Electronic Supplementary Material (ESI) for ChemComm.

Diastereo- and enantioselective synthesis of biaryl aldehydes bearing both axial and central chirality

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Supplementary Information

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I. General information

^{1}H, **^{13}C**, **^{19}F**, and **^{31}P** spectra were recorded on a JNM-ECZ 400S (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^{1}H ($CDCl_3$ δ 7.26; DMSO-d_6 δ 2.50), ^{13}C ($CDCl_3$ δ 77.16; DMSO-d_6 δ 39.52). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), and integration. Melting point (**MP**) was obtained on Buchi M-560. For thin-layer chromatography (**TLC**), Huanghai TLC plates (HSGF 254) were used, and compounds were visualized with UV light at 254 nm. Preparative HPLC was conducted on an Agilent HPLC 1260 Infinity II using an Agilent Prep column (10 μm, Prep-C18, 100 Å, 250 × 21.2 mm). High-resolution mass spectra (**HRMS**) were obtained on an Agilent 1290-6530 Q-TOF spectrometer. X-ray diffraction analysis was performed on a Bruker D8 Venture diffractometer. **Optical rotations** were recorded on an InsMark IP-digi 300 automatic polarimeter. Enantiomeric ratios (**er**) were determined by HPLC analysis on an Agilent HPLC 1260 Infinity II; column, Chiralpak IA, IB N-5, ID, and IF.

Unless otherwise noted, all reactions were carried out under an ambient atmosphere; exclusion of air or moisture was not required. Anhydrous and deuterated solvents were purchased from commercial suppliers and used as received without further purification. Prochiral biaryl dialdehydes **1**[1] and ligands **L1**,[2] **L4**-**L7**[3] were prepared according to literature procedures. Ligands **L2**, **L3**, and **L8** were purchased from commercial suppliers and used as received without further purification. The relative and absolute configurations of **3a** and **3a'** were unambiguously assigned by single-crystal X-ray diffraction analysis (CCDC 2181106 and 2241542, respectively), and those of other products were assigned by analogy.

II. Preparation of activated isocyanides 2

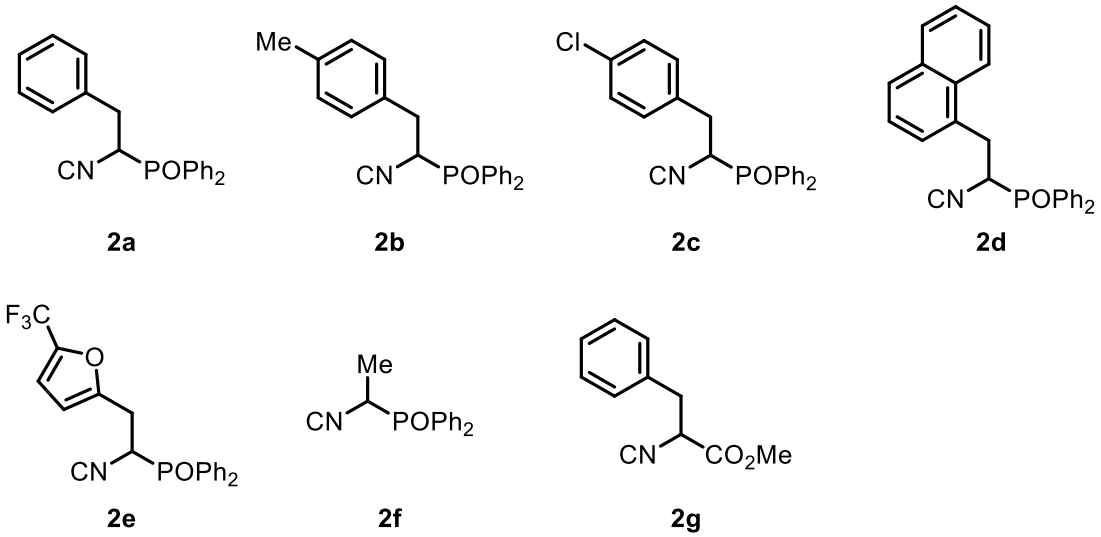
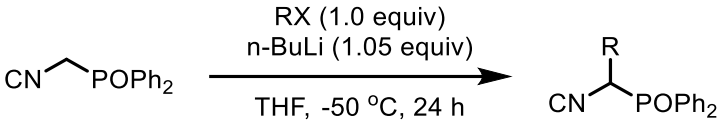


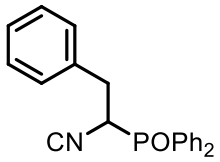
Figure S1. Activated isocyanides involved in this study

Isocyanoacetate **2g** is a known compound and was prepared according to the literature procedure.[4] Isocyanides **2a-2f** were prepared from α-isocyanomethyldiphenylphosphine oxide[5] and the corresponding halides according to the following procedure.



General procedure. To a solution of α-isocyanomethyldiphenylphosphine oxide (1.0 equiv) in THF (0.02 M) under a nitrogen atmosphere was slowly added n-BuLi (2.5 M in hexane, 1.05 equiv) at -50 °C and stirred for 0.5 h, then the corresponding halide (1.0 equiv) was added. After another 24 h, the reaction mixture was warmed to room temperature and filtered to remove insoluble solids. The filtrate was concentrated and the residue was purified by flash column chromatography to afford the corresponding activated isocyanide.

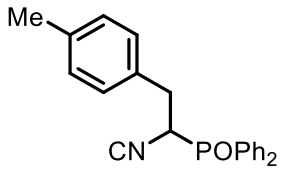
(1-Isocyano-2-phenylethyl)diphenylphosphine oxide (2a)



2a

Purified by flash column chromatography (PE/EtOAc 1:1). White solid, 680 mg, 66% yield. **MP**: 185-186 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04-7.97 (m, 2H), 7.93-7.86 (m, 2H), 7.71-7.52 (m, 6H), 7.34-7.27 (m, 3H), 7.25-7.21 (m, 2H), 4.51-4.43 (m, 1H), 3.47-3.38 (m, 1H), 2.82-2.72 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.6 (d, *J* = 3.0 Hz), 135.8 (d, *J* = 11.2 Hz), 133.4 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 8.9 Hz), 131.6 (d, *J* = 9.5 Hz), 129.3, 129.24, 129.19 (d, *J* = 102.6 Hz), 129.1 (d, *J* = 7.7 Hz), 129.0, 128.9, 127.7, 126.7, 56.1 (d, *J* = 70.7 Hz), 34.9; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.5; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}NNaOP$ 354.1018; Found 354.1018.

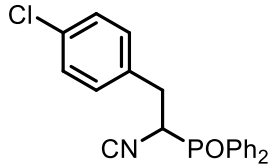
(1-Isocyano-2-(*p*-tolyl)ethyl)diphenylphosphine oxide (2b)



2b

Purified by flash column chromatography (EtOAc). White solid, 250 mg, 72% yield. **MP**: 174-175 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04-7.96 (m, 2H), 7.92-7.85 (m, 2H), 7.70-7.51 (m, 6H), 7.11 (d, *J* = 0.7 Hz, 4H), 4.49-4.40 (m, 1H), 3.43-3.34 (m, 1H), 2.78-2.68 (m, 1H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.5, 137.3, 133.3 (d, *J* = 2.8 Hz), 133.2 (d, *J* = 2.9 Hz), 132.7 (d, *J* = 11.5 Hz), 132.5 (d, *J* = 9.0 Hz), 131.5 (d, *J* = 9.5 Hz), 129.6, 129.22 (d, *J* = 102.4 Hz), 129.18 (d, *J* = 12.2 Hz), 129.1, 129.0 (d, *J* = 12.1 Hz), 127.2 (d, *J* = 100.9 Hz), 56.1 (d, *J* = 70.8 Hz), 34.5, 21.2; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.6; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}NNaOP$ 368.1175; Found 368.1177.

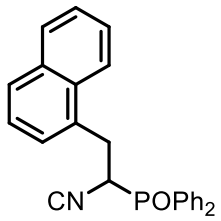
(2-(4-Chlorophenyl)-1-isocyanoethyl)diphenylphosphine oxide (2c)



2c

Purified by flash column chromatography (EtOAc). White solid, 200 mg, 55% yield. **MP**: 140-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 2H), 7.87-7.81 (m, 2H), 7.67-7.48 (m, 6H), 7.25-7.21 (m, 2H), 7.14-7.10 (m, 2H), 4.44-4.36 (m, 1H), 3.39-3.31 (m, 1H), 2.76-2.66 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.9, 134.2 (d, *J* = 11.2 Hz), 133.7, 133.4 (d, *J* = 2.8 Hz), 133.3 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 8.9 Hz), 131.5 (d, *J* = 9.5 Hz), 130.6, 129.3 (d, *J* = 12.3 Hz), 129.09, 129.06 (d, *J* = 12.3 Hz), 129.0 (d, *J* = 102.9 Hz), 127.0 (d, *J* = 101.1 Hz), 55.8 (d, *J* = 70.3 Hz), 34.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.3; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}ClNNaOP$ 388.0628; Found 388.0631.

(1-Isocyano-2-(naphthalen-1-yl)ethyl)diphenylphosphine oxide (2d)

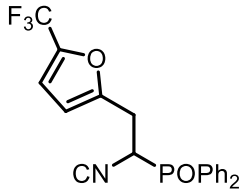


2d

Purified by flash column chromatography (EtOAc). White solid, 200 mg, 53% yield. **MP**: 170-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10-8.04 (m, 2H), 7.94-7.83 (m, 4H), 7.80 (dd, *J* = 6.8, 2.7 Hz, 1H), 7.73-7.68 (m, 1H), 7.66-7.60 (m, 3H), 7.58-7.49 (m, 4H), 7.43-7.37 (m, 2H), 4.67-4.59 (m, 1H), 4.17-4.09 (m, 1H), 3.08-2.98 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.4, 134.1, 133.4 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 9.0 Hz), 131.6 (d, *J* = 9.5 Hz), 131.3 (d, *J* = 10.9 Hz), 131.2, 129.3 (d, *J* = 3.4 Hz), 129.18 (d, *J* = 102.5 Hz), 129.15, 129.0, 128.6 (d, *J* = 9.3 Hz), 127.2 (d, *J* = 100.7 Hz), 126.9, 126.0, 125.6, 122.8, 54.8 (d, *J* = 70.5 Hz), 32.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{20}NNaOP$

404.1175; Found 404.1175.

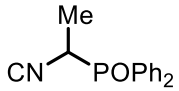
(1-Isocyano-2-(5-(trifluoromethyl)furan-2-yl)ethyl)diphenylphosphine oxide (2e)



2e

Purified by flash column chromatography (EtOAc). Yellow wax, 150 mg, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.91-7.85 (m, 2H), 7.70-7.53 (m, 6H), 6.68-6.65 (m, 1H), 6.29 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.70-4.63 (m, 1H), 3.49-3.39 (m, 1H), 3.08-2.98 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.2, 151.9 (d, *J* = 12.0 Hz), 141.9 (q, *J* = 42.7 Hz), 133.6 (d, *J* = 2.9 Hz), 133.5 (d, *J* = 2.8 Hz), 132.4 (d, *J* = 9.2 Hz), 131.5 (d, *J* = 9.6 Hz), 129.4 (d, *J* = 12.4 Hz), 129.2 (d, *J* = 12.4 Hz), 128.1, 126.8 (d, *J* = 101.8 Hz), 119.0 (q, *J* = 267.0 Hz), 112.7 (q, *J* = 3.0 Hz), 110.0, 52.6 (d, *J* = 70.0 Hz), 28.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -64.0; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{15}F_3NNaO_2P$ 412.0685; Found 412.0687.

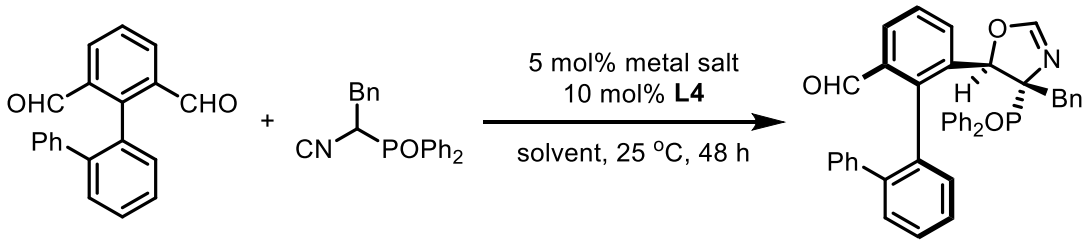
(1-Isocyanoethyl)diphenylphosphine oxide (2f)



2f

Purified by flash column chromatography (PE/EtOAc 1:1). White solid, 200 mg, 78% yield. **MP**: 159-160 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98-7.91 (m, 2H), 7.89-7.82 (m, 2H), 7.68-7.50 (m, 6H), 4.48-4.38 (m, 1H), 1.60 (dd, *J* = 13.4, 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 161.2, 133.3 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 8.7 Hz), 131.6 (d, *J* = 9.6 Hz), 129.18 (d, *J* = 102.2 Hz), 129.16 (d, *J* = 12.3 Hz), 128.9 (d, *J* = 12.2 Hz), 126.9 (d, *J* = 101.1 Hz), 48.6 (d, *J* = 73.3 Hz), 15.4; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.6; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}NNaOP$ 278.0705; Found 278.0706.

III. Metal salt and solvent screening[a]

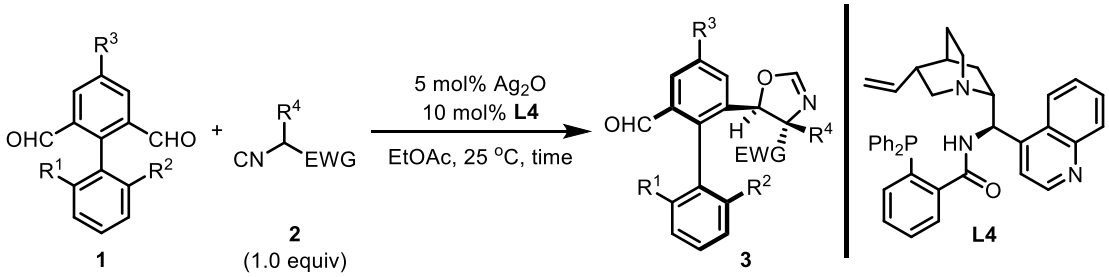


1a **2a** (1.0 equiv) **3a**

Entry	Metal salt	Solvent	dr (**3a**/**3a'**)[b]	Yield (%)[c]	er[d]
1	Ag_2CO_3	EtOAc	8:1	68	99:1
2	AgOAc	EtOAc	9:1	36	99:1
3	$Cu(OAc)_2$	EtOAc	/	<5	/
4	Cu_2O	EtOAc	/	<5	/
5	Ag_2O	THF	9:1	50	99:1
6	Ag_2O	CH_2Cl_2	8:1	56	99:1
7	Ag_2O	DCE	8:1	53	99:1
8	Ag_2O	toluene	9:1	65	99:1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), metal salt (5 mol%), and **L4** (10 mol%) in 1.0 mL of solvent at 25 °C for 48 h. [b] Determined by crude ^{1}H NMR. [c] Isolated yields. [d] Determined by chiral HPLC.

IV. Silver-catalyzed desymmetric [3+2] cycloaddition reaction



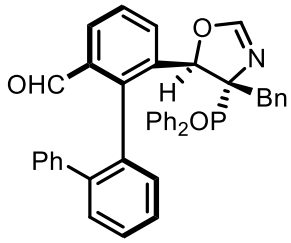
1 **2** (1.0 equiv) **3** **L4**

General procedure. To a 10 mL vial charged with **L4** (5.81 mg, 0.010 mmol, 10 mol%) and Ag_2O (1.16 mg, 0.005 mmol, 5 mol%) was added anhydrous EtOAc (1.0 mL, 0.1 M). The mixture was stirred at ambient temperature for 5 min, then prochiral biaryl dialdehyde **1** (0.10 mmol) and activated isocyanide **2** (0.10 mmol) were added

successively in one portion. The reaction mixture was stirred at 25 ℃ for the given time, then concentrated and purified by flash column chromatography to afford **3**.

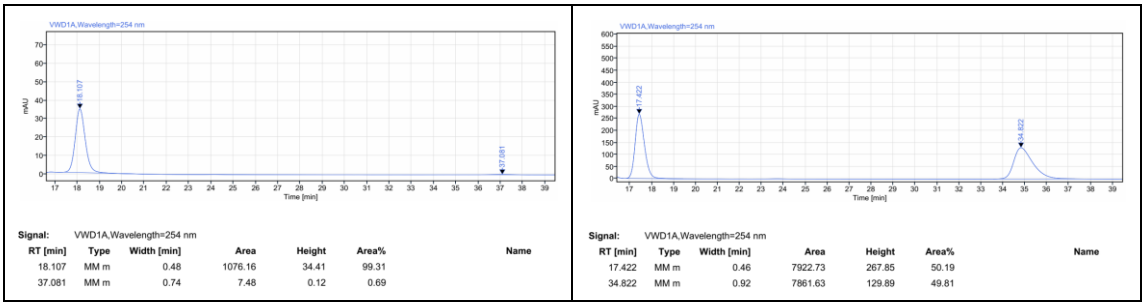
V. Characterization of compounds 3

(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-[1,1':2', 1''-terphenyl]-2-carbaldehyde (3a)

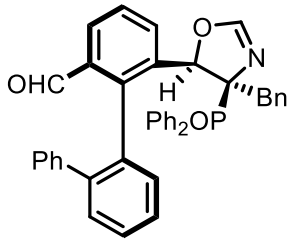


3a

With **2a** (1.0 equiv) for 48 h. 8:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 46.9 mg, 76% yield. **MP**: 227-228 ℃; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.66 (s, 1H), 7.84-7.75 (m, 4H), 7.73-7.65 (m, 2H), 7.55-7.45 (m, 3H), 7.40-7.15 (m, 9H), 7.06-6.95 (m, 5H), 6.84-6.76 (m, 3H), 6.69-6.64 (m, 2H), 5.58 (d, *J* = 19.2 Hz, 1H), 2.94 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.81 (dd, *J* = 20.7, 14.1 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 191.4, 157.1 (d, *J* = 7.7 Hz), 143.1, 140.6, 139.9, 135.2 (d, *J* = 4.5 Hz), 135.1, 134.1 (d, *J* = 7.6 Hz), 133.2, 132.5, 132.0 (d, *J* = 7.7 Hz), 131.8, 131.6, 131.53, 131.45, 131.1, 130.8, 130.5, 129.6, 129.0, 128.6, 128.5, 128.0 (d, *J* = 10.8 Hz), 127.7, 127.6 (d, *J* = 11.5 Hz), 127.4, 126.9, 126.8, 126.1, 79.9 (d, *J* = 7.7 Hz), 78.9 (d, *J* = 81.0 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 26.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{32}NNaO_3P$ 640.2012; Found 640.2026. **Optical Rotation**: $[\alpha]^{20}_D$ = +128.4 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IF column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 18.1 min for major isomer, t_R = 37.1 min for minor isomer).

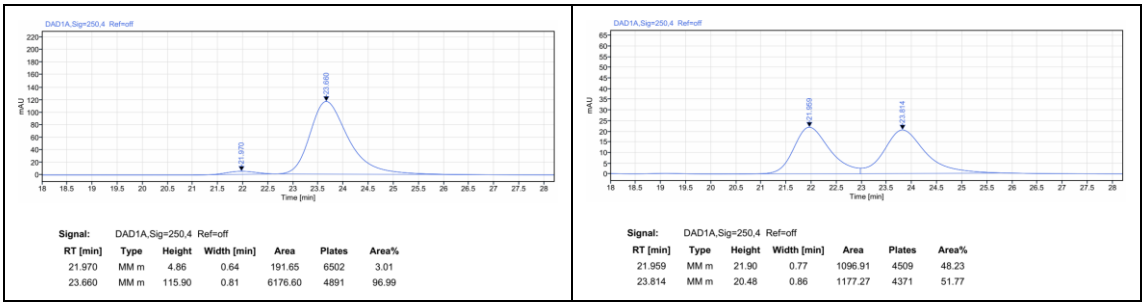


(*S*)-6-((4*S*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (3a')



3a'

The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 5.9 mg, 10% yield. **MP**: 137-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.62 (d, *J* = 7.5 Hz, 1H), 8.33-8.24 (m, 2H), 7.77-7.66 (m, 4H), 7.60 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.53 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49-7.40 (m, 4H), 7.30-7.24 (m, 2H), 7.19-7.08 (m, 3H), 7.01-6.90 (m, 4H), 6.68-6.63 (m, 2H), 6.45 (t, *J* = 7.7 Hz, 1H), 6.40-6.35 (m, 2H), 6.21 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.50 (d, *J* = 13.9 Hz, 1H), 3.04-2.91 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.2, 155.8 (d, *J* = 13.6 Hz), 144.2, 142.4, 140.2, 134.9 (d, *J* = 6.2 Hz), 134.1 (d, *J* = 7.8 Hz), 133.9 (d, *J* = 12.6 Hz), 133.3 (d, *J* = 6.2 Hz), 133.0 (d, *J* = 16.0 Hz), 132.4 (d, *J* = 7.8 Hz), 132.0, 131.9, 131.6, 131.4, 130.0, 129.2, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.84, 127.79, 127.1, 126.8, 126.7, 126.4, 81.4 (d, *J* = 4.2 Hz), 78.5 (d, *J* = 87.0 Hz), 40.5 (d, *J* = 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 24.3; **HRMS** (ESI) m/z: $[M+K]^+$ Calcd for $C_{41}H_{32}KNO_3P$ 656.1751; Found 656.1755. **Optical Rotation**: $[\alpha]^{20}_D$ = -52.9 (c = 0.4, CH_2Cl_2). 97:3 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 22.0 min for minor isomer, t_R = 23.7 min for major isomer).



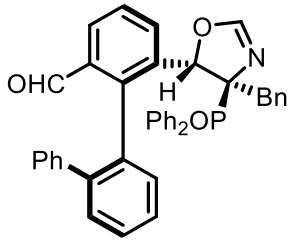
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Height	Width [min]	Area	Plates	Area%
21.970	MM m	4.86	0.64	191.65	6502	3.01
23.660	MM m	115.90	0.81	6176.60	4891	96.99

Signal: DAD1A,Sig=250,4 Ref=off

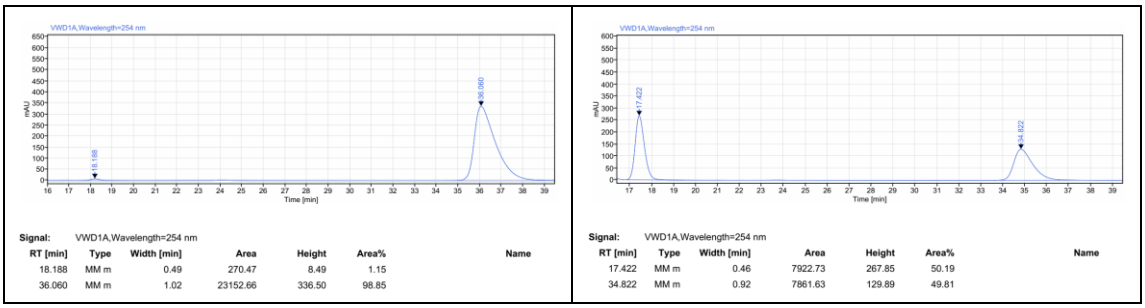
RT [min]	Type	Height	Width [min]	Area	Plates	Area%
21.959	MM m	21.90	0.77	1096.91	4509	48.23
23.814	MM m	20.48	0.86	1177.27	4371	51.77

(*R*)-6-((4*S*,5*S*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (*ent*-3a)



***ent*-3a**

With **2a** (1.0 equiv) and **L6** for 48 h. 8:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 43.8 mg, 71% yield. **Optical Rotation**: $[\alpha]^{20}_D$ = -126.1 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IF column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 18.2 min for minor isomer, t_R = 36.1 min for major isomer).



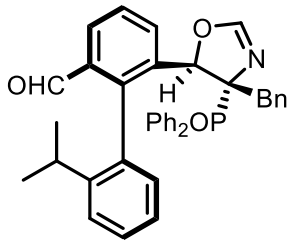
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
18.188	MM m	0.49	270.47	8.49	1.15	
36.060	MM m	1.02	23152.66	336.50	98.85	

Signal: VWD1A,Wavelength=254 nm

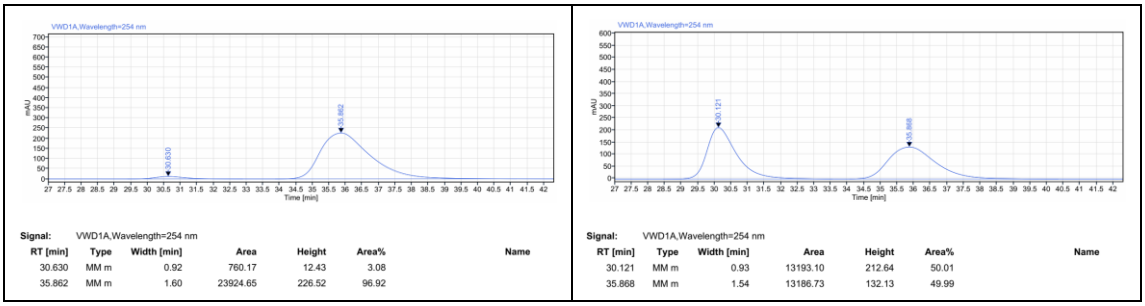
RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.422	MM m	0.46	7922.73	267.85	50.19	
34.822	MM m	0.92	7861.63	129.89	49.81	

(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-isopropyl-[1,1'-biphenyl]-2-carbaldehyde (3b)

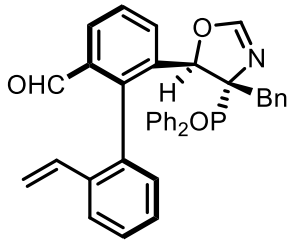


3b

With **2a** (1.0 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White wax, 32.2 mg, 55% yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.52 (s, 1H), 7.89 (dd, J = 7.2, 1.7 Hz, 1H), 7.82-7.75 (m, 2H), 7.71-7.65 (m, 1H), 7.61-7.52 (m, 3H), 7.51-7.38 (m, 4H), 7.30-7.22 (m, 3H), 7.19-7.13 (m, 2H), 7.08-7.00 (m, 4H), 6.84-6.77 (m, 3H), 5.52 (d, J = 19.4 Hz, 1H), 2.97-2.84 (m, 2H), 2.20-2.08 (m, 1H), 0.84 (d, J = 6.9 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 191.3, 157.0 (d, J = 7.7 Hz), 145.7, 143.6, 135.4 (d, J = 11.2 Hz), 135.2 (d, J = 4.8 Hz), 134.6, 134.0, 132.4, 132.0, 131.8 (d, J = 7.7 Hz), 131.5 (d, J = 6.5 Hz), 131.4 (d, J = 6.8 Hz), 131.2, 130.7, 130.3, 129.4, 129.1, 128.0, 127.9, 127.6, 127.5, 126.9, 126.7, 126.1, 125.3, 79.7 (d, J = 7.6 Hz), 78.8 (d, J = 81.2 Hz), 29.6, 23.8, 22.5; **^{31}P NMR** (162 MHz, DMSO-d_6): δ 26.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{34}NNaO_3P$ 606.2169; Found 606.2164. **Optical Rotation**: $[\alpha]^{20}_D$ = +147.4 (c = 0.4, CH_2Cl_2). 97:3 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 30.6 min for minor isomer, t_R = 35.9 min for major isomer).

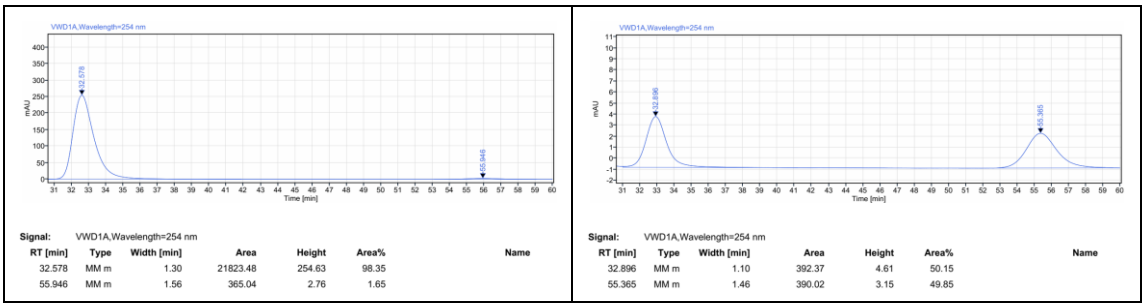


(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-vinyl-[1,1'-biphenyl]-2-carbaldehyde (3c)

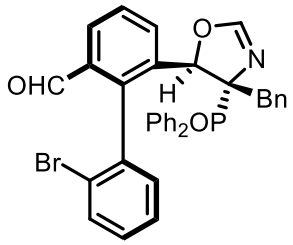


3c

With **2a** (1.2 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). White solid, 26.6 mg, 47% yield. **MP**: 170-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.61 (d, *J* = 0.8 Hz, 1H), 8.00-7.93 (m, 3H), 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.79-7.67 (m, 2H), 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42-7.36 (m, 1H), 7.30-7.22 (m, 6H), 7.20-7.14 (m, 3H), 7.02-6.97 (m, 2H), 6.92 (d, *J* = 3.7 Hz, 1H), 6.88-6.81 (m, 3H), 6.11 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.73 (d, *J* = 19.1 Hz, 1H), 5.61 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.04 (dd, *J* = 11.0, 1.1 Hz, 1H), 3.18 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.94 (dd, *J* = 18.2, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.0, 156.0 (d, *J* = 7.5 Hz), 143.4, 136.4, 135.7 (d, *J* = 11.6 Hz), 135.5 (d, *J* = 6.2 Hz), 134.7, 134.2, 134.0, 133.1, 132.5 (d, *J* = 8.0 Hz), 132.24, 132.16 (d, *J* = 8.3 Hz), 131.7 (d, *J* = 2.8 Hz), 131.21, 131.16 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 95.3 Hz), 129.5, 129.2 (d, *J* = 92.3 Hz), 129.0, 128.0, 127.9, 127.80, 127.75, 127.4, 126.4, 125.3, 116.5, 80.7 (d, *J* = 6.8 Hz), 79.4 (d, *J* = 80.3 Hz), 38.6 (d, *J* = 3.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.8; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{30}NNaO_3P$ 590.1856; Found 590.1886. **Optical Rotation**: $[\alpha]^{20}_D$ = +104.0 (c = 0.1, CH_2Cl_2). 98:2 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 32.6 min for major isomer, t_R = 55.9 min for minor isomer).

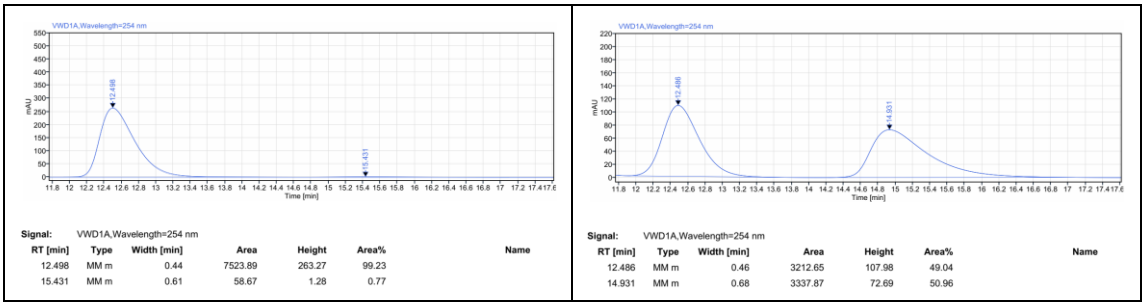


(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-brom o-[1,1'-biphenyl]-2-carbaldehyde (3d)

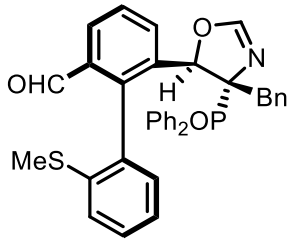


3d

With **2a** (1.2 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). White solid, 24.4 mg, 39% yield. **MP**: 121-122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 8.01-7.94 (m, 3H), 7.89 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85-7.80 (m, 1H), 7.65-7.56 (m, 2H), 7.46-7.40 (m, 1H), 7.34-7.24 (m, 6H), 7.22-7.15 (m, 3H), 7.01-6.96 (m, 2H), 6.93 (d, *J* = 3.7 Hz, 1H), 6.89-6.81 (m, 3H), 5.76 (d, *J* = 19.1 Hz, 1H), 3.17 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.94 (dd, *J* = 18.2, 14.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 191.4, 156.0 (d, *J* = 7.7 Hz), 143.3, 135.40 (d, *J* = 3.4 Hz), 135.35, 135.3, 134.9, 134.5, 134.2, 132.6, 132.4 (d, *J* = 7.8 Hz), 132.1 (d, *J* = 8.3 Hz), 131.9 (d, *J* = 2.8 Hz), 131.24, 131.20, 130.93 (d, *J* = 95.4 Hz), 130.85, 129.1 (d, *J* = 92.4 Hz), 128.7, 128.3, 128.2, 127.9 (d, *J* = 5.1 Hz), 127.8 (d, *J* = 5.7 Hz), 127.4, 126.5, 123.5, 80.9 (d, *J* = 6.8 Hz), 79.4 (d, *J* = 80.3 Hz), 38.7 (d, *J* = 3.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{27}BrNNaO_3P$ 642.0804; Found 642.0809. **Optical Rotation**: $[\alpha]^{20}_D$ = +121.8 (c = 0.5, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 12.5 min for major isomer, t_R = 15.4 min for minor isomer).



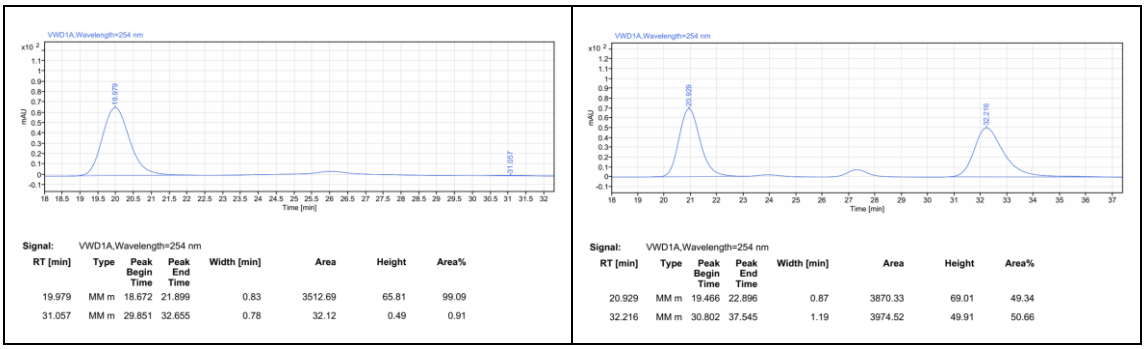
(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-(methylthio)-[1,1'-biphenyl]-2-carbaldehyde (3e)



3e

With **2a** (1.0 equiv) for 24 h. 5:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 22.5 mg, 38% yield. **MP**: 124-125 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.02-7.94 (m, 3H), 7.75-7.65 (m, 2H), 7.55 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.46-7.38 (m, 2H), 7.36-7.15 (m, 9H), 7.06-7.00 (m, 2H), 6.97 (d, *J* = 3.7 Hz, 1H), 6.91-6.82 (m, 3H), 5.75 (d, *J* = 19.3 Hz, 1H), 3.20 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.99 (dd, *J* = 18.8, 14.4 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.0, 156.1 (d, *J* = 7.5 Hz), 142.6, 137.9, 135.8 (d, *J* = 11.5 Hz), 135.5 (d, *J* = 5.9 Hz), 134.6, 134.3, 133.3, 132.5 (d, *J* = 7.9 Hz), 132.2 (d, *J* = 8.3 Hz), 131.8, 131.7 (d, *J* = 2.7 Hz), 131.3, 131.2 (d, *J* = 95.3 Hz), 131.1 (d, *J* = 2.9 Hz), 129.9, 129.5 (d, *J* = 92.1 Hz), 128.2, 128.0, 127.8 (d, *J* = 6.8 Hz), 127.7 (d, *J* = 6.5 Hz), 127.4, 126.5, 125.9, 124.0, 81.0 (d, *J* = 7.0 Hz), 79.4 (d, *J* = 80.5 Hz), 38.9 (d, *J* = 2.9 Hz), 15.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.6; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{30}NNaO_3PS$ 610.1576; Found 610.1578. **Optical Rotation**: $[\alpha]^{20}_D$ = +149.4 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 20.0 min for major isomer, t_R = 31.1 min for minor

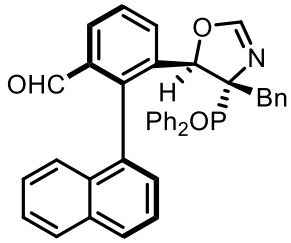
isomer).



Signal: VWD1A,Wavelength=254 nm							
RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
19.979	MM m	18.672	21.899	0.83	3512.69	65.81	99.09
31.057	MM m	29.851	32.655	0.78	32.12	0.49	0.91

Signal: VWD1A,Wavelength=254 nm							
RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
20.929	MM m	19.466	22.896	0.87	3870.33	69.01	49.34
32.216	MM m	30.802	37.545	1.19	3974.52	49.91	50.66

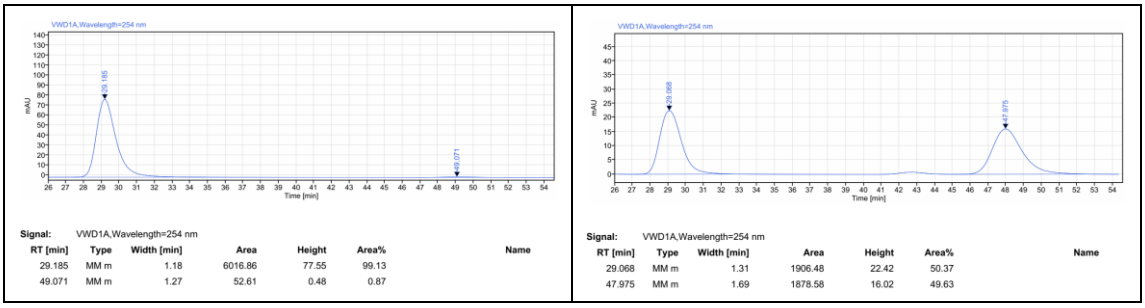
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(naphthalen-1-yl)benzaldehyde (3f)



3f

With **2a** (1.0 equiv) for 48 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 43.1 mg, 73% yield. **MP**: 118-119 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.42 (d, J = 0.7 Hz, 1H), 8.31-8.23 (m, 2H), 7.95 (dd, J = 7.7, 1.4 Hz, 1H), 7.88 (dd, J = 8.3, 7.0 Hz, 1H), 7.80-7.73 (m, 3H), 7.69-7.64 (m, 1H), 7.54-7.48 (m, 1H), 7.44-7.35 (m, 3H), 7.31-7.13 (m, 4H), 7.03 (dd, J = 8.5, 1.1 Hz, 1H), 6.98-6.94 (m, 2H), 6.92-6.86 (m, 2H), 6.85-6.78 (m, 3H), 6.63-6.56 (m, 2H), 5.39 (d, J = 19.3 Hz, 1H), 2.98 (dd, J = 14.2, 7.4 Hz, 1H), 2.81 (dd, J = 19.4, 14.1 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 191.3, 156.9 (d, J = 7.7 Hz), 141.9, 136.3 (d, J = 11.5 Hz), 135.2 (d, J = 5.6 Hz), 134.8, 134.0, 133.3, 131.6, 131.51 (d, J = 93.7 Hz), 131.49, 131.4 (d, J = 5.3 Hz), 131.3, 131.0, 130.9, 130.3, 129.2 (d, J = 90.9 Hz), 128.9, 128.7, 128.2, 127.7 (d, J = 3.5 Hz), 127.6, 127.4 (d, J = 10.7 Hz), 127.1, 126.9, 126.6, 126.1 (d, J = 8.7 Hz), 124.4, 79.7 (d, J = 7.2 Hz), 78.8 (d, J = 80.6 Hz), 38.3; **^{31}P NMR** (162 MHz, DMSO-d_6): δ 27.3; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{30}NNaO_3P$ 614.1856; Found 614.1859. **Optical Rotation**: $[\alpha]^{20}_D$ = +61.8 (c = 0.3, CH_2Cl_2). 99:1 er (HPLC

condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 29.2 min for major isomer, t_R = 49.1 min for minor isomer).



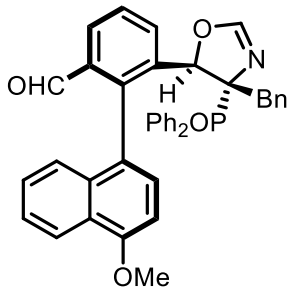
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
29.185	MM m	1.18	6016.86	77.55	99.13	
49.071	MM m	1.27	52.61	0.48	0.87	

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
29.068	MM m	1.31	1906.48	22.42	50.37	
47.975	MM m	1.69	1878.58	16.02	49.63	

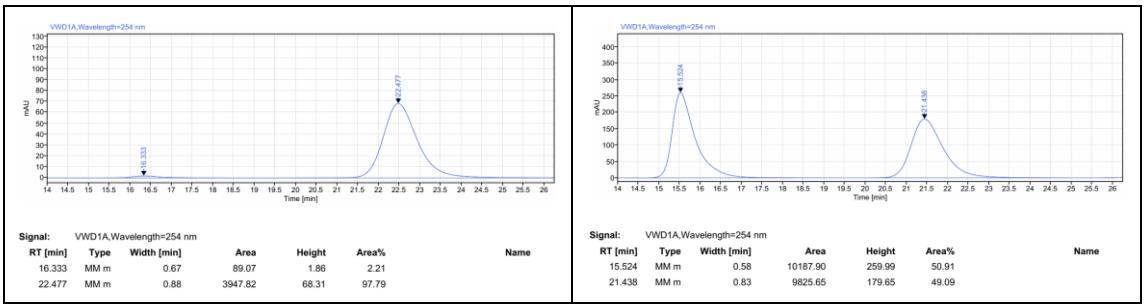
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(4-methoxynaphthalen-1-yl)benzaldehyde (3g)



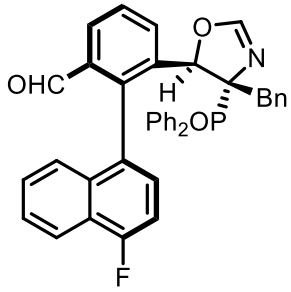
3g

With **2a** (1.2 equiv) for 24 h. 5:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). White solid, 38.4 mg, 62% yield. **MP**: 130-131 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.54 (d, *J* = 0.8 Hz, 1H), 8.58-8.54 (m, 1H), 8.01 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.93-7.86 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.61-7.55 (m, 1H), 7.39-7.29 (m, 3H), 7.27-7.21 (m, 2H), 7.19-7.11 (m, 3H), 7.08-7.01 (m, 3H), 6.91-6.82 (m, 6H), 6.77-6.70 (m, 2H), 5.65 (d, *J* = 19.4 Hz, 1H), 4.23 (s, 3H), 3.20 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.99 (dd, *J* = 18.7, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.5, 156.4, 155.9 (d, *J* = 7.7 Hz), 143.3, 136.7 (d, *J* = 11.3 Hz), 135.9, 135.5 (d, *J* = 5.9 Hz), 134.1, 133.1, 132.2 (d, *J* = 8.4 Hz), 132.0, 131.9 (d, *J* = 4.0 Hz), 131.4 (d, *J* = 2.5 Hz), 131.3, 131.11 (d, *J* = 95.1 Hz), 131.09 (d, *J* = 2.9 Hz), 128.8 (d, *J* = 92.6 Hz), 128.0, 127.8 (d, *J* = 2.3 Hz), 127.7 (d, *J* = 3.3 Hz), 127.61, 127.55, 127.4, 126.5, 125.9,

125.6, 125.1, 122.9, 122.7, 104.5, 80.9 (d, J = 7.1 Hz), 79.3 (d, J = 80.5 Hz), 56.1, 38.7 (d, J = 3.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{32}NNaO_4P$ 644.1961; Found 644.1961. **Optical Rotation**: $[\alpha]^{20}_D$ = +81.1 (c = 0.4, CH_2Cl_2). 98:2 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 16.3 min for minor isomer, t_R = 22.5 min for major isomer).



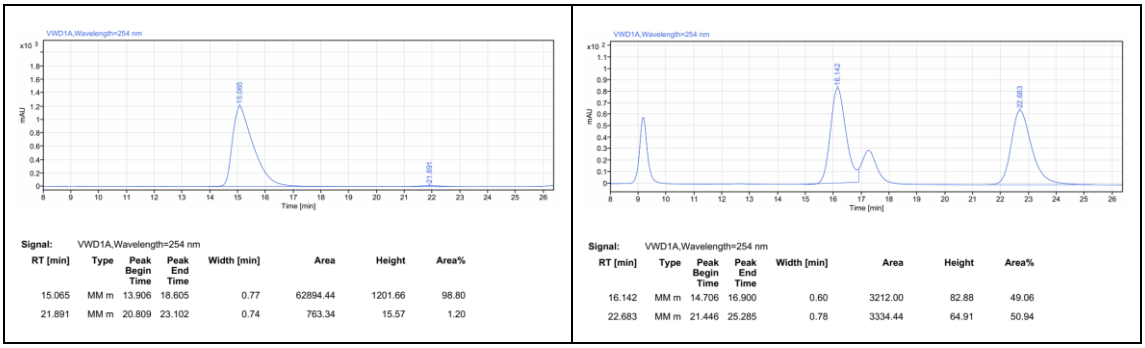
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(4-fluoronaphthalen-1-yl)benzaldehyde (3h)



3h

With **2a** (1.2 equiv) for 24 h. 5:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). White solid, 34.7 mg, 57% yield. **MP**: 200-201 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.03 (dd, J = 7.7, 1.4 Hz, 1H), 7.94-7.87 (m, 2H), 7.72-7.63 (m, 3H), 7.45-7.35 (m, 2H), 7.28-7.23 (m, 2H), 7.21-7.12 (m, 4H), 7.02-6.98 (m, 2H), 6.92-6.82 (m, 6H), 6.79-6.72 (m, 2H), 5.56 (d, J = 19.3 Hz, 1H), 3.19 (dd, J = 14.4, 7.9 Hz, 1H), 2.96 (dd, J = 18.3, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 191.8, 159.5 (d, J = 254.2 Hz), 155.8 (d, J = 7.7 Hz), 142.1, 136.6 (d, J = 11.4 Hz), 135.6, 135.4 (d, J = 6.1 Hz), 134.1, 133.5 (d, J = 4.8

Hz), 132.1 (d, J = 8.5 Hz), 131.9 (d, J = 8.2 Hz), 131.6 (d, J = 8.9 Hz), 131.4 (d, J = 2.8 Hz), 131.23, 131.18 (d, J = 2.9 Hz), 130.9 (d, J = 95.3 Hz), 128.8 (d, J = 92.5 Hz), 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 126.73 (d, J = 4.5 Hz), 126.67, 126.5, 125.3 (d, J = 2.6 Hz), 124.1 (d, J = 16.5 Hz), 121.4 (d, J = 5.3 Hz), 110.4 (d, J = 20.3 Hz), 80.7 (d, J = 7.0 Hz), 79.4 (d, J = 80.4 Hz), 38.6 (d, J = 3.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ -120.8; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.8; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{29}FNNaO_3P$ 632.1761; Found 632.1759. **Optical Rotation**: $[\alpha]^{20}_D$ = +53.0 (c = 0.7, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 15.1 min for major isomer, t_R = 21.9 min for minor isomer).



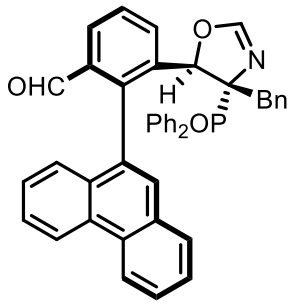
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
15.065	MM m	13.906	18.605	0.77	62894.44	1201.66	98.80
21.891	MM m	20.809	23.102	0.74	763.34	15.57	1.20

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
16.142	MM m	14.706	16.900	0.60	3212.00	82.88	49.06
22.683	MM m	21.446	25.285	0.78	3334.44	64.91	50.94

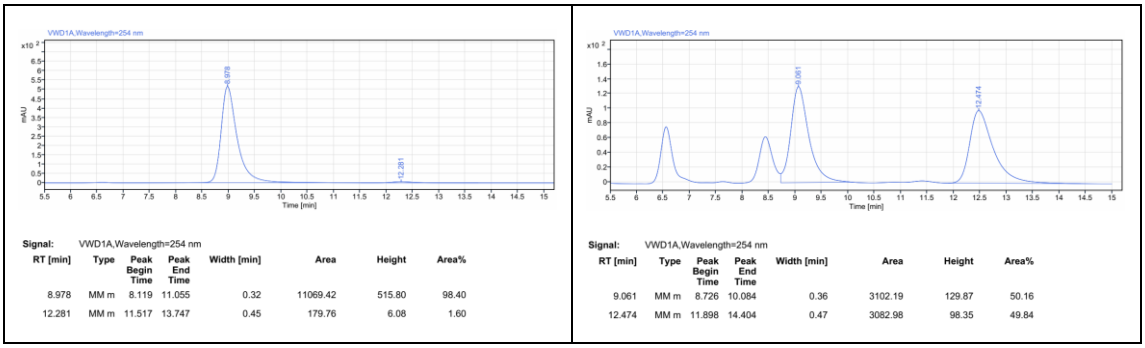
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(phenanthren-9-yl)benzaldehyde (3i)



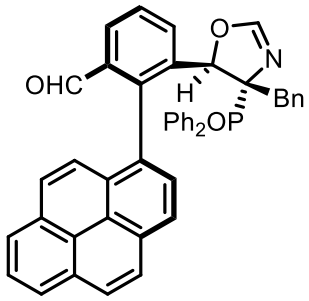
3i

With **2a** (1.2 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). White solid, 32.9 mg, 51% yield. **MP**: 155-156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 9.00-8.95 (m, 1H), 8.91 (d, J = 8.1 Hz, 1H), 8.23 (dd, J = 7.7,

1.6 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.5 Hz, 1H), 8.00 (s, 1H), 7.87-7.74 (m, 5H), 7.48-7.38 (m, 2H), 7.33 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.24-7.18 (m, 2H), 7.16-7.08 (m, 3H), 7.05-7.01 (m, 2H), 6.95-6.79 (m, 6H), 6.69-6.63 (m, 2H), 5.72 (d, *J* = 19.2 Hz, 1H), 3.28 (dd, *J* = 14.4, 8.3 Hz, 1H), 3.06 (dd, *J* = 17.9, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.1, 155.7 (d, *J* = 7.7 Hz), 142.9, 136.6 (d, *J* = 11.2 Hz), 135.7, 135.6 (d, *J* = 6.0 Hz), 134.3, 132.9, 132.2 (d, *J* = 8.5 Hz), 131.9 (d, *J* = 8.1 Hz), 131.6, 131.4, 131.32, 131.26 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 95.2 Hz), 130.8, 130.6, 129.9, 129.3, 129.0 (d, *J* = 92.6 Hz), 128.1 (d, *J* = 3.4 Hz), 127.8, 127.7 (d, *J* = 2.8 Hz), 127.6, 127.5, 127.4, 127.1, 126.5, 126.3, 123.4, 122.7, 81.0 (d, *J* = 7.1 Hz), 79.3 (d, *J* = 80.3 Hz), 38.6 (d, *J* = 3.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{43}H_{33}NO_3P$ 642.2193; Found 642.2198. **Optical Rotation**: $[\alpha]^{20}_D$ = +59.7 (c = 0.8, CH_2Cl_2). 98:2 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 9.0 min for major isomer, t_R = 12.3 min for minor isomer).



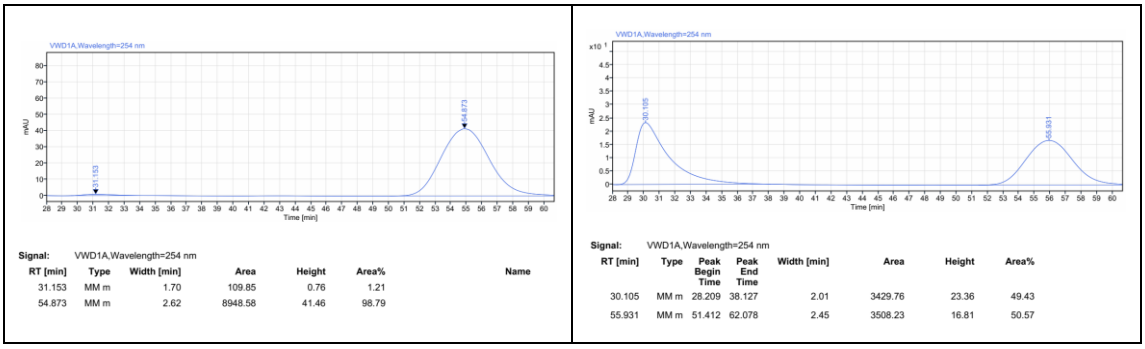
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(pyren-1-yl)benzaldehyde (3j)



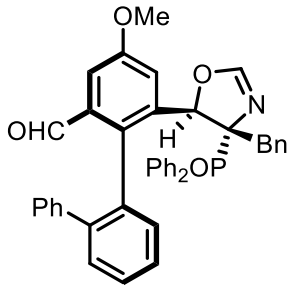
3j

With **2a** (1.2 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude

reaction mixture was purified by preparative HPLC (gradient (0.1% HCOOH in H_2O/MeCN) 0 min; 40:60, 15 min; 0:100, 25 min; 0:100, 25.1 min; 40:60, 30 min; 40:60). Yellow solid, 30.9 mg, 46% yield. **MP**: 158-159 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.53 (d, *J* = 0.8 Hz, 1H), 8.70 (d, *J* = 7.8 Hz, 1H), 8.39-8.33 (m, 2H), 8.27 (d, *J* = 8.3 Hz, 2H), 8.22 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.15-8.10 (m, 2H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.78-7.71 (m, 2H), 7.51-7.46 (m, 1H), 7.42-7.37 (m, 2H), 7.20-7.14 (m, 1H), 7.09-7.02 (m, 4H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.89-6.82 (m, 3H), 6.76-6.70 (m, 1H), 6.31-6.24 (m, 2H), 6.09-6.03 (m, 2H), 5.60 (d, *J* = 19.5 Hz, 1H), 3.19 (dd, *J* = 14.3, 7.2 Hz, 1H), 3.01 (dd, *J* = 19.8, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 191.9, 155.9 (d, *J* = 7.7 Hz), 143.7, 136.5 (d, *J* = 11.4 Hz), 135.6, 135.4 (d, *J* = 5.5 Hz), 134.3, 132.0, 131.92, 131.89, 131.7, 131.5, 131.44, 131.41, 131.0, 130.9 (d, *J* = 3.2 Hz), 130.8, 130.7, 129.3, 129.2, 128.8, 128.4, 128.23, 128.20, 128.17, 128.1, 127.6 (d, *J* = 11.6 Hz), 127.4, 127.1 (d, *J* = 11.2 Hz), 126.6 (d, *J* = 3.8 Hz), 126.0, 125.8, 125.5, 124.8 (d, *J* = 9.9 Hz), 124.0, 81.0 (d, *J* = 7.5 Hz), 79.4 (d, *J* = 80.9 Hz), 39.2 (d, *J* = 2.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.8; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{45}H_{33}NO_3P$ 666.2193; Found 666.2189. **Optical Rotation**: $[\alpha]^{20}_D$ = -15.1 (c = 0.4, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 31.2 min for minor isomer, t_R = 54.9 min for major isomer).

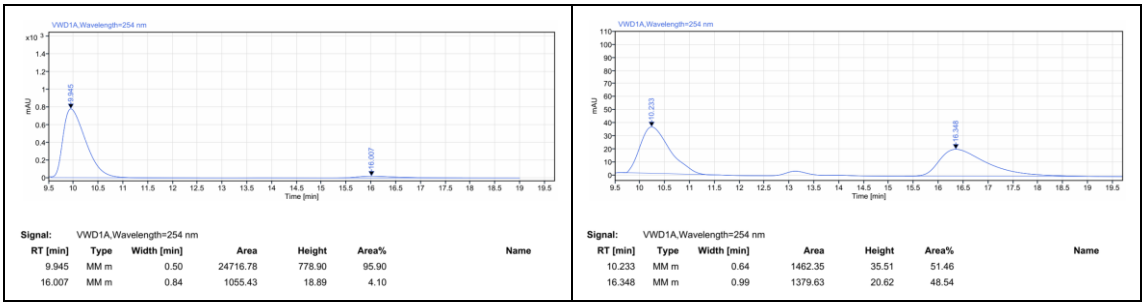


(*S*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-4-methoxy-[1,1':2',1''-terphenyl]-2-carbaldehyde (3k)



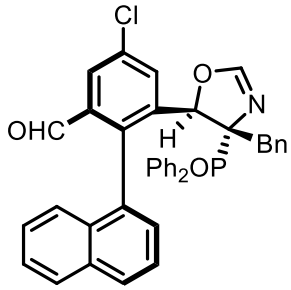
3k

With **2a** (1.0 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 27.0 mg, 42% yield. **MP**: 104-105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.01-7.94 (m, 2H), 7.90-7.85 (m, 1H), 7.79-7.70 (m, 2H), 7.55 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46-7.41 (m, 1H), 7.35-7.25 (m, 6H), 7.21-7.15 (m, 2H), 7.08-6.97 (m, 5H), 6.90-6.82 (m, 4H), 6.74-6.70 (m, 2H), 6.51 (d, *J* = 2.8 Hz, 1H), 5.72 (d, *J* = 19.2 Hz, 1H), 3.66 (s, 3H), 3.20 (dd, *J* = 14.5, 8.2 Hz, 1H), 3.00 (dd, *J* = 18.1, 14.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.1, 158.5, 156.1 (d, *J* = 7.7 Hz), 142.1, 140.4, 137.2, 136.8 (d, *J* = 11.6 Hz), 135.8, 135.6 (d, *J* = 6.2 Hz), 133.9, 132.6 (d, *J* = 7.9 Hz), 132.2 (d, *J* = 8.5 Hz), 132.0, 131.8 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 95.1 Hz), 131.3, 131.2 (d, *J* = 2.9 Hz), 130.1, 129.7 (d, *J* = 91.9 Hz), 129.3, 129.1, 128.6, 128.0 (d, *J* = 11.1 Hz), 127.9, 127.8, 127.3, 126.8, 126.4, 121.8, 110.6, 80.7 (d, *J* = 7.2 Hz), 79.5 (d, *J* = 80.4 Hz), 55.4, 38.7 (d, *J* = 3.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.4; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{34}NNaO_4P$ 670.2118; Found 670.2116. **Optical Rotation**: $[\alpha]^{20}_D$ = +155.2 (c = 0.2, CH_2Cl_2). 96:4 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 9.9 min for major isomer, t_R = 16.0 min for minor isomer).



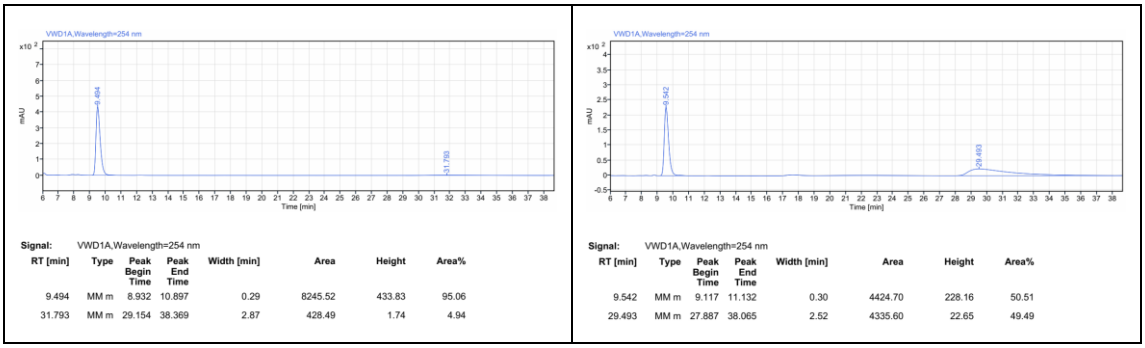
(*S*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-5-chloro

-2-(naphthalen-1-yl)benzaldehyde (3l)



3l

With **2a** (1.0 equiv) for 24 h. 1:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). Yellow solid, 27.3 mg, 44% yield. **MP**: 119-120 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 8.29-8.25 (m, 1H), 8.19-8.15 (m, 1H), 8.07-7.94 (m, 4H), 7.76 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.67-7.62 (m, 1H), 7.43-7.38 (m, 1H), 7.35-7.30 (m, 1H), 7.27-7.18 (m, 3H), 7.15 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.01-6.93 (m, 6H), 6.92-6.86 (m, 2H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.69-6.62 (m, 2H), 5.56 (d, *J* = 19.4 Hz, 1H), 3.30 (dd, *J* = 14.7, 8.8 Hz, 1H), 2.97 (dd, *J* = 14.7, 13.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 190.8, 155.5 (d, *J* = 7.5 Hz), 141.1, 138.6 (d, *J* = 11.9 Hz), 136.4, 135.3 (d, *J* = 8.4 Hz), 134.7, 134.1, 133.9, 132.5 (d, *J* = 8.4 Hz), 132.1 (d, *J* = 7.8 Hz), 131.9, 131.7, 131.58, 131.57 (d, *J* = 8.2 Hz), 130.7, 129.92, 129.87, 129.8, 129.1, 128.2 (d, *J* = 92.4 Hz), 128.1, 128.0 (d, *J* = 7.4 Hz), 127.7, 127.6, 127.5, 127.0, 126.7, 126.5, 125.0, 79.9 (d, *J* = 7.1 Hz), 79.4 (d, *J* = 79.3 Hz), 37.6 (d, *J* = 3.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.7; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{29}ClNNaO_3P$ 648.1466; Found 648.1461. **Optical Rotation**: $[\alpha]^{20}_D$ = +88.4 (c = 0.1, CH_2Cl_2). 95:5 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 9.5 min for major isomer, t_R = 31.8 min for minor isomer).



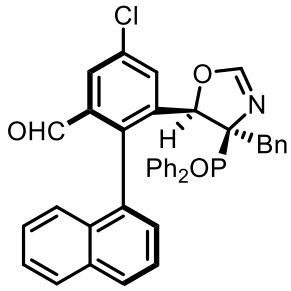
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
9.494	MM m	8.932	10.897	0.29	8245.52	433.83	95.06
31.793	MM m	29.154	38.369	2.87	428.49	1.74	4.94

Signal: VWD1A,Wavelength=254 nm

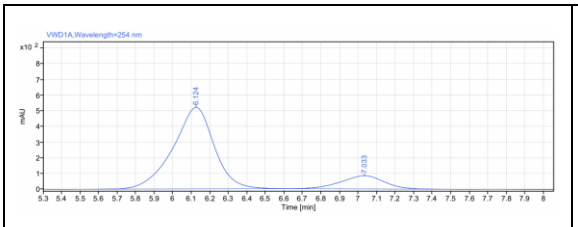
RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
9.542	MM m	9.117	11.132	0.30	4424.70	228.16	50.51
29.493	MM m	27.887	38.065	2.52	4335.60	22.65	49.49

(*S*)-3-((4*S*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-5-chloro-2-(naphthalen-1-yl)benzaldehyde (3l')



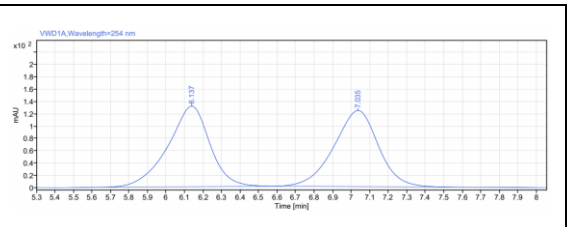
3l'

The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 20.9 mg, 33% yield. **MP**: 153-154 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.67 (dd, *J* = 7.1, 1.1 Hz, 1H), 8.32-8.25 (m, 2H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.80-7.74 (m, 2H), 7.58-7.39 (m, 7H), 7.35-7.30 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.92-6.87 (m, 2H), 6.66 (t, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 2.3 Hz, 1H), 5.78-5.73 (m, 2H), 5.17 (d, *J* = 15.2 Hz, 1H), 2.85 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.61 (dd, *J* = 13.6, 4.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 190.9, 155.3 (d, *J* = 12.9 Hz), 141.9, 138.4 (d, *J* = 6.2 Hz), 136.0, 133.9, 133.8, 133.6, 133.3 (d, *J* = 96.4 Hz), 133.2, 133.0, 132.7, 132.3 (d, *J* = 3.0 Hz), 132.1, 132.0 (d, *J* = 5.7 Hz), 131.9, 131.7, 131.3, 130.9, 129.6, 128.7 (d, *J* = 3.3 Hz), 128.6, 128.4, 127.7, 127.5, 127.4, 126.8, 126.6, 125.8, 124.9, 80.8 (d, *J* = 3.8 Hz), 78.4 (d, *J* = 85.6 Hz), 40.1 (d, *J* = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 24.2; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{29}ClNNaO_3P$ 648.1466; Found 648.1468. **Optical Rotation**: $[\alpha]^{20}_D$ = -61.7 (c = 0.3, CH_2Cl_2). 85:15 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 6.1 min for major isomer, t_R = 7.0 min for minor isomer).



Signal: VWD1A,Wavelength=254 nm

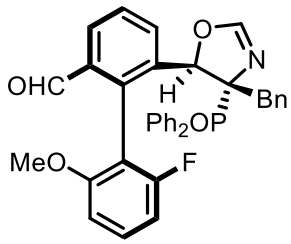
RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
6.124	MM m	5.588	6.594	0.23	8038.86	519.48	85.43
7.033	MM m	6.594	7.575	0.24	1371.06	84.24	14.57



Signal: VWD1A,Wavelength=254 nm

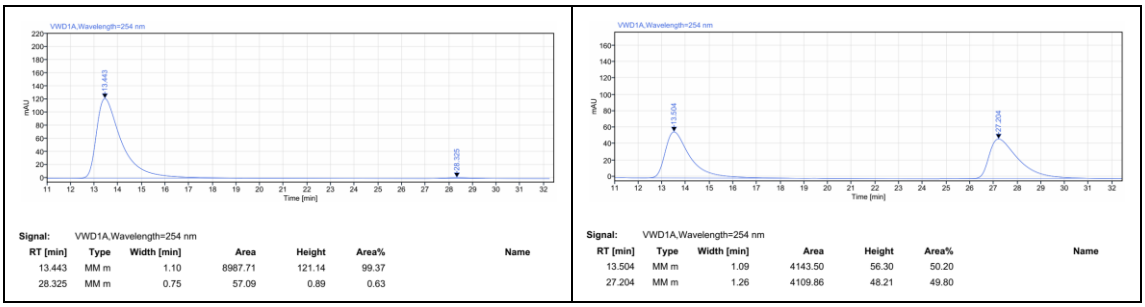
RT [min]	Type	Peak Begin Time	Peak End Time	Width [min]	Area	Height	Area%
6.137	MM m	5.559	6.611	0.23	2051.31	130.18	49.97
7.035	MM m	6.611	8.005	0.25	2053.98	122.88	50.03

(*R*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-fluoro-6'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (3m)

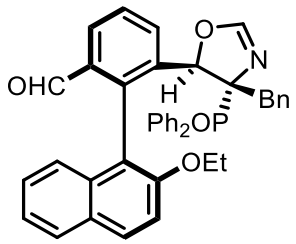


3m

With **2a** (1.0 equiv) for 24 h. >20:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 44.7 mg, 76% yield. **MP**: 101-102 ℃; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.63 (s, 1H), 7.88 (dd, J = 7.6, 1.4 Hz, 1H), 7.81-7.70 (m, 3H), 7.54-7.43 (m, 3H), 7.40-7.34 (m, 3H), 7.29-7.23 (m, 2H), 7.22-7.09 (m, 5H), 7.01-6.95 (m, 2H), 6.82-6.77 (m, 3H), 5.55 (d, J = 19.4 Hz, 1H), 3.98 (s, 3H), 2.95 (dd, J = 14.1, 5.9 Hz, 1H), 2.64 (dd, J = 21.2, 14.1 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 191.6, 159.4 (d, J = 6.5 Hz), 158.7 (d, J = 241.0 Hz), 157.0 (d, J = 7.7 Hz), 136.2 (d, J = 11.3 Hz), 135.4 (d, J = 5.4 Hz), 134.1, 134.0, 133.8, 131.9 (d, J = 7.7 Hz), 131.81 (d, J = 102.8 Hz), 131.76, 131.5, 131.4, 131.0, 130.7, 129.8 (d, J = 90.6 Hz), 128.4, 128.0, 127.9, 127.6 (d, J = 11.5 Hz), 127.0, 126.1, 110.1 (d, J = 19.6 Hz), 108.9, 107.3 (d, J = 21.9 Hz), 80.0 (d, J = 7.3 Hz), 79.2 (d, J = 80.9 Hz), 56.2, 37.5; **^{19}F NMR** (376 MHz, DMSO-d_6): δ -114.0; **^{31}P NMR** (162 MHz, DMSO-d_6): δ 26.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{29}FNNaO_4P$ 612.1710; Found 612.1708. **Optical Rotation**: $[\alpha]^{20}_D$ = +128.5 (c = 0.3, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak ID column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 13.4 min for major isomer, t_R = 28.3 min for minor isomer).

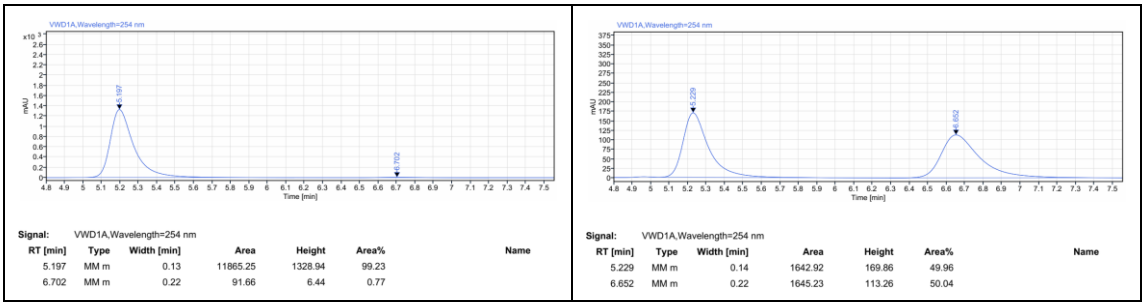


(*R*)-3-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2-(2-ethoxynaphthalen-1-yl)benzaldehyde (3n)

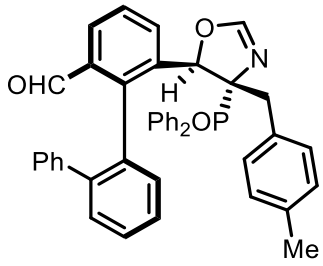


3n

With **2a** (1.0 equiv) for 16 h. >20:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 48.0 mg, 76% yield. **MP**: 258-259 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.63 (d, *J* = 0.8 Hz, 1H), 8.27 (d, *J* = 9.1 Hz, 1H), 8.09 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.04 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.99-7.92 (m, 2H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.49-7.44 (m, 1H), 7.33-7.24 (m, 3H), 7.21-7.11 (m, 4H), 7.02-6.96 (m, 3H), 6.90-6.83 (m, 6H), 6.68-6.61 (m, 2H), 5.56 (d, *J* = 19.6 Hz, 1H), 4.58-4.48 (m, 1H), 4.42-4.32 (m, 1H), 3.26 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.95 (dd, *J* = 16.3, 14.5 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.2, 156.2, 155.9 (d, *J* = 7.5 Hz), 139.8, 136.8 (d, *J* = 11.7 Hz), 136.0 (d, *J* = 7.2 Hz), 135.0, 134.2, 133.1, 132.4 (d, *J* = 8.4 Hz), 132.0 (d, *J* = 8.1 Hz), 131.4, 131.3 (d, *J* = 2.7 Hz), 131.2, 131.11 (d, *J* = 95.0 Hz), 131.07 (d, *J* = 2.9 Hz), 129.0, 128.8 (d, *J* = 91.7 Hz), 128.6, 127.8, 127.7, 127.62, 127.56, 127.5, 127.4, 127.3, 126.2, 123.7 (d, *J* = 5.6 Hz), 114.7, 80.7 (d, *J* = 6.7 Hz), 79.5 (d, *J* = 80.0 Hz), 64.2, 36.4 (d, *J* = 3.1 Hz), 15.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{34}NNaO_4P$ 658.2118; Found 658.2122. **Optical Rotation**: $[\alpha]^{20}_D$ = +6.7 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 5.2 min for major isomer, t_R = 6.7 min for minor isomer).



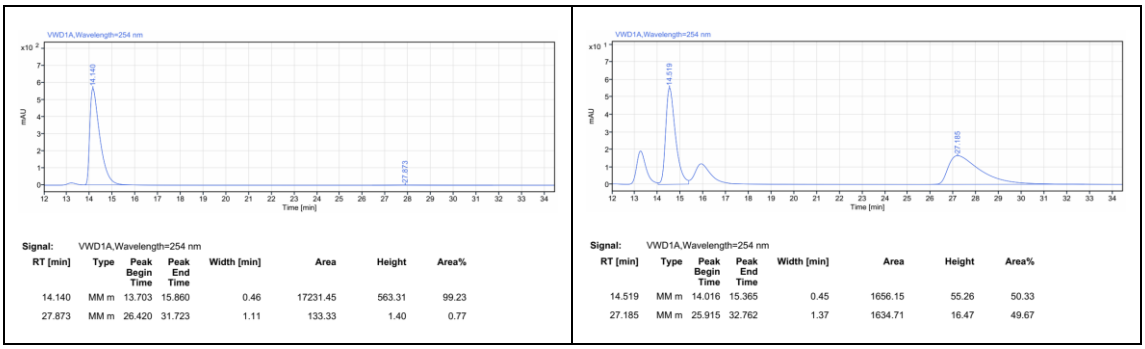
(*S*)-6-((4*R*,5*R*)-4-(diphenylphosphoryl)-4-(4-methylbenzyl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (3o)



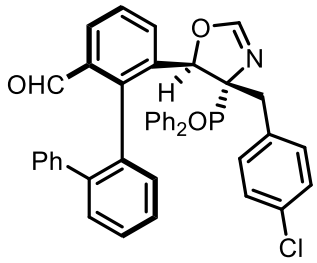
3o

With **2b** (1.0 equiv) for 48 h. 7:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 34.7 mg, 55% yield. **MP**: 282-283 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.72 (d, *J* = 0.8 Hz, 1H), 7.88-7.81 (m, 3H), 7.77-7.66 (m, 3H), 7.49 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.39-7.33 (m, 1H), 7.25-7.17 (m, 5H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.10-7.04 (m, 3H), 7.01-6.90 (m, 3H), 6.88-6.84 (m, 3H), 6.67-6.63 (m, 2H), 6.55 (d, *J* = 7.8 Hz, 2H), 5.71 (d, *J* = 19.3 Hz, 1H), 3.04 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.87 (dd, *J* = 20.6, 14.3 Hz, 1H), 2.02 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.1, 156.1 (d, *J* = 7.7 Hz), 144.2, 141.6, 140.2, 135.9, 135.4 (d, *J* = 11.3 Hz), 134.7, 134.2, 133.4, 132.5 (d, *J* = 8.0 Hz), 132.2, 132.1 (d, *J* = 10.4 Hz), 132.0 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 95.4 Hz), 131.3, 130.5 (d, *J* = 2.9 Hz), 129.9, 129.8 (d, *J* = 91.8 Hz), 129.3, 129.0, 128.6, 128.04, 128.01, 127.93, 127.85, 127.7, 127.5 (d, *J* = 10.6 Hz), 126.8, 80.9 (d, *J* = 7.2 Hz), 79.8 (d, *J* = 81.3 Hz), 39.0 (d, *J* = 2.9 Hz), 20.9; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.9; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}NO_3P$ 632.2349; Found 632.2355. **Optical Rotation**: $[\alpha]^{20}_D$ = +128.7 (c = 0.2, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 95:5, flow

rate = 1 mL/min, wavelength = 254 nm, t_R = 14.1 min for major isomer, t_R = 27.9 min for minor isomer).



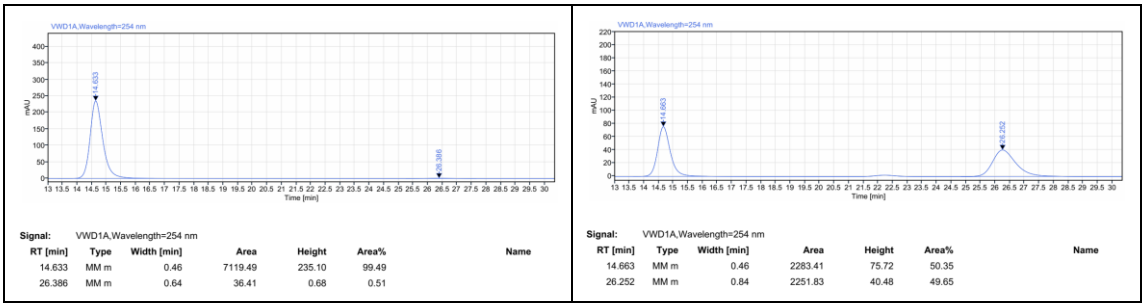
(*S*)-6-((4*R*,5*R*)-4-(4-chlorobenzyl)-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (3p)



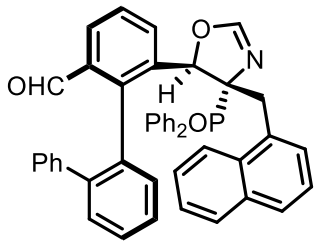
3p

With **2c** (1.0 equiv) for 24 h. 11:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 50.0 mg, 77% yield. **MP**: 191-192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (d, *J* = 0.8 Hz, 1H), 7.93-7.81 (m, 4H), 7.80-7.75 (m, 1H), 7.73 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.56-7.53 (m, 1H), 7.46-7.40 (m, 1H), 7.33-7.24 (m, 6H), 7.18-7.12 (m, 3H), 7.06-6.95 (m, 6H), 6.76-6.72 (m, 2H), 6.69-6.65 (m, 2H), 5.75 (d, *J* = 19.1 Hz, 1H), 3.04 (dd, *J* = 14.2, 6.3 Hz, 1H), 2.89 (dd, *J* = 22.0, 14.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.0, 156.3 (d, *J* = 7.6 Hz), 144.2, 141.7, 140.1, 135.2 (d, *J* = 11.2 Hz), 134.9, 134.0, 133.8 (d, *J* = 4.7 Hz), 133.3, 132.9, 132.5, 132.4 (d, *J* = 8.0 Hz), 132.1, 131.9 (d, *J* = 8.2 Hz), 131.8 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 95.1 Hz), 130.9 (d, *J* = 2.9 Hz), 130.0, 129.7 (d, *J* = 92.3 Hz), 129.4, 129.0, 128.6, 128.1 (d, *J* = 11.2 Hz), 127.9, 127.8, 127.7 (d, *J* = 9.5 Hz), 127.4, 126.9, 81.0 (d, *J* = 7.3 Hz), 79.5 (d, *J* = 81.3 Hz), 39.2 (d, *J* = 2.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}ClNO_3P$ 652.1803; Found 652.1799. **Optical Rotation**: $[\alpha]^{20}_D$ =

+33.0 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IA column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 14.6 min for major isomer, t_R = 26.4 min for minor isomer).



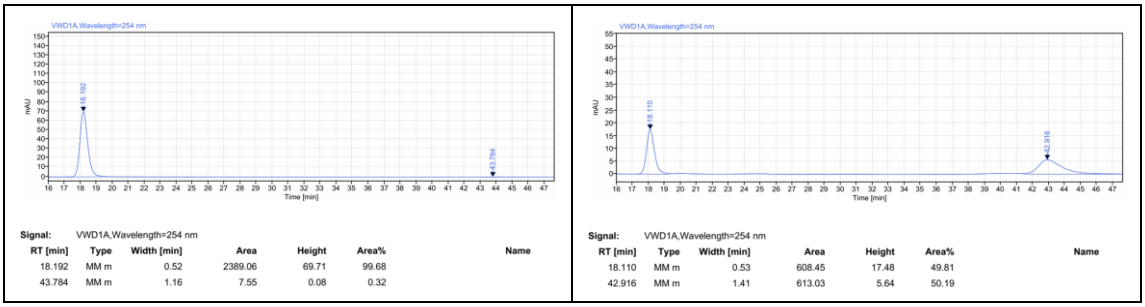
(*S*)-6-((4*R*,5*R*)-4-(diphenylphosphoryl)-4-(naphthalen-1-ylmethyl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (3q)



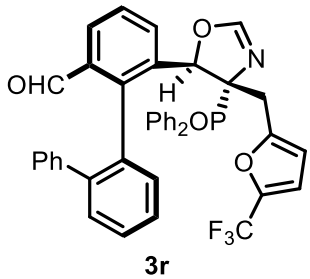
3q

With **2d** (1.0 equiv) for 72 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 39.4 mg, 59% yield. **MP**: 138-139 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.02-7.96 (m, 1H), 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.84-7.79 (m, 1H), 7.75 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.62-7.49 (m, 5H), 7.44-7.20 (m, 10H), 7.06-6.90 (m, 6H), 6.81-6.74 (m, 4H), 5.89 (d, *J* = 18.9 Hz, 1H), 3.54-3.42 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.0, 156.2 (d, *J* = 7.6 Hz), 144.2, 141.7, 140.2, 135.4 (d, *J* = 11.1 Hz), 134.9, 133.9, 133.5, 133.4, 133.0, 132.6 (d, *J* = 8.0 Hz), 132.2, 132.1 (d, *J* = 4.3 Hz), 131.6 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 8.6 Hz), 131.0, 130.6, 130.5 (d, *J* = 2.9 Hz), 130.0, 129.7 (d, *J* = 92.1 Hz), 129.4, 129.1, 128.7, 128.1, 127.91, 127.88, 127.80, 127.75, 127.5, 127.1, 126.9 (d, *J* = 7.4 Hz), 125.5, 125.2, 125.0, 124.6, 81.1 (d, *J* = 6.6 Hz), 80.2 (d, *J* = 81.4 Hz), 36.1 (d, *J* = 2.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{45}H_{35}NO_3P$

668.2349; Found 668.2350. **Optical Rotation**: $[\alpha]^{20}_{D}$ = +143.0 (c = 0.1, CH_2Cl_2). 99.5:0.5 er (HPLC condition: Chiralpak IF column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 18.2 min for major isomer, t_R = 43.8 min for minor isomer).



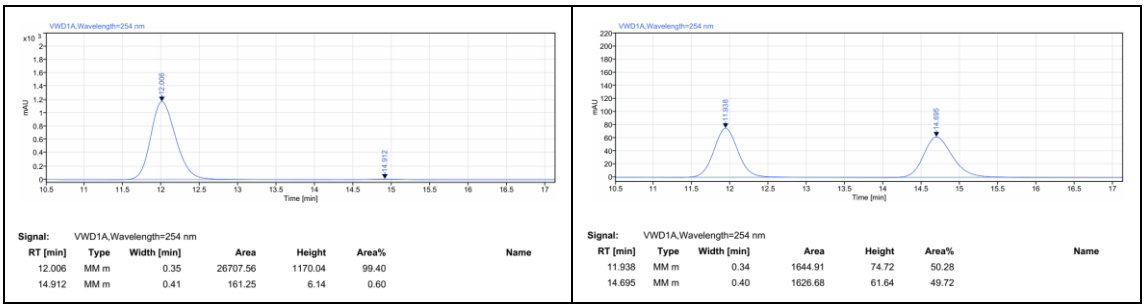
(*S*)-6-((4*R*,5*R*)-4-(diphenylphosphoryl)-4-((5-(trifluoromethyl)furan-2-yl)methyl)-4,5-dihydrooxazol-5-yl)-[1,1':2',1''-terphenyl]-2-carbaldehyde (3r)



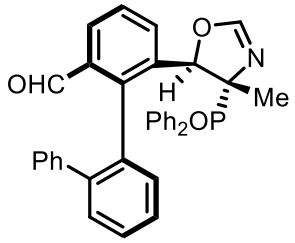
3r

With **2e** (1.0 equiv) for 48 h. 8:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White wax, 31.7 mg, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (d, *J* = 0.7 Hz, 1H), 8.13-8.05 (m, 2H), 7.89-7.82 (m, 2H), 7.77-7.73 (m, 1H), 7.65 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49-7.43 (m, 1H), 7.37-7.27 (m, 8H), 7.19 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.07-6.95 (m, 3H), 6.93 (d, *J* = 3.4 Hz, 1H), 6.71-6.66 (m, 2H), 6.19-6.15 (m, 1H), 5.92 (d, *J* = 3.4 Hz, 1H), 5.74 (d, *J* = 18.9 Hz, 1H), 3.21 (dd, *J* = 15.5, 8.2 Hz, 1H), 2.98 (dd, *J* = 18.2, 15.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.0, 156.7 (d, *J* = 7.6 Hz), 152.3 (d, *J* = 5.8 Hz), 144.2, 141.7, 140.6 (d, *J* = 42.4 Hz), 140.1, 134.9, 134.7 (d, *J* = 10.7 Hz), 133.7, 133.3, 132.6 (d, *J* = 8.0 Hz), 132.1, 132.0 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 8.5 Hz), 131.5 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 95.6 Hz), 130.1, 129.4, 129.1, 128.6, 128.5, 128.3, 128.2, 128.1 (d, *J* = 5.2 Hz), 127.9, 127.7, 126.9, 119.1 (d, *J* = 266.7 Hz), 112.0 (d, *J* = 3.1 Hz), 111.4, 80.5 (d, *J* = 7.0

Hz), 78.2 (d, J = 81.4 Hz), 31.8 (d, J = 3.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.4; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.1; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{29}F_3NNaO_4P$ 698.1679; Found 698.1678. **Optical Rotation**: $[\alpha]^{20}_D$ = +67.4 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IF column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 12.0 min for major isomer, t_R = 14.9 min for minor isomer).



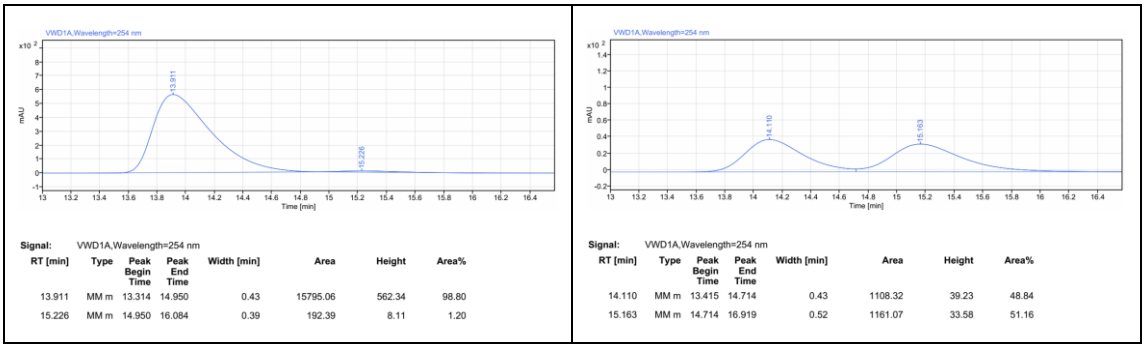
(*S*)-6-((4*R*,5*R*)-4-(diphenylphosphoryl)-4-methyl-4,5-dihydrooxazol-5-yl)-[1,1':2', 1''-terphenyl]-2-carbaldehyde (3s)



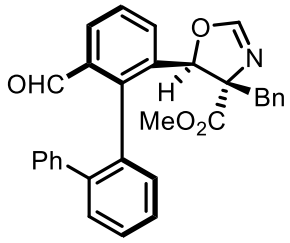
3s

With **2f** (1.0 equiv) for 24 h. 13:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 38.4 mg, 71% yield. **MP**: 106-107 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.71 (d, J = 0.8 Hz, 1H), 8.25-8.18 (m, 2H), 7.80 (dd, J = 7.7, 1.4 Hz, 1H), 7.76-7.71 (m, 1H), 7.67-7.64 (m, 1H), 7.53 (dd, J = 7.4, 1.4 Hz, 1H), 7.49-7.25 (m, 10H), 7.21-7.18 (m, 1H), 7.02-6.92 (m, 3H), 6.73-6.68 (m, 3H), 5.65 (d, J = 19.0 Hz, 1H), 1.26 (d, J = 14.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.1, 156.0 (d, J = 7.9 Hz), 144.2, 141.6, 140.2, 135.3 (d, J = 10.8 Hz), 134.9, 133.6 (d, J = 6.5 Hz), 132.7 (d, J = 4.1 Hz), 132.6 (d, J = 3.7 Hz), 132.2 (d, J = 2.8 Hz), 132.1, 132.0, 130.1 (d, J = 95.3 Hz), 129.9, 129.3, 129.2, 128.61 (d, J = 93.2 Hz), 128.59, 128.5, 128.4, 128.1, 127.93, 127.88, 127.7, 126.9, 79.8 (d, J = 7.1 Hz), 75.3 (d, J = 81.4 Hz), 19.3 (d, J =

2.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{28}NNaO_3P$ 564.1699; Found 564.1701. **Optical Rotation**: $[\alpha]^{20}_D$ = +465.1 (c = 0.3, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 13.9 min for major isomer, t_R = 15.2 min for minor isomer).



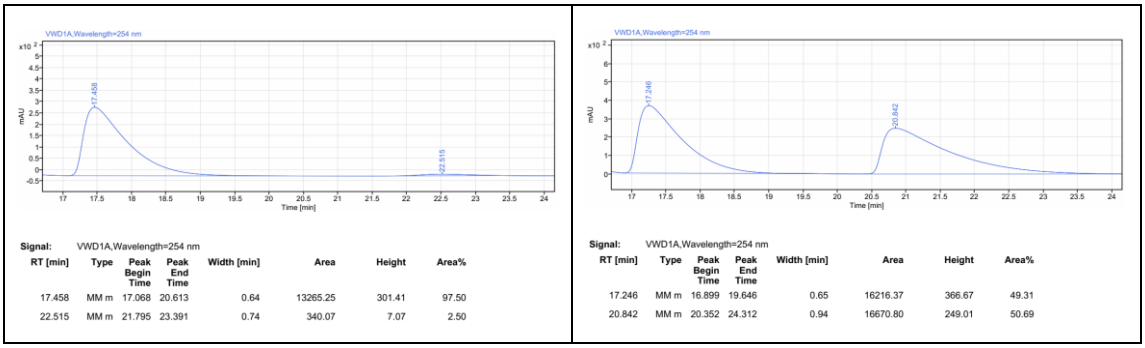
Methyl (4*S*,5*R*)-4-benzyl-5-((*S*)-6-formyl-[1,1':2',1''-terphenyl]-2-yl)-4,5-dihydrooxazole-4-carboxylate (3t)



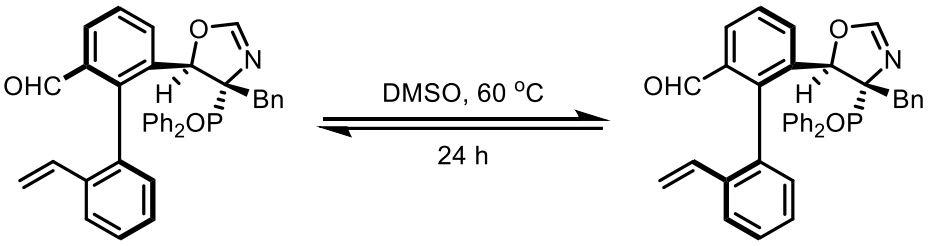
3t

With **2g** (1.0 equiv) for 24 h. 4:1 dr (determined by crude ^{1}H NMR). The crude reaction mixture was purified by flash column chromatography (PE/EtOAc 4:1). White solid, 34.2 mg, 72% yield. **MP**: 100-101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (d, *J* = 0.8 Hz, 1H), 7.84 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.74-7.65 (m, 3H), 7.62-7.59 (m, 1H), 7.37-7.31 (m, 1H), 7.26-7.23 (m, 1H), 7.22-7.16 (m, 3H), 7.11-7.04 (m, 3H), 6.90-6.84 (m, 3H), 6.68-6.63 (m, 2H), 5.22 (s, 1H), 3.30 (s, 3H), 3.10 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 191.9, 171.3, 155.6, 143.4, 142.2, 139.8, 136.6, 134.4, 134.3, 133.4, 132.7, 131.5, 131.2, 130.5, 129.5, 129.1, 128.2, 128.1, 127.9, 127.81, 127.76, 127.3, 83.0, 81.0, 52.4, 43.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{26}NO_4$ 476.1856; Found 476.1857. **Optical Rotation**:

$[\alpha]^{20}_D$ = +13.6 (c = 0.3, CH_2Cl_2). 97.5:2.5 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 17.5 min for major isomer, t_R = 22.5 min for minor isomer).

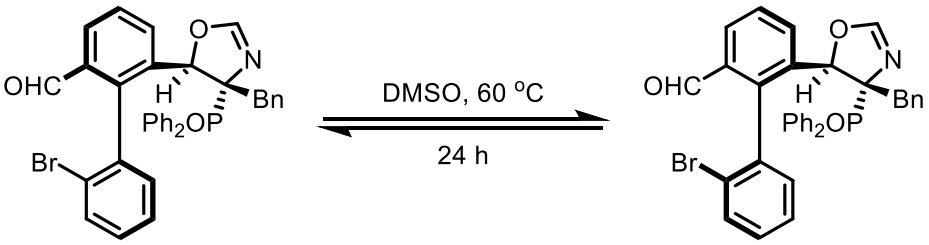


VI. Evaluation of the thermal stability of the chiral axis



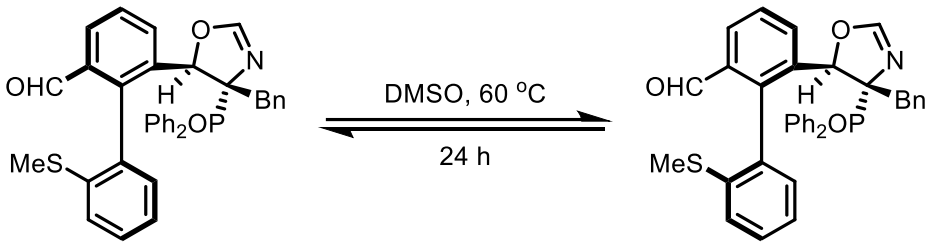
3c **3c"**

To a 10 mL vial charged with **3c** (0.010 mmol) was added anhydrous DMSO (1.0 mL). After stirring at 60 °C for 24 h, no **3c"** was detected by ^{1}H NMR spectroscopy, and the ee value of **3c** remained unchanged.



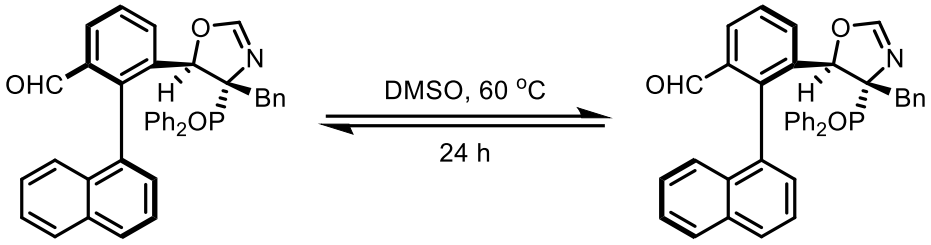
3d **3d"**

To a 10 mL vial charged with **3d** (0.010 mmol) was added anhydrous DMSO (1.0 mL). After stirring at 60 °C for 24 h, no **3d"** was detected by ^{1}H NMR spectroscopy, and the ee value of **3d** remained unchanged.



3e **3e"**

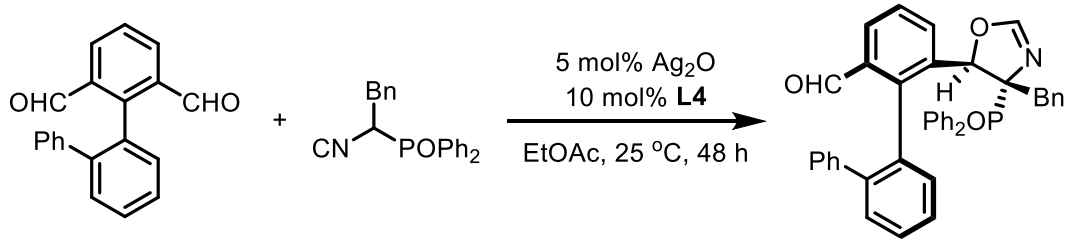
To a 10 mL vial charged with **3e** (0.010 mmol) was added anhydrous DMSO (1.0 mL). After stirring at 60 °C for 24 h, no **3e"** was detected by ^{1}H NMR spectroscopy, and the ee value of **3e** remained unchanged.



3f **3f"**

To a 10 mL vial charged with **3f** (0.010 mmol) was added anhydrous DMSO (1.0 mL). After stirring at 60 °C for 24 h, no **3f"** was detected by ^{1}H NMR spectroscopy, and the ee value of **3f** remained unchanged.

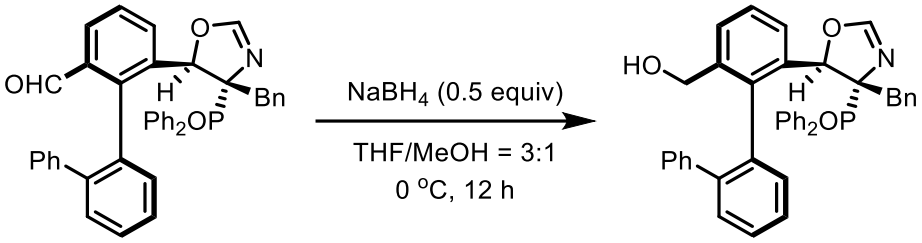
VII. Gram-scale reaction and derivatization



1a 2.5 mmol **2a** (1.0 equiv) **3a**: dr = 8:1, 1.14 g 74%, 99:1 er

To a 50 mL round-bottom flask charged with **L4** (145.3 mg, 0.25 mmol) and Ag_2O (29.0 mg, 0.125 mmol) was added anhydrous EtOAc (25.0 mL). The mixture was stirred at ambient temperature for 5 min, then **1a** (715.0 mg, 2.5 mmol) and **2a** (827.5 mg, 2.5 mmol) were added successively in one portion. The reaction mixture was

stirred at 25 ℃ for 48 h, then concentrated and purified by flash column chromatography (PE/EtOAc 4:1) to afford **3a**.

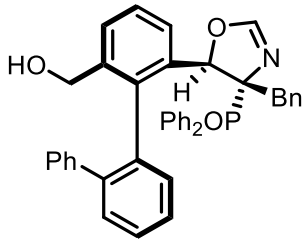


3a: 99:1 er

4: 98%, 99:1 er

To a suspension of $NaBH_4$ (1.9 mg, 0.05 mmol) in THF/MeOH = 3:1 (1.0 mL) under nitrogen atmosphere was added a solution of **3a** (61.7 mg, 0.10 mmol) in THF/MeOH = 3:1 (1.0 mL). The reaction mixture was stirred at 0 ℃ for 12 h and then concentrated and purified by flash column chromatography (EtOAc) to afford **4**.

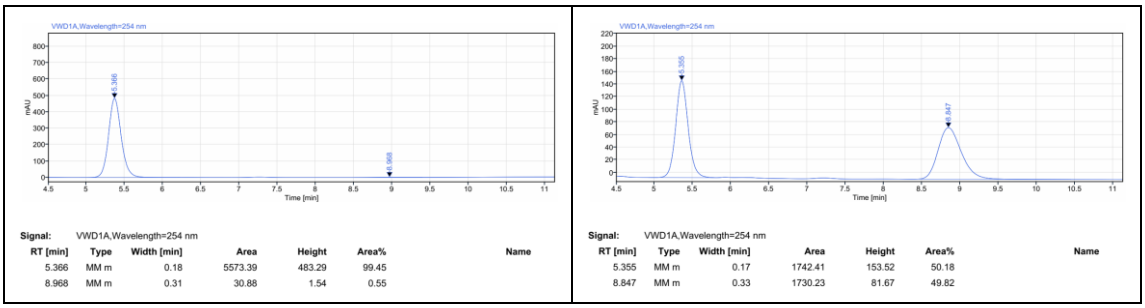
((4*R*,5*R*)-4-benzyl-5-((*R*)-6-(hydroxymethyl)-[1,1':2',1''-terphenyl]-2-yl)-4,5-dihydrooxazol-4-yl)diphenylphosphine oxide (4)

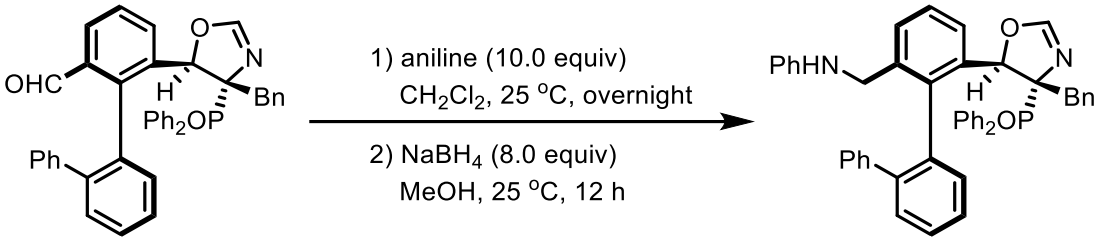


4

White solid, 60.6 mg, 98% yield. **MP**: 245-246 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89-7.81 (m, 3H), 7.72-7.66 (m, 1H), 7.61-7.57 (m, 1H), 7.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.40-7.34 (m, 1H), 7.25-7.16 (m, 6H), 7.11-7.02 (m, 5H), 7.01-6.95 (m, 2H), 6.94-6.90 (m, 2H), 6.83-6.76 (m, 5H), 5.68 (d, *J* = 19.4 Hz, 1H), 4.46 (d, *J* = 13.6 Hz, 1H), 4.28 (d, *J* = 13.6 Hz, 1H), 3.13-2.96 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.4 (d, *J* = 7.7 Hz), 140.6 (d, *J* = 4.8 Hz), 139.9, 139.1, 135.7 (d, *J* = 4.2 Hz), 134.7, 134.0 (d, *J* = 10.8 Hz), 132.7, 132.4 (d, *J* = 7.9 Hz), 132.0 (d, *J* = 8.4 Hz), 131.8 (d, *J* = 94.8 Hz), 131.6, 131.5 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 2.9 Hz), 130.1, 130.0 (d, *J* = 92.2 Hz), 129.0, 128.8, 128.7, 128.0, 127.9, 127.67,

127.65, 127.6, 127.54, 127.48, 127.2, 126.7, 126.4, 82.0 (d, J = 7.1 Hz), 79.4 (d, J = 81.4 Hz), 63.3, 39.4 (d, J = 2.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.6; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{34}NNaO_3P$ 642.2169; Found 642.2167. **Optical Rotation**: $[\alpha]^{20}_D$ = +76.7 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 5.4 min for major isomer, t_R = 9.0 min for minor isomer).



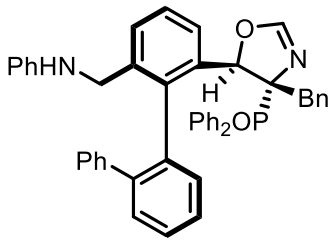


3a: 99:1 er

5: 83%, 99.5:0.5 er

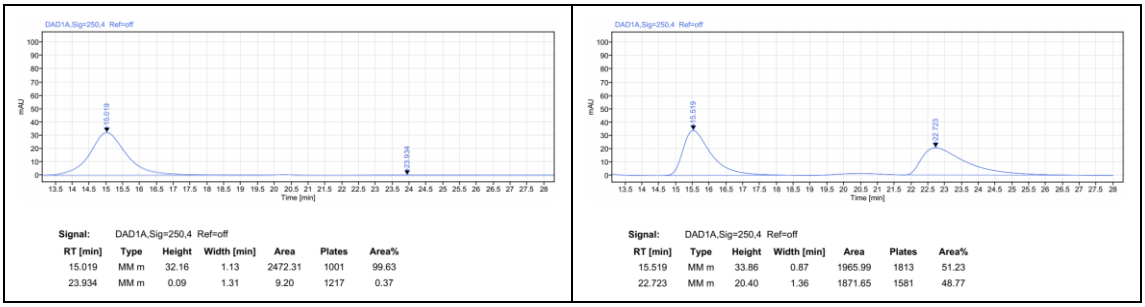
To a solution of **3a** (30.9 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was added aniline (46.6 mg, 0.5 mmol). The reaction mixture was stirred at 25 °C overnight, after which $NaBH_4$ (15.1 mg, 0.4 mmol) and MeOH (1.0 mL) were added and the mixture was stirred for an additional 12 h. After completion of the reaction, the solvent was removed under reduced pressure. To the residue, water was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc 4:1) to afford **5**.

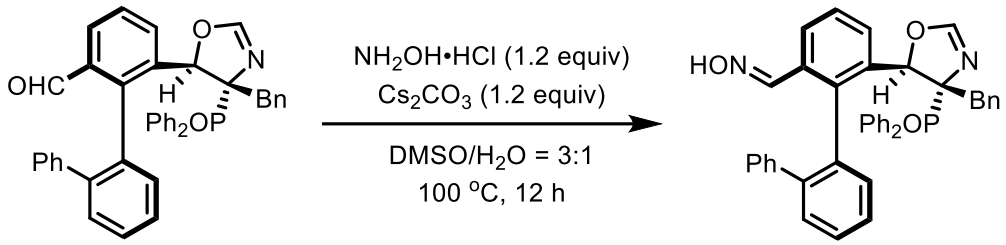
((4*R*,5*R*)-4-benzyl-5-((*R*)-6-((phenylamino)methyl)-[1,1':2',1''-terphenyl]-2-yl)-4,5-dihydrooxazol-4-yl)diphenylphosphine oxide (5)



5

White solid, 29.0 mg, 83% yield. **MP**: 127-128 ℃; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.83-7.70 (m, 4H), 7.60-7.54 (m, 2H), 7.47 (d, J = 3.5 Hz, 1H), 7.44-7.39 (m, 1H), 7.30-7.24 (m, 3H), 7.18-7.11 (m, 7H), 7.08-7.03 (m, 4H), 6.94-6.85 (m, 5H), 6.82-6.76 (m, 3H), 6.48-6.42 (m, 1H), 6.17-6.12 (m, 2H), 5.62 (d, J = 19.4 Hz, 1H), 3.83 (d, J = 16.5 Hz, 1H), 3.58 (d, J = 16.5 Hz, 1H), 3.05-2.90 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 157.2 (d, J = 7.6 Hz), 148.4, 140.4, 139.7, 139.1, 137.6, 135.4 (d, J = 4.2 Hz), 134.3, 134.2, 132.4, 132.2 (d, J = 93.6 Hz), 131.9 (d, J = 7.8 Hz), 131.6, 131.5, 131.3, 130.7, 129.82, 129.75, 128.81, 128.78, 128.7, 128.4, 127.8 (d, J = 10.6 Hz), 127.7, 127.5 (d, J = 11.2 Hz), 127.0, 126.8, 126.7 (d, J = 4.1 Hz), 126.5, 126.1, 115.8, 112.0, 81.1 (d, J = 7.2 Hz), 78.8 (d, J = 81.0 Hz), 45.2; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{47}H_{39}N_2NaO_2P$ 717.2641; Found 717.2640. **Optical Rotation**: $[\alpha]^{14}_D$ = +104.1 (c = 0.7, CH_2Cl_2). 99.5:0.5 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 15.0 min for major isomer, t_R = 23.9 min for minor isomer).



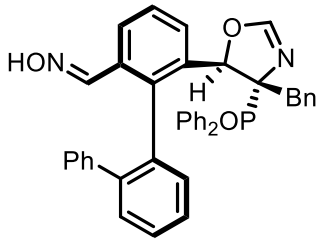


3a: 99:1 er

6: 87%, 99.5:0.5 er

To a mixture of **3a** (61.7 mg, 0.10 mmol) and Cs_2CO_3 (39.1 mg, 0.12 mmol) in DMSO/H_2O = 3:1 (1.0 mL) was added a solution of NH_2OH·HCl (8.3 mg, 0.12 mmol) in DMSO/H_2O = 3:1 (1.0 mL). The reaction mixture was stirred at 100 ℃ for 12 h. After completion, the reaction mixture was cooled to room temperature and treated with water (2 × 5 mL). The resulting mixture was extracted with ethyl acetate (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc 4:1) to afford **6**.

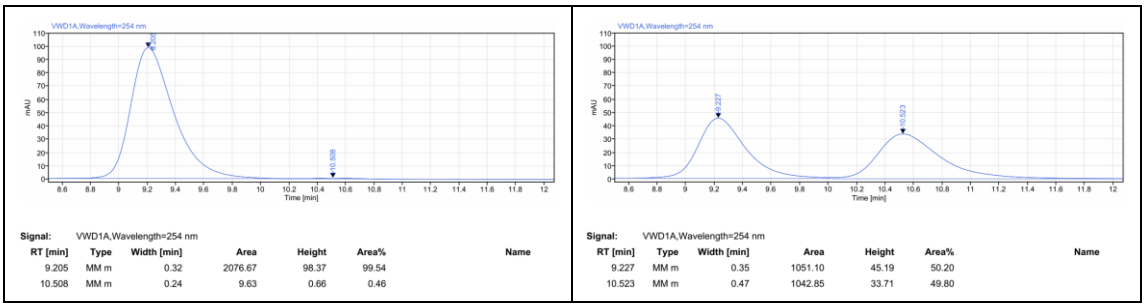
(*E*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-[1,1':2', 1''-terphenyl]-2-carbaldehyde oxime (6)

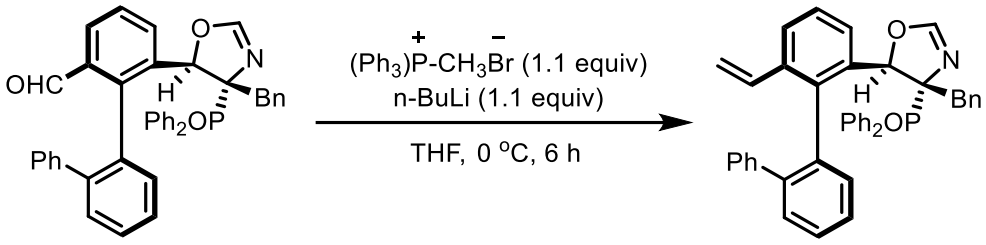


6

White solid, 55.0 mg, 87% yield. **MP**: 157-158 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.33 (d, *J* = 1.9 Hz, 1H), 8.02 (s, 1H), 7.91-7.80 (m, 3H), 7.74-7.69 (m, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.56-7.49 (m, 2H), 7.48-7.43 (m, 1H), 7.36-7.30 (m, 2H), 7.28-7.17 (m, 3H), 7.13-7.06 (m, 4H), 7.04-6.99 (m, 1H), 6.96-6.89 (m, 4H), 6.83-6.76 (m, 4H), 6.70-6.66 (m, 2H), 5.62 (d, *J* = 19.8 Hz, 1H), 3.24 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.95 (dd, *J* = 23.1, 14.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.4 (d, *J* = 8.2 Hz), 148.9, 140.8, 140.5, 140.4, 135.8 (d, *J* = 4.5 Hz), 134.2, 133.8, 133.7 (d, *J* = 10.8 Hz), 132.7, 132.5 (d, *J* = 8.1 Hz), 131.9 (d, *J* = 8.0 Hz), 131.7, 131.6,

130.9 (d, J = 3.8 Hz), 129.9, 129.6 (d, J = 93.3 Hz), 129.4, 129.1, 129.0, 128.8, 128.2, 128.0, 127.8, 127.7, 127.6, 127.2, 127.0, 126.5, 126.3, 81.7 (d, J = 7.5 Hz), 79.4 (d, J = 82.5 Hz), 38.8 (d, J = 2.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{33}N_2NaO_3P$ 655.2121; Found 655.2121. **Optical Rotation**: $[\alpha]^{20}_D$ = +185.4 (c = 0.1, CH_2Cl_2). 99.5:0.5 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 9.2 min for major isomer, t_R = 10.5 min for minor isomer).



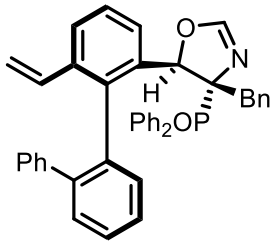


3a: 99:1 er

7: 89%, 99:1 er

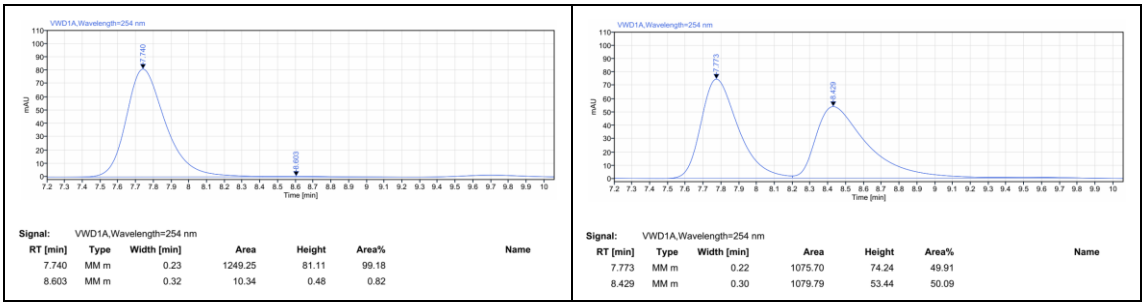
To a stirred solution of methyltriphenylphosphonium bromide (39.3 mg, 0.11 mmol) in anhydrous THF (0.5 mL) was added n-BuLi (2.5 M in hexane, 45 μL, 0.11 mmol) dropwise at 0 °C under nitrogen atmosphere and stirred for 0.5 h. Then a solution of **3a** (61.7 mg, 0.1 mmol) in THF (0.5 mL) was added and stirred at °C for 6 h. After completion, the reaction mixture was quenched with water (3 mL), and extracted with ethyl acetate (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc 4:1) to afford **7**.

((4*R*,5*R*)-4-benzyl-5-((*R*)-6-vinyl-[1,1':2',1''-terphenyl]-2-yl)-4,5-dihydrooxazol-4-yl)diphenylphosphine oxide (7)

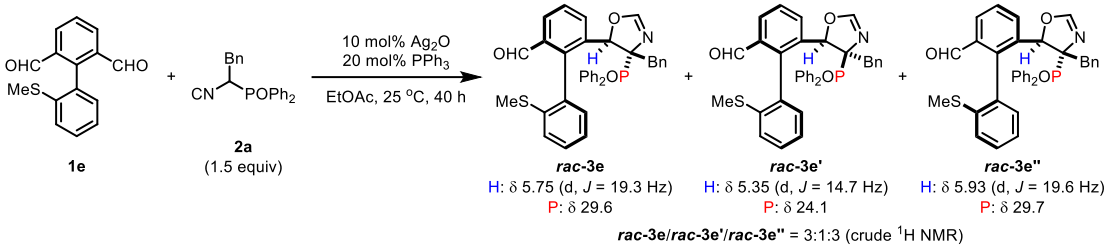


7

White solid, 54.8 mg, 89% yield. **MP**: 222-223 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.76 (m, 3H), 7.67-7.62 (m, 1H), 7.51 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.47-7.41 (m, 2H), 7.39-7.34 (m, 1H), 7.27-7.17 (m, 4H), 7.15-7.10 (m, 1H), 7.05-6.94 (m, 6H), 6.92-6.87 (m, 2H), 6.82 (d, *J* = 3.6 Hz, 1H), 6.76-6.65 (m, 6H), 6.46 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.57-5.54 (m, 1H), 5.53-5.50 (m, 1H), 5.08 (dd, *J* = 11.1, 1.2 Hz, 1H), 3.00 (dd, *J* = 14.3, 7.5 Hz, 1H), 2.86 (dd, *J* = 21.9, 14.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.4 (d, *J* = 7.7 Hz), 141.0, 140.8, 139.5, 137.6, 135.8 (d, *J* = 4.5 Hz), 135.7, 135.3, 134.0 (d, *J* = 11.1 Hz), 133.1, 132.5 (d, *J* = 8.0 Hz), 132.4, 132.0 (d, *J* = 8.3 Hz), 131.6, 131.5 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 3.3 Hz), 129.9, 129.8, 129.0, 128.6, 128.4, 127.9 (d, *J* = 11.1 Hz), 127.7 (d, *J* = 11.5 Hz), 127.5, 127.4, 127.19, 127.15, 126.5, 126.3, 125.2, 115.4, 82.0 (d, *J* = 7.1 Hz), 79.5 (d, *J* = 81.3 Hz), 39.2 (d, *J* = 2.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}NO_2P$ 616.2400; Found 616.2396. **Optical Rotation**: $[\alpha]^{20}_D$ = +216.1 (c = 0.1, CH_2Cl_2). 99:1 er (HPLC condition: Chiralpak IB N-5 column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 7.7 min for major isomer, t_R = 8.6 min for minor isomer).

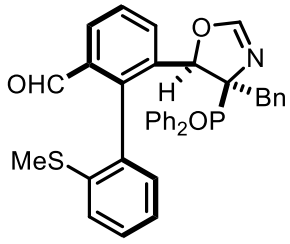


VIII. Isolation of *rac*-3e' and *rac*-3e''



To a 10 mL vial charged with PPh_3 (5.24 mg, 0.02 mmol) and Ag_2O (2.32 mg, 0.01 mmol) was added anhydrous EtOAc (1.0 mL). The mixture was stirred at ambient temperature for 5 min, then **1e** (25.6 mg, 0.10 mmol) and **2a** (49.7 mg, 0.15 mmol) were added successively in one portion. The reaction mixture was stirred at 25 °C for 40 h, then concentrated and purified by flash column chromatography (PE/EtOAc 5:1) to afford ***rac*-3e'** and ***rac*-3e''**.

(±)-(*S*)-6-((4*S*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-(methylthio)-[1,1'-biphenyl]-2-carbaldehyde (*rac*-3e')

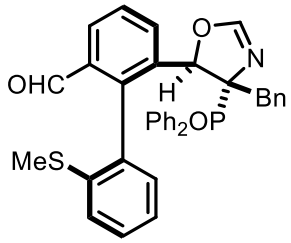


***rac*-3e'**

White solid. **MP**: 131-132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.51 (d, *J* = 0.8 Hz, 1H), 8.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.32-8.23 (m, 2H), 7.83 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.75-7.68 (m, 2H), 7.63-7.57 (m, 1H), 7.54-7.43 (m, 5H), 7.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.34-7.28 (m, 2H), 7.15-7.03 (m, 3H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.70 (t, *J* = 7.8 Hz, 1H), 6.43 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.29-6.24 (m, 2H), 5.35 (d, *J* = 14.7 Hz, 1H), 2.93 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.83 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.2, 155.8 (d, *J* = 13.1 Hz), 143.0, 139.2, 135.2 (d, *J* = 6.3 Hz), 134.1, 133.8 (d, *J* = 12.6 Hz), 133.7, 133.5, 133.2, 133.0 (d, *J* = 16.5 Hz), 132.5 (d, *J* = 7.9 Hz), 132.0 (d, *J* = 8.0 Hz), 131.6 (d, *J* = 2.8 Hz), 131.5, 131.4, 129.7, 128.6, 128.5, 128.2, 128.1, 127.8, 127.2, 127.1 (d, *J* = 2.9 Hz), 124.8, 123.6, 81.3 (d, *J* = 4.2 Hz), 78.5 (d, *J* = 86.5 Hz), 40.4 (d, *J* = 5.7 Hz), 15.2; **^{31}P NMR** (162 MHz,

$CDCl_3$): δ 24.1; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{30}NNaO_3PS$ 610.1576; Found 610.1580.

(±)-(*R*)-6-((4*R*,5*R*)-4-benzyl-4-(diphenylphosphoryl)-4,5-dihydrooxazol-5-yl)-2'-(methylthio)-[1,1'-biphenyl]-2-carbaldehyde (*rac*-3e")



***rac*-3e"**

White solid. **MP**: 110-111 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 8.03-7.95 (m, 3H), 7.60-7.54 (m, 1H), 7.51-7.36 (m, 6H), 7.33-7.17 (m, 6H), 6.95-6.83 (m, 5H), 6.70-6.54 (m, 2H), 5.93 (d, *J* = 19.6 Hz, 1H), 3.44 (dd, *J* = 14.6, 8.0 Hz, 1H), 3.07 (dd, *J* = 17.0, 14.6 Hz, 1H), 2.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.3, 155.7 (d, *J* = 7.8 Hz), 142.6, 140.8, 135.9 (d, *J* = 6.9 Hz), 135.3 (d, *J* = 11.2 Hz), 134.9, 134.8, 133.1, 132.7 (d, *J* = 7.8 Hz), 132.1 (d, *J* = 8.3 Hz), 131.8, 131.5, 131.24 (d, *J* = 2.8 Hz), 131.16 (d, *J* = 96.0 Hz), 129.6, 129.32 (d, *J* = 92.0 Hz), 129.30, 128.1, 128.0 (d, *J* = 5.4 Hz), 127.9 (d, *J* = 4.8 Hz), 127.5, 127.3, 126.5, 125.4, 124.0, 81.2, 79.6 (d, *J* = 80.6 Hz), 37.1 (d, *J* = 3.4 Hz), 15.7; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.7; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{30}NNaO_3PS$ 610.1576; Found 610.1574.

IX. Crystal structure data of 3a and 3a'

The relative and absolute configurations of **3a** (*S*,4*R*,5*R*) were assigned by X-ray crystallographic analysis of a single crystal of **3a** (Figure S2). The crystal was prepared from the solution of **3a** in PE/EtOAc/CH_2Cl_2 = 4:1:1 at 25 ℃.

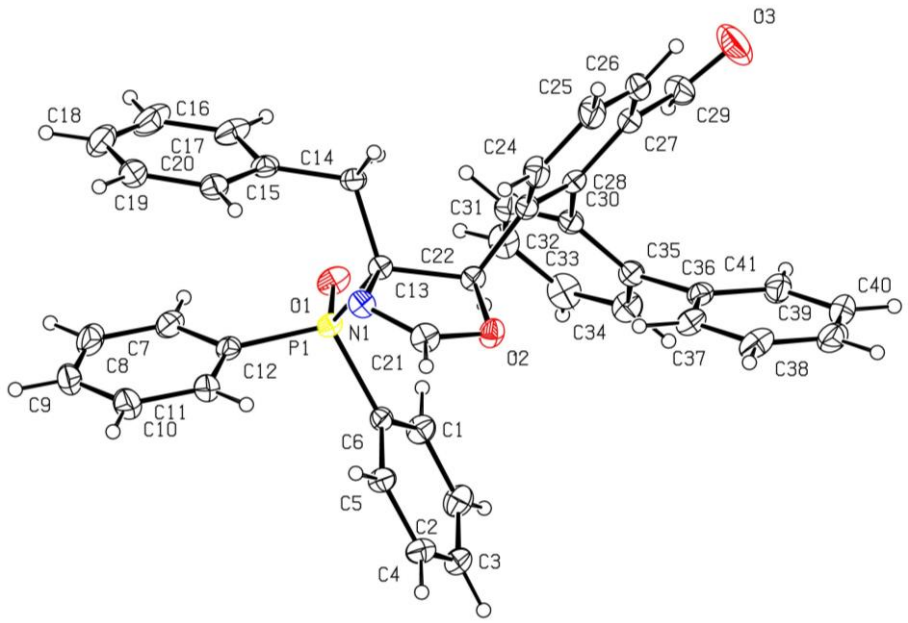


Figure S2. X-ray structure of **3a** (ellipsoid contour at 30% probability)

Table S1. Crystal data and structure refinement for mo_220412_HF_0m_tw

Identification code	mo_220412_HF_0m_tw
Empirical formula	$C_{41}H_{32}NO_3P$
Formula weight	617.64
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.582(4)
b/Å	14.754(3)
c/Å	15.384(4)
α/°	90
β/°	95.337(13)
γ/°	90
Volume/Å^3	3295.6(14)
Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.124

F(000)	1296.0
Crystal size/mm^3	0.28 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.832 to 54.308
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -2 ≤ l ≤ 19
Reflections collected	14509
Independent reflections	14509 [R_{int} = 0.0529, R_{sigma} = 0.0552]
Data/restraints/parameters	14509/1/830
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0865
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.0902
Largest diff. peak/hole / e Å^{-3}	0.33/-0.22
Flack parameter	0.04(2)

The relative and absolute configurations of **3a'** (*S*,4*S*,5*R*) were assigned by X-ray crystallographic analysis of a single crystal of **3a'** (Figure S3). The crystal was prepared from the solution of **3a'** in PE/EtOAc = 3:1 at 25 ℃.

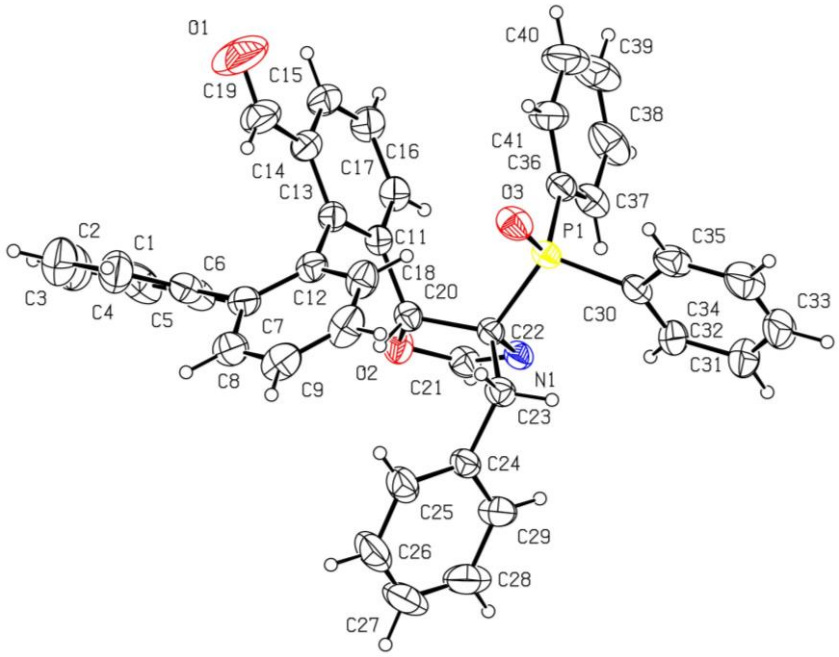


Figure S3. X-ray structure of **3a'** (ellipsoid contour at 30% probability)

Table S2. Crystal data and structure refinement for cu_221208_HF_Ph_model_dr_sq

Identification code	cu_221208_HF_Ph_model_dr_sq
Empirical formula	$C_{41}H_{32}NO_3P$
Formula weight	617.64
Temperature/K	298.00
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	13.7964(3)
b/Å	25.0930(6)
c/Å	10.7544(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3723.10(16)
Z	4
ρ_{calc}g/cm^3	1.102
μ/mm^{-1}	0.932
F(000)	1296.0
Crystal size/mm^3	0.45 × 0.3 × 0.26
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.222 to 136.244
Index ranges	-16 ≤ h ≤ 16, -29 ≤ k ≤ 30, -12 ≤ l ≤ 12
Reflections collected	35451
Independent reflections	6754 [R_{int} = 0.0406, R_{sigma} = 0.0306]
Data/restraints/parameters	6754/0/415
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0854

Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0882
Largest diff. peak/hole / e Å^{-3}	0.14/-0.23
Flack parameter	0.023(8)

X. References

1 Y. Wu, M. Li, J. Sun, G. Zheng and Q. Zhang, *Angew. Chem. Int. Ed.*, 2022, **61**, e202117340.

2 Y. Xiong, Z. Du, H. Chen, Z. Yang, Q. Tan, C. Zhang, L. Zhu, Y. Lan and M. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 961-971.

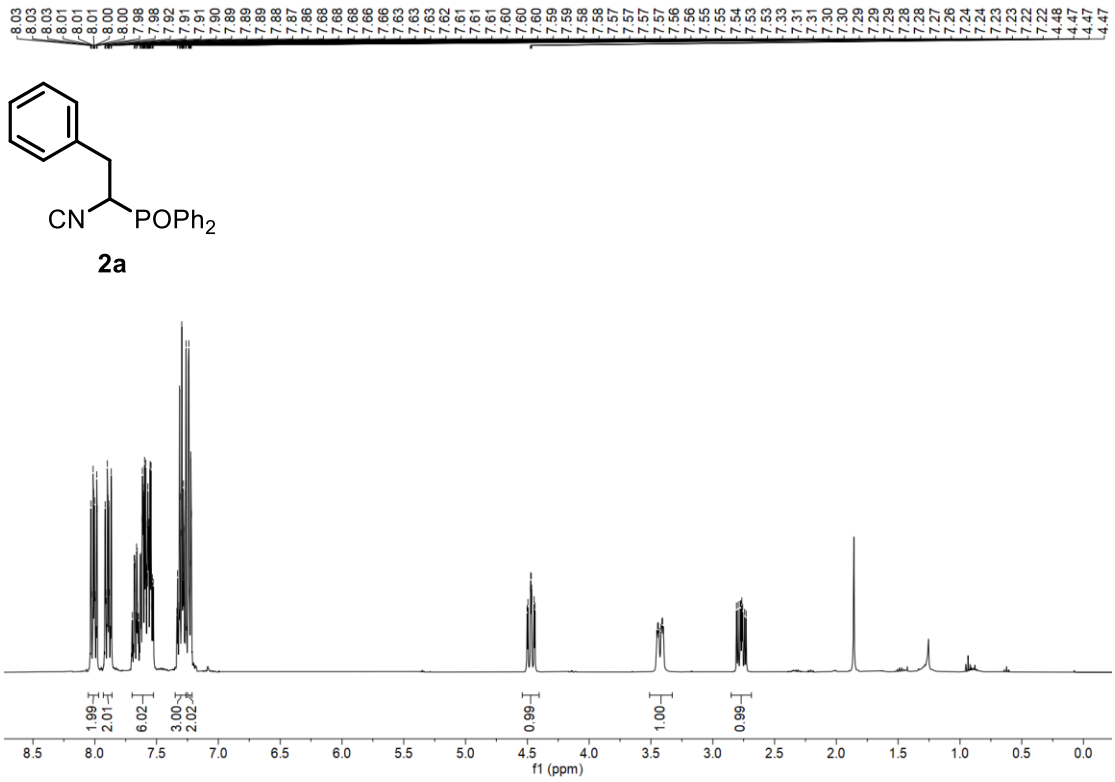
3 (*a*) F. Sladojevich, A. Trabocchi, A. Guarna and D. J. Dixon, *J. Am. Chem. Soc.*, 2011, **133**, 1710-1713; (*b*) P.-L. Shao, J.-Y. Liao, Y. A. Ho and Y. Zhao, *Angew. Chem. Int. Ed.*, 2014, **53**, 5435-5439.

4 Z.-P. Wang, Q. Wu, J. Jiang, Z.-R. Li, X.-J. Peng, P.-L. Shao and Y. He, *Org. Chem. Front.*, 2018, **5**, 36-40.

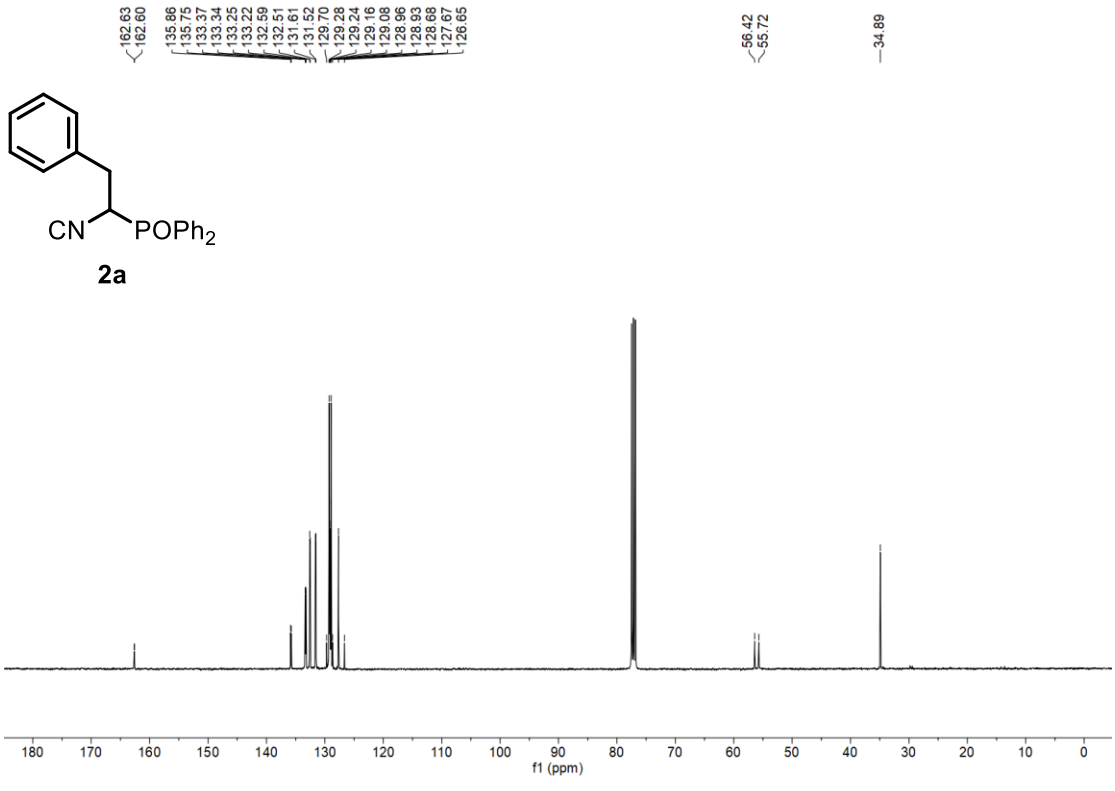
5 X.-L. He, H.-R. Zhao, X. Song, B. Jiang, W. Du and Y.-C. Chen, *ACS Catal.*, 2019, **9**, 4374-4381.

XI. NMR spectra

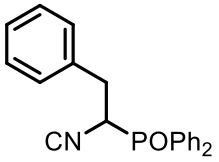
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

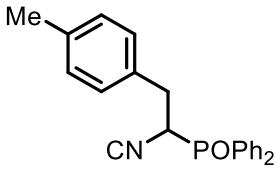


^{31}P NMR (162 MHz, $CDCl_3$)

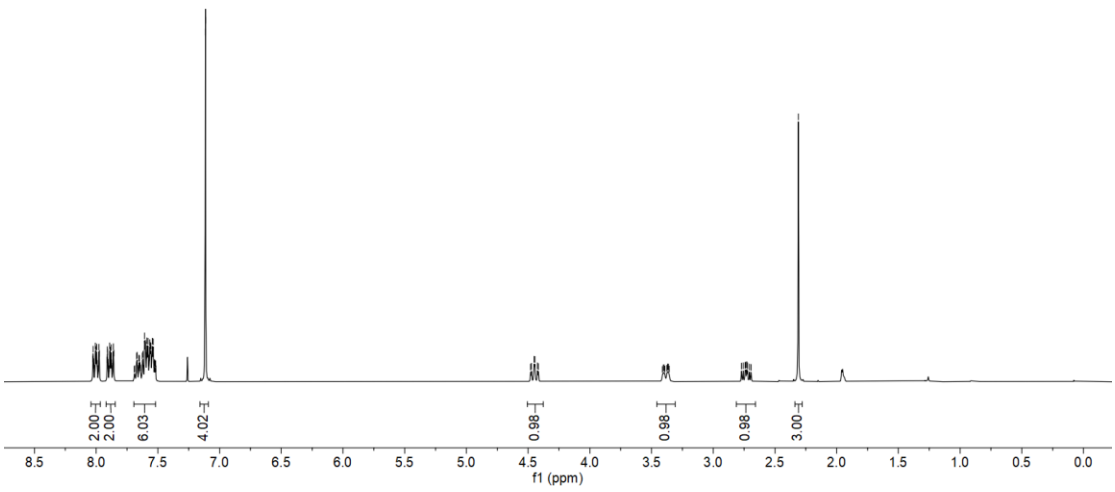


2a

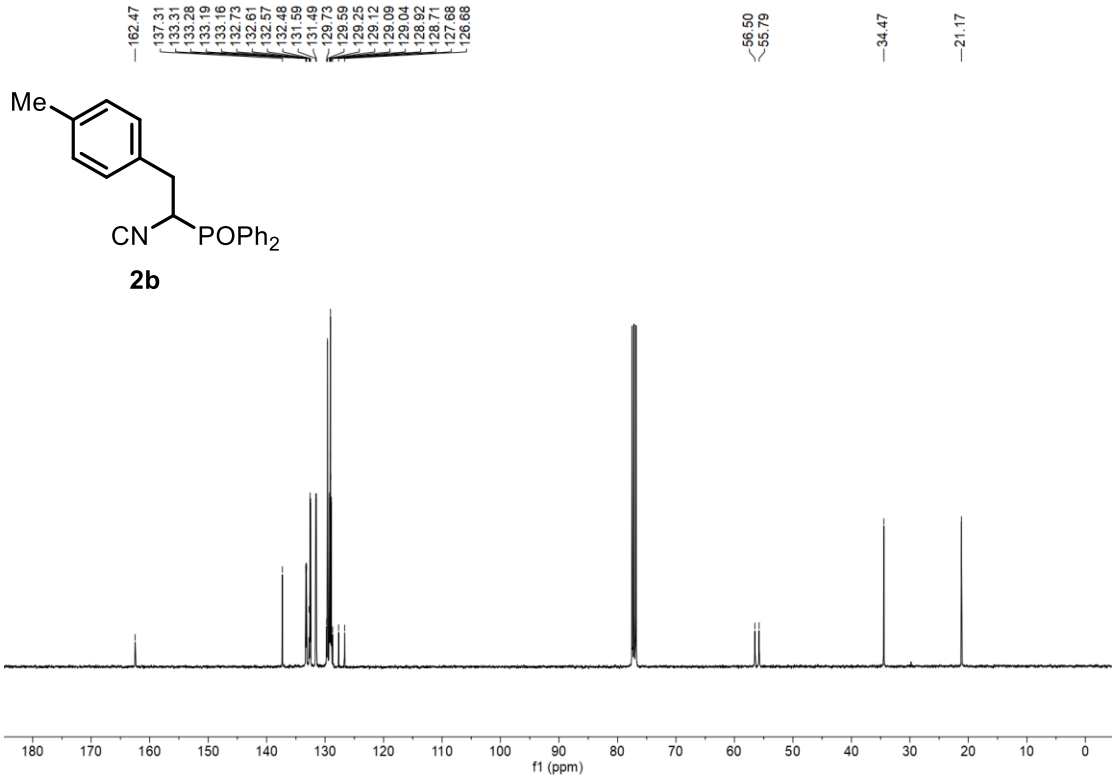
^{1}H NMR (400 MHz, $CDCl_3$)



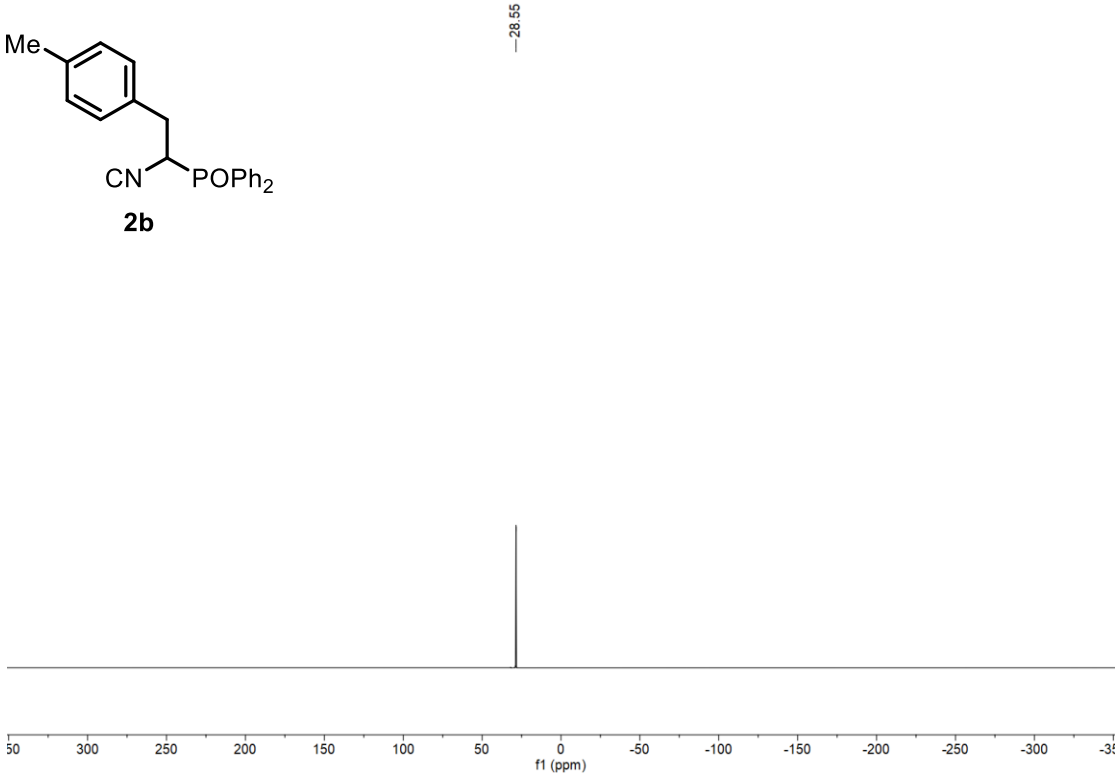
2b



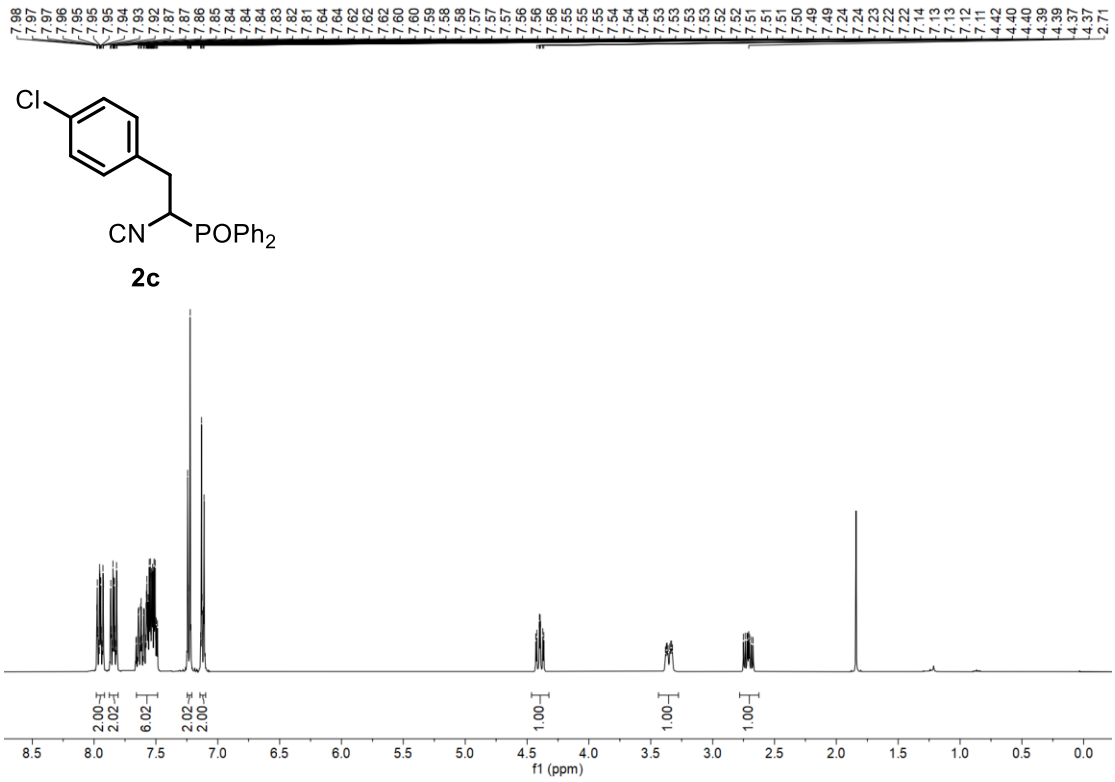
^{13}C NMR (101 MHz, $CDCl_3$)



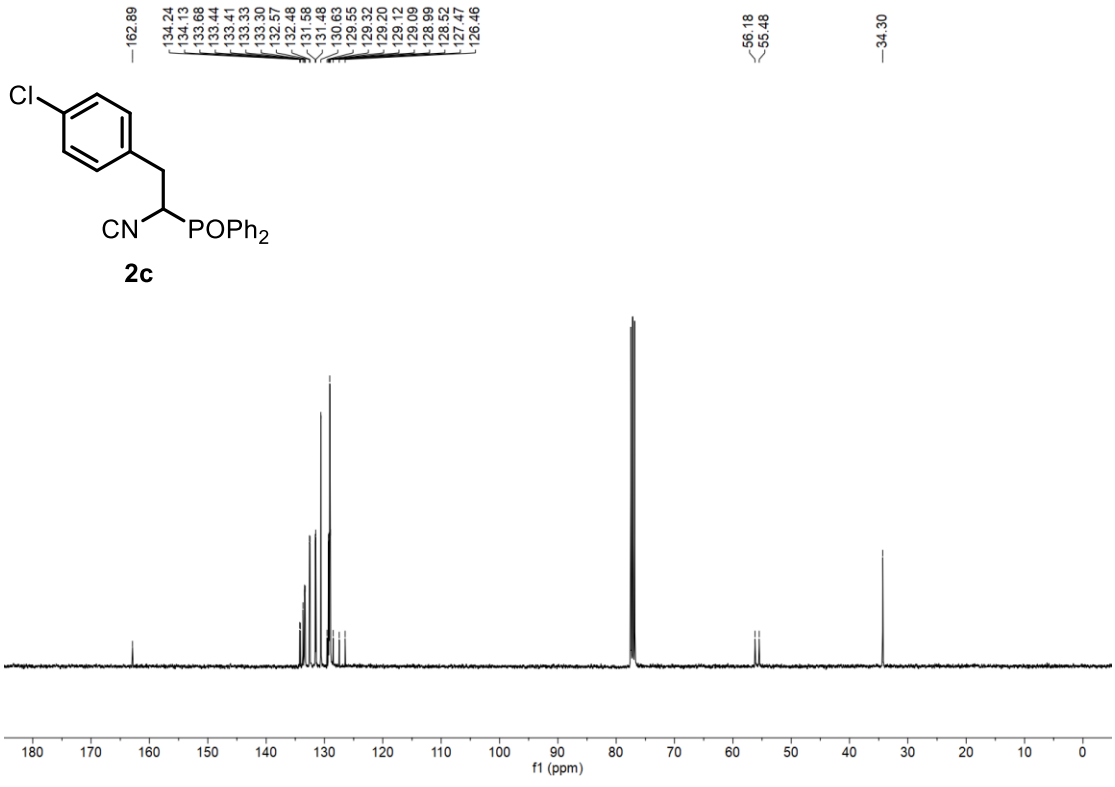
^{31}P NMR (162 MHz, $CDCl_3$)



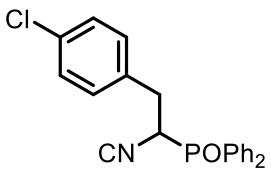
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

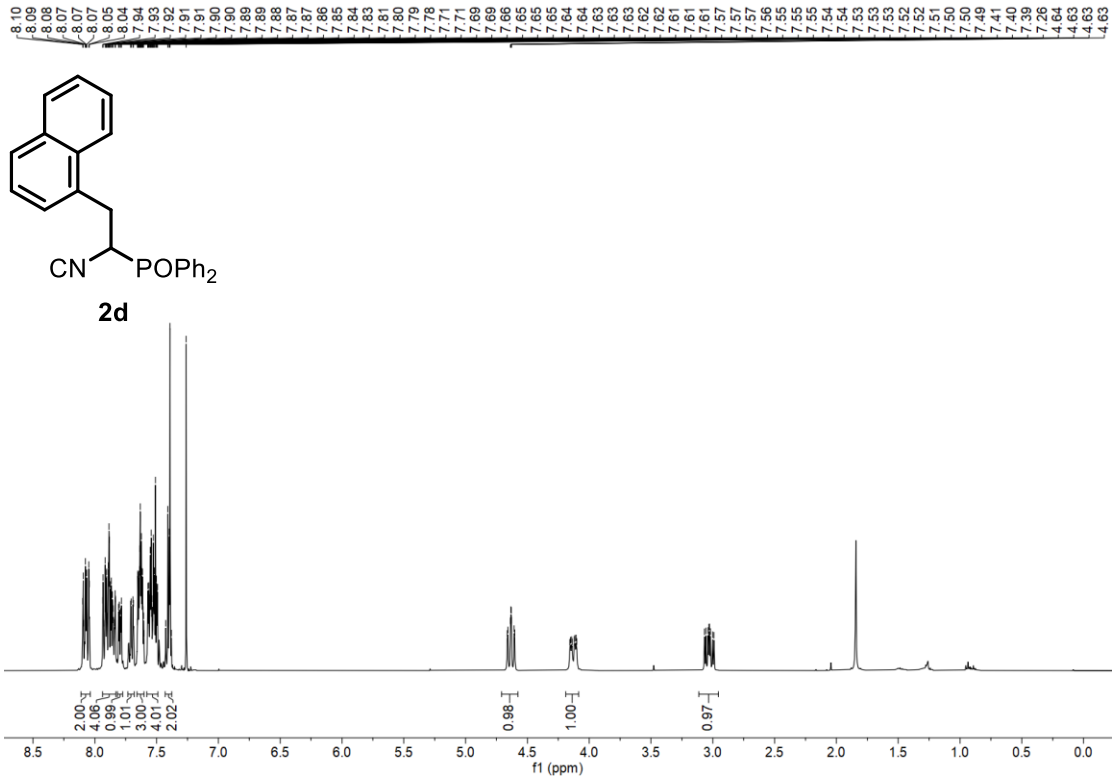


^{31}P NMR (162 MHz, $CDCl_3$)



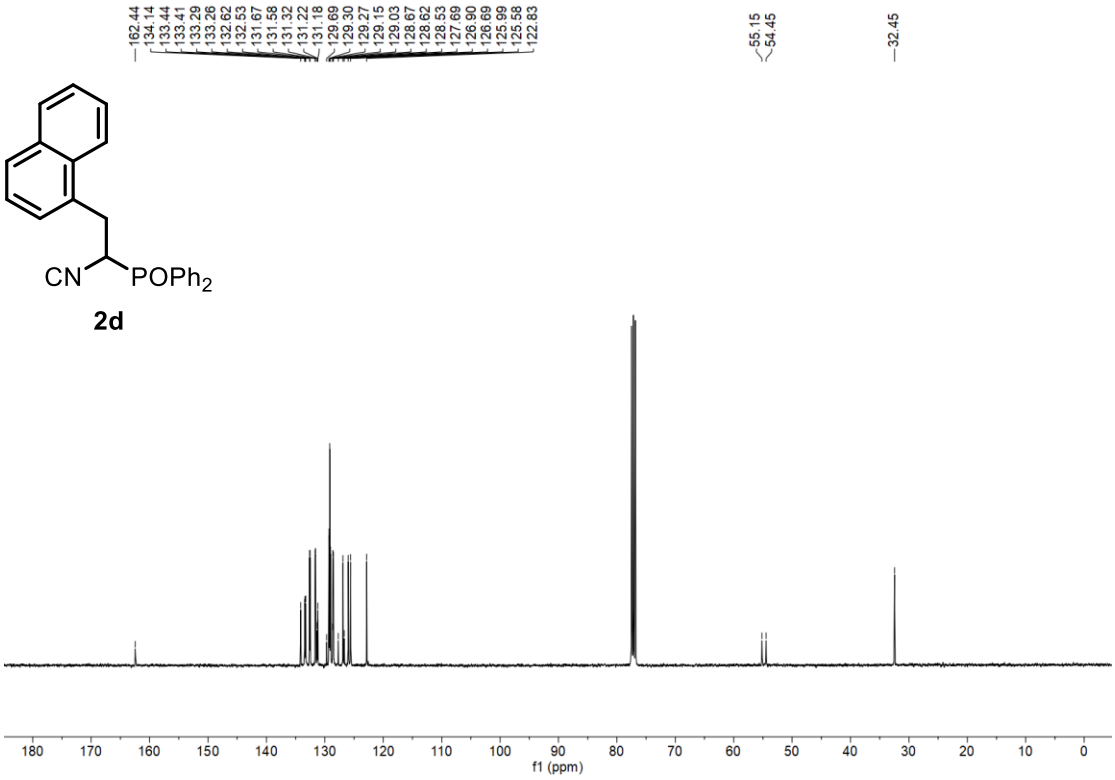
2c

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

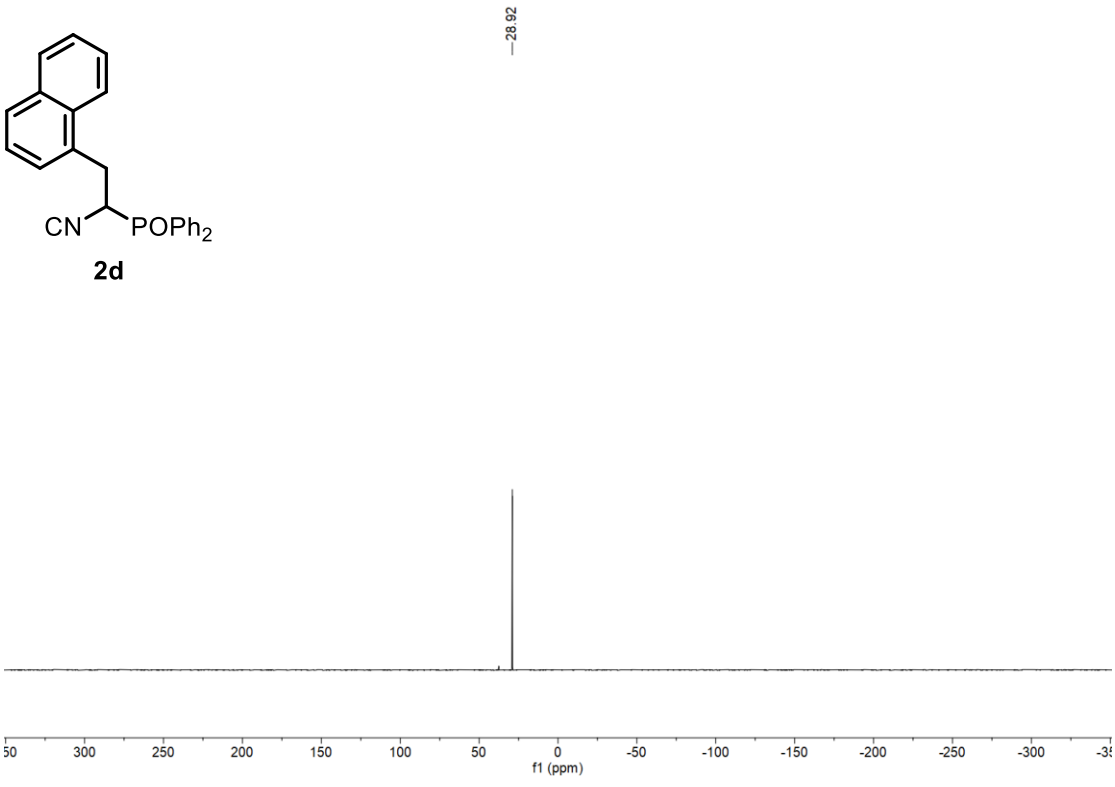


2d

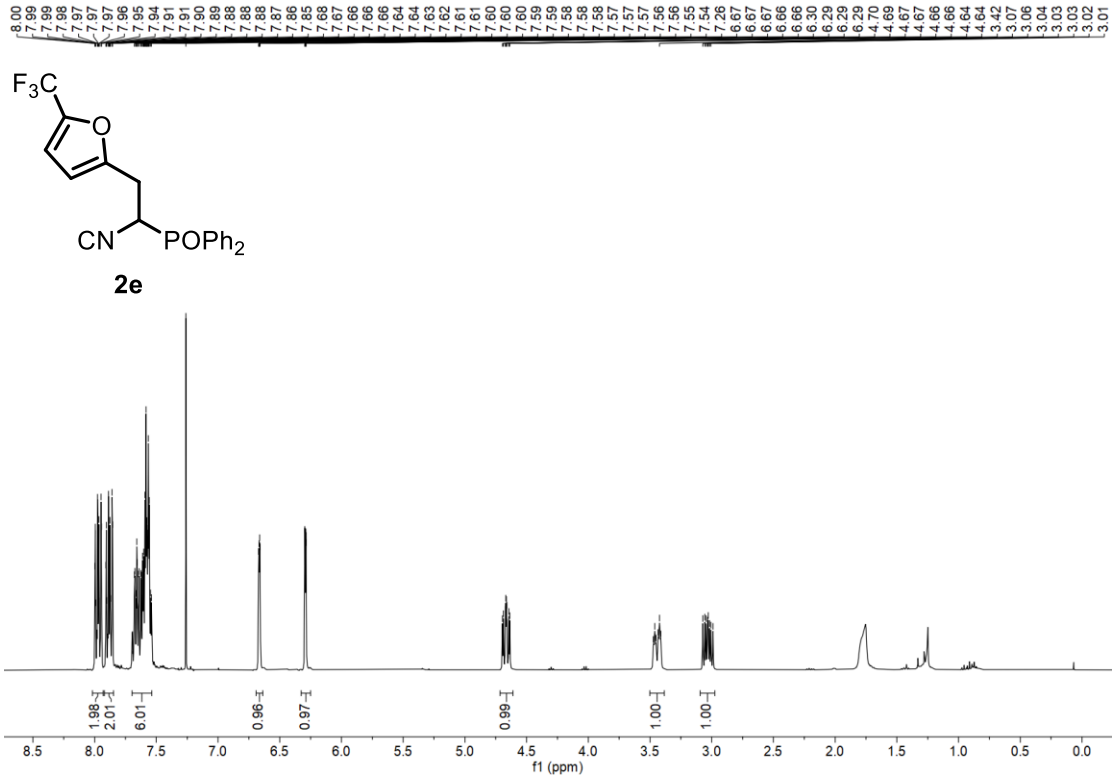
^{13}C NMR (101 MHz, $CDCl_3$)



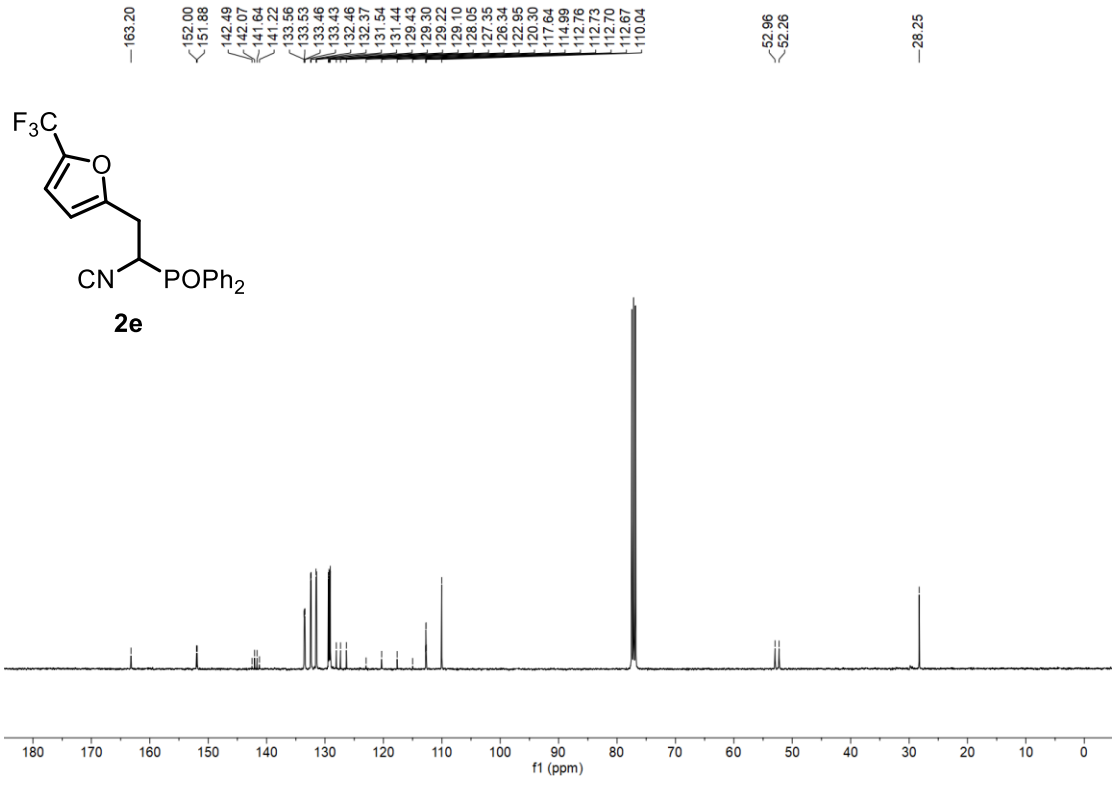
^{31}P NMR (162 MHz, $CDCl_3$)



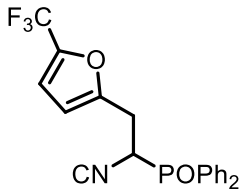
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

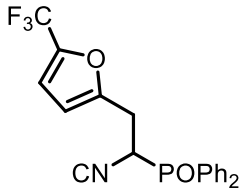


^{19}F NMR (376 MHz, $CDCl_3$)



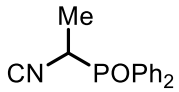
2e

^{31}P NMR (162 MHz, $CDCl_3$)

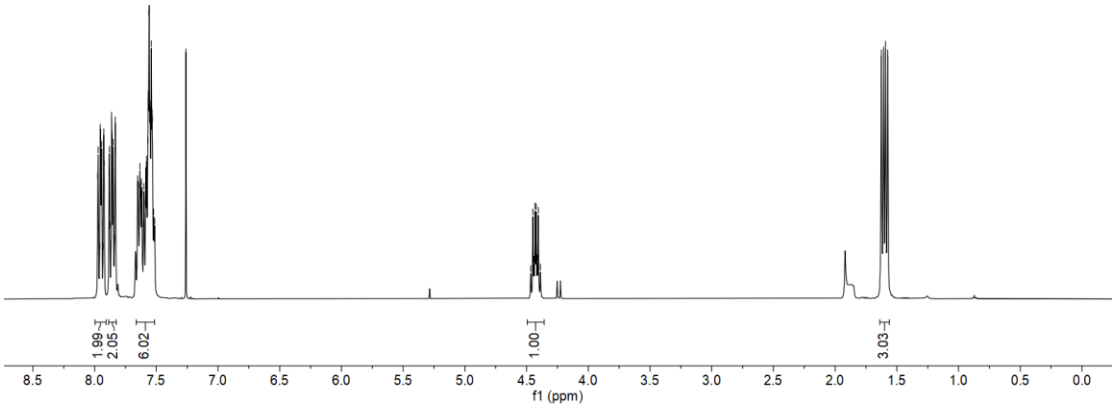


2e

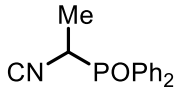
^{1}H NMR (400 MHz, $CDCl_3$)



2f



^{13}C NMR (101 MHz, $CDCl_3$)



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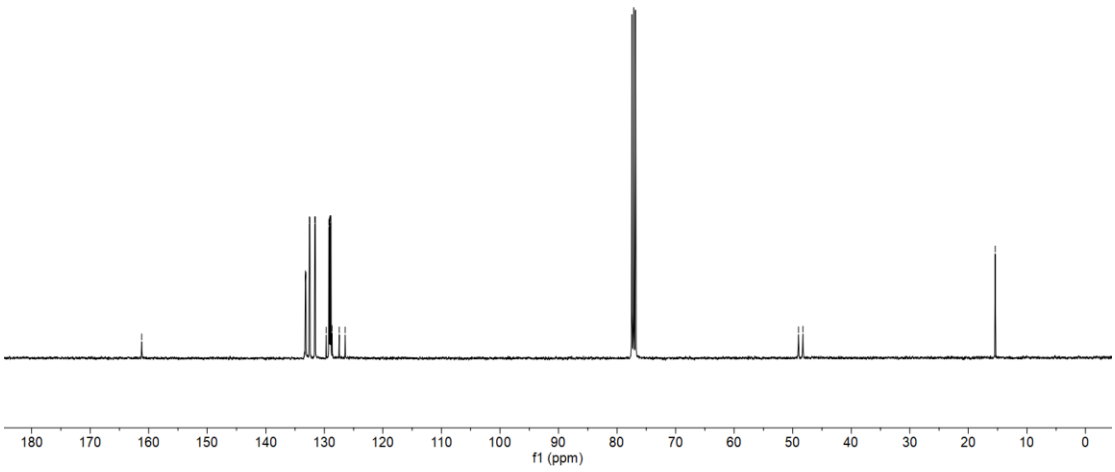
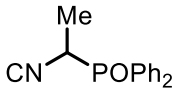
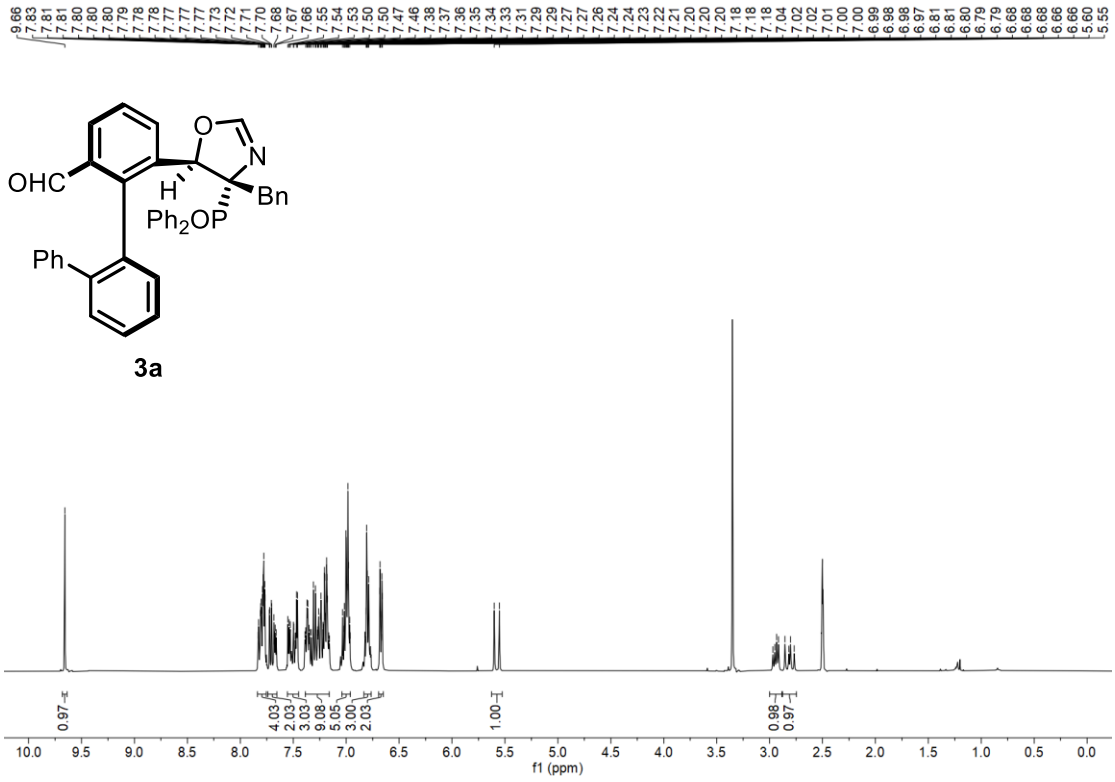


^{31}P NMR (162 MHz, $CDCl_3$)



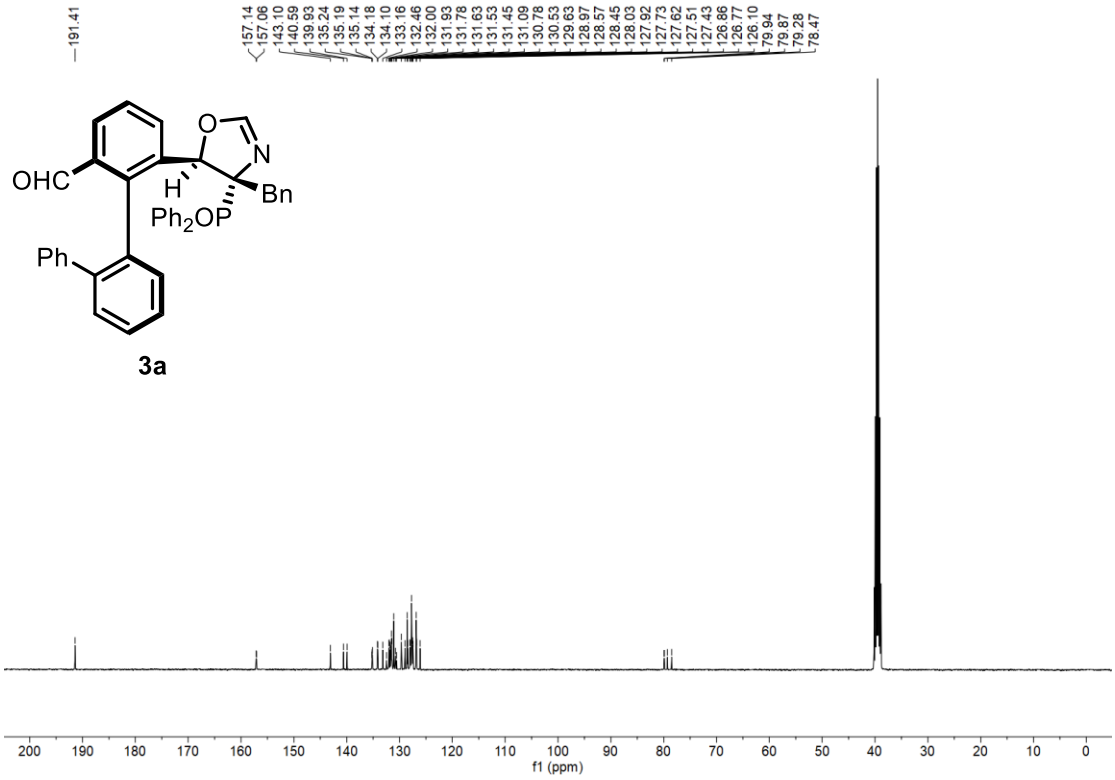
2f

^{1}H NMR (400 MHz, DMSO-d_6)

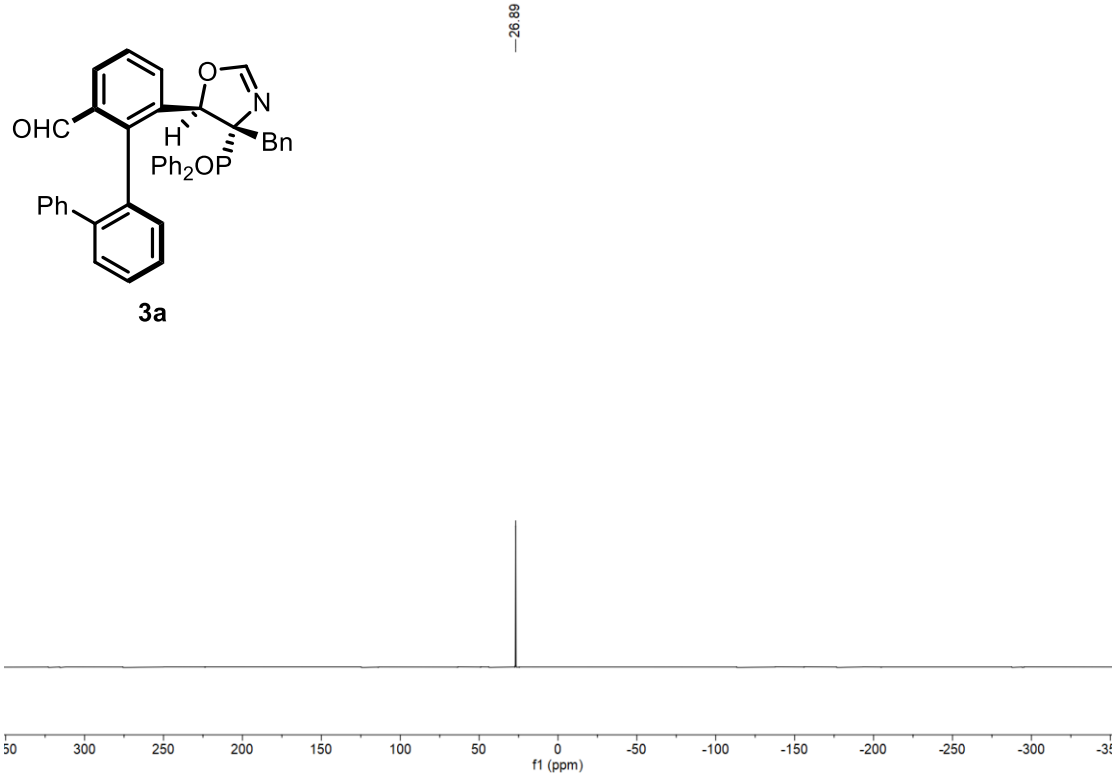


3a

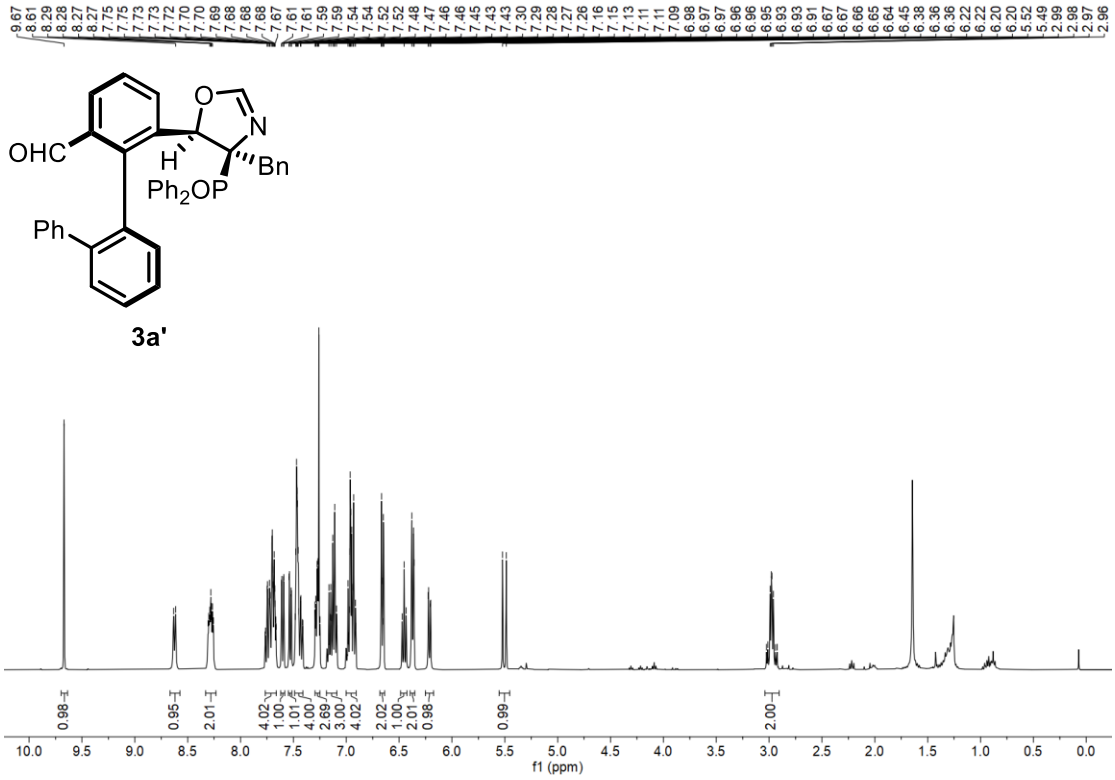
^{13}C NMR (101 MHz, DMSO-d_6)



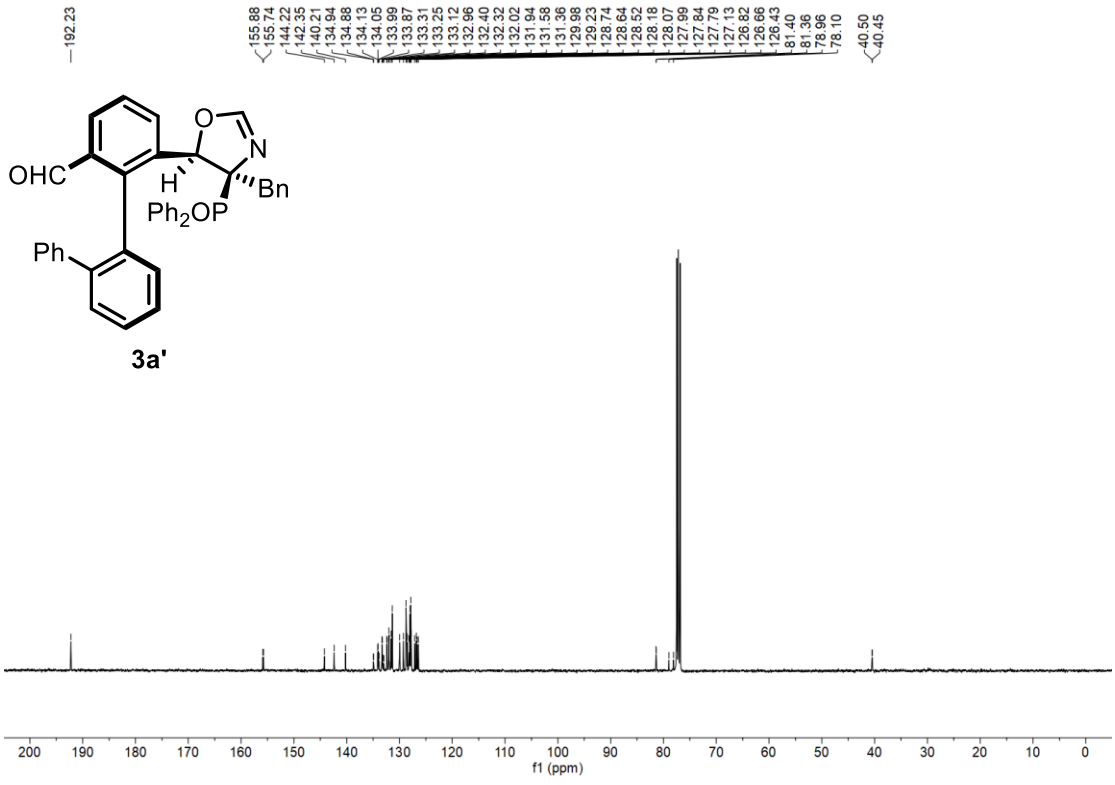
^{31}P NMR (162 MHz, DMSO-d_6)



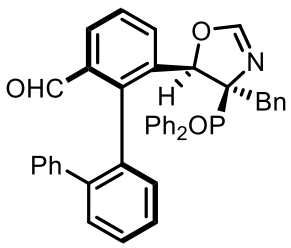
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

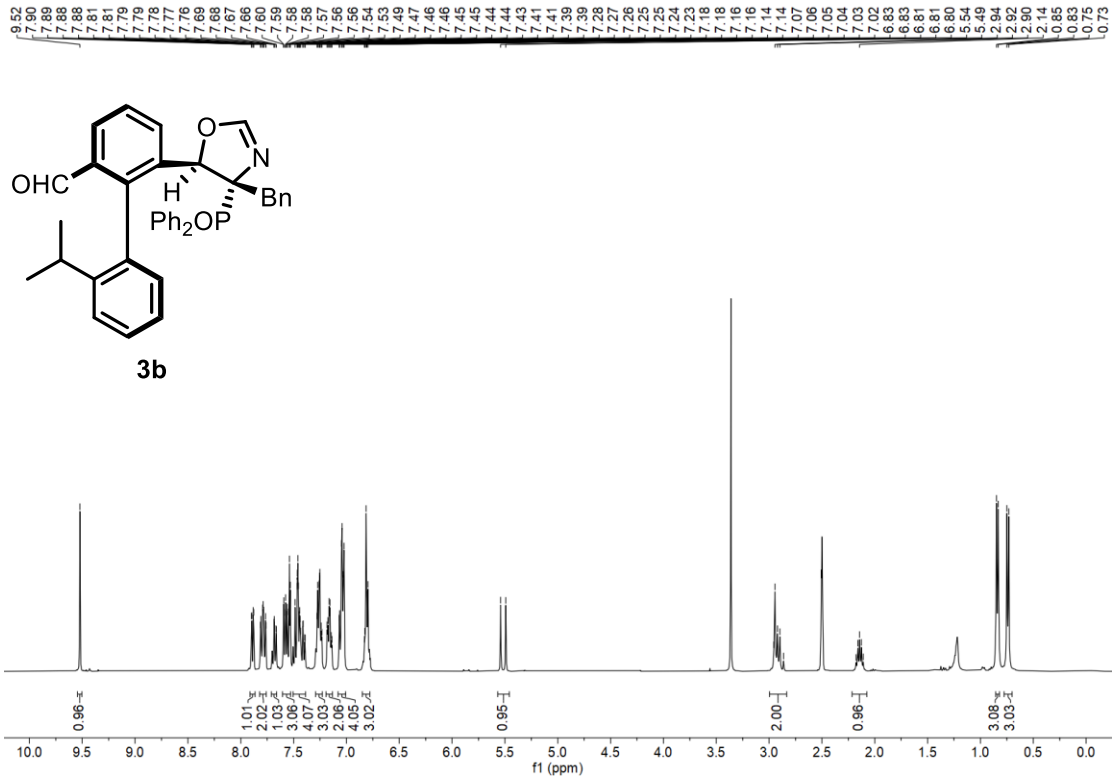


^{31}P NMR (162 MHz, $CDCl_3$)



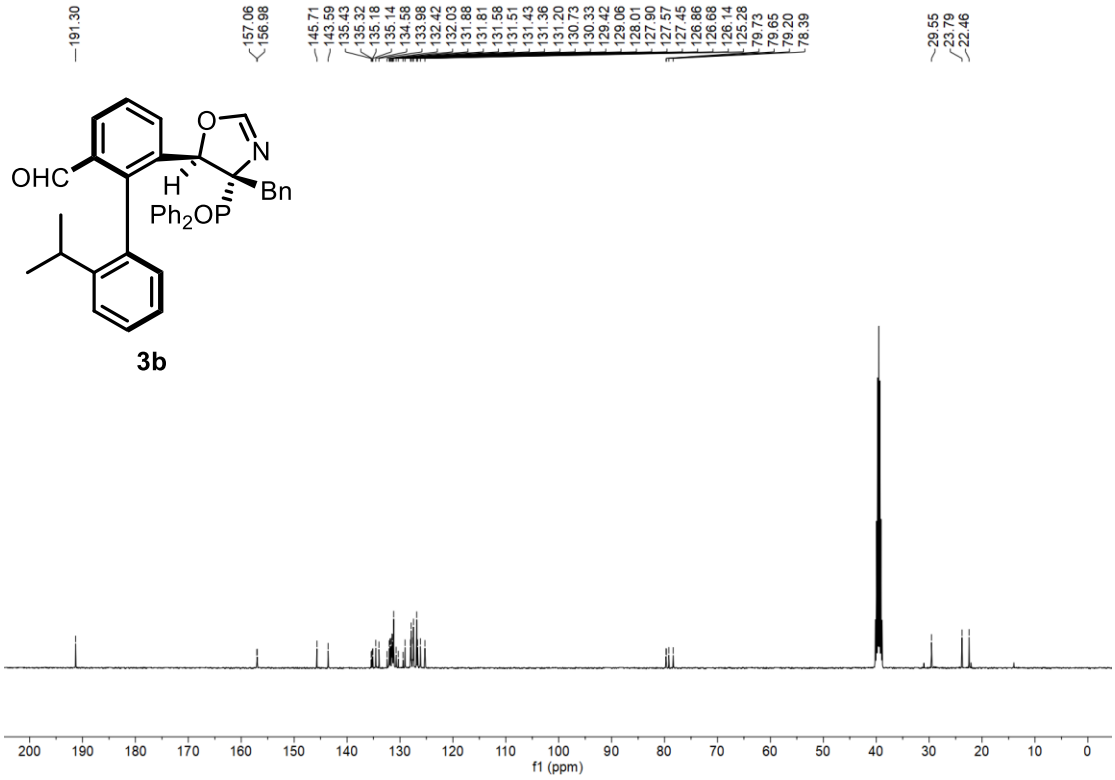
3a'

^{1}H NMR (400 MHz, DMSO-d_6)

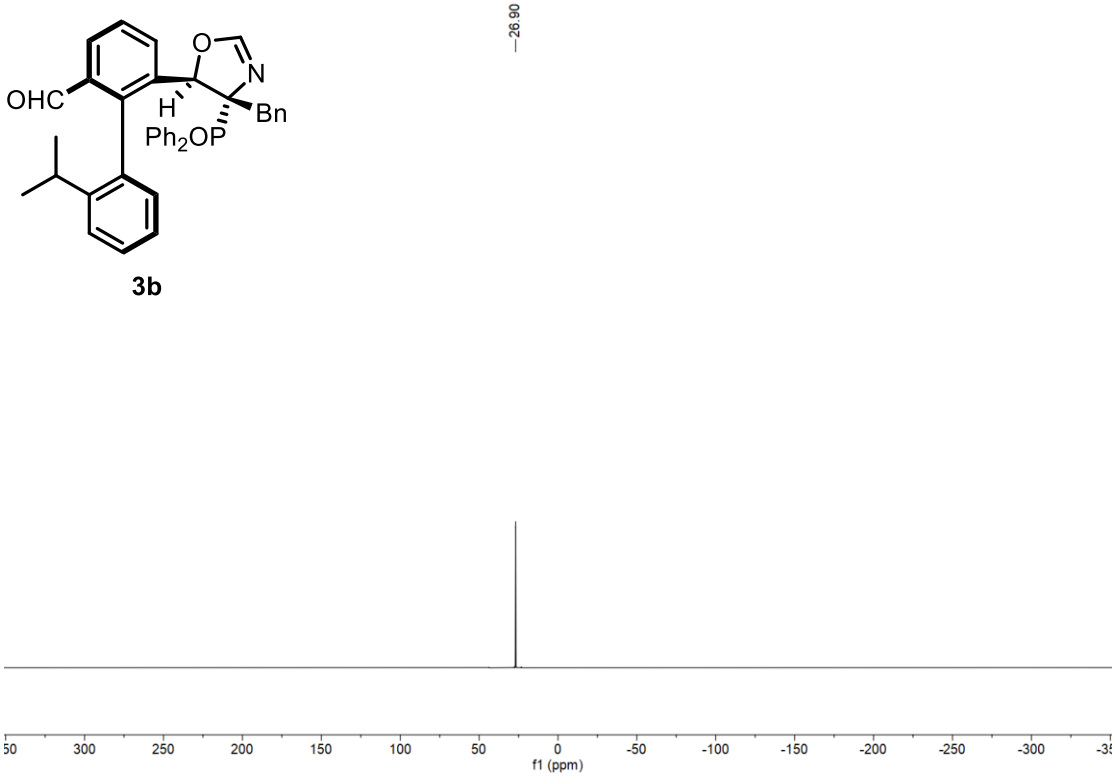


3b

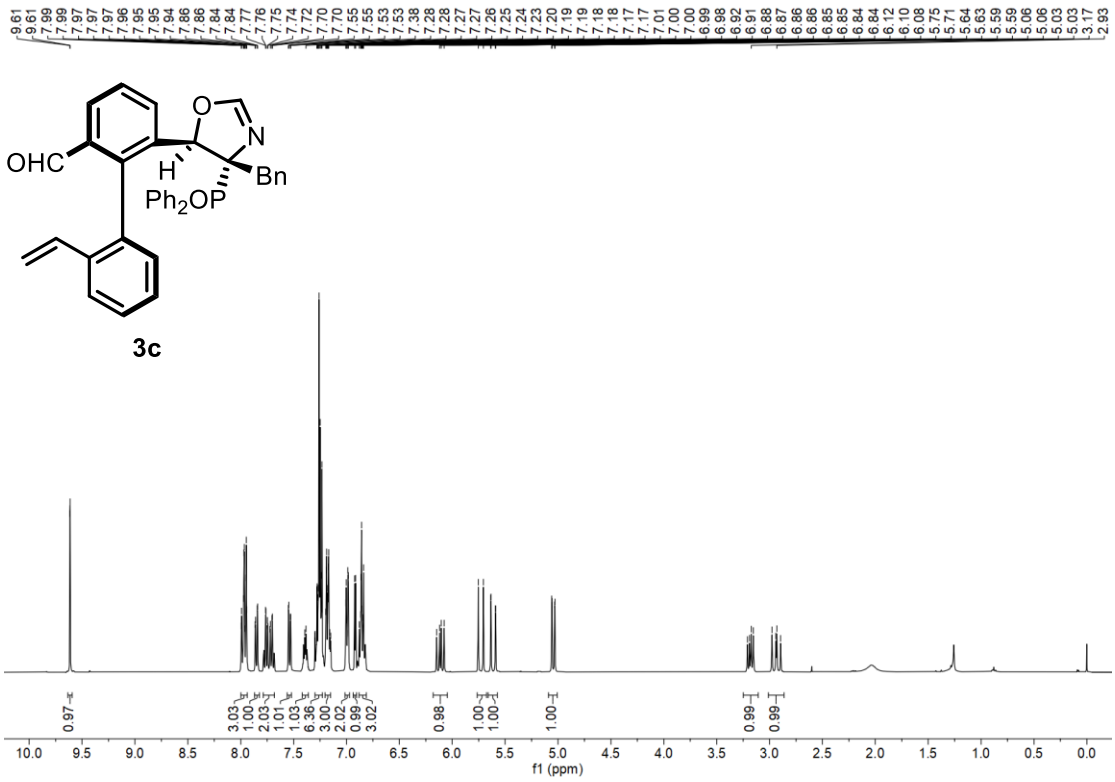
^{13}C NMR (101 MHz, DMSO-d_6)



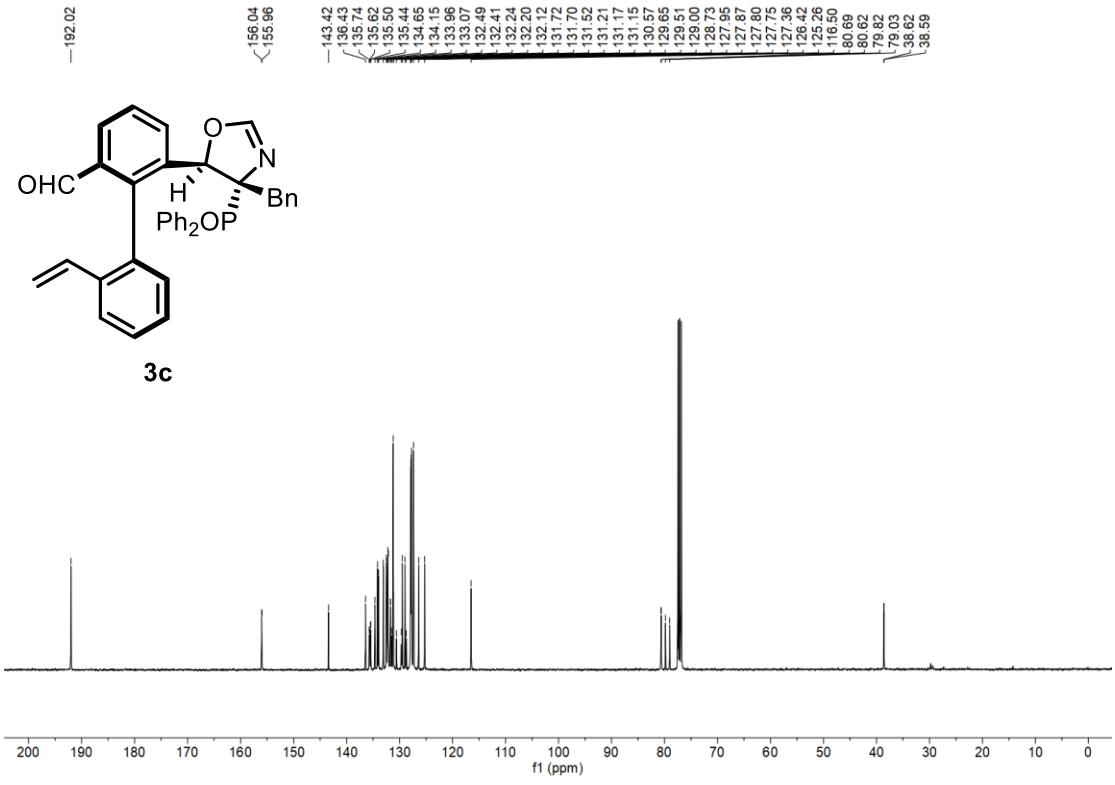
^{31}P NMR (162 MHz, DMSO-d_6)



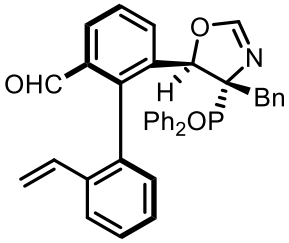
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

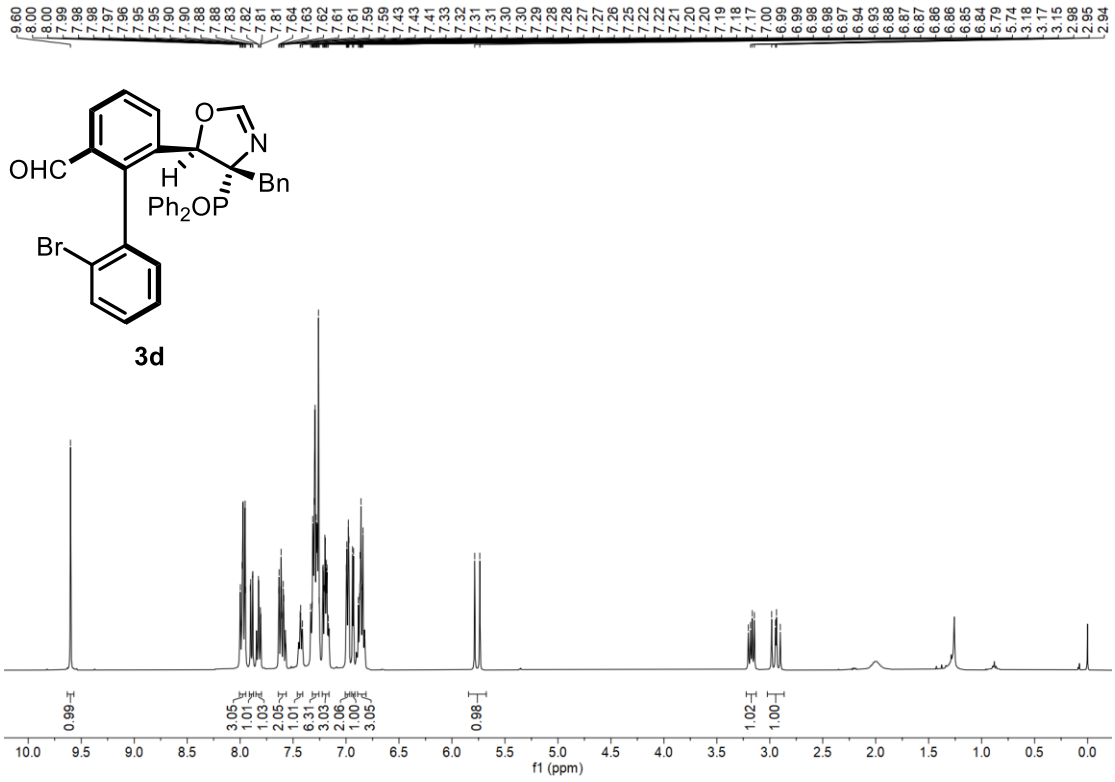


^{31}P NMR (162 MHz, $CDCl_3$)



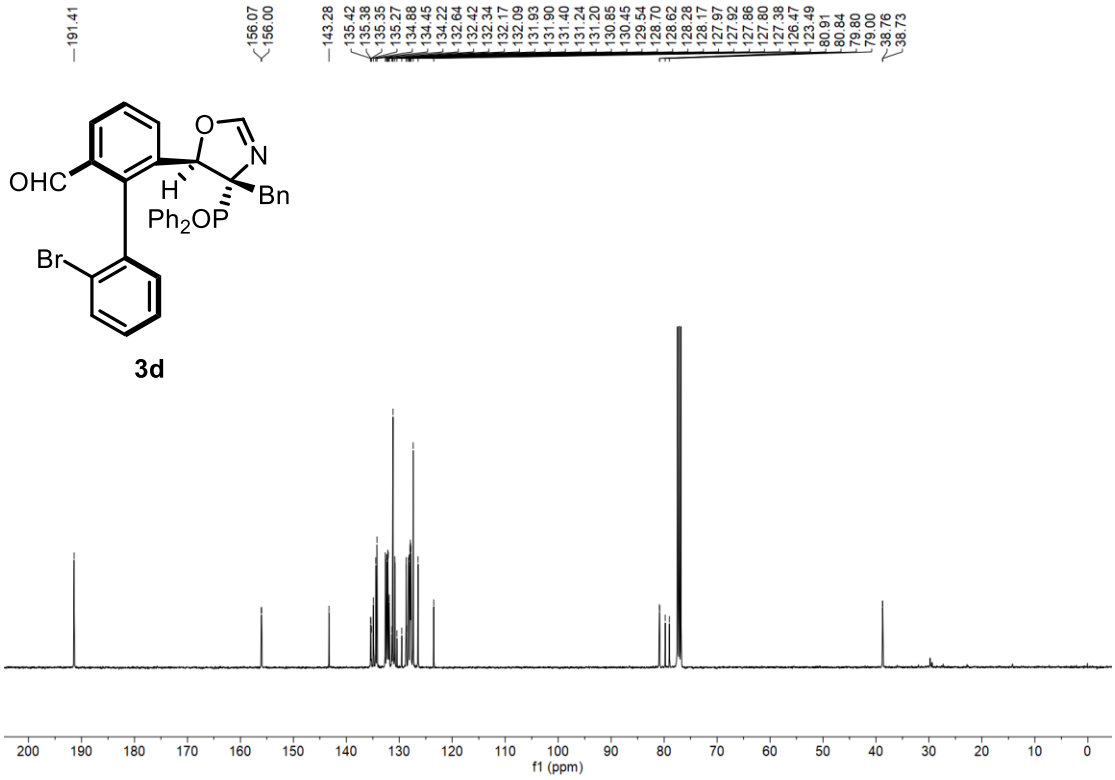
3c

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

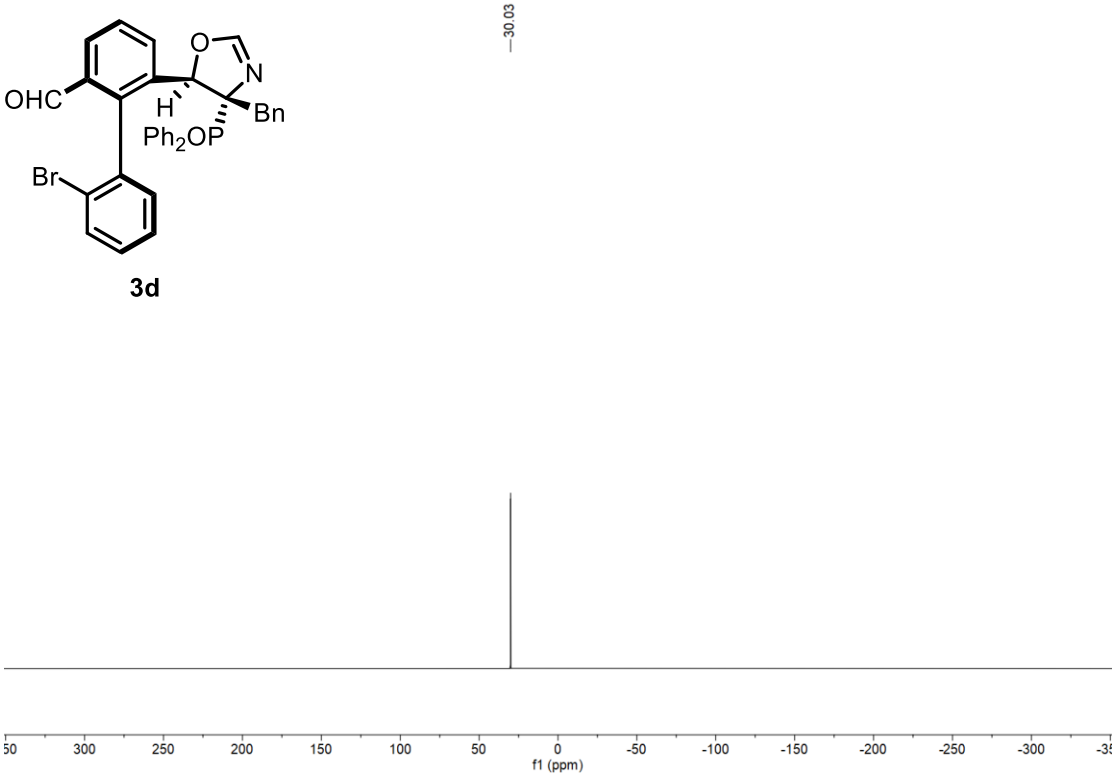


3d

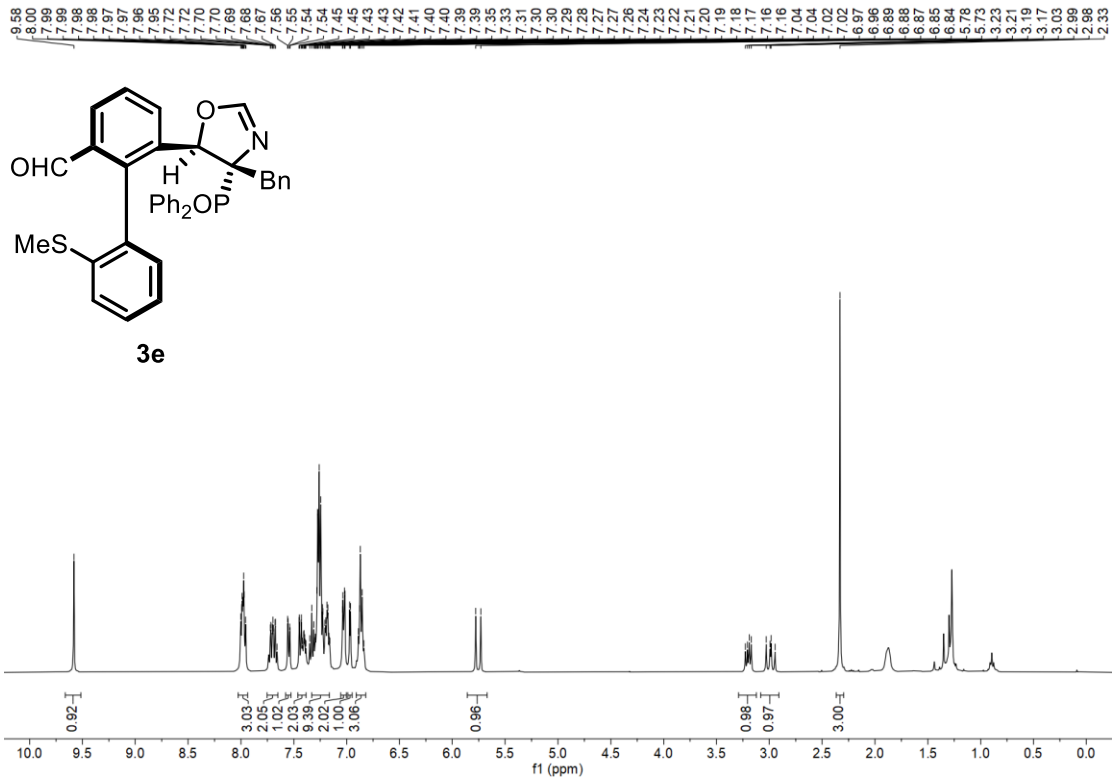
^{13}C NMR (101 MHz, $CDCl_3$)



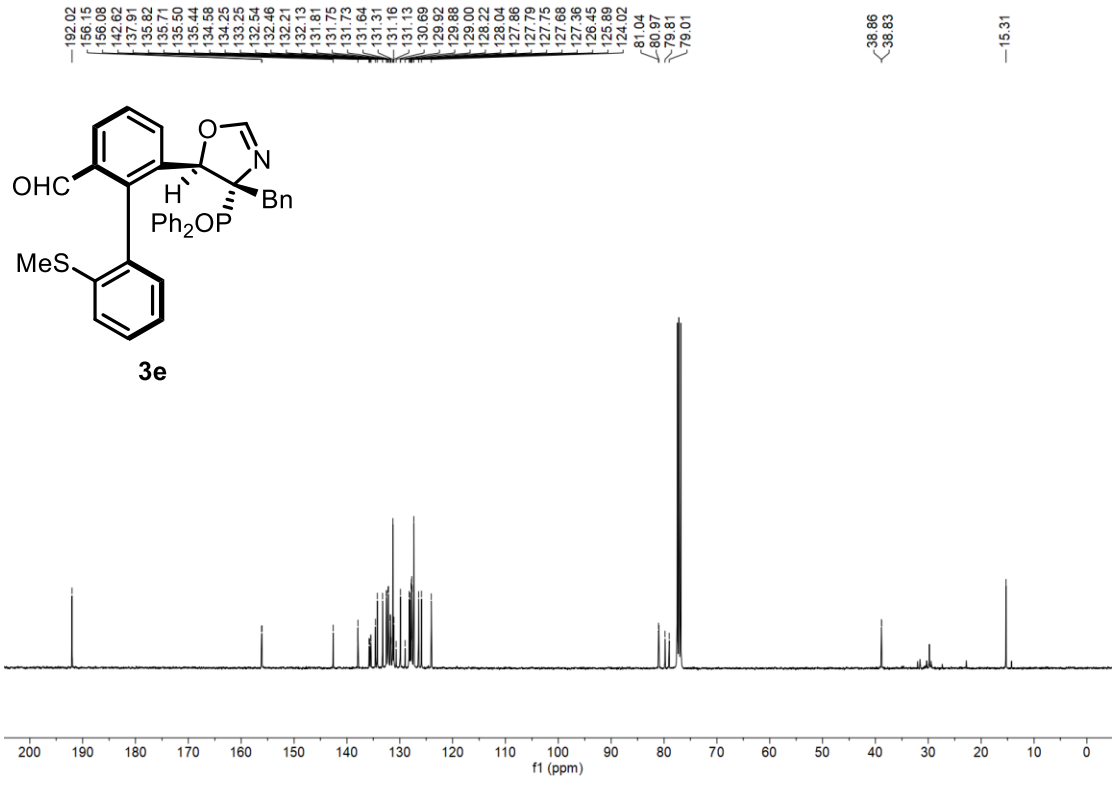
^{31}P NMR (162 MHz, $CDCl_3$)



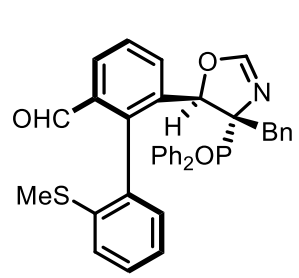
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

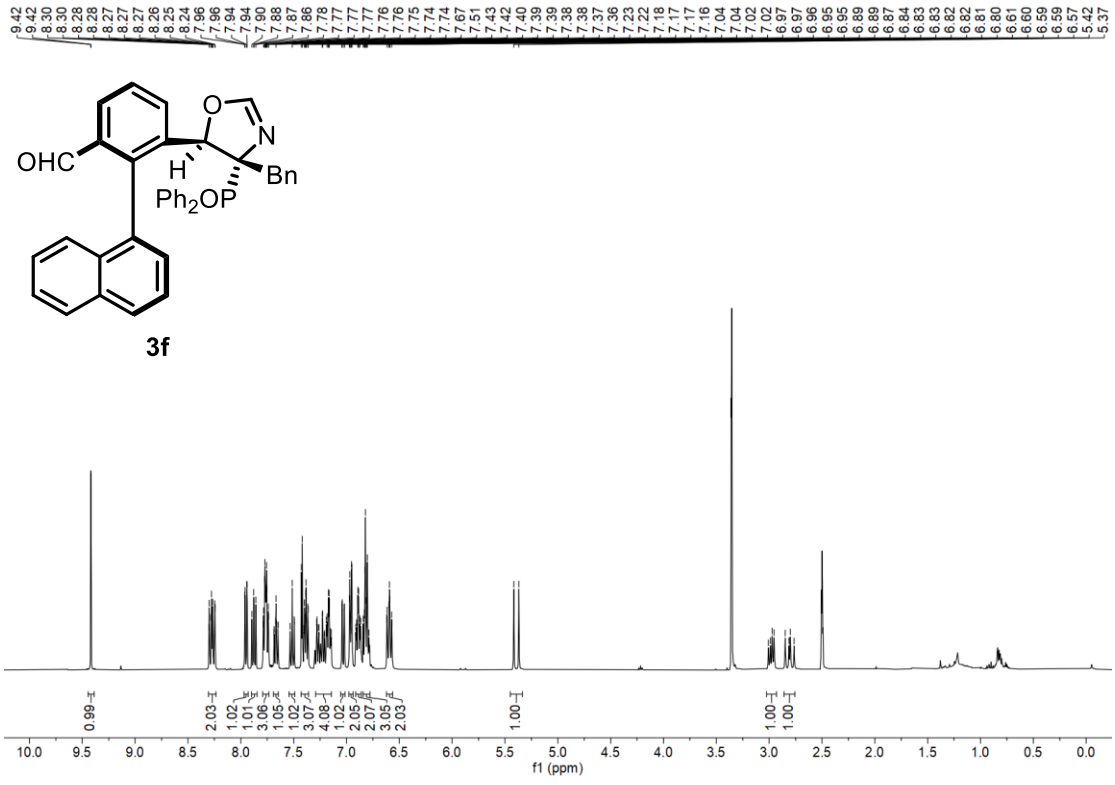


^{31}P NMR (162 MHz, $CDCl_3$)



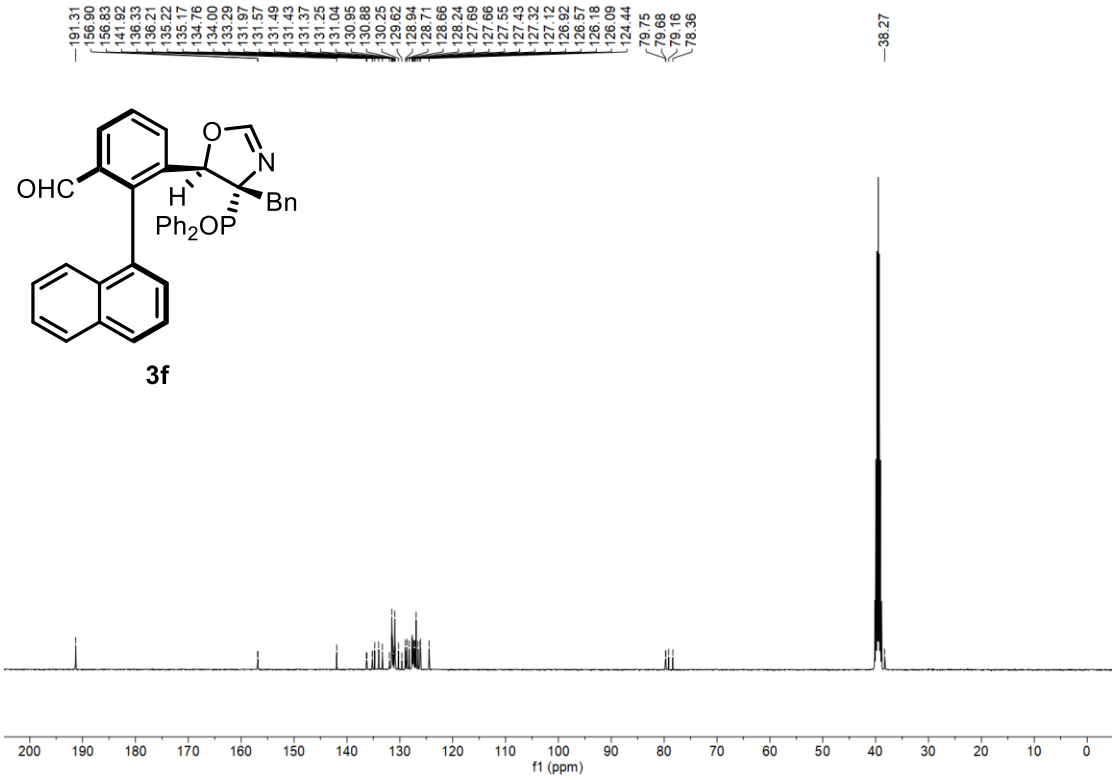
3e

^{1}H NMR (400 MHz, DMSO-d_6)

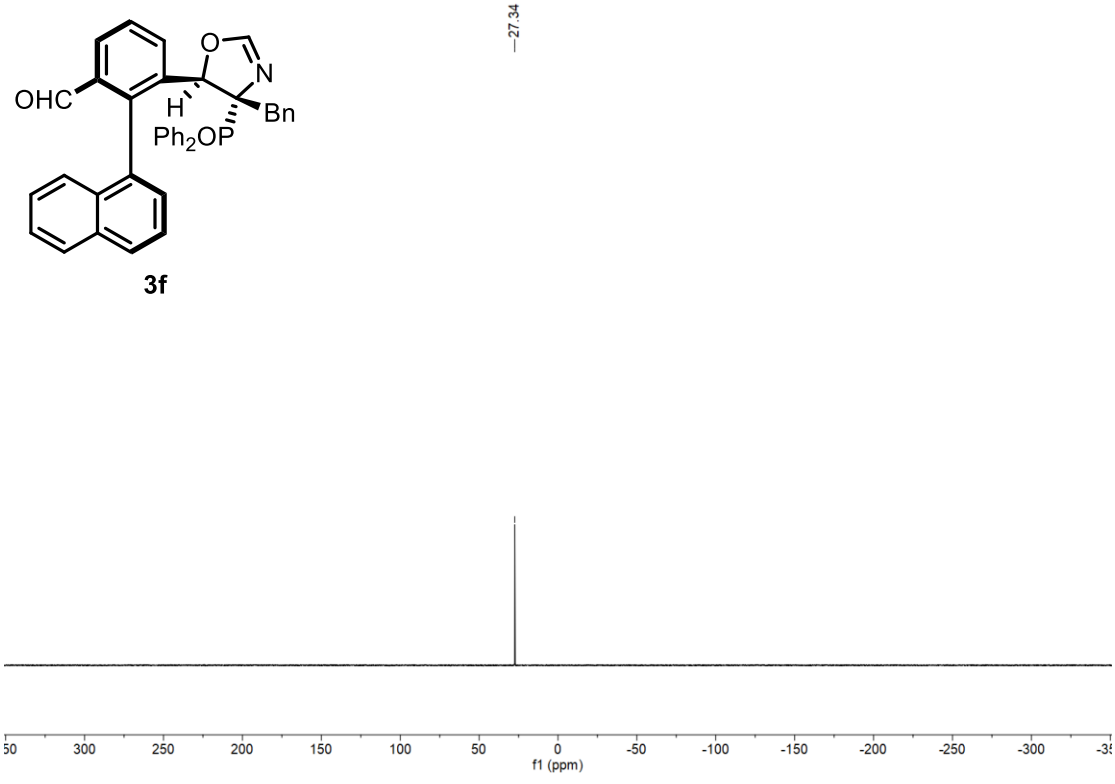


3f

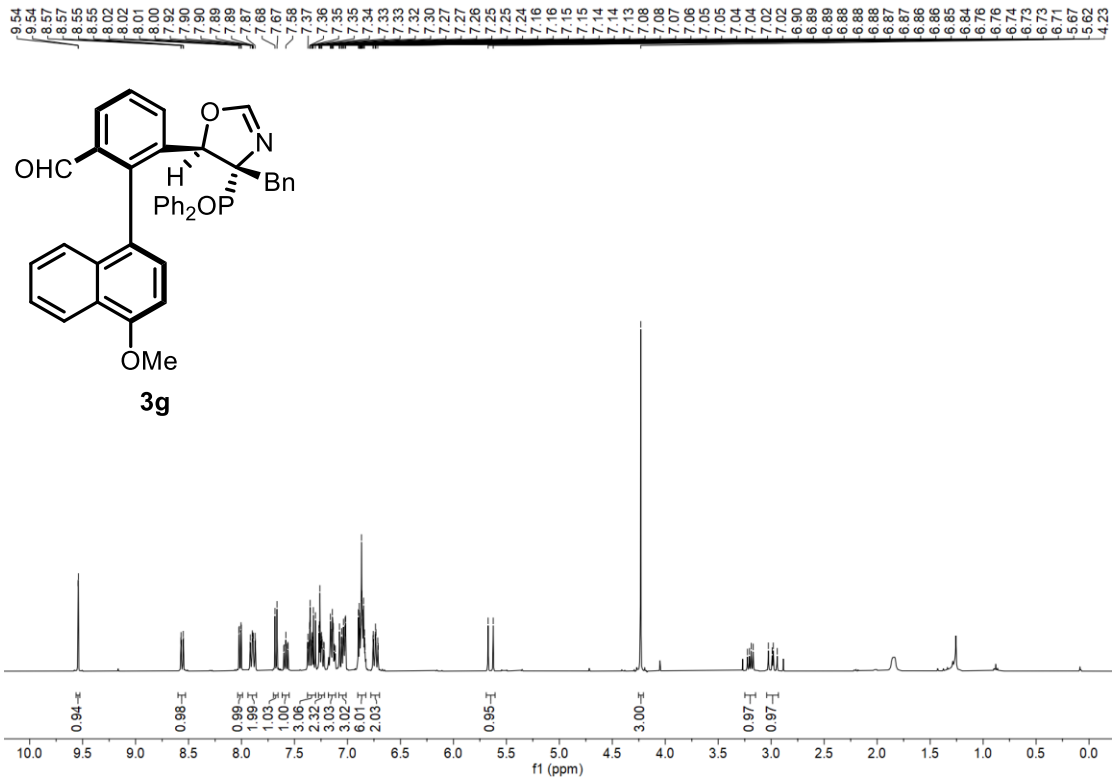
^{13}C NMR (101 MHz, DMSO-d_6)



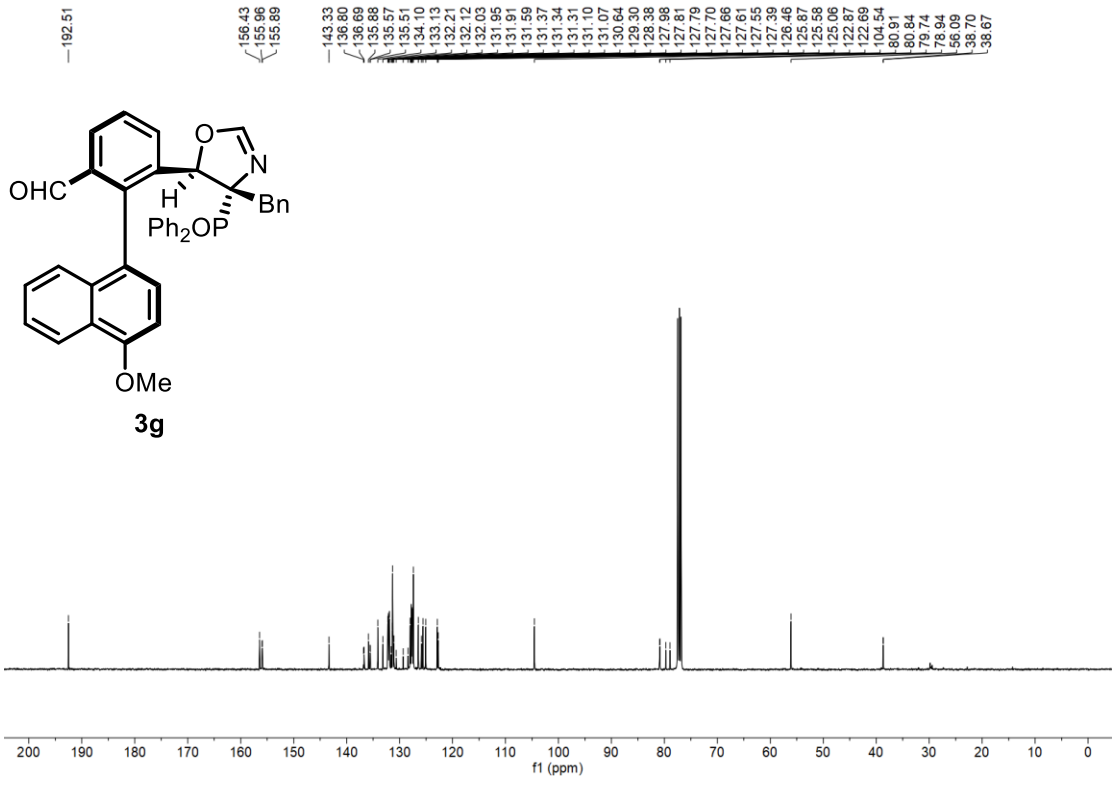
^{31}P NMR (162 MHz, DMSO-d_6)



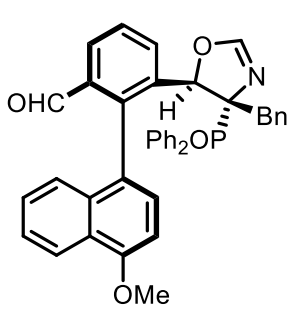
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

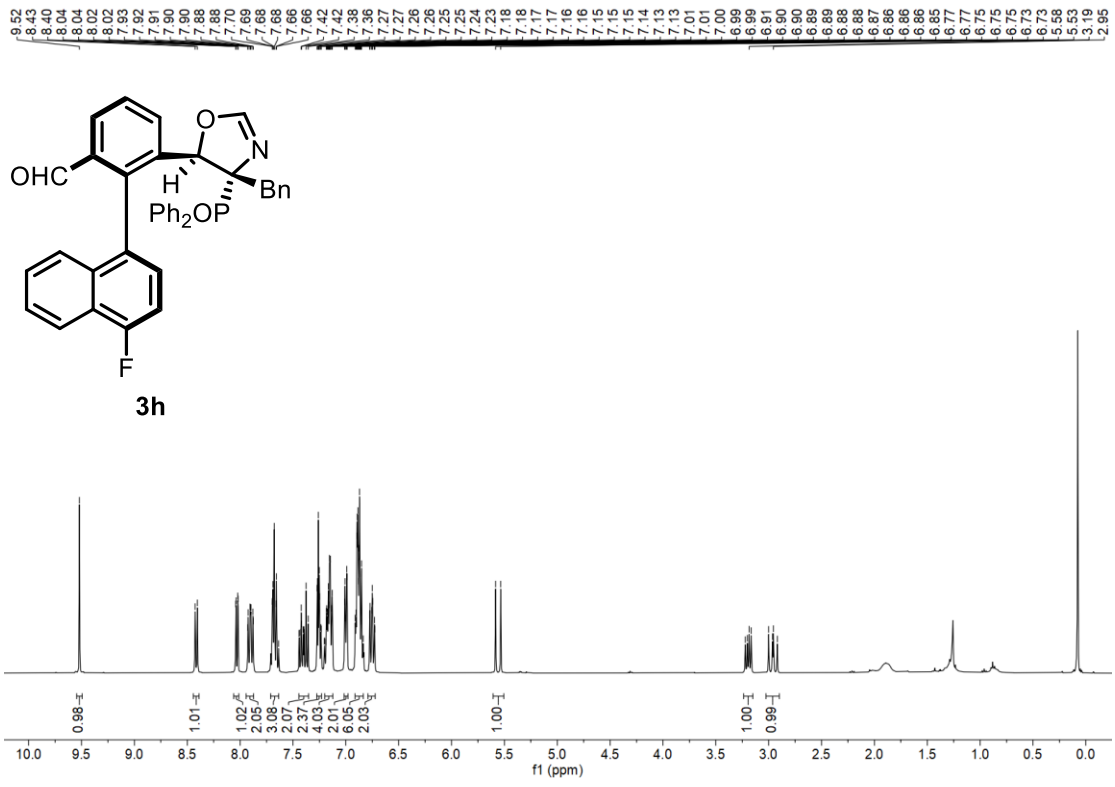


^{31}P NMR (162 MHz, $CDCl_3$)



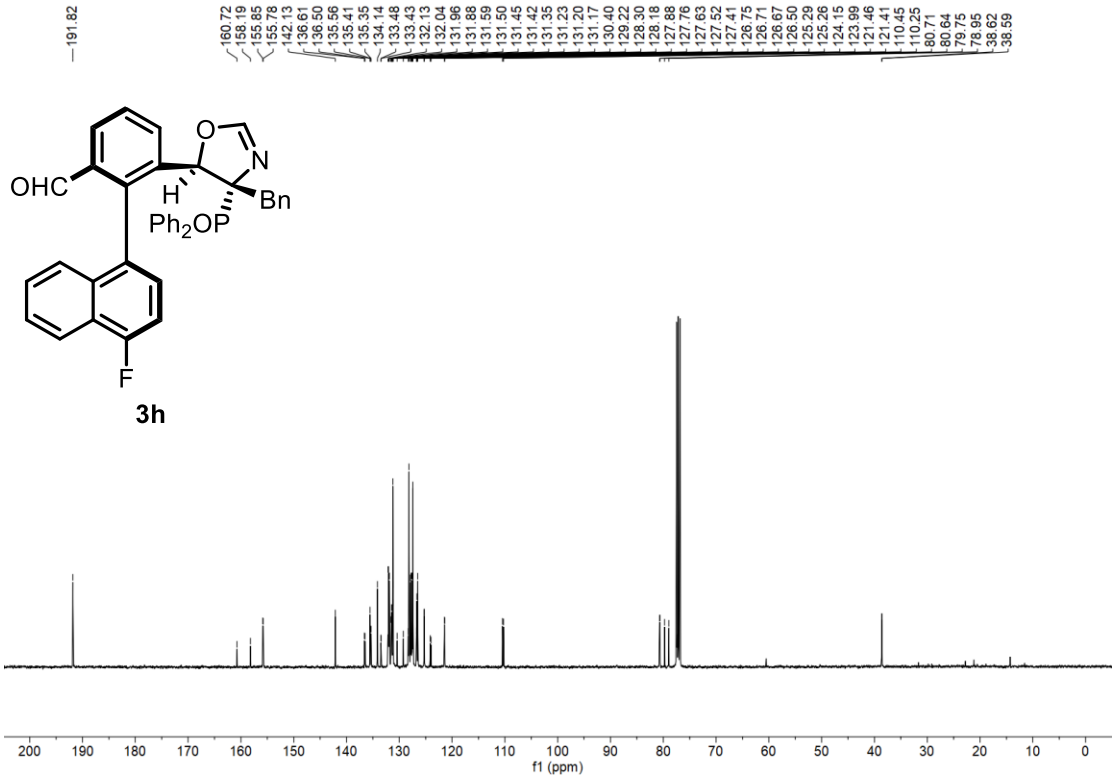
3g

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

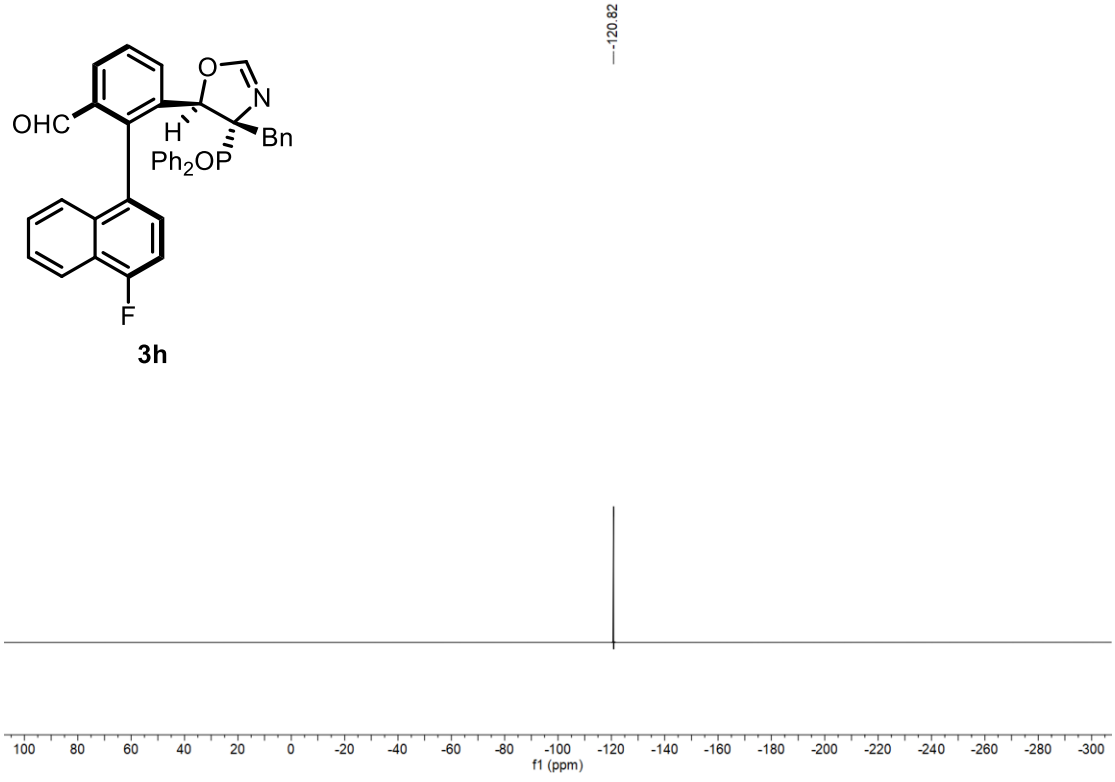


3h

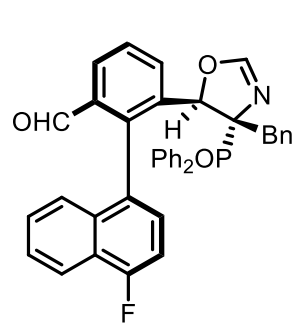
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

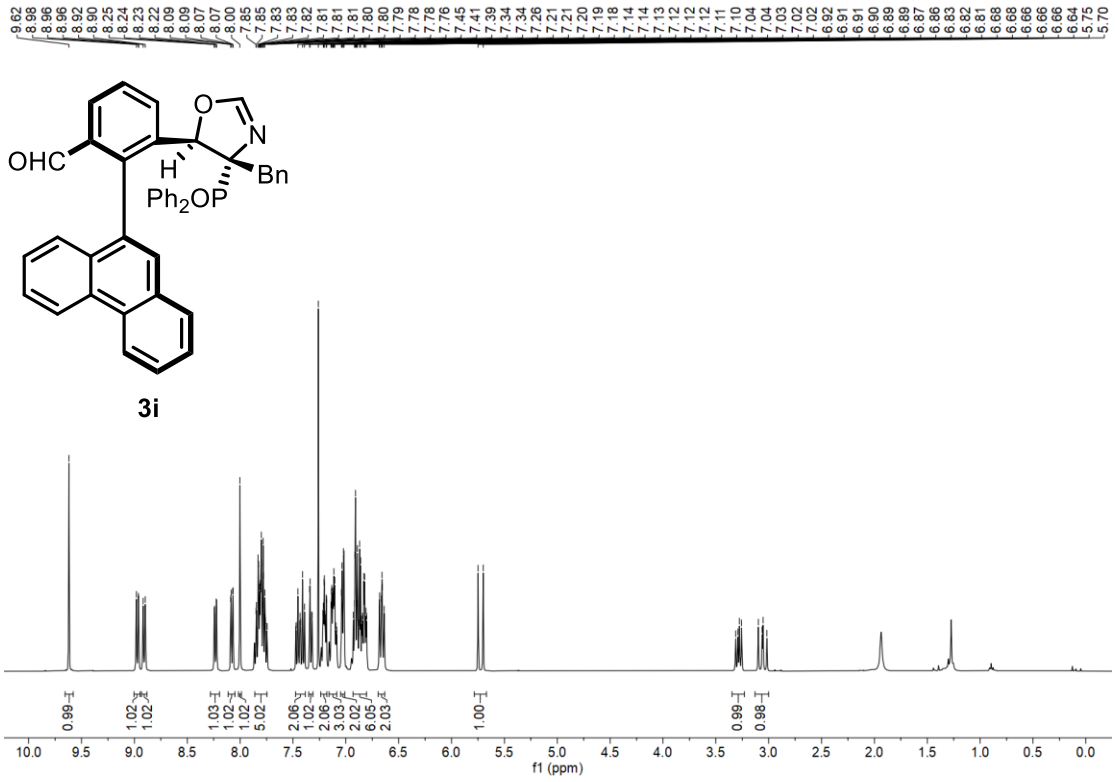


^{31}P NMR (162 MHz, $CDCl_3$)



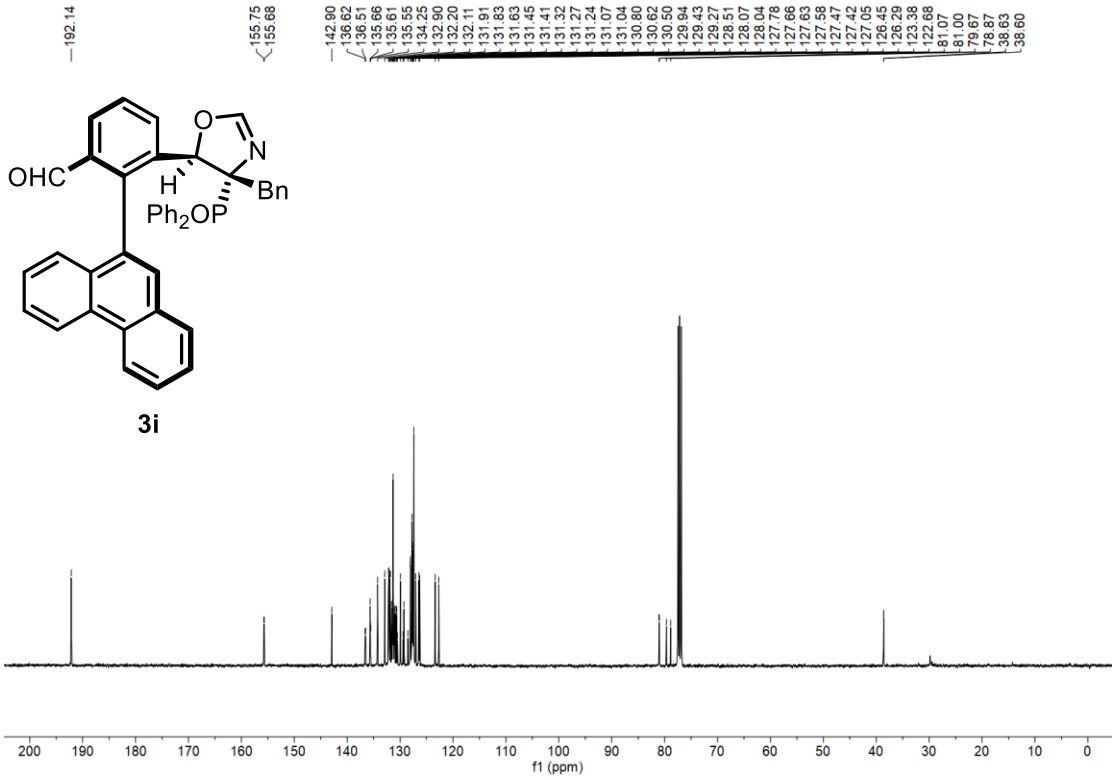
3h

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



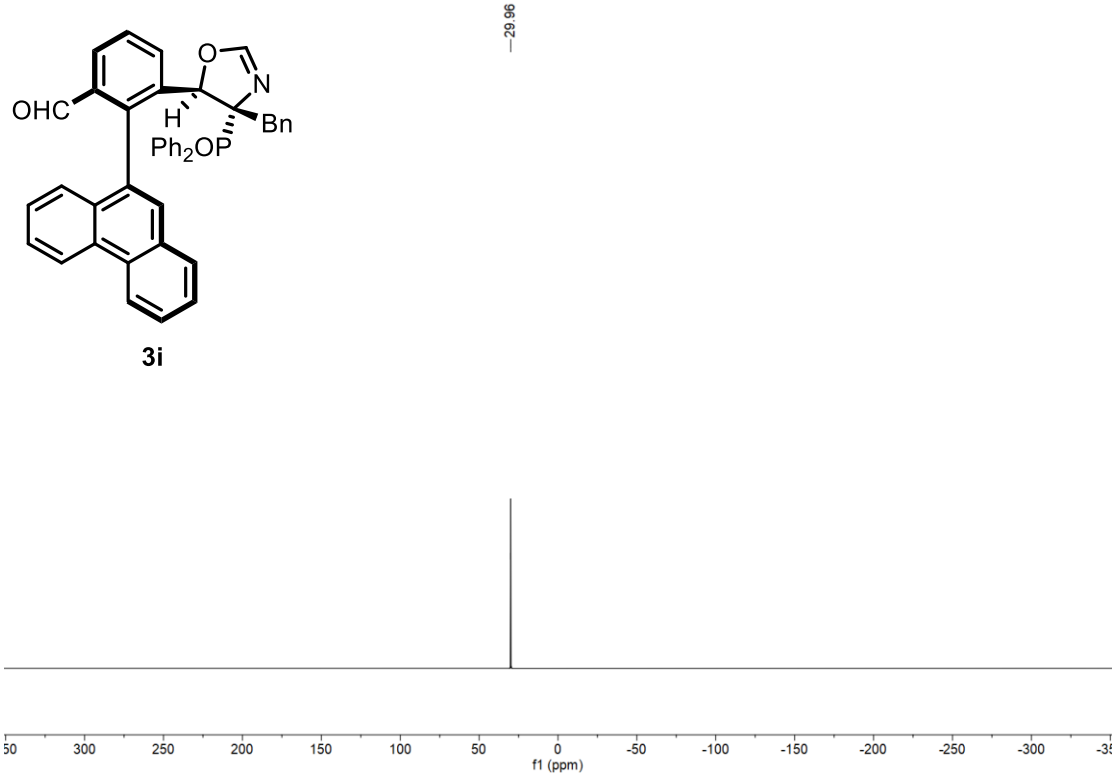
3i

^{13}C NMR (101 MHz, $CDCl_3$)



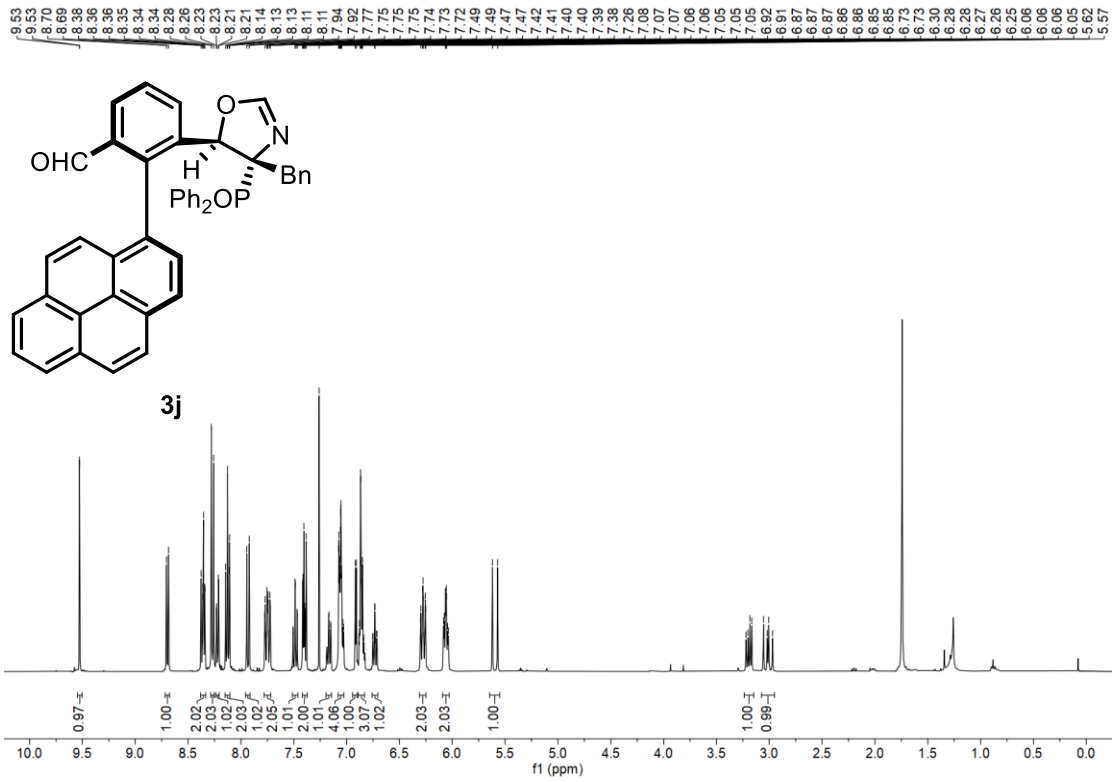
3i

^{31}P NMR (162 MHz, $CDCl_3$)

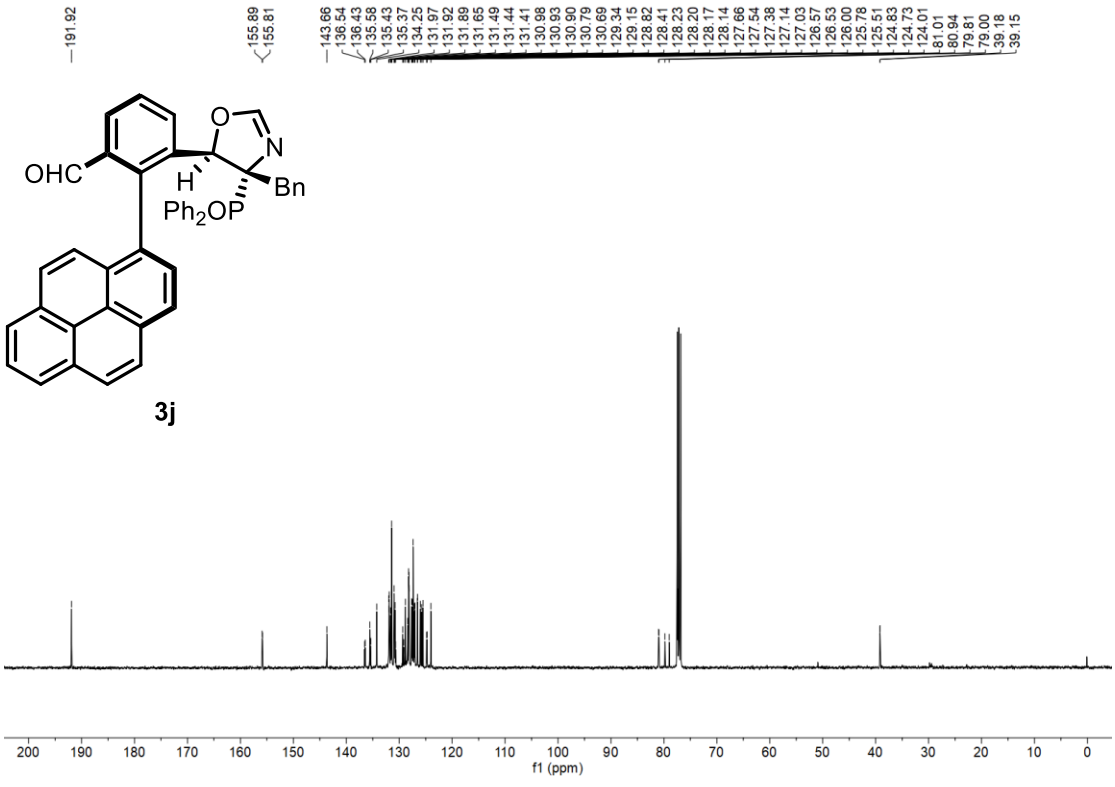


3i

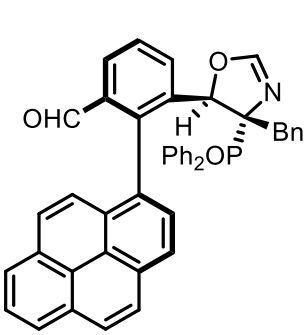
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

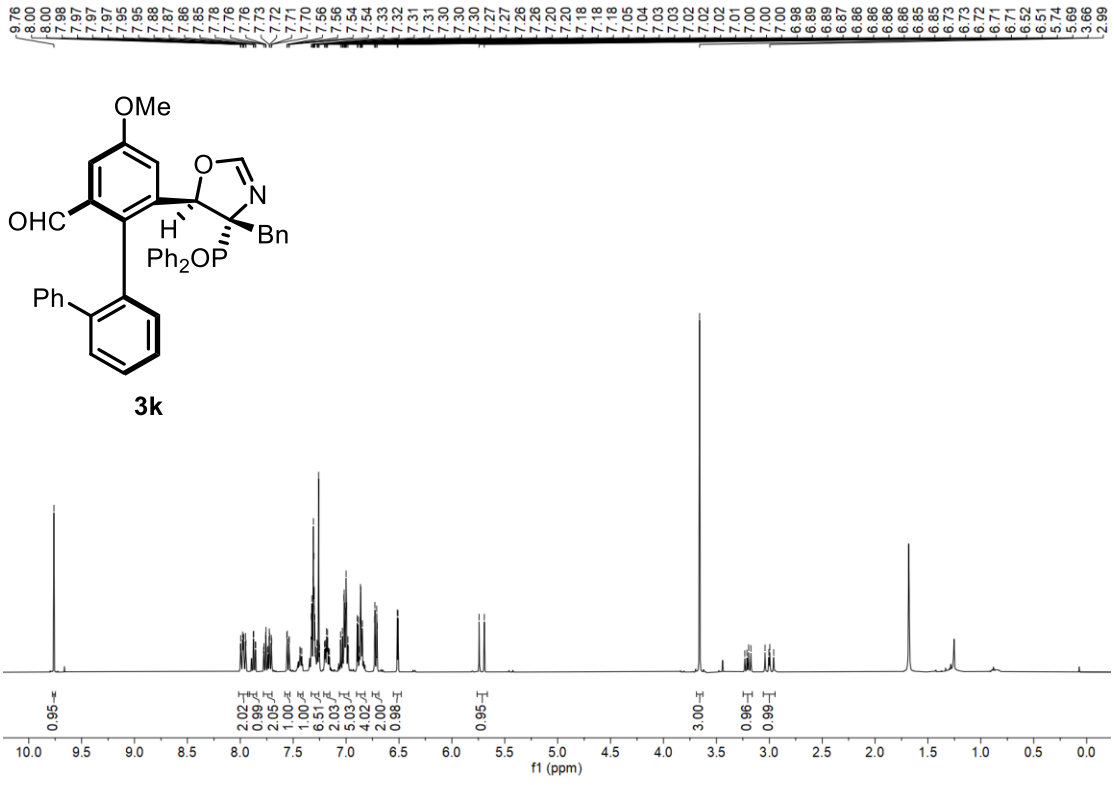


^{31}P NMR (162 MHz, $CDCl_3$)



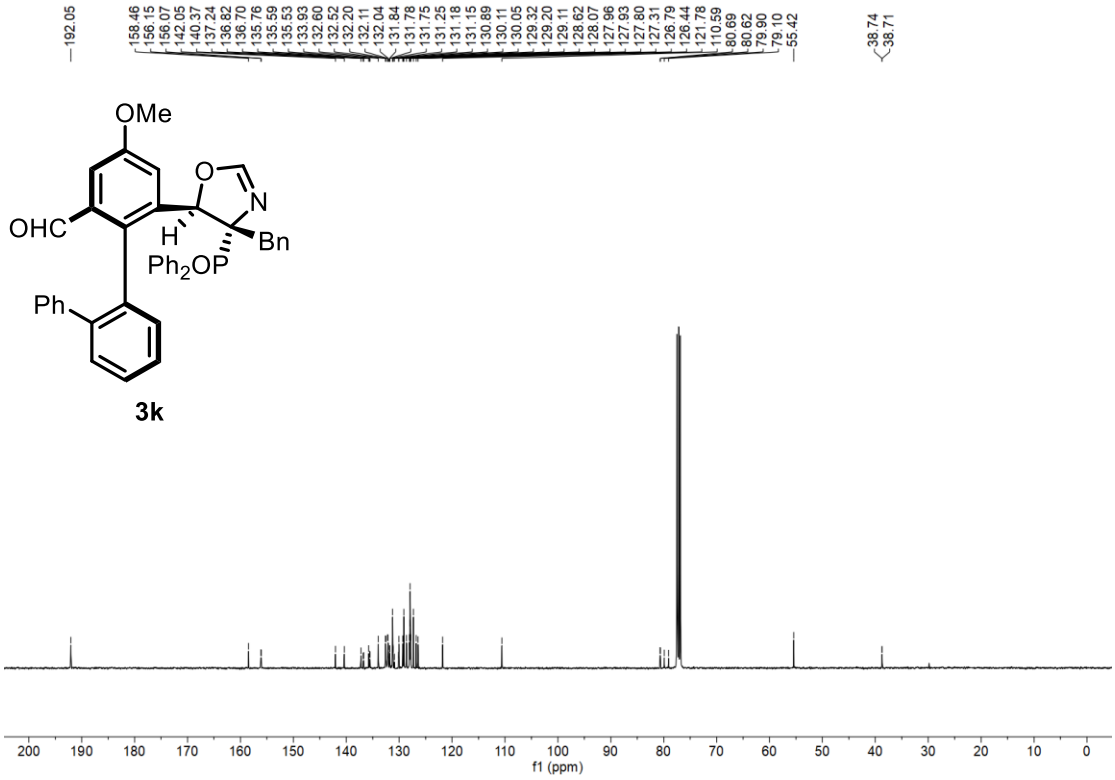
3j

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

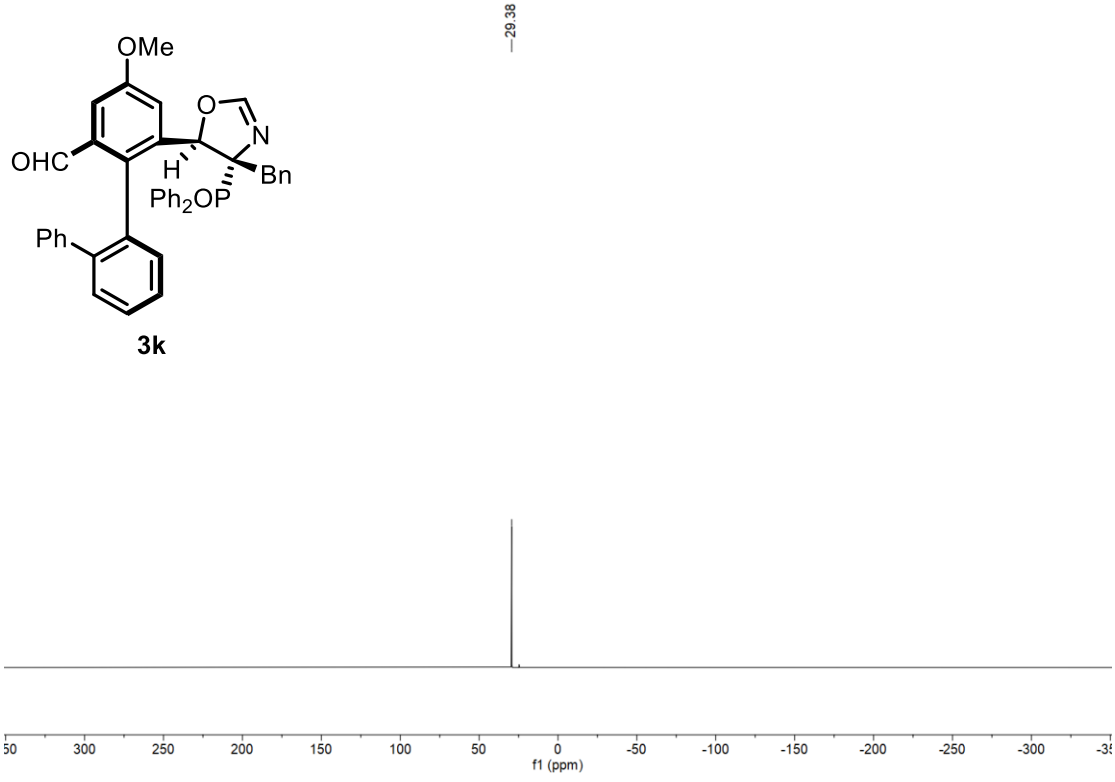


3k

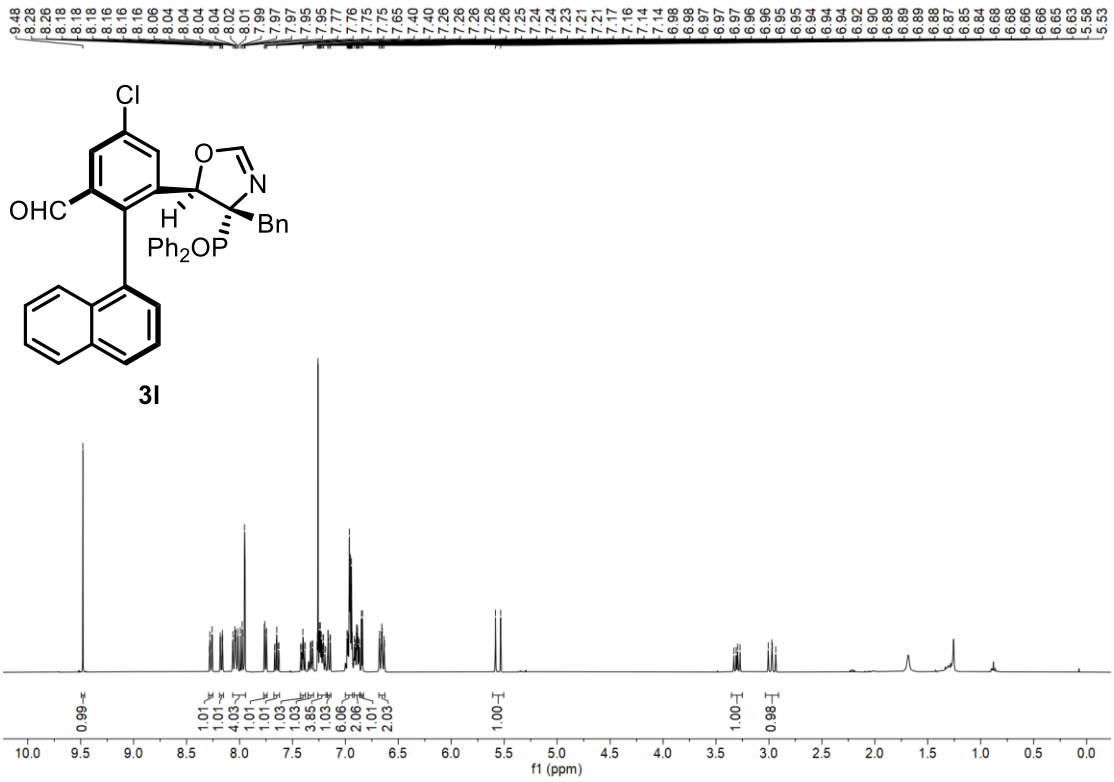
^{13}C NMR (101 MHz, $CDCl_3$)



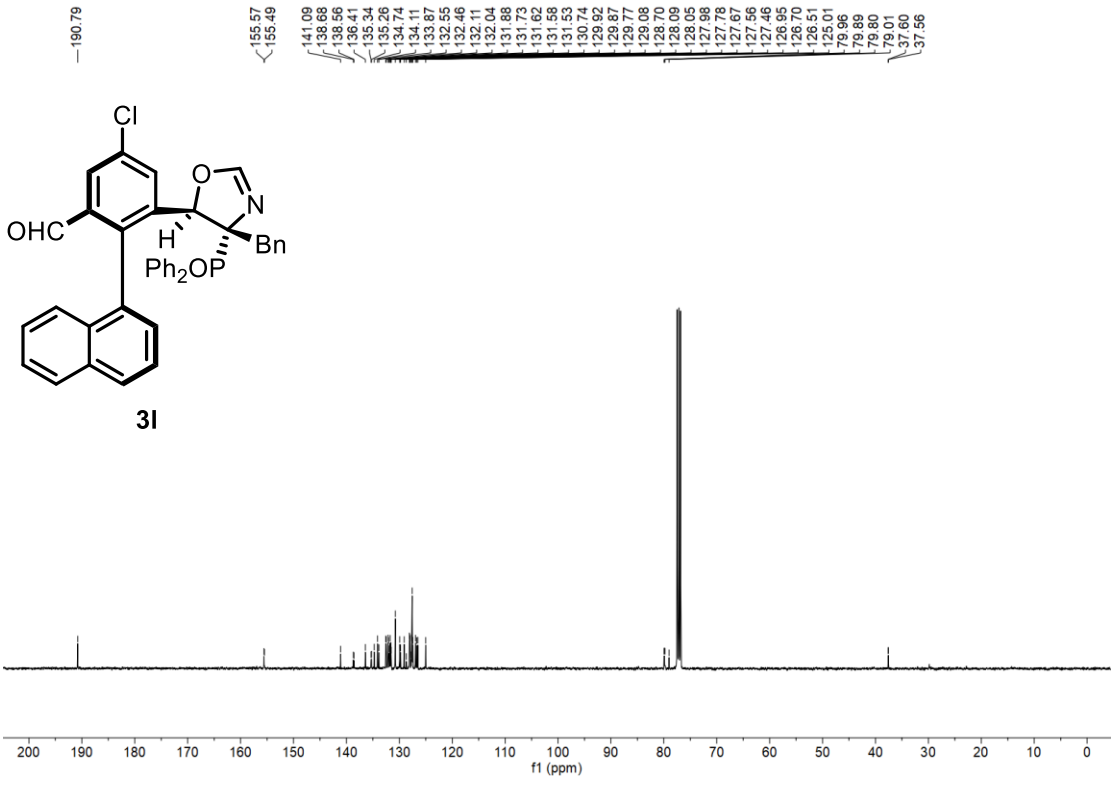
^{31}P NMR (162 MHz, $CDCl_3$)



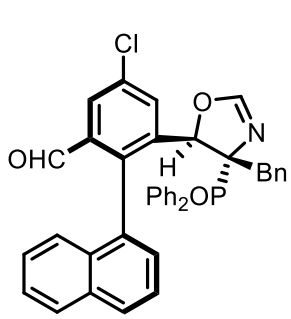
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

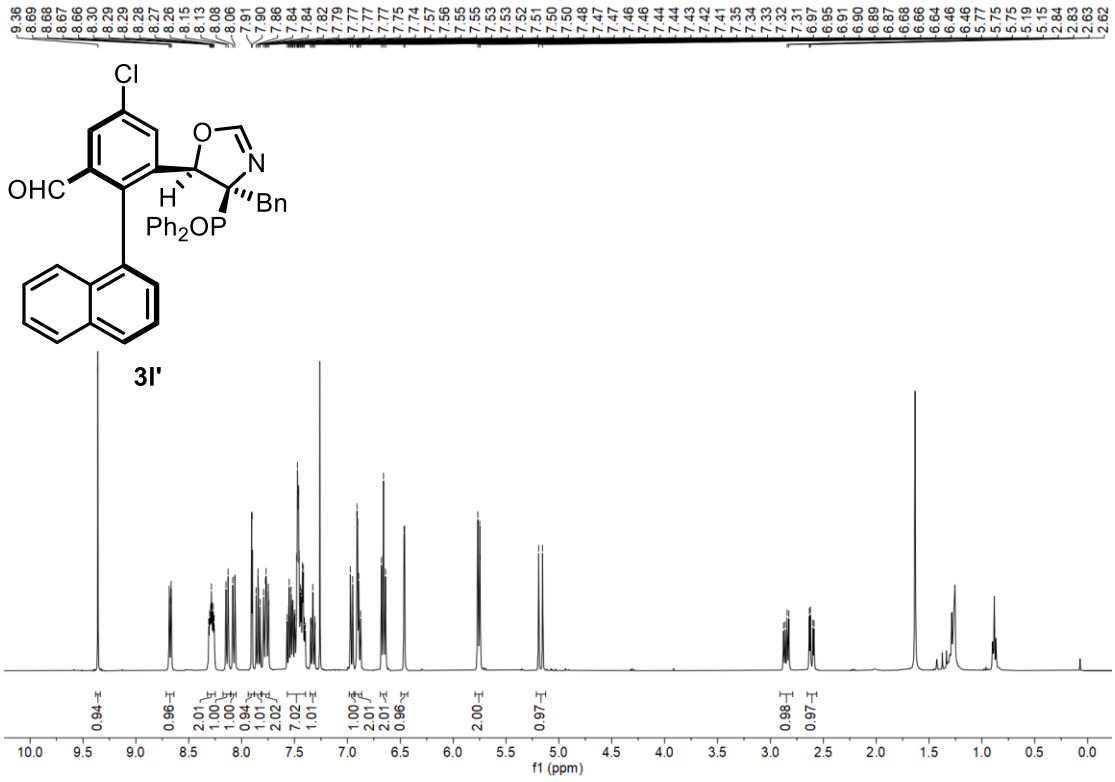


^{31}P NMR (162 MHz, $CDCl_3$)



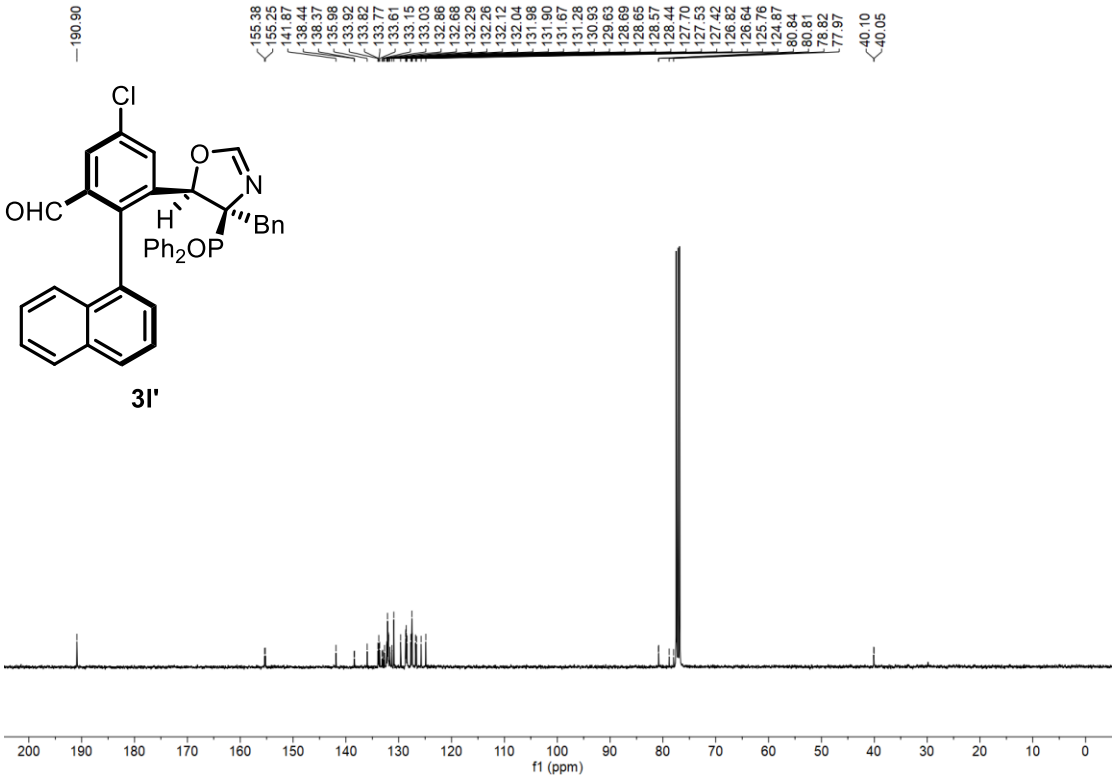
3l

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

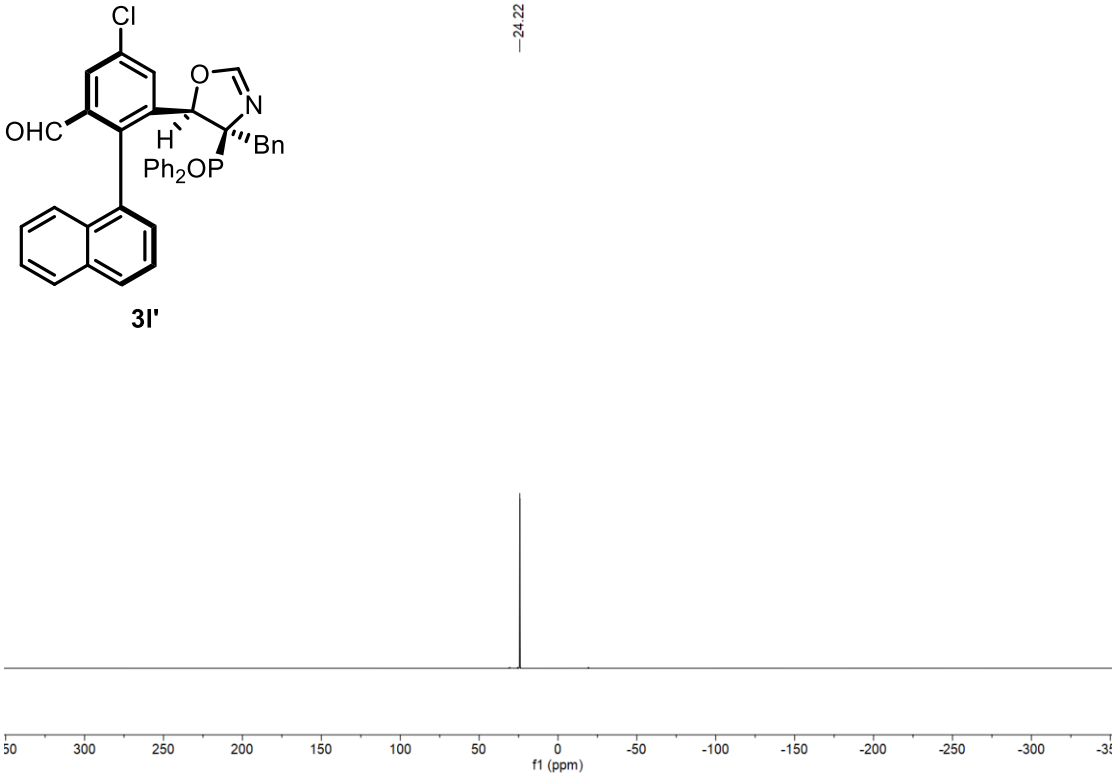


3l'

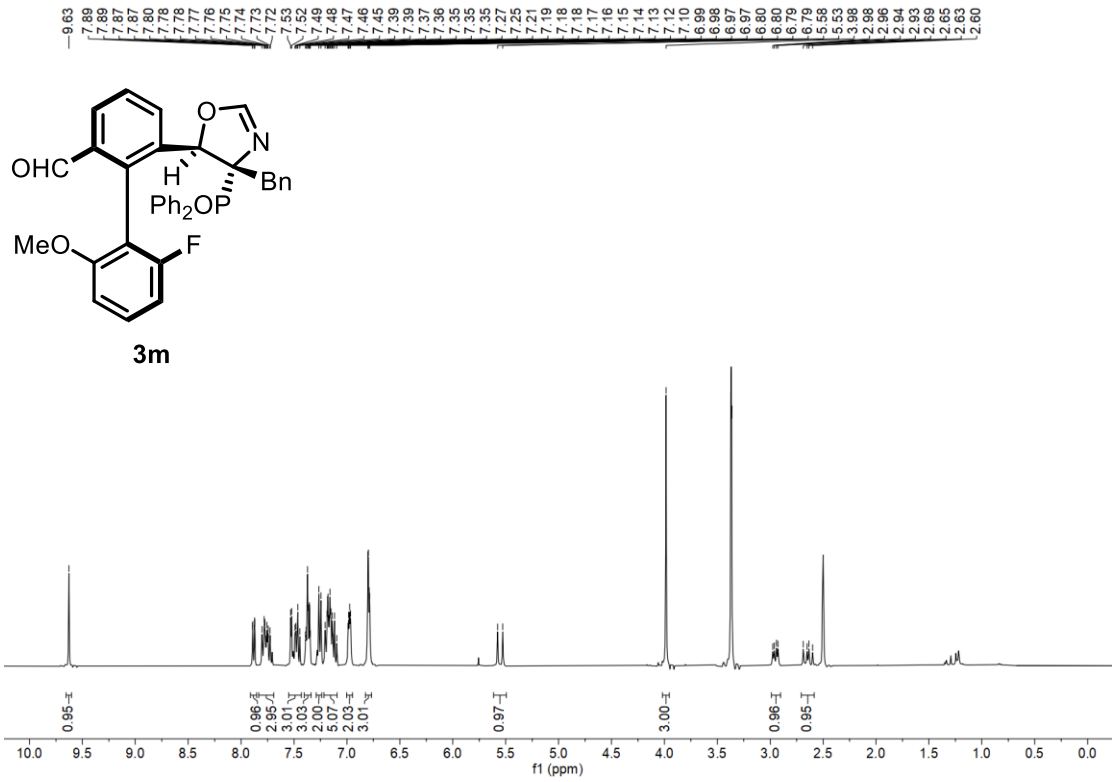
^{13}C NMR (101 MHz, $CDCl_3$)



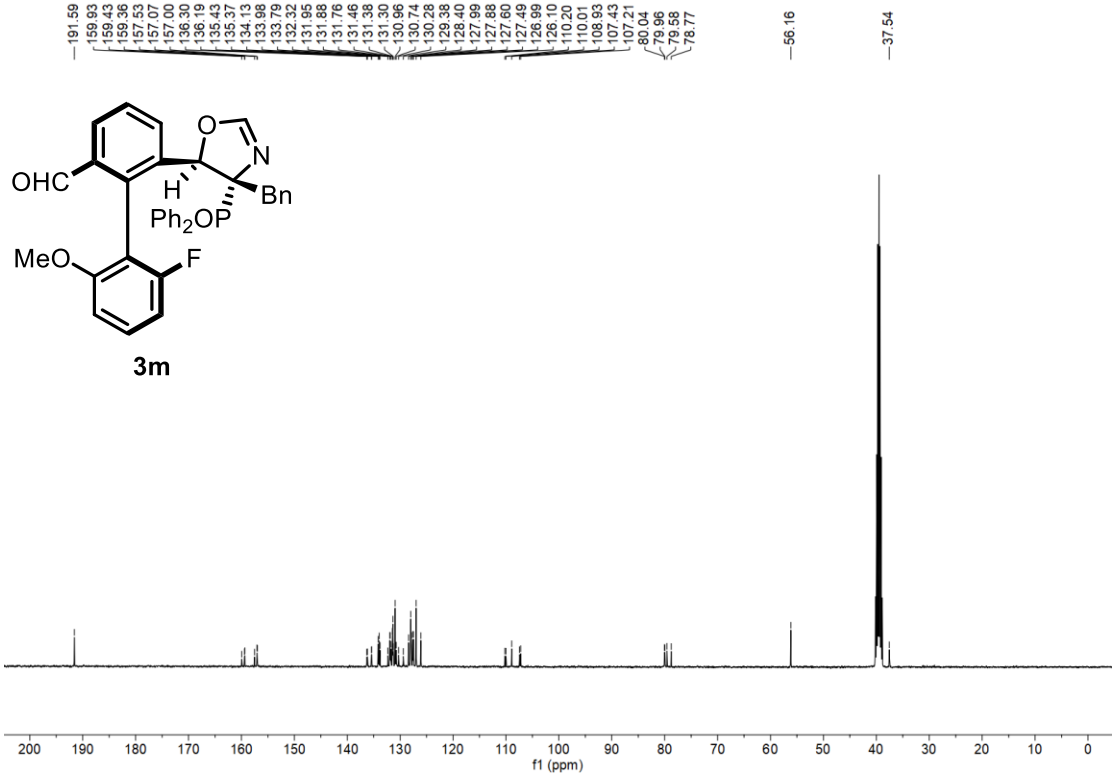
^{31}P NMR (162 MHz, $CDCl_3$)



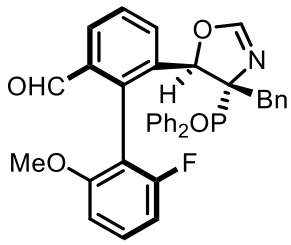
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

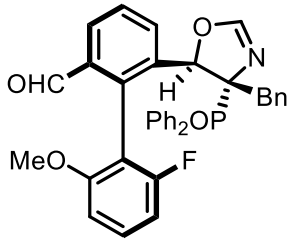


^{19}F NMR (376 MHz, DMSO-d_6)



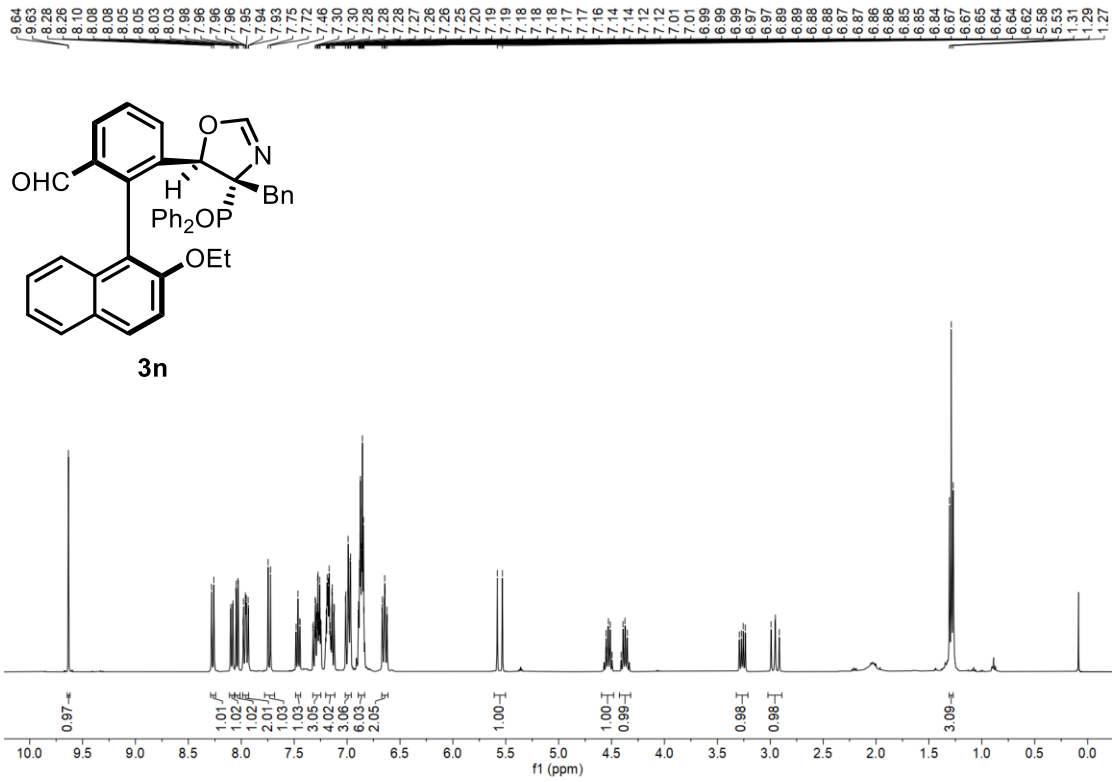
3m

^{31}P NMR (162 MHz, DMSO-d_6)

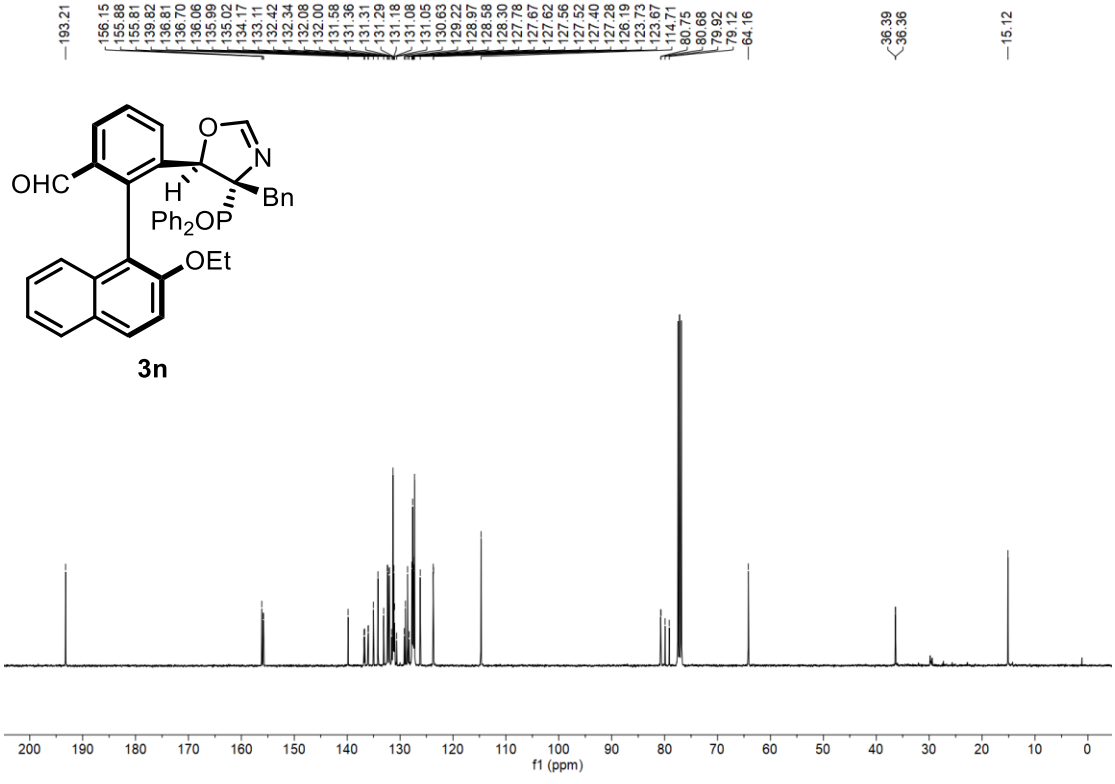


3m

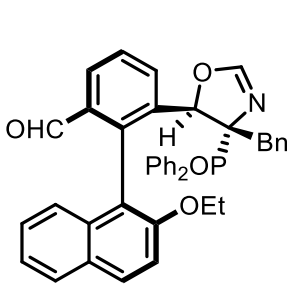
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

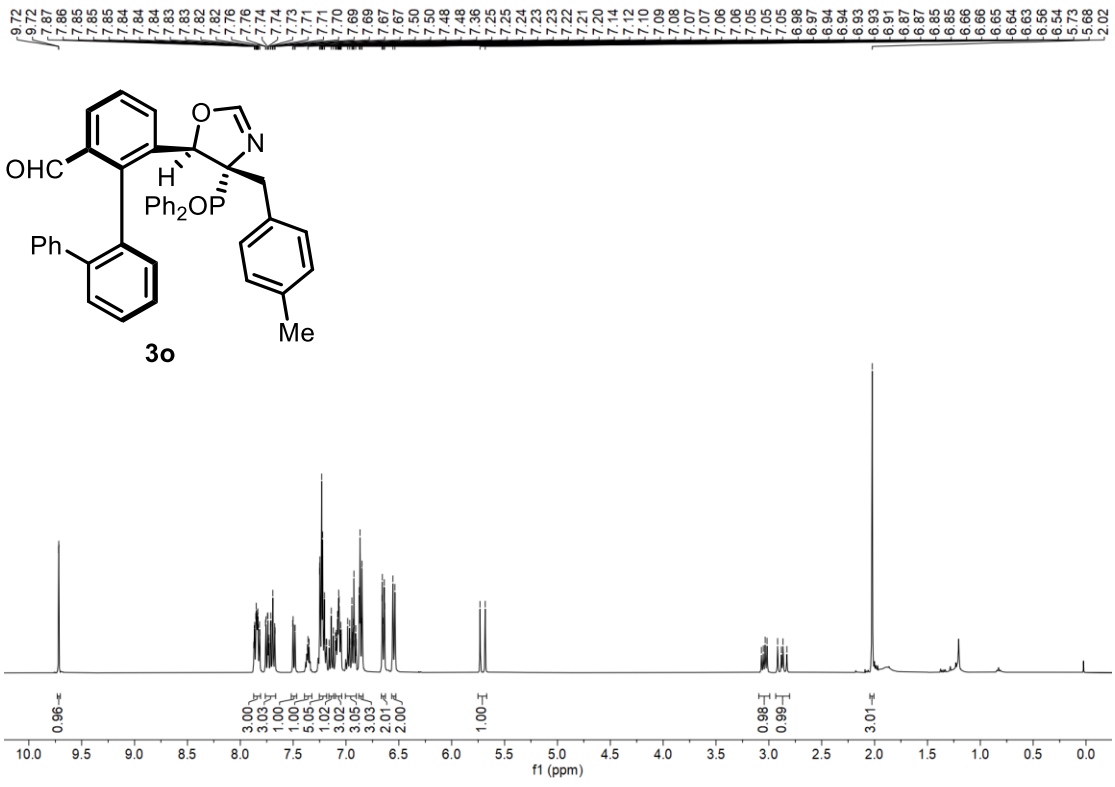


^{31}P NMR (162 MHz, $CDCl_3$)



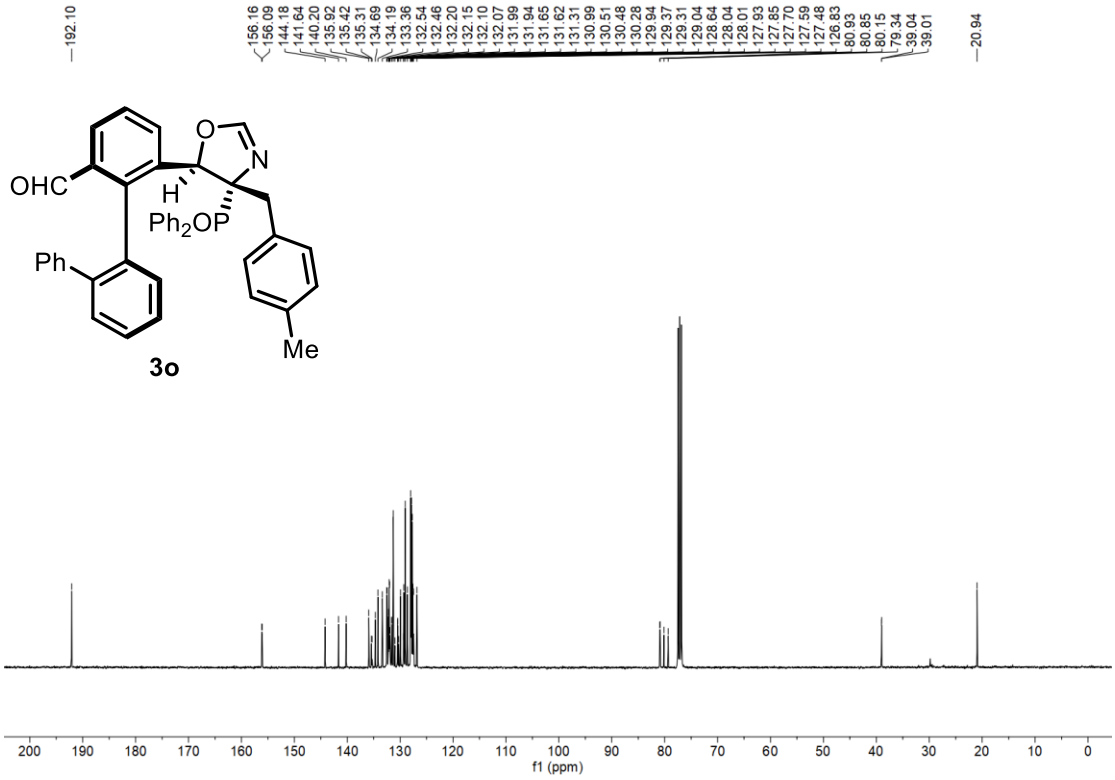
3n

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

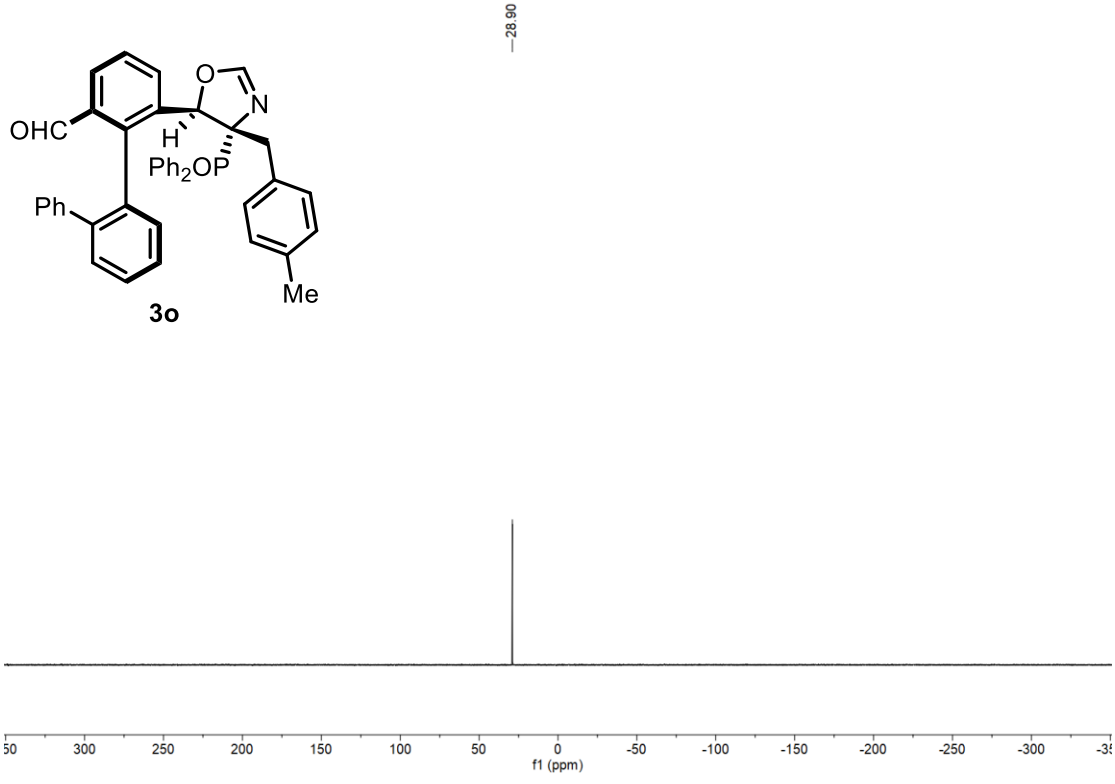


3o

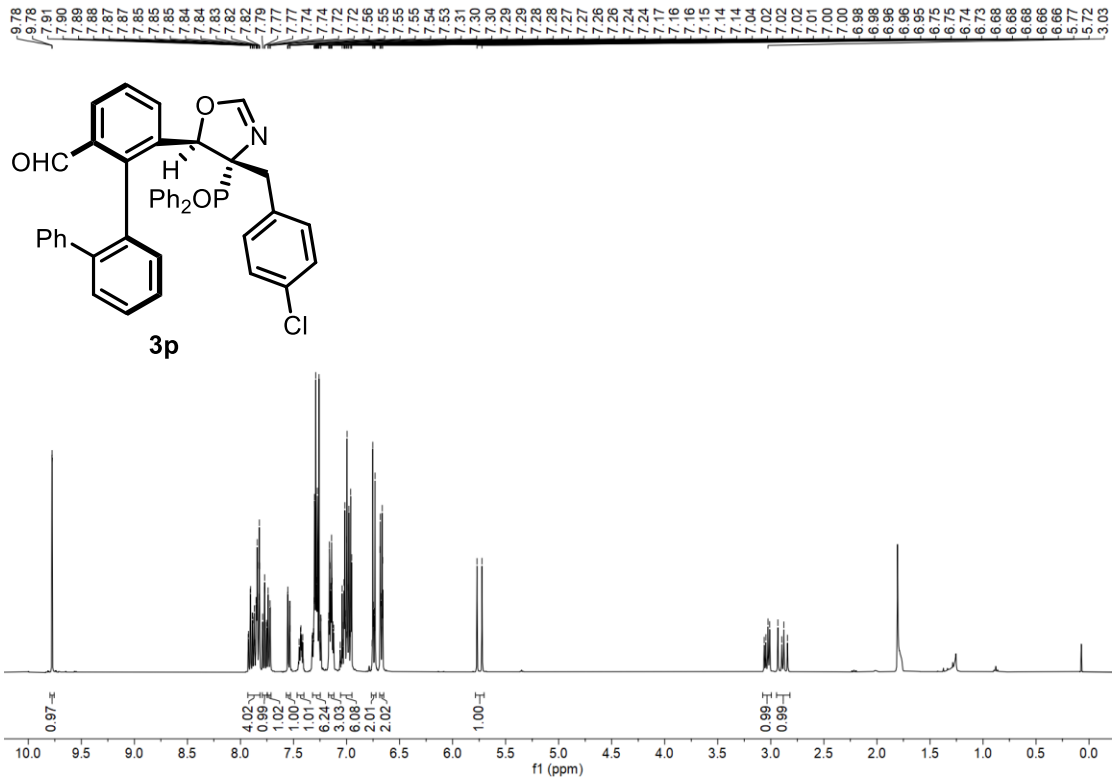
^{13}C NMR (101 MHz, $CDCl_3$)



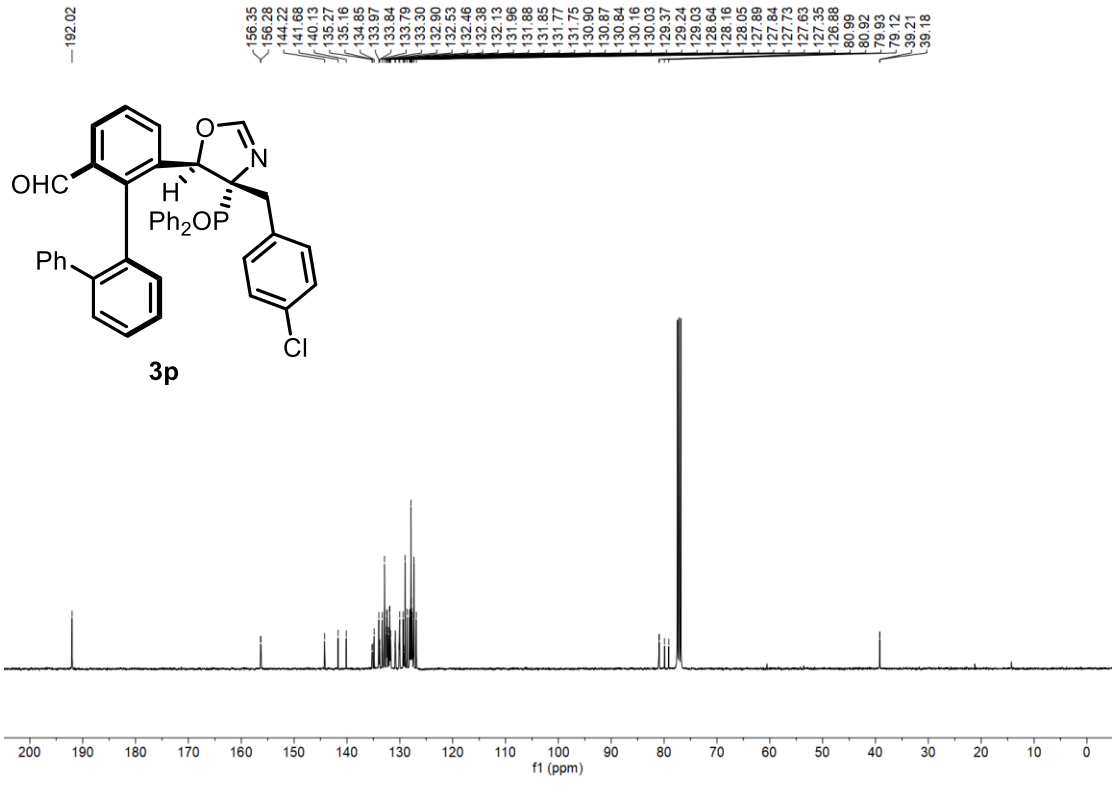
^{31}P NMR (162 MHz, $CDCl_3$)



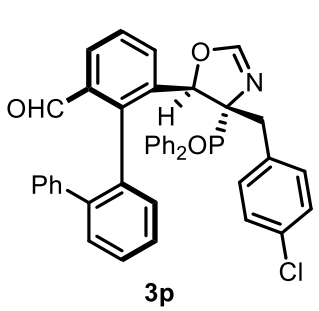
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

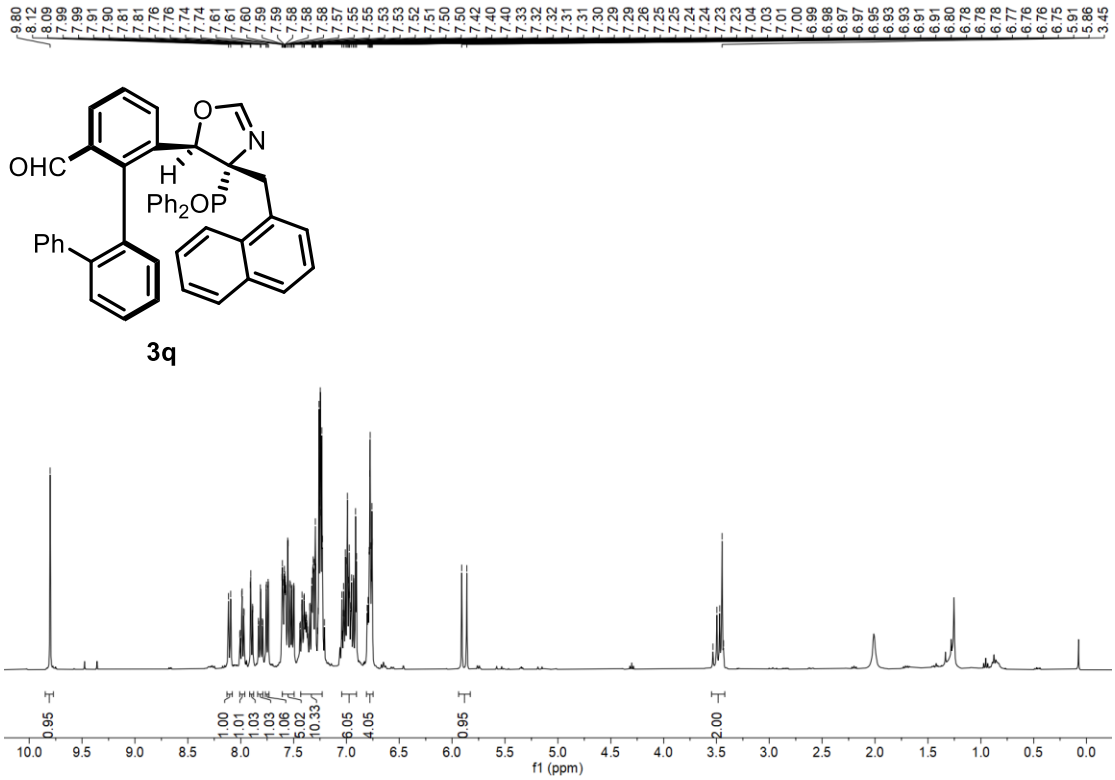


^{31}P NMR (162 MHz, $CDCl_3$)



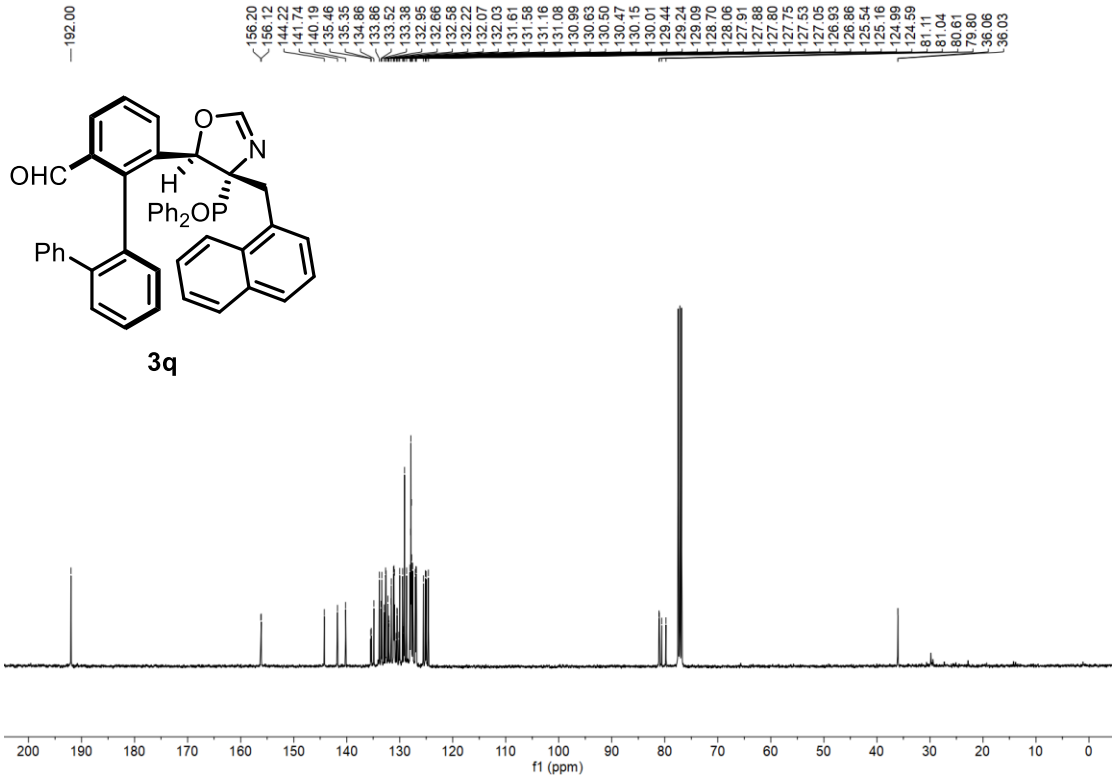
3p

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

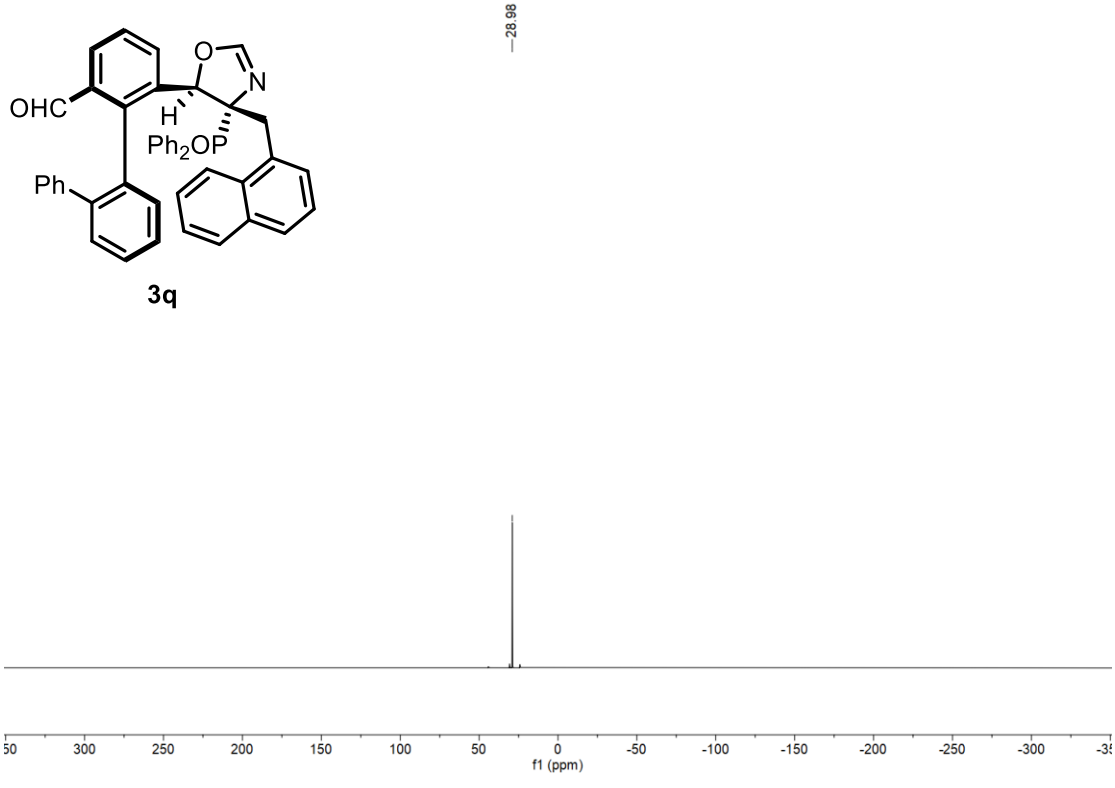


3q

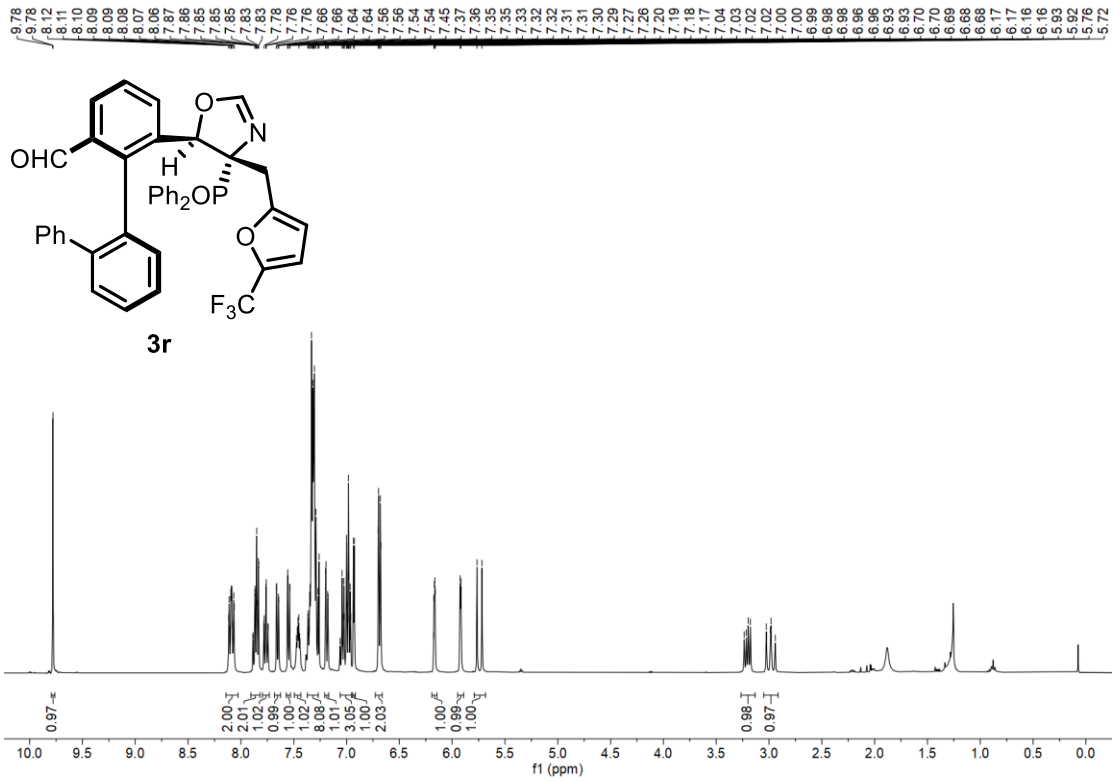
^{13}C NMR (101 MHz, $CDCl_3$)



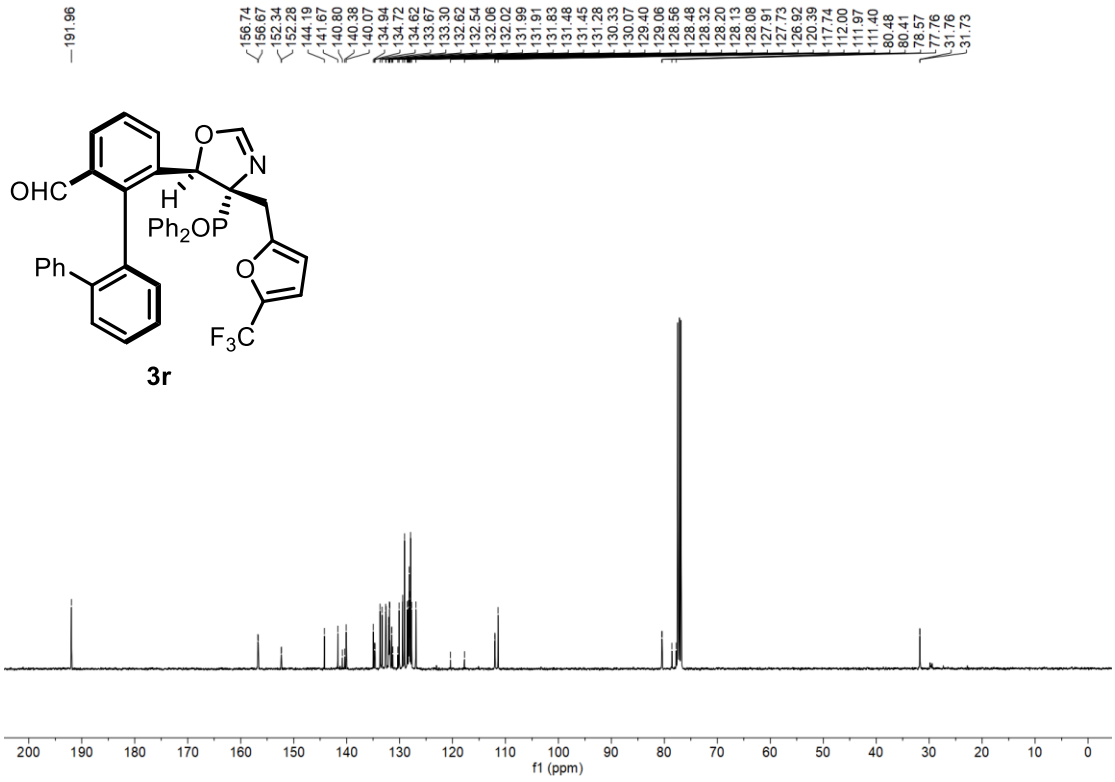
^{31}P NMR (162 MHz, $CDCl_3$)



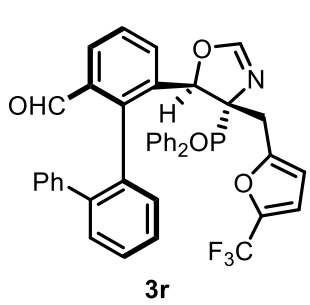
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

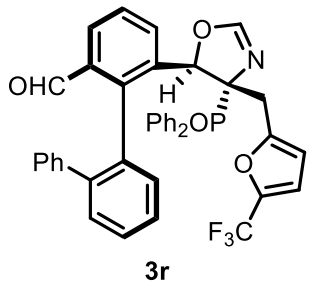


^{19}F NMR (376 MHz, $CDCl_3$)



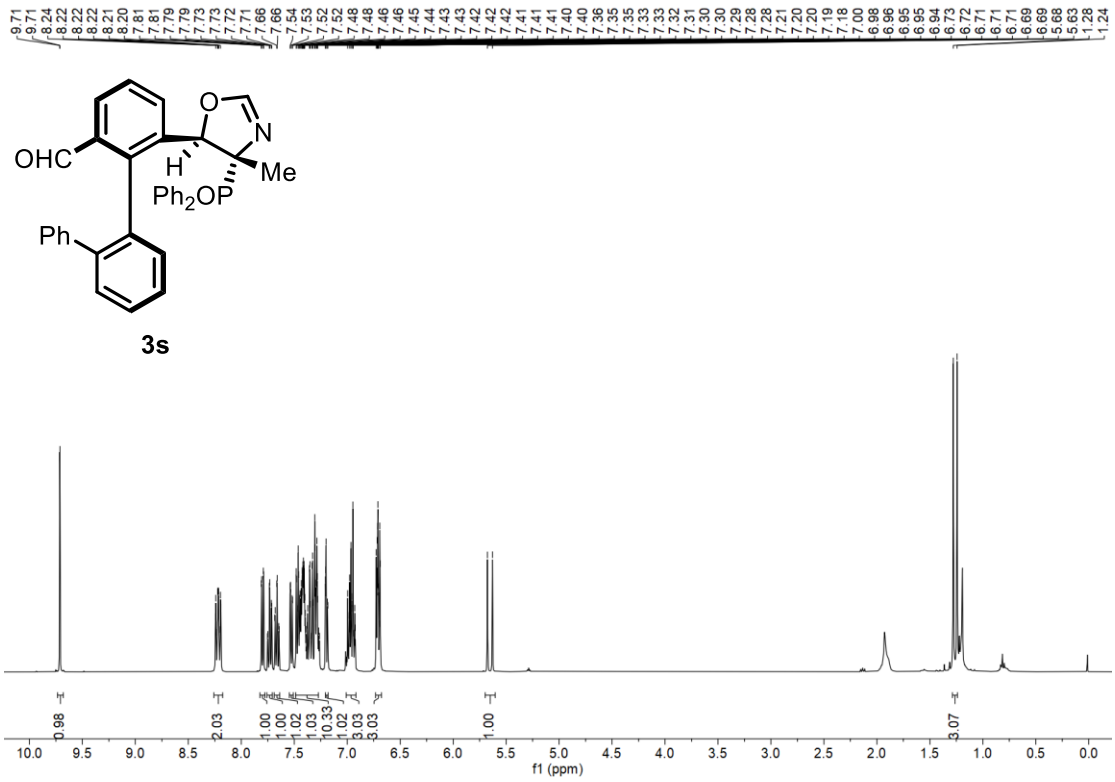
3r

^{31}P NMR (162 MHz, $CDCl_3$)



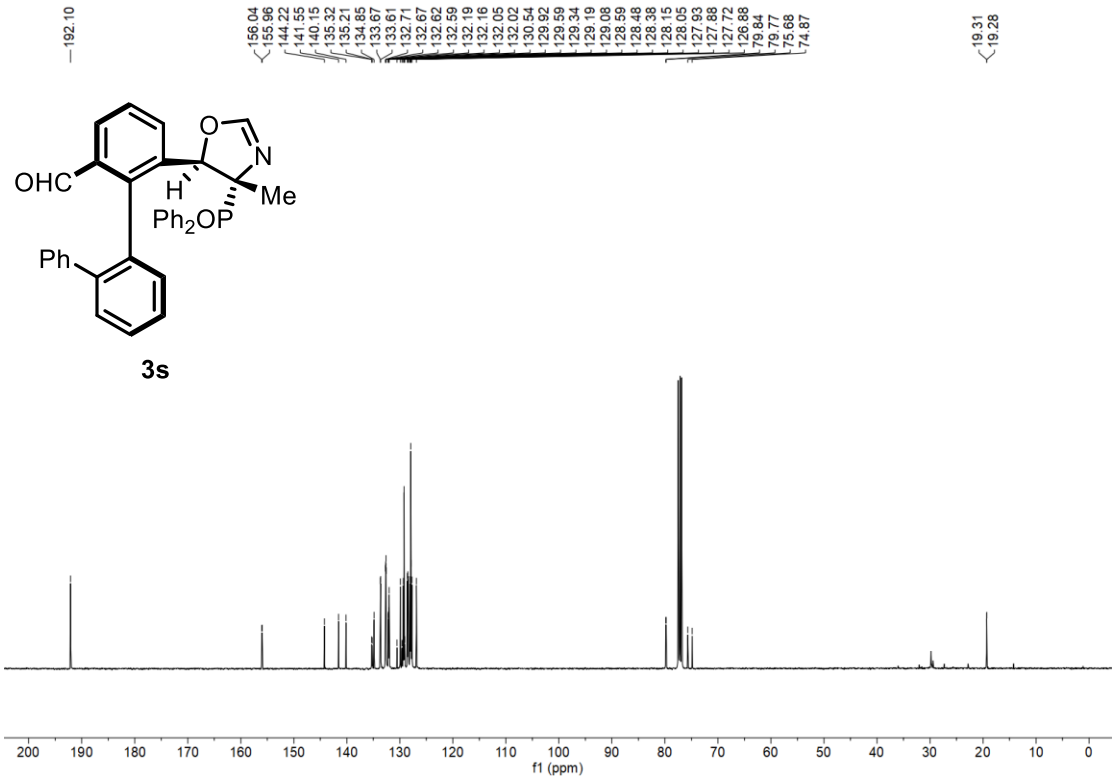
3r

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



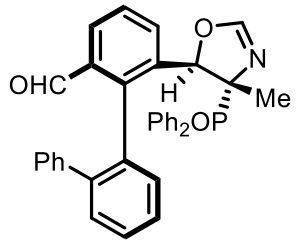
3s

^{13}C NMR (101 MHz, $CDCl_3$)



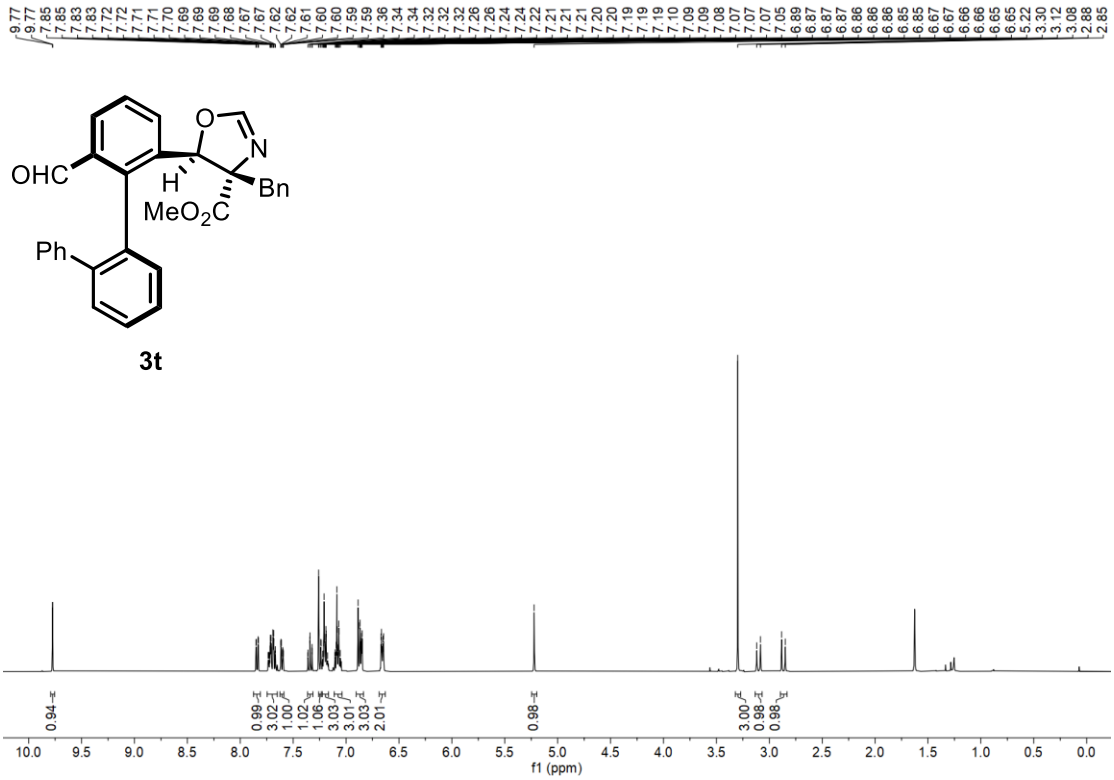
3s

^{31}P NMR (162 MHz, $CDCl_3$)



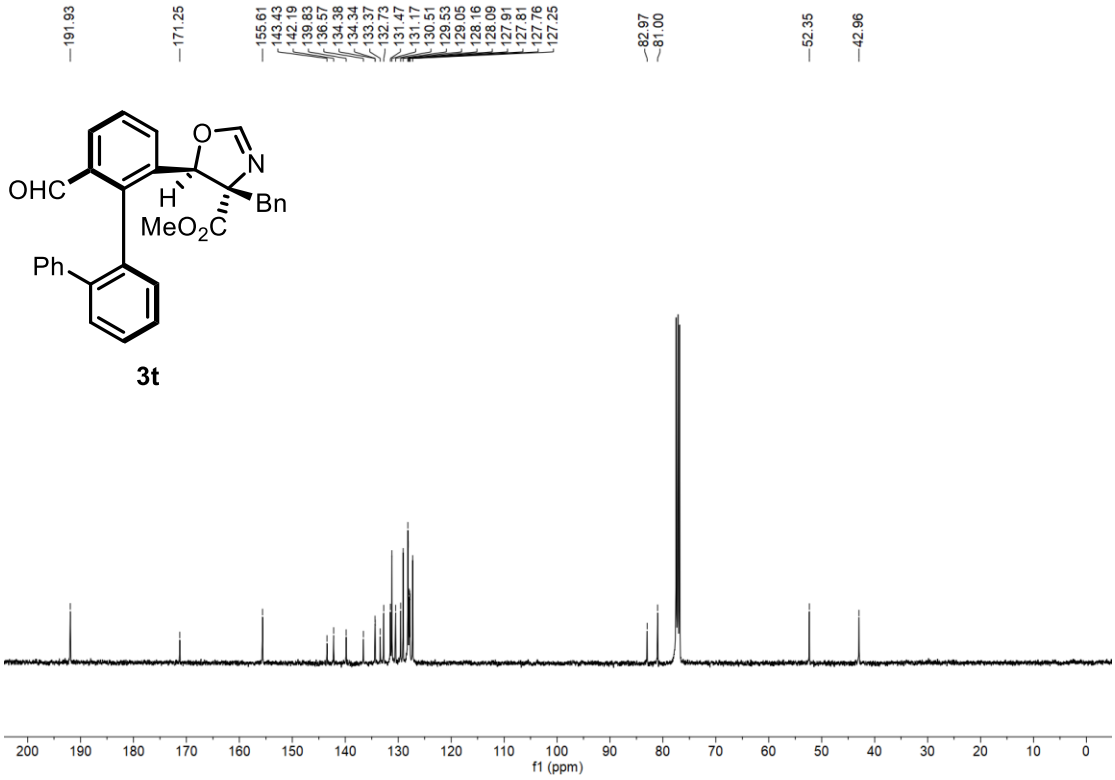
3s

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

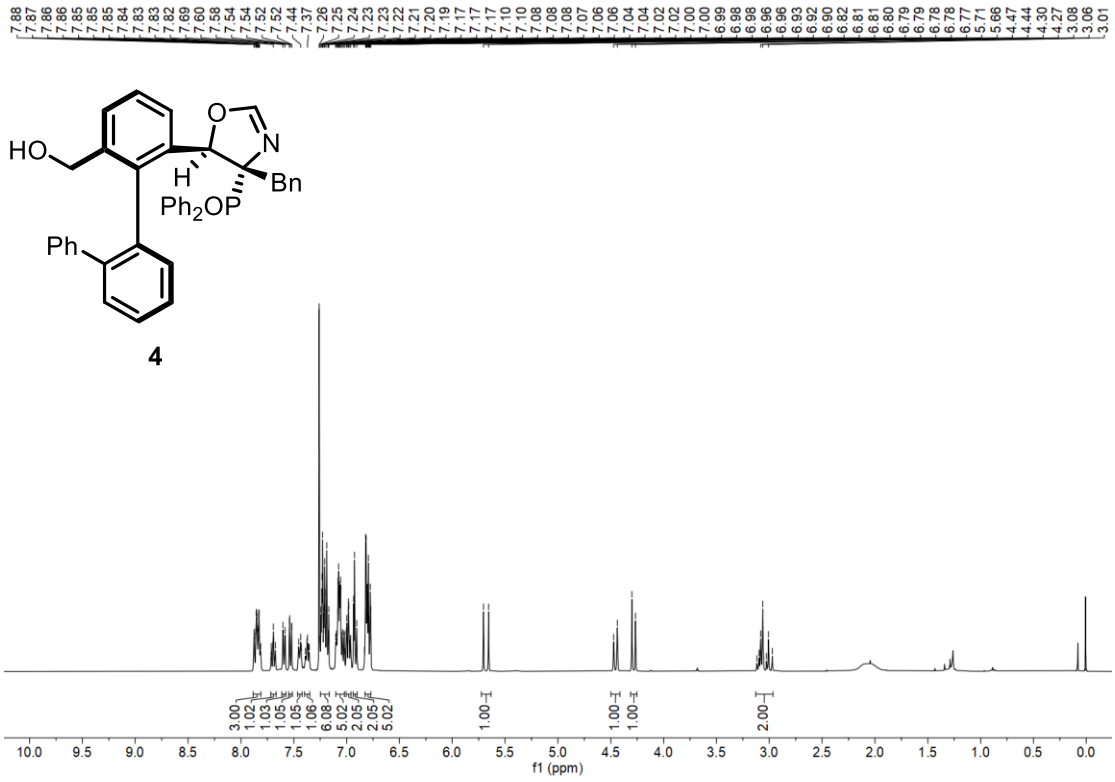


3t

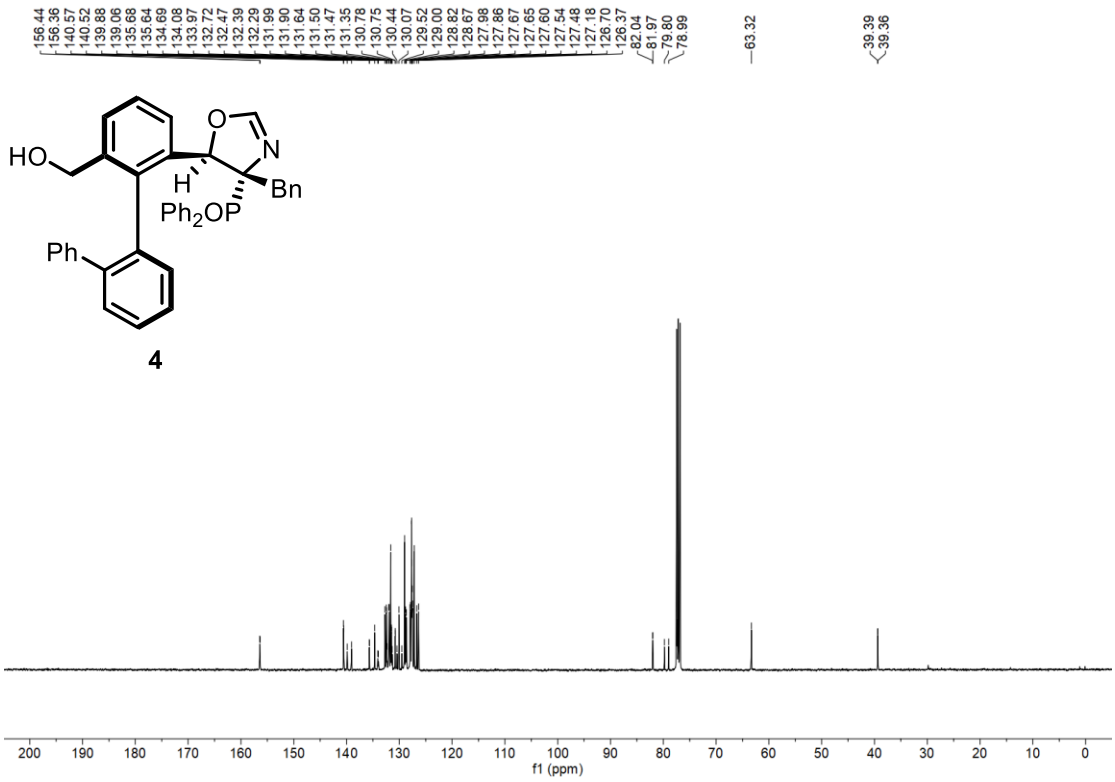
^{13}C NMR (101 MHz, $CDCl_3$)



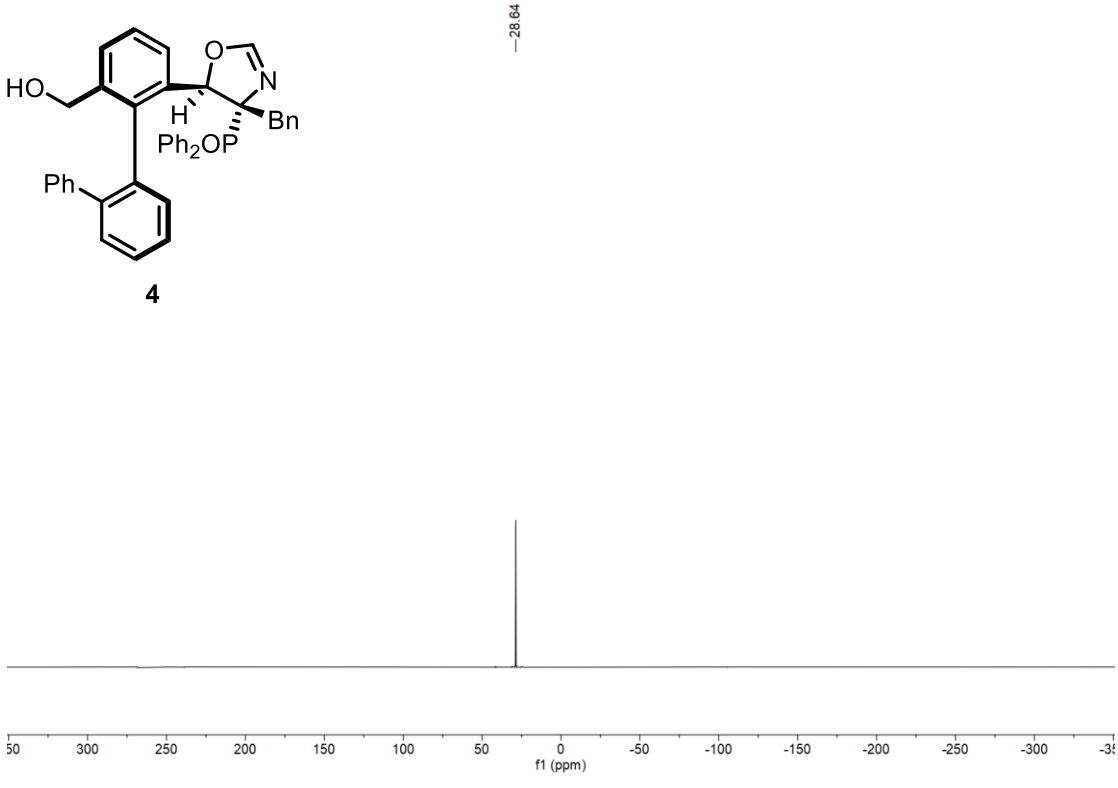
^{1}H NMR (400 MHz, $CDCl_3$)



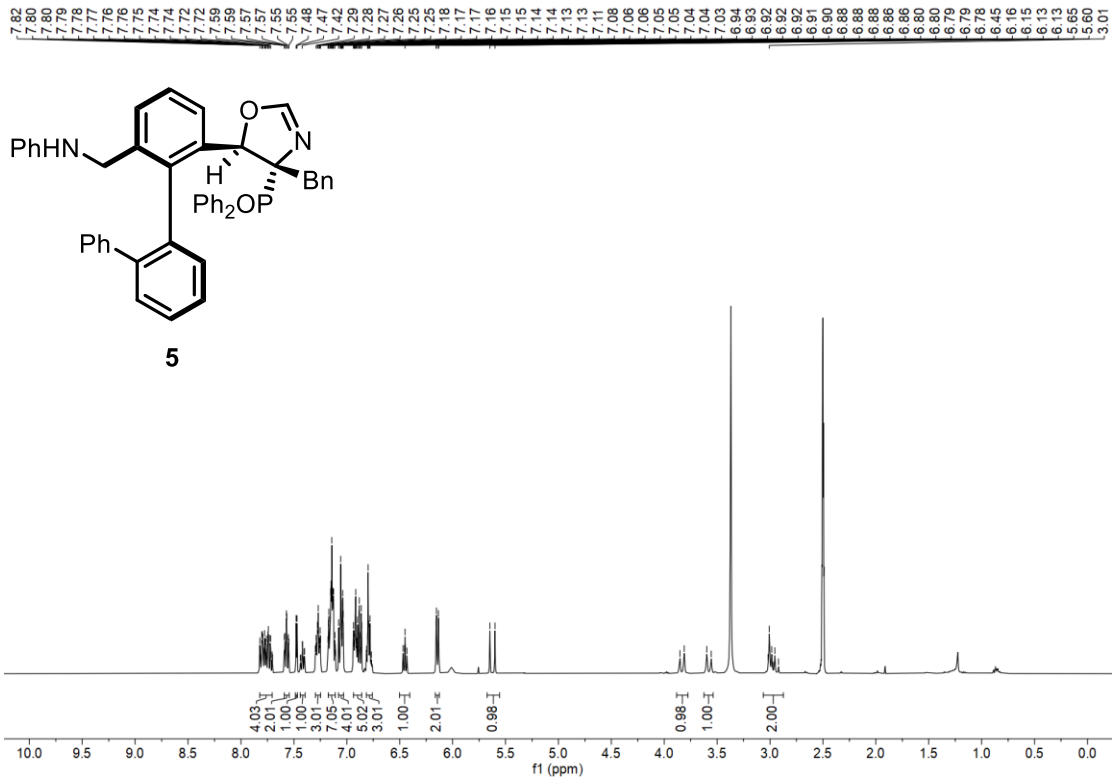
^{13}C NMR (101 MHz, $CDCl_3$)



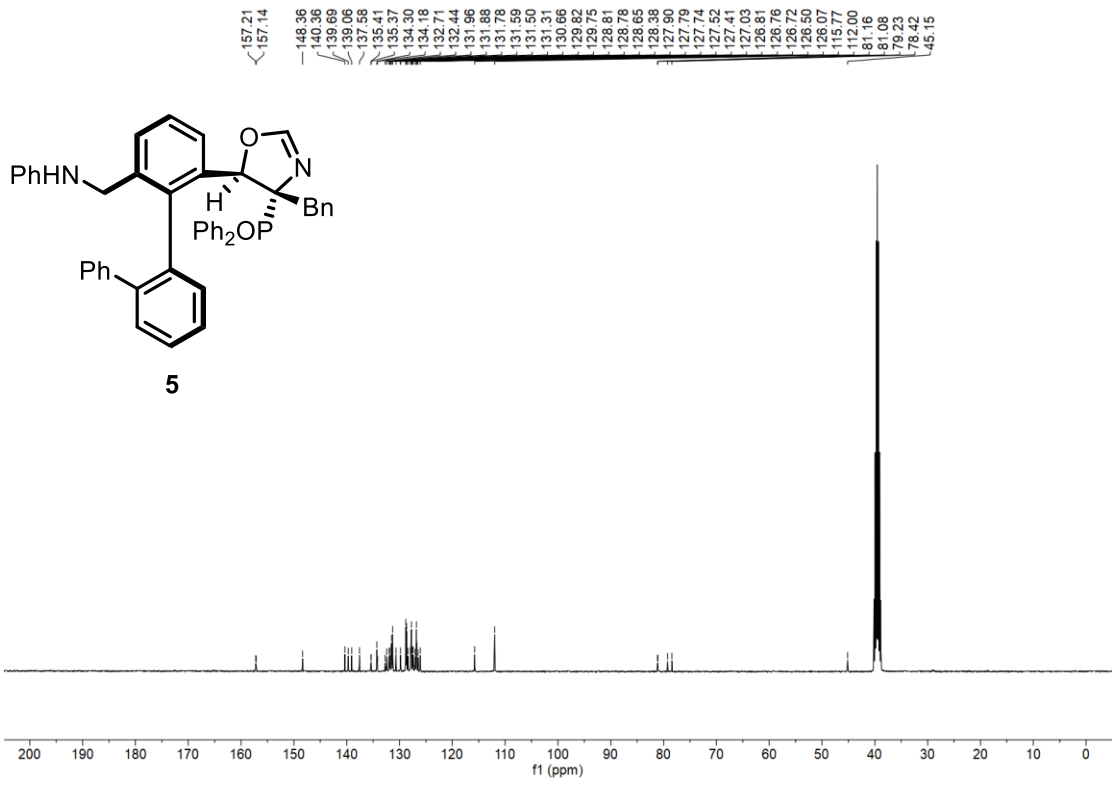
^{31}P NMR (162 MHz, $CDCl_3$)



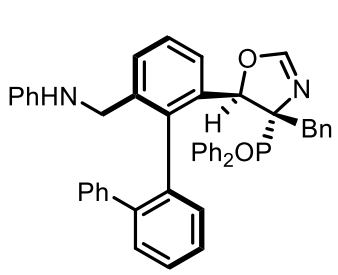
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)

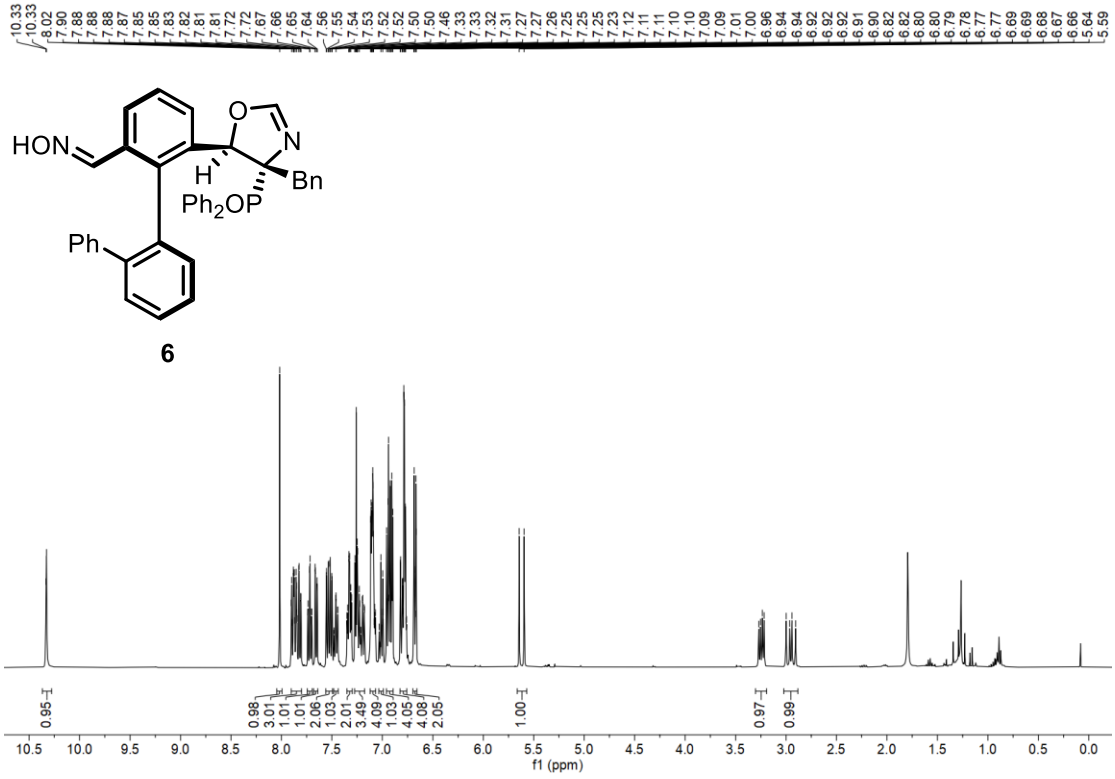


^{31}P NMR (162 MHz, $CDCl_3$)



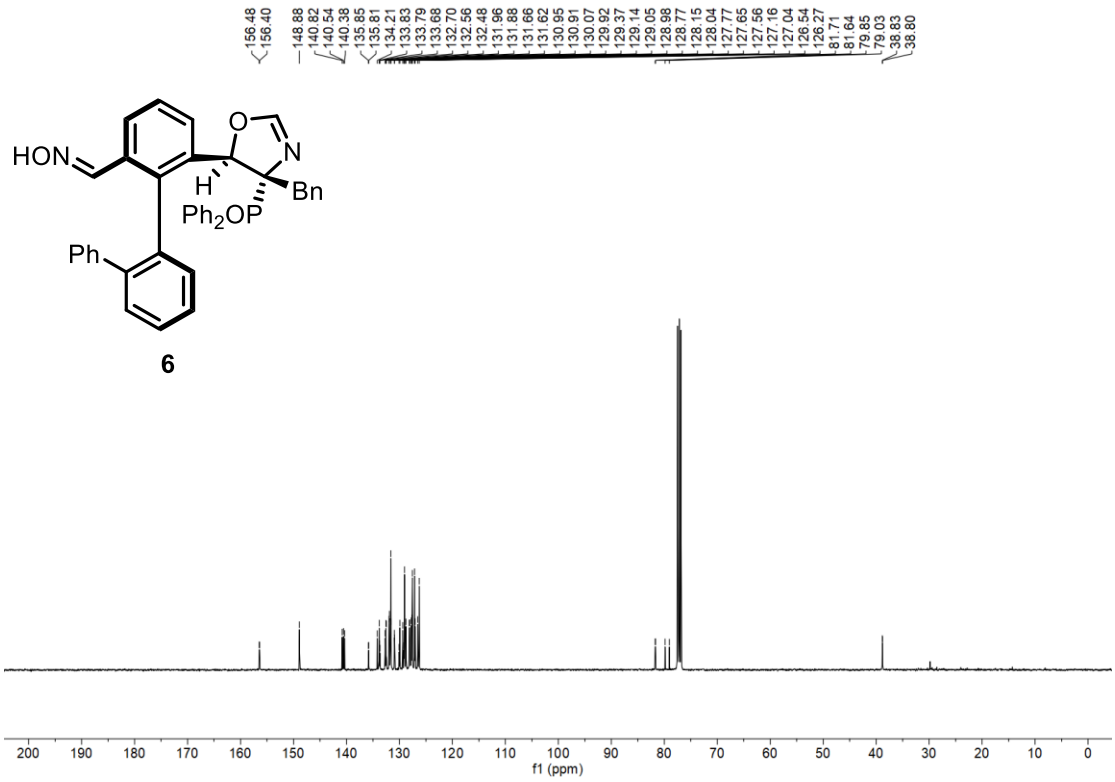
5

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



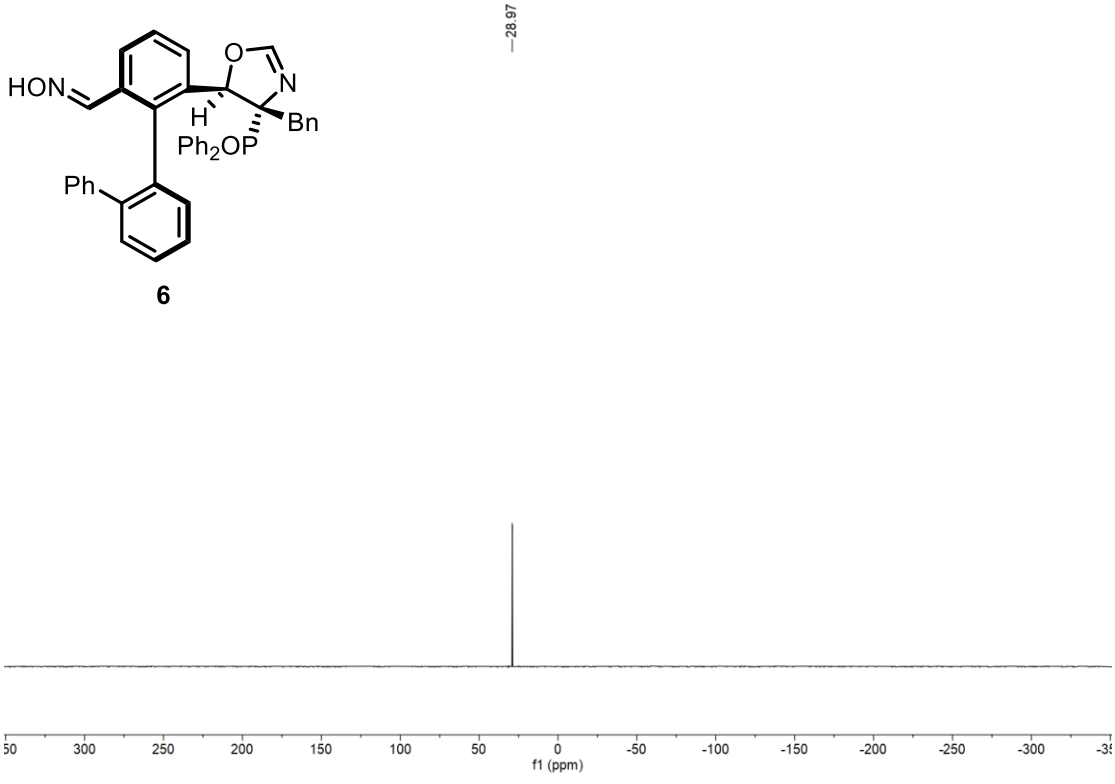
6

^{13}C NMR (101 MHz, $CDCl_3$)



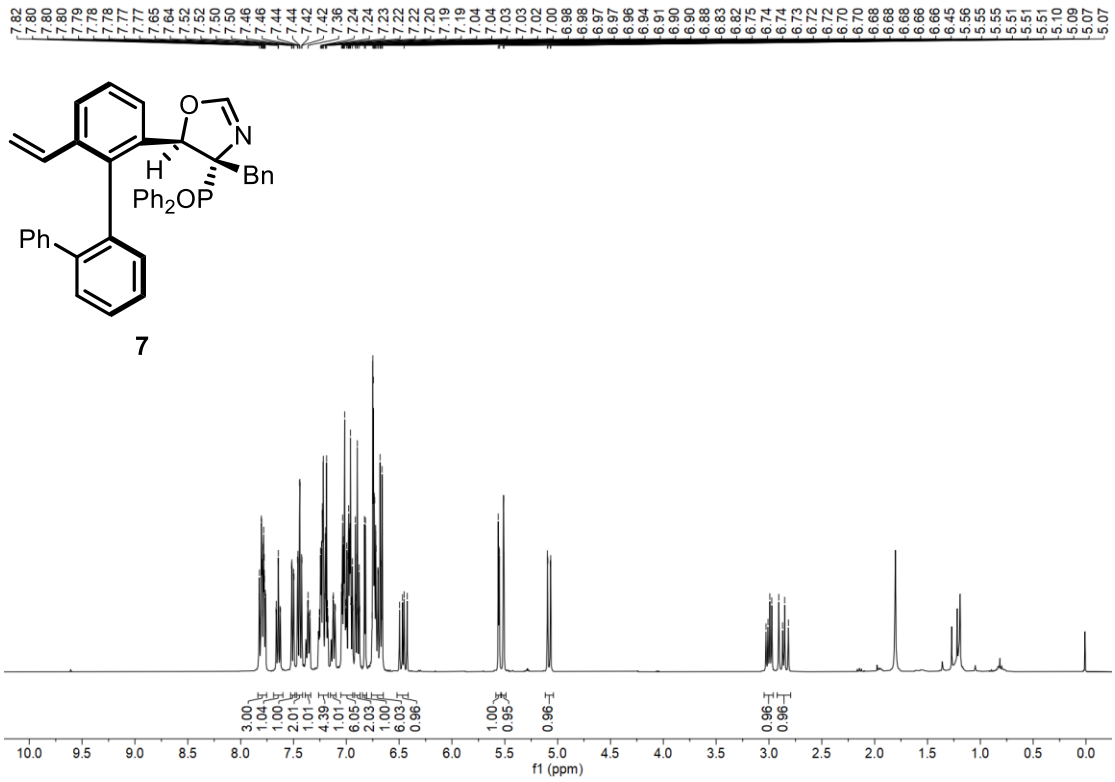
6

^{31}P NMR (162 MHz, $CDCl_3$)

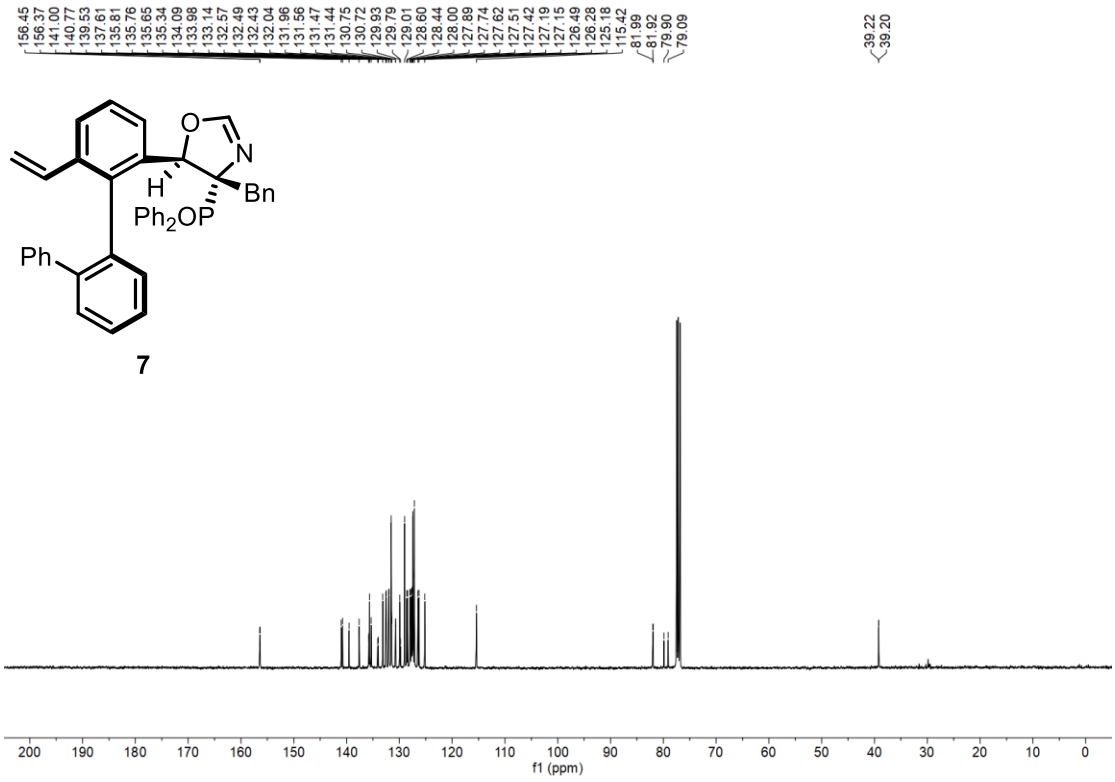


6

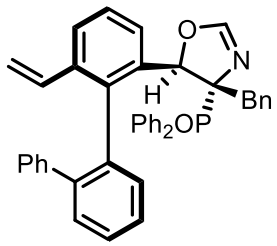
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

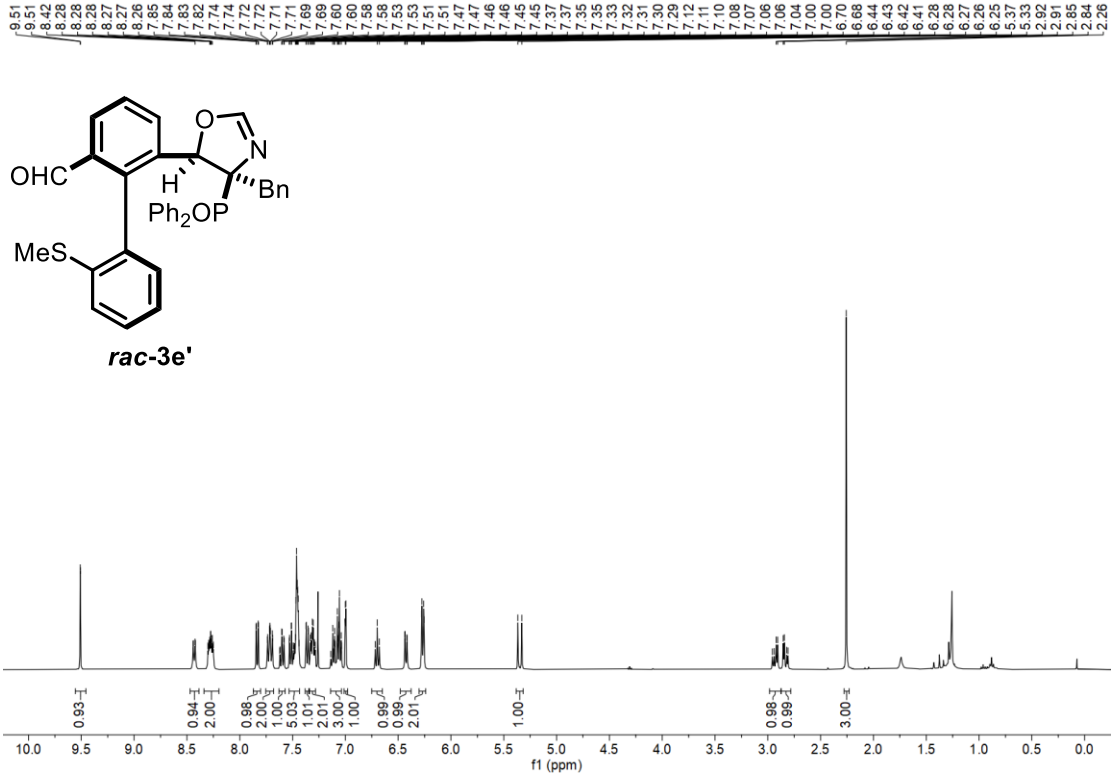


^{31}P NMR (162 MHz, $CDCl_3$)



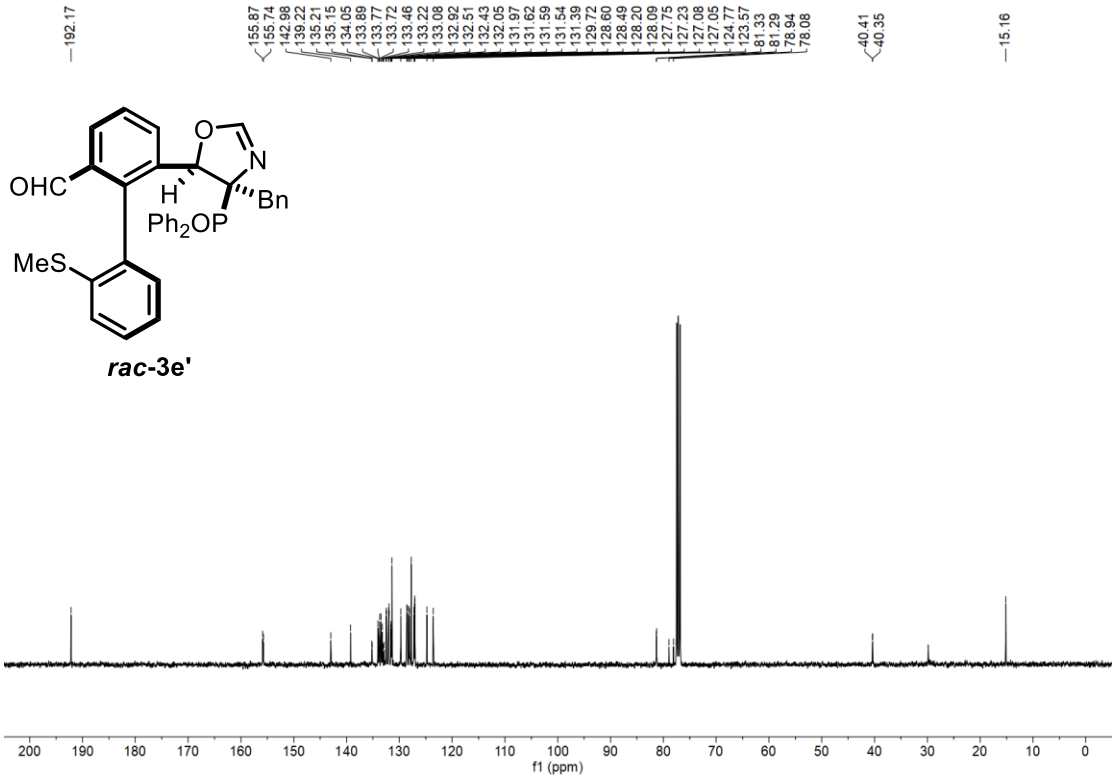
7

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

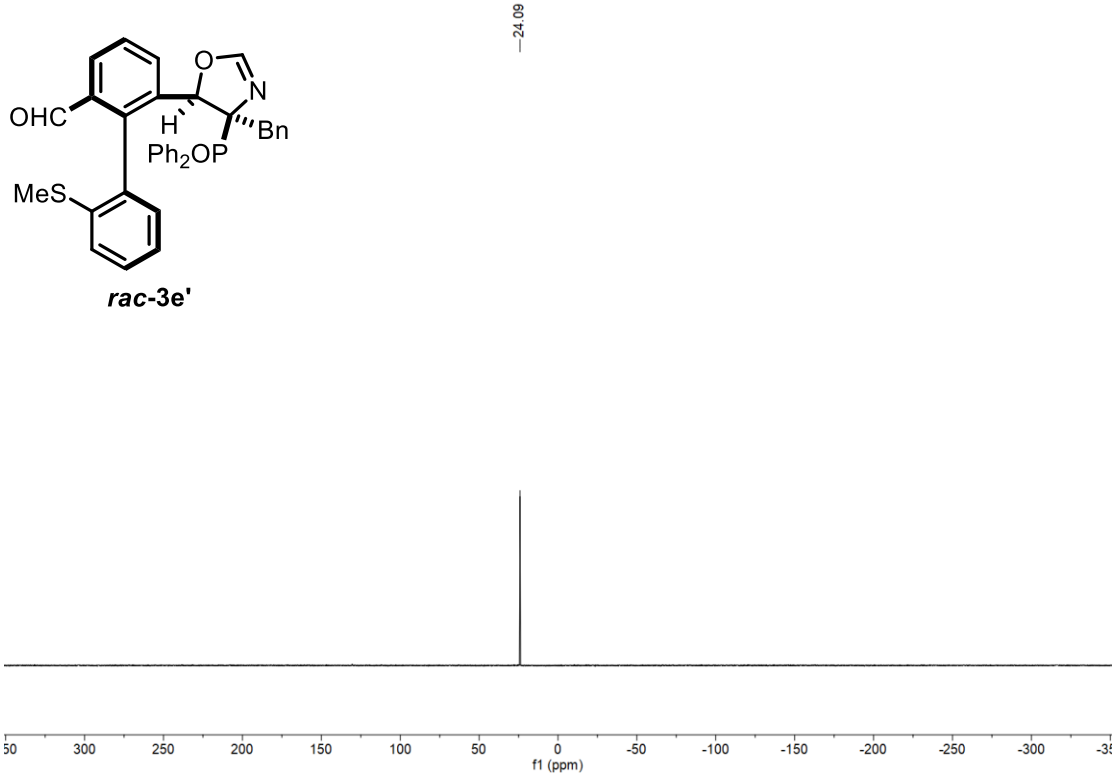


***rac*-3e'**

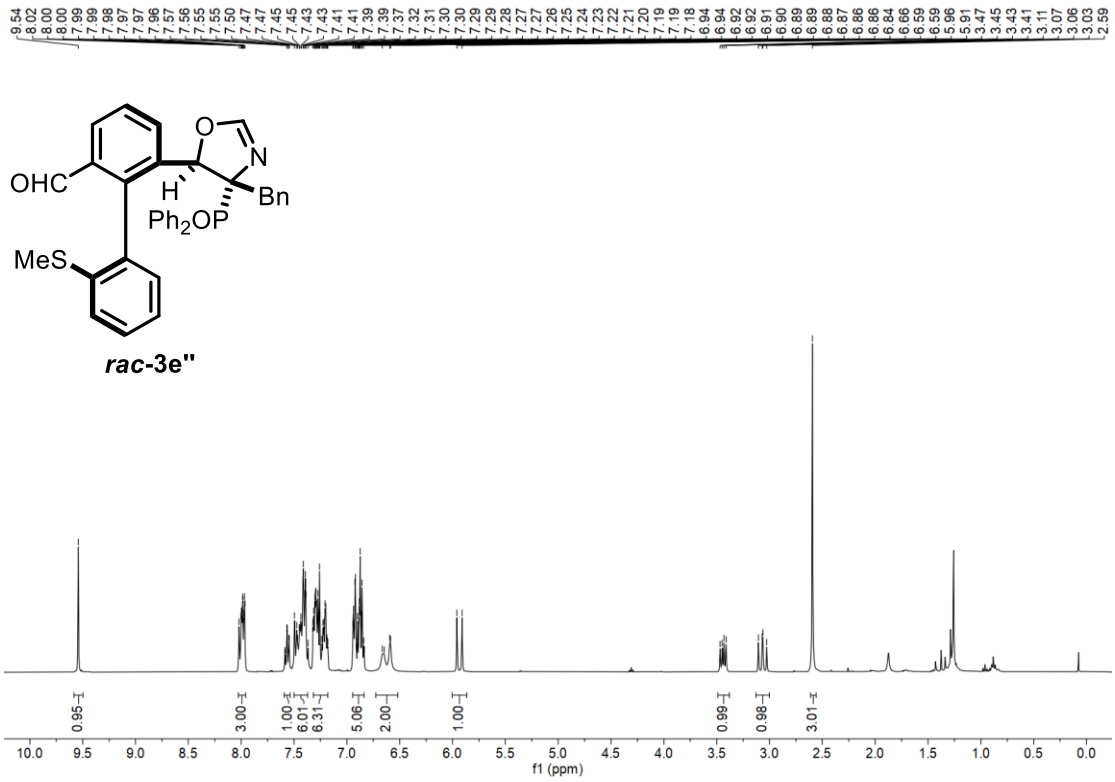
^{13}C NMR (101 MHz, $CDCl_3$)



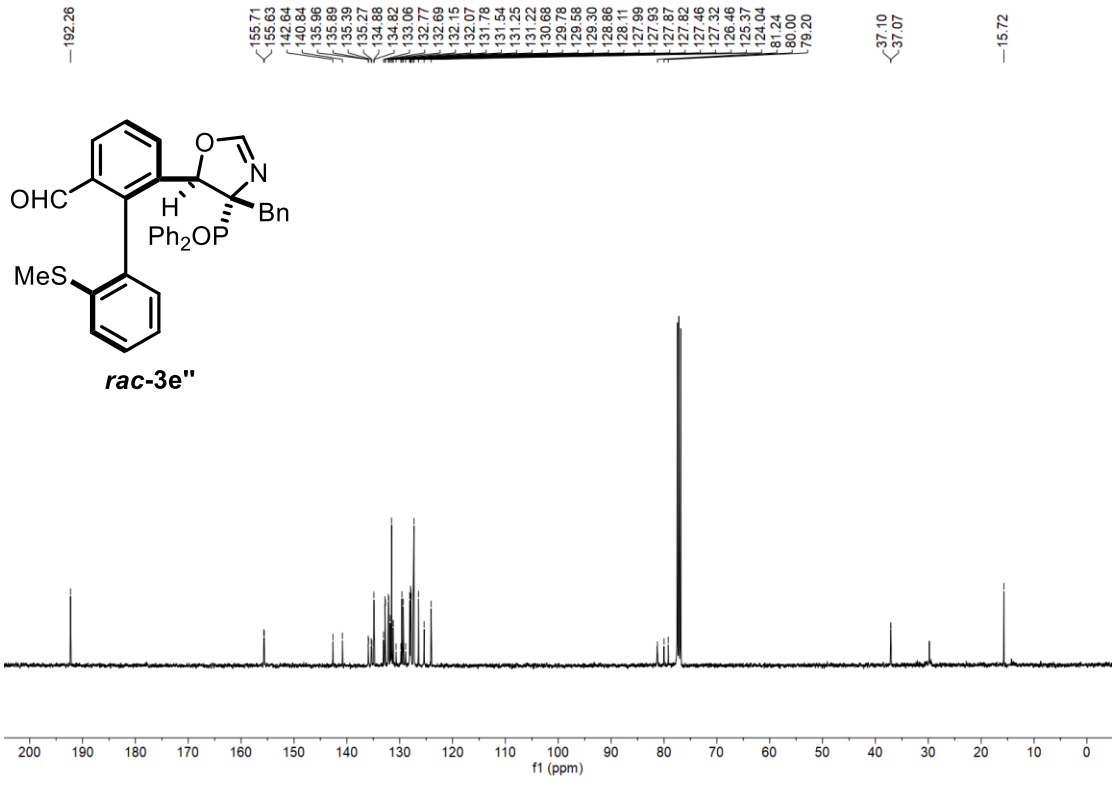
^{31}P NMR (162 MHz, $CDCl_3$)



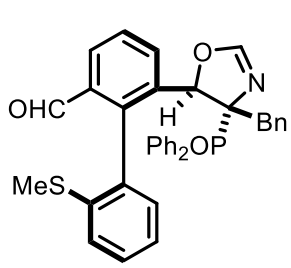
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



***rac*-3e''**