Supporting Information

Imine Amidation Catalyzed by a Chiral VAPOL Calcium Phosphate

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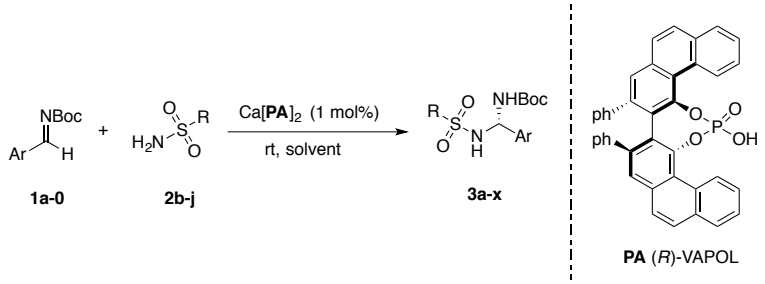
General considerations: All reactions were carried out in flame or oven-dried reaction test tubes and run under a dry argon atmosphere with magnetic stirring. Dry ether and dry toluene was obtained by filtration of reagent-grade solvent through an Innovative Technologies solvent drying system. (*R*)-VAPOL was synthesized according to the literature procedure and used for all catalysts.[1] Ca[(*R*)-**PA**]$_2$ was prepared as the reported procedures.[2] All imines were synthesized according to the literature procedure[3] and distilled before use. Sulfonamides and BINOL were purchased from commercial sources.

Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Visualization was accomplished UV light (254nm), flash column chromatography was performed with silica gel (200-300 mesh). The HRMS data were measured on a Thermo Fisher Q Exactive HF LC-MS. The mass analyzer type used for the HRMS measurements was Q-TOF. Optical rotations were measured on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-μL cell with a path length of 0.5 dm. Melting points were determined with a Micromelting point apparatus without correction. Enantiomeric excess (*ee*) was determined using a Shimadzu HPLC LC-20AT, SPD-20A UV/VIS detector, and CTO-20A column oven. Column conditions are reported in the experimental section below. H and C NMR spectra were recorded on 400 MHz or 600 MHz spectrometer at 25 ℃. Bruker Avance Ⅲ instrument with chemical shifts reported relative to tetramethylsilane (TMS). The absolute configuration of 3a-3x were determined to be "(*S*)" by HPLC spectrum to the reported literature values and X-ray. Compounds synthetized in the literature were characterized by matching their data with the reported values.

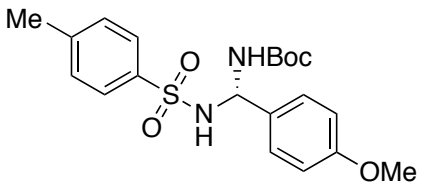
General procedure for the amidation of imines



The BOC-imine (0.25 mmol), nucleophile (0.125 mmol) and the catalyst Ca[(*R*)-**PA**]$_2$ (1-5mol%) were weighted into a dry test tube. The atmosphere was exchanged with argon three times, and anhydrous toluene or ether (2.0 mL) was added *via* syringe. The reaction mixture was stirred at ambient temperature for the desired reaction time as judged by TLC. Upon completion, solvent was removed under vacuo and the residue was purified by silica gel chromatography (Hexane/Acetone = 10/1 to 4/1) to provide chiral product **3a-x**. All racemic samples were

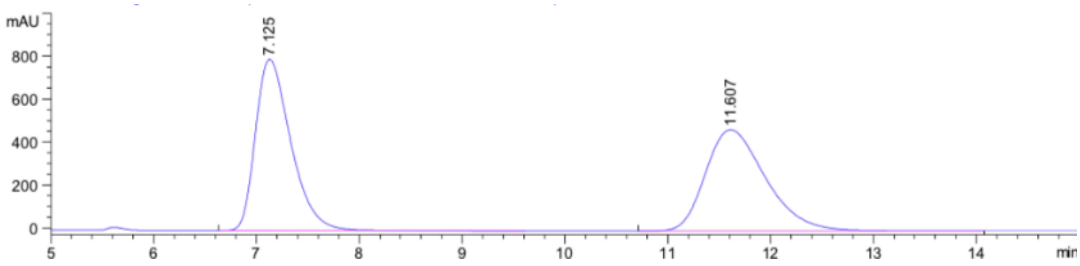
prepared by using calcium BINOL phosphate salt (20 mol%) as catalyst and their chiral HPLC retention time data were compared just prior to authentic samples with enantiomeric excess.

Characterization data for aminal products (3a-3x)



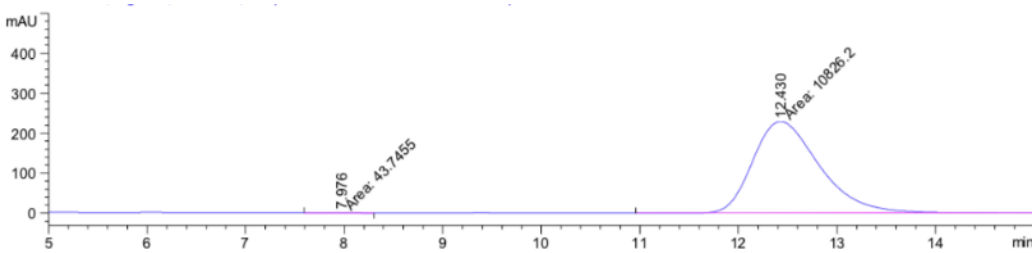
3a

(*S*)-*tert*-butyl (4-methoxyphenyl)(4-methylphenylsulfonamidomethyl)carbamate (3a) The reaction was performed in 0.125mmol scale for 15h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 6:1) as a white solid 25mg, 99% yield, >99% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 80:20 hexanes/iPrOH): t_R(minor) = 7.97 min, t_R(major) = 12.43 min. $[\alpha]_D^{20}$ = +5.67 (*c* = 0.275, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.55 (s, 1H), 6.13 (s, 1H), 3.78 (s, 3H), 2.42 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 160.4, 155.2, 143.6, 140.3, 133.1, 130.2, 128.3, 128.0, 114.5, 79.5, 64.1, 55.6, 28.5, 21.4. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_5S$ ([M+Na]$^+$) 429.1455, found 429.1459.



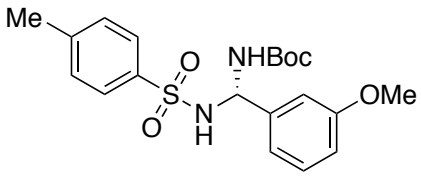
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.125	BB	0.3663	1.90102e4	797.02075	49.8836
2	11.607	BB	0.6278	1.90989e4	470.25076	50.1164
Totals :				3.81091e4	1267.27151	



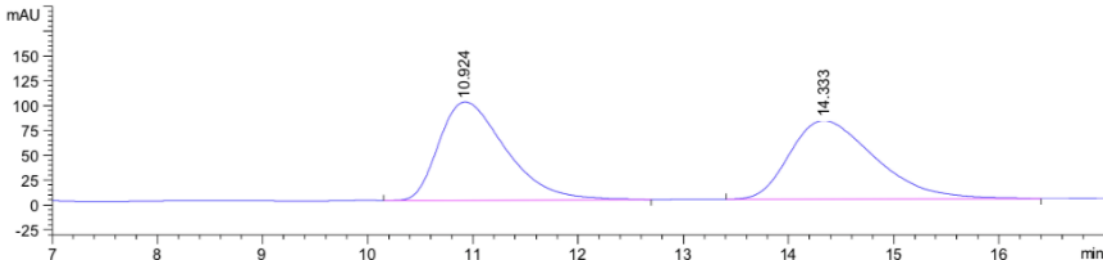
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.976	MM	0.5735	43.74552	1.27134	0.4024
2	12.430	MM	0.7866	1.08262e4	229.39241	99.5976
Totals :				1.08699e4	230.66375	



3b

(*S*)-*tert*-butyl (3-methoxyphenyl)(4-methylphenylsulfonamido)methylcarbamate (3b) The reaction was performed in 0.125mmol scale for 50h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 6:1) as a white solid 23mg, 91% yield, 97% *ee*. M.P.: 137-138 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 10.86 min, t_R(major) = 14.21 min. $[\alpha]_D^{20}$ = -1.52 (*c* = 0.290, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 – 7.75 (m, 2H), 7.36 (d, *J* = 5.8 Hz, 2H), 7.24 (t, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.84 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.67 (s, 1H), 6.16 (t, *J* = 9.0 Hz, 1H), 3.75 (s, 3H), 2.42 (s, 3H), 1.33 (s, 9H).^{13}C NMR (150 MHz, Acetone-d_6) δ 160.8, 155.2, 143.7, 142.6, 140.3, 130.3, 130.3, 128.0, 119.2, 114.3, 112.7, 79.6, 64.4, 55.5, 28.5, 21.4. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_5S$ ([M+Na]$^+$) 429.1455, found 429.1449.



Signal 2: DAD1 B, Sig=220,4 Ref=off

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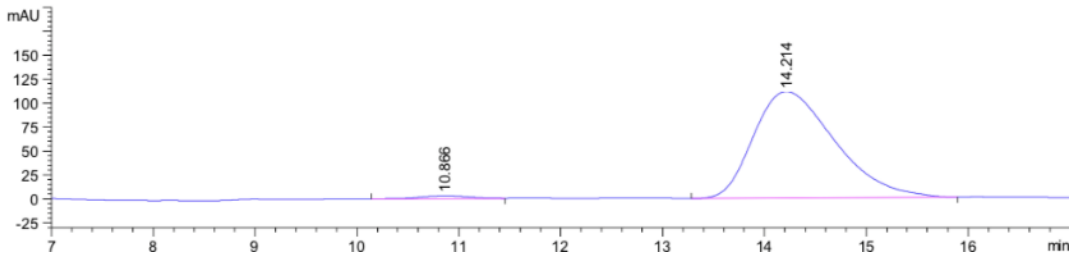
1	10.924	BB	0.6755	4371.80273	98.94780	49.4214
2	14.333	BB	0.8719	4474.17139	79.09678	50.5786

Totals : 8845.97412 178.04458



Signal 2: DAD1 B, Sig=220,4 Ref=off

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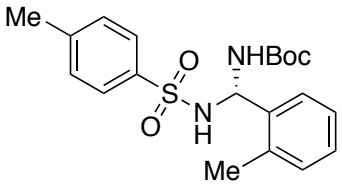
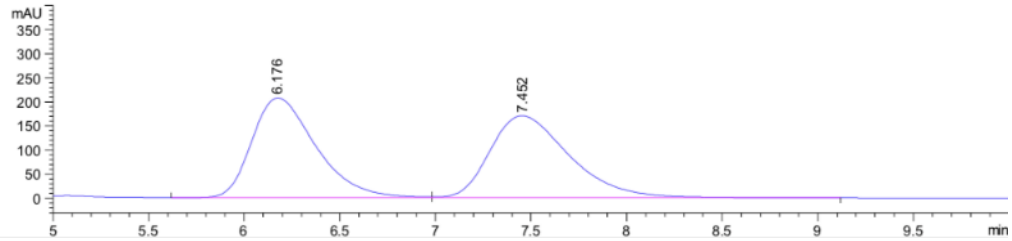
1	10.866	BB	0.4877	97.67110	2.96995	1.5562
2	14.214	BB	0.8759	6178.64893	111.26063	98.4438

Totals : 6276.32002 114.23057



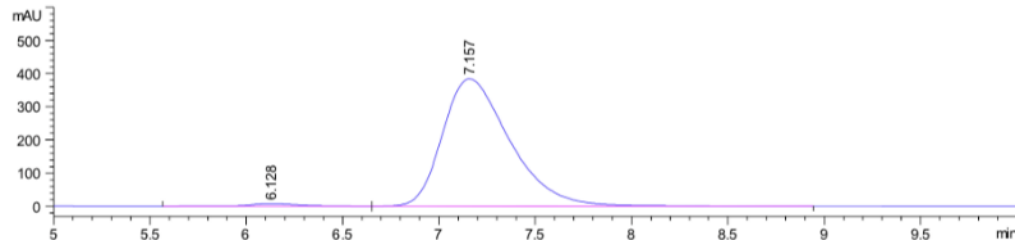
3c

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(*o*-tolylmethyl)carbamate (3c) The reaction was performed in 0.125mmol scale for 9h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 21mg, 88% yield, 97% *ee*. M.P.: 168-169 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 6.13 min, t_R(major) = 7.16 min. $[\alpha]_D^{20}$ = -1.90 (*c* = 0.315, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.20 – 7.12 (m, 3H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.42 (t, *J* = 7.3 Hz, 1H), 2.43 (s, 3H), 2.28 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 154.9, 143.6, 140.2, 139.2, 136.0, 131.2, 130.2, 128.8, 128.1, 126.9, 126.6, 79.5, 61.7, 28.5, 21.4, 19.0. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_4S$ ([M+Na]$^+$) 413.1505, found 413.1505.



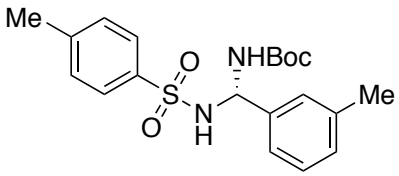
Signal 3: DAD1 C, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.176	BV	0.3562	4830.24414	206.99649	49.4947
2	7.452	VB	0.4443	4928.87256	170.00095	50.5053
Totals :				9759.11670	376.99744	



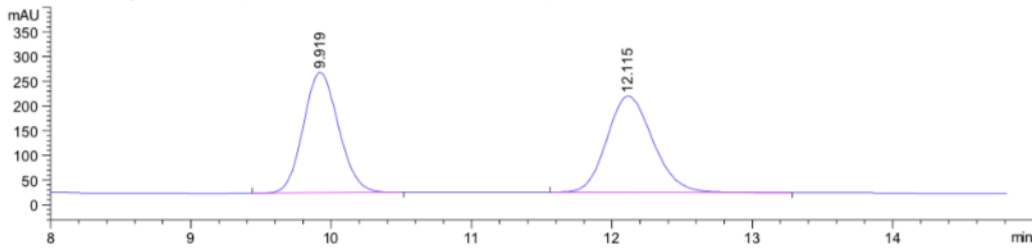
Signal 3: DAD1 C, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.128	BB	0.2894	154.91367	8.01692	1.6322
2	7.157	BB	0.3720	9336.24902	383.47876	98.3678
Totals :				9491.16269	391.49568	



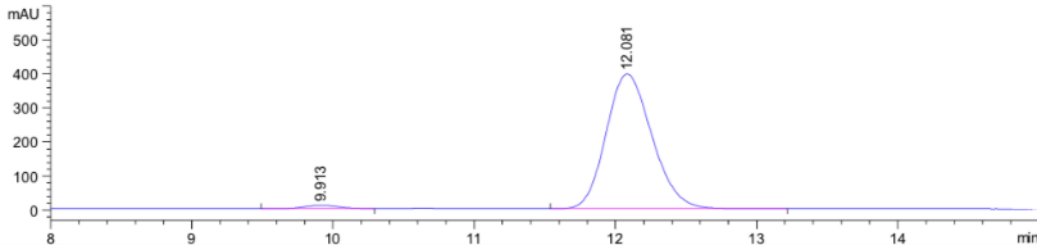
3d

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(*m*-tolylmethyl)carbamate (3d) The reaction was performed in 0.125mmol scale for 8h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 24mg, 99% yield, 96% *ee*. M.P.: 149-150 ^{o}C. HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 80:20 hexanes/iPrOH): t_R(minor) = 9.91 min, t_R(major) = 12.08 min. $[\alpha]_D^{20}$ = -1.04 (*c* = 0.230, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 – 7.74 (m, 2H), 7.39 – 7.33 (m, 2H), 7.20 (td, *J* = 8.2, 5.9 Hz, 3H), 7.15 – 7.06 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.17 (t, *J* = 8.6 Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.1, 143.6, 141.0, 140.3, 138.7, 130.2, 129.4, 129.2, 128.0, 127.8, 124.1, 79.5, 64.4, 28.5, 21.4, 21.4. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_4S$ ($[M+Na]^+$) 413.1505, found 413.1491.



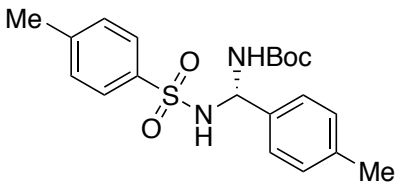
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.919	BB	0.2724	4260.58496	243.21579	49.0680
2	12.115	BB	0.3537	4422.42871	194.19868	50.9320
Totals :				8683.01367	437.41447	



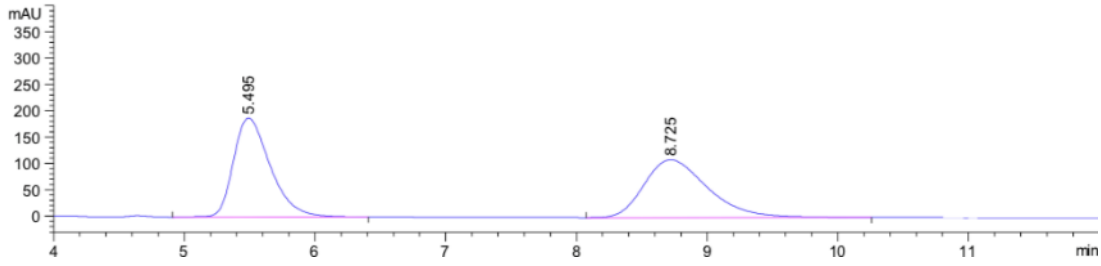
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.913	BB	0.2648	170.68063	10.12074	1.8691
2	12.081	BB	0.3518	8961.11035	396.34409	98.1309
Totals :				9131.79099	406.46482	



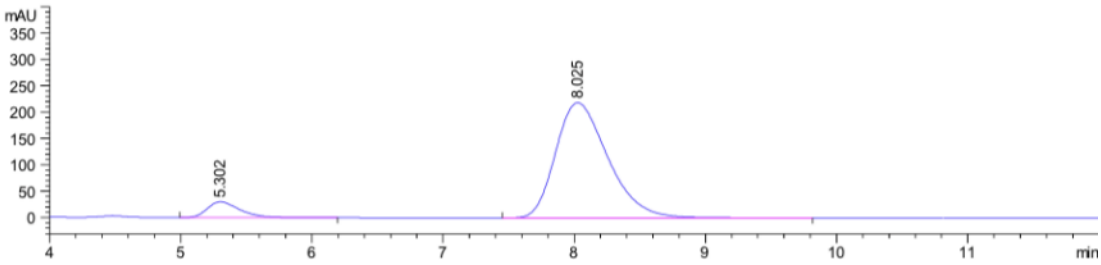
3e

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(*p*-tolylmethyl)carbamate (3e) The reaction was performed in 0.125mmol scale for 24h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 24mg, 98% yield, 84% *ee*. M.P.: 153-154 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 80:20 hexanes/iPrOH): t_R(minor) = 5.30 min, t_R(major) = 8.03 min. $[\alpha]_D^{20}$ = +1.87 (*c* = 0.160, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 – 7.75 (m, 2H), 7.39 – 7.32 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.16 – 7.10 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.56 (s, 1H), 6.15 (s, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.0, 143.6, 140.3, 138.3, 138.2, 130.2, 130.2, 129.8, 128.0 127.0, 79.5, 64.3, 28.5, 21.4, 21.0. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_4S$ ([M+Na]$^+$) 413.1505, found 413.1498.



Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.495	BB	0.3011	3686.95337	187.71642	49.8025
2	8.725	BB	0.5214	3716.20020	109.64300	50.1975
Totals :				7403.15356	297.35941	



Signal 3: DAD1 C, Sig=220,4 Ref=off

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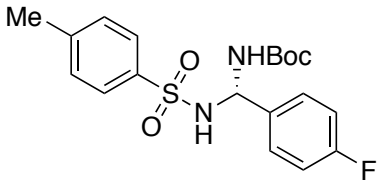
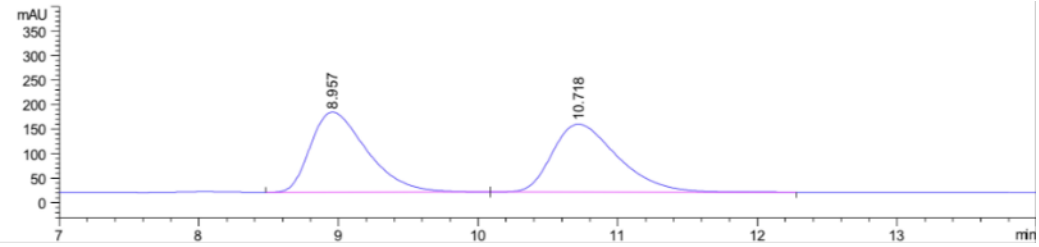
1	5.302	BB	0.2618	516.46619	29.86362	7.8401
2	8.025	BB	0.4284	6071.01367	218.30373	92.1599
Totals :				6587.47986	248.16734	



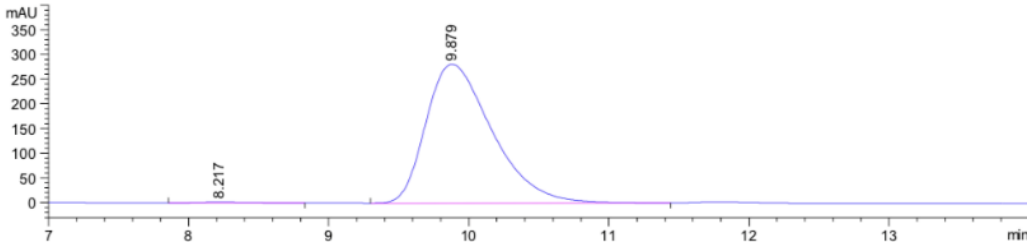
3f

(*S*)-*tert*-butyl (4-fluorophenyl)((4-methylphenylsulfonamidomethyl)carbamate (3f) The reaction was performed in 0.25mmol scale for 14h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 49mg, 99% yield, 99% *ee*. M.P.: 157-158 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 8.22 min, t_R(major) = 9.88 min. $[\alpha]_D^{20}$ = +3.26 (*c* = 0.245, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.81 – 7.76 (m, 2H), 7.44 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 6.18 (t, *J* = 9.1 Hz, 1H), 2.42 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 164.0, 162.4, 155.2, 143.7, 140.2, 137.3, 130.3, 129.2, 129.2, 128.0, 115.9, 115.8, 79.7, 63.9, 28.5, 21.4. HRMS (ESI) Calcd for $C_{19}H_{23}FN_2NaO_4S$ ([M+Na]$^+$) 417.1255, found 417.1264.



Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.957	VB	0.4317	4579.30029	163.01512	50.4331
2	10.718	BB	0.4997	4500.65869	138.28102	49.5669
Totals :				9079.95898	301.29614	



Signal 2: DAD1 B, Sig=220,4 Ref=off

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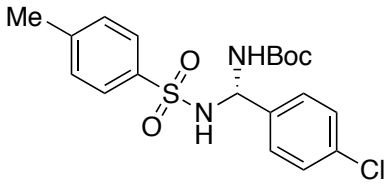
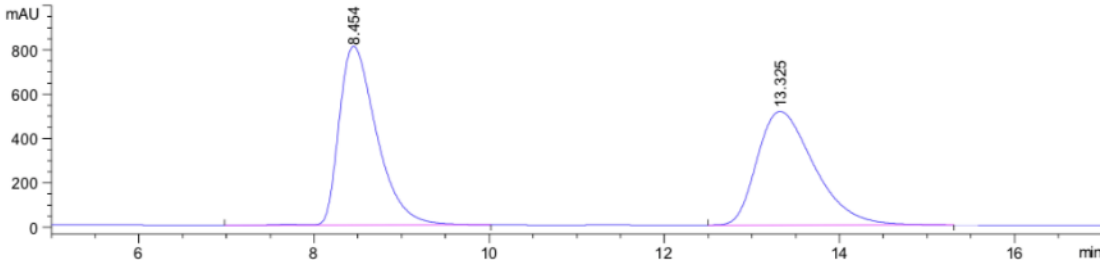
1	8.217	BB	0.3711	46.64305	1.85631	0.5031
2	9.879	BB	0.5050	9224.91309	280.98706	99.4969
Totals :				9271.55614	282.84337	



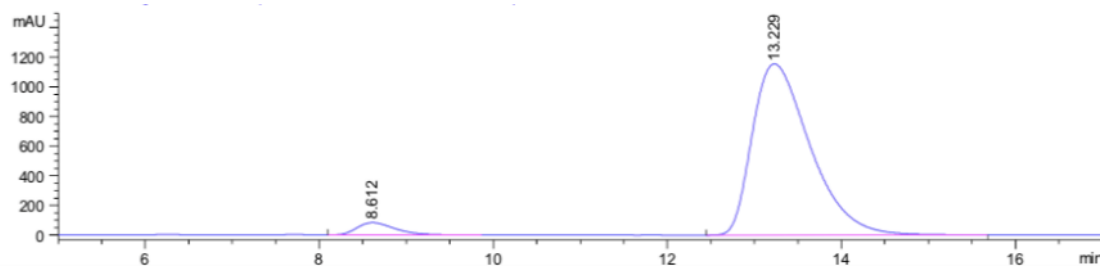
3g

(*S*)-*tert*-butyl (4-chlorophenyl)(4-methylphenylsulfonamidomethyl)carbamate (3g) The reaction was performed in 0.25mmol scale for 16h using 1 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 48mg, 94% yield, 91% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 8.61 min, t_R(major) = 13.23 min. $[\alpha]_D^{20}$ = -10.1 (*c* = 0.295, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.80 – 7.75 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (dt, *J* = 8.4, 2.5 Hz, 4H), 7.28 – 7.19 (m, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.18 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 143.8, 140.1, 140.0, 134.1, 130.3, 129.3, 129.0, 128.0, 79.8, 63.9, 28.5, 21.5. HRMS (ESI) Calcd for $C_{19}H_{23}ClN_2NaO_4S$ ([M+Na]$^+$) 433.0959, found 433.0969.



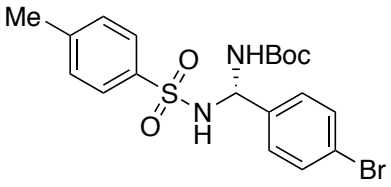
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.454	VB R	0.4582	2.40511e4	807.17743	50.9172
2	13.325	BB	0.7000	2.31846e4	512.29926	49.0828
Totals :				4.72357e4	1319.47668	



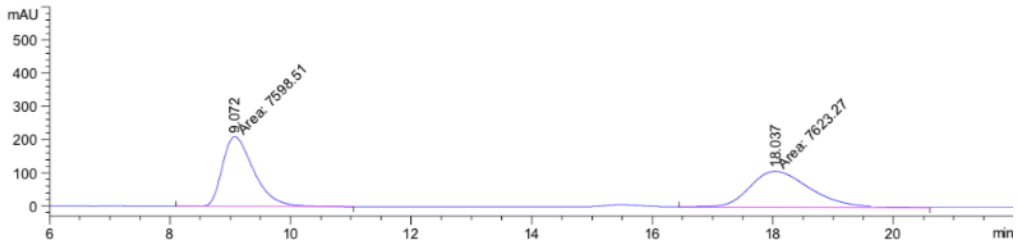
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.612	BB	0.4711	2533.95703	82.77647	4.5252
2	13.229	BB	0.7172	5.34627e4	1156.72327	95.4748
Totals :				5.59967e4	1239.49973	



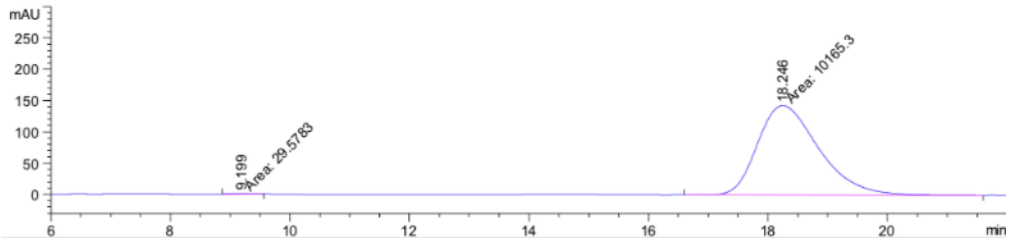
3h

(*S*)-*tert*-butyl (4-bromophenyl)(4-methylphenylsulfonamidomethyl)carbamate (3h) The reaction was performed in 0. 25mmol scale for 24h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 55mg, 96% yield, >99% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 9.20 min, t_R(major) = 18.25 min. $[\alpha]_D^{20}$ = +0.55 (*c* = 0.290, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 – 7.71 (m, 2H), 7.56 – 7.49 (m, 2H), 7.36 (dd, *J* = 8.4, 3.6 Hz, 4H), 7.25 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.15 (t, *J* = 9.0 Hz, 1H), 2.43 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 143.8, 140.5, 140.1, 132.2, 130.3, 129.3, 128.0, 122.3, 79.8, 64.0, 28.5, 21.4. HRMS (ESI) Calcd for $C_{19}H_{23}BrN_2NaO_4S$ ([M+Na]$^+$) 477.0454, found 477.0459.



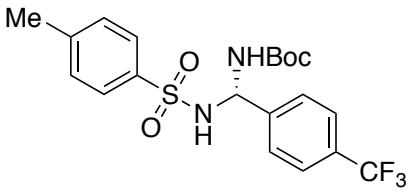
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.072	MM	0.6049	7598.51416	209.35927	49.9187
2	18.037	MM	1.1684	7623.27246	108.73913	50.0813
Totals :				1.52218e4	318.09840	



Signal 1: DAD1 A, Sig=220,4 Ref=off

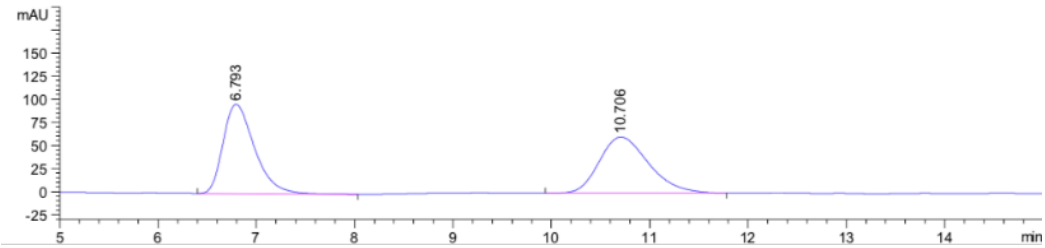
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.199	MM	0.4027	29.57825	1.22414	0.2901
2	18.246	MM	1.1876	1.01653e4	142.65549	99.7099
Totals :				1.01949e4	143.87962	



3i

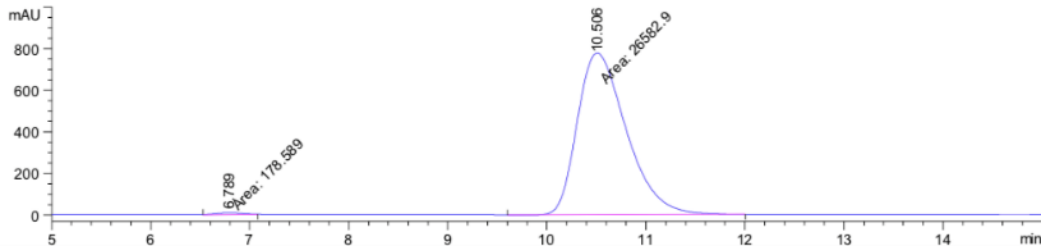
(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(4-trifluoromethylphenylmethyl)carbamate (3i)

The reaction was performed in 0. 25mmol scale for 20h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 55mg, 99% yield, 99% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 6.79 min, t_R(major) = 10.51 min. $[\alpha]_D^{20}$ = -13.75 (*c* = 0.305, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 3H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.26 (t, *J* = 9.2 Hz, 1H), 2.42 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 145. 5, 143.8, 140.1, 130.5, 130.3, 130.2, 128.0, 128.0, 126.2 (q, *J* = 3.7 Hz), 79.8, 64.0, 28.5, 21.4. HRMS (ESI) Calcd for $C_{20}H_{23}F_3N_2NaO_4S$ ([M+Na]$^+$) 467.1223, found 467.1229.



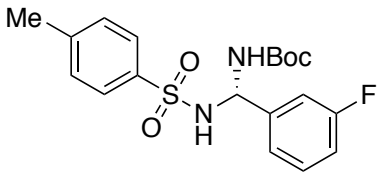
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.793	BB	0.3418	2153.20850	96.70289	50.4196
2	10.706	BB	0.5390	2117.37256	60.69666	49.5804
Totals :				4270.58105	157.39955	



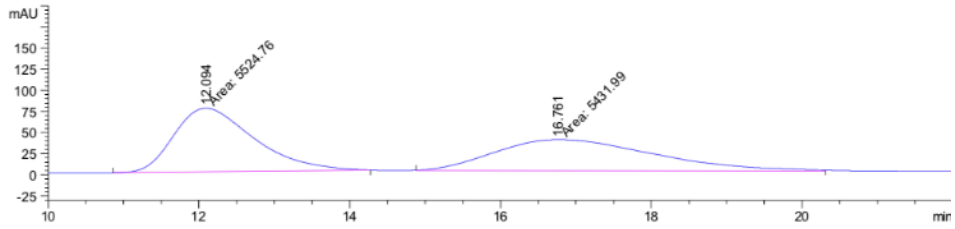
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.789	MM	0.3235	178.58879	9.19974	0.6673
2	10.506	MM	0.5712	2.65829e4	775.58008	99.3327
Totals :				2.67615e4	784.77982	



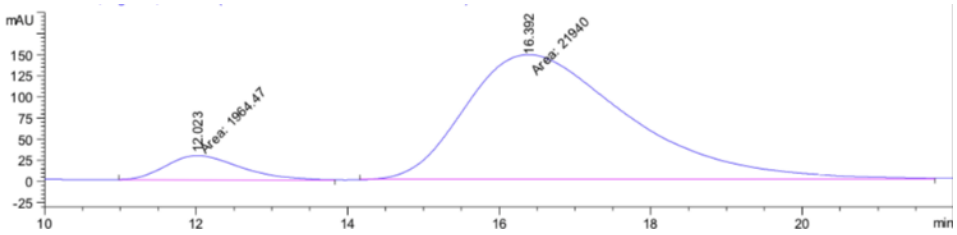
3j

(*S*)-*tert*-butyl ((3-fluorophenyl)(4-methylphenylsulfonamidomethyl)carbamate (3j) The reaction was performed in 0. 125mmol scale for 18h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 23mg, 94% yield, 85% *ee*. M.P.: 150-151 ^{o}C. HPLC analysis (Chiralcel OJ-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 12.03 min, t_R(major) = 16.39 min. $[\alpha]_D^{20}$ = -8.09 (*c* = 0.220, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.79 (d, 2H), 7.42 – 7.35 (m, 3H), 7.25 (dd, *J* = 17.8, 8.4 Hz, 2H), 7.18 (dt, *J* = 10.4, 2.2 Hz, 1H), 7.06 (tdd, *J* = 8.5, 2.7, 0.8 Hz, 1H), 6.78 (s, 1H), 6.21 (t, *J* = 8.9 Hz, 1H), 2.42 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 163.64 (d, *J* = 244.0 Hz), 155.17, 143.99 (d, *J* = 6.9 Hz), 143.79, 140.13, 131.17 (d, *J* = 8.2 Hz), 130.3, 128.0, 123.2, 115.5 (d, *J* = 21.2 Hz), 114.0 (d, *J* = 23.1 Hz), 79.8, 63.9, 28.5, 21.4. HRMS (ESI) Calcd for $C_{19}H_{23}FN_2NaO_4S$ ([M+Na]$^+$) 417.1255, found 417.1273.



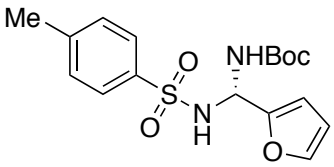
Signal 3: DAD1 C, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.094	MM	1.2262	5524.76221	75.09027	50.4234
2	16.761	MF	2.4482	5431.98975	36.97984	49.5766
Totals :				1.09568e4	112.07011	



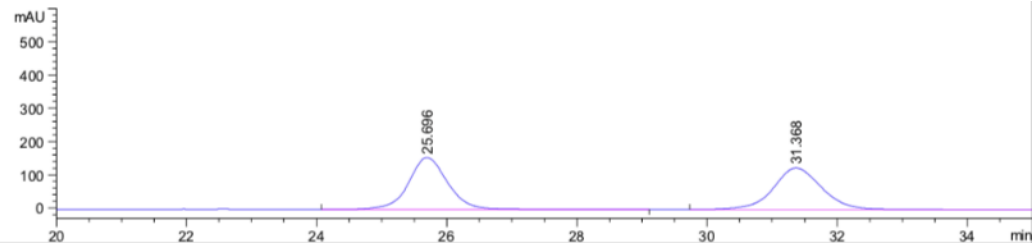
Signal 3: DAD1 C, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.023	MM	1.1414	1964.47131	28.68607	8.2180
2	16.392	MM	2.4833	2.19400e4	147.24892	91.7820
Totals :				2.39044e4	175.93498	



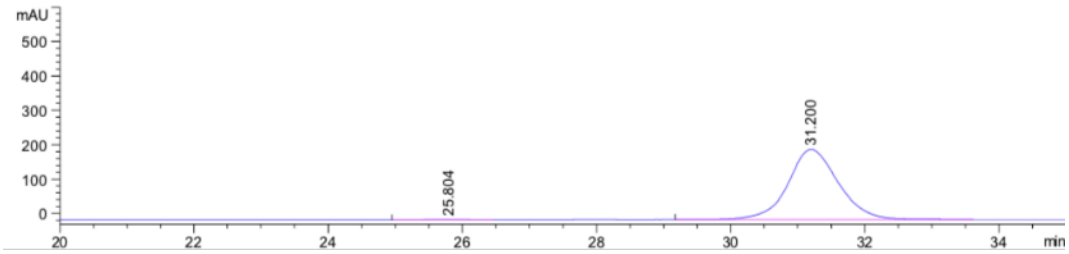
3k

(*S*)-*tert*-butyl (furan-2-yl)4-methylphenylsulfonamidomethyl)carbamate (3k) The reaction was performed in 0. 125mmol scale for 24h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 22mg, 99% yield, 99% *ee*. M.P.: 152-153 ^{o}C. HPLC analysis (Chiralcel IA-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 25.80 min, t_R(major) = 31.20min. $[\alpha]_D^{20}$ = -3.125 (*c* = 0.160, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.78 (td, 2H), 7.45 (t, *J* = 1.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 1H), 6.75 – 6.66 (m, 1H), 6.39 – 6.32 (m, 2H), 6.25 (t, *J* = 8.8 Hz, 1H), 2.41 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 153.0, 143.6, 143.5, 140.4, 130.2, 127.9, 111.2, 107.9, 79.8, 59.5, 28.5, 21.4. HRMS (ESI) Calcd for $C_{17}H_{22}N_2NaO_5S$ ([M+Na]$^+$) 389.1142, found 389.1150.



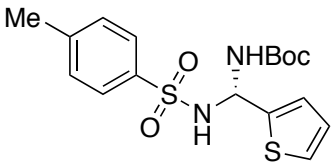
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.696	BV R	0.6411	6633.16406	156.19527	50.3333
2	31.368	BV R	0.7833	6545.30566	124.76031	49.6667
Totals :				1.31785e4	280.95557	



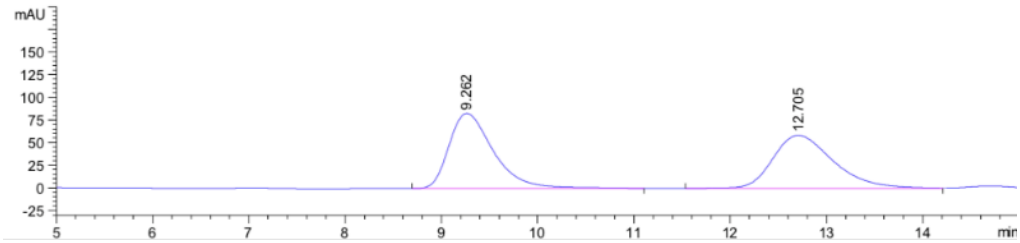
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.804	BB	0.5397	53.28258	1.40096	0.4940
2	31.200	BB	0.7978	1.07319e4	203.98979	99.5060
Totals :				1.07852e4	205.39075	



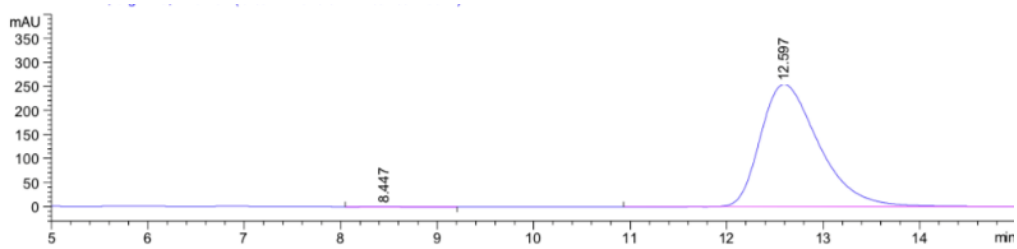
3l

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(thiophen-2-yl)methylcarbamate (3l) The reaction was performed in 0. 25mmol scale for 12h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 23mg, 99% yield, >99% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 8.45 min, t_R(major) = 12.60 min. $[\alpha]_D^{20}$ = -14.93 (*c* = 0.365, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 – 7.78 (m, 2H), 7.40 – 7.34 (m, 3H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.02 (dt, *J* = 3.6, 1.3 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.73 (s, 1H), 6.38 (t, *J* = 9.4 Hz, 1H), 2.42 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.0, 145.6, 143.8, 140.2, 130.3, 128.0, 127.8, 126.5, 125.7, 79.9, 61.5, 28.5, 21.4. HRMS (ESI) Calcd for $C_{17}H_{22}N_2NaO_4S_2$ ([M+Na]$^+$) 405.0913, found 405.0905.



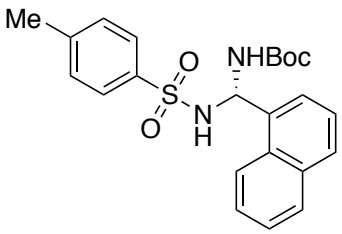
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.262	BB	0.4907	2661.11914	82.86712	51.1067
2	12.705	BB	0.6680	2545.86499	58.46561	48.8933
Totals :				5206.98413	141.33273	



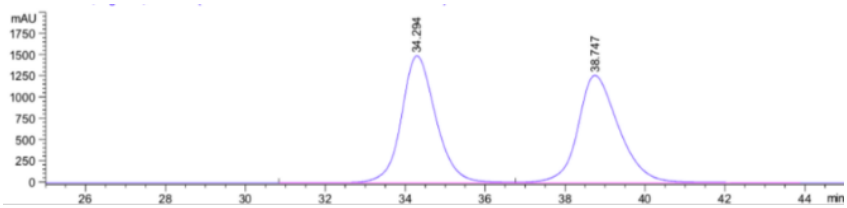
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.447	BB	0.3584	15.47902	6.39457e-1	0.1440
2	12.597	BB	0.6472	1.07368e4	255.01836	99.8560
Totals :				1.07523e4	255.65781	



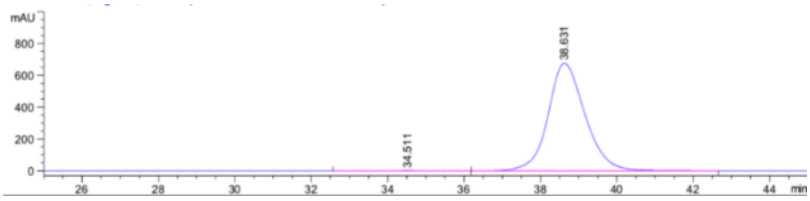
3m

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(naphthalen-1-yl)methylcarbamate (3m) The reaction was performed in 0. 125mmol scale for 10h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 26mg, 98% yield, >99% *ee*. M.P.: 158-159 ^{o}C. HPLC analysis (Chiralcel IA-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 34.51 min, t_R(major) = 38.63 min. $[\alpha]_D^{20}$ = +4.04 (*c* = 0.425, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.17 – 8.10 (m, 1H), 7.94 – 7.88 (m, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 8.7 Hz, 1H), 6.84 – 6.73 (m, 1H), 2.43 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.1, 143.7, 140.2, 136.3, 134.8, 131.2, 130.2, 129.7, 129.5, 128.1, 127.3, 126.7, 125.9, 124.6, 124.1, 78.0, 61.6, 28.5, 21.4. HRMS (ESI) Calcd for $C_{23}H_{26}N_2NaO_4S$ ([M+Na]$^+$) 449.1505, found 449.1504.



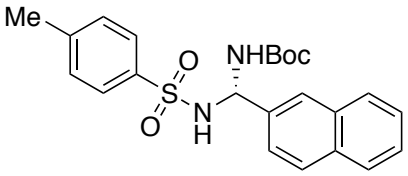
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.294	VV R	0.9127	8.93004e4	1494.62781	49.8191
2	38.747	VB	1.0705	8.99490e4	1263.63098	50.1809
Totals :				1.79249e5	2758.25879	



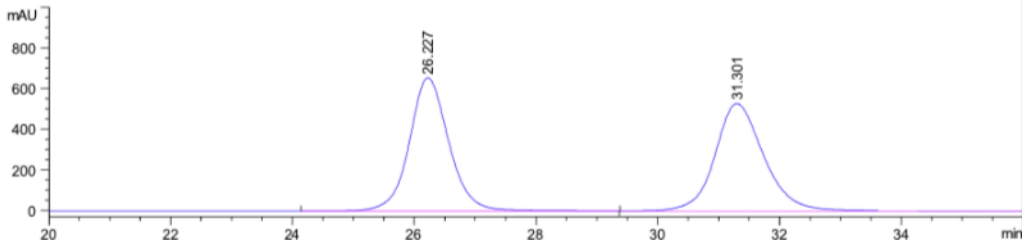
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.511	VB	1.2885	150.05591	1.57360	0.3272
2	38.631	BB	1.0206	4.57118e4	676.25269	99.6728
Totals :				4.58618e4	677.82629	



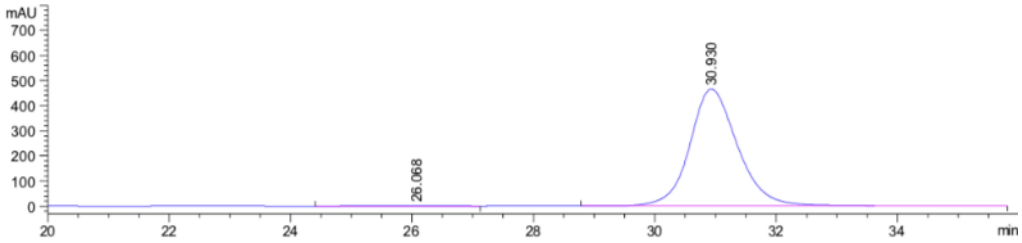
3n

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(naphthalen-2-yl)methylcarbamate (3n) The reaction was performed in 0. 125mmol scale for 17h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 24mg, 90% yield, >99% *ee*. M.P.: 151-152 ^{o}C. HPLC analysis (Chiralcel IA-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 20.07 min, t_R(minor) = 30.93 min. $[\alpha]_D^{20}$ = +10.55 (*c* = 0.280, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.90 – 7.84 (m, 4H), 7.83 – 7.79 (m, 2H), 7.55 – 7.48 (m, 3H), 7.36 – 7.31 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.76 (s, 1H), 6.36 (s, 1H), 2.40 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 143.7, 140.3, 138.4, 134.0, 134.0, 130.3, 129.1, 129.0, 128.4, 128.0, 127.2, 127.1, 125.8, 125.4, 79.7, 64.7, 28.5, 21.4. HRMS (ESI) Calcd for $C_{23}H_{26}N_2NaO_4S$ ([M+Na]$^+$) 449.1505, found 449.1517.



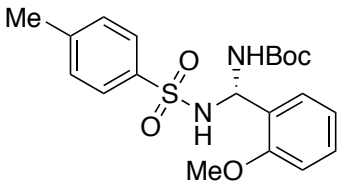
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.227	BB	0.6861	2.95211e4	654.63531	50.0284
2	31.301	BB	0.8438	2.94877e4	527.80292	49.9716
Totals :				5.90088e4	1182.43823	



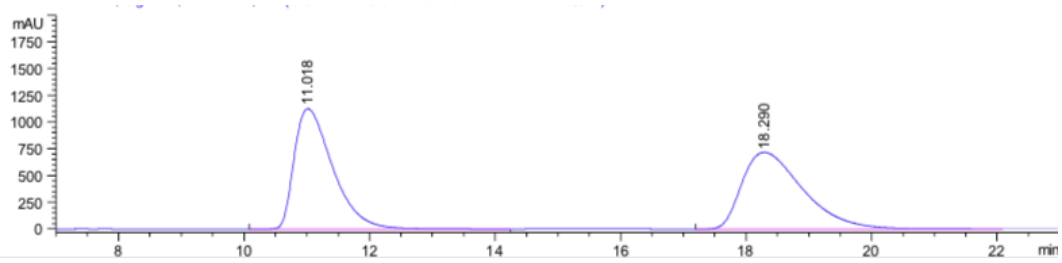
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.068	BB	0.8755	39.58795	6.41957e-1	0.1537
2	30.930	BB	0.8360	2.57163e4	465.91098	99.8463
Totals :				2.57559e4	466.55294	



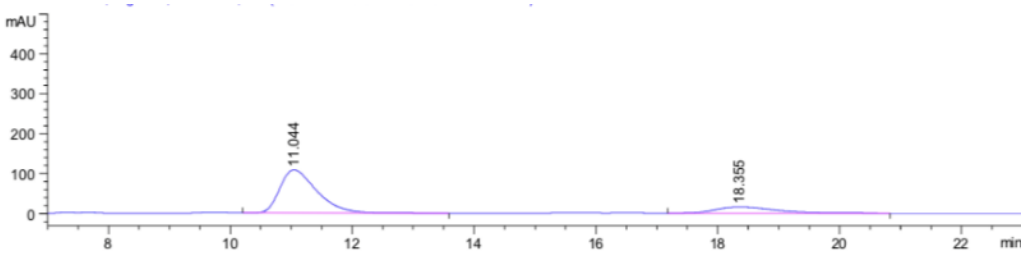
3o

(*S*)-*tert*-butyl (2-methoxyphenyl)(4-methylphenylsulfonamidomethyl)carbamate (3o) The reaction was performed in 0. 125mmol scale for 36h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 20mg, 79% yield, 67% *ee*. M.P.: 169-170 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 11.04 min, t_R(major) = 18.36 min. $[\alpha]_D^{20}$ = -24.23 (*c* = 0.085, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 3H), 7.24 (td, *J* = 7.8, 1.7 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.83 (m, 2H), 6.49 – 6.40 (m, 1H), 6.27 (t, *J* = 8.9 Hz, 1H), 3.74 (s, 3H), 2.40 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 157.3, 154.8, 143.3, 140.2, 130.3, 130.0, 128.6, 128.5, 128.0, 121.2, 111.8, 79.5, 62.6, 55.7, 28.5, 21.4. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_5S$ ($[M+Na]^+$) 429.1455, found 429.1444.



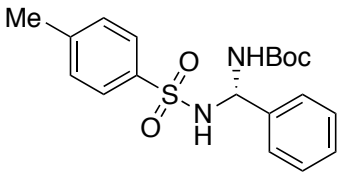
Signal 3: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.018	BB	0.6596	4.80020e4	1125.43579	49.7417
2	18.290	BB	1.0482	4.85005e4	717.84839	50.2583
Totals :				9.65026e4	1843.28418	



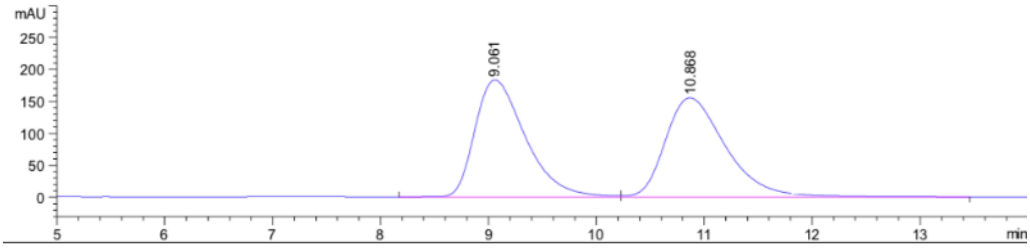
Signal 3: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.044	BB	0.6423	4575.87939	107.99270	81.3938
2	18.355	BB	0.9498	1046.02246	15.56971	18.6062
Totals :				5621.90186	123.56240	



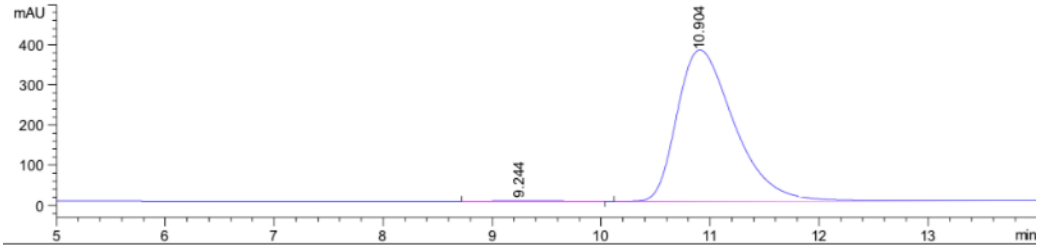
3p

(*S*)-*tert*-butyl (4-methylphenylsulfonamido)(phenyl)methylcarbamate (3p) The reaction was performed in 0.25mmol scale for 3h using 1 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 47mg, 99% yield, >99% *ee*. M.P.: 170-171 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 9.24 min, t_R(major) = 10.90 min. $[\alpha]_D^{20}$ = -6.69 (*c* = 0.260, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.27 (m, 8H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.70 (s, 1H), 6.22 (t, *J* = 9.1 Hz, 1H), 2.43 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 143.7, 141.1, 140.3, 130.3, 129.2, 128.7, 128.0, 127.1, 79.6, 64.4, 28.5, 21.4. HRMS (ESI) Calcd for $C_{19}H_{24}N_2NaO_4S$ ($[M+Na]^+$) 399.1349, found 399.1360.



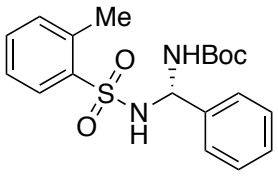
Signal 3: DAD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.061	BV	0.4997	5957.33887	183.06398	49.7110
2	10.868	VB	0.5952	6026.60498	155.13988	50.2890
Totals :				1.19839e4	338.20386	



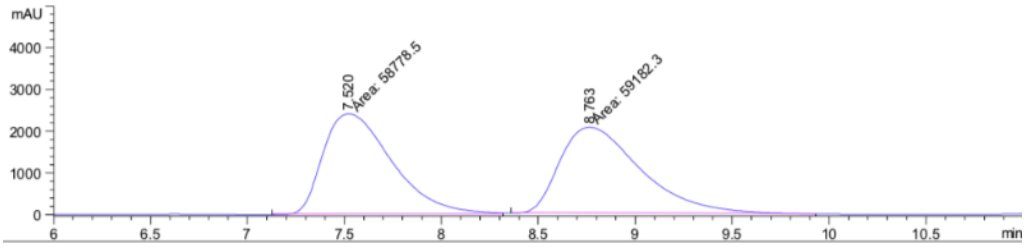
Signal 3: DAD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.244	BB	0.4938	26.22846	6.74327e-1	0.1906
2	10.904	BV R	0.5605	1.37357e4	376.49841	99.8094
Totals :				1.37620e4	377.17274	



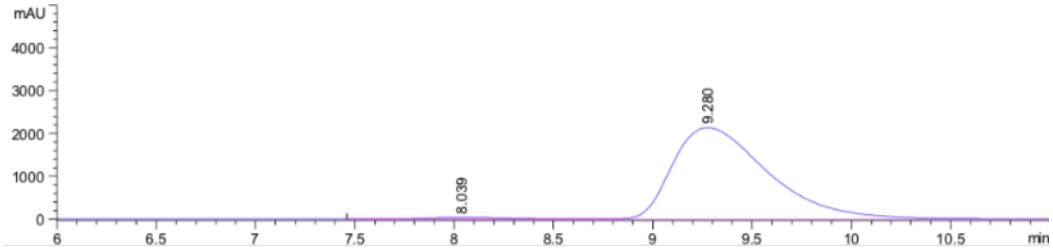
3q

(*S*)-*tert*-butyl (2-methylphenylsulfonamido)(phenylmethyl)carbamate (3q) The reaction was performed in 0.125mmol scale for 15h using 1 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 23mg, 99% yield, 97% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 8.04 min, t_R(major) = 9.28 min. $[\alpha]_D^{20}$ = +7.33 (*c* = 0.320, $CHCl_3$). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.97 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 – 7.20 (m, 8H), 6.74 (s, 1H), 6.14 (t, *J* = 8.8 Hz, 1H), 2.65 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 139.9, 136.9, 132.3, 132.2, 129.2, 128.3, 127.9, 126.2, 126.0, 78.7, 63.3, 27.6, 19.6. HRMS (ESI) Calcd for $C_{19}H_{24}N_2NaO_4S$ ($[M+Na]^+$) 399.1349, found 399.1340.



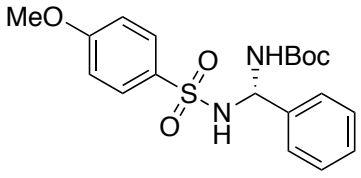
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.520	MM	0.4084	5.87785e4	2398.46484	49.8288
2	8.763	MM	0.4807	5.91823e4	2052.13135	50.1712
Totals :				1.17961e5	4450.59619	



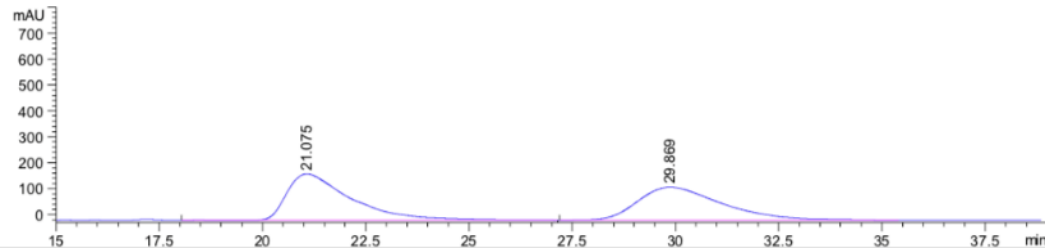
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.039	BV E	0.4403	1205.02185	41.80830	1.6160
2	9.280	VV R	0.5179	7.33648e4	2129.98462	98.3840
Totals :				7.45698e4	2171.79292	



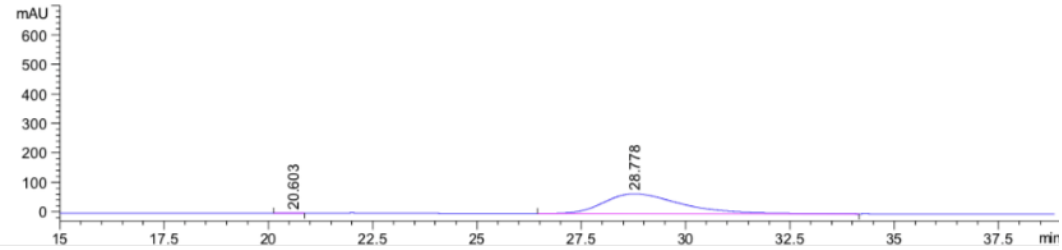
3r

(*S*)-*tert*-butyl (4-methoxyphenylsulfonamido)(phenylmethyl)carbamate (3r) The reaction was performed on a 0.125 mmol scale for 5 h using 5 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 23mg, 95% yield, >99% *ee*. HPLC analysis (Chiralcel OJ-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 20.60 min, t_R(major) = 28.78 min. $[\alpha]_D^{20}$ = -5.07 (*c* = 0.205, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.84 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 (td, *J* = 7.1, 6.2, 1.2 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.13 – 7.04 (m, 3H), 6.69 (d, *J* = 9.0 Hz, 1H), 6.19 (t, *J* = 8.8 Hz, 1H), 3.90 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 163.6, 155.2, 141.2, 134.7, 130.1, 129.2, 128.7, 127.1, 114.9, 79.6, 64.3, 56.1, 28.5. HRMS (ESI) Calcd for $C_{19}H_{24}N_2NaO_5S$ ([M+Na]$^+$) 415.1298, found 415.1299.



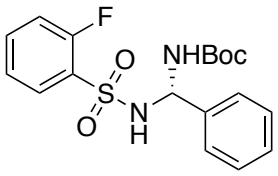
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.075	VV R	1.6207	1.92930e4	178.86012	51.7781
2	29.869	BB	2.1196	1.79679e4	127.23364	48.2219
Totals :				3.72610e4	306.09377	



Signal 4: DAD1 D, Sig=210,4 Ref=360,100

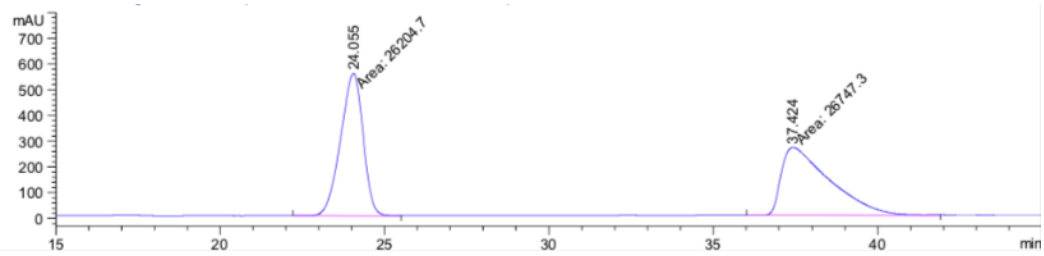
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.603	BB	0.2933	5.99921	3.16205e-1	0.0696
2	28.778	BB	1.9175	8614.58691	67.29176	99.9304
Totals :				8620.58612	67.60797	



3s

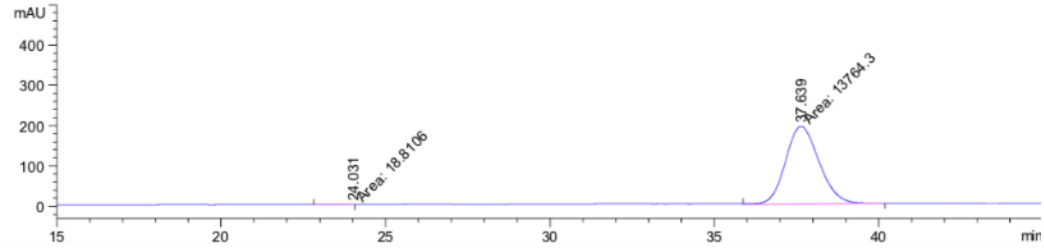
(*S*)-*tert*-butyl(2-fluorophenylsulfonamide)(phenylmethyl)carbamate (3s) The reaction was performed on a 0.125 mmol scale for 20 h using 1 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 47mg, 99% yield, >99% *ee*. M.P.: 160-161 ^{o}C. HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 24.03 min, t_R(major) = 37.64 min. $[\alpha]_D^{20}$ = -2.15 (*c* = 0.090, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.89 (td, *J* = 7.6, 1.8 Hz, 1H), 7.77 – 7.56 (m, 1H), 7.44 (dd, *J* = 23.2, 7.9 Hz, 3H), 7.38 – 7.26 (m, 5H), 6.76 (s, 1H), 6.19 (t, *J* = 9.0 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 159.8 (d, *J* = 253.5 Hz), 155.1, 140.6, 135.8 (d, *J* = 8.5 Hz), 131.0, 130.6 (d, *J* =

13.8 Hz), 129.2, 128.8, 127.1, 125.4 (d, J = 3.6 Hz), 117.6 (d, J = 21.1 Hz), 79.8, 64.4, 28.5. HRMS (ESI) Calcd for $C_{18}H_{21}FN_2NaO_4S$ ($[M+Na]^+$) 403.1098, found 403.1109.



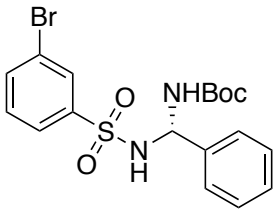
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.055	MM	0.7911	2.62047e4	552.06421	49.4877
2	37.424	MM	1.6998	2.67473e4	262.26611	50.5123
Totals :				5.29520e4	814.33032	



Signal 2: DAD1 B, Sig=220,4 Ref=off

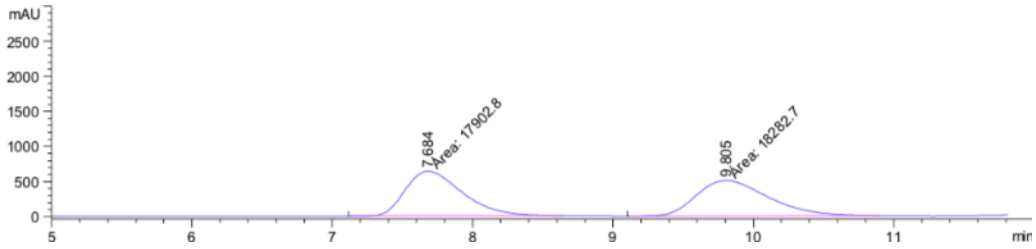
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.031	MM	0.9701	18.81063	3.23163e-1	0.1365
2	37.639	MM	1.1912	1.37643e4	192.57817	99.8635
Totals :				1.37831e4	192.90133	



3t

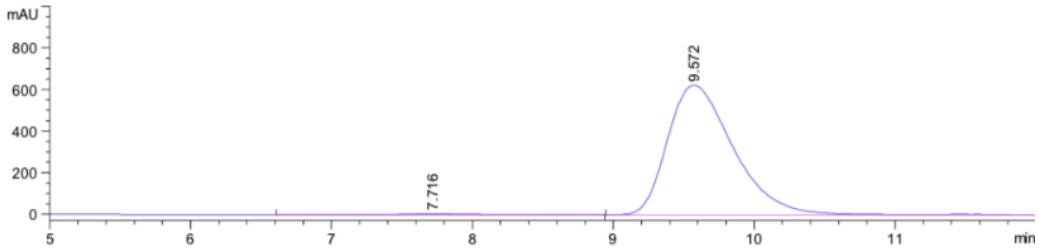
(*S*)-*tert*-butyl (3-bromophenylsulfonamido)(phenylmethyl)carbamate (3t) The reaction was performed in 0.25mmol scale for 22h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 53mg, 96% yield, 99% *ee*. M.P.: 124-125 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 7.72 min, t_R(major) = 9.57 min. $[\alpha]_D^{20}$ = -3.63 (c = 0.270, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.03 (t, J = 1.9 Hz, 1H), 7.91 (dt, J = 7.9, 1.3 Hz, 1H), 7.80 (ddd, J = 8.1, 2.0, 1.0 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.38 – 7.32

(m, 2H), 7.32 – 7.28 (m, 1H), 6.89 – 6.79 (m, 1H), 6.24 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 145.2, 140.6, 136.0, 131.8, 130.7, 129.3, 129.0, 127.1, 126.8, 123.0, 79.9, 64.5, 28.6. HRMS (ESI) Calcd for $C_{18}H_{21}BrN_2NaO_4S$ ([M+Na]$^+$) 463.0298, found 463.0298.



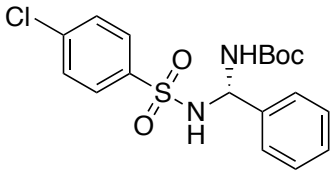
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.684	MM	0.4707	1.79028e4	633.87115	49.4750
2	9.805	MM	0.6004	1.82827e4	507.52985	50.5250
Totals :				3.61855e4	1141.40100	



Signal 3: DAD1 C, Sig=220,4 Ref=off

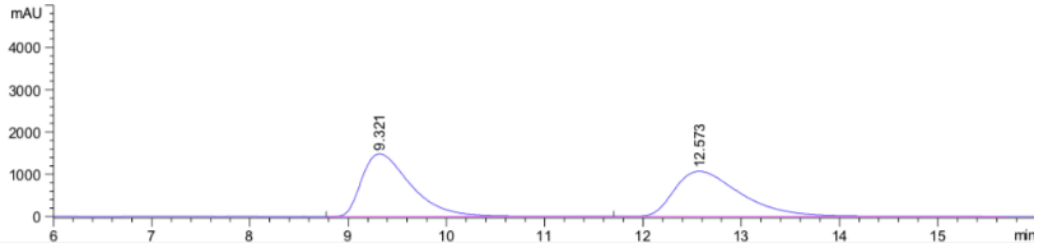
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.716	VB R	0.4573	140.37172	4.28236	0.6849
2	9.572	BV R	0.5067	2.03546e4	622.62317	99.3151
Totals :				2.04950e4	626.90553	



3u

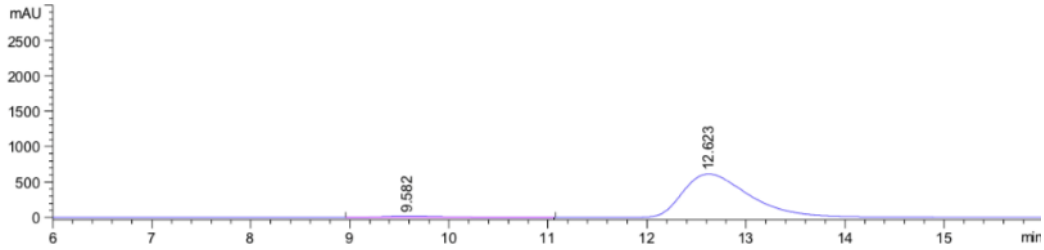
(*S*)-*tert*-butyl (4-chlorophenylsulfonamido)(phenylmethyl)carbamate (3u) The reaction was performed in 0.125mmol scale for 15h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 24mg, 99% yield, 95% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 9.58 min, t_R(major) = 12.26 min. $[\alpha]_D^{20}$ = -11.15 (*c* = 0.160, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.93 – 7.87 (m, 2H), 7.62 – 7.55 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.32 – 7.27 (m, 1H), 6.72 (s, 1H), 6.23 (t, *J* = 8.8 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6)

δ 155.2, 142.0, 140.8, 138.7, 129.9, 129.8, 129.3, 128.8, 127.1, 79.8, 64.4, 28.5. HRMS (ESI) Calcd for $C_{18}H_{21}ClN_2NaO_4S$ ([M+Na]$^+$) 419.0803, found 419.0804.



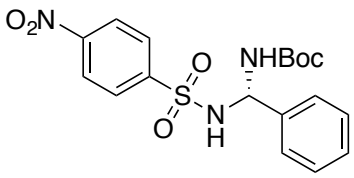
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.321	VB	0.5323	5.13444e4	1481.76953	50.5758
2	12.573	BB	0.7251	5.01754e4	1066.08545	49.4242
Totals :				1.01520e5	2547.85498	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

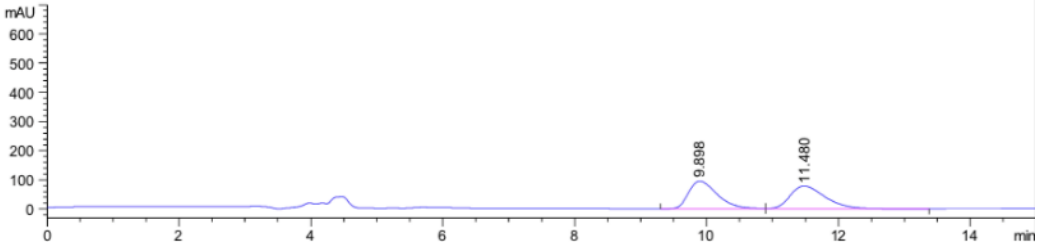
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.582	BB	0.5700	761.34729	20.46556	2.5552
2	12.623	BBA	0.7282	2.90352e4	613.43097	97.4448
Totals :				2.97965e4	633.89653	



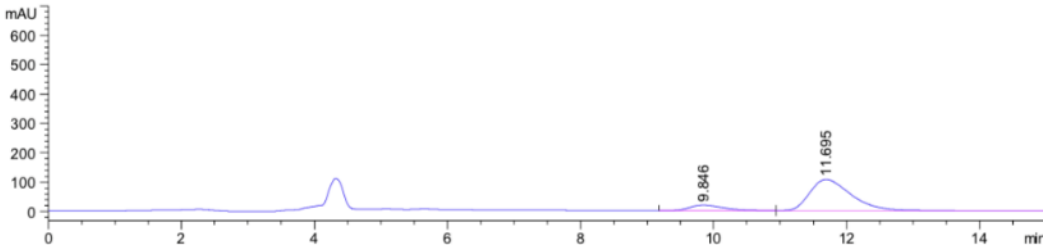
3v

(*S*)-*tert*-butyl (4-nitrophenylsulfonamido)(phenylmethyl)carbamate (3v) The reaction was performed in 0.125mmol scale for 50h using 1 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 21mg, 84% yield, 75% *ee*. M.P.: 136-137 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 80:20 hexanes/iPrOH): t_R(minor) = 9.85 min, t_R(major) = 11.70 min. $[\alpha]_D^{20}$ = +10.93 (*c* = 0.320, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.43 – 8.36 (m, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 (dd, *J* = 8.4, 6.1 Hz, 1H), 6.82 (s, 1H), 6.27 (t, *J* = 8.7 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, Acetone-d_6) δ 155.2, 150.9, 148.7, 140.3, 129.5, 129.4, 129.0, 127.1, 124.9, 79.9, 64.7, 28.4. HRMS (ESI) Calcd for $C_{18}H_{21}N_3NaO_6S$ ([M+Na]$^+$) 430.1043, found 430.1042.

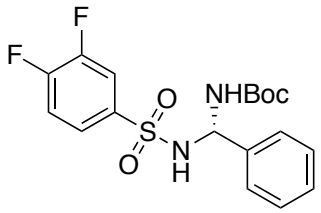


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.898	BV	0.4695	2897.25757	95.08879	49.6369
2	11.480	VB	0.5764	2939.64648	78.23058	50.3631
Totals :				5836.90405	173.31937	



Signal 2: DAD1 B, Sig=220,4 Ref=off

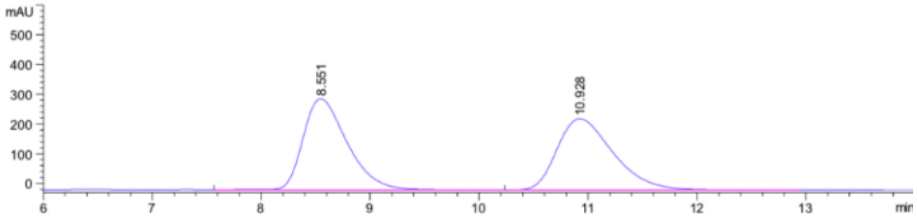
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.846	BV	0.5561	670.68481	18.44890	12.5653
2	11.695	VV R	0.6728	4666.90869	105.85408	87.4347
Totals :				5337.59351	124.30298	



3w

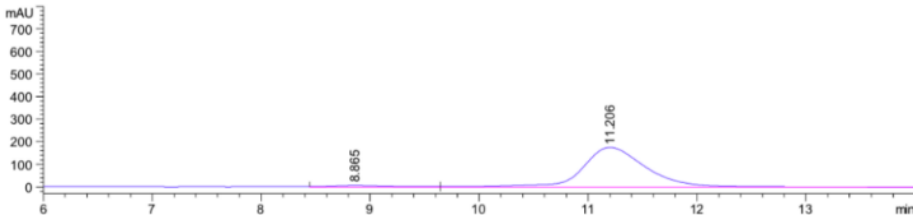
(*S*)-*tert*-butyl (3,4-difluorophenylsulfonamido)(phenylmethyl)carbamate (3w) The reaction was performed in 0.125mmol scale for 5h using 5 mol% Ca[(*R*)-**PA**]$_2$ in toluene. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 24mg, 96% yield, 95% *ee*. M.P.: 141-142 ^{o}C. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 8.87 min, t_R(major) = 11.21 min. $[\alpha]_D^{20}$ = +10.20 (*c* = 0.445, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.82 (td, *J* = 7.4, 3.5 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.54 (dt, *J* = 10.4, 8.2 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.29 (m, 1H),

6.83 (s, 1H), 6.23 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 155.3, 153.4 (dd, J = 252.7, 12.7 Hz), 150.5 (dd, J = 255.8, 13.4 Hz), 140.5, 140.3, 129.3, 128.9, 125.6 (d, J = 7.0 Hz), 118.9 (d, J = 19.7 Hz), 117.8 (d, J = 20.8 Hz), 79.8, 64.5, 28.4. HRMS (ESI) Calcd for $C_{18}H_{20}F_2N_2NaO_4S$ ([M+Na]$^+$) 421.1004, found 421.1001.



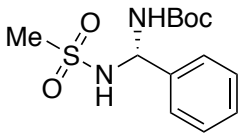
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.551	VB R	0.4308	8597.42676	305.78113	50.1878
2	10.928	BB	0.5445	8533.06836	239.04318	49.8122
Totals :				1.71305e4	544.82431	



Signal 2: DAD1 B, Sig=220,4 Ref=off

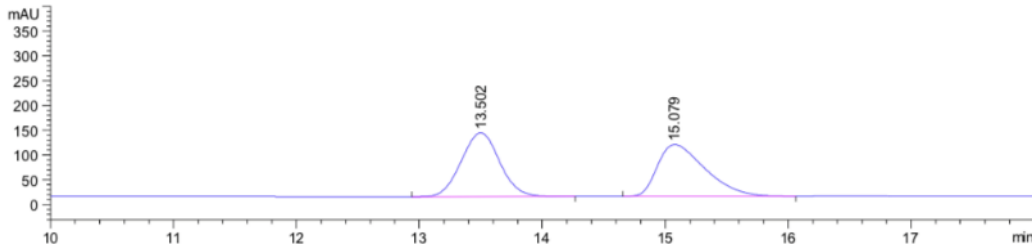
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.865	VV	0.4640	175.76302	5.69625	2.4796
2	11.206	VBA	0.5988	6912.50000	174.25714	97.5204
Totals :				7088.26302	179.95339	



3x

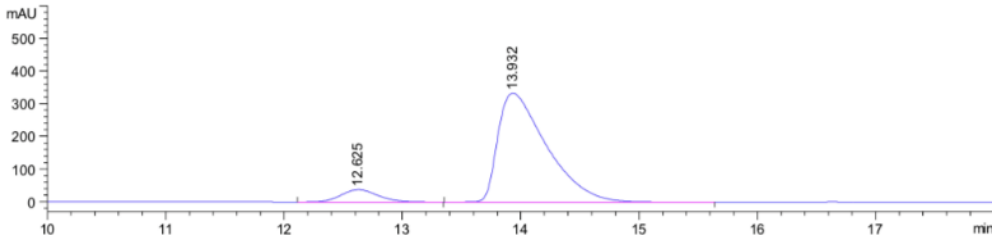
(*S*)-*tert*-butyl (4-methylsulfonamido)(phenylmethyl)carbamate (3x) The reaction was performed in 0.25mmol scale for 3h using 5 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 35mg, 94% yield, 84% *ee*. M.P.: 143-144 ^{o}C. HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 12.63 min, t_R(major) = 13.93 min. $[\alpha]_D^{20}$ = +1.64 (c = 0.340, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.53 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.3 Hz, 1H), 7.05 (d, J = 8.9 Hz, 1H), 6.89 (d, J = 9.0 Hz, 1H), 6.25 (t, J = 9.1 Hz, 1H), 3.06 (s, 3H), 1.45 (s,

9H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.1, 141.0, 129.3, 128.8, 127.2, 80.1, 64.4, 42.0, 28.5. HRMS (ESI) Calcd for $C_{13}H_{20}N_2NaO_4S$ ([M+Na]$^+$) 323.1036, found 323.1048.



Signal 3: DAD1 C, Sig=220,4 Ref=360,100

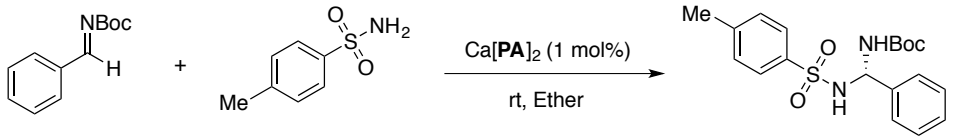
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.502	BB	0.3402	2799.68726	128.48338	49.8816
2	15.079	BB	0.4147	2812.98364	104.29829	50.1184
Totals :				5612.67090	232.78167	



Signal 3: DAD1 C, Sig=220,4 Ref=off

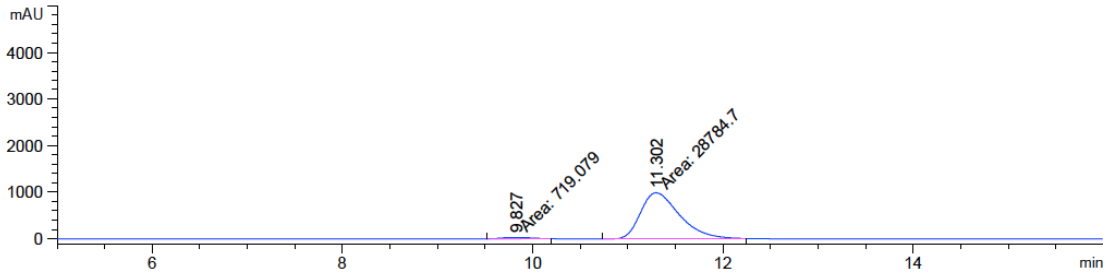
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.625	BB	0.3326	806.94025	37.56426	7.7973
2	13.932	BB	0.4279	9542.06738	333.39578	92.2027
Totals :				1.03490e4	370.96004	

Large scale reaction producing product 3p



1p, 1 mmol **2a,** 0.5 mmol **3p,** 97%, 95% *ee*

The reaction was performed in a 1 mmol scale (imine). The reaction was run for 4h using 1 mol% Ca[(*R*)-**PA**]$_2$ in ether. The product was obtained by flash chromatography (hexane: acetone = 4:1) as a white solid 183.6 mg, 97% yield, 95% *ee*. HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(minor) = 9.83 min, t_R(major) = 11.30 min.



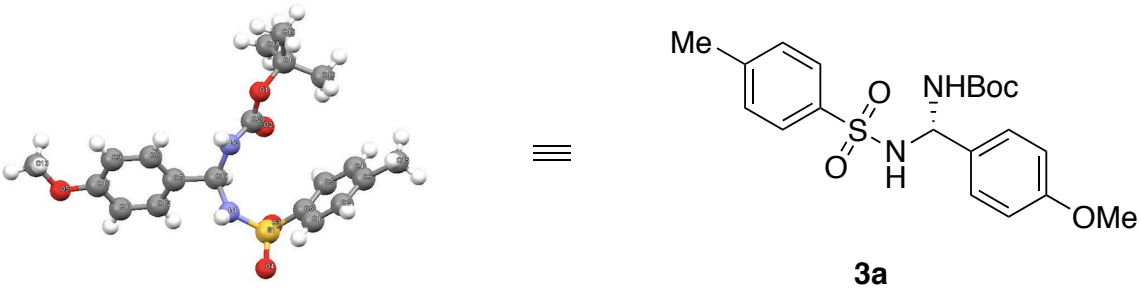

```
Signal 2: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.827 MM    0.3621  719.07947   33.10196   2.4372
   2  11.302 MM    0.4826 2.87847e4   994.14484  97.5628

Totals :                 2.95038e4  1027.24679
```

Crystal growth conditions and data

Crystal growth conditions of 3a

After dissolving the compound **3a** in minimal acetone, an appropriate amount of hexanes was added and then allowed to stand at room temperature. Some small holes were punctured into the sealing film on the bottle. After leaving it in a cool place for some time, slow evaporation of the solvent allowed for X-ray quality crystals to form.

X-ray structure of 3a



3a

Craystal measurement and data for 3a

Bond precision:	C-C = 0.0085 A		Wavelength=1.54184
Cell:	a=5.1266(2)	b=20.3732(11)	c=20.4123(12)
	alpha=90	beta=90	gamma=90
Temperature:	160 K		

	Calculated	Reported
Volume Space group Hall group	2131.97(19) P 21 21 21	2131.97(19) P 21 21 21
Moiety formula	P 2ac 2ab C20 $H_{20}H_{26}N_2O_5S$	P 2ac 2ab $C_{20}H_{26}N_2O_5S$
Sum formula	$C_{20}H_{26}N_2O_5S$	$C_{20}H_{26}N_2O_5S$
Mr	406.49	406.49
Dx,g cm^{-3}	1.266	1.266
Z	4	4
Mu (mm-1)	1.623	1.623
F000	864.0	864.0
F000’	867.90	
h,k,lmax	6,25,25	6,25,25

Nref	4540[2648]	4273
Tmin,Tmax	0.943,0.952	0.378,1.000
Tmin’	0.922	

Correction method= # Reported T Limits: Tmin=0.378 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.61/0.94 Theta(max)= 77.396

R(reflections)= 0.0501(3093) wR2(reflections)= 0.1485(4273)

S = 1.051 Npar= 267

References

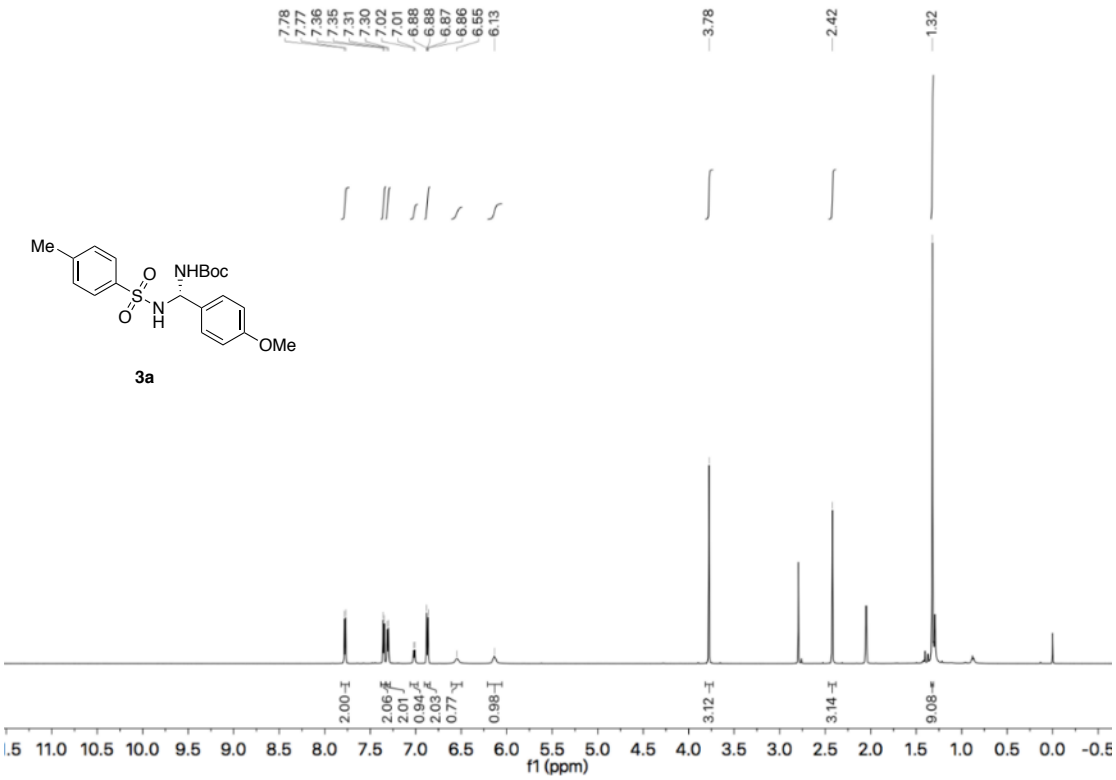
1. (a) Ding, Z. S.; Osminski, W. E. G.; Ren, H.; Wulff, W. D. Scalable Syntheses of the Vaulted Biaryl Ligands VAPOL and VANOL via the Cycloaddition/Electrocyclization Cascade. *Org. Process Res. Dev.* **2011**, *15*, 1089. (b) Desai, A. A.; Huang, L.; Wulff, W. D.; Rowland, G. B.; Antilla, J. C. Gram-Scale Preparation of VAPOL Hydrogenphosphate: A Structurally Distinct Chiral Brønsted Acid. *Synthesis* **2010**, 2106. (c) Gupta, A. K.; Zhang, X.; Staples, R. J.; Wulff, W. D. The *iso*-VAPOL Ligand: Synthesis, Solid-State Structure and its Evaluation as a BOROX Catalyst. *Catal. Sci. Technol.* **2014**, *4*, 4406.

2. Zheng, W. H.; Zhang, Z. H.; Kaplan, M. J.; Antilla, J. C. Chiral Calcium VAPOL Phosphate Mediated Asymmetric Chlorination and Michael Reactions of 3-Substituted Oxindoles. *J. Am. Chem. Soc.* **2011**, *133*, 3339.

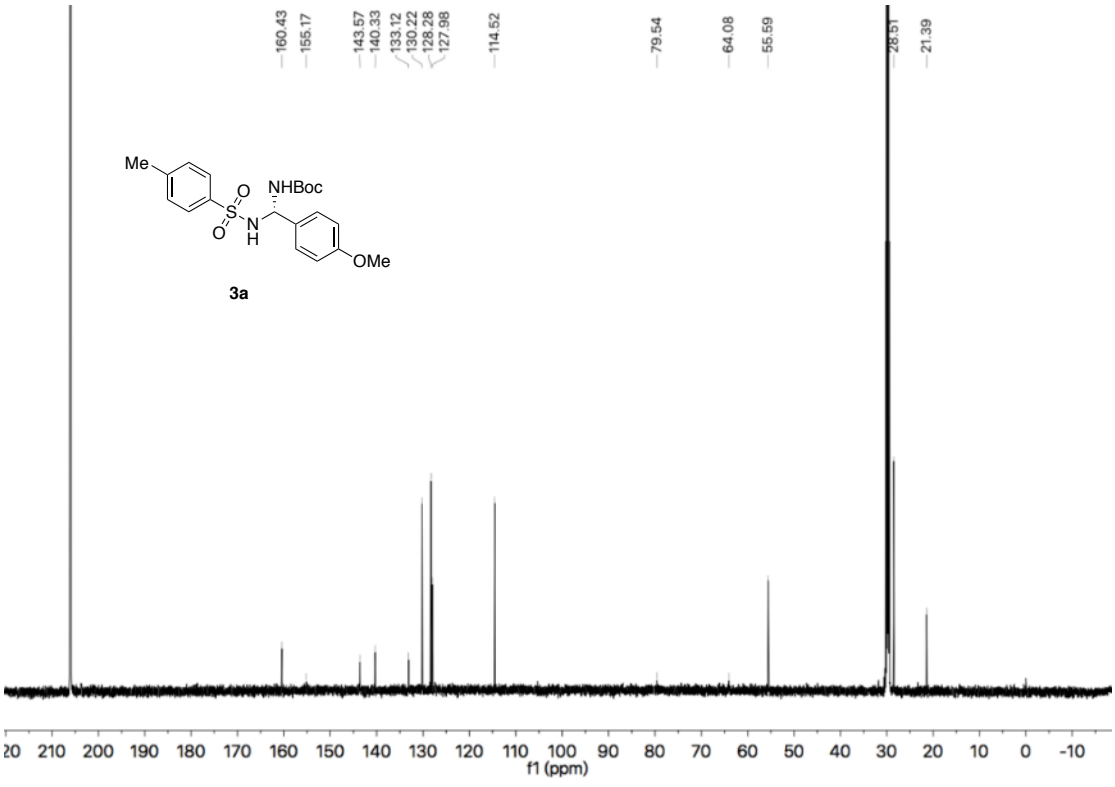
3. Wenzel, A. G.; Jacobsen, E. N. Asymmetric catalytic Mannich reactions catalyzed by urea derivatives: Enantioselective synthesis of beta-aryl-beta-amino acids. *J. Am. Chem. Soc.* **2002**, *124*, 12964.

^{1}H-NMR, ^{13}C-NMR spectra data

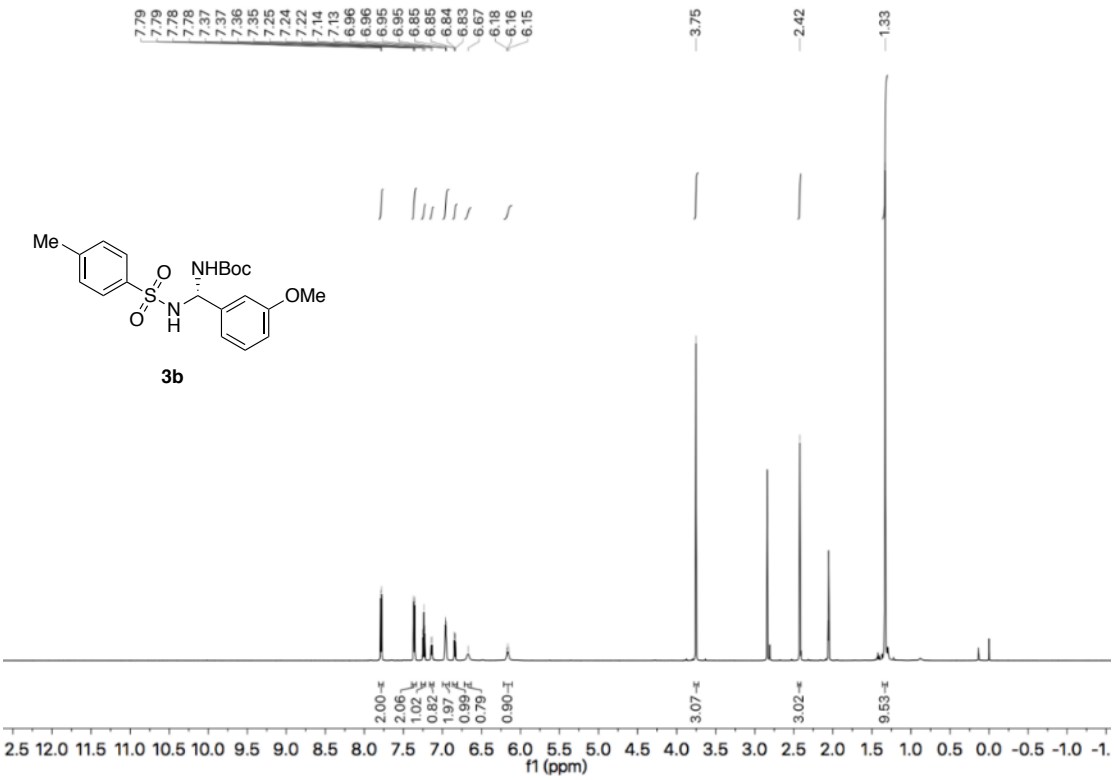
[1]H-NMR (600 MHz, Acetone-d_6) of compound of **3a**



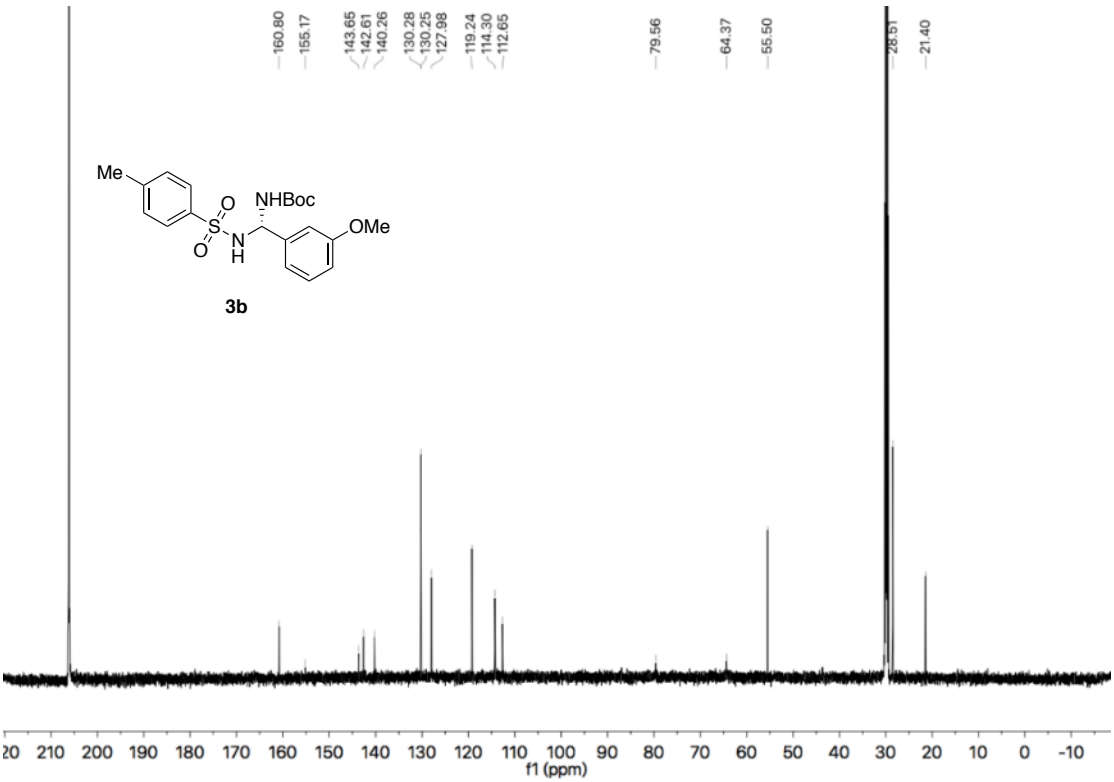
[13]C-NMR (150 MHz, Acetone-d_6) of compound of **3a**



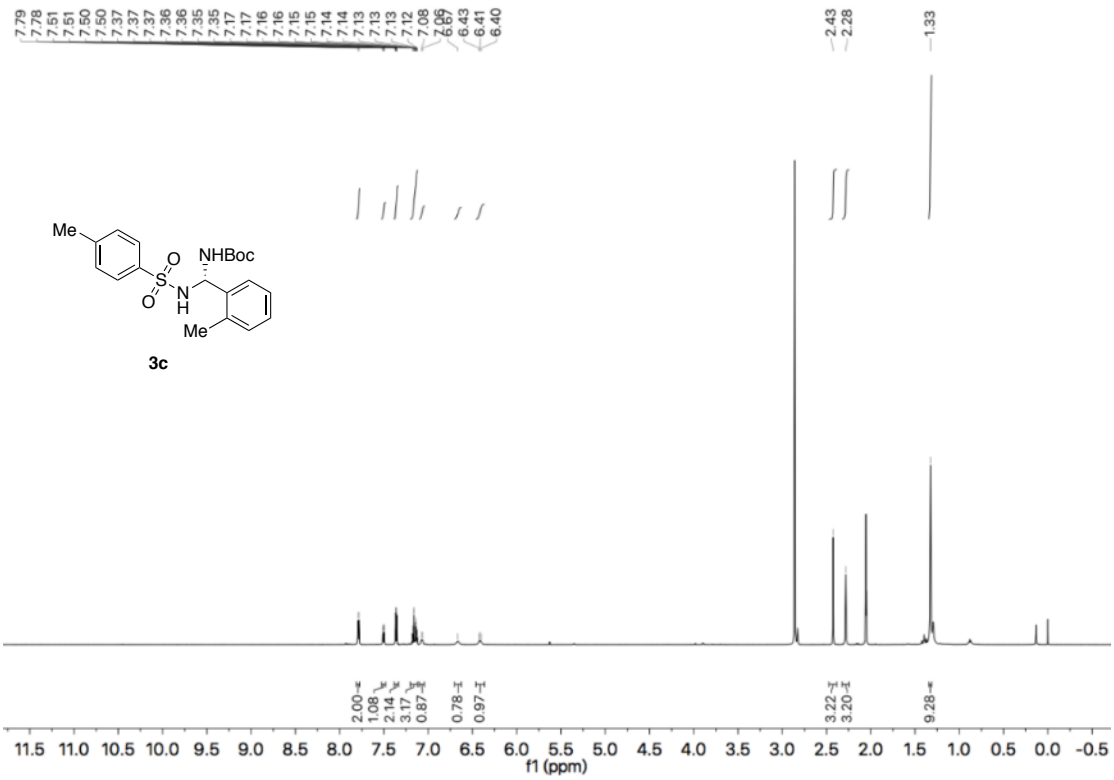
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3b**



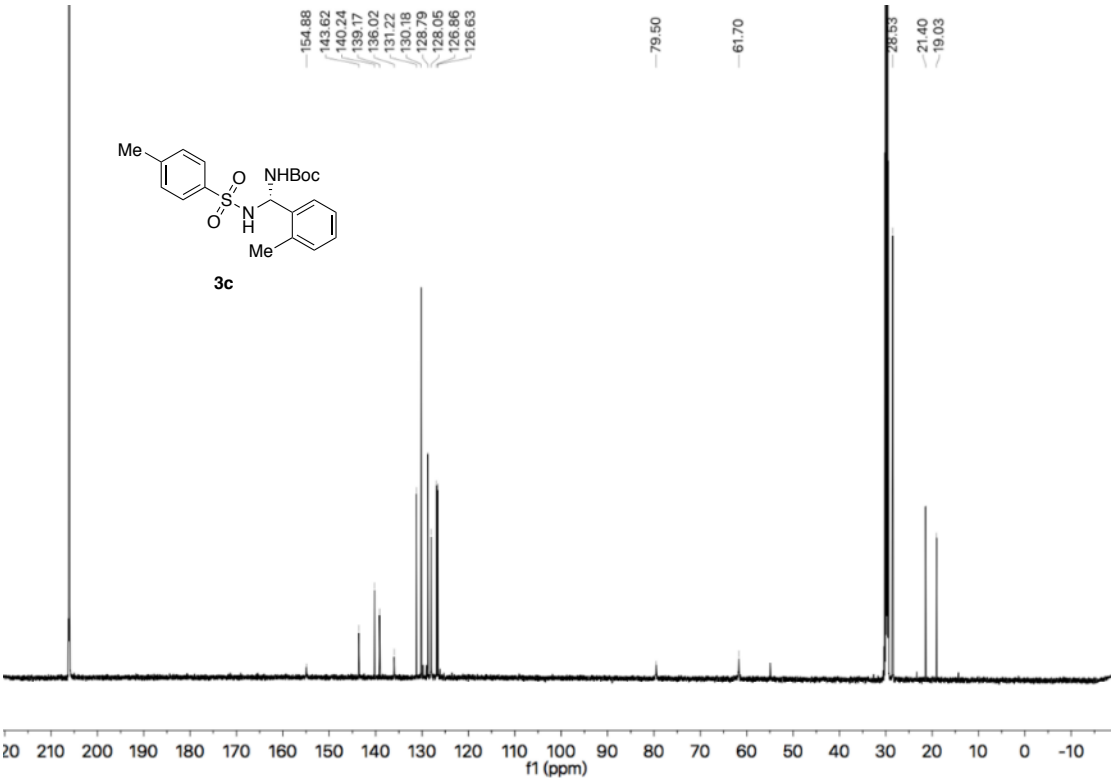
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3b**



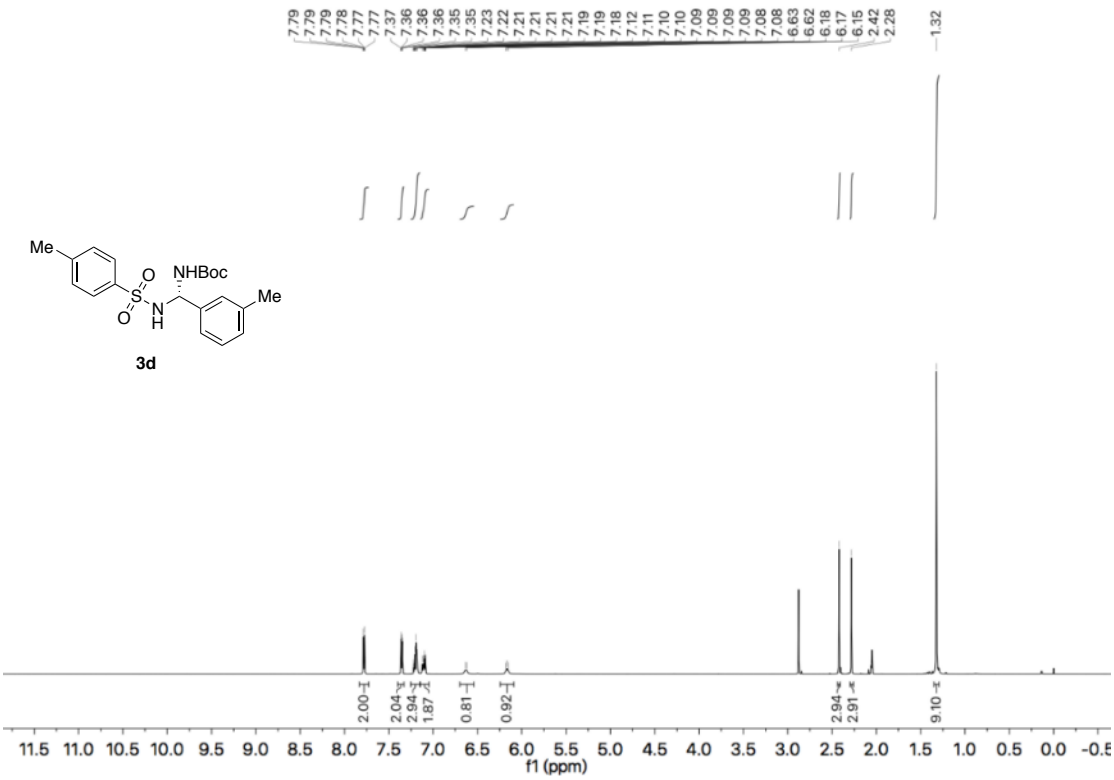
[1]H-NMR of (600 MHz, Acetone-d_6) compound of **3c**



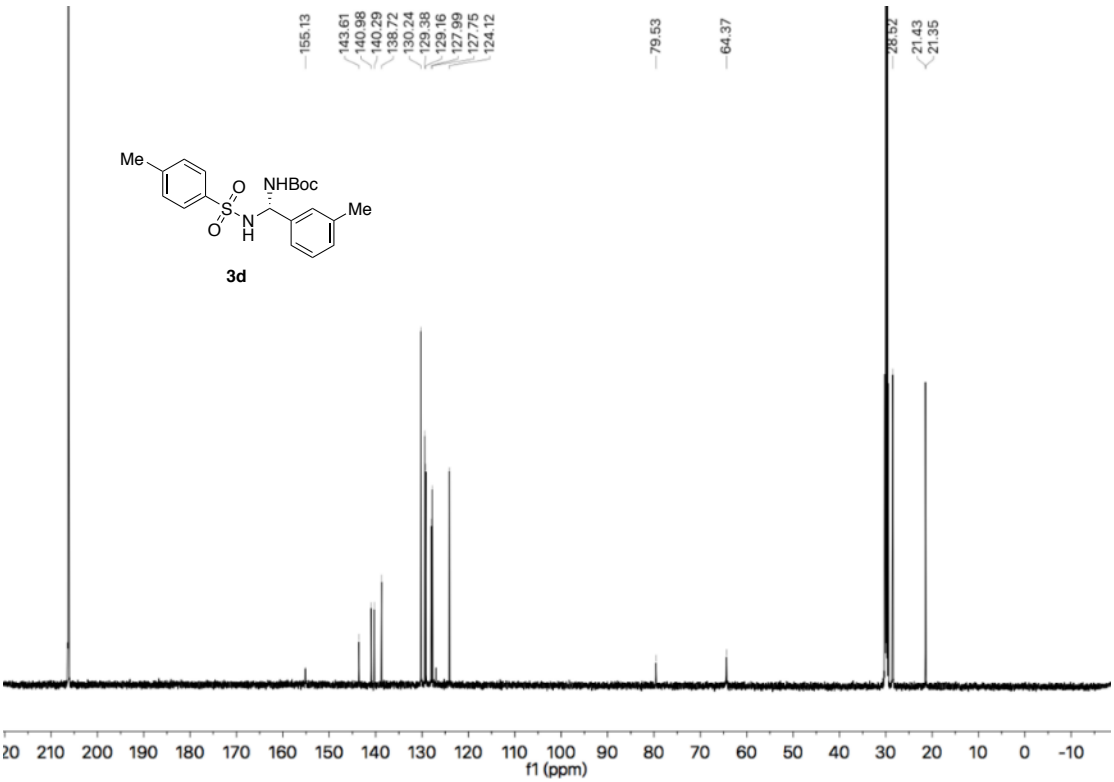
[13]C-NMR (150 MHz, Acetone-d_6) of compound of **3c**



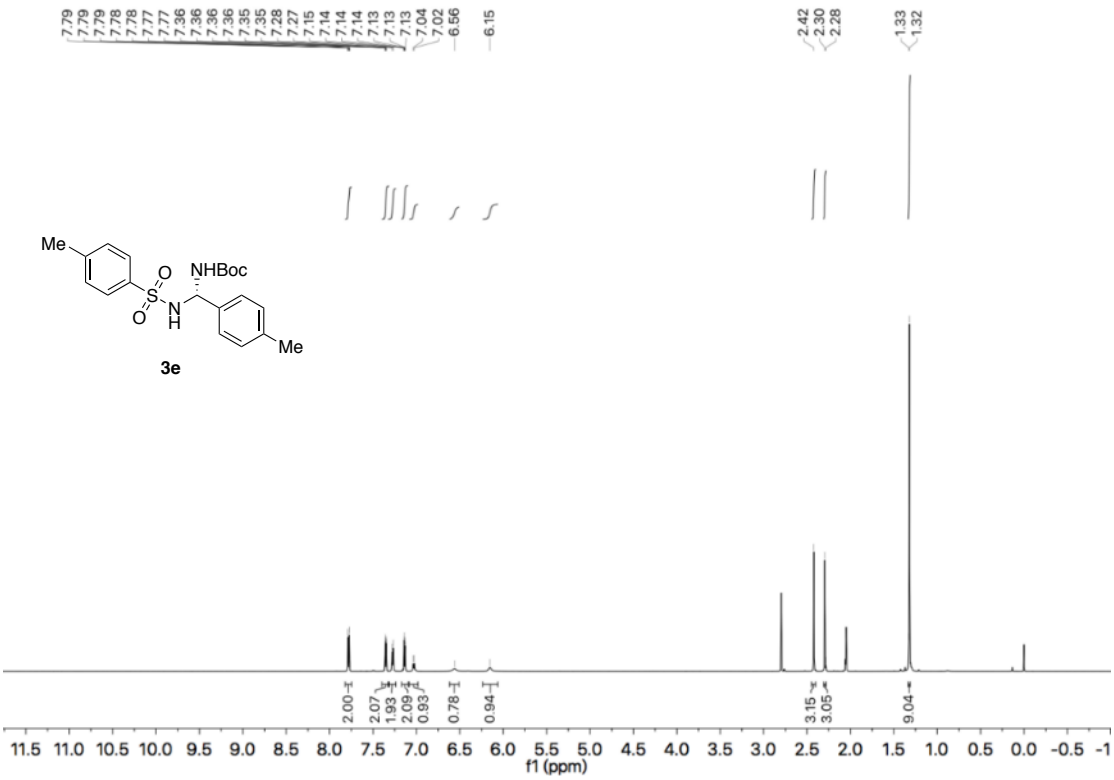
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3d**



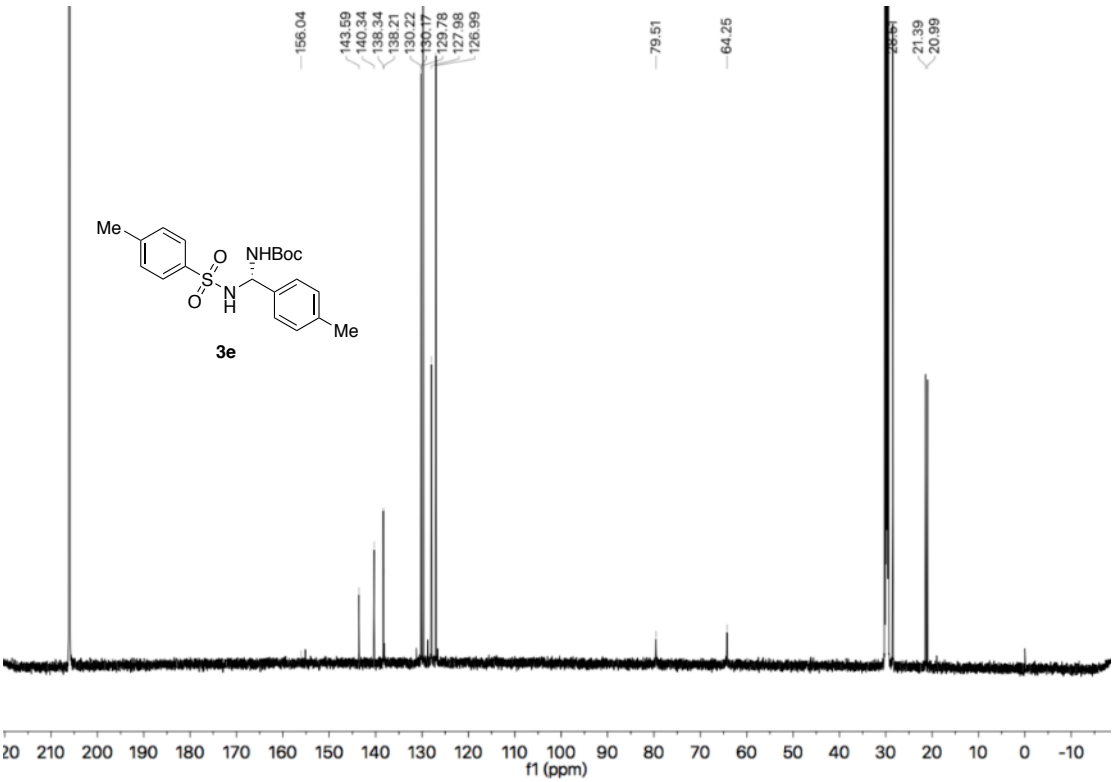
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3d**



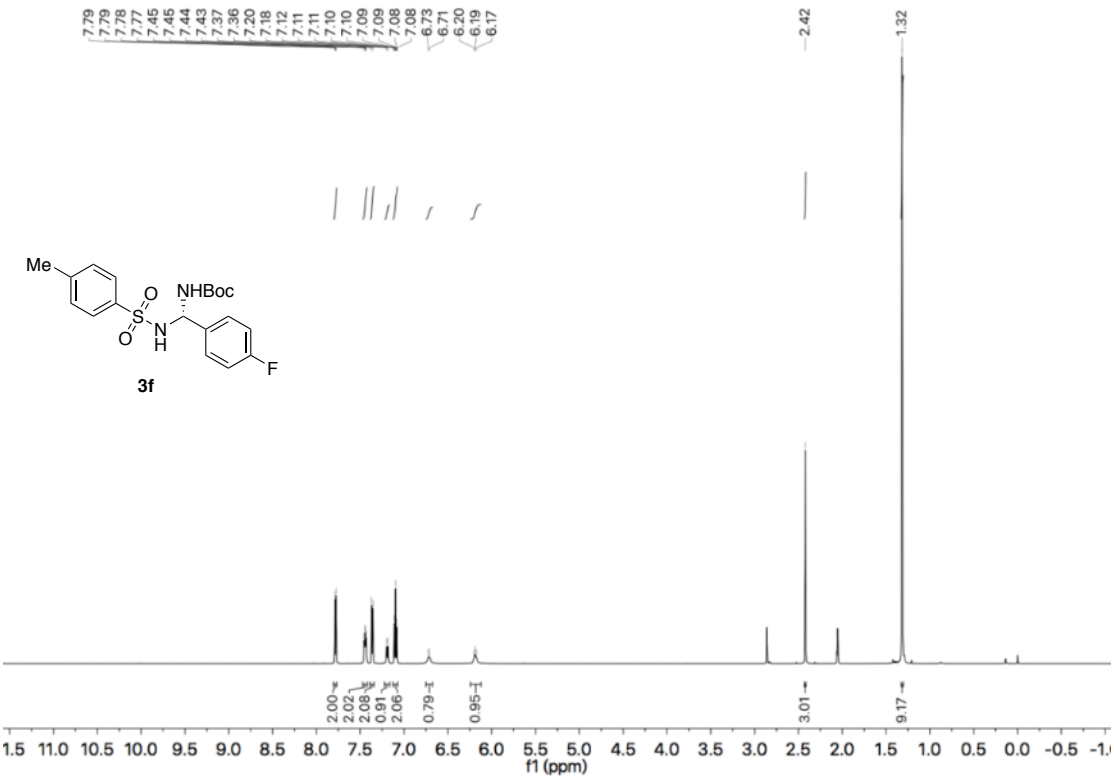
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3e**



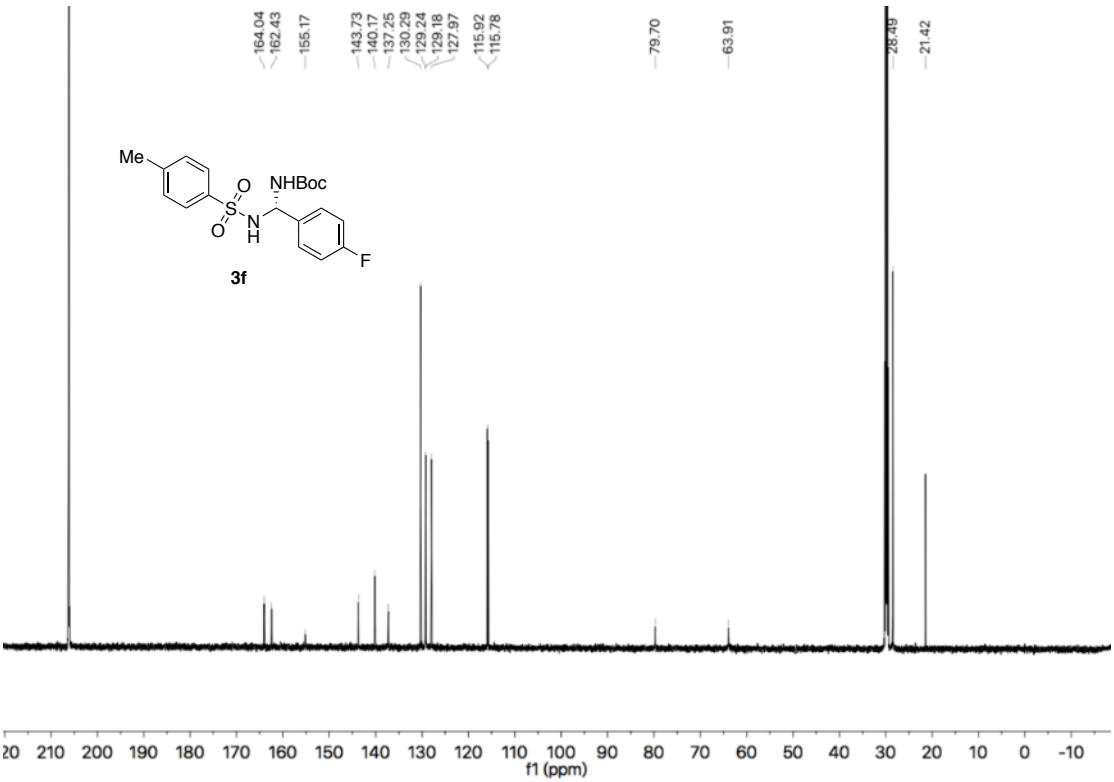
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3e**



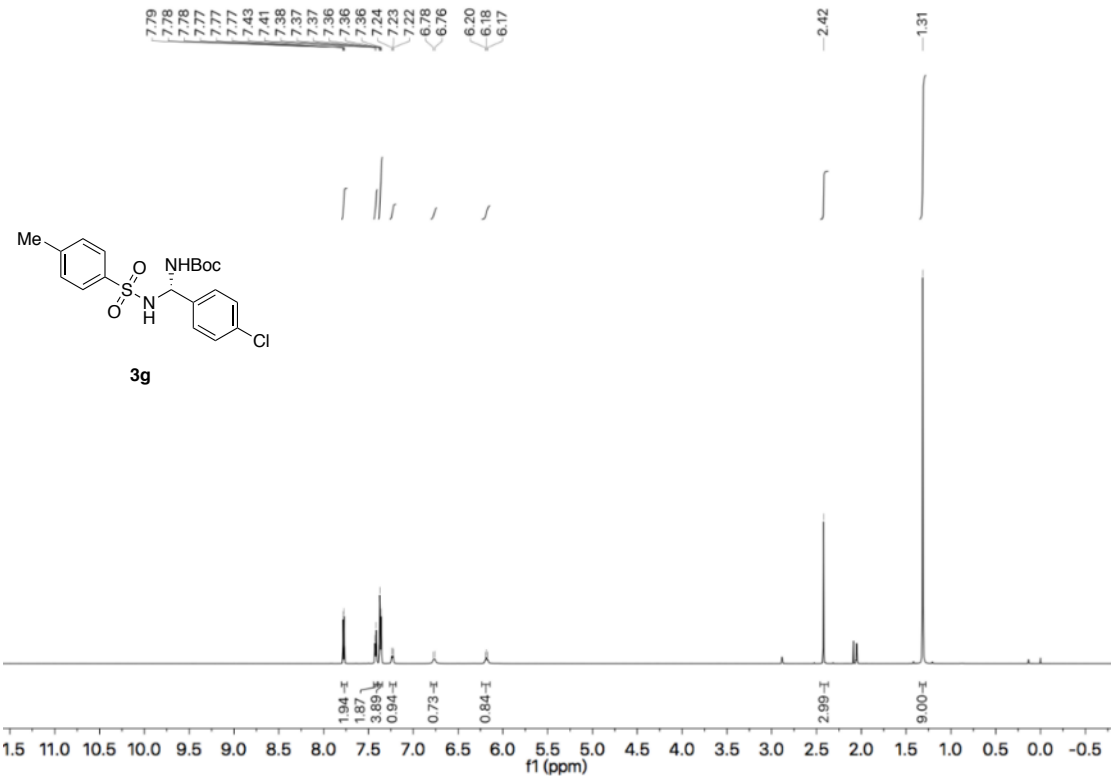
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3f**



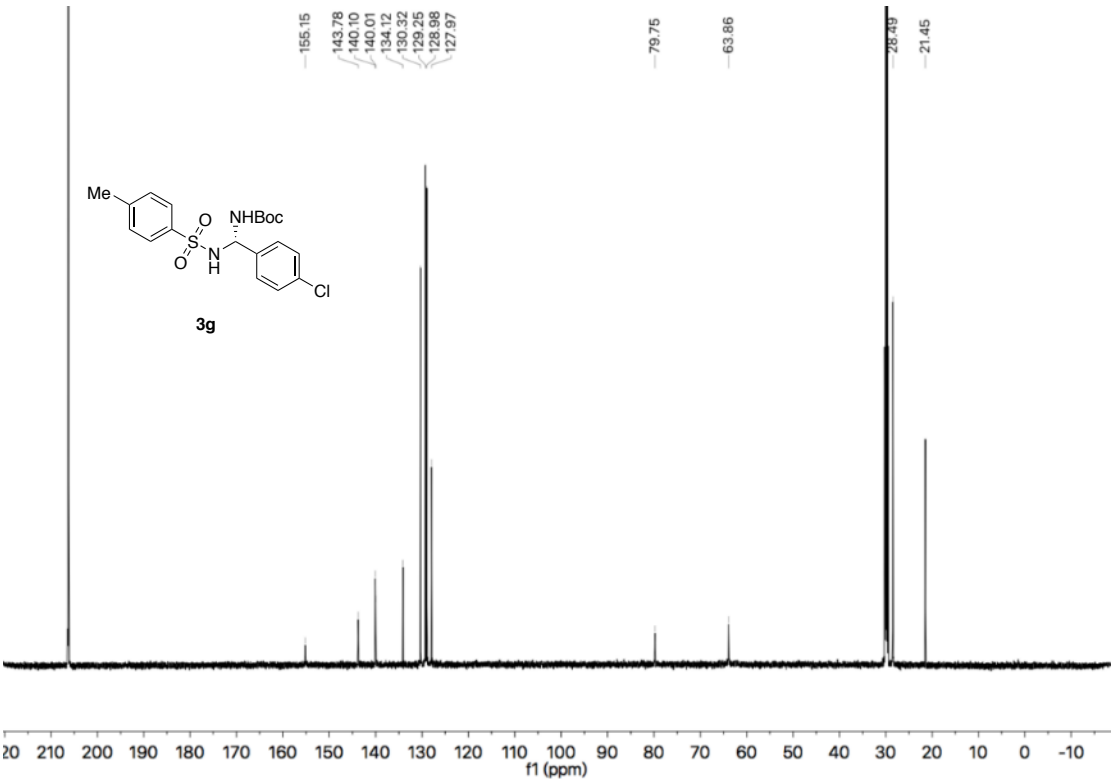
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3f**



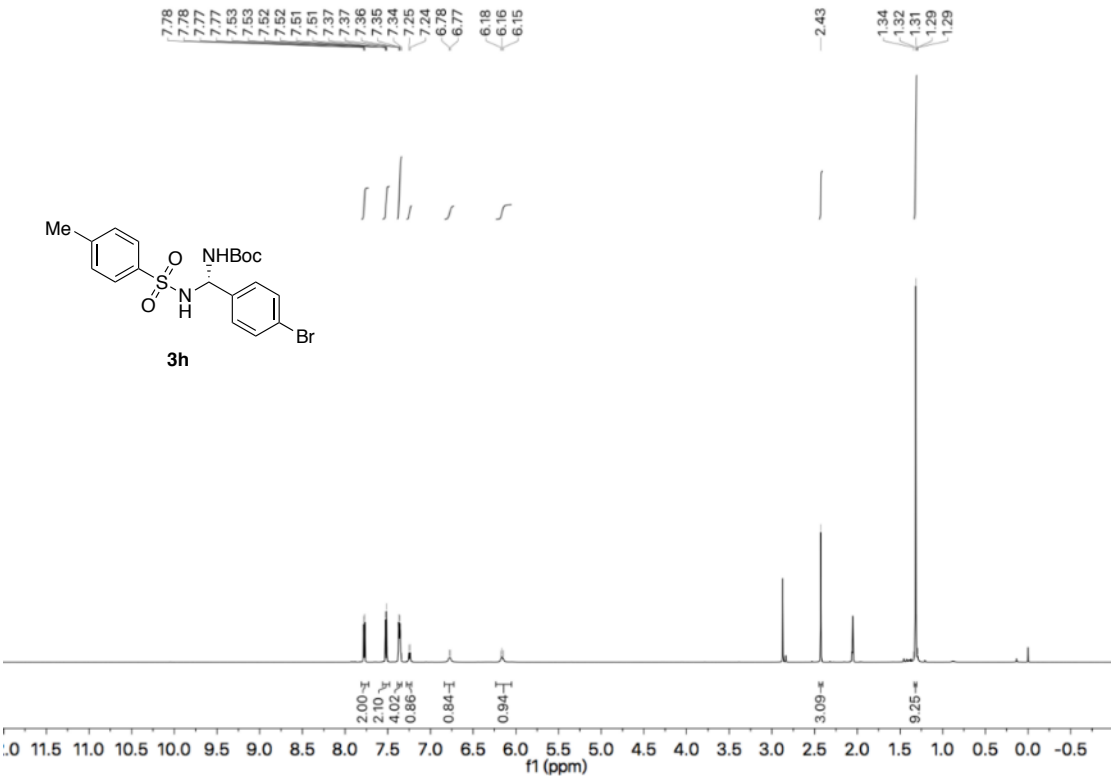
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3g**



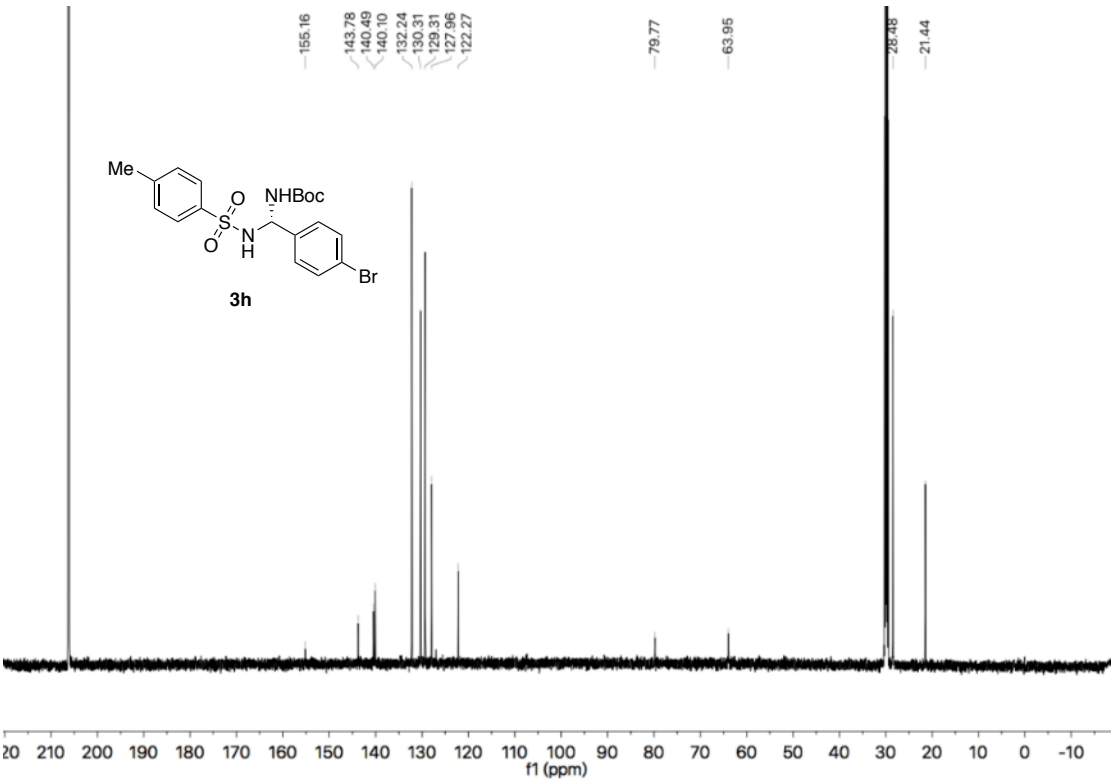
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3g**



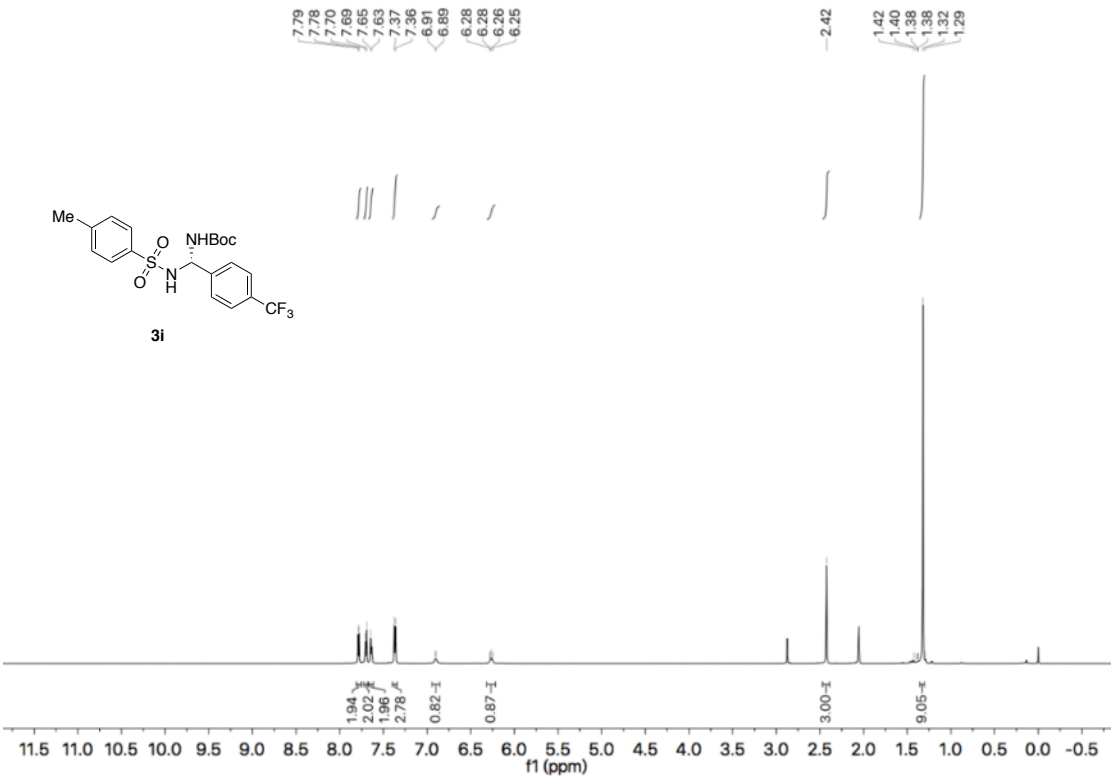
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3h**



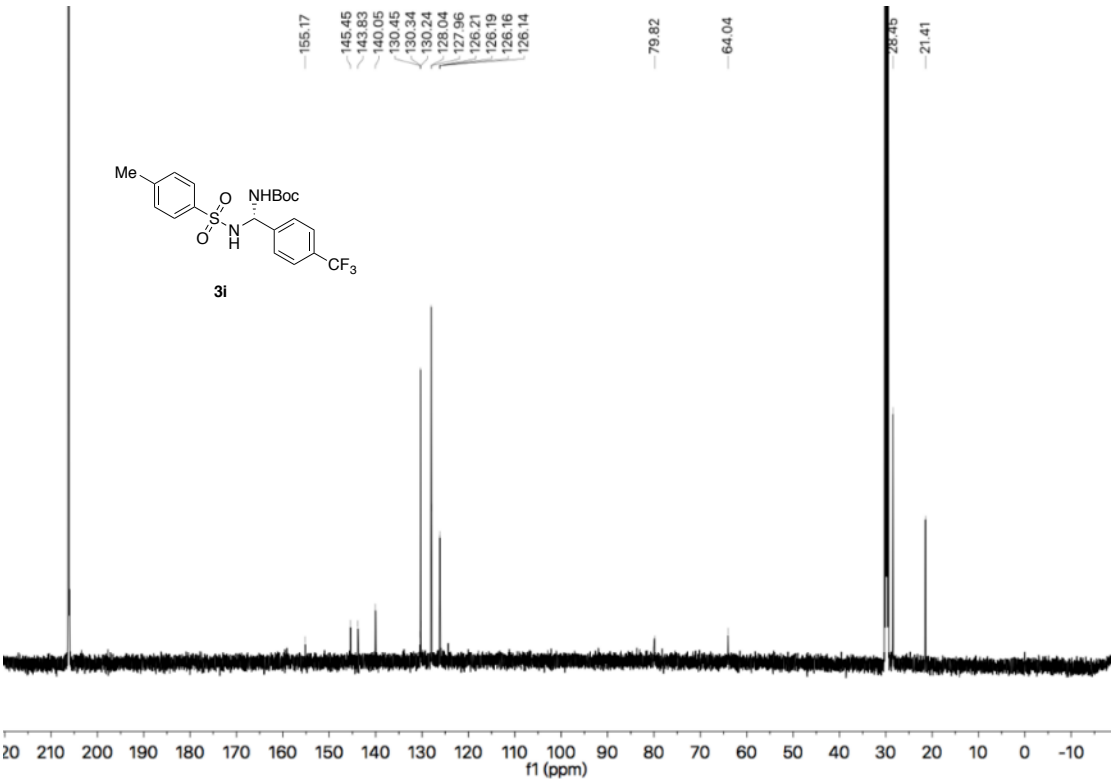
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3h**



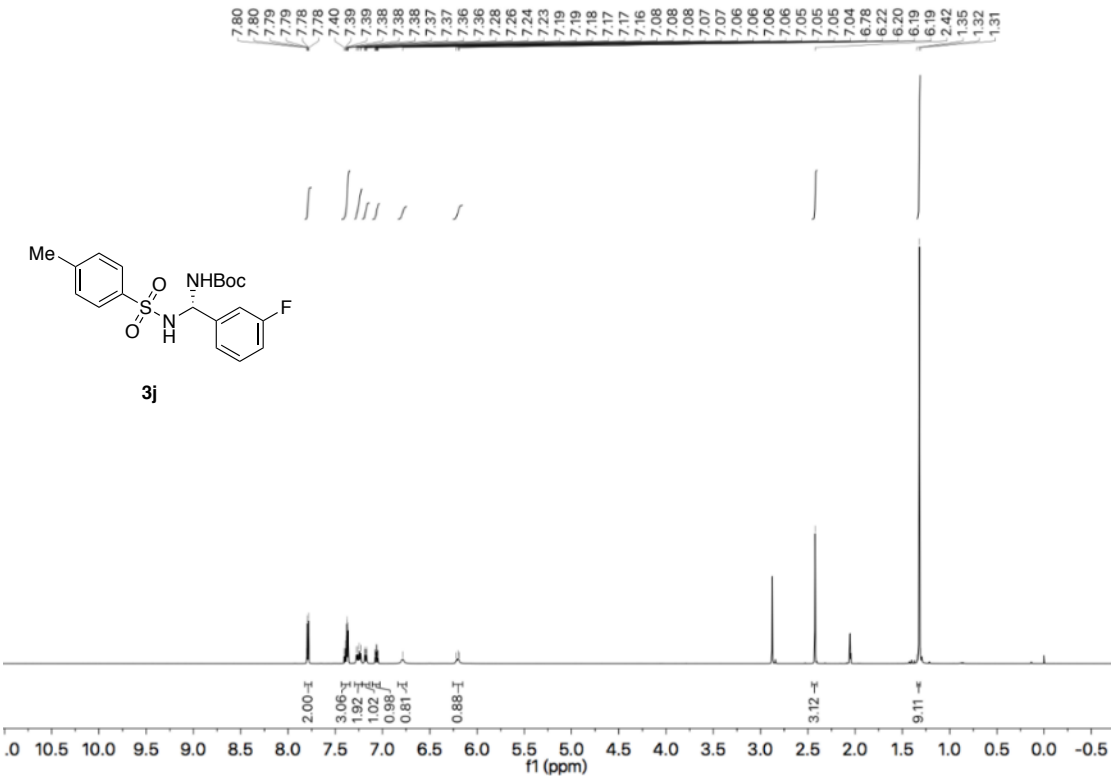
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3i**



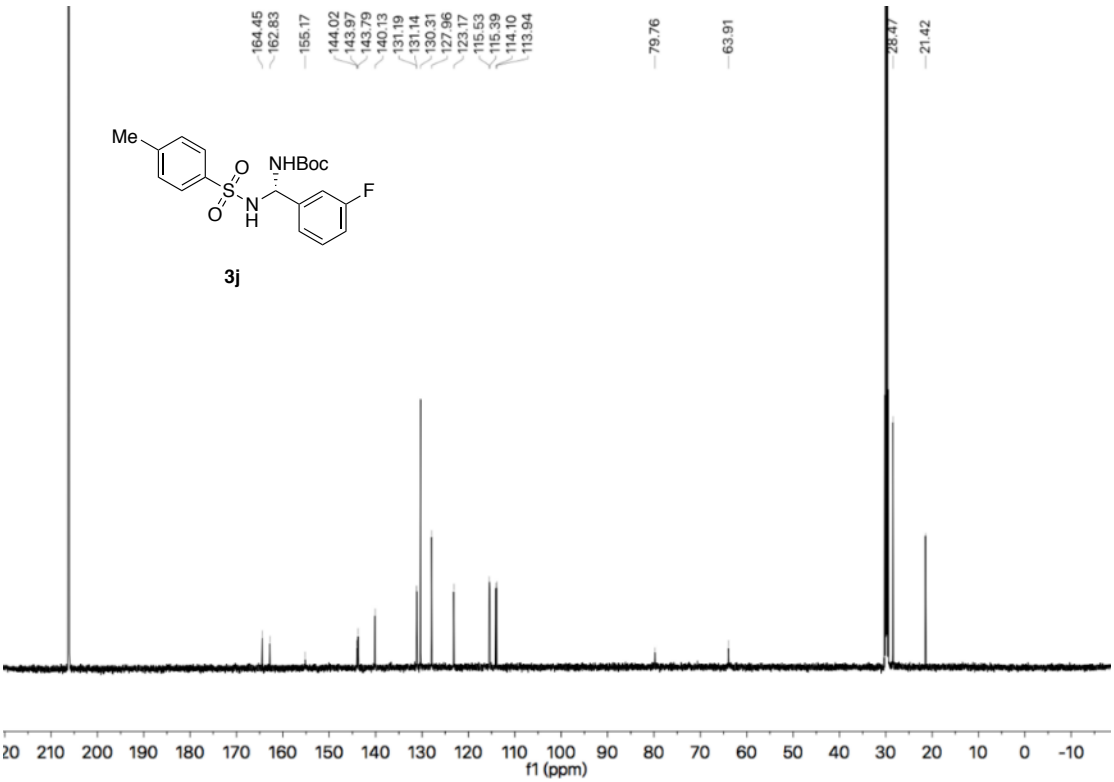
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3i**



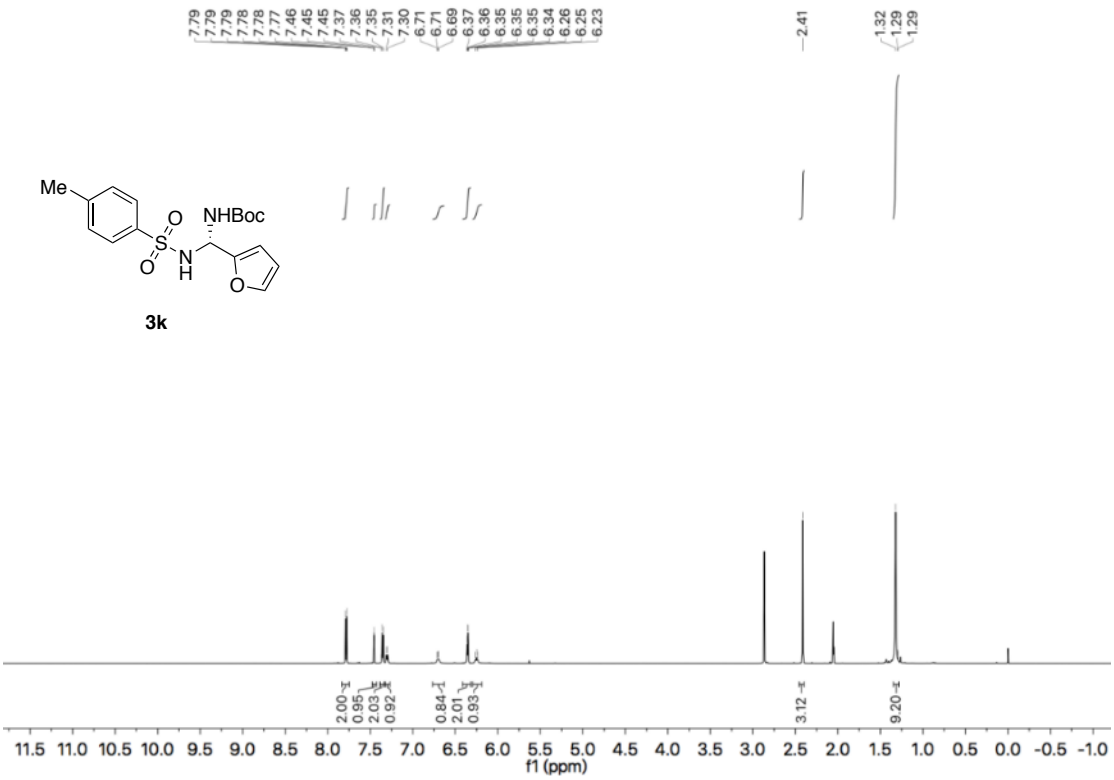
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3j**



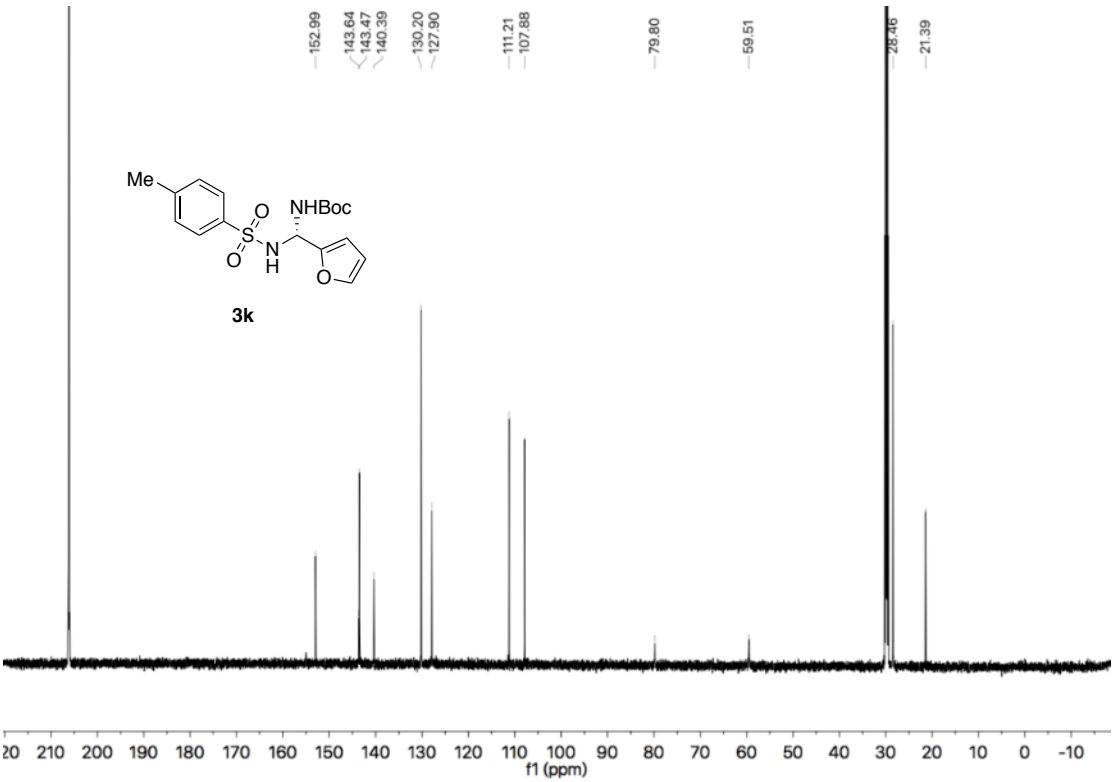
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3j**



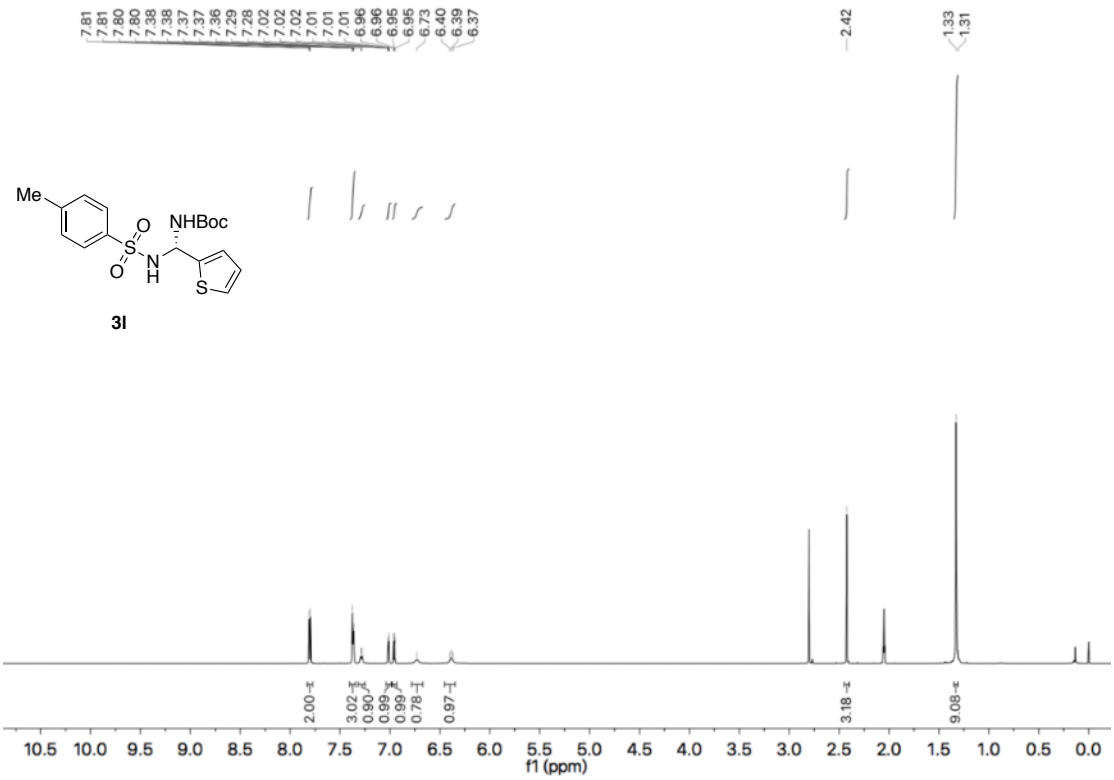
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3k**



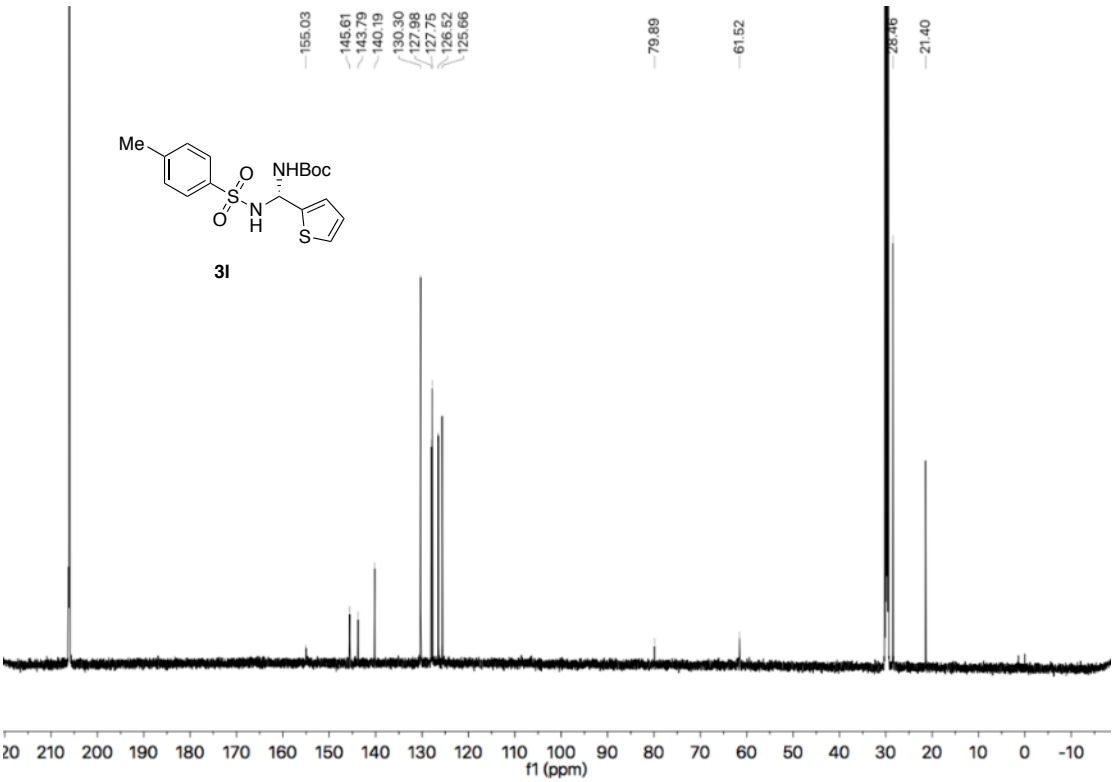
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3k**



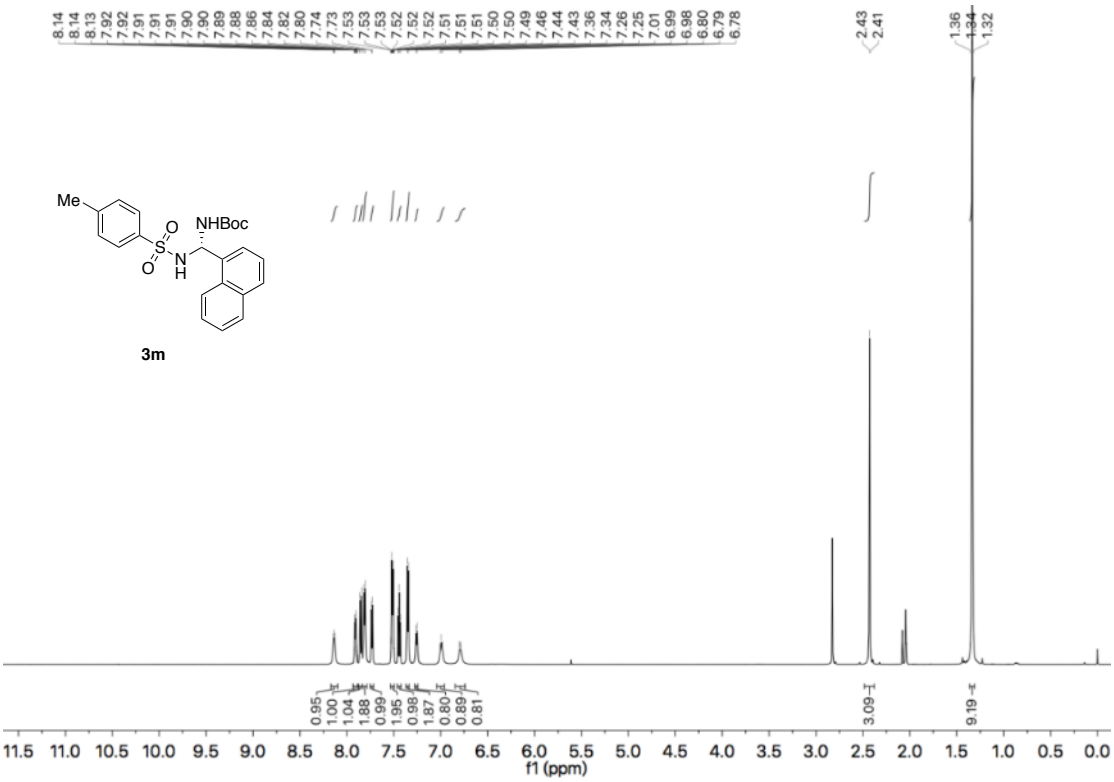
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3l**



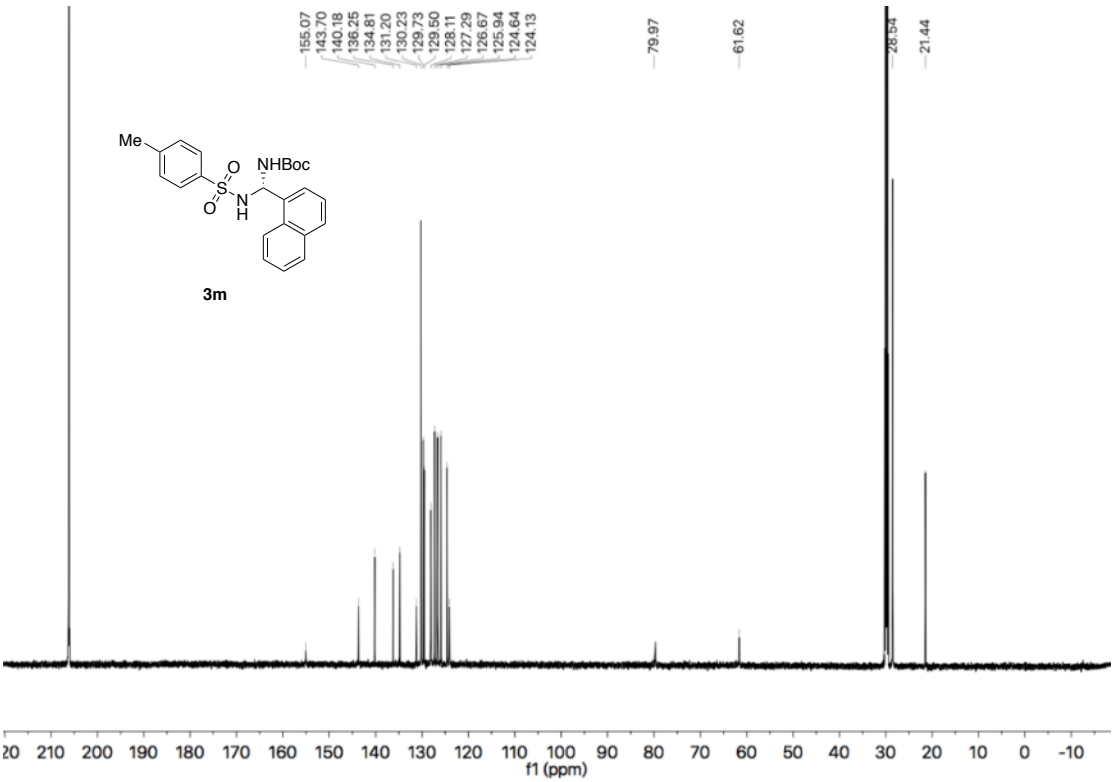
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3l**



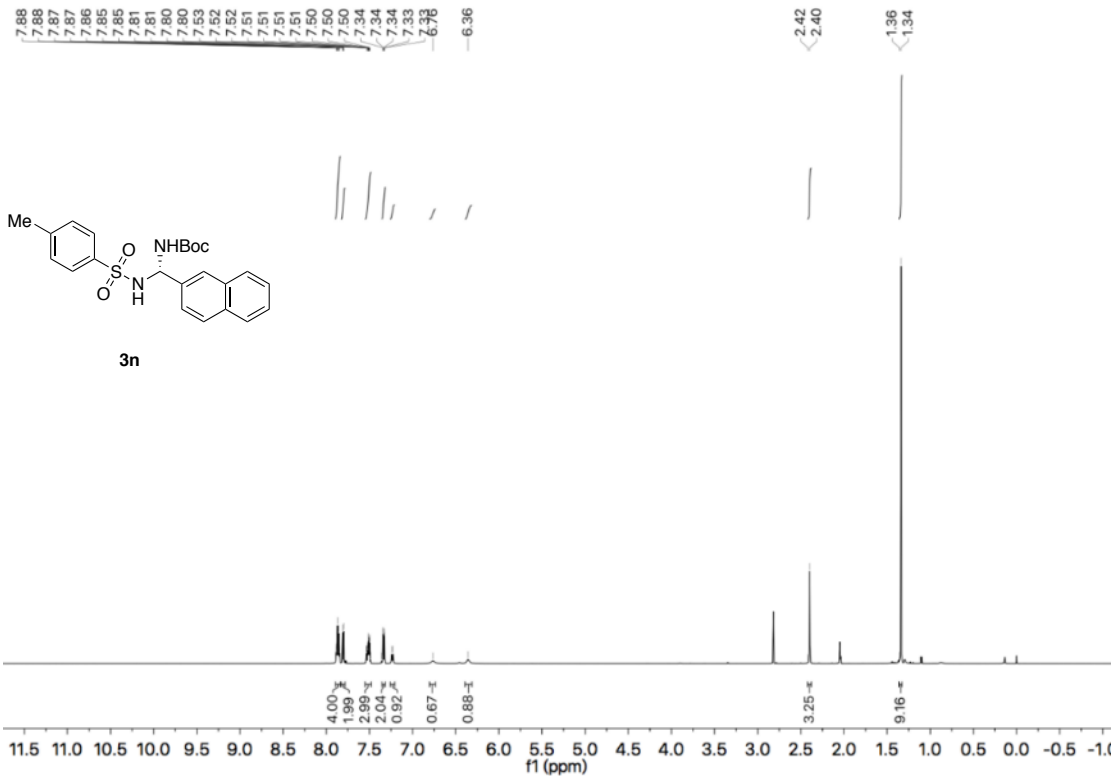
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3m**



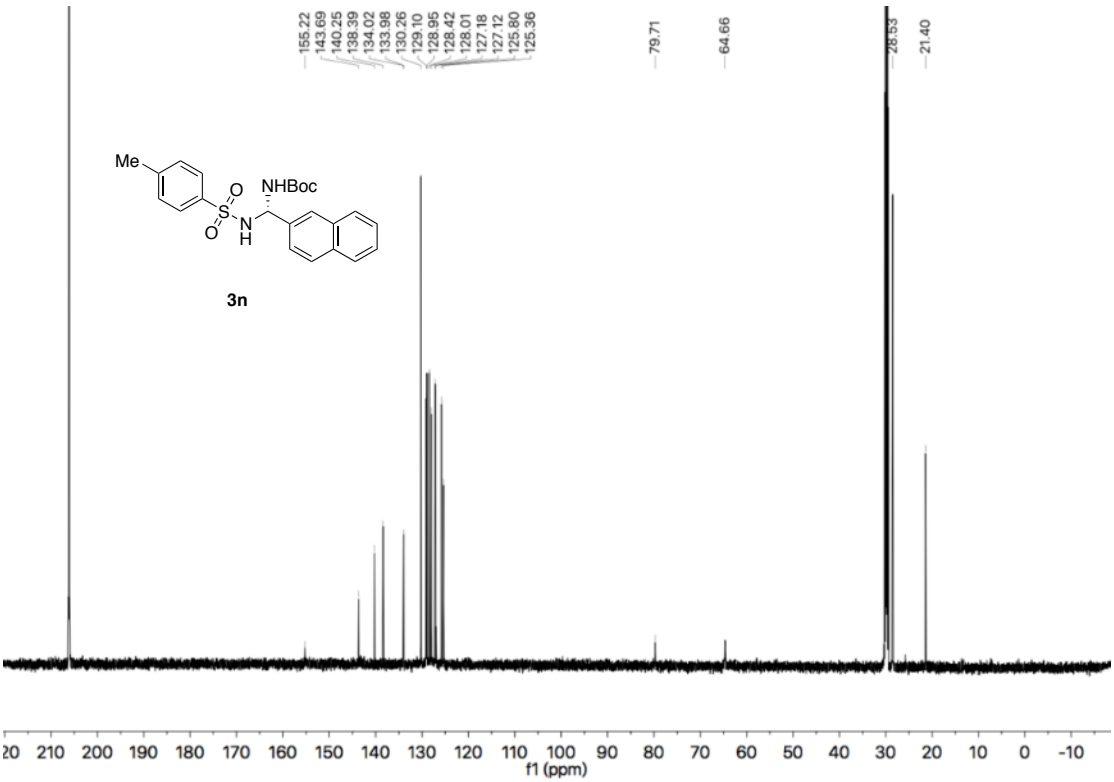
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3m**



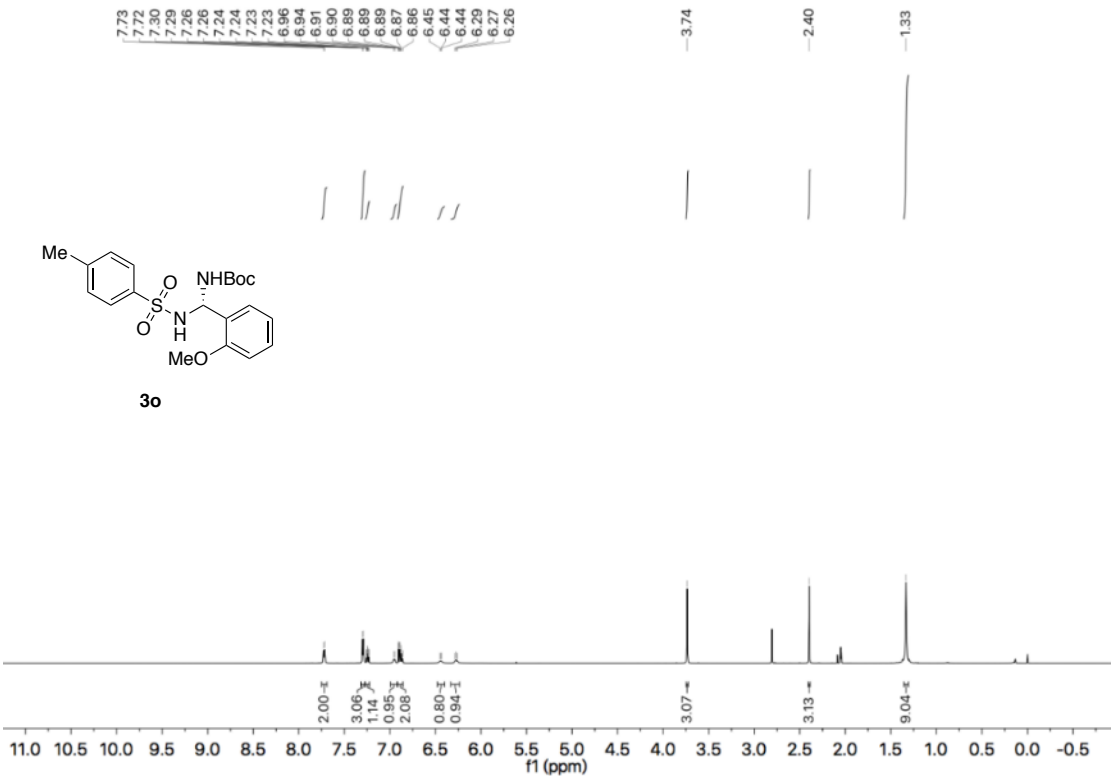
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3n**



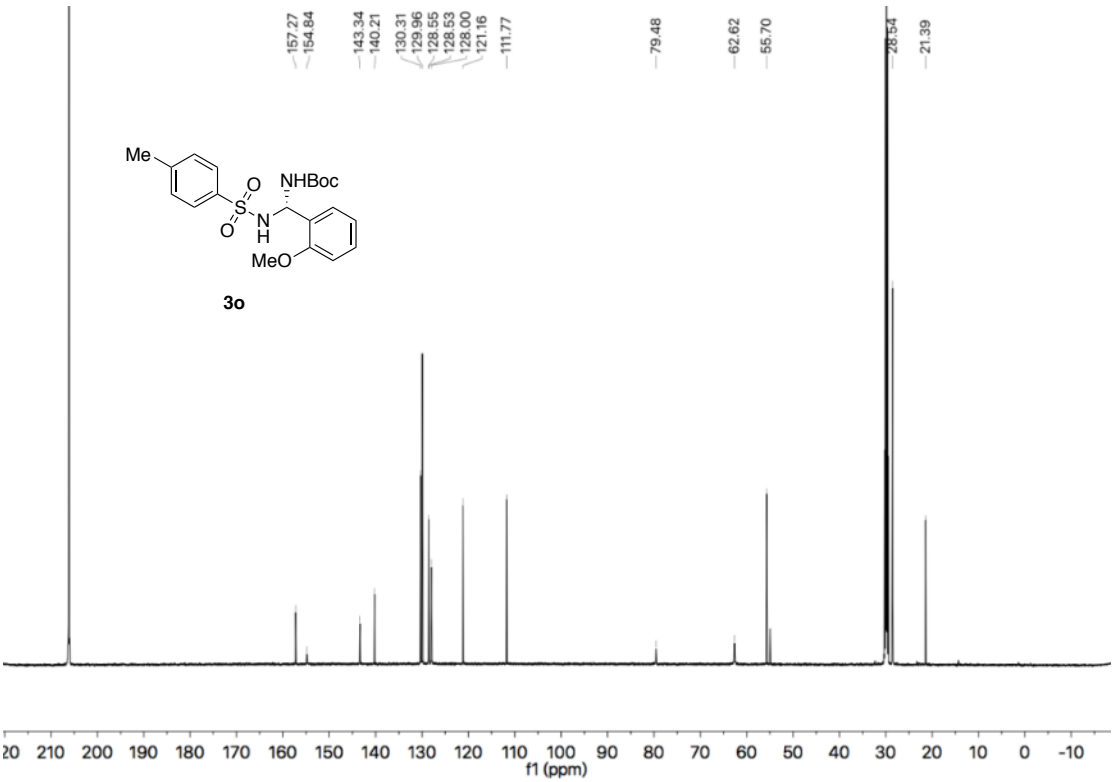
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3n**



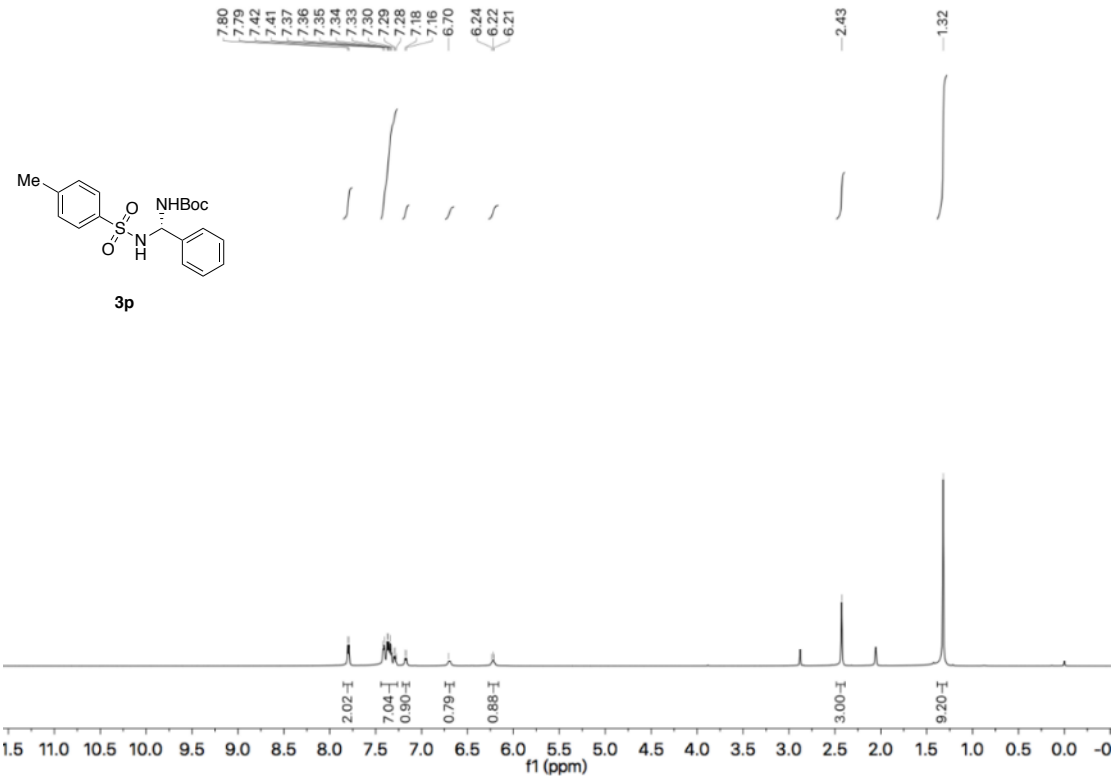
[1]H-NMR (600 MHz, Acetone-d_6) of compound of **3o**



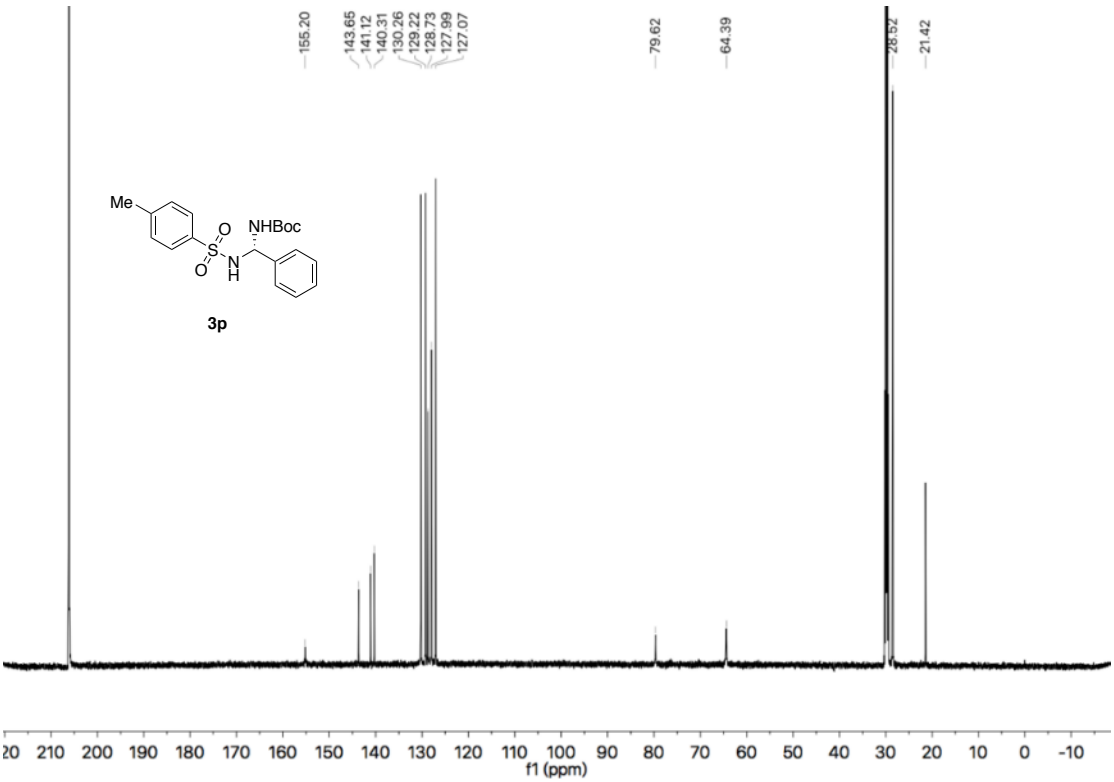
[13]C-NMR (150 MHz, Acetone-d_6) of compound of **3o**



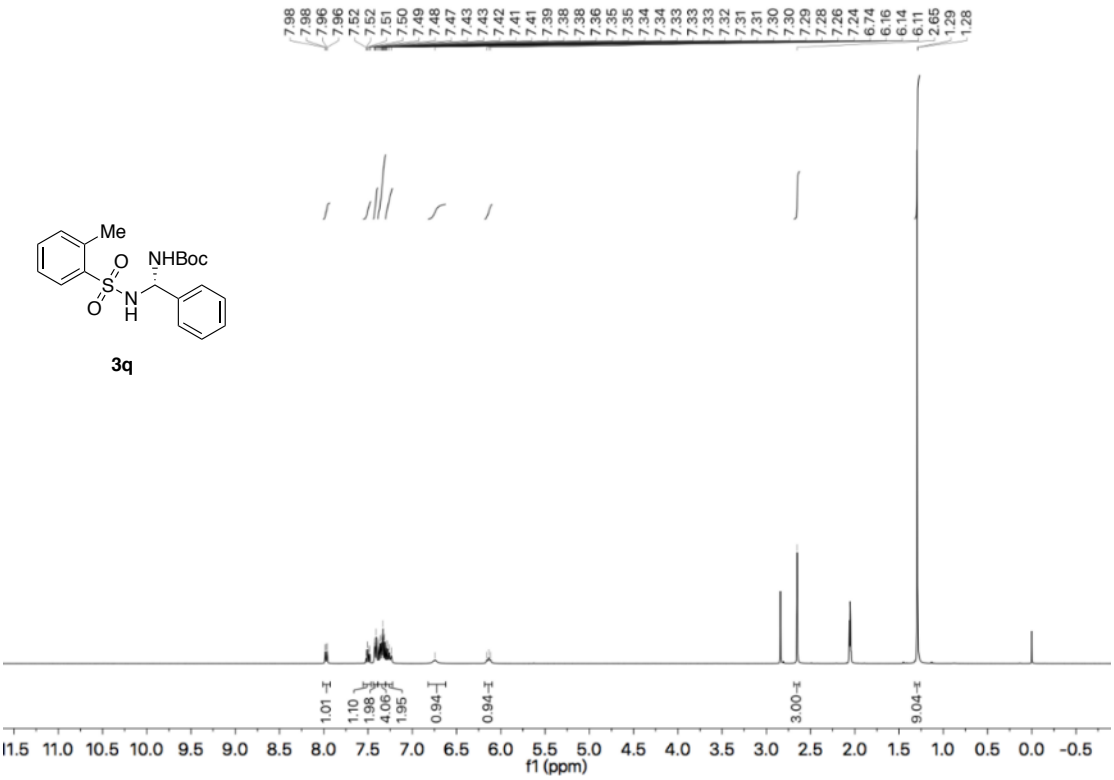
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3p**



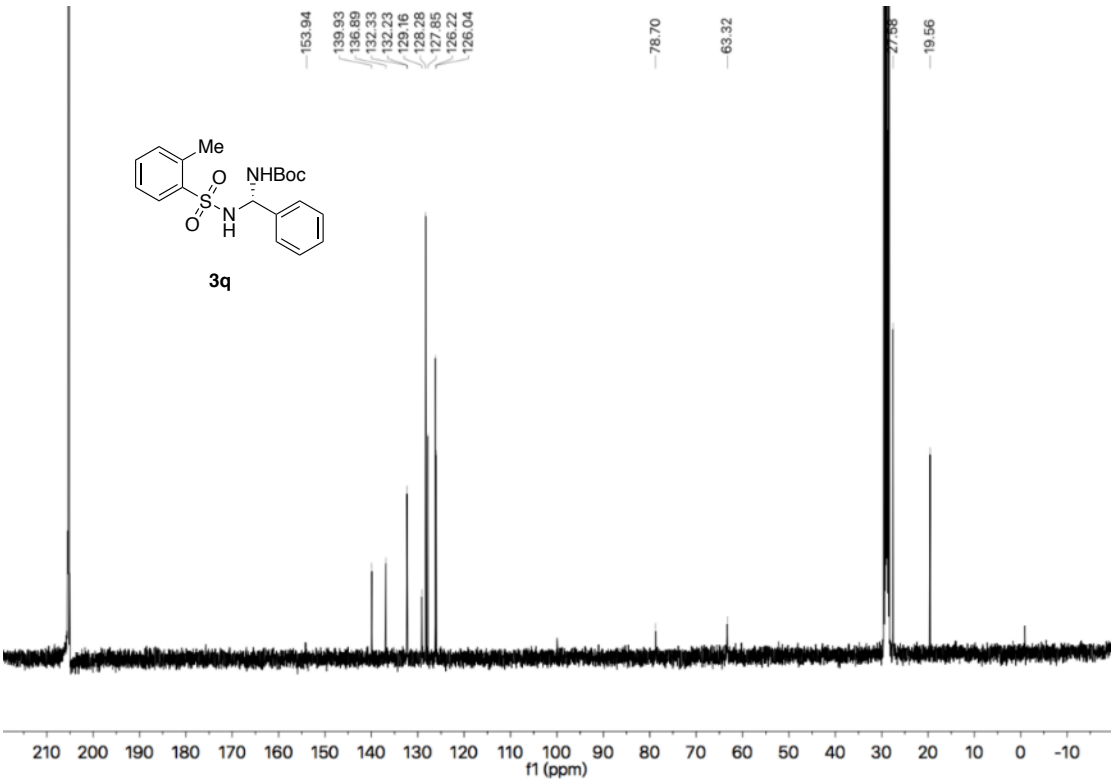
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3p**



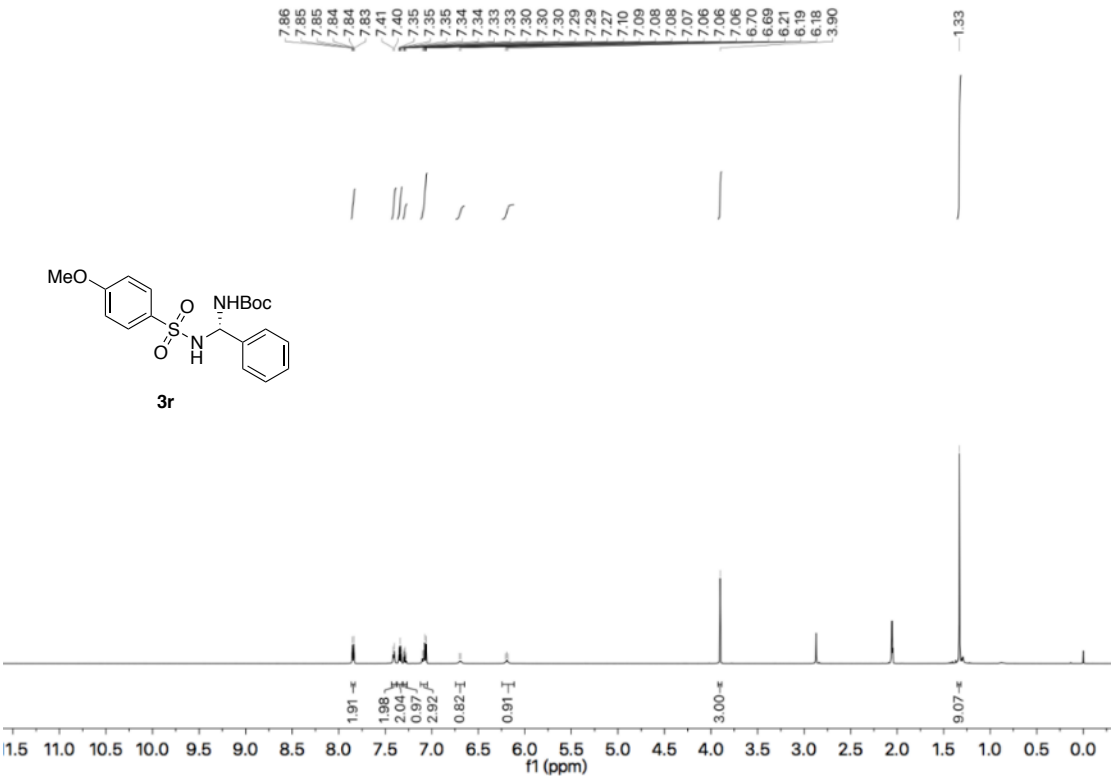
[1]H-NMR (400 MHz, Acetone-d_6) of compound of **3q**



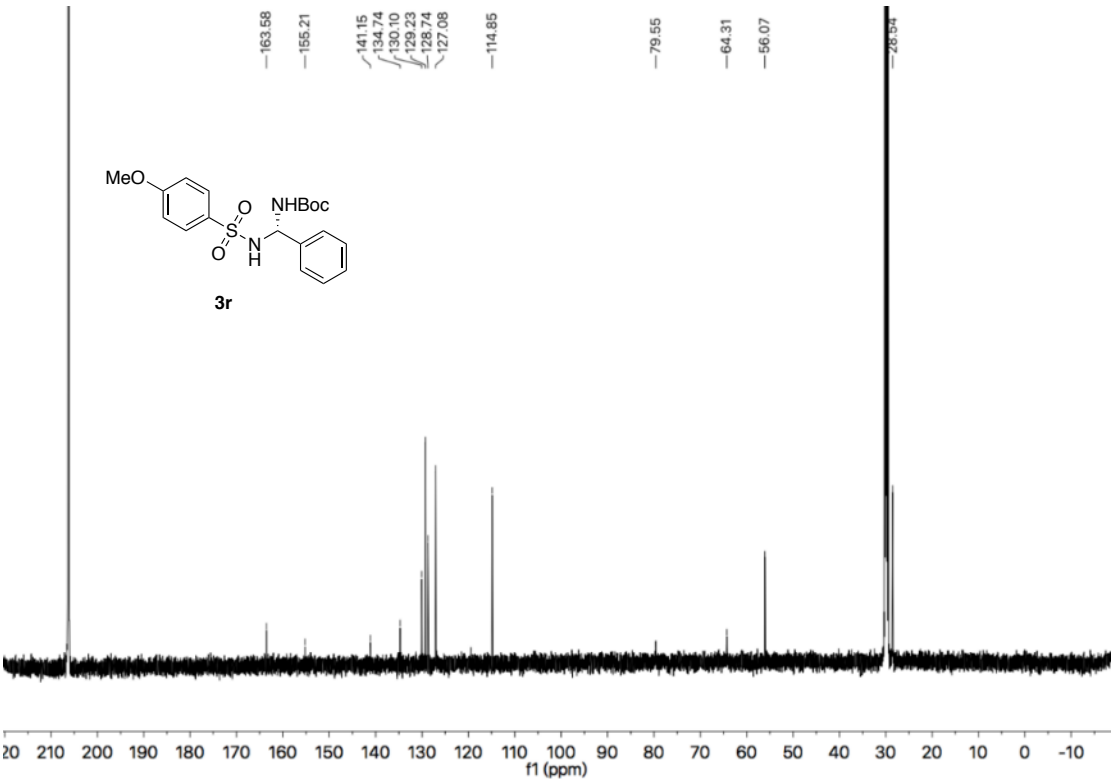
[13]C-NMR (100 MHz, Acetone-d_6) of compound of **3q**



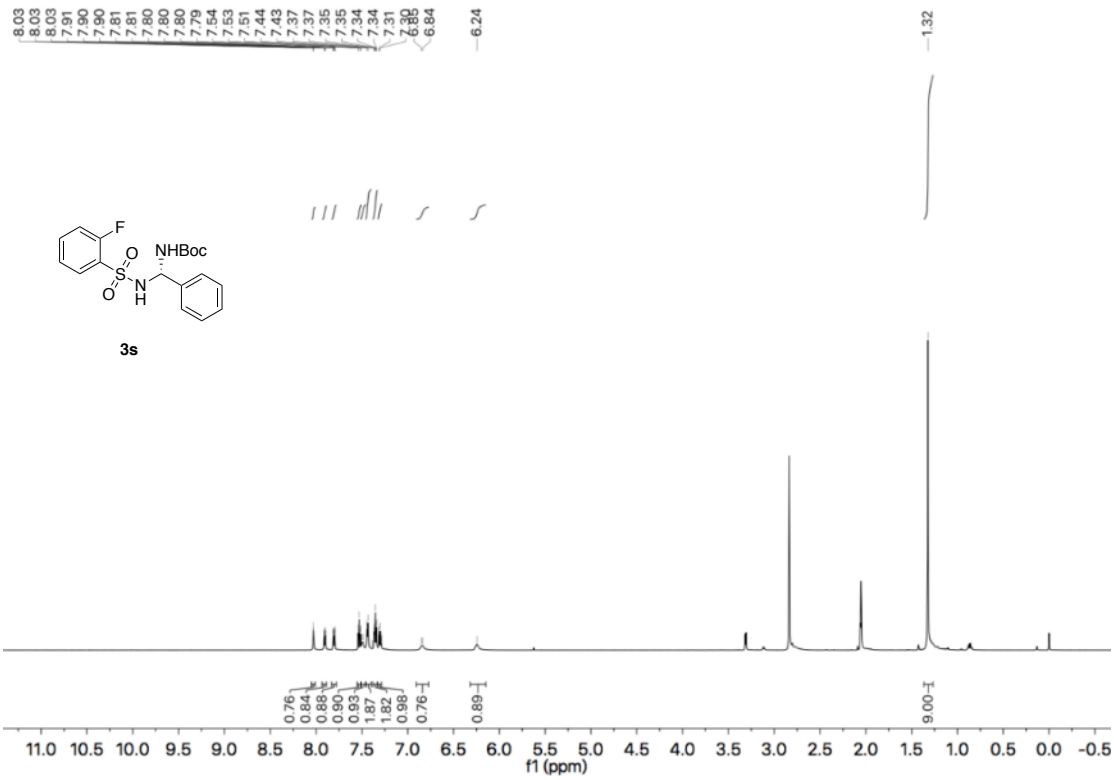
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3r**



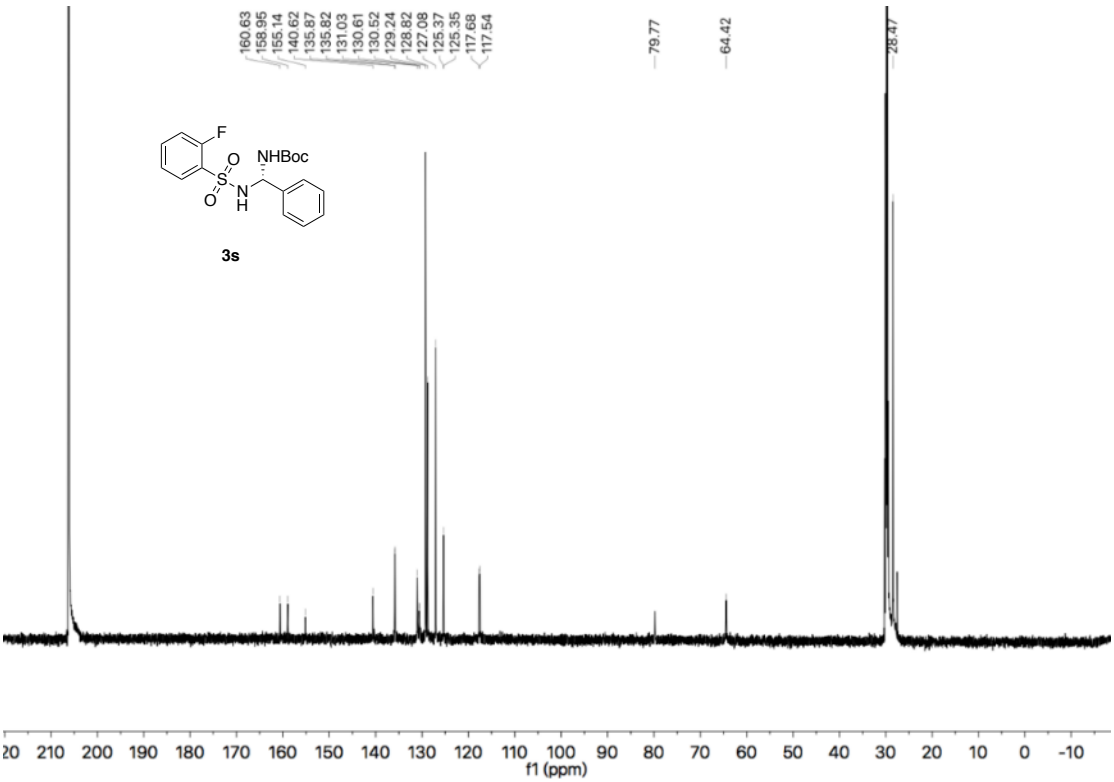
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3r**



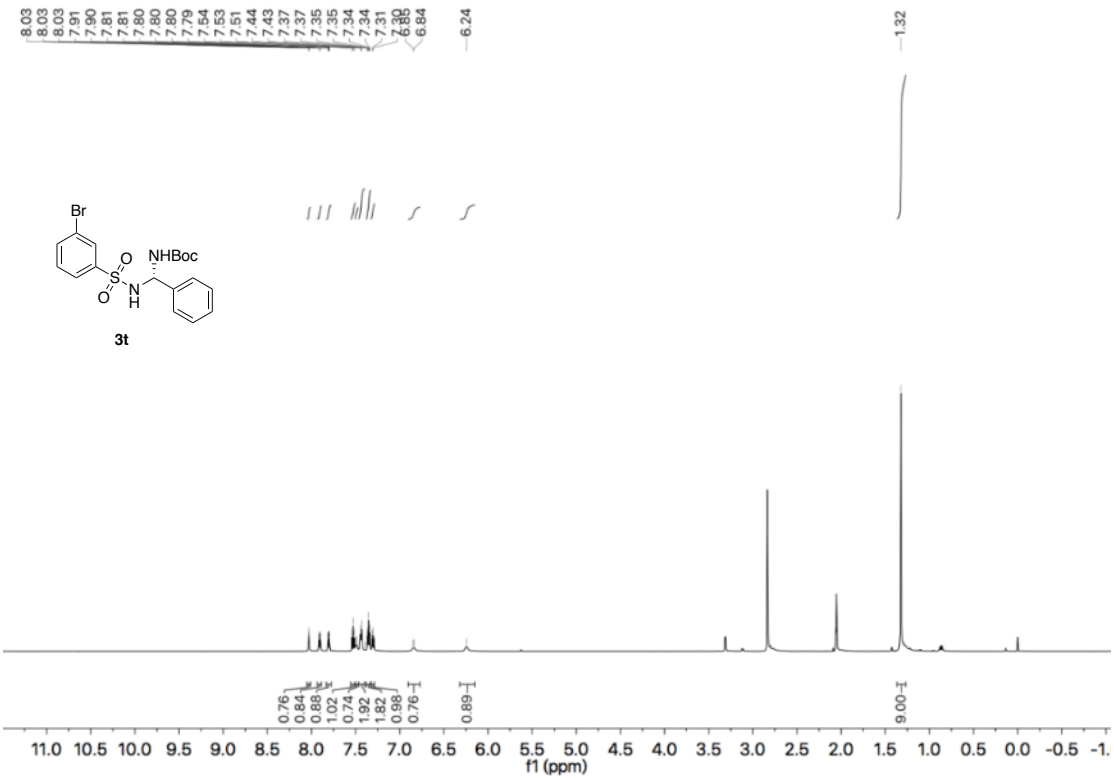
[1]H-NMR (600 MHz, Acetone-d_6) of compound of **3s**



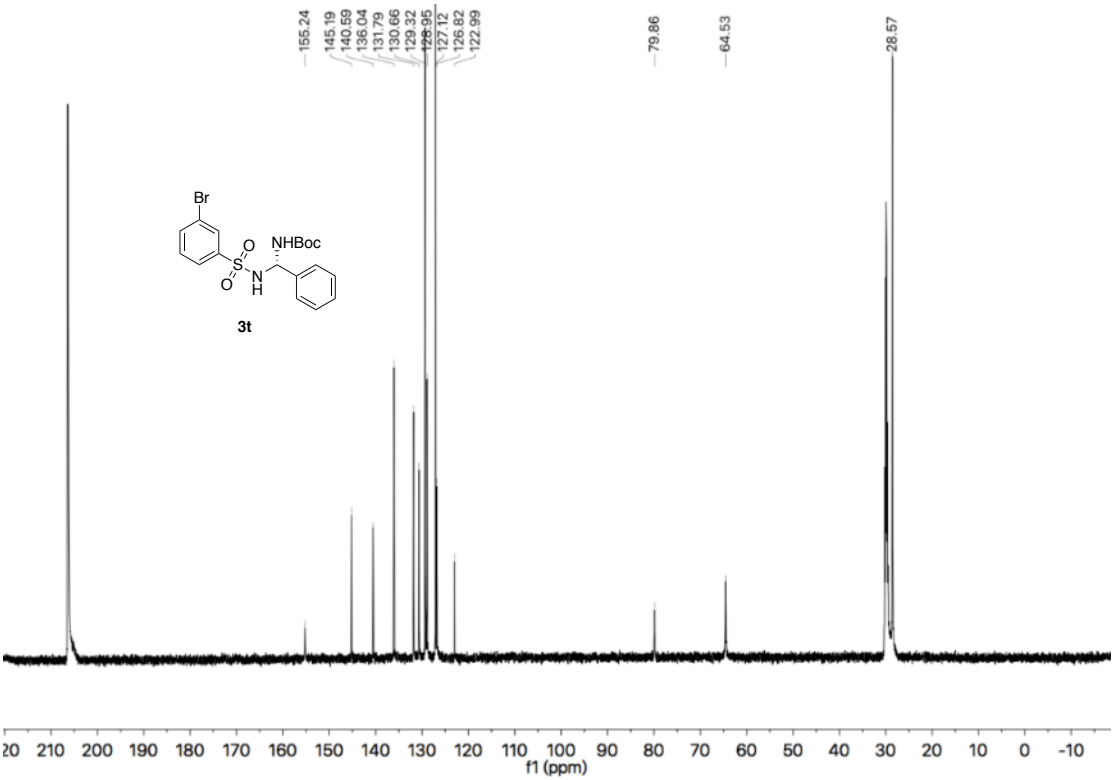
[13]C-NMR (150 MHz, Acetone-d_6) of compound of **3s**



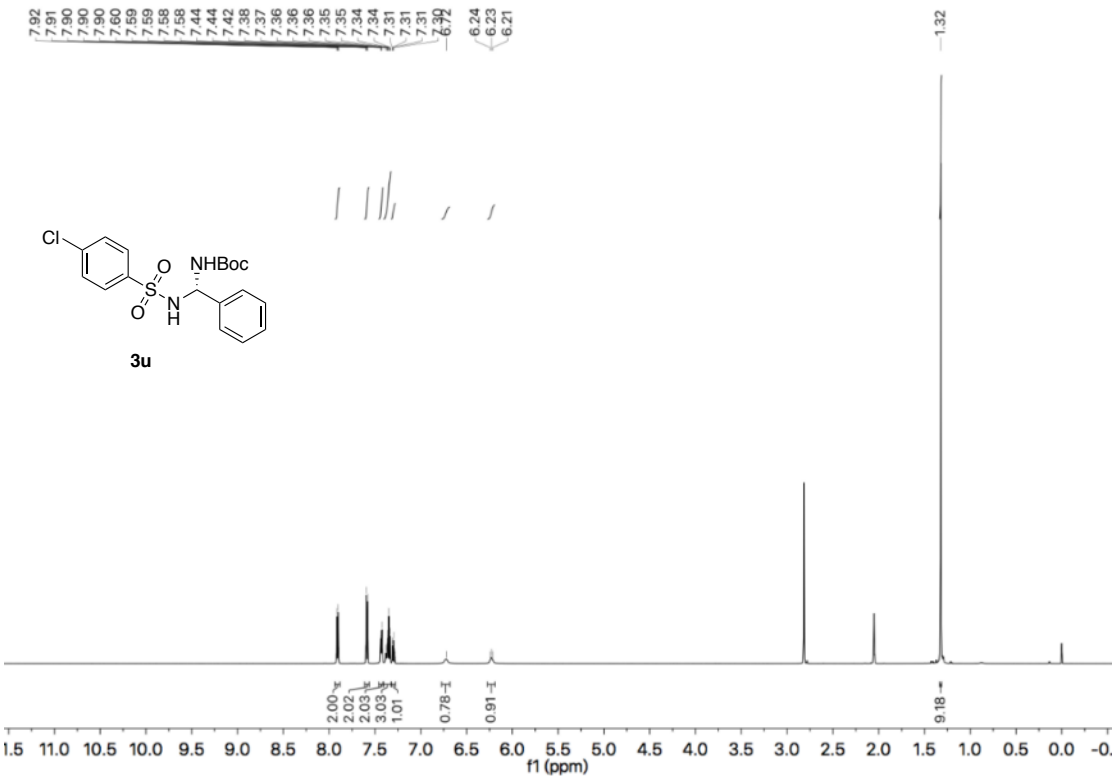
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3t**



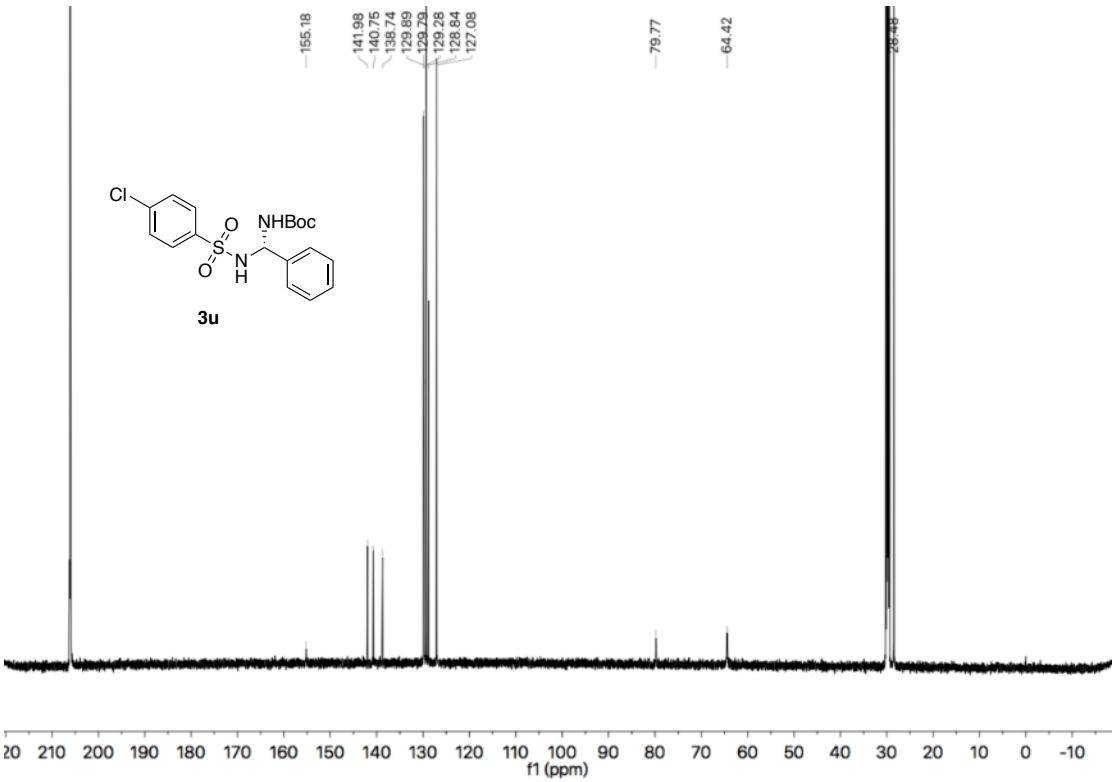
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3t**



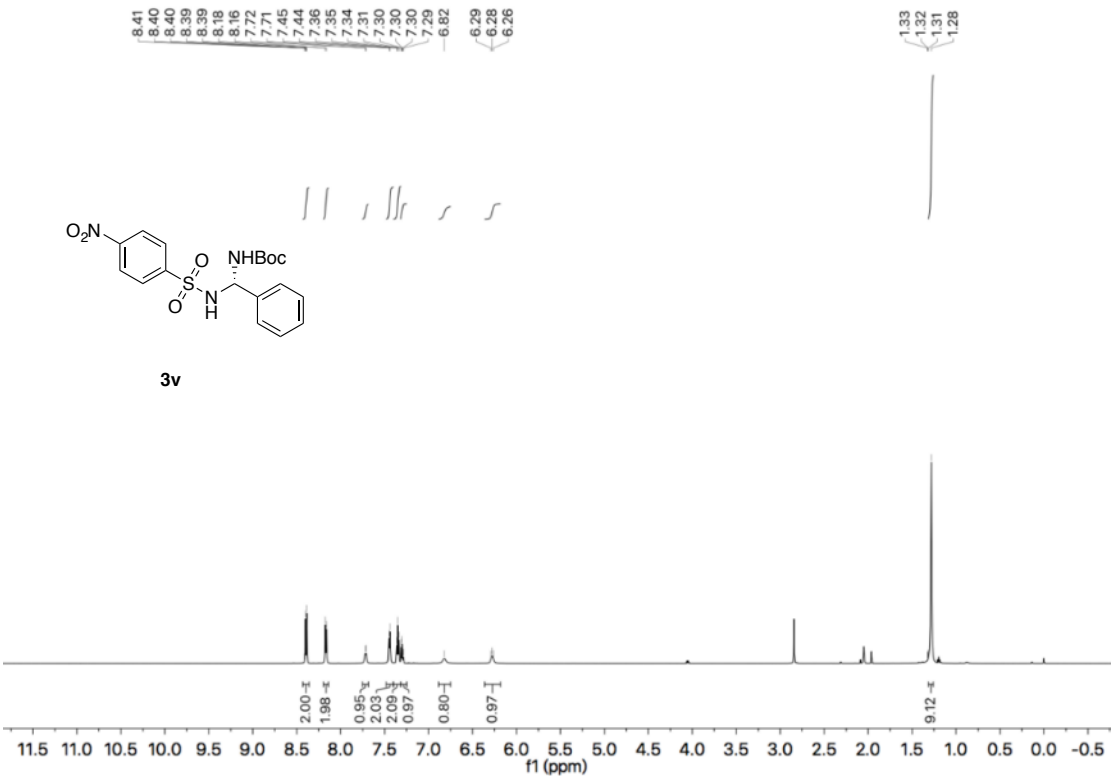
[1]H-NMR (600 MHz, Acetone-d_6) of compound of **3u**



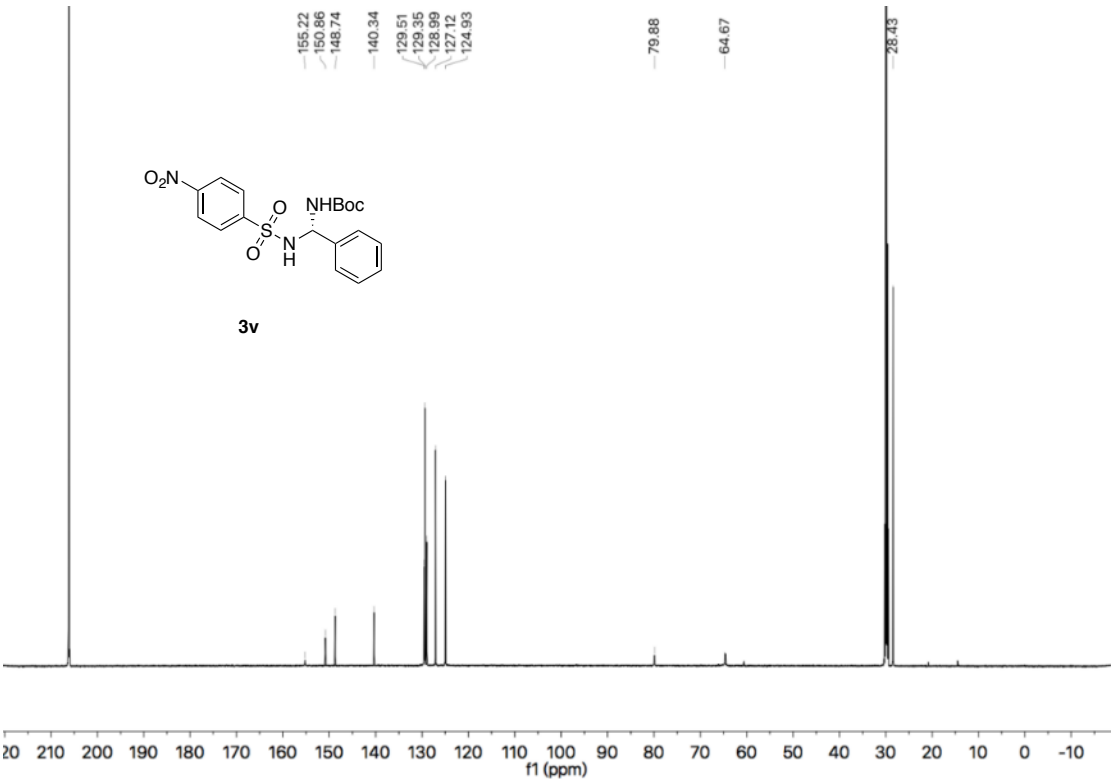
[13]C-NMR (150 MHz, Acetone-d_6) of compound of **3u**



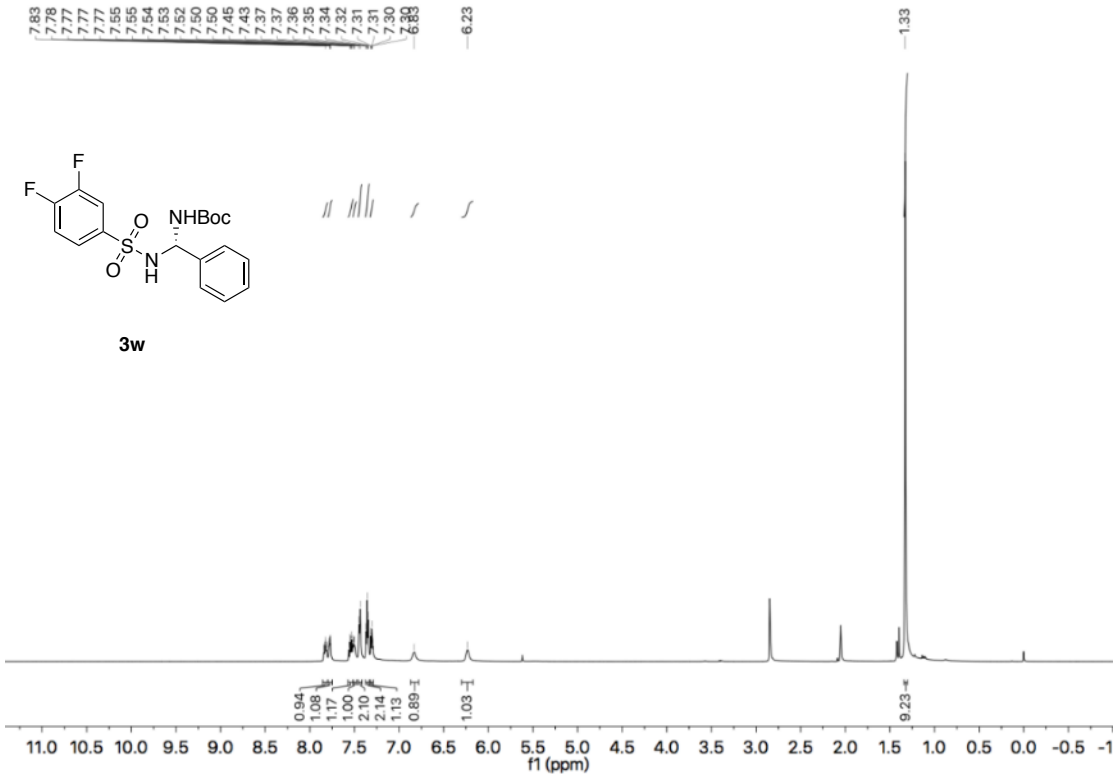
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3v**



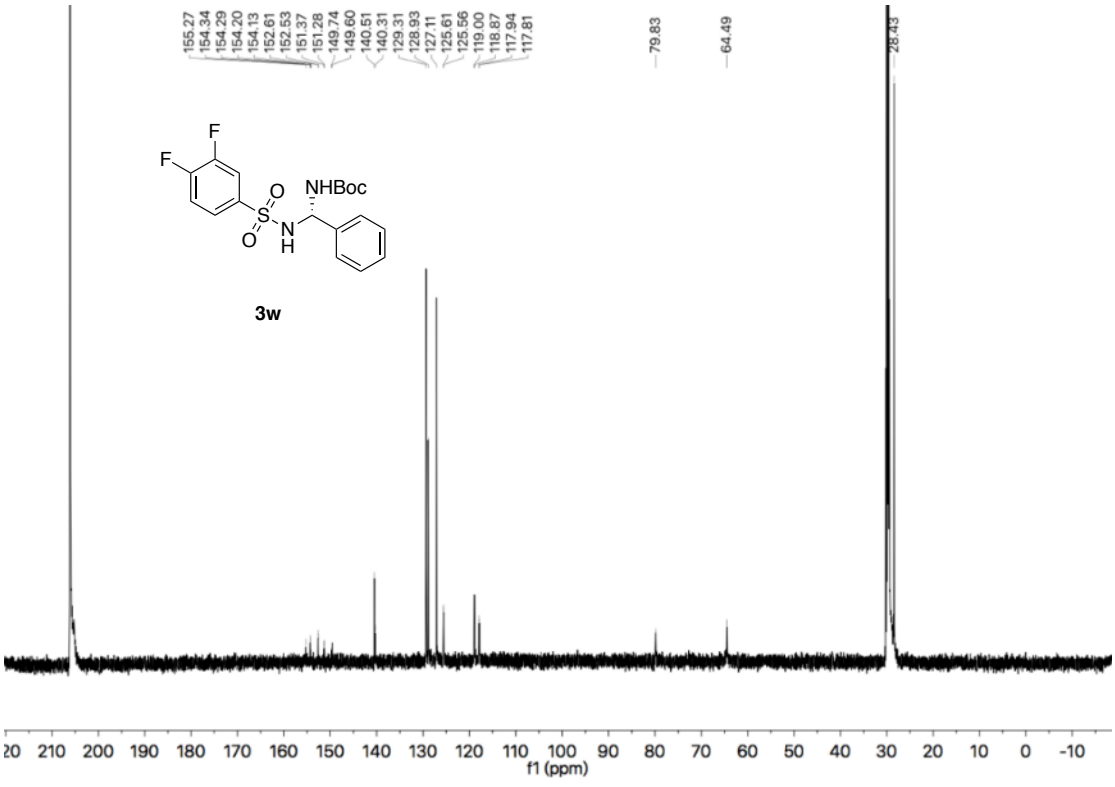
^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3v**



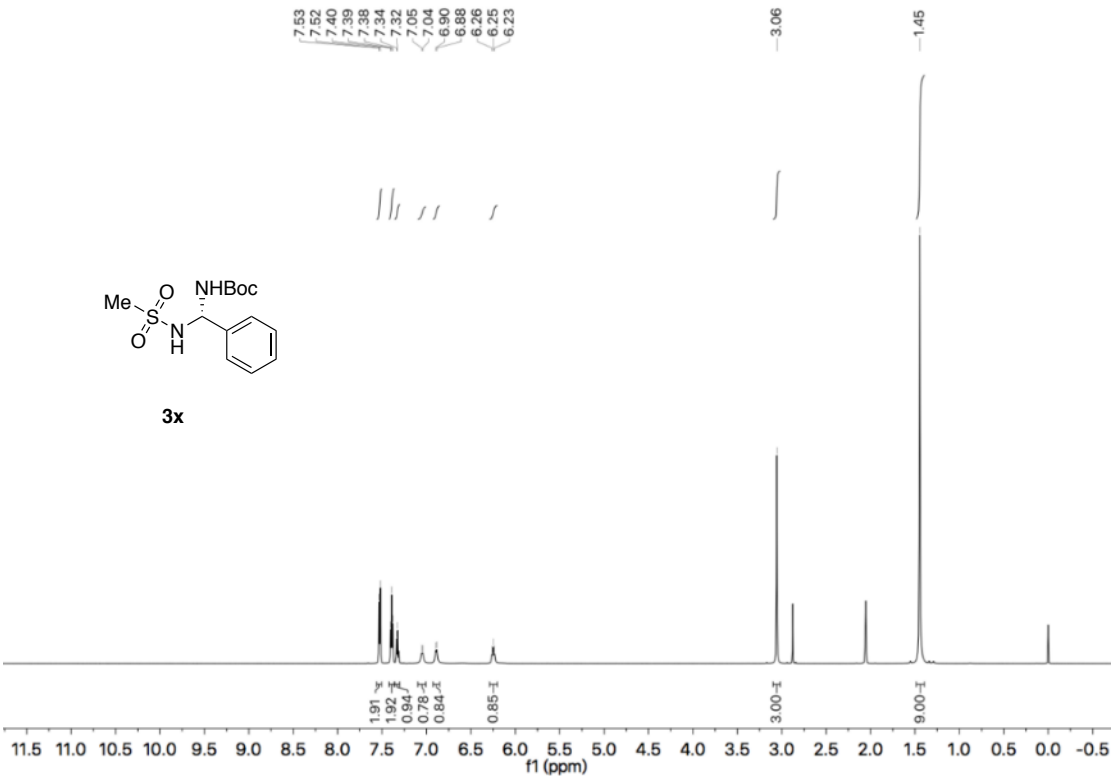
^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3w**



^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3w**



^{1}H-NMR (600 MHz, Acetone-d_6) of compound of **3x**



^{13}C-NMR (150 MHz, Acetone-d_6) of compound of **3x**