 7.49-7.43 (m, 6H), 7.40-7.35 (m, 2H), 7.31-7.29 (m, 1H), 7.25-7.22 (m, 2H), 7.21-7.19 (m, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 4.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 6.12 (d, *J* = 20.0 Hz, 1H), 2.31 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.8, 142.5, 140.7, 140.6, 138.8, 138.2 (d, *J* = 10.1 Hz), 132.8, 132.4, 132.2 (d, *J* = 9.3 Hz), 131.6, 131.4 (d, *J* = 2.8 Hz), 131.3, 131.2 (d, *J* = 5.6 Hz), 129.9, 128.9, 128.8, 128.3, 128.2 (d, *J* = 4.1 Hz), 128.1, 128.0, 127.7, 126.0, 125.8, 72.2, 22.6, 21.6. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.0 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{31}BrO_2P^+$: 629.1240, Found: 629.1226.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-7-methyl-4-phenyl-2-(m-tolyl)naphthalen-1(2H)-one**

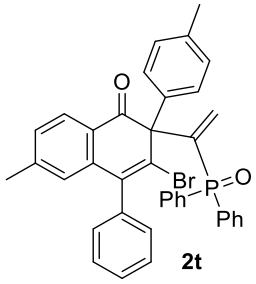
**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-5-methyl-4-phenyl-2-(m-tolyl)naphthalen-1(2H)-one (2s+2s')**



**2s** **2s'** (Mixture which cannot be separated)

Yellow oil, (33.9 mg, 54% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.85-7.70 (m, 3H), 7.58-7.49 (m, 7H), 7.48-7.37 (m, 6H), 7.25-7.22 (m, 1H), 7.13-7.09 (m, 2H), 6.67 (d, *J* = 5.0 Hz, 1H), 6.10-5.79 (m, 2H), 2.35 (s, 3H), 2.27-2.23 (m, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.3 (d, *J* = 1.9 Hz), 148.0 (d, *J* = 94.5 Hz), 140.6 (d, *J* = 24.3 Hz), 138.2 (d, *J* = 37.5 Hz), 135.8, 135.5 (d, *J* = 9.7 Hz), 135.3 (d, *J* = 7.6 Hz), 134.6, 134.1, 133.6, 133.1, 132.4 (d, *J* = 9.3 Hz), 132.2 (d, *J* = 10.2 Hz), 131.7 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 2.6 Hz), 130.7, 129.4 (d, *J* = 11.8 Hz), 129.0, 128.5 (d, *J* = 6.6 Hz), 128.4 (d, *J* = 4.1 Hz), 128.2 (d, *J* = 5.0 Hz), 128.1 (d, *J* = 12.2 Hz), 127.7 (d, *J* = 6.1 Hz), 127.3, 69.7 (d, *J* = 9.0 Hz), 21.9, 21.1. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.1:30.7 = 4.3:1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{31}BrO_2P^+$: 629.1240, Found: 629.1234.

**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-6-methyl-4-phenyl-2-(p-tolyl)naphthalen-1(2H)-one (2t)**

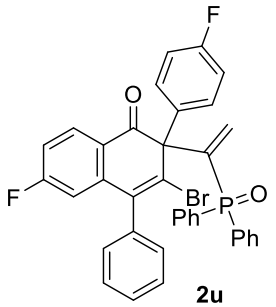


**2t**

White solids, *m.p.*: 224.7-226.3 ℃ (29.5 mg, 47% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.91 (m, 2H), 7.85-7.77 (m, 3H), 7.63-7.58 (m, 3H), 7.57-7.53 (m, 4H), 7.51-7.46 (m, 3H), 7.44-7.38 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 6.11 (d, *J* = 12.0 Hz, 1H), 6.03 (d, *J* = 12.0 Hz, 1H), 2.33 (s, 3H), 2.21 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 195.7, 148.0 (d, *J* = 94.1 Hz), 144.6, 140.6 (d, *J* = 42.6 Hz), 138.1 (d, *J* = 33.6 Hz), 135.4 (d, *J* = 9.7 Hz), 134.4 (d, *J* = 41.5 Hz), 133.7 (d, *J* = 40.8 Hz), 132.5 (d, *J* = 7.9 Hz), 132.4 (d, *J* = 9.1 Hz), 132.1 (d, *J* = 10.4 Hz), 131.5 (d, *J* = 10.7 Hz), 130.0, 129.5, 129.4, 129.2, 129.0 (d, *J* = 23.8 Hz), 128.4, 128.2 (d, *J* = 12.2 Hz),

128.1, 127.9 (d, $J$ = 38.0 Hz), 126.5, 69.4 (d, $J$ = 9.1 Hz), 21.9, 21.0. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{31}BrO_2P^+$: 629.1240, Found: 629.1242.

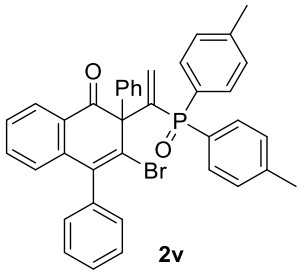
**3-bromo-2-(1-(diphenylphosphoryl)vinyl)-6-fluoro-2-(4-fluorophenyl)-4-phenyln aphthalen-1(2H)-one (2u)**




**2u**

White solids, *m.p.*: 184.5-186.3 ℃ (27.4 mg, 43% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.95-7.92 (m, 1H), 7.90-7.86 (m, 2H), 7.77-7.73 (m, 2H), 7.69-7.65 (m, 2H), 7.59-7.55 (m, 2H), 7.53-7.50 (m, 3H), 7.49-7.45 (m, 2H), 7.42-7.38 (m, 3H), 7.35-7.33 (m, 1H), 7.05-7.02 (m, 2H), 6.95-6.92 (m, 1H), 6.47-6.44 (m, 1H), 6.07-5.96 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 194.5, 166.4 (d, $J$ = 254.5 Hz), 162.7 (d, $J$ = 248.8 Hz), 148.0 (d, $J$ = 94.2 Hz), 140.9 (d, $J$ = 9.4 Hz), 140.4, 139.5, 135.6 (d, $J$ = 9.7 Hz), 133.5 (dd, $J$ = 103.7, 65.0 Hz), 132.2 (dd, $J$ = 28.9, 9.8 Hz), 132.0 (d, $J$ = 16.4 Hz), 131.9, (d, $J$ = 2.5 Hz), 131.0 (d, $J$ = 9.7 Hz), 130.5, 129.3 (d, $J$ = 5.2 Hz), 129.0 (d, $J$ = 47.9 Hz), 128.4 (d, $J$ = 12.4 Hz), 128.3, 128.2, 125.2, 115.7 (d, $J$ = 22.3 Hz), 115.6 (d, $J$ = 21.5 Hz), 114.7 (d, $J$ = 24.5 Hz), 69.0 (d, $J$ = 9.5 Hz). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -102.9 (s), -113.5 (s). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{25}BrF_2O_2P^+$: 637.0738, Found: 637.0736.

**3-bromo-2-(1-(di-p-tolylphosphoryl)vinyl)-2,4-diphenylnaphthalen-1(2H)-one (2v)**

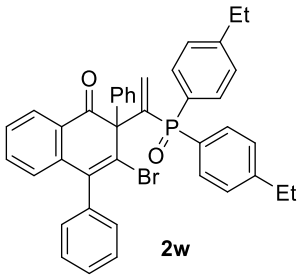



**2v**

White solids, *m.p.*: 243.0-244.8 ℃ (46.5 mg, 74% yield). TLC ($R_f$ = 0.25, petroleum

ether/ethyl acetate=3:1). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.90-7.84 (m, 2H), 7.80 (d, *J* = 4.0 Hz, 2H), 7.75-7.70 (m, 2H), 7.62-7.56 (m, 2H), 7.52-7.45 (m, 3H), 7.40-7.32 (m, 6H), 7.30-7.23 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.14-6.00 (m, 2H), 2.47 (s, 3H), 2.39 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.0, 148.4 (d, *J* = 94.3 Hz), 141.9 (d, *J* = 6.8 Hz), 140.6 (d, *J* = 34.5 Hz), 138.2, 135.5 (d, *J* = 7.6 Hz), 135.4 (d, *J* = 9.7 Hz), 133.8, 132.4 (d, *J* = 9.7 Hz), 132.2 (d, *J* = 10.5 Hz), 131.4 (d, *J* = 21.9 Hz), 130.4 (d, *J* = 21.2 Hz), 130.2, 129.5 (d, *J* = 20.5 Hz), 129.1, 128.9 (d, *J* = 2.0 Hz), 128.8, 128.7, 128.5, 128.2 (d, *J* = 4.8 Hz), 127.9 (d, *J* = 6.1 Hz), 127.6, 69.7 (d, *J* = 9.2 Hz), 21.7 (d, *J* = 11.0 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{38}H_{30}BrNaO_2P^+$: 651.1059, Found: 651.1052.

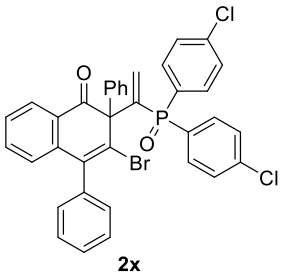
**2-(1-(bis(4-ethylphenyl)phosphoryl)vinyl)-3-bromo-2,4-diphenylnaphthalen-1(2H)-one (2w)**



**2w**

White solids, *m.p.*: 158.5-160.3 ℃ (49.9 mg, 76% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 1H), 7.90-7.85 (m, 2H), 7.79-7.71 (m, 4H), 7.61-7.54 (m, 2H), 7.51-7.47 (m, 2H), 7.44-7.42 (m, 1H), 7.40-7.36 (m, 4H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 3H), 6.80 (d, *J* = 8 Hz, 1H), 6.14-6.00 (m, 2H), 2.76 (q, *J* = 8 Hz, 16Hz, 2H), 2.69 (q, *J* = 8 Hz, 16Hz, 2H), 1.31 (t, *J* = 8 Hz, 3H), 1.25 (t, *J* = 8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.0, 148.3 (d, *J* = 94.2 Hz), 148.0, 140.6 (d, *J* = 42.9 Hz), 138.2, 135.5, 135.4 (d, *J* = 18.0 Hz), 133.8, 132.5 (d, *J* = 9.7 Hz), 132.3 (d, *J* = 10.6 Hz), 131.5 (d, *J* = 30.4 Hz), 130.4 (d, *J* = 29.5 Hz), 130.2, 129.4 (d, *J* = 16.6 Hz), 129.1, 129.0, 128.7, 128.5, 128.2 (d, *J* = 6.6 Hz), 127.9, 127.8, 127.7 (d, *J* = 3.1 Hz), 127.6 (d, *J* = 5.5 Hz), 69.7 (d, *J* = 9.3 Hz), 28.9 (d, *J* = 10.4 Hz), 15.2. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{35}BrO_2P^+$: 657.1553, Found: 657.1539.

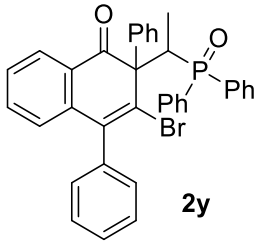
**2-(1-(bis(4-chlorophenyl)phosphoryl)vinyl)-3-bromo-2,4-diphenylnaphthalen-1(2H)-one (2x)**




**2x**

White solids, *m.p.*: 127.5-129.2 ℃ (48.1 mg, 72% yield). TLC ($R_f$ = 0.25, petroleum ether/ethy acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.86 (m, 3H), 7.75-7.70 (m, 4H), 7.62-7.48 (m, 6H), 7.44-7.37 (m, 4H), 7.36-7.31 (m, 2H), 7.29-7.25 (m, 2H), 6.81 (d, *J* = 8 Hz, 1H), 6.10 (d, *J* = 8 Hz, 1H), 6.03 (d, *J* = 16 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.3, 147.6 (d, *J* = 96.1 Hz), 140.5 (d, *J* = 85.0 Hz), 138.5, 138.4 (d, *J* = 6.4 Hz), 138.1, 136.0 (d, *J* = 9.8 Hz), 134.9 (d, *J* = 7.7 Hz), 134.1, 133.7 (d, *J* = 10.3 Hz), 133.5 (d, *J* = 11.1 Hz), 132.6 (d, *J* = 17.9 Hz), 131.5 (d, *J* = 16.7 Hz), 129.7 (d, *J* = 46.1 Hz), 129.1 (d, *J* = 4.9 Hz), 128.8, 128.7, 128.6 (d, *J* = 5.6 Hz), 128.5, 128.4 (d, *J* = 2.2 Hz), 128.0, 127.8 (d, *J* = 12.4 Hz), 69.8 (d, *J* = 9.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{24}BrCl_2NaO_2P^+$: 690.9967, Found: 690.9962.

**3-bromo-2-(1-(diphenylphosphoryl)ethyl)-2,4-diphenylnaphthalen-1(2H)-one (2y)**

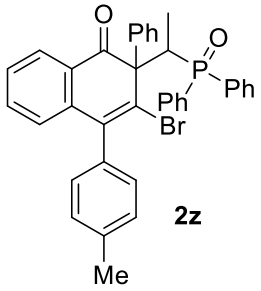



**2y**

White solids, *m.p.*: 241.7-243.3 ℃ (45.2 mg, 75% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 2H), 7.88 (d, *J* = 8 Hz, 1H), 7.78-7.73 (m, 2H), 7.67 (t, *J* = 8 Hz, 1H), 7.59-7.56 (m, 3H), 7.55-7.50 (m, 5H), 7.37-7.32 (m, 3H), 7.30-7.27 (m, 2H), 7.11 (t, *J* = 8 Hz, 1H), 7.07-7.03 (m, 3H), 6.78 (d, *J* = 8 Hz, 1H), 4.89-4.80 (m, 1H), 1.64 (dd, *J* = 8 Hz, 16 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.4, 140.1 (d, *J* = 80.0 Hz), 138.1, 137.2 (d, *J* = 11.6 Hz), 134.2, 133.5, 132.6 (d, *J* = 9.2 Hz), 132.1, 131.6 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 7.9 Hz), 130.7 (d, *J* = 3.7 Hz), 130.2, 129.2 (d, *J* = 21.7 Hz), 128.7 (d, *J* = 19.8 Hz), 128.5 (d, *J* = 4.5 Hz), 128.4, 127.9 (d, *J* = 18.7 Hz), 127.7 (d, *J* = 17.2 Hz), 127.5, 127.1, 64.4, 42.9 (d, *J* = 67.6 Hz), 13.4. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.2 (s). **HRMS**

**(ESI):** ([M+H]$^+$) Calcd for $C_{36}H_{29}BrO_2P^+$: 603.1083, Found: 603.1076.

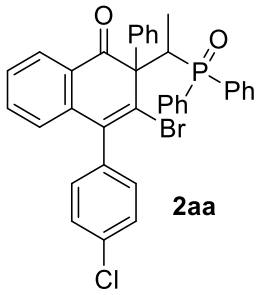
**3-bromo-2-(1-(diphenylphosphoryl)ethyl)-2-phenyl-4-(p-tolyl)naphthalen-1(2H)-one (2z)**




**2z**

White solids, *m.p.*: 240.5-242.2 ℃ (43.1 mg, 70% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 2H), 7.77-7.72 (m, 3H), 7.58-7.51 (m, 6H), 7.48 (d, *J* = 8 Hz, 1H), 7.39-7.32 (m, 3H), 7.30-7.23 (m, 3H), 7.12-7.09 (m, 1H), 7.06-7.01 (m, 3H), 6.81 (d, *J* = 8 Hz, 1H), 4.89-4.80 (m, 1H), 2.52 (s, 3H), 1.64 (dd, *J* = 8 Hz, 16 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.5, 140.6, 138.0 (d, *J* = 59.8 Hz), 137.2 (d, *J* = 11.6 Hz), 136.7, 134.1, 133.4, 132.6 (d, *J* = 9.2 Hz), 132.4, 132.1, 131.6 (d, *J* = 8.1 Hz), 131.5 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 3.6 Hz), 130.0 (d, *J* = 3.8 Hz), 129.1 (d, *J* = 32.6 Hz), 128.7 (d, *J* = 16.7 Hz), 128.4 (d, *J* = 14.4 Hz), 127.7 (d, *J* = 9.7 Hz), 127.5 (d, *J* = 4.8 Hz), 127.4, 127.1, 64.5, 42.9 (d, *J* = 67.6 Hz), 21.6, 13.3. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.2 (s). **HRMS (ESI):** ([M+H]$^+$) Calcd for $C_{37}H_{31}BrO_2P^+$: 617.1240, Found: 617.1242.

**3-bromo-4-(4-chlorophenyl)-2-(1-(diphenylphosphoryl)ethyl)-2-phenylnaphthalen-1(2H)-one (2aa)**

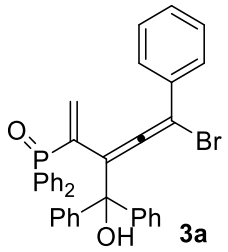



**2aa**

White solids, *m.p.*: 231.7-233.5 ℃ (40.1 mg, 63% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.83-7.81 (m, 1H), 7.71-7.66 (m, 2H), 7.63-7.61 (m, 1H), 7.53-7.47 (m, 7H), 7.33-7.29 (m, 2H), 7.28-7.22 (m, 3H), 7.09-7.06 (m, 1H), 7.05-6.97 (m, 3H), 6.73 (d, *J* = 8 Hz, 1H), 4.82-4.75 (m, 1H), 1.61 (dd, *J* = 5 Hz, 15 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ

196.3, 139.5, 138.0 (d, *J* = 37.9 Hz), 137.1 (d, *J* = 11.7 Hz), 134.3, 134.1, 133.4, 132.5 (d, *J* = 9.3 Hz), 132.0, 131.9, 131.7 (d, *J* = 13.0 Hz), 131.5 (d, *J* = 8.2 Hz), 131.3, 130.2 (d, *J* = 110.6 Hz), 128.9, 128.7, 128.6, 127.9 (d, *J* = 7.9 Hz), 127.6 (d, *J* = 11.5 Hz), 127.1 (d, *J* = 15.1 Hz), 64.4, 43.0 (d, *J* = 67.5 Hz), 13.4. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.0 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{28}BrClO_2P^+$: 637.0693, Found: 637.0690.

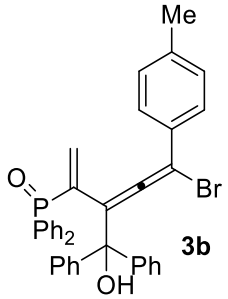
**(5-bromo-3-(hydroxydiphenylmethyl)-5-phenylpenta-1,3,4-trien-2-yl)diphenylphosphine oxide (3a)**



**3a**

White solids, *m.p.*: 165.0-166.2 ℃ (56.0 mg, 93% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.62 (m, 6H), 7.54-7.47 (m, 5H), 7.37-7.28 (m, 6H), 7.20-7.10 (m, 6H), 6.90-6.88 (m, 2H), 6.01 (d, *J* = 44.0 Hz, 1H), 5.42 (d, *J* = 20.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.4 (d, *J* = 6.7 Hz), 146.0, 144.3, 138.9 (d, *J* = 91.7 Hz), 134.2 (d, *J* = 10.4 Hz), 133.1, 132.4 (d, *J* = 14.0 Hz), 132.1 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 10.2 Hz), 130.4, 129.5 (d, *J* = 25.8 Hz), 128.8 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.5 Hz), 128.3, 127.9 (d, *J* = 7.7 Hz), 127.7 (d, *J* = 7.8 Hz), 127.1 (d, *J* = 24.2 Hz), 127.0, 118.8 (d, *J* = 6.8 Hz), 96.3, 80.8. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{28}BrNaO_2P^+$: 625.0903, Found: 625.0886.

**(5-bromo-3-(hydroxydiphenylmethyl)-5-(p-tolyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3b)**

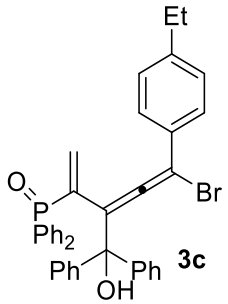


**3b**

White solids, *m.p.*: 155.3-157.0 ℃ (54.8 mg, 89% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 2H), 7.66-7.61

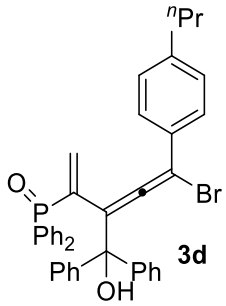
(m, 4H), 7.59-7.55 (m, 1H), 7.51-7.46 (m, 4H), 7.42-7.38 (m, 1H), 7.36-7.26 (m, 5H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.14-7.11 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.77-6.74 (m, 2H), 5.99 (d, *J* = 40.0 Hz, 1H), 5.41 (d, *J* = 20.0 Hz, 1H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.2 (d, *J* = 6.9 Hz), 146.0, 144.4, 139.1 (d, *J* = 91.4 Hz), 138.3, 134.2 (d, *J* = 10.5 Hz), 132.3 (d, *J* = 15.0 Hz), 132.1, 132.0, 131.9, 130.3 (d, *J* = 9.5 Hz), 129.5 (d, *J* = 38.2 Hz), 128.7 (d, *J* = 12.6 Hz), 128.6, 128.5 (d, *J* = 12.5 Hz), 127.8 (d, *J* = 9.6 Hz), 127.6, 127.2, 126.9 (d, *J* = 10.2 Hz), 118.7 (d, *J* = 7.2 Hz), 96.3, 80.7, 21.2. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.1 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{37}H_{30}BrNaO_2P^+$: 639.1059, Found: 639.1047.

**(5-bromo-5-(4-ethylphenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3c)**




White solids, *m.p.*: 135.9-137.8 ℃ (54.2 mg, 86% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.60-7.55 (m, 4H), 7.50-7.48 (m, 1H), 7.46-7.44 (m, 2H), 7.41-7.38 (m, 2H), 7.31-7.29 (m, 1H), 7.26-7.22 (m, 4H), 7.21-7.18 (m, 1H), 7.13 (t, *J* = 6.0 Hz, 2H), 7.07-7.04 (m, 1H), 6.87 (d, *J* = 12.0 Hz, 2H), 6.72 (d, *J* = 6.0 Hz, 2H), 5.92 (d, *J* = 36.0 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 2.54 (q, *J* = 6.0 Hz, 2H), 1.17 (t, *J* = 6.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.2 (d, *J* = 6.6 Hz), 146.0, 144.7, 144.4, 139.0 (d, *J* = 91.6 Hz), 134.1 (d, *J* = 10.6 Hz), 132.4 (d, *J* = 2.2 Hz), 132.3 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 9.9 Hz), 130.5, 130.2, 129.5 (d, *J* = 3.7 Hz), 128.8 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.2 Hz), 127.8 (d, *J* = 18.0 Hz), 127.6 (d, *J* = 25.2 Hz), 127.2, 127.0, 118.5 (d, *J* = 7.1 Hz), 96.5, 80.7, 28.5, 15.6. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{38}H_{32}BrNaO_2P^+$: 653.1216, Found: 653.1210.

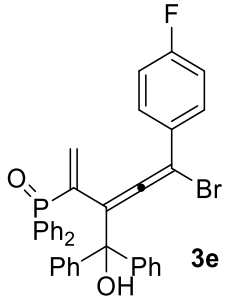
**(5-bromo-3-(hydroxydiphenylmethyl)-5-(4-propylphenyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3d)**



**3d**

White solids, *m.p.*: 150.7-152.1 ℃ (54.7 mg, 85% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 2H), 7.67-7.61 (m, 4H), 7.59-7.55 (m, 1H), 7.51-7.45 (m, 4H), 7.40-7.36 (m, 1H), 7.34-7.24 (m, 5H), 7.21-7.17 (m, 2H), 7.13-7.10 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.98 (d, *J* = 40.0 Hz, 1H), 5.40 (d, *J* = 16.0 Hz, 1H), 2.55 (t, *J* = 8.0 Hz, 2H), 1.69-1.59 (m, 2H), 0.98 (t, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.2 (d, *J* = 6.8 Hz), 146.0, 144.4, 143.1, 139.0 (d, *J* = 91.6 Hz), 134.1 (d, *J* = 10.6 Hz), 132.4 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 2.7 Hz), 132.1, 132.0 (d, *J* = 1.9 Hz), 131.9, 130.4 (d, *J* = 6.0 Hz), 129.5 (d, *J* = 31.3 Hz), 128.7 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.4 Hz), 127.9 (d, *J* = 22.0 Hz), 127.7 (d, *J* = 11.2 Hz), 127.2, 126.9 (d, *J* = 10.8 Hz), 118.5 (d, *J* = 7.0 Hz), 96.4, 80.7, 37.7, 24.5, 13.9. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{39}H_{34}BrNaO_2P^+$: 667.1372, Found: 667.1362.

**(5-bromo-5-(4-fluorophenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3e)**

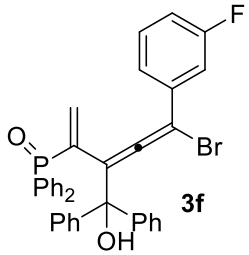


**3e**

White solids, *m.p.*: 164.4-165.8 ℃ (55.8 mg, 90% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.67 (m, 4H), 7.63-7.58 (m, 2H), 7.56-7.53 (m, 1H), 7.50-7.43 (m, 4H), 7.37-7.25 (m, 6H), 7.19-7.15 (m, 2H), 7.12-7.08 (m, 1H), 6.77 (s, 2H), 6.75 (s, 2H), 5.97 (d, *J* = 40.0 Hz, 1H), 5.40 (d, *J* = 16.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.1 (d, *J* = 6.5 Hz), 162.5 (d, *J* = 248.8 Hz), 145.1 (d, *J* = 214.2 Hz), 138.7 (d, *J* = 91.9 Hz), 134.0 (d, *J* = 10.4 Hz), 132.5 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 2.8 Hz), 132.0 (dd, *J* = 15.8, 10.0 Hz), 130.3,

129.4 (d, *J* = 12.0 Hz), 129.1, 128.7 (d, *J* = 11.9 Hz), 128.6 (d, *J* = 8.4 Hz), 128.4, 127.9, 127.6 (d, *J* = 1.5 Hz), 127.1 (d, *J* = 28.5 Hz), 126.8, 118.7 (d, *J* = 6.9 Hz), 114.8 (d, *J* = 21.9 Hz), 95.0, 80.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -113.2 (s). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.4 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{27}BrFNaO_2P^+$: 643.0808, Found: 643.0802.

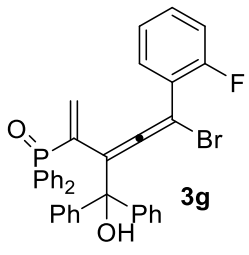
**(5-bromo-5-(3-fluorophenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3f)**



**3f**

White solids, *m.p.*: 167.0-168.8 ℃ (41.5 mg, 67% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.61-7.60 (m, 2H), 7.58-7.52 (m, 3H), 7.44-7.41 (m, 4H), 7.34-7.32 (m, 1H), 7.30-7.26 (m, 4H), 7.24-7.22 (m, 1H), 7.15-7.13 (m, 2H), 7.08-7.05 (m, 1H), 7.00-6.96 (m, 1H), 6.81-6.77 (m, 1H), 6.56-6.55 (m, 1H), 6.46-6.44 (m, 1H), 5.92 (d, *J* = 42.0 Hz, 1H), 5.36 (d, *J* = 24.0 Hz, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.4 (d, *J* = 6.7 Hz), 162.2 (d, *J* = 246.0 Hz), 145.0 (d, *J* = 316.0 Hz), 138.6 (d, *J* = 91.8 Hz), 135.4 (d, *J* = 7.9 Hz), 134.0 (d, *J* = 10.5 Hz), 132.5 (d, *J* = 2.3 Hz), 132.3 (d, *J* = 2.5 Hz), 132.1 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 9.9 Hz), 130.1, 129.2 ((q, *J* = 15.1 Hz), 128.7 (d, *J* = 12.8 Hz), 128.5 (d, *J* = 12.6 Hz), 127.9, 127.7 (d, *J* = 5.3 Hz), 127.2 (d, *J* = 34.6 Hz), 126.8, 122.6 (d, *J* = 2.2 Hz), 119.1 (d, *J* = 6.7 Hz), 115.0 (d, *J* = 21.1 Hz), 113.9 (d, *J* = 24.0 Hz), 94.6, 80.7. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -113.4 (s). **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{27}BrFNaO_2P^+$: 643.0808, Found: 643.0803.

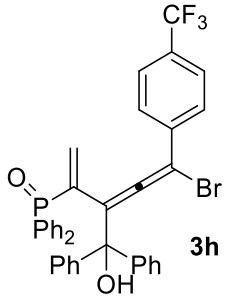
**(5-bromo-5-(2-fluorophenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3g)**



**3g**

White solids, *m.p.*: 155.3-157.0 ℃ (39.1 mg, 63% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71-7.60 (m, 4H), 7.58-7.56 (m, 1H), 7.54-7.43 (m, 7H), 7.39-7.35 (m, 2H), 7.28-7.17 (m, 7H), 6.97-6.90 (m, 2H), 6.72-6.68 (m, 1H), 6.04 (d, *J* = 40.0 Hz, 1H), 5.44 (d, *J* = 20.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.1 (d, *J* = 7.3 Hz), 160.3, 157.8, 144.9 (d, *J* = 32.6 Hz), 138.4 (d, *J* = 91.8 Hz), 135.0 (d, *J* = 10.3 Hz), 132.3 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.2 Hz), 132.0 (d, *J* = 2.1 Hz), 130.7 (d, *J* = 1.5 Hz), 130.2 (d, *J* = 8.6 Hz), 129.2 (d, *J* = 1.8 Hz), 128.7 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.4 Hz), 127.6 (d, *J* = 2.9 Hz), 127.4 (d, *J* = 23.1 Hz), 127.0 (d, *J* = 16.4 Hz), 123.9 (d, *J* = 3.7 Hz), 122.1 (d, *J* = 11.4 Hz), 117.1 (d, *J* = 7.5 Hz), 115.6 (d, *J* = 21.4 Hz), 87.3, 80.6. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -110.0 (s). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.1 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{27}BrFNaO_2P^+$: 643.0808, Found: 643.0804.

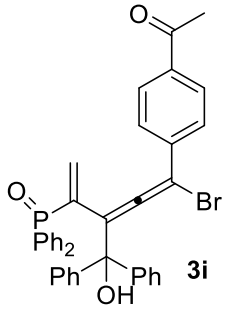
**(5-bromo-3-(hydroxydiphenylmethyl)-5-(4-(trifluoromethyl)phenyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3h)**




**3h**

White solids, *m.p.*: 171.7-173.5 ℃ (55.6 mg, 83% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.67-7.63 (m, 4H), 7.57-7.51 (m, 3H), 7.47-7.45 (m, 3H), 7.43-7.40 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.20 (m, 5H), 7.16-7.13 (m, 2H), 7.08-7.05 (m, 1H), 6.82 (d, *J* = 10.0 Hz, 2H), 5.93 (d, *J* = 40.0 Hz, 1H), 5.36 (d, *J* = 20.0 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.9 (d, *J* = 6.4 Hz), 145.0 (d, *J* = 288.0 Hz), 138.3 (d, *J* = 92.1 Hz), 136.8, 134.1 (d, *J* = 10.2 Hz), 132.7 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 10.1 Hz), 131.9 (d, *J* = 10.0 Hz), 130.1 (d, *J* = 10.9 Hz), 129.8, 129.2 (d, *J* = 34.0 Hz), 128.8 (d, *J* = 12.6 Hz), 128.5 (d, *J* = 12.6 Hz), 128.1, 127.7 (d, *J* = 14.5 Hz), 127.3 (d, *J* = 33.0 Hz), 126.9 (d, *J* = 41.4 Hz), 124.8 (q, *J* = 3.8 Hz), 124.0 (d, *J* = 272.1 Hz), 119.1 (d, *J* = 6.7 Hz), 94.5, 80.8. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -62.5 (s). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 36.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{37}H_{27}BrF_3NaO_2P^+$: 693.0776, Found: 693.0769.

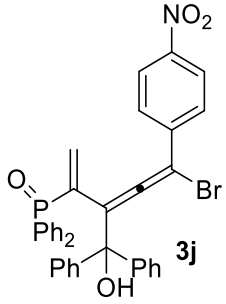
**1-(4-(1-bromo-4-(diphenylphosphoryl)-3-(hydroxydiphenylmethyl)penta-1,2,4-trien-1-yl)phenyl)ethan-1-one (3i)**



**3i**

White solids, *m.p.*: 167.5-168.2 ℃ (50.9 mg, 79% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.66-7.59 (m, 5H), 7.58-7.54 (m, 2H), 7.47-7.43 (m, 4H), 7.34-7.26 (m, 6H), 7.18-7.14 (m, 2H), 7.10-7.06 (m, 1H), 6.90 (d, *J* = 12.0 Hz, 2H), 5.96 (d, *J* = 40.0 Hz, 1H), 5.40 (d, *J* = 20.0 Hz, 1H), 2.57 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.1 (d, *J* = 6.6 Hz), 197.4, 145.9, 143.9, 138.8, 137.8 (d, *J* = 21.7 Hz), 136.3, 134.3 (d, *J* = 10.3 Hz), 132.4 (d, *J* = 18.2 Hz), 132.0 (d, *J* = 10.1 Hz), 131.9 (d, *J* = 10.1 Hz), 130.2, 129.4, 129.2, 128.8 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.5 Hz), 127.9 (d, *J* = 1.8 Hz), 127.6 (d, *J* = 6.5 Hz), 127.2 (d, *J* = 24.3 Hz), 126.8 (d, *J* = 19.5 Hz), 119.2 (d, *J* = 6.8 Hz), 94.9, 80.8, 26.7. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+H-H_2O]^+$) Calcd for $C_{38}H_{29}BrO_2P^+$: 627.1083, Found: 627.1073.

**(5-bromo-3-(hydroxydiphenylmethyl)-5-(4-nitrophenyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3j)**

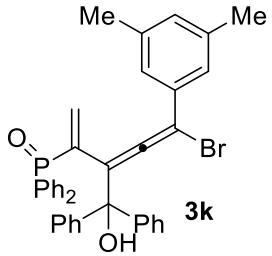


**3j**

White solids, *m.p.*: 164.3-166.0 ℃ (45.3 mg, 70% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.85-7.84 (m, 2H), 7.69-7.66 (m, 2H), 7.64-7.62 (m, 2H), 7.56-7.53 (m, 3H), 7.45-7.42 (m, 4H), 7.36-7.30 (m, 3H), 7.29-7.26 (m, 3H), 7.13 (t, *J* = 6.0 Hz, 2H), 7.06-7.04 (m, 1H), 6.90 (d, *J* = 6.0 Hz, 2H), 5.94 (d, *J* = 42.0 Hz, 1H), 5.39 (d, *J* = 18.0 Hz, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 203.5 (d, *J* = 6.5 Hz), 146.0, 145.3 (d, *J* = 542.8 Hz), 139.5, 137.9 (d, *J* = 89.6 Hz), 134.2 (d, *J* = 10.1 Hz), 132.5 (d, *J* = 36.6 Hz), 132.1 (d, *J* = 10.8 Hz), 131.9

(d, *J* = 9.8 Hz), 130.0, 129.2 (d, *J* = 27.6 Hz), 128.8 (d, *J* = 12.8 Hz), 128.5 (d, *J* = 12.2 Hz), 127.9 (d, *J* = 43.6 Hz), 127.6, 127.4 (d, *J* = 3.4 Hz), 127.2, 126.6, 123.0, 119.5, 93.6, 80.9. **$^{31}$P NMR** (243 MHz, $CDCl_3$) δ 35.5 (s). **HRMS(ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{28}BrNO_4P^+$: 648.0934, Found: 648.0923.

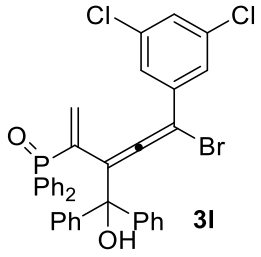
**(5-bromo-5-(3,5-dimethylphenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3k)**



**3k**

White solids, *m.p.*: 135.0-136.8 ℃ (54.8 mg, 87% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2H), 7.67-7.63 (m, 4H), 7.60-7.56 (m, 1H), 7.53-7.47 (m, 5H), 7.39-7.36 (m, 1H), 7.33-7.27 (m, 4H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 1H), 6.81 (s, 1H), 6.44 (s, 2H), 6.00 (d, *J* = 40.0 Hz, 1H), 5.43 (d, *J* = 20.0 Hz, 1H), 2.20 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.4 (d, *J* = 7.0 Hz), 145.3 (d, *J* = 194.3 Hz), 139.2 (d, *J* = 91.3 Hz), 137.4, 134.1 (d, *J* = 10.7 Hz), 133.0, 132.4 (d, *J* = 2.8 Hz), 132.1, 132.0, 131.9 (d, *J* = 10.0 Hz), 130.3, 130.1, 129.4 (d, *J* = 40.7 Hz), 128.7, 128.4 (d, *J* = 12.5 Hz), 127.8 (d, *J* = 13.1 Hz), 127.3 (d, *J* = 74.6 Hz), 127.2, 124.8, 118.5 (d, *J* = 7.1 Hz), 96.4, 80.6, 21.2. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{38}H_{32}BrNaO_2P^+$: 653.1216, Found: 653.1209.

**(5-bromo-5-(3,5-dichlorophenyl)-3-(hydroxydiphenylmethyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (3l)**

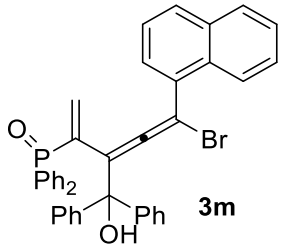


**3l**

Yellow oil, (44.9 mg, 67% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 4H), 7.64-7.54 (m, 3H), 7.48-7.42 (m, 4H), 7.38-7.28 (m, 6H), 7.22-7.19 (m, 2H), 7.14-7.10 (m, 2H), 6.58 (d, *J* = 4.0 Hz,

2H), 5.92 (d, *J* = 40.0 Hz, 1H), 5.41 (d, *J* = 28.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.5 (d, *J* = 6.4 Hz), 146.2, 143.5, 138.2 (d, *J* = 92.1 Hz), 136.2, 134.4, 133.7 (d, *J* = 10.0 Hz), 132.6 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 10.1 Hz), 131.7 (d, *J* = 10.1 Hz), 130.0, 128.9 (d, *J* = 3.8 Hz), 128.8 (d, *J* = 12.7 Hz), 128.5 (d, *J* = 12.5 Hz), 128.0 (d, *J* = 5.5 Hz), 127.7 (d, *J* = 27.1 Hz), 127.4 (d, *J* = 20.3 Hz), 126.6, 125.1, 119.4 (d, *J* = 6.5 Hz), 93.0 (d, *J* = 1.7 Hz), 80.8. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{26}BrCl_2NaO_2P^+$: 693.0123, Found: 693.0115.

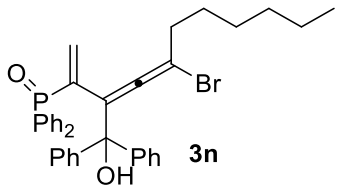
**(5-bromo-3-(hydroxydiphenylmethyl)-5-(naphthalen-1-yl)penta-1,3,4-trien-2-yl) diphenylphosphine oxide (3m)**



**3m**

White solids, *m.p.*: 115.3-117.0 ℃ (32.6 mg, 50% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.72-7.67 (m, 2H), 7.59-7.49 (m, 7H), 7.48-7.43 (m, 2H), 7.38-7.29 (m, 7H), 7.25-7.22 (m, 2H), 7.19-7.11 (m, 4H), 6.65-6.62 (m, 1H), 5.92 (d, *J* = 40.0 Hz, 1H), 5.41 (d, *J* = 25.0 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 201.4, 145.2, 144.5, 139.8, 139.0, 134.9 (d, *J* = 10.6 Hz), 133.7, 132.5, 132.3, 132.2, 132.0 (d, *J* = 9.9 Hz), 130.3 (d, *J* = 12.6 Hz), 129.6, 129.4 (d, *J* = 10.1 Hz), 128.9 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.4 Hz), 128.3, 128.0 (d, *J* = 14.6 Hz), 127.7 (d, *J* = 13.6 Hz), 127.4, 127.1 (d, *J* = 21.9 Hz), 126.3 (d, *J* = 20.5 Hz), 125.7, 125.2, 117.1 (d, *J* = 7.4 Hz), 90.3, 80.7. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{31}BrO_2P^+$: 653.1240, Found: 653.1231.

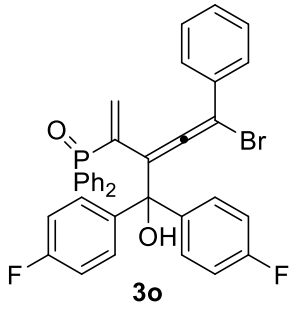
**(5-bromo-3-(hydroxydiphenylmethyl)undeca-1,3,4-trien-2-yl)diphenylphosphine oxide (3n)**



**3n**

White solids, *m.p.*: 126.0-127.3 ℃ (50.6 mg, 83% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.58-7.51 (m, 5H), 7.49-7.44 (m, 2H), 7.43-7.39 (m, 2H), 7.38-7.36 (m, 2H), 7.25-7.18 (m, 5H), 7.17-7.13 (m, 2H), 5.87 (d, *J* = 40.0 Hz, 1H), 5.33 (d, *J* = 20.0 Hz, 1H), 1.81-1.71 (m, 2H), 1.23-1.15 (m, 2H), 1.09-1.03 (m, 2H), 0.95-0.88 (m, 2H), 0.86-0.84 (m, 4H), 0.77-0.68 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 200.2 (d, *J* = 6.9 Hz), 146.4, 144.3, 139.3, 138.6, 134.2 (d, *J* = 10.6 Hz), 132.4 (dd, *J* = 5.4, 2.8 Hz), 132.1 (dd, *J* = 12.9, 9.9 Hz), 130.4 (d, *J* = 34.2 Hz), 129.6 (d, *J* = 34.7 Hz), 128.7 (dd, *J* = 12.4, 9.0 Hz), 127.8 (d, *J* = 4.4 Hz), 127.4 (d, *J* = 32.5 Hz), 127.0 (d, *J* = 23.3 Hz), 116.8 (d, *J* = 6.9 Hz), 97.1, 80.5, 37.4, 31.5, 28.3, 27.4, 22.5, 14.2. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 35.5 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{36}BrNaO_2P^+$: 633.1529, Found: 633.1457.

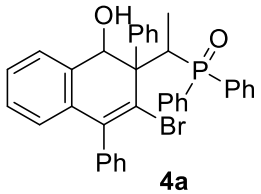
**(3-(bis(4-fluorophenyl)(hydroxy)methyl)-5-bromo-5-phenylpenta-1,3,4-trien-2-yl )diphenylphosphine oxide (3o)**




**3o**

White solids, *m.p.*: 183.8-184.4 ℃ (33.8 mg, 53% yield). TLC ($R_f$= 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.65 (m, 2H), 7.62-7.57 (m, 4H), 7.56-7.48 (m, 3H), 7.45-7.33 (m, 5H), 7.20-7.10 (m, 3H), 6.95 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 40.0 Hz, 1H), 5.40 (d, *J* = 20.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.3 (d, *J* = 7.1 Hz), 163.1, 160.7 (d, *J* = 17.9 Hz), 140.8 (d, *J* = 175.3 Hz), 138.9 (d, *J* = 90.9 Hz), 134.5 (d, *J* = 10.7 Hz), 132.7, 132.5 (d, *J* = 9.8 Hz), 132.0 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 3.1 Hz), 130.1, 129.4 (d, *J* = 8.1 Hz), 128.8 (d, *J* = 12.5 Hz), 128.7, 128.6 (d, *J* = 6.2 Hz), 128.5 (d, *J* = 4.5 Hz), 127.4 (d, *J* = 131.4 Hz), 119.1, 114.6 (d, *J* = 21.3 Hz), 114.3 (d, *J* = 21.4 Hz), 96.2, 79.9. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -115.7 (s), -116.0 (s). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 35.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{26}BrF_2NaO_2P^+$: 661.0714, Found: 661.0707.

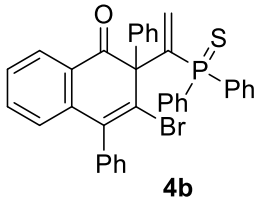
**(1-(3-bromo-1-hydroxy-2,4-diphenyl-1,2-dihydronaphthalen-2-yl)ethyl)diphenyl phosphine oxide (4a)**




**4a**

White solids, *m.p.*: 231.9-232.3 ℃ (79.7 mg, 66% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.02-7.99 (m, 1H), 7.88-7.84 (m, 2H), 7.60-7.58 (m, 2H), 7.49-7.46 (m, 3H), 7.38-7.32 (m, 5H), 7.30-7.27 (m, 1H), 7.14-7.11 (m, 1H), 7.05-6.99 (m, 4H), 6.92-6.88 (m, 1H), 6.64-6.58 (m, 3H), 6.28 (d, *J* = 10.0 Hz, 1H), 5.76 (s, 1H), 4.15-4.09 (m, 1H), 1.57 (dd, *J* = 5.0 Hz, 15Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.4 (d, *J* = 75.9 Hz), 138.7 (d, *J* = 97.1 Hz), 134.3 (d, *J* = 14.9 Hz), 132.9 (d, *J* = 99.8 Hz), 132.4, 131.8 (d, *J* = 98.7 Hz), 131.7 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 4.4 Hz), 130.7 (d, *J* = 5.6 Hz), 130.6 (d, *J* = 2.9 Hz), 130.0, 129.0 (d, *J* = 11.5 Hz), 128.9, 128.8 (d, *J* = 7.4 Hz), 128.4 (d, *J* = 41.6 Hz), 127.9 (d, *J* = 12.1 Hz), 127.5 (d, *J* = 33.8 Hz), 127.0, 126.4 (d, *J* = 2.8 Hz), 124.9, 70.9, 57.8, 43.3 (d, *J* = 68.2 Hz), 14.7. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 39.6 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{30}BrNaO_2P^+$: 627.1059, Found: 627.1049.

**3-bromo-2-(1-(diphenylphosphorothioyl)vinyl)-2,4-diphenylnaphthalen-1(2H)-one (4b)**

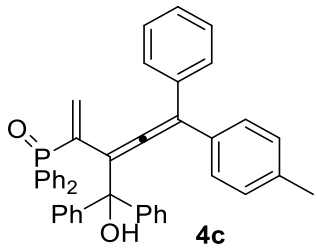



**4b**

White solids, *m.p.*: 228.2-230.0 ℃ (53.0 mg, 43% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=3:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.14-8.10 (m, 2H), 7.84-7.82 (m, 1H), 7.74-7.67 (m, 4H), 7.62-7.54 (m, 6H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.35-7.29 (m, 5H), 7.28-7.25 (m, 1H), 7.23-7.20 (m, 1H), 6.77 (d, *J* = 20.0 Hz, 1H), 6.01 (d, *J* = 20.0 Hz, 1H), 5.94 (d, *J* = 40.0 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 195.6, 147.5 (d, *J* = 74.6 Hz), 140.1 (d, *J* = 174.5 Hz), 138.7 (d, *J* = 7.4 Hz), 138.3, 136.3 (d, *J* = 21.8 Hz), 136.0 (d, *J* = 55.6 Hz), 133.9, 133.1 (d, *J* = 86.3 Hz), 132.4 (d, *J* = 10.4 Hz), 132.1 (d, *J* = 10.7 Hz), 131.4 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 3.0 Hz), 131.0, 129.4 (d, *J* = 14.9 Hz), 129.2, 129.0, 128.7, 128.5 (d, *J* = 9.8 Hz), 128.4 (d, *J* =

5.4 Hz), 128.3 (d, *J* = 5.4 Hz), 128.0, 127.7 (d, *J* = 2.9 Hz), 70.8 (d, *J* = 11.9 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 46.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{27}BrOPS^+$: 617.0698, Found: 617.0693.

**(3-(hydroxydiphenylmethyl)-5-phenyl-5-(p-tolyl)penta-1,3,4-trien-2-yl)diphenylphosphine oxide (4c)**

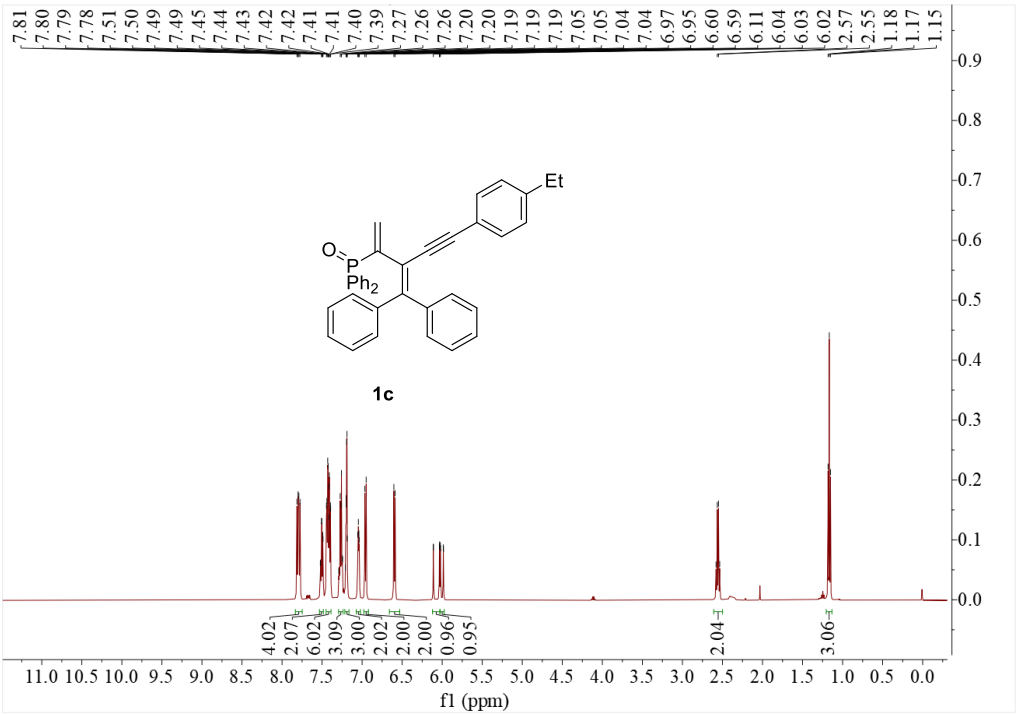



**4c**

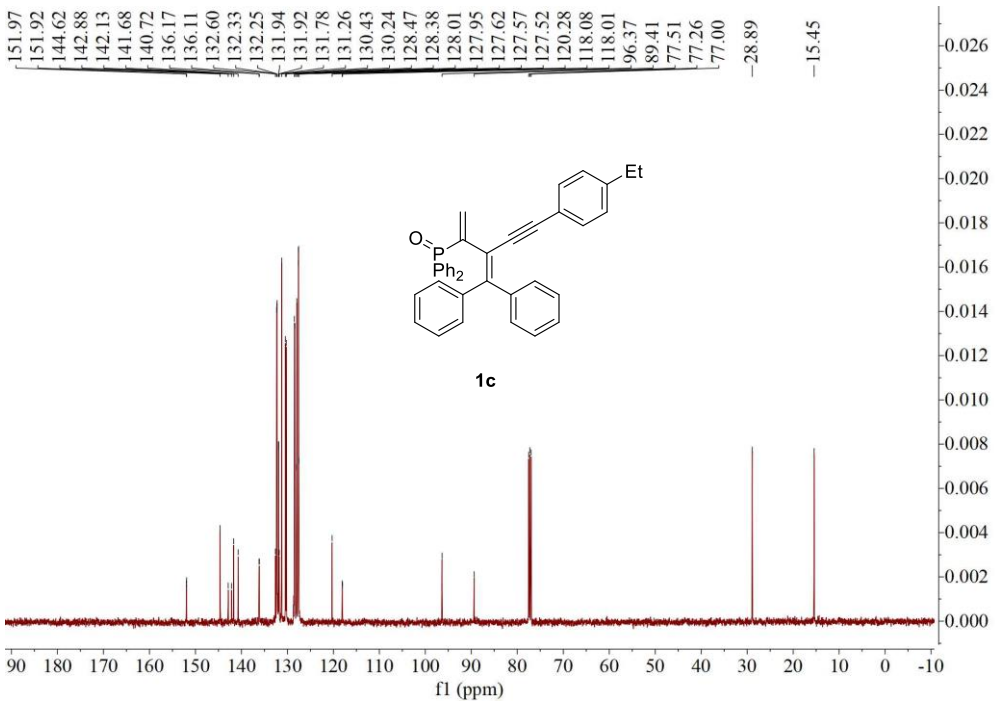
White solids, *m.p.*: 93.2-95.2 ℃ (65.0 mg, 54% yield). TLC ($R_f$ = 0.25, petroleum ether/ethyl acetate=5:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.55 (m, 4H), 7.45-7.41 (m, 4H), 7.36-7.32 (m, 2H), 7.28-7.23 (m, 4H), 7.20-7.15 (m, 2H), 7.14-7.10 (m, 7H), 6.96 (d, *J* = 10.0 Hz, 2H), 6.70 (d, *J* = 5.0 Hz, 2H), 6.63 (d, *J* = 10.0 Hz, 2H), 5.96 (d, *J* = 40.0 Hz, 1H), 5.39 (d, *J* = 20.0 Hz, 1H), 2.33 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 206.1, 145.7 (d, *J* = 4.3 Hz), 139.7, 137.1, 136.0, 134.2, 133.5 (d, *J* = 11.5 Hz), 132.9, 132.2, 132.1, 132.0 (d, *J* = 3.9 Hz), 130.1 (d, *J* = 17.3 Hz), 129.2 (d, *J* = 17.9 Hz), 128.9, 128.5, 128.4, 128.3 (d, *J* = 8.0 Hz), 128.1, 128.1, 127.6 (d, *J* = 3.9 Hz), 127.4 (d, *J* = 3.3 Hz), 127.3, 126.8, 112.4, 81.1, 21.3. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 36.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{43}H_{36}O_2P^+$: 615.2447, Found: 615.2433.

# 9 $^{1}$H-NMR, $^{13}$C-NMR, $^{31}$P-NMR, $^{19}$F-NMR, and HRMS spectra for Substrates and Products

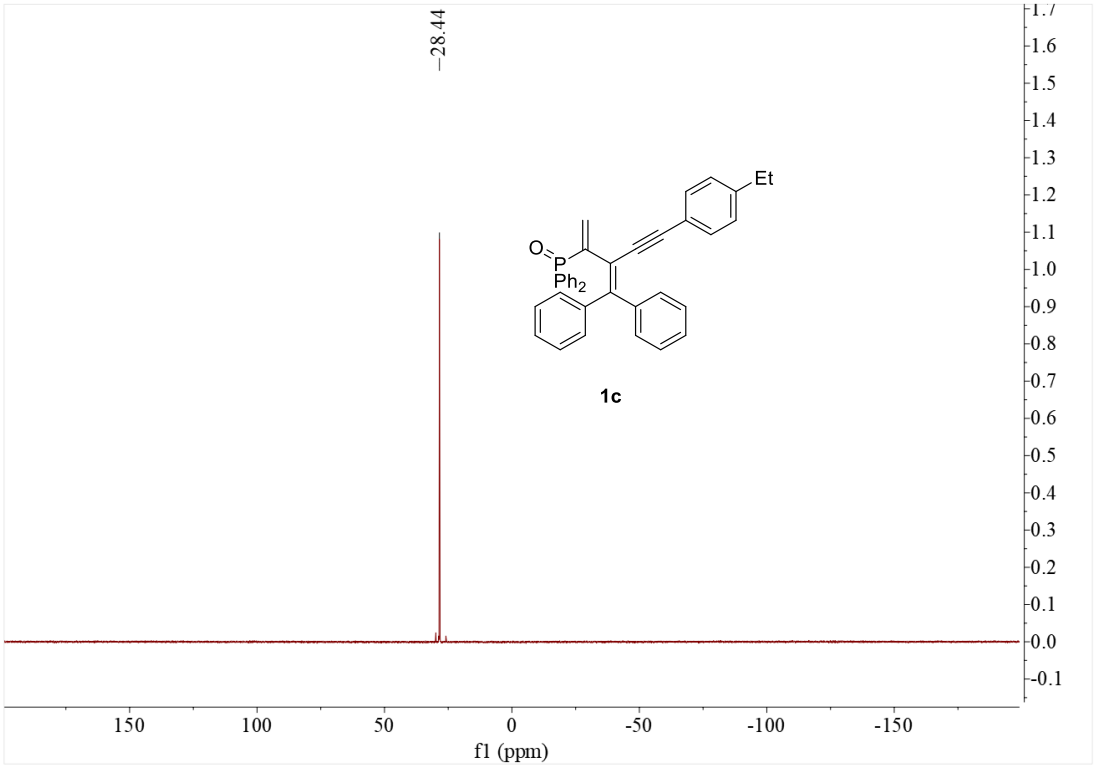
**Compound 1c ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



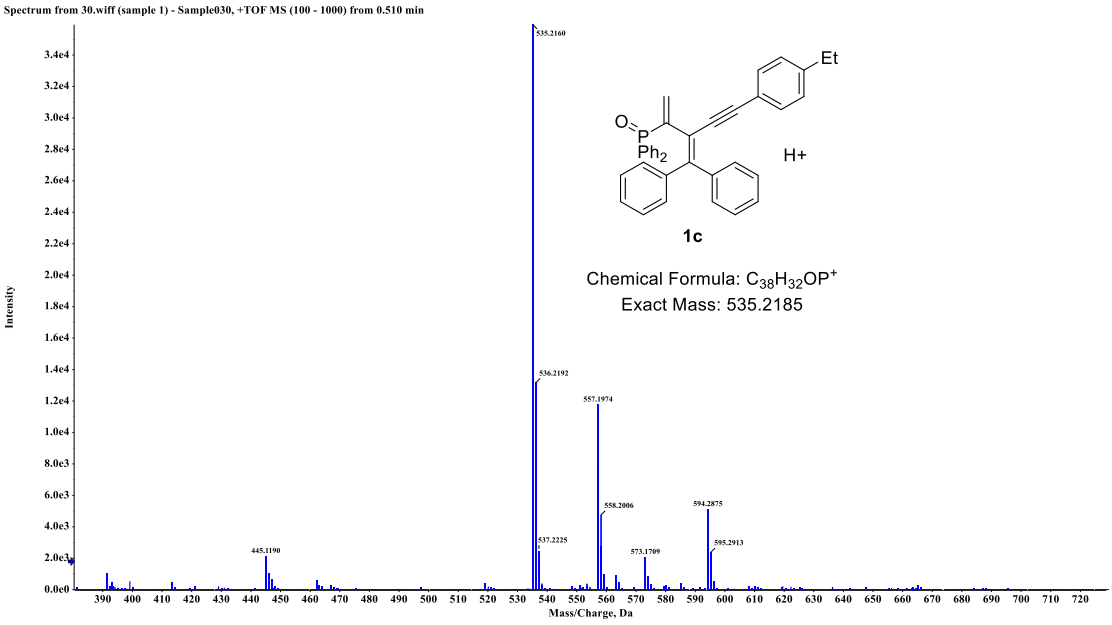

$^{1}$H NMR (500 MHz, $CDCl_3$) of **1c**



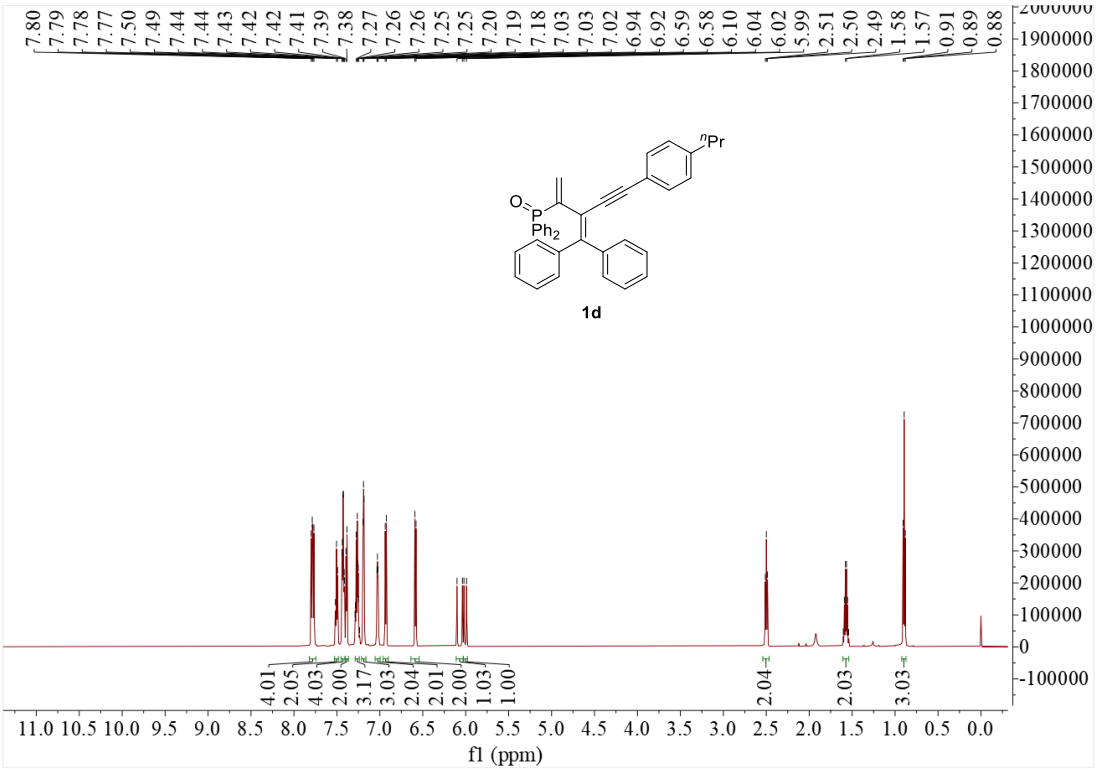

$^{13}$C NMR (126 MHz, $CDCl_3$) **of 1c**



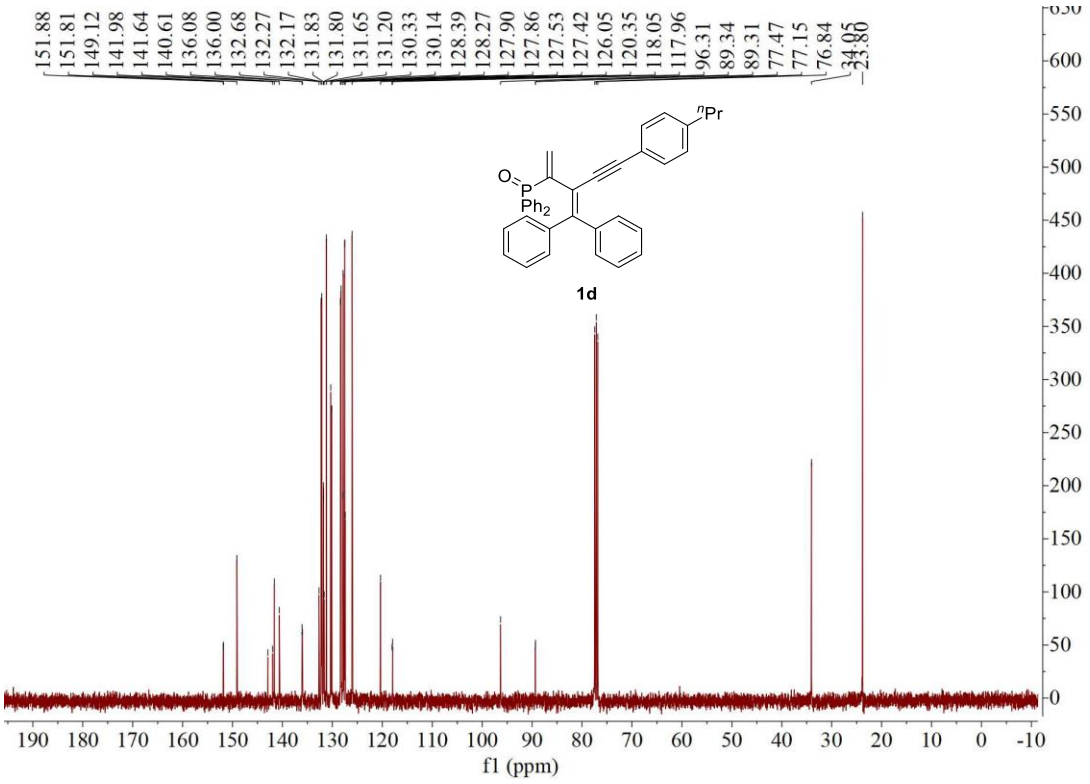

$^{31}$P NMR (202 MHz, $CDCl_3$) of **1c**



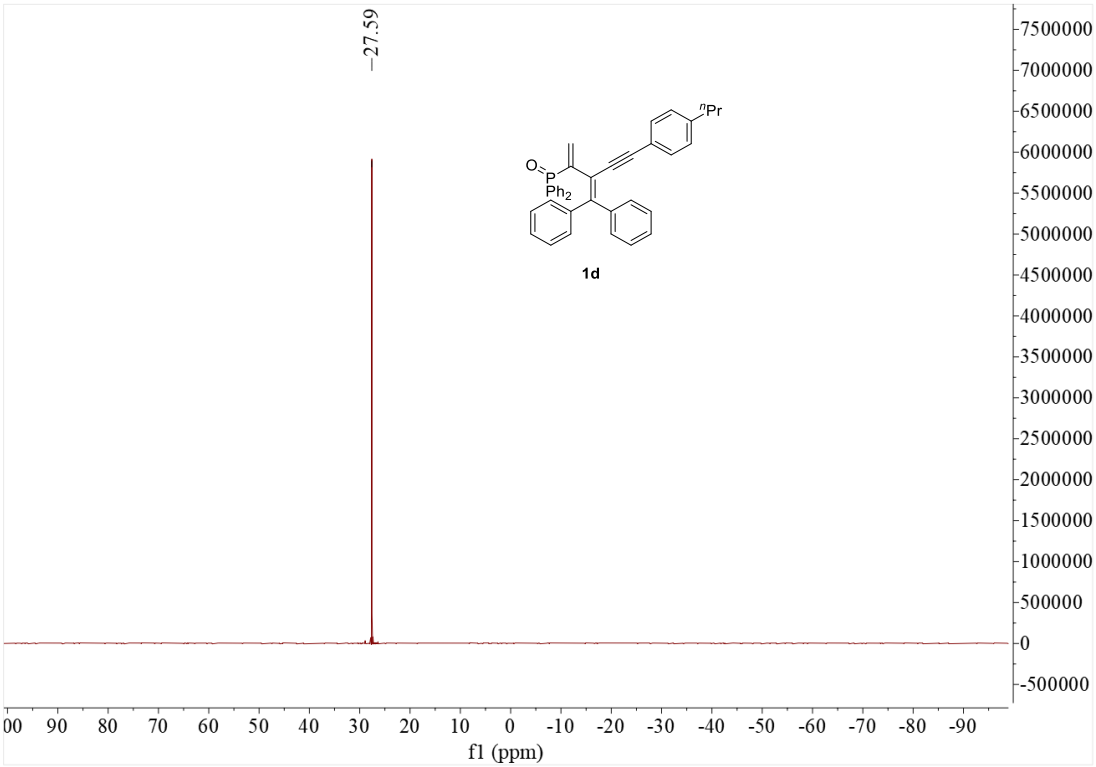
**Compound 1d ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



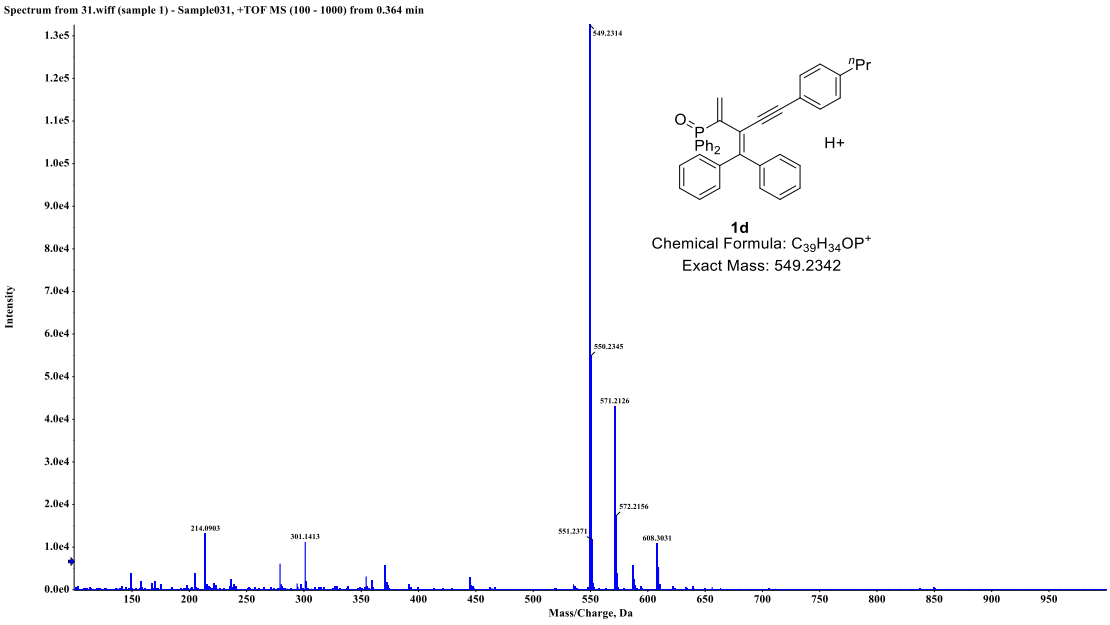

$^{1}$H NMR (600 MHz, $CDCl_3$) of **1d**



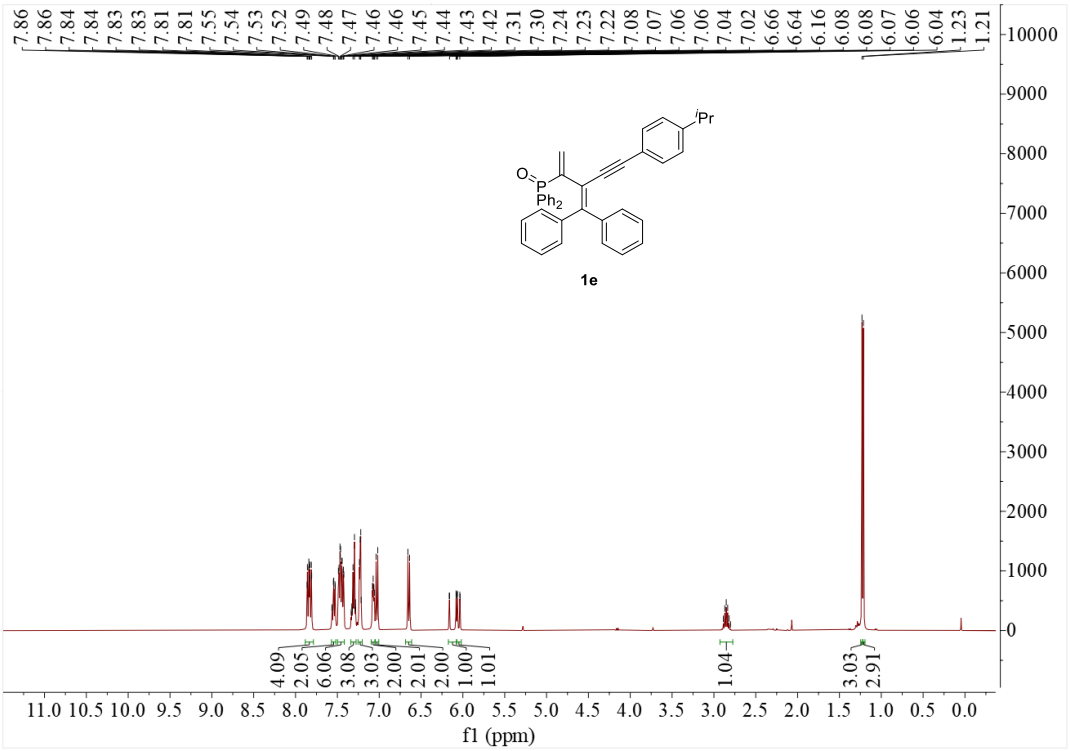

$^{13}$C NMR (151 MHz, $CDCl_3$) of **1d**



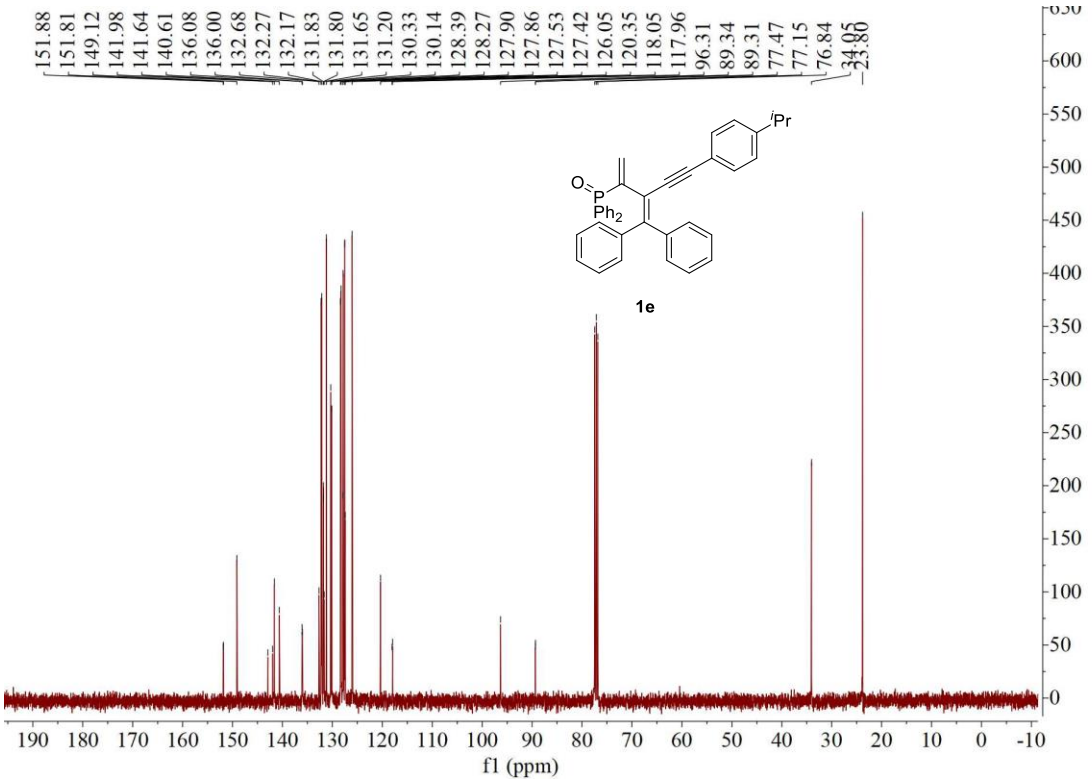

$^{31}$P NMR (243 MHz, $CDCl_3$) of **1d**



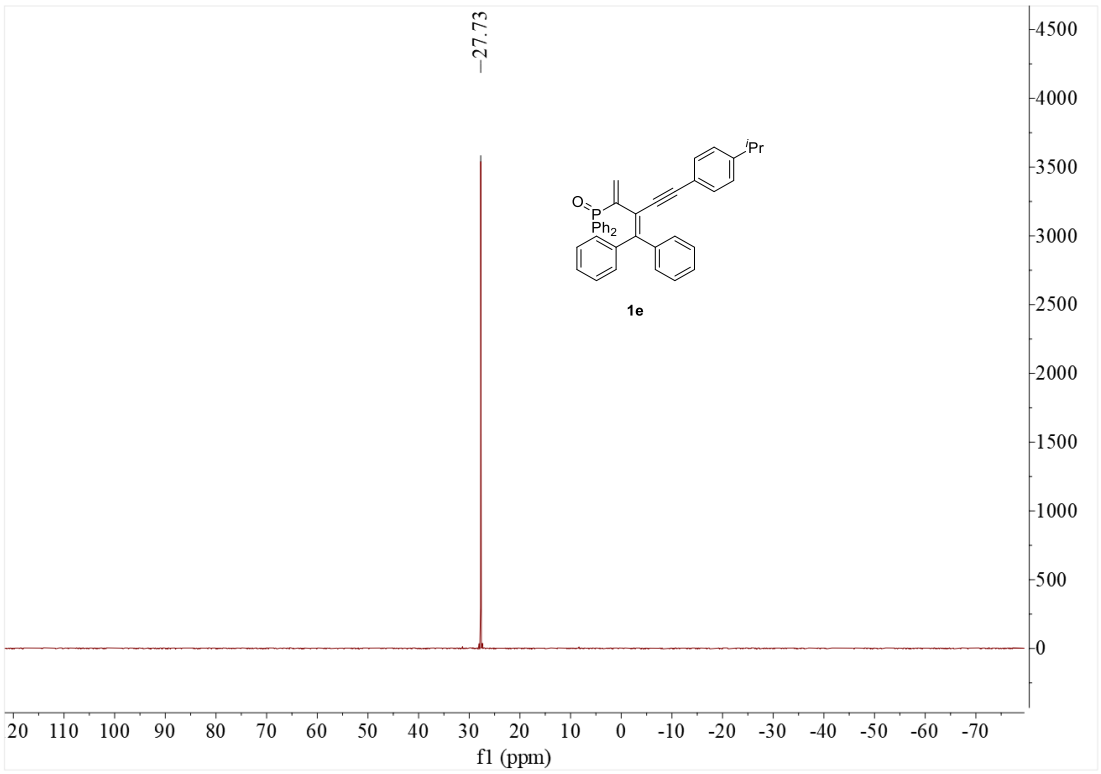
**Compound 1e ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



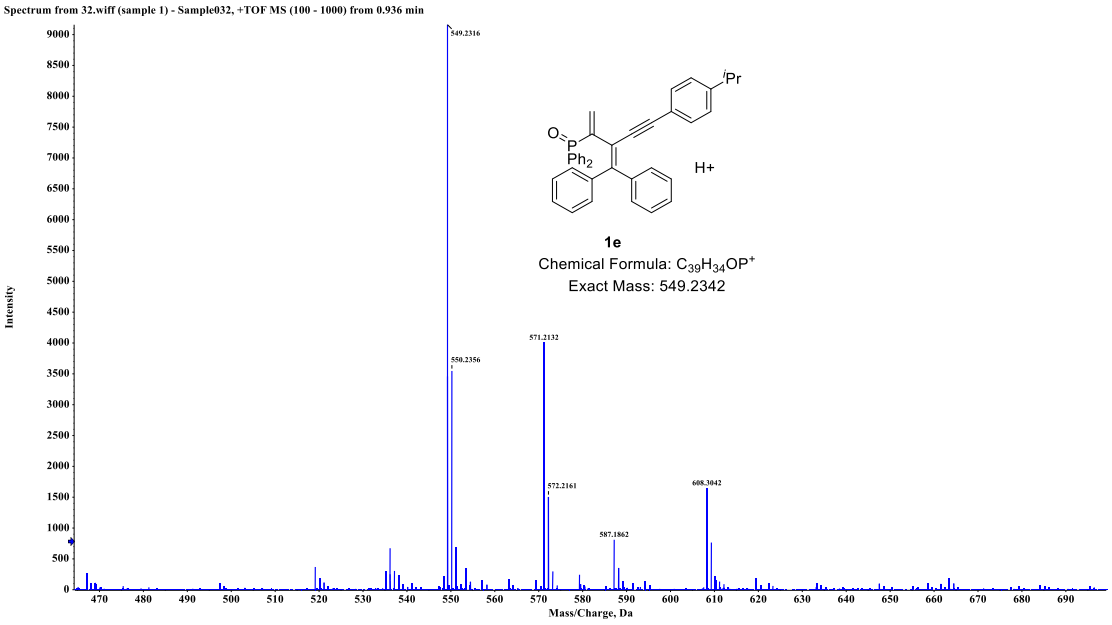

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1e**



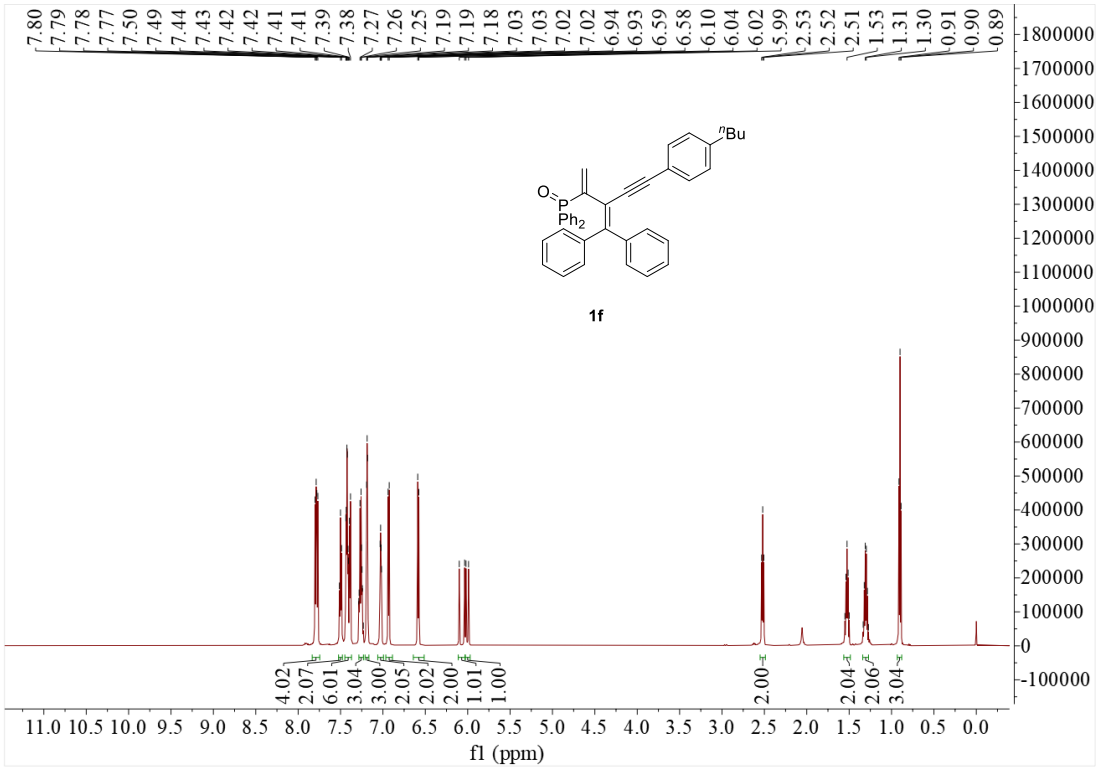

$^{13}$C NMR (101 MHz, $CDCl_3$) of **1e**



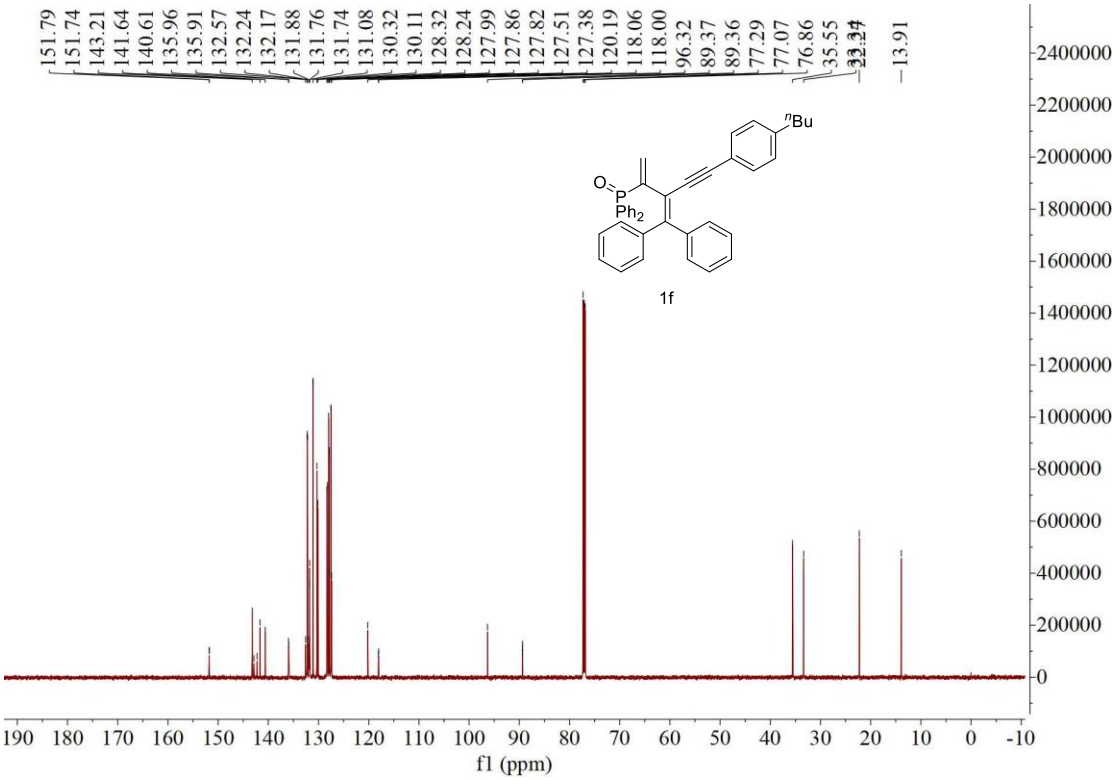

$^{31}$P NMR (162 MHz, $CDCl_3$) of **1e**



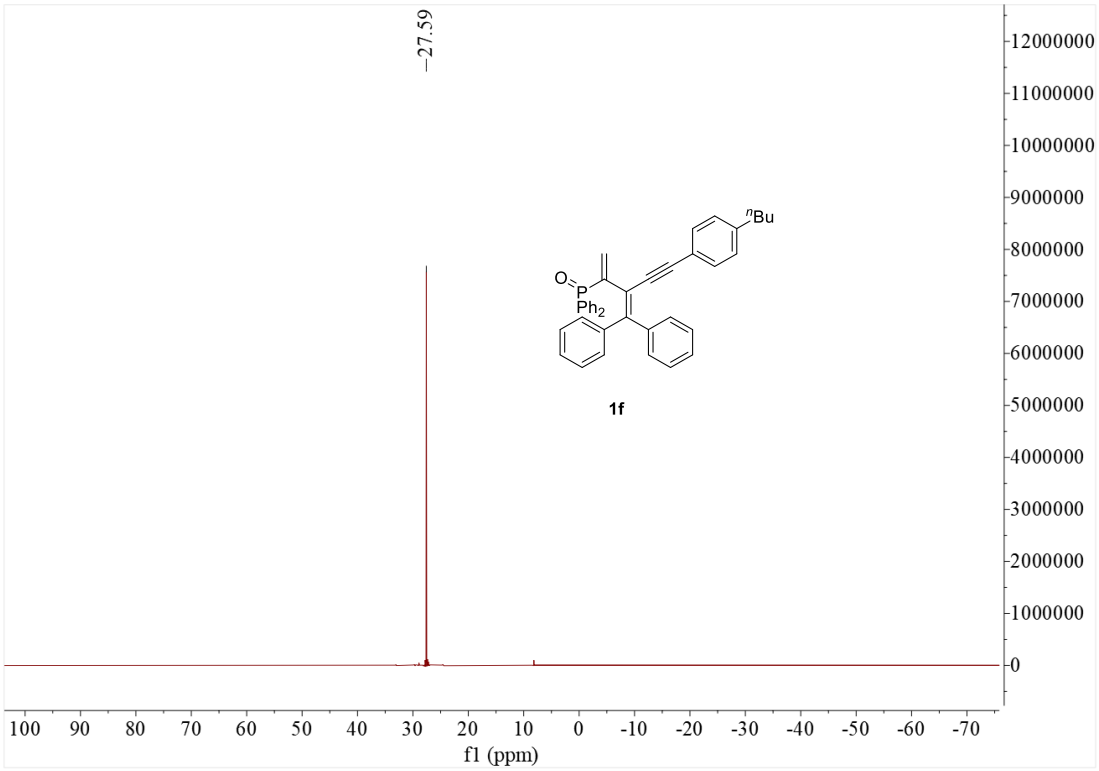
**Compound 1f ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



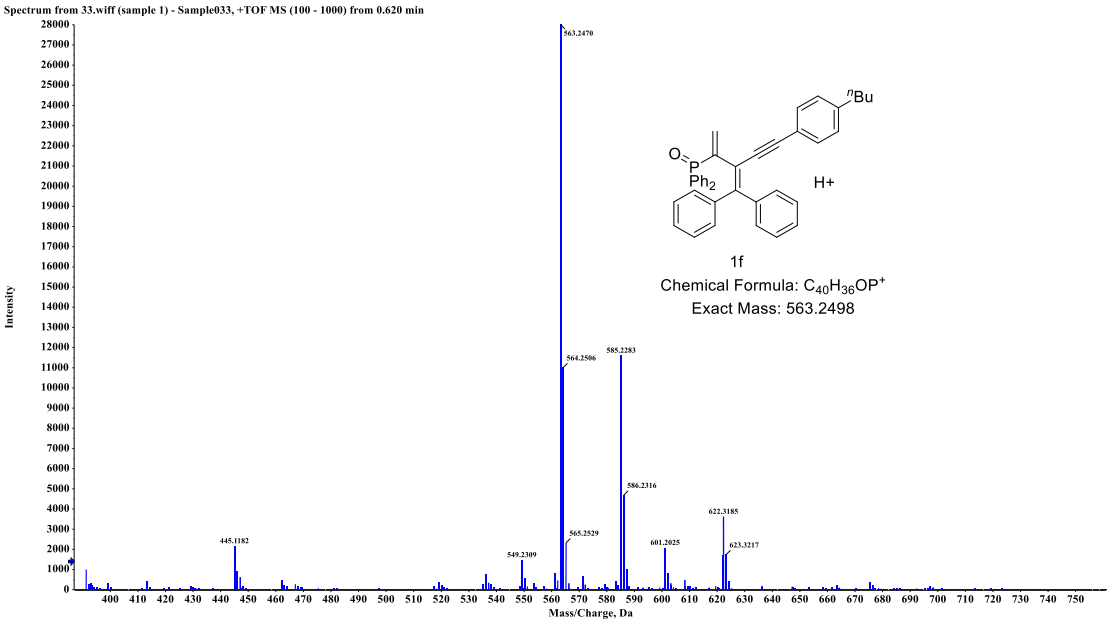

$^{1}$H NMR (600 MHz, $CDCl_3$) of **1f**



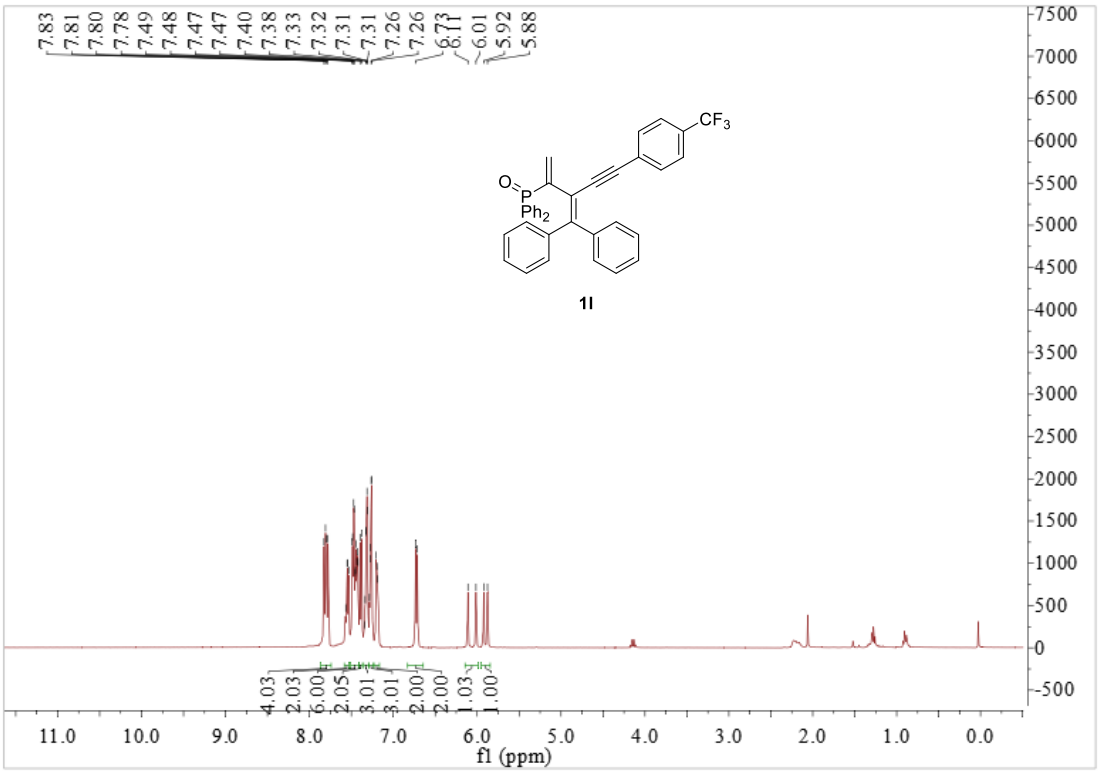

$^{13}$C NMR (151 MHz, $CDCl_3$) of **1f**



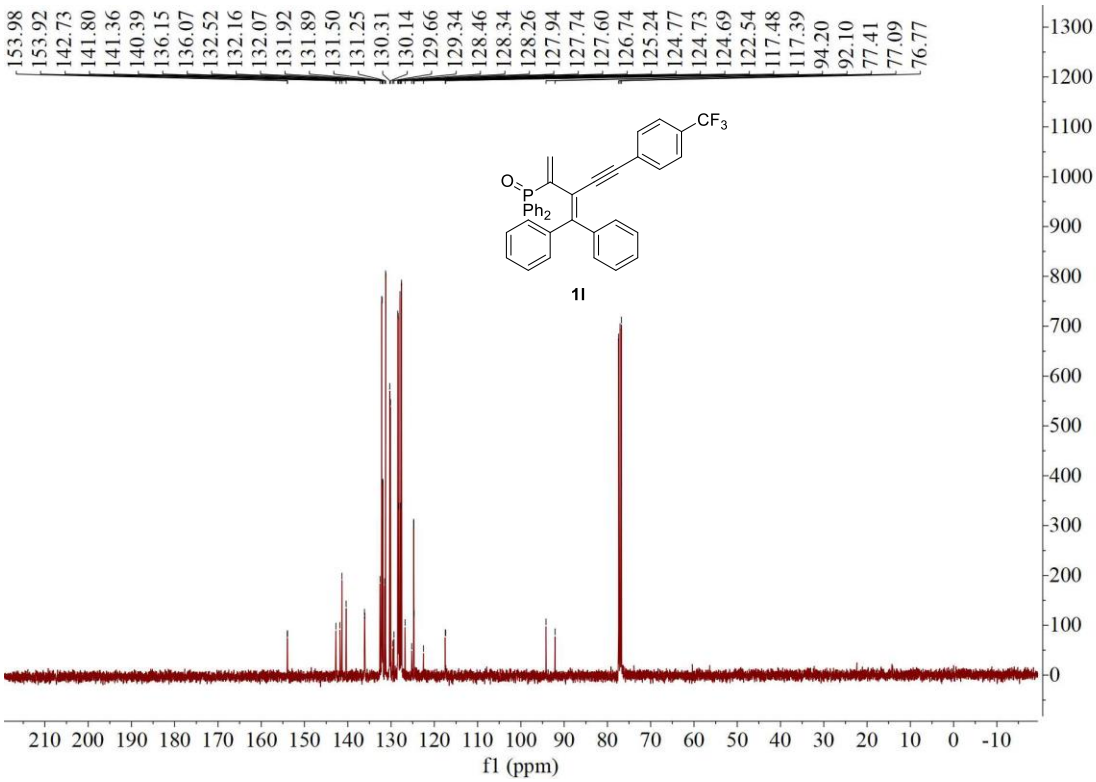

$^{31}$P NMR (243 MHz, $CDCl_3$) of **1f**



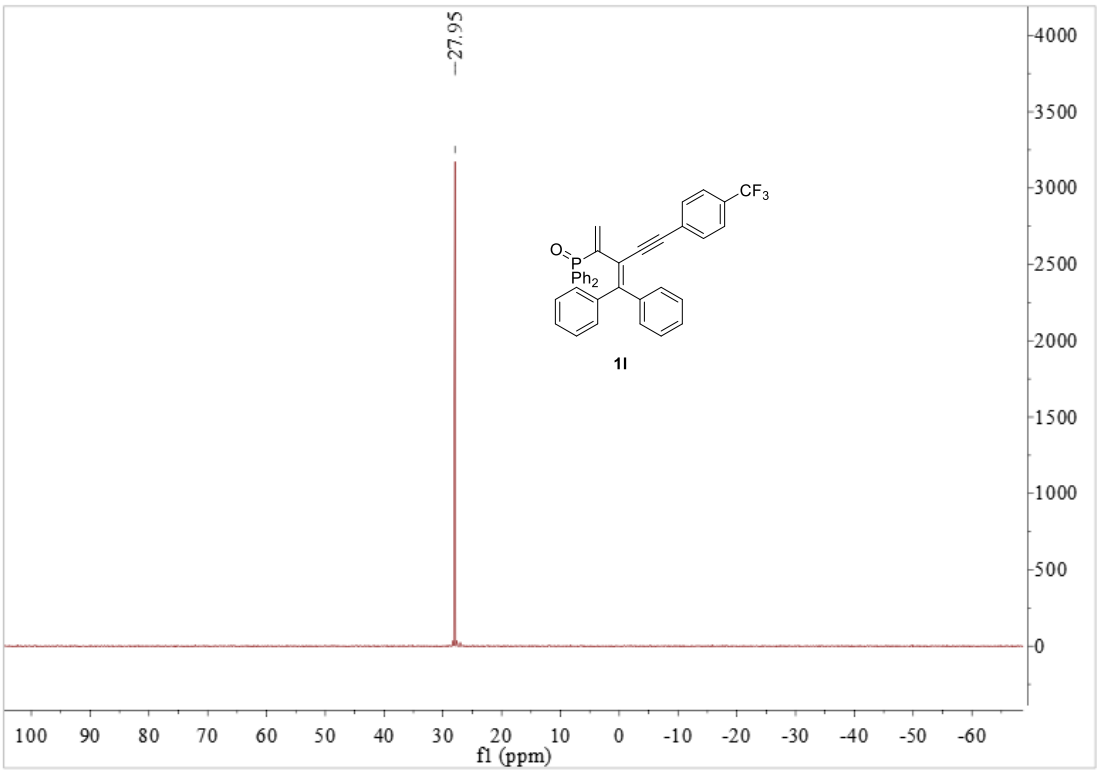
**Compound 1l ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$; $^{19}$F NMR, 376 MHz, $CDCl_3$)**



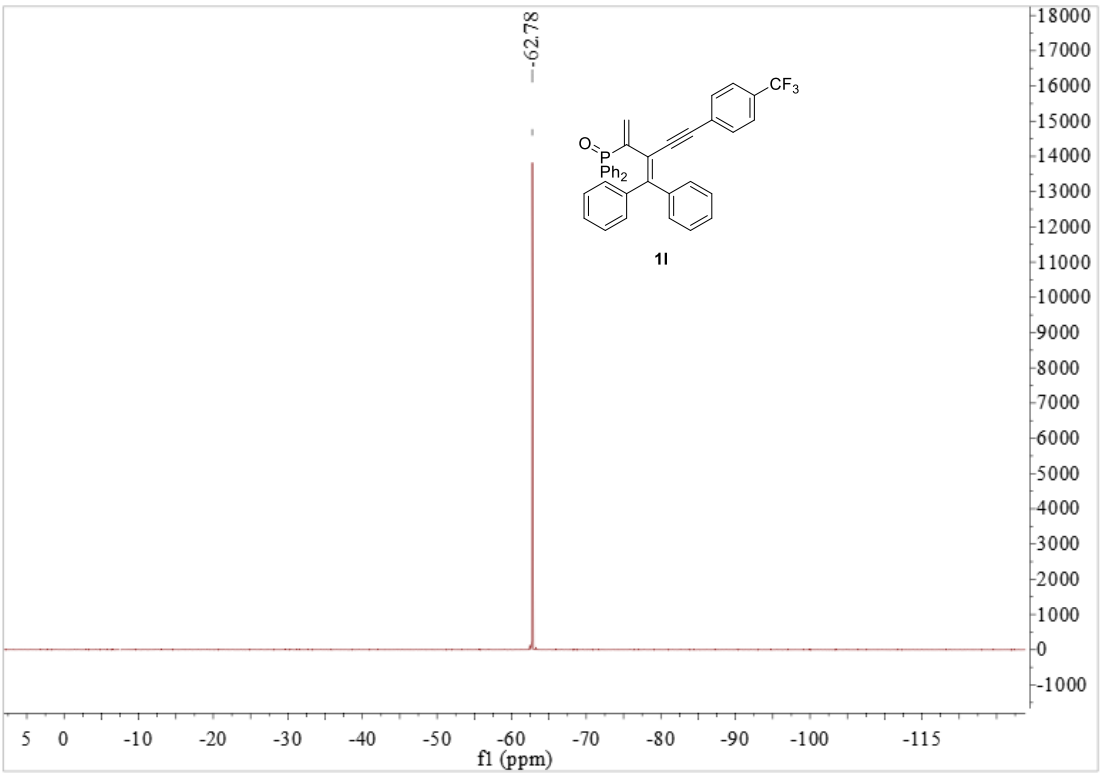

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1l**



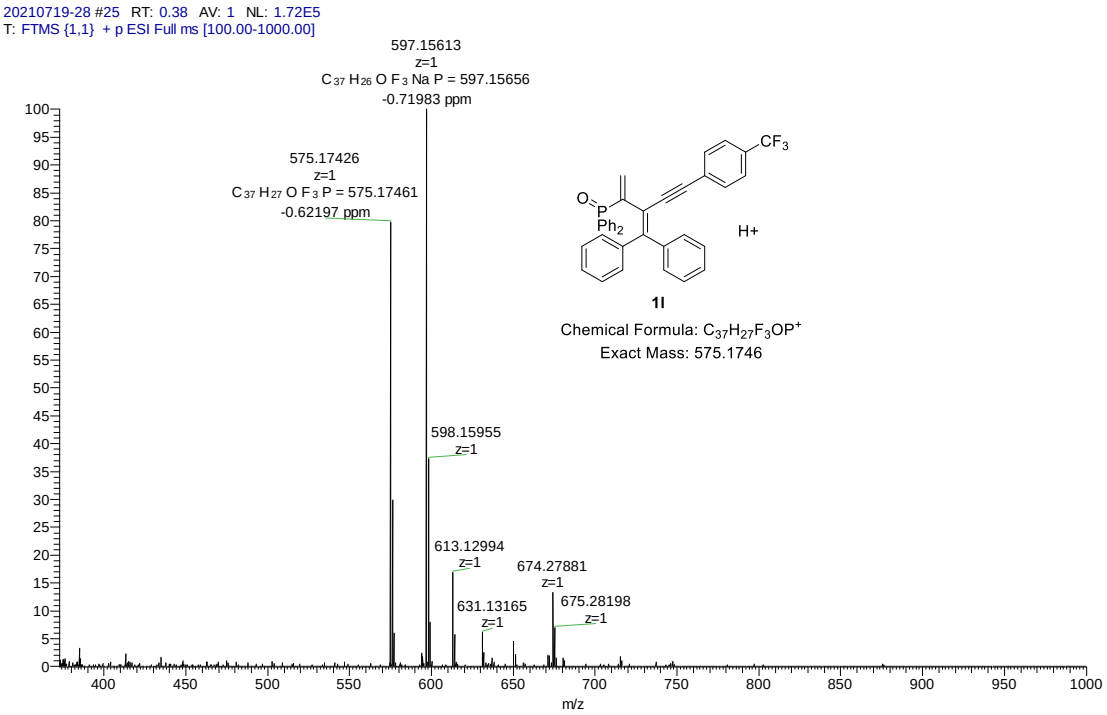

$^{13}$C NMR (101 MHz, $CDCl_3$) of **1l**



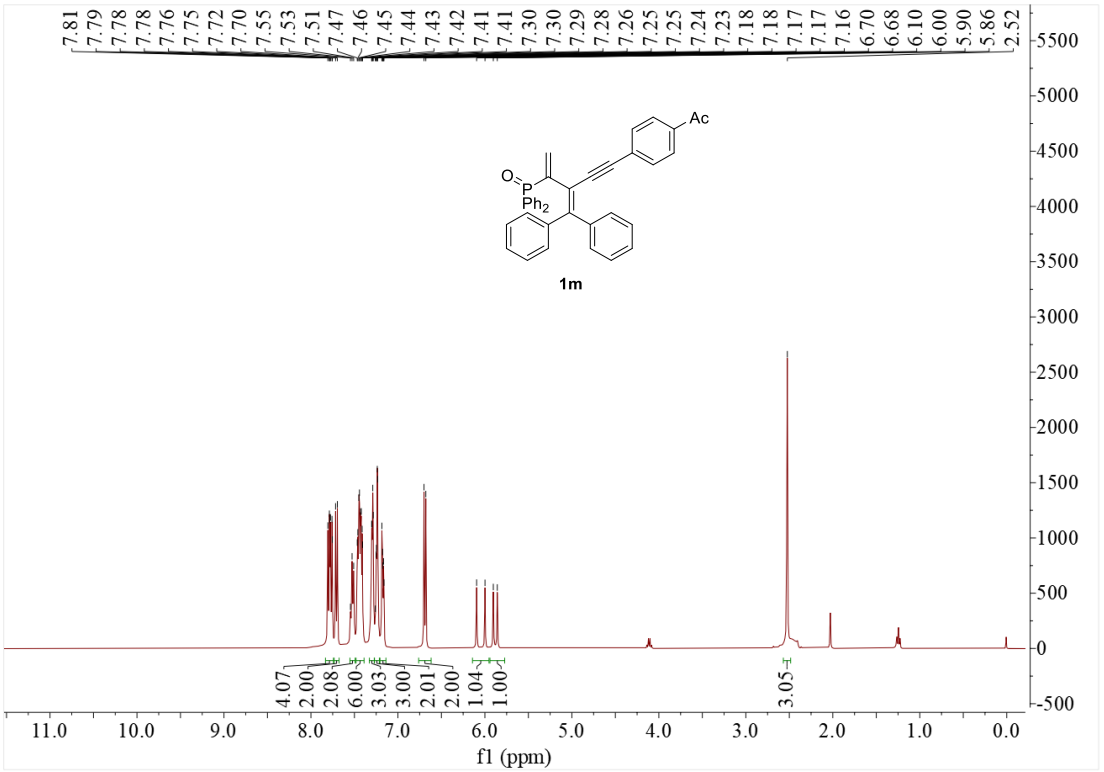

$^{31}$P NMR (162 MHz, $CDCl_3$) of **1l**



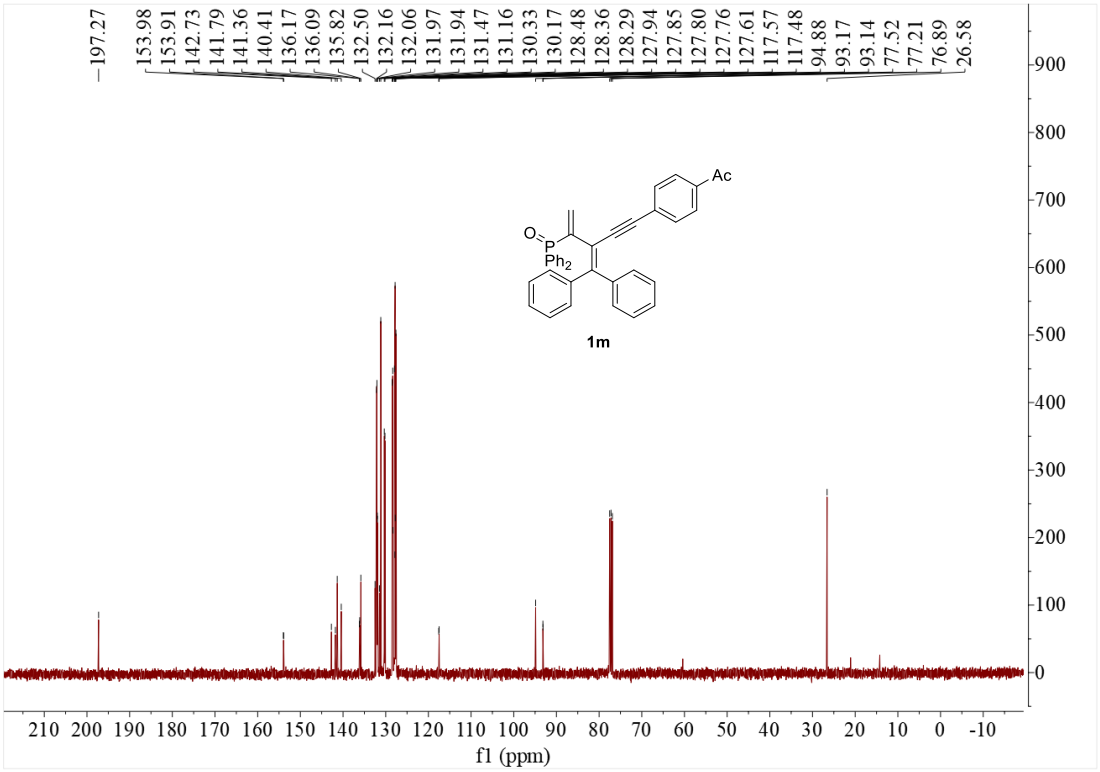

$^{19}$F NMR (376 MHz, $CDCl_3$) of **1l**



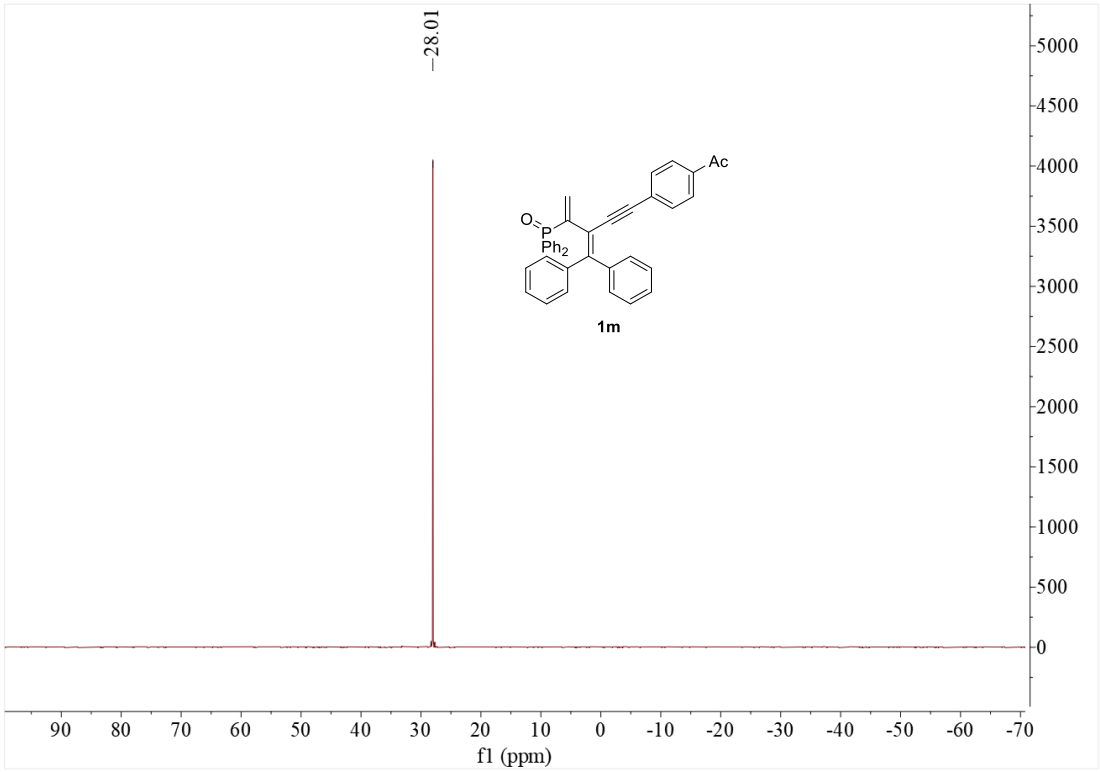

**Compound 1m ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



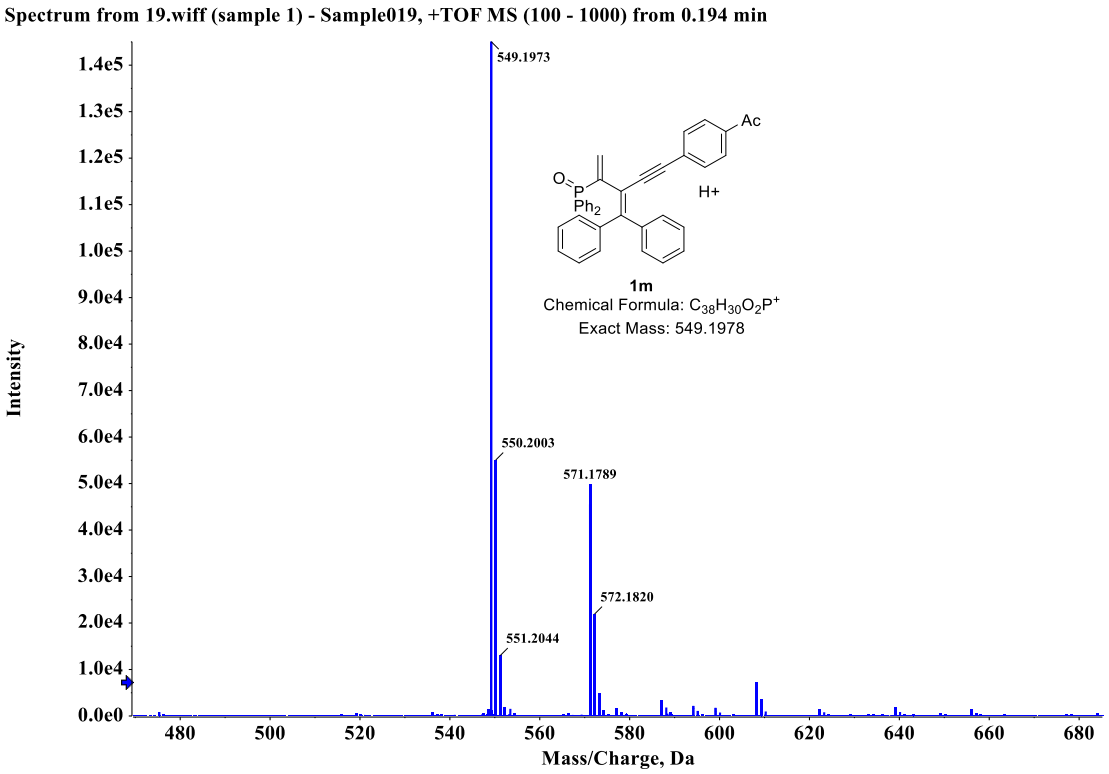

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1m**



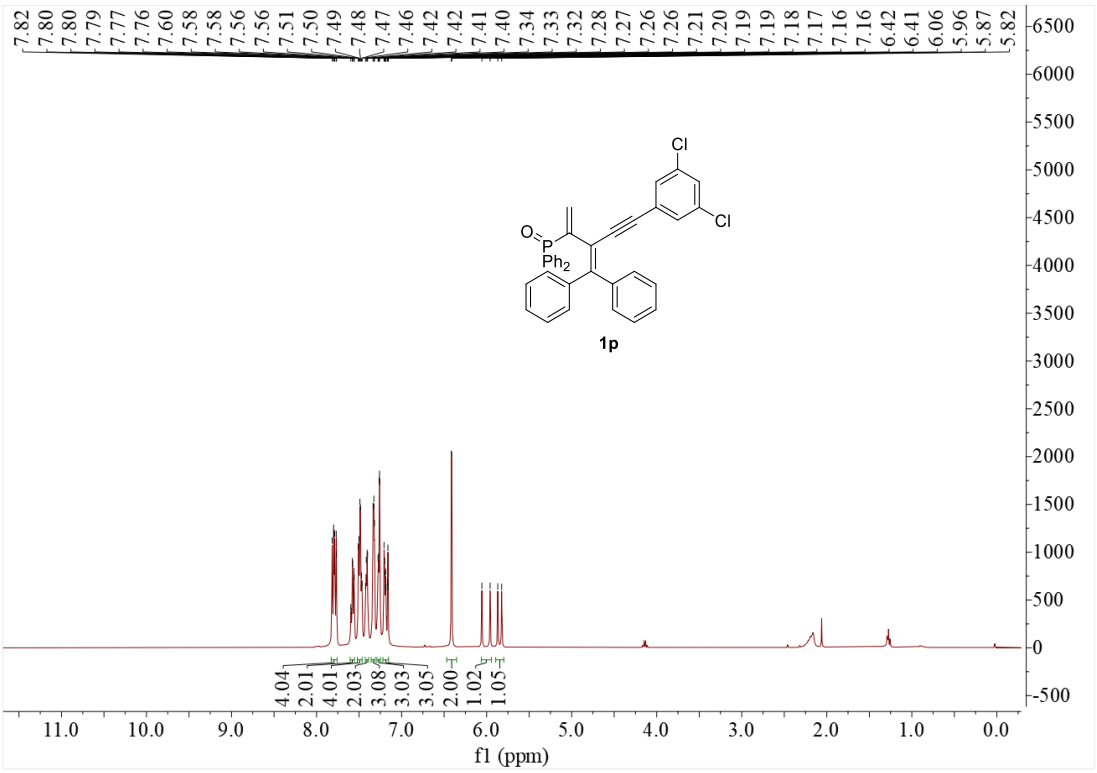

$^{13}$C NMR (101 MHz, $CDCl_3$) of **1m**



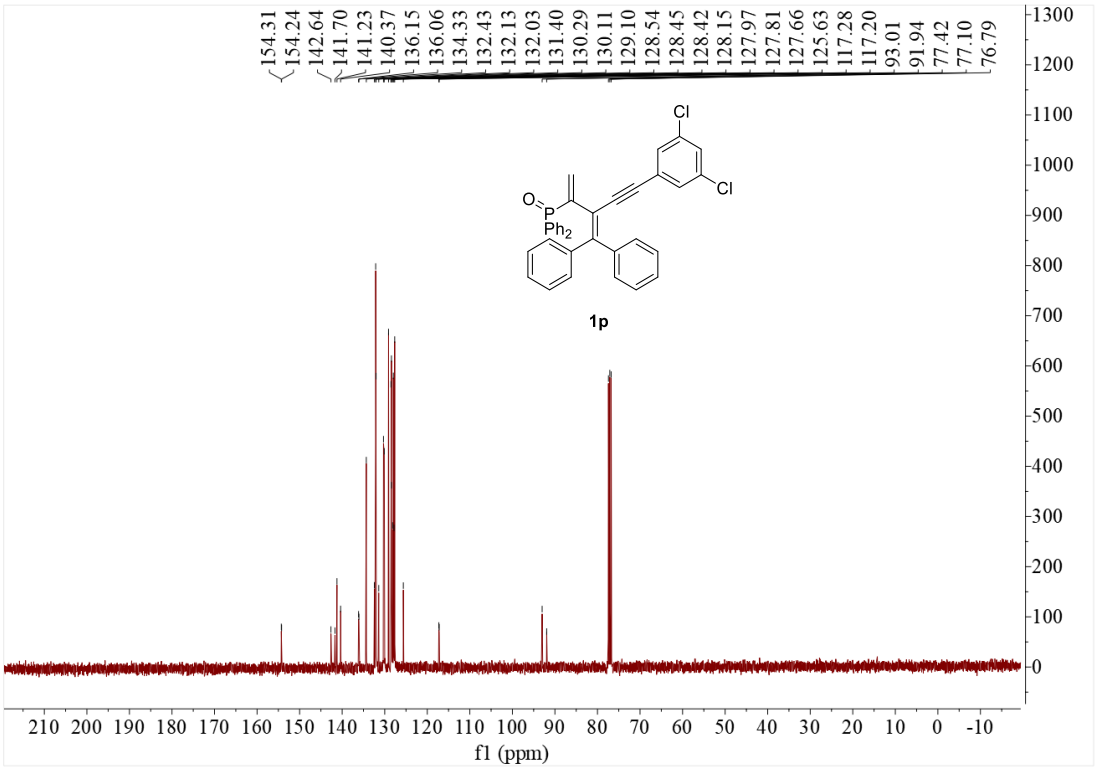

$^{31}$P NMR (162 MHz, $CDCl_3$) of **1m**



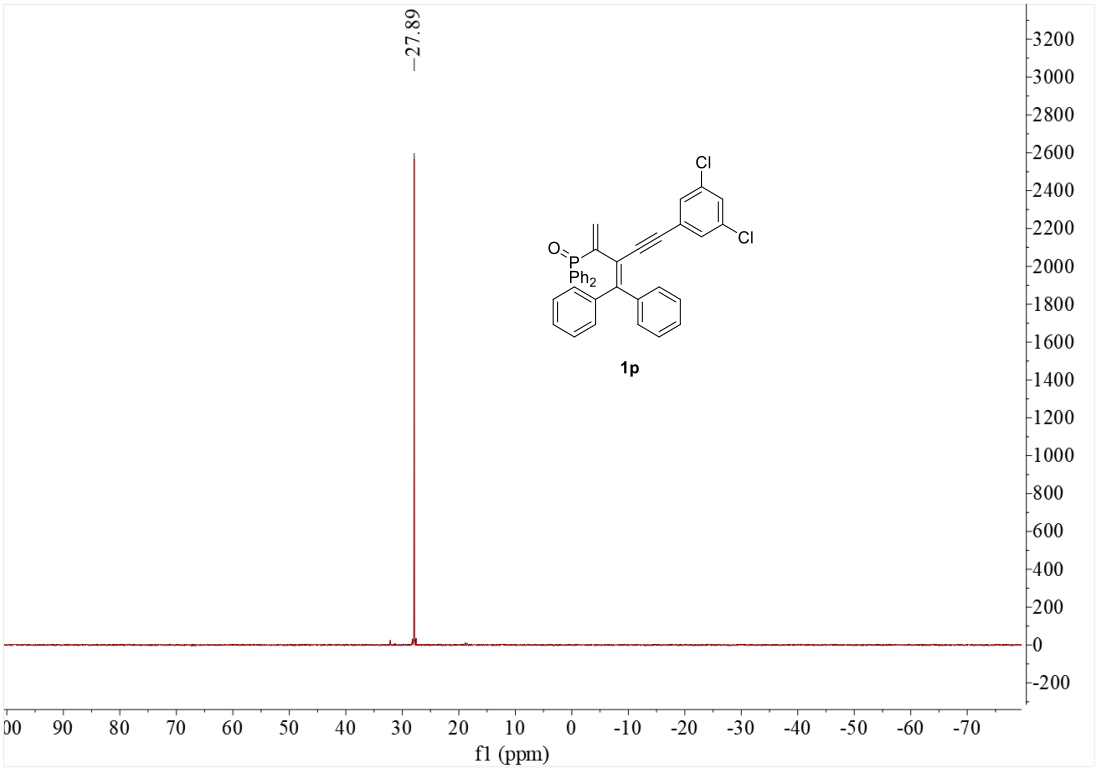

**Compound 1p ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



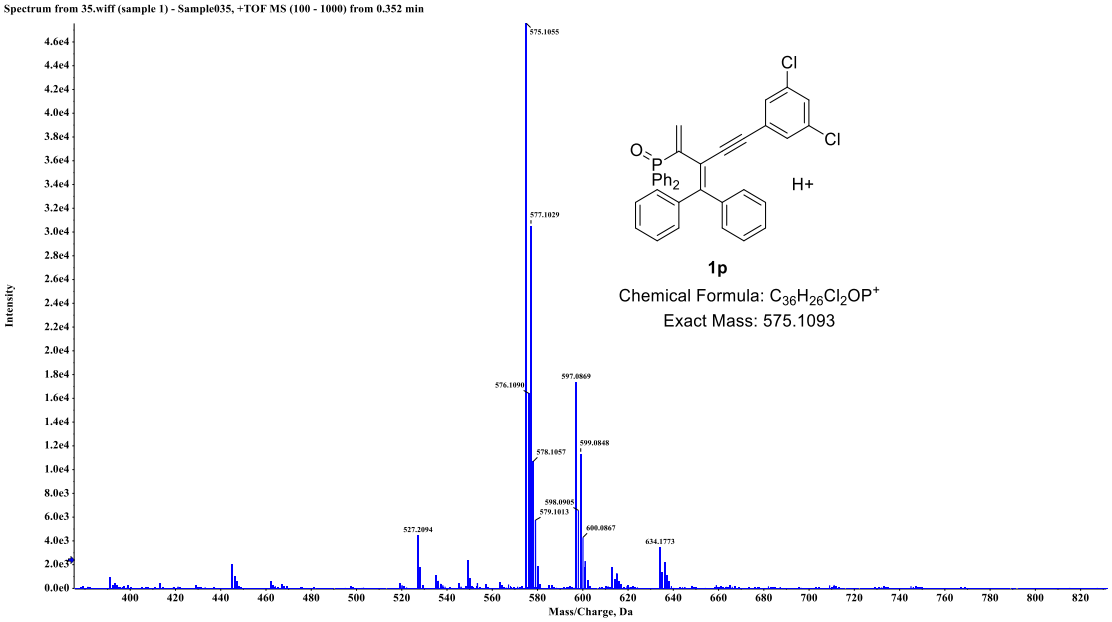

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1p**



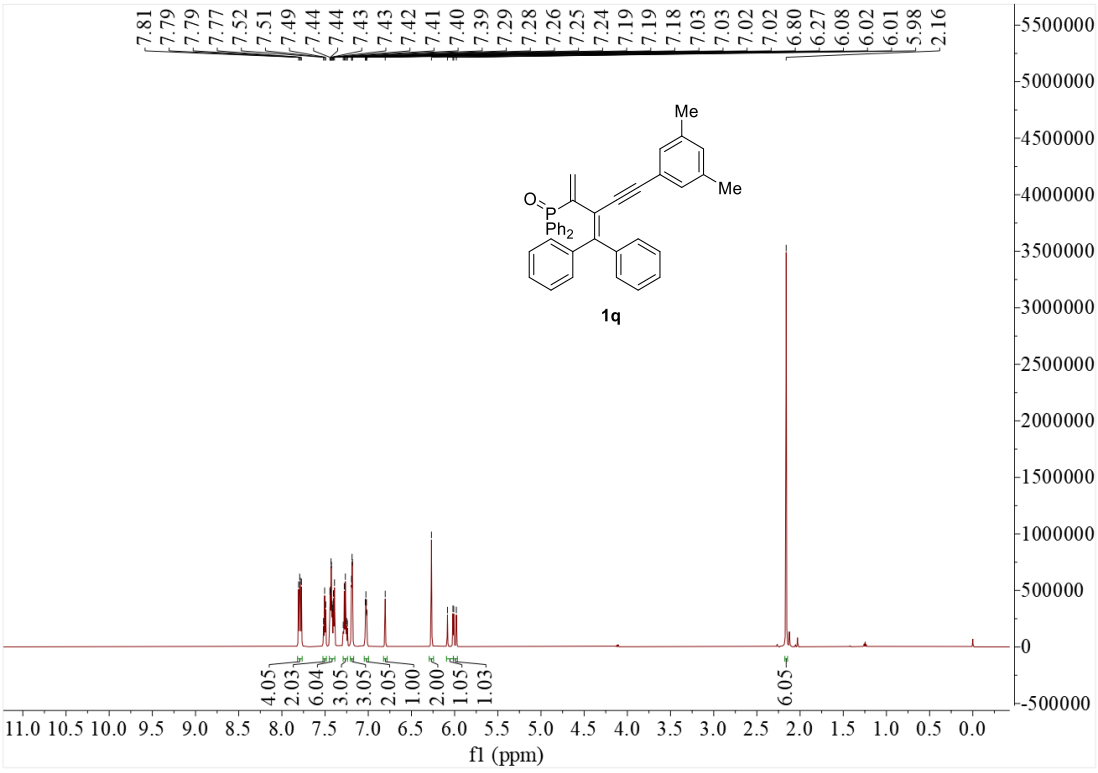

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **1p**



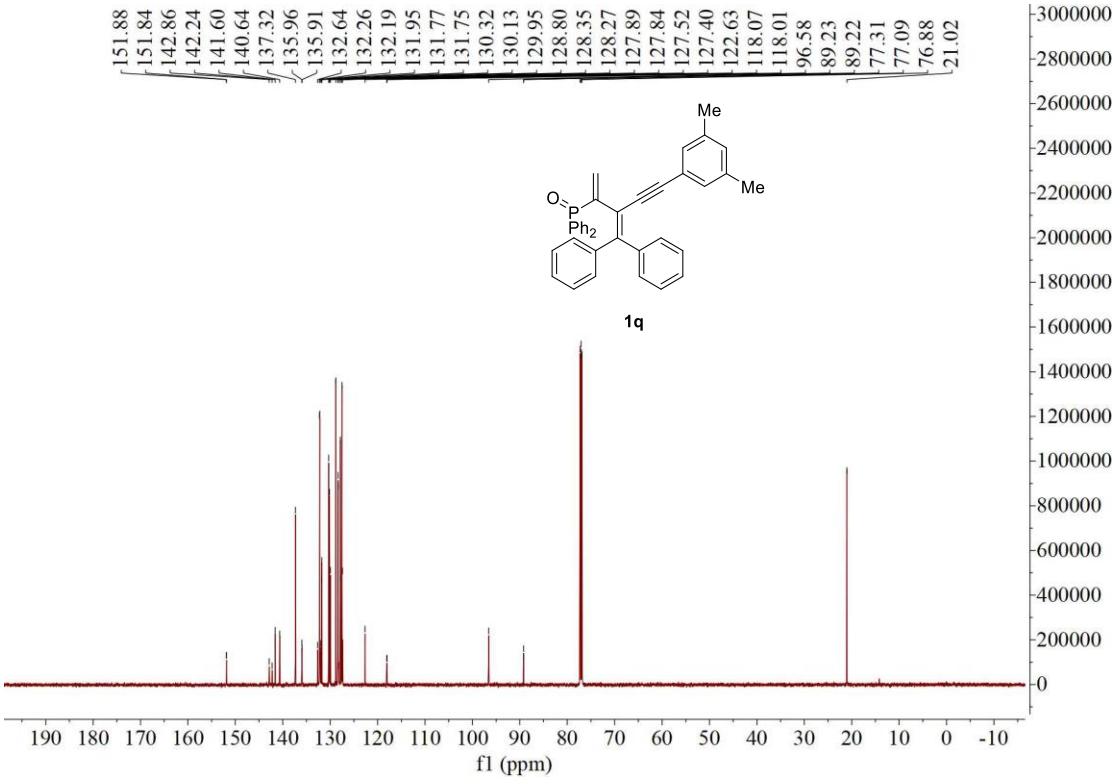

$^{31}P$ NMR (162 MHz, $CDCl_3$) of **1p**



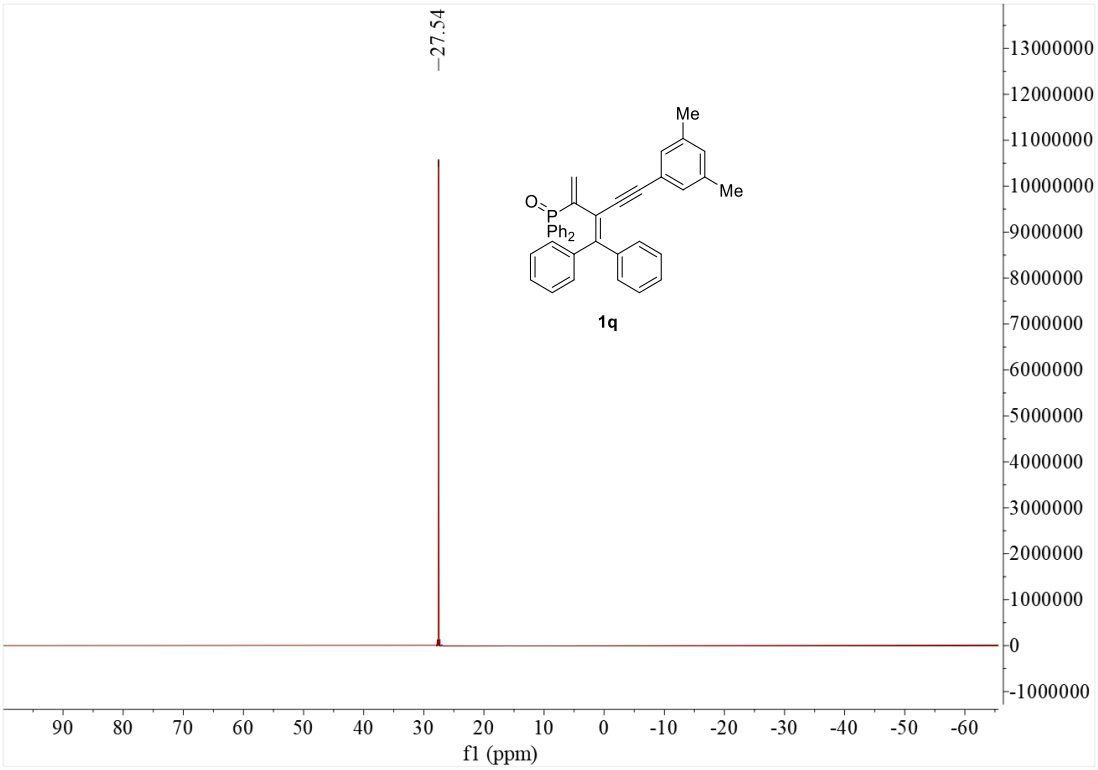

**Compound 1q ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



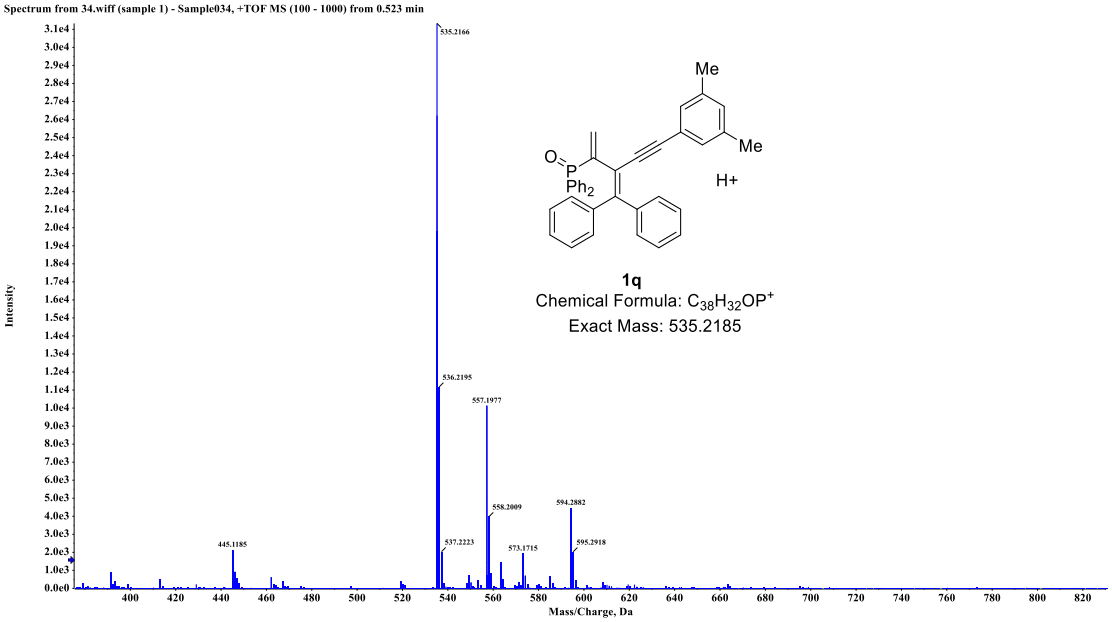

$^{1}$H NMR (600 MHz, $CDCl_3$) of **1q**



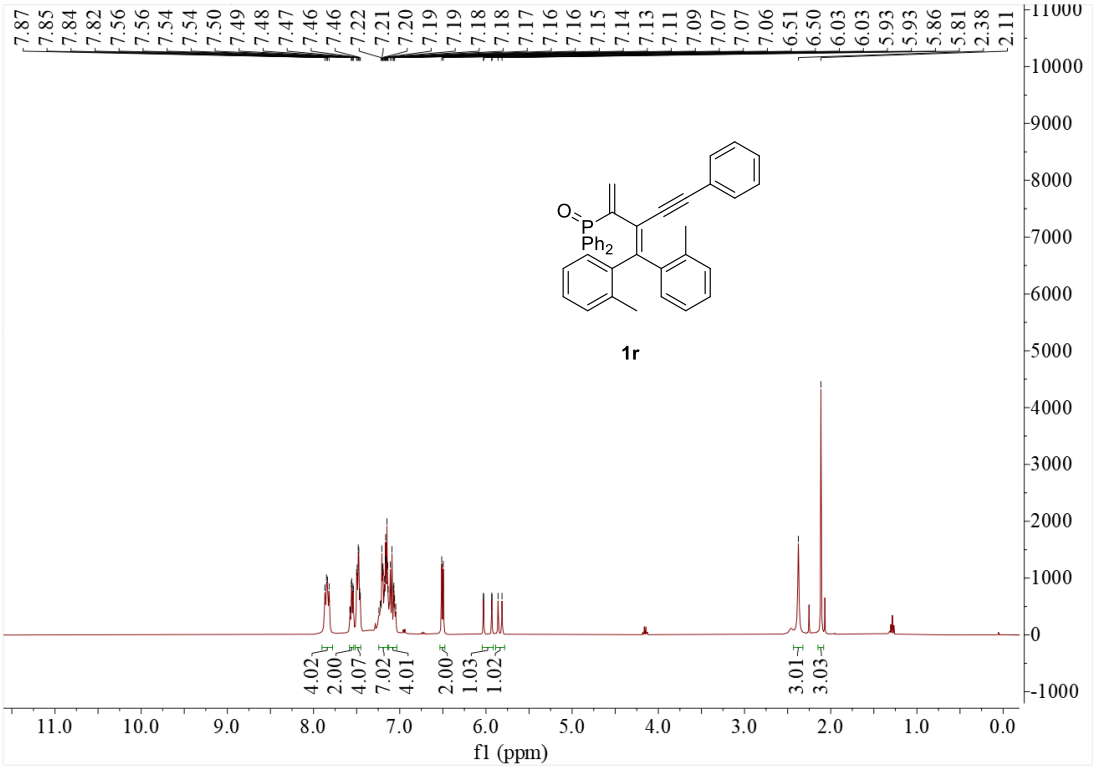

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **1q**



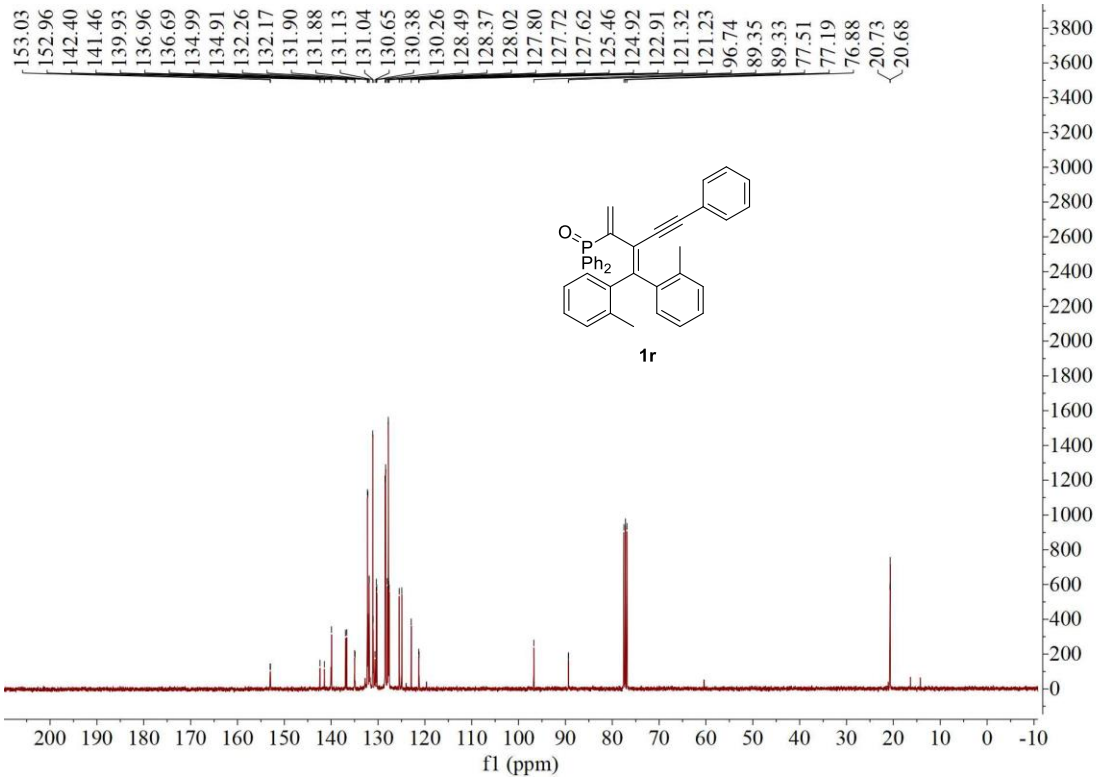

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **1q**



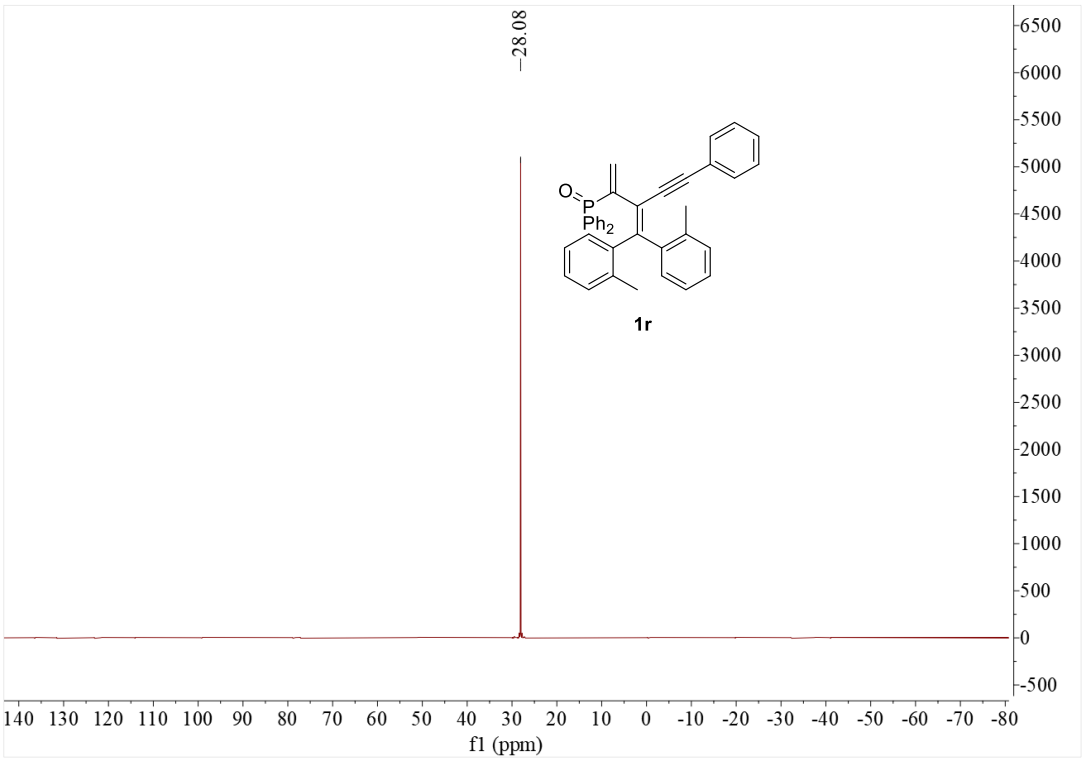

**Compound 1r ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



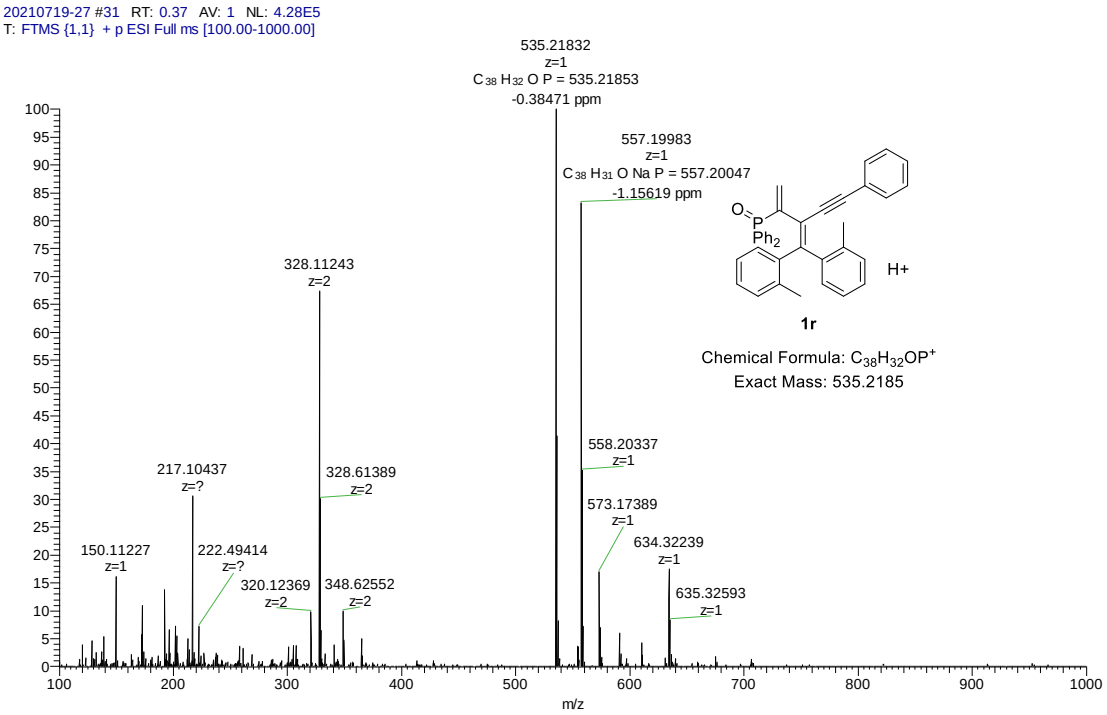

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1r**



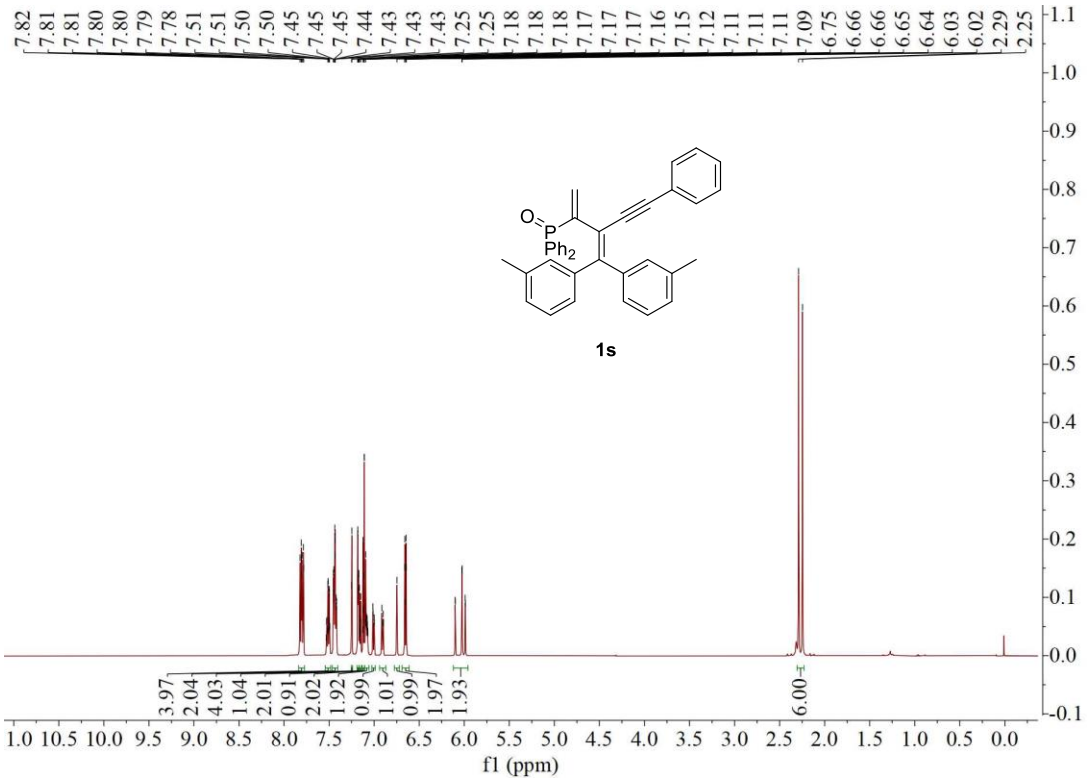

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **1r**



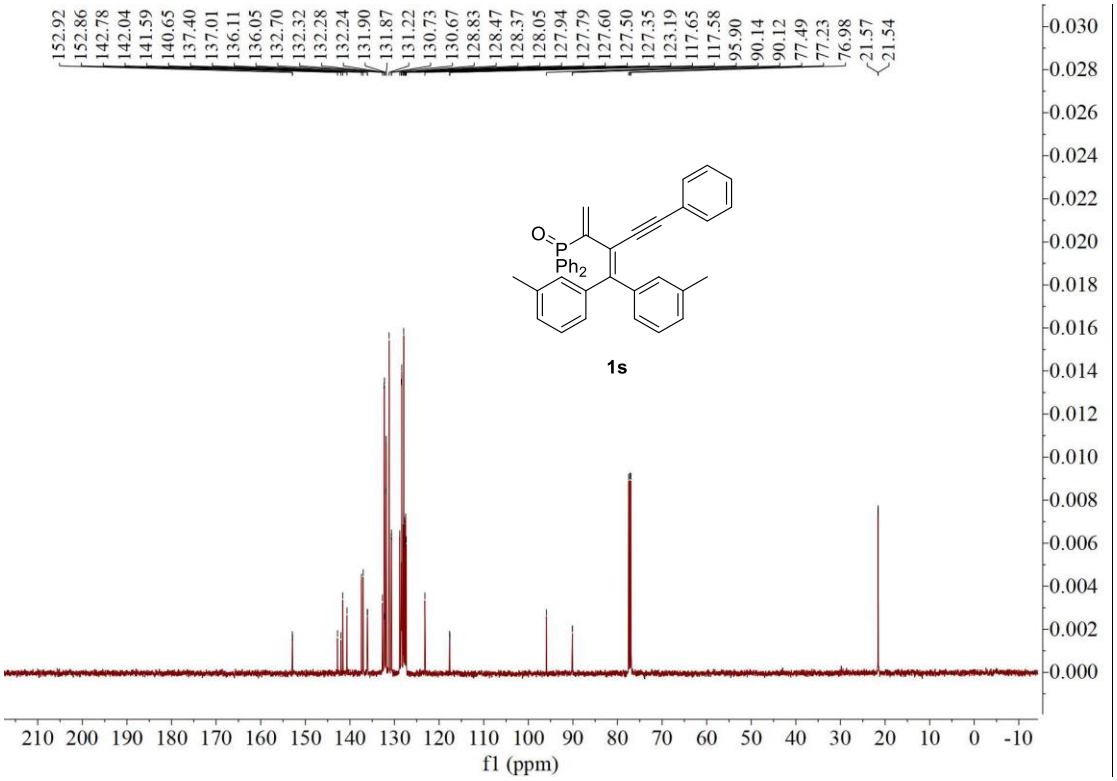

$^{31}P$ NMR (162 MHz, $CDCl_3$) of **1r**



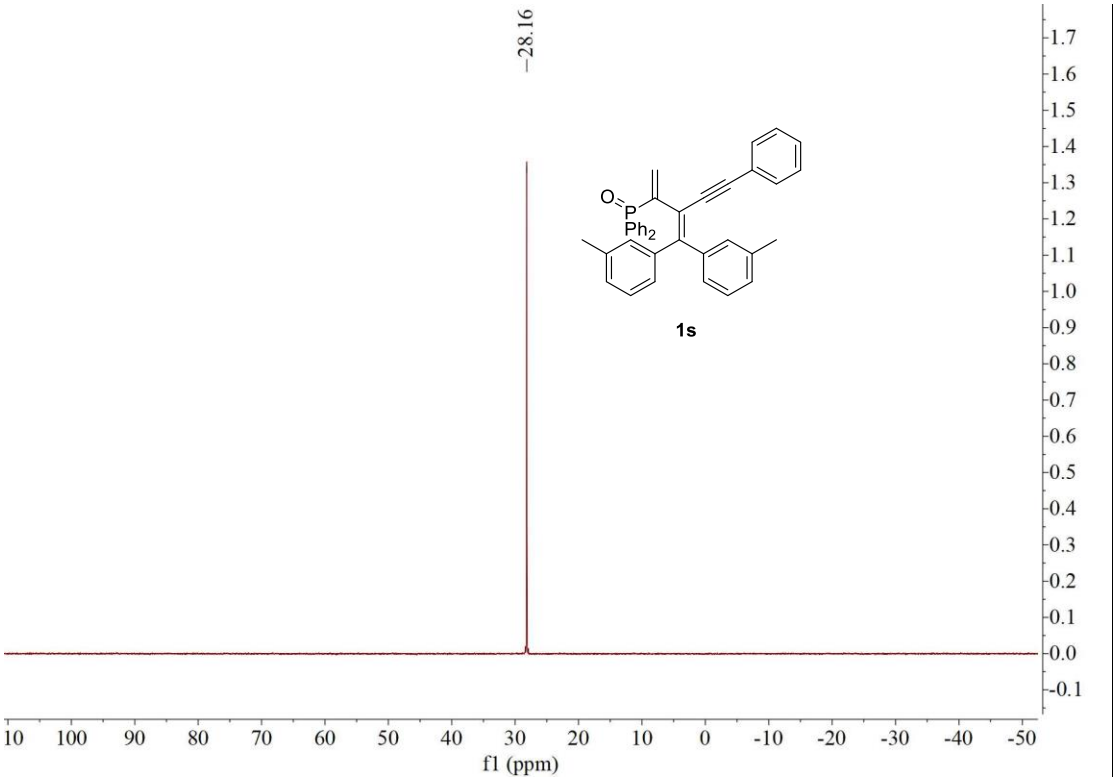

**Compound 1s ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**




$^{1}$H NMR (500 MHz, $CDCl_3$) of **1s**

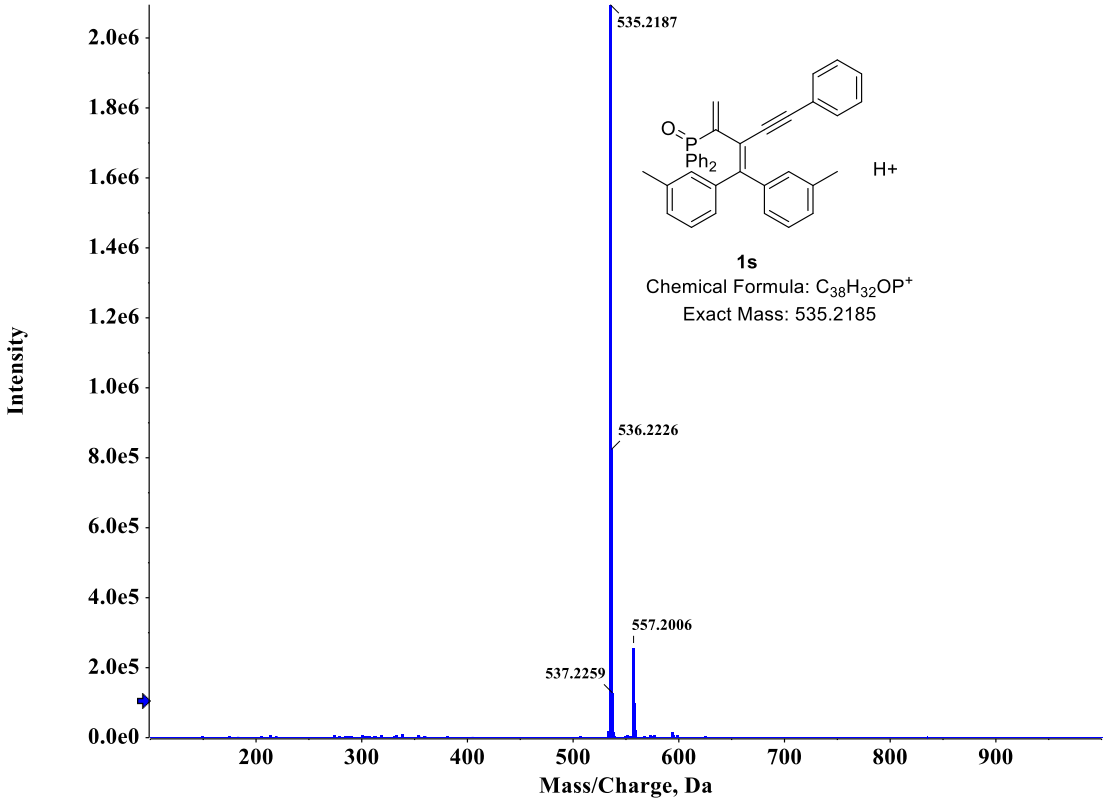



$^{13}C$ NMR (126 MHz, $CDCl_3$) of **1s**

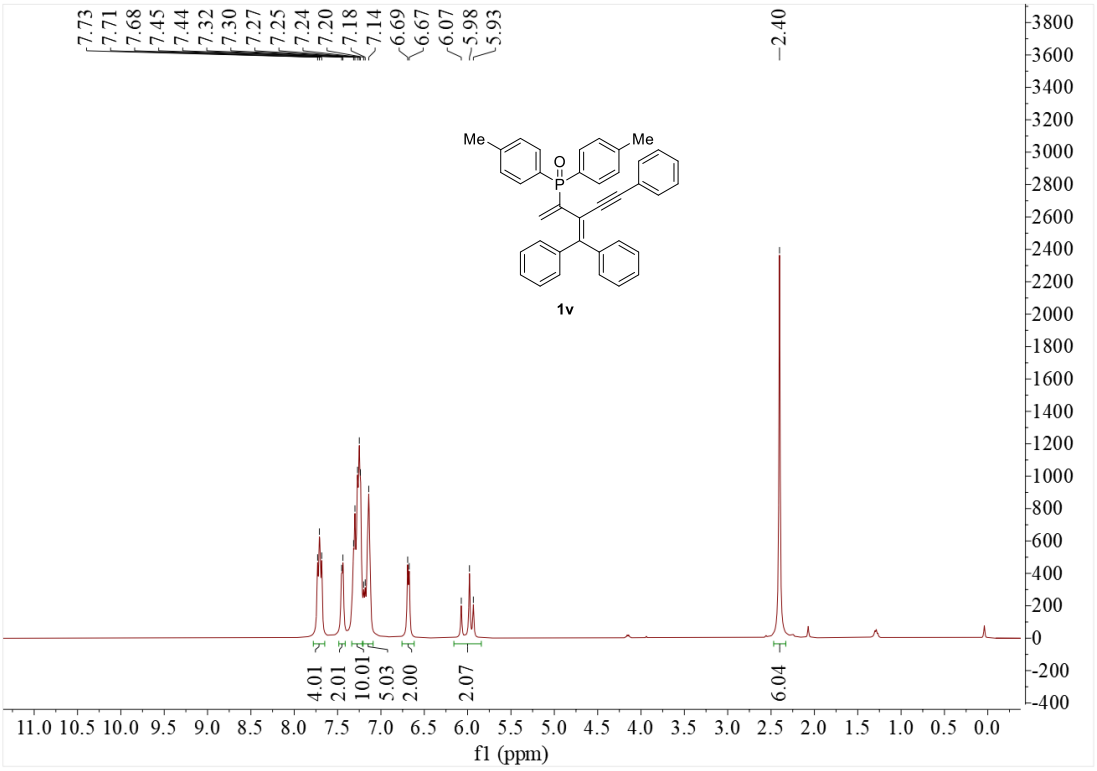



$^{31}P$ NMR (202 MHz, $CDCl_3$) of **1s**

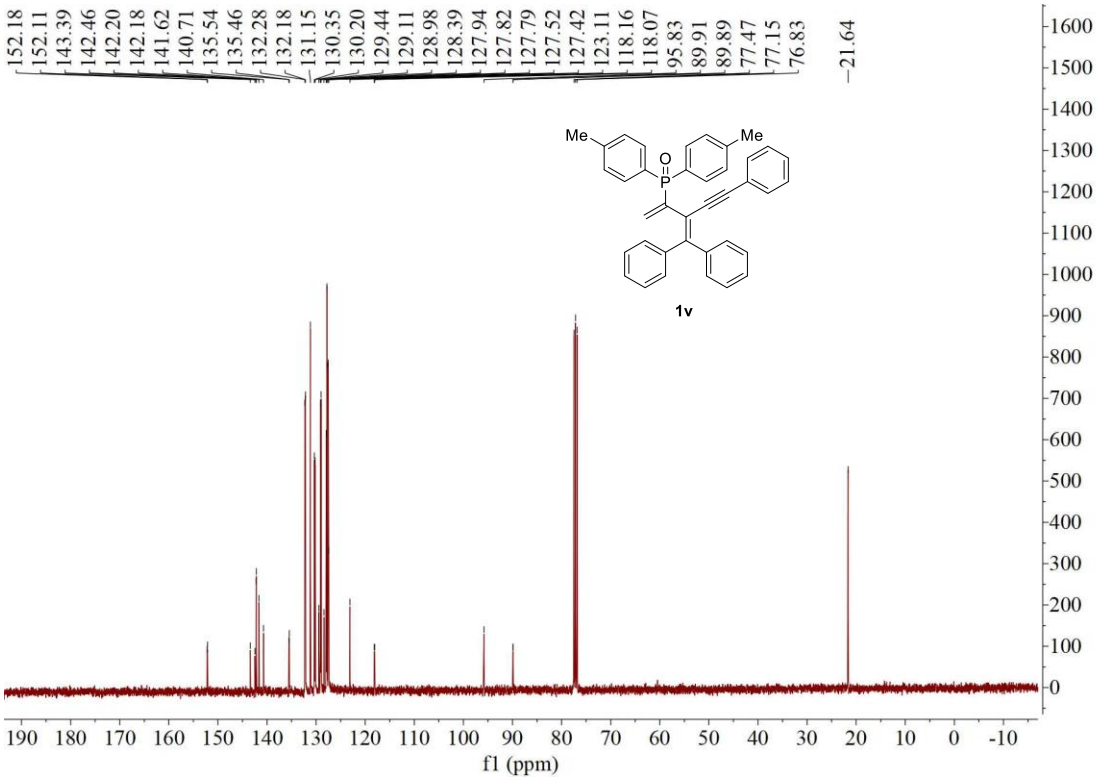
**Spectrum from 21.wiff (sample 1) - Sample021, +TOF MS (100 - 1000) from 0.146 min**



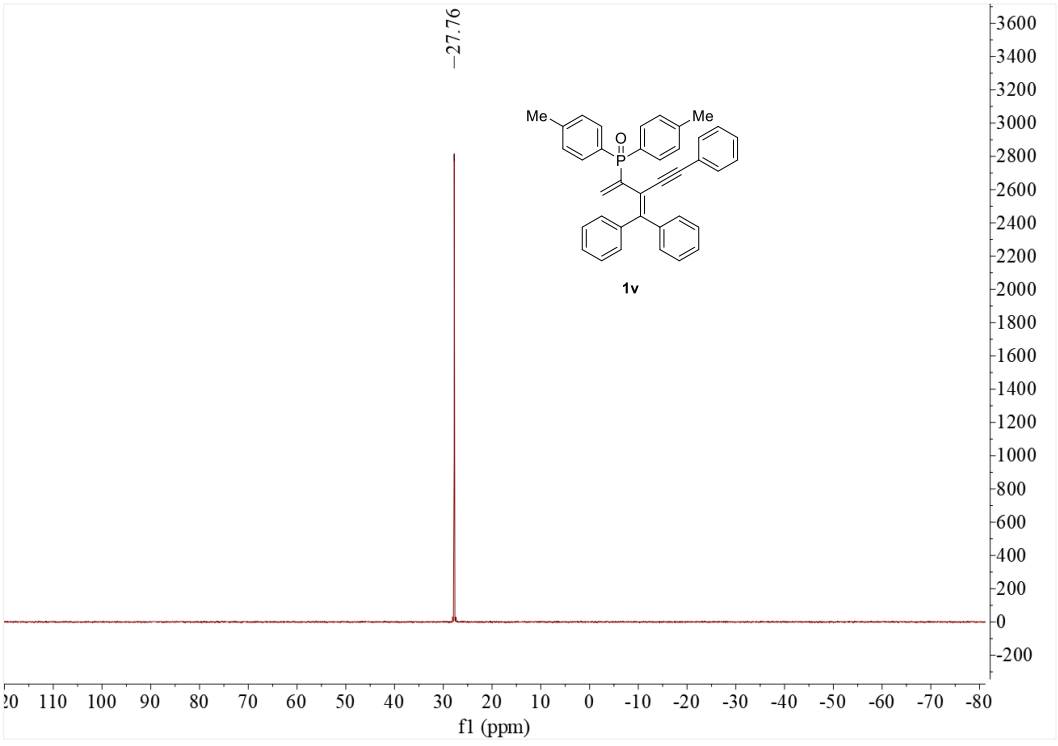

**Compound 1v ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



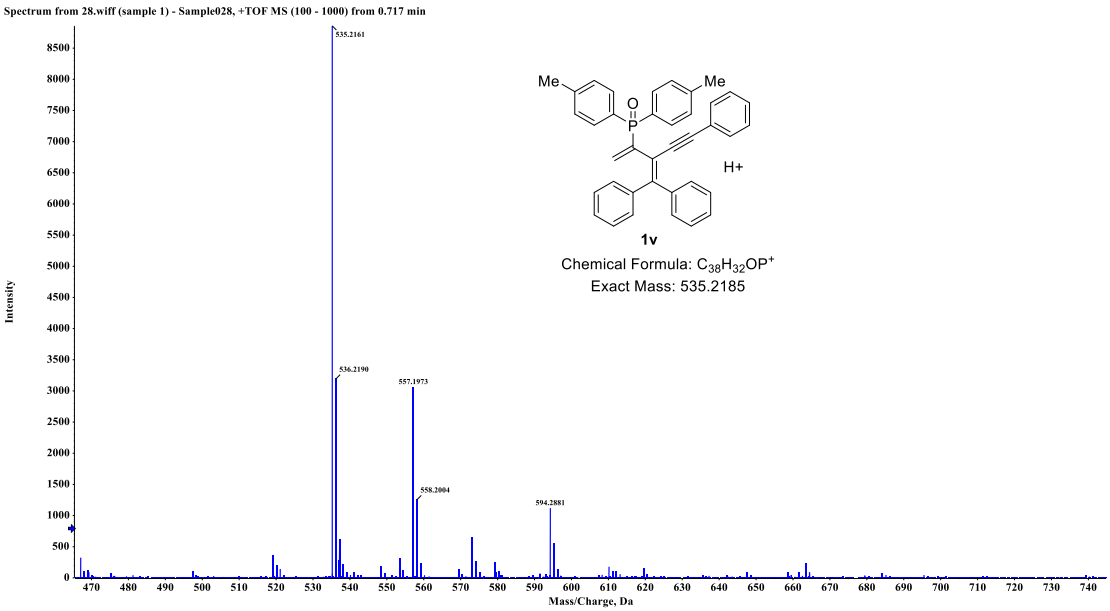

$^{1}$H NMR (400 MHz, $CDCl_3$) of **1v**



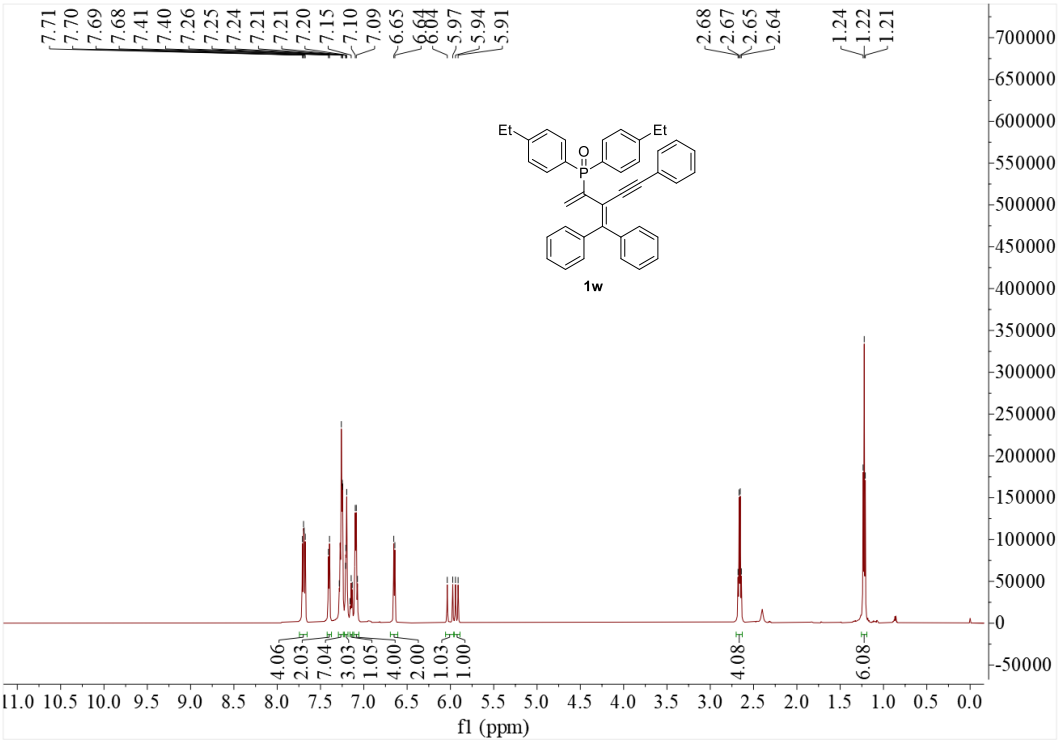

$^{13}$C NMR (101 MHz, $CDCl_3$) of **1v**



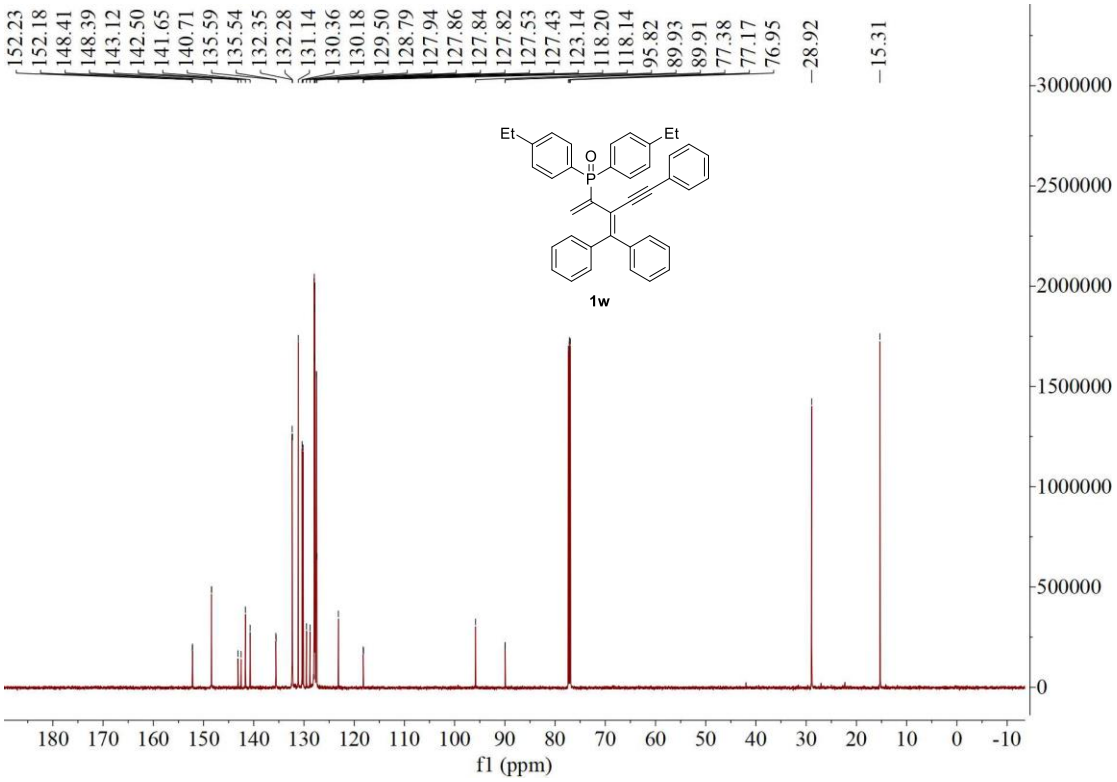

$^{31}$P NMR (162 MHz, $CDCl_3$) of **1v**



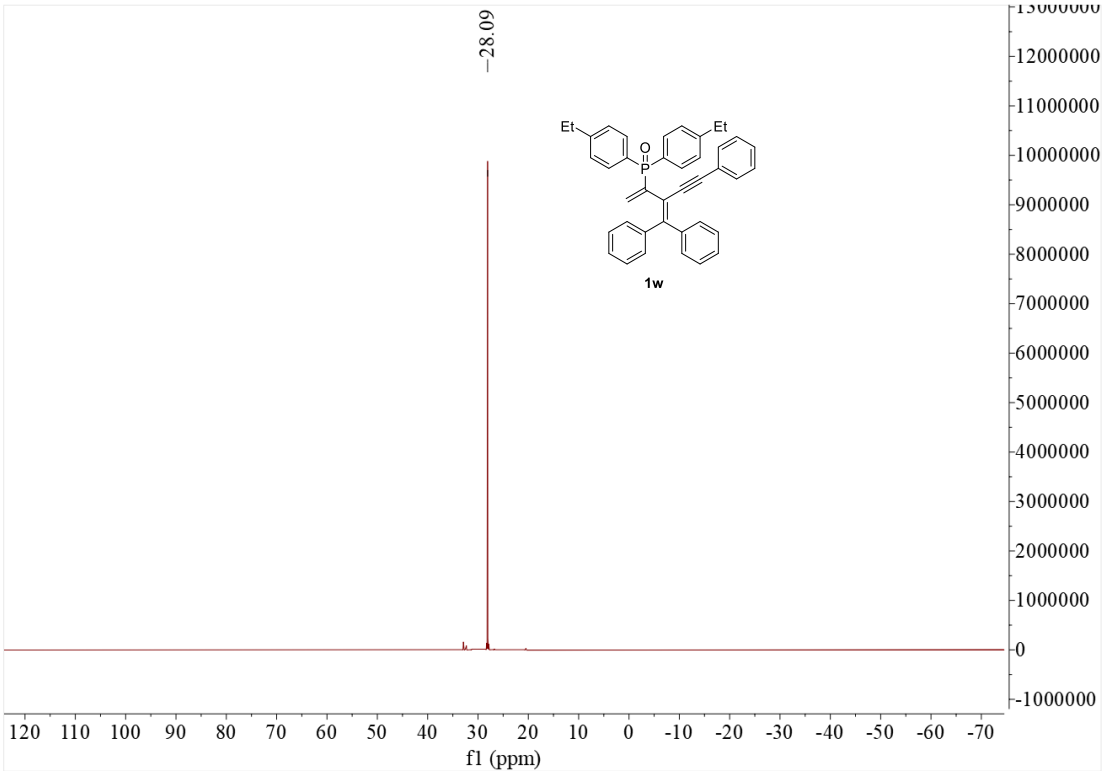

**Compound 1w ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



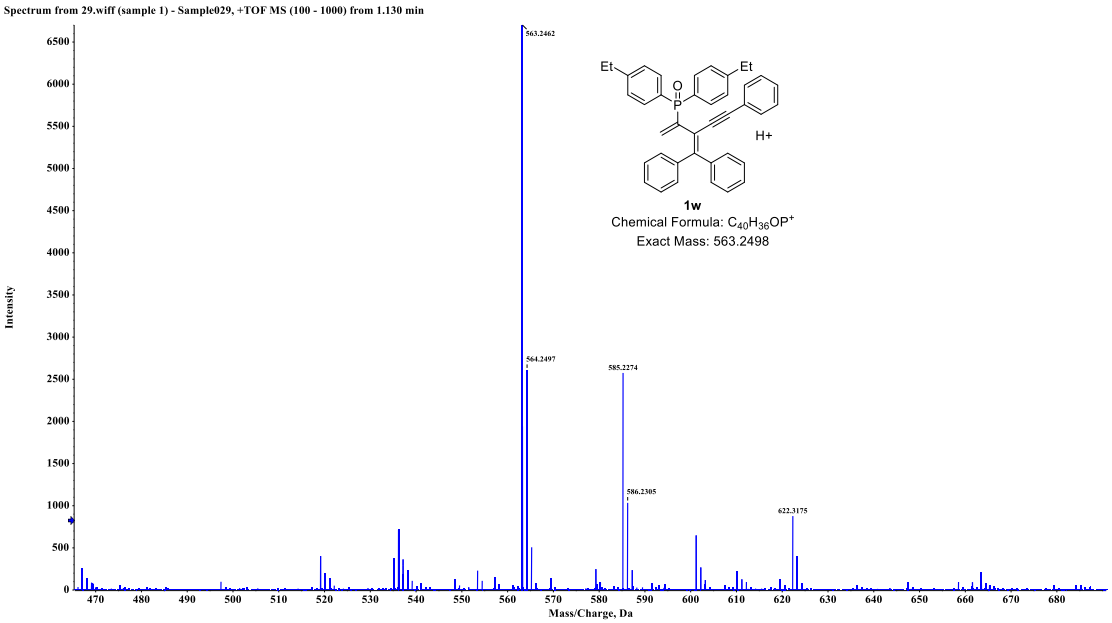
$^{1}$H NMR (600 MHz, $CDCl_3$) of **1w**



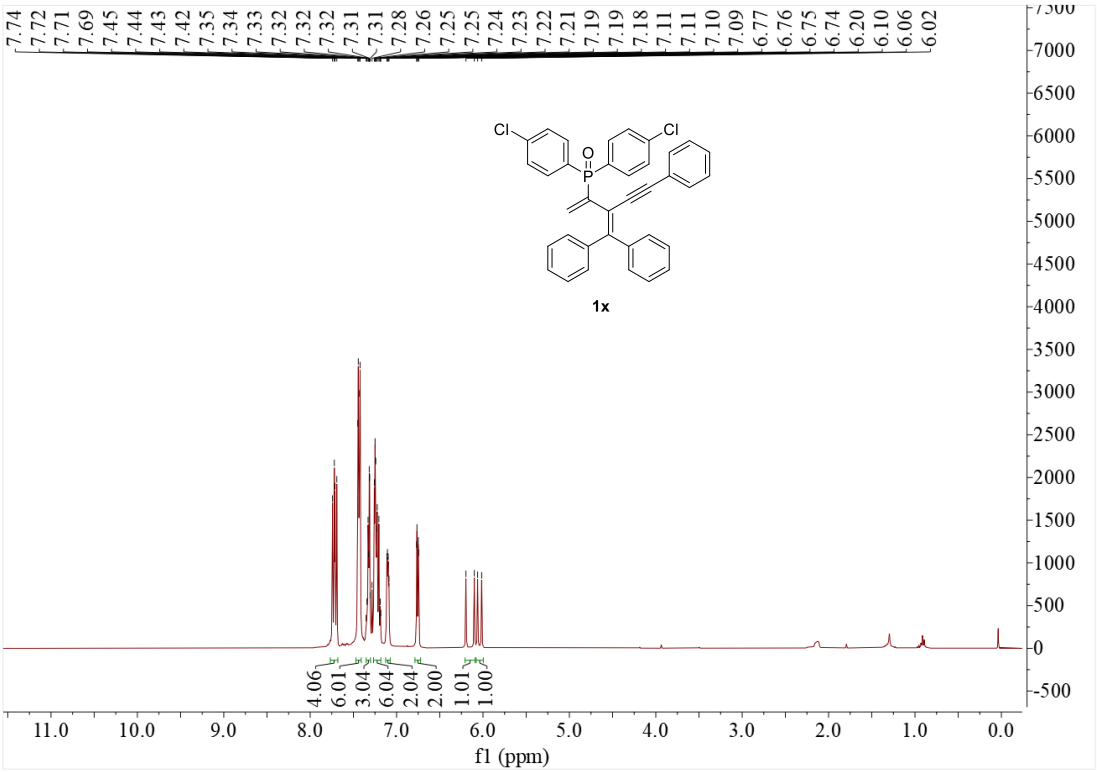

$^{13}$C NMR (151 MHz, $CDCl_3$) of **1w**



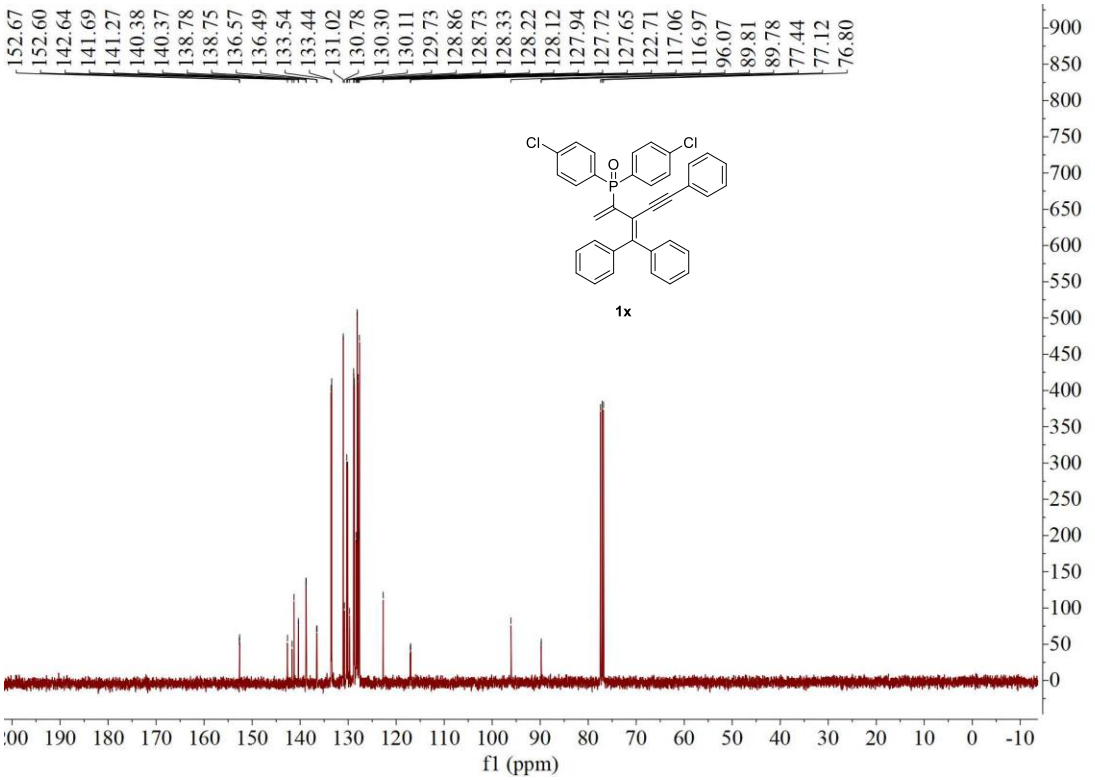
$^{31}$P NMR (243 MHz, $CDCl_3$) of **1w**



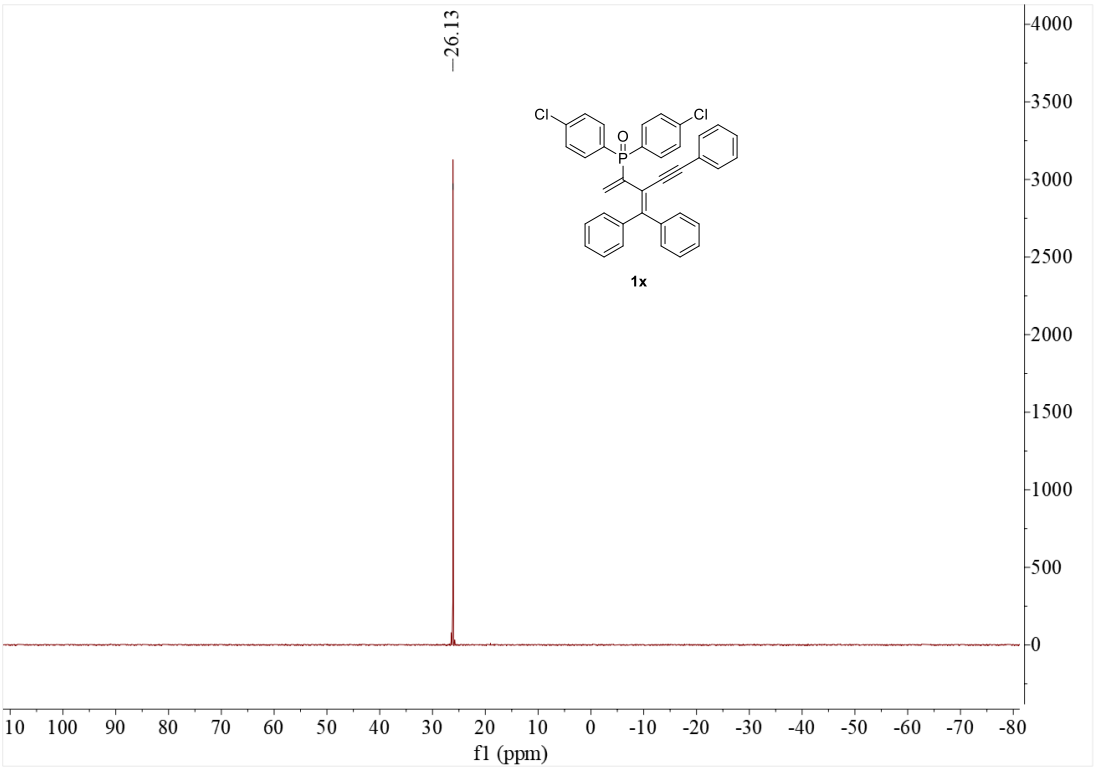

**Compound 1x ($^1$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



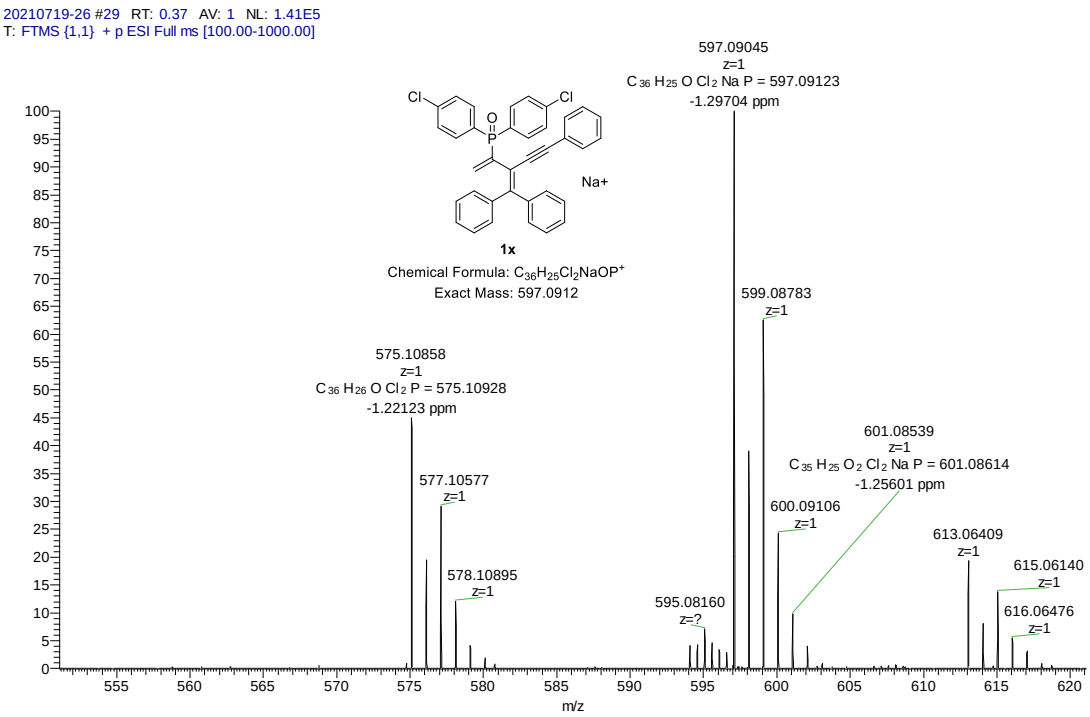

$^1$H NMR (400 MHz, $CDCl_3$) of **1x**



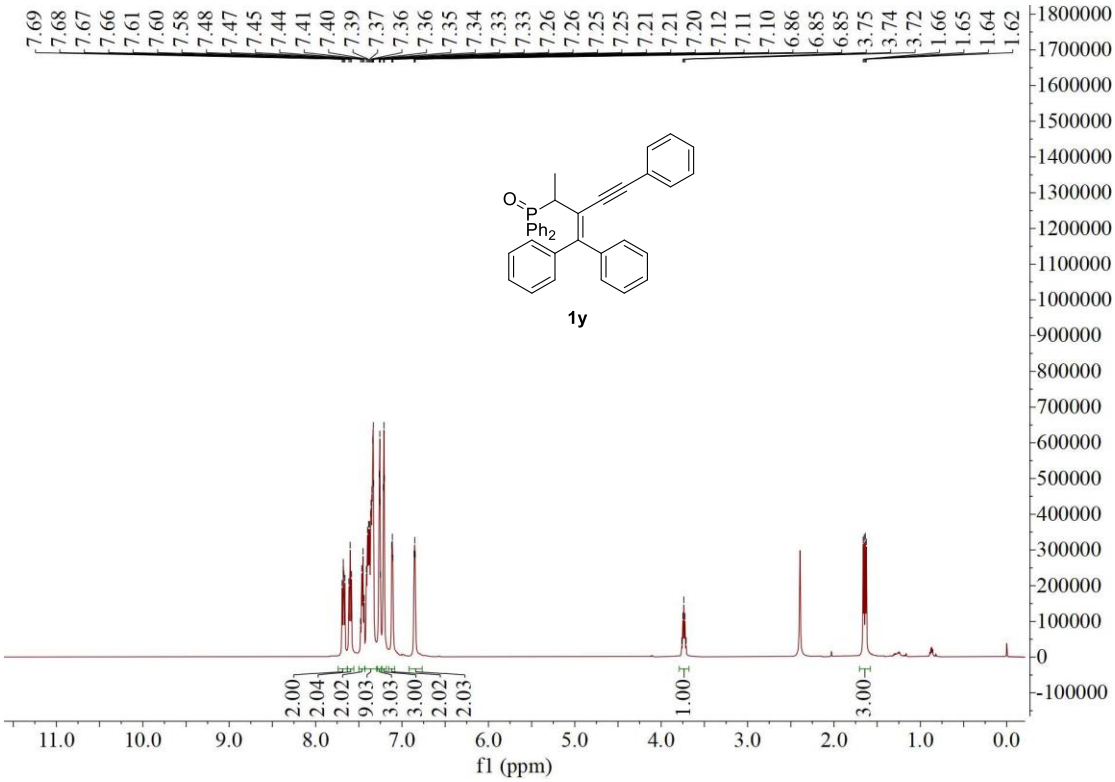

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **1x**



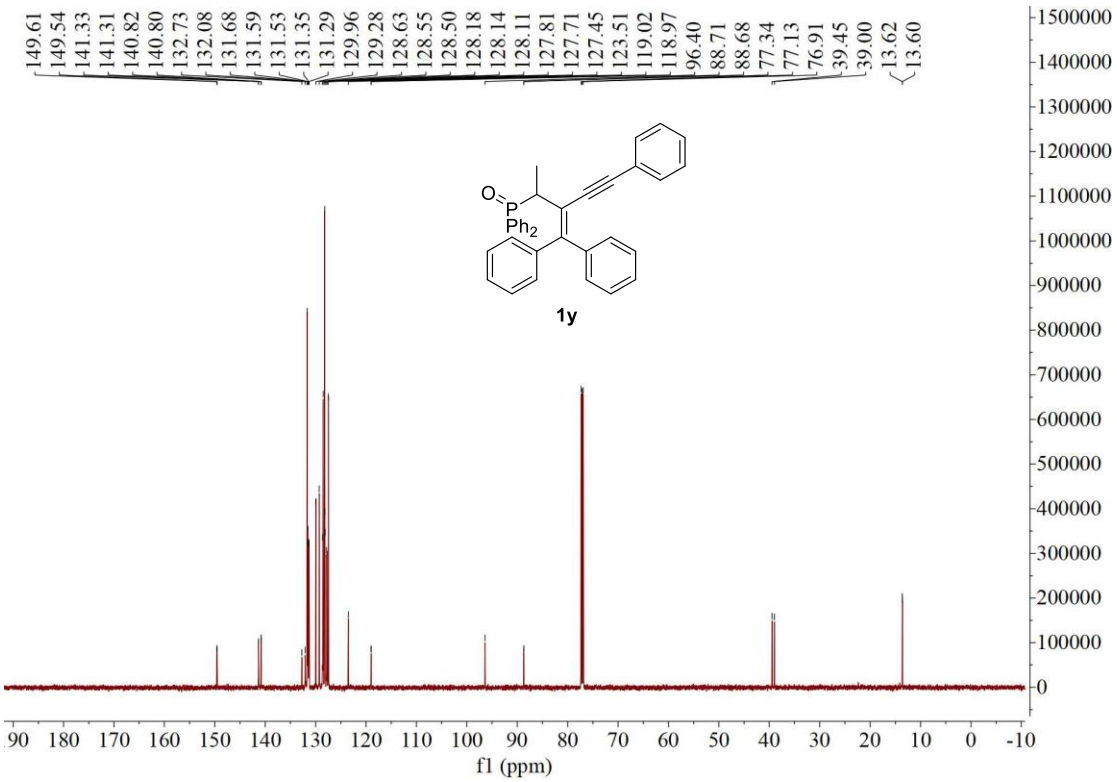

$^{31}P$ NMR (162 MHz, $CDCl_3$) of **1x**



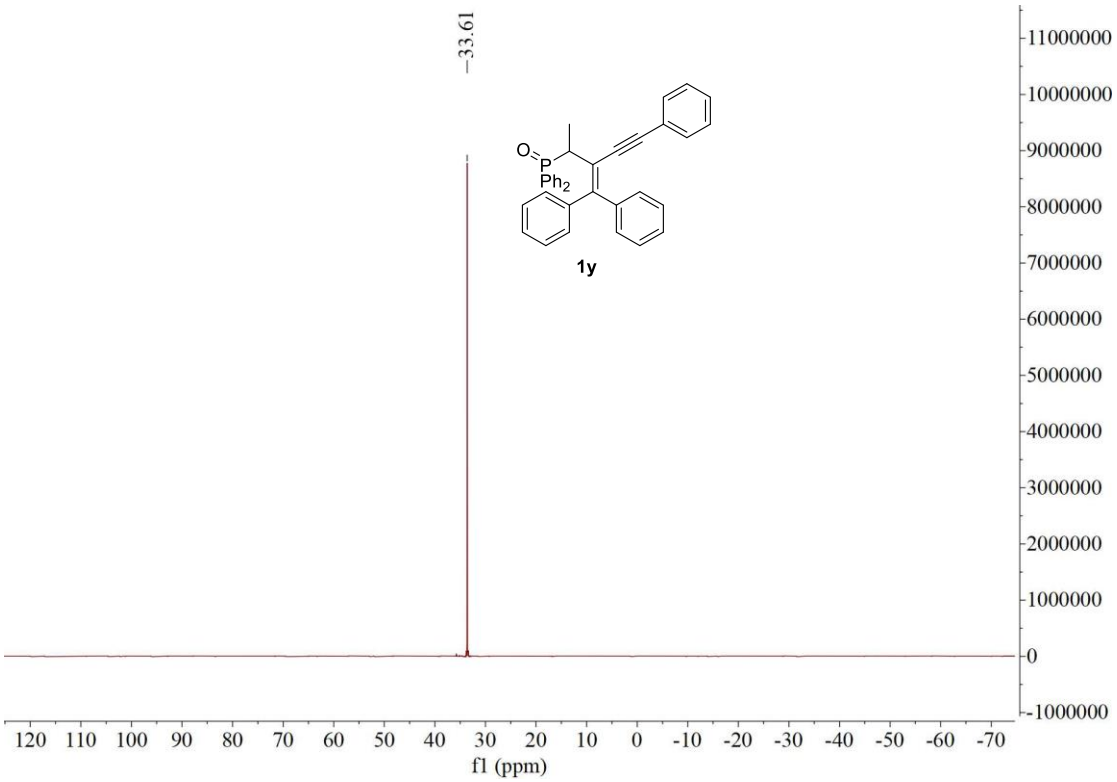

**Compound 1y ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



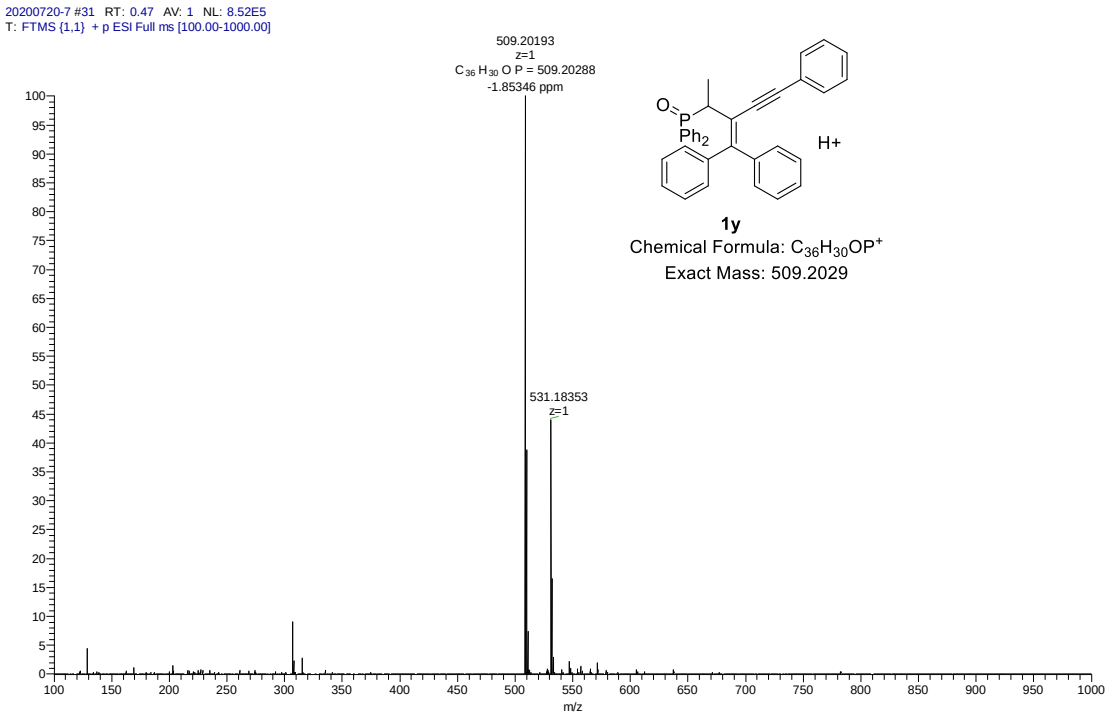

$^{1}$H NMR (600 MHz, $CDCl_3$) of **1y**



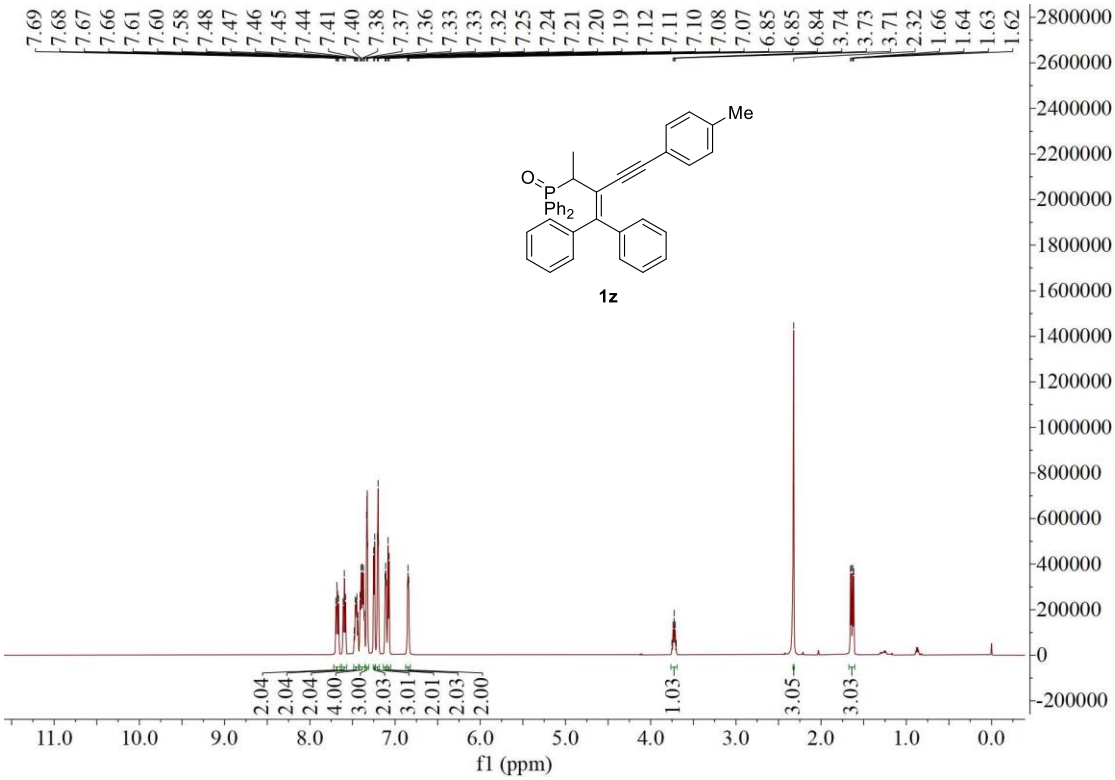

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **1y**



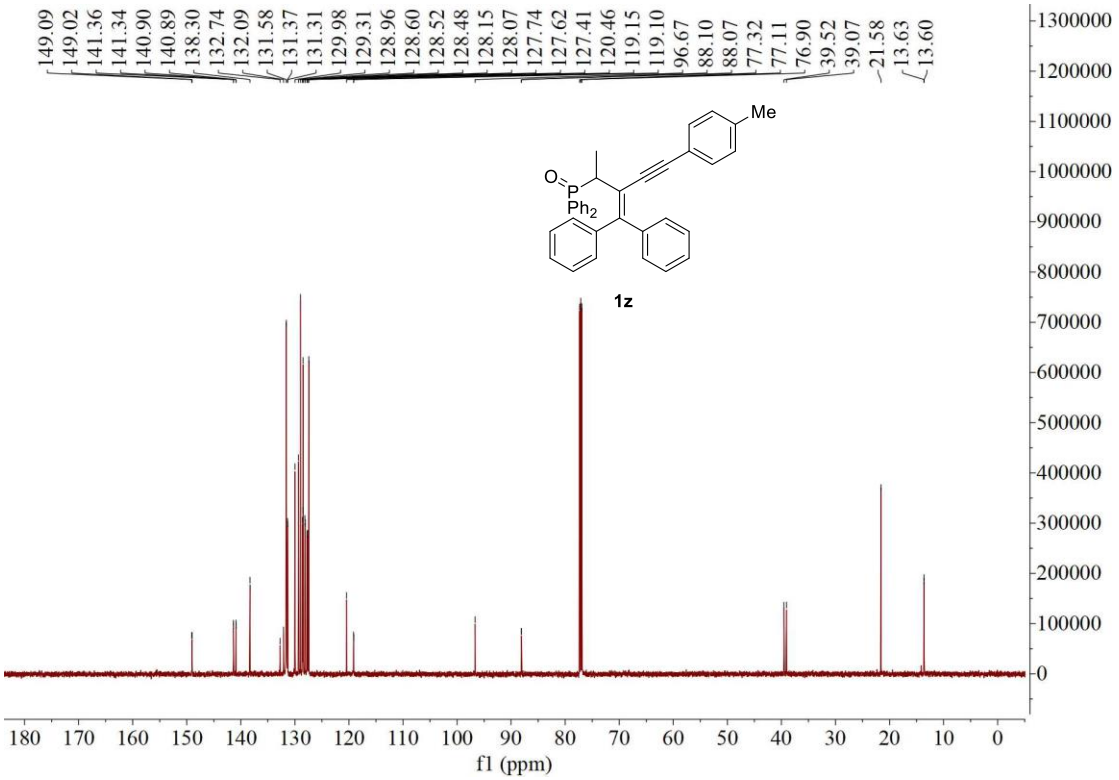
$^{31}$P NMR (243 MHz, $CDCl_3$) of **1y**



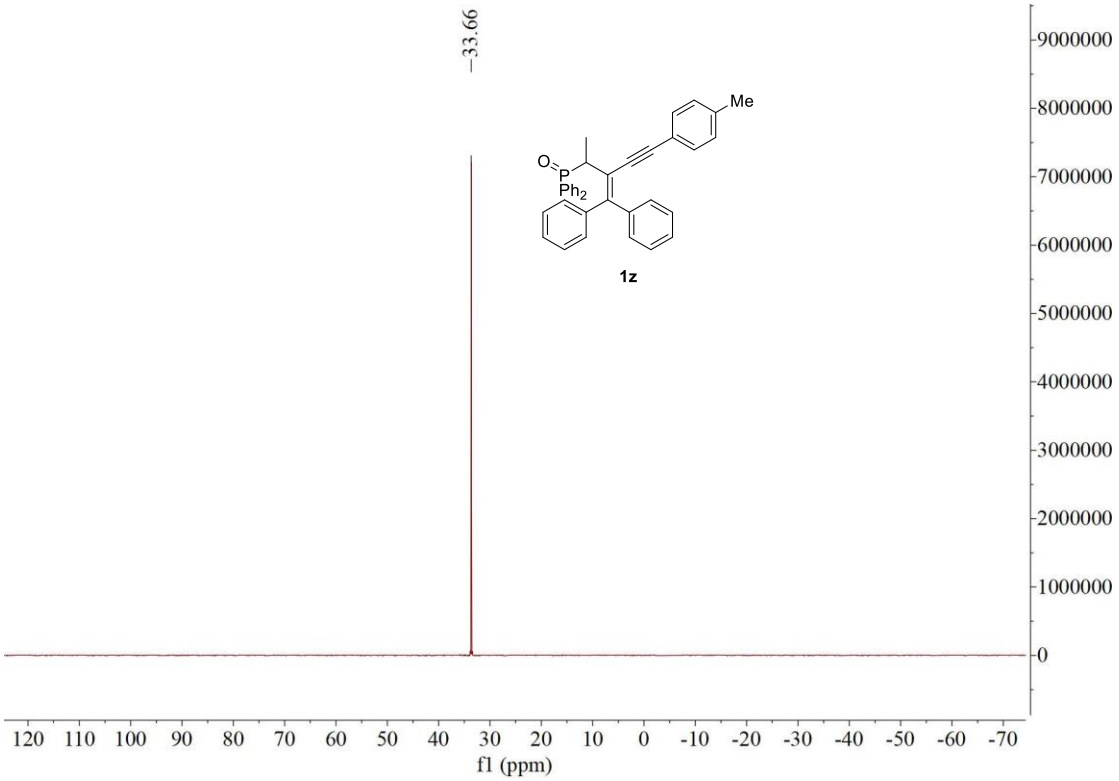

**Compound 1z ($^1$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



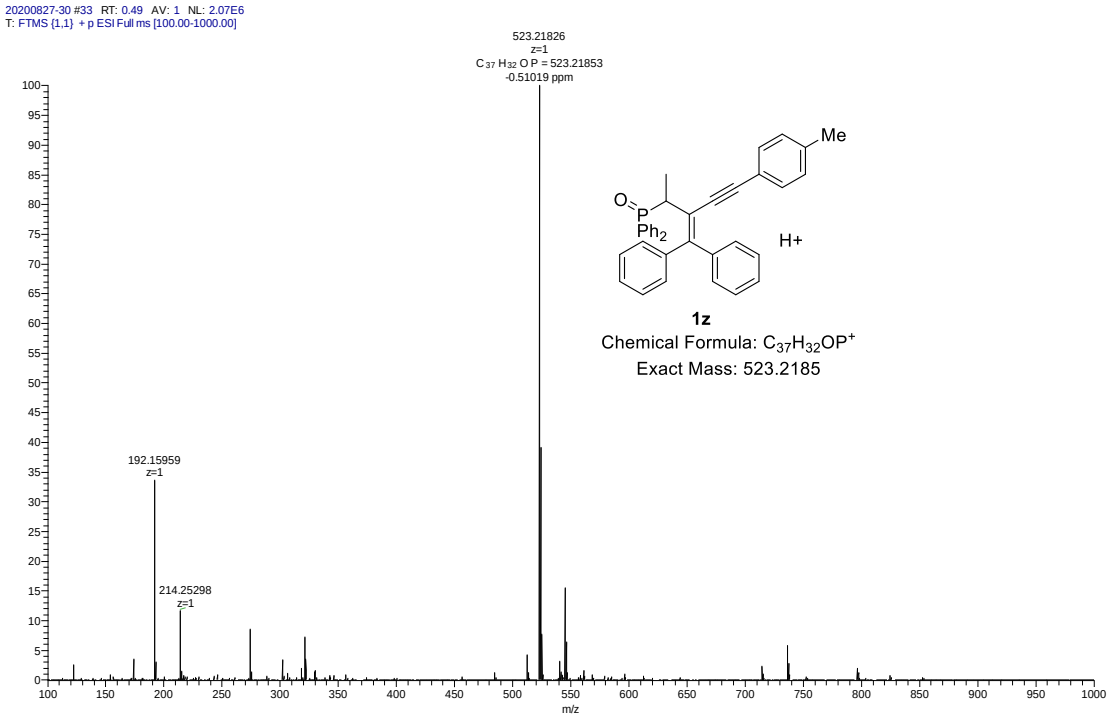

$^1$H NMR (600 MHz, $CDCl_3$) of **1z**



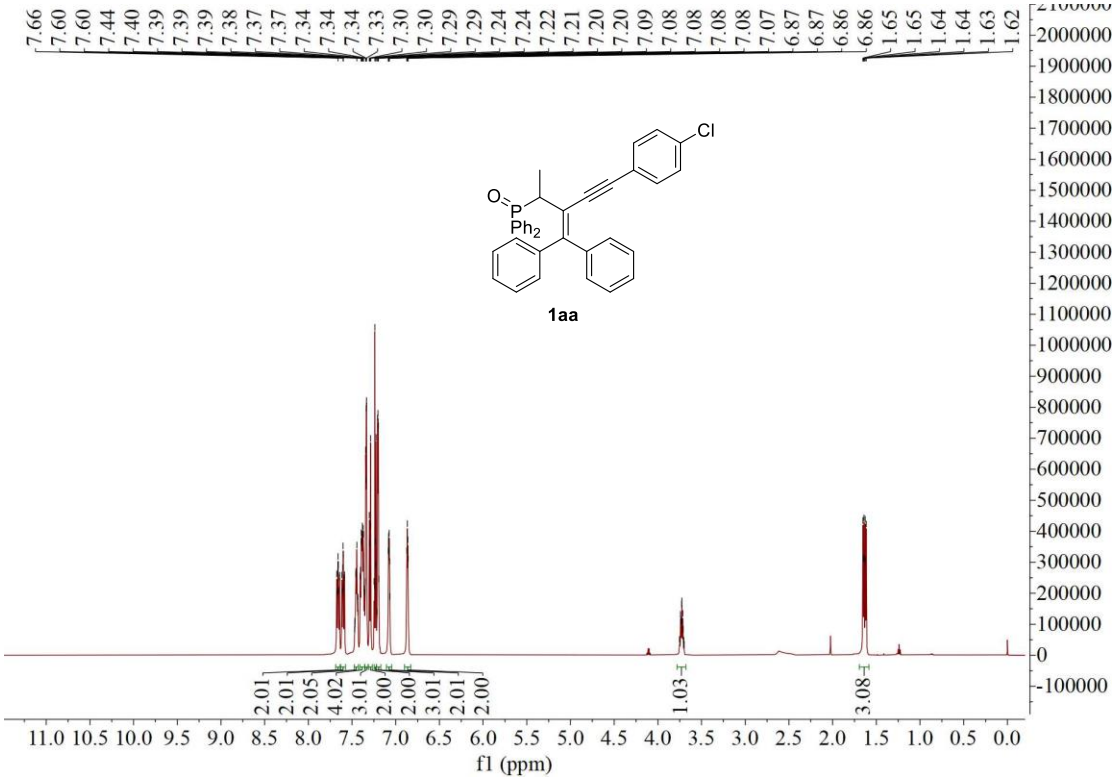

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **1z**



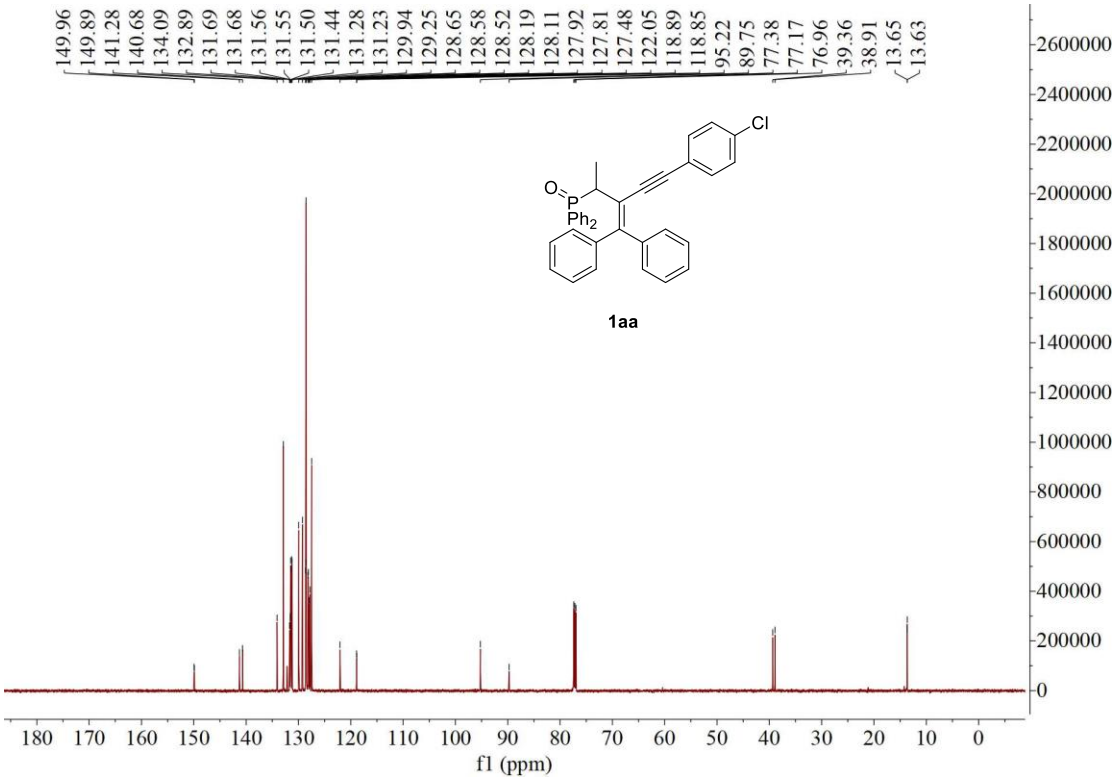
$^{31}$P NMR (243 MHz, $CDCl_3$) of **1z**



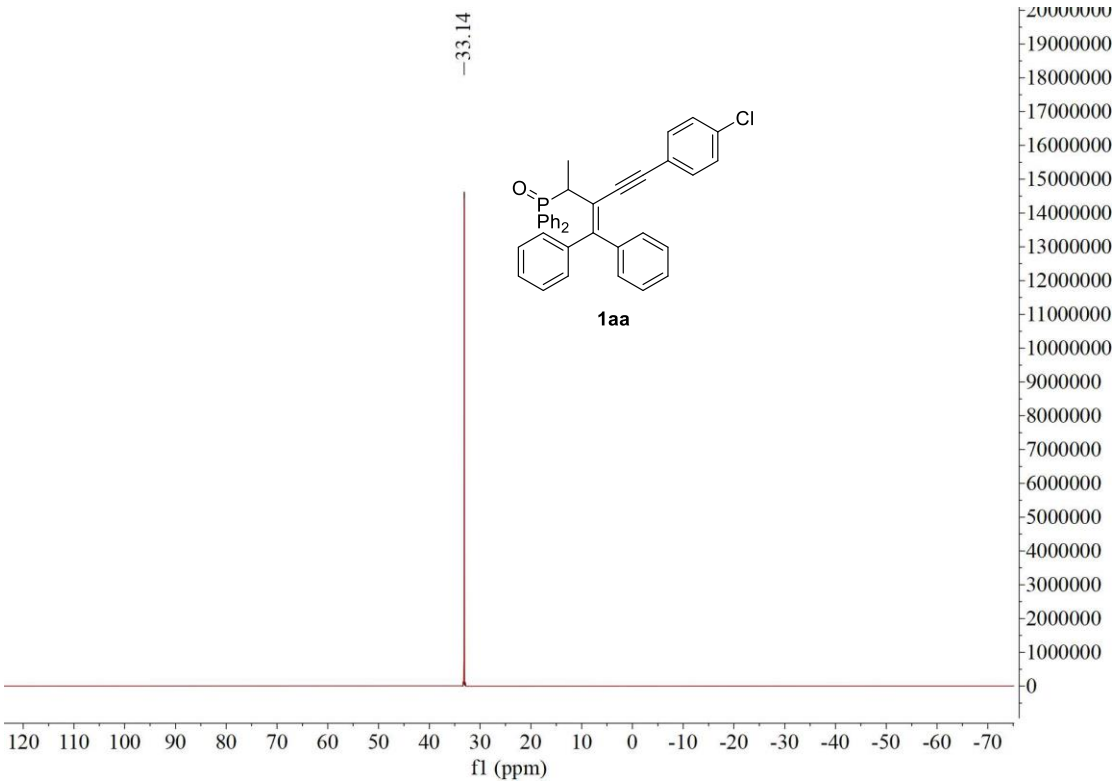

**Compound 1aa ($^1$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



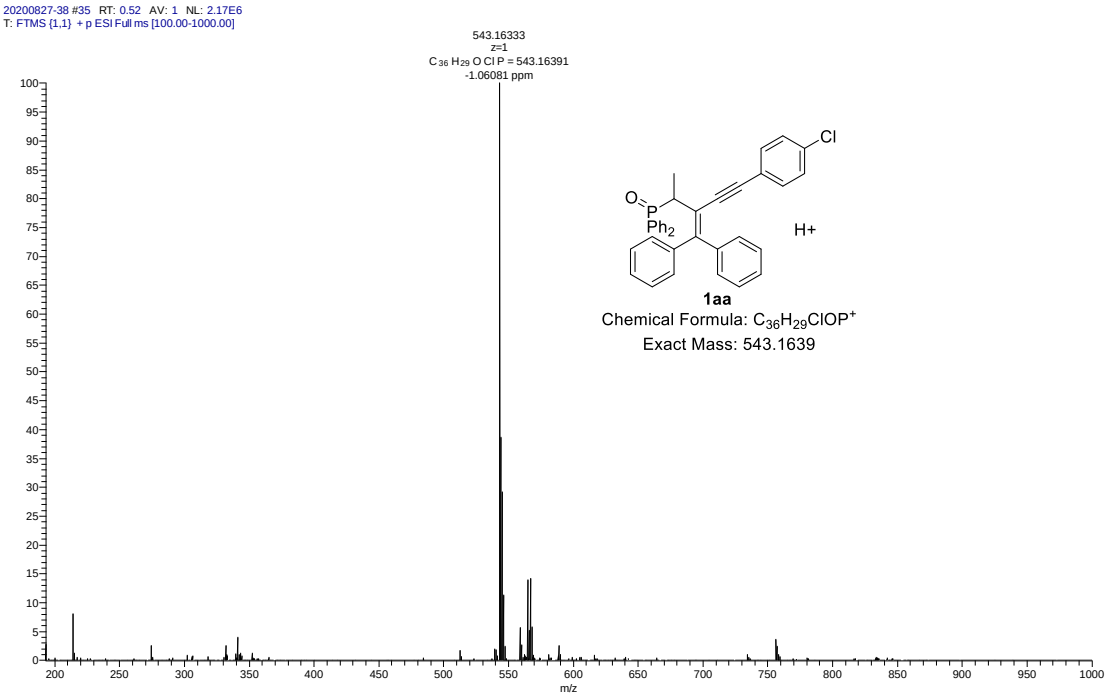

$^1$H NMR (600 MHz, $CDCl_3$) of **1aa**



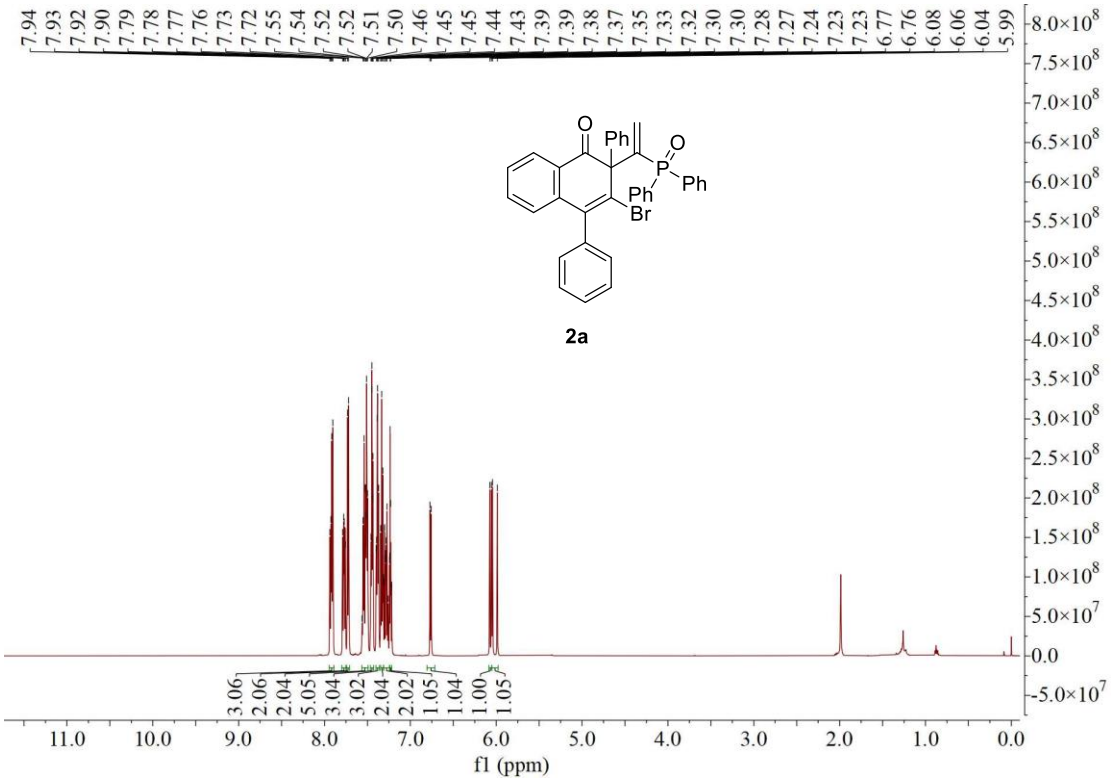

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **1aa**



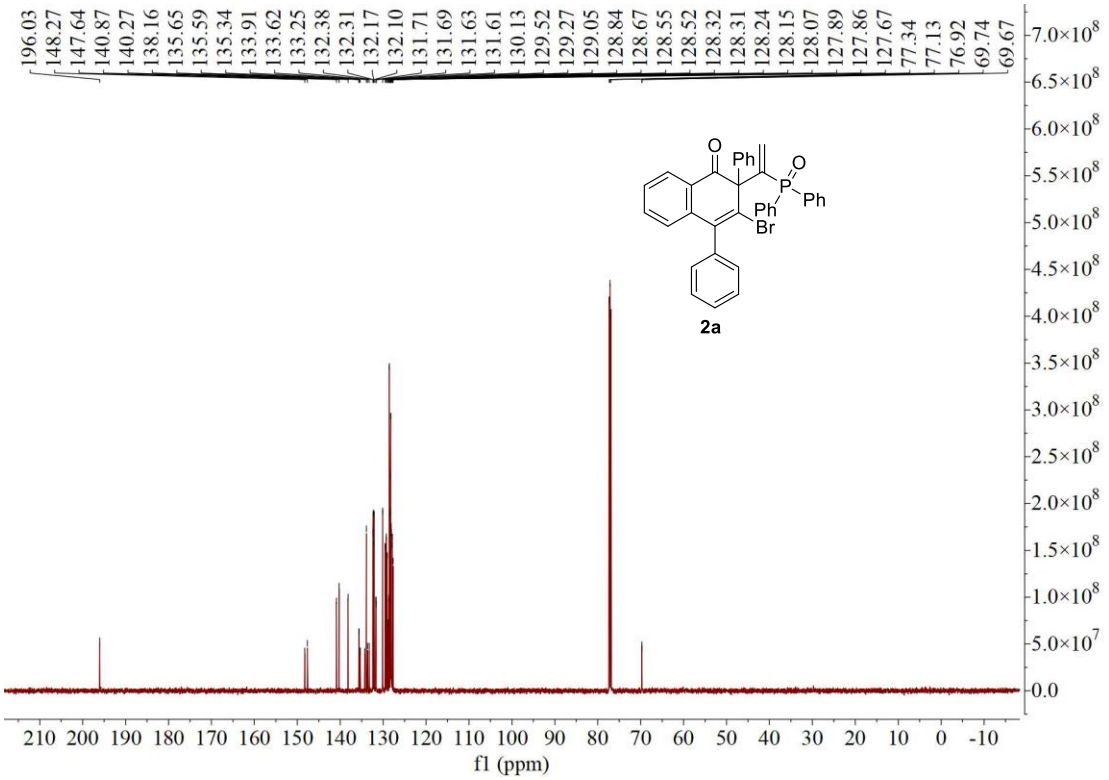

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **1aa**



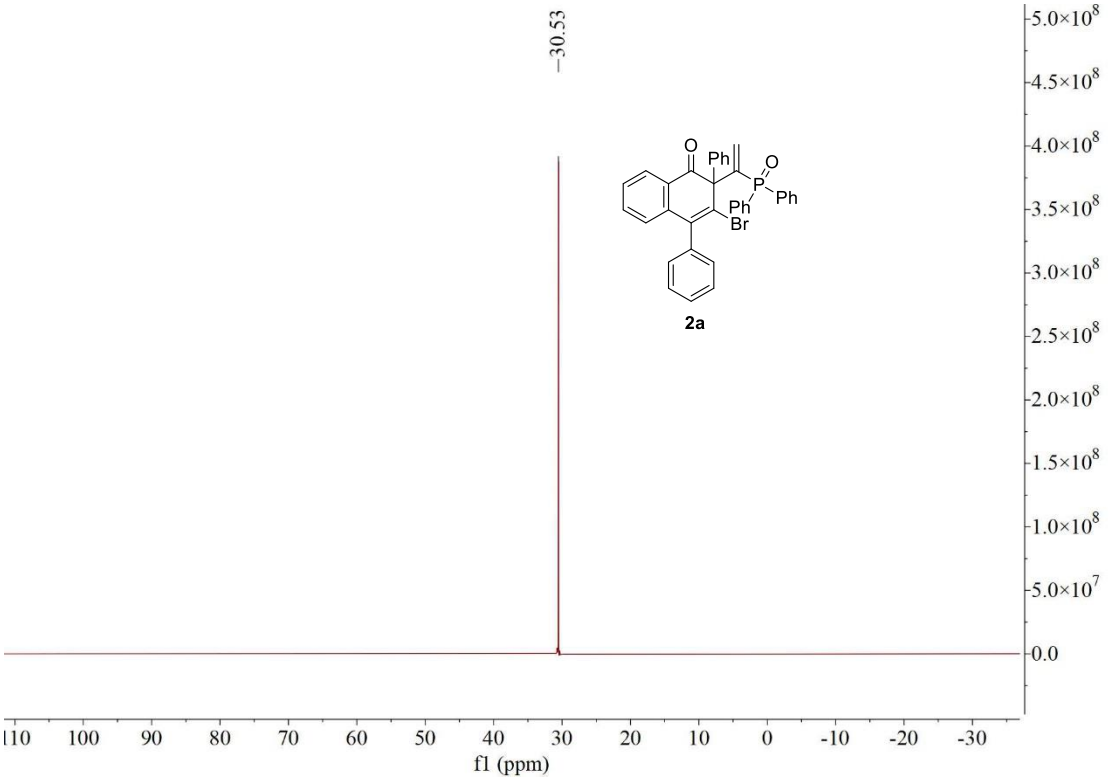

**Compound 2a ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



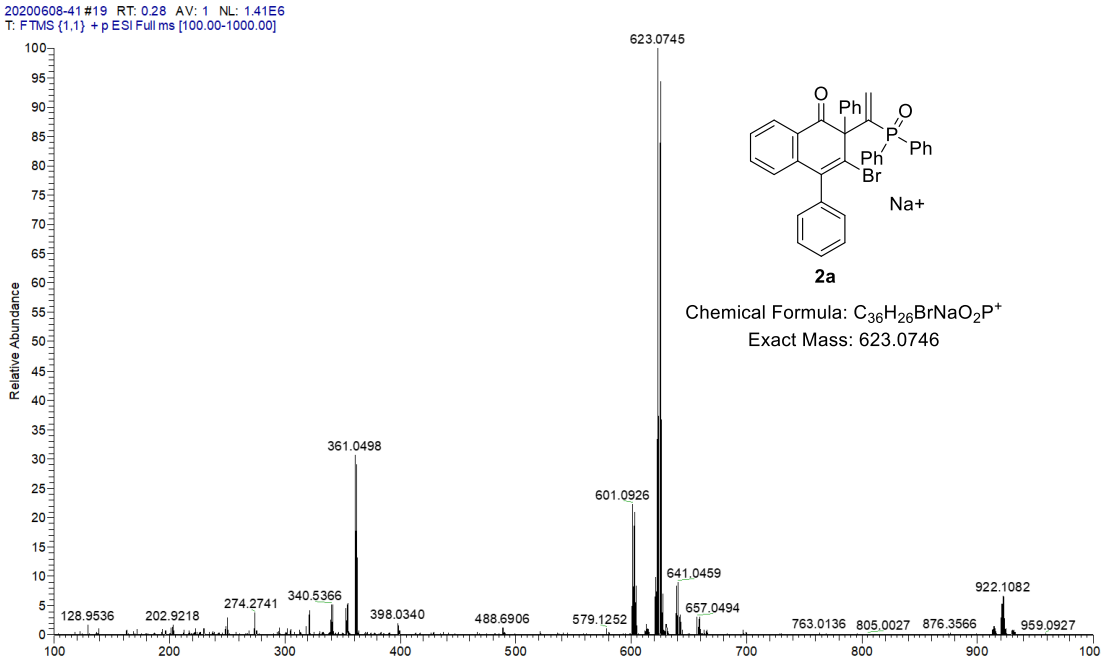

$^{1}$H NMR (600 MHz, $CDCl_3$) of **2a**



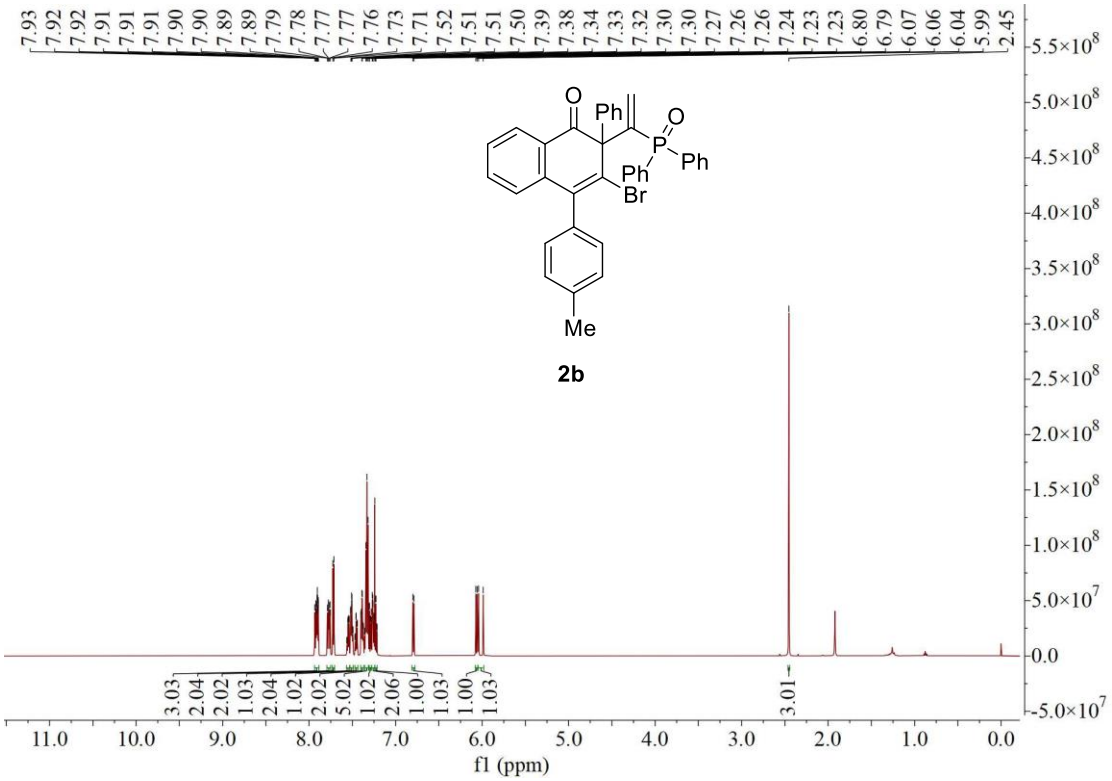

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **2a**



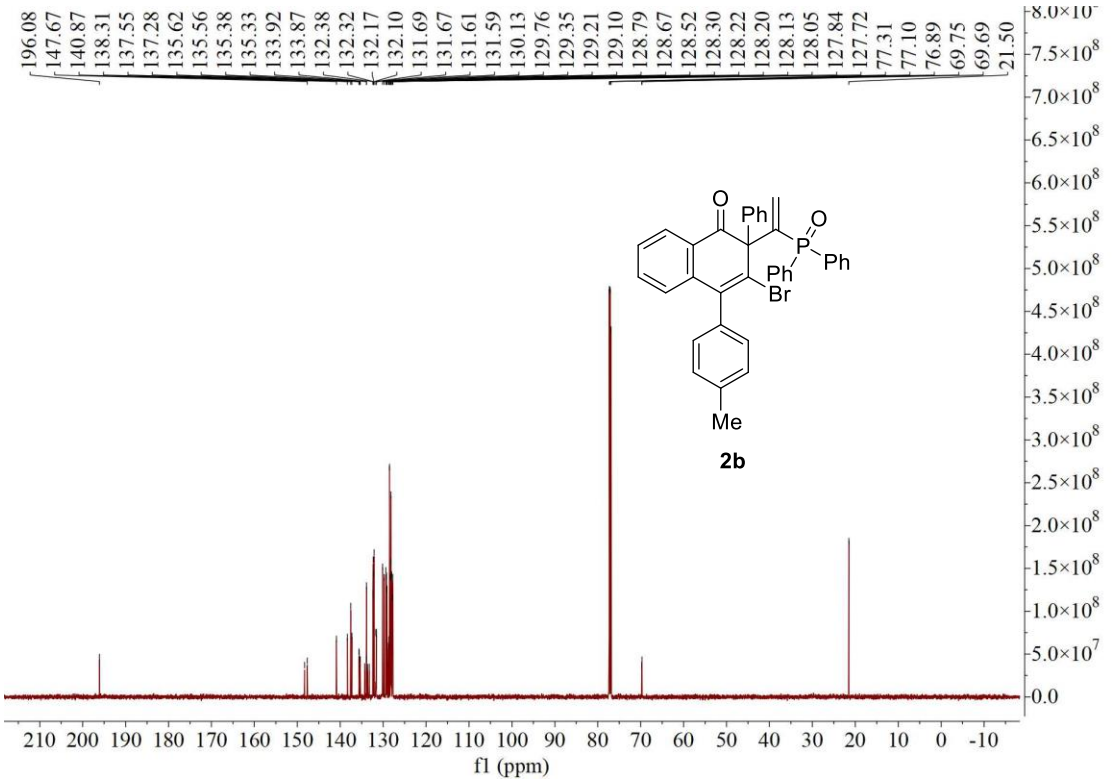

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **2a**



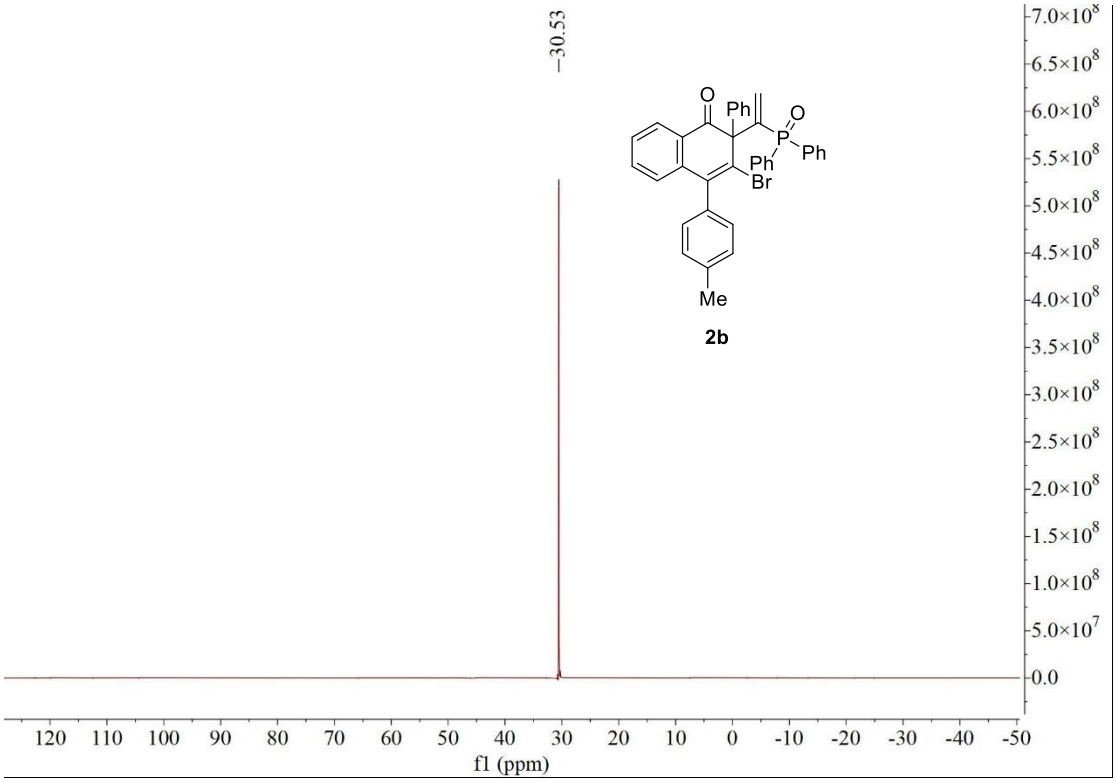

**Compound 2b ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



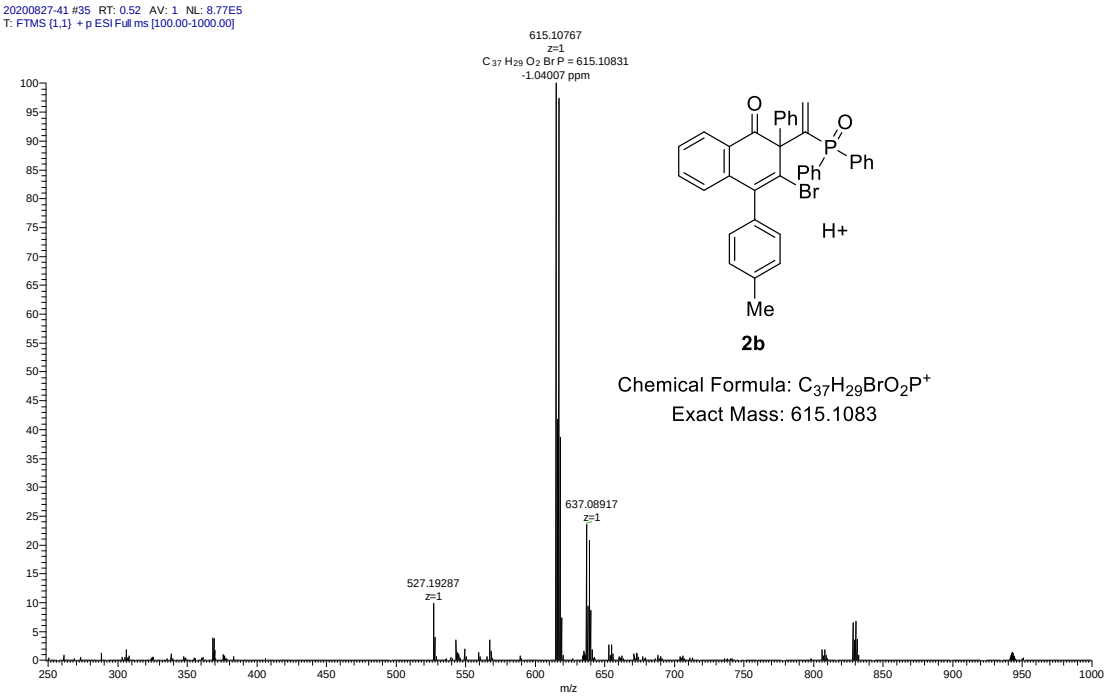

$^{1}$H NMR (600 MHz, $CDCl_3$) of **2b**



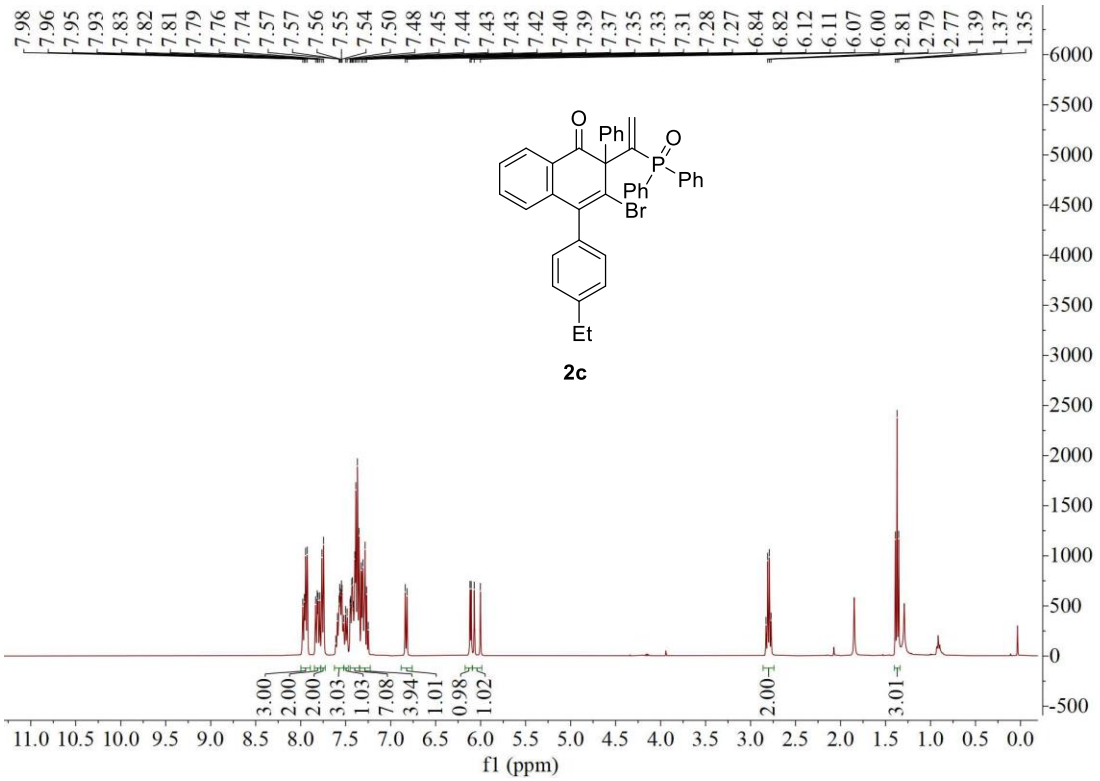

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **2b**



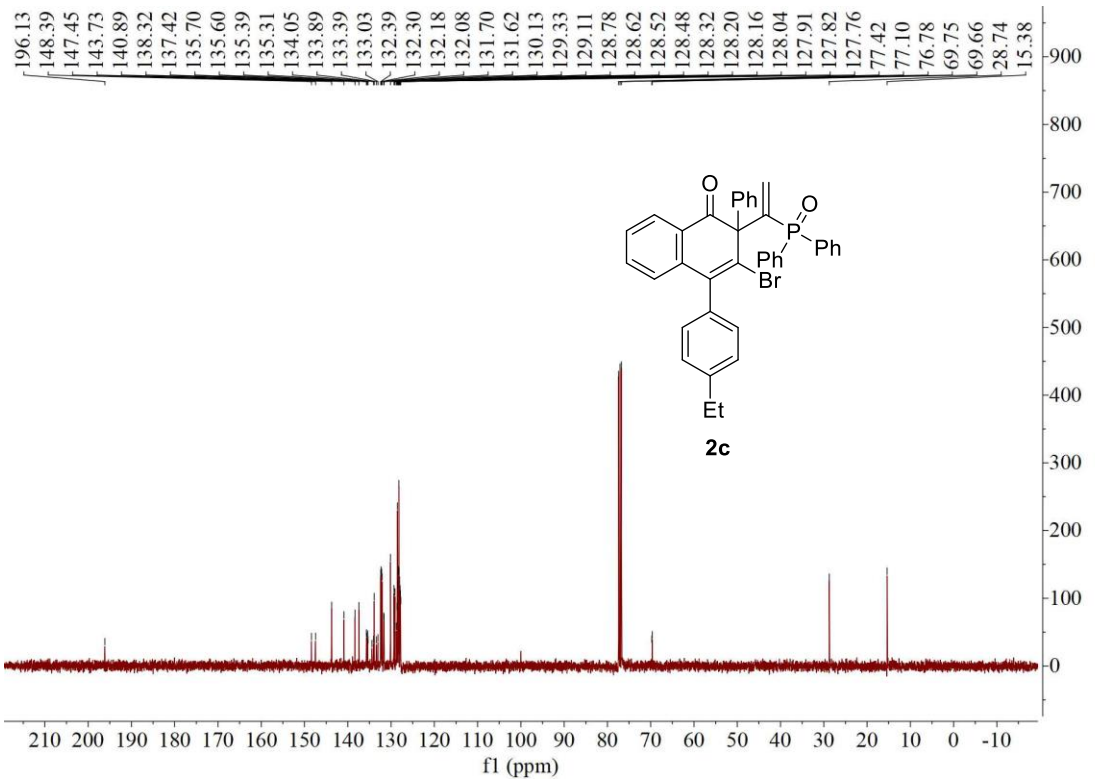

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **2b**



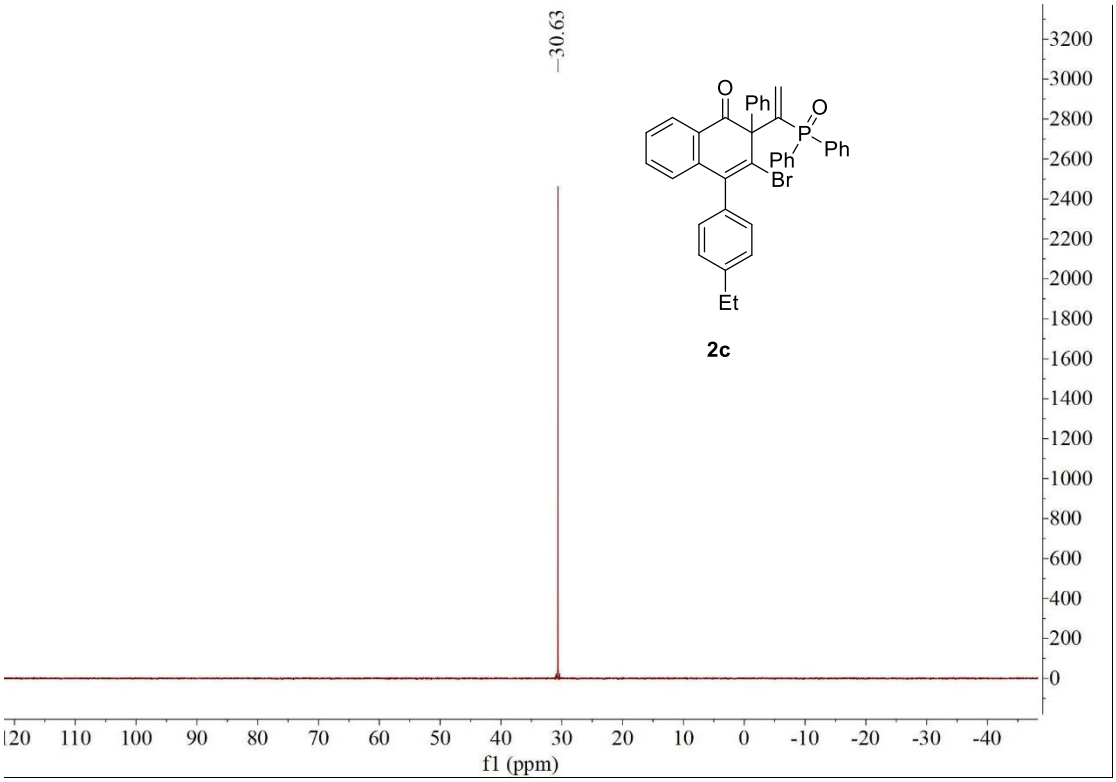

**Compound 2c ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



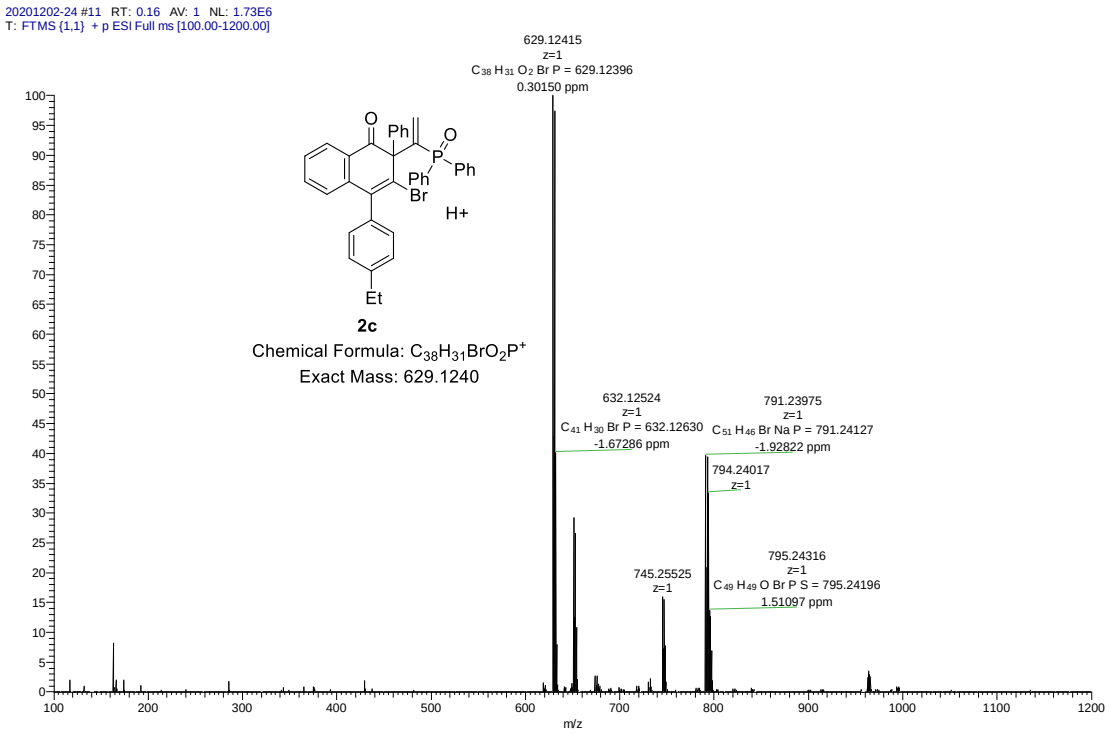

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2c**



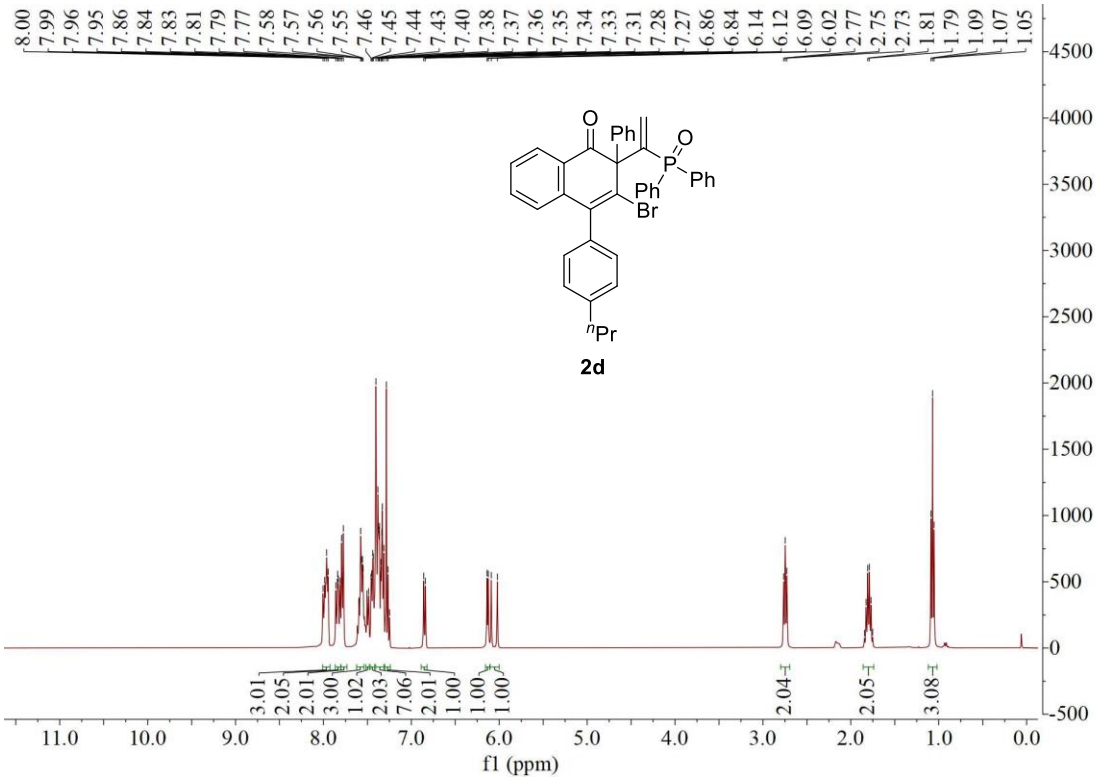

$^{13}C$ NMR (101MHz, $CDCl_3$) of **2c**



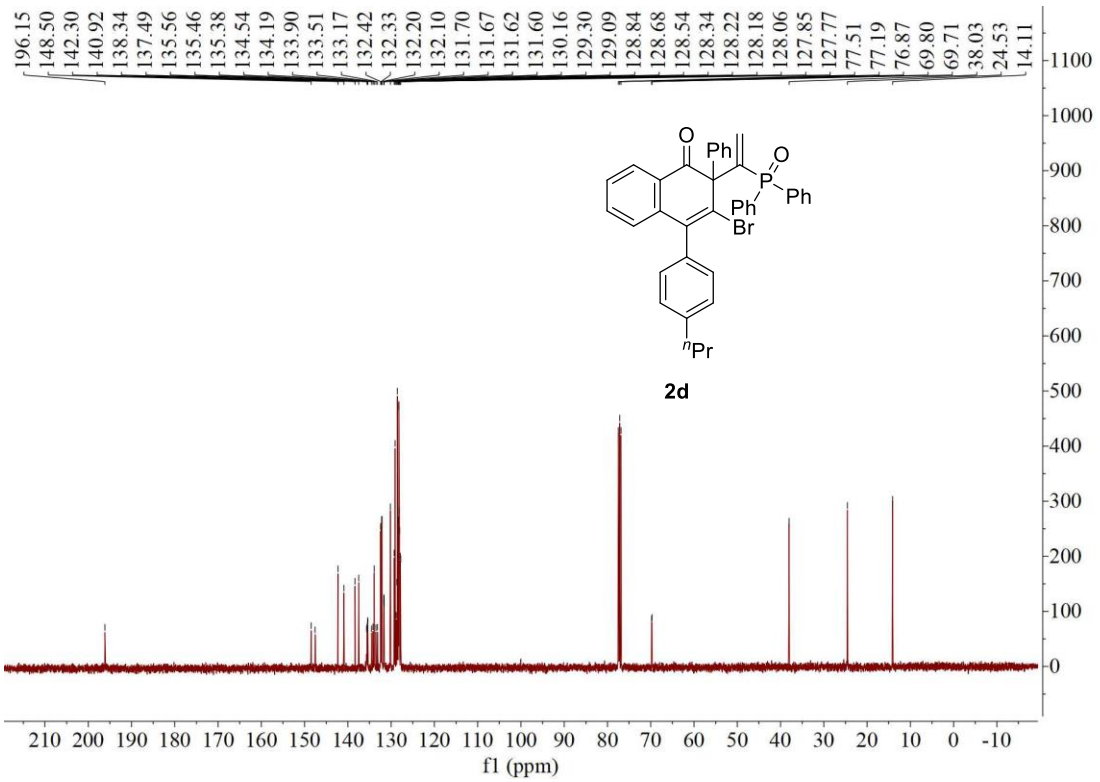

$^{31}P$ NMR (162 MHz, $CDCl_3$) of **2c**



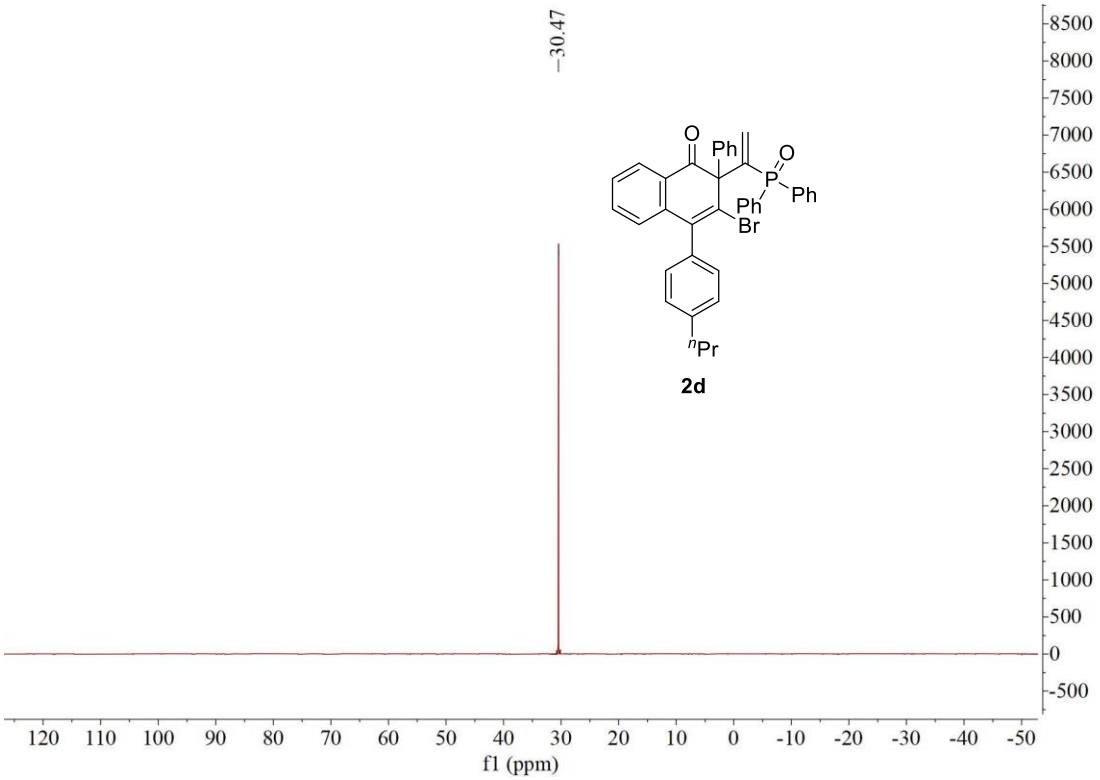

**Compound 2d ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



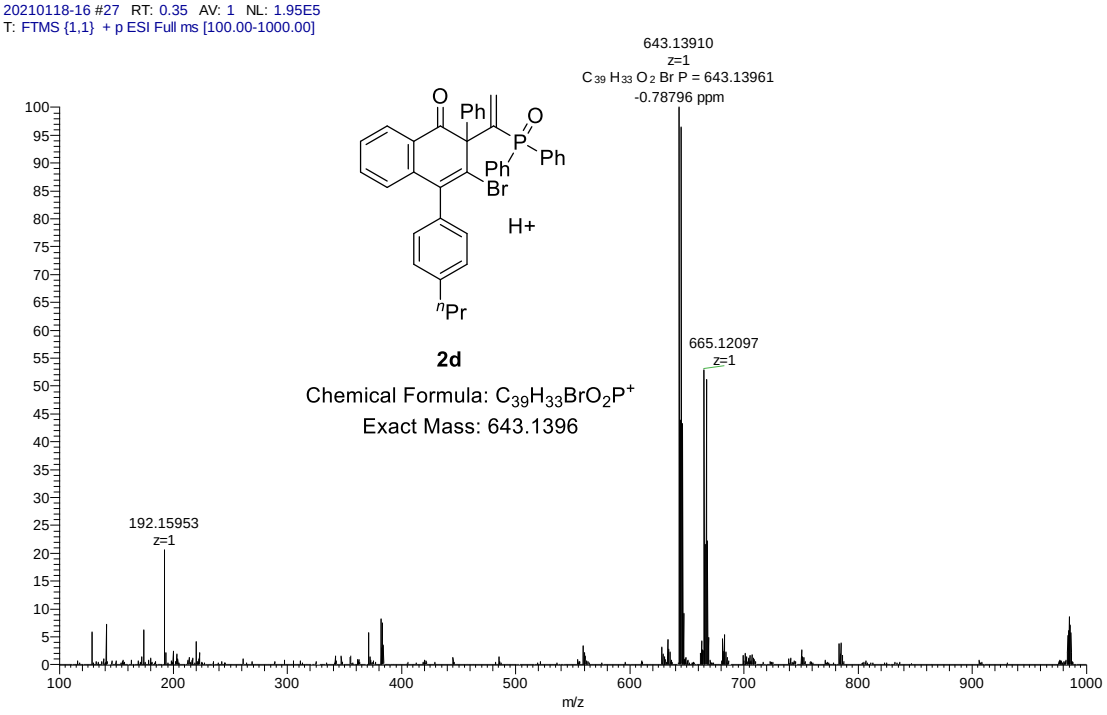

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2d**



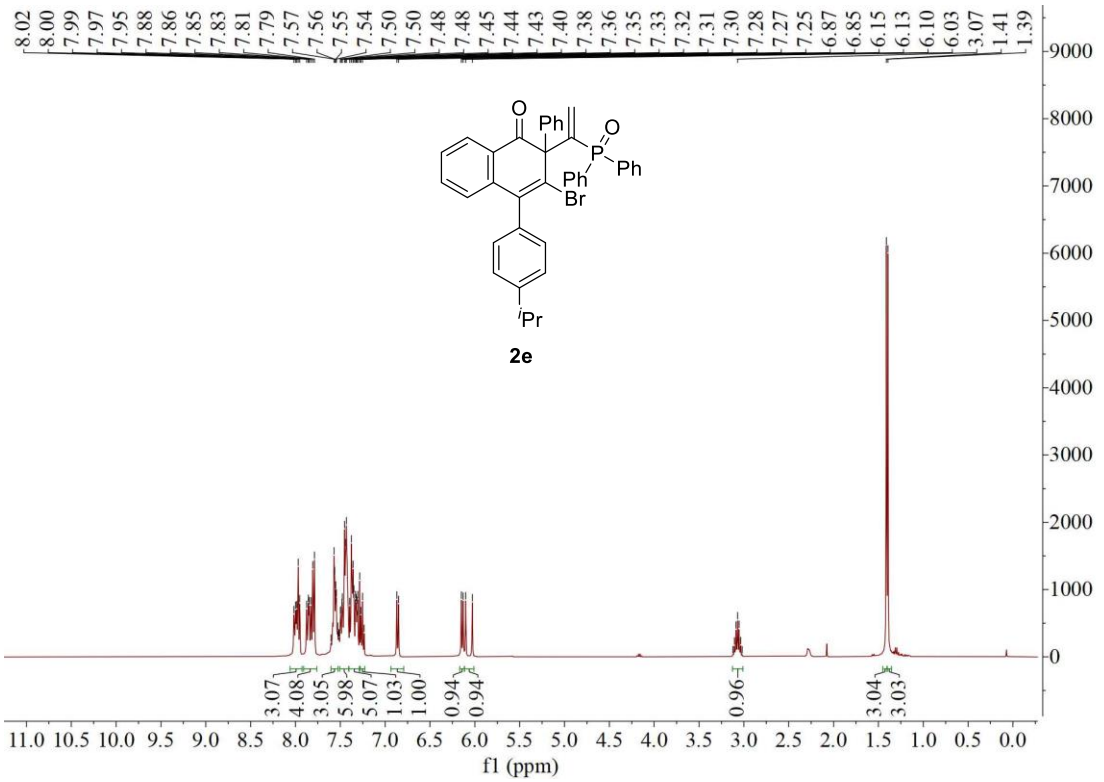

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2d**



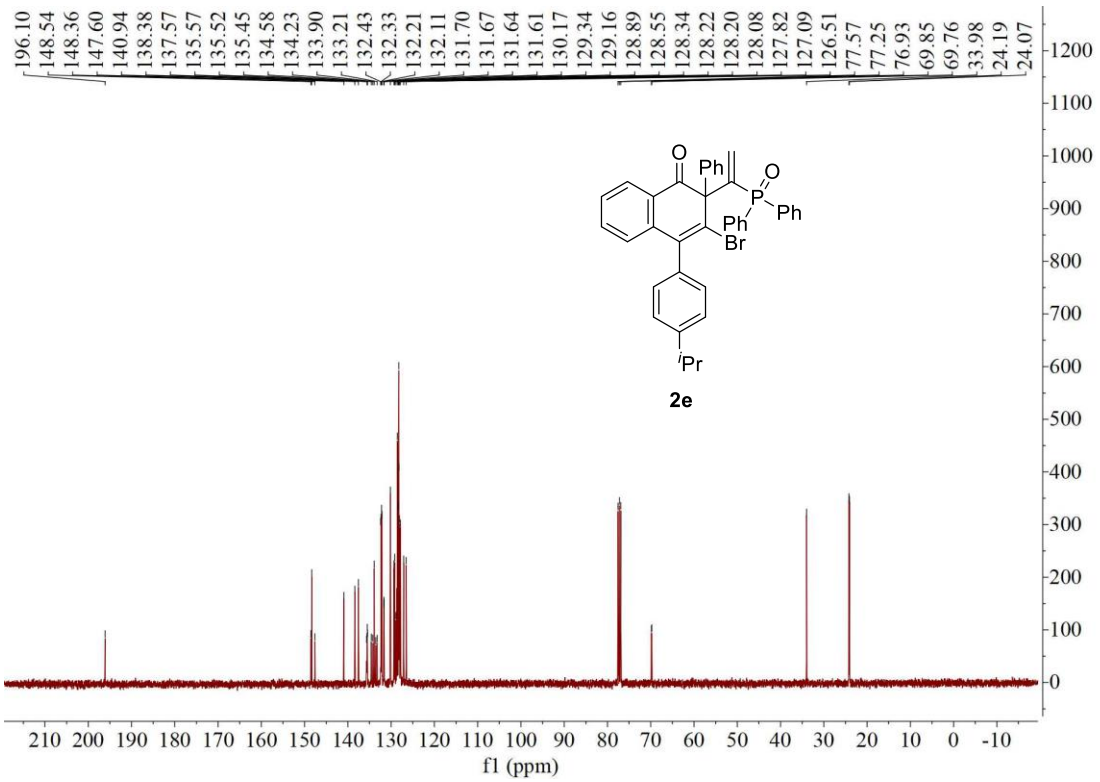

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2d**



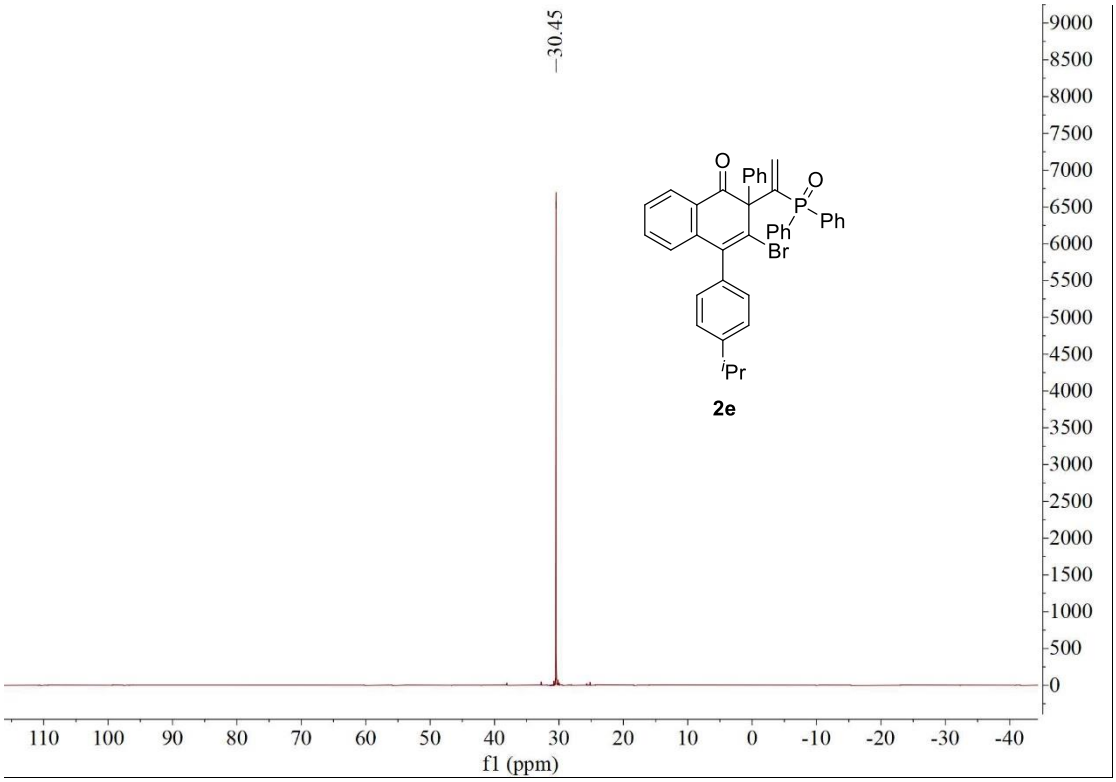

**Compound 2e ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



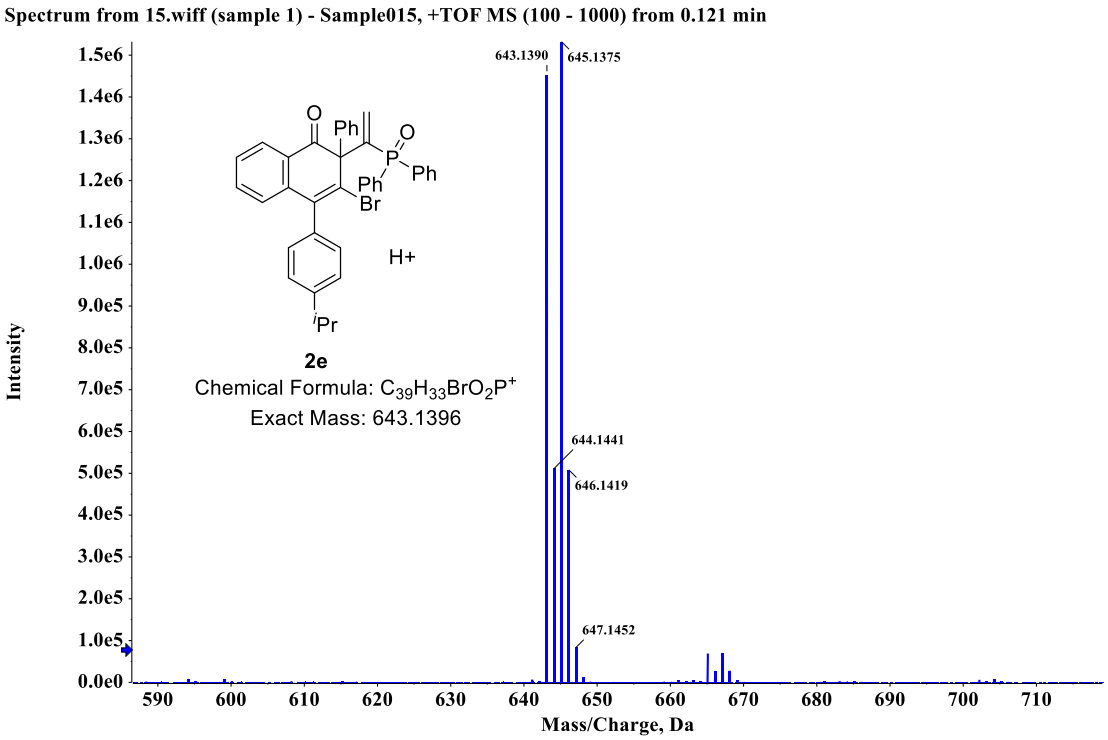

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2e**



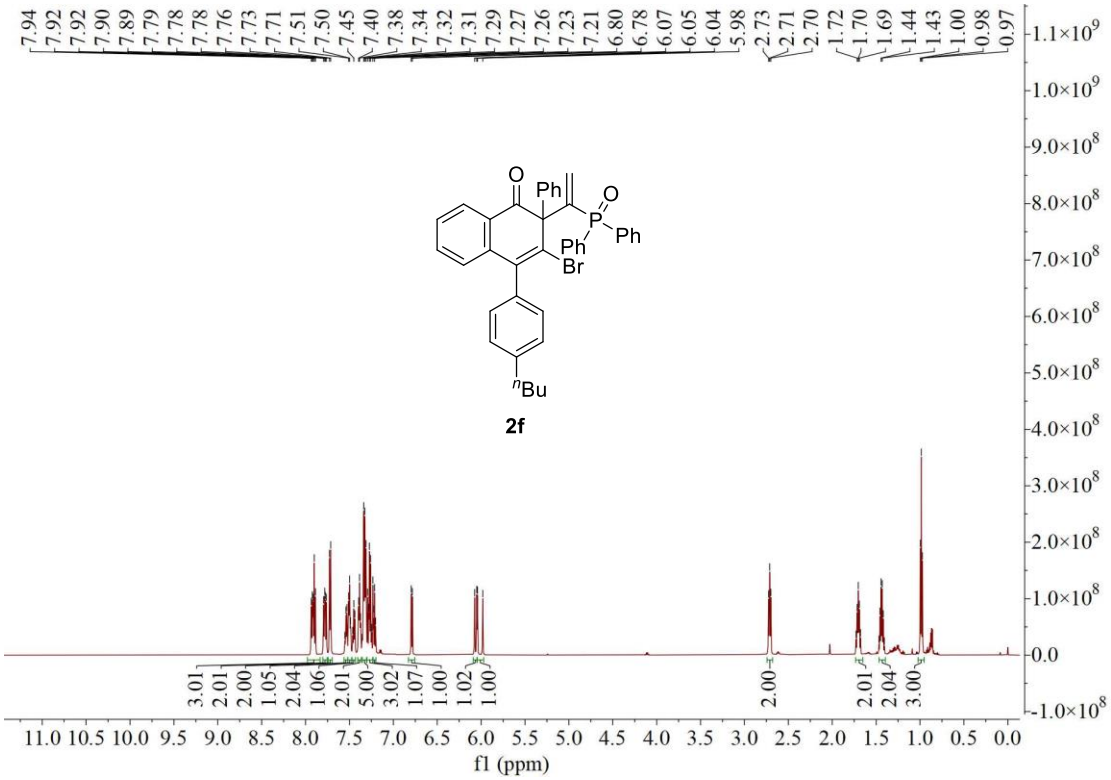

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2e**



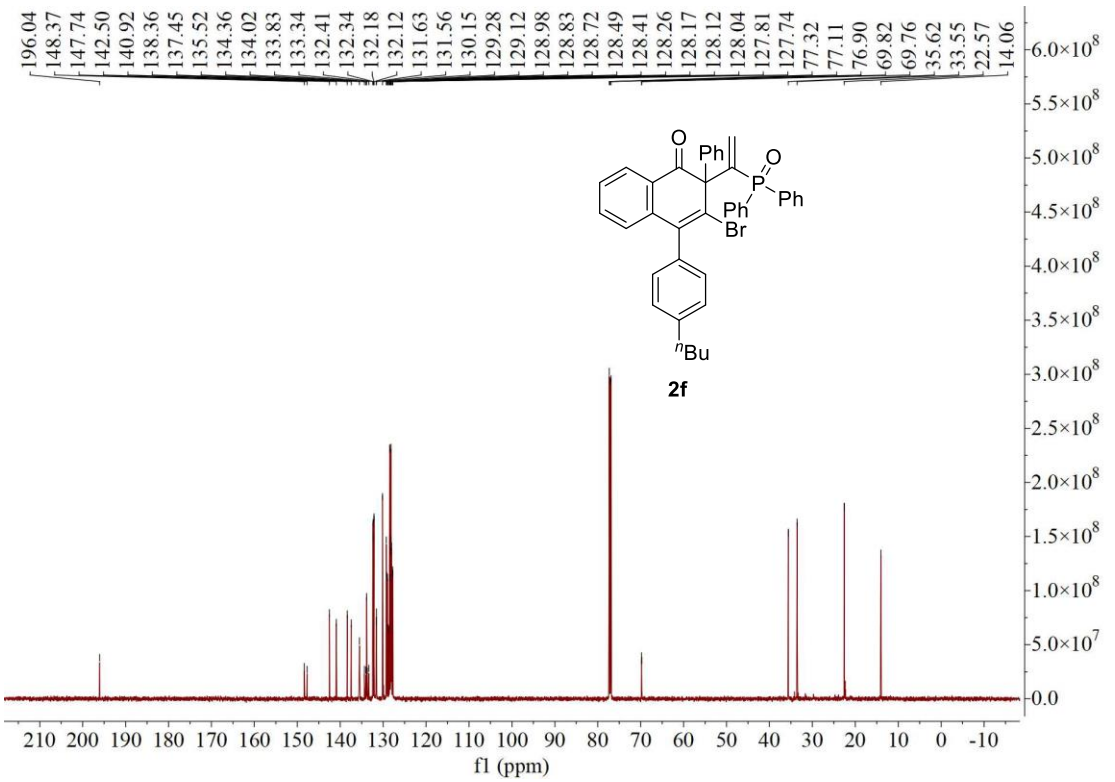

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2e**



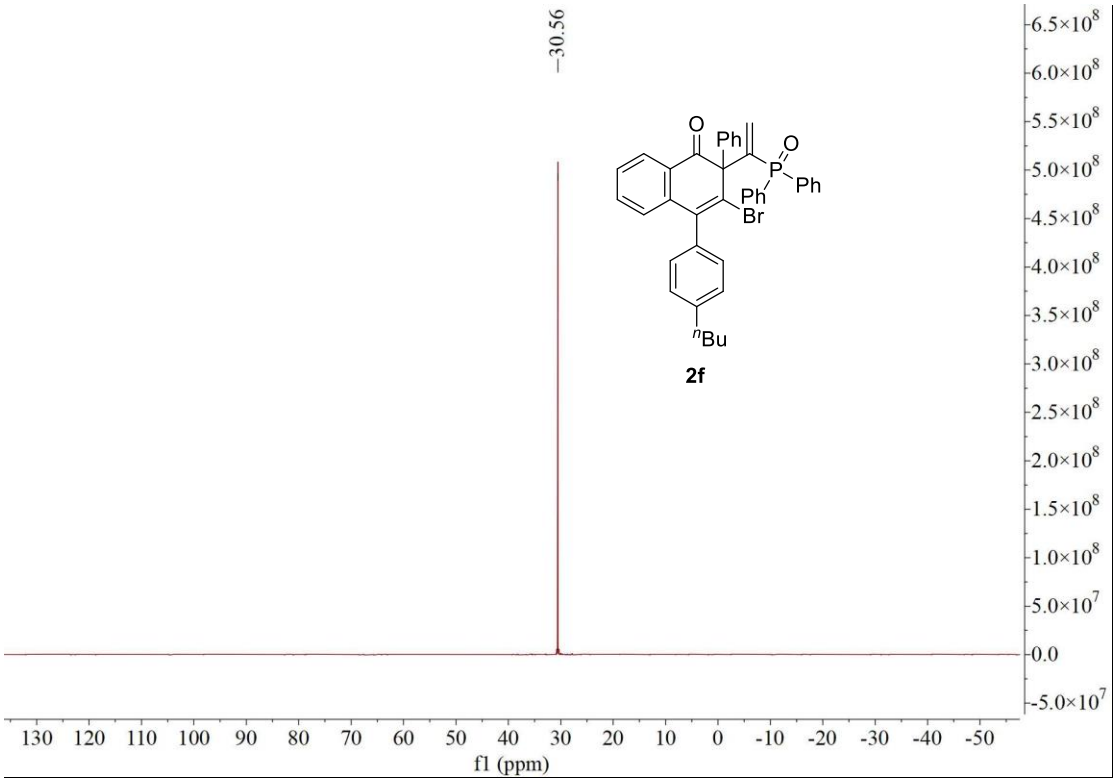

**Compound 2f ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



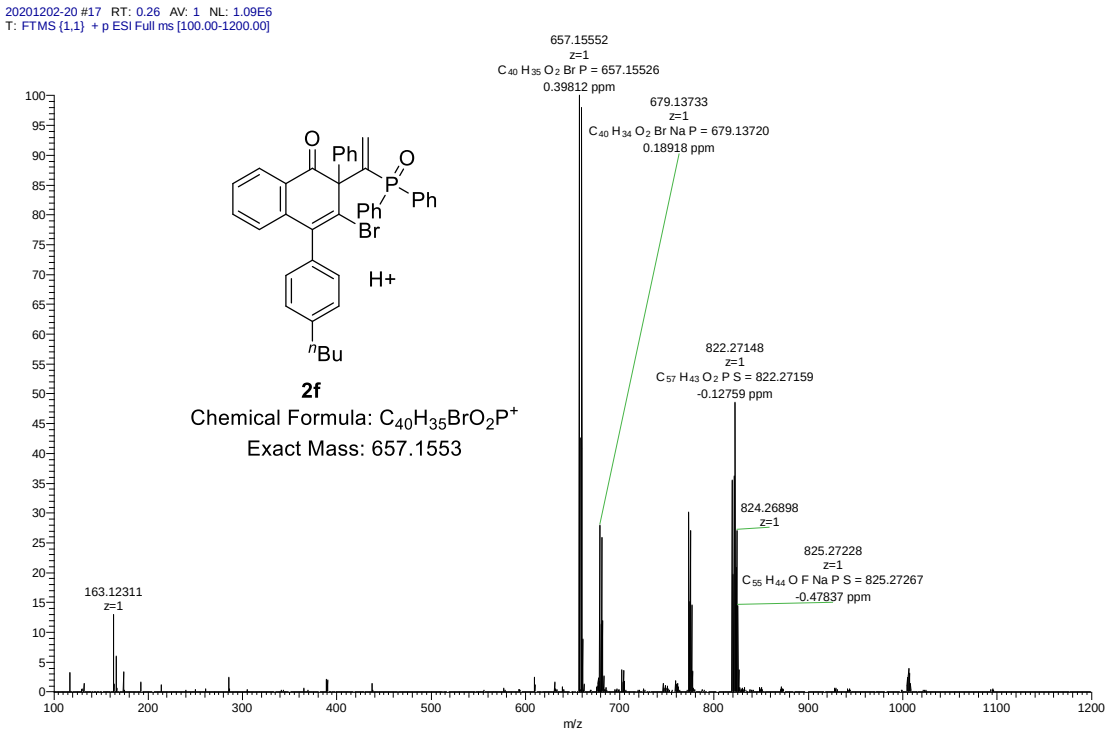

$^{1}$H NMR (600 MHz, $CDCl_3$) of **2f**



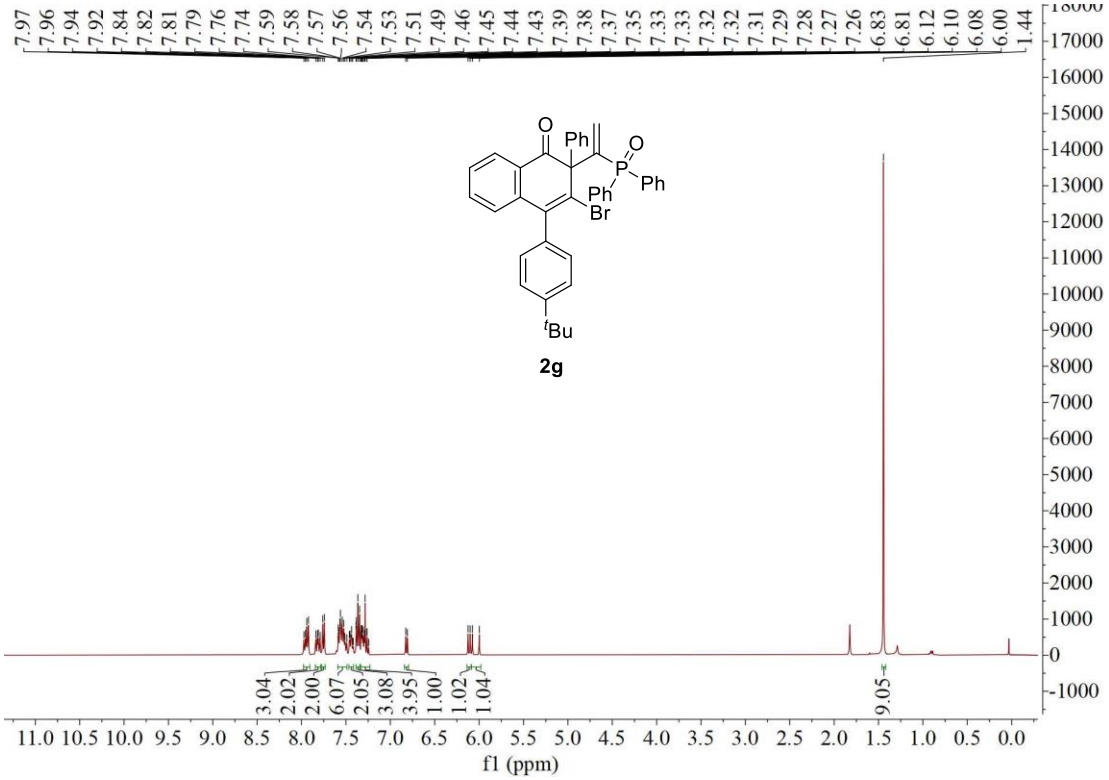

$^{13}$C NMR (151 MHz, $CDCl_3$) of **2f**



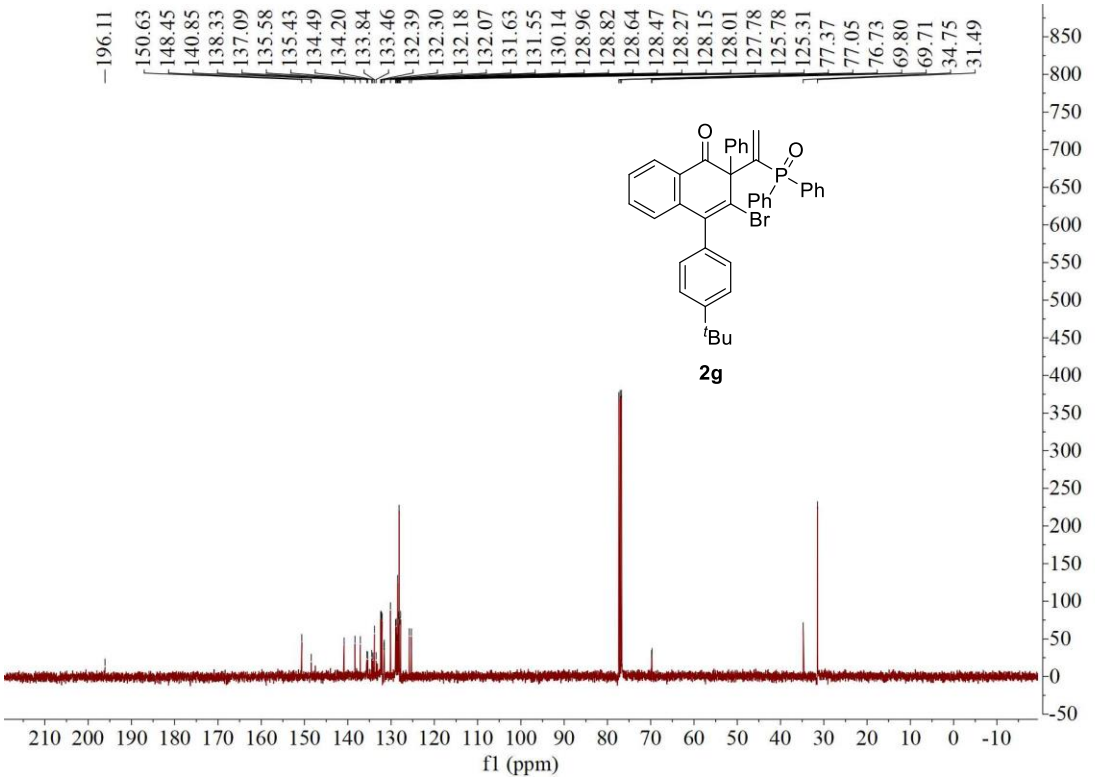

$^{31}$P NMR (243 MHz, $CDCl_3$) of **2f**



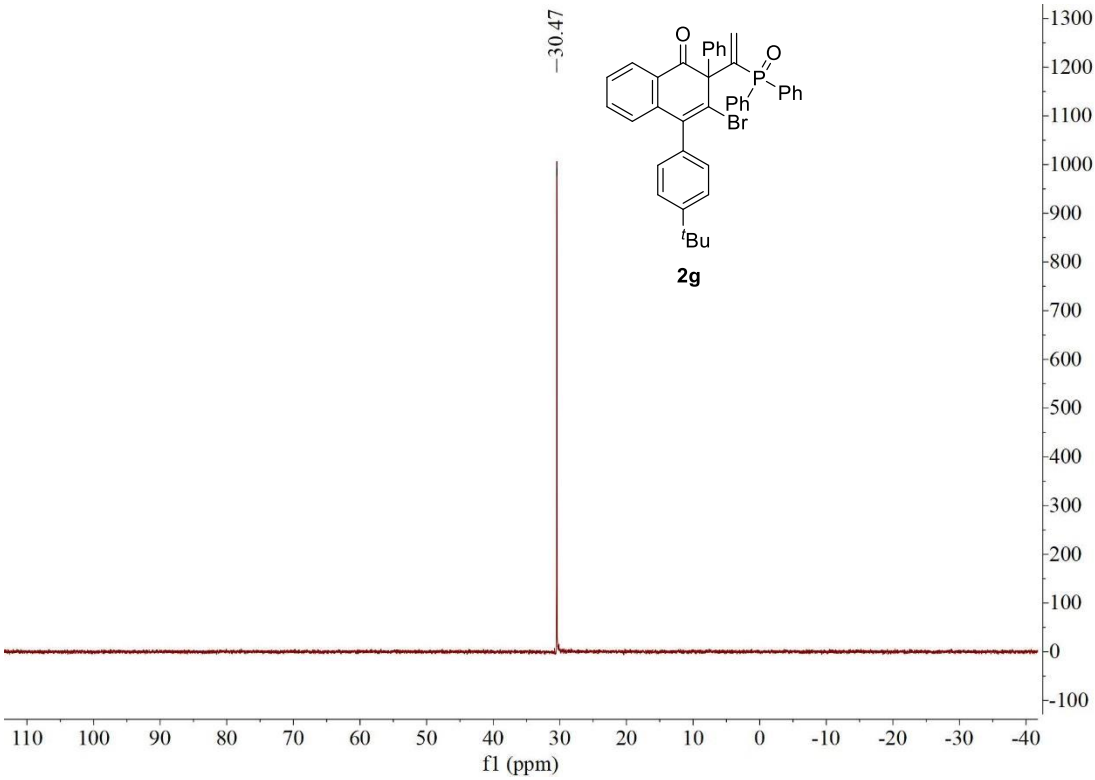

**Compound 2g ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



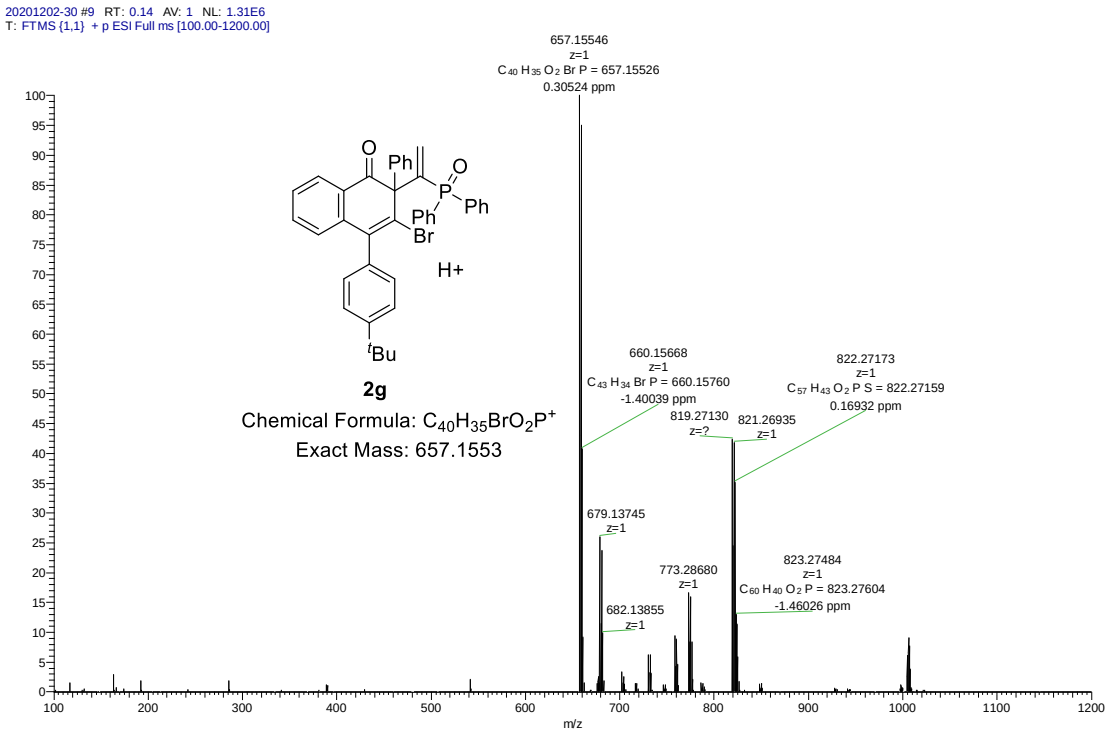

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2g**



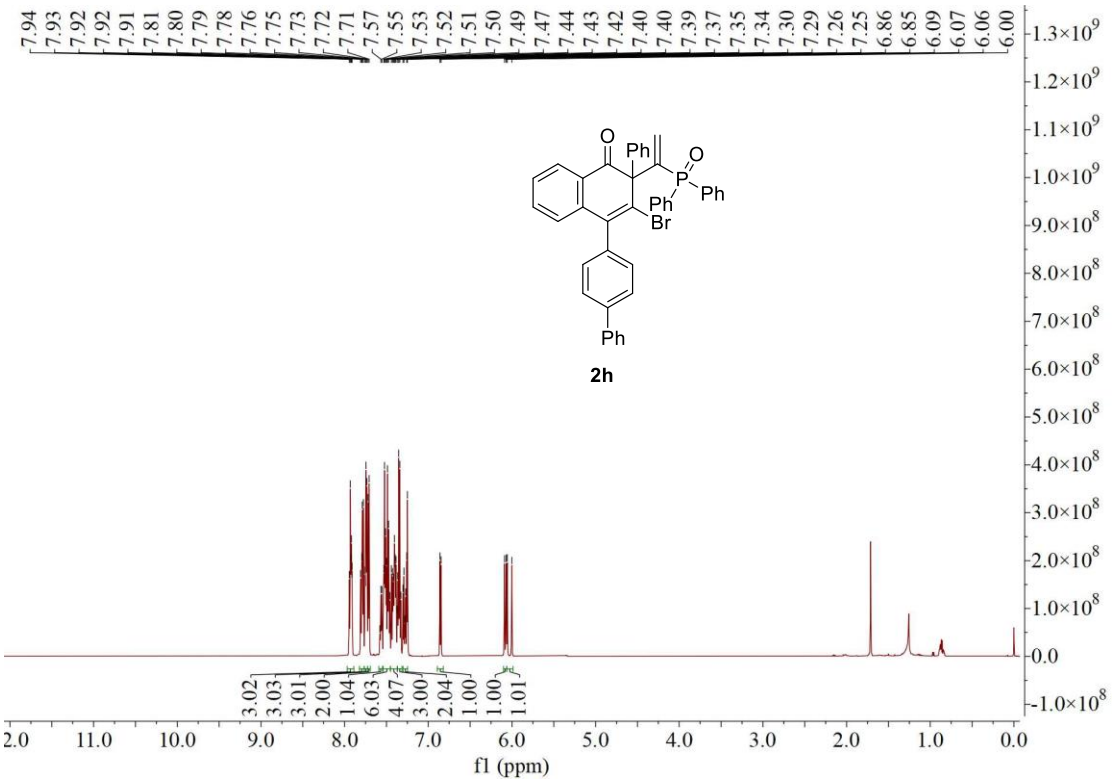

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2g**



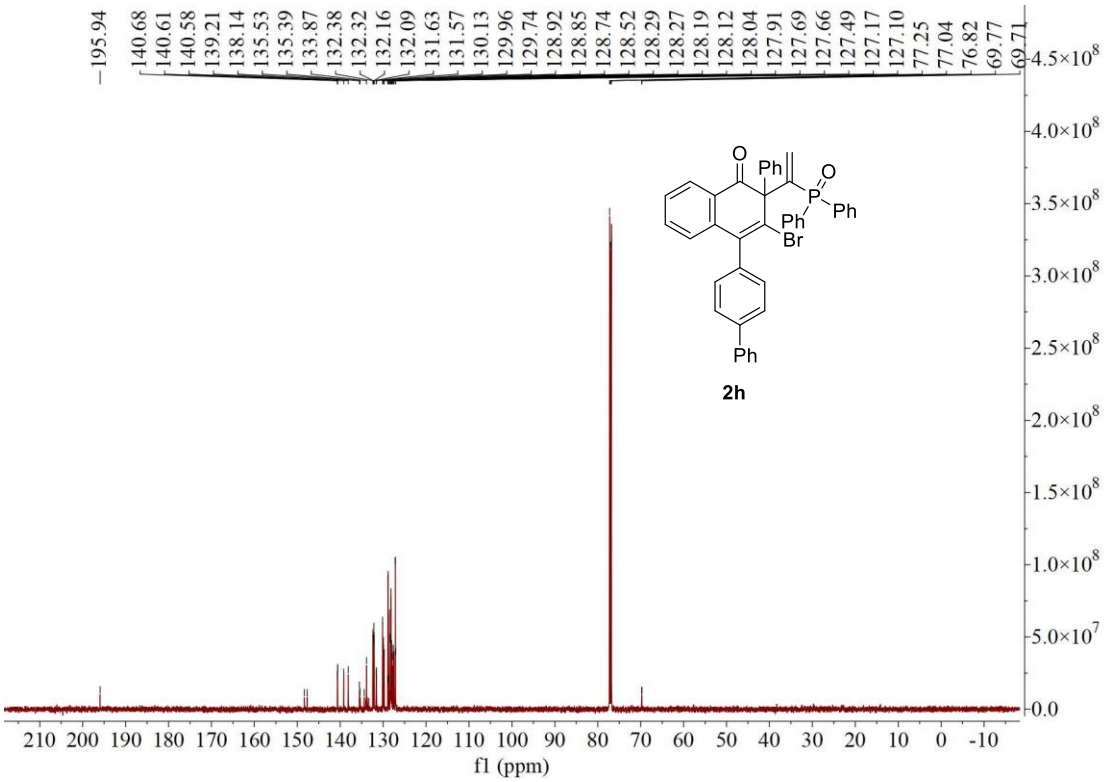

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2g**



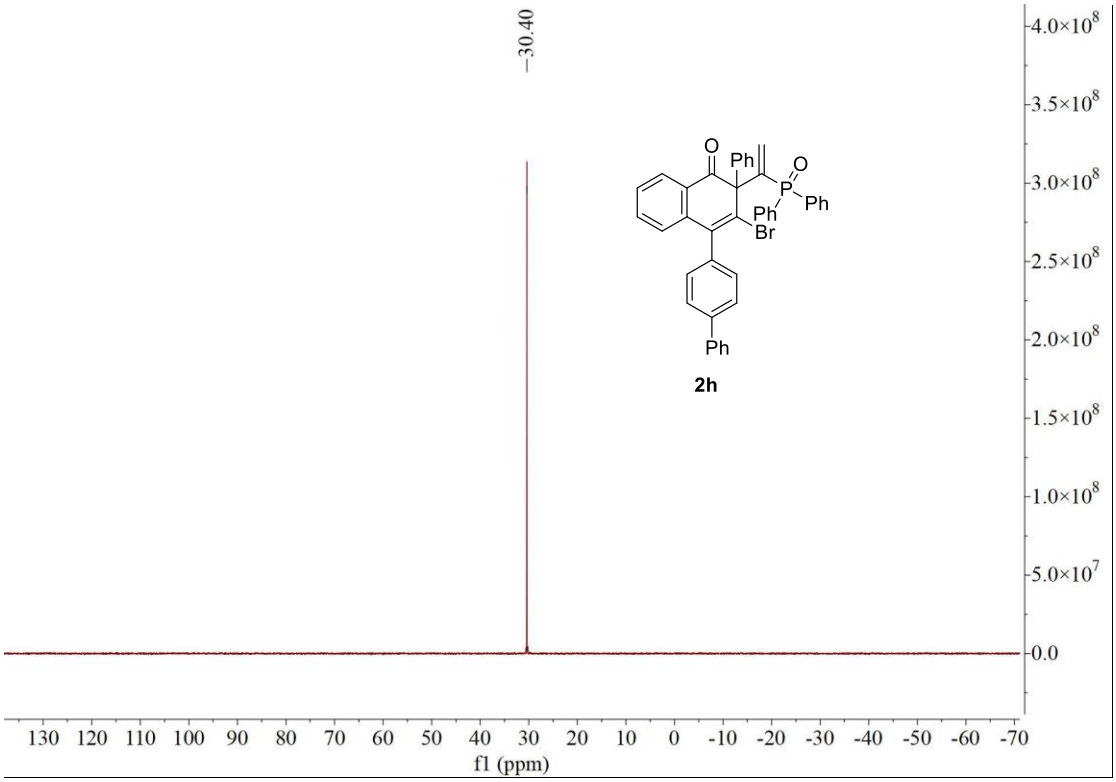

**Compound 2h ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



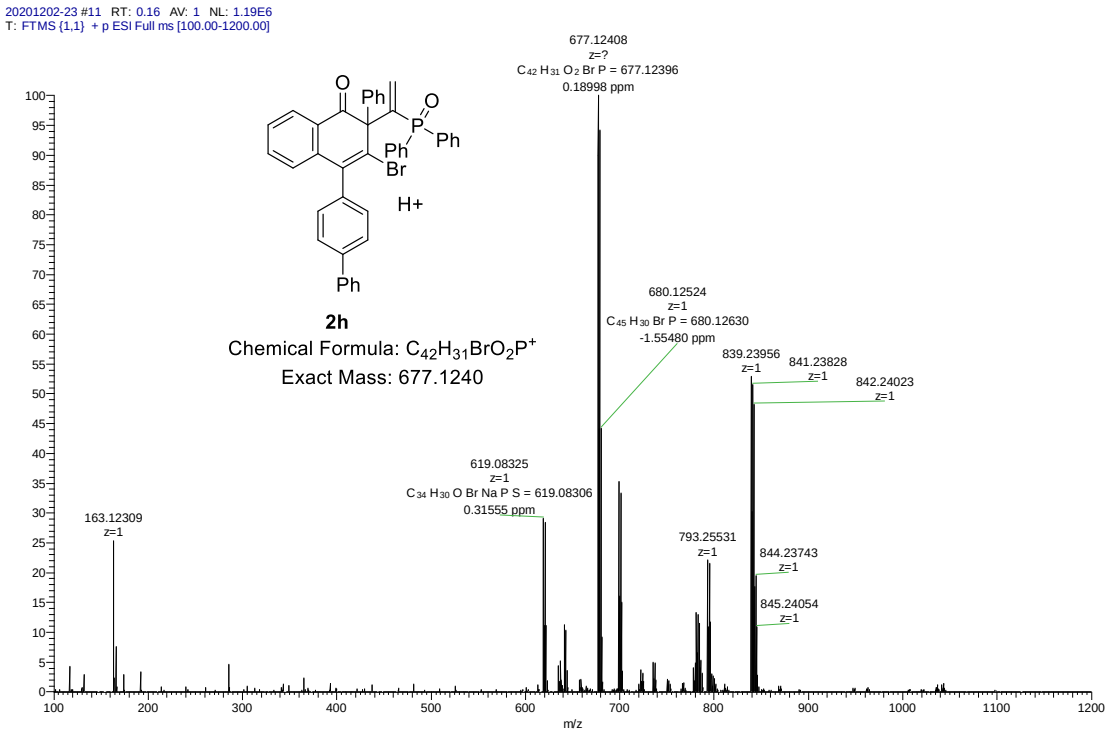

$^{1}$H NMR (600 MHz, $CDCl_3$) of **2h**



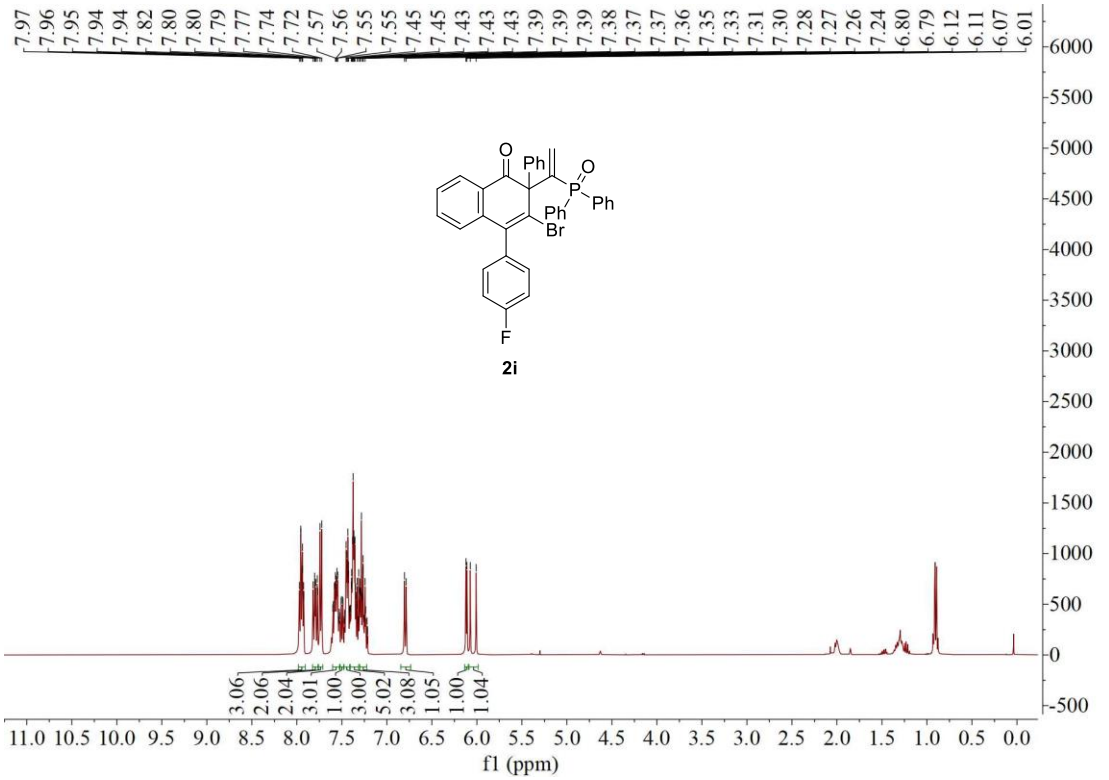

$^{13}$C NMR (151 MHz, $CDCl_3$) of **2h**



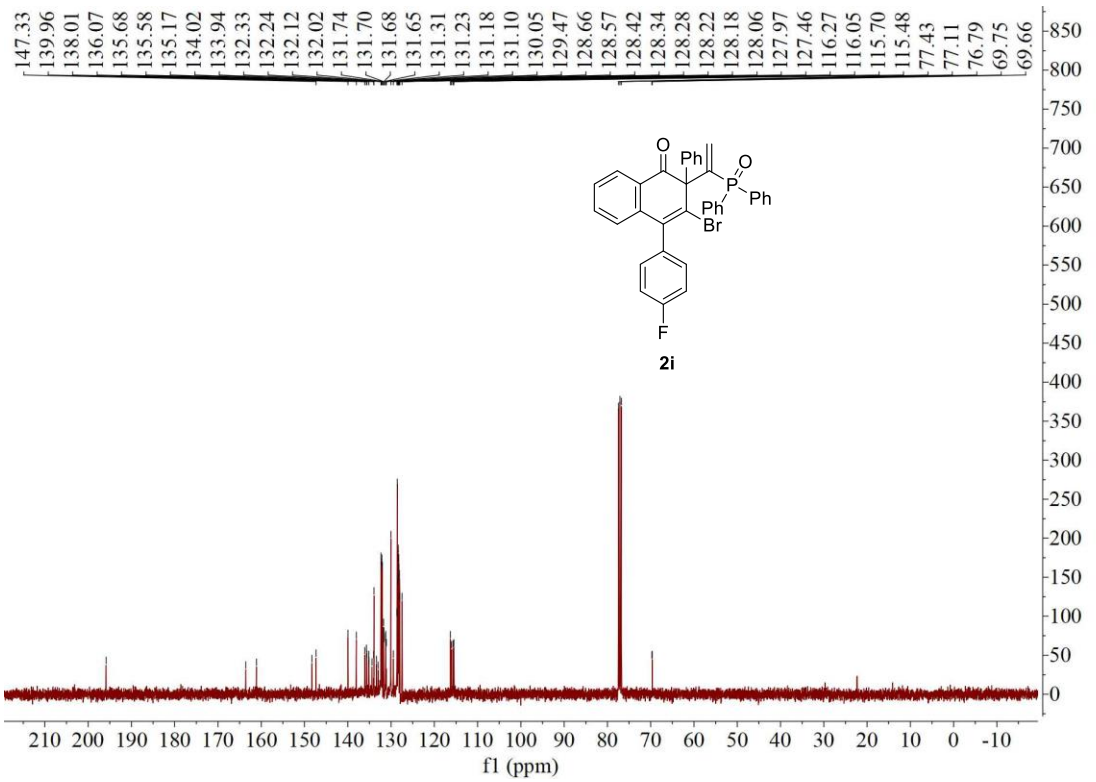

$^{31}$P NMR (243 MHz, $CDCl_3$) of **2h**



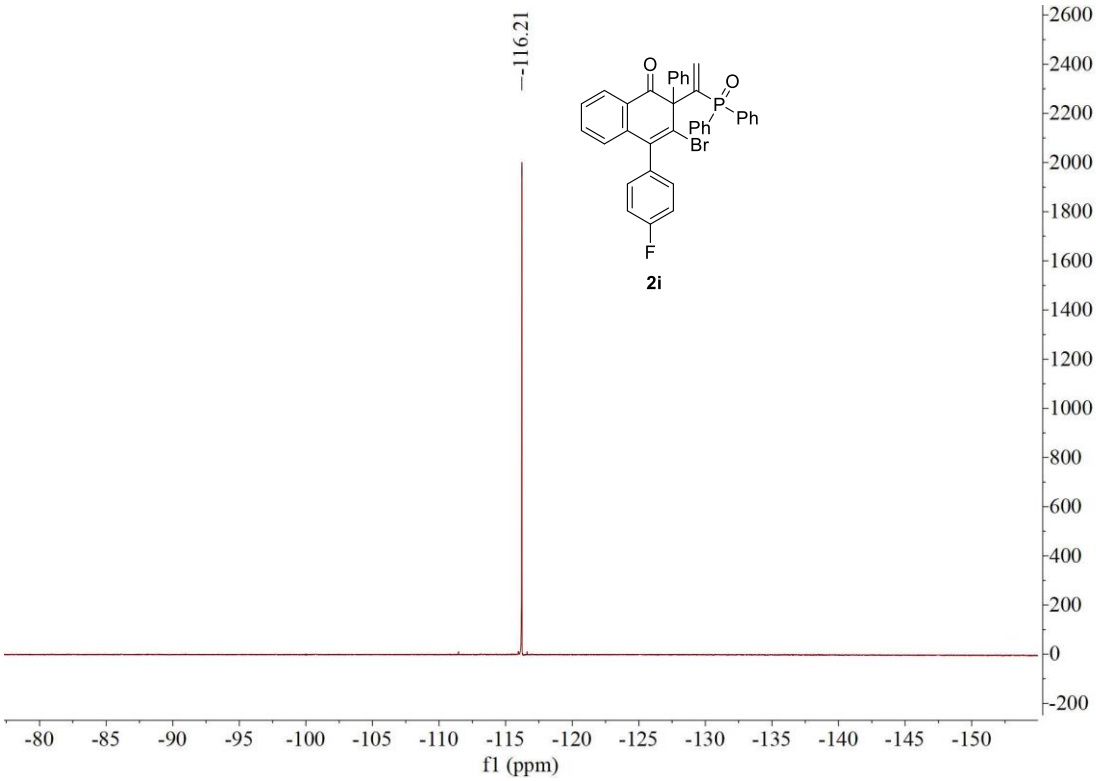

**Compound 2i ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$; $^{19}$F NMR, 376 MHz, $CDCl_3$)**



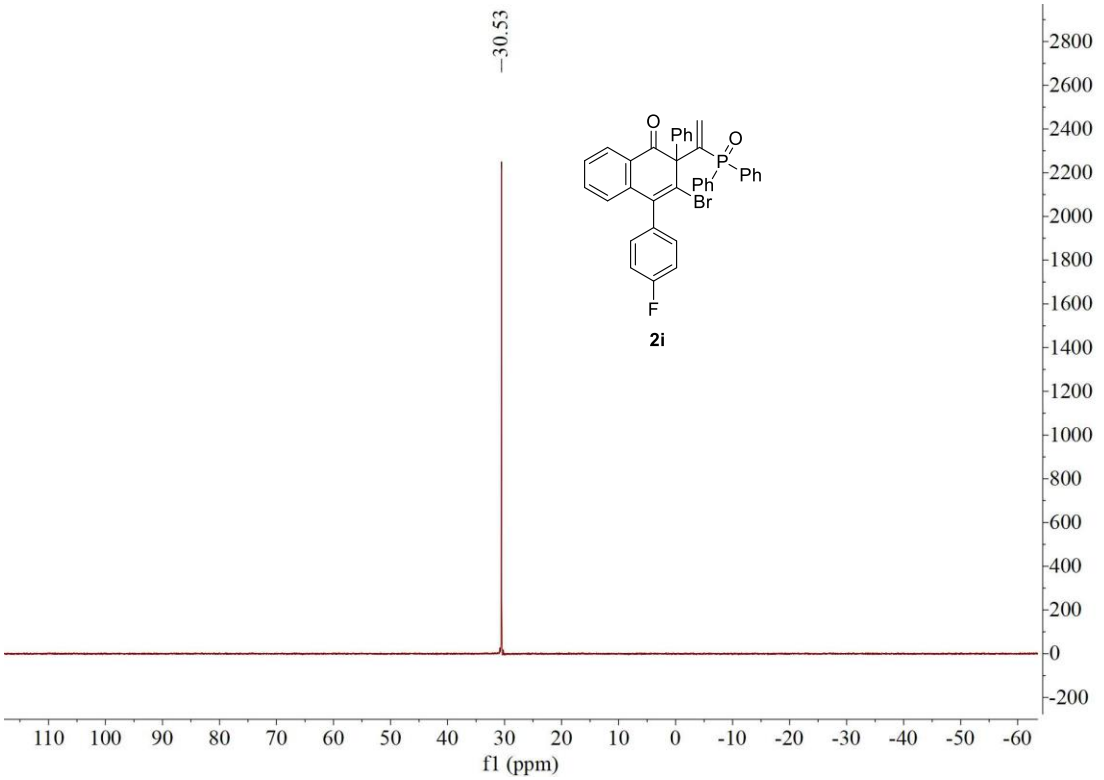

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2i**



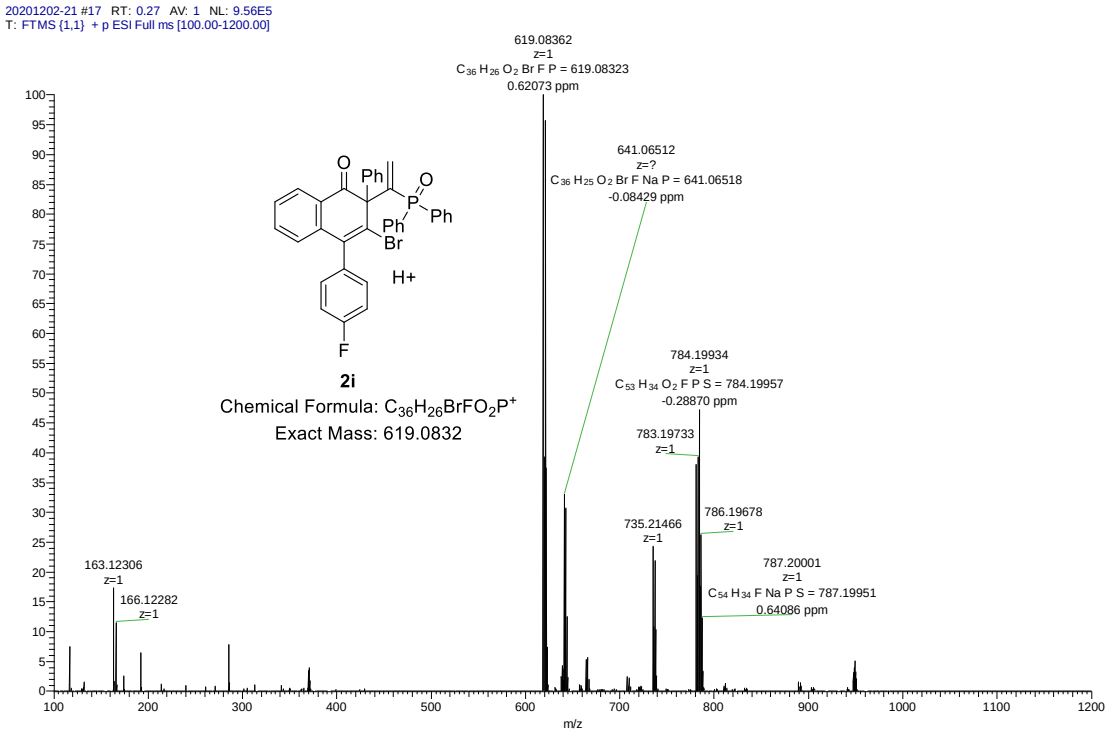

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **2i**



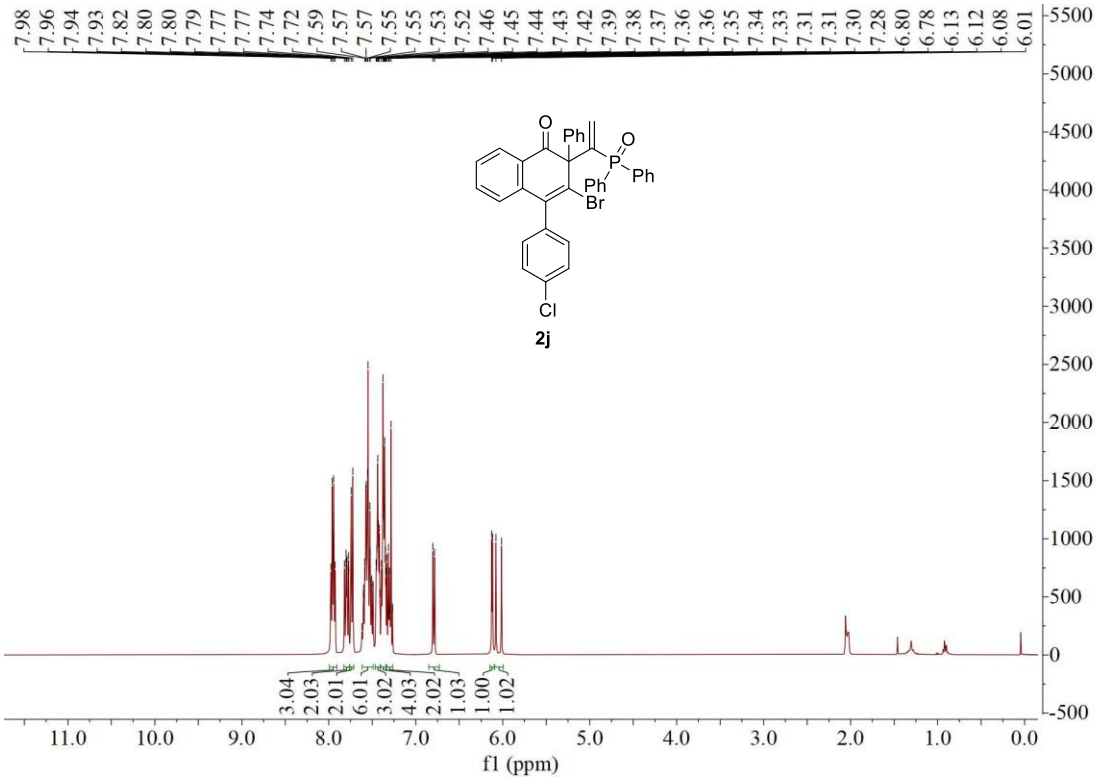

$^{19}F$ NMR (376 MHz, $CDCl_3$) of **2i**



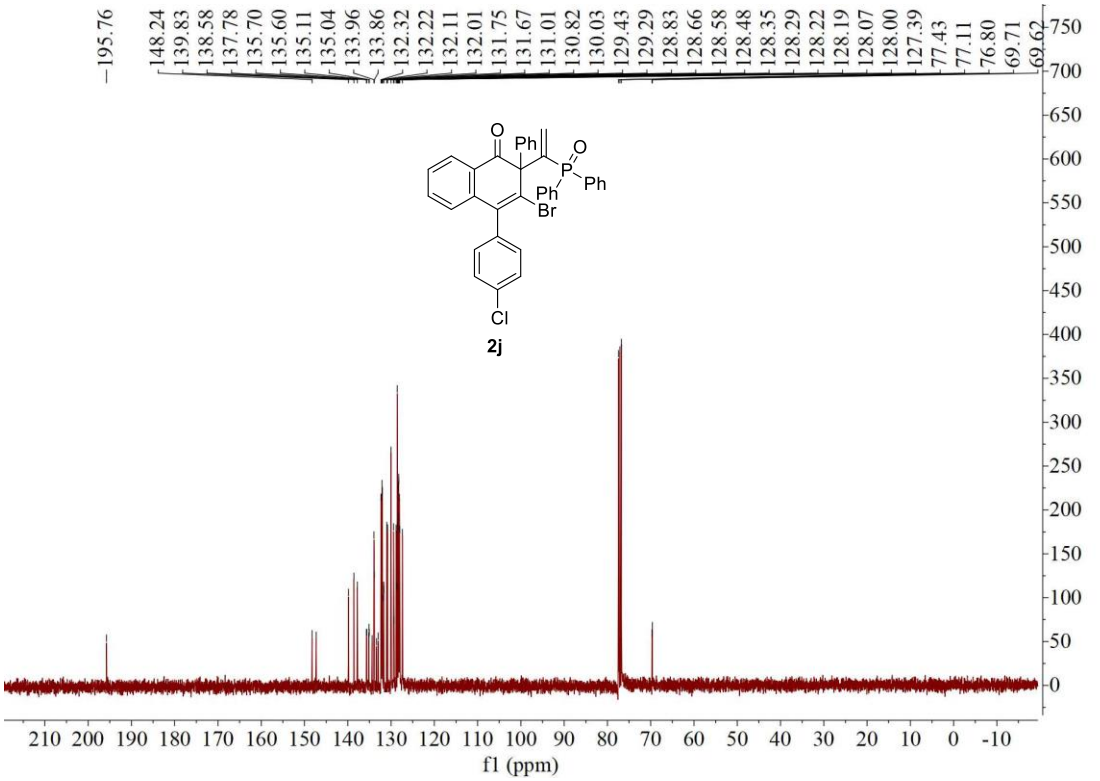

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2i**



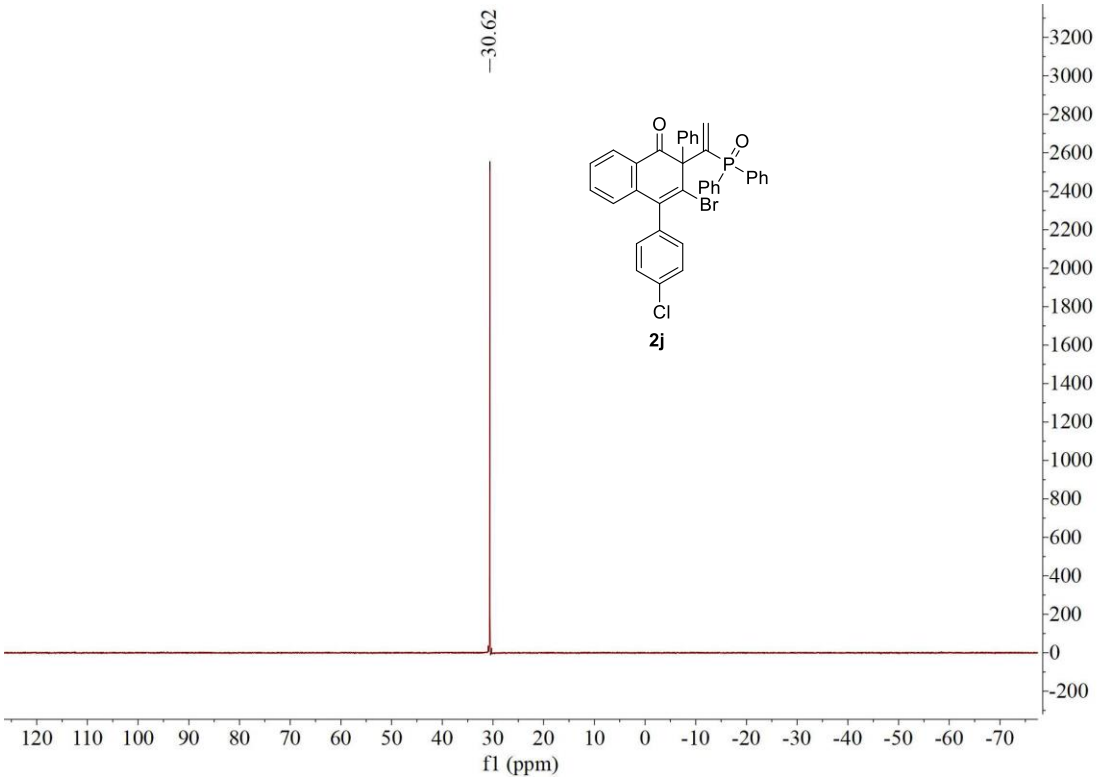
**Compound 2j ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



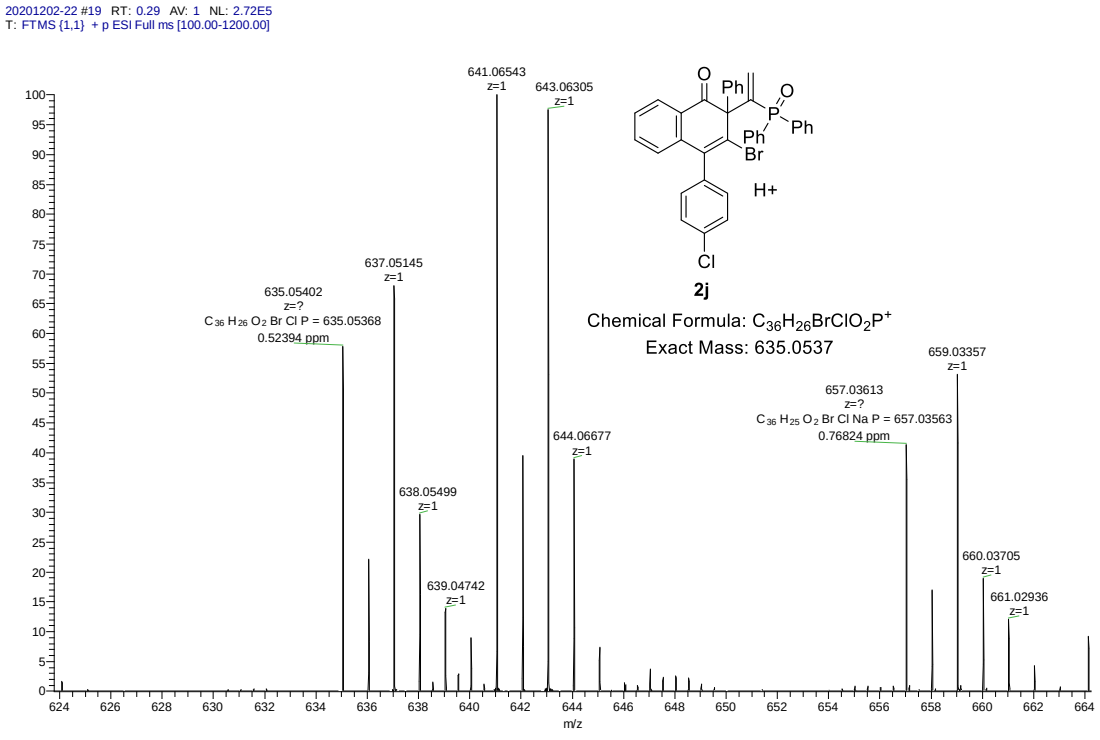

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2j**



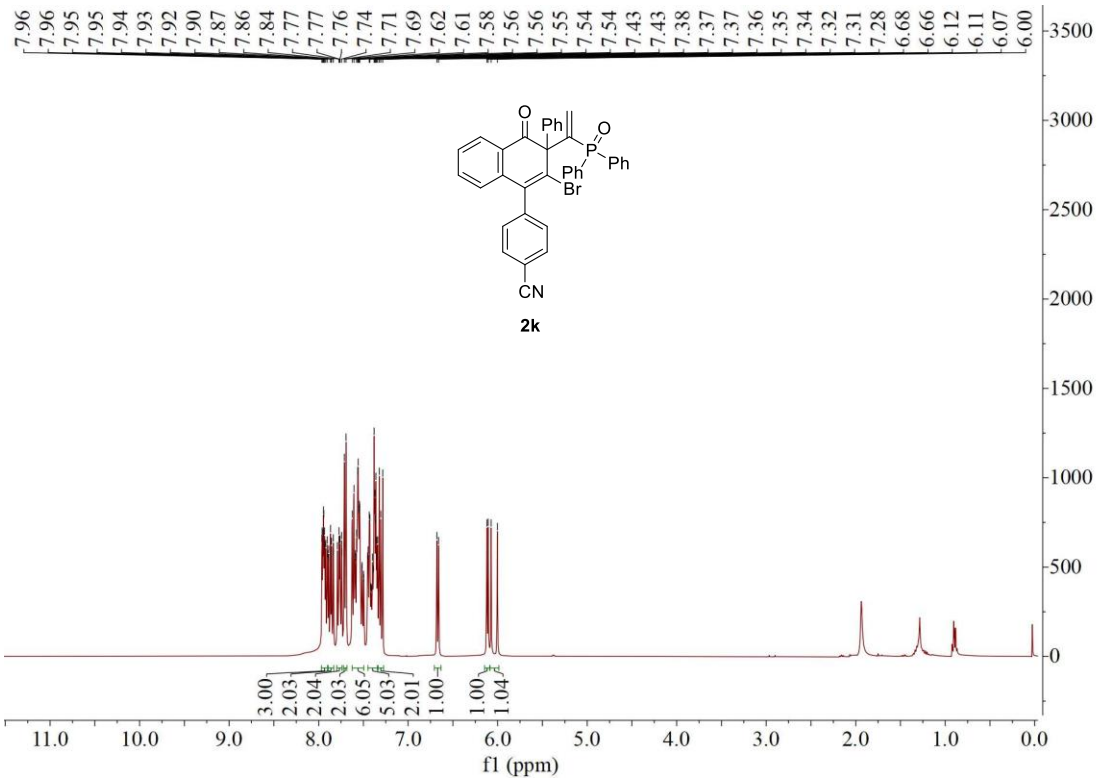

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2j**



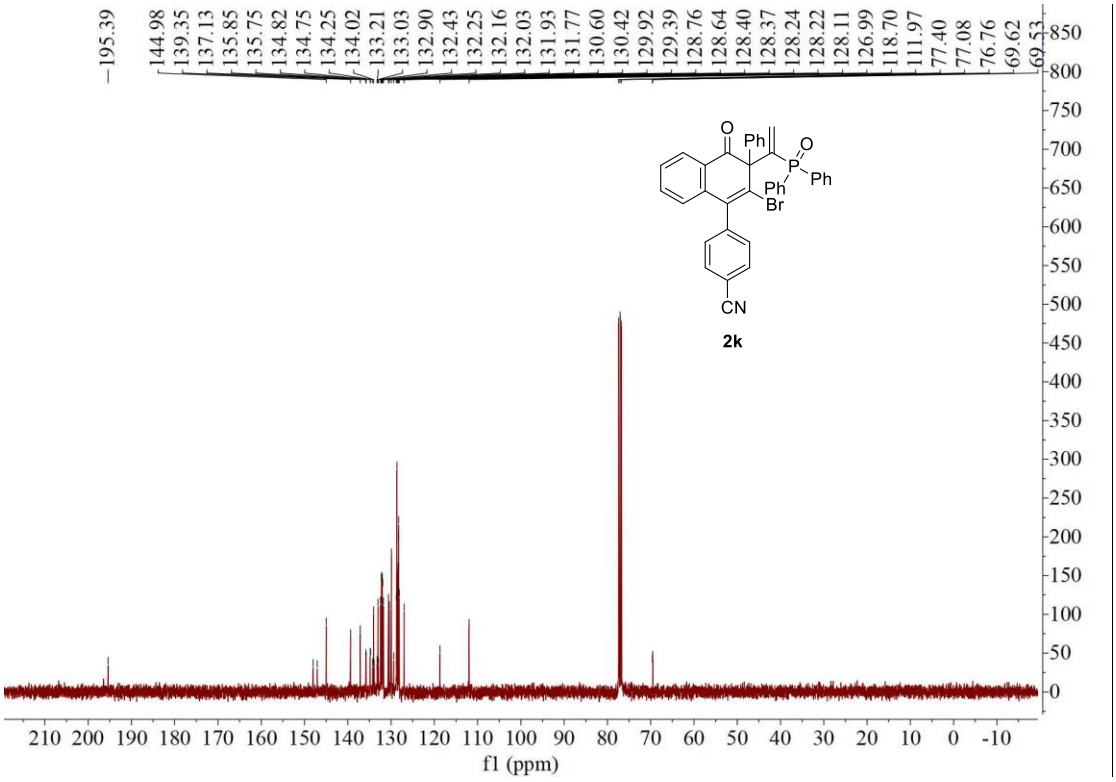

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2j**



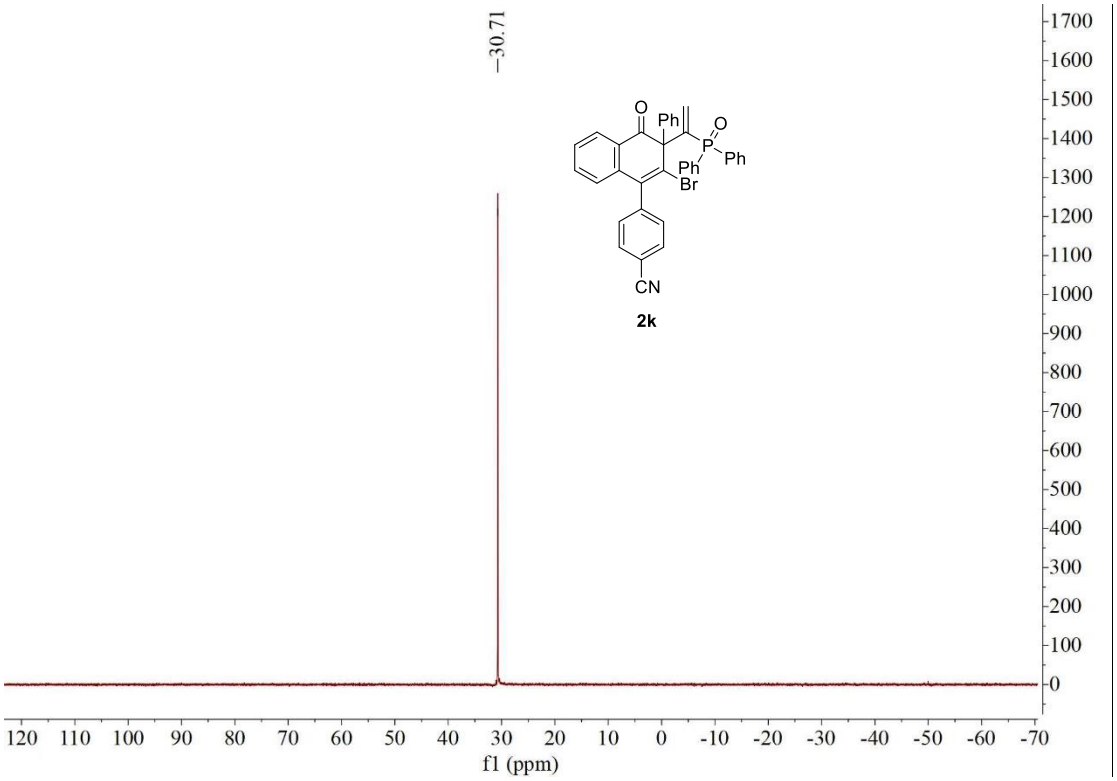
**Compound 2k ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



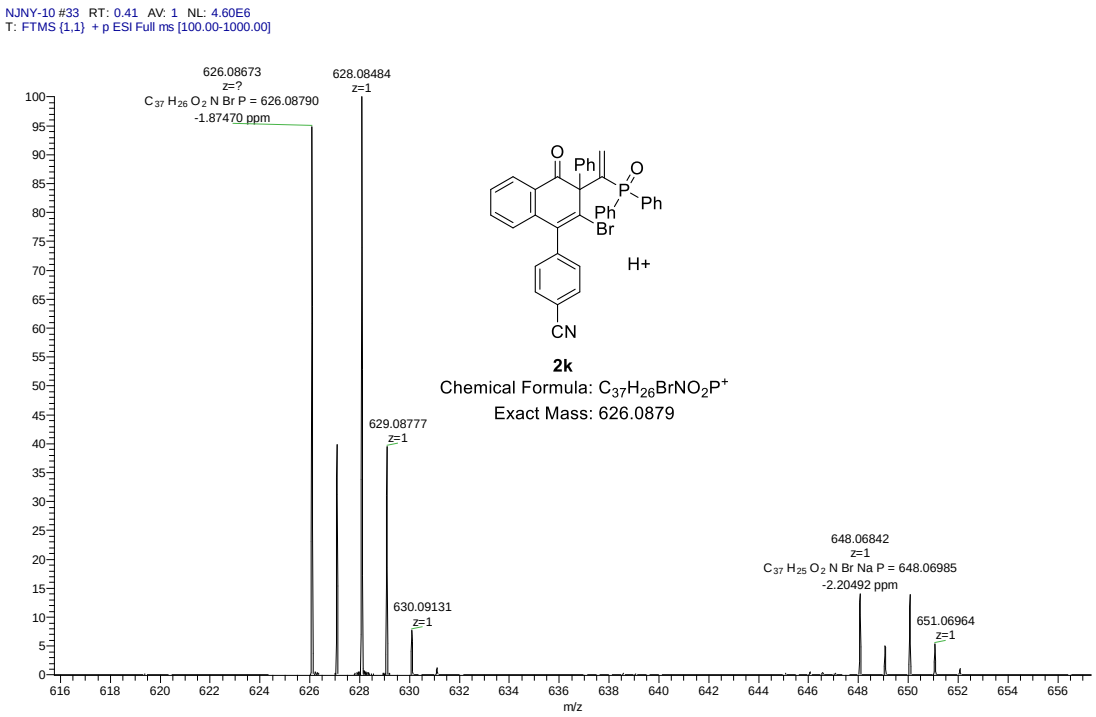

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2k**



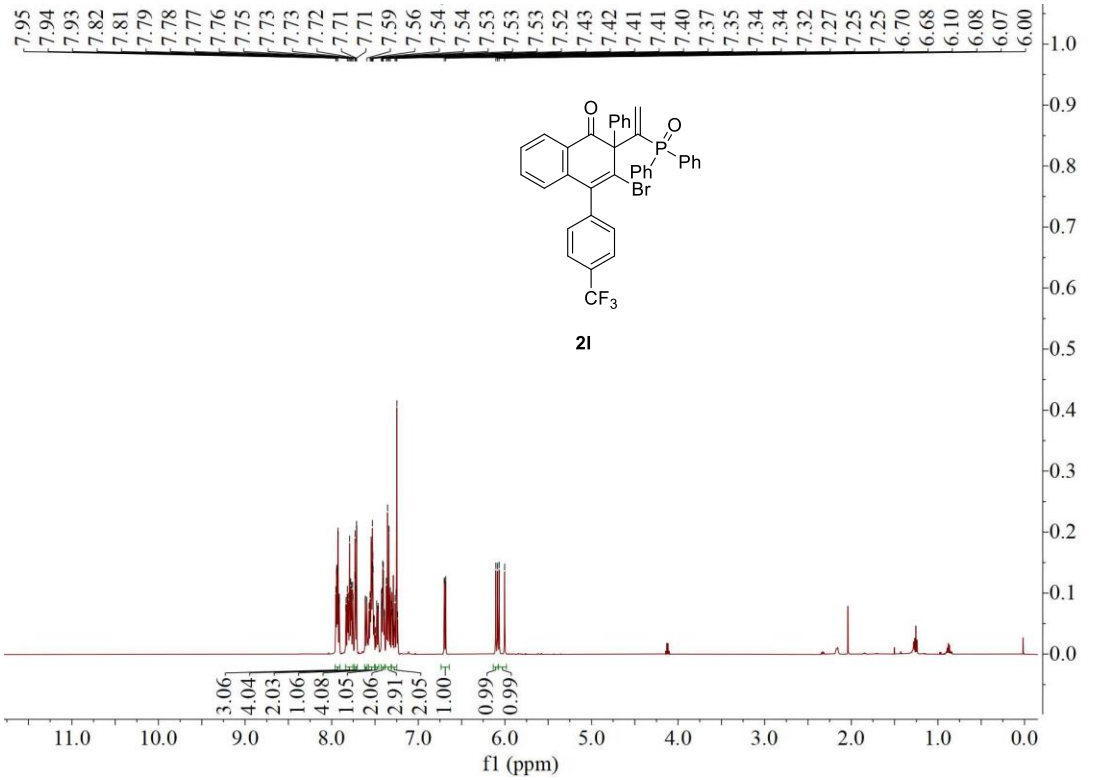

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2k**



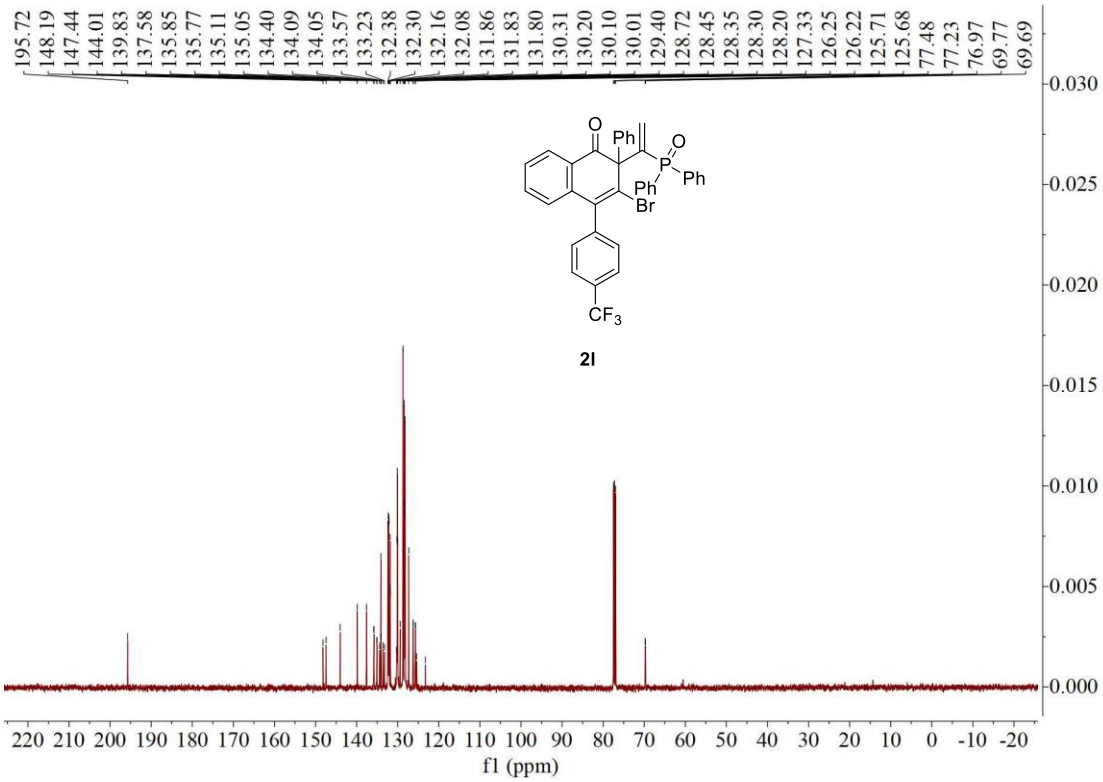

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2k**



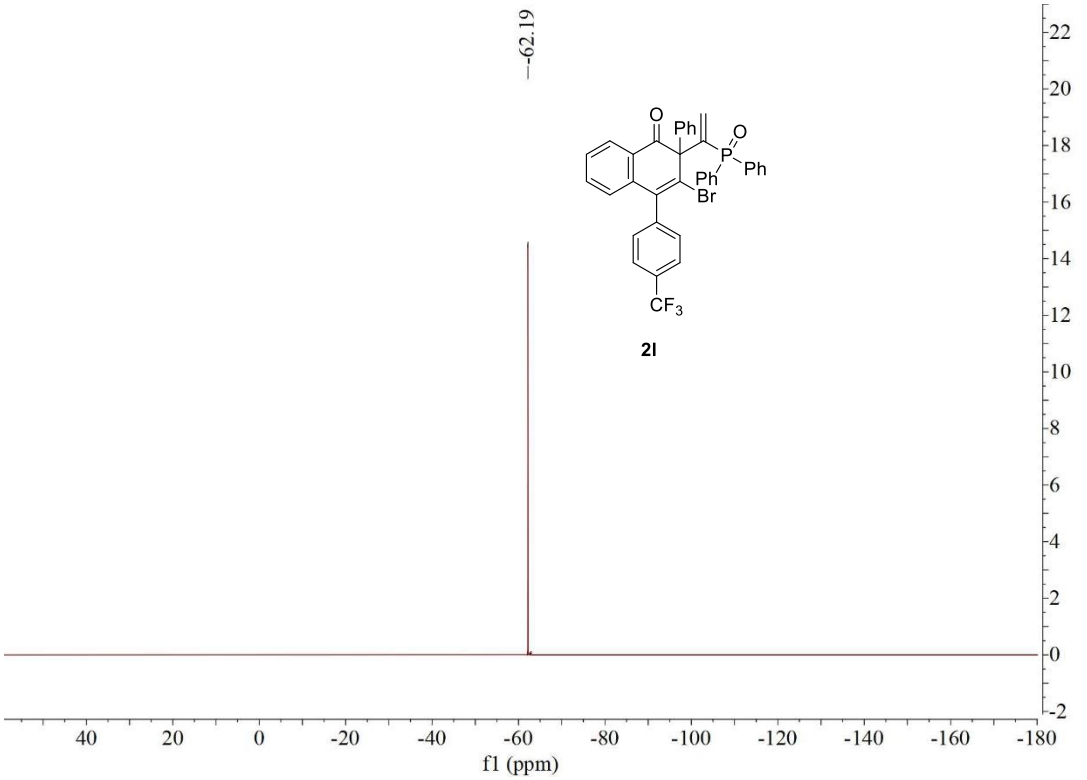
**Compound 2l ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$; $^{19}$F NMR, 471 MHz, $CDCl_3$)**



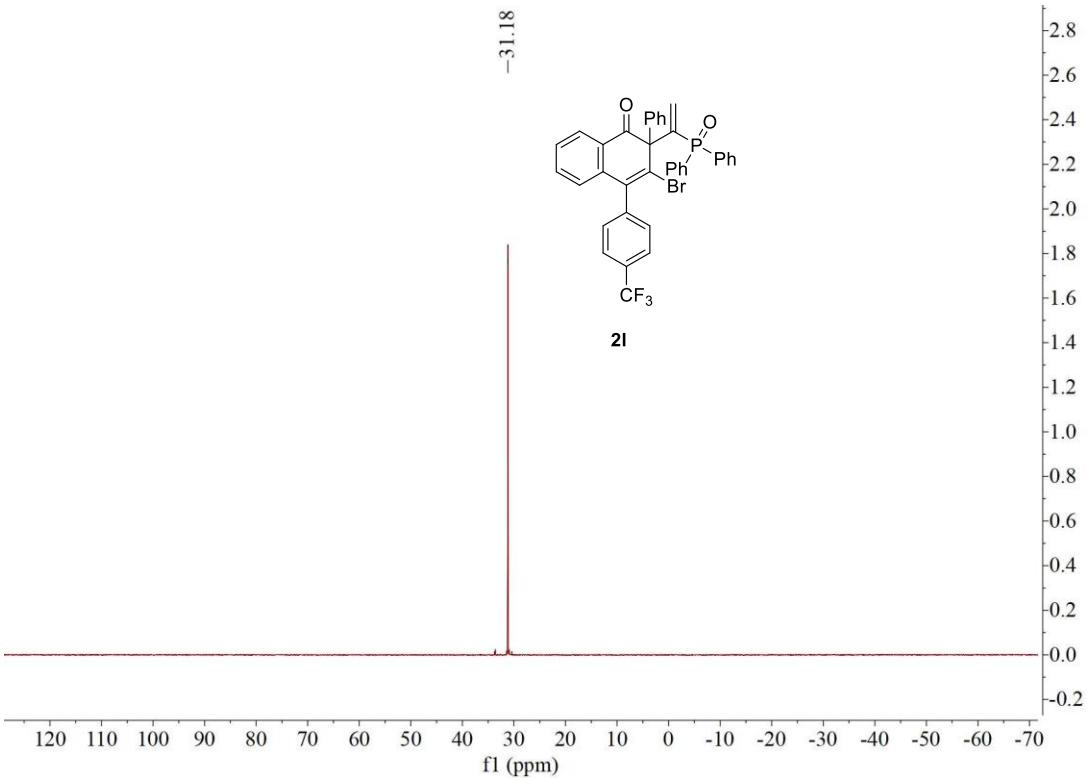

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2l**



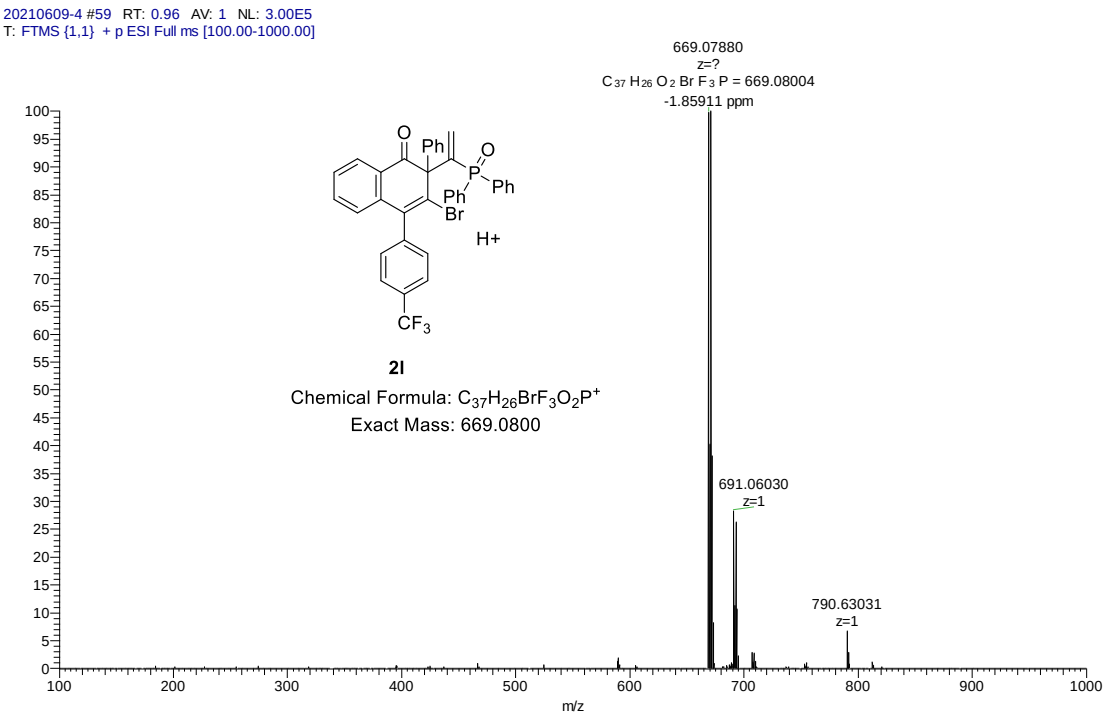

$^{13}$C NMR (126 MHz, $CDCl_3$) of **2l**



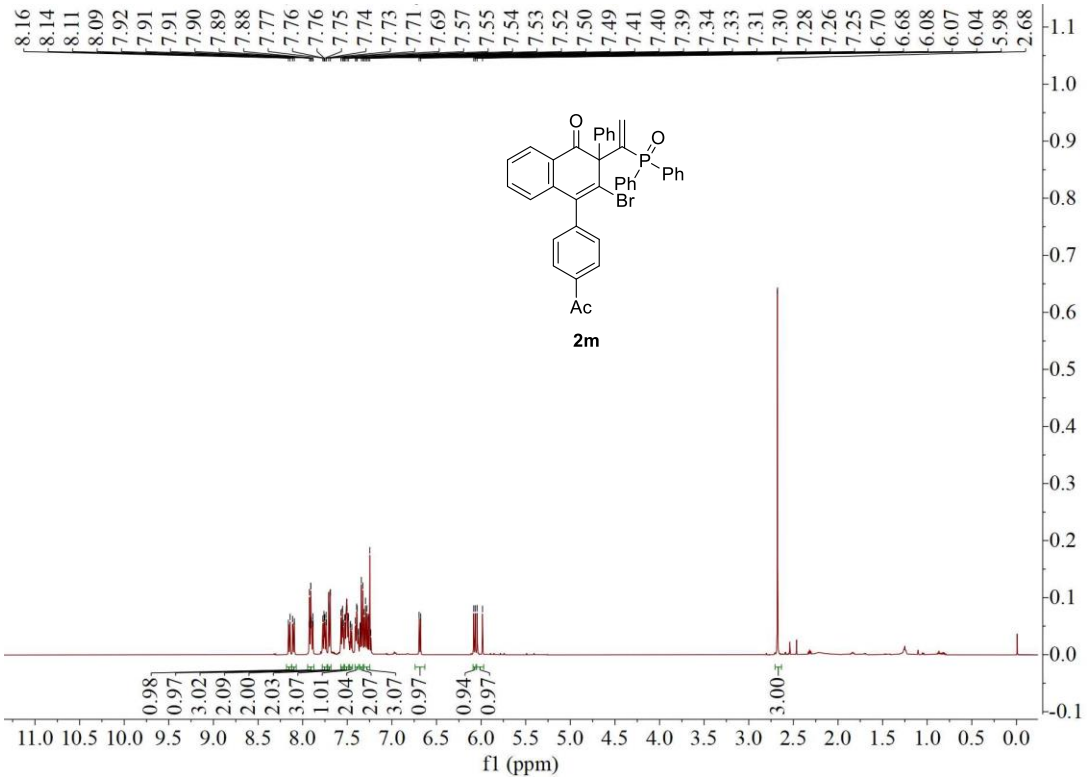

$^{19}$F NMR (471 MHz, $CDCl_3$) of **2l**



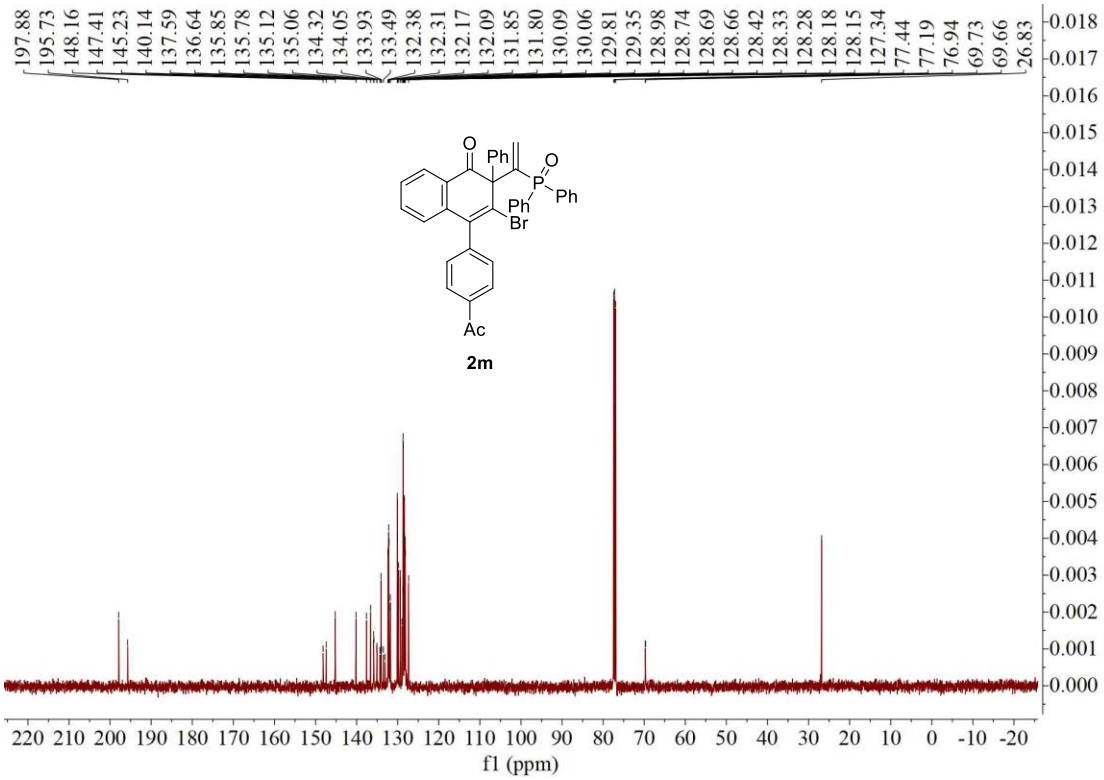

$^{31}$P NMR (202 MHz, $CDCl_3$) of **2l**



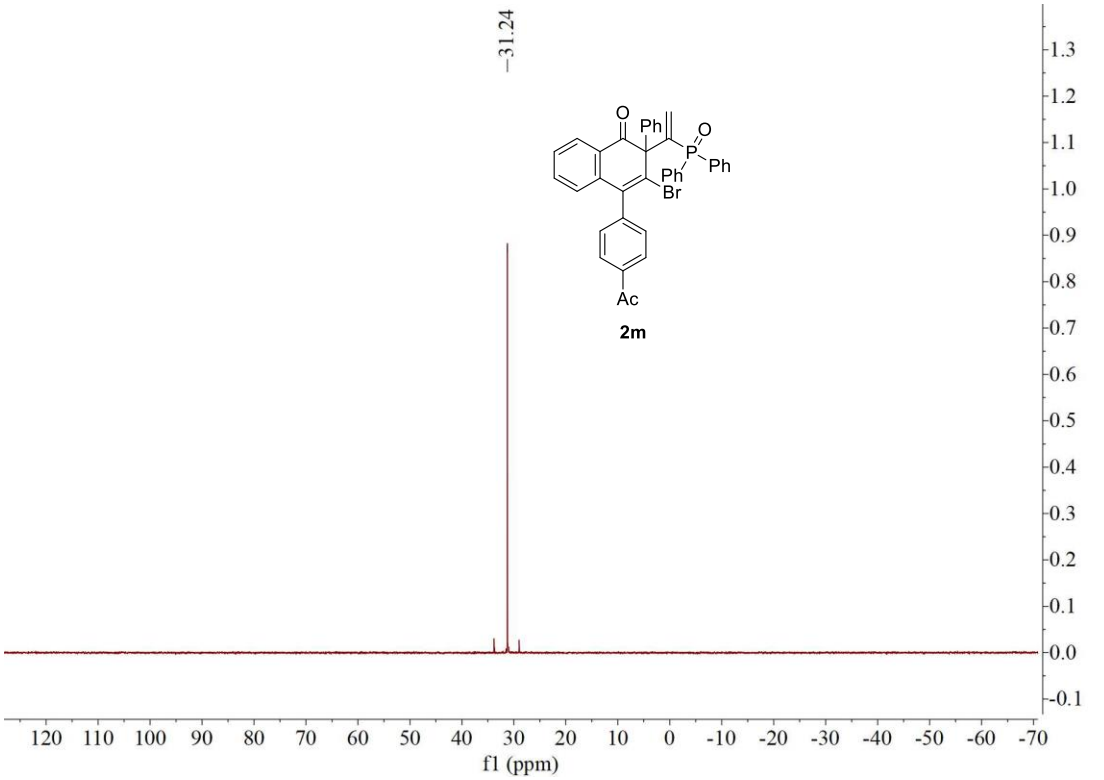

**Compound 2m ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



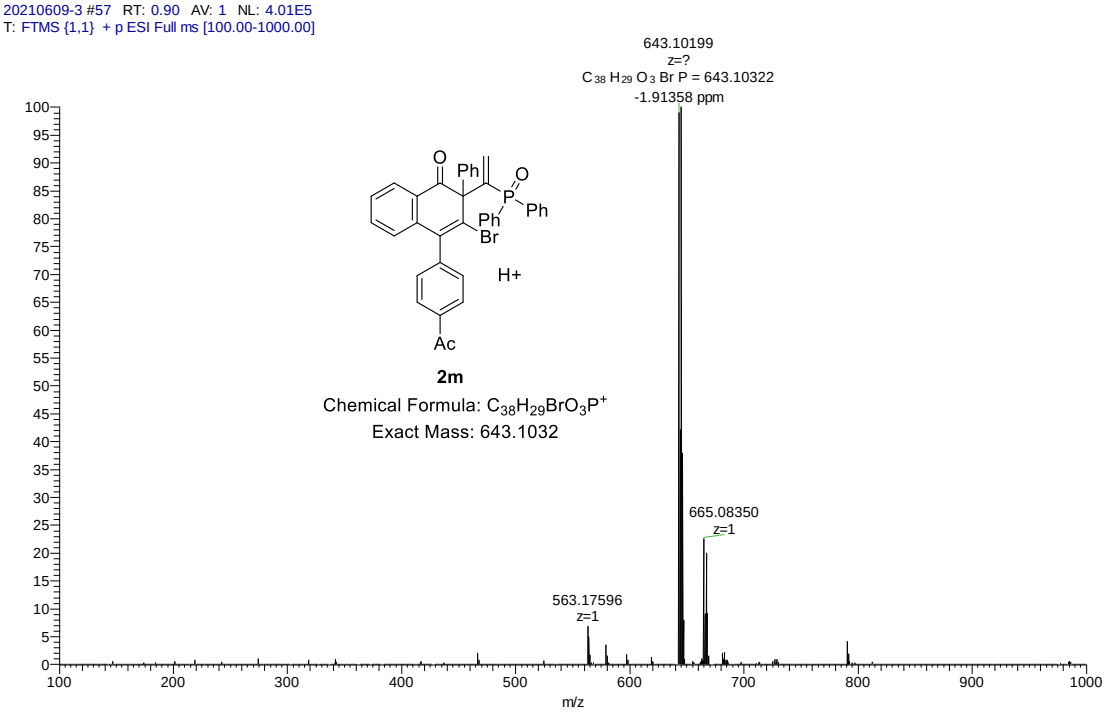

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2m**



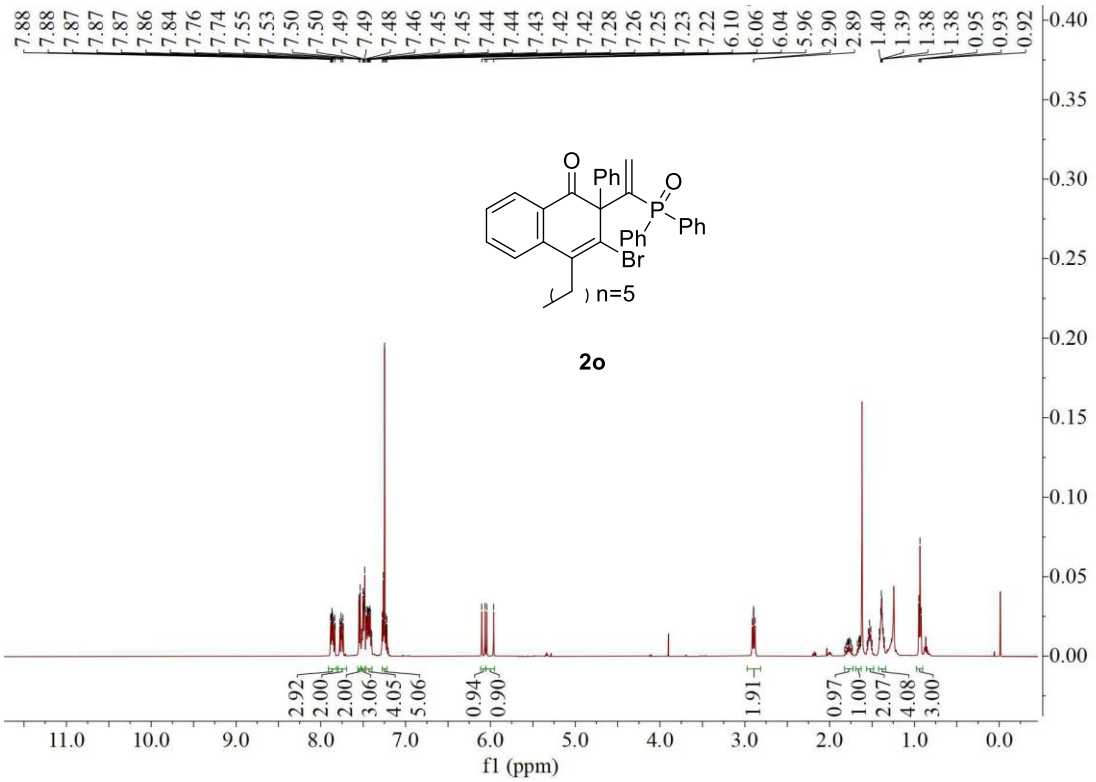

$^{13}$C NMR (126 MHz, $CDCl_3$) of **2m**



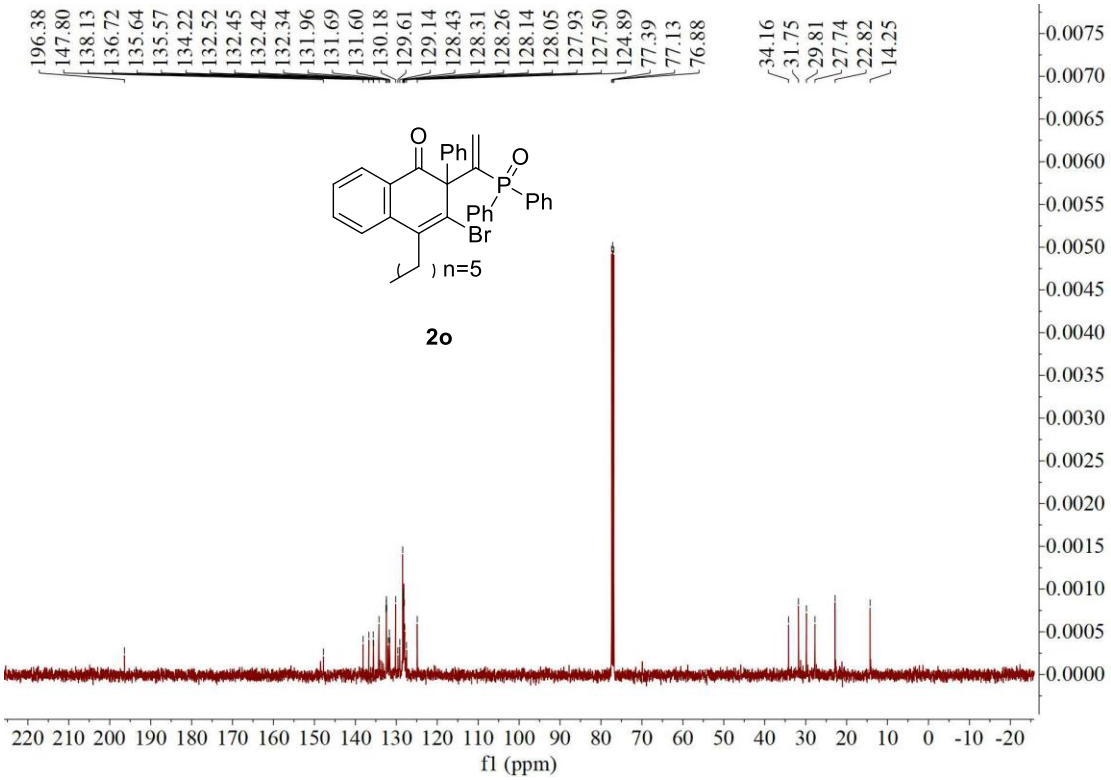

$^{31}$P NMR (202 MHz, $CDCl_3$) of **2m**



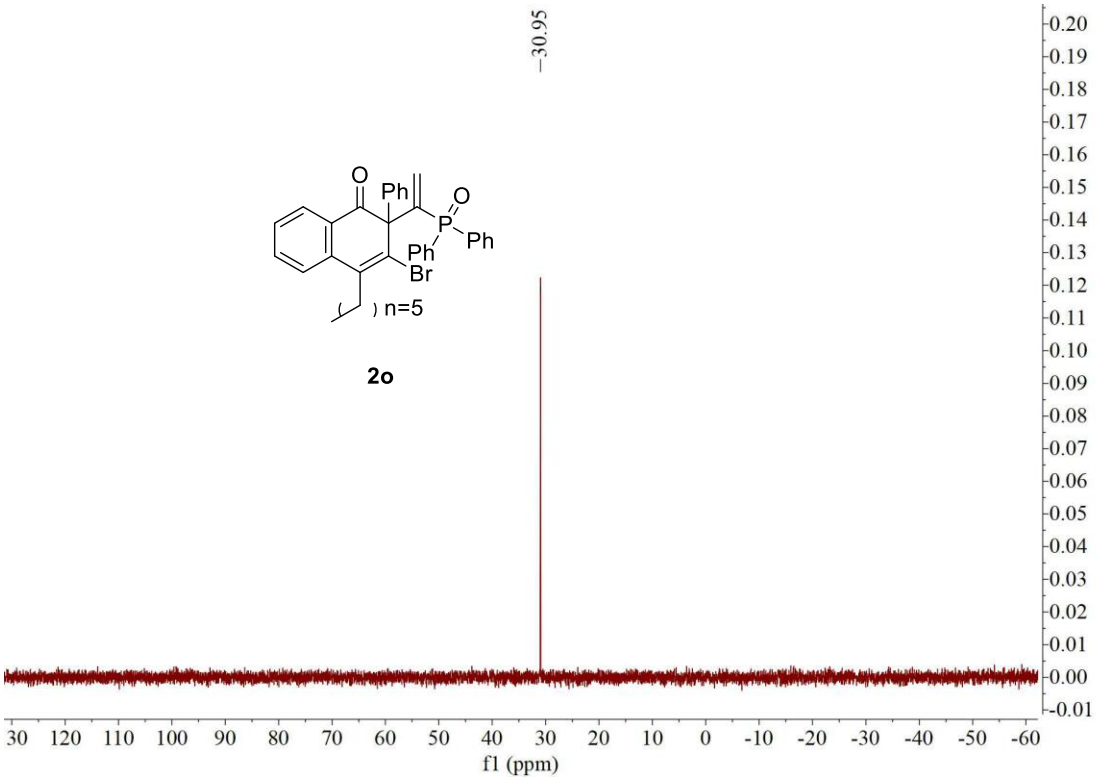

**Compound 2o ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



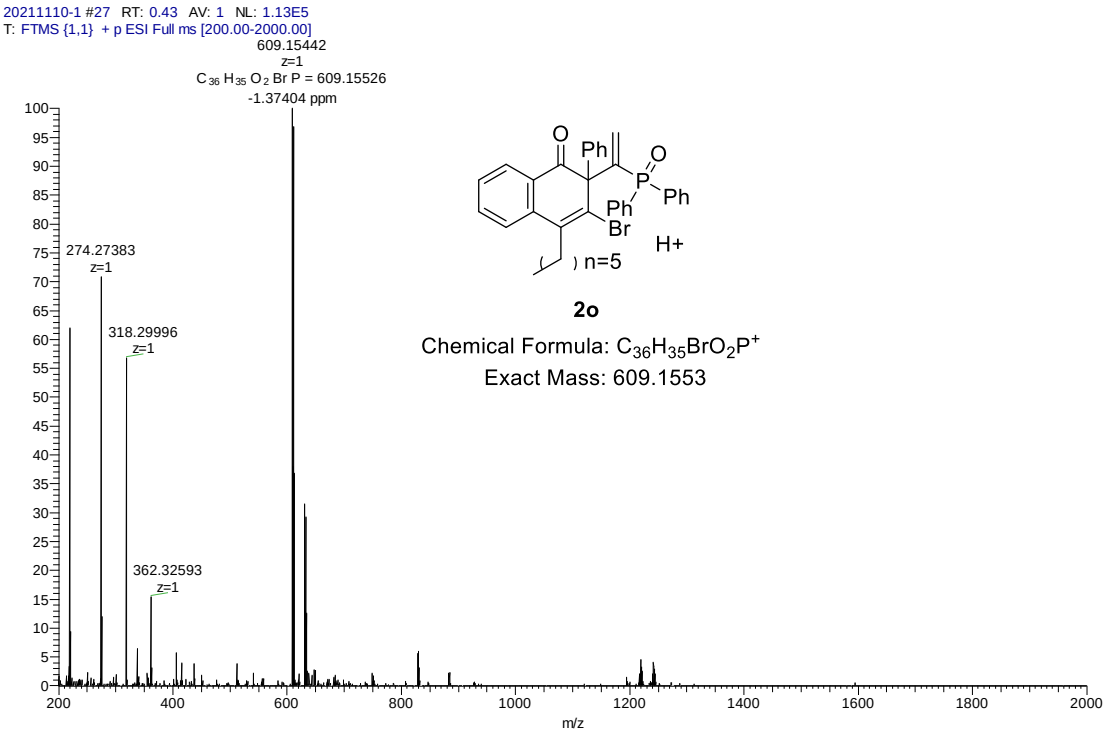

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2o**



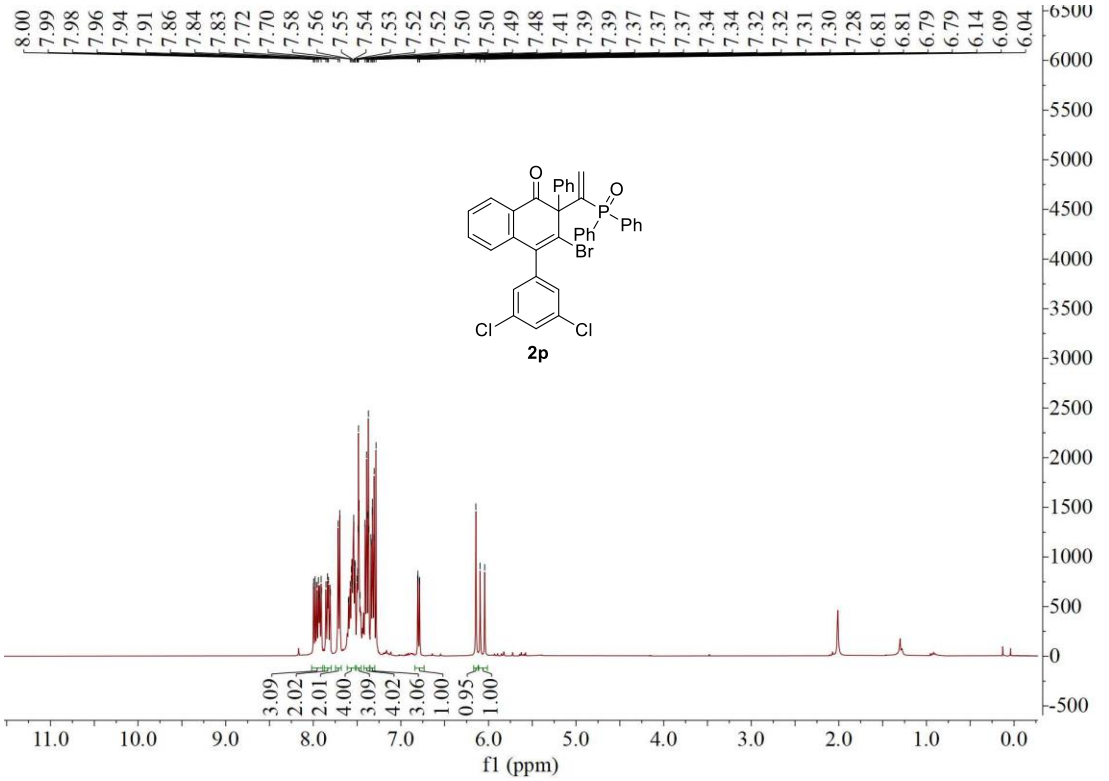

$^{13}$C NMR (126 MHz, $CDCl_3$) of **2o**



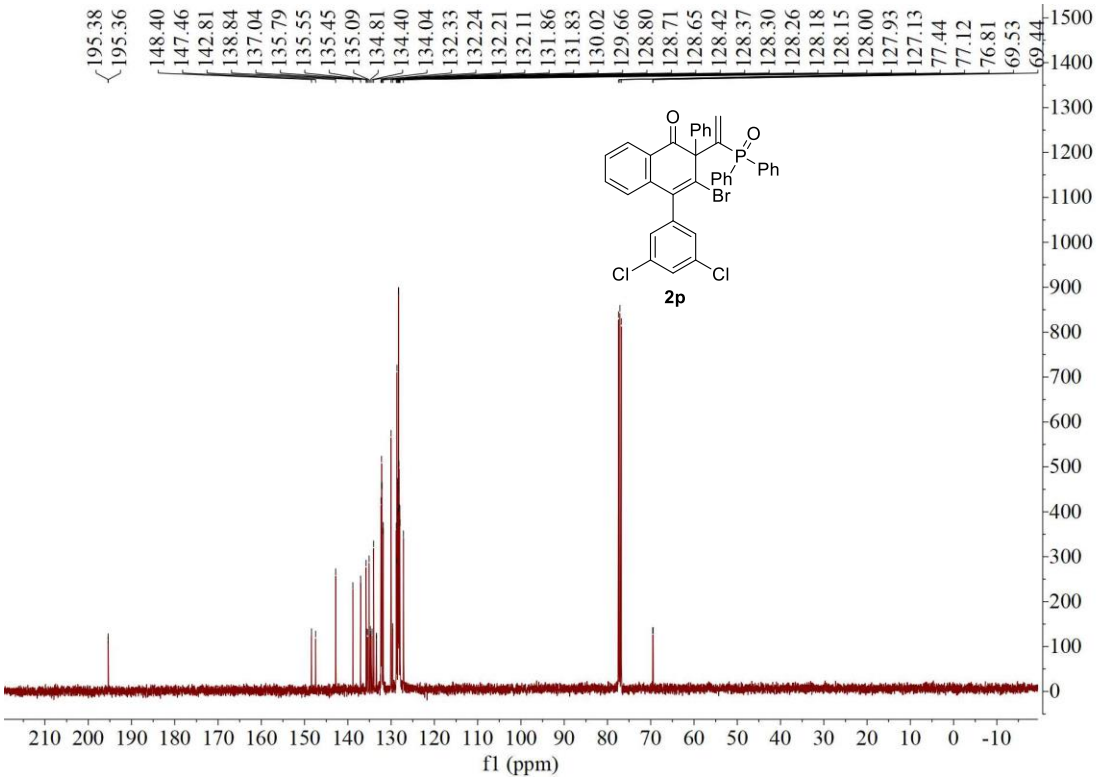

$^{31}$P NMR (202 MHz, $CDCl_3$) of **2o**



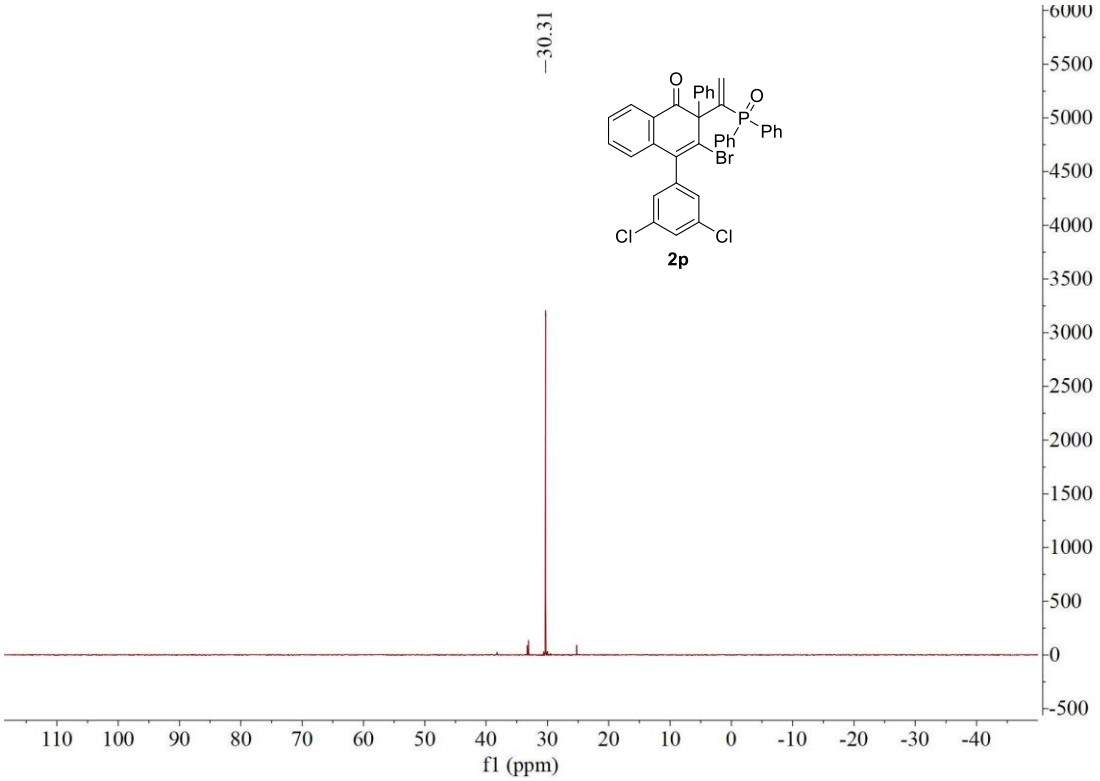

**Compound 2p ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



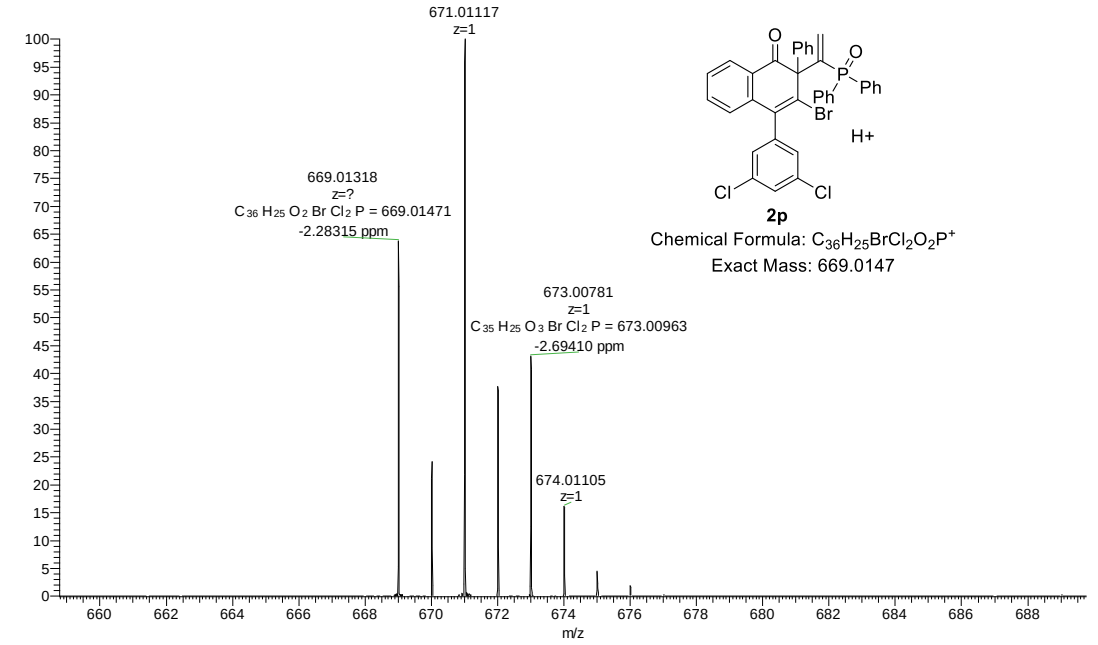

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2p**



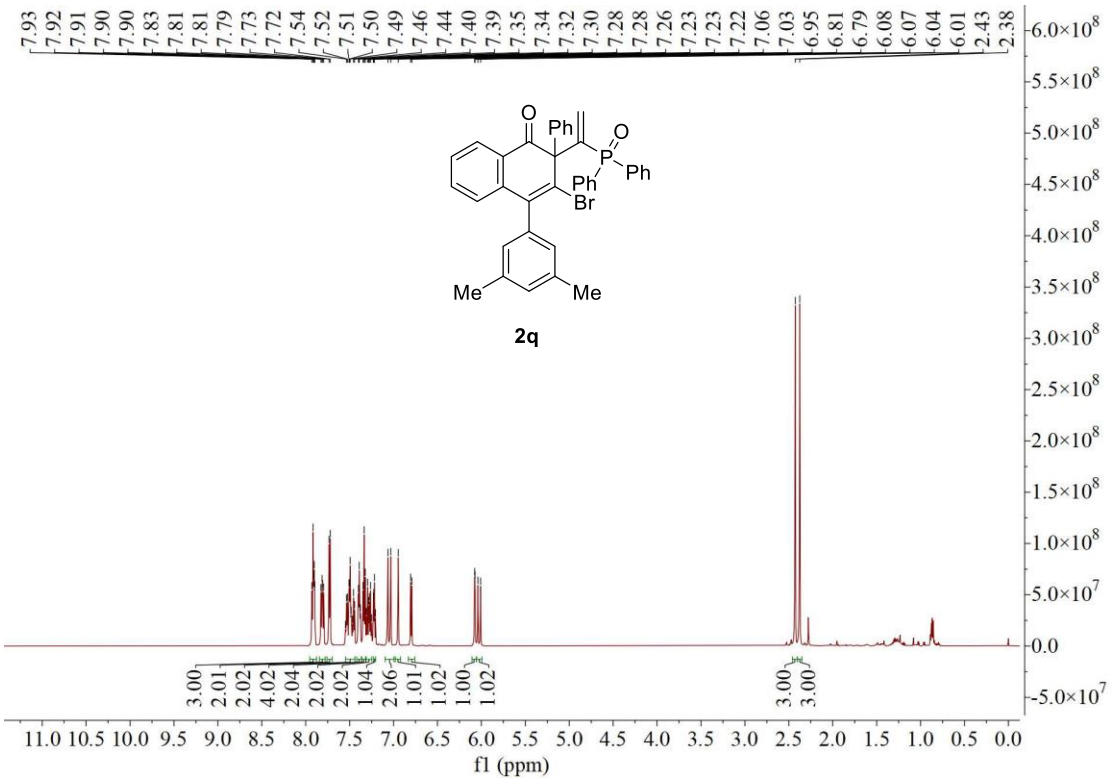

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2p**



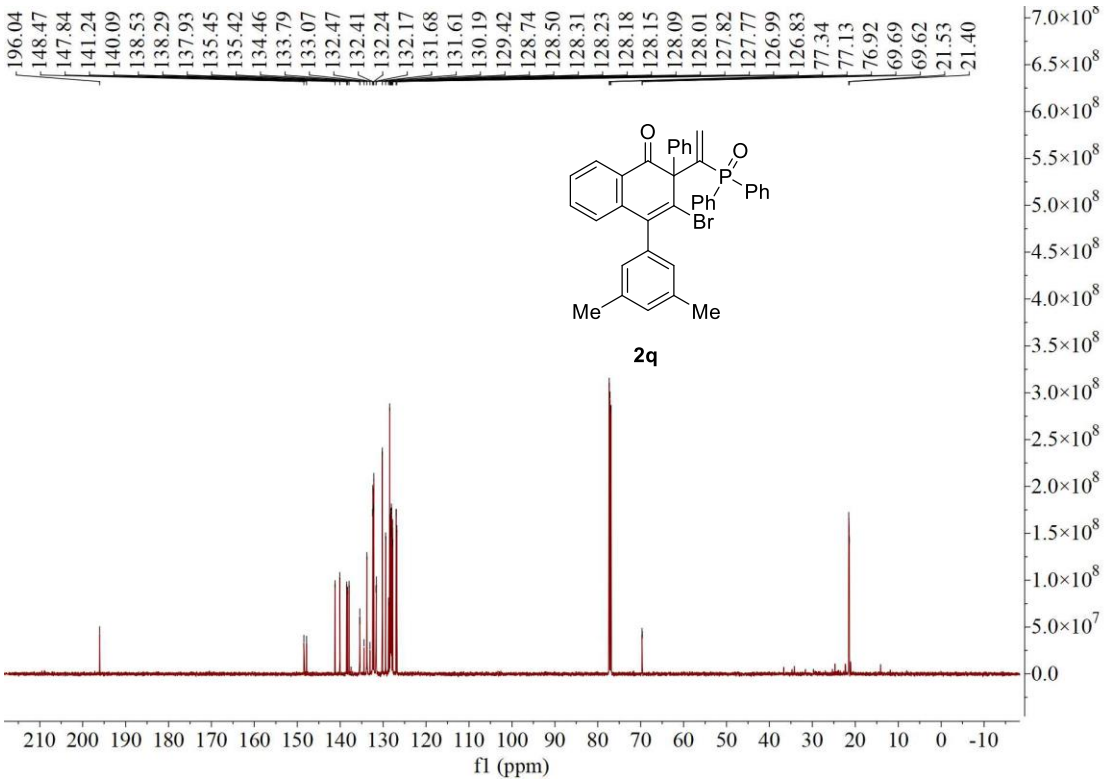

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2p**



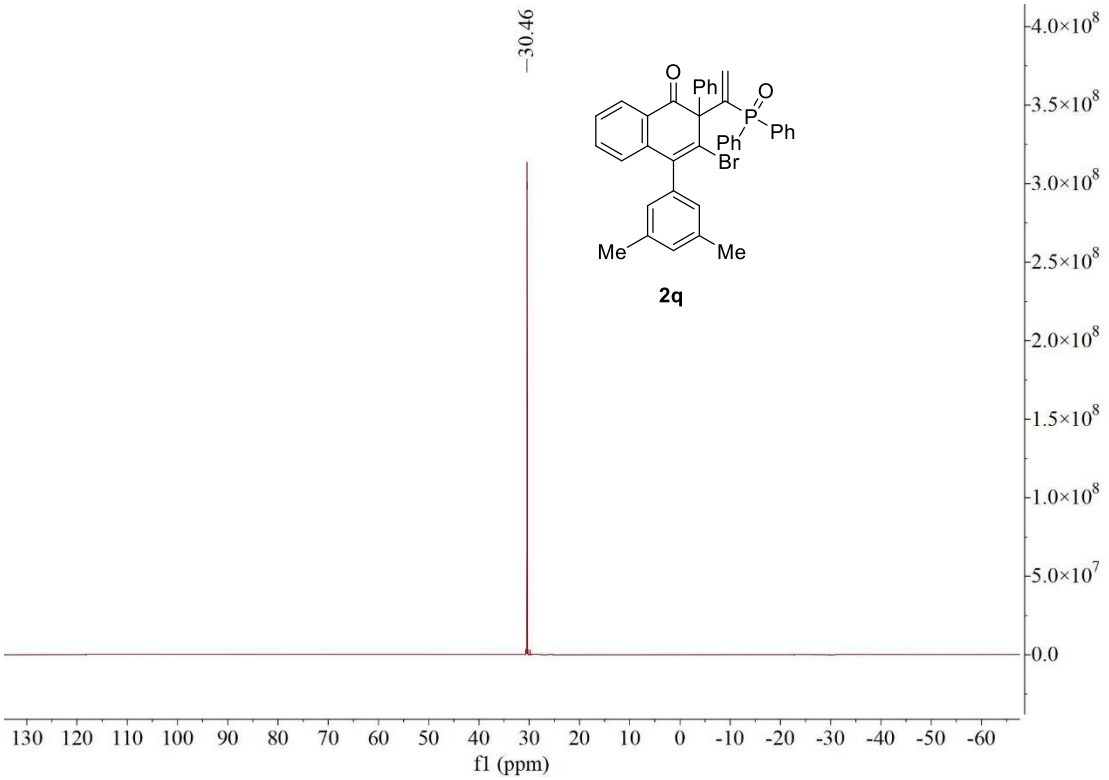

**Compound 2q ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



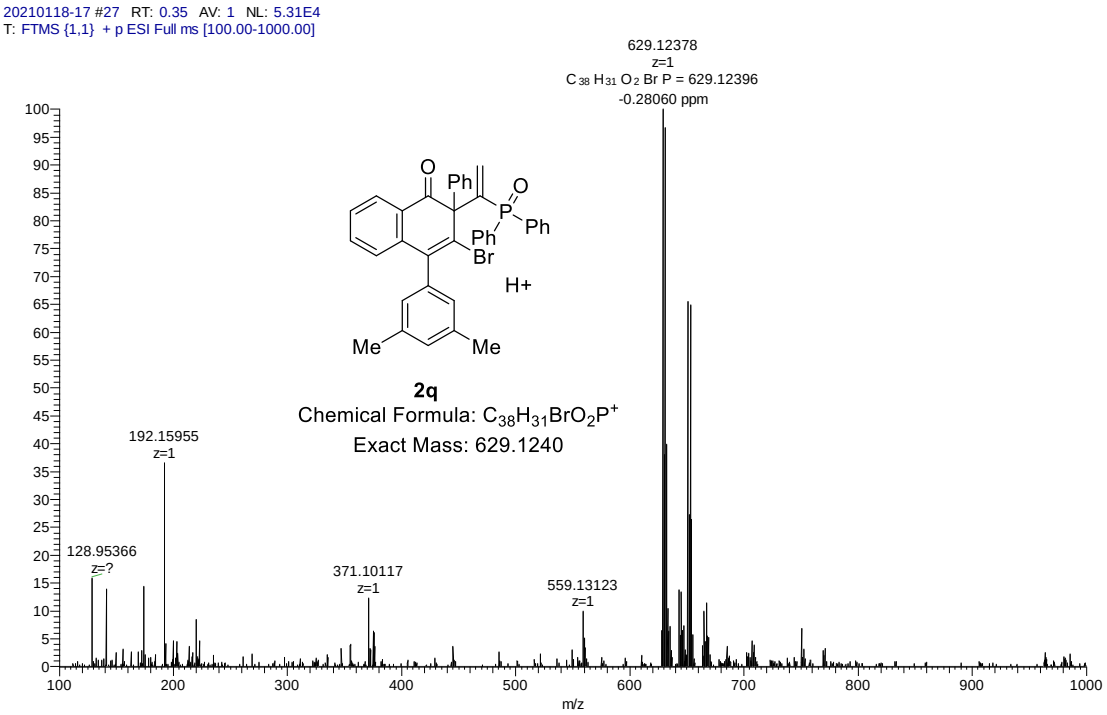

$^{1}$H NMR (600 MHz, $CDCl_3$) of **2q**



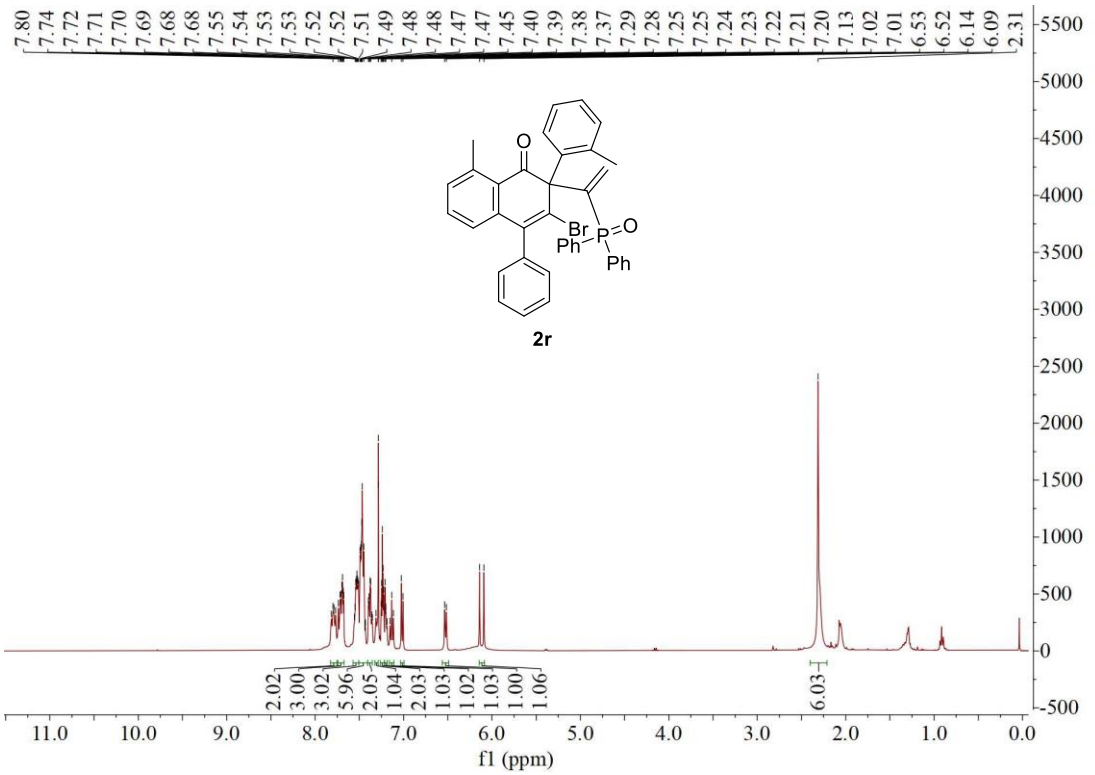

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **2q**



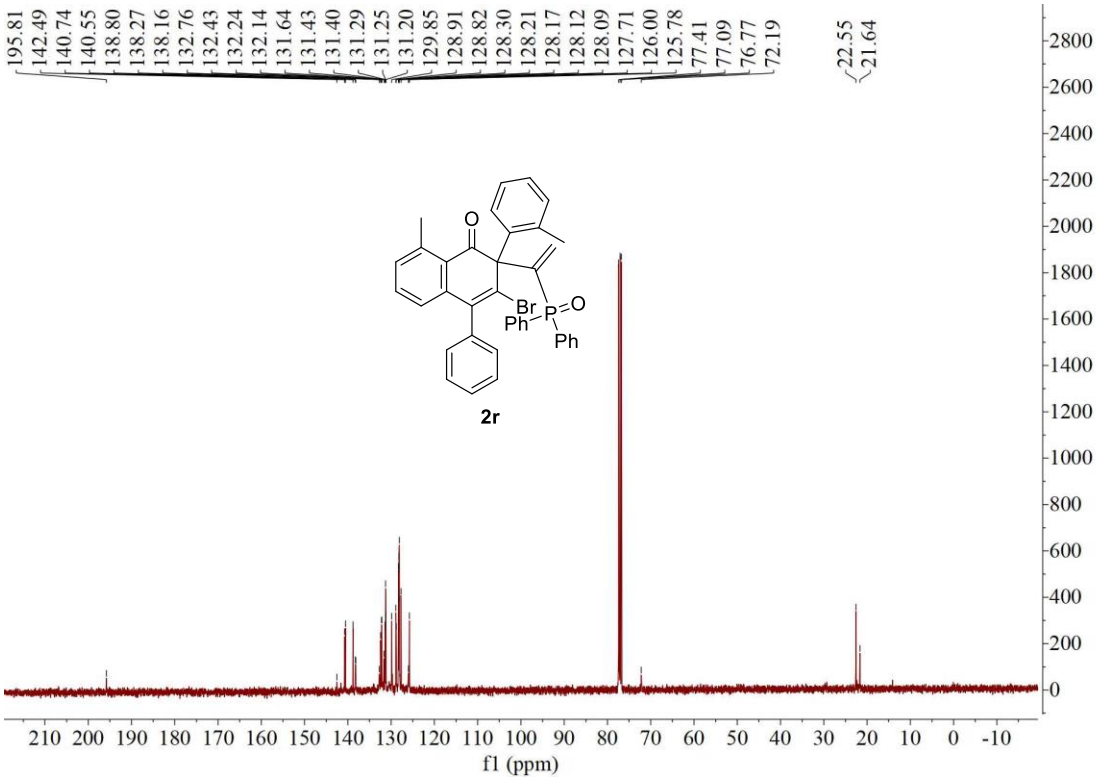

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **2q**



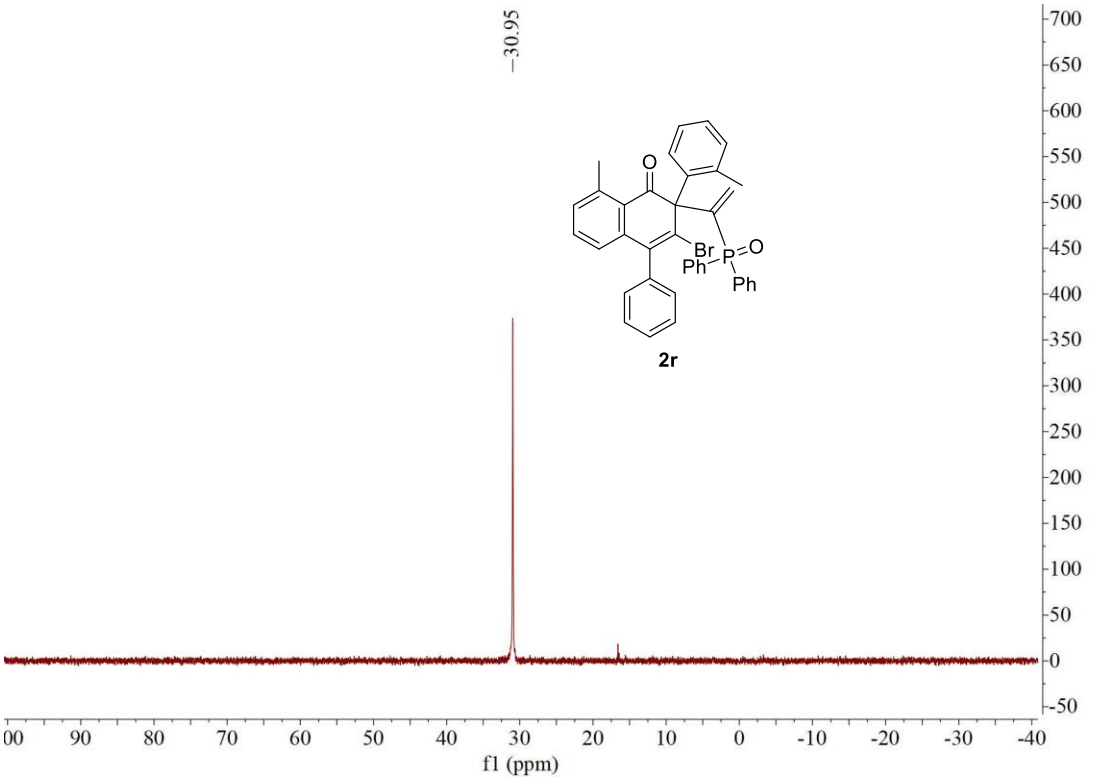

**Compound 2r ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



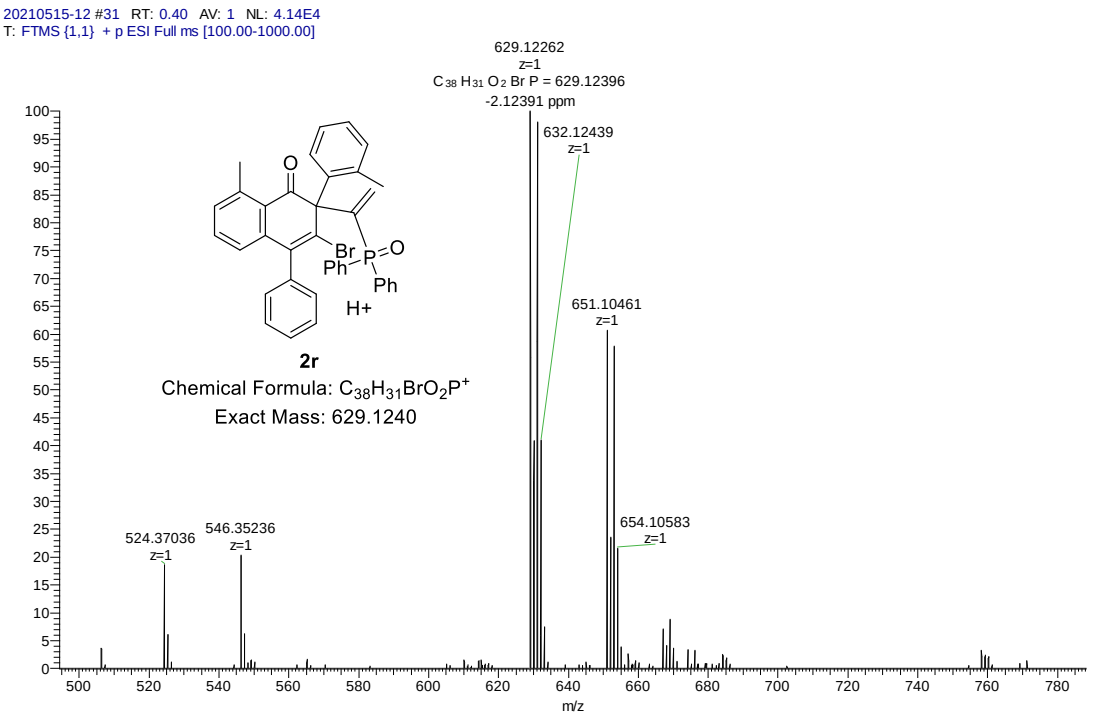

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2r**



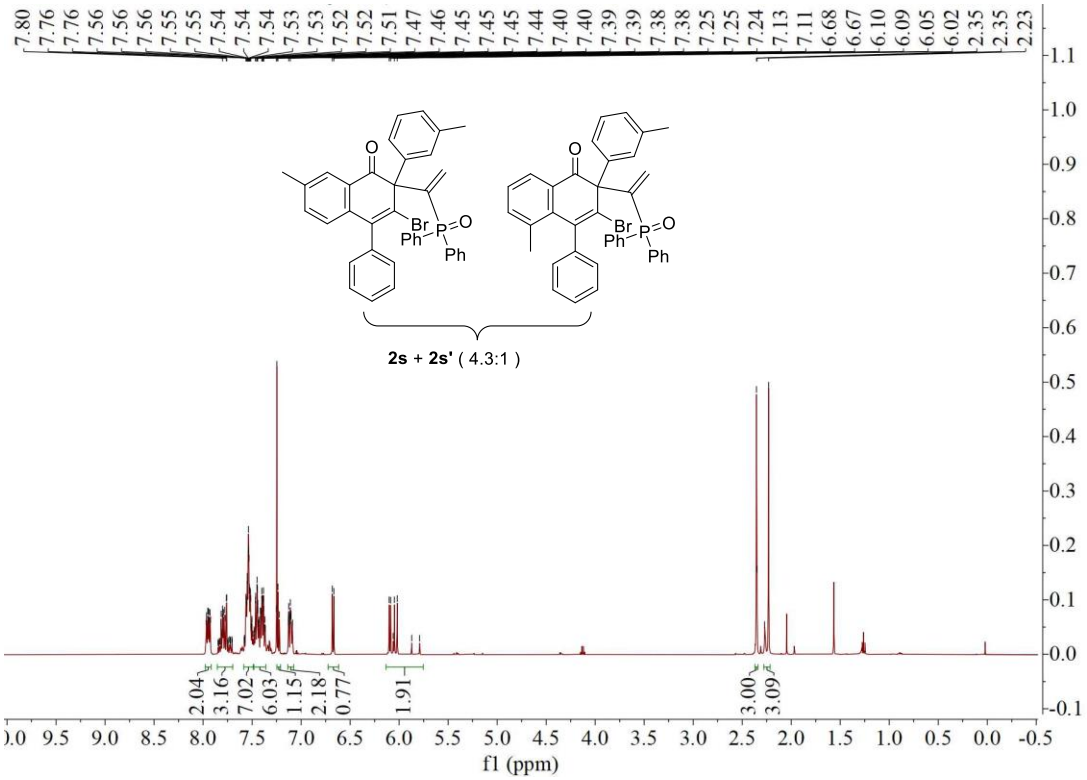

$^{13}C$ NMR (101 MHz, $CDCl_3$) of **2r**



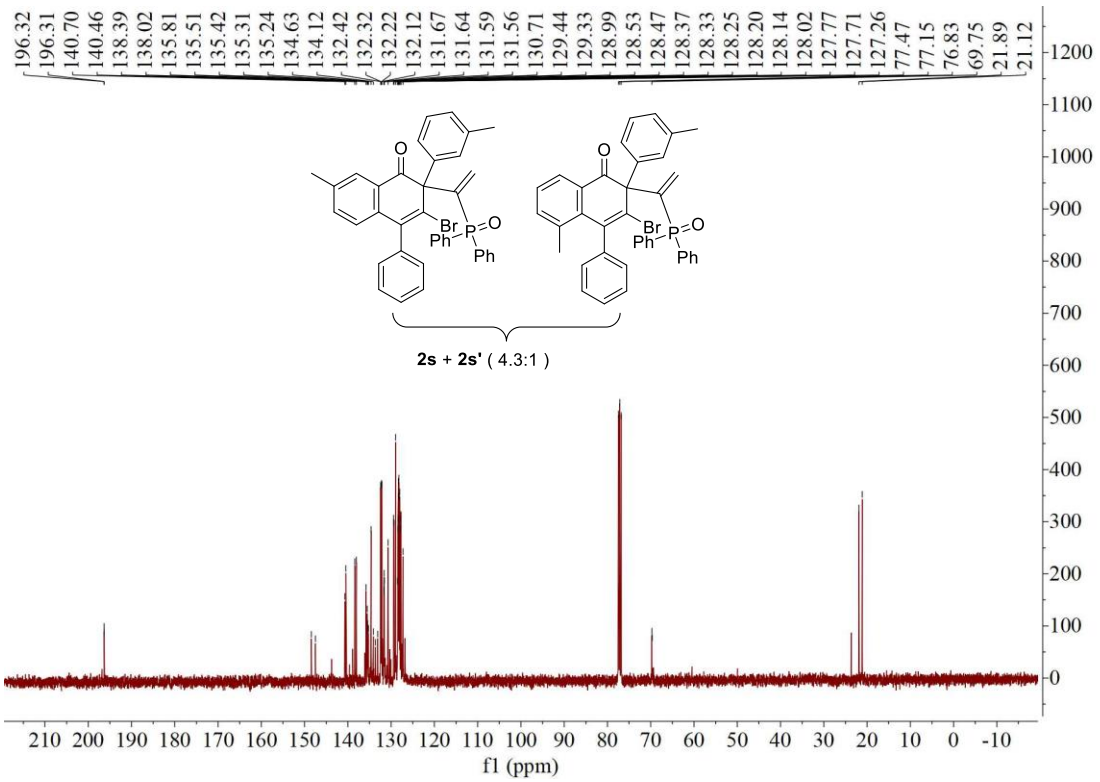

$^{31}P$ NMR (162 MHz, $CDCl_3$) of **2r**



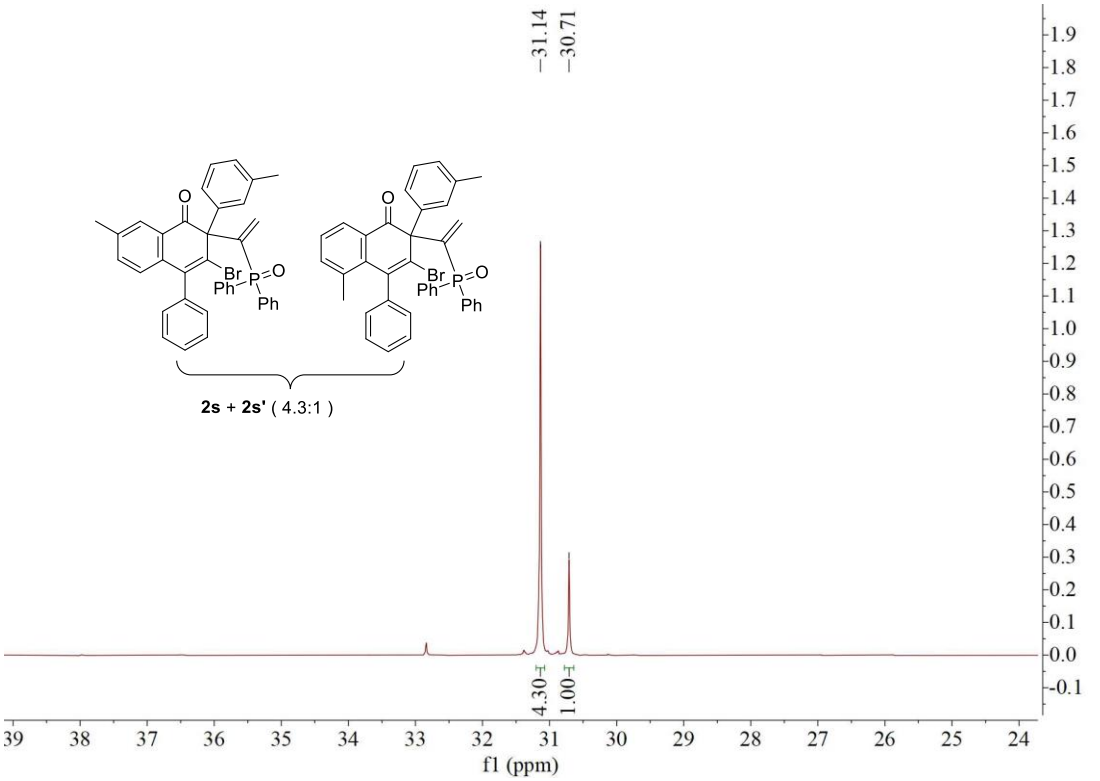

**Compound 2s and 2s' ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



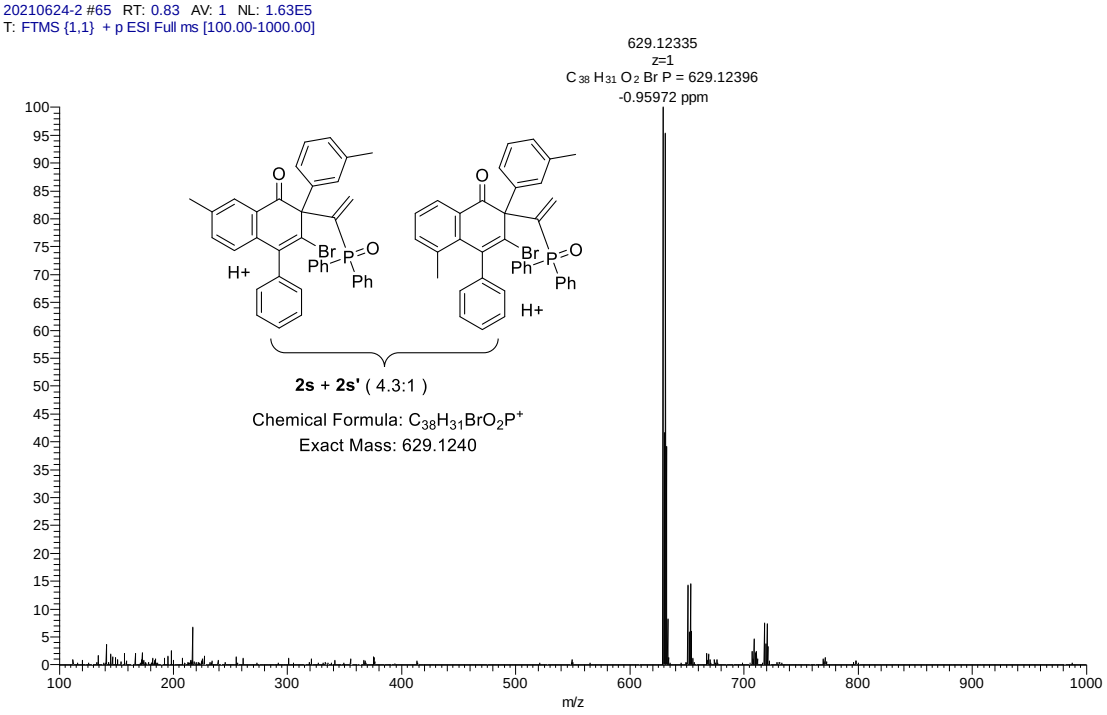

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2s** and **2s'**



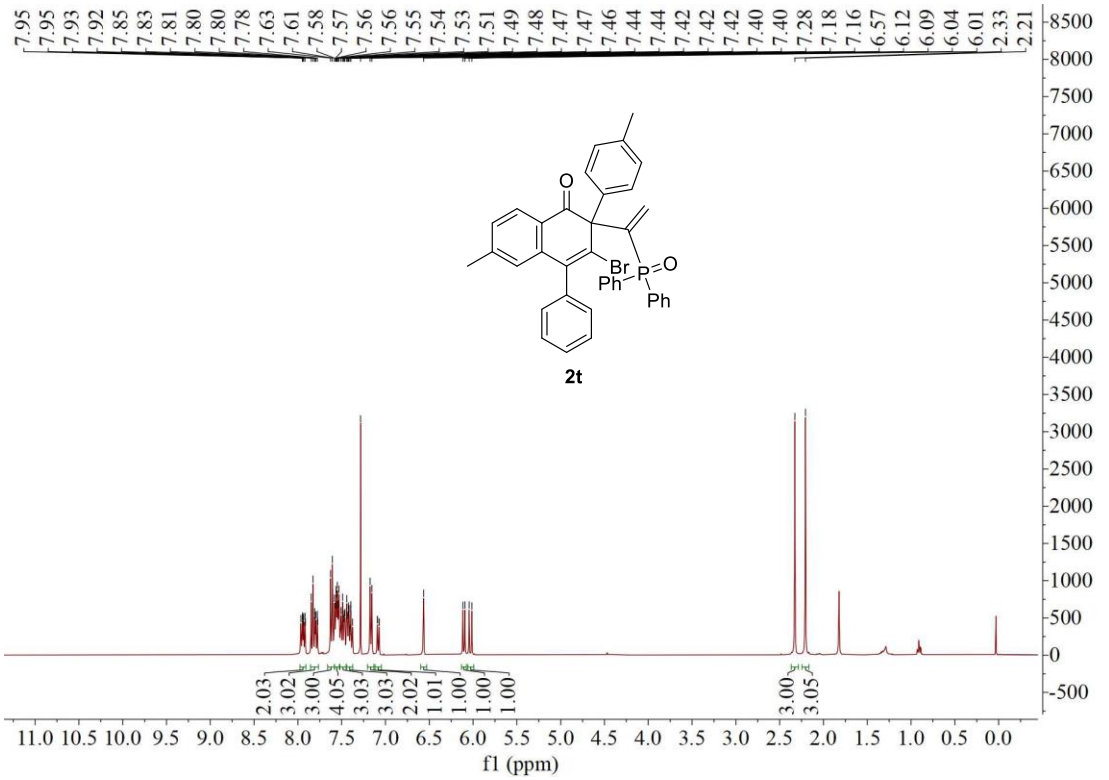

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2s** and **2s'**



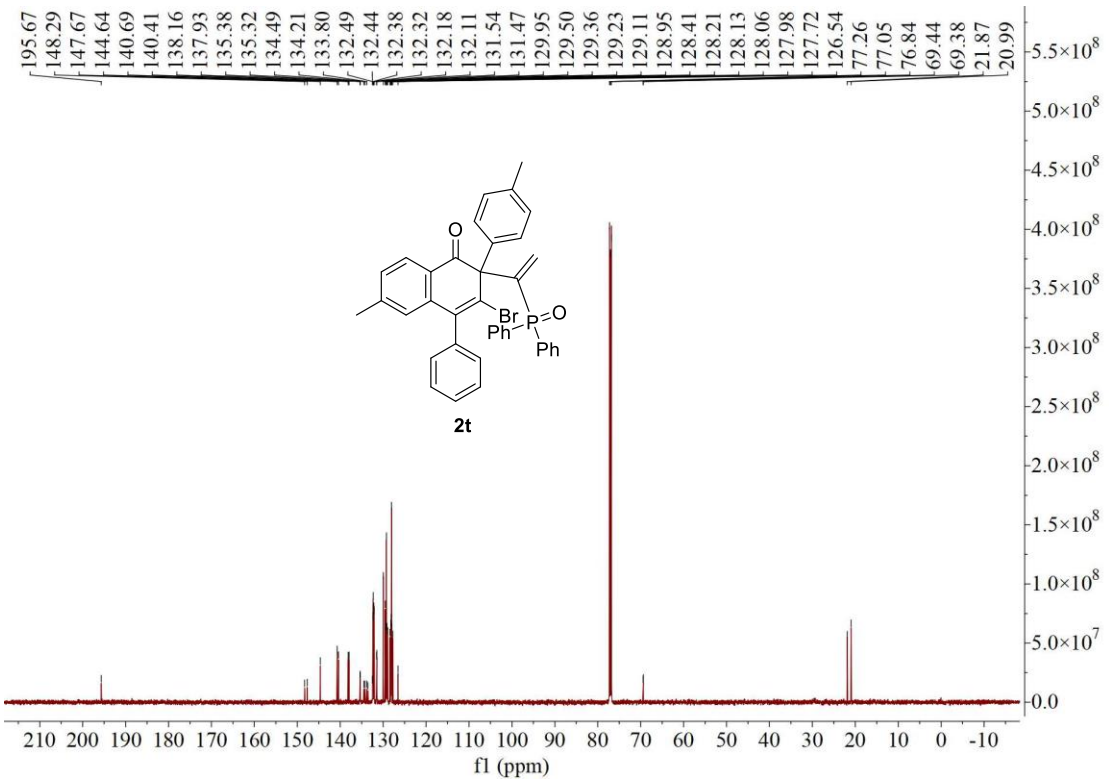

$^{31}$P NMR (202 MHz, $CDCl_3$) of **2s** and **2s'**



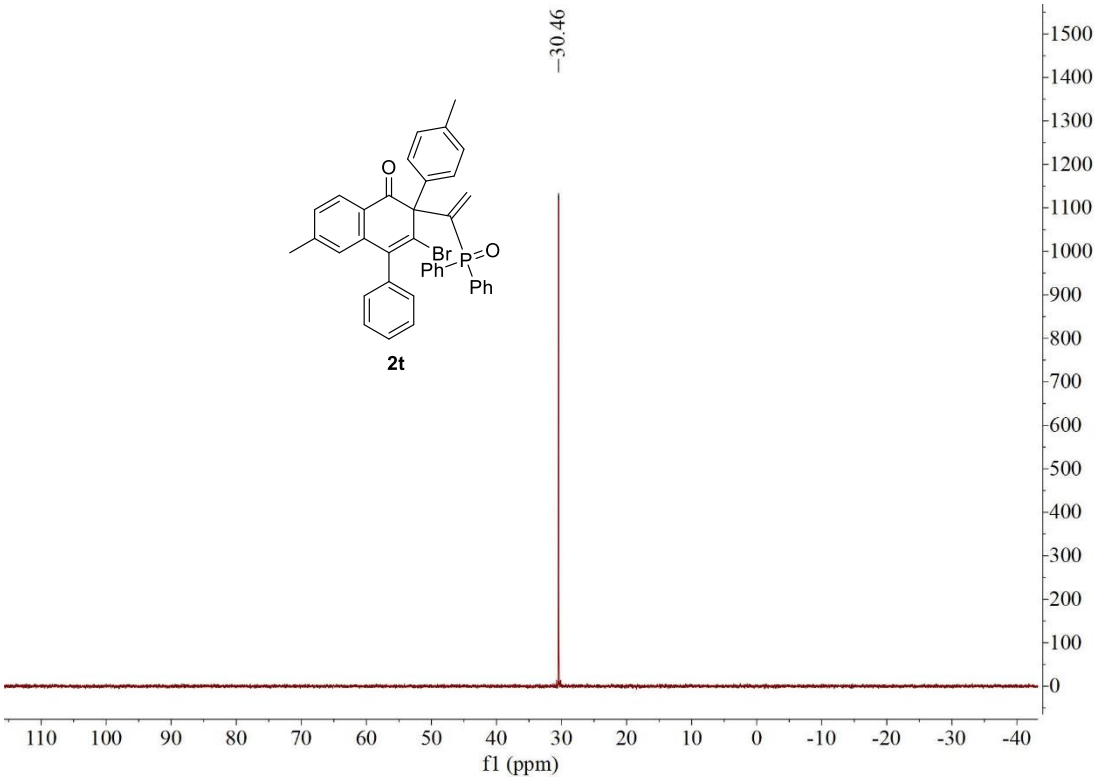

**Compound 2t ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



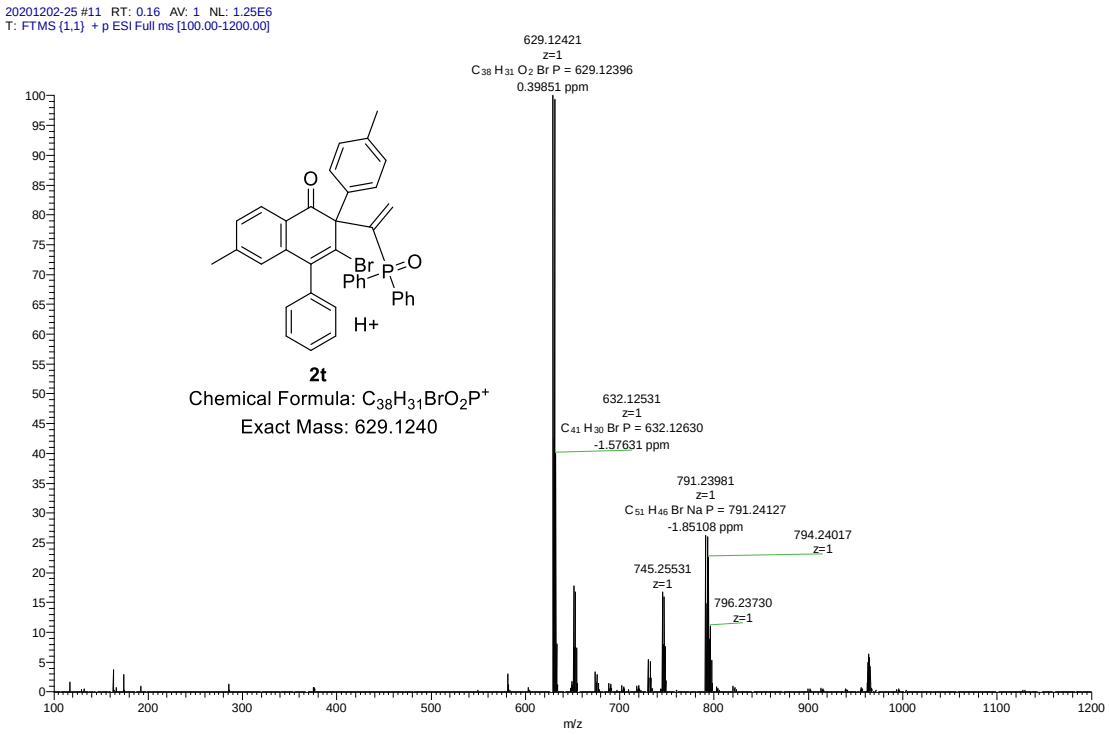

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2t**



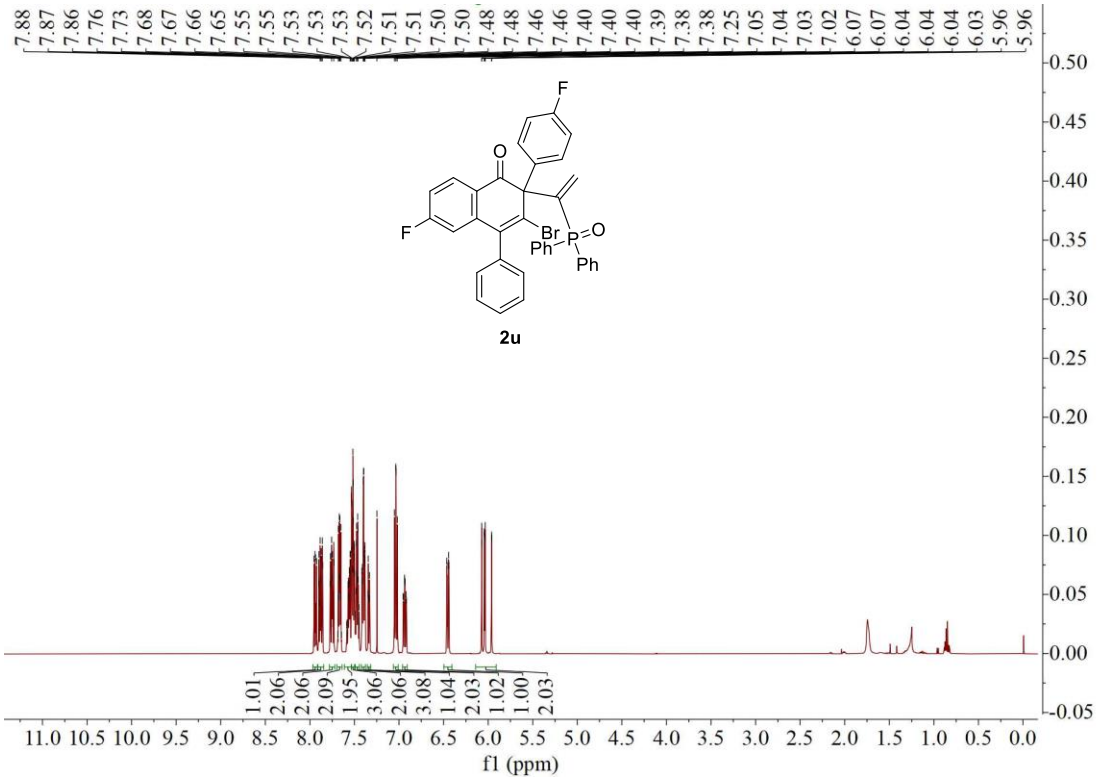

$^{13}$C NMR (151 MHz, $CDCl_3$) of **2t**



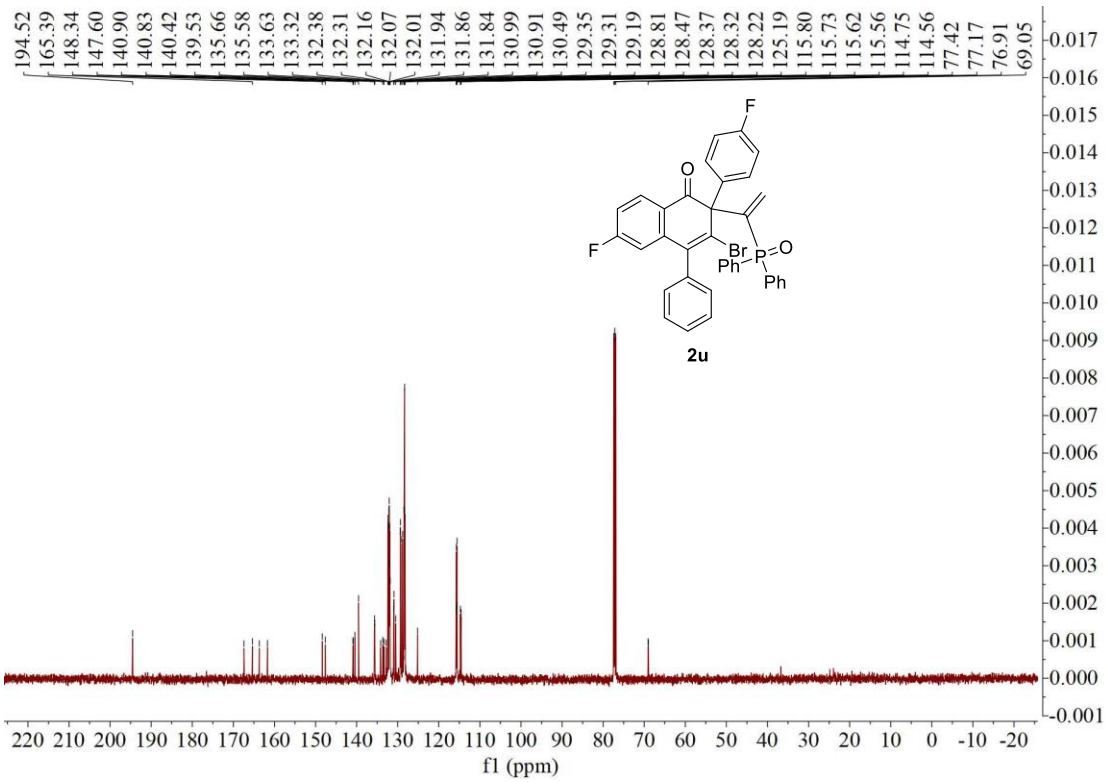

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2t**



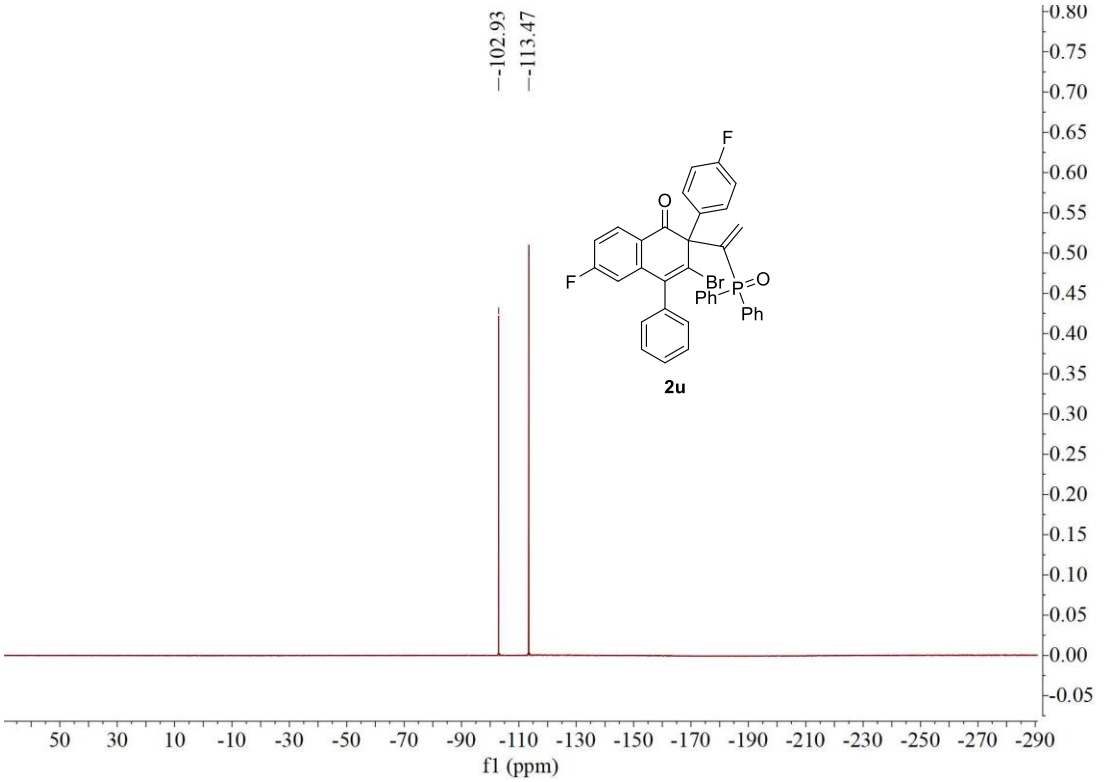

**Compound 2u ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$; $^{19}$F NMR, 471 MHz, $CDCl_3$)**



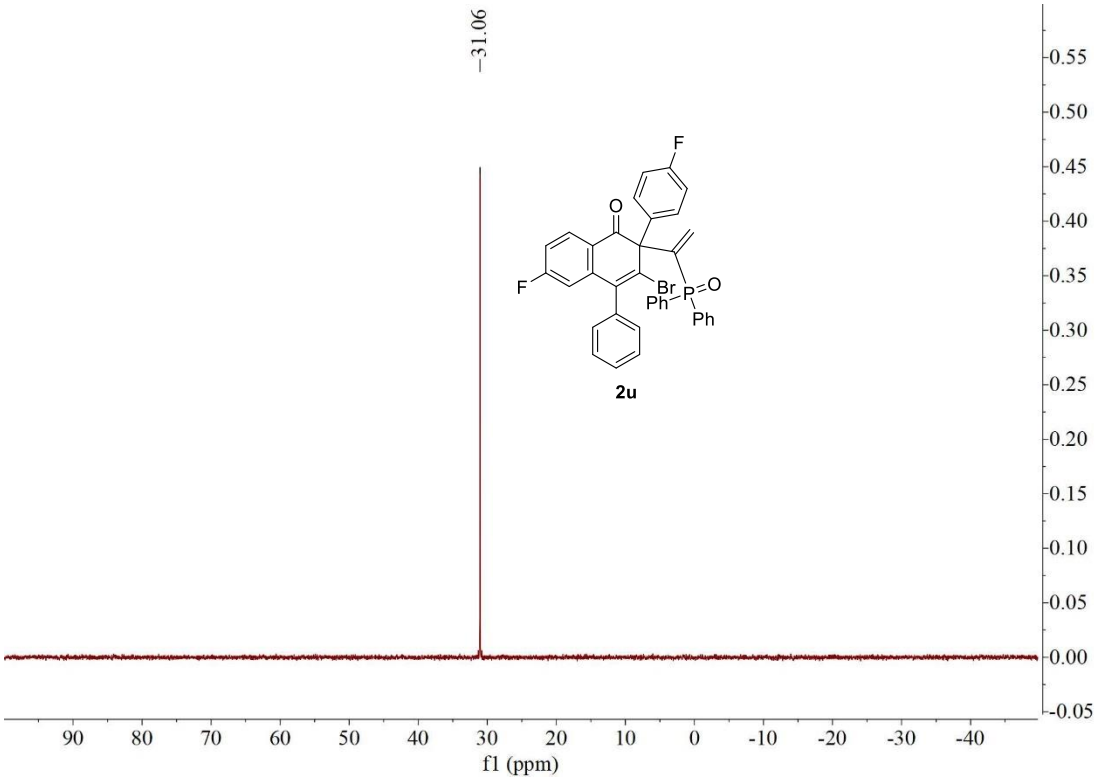

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2u**




$^{13}C$ NMR (126 MHz, $CDCl_3$) of **2u**

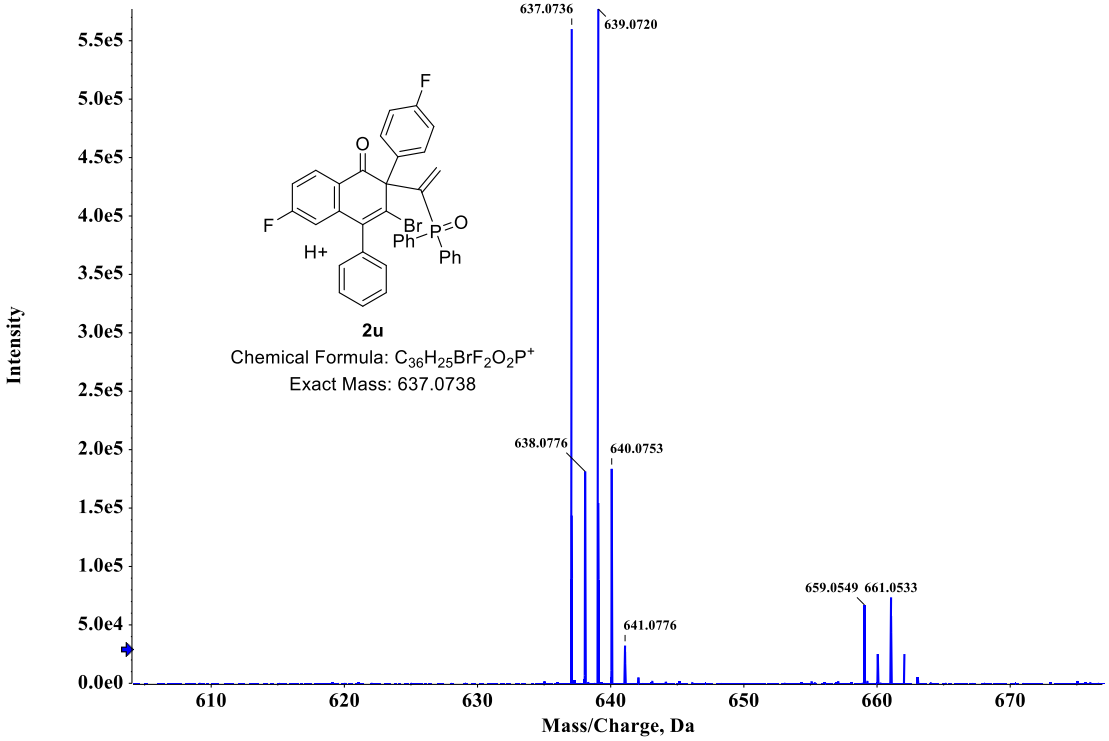



$^{19}F$ NMR (471 MHz, $CDCl_3$) of **2u**

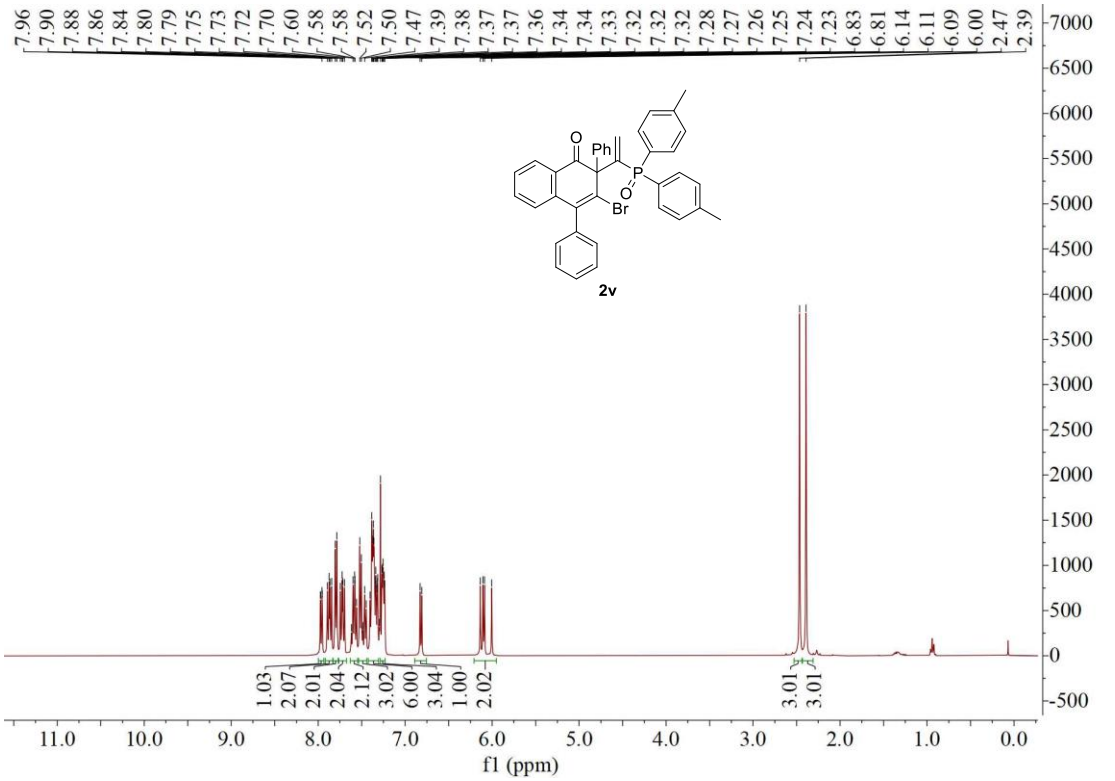



$^{31}P$ NMR (202 MHz, $CDCl_3$) of **2u**

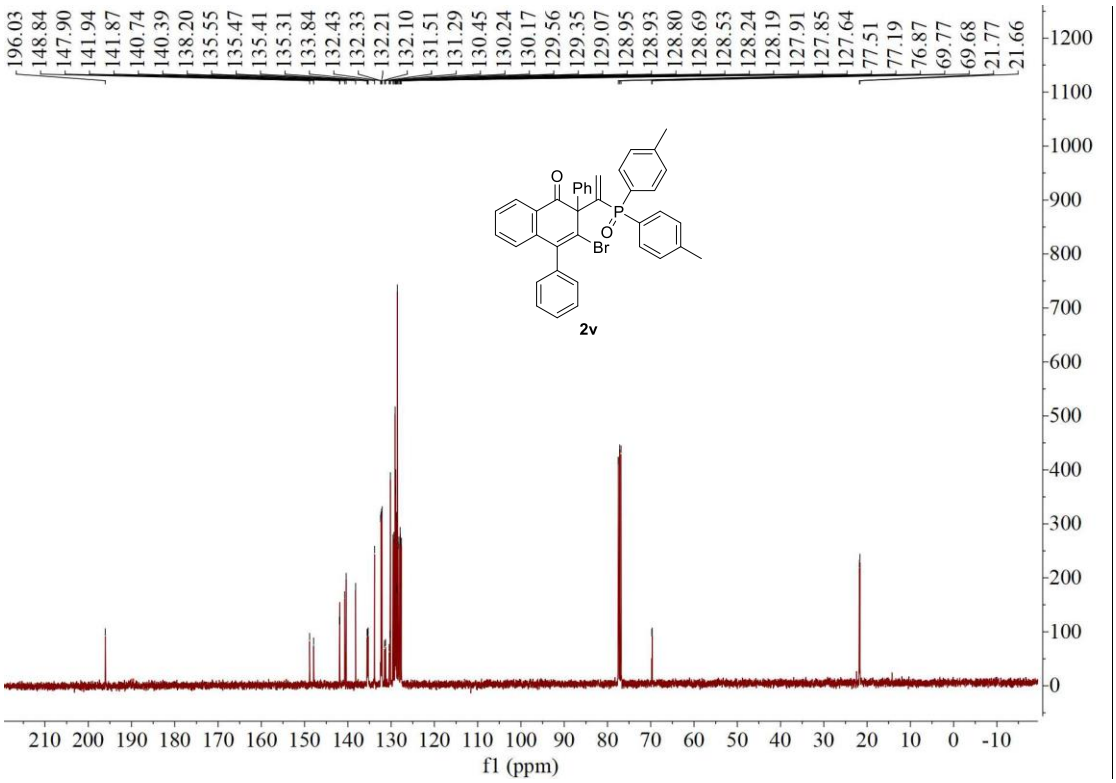
**Spectrum from 16.wiff (sample 1) - Sample016, +TOF MS (100 - 1000) from 0.158 min**



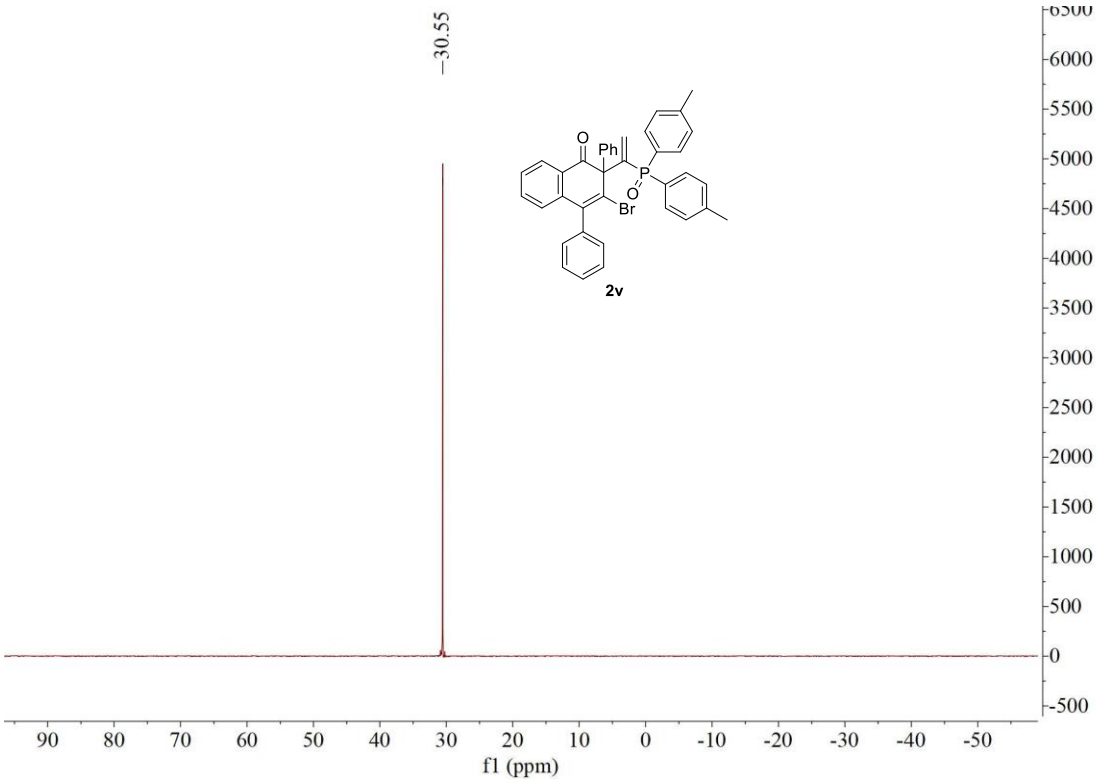
**Compound 2v ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



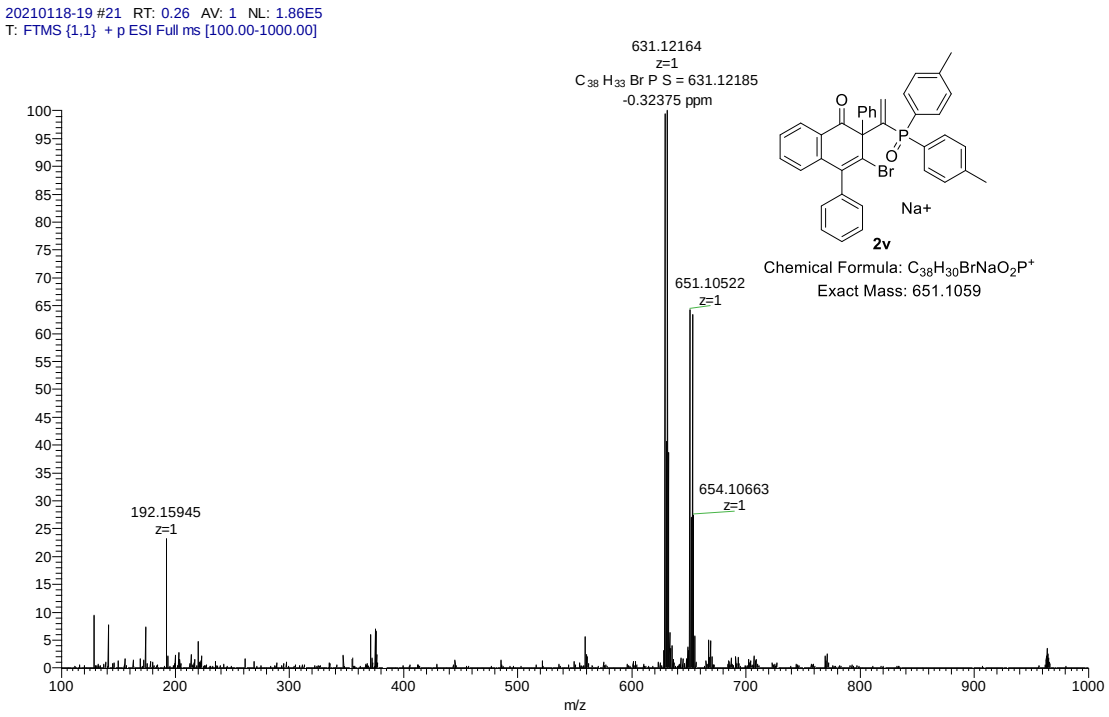

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2v**



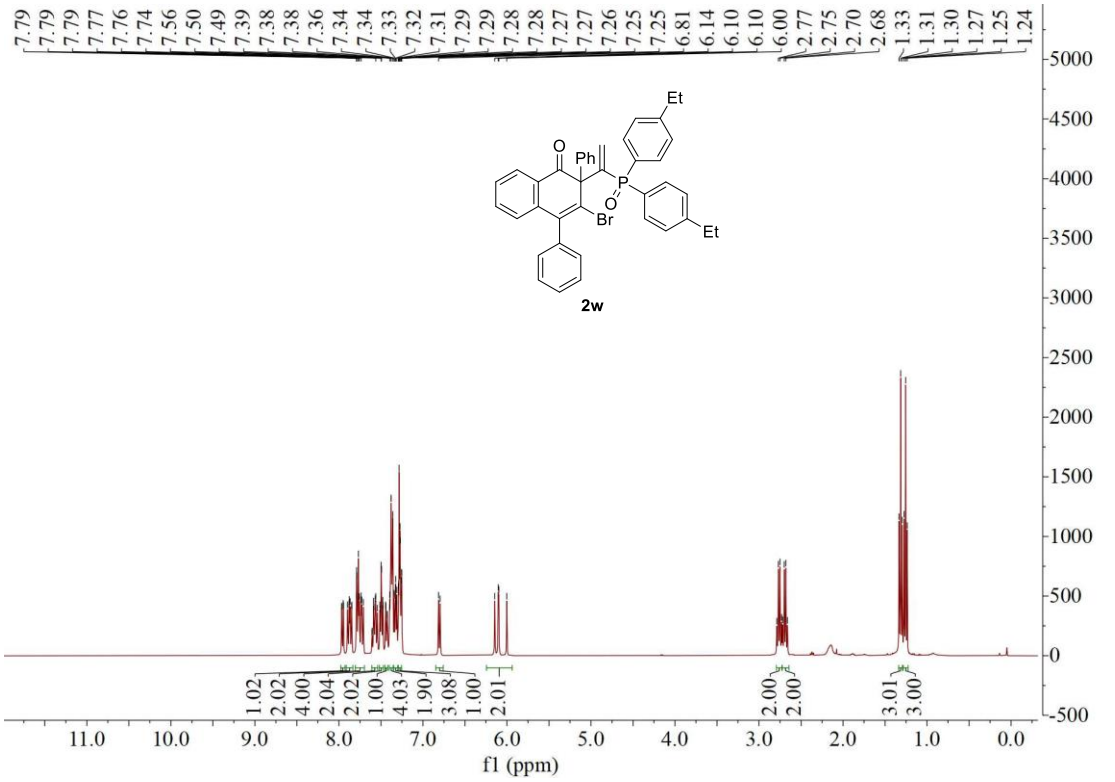

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2v**



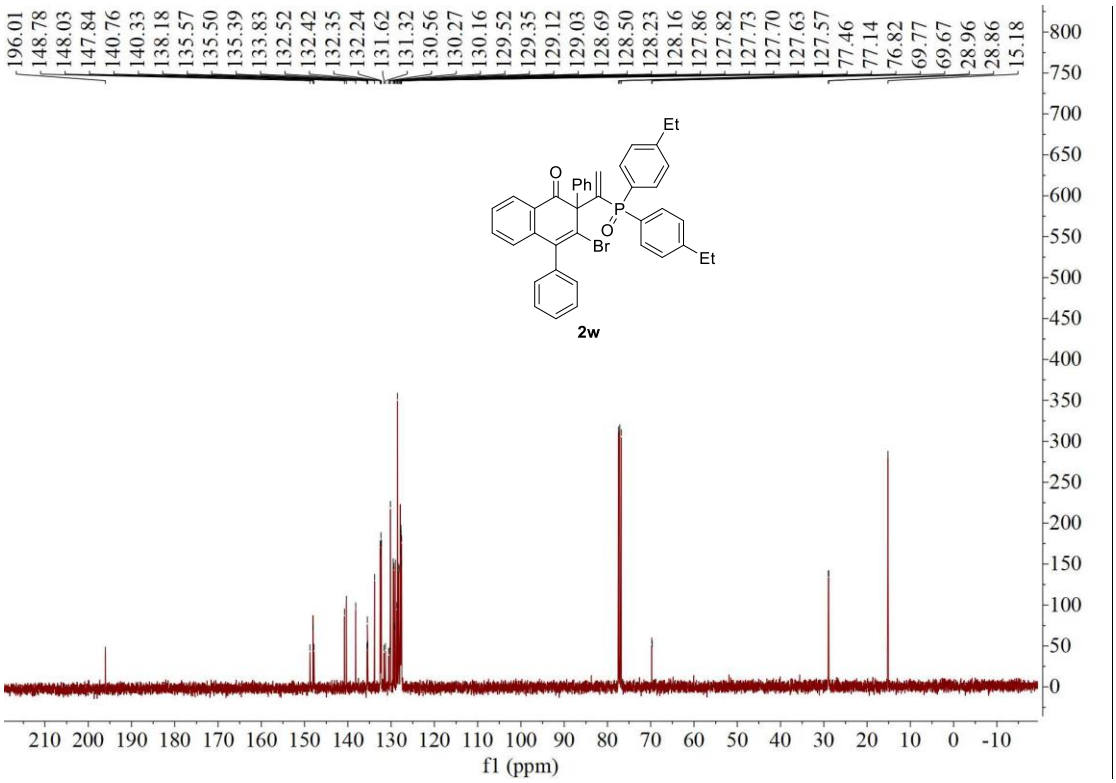

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2v**



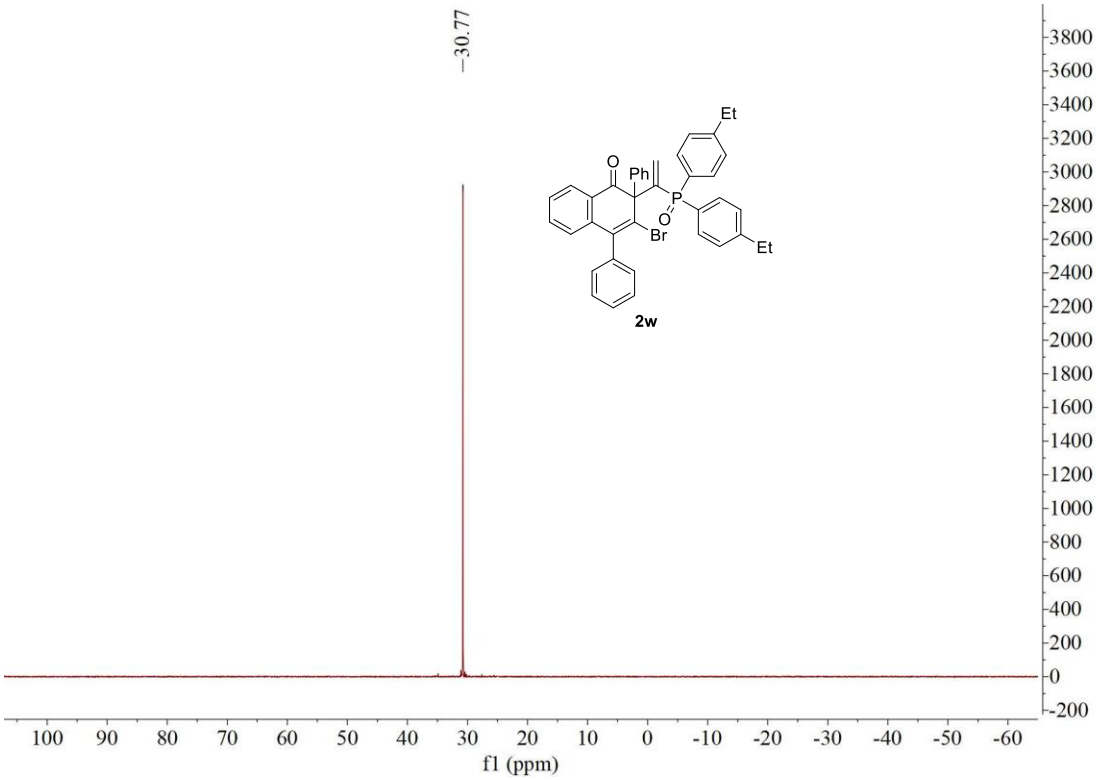
**Compound 2w ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



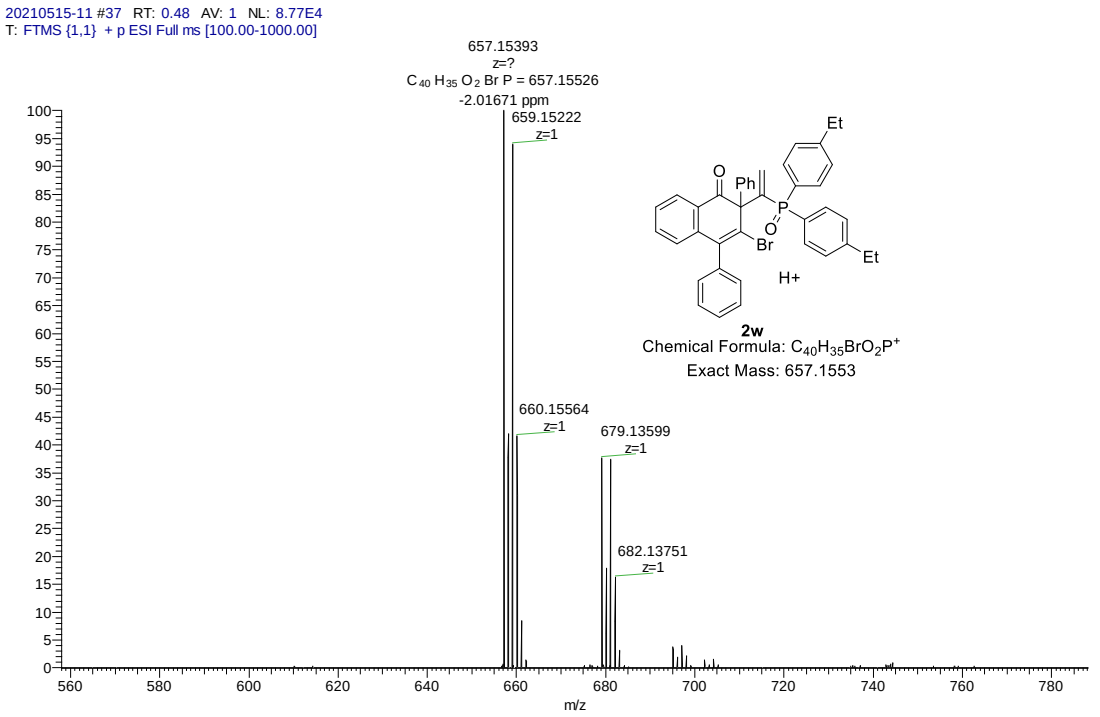

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2w**



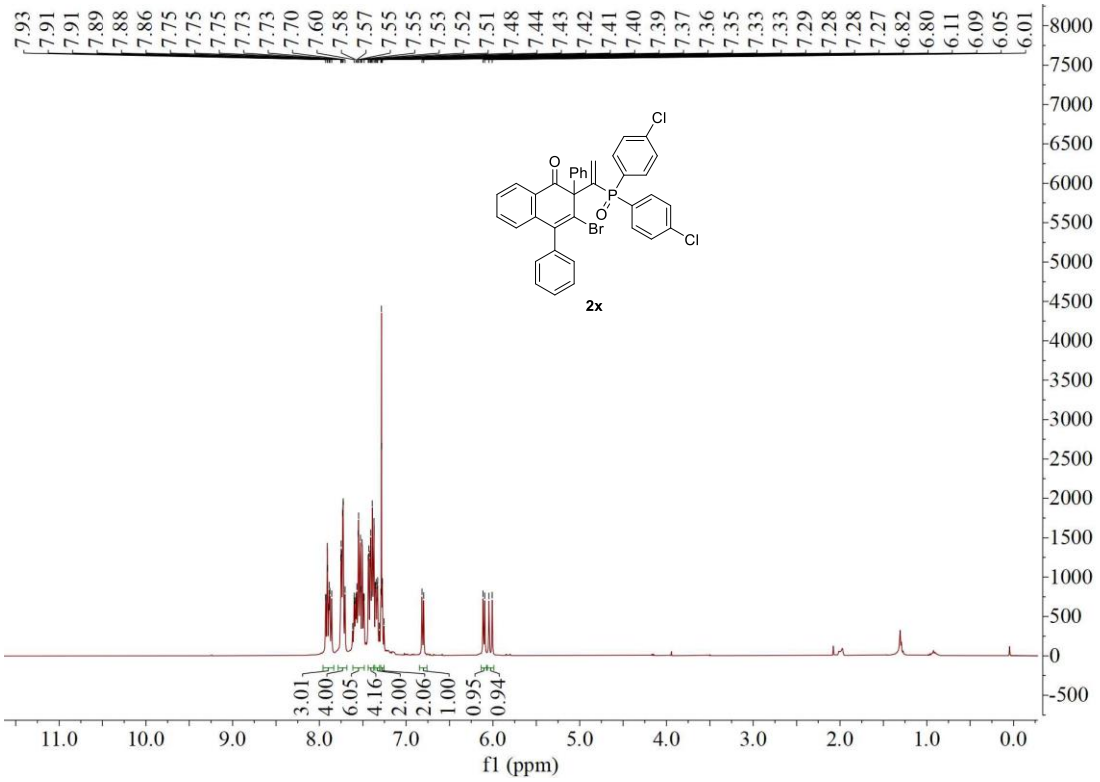

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2w**



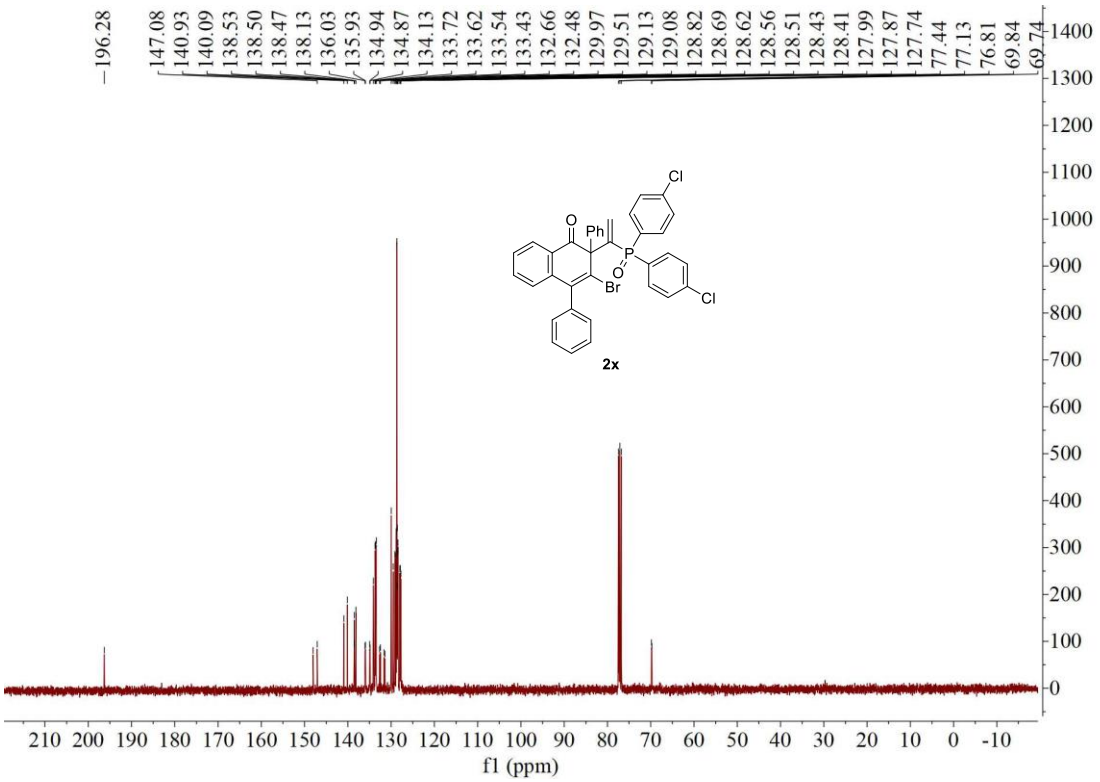

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2w**



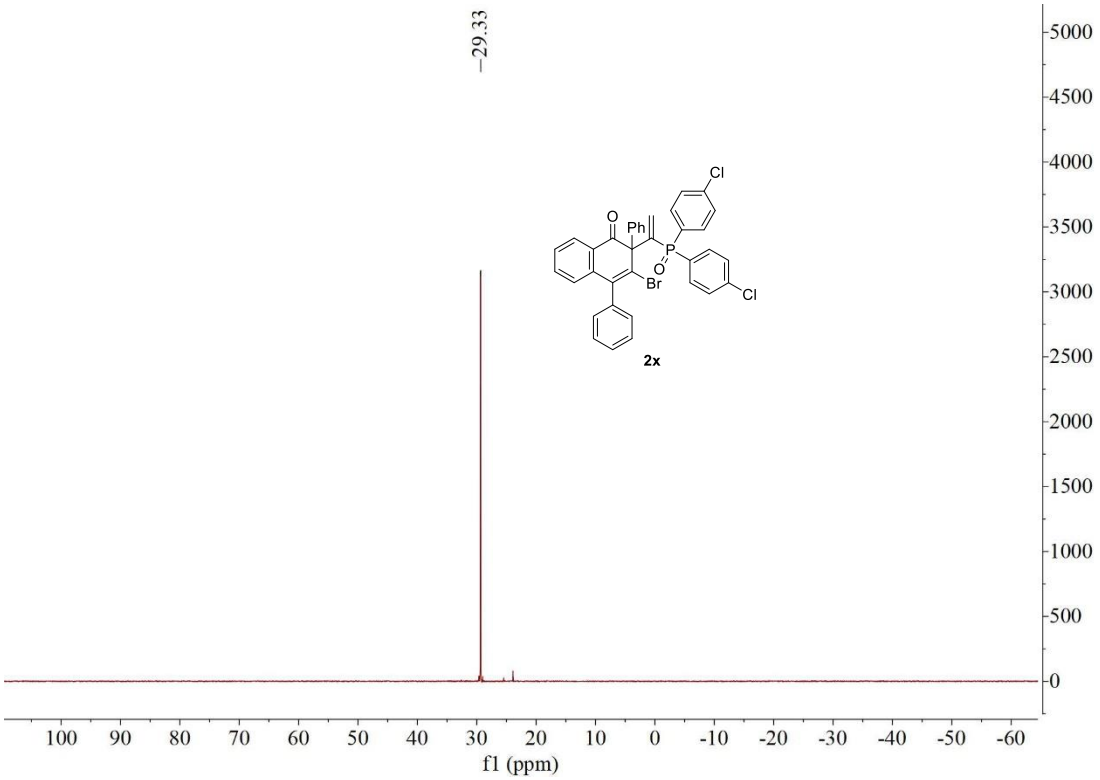
**Compound 2x ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



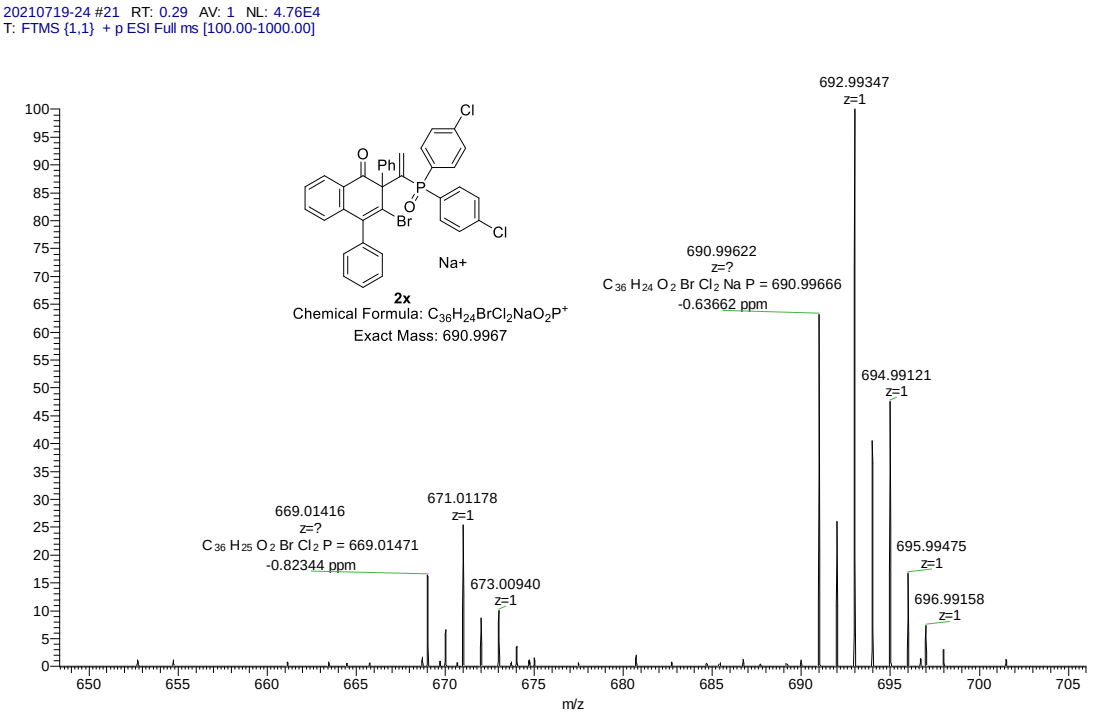

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2x**



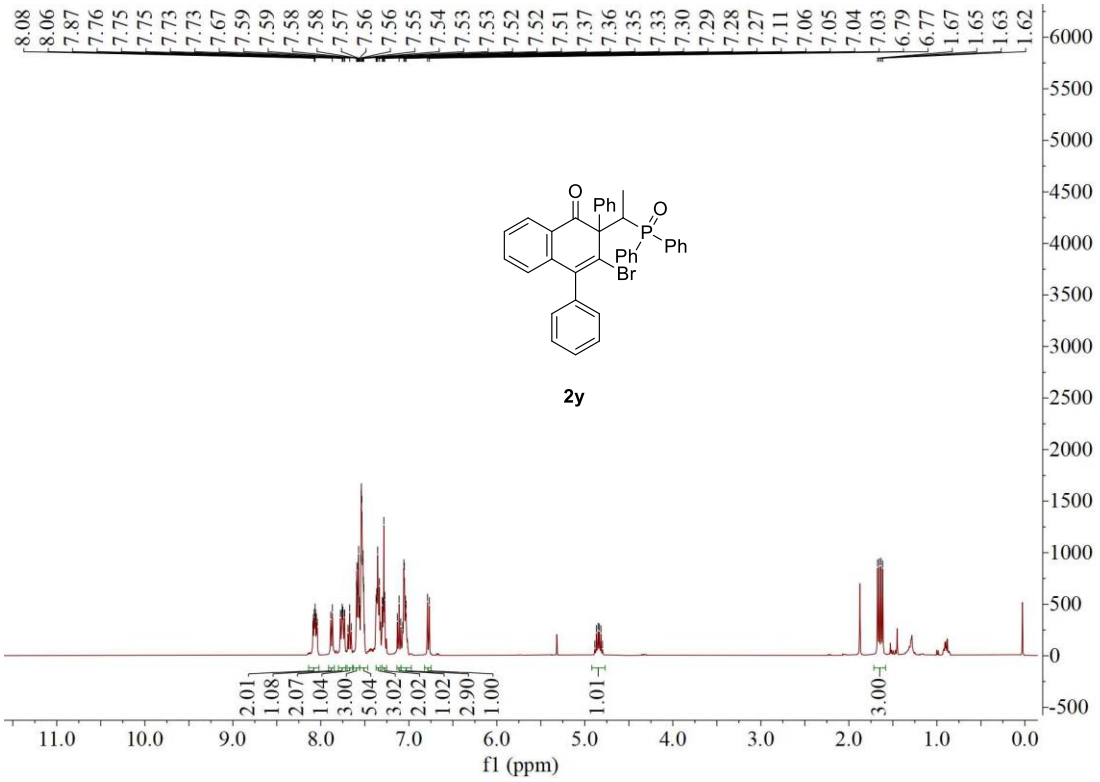

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2x**



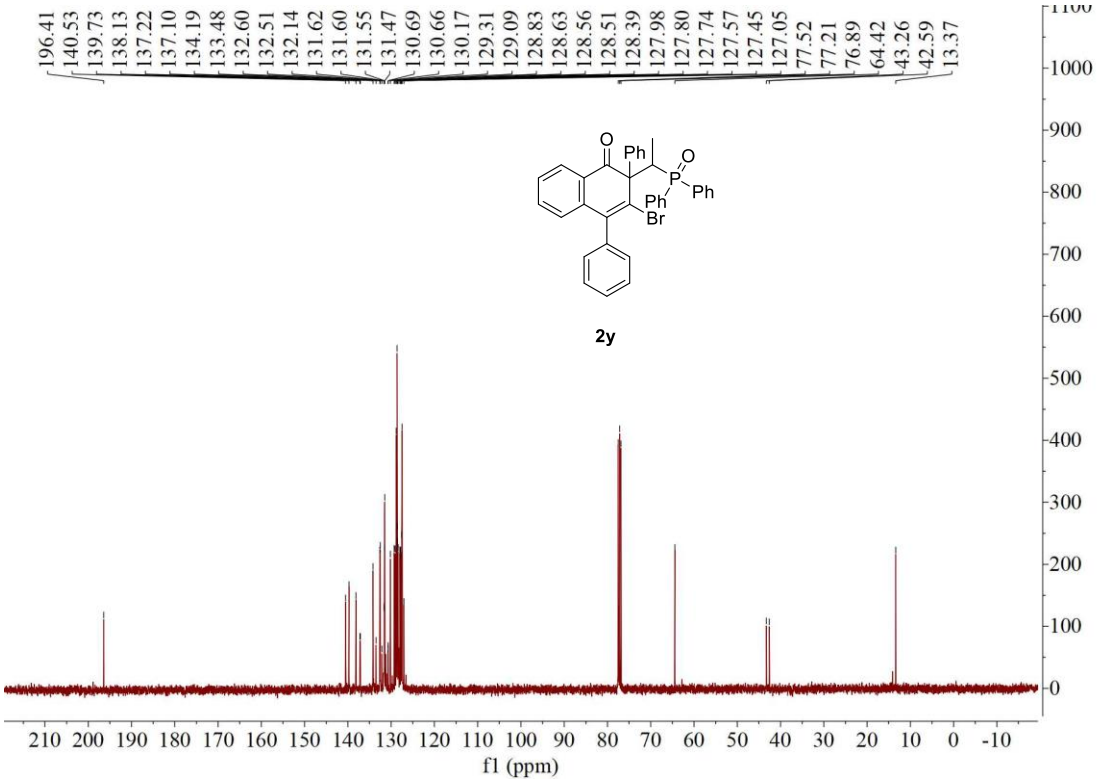

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2x**



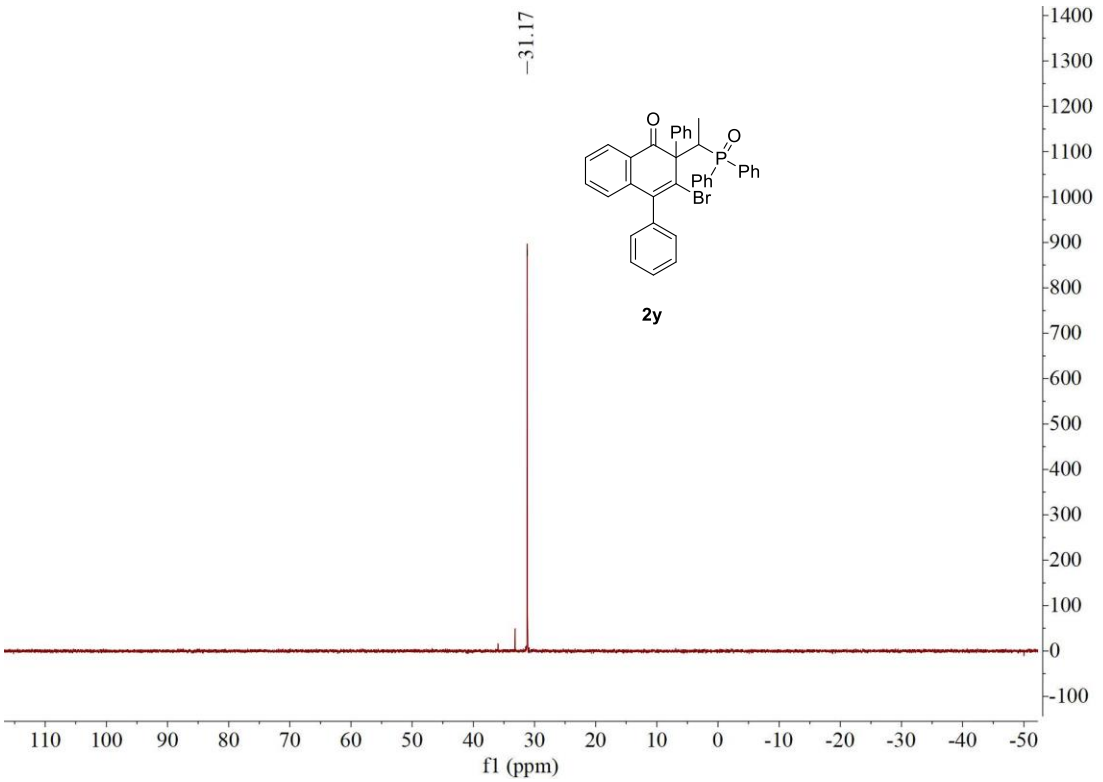
**Compound 2y ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



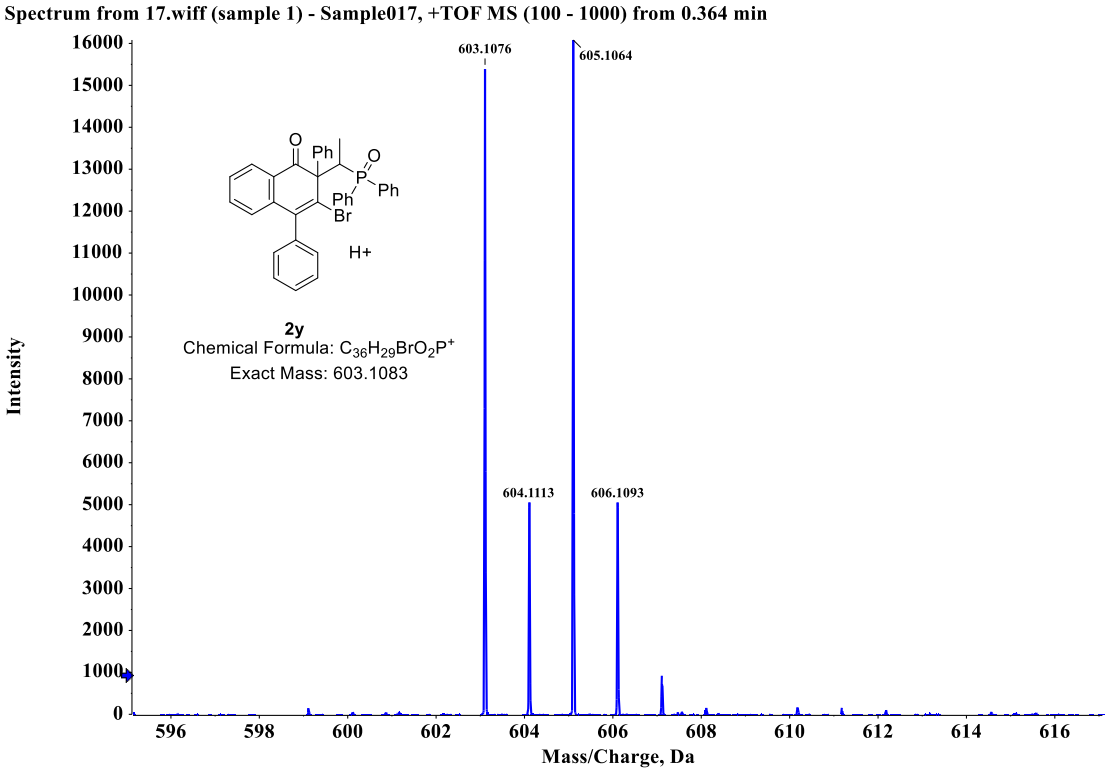

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2y**



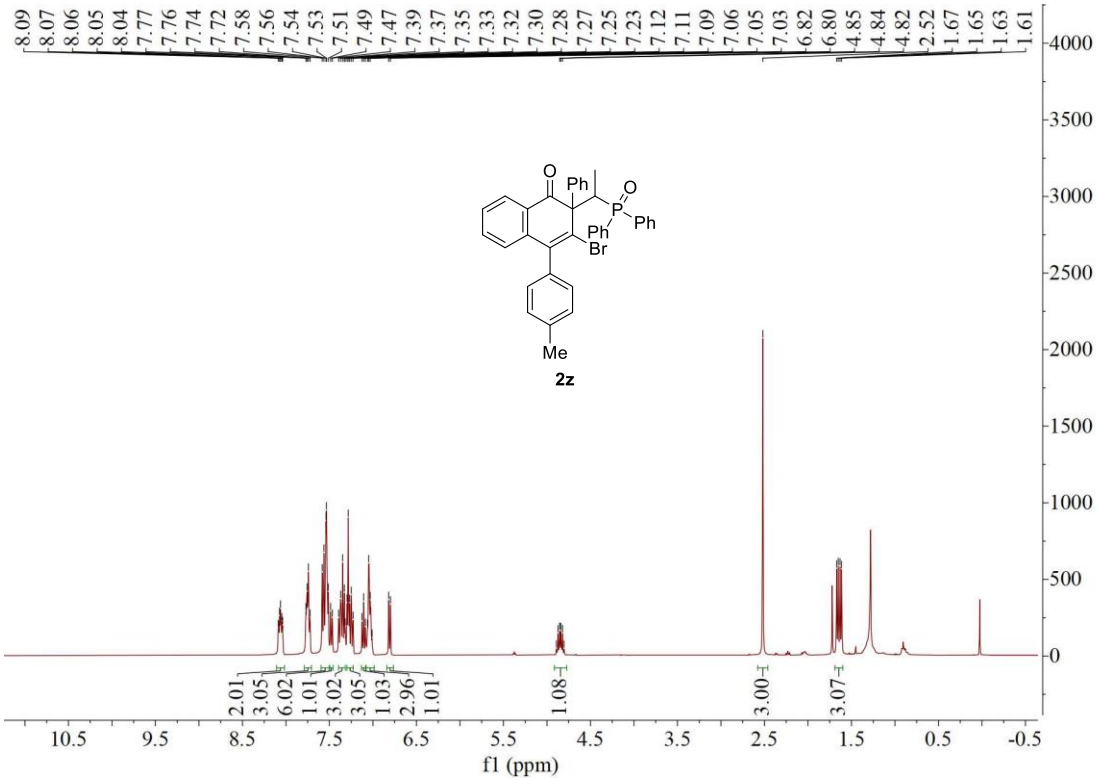

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2y**



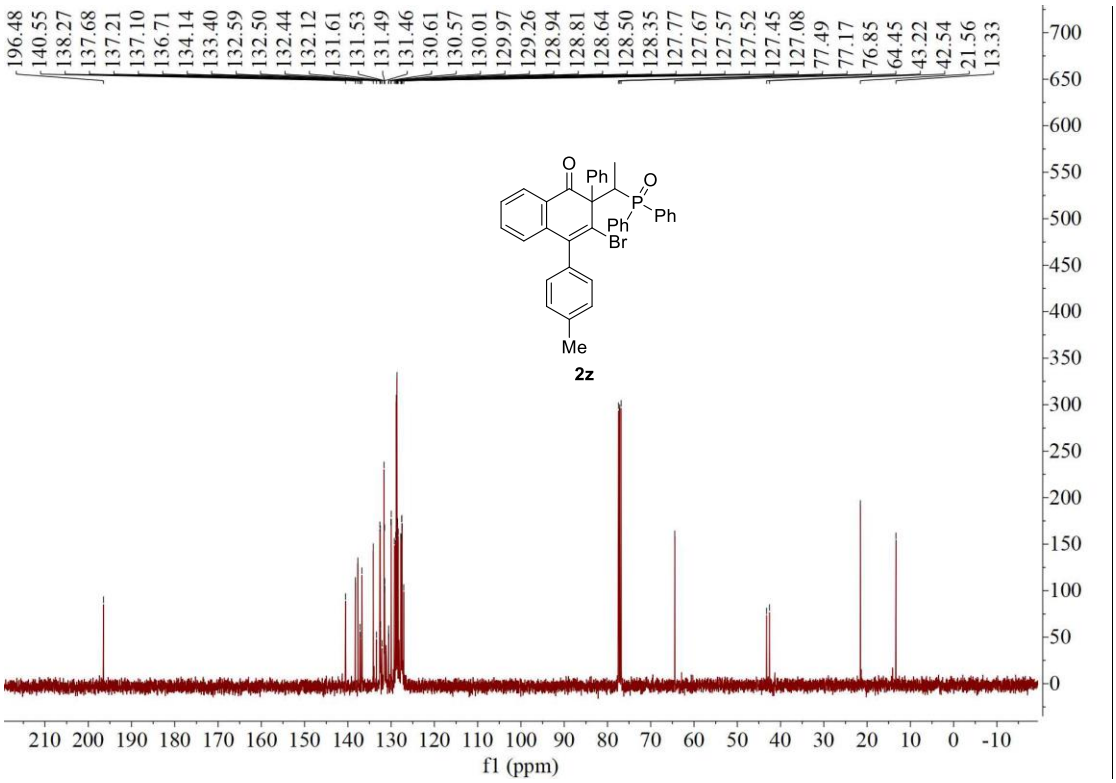

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2y**



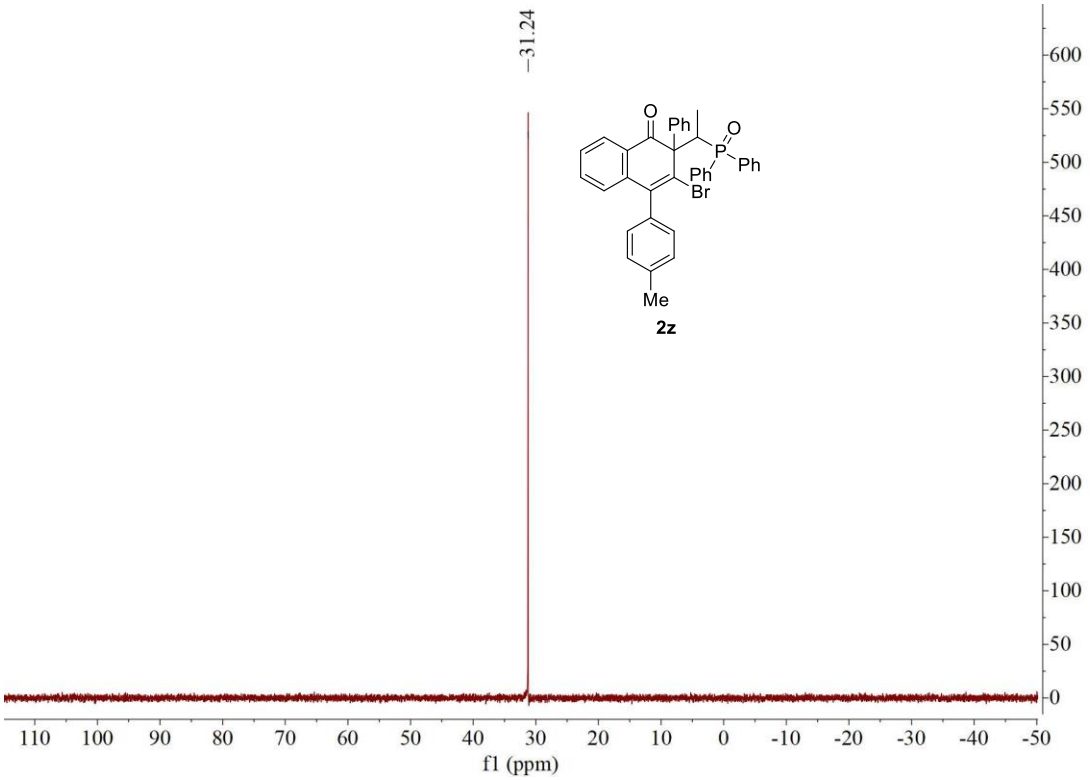
**Compound 2z ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



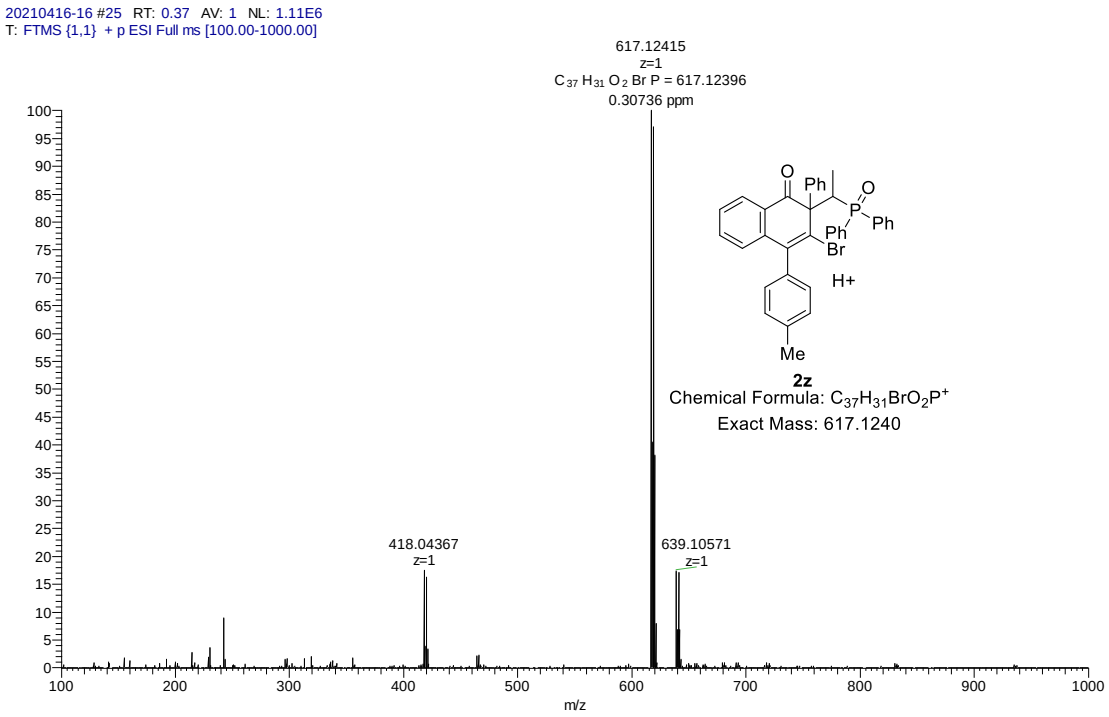

$^{1}$H NMR (400 MHz, $CDCl_3$) of **2z**



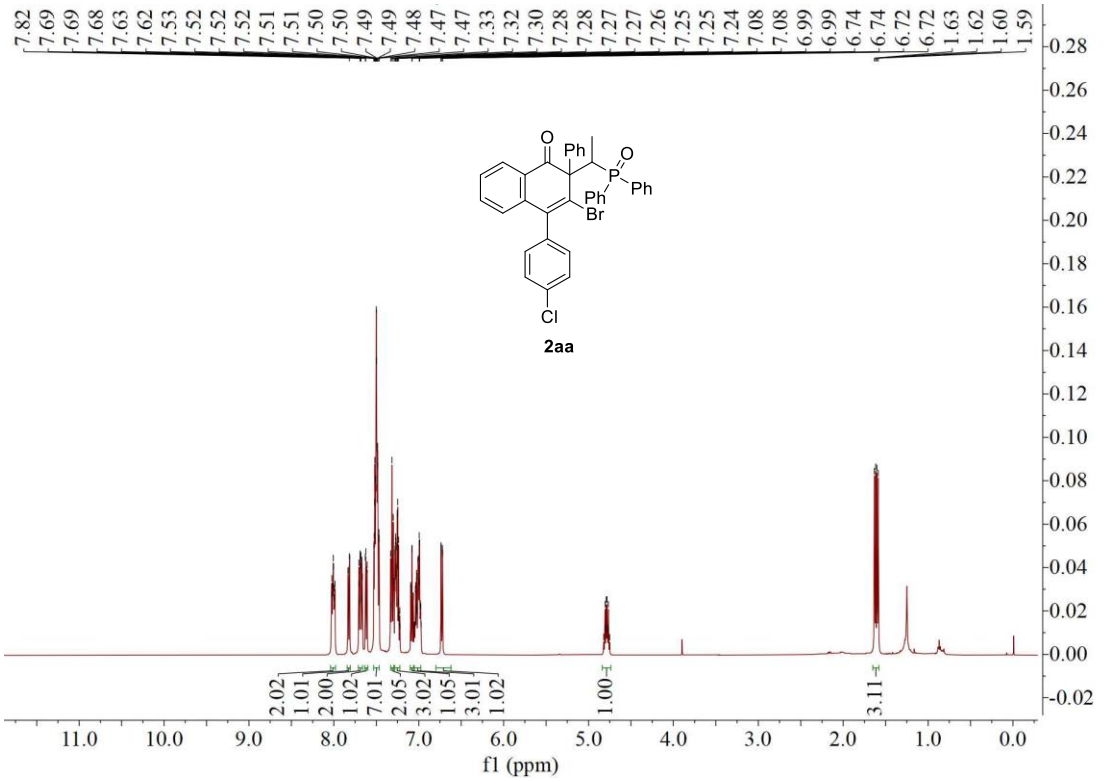

$^{13}$C NMR (101 MHz, $CDCl_3$) of **2z**



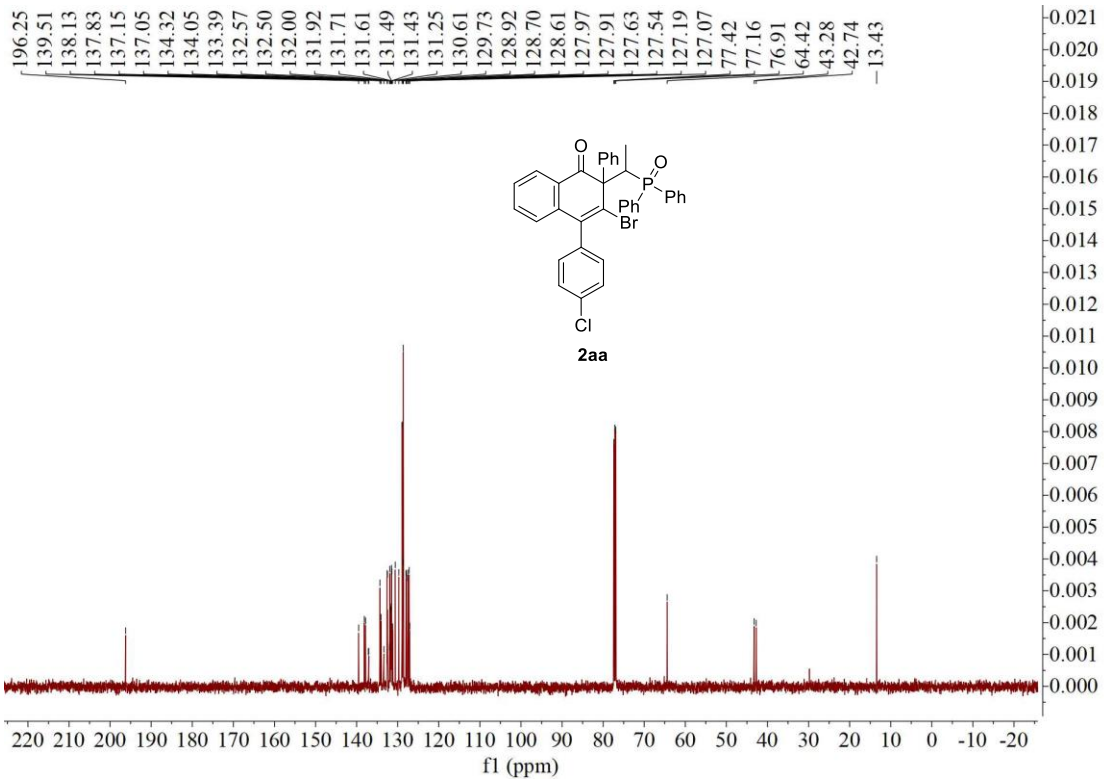

$^{31}$P NMR (162 MHz, $CDCl_3$) of **2z**



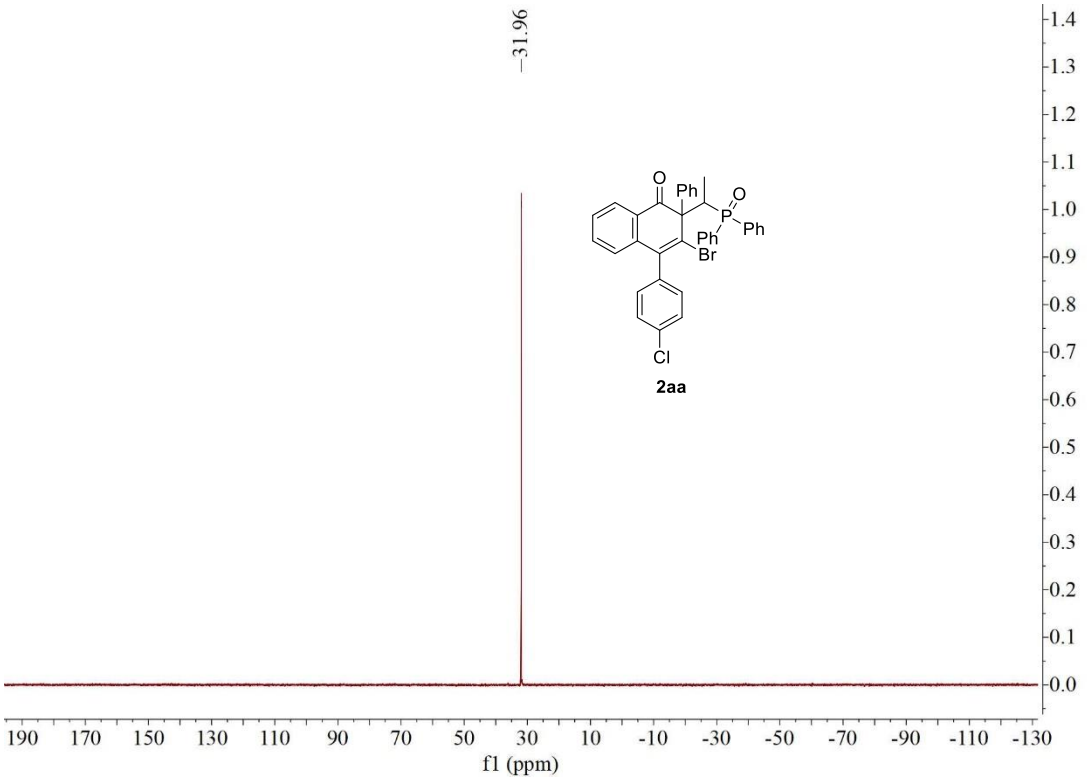
**Compound 2aa ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



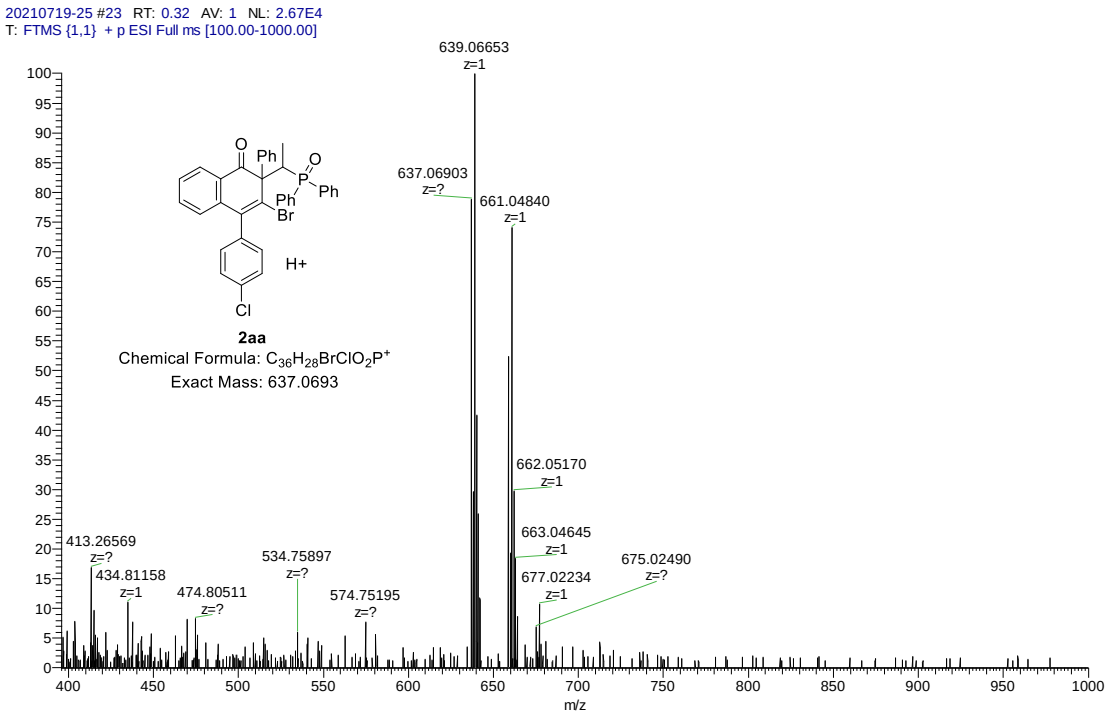

$^{1}$H NMR (500 MHz, $CDCl_3$) of **2aa**



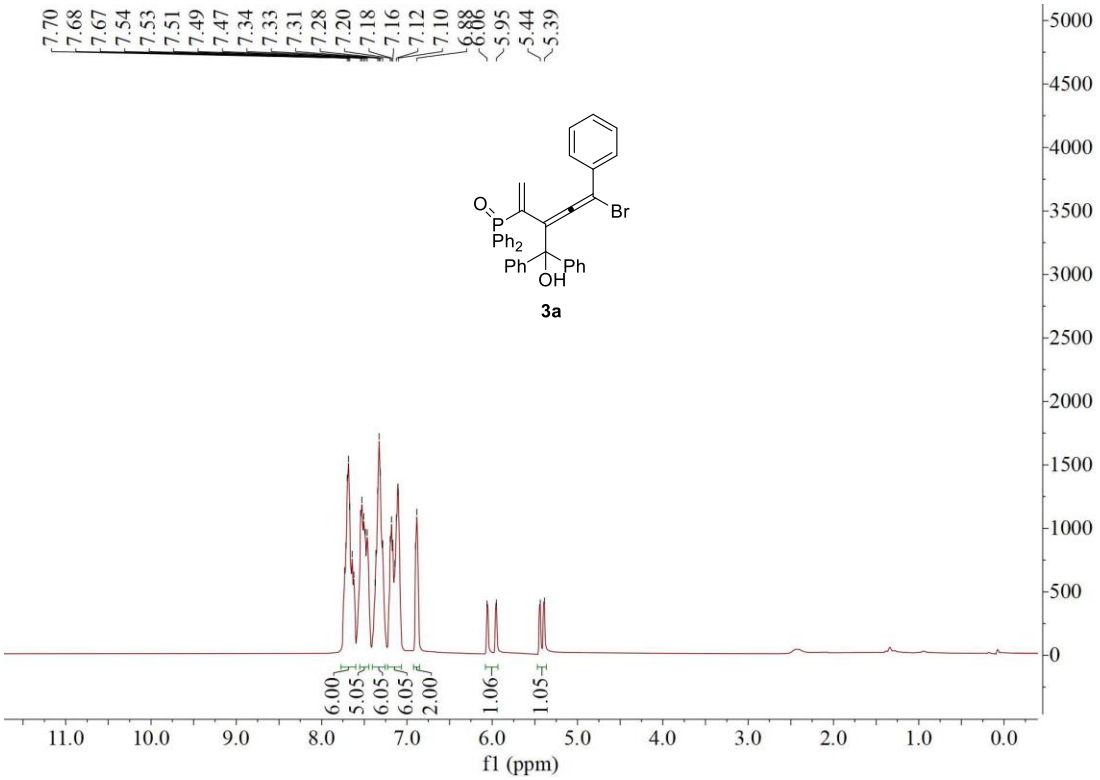

$^{13}$C NMR (126 MHz, $CDCl_3$) of **2aa**



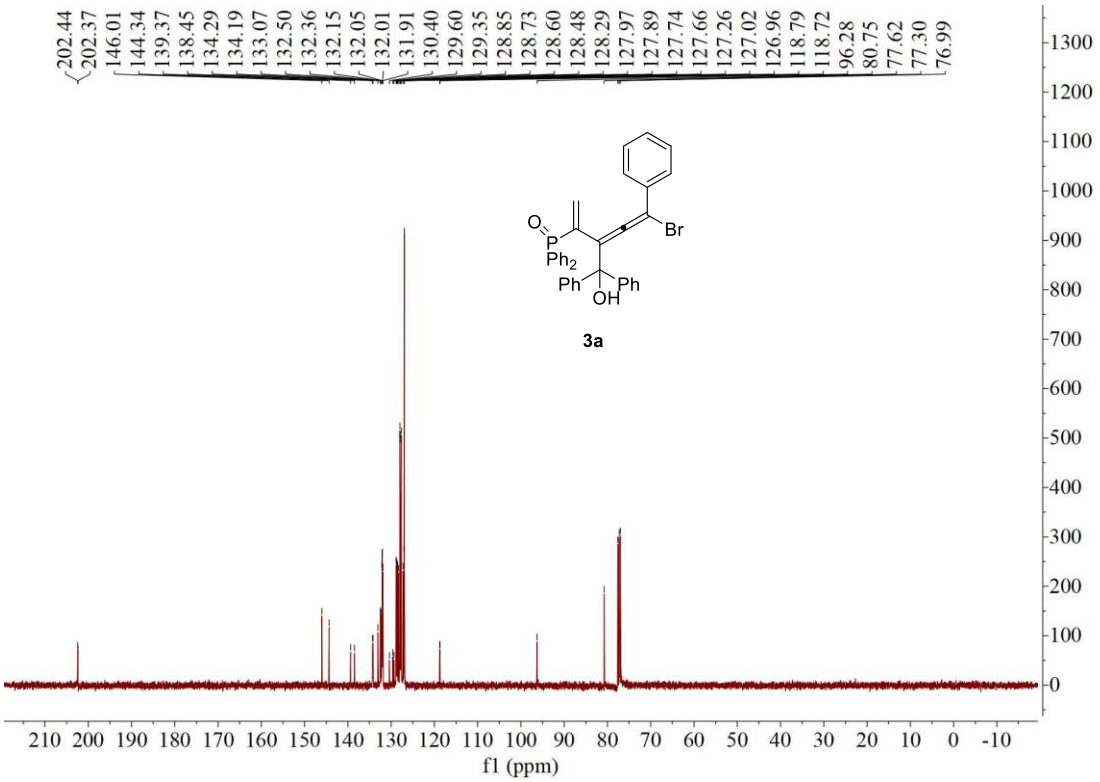

$^{31}$P NMR (202 MHz, $CDCl_3$) of **2aa**



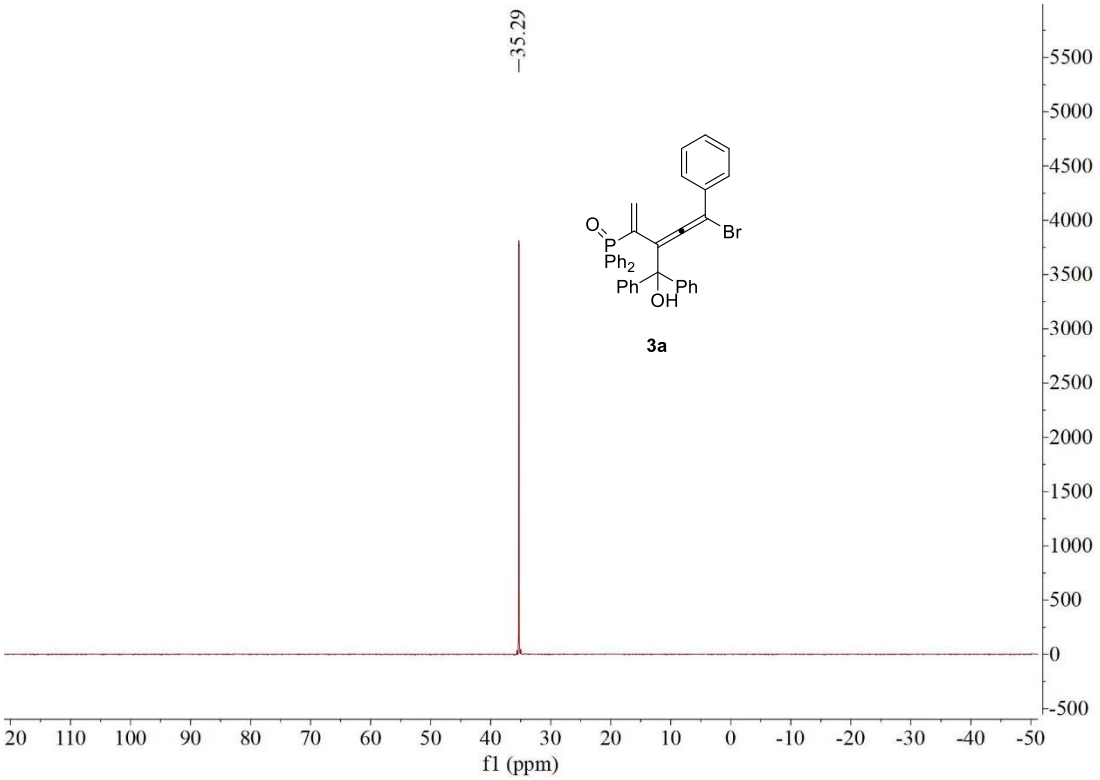
**Compound 3a ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



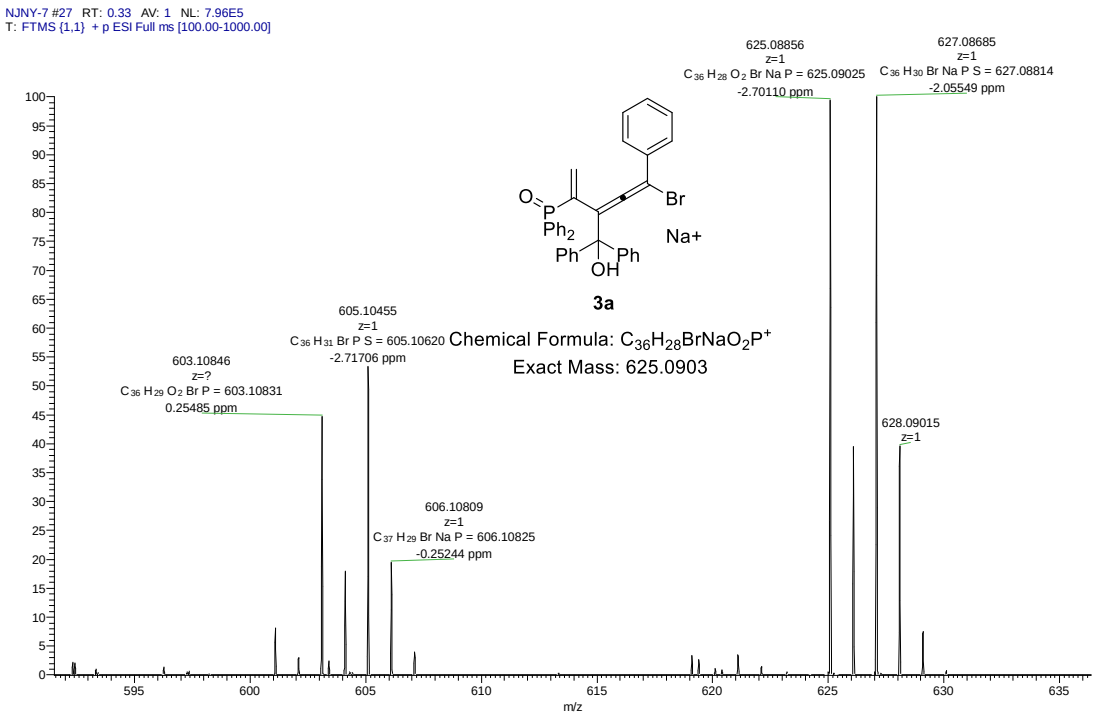

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3a**



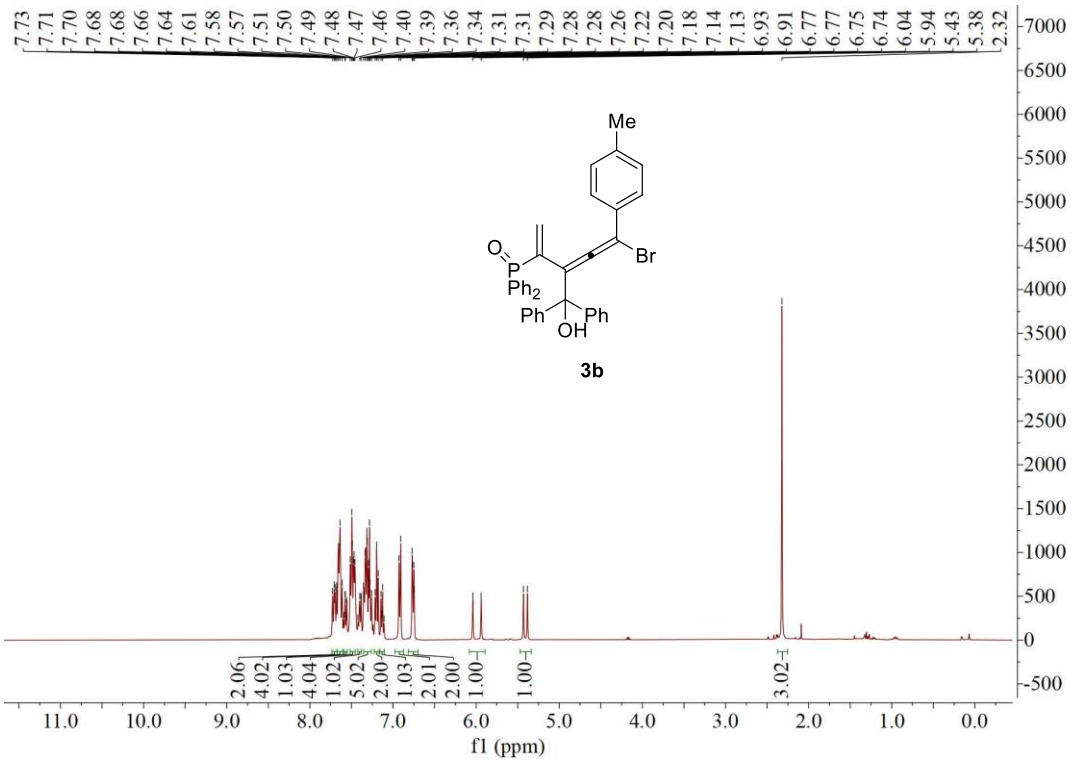

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3a**



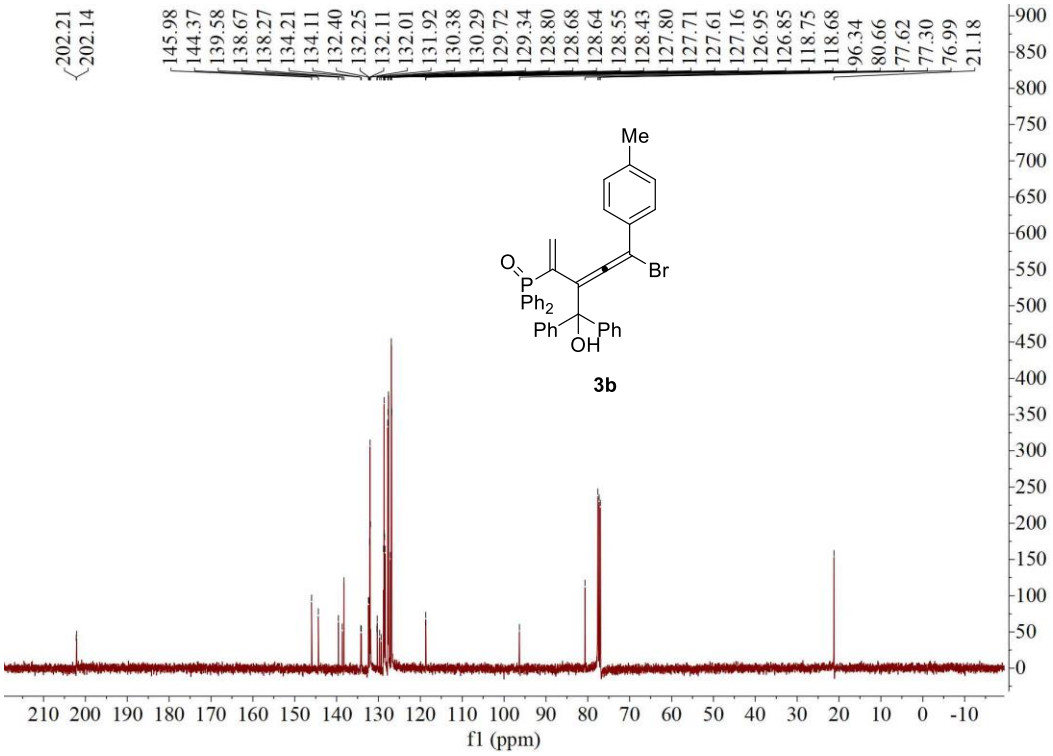

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3a**



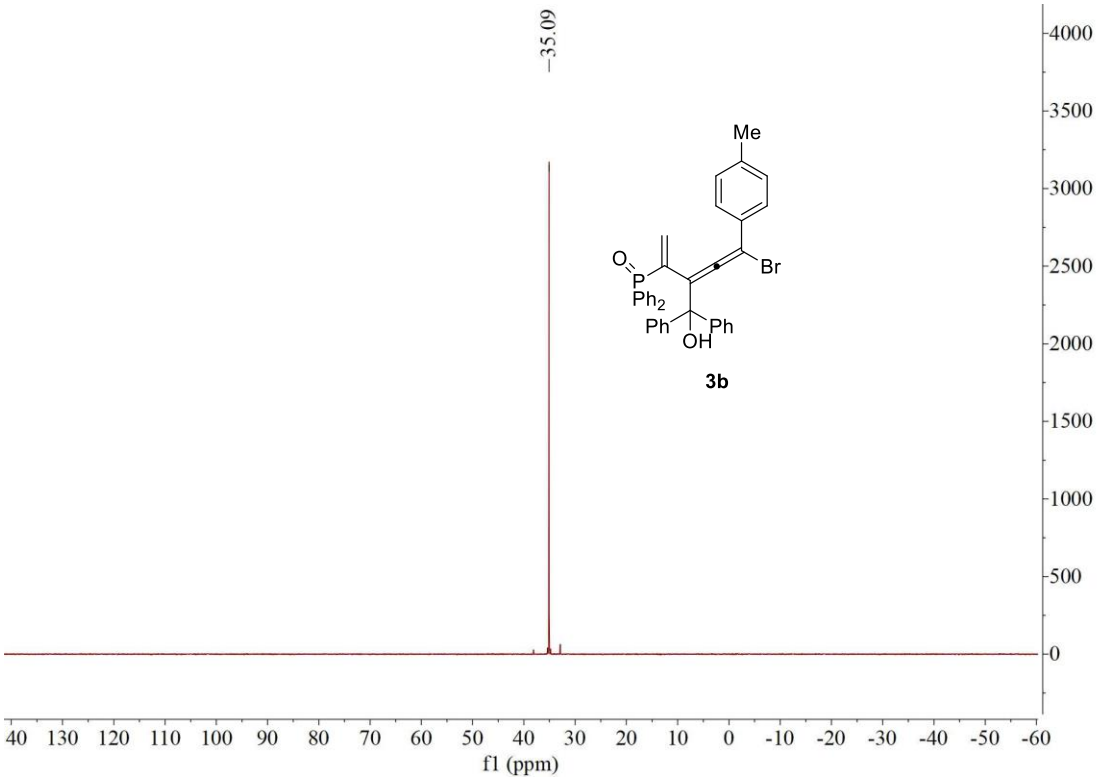
**Compound 3b ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



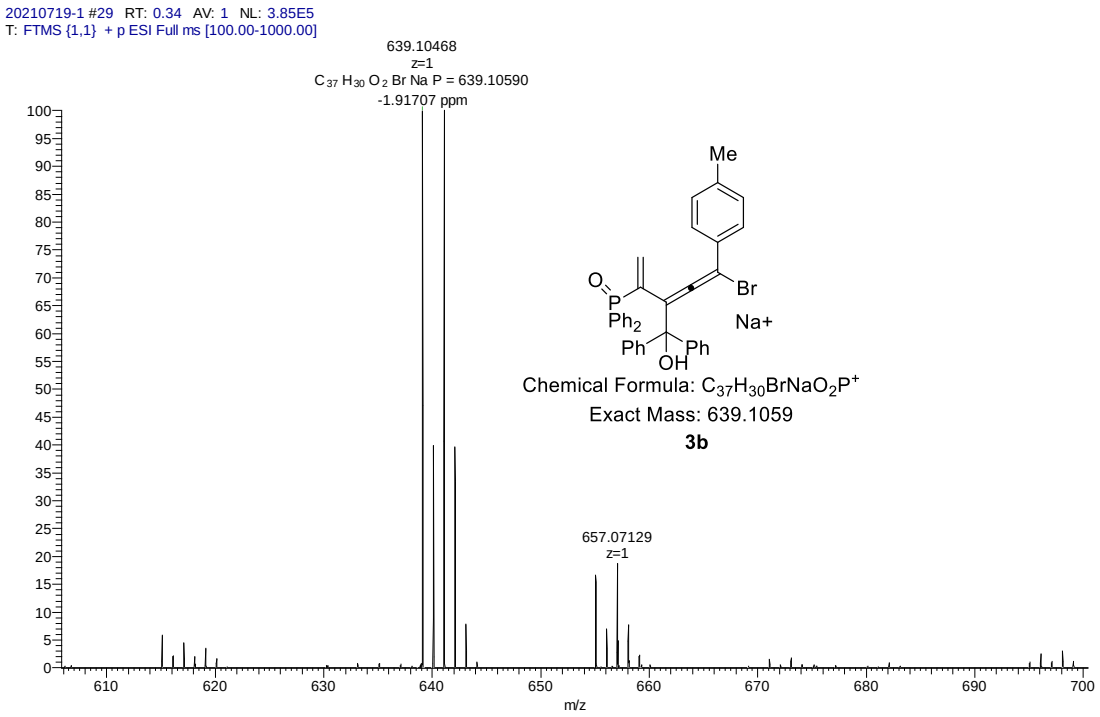

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3b**



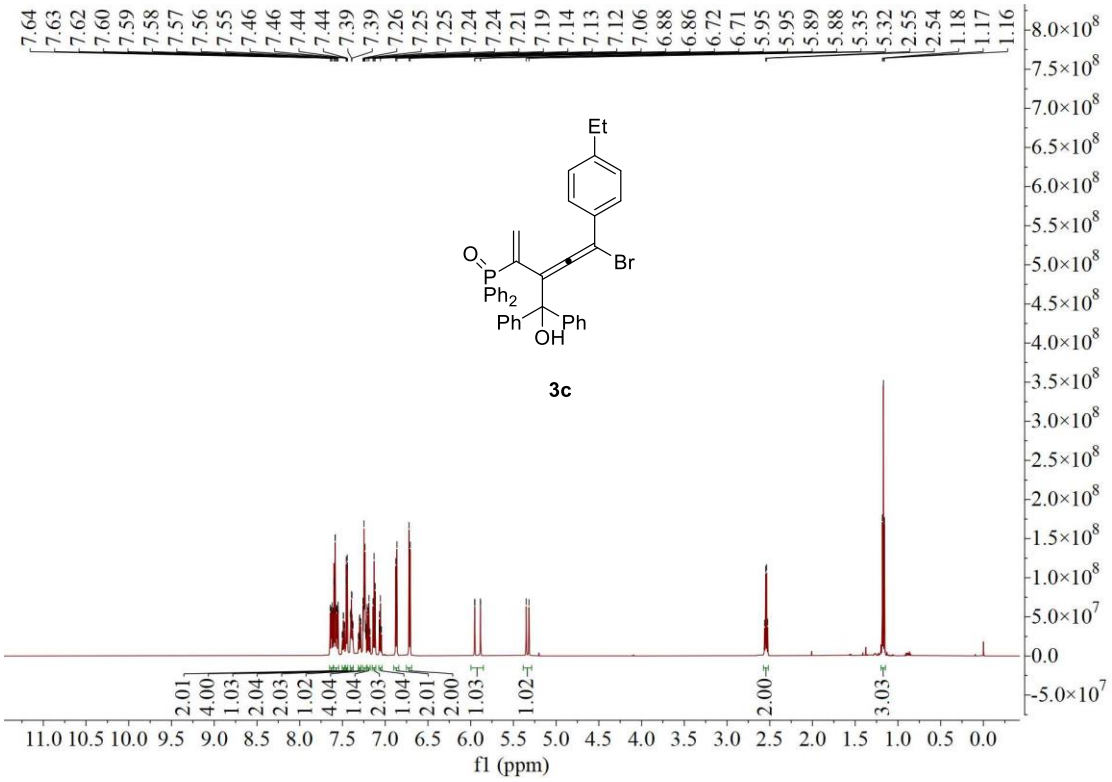

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3b**



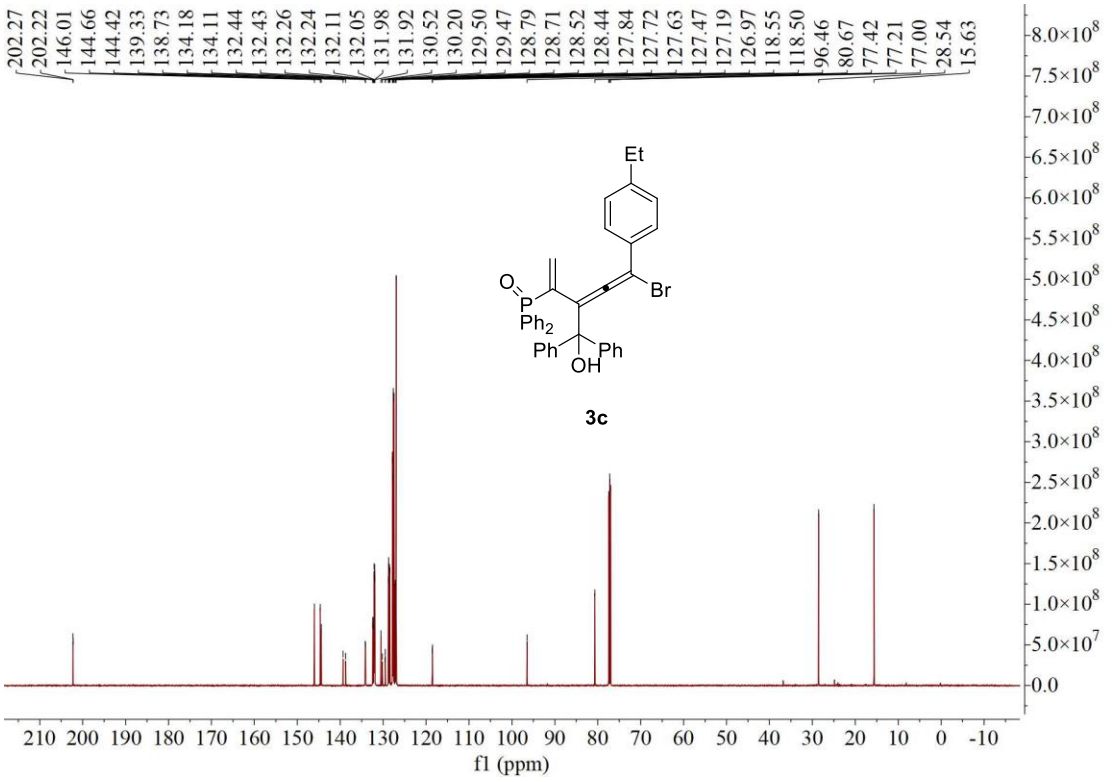

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3b**



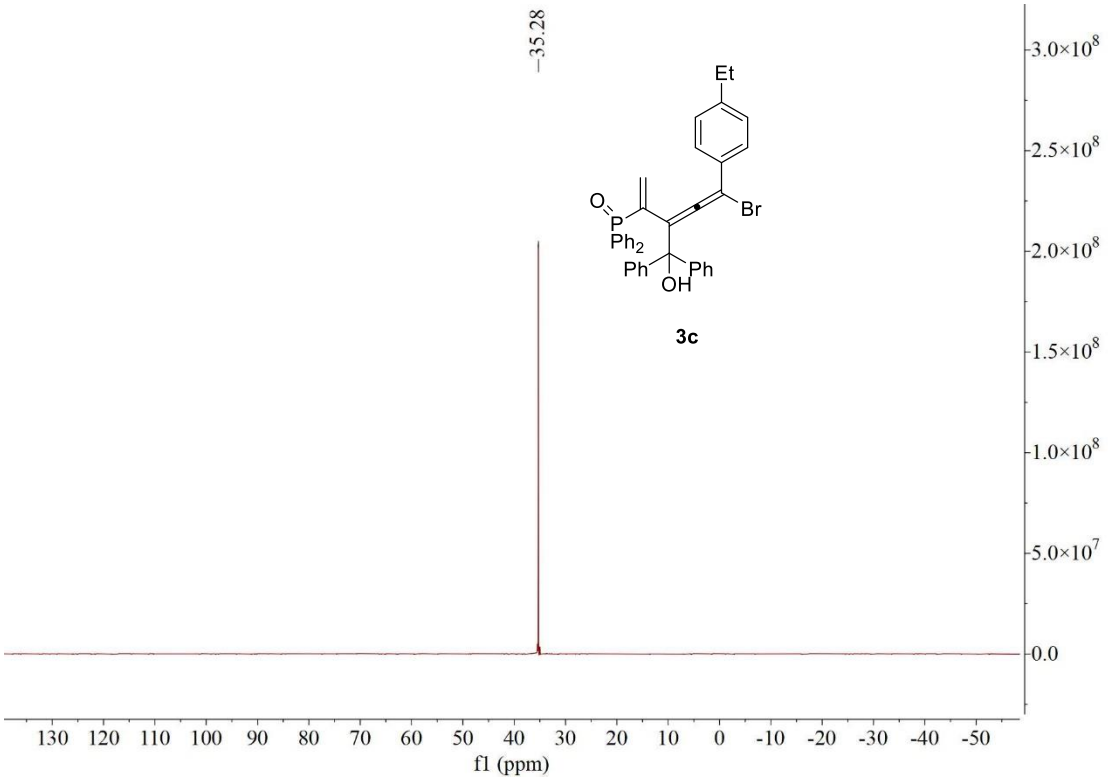
**Compound 3c ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



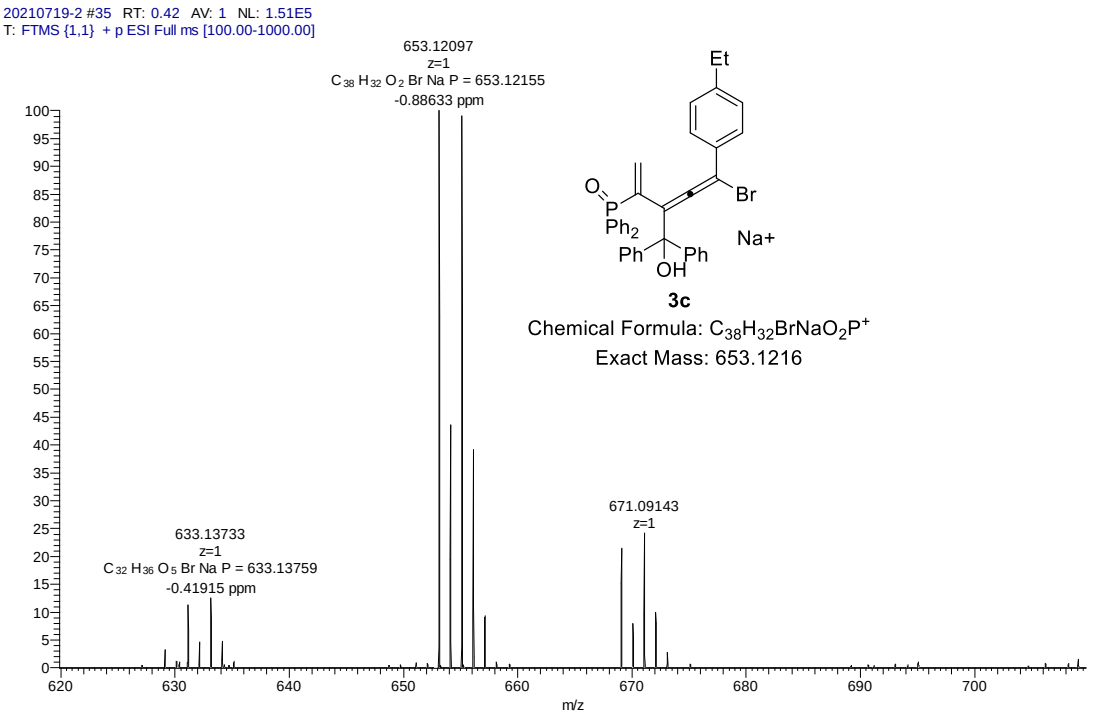

$^{1}$H NMR (600 MHz, $CDCl_3$) of **3c**



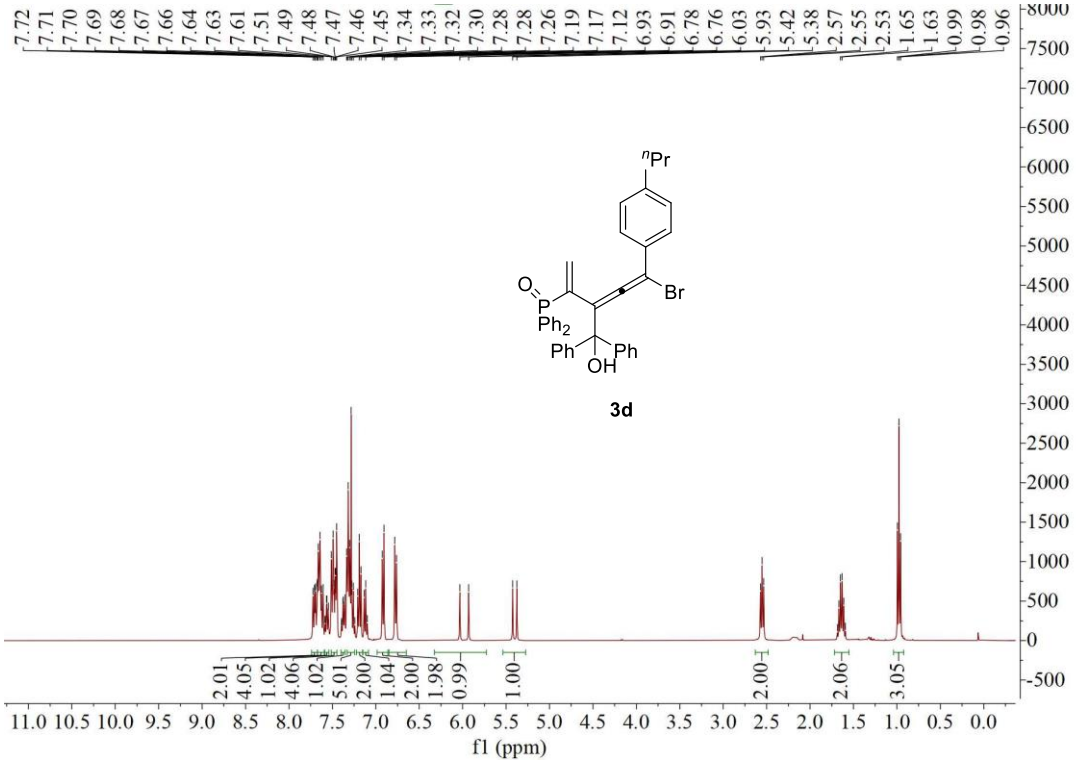

$^{13}$C NMR (151 MHz, $CDCl_3$) of **3c**



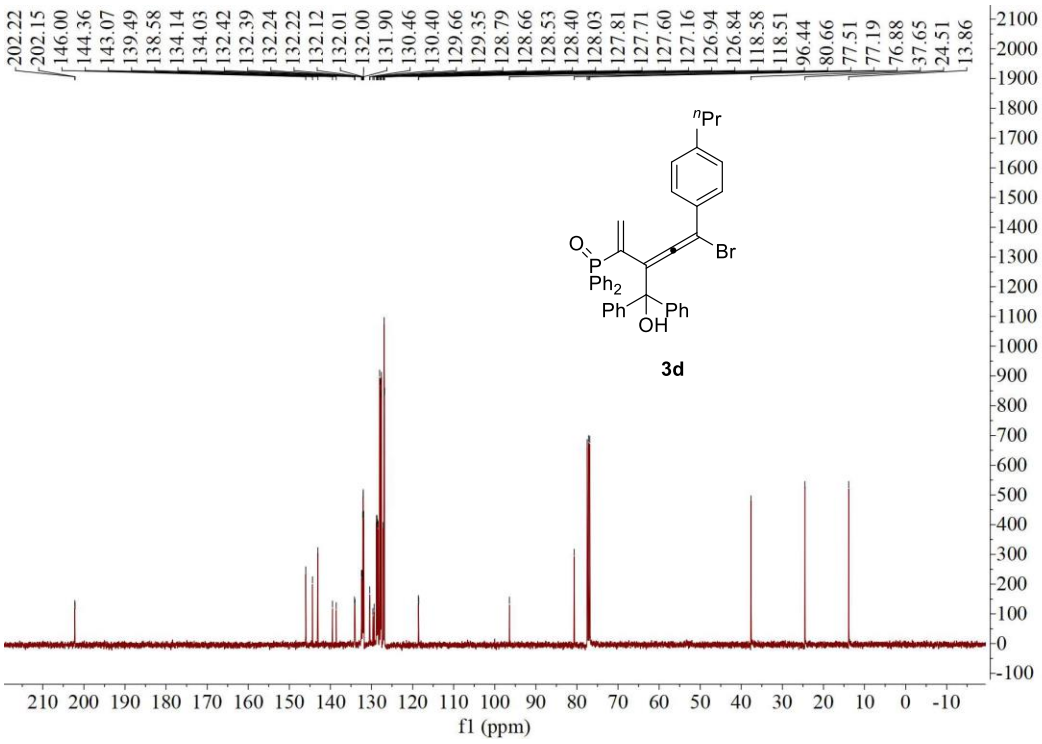

$^{31}$P NMR (243 MHz, $CDCl_3$) of **3c**



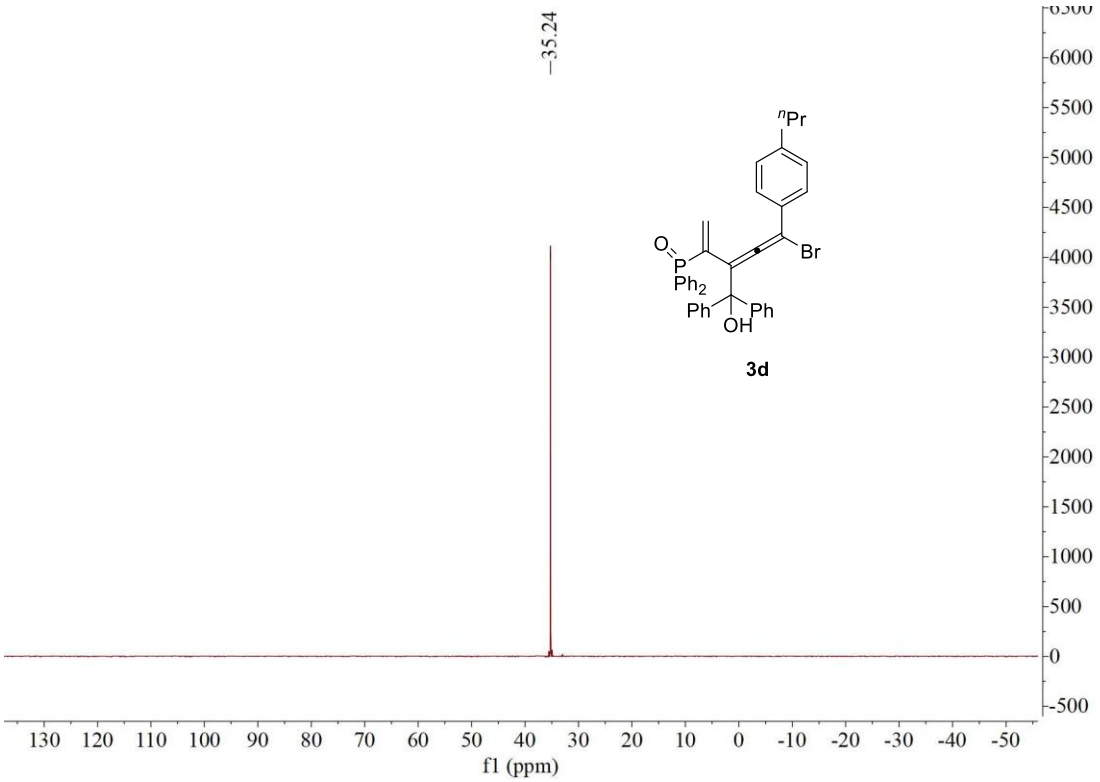
**Compound 3d ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



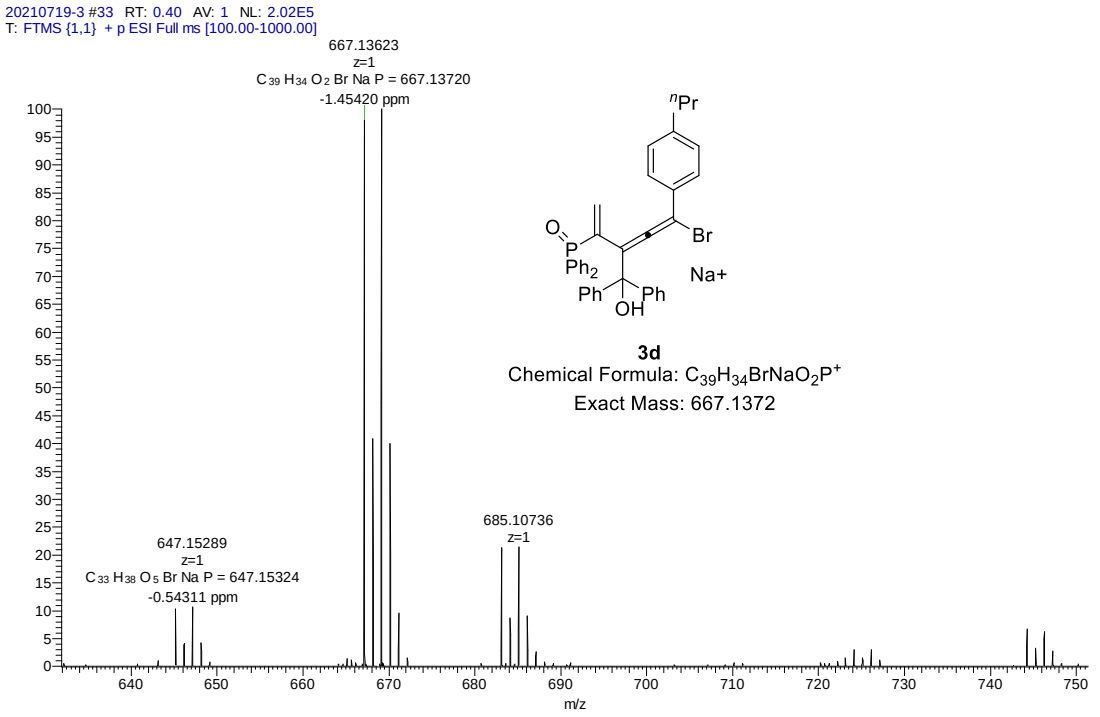

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3d**



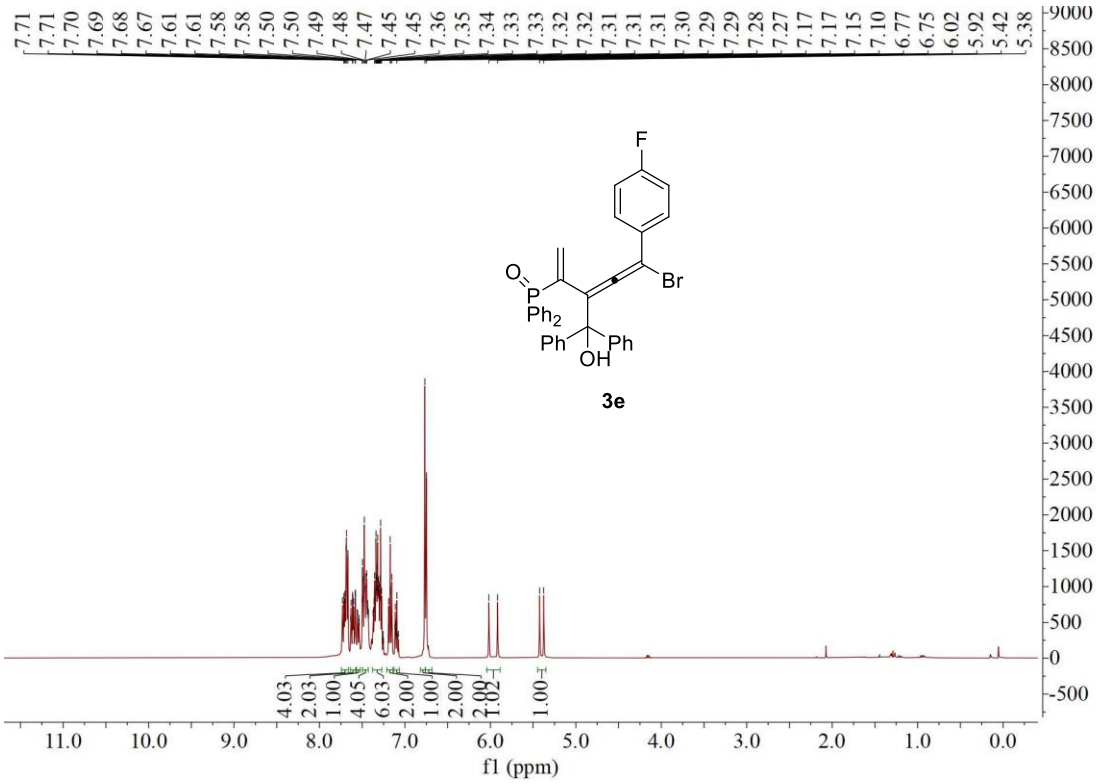

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3d**



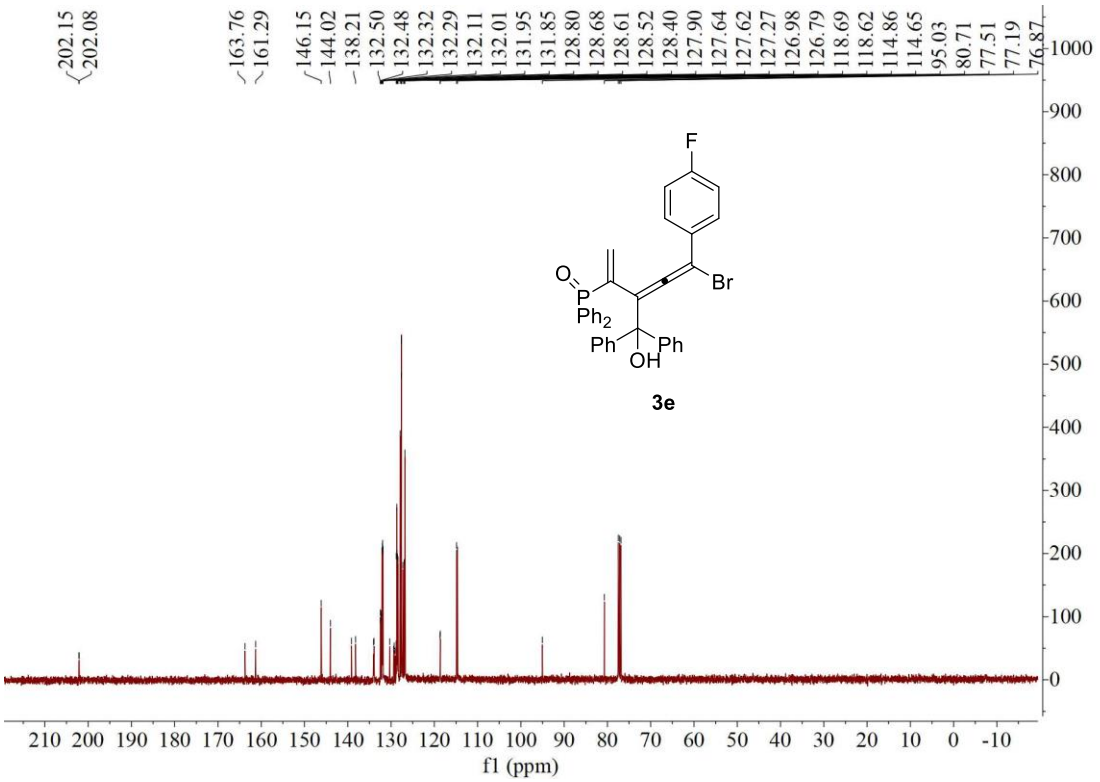

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3d**



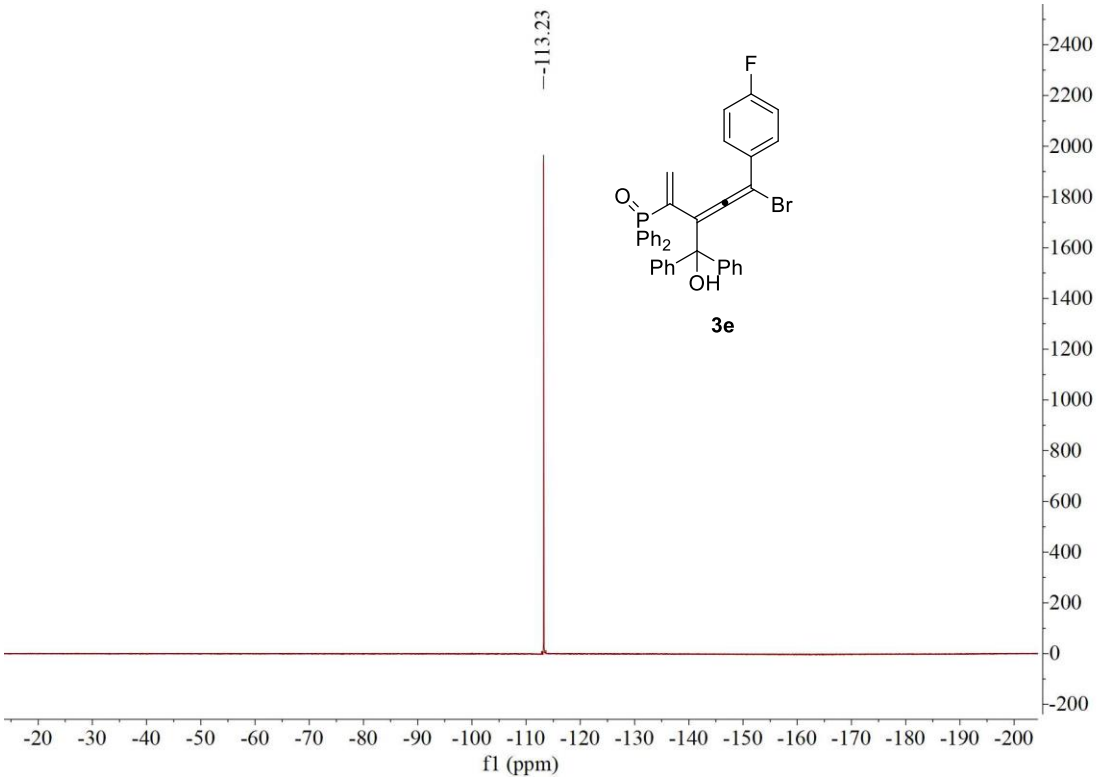
**Compound 3e ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$; $^{19}$F NMR, 376 MHz, $CDCl_3$)**



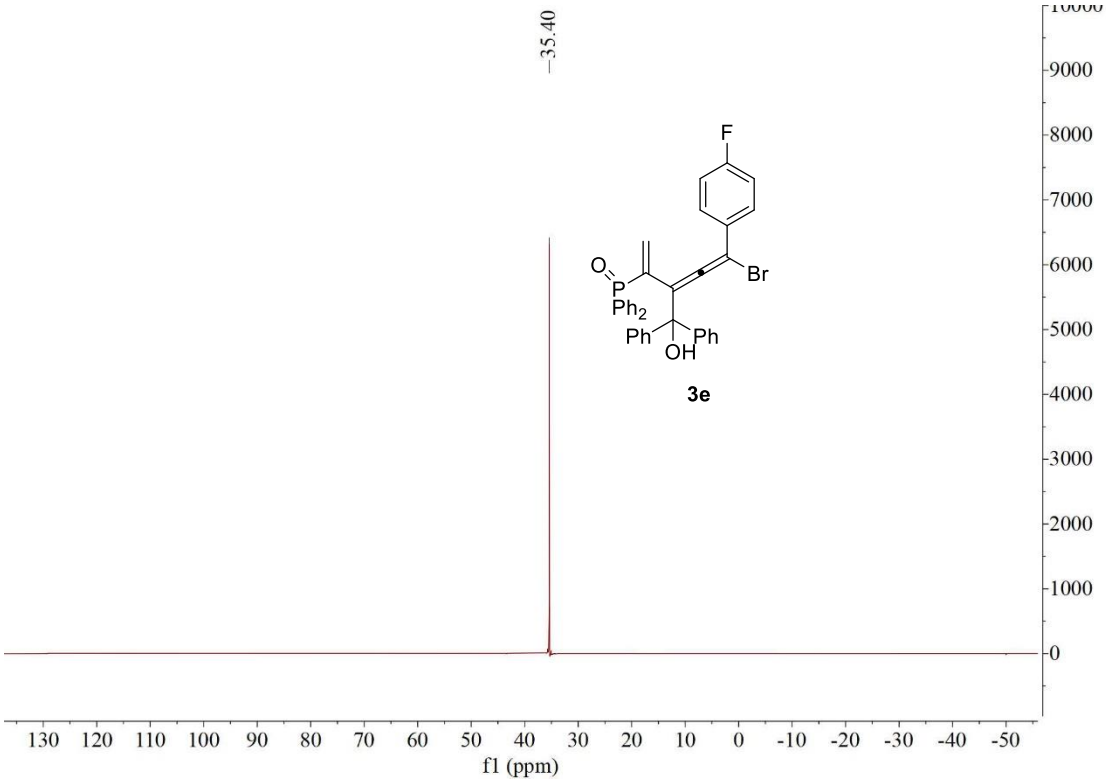

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3e**



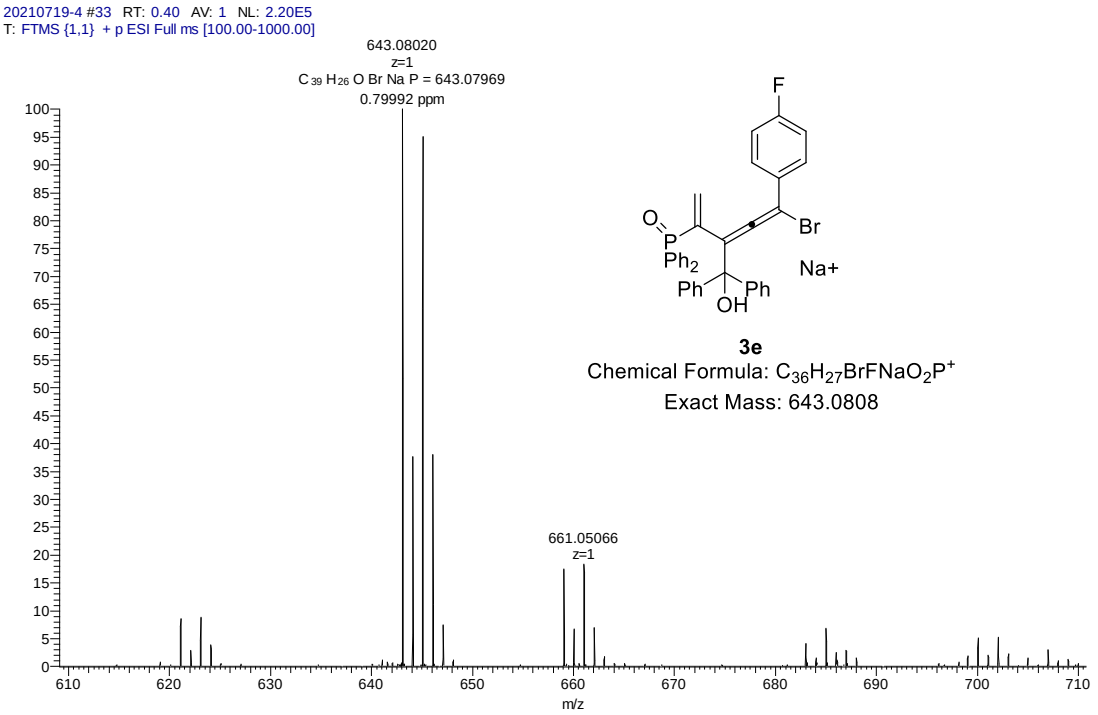

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3e**



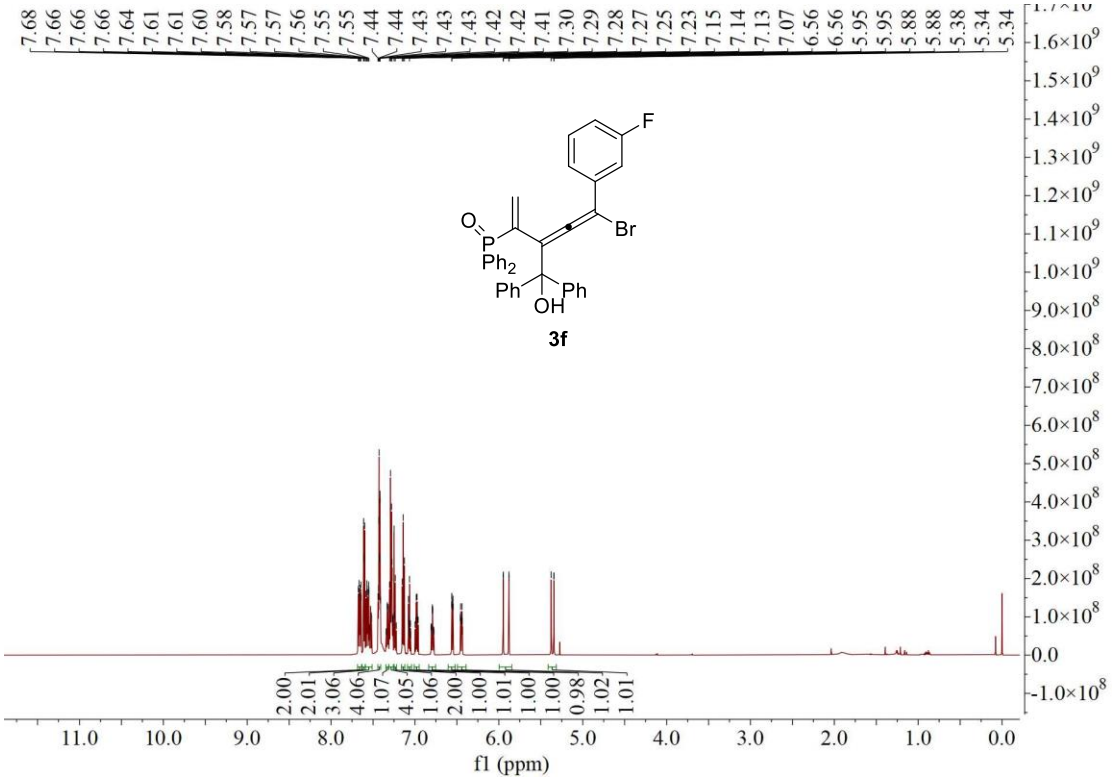

$^{19}$F NMR (376 MHz, $CDCl_3$) of **3e**



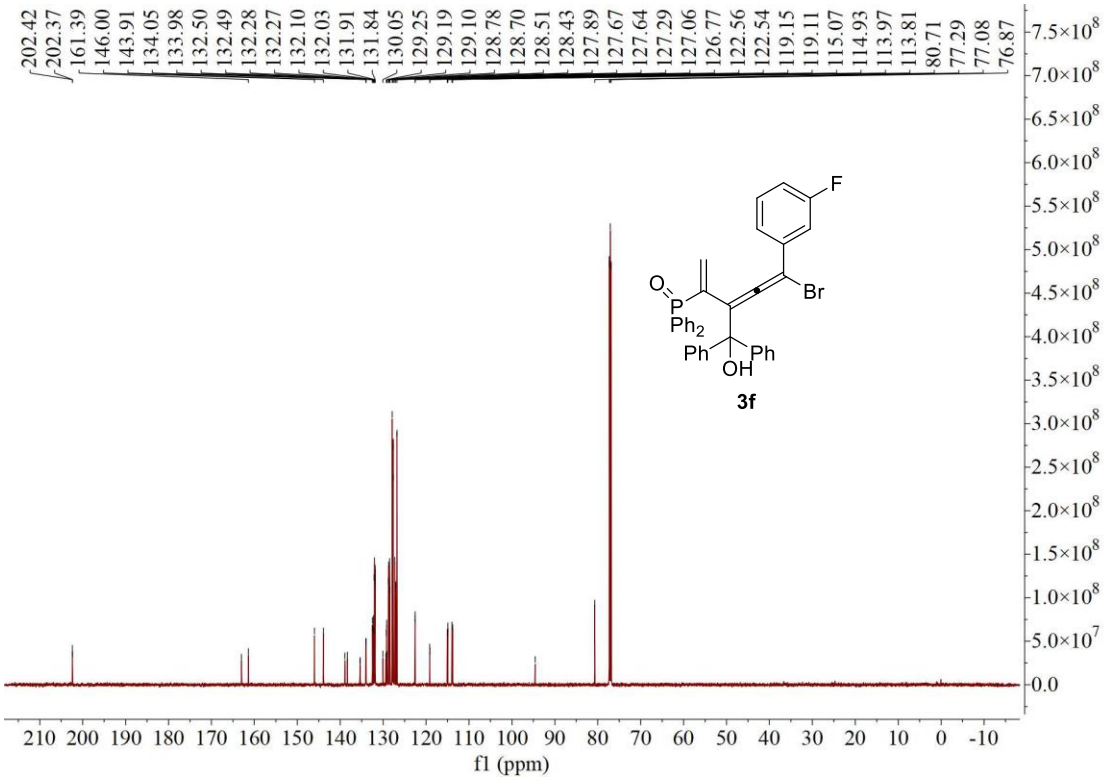

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3e**



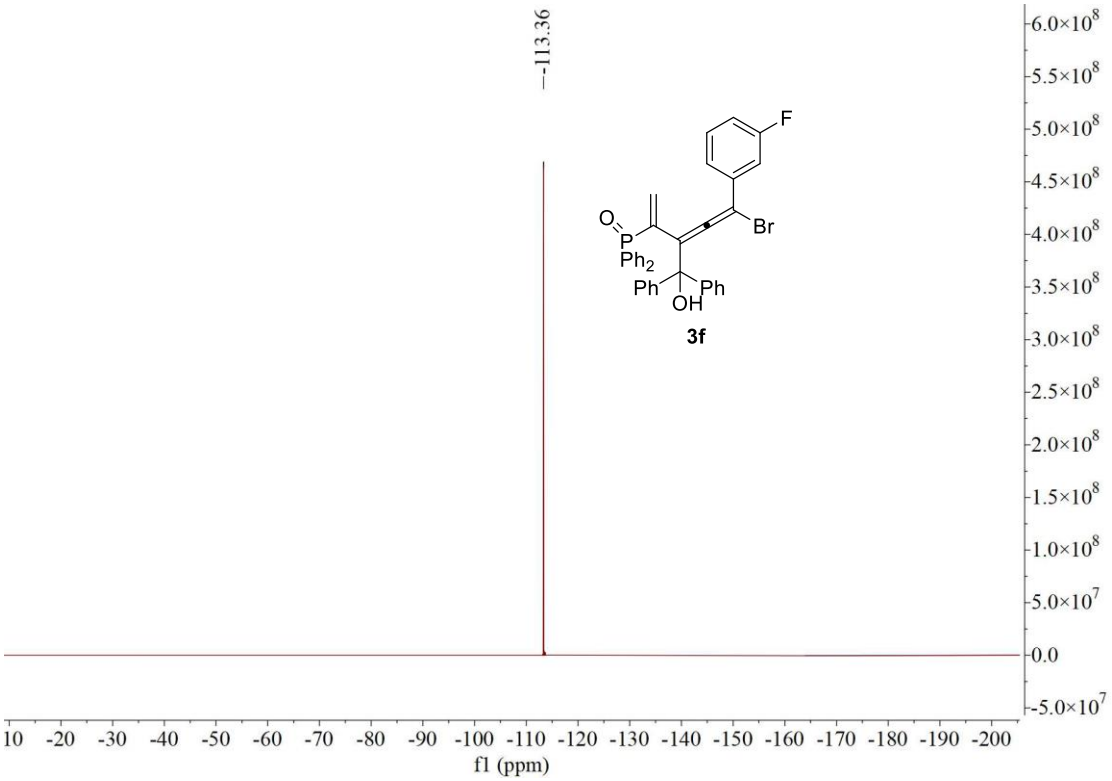

**Compound 3f ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$; $^{19}$F NMR, 565 MHz, $CDCl_3$)**



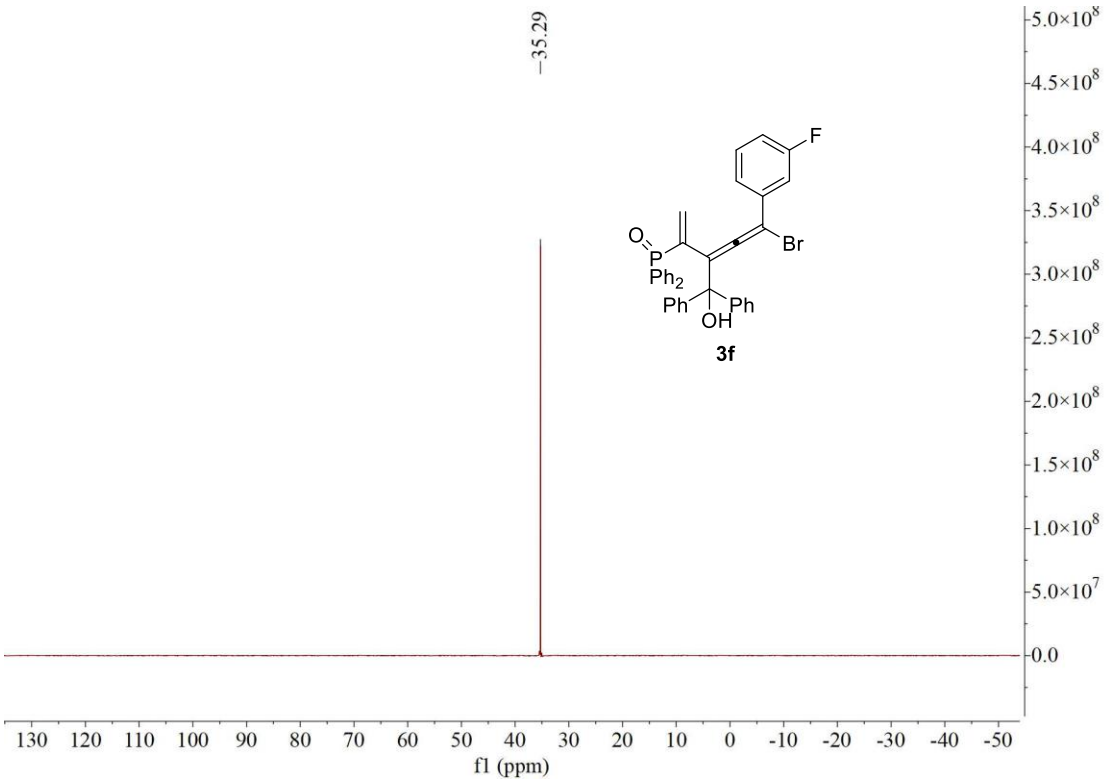

$^{1}$H NMR (600 MHz, $CDCl_3$) of **3f**



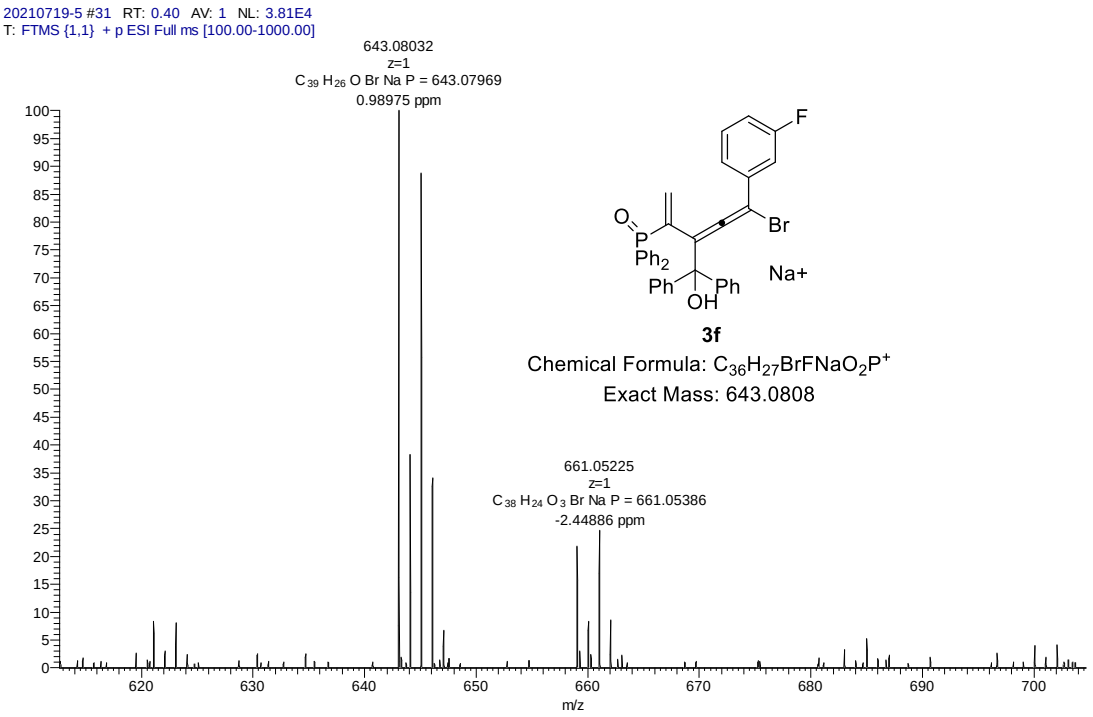

$^{13}C$ NMR (151 MHz, $CDCl_3$) of **3f**



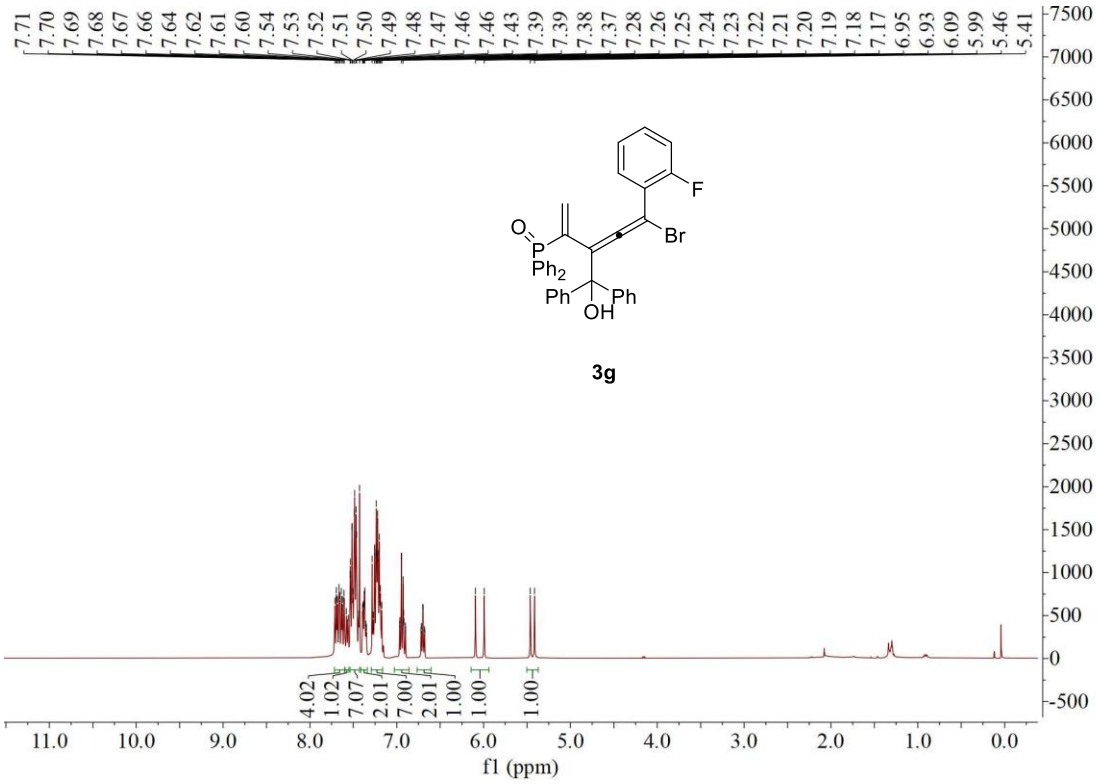

$^{19}F$ NMR (565 MHz, $CDCl_3$) of **3f**



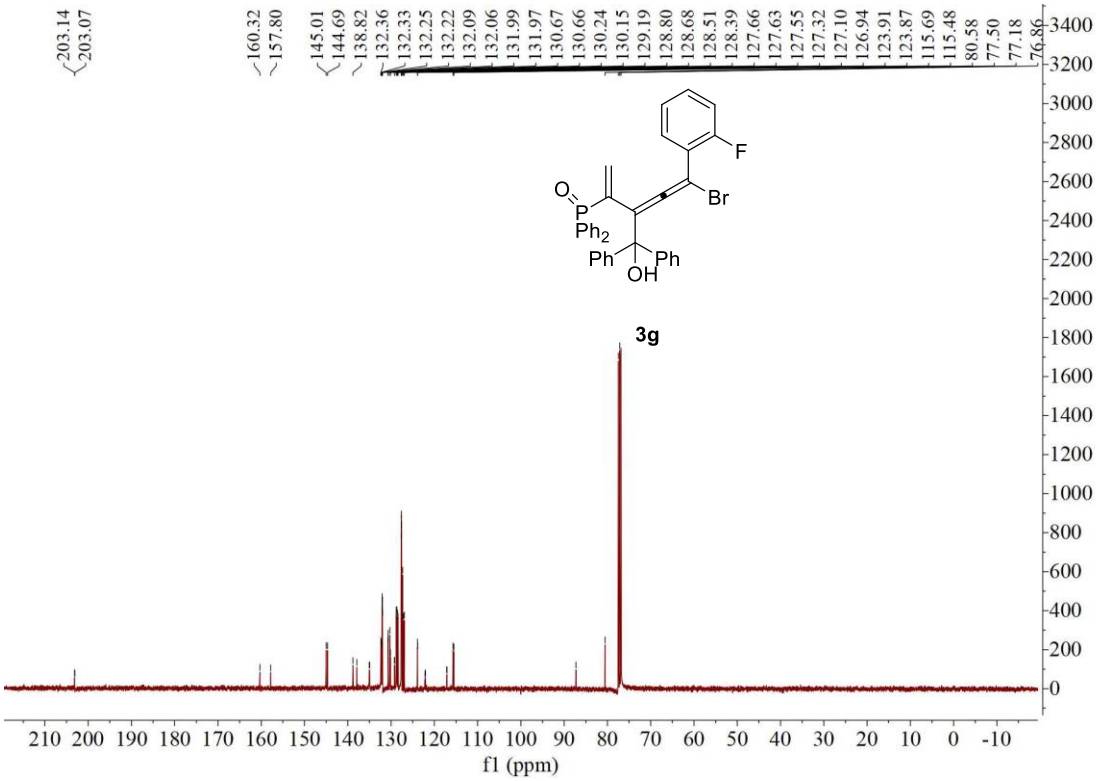

$^{31}$P NMR (243 MHz, $CDCl_3$) of **3f**



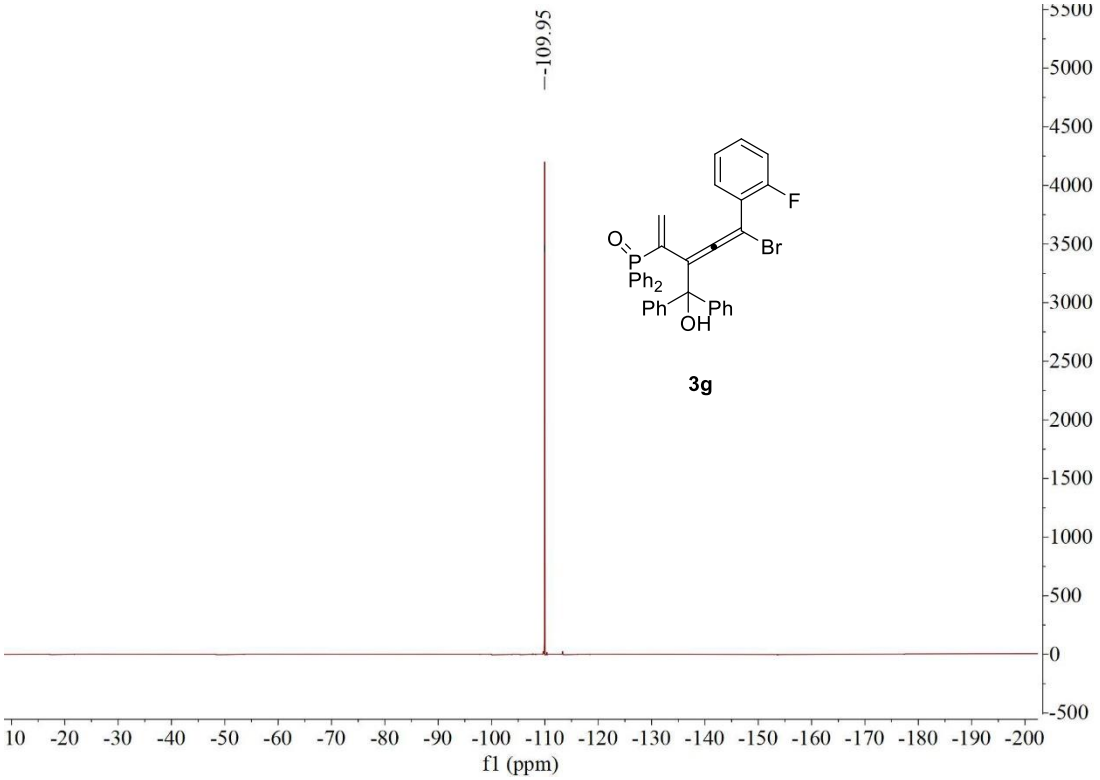
**Compound 3g ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$; $^{19}$F NMR, 376 MHz, $CDCl_3$)**



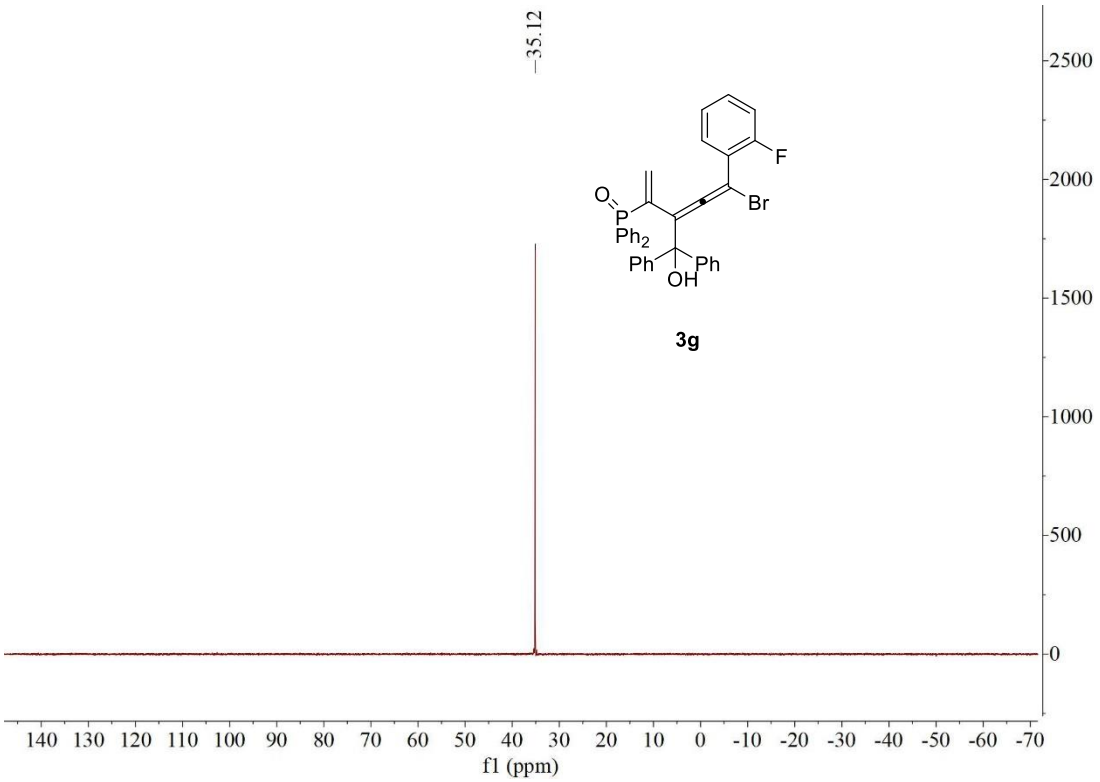

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3g**



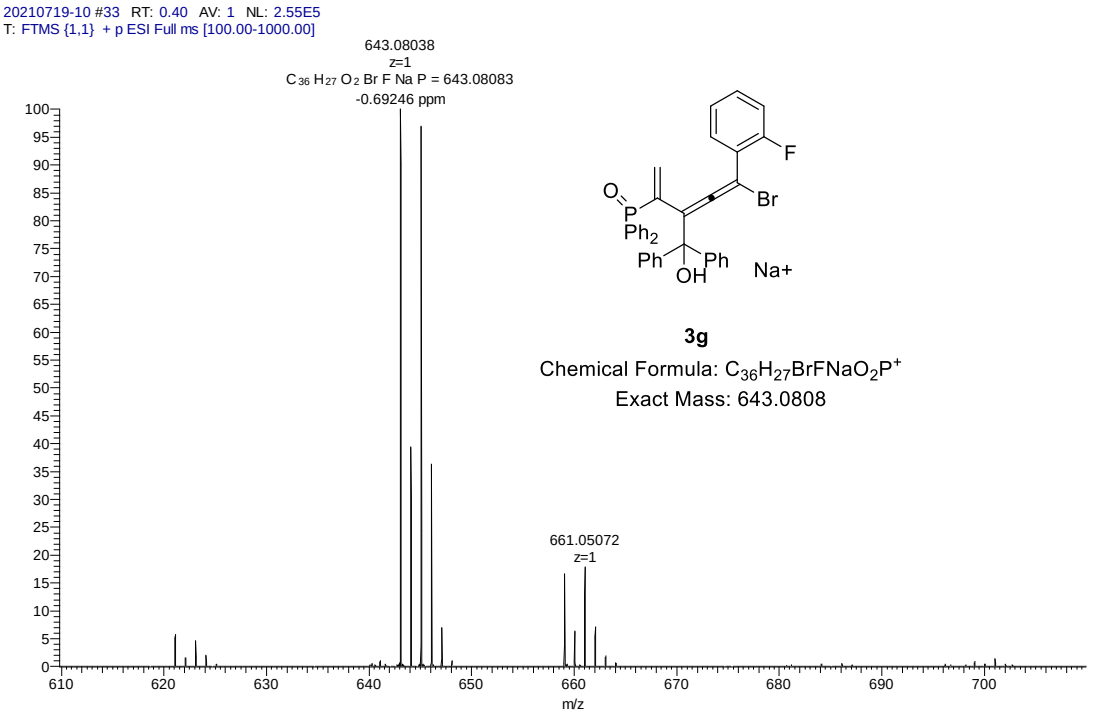

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3g**



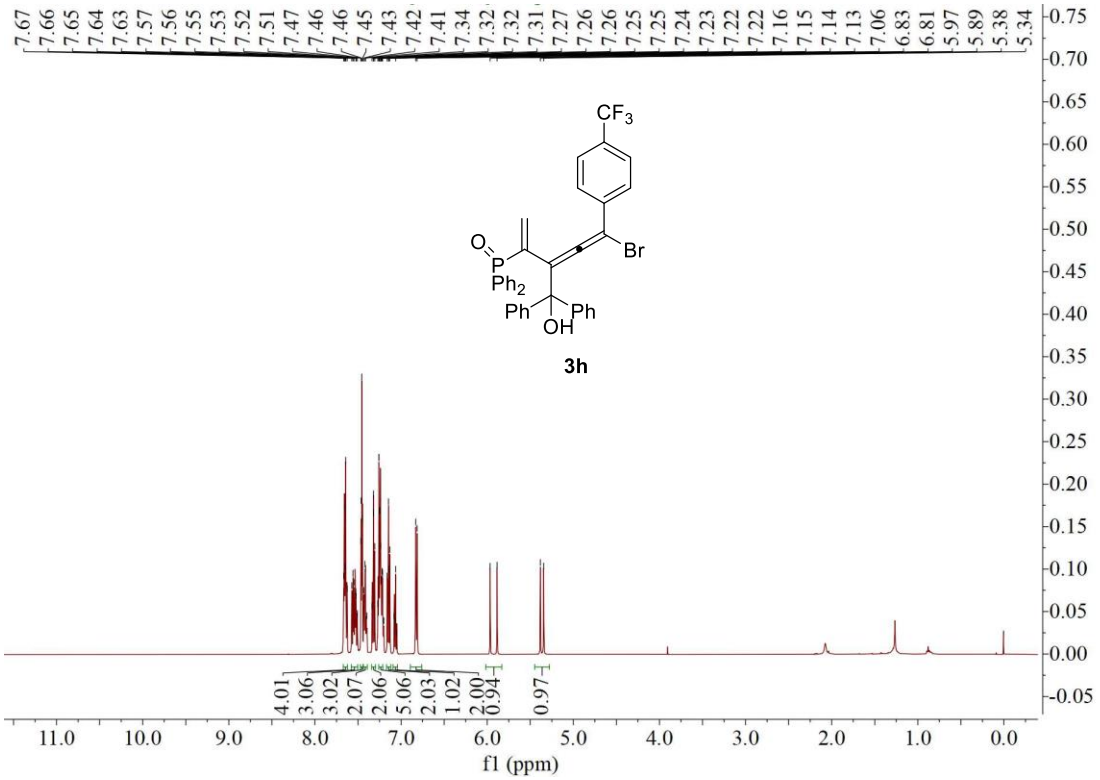

$^{19}$F NMR (376 MHz, $CDCl_3$) of **3g**



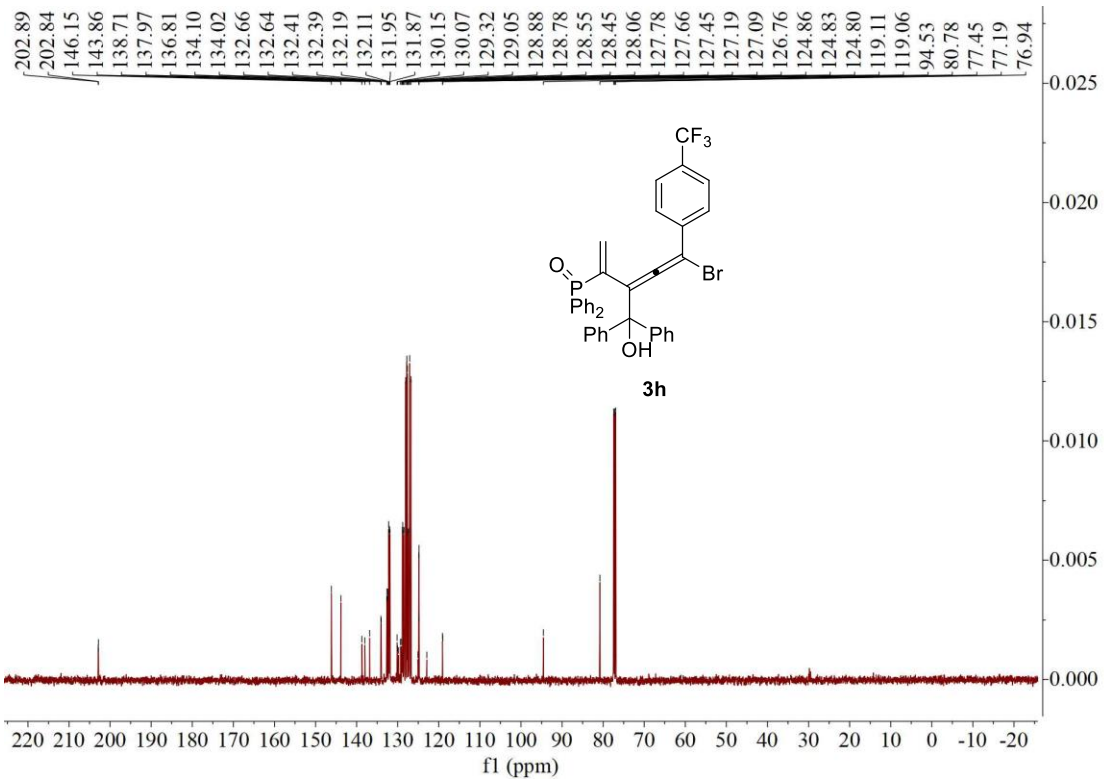

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3g**



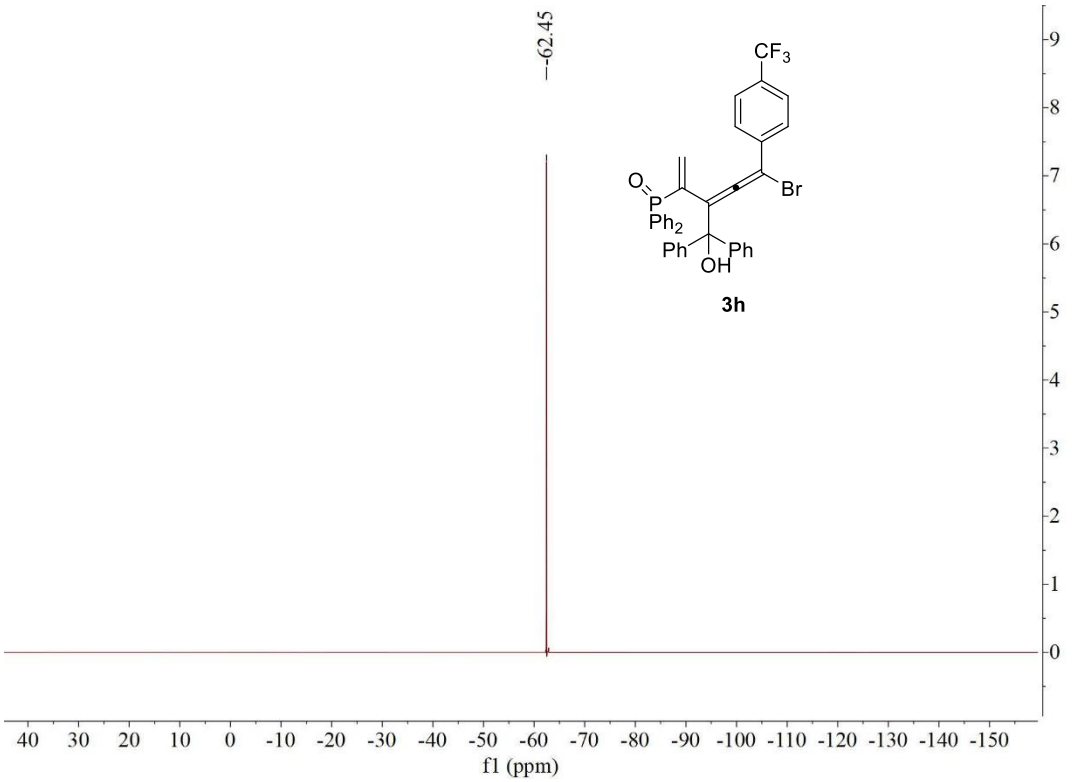

**Compound 3h ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$; $^{19}$F NMR, 471 MHz, $CDCl_3$)**



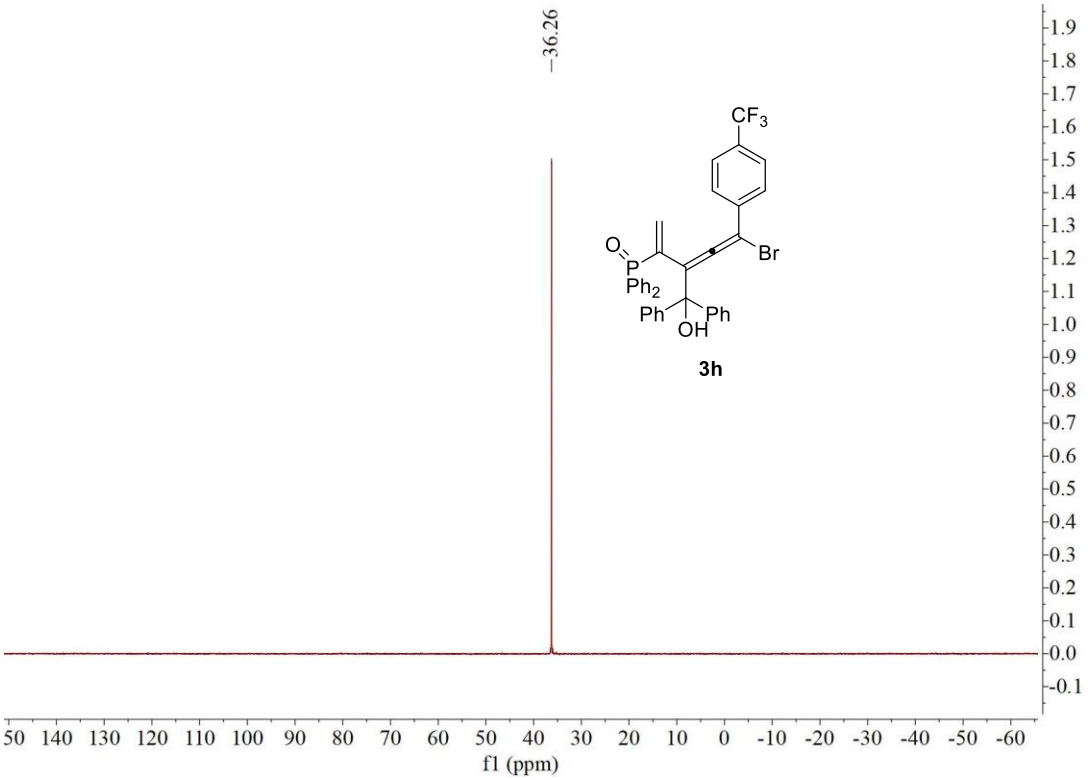

$^{1}$H NMR (500 MHz, $CDCl_3$) of **3h**



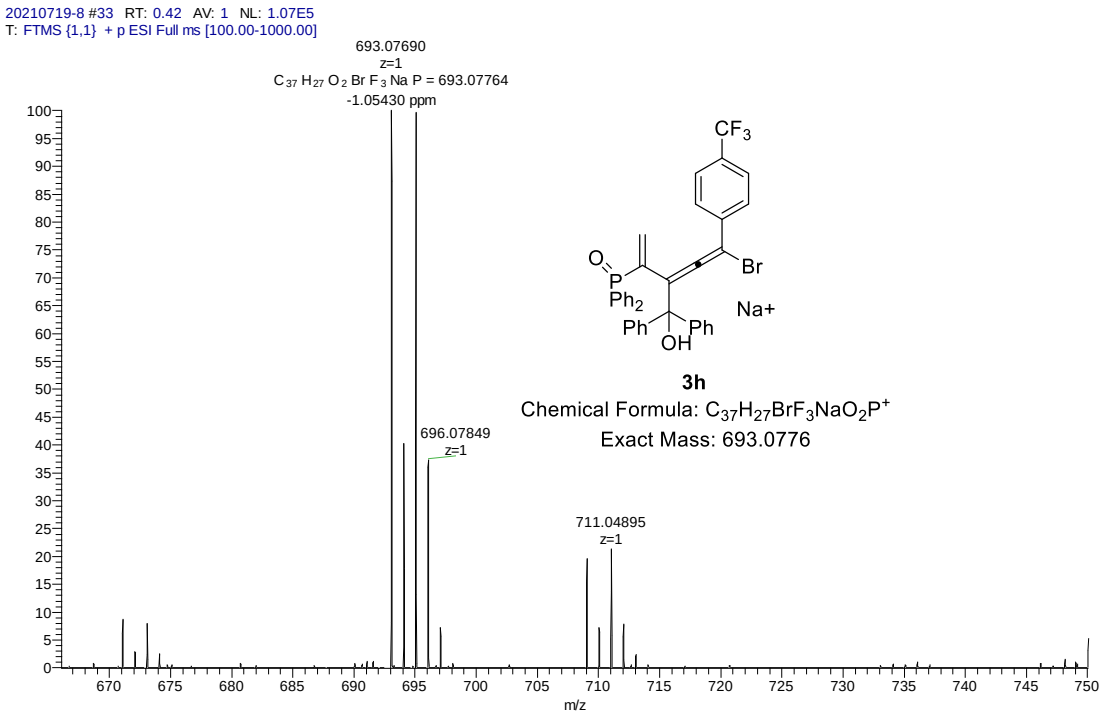

$^{13}$C NMR (126 MHz, $CDCl_3$) of **3h**



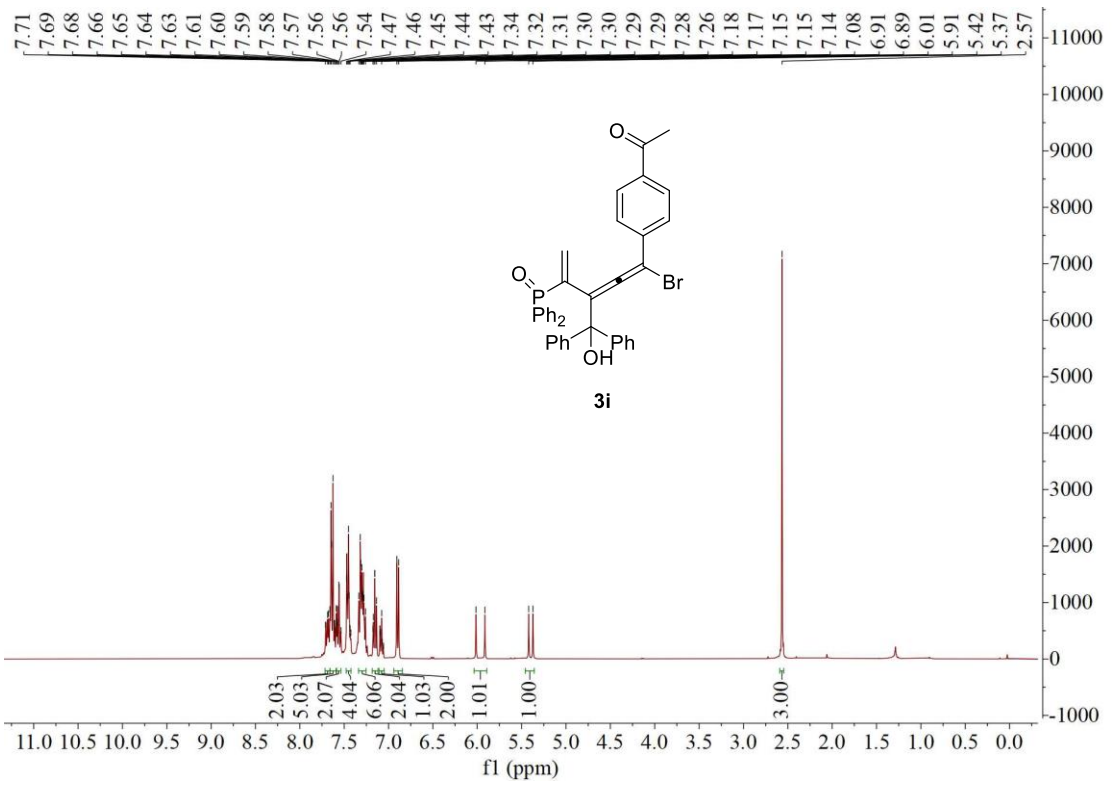

$^{19}$F NMR (471 MHz, $CDCl_3$) of **3h**



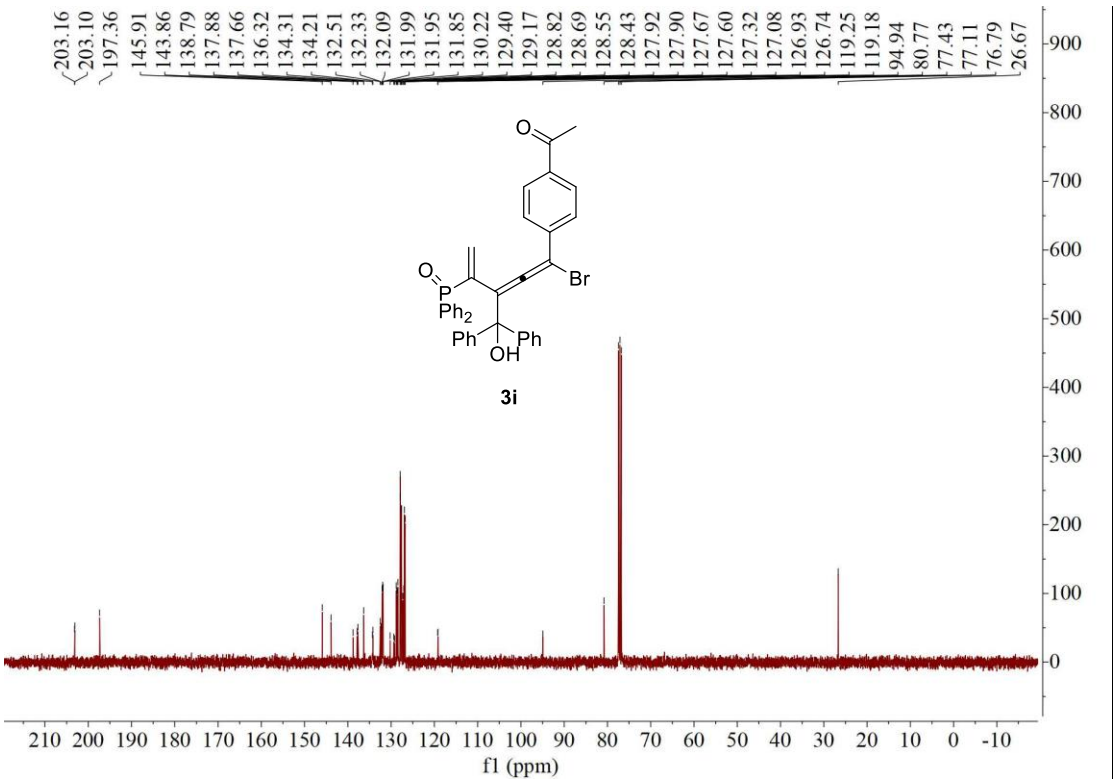

$^{31}$P NMR (202 MHz, $CDCl_3$) of **3h**



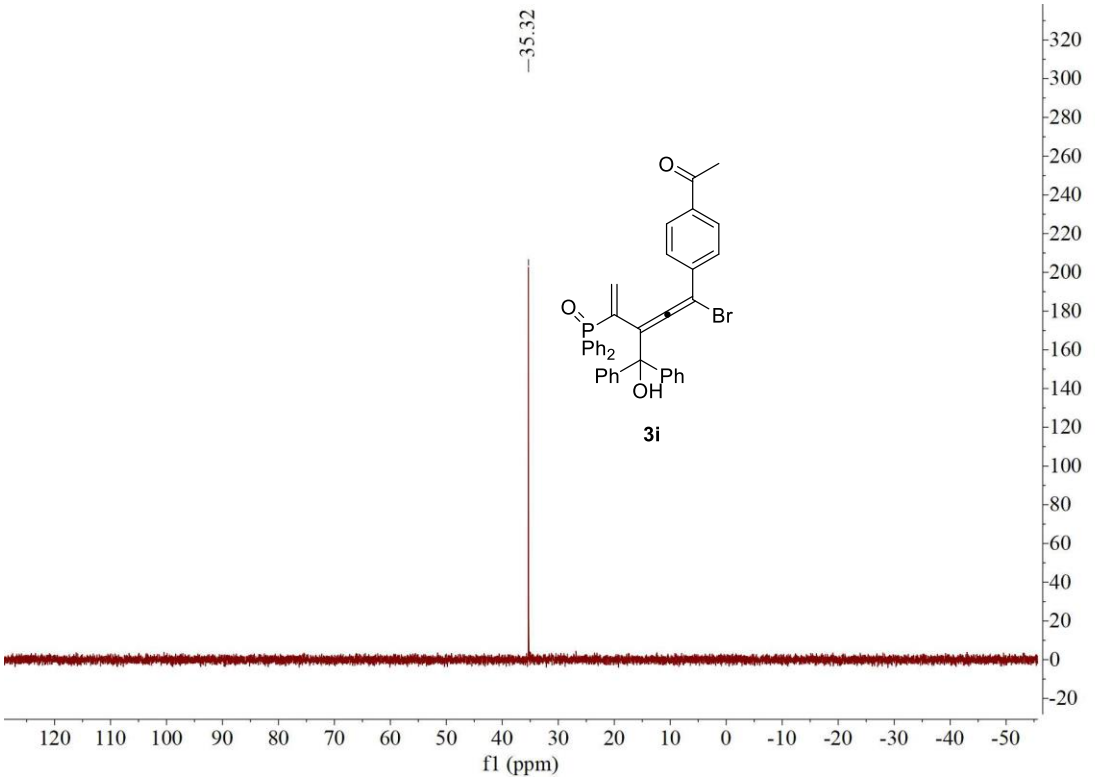
**Compound 3i ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**




$^{1}$H NMR (400 MHz, $CDCl_3$) of **3i**

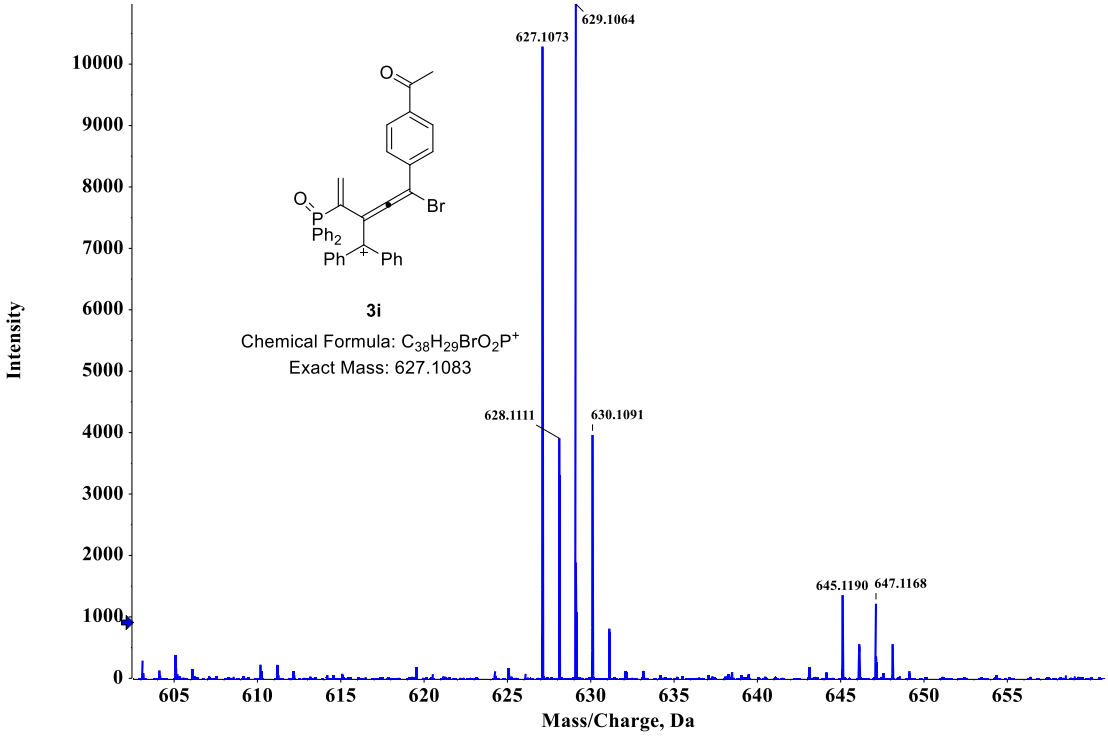



$^{13}$C NMR (101 MHz, $CDCl_3$) of **3i**

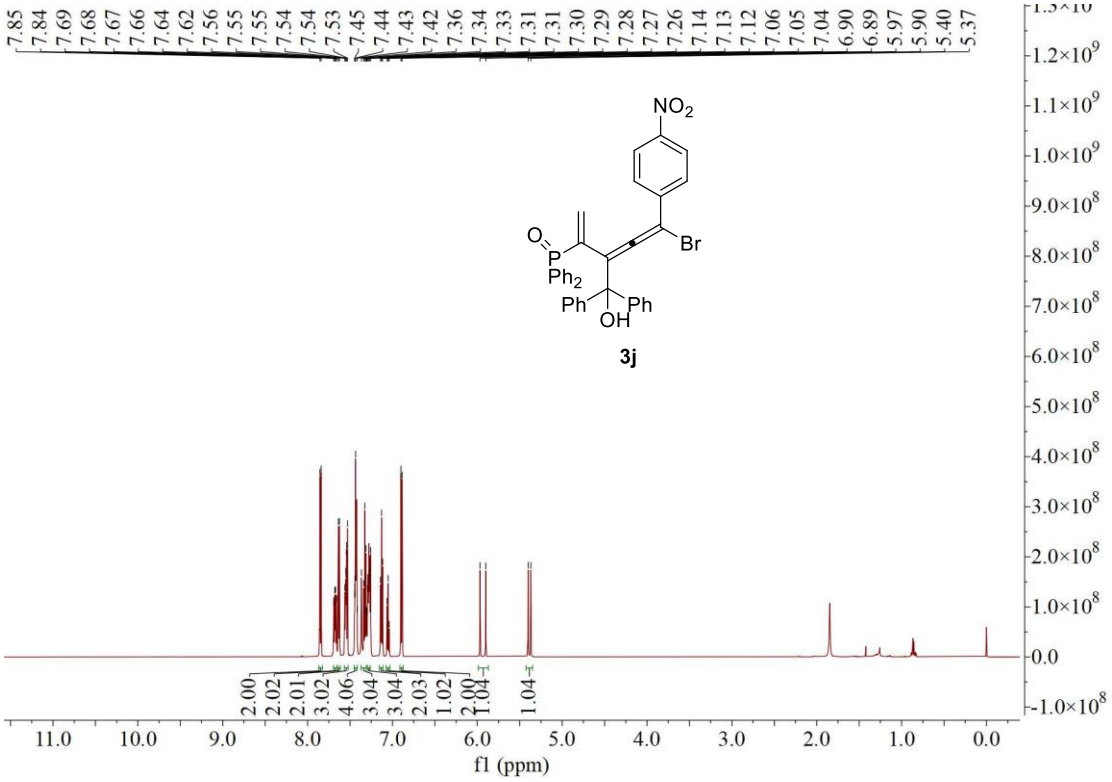



$^{31}$P NMR (162 MHz, $CDCl_3$) of **3i**

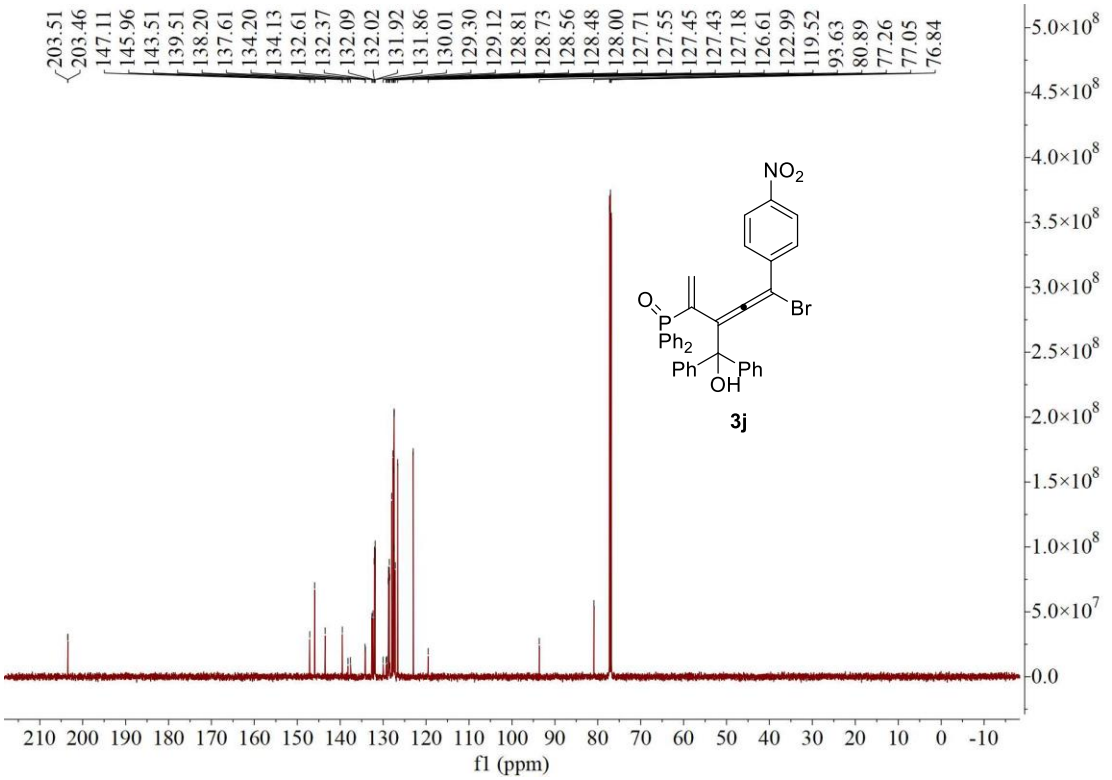
**Spectrum from 18.wiff (sample 1) - Sample018, +TOF MS (100 - 1000) from 0.206 min**



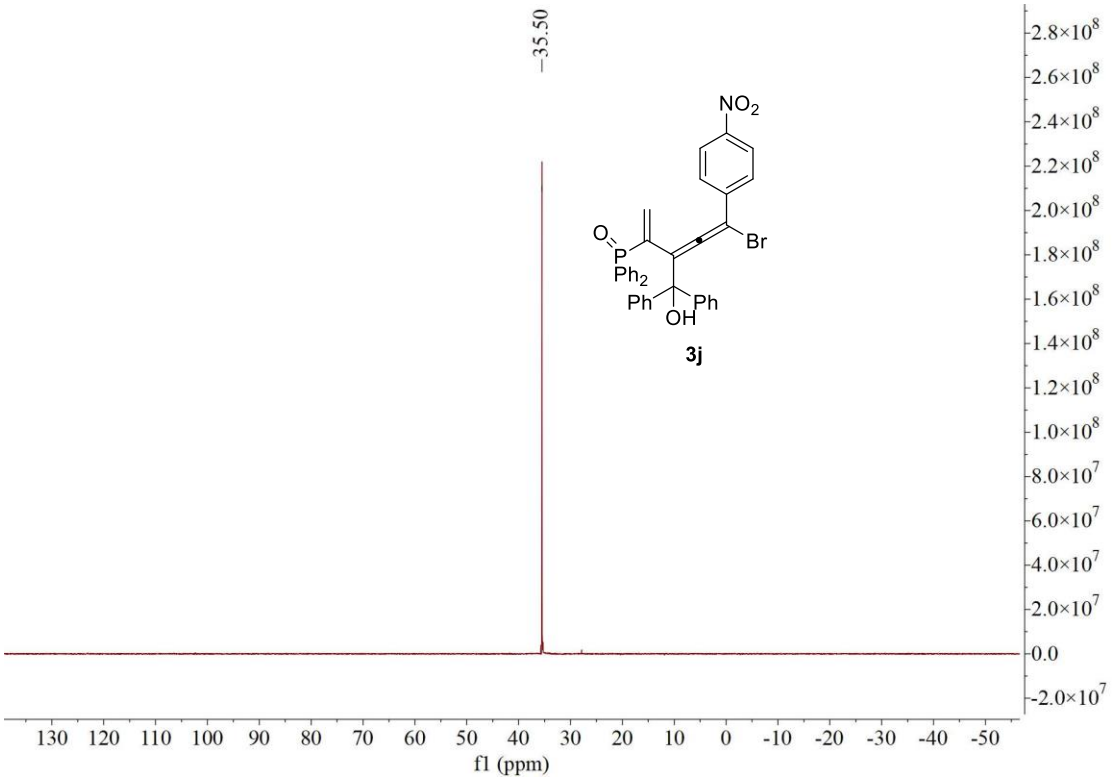
**Compound 3j ($^{1}$H NMR, 600 MHz, $CDCl_3$; $^{13}$C NMR, 151 MHz, $CDCl_3$; $^{31}$P NMR, 243 MHz, $CDCl_3$)**



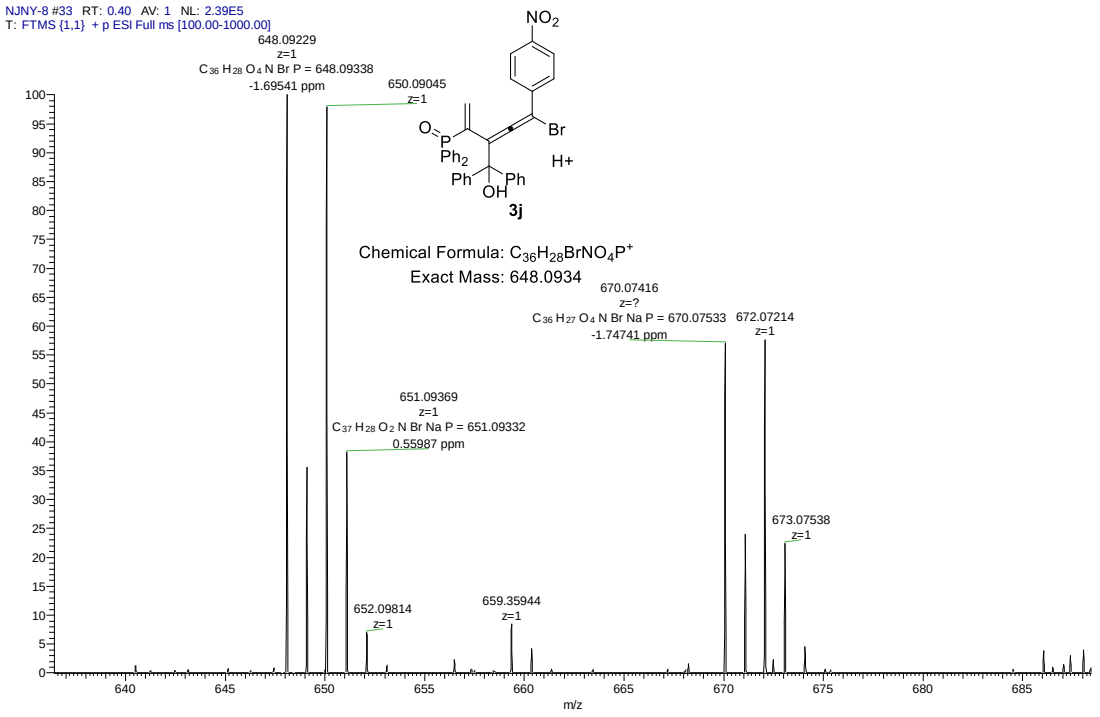

$^{1}$H NMR (600 MHz, $CDCl_3$) of **3j**



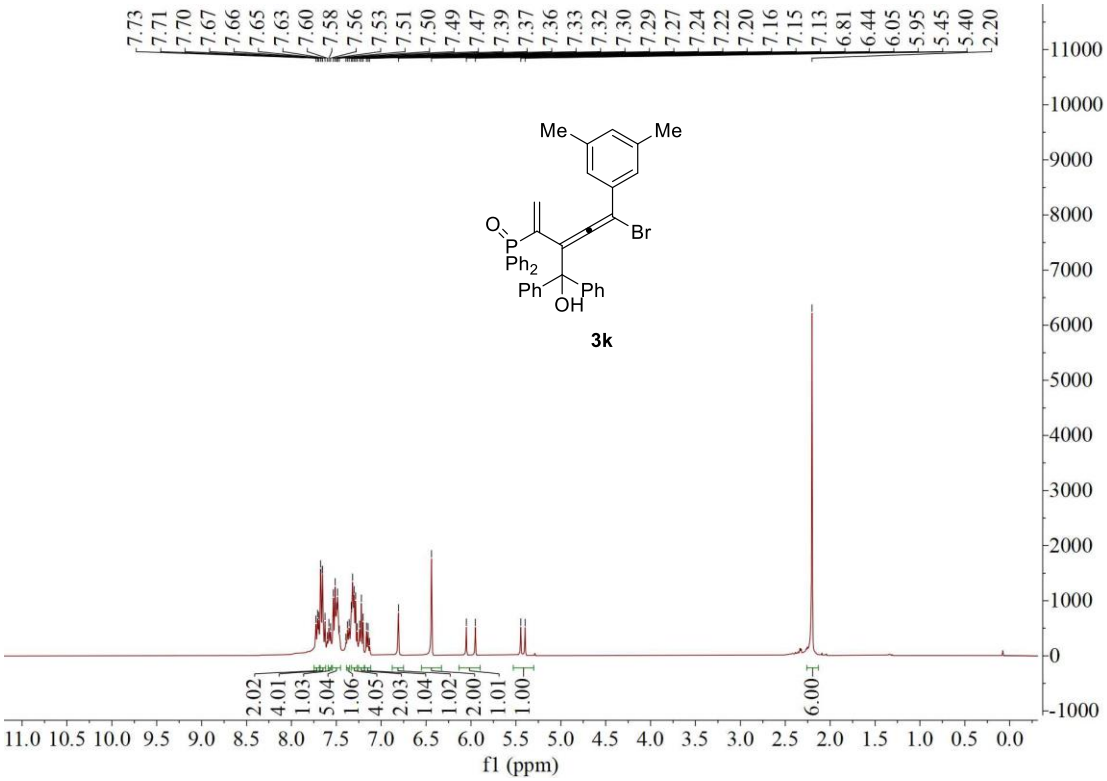

$^{13}$C NMR (151 MHz, $CDCl_3$) of **3j**



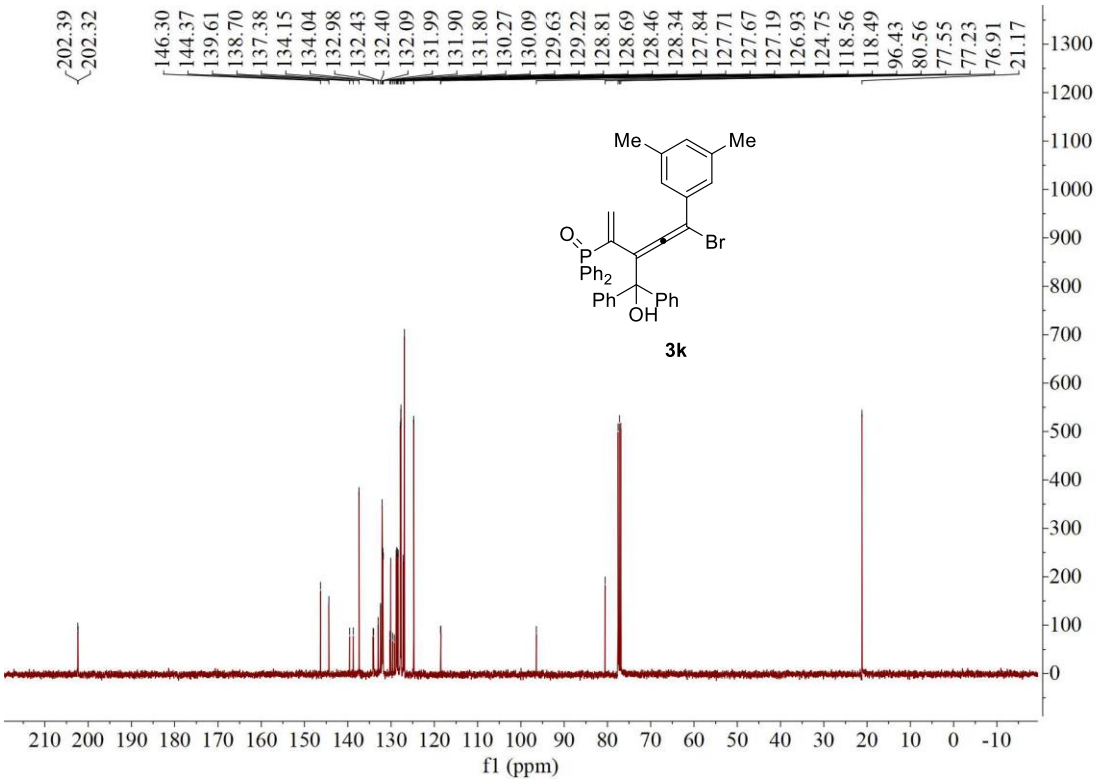

$^{31}P$ NMR (243 MHz, $CDCl_3$) of **3j**



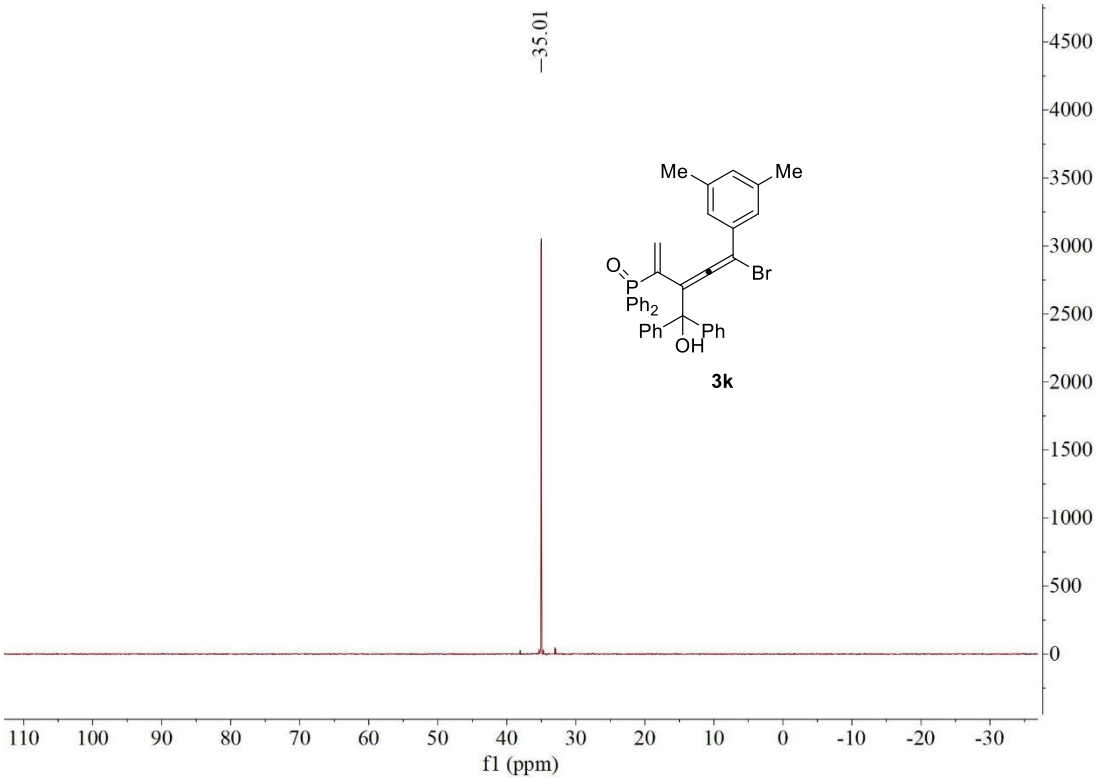
**Compound 3k ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



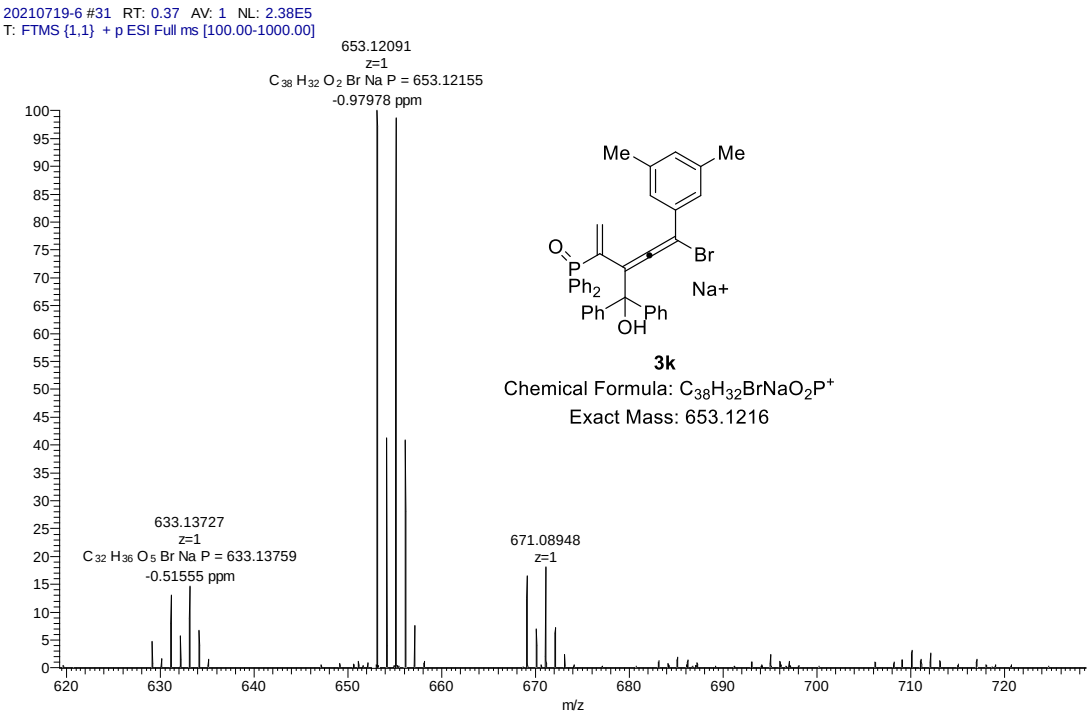

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3k**



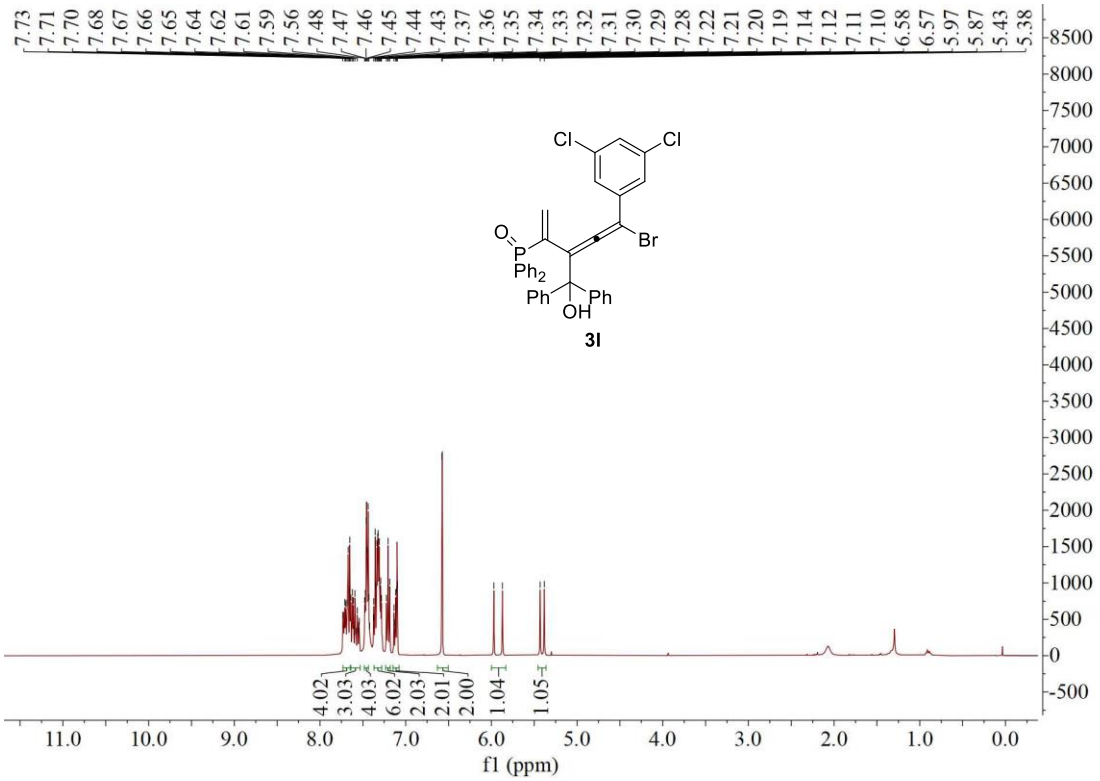

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3k**



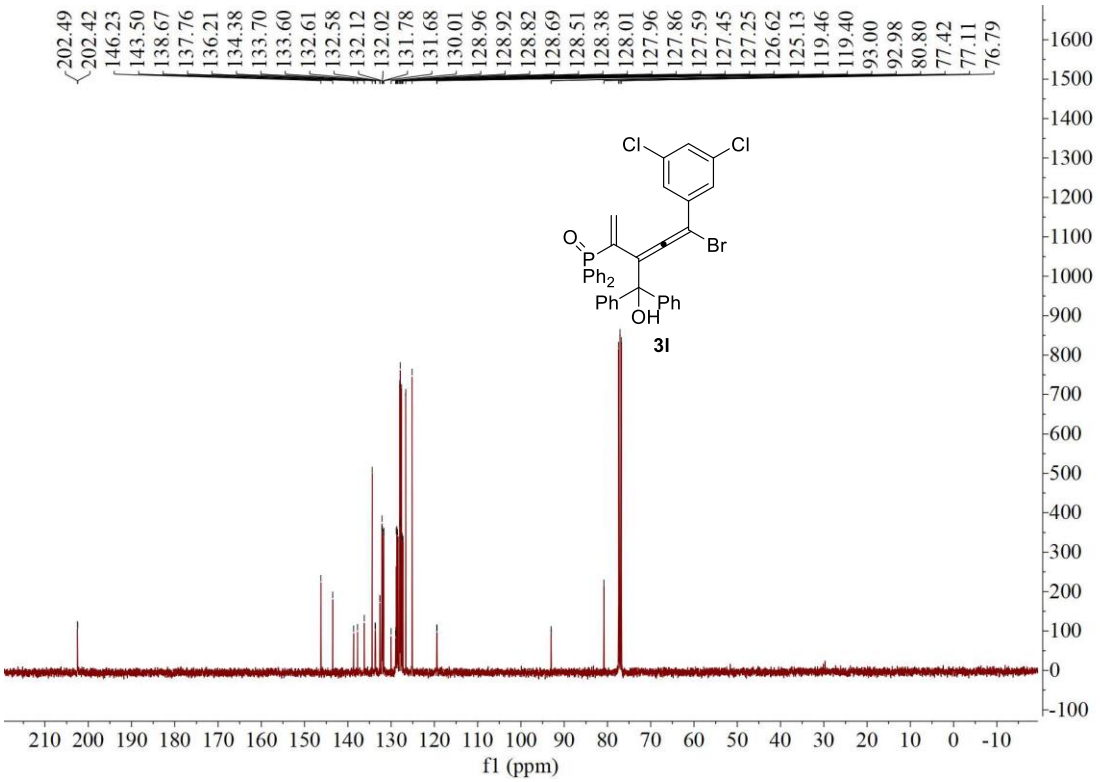

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3k**



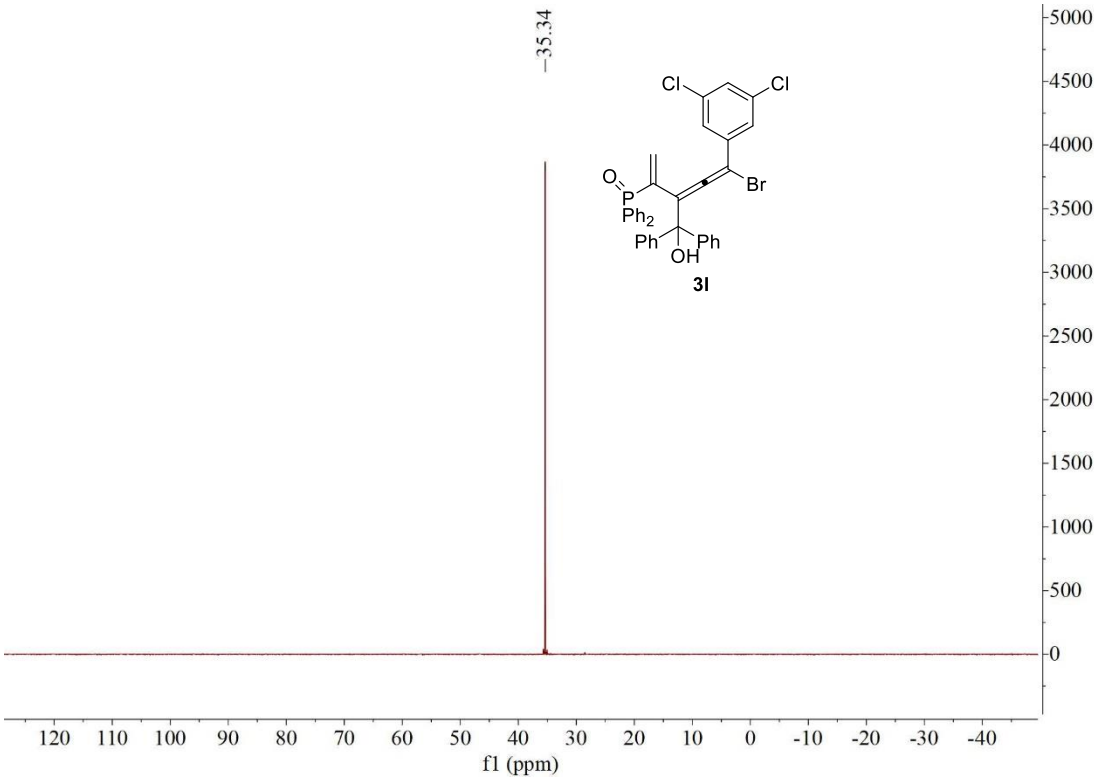
**Compound 3l ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$)**



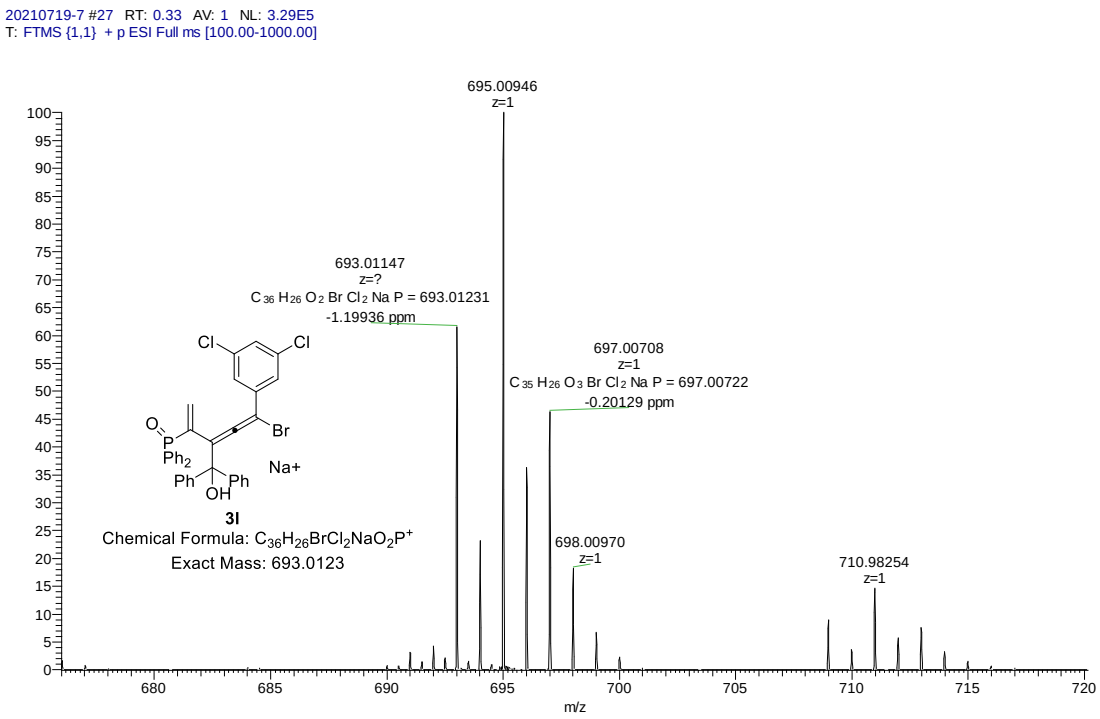

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3l**



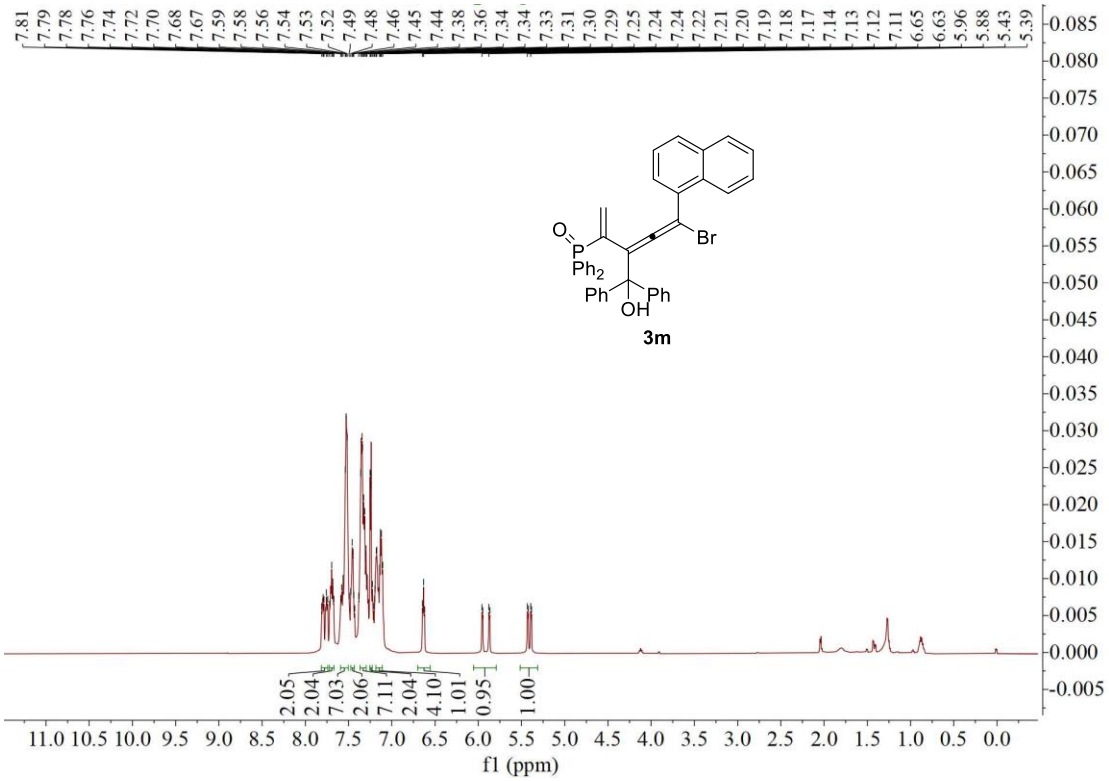

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3l**



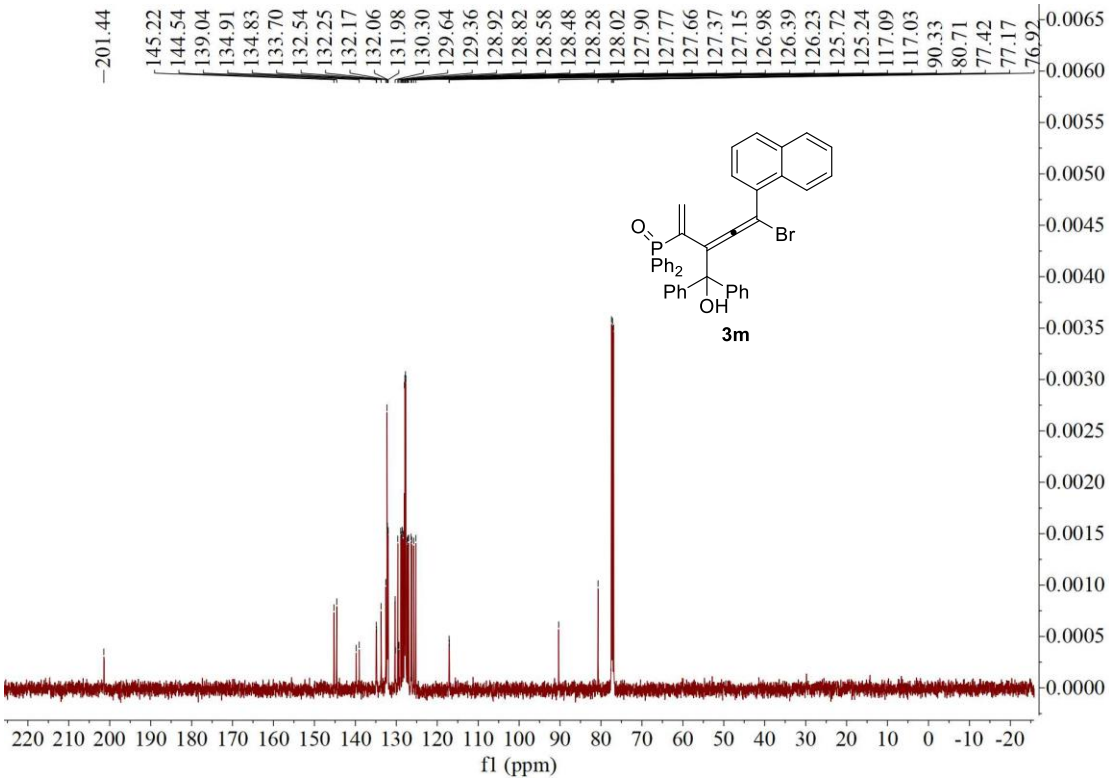

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3l**



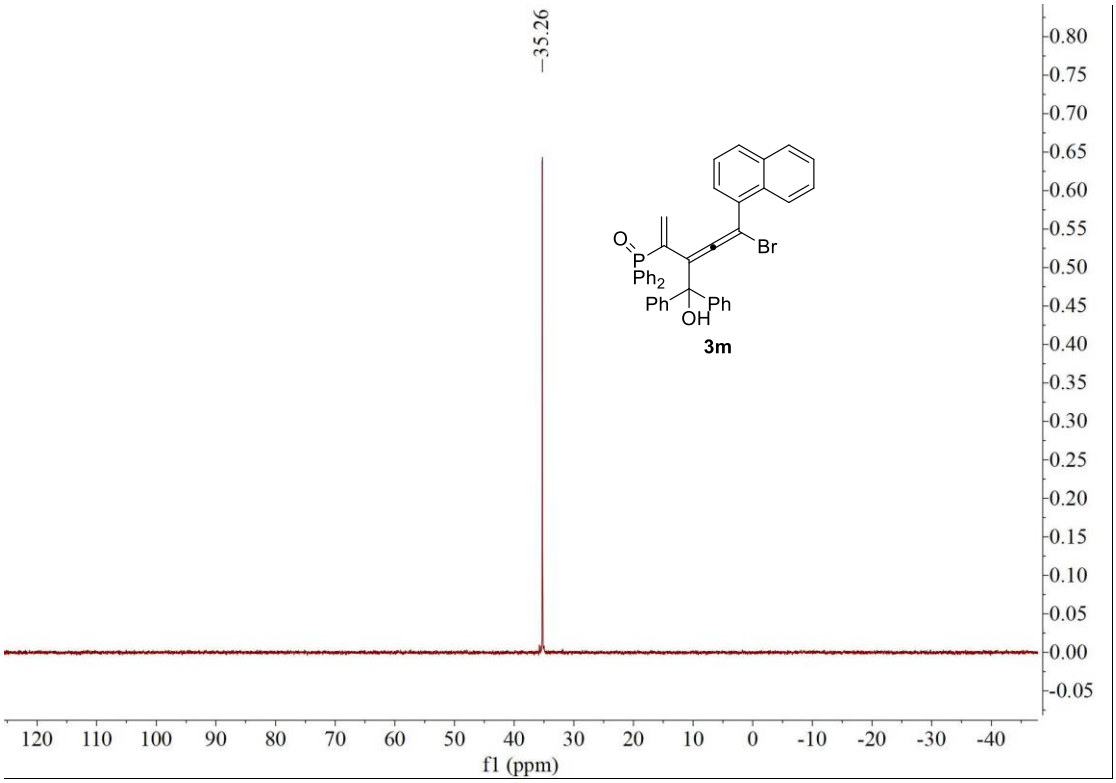
**Compound 3m ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



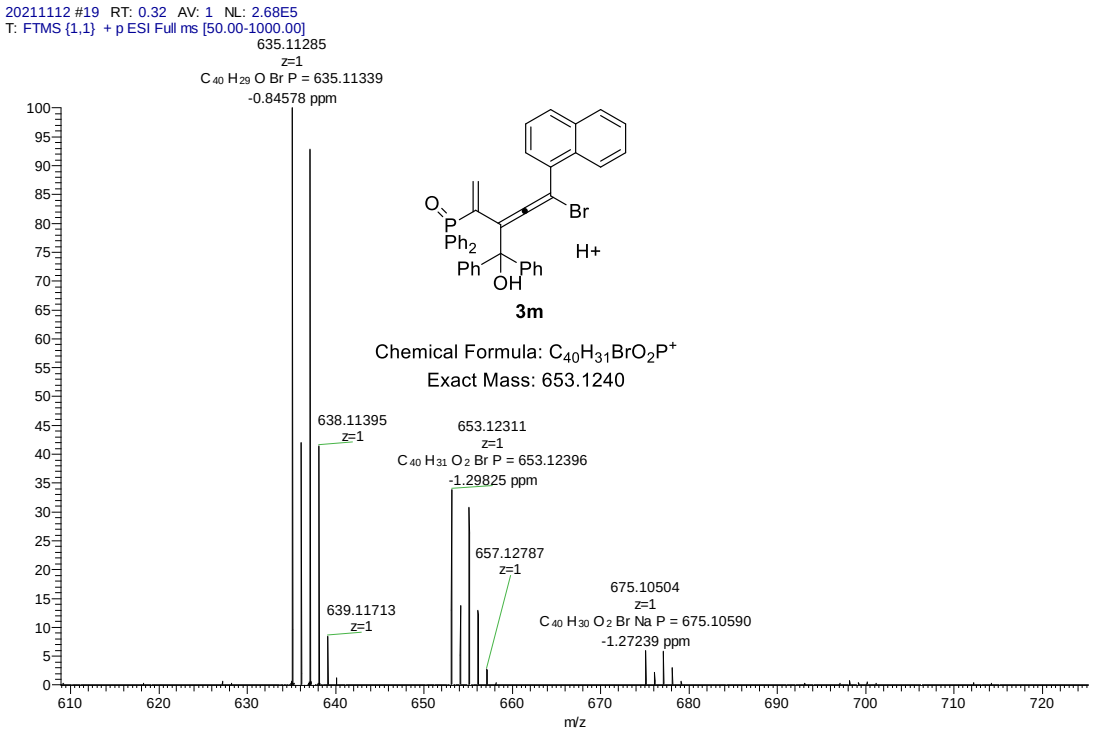

$^{1}$H NMR (500 MHz, $CDCl_3$) of **3m**



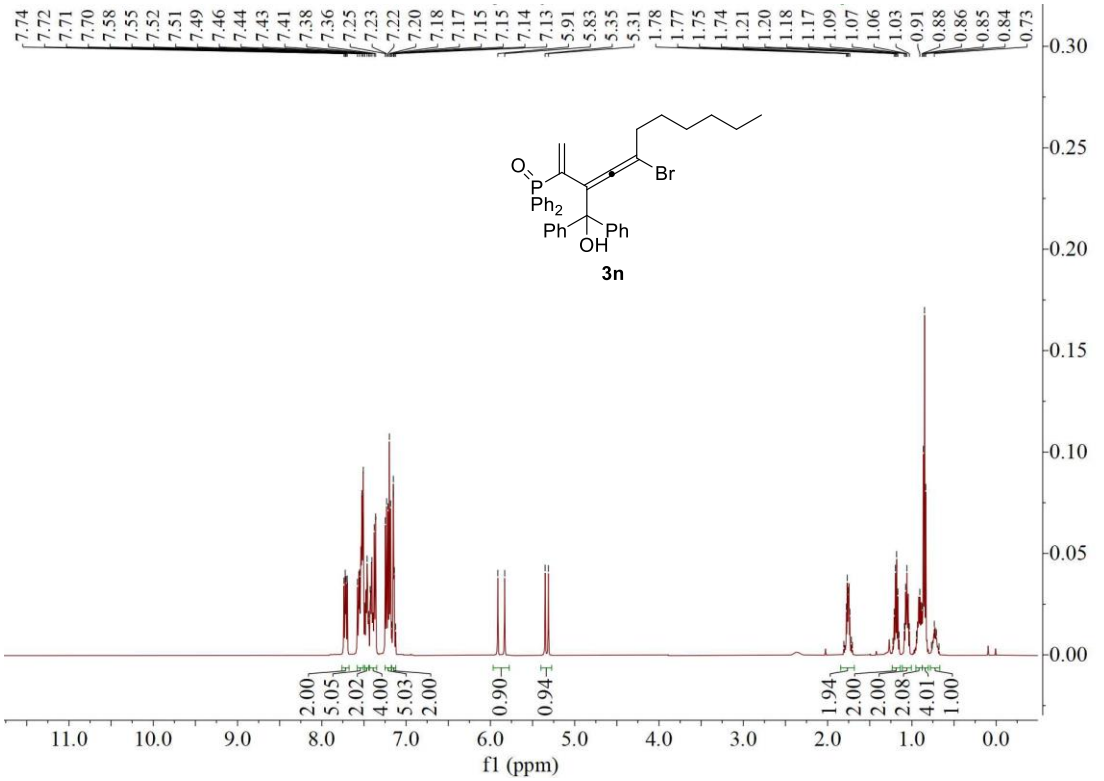

$^{13}$C NMR (126 MHz, $CDCl_3$) of **3m**



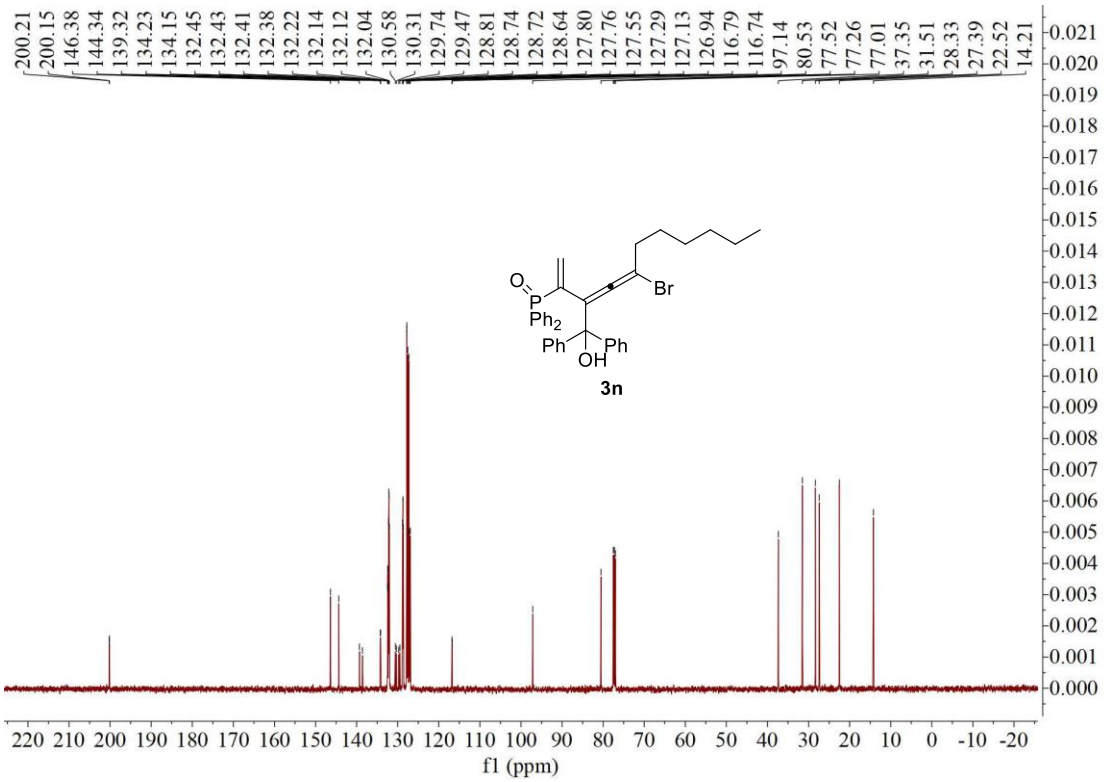

$^{31}$P NMR (202 MHz, $CDCl_3$) of **3m**



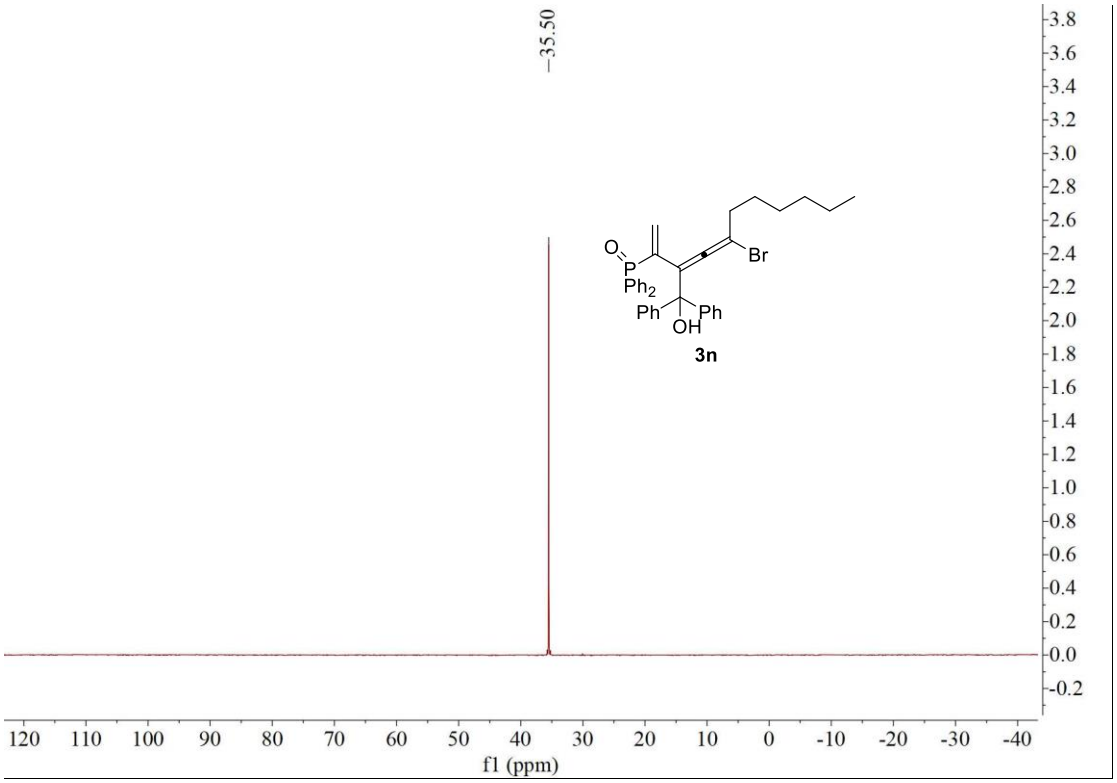
**Compound 3n ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**




$^{1}$H NMR (500 MHz, $CDCl_3$) of **3n**

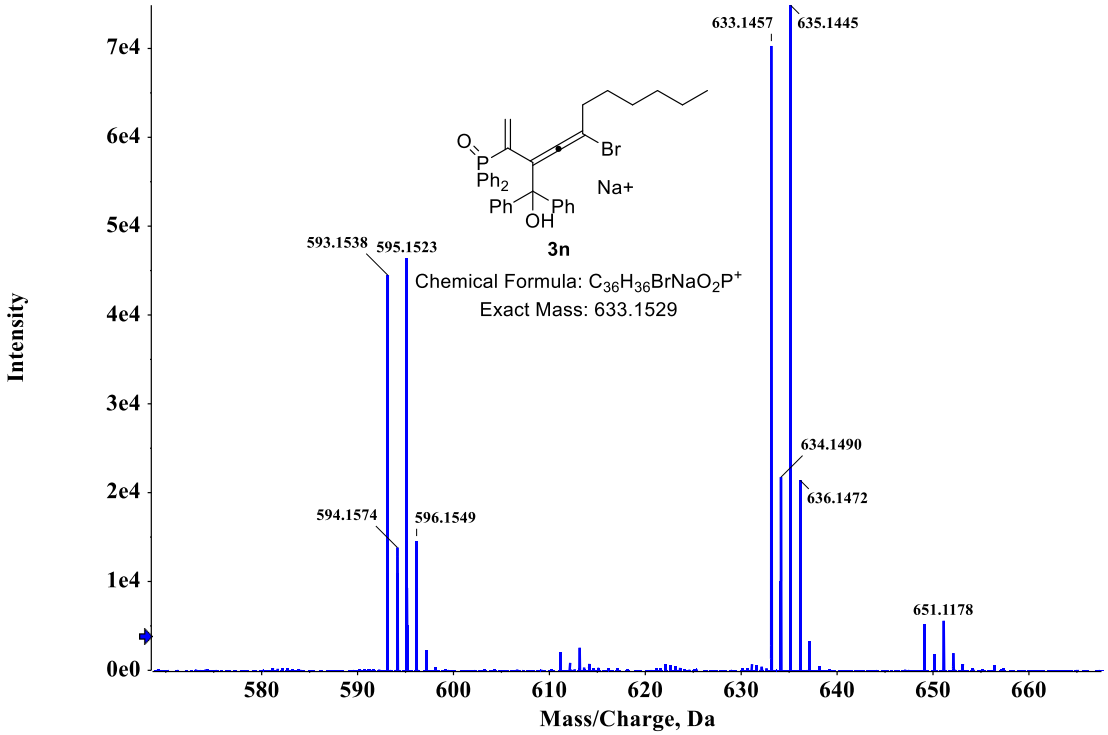



$^{13}$C NMR (126 MHz, $CDCl_3$) of **3n**

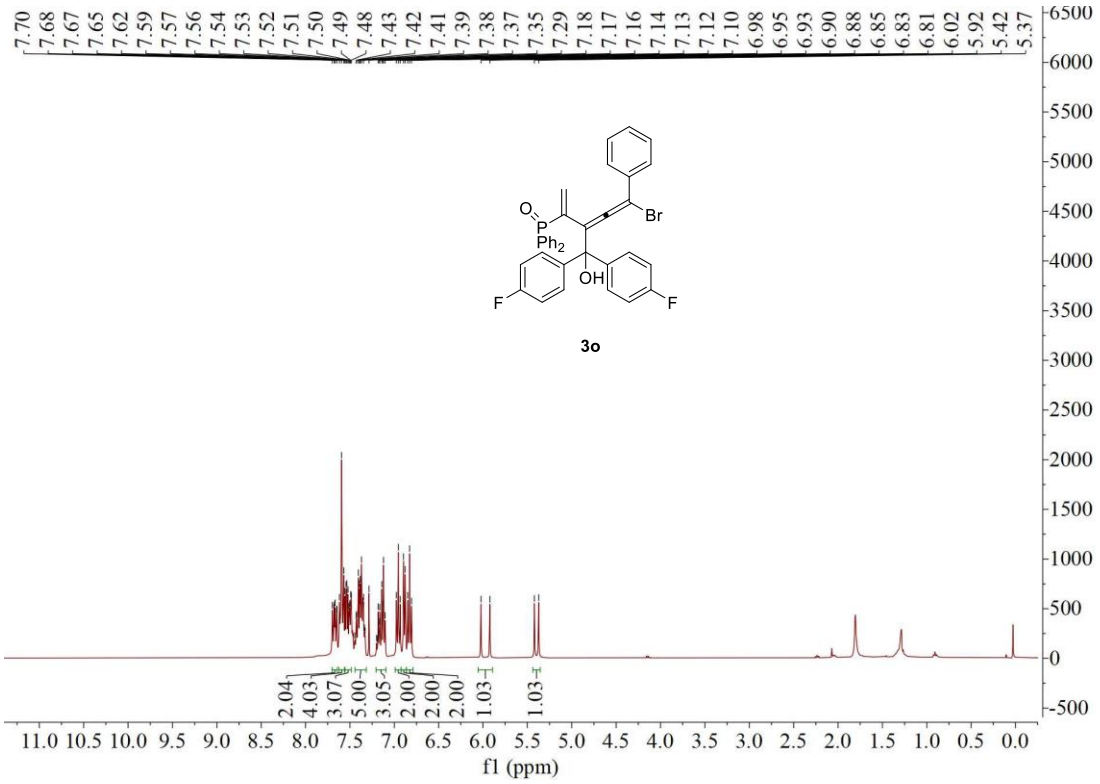



$^{31}$P NMR (202 MHz, $CDCl_3$) of **3n**

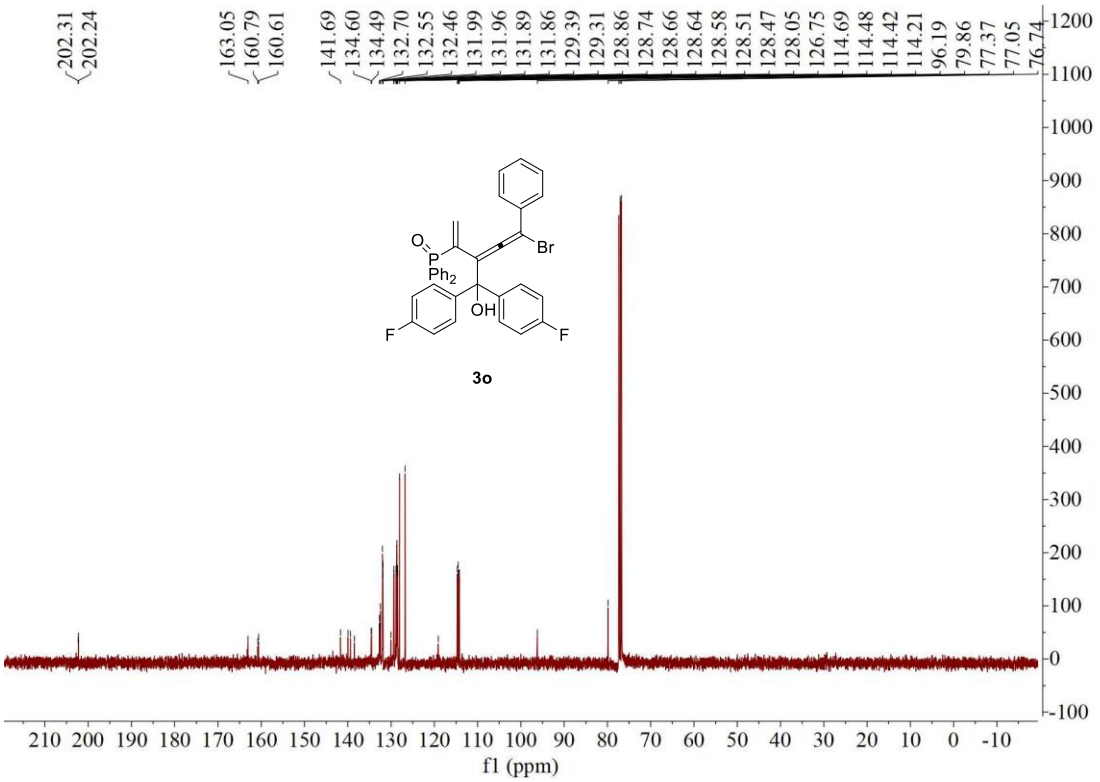
**Spectrum from 1.wiff (sample 1) - Sample001, +TOF MS (100 - 1000) from 0.352 min**



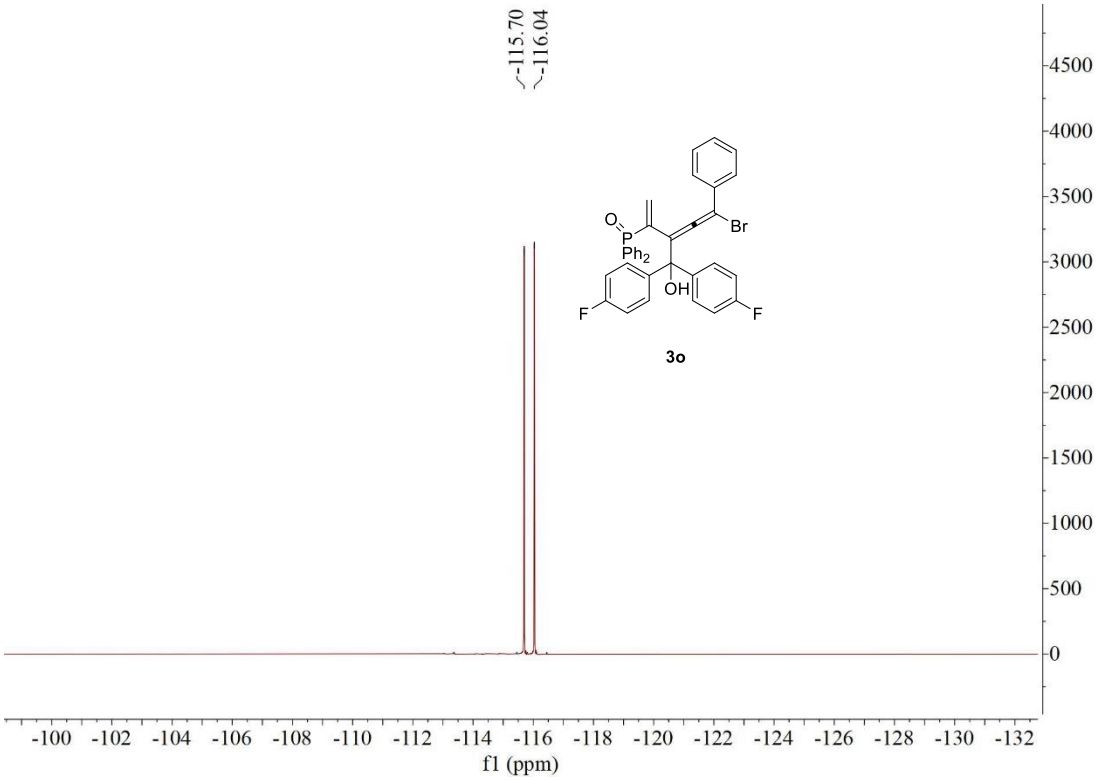
**Compound 3o ($^{1}$H NMR, 400 MHz, $CDCl_3$; $^{13}$C NMR, 101 MHz, $CDCl_3$; $^{31}$P NMR, 162 MHz, $CDCl_3$; $^{19}$F NMR, 376 MHz, $CDCl_3$)**



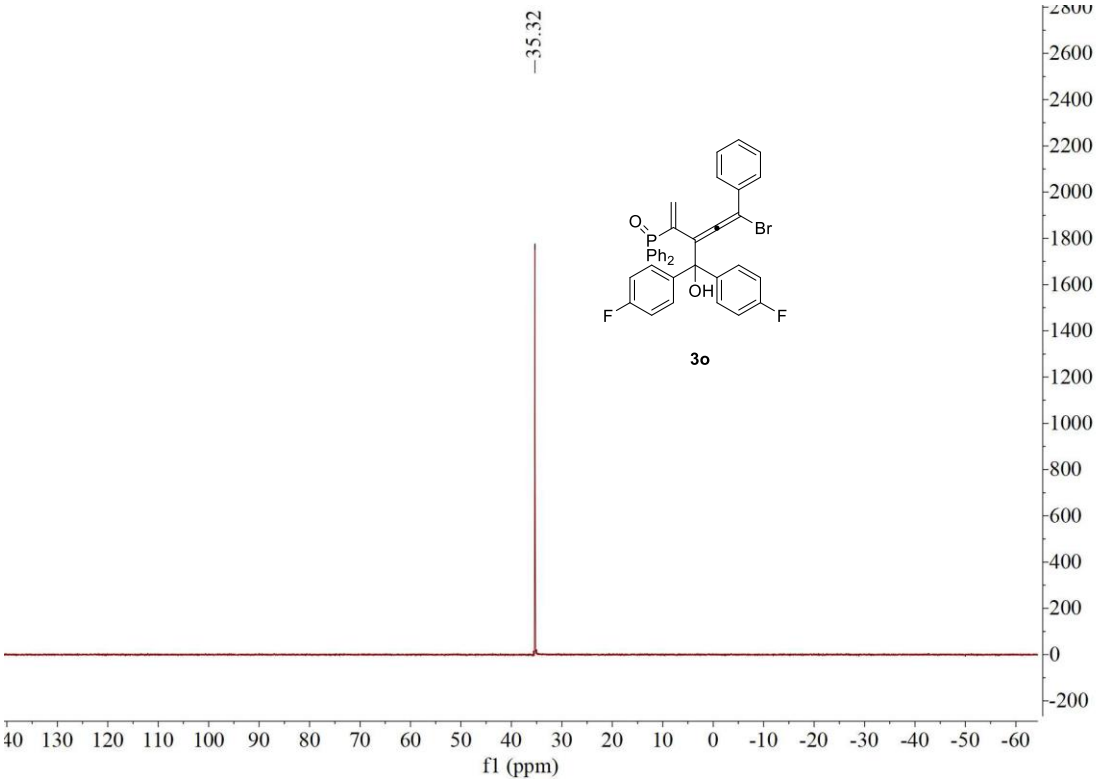

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3o**



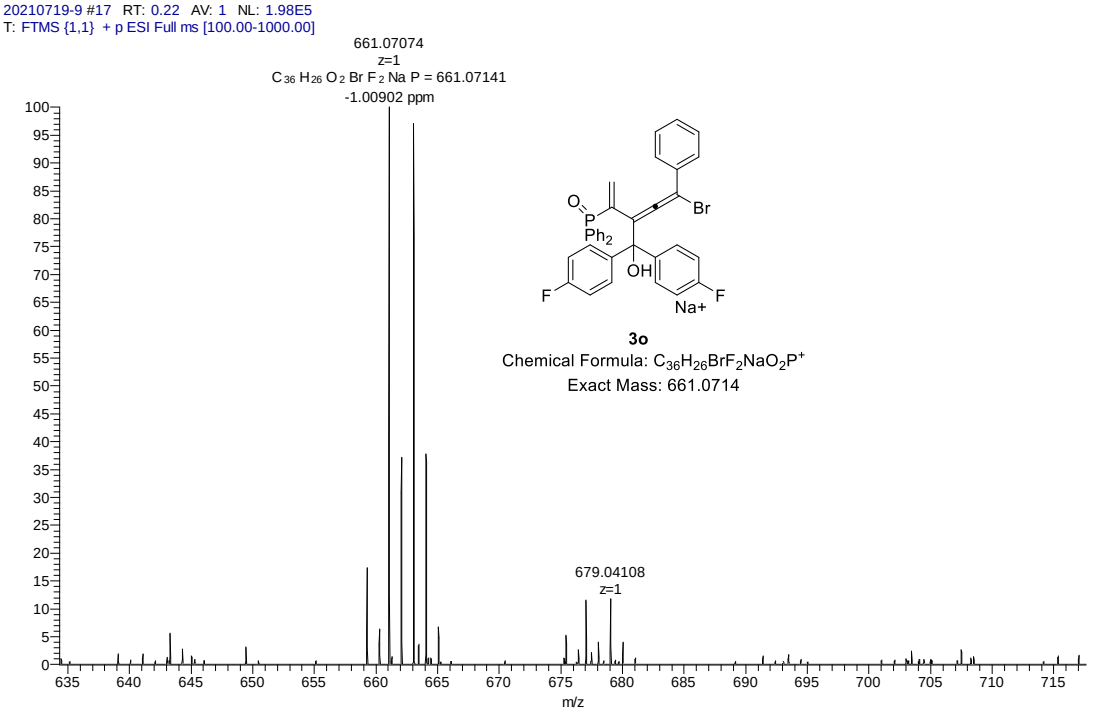

$^{13}$C NMR (101 MHz, $CDCl_3$) of **3o**



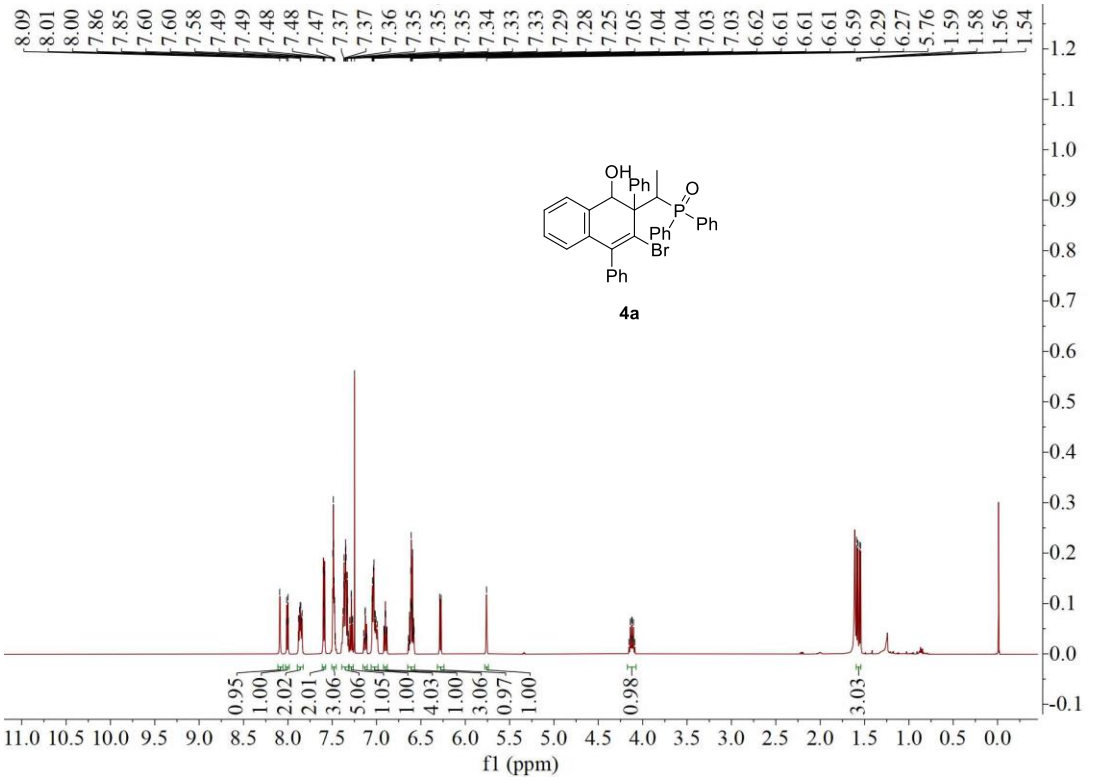

$^{19}$F NMR (376 MHz, $CDCl_3$) of **3o**



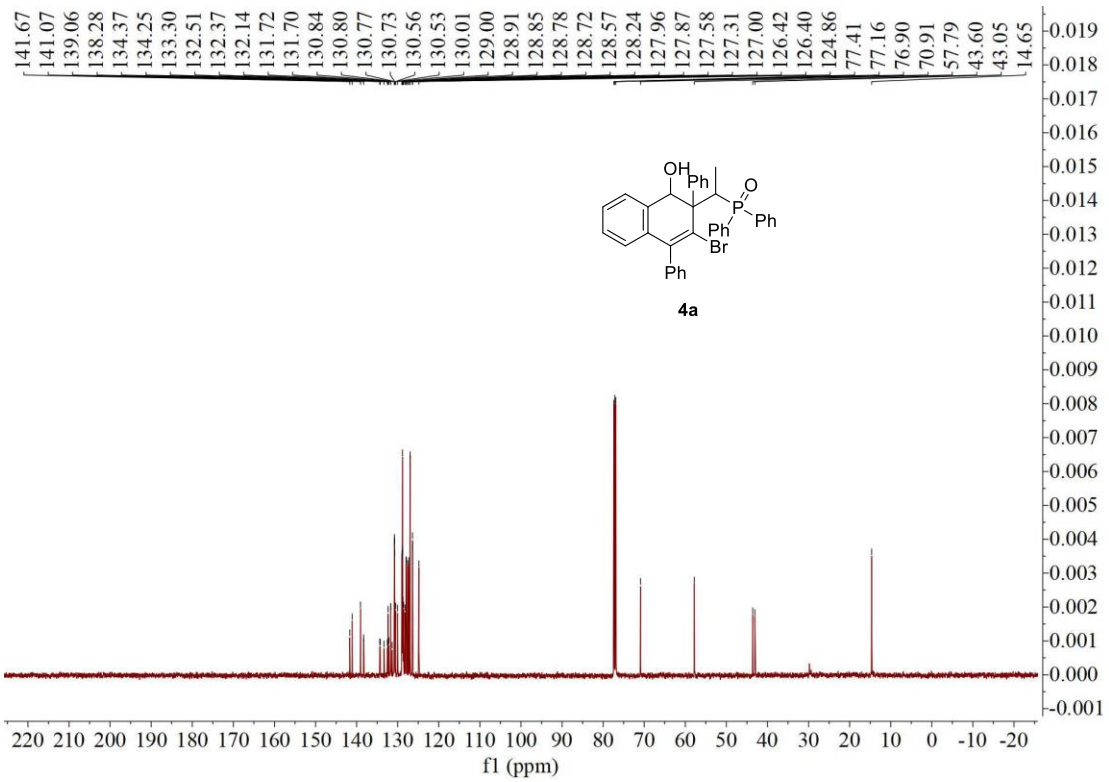

$^{31}$P NMR (162 MHz, $CDCl_3$) of **3o**



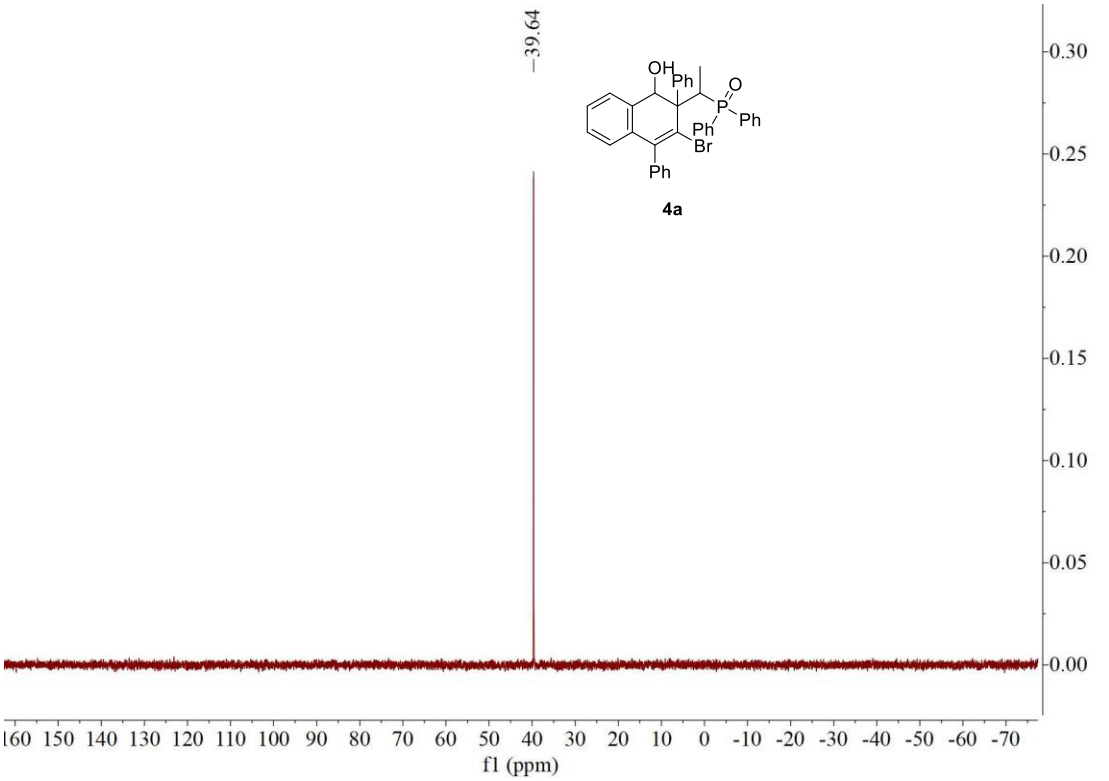

**Compound 4a ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



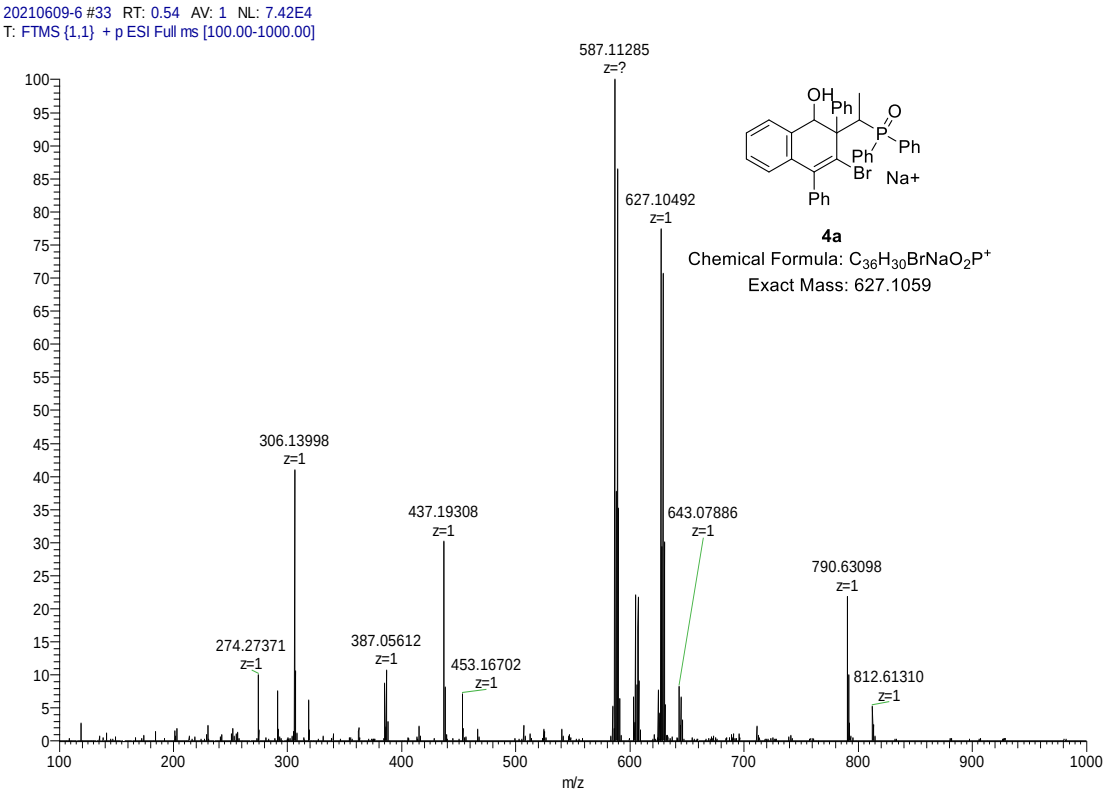

$^{1}$H NMR (500 MHz, $CDCl_3$) of **4a**



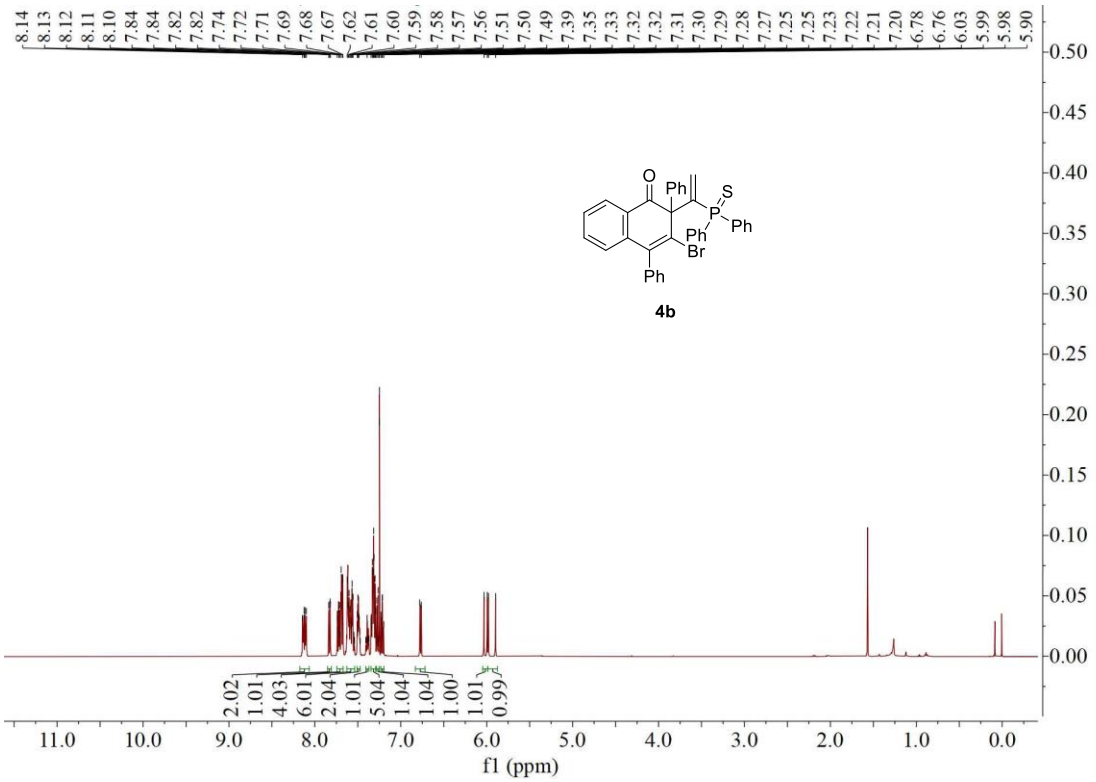

$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4a**



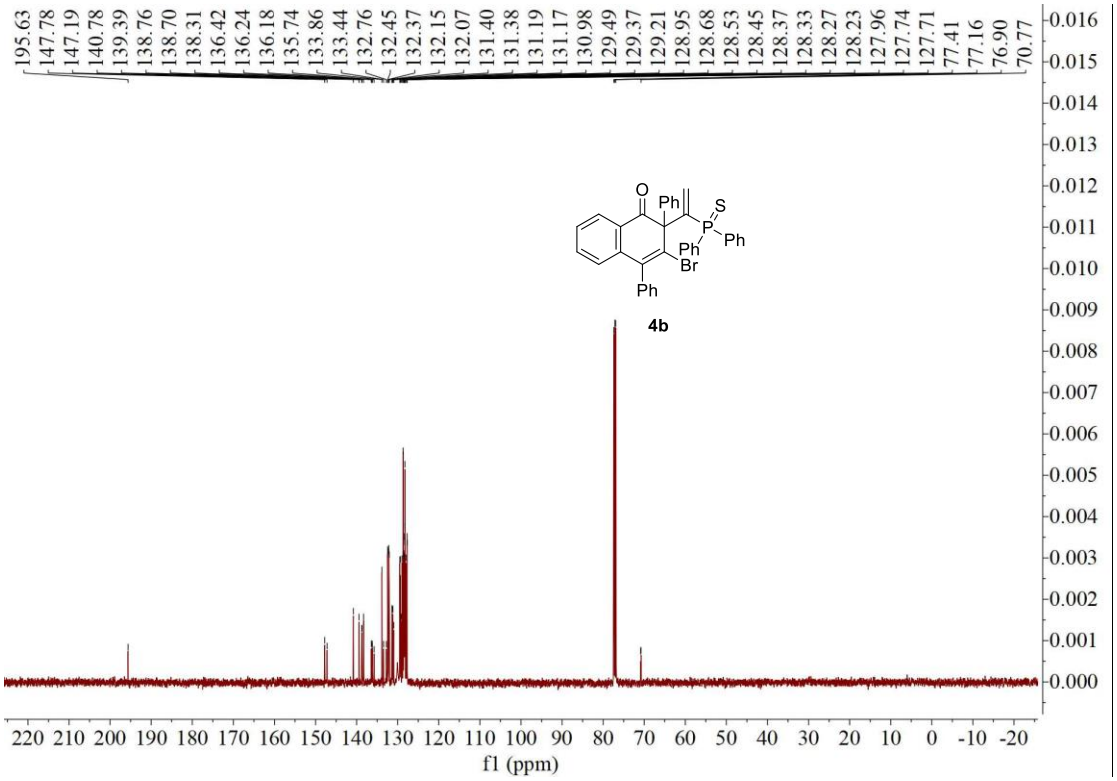

$^{31}P$ NMR (202 MHz, $CDCl_3$) of **4a**



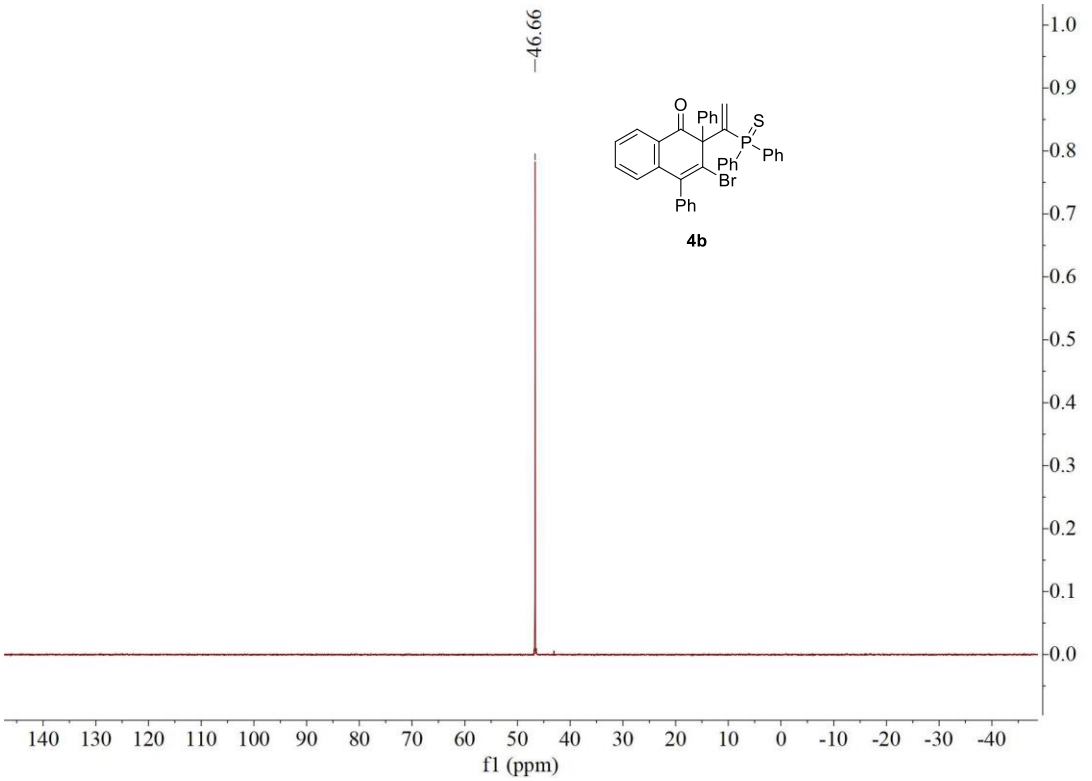

**Compound 4b ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



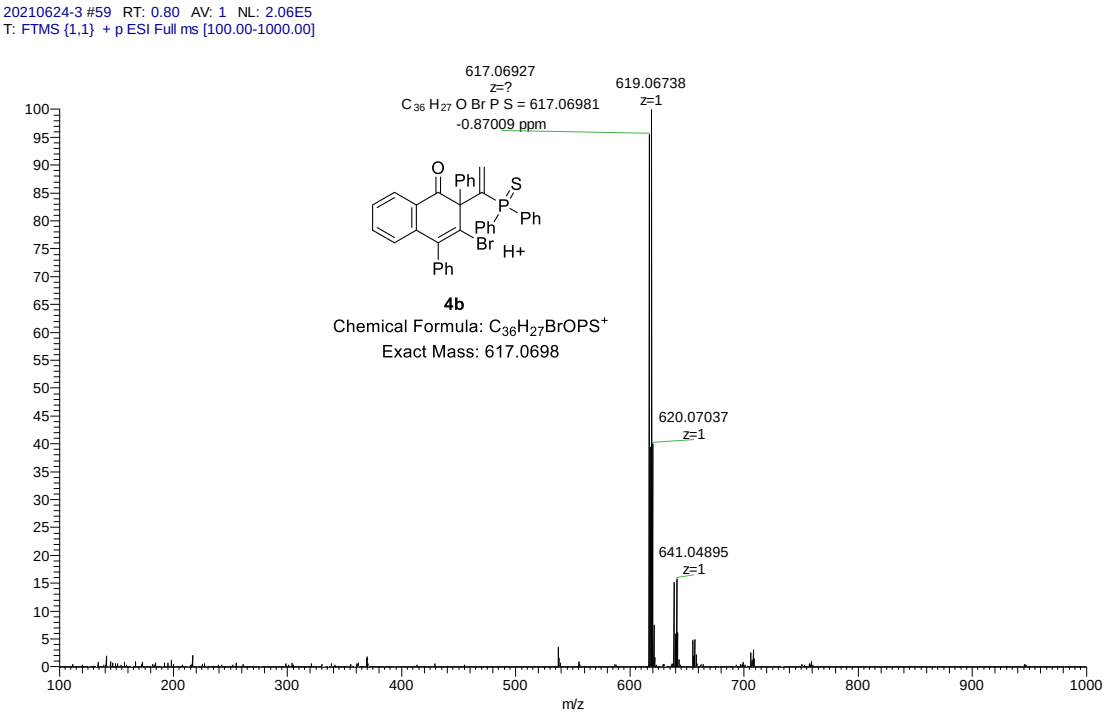

$^{1}$H NMR (500 MHz, $CDCl_3$) of **4b**



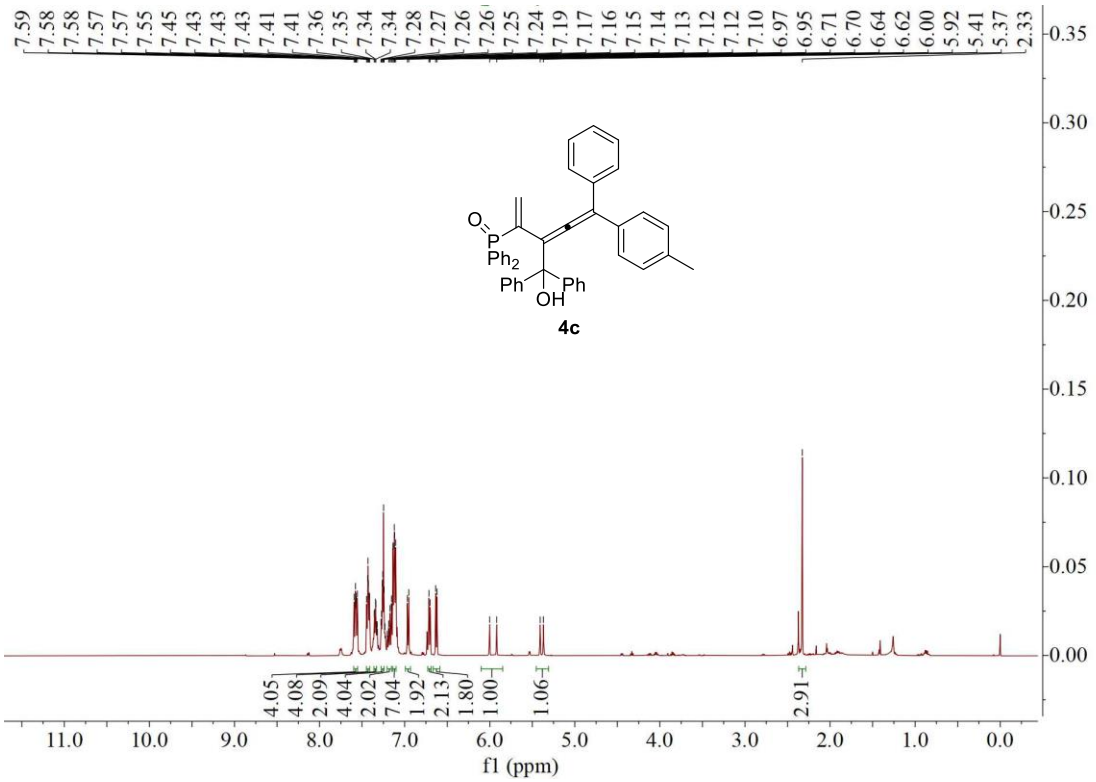

$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4b**



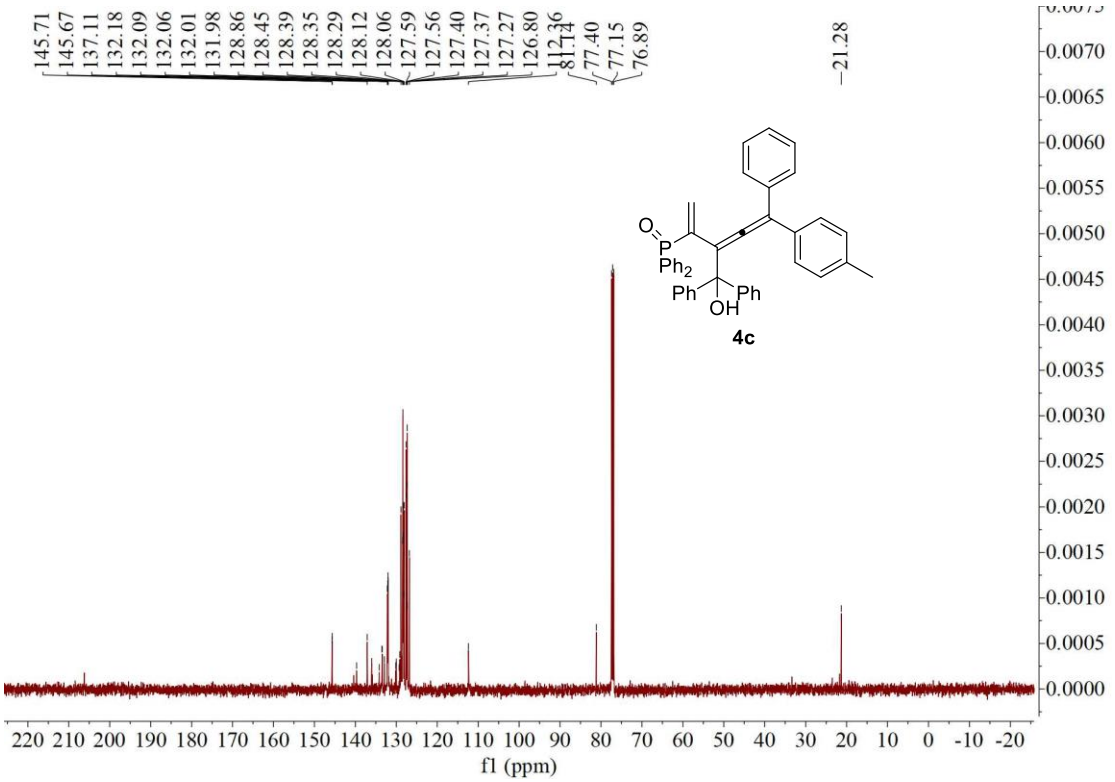

$^{31}P$ NMR (202 MHz, $CDCl_3$) of **4b**



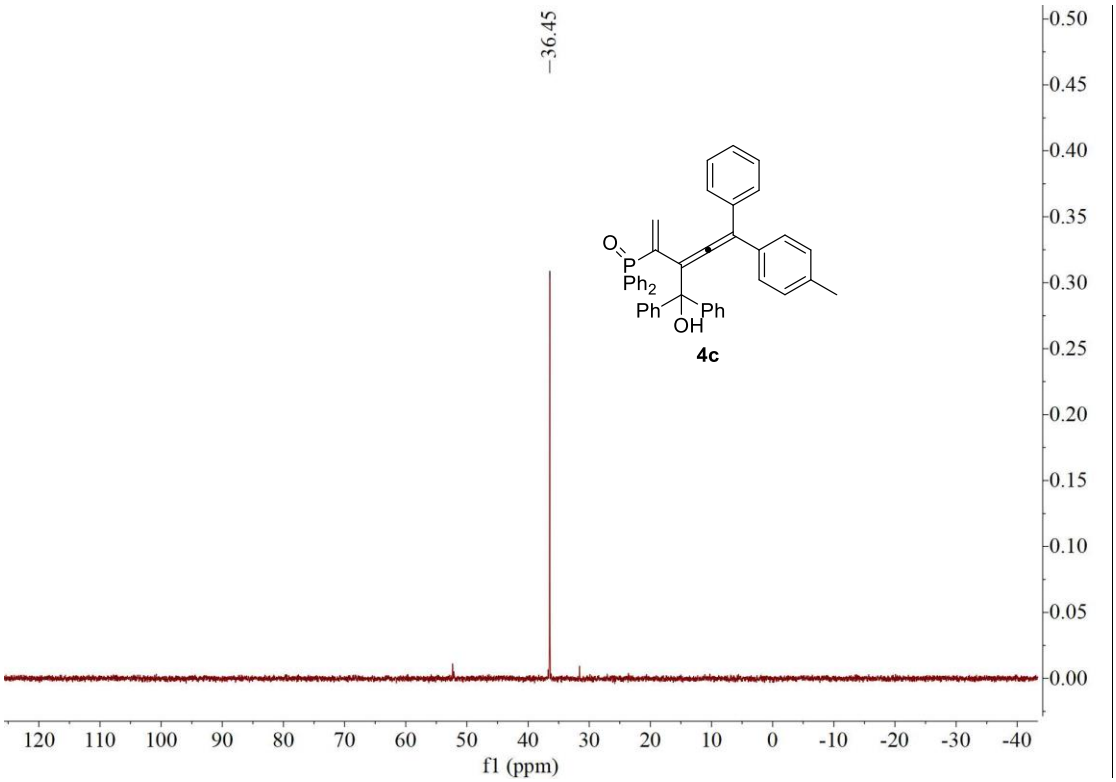

**Compound 4c ($^{1}$H NMR, 500 MHz, $CDCl_3$; $^{13}$C NMR, 126 MHz, $CDCl_3$; $^{31}$P NMR, 202 MHz, $CDCl_3$)**



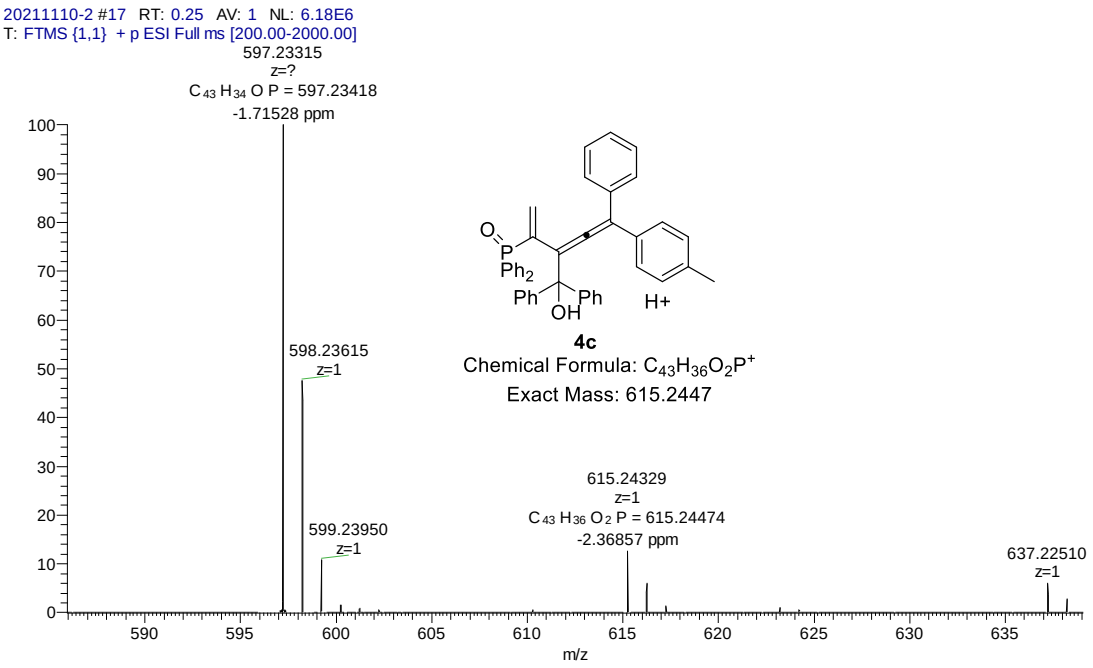

$^{1}$H NMR (500 MHz, $CDCl_3$) of **4c**




$^{13}$C NMR (126 MHz, $CDCl_3$) of **4c**




$^{31}$P NMR (202 MHz, $CDCl_3$) of **4c**


20211110-2 #17 RT: 0.25 AV: 1 NL: 6.18E6
T: FTMS {1,1} + p ESI Full ms [200.00-2000.00]
597.23315
z=?
C 43 H 34 O P = 597.23418
-1.71528 ppm
598.23615
z=1
599.23950
z=1
615.24329
z=1
C 43 H 36 O 2 P = 615.24474
-2.36857 ppm
637.22510
z=1
O
P
Ph2
Ph
OH
Ph
H+
4c
Chemical Formula: C43H36O2P+
Exact Mass: 615.2447
m/z