Supporting Information

A Dynamic Kinetic C–P Cross–Coupling for the Asymmetric Synthesis of Axially Chiral P,N Ligands

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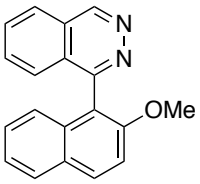
General Information.

^{1}H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz; ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz with the solvent peak used as the internal reference (7.26 and 77.0 ppm for ^{1}H and ^{13}C respectively for $CDCl_3$; 5.32 and 53.8 ppm for ^{1}H and ^{13}C respectively for CD_2Cl_2; 7.16 and 128.1 ppm for ^{1}H and ^{13}C respectively for C_6D_6.); Column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminum backed plates (1.5 × 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24}\cdot 4\ H_2O$ in 95% EtOH (w/v) or followed by heating.

The silylphosphines used in this paper are moisture-sensitive compounds, and were stored in a nitrogen-filled glovebox and manipulated in flame-dried glassware using standard Schlenk techniques. Purging refers to an evacuation/argon refilling procedure carried out three times. Anhydrous 1,4-dioxane and THF were obtained by distillation from sodium using benzophenone as indicator. Anhydrous CsF was purchased from Aldrich and stored in a nitrogen-filled glovebox. $Pd(dba)_2$ was purchased from Aldrich, ligands **L1**,[1] **L2**,[2] **L3**[3] and **L4**[4] were prepared following described procedures, and ligands **L5-L18** were purchased from Aldrich. Triflates **(±)-1A**[5], **(±)-1B-C**[6] and silylphosphines **2** and **4**[7] were synthesized following literature procedures.

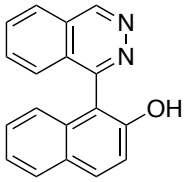
1-(2-methoxynaphthalen-1-yl)phthalazine.



A dried Schlenk tube was charged with $Pd(PPh_3)_4$ (5 mol%) and 1-chlorophthalazine (9.11 mmol, 1.5 g), and after three cycles of vacuum-argon flushing, DME (18 mL) was added and reaction mixture was stirred for 30 min at room temperature. (2-Methoxynaphthalen-1-yl)boronic acid (1.2 eq.) and 11 mL of Na_2CO_3 (2M, aq.) were then sequentially added and the reaction mixture was refluxed overnight, then cooled to room temperature, quenched with H_2O (10 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, concentrated, and

the residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane 2:1 Et_3N 1%) to afford 1-(2-methoxynaphthalen-1-yl)phthalazine (1.62 g, 62%) as a light brown foam. ^1H NMR (500 MHz, $CDCl_3$): δ 9.65 (d, 1H, *J* = 0.6 Hz), 8.06 (d, 2H, *J* = 8.6 Hz), 7.91-7.87 (m, 2H), 7.71 (td, 1H, *J* = 7.0 and 1.1 Hz), 7.49 (dd, 1H, *J* = 8.3 and 0.6 Hz), 7.45 (d, 1H, *J* = 9.1 Hz), 7.35 (td, 1H, *J* = 6.8 and 1.1 Hz), 7.28 (td, 1H, *J* = 6.8 and 1.1 Hz), 7.10 (d, 1H, *J* = 8.6 Hz), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 155.4, 151.0, 133.9, 132.6, 132.4, 131.4, 129.2, 128.2, 127.6, 127.3, 126.8, 126.6, 126.4, 124.7, 124.0, 118.7, 113.5, 56.8. HRMS (EI) calcd. for $C_{19}H_{14}N_2O$ (M^+) 286.1106. Found 286.1104.

1-(phthalazin-1-yl)naphthalen-2-ol.

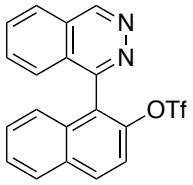


BBr_3 (1.2 eq.) was carefully added to a solution of 1-(2-methoxynaphthalen-1-yl)phthalazine (2.97 mmol, 850 mg) in dry CH_2Cl_2 (12 mL) under argon. The reaction mixture was refluxed for 1 hour and stirred overnight at room temperature. The resulting mixture was cooled to 0 °C, quenched with H_2O, and the formed precipitated was vigorously stirred in a CH_2Cl_2/Na_2CO_3 (2M, aq.) mixture. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried ($MgSO_4$), filtered, concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2:MeOH 50:2 Et_3N 1%) to afford 1-(phthalazin-1-yl)naphthalen-2-ol (646 mg, 80%) as a brown solid. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ 9.91 (br s, 1H), 9.78 (s, 1H), 8.27 (d, 1H, *J* = 8.1 Hz), 8.02-7.99 (m, 2H), 7.92 (d, 1H, *J* = 7.8 Hz), 7.85 (t, 1H, *J* = 8.1 Hz), 7.42 (d, 1H, *J* = 8.8 Hz), 7.40 (d, 1H, *J* = 9.0 Hz), 7.30 (td, 1H, *J* = 7.5 and 1.0 Hz), 7.25 (td, 1H, *J* = 7.7 and 1.3 Hz), 6.90 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ 157.5, 153.2, 150.7, 133.6, 133.0, 132.6, 130.6, 128.1, 127.8, 126.8, 126.7, 126.4, 126.2, 125.5, 123.6, 122.9, 118.2, 115.1. HRMS (EI) calcd. for $C_{18}H_{12}N_2O$ (M^+) 272.0950. Found 272.0947.

Synthesis of triflates (±)-1D and (±)-9. General procedure.

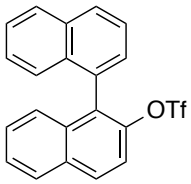
Following a described procedure,[6b] triflic anhydride (1.2 eq.) was carefully dropwise added to an under argon solution containing the corresponding alcohol**,** dry pyridine (1.2 eq.) and DMAP (cat.) in dry CH_2Cl_2 (5 mL/mmol). The reaction mixture was stirred at room temperature overnight, then quenched with $NaHCO_3$ (sat. aq.) and the organic phase was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was dried ($MgSO_4$), filtered, concentrated, and the residue was purified by column chromatography on silica gel using EtOAc/*n*-hexane mixtures.

1-(phthalazin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (±)-1D.



Following the general procedure starting from 1-(phthalazin-1-yl)naphthalen-2-ol (2.28 mmol, 620 mg), column chromatography (EtOAc/*n*-hexane 1:5→1.1) afforded **(±)-1D** (552 mg, 60%) as a light brown foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 8.15 (d, 1H, *J* = 9.1 Hz), 8.12 (d, 1H, *J* = 8.1 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 7.96 (t, 1H, *J* = 7.7 Hz), 7.78 (t, 1H, *J* = 7.6 Hz), 7.64 (d, 1H, *J* = 9.1 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 7.46-7.41 (m, 2H), 7.28 (d, 1H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 151.4, 145.2, 133.0, 133.0, 132.9, 132.4, 132.0, 128.3, 128.2, 127.4, 126.9, 126.7, 126.4, 126.1, 126.1, 125.6, 119.5, 118.1 (q, $J_{C,F}$ = 310 Hz). HRMS (EI) calcd. for $C_{19}H_{12}F_3N_2O_3S$ (M^++1) 405.0519. Found 405.0521.

[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (±)-9.

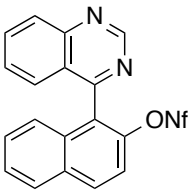


Following the general procedure starting from [1,1'-binaphthalen]-2-ol **(±)-10**[8] (1.0 mmol, 270 mg), column chromatography (EtOAc/*n*-hexane 1:10) afforded **(±)-9** (342 mg, 85%) as a colourless viscous oil. Spectroscopic data matched those reported in the literature for the (*R*)-enantiomer.[9]

Synthesis of Nonaflates (±)-8C-D and (±)-11. General procedure.

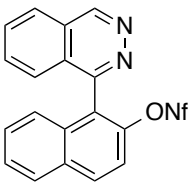
Following a described procedure,[10] over a suspension of the corresponding alcohol (1.0 equiv) and K_2CO_3 (1.5 equiv) in acetonitrile (0.5 M), perfluorobutanesulfonyl fluoride (90%, 1.2 equiv) was added in one portion, and the resulting mixture was vigorously stirred for 24 h. After completion (TLC monitoring), the reaction mixture was filtered through a Celite pad, the solvent was removed in vacuum, and the residue was purified by flash column chromatography over silica gel.

1-(quinazolin-4-yl)naphthalen-2-yl nonaflate (±)-8C.



Following the general procedure starting from 1-(quinazolin-4-yl)naphthalen-2-ol[¡Error! Marcador no definido.b] (1.43 mmol, 390 mg), column chromatography (EtOAc/*n*-hexane 2:1) afforded **(±)-8C** (708 mg, 90%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 8.21 (d, 1H, *J* = 8.4 Hz), 8.15 (d, 1H, *J* = 9.1 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 7.96 (t, 1H, *J* = 8.0 Hz), 7.65-7.58 (m, 2H), 7.53 (t, 1H, *J* = 8.0 Hz), 7.47-7.43 (m, 2H), 7.27 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 154.8, 150.6, 144.6, 134.5, 132.4, 132.3, 132.1, 129.0, 128.4, 128.3, 128.3, 127.5, 126.9, 126.4, 125.9, 125.0, 119.4, (nanoflate group not observed). ^{19}F NMR (377 MHz, $CDCl_3$): –80.7 (t, $J_{F\text{-}P}$ = 11 Hz), –110.0 (q, $J_{F\text{-}P}$ = 15 Hz), –121.1 (m), –126.0 (m). HRMS (ESI) calcd. for $C_{22}H_{12}F_9N_2O_3S$ ($M + H^+$) 555.0419. Found 555.0412.

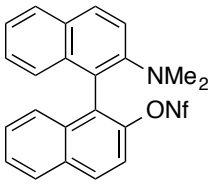
1-(phthalazin-1-yl)naphthalen-2-yl nonaflate (±)-8D.



Following the general procedure starting from 1-(phthalazin-1-yl)naphthalen-2-ol (3.9 mmol, 1.07 g), column chromatography (CH_2Cl_2/MeOH 50:1) afforded **(±)-8D** (1.2 g, 56%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 8.16 (d, 1H, *J* = 9.1 Hz), 8.11 (d, 1H, *J* = 8.1 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 7.96 (t, 1H, *J* = 7.6 Hz), 7.78 (t, 1H, *J* = 7.6 Hz), 7.64 (d, 1H, *J* = 9.2 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 7.47-7.41 (m, 2H), 7.28 (d, 1H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 151.4, 145.2, 133.0, 133.0, 132.9, 132.4, 132.0, 128.3, 128.2, 127.4, 126.9, 126.7, 126.4, 126.2, 126.2, 125.6, 119.5, (nanoflate

group not observed). ^{19}F NMR (377 MHz, $CDCl_3$): –80.7 (t, J_{F-P} = 11 Hz), –110.0 (t, J_{F-P} = 15 Hz), –121.2 (m), –126.0 (m). HRMS (ESI) calcd. for $C_{22}H_{12}F_9N_2O_3S$ (M + H^+): 555.0419. Found: 555.0414.

2'-(dimethylamino)-[1,1'-binaphthalen]-2-yl nonaflate (±)-11.



Following the general procedure starting from 2'-(dimethylamino)-[1,1'-binaphthalen]-2-ol **(±)-12**[11] (0.782 mmol, 245 mg), column chromatography (EtOAc/*n*-hexane 9:1) afforded **(±)-11** (430 mg, 92%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 9.1 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.61-7.52 (m, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.47-7.35 (m, 2H), 7.35-7.28 (m, 1H), 7.18 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 145.6, 134.2, 133.6, 132.5, 130.2, 129.9, 129.7, 129.6, 128.3, 127.9, 127.5, 127.3, 126.7, 126.3, 125.2, 123.7, 120.0, 119.8, 119.4, 43.5 (nanoflate group not observed). ^{19}F NMR (377 MHz, $CDCl_3$): –80.7 (t, J_{F-P} = 11 Hz), –110.6 (q, J_{F-P} = 11 Hz), –121.2 (m), –126.1 (m). HRMS (ESI) calcd. for $C_{26}H_{19}F_9NO_3S$ (M + H^+) 596.0936. Found 596.0926.

Synthesis of Silylphosphines 5a-e. General procedure.

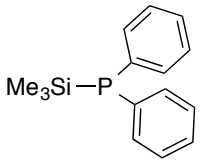
A flamed-dried Schlenk tube was charged with the corresponding phosphine (1 equiv.). After purging with argon, dry THF was added (1.5 mL/mmol phosphine) and the resulting solution was cooled to –78 °C. *n*-BuLi (1.5 equiv) was then added dropwise, the resulting mixture was allowed to reach –60 °C (for aromatic phosphines) or –40 °C (for aliphatic phosphines), stirred for 20 min and cooled again to –78 °C. Finally, Me_3SiCl (1.5 equiv) was added dropwise and the crude mixture was allowed to reach room temperature. and concentrated to dryness. Dry pentane was added to complete precipitation of LiCl and the reaction crude filtered via filter-cannula under Ar. This extraction process was repeated twice, the solvents were removed under vacuum and the residue was either distilled or washed with pentane.

*Note: The purity of silylphophines **5a-e** (HPR_2 free) is crucial to get high and reproducible enantioselectivities in the C-P coupling reactions. Different commercially*

available Me_3SiPPh_2 samples were checked and did not fulfill the purity requirements for this study.

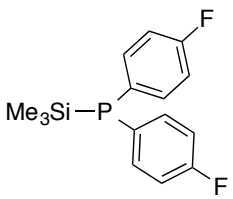
Yields, procedure details and characterization data for silylphosphines **5a-e** are as follows:

Diphenyl(trimethylsilyl)phosphine 5a.



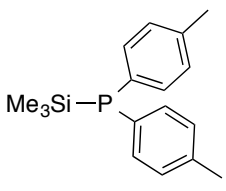
Following the general procedure starting from diphenylphosphine (7.3 g, 39.21 mmol), further distillation of the oily crude afforded **5a** (8.95 g, 88%) as a colorless liquid. Spectroscopic and physical data matched those of a commercial sample.[12]

Di(4-fluorophenyl)(trimethylsilyl)phosphine 5b.



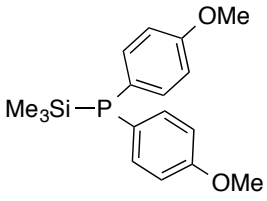
Following the general procedure starting from di(4-fluorophenyl)phosphine (4.20 g, 18.90 mmol), further distillation (117°C/2·10^{-4} mbar) of the oily crude afforded **5b** (3.95 g, 71%) as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.23 (q, 4H, $J_{H,H}$ = $J_{H,F}$ = $J_{H,P}$ = 6.8 Hz), 6.74 (t, 4H, $J_{H,H}$ = $J_{H,F}$ = 8.4 Hz), 0,06 (d, 9H, $J_{H,P}$ = 6.5 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 163.2 (d, $J_{C\text{-}F}$ = 246 Hz, 2C), 135.8 (dd, $J_{C\text{-}P}$ = 18 and $J_{C\text{-}F}$ = 8 Hz, 4C), 131.6 (dd, $J_{C\text{-}P}$ = 17 and $J_{C\text{-}F}$ = 4 Hz, 2C), 115.9 (dd, $J_{C\text{-}F}$ = 21 and $J_{C\text{-}P}$ = 7 Hz, 4C), –1.3 (d, $J_{C\text{-}P}$ = 13 Hz, 3C). ^{31}P NMR (161 MHz, C_6D_6): –59.3 (t, $J_{P\text{-}F}$ = 4 Hz). ^{19}F NMR (377 MHz, C_6D_6): –114.0 (d, $J_{F\text{-}P}$ = 4 Hz).

Di-*p*-tolyl(trimethylsilyl)phosphine 5c.



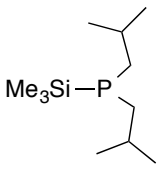
Following the general procedure starting from di-*p*-tolylphosphine (3.94 g, 18.39 mmol), further washing with pentane of the solid crude obtained afforded **5c** (4.38 g, 83 %) as a colorless solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (t, 4H, $J_{H,H}$ = $J_{H,P}$ = 7.7 Hz), 6.95 (d, 4H, $J_{H,H}$ = 7.7 Hz), 2.07 (s, 6H), 0.20 (d, 9H, $J_{H,P}$ = 4.7 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 137.3 (2C), 134.3 (d, $J_{C\text{-}P}$ = 17 Hz, 4C), 133.1 (d, $J_{C\text{-}P}$ = 15 Hz, 2C), 129.6 (d, $J_{C\text{-}P}$ = 7 Hz, 4C), 21.2 (2C), –1.0 (d, $J_{C\text{-}P}$ = 11 Hz, 3C). ^{31}P NMR (161 MHz, C_6D_6): –59.6.

Di(4-methoxyphenyl)(trimethylsilyl)phosphine 5d.



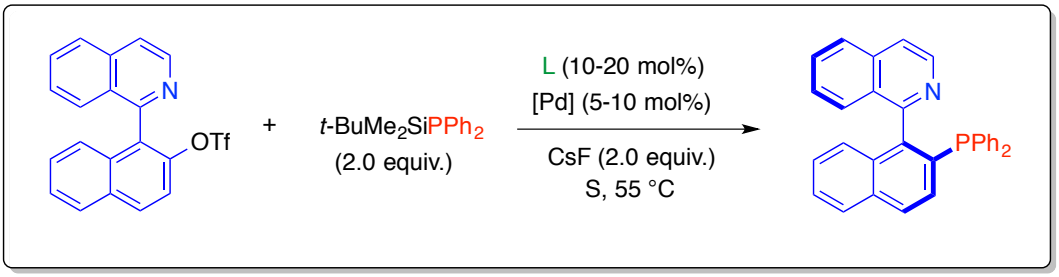
Following the general procedure, starting from di(4-methoxyphenyl)phosphine (2.0 g, 8.12 mmol), further washing with pentane of the solid crude afforfded **5d** (1.90 g, 73%) as a colorless solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (t, 4H, $J_{H,H}$ = $J_{H,P}$ = 7.8 Hz), 6.76 (d, 4H, $J_{H,H}$ = 8.2 Hz), 3.27 (s, 6H), 0.21 (d, 9H, $J_{H,P}$ = 4.7 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 160.0 (2C), 135.6 (d, $J_{C\text{-}P}$= 18 Hz, 4C), 127.2 (d, $J_{C\text{-}P}$ = 14 Hz, 2C), 114.6 (d, $J_{C\text{-}P}$ = 7 Hz, 4C), 54.7 (2C), –1.0 (d, $J_{C\text{-}P}$ = 13 Hz, 3C). ^{31}P NMR (161 MHz, $CDCl_3$): –62.0.

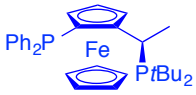
Diisobutyl(trimethylsilyl)phosphine 5e.

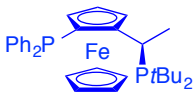
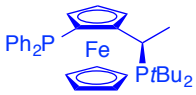
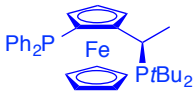
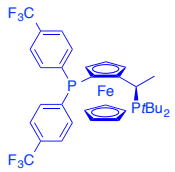
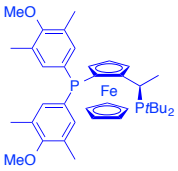
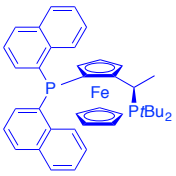
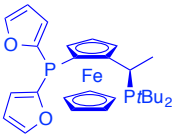
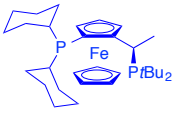
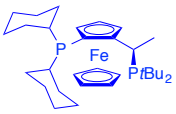
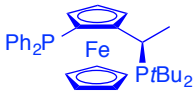


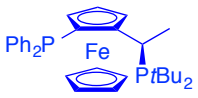
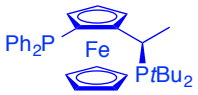
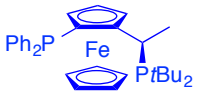
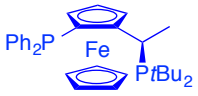
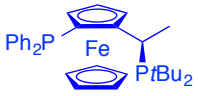
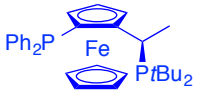
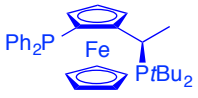
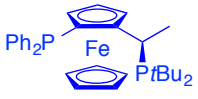
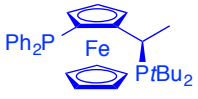
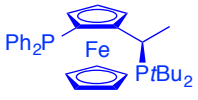
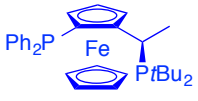
Following the general procedure starting from diisobutylphosphine (5.17 g, 35.36 mmol), further distillation (55°C/1.2·10^{-1} mbar) of the oily crude afforded **3e** (7.12 g, 92%) as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 1.69 (m, 2H) 1.46-1.34 (m, 4H), 1.05 (t, 12H, $J_{H\text{-}H}$ = $J_{H\text{-}P}$= 7.6 Hz), 0.13 (br s, 9H). ^{13}C NMR (100 MHz, C_6D_6): δ 33.4 (d, $J_{C\text{-}P}$ = 16 Hz, 2C), 28.9 (d, $J_{C\text{-}P}$ = 15 Hz, 2C), 24.5 (d, $J_{C\text{-}P}$ = 9 Hz, 2C), 23.8 (d, $J_{C\text{-}P}$ = 10 Hz, 2C), –2.0 (d, $J_{C\text{-}P}$ = 11 Hz, 3C). ^{31}P NMR (161 MHz, C_6D_6): –113.5.

Table 1. Screening of Josiphos ligands and different solvents using *t*BuMe$_2$SiPPh$_2$:



Ligand (mol%)		[Pd] (mol%)	t (h)	Solvent (*c*)	C[a] (%)	e.r.
	(10)	Pd(dba)$_2$ (10)	15	THF (0.05M)	78	70:30

	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	58	77:23
	(10)	$Pd(dba)_2$ 10%	6	THF (0.05M)	66	74.5:25.5
	(20)	$Pd(dba)_2$ 10%	6	THF (0.05M)	57	77:23
	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	70	67:33
	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	30	78.5:21.5
	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	traces	nd
	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	65	67:33
	(10)	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	traces	nd
	10%	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	8	nd
	10%	$Pd_2(dba)_3$ 5%	6	THF (0.0125M)	50	75.5:24.5

	10%	$Pd_2(dba)_3$ 5%	6	THF (0.05M)	-	73.5:26.5
	10%	$Pd(OAc)_2$ 10%	6	THF (0.05M)	61	73:27
	10%	$Pd_2(dba)_3$ 5%	6	DME (0.025M)	63	72.5:27.5
	10%	$Pd_2(dba)_3$ 5%	6	DMF (0.025M)	88[b]	70.5:29.5
	10%	$Pd_2(dba)_3$ 5%	6	Toluene (0.025M)	43	77:23
	10%	$Pd_2(dba)_3$ 5%	6	1,2-DCE (0.025M)	21	86:14
	10%	$Pd_2(dba)_3$ 5%	6	DMSO (0.025M)	94[b]	87.5:12.5
	10%	$Pd_2(dba)_3$ 5%	6	1,4-dioxane (0.025M)	39	82:18
	10%	$Pd_2(dba)_3$ 5%	6	$CHCl_3$ (0.025M)	traces	nd
	10%	$Pd_2(dba)_3$ 5%	6	EtOH (0.025M)	12	94.5:5.5
	10%	$Pd_2(dba)_3$ 5%	6	MeCN (0.025M)	66	80:20

[a] Conversion was estimated by ^1H NMR. The exclusive formation of QUINAP + QUINAPO is assumed. [b] High consumption of the starting triflate was observed but the major product was the hydrolyzed triflate.

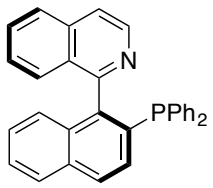
Dynamic Kinetic Asymmetric C-P Cross–Coupling. General procedure:

A flame-dried Schlenk tube was charged with triflate **(±)-1A-D** or nonaflate **(±)-8C-D** (0.1 mmol), $Pd(dba)_2$ (10 mol%) and the required ligand (**L12** or **L16**) (10 mol%). After purging with argon, the tube was introduced in a nitrogen-filled glovebox and anhydrous CsF (0.2 mmol), deoxygenated dry THF (2 mL) and the appropriate silylphosphine (0.2 mmol) were sequentially added. The sealed Schlenk tube was brought out of the glovebox and placed into a preheated oil-bath at 40 °C until completion of the reaction (TLC monitoring). After reaching room temperature, the reaction crude was filtered through a pad of Celite and the solvents were removed under vacuum. The resulting residue was purified by column chromatography over silica gel under nitrogen. Starting materials, yields, reaction times, solvents used for chromatography, and characterization data for phosphines **3** are as follows:

*Note: Partial oxidation of phosphine **3** was observed inside HPLC chiral columns. Therefore, phosphine samples were oxidized (H_2O_2 in acetone) to the corresponding phosphine oxides in order to determine the er´s. The racemic phosphine oxides references were directly prepared by heating a mixture of the corresponding starting triflates (0.1 mmol, 1.0 equiv.) and $HP(O)Ar_2$ (0.11 mmol, 1.1 equiv.), dppp (5 mol%), $Pd(OAc)_2$ (5 mol%), iPr_2NEt (0.4 mmol, 4.0 equiv.) in DMSO (0.5 mL) at 100 °C overnight.*

Characterization of products 3Aa-Ce:

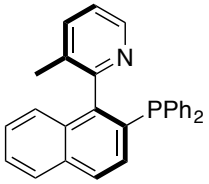
(*S*)-1-(2-(diphenylphosphanyl)naphthalen-1-yl)isoquinoline 3Aa.



Following the general procedure using triflate **(±)-1A** and **5a** as starting materials and **L12** as the ligand, after 15 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM/*n*-hexane 7:3 to DCM) afforded **3Aa** (41.5 mg, 95%) as a white solid. Spectroscopic and physical data matched those reported in the literature.[¡Error! Marcador no definido.] $[\alpha]^{20}_D$ –138.0 (*c* 1.0, $CHCl_3$) for er 95.5:4.5. [Lit.:[¡Error! Marcador no definido.] $[\alpha]^{25}_D$= –165.0 (*c* 1.0, $CHCl_3$) for (*S*)-enantiomer (er 99.5:0.5)]. HPLC (IA column, Hex:Isop 85:15, T= 30°C, F= 1mL/min): t_R 23.59 min (major) and 30.78 min (minor).

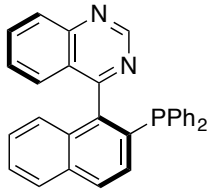
Note: A sample of **3Aa** *with er* 95.5:4.5 *was crystallized from a hot Toluene/CH_2Cl_2 10:1 mixture, affording the enantioenriched product* **3Aa** *with er >99.5:0.5.*

(*S*)-2-(2-(diphenylphosphanyl)naphthalen-1-yl)-3-methylpyridine 3Ba.



Following the general procedure using triflate **(±)-1B** and **5a** as starting materials and **L12** as the ligand, after 15 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM/*n*-hexane 7:3 to DCM) afforded **3Ba** (36.0 mg, 89%) as a white solid. $[\alpha]^{20}_D$ –27.5 (*c* 1.0, $CHCl_3$) for er 95:5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, 1H, *J* = 4.0 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.81 (d, 1H, *J* = 8.4 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.48 (t, 1H, *J* = 7.6 Hz), 7.36 (t, 1H, *J* = 8.0 Hz), 7.33-7.23 (m, 12H), 7.19 (d, 1H, *J* = 8.4 Hz), 1.94 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 157.0 (d, J_{C-P} = 6 Hz), 146.0, 145.0 (d, J_{C-P} = 34 Hz), 137.1 (d, J_{C-P} = 13 Hz), 136.6 (d, J_{C-P} = 12 Hz), 136.6, 133.0, 133.0, 132.8, 132.7, 132.5 (d, J_{C-P} = 10 Hz), 132.5, 132.4 (d, J_{C-P} = 2 Hz), 131.0 (d, J_{C-P} = 8 Hz), 129.3 (d, J_{C-P} = 2 Hz), 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 126.2, 125.9, 125.1 (d, J_{C-P} = 2 Hz), 122.0, 18.1 (d, J_{C-P} = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –13.6. HRMS (ESI) calcd. for $C_{28}H_{23}NP$ (M + H^+) 404.1563. Found 404.1558. HPLC (IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min): t_R 10.20 min (major) and 13.06 min (minor).

(*S*)-4-(2-(diphenylphosphanyl)naphthalen-1-yl)quinazoline 3Ca.

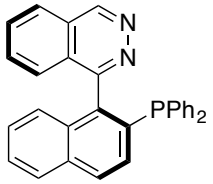


Following the general procedure using triflate **(±)-1C** and **5a** as starting materials and **L12** as the ligand, after 20 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 3:7) afforded **3Ca** (39.2 mg, 89%) as a light yellow solid. $[\alpha]^{20}_D$ –152 (*c* 1.0, $CHCl_3$) for er 95:5. After washing with acetone, a white solid is obtained (er >99.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H), 8.16 (d, 1H, *J* = 8.5 Hz), 7.95 (d, 1H, *J* = 8.5 Hz), 7.92 (d, 1H, *J* = 8.2 Hz), 7.86 (ddd, 1H, *J* = 8.4, 5.2 and 3.2 Hz), 7.52 (t, 1H, *J* = 7.6 Hz), 7.46 (dd, 1H, J_{H-H} = 8.5 and J_{H-P} = 3.2 Hz), 7.35-7.16 (m, 13H), 7.09 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4 (d, J_{C-P} = 7 Hz), 154.7, 150.1, 141.5 (d, J_{C-P} = 33 Hz), 136.7 (d, J_{C-P} = 10 Hz), 136.5 (d, J_{C-P} = 11 Hz), 134.6 (d, J_{C-P}

= 15 Hz), 133.9, 133.8, 133.6, 133.4, 133.3, 133.1, 131.8 (d, $J_{C\text{-}P}$ = 8 Hz), 129.8, 129.3, 128.7, 128.6, 128.4, 128.3, 128.3, 128.3, 128.1, 127.5, 127.1, 127.0, 127.0, 126.0 (d, $J_{C\text{-}P}$ = 2 Hz), 125.7 (d, $J_{C\text{-}P}$ = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –14.0. HRMS (ESI) calcd. for $C_{30}H_{22}N_2P$ (M + H^+) 441.1515. Found 441.1506. HPLC for phosphine oxide (IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min): t_R 20.30 min (major) and 26.28 min (minor).

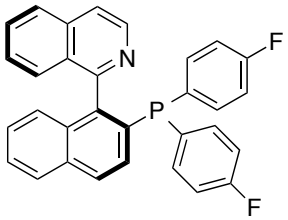
Note: A lack of reproducibility was observed in terms of enantioselectivity most probably due to undetectable impurities accompanying triflate ***(±)-1C****. Replacement of triflate* ***(±)-1C*** *by nonaflate* ***(±)-8C*** *gave rise to high levels of enantioselectivity and consistent reproducibility (er 94.5:5.5, 90% isolated yield).*

(*S*)-1-(2-(diphenylphosphanyl)naphthalen-1-yl)phthalazine 3Da.



Following the general procedure using triflate **(±)-1D** and **5a** as starting materials and **L12** as the ligand, after 20 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 2:3) afforded **3Da** (31.1 mg, 71%) as a white solid. $[\alpha]^{20}_D$ –77.3 (*c* 1.2, CH_2Cl_2) for er 85.5:14.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 8.05 (d, 1H, *J* = 8.4 Hz), 7.95 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 8.0 Hz), 7.85 (t, 1H, *J* = 8.0 Hz), 7.57-7.45 (m, 3H), 7.33-7.19 (m, 11H), 7.17-7.11 (m 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.6 (d, $J_{C\text{-}P}$ = 6 Hz), 151.3, 141.3 (d, $J_{C\text{-}P}$ = 33 Hz), 137.5 (d, $J_{C\text{-}P}$ = 13 Hz), 137.1 (d, $J_{C\text{-}P}$ = 11 Hz), 135.9 (d, $J_{C\text{-}P}$ = 14 Hz), 134.0, 134.0, 133.8, 133.7, 133.5, 133.1 (d, $J_{C\text{-}P}$ = 8 Hz), 132.9, 132.7, 130.4, 129.7, 129.0, 128.8, 128.8, 128.7, 128.7, 128.5, 127.9 (d, $J_{C\text{-}P}$ = 3 Hz), 127.5, 127.3, 126.9, 126.7, 126.5 (d, $J_{C\text{-}P}$ = 2 Hz), 126.2. ^{31}P NMR (161 MHz, $CDCl_3$): –14.1. HRMS (ESI) calcd. for $C_{30}H_{22}N_2P$ (M + H^+) 441.1515. Found 441.1509. HPLC (IA column, Hex:Isop 50:50, T= 30°C, F= 1mL/min): t_R 14.56 min (minor) and 27.94 min (major).

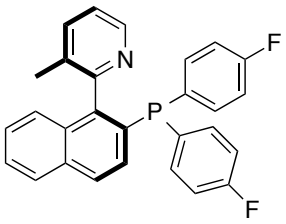
(*S*)-1-(2-(bis(4-fluorophenyl)phosphanyl)naphthalen-1-yl)isoquinoline 3Ab.



Following the general procedure using triflate **(±)-1A** and **5b** as starting materials and **L12** as the ligand, after 18 hours at 40

°C purification of the reaction crude through a short pad of SiO_2 (DCM/*n*-hexane 7:3 to DCM) afforded **3Ab** (41.9 mg, 88%) as a white foam. $[\alpha]^{20}_D$ –98.2 (*c* 0.8, $CHCl_3$) for er 90:10. ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, 1H, *J* = 5.6 Hz), 7.94-7.90 (m, 3H), 7.76 (d, 1H, *J* = 5.6 Hz), 7.64-7.62 (m, 1H), 7.50 (t, 1H, *J* = 8.0 Hz), 7.36 (d, 1H, *J* = 8.4 Hz), 7.31-7.18 (m, 5H), 7.14-7.10 (m, 3H), 6.99 (t, 2H, $J_{H,H} = J_{H,F}$ = 8.4 Hz), 6.91 (t, 2H, $J_{H,H} = J_{H,F}$ = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 (d, J_{C-F} = 247 Hz), 163.0 (d, J_{C-F} = 247 Hz), 160.1 (d, J_{C-P} = 6 Hz), 144.0 (d, J_{C-P} = 32 Hz), 142.2, 135.9, 135.6 (dd, J_{C-P} = 22 and J_{C-F} = 8 Hz, 2C), 135.1 (dd, J_{C-P} = 20 and J_{C-P} = 8 Hz), 134.4 (d, J_{C-P} = 33 Hz), 132.7-132.4 (5C), 130.0, 129.3, 128.9, 127.9, 127.3, 127.0, 127.0, 126.9, 126.8, 126.5 (d, J_{C-P} = 2 Hz), 120.4, 115.6 (dd, J_{C-F} = 21 and J_{C-P} = 1 Hz, 2C), 115.5 (dd, J_{C-F} = 21 and J_{C-P} = 2 Hz, 2C). ^{31}P NMR (161 MHz, $CDCl_3$): –15.9 (t, J_{P-F} = 4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): –112.0 (d, J_{F-P} = 4 Hz), –113.1 (d, J_{F-P} = 5 Hz). HRMS (ESI) calcd. for $C_{31}H_{21}F_2NP$ ($M + H^+$) 476.1374. Found 476.1366. HPLC for phosphine oxide (IA column, Hex:Isop 85:15, T= 30°C, F= 1mL/min): t_R 22.99 min (major) and 39.58 min (minor).

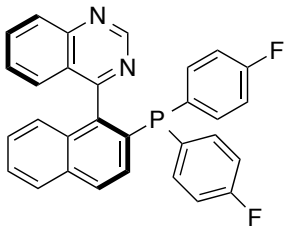
(*S*)-2-(2-(bis(4-fluorophenyl)phosphanyl)naphthalen-1-yl)-3-methylpyridine 3Bb.



Following the general procedure using triflate **(±)-1B** and **5b** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM/*n*-hexane 7:3 to DCM) afforded **3Bb** (35.8 mg, 82%) as a white foam. $[\alpha]^{20}_D$ –88.9 (*c* 1.4, $CHCl_3$) for er 92.5:7.5. ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, 1H, *J* = 4.6 Hz), 7.86 (d, 1H, *J* = 8.2 Hz), 7.83 (d, 1H, *J* = 8.5 Hz), 7.62 (d, 1H, *J* = 7.6 Hz), 7.50 (t, 1H, *J* = 8.0 Hz), 7.37 (t, 1H, *J* = 8.0 Hz), 7.29-7.22 (m, 4H), 7.20-7.17 (m, 3H), 7.03 (t, 2H, $J_{H,H} = J_{H,F}$ = 8.6 Hz), 6.97 (t, 2H, $J_{H,H} = J_{H,F}$ = 8.6 Hz), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 (d, J_{C-F} = 248 Hz), 163.1 (d, J_{C-F} = 247 Hz), 157.8 (d, J_{C-P} = 6 Hz), 146.8, 144.2 (d, J_{C-P} = 33 Hz), 137.4, 135.5 (dd, J_{C-P} = 22 and J_{C-F} = 8 Hz, 2C), 135.2 (dd, J_{C-P} = 21 and J_{C-F} = 8 Hz, 2C), 133.7, 133.1 (d, J_{C-P} = 2 Hz), 132.9 (d, J_{C-P} = 12 Hz), 132.8 (dd, J_{C-P} = 13 and J_{C-F} = 4 Hz), 132.3 (dd, J_{C-P} = 11 and J_{C-F} = 4 Hz), 131.7 (d, J_{C-P} = 8 Hz), 129.2, 128.5, 128.1, 127.0, 126.8, 125.7 (d, J_{C-P} = 2 Hz), 122.8,

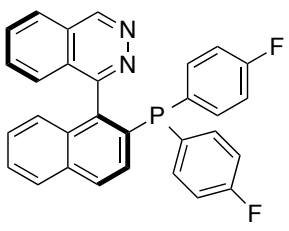
115.7 (dd, $J_{C\text{-}F}$ = 21 and $J_{C\text{-}P}$ = 7 Hz, 2C), 115.0 (dd, $J_{C\text{-}F}$ = 21 and $J_{C\text{-}P}$ = 8 Hz, 2C), 19.0 (d, $J_{C\text{-}P}$ = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –15.4 (t, $J_{P\text{-}F}$ = 5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): –112.4 (d, $J_{F\text{-}P}$ = 5 Hz), –113.0 (d, $J_{F\text{-}P}$ = 5 Hz). HRMS (ESI) calcd. for $C_{28}H_{21}F_2NP$ (M + H^+) 440.1374. Found 440.1366. HPLC for phosphine oxide (IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min): t_R 9.98 min (major) and 16.49 min (minor).

(*S*)-4-(2-(bis(4-fluorophenyl)phosphanyl)naphthalen-1-yl)quinazoline 3Cb.



Following the general procedure and using nonaflate **(±)-8C** and **5b** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 3:7) afforded **3Cb** (41.6 mg, 87%) as a white foam. $[\alpha]^{20}_D$ –48.0 (*c* 0.5, $CHCl_3$) for er 93:7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.10 (d, 1H, *J* = 8.0 Hz), 7.91 (d, 1H, *J* = 8.5 Hz), 7.87 (d, 1H, *J* = 8.0 Hz), 7.82 (t, 1H, *J* = 8.0 Hz), 7.48 (t, 1H, *J* = 8.0 Hz), 7.31 (dd, 1H, $J_{H\text{-}H}$ = 8.4 and $J_{H\text{-}P}$ = 3 Hz), 7.30-7.24 (m, 2H), 7.24-7.18 (m, 1H), 7.13 (m, 2H), 7.12-7.04 (m, 3H), 6.95 (t, 2H, $J_{H,H}$ = $J_{H,F}$ = 8.6 Hz), 6.87 (t, 2H, $J_{H,H}$ = $J_{H,F}$ = 8.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (d, $J_{C\text{-}P}$ = 6 Hz), 163.3 (d, $J_{C\text{-}F}$ = 248 Hz), 163.2 (d, $J_{C\text{-}F}$ = 247 Hz), 154.7, 150.2, 141.3 (d, $J_{C\text{-}P}$ = 32 Hz), 135.6 (dd, $J_{C\text{-}P}$ = 22 and $J_{C\text{-}F}$ = 8 Hz, 2C), 135.1 (dd, $J_{C\text{-}P}$ = 21 and $J_{C\text{-}P}$ = 8 Hz, 2C), 134.2 (d, $J_{C\text{-}P}$ = 15 Hz), 134.0, 133.4, 132.0-131.7 (3C), 129.5, 129.2, 128.8, 128.1, 127.6, 127.3, 127.2, 126.8, 125.9 (d, $J_{C\text{-}P}$ = 2 Hz), 125.5 (d, $J_{C\text{-}P}$ = 3 Hz), 115.8 (dd, $J_{C\text{-}F}$ = 21 and $J_{C\text{-}P}$ = 2 Hz, 2C), 115.7 (dd, $J_{C\text{-}F}$ = 21 and $J_{C\text{-}P}$ = 3 Hz, 2C). ^{31}P NMR (161 MHz, $CDCl_3$): –16.0 (t, $J_{P\text{-}F}$ = 4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): –111.9 (d, $J_{F\text{-}P}$ = 4 Hz), –112.5 (d, $J_{F\text{-}P}$ = 5 Hz). HRMS (ESI) calcd. for $C_{30}H_{20}F_2N_2P$ (M + H^+) 477.1327. Found 477.1324. HPLC (IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min): t_R 11.18 min (major) and 19.33 min (minor).

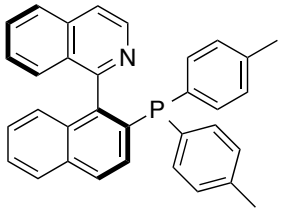
(*S*)-1-(2-(bis(4-fluorophenyl)phosphanyl)naphthalen-1-yl)phthalazine 3Db.



Following the general procedure and using triflate **(±)-1D** and **5b** as starting materials and **L12** as the ligand, after 20 hours at 40 °C purification of the reaction crude through a short pad

of SiO_2 (EtOAc/*n*-hexane 1:4 to 2:3) afforded **3Db** (34.6 mg, 73%) as a light yellow solid. $[\alpha]^{20}_D$ –120.0 (*c* 0.4, $CHCl_3$) for er 91:9. ^1H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 8.05 (d, 1H, *J* = 8.0 Hz), 7.97 (d, 1H, *J* = 8.0 Hz), 7.92 (d, 1H, *J* = 8.0 Hz), 7.87 (t, 1H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.52 (t, 1H, *J* = 7.6 Hz), 7.38 (dd, 1H, $J_{H,H}$ = 8.4 and $J_{H,P}$ = 3.3 Hz), 7.31 (t, 1H, *J* = 8.0 Hz), 7.24-7.18 (m, 3H), 7.12-7.07 (m, 3H), 6.98 (t, 2H, $J_{H,H}$ = $J_{H,F}$ = 8.4 Hz), 6.91 (t, 2H, $J_{H,H}$ = $J_{H,F}$ = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 (d, J_{C-F} = 248 Hz), 163.1 (d, J_{C-F} = 247 Hz), 160.0 (d, J_{C-P} = 6 Hz), 150.9, 140.4 (d, J_{C-P} = 32 Hz), 135.5 (dd, J_{C-P} = 22 and J_{C-F} = 8 Hz, 2C), 135.3 (d, J_{C-P} = 14 Hz), 135.1 (dd, J_{C-P} = 20 and J_{C-P} = 8 Hz, 2C), 133.5, 132.6 (d, J_{C-P} = 7 Hz), 132.4 (d, J_{C-P} = 4 Hz), 132.4, 132.3, 131.7 (dd, J_{C-P} = 11 and J_{C-F} = 4 Hz), 129.6, 129.4, 128.1, 127.5 (d, J_{C-P} = 3 Hz), 127.2, 127.1, 126.5, 126.2, 126.1, 125.9, 115.7 (dd, J_{C-F} = 7 and J_{C-P} = 7 Hz, 2C), 115.5 (dd, J_{C-F} = 7 and J_{C-P} = 6 Hz, 2C). ^{31}P NMR (161 MHz, $CDCl_3$): –15.8 (t, J_{P-F} = 4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): –112.2 (d, J_{F-P} = 5 Hz), –112.6 (d, J_{F-P} = 5 Hz). HRMS (ESI) calcd. for $C_{30}H_{20}F_2N_2P$ ($M + H^+$) 477.1327. Found 477.1321. HPLC (IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min): t_R 19.51 min (minor) and 23.49 min (major).

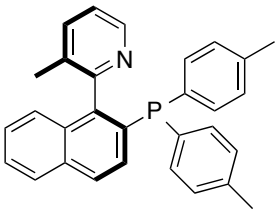
(*S*)-1-(2-(Di-*p*-tolylphosphanyl)naphthalen-1-yl)isoquinoline 3Ac.



Following the general procedure using triflate **(±)-1A** and **5c** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM/*n*-hexane 7:3 to DCM) afforded **3Ac** (39.3 mg, 84%) as a white solid. Spectroscopic and physical data matched those reported in the literature.[13] $[\alpha]^{20}_D$ –82.5 (*c* 0.6, $CHCl_3$) for er 92:8. [Lit.:**¡Error! Marcador no definido.** $[\alpha]^{25}_D$= –86.1 (*c* 2.0, $CHCl_3$) for (*S*)-enantiomer (er 96:4)]. HPLC for phosphine oxide (ADH column, Hex:Isop 70:30, T= 30°C, F= 1mL/min): t_R 14.74 min (major) and 16.53 min (minor).

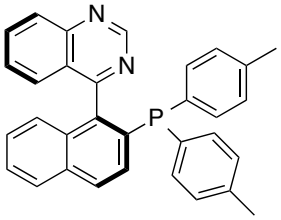
Note: A sample of **3Ac** *with er 89:11 was crystallized by slow diffusion of n-hexane in a solution of the product in OEtAc, affording the formation of racemic crystals and the enantioenriched product* **3Ac** *(er 97.5:2.5, 80% yield) was obtained from the mother liquor.*

(*S*)-2-(2-(Di-*p*-tolylphosphanyl)naphthalen-1-yl)-3-methylpyridine 3Bc.



Following the general procedure using triflate **(±)-1B** and **5c** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM to DCM/MeOH 100:1) afforded **3Bc** (35.2 mg, 81%) as a light white foam. $[\alpha]^{20}_D$ –84.6 (*c* 1.3, $CHCl_3$) for er 93:7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, 1H, *J* = 4.8 Hz), 7.86 (d, 1H, *J* = 8.2 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.63 (d, 1H, *J* = 7.7 Hz), 7.49 (t, 1H, *J* = 8.2 Hz), 7.39-7.35 (m, 2H), 7.29 (m, 1H), 7.24-7.09 (m, 9H), 2.37 (s, 3H), 2.33 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3 (d, J_{C-P} = 6 Hz), 146.7, 145.0 (d, J_{C-P} = 33 Hz), 138.3, 137.9, 137.3, 134.1 (d, J_{C-P} = 11 Hz), 133.9 (d, J_{C-P} = 14 Hz), 133.8 (d, J_{C-P} = 20 Hz, 2C), 133.3 (d, J_{C-P} = 19 Hz, 2C), 133.1 (d, J_{C-P} = 3 Hz), 131.7 (d, J_{C-P} = 8 Hz), 129.8 (d, J_{C-P} = 2 Hz, 2C), 129.1 (d, J_{C-P} = 7 Hz, 2C), 129.0 (d, J_{C-P} = 7 Hz, 2C), 128.1, 127.9, 126.6, 126.5, 125.8 (d, J_{C-P} = 2 Hz, 2C), 122.6, 21.3, 21,2, 19.0 (d, J_{C-P} = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –15.2. HRMS (ESI) calcd. for $C_{30}H_{27}NP$ ($M + H^+$) 432.1876. Found 432.1867. HPLC for phosphine oxide (IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min): t_R 11.13 min (major) and 17.55 min (minor).

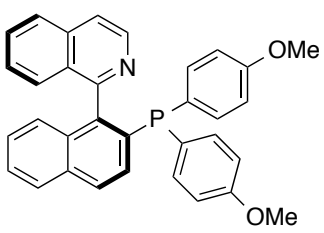
(*S*)-4-(2-(di-*p*-tolylphosphanyl)naphthalen-1-yl)quinazoline 3Cc.



Following the general procedure and using nonaflate **(±)-8C** and **5c** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 3:7) afforded **3Cc** (41.6 mg, 89%) as a light white foam. $[\alpha]^{20}_D$ –102.1 (*c* 0.9, $CHCl_3$) for er 93:7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (s, 1H), 8.13 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 8.7 Hz), 7.90 (d, 1H, *J* = 8.4 Hz), 7.84 (m, 1H), 7.50 (t, 1H, *J* = 7.6 Hz), 7.44 (dd, 1H, $J_{H,H}$ = 8.5 and $J_{H,P}$ = 3.3 Hz), 7.32-7.28 (m, 3H), 7.14-7.09 (m, 4H), 7.06-7.00 (m, 5H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4 (d, J_{C-P} = 7 Hz), 154.7, 150.1, 141.0 (d, J_{C-P} = 32 Hz), 138.6, 138.2, 135.3 (d, J_{C-P} = 16 Hz), 133.8, 133.7, 133.6, 133.3, 133.3, 133.2, 133.1, 133.0 (d, J_{C-P} = 5 Hz), 131.8 (d, J_{C-P} = 7 Hz), 129.7, 129.2, 129.1, 129.1, 129.0, 128.6, 128.0, 127.4, 127.1, 126.9, 125.9 (d, J_{C-P} = 2 Hz), 125.6 (d, J_{C-P} = 3 Hz), 21.2, 21.2. ^{31}P

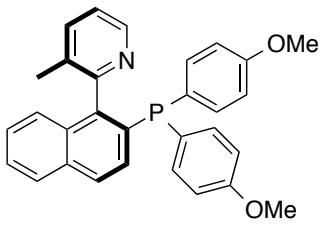
NMR (161 MHz, $CDCl_3$): –15.2. HRMS (ESI) calcd. for $C_{32}H_{26}N_2P$ (M + H^+) 469.1828. Found 469.1818. HPLC for phosphine oxide (IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min): t_R 18.19 min (major) and 25.41 min (minor).

(*S*)-1-(2-(bis(4-methoxyphenyl)phosphanyl)naphthalen-1-yl)isoquinoline 3Ad.



Following the general procedure using triflate **(±)-1A** and **5d** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 3:7) afforded **3Ad** (37.2 mg, 74%) as a white foam. $[\alpha]^{20}_D$ –40.0 (*c* 1.0, $CHCl_3$) for er 78:22. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, 1H, *J* = 5.6 Hz), 7.92-7.89 (m, 3H), 7.74 (d, 1H, *J* = 5.6 Hz), 7.61 (t, 1H, *J* = 7.3 Hz), 7.49-7.43 (m, 2H), 7.29-7.17 (m, 5H), 7.11-7.07 (m, 3H), 6.88 (d, 2H, *J* = 8.2 Hz), 6.74 (d, 2H, *J* = 8.2 Hz), 3.79 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4 (d, $J_{C\text{-}P}$ = 6 Hz), 159.9, 159.7, 143.3 (d, $J_{C\text{-}P}$ = 32 Hz), 142.2, 135.9 (d, $J_{C\text{-}P}$ = 14 Hz), 135.8, 135.2 (d, $J_{C\text{-}P}$ = 22 Hz, 2C), 134.7 (d, $J_{C\text{-}P}$ = 20 Hz, 2C), 133.4, 132.6 (d, $J_{C\text{-}P}$ = 7 Hz), 129.9, 129.6, 128.9 (d, $J_{C\text{-}P}$ = 3 Hz), 128.5, 128.3, 128.2 (d, $J_{C\text{-}P}$ = 1 Hz), 127.8, 127.5, 126.8, 126.7, 126.6, 126.5, 126.4 (d, $J_{C\text{-}P}$ = 2 Hz), 120.2, 113.9 (d, $J_{C\text{-}P}$ = 7 Hz, 2C), 113.8 (d, $J_{C\text{-}P}$ = 7 Hz, 2C), 55.1 (2C). ^{31}P NMR (161 MHz, $CDCl_3$): –16.6. HRMS (ESI) calcd. for $C_{33}H_{27}NO_2P$ (M + H^+) 500.1774. Found 500.1763. HPLC (IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min): t_R 17.78 min (major) and 22.36 min (minor).

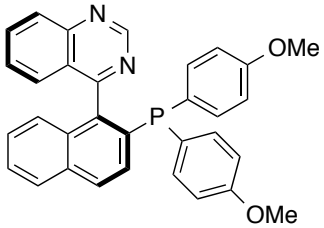
(*S*)-2-(2-(bis(4-methoxyphenyl)phosphanyl)naphthalen-1-yl)-3-methylpyridine 3Bd.



Following the general procedure using triflate **(±)-1B** and **5d** as starting materials and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a very short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 3:7) afforded **3Bd** (35.8 mg, 77%) as a light yellow foam. $[\alpha]^{20}_D$ –10.4 (*c* 1.3, $CHCl_3$) for er 85:15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, 1H, *J* = 4.8 Hz), 7.87 (d,

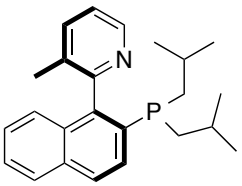
1H, *J* = 8.2 Hz), 7.84 (d, 1H, *J* = 8.4 Hz), 7.63 (d, 1H, *J* = 7.6 Hz), 7.50 (t, 1H, *J* = 7.6 Hz), 7.39-7.32 (m, 2H), 7.30-7.24 (m, 3H), 7.21-7.17 (m, 3H), 6.90 (d, 2H, *J* = 8.1 Hz), 6.85 (d, 2H, *J* = 8.2 Hz), 3.83 (s, 3H), 3.80 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 159.7, 158.1 (d, $J_{C\text{-}P}$ = 6 Hz), 146.7, 144.5 (d, $J_{C\text{-}P}$ = 32 Hz), 137.3, 135.2 (d, $J_{C\text{-}P}$ = 21 Hz, 2C), 134.8 (d, $J_{C\text{-}P}$ = 20 Hz, 2C), 134.3 (d, $J_{C\text{-}P}$ = 13 Hz), 133.6, 133.1 (d, $J_{C\text{-}P}$ = 3 Hz), 131.7 (d, $J_{C\text{-}P}$ = 7 Hz), 129.5, 128.4 (d, $J_{C\text{-}P}$ = 9 Hz), 128.2 (d, $J_{C\text{-}P}$ = 8 Hz), 128.0, 128.0, 126.5 (d, $J_{C\text{-}P}$ = 2 Hz), 125.7 (d, $J_{C\text{-}P}$ = 3 Hz), 122.6, 114.0 (d, $J_{C\text{-}P}$ = 7 Hz, 2C), 113.8 (d, $J_{C\text{-}P}$ = 7 Hz, 2C), 55.1, 55.1, 19.0 (d, $J_{C\text{-}P}$ = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –16.3. HRMS (ESI) calcd. for $C_{30}H_{27}NO_2P$ (M + H^+) 464.1774. Found 464.1763. HPLC for phosphine oxide (IA column, Hex:Isop 50:50, T= 30°C, F= 1mL/min): t_R 8.40 min (major) and 16.43 min (minor).

(*S*)-4-(2-(bis(4-methoxyphenyl)phosphanyl)naphthalen-1-yl)quinazoline 3Cd.



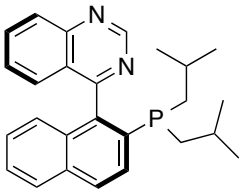
Following the general procedure and using nonaflate **(±)-8C** as starting material and **L12** as the ligand, after 18 hours at 40 °C purification of the reaction crude through a very short pad of SiO_2 (EtOAc/*n*-hexane 1:4 to 35:65) afforded **3Cd** (37.0 mg, 74%) as a light yellow foam. $[\alpha]^{20}_D$ –39.4 (*c* 0.5, $CHCl_3$) for er 89.5:10.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (s, 1H), 8.12 (d, 1H, *J* = 8.5 Hz), 7.93 (d, 1H, *J* = 9.1 Hz), 7.90 (d, 1H, *J* = 9.4 Hz), 7.84 (m, 1H), 7.49 (t, 1H, *J* = 7.8 Hz), 7.42 (dd, 1H, $J_{H\text{-}H}$ = 8.5 and $J_{H\text{-}P}$ = 3.4 Hz), 7.32-7.23 (m, 3H), 7.16 (d, 1H, *J* = 7.4 Hz), 7.14 (d, 1H, *J* = 7.4 Hz), 7.09-7.04 (m, 3H), 6.84 (d, 2H, *J* = 7.9 Hz), 6.73 (d, 2H, *J* = 8.6 Hz), 3.79 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4 (d, $J_{C\text{-}P}$ = 6 Hz), 160.1, 159.9, 154.8, 150.1, 140.5 (d, $J_{C\text{-}P}$ = 31 Hz), 135.9 (d, $J_{C\text{-}P}$ = 16 Hz), 135.3 (d, $J_{C\text{-}P}$ = 22 Hz, 2C), 134.8 (d, $J_{C\text{-}P}$ = 22 Hz, 2C), 133.7, 133.3, 131.8 (d, $J_{C\text{-}P}$ = 7 Hz), 129.5, 129.1, 128.6, 128.1, 127.6 (d, $J_{C\text{-}P}$ = 2 Hz), 127.5, 127.4, 127.1, 126.9, 126.8, 125.8 (d, $J_{C\text{-}P}$ = 2 Hz), 125.6 (d, $J_{C\text{-}P}$ = 3 Hz), 114.1 (d, $J_{C\text{-}P}$ = 8 Hz, 2C), 114.0 (d, $J_{C\text{-}P}$ = 8 Hz, 2C), 55.1, 55.1. ^{31}P NMR (161 MHz, $CDCl_3$): –16.3. HRMS (ESI) calcd. for $C_{32}H_{26}N_2O_2P$ (M + H^+) 501.1726. Found 501.1700. HPLC for phosphine oxide (IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min): t_R 17.29 min (major) and 27.00 min (minor).

(*S*)-2-(2-(diisobutylphosphanyl)naphthalen-1-yl)-3-methylpyridine 3Be.



Following the general procedure using triflate **(±)-1B** and **5e** as starting materials and **L16** as the ligand, after 40 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (EtOAc/*n*-hexane 5:95 to 1:9) afforded **3Be** (33.8 mg, 93%) as a white foam. $[\alpha]^{20}_D$ –73.7 (*c* 1.1, $CHCl_3$) for er 85:15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, 1H, *J* = 3 Hz), 7.91 (d, 1H, *J* = 8.4 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 7.70 (d, 1H, *J* = 8.4 Hz), 7.64 (d, 1H, *J* = 7.6 Hz), 7.46 (t, 1H, *J* = 7.9 Hz), 7.35-7.30 (m, 2H), 7.13 (d, 1H, *J* = 8.3 Hz), 2.01 (s, 3H), 1.84 (m, 1H), 1.71 (m, 1H), 1.60-1.49 (m, 3H), 1.39 (m, 1H), 0.95 (d, 3H, *J* = 6.4 Hz), 0.92 (d, 3H, *J* = 6.3 Hz), 0.82 (d, 3H, *J* = 6.3 Hz), 0.78 (d, 3H, *J* = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (d, $J_{C\text{-}P}$ = 6 Hz), 146.7, 145.2 (d, $J_{C\text{-}P}$ = 32 Hz), 137.4, 135.9 (d, $J_{C\text{-}P}$ = 17 Hz), 133.8, 133.0 (d, $J_{C\text{-}P}$ = 3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 7 Hz), 128.3, 128.1, 126.6, 126.5, 126.4 (d, $J_{C\text{-}P}$ = 3 Hz), 126.0 (d, $J_{C\text{-}P}$ = 2 Hz), 122.7, 41.5 (d, $J_{C\text{-}P}$ = 13 Hz), 38.7 (d, $J_{C\text{-}P}$ = 14 Hz), 26.7 (d, $J_{C\text{-}P}$ = 14 Hz), 26.1 (d, $J_{C\text{-}P}$ = 13 Hz), 25.0 (d, $J_{C\text{-}P}$ = 8 Hz), 24.6 (d, $J_{C\text{-}P}$ = 9 Hz), 24.2 (d, $J_{C\text{-}P}$ = 10 Hz), 24.0 (d, $J_{C\text{-}P}$ = 9 Hz), 19.1 (d, $J_{C\text{-}P}$ = 3 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –43.9. HRMS (ESI) calcd. for $C_{24}H_{30}NP$ (M + H^+) 364.2189. Found 364.2177. HPLC (ADH column, Hex:Isop 95:5, T= 30°C, F= 1mL/min): t_R 17.49 min (major) and 18.32 min (minor).

(*S*)-4-(2-(diisobutylphosphanyl)naphthalen-1-yl)quinazoline 3Ce.



Following the general procedure and using nonaflate **(±)-8C** and **5e** as starting materials and **L16** as the ligand, after 40 hours at 40 °C purification of the reaction crude through a short pad of SiO_2 (DCM to DCM/MeOH 50:1) afforded **3Ce** (28.8 mg, 72%) as a white solid. $[\alpha]^{20}_D$ –29.5 (*c* 1.0, $CHCl_3$) for er 72.5:27.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.18 (d, 1H, *J* = 8.5 Hz), 8.05 (d, 1H, *J* = 8.5 Hz), 7.94 (d, 1H, *J* = 8.2 Hz), 7.89 (t, 1H, *J* = 7.7 Hz), 7.80 (d, 1H, *J* = 8.6 Hz), 7.50 (t, 1H, *J* = 7.5 Hz), 7.44-7.38 (m, 2H), 7.31 (t, 1H, *J* = 7.8 Hz), 7.06 (d, 1H, *J* = 8.5 Hz), 1.79-1.76 (m, 2H), 1.55 (m, 1H), 1.43-1.37 (m, 3H), 0.87 (d, 3H, *J* = 6.5 Hz), 0.83 (d, 3H, *J* = 6.5 Hz), 0.74 (d, 3H, *J* = 5.8 Hz), 0.62 (d, 3H, *J* = 5.7Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (d, $J_{C\text{-}P}$ = 7 Hz), 154.6, 150.0,

141.7 (d, $J_{C\text{-}P}$ = 33 Hz), 137.0 (d, $J_{C\text{-}P}$ = 19 Hz), 133.8, 133.4, 131.6 (d, $J_{C\text{-}P}$ = 8 Hz), 129.3, 128.7, 128.0, 127.6, 127.0, 126.9, 126.7, 126.2 (d, $J_{C\text{-}P}$ = 3 Hz), 126.0, 126.0, 40.8 (d, $J_{C\text{-}P}$ = 13 Hz), 38.9 (d, $J_{C\text{-}P}$ = 13 Hz), 26.2 (d, $J_{C\text{-}P}$ = 14 Hz), 26.0 (d, $J_{C\text{-}P}$ = 13 Hz), 24.7 (d, $J_{C\text{-}P}$ = 8 Hz), 24.5 (d, $J_{C\text{-}P}$ = 9 Hz), 23.8 (d, $J_{C\text{-}P}$ = 9 Hz), 23.7 (d, $J_{C\text{-}P}$ = 10 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): –44.3. HRMS (ESI) calcd. for $C_{26}H_{30}N_2P$ (M + H^+) 401.2141. Found 401.2132. HPLC (ADH column, Hex:Isop 85:15, T= 30°C, F= 1mL/min): t_R 5.79 min (minor) and 6.33 min (major).

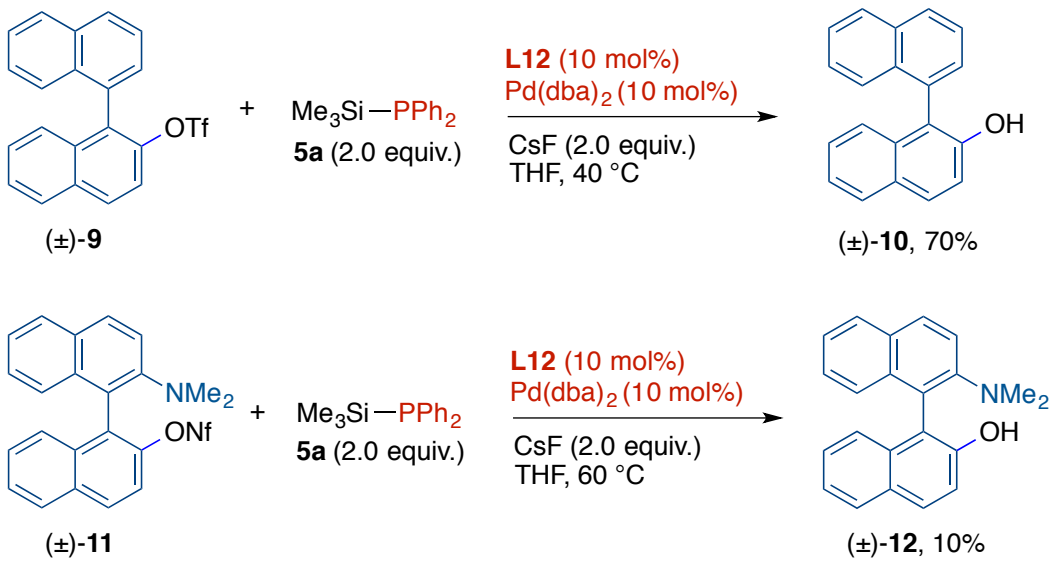


Figure S1. Experiments with Triflate **9** and Nonaflate **11**.

Following the general procedure for the Dynamic Kinetic Asymmetric C-P Cross–Coupling using **L12** as the ligand and triflate **9** or nonaflate **11** as the starting materials, after 18 hours at 40 °C and 60 °C respectively, the formation of the hydrolisis products **10**, **12** together with the starting materials was observed.

NMR spectra and HPLC traces:

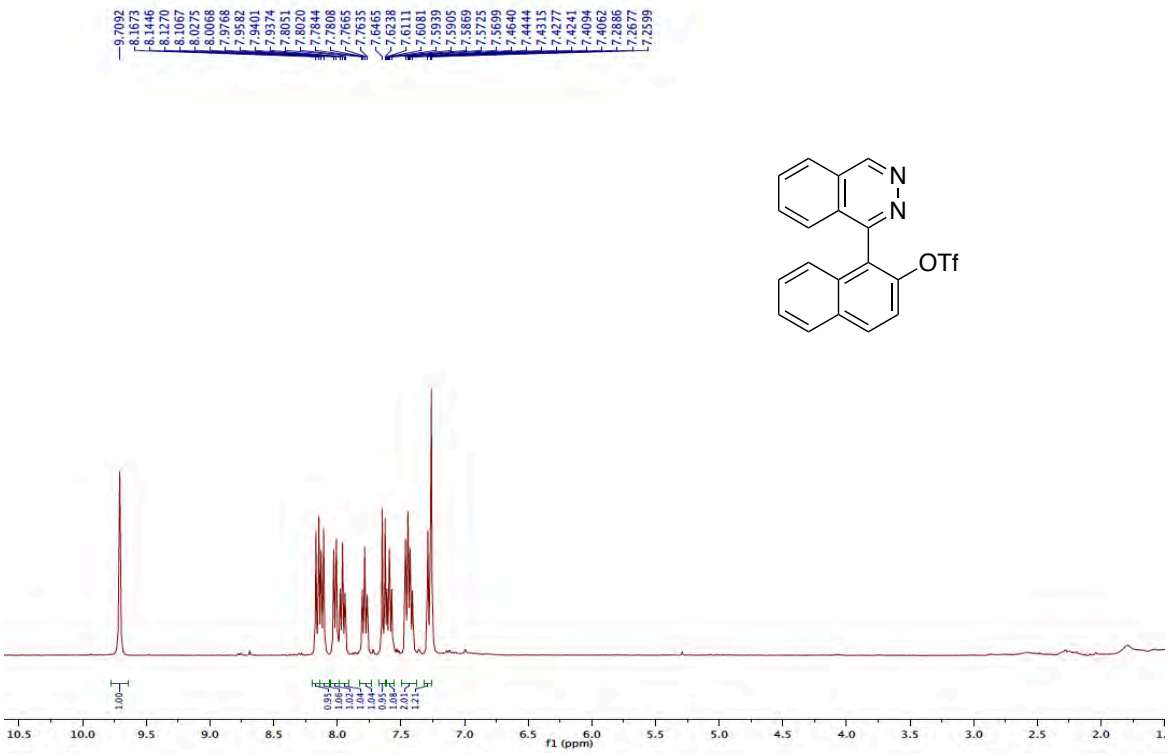


Figure S2. ^{1}HNMR ($CDCl_3$, 400 MHz) of **(±)-1D**

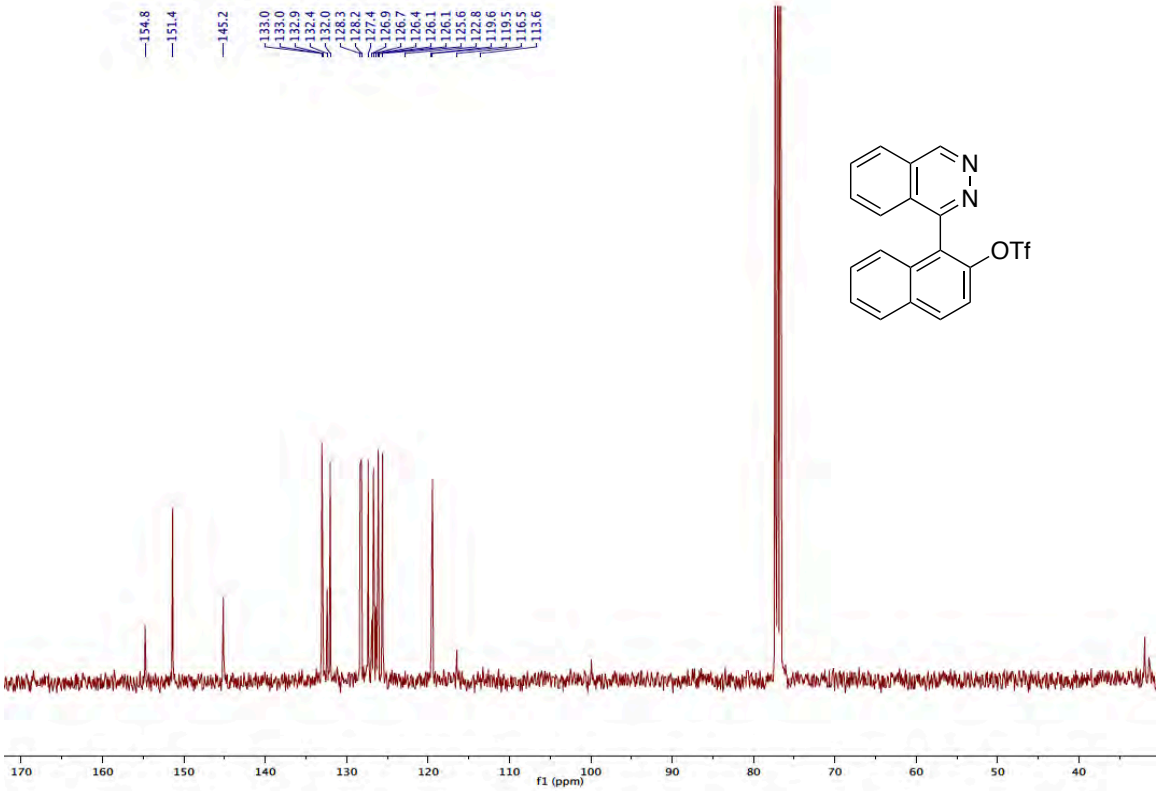


Figure S3. ^{13}C NMR ($CDCl_3$, 100 MHz) of **(±)-1D**

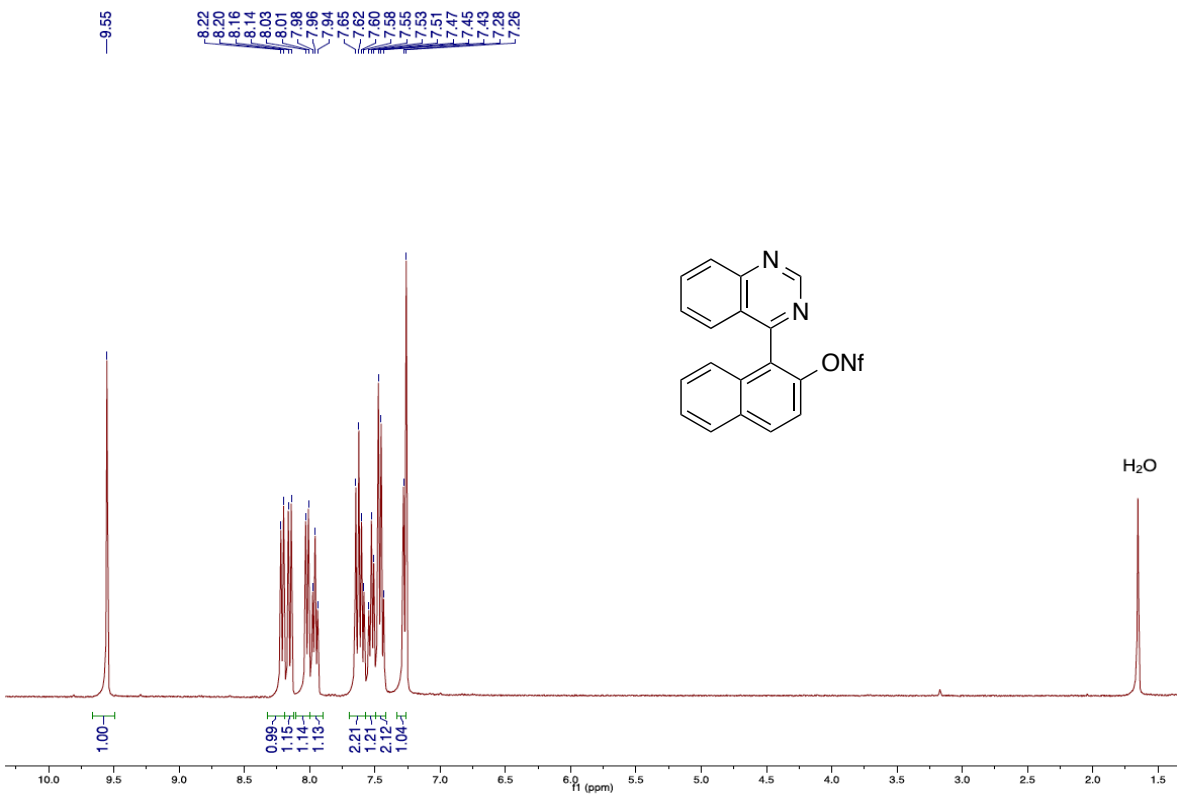


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) of **(±)-8C**

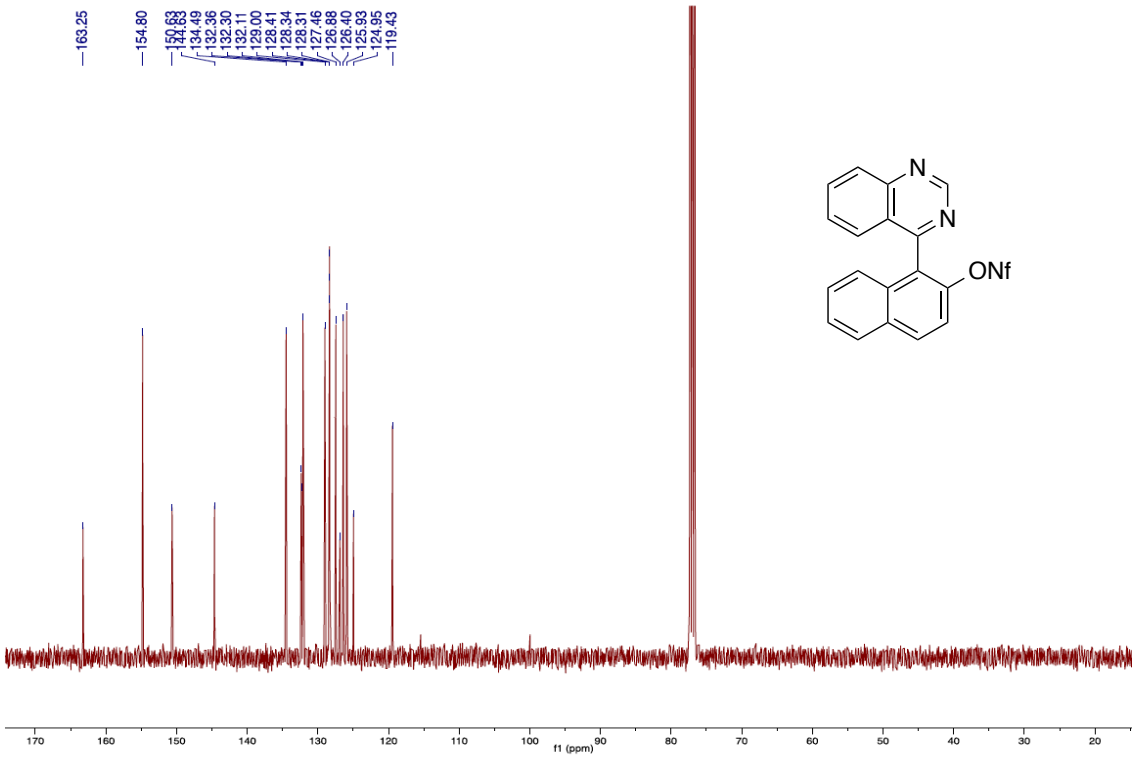


Figure S5. ^{13}C NMR ($CDCl_3$, 100 MHz) of **(±)-8C**

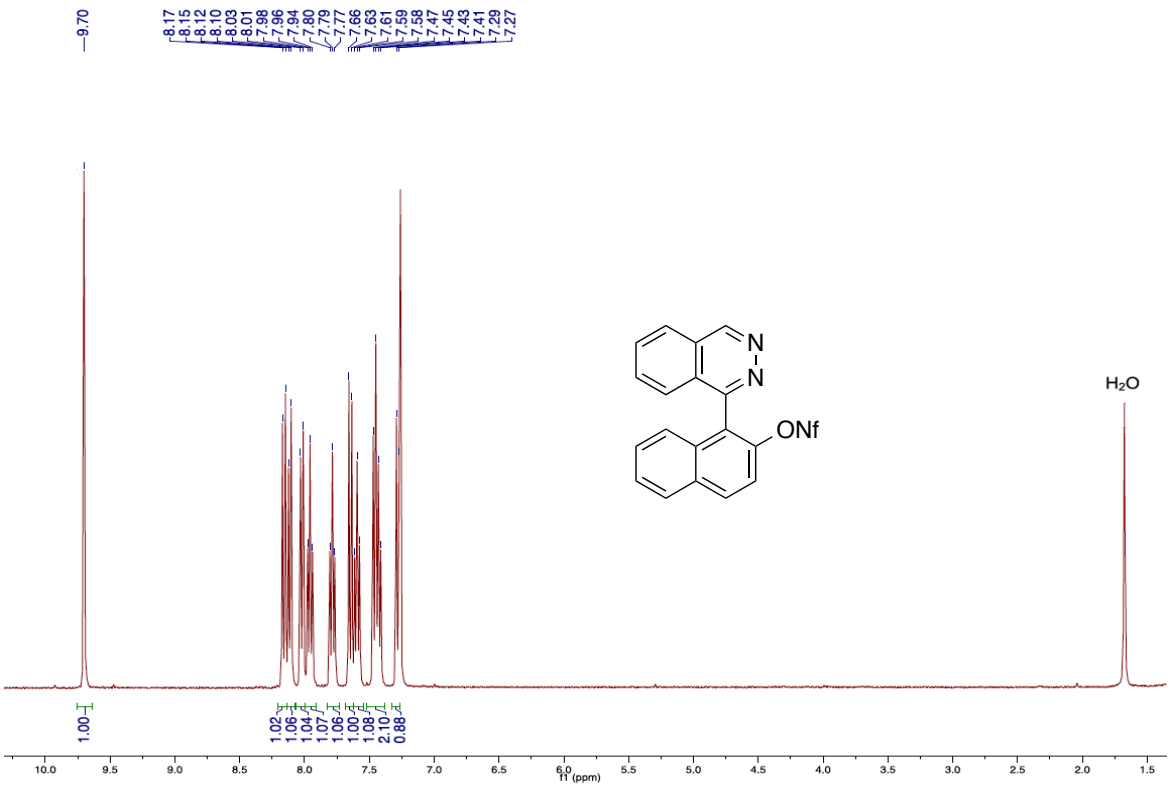


Figure S6. ^{1}H NMR ($CDCl_3$, 400 MHz) of **(±)-8D**

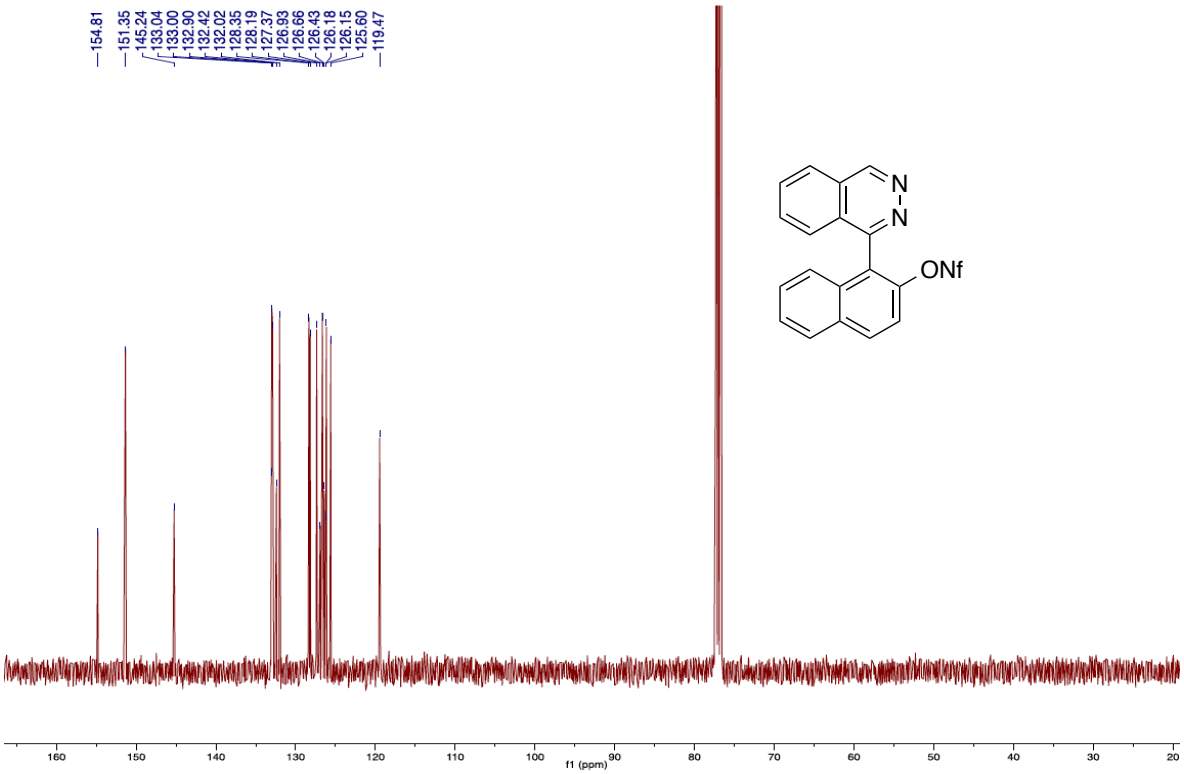


Figure S7. ^{13}C NMR ($CDCl_3$, 100 MHz) of **(±)-8D**

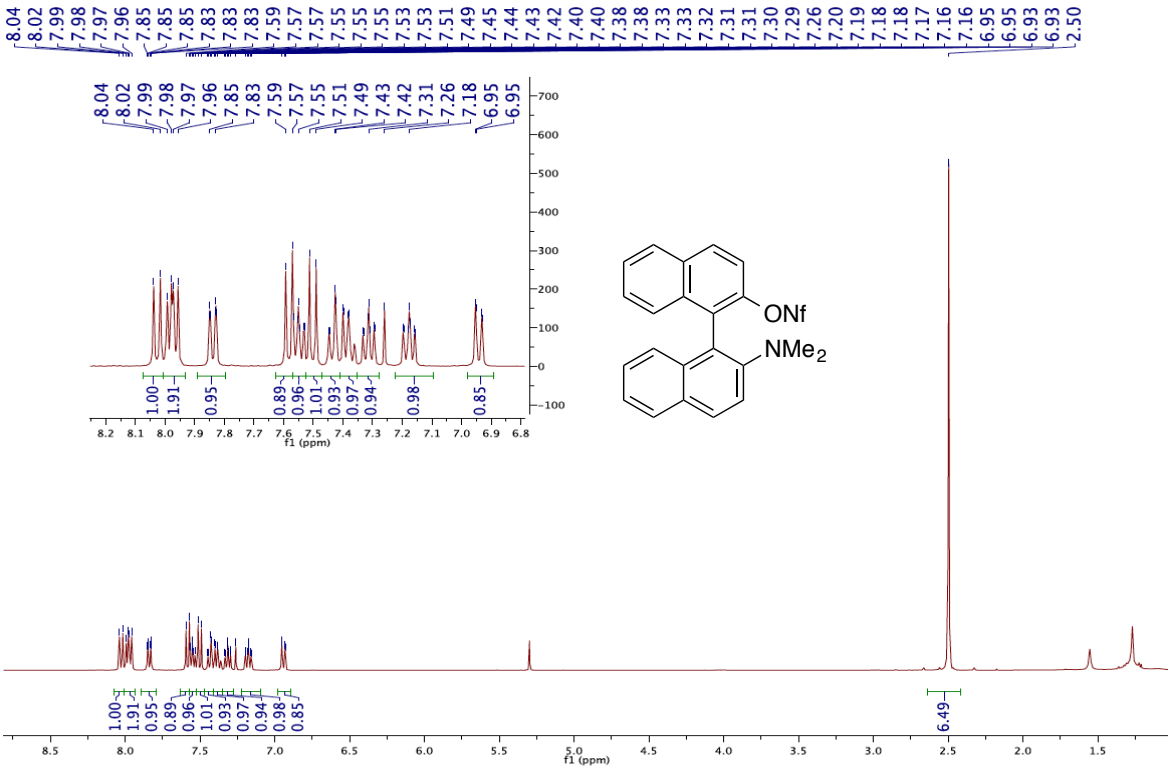


Figure S8. ^{1}H NMR ($CDCl_3$, 400 MHz) of **(±)-11**

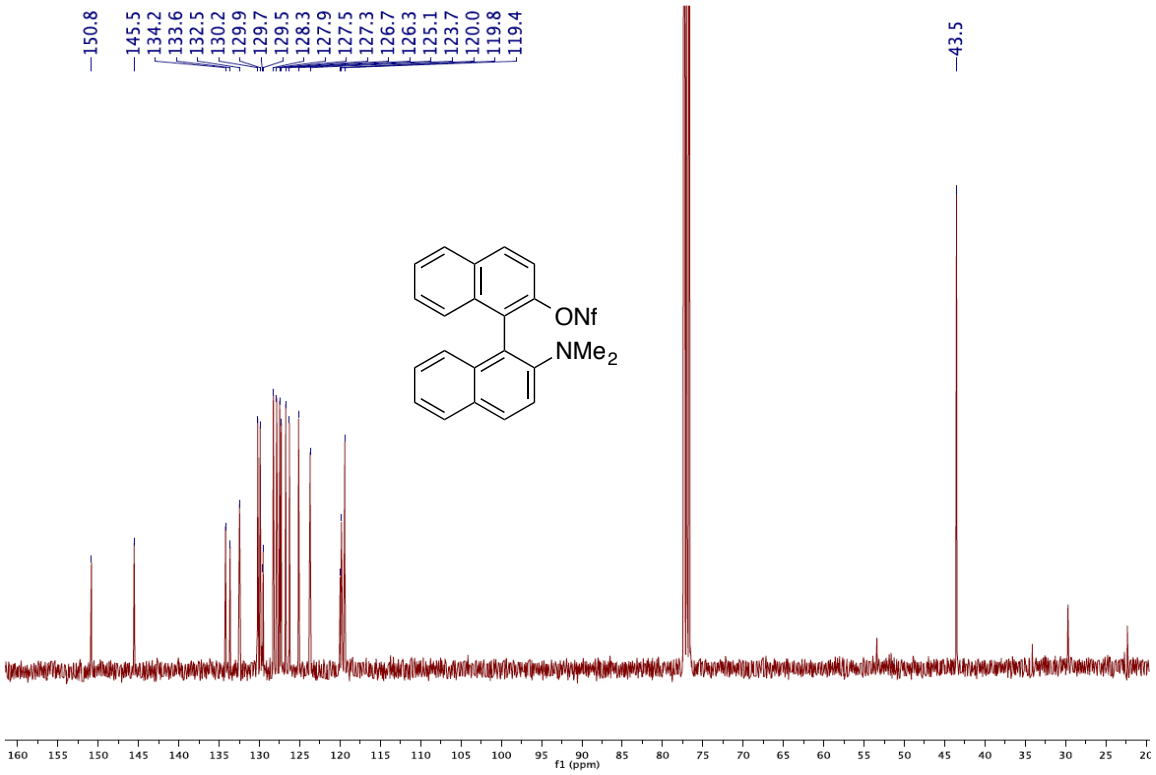


Figure S9. ^{13}C NMR ($CDCl_3$, 100 MHz) of **(±)-11**

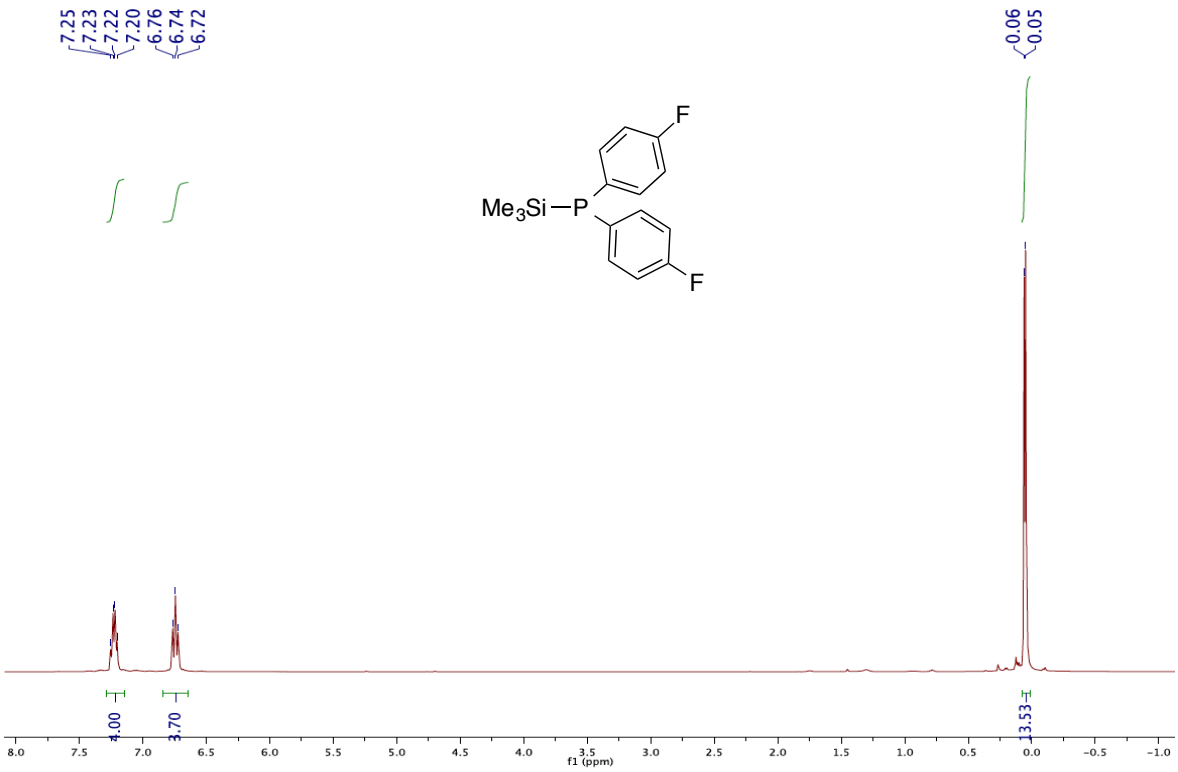


Figure S10. ^{1}H NMR (400 MHz, C_6D_6) of **5b**

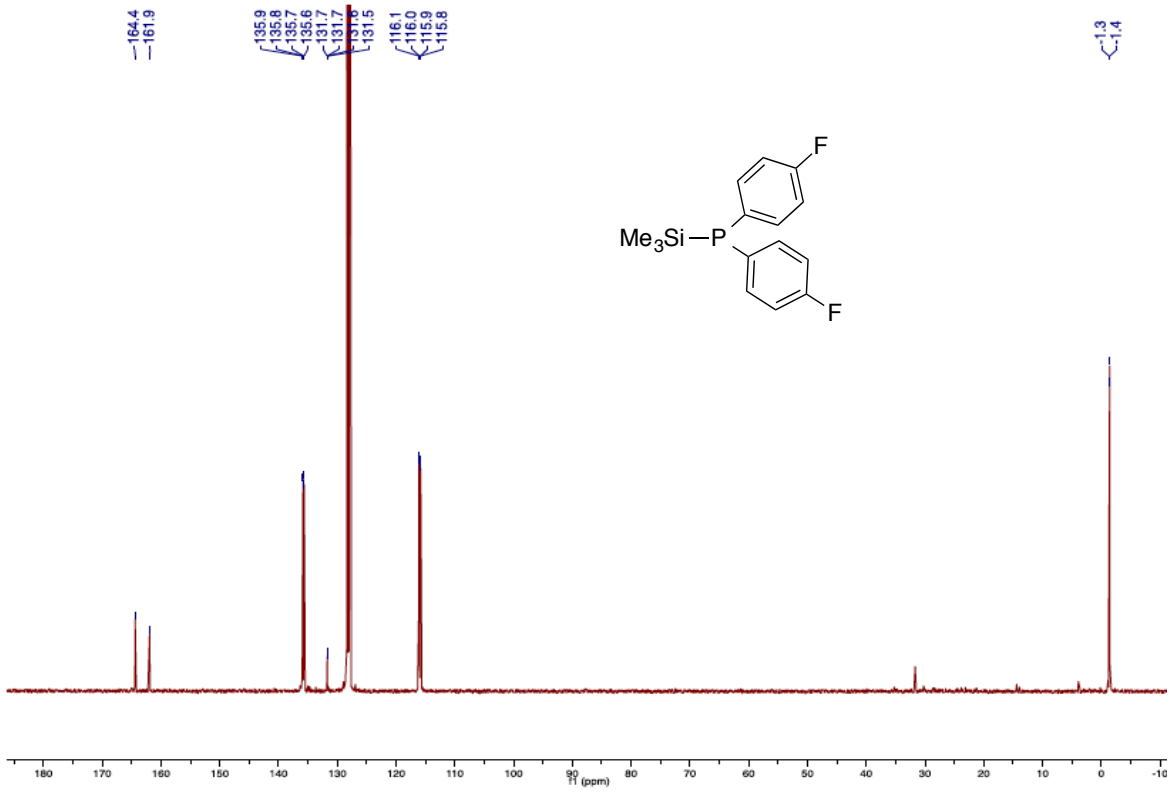


Figure S11. ^{13}C NMR (100 MHz, C_6D_6) of **5b**

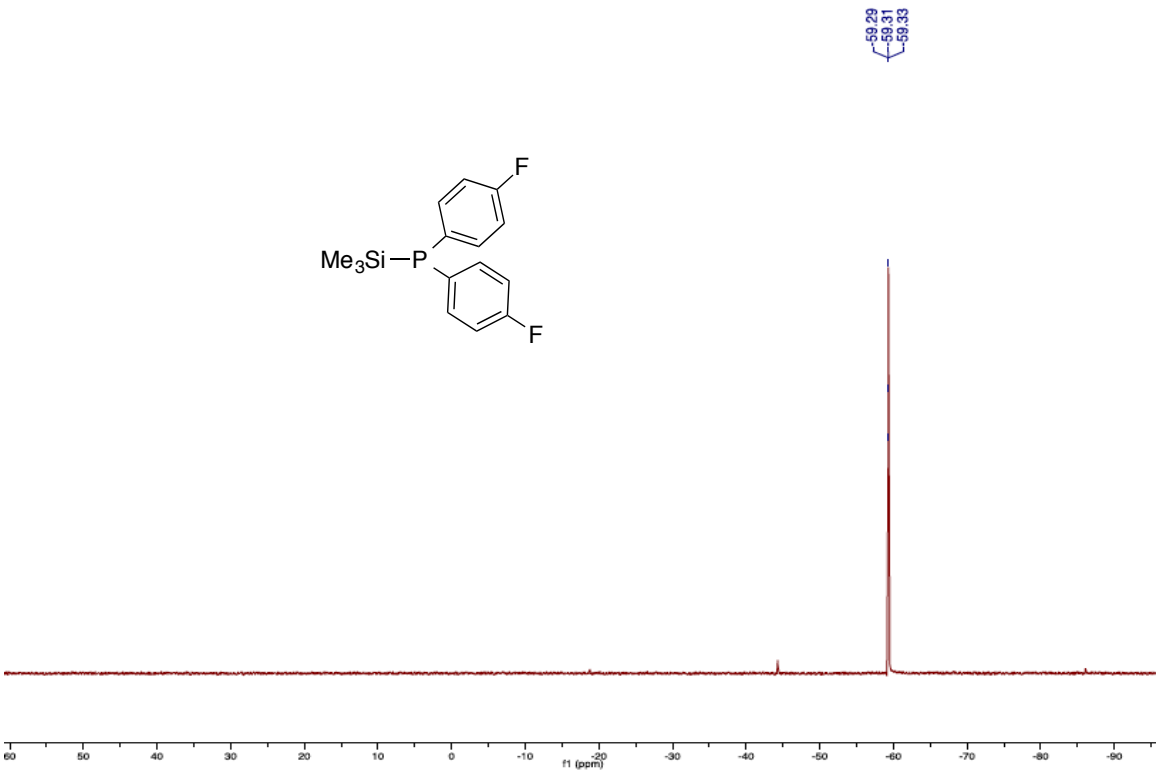


Figure S12. ^{31}P NMR (161 MHz, C_6D_6) of **5b**

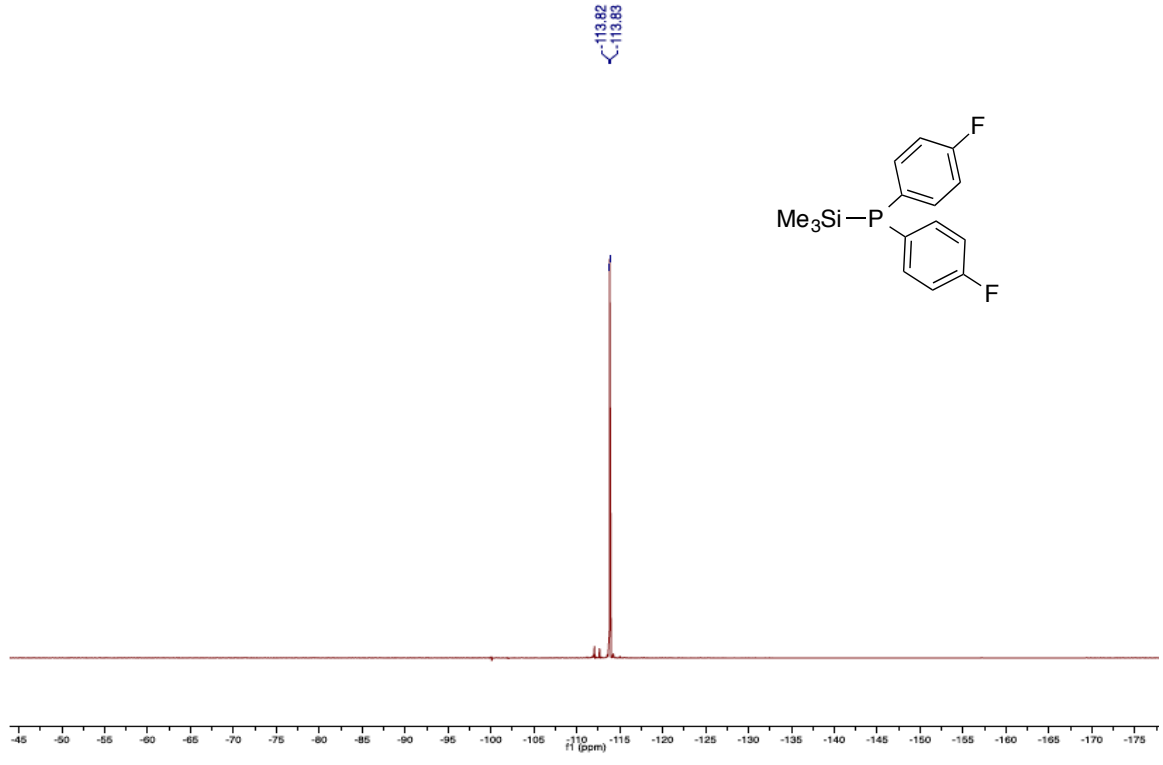


Figure S13. ^{19}F NMR (377 MHz, C_6D_6) of **5b**

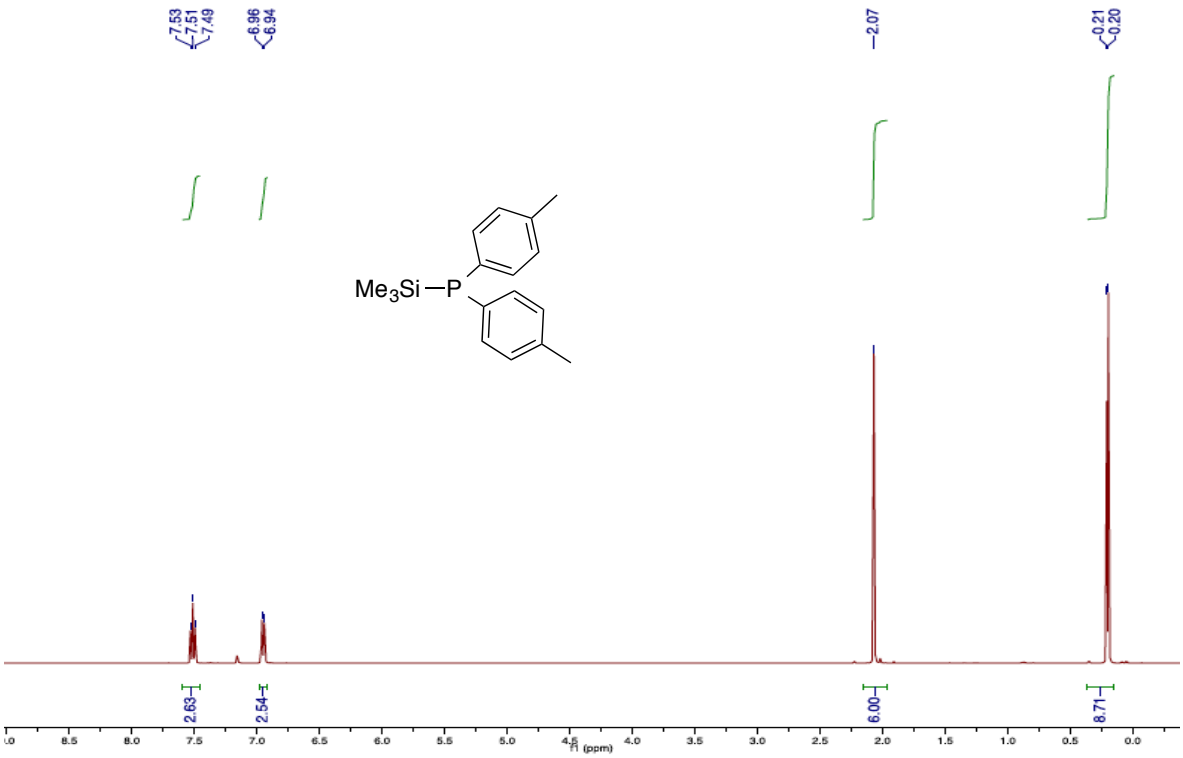


Figure S14. ^{1}H NMR (400 MHz, C_6D_6) of **5c**

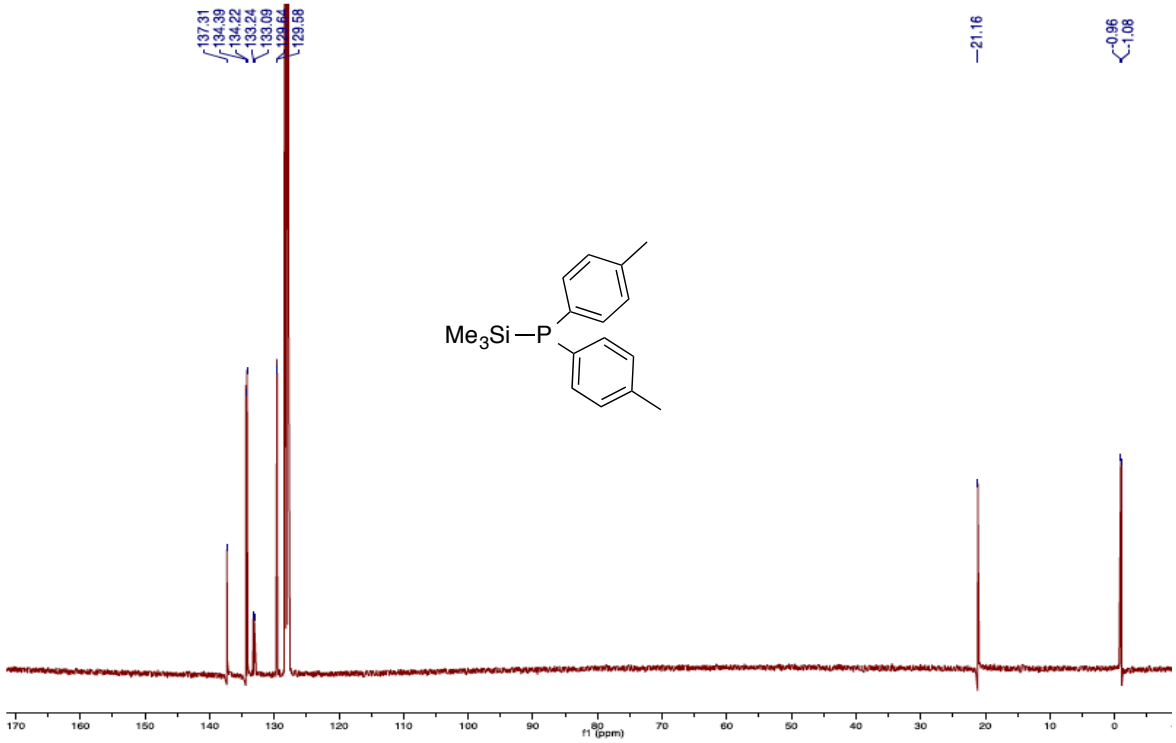


Figure S15. ^{13}C NMR (100 MHz, C_6D_6) of **5c**

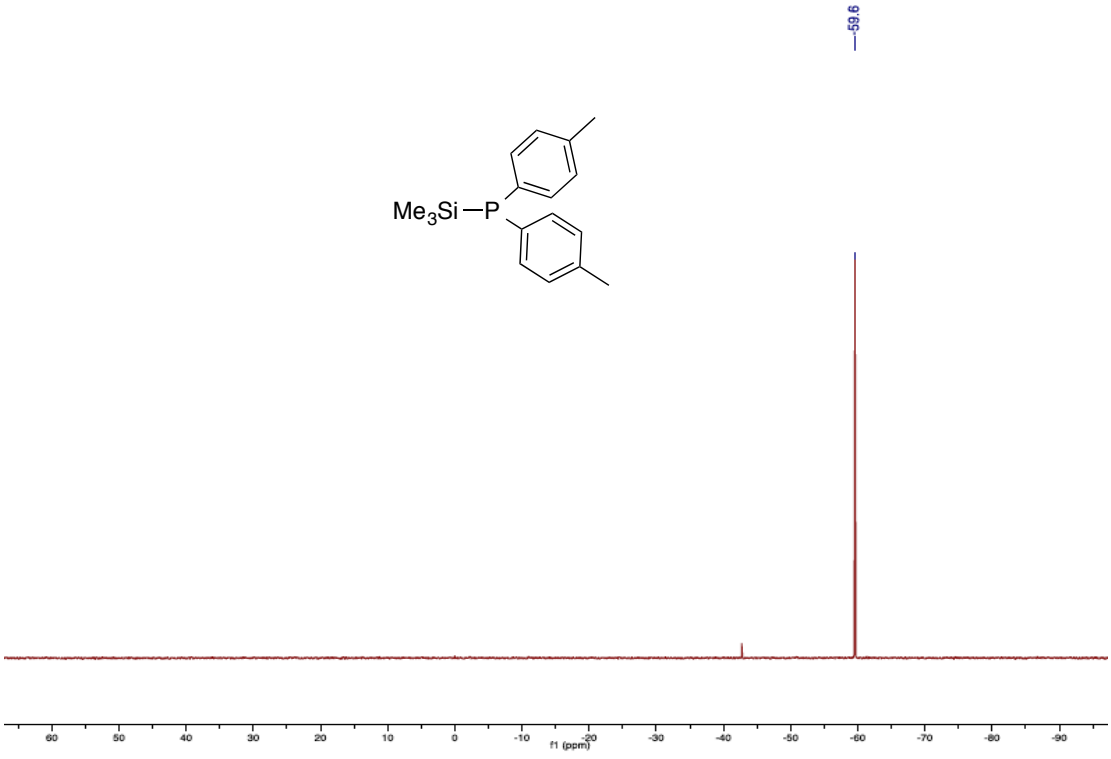


Figure S16. ^{31}P NMR (161 MHz, C_6D_6) of **5c**

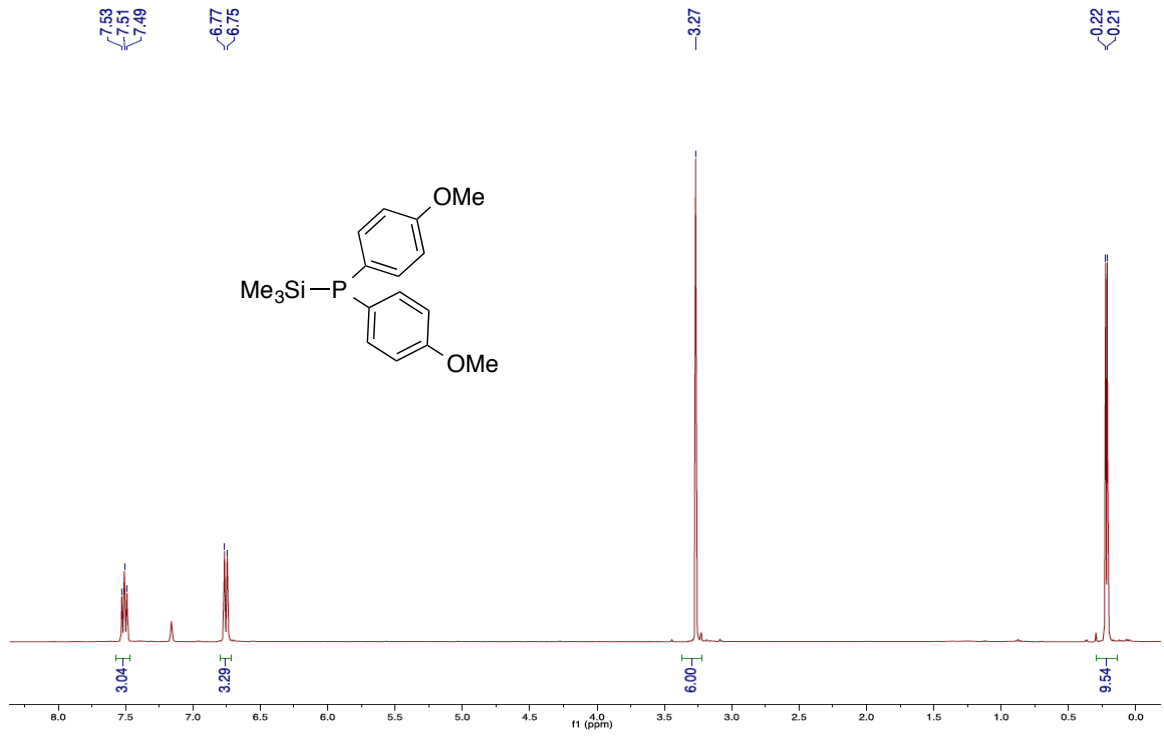


Figure S17. ^{1}H NMR (400 MHz, C_6D_6) of **5d**

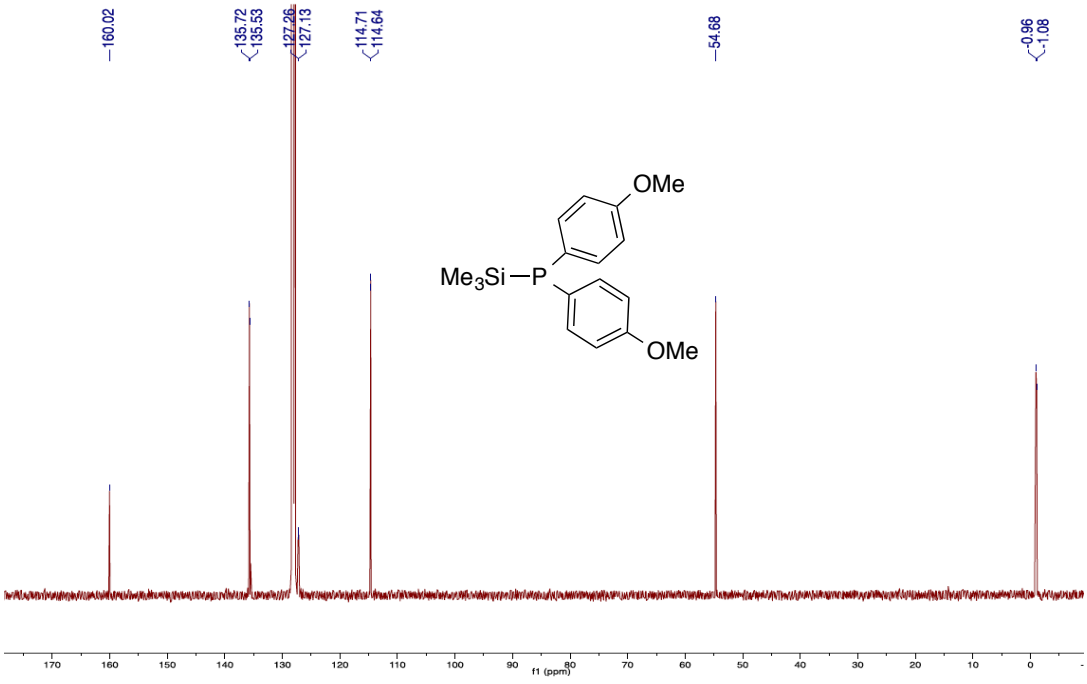


Figure S18. ^{13}C NMR (100 MHz, C_6D_6) of **5d**

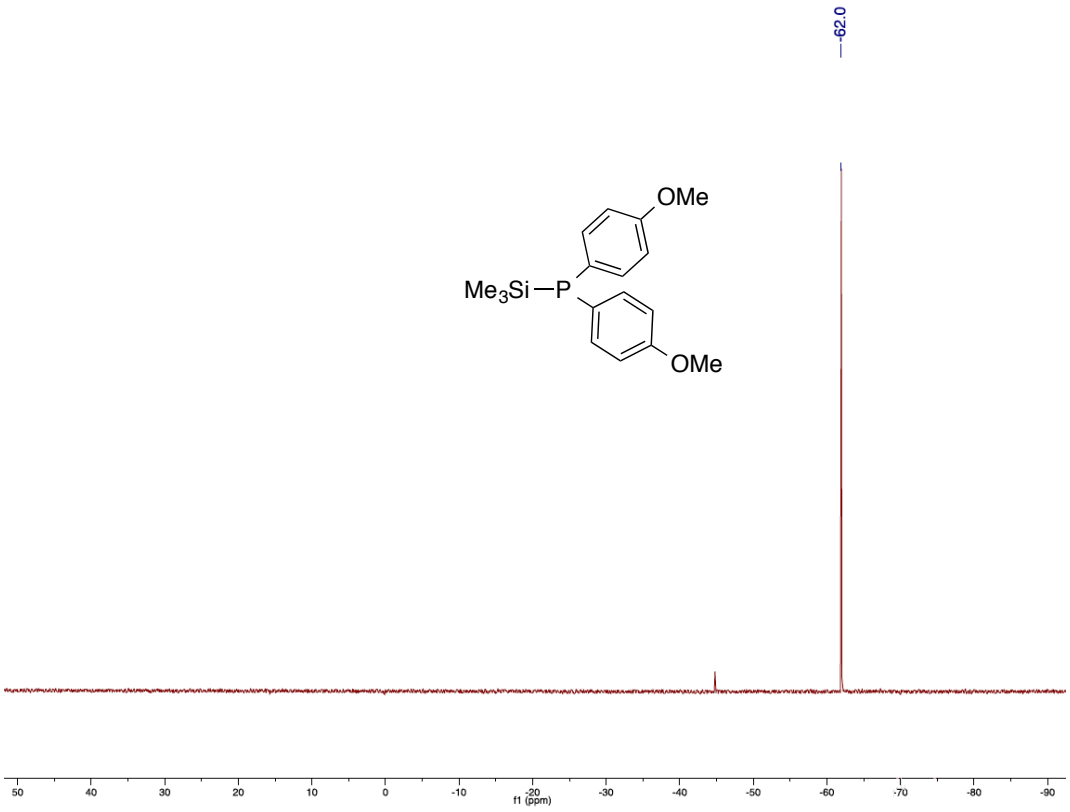


Figure S19. ^{31}P NMR (161 MHz, C_6D_6) of **5d**

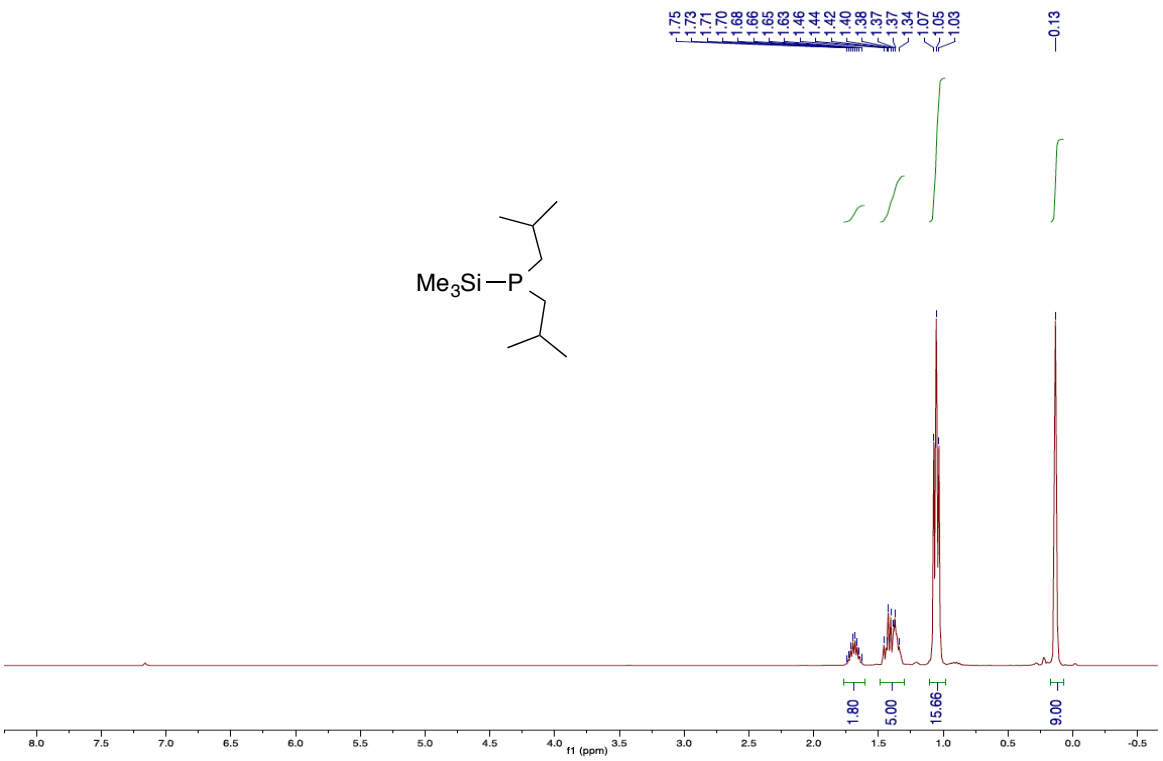


Figure S20. ^{1}H NMR (400 MHz, C_6D_6) of **5e**

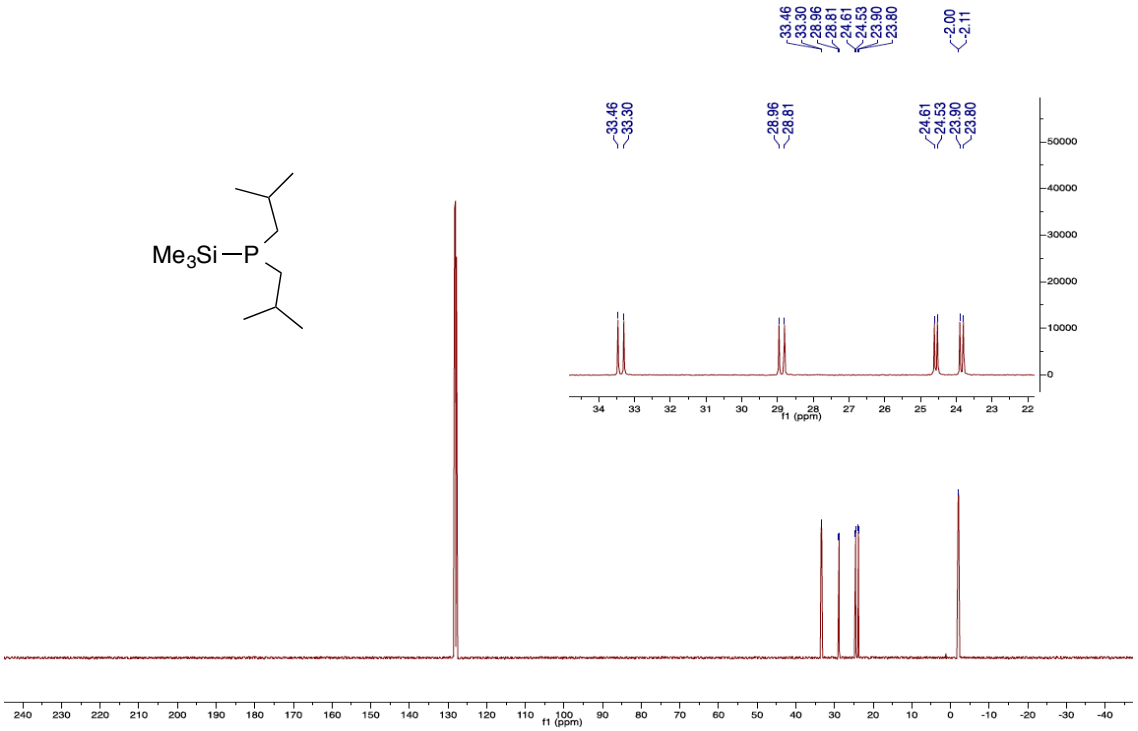


Figure S21. ^{13}C NMR (100 MHz, C_6D_6) of **5e**

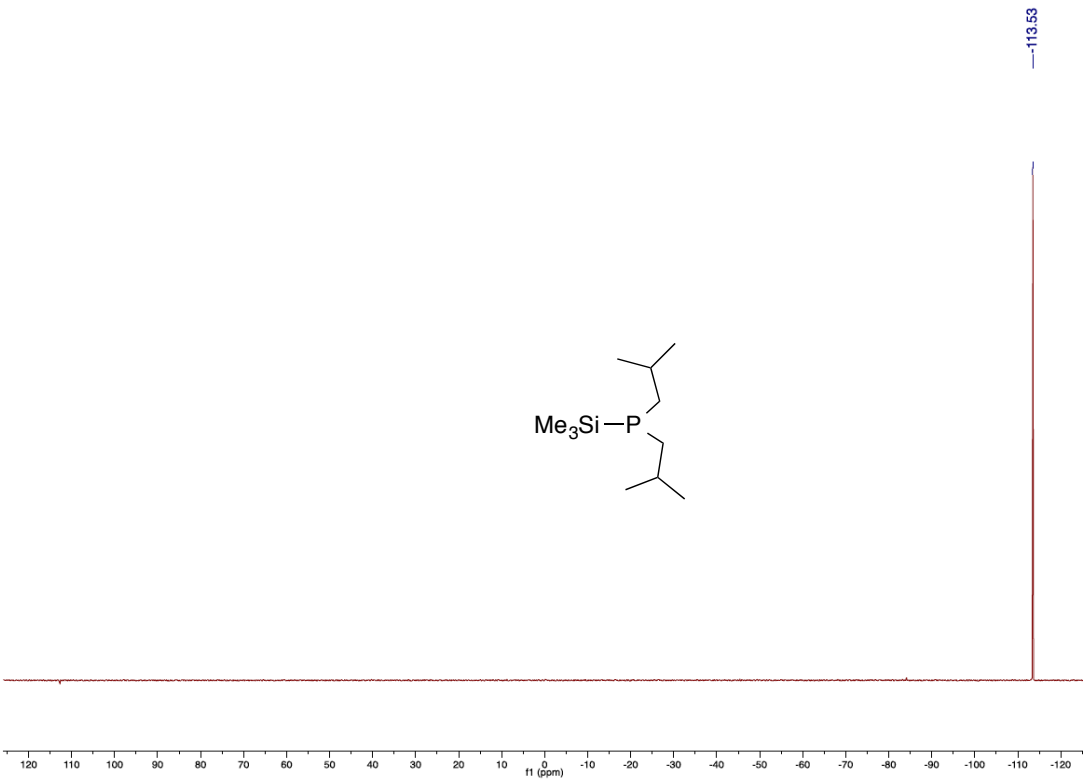


Figure S22. ^{31}P NMR (161 MHz, C_6D_6) of **5e**

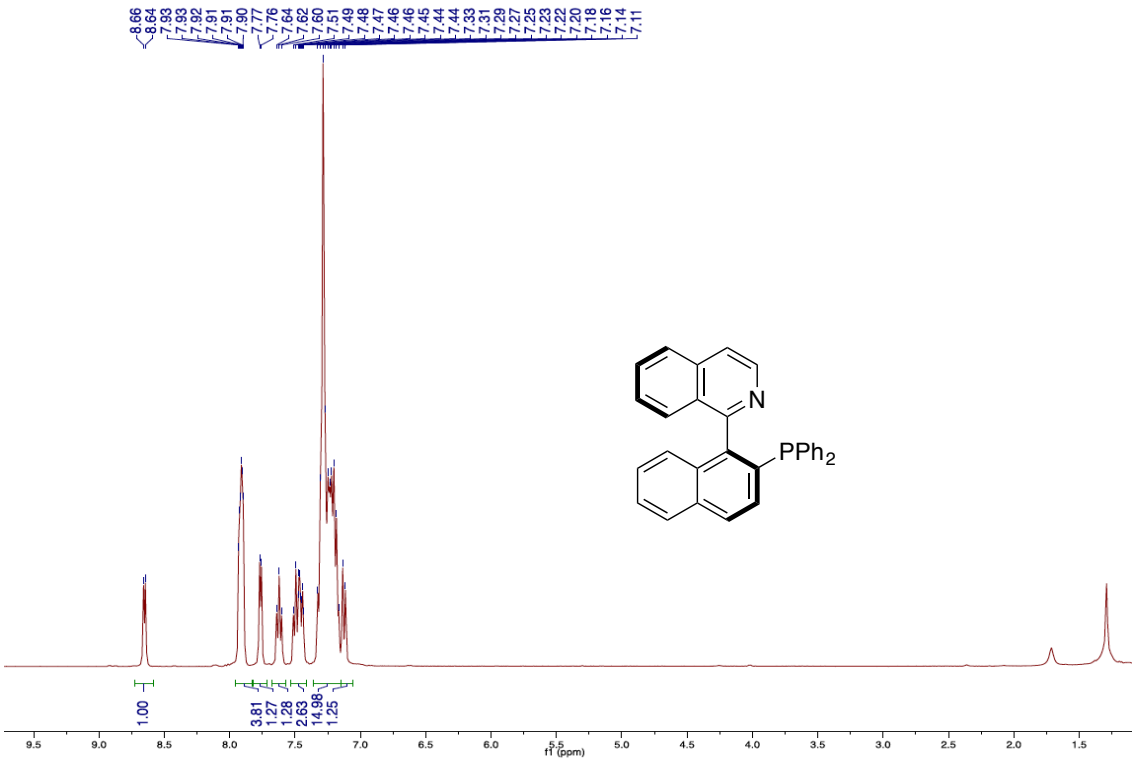


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Aa**

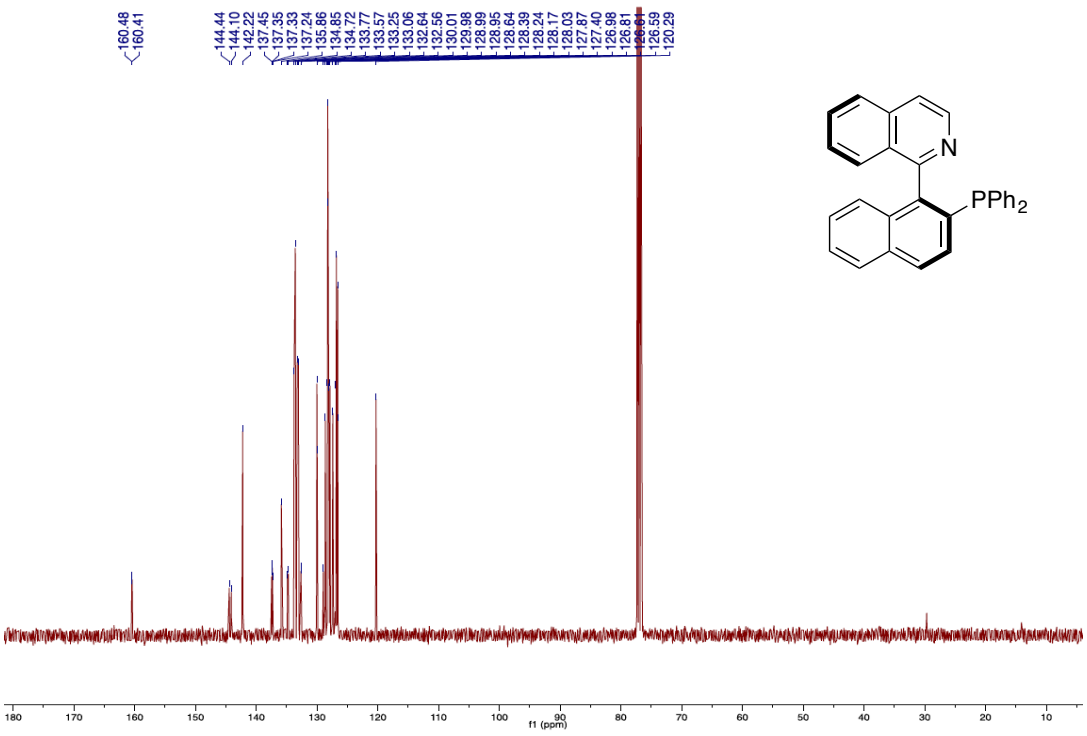


Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Aa**

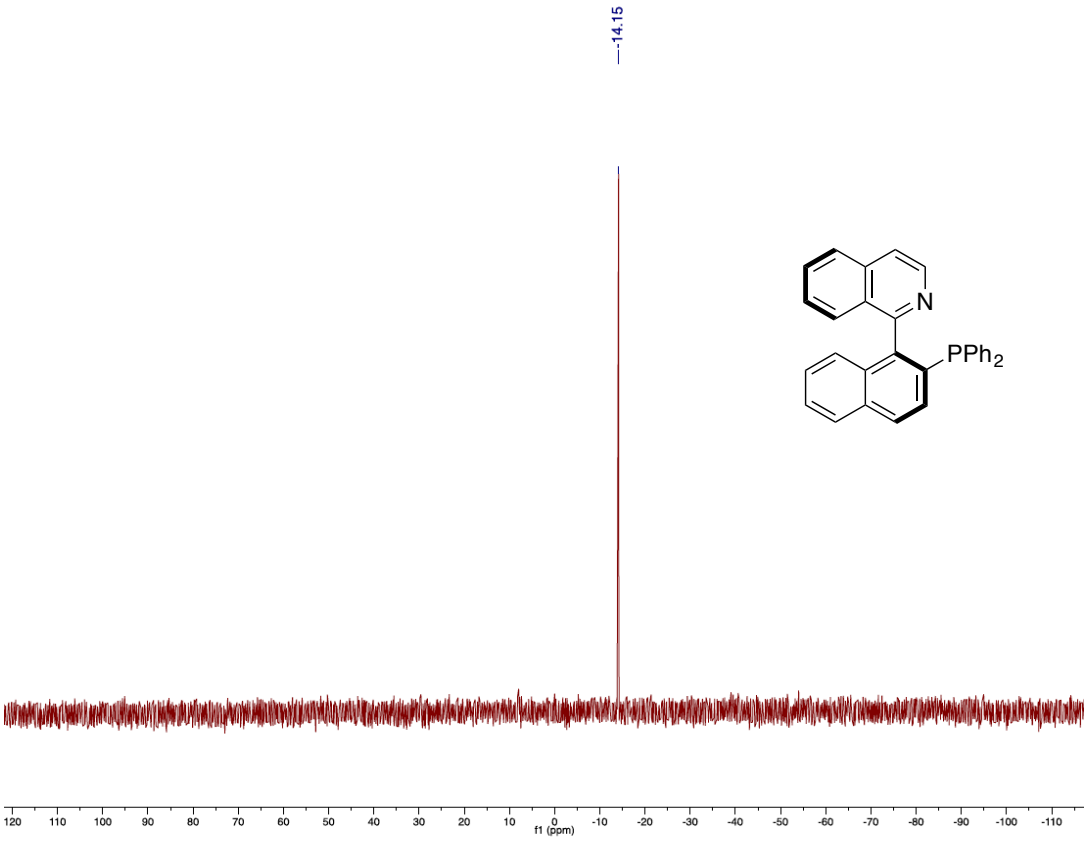
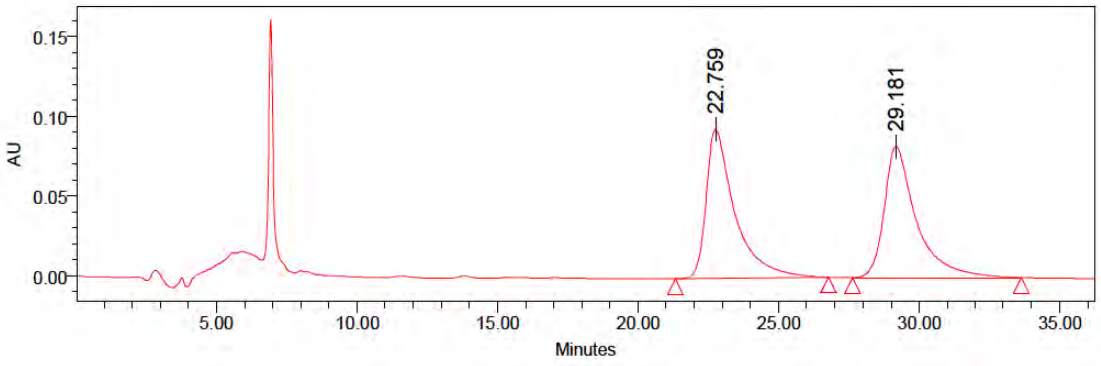
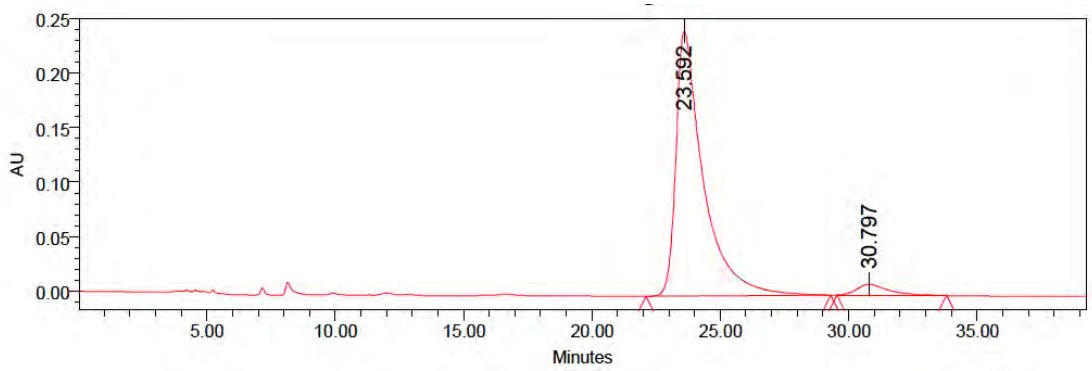


Figure S25. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Aa**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 228.5 nm	22.759	6609456	50.29	93386
2	PDA 228.5 nm	29.181	6532200	49.71	82031

Figure S26. Phosphine oxide racemic sample: IA column, Hex:Isop 85:15, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 228.5 nm	23.592	17977575	95.53	242809
2	PDA 228.5 nm	30.797	840444	4.47	10000

Figure S27. Phosphine oxide enantioriched sample: er 95.5:4.5.

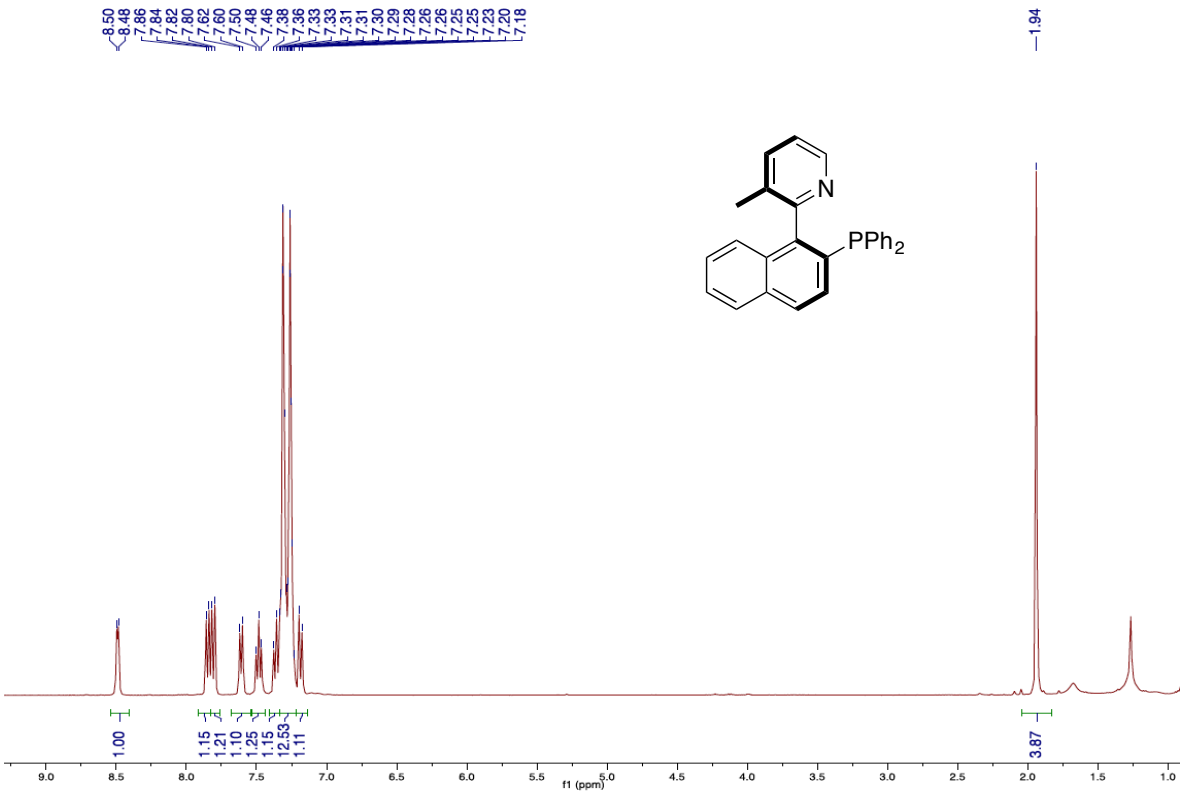


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of ***(S)*-3Ba**

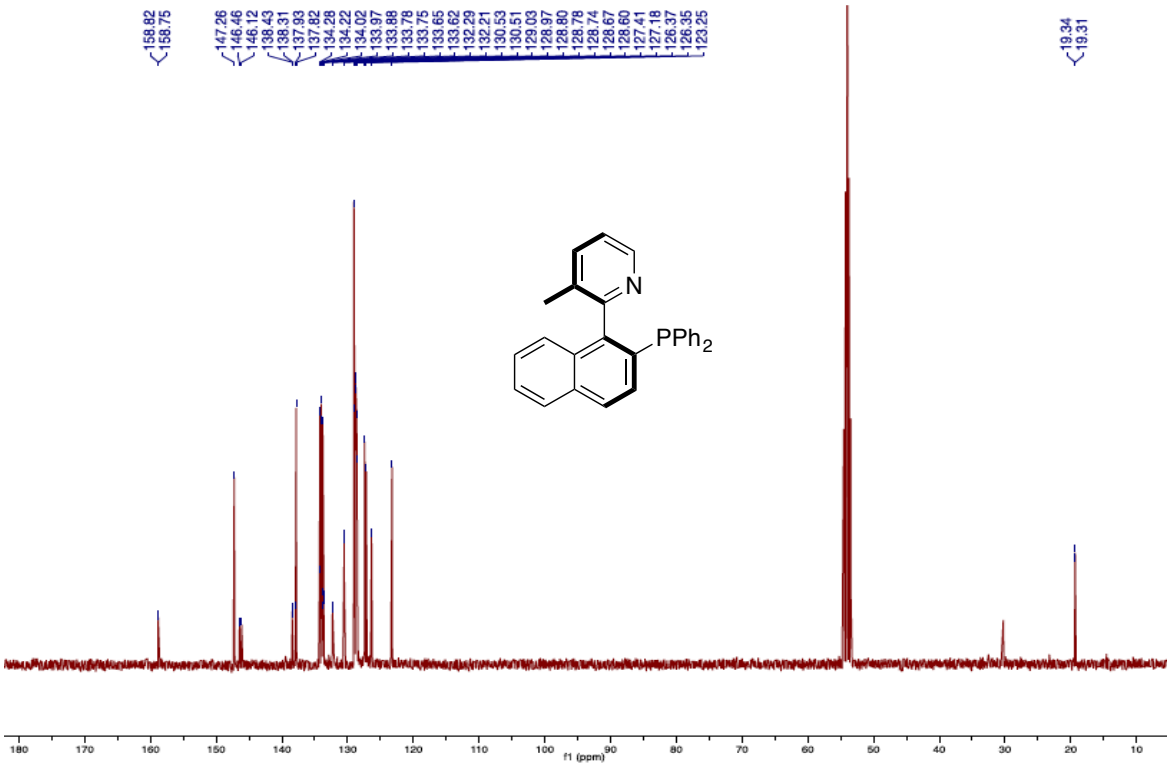


Figure S29. ^{13}C NMR (100 MHz, CD_2Cl_2) of ***(S)*-3Ba**

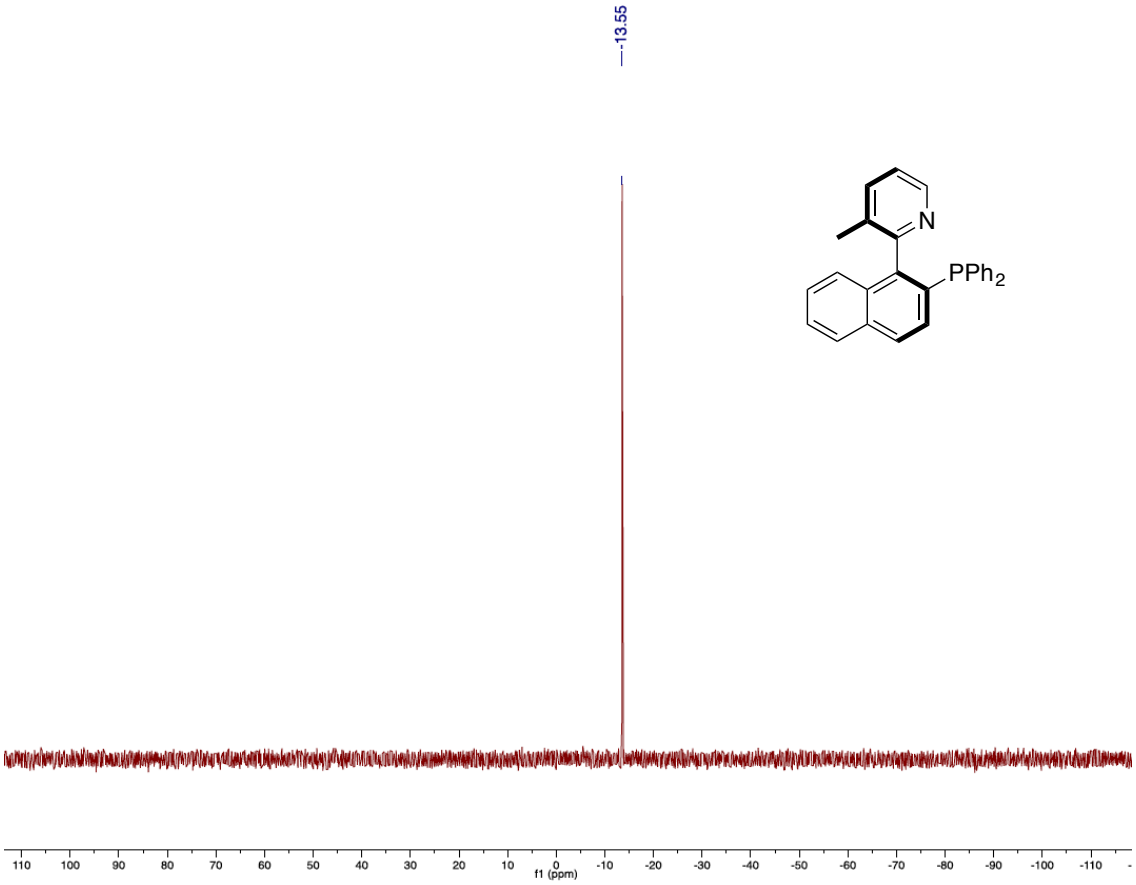
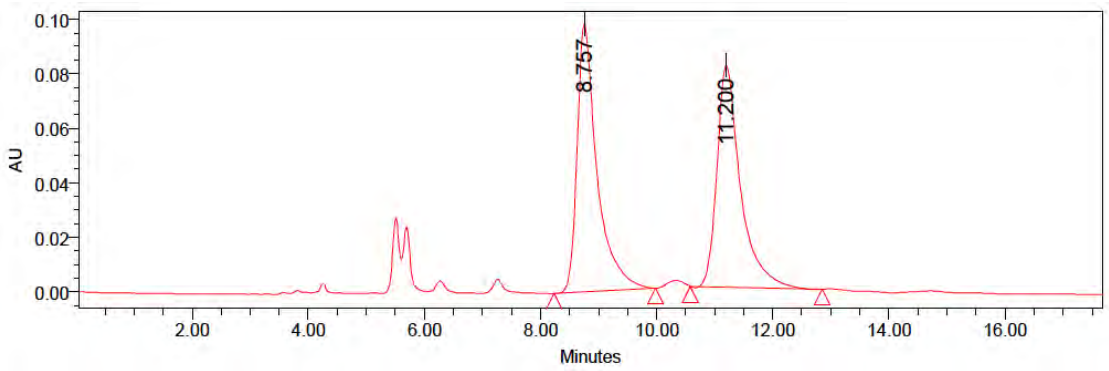
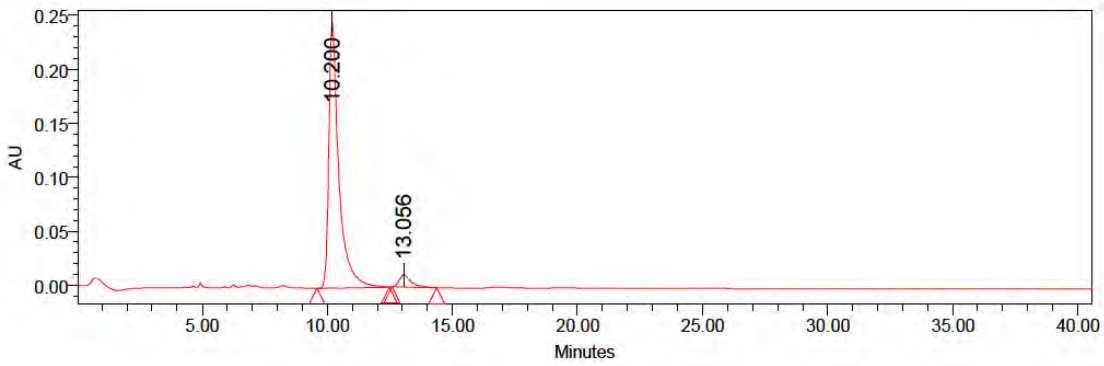


Figure S30. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ba**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.6 nm	8.757	2352809	50.63	98419
2	PDA 235.6 nm	11.200	2294466	49.37	81592

Figure S31. Phosphine oxide racemic sample: IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.6 nm	10.200	6844888	95.00	245129
2	PDA 235.6 nm	13.056	360609	5.00	11078

Figure S32. Phosphine oxide enantioriched sample: er 95:5.

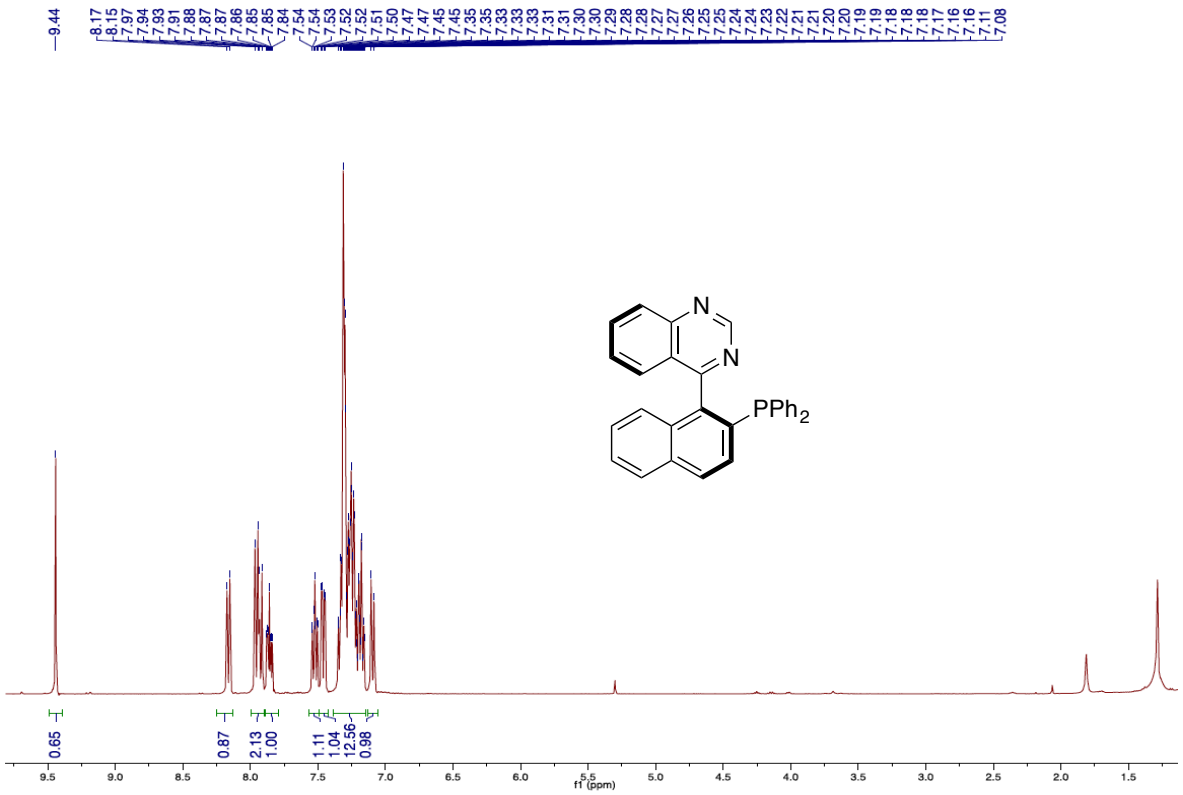


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Ca**

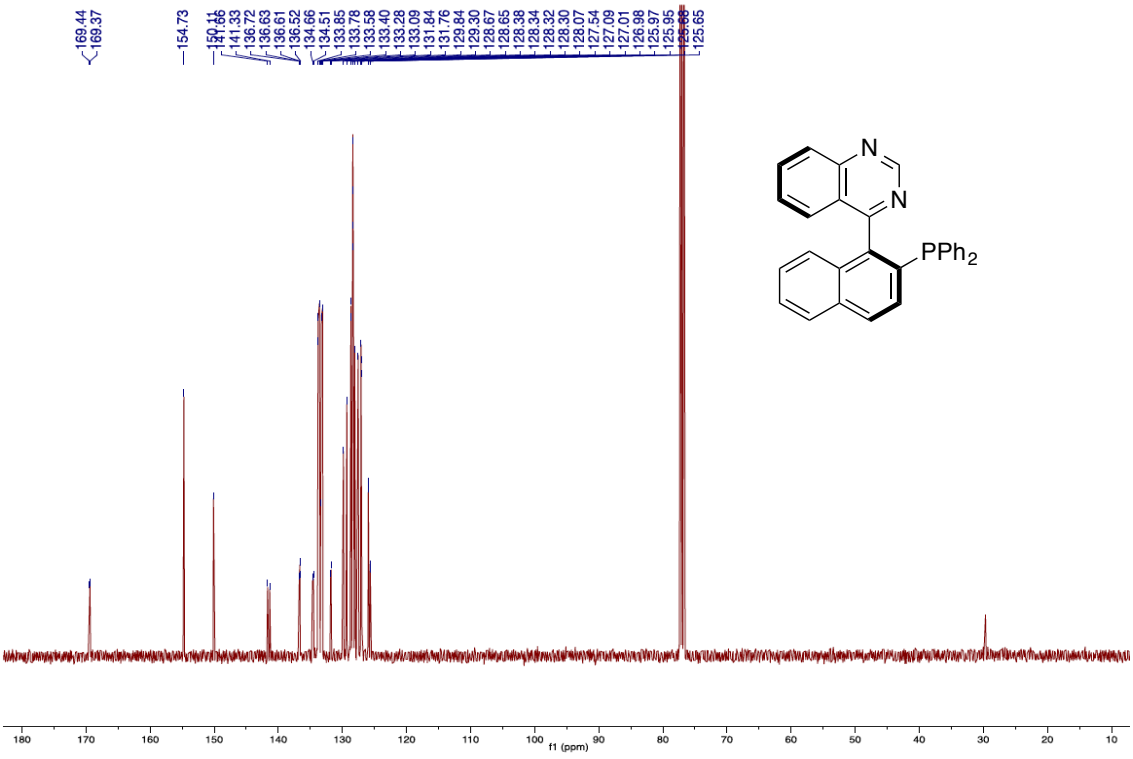


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Ca**

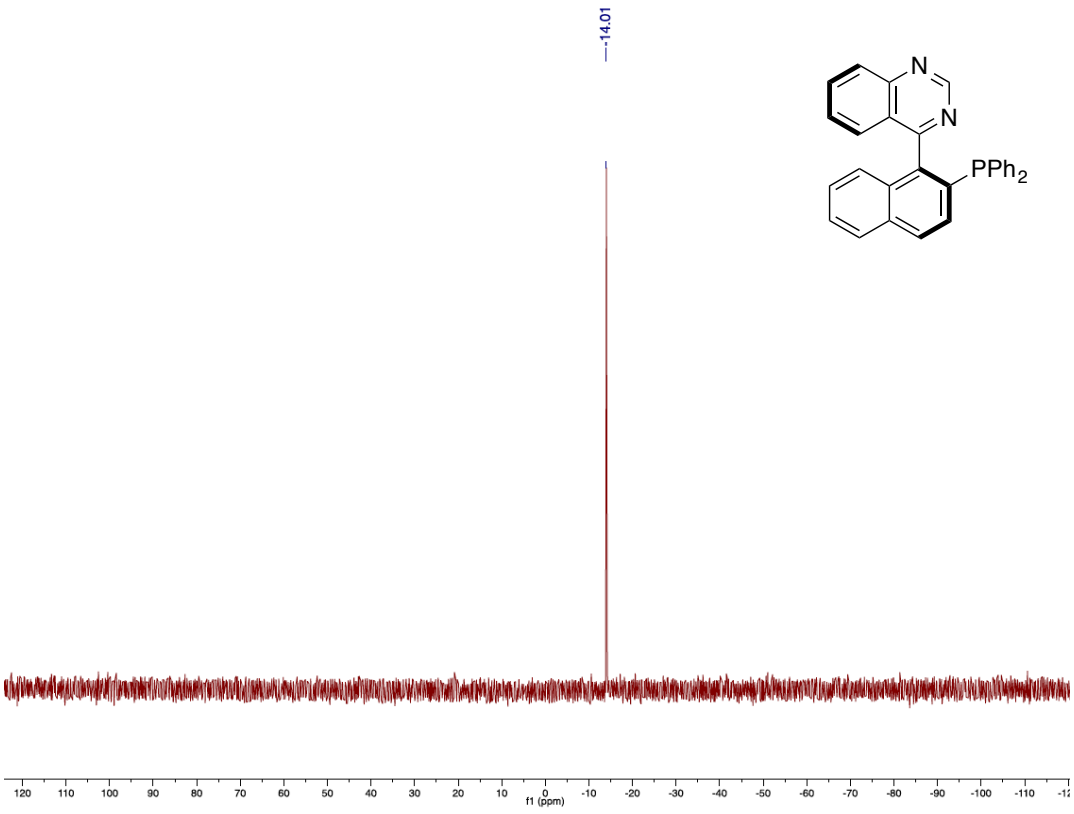
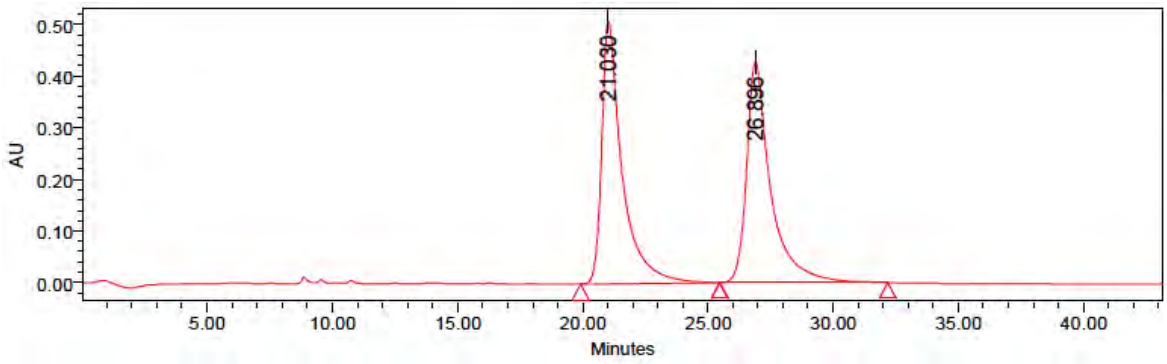
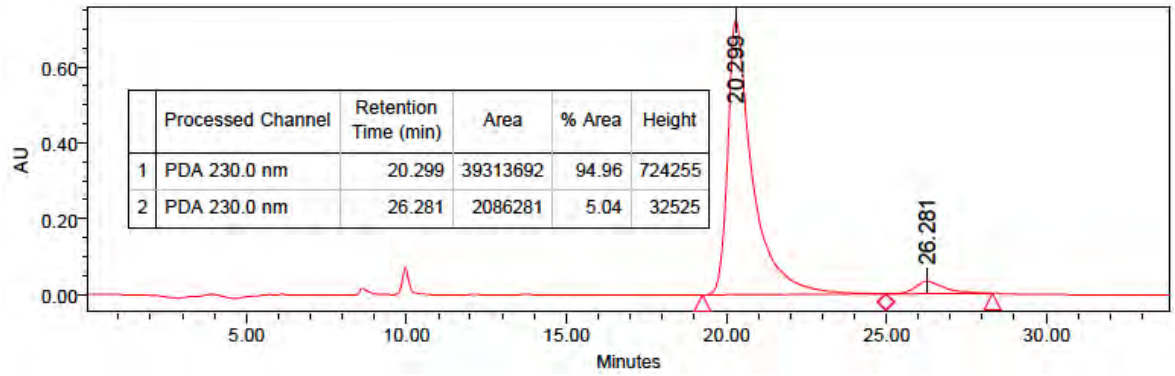


Figure S35. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ca**



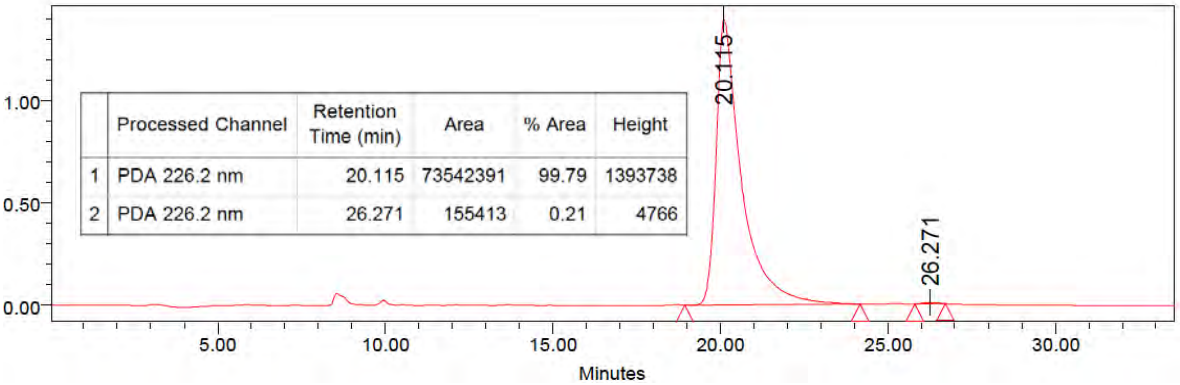
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	21.030	28698078	50.22	507467
2	PDA 230.0 nm	26.896	28444144	49.78	426593

Figure S36. Phosphine oxide racemic sample: IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	20.299	39313692	94.96	724255
2	PDA 230.0 nm	26.281	2086281	5.04	32525

Figure S37. Phosphine oxide enantioriched sample: er 95:5.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 226.2 nm	20.115	73542391	99.79	1393738
2	PDA 226.2 nm	26.271	155413	0.21	4766

Figure S38. After washing with acetone, er >99:1.

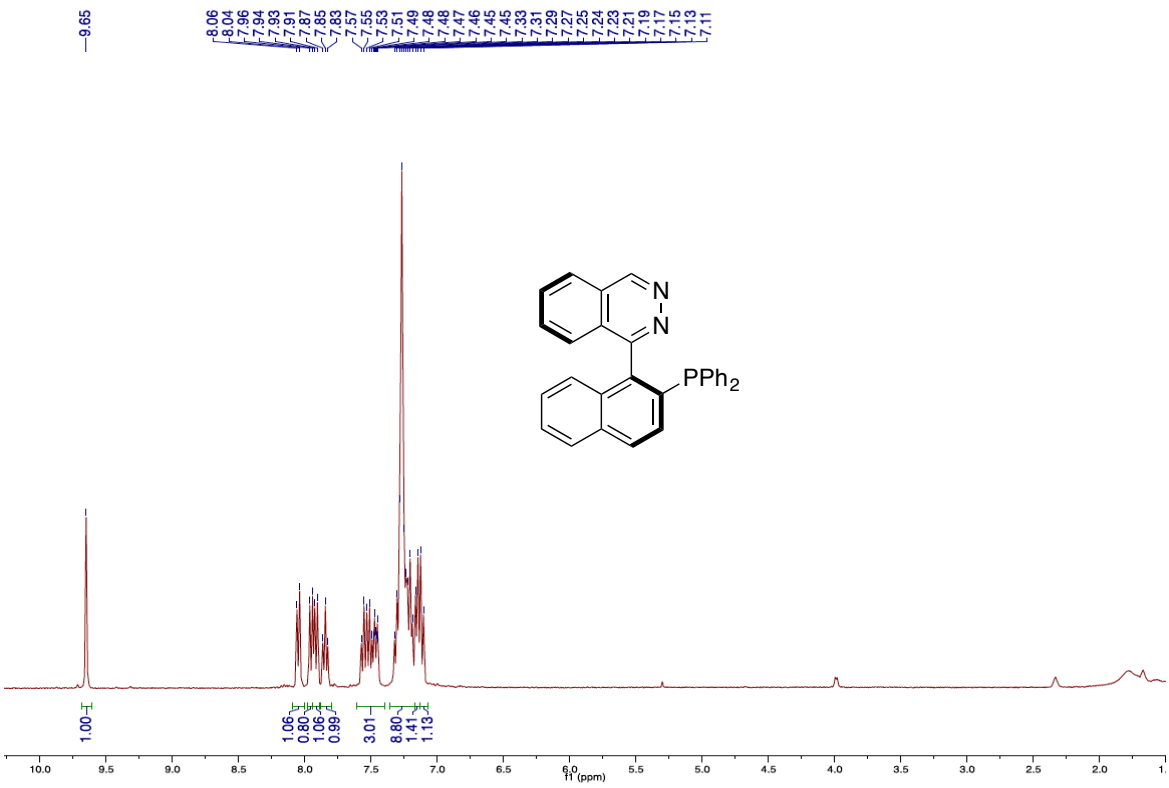


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Da**

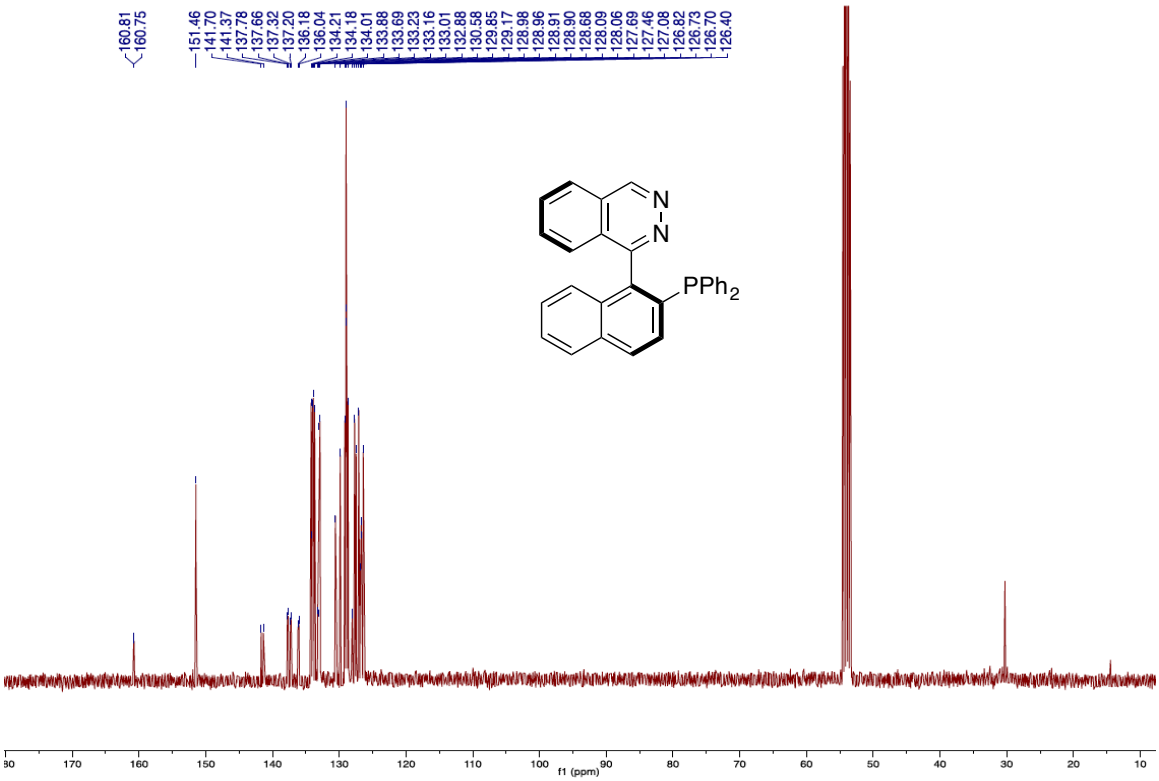


Figure S40. ^{13}C NMR (100 MHz, CD_2Cl_2) of **(*S*)-3Da**

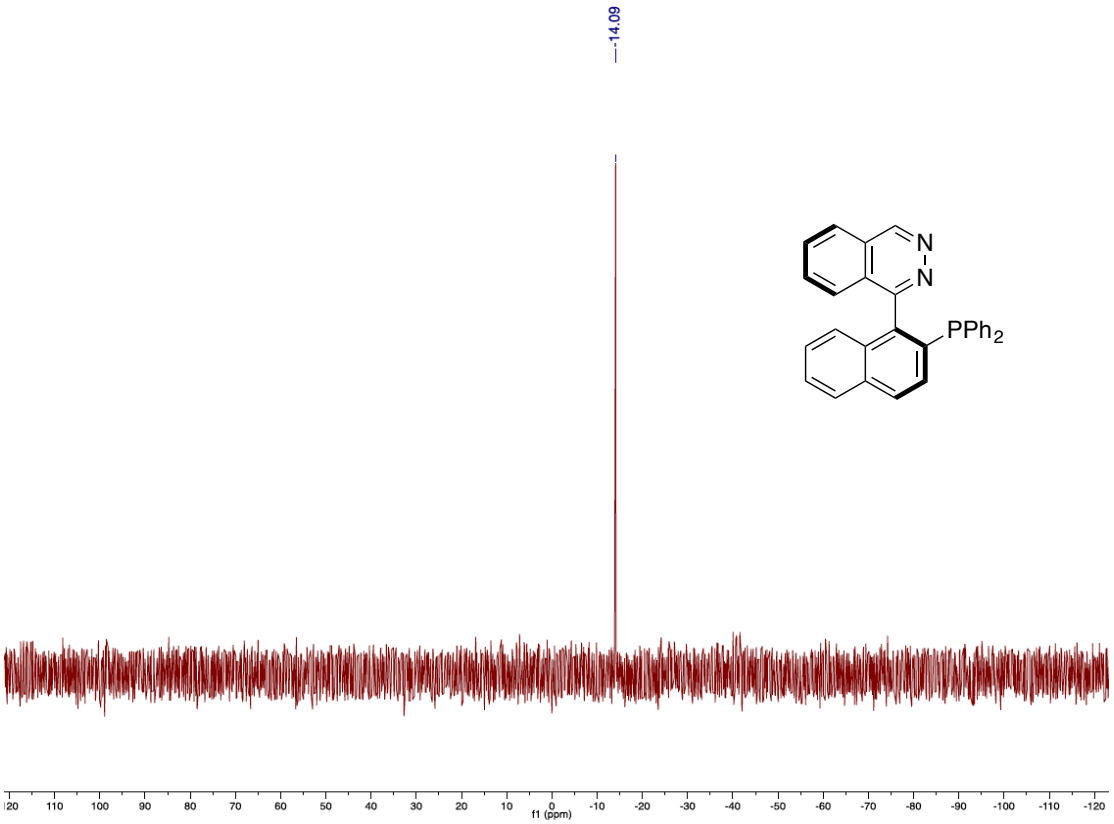
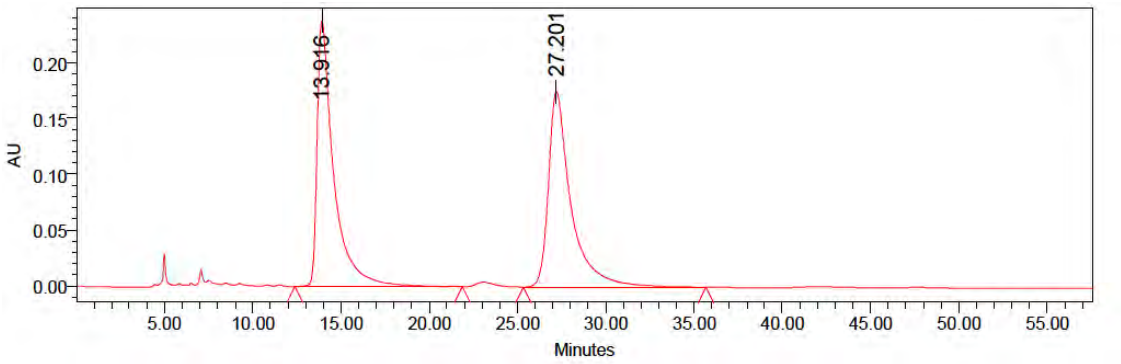
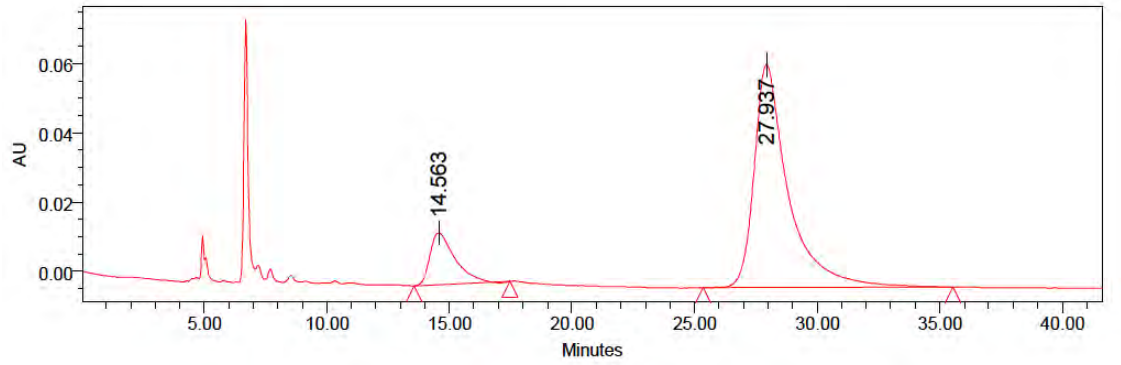


Figure S41. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Da**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	13.916	15512012	49.95	237559
2	PDA 229.7 nm	27.201	15542469	50.05	174951

Figure S42. Phosphine oxide racemic sample: IA column, Hex:Isop 50:50, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	14.563	1060759	14.52	14936
2	PDA 229.7 nm	27.937	6244818	85.48	64318

Figure S43. Phosphine oxide enantioriched sample: er 14.5:85.5.

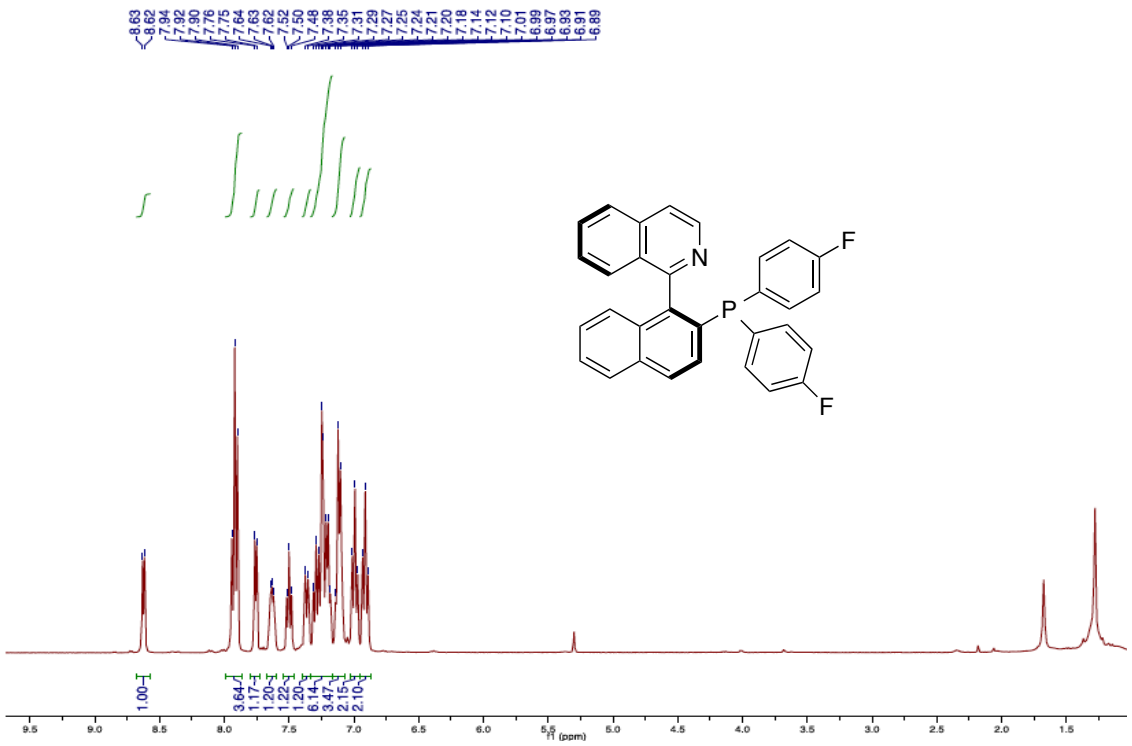


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Ab**

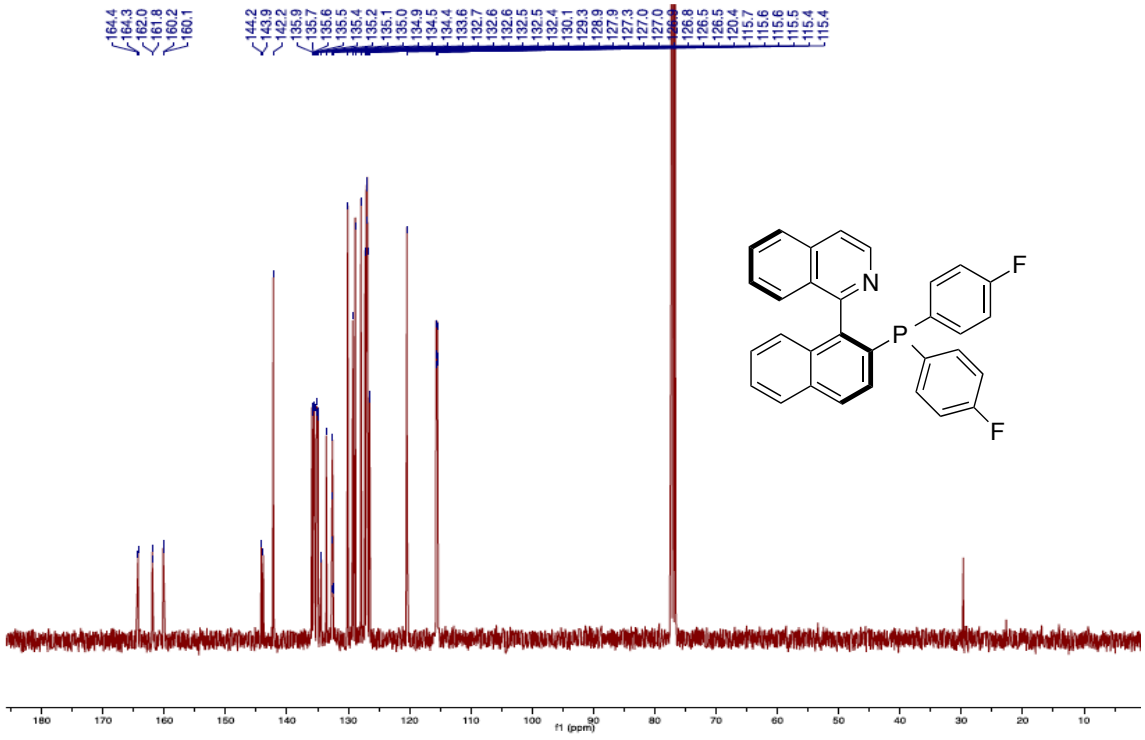


Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Ab**

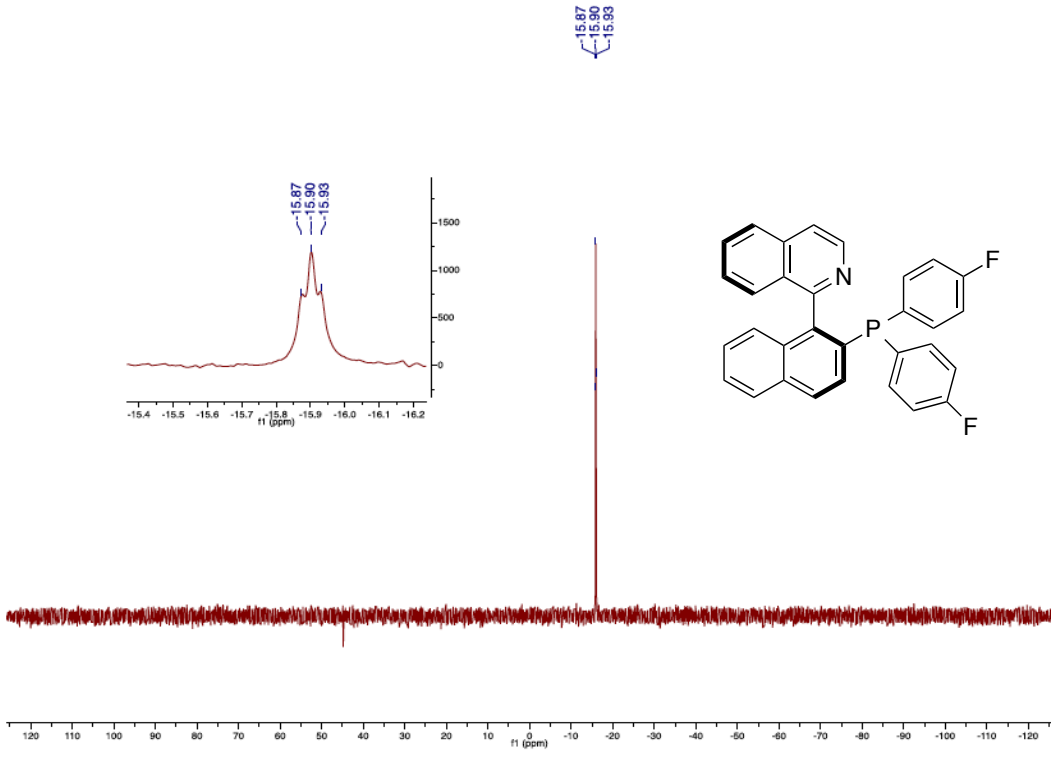


Figure S46. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ab**

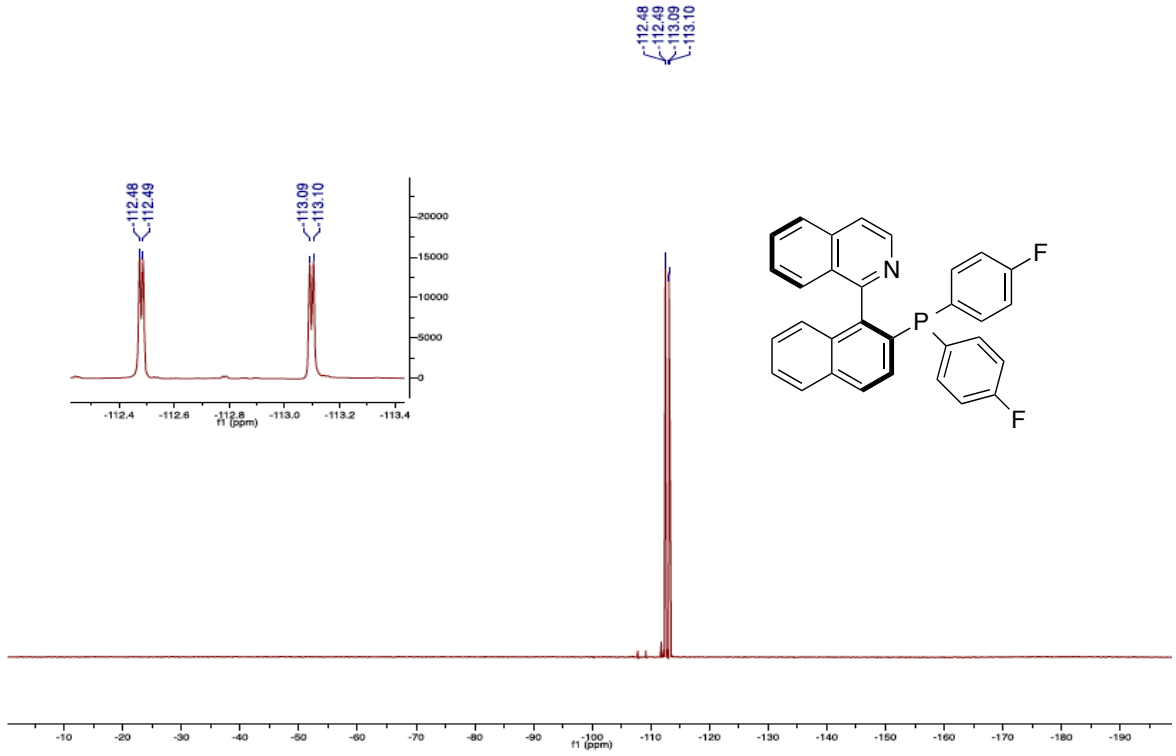
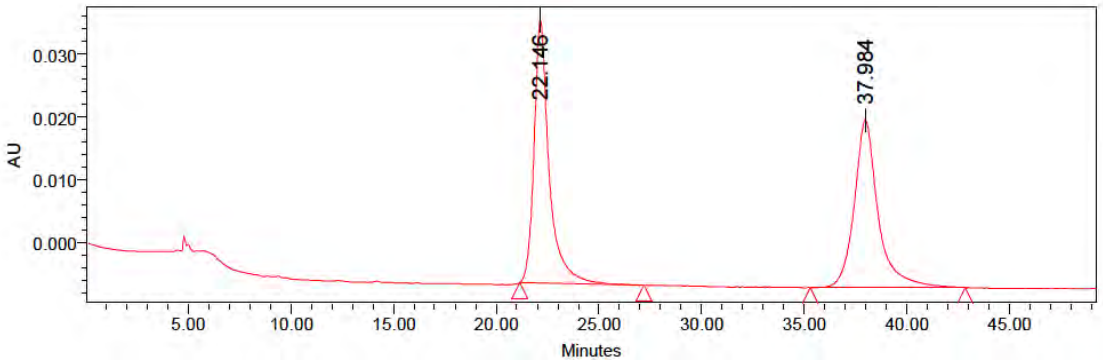
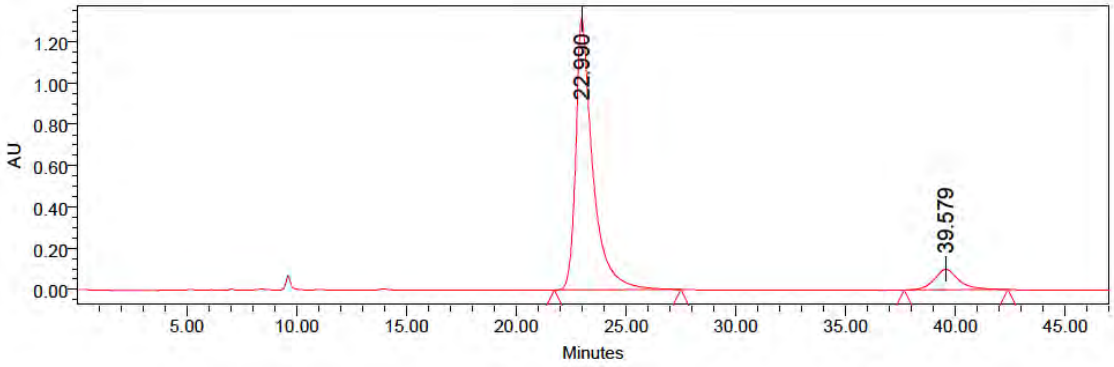


Figure S47. ^{19}F NMR (377 MHz, $CDCl_3$) of **(*S*)-3Ab**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 221.5 nm	22.146	2143439	49.71	41856
2	PDA 221.5 nm	37.984	2168742	50.29	26631

Figure S48. Phosphine oxide racemic sample: IA column, Hex:Isop 85:15, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 221.5 nm	22.990	70857057	90.07	1313590
2	PDA 221.5 nm	39.579	7811885	9.93	99783

Figure S49. Phosphine oxide enantioriched sample: er 90:10.

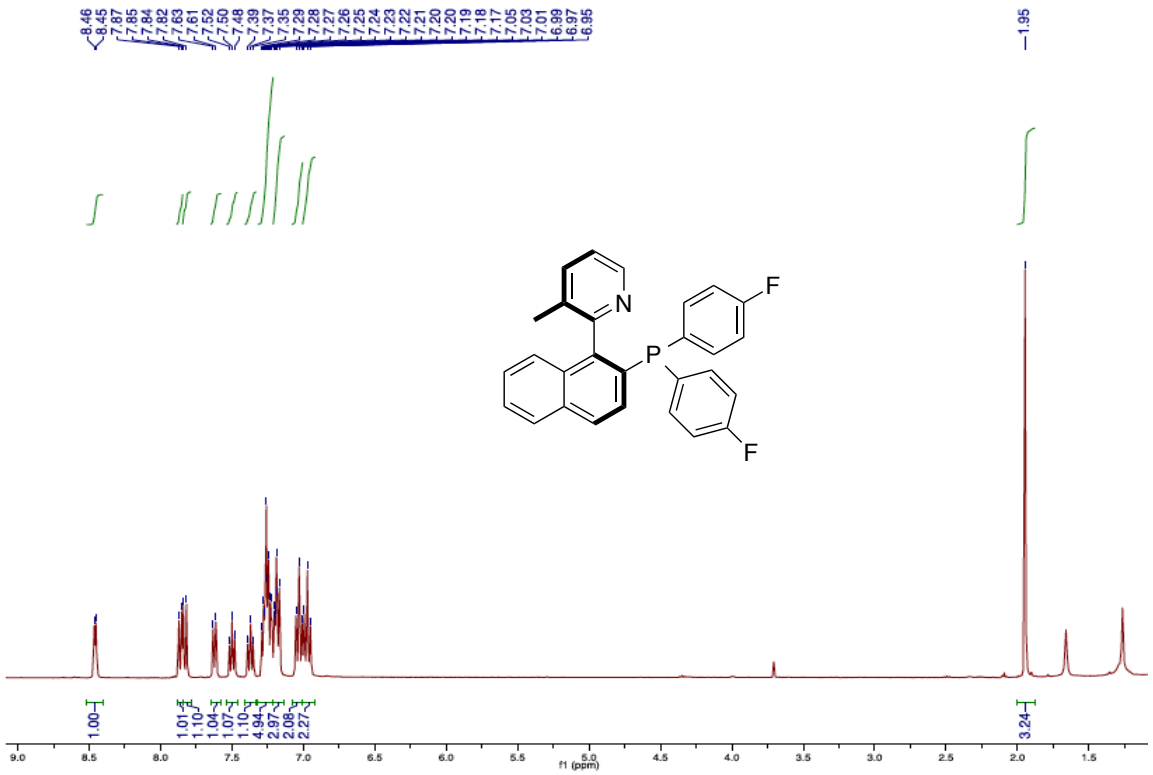


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Bb**

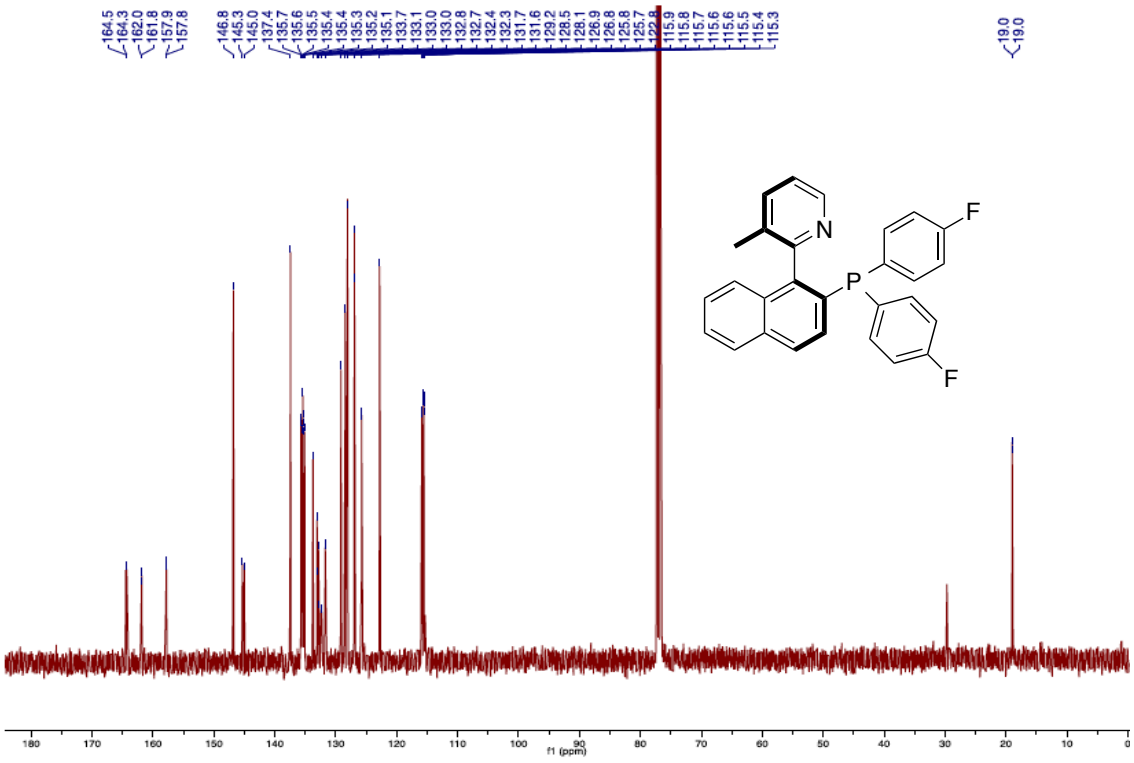


Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Bb**

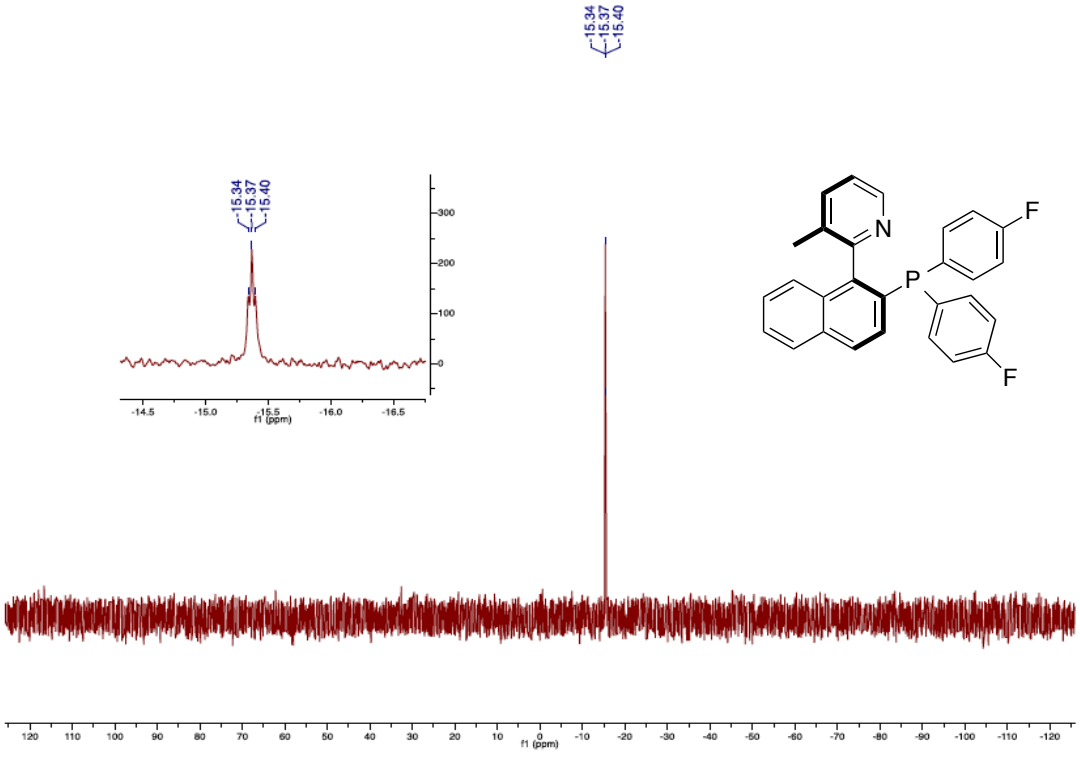


Figure S52. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Bb**

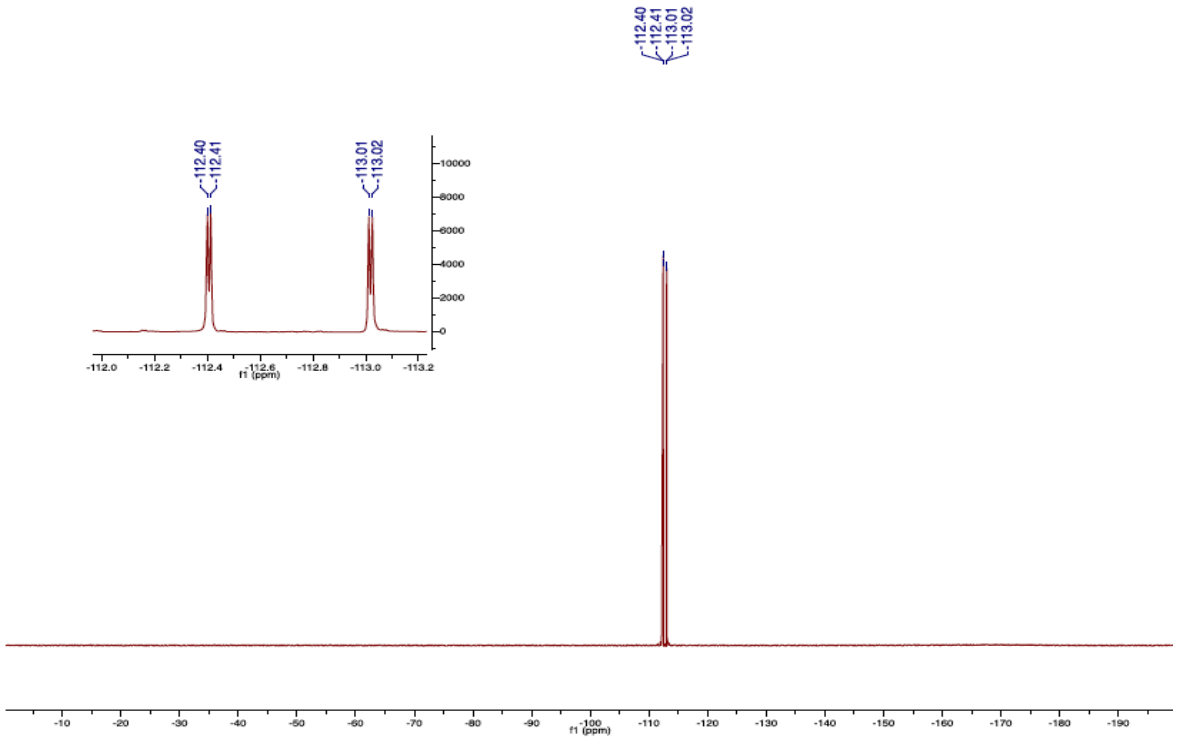
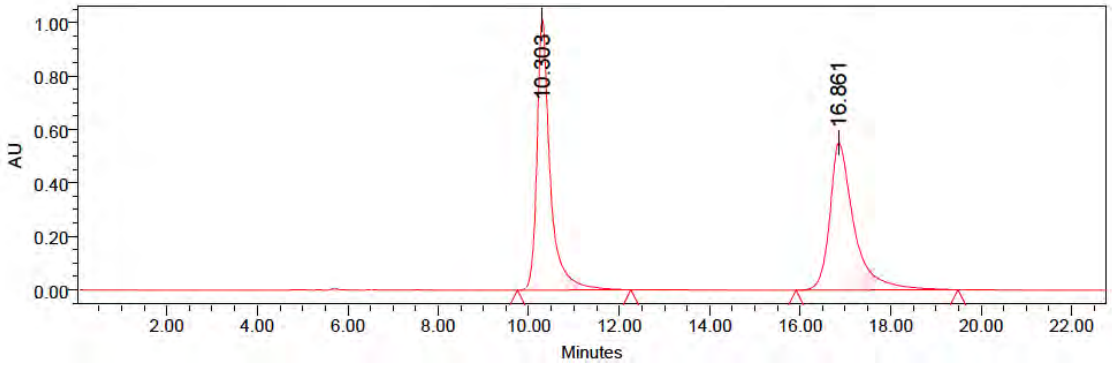
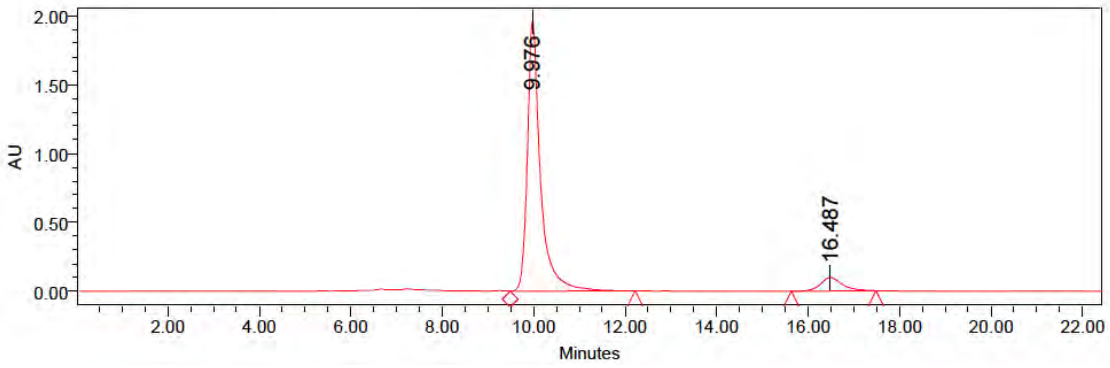


Figure S53. ^{19}F NMR (377 MHz, $CDCl_3$) of **(*S*)-3Bb**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	10.303	20435412	50.06	1013596
2	PDA 236.0 nm	16.861	20383602	49.94	550335

Figure S54. Phosphine oxide racemic sample: IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	9.976	38904508	92.57	1960137
2	PDA 236.0 nm	16.487	3124873	7.43	96937

Figure S55. Phosphine oxide enantioriched sample: er 92.5:7.5.

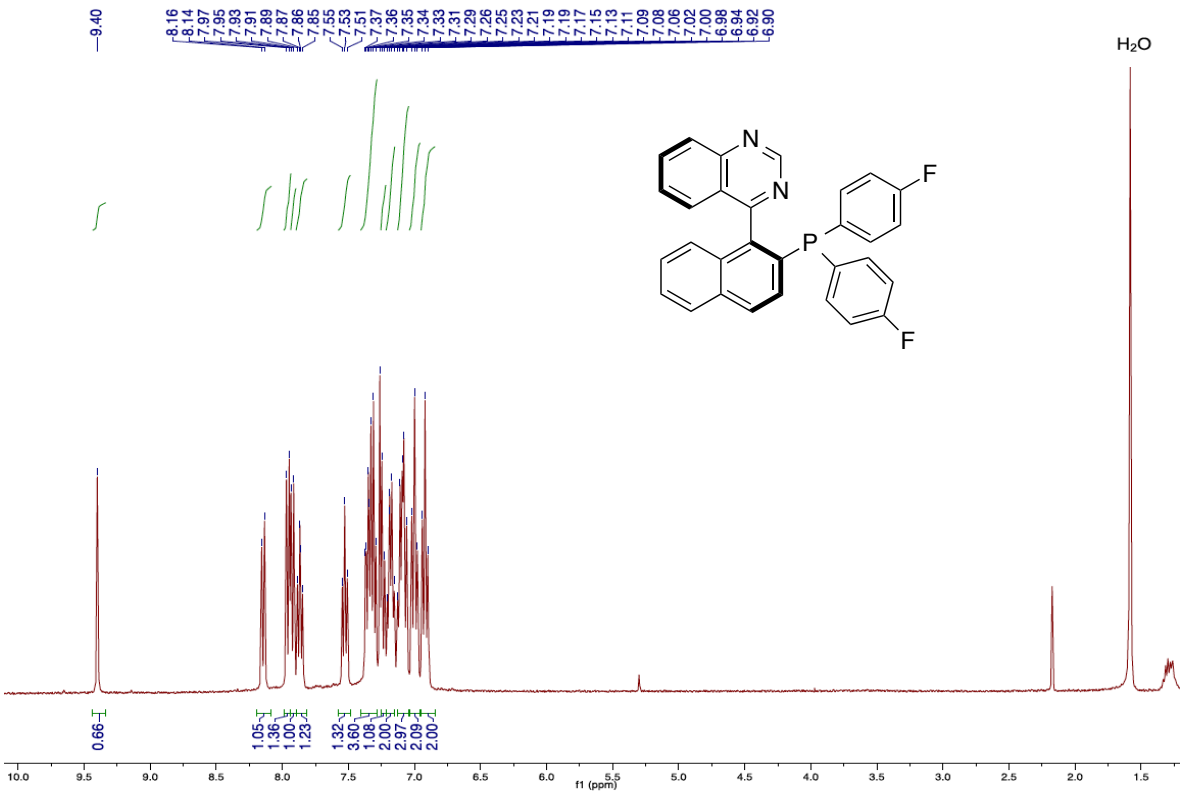


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Cb**

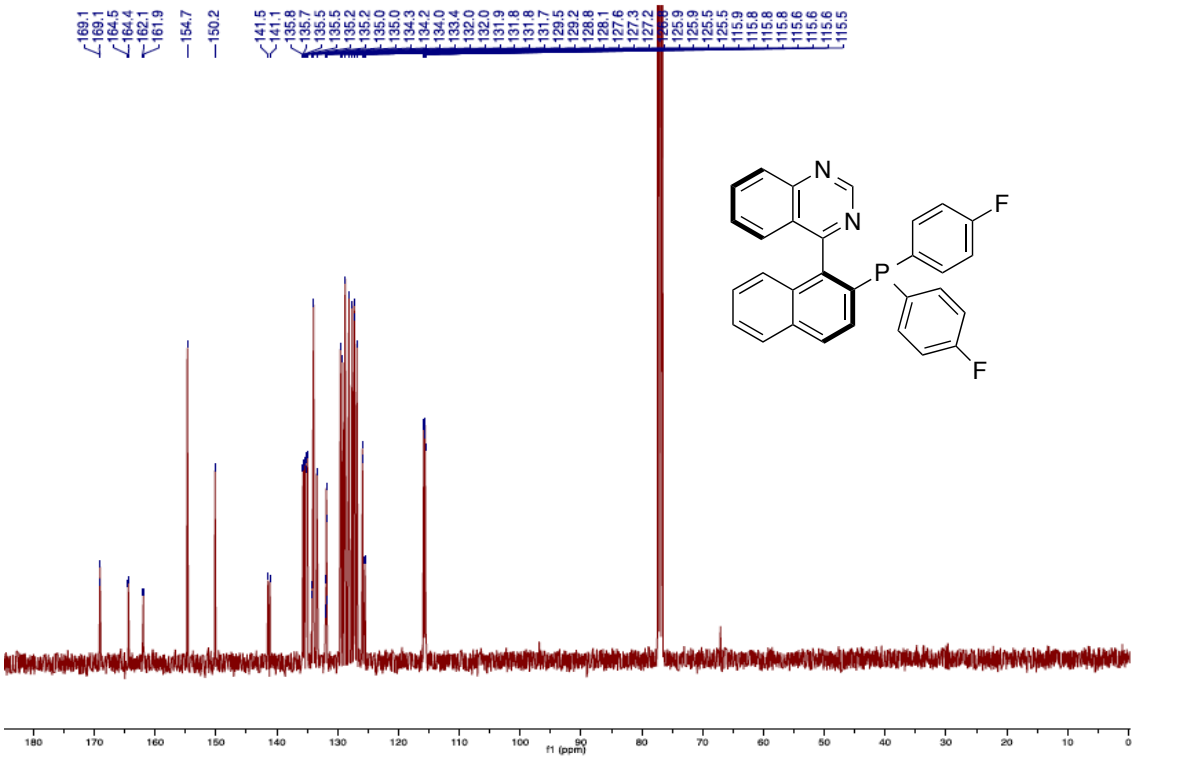


Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Cb**

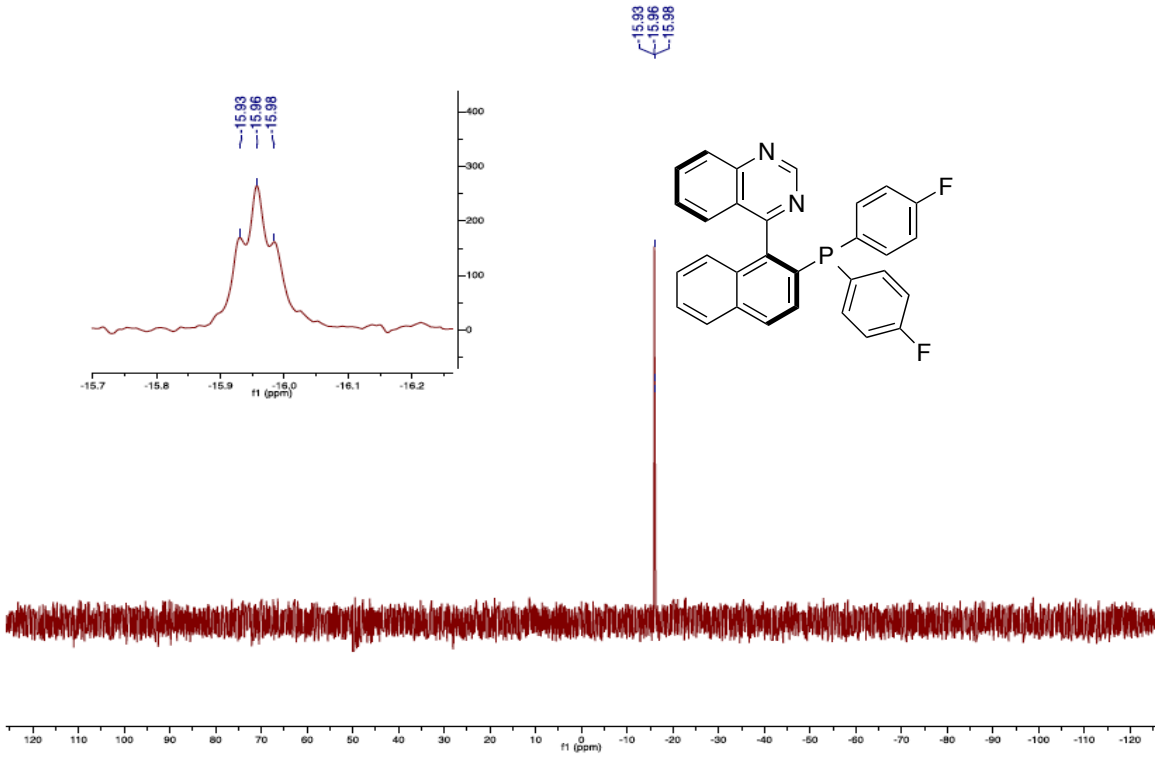


Figure S58. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Cb**

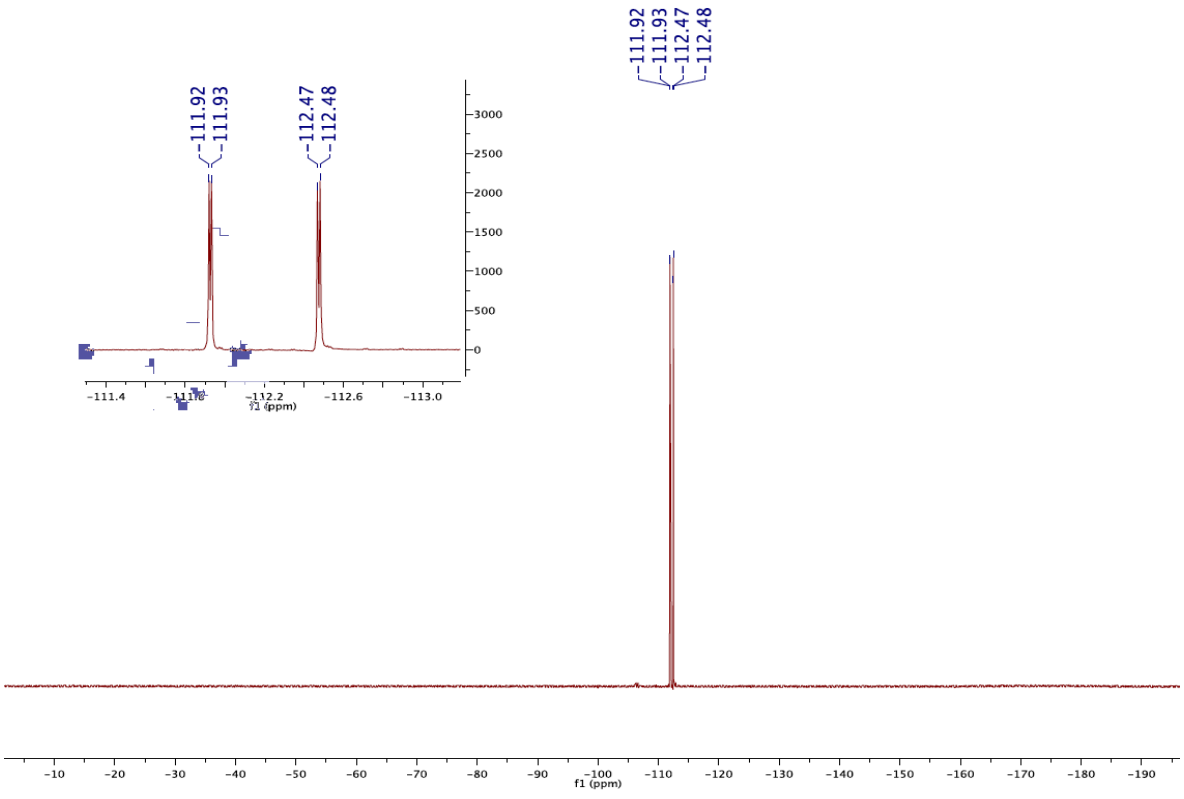
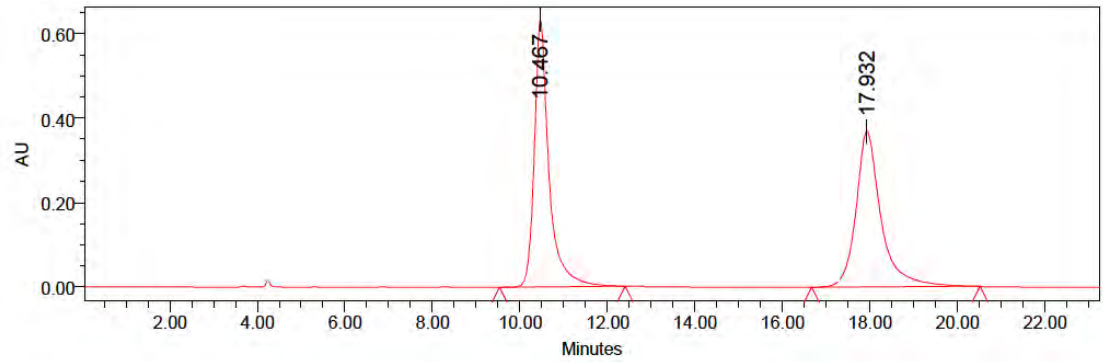
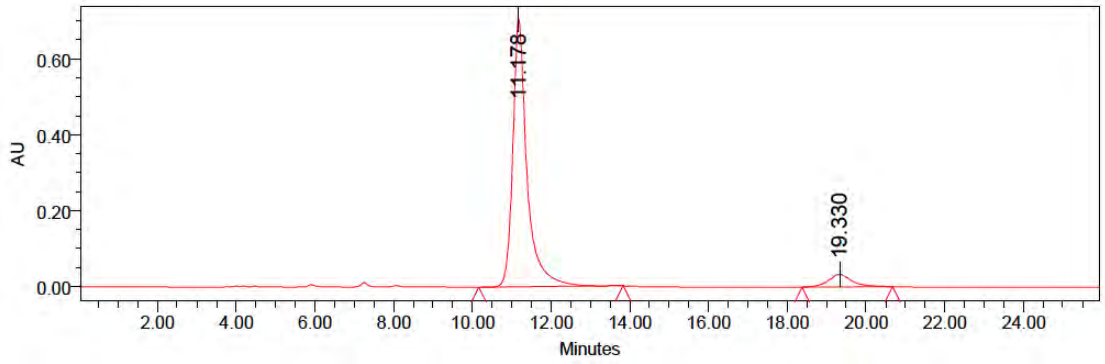


Figure S59. ^{19}F NMR (377 MHz, $CDCl_3$) of **(*S*)-3Cb**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	10.467	14737393	50.11	633265
2	PDA 229.7 nm	17.932	14673815	49.89	368205

Figure S60. Phosphine oxide racemic sample: IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	11.178	17727710	92.99	705953
2	PDA 229.7 nm	19.330	1336010	7.01	32517

Figure S61. Phosphine oxide enantioriched sample: er 93:7.

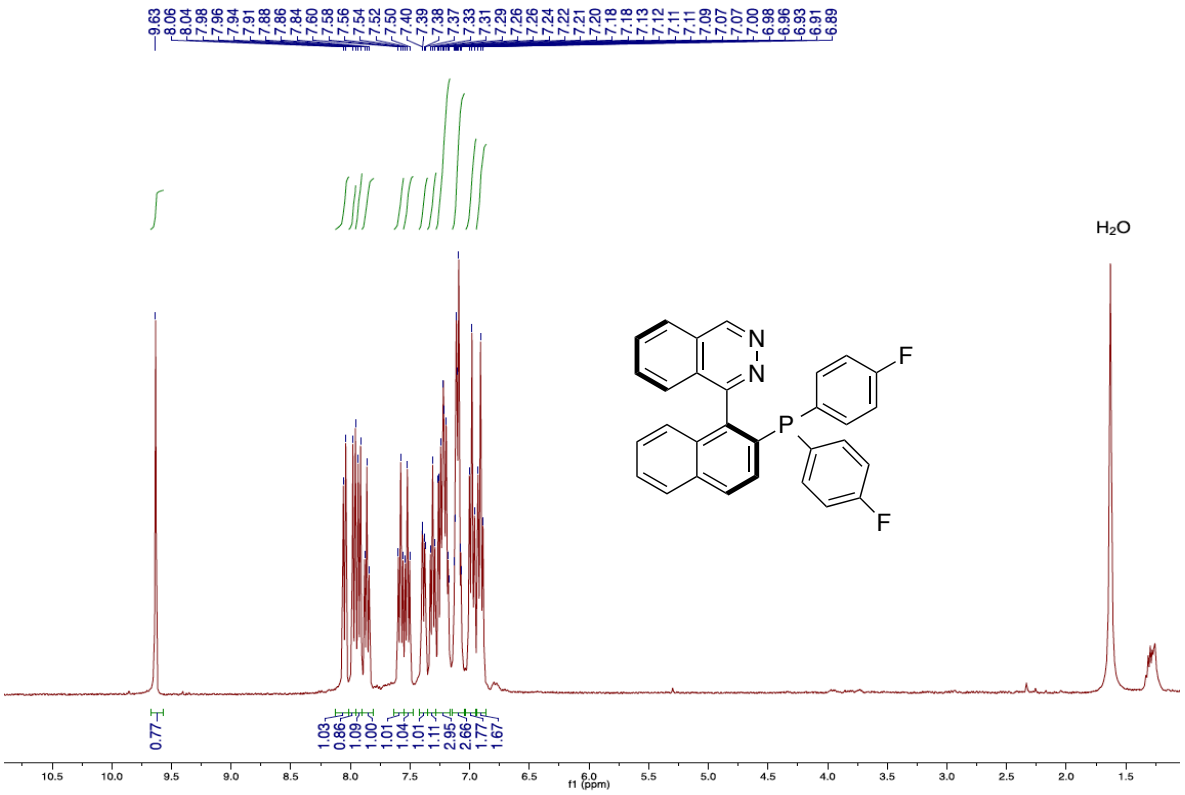


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Db**

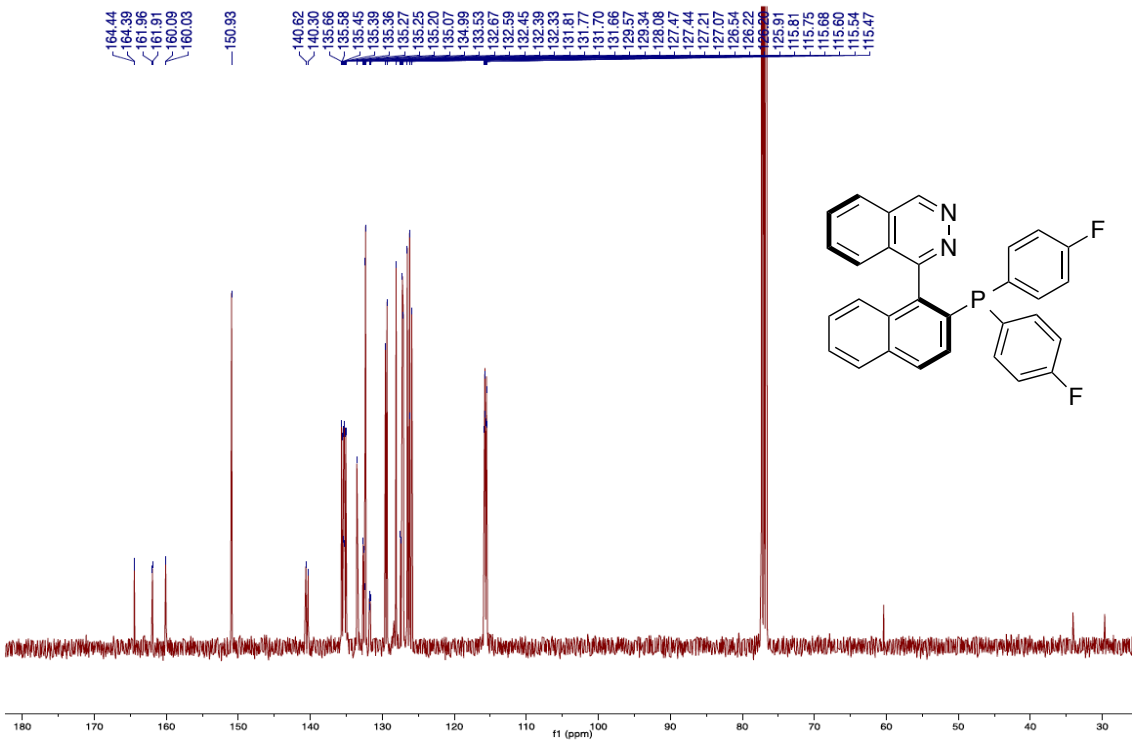


Figure S63. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Db**

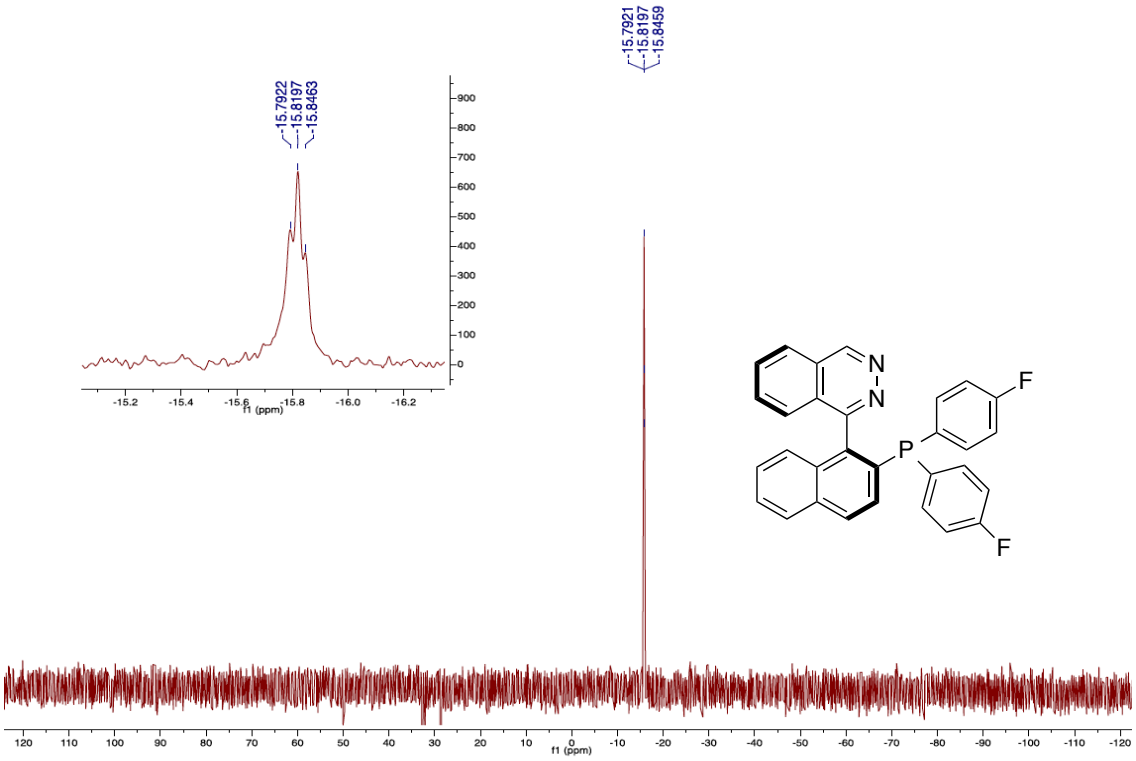


Figure S64. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Db**

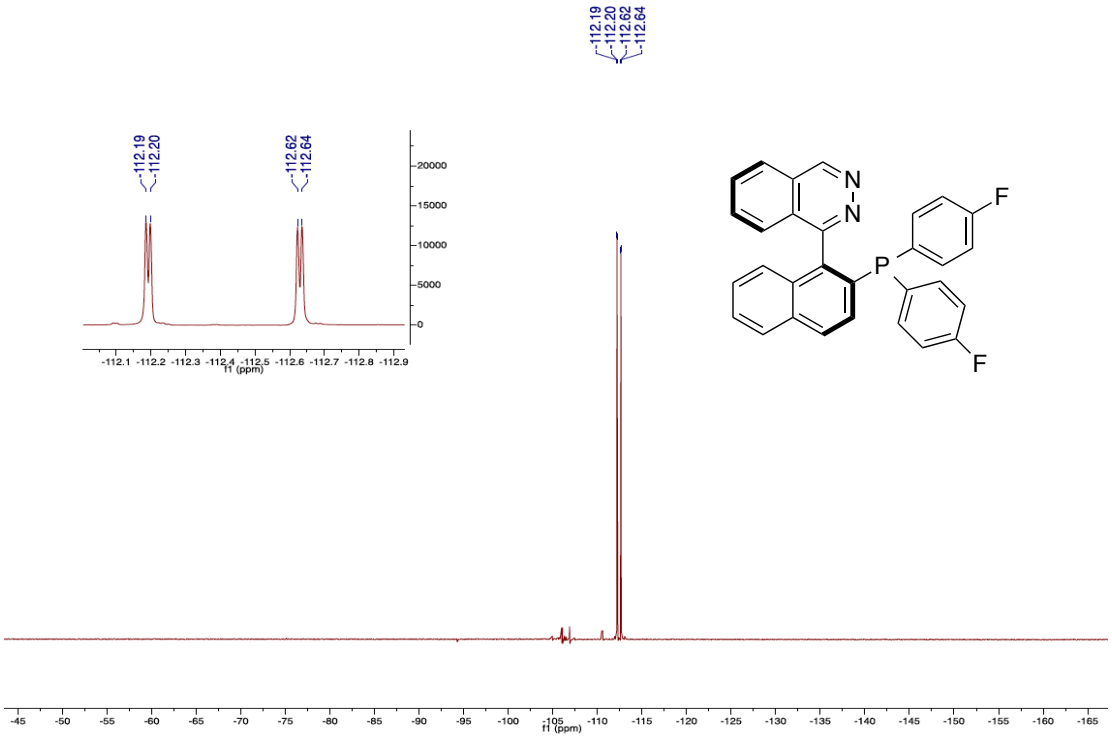
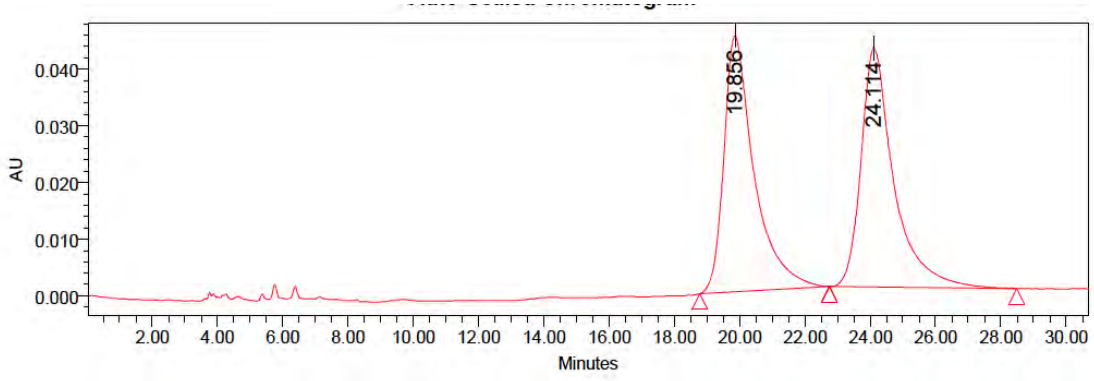
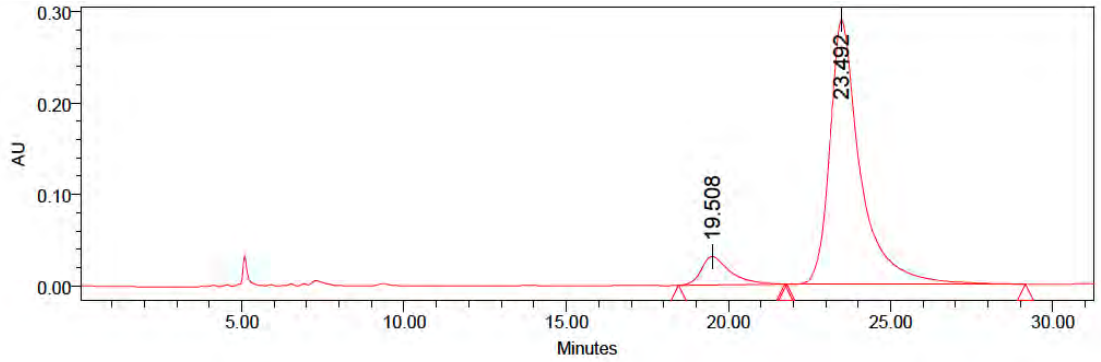


Figure S65. ^{19}F NMR (377 MHz, $CDCl_3$) of **(*S*)-3Db**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	19.856	2913477	49.71	45184
2	PDA 229.0 nm	24.114	2947758	50.29	42191

Figure S66. Phosphine oxide racemic sample: IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	19.508	1924647	9.18	31141
2	PDA 229.0 nm	23.492	19029852	90.82	289036

Figure S67. Phosphine oxide enantioriched sample: er 9:91.

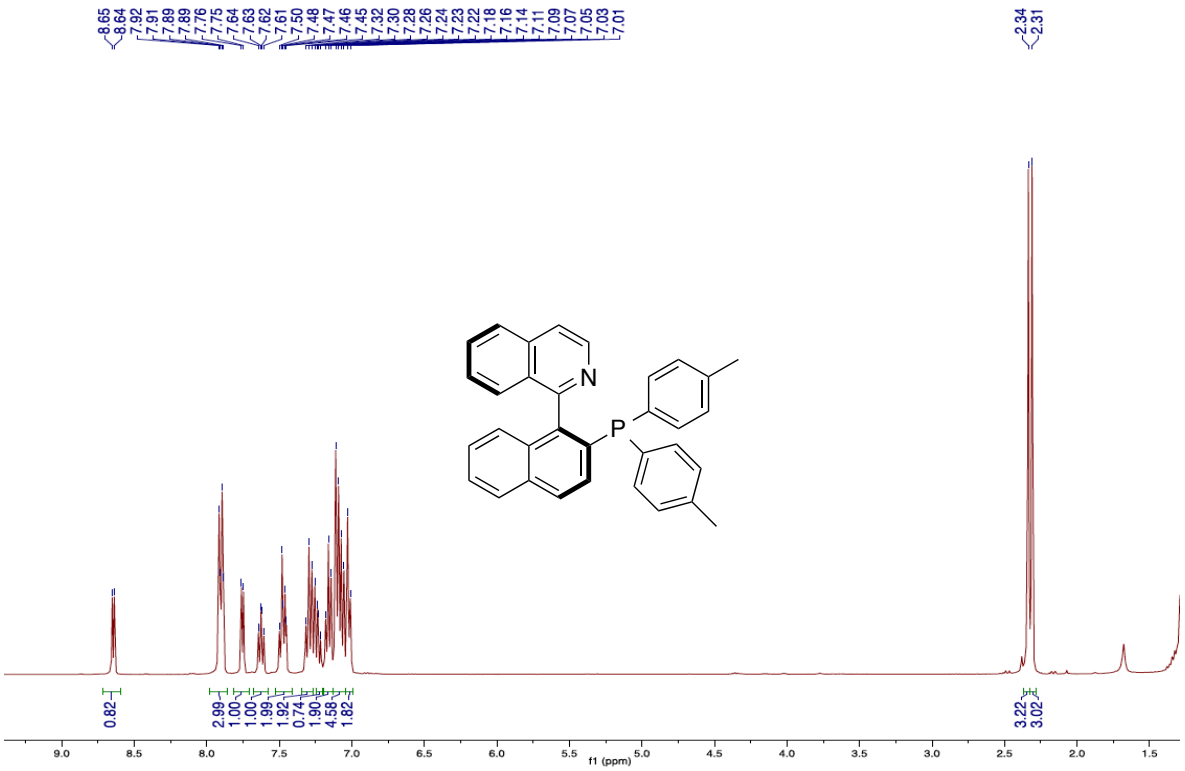


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Ac**

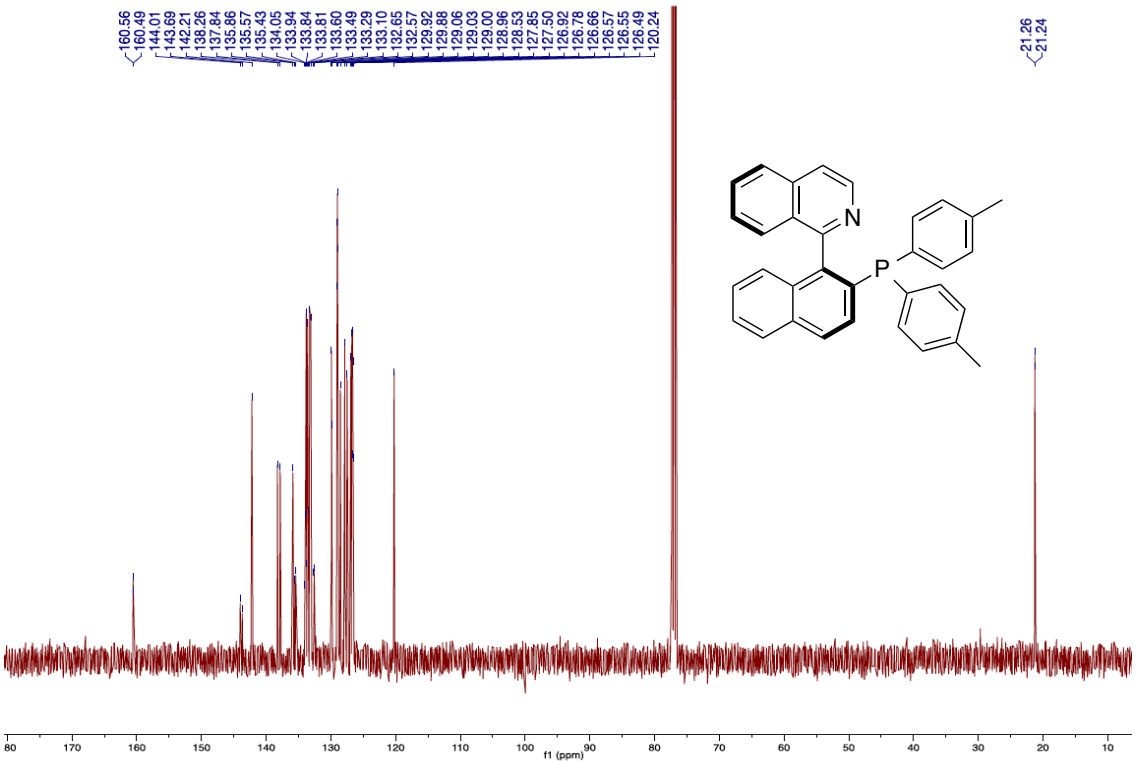


Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Ac**

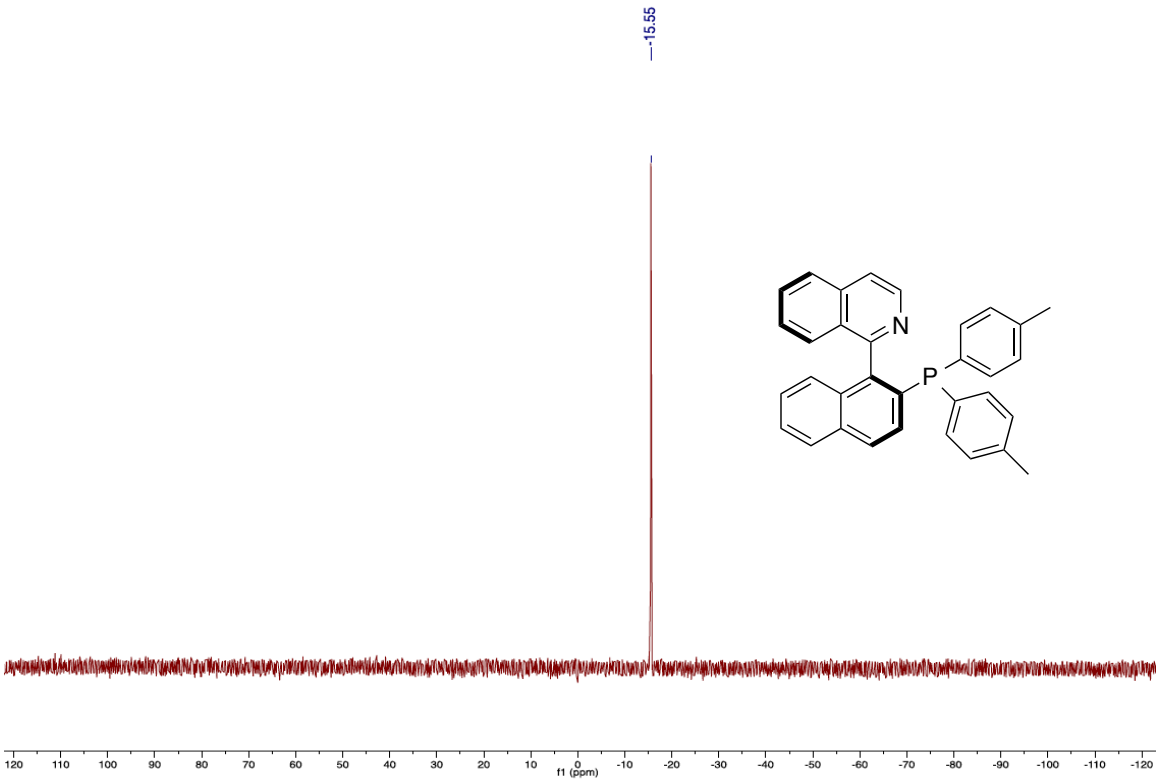
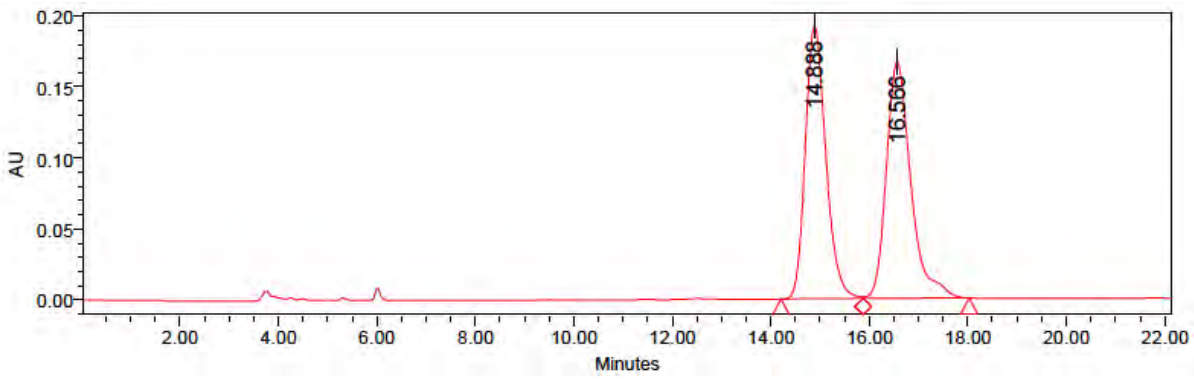
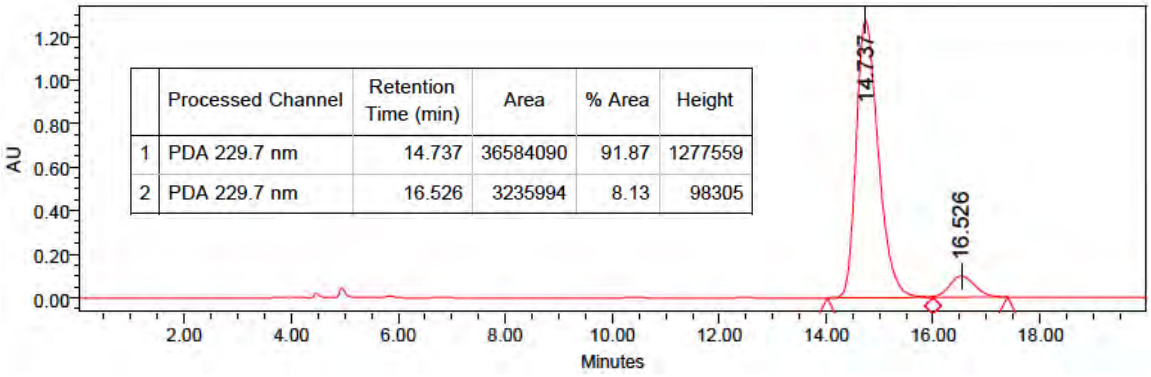


Figure S70. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ac**



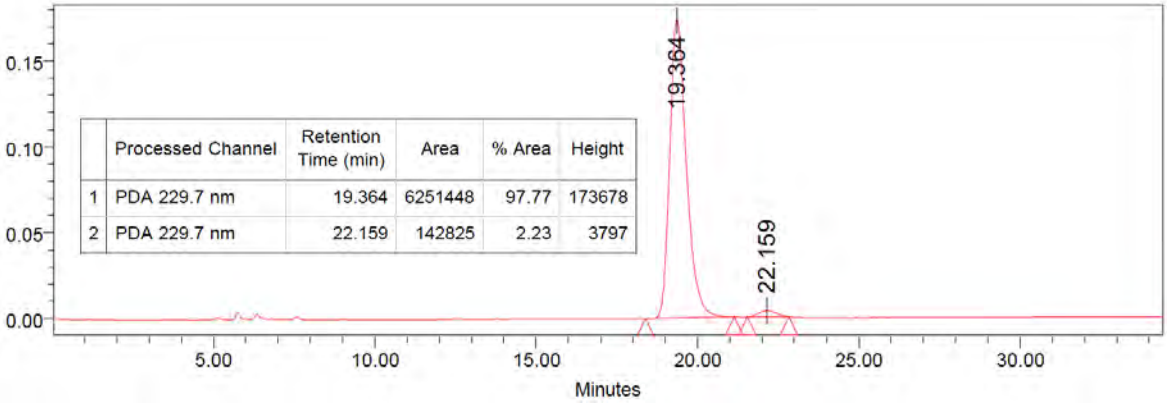
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 228.0 nm	14.888	5565129	49.05	191802
2	PDA 228.0 nm	16.566	5779991	50.95	166590

Figure S71. Phosphine oxide racemic sample: AD-H column, Hex:Isop 70:30, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	14.737	36584090	91.87	1277559
2	PDA 229.7 nm	16.526	3235994	8.13	98305

Figure S72. Phosphine oxide enantioriched sample: er 92:8.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	19.364	6251448	97.77	173678
2	PDA 229.7 nm	22.159	142825	2.23	3797

Figure S73. Enantioenriched product (er 97:5:2.5) from the mother liquor after crystallization from a EtOAc/*n*-hexane mixture.

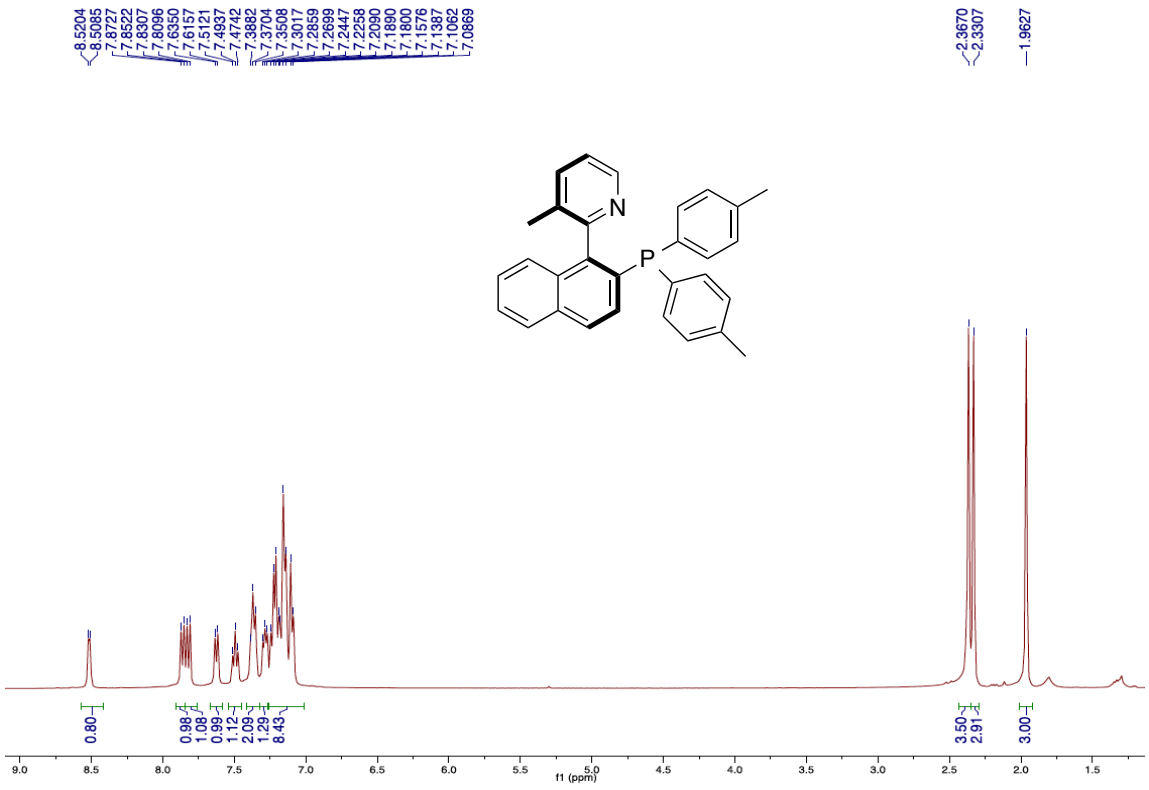


Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Bc**

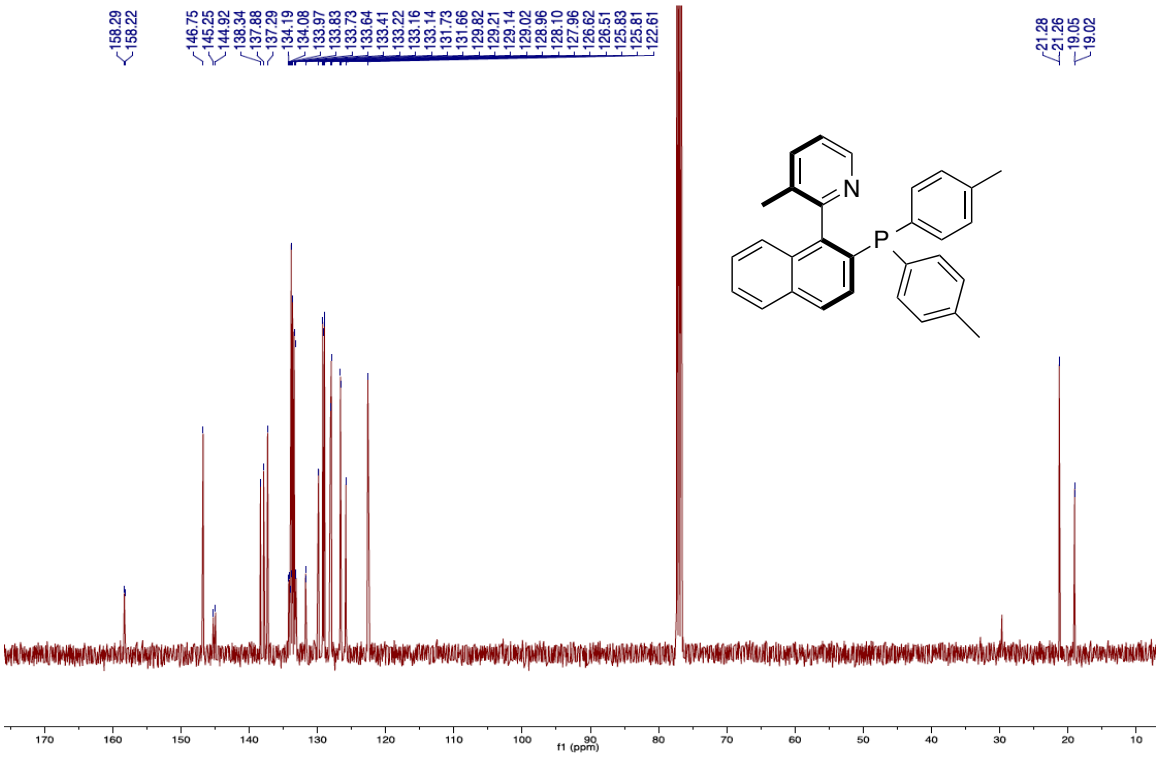


Figure S75. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Bc**

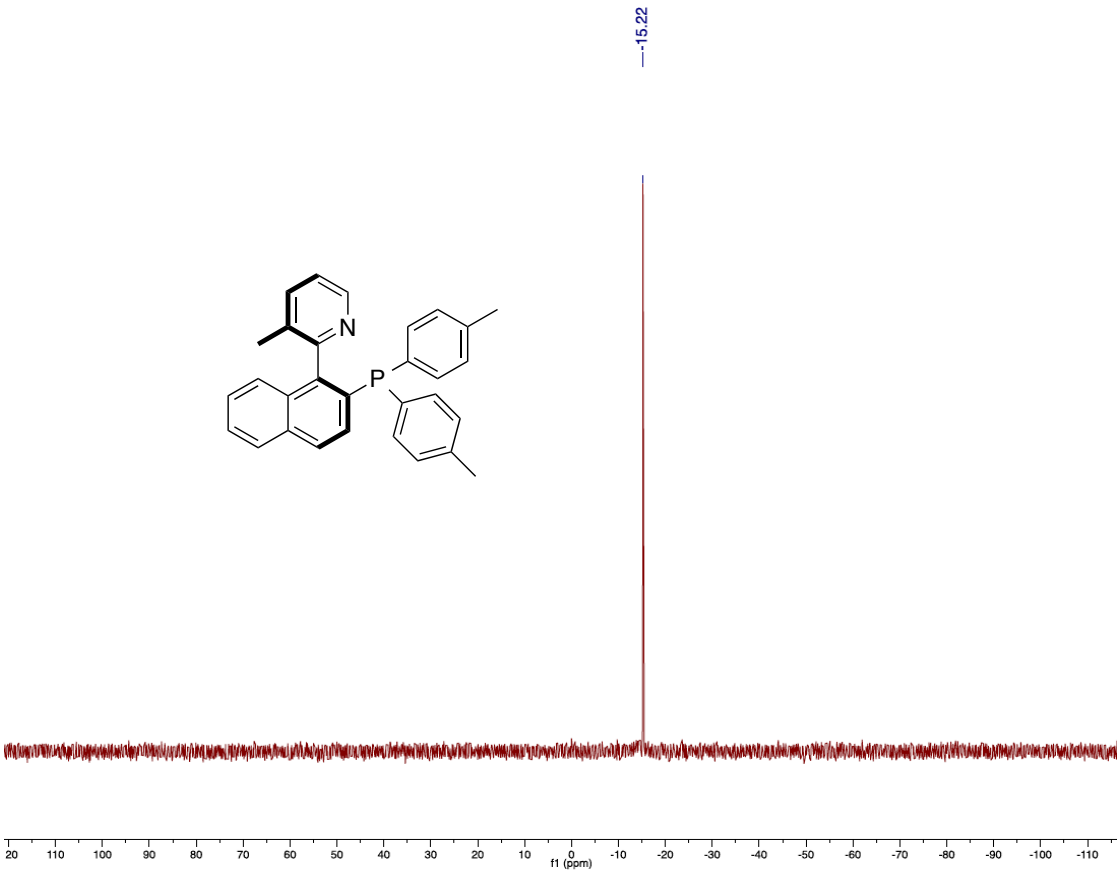
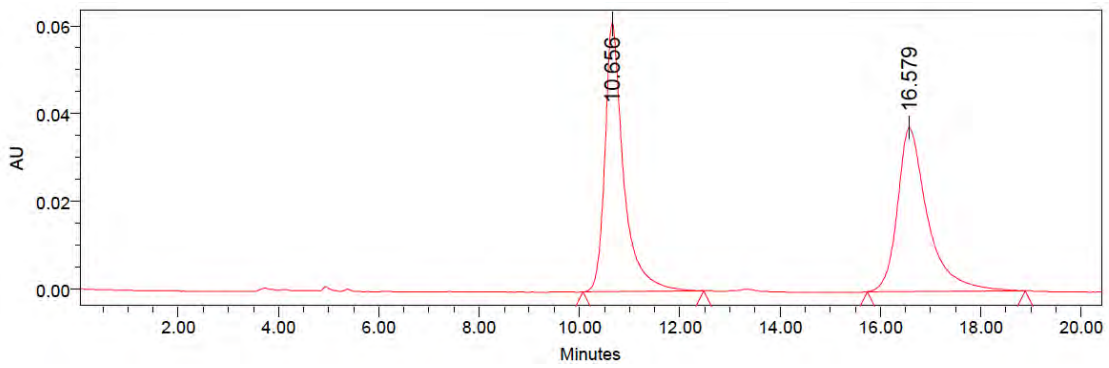
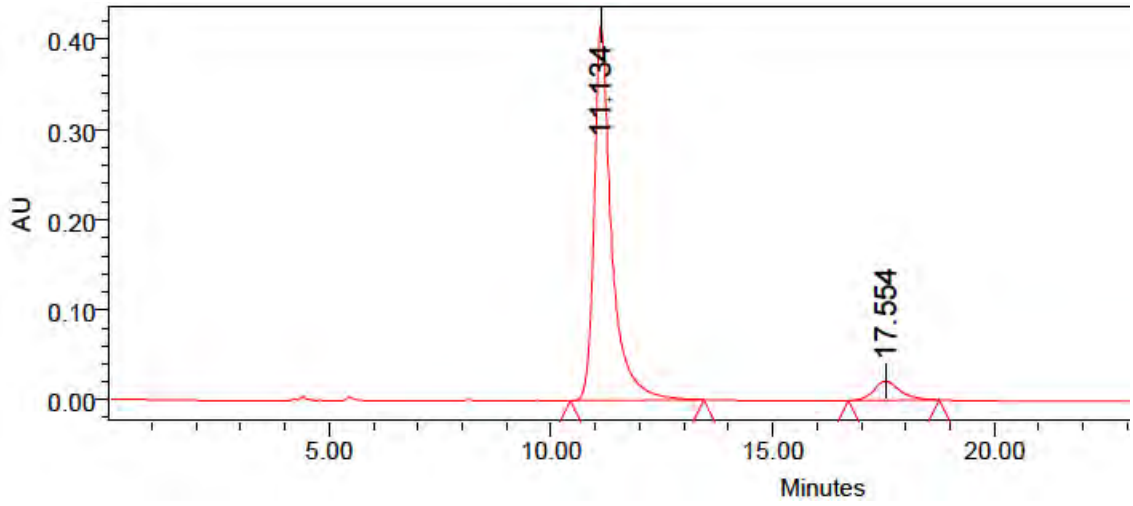


Figure S76. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Bc**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 253.5 nm	10.656	1585406	50.45	61209
2	PDA 253.5 nm	16.579	1557357	49.55	37271

Figure S77. Phosphine oxide racemic sample: IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	11.134	11303460	92.90	417832
2	PDA 236.0 nm	17.554	864290	7.10	21216

Figure S78. Phosphine oxide enantioriched sample: er 93:7.

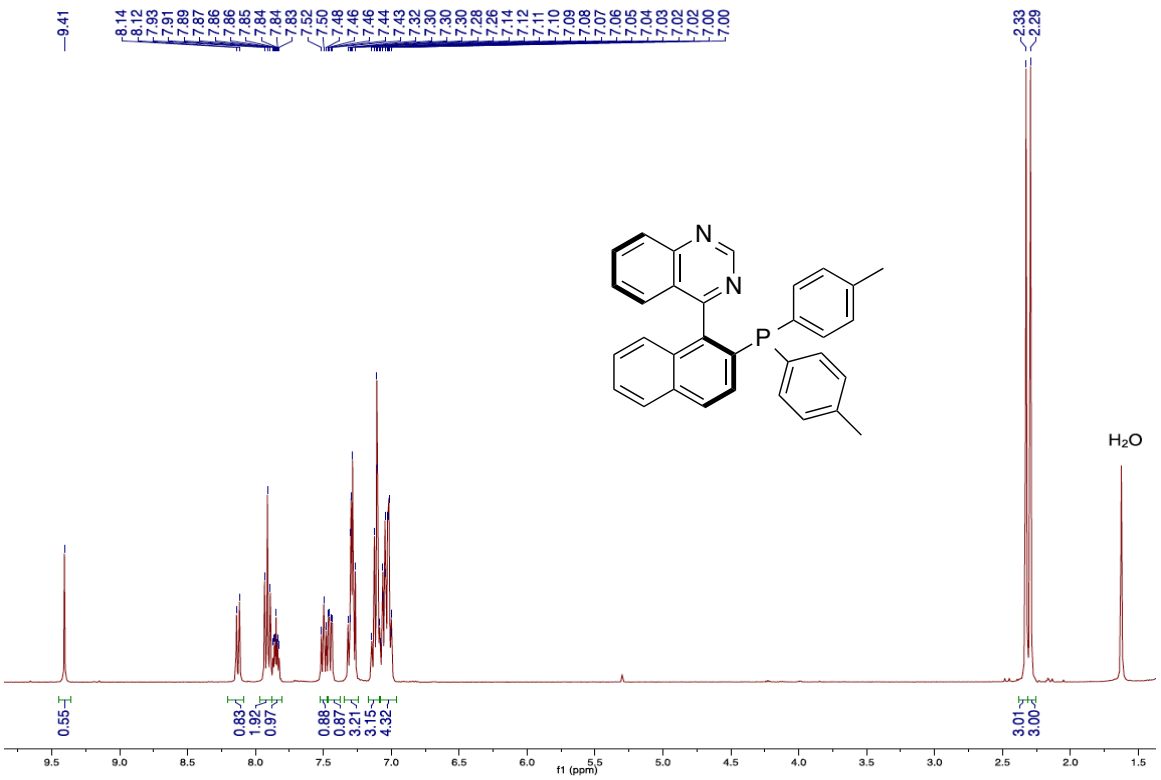


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Cc**

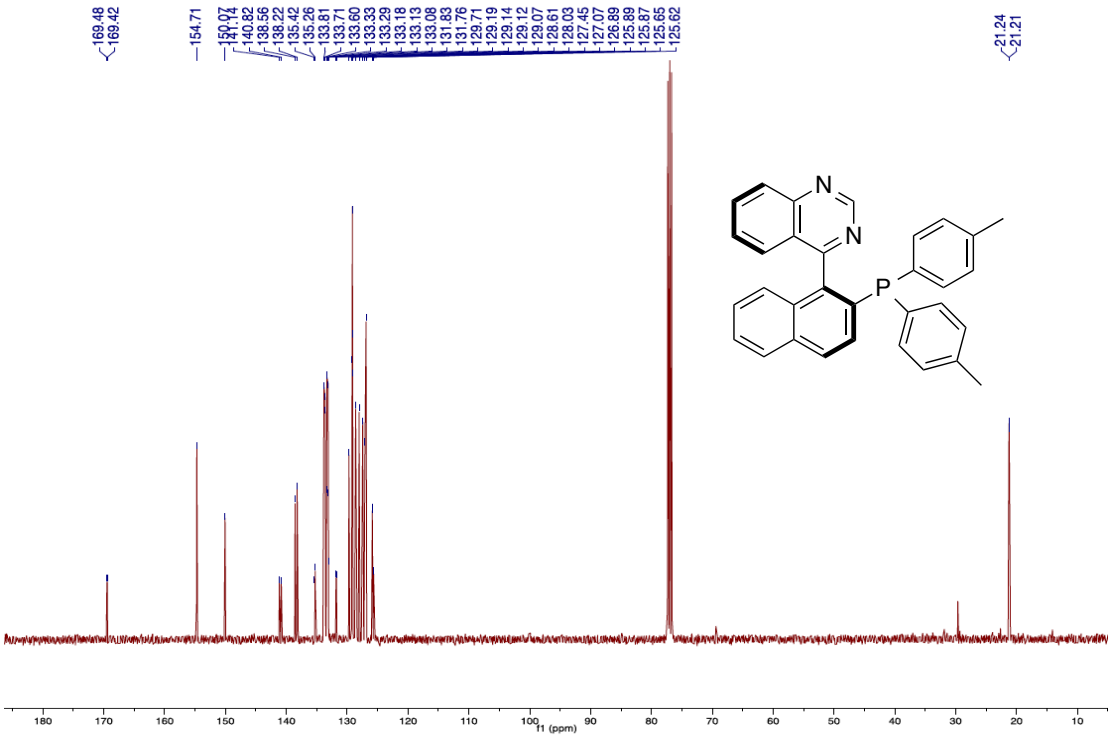


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Cc**

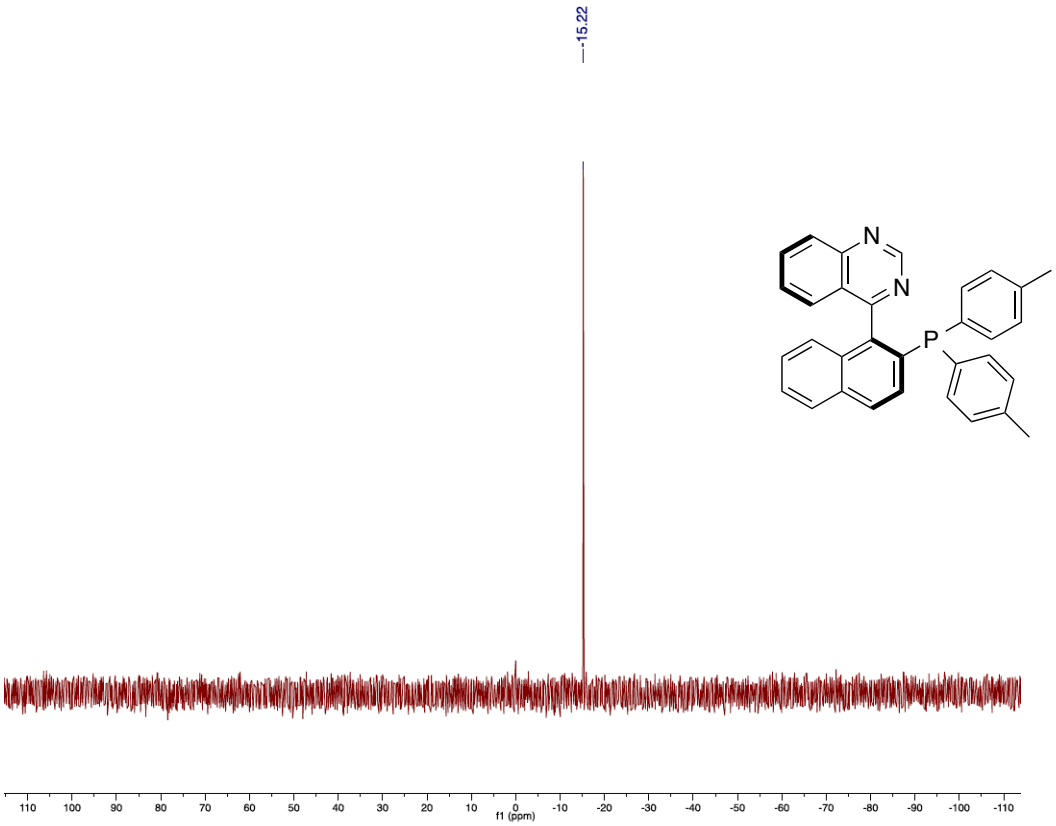
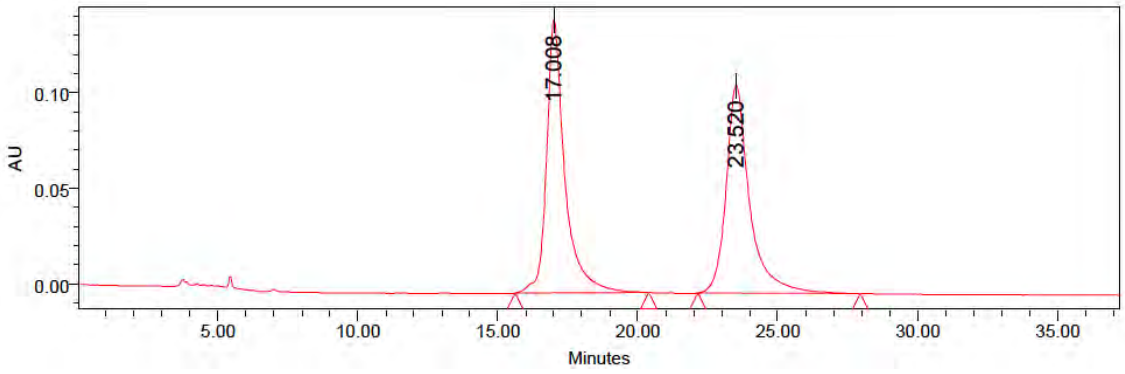
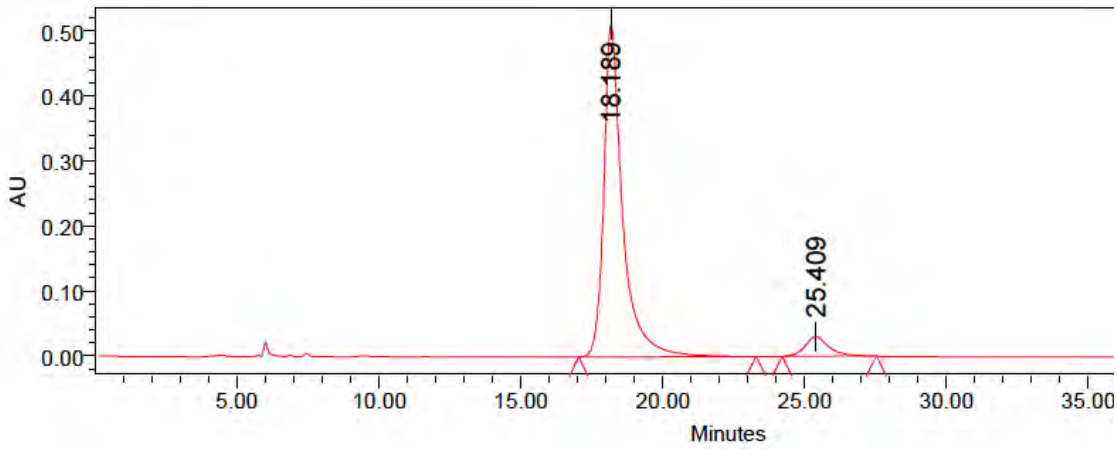


Figure S81. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Cc**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	17.008	6508012	50.54	142553
2	PDA 229.7 nm	23.520	6367723	49.46	108542

Figure S82. Phosphine oxide racemic sample: IA column, Hex:Isop 75:25, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.7 nm	18.189	23495973	92.95	511713
2	PDA 229.7 nm	25.409	1781334	7.05	30251

Figure S83. Phosphine oxide enantioriched sample: er 93:7.

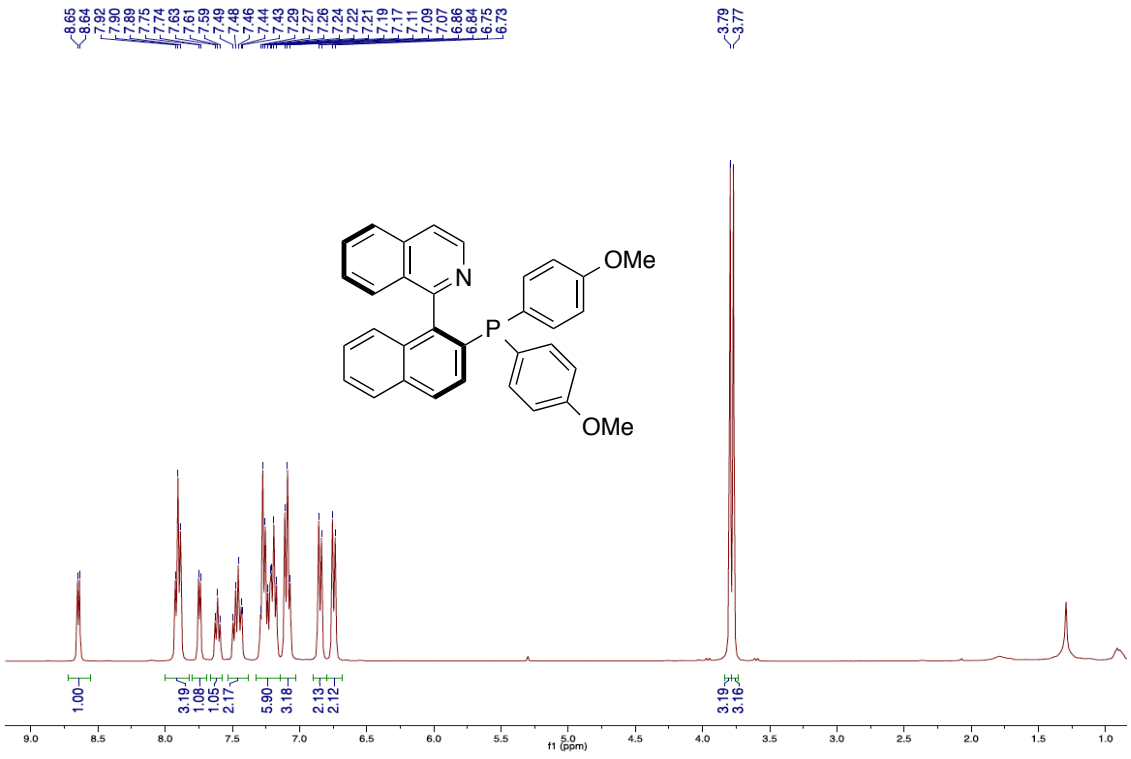


Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Ad**

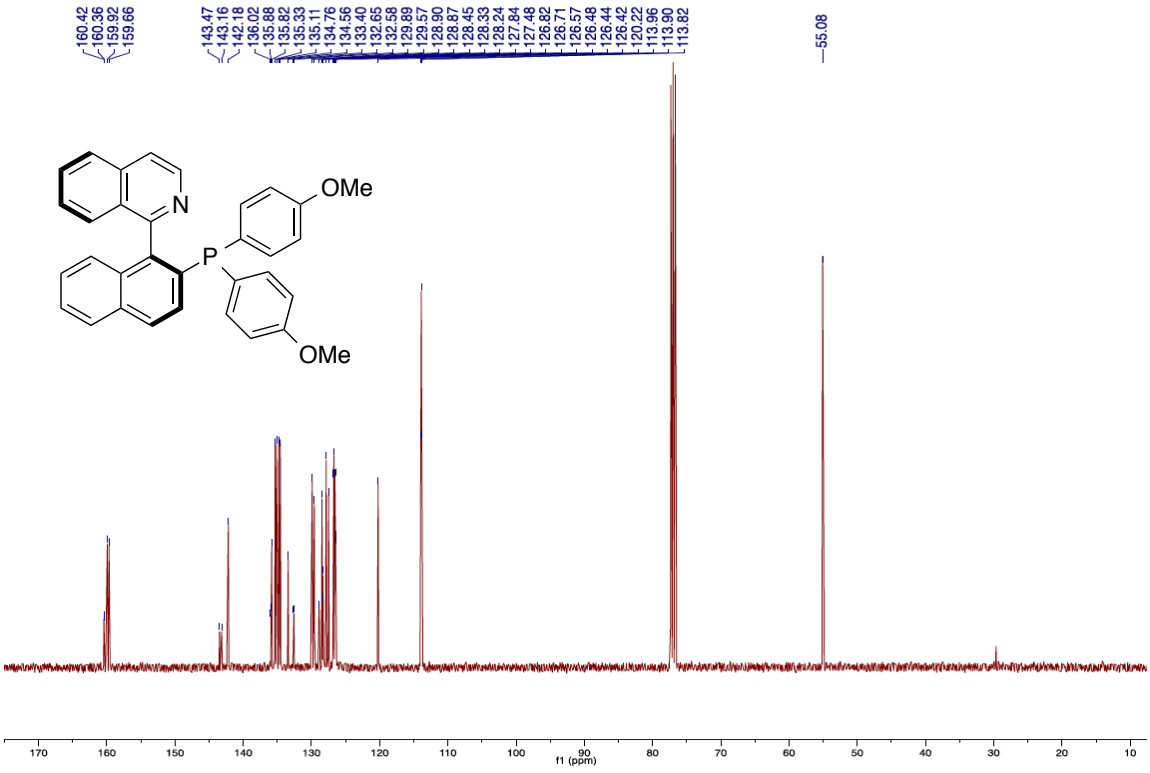


Figure S85. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Ad**

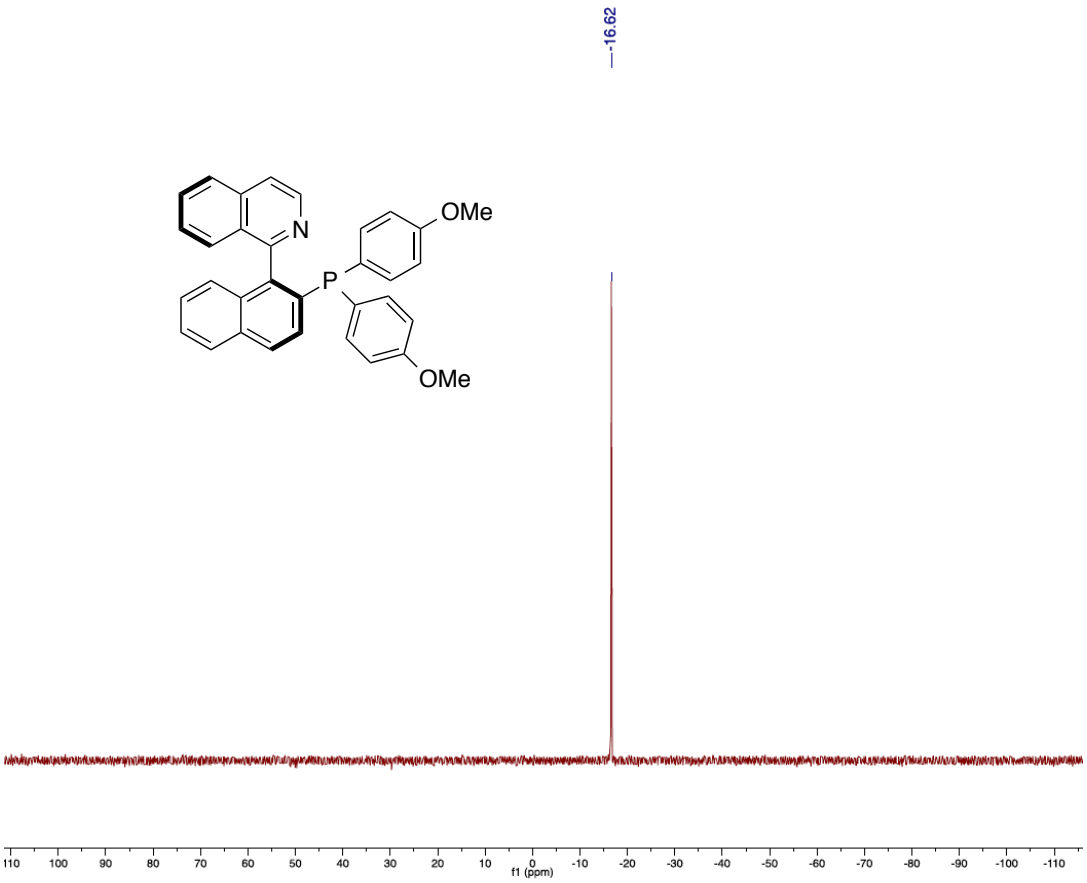
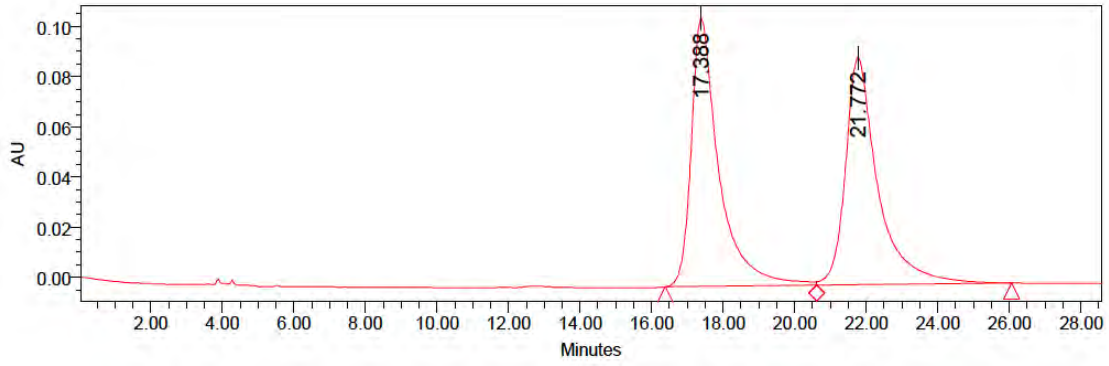
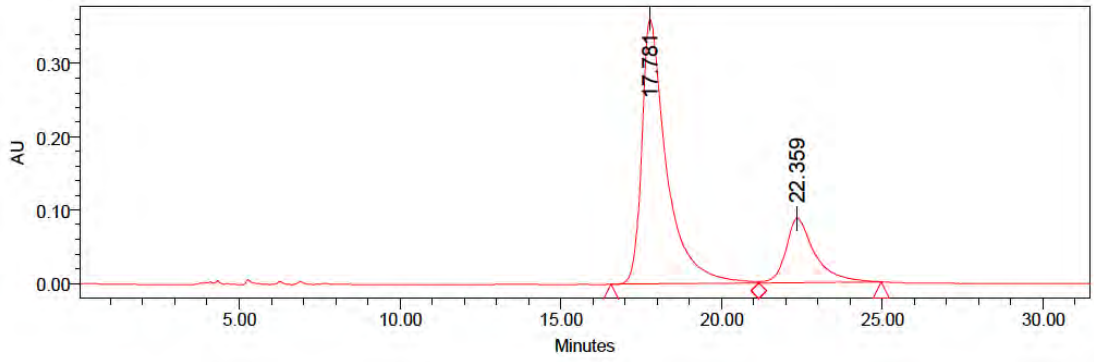


Figure S86. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ad**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	17.388	5762027	50.20	106780
2	PDA 229.0 nm	21.772	5715941	49.80	90455

Figure S87. Phosphine oxide racemic sample: IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	17.781	19452027	78.05	361366
2	PDA 229.0 nm	22.359	5469834	21.95	87322

Figure S88. Phosphine oxide enantioriched sample: er 78:22.

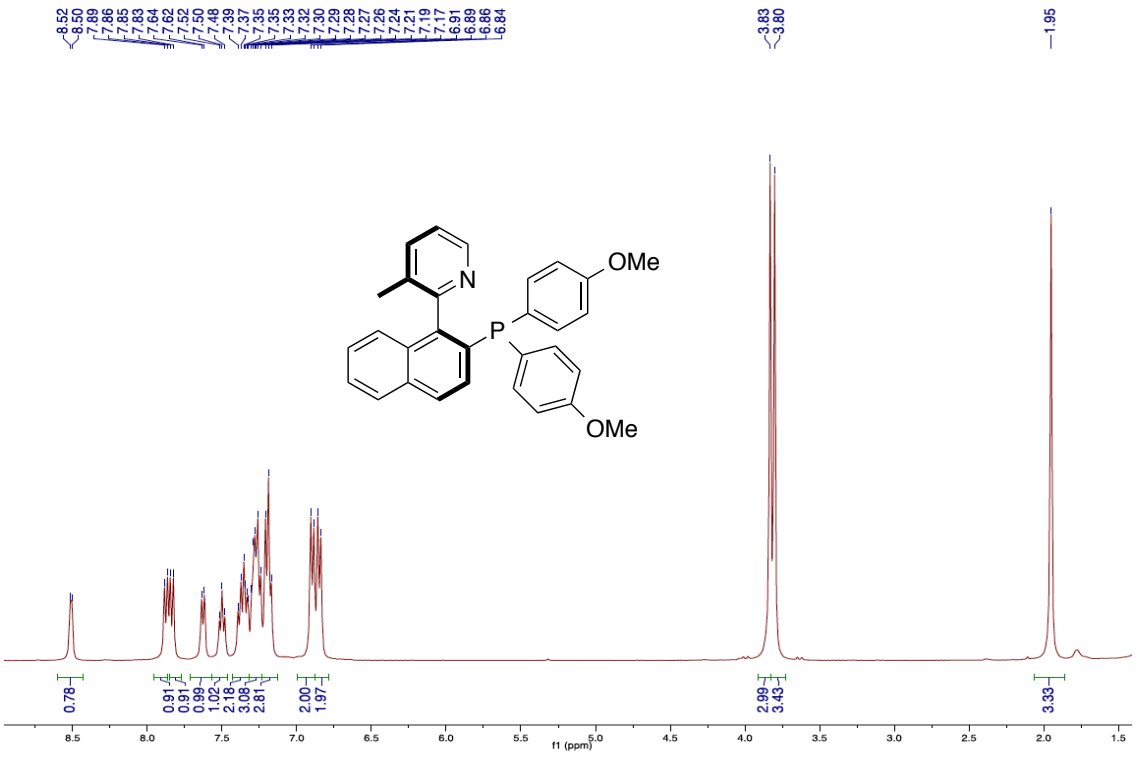


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Bd**

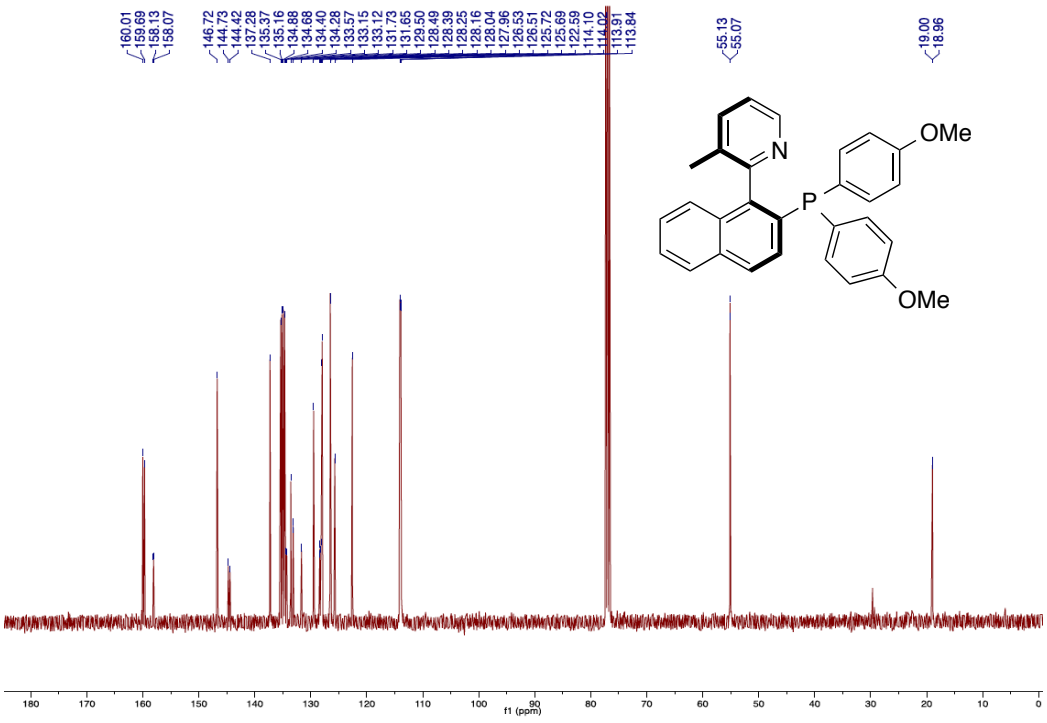


Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Bd**

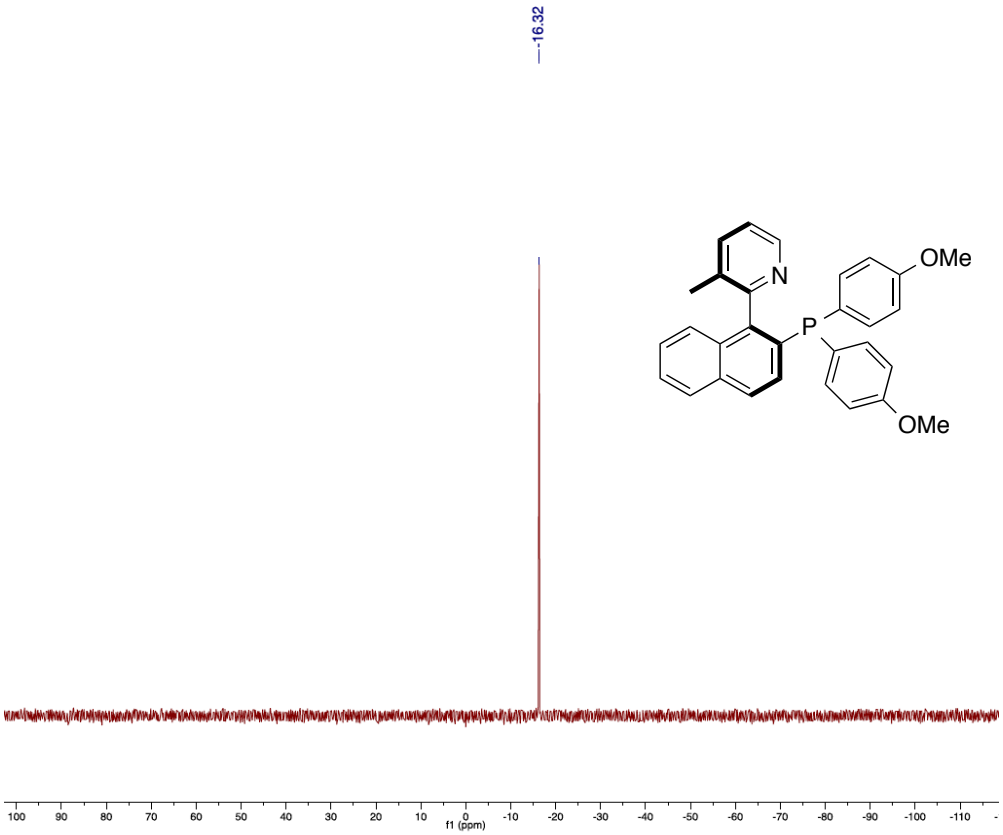
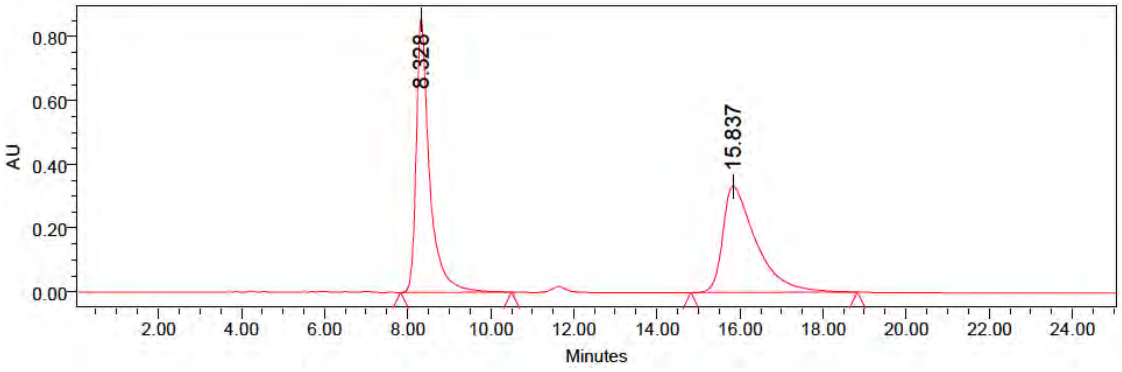
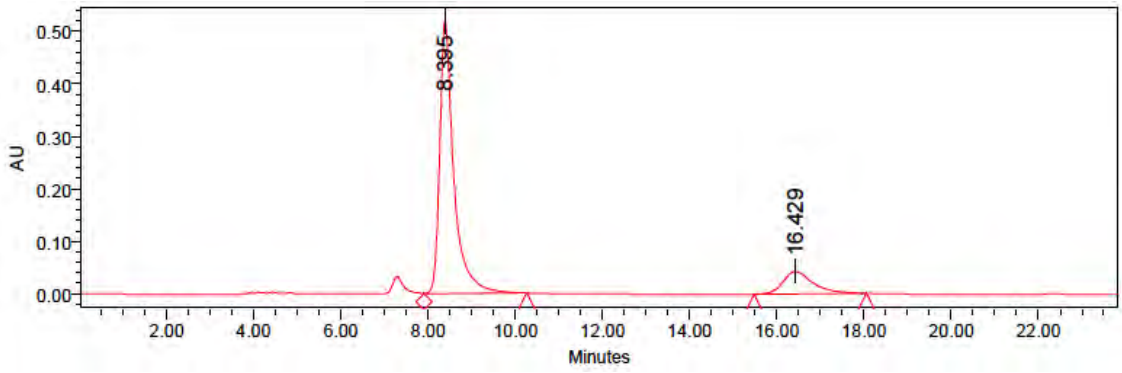


Figure S91. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Bd**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 238.0 nm	8.328	19028007	50.66	856237
2	PDA 238.0 nm	15.837	18529928	49.34	332887

Figure S92. Phosphine oxide racemic sample: IA column, Hex:Isop 50:50, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 238.0 nm	8.395	11594275	85.02	518637
2	PDA 238.0 nm	16.429	2043144	14.98	42678

Figure S93. Phosphine oxide enantioriched sample: er 85:15.

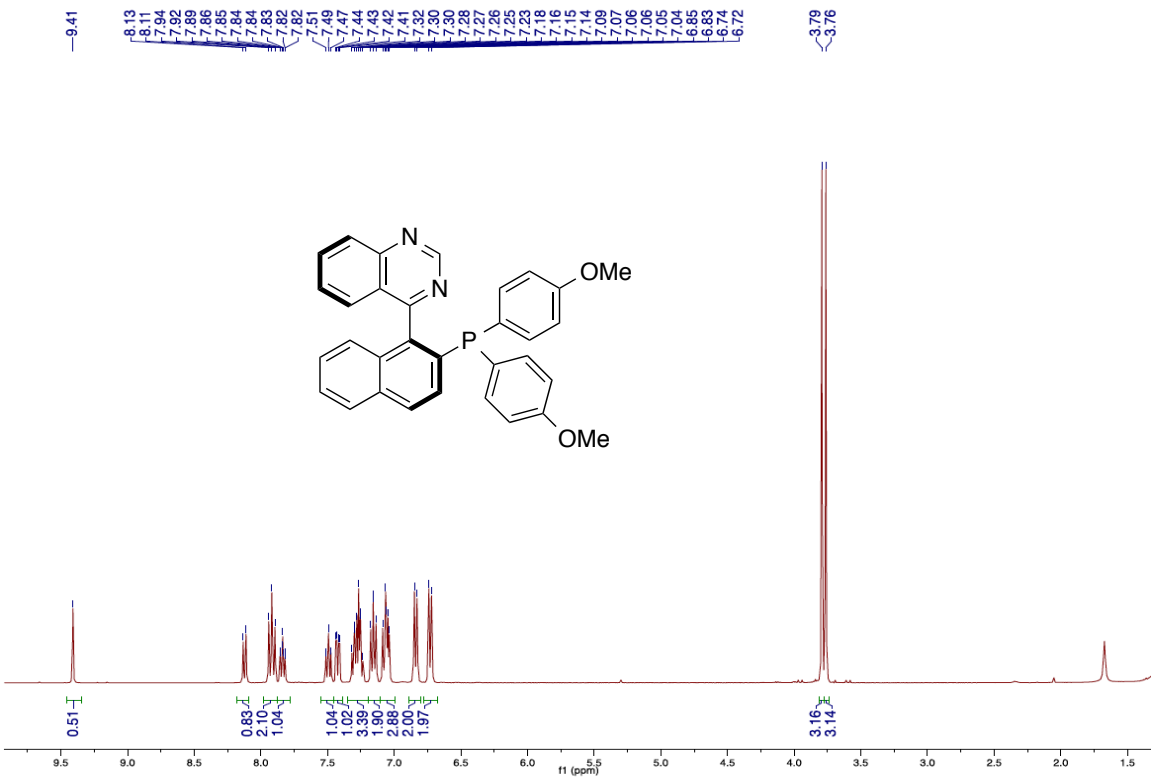


Figure S94. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Cd**

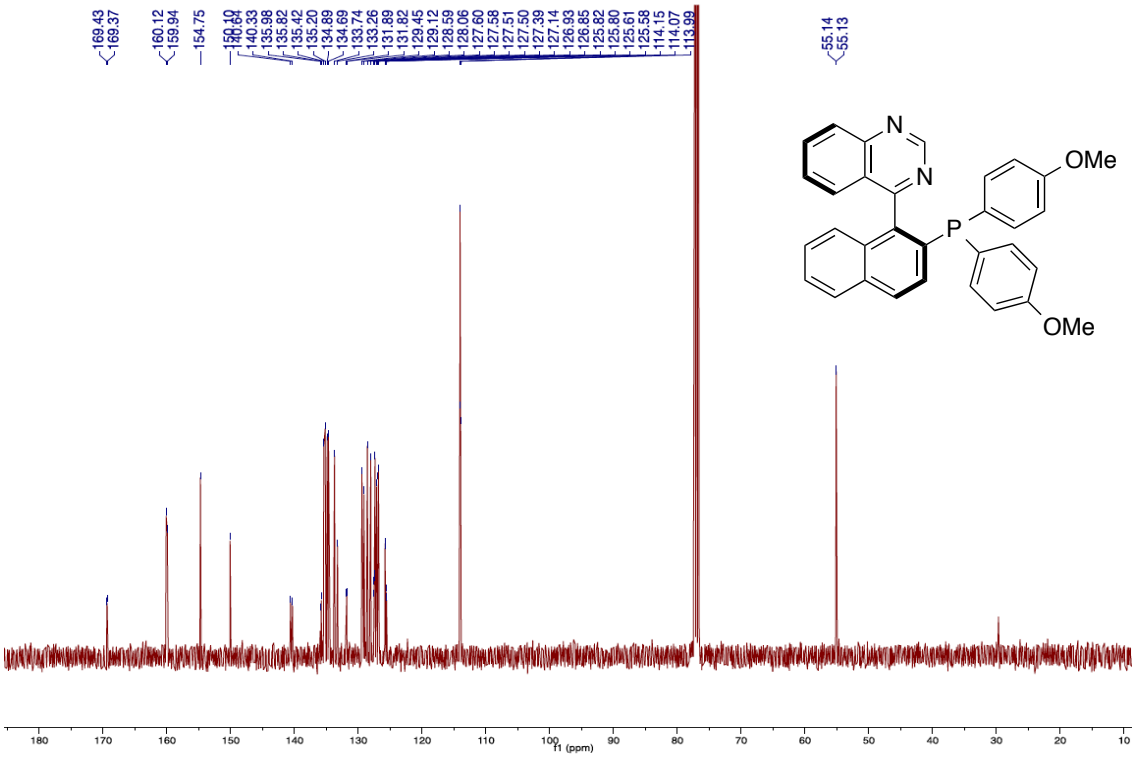


Figure S95. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Cd**

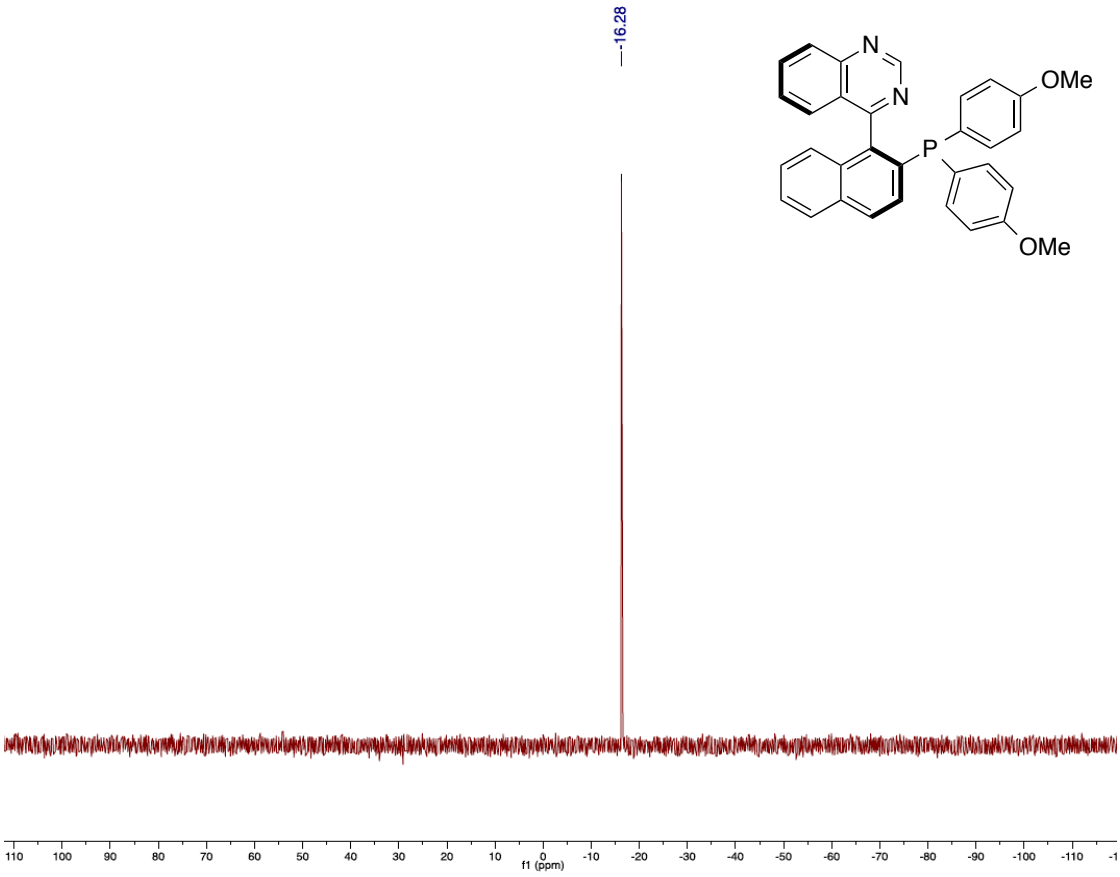
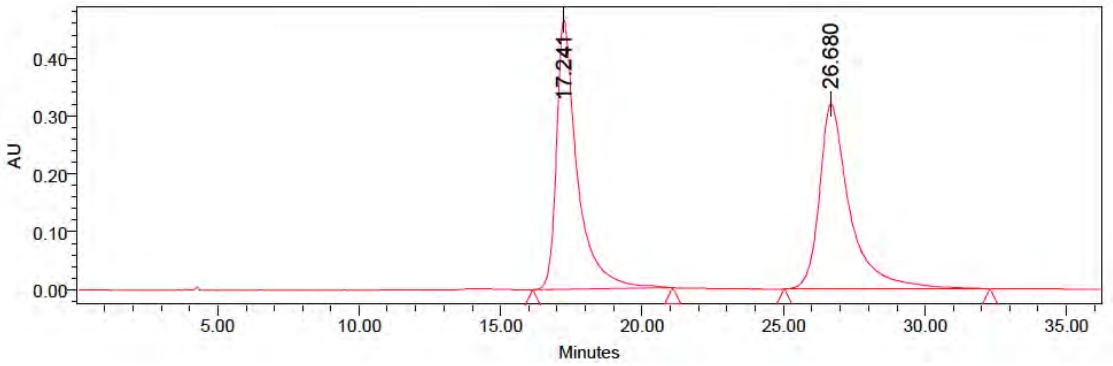
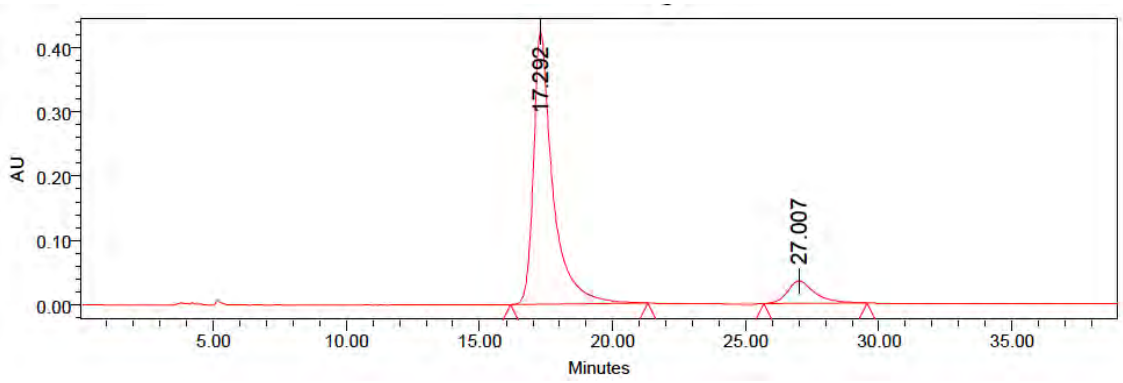


Figure S96. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Cd**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	17.241	23808678	49.98	465123
2	PDA 229.0 nm	26.680	23832362	50.02	319410

Figure S97. Phosphine oxide racemic sample: IA column, Hex:Isop 70:30, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 229.0 nm	17.292	21425075	89.49	424651
2	PDA 229.0 nm	27.007	2515103	10.51	35062

Figure S98. Phosphine oxide enantioriched sample: er 89.5:10.5.

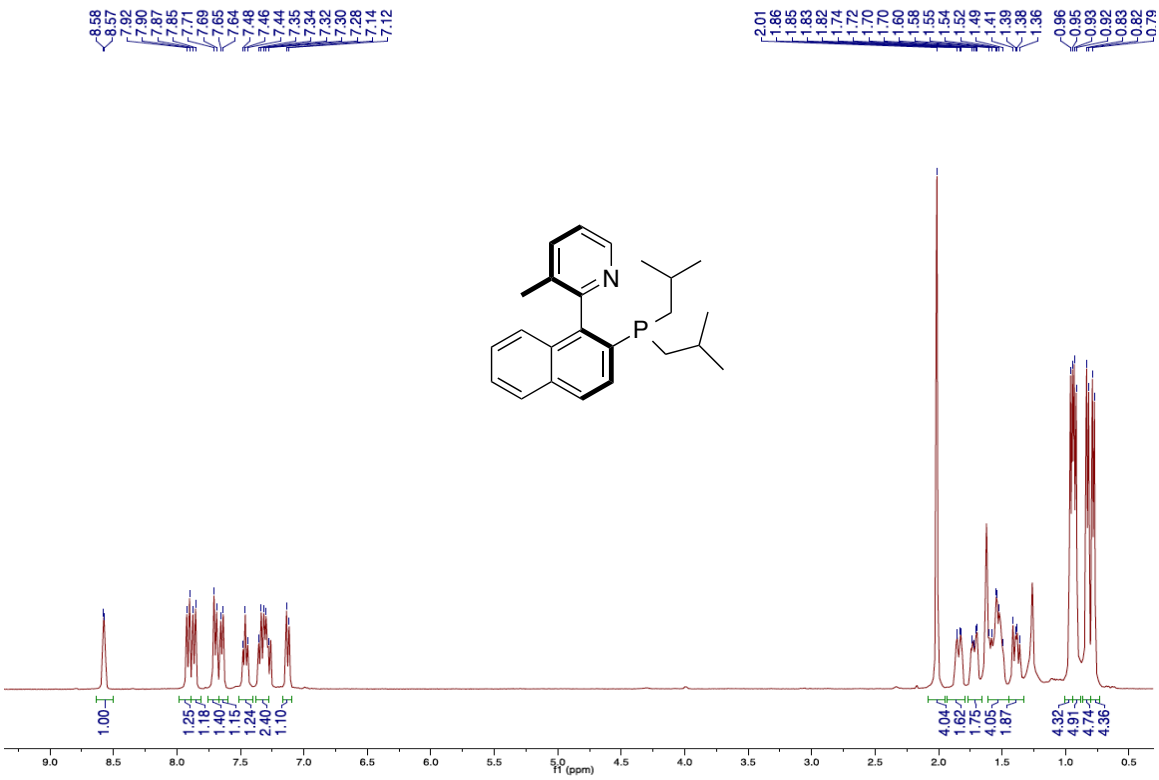


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Be**

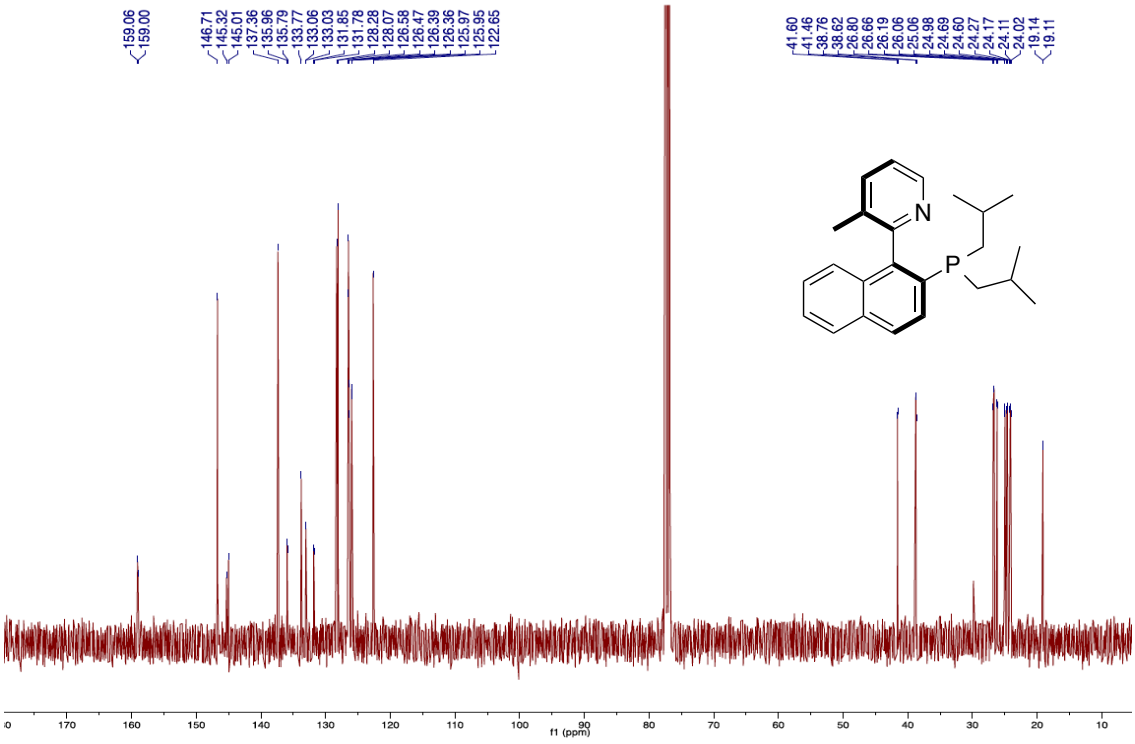


Figure S100. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Be**

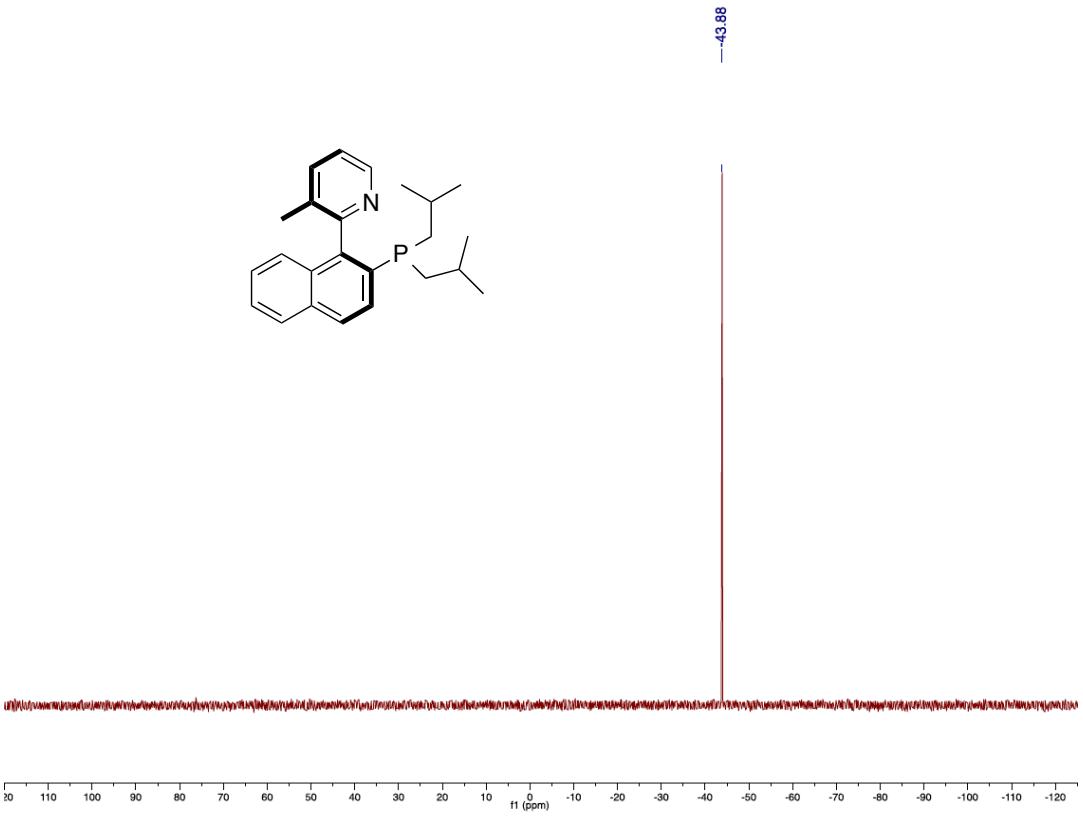
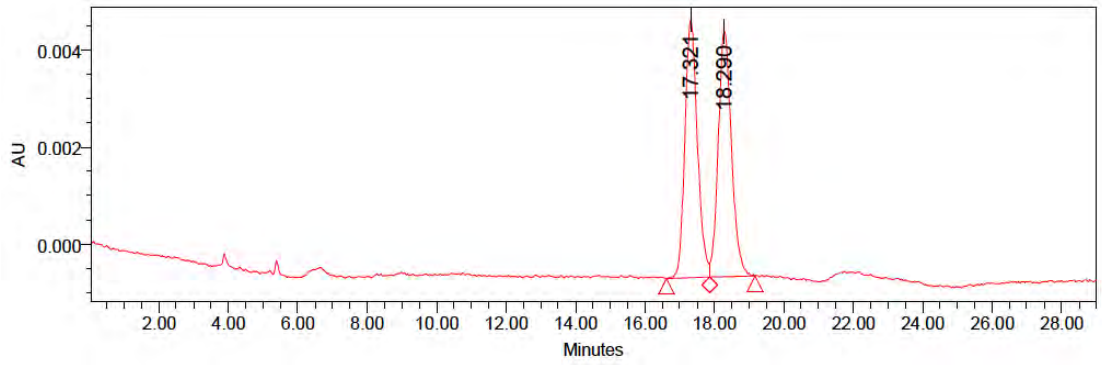
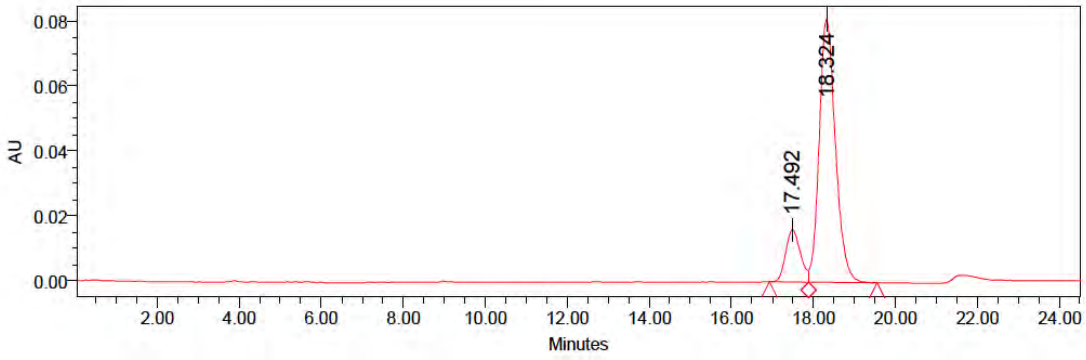


Figure S101. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Be**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 271.9 nm	17.321	132813	49.83	5314
2	PDA 271.9 nm	18.290	133736	50.17	5058

Figure S102. Phosphine oxide racemic sample: ADH column, Hex:Isop 95:5, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 271.9 nm	17.492	399179	15.24	16014
2	PDA 271.9 nm	18.324	2219890	84.76	81084

Figure S103. Phosphine oxide enantioriched sample: er 15:85.

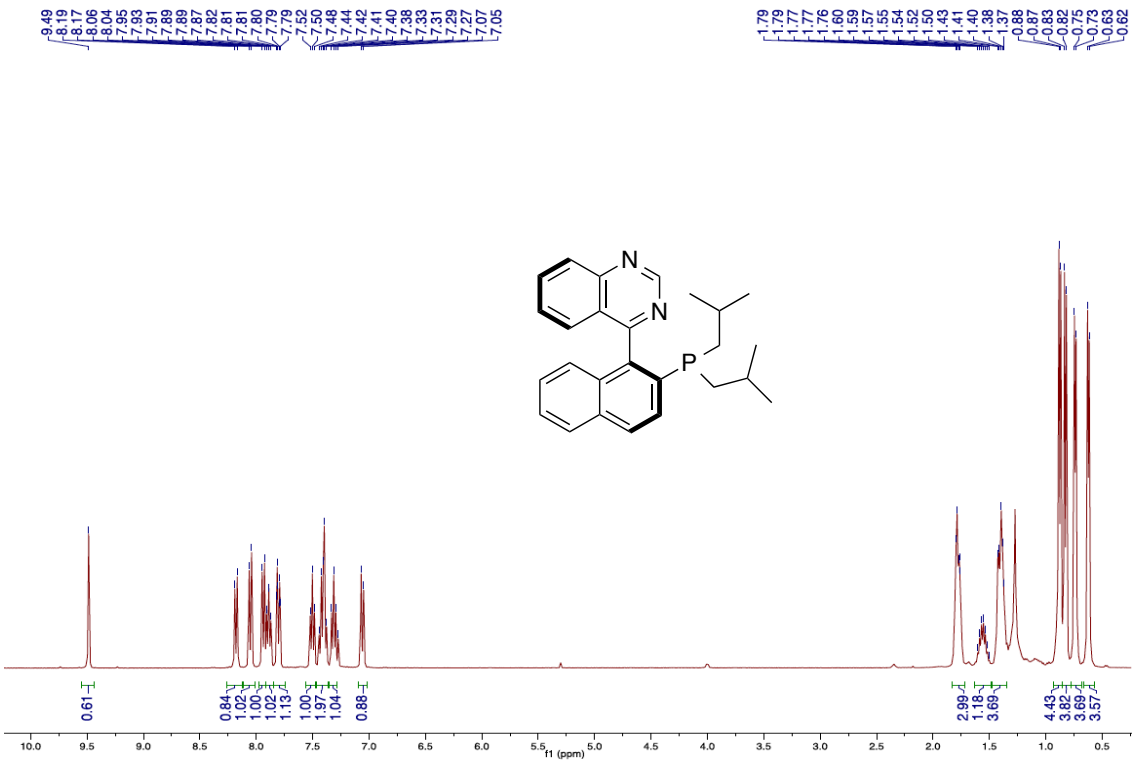


Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) of **(*S*)-3Ce**

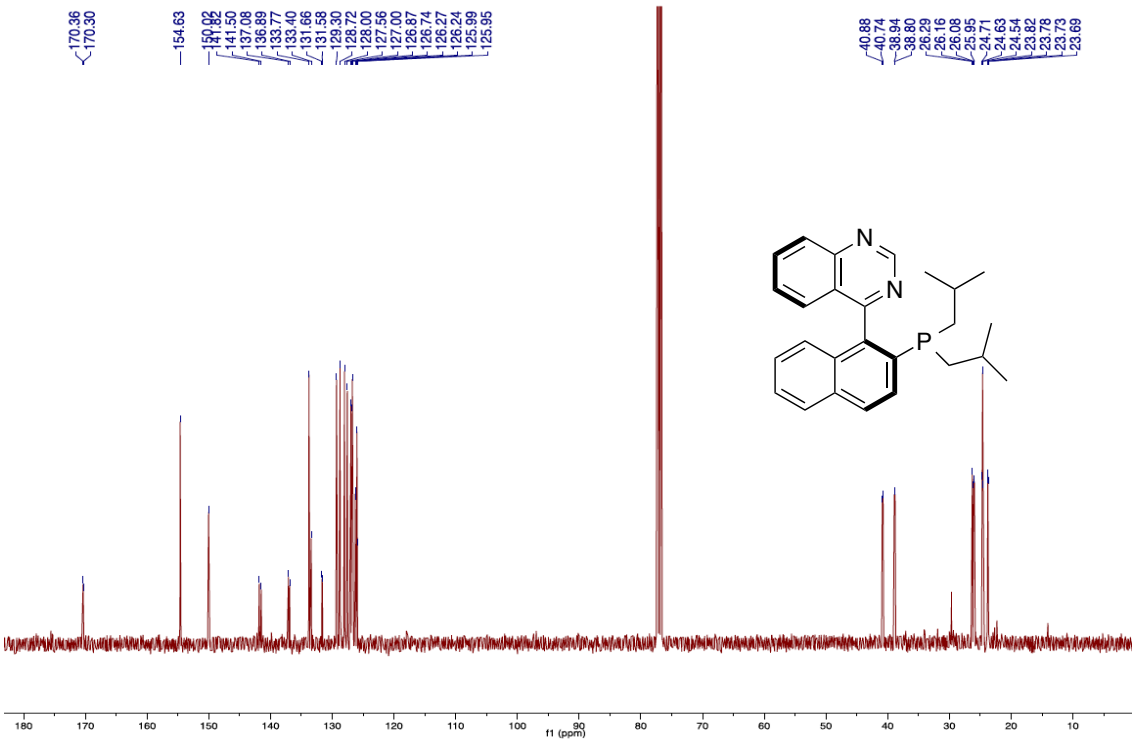


Figure S105. ^{13}C NMR (100 MHz, $CDCl_3$) of **(*S*)-3Ce**

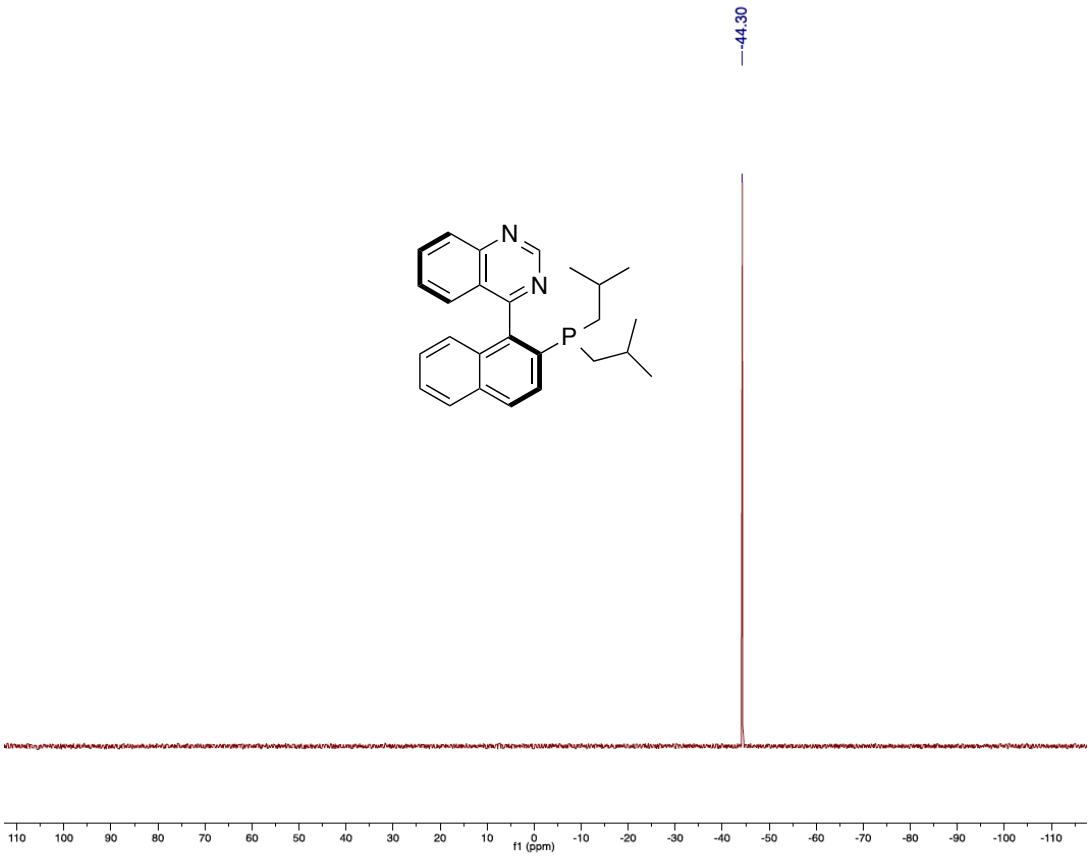
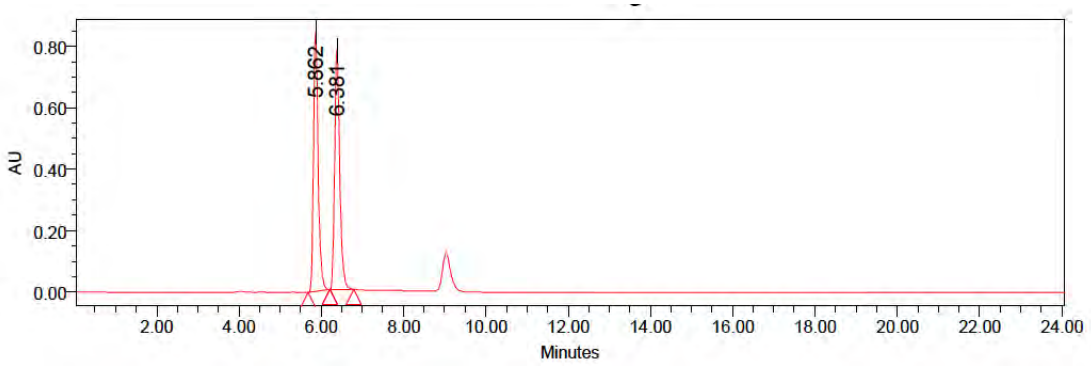
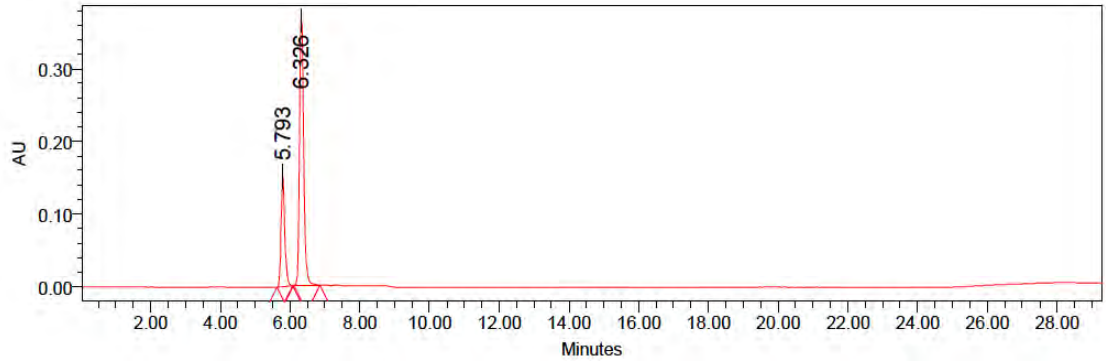


Figure S106. ^{31}P NMR (161 MHz, $CDCl_3$) of **(*S*)-3Ce**



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 225.0 nm	5.862	6595494	49.51	841443
2	PDA 225.0 nm	6.381	6726011	50.49	783165

Figure S107. Phosphine racemic sample: ADH column, Hex:Isop 85:15, T= 30°C, F= 1mL/min.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 225.0 nm	5.793	1132601	27.31	152813
2	PDA 225.0 nm	6.326	3015055	72.69	367993

Figure S108. Phosphine enantioriched sample: er 27.5:72.5.

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