Supporting information for

Stepwise Photosensitized C(sp^3)-C(CO) Bond Cleavage and C-P Bond Formation of 1,3-Dicarbonyls with Arylphosphine Oxides

Xiuli Zhao,[#] Mengmeng Huang,[#] Yabo Li, Jianye Zhang, Jung Keun Kim,* and Yangjie Wu*

College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P.R. China.

Contents:

1. General information

All reactions were performed under Ar atmosphere using quartz tube. Organophosphorous reagents **2a-c** and 1,3-dicarbonyl compound **1a** were purchased from commercial suppliers and used without further purification. (Hetero)Aryl substituted 1,3-diketones **1b-1s** were prepared according to the literature procedures.[1] Silica gel was purchased from Qing Dao Hai Yang Chemical Industry. ^{1}H NMR and ^{13}C NMR spectra was recorded on a Bruker DPX-400 spectrometer with solvent signals as internal reference .^{31}P NMR spectra was recorded at 160 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to H_3PO_4 (δ = 0 ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. Coupling constants *J* are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/VIS Absorption spectra was recorded in DMSO on a Perkin Elmer Lambda 35 Spectrometer. The Cyclic voltammetry (CV) was recorded in DMSO by CHI650A. The Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer in DMSO.

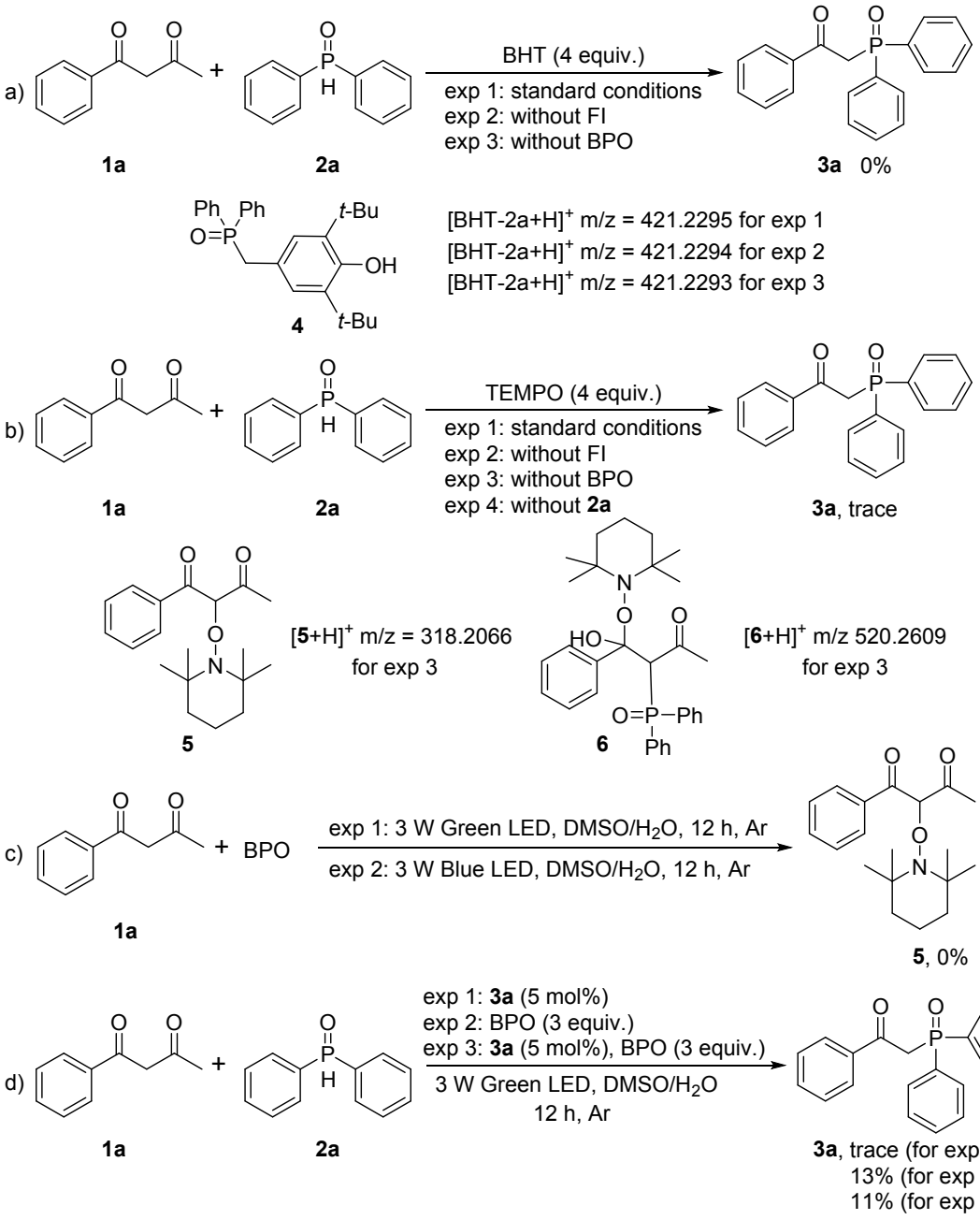
2. Experimental Procedure

Synthesis of *β*-ketophosphine oxides (3). 1-phenylbutane-1,3-dione (0.2 mmol), diphenylphosphine oxide (0.6 mmol), FI (0.01 mmol) and benzoyl peroxide (BPO) (wetted with ca. 25% H_2O, 0.6 mmol) were combined in DMSO / H_2O (1.6 mL / 0.4 mL) in Ar atmosphere. The mixture was stirred at room temperature under green LED lamp (3 W) for 12 hours. The reaction mixture was purified by chromatography on silica gel (elute: EtOAc / Petroleum ether 1 / 1-3 / 1, v / v) to give the desired product.

Synthesis of 3-$EuCl_3$ (7) complexes. General procedure for $EuCl_3$-**3** complexes described here. β-Ketophosphine oxides **3** (50 mg, 0.15 mmol) and 1/3 molar equivalent of $EuCl_3 \cdot 6H_2O$ were dissolved in CH_3CN (~15 mL) and stirred at room temperature for thirty minutes. The solvent was removed under reduced pressure, and the crude product is washed three times with ether to obtain white powders**.**

3. Control Experiments

Scheme S1. Control experiments



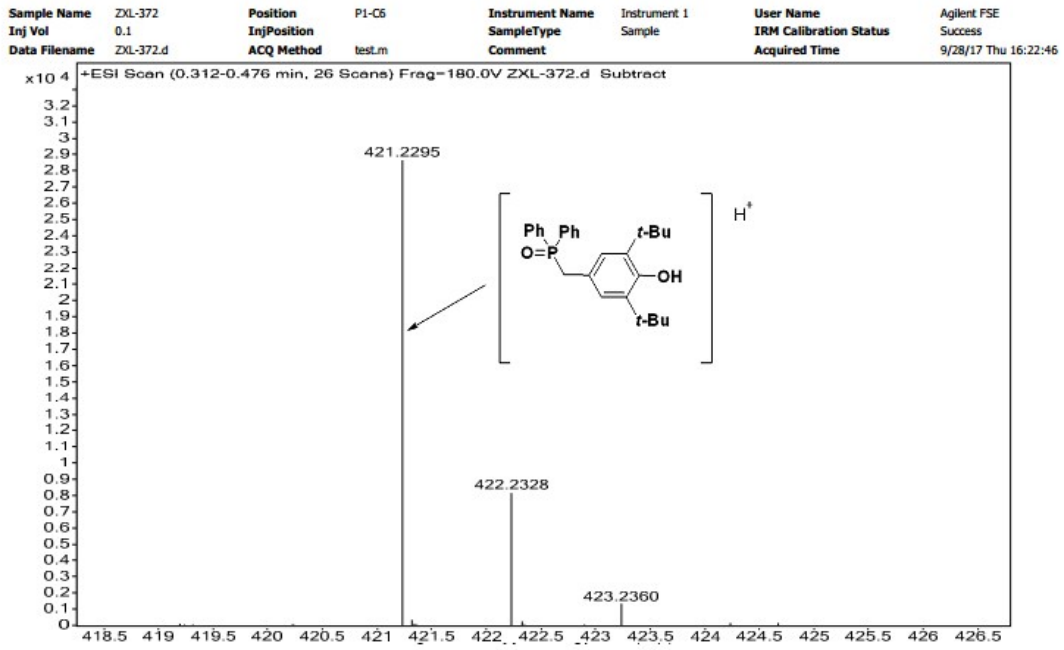


Figure S1 HRMS spectrum of compound [**4**+H]$^+$ for exp 1

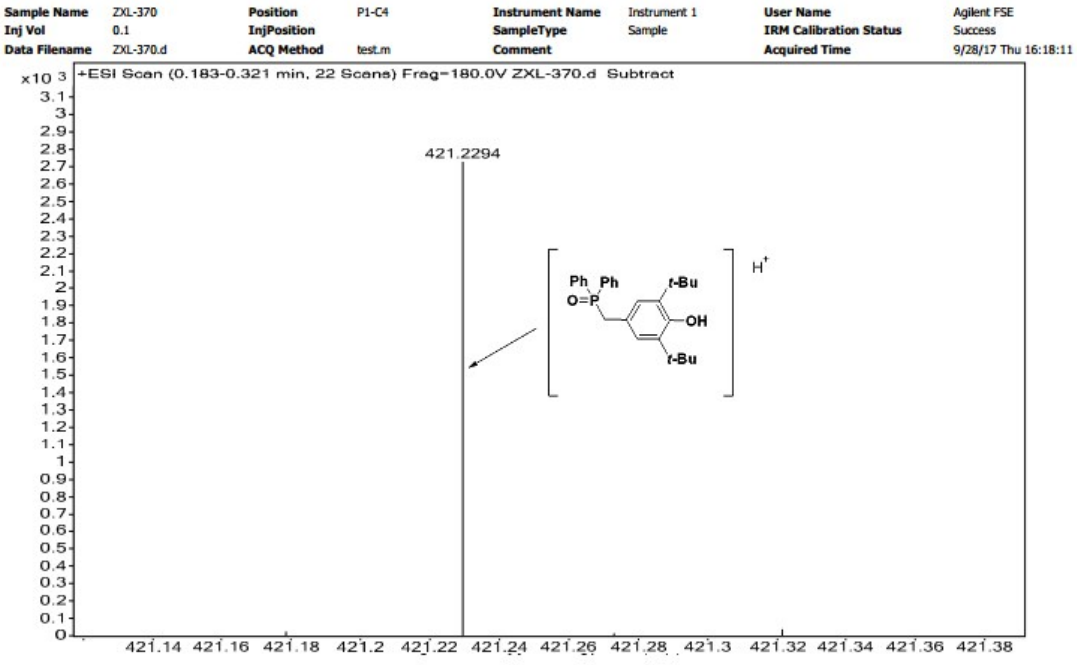


Figure S2 HRMS spectrum of compound [**4**+H]$^+$ for exp 2

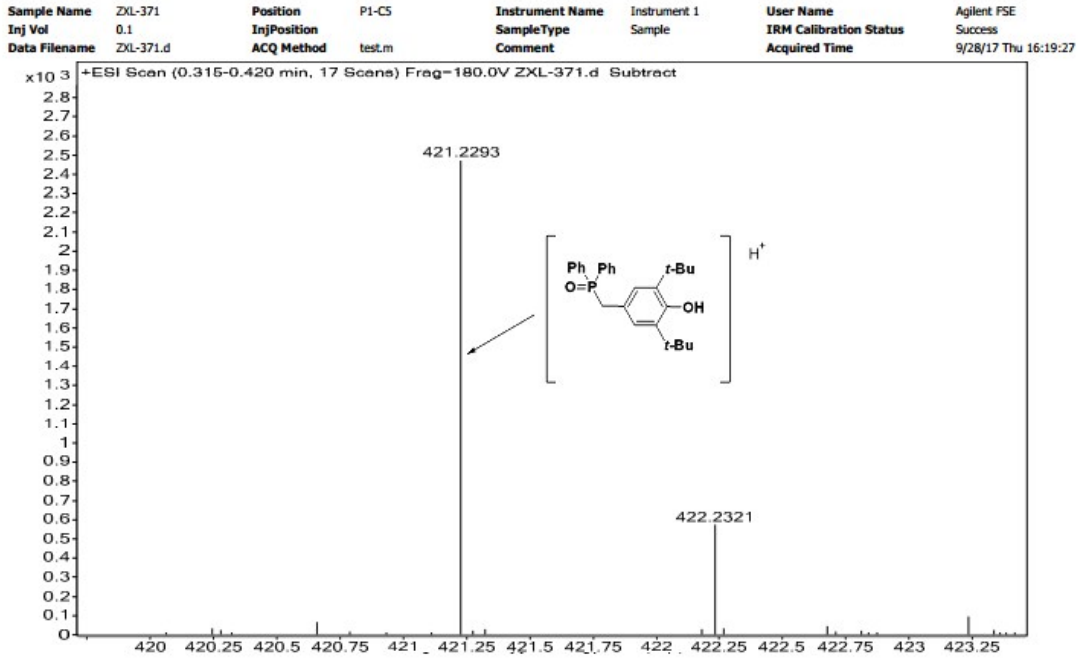


Figure S3 HRMS spectrum of compound [**4**+H]$^+$ for exp 3

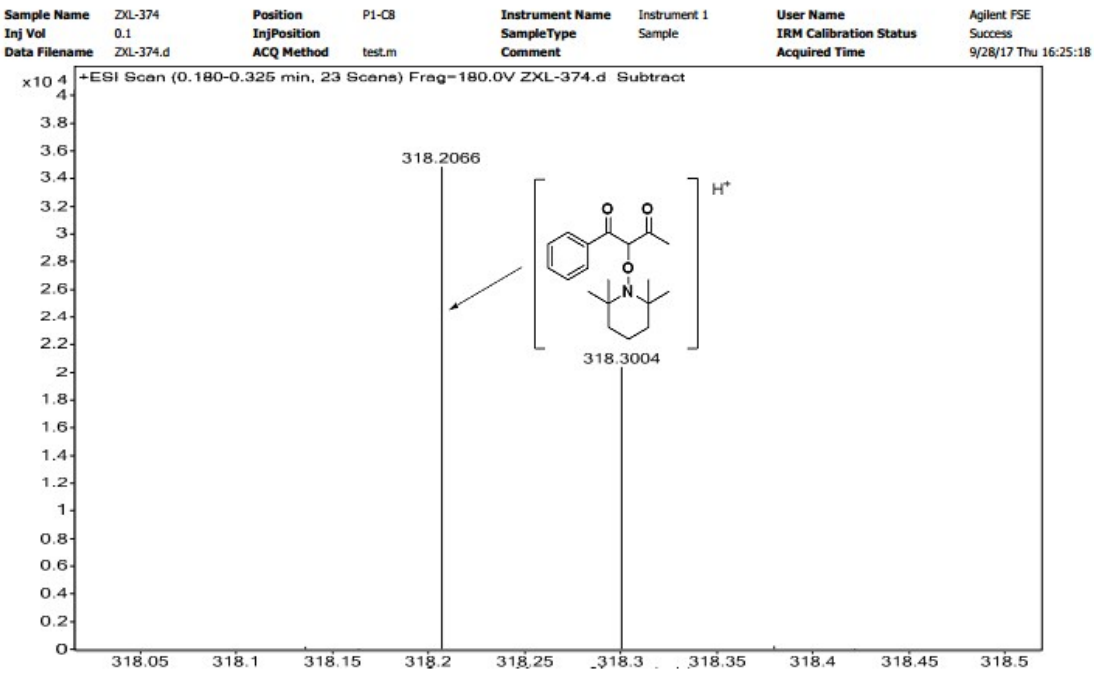


Figure S4 HRMS spectrum of compound [**5**+H]$^+$ for exp 3

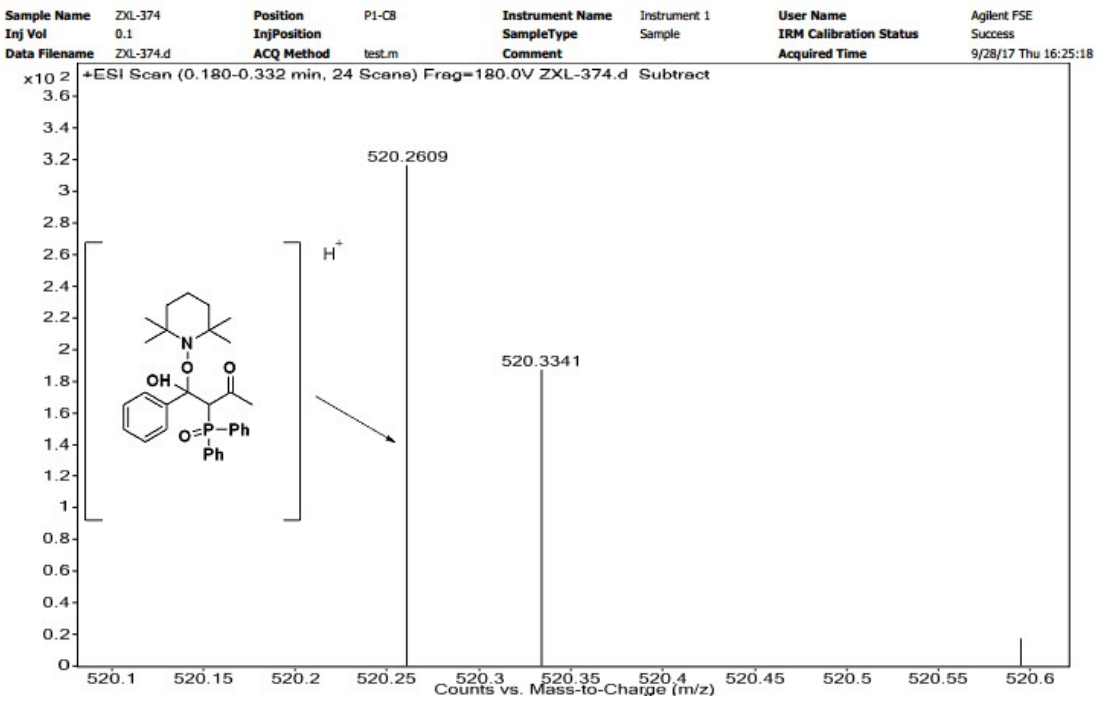
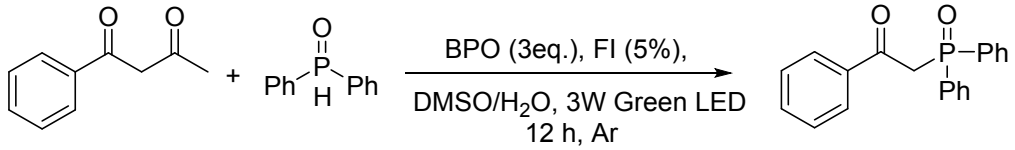


Figure S5 HRMS spectrum of compound [**6**+H]$^+$ for exp 3

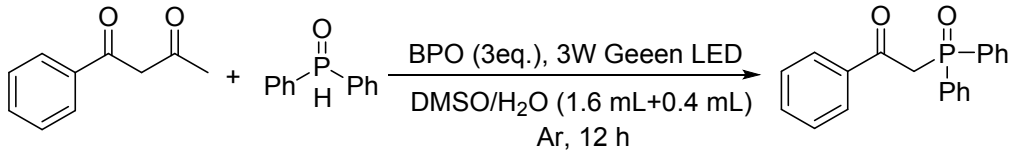
Scheme S2. The Yield of **3a** use different volume ratio of DMSO and H_2O



1a **2a** **3a**

entry	solvent	Yield (%)
1	DMSO	48
2	DMSO/H_2O (1.95 mL+0.05 mL)	49
3	DMSO/H_2O (1.90 mL+0.10 mL)	60
4	DMSO/H_2O (1.85 mL+0.15 mL)	60
5	DMSO/H_2O (1.80 mL+0.20 mL)	62
6	DMSO/H_2O (1.60 mL+0.40 mL)	77
7	DMSO/H_2O (1.50 mL+0.50 mL)	60

Scheme S3. Photocatalytic activity of BPO



1a **2a** **3a**

entry	Light	Yield(%)
1	3W green LED	13%
2	3W blue LED	71%
3	3W yellow-green LED	18%

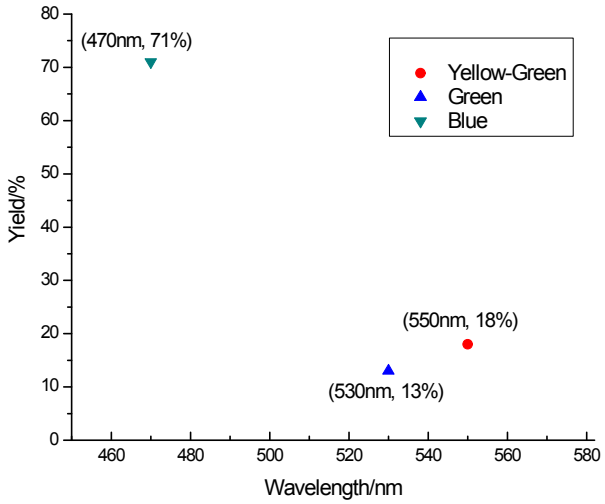


Figure S6. Photocatalytic activity of BPO

4. UV/VIS Absorption spectra, Cyclic Voltammetry, Luminescence Quenching Experiments and Data processing of compounds 3

1) UV/VIS Absorption spectra

The UV/VIS Absorption spectra was recorded in DMSO of a 0.1 M solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

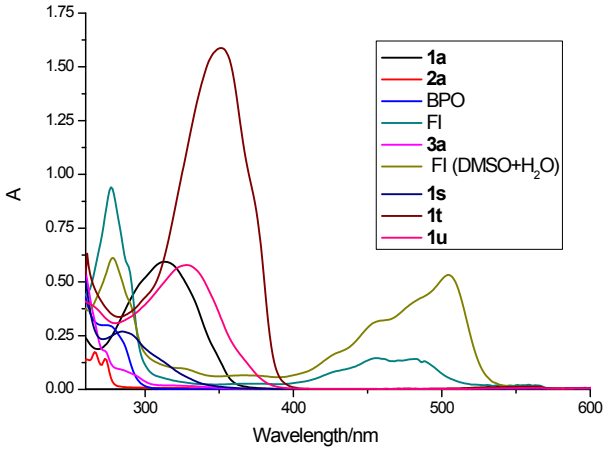


Figure S7. Absorption spectra of 1-phenylbutane-1,3-dione **1a** (λ_{max} = 357 nm), diphenylphosphine oxide **2a** (λ_{max} = 281 nm), **FI**(λ_{max} = 512 nm), **BPO** (λ_{max} = 298 nm), **3a** (λ_{max} = 259nm), ethyl 3-oxo-3-phenylpropanoate **1s** (λ_{max} = 335 nm), 1,3-diphenylpropane-1,3-dione **1t** (λ_{max} = 335 nm), 1-(thiophen-2-yl)butane-1,3-dione **1u** (λ_{max} = 391 nm), in DMSO (0.1 mM). **FI** (λmax = 531 nm, in DMSO/H_2O, 0.1 mM).

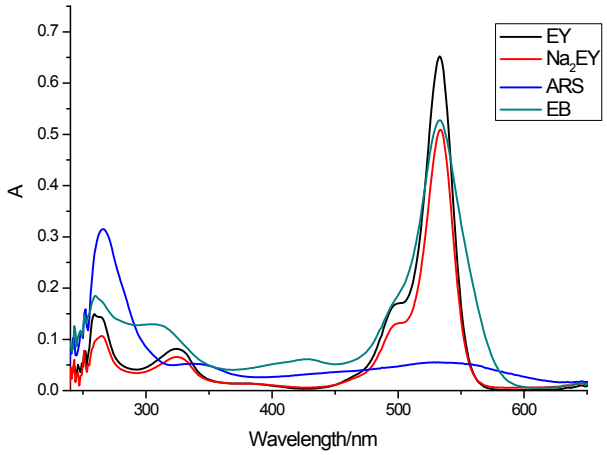


Figure S8. Absorption spectras of different photocatalyst: EY (λmax = 557 nm), Na_2EY (λmax = 556 nm), ARS (λ_{max} = 620 nm), EB (λ_{max} = 579 nm), in DMSO (0.1 mM)

2) Cyclic Voltammetry

Cyclic voltammetry was measured under Ar atmosphere with a Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M $TBAPF_6$ in DMSO) at 50 mV/sec of scan rate.

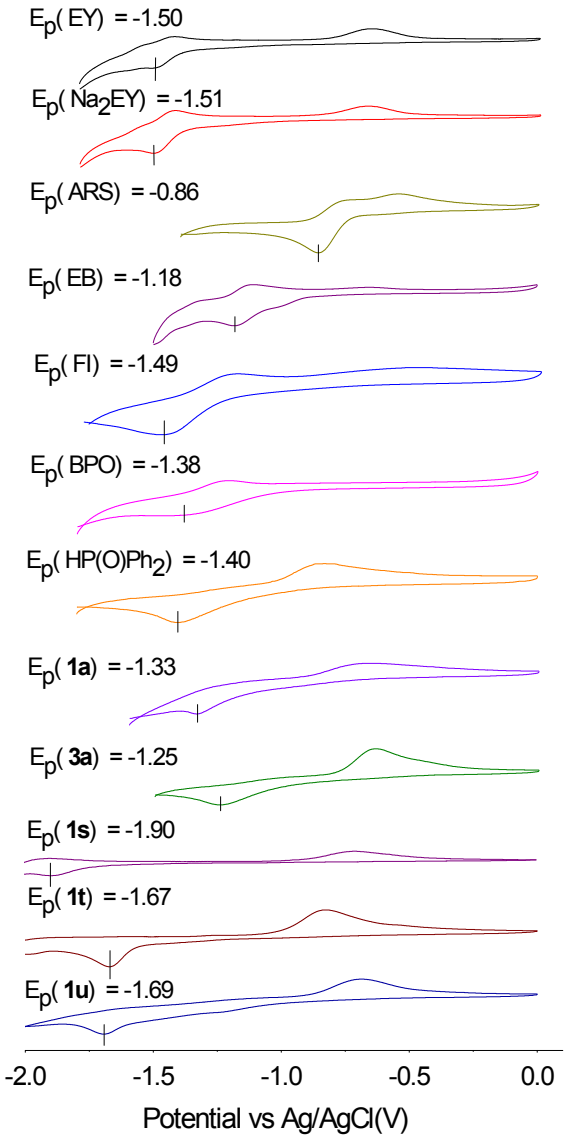


Figure S9. CV of Reaction reagents (1 mM in DMSO)

3) Luminescence Quenching Experiments

Emission intensities were recorded using a F-4500 FL Spectrophotometer. First, all FI solutions were excited at 450 nm and the emission intensity at 460 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of FI and different concentration of 1-phenylbutane-1,3-dione **1a**, diphenylphosphine oxide **2a** and BPO in DMSO in 10 mm path length quartz cuvette was collected. The BPO solution was excited at 260 nm and the emission intensity at 280 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of BPO and different concentration (0.010~0.125 mM) of diphenylphosphine oxide **2a** in DMSO in 10 mm path length quartz cuvette was collected.

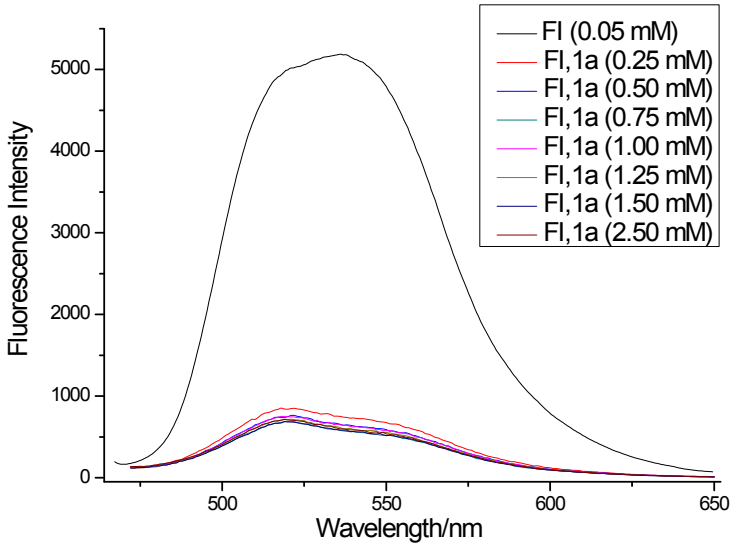


Figure S10. Luminescence quenching experiments of FI with **1a**

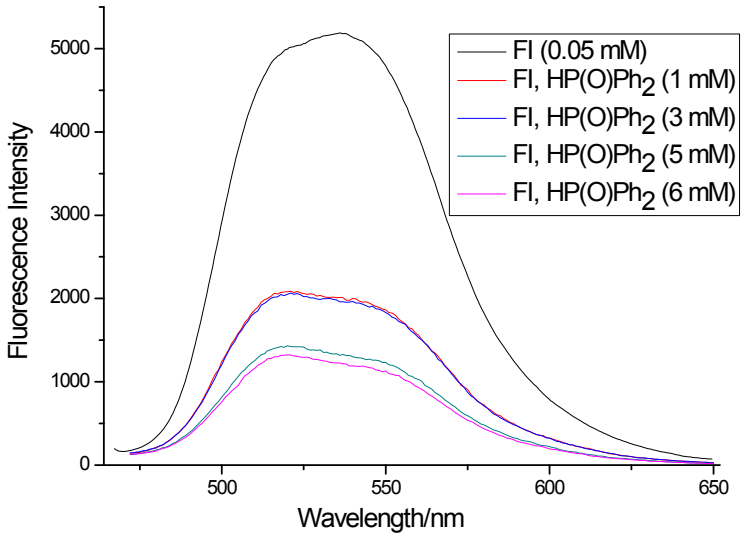


Figure S11. Luminescence quenching experiments of FI with **2a**

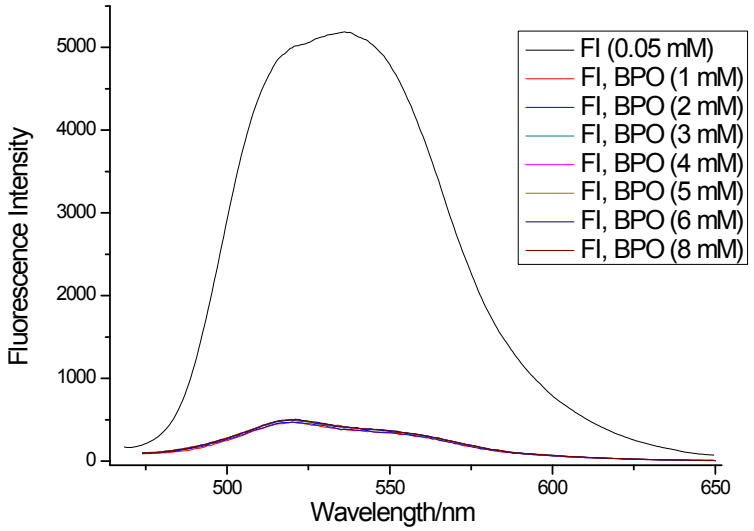


Figure S12. Luminescence quenching experiments of FI with BPO

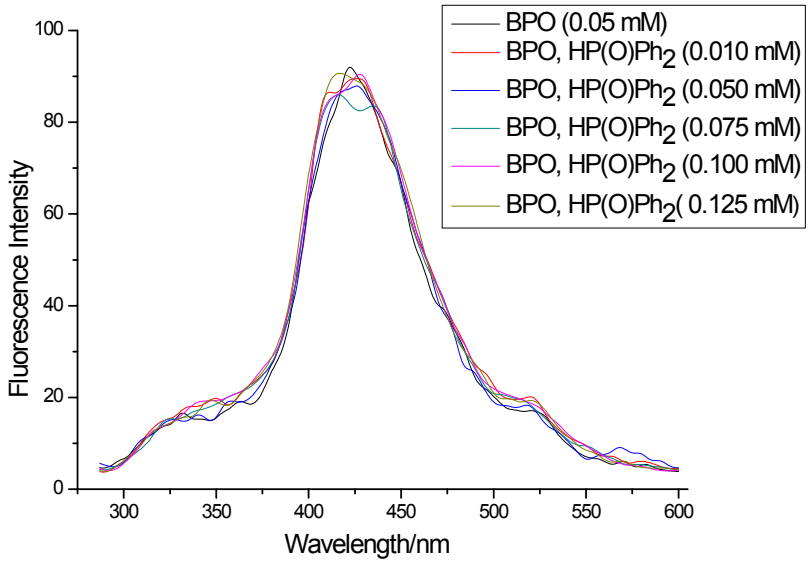


Figure S13. Luminescence quenching experiments of BPO with **2a**

4) Data processing

With the reversible reduction waves of all the reagents in hand, we calculated the excited redox potential, E_g of different reagents.

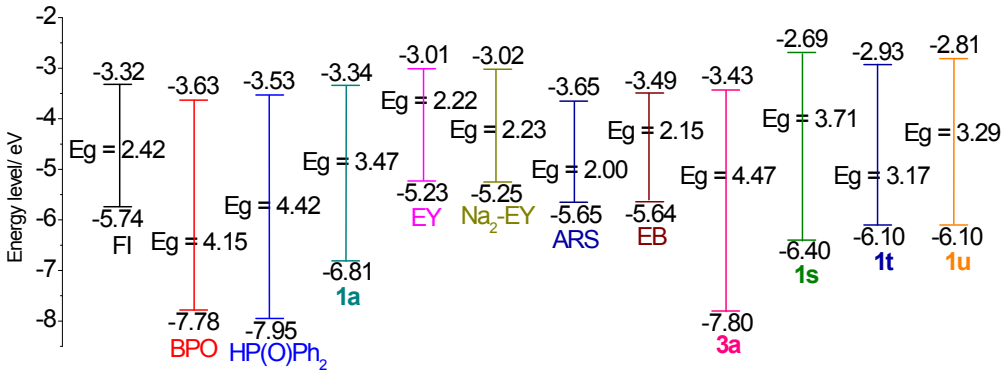


Figure S14. The E_{HOMO}, E_{LUMO} and E_g of different reagents

5. UV/VIS Absorption spectra, Luminescence excitation spectra, and Elemental analysis of the complexes 7

1) UV/VIS Absorption spectra

The UV/VIS absorption spectra of the **3**-$EuCl_3$(**7**) complexes were recorded in CH_3CN of a 2 M solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

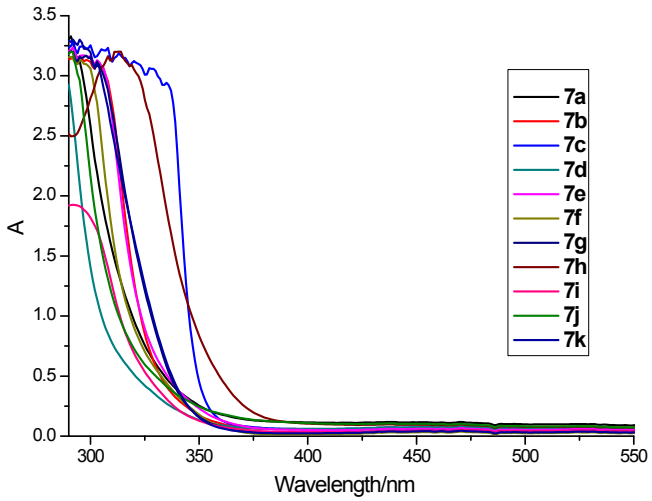


Figure S15. Absorption spectra of 7**a** (λ_{max} = 327 nm), 7**b** (λ_{max} = 328 nm), 7**c** (λ_{max} = 351 nm), 7**d** (λ_{max} = 310 nm), **7e** (λ_{max} = 330 nm), **7f** (λ_{max} = 321 nm), **7g** (λ_{max} = 341 nm), **7h** (λ_{max} = 351 nm), **7i** (λ_{max} = 327 nm), **7j** (λ_{max} = 317 nm), **7k** (λ_{max} = 341 nm) in CH_3CN (2 mM).

2) Luminescence excitation spectra

Luminescence excitation spectra of the **3**-$EuCl_3$ (**7**) complexes were recorded in CH_3CN of a 2 M solution in 10 mm path length quartz cuvette on a F-4500 FL Spectrophotometer. The excited wavelength was 350 nm.

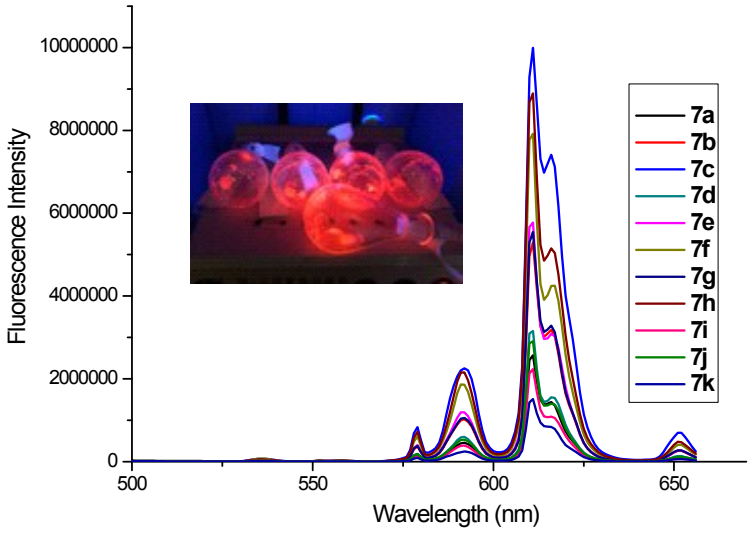


Figure S16. Luminescence excitation spectra of the $3EuCl_3$-**3** complexes

The quantum yield values of the $3EuCl_3$-**3** complexes excited at 300 nm in CH_3CN.

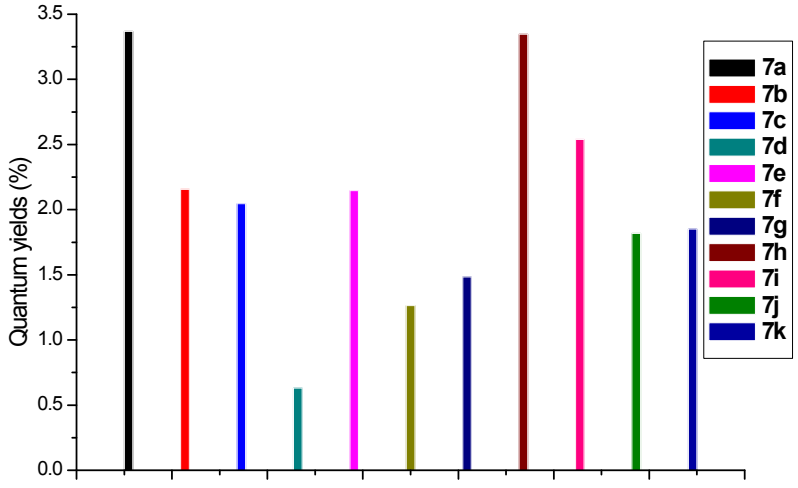


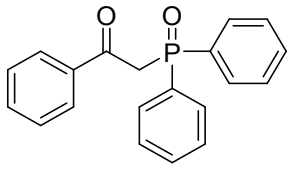
Figure S17. The quantum yield values of the complexes **7**

3) Scheme S4. Elemental analysis

proudct	structure	C(fond)	H(fond)	anal. calcd C	anal. calcd H
7a	$EuCl_3$-(**3a**)$_2(H_2O)_{10}$	44.53	4.70	44.52	5.04
7b	$EuCl_3$-(**3b**)$_3(H_2O)_5$	56.14	4.78	55.99	5.00
7c	$EuCl_3$-(**3c**)$_3(H_2O)_6$	52.95	4.59	53.38	4.91
7d	$EuCl_3$-(**3d**)$_3(H_2O)_6$	52.17	4.30	52.17	4.38
7e	$EuCl_3$-(**3f**)$_2(H_2O)_3$	47.84	3.55	47.71	4.00
7f	$EuCl_3$-(**3g**)$_3(H_2O)_5(CH_3CN)_{13}$	52.55	4.55	52.22	4.78
7g	$EuCl_3$- (**3i**)$_3(H_2O)_6$	55.44	4.75	55.25	5.08
7h	$EuCl_3$- (**3j**)$_3(H_2O)_5$	54.36	4.83	54.07	4.83
7i	$EuCl_3$- (**3j**)$_2(H_2O)_5(CH_3CN)_2$	43.27	4.13	43.00	3.94
7j	$EuCl_3$- (**3d**)$_3(H_2O)_6$	48.72	4.10	48.75	3.95
7k	$EuCl_3$- (**3i**)$_3(H_2O)_7$	54.19	4.73	54.54	5.16

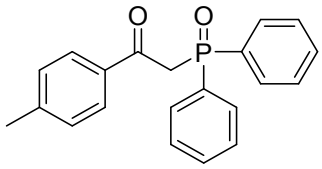
6. Characterization data

2-(diphenylphosphoryl)-1-phenylethan-1-one (3a)[2]



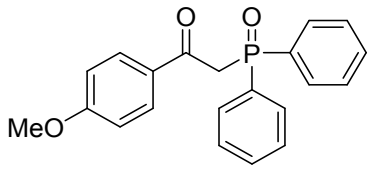
White solid; mp. 134.6-136.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.82-7.78 (m, 4H), 7.52-7.39 (m, 9H), 4.14 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.9 (d, *J* = 5.9 Hz), 137.0, 133.7, 132.2 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 103.4 Hz), 131.1 (d, *J* =9.5 Hz), 129.3, 128.7 (d, *J* = 11.7 Hz), 128.6, 43.3 (d, *J* = 58.0 Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 27.0.
HRMS (ESI) calcd. for $C_{20}H_{18}O_2P$ $(M+H)^+$: 321.1039, found: 321.1045.

2-(diphenylphosphoryl)-1-(p-tolyl)ethan-1-one (3b)[2]



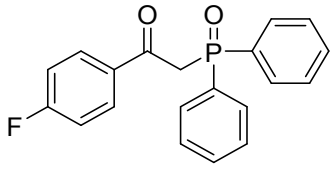
White solid; mp. 144.2-146.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.83-7.77 (m, 4H), 7.53-7.49 (m, 2H), 7.47-7.42 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.11 (d, *J* = 15.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 192.4 (d, *J* = 5.1 Hz), 144.7, 134.5, 132.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 103.4 Hz), 131.2 (d, *J* = 9.5 Hz), 129.4, 129.3, 128.6 (d, *J* = 11.7 Hz), 43.2 (d, *J* = 58.0 Hz), 21.7; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1.
HRMS (ESI) calcd. for $C_{21}H_{20}O_2P$ $(M+H)^+$: 335.1195, found: 335.1195.

2-(diphenylphosphoryl)-1-(4-methoxyphenyl)ethan-1-one (3c)[2]



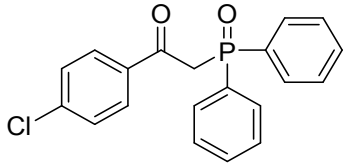
White solid; mp. 154.5-156.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99-7.97 (m, 2H), 7.82-7.77 (m, 4H), 7.53-7.49 (m, 2H), 7.47-7.42 (m, 4H), 6.89-6.87 (m, 2H), 4.08 (d, *J* = 15.4 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.1 (d, *J* = 5.1 Hz), 164.0, 132.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* =102.7 Hz), 131.8, 131.1 (d, *J* = 10.3 Hz), 130.1, 128.6 (d, *J* = 11.7 Hz), 113.7, 55.5, 43.2 (d, *J* = 58.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1
HRMS (ESI) calcd. for $C_{21}H_{20}O_3P$ $(M+H)^+$: 351.1145, found: 351.1145.

2-(diphenylphosphoryl)-1-(4-fluorophenyl)ethan-1-one (3d)[2]



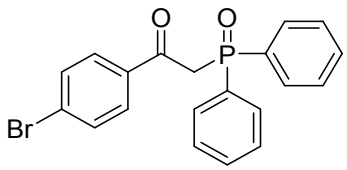
White solid; mp. 167.4-168.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06-8.02 (m, 2H), 7.82-7.76 (m, 4H), 7.55-7.51 (m, 2H), 7.49-7.44 (m, 4H), 7.10-7.06 (m, 2H), 4.10 (d, *J* = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.3 (d, *J* = 5.9 Hz), 166.1 (d, *J* = 256.0 Hz), 133.4 (d, *J* =2.9 Hz), 132.3 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 9.5 Hz), 131.7 (d, *J* = 103.4.0 Hz), 131.1 (d, *J* = 10.3 Hz), 128.7 (d, *J* = 12.5 Hz), 115.7 (d, *J* = 22.0 Hz), 43.6 (d, *J* = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.1.
HRMS (ESI) calcd. for $C_{20}H_{17}FO_2P$ $(M+H)^+$: 339.0945, found: 339. 0945.

1-(4-chlorophenyl)-2-(diphenylphosphoryl)ethan-1-one (3e)[2]



White solid; mp. 146.6-148.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98-7.95 (m, 2H), 7.82-7.77 (m, 4H), 7.56-7.52 (m, 2H), 7.50-7.45 (m, 4H), 7.41-7.38 (m, 2H), 4.11 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$,100 MHz): δ 191.7 (d, *J* = 5.1 Hz), 140.3, 135.3, 132.3 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 103.4 Hz), 131.1 (d, *J* = 9.5 Hz), 130.8, 128.9, 128.7 (d, *J* = 12.5 Hz), 43.6 (d, *J* = 56.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.8.
HRMS (ESI) calcd. for $C_{20}H_{17}ClO_2P$ $(M+H)^+$: 355.0649, found: 355. 0650.

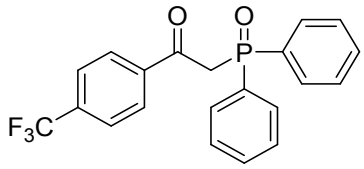
1-(4-bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (3f)[2]



White solid; mp. 142.5-143.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.87 (m, 2H), 7.82-7.76 (m, 4H), 7.58-7.52 (m, 4H), 7.50-7.45 (m, 4H), 4.10 (d, *J* = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.9 (d, *J* = 5.9 Hz), 135.7, 132.3 (d, *J* = 2.9 Hz), 132.2,

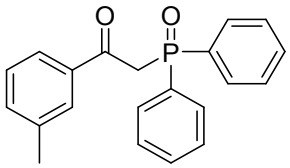
131.4 (d, J = 100.5 Hz), 131.1 (d, J =9.5 Hz), 129.2, 128.7 (d, J = 11.7 Hz), 43.6 (d, J = 56.5 Hz); ^{31}P NMR ($CDCl_3$, 162MHz): δ 26.8.
HRMS (ESI) calcd. for $C_{20}H_{17}BrO_2P$ $(M+H)^+$: 399.0144, found: 399. 0145.

2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3g)[2]



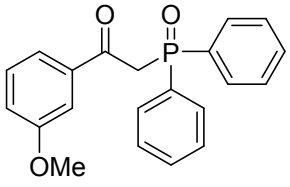
White solid; mp. 138.6-140.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, J = 8.2 Hz, 2H), 7.81-7.76 (m, 4H), 7.68 (d, J = 8.3 Hz, 2H), 7.56-7.52 (m, 2H), 7.50-7.45 (m, 4H), 4.16 (d, J =15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.1 (d, J = 5.9 Hz), 139.5, 134.7 (d, J = 33.0 Hz), 132.4 (d, J = 2.9 Hz), 132.0, 131.1 (d, J = 9.5 Hz), 129.7, 128.7 (d, J = 12.5 Hz), 125.6 (q, J = 3.7 Hz), 123.5 (d, J = 272.9 Hz) 43.9 (d, J = 55.8 Hz); ^{31}P NMR (CDCl3, 162 MHz): δ 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.
HRMS (ESI) calcd. for $C_{21}H_{17}F_3O_2P$ $(M+H)^+$: 389.0913, found: 389. 0911.

2-(diphenylphosphoryl)-1-(m-tolyl)ethan-1-one (3i)[2]



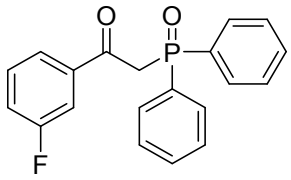
White solid; mp. 122.8-124.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.78 (m, 5H), 7.73 (s, 1H), 7.55-7.50 (m, 2H), 7.48-7.43 (m, 4H), 7.36-7.28 (m, 2H), 4.14 (d, J = 15.5 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.0 (d, J = 5.9 Hz), 138.3, 137.0, 134.5, 132.5 (d, J = 103.4 Hz), 132.2 (d, J = 2.9 Hz), 131.1 (d, J = 9.5 Hz), 129.6, 128.6 (d, J = 11.7 Hz), 128.5, 126.6, 43.2 (d, J = 58.0 Hz), 21.3; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1
HRMS (ESI) calcd. for $C_{21}H_{20}O_2P$ $(M+H)^+$: 335.1195, found: 335.1194.

2-(diphenylphosphoryl)-1-(3-methoxyphenyl)ethan-1-one (3j)[2]



White solid; mp. 100.7-102.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 4H), 7.59 (d, J = 7.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.47-7.43 (m, 5H), 7.32 (t, J =7.9 Hz, 1H), 7.08 (dd, J_1 = 2.1 Hz, J_2 = 8.2 Hz, 1H), 4.13 (d, J = 15.3 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.7 (d, J = 5.1 Hz), 159.7, 138.3, 132.2 (d, J = 2.9 Hz), 131.9 (d, J = 103.4 Hz), 131.2 (d, J = 10.3 Hz), 129.6, 128.7 (d, J = 12.3 Hz), 122.3, 120.6, 112.7, 55.5, 43.4 (d, J = 58.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1
HRMS (ESI) calcd. for $C_{21}H_{20}O_3P$ $(M+H)^+$: 351.1145, found: 351.1145.

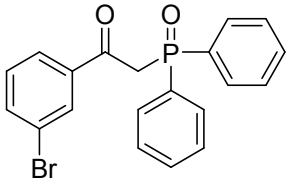
2-(diphenylphosphoryl)-1-(3-fluorophenyl)ethan-1-one (3k)[2]



White solid; mp. 130.2-132.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 5H), 7.64-7.61 (m, 1H), 7.55–7.51 (m, 2H), 7.48-7.42 (m, 4H), 7.40-7.37 (m, 1H), 7.25-7.20 (m, 1H), 4.11 (d, J = 15.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7 (dd, J_1 = 2.2 Hz, J_2 = 5.1 Hz), 162.7 (d, J = 248.0 Hz), 139.0 (d, J = 5.9 Hz), 132.3 (d, J =2.9 Hz), 132.2 (d, J =104.2 Hz), 131.1 (d, J = 9.5 Hz), 130.3 (d, J = 8.1 Hz), 128.7 (d, J = 11.7 Hz), 125.4 (d, J =2.9 Hz), 120.7 (d, J = 21.3 Hz), 115.7 (d, J = 22.7 Hz), 43.6 (d, J = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8.

HRMS (ESI) calcd. for $C_{20}H_{17}FO_2P$ $(M+H)^+$: 339.0945, found: 339. 0945.

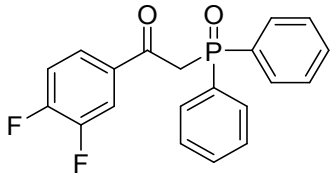
1-(3-bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (3l)[2]



White solid; mp. 120.1-122.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.81-7.76 (m, 4H), 7.64 (d, J =7.8 Hz, 1H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.29 (t, J = 8.0 Hz, 1H), 4.11 (d, J = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7 (d, J = 5.1 Hz), 138.6, 136.4, 132.4 (d, J = 2.9 Hz), 131.9, 131.6 (d, J = 104.2 Hz), 131.1 (d, J = 9.5 Hz), 130.2, 128.7 (d, J =12.5 Hz), 128.1, 122.9, 43.5 (d, J = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7.

HRMS (ESI) calcd. for $C_{20}H_{17}BrO_2P$ $(M+H)^+$: 399.0144, found: 399. 0140.

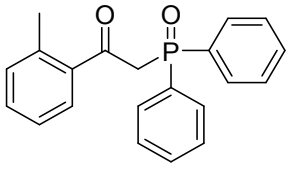
1-(3,4-difluorophenyl)-2-(diphenylphosphoryl)ethan-1-one (3m)



White solid; mp. 144.7-146.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.84-7.77 (m, 5H), 7.58 – 7.53 (m, 2H), 7.51-7.46 (m, 4H), 7.24-7.19 (m, 1H), 4.08 (d, J = 15.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.5 (d, J = 4.4 Hz), 154.0 (dd, J_1 = 13.2, J_2 = 258.2 Hz), 150.2 (dd, J_1 = 12.5, J_2 = 250.9 Hz), 134.0 (t, J = 3.7 Hz), 132.4 (d, J =2.9 Hz), 132.0, 131.0 (d, J =10.3 Hz), 128.8 (d, J = 11.7 Hz), 126.9 (q, J = 3.7 Hz), 118.4 (dd, J_1 = 1.47 Hz, J_2 = 18.3 Hz), 117.5 (d, J = 17.6 Hz), 43.7 (d, J = 56.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.6 (d, J = 20.4 Hz), -135.9 (d, J = 20.4 Hz).

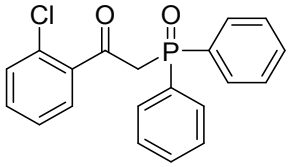
HRMS (ESI) calcd. for $C_{20}H_{16}F_2O_2P$ $(M+H)^+$: 357.0850, found: 357.0848.

2-(diphenylphosphoryl)-1-(o-tolyl)ethan-1-one (3n)[2]



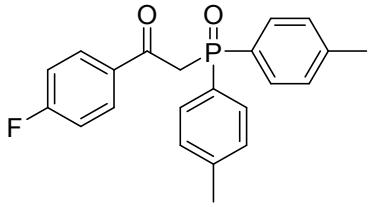
White solid; mp. 78.9-80.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.81-7.76 (m, 4H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.36-7.32 (m, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 4.10 (d, *J* = 15.3 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.7 (d, *J* = 5.8 Hz), 139.0, 137.8, 132.1 (d, *J* = 103.4 Hz), 132.1 (d, *J* = 2.9 Hz), 132.01, 131.9, 131.1 (d, *J* = 10.3 Hz), 130.4, 128.7 (d, *J* = 12.5Hz), 125.8, 45.6 (d, *J* = 56.7 Hz), 21.3; ^{31}P NMR ($CDCl_3$,162 MHz): δ 27.2.
HRMS (ESI) calcd. for $C_{21}H_{20}O_2P$ $(M+H)^+$: 335.1195, found: 335.1193.

1-(2-chlorophenyl)-2-(diphenylphosphoryl)ethan-1-one (3o)[2]



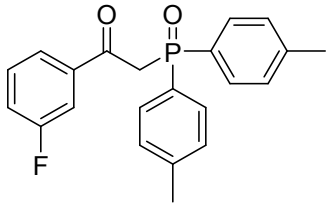
White solid; mp. 80.5-82.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.79-7.74 (m, 4H), 7.55-7.51 (m, *J* = 7.8 Hz, 2H), 7.48-7.43 (m, 4H), 7.35-7.29 (m, 2H), 7.26-7.22 (m, 1H), 4.24 (d, *J* = 14.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.0 (d, *J* = 5.9 Hz), 139.0, 132.2 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 103.4 Hz), 131.1 (d, *J* = 10.3 Hz), 131.0, 130.3, 130.1, 128.7 (d, *J* =12.5 Hz), 127.1, 47.7 (d, *J* = 58.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1
HRMS (ESI) calcd. for $C_{20}H_{17}ClO_2P$ $(M+H)^+$: 355.0649, found: 355. 0648.

2-(di-p-tolylphosphoryl)-1-(4-fluorophenyl)ethan-1-one (3p)



White solid; mp. 108.6-110.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08-8.04 (m, 2H), 7.68-7.63 (m, 4H), 7.28-7.25 (m, 4H), 7.09 (t, *J* = 8.6 Hz, 2H), 4.07 (d, *J* = 15.3 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5 (d, *J* = 5.9 Hz), 166.1 (d, *J* = 256.0 Hz), 142.8 (d, *J* =2.9 Hz), 133.5 (d, *J* = 2.2 Hz), 131.1 (d, *J* = 10.3 Hz), 129.5, 129.3, 128.6 (d, *J* = 106.4 Hz), 115.6 (d, *J* = 22.0 Hz), 43.8 (d, *J* = 56.5 Hz), 21,6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.3.
HRMS (ESI) calcd. for $C_{22}H_{21}FO_2P$ $(M+H)^+$: 367.1258, found: 367.1256.

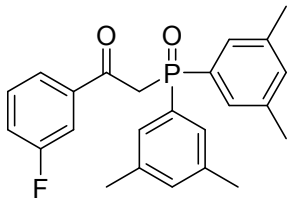
2-(di-p-tolylphosphoryl)-1-(3-fluorophenyl)ethan-1-one (3q)



White solid; mp. 110.8.-112.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.83 (m, 1H), 7.69-7.62 (m, 5H), 7.44-7.39 (m, 1H), 7.28-7.28 (m, 4H), 7.24-7.22 (m, 1H), 4.07 (d, J = 15.3 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.0 (dd, J_1 = 2.2, J_2 = 5.9 Hz), 162.7 (d, J = 248.0 Hz), 142.8 (d, J =2.9 Hz), 139.1 (d, J =6.6 Hz), 131.1 (d, J = 10.3 Hz), 130.2 (d, J = 7.3 Hz), 129.4 (d, J = 12.5 Hz), 128.6 (d, J = 106.4 Hz), 125.5 (d, J = 2.9 Hz), 120.6 (d, J=21.3), 115.7 (d, J = 22.7 Hz), 43.9 (d, J = 56.5 Hz), 21.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9.

HRMS (ESI) calcd. for $C_{22}H_{21}FO_2P$ $(M+H)^+$: 367.1258, found: 367.1254.

2-(bis(3,5-dimethylphenyl)phosphoryl)-1-(3-fluorophenyl)ethan-1-one (3r)



White solid; mp. 100.5.-102.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, J = 7.8 Hz 1H), 7.64-7.60 (m, 1H), 7.43-7.36 (m, 5H), 7.25-7.22 (m, 1H), 7.14 (s, 1H), 4.07 (d, J = 15.2 Hz, 2H), 2.32 (s, 12H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 191.9 (dd, J_1 = 2.2, J_2 = 5.14 Hz), 162.7 (d, J = 248.9 Hz), 139.2 (d, J =5.9 Hz), 138.5 (d, J =13.2 Hz), 134.0 (d, J =2.9 Hz), 131.5 (d, J = 102.7 Hz), 130.2 (d, J =7.34 Hz), 128.6 (d, J = 9.54 Hz), 125.4 (d, J= 2.2 Hz), 120.5 (d, J = 21.3), 115.7 (d, J = 22.0 Hz), 43.7 (d, J = 55.8 Hz), 21,3; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0.

HRMS (ESI) calcd. for $C_{24}H_{25}FO_2P$ $(M+H)^+$: 395.1571, found: 395.1571.

7a. FT-IR v (KBr, cm^{-1}): 1675.67 (C=O), 1140.05 (P=O); anal. calcd for $Eu(C_{20}H_{17}O_2P)_2Cl_3(H_2O)_{10}$: C, 44.52; H, 5.04. Found: C, 44.53; H, 4.70.

7b. FT-IR v (KBr, cm^{-1}): 1672.01 (C=O), 1139.6 (P=O); anal. calcd for $EuC_{63}H_{57}O_6P_3Cl_3(H_2O)_5$: C 55.99; H 5.00. Fond: C, 56.14; H, 4.77.

7c. FT-IR v (KBr, cm^{-1}): 1666.08 (C=O), 1095.18 (P=O); anal. calcd for $EuC_{63}H_{57}O_9P_3Cl_3(H_2O)_6$: C, 53.38; H, 4.59. Found: C, 52.95; H, 4.59.

7d. FT-IR v (KBr, cm^{-1}): 1675.94 (C=O), 1158.48 (P=O); anal. calcd for $EuC_{60}H_{48}F_3O_6P_3Cl_3(H_2O)_6$: C, 52.17; H, 4.38. Found: C, 52.17; H, 4.30.

7e. Yield: 58% (42 mg). FT-IR v (KBr, cm^{-1}): 1677.02 (C=O), 1142.57 (P=O); anal. calcd for $EuC_{40}H_{32}Br_3O_4P_2Cl_3(H_2O)_3$: C, 47.71; H, 4.00. Found C, 47.84; H, 3.55.

7f. FT-IR v (KBr, cm^{-1}): 1674.69 (C=O), 1151.60 (P=O); anal. calcd for $EuC_{63}H_{48}F_3O_6P_3Cl_3(CH_3CN)_{13}(H_2O)_5$: C, 52.22; H, 4.78. Found: C, 52.55; H, 4.55.

7g. FT-IR v (KBr, cm^{-1}): 1674.20 (C=O), 1139.90 (P=O); anal. calcd for $EuC_{63}H_{57}O_6P_3Cl_3(H_2O)_6$: C, 55.25; H, 5.08. Found: C, 55.44; H, 4.75.

7h. FT-IR *v* (KBr, cm^{-1}): 1675.23 (C=O), 1139.26 (P=O); anal. calcd for $EuC_{63}H_{57}O_9P_3Cl_3(H_2O)_5$: C, 54.07; H, 4.83. Found: C, 54.36; H, 4.83.

7i. FT-IR *v* (KBr, cm^{-1}): 1679.25 (C=O), 1137.68 (P=O); anal. calcd for $EuC_{40}H_{32}Br_3O_4P_2Cl_3(CH_3CN)_2(H_2O)_5$: C, 43.00; H, 3.94. Found: C, 43.27; H, 4.13.

7j. FT-IR *v* (KBr, cm^{-1}): 1650.63 (C=O), 1155.67 (P=O); anal. calcd for $EuC_{60}H_{45}F_6O_6P_3Cl_3(H_2O)_6$: C, 48.75; H, 3.95. Found: C, 48.72; H, 4.10.

7k. FT-IR *v* (KBr, cm^{-1}): 1676.16 (C=O), 1137.41 (P=O); anal. calcd for $EuC_{63}H_{57}O_6P_3Cl_3(H_2O)_7$: C, 54.54; H, 5.16. Found: C, 54.19; H, 4.73.

References:

[1] Bai Y.; Chen W.;, Chen Y.; Huang H.; Xiao F.; Deng G. *RSC Adv.*, **2015**, *5*, 8002.

[2] Zhang, P.; Zhang, L.; Gao, Y.; Xu, J.; Fang, H.; Tang, G.; Zhao, Y. *Chem. Commun.*, **2015**, *51*, 7839.

7. The NMR spectra

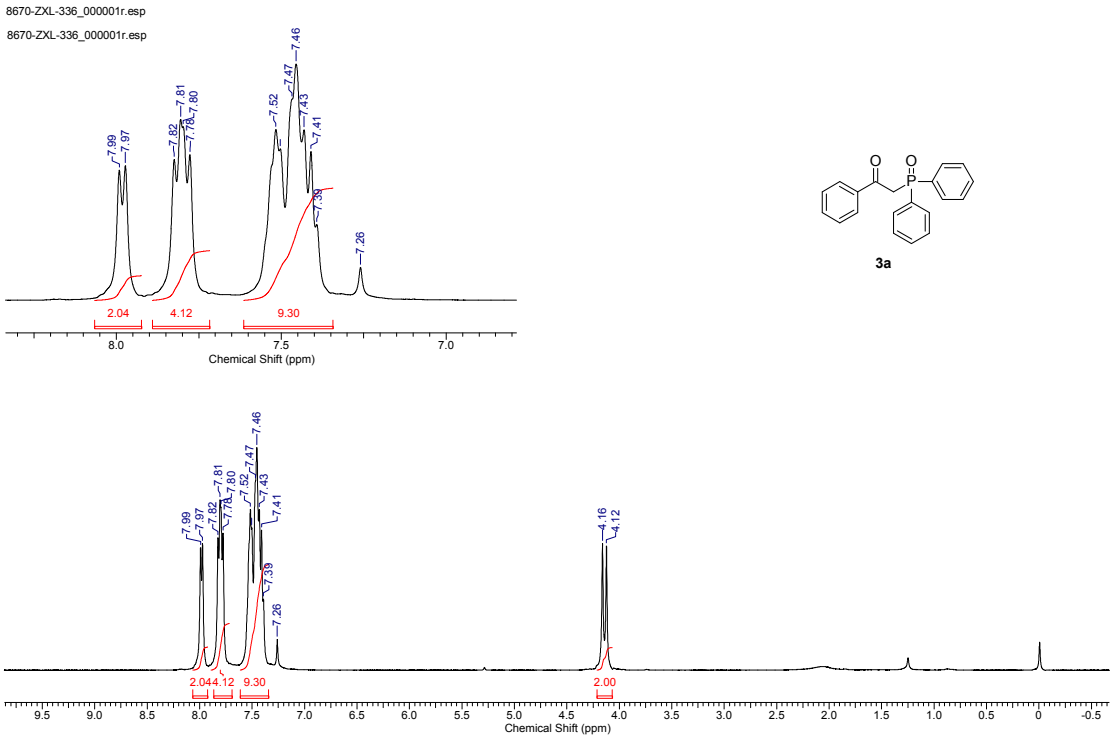


Figure S18. ^1H NMR spectrum of compound **3a**

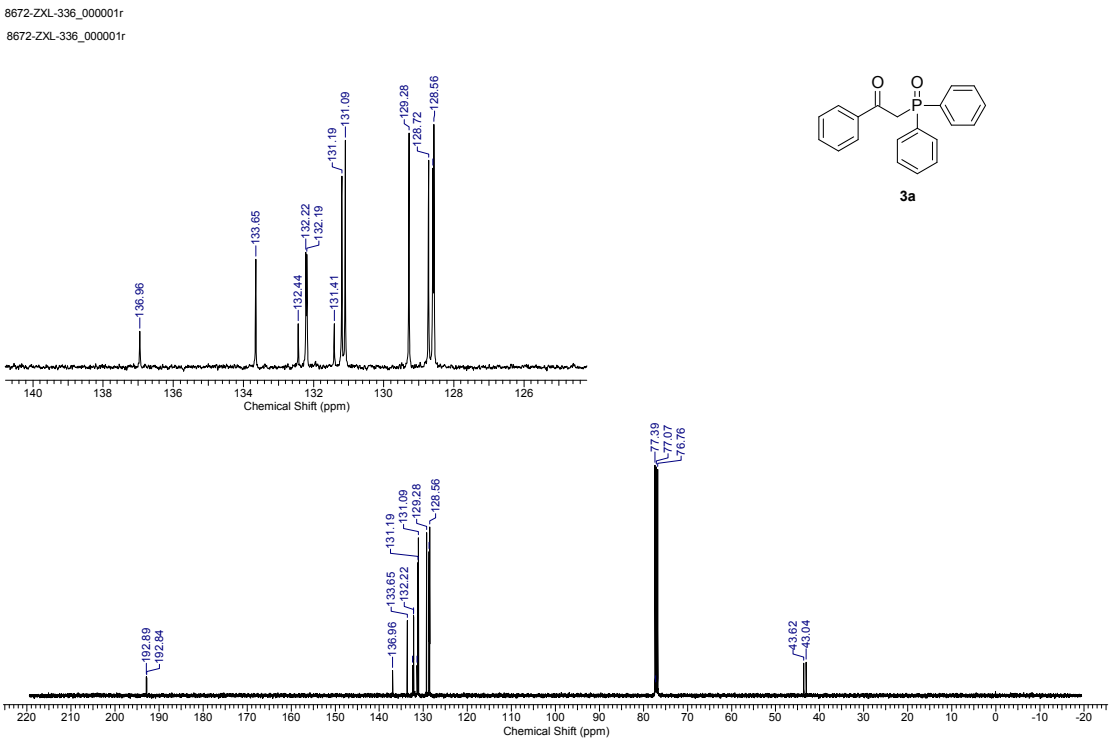


Figure S19. ^{13}C NMR spectrum of compound **3a**

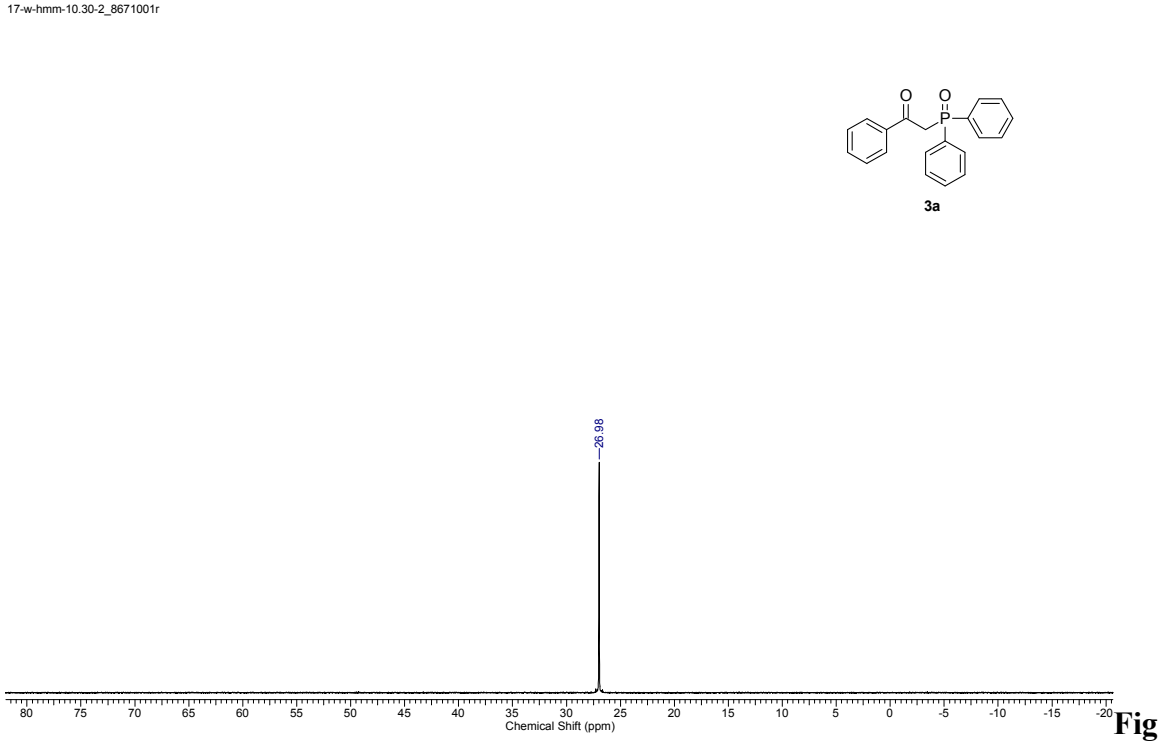


Figure S20. ^{31}P NMR spectrum of compound **3a**

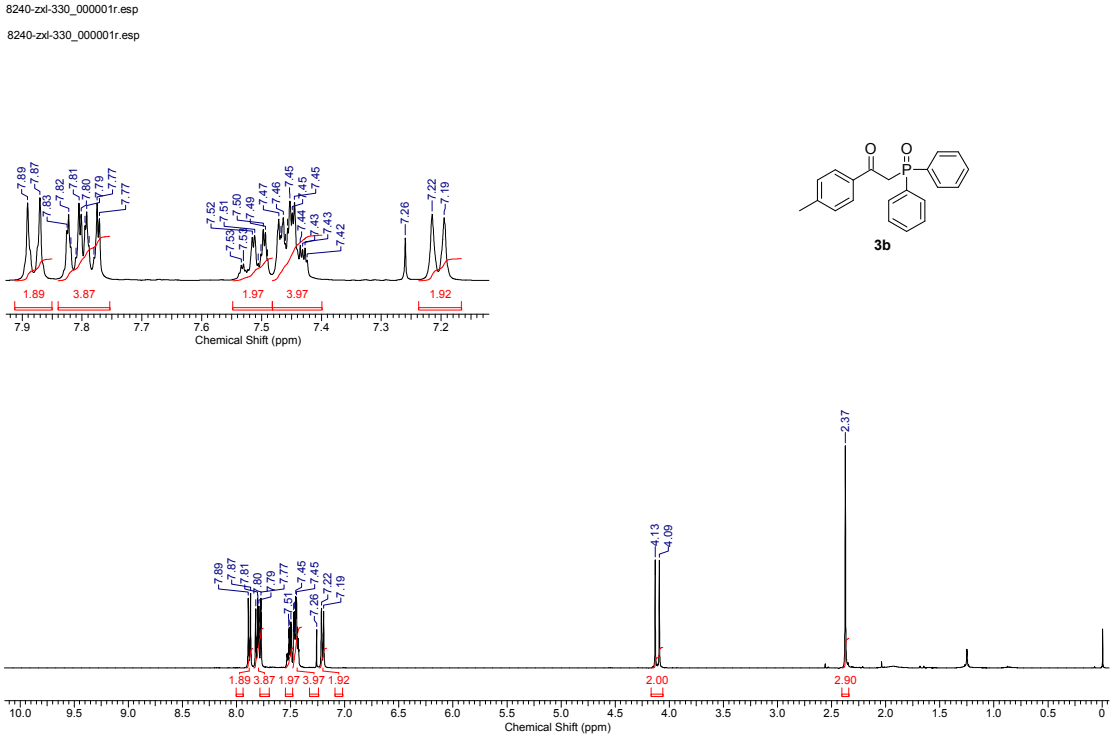


Figure S21. ^{1}H NMR spectrum of compound 3b

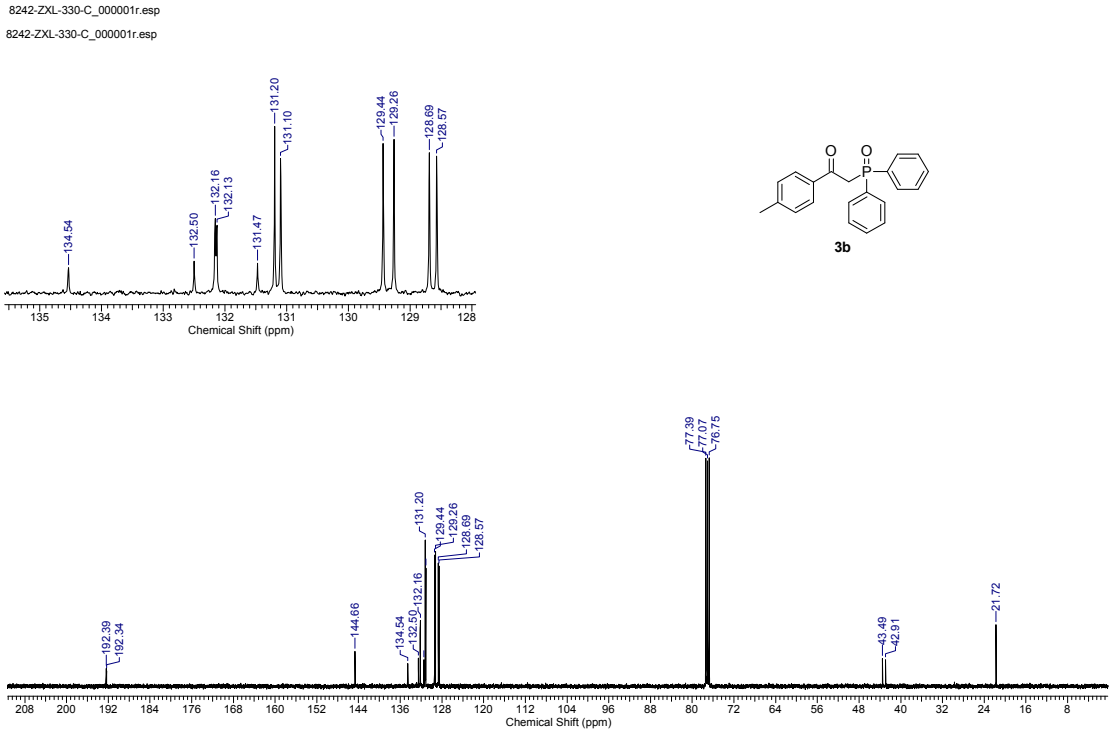


Figure S22. ^{13}C NMR spectrum of compound **3b**

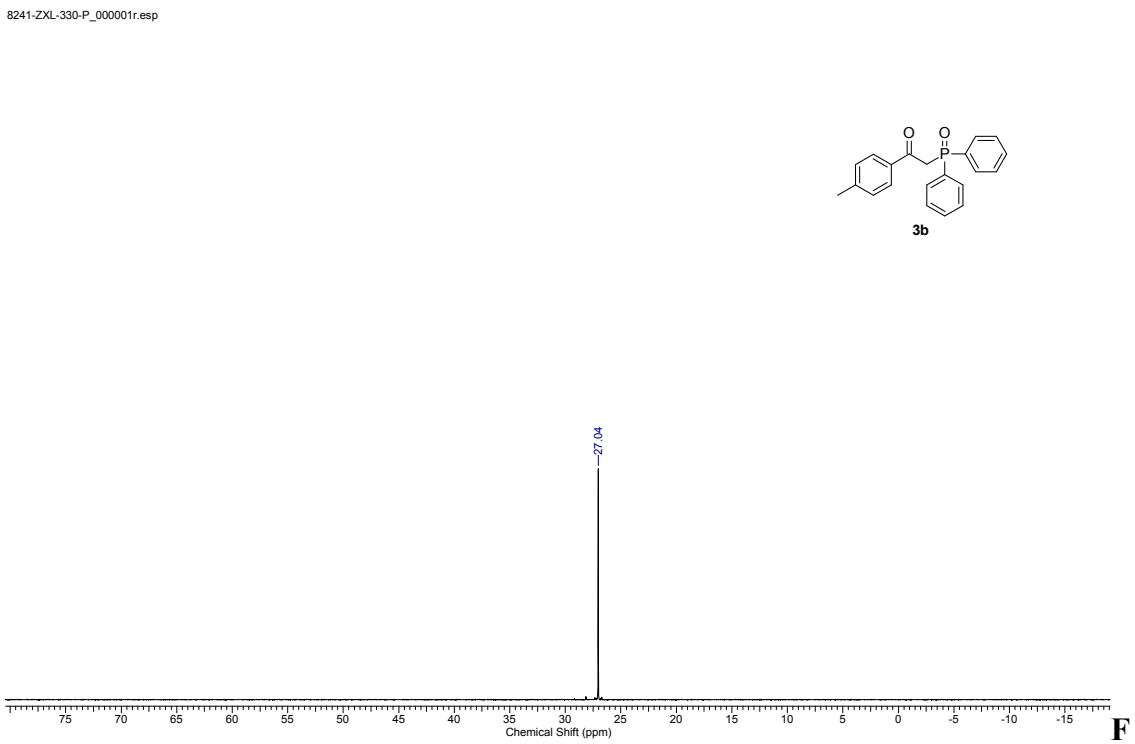


Figure S23. ^{31}P NMR spectrum of compound **3b**

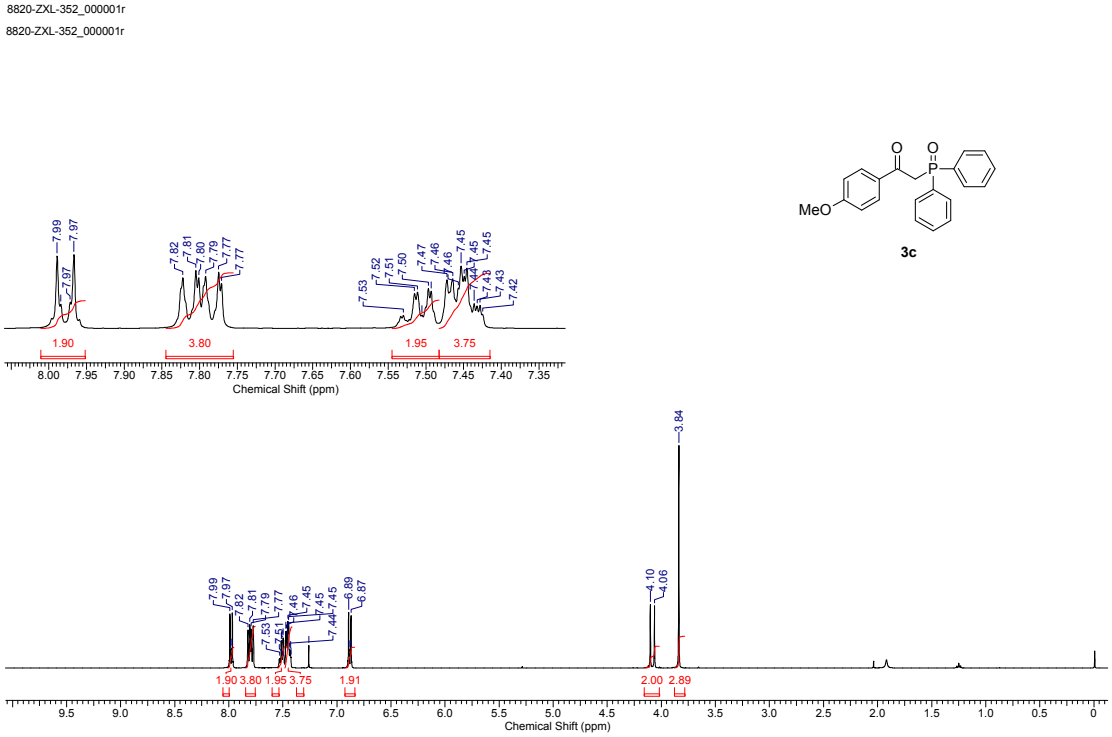


Figure S24. ^{1}H NMR spectrum of compound **3c**

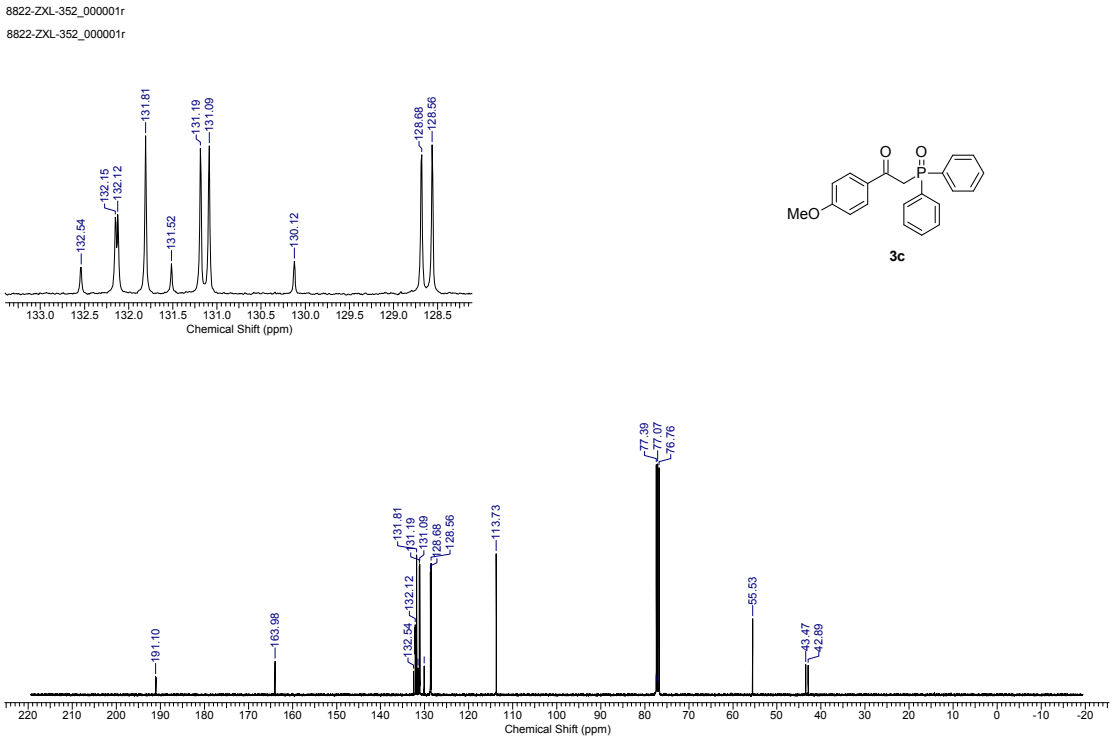


Figure S25. ^{13}C NMR spectrum of compound **3c**

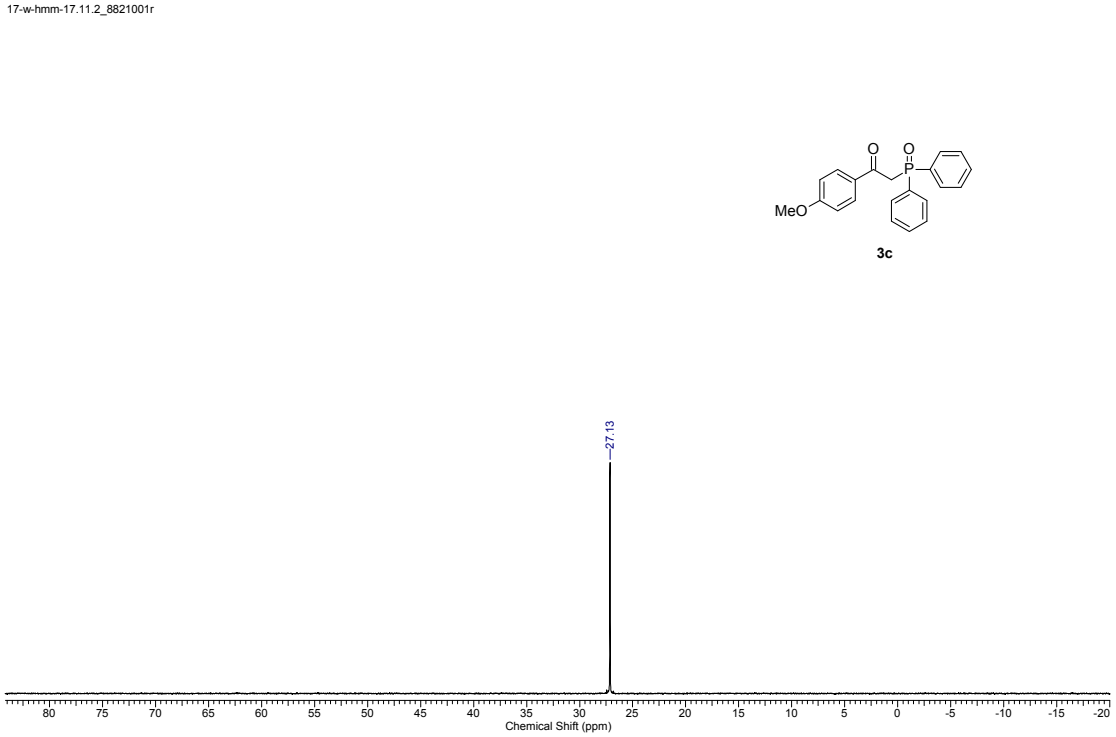


Figure S26. ^{31}P NMR spectrum of compound **3c**

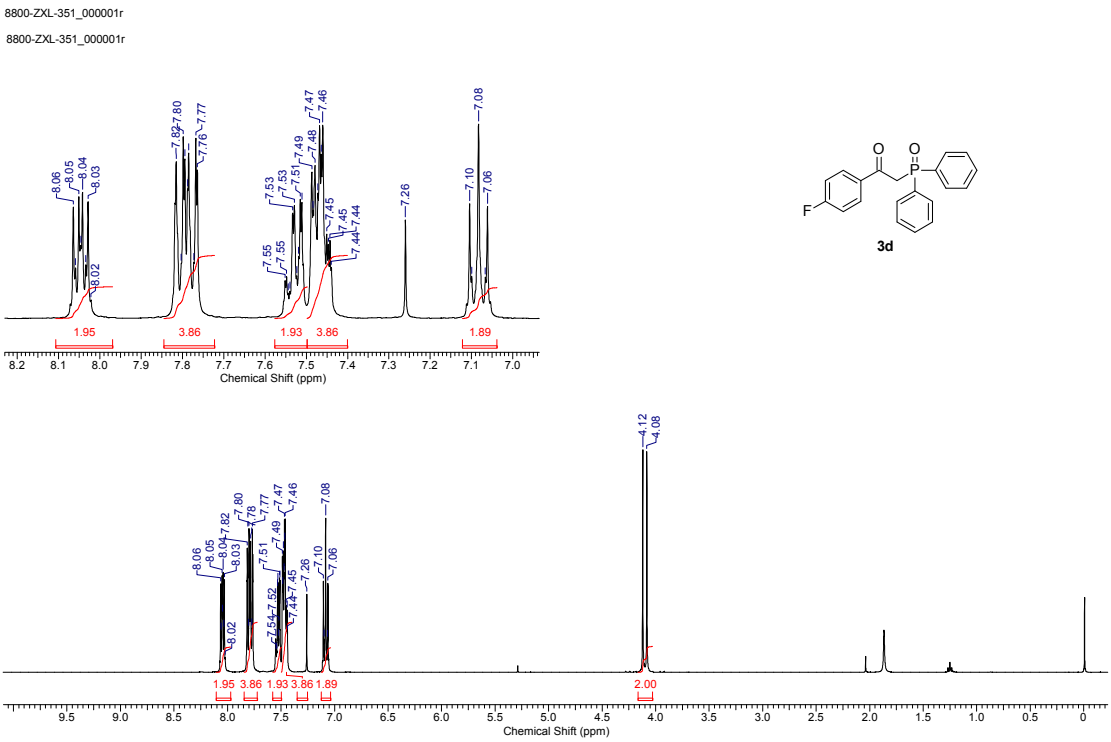


Figure S27. ^{1}H NMR spectrum of compound **3d**

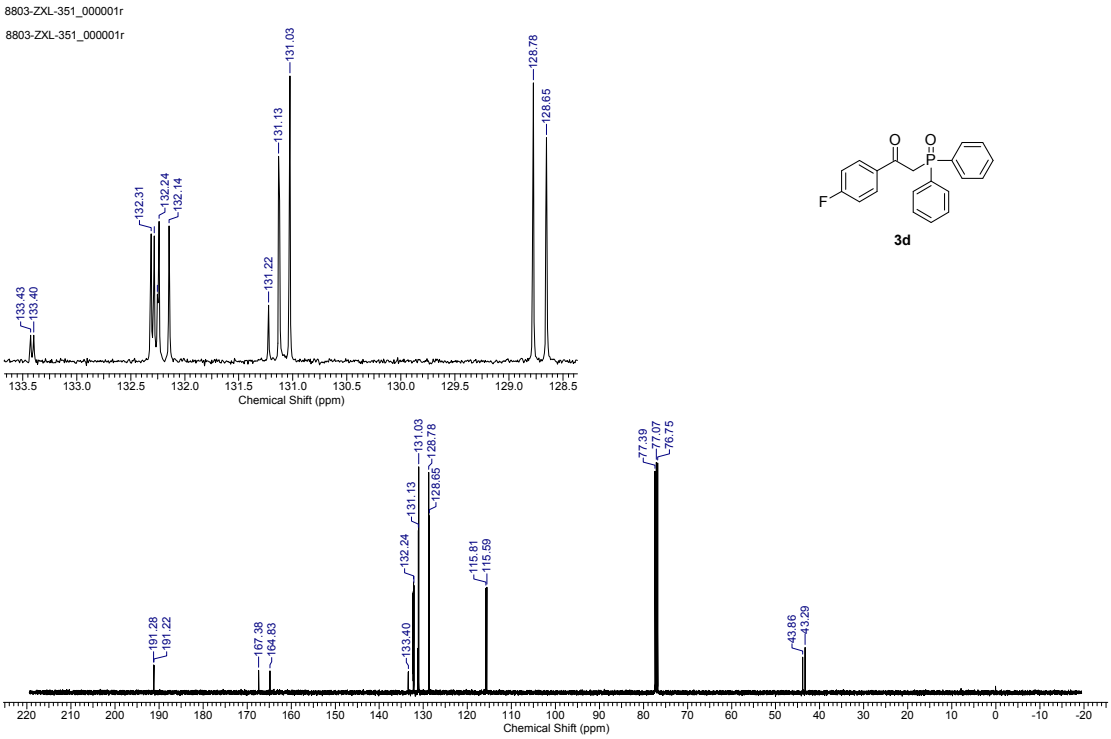


Figure S28. ^{13}C NMR spectrum of compound **3d**

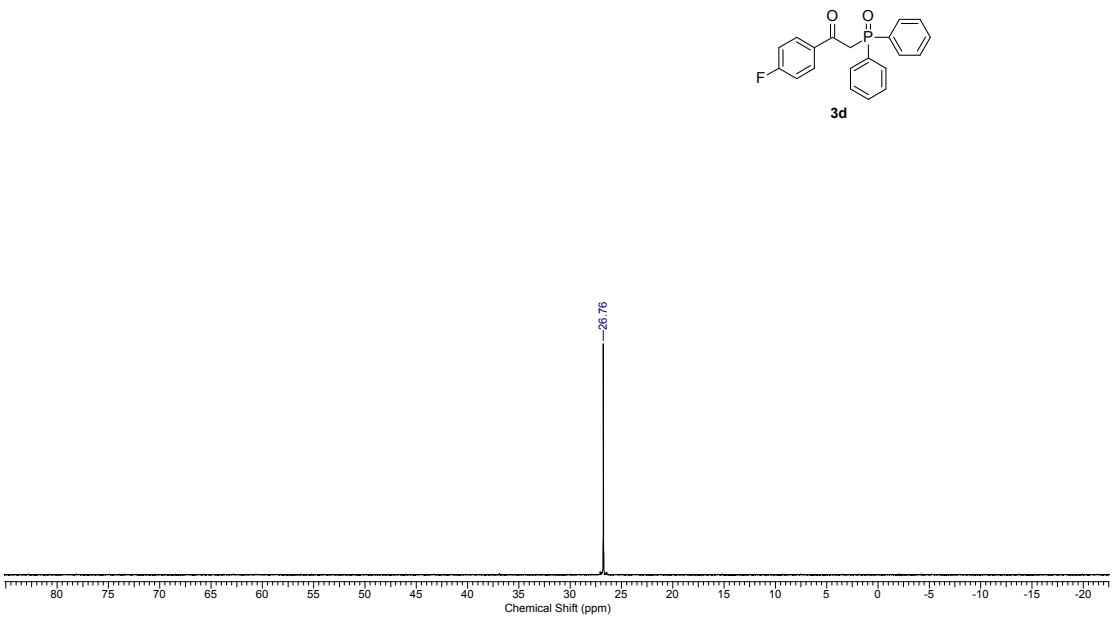


Figure S29. ^{31}P NMR spectrum of compound **3d**

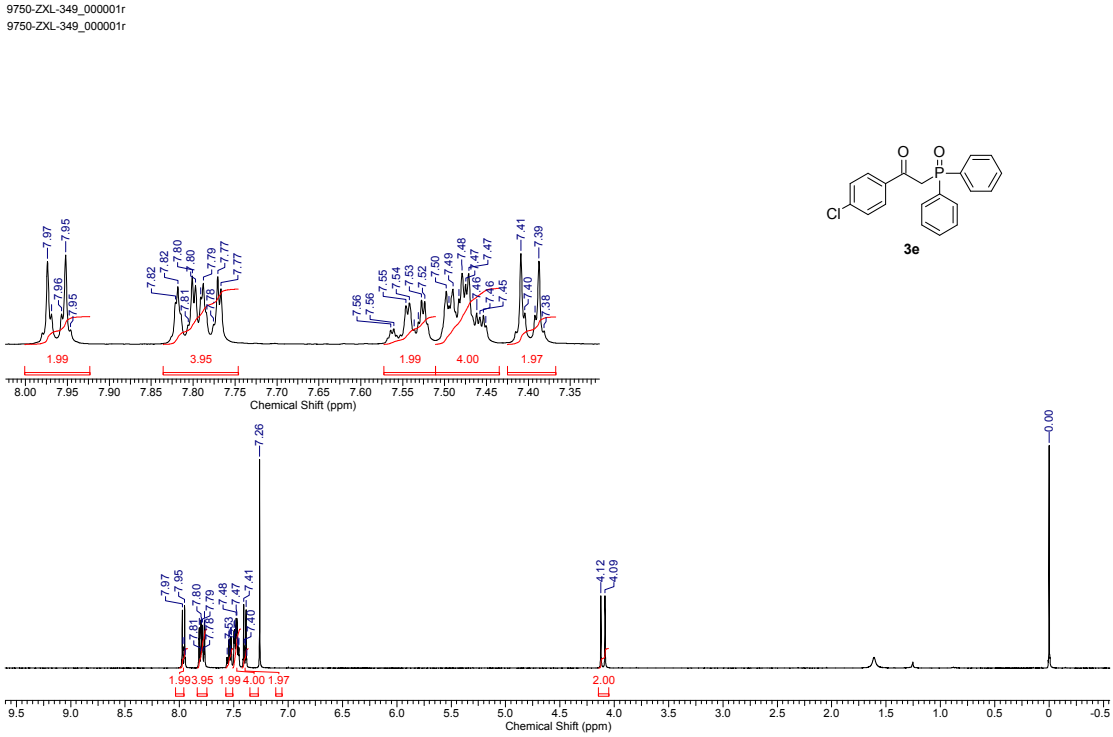


Figure S30. ^{1}H NMR spectrum of compound **3e**

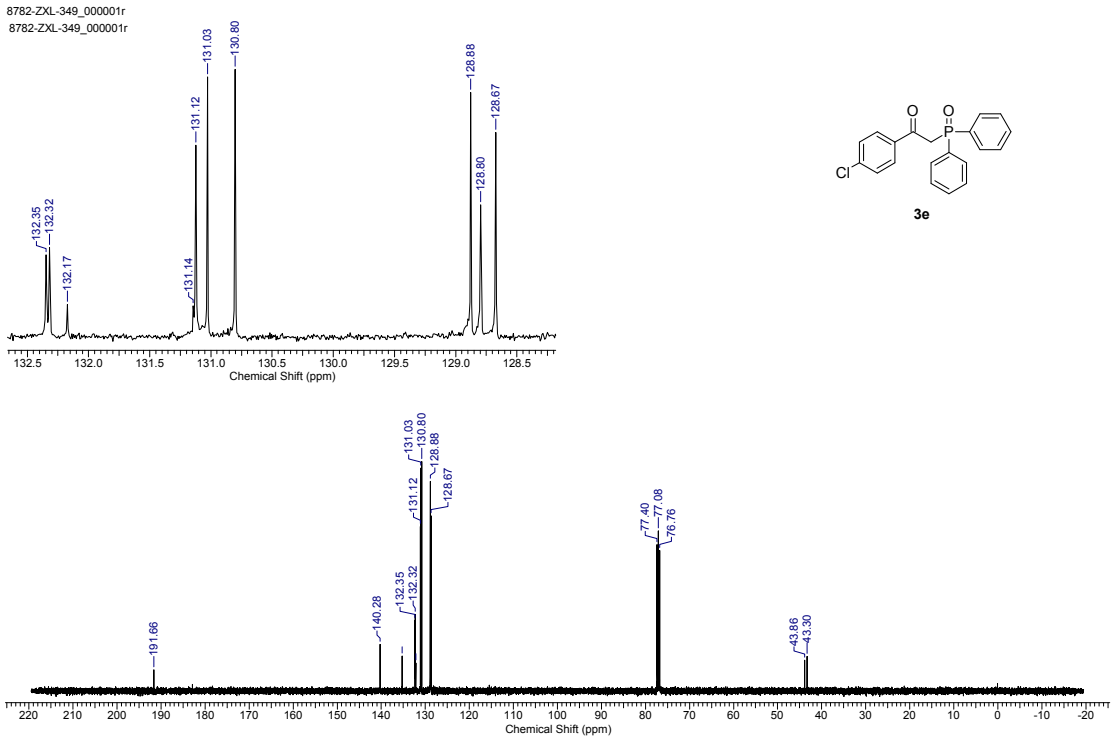


Figure S31. ^{13}C NMR spectrum of compound **3e**

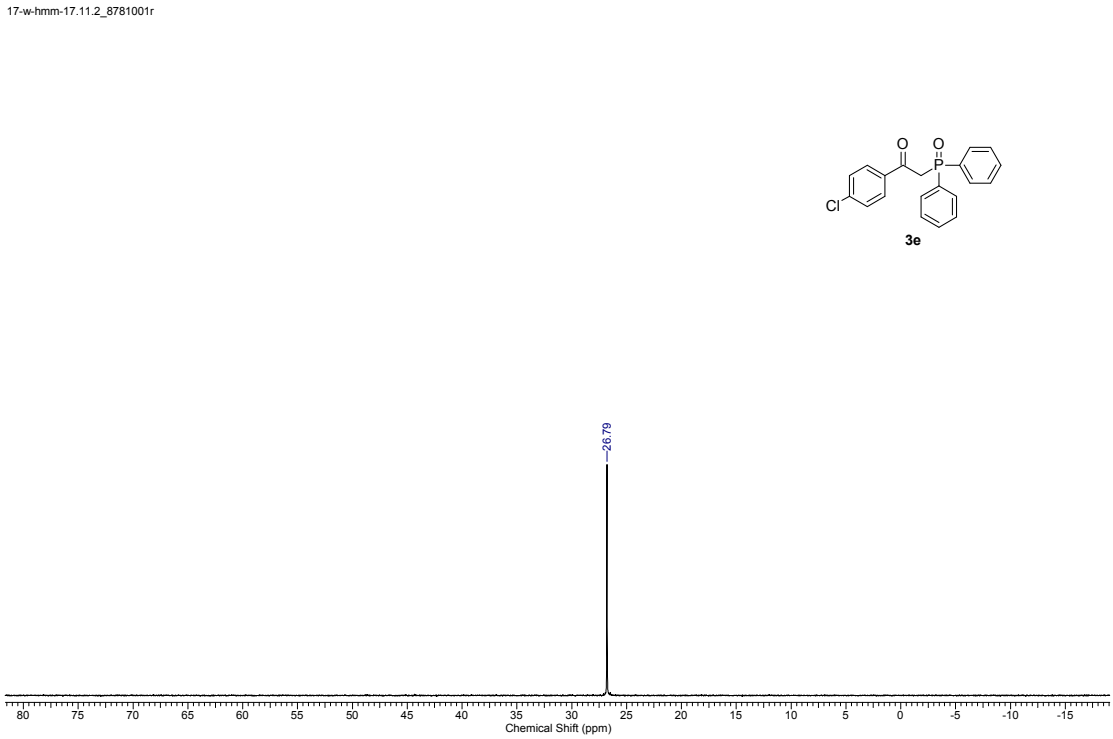


Figure S32. ^{31}P NMR spectrum of compound **3e**

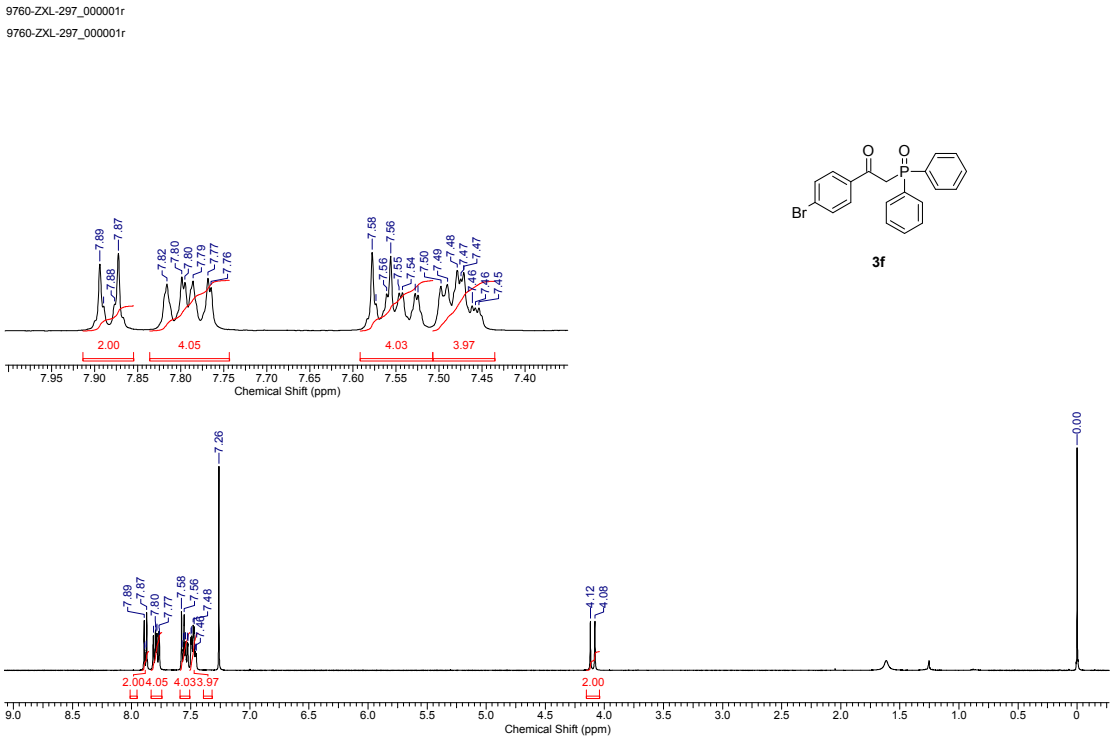


Figure S33. ^{1}H NMR spectrum of compound **3f**

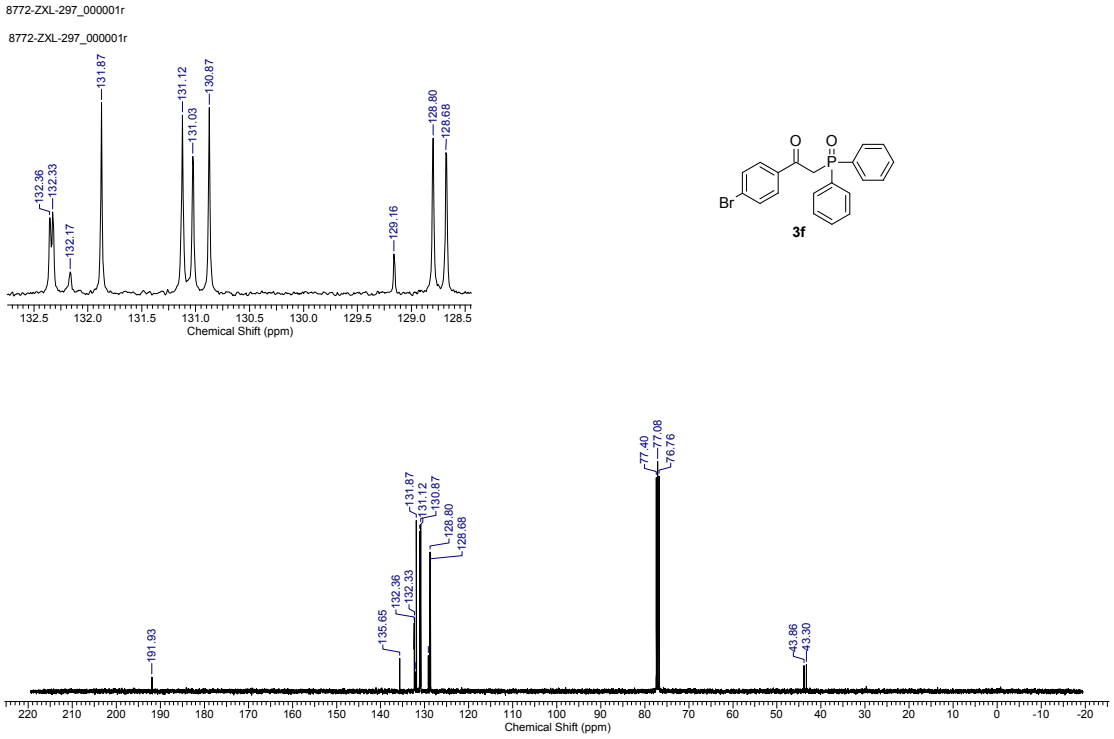


Figure S34. ^{13}C NMR spectrum of compound **3f**

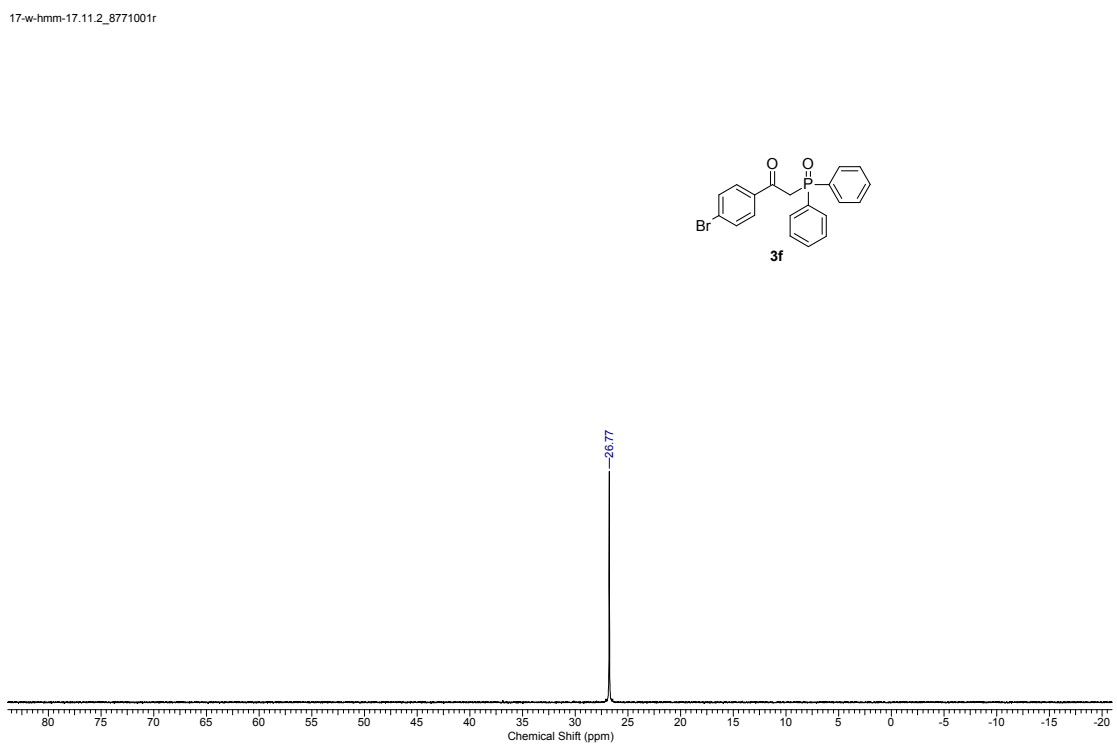


Figure S35. ^{31}P NMR spectrum of compound **3f**

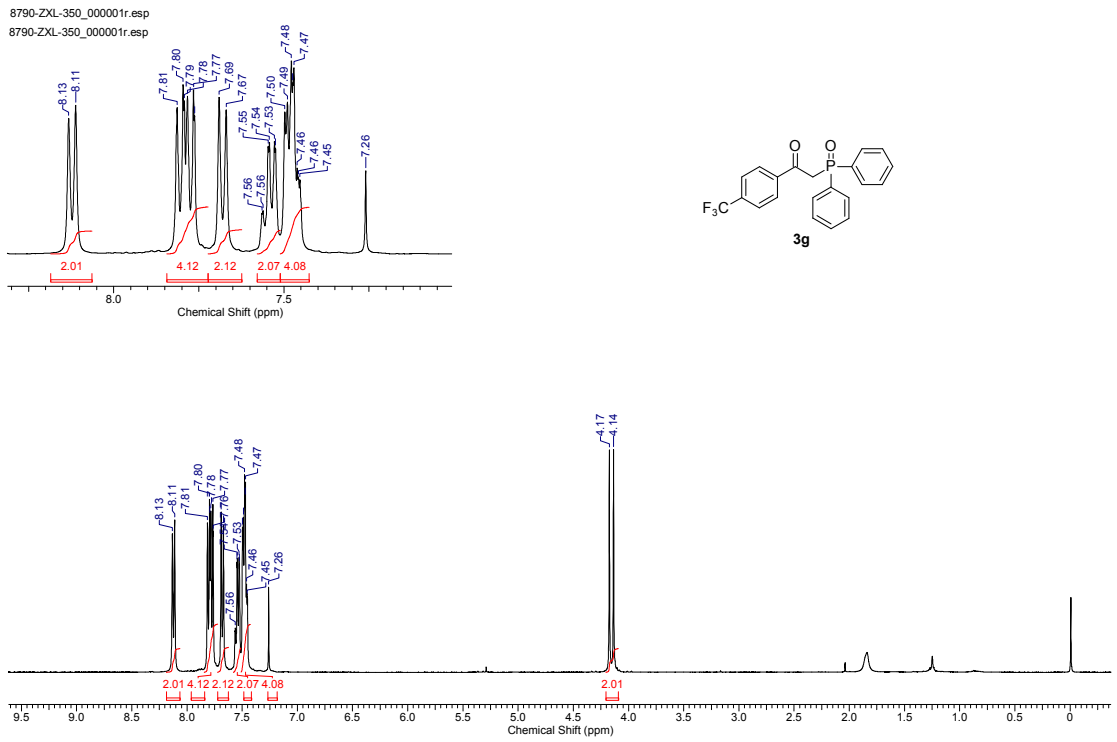


Figure S36. ^{1}H NMR spectrum of compound **3g**

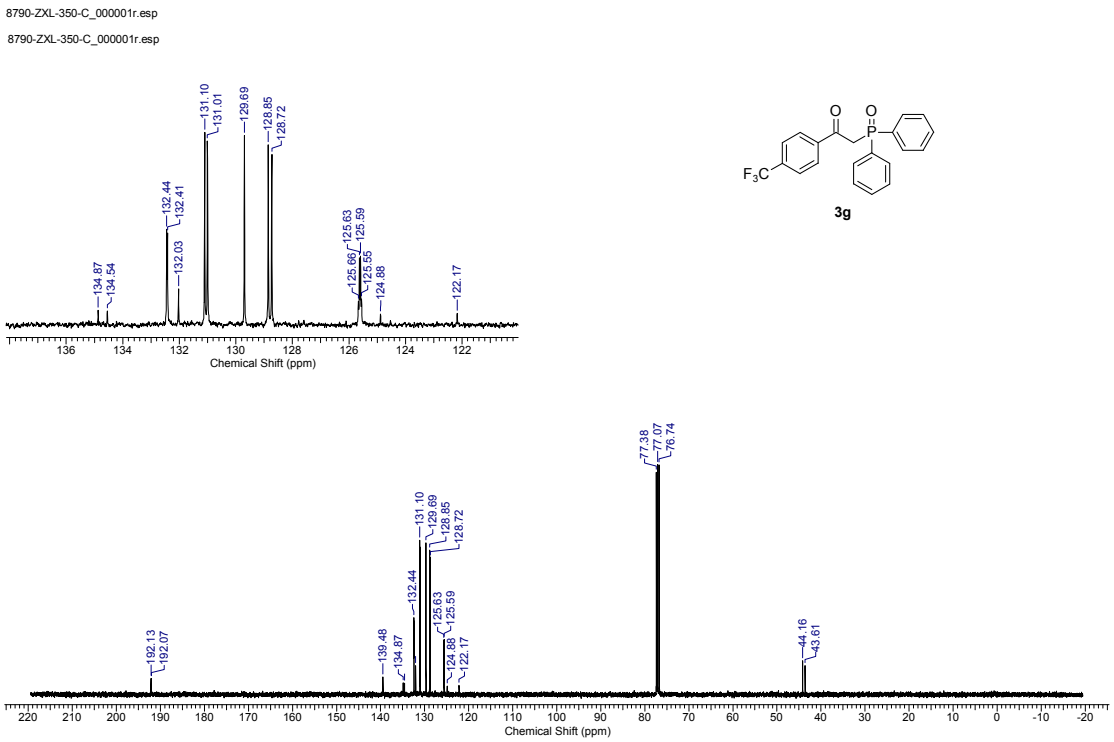


Figure S37. ^{13}C NMR spectrum of compound **3g**

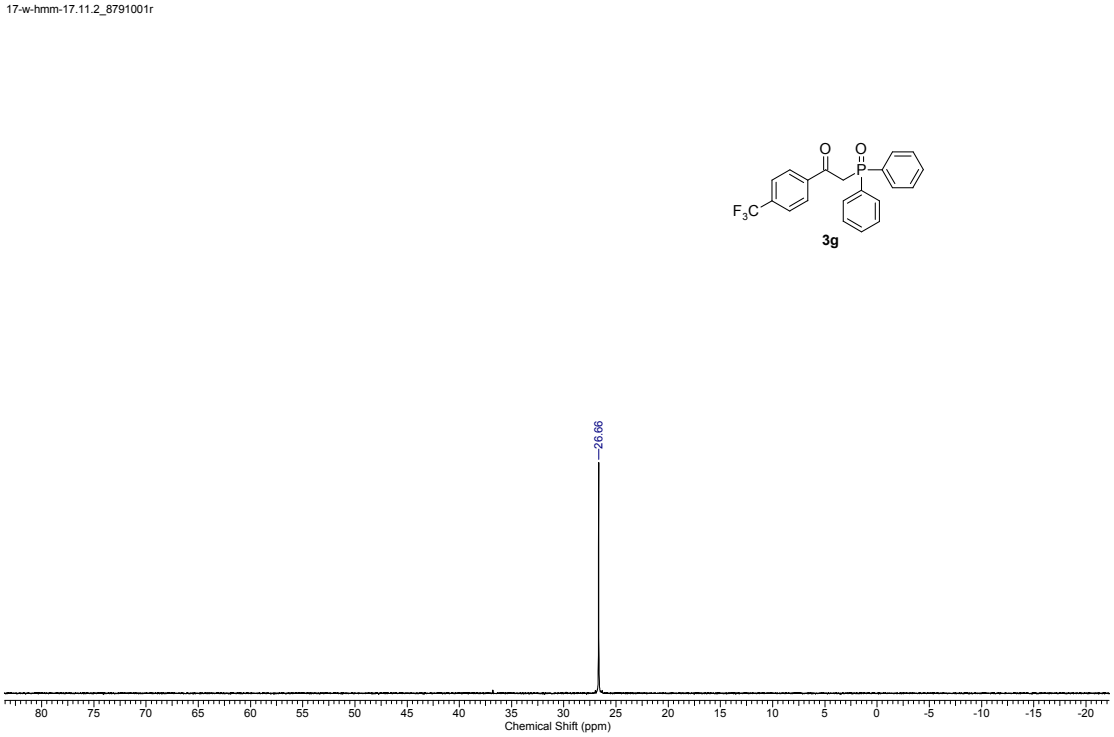


Figure S38. ^{31}P NMR spectrum of compound **3g**

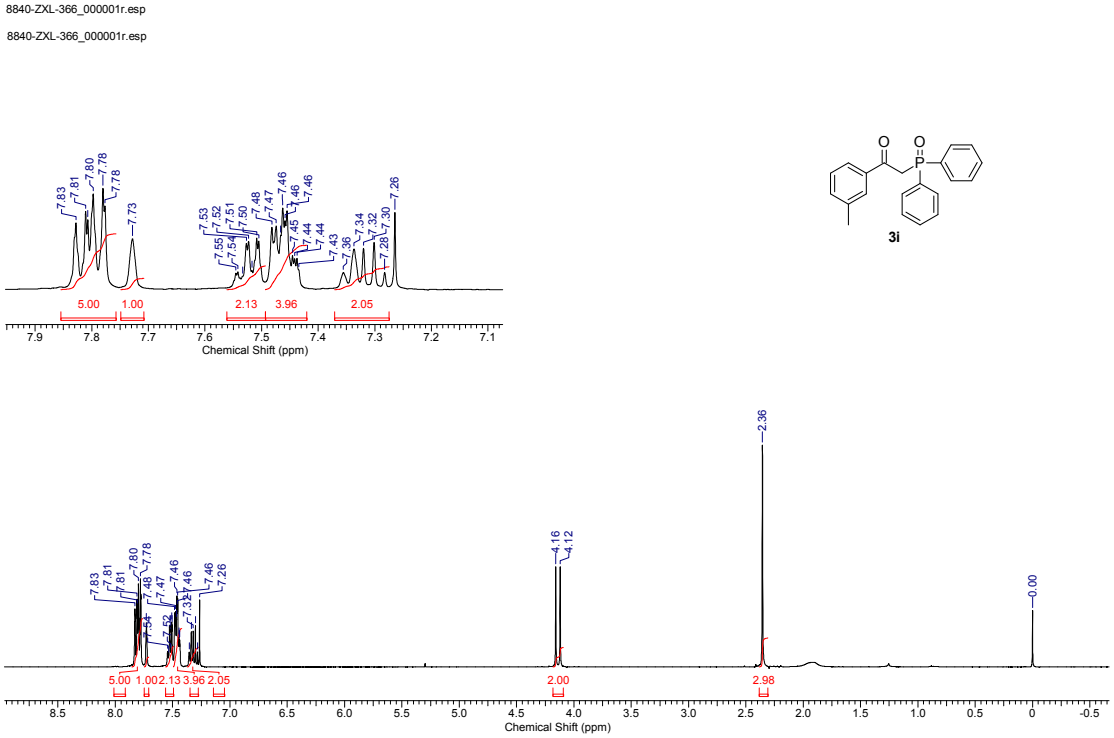


Figure S39. ^{1}H NMR spectrum of compound **3i**

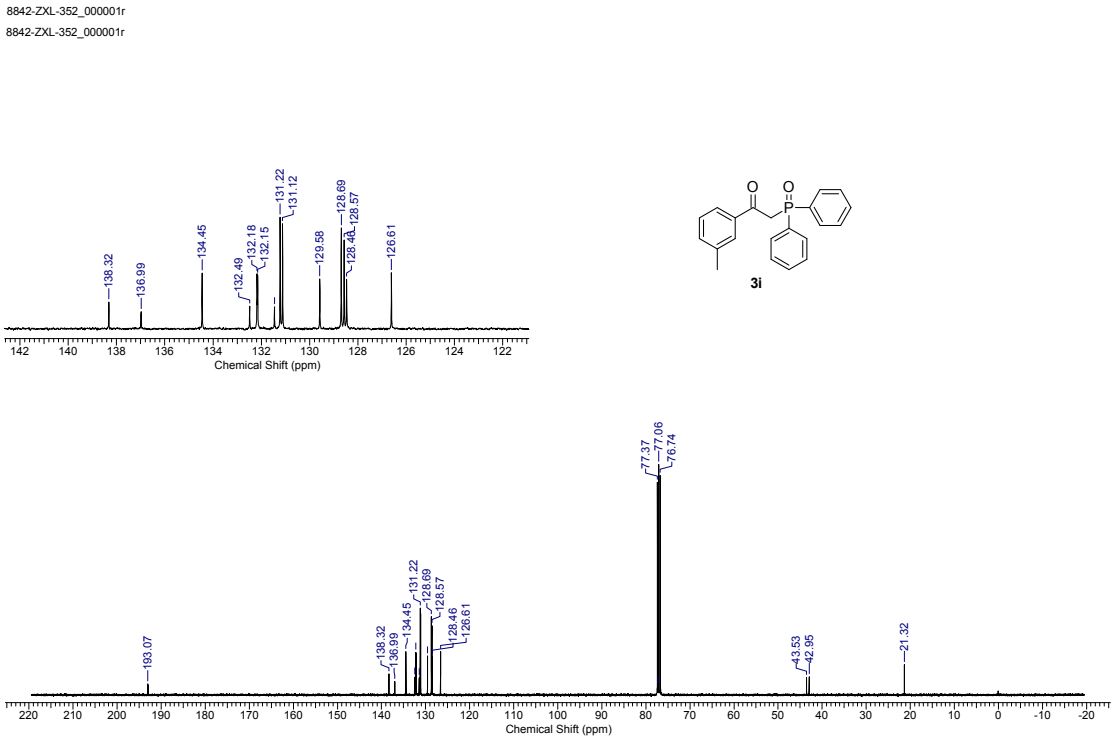


Figure S40. ^{13}C NMR spectrum of compound **3i**

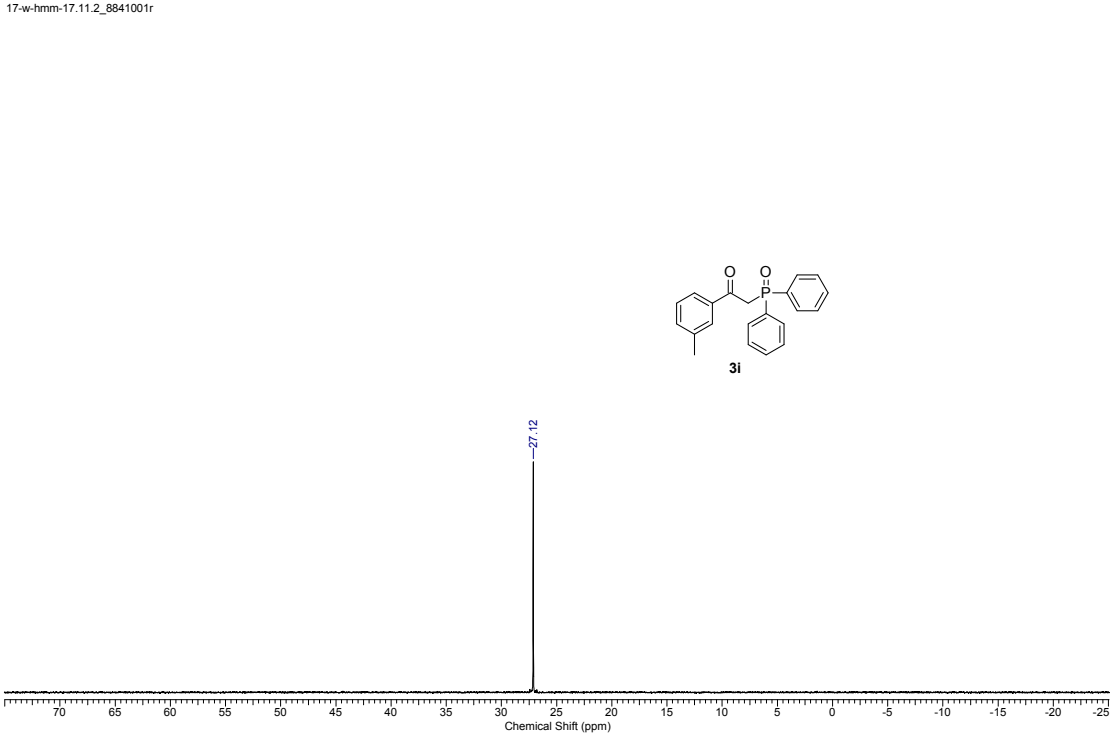


Figure S41. ^{31}P NMR spectrum of compound **3i**

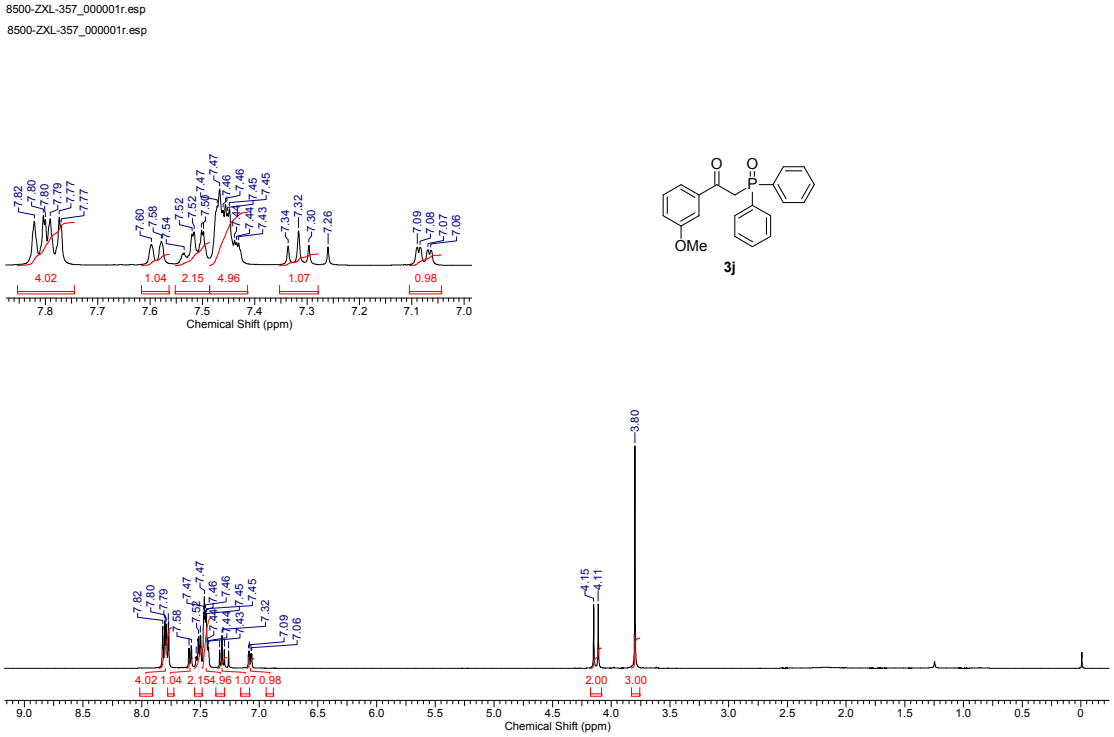


Figure S42. ^{1}H NMR spectrum of compound **3j**

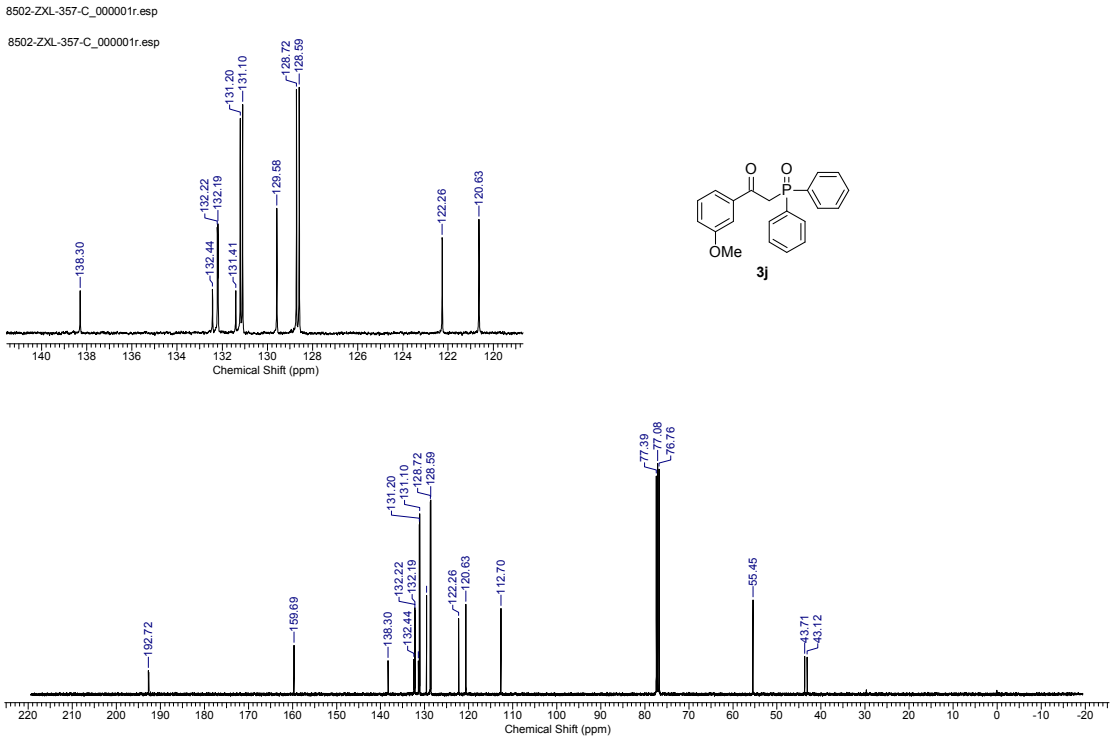


Figure S43. ^{13}C NMR spectrum of compound **3j**

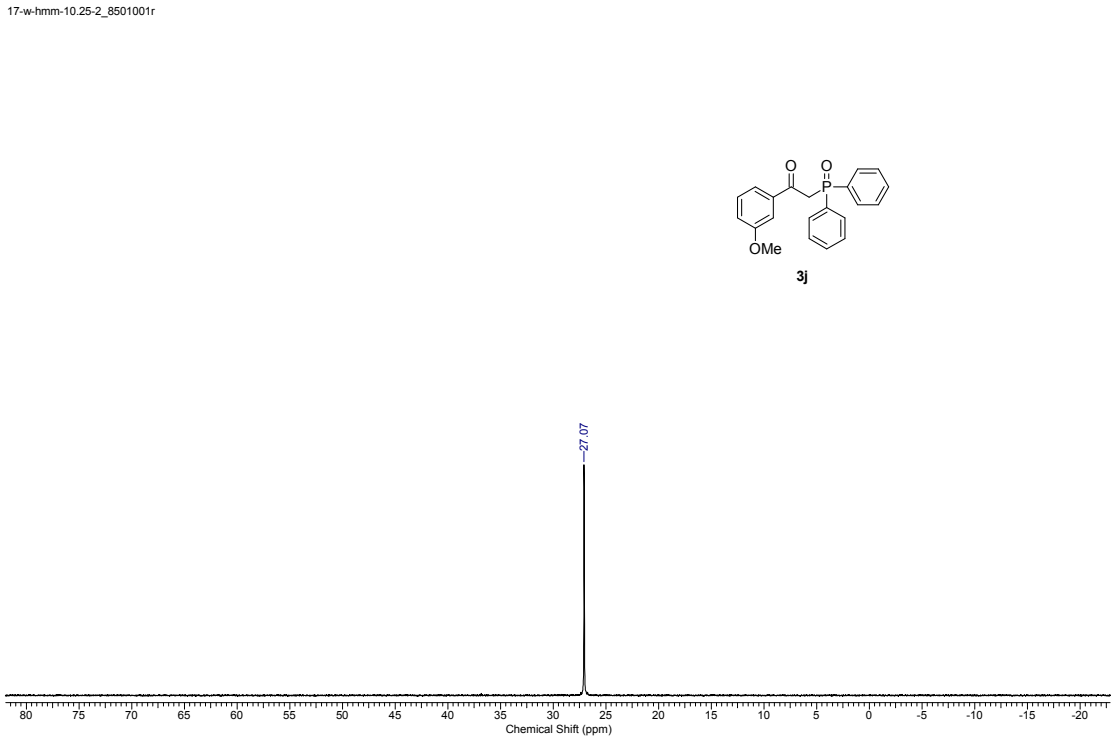


Figure S44. ^{31}P NMR spectrum of compound **3j**

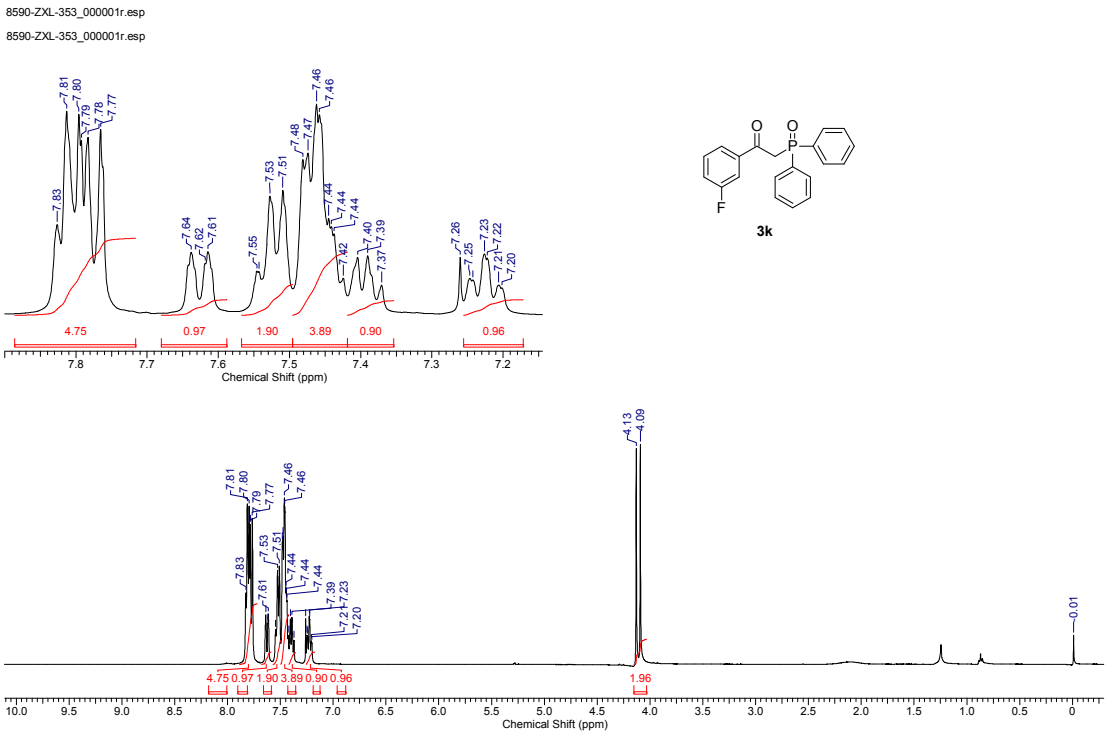


Figure S45. ^{1}H NMR spectrum of compound **3k**

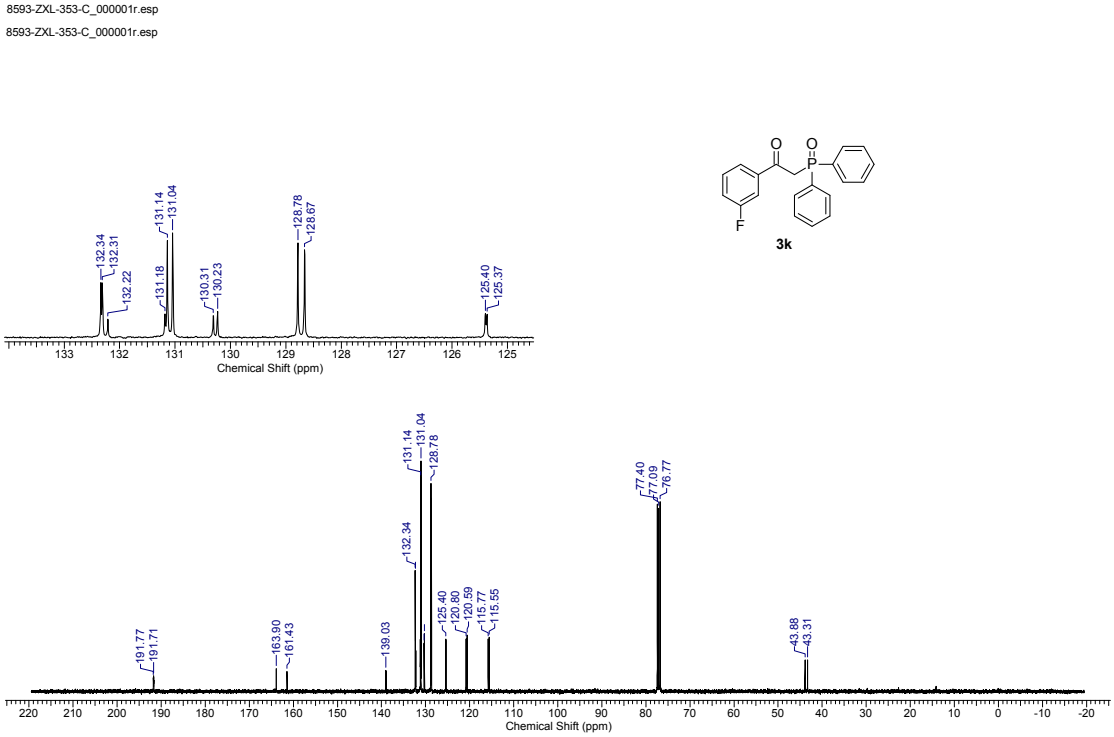


Figure S46. ^{13}C NMR spectrum of compound **3k**

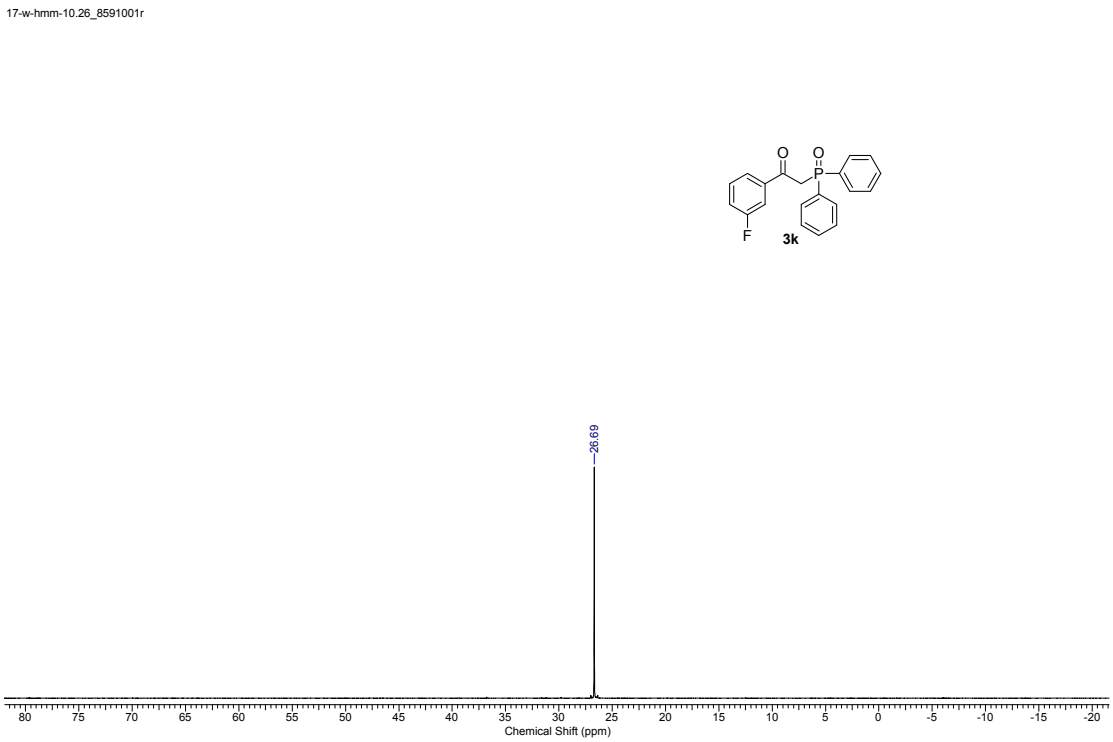


Figure S47. ^{31}P NMR spectrum of compound **3k**

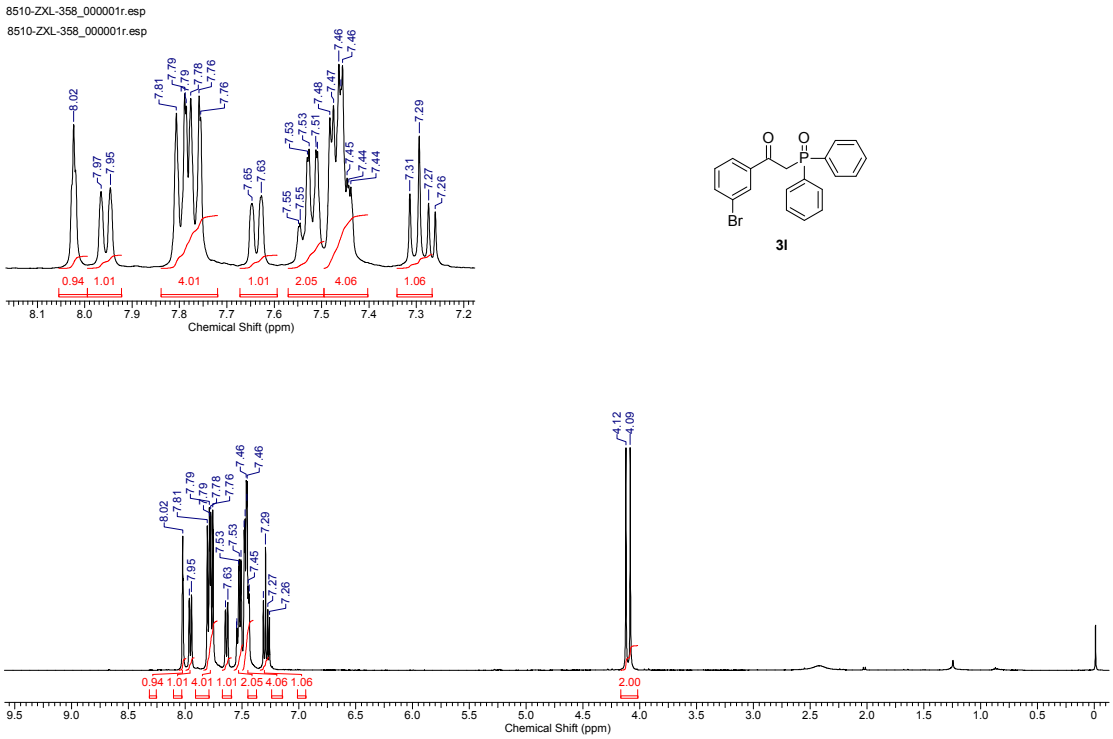


Figure S48. ^{1}H NMR spectrum of compound **3l**

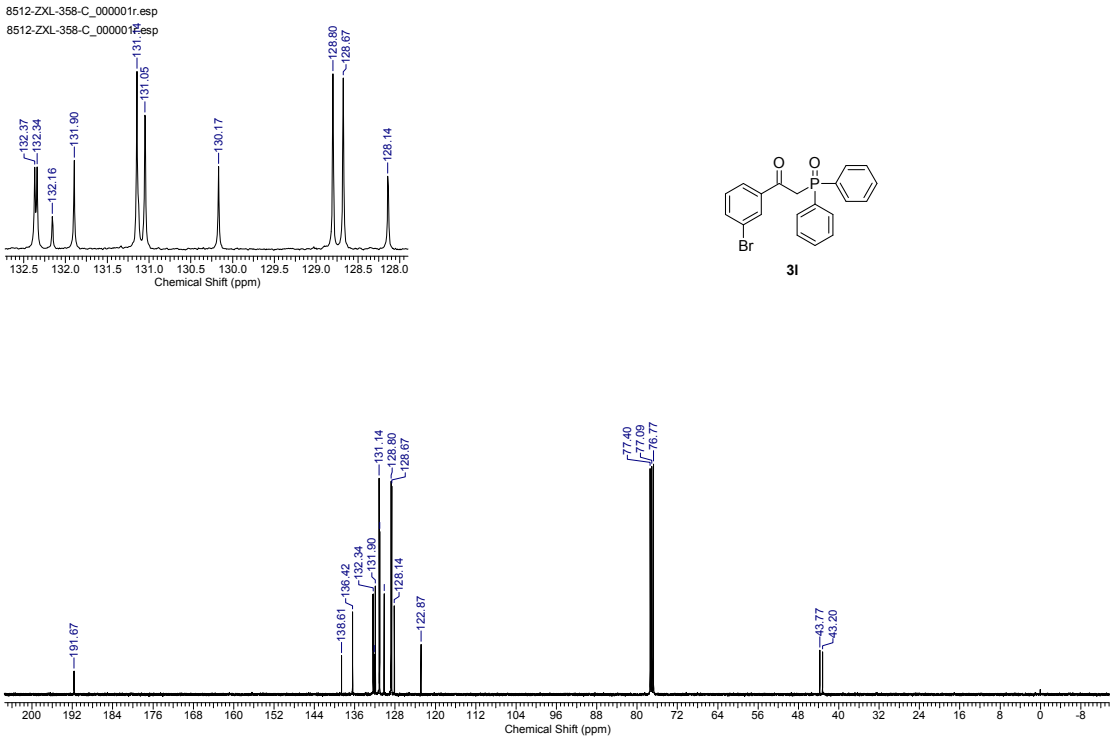


Figure S49. ^{13}C NMR spectrum of compound **3l**

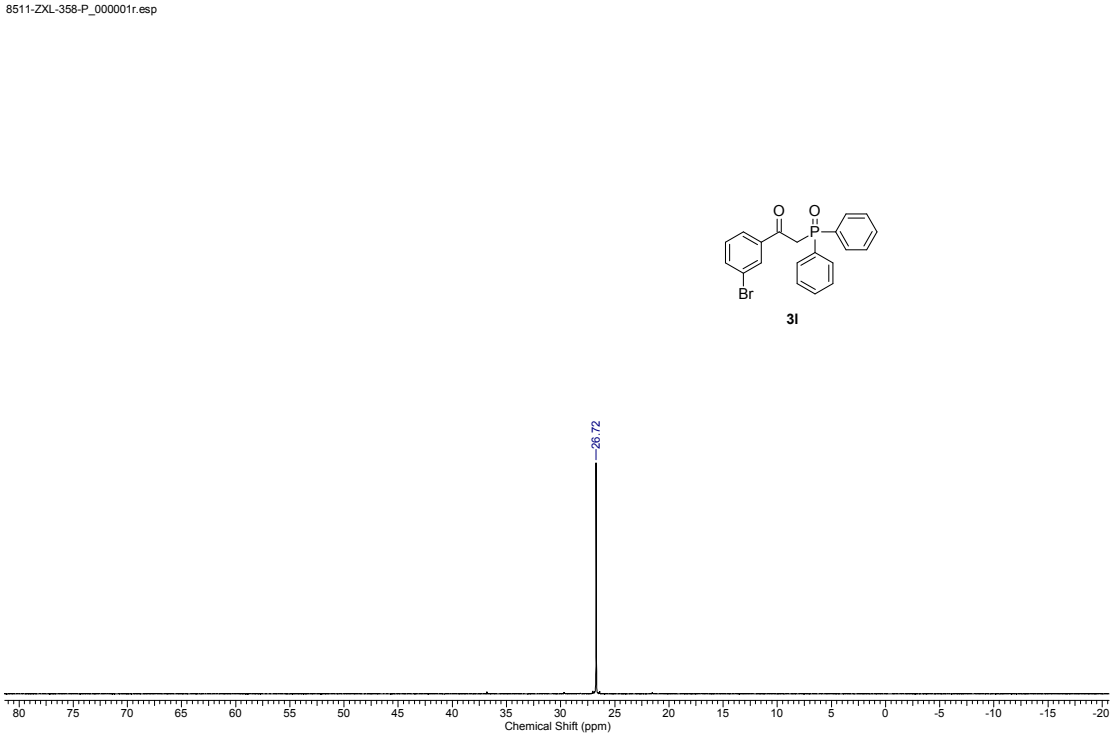


Figure S50. ^{31}P NMR spectrum of compound **3l**

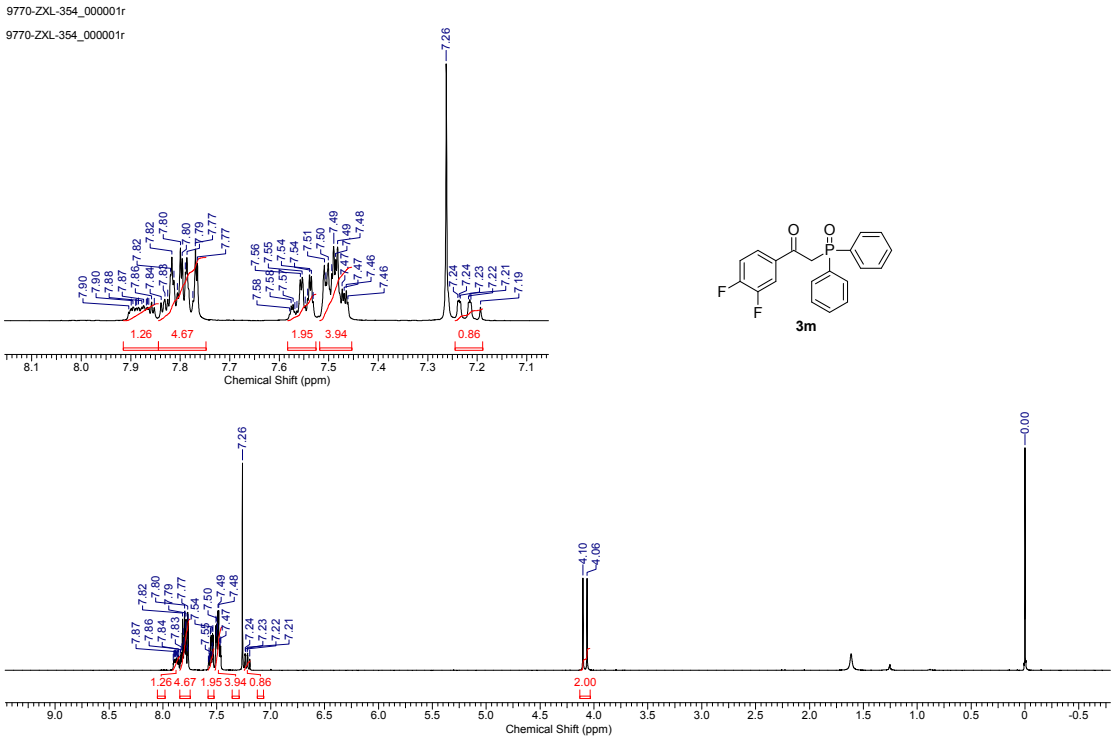


Figure S51. ^{1}H NMR spectrum of compound **3m**

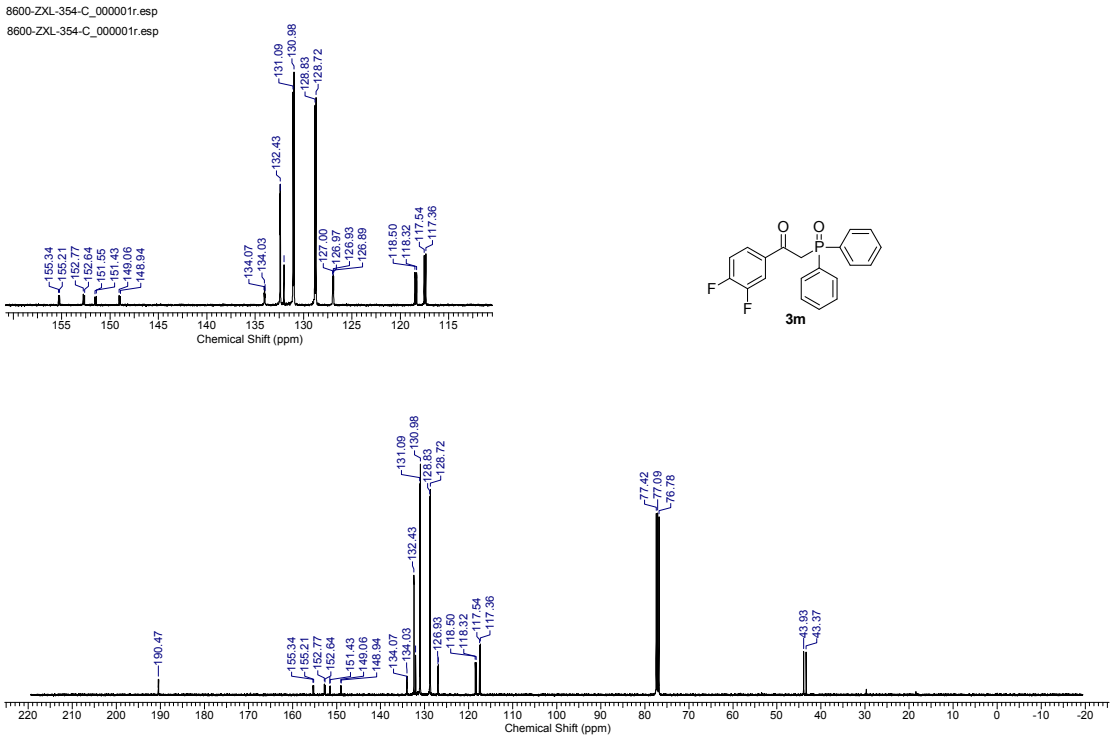


Figure S52. ^{13}C NMR spectrum of compound **3m**

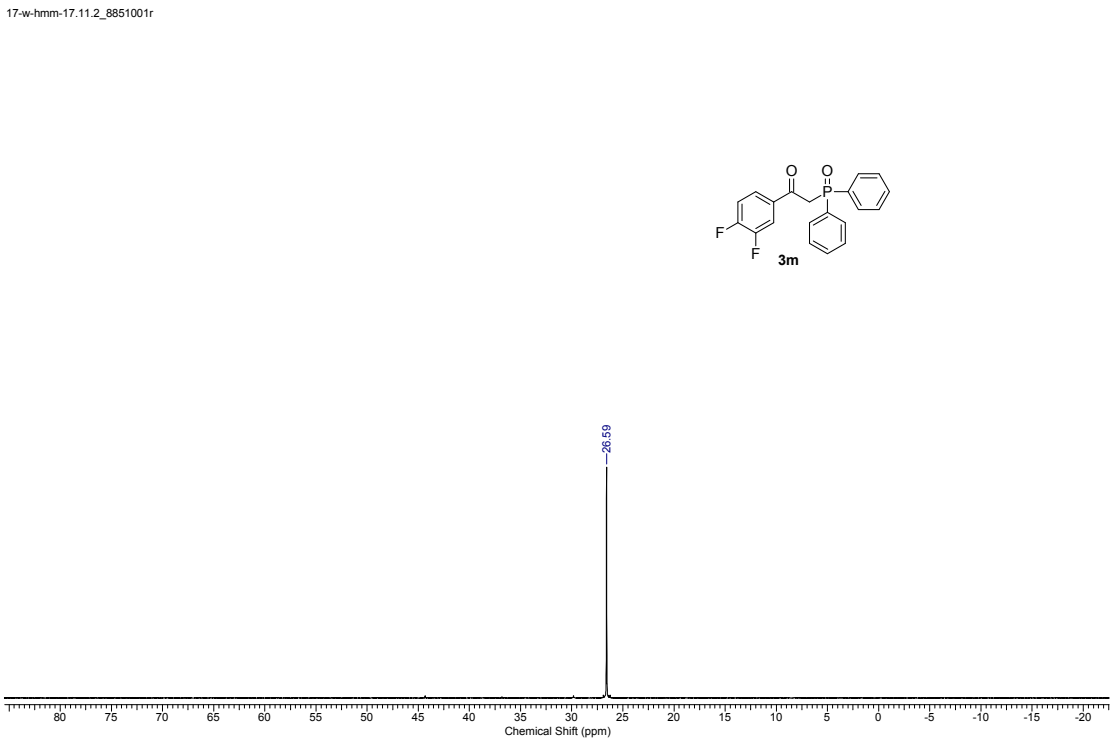


Figure S53. ^{31}P NMR spectrum of compound **3m**

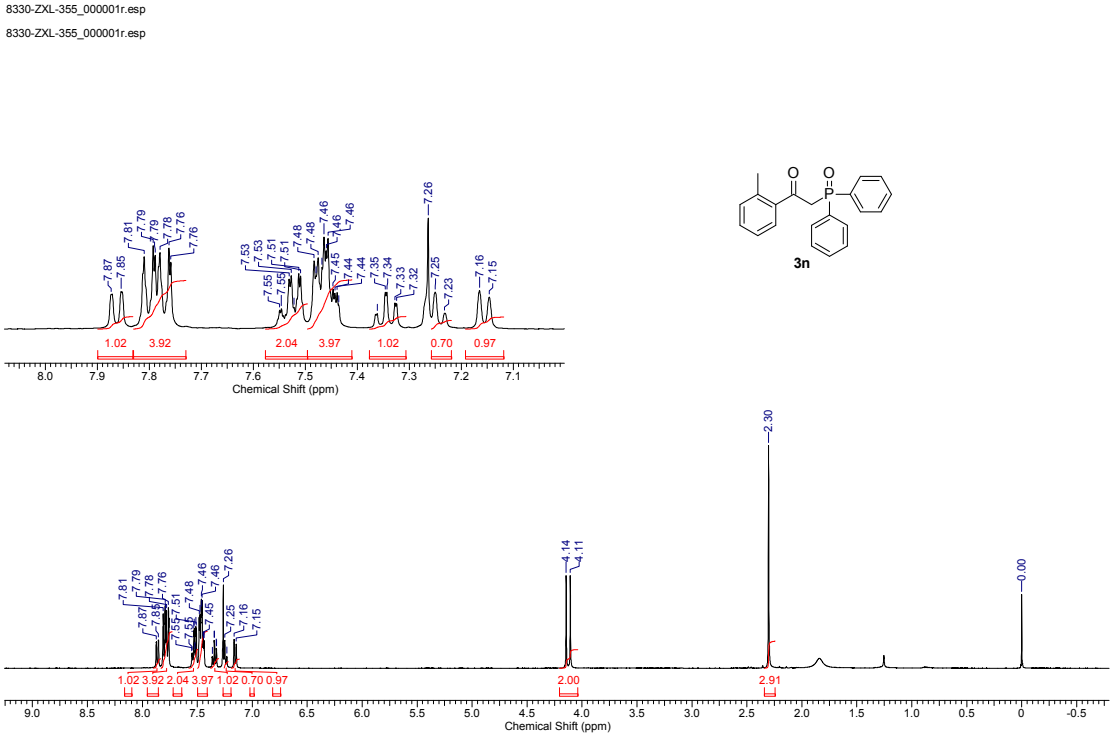


Figure S54. ^{1}H NMR spectrum of compound **3n**

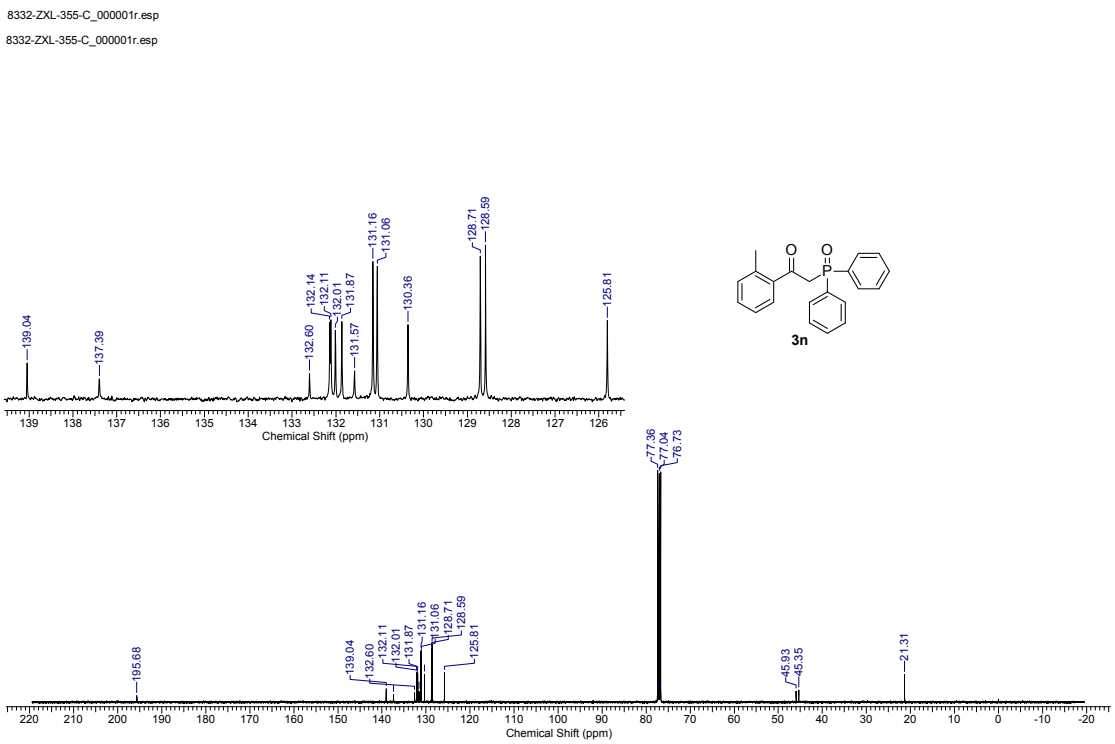


Figure S55. ^{13}C NMR spectrum of compound **3n**

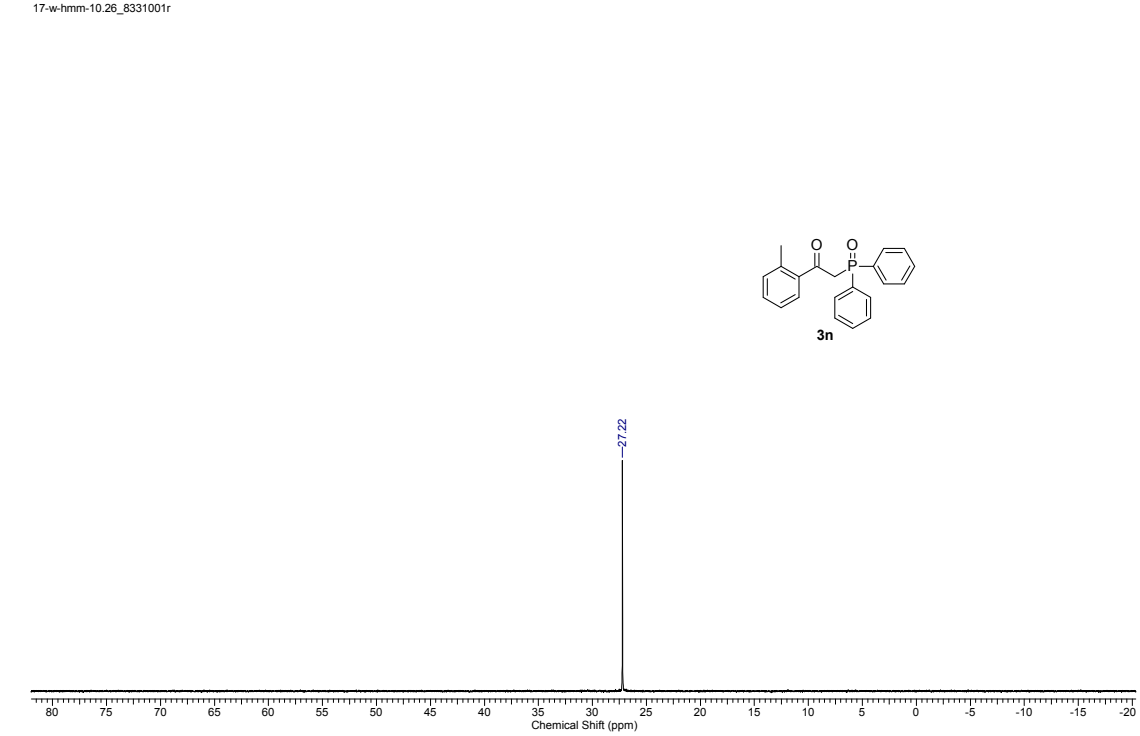


Figure S56. ^{31}P NMR spectrum of compound **3n**

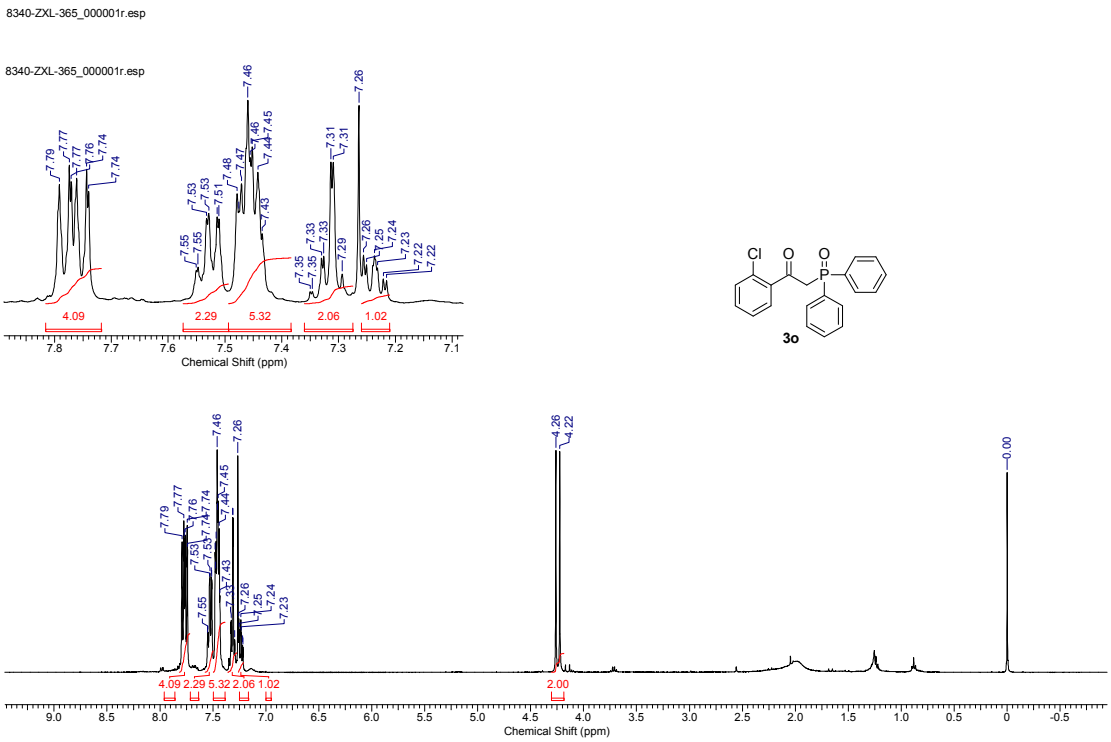


Figure S57. ^{1}H NMR spectrum of compound **3o**

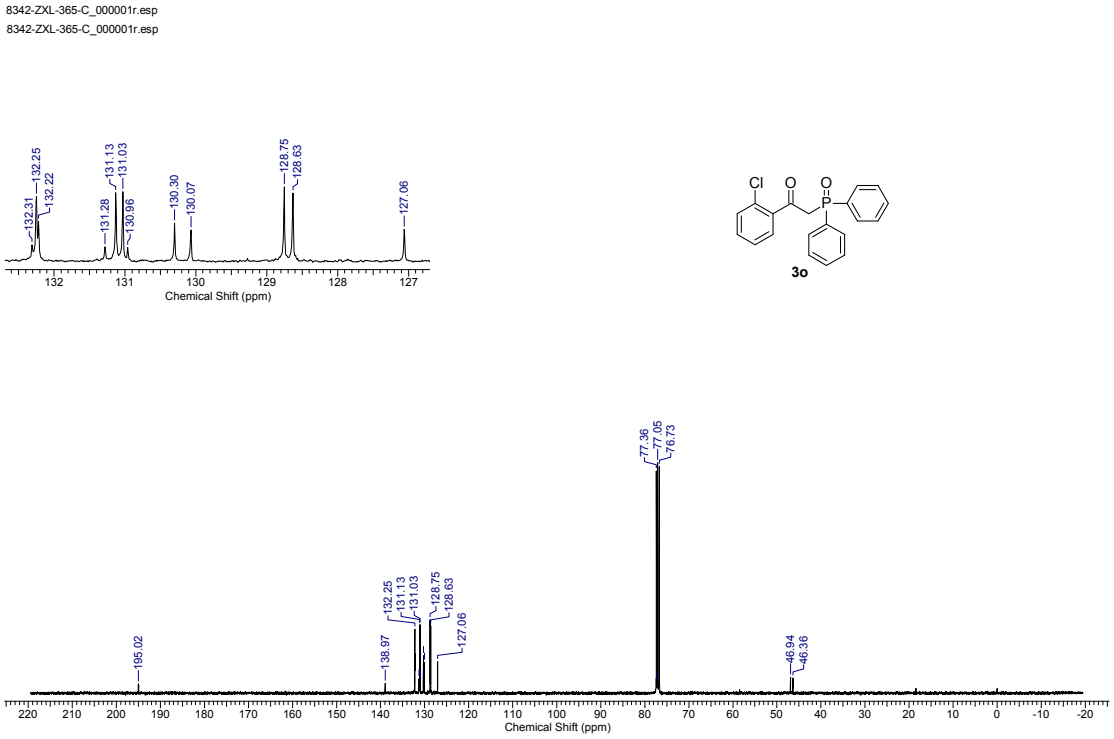


Figure S58. ^{13}C NMR spectrum of compound **3o**

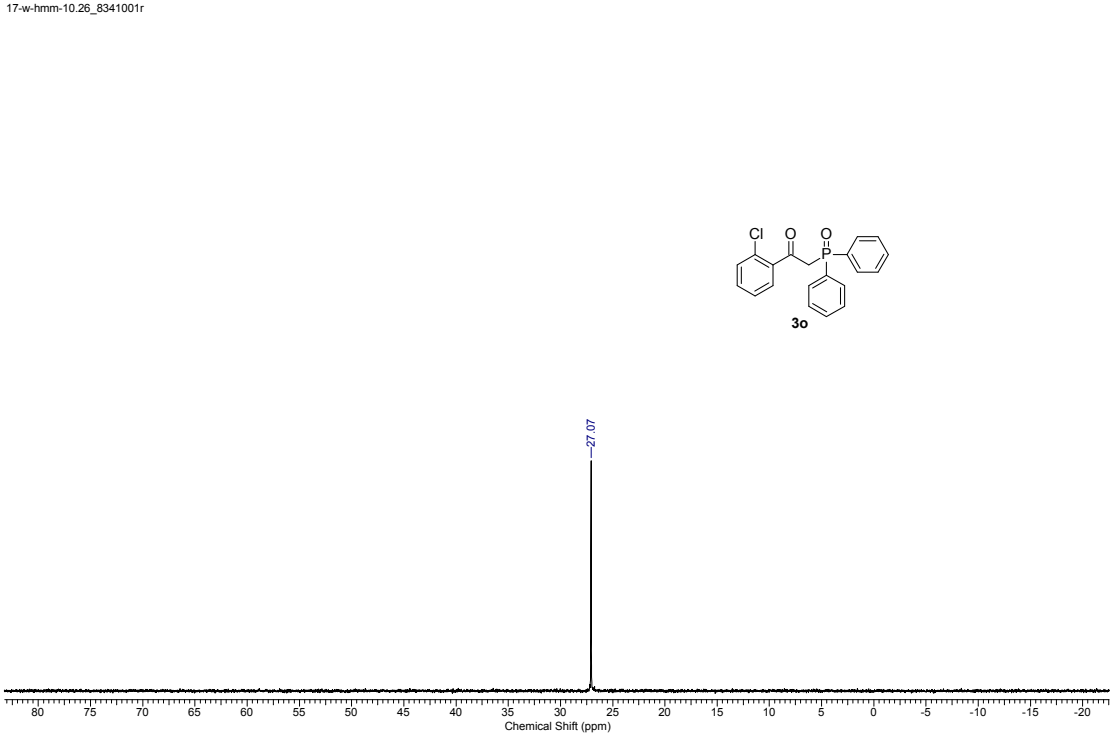


Figure S59. ^{31}P NMR spectrum of compound **3o**

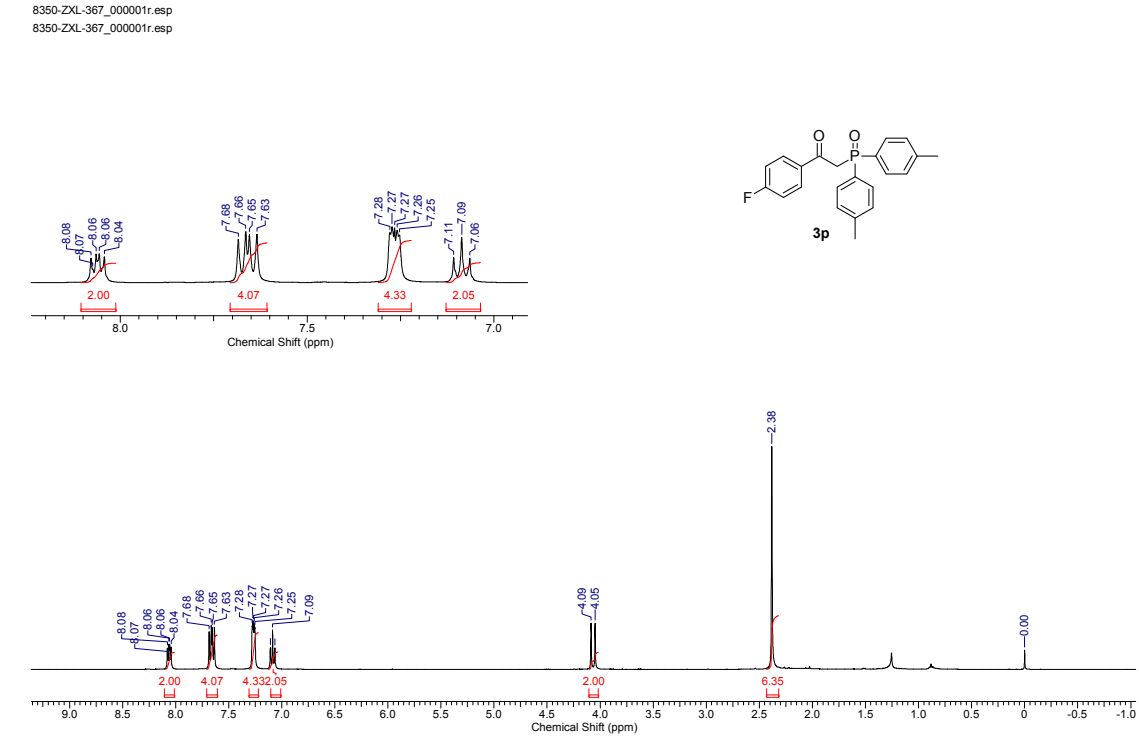


Figure S60. ^{1}H NMR spectrum of compound **3p**

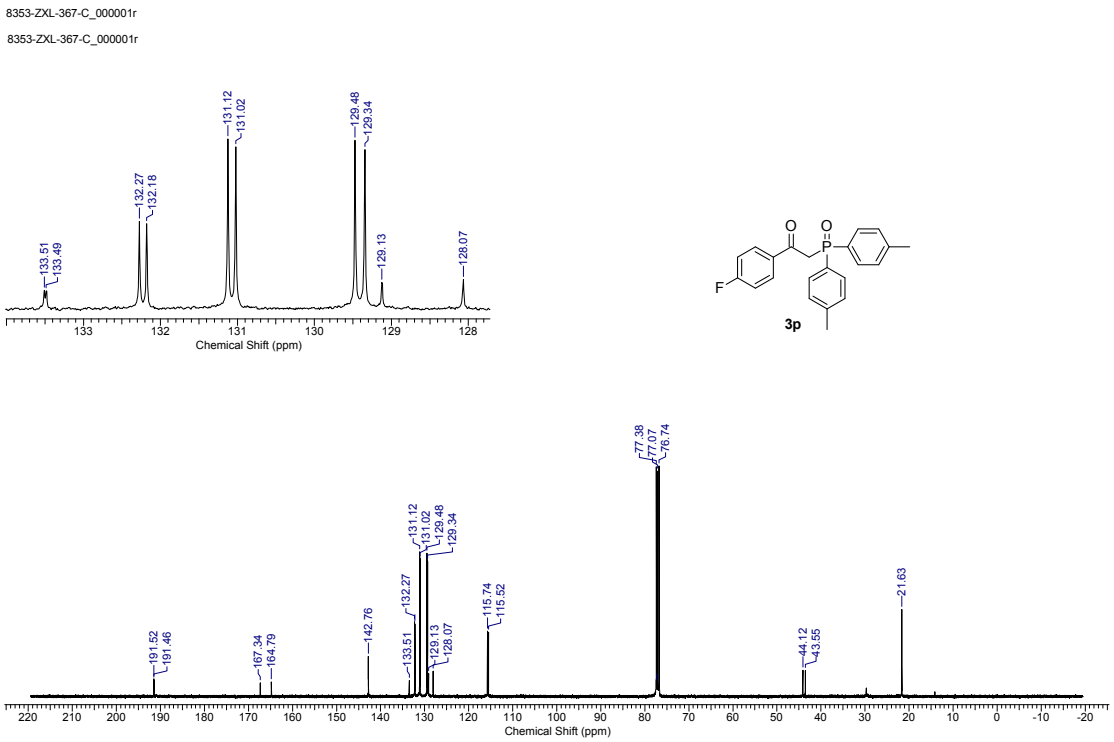


Figure S61. ^{13}C NMR spectrum of compound **3p**

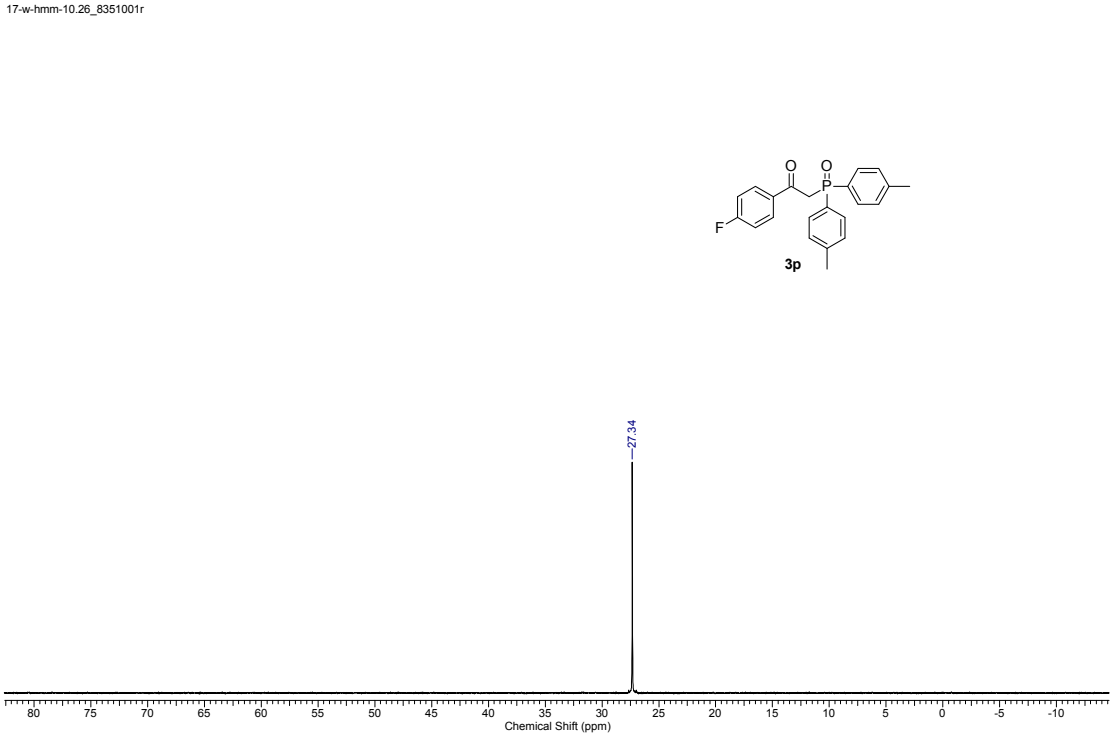


Figure S62. ^{31}P NMR spectrum of compound **3p**

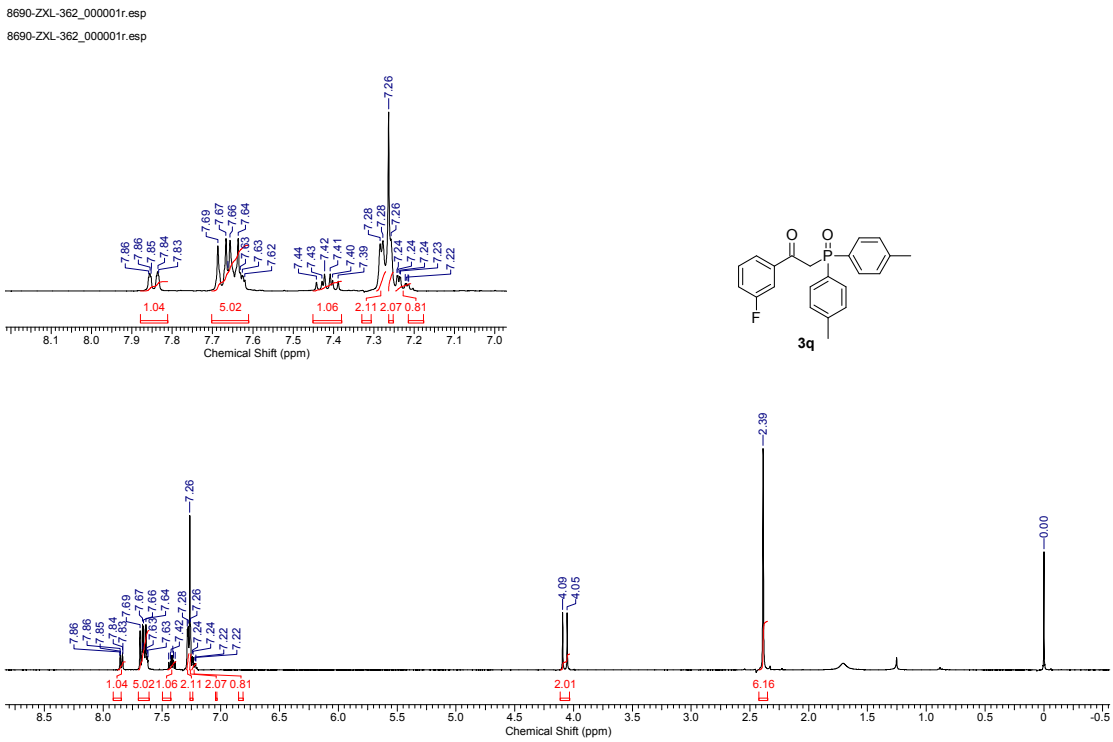


Figure S63. ^{1}H NMR spectrum of compound **3q**

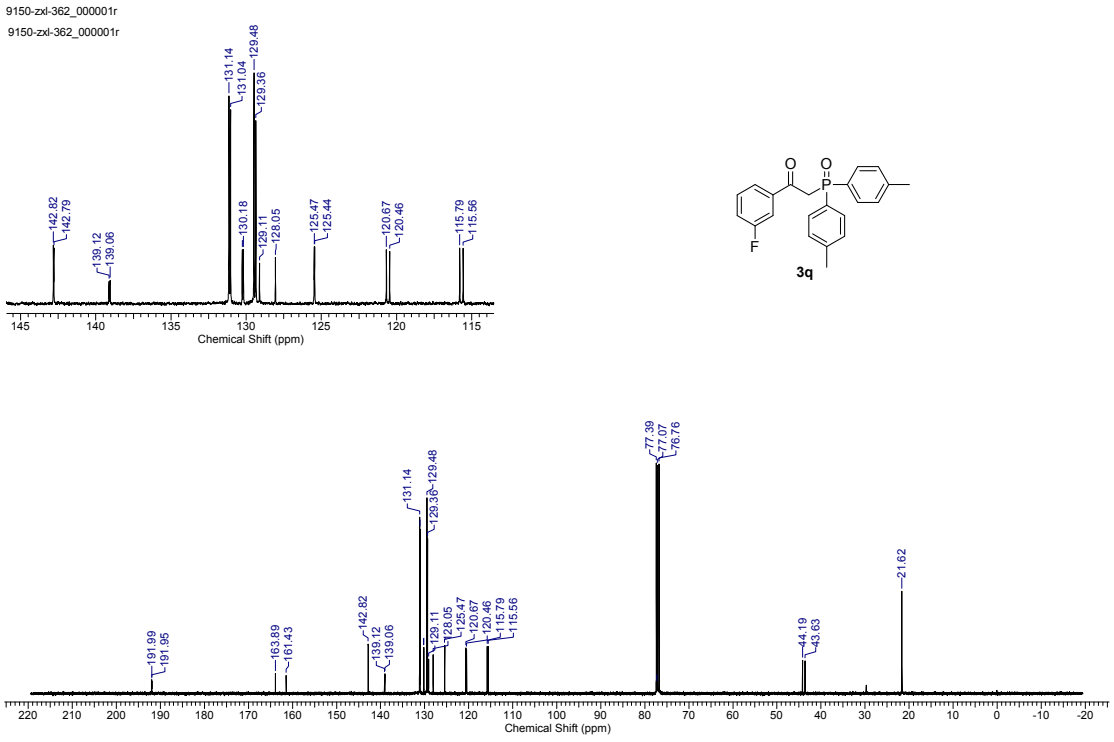


Figure S64. ^{13}C NMR spectrum of compound **3q**

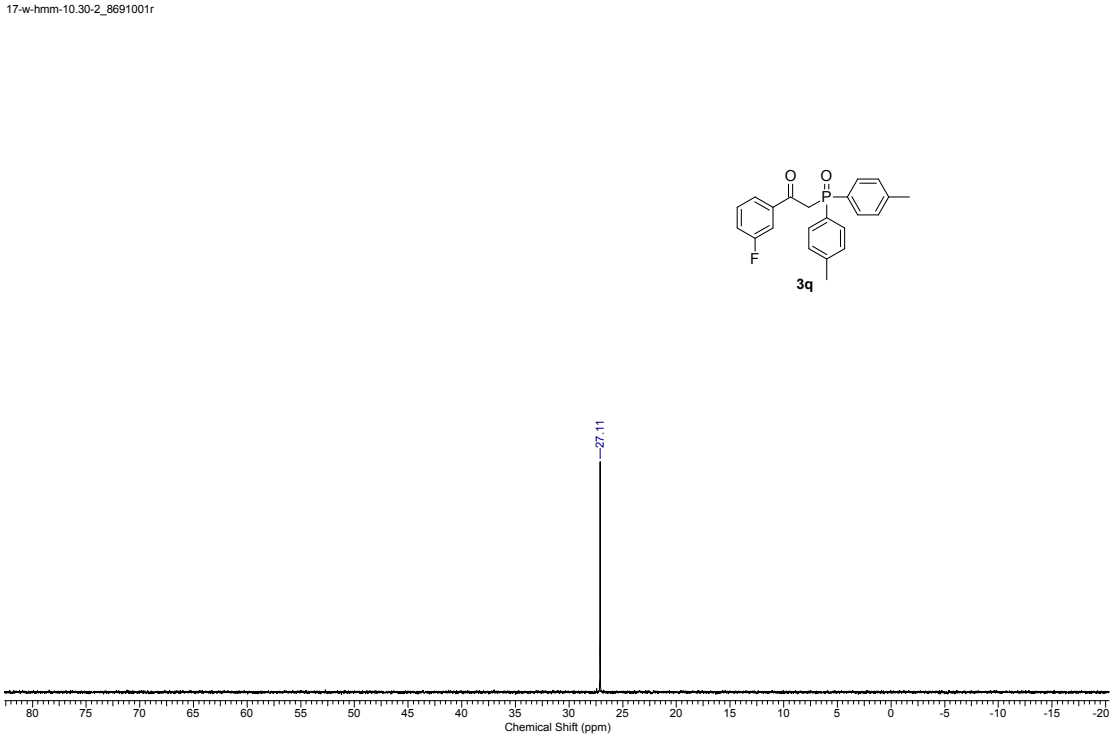


Figure S65. ^{31}P NMR spectrum of compound **3q**

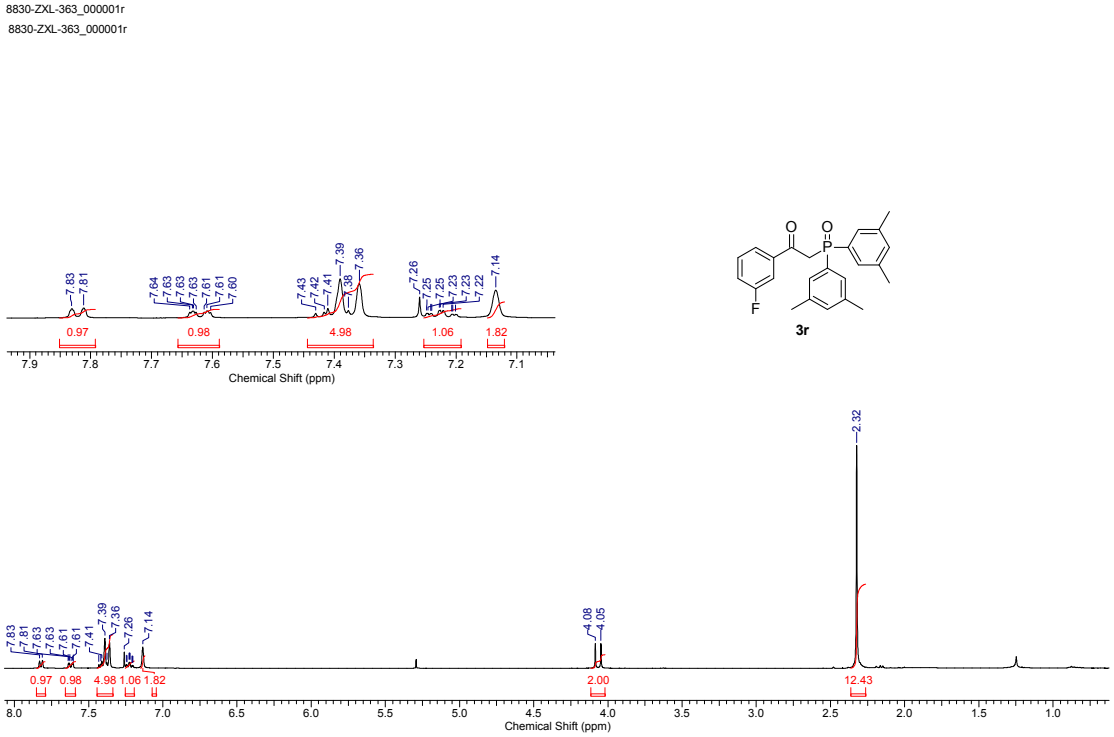


Figure S66. ^{1}H NMR spectrum of compound **3r**

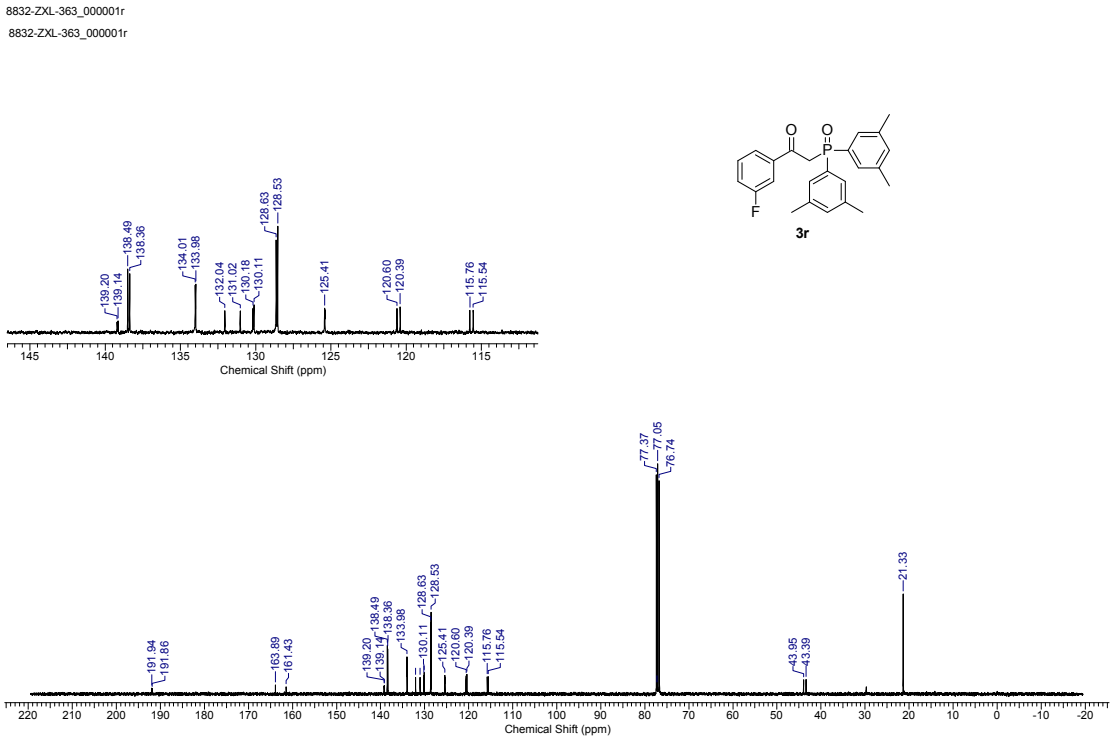


Figure S67. ^{13}C NMR spectrum of compound **3r**

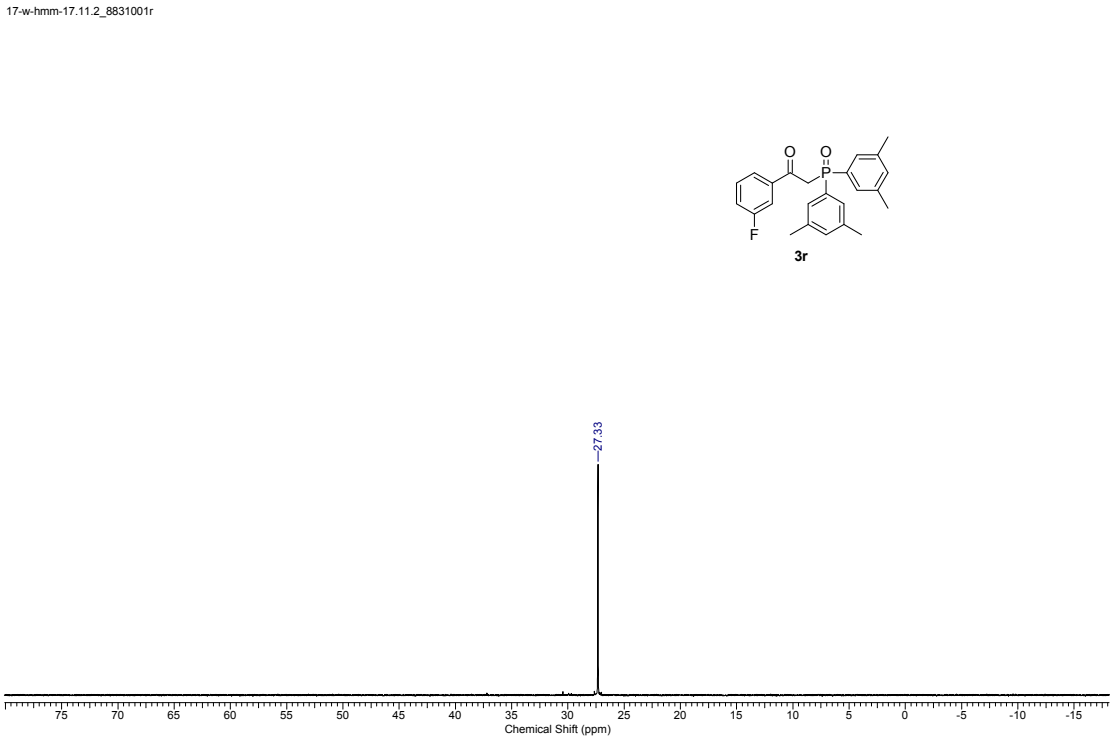


Figure S68. ^{31}P NMR spectrum of compound **3r**

8. The IR spectra of the complexes 7

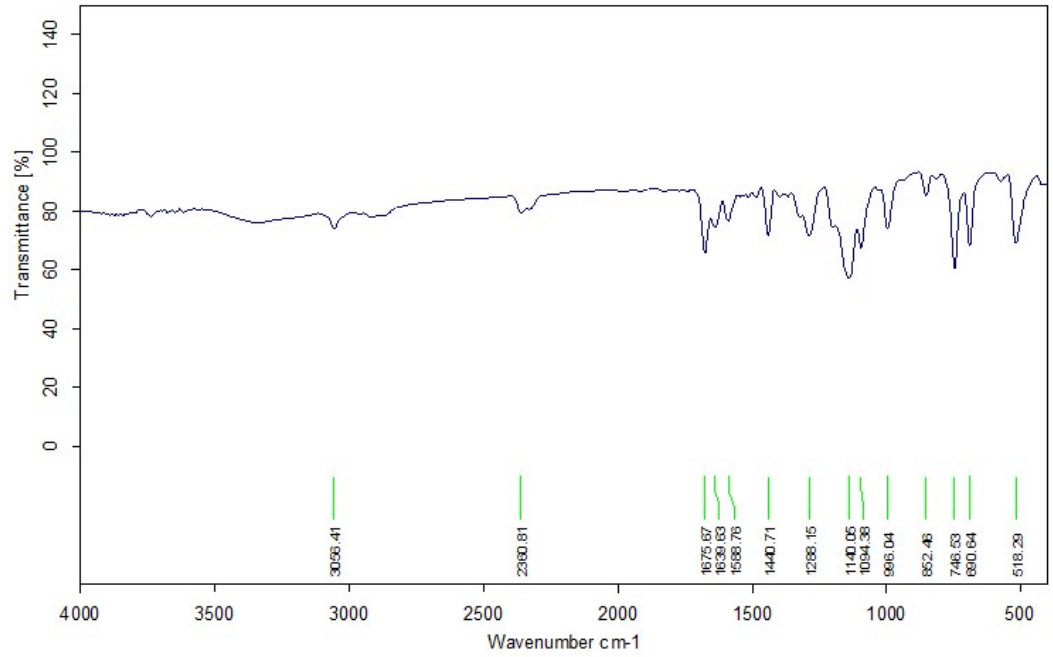


Figure S69. IR spectra of compound **7a**

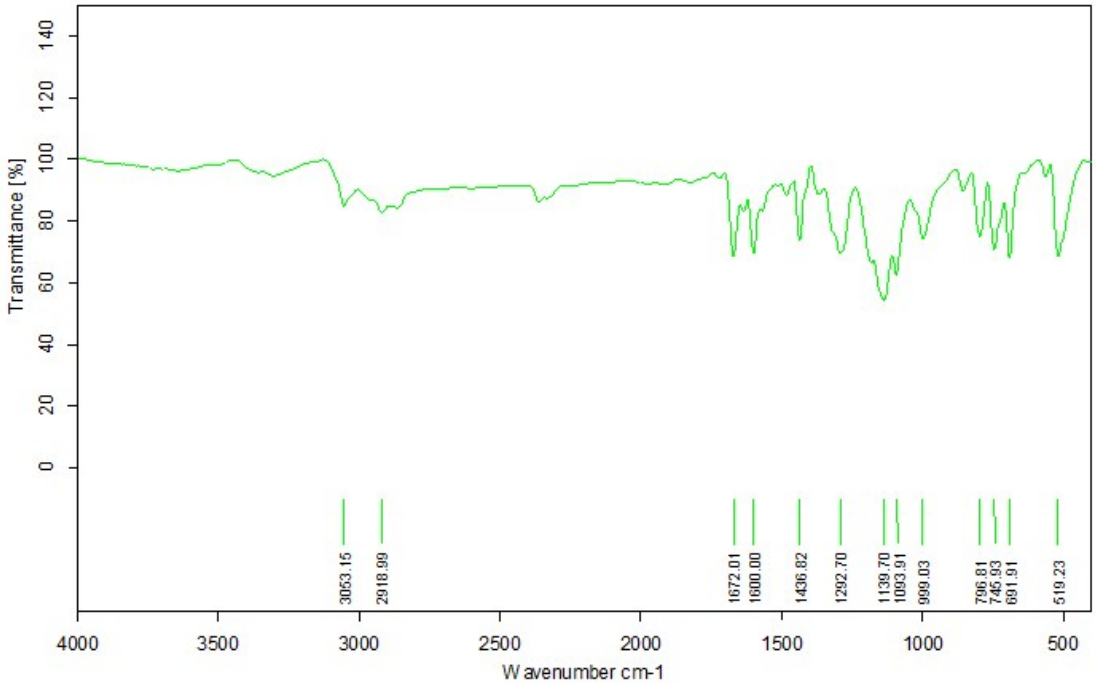


Figure S70. IR spectra of compound **7b**

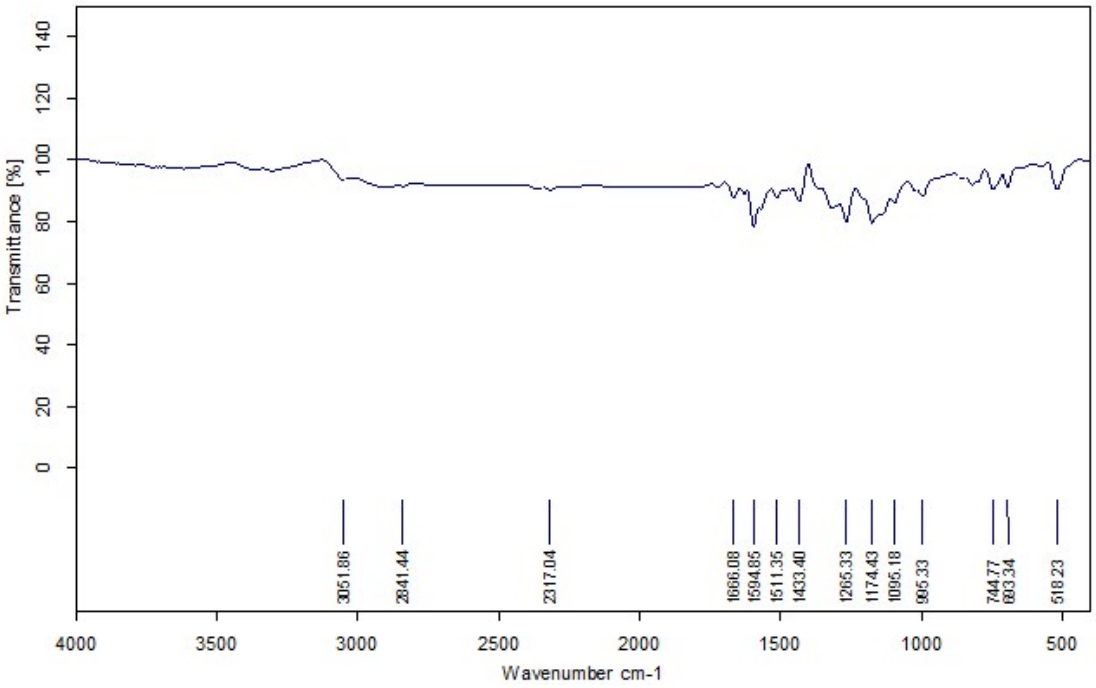


Figure S71. IR spectra of compound **7c**

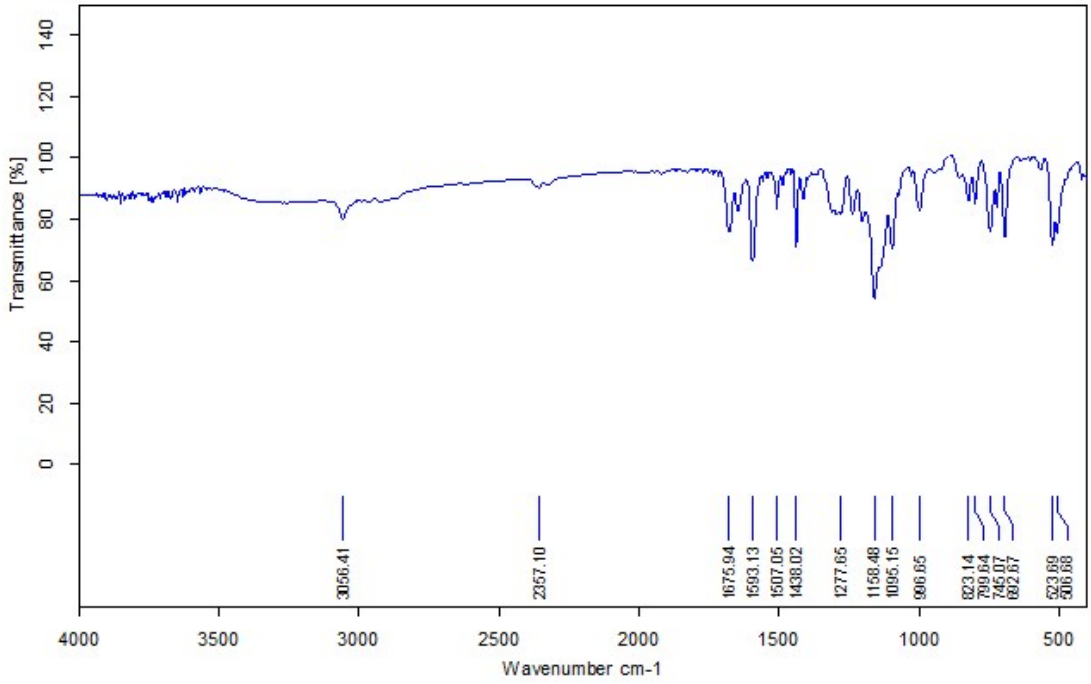


Figure S72. IR spectra of compound **7d**

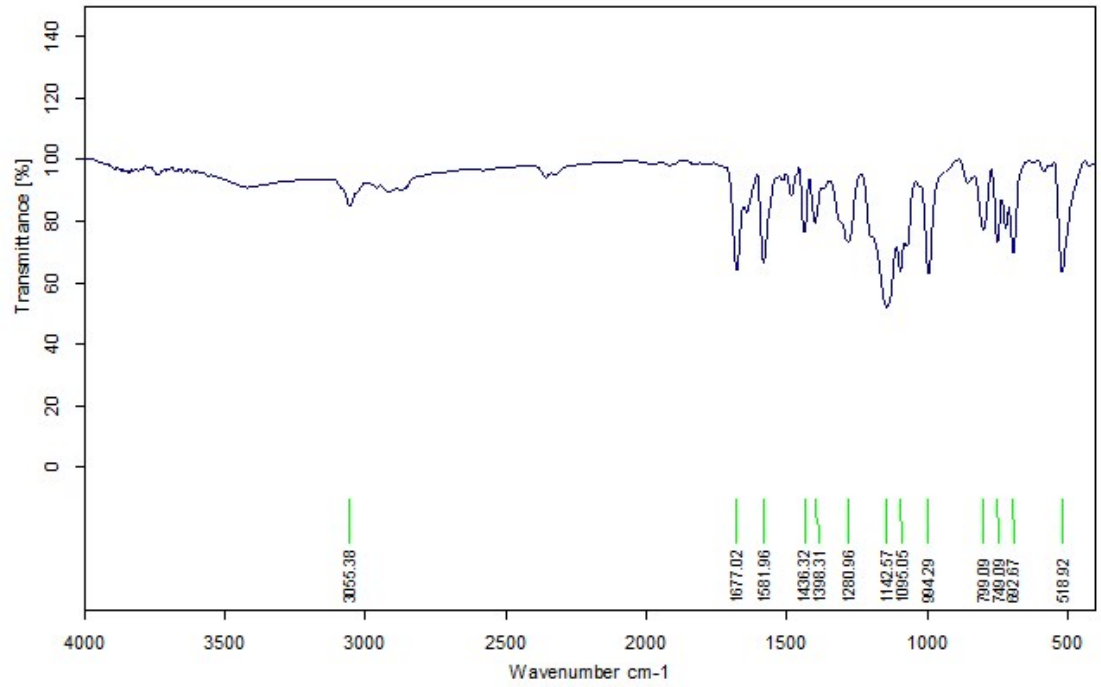


Figure S73. IR spectra of compound **7e**

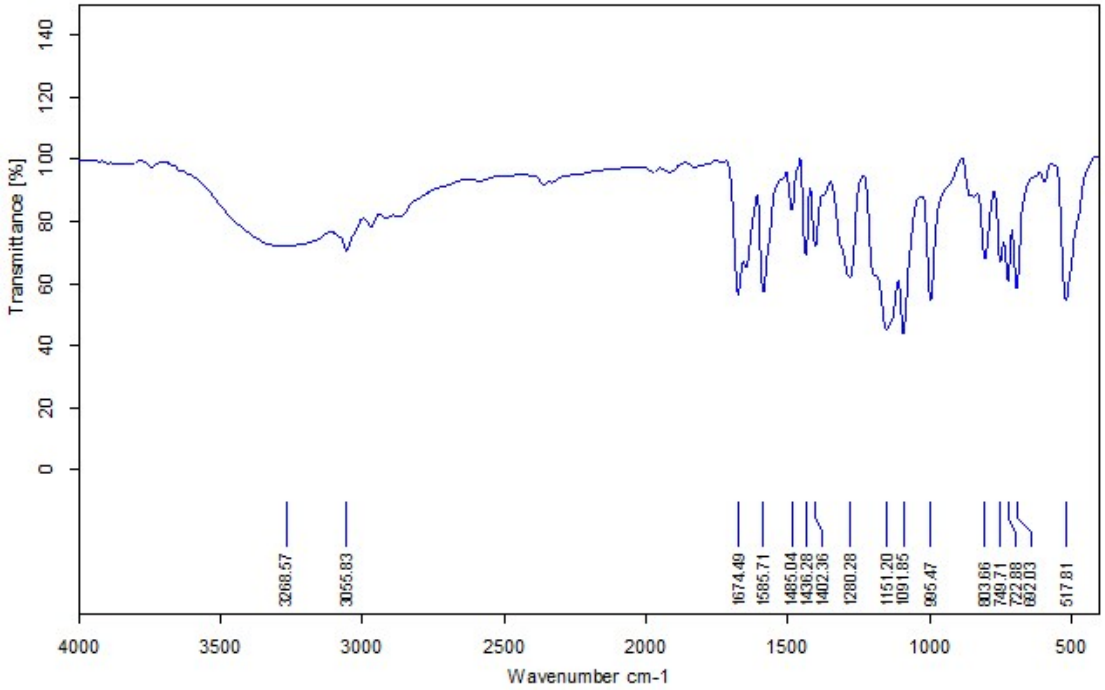


Figure S74. IR spectra of compound **7f**

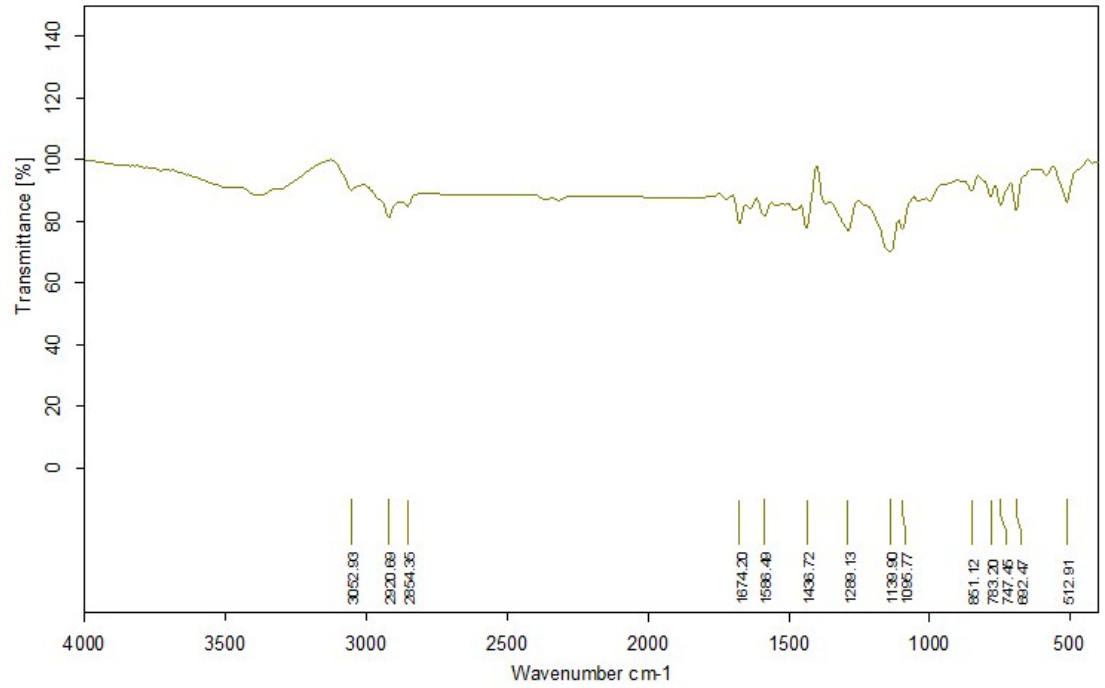


Figure S75. IR spectra of compound **7g**

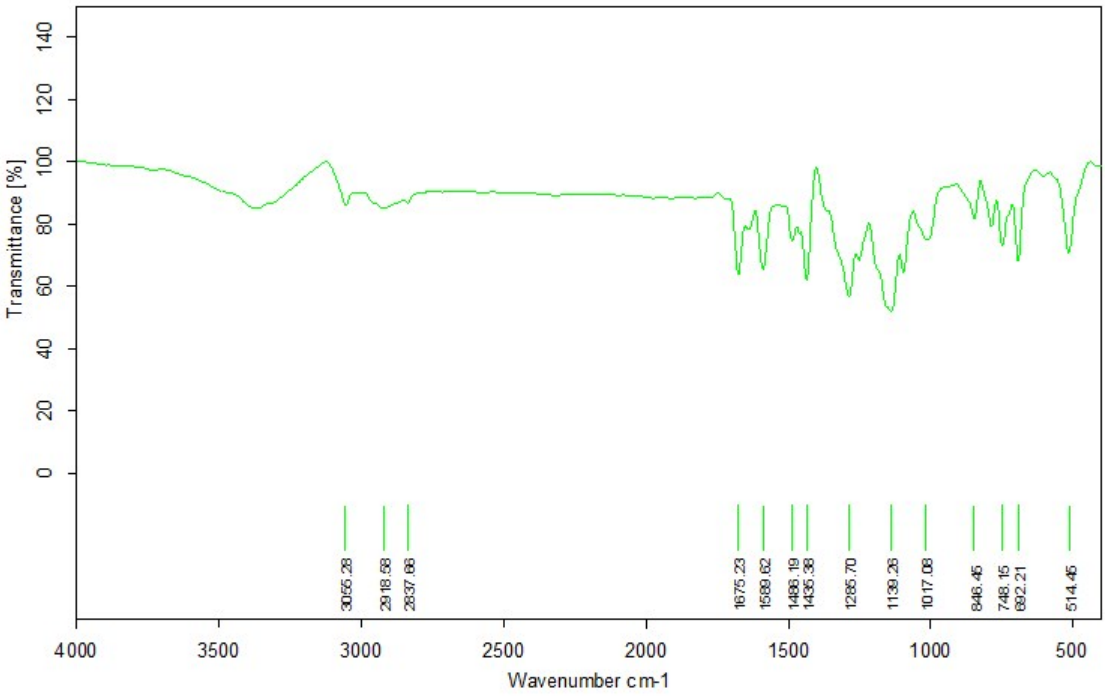


Figure S76. IR spectra of compound **7h**

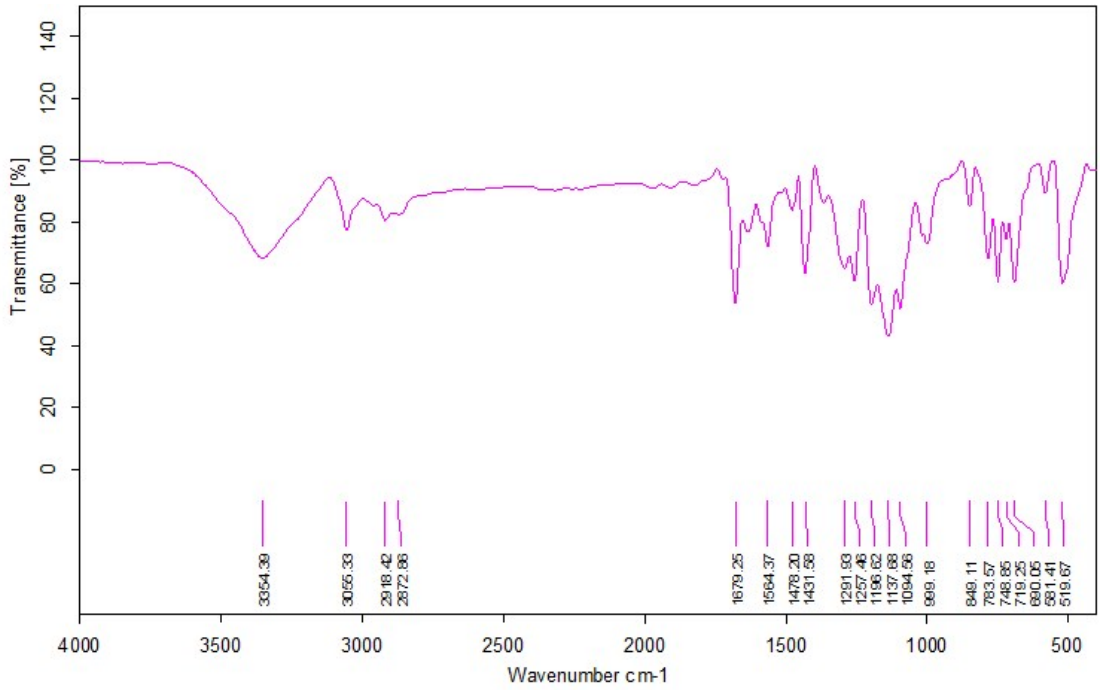


Figure S77. IR spectra of compound **7i**

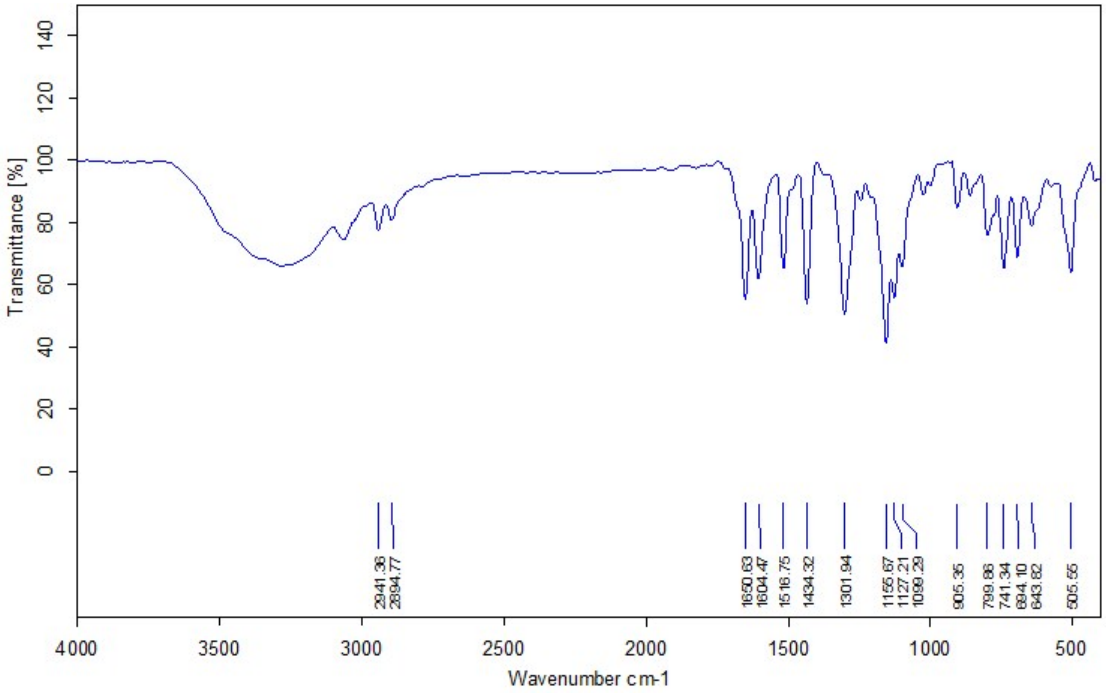


Figure S78. IR spectra of compound **7j**

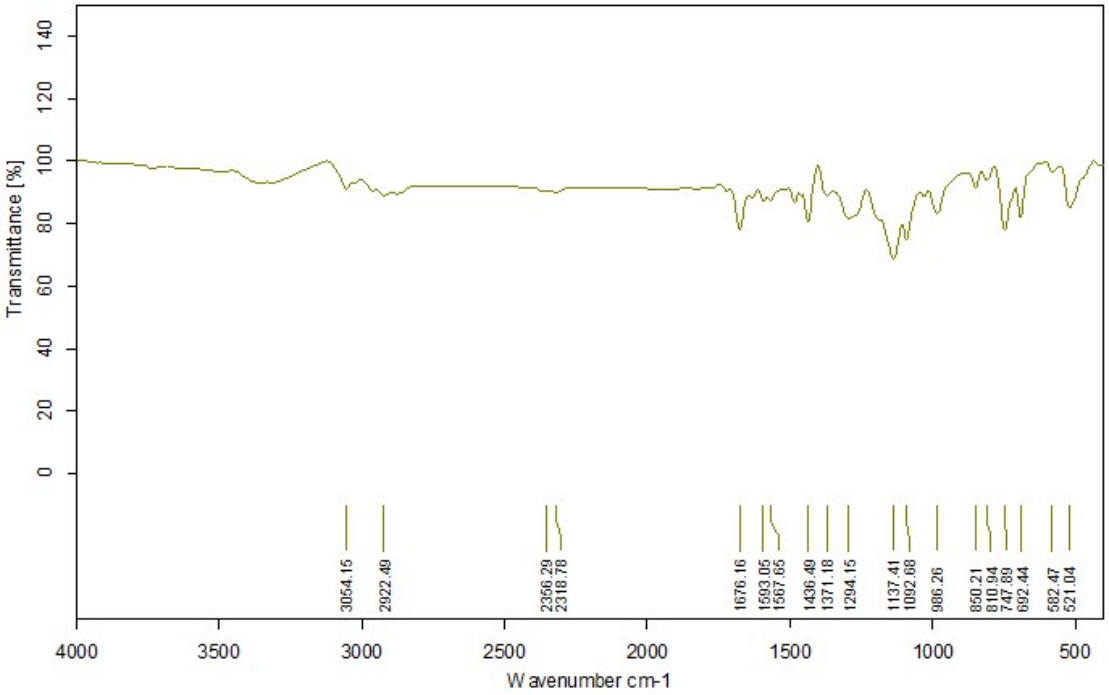


Figure S79. IR spectra of compound **7k**

9. Determination of Structure of 3a

The structure of **3a** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane. Further information can be found in the CIF file. The crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1811537.**

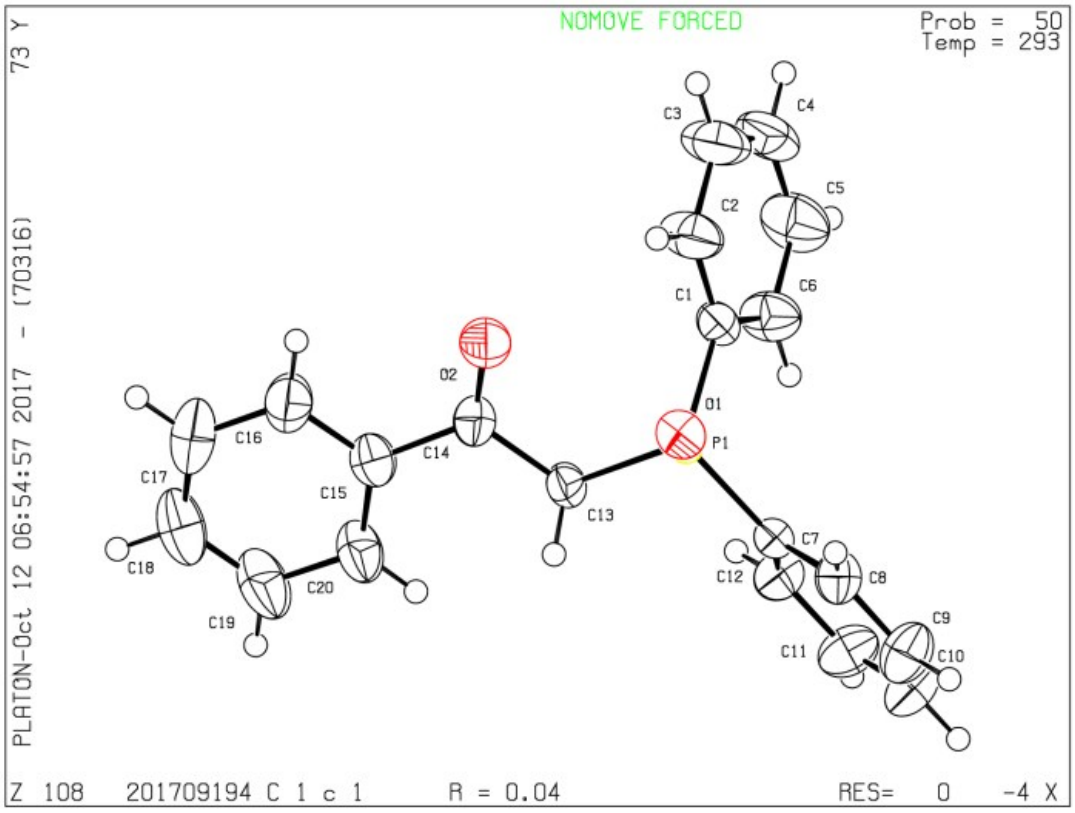


Table 1 Crystal data and structure refinement for 3a.

Identification code	201709194
Empirical formula	$C_{20}H_{17}O_2P$
Formula weight	320.30
Temperature/K	293(2)
Crystal system	monoclinic
Space group	Cc
a/Å	16.191(2)
b/Å	17.7337(7)
c/Å	8.5986(11)
α/°	90
β/°	137.72(3)
γ/°	90
Volume/Å^3	1660.8(6)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	1.517
F(000)	672.0
Crystal size/mm^3	0.22 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.53 to 134.066
Index ranges	$-19 \le h \le 16$, $-16 \le k \le 21$, $-10 \le l \le 10$
Reflections collected	2986
Independent reflections	1764 [R_{int} = 0.0225, R_{sigma} = 0.0358]
Data/restraints/parameters	1764/2/208
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0969
Largest diff. peak/hole / e Å^{-3}	0.29/-0.24
Flack parameter	0.07(3)