Chiral Phosphoric Acid-Catalyzed Enantioselective Phosphinylation of 3,4-Dihydroisoquinolines with diarylphosphine oxides: Access to cyclic chiral α-amino diarylphosphine oxides

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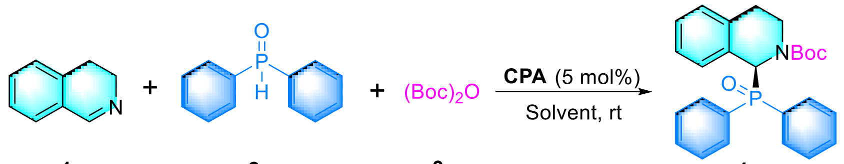
Table of Contents

1. General information

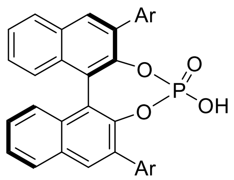
General information: Reagents and solvents were purchased from common commercial suppliers and were used without further purification. Column chromatography was generally performed on silica gel (200-300 mesh). Melting points were determined with a Büchi B-545 melting-point apparatus. 600MHz ^{1}H NMR and 151MHz ^{13}C NMR spectra were recorded on Varian VMS-600 spectrometers, respectively. The chemical shifts are reported in ppm (δ scale) relative to internal tetramethylsilane, and coupling constants are reported in hertz (Hz). High-resolution mass spectra (HRMS) were obtained on Agilent 6502 Q-TOF HPLC and mass spectrometry.

2. Reaction conditions optimization for the enantioselective phosphinylation of 3,4-dihydroisoquinoline.

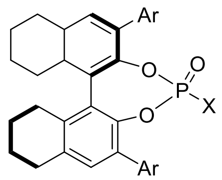
Table S1. Chiral Brønsted Acid Catalyst Evaluation[a]



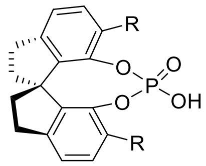
1a **2a** **3a** **4aaa**



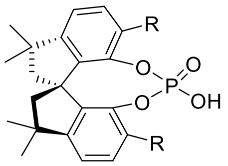
cat.1a, R = Ph, X = OH;
cat.1b, R = adamantane, X = OH;
cat.1c, R = 1-naphthyl, X = OH;
cat.1d, R = 2-naphthyl, X = OH;
cat.1e, R = 9-anthracenyl, X = OH;
cat.1f, R = 9-phenanthryl, X = OH;
cat.1g, R = 1-pyrenyl, X = OH;
cat.1h, R = $SiPh_3$, X = OH;
cat.1i, R = 4-$NO_2C_6H_4$, X = OH;
cat.1j, R = 4-$CF_3C_6H_4$, X = OH;
cat.1k, R = 4-PhC_6H_4, X = OH;
cat.1l, R = 4-*t*-BuC_6H_4, X = OH;
cat.1m,R = 4-$OMeC_6H_4$, X = OH;
cat.1n, R = 4-(2-naphthyl)C_6H_4, X = OH;
cat.1o, R = 2-OMe-5-*t*-BuC_6H_3, X = OH;
cat.1p, R = 2,6-$OMe_2C_6H_3$, X = OH;
cat.1q, R = 3,5-$(CF_3)_2C_6H_3$, X = OH;
cat.1r, R = 3,5-$Cl_2C_6H_3$, X = OH;
cat.1s, R = 3,5-$Me_2C_6H_3$, X = OH;
cat.1t, R = 3,5-*t*-$Bu_2C_6H_3$, X = OH;
cat.1u, R = 3,5-(3,5-*t*-$Bu_2C_6H_3)_2C_6H_3$, X = OH;
cat.1v, R = 3,5-*t*-Bu_2-4-$OMeC_6H_2$, X = OH;
cat.1w,R = 2,4,6-$Me_3C_6H_2$, X = OH;
cat.1x, R = 2,4,6-*i*-$Pr_3C_6H_2$, X = OH;
cat.1y, R = 2,4,6-$Ph_3C_6H_2$, X = OH;
cat.1z, R = 2,4,6-$Cy_3C_6H_2$, X = OH;
cat.1a', R = 2,4,6-$OMe_3C_6H_2$, X = OH;
cat.1b', R = 2,6-*i*-Pr_2-4-(9-anthracenyl)C_6H_2, X = OH;
cat.5a, R = 9-anthracenyl, X = NTf;
cat.5b, R = 9-phenanthryl, X = NTf;



cat.2a, R = Ph, X = OH;
cat.2b, R = 1-naphthyl, X = OH;
cat.2c, R = 2-naphthyl, X = OH;
cat.2d, R = 9-anthracenyl, X = OH;
cat.2e, R = 9-phenanthryl, X = OH;
cat.2f, R = 1-pyrenyl, X = OH;
cat.2g, R = $SiPh_3$, X = OH;
cat.2h, R = 4-ClC_6H_4, X = OH;
cat.2i, R = 4-$NO_2C_6H_4$, X = OH;
cat.2j, R = 4-$CF_3C_6H_4$, X = OH;
cat.2k, R = 4-PhC_6H_4, X = OH;
cat.2l, R = 4-*t*-BuC_6H_4, X = OH;
cat.2m,R = 4-$OMeC_6H_4$, X = OH;
cat.2n, R = 4-(2-naphthyl)C_6H_4, X = OH;
cat.2o, R = 3,5-$(CF_3)_2C_6H_3$, X = OH;
cat.2p, R = 3,5-$Me_2C_6H_3$, X = OH;
cat.2q, R = 3,5-$Ph_2C_6H_3$, X = OH;
cat.2r,R = 2,4,6-$Me_3C_6H_2$, X = OH;
cat.2s, R = 2,4,6-*i*-$Pr_3C_6H_2$, X = OH;
cat.2t, R = 3,5-*t*-Bu_2-4-$OMeC_6H_2$, X = OH;
cat.6a, R = 9-anthracenyl, X = NTf;
cat.6b, R = 9-phenanthryl, X = NTf;



cat.4a, R = 9-anthracenyl
cat.4b, R = 9-phenanthryl
cat.4c, R = 1-pyrenyl
cat.4d, R = $SiPh_3$
cat.4e, R = 4-$CF_3C_6H_4$
cat.4f, R = 4-PhC_6H_4
cat.4g, R = 4-*t*-BuC_6H_4
cat.4h, R = 4-(2-naphthyl)C_6H_4
cat.4i, R = 3,5-$(CF_3)_2C_6H_3$
cat.4j, R = 3,5-$Cl_2C_6H_3$
cat.4k, R = 3,5-$Me_2C_6H_3$
cat.4l, R = 3,5-$Ph_2C_6H_3$
cat.4m,R = 3,5-*t*-Bu_2-4-$OMeC_6H_2$
cat.4n, R = 2,4,6-$Me_3C_6H_2$
cat.4o, R = 2,4,6-*i*-$Pr_3C_6H_2$



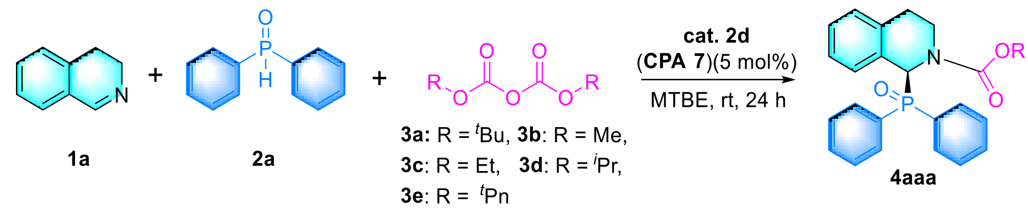
cat.3a, R = 9-anthracenyl
cat.3b, R = 9-phenanthryl
cat.3c, R = 2-naphthyl
cat.3d, R = 3,5-*t*-Bu_2-4-$OMeC_6H_2$
cat.3e,R = 2,4,6-$Me_3C_6H_2$
cat.3f, R = 2,4,6-*i*-$Pr_3C_6H_2$

Entry	cat.	Yield (%)[b]	ee (%)[c]
1	-	60	0
2	**cat.1a**	99	7
3	**cat.1b**	86	1
4	**cat.1c**	46	4
5	**cat.1d**	89	17
6	**cat.1e**	99	16
7	**cat.1f**	65	22
8	**cat.1g**	83	10
9	**cat.1h**	94	5
10	**cat.1i**	92	5
11	**cat.1j**	85	9
12	**cat.1k**	89	1
13	**cat.1l**	96	2
14	**cat.1m**	87	2
15	**cat.1n**	95	1
16	**cat.1o**	99	2
17	**cat.1p**	96	5
18	**cat.1q**	98	1
19	**cat.1r**	79	10
20	**cat.1s**	94	10
21	**cat.1t**	88	3
22	**cat.1u**	90	4
23	**cat.1v**	95	12
24	**cat.1w**	93	10
25	**cat.1x**	87	6
26	**cat.1y**	93	1
27	**cat.1z**	99	1
28	**cat.1a’**	87	1
29	**cat.1b’**	90	1
30	**cat.2a**	94	6
31	**cat.2b**	95	31
32	**cat.2c**	99	17
33	**cat.2d (CPA 7)**	**90**	**44**
34	**cat.2e**	99	34
35	**cat.2f**	99	39
36	**cat.2g**	80	0
37	**cat.2h**	95	16
38	**cat.2i**	80	0
39	**cat.2j**	98	6
40	**cat.2k**	95	8
41	**cat.2l**	99	6
42	**cat.2m**	97	6

43	**cat.2n**	95	6
44	**cat.2o**	95	0
45	**cat.2p**	88	4
46	**cat.2q**	90	25
47	**cat.2r**	96	33
48	**cat.2s**	99	6
49	**cat.2t**	98	4
50	**cat.3a**	84	22
51	**cat.3b**	99	2
52	**cat.3c**	85	1
53	**cat.3d**	90	1
54	**cat.3e**	93	0
55	**cat.3f**	99	3
56	**cat.4a**	95	0
57	**cat.4b**	90	2
58	**cat.4c**	99	1
59	**cat.4d**	98	0
60	**cat.4e**	92	2
61	**cat.4f**	90	1
62	**cat.4g**	84	0
63	**cat.4h**	88	1
64	**cat.4i**	96	1
65	**cat.4j**	99	8
66	**cat.4k**	87	1
67	**cat.4l**	95	1
68	**cat.4m**	98	0
69	**cat.4n**	99	0
70	**cat.4o**	99	0
71	**cat.5a**	89	19
72	**cat.5b**	95	27
73	**cat.6a**	70	17
74	**cat.6b**	63	15

[a]Reaction conditions: **1a** (0.2 mmol), **3a** (0.6 mmol) and **cat.1-6** (5 mol%) at 50°C for 0.5 h. Solvent (2 mL) and **2a** was added, and the mixture was stirred at rt for 24 h. [b]Yield was determined by HPLC analysis. [c]Determined by HPLC (Chiralcel OD-RH).

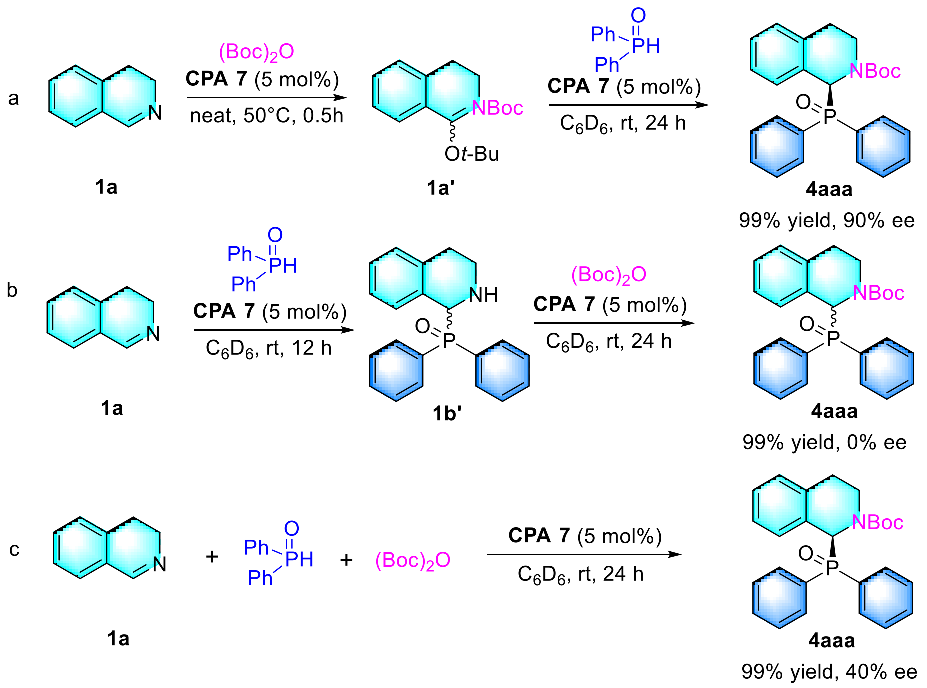
Table S2. Additional efforts at reaction optimization (solvent, temperature, additive, catalyst loading, concentration and activating reagents)[a]



Entry	Solvent	additive	Temp. (°C)	Yield (%)[b]	ee (%)[c]
1	PhMe	-	25	90	44
2	PhH	-	25	81	63
3	PhCl	-	25	52	27
4	$PhNO_2$	-	25	78	5
5	PhOMe	-	25	77	24
6	PhOEt	-	25	80	36
7	CCl_4	-	25	99	2
8	CH_2Cl_2	-	25	92	16
9	EA	-	25	99	21
10	CH_3CN	-	25	99	2
11	Acetone	-	25	22	16
12	Et_2O	-	25	35	14
13	*n*-Pr_2O	-	25	95	56
14	*i*-Pr_2O	-	25	98	47
15	*n*-Bu_2O	-	25	96	67
16	MTBE	-	25	96	79
17	THF	-	25	95	23
18	2-MeTHF	-	25	82	46
19	1,4-Dioxane	-	25	57	12
20	MTBE	3Å MS	25	99	88
21	MTBE	4Å MS	25	99	91
22	MTBE	5Å MS	25	99	85
23	MTBE	13X MS	25	99	88
24	MTBE	4Å MS	0	70(99[d])	91
25[e]	MTBE	4Å MS	35	99	85
26[f]	MTBE	4Å MS	25	60	90
27[g]	MTBE	4Å MS	25	99	91
26[h]	MTBE	4Å MS	25	73	91
27[i]	MTBE	4Å MS	25	99	89
28	PhH	4Å MS	25	99	90
29[j]	MTBE	4Å MS	25	95	30
30[k]	MTBE	4Å MS	25	80	40
31[l]	MTBE	4Å MS	25	87	73
32[m]	MTBE	4Å MS	25	99	80

[a]Reaction conditions: **1a** (0.2 mmol), 3 (0.3 mmol) and **cat.2d** (5 mol%) at 50°C for 0.5 h. Solvent (2 mL) and **2a** was added, and the mixture was stirred at rt for 24 h. [b]Yield was determined by HPLC analysis. [c]Determined by HPLC (Chiralcel OD-RH). [d]48 h. [e]12h. [f]**cat.2d** (2.5 mol%). [g]**cat.2d** (10 mol%), 12h. [h]0.05M. [i]0.2M. [j]**3b** was used. [k]**3c** was used. [l]**3d** was used. [m]**3e** was used.

3. Control and NMR tracking experiments



Scheme S1. Control experiments

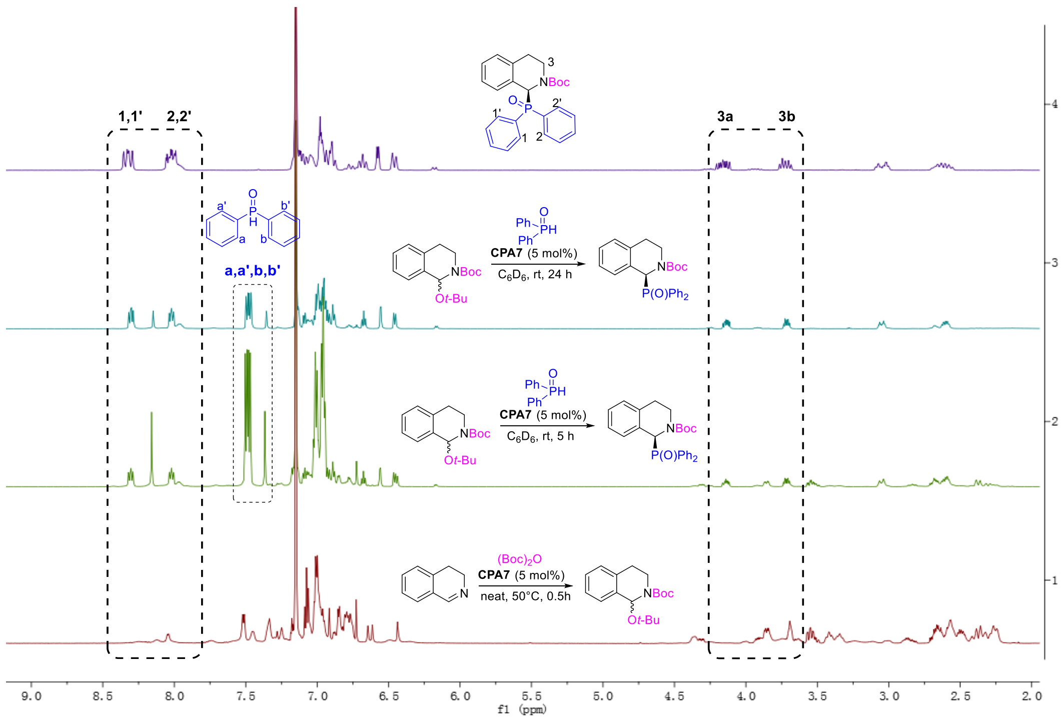


Figure S1 ^{1}H NMR of mixture at different reaction processes and times of **Schem S1a**.

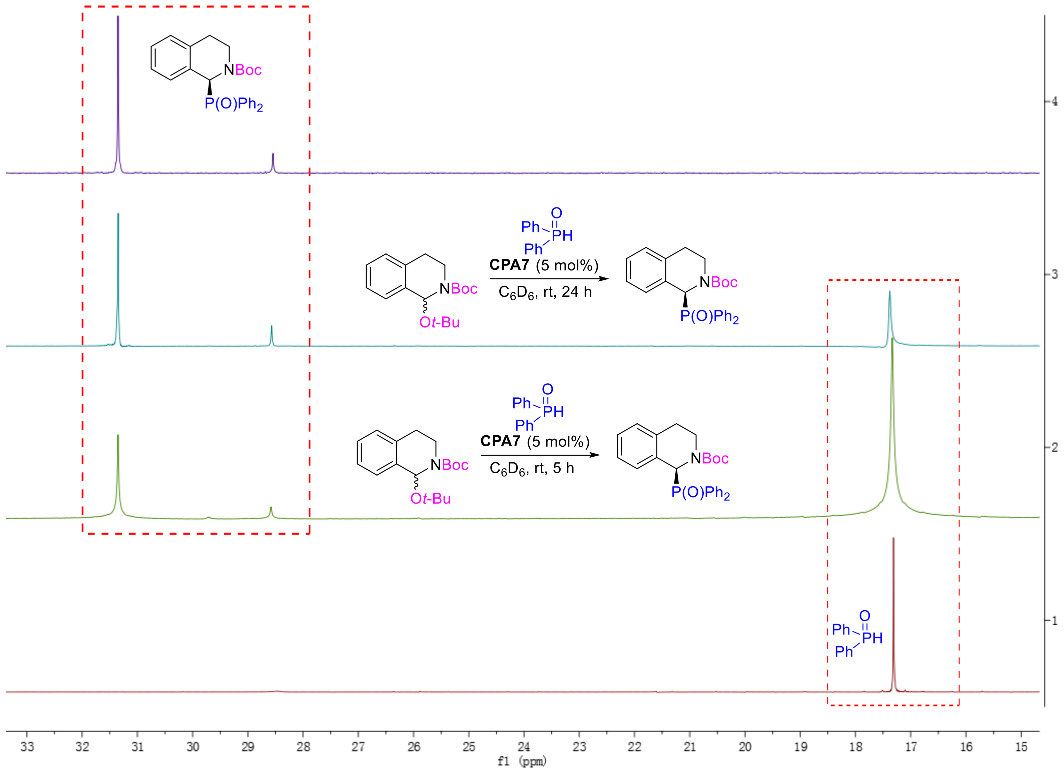


Figure S2. ^{31}P NMR of mixture at different reaction processes and times of **Schem S1a**.

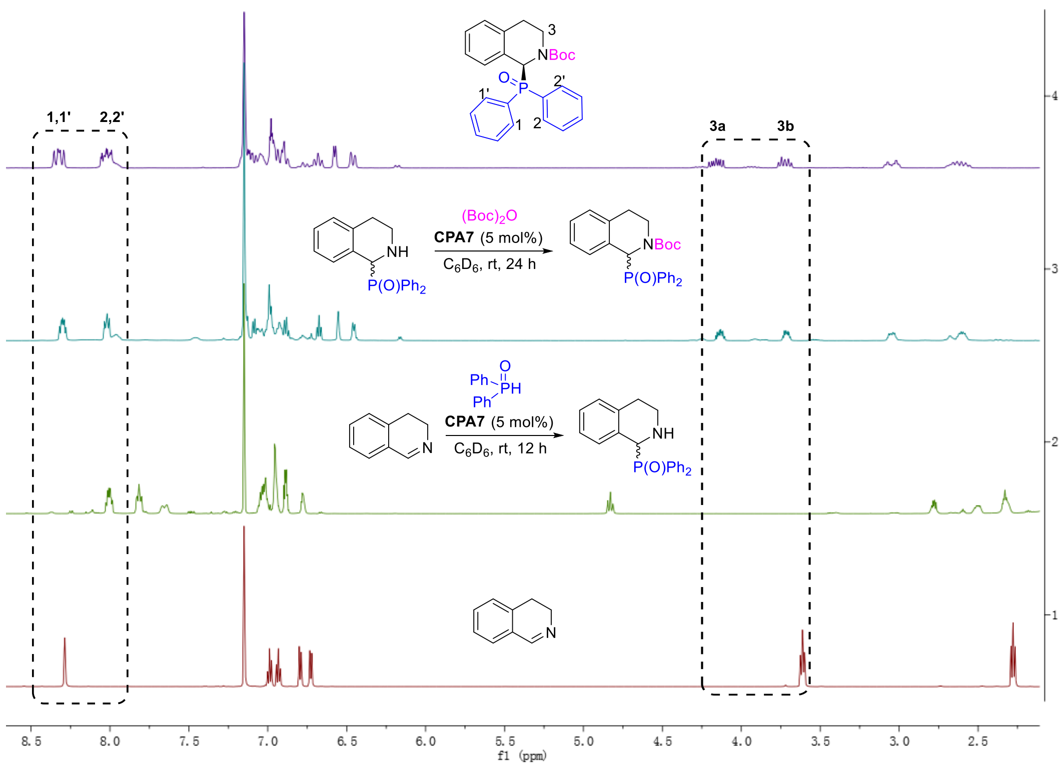


Figure S3. ^{1}H NMR of mixture at different reaction processes and times of **Schem S1b**.

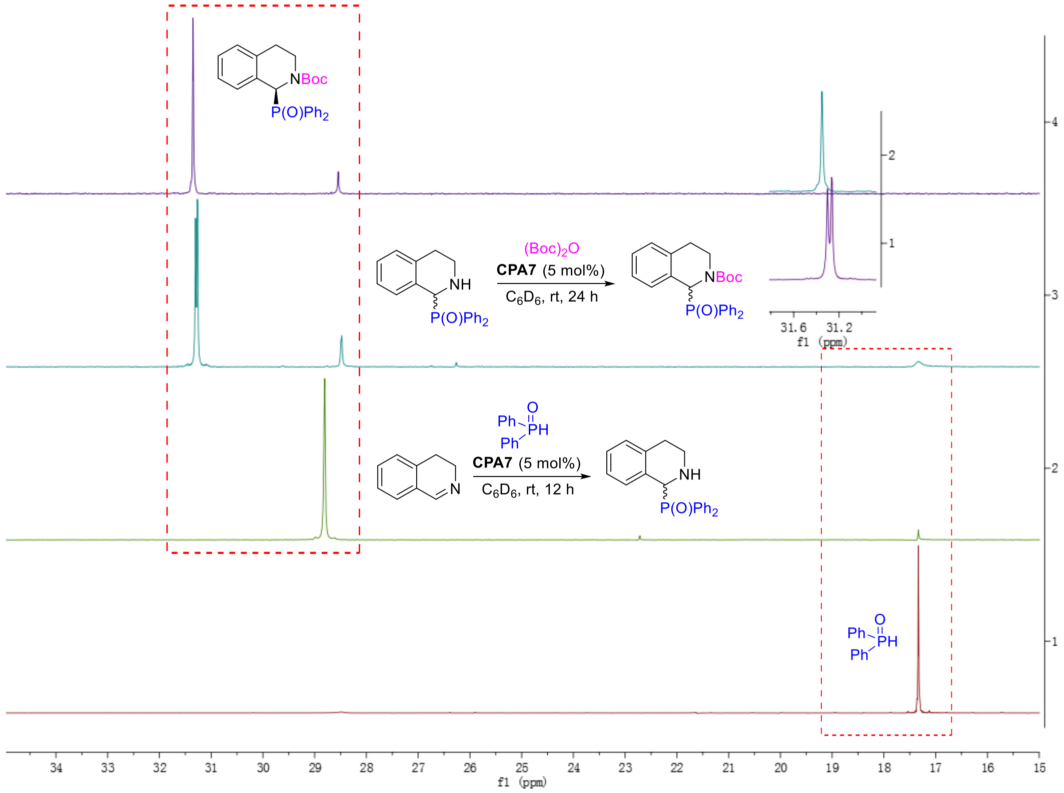


Figure S4. ^{31}P NMR of mixture at different reaction processes and times of **Schem S1b**.

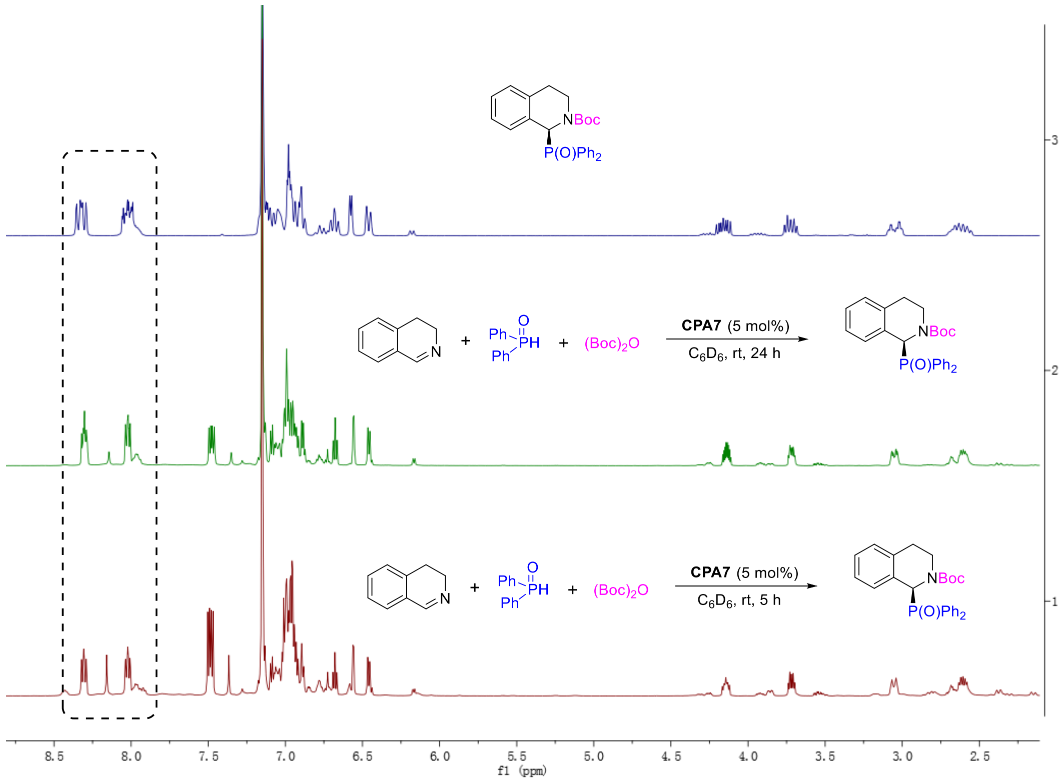


Figure S5 ^{1}H NMR of mixture at different reaction processes and times of **Schem S1c**.

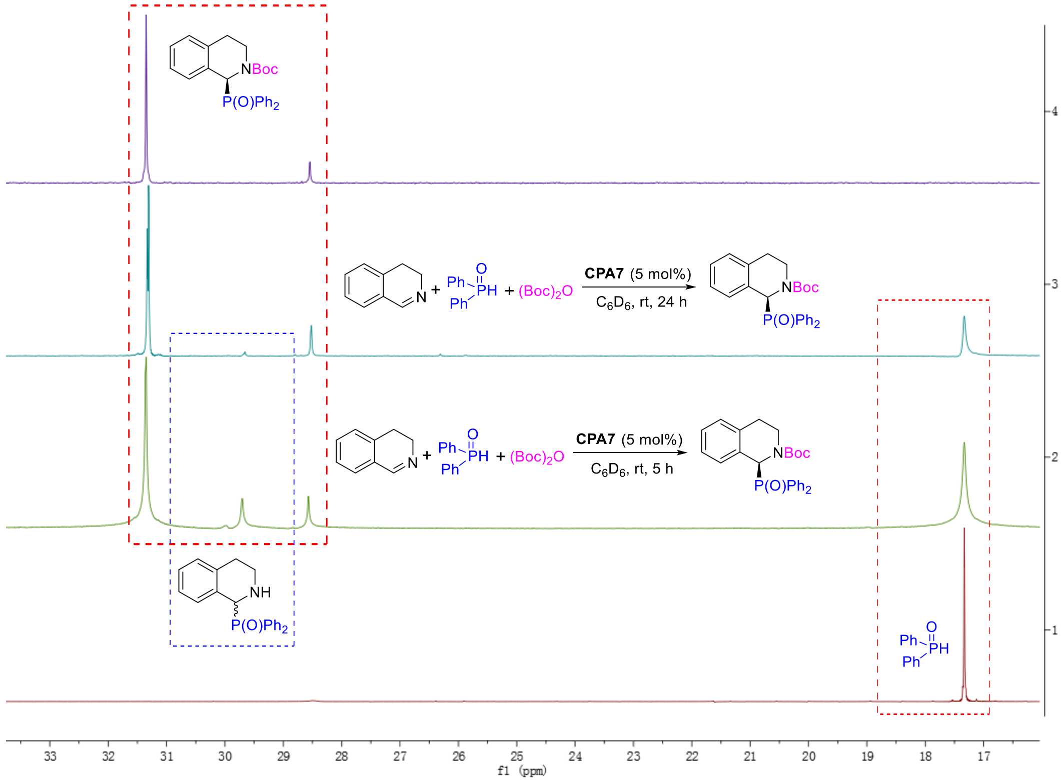
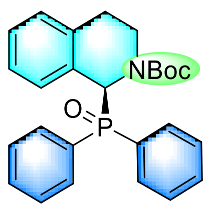


Figure S6 ^{31}P NMR of mixture at different reaction processes and times of **Schem S1c**.

4. General Procedure for Synthesis of *tert*-butyl-1-(diarylphosphoryl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylates.

A mixture of 3,4-dihydroisoquinoline **1** (0.2 mmol), catalyst **CPA7** (5 mol%) and $(Boc)_2O$ (0.3mmol) was stirred at 50℃ for 0.5 h. Then 4Å MS (50 mg), MTBE or benzene (2 mL) and diarylphosphine oxide **2** (0.24mmol) was added, and the reaction was stirred at room temperature for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography with PE/EA (2/1) to obtain tert-butyl-1-(diphenylphosphoryl)-3,4- dihydroisoquinoline-2(1H)-carboxylates **4**.

5. Characterization of products



4aaa

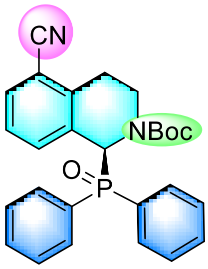
99% yield, 91% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.37 - 8.24 (m, 2H), 8.02 (ddd, *J* = 10.5, 7.8, 1.6 Hz, 2H), 7.76 - 7.73 (m, 2H), 7.11 - 7.02 (m, 2H), 7.01 - 6.95 (m, 2H), 6.91 (dd, *J* = 21.5, 7.4 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 4.14 (ddd, *J* = 12.9, 8.9, 5.3 Hz, 1H), 3.77 - 3.67 (m, 1H), 3.05 (ddd, *J* = 15.9, 5.0, 3.4 Hz, 1H), 2.64 - 2.53 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 155.26 (d, *J* = 3.3 Hz), 137.33 (d, *J* = 3.9 Hz), 133.85 (d, *J* = 18.4 Hz), 133.23 (d, *J* = 24.4 Hz), 132.49, 132.45, 132.43, 132.39, 132.03 (d, *J* = 2.7 Hz), 131.85 (d, *J* = 3.0 Hz), 131.22, 129.68 (d, *J* = 2.6 Hz), 129.06 (d, *J* = 11.2 Hz), 128.60, 128.47, 128.31, 128.01 (d, J = 3.3 Hz), 127.93 (d, J = 2.8 Hz), 126.10 (d, J = 2.6 Hz), 80.2, 57.3 (d, J = 73.9 Hz), 41.8, 28.8, 28.7 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.5 (for major rotamer), 28.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{28}NO_3PNa$ $[M+Na]^+$ 456.1699, found 456.1704; $[\alpha]_D^{25}$ = + 6.1 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 60/40, v/v, 1.0 mL/min, 280 nm, t_R (major) = 17.4 min, t_R (minor) = 19.1 min), 91% *ee*.



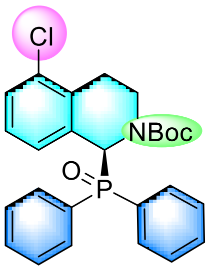
4baa
86% yield, 92% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.27 - 8.18 (m, 2H), 7.97 - 7.90 (m, 2H), 7.12 (m, 2H), 7.09 - 7.04 (m, 1H), 7.03 - 6.92 (m, 3H), 6.71 (s, 1H), 6.49 (d, J = 7.9 Hz, 1H), 6.38 (d, J = 4.7 Hz, 1H), 6.10 (d, J = 7.2 Hz, 1H), 3.98 (ddd, J = 13.2, 9.1, 5.3 Hz, 1H), 3.66 - 3.54 (m, 1H), 2.71 (d, J = 15.3 Hz, 1H), 2.32 - 2.23 (m, 1H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 155.00 (d, J = 3.2 Hz), 138.29 (d, J = 3.7 Hz), 136.03, 133.24, 133.08 (d, J = 1.8 Hz), 132.95, 132.64, 132.55 (d, J = 2.8 Hz), 132.38, 132.33 (d, J = 9.5 Hz), 132.20 (d, J = 8.7 Hz), 129.25 (d, J = 11.3 Hz), 128.76 (d, J = 11.7 Hz). 129.25 (d, J = 2.3 Hz), 128.68, 128.47, 128.31, 119.01, 112.17 (d, J = 2.7 Hz), 80.69, 57.13 (d, J = 72.0 Hz), 41.00, 28.52 (3), 28.18.

^{31}P NMR (243 MHz, C_6D_6): δ 31.7 (for major rotamer), 28.9 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{27}N_2O_3PNa$ $[M+Na]^+$ 481.1652, found:481.1659; $[\alpha]_D^{25}$ = + 15.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 65/35, v/v, 1.0 mL/min, 280 nm, t_R (major) = 13.0 min, t_R (minor) = 15.0 min), 92% *ee*.



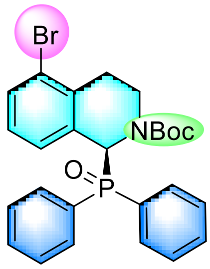
4caa
83% yield, 95% ee

^{1}H NMR (600 MHz, C_6D_6) δ: 8.41 - 8.20 (m, 2H), 8.00 (ddd, J = 10.6, 7.8, 1.5 Hz, 2H), 7.14 - 7.11 (m, 2H), 7.10 - 7.04 (m, 1H), 7.04 - 6.95 (m, 4H), 6.51 (d, J = 4.2 Hz, 1H), 6.39 (t, J = 7.8 Hz, 1H), 6.27 (d, J = 7.7 Hz, 1H), 4.11 (ddd, J = 13.4, 10.3, 5.1 Hz, 1H), 3.90 - 3.72 (m, 1H), 3.11 - 2.96 (m, 1H), 2.76 - 2.64 (m, 1H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 154.97 (d, J = 3.7 Hz), 135.39 (d, J = 2.2 Hz), 135.05 (d, J = 3.8 Hz), 134.00, 133.38(d, J = 4.6 Hz), 133.37, 132.73, 132.34 (d, J = 7.2 Hz), 132.28 (d, J = 6.6 Hz), 132.15 (d, J = 2.6 Hz), 132.01 (d, J = 2.6 Hz), 129.17 (d, J = 11.2 Hz), 128.75 (d, J = 8.4 Hz), 128.68, 128.47, 128.31, 126.81 (d, J = 2.4 Hz), 126.42 (d, J = 2.9 Hz), 80.44, 56.78 (d, J = 73.1 Hz), 40.81, 28.54 (3), 26.76.

^{31}P NMR (243 MHz, C_6D_6): δ 31.6 (for major rotamer), 28.7 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}ClNO_3PNa$ $[M+Na]^+$ 490.1309, found 490.1316; $[\alpha]_D^{25}$ = + 36.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 55/45, v/v, 1.0 mL/min, 280 nm, t_R (major) = 8.1 min, t_R (minor) = 9.2 min), 95% *ee*.



4daa

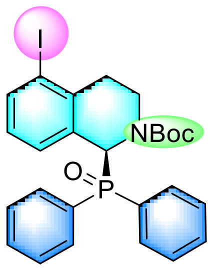
91% yield, 97% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.37 – 8.18 (m, 2H), 8.00 (ddd, J = 10.6, 7.8, 1.5 Hz, 2H), 7.18 (dt, J = 7.6, 2.2 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 6.94 (m, 4H), 6.49 (d, J = 4.2 Hz, 1H), 6.30 (d, J = 5.2 Hz, 2H), 4.09 (ddd, J = 13.4, 10.2, 5.1 Hz, 1H), 3.83 – 3.69 (m, 1H), 3.12 – 2.96 (m, 1H), 2.81 – 2.64 (m, 1H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 154.95 (d, J = 3.6 Hz), 136.63 (d, J = 3.8 Hz), 133.97, 133.60, 133.36 (d, J = 4.3 Hz), 132.71, 132.34 (d, J = 7.9 Hz), 132.29 (d, J = 7.3 Hz), 132.15 (d, J = 2.6 Hz), 132.06 (d, J = 2.6 Hz), 132.01 (d, J = 2.6 Hz), 129.17 (d, J = 11.3 Hz), 128.73 (d, J = 11.3 Hz), 128.68, 128.47, 128.31, 127.20 (d, J = 2.3 Hz), 127.07 (d, J = 2.9 Hz), 126.36 (d, J = 2.2 Hz), 80.45, 56.91 (d, J = 73.1 Hz), 41.05, 29.69, 28.54 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.7 (for major rotamer), 28.8 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}ClNO_3PNa$ $[M+Na]^+$ 534.0804, found 534.0808; $[\alpha]_D^{25}$ = + 50.2 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 65/35, v/v, 1.0 mL/min, 280 nm, t_R (major) = 33.6 min, t_R (minor) = 36.6 min), 97% *ee*.



4eaa

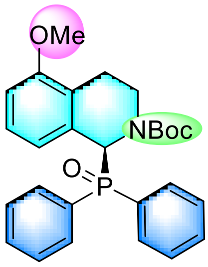
83% yield, 95% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.36 – 8.21 (m, 2H), 8.07 – 7.95 (m, 2H), 7.47 (d, J = 7.9 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 7.03 (m, 1H), 6.99 (tt, J = 8.7, 6.1 Hz, 3H), 6.45 (d, J = 4.0 Hz, 1H), 6.33 (d, J = 7.6 Hz, 1H), 6.14 (t, J = 7.7 Hz, 1H), 4.07 (ddd, J = 13.4, 10.0, 5.2 Hz, 1H), 3.74 (ddd, J = 10.4, 5.6, 3.7 Hz, 1H), 3.02 (d, J = 16.6 Hz, 1H), 2.70 (dt, J = 16.4, 7.2 Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 154.92 (d, J = 3.6 Hz), 139.63 (d, J = 3.8 Hz), 138.82 (d, J = 2.6 Hz), 133.97, 133.37, 133.22, 132.73, 132.35 (d, J = 8.8 Hz), 132.30 (d, J = 7.8 Hz), 132.13 (d, J = 2.6 Hz), 131.99 (d, J = 2.6 Hz), 129.16 (d, J = 11.2 Hz), 128.72 (d, J = 12.0 Hz), 128.68, 128.47, 128.31, 128.00 (d, J = 2.9 Hz), 127.61 (d, J = 2.2 Hz), 103.36 (d, J = 2.2 Hz), 80.44, 57.12 (d, J = 73.0 Hz), 41.58, 35.17, 28.54 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.6 (for major rotamer), 28.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}INO_3PNa$ $[M+Na]^+$ 582.0665, found 582.0669; $[\alpha]_D^{25}$ = + 53.4 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 50/50, v/v, 1.0 mL/min, 280 nm, t_R (major) = 9.8 min, t_R (minor) = 11.2 min), 95% *ee*.



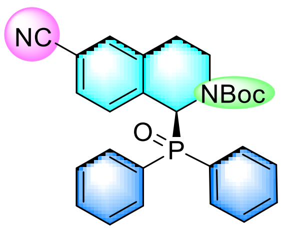
4faa
92% yield, 89% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.37 – 8.29 (m, 2H), 8.11 – 8.04 (m, 2H), 7.15 – 7.11 (m, 1H), 7.10 – 7.03 (m, 2H), 7.01 (dt, J = 7.6, 3.5 Hz, 3H), 6.68 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 4.2 Hz, 1H), 6.29 (d, J = 8.3 Hz, 1H), 6.19 (d, J = 7.8 Hz, 1H), 4.28 – 4.19 (m, 1H), 4.00 – 3.89 (m, 1H), 3.23 (s, 3H), 3.15 – 3.07 (m, 1H), 2.89 – 2.81 (m, 1H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 158.02 (d, J = 2.1 Hz), 155.21 (d, J = 3.9 Hz), 134.51, 133.92, 133.28, 132.40 (d, J = 2.6 Hz), 132.34 (d, J = 3.1 Hz), 132.14, 131.98 (d, J = 2.7 Hz), 131.83 (d, J = 2.6 Hz), 129.10 (d, J = 11.2 Hz), 128.68 (d, J = 11.4 Hz), 128.68, 128.47, 128.31, 126.48 (d, J = 2.4 Hz), 125.89 (d, J = 3.9 Hz), 120.29 (d, J = 2.8 Hz), 109.24 (d, J = 2.6 Hz), 80.12, 56.76 (d, J = 73.8 Hz), 55.12, 41.06, 28.58 (3), 23.01.

^{31}P NMR (243 MHz, C_6D_6): δ 31.5 (for major rotamer), 28.7 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{30}NO_4PNa$ $[M+Na]^+$ 486.1805, found 486.1810; $[\alpha]_D^{25}$ = + 34.8 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 50/50, v/v, 1.0 mL/min, 280 nm, t_R (major) = 5.4 min, t_R (minor) = 6.6 min), 89% *ee*.
C27H30NO4P+Na,Clac:486.1805, Found:486.1810



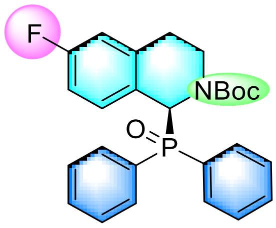
4gaa
90% yield, 89% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.23 – 8.16 (m, 2H), 7.98 (ddd, J = 10.5, 7.6, 1.7 Hz, 2H), 7.11 (ddd, J = 9.0, 5.3, 2.2 Hz, 2H), 7.06 (td, J = 7.3, 1.2 Hz, 1H), 7.03 – 6.96 (m, 3H), 6.85 (d, J = 7.6 Hz, 1H), 6.39 (d, J = 4.2 Hz, 1H), 6.35 (d, J = 7.8 Hz, 1H), 6.25 (t, J = 7.7 Hz, 1H), 3.89 (ddd, J = 13.4, 9.8, 5.1 Hz, 1H), 3.66 – 3.57 (m, 1H), 3.12 (dt, J = 10.9, 5.0 Hz, 1H), 2.78 – 2.67 (m, 1H), 1.22 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 154.87 (d, J = 3.1 Hz), 140.63 (d, J = 3.8 Hz), 133.44, 132.84, 132.69, 132.55, 132.37 (d, J = 2.6 Hz), 132.29 (d, J = 9.2 Hz), 132.23 (d, J = 8.8 Hz), 132.19, 131.94 (d, J = 2.3 Hz), 131.44 (d, J = 2.9 Hz), 129.28 (d, J = 11.3 Hz), 128.78 (d, J = 11.7 Hz), 128.68, 128.47, 128.31. 126.15 (d, J = 2.1 Hz), 117.76, 114.26 (d, J = 1.9 Hz), 80.70, 56.69 (d, J = 72.5 Hz), 40.48, 28.50 (3), 27.54.

^{31}P NMR (243 MHz, C_6D_6): δ 32.1 (for major rotamer), 29.1 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{27}NO_3PNa$ $[M+Na]^+$ 481.1652, found 481.1658; $[\alpha]_D^{25}$ = + 26.6 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 68/32, v/v, 1.0 mL/min, 280 nm, t_R (major) = 65.5 min, t_R (minor) = 70.6 min), 89% *ee*.



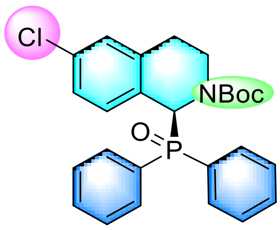
4haa
93% yield, 88% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.47 – 8.19 (m, 2H), 8.10 – 7.77 (m, 2H), 7.15 – 7.10 (m, 1H), 7.10 – 7.01 (m, 2H), 7.01 – 6.92 (m, 3H), 6.57 (dd, J = 9.2, 2.3 Hz, 1H), 6.46 (d, J = 2.9 Hz, 1H), 6.32 (td, J = 8.5, 2.5 Hz, 1H), 6.27 – 6.20 (m, 1H), 4.07 (ddd, J = 13.1, 8.9, 5.3 Hz, 1H), 3.71 – 3.57 (m, 1H), 2.90 (dt, J = 16.0, 4.2 Hz, 1H), 2.47 – 2.38 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 162.74 (dd, $J_{C\text{-}F}$ = 245.7, $J_{C\text{-}P}$ = 2.9 Hz), 155.18 (d, J = 3.5 Hz), 139.78 (dd, $J_{C\text{-}F}$ = 7.8, $J_{C\text{-}P}$ = 3.7 Hz), 133.61 (d, $J_{C\text{-}F}$ = 29.1 Hz), 133.11, 132.87, 132.42 (d, J = 9.3 Hz), 132.33 (d, J = 8.6 Hz), 132.12 (d, J = 2.6 Hz), 131.95 (d, J = 2.7 Hz), 129.45 (dd, $J_{C\text{-}F}$ = 8.2, $J_{C\text{-}P}$ = 3.2 Hz), 129.11 (d, J = 11.1 Hz), 128.70 (d, J = 11.1 Hz), 128.68, 128.47, 128.31, 126.86 (d, J = 2.7 Hz), 116.31 (d, J = 21.3 Hz), 113.39 – 112.70 (m), 80.36, 56.66 (d, J = 74.4 Hz), 41.22, 28.72, 28.57 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.2 (d, $J_{P\text{-}F}$ = 4.3 Hz), 28.4 (d, $J_{P\text{-}F}$ = 3.9 Hz).

HRMS (m/z) calcd for $C_{26}H_{27}FNO_3PNa$ $[M+Na]^+$ 474.1605, found 474.1613; $[\alpha]_D^{25}$ = + 18.4(c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.0 min, t_R (minor) = 6.1 min), 88% *ee*.



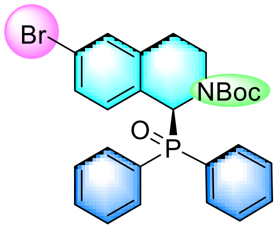
4iaa
91% yield, 93% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.31 – 8.20 (m, 2H), 7.96 (ddd, J = 10.6, 7.8, 1.5 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.10 – 7.00 (m, 2H), 7.00 – 6.94 (m, 3H), 6.88 (s, 1H), 6.60 (dd, J = 8.2, 1.9 Hz, 1H), 6.42 (d, J = 3.4 Hz, 1H), 6.16 (dd, J = 8.2, 1.3 Hz, 1H), 4.02 (ddd, J = 13.1, 9.1, 5.3 Hz, 1H), 3.68 – 3.60 (m, 1H), 2.88 – 2.80 (m, 1H), 2.44 – 2.36 (m, 1H), 1.24 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.14 (d, J = 3.3 Hz), 139.25 (d, J = 3.8 Hz), 133.79 (d, J = 3.3 Hz), 133.11, 132.90, 132.38 (d, J = 9.7 Hz), 132.38 – 132.27 (m), 132.28 (d, J = 8.0 Hz), 132.11 (d, J = 2.6 Hz), 129.80 (d, J = 1.8 Hz), 129.39, 129.20 (d, J = 11.3 Hz), 129.12 (d, J = 3.2 Hz), 128.75 (d, J = 11.7 Hz), 128.68, 128.47, 128.31, 126.28 (d, J = 2.4 Hz), 104.67 (d, J = 2.8 Hz), 80.51, 56.71 (d, J = 73.8 Hz), 41.18, 28.54 (3), 28.45.

^{31}P NMR (243 MHz, C_6D_6): δ 32.4 (for major rotamer), 29.4 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}ClNO_3PNa$ $[M+Na]^+$ 490.1309, found 490.1313; $[\alpha]_D^{25}$ = + 20.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 5.1 min, t_R (minor) = 8.1 min), 93% *ee*.



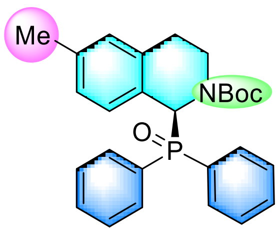
4jaa
93% yield, 93% ee

^{1}H NMR (600 MHz, C_6D_6): δ 8.32 – 8.20 (m, 2H), 8.02 – 7.80 (m, 2H), 7.14 – 7.11 (m, 1H), 7.08 (td, J = 7.4, 1.2 Hz, 1H), 7.02 (s, 2H), 7.00 – 6.92 (m, 3H), 6.75 (dd, J = 8.2, 1.6 Hz, 1H), 6.41 (d, J = 3.8 Hz, 1H), 6.09 (dd, J = 8.2, 1.3 Hz, 1H), 4.06 (ddd, J = 13.0, 9.1, 5.3 Hz, 1H), 3.68 – 3.58 (m, 1H), 2.89 – 2.76 (m, 1H), 2.43 – 2.31 (m, 1H), 1.24 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 155.15 (d, J = 3.5 Hz), 139.65 (d, J = 3.8 Hz), 133.48 (d, J = 26.5 Hz), 132.97, 132.75, 132.68 (d, J = 1.9 Hz), 132.39 (d, J = 9.3 Hz), 132.30 (d, J = 8.7 Hz), 132.16 (d, J = 2.6 Hz), 131.99 (d, J = 2.6 Hz), 130.19, 129.43 (d, J = 3.2 Hz), 129.13 (d, J = 2.3 Hz), 129.12 (d, J = 11.2 Hz), 128.71 (d, J = 8.8 Hz), 128.68, 128.47 , 128.31, 121.94 (d, J = 3.4 Hz), 80.42, 56.76 (d, J = 73.7 Hz), 41.19, 28.56 (3), 28.40.

^{31}P NMR (243 MHz, C_6D_6): δ 31.1 (for major rotamer), 28.3 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}BrNO_3PNa$ $[M+Na]^+$ 534.0804, found 534.0806; $[\alpha]_D^{25}$ = + 24.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 55/45 v/v, 1.0 mL/min, 280 nm, t_R (major) = 8.5 min, t_R (minor) = 12.6 min), 93% *ee*.



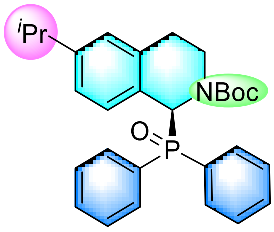
4kaa
99% yield, 79% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.38 – 8.27 (m, 2H), 8.03 (ddd, J = 10.5, 7.7, 1.6 Hz, 2H), 7.20 – 7.13 (m, 1H), 7.11 – 7.03 (m, 2H), 7.03 – 6.95 (m, 3H), 6.70 (s, 1H), 6.57 (d, J = 3.2 Hz, 1H), 6.50 (d, J = 7.7 Hz, 1H), 6.37 (dd, J = 7.8, 1.3 Hz, 1H), 4.21 (ddd, J = 12.9, 9.0, 5.3 Hz, 1H), 3.83 – 3.71 (m, 1H), 3.06 (ddd, J = 15.9, 4.9, 3.3 Hz, 1H), 2.68 – 2.57 (m, 1H), 2.00 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.32 (d, J = 3.7 Hz), 137.34 (d, J = 2.8 Hz), 137.13 (d, J = 3.8 Hz), 134.13, 133.98, 133.53, 133.35, 132.48 (d, J = 3.8 Hz), 132.42 (d, J = 3.2 Hz), 131.95 (d, J = 2.6 Hz), 131.80 (d, J = 2.6 Hz), 130.41 (d, J = 2.0 Hz), 129.03 (d, J = 11.1 Hz), 128.67, 128.47, 128.31, 128.12, 127.88 (d, J = 3.3 Hz), 126.93 (d, J = 2.3 Hz), 80.14, 57.01 (d, J = 74.5 Hz), 41.80, 28.81, 28.61 (3), 21.37.

^{31}P NMR (243 MHz, C_6D_6): δ 31.1 (for major rotamer), 28.4 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{30}NO_3PNa$ $[M+Na]^+$ 470.1856, found 470.1862; $[\alpha]_D^{25}$ = + 12.9 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.1 min, t_R (minor) = 5.4 min), 79% *ee*.



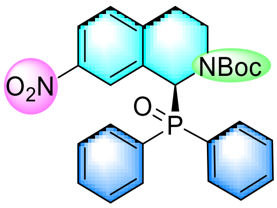
4laa
86% yield, 42% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.38 – 8.27 (m, 2H), 8.04 (ddd, *J* = 10.5, 7.8, 1.5 Hz, 2H), 7.19 – 7.12 (m, 1H), 7.12 – 7.03 (m, 2H), 7.02 – 6.96 (m, 3H), 6.87 (s, 1H), 6.59 (dd, *J* = 9.6, 2.1 Hz, 2H), 6.45 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.83 – 3.71 (m, 1H), 3.08 (ddd, *J* = 15.9, 4.9, 3.2 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.58 (ddt, *J* = 20.3, 13.6, 6.9 Hz, 1H), 1.26 (s, 9H), 1.11 – 1.04 (m, 6H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.30 (d, *J* = 3.5 Hz), 148.37 (d, *J* = 2.8 Hz), 137.12 (d, *J* = 3.8 Hz), 134.08, 133.96, 133.49, 133.33, 132.48 (d, *J* = 4.2 Hz), 132.42 (d, *J* = 4.9 Hz), 131.97 (d, *J* = 2.6 Hz), 131.80 (d, *J* = 2.7 Hz), 129.05 (d, *J* = 11.1 Hz), 128.67, 128.65 (d, *J* = 11.1 Hz), 128.47, 128.31, 128.01 (d, *J* = 3.2 Hz), 127.78 (d, *J* = 1.8 Hz), 124.38 (d, *J* = 2.3 Hz), 80.15, 57.00 (d, *J* = 74.5 Hz), 41.82, 34.41, 28.98, 28.62 (3), 24.39, 24.32.

^{31}P NMR (243 MHz, C_6D_6): δ 31.3 (for major rotamer), 28.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{29}H_{34}NO_3PNa$ $[M+Na]^+$ 498.2169, found 498.2175; $[\alpha]_D^{25}$ = + 12.3 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 55/45 v/v, 1.0 mL/min, 280 nm, t_R (major) = 8.3 min, t_R (minor) = 9.6 min), 42% *ee*.



4maa
52% yield, 89% ee

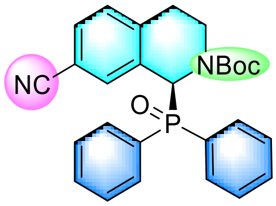
^{1}H NMR (600 MHz, C_6D_6) δ 8.30 – 8.20 (m, 2H), 7.89 – 7.80 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.11 – 7.02 (m, 4H), 6.99 (td, *J* = 7.5, 2.8 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 4.0 Hz, 1H), 4.19 (ddd, *J* = 13.2, 9.5, 5.2 Hz, 1H), 3.78 – 3.60 (m, 1H), 2.79 (d, *J* = 16.3 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 167.84, 154.95 (d, *J* = 3.5 Hz), 146.32, 144.35 (d, *J* = 3.5 Hz), 132.85 (d, *J* = 2.6 Hz), 132.42 (d, *J* = 9.4 Hz), 132.33, 132.22 (d, *J* = 2.6 Hz), 132.04 (d, *J* = 8.6 Hz), 131.11, 130.22, 129.49 (d, *J* = 11.4 Hz), 128.79 (d, *J* = 11.6 Hz), 128.68, 128.47, 128.31, 122.97 (d, *J* = 2.9 Hz), 122.41 (d, *J* = 2.3 Hz), 80.73, 56.67 (d, *J* = 73.0 Hz), 40.83, 28.75, 28.50 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.8 (for major rotamer), 29.7 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}N_2O_5PNa$ $[M+Na]^+$ 501.1550, found 501.1556; $[\alpha]_D^{25}$ = + 12.7 (c

= 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 70/30 v/v, 1.0 mL/min, 280 nm, t_R (major) = 41.3 min, t_R (minor) = 44.4 min), 89% *ee*.



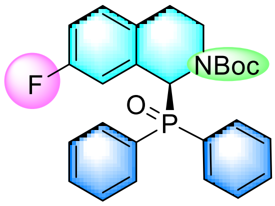
4naa
86% yield, 90% ee

^{1}H NMR (600 MHz, C_6D_6) δ 7.88 (dd, J = 11.4, 7.6 Hz, 2H), 7.81 (dd, J = 10.8, 7.7 Hz, 2H), 7.53 (q, J = 10.0, 8.7 Hz, 1H), 7.47 (td, J = 7.7, 2.7 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.36 (td, J = 7.6, 2.7 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.19 – 7.07 (m, 1H), 6.41 (s, 1H), 6.06 (d, J = 3.8 Hz, 1H), 3.84 – 3.66 (m, 2H), 3.11 – 3.04 (m, 1H), 2.79 (dt, J = 16.2, 7.5 Hz, 1H), 1.17 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.32, 141.00, 131.78 (d, J = 2.8 Hz), 131.03 (d, J = 2.7 Hz), 130.59, 130.55, 130.53, 130.51, 130.46, 129.87 (d, J = 3.0 Hz), 129.60 (d, J = 5.0 Hz), 129.56, 129.01, 128.08, 128.01, 127.38, 127.30, 117.39, 108.47 (d, J = 2.4 Hz), 79.91, 54.92 (d, J = 72.7 Hz), 39.20, 27.43, 27.12(2), 27.02.

^{31}P NMR (243 MHz, C_6D_6): δ 32.5 (for major rotamer), 29.9 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{27}N_2O_3PNa$ $[M+Na]^+$ 481.1652, found 481.1656; $[\alpha]_D^{25}$ = + 37.1 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 72/28 v/v, 1.0 mL/min, 280 nm, t_R (major) = 34.2 min, t_R (minor) = 36.9 min), 90% *ee*.



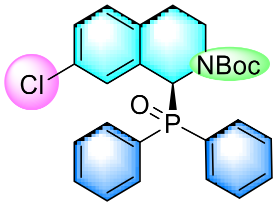
4oaa
92% yield, 94% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.36 – 8.21 (m, 2H), 7.94 (ddt, J = 10.8, 6.7, 1.6 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.08 (dq, J = 8.4, 2.3, 1.9 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.99 – 6.89 (m, 3H), 6.64 – 6.60 (m, 2H), 6.46 (d, J = 4.2 Hz, 1H), 6.13 – 6.08 (m, 1H), 4.17 (ddd, J = 12.9, 9.5, 5.1 Hz, 1H), 3.74 (dddd, J = 13.0, 6.0, 4.6, 1.1 Hz, 1H), 2.89 – 2.76 (m, 1H), 2.61 – 2.40 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 160.48 (d, J = 2.8 Hz), 158.87 (d, J = 2.7 Hz), 153.60 (d, J = 3.5 Hz), 131.84 (d, J = 4.2 Hz), 131.38 (d, J = 7.3 Hz), 131.26 (d, J = 3.2 Hz), 131.20 (d, J = 5.6 Hz), 130.90, 130.84, 130.76 (d, J = 2.6 Hz), 130.70, 130.65, 130.44 (d, J = 3.2 Hz), 129.47 (d, J = 8.4 Hz), 127.65(d, J = 11.2 Hz), 127.18, 127.12 (d, J = 3.9 Hz), 126.92, 126.77 – 126.75, 113.26 (ddd, J = 22.9, 10.5, 3.0 Hz), 78.84, 55.42 (d, J = 73.8 Hz), 40.02, 27.02(3), 26.51.

^{31}P NMR (243 MHz, C_6D_6): δ 31.3 (for major rotamer), 28.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}FNO_3PNa$ $[M+Na]^+$ 474.1605, found 474.1613; $[\alpha]_D^{25}$ = + 48.0 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 60/40 v/v, 1.0 mL/min, 280 nm, t_R (major) = 8.0 min, t_R (minor) = 9.7 min), 94% *ee*.



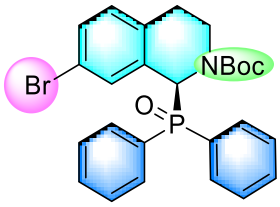
4paa
76% yield, 95% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.29 (ddt, *J* = 11.1, 6.2, 1.3 Hz, 2H), 7.90 (ddt, *J* = 9.7, 6.9, 1.4 Hz, 2H), 7.13 (dt, *J* = 6.4, 1.5 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.06 – 7.03 (m, 1H), 7.03 – 6.98 (m, 1H), 6.98 – 6.94 (m, 2H), 6.91 (dt, *J* = 8.1, 2.0 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 4.1 Hz, 1H), 6.30 (d, *J* = 2.1 Hz, 1H), 4.20 (ddd, *J* = 13.0, 9.5, 5.1 Hz, 1H), 3.73 (dddd, *J* = 13.0, 6.0, 4.6, 1.1 Hz, 1H), 2.82 (dtd, *J* = 16.5, 5.0, 2.1 Hz, 1H), 2.46 (dddd, *J* = 16.0, 9.2, 6.3, 2.3 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 153.61 (d, *J* = 3.8 Hz), 134.16 (d, *J* = 3.8 Hz), 131.66, 131.30, 131.04 (d, *J* = 6.6 Hz), 130.93, 130.87, 130.79 (d, *J* = 2.6 Hz), 130.73, 130.67, 130.49 (d, *J* = 3.2 Hz), 130.05 (d, *J* = 2.8 Hz), 129.38, 127.65 (d, *J* = 11.1 Hz), 127.17 (d, *J* = 11.1 Hz), 126.93, 126.76, 126.59 (d, *J* = 3.1 Hz), 126.38 (d, *J* = 2.8 Hz), 78.89, 55.18 (d, *J* = 73.6 Hz), 39.84, 27.01(3), 26.59.

^{31}P NMR (243 MHz, C_6D_6): δ 31.5 (for major rotamer), 28.9 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}ClNO_3PNa$ $[M+Na]^+$ 490.1316, found:490.1313; $[\alpha]_D^{25}$ = +22.2 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 65/35 v/v, 1.0 mL/min, 280 nm, t_R (major) = 22.2 min, t_R (minor) = 24.7 min), 89% *ee*.



4qaa
56%yield, 76% ee

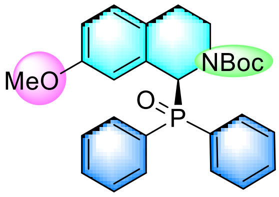
^{1}H NMR (600 MHz, C_6D_6) δ 8.29 (ddt, *J* = 11.1, 6.3, 1.3 Hz, 2H), 7.93 – 7.79 (m, 2H), 7.14 – 7.12 (m, 1H), 7.11 – 7.07 (m, 1H), 7.05 (dtd, *J* = 6.9, 5.2, 1.6 Hz, 2H), 7.03 – 7.00 (m, 1H), 7.00 – 6.94 (m, 2H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 2.1 Hz, 1H), 6.39 (d, *J* = 4.2 Hz, 1H), 4.21 (ddd, *J* = 12.9, 9.5, 5.2 Hz, 1H), 3.79 – 3.62 (m, 1H), 2.80 (ddt, *J* = 14.5, 5.3, 2.6 Hz, 1H), 2.43 (dddd, *J* = 16.1, 9.2, 6.3, 2.3 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 153.61 (d, *J* = 3.6 Hz), 134.65 (d, *J* = 3.8 Hz), 131.61 (d, *J* = 4.4 Hz), 130.94, 130.88, 130.80 (d, *J* = 2.8 Hz), 130.73, 130.67, 130.50 (d, *J* = 2.8 Hz), 129.68, 129.53 (d, *J* = 3.2 Hz), 129.27 (d, *J* = 2.8 Hz), 127.66 (d, *J* = 11.4 Hz), 127.17 (d, *J* = 11.9 Hz), 127.13, 126.92, 126.76, 118.01 (d, *J* = 2.9 Hz), 78.90, 55.06 (d, *J* = 73.7 Hz), 39.77 , 27.00(3), 26.63 .

^{31}P NMR (243 MHz, C_6D_6): δ 31.6 (for major rotamer), 28.9 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}BrNO_3PNa$ $[M+Na]^+$ 534.0804, found 534.0804; $[\alpha]_D^{25}$ = + 17.0 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH-3um, CH_3CN/H_2O

= 65/35 v/v, 0.6 mL/min, 280 nm, t_R (major) = 32.0 min, t_R (minor) = 34.5 min), 76% *ee*.



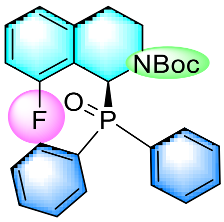
4raa
82% yield, 95% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.41 – 8.30 (m, 2H), 7.98 (ddt, *J* = 10.2, 4.8, 2.3 Hz, 2H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.05 – 6.99 (m, 1H), 6.95 – 6.87 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.75 – 6.71 (m, 1H), 6.56 (d, *J* = 3.9 Hz, 1H), 5.98 (s, 1H), 4.35 – 4.21 (m, 1H), 3.90 – 3.82 (m, 1H), 2.99 (s, 3H), 2.83 (d, *J* = 15.7 Hz, 1H), 2.69 – 2.59 (m, 1H), 1.26 (s, 9H).

^{13}C NMR (151 MHz, Benzene-d_6) δ 158.11 (d, *J* = 2.4 Hz), 155.33 (d, *J* = 4.0 Hz), 134.37, 133.79 (d, *J* = 4.8 Hz), 133.17, 132.48, 132.43 (d, *J* = 2.7 Hz), 132.38, 131.89 (d, *J* = 2.6 Hz), 131.82 (d, *J* = 2.6 Hz), 131.71, 130.78 (d, *J* = 1.7 Hz), 129.05 (d, *J* = 11.1 Hz), 128.70 (d, *J* = 6.4 Hz), 128.65, 128.47, 128.31, 115.37 (d, *J* = 2.6 Hz), 112.24 (d, *J* = 2.9 Hz), 80.22, 57.09 (d, *J* = 74.3 Hz), 54.71, 41.84, 28.59(3), 27.97.

^{31}P NMR (243 MHz, C_6D_6): δ 31.0 (for major rotamer), 28.3 (for minor rotamer).

HRMS (m/z) calcd for $C_{27}H_{30}NO_4PNa$ $[M+Na]^+$ 486.1810, found 486.1805; $[\alpha]_D^{25}$ = + 22.6 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 65/35 v/v, 1.0 mL/min, 280 nm, t_R (major) = 12.3 min, t_R (minor) = 13.4 min), 95% *ee*.



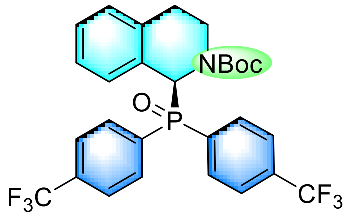
4saa
53% yield, 3% ee

^{1}H NMR (600 MHz, Benzene-d_6) δ 8.29 (ddt, *J* = 11.2, 6.1, 1.4 Hz, 2H), 8.21 (ddt, *J* = 10.9, 7.2, 2.0 Hz, 2H), 7.12 (ddd, *J* = 9.1, 5.3, 2.3 Hz, 2H), 7.07 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.06 – 6.99 (m, 3H), 6.91 (d, *J* = 3.7 Hz, 1H), 6.70 (tdd, *J* = 7.6, 5.5, 1.6 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.42 (t, *J* = 8.7 Hz, 1H), 3.76 (dtd, *J* = 12.2, 6.1, 1.0 Hz, 1H), 3.50 (dt, *J* = 14.9, 7.0 Hz, 1H), 3.40 (ddd, *J* = 12.2, 8.1, 5.9 Hz, 1H), 2.46 (dt, *J* = 15.5, 6.1 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 157.98 (dd, *J* = 246.8, 4.1 Hz), 153.71, 138.56, 131.96, 131.32, 131.13, 131.07, 130.77, 130.71, 130.54 (d, *J* = 3.2 Hz), 130.28 (d, *J* = 2.9 Hz), 127.58 (dd, *J* = 8.7, 2.8 Hz), 127.27 (d, *J* = 11.5 Hz), 127.15, 126.94, 126.77, 122.91 (t, *J* = 2.7 Hz), 118.49 (d, *J* = 17.0 Hz), 111.77 (d, *J* = 22.0 Hz), 78.83, 51.09 (d, *J* = 73.6 Hz), 40.45, 27.07(4).

^{31}P NMR (243 MHz, C_6D_6): δ 31.8 (for major rotamer), 29.9 (for minor rotamer).

HRMS (m/z) calcd for $C_{26}H_{27}FNO_3PNa$ $[M+Na]^+$ 474.1605, found 474.1611; $[\alpha]_D^{25}$ = 0 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.1 min, t_R (minor) = 9.7 min), 3% *ee*.



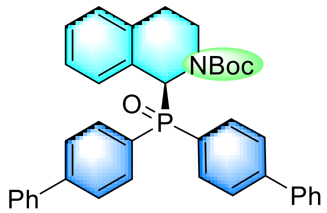
4aba, 92% yield, 79% *ee*

[1]H NMR (600 MHz, C_6D_6) δ 8.15 (dd, *J* = 10.4, 8.4 Hz, 2H), 7.95 – 7.82 (m, 2H), 7.39 (d, *J* = 6.6 Hz, 2H), 7.20 (d, *J* = 6.6 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 3.94 (ddd, *J* = 13.0, 7.9, 5.4 Hz, 1H), 3.56 (dt, *J* = 12.4, 6.1 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.57 – 2.47 (m, 1H), 1.17 (s, 9H).

[13]C NMR (151 MHz, C_6D_6) δ 155.22 (d, *J* = 2.9 Hz), 137.51 (d, *J* = 3.9 Hz), 137.18 (d, *J* = 11.0 Hz), 136.59 (d, *J* = 4.1 Hz), 134.23, 134.22 (d, *J* = 2.8 Hz), 134.03 (d, *J* = 3.5 Hz), 134.01 (d, *J* = 3.2 Hz), 133.82 (d, *J* = 2.8 Hz), 133.01 (d, *J* = 10.8 Hz), 132.82 (d, *J* = 11.2 Hz), 130.12, 129.73 (d, *J* = 2.0 Hz), 128.68, 128.47, 128.31, 127.69 (d, *J* = 3.6 Hz), 126.40 (d, *J* = 2.3 Hz), 126.17 – 125.91 (m), 125.47 - 125.37 (m), 80.80, 57.35 (d, *J* = 75.4 Hz), 41.90, 28.73, 28.37 (3).

[31]P NMR (243 MHz, C_6D_6): δ 29.5 (for major rotamer), 26.7 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{26}F_6NO_3PNa$ $[M+Na]^+$ 592.1447, found 592.1454; $[\alpha]_D^{25}$ = + 7.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 45/55 v/v, 1.0 mL/min, 280 nm, t_R (major) = 11.0 min, t_R (minor) = 13.0 min), 79% *ee*.



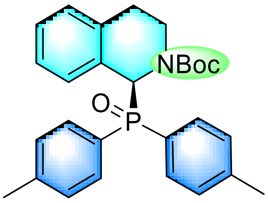
4aca, 88% yield, 82% ee

[1]H NMR (600 MHz, C_6D_6) δ 9.53 (d, *J* = 8.6 Hz, 1H), 9.41 (d, *J* = 8.6 Hz, 1H), 8.72 (dd, *J* = 14.5, 7.1 Hz, 1H), 8.10 (dd, *J* = 14.2, 6.9 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.29 (td, *J* = 8.0, 2.3 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 9.5 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.95 (d, *J* = 3.9 Hz, 1H), 6.91 (dd, *J* = 12.5, 7.0 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 2H), 6.25 (t, *J* = 7.4 Hz, 1H), 5.95 (d, *J* = 7.6 Hz, 1H), 4.74 – 4.64 (m, 1H), 3.80 – 3.72 (m, 1H), 3.40 (d, *J* = 15.7 Hz, 1H), 2.77 – 2.67 (m, 1H), 1.24 (s, 9H).

[13]C NMR (151 MHz, C_6D_6) δ 156.15 (d, *J* = 4.9 Hz), 137.91 (d, *J* = 3.7 Hz), 135.80 (d, *J* = 8.0 Hz), 135.56 (d, *J* = 7.5 Hz), 135.05 (d, *J* = 8.7 Hz), 134.60 (d, *J* = 7.7 Hz), 134.33 (d, *J* = 8.9 Hz), 133.53 (d, *J* = 2.8 Hz), 133.48 (d, *J* = 2.7 Hz), 132.81 (d, *J* = 11.7 Hz), 131.07, 130.46, 130.16, 129.85, 129.59, 129.38 (d, *J* = 1.5 Hz), 129.27, 128.74 (d, *J* = 4.1 Hz), 128.68, 128.47, 128.31, 127.88 (d, *J* = 2.7 Hz), 127.83, 127.44, 126.69 (d, *J* = 9.8 Hz), 125.57, 125.31, 125.22, 124.86, 124.77, 80.41, 58.05 (d, *J* = 76.8 Hz), 42.07, 28.74, 28.47 (3).

[31]P NMR (243 MHz, C_6D_6): δ 39.5 (for major rotamer), 25.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{38}H_{36}NO_3PNa$ $[M+Na]^+$ 608.2325, found 608.2328; $[\alpha]_D^{25}$ = + 9.9 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 35/65 v/v, 1.0 mL/min, 280 nm, t_R (major) = 16.8 min, t_R (minor) = 20.9 min), 82% *ee*.



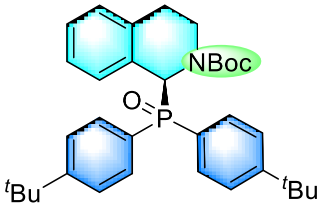
4ada, 85% yield, 88% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.26 (dd, J = 10.8, 8.1 Hz, 2H), 7.99 (dd, J = 10.4, 8.1 Hz, 2H), 7.01 (dd, J = 8.0, 2.2 Hz, 2H), 6.96 - 6.90(m, 3H), 6.84 (dd, J = 8.0, 2.1 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.59 (t, J = 5.6 Hz, 1H), 4.20 (ddd, J = 12.9, 9.0, 5.3 Hz, 1H), 3.83 – 3.72 (m, 1H), 3.07 (ddd, J = 15.9, 4.8, 3.3 Hz, 1H), 2.68 – 2.57 (m, 1H), 1.99 (s, 3H), 1.90 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.28 (d, J = 3.4 Hz), 142.34 (d, J = 2.6 Hz), 142.01 (d, J = 2.7 Hz), 137.30 (d, J = 3.8 Hz), 132.54 (d, J = 1.3 Hz), 132.48, 131.54, 129.90 (d, J = 11.5 Hz), 129.70 (d, J = 1.9 Hz), 129.44 (d, J = 11.9 Hz), 128.68, 128.47, 128.31, 128.09 (d, J = 3.3 Hz), 127.84 (d, J = 2.5 Hz), 127.92 (d, J = 5.8 Hz), 126.09 (d, J = 2.2 Hz), 80.08, 57.35 (d, J = 73.8 Hz), 41.73, 28.83, 28.59 (3), 21.63 (2).

^{31}P NMR (243 MHz, C_6D_6): δ 31.9 (for major rotamer), 29.0 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{32}NO_3PNa$ $[M+Na]^+$ 484.2012, found 484.2016; $[\alpha]_D^{25}$ = + 12.6 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 55/45 v/v, 1.0 mL/min, 280 nm, t_R (major) = 17.2 min, t_R (minor) = 19.5 min), 88% *ee*.



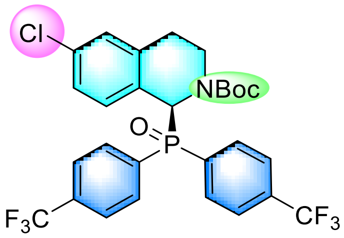
4a**ea**, 88% yield, 91% ee

^{1}H NMR (600 MHz, C_6D_6) δ 8.32 (dd, J = 10.7, 8.4 Hz, 2H), 8.10 (dd, J = 10.3, 8.4 Hz, 2H), 7.30 (dd, J = 8.4, 2.4 Hz, 2H), 7.17 – 7.15 (m, 2H), 6.97 – 6.88 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 3.6 Hz, 1H), 6.58 (d, J = 7.7 Hz, 1H), 4.20 (ddd, J = 12.9, 9.0, 5.2 Hz, 1H), 3.85 – 3.68 (m, 1H), 3.17 – 2.99 (m, 1H), 2.63 (dd, J = 15.4, 7.4 Hz, 1H), 1.27 (s, 9H), 1.13 (s, 9H), 1.07 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.30 (d, J = 2.7 Hz), 155.22 (d, J = 3.1 Hz), 154.79 (d, J = 2.7 Hz), 137.28 (d, J = 3.7 Hz), 132.52 (d, J = 9.8 Hz), 132.45 (d, J = 9.3 Hz), 131.58, 131.15, 130.97, 130.54, 130.32, 129.65 (d, J = 1.8 Hz), 128.68, 128.47, 128.31, 128.13 (d, J = 3.3 Hz), 127.81 (d, J = 2.5 Hz), 126.19 (d, J = 11.6 Hz), 125.71 (d, J = 11.7 Hz), 80.01, 57.42 (d, J = 73.5 Hz), 41.80, 35.14, 35.12, 31.47 (3), 31.41 (3), 28.91, 28.71 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.9 (for major rotamer), 28.8 (for minor rotamer).

HRMS (m/z) calcd for $C_{34}H_{44}NO_3PNa$ $[M+Na]^+$ 568.2951, found 568.2955; $[\alpha]_D^{25}$ = + 13.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 45/55 v/v, 1.0 mL/min, 280 nm, t_R (major) = 19.4 min, t_R (minor) = 21.7 min), 91% *ee*.



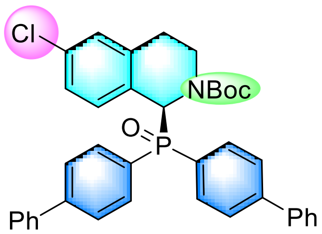
4iba, 98% yield, 86% *ee*

^{1}H NMR (600 MHz, C_6D_6): δ 8.12 (dd, *J* = 10.5, 8.4 Hz, 2H), 7.93 – 7.75 (m, 2H), 7.47 – 7.35 (m, 2H), 7.20 (d, *J* = 6.6 Hz, 2H), 6.86 (s, 1H), 6.58 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.03 (dd, *J* = 8.2, 1.5 Hz, 1H), 3.93 – 3.75 (m, 1H), 3.49 (dt, *J* = 12.4, 6.0 Hz, 1H), 2.88 (dt, *J* = 14.7, 4.9 Hz, 1H), 2.43 – 2.22 (m, 1H), 1.16 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 155.10 (d, *J* = 3.0 Hz), 139.43 (d, *J* = 3.9 Hz), 136.79, 136.20 (d, *J* = 7.3 Hz), 134.39 (d, *J* = 2.8 Hz), 134.32 (d, *J* = 3.5 Hz), 134.18 (t, *J* = 2.9 Hz), 133.98 (d, *J* = 2.7 Hz), 132.99 (d, *J* = 9.6 Hz), 132.76 (d, *J* = 9.0 Hz), 129.87 (d, *J* = 1.9 Hz), 128.79 (d, *J* = 3.5 Hz), 128.68, 128.48, 128.31, 127.94, 126.54 (d, *J* = 2.3 Hz), 126.25 – 125.97 (m), 125.66 – 125.38 (m), 125.37, 123.67 (d, *J* = 31.7 Hz), 81.05, 56.77 (d, *J* = 75.3 Hz), 41.35, 28.41, 28.34 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 29.4 (for major rotamer), 26.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{25}ClF_6NO_3PNa$ $[M+Na]^+$ 626.1062, found 626.1060; $[\alpha]_D^{25}$ = + 3.7 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 45/55 v/v, 1.0 mL/min, 280 nm, t_R (major) = 6.6 min, t_R (minor) = 8.0 min), 86% *ee*.



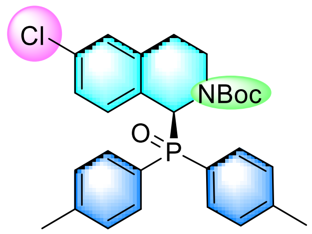
4ica, 93% yield, 93% *ee*

^{1}H NMR (600 MHz, C_6D_6): δ 8.42 (dd, *J* = 10.7, 8.3 Hz, 2H), 8.12 (dd, *J* = 10.3, 8.3 Hz, 2H), 7.54 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.37 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.18 (dd, *J* = 15.4, 7.4 Hz, 3H), 7.11 (dd, *J* = 15.7, 7.4 Hz, 3H), 6.91 (s, 1H), 6.65 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.55 (d, *J* = 3.4 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 4.17 (ddd, *J* = 13.0, 9.0, 5.3 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.97 – 2.86 (m, 1H), 2.49 – 2.39 (m, 1H), 1.24 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.22 (d, *J* = 3.3 Hz), 145.21 (d, *J* = 2.6 Hz), 145.11 (d, *J* = 2.6 Hz), 140.93, 140.46, 139.37 (d, *J* = 3.6 Hz), 133.81, 133.08 (d, *J* = 9.5 Hz), 132.96 (d, *J* = 8.9 Hz), 132.22 (d, *J* = 6.4 Hz), 131.63, 131.55, 129.82 (d, *J* = 1.5 Hz), 129.75, 129.52, 129.50 (d, *J* = 5.8 Hz), 129.26 (d, *J* = 2.9 Hz), 128.80, 128.68, 128.65, 128.47, 128.31, 127.93 (d, *J* = 14.6 Hz), 127.88, 127.54 (d, *J* = 11.8 Hz), 126.37, 80.51, 56.93 (d, *J* = 74.0 Hz), 41.31, 28.57, 28.55 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.5 (for major rotamer), 28.5 (for minor rotamer).

HRMS (m/z) calcd for $C_{38}H_{52}ClNO_3PNa$ $[M+Na]^+$ 642.1941, found 642.1936; $[\alpha]_D^{25}$ = + 22.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 25/75 v/v, 1.0 mL/min, 280 nm, t_R (major) = 11.6 min, t_R (minor) = 17.6 min), 93% *ee*.



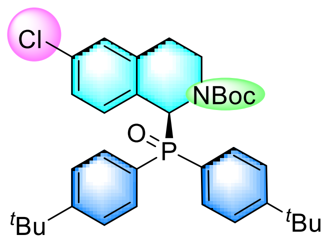
4ida, 83% yield, 90% *ee*

^{1}H NMR (600 MHz, C_6D_6): δ 8.23 (dd, J = 10.8, 8.1 Hz, 2H), 8.03 – 7.79 (m, 2H), 7.01 (dd, J = 8.0, 2.1 Hz, 2H), 6.88 (s, 1H), 6.83 (dd, J = 7.9, 2.0 Hz, 2H), 6.64 (dd, J = 8.1, 1.8 Hz, 1H), 6.46 (d, J = 3.9 Hz, 1H), 6.33 – 6.26 (m, 1H), 4.22 – 4.02 (m, 1H), 3.80 – 3.61 (m, 1H), 2.85 (d, J = 15.3 Hz, 1H), 2.54 – 2.30 (m, 1H), 1.98 (s, 3H), 1.91 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6): δ 155.17 (d, J = 3.5 Hz), 142.53 (d, J = 2.7 Hz), 142.20 (d, J = 2.7 Hz), 139.30 (d, J = 3.7 Hz), 133.61 (d, J = 3.2 Hz), 132.82 (d, J = 8.4 Hz), 132.45 (d, J = 7.5 Hz), 132.39 (d, J = 6.9 Hz), 130.70, 130.57, 130.08, 129.96 (d, J = 11.7 Hz), 129.76 (d, J = 1.9 Hz), 129.50 (d, J = 11.9 Hz), 129.26 (d, J = 3.1 Hz), 128.68, 128.47, 128.31, 126.21 (d, J = 2.1 Hz), 80.30, 56.80 (d, J = 73.7 Hz), 41.19, 28.56 (3), 28.51, 21.63 (2).

^{31}P NMR (243 MHz, C_6D_6): δ 31.6 (for major rotamer), 28.8 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{31}ClNO_3PNa$ $[M+Na]^+$ 518.1628, found 518.1628; $[\alpha]_D^{25}$ = + 19.2 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 40/60 v/v, 1.0 mL/min, 280 nm, t_R (major) = 7.3 min, t_R (minor) = 8.5 min), 90% *ee*.



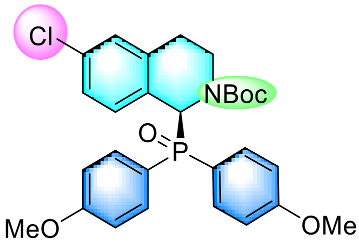
4iea, 85% yield, 95% *ee*

^{1}H NMR (600 MHz, C_6D_6): δ 8.30 (dd, J = 10.8, 8.4 Hz, 2H), 8.03 (dd, J = 10.3, 8.4 Hz, 2H), 7.30 (dd, J = 8.4, 2.4 Hz, 2H), 7.14 (dd, J = 8.4, 2.4 Hz, 2H), 6.88 (s, 1H), 6.61 (dd, J = 8.2, 1.9 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 6.32 – 6.25 (m, 1H), 4.13 (ddd, J = 13.0, 9.2, 5.2 Hz, 1H), 3.75 – 3.63 (m, 1H), 2.85 (d, J = 15.3 Hz, 1H), 2.47 – 2.34 (m, 1H), 1.27 (s, 9H), 1.12 (s, 9H), 1.07 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.55 (d, J = 2.6 Hz), 155.11 (d, J = 3.2 Hz), 155.01 (d, J = 2.7 Hz), 133.59 (d, J = 3.1 Hz), 132.46 (d, J = 9.5 Hz), 132.36 (d, J = 9.0 Hz), 130.79, 130.56, 130.18, 130.04, 129.91, 129.72, 129.30 (d, J = 3.0 Hz), 128.68, 128.47, 128.31, 126.27 (d, J = 11.3 Hz), 126.23, 125.79 (d, J = 11.7 Hz), 80.24, 56.86 (d, J = 73.4 Hz), 41.25, 35.16, 35.14, 31.45 (3), 31.40 (3), 28.67 (3), 28.59.

^{31}P NMR (243 MHz, C_6D_6): δ 31.7 (for major rotamer), 28.7 (for minor rotamer).

HRMS (m/z) calcd for $C_{34}H_{43}ClNO_3PNa$ $[M+Na]^+$ 602.2567, found 602.2563; $[\alpha]_D^{25}$ = + 24.3 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 45/55 v/v, 1.0 mL/min, 280 nm, t_R (major) = 9.8 min, t_R (minor) = 10.9 min), 95% *ee*.



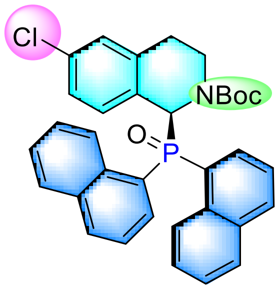
4ifa, 80% yield, 83% *ee*

^{1}H NMR (600 MHz, C_6D_6): δ 8.23 (dd, *J* = 10.4, 8.8 Hz, 2H), 7.95 – 7.89 (m, 2H), 6.90 (s, 1H), 6.80 (dd, *J* = 8.6, 1.9 Hz, 2H), 6.68 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.62 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.40 (d, *J* = 3.9 Hz, 1H), 6.31 (d, *J* = 7.9 Hz, 1H), 4.14 (ddd, *J* = 14.1, 9.2, 5.3 Hz, 1H), 3.78 – 3.68 (m, 1H), 3.19 (s, 3H), 3.11 (s, 3H), 2.87 (d, *J* = 15.8 Hz, 1H), 2.50 – 2.40 (m, 1H), 1.27 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 163.10, 155.18 (d, *J* = 3.3 Hz), 139.29 (d, *J* = 3.6 Hz), 134.24 (d, *J* = 5.0 Hz), 134.17 (d, *J* = 4.4 Hz), 133.56 (d, *J* = 3.1 Hz), 130.09, 129.73, 129.34 (d, *J* = 2.9 Hz), 128.68, 128.47, 128.31, 126.19 (d, *J* = 1.9 Hz), 124.82 (s), 124.16 (d, *J* = 5.8 Hz), 114.88 (d, *J* = 12.2 Hz), 114.47 (d, *J* = 12.5 Hz), 80.34, 56.89 (d, *J* = 74.1 Hz), 55.09 (2), 41.16, 28.60 (3), 28.54.

^{31}P NMR (243 MHz, C_6D_6): δ 31.7 (for major rotamer), 28.6 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{31}ClNO_5PNa$ $[M+Na]^+$ 550.1526, found 550.1521; $[\alpha]_D^{25}$ = + 23.9 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 55/45 v/v, 1.0 mL/min, 280 nm, t_R (major) = 11.7 min, t_R (minor) = 13.9 min), 83% *ee*.



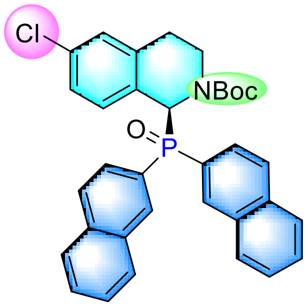
4iga, 80% yield, 91% *ee*

^{1}H NMR (600 MHz, C_6D_6) δ 9.48 (d, *J* = 8.6 Hz, 1H), 9.34 (d, *J* = 8.6 Hz, 1H), 8.68 (dd, *J* = 14.5, 7.0 Hz, 1H), 8.05 (dd, *J* = 14.0, 6.5 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.29 (td, *J* = 8.0, 2.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 11.9, 7.2 Hz, 2H), 6.88 (s, 2H), 6.81 (d, *J* = 4.1 Hz, 1H), 6.20 – 6.09 (m, 1H), 5.64 (d, *J* = 7.4 Hz, 1H), 4.67 – 4.53 (m, 1H), 3.72 – 3.61 (m, 1H), 3.19 (d, *J* = 15.9 Hz, 1H), 2.54 – 2.45 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 156.03 (d, *J* = 4.9 Hz), 139.87 (d, *J* = 3.8 Hz), 135.64 (d, *J* = 7.3 Hz), 135.49 (d, *J* = 7.6 Hz), 135.04 (d, *J* = 8.8 Hz), 134.56 (d, *J* = 11.9 Hz), 134.29 (d, *J* = 8.9 Hz), 133.71 (d, *J* = 3.3 Hz), 133.66 (d, *J* = 2.8 Hz), 133.62 (d, *J* = 2.7 Hz), 132.74 (d, *J* = 11.6 Hz), 129.78 (d, *J* = 3.2 Hz), 129.55, 129.41 (d, *J* = 1.5 Hz), 129.36, 129.31, 128.68, 128.47, 128.31, 128.02 (d, *J* = 2.2 Hz), 127.95, 127.52, 126.85, 126.74, 125.62 (d, *J* = 1.9 Hz), 125.27 (d, *J* = 13.1 Hz), 124.78 (d, *J* = 13.8 Hz), 80.65, 57.52 (d, *J* = 76.6 Hz), 41.53, 28.71, 28.45 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 39.2 (for major rotamer), 35.3 (for minor rotamer).

HRMS (m/z) calcd for $C_{34}H_{31}ClNO_3PNa$ $[M+Na]^+$ 590.1628, found 590.1623; $[\alpha]_D^{25}$ = + 12.9 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 16.0 min, t_R (minor) = 17.8 min), 91% *ee*.



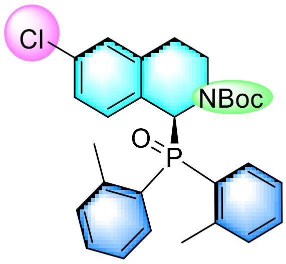
4iha, 98% yield, 96% *ee*

^{1}H NMR (600 MHz, C_6D_6) δ 9.04 (d, *J* = 12.9 Hz, 1H), 8.76 (d, *J* = 12.7 Hz, 1H), 8.50 – 8.40 (m, 1H), 8.08 (td, *J* = 8.5, 1.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.17 (d, *J* = 3.9 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.88 (s, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 6.41 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 1H), 4.22 (ddd, *J* = 13.0, 9.3, 5.2 Hz, 1H), 3.77 – 3.66 (m, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.54 – 2.35 (m, 1H), 1.14 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 155.32 (d, *J* = 3.6 Hz), 139.24 (d, *J* = 3.7 Hz), 135.60, 135.38 (d, *J* = 2.1 Hz), 135.12 (d, *J* = 7.3 Hz), 134.30 (d, *J* = 8.7 Hz), 133.77 (d, *J* = 3.2 Hz), 133.50 (d, *J* = 3.8 Hz), 133.42 (d, *J* = 3.3 Hz), 130.85 (d, *J* = 2.5 Hz), 130.23 (d, *J* = 3.3 Hz), 129.83, 129.73, 129.62, 129.25 (d, *J* = 11.6 Hz), 129.20 (d, *J* = 3.4 Hz), 128.68, 128.63, 128.47, 128.31, 127.59 (d, *J* = 10.0 Hz), 127.48, 127.12, 126.76 (d, *J* = 10.3 Hz), 126.33 (d, *J* = 2.2 Hz), 80.53, 56.65 (d, *J* = 74.0 Hz), 41.27, 28.50, 28.41 (3).

^{31}P NMR (243 MHz, C_6D_6): δ 31.9 (for major rotamer), 28.8 (for minor rotamer).

HRMS (m/z) calcd for $C_{34}H_{31}ClNO_3PNa$ $[M+Na]^+$ 590.1628, found 590.1624; $[\alpha]_D^{25}$ = + 23.0 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 45/55 v/v, 1.0 mL/min, 280 nm, t_R (major) = 9.2 min, t_R (minor) = 12.1 min), 96% *ee*.



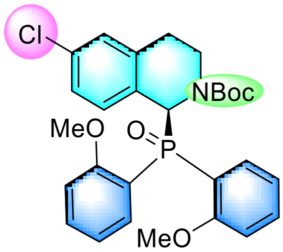
4iia, 88% yield, 90% *ee*

^{1}H NMR (600 MHz, C_6D_6) δ 8.58 (dd, *J* = 11.5, 7.8 Hz, 1H), 7.52 (dd, *J* = 13.1, 7.7 Hz, 1H), 7.24 (t, *J* = 6.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (dd, *J* = 7.3, 3.8 Hz, 1H), 6.86 (s, 1H), 6.75 – 6.68 (m, 2H), 6.55 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 5.6 Hz, 1H), 5.81 (d, *J* = 8.0 Hz, 1H), 4.78 (ddd, *J* = 13.6, 10.8, 5.3 Hz, 1H), 4.01 – 3.84 (m, 1H), 2.73 – 2.59 (m, 1H), 2.57 – 2.52 (m, 1H), 2.51 (s, 3H), 2.26 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ 156.23 (d, *J* = 6.7 Hz), 144.35 (d, *J* = 7.5 Hz), 139.83 (d, *J* = 3.7 Hz), 133.68, 133.51 (d, *J* = 12.0 Hz), 132.99 (d, *J* = 10.2 Hz), 132.55 (d, *J* = 11.3 Hz), 132.35 (d, *J* = 10.5 Hz), 132.23 (d, *J* = 2.4 Hz), 132.17, 129.97, 129.93 (d, *J* = 2.7 Hz), 129.41, 128.68, 128.47, 128.31, 126.21 (d, *J* = 12.1 Hz), 125.61 (d, *J* = 11.8 Hz), 125.57, 80.87, 55.57 (d, *J* = 76.4 Hz), 40.89, 28.60 (3), 27.98, 22.07 (d, J = 3.9 Hz), 21.65 (d, J = 2.2 Hz).

^{31}P NMR (243 MHz, C_6D_6): δ 38.4 (for major rotamer), 24.8 (for minor rotamer).

HRMS (m/z) calcd for $C_{28}H_{31}ClNO_3PNa$ $[M+Na]^+$ 518.1628, found 518.1625; $[\alpha]_D^{25}$ = + 124.8 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH-3um, CH_3CN/H_2O = 50/50 v/v, 0.6 mL/min, 280 nm, t_R (major) = 38.1 min, t_R (minor) = 40.0 min), 90% *ee*.



4ija, 78% yield, 86% ee

Major rotamer : ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 13.5, 7.6 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.48 (q, J = 7.5 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.16 – 7.13 (m, 1H), 7.11 – 7.06 (m, 1H), 7.01 (dd, J = 8.4, 5.3 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.79 – 6.75 (m, 1H), 6.74 – 6.70 (m, 1H), 6.59 (dd, J = 9.0, 1.8 Hz, 1H), 6.34 (d, J = 8.3 Hz, 1H), 4.36 – 4.29 (m, 1H), 4.14 – 4.06 (m, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.03 (t, J = 14.9 Hz, 2H), 2.98 (d, J = 4.6 Hz, 3H), 1.09 (s, 9H).

^{31}P NMR (243 MHz, C_6D_6): δ 40.8.

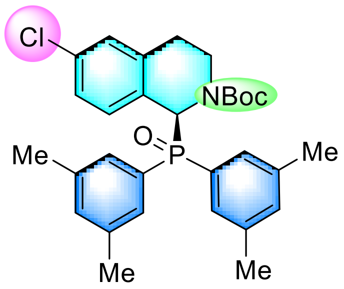
^{13}C NMR (151 MHz, $CDCl_3$) 161.10, 153.96, 138.16, 135.18, 134.86 (d, J = 7.0 Hz), 134.35, 134.33, 133.98, 132.26, 130.53, 128.77, 128.31, 127.75, 124.87 (d, J = 3.2 Hz), 121.03 (d, J = 2.9 Hz), 120.79 (d, J = 11.7 Hz), 111.16 (d, J = 6.6 Hz), 110.54 (d, J = 6.6 Hz), 79.90, 56.39 (d, J = 73.3 Hz), 55.63, 55.00, 40.66, 28.06, 27.90 (3).

Minor rotamer : ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 1H), 7.62 – 7.57 (m, 1H), 7.48 (q, J = 7.5 Hz, 2H), 7.13 – 7.11 (m, 1H), 7.06 – 7.02 (m, 1H), 6.99 – 6.95 (m, 1H), 6.92 (dd, J = 8.3, 5.3 Hz, 1H), 6.82 (dd, J = 8.4, 5.3 Hz, 1H), 6.78 (dd, J = 8.4, 4.7 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.56 – 6.51 (m, 1H), 4.23 (ddd, J = 15.1, 10.6, 4.9 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.94 (dd, J = 10.3, 6.3 Hz, 1H), 2.85 (q, J = 9.0, 8.0 Hz, 2H), 1.35 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.36, 154.92, 138.13, 135.13, 134.97 (d, J = 7.1 Hz), 134.40, 134.08, 133.74, 132.26, 130.26, 128.77, 128.31, 127.73, 125.17, 120.96 (d, J = 2.8 Hz), 120.54 (d, J = 11.9 Hz), 111.16 (d, J = 6.6 Hz), 110.54 (d, J = 6.6 Hz), 80.06, 55.68, 55.24, 54.68 (d, J = 77.9 Hz), 39.14, 28.25(3), 27.99 .

^{31}P NMR (243 MHz, C_6D_6): δ 37.0

HRMS (m/z) calcd for $C_{28}H_{31}ClNO_5PNa$ $[M+Na]^+$ 550.1526, found 550.1524; $[\alpha]_D^{25}$ = + 83.6 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 9.0 min, t_R (minor) = 10.1 min), 86% *ee*.



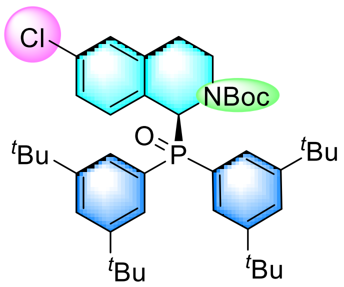
3ika, 85% yield, 94% *ee*

[1]H NMR (600 MHz, C_6D_6) δ 8.09 (d, *J* = 11.3 Hz, 2H), 7.77 (d, *J* = 10.9 Hz, 2H), 6.88 (s, 1H), 6.81 (s, 1H), 6.70 (s, 1H), 6.64 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.60 (d, *J* = 4.1 Hz, 1H), 6.39 – 6.30 (m, 1H), 4.32 – 4.19 (m, 1H), 3.77 (ddd, *J* = 10.8, 5.6, 4.4 Hz, 1H), 2.79 (d, *J* = 16.5 Hz, 1H), 2.54 – 2.41 (m, 1H), 2.13 (s, 6H), 1.91 (s, 6H), 1.28 (s, 9H).

[13]C NMR (151 MHz, C_6D_6) δ 155.31 (d, *J* = 3.9 Hz), 139.29 (d, *J* = 3.7 Hz), 138.98 (d, *J* = 11.8 Hz), 138.39 (d, *J* = 12.2 Hz), 134.12 (d, *J* = 2.7 Hz), 133.95 (d, *J* = 2.4 Hz), 133.65 (d, *J* = 3.0 Hz), 133.45, 133.35, 132.81, 130.05 (d, *J* = 6.1 Hz), 130.00 (d, *J* = 5.6 Hz), 129.93, 129.88, 129.37 (d, *J* = 2.9 Hz), 128.68, 128.47, 128.31, 126.10 (d, *J* = 2.1 Hz), 80.34, 56.46 (d, *J* = 73.5 Hz), 41.17, 28.54 (3), 28.44, 21.62 (2), 21.39 (2).

[31]P NMR (243 MHz, C_6D_6): δ 32.3 (for major rotamer), 29.2 (for minor rotamer).

HRMS (m/z) calcd for $C_{30}H_{35}ClNO_3PNa$ $[M+Na]^+$ 546.1941, found 456.1938; $[\alpha]_D^{25}$ = + 22.2 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OX-RH, CH_3CN/H_2O = 35/65 v/v, 1.0 mL/min, 280 nm, t_R (major) = 12.6 min, t_R (minor) = 14.3 min), 94% *ee*.



4ila, 60% yield, 96% *ee*

Major rotamer : [1]H NMR (600 MHz, C_6D_6) δ 8.43 (dd, *J* = 11.7, 1.7 Hz, 2H), 8.11 (dd, *J* = 11.4, 1.8 Hz, 2H), 7.68 (s, 1H), 7.58 (s, 1H), 6.89 (s, 1H), 6.65 – 6.56 (m, 2H), 6.17 (d, *J* = 8.2 Hz, 1H), 4.43 (ddd, *J* = 13.1, 9.7, 5.2 Hz, 1H), 3.83 – 3.74 (m, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 2.53 – 2.43 (m, 1H), 1.33 (s, 18H), 1.21 (s, 9H), 1.16 (s, 18H).

[13]C NMR (151 MHz, C_6D_6) δ 155.49 (d, *J* = 4.6 Hz), 152.02 (d, *J* = 10.9 Hz), 151.39 (d, *J* = 11.3 Hz), 139.38 (d, *J* = 3.6 Hz), 133.53 (d, *J* = 3.0 Hz), 133.37, 132.77, 132.62, 131.98, 130.10, 129.86 (d, *J* = 1.4 Hz), 129.50 (d, *J* = 2.7 Hz), 128.68, 128.47, 128.31, 126.92 (d, *J* = 9.5 Hz), 126.68 (d, *J* = 2.5 Hz), 126.30 (d, *J* = 2.4 Hz), 125.97 (d, *J* = 1.9 Hz), 80.25, 56.87 (d, *J* = 73.8 Hz), 41.40, 35.63 (2), 35.46 (2), 31.91 (6), 31.68 (6), 28.62 (3), 28.37. [31]P NMR (243 MHz, C_6D_6): δ 32.3.

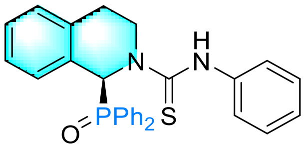
[13]C NMR (151 MHz, Benzene-d_6) δ 80.18, 59.85 (d, *J* = 70.0 Hz), 39.81, 35.57 , 35.52 , 31.78 , 31.76 , 28.44, 28.37 .

Minor rotamer : ^{1}H NMR (600 MHz, C_6D_6) δ 8.08 (dd, *J* = 10.9, 1.6 Hz, 2H), 7.89 (dd, *J* = 11.5, 1.5 Hz, 2H), 7.71 (s, 1H), 7.58 (s, 1H), 6.76 (m, 3H), 6.08 (d, *J* = 8.5 Hz, 1H), 4.34 – 4.26 (m, 1H), 4.00 – 3.91 (m, 1H), 2.57 (d, *J* = 15.9 Hz, 1H), 2.52 – 2.45 (m, 1H), 1.26 (s, 18H), 1.21 (s, 18H), 1.18 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ154.07, 151.95 (d, *J* = 9.6 Hz), 151.46 (d, *J* = 11.3 Hz), 138.93 (d, *J* = 3.1 Hz), 133.71 (d, *J* = 3.1 Hz), 133.37, 132.73, 132.62, 131.98, 130.24, 129.90, 129.09 (d, *J* = 2.6 Hz), 128.68, 128.47, 128.31, 126.92 (d, *J* = 9.5 Hz), 126.59 (d, *J* = 2.1 Hz), 126.35 (d, *J* = 2.0 Hz), 125.97 (d, *J* = 1.9 Hz), 80.18, 59.85 (d, *J* = 70.0 Hz), 39.81, 35.57 (2), 35.52 (2), 31.78 (6), 31.76 (6), 28.44 (3), 28.37.

^{31}P NMR (243 MHz, C_6D_6): δ 29.2.

HRMS (m/z) calcd for $C_{42}H_{59}ClNO_3PNa$ $[M+Na]^+$ 714.3819, found 714.3820; $[\alpha]_D^{25}$ = +12.8 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OX-RH, CH_3CN/H_2O = 20/80 v/v, 1.0 mL/min, 280 nm, t_R (major) = 8.0 min, t_R (minor) = 9.9 min), 96% *ee*.



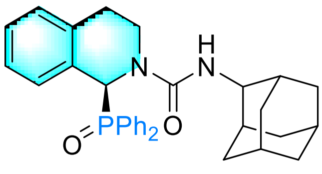
6aaa, 85% yield, 97% ee

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.86 (dd, *J* = 11.1, 7.7 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.61 (tdd, *J* = 7.3, 4.4, 1.4 Hz, 2H), 7.49 (dtd, *J* = 13.0, 7.7, 3.0 Hz, 4H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.22 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.15 (tt, *J* = 7.7, 1.7 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 7.7 Hz, 1H), 4.11 (dt, *J* = 12.9, 6.4 Hz, 1H), 3.77 – 3.63 (m, 1H), 2.93 – 2.76 (m, 1H), 2.59 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 185.52, 140.33, 136.21, 132.86 (d, *J* = 2.8 Hz), 132.64 (d, *J* = 2.8 Hz), 132.36 (d, *J* = 8.8 Hz), 131.92 (d, *J* = 9.3 Hz), 130.33 (d, *J* = 95.3 Hz), 129.07, 128.74 (d, *J* = 8.2 Hz), 128.69 (9), 128.62, 128.24 (d, *J* = 2.9 Hz), 127.55 (d, *J* = 3.5 Hz), 126.13 (d, *J* = 2.2 Hz), 124.94, 124.02. 64.91 (d, *J* = 70.9 Hz), 45.94, 27.92.

^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

HRMS (m/z) calcd for $C_{28}H_{25}N_2OPSNa$ $[M+Na]^+$ 491.1323, found 491.1329; $[\alpha]_D^{25}$ = +103.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 40/60 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.7 min, t_R (minor) = 5.9 min), 97% *ee*.



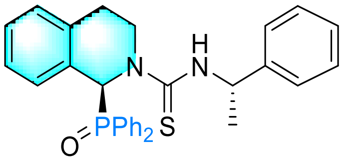
6aab, 88% yield, 99% ee

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 2H), 7.89 – 7.81 (m, 2H), 7.57 – 7.52 (m, 2H), 7.52 – 7.42 (m, 4H), 7.18 – 7.11 (m, 2H), 6.90 (dt, *J* = 8.3, 4.2 Hz, 1H), 6.45 (t, *J* = 5.4 Hz, 2H), 3.78 – 3.72 (m, 1H), 3.32 (q, *J* = 8.6, 7.9 Hz, 2H), 2.90 – 2.71 (m, 1H), 2.03 (s, 3H), 1.81 (d, *J* = 14.7 Hz, 6H), 1.64 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.06, 136.55 (d, *J* = 3.8 Hz), 132.01 (d, *J* = 2.7 Hz), 131.93 , 131.88 , 131.63 (d, *J* = 2.7 Hz), 131.57 , 131.51 , 131.12 , 130.75 , 130.73 (d, *J* = 90.7 Hz), 128.52 , 128.45 , 128.32 (d, J = 2.2 Hz), 128.25 , 128.18 , 127.67 (d, J = 2.8 Hz), 127.52 (d, J = 3.9 Hz), 125.87 (d, J = 2.2 Hz), 58.42, 51.34, 42.15 (2), 41.89, 36.39 (2), 29.52 (4), 28.01, 18.40.

^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

HRMS (m/z) calcd for $C_{32}H_{35}N_2O_2PNa$ $[M+Na]^+$ 533.2334, found 533.2335; $[\alpha]_D^{25}$ = +63.6 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OD-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 13.9 min, t_R (minor) = 15.6 min), 99% *ee*.



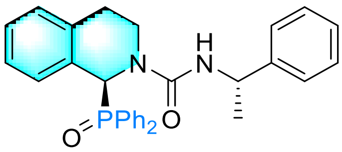
6aac, 93% yield, 98% ee

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.96 – 7.91 (m, 2H), 7.60 (td, J = 7.4, 1.5 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.45 (td, J = 7.7, 2.9 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.24 (tt, J = 6.2, 2.2 Hz, 1H), 7.17 (tt, J = 7.4, 1.5 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.53 (d, J = 7.7 Hz, 1H), 5.58 (p, J = 7.1 Hz, 1H), 3.85 (dt, J = 11.8, 5.9 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.26 (s, 1H), 2.84 (dt, J = 15.7, 5.7 Hz, 1H), 1.42 (d, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 182.34, 142.86, 135.87, 132.44, 132.25, 132.19, 131.99, 131.72, 131.66, 128.73, 128.65, 128.29 (d, J = 3.0 Hz), 128.23, 128.15, 128.05 (d, J = 3.3 Hz), 127.50 (d, J = 4.3 Hz), 127.34, 126.44, 126.26 (d, J = 2.8 Hz), 63.62 (d, J = 71.1 Hz), 54.92, 44.38, 27.88, 21.47.

^{31}P NMR (243 MHz, $CDCl_3$): δ 34.2.

HRMS (m/z) calcd for $C_{30}H_{29}N_2OPSNa$ $[M+Na]^+$ 519.1630, found 519.1632; $[\alpha]_D^{25}$ = +103.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak OJ-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 6.6 min, t_R (minor) = 7.9 min), 98% *ee*.



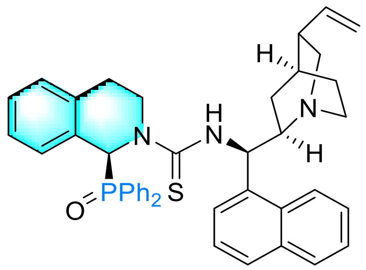
6aad, 96% yield, 98% ee

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.78 – 7.70 (m, 2H), 7.48 – 7.39 (m, 2H), 7.36 (td, J = 7.7, 2.6 Hz, 4H), 7.20 – 7.12 (m, 4H), 7.12 – 7.07 (m, 1H), 7.06 – 6.99 (m, 2H), 6.83 – 6.74 (m, 1H), 6.35 (d, J = 6.8 Hz, 2H), 4.70 (s, 1H), 3.65 (dt, J = 10.9, 5.5 Hz, 1H), 3.25 (td, J = 10.3, 9.7, 5.6 Hz, 1H), 3.16 (s, 1H), 2.69 (dt, J = 15.4, 5.4 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.62, 143.90, 136.21 (d, J = 3.7 Hz), 132.10 (d, J = 2.6 Hz), 131.99, 131.93, 131.72 (d, J = 2.7 Hz), 131.64, 131.58, 131.10, 130.52, 130.44 (d, J = 91.2 Hz), 128.55 (2), 128.47, 128.28 (d, J = 2.3 Hz), 128.21, 128.13, 127.75 (d, J = 2.7 Hz), 127.48 (d, J = 3.9 Hz), 127.10, 126.03 (2), 125.97 (d, J = 2.1 Hz), 58.36 , 50.28 , 41.57, 28.01, 22.44, 18.39 .

^{31}P NMR (243 MHz, $CDCl_3$): δ 34.0.

HRMS (m/z) calcd for $C_{30}H_{29}N_2O_2PNa$ $[M+Na]^+$ 503.1859, found 503.1865; $[\alpha]_D^{25}$ = +83.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.1 min, t_R (minor) = 4.8 min), 98% *ee*.



6aae, 86% yield, 99% ee

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, J = 4.5 Hz, 1H), 8.17 – 7.98 (m, 4H), 7.84 – 7.74 (m, 3H), 7.67 (d, J = 41.0 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.46 (td, J = 7.7, 2.8 Hz, 2H), 7.38 (dd, J = 9.2, 2.6 Hz, 1H), 7.29 (s, 1H), 7.22 – 7.14 (m, 2H), 7.11 – 6.89 (m, 3H), 6.48 (d, J = 7.6 Hz, 1H), 5.89 (ddd, J = 16.9, 10.6, 5.9 Hz, 1H), 5.14 (t, J = 12.7 Hz, 2H), 4.11 (s, 1H), 3.96 (s, 2H), 3.82 (s, 1H), 3.47 (s, 1H), 2.95 (t, J = 28.4 Hz, 6H), 2.32 (s, 1H), 1.68 (s, 1H), 1.57 (s, 1H), 1.51 – 1.37 (m, 2H), 1.32 – 1.18 (m, 1H), 0.99 – 0.81 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.71, 155.74, 145.77, 137.93, 133.59, 130.22, 129.98, 129.65, 129.42, 128.83 (6), 126.80, 126.72 (6), 125.91 (3), 125.31, 124.42 (d, J = 2.2 Hz), 120.26, 116.55, 113.30, 100.05, 60.99 (d, J = 70.9 Hz), 60.16, 53.98, 53.58, 47.18, 44.83, 41.60, 36.71, 26.22, 25.16, 24.50.

^{31}P NMR (243 MHz, $CDCl_3$): δ 34.9.

HRMS (m/z) calcd for $C_{42}H_{42}N_3OPSNa$ $[M+Na]^+$ 690.2684, found 690.2688; $[\alpha]_D^{25}$ = +153.5 (c = 0.20, $CHCl_3$); The *ee* was determined by HPLC analysis (Chiralpak AS-RH, CH_3CN/H_2O = 50/50 v/v, 1.0 mL/min, 280 nm, t_R (major) = 4.8 min, t_R (minor) = 5.3 min), 99% *ee*.

6. DFT Calculations

DFT calculations were performed using the Gaussian 16 package.[1] All the structures were optimized at the B3LYP/6-31G* level,2-5 which has been found to produce reliable results for the phosphoric acid catalyzed reactions.[6-7] Vibrational analyses were performed to ensure intermediates to have no imaginary frequencies and the transition state structures to have only one imaginary frequency. Transition state structures were confirmed to connect appropriate reactants or products by intrinsic reaction coordinate (IRC) calculations.[8] Solvent effects were considered using diisopropylether with the SMD[9] model at the M06-2X/6-311++G** level.[5, 10-13]. We also performed single-point energy calculations using various methods including M062X-D3, B3LYP, B3LYP-D3 and B3LYP-D3(BJ) with basis set 6-311++G** for the transition states **TS5(S)** and **TS5(R)** presented in **Figure 3** in the main text.

Table S3. The energies of calculated structures.

	E(gas)	G(gas)	E(sol)	G(sol)
CPA7	-2493.7487	-2493.0974	-2493.5260	-2492.8747
1a	-403.1082	-402.9808	-403.0521	-402.9247
$(BOC)_2O$	-768.0602	-767.8272	-767.9921	-767.7591
TS1	-3664.9223	-3663.8675	-3664.5868	-3663.5320
1a-1	-1171.2032	-1170.8167	-1171.0885	-1170.7020
TS2	-3664.9511	-3663.8968	-3664.6145	-3663.5603
1a-2	-3664.9540	-3663.8991	-3664.6205	-3663.5656
TS3	-3664.9250	-3663.8659	-3664.5874	-3663.5283
CO_2	-188.5776	-188.5867	-188.5755	-188.5846

1a'	-982.6266	-982.2504	-982.5128	-982.1367
$Ph_2P(O)H$	-880.4756	-880.3190	-880.4059	-880.2492
TS4	-4356.8524	-4355.6245	-4356.4628	-4355.2349
1a'-1	-4123.1926	-4122.0932	-4122.8304	-4121.7310
TS5(*S*)	-4123.1743	-4122.0767	-4122.8162	-4121.7186
TS5(*R*)	-4123.1731	-4122.0738	-4122.8134	-4121.7140
^{t}BuOH	-233.6667	-233.5596	-233.6385	-233.5314

Table S4. Comparison of results from single-point energy calculations using different DFT methods for the relative energy difference of **TS5(S)** and **TS5(R)** presented in **Figure 3** in the main text.

	B3LYP[a)]	B3LYP	B3LYP-D3	B3LYP-D3(BJ)	M062X	M062X-D3	Experimental
$\Delta\Delta G^{*}$[b)]	1.9	2.6	3.0	2.1	2.9	3.2	1.8
ee	91.6%	97.5%	98.7%	94.1%	98.4%	99.1%	91%

[a)] data from gas phase calculation.

[b)] $\Delta\Delta G^* = \Delta G^*$**TS5(*R*) -** ΔG^***TS5(*S*)**, Relative free energies are given in kcal/mol.

Remarks on **Table S4**:

The results shown in **Table S4** indicate that different DFT methods give approximately consistent results and correctly reproduce the enantiomeric preference observed experimentally.

7. Reference

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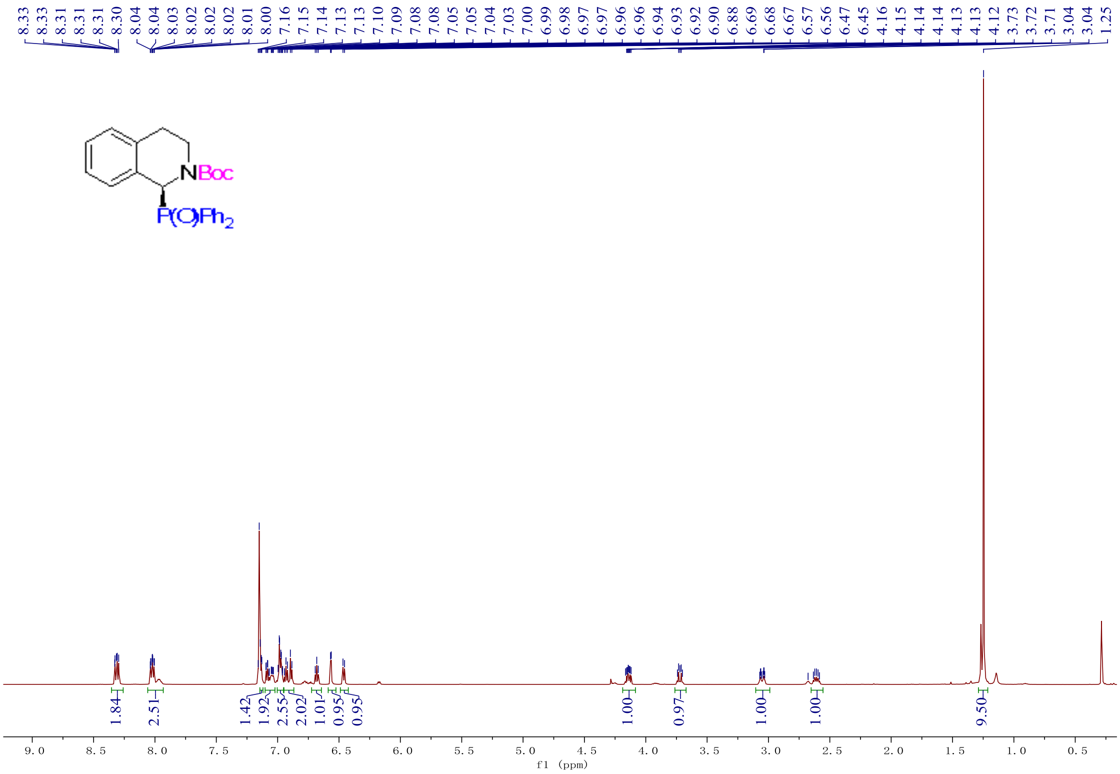
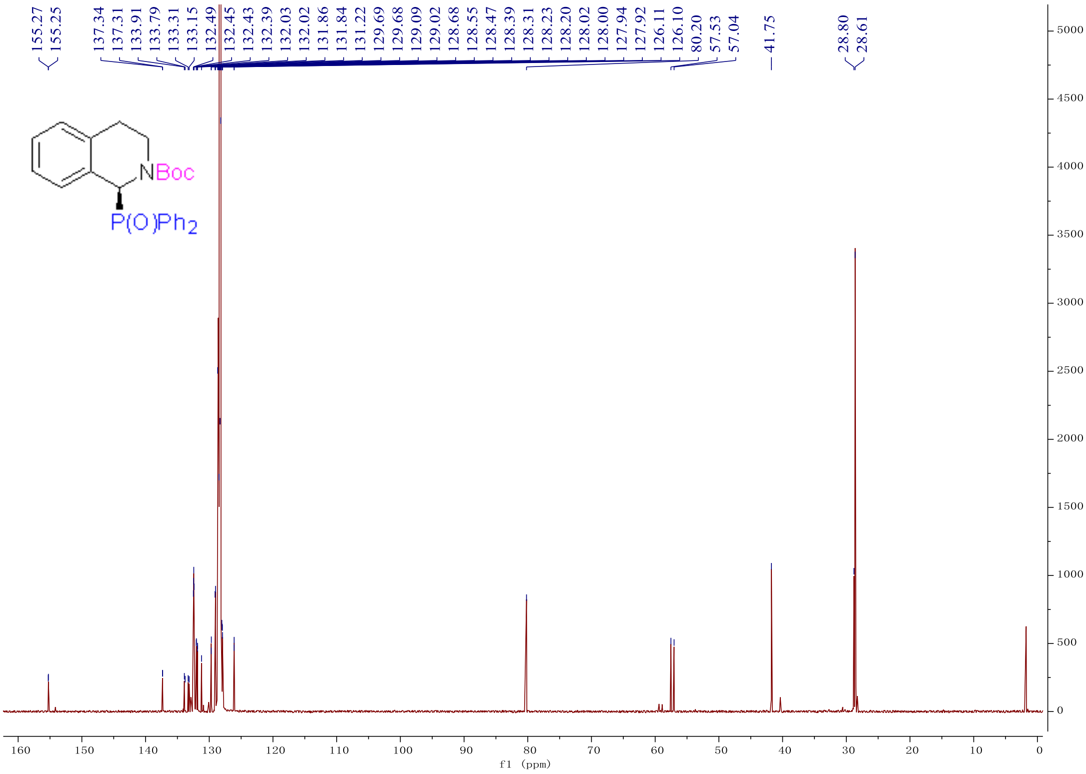
8. The spectra of NMR



^{1}H NMR of compound **4aaa**



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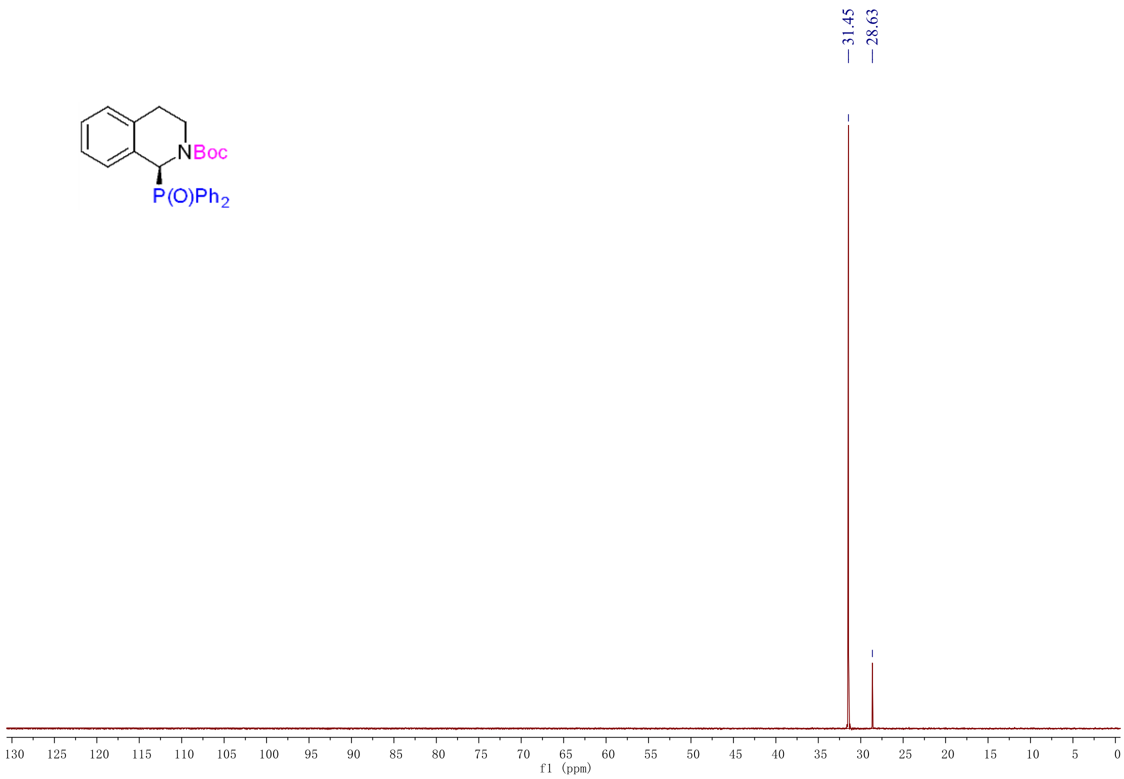

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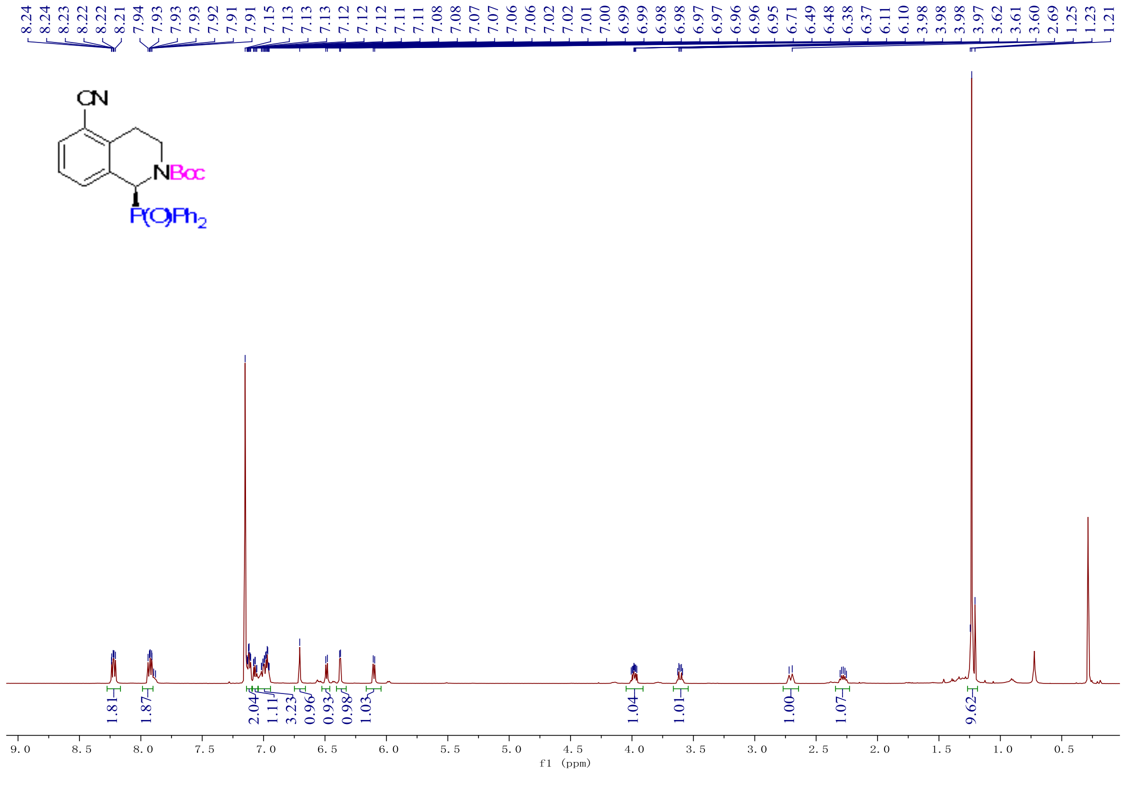

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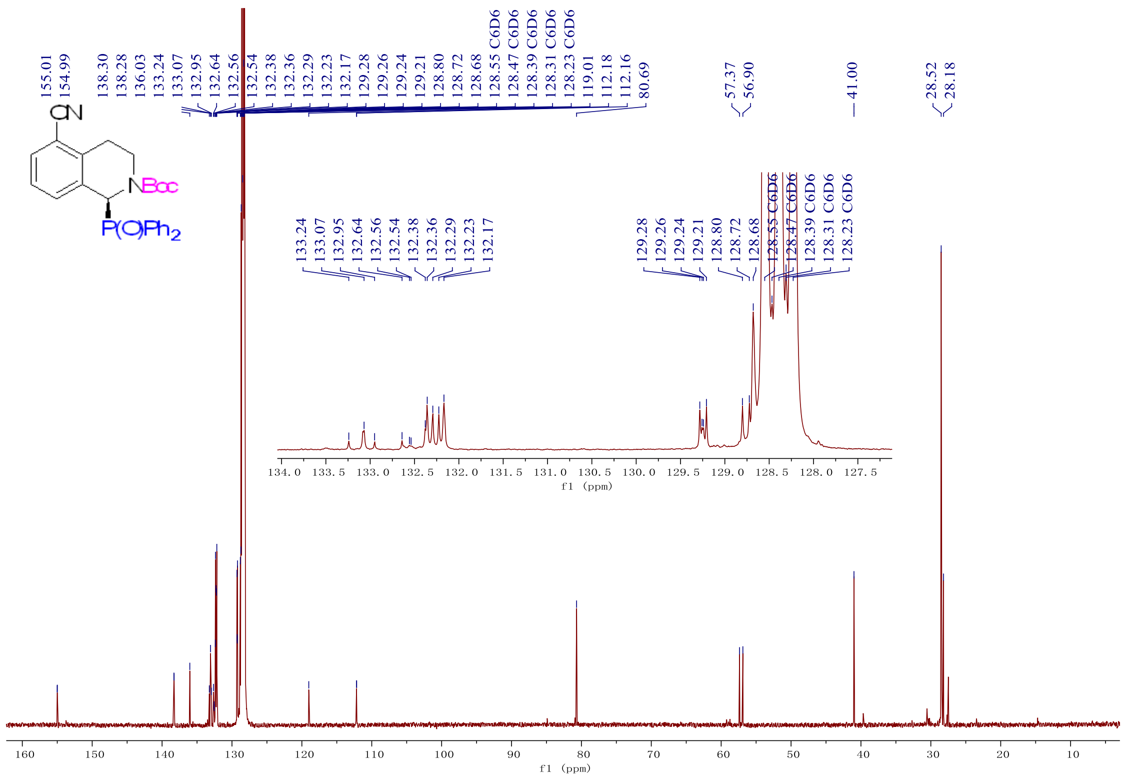

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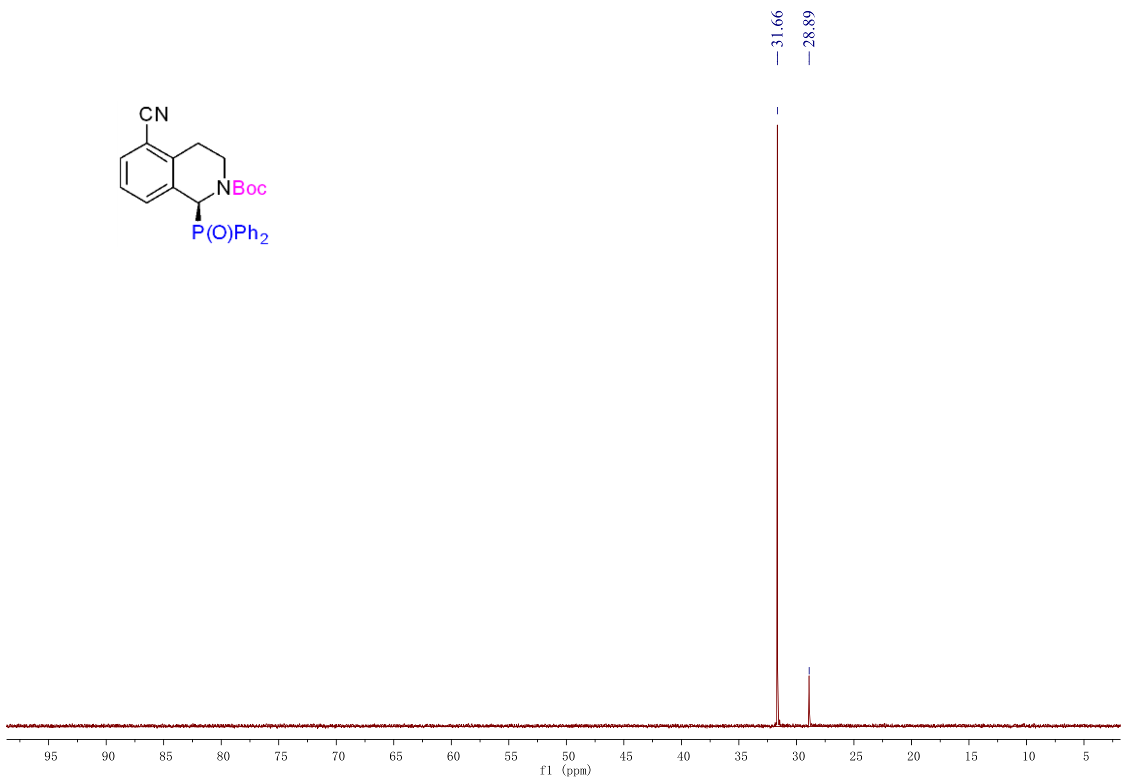

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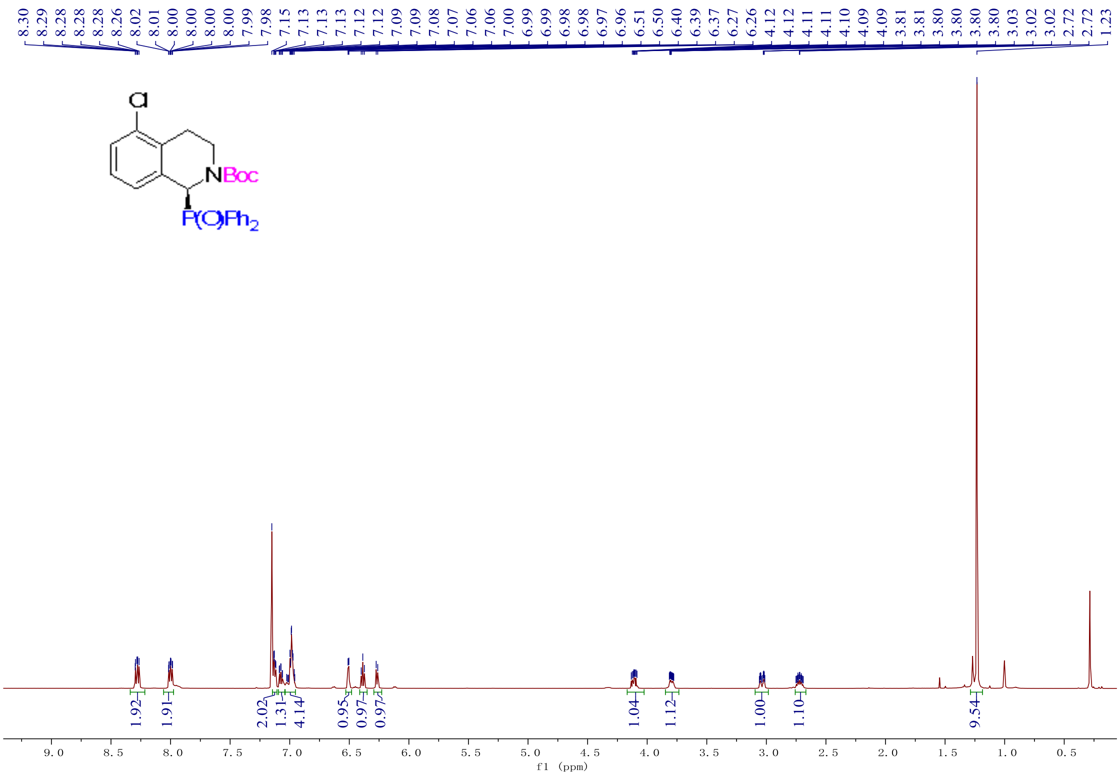

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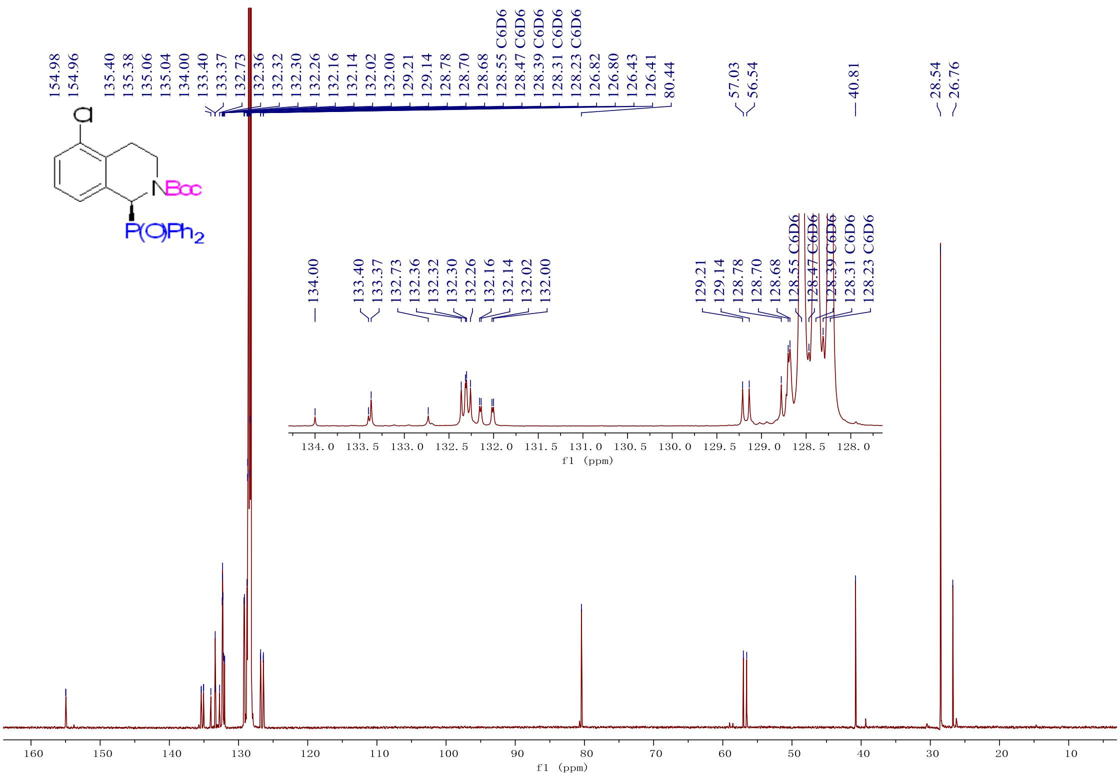

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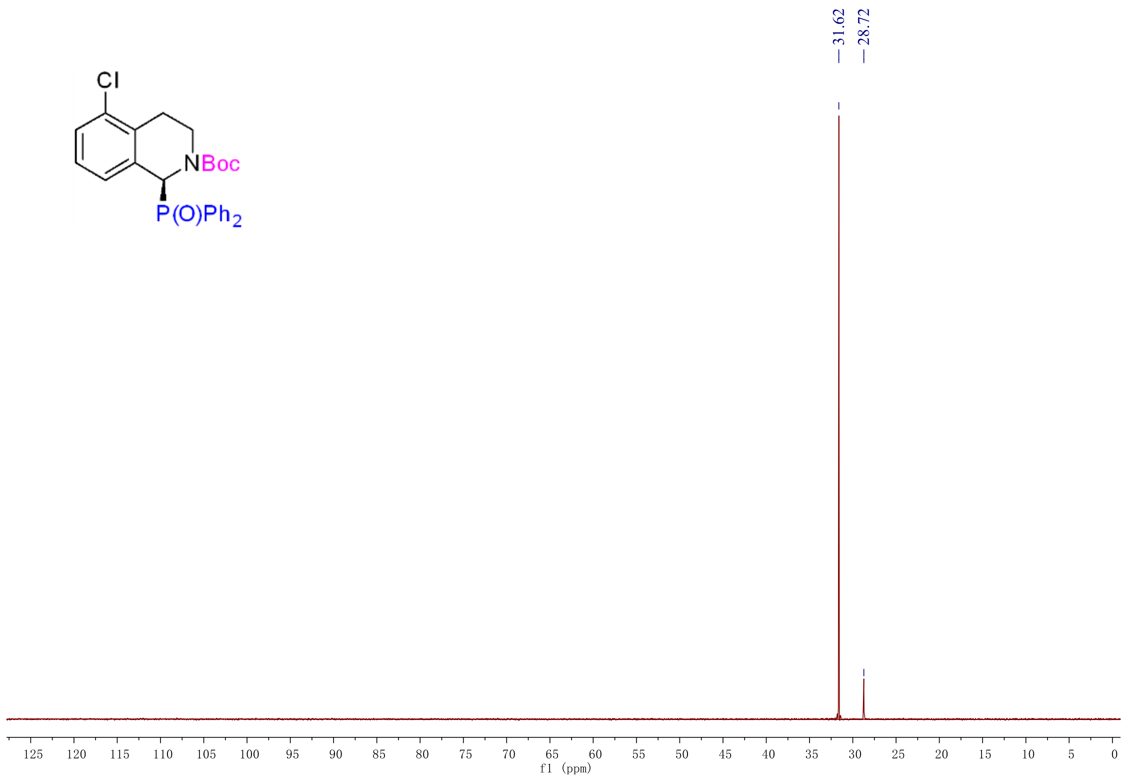

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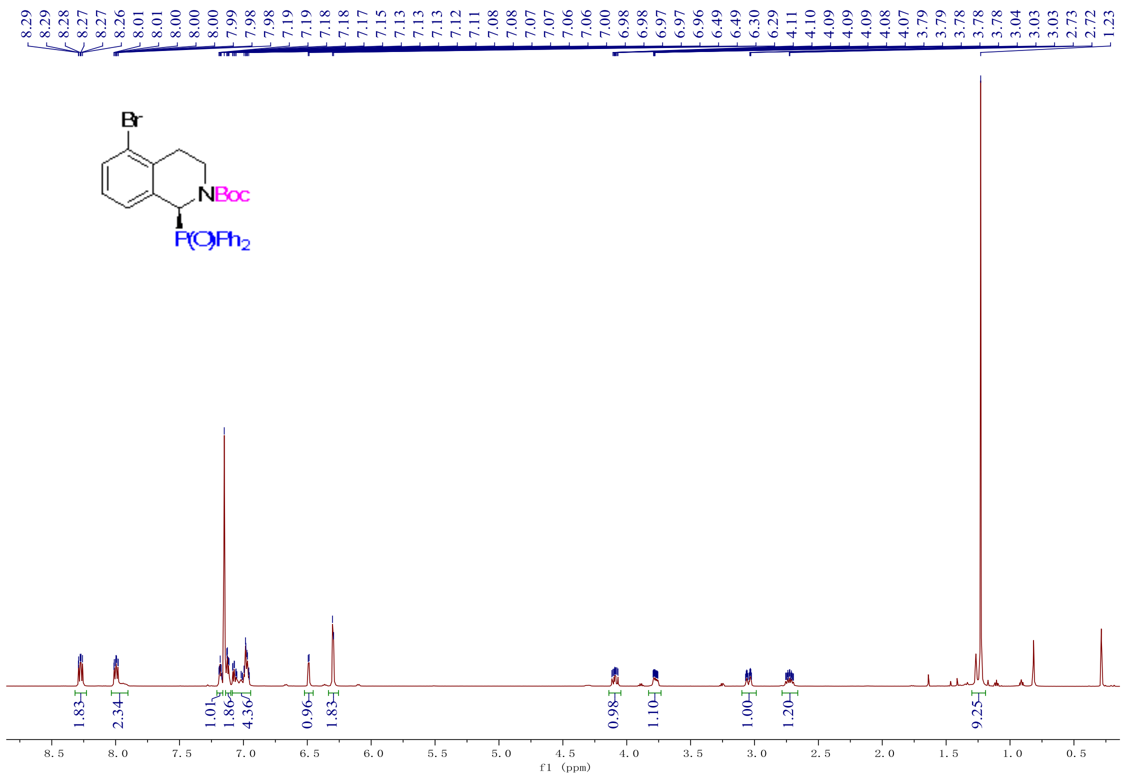

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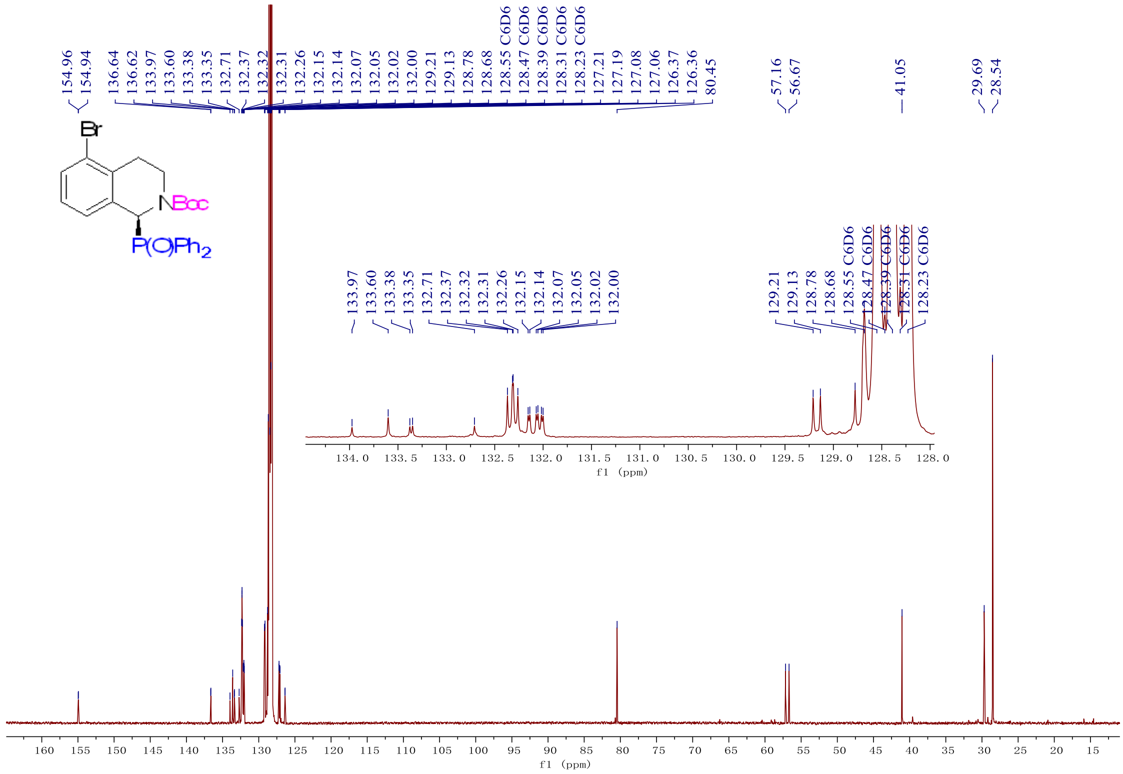

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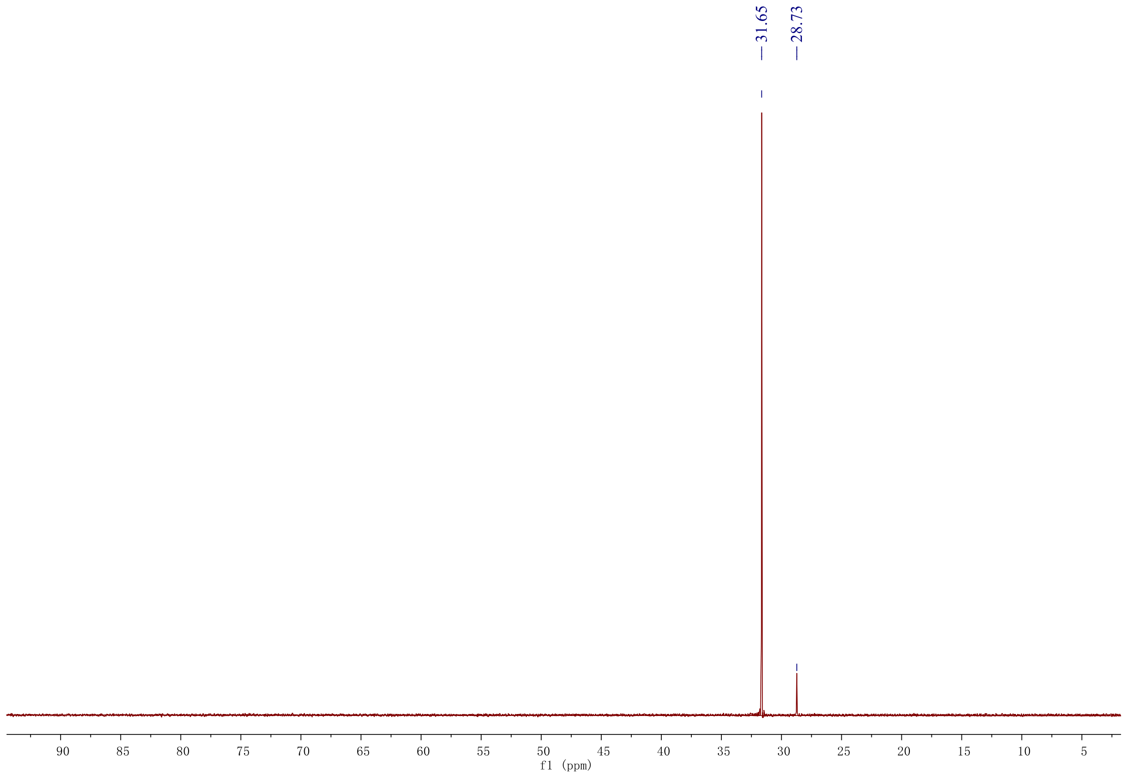

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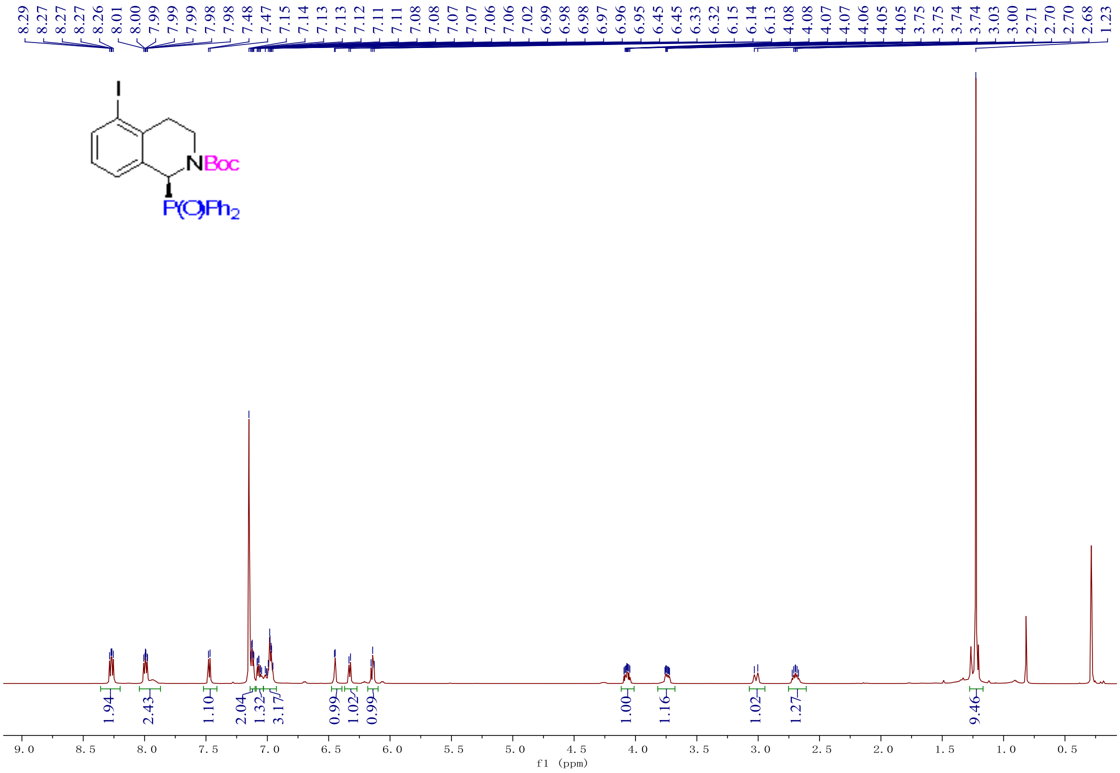

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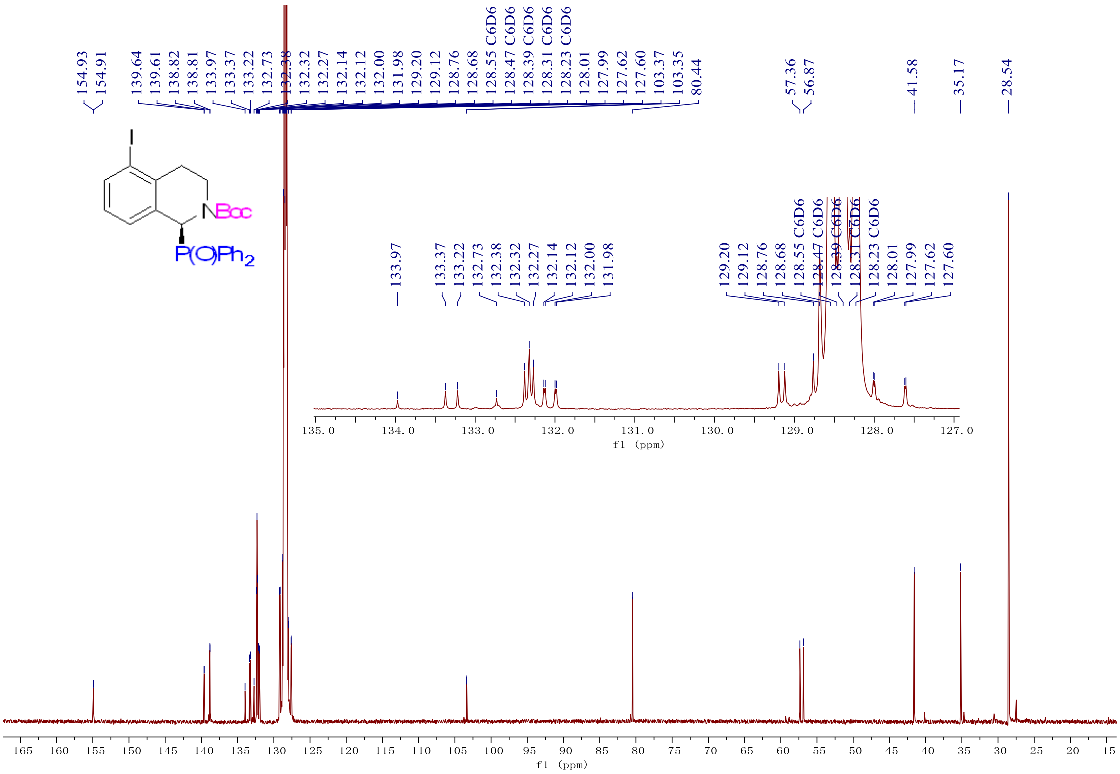

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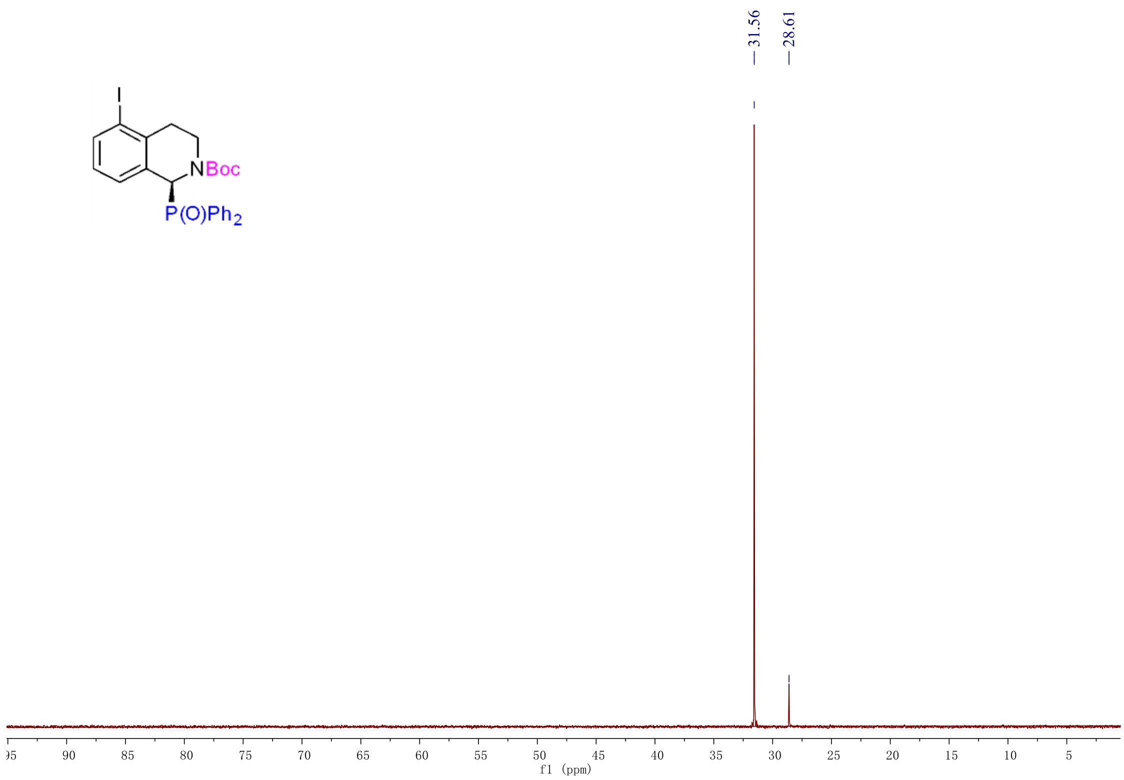

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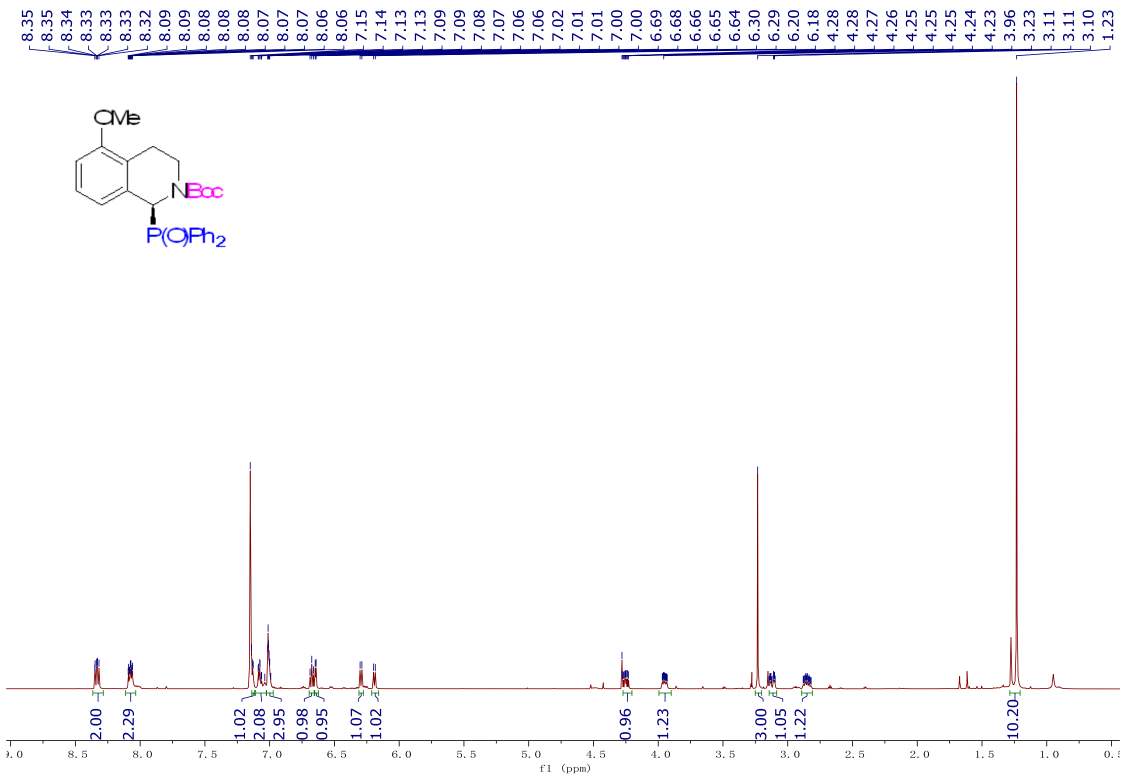

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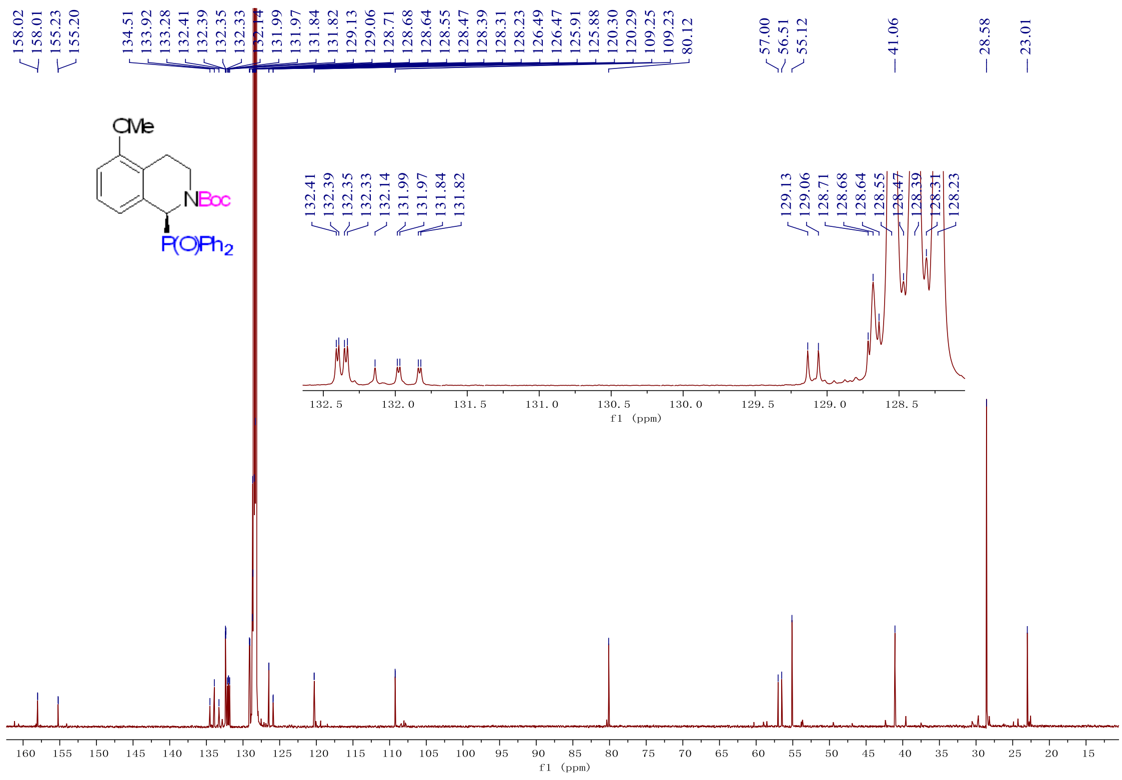

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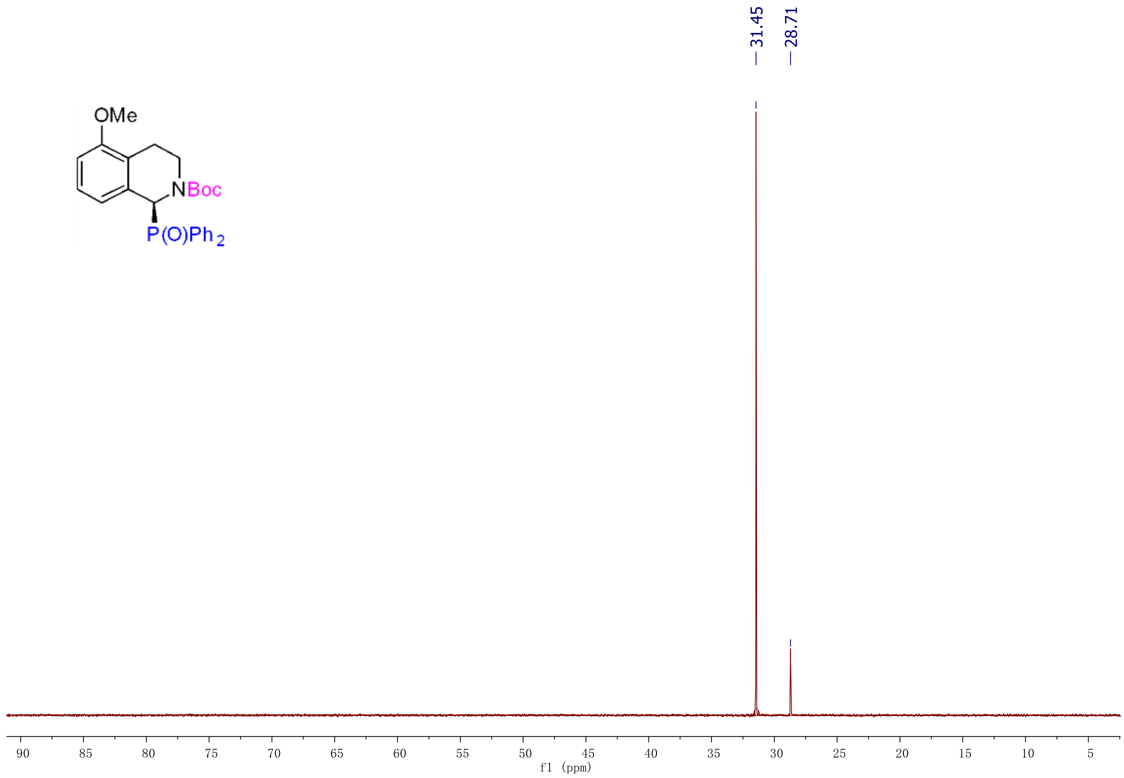

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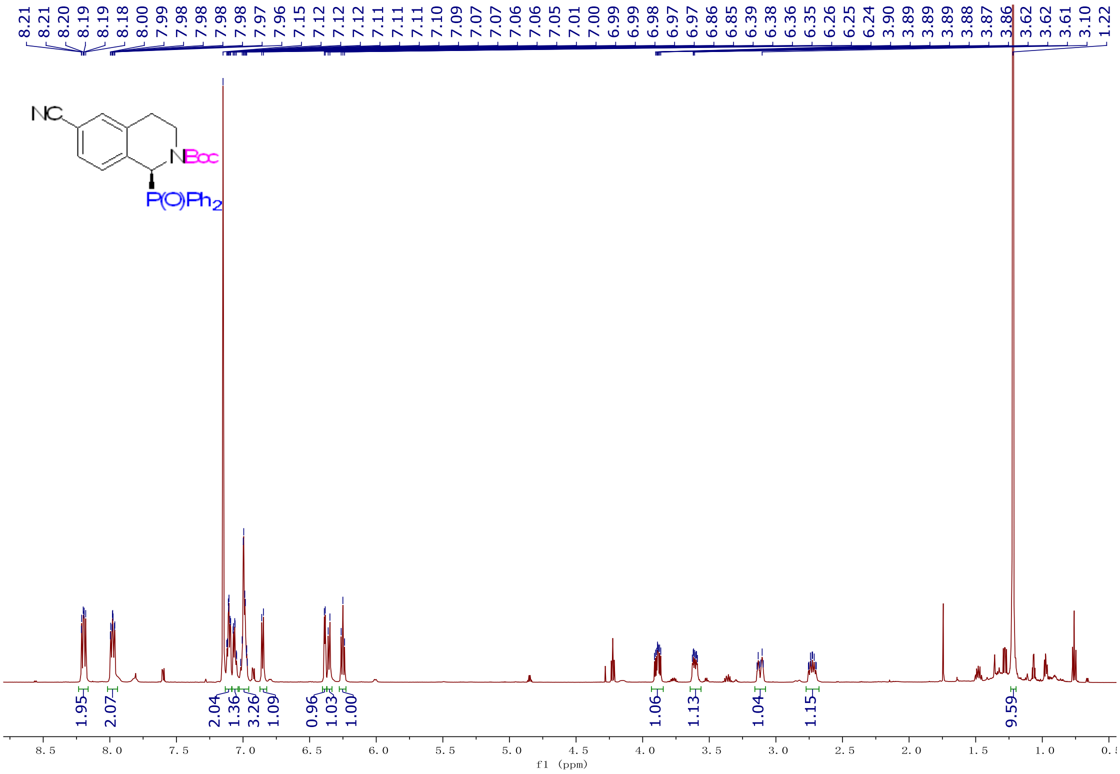

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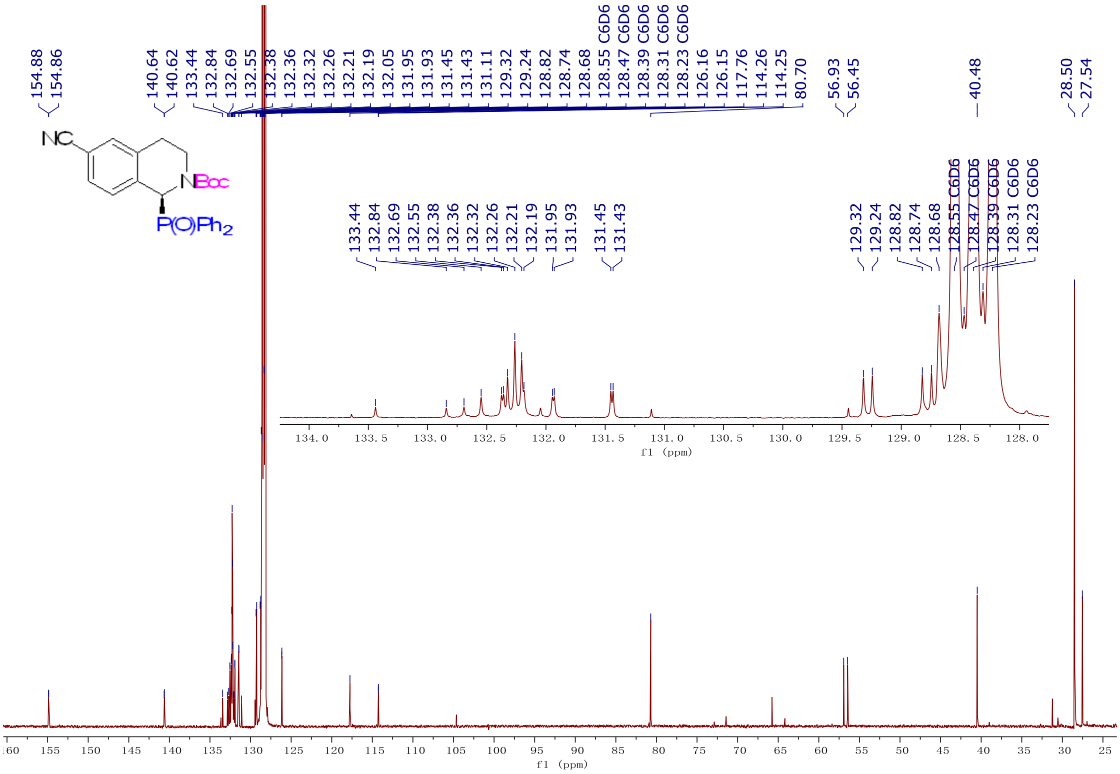

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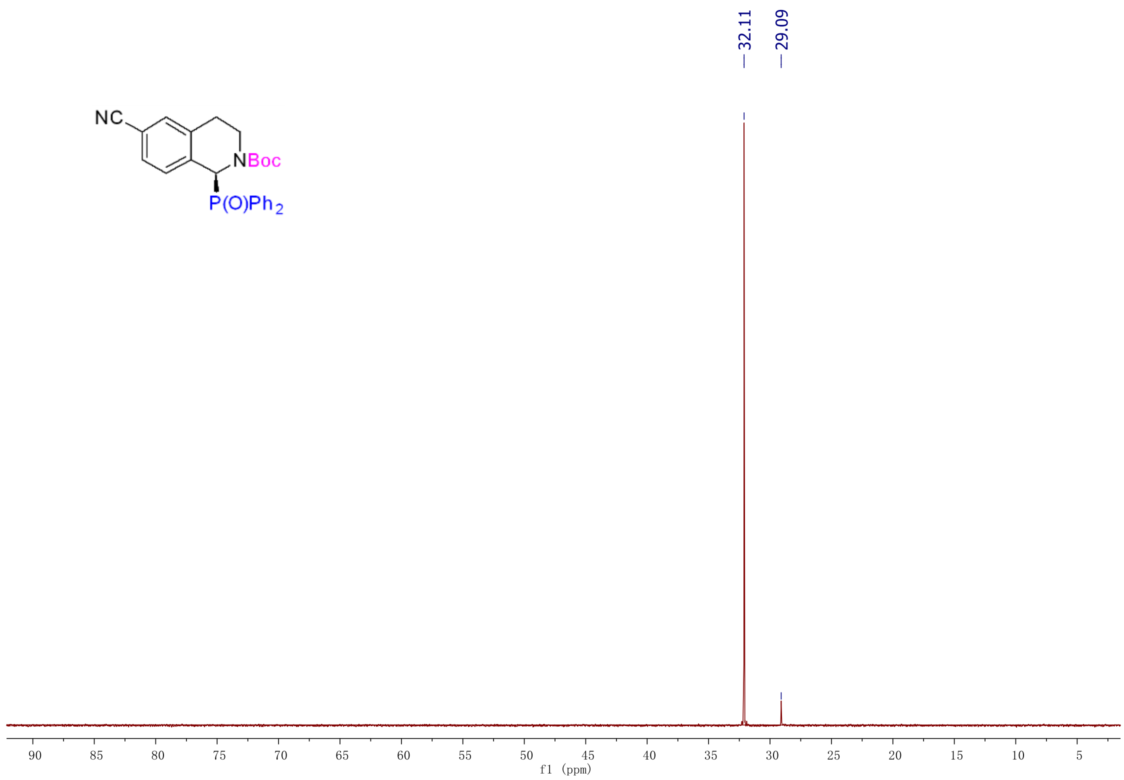

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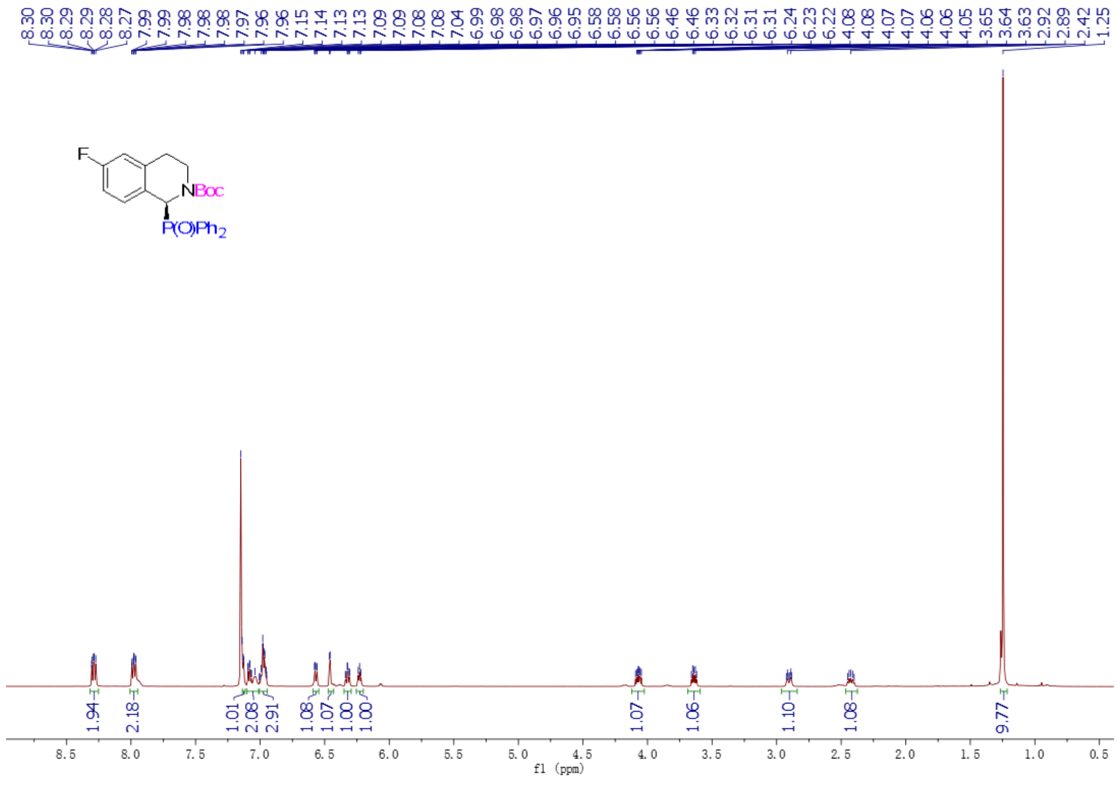

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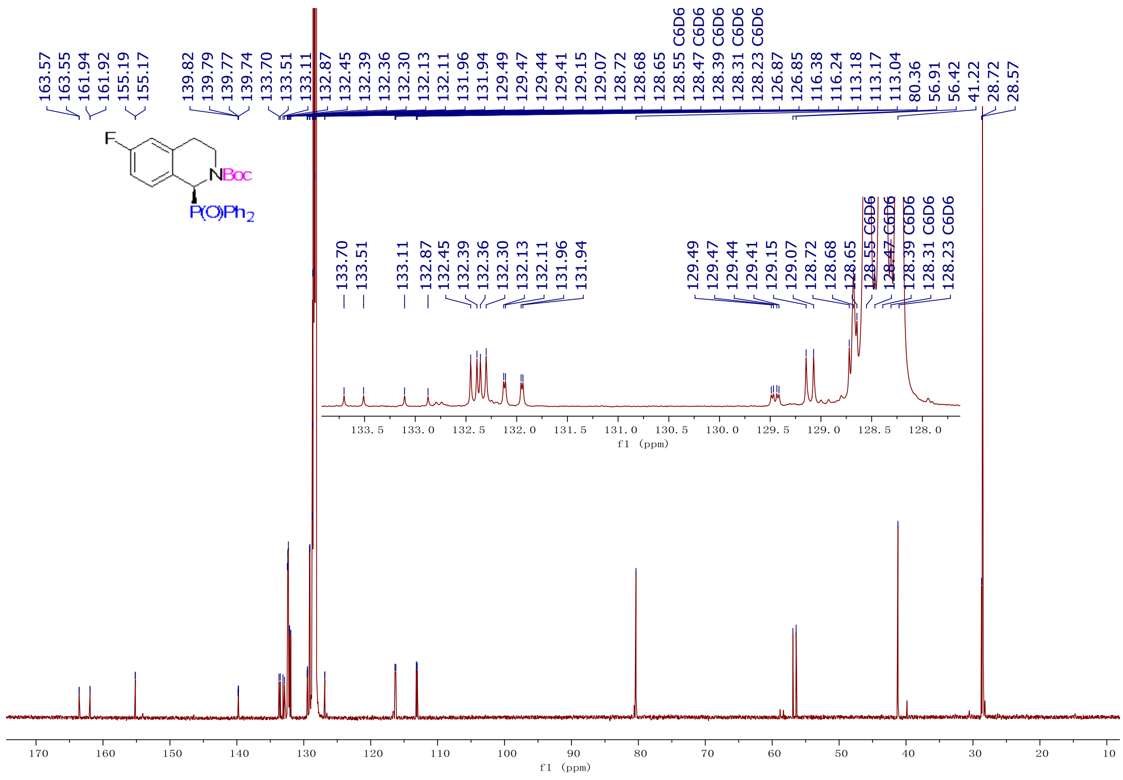

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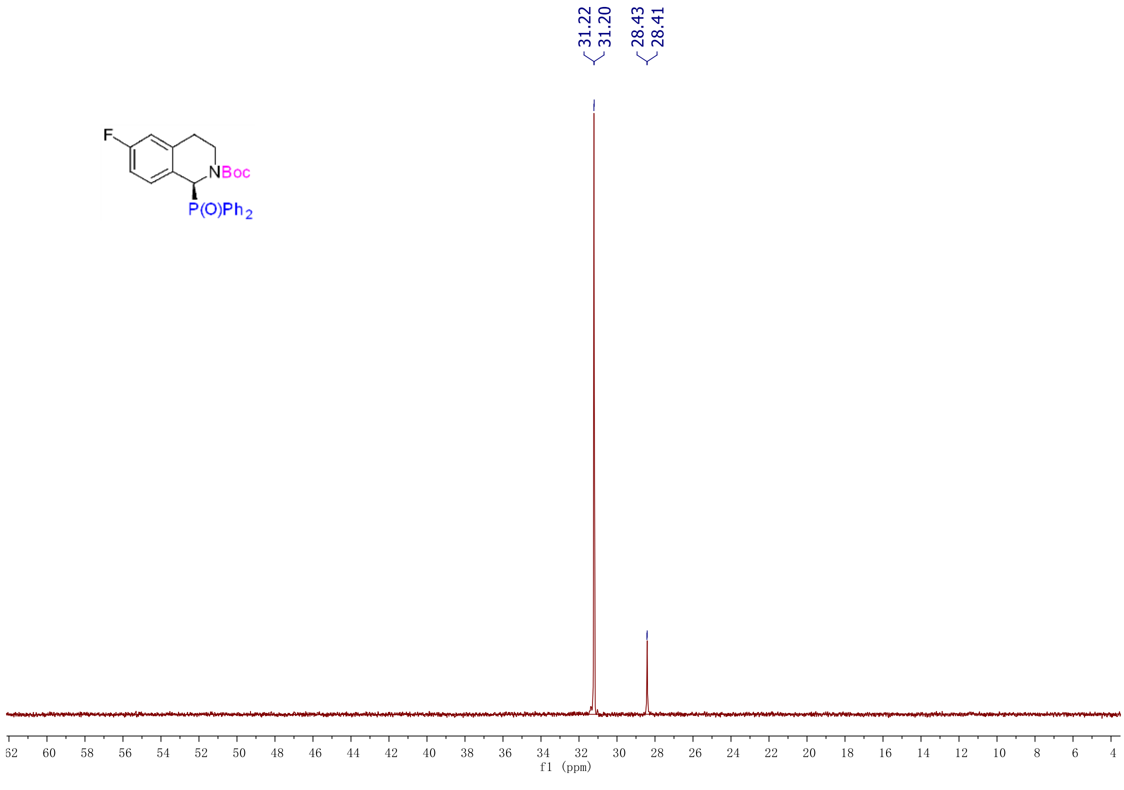

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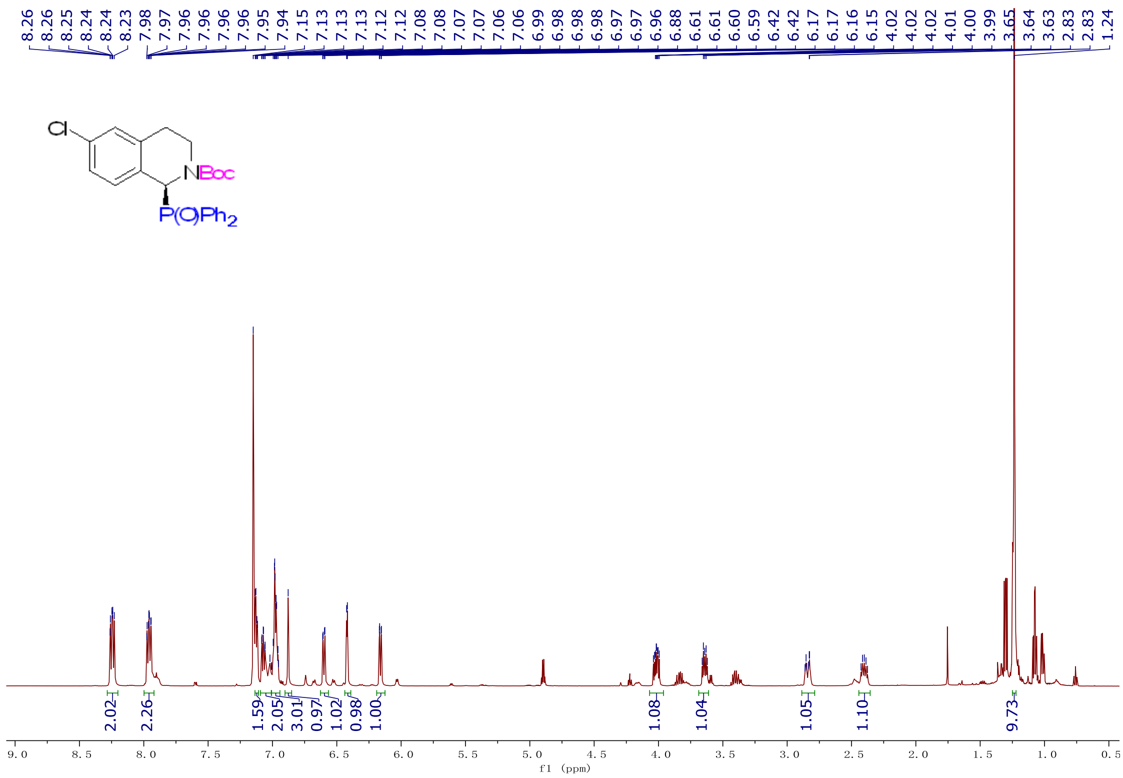

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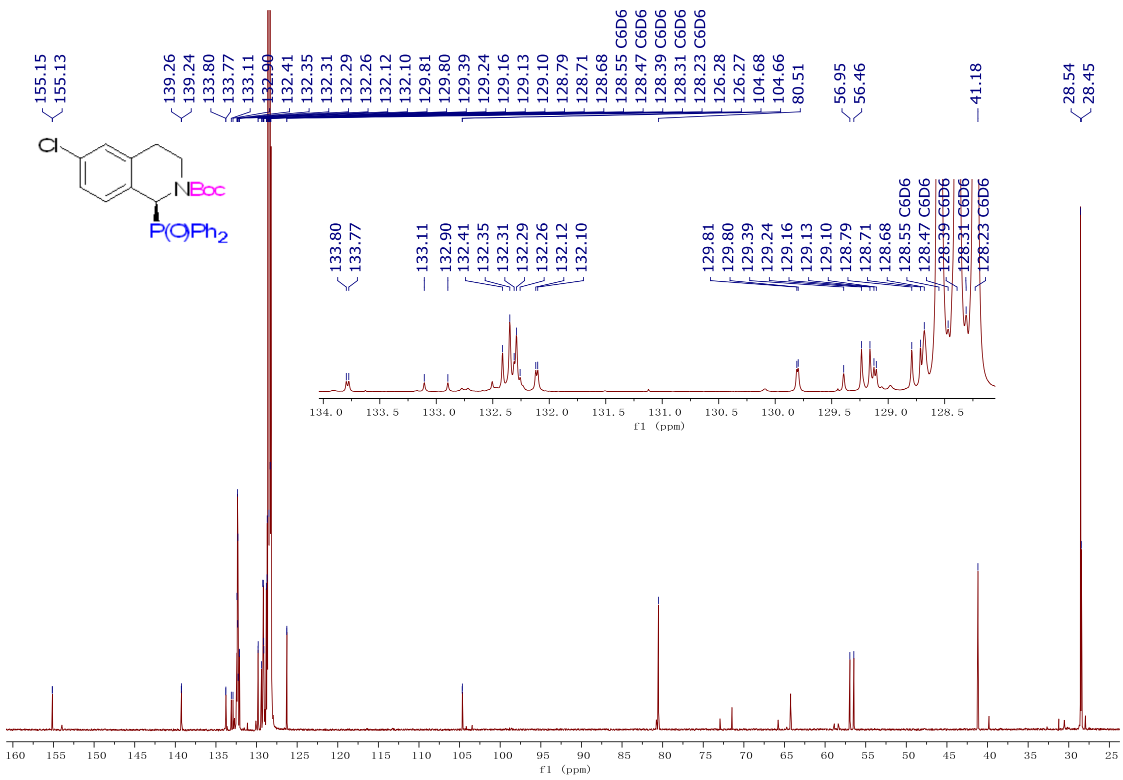

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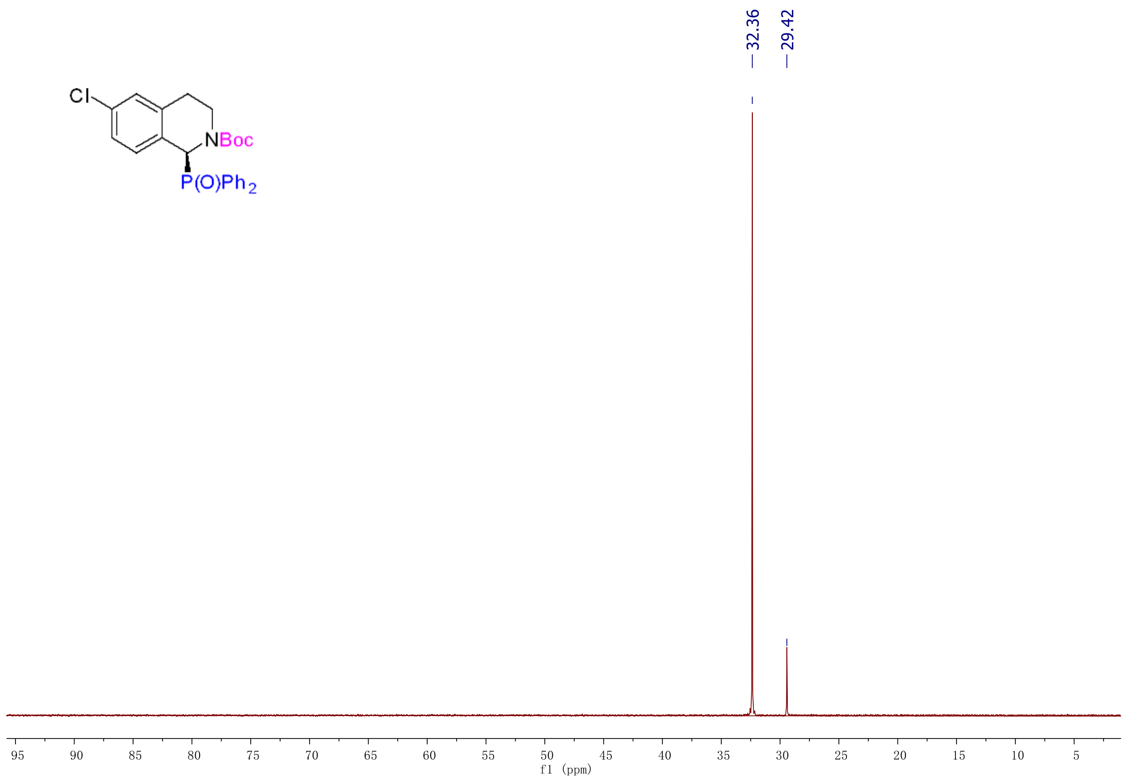

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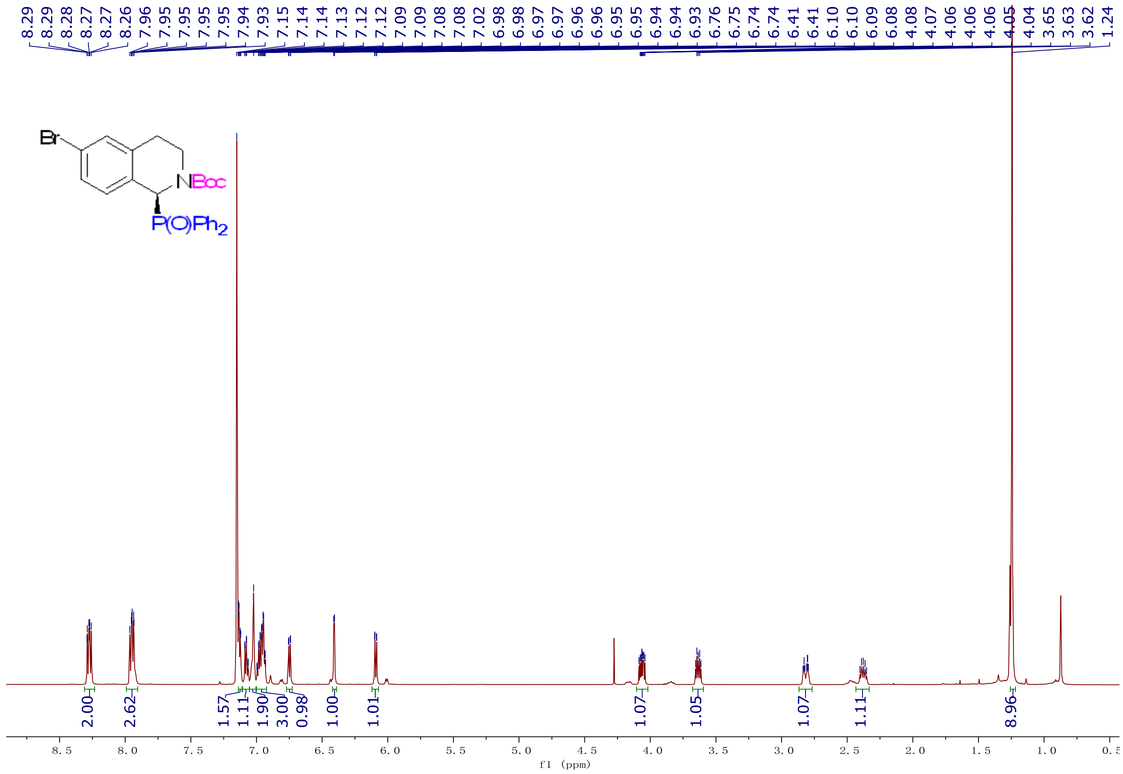

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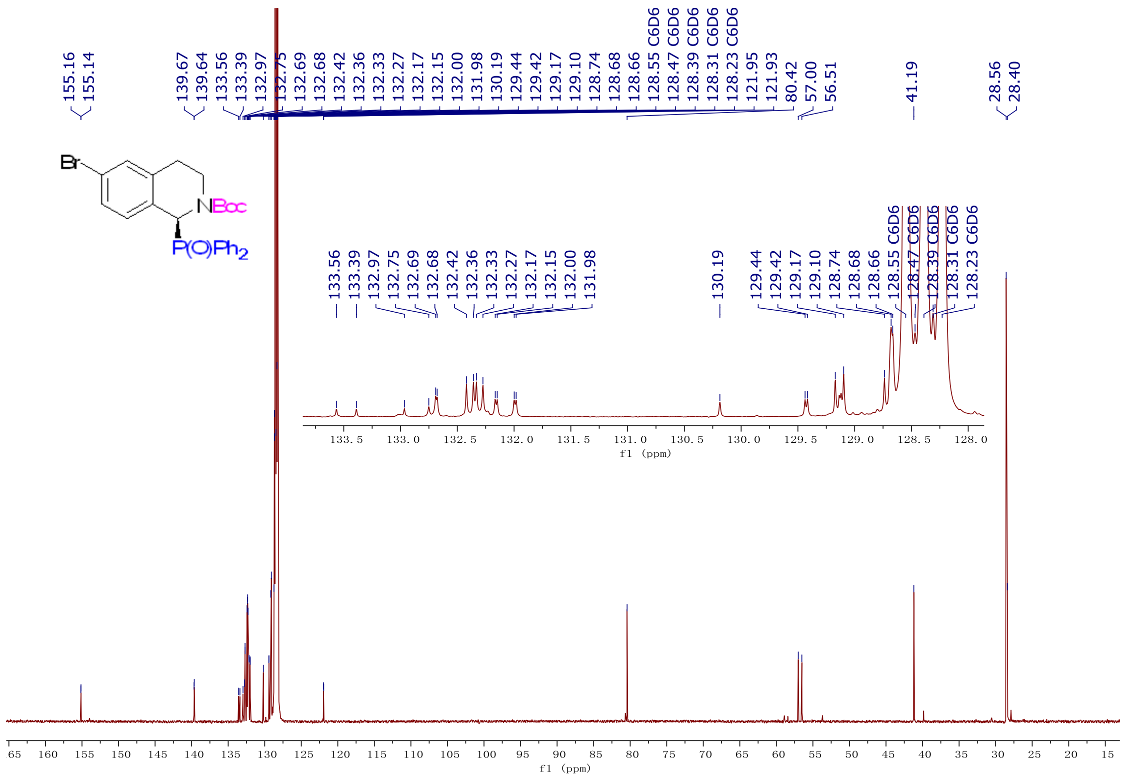

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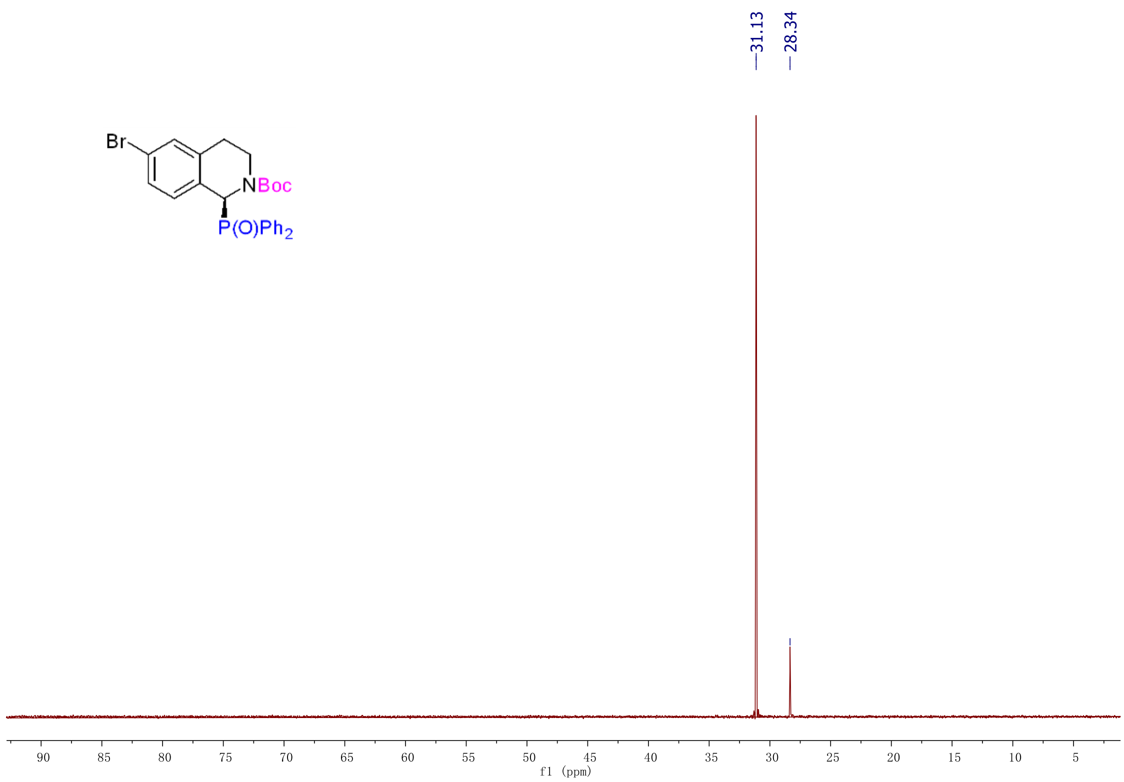

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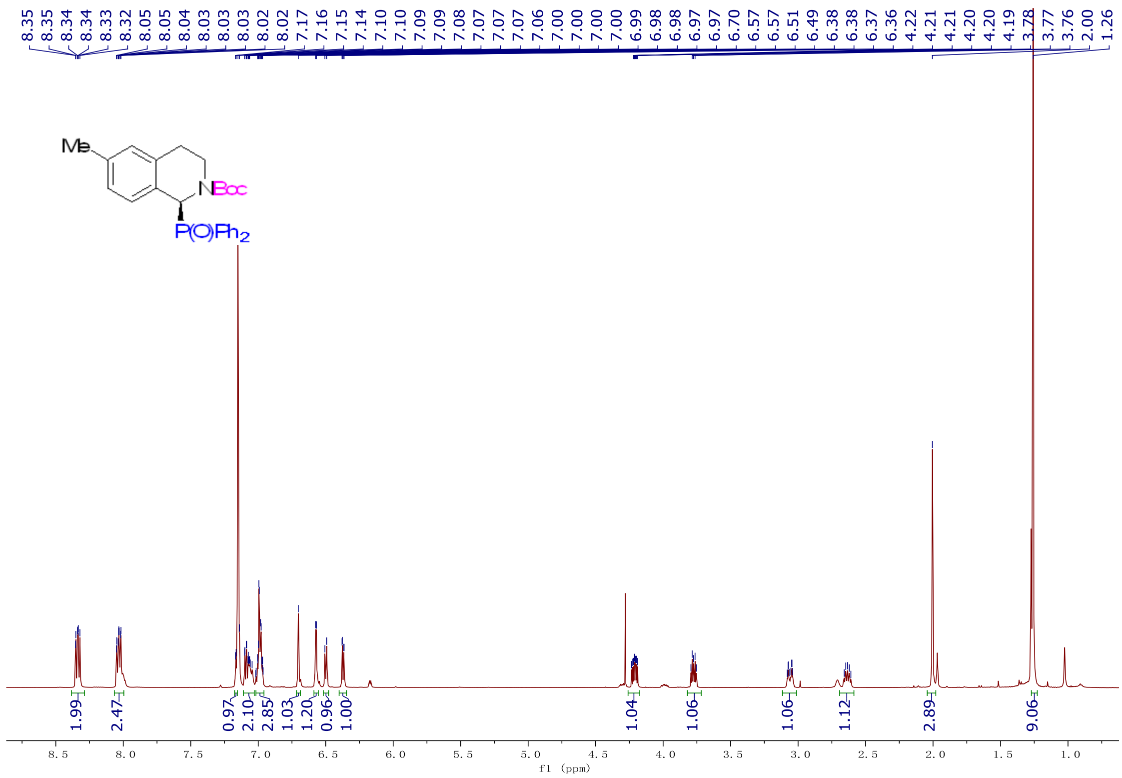

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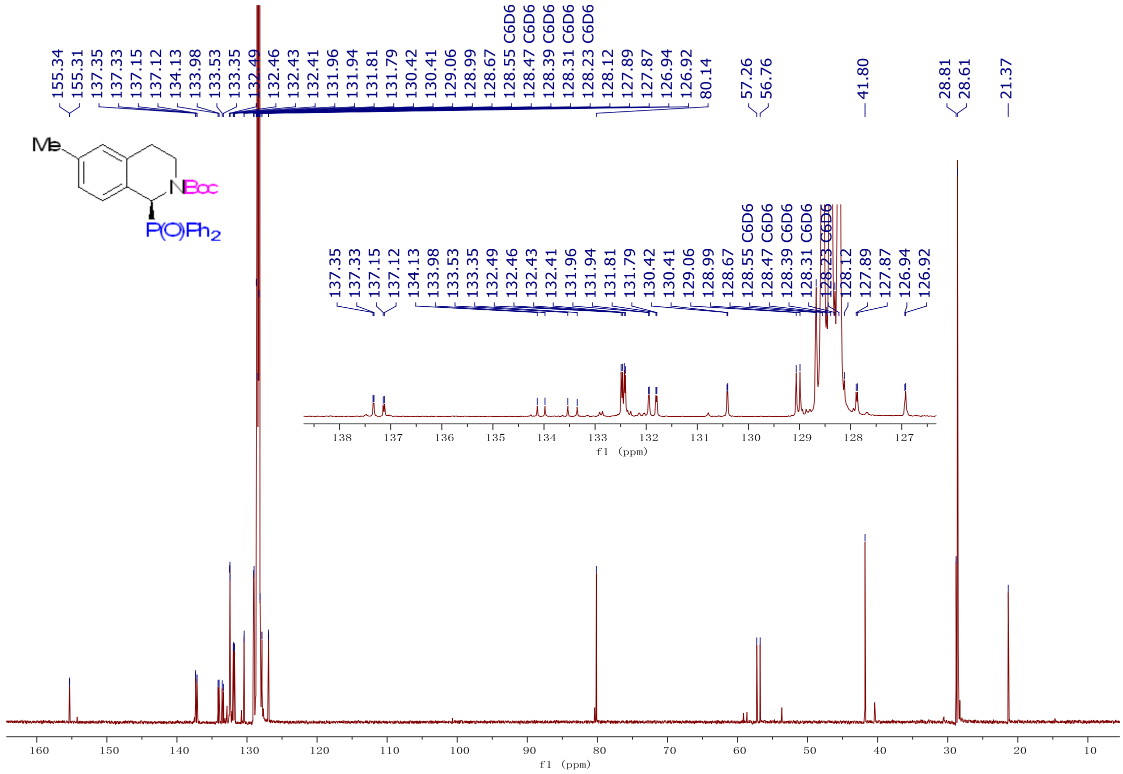

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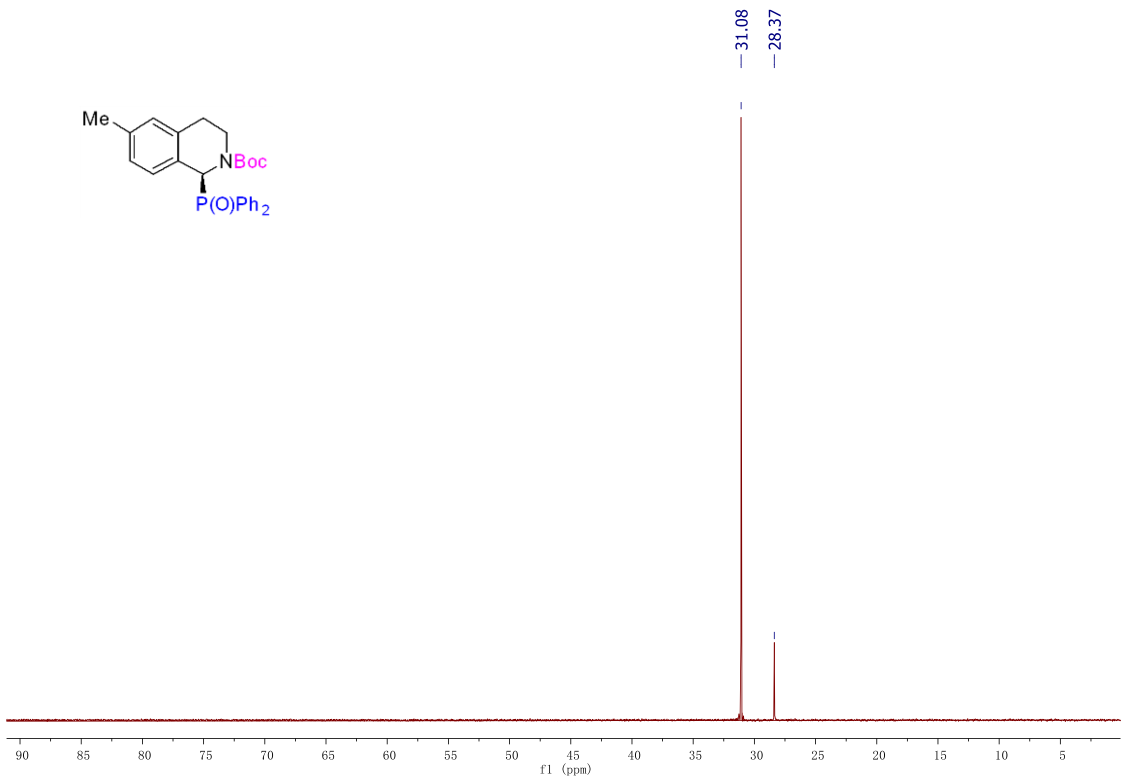

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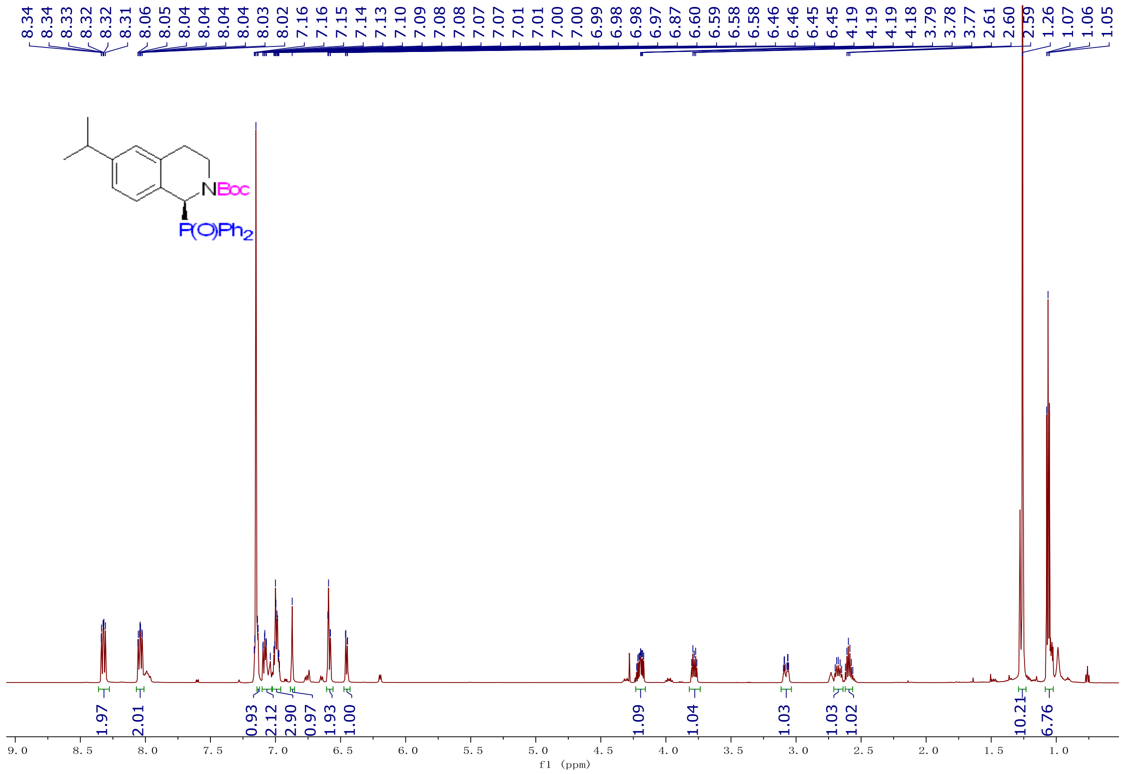

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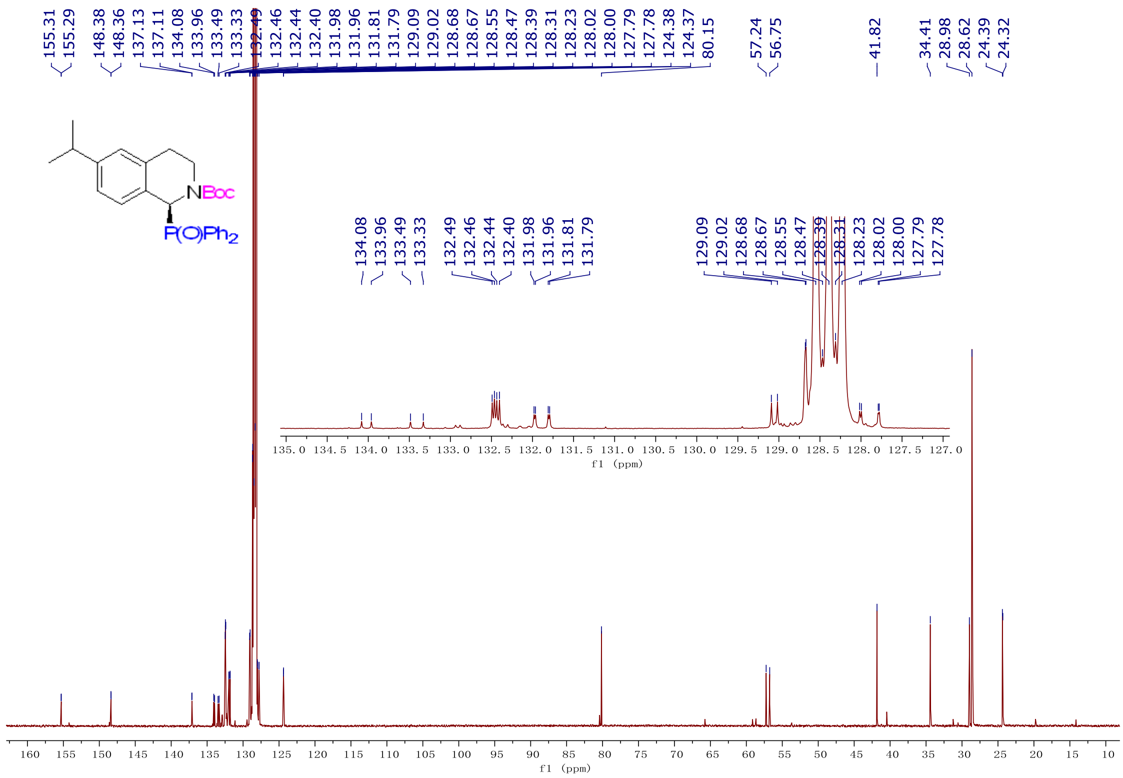

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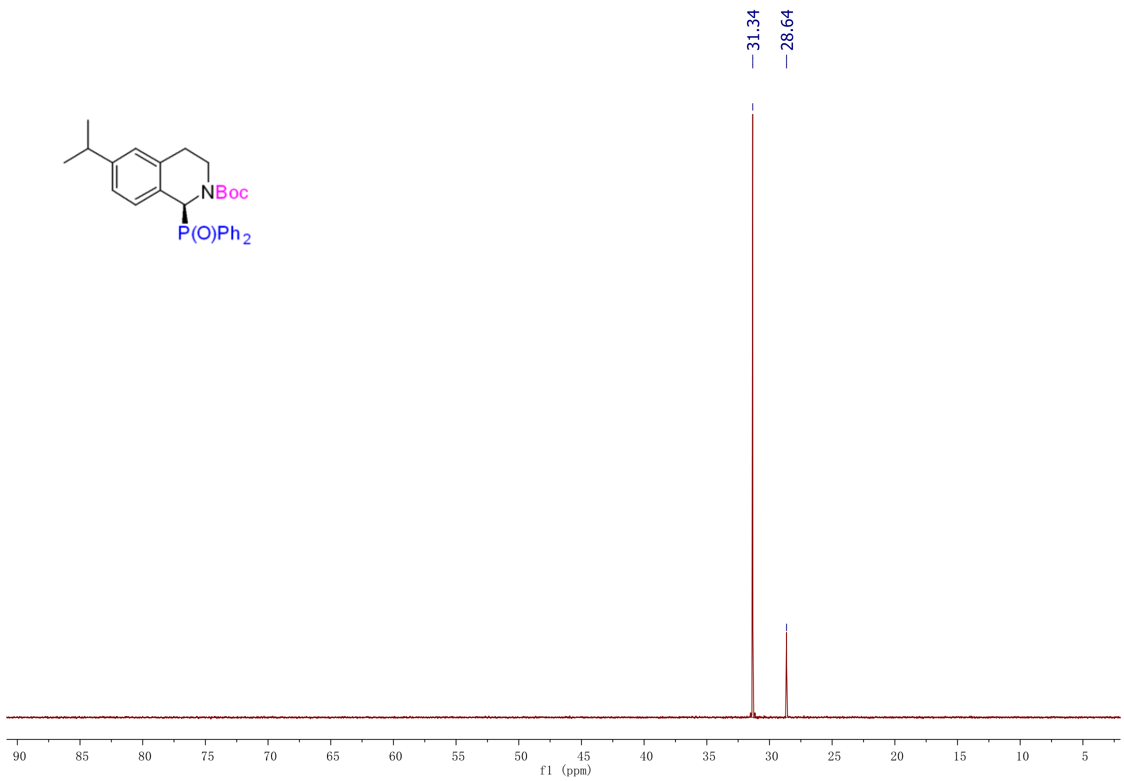

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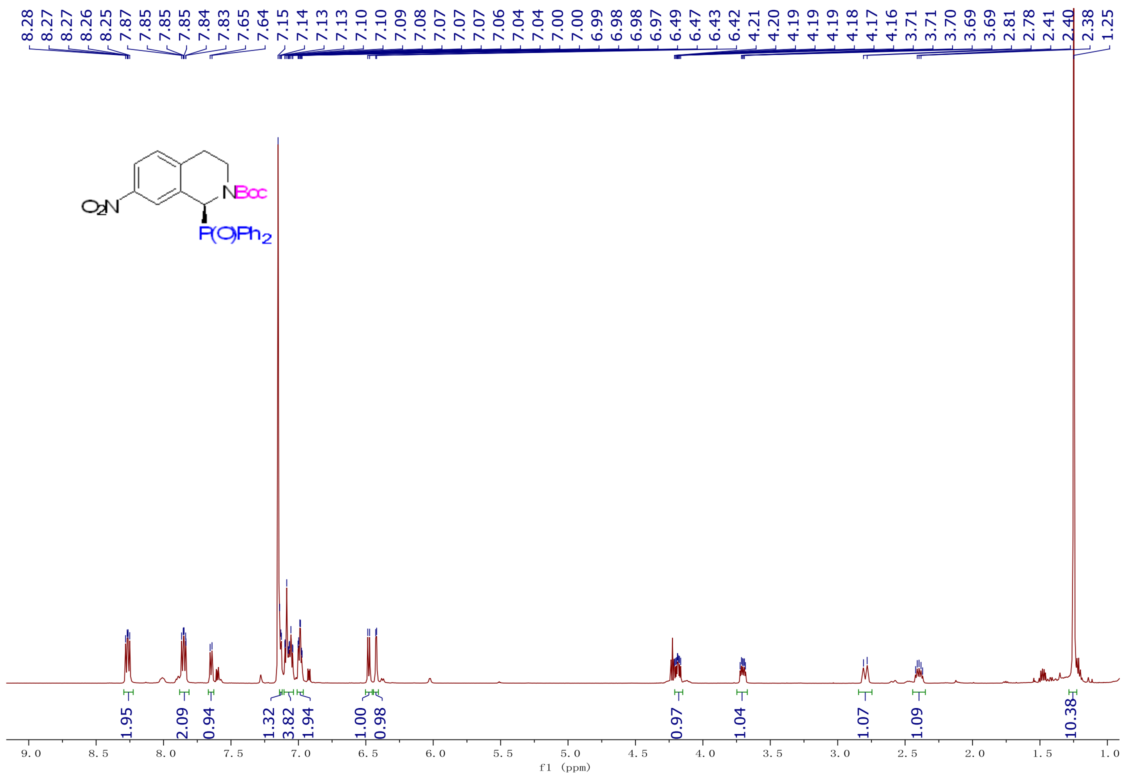

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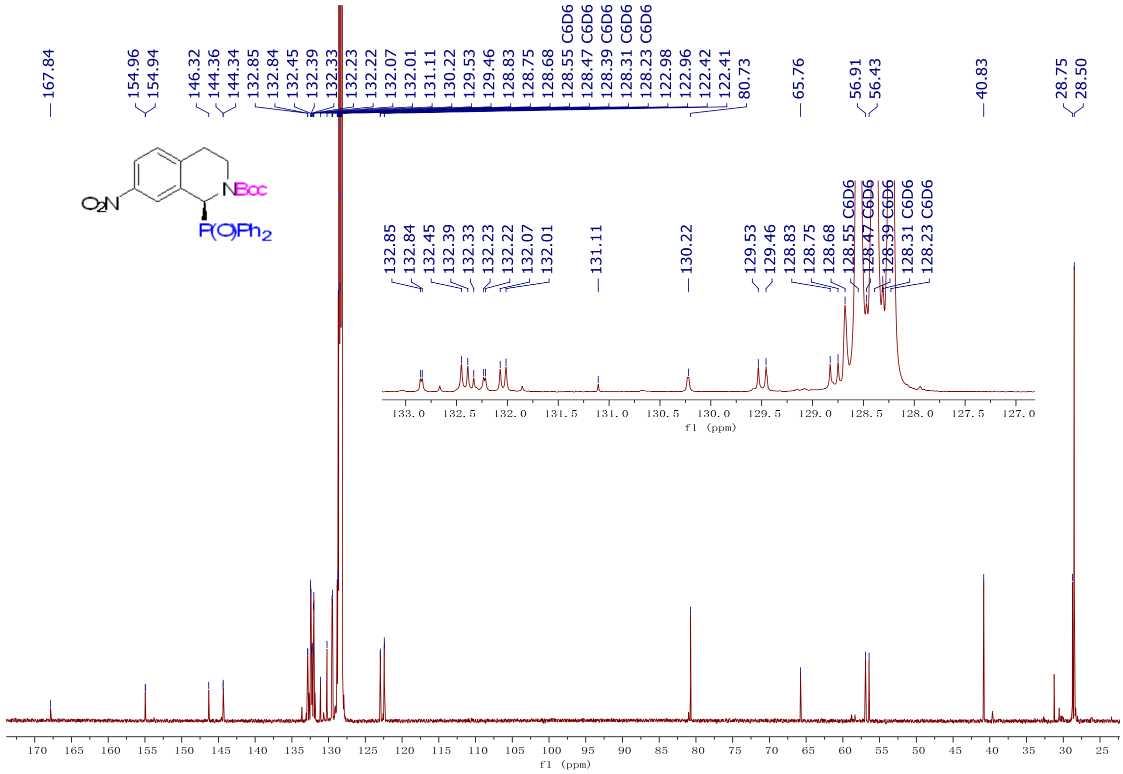

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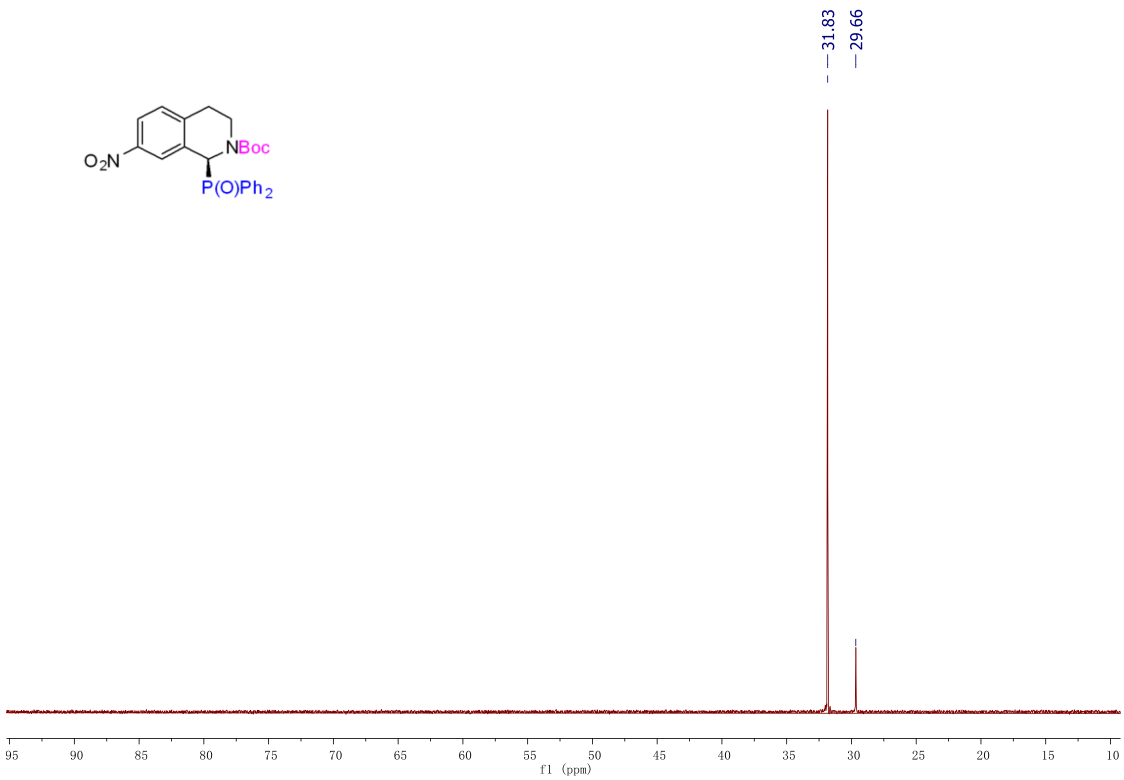

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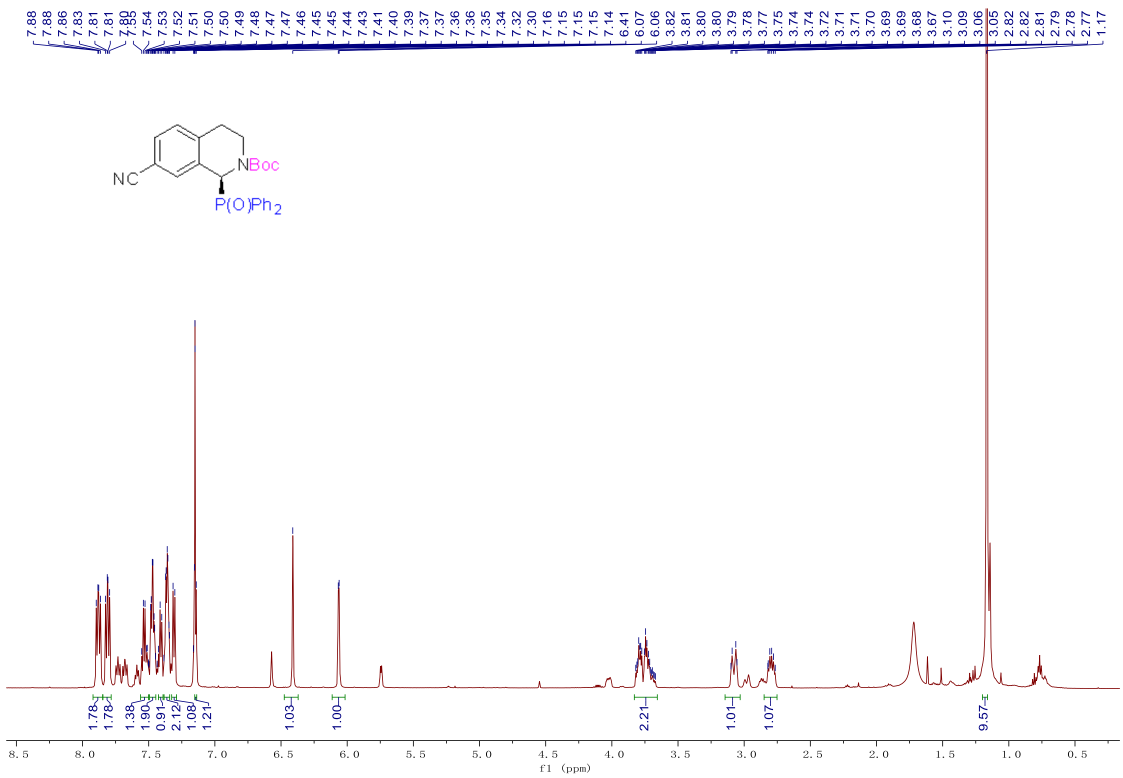

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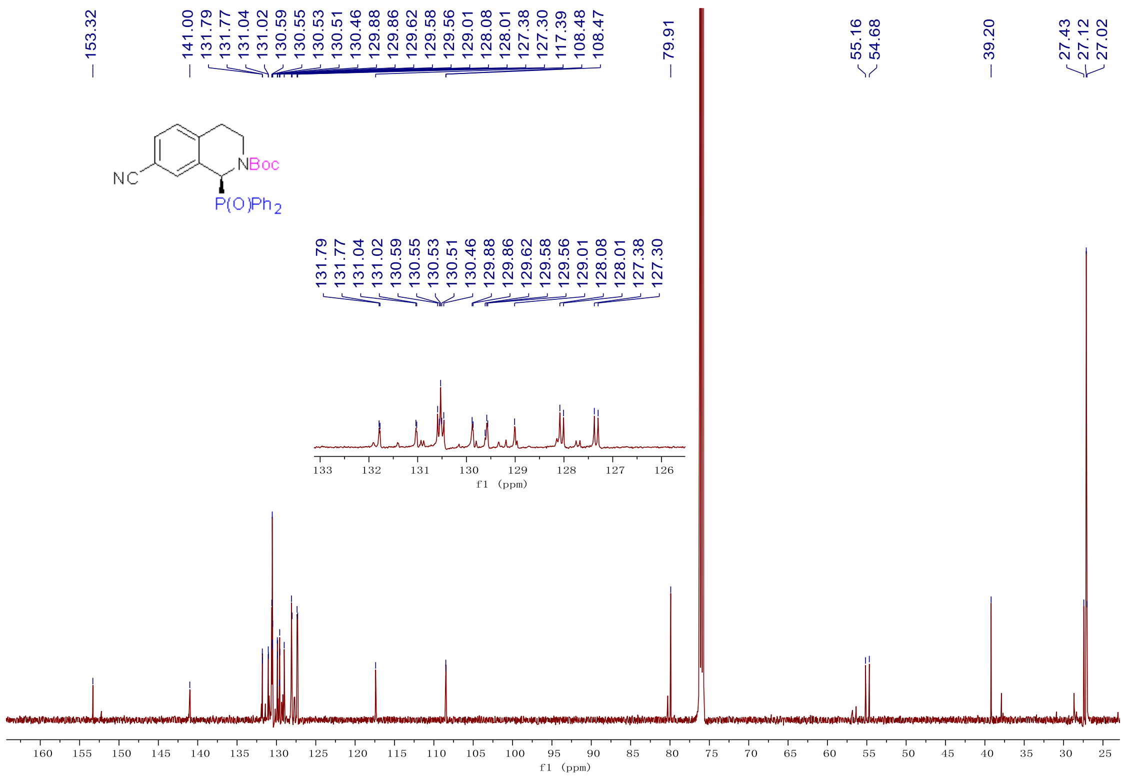

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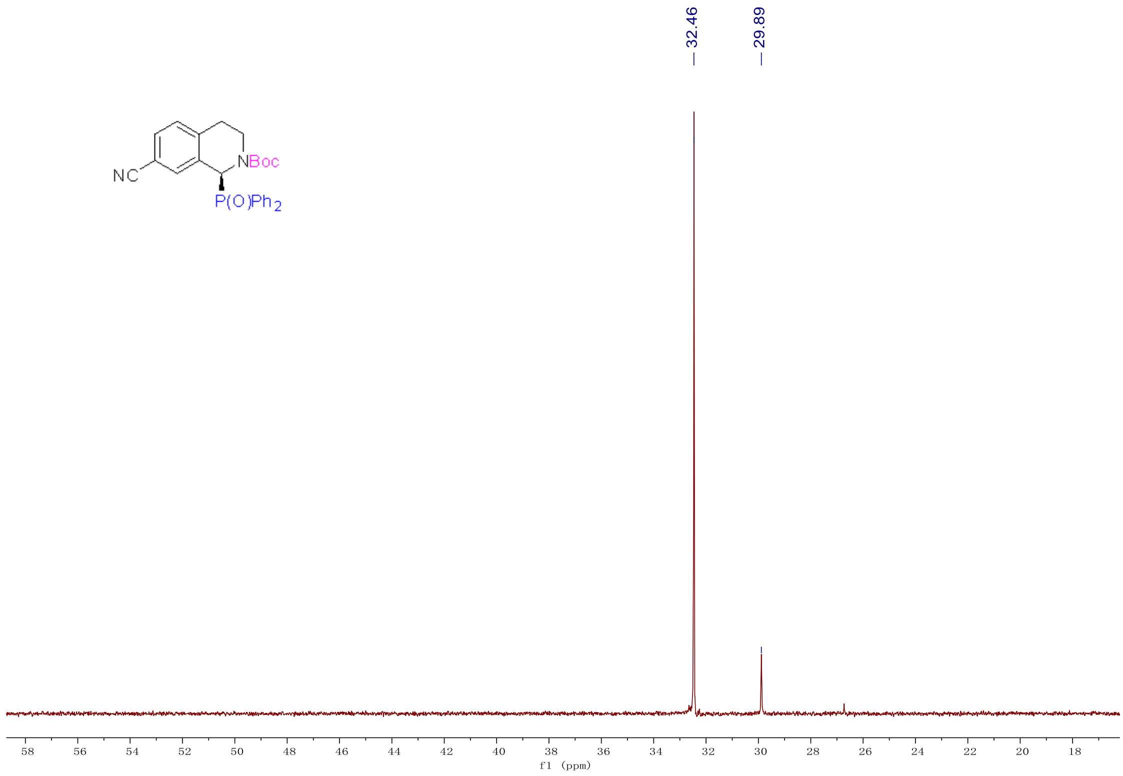

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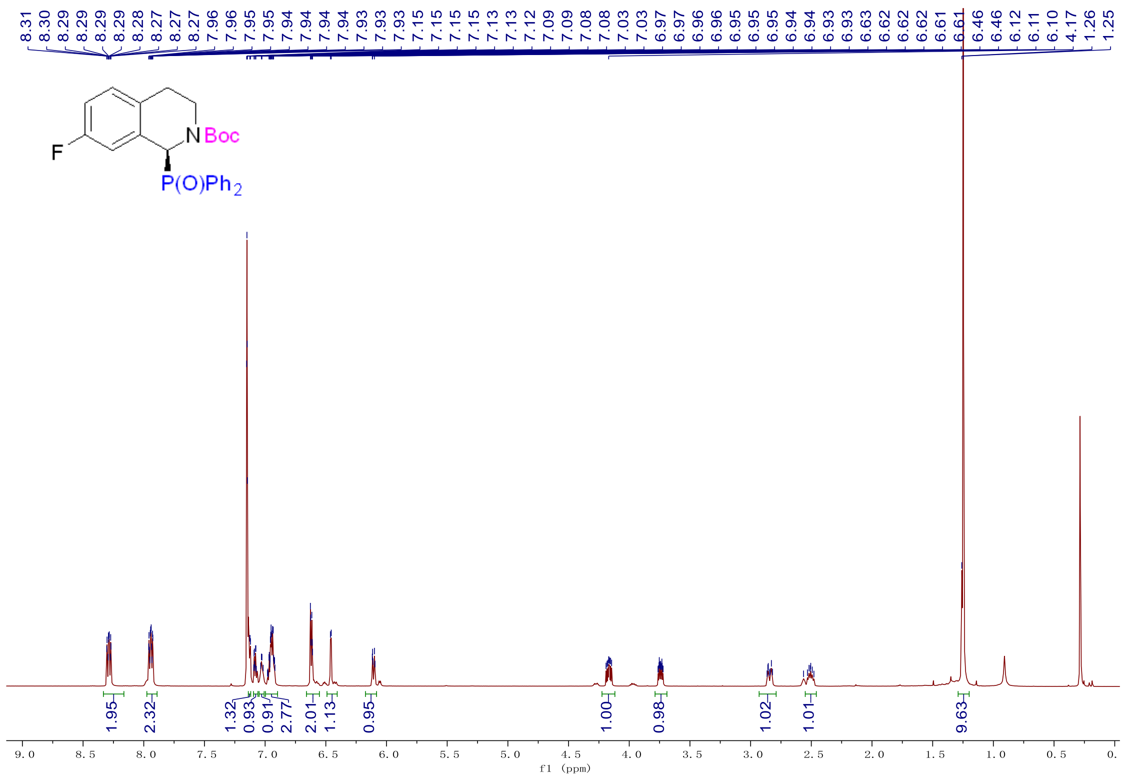

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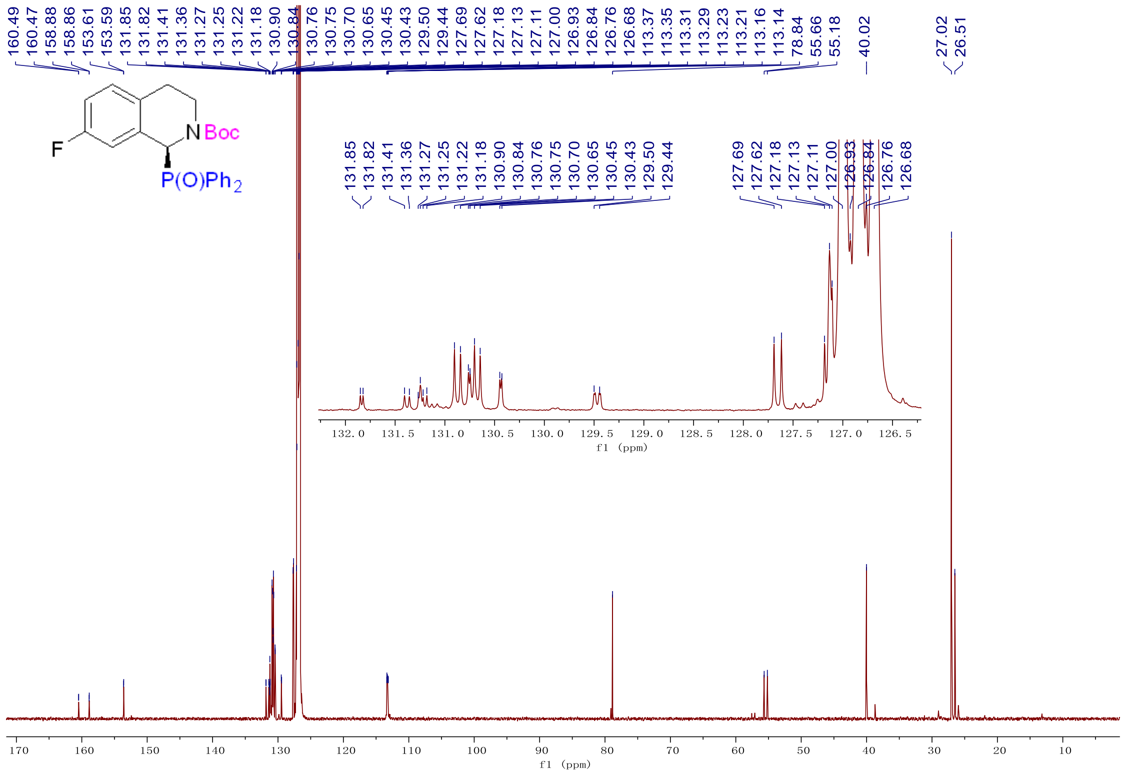

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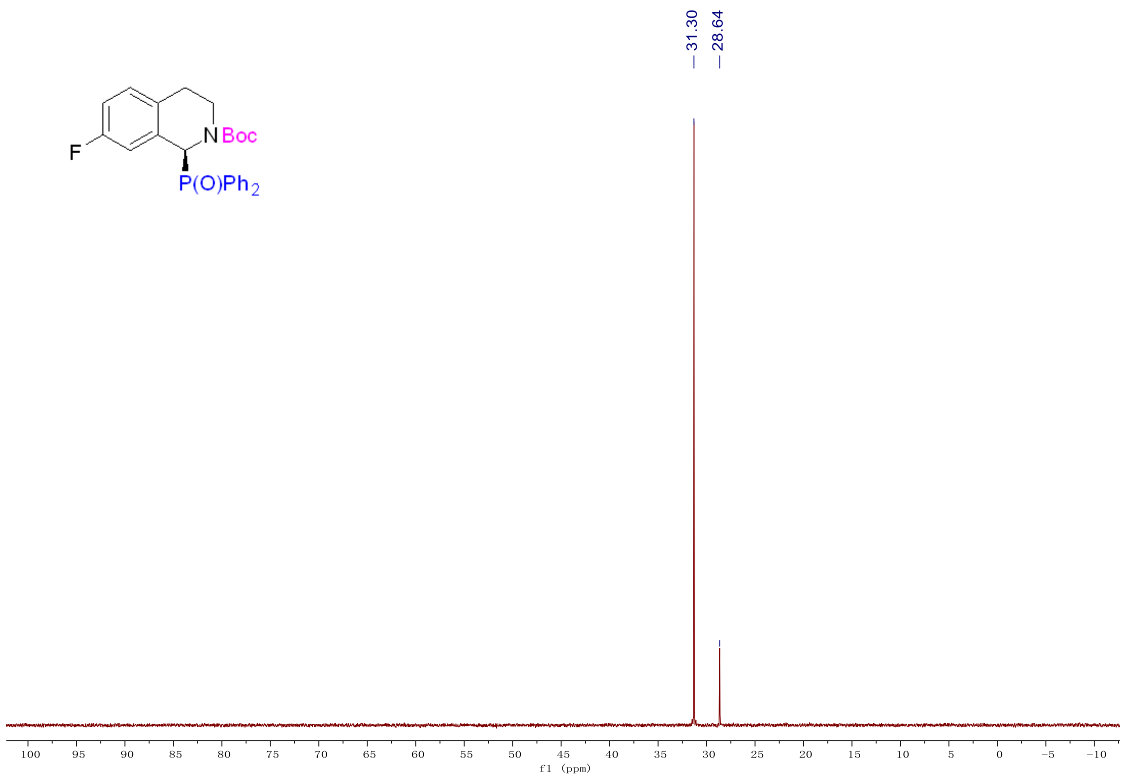

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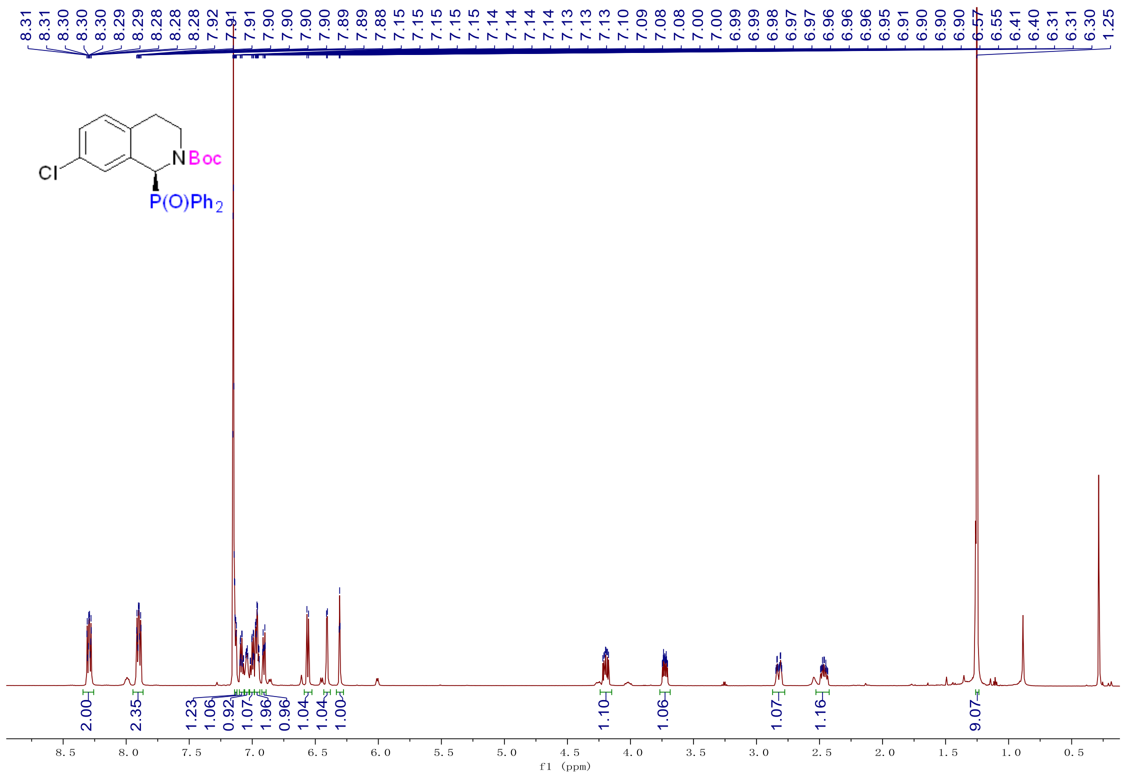

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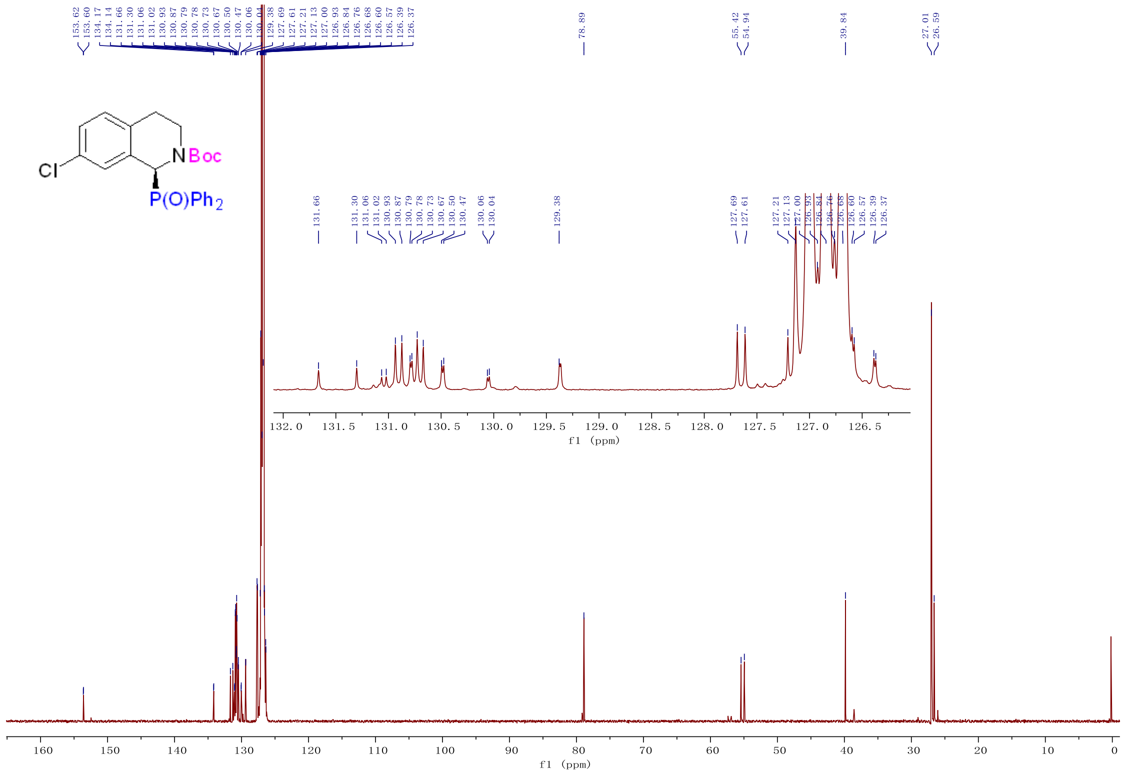

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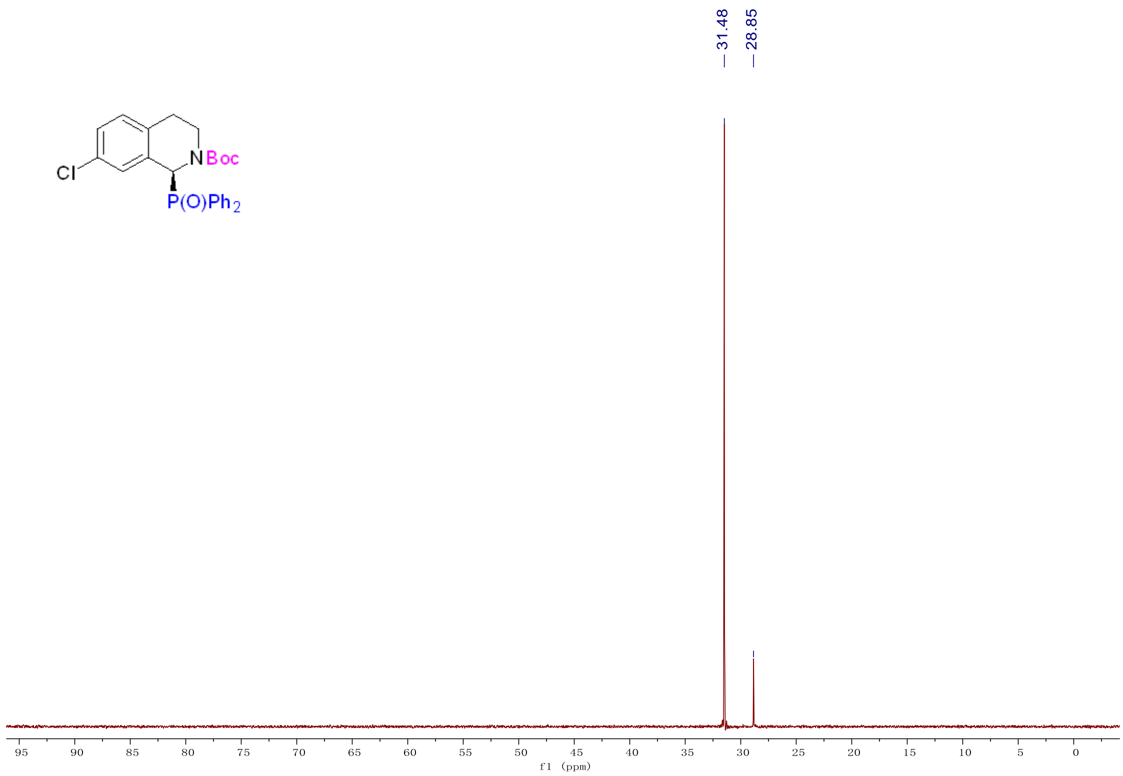

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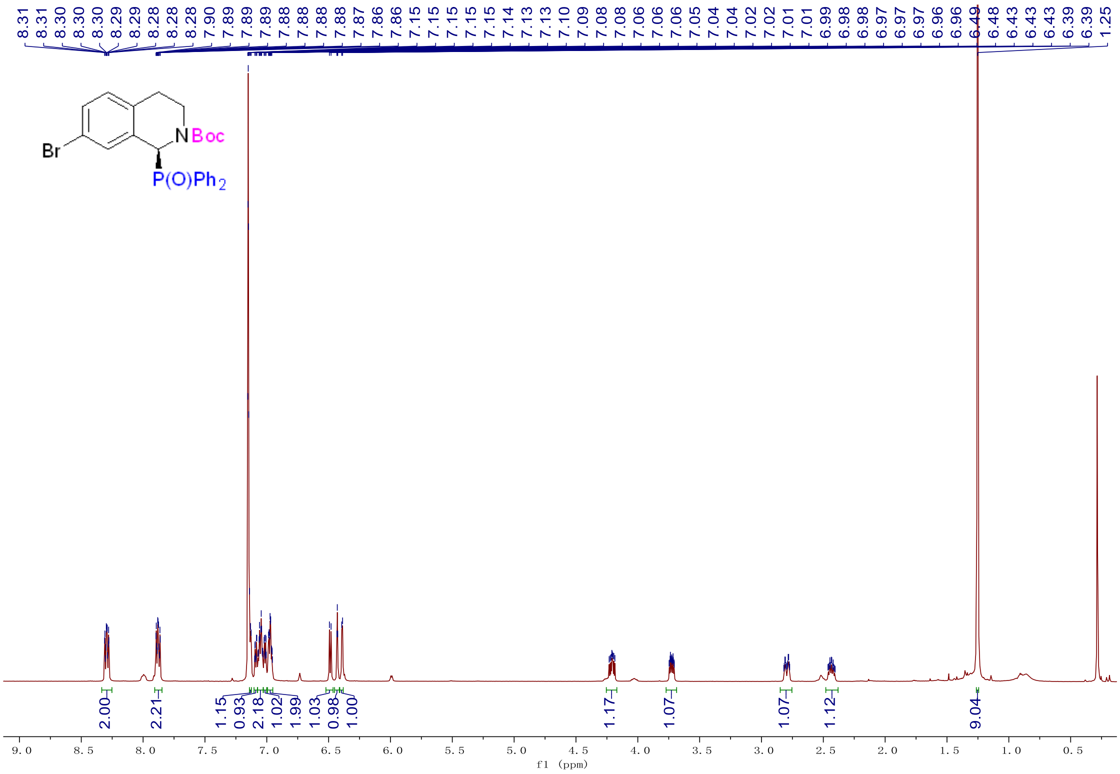

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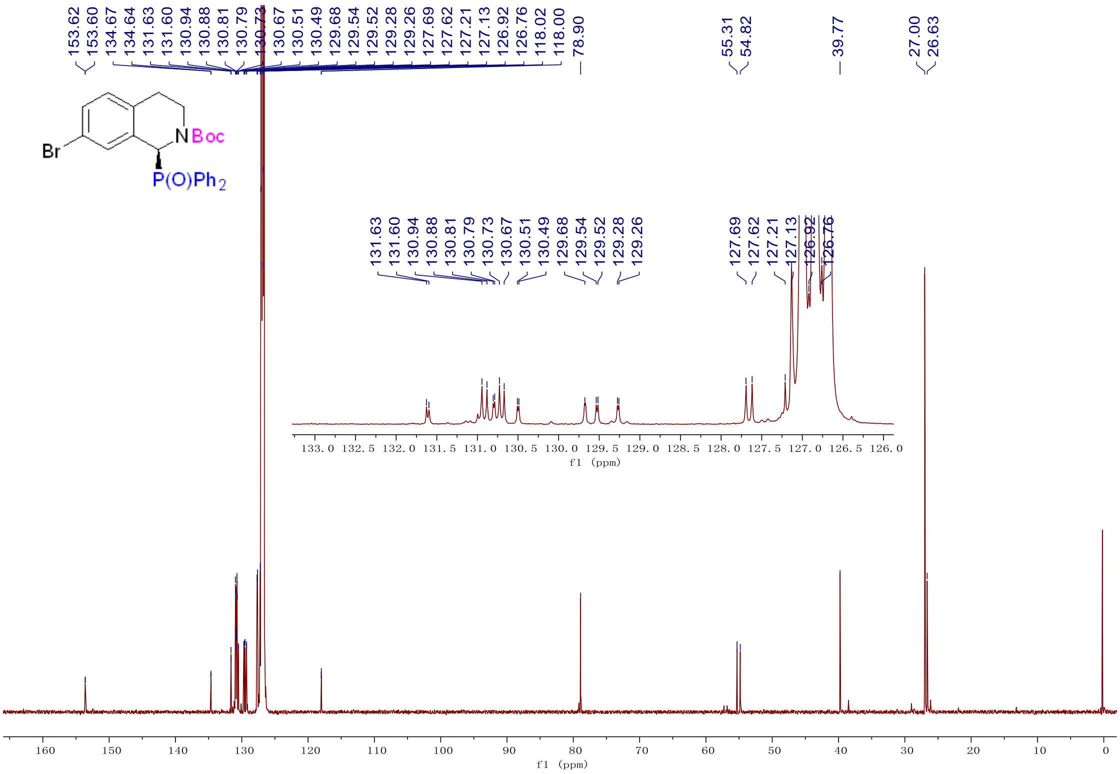

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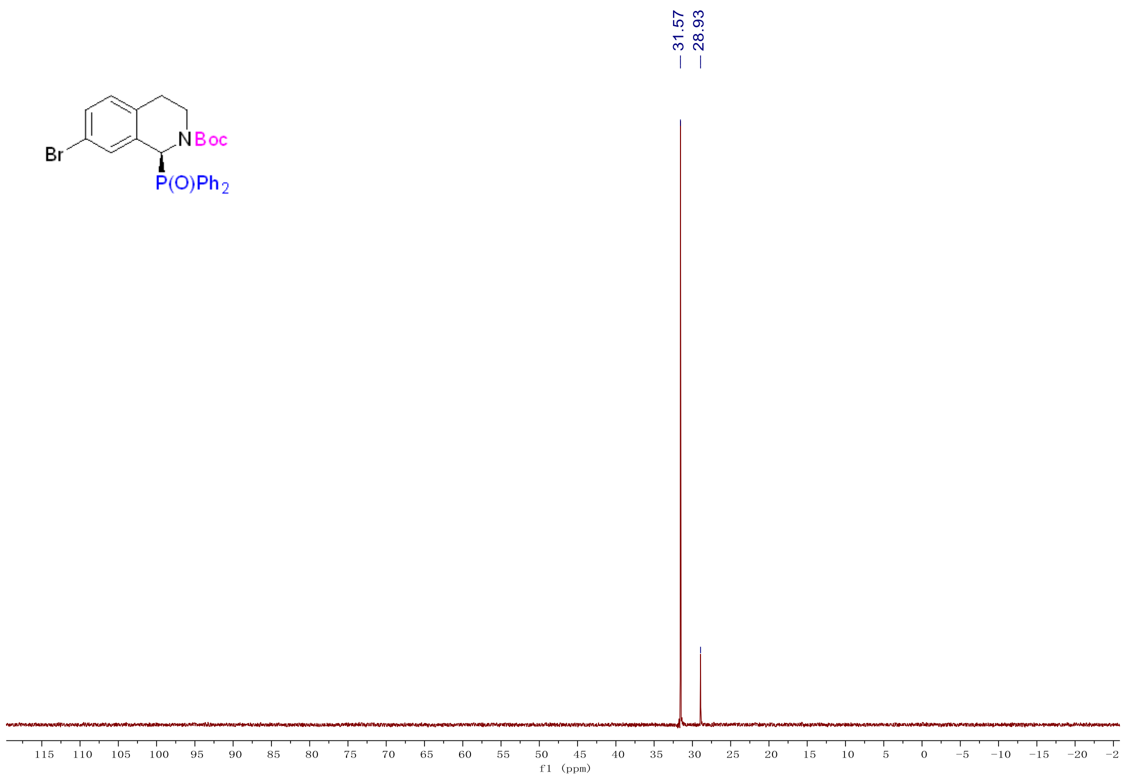

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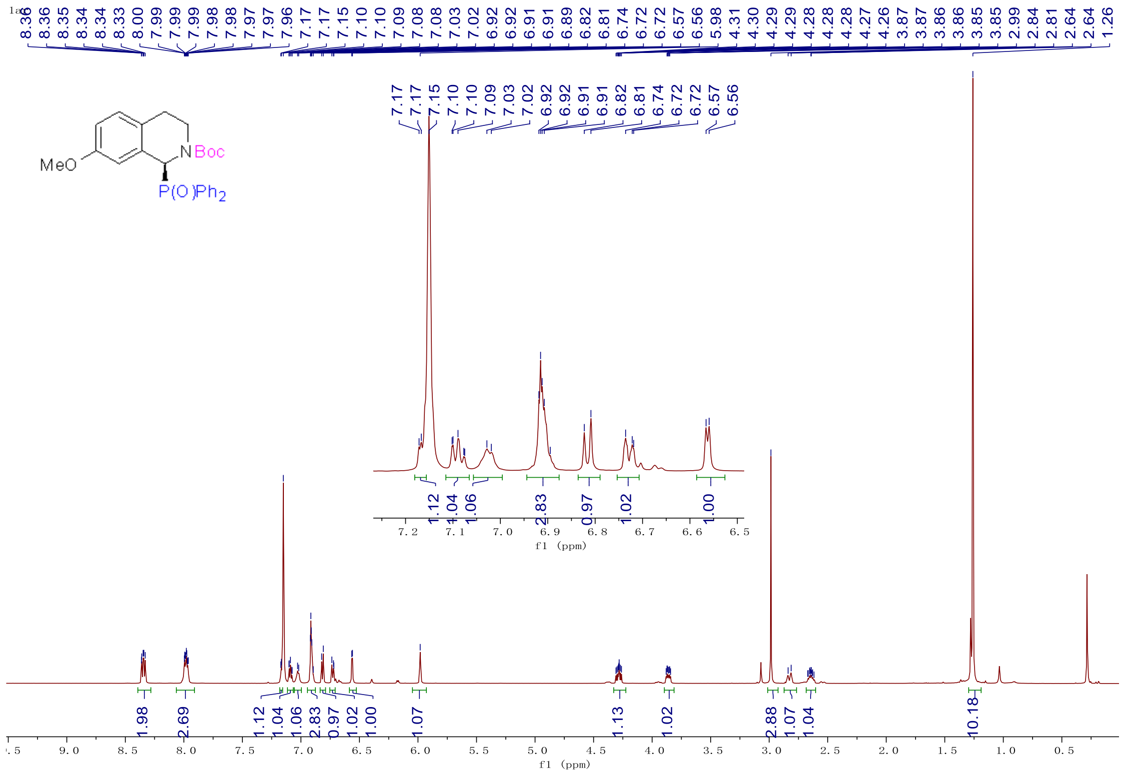

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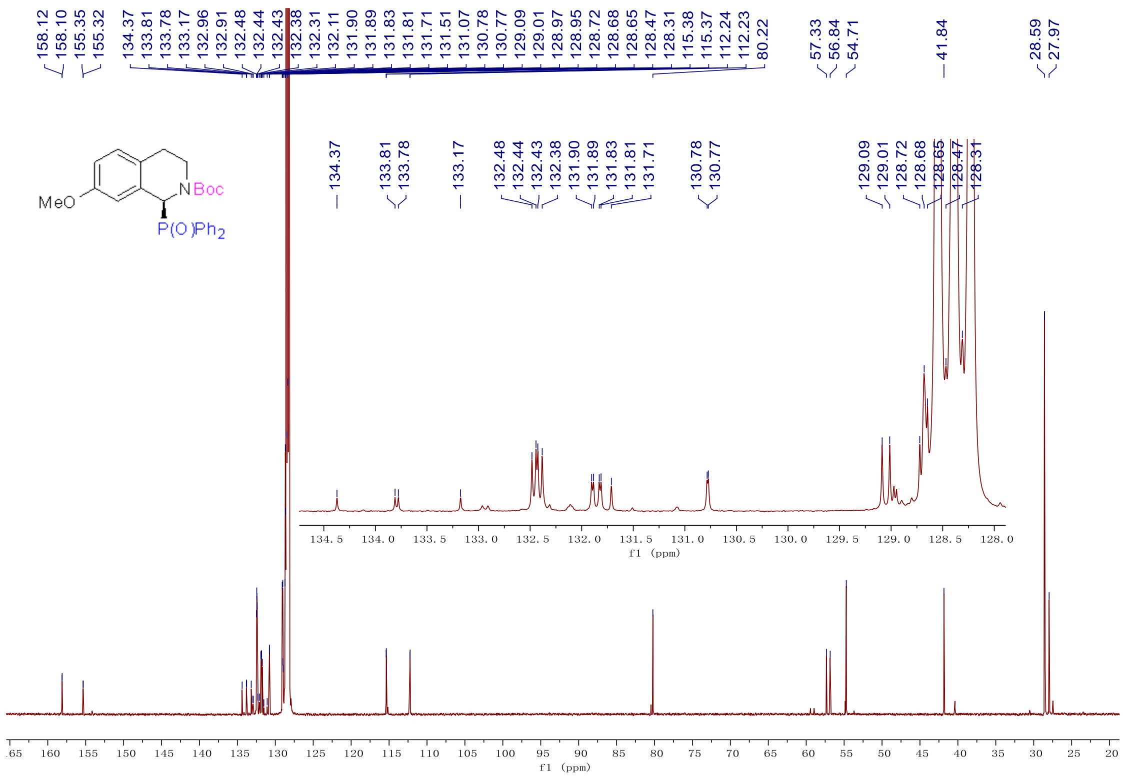

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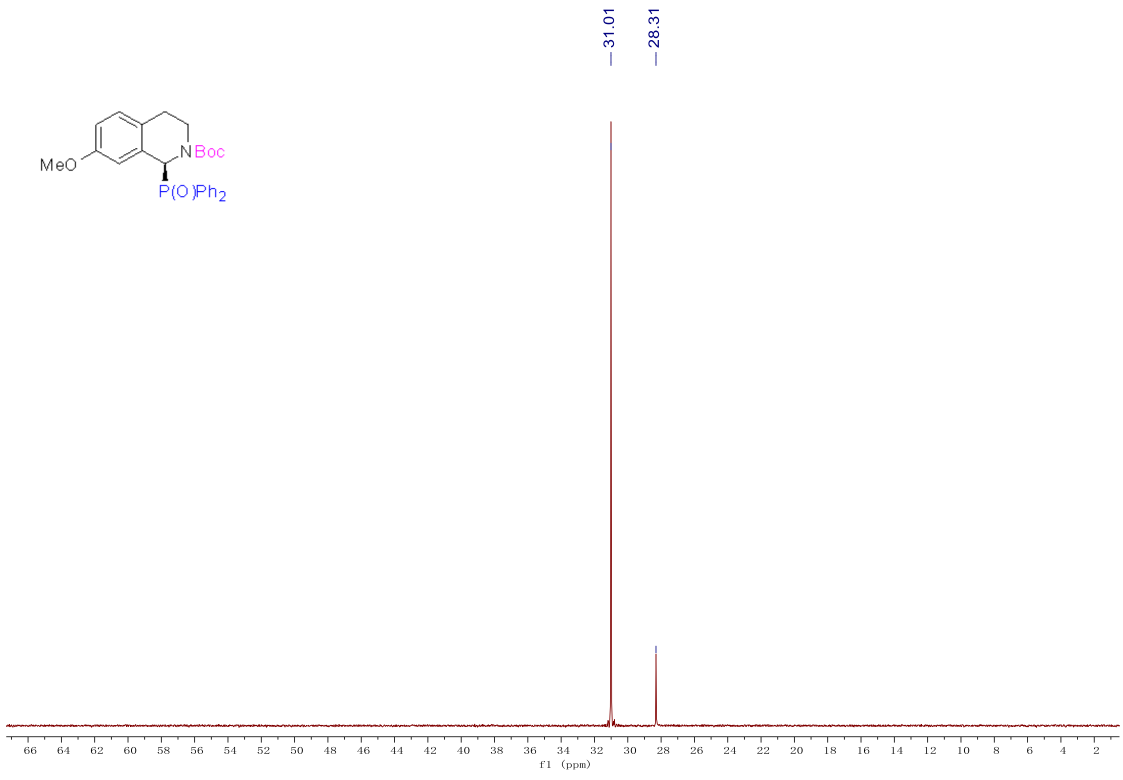

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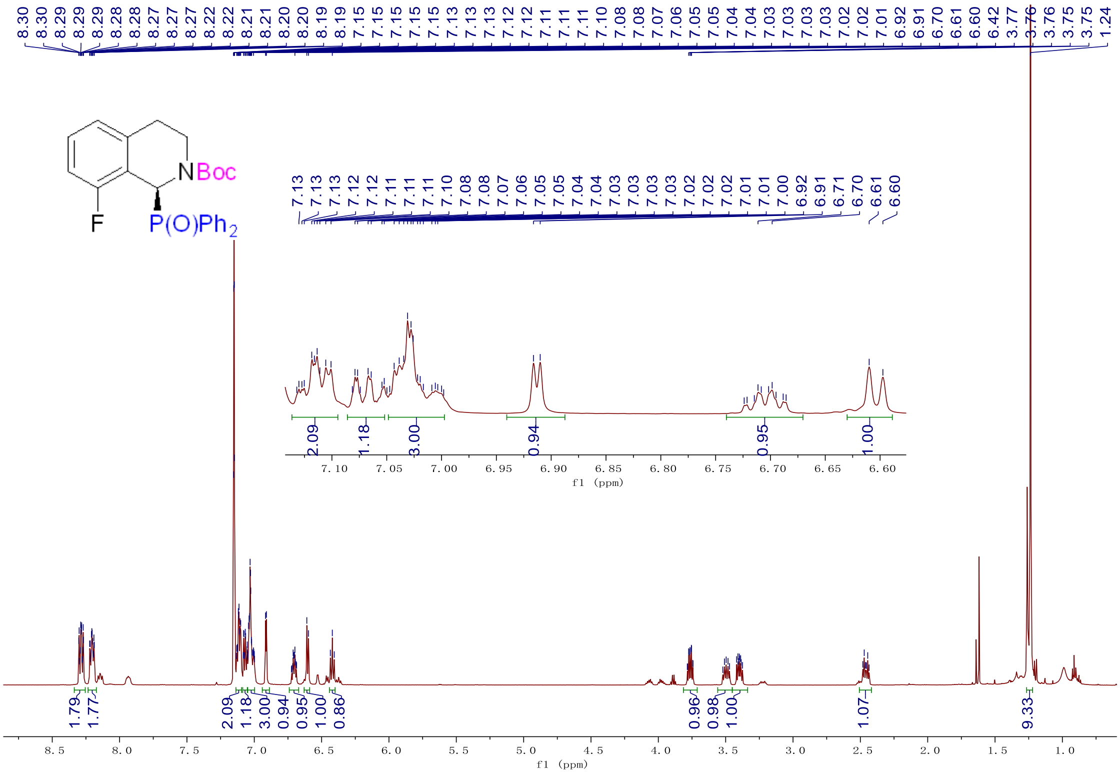

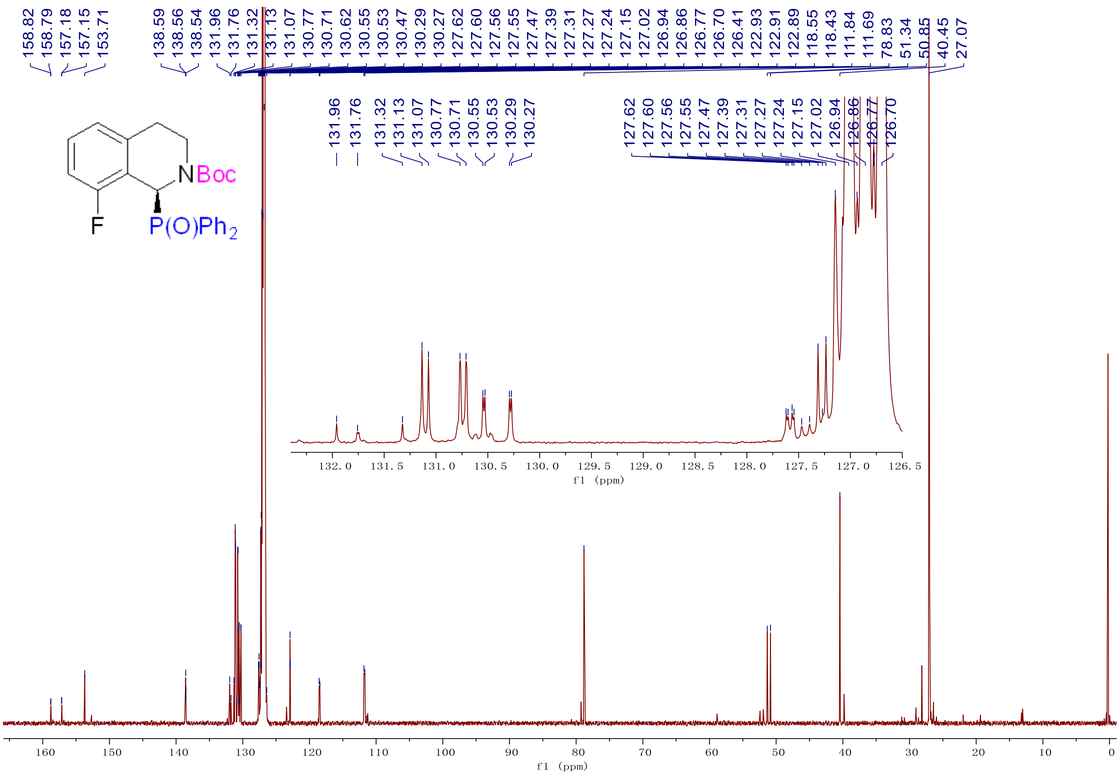

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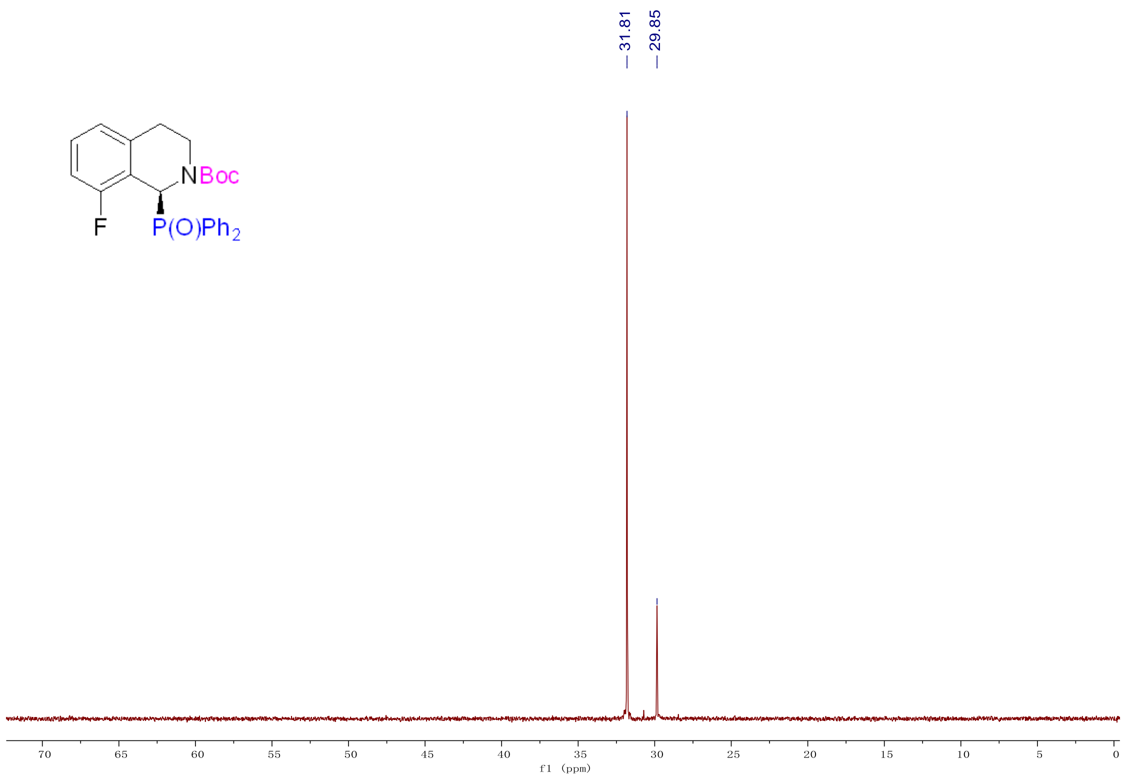

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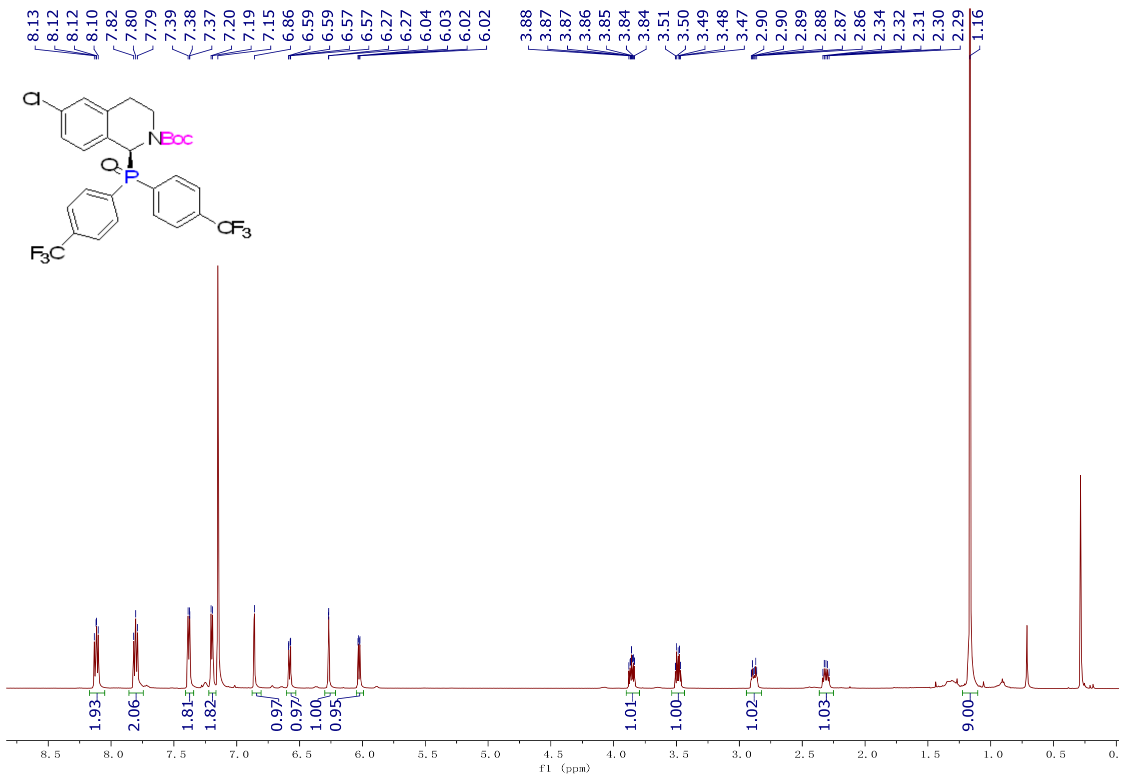
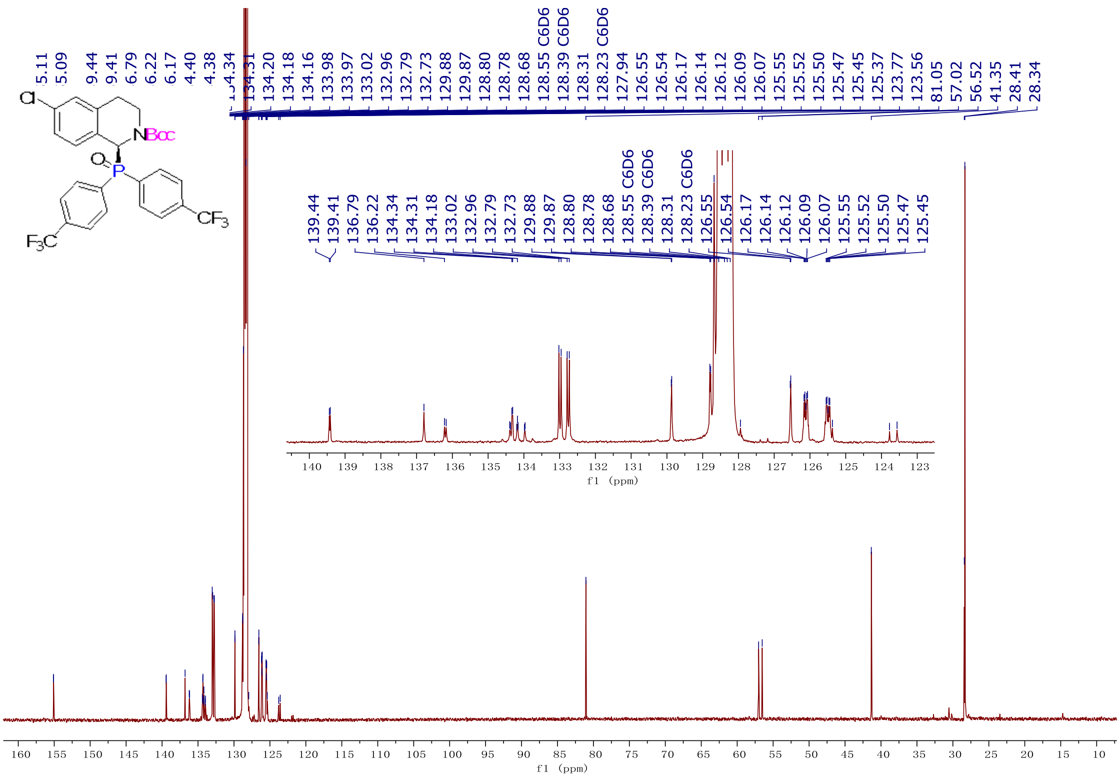
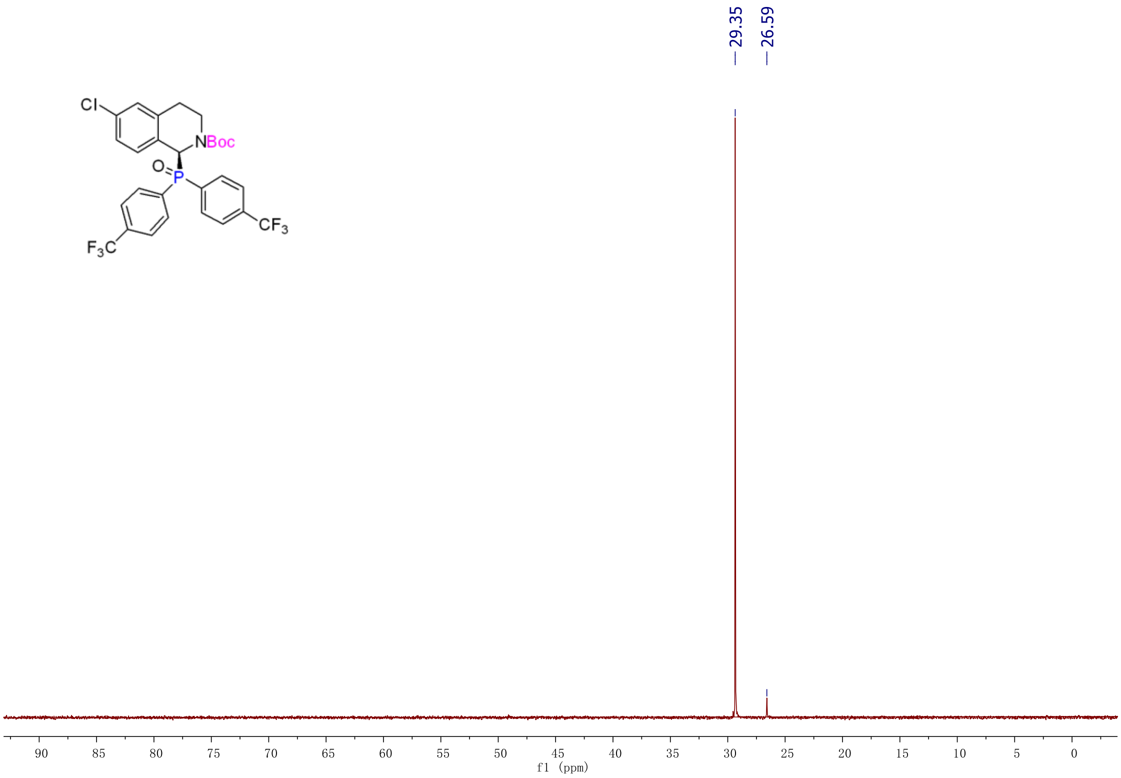


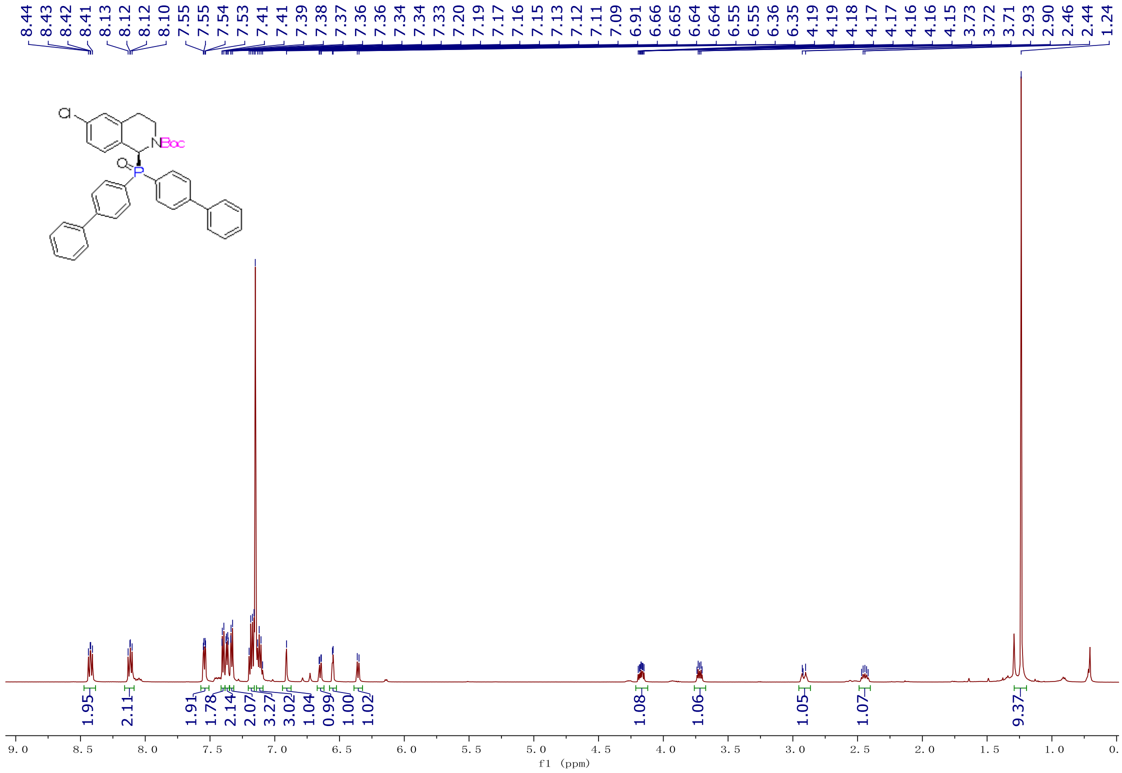
^{1}H NMR of compound **4iba**



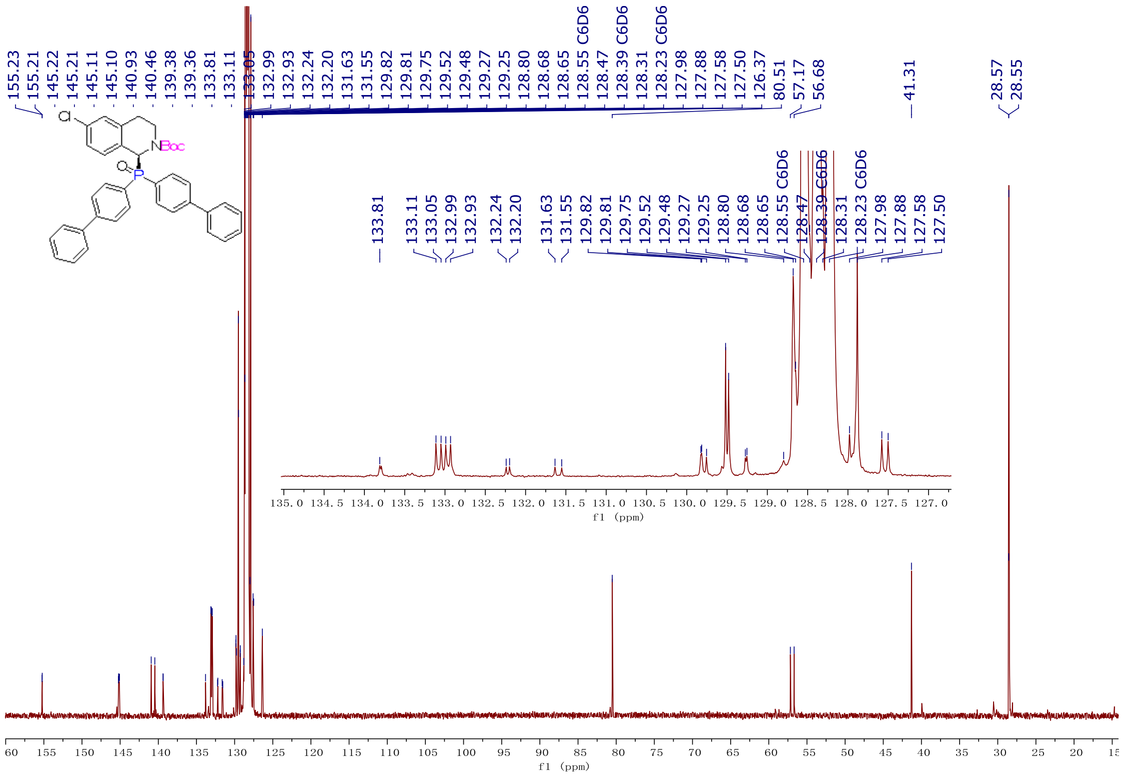
^{13}C NMR of compound **4iba**



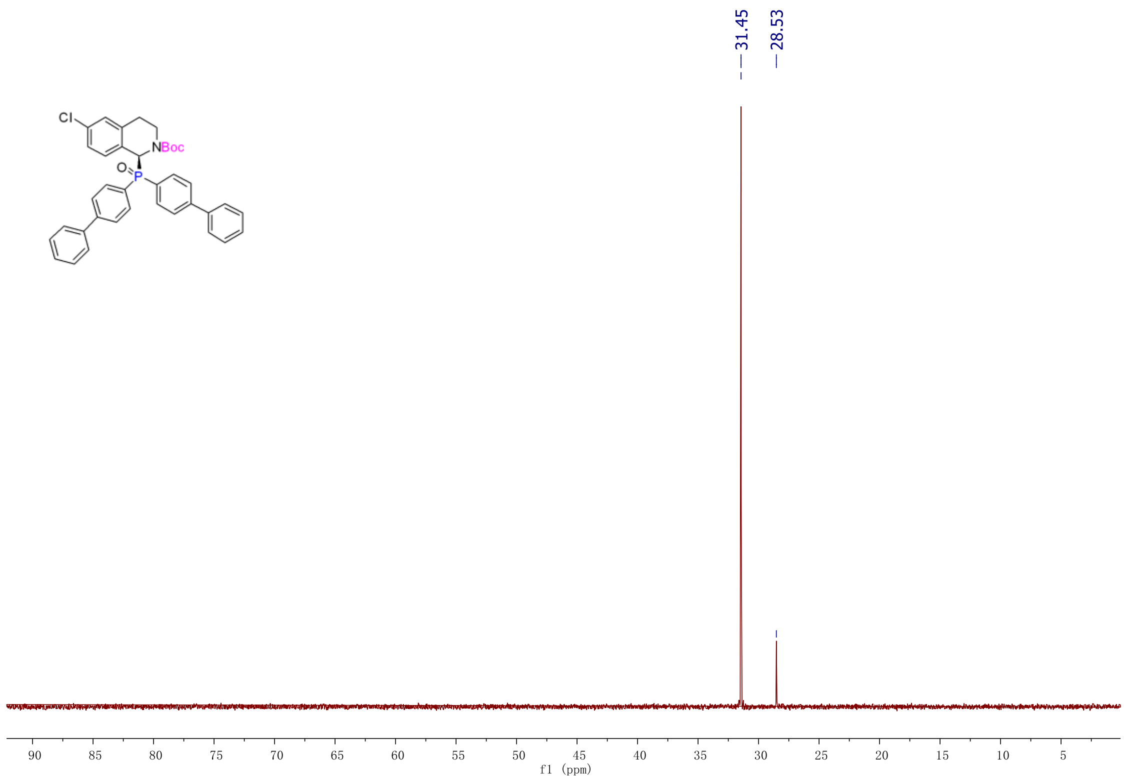
^{31}P NMR of compound **4iba**



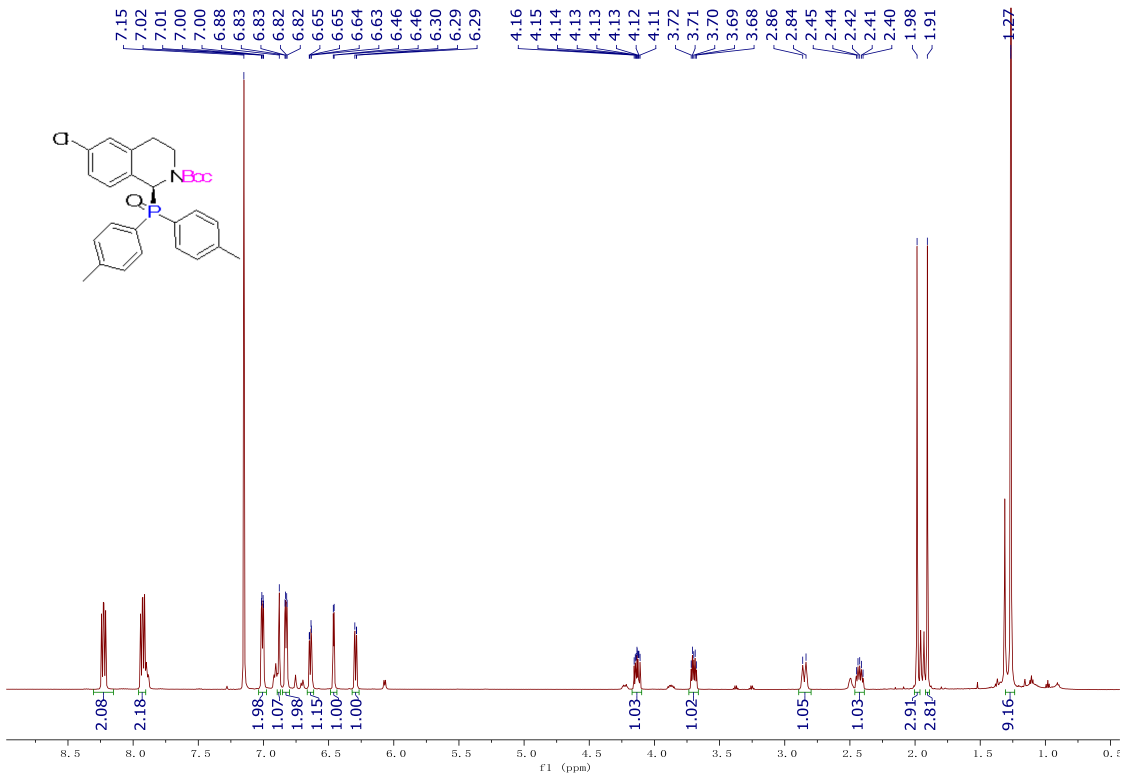
^{1}H NMR of compound **4ica**



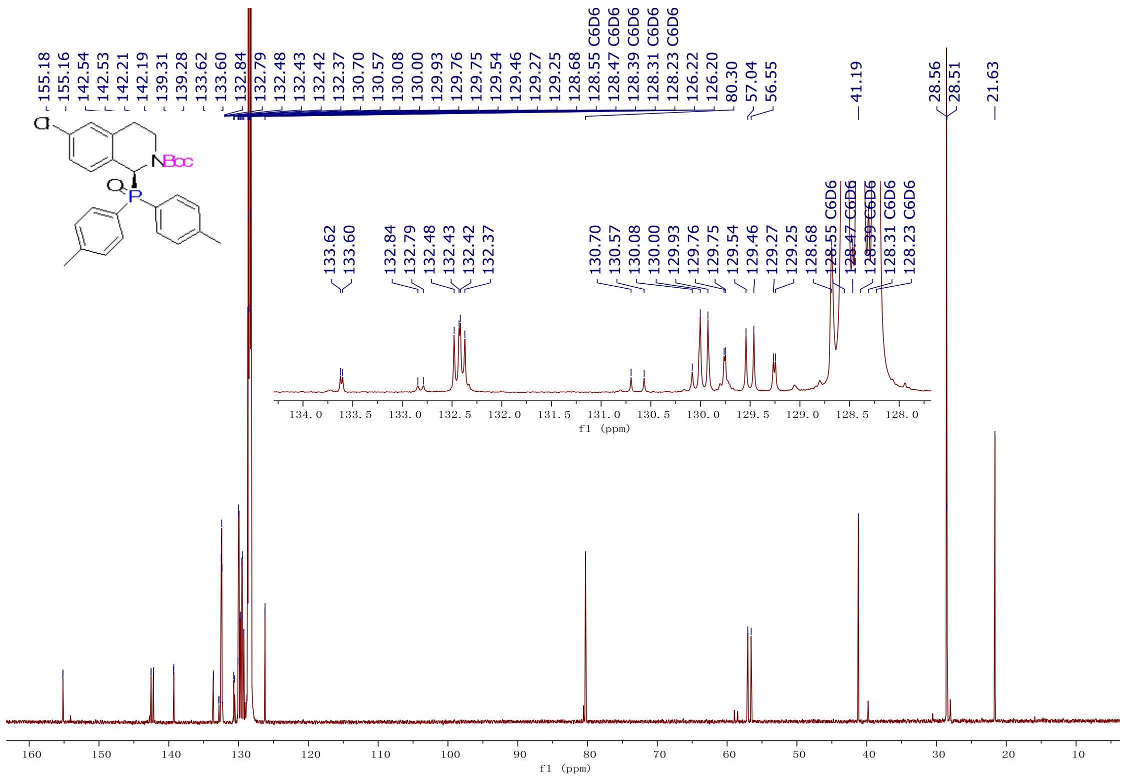
^{13}C NMR of compound **4ica**



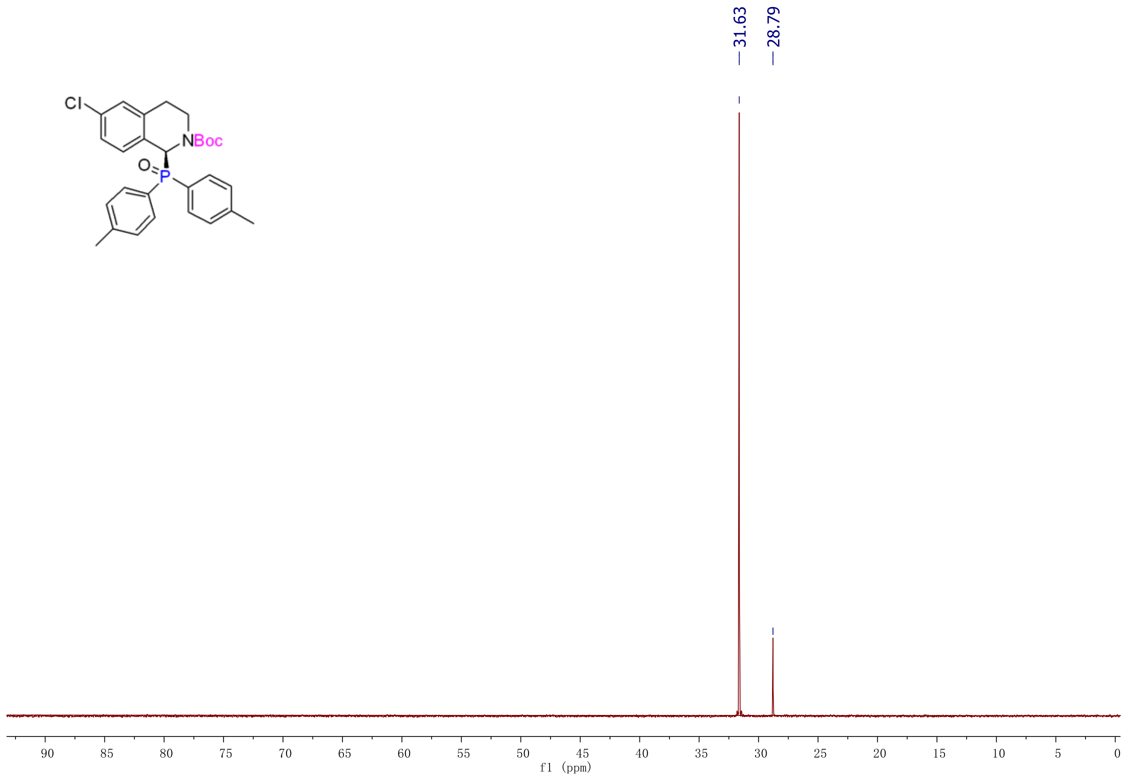
^{31}P NMR of compound **4ica**



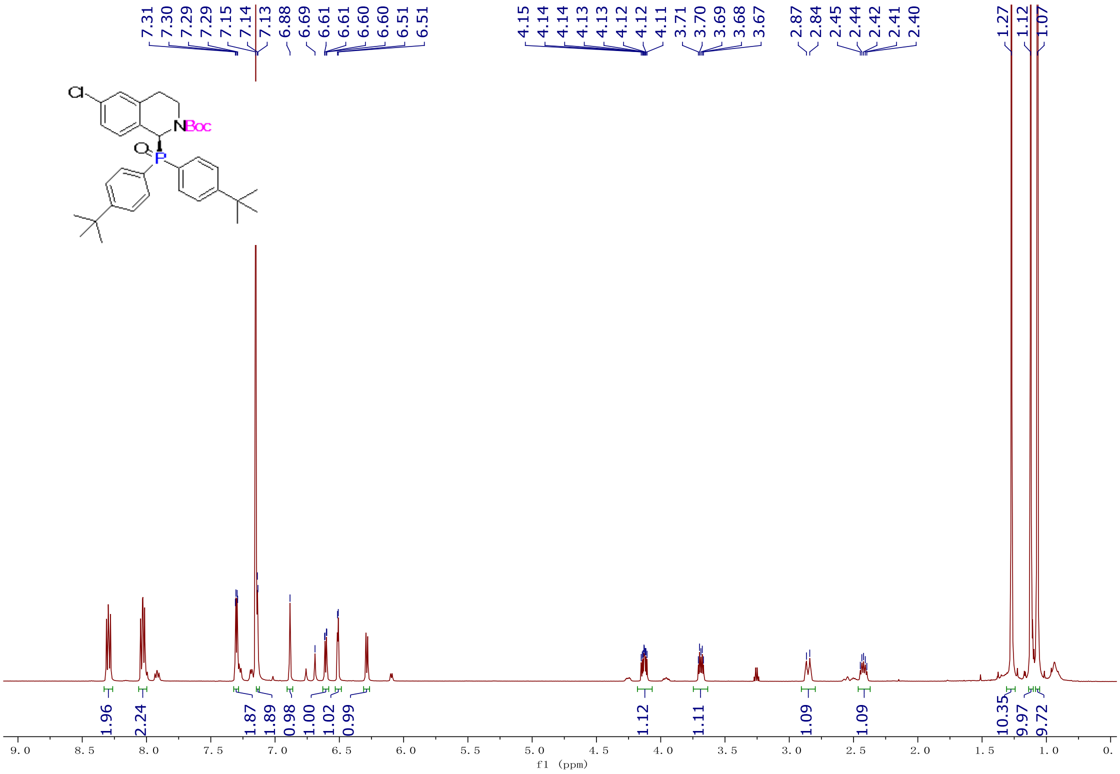
^{1}H NMR of compound **4ida**



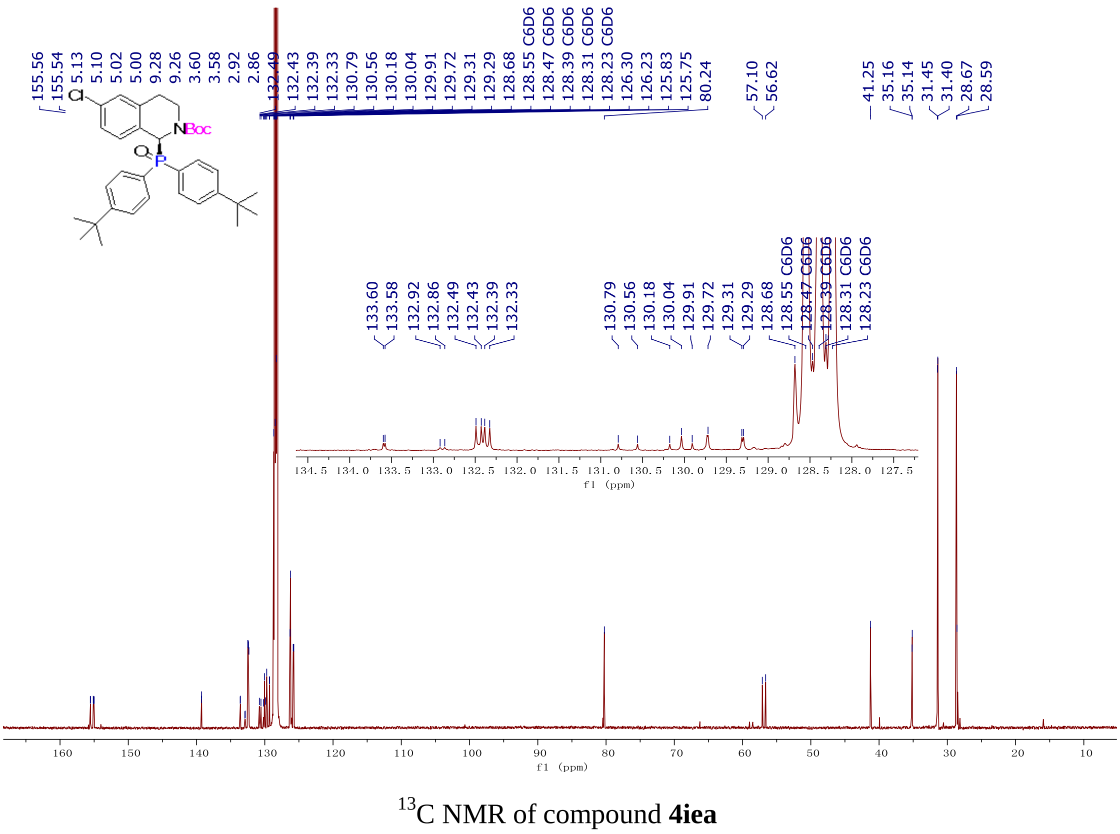
^{13}C NMR of compound **4ida**



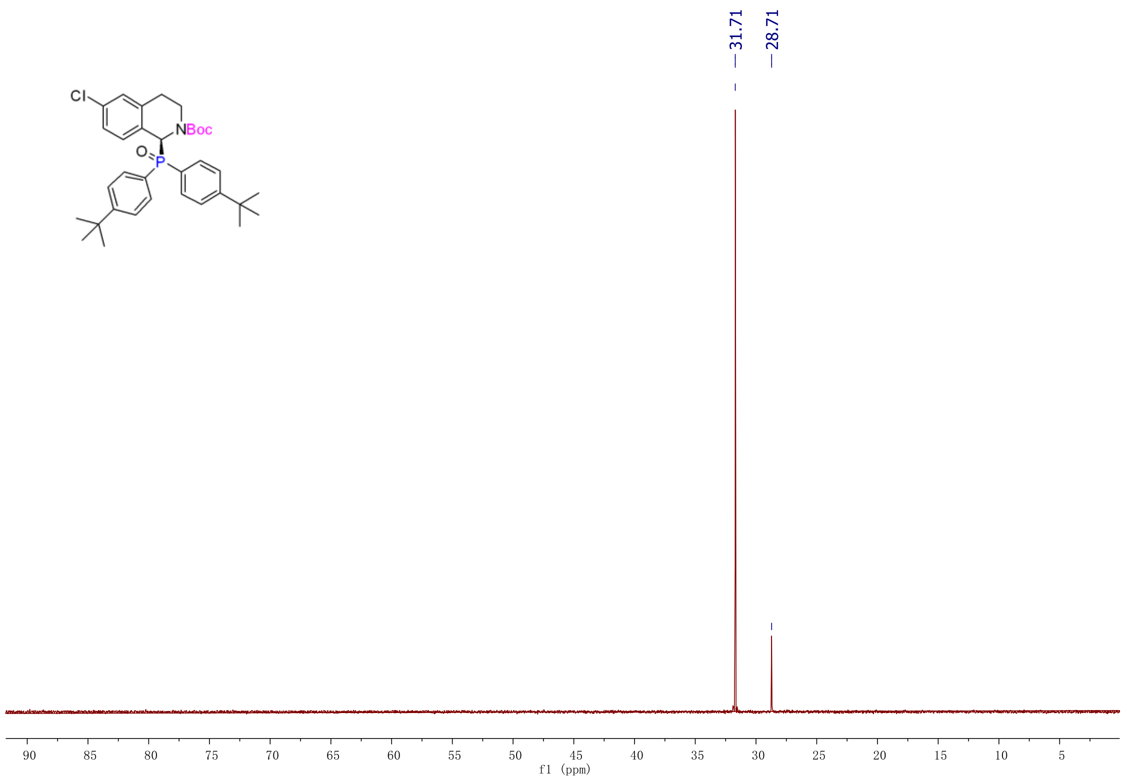
^{31}P NMR of compound **4ida**



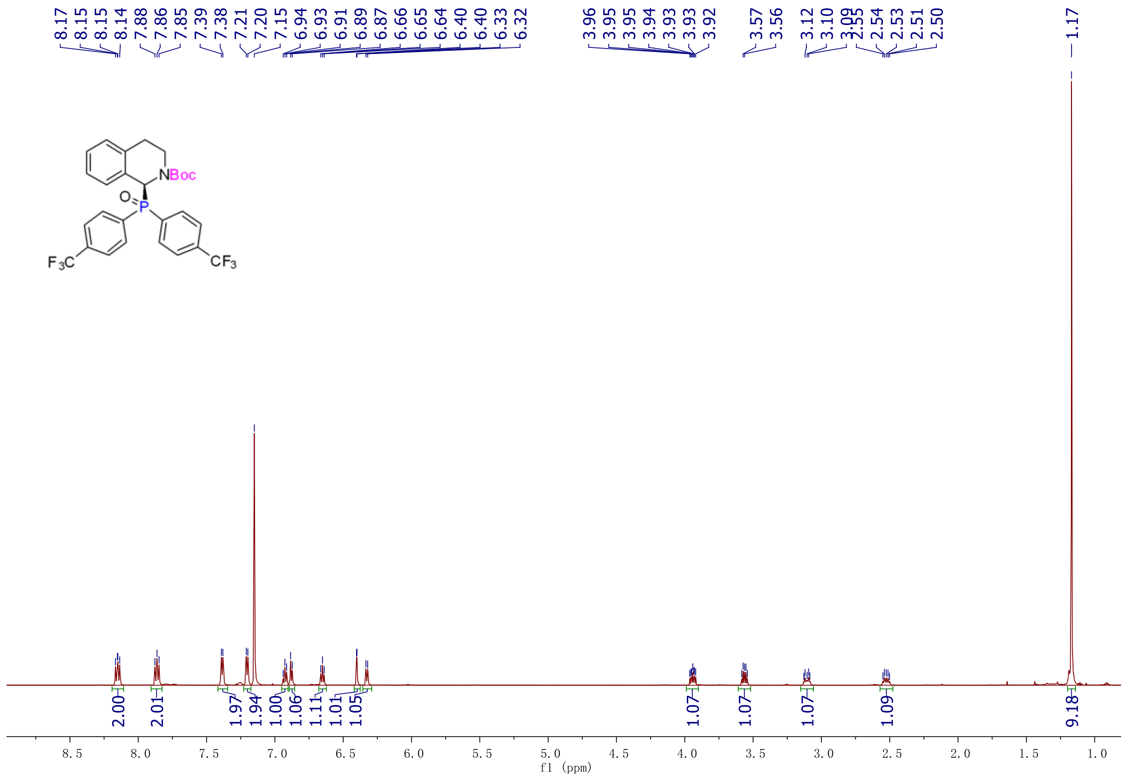
^{1}H NMR of compound **4iea**



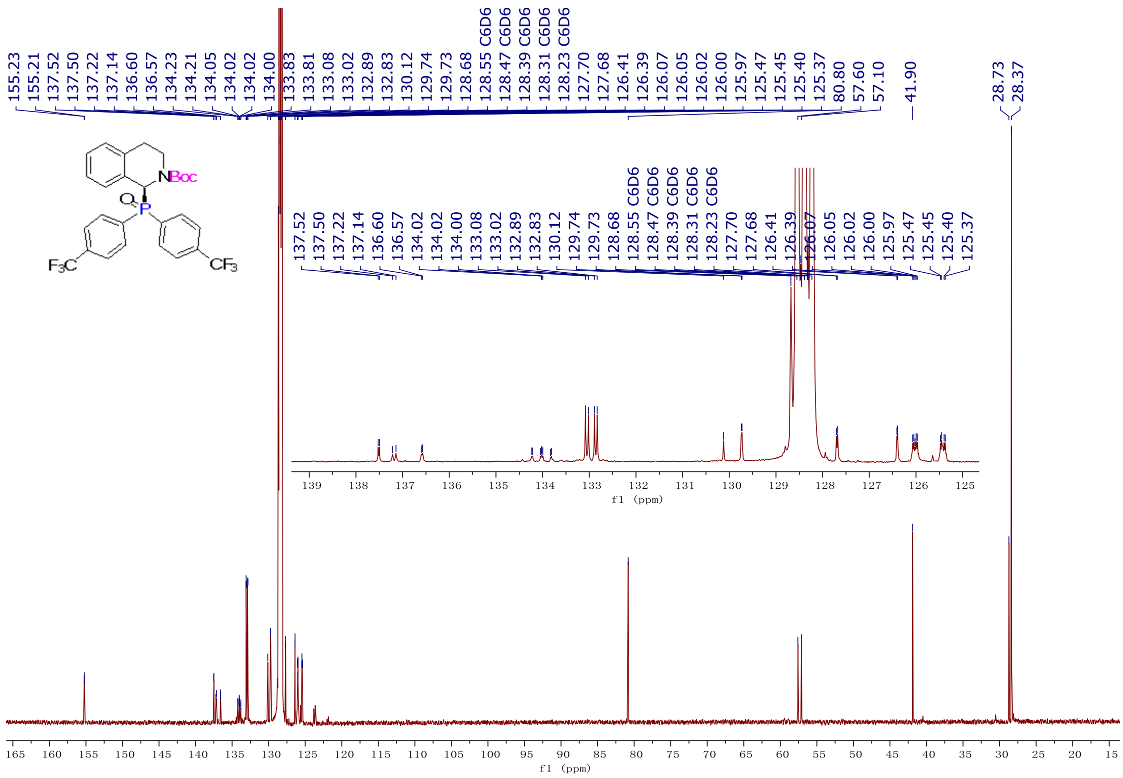
^{13}C NMR of compound **4iea**



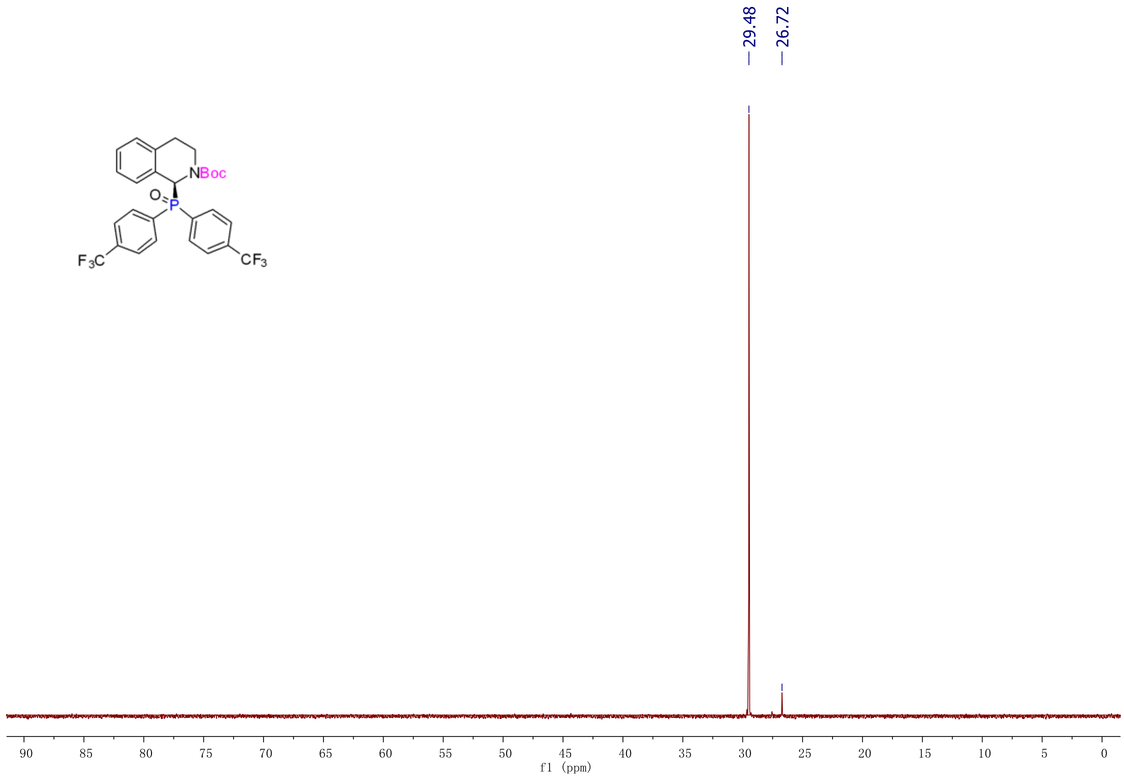
^{31}P NMR of compound **4iea**



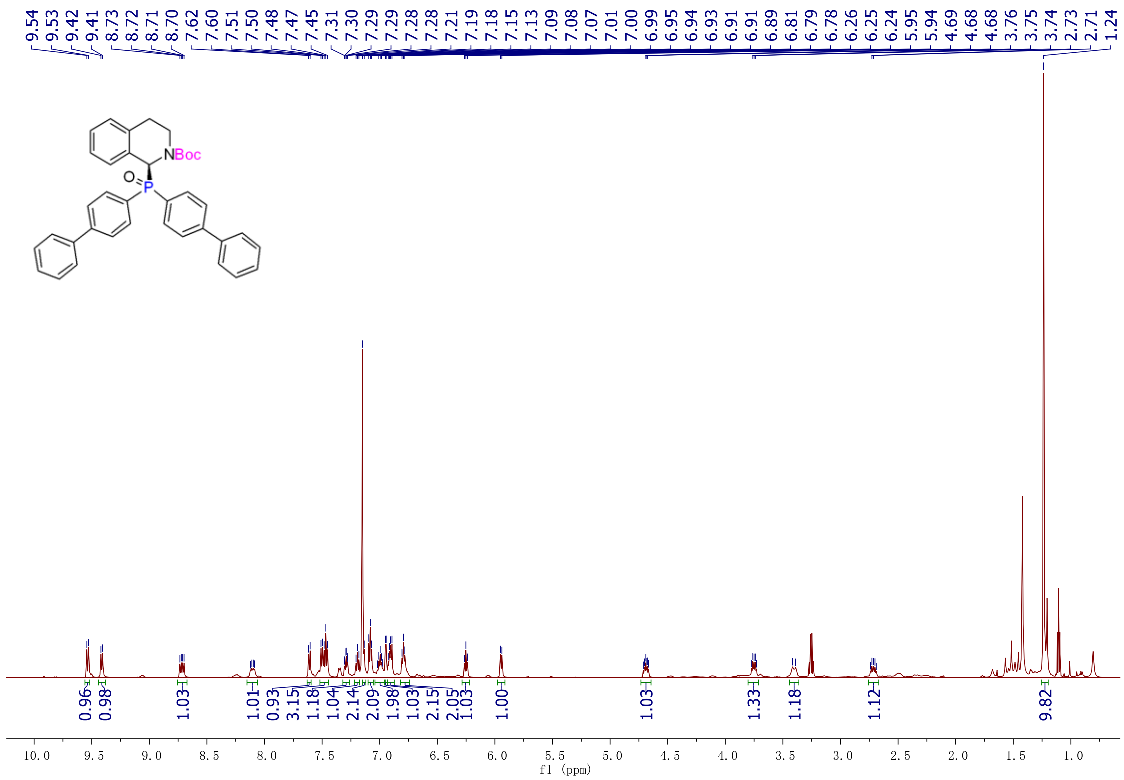
^{1}H NMR of compound **4aba**



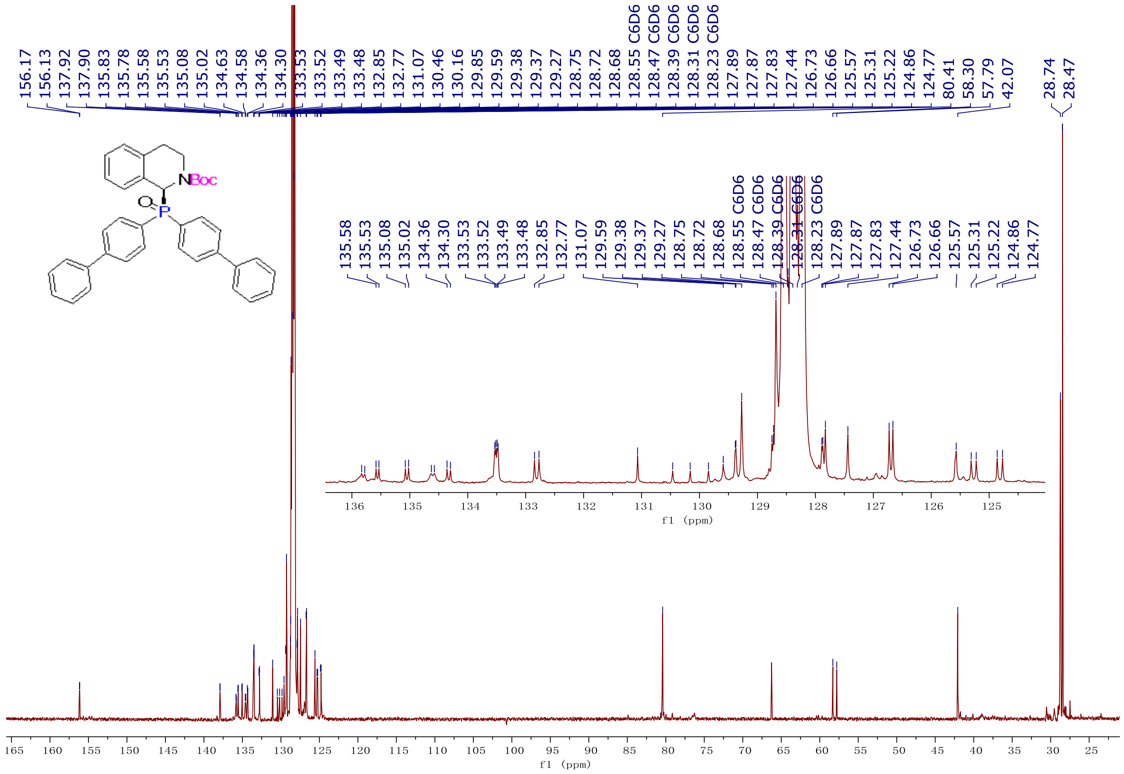
[13]C NMR of compound **4aba**



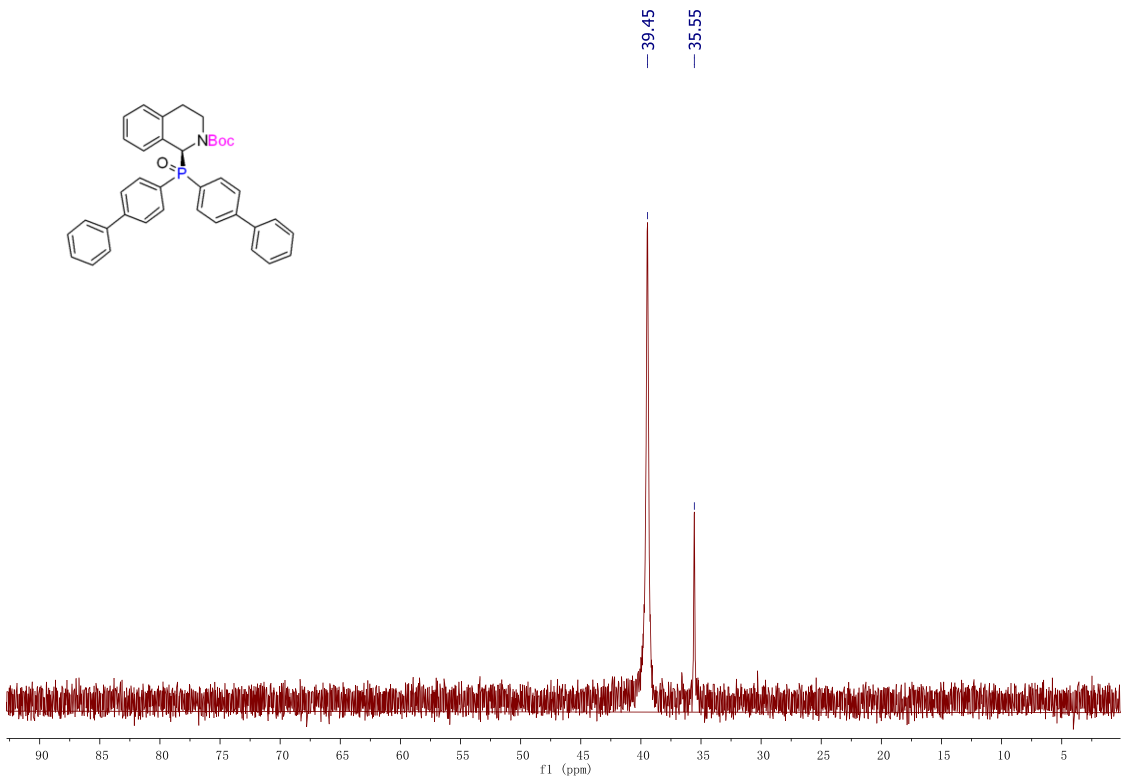
[31]P NMR of compound **4aba**



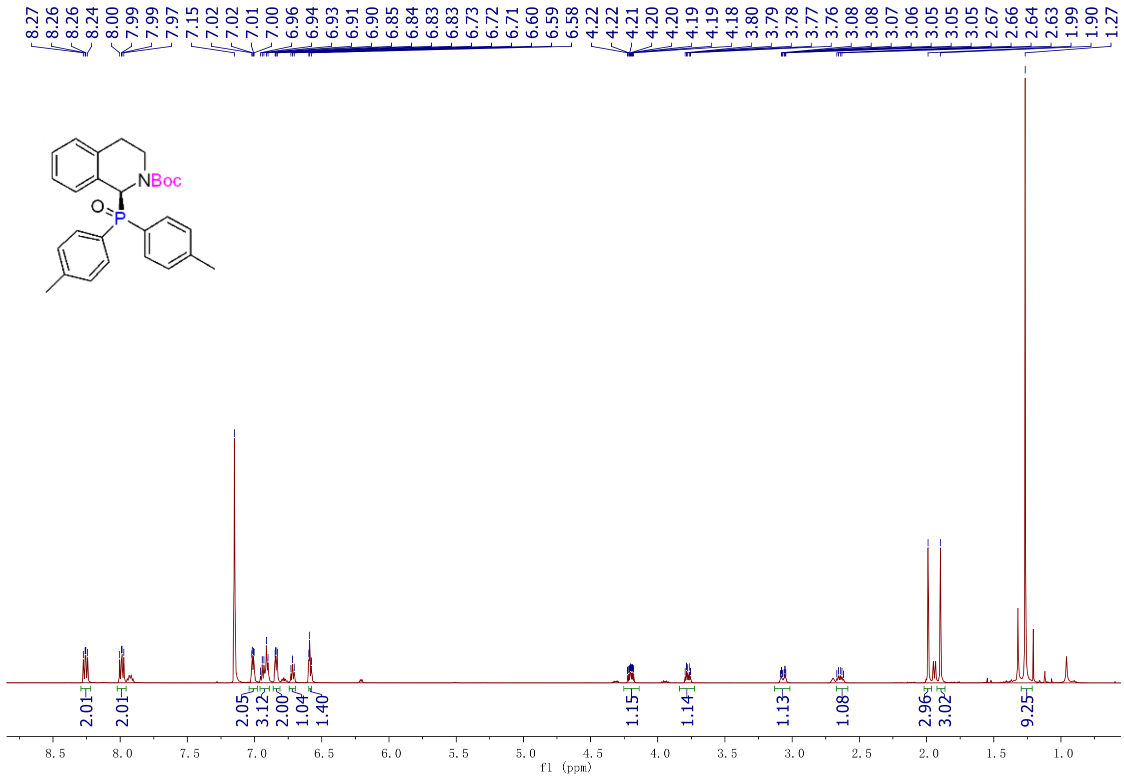
[1]H NMR of compound **4aca**



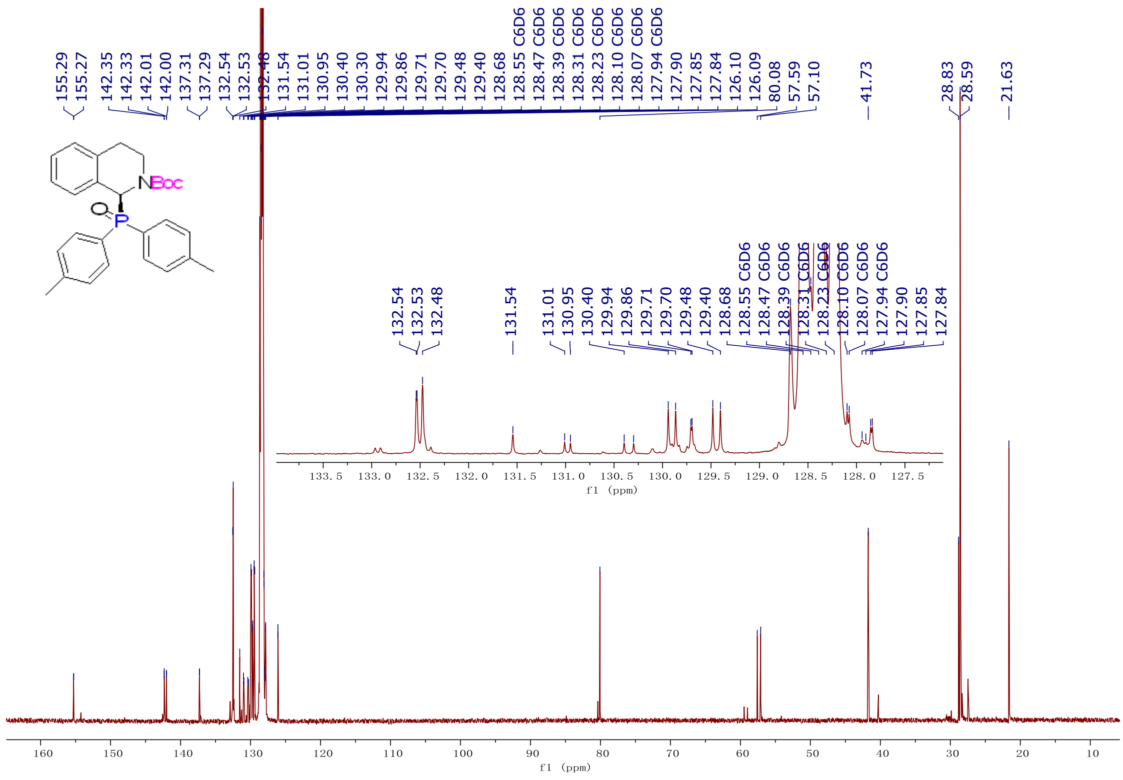
[13]C NMR of compound **4aca**



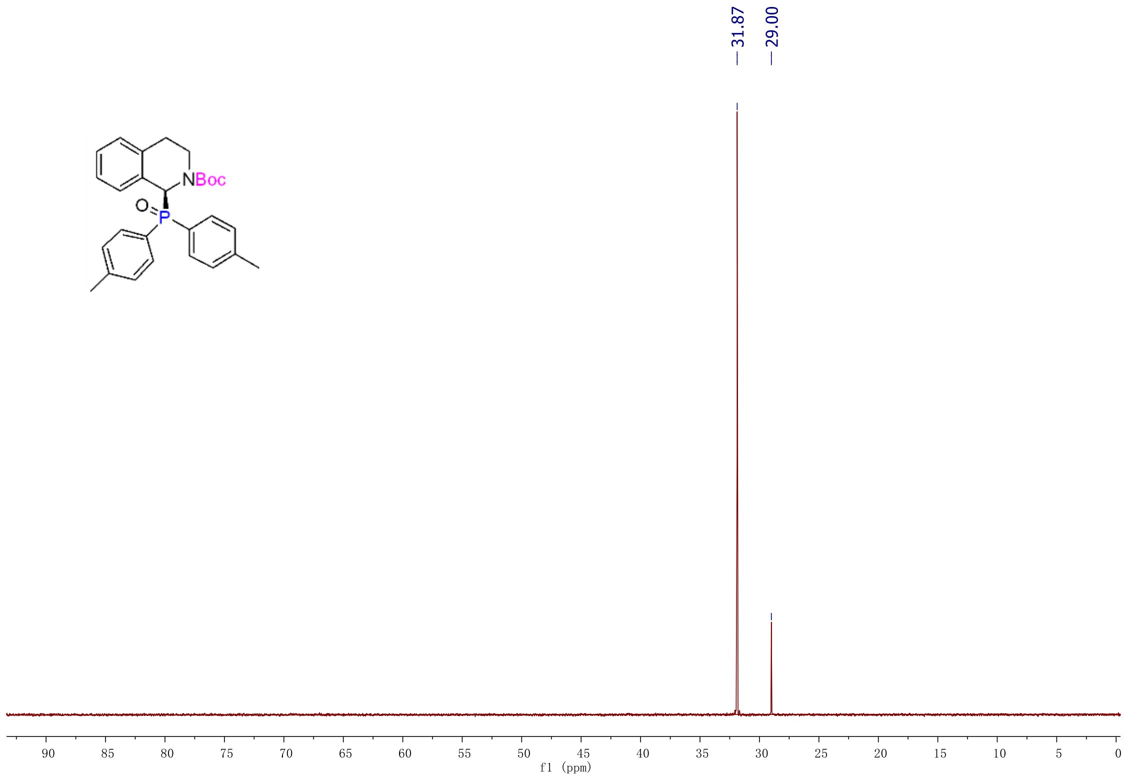
^{31}P NMR of compound **4aca**



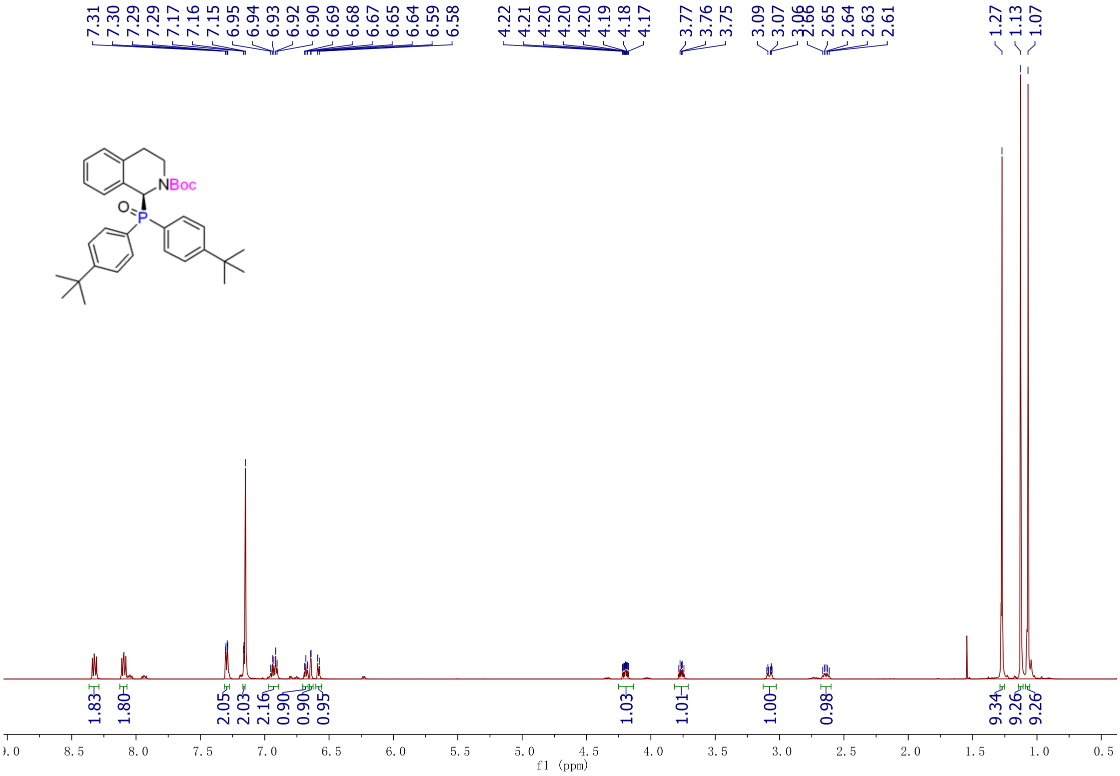
^{1}H NMR of compound **4ada**



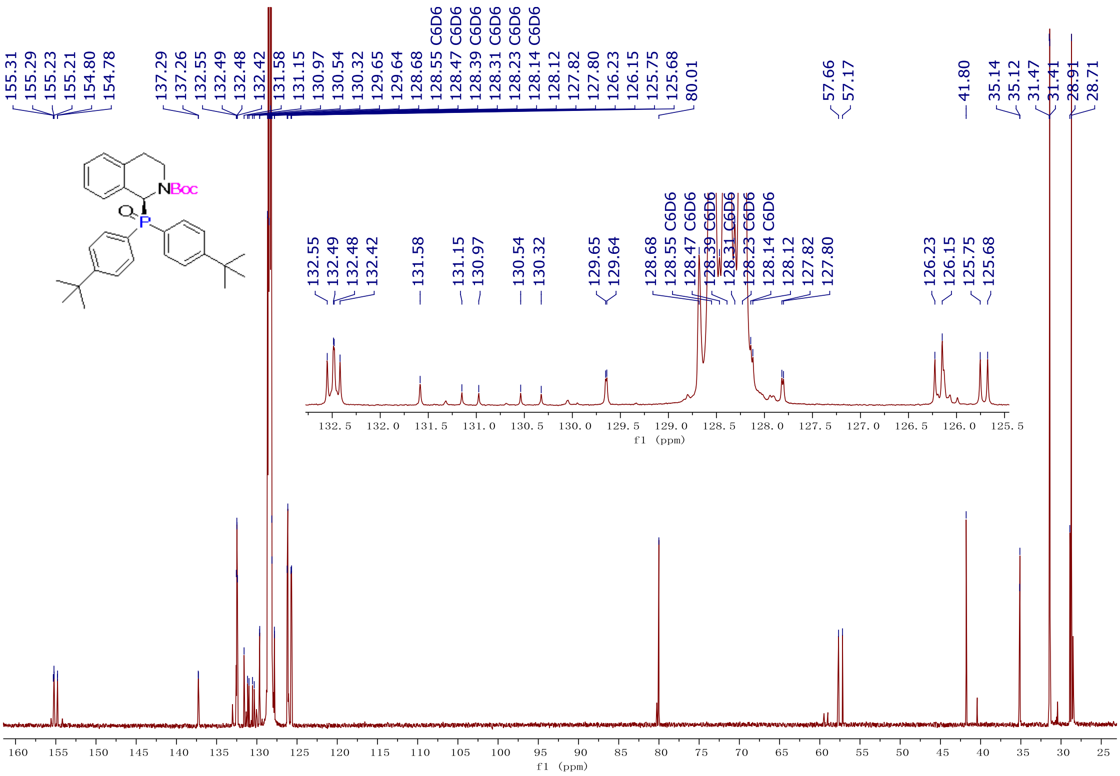
^{13}C NMR of compound **4ada**



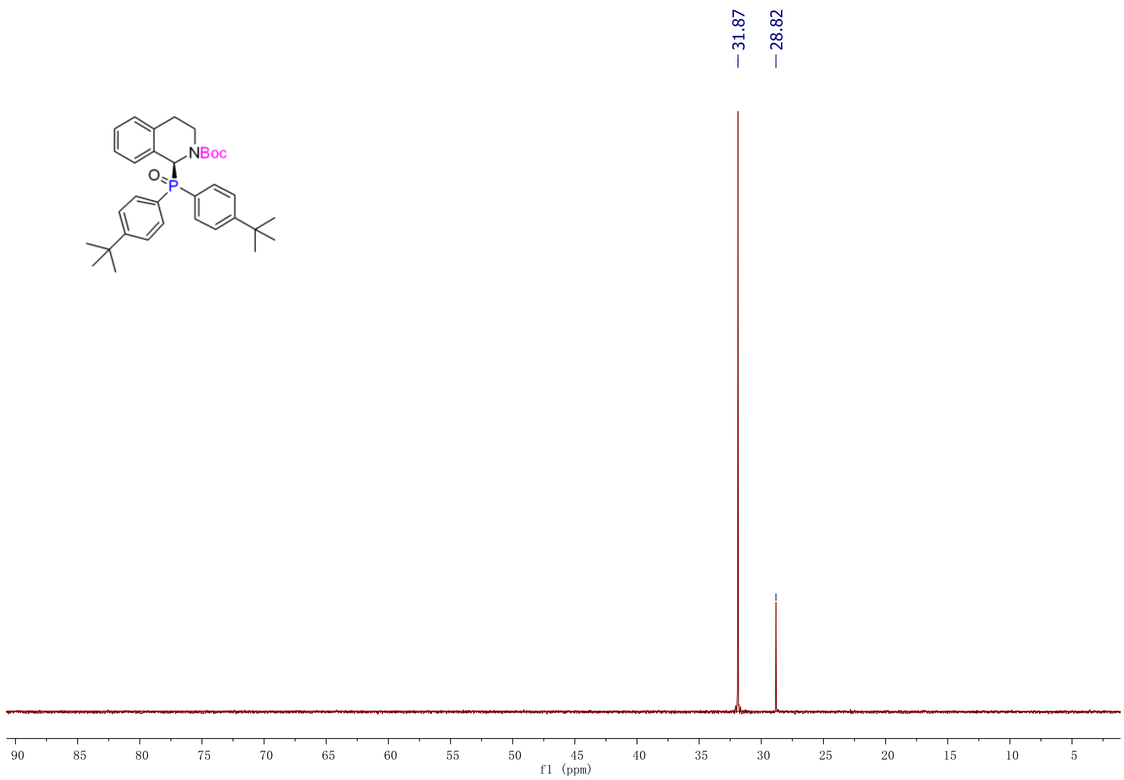
^{31}P NMR of compound **4ada**



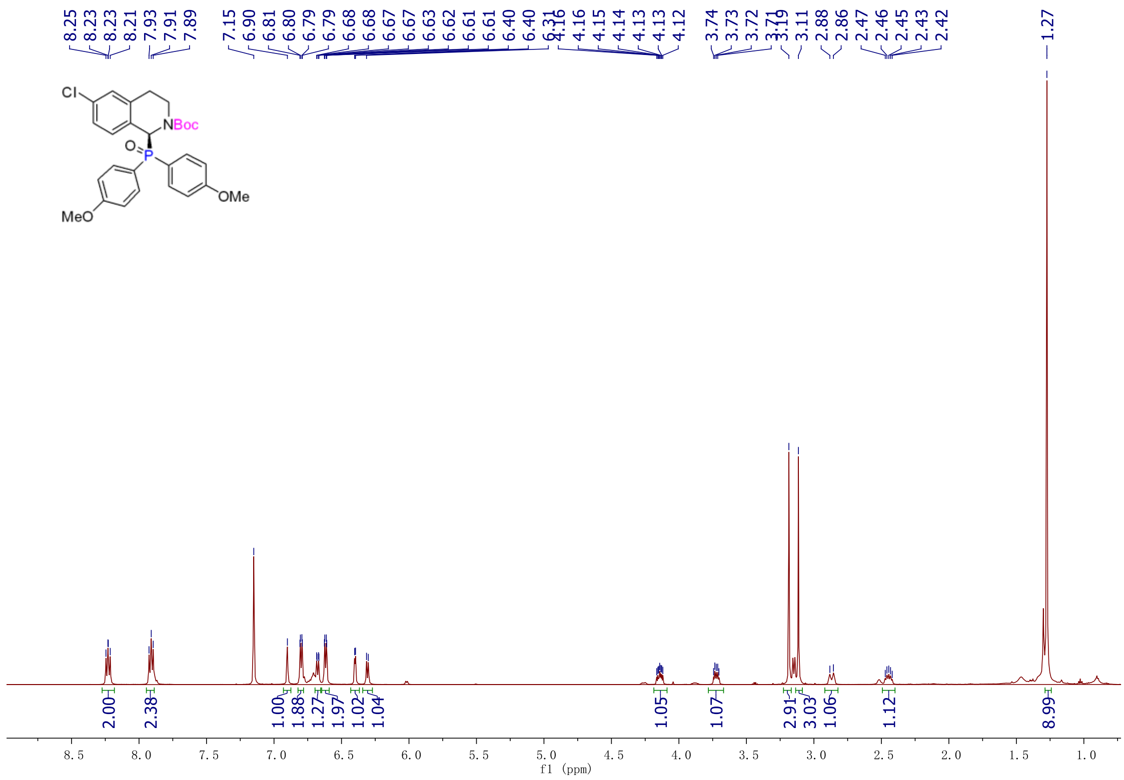
^{1}H NMR of compound **4aea**



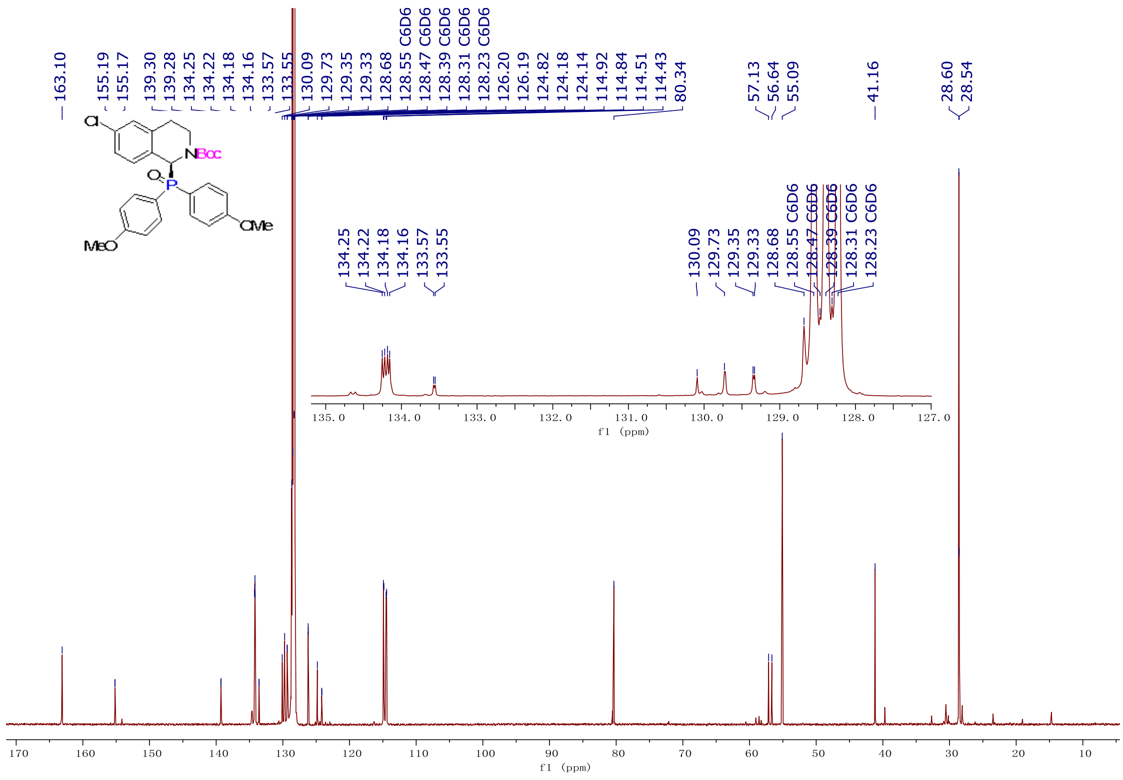
^{13}C NMR of compound **4aea**



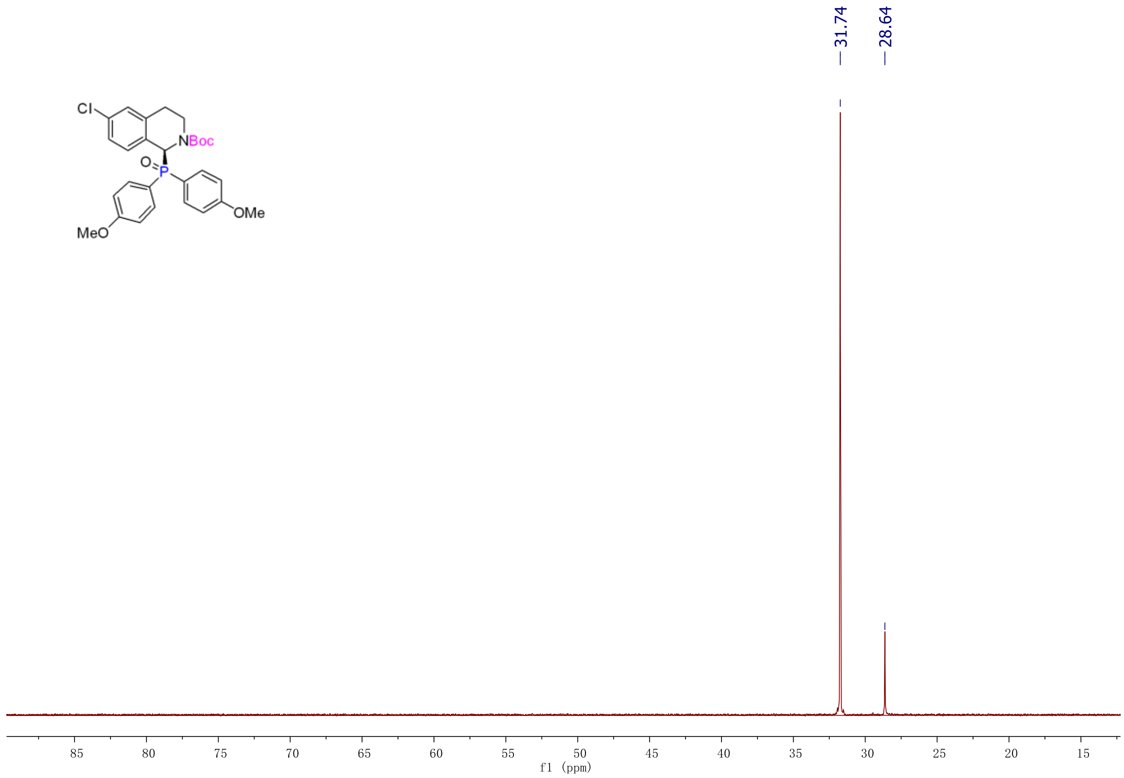
^{31}P NMR of compound **4aea**



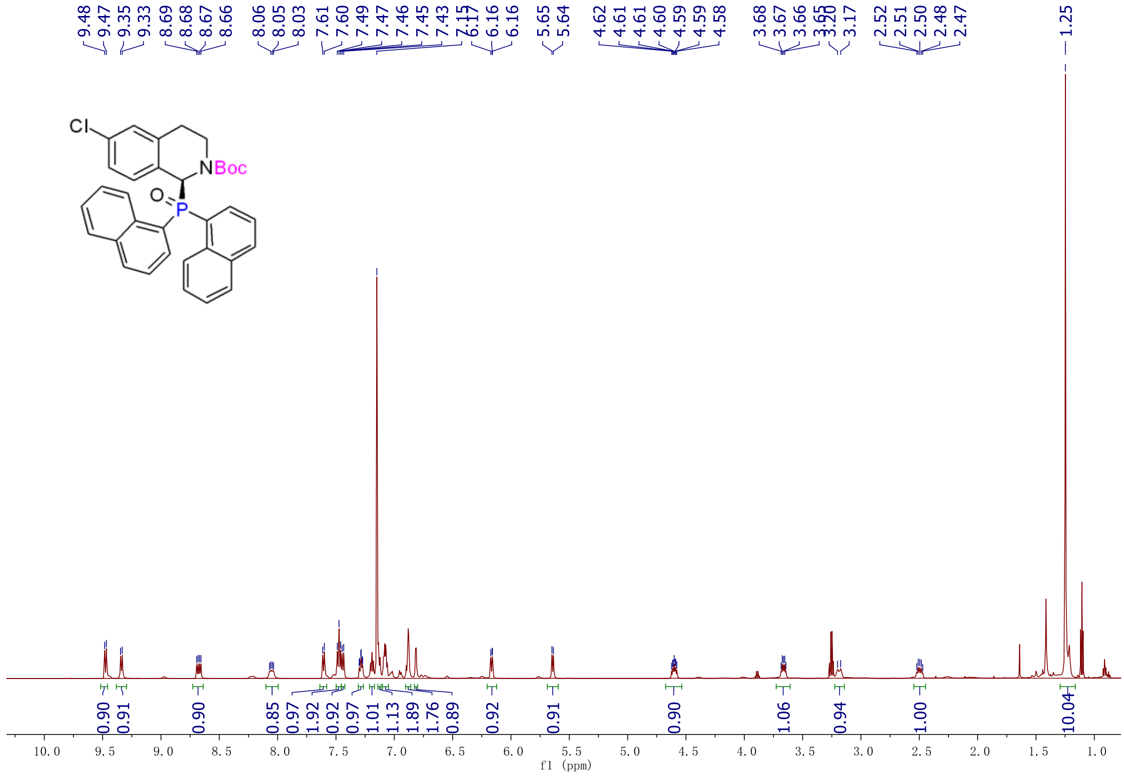
^{1}H NMR of compound **4ifa**



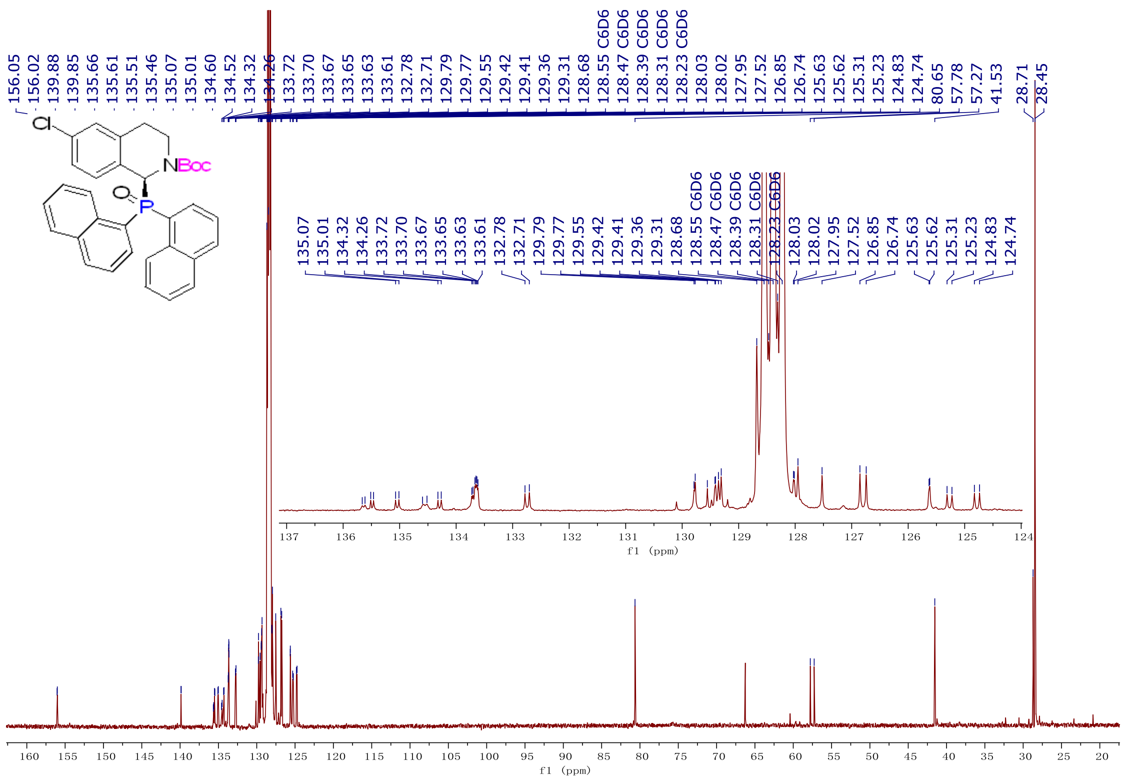
^{13}C NMR of compound **4ifa**



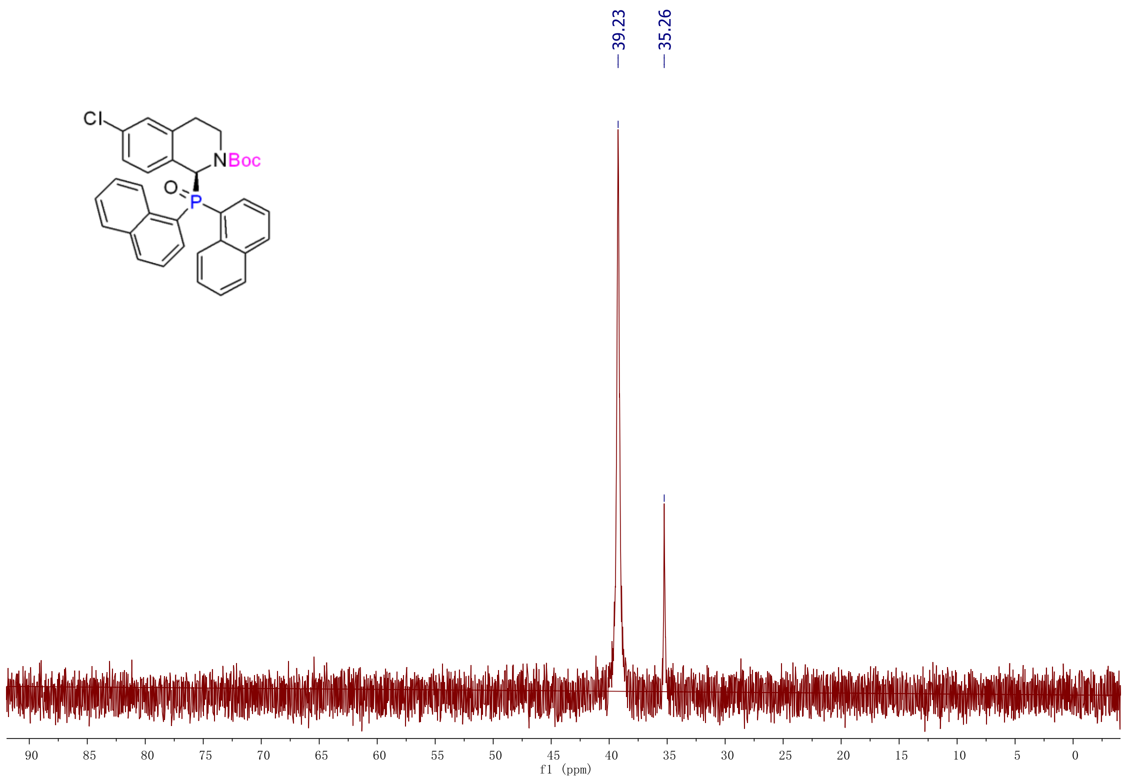
^{31}P NMR of compound **4ifa**



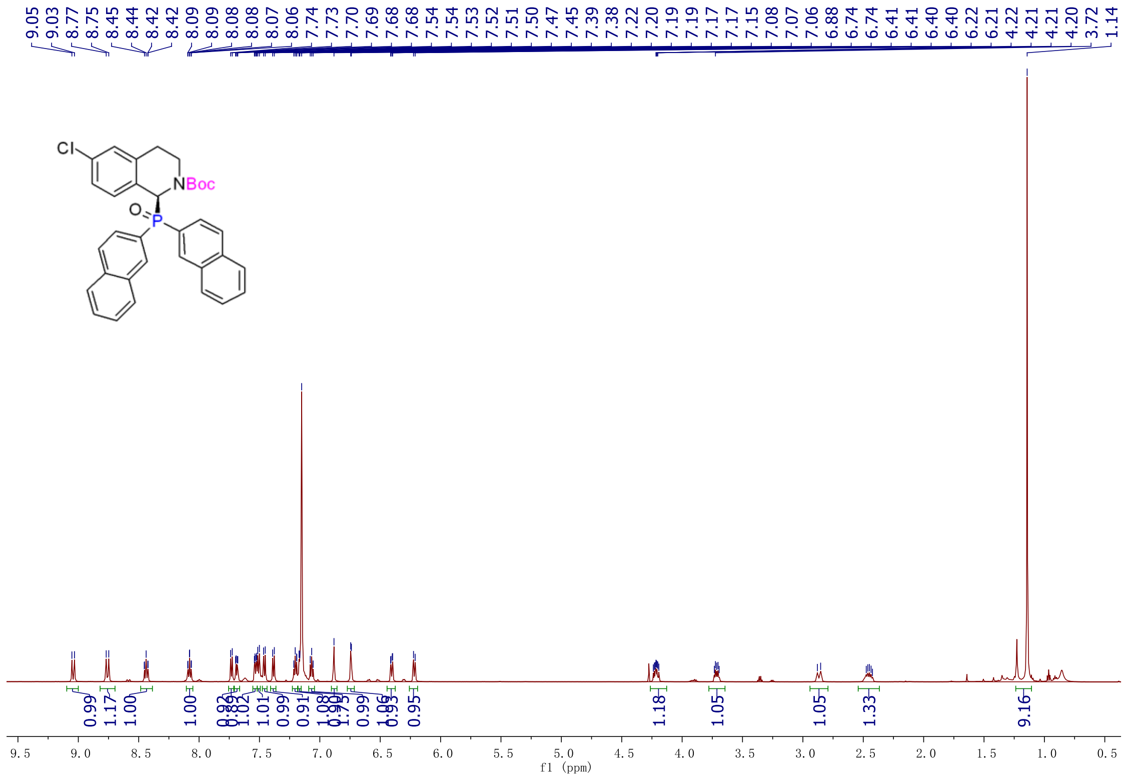
[1]H NMR of compound **4iga**



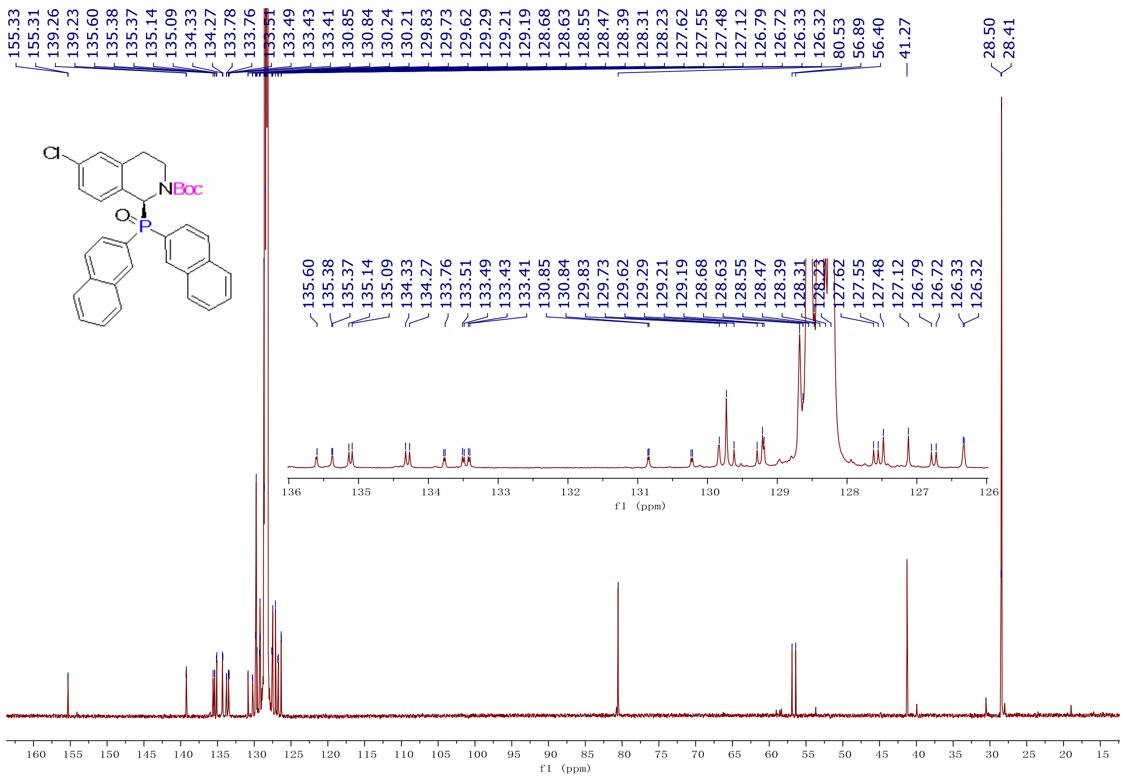
[13]C NMR of compound **4iga**



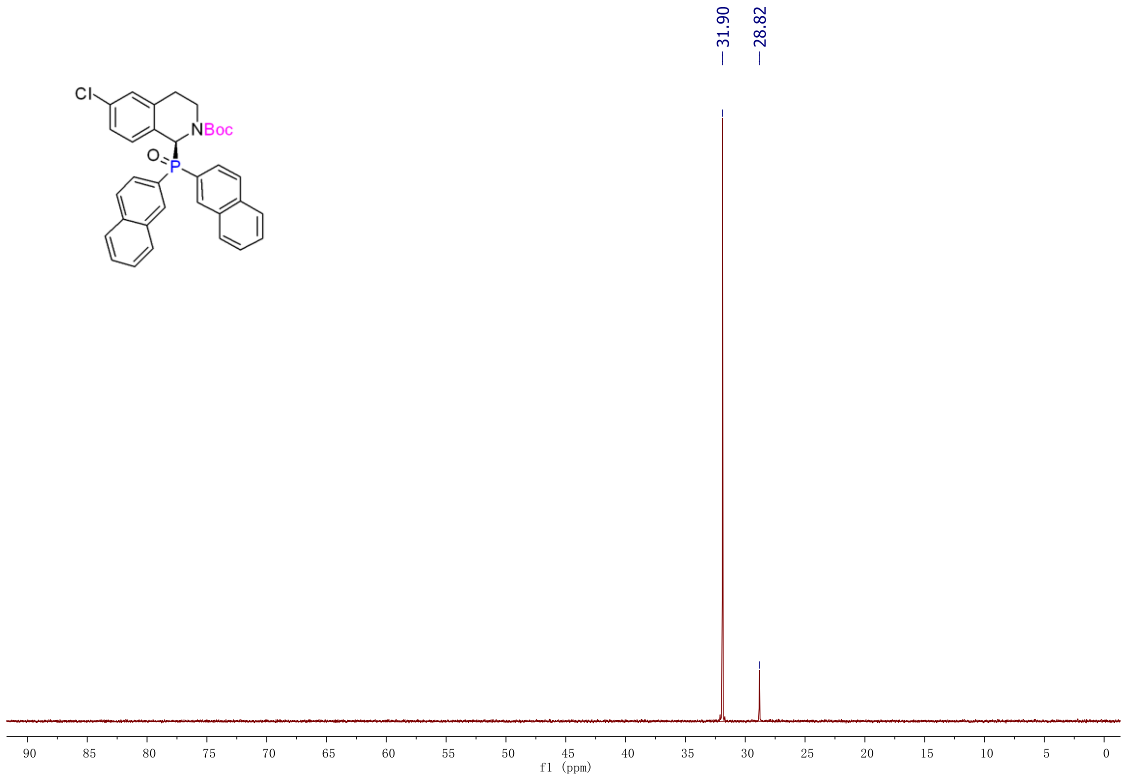
^{31}P NMR of compound **4iga**



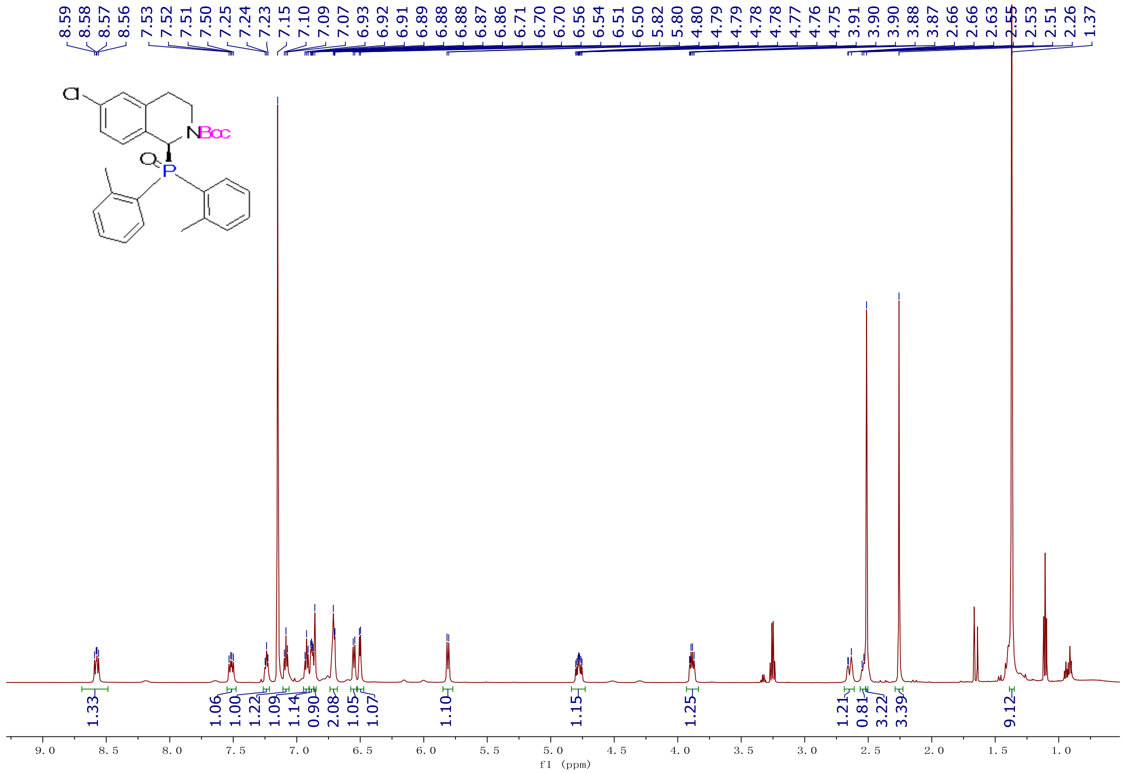
^{1}H NMR of compound **4iha**



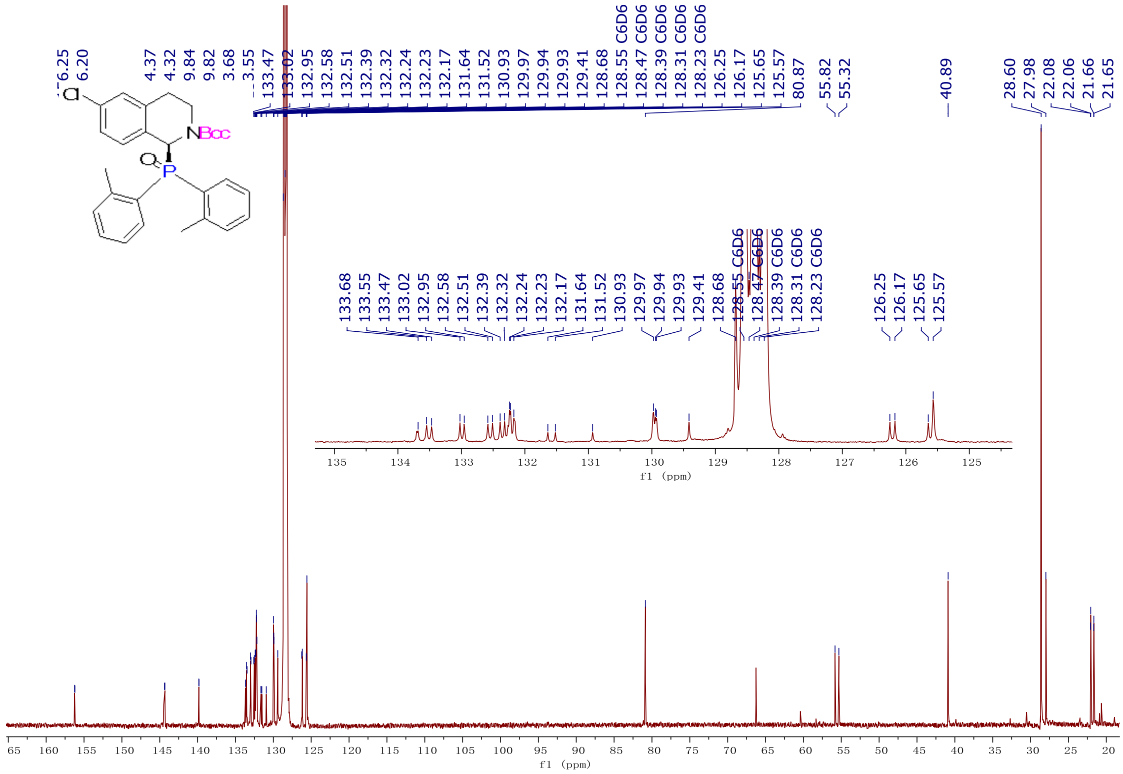
^{13}C NMR of compound **4iha**



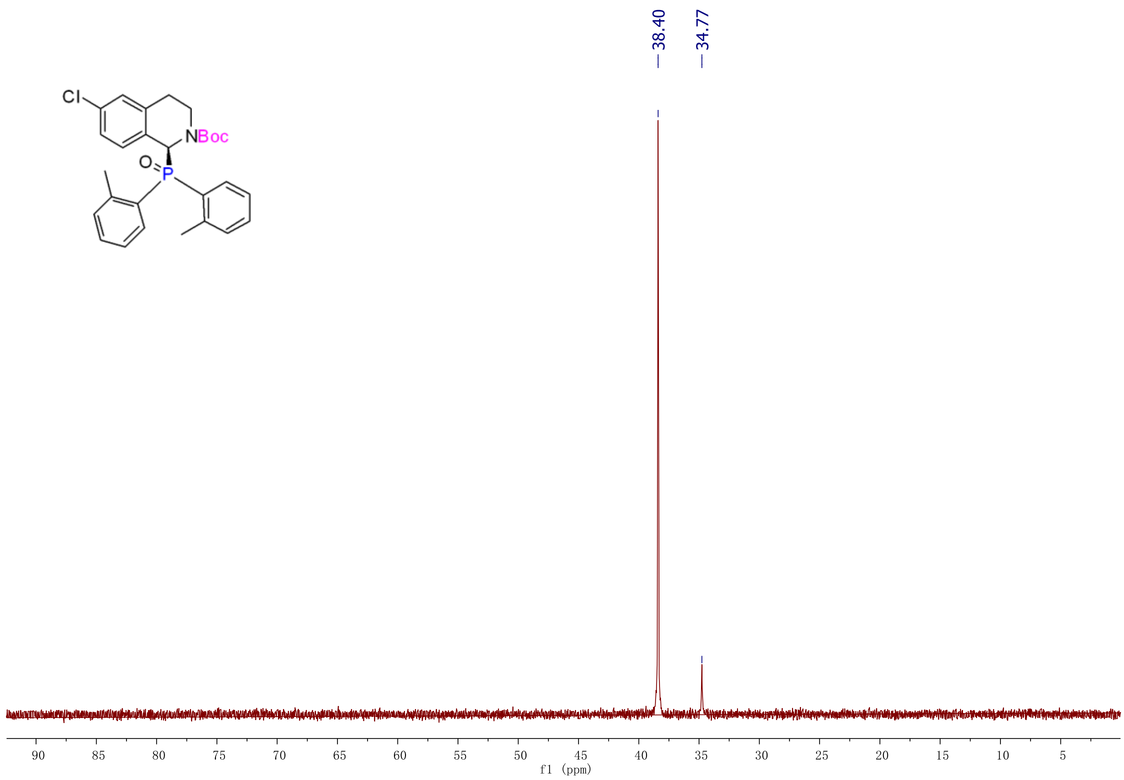
^{31}P NMR of compound **4iha**



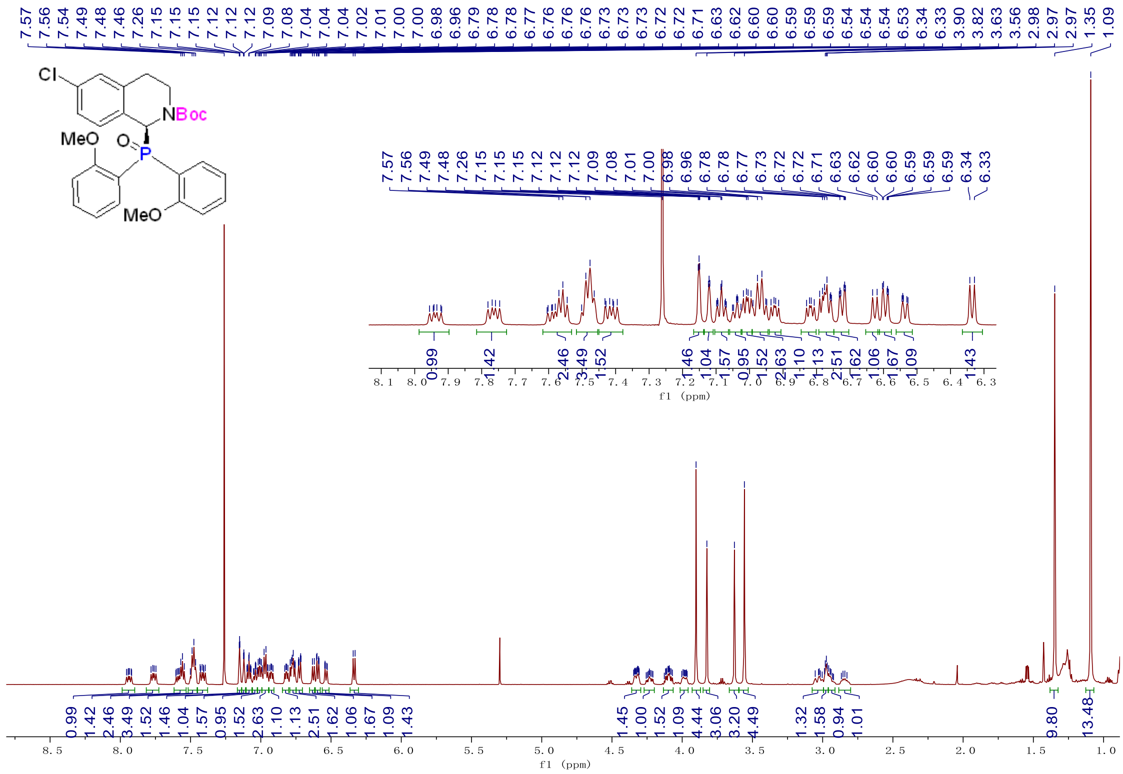
[1]H NMR of compound **4iia**



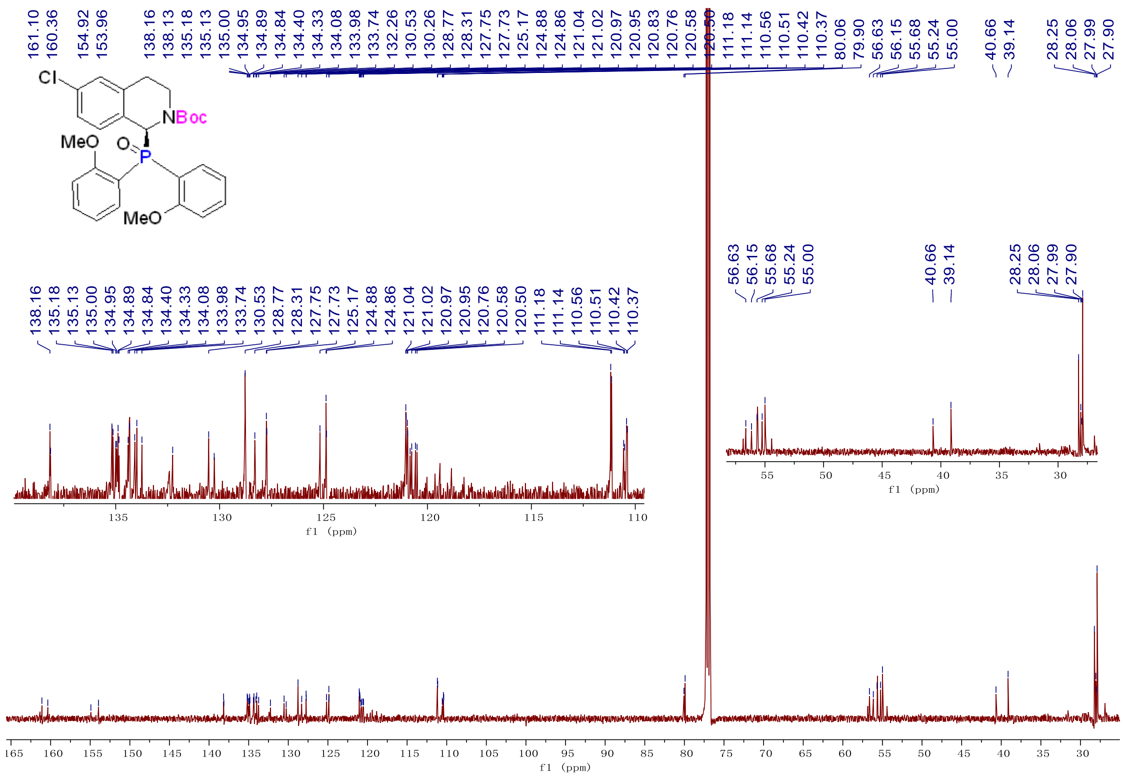
[13]C NMR of compound **4iia**



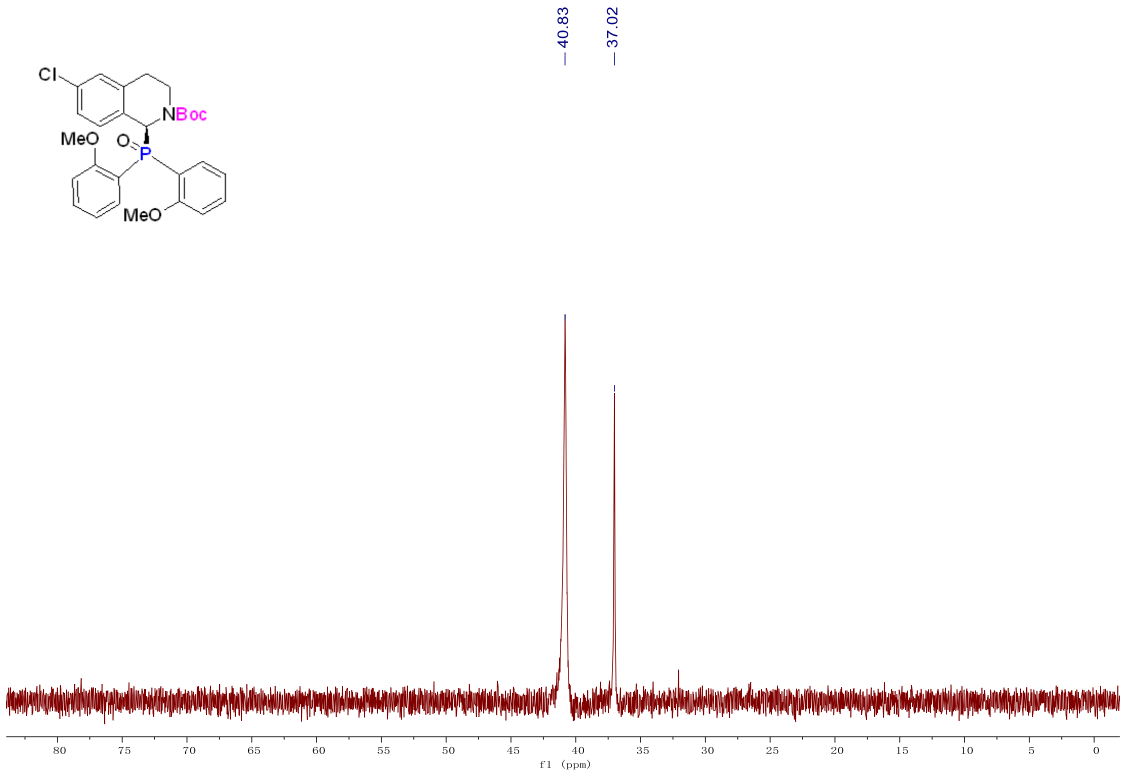
^{31}P NMR of compound **4iia**



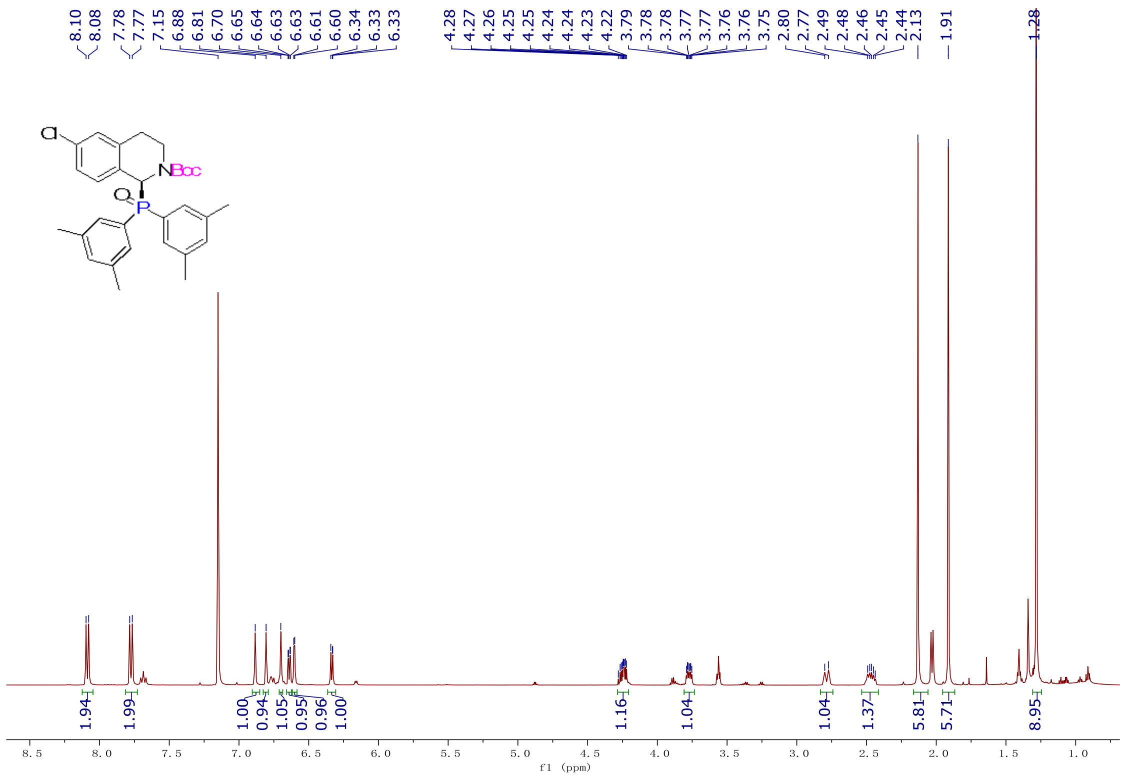
^{1}H NMR of compound **4ija**



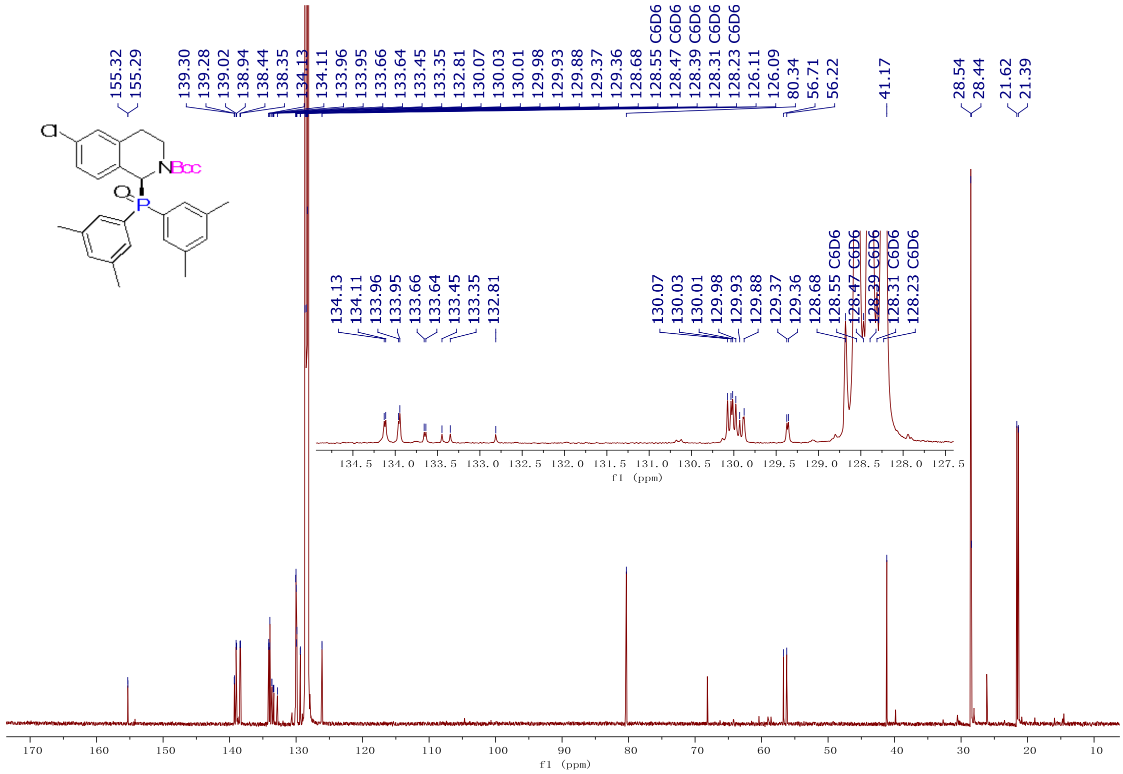
^{13}C NMR of compound **4ija**



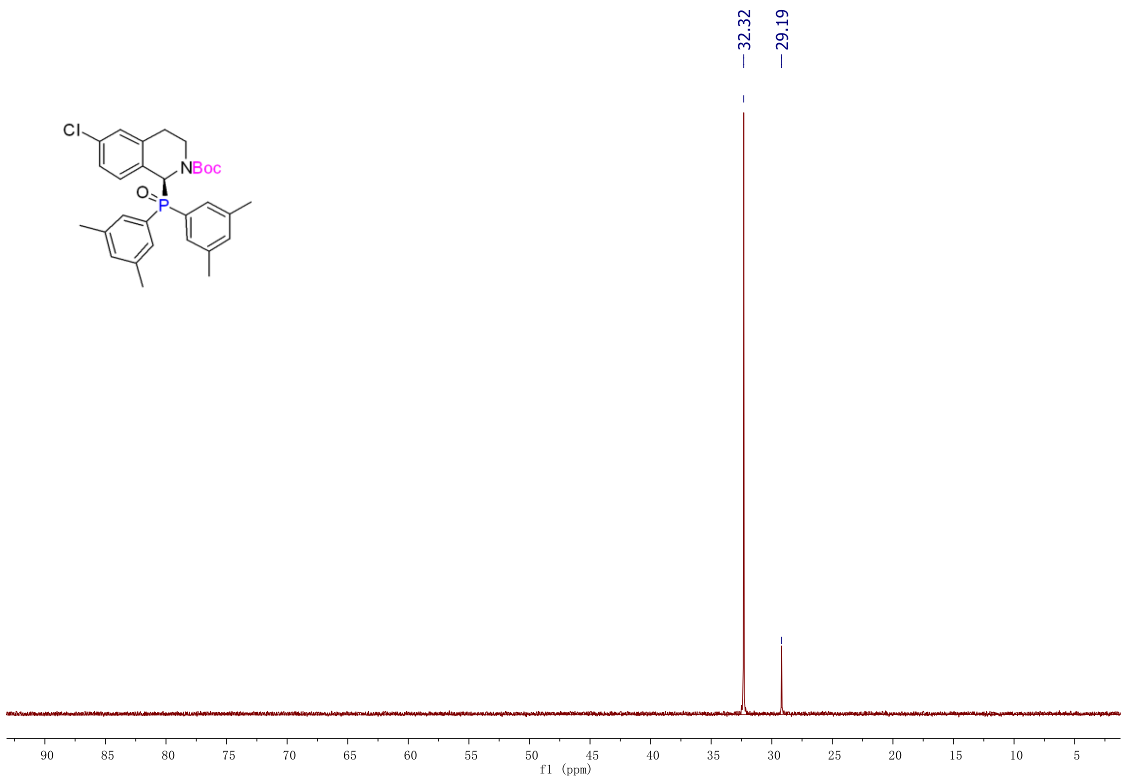
^{31}P NMR of compound **4ija**



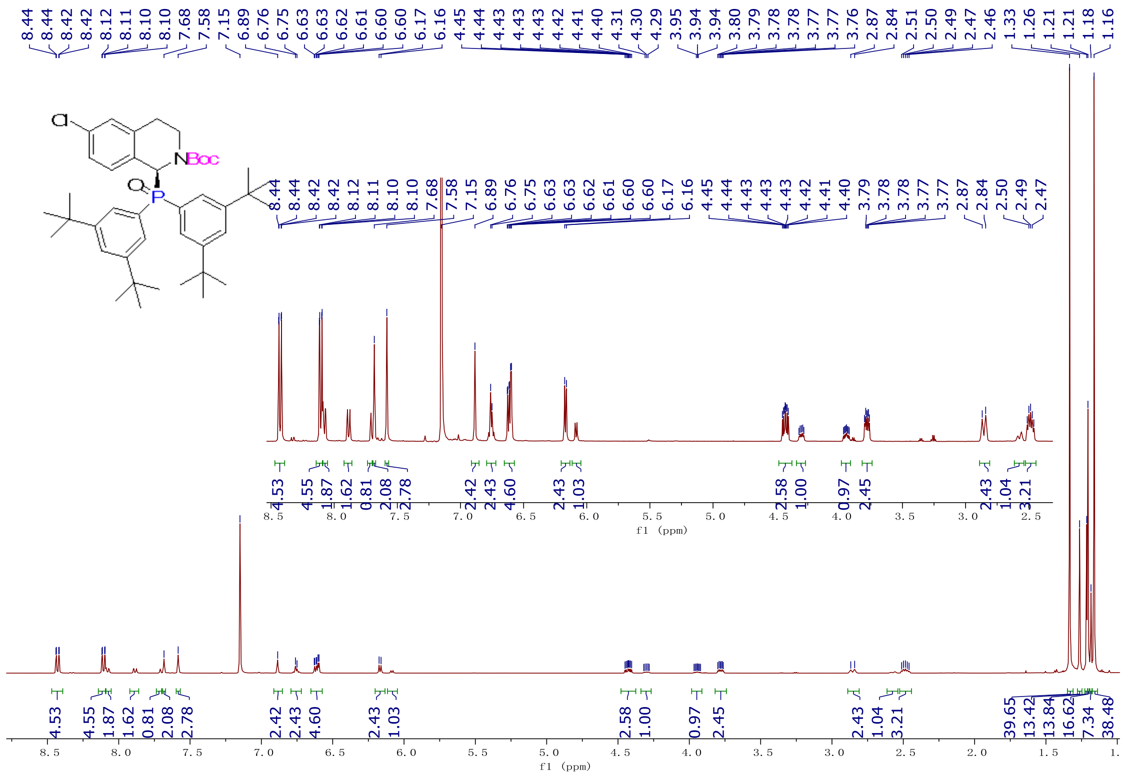
^{1}H NMR of compound **4ika**



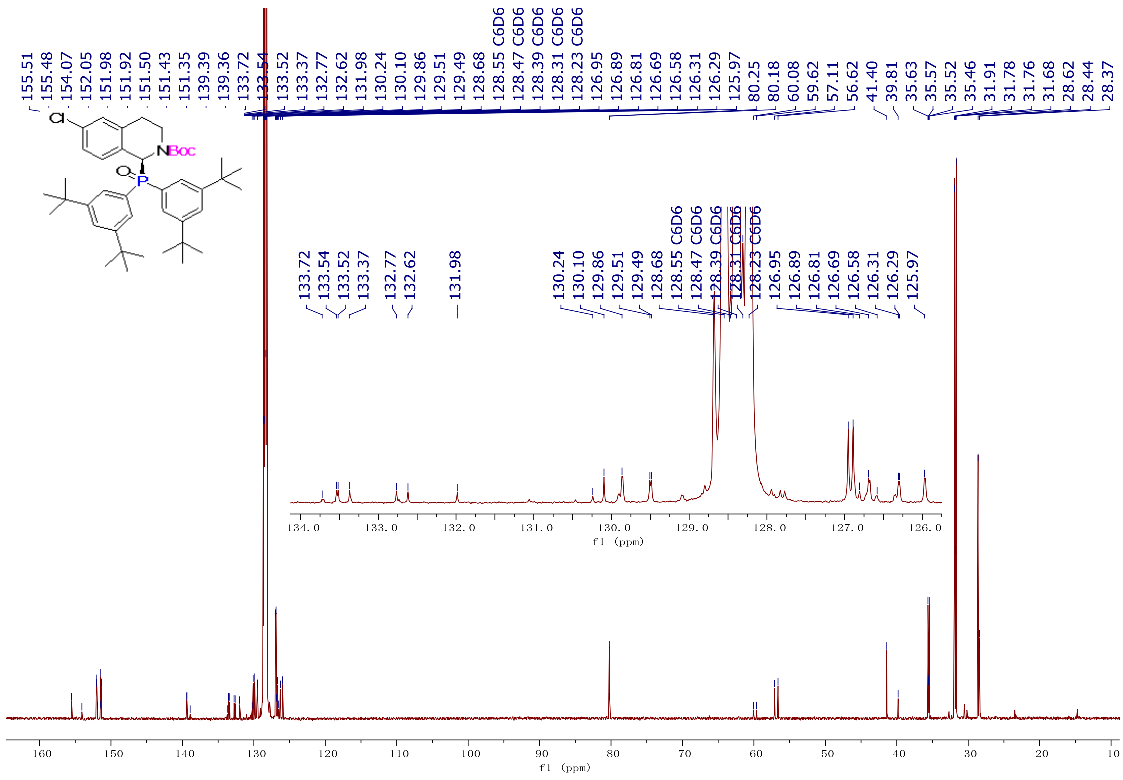
^{13}C NMR of compound **4ika**



^{31}P NMR of compound **4ika**



^{1}H NMR of compound **4ika**



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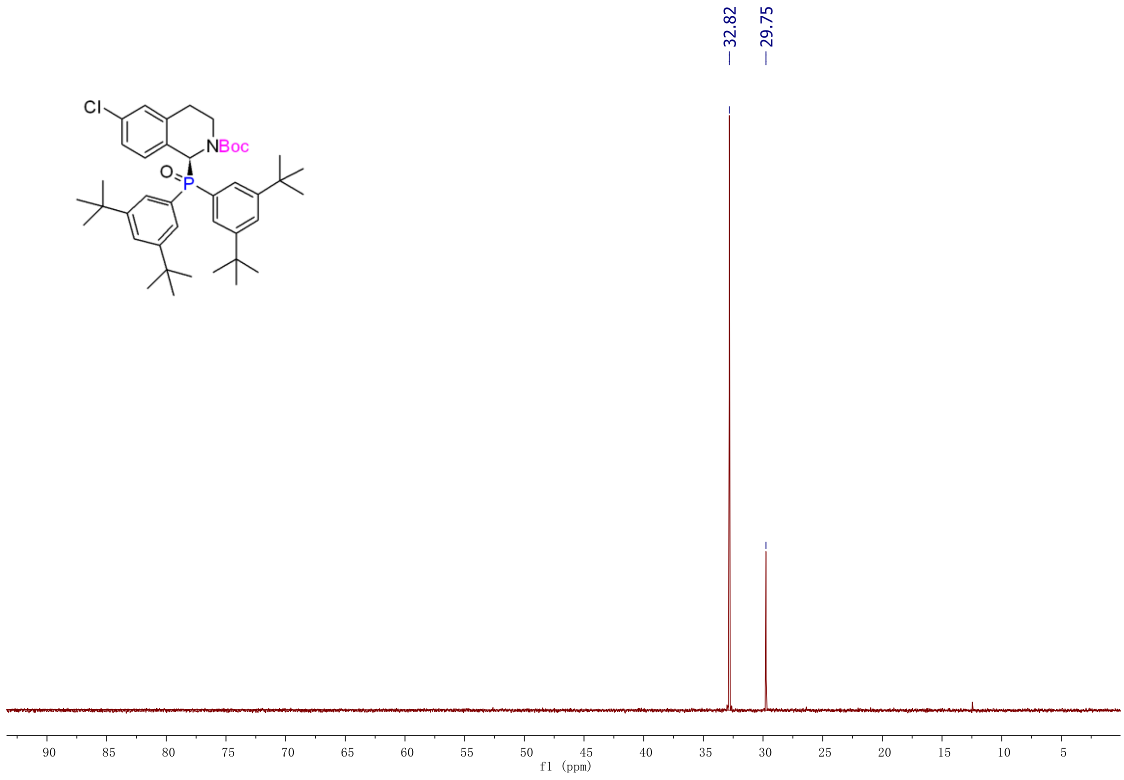
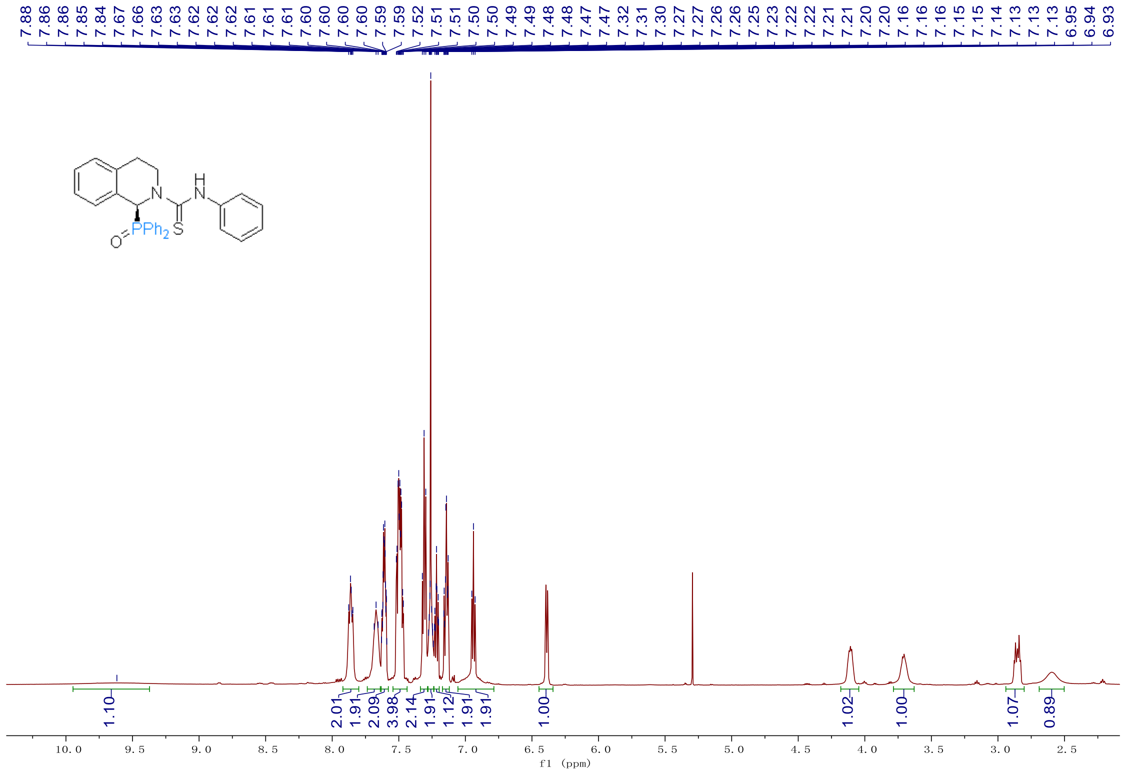
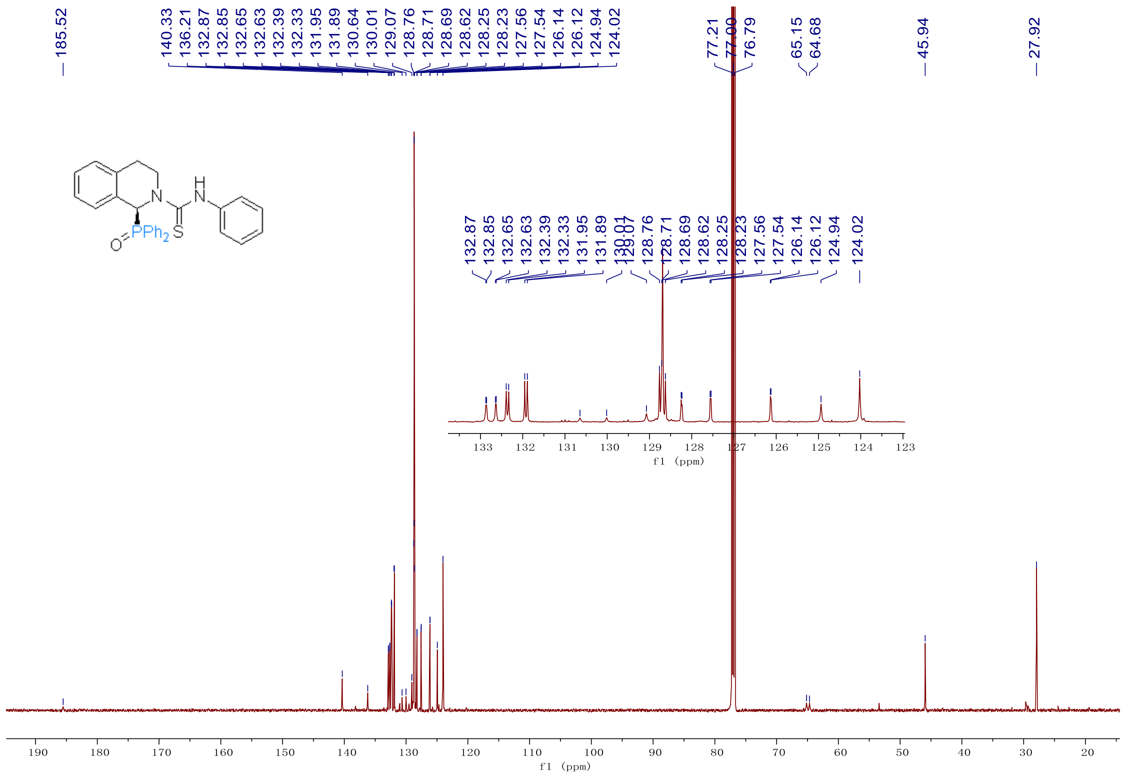


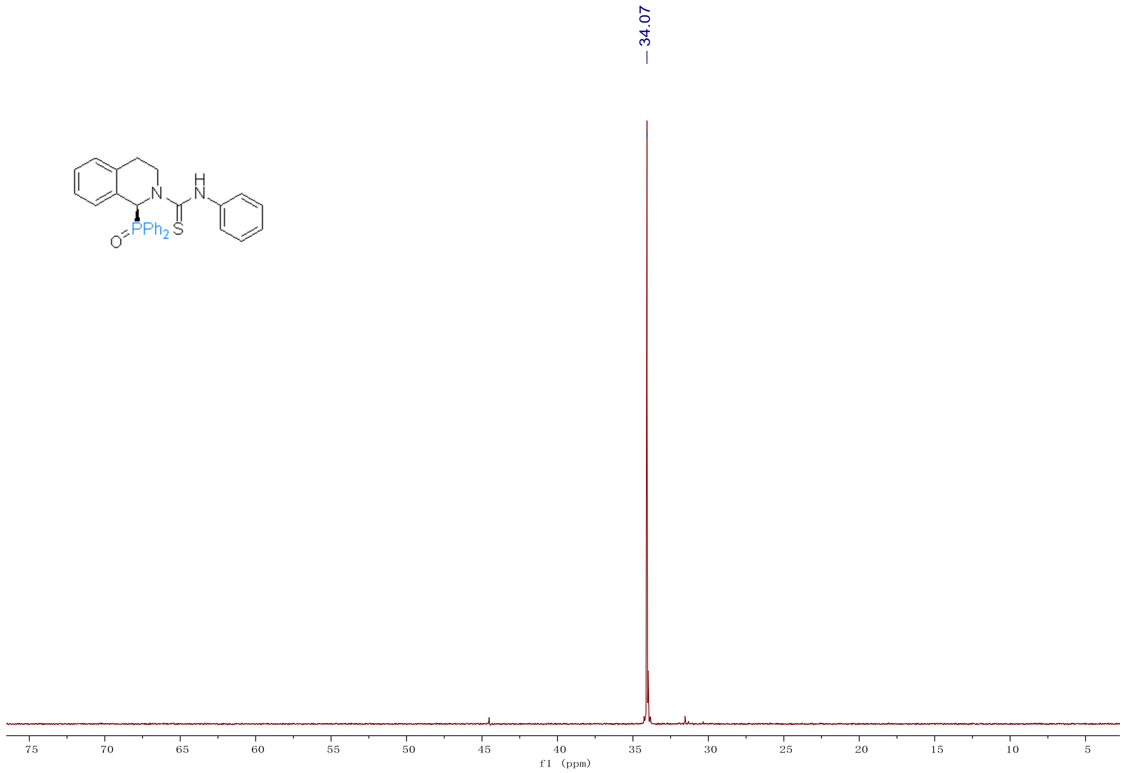
^{31}P NMR of compound **4ika**



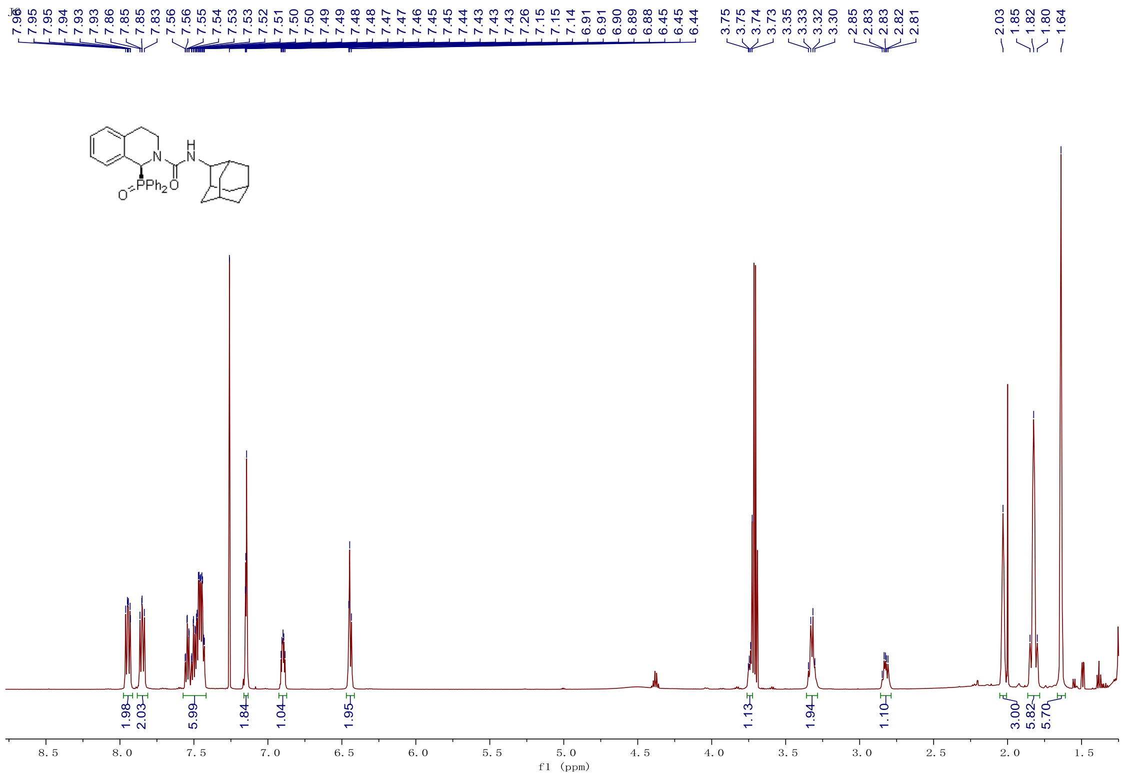
[1]H NMR of compound **6aaa**



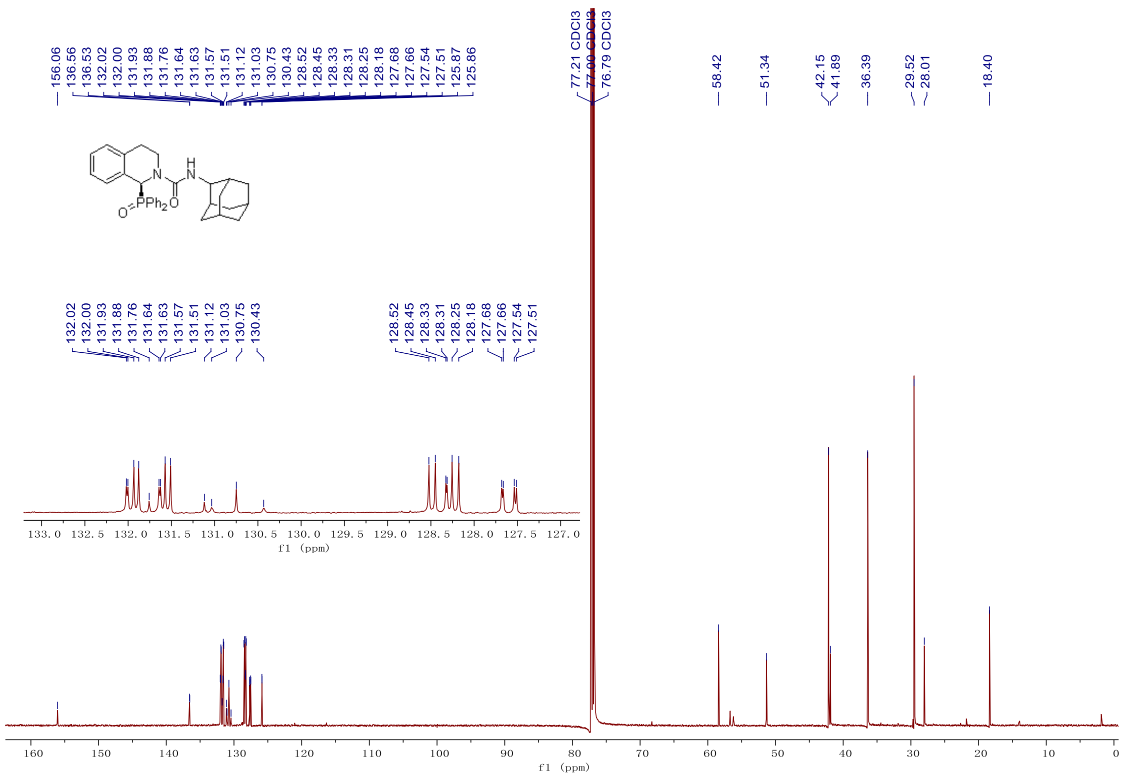
[13]C NMR of compound **6aaa**



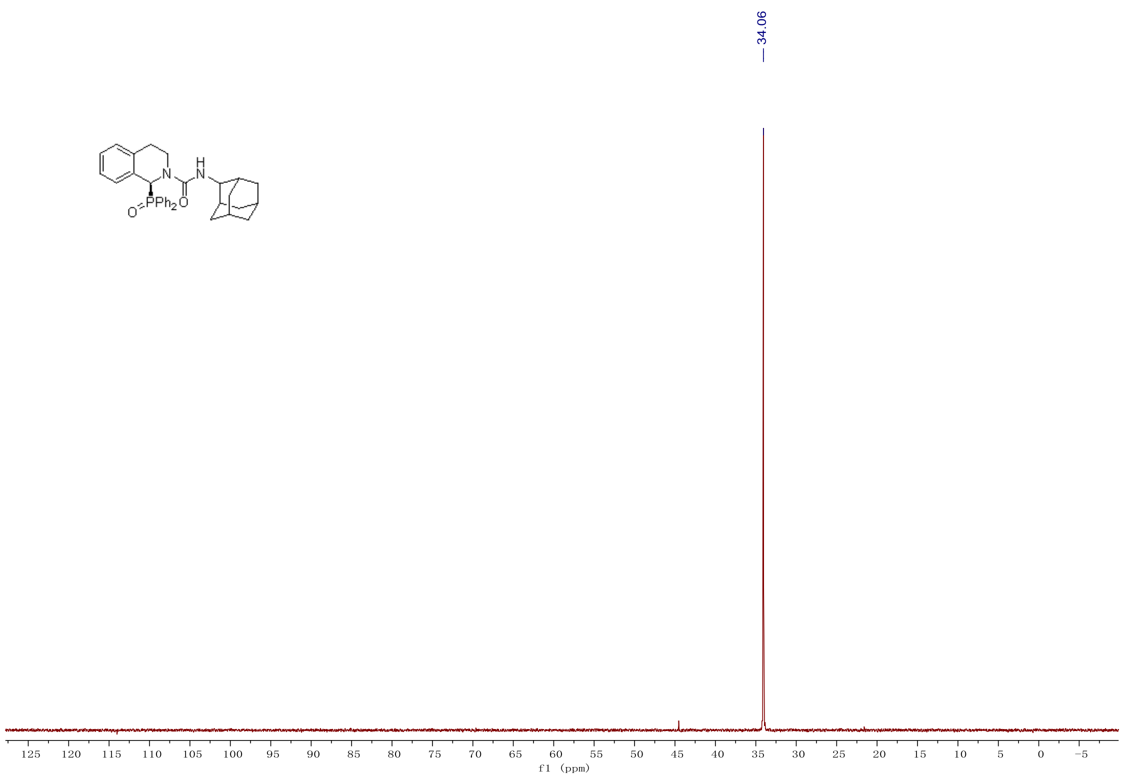
^{31}P NMR of compound **6aaa**



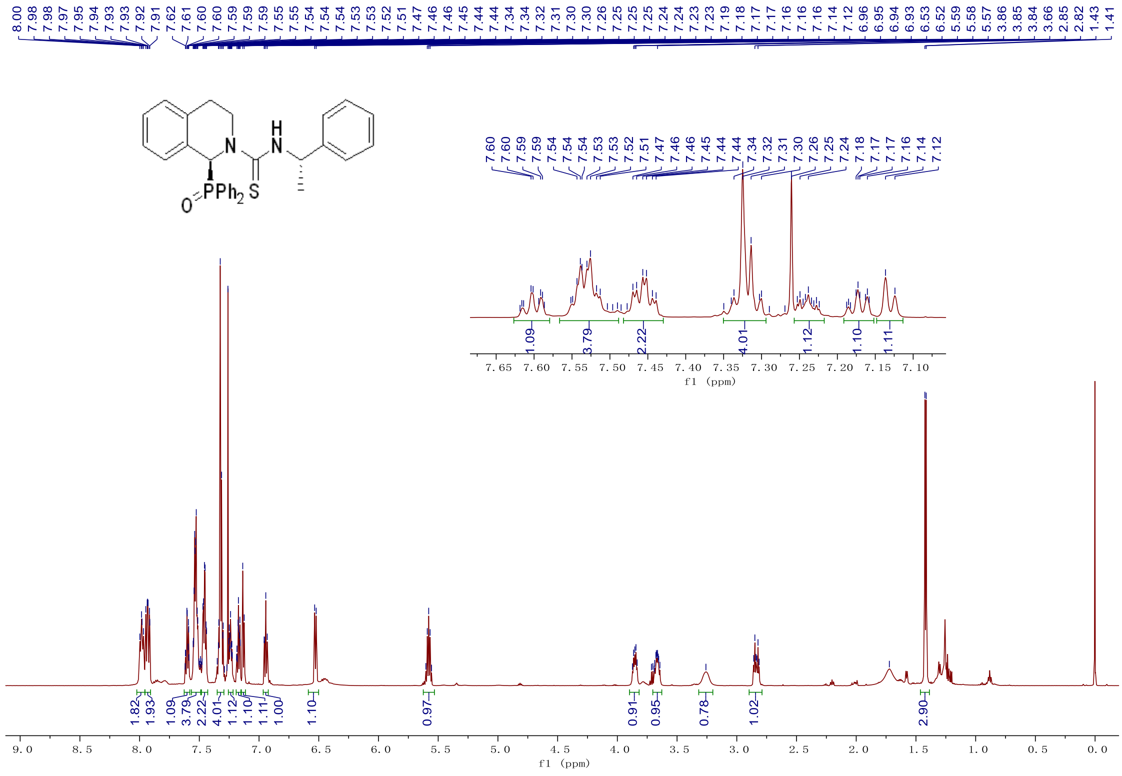
^{1}H NMR of compound **6aab**



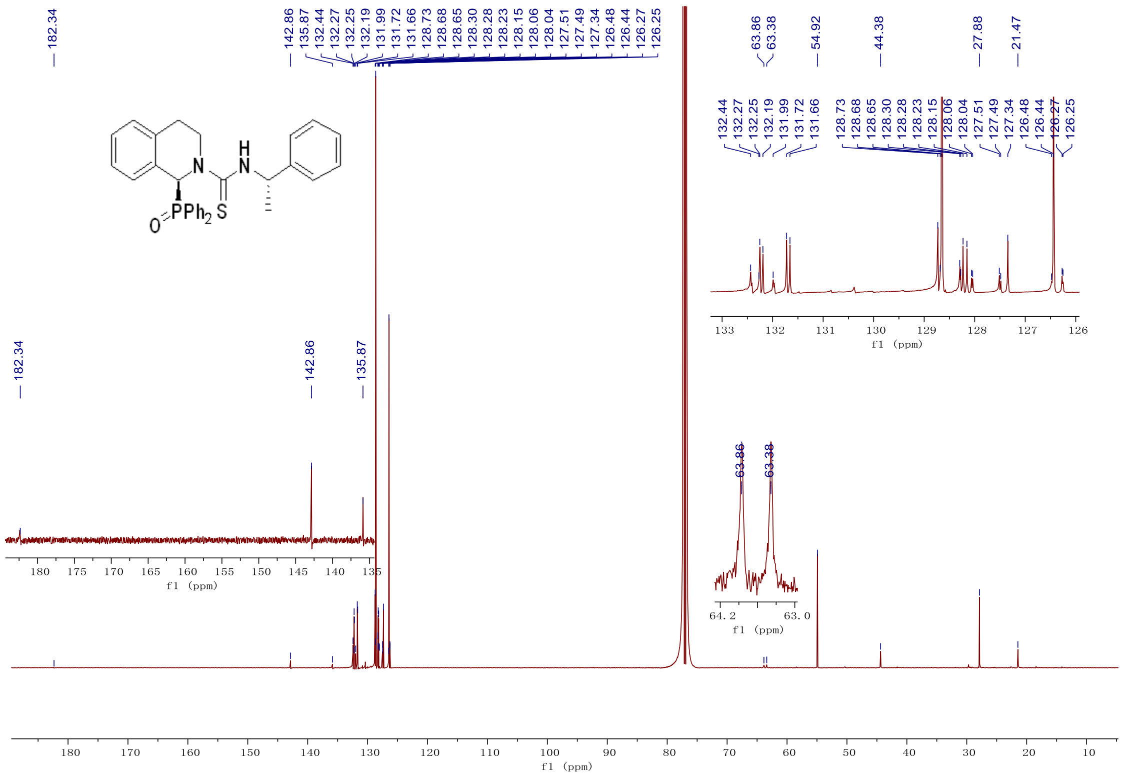
^{13}C NMR of compound **6aab**



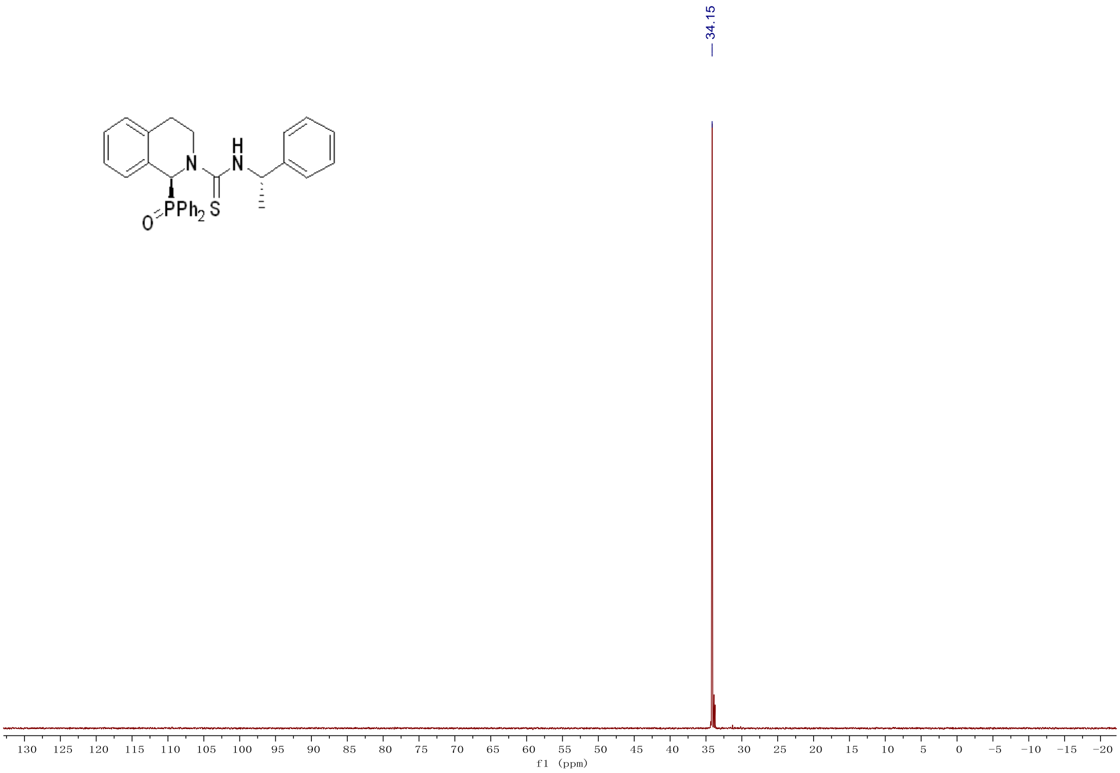
^{31}P NMR of compound **6aab**



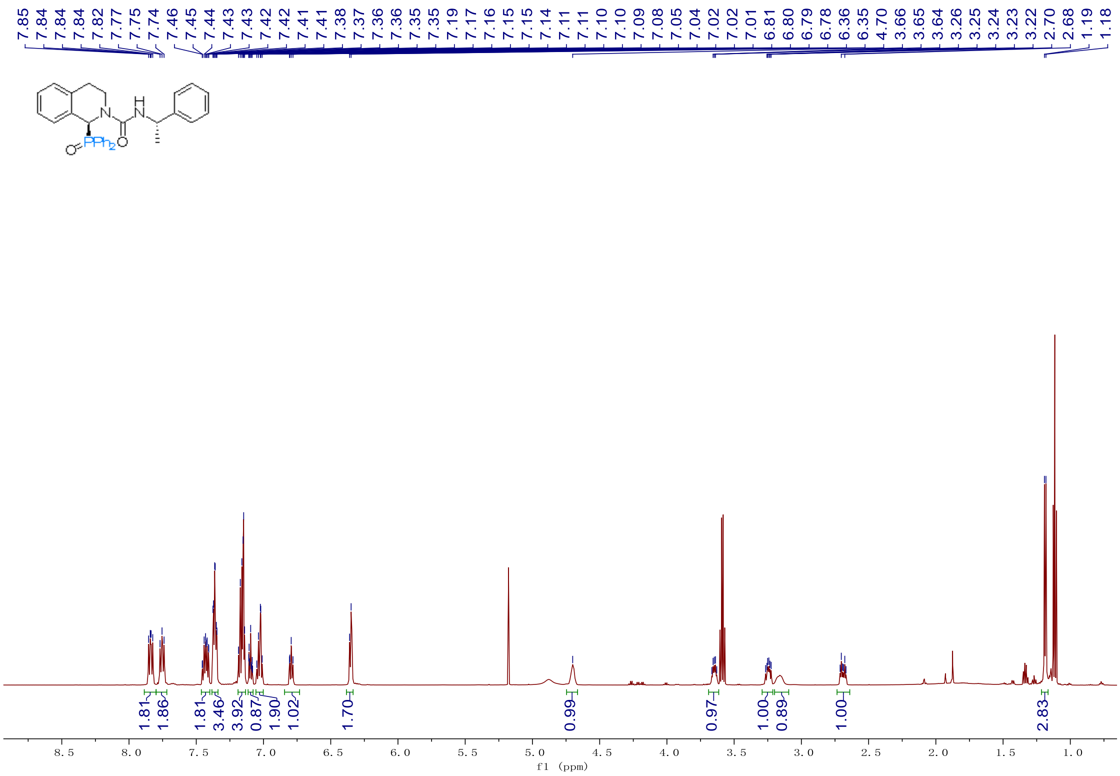
[1]H NMR of compound **6aac**



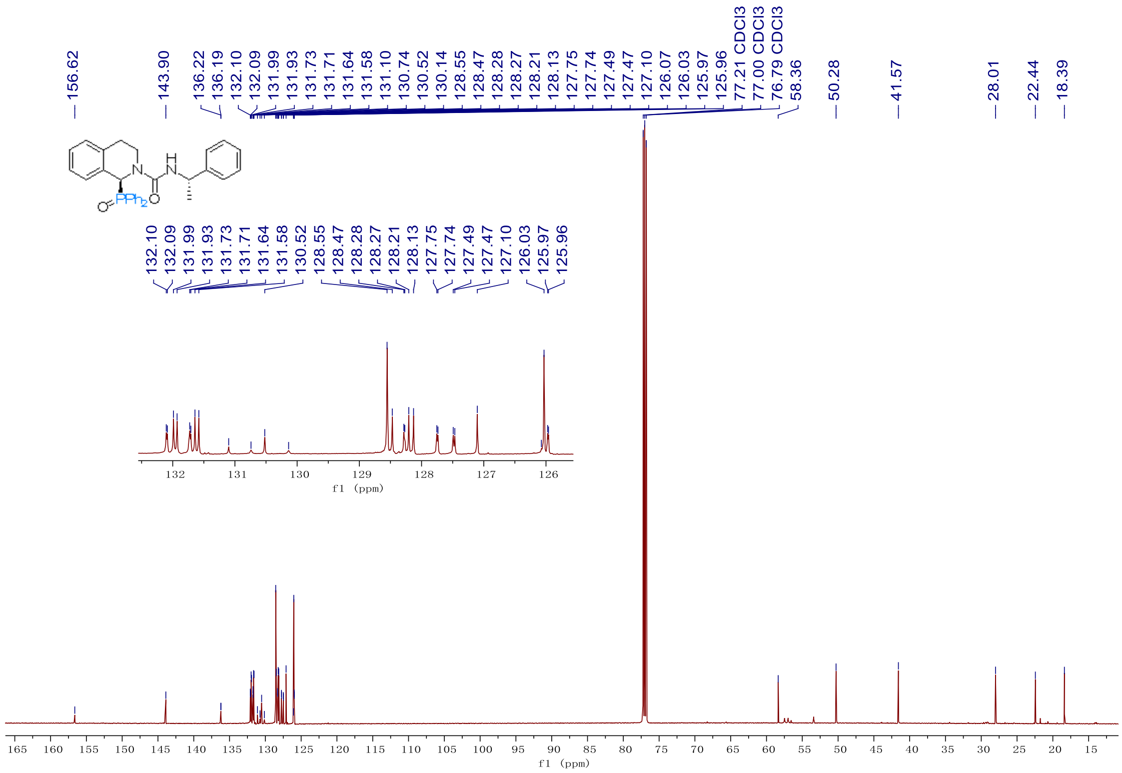
[13]C NMR of compound **6aac**



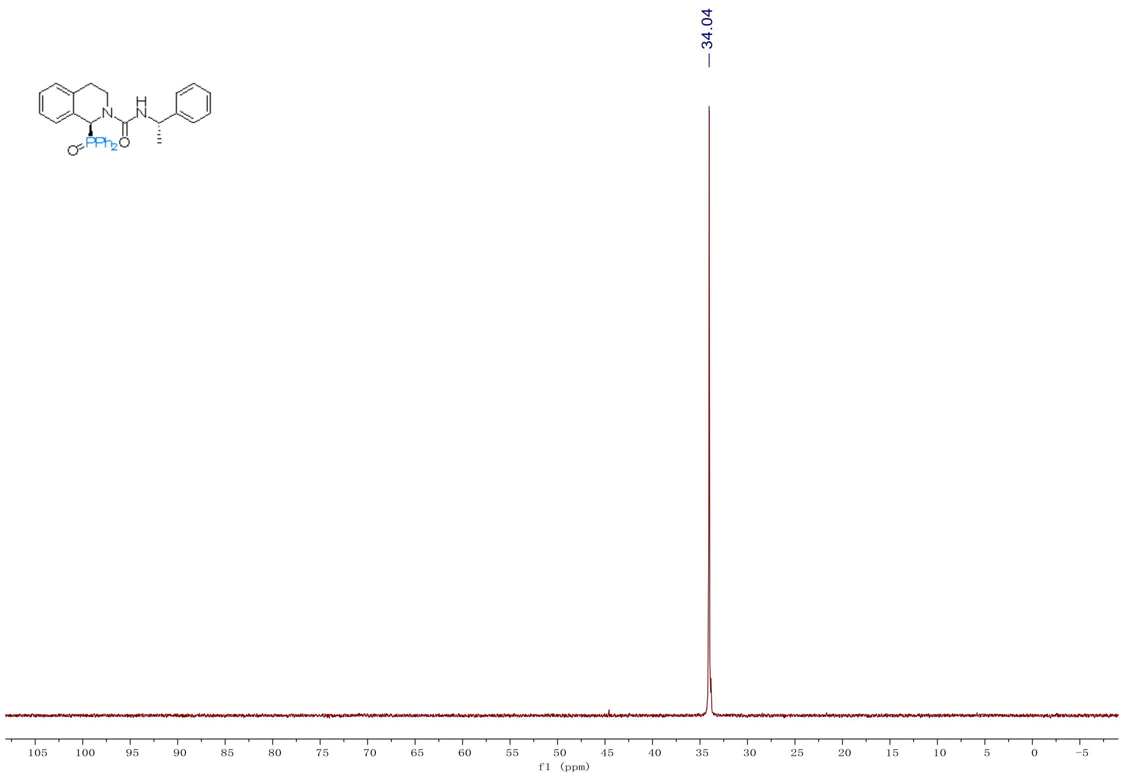
^{31}P NMR of compound **6aac**



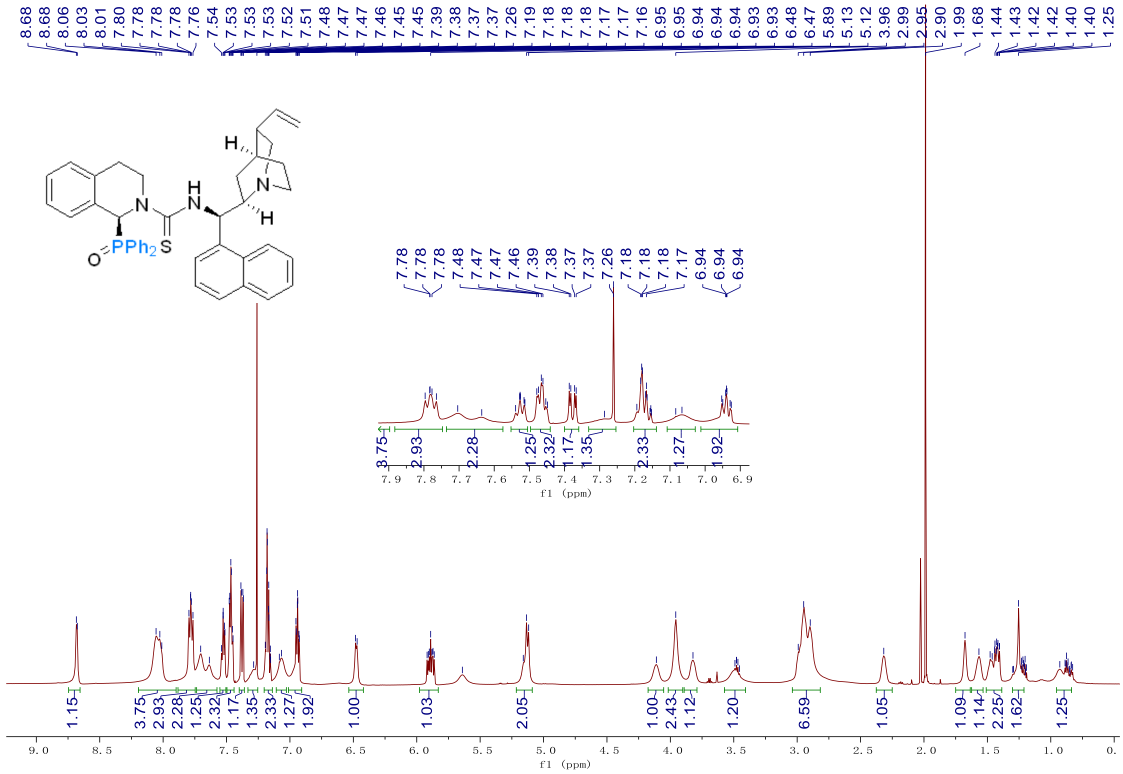
^{1}H NMR of compound **6aad**



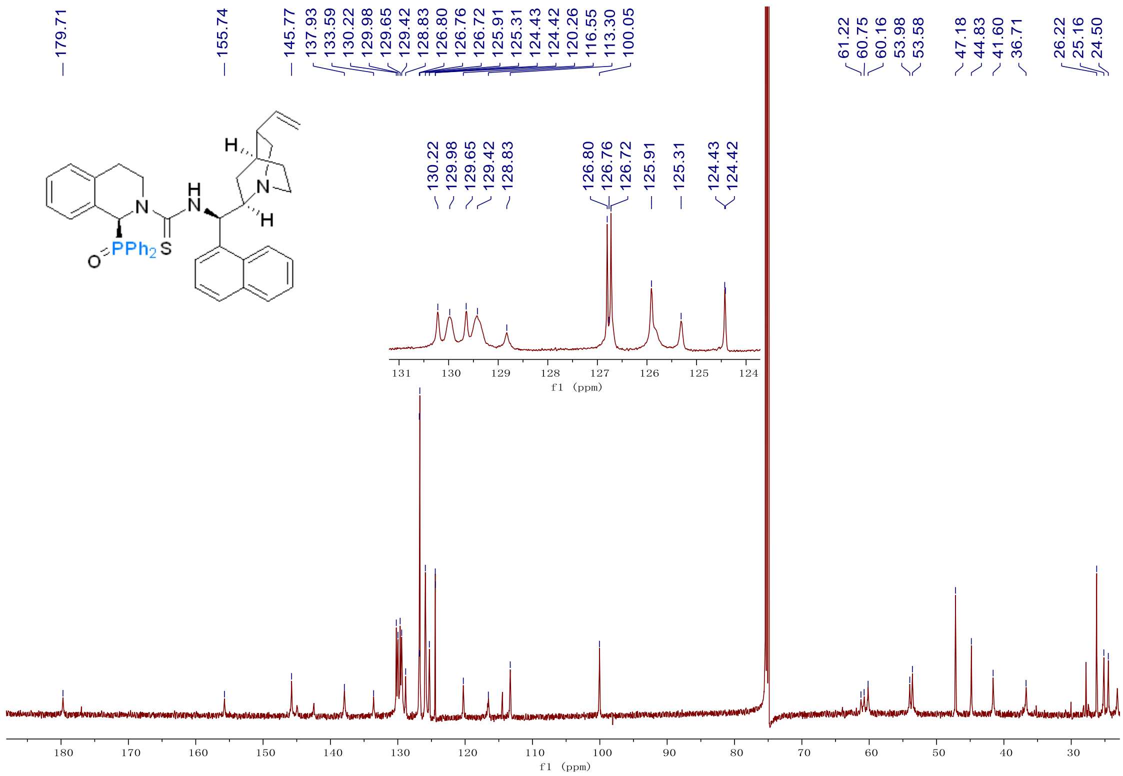
^{13}C NMR of compound **6aad**



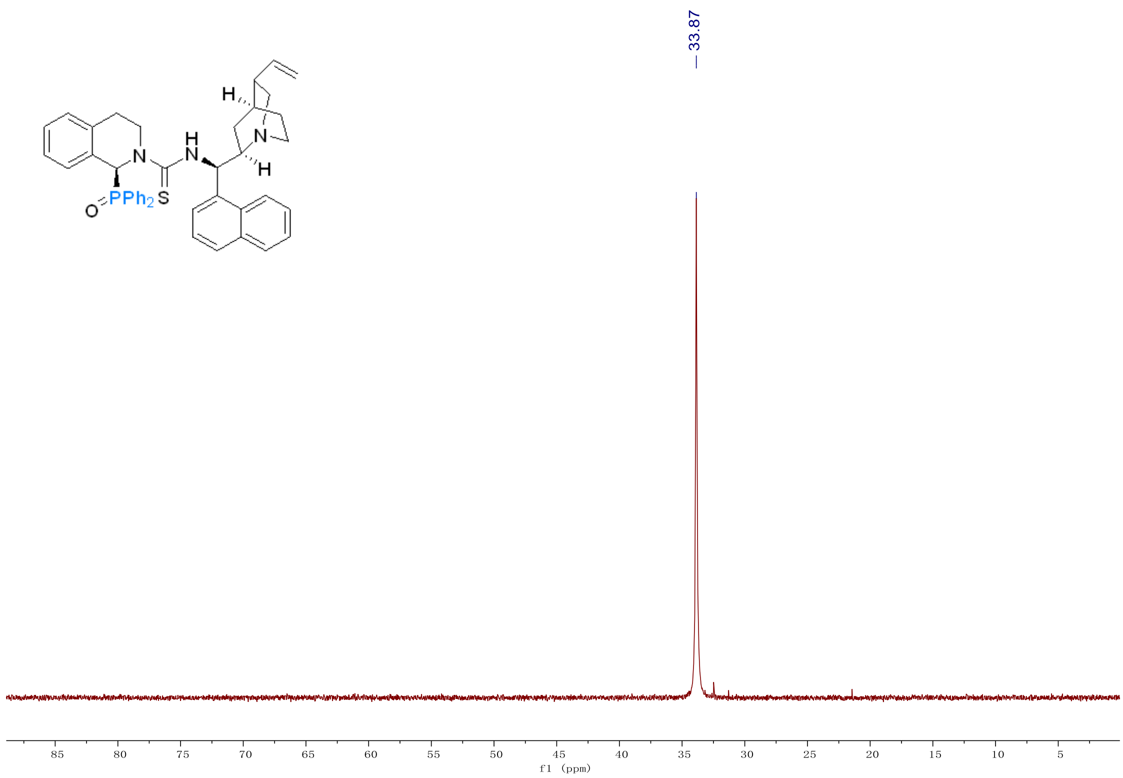
^{31}P NMR of compound **6aad**



[1]H NMR of compound **6aae**

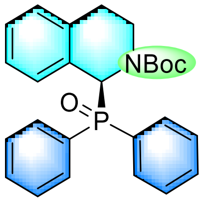


[13]C NMR of compound **6aad**



^{31}P NMR of compound **6aad**

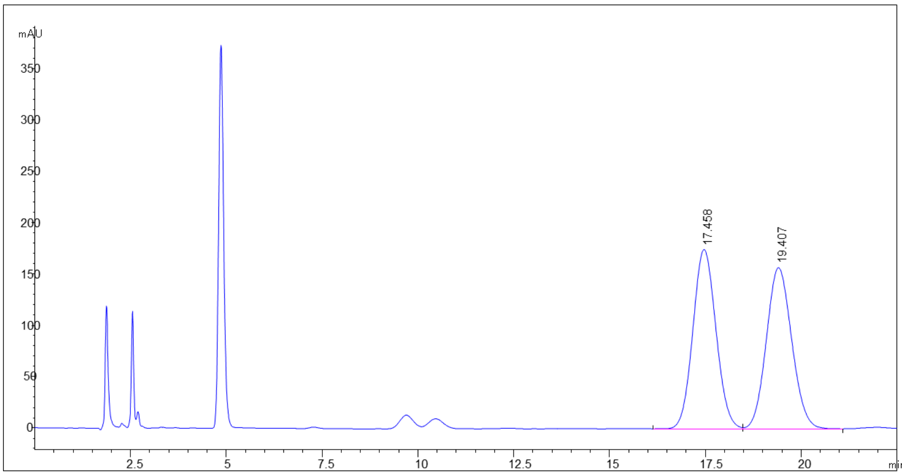
9. The spectra of HPLC



4aaa

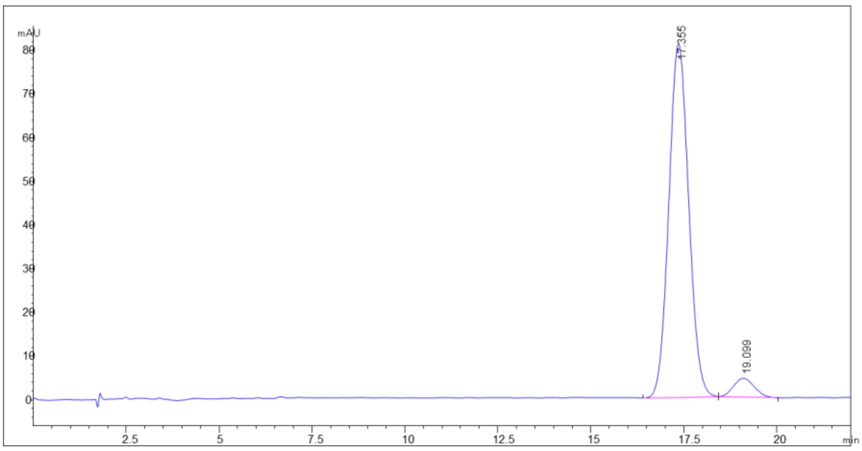
99% yield, 91% ee

Chiralpak OD-RH column, MeCN/H_2O= 60/40, flow rate 1.0 mL/min



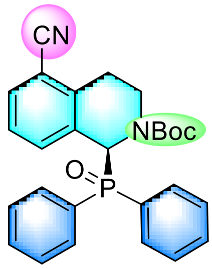
Peak	Retention time	Area	% Area
1	17.458	7399.4	50.228
2	19.407	7332.2	49.772

HPLC for racemic compound **4aaa**



Peak	Retention time	Area	% Area
1	17.355	3011.1	95.35
2	19.099	146.8	4.65

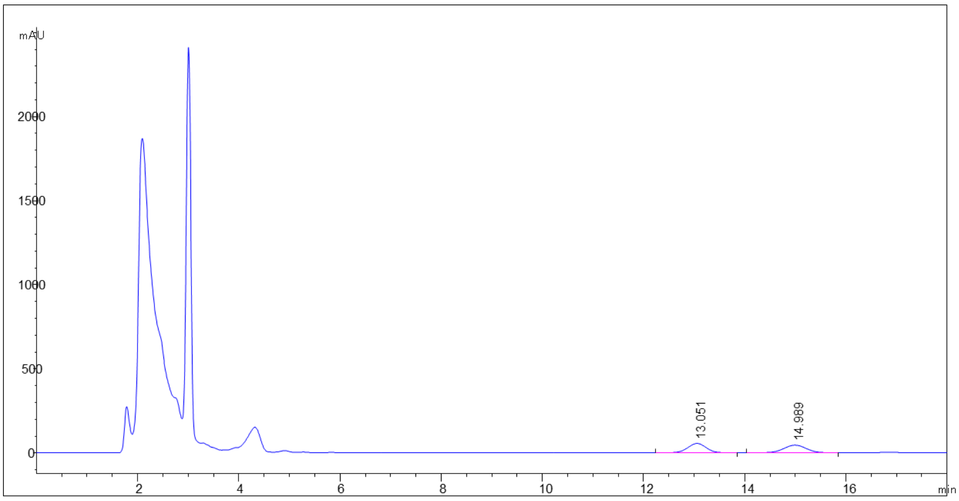
HPLC for pure enantioenriched compound **4aaa**



4baa

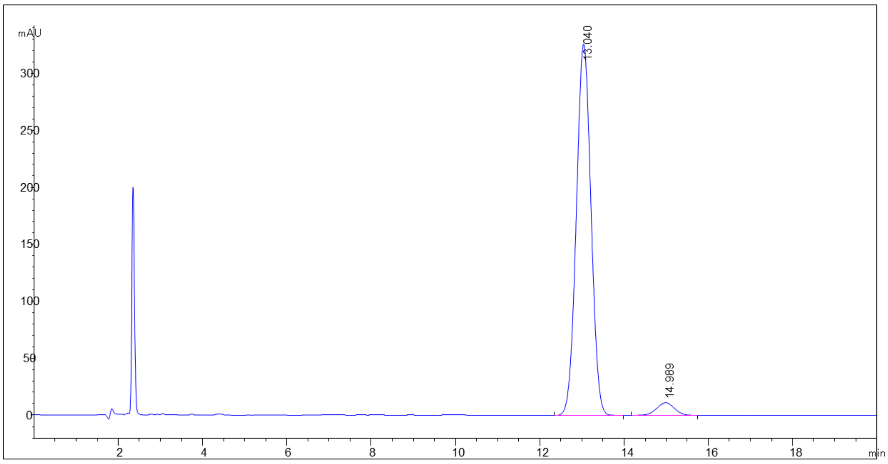
86% yield, 92% ee

Chiralpak OJ-RH column, MeCN/H_2O= 65/35, flow rate 1.0 mL/min



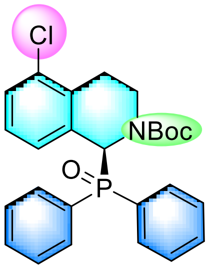
Peak	Retention time	Area	% Area
1	13.050	1408.4	49.832
2	14.989	1417.9	50.168

HPLC for racemic compound **4baa**



Peak	Retention time	Area	% Area
1	13.040	7888.8	95.915
2	14.989	336	4.085

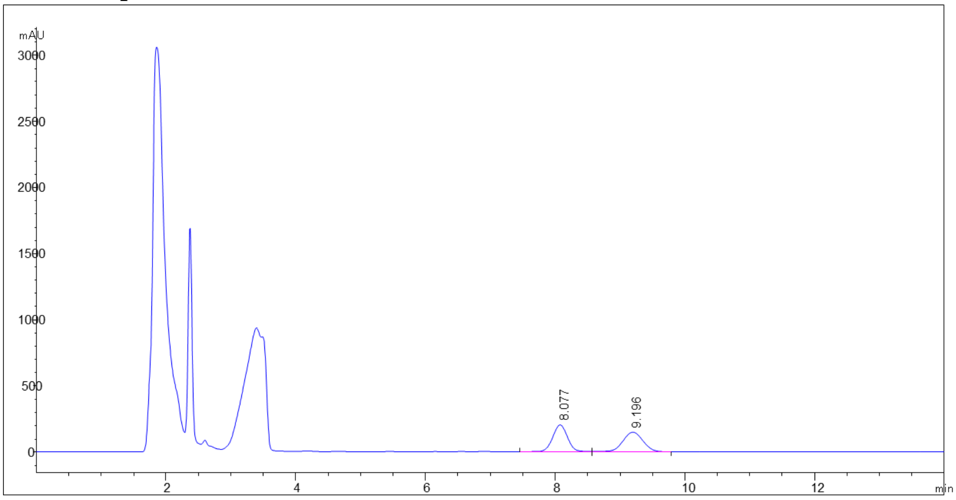
HPLC for pure enantioenriched compound **4baa**



4caa

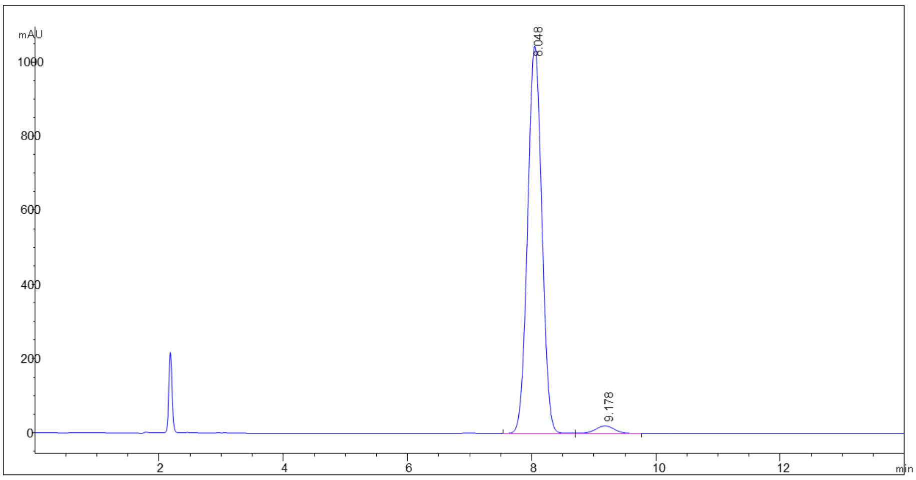
83% yield, 95% ee

Chiralpak OJ-RH column, MeCN/H_2O= 55/45, flow rate 1.0 mL/min



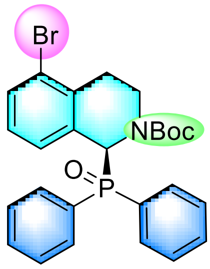
Peak	Retention time	Area	% Area
1	8.077	3245.6	50.260
2	9.196	3212	49.740

HPLC for racemic compound **4caa**



Peak	Retention time	Area	% Area
1	8.048	16570.2	97.556
2	9.178	415.1	2.444

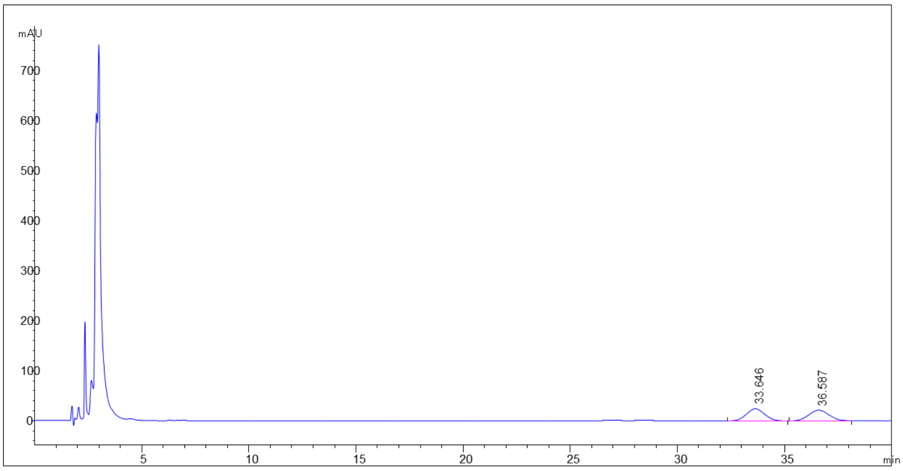
HPLC for pure enantioenriched compound **4caa**



4daa

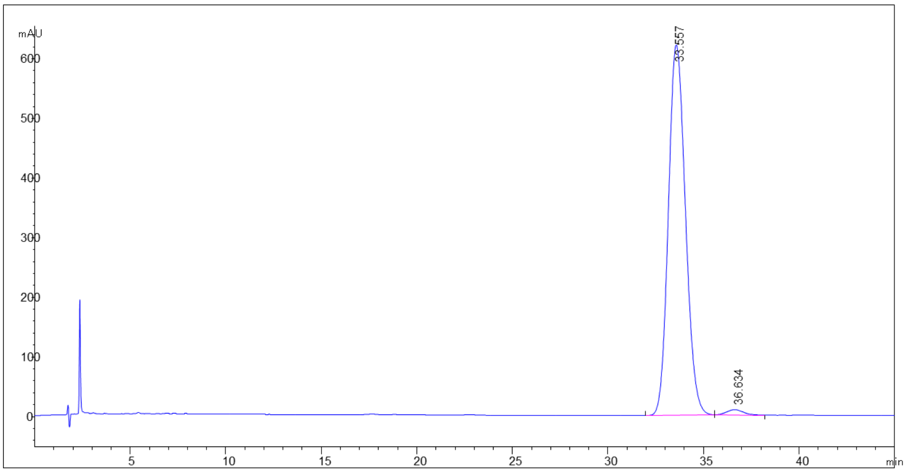
91% yield, 97% ee

Chiralpak OJ-RH column, MeCN/H_2O= 65/35, flow rate 1.0 mL/min



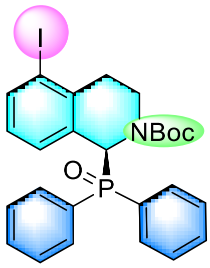
Peak	Retention time	Area	% Area
1	33.646	1445.3	49.975
2	36.587	1446.7	50.025

HPLC for racemic compound **4daa**



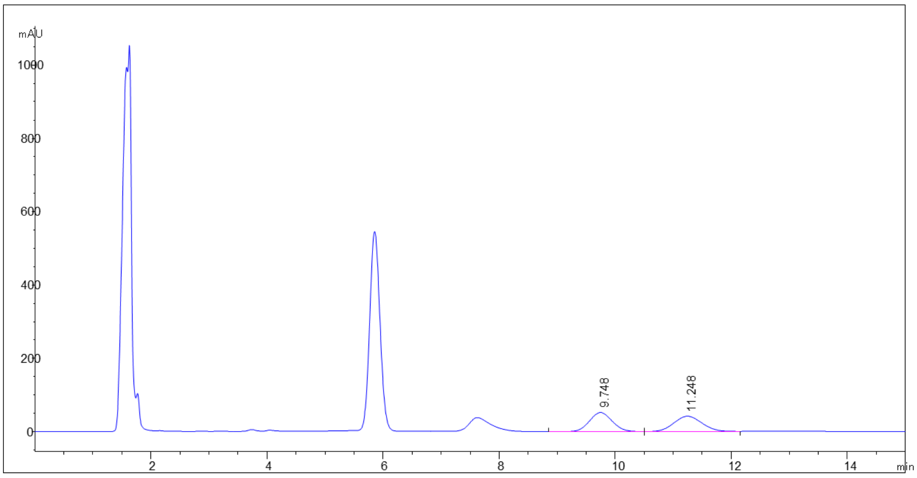
Peak	Retention time	Area	% Area
1	33.557	38390.7	98.566
2	36.634	558.6	1.434

HPLC for pure enantioenriched compound **4daa**



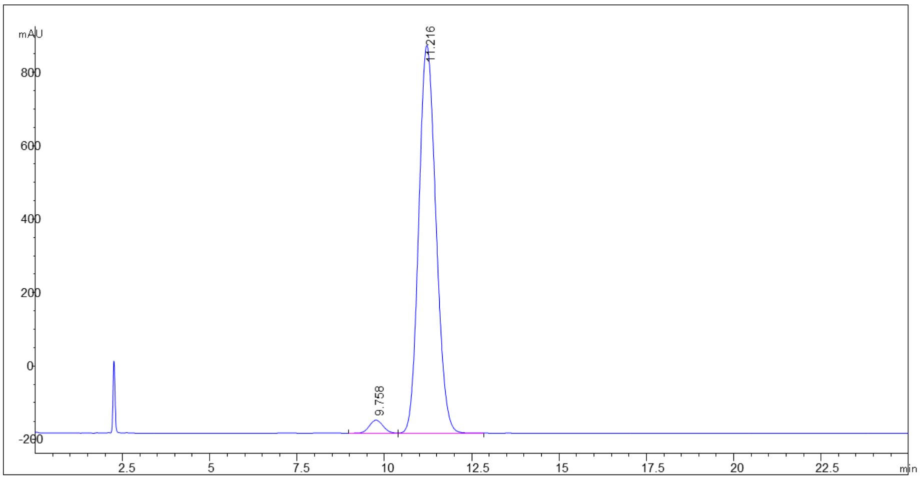
4eaa
83% yield, 95% ee

Chiralpak AS-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



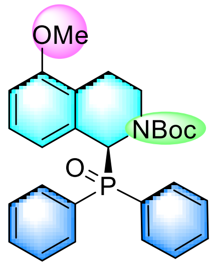
Peak	Retention time	Area	% Area
1	9.748	1465.3	50.459
2	11.248	1438.7	49.541

HPLC for racemic compound **4eaa**



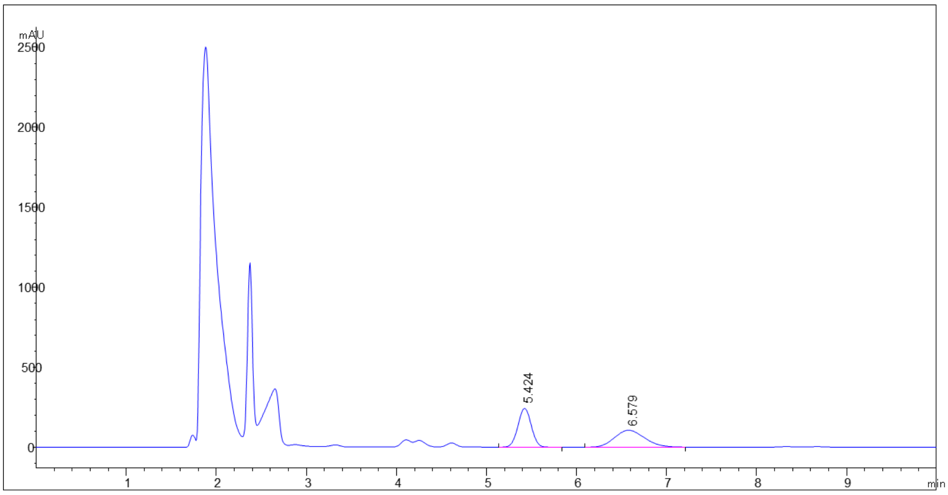
Peak	Retention time	Area	% Area
1	9.758	999.2	2.683
2	11.216	36243.5	97.317

HPLC for pure enantioenriched compound **4eaa**



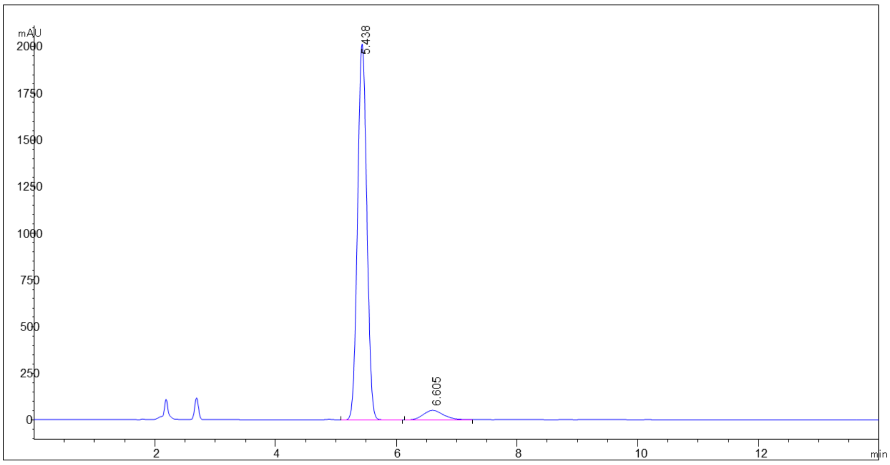
4faa
92% yield, 89% ee

Chiralpak AS-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



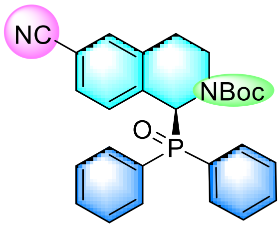
Peak	Retention time	Area	% Area
1	5.424	2543.6	50.294
2	6.579	2513.9	49.706

HPLC for racemic compound **4faa**



Peak	Retention time	Area	% Area
1	5.438	21480.3	94.655
2	6.605	1213.1	5.345

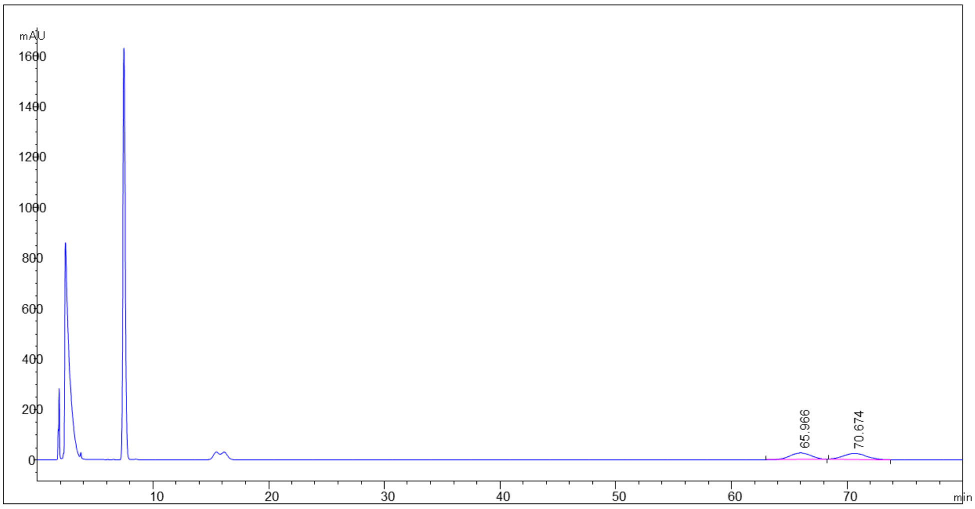
HPLC for pure enantioenriched compound **4faa**



4gaa

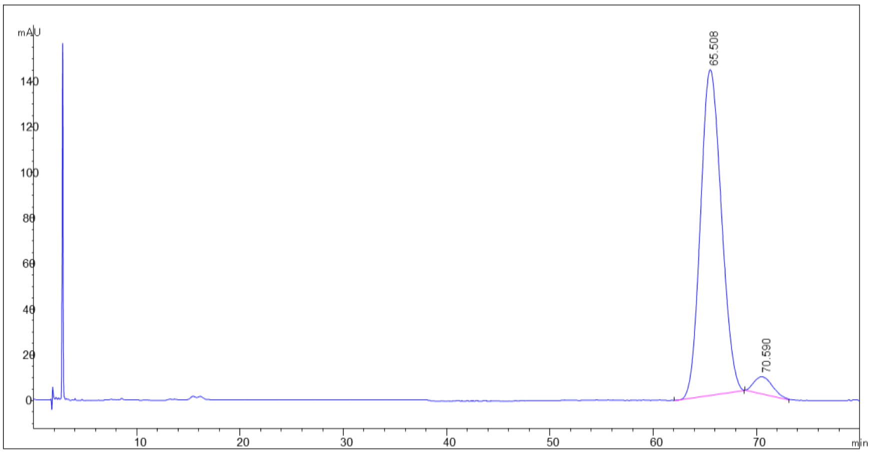
90% yield, 89% ee

Chiralpak OD-RH column, MeCN/H_2O= 68/32, flow rate 1.0 mL/min



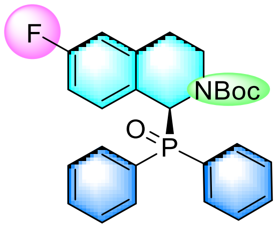
Peak	Retention time	Area	% Area
1	65.966	3356.2	50.324
2	70.674	3313	49.676

HPLC for racemic compound **4gaa**



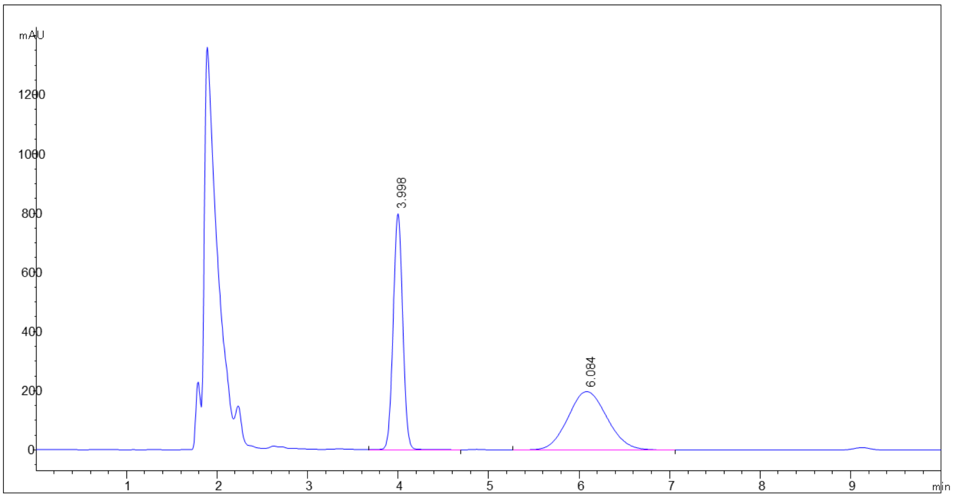
Peak	Retention time	Area	% Area
1	65.508	20089	95.498
2	70.590	947.1	4.502

HPLC for pure enantioenriched compound **4gaa**



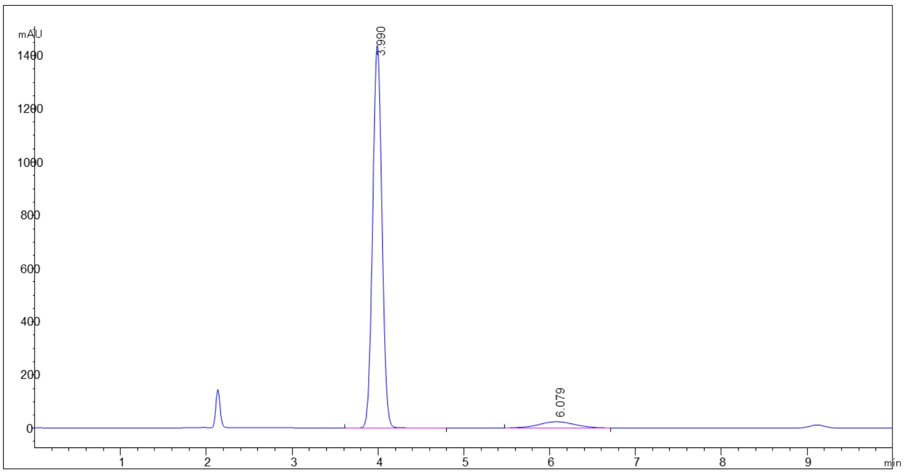
4haa
93% yield, 88% ee

Chiralpak OJ-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



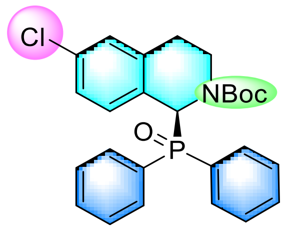
Peak	Retention time	Area	% Area
1	3.998	5871.5	49.727
2	6.084	5936.1	50.273

HPLC for racemic compound **4haa**



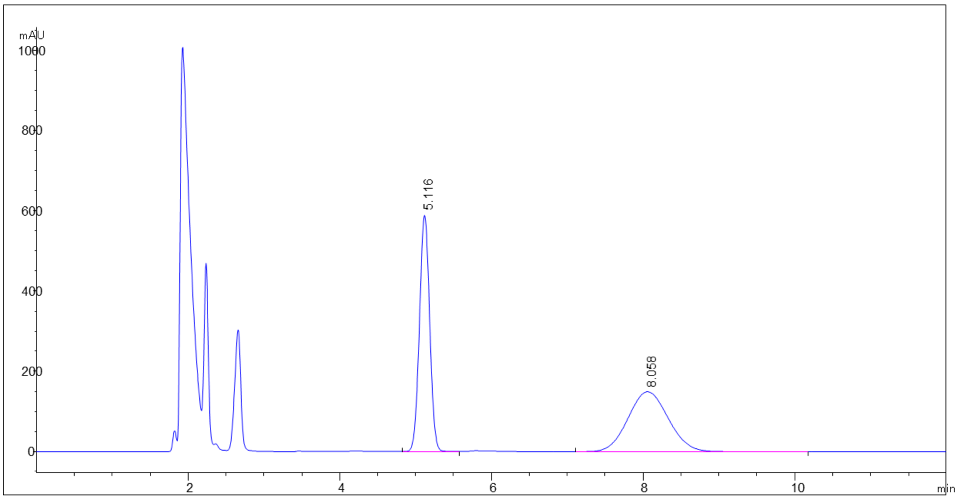
Peak	Retention time	Area	% Area
1	3.990	10861	93.942
2	6.079	700.4	6.058

HPLC for pure enantioenriched compound **4haa**



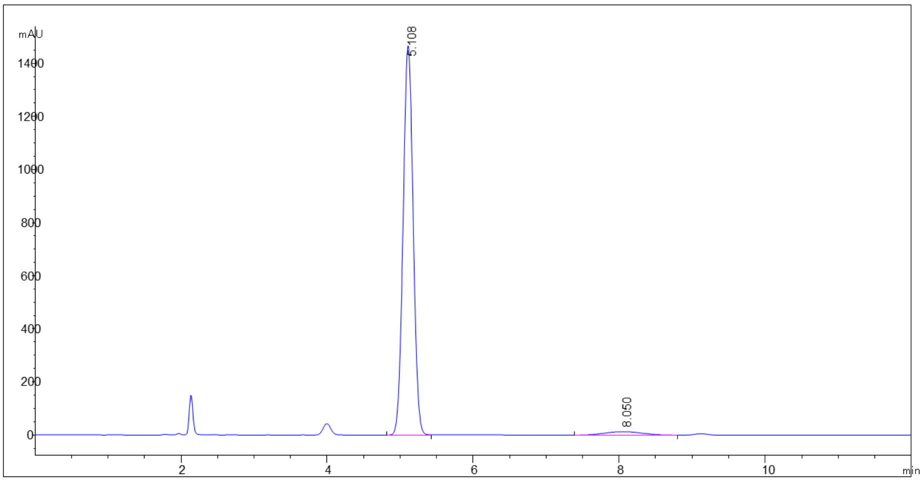
4iaa
91% yield, 93% ee

Chiralpak OJ-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



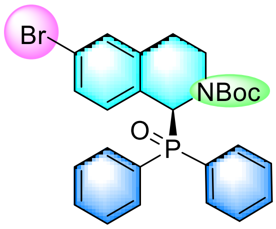
Peak	Retention time	Area	% Area
1	5.116	5525.7	49.819
2	8.058	5565.8	50.181

HPLC for racemic compound **4iaa**



Peak	Retention time	Area	% Area
1	5.108	14023.4	96.391
2	8.050	525.1	3.609

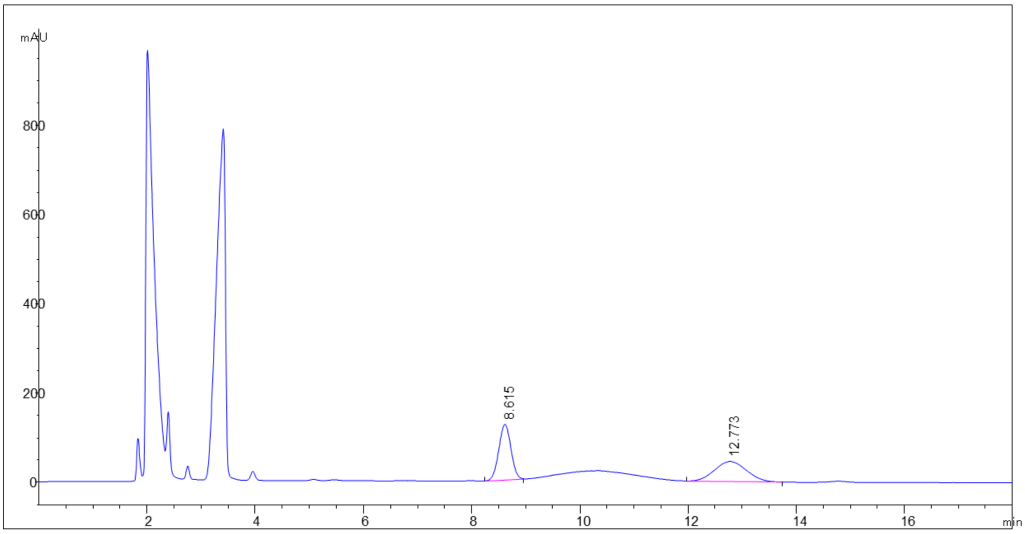
HPLC for pure enantioenriched compound **4iaa**



4jaa

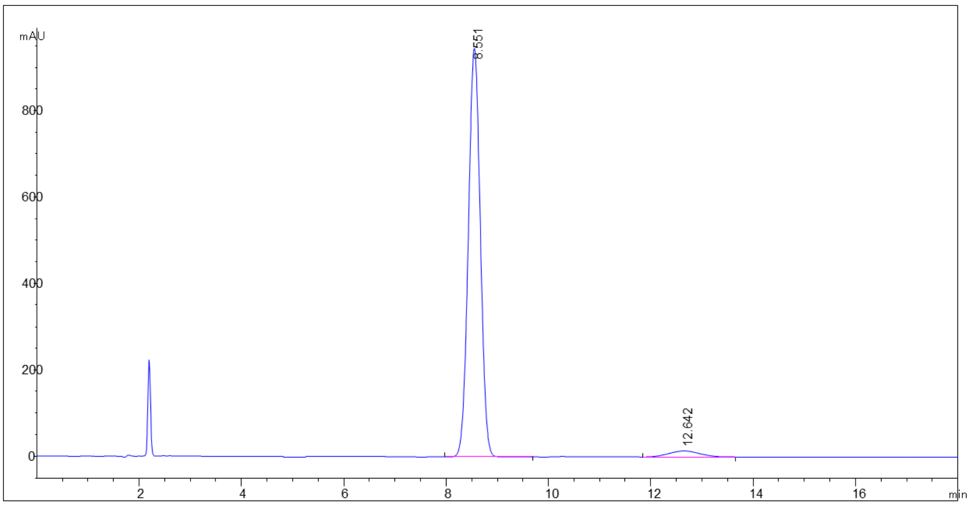
93% yield, 93% ee

Chiralpak OJ-RH column, MeCN/H_2O= 55/45, flow rate 1.0 mL/min



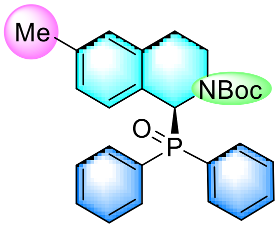
Peak	Retention time	Area	% Area
1	8.615	1962.8	51.130
2	12.773	1876	48.870

HPLC for racemic compound **4jaa**



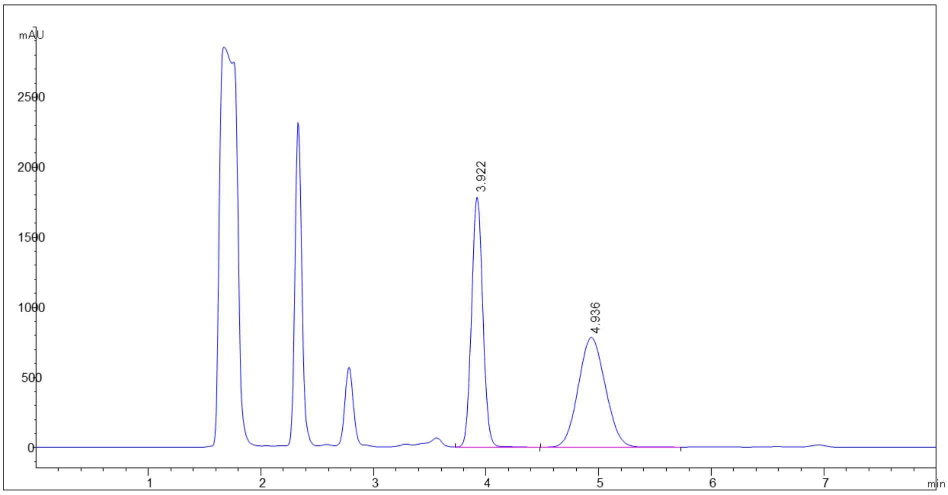
Peak	Retention time	Area	% Area
1	8.551	15352.6	96.254
2	12.642	594.2	3.746

HPLC for pure enantioenriched compound **4jaa**



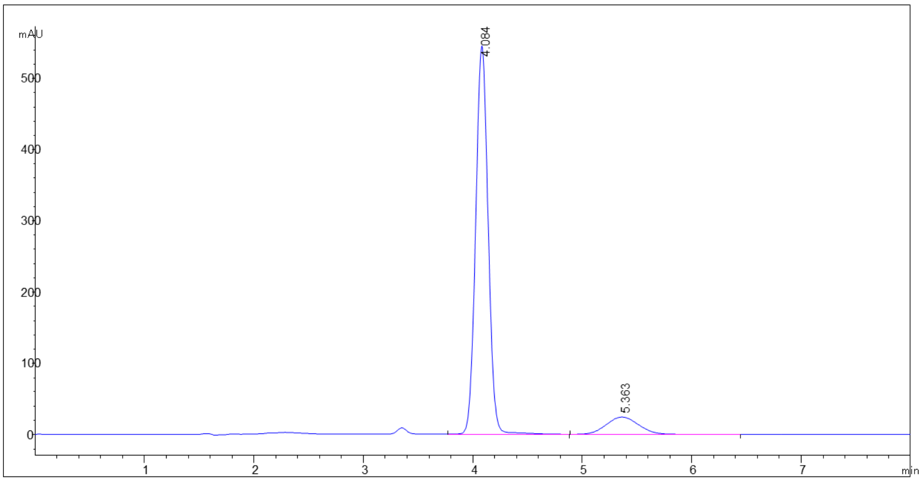
4kaa
99% yield, 79% ee

Chiralpak OJ-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



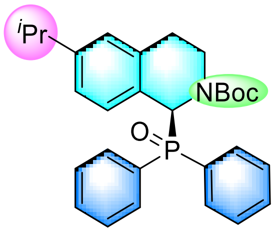
Peak	Retention time	Area	% Area
1	3.922	12405.7	48.708
2	4.936	13063.5	51.292

HPLC for racemic compound **4kaa**



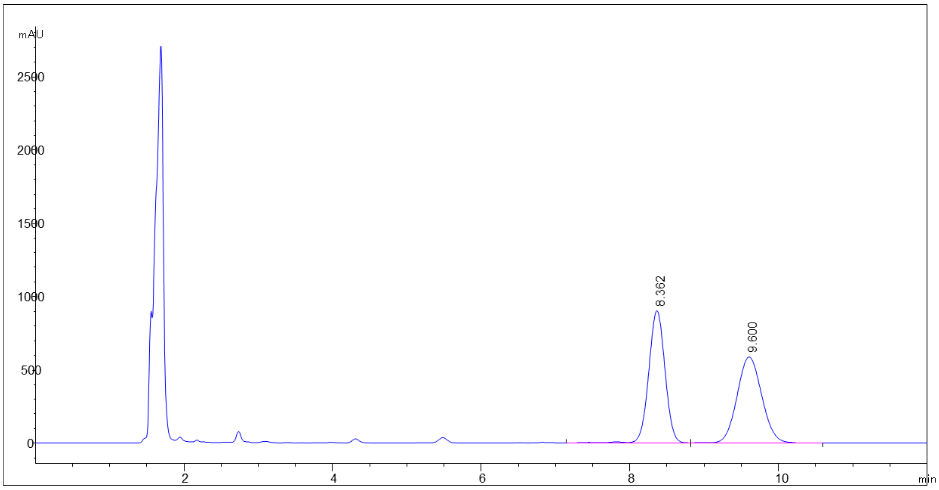
Peak	Retention time	Area	% Area
1	4.084	4302.5	89.534
2	5.363	502.9	10.466

HPLC for pure enantioenriched compound **4kaa**



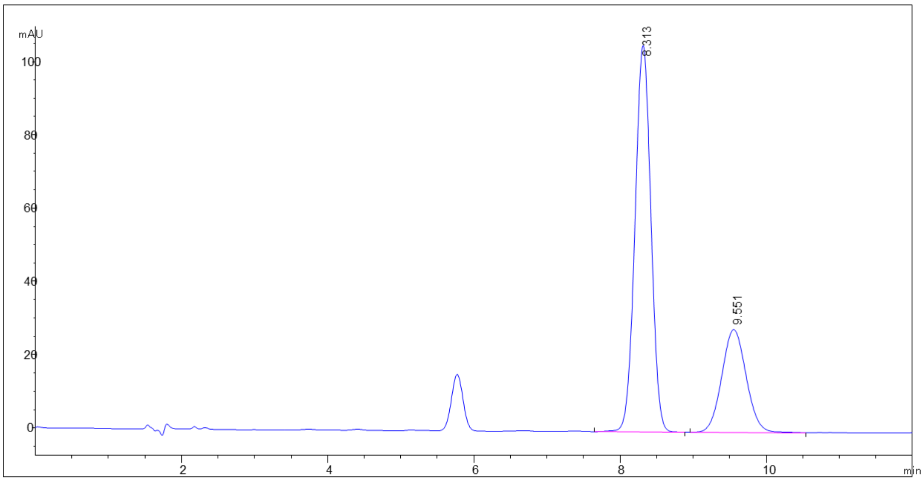
4laa
86% yield, 42% ee

Chiralpak OJ-RH column, MeCN/H_2O= 55/45, flow rate 1.0 mL/min



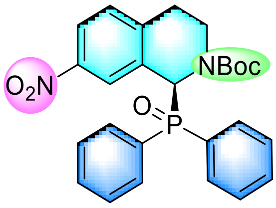
Peak	Retention time	Area	% Area
1	8.362	13706.4	50.382
2	9.600	13498.8	49.618

HPLC for racemic compound **4laa**



Peak	Retention time	Area	% Area
1	8.313	1975.5	71.086
2	9.551	649.8	28.914

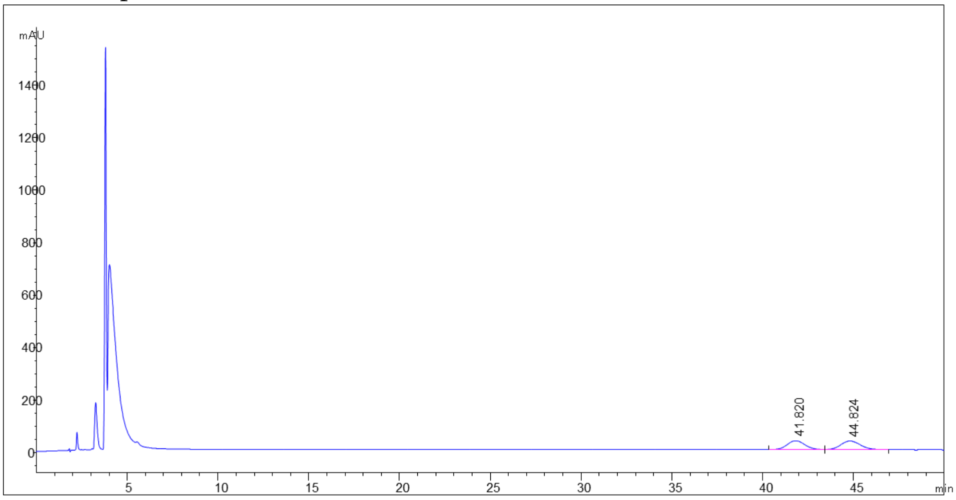
HPLC for pure enantioenriched compound **4laa**



4maa

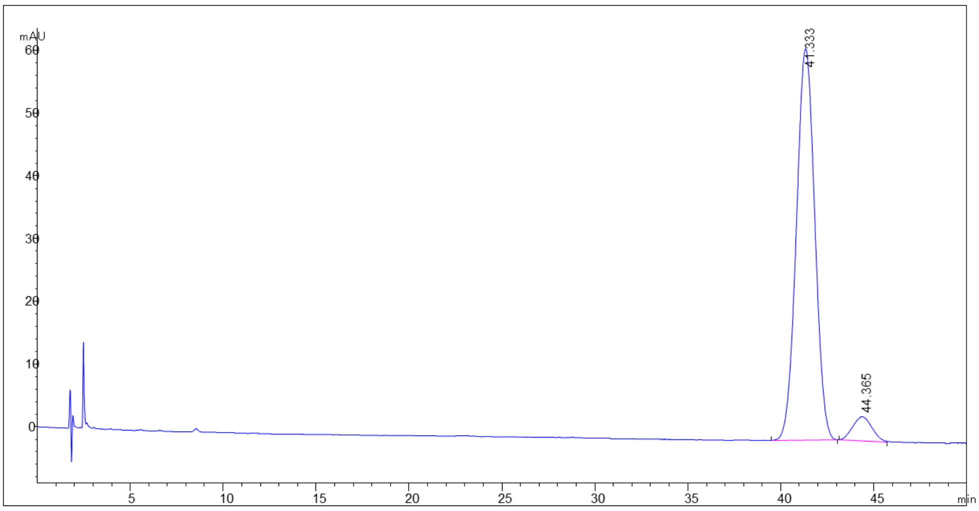
52% yield, 89% ee

Chiralpak OJ-RH column, MeCN/H_2O= 70/30, flow rate 1.0 mL/min



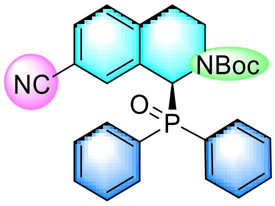
Peak	Retention time	Area	% Area
1	41.820	2387.3	50.096
2	44.824	2378.2	49.904

HPLC for racemic compound **4maa**



Peak	Retention time	Area	% Area
1	41.333	5262.7	94.503
2	44.365	361.2	5.497

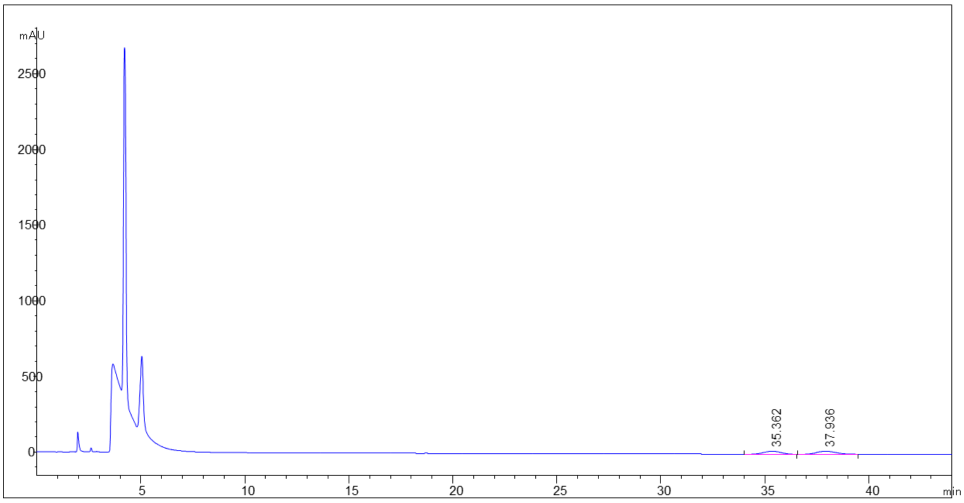
HPLC for pure enantioenriched compound **4maa**



4naa

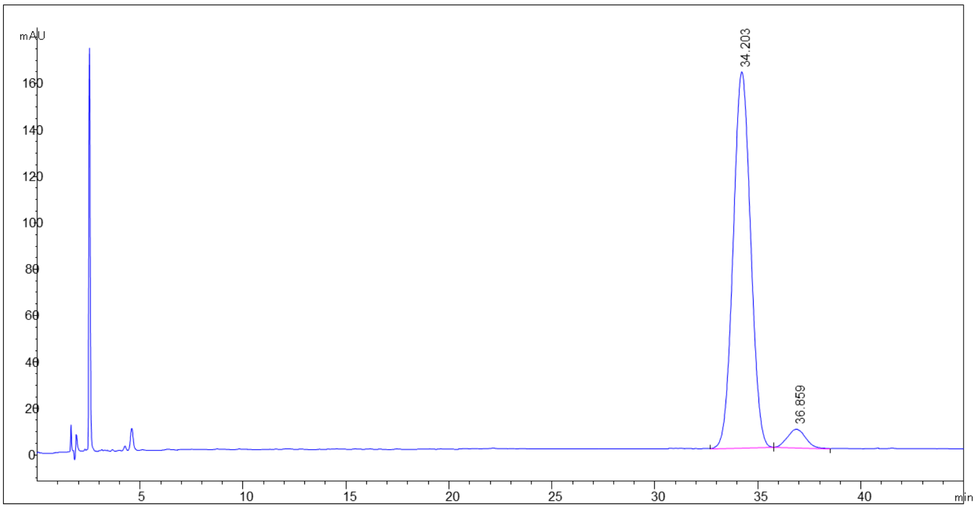
86% yield, 90% ee

Chiralpak OJ-RH column, MeCN/H_2O= 72/28, flow rate 1.0 mL/min



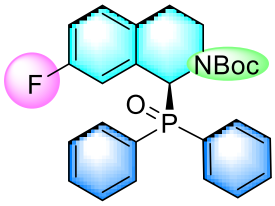
Peak	Retention time	Area	% Area
1	35.262	1305.4	49.409
2	37.936	1336.6	50.091

HPLC for racemic compound **4naa**



Peak	Retention time	Area	% Area
1	34.203	9554.1	95.044
2	36.859	498.2	4.956

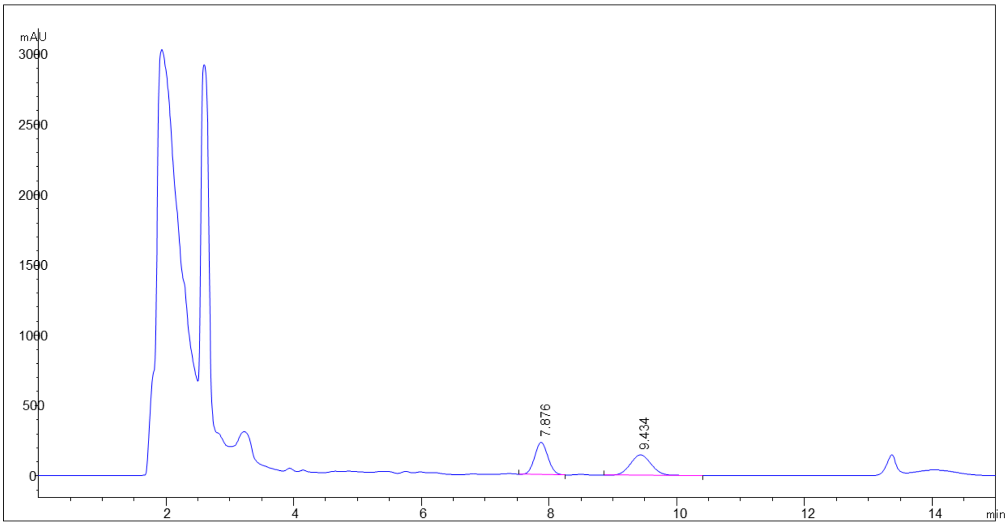
HPLC for pure enantioenriched compound **4naa**



4oaa

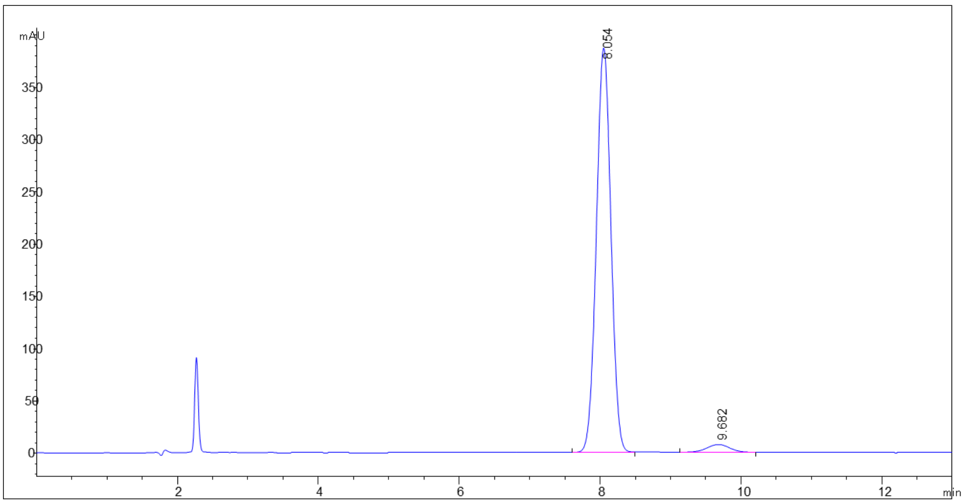
92% yield, 94% ee

Chiralpak OJ-RH column, MeCN/H_2O= 60/40, flow rate 1.0 mL/min



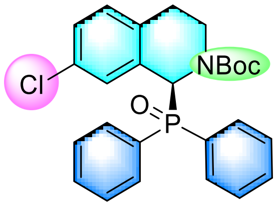
Peak	Retention time	Area	% Area
1	7.876	3337.6	50.083
2	9.434	3326.6	49.917

HPLC for racemic compound **4oaa**



Peak	Retention time	Area	% Area
1	8.054	5551.9	97.088
2	9.682	166.5	2.912

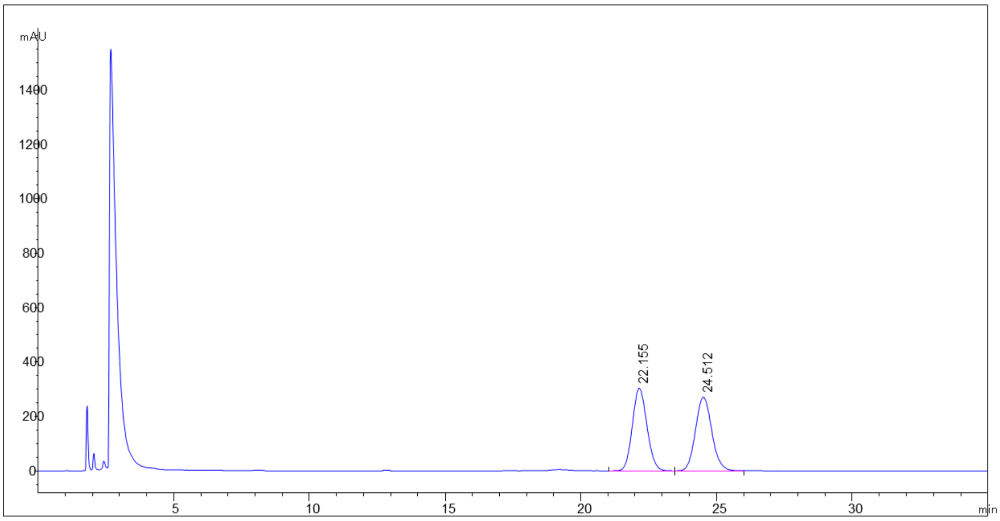
HPLC for pure enantioenriched compound **4oaa**



4paa

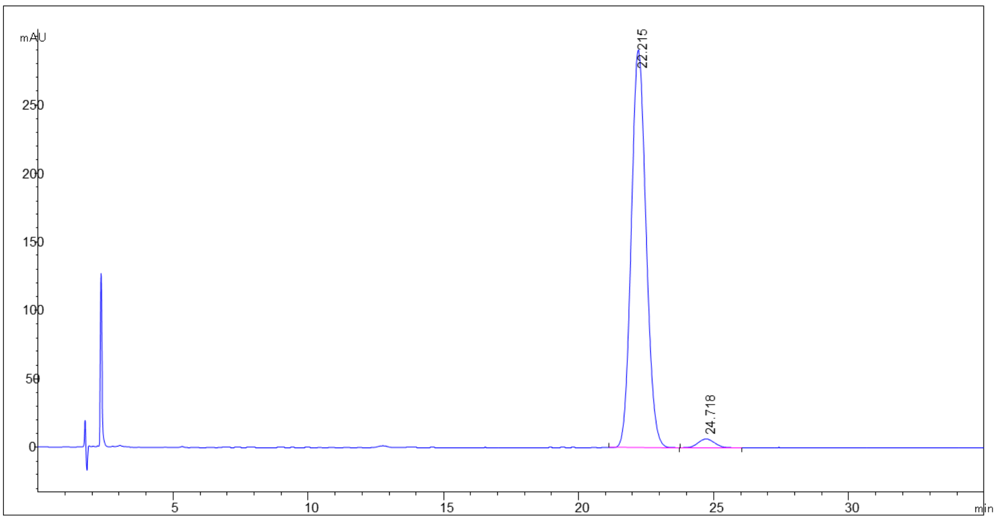
76% yield, 95% ee

Chiralpak OJ-RH column, MeCN/H_2O= 65/35, flow rate 1.0 mL/min



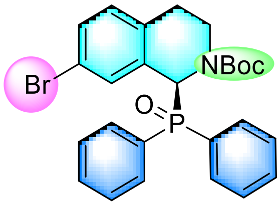
Peak	Retention time	Area	% Area
1	22.155	303.7	50.072
2	24.512	271.1	49.928

HPLC for racemic compound **4paa**



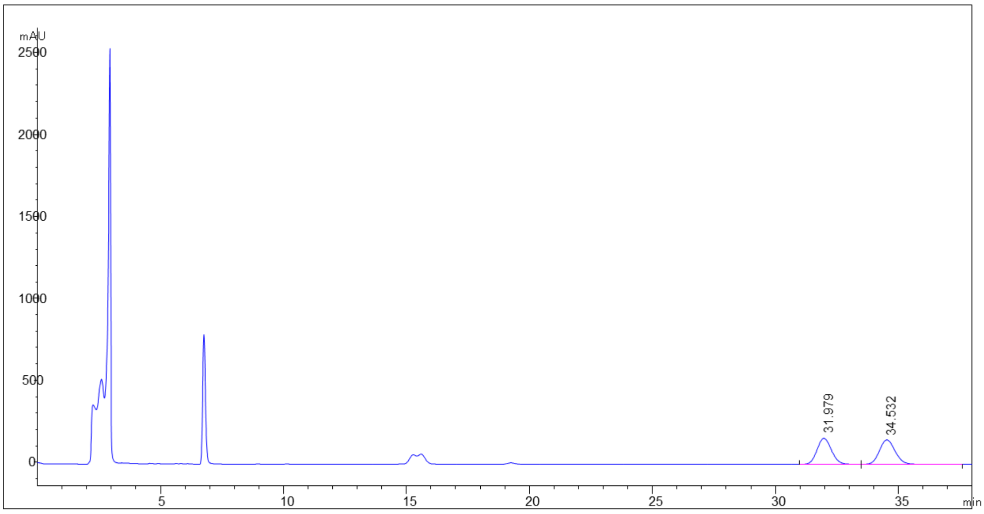
Peak	Retention time	Area	% Area
1	22.215	11017.5	97.543
2	24.718	277.6	2.457

HPLC for pure enantioenriched compound **4paa**



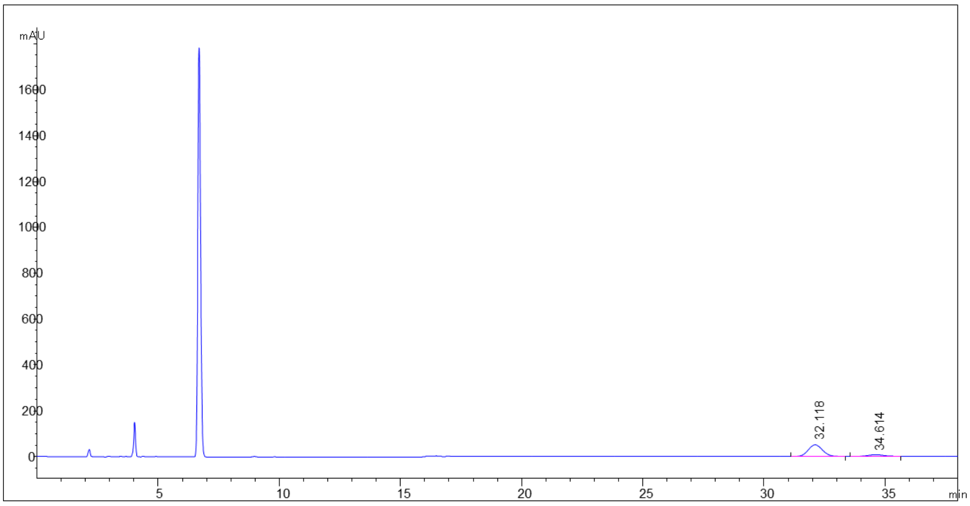
4qaa
56%yield, 76% ee

Chiralpak OD-RH-3um column, MeCN/H_2O= 65/35, flow rate 0.6 mL/min



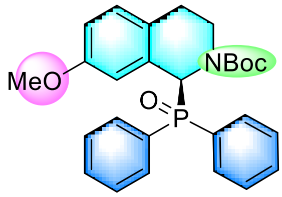
Peak	Retention time	Area	% Area
1	31.979	6644	49.917
2	34.532	6666.1	50.083

HPLC for racemic compound **4qaa**



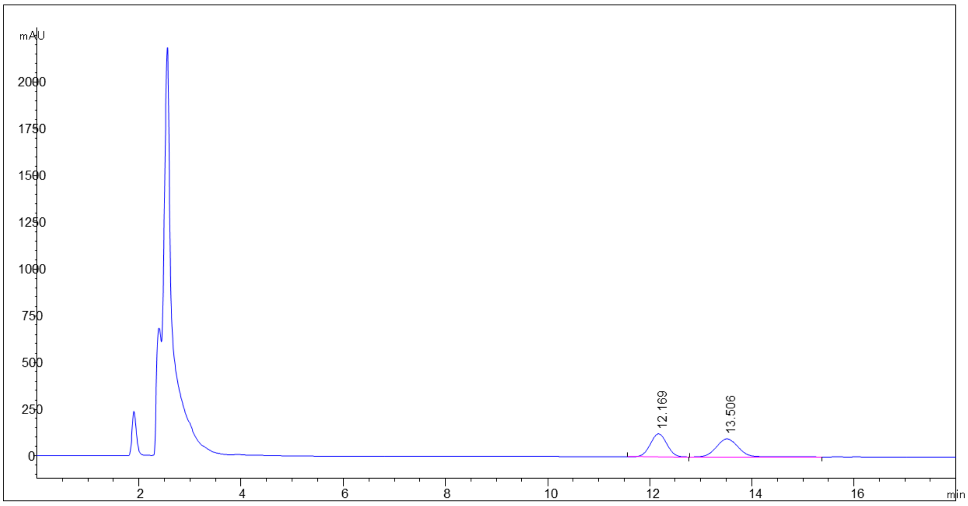
Peak	Retention time	Area	% Area
1	32.118	2160	87.846
2	34.614	298.8	12.154

HPLC for pure enantioenriched compound **4qaa**



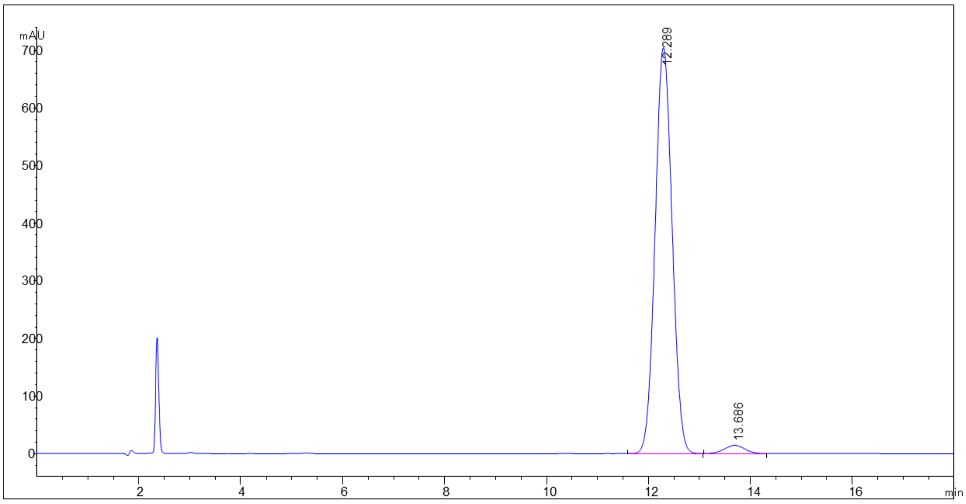
4raa
82% yield, 95% ee

Chiralpak OJ-RH column, MeCN/H_2O= 65/35, flow rate 1.0 mL/min



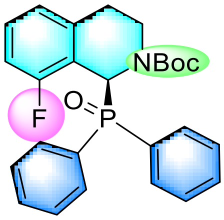
Peak	Retention time	Area	% Area
1	12.169	2814	49.263
2	13.506	2898.2	50.737

HPLC for racemic compound **4raa**



Peak	Retention time	Area	% Area
1	12.289	16291.4	97.682
2	13.686	386.7	2.318

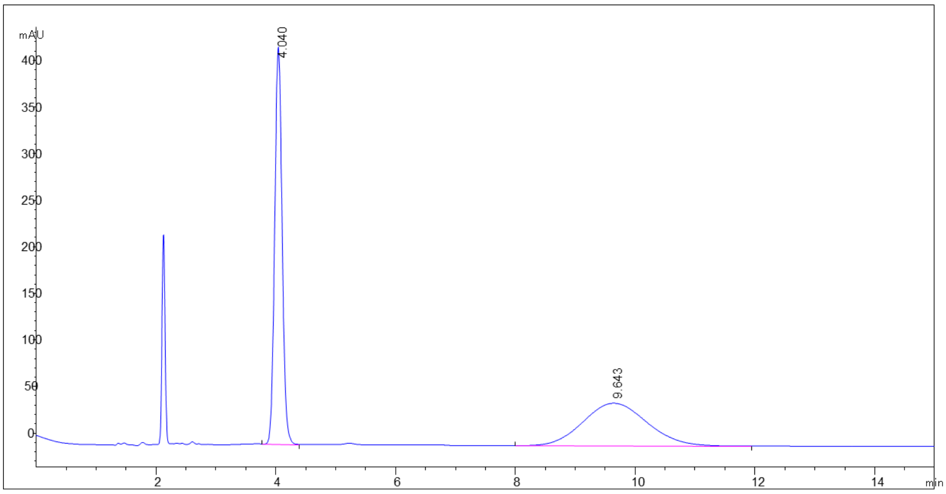
HPLC for pure enantioenriched compound **4raa**



4saa

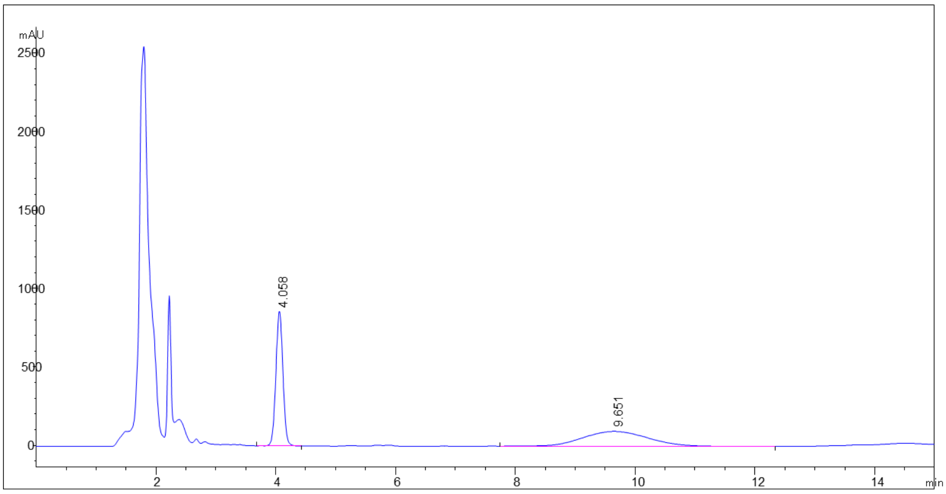
53% yield, 3% ee

Chiralpak AS-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



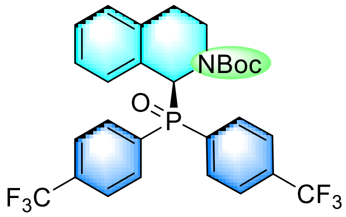
Peak	Retention time	Area	% Area
1	4.040	7044.6	49.645
2	9.643	7145.5	50.355

HPLC for racemic compound **4saa**



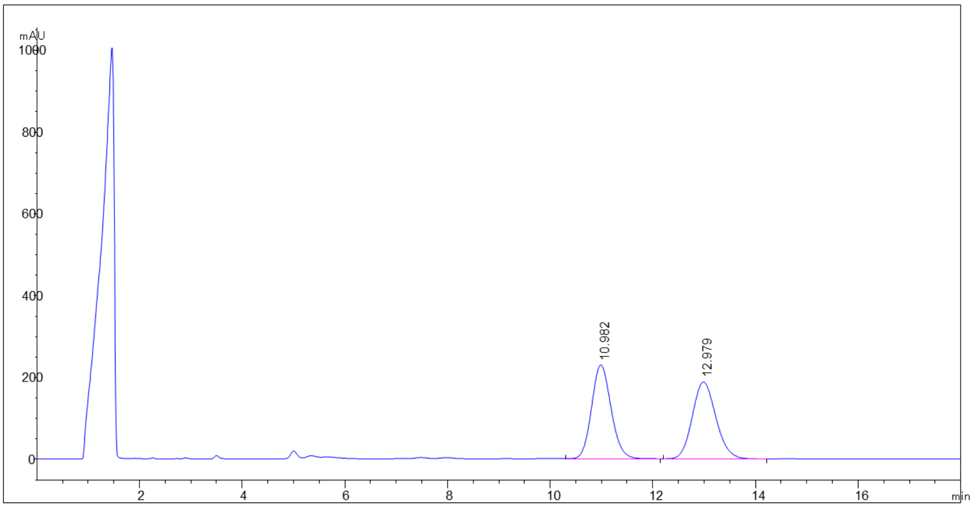
Peak	Retention time	Area	% Area
1	4.058	3679	51.674
2	9.651	3440.6	48.326

HPLC for pure enantioenriched compound **4saa**



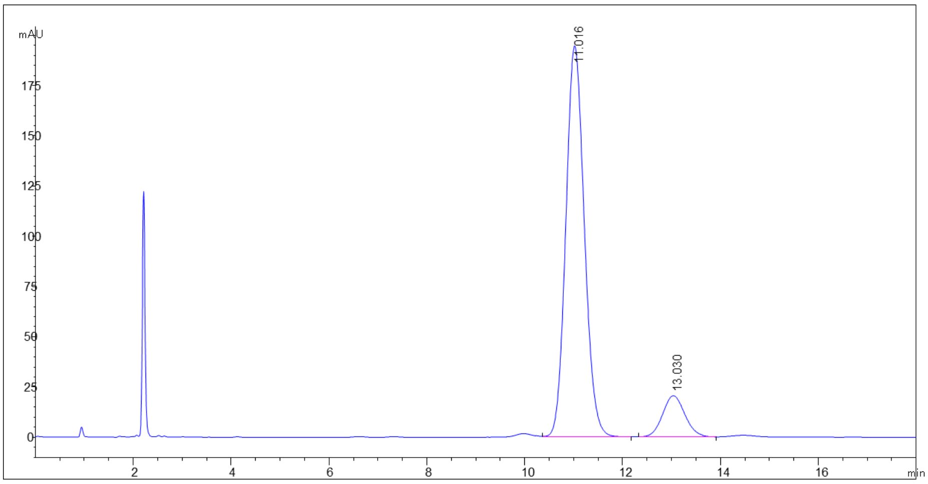
4**aba,** 92% yield, 79% *ee*

Chiralpak OD-RH column, MeCN/H_2O= 45/55, flow rate 1.0 mL/min



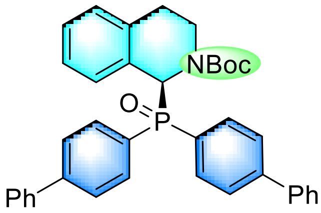
Peak	Retention time	Area	% Area
1	10.982	6085.4	50.166
2	12.979	6045.3	49.834

HPLC for racemic compound **4aba**



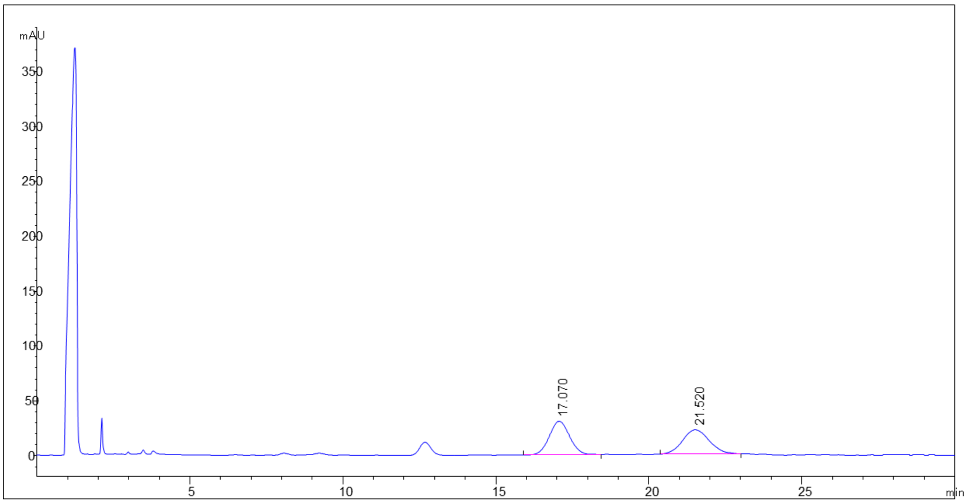
Peak	Retention time	Area	% Area
1	11.016	5530.4	89.587
2	13.030	642.8	10.413

HPLC for pure enantioenriched compound **4aba**



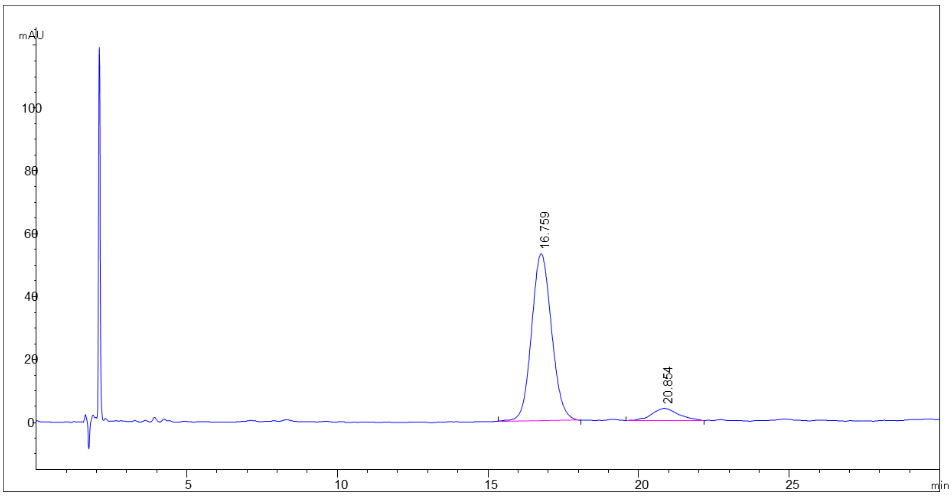
4aca, 88% yield, 82% ee

Chiralpak OD-RH column, MeCN/H_2O= 35/65, flow rate 1.0 mL/min



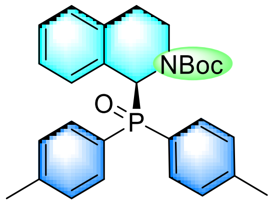
Peak	Retention time	Area	% Area
1	17.070	1419.9	50.945
2	21.520	1367.2	49.055

HPLC for racemic compound **4aca**



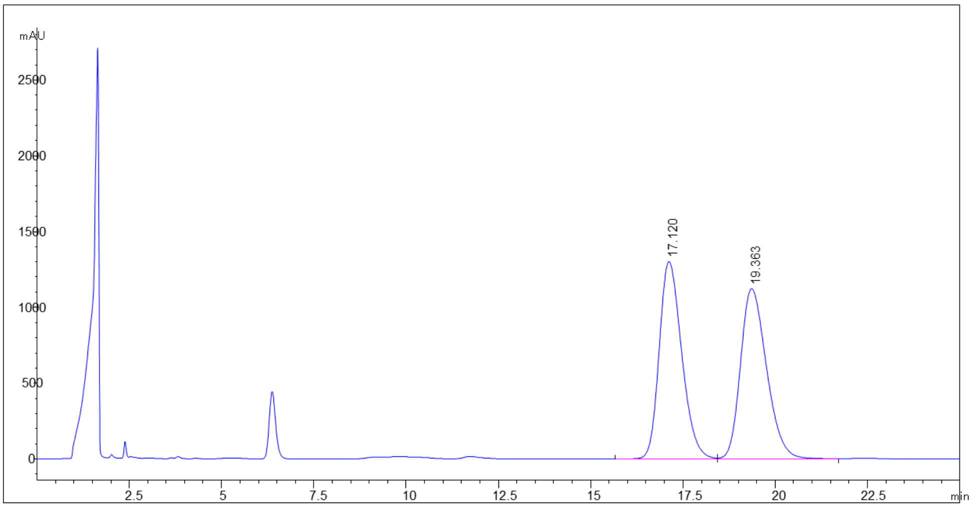
Peak	Retention time	Area	% Area
1	16.759	2451.4	90.986
2	20.854	242.9	9.014

HPLC for pure enantioenriched compound **4aca**



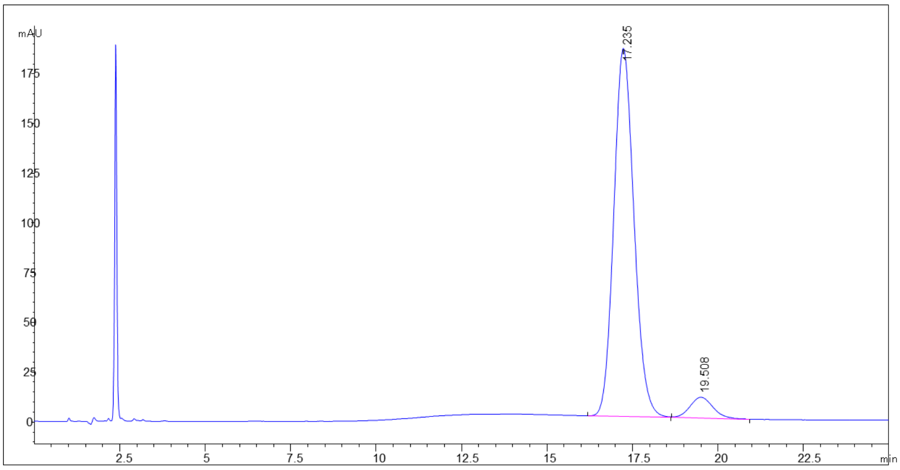
4ada, 85% yield, 88% ee

Chiralpak OD-RH column, MeCN/H_2O= 55/45, flow rate 1.0 mL/min



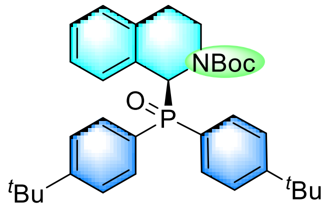
Peak	Retention time	Area	% Area
1	17.120	55243.3	50.063
2	19.363	55104.2	49.937

HPLC for racemic compound **4ada**



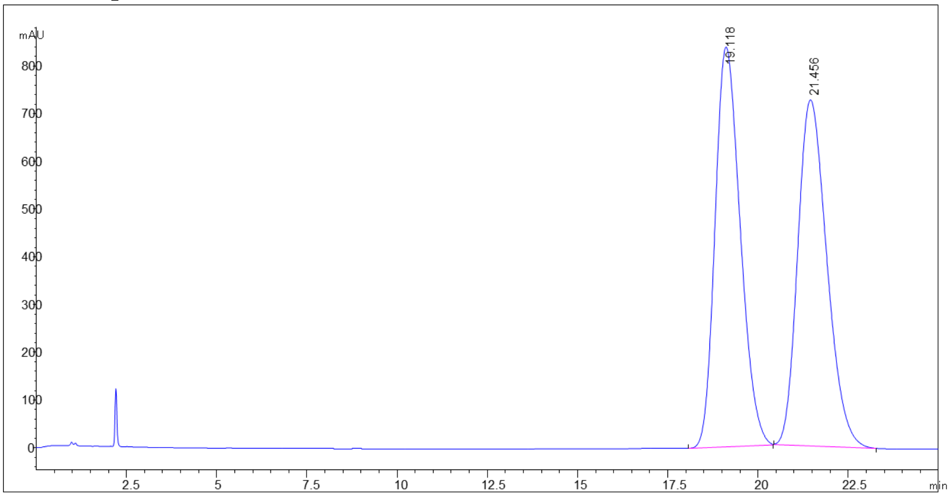
Peak	Retention time	Area	% Area
1	17.235	7610.8	94.179
2	19.508	470.4	5.821

HPLC for pure enantioenriched compound **4ada**



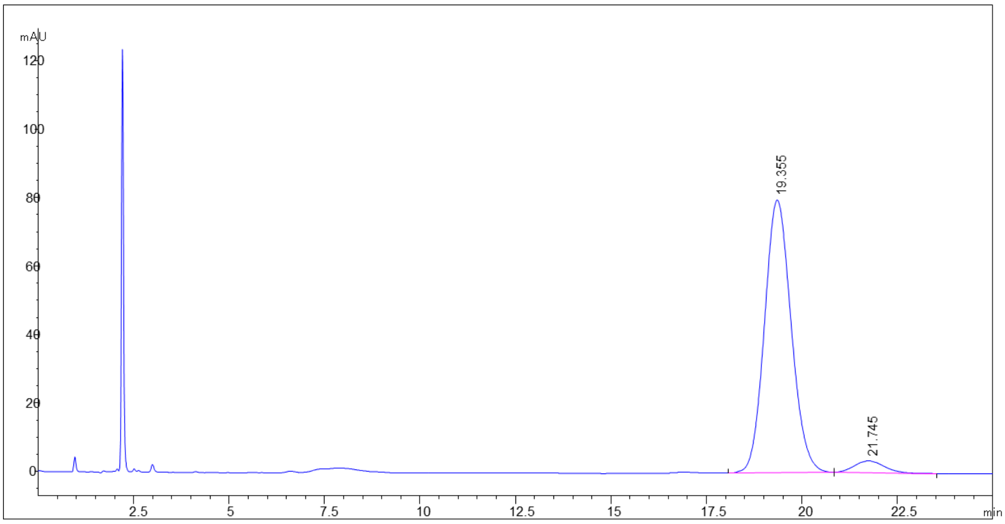
4a**ea**, 88% yield, 91% ee

Chiralpak OD-RH column, MeCN/H_2O= 45/55, flow rate 1.0 mL/min



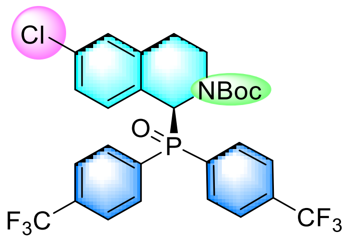
Peak	Retention time	Area	% Area
1	19.118	40659.4	50.054
2	21.456	40571.7	49.946

HPLC for racemic compound **4aea**



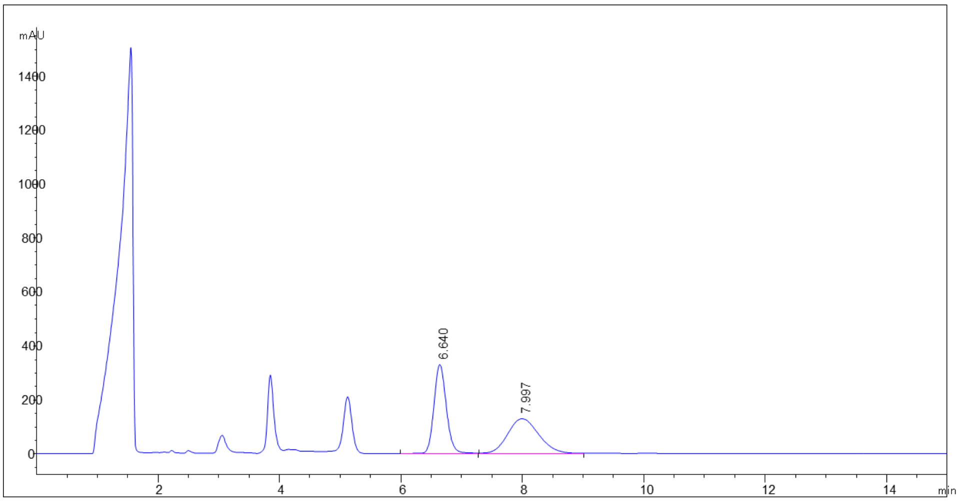
Peak	Retention time	Area	% Area
1	19.355	3861.5	95.220
2	21.745	193.9	4.780

HPLC for pure enantioenriched compound **4aea**



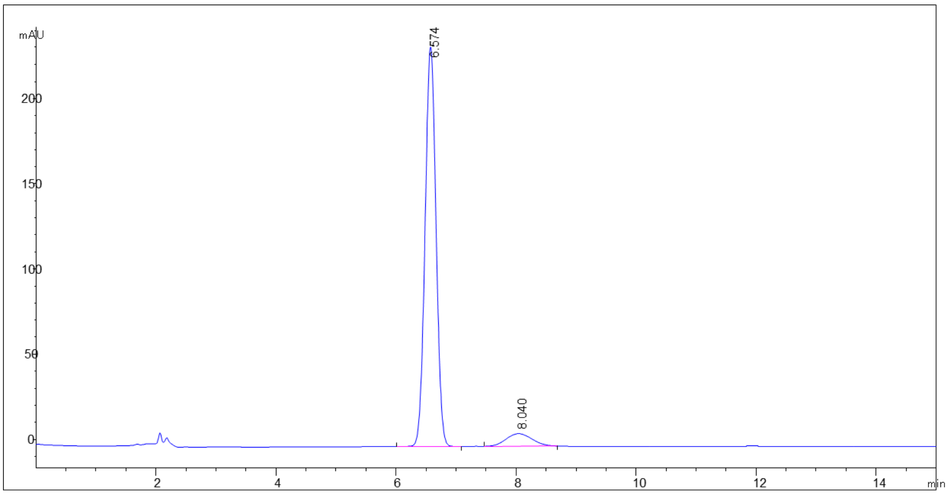
4iba, 98% yield, 86% *ee*

Chiralpak OJ-RH column, MeCN/H_2O= 45/55, flow rate 1.0 mL/min



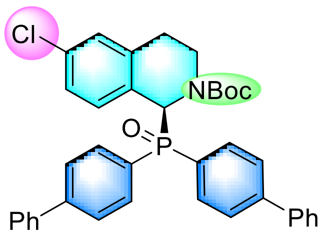
Peak	Retention time	Area	% Area
1	6.640	4644.6	50.507
2	7.997	4551.2	49.493

HPLC for racemic compound **4iba**



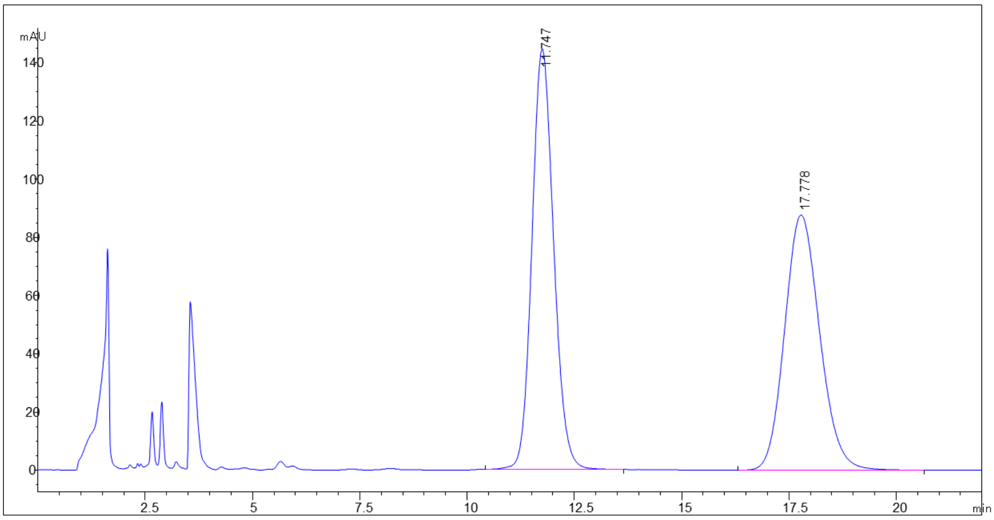
Peak	Retention time	Area	% Area
1	6.574	2976.4	92.955
2	8.040	225.6	7.045

HPLC for pure enantioenriched compound **4iba**



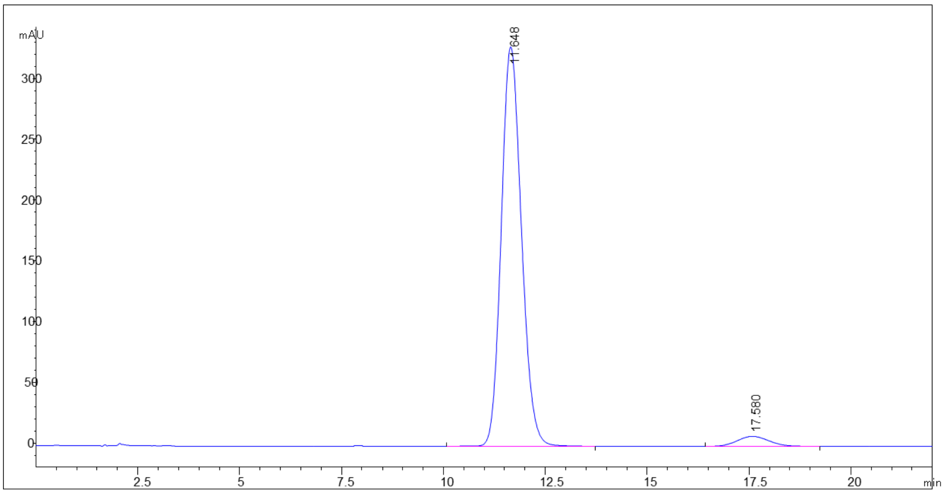
4ica, 93% yield, 93% *ee*

Chiralpak OD-RH column, MeCN/H_2O= 25/75, flow rate 1.0 mL/min



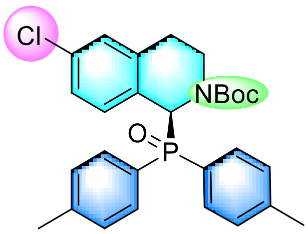
Peak	Retention time	Area	% Area
1	11.747	5080	50.372
2	17.778	5005	49.628

HPLC for racemic compound **4ica**



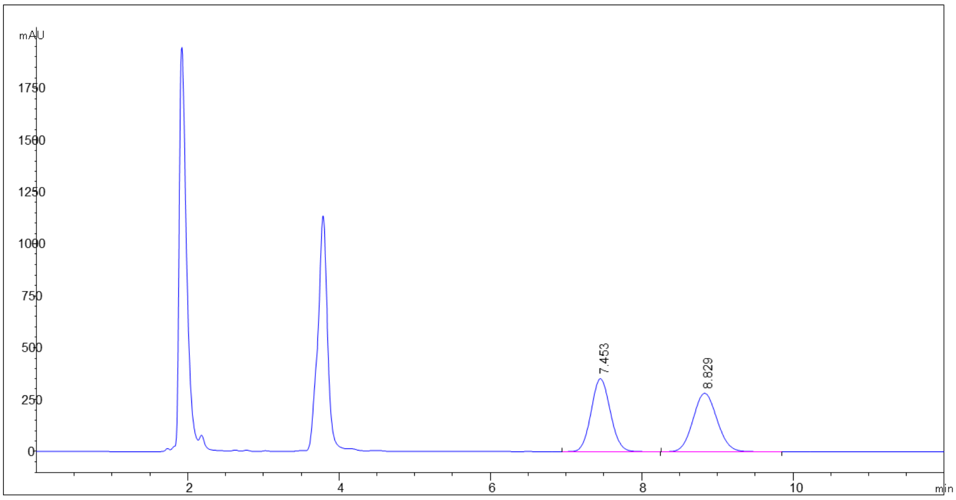
Peak	Retention time	Area	% Area
1	11.648	11304.6	96.290
2	17.580	435.6	3.710

HPLC for pure enantioenriched compound **4ica**



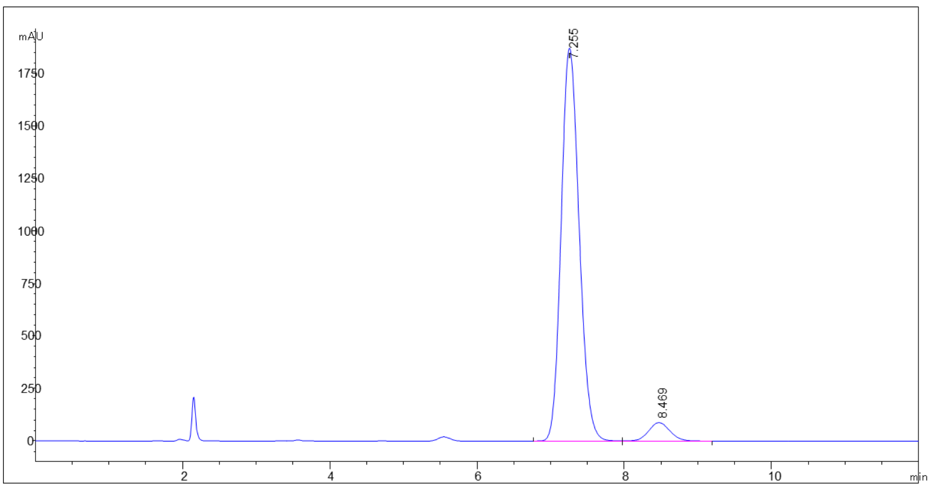
4ida, 83% yield, 90% *ee*

Chiralpak OD-RH column, MeCN/H2O= 40/60, flow rate 1.0 mL/min



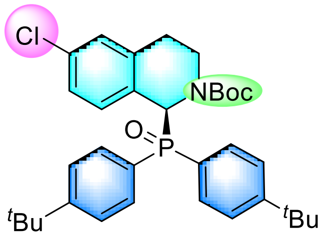
Peak	Retention time	Area	% Area
1	7.453	6211.8	49.987
2	8.829	6215	50.013

HPLC for racemic compound **4ida**



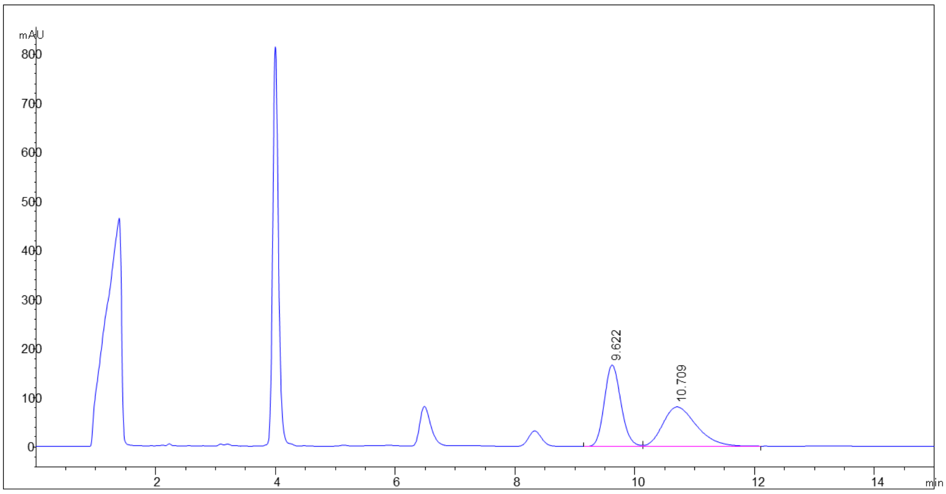
Peak	Retention time	Area	% Area
1	7.255	31719.9	94.781
2	8.469	1746.6	5.219

HPLC for pure enantioenriched compound **4ida**



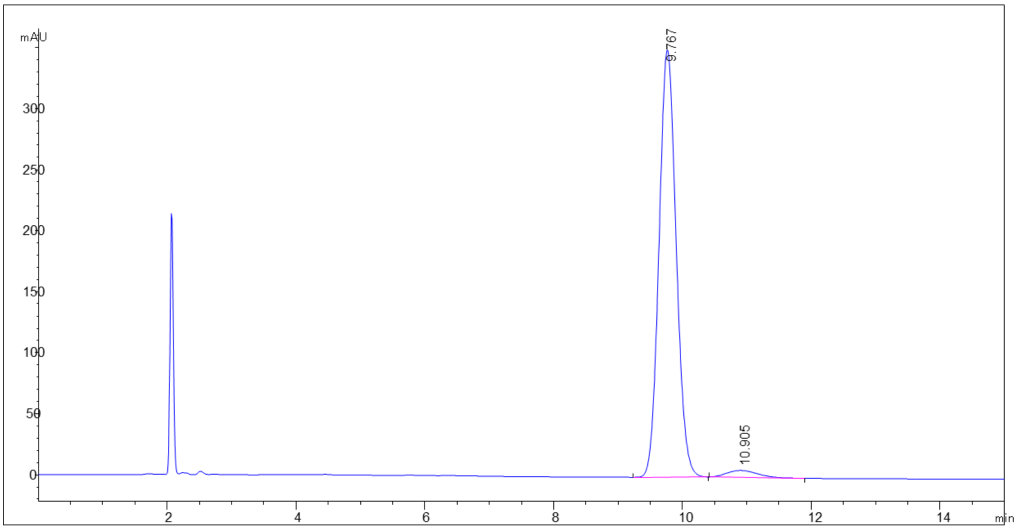
4iea, 85% yield, 95% *ee*

Chiralpak OJ-RH column, MeCN/H_2O= 45/55, flow rate 1.0 mL/min



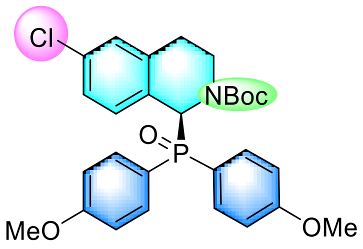
Peak	Retention time	Area	% Area
1	9.622	3193.2	50.211
2	10.709	3166.3	49.789

HPLC for racemic compound **4iea**



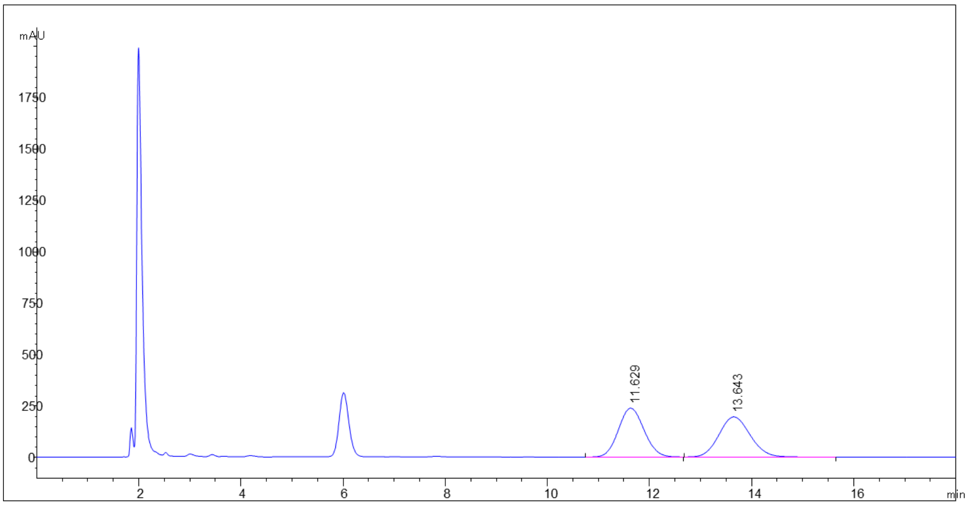
Peak	Retention time	Area	% Area
1	9.767	6472.1	97.398
2	10.905	173.9	2.602

HPLC for pure enantioenriched compound **4iea**



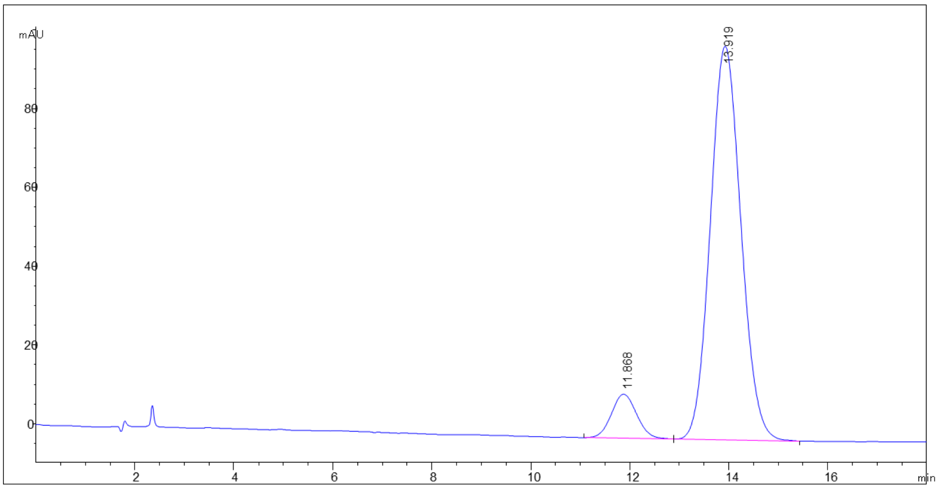
4ifa, 80% yield, 83% *ee*

Chiralpak AS-RH column, MeCN/H_2O= 55/45, flow rate 1.0 mL/min



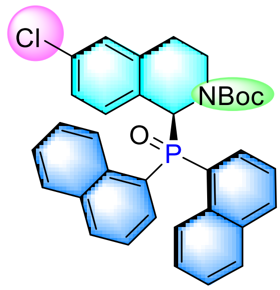
Peak	Retention time	Area	% Area
1	11.629	8360.8	49.931
2	13.643	8363.8	50.069

HPLC for racemic compound **4ifa**



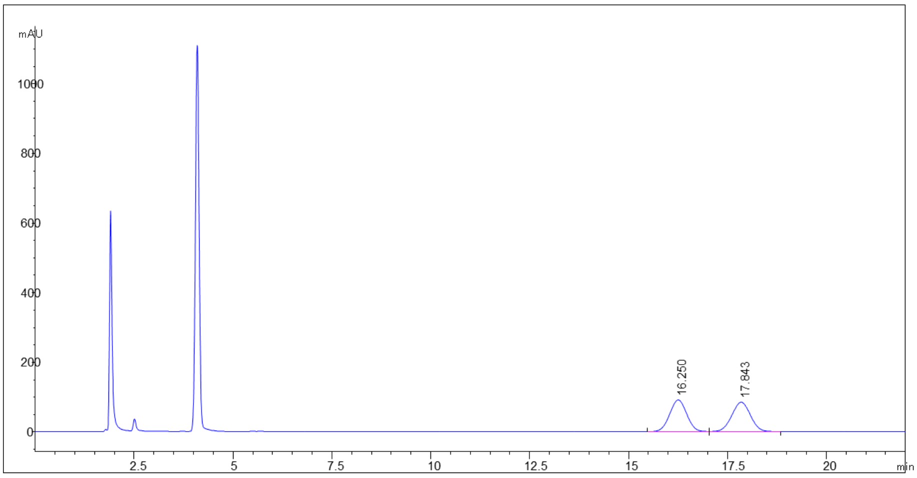
Peak	Retention time	Area	% Area
1	11.686	397	8.467
2	13.919	4292.2	91.533

HPLC for pure enantioenriched compound **4ifa**



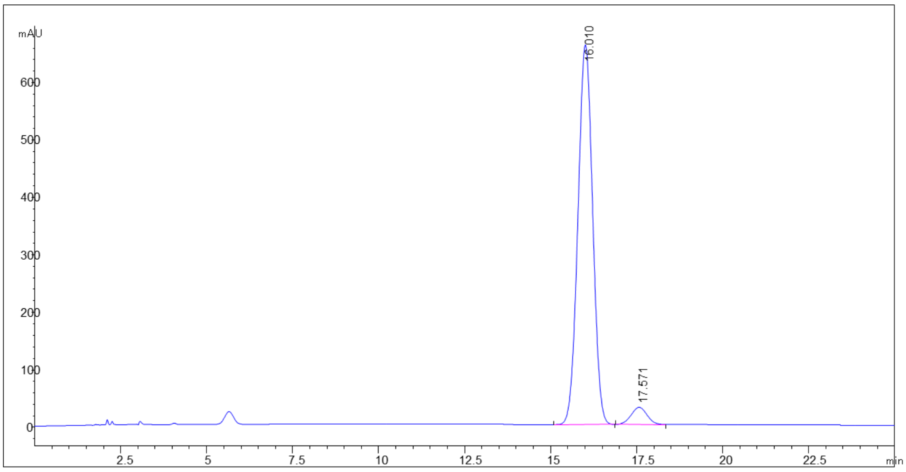
4iga, 80% yield, 91% *ee*

Chiralpak OJ-RH column, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



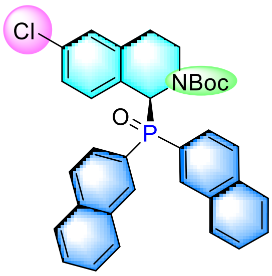
Peak	Retention time	Area	% Area
1	16.250	2754.7	50.006
2	17.751	2754	40.994

HPLC for racemic compound **4iga**



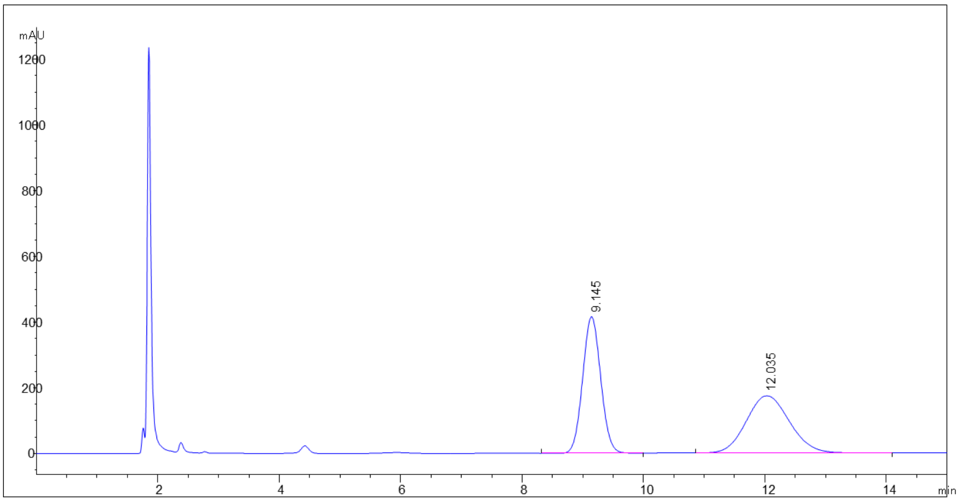
Peak	Retention time	Area	% Area
1	16.010	19623.5	95.343
2	17.778	958.4	4.657

HPLC for pure enantioenriched compound **4iea**



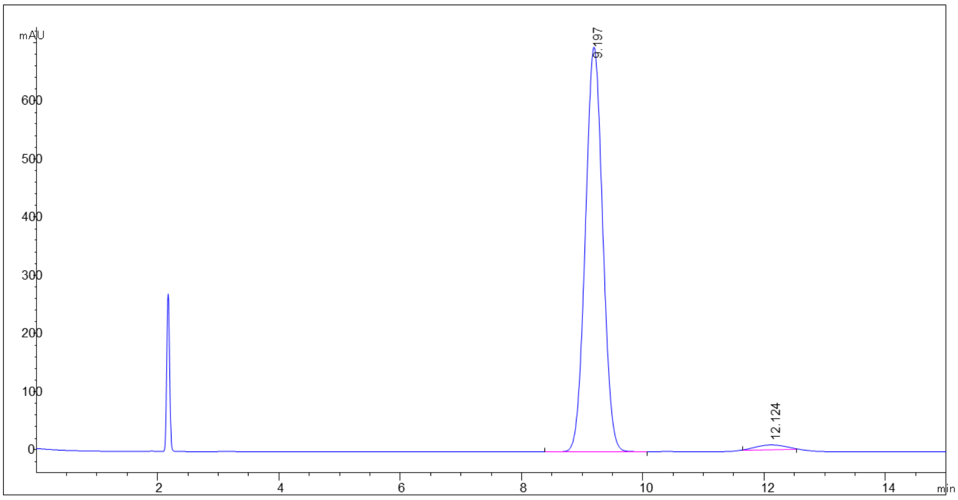
4iha, 98% yield, 96% *ee*

Chiralpak OJ-RH column, MeCN/H_2O= 45/55, flow rate 1.0 mL/min



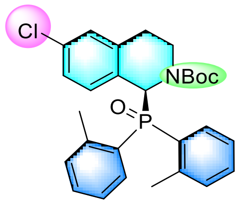
Peak	Retention time	Area	% Area
1	9.145	8614.4	49.892
2	12.035	8651.9	50.108

HPLC for racemic compound **4iha**



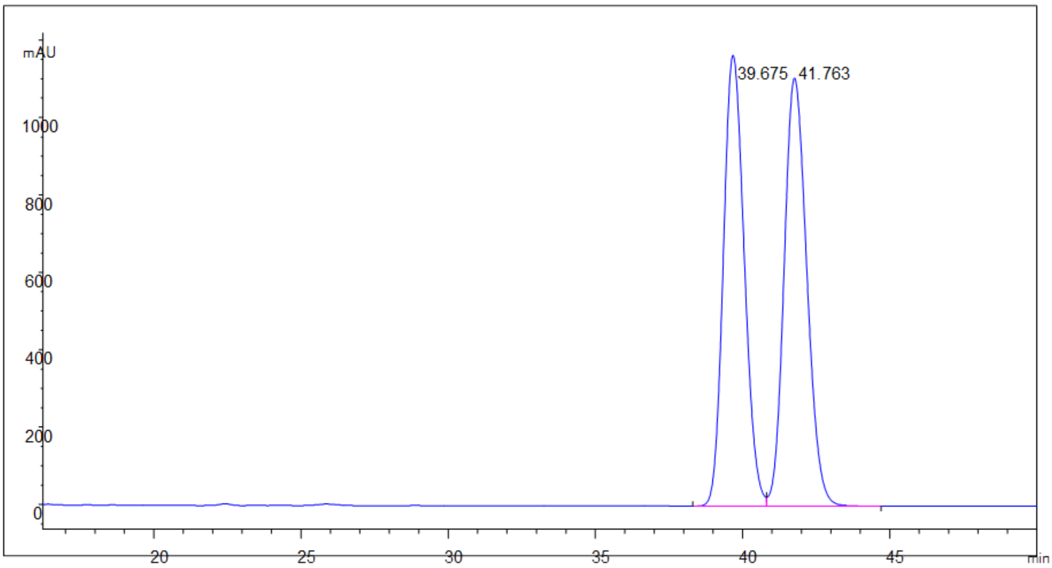
Peak	Retention time	Area	% Area
1	9.197	13814.8	98.193
2	12.124	254.3	1.807

HPLC for pure enantioenriched compound **4iha**



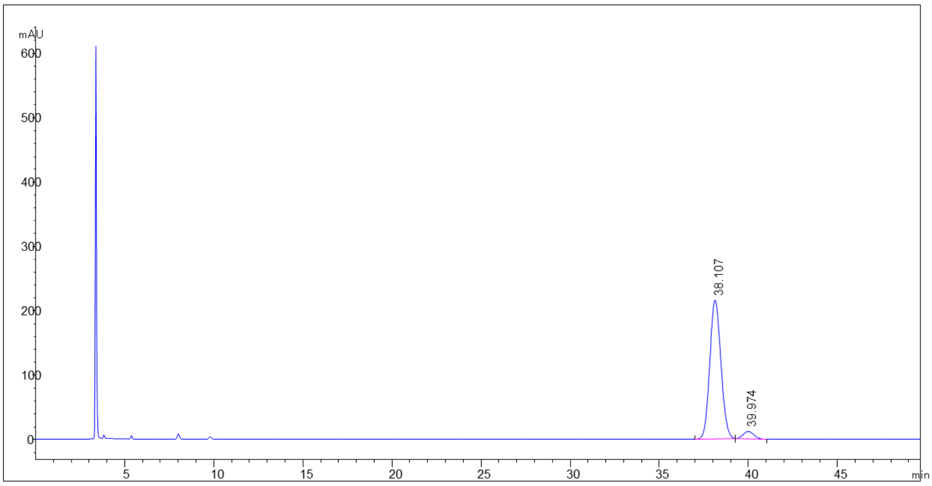
4iia, 88% yield, 90% *ee*

Chiralpak OD-RH-3um, CH_3CN/H_2O = 50/50 v/v, flow rate 0.6 mL/min



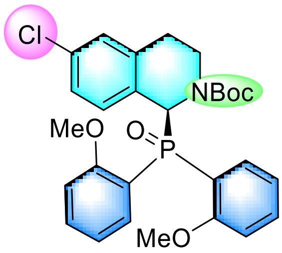
Peak	Retention time	Area	% Area
1	39.675	57449	49.197
2	41.763	59324	50.803

HPLC for racemic compound **4iia**



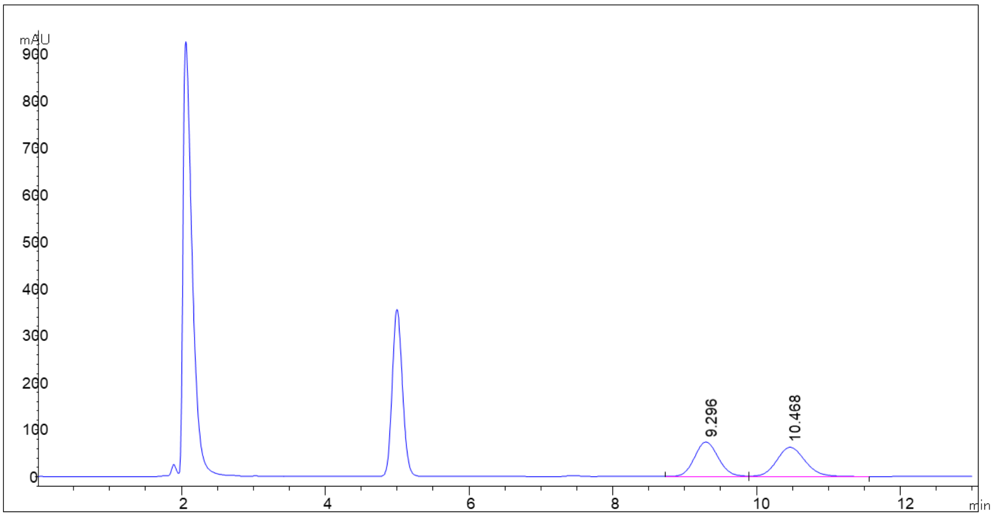
Peak	Retention time	Area	% Area
1	38.107	9399.9	95.084
2	39.974	486	4.916

HPLC for pure enantioenriched compound **4iia**



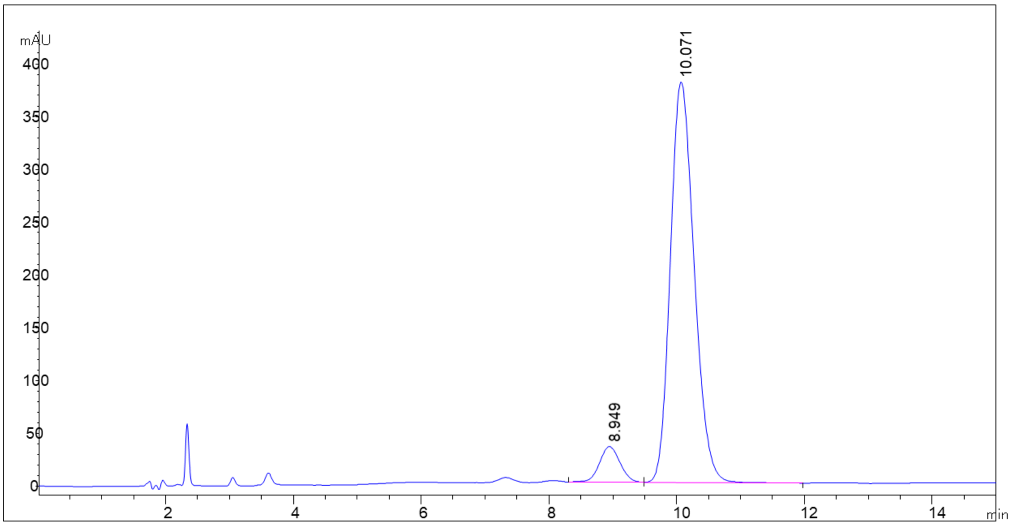
4ija, 78% yield, 86% ee

Chiralpak OX-RH column, MeCN/H_2O= 35/65, flow rate 1.0 mL/min



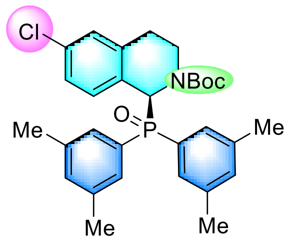
Peak	Ret. Time	Area	Area %
1	9.296	1675.4	49.145
2	10.468	1733.7	50.855

HPLC for racemic compound **4ija**



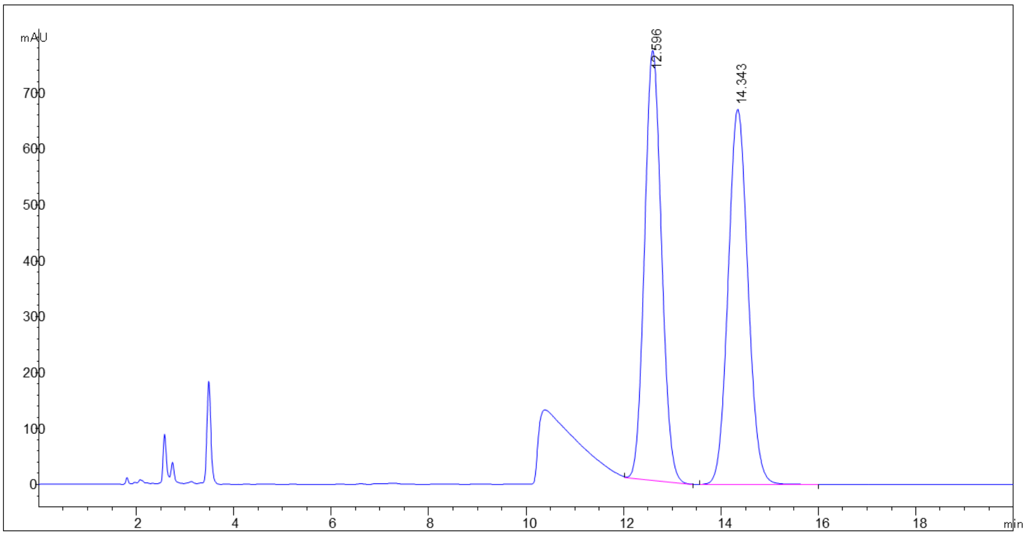
Peak	Ret. Time	Area	Area %
1	8.949	755	7.122
2	10.071	9846.8	92.878

HPLC for pure enantioenriched compound **4ija**



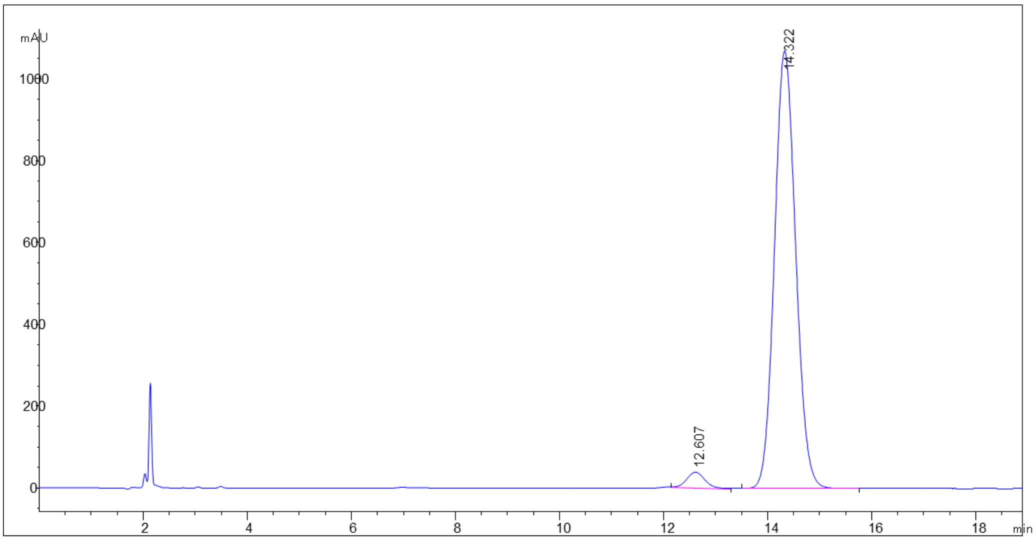
3ika, 85% yield, 94% *ee*

Chiralpak OX-RH column, MeCN/H_2O= 35/65, flow rate 1.0 mL/min



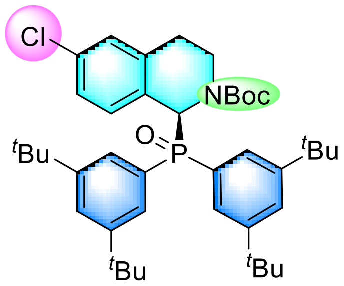
Peak	Retention time	Area	% Area
1	12.596	18604.8	49.531
2	14.343	18957.4	50.469

HPLC for racemic compound **4ika**



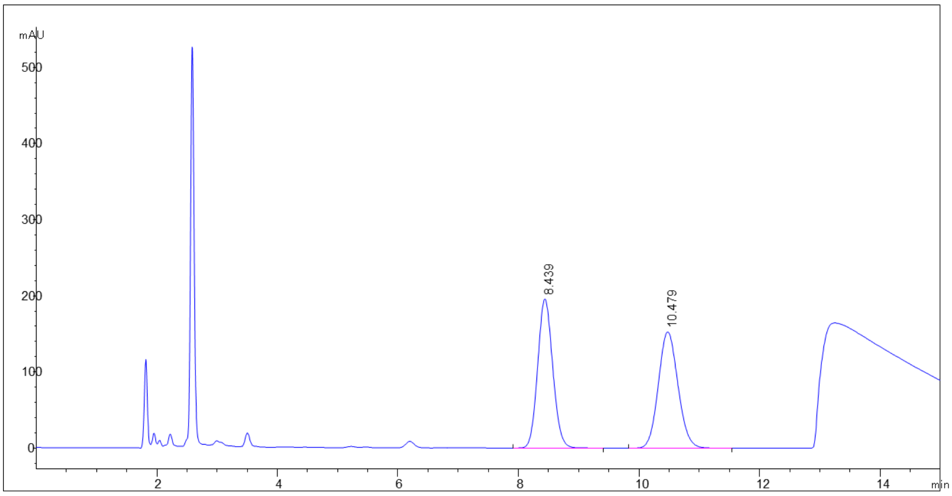
Peak	Retention time	Area	% Area
1	12.607	904.2	2.892
2	14.322	30362	97.108

HPLC for pure enantioenriched compound **4ika**



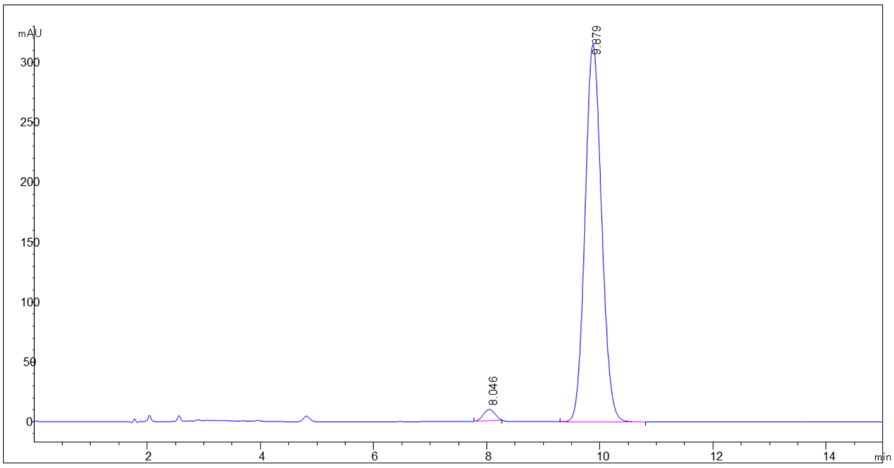
4ila, 60% yield, 96% *ee*

Chiralpak OX-RH column, MeCN/H_2O= 20/80, flow rate 1.0 mL/min



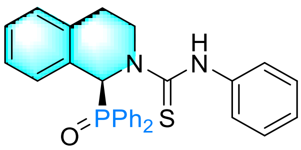
Peak	Retention time	Area	% Area
1	8.439	3396.8	49.637
2	10.479	3446.6	50.363

HPLC for racemic compound **4ila**



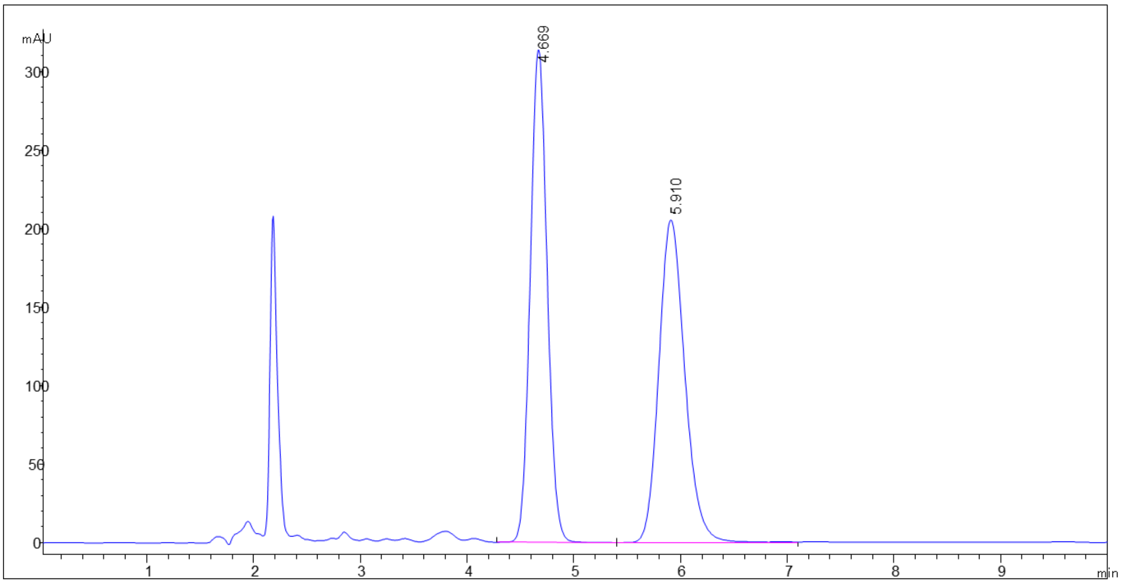
Peak	Retention time	Area	% Area
1	8.046	130	1.988
2	9.879	6046.8	98.012

HPLC for pure enantioenriched compound **4ila**



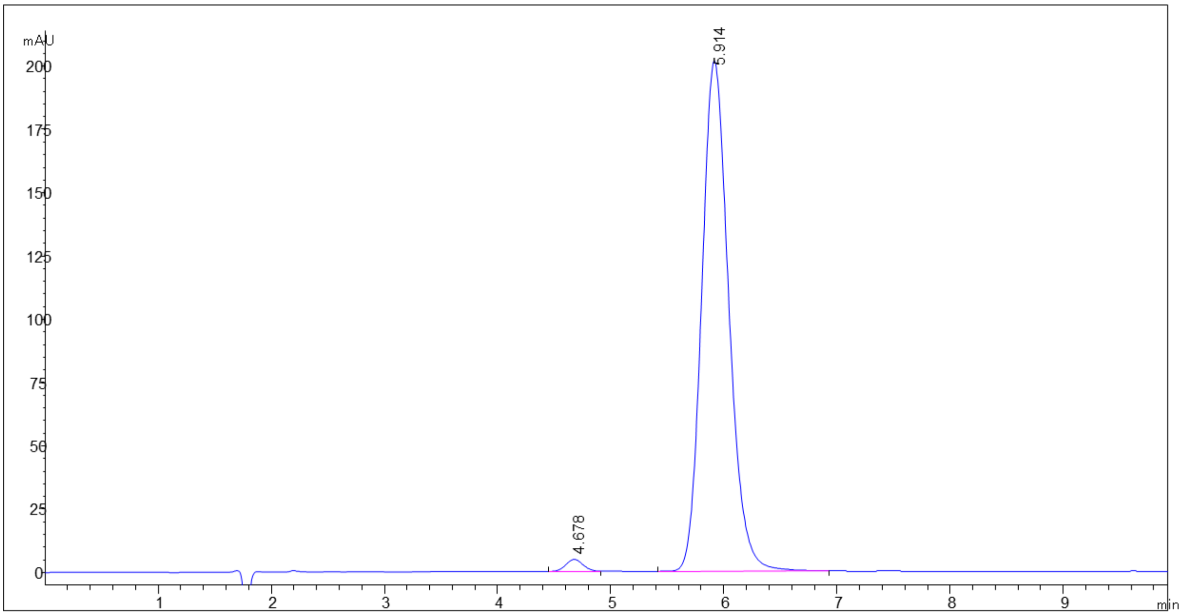
6aaa, 85% yield, 98% ee

Chiralpak OD-RH, MeCN/H_2O= 40/60, flow rate 1.0 mL/min



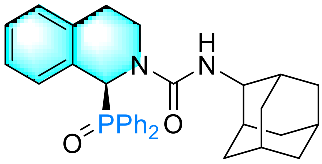
Peak	Ret. Time	Area	Area %
1	4.669	3455.3	49.845
2	5.91	3476.9	50.155

HPLC for racemic compound **6aab**



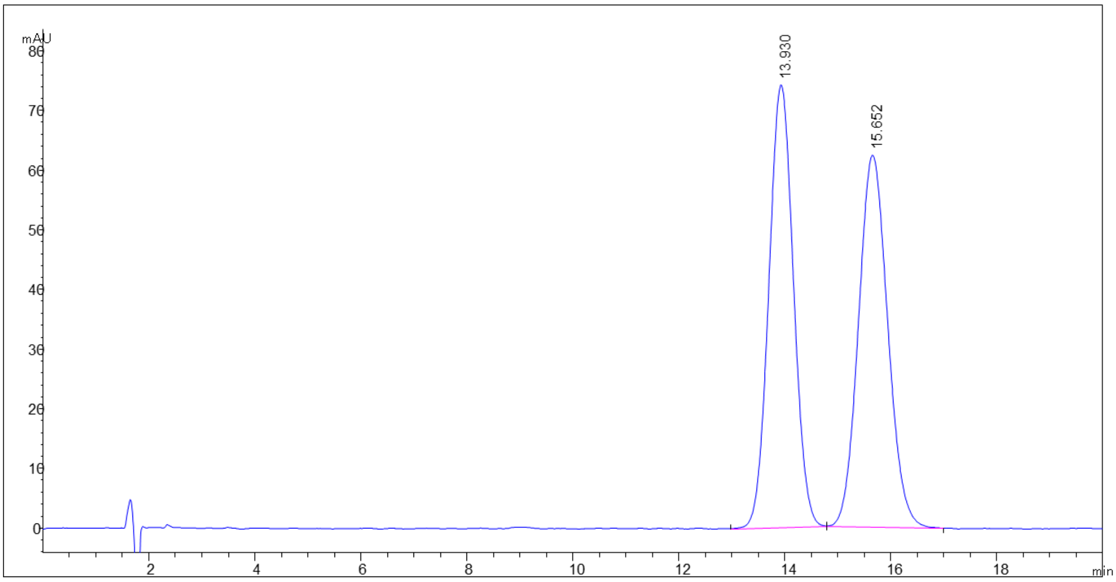
Peak	Ret. Time	Area	Area %
1	4.678	51.2	1.513
2	5.914	3334.7	98.487

HPLC for pure enantioenriched compound **6aab**



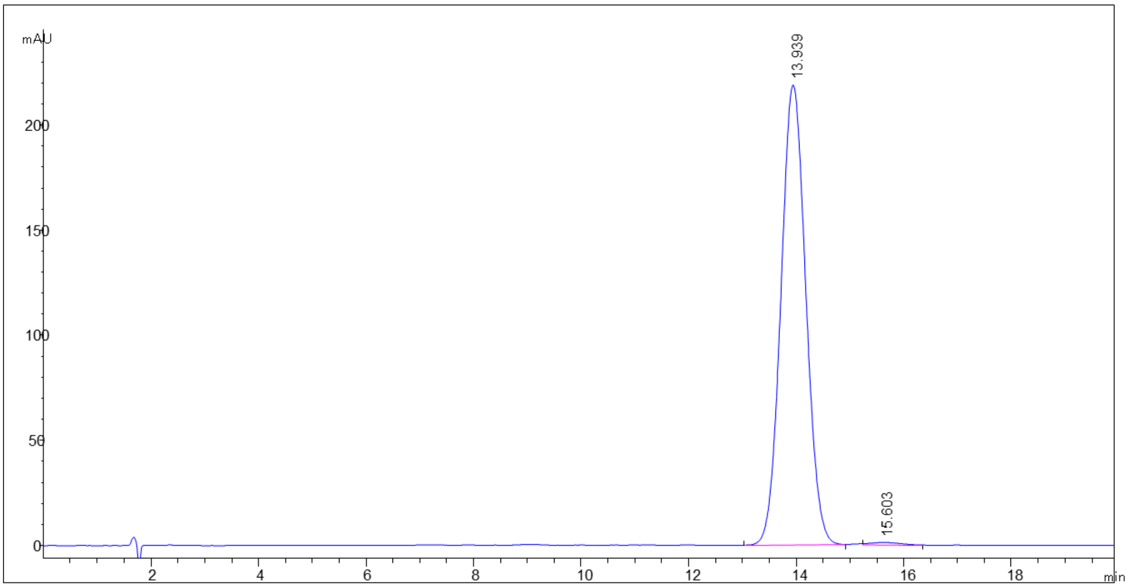
6aab, 88% yield, 99% ee

Chiralpak OD-RH, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



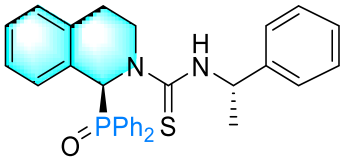
Peak	Ret. Time	Area	Area %
1	13.93	2384.4	50.015
2	15.652	2383	49.985

HPLC for racemic compound **6aab**



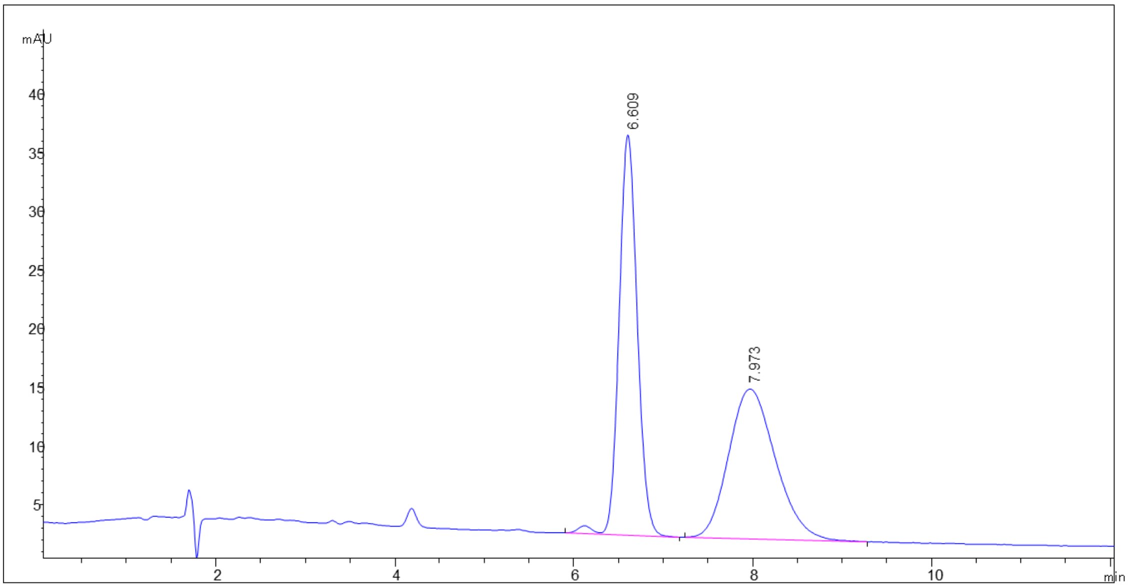
Peak	Ret. Time	Area	Area %
1	13.939	7031.2	99.414
2	15.603	41.4	0.586

HPLC for pure enantioenriched compound **6aab**



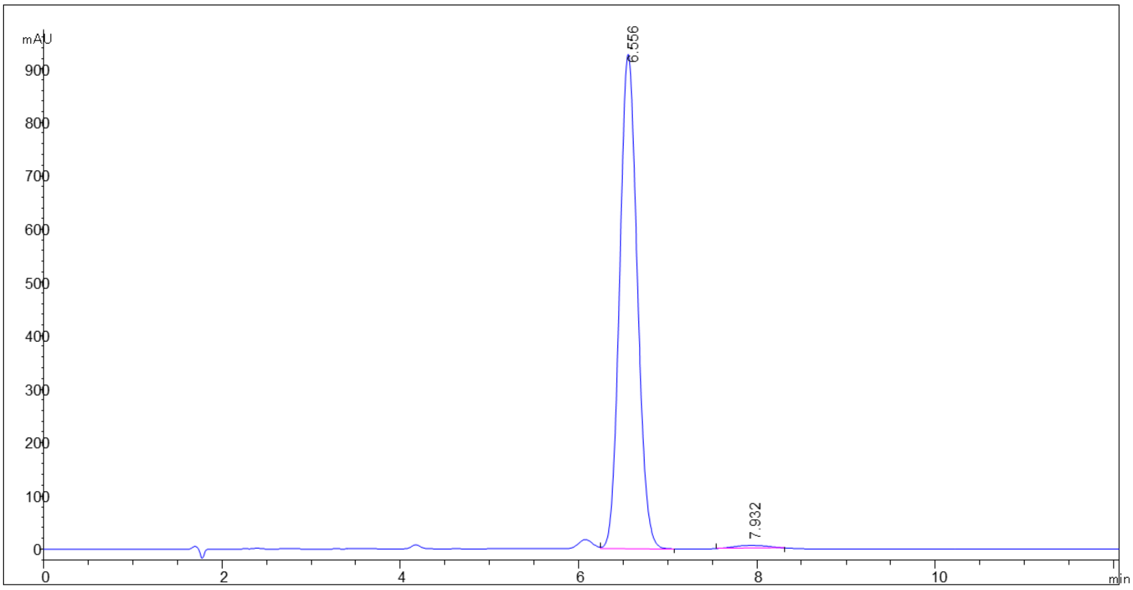
6aac, 93% yield, 98% ee

Chiralpak OJ-RH, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



Peak	Ret. Time	Area	Area %
1	6.609	485.7	51.072
2	7.973	465.4	48.928

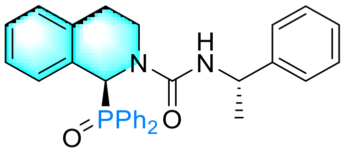
HPLC for racemic compound **6aac**



Peak	Ret. Time	Area	Area %
1	6.556	12715.8	98.761

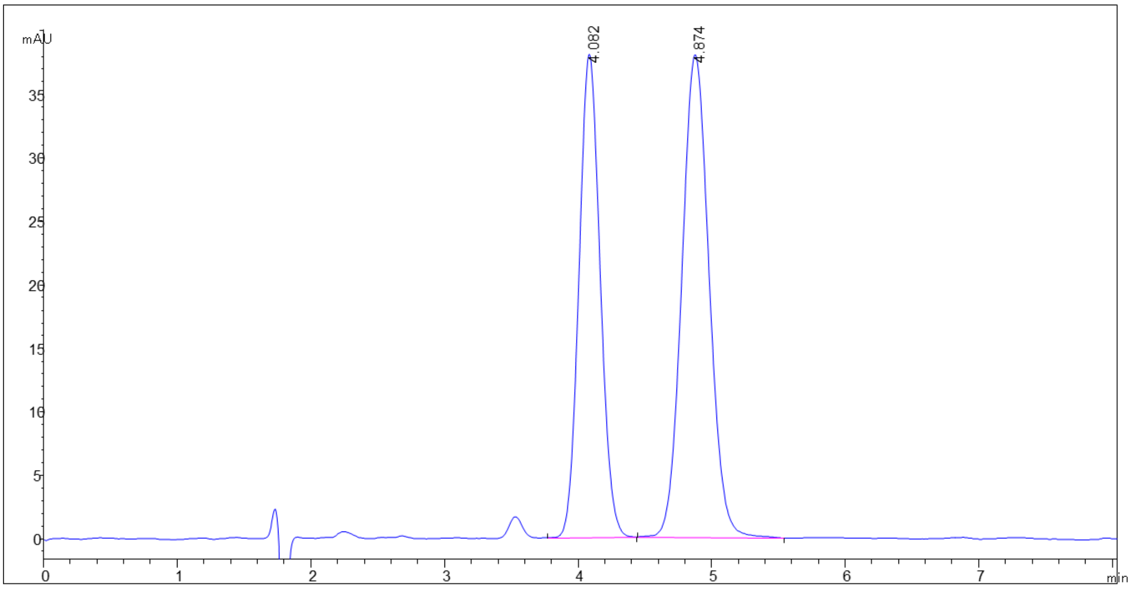
2	7.932	159.6	1.239

HPLC for pure enantioenriched compound **6aac**



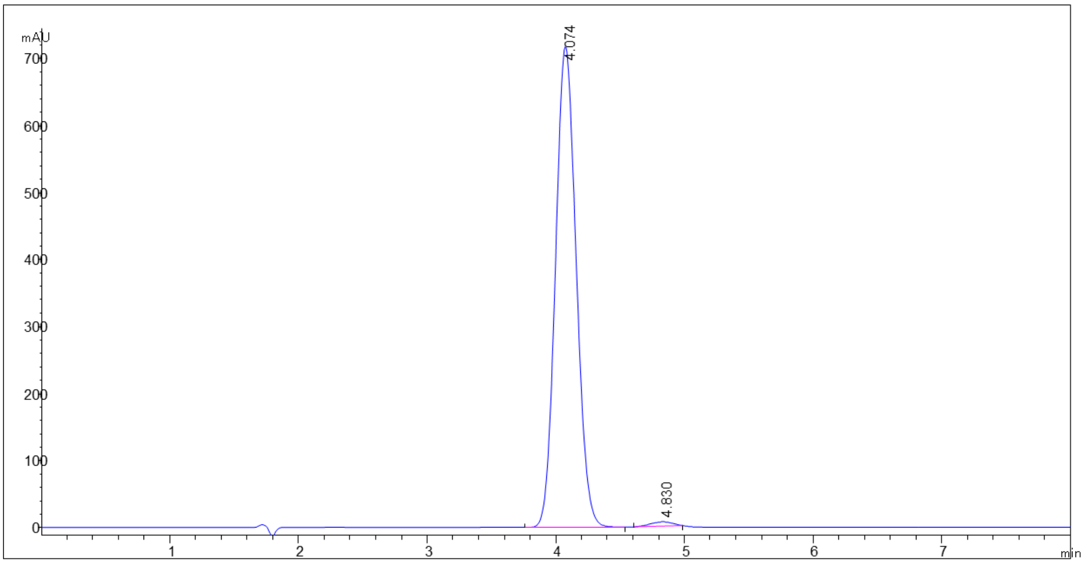
6aad, 96% yield, 98% ee

Chiralpak AS-RH, MeCN/H_2O= 50/50, flow rate 1.0 mL/min



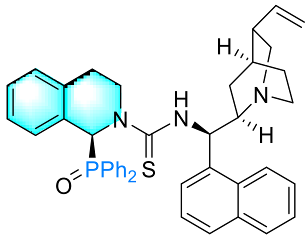
Peak	Ret. Time	Area	Area %
1	4.082	420	43.91
2	4.874	536.5	56.09

HPLC for racemic compound **6aad**



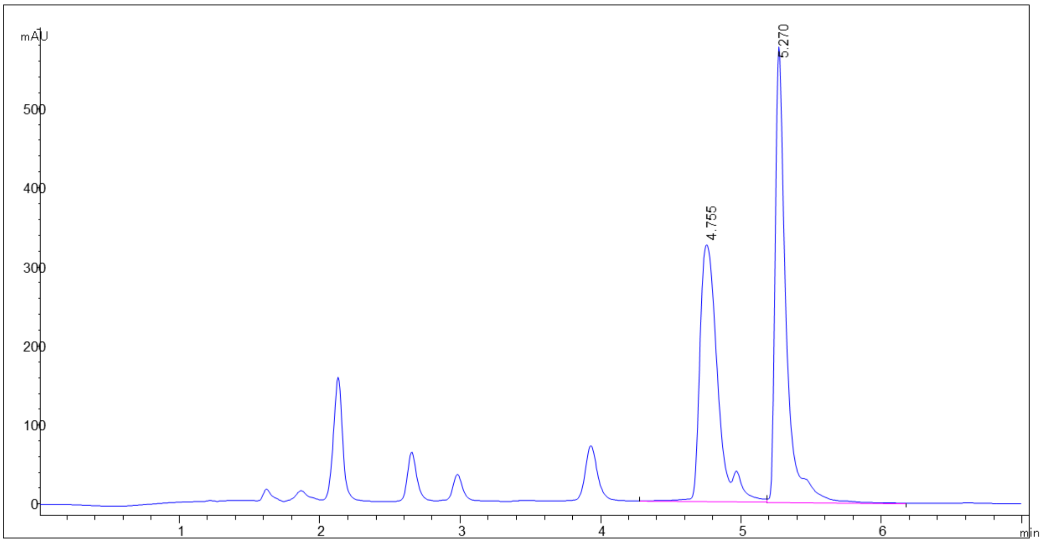
Peak	Ret. Time	Area	Area %
1	4.074	7962.4	99.028
2	4.83	78.2	0.972

HPLC for pure enantioenriched compound **6aad**



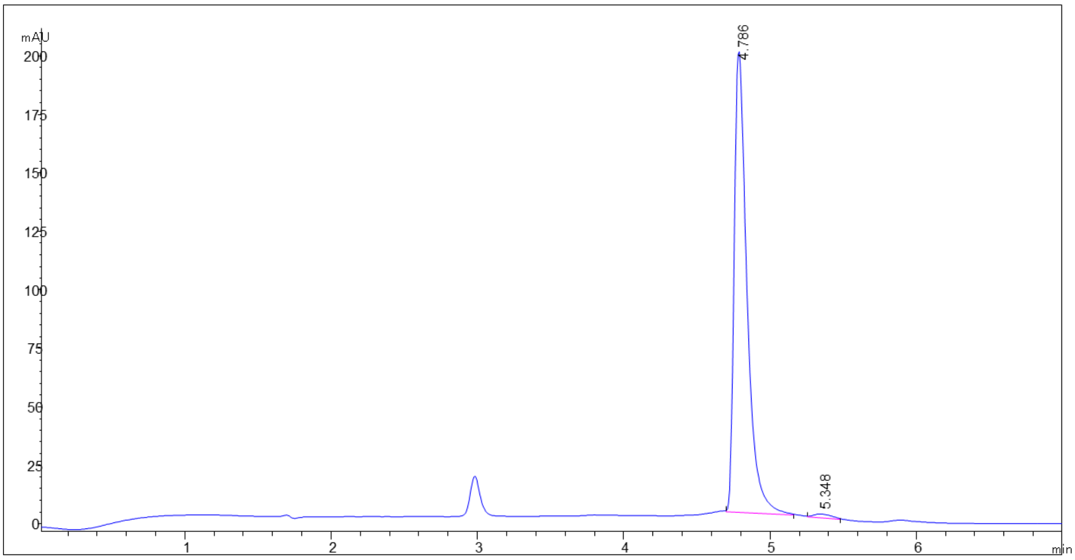
6aae, 86% yield, 99% ee

C8 column, MeCN/H_2O= 60/40, flow rate 1.0 mL/min



Peak	Ret. Time	Area	Area %
1	4.755	2899.4	48.33
2	5.27	3099.8	51.67

HPLC for racemic compound **6aae**



Peak	Ret. Time	Area	Area %
1	4.786	1245.1	99.347

2	5.348	8.2	0.653

HPLC for pure enantioenriched compound **6aae**