Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Cobalt-Catalyzed Asymmetric Phospha-Michael Reaction of Diarylphosphine Oxides for the Synthesis of Chiral Organophosphorus Compounds

Xu-Hui Yu,[a] Liang-Qiu Lu,[a] Zhi-Han Zhang,[a] De-Qing Shi*,[a] and Wen-Jing Xiao[a,b]

[a] Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, CCNU-uOttawa Joint Research Centre, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan 430079, Hubei, China

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, China

Corresponding author: chshidq@ccnu.edu.cn (Prof. Dr. De-Qing Shi)

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1. General Information

N-phenylimidazole α, β-unsaturated ketones **1**, diaryl phosphine oxides **2** were synthesized according to the reported procedures. [1, 2]

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. All of the reactions were carried out using a schlenk borosilicate reaction tube (10 mL) without special photochemical equipment.^{1}H NMR spectra were recorded on 400 MHz spectrophotometer. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR (100 MHz)、^{31}P NMR (162 MHz)、^{19}F NMR (376 MHz) spectra were recorded on Varian Mercury 400 with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Enantiomeric ratio (ee) values were determined by chiral HPLC with chiral OD-H, AS-H columns with hexane and *i*-PrOH as eluent.

References:

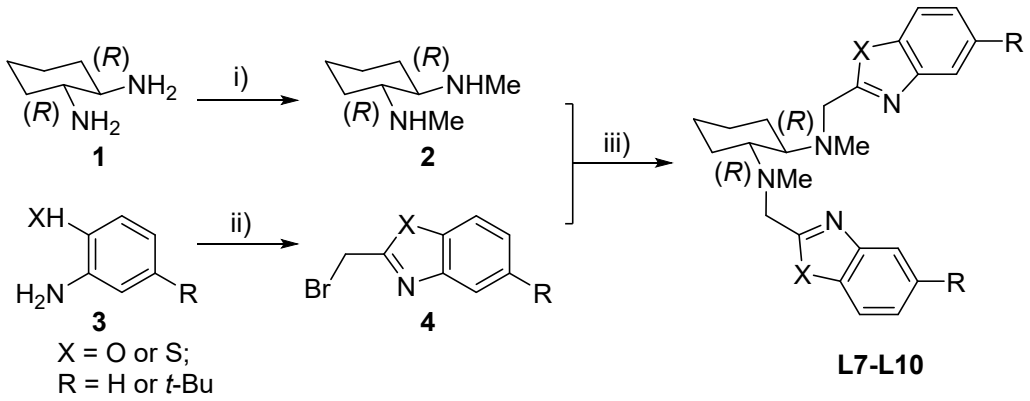
[1] a) D. Evans, K. R. Fandrick, Catalytic Enantioselective Pyrrole Alkylations of α,β-Unsaturated 2-Acyl Imidazoles, *Org. Lett*., 2006, **8**, 2249-2252; b) H.-H. Huo, K. Harms, E. Meggers, Catalytic, Enantioselective Addition of Alkyl Radicals to Alkenes via Visible-Light-Activated Photoredox Catalysis with a Chiral Rhodium Complex, *J. Am. Chem. Soc*., 2016, **138**, 6936-6939.

[2] C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, A Superior Method for the Reduction of Secondary Phosphine Oxides, *Org. Lett*., 2005, **7**, 4277-4280.

[3] K. Zhang, L.-Q. Lu, Y. Jia, Y. Wang, F.-D. Lu, F. Pan, W.-J. Xiao, Exploration of Chiral Cobalt Catalyst for Visible-Light-Induced Enantioselective Radical Conjugate Addition, *Angew. Chem. Int. Ed*., 2019, **58**, 13375-13379.

2. Preparation and Characterization of Chiral N4 ligands containing benzoxazolyl or benzothiazolyl moiety and its Cobalt complexes

2.1 Procedures for chiral ligands L7 – L10



i) Ethyl formate, then $LiAlH_4$; ii) $BrCH_2C(OEt)_3$, HBF_4-SiO_2; iii) NaH in THF

2 was synthesized according to our previous reported method. [3]

Synthesis of **4**[4]

A mixture of triethyl bromoorthoacetate (10 mmol, 2 equiv.) and substituted *o*-aminothiophenol (5 mmol) was stirred at room temperature in presence of catalytic amount of HBF_4-SiO_2 (200 mg, 0.05 mmol, 2 mol %) for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 30 mL of ethyl acetate and filtered through a plug of cotton. The cotton plug was washed with ethyl acetate (10 mL × 3). The combined ethyl acetate layer was concentrated under reduced pressure to afford the crude product, which was purified further by column chromatography (n-hexane: ethyl acetate 7:3) to afford **4** as an oil (yield: 88-94%).

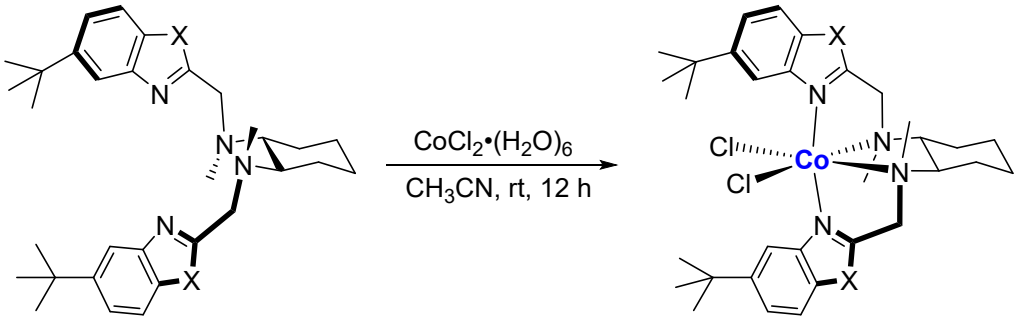
[4] Patil, A. V.; Bandgar, B. P.; Lee, S.-H. Silica supported fluoroboric acid: an efficient and reusable heterogeneous catalyst for facile synthesis of 2-aliphatic benzothiazoles, benzoxazoles, benzimidazoles and imidazo[4,5-*b*]pyridines. *Bull. Korean Chem. Soc.* **2010**, *31*, 1719-1722.

Synthesis of ligands **L7-L10**

Under argon atmosphere, to a dried 25 mL Schlenk flask was treated with **NaH** (2 mmol, 2.0 equiv.) and 10 mL of anhydrous THF, the mixture was cooled in ice-bath.

Then, **2** (1 mmol) in anhydrous THF (2 mL) was added dropwise with a syringe. 30 min later, **4** (2 mmol) in anhydrous THF (2 mL) was added dropwise slowly. The solution was stirred at ambient temperature and monitored by TLC analysis. The workup includes addition of saturated NH_4Cl solution (2 mL), extraction into ethyl acetate (2 mL*3). After phase separation, drying over Na_2SO_4 and removal of solvent under reduced pressure, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the desired product (yield: 40-62%).

2.2 General procedure for synthesis of chiral Co(II)-complexes ΛCo9 and ΛCo10

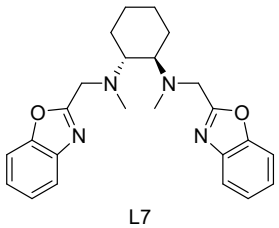


L9 (X = O), **L10** (X = S)

Under argon atmosphere, to an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $CoCl_2•(H_2O)_6$ (0.25 mmol, 59.48 mg) and the corresponding chiral ligand **L9** or **L10** (0.25 mmol) in 3 mL of CH_3CN. The solution was stirred at room temperature for 12 h. After the solvent was removed under vacuum, a purple pink crude cobalt complex was obtained, which was purified further by washing with ethyl ether and drying under a reduce pressure to obtain cobalt catalyst ΛCo9 or ΛCo10.

2.3 Characterization of chiral ligands L7-L10

(1*R*,2*R*)-N^1,N^2-bis(benzo[*d*]oxazol-2-ylmethyl)-N^1,N^2-dimethylcyclohexane-1,2-diamine (L7)

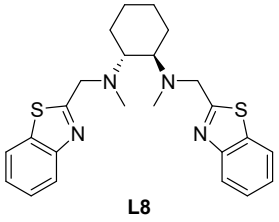


L7

Yellow oil, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.70 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.49 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.30 (dd, *J* = 6.0, 3.2 Hz, 4H), 4.21 – 4.05 (m, 4H), 2.74 – 2.69 (m, 2H), 2.47 (s, 6H), 1.86 (d, *J* = 12.0 Hz, 2H), 1.71 (d, *J* = 7.6 Hz, 2H), 1.30 – 1.22 (m, 2H), 1.19 – 1.09 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 165.2, 150.9, 141.0, 124.8, 124.1,

119.9, 110.6, 63.6, 52.2, 37.0, 27.0, 25.5; **HRMS** (ESI) for: $C_{24}H_{29}N_4O_2$ $[M+H]^+$: calcd 405.2285, found 405.2285.

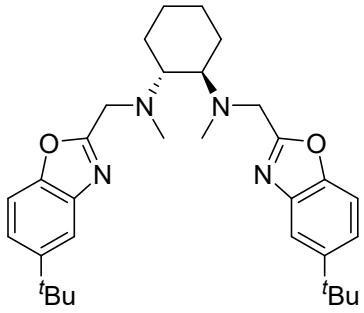
(1*R*,2*R*)-N^1,N^2-bis(benzo[*d*]thiazol-2-ylmethyl)-N^1,N^2-dimethylcyclohexane-1,2-diamine (L8)



L8

Orange solid, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 2H), 4.35 – 4.08 (m, 4H), 2.75 (d, *J* = 7.3 Hz, 2H), 2.47 (s, 6H), 1.96 (d, *J* = 12.0 Hz, 2H), 1.77 (d, *J* = 6.8 Hz, 2H), 1.44 – 1.27 (m, 2H), 1.23 – 1.12 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 176.1, 153.4, 135.4, 125.5, 124.5, 122.4, 121.7, 64.8, 58.3, 36.3, 27.0, 25.5. **HRMS** (ESI) for: $C_{24}H_{29}N_4S_2$ $[M+H]^+$: calcd 437.1828, found 437.1834.

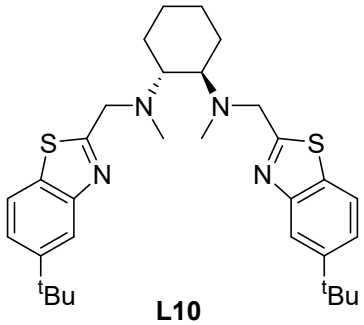
(1*R*,2*R*)-N^1,N^2-bis((5-(tert-butyl)benzo[*d*]oxazol-2-yl)methyl)-N^1,N^2-dimethylcyclohexane-1,2-diamine (L9)



L9

Yellow oil, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 1.7 Hz, 2H), 7.42 – 7.34 (m, 4H), 4.21 – 4.02 (m, 4H), 2.74 – 2.67 (m, 2H), 2.46 (s, 6H), 1.91 – 1.81 (m, 2H), 1.75 – 1.66 (m, 2H), 1.37 (s, 18H), 1.30 – 1.21 (m, 2H), 1.16 – 1.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 165.4, 148.9, 147.6, 141.0, 122.4, 116.3, 109.7, 63.5, 52.3, 37.0, 34.8, 31.8, 27.1, 25.5; **HRMS** (ESI) for: $C_{32}H_{45}N_4O_2$ $[M+H]^+$: calcd 517.3537, found 517.3541.

(1*R*,2*R*)-N^1,N^2-bis((5-(tert-butyl)benzo[*d*]thiazol-2-yl)methyl)-N^1,N^2-dimethylcyclohexane-1,2-diamine (L10)



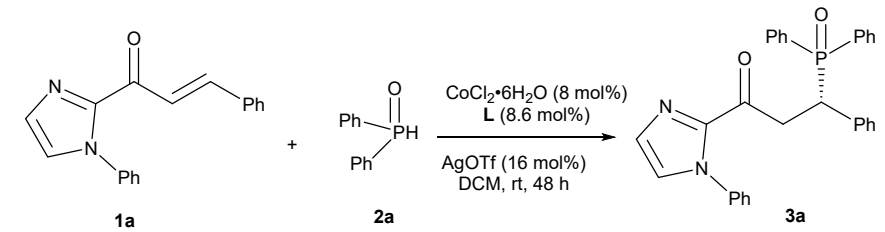
L10

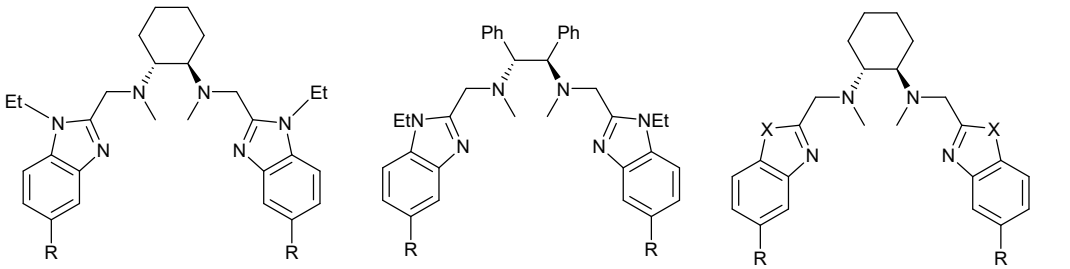
Pure yellow solid, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J* = 1.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.33 (m, 2H), 4.40 – 3.92 (m, 4H), 2.77 (d, *J* = 9.1 Hz, 2H), 2.47 (s, 6H), 1.98 (d, *J* = 12.6 Hz, 2H), 1.78 (d, *J* = 7.9 Hz, 2H), 1.40 (s, 18H), 1.21 – 1.17 (m, 2H), 0.87 – 0.83 (m, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 176.2, 153.7, 149.2, 132.4, 122.7, 121.1, 119.0, 64.8, 58.5, 36.4, 34.8, 31.6, 27.2, 25.6; **HRMS** (ESI) for: $C_{32}H_{45}N_4S_2$ $[M+H]^+$: calcd 549.3080, found 549.3075.

3. Optimization of the Reaction Conditions

3.1 Impact of Ligands

Table S1[a]



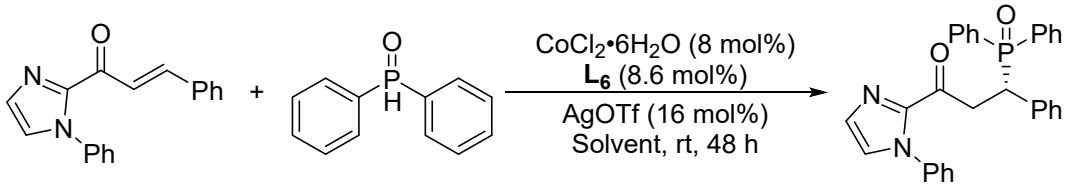


Entry	Chiral Ligand	Yield (%)[b]	ee (%)[c]
1	**L1**	99	49
2	**L2**	99	53
3	**L3**	99	48
4	**L4**	99	86
5	**L5**	88	91
6	**L6**	**98**	**93**
7	**L7**	42	3
8	**L8**	59	43
9	**L9**	36	24
10	**L10**	40	47

[a] Reactions conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), $CoCl_2$•6H2O (8 mol%), L (8.6 mol%), AgOTf (16 mol%) in DCM (1.0 mL) at rt. [b] Determined by ^1H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis.

3.2 Impact of Solvents

Table S2[a]



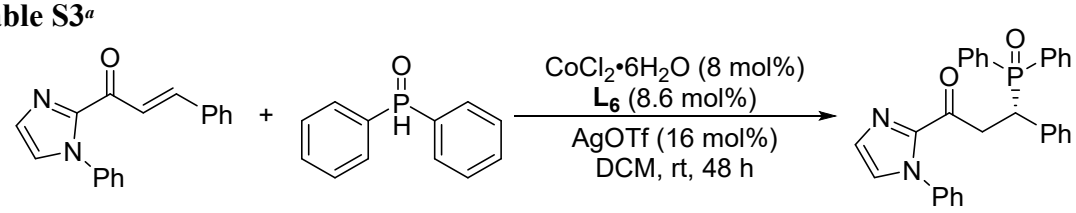
1a **2a** **3a**

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	MeCN	75	48
2	Ethyl Acetate	93	6
3	$CHCl_3$	92	84
4	THF	99	18
5	Et_2O	80	2
6	Dioxane	85	15
7	**DCM**	**98**	**93**
8[d]	DCM	96	86
9[e]	DCM	94	88

[a] Reactions conditions: 1a (0.1 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), CoCl2•6H2O (8 mol%), L6 (8.6 mol%), AgOTf (16 mol%) in solvent (1.0 mL) at rt. [b] Determined by 1H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis. [d] In DCM (2.0 mL). [e] In DCM (3.0 mL).

3.3 Impact of the amount of reactant

Table S3[a]



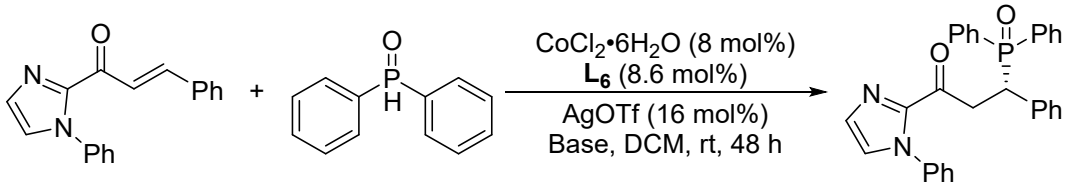
1a **2a** **3a**

Entry	X:Y	Yield (%)[b]	ee (%)[c]
1	1:1	94	93
2	**1:1.5**	**98**	**93**
3	1:2	95	85
4	1:3	91	81

[a] Reactions conditions: the molecular ratio of **1a** and **2a** = X:Y, $CoCl_2$•$6H_2O$ (8 mol%), **L6** (8.6 mol%), AgOTf (16 mol%) in DCM (1.0 mL) at r.t. [b] Determined by ^1H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis.

3.4 Impact of Bases

Table S4[a]



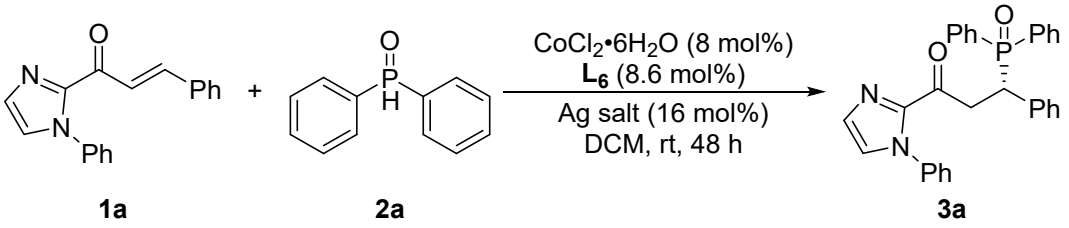
1a **2a** **3a**

Entry	Base[d]	Yield (%)[b]	ee (%)[c]
1	Na_2CO_3	87	87
2	$^{i}Pr_2NEt$	35	26
3	DBU	91	3
4	Cy_2NMe	53	26
5	w/o[e]	**98**	**93**

[a] Reactions conditions:**1a** (0.1 mmol, 1.0 equiv),**2a** (0.15 mmol, 1.5 equiv.), $CoCl_2$•$6H_2O$ (8 mol%), **L6** (8.6 mol%), AgOTf (16 mol%) in DCM (1.0 mL) at rt. [b] Determined by ^{1}H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis. [d] Base (10 mol%). [e] w/o = without

3.5 Impact of the counter anion

Table S5[a]

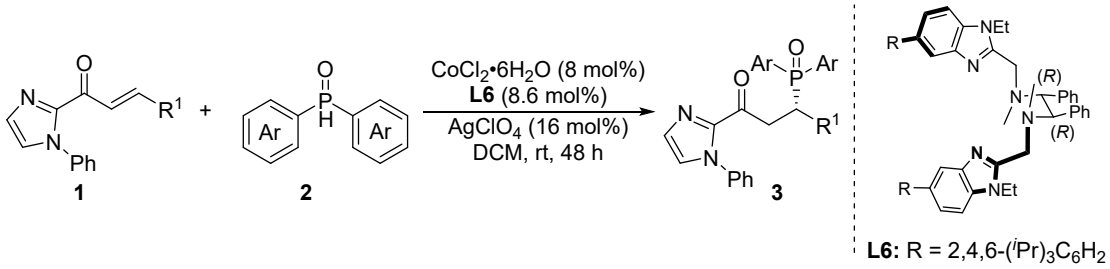


Entry	Ag salt	Yield (%)[b]	ee (%)[c]
1	AgOTf	98	93
2	**$AgClO_4$**	**99**	**96**

[a] Reactions conditions:**1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), $CoCl_2$•$6H_2O$ (8 mol%), **L6** (8.6 mol%), Ag salt (16 mol%) in DCM (1.0 mL) at r.t. [b] Determined by ^{1}H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis.

4. General Procedure and Spectral Data of the Products

4.1 General procedure for the synthesis of products 3.

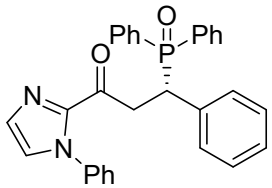


Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $CoCl_2$•$6H_2O$ (0.016 mmol, 8 mol%) and L6 (0.0172 mmol, 8.6 mol%) and 2 mL of DCM under air, after 12 h of stirring at room temperature, $AgClO_4$ (0.032 mmol, 16 mol%) was added, the mixture was stirred for 1 h at room temperature. After

AgCl was filtered by syringe with a filter head, substrate **1** (0.2 mmol, 1.0 eq) was added continue to stir 0.5 h, then substrate **2** (0.3 mmol, 1.5 equiv.) was added to the mixture under air. The solution was stirred at room temperature for about 48 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel to give product **3**. All the products **3** were prepared according to the above procedure.

4.2 Spectral data of products 3

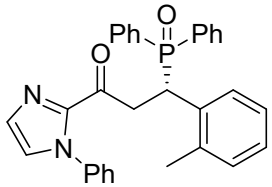
(*S*)-3-(diphenylphosphoryl)-3-phenyl-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3a)



3a

87.7 mg, white solid, 92% yield, $[\alpha]_D^{25}$ = -110.47 (c = 1.01 in $CHCl_3$); 96% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 7.27 min, t_R (minor) = 9.92 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.01 – 7.93 (m, 2H), 7.57 – 7.42 (m, 5H), 7.41 – 7.31 (m, 4H), 7.25 – 7.19 (m, 5H), 7.14 – 7.09 (m, 3H), 7.08 (d, *J* = 1.0 Hz, 1H), 6.95 – 6.90 (m, 2H), 4.47 – 4.38 (m, 1H), 4.18 (ddd, *J* = 17.3, 10.7, 6.3 Hz, 1H), 3.50 (ddd, *J* = 17.4, 10.0, 3.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.9 (d, *J* = 14.2 Hz), 142.3, 137.8, 135.2 (d, *J* = 5.5 Hz), 131.9 (d, *J* = 2.9 Hz), 131.6, 131.5, 131.5, 131.4 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 15.1 Hz), 130.0 (d, *J* = 5.3 Hz), 129.5, 128.8 (d, *J* = 5.2 Hz), 128.6 (d, *J* = 2.6 Hz), 128.1 (d, *J* = 2.0 Hz), 128.1, 127.9, 127.0 (d, *J* = 2.9 Hz), 125.5, 41.7 (d, *J* = 68.2 Hz), 39.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 37.74. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{26}N_2O_2P$: 477.1726, found:477.1719.

(*S*)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3b)

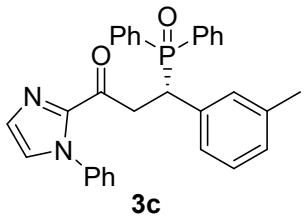


3b

97.1 mg, white solid, 99% yield; $[\alpha]_D^{25}$ = -100.32 (*c* = 1.21 in $CHCl_3$); 98% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 5.30 min, t_R (minor) = 6.90 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.03 (dd, *J* = 10.5, 7.6 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.57 (h, *J* = 6.9 Hz, 3H), 7.30 (tt, *J* = 13.2, 5.8 Hz, 6H), 7.22 – 7.11 (m, 4H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 4.67 (ddd, *J* = 11.5, 8.5, 3.4 Hz, 1H), 4.11 (ddd, *J* = 17.4, 11.0, 7.0 Hz, 1H), 3.53 (ddd, *J* = 16.9, 9.1, 3.5 Hz, 1H), 1.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.3 (d, *J* = 14.7 Hz), 142.4, 137.8, 137.2 (d, *J* = 6.1 Hz), 133.4 (d, *J* = 5.7 Hz), 132.4 , 132.0 (d, *J* = 2.2 Hz), 131.9 (d, *J* = 8.4 Hz), 131.4 (d, *J* = 2.6 Hz), 131.0 (d, *J* = 9.2 Hz), 130.8, 129.8 (d, *J* = 7.4 Hz), 129.6 , 128.8 , 128.8 , 128.7 , 128.4 , 127.8 (d, *J* = 11.6 Hz), 127.0 (d, *J* = 2.0 Hz), 126.8 , 126.2, 125.3, 40.2, 37.1

(d, *J* = 68.9 Hz), 19.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.31. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}N_2O_2P$: 491.1883, found:491.1875.

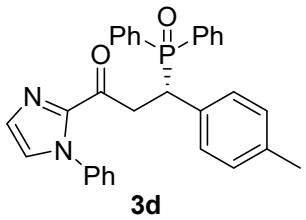
(*S*)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(m-tolyl)propan-1-one (3c)



3c

92.2 mg, white solid, 94% yield, $[\alpha]_D^{25}$ = -88.77 (*c* = 1.21 in $CHCl_3$); 92% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 25.19 min, t_R (minor) = 36.43 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 10.2, 7.9 Hz, 2H), 7.49 (ddd, J = 23.4, 10.4, 7.0 Hz, 5H), 7.37 (dq, J = 8.7, 7.0, 6.6 Hz, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.22 (s, 1H), 7.08 (s, 1H), 7.00 (d, J = 4.0 Hz, 3H), 6.96–6.90 (m, 3H), 4.47–4.32 (m, 1H), 4.15 (ddd, J = 17.1, 10.6, 6.5 Hz, 1H), 3.51 (ddd, J = 17.6, 10.4, 3.4 Hz, 1H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.1 (d, *J* = 14.1 Hz), 142.5, 137.7 (d, *J* = 34.1 Hz), 135.0 (d, *J* = 5.4 Hz), 131.9, 131.8, 131.8 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 8.6 Hz), 131.3 (d, *J* = 2.4 Hz), 131.2 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 5.5 Hz), 129.7, 128.8, 128.7, 128.6 (d, *J* = 3.3 Hz), 128.0, 127.9, 127.8, 127.7 (d, *J* = 2.1 Hz), 127.1 (d, *J* = 5.3 Hz), 126.9, 125.5, 41.6 (d, *J* = 68.1 Hz), 39.2, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.12. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}N_2O_2P$: 491.1883, found:491.1873.

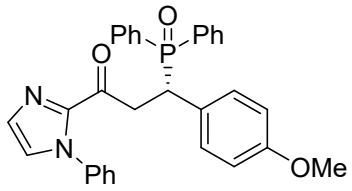
(*S*)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(p-tolyl)propan-1-one (3d)



3d

97.1 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = 24.9 (*c* = 1.05 in $CHCl_3$); 94% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 11.69 min, t_R (minor) = 18.10 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.86 (m, 2H), 7.56 – 7.42 (m, 5H), 7.41 – 7.30 (m, 4H), 7.29 – 7.22 (m, 2H), 7.21 (d, *J* = 1.0 Hz, 1H), 7.13 – 7.06 (m, 3H), 6.96 – 6.89 (m, 4H), 4.41 (ddd, *J* = 11.7, 8.6, 3.4 Hz, 1H), 4.14 (ddd, *J* = 17.3, 10.9, 6.5 Hz, 1H), 3.48 (ddd, *J* = 17.3, 9.9, 3.4 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.2 (d, *J* = 14.5 Hz), 158.5, 142.5, 137.9, 132.1, 131.9, 131.7, 131.4 (d, *J* = 8.6 Hz), 131.3, 131.1, 131.0, 129.7, 128.8, 128.7, 128.6 (d, *J* = 5.2 Hz), 128.0 (d, *J* = 11.6 Hz), 127.0 (d, *J* = 5.8 Hz), 126.9, 125.5, 113.5, 41.2 (d, *J* = 68.6 Hz), 39.4, 21.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.00. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}N_2O_2P$: 491.1883, found:491.1877.

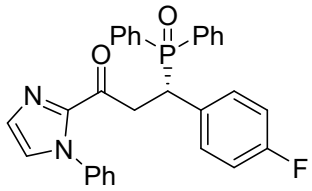
(*S*)-3-(diphenylphosphoryl)-3-(4-methoxyphenyl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3e)



3e

82.1 mg, white solid, 81% yield, $[\alpha]_D^{25}$ = -36.63 (*c* = 1.25 in $CHCl_3$); 94% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 18.85 min, t_R (minor) = 26.22 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.99–7.91 (m, 2H), 7.56–7.43 (m, 5H), 7.42–7.31 (m, 4H), 7.27 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 7.14 (dt, J = 8.7, 2.0 Hz, 2H), 7.08 (s, 1H), 6.95 (dt, J = 8.4, 1.7 Hz, 2H), 6.69–6.62 (m, 2H), 4.38 (t, J = 9.5 Hz, 1H), 4.21–4.06 (m, 1H), 3.71 (s, 3H), 3.51–3.34 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.2 (d, *J* = 14.6 Hz), 158.5, 142.5, 137.9, 132.1, 131.9, 131.7, 131.4 (d, *J* = 8.6 Hz), 131.3 (d, *J* = 2.3 Hz), 131.1, 131.0, 129.7, 128.8, 128.7, 128.6 (d, *J* = 5.1 Hz), 128.0 (d, *J* = 11.6 Hz), 127.0 (d, *J* = 5.8 Hz), 126.9, 125.5, 113.5, 55.0, 40.8 (d, *J* = 68.9 Hz), 39.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) δ 33.43. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{31}H_{27}N_2O_3PNa$: 529.1652, found:529.1654.

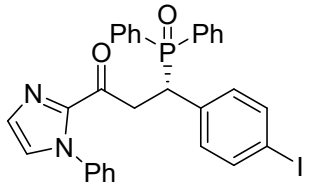
(*S*)-3-(diphenylphosphoryl)-3-(4-fluorophenyl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3f)



3f

94.0 mg, white solid, 95% yield, $[\alpha]_D^{25}$ = -100.5 (*c* = 1.12 in $CHCl_3$); 95% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 7.27 min, t_R (minor) = 12.32 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.02 – 7.88 (m, 2H), 7.57 – 7.43 (m,5H), 7.41-7.34 (m, 4H), 7.29 – 7.18 (m, 5H), 7.09 (s, 1H), 7.00 – 6.93 (m, 2H), 6.81 (t, *J* = 8.5 Hz, 2H), 4.39 (ddd, *J* = 11.2, 8.0, 3.1 Hz, 1H), 4.17 (ddd, *J* = 17.1, 11.0, 5.9 Hz, 1H), 3.44 (ddd, *J* = 17.5, 9.8, 3.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.8 (d, *J* = 14.4 Hz), 142.4, 137.9, 131.9 (d, *J* = 2.8 Hz), 131.9, 131.6, 131.5, 131.5, 131.4, 131.0, 130.9, 130.6, 129.7, 128.8 (d, *J* = 2.4 Hz), 128.7, 128.1 (d, *J* = 11.7 Hz), 127.1, 125.6, 115.1 (d, *J* = 2.1 Hz), 114.9 (d, *J* = 2.0 Hz), 40.8 (d, J = 68.7 Hz), 39.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.42 (d, *J* = 4.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -115.47 (d, *J* = 4.6 Hz). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{24}FN_2O_2PNa$: 517.1452, found:517.1452.

(*S*)-3-(diphenylphosphoryl)-3-(4-iodophenyl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3g)

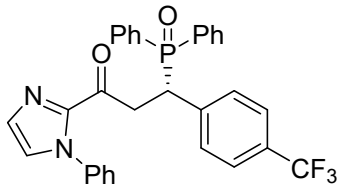


3g

119.3 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = -68.3 (*c* = 1.14 in $CHCl_3$); 94% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 7.98 min, t_R (minor) = 14.08 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.97 – 7.92 (m, 2H), 7.53 – 7.47 (m,5H), 7.43 (d, *J* = 8.1 Hz, 2H),

7.37 (q, *J* = 7.5 Hz, 4H), 7.29 – 7.25 (m, 2H), 7.21 (s, 1H), 7.08 (s, 1H), 6.97 (dd, *J* = 13.5, 7.7 Hz, 4H), 4.36 (ddd, *J* = 11.2, 8.2, 3.1 Hz, 1H), 4.14 (ddd, *J* = 17.3, 11.0, 6.1 Hz, 1H), 3.45 (ddd, *J* = 17.4, 9.7, 3.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.6 (d, *J* = 14.3 Hz), 142.3, 137.8, 137.2 (d, *J* = 2.0 Hz), 135.2 (d, *J* = 5.5 Hz), 132.0, 131.9, 131.8, 131.5 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 8.7 Hz), 131.0 (d, *J* = 8.8 Hz), 130.7 (d, *J* = 26.0 Hz), 129.6, 128.9, 128.8, 128.7, 128.2 (d, *J* = 11.8 Hz), 127.1, 125.6, 92.7 (d, *J* = 3.5 Hz), 41.3 (d, *J* = 67.8 Hz), 39.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.60. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{24}IN_2O_2P$: 625.0512, found:625.0510.

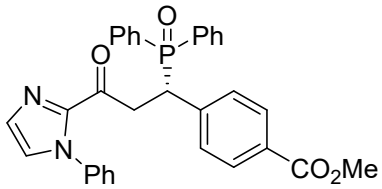
(*S*)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (3h)



3h

95.8 mg, white solid, 88% yield, $[\alpha]_D^{25}$ = 0.3 (*c* = 1.07 in $CHCl_3$); 89% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 9.06 min, t_R (minor) = 17.99 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.02 – 7.92 (m, 2H), 7.59 – 7.44 (m, 6H), 7.43 – 7.33 (m, 8H), 7.31 – 7.27 (m, 1H), 7.22 (s, 1H), 7.09 (s, 1H), 6.98 – 6.93 (m, 2H), 4.47 (ddd, *J* = 11.2, 8.1, 3.2 Hz, 1H), 4.22 (ddd, *J* = 17.2, 11.0, 6.0 Hz, 1H), 3.49 (ddd, *J* = 17.7, 9.9, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.5 (d, *J* = 14.1 Hz), 142.2, 139.7 (d, *J* = 5.0 Hz), 137.8, 132.1 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 2.8 Hz), 131.6, 131.4 (d, *J* = 8.7 Hz), 131.2, 130.9 (d, *J* = 8.8 Hz), 130.6, 130.3 (d, *J* = 5.3 Hz), 130.2, 129.8, 129.2 (d, *J* = 2.6 Hz), 128.9, 128.9, 128.8 (d, *J* = 3.9 Hz), 128.2 (d, *J* = 11.8 Hz), 127.2, 125.5, 125.4, 124.9 (dd, *J* = 3.9, 2.1 Hz), 122.7, 41.6 (d, *J* = 67.2 Hz), 39.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -62.52. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{25}F_3N_2O_2P$: 545.1600, found:545.1598.

Methyl-(*S*)-4-(1-(diphenylphosphoryl)-3-oxo-3-(1-phenyl-1H-imidazol-2-yl)propyl)benzoate (3i)

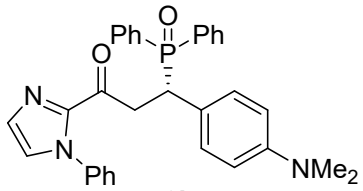


3i

72.7 mg, white solid, 68% yield, $[\alpha]_D^{25}$ = 0.57 (*c* = 1.23 in $CHCl_3$); 95% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =25.67min, t_R (minor) = 39.12 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.04 – 8.00 (m, 2 H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.50 (m, 5H), 7.49 – 7.35 (m, 6H), 7.31 (q, *J* = 3.4, 2.8 Hz, 3H), 7.14 (s, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 4.52 (td, *J* = 9.8, 8.6, 2.9 Hz, 1H), 4.30 (ddd, *J* = 17.2, 10.9, 5.9 Hz, 1H), 3.91 (s, 3H), 3.54 (ddd, *J* = 17.7, 10.1, 3.2 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.6 (d, *J* = 14.2 Hz), 166.8, 142.3, 141.0 (d, *J* = 5.6 Hz), 137.8, 132.0 (d, *J* = 2.2 Hz), 131.6, 131.5, 131.4, 131.3, 130.9 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 21.1 Hz), 130.0 (d, *J* = 5.3 Hz), 129.8, 129.2, 128.8, 128.7 (d, *J* = 5.3 Hz), 128.1 (d, *J* = 11.8 Hz), 127.1, 125.5, 51.9, 41.8 (d, *J* = 67.2 Hz), 39.1. **^{31}P NMR** (162 MHz,

$CDCl_3$) δ (ppm) 32.67. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{28}N_2O_4P$: 535.1781, found:535.1778.

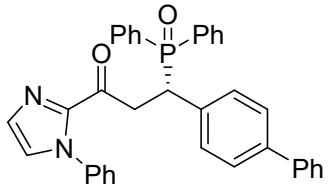
(*S*)-3-(4-(dimethylamino)phenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3j)



3j

84.3 mg, yellow oil, 81% yield, $[\alpha]_D^{25}$ = -87.77 (*c* = 1.25 in $CHCl_3$); 92% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 14.51 min, t_R (minor) = 23.63 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.02 – 7.96 (m, 2H), 7.58 – 7.49 (m, 5H), 7.46 –7.35 (m, 4H), 7.33 – 7.27 (m, 3H), 7.12 –7.05 (m, 3H), 7.00 – 6.94 (m, 2H), 6.58 – 6.50 (m, 2H), 4.44 – 4.38 (m, 1H), 4.14 – 4.09 (m, 1H), 3.51 (ddd, *J* = 17.1, 9.5, 3.4 Hz, 1H), 2.89 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.5 (d, *J* = 14.7 Hz), 149.5 (d, *J* = 1.7 Hz), 142.7, 138.0, 132.3 (d, *J* = 6.1 Hz), 131.6 (d, *J* = 3.9 Hz), 131.5, 131.3, 131.3, 131.2 (d, *J* = 2.3 Hz), 130.7 (d, *J* = 5.3 Hz), 129.6, 128.7, 128.6, 128.5 (d, *J* = 6.4 Hz), 127.9 (d, *J* = 11.6 Hz), 126.7, 125.6, 122.4 (d, *J* = 6.0 Hz), 112.3, 40.8 (d, *J* = 69.69 Hz), 40.5, 39.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.46. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{31}N_3O_2P$: 520.2148, found:520.2145.

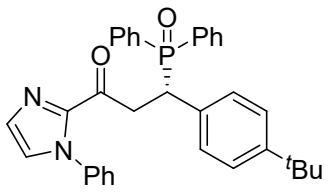
(*S*)-3-([1,1'-biphenyl]-4-yl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3k)



3k

107.2 mg, white solid, 97% yield, $[\alpha]_D^{25}$ = -330.67 (*c* = 1.27 in $CHCl_3$); 90% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 8.35 min, t_R (minor) = 13.84 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.04 – 7.91 (m, 2H), 7.57 – 7.48 (m, 7H), 7.43 – 7.31 (m, 8H), 7.31 – 7.25 (m, 5H), 7.23 (s, 1H), 7.09 (s, 1H), 6.94 (d, *J* = 7.1 Hz, 2H), 4.49 (ddd, *J* = 11.3, 8.5, 3.3 Hz, 1H), 4.21 (ddd, *J* = 17.3, 10.9, 6.4 Hz, 1H), 3.53 (ddd, *J* = 17.3, 9.8, 3.4 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.0 (d, *J* = 14.3 Hz), 142.4, 140.5, 139.6 (d, *J* = 2.0 Hz), 137.8, 134.3 (d, *J* = 5.9 Hz), 131.9, 131.7, 131.6, 131.5, 131.1 (d, *J* = 9.0 Hz), 130.9, 130.7, 130.4 (d, *J* = 5.3 Hz), 129.6, 128.8 (d, *J* = 2.5 Hz), 128.7, 128.6, 128.1 (d, *J* = 11.7 Hz), 127.2, 127.0, 126.8, 126.7, 125.5, 41.5 (d, *J* = 67.7 Hz), 39.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.39. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{30}N_2O_2P$: 553.2039, found:553.2035.

(*S*)-3-(4-(tert-butyl)phenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3l)

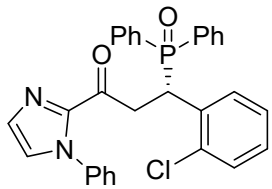


3l

105.5 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = 3.00 (*c* = 1.03 in $CHCl_3$); 94% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =20.33min, t_R

(minor) = 38.06 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.01 – 7.88 (m, 2H), 7.56 – 7.46 (m, 3H), 7.42 (dd, *J* = 11.1, 7.7 Hz, 2H), 7.33 (dd, *J* = 14.5, 7.2 Hz, 4H), 7.21 (td, *J* = 7.5, 2.8 Hz, 3H), 7.15 – 7.08 (m, 4H), 7.06 (s, 1H), 6.87 (d, *J* = 7.6 Hz, 2H), 4.52 – 4.34 (m, 1H), 4.11 (ddd, *J* = 17.5, 10.7, 6.9 Hz, 1H), 3.52 (ddd, *J* = 17.2, 9.9, 3.5 Hz, 1H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.1 (d, *J* = 14.3 Hz), 149.8 (d, *J* = 2.8 Hz), 142.4, 137.9, 132.0, 131.8 (d, *J* = 2.8 Hz), 131.7, 131.5 (d, *J* = 8.6 Hz), 131.2 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 8.8 Hz), 130.9 (d, *J* = 27.2 Hz), 129.6 (d, *J* = 5.3 Hz), 129.5, 128.8, 128.7, 128.5 (d, *J* = 8.1 Hz), 127.8 (d, *J* = 11.7 Hz), 126.7, 125.4, 125.0 (d, *J* = 2.1 Hz), 41.3 (d, *J* = 68.3 Hz), 39.3, 34.3, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 37.12. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{34}H_{34}N_2O_2P$: 533.2352, found:533.2348.

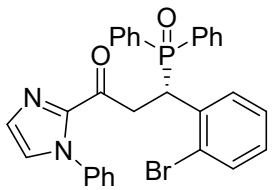
(S)-3-(2-chlorophenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3m)



3m

93.0 mg, white solid, 91% yield, $[\alpha]_D^{25}$ = 4.27 (*c* = 1.03 in $CHCl_3$); 91% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 6.01 min, t_R (minor) = 8.07 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.11 (dd, *J* = 10.8, 7.1 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.44 – 7.39 (m, 2H), 7.36 – 7.28 (m, 4H), 7.26 – 7.13 (m, 4H), 7.08 – 7.03 (m, 3H), 6.90 (d, *J* = 7.6 Hz, 2H), 5.13 (ddd, *J* = 11.0, 7.3, 3.7 Hz, 1H), 4.02 (ddd, *J* = 17.4, 10.6, 7.4 Hz, 1H), 3.65 (ddd, *J* = 16.5, 9.3, 3.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.6 (d, *J* = 13.8 Hz), 142.2, 137.8, 134.5 (d, *J* = 7.2 Hz), 133.4 (d, *J* = 4.9 Hz), 132.0 (d, *J* = 2.4 Hz), 131.8, 131.7 (d, *J* = 8.7 Hz), 131.4 (d, *J* = 2.5 Hz), 131.1 (d, *J* = 4.0 Hz), 130.9 (d, *J* = 9.5 Hz), 130.1, 129.6, 128.9, 128.8 (d, *J* = 4.3 Hz), 128.7, 128.5, 128.2, 127.8 (d, *J* = 11.9 Hz), 127.1, 126.9, 125.4, 39.8, 37.4 (d, *J* = 67.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.65. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{24}ClN_2O_2PNa$: 533.1156, found:533.1160.

(S)-3-(2-bromophenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3n)

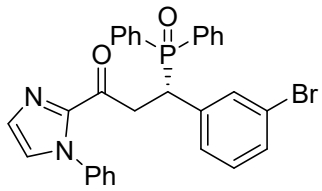


3n

109.9 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = -92.10(*c* = 1.06 in $CHCl_3$); 87% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) = 12.49 min, t_R (minor) = 16.60 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.18 – 8.09 (m, 2H), 7.94 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.43 – 7.35 (m, 3H), 7.35 – 7.28 (m, 5H), 7.25 – 7.22 (m, 1H), 7.18 (td, *J* = 7.7, 3.0 Hz, 2H), 7.08 (d, *J* = 1.0 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.93 – 6.87 (m, 2H), 5.11 (ddd, *J* = 11.0, 7.4, 3.9 Hz, 1H), 3.94 (ddd, *J* = 16.1, 10.7, 7.6 Hz, 1H), 3.66 (ddd, *J* = 16.1, 9.2, 3.9 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.7 (d, *J* = 14.4 Hz), 142.3, 137.8, 135.1

(d, *J* = 4.7 Hz), 132.3, 132.1, 131.8, 131.7, 131.5 (d, *J* = 2.4 Hz), 131.4 (d, *J* = 4.2 Hz), 131.1 (d, *J* = 9.4 Hz), 129.7, 128.8, 128.8, 128.7, 128.6, 128.5, 127.8, 127.7, 127.0, 125.9 (d, *J* = 7.5 Hz), 125.4, 40.5 (d, *J* = 66.8 Hz), 40.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.57. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{25}BrN_2O_2P$: 555.0832, found:555.0830.

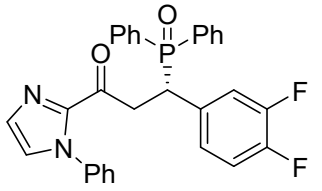
(*S*)-3-(3-bromophenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3o)



3o

105.5 mg, white solid, 95% yield, $[\alpha]_D^{25}$ = -29.63(*c* = 1.12 in $CHCl_3$); 88% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 8.12 min, t_R (minor) = 11.56 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.91 (m, 2H), 7.58 – 7.44 (m, 5H), 7.42 – 7.36 (m, 4H), 7.31 – 7.27 (m, 3H), 7.25 (s, 2H), 7.23 (s, 1H), 7.10 (d, *J* = 0.9 Hz, 1H), 7.04 – 6.98 (m, 3H), 4.39 – 4.30 (m, 1H), 4.16 (ddd, *J* = 17.0, 10.8, 6.0 Hz, 1H), 3.48 (ddd, *J* = 17.6, 10.3, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.6 (d, *J* = 14.0 Hz), 142.3, 137.8 (d, *J* = 5.4 Hz), 133.0 (d, *J* = 5.7 Hz), 132.6, 132.0 (d, *J* = 2.3 Hz), 131.6, 131.4 (d, *J* = 8.7 Hz), 131.3, 131.0 (d, *J* = 8.8 Hz), 130.6 (d, *J* = 11.9 Hz), 130.3, 130.1 (d, *J* = 2.2 Hz), 129.8, 129.6, 128.8 (d, *J* = 4.2 Hz), 128.7 (d, *J* = 3.0 Hz), 128.5 (d, *J* = 5.2 Hz), 128.2 (d, *J* = 11.7 Hz), 127.1, 125.6, 121.9 (d, *J* = 2.0 Hz), 41.4 (d, *J* = 68.1 Hz), 39.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.91. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{24}BrN_2O_2PNa$: 577.0651, found:577.0651.

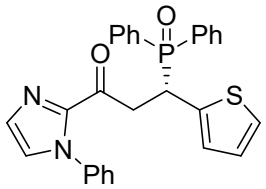
(S)-3-(3,4-difluorophenyl)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3p)



3p

97.4 mg, white solid, 95% yield, $[\alpha]_D^{25}$ = -94.9 (*c* = 1.17 in $CHCl_3$); 92% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 9.33 min, t_R (minor) = 11.55 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.95 (t, J = 9.0 Hz, 2H), 7.51 (q, J = 9.3, 8.8 Hz, 5H), 7.38 (dd, J = 13.9, 7.3 Hz, 4H), 7.30 (s, 1H), 7.28 (s, 1H), 7.21 (s, 1H), 7.12 (d, J = 12.0 Hz, 2H), 7.02 (t, J = 8.0 Hz, 3H), 6.89 (q, J = 8.9 Hz, 1H), 4.35 (t, J = 9.5 Hz, 1H), 4.17 (ddd, J = 17.1, 10.9, 5.5 Hz, 1H), 3.43 (dd, J = 17.7, 10.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.5 (d, *J* = 13.9 Hz), 150.9 (d, *J* = 12.6 Hz), 150.6 (d, *J* = 9.7 Hz), 148.5 (d, *J* = 13.3 Hz), 148.1 (d, *J* = 14.4 Hz), 142.2, 137.8, 132.5, 132.0, 131.6, 131.3 (d, *J* = 8.7 Hz), 130.8 (d, *J* = 8.9 Hz), 129.8, 128.9, 128.8, 128.2 (d, *J* = 11.6 Hz), 127.3, 126.0, 125.6, 119.0 (d, *J* = 5.0 Hz), 118.8 (d, *J* = 5.4 Hz), 116.8 (d, *J* = 16.9 Hz), 40.7 (d, *J* = 68.4 Hz), 39.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.68. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -137.62 (d, *J* = 21.3 Hz), -139.85 (dd, *J* = 21.4, 4.1 Hz). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{23}F_2N_2O_2PNa$: 535.1357, found:535.1355.

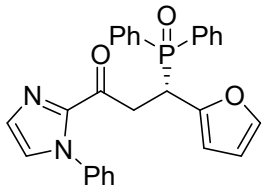
(*S*)-3-(diphenylphosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(thiophen-2-yl)propan-1-one (3q)



3q

95.5 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = -12.9 (*c* = 1.12 in $CHCl_3$); 98% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =8.84 min, t_R (minor) = 11.32 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.90 (m, 2H), 7.58 – 7.45 (m, 5H), 7.41 – 7.34 (m, 4H), 7.33 – 7.26 (m, 2H), 7.22 (s, 1H), 7.10 (s, 1H), 7.02 (d, *J* = 6.4 Hz, 3H), 6.91 (s, 1H), 6.78 (t, *J* = 4.4 Hz, 1H), 4.80 (td, *J* = 10.3, 3.1 Hz, 1H), 4.12 (ddd, *J* = 17.4, 11.0, 6.0 Hz, 1H), 3.53 (ddd, *J* = 17.4, 9.5, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.3 (d, *J* = 13.6 Hz), 142.2, 137.8, 137.0 (d, *J* = 6.3 Hz), 132.0 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 8.8 Hz), 131.2, 131.1, 130.3 (d, *J* = 5.1 Hz), 129.5, 128.8, 128.7, 128.6 (d, *J* = 2.1 Hz), 128.1 (d, *J* = 11.7 Hz), 127.5 (d, *J* = 6.3 Hz), 127.0, 126.6 (d, *J* = 2.7 Hz), 125.5, 124.7 (d, *J* = 3.0 Hz), 40.3, 37.1 (d, *J* = 70.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.79. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{23}N_2O_2PSNa$: 505.1110, found:505.1114.

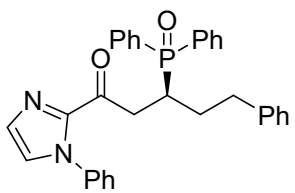
(*S*)-3-(diphenylphosphoryl)-3-(furan-2-yl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3r)



3r

79.3 mg, white solid, 85% yield, $[\alpha]_D^{25}$ = -19.10 (*c* = 1.01 in $CHCl_3$); 94% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =21.56 min, t_R (minor) = 28.93 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.85 (dd, *J* = 11.2, 7.5 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.46 (td, *J* = 7.3, 4.0 Hz, 3H), 7.41 – 7.31 (m, 5H), 7.23 (s, 1H), 7.14 – 7.11 (m, 4H), 6.15 (dt, *J* = 3.3, 1.6 Hz, 1H), 6.02 (t, *J* = 3.3 Hz, 1H), 4.68 (td, *J* = 11.4, 3.5 Hz, 1H), 4.08 (ddd, *J* = 17.2, 10.7, 6.2 Hz, 1H), 3.61 (ddd, *J* = 17.7, 9.9, 3.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.5 (d, *J* = 13.0 Hz), 148.9 (d, *J* = 6.5 Hz), 142.3, 141.6 (d, *J* = 3.0 Hz), 137.9, 131.9 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 2.5 Hz), 131.5, 131.4, 130.8 (d, *J* = 16.1 Hz), 129.9, 129.8, 128.8, 128.6, 128.5, 128.1 (d, *J* = 11.8 Hz), 127.1, 125.6, 110.6 (d, *J* = 3.2 Hz), 108.9 (d, *J* = 6.0 Hz), 37.0, 36.1 (d, *J* = 70.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.27. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{23}N_2O_3PNa$: 489.1339, found:489.1340.

(*S*)-3-(diphenylphosphoryl)-5-phenyl-1-(1-phenyl-1H-imidazol-2-yl)pentan-1-one (3s)

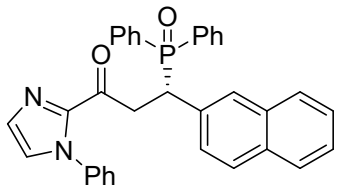


3s

50.5 mg, white solid, 50% yield, $[\alpha]_D^{25}$ = -7.97 (*c* = 1.08 in $CHCl_3$); >99% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =14.46min, t_R (minor) = 24.87 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.80 – 7.71

(m, 4H), 7.53 – 7.34 (m, 9H), 7.25 (s, 1H), 7.21 – 7.09 (m, 6H), 6.95 (d, *J* = 7.3 Hz, 2H), 3.66 (dt, *J* = 17.1, 8.2 Hz, 1H), 3.46 (ddd, *J* = 18.6, 15.1, 4.2 Hz, 1H), 3.33 (tt, *J* = 8.4, 4.3 Hz, 1H), 2.66 (ddd, *J* = 14.9, 10.3, 5.0 Hz,1H), 2.45 (ddd, *J* = 13.7, 10.2, 6.6 Hz, 1H), 2.05 – 1.80 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.6 (d, *J* = 10.7 Hz), 142.4, 141.2, 138.1, 132.4 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 2.8 Hz), 131.3, 131.2, 131.1 (d, *J* = 8.6 Hz), 129.8, 128.9, 128.8, 128.6, 128.5, 128.4 (d, *J* = 2.1 Hz), 128.2, 127.2, 125.9, 125.8, 37.6, 33.8 (d, *J* = 10.7 Hz), 31.8 (d, *J* = 72.6 Hz), 30.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 37.12. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{32}H_{29}N_2O_2PNa$: 527.1859, found:527.1860.

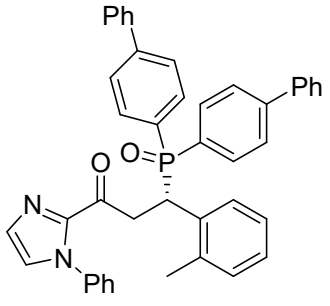
(*S*)-3-(diphenylphosphoryl)-3-(naphthalen-2-yl)-1-(1-phenyl-1H-imidazol-2-yl)propan-1-one (3t)



3t

104.3 mg, white solid, 99% yield, $[\alpha]_D^{25}$ = -27.67(*c* = 1.17 in $CHCl_3$); 84% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 11.57 min, t_R (minor) = 16.30 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.05 – 7.91 (m, 2H), 7.71 – 7.65 (m, 3H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.44 (m, 5H), 7.41 – 7.35 (m, 3H), 7.34 – 7.24 (m, 2H), 7.24 – 7.15 (m, 5H), 7.02 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 4.60 (ddd, *J* = 11.5, 8.5, 3.2 Hz, 1H), 4.32 (ddd, *J* = 17.2, 10.9, 6.2 Hz, 1H), 3.56 (ddd, *J* = 17.4, 9.8, 3.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.0 (d, *J* = 14.4 Hz), 142.5, 137.8, 133.0, 133.0, 132.3, 131.9, 131.5 (d, *J* = 8.6 Hz), 131.4, 131.1 (d, *J* = 8.8 Hz), 130.9, 129.7, 129.1 (d, *J* = 6.8 Hz), 128.8, 128.7, 128.7, 128.5, 128.1 (d, *J* = 4.4 Hz), 128.0 (d, *J* = 2.5 Hz), 127.8, 127.7, 127.4, 127.0, 125.7, 125.7, 125.5, 41.8 (d, *J* = 68.4 Hz), 39.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.37. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{34}H_{28}N_2O_2P$: 527.1883, found:527.1882.

(*S*)-3-(di([1,1'-biphenyl]-4-yl)phosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3u)

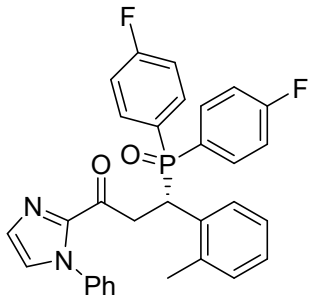


3u

124.7 mg, white solid, 97% yield, $[\alpha]_D^{25}$ = -279.87 (*c* = 1.27 in $CHCl_3$); 93% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) =22.20 min, t_R (minor) = 39.66 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.13 (dd, *J* = 10.3, 7.9 Hz, 2H), 7.78 (dt, *J* = 8.2, 4.9 Hz, 3H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.33 (m, 12H), 7.30 (t, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.20 (s, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 2H), 4.77 (ddd, *J* = 11.6, 8.6, 3.6 Hz, 1H), 4.16 (ddd, *J* = 17.5, 10.8, 7.2 Hz, 1H), 3.65 (ddd, *J* = 16.8, 9.2, 3.6 Hz, 1H), 1.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.2 (d, *J* = 14.7 Hz), 144.6 (d, *J* = 2.7 Hz), 143.9 (d, *J* = 2.7 Hz), 142.3, 139.6 (d, *J* =

5.1 Hz), 137.6, 137.2 (d, *J* = 6.2 Hz), 133.5 (d, *J* = 5.6 Hz), 132.3 (d, *J* = 8.6 Hz), 131.5 (d, *J* = 9.5 Hz), 131.1, 130.1, 129.8, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 127.3, 127.2, 127.1, 126.9, 126.7, 126.4, 126.2 (d, *J* = 5.5 Hz), 125.2, 40.3, 37.3 (d, *J* = 70.1 Hz), 19.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.70. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{43}H_{36}N_2O_2P$: 643.2509, found:643.2504.

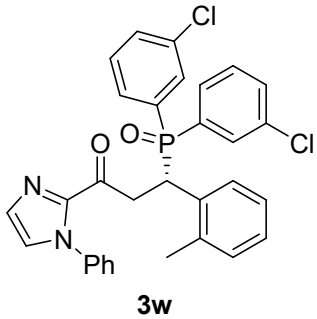
(S)-3-(bis(4-fluorophenyl)phosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3v)



3v

102.1 mg, white solid, 97% yield, $[\alpha]_D^{25}$ = -103.87 (*c* = 1.16 in $CHCl_3$); >99% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) =42.07min, t_R (minor) = 65.58 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.03 (td, *J* = 9.1, 5.5 Hz, 2H), 7.73 – 7.70 (m, 1H), 7.39 – 7.30 (m, 3H), 7.28 (dd, *J* = 5.0, 2.7 Hz, 1H), 7.25 – 7.15 (m,5H), 7.11 – 7.08 (m, 2H), 6.90 – 6.61 (m, 5H), 4.64 (ddd, *J* = 11.8, 8.5, 3.8 Hz, 1H), 4.04 (ddd, *J* = 17.5, 10.5, 7.6 Hz, 1H), 3.57 (ddd, *J* = 16.9, 9.7, 3.7 Hz, 1H), 1.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.0 (d, *J* = 14.6 Hz), 166.4 (d, *J* = 3.1 Hz), 165.9 (d, *J* = 2.9 Hz), 163.9 (d, *J* = 2.9 Hz), 163.4 (d, *J* = 2.8 Hz), 142.3, 137.7, 137.0 (d, *J* = 5.8 Hz), 134.3 (t, *J* = 9.2 Hz), 133.4 (t, *J* = 9.6 Hz), 133.2(d, *J* = 5.4 Hz), 129.9, 129.7 (d, *J* = 8.7 Hz), 128.8, 128.5, 128.4 (d, *J* = 2.9 Hz), 127.2 (d, *J* = 2.5 Hz), 126.9, 126.4, 125.3, 116.2 (dd, *J* = 21.4, 12.3 Hz), 115.2 (dd, *J* = 21.2, 12.8 Hz), 40.2, 37.3 (d, *J* = 68.2 Hz), 19.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.22. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -106.23 (m), -107.01 (m). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{31}H_{25}F_2N_2O_2PNa$: 549.1514, found:549.1518.

(S)-3-(bis(3-chlorophenyl)phosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3w)

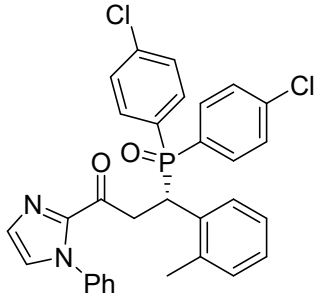


3w

106.3 mg, white solid, 95% yield, $[\alpha]_D^{25}$ = -134.33 (*c* = 1.09 in $CHCl_3$); >99% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) =36.41 min, t_R (minor) = 45.82 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.06 (dt, *J* = 10.9, 1.6 Hz, 1H), 7.93 – 7.83 (m, 1H), 7.76 – 7.72 (m, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.52 (td, *J* = 7.8, 3.4 Hz, 1H), 7.38 – 7.29 (m, 4H),7.25 – 7.16 (m, 3H), 7.16 – 7.11 (m, 2H), 7.10 – 7.08 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.80 (m, 2H), 4.68 (ddd, *J* = 11.3, 8.1, 3.6 Hz, 1H), 4.03 (ddd, *J* = 17.5, 10.6, 7.4 Hz, 1H), 3.58 (ddd, *J* = 16.7, 9.9, 3.6 Hz, 1H), 1.80 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.7 (d, *J* = 14.8 Hz), 142.2, 137.7, 136.9, 135.5 (d, *J* = 14.7 Hz), 134.4, 134.3 (d, *J* = 5.9 Hz), 133.3, 132.9 (d, *J* = 16.4 Hz), 132.7 (d, *J* = 5.7 Hz), 132.5 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 8.8 Hz), 131.7 (d, *J* = 3.4 Hz), 130.8 (d, *J* = 10.0 Hz), 130.3 (d, *J* = 12.2 Hz),

130.0, 129.7, 129.6 (d, J = 8.4 Hz), 129.3 (d, J = 12.7 Hz), 128.9, 128.8 (d, J = 3.0 Hz), 128.5, 127.4 (d, J = 2.7 Hz), 126.9, 126.5, 125.3, 40.2, 37.0 (d, J = 70.2 Hz), 19.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.54. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{26}Cl_2N_2O_2P$: 559.1103, found:559.1100.

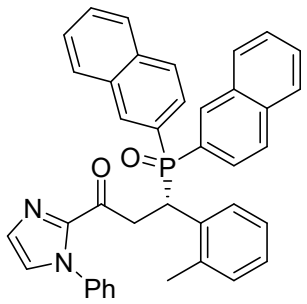
(S)-3-(bis(4-chlorophenyl)phosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3x)



3x

102.9 mg, white solid, 92% yield, $[\alpha]_D^{25}$ = -109.67 (c = 1.15 in $CHCl_3$); >99% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) =17.56min, t_R (minor) = 22.77 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.86 (dd, J = 10.3, 8.1 Hz, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.46 (dd, J = 8.4, 2.3 Hz, 2H), 7.33 – 7.21 (m, 2H), 7.19 (s, 1H), 7.14 (s, 2H), 7.09 (d, J = 6.6 Hz, 4H), 7.01 (d, J = 7.1 Hz, 2H), 6.83 (d, J = 7.5 Hz, 1H), 6.76 (dd, J = 7.3, 2.0 Hz, 2H), 4.57 (td, J = 9.8, 3.7 Hz, 1H), 3.94 (ddd, J = 17.7, 10.2, 7.9 Hz, 1H), 3.51 (ddd, J = 16.9, 10.2, 3.9 Hz, 1H), 1.72 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 187.8 (d, J = 14.3 Hz), 142.2, 138.8 (d, J = 3.2 Hz), 138.1 (d, J = 3.4 Hz), 137.7, 136.9 (d, J = 6.4 Hz), 133.2 (d, J = 9.2 Hz), 133.0 (d, J = 5.7 Hz), 132.3 (d, J = 10.0 Hz), 130.7, 130.0, 129.7 (d, J = 7.2 Hz), 129.2, 129.1, 128.8, 128.5, 128.2, 128.1, 127.2 (d, J = 2.8 Hz), 126.9, 126.4, 125.3, 40.1, 36.9 (d, J = 69.4 Hz), 19.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 31.90. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{26}Cl_2N_2O_2P$: 559.1103, found:559.1098.

(S)-3-(di(naphthalen-2-yl)phosphoryl)-1-(1-phenyl-1H-imidazol-2-yl)-3-(o-tolyl)propan-1-one (3y)



3y

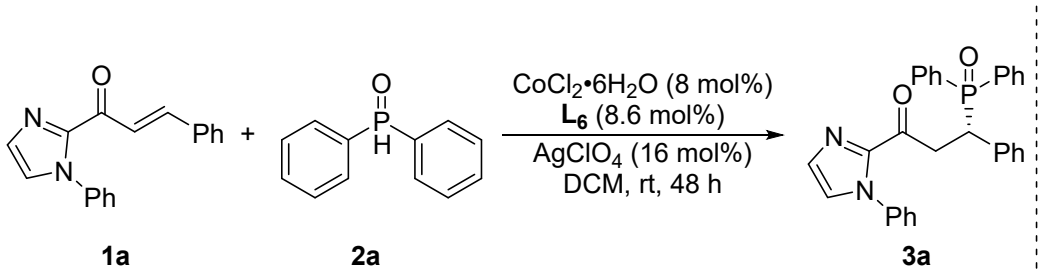
115.8 mg, white solid, 98% yield, $[\alpha]_D^{25}$ = -198.30 (c = 1.13 in $CHCl_3$); >99% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), t_R (major) =12.92min, t_R (minor) = 21.51 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.74 (d, J = 12.6 Hz, 1H), 8.00 (t, J = 6.9 Hz, 3H), 7.94 – 7.80 (m, 3H), 7.71 (d, J = 8.1 Hz, 1H), 7.65 – 7.52 (m, 5H), 7.46 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 (s, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H), 6.81 (d, J = 7.5 Hz, 1H), 6.74 – 6.72 (m, 2H), 4.90 (ddd, J = 10.3, 8.3, 3.9 Hz, 1H), 4.12 (ddd, J = 17.6, 10.4, 7.7 Hz, 1H), 3.71 (ddd, J = 16.9, 9.6, 3.9 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 188.2 (d, J = 14.3 Hz), 142.4, 137.7, 137.1 (d, J = 6.2 Hz), 134.7 (d, J = 2.4 Hz), 134.4 (d, J = 7.6 Hz), 134.3 (d, J = 2.3 Hz), 133.7 (d, J = 5.6 Hz), 133.1 (d, J = 8.6 Hz), 132.7, 132.6, 132.0 (d, J = 12.8 Hz), 129.9, 129.8, 129.6, 129.0, 128.8 (d, J = 2.9 Hz), 128.7, 128.5, 128.4, 128.2 (d, J = 3.9 Hz), 127.8, 127.7, 127.5, 127.4, 127.3, 127.0 (d, J = 2.5 Hz), 126.9, 126.8, 126.4 (d, J = 4.2 Hz), 126.4, 126.0,

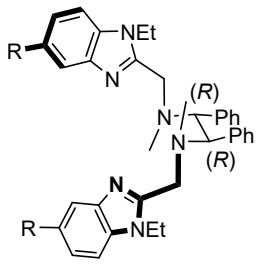
125.9, 125.3, 40.5, 37.2 (d, J = 67.0 Hz), 19.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.76. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{39}H_{31}N_2O_2PNa$: 613.2015, found:613.2014.

5. Mechanism Investigation

5.1 The control experiments

Table S6[a]

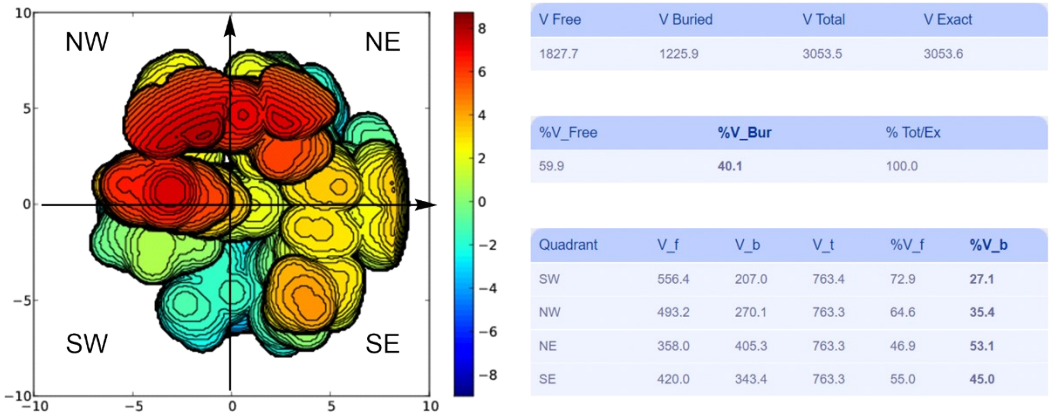




L6: R = 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$

Entry	$CoCl_2$•$6H_2O$	L	$AgClO_4$	Yield (%)[b]	ee (%)[c]
1	×	×	×	66	0
2	√	×	×	47	0
3	√	√	×	20	0
4	×	×	√	36	0
5	×	√	√	40	0
6	√	√	√	99(92)[d]	96

[a] Reactions conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), $CoCl_2$•$6H_2O$ (8 mol%), L6 (8.6 mol%), $AgClO_4$ (16 mol%) in DCM (1.0 mL) at r.t. [b] Determined by ^{1}H NMR using triphenylmethane as an internal standard. [c] Determined by chiral HPLC analysis. [d] Isolated yield in parentheses.



V Free	V Buried	V Total	V Exact
1827.7	1225.9	3053.5	3053.6

%V_Free	%V_Bur	% Tot/Ex
59.9	**40.1**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	556.4	207.0	763.4	72.9	**27.1**
NW	493.2	270.1	763.3	64.6	**35.4**
NE	358.0	405.3	763.3	46.9	**53.1**
SE	420.0	343.4	763.3	55.0	**45.0**

Figure S1. The computed steric map and buried volume for **Int-1** with **L6** ligand. The computed buried volume for SW quadrant is much smaller than that for NW quadrant, consistent with the experimentally observed nucleophilic attack region. Geometry optimizations were carried out at the M06L/def2SVP(Co)-6-31G(d) level.

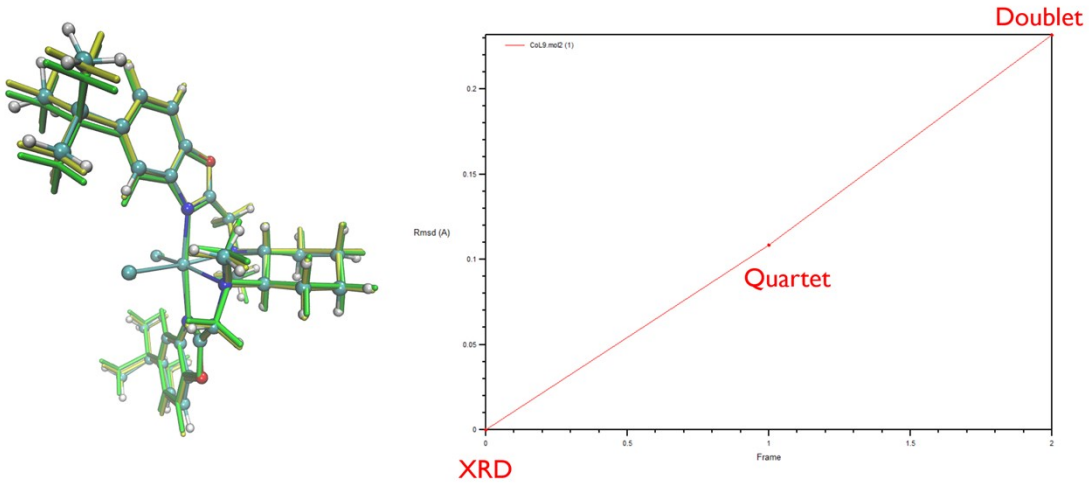
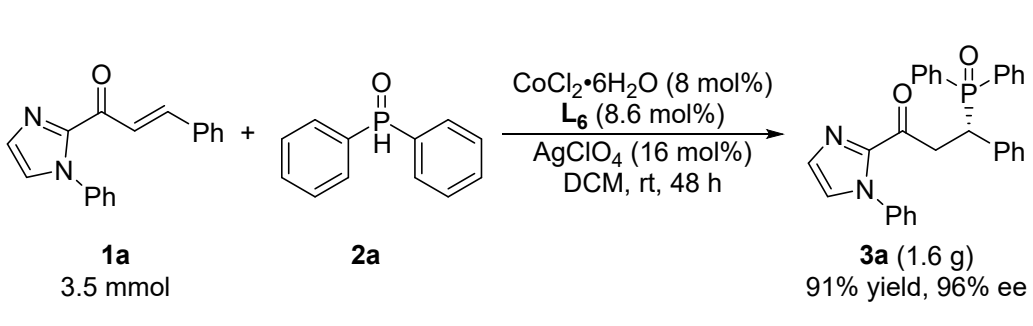


Figure S2. Comparison of XRD structure and calculated quartet (yellow) and doublet (green) structures of **ΛCo9**. Structure optimizations were carried at the M06L/def2SVP level.

Comments on **Figure S2**: The optimized structure of quartet **ΛCo9** complex deviates much less from the experimental structure than that of doublet complex. In the meanwhile, the quartet complex is much more stable than doublet complex by 14.0 kcal/mol. The above results convinced us to consider **Int-1** as quartet.

6. Preparative Utility of the Methodology

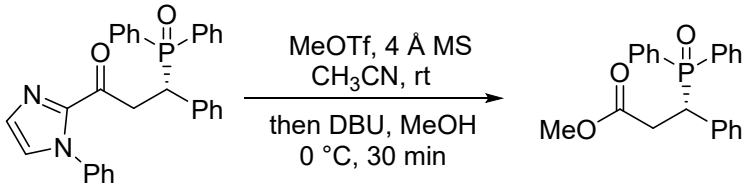
6.1 The gram-scale preparation



Under air conditions, take a clean 100 mL round-bottomed flask, fill with a suitable magnet, and add $CoCl_2$•$6H_2O$ (0.28 mmol, 8 mol%), **L6** (0.30 mmol, 8.6 mol%) and anhydrous dichloromethane (35 mL), stirred for 12 hours at room temperature (obvious color change of the system was observed: blue and transparent to purple-pink and slightly turbid). Then, $AgClO_4$ (0.56 mmol, 16 mol%) was rapidly added to the reaction system. After 1 h, the reaction mixture changed from a purplish-pink slightly turbid solution to pale pink accompanied by off-white flocculents. At room temperature, take a 50-mL syringe, remove the needle, add a needle filter, draw all the supernatant in the system into another clean 100-mL round-bottom flask, and then add substrate 1a (3.5 mmol, 1.0 eq.), stirred for 30 minutes (the reaction system changed from pale pink to orange), then the substrate 2a (5.25 mmol, 1.5 eq.) was added to the reaction system (the reaction system changed from orange to pale yellow) ,stirred at rt for 48 hours, and monitor the reaction progress by TLC. After the substrate1a was completely converted, the solvent in the reaction was removed under reduced pressure. The obtained crude product was separated by column chromatography (DCM/EA=1:1) to obtain 1.6 g of pure target compound **3a**.

6.2 The synthetic transformations of product

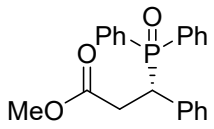
6.2.1 Preparation of chiral ester 4a from 3a



To a solution of **3a** (0.1 mmol: 96% ee, 1.0 eq) in CH_3CN (1 mL) was added 4Å MS (200 mg, 100 mg/0.1 mmol of **3a**) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of nitrogen for 2 h at room temperature, then methyl trifluoromethansulfonate (0.3 mmol, 3.0 eq) was added at room temperature. After being stirred at room temperature for 2 h, MeOH (1.00 mL) and DBU (0.50 mL) were subsequently added to the reaction mixture at 0 °C. After being stirred at 0 °C for

0.5 h, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE/Et_2O) to give **4a** (93% yield, 81% ee) as a white solid.

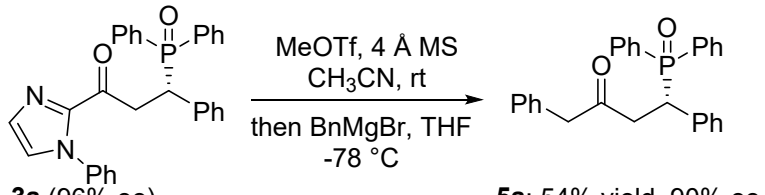
Methyl (S)-3-(diphenylphosphoryl)-3-phenylpropanoate (4a)



4a

33.9 mg, white solid, 93% yield, $[\alpha]_D^{25}$ = -108.3 (*c* = 1.02 in $CHCl_3$); 81% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) =37.84 min, t_R (minor) = 41.92 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.98 – 7.93 (m, 2H), 7.60 – 7.50 (m, 3H), 7.45 (dd, *J* = 11.3, 7.6 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.29 – 7.22 (m, 4H), 7.17 (d, *J* = 6.7 Hz, 3H), 4.08 (ddd, *J* = 11.1, 7.8, 3.3 Hz, 1H), 3.47 (s, 3H), 3.12 (ddd, *J* = 17.0, 11.1, 6.1 Hz, 1H), 2.91 (ddd, *J* = 16.6, 9.5, 3.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 171.8 (d, *J* = 17.2 Hz), 135.0 (d, *J* = 5.5 Hz), 132.0 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 15.6 Hz), 131.5 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 8.5 Hz), 131.0 (d, *J* = 8.9 Hz), 130.7 (d, *J* = 9.8 Hz), 129.6 (d, *J* = 5.5 Hz), 128.9 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 2.0 Hz), 128.1 (d, *J* = 11.8 Hz), 127.3 (d, *J* = 2.5 Hz), 51.9 , 42.8 (d, *J* = 68.2 Hz), 34.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 32.71. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}O_3P$: 365.1301, found:365.1305.

6.2.2 Preparation of chiral ketone 5a

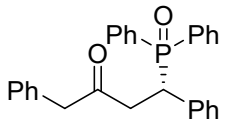


3a (96% ee) **5a**: 54% yield, 90% ee

To a solution of **3a** (0.2 mmol, 1.0 eq, 96% ee), 4Å molecular sieves (200 mg), and acetonitrile (2.0 ml) were combined in an oven dried airtight flask. The suspension was stirred vigorously under a positive pressure of nitrogen for 2 hours. Then methyl trifluoromethanesulfonate (0.6 mmol, 3.00 eq) was added stirred an additional 2 hours. Then the reaction mixture was filtered through a short plug of oven dried Celite. The vial and Celite were washed with 1 ml EtOAc and the solvent was removed in vacuo. The resulting solid was dissolved in THF (3 ml) and the vial cooled to –78 °C before benzylmagnesium bromide (1 M, 0.5 mmol, 2.5 eq.) was added very slowly. The reaction was then stirred for 30 min before quenched by saturated aqueous $NaHCO_3$ (2 ml) and water (10 ml) and the reaction allowed to warm to ambient temperature with stirring. The aqueous layer was then extracted with diethyl ether (3 x 15 ml) and the combined organic dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo.

The product was purified by flash chromatography (PE: Et_2O) to give the title compound **5a**.

(S)-4-(diphenylphosphoryl)-1,4-diphenylbutan-2-one (5a)

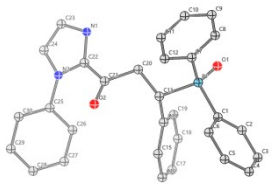
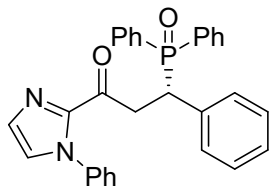


5a

45.8 mg, white solid, 54% yield, $[\alpha]_D^{25}$ = -72.6 (*c* = 1.13 in $CHCl_3$); 90% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C), t_R (major) =41.01 min, t_R (minor) = 49.37 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.94 – 7.84 (m, 2H), 7.60 – 7.47 (m, 3H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 1H), 7.24 – 7.17 (m, 7H), 7.13 – 7.09 (m, 3H), 6.88-6.86 (m, 2H), 4.19 (ddd, J = 10.2, 7.0, 2.9 Hz, 1H), 3.47 (d, J = 6.0 Hz, 2H), 3.36 (ddd, J = 17.5, 10.3, 5.4 Hz, 1H), 2.92 (ddd, J = 17.8, 11.0, 2.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 205.1 (d, *J* = 13.1 Hz), 135.3 (d, *J* = 5.7 Hz), 133.0, 132.0 (d, *J* = 2.3 Hz), 131.7 (d, *J* = 24.2 Hz), 131.4 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 8.5 Hz), 130.7, 129.6 (d, *J* = 5.6 Hz), 129.2, 128.8 (d, *J* = 11.3 Hz), 128.6, 128.2, 128.0 (d, *J* = 11.8 Hz), 127.0, 126.9, 50.5, 41.8, 41.2 (d, *J* = 68.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ (ppm) 33.60. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{26}O_2P^+$: 425.1665, found:425.1668.

7. X-Ray Diagrams

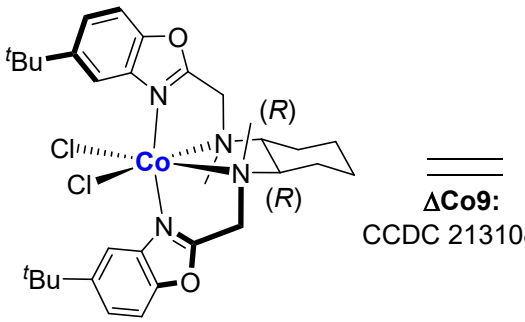
(1) X-Ray structure of **3a**

 CCDC 2131091	 **3a**

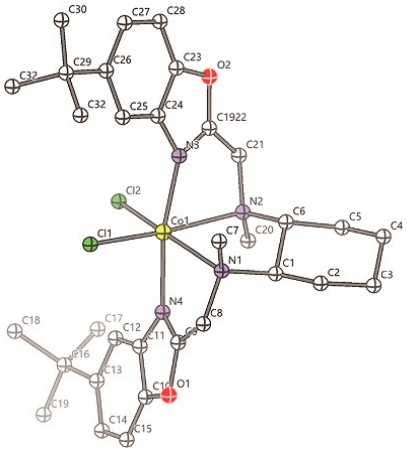
Single crystals of **3a** were obtained from the mixed dichloromethane and ethyl acetate. CCDC: 2131091 contain the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data (CCDC 2131091)**.** $C_{30}H_{25}N_2O_2P$, *M* = 476.49, triclinic: a = 12.0468(10) Å, b = 5.7528(5) Å, c = 17.6094(14) Å, *V* = 1206.27(17) Å^3.

(2) X-Ray structure of **ΛCo9**



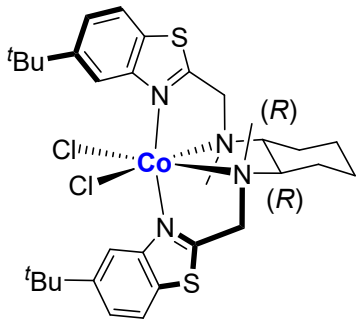
ΔCo9:
CCDC 2131088



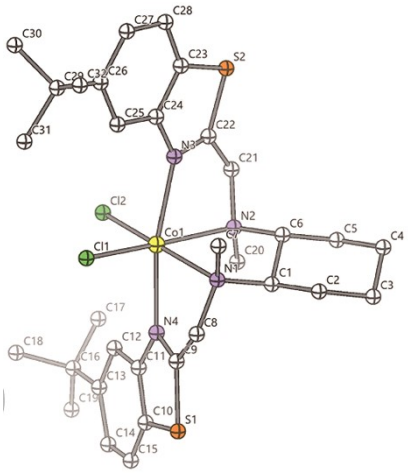
Single crystals of **ΛCo9** were obtained from the mixed dichloromethane and ethyl acetate. CCDC: 2131088 contain the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data (CCDC 2131088)**.** $C_{32}H_{44}Cl_2CoN_4O_2$, M = 646.54, triclinic: a = 42.695(10) Å, b = 24.761(6) Å, c = 25.350(7) Å , V = 25854(11) Å^3.

(3) X-Ray structure of **ΛCo10**



ΔCo10:
CCDC 2131089



Single crystals of **ΛCo10** were obtained from the mixed dichloromethane and ethyl acetate. CCDC: 2131089 contain the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data (CCDC 2131089)**.** $C_{32}H_{44}Cl_2CoN_4S_2$, M = 766.76, triclinic: a = 15.7111(9) Å. b = 25.1439(15) Å. c = 11.3621(6)Å , V = 4488.5(4) Å^3.

8. NMR Spectra of products 3, 4a and 5a.

Figure S3: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3a

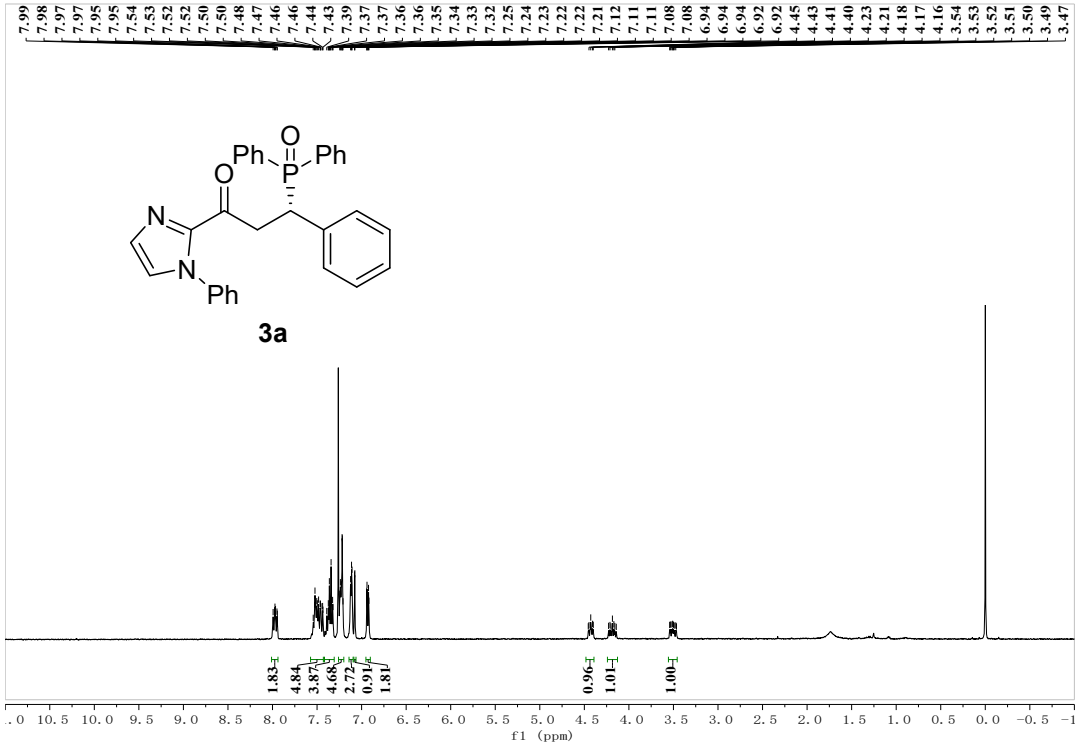


Figure S4: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3a

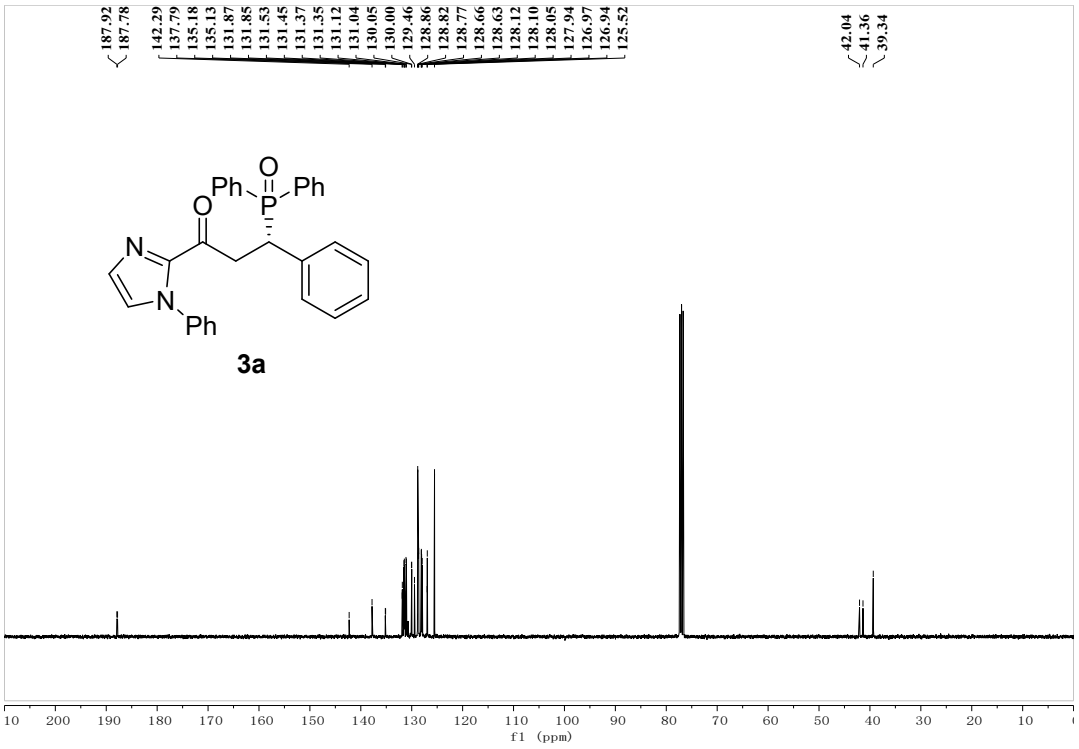


Figure S5: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3a

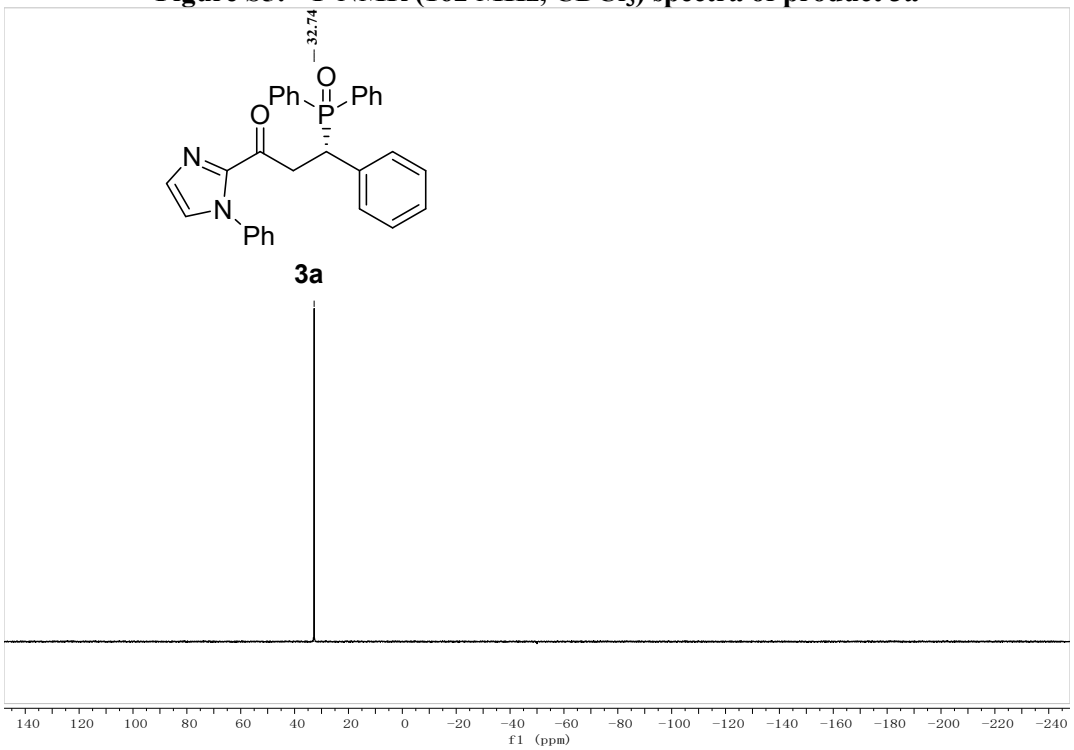


Figure S6: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3b

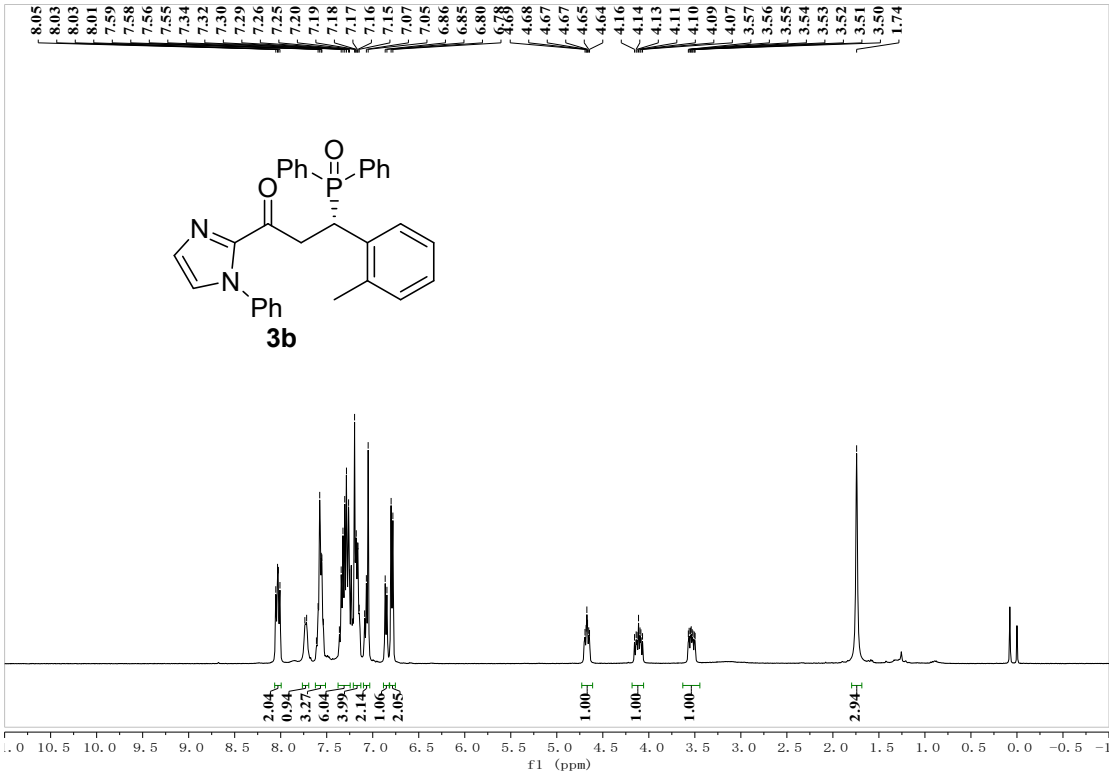


Figure S7: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3b

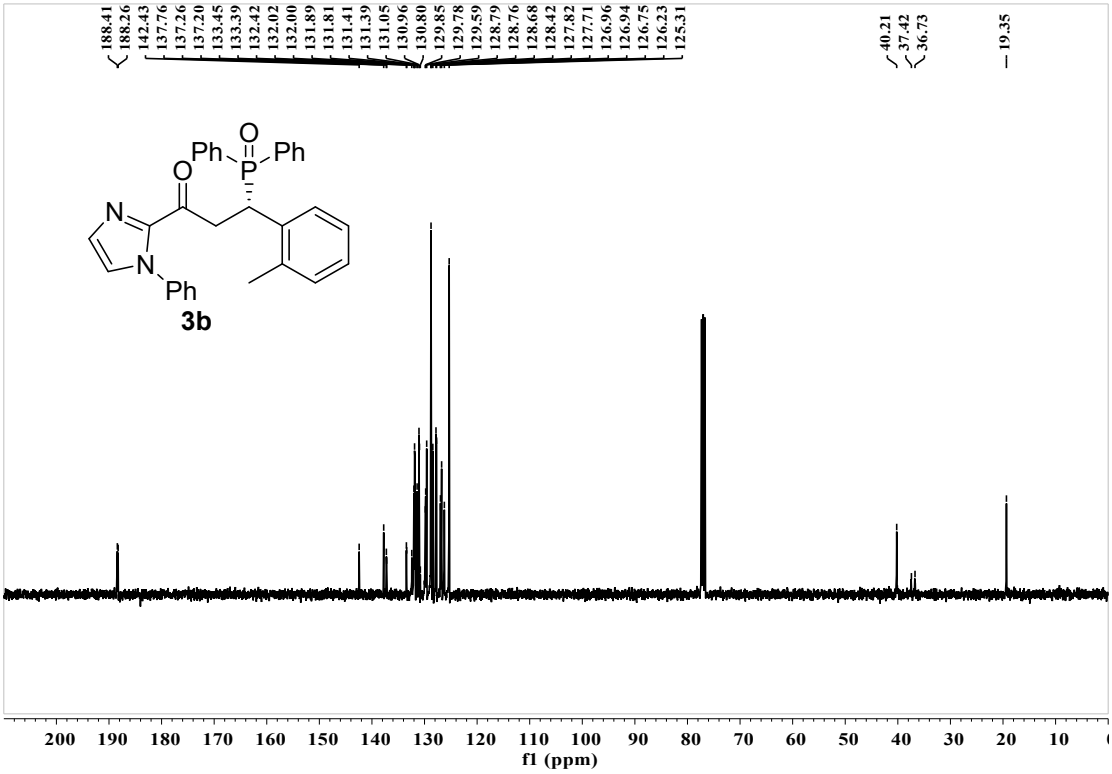


Figure S8: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3b

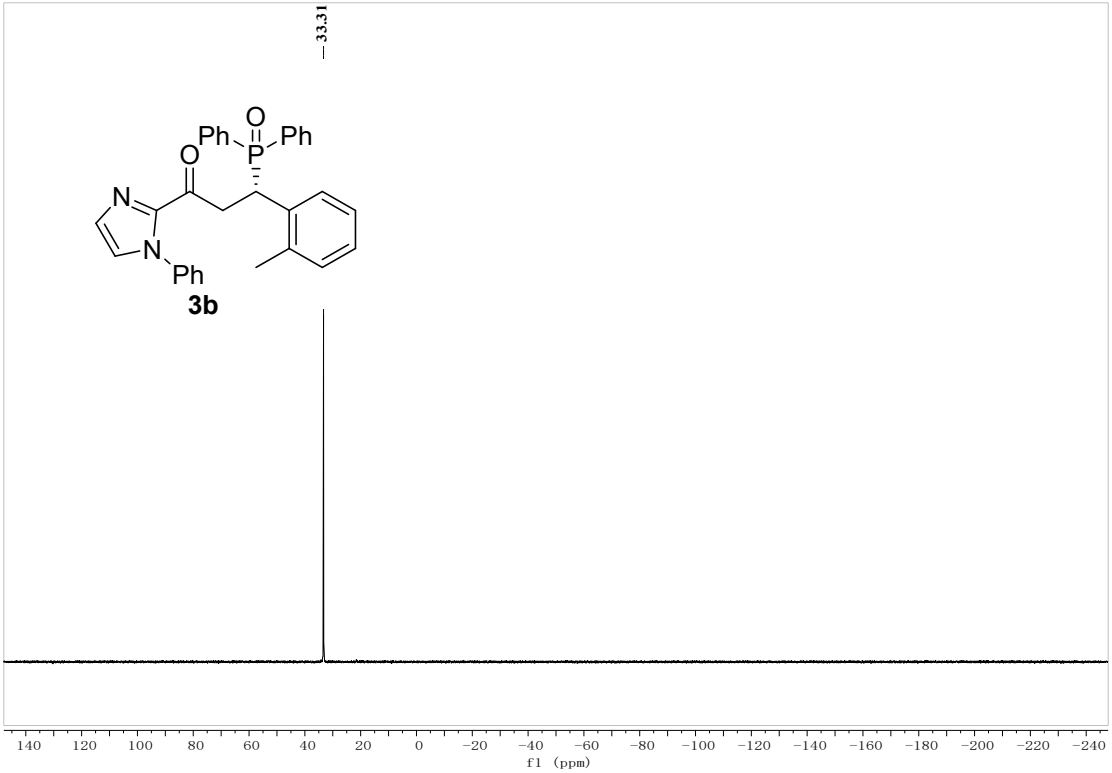


Figure S9: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3c

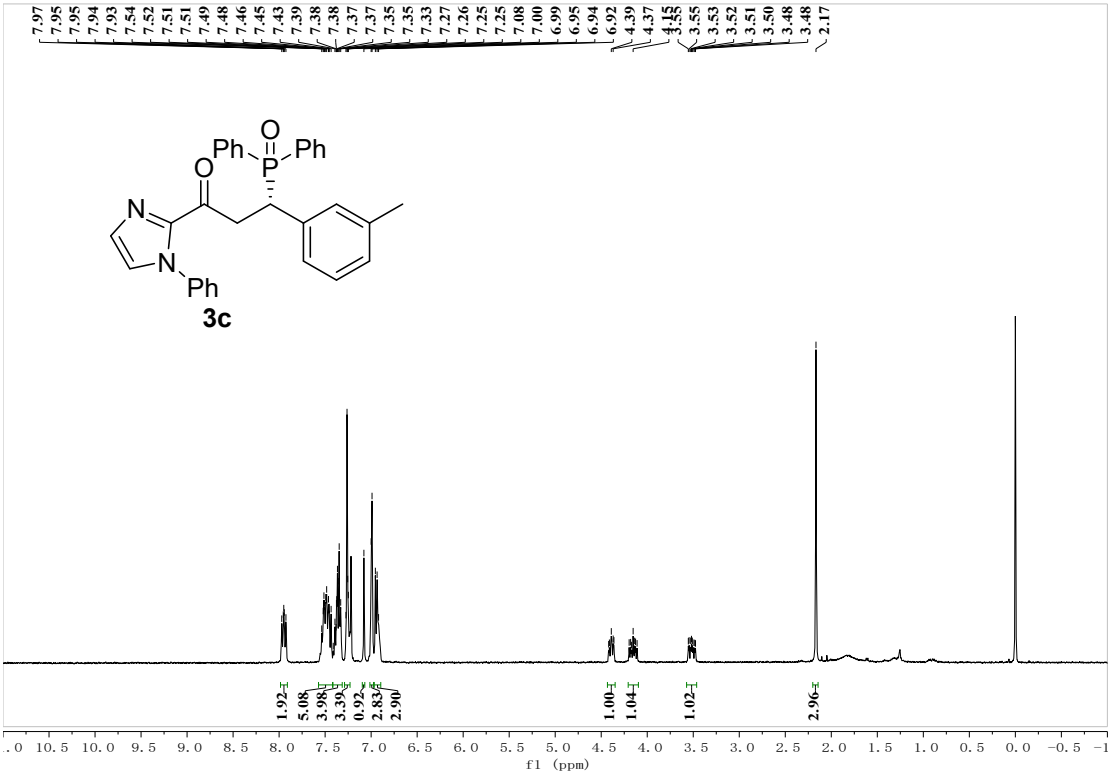


Figure S10: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3c

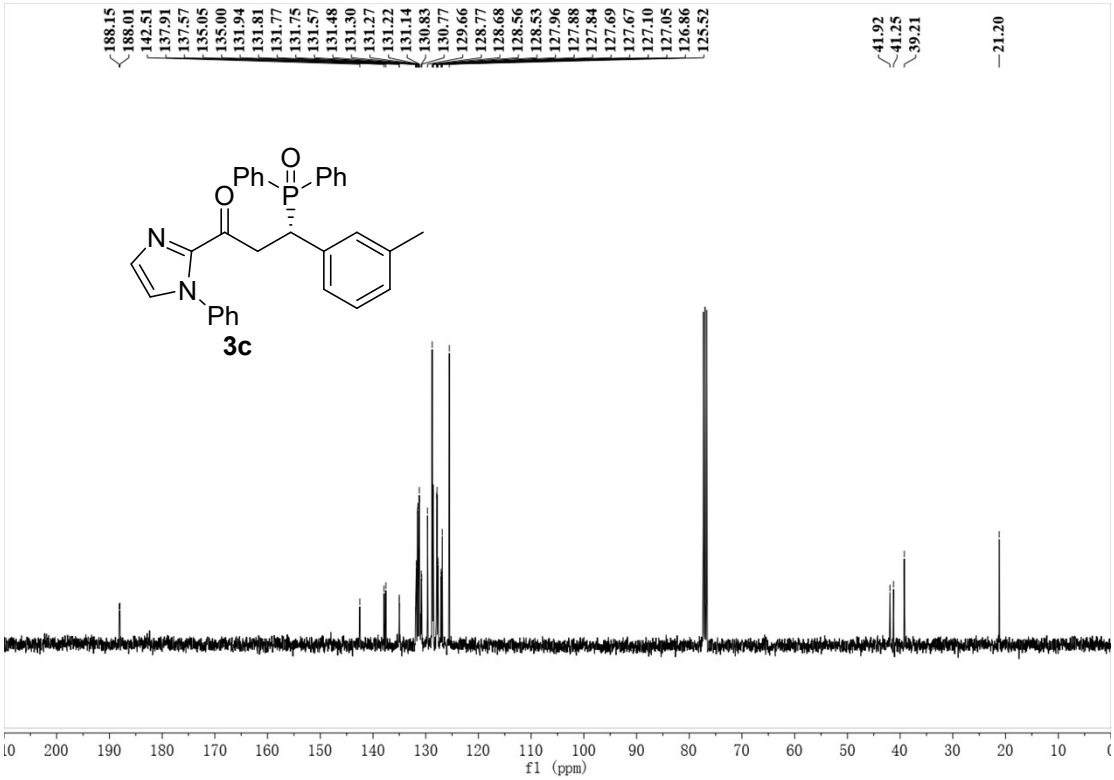


Figure S11: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3c

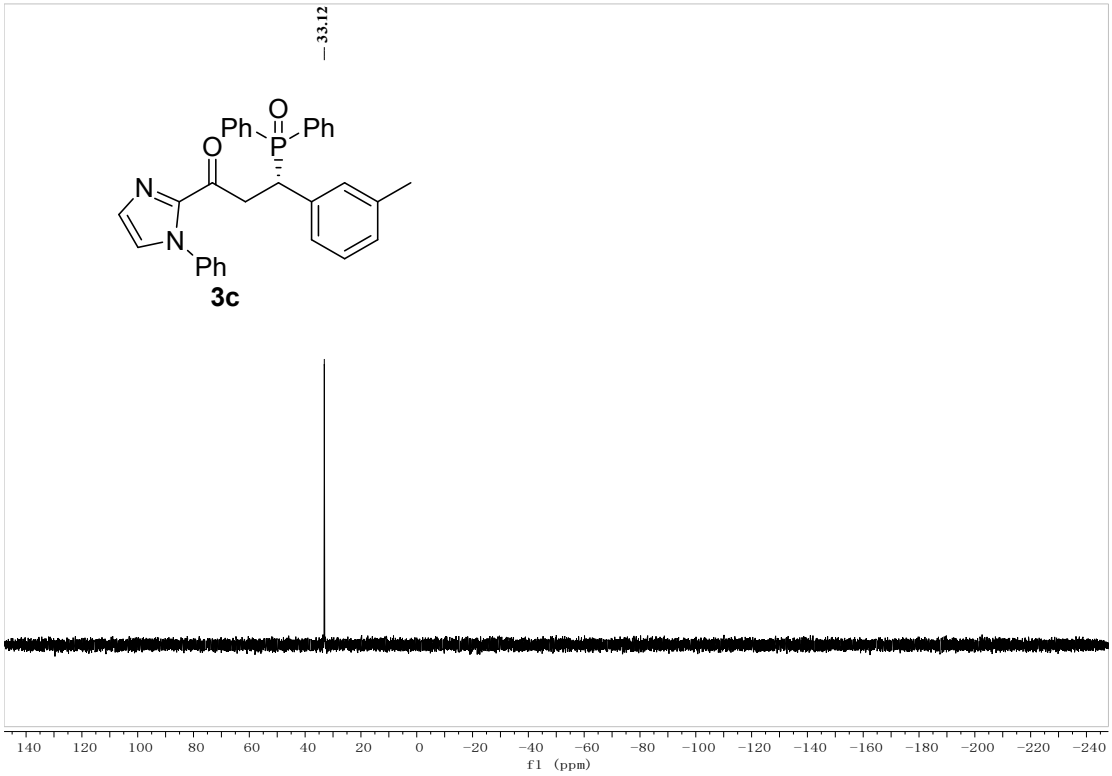


Figure S12: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3d

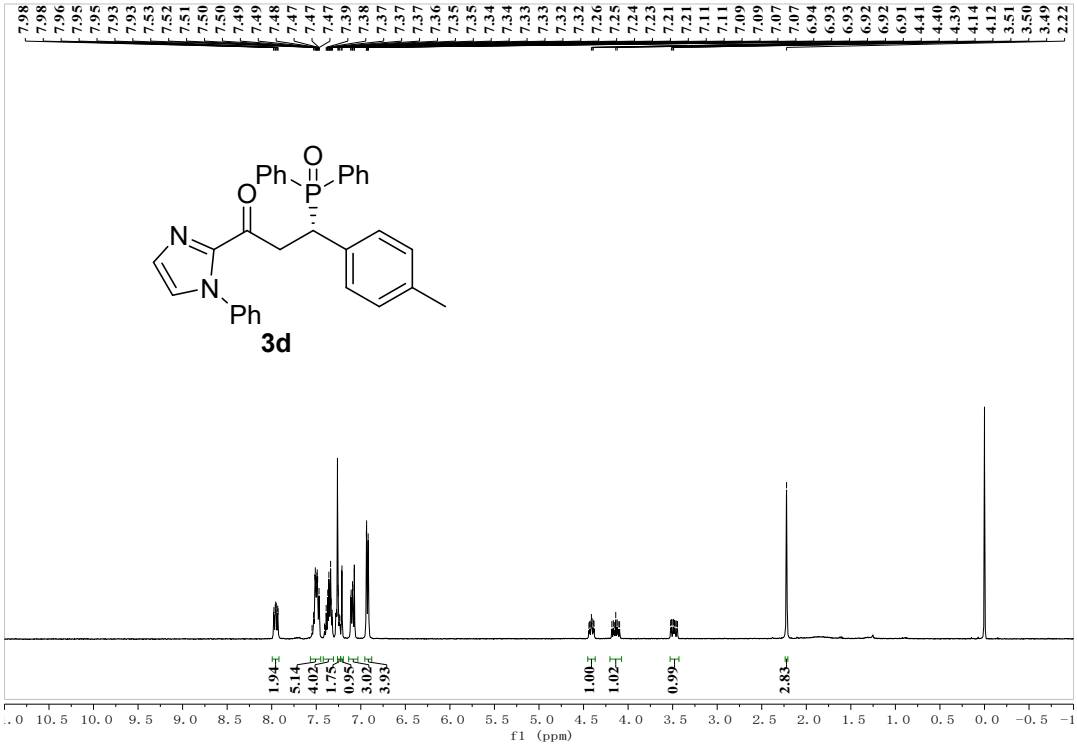


Figure S13: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3d

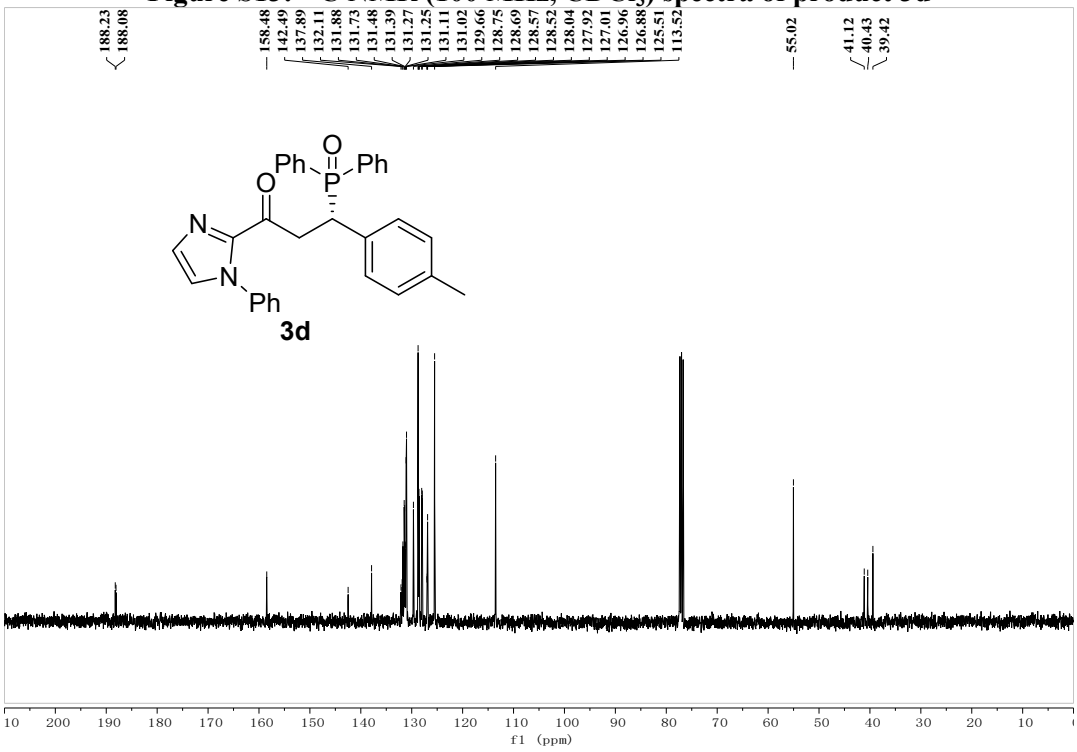


Figure S14: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3d

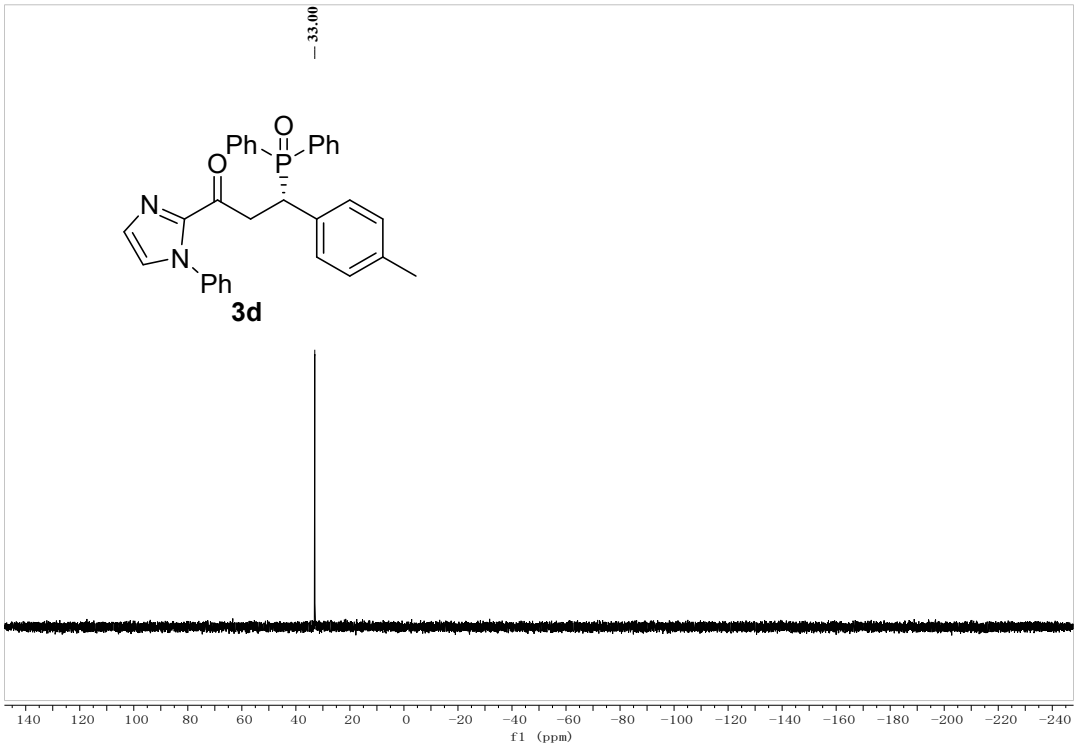


Figure S15: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3e

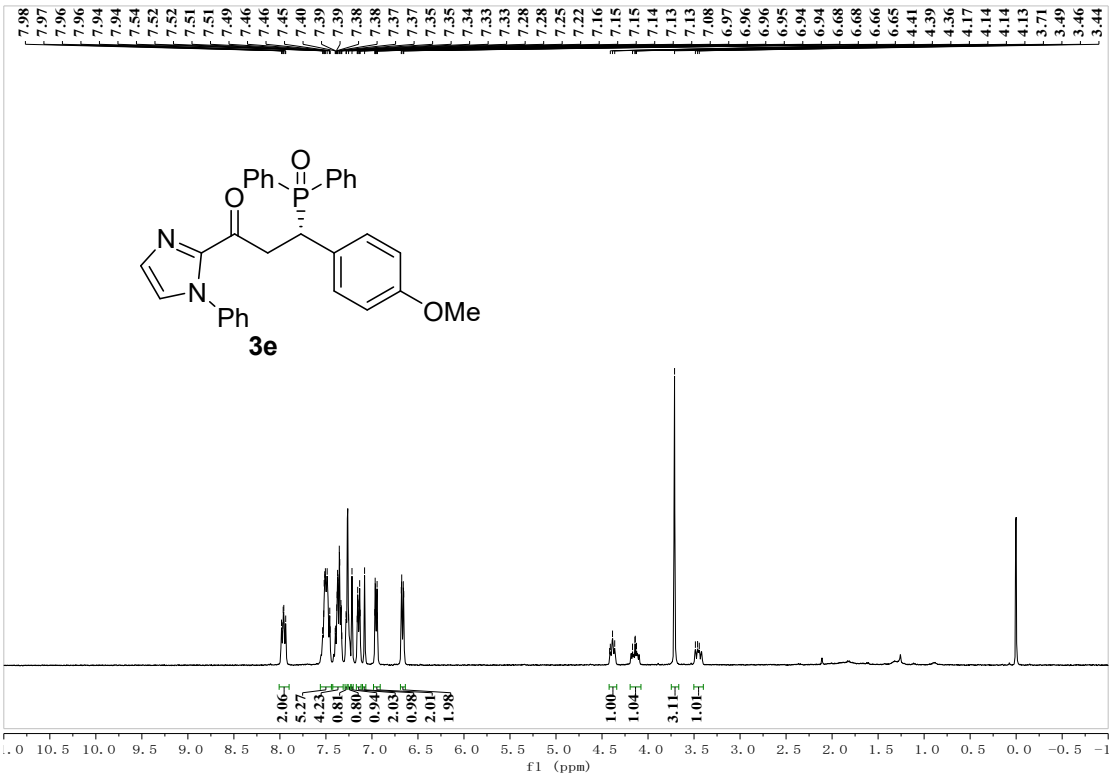


Figure S16: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3e

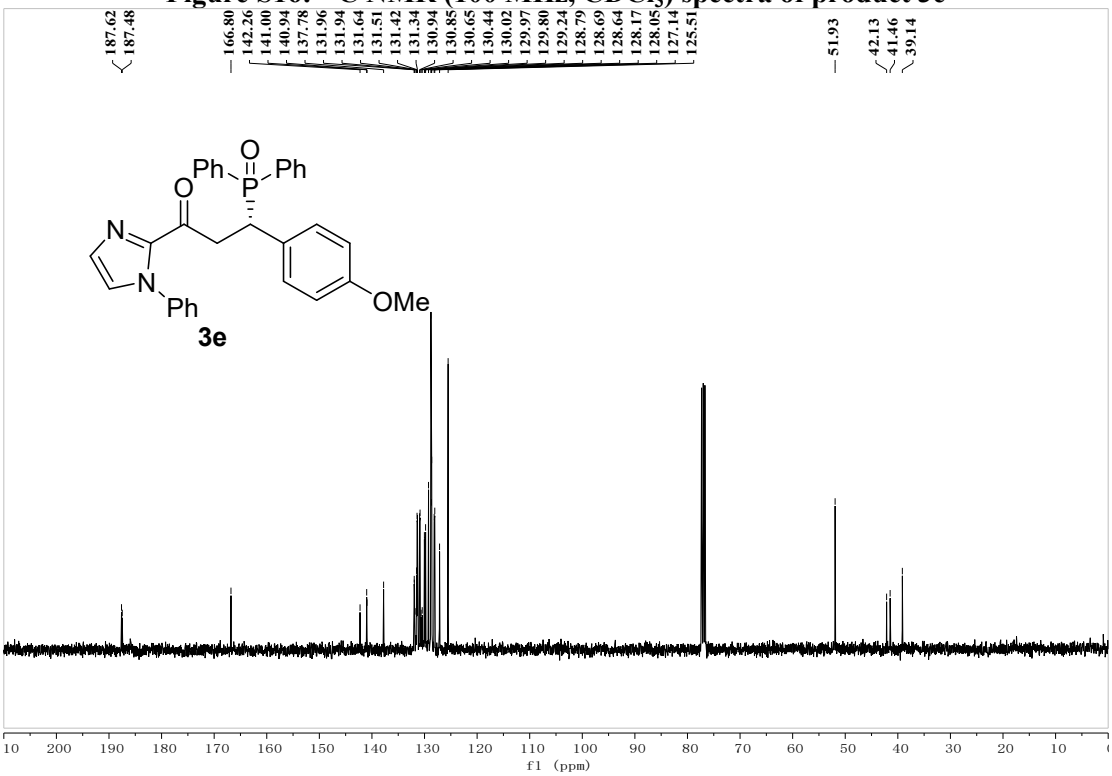


Figure S17: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3e

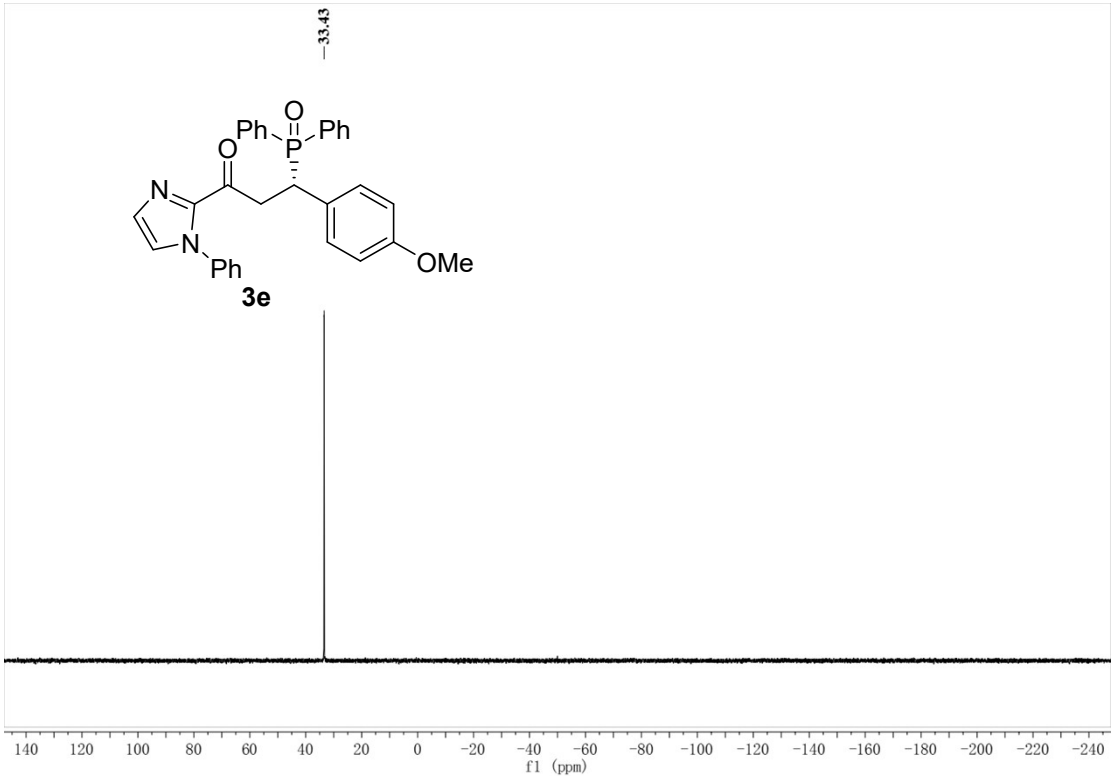


Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3f

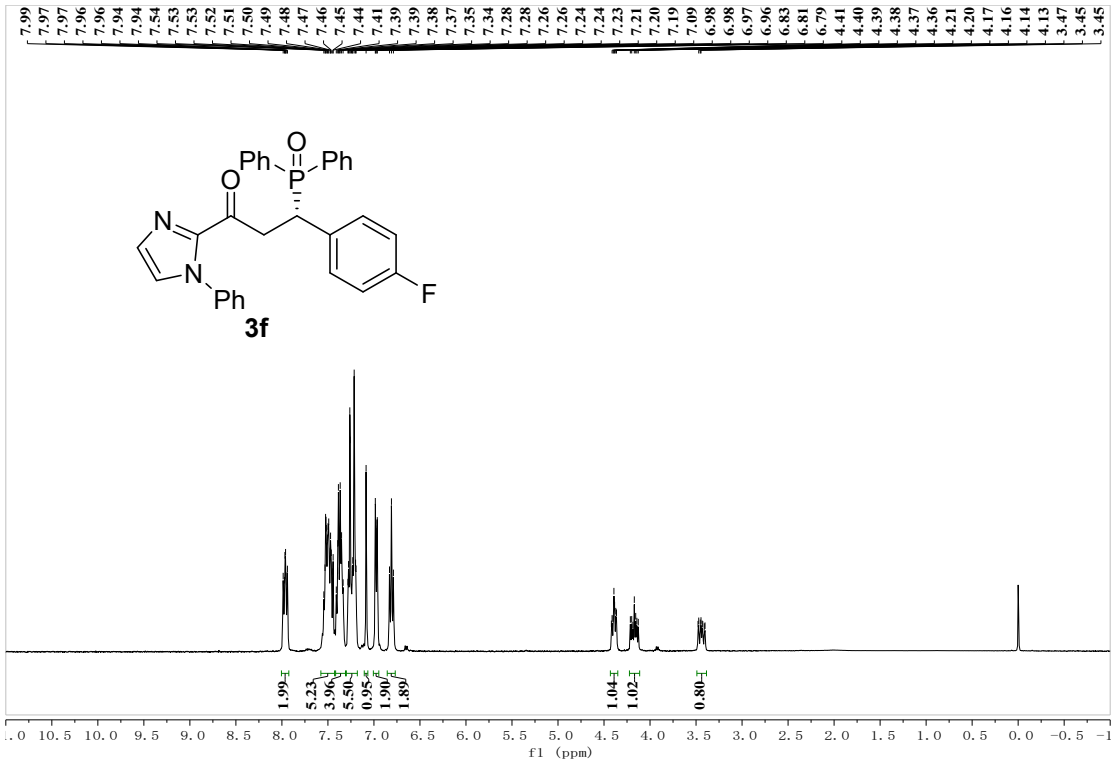


Figure S19: ^{13}C NMR (100 MHz, CDCl3) spectra of product 3f

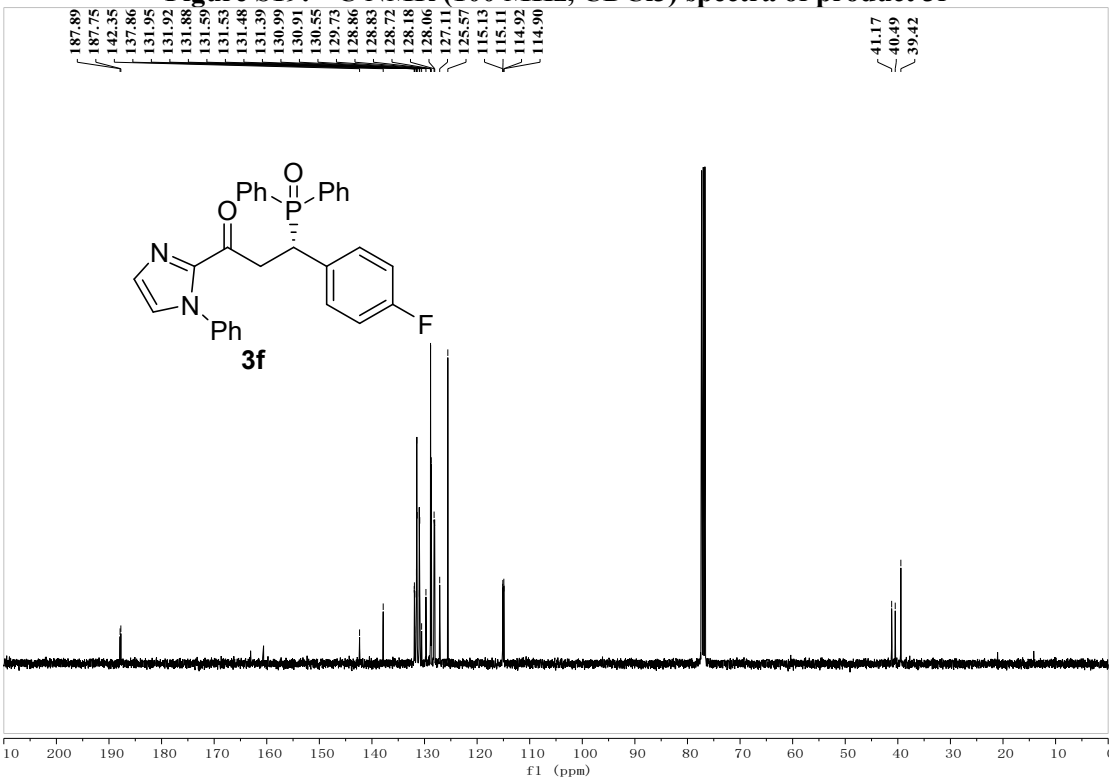


Figure S20: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3f

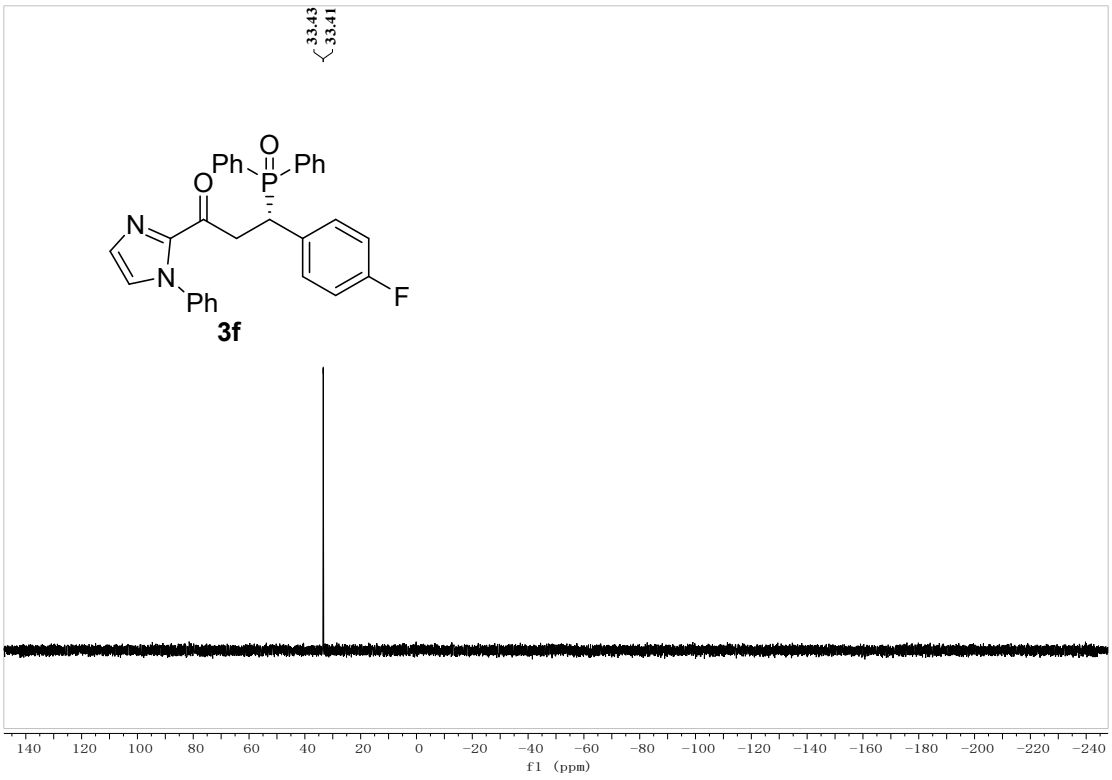


Figure S21: ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3f

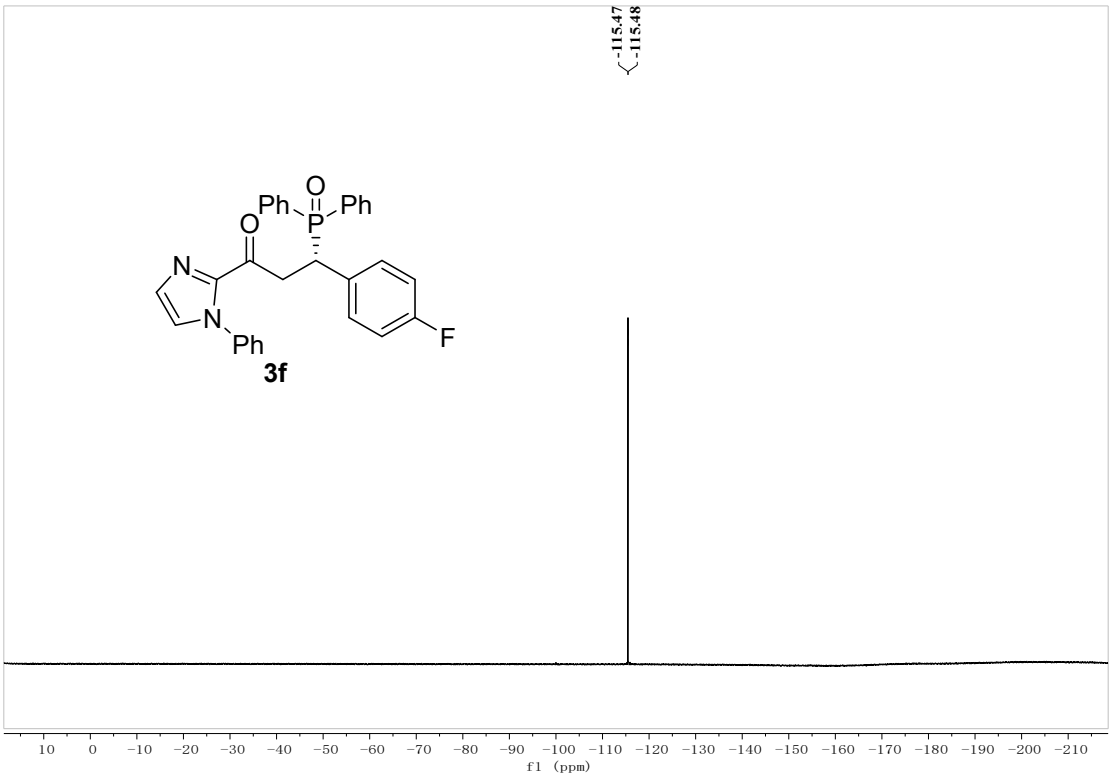


Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3g

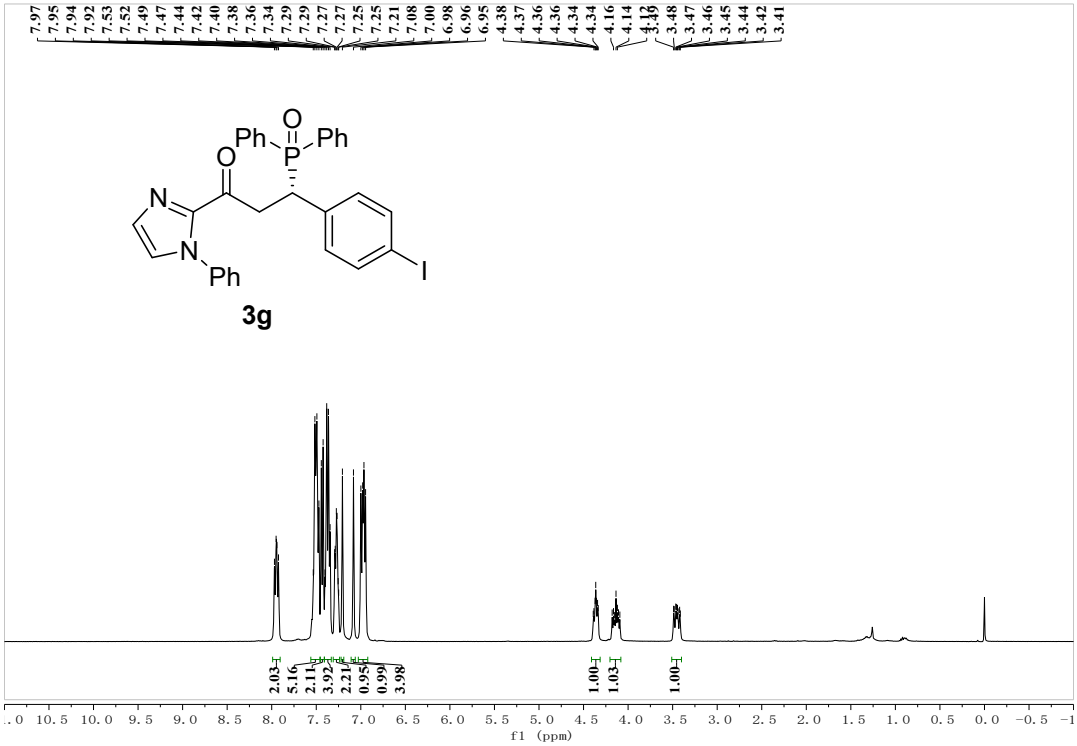


Figure S23: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3g

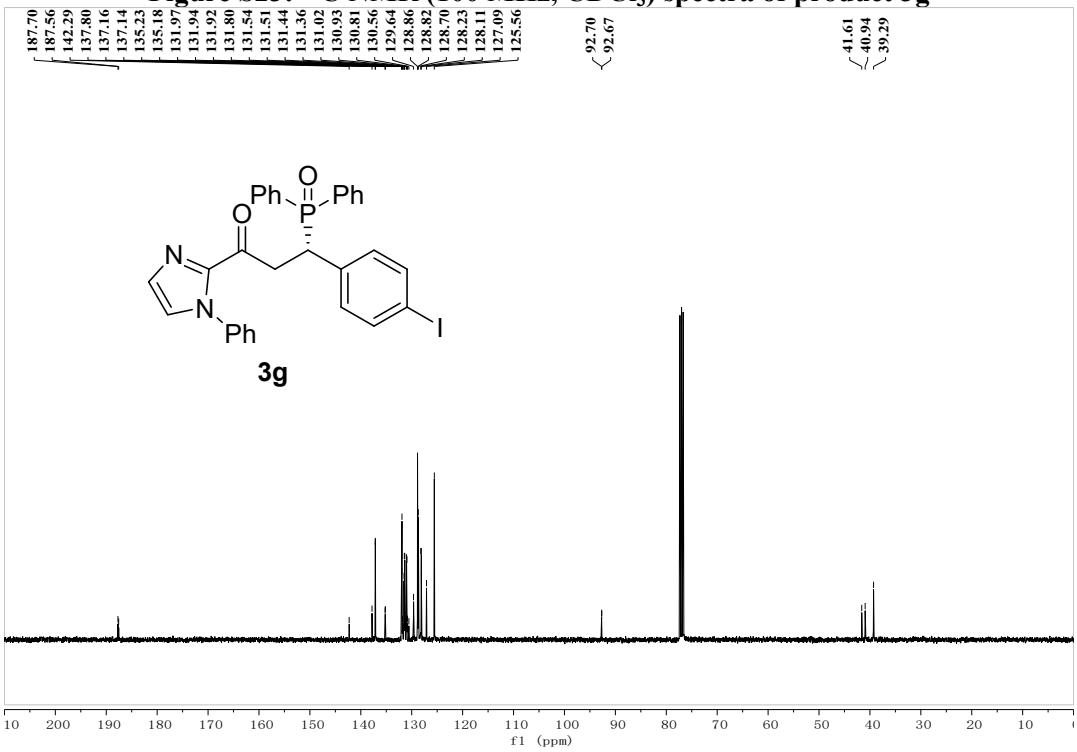


Figure S24: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3g

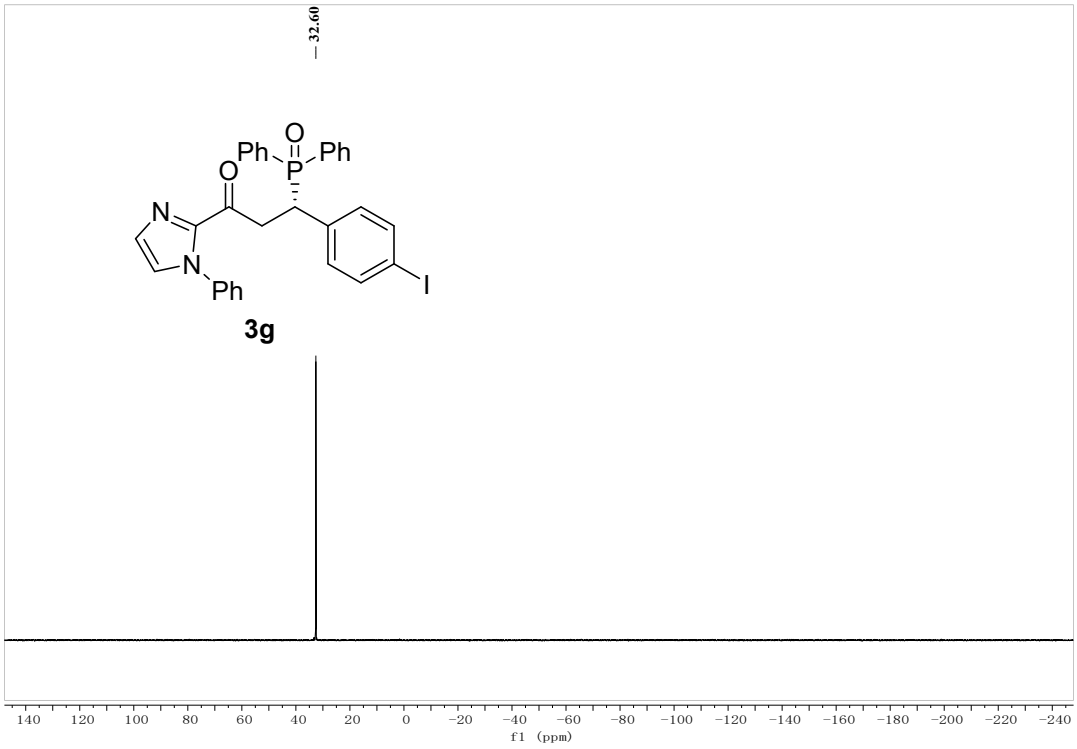


Figure S25: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3h

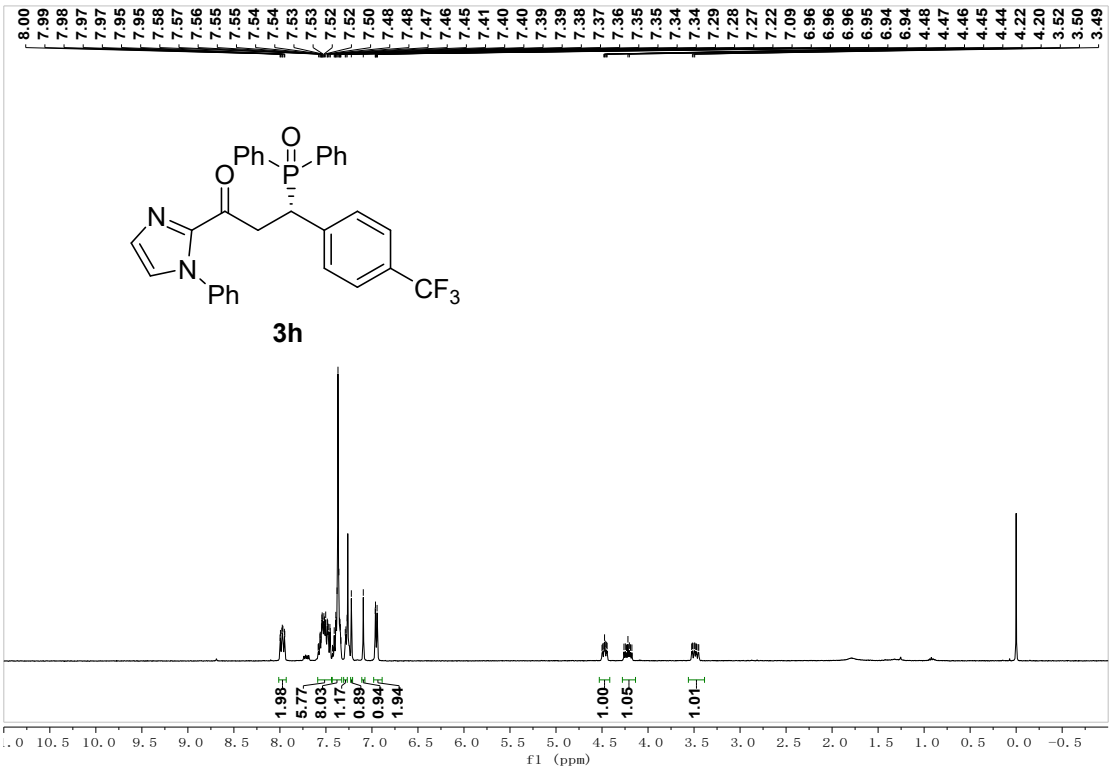


Figure S26: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3h

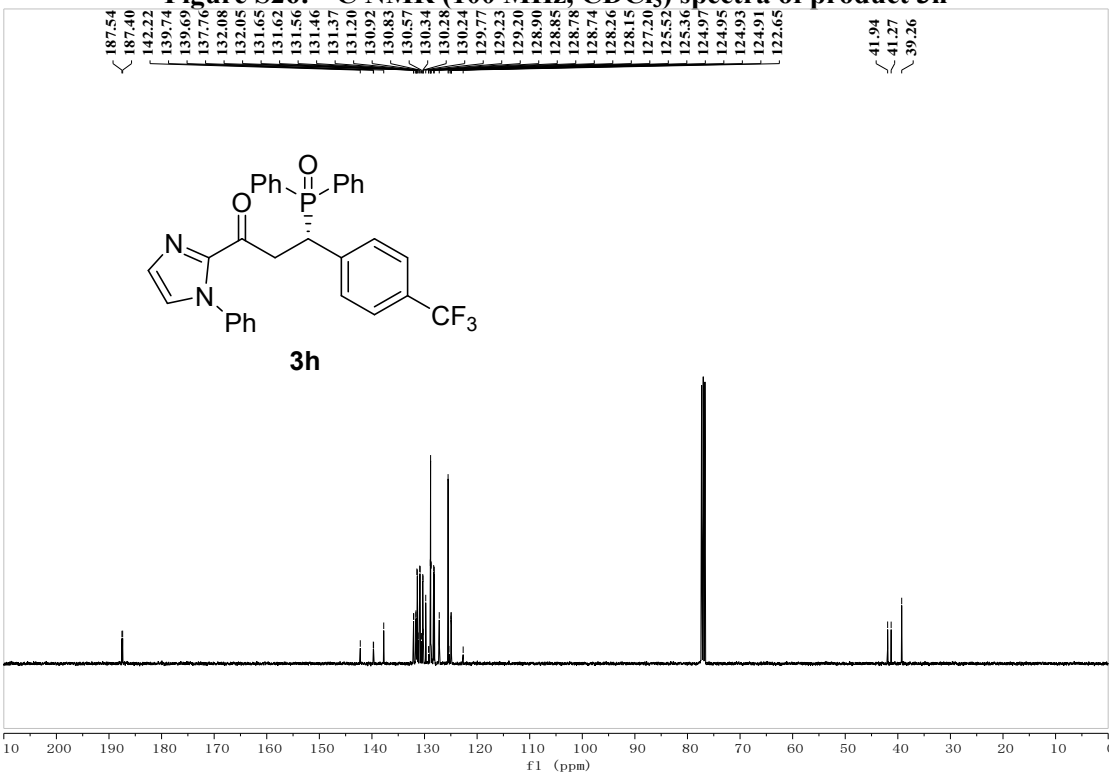


Figure S27: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3h

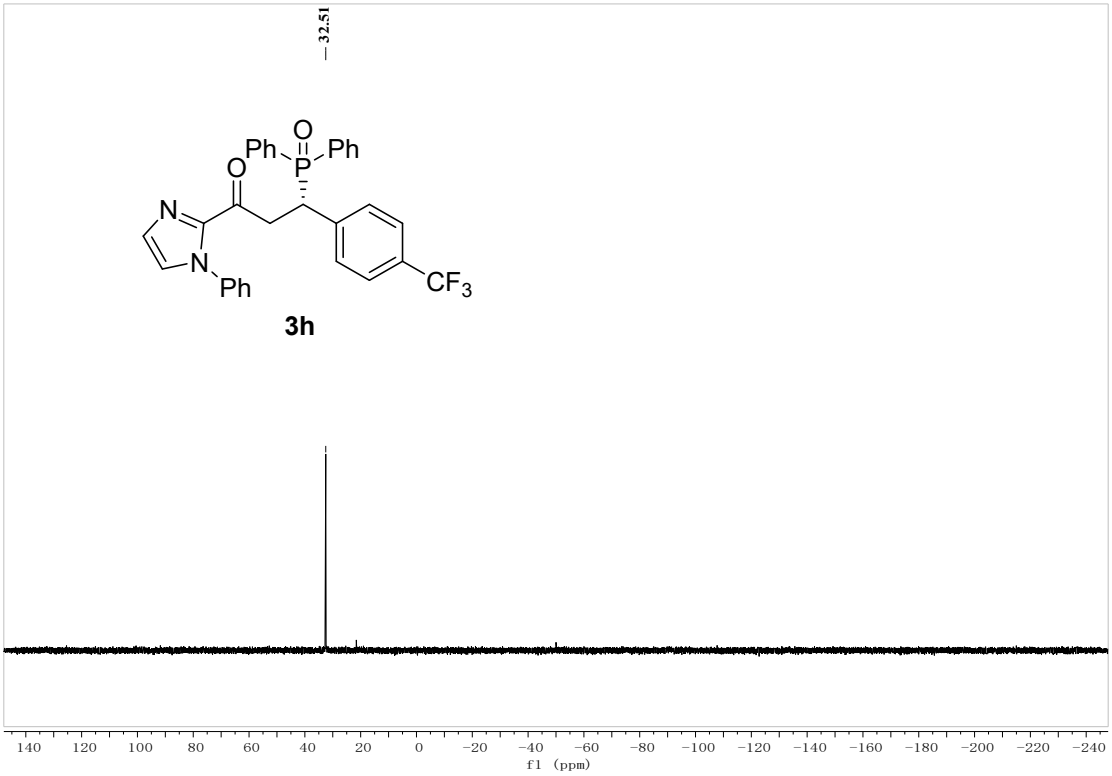


Figure S28: ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3h

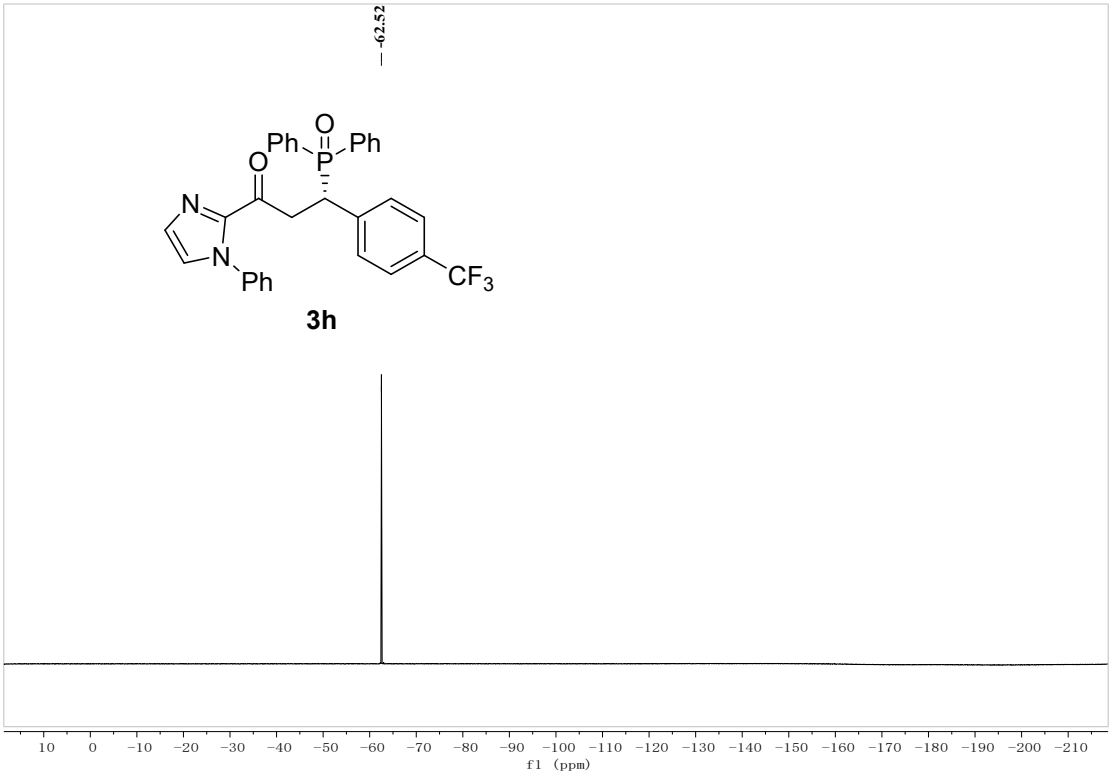


Figure S29: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3i

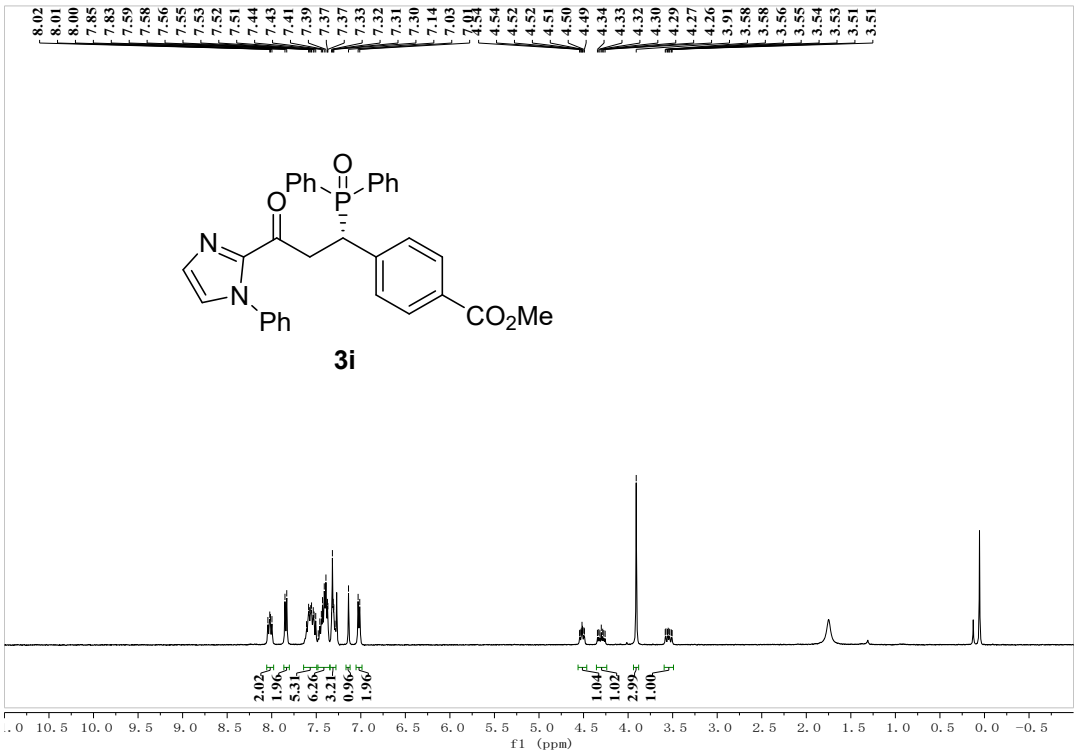


Figure S30: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3i

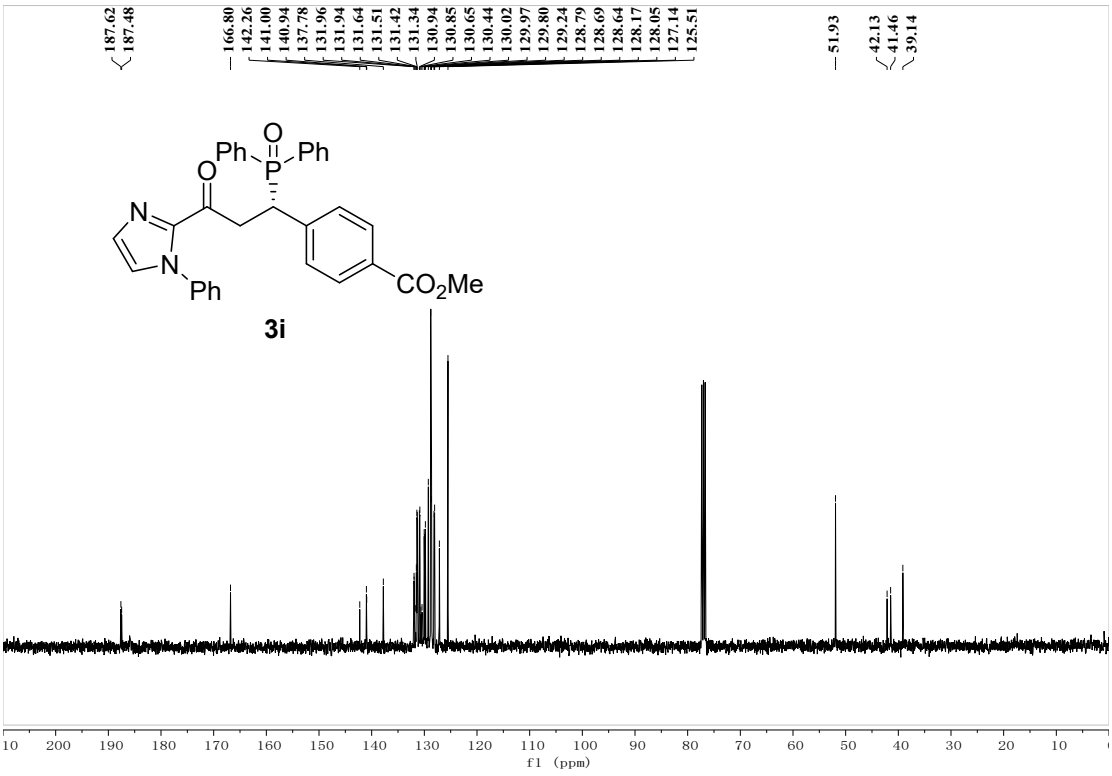


Figure S31: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3i

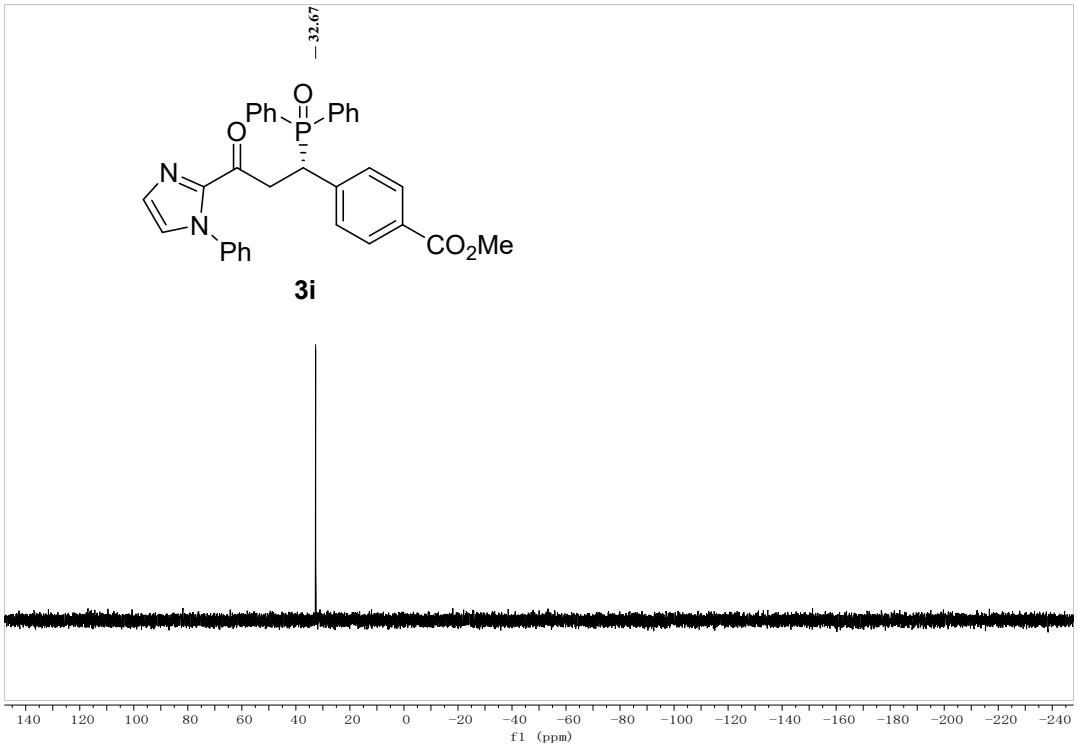


Figure S32: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3j

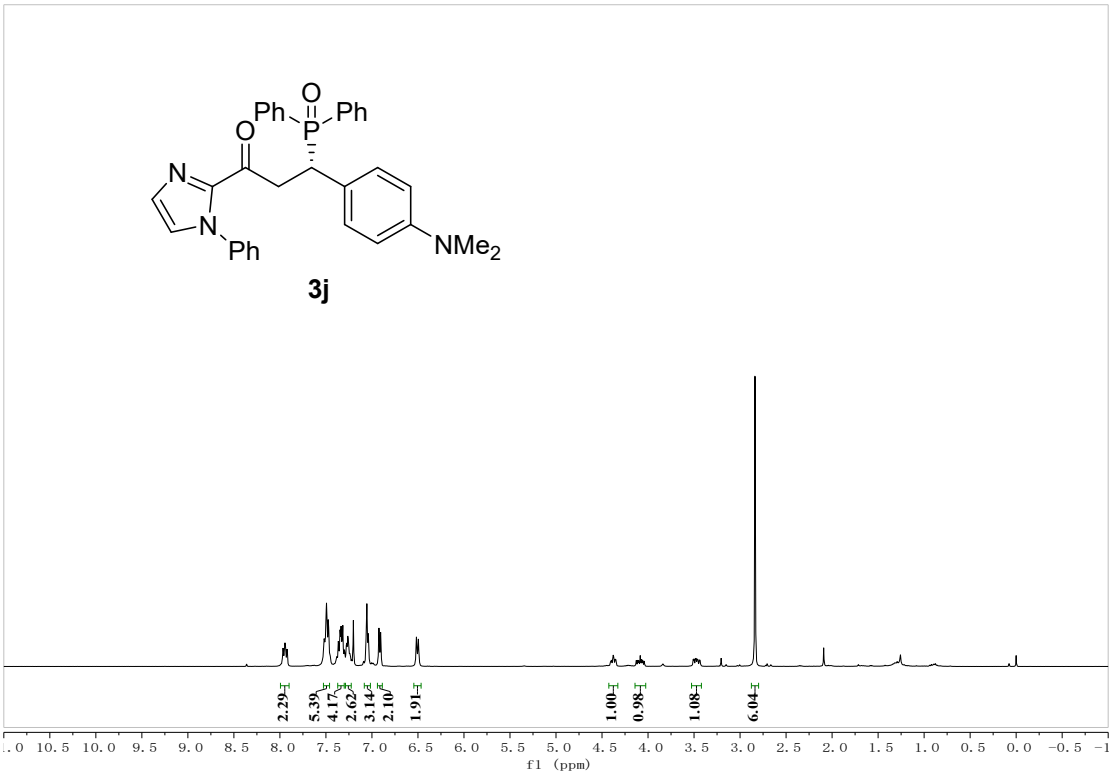


Figure S33: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3j

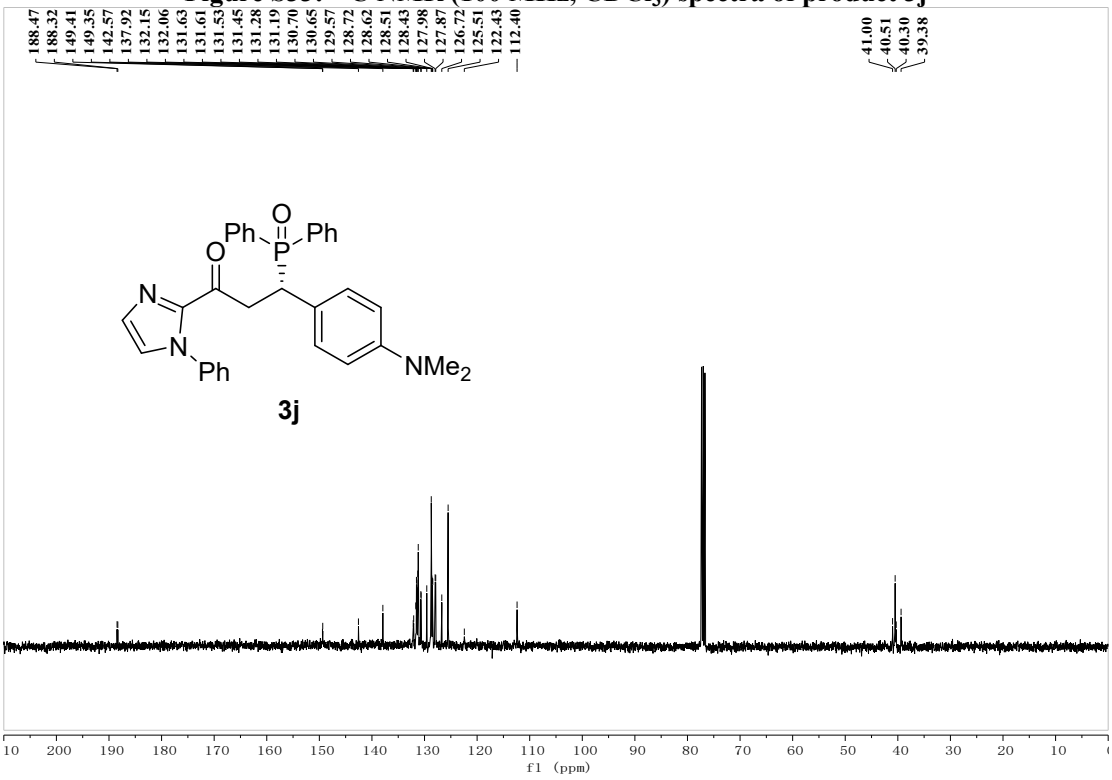


Figure S34: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3j

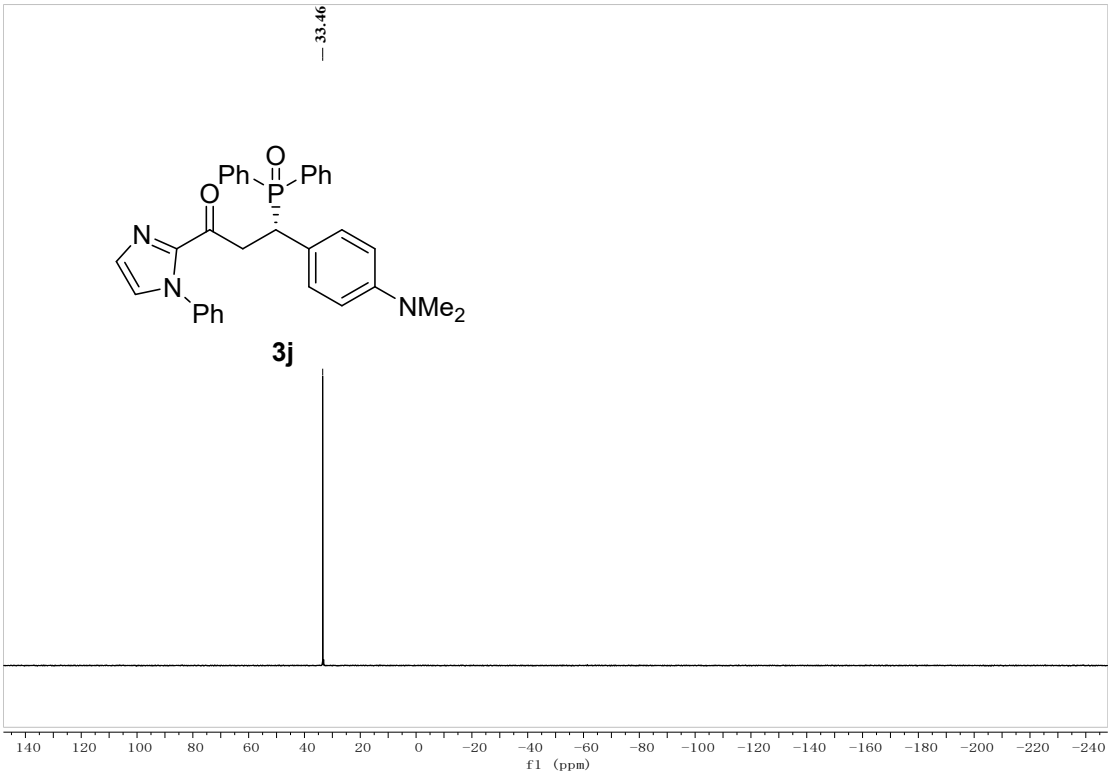


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3k

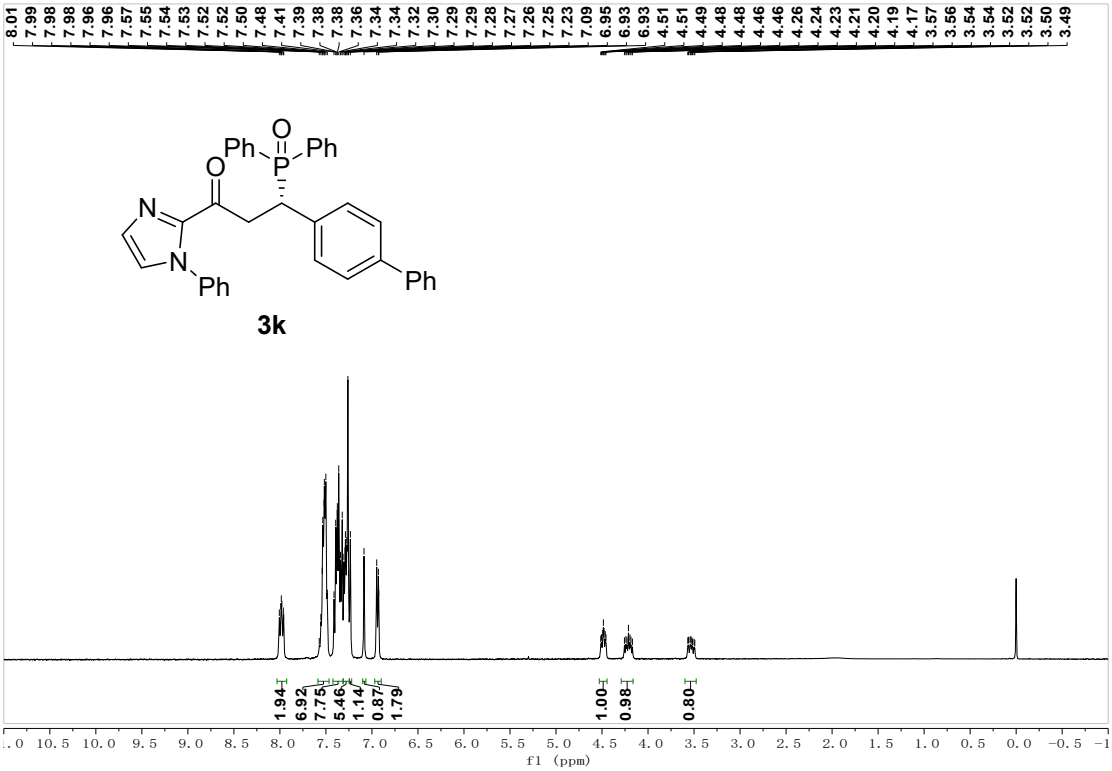


Figure S36: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3k

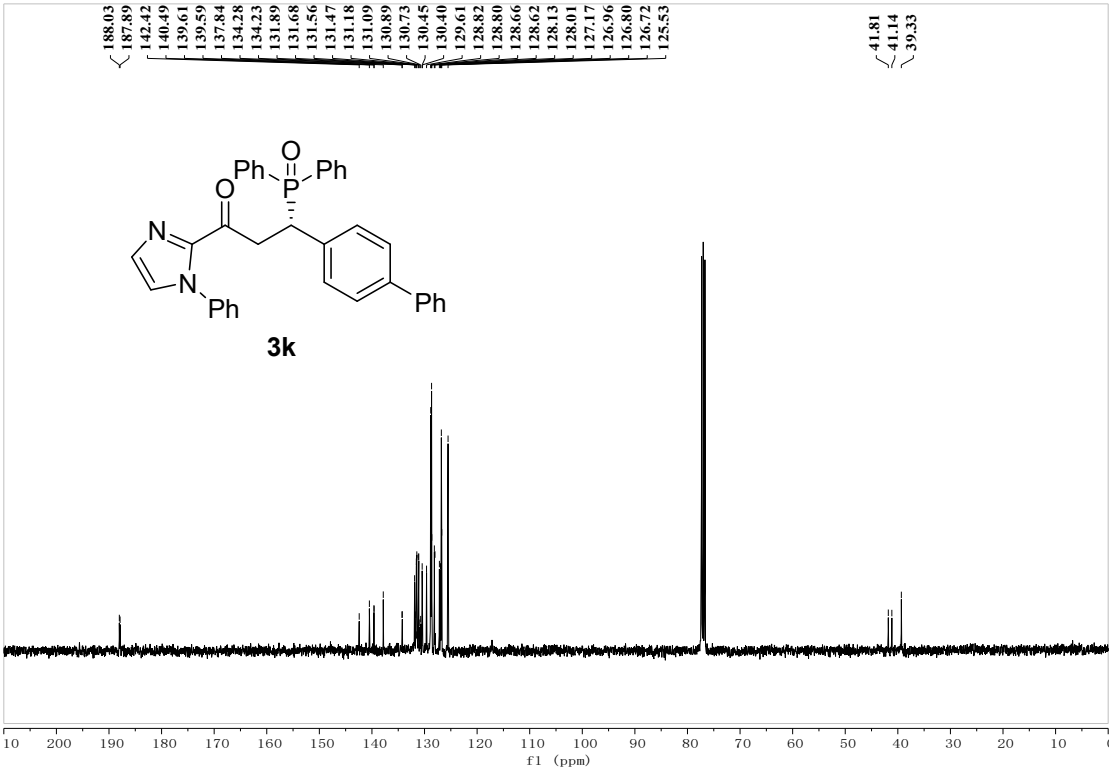


Figure S37: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3k

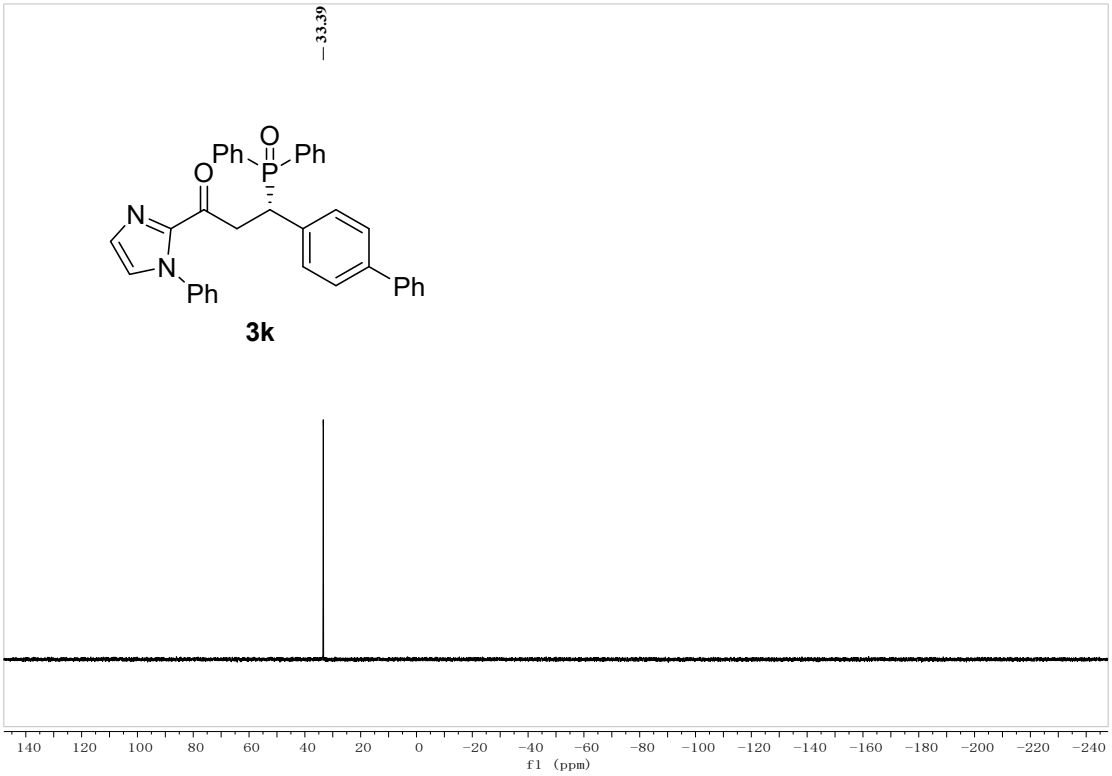


Figure S38: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3l

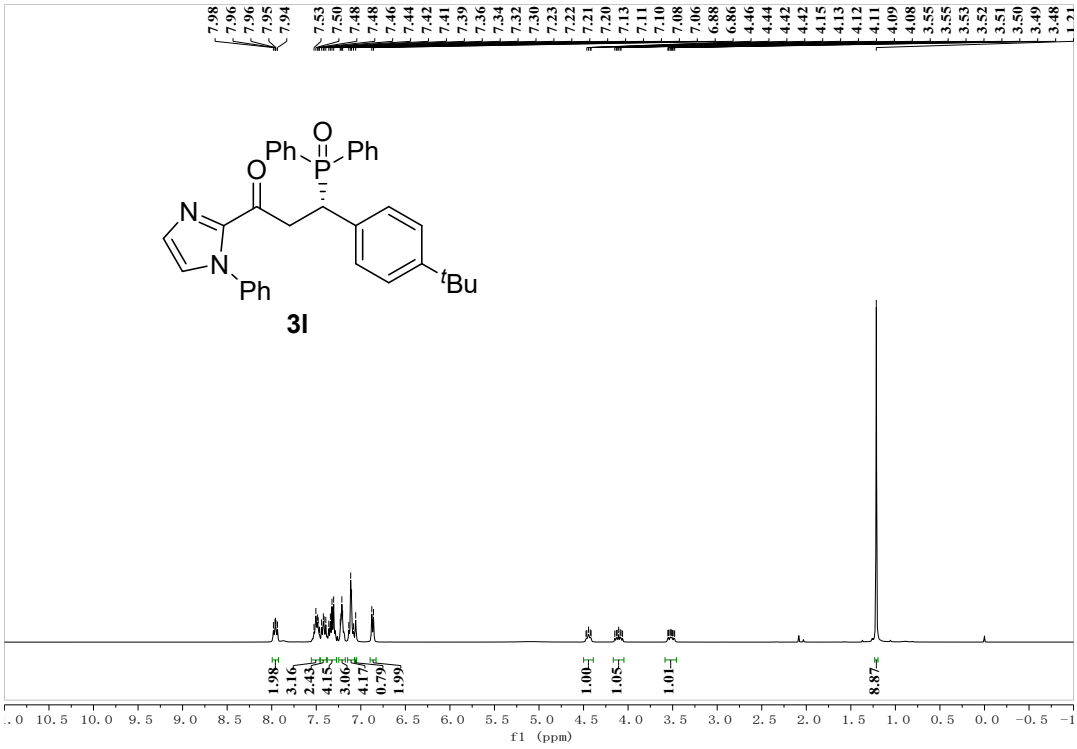


Figure S39: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3l

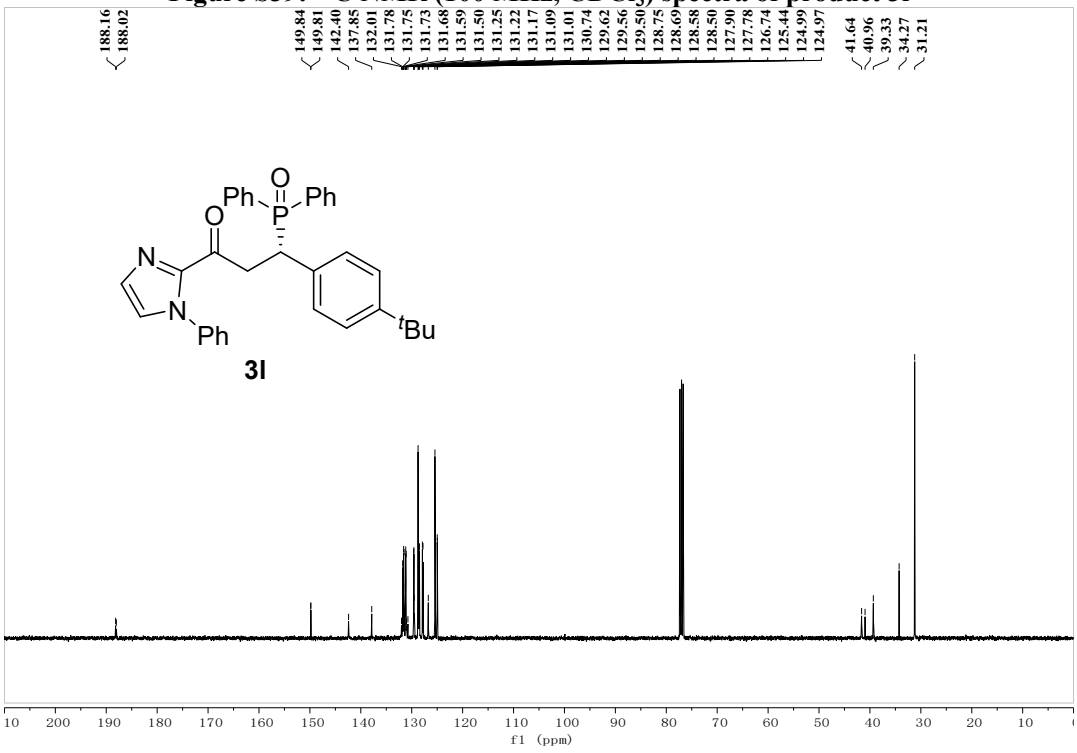


Figure S40: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3l

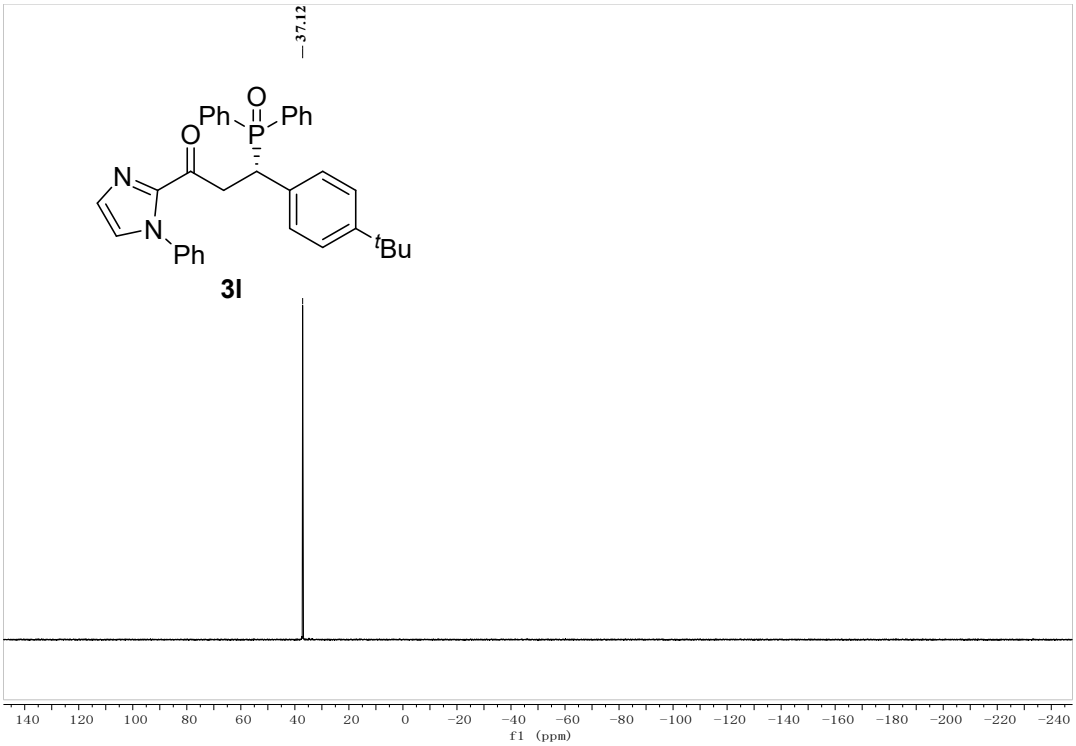


Figure S41: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3m

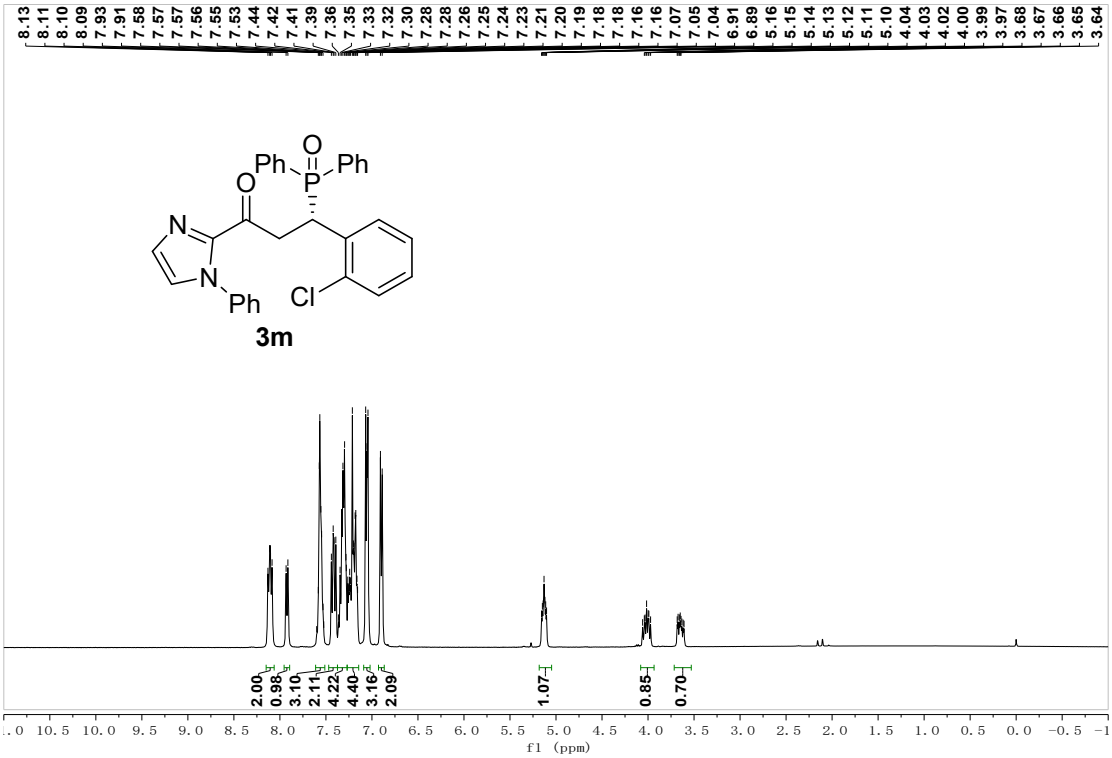


Figure S42: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3m

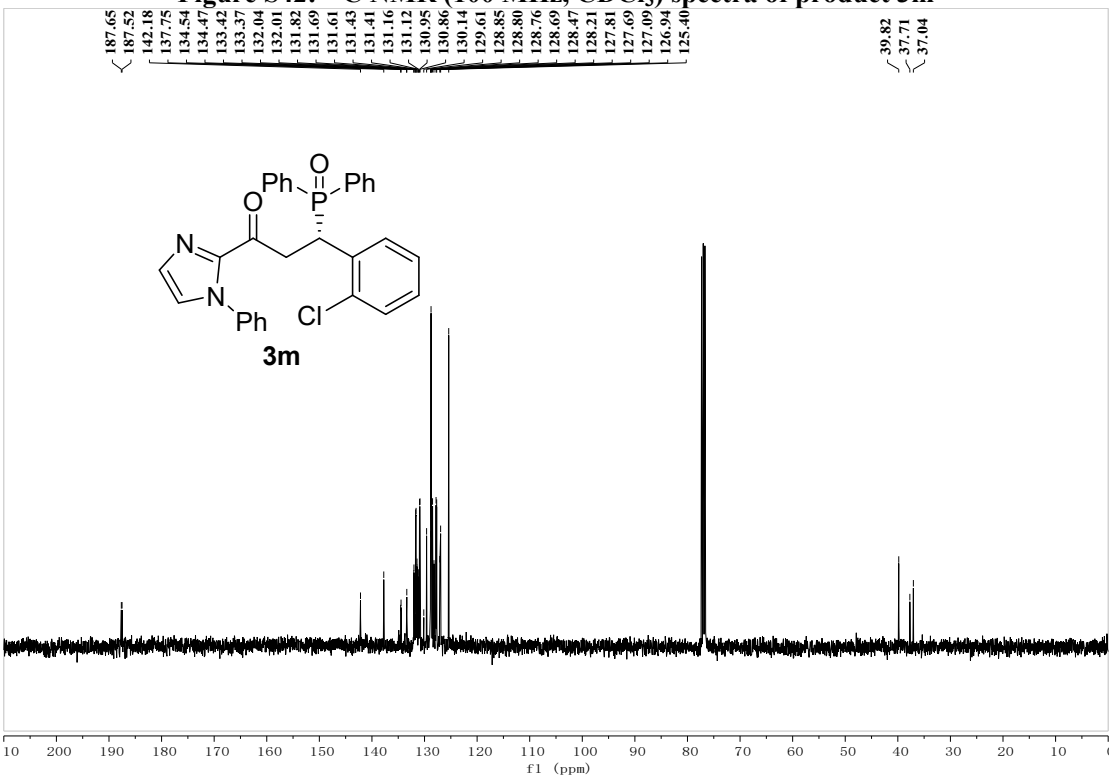


Figure S43: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3m

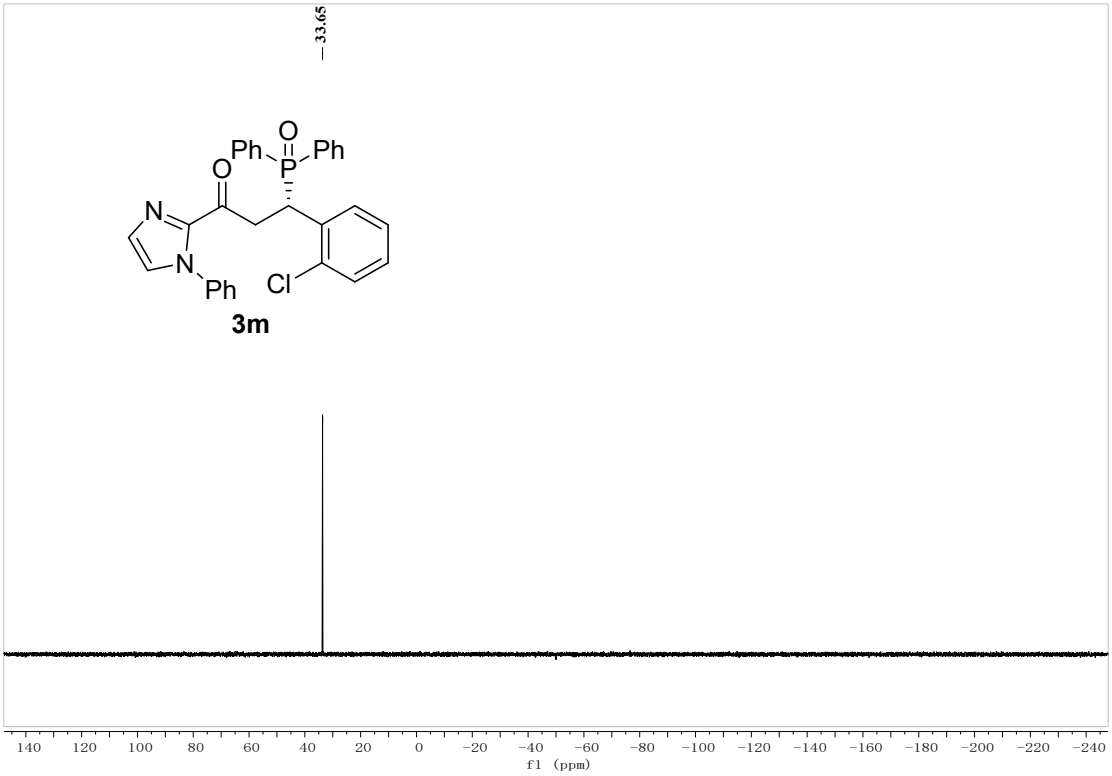


Figure S44: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3n

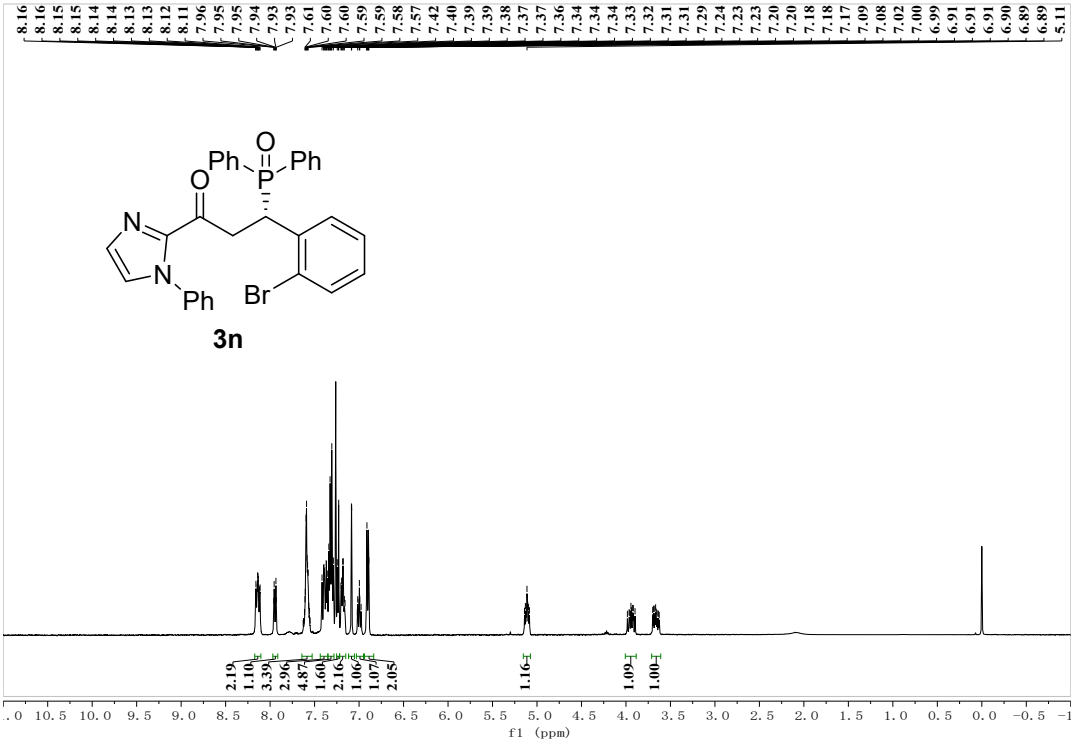


Figure S45: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3n

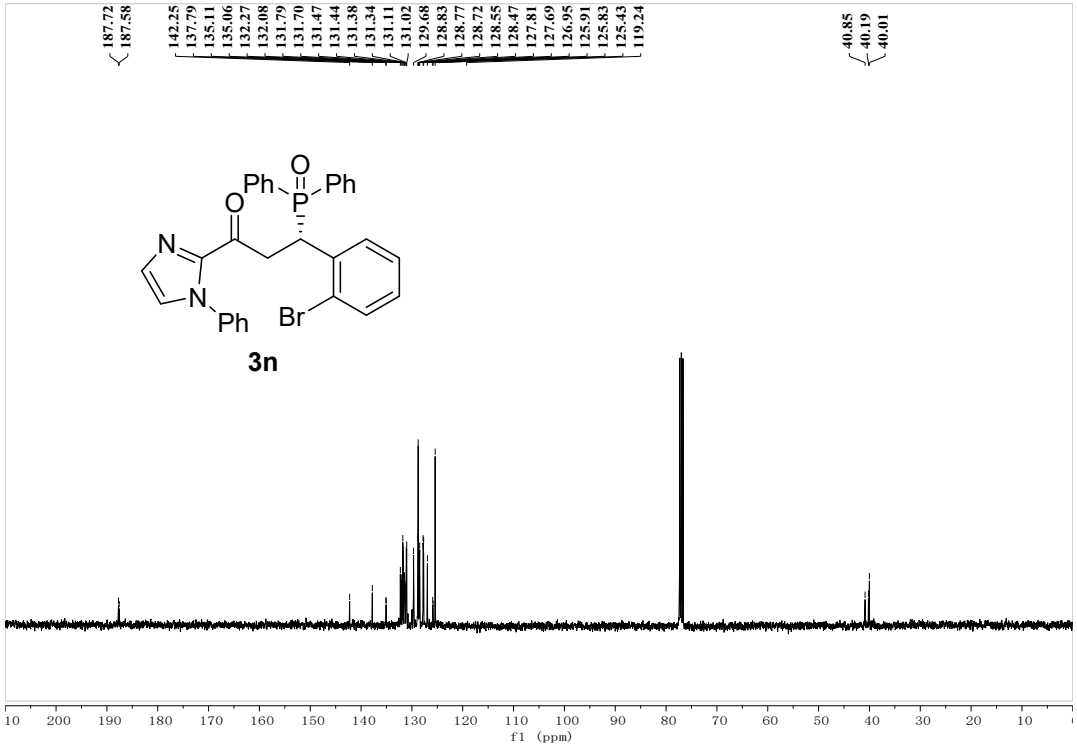


Figure S46: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3n

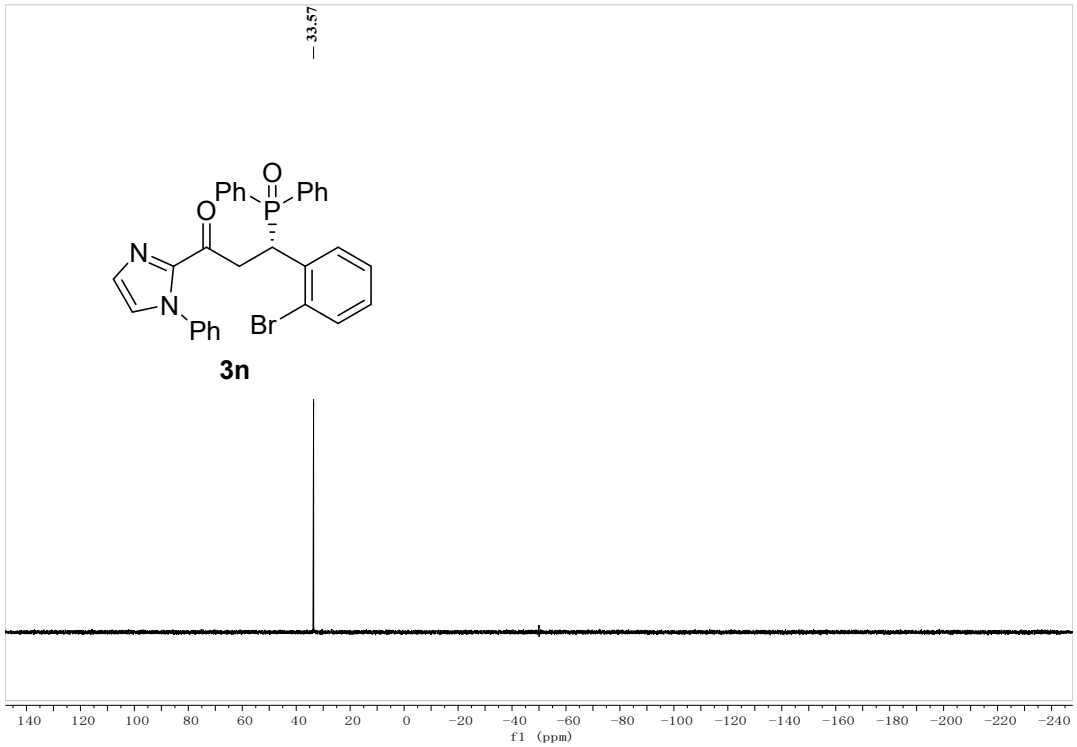


Figure S47: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3o

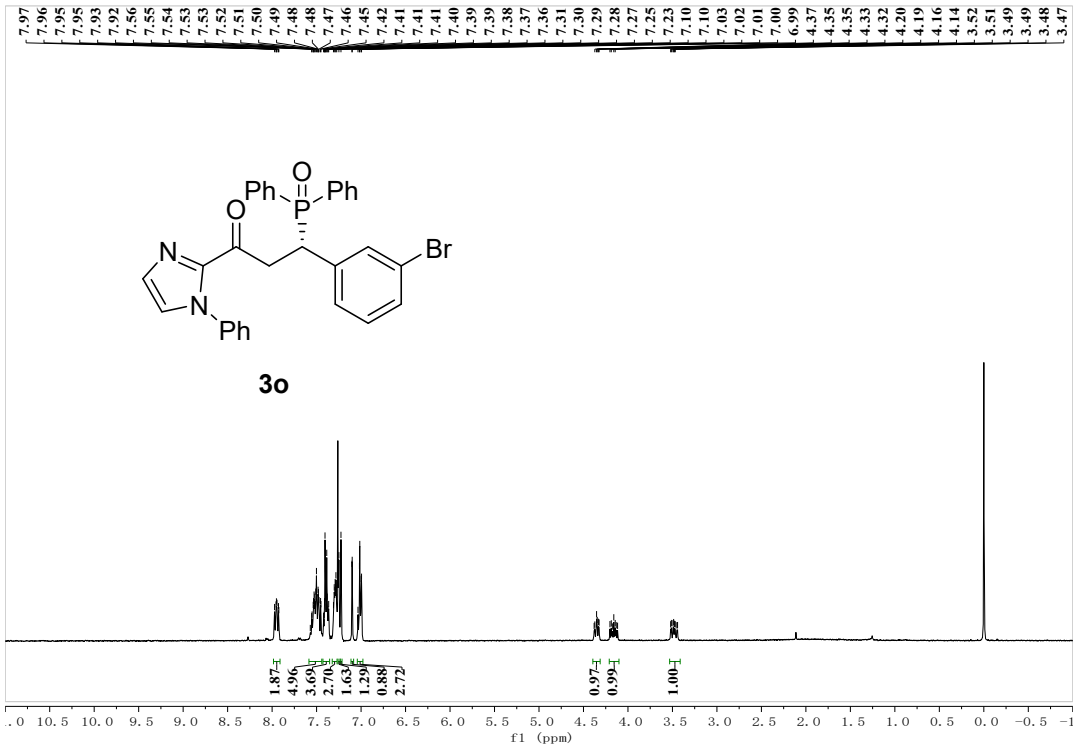


Figure S48: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3o

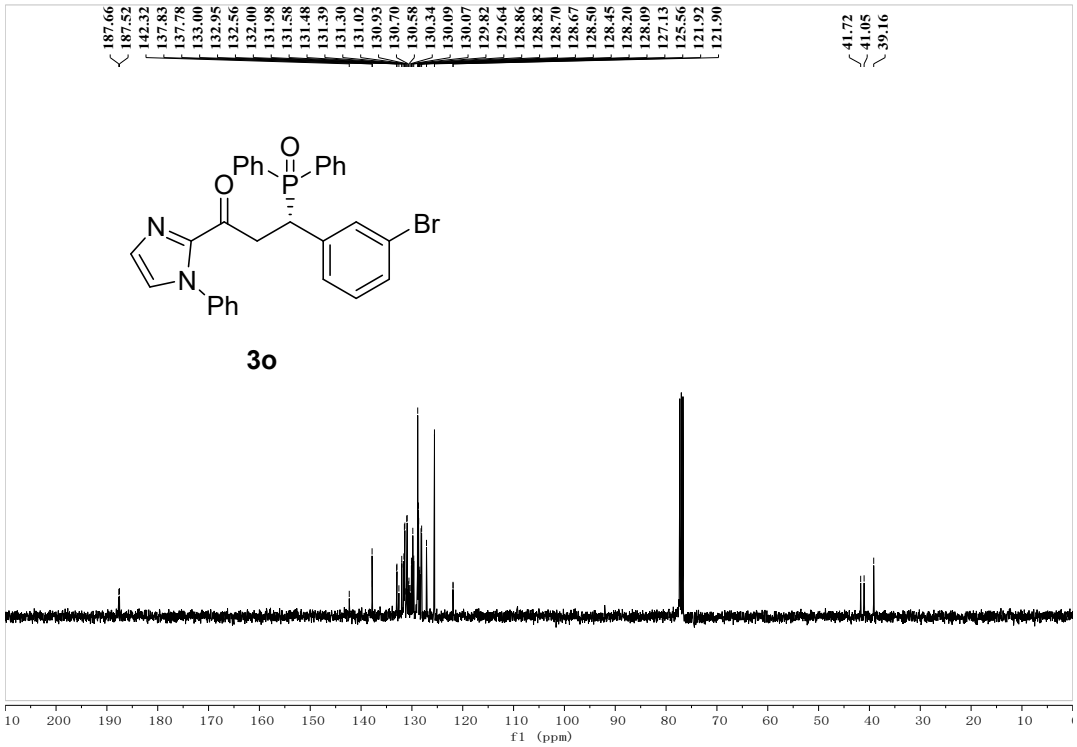


Figure S49: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3o

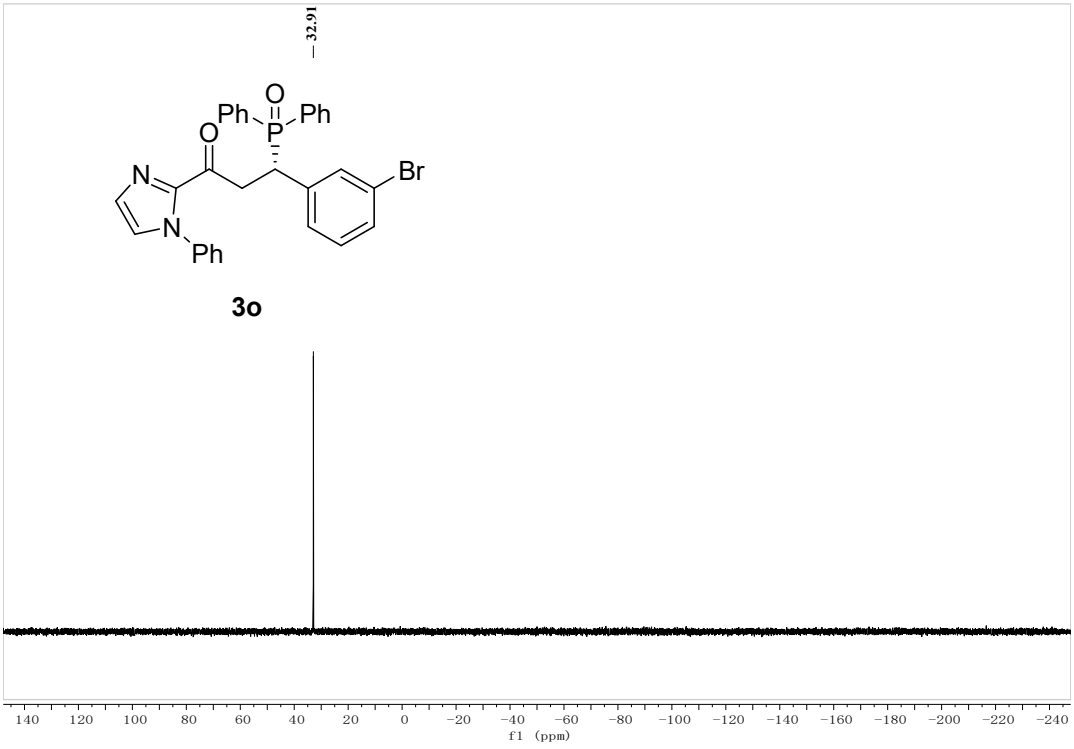


Figure S50: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3p

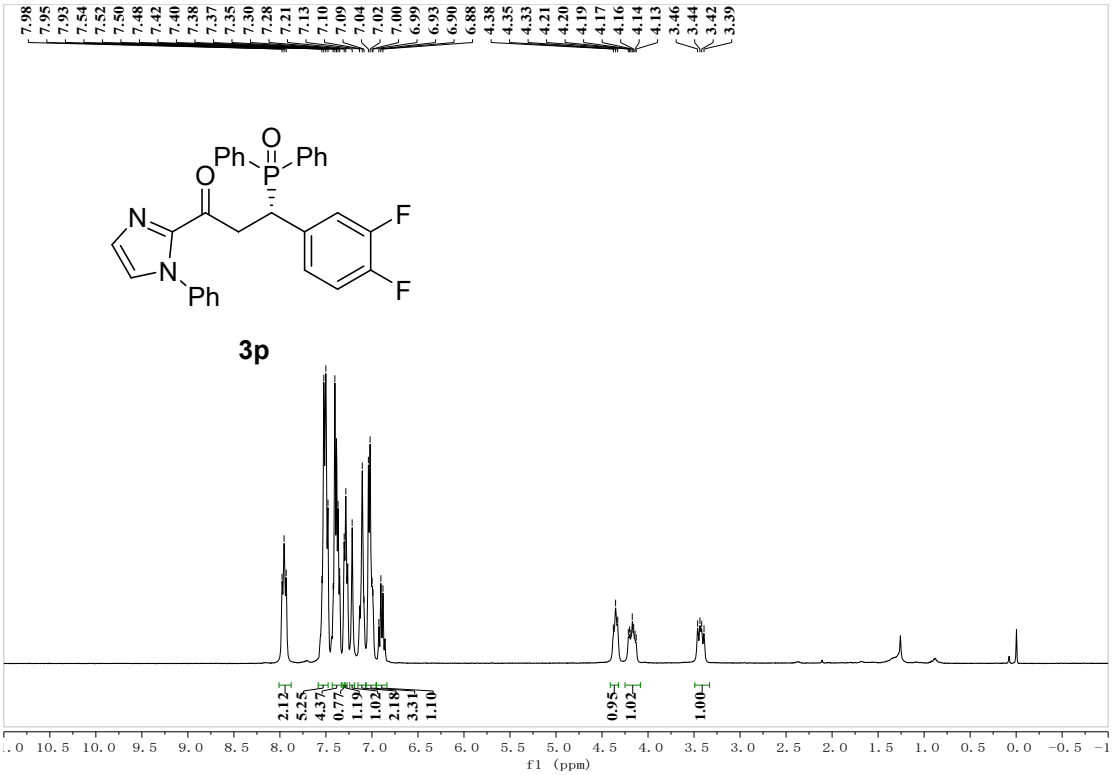


Figure S51: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3p

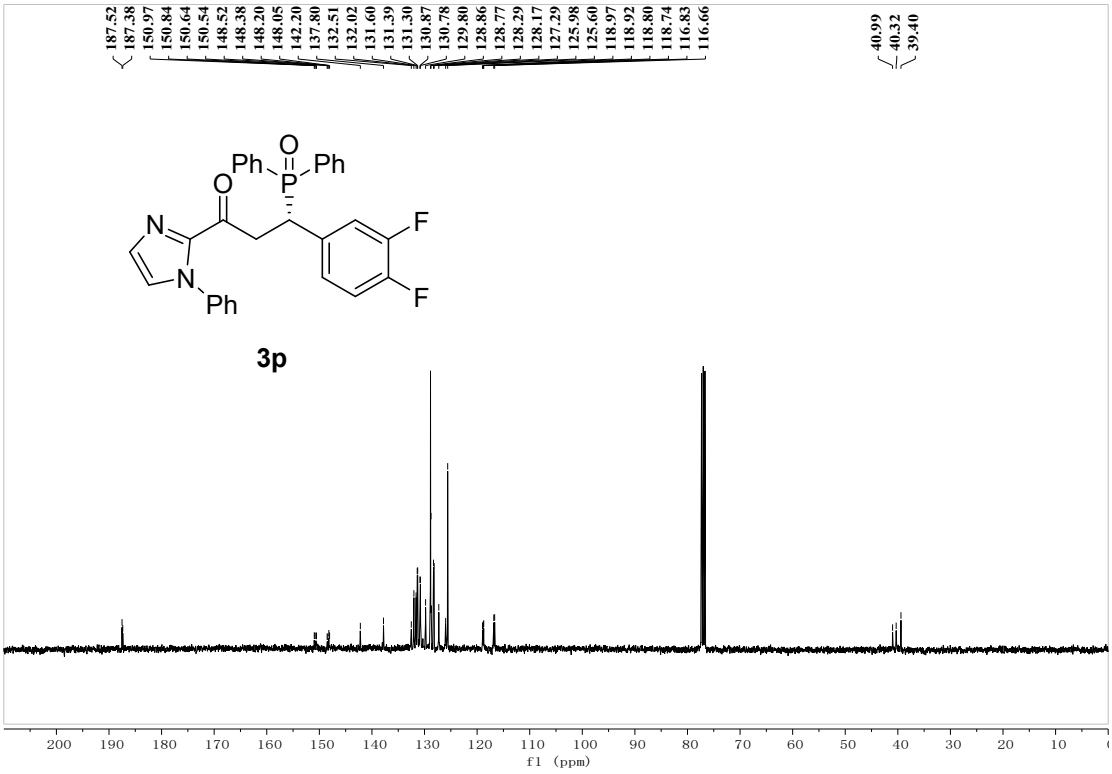


Figure S52: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3p

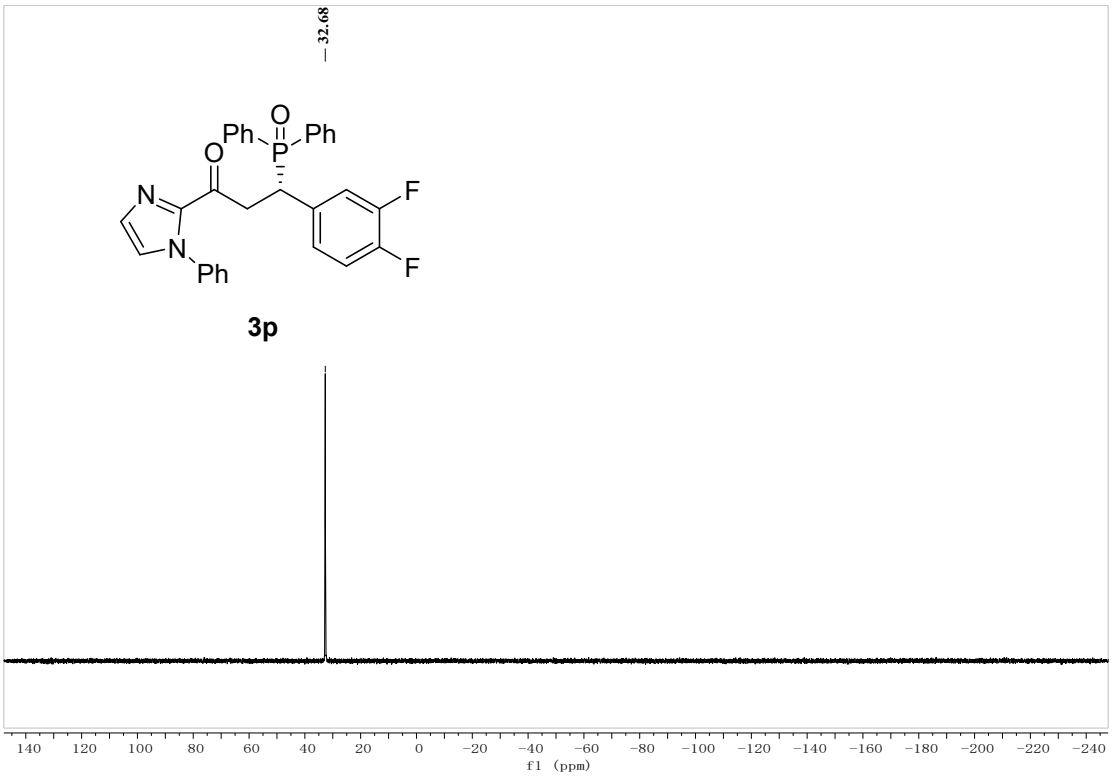


Figure S53: ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3p

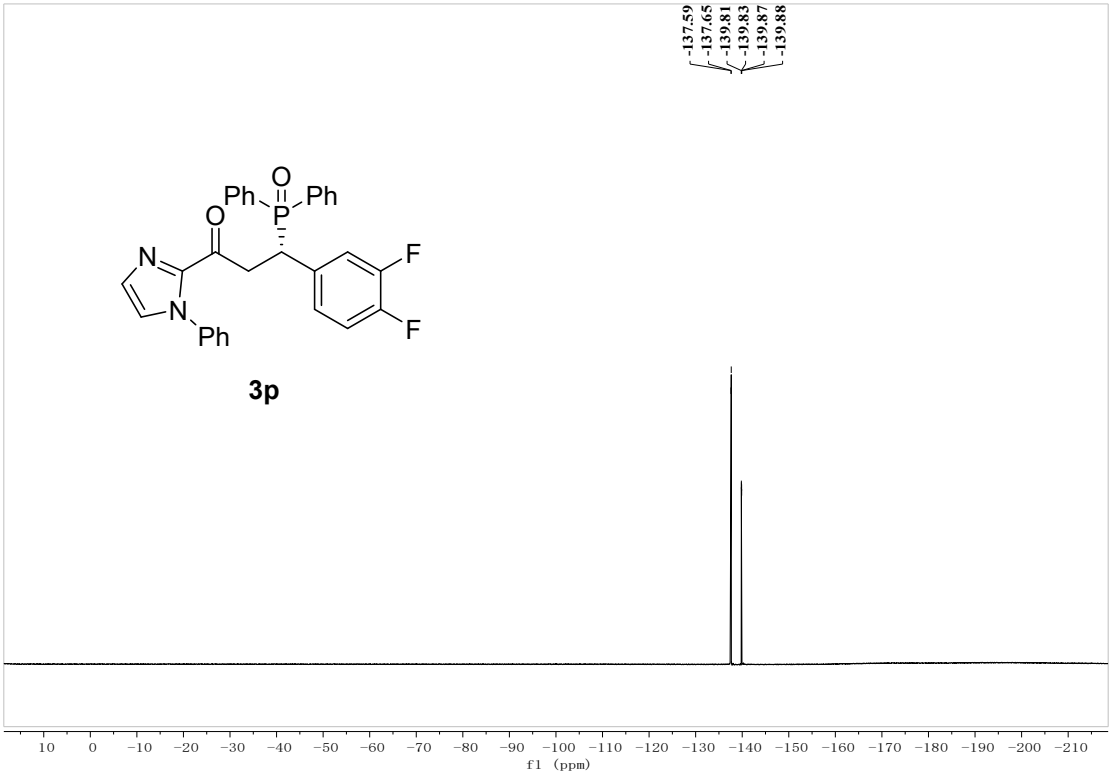


Figure S54: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3q

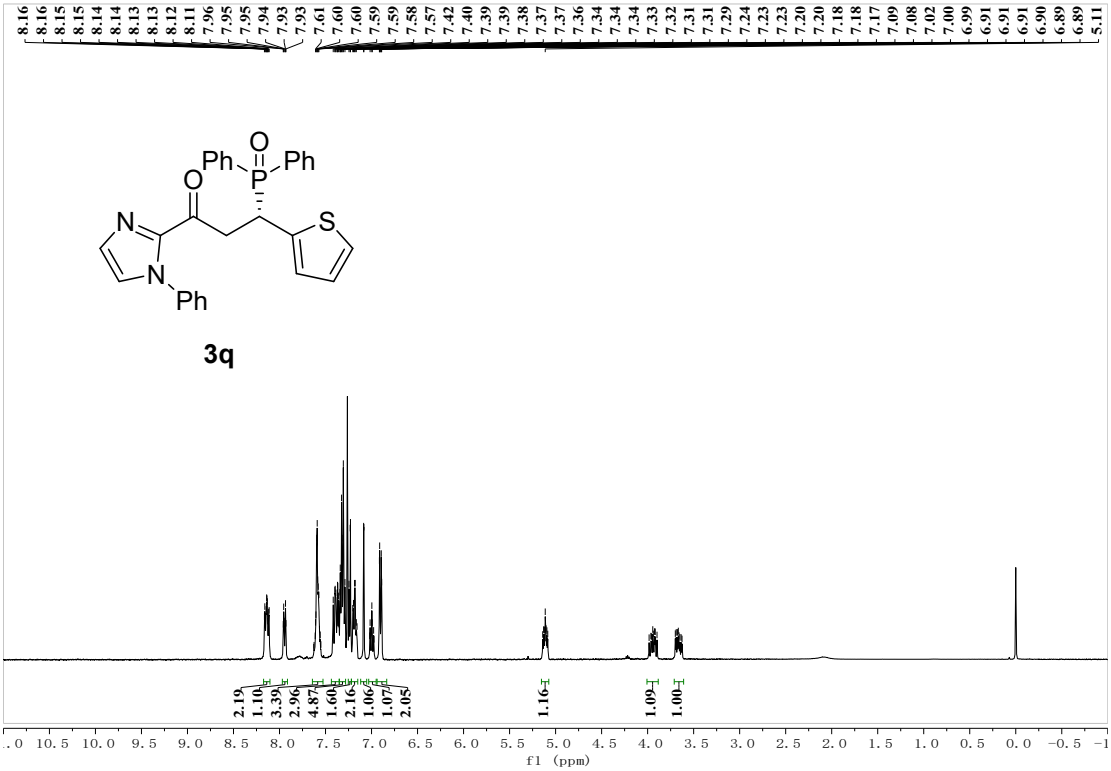


Figure S55: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3q

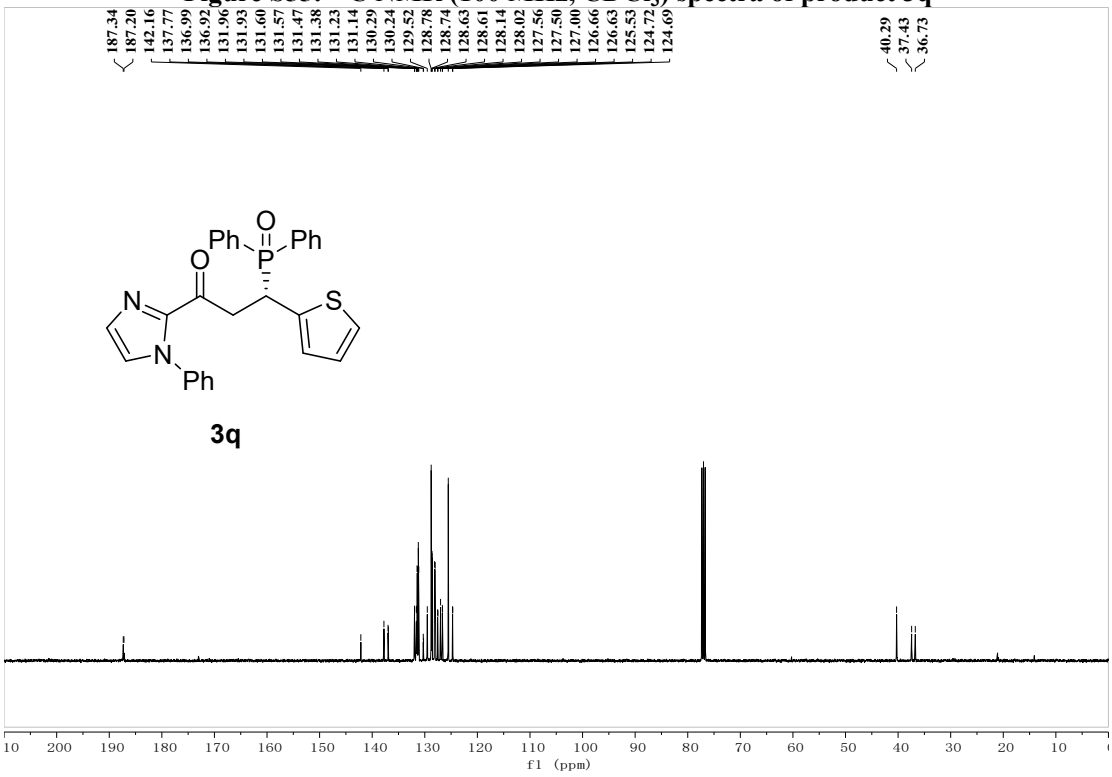


Figure S56: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3q

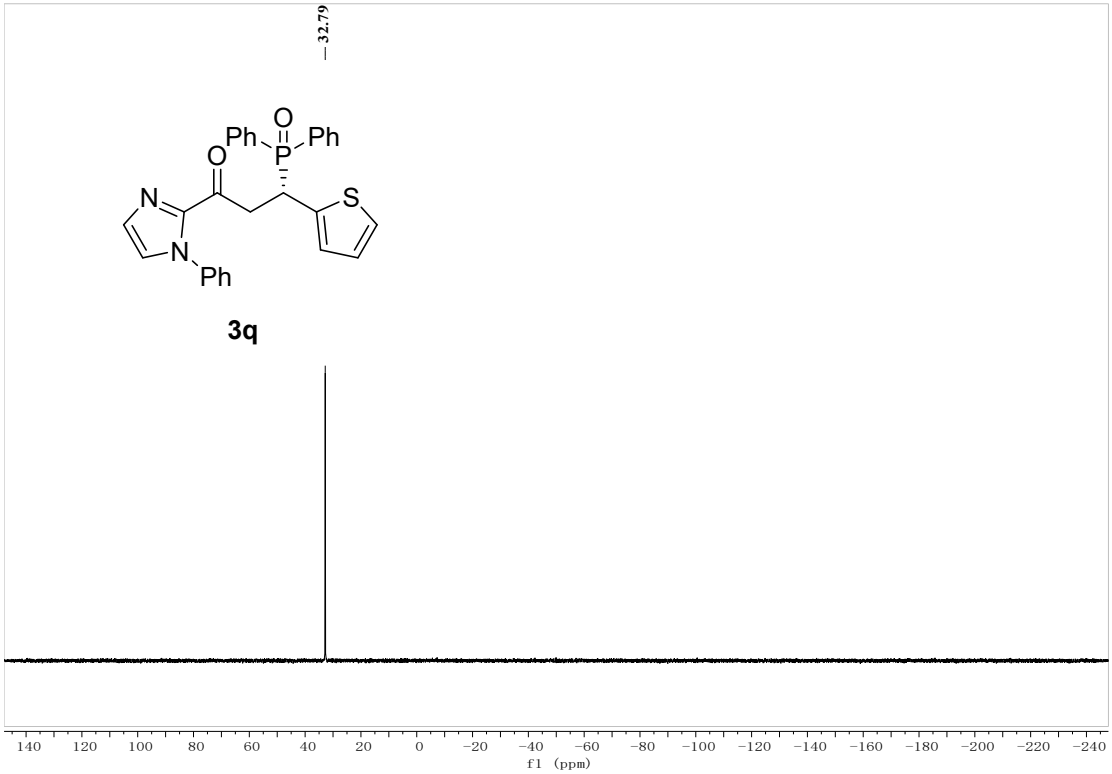


Figure S57: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3r

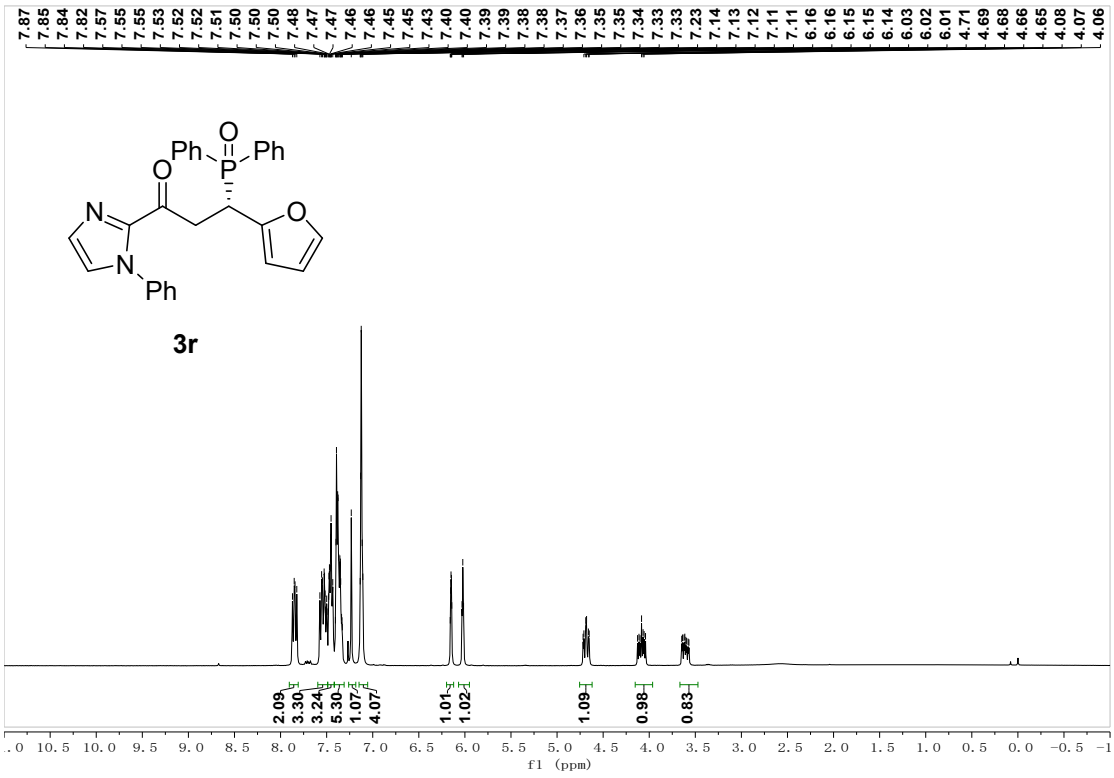


Figure S58: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3r

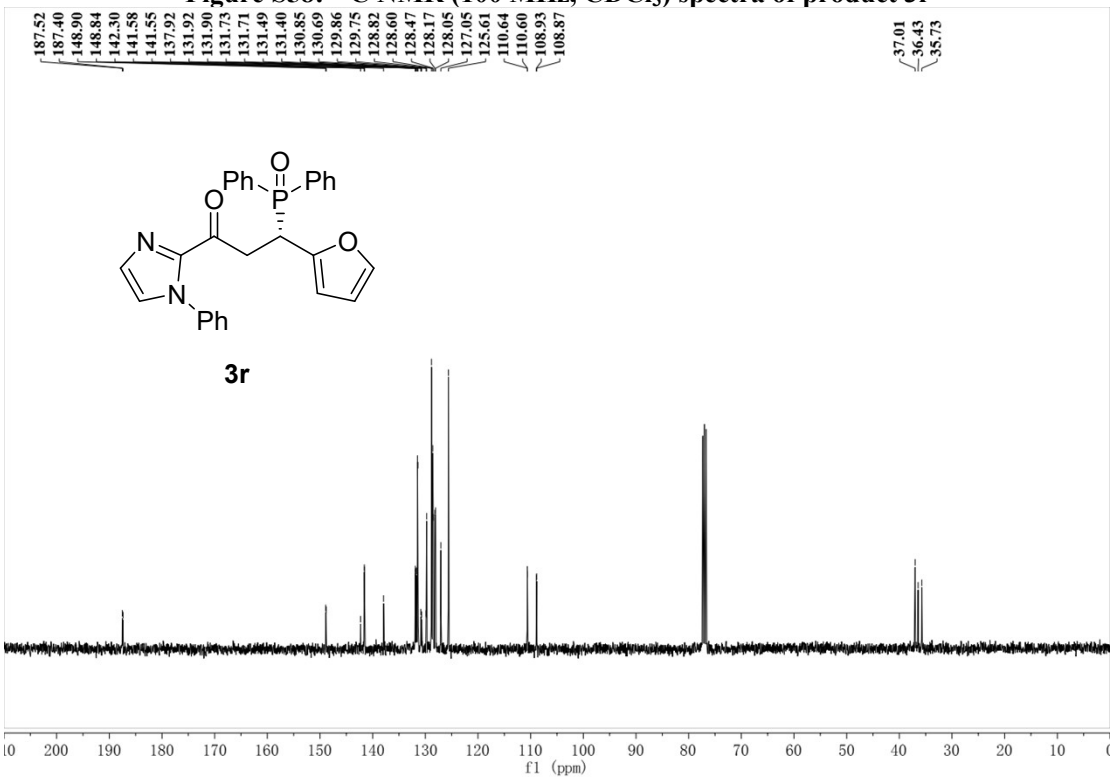


Figure S59: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3r

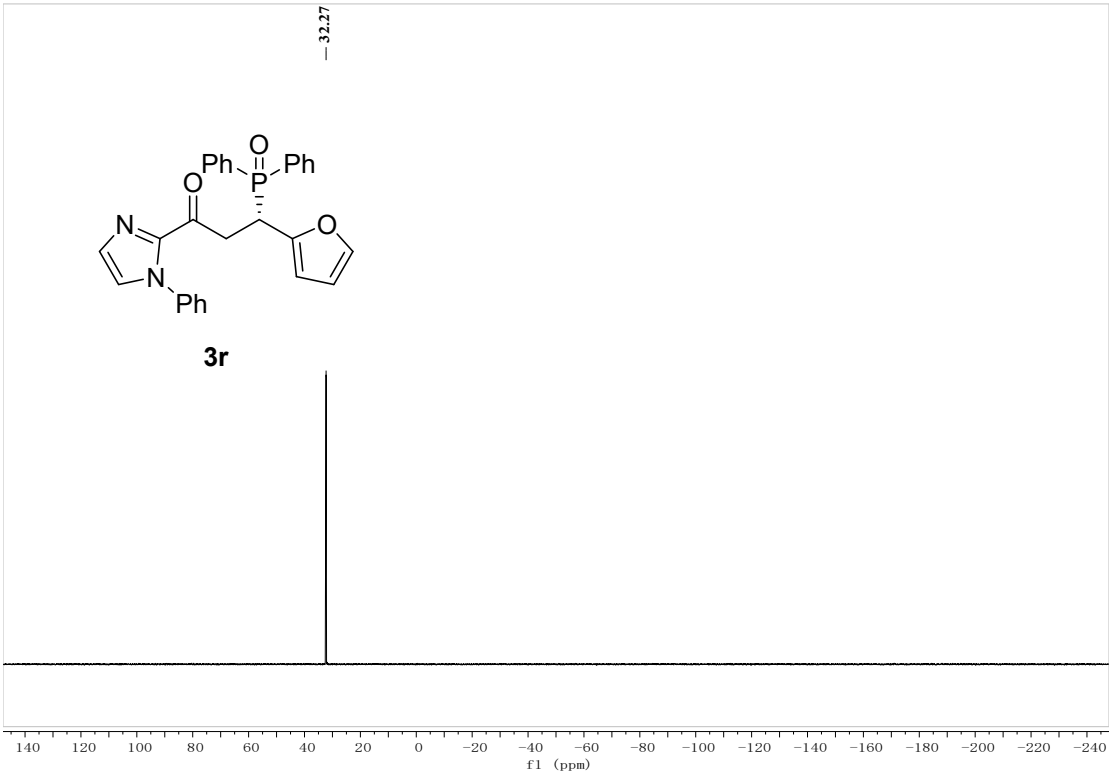


Figure S60: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3s

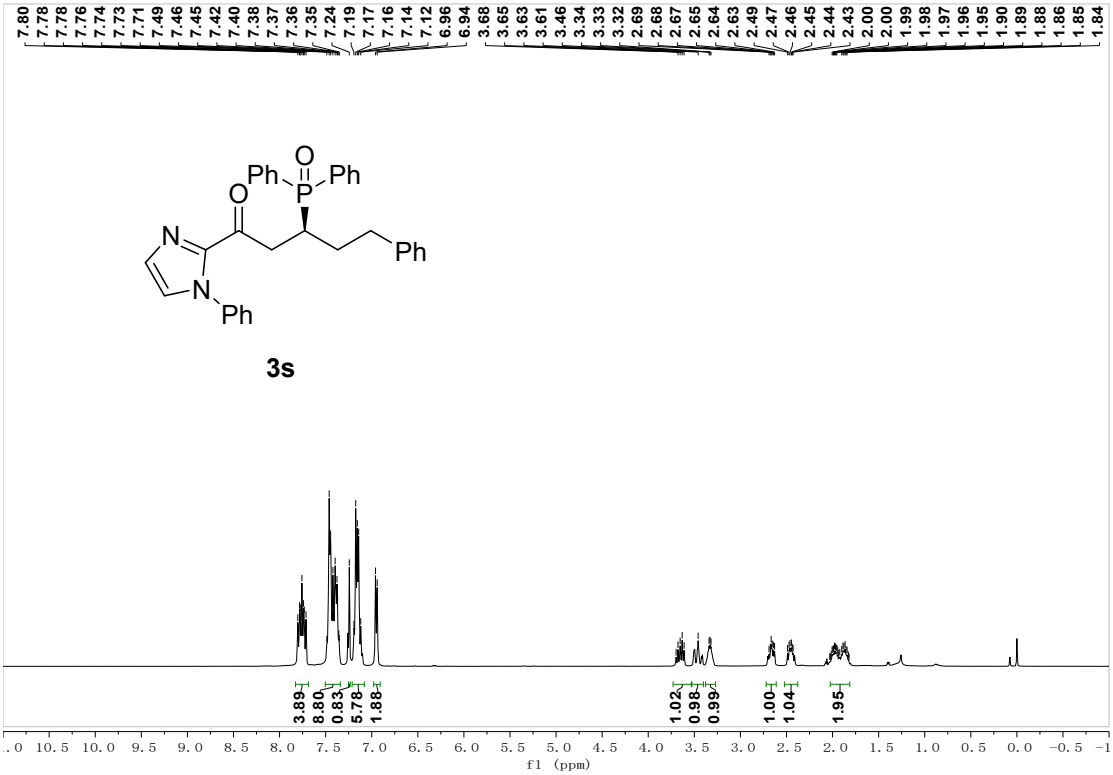


Figure S61: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3s

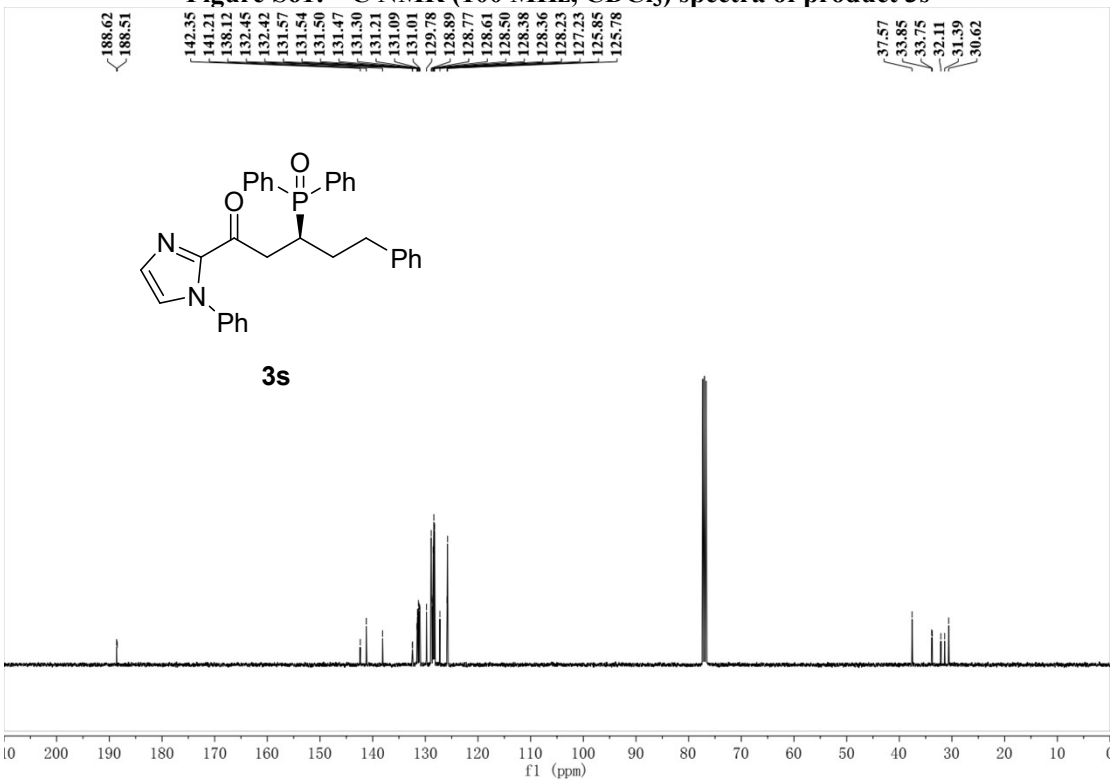


Figure S62: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3s

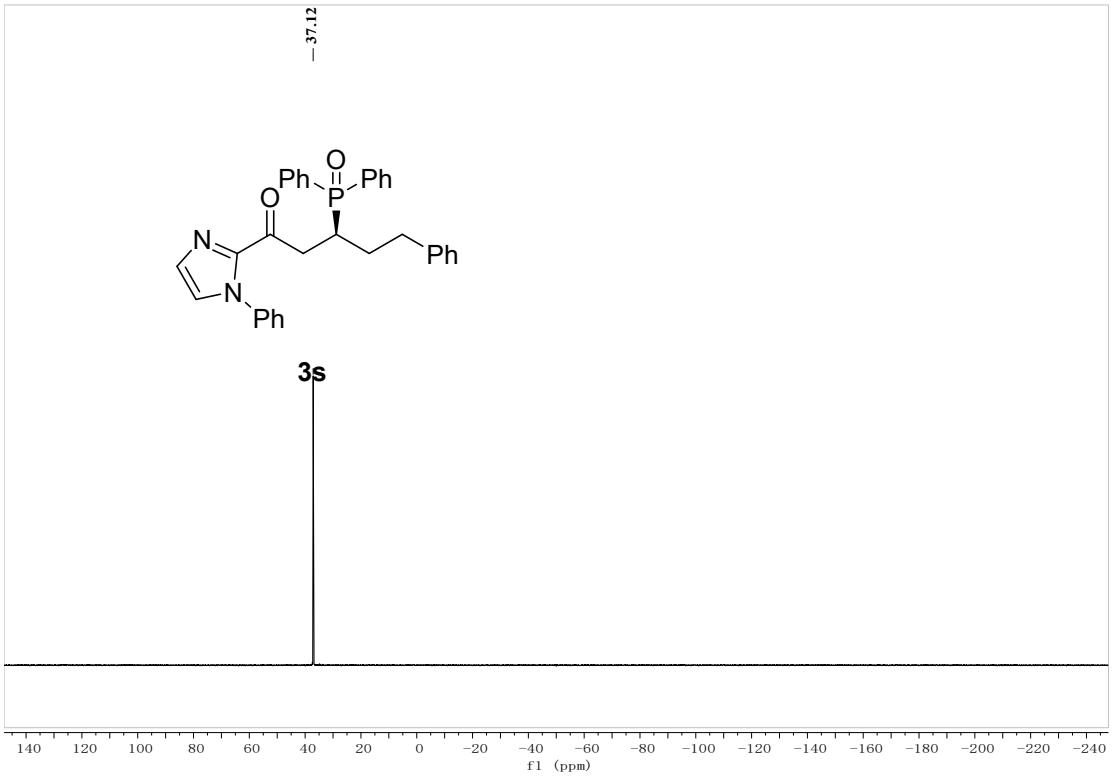


Figure S63: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3t

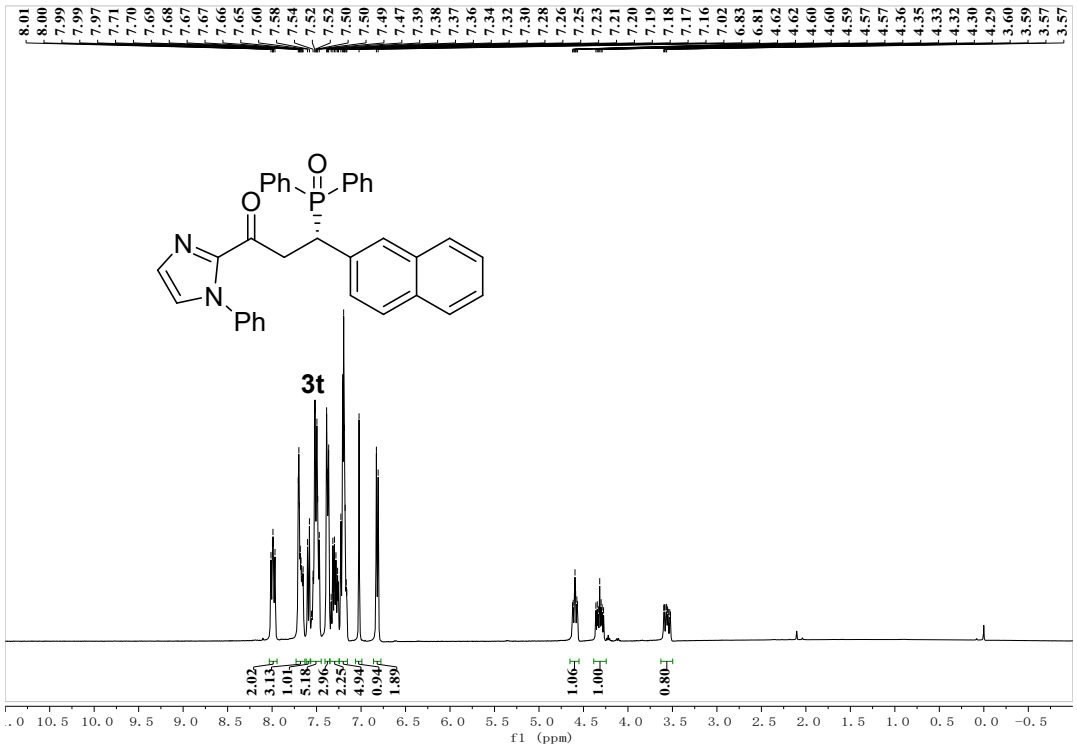


Figure S64: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3t

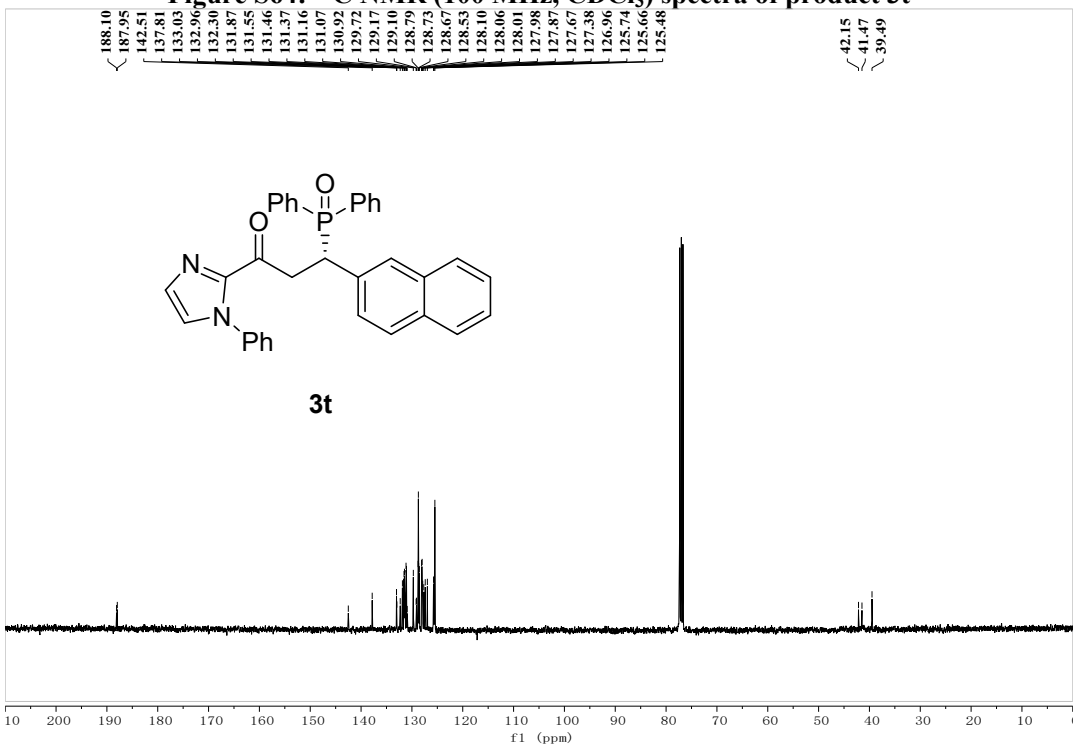


Figure S65: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3t

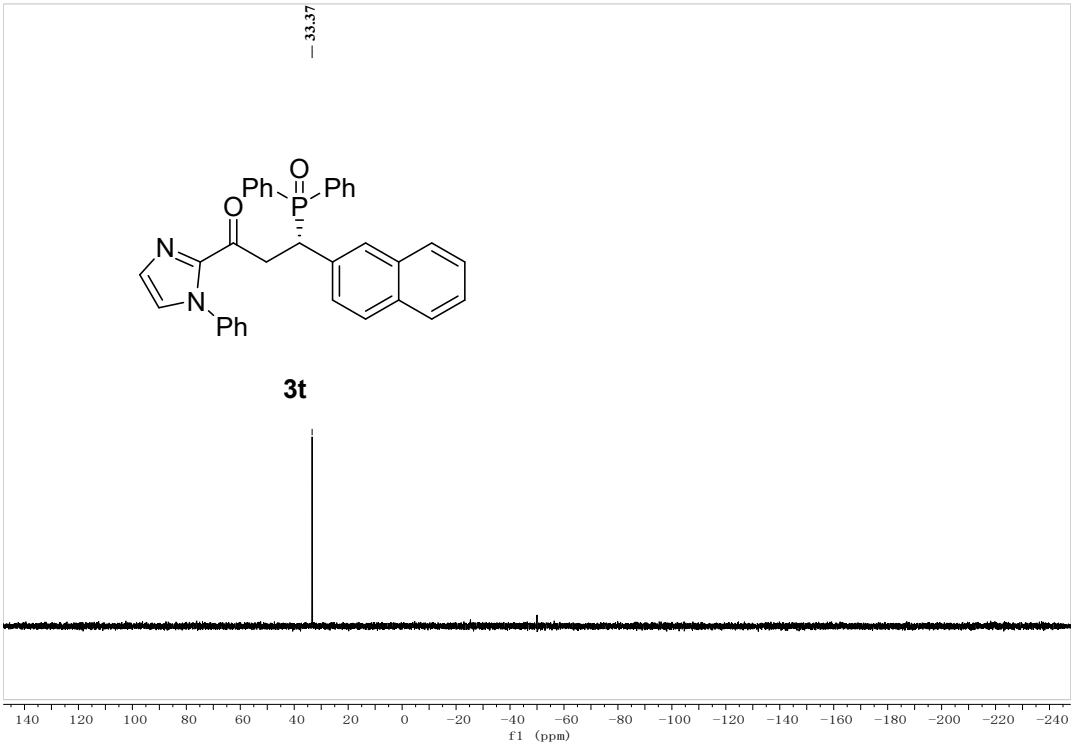


Figure S66: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3u

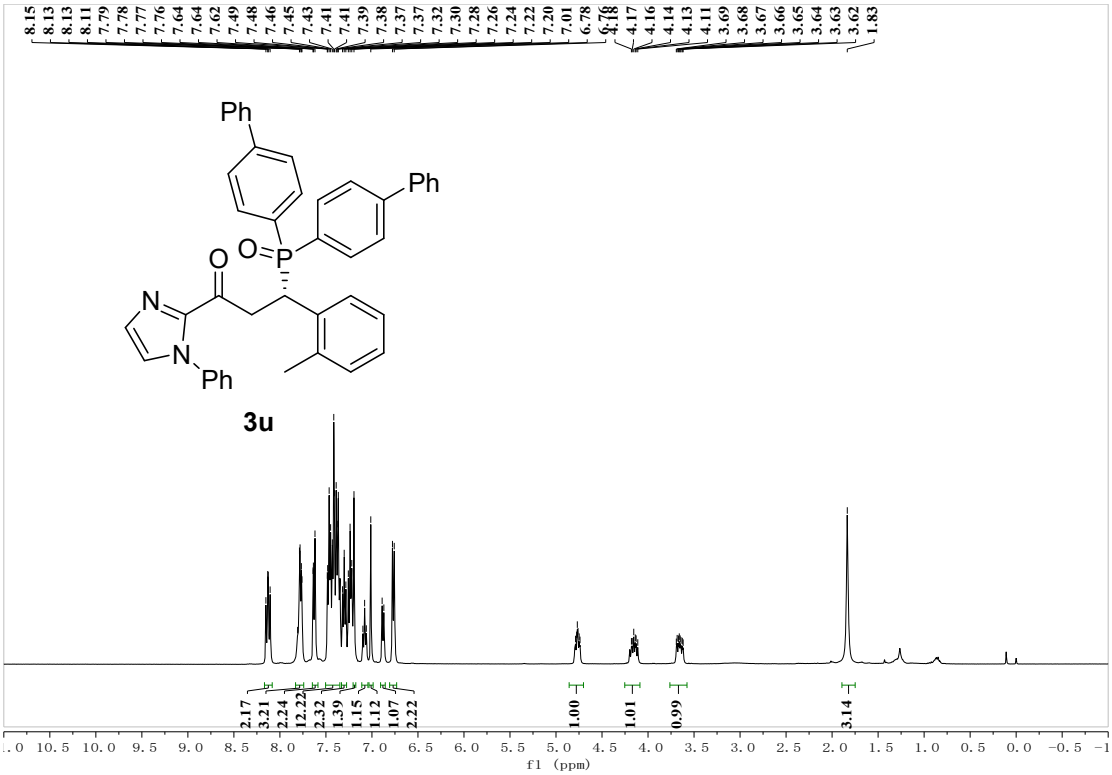


Figure S67: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3u

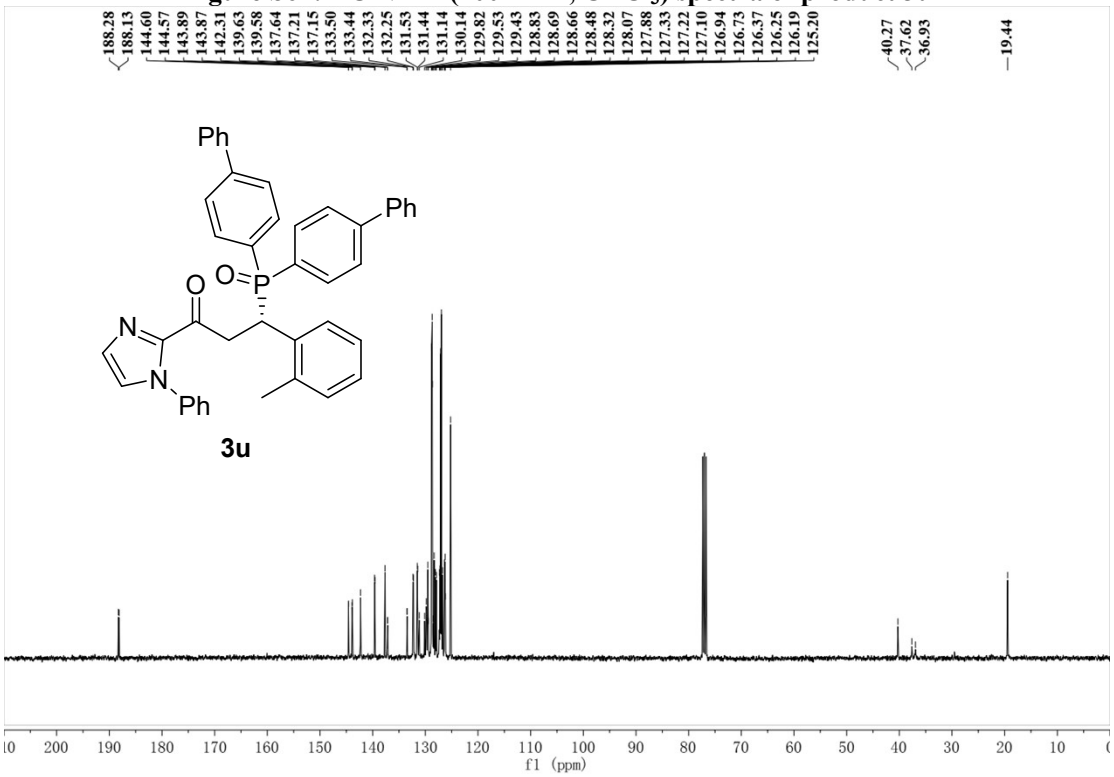


Figure S68: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3u

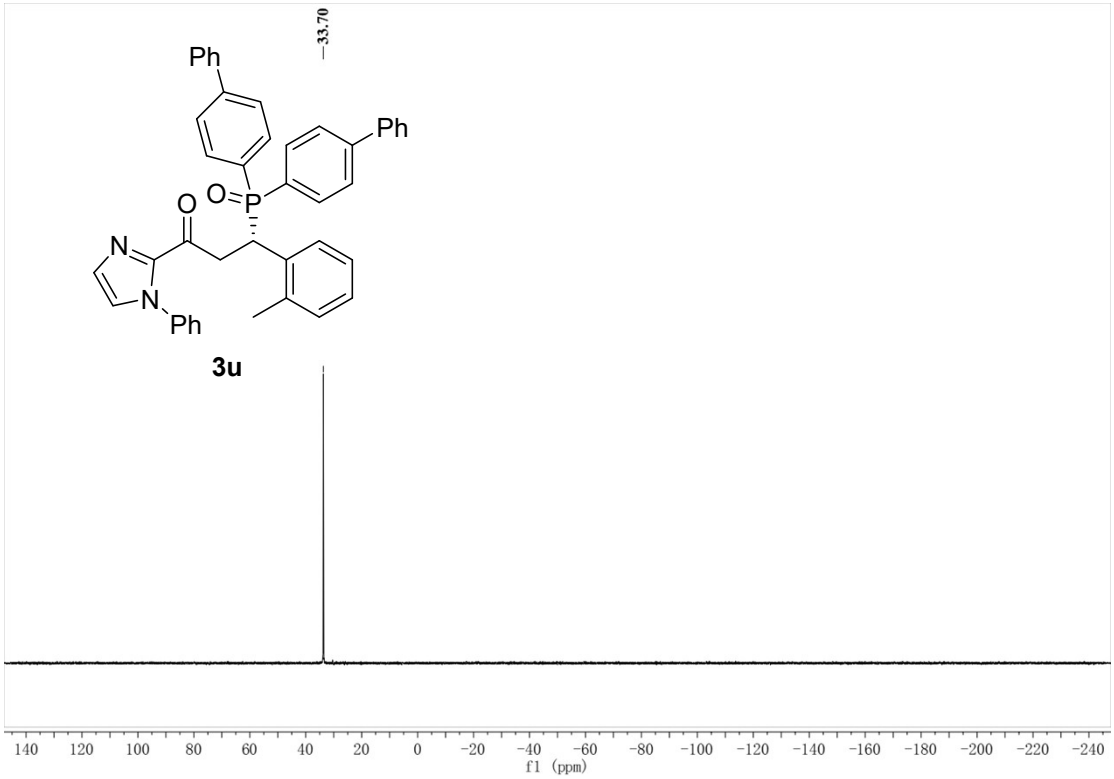


Figure S69: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3v

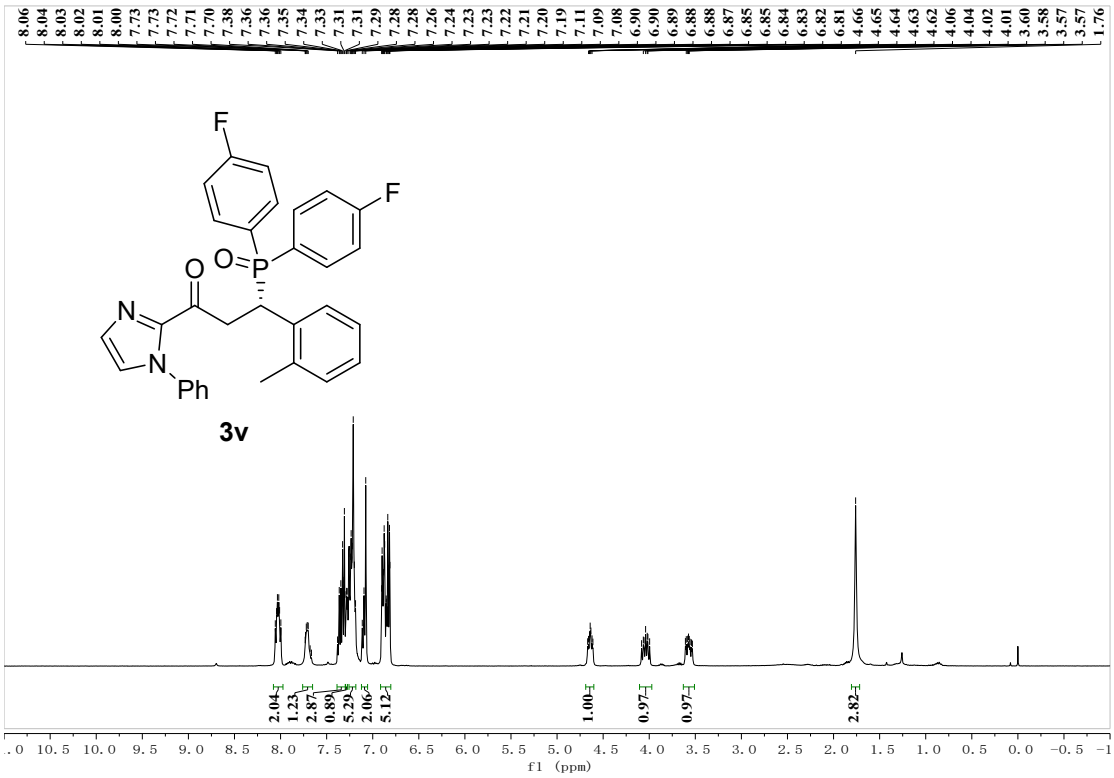


Figure S70: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3v

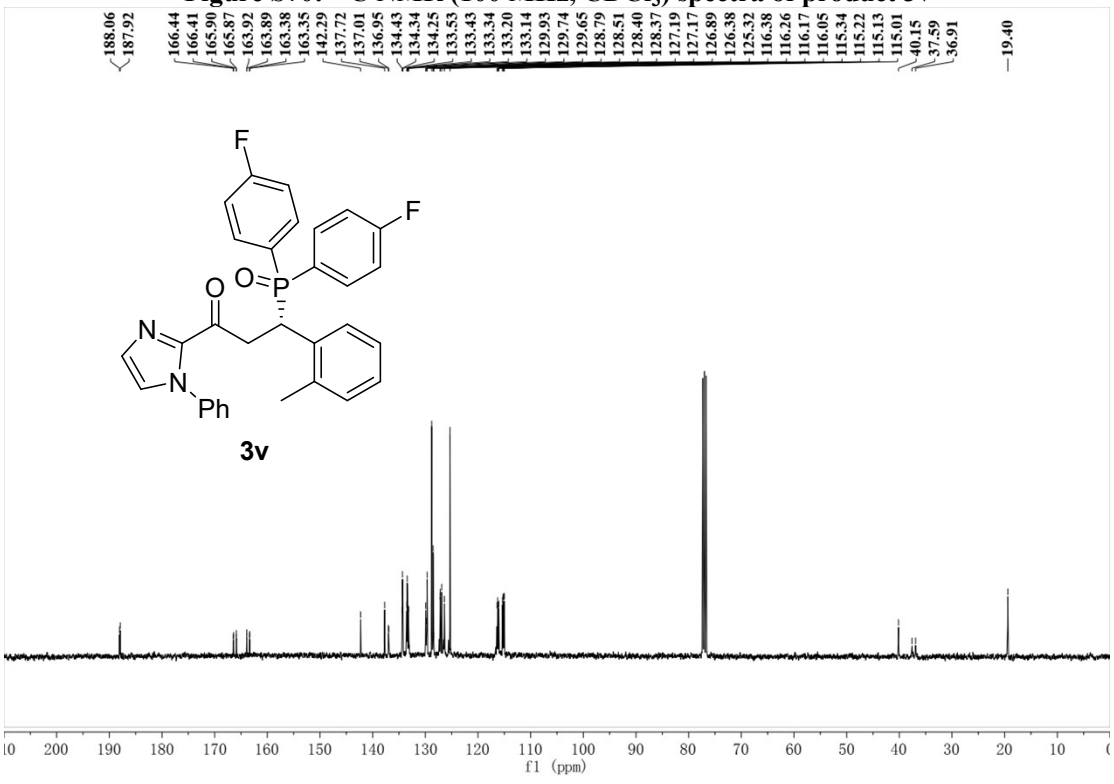


Figure S71: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3v

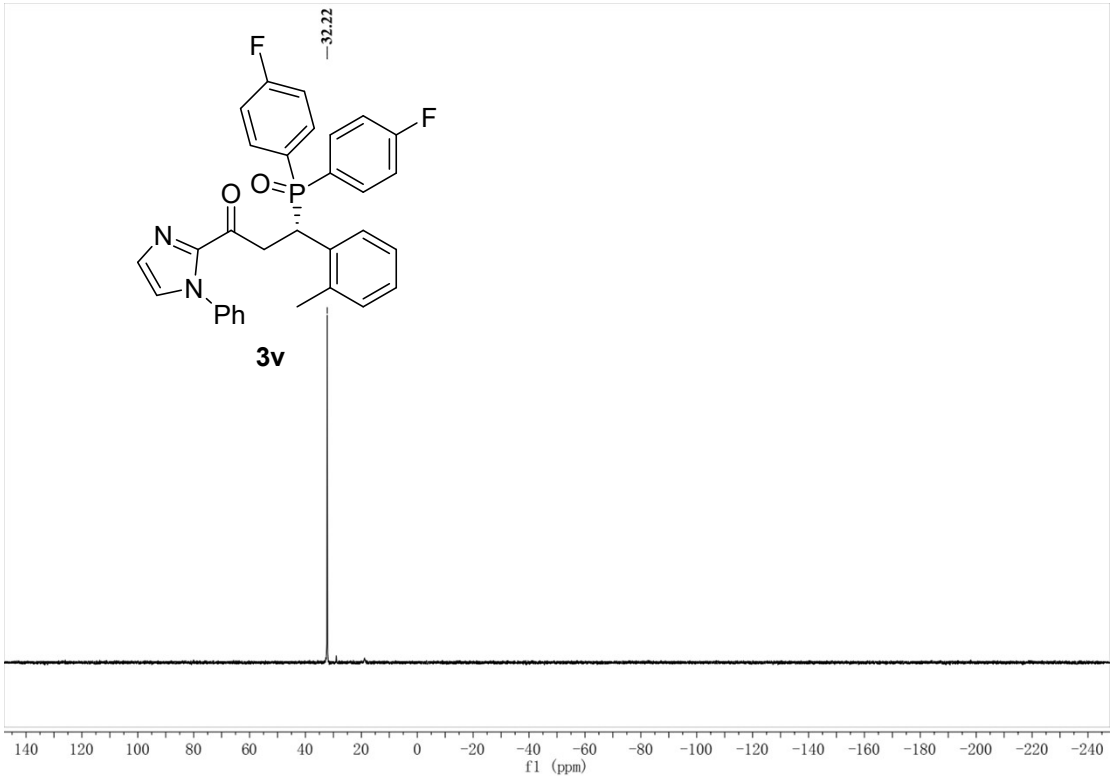


Figure S72: ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3v

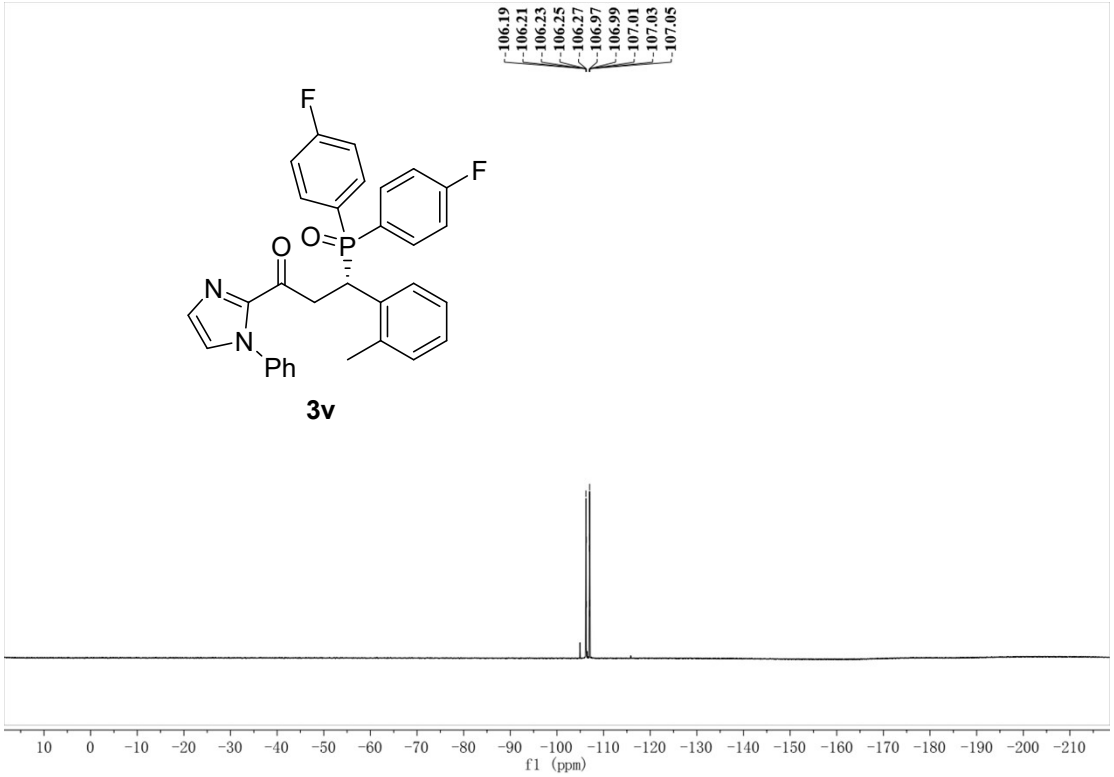


Figure S73: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3w

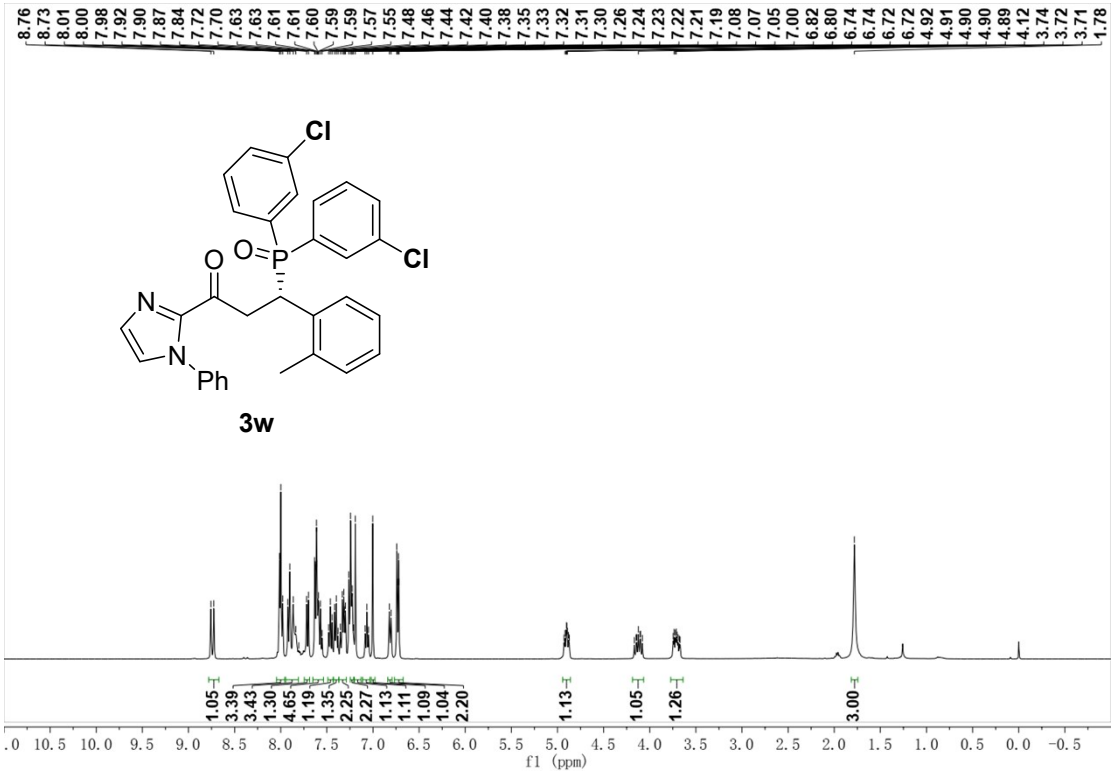


Figure S74: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3w

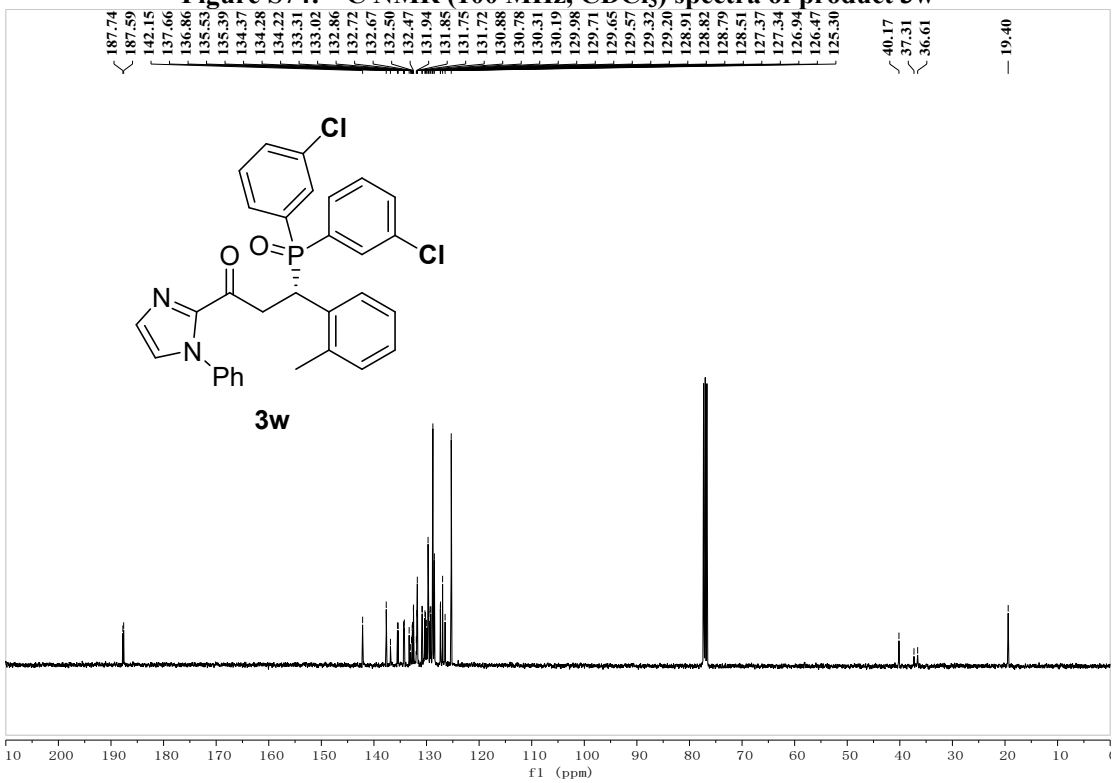


Figure S75: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3w

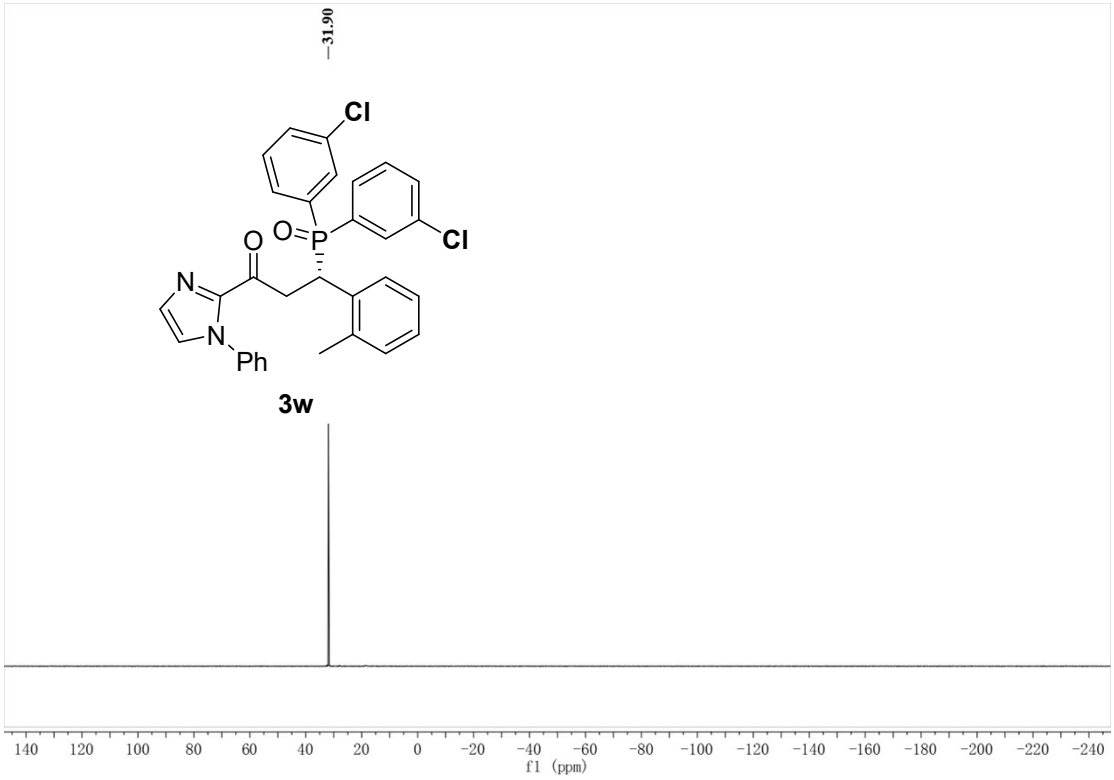


Figure S76: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3x

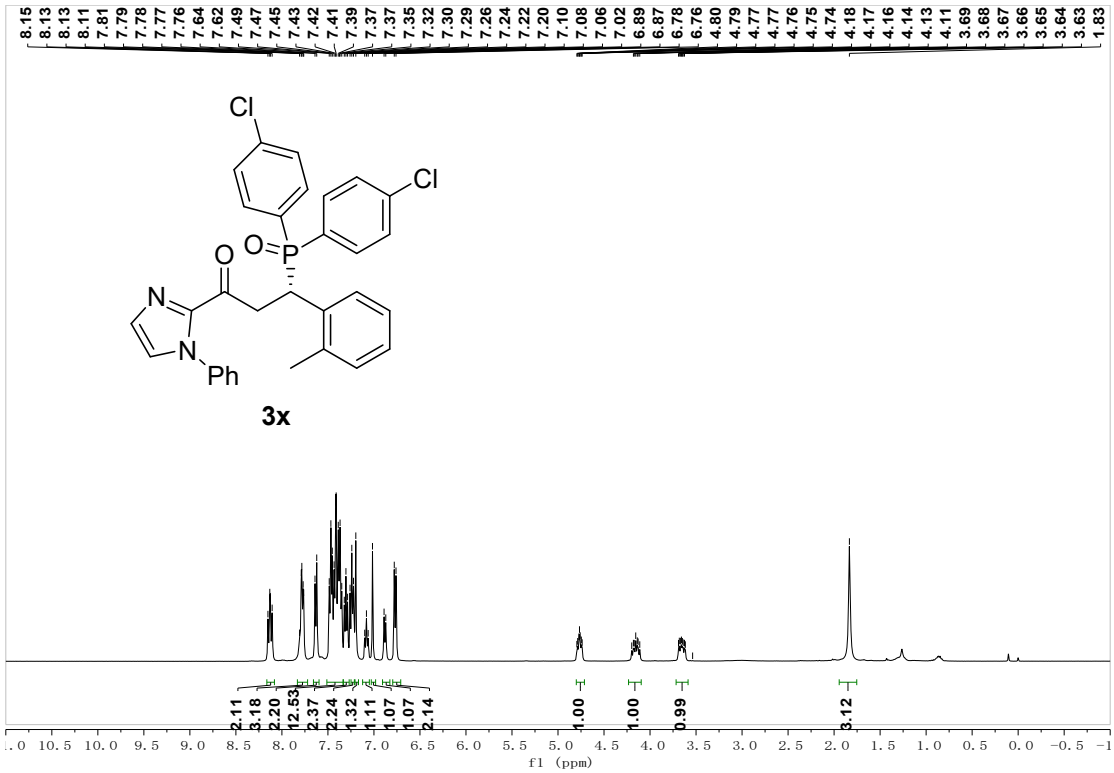


Figure S77: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3x

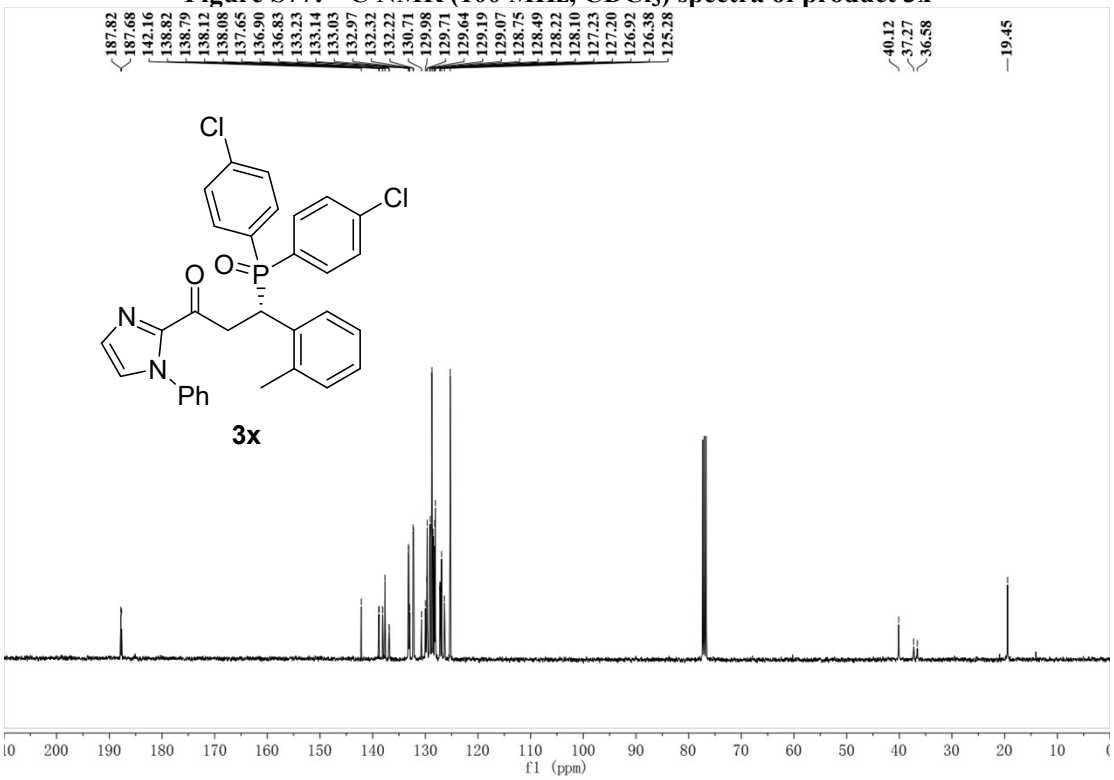


Figure S78: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3x

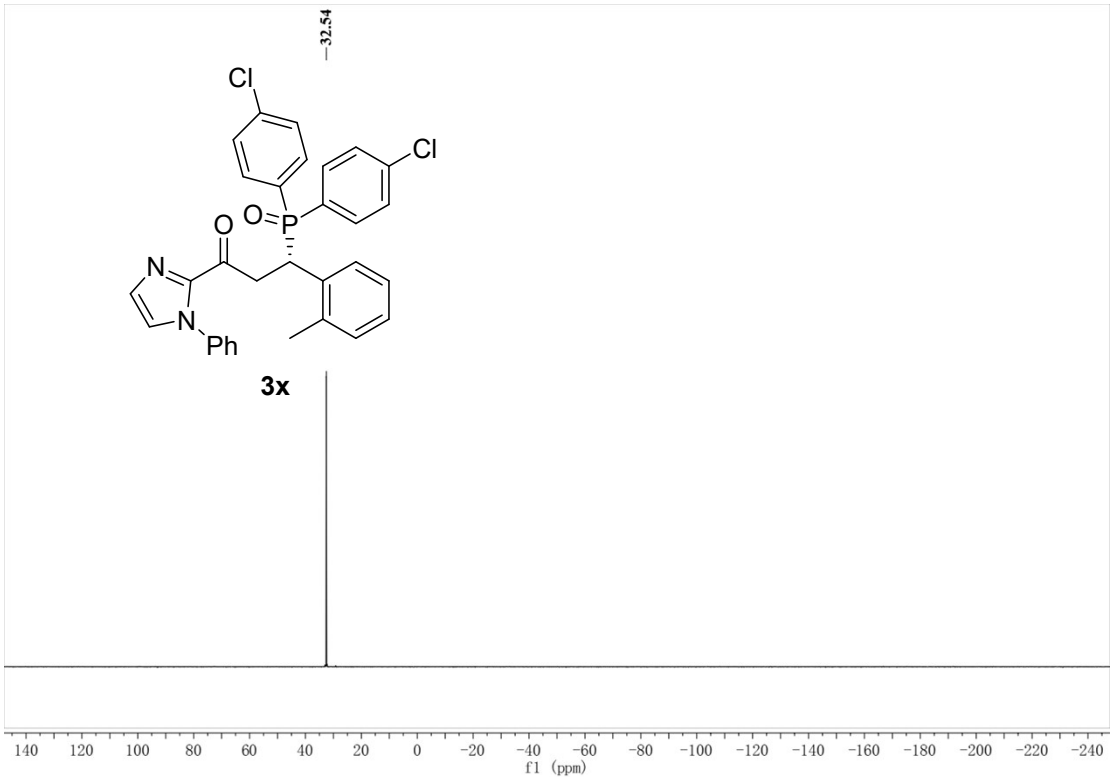


Figure S79: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 3y

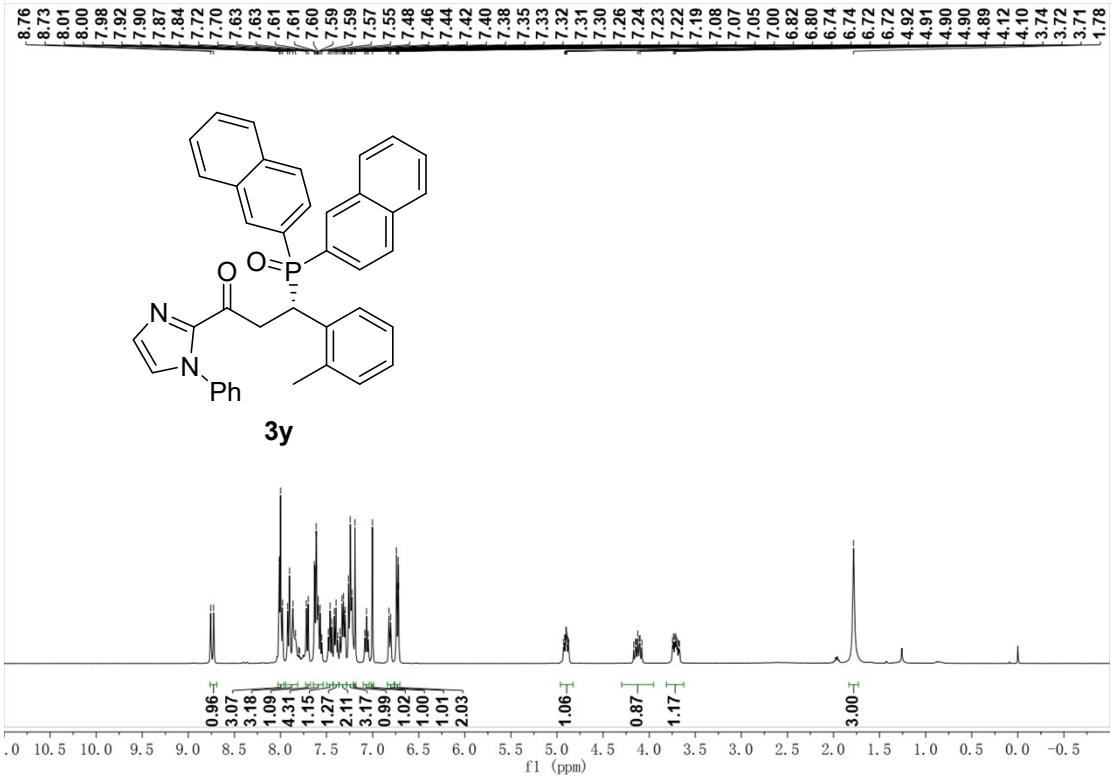


Figure S80: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3y

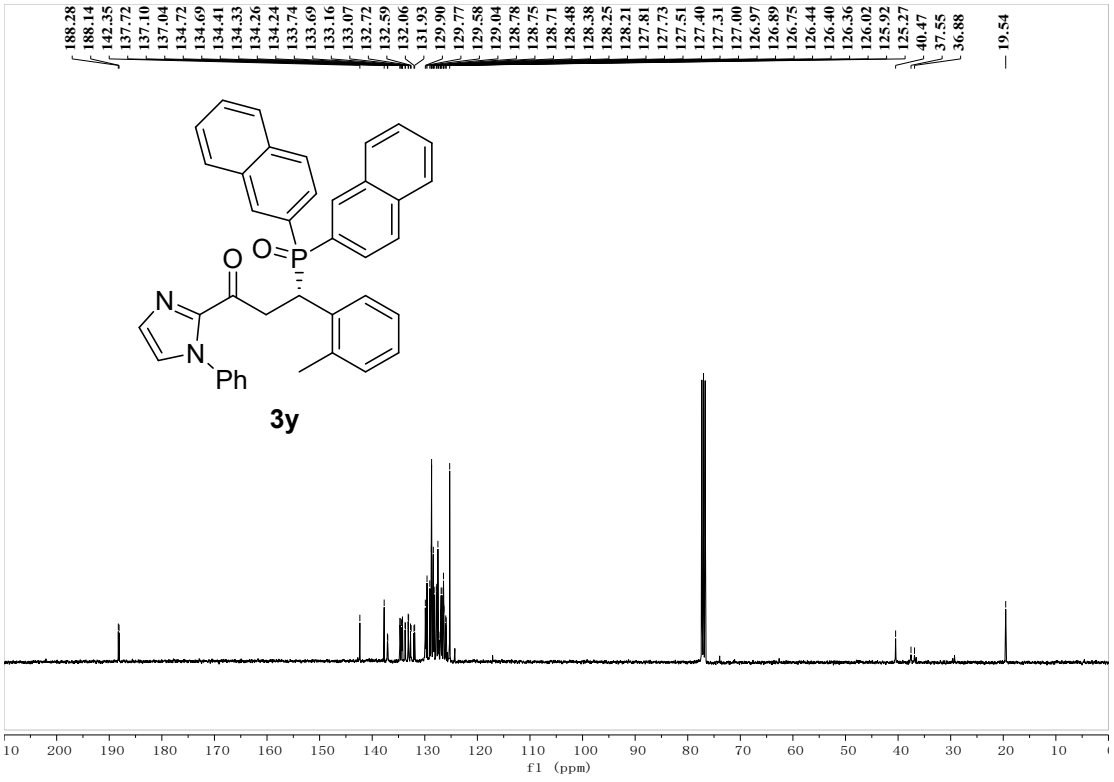


Figure S81: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 3y

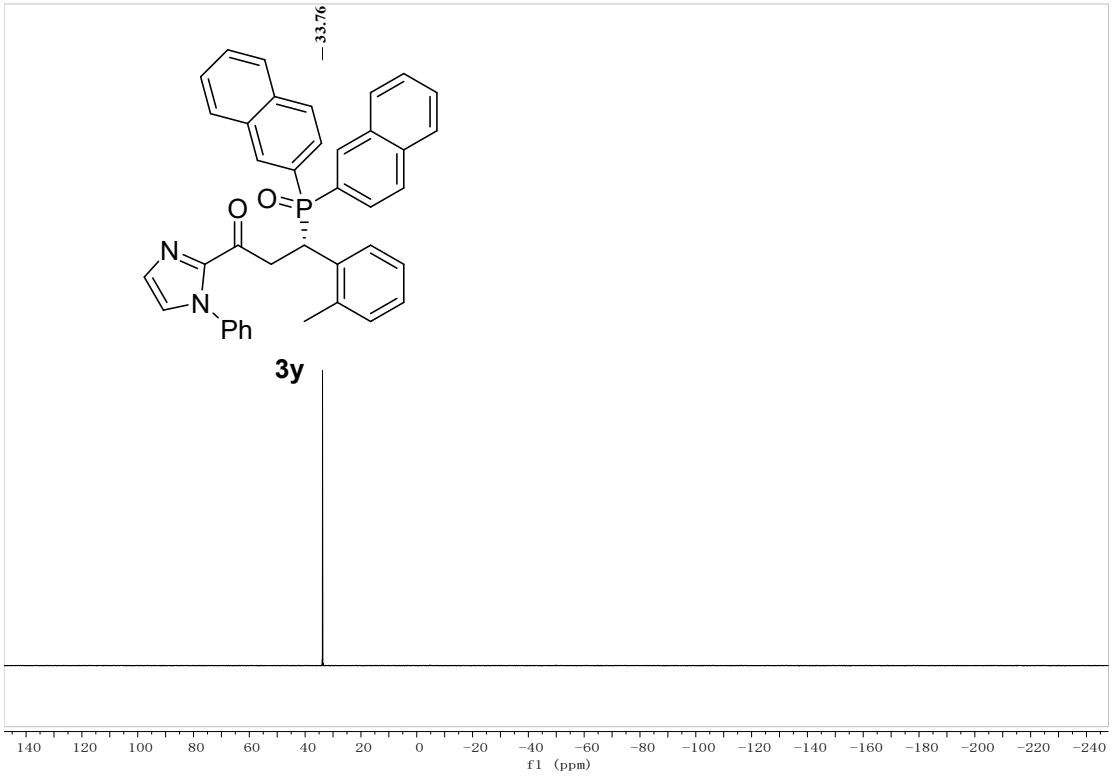


Figure S82: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 4a

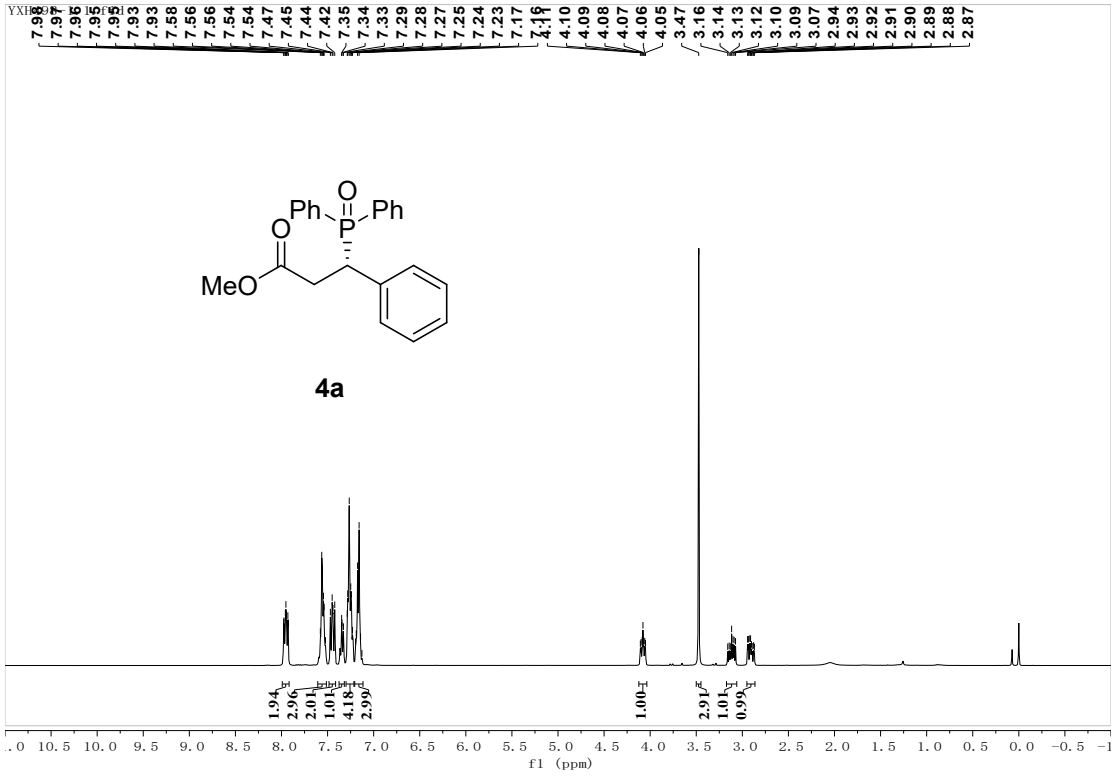


Figure S83: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4a

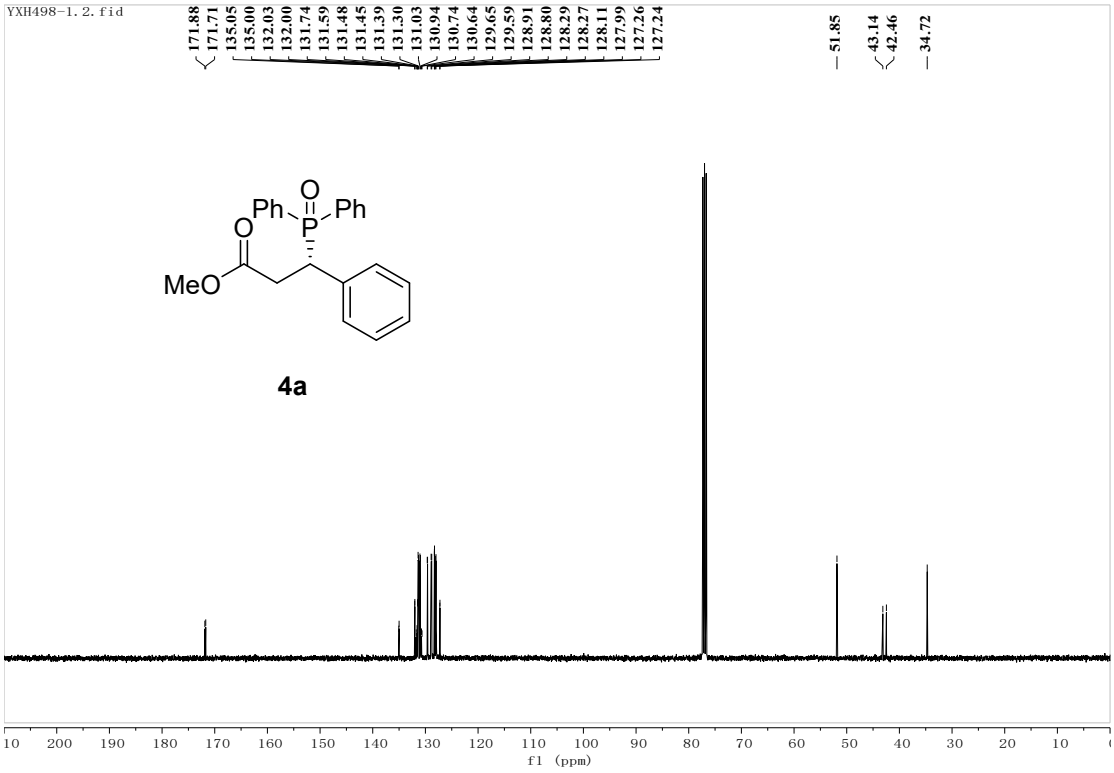


Figure S84: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 4a

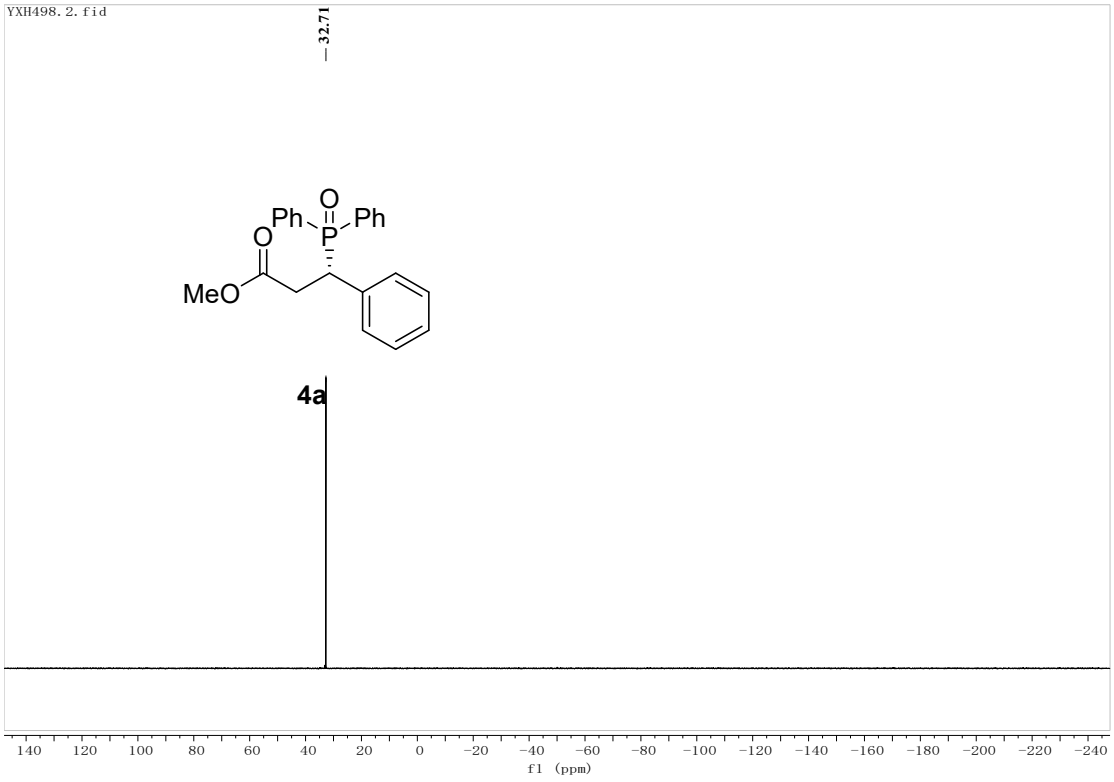


Figure S85: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of product 5a

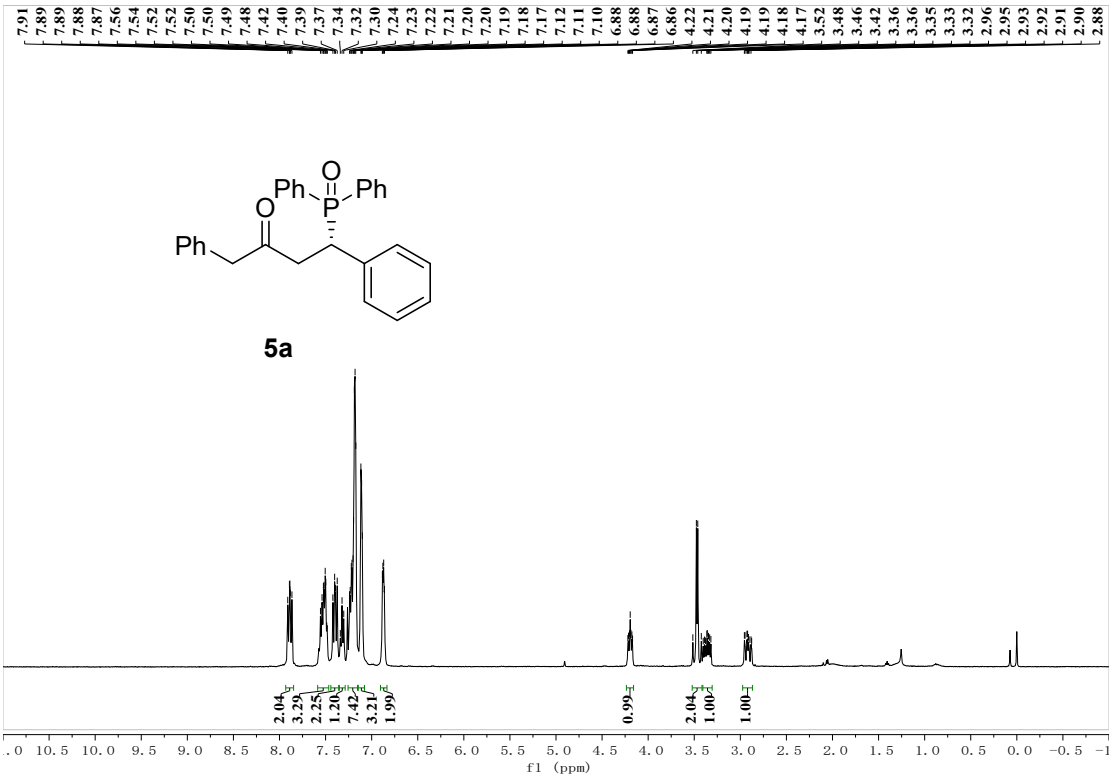


Figure S86: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5a

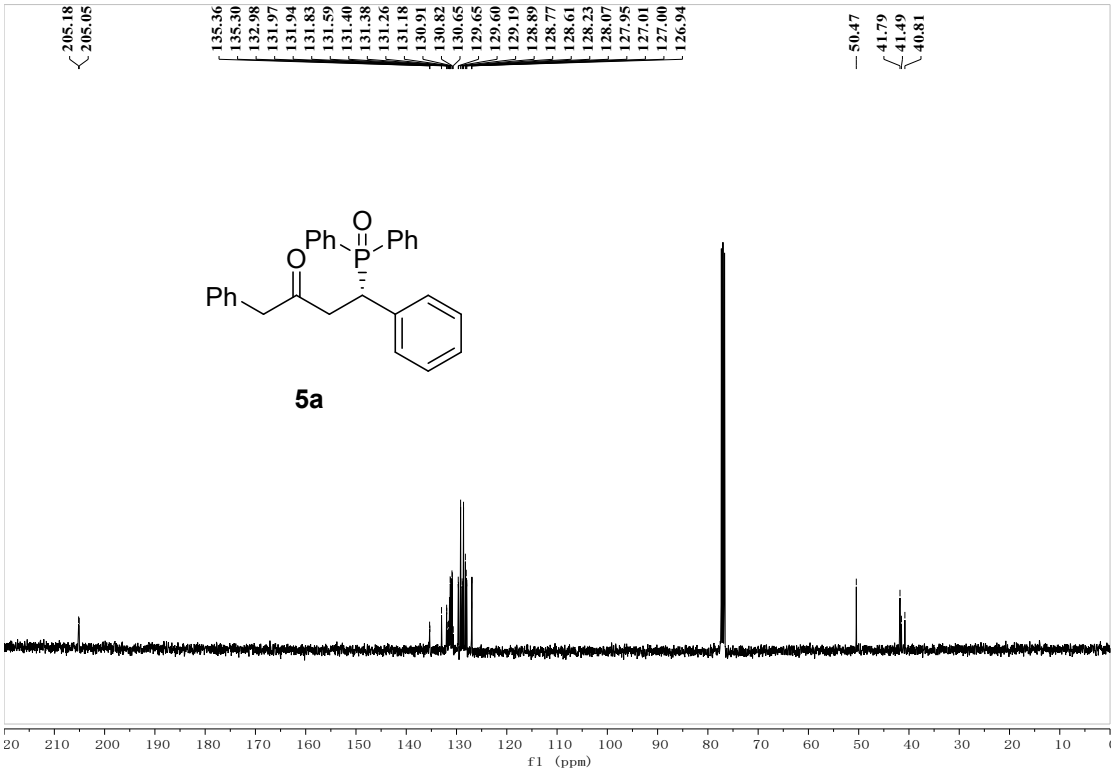
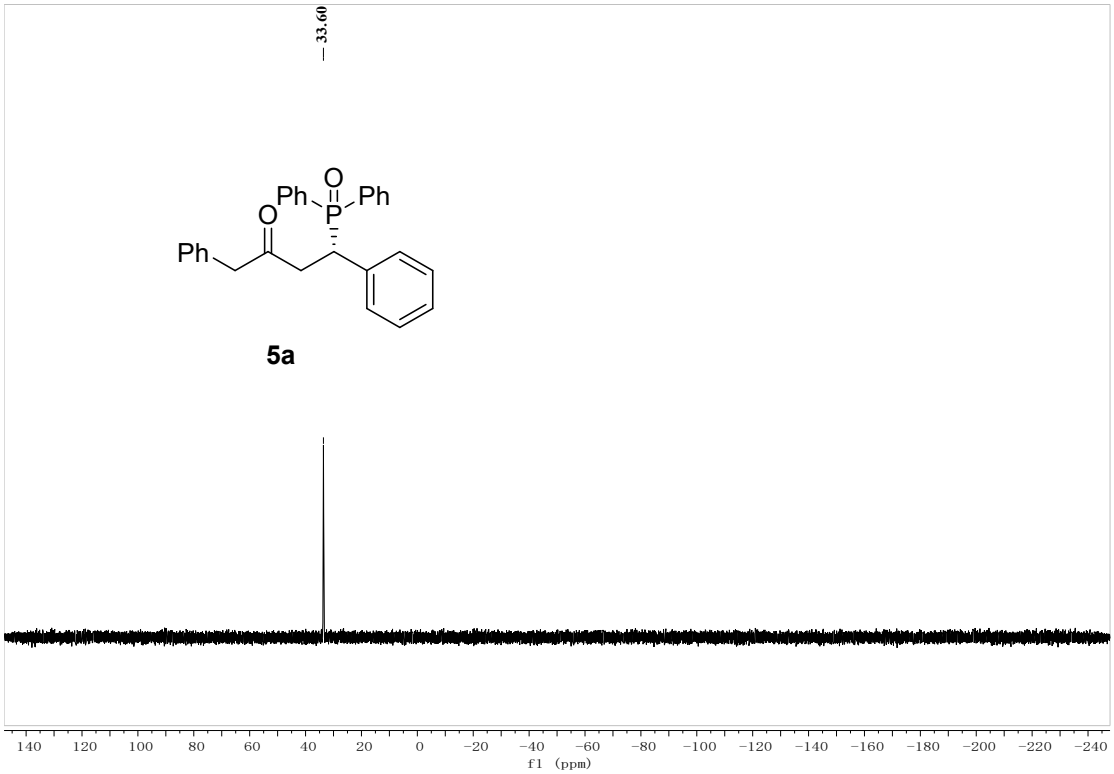
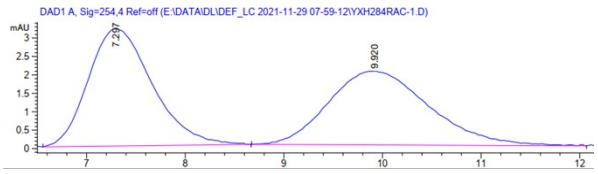


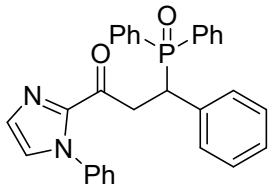
Figure S87: ^{31}P NMR (162 MHz, $CDCl_3$) spectra of product 5a



9. Copies of HPLC Chromatograms

Chiral HPLC spectrum of racemic 3a





***rac*-3a**

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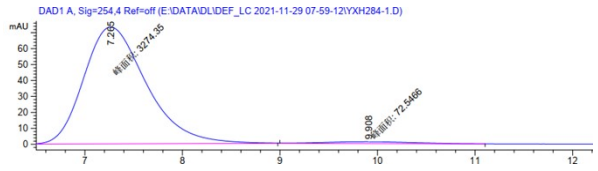
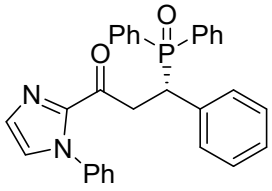
2	9.920	BB	0.8371	141.56355	2.00164	49.6442

Chiral HPLC spectrum of 3a

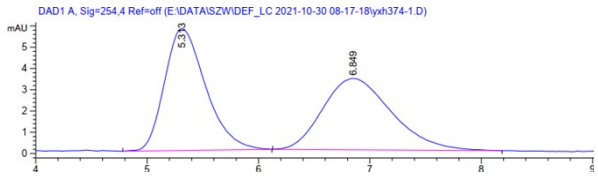


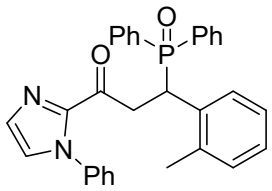


3a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.265	MM	0.7439	3274.34741	73.35912	97.8324
2	9.908	MM	1.0595	72.54664	1.14120	2.1676

Chiral HPLC spectrum of racemic 3b

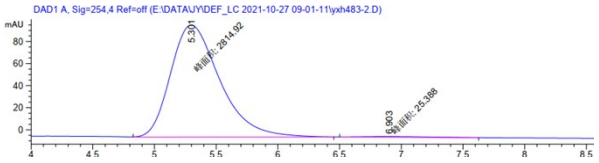


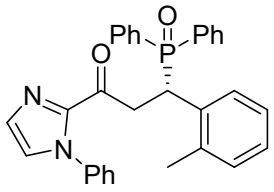


***rac*-3b**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.313	BB	0.3871	146.80138	5.72573	50.5057
2	6.849	BB	0.5182	143.86177	3.35511	49.4943

Chiral HPLC spectrum of 3b

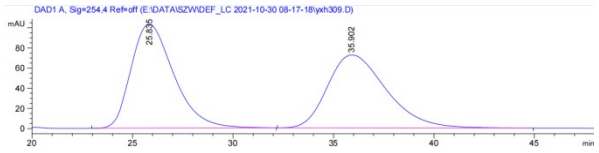


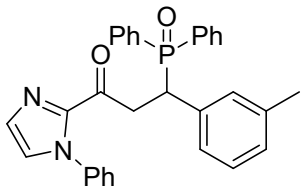


3b

1	5.301	MM	0.4626	2814.91650	101.40684	99.1062
2	6.903	MM	0.6173	25.38800	6.85437e-1	0.8938

Chiral HPLC spectrum of racemic 3c

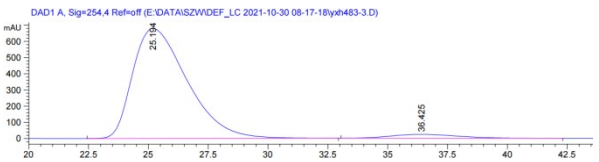


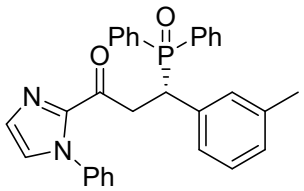


***rac*-3c**

1	25.835	BB	2.1886	1.52288e4	103.14180	50.8448
2	35.902	BB	2.7095	1.47228e4	72.30677	49.1552

Chiral HPLC spectrum of 3c

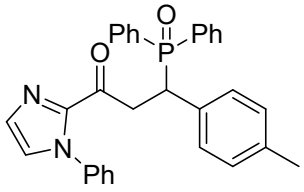




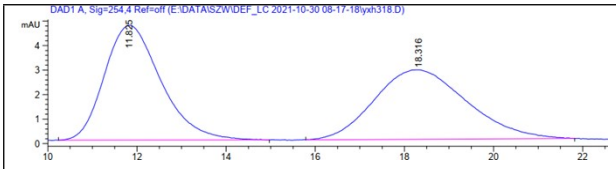
3c

1	25.194	BB	2.4369	1.07237e5	681.07306	95.9663
2	36.425	BB	2.3196	4507.37402	23.56472	4.0337

Chiral HPLC spectrum of racemic 3d

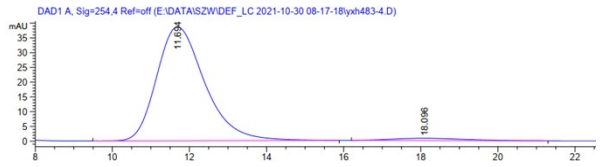


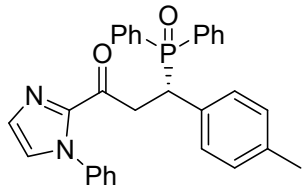
***rac*-3d**



1	11.825	BB	1.0950	412.12143	4.68160	50.2235
2	18.316	BB	1.7174	408.45279	2.83417	49.7765

Chiral HPLC spectrum of 3d

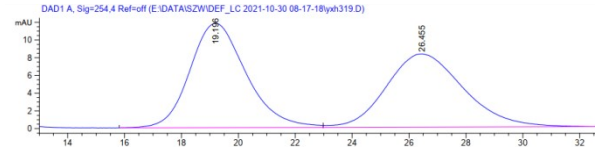


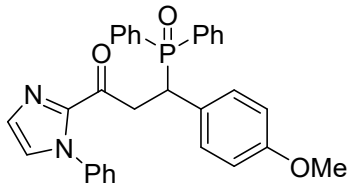


3d

1	11.694	BB	1.3129	3345.58398	38.53442	97.0300
2	18.096	BB	1.5533	102.40508	7.77145e-1	2.9700

Chiral HPLC spectrum of racemic 3e

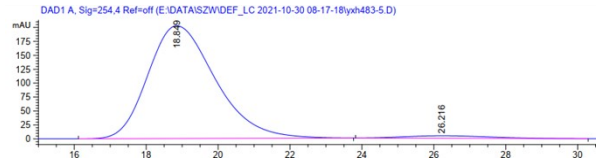


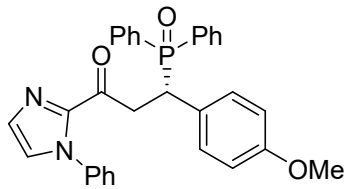


***rac*-3e**

1	19.196	BV	1.9869	1618.67273	11.78147	50.9860
2	26.455	VBA	2.2958	1556.06909	8.25256	49.0140

Chiral HPLC spectrum of 3e

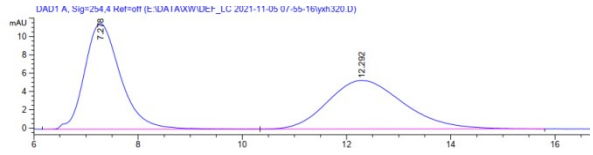


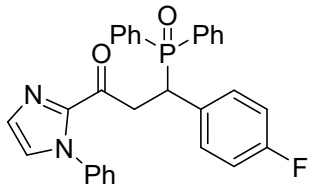


3e

1	18.849	BB	1.9955	2.63625e4	202.40791	97.2982
2	26.216	BB	1.9428	732.04877	4.43706	2.7018

Chiral HPLC spectrum of racemic 3f

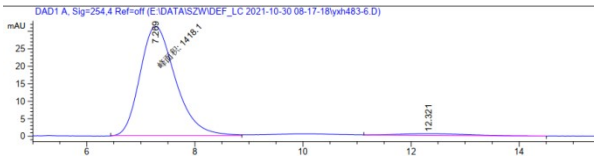


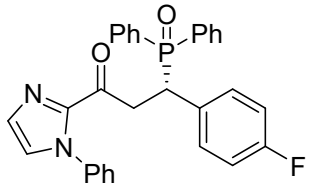


***rac*-3f**

1	7.278	BB	0.7297	552.53955	11.55907	50.6341
2	12.292	BB	1.3402	538.70032	5.30712	49.3659

Chiral HPLC spectrum of 3f

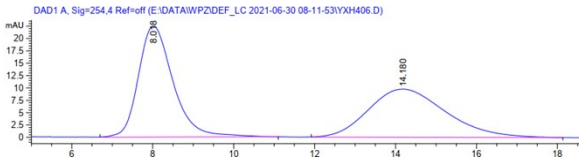


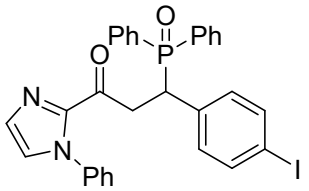


3f

1	7.269	MM	0.7575	1418.10413	31.20138	97.3140
2	12.321	BB	1.0441	39.14185	4.60297e-1	2.6860

Chiral HPLC spectrum of racemic 3g

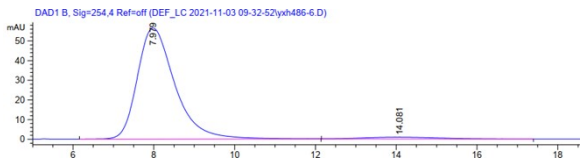


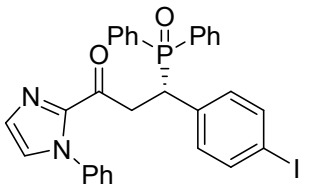


***rac*-3g**

1	8.018	BB	0.8802	1334.97949	22.49907	50.8522
2	14.180	BB	1.5517	1290.23364	9.73866	49.1478

Chiral HPLC spectrum of 3g

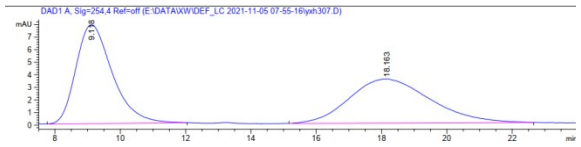
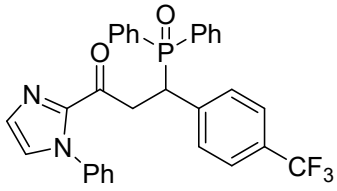




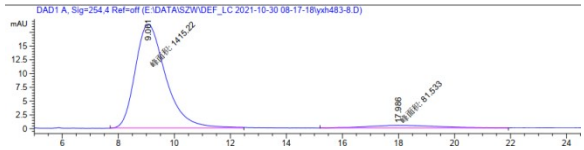
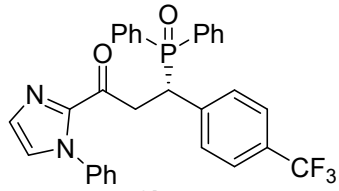
3g

	1 7.979 BB 0.9829 3632.32446 56.43537 96.9923 2 14.081 BB 1.5159 112.63776 8.87960e-1 3.0077

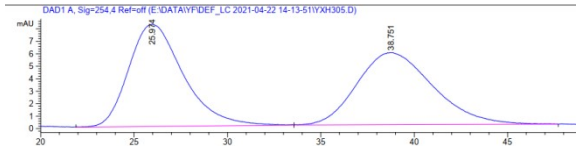
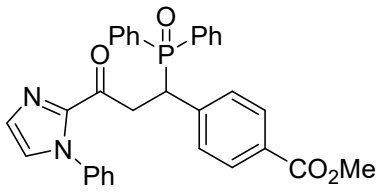
Chiral HPLC spectrum of racemic 3h

	 ***rac*-3h**
	1 9.118 BB 1.1260 607.97571 7.86338 50.2367 2 18.163 BB 2.0189 602.24683 3.50106 49.7633

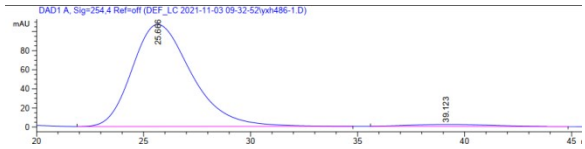
Chiral HPLC spectrum of 3h

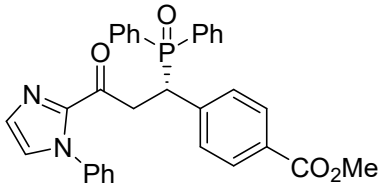
	 **3h**
	1 9.061 MM 1.2555 1415.21521 18.78668 94.5527 2 17.986 MM 2.8347 81.53301 4.79368e-1 5.4473

Chiral HPLC spectrum of racemic 3i

	 ***rac*-3i**
	1 25.974 BB 2.8492 1663.58240 8.19205 50.4691 2 38.751 BB 3.4305 1632.65796 5.76772 49.5309

Chiral HPLC spectrum of 3i

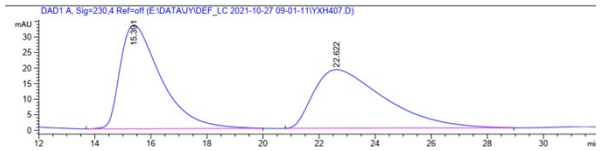


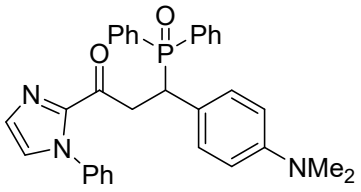


3i

1	25.666	BB	2.8886	2.06745e4	106.88925	97.5230
2	39.123	BB	3.0807	525.11169	1.99635	2.4770

Chiral HPLC spectrum of racemic 3j

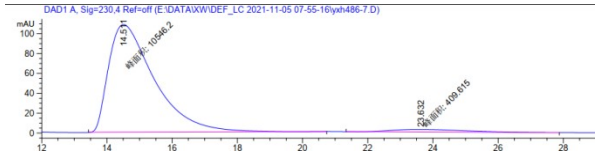


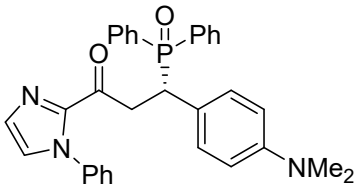


***rac*-3j**

1	15.391	BB	1.4460	3349.28540	33.28315	50.2767
2	22.622	BB	2.0653	3312.42261	18.83905	49.7233

Chiral HPLC spectrum of 3j

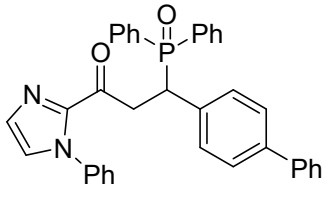




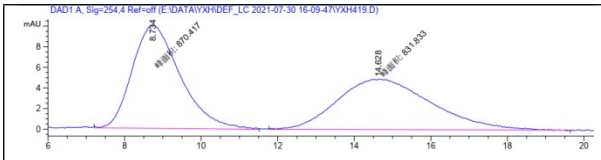
3j

1	14.511	MM	1.6220	1.05462e4	108.36304	96.2612
2	23.632	MM	2.6284	409.61526	2.59741	3.7388

Chiral HPLC spectrum of racemic 3k

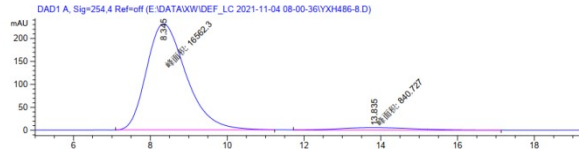


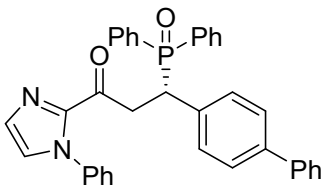
***rac*-3k**



1	8.734	MM	1.4417	870.41687	10.06262	51.1333
2	14.628	MM	2.8371	831.83276	4.88660	48.8667

Chiral HPLC spectrum of 3k

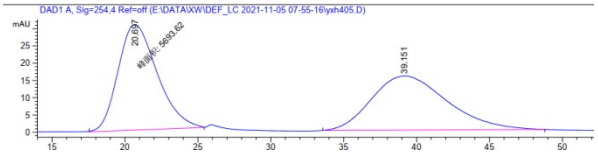


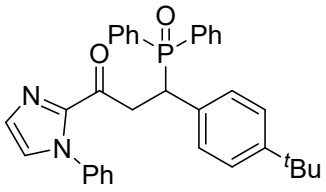


3k

1	8.345	MM	1.1966	1.65623e4	230.67975	95.1691
2	13.835	MM	2.4608	840.72699	5.69404	4.8309

Chiral HPLC spectrum of racemic 3l

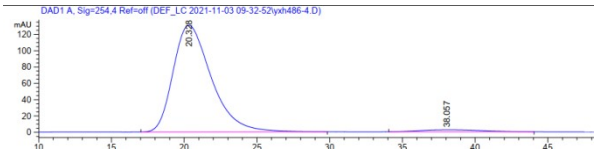


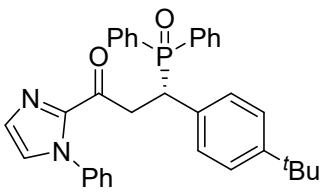


***rac*-3l**

1	20.697	MM	3.1086	5693.61768	30.52610	50.2387
2	39.151	BB	4.2015	5639.52441	15.68225	49.7613

Chiral HPLC spectrum of 3l

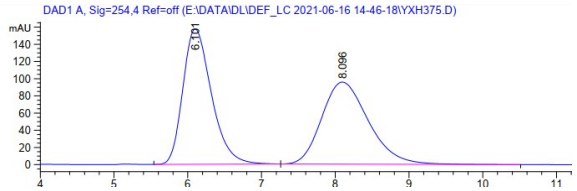


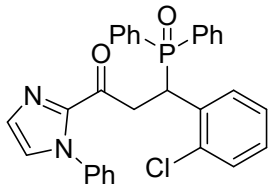


3l

1	20.328	BB	2.5087	2.38841e4	130.77698	97.0754
2	38.057	BB	3.4818	719.56342	2.41801	2.9246

Chiral HPLC spectrum of racemic 3m

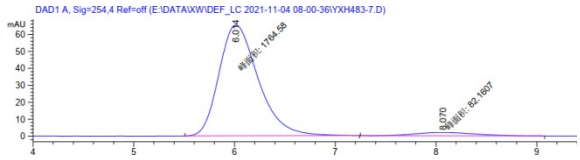


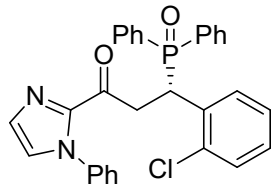


***rac*-3m**

1	6.101	BB	0.4136	4231.25488	157.43309	50.1534
2	8.096	BB	0.6822	4205.37646	95.41991	49.8466

Chiral HPLC spectrum of 3m

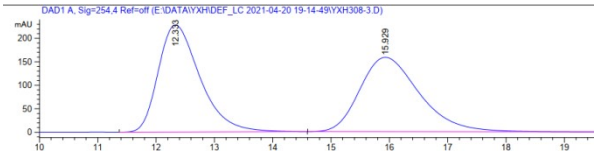


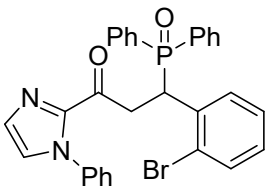


3m

1	6.014	MM	0.4501	1764.57861	65.34328	95.5510
2	8.070	MM	0.7032	82.16070	1.94724	4.4490

Chiral HPLC spectrum of racemic 3n

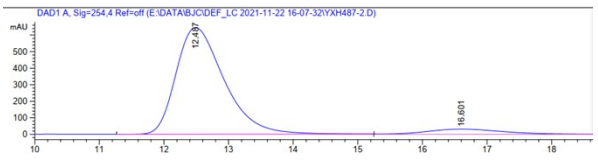


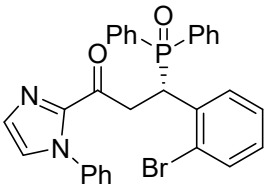


***rac*-3n**

1	12.333	BB	0.7629	1.13101e4	227.91826	50.0887
2	15.929	BB	1.0923	1.12700e4	158.35271	49.9113

Chiral HPLC spectrum of 3n

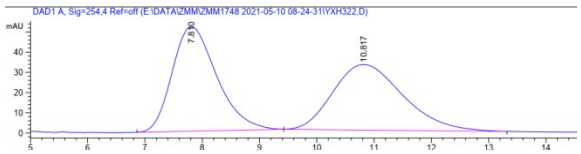


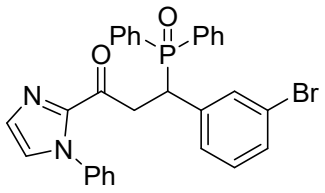


3n

	1	12.487	BB	0.7932	3.32130e4	644.49701	93.4250
	2	16.601	BBA	1.1060	2337.45410	29.90220	6.5750

Chiral HPLC spectrum of racemic 3o

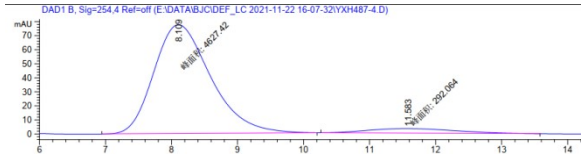


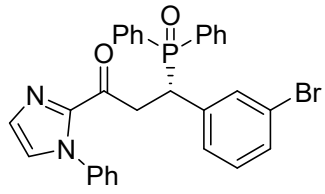


***rac*-3o**

	1	7.810	BB	0.8230	2791.53931	51.77766	50.3074
	2	10.817	BB	1.0671	2757.42017	32.45793	49.6926

Chiral HPLC spectrum of 3o

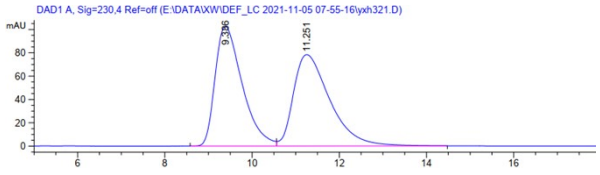


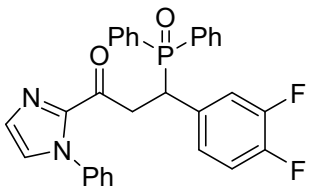


3o

	1	8.109	MM	0.9952	4627.42480	77.49568	94.0631
	2	11.583	MM	1.5089	292.06403	3.22599	5.9369

Chiral HPLC spectrum of racemic 3p

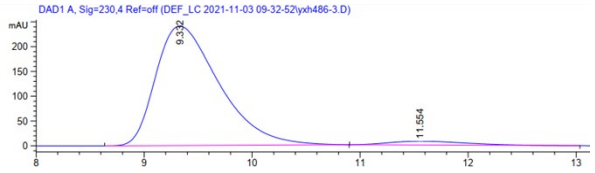


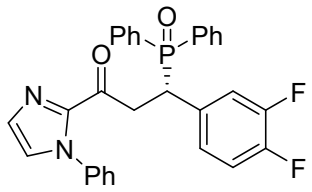


***rac*-3p**

	1	9.386	BV	0.6564	4421.74121	102.67593	49.3863
	2	11.251	VB	0.8734	4531.63916	78.28185	50.6137

Chiral HPLC spectrum of 3p

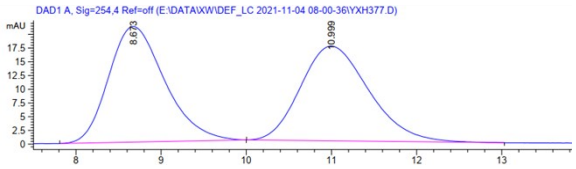


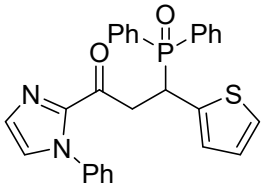


3p

1	9.332	BB	0.6248	9807.13770	240.99039	96.2938
2	11.554	BB	0.7076	377.46478	7.54637	3.7062

Chiral HPLC spectrum of racemic 3q

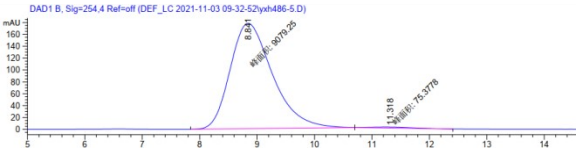


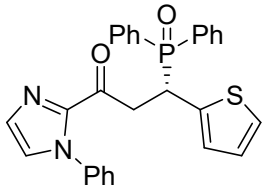


***rac*-3q**

1	8.673	BB	0.6818	963.77271	21.06579	50.0033
2	10.999	BB	0.8128	963.64496	17.27482	49.9967

Chiral HPLC spectrum of 3q

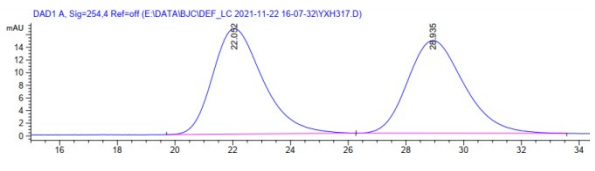


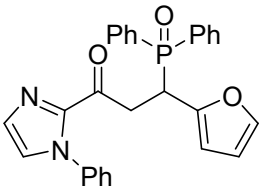


3q

1	8.841	MM	0.8540	9079.24609	177.18825	99.1766
2	11.318	MM	0.7843	75.37778	1.60185	0.8234

Chiral HPLC spectrum of racemic 3r

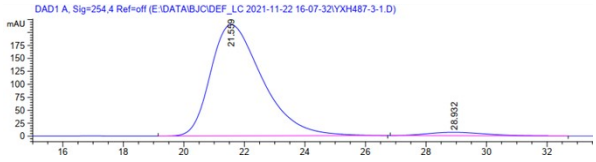
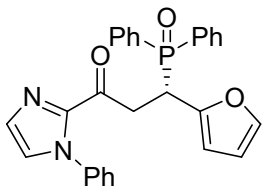




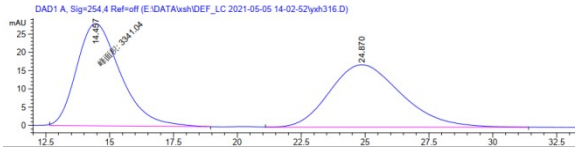
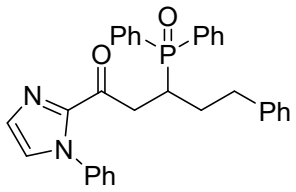
***rac*-3r**

	1 22.052 BB 1.6887 2008.53845 16.68181 50.2451 2 28.935 BB 1.6139 1988.94543 14.66844 49.7549

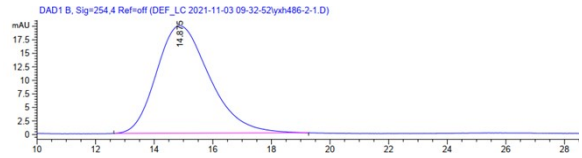
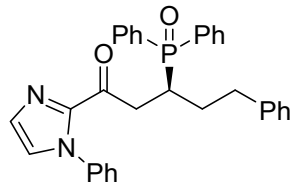
Chiral HPLC spectrum of 3r

	 **3r**
	1 21.559 BB 1.8091 2.54228e4 214.75020 96.8075 2 28.932 BB 1.5318 838.38580 6.45273 3.1925

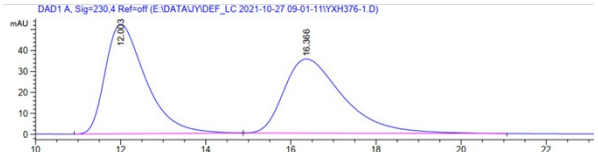
Chiral HPLC spectrum of racemic 3s

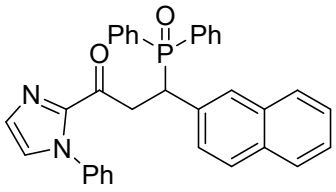
	 ***rac*-3s**
	1 14.457 MM 1.9875 3341.04004 28.01695 49.9668 2 24.870 BB 2.3420 3345.48486 17.07411 50.0332

Chiral HPLC spectrum of 3s

	 **3s**
	1 14.875 BB 1.4965 2502.19897 19.87931 100.0000

Chiral HPLC spectrum of racemic 3t

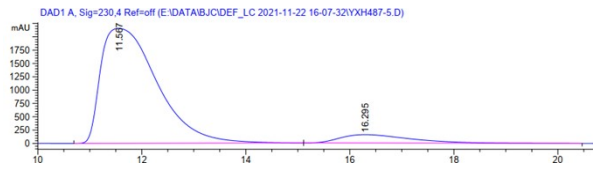


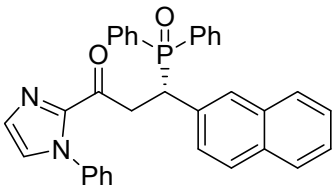


***rac*-3t**

1	12.003	BB	0.9831	3439.32593	52.30711	50.2066
2	16.366	BB	1.3805	3411.02368	35.38856	49.7934

Chiral HPLC spectrum of 3t

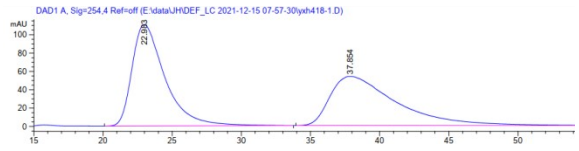


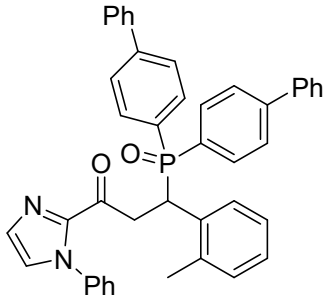


3t

1	11.567	BB	0.8949	1.62269e5	2153.96021	91.7089
2	16.295	BB	1.3991	1.46702e4	156.57057	8.2911

Chiral HPLC spectrum of racemic 3u

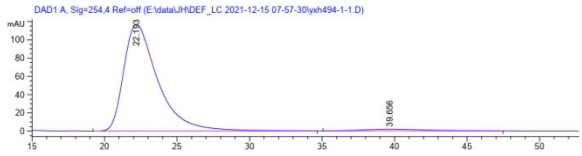


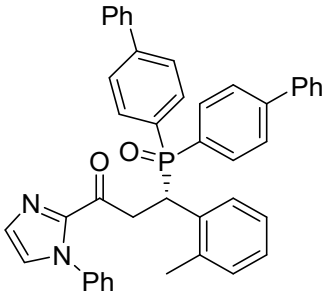


***rac*-3u**

1	22.983	BB	2.3328	1.83114e4	110.53043	50.6702
2	37.854	BB	3.9516	1.78270e4	53.49834	49.3298

Chiral HPLC spectrum of 3u

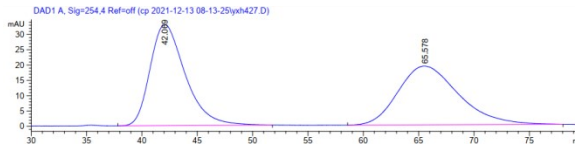


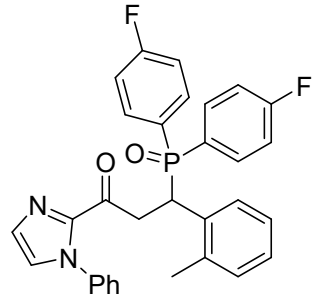


3u

1	22.193	BB	2.4154	1.92157e4	116.79686	96.6999
2	39.656	BB	3.8287	655.77277	2.00455	3.3001

Chiral HPLC spectrum of racemic 3v

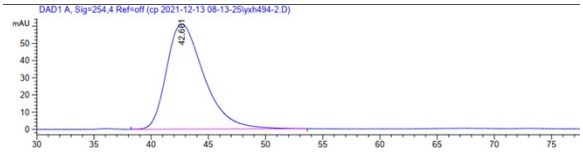


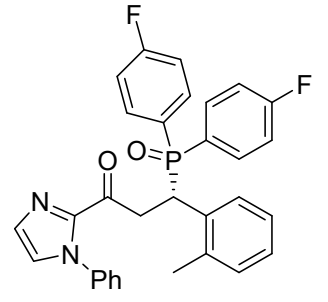


***rac*-3v**

1	42.069	BB	2.9129	7297.34521	32.98690	50.0153
2	65.578	BB	4.4614	7292.89014	19.17440	49.9847

Chiral HPLC spectrum of 3v

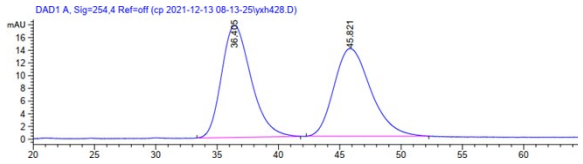


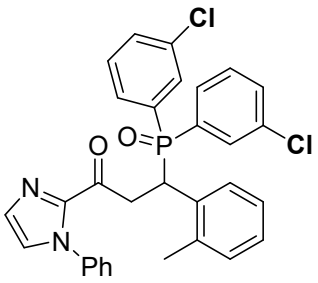


3v

1	42.661	BB	3.2693	1.39115e4	61.16967	100.0000

Chiral HPLC spectrum of racemic 3w

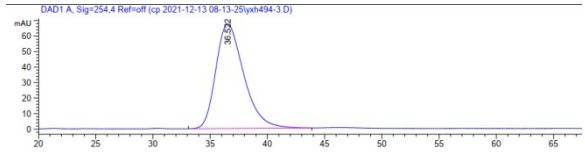


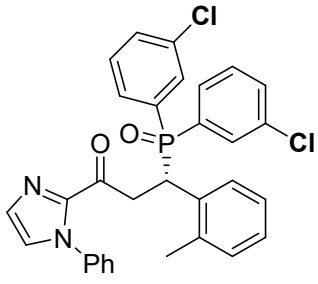


***rac*-3w**

1	36.405	BB	2.0031	2944.97192	17.62730	50.5244
2	45.821	BB	2.4508	2883.84326	13.80721	49.4756

Chiral HPLC spectrum of 3w

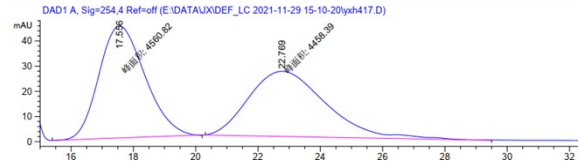


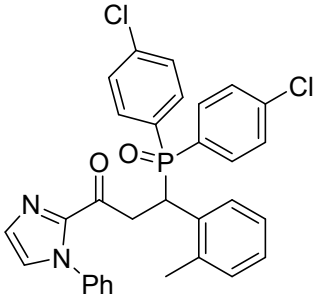


3w

1	36.522	BB	2.5806	1.14230e4	67.42413	100.0000

Chiral HPLC spectrum of racemic 3x

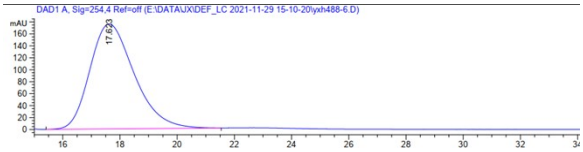


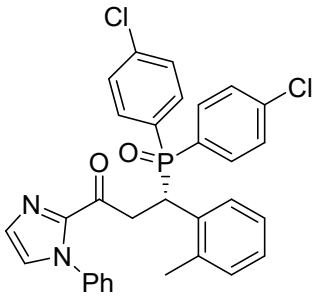


***rac*-3x**

1	17.556	MM	1.7096	4560.81885	44.46276	50.5678
2	22.769	MM	2.8745	4458.39209	25.85032	49.4322

Chiral HPLC spectrum of 3x

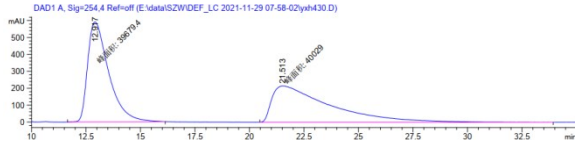


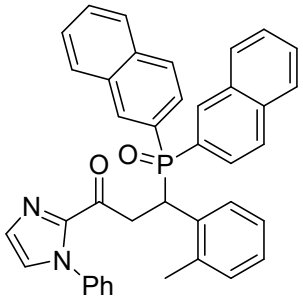


3x

1	17.623	BB	1.6641	1.88697e4	175.26846	100.0000

Chiral HPLC spectrum of racemic 3y

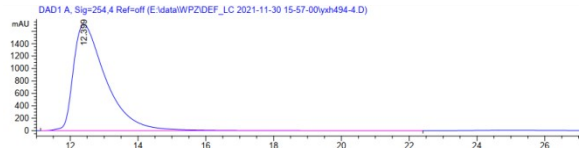


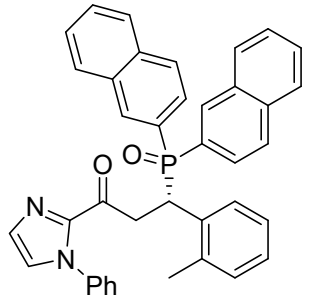


***rac*-3y**

1	12.917	MM	1.1185	3.96794e4	591.26788	49.7807
2	21.513	MM	3.1006	4.00290e4	215.16611	50.2193

Chiral HPLC spectrum of 3y

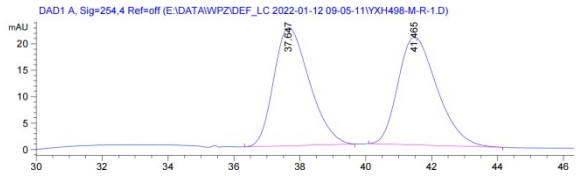


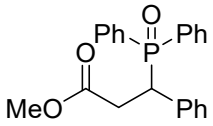


3y

1	12.399	VB	1.0005	1.14316e5	1708.82251	100.0000

Chiral HPLC spectrum of racemic 4a

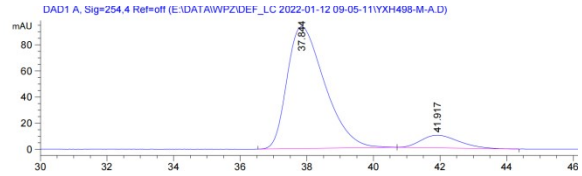


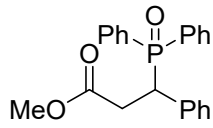


***rac*-4a**

1	37.647	BB	0.8923	1677.95093	22.34071	49.9442
2	41.465	BB	0.9994	1681.70142	20.44953	50.0558

Chiral HPLC spectrum of 4a

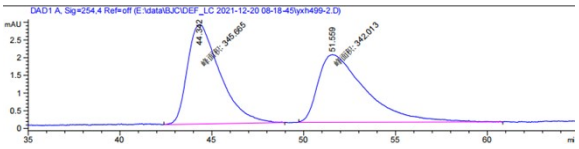


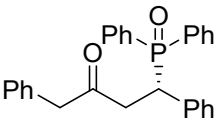


4a

1	37.844	BB	1.1695	7326.01514	93.36007	90.5483
2	41.917	BB	0.9442	764.71484	9.73781	9.4517

Chiral HPLC spectrum of racemic 5a

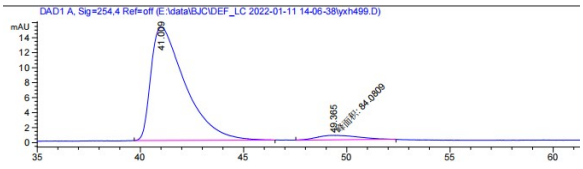


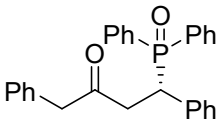


***rac*-5a**

1	44.342	MM	2.0537	345.66528	2.80516	50.2655
2	51.559	MM	2.9847	342.01346	1.90981	49.7345

Chiral HPLC spectrum of 5a





5a

1	41.009	BB	1.5849	1742.36304	15.11512	95.3965
2	49.365	MM	2.3009	84.08093	6.09050e-1	4.6035