Electronic Supplementary Material (ESI) for ChemComm.

Palladium-Catalyzed Enantioselective Arylation of Trichloroacetaldimine or Tri-/Difluoro- Precursors

Supporting Information

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General remarks

All the manipulations were performed in air, unless mentioned otherwise. *n*-Hexane, 1,2-dichloroethane were purchased from J&K Chemicals and used without further purification. The following chemicals were purchased and used as received: $AgSbF_6$ (Energy Chemicals), Pd $(TFA)_2$ (99%, Sigma-Aldrich), (*S*)-^{t}Bu-PyOX (99%, Bide Chemicals). All *N*, *O*-acetals[1] and boroxine[2] were prepared by literature report procedure.

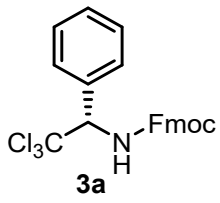
^{1}H, ^{13}C, ^{19}F NMR spectra were recorded using Agilent Technologies 600 MHz NMR, Bruker 400 MHz and 600 MHz NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were referenced to resonances of the residual protons in the deuterated solvents. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, br = broad singlet and m = multiplet. HR-MS analyses were performed at a Thermo Scientific Exactive-TOF (ESI ionization source). Optical rotation were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). Enantiomeric ratios were determined by HPLC using Agilent technologies 1260 infinity, using *n*-hexane/*i*-PrOH as a mobile phase and detected by UV at 254~210 nm.

General procedure for chiral α-aryl trichloroethylamines

In a flame dried round bottom flask, Pd $(TFA)_2$ (1.7 mg, 0.005 mmol), (*S*)-^{t}Bu-PyOX (1.2 mg, 0.006 mmol), $AgSbF_6$ (6.7 mg, 0.02 mmol), *N*, *O*-acetal (0.10 mmol), boroxine (0.20 mmol) and DCE (1 mL) were added under air. The reaction mixture was stirred at 70 °C for 12 h and the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1:30 - 1:5) as eluent, and data for characterization of the products are listed below.

Characterization and HPLC data of chiral α-aryl trichloroethylamines

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-phenylethyl)carbamate (3a)

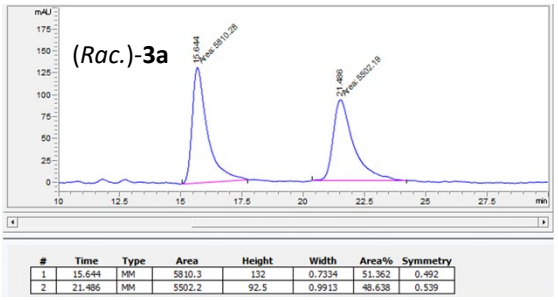


3a

The title compound was isolated [(*S*)-**3a**: 36.6 mg, 82%, 98% *ee*; (*R*)-**3a**: 35.7 mg, 80%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.58 (dd, *J* = 7.8, 4.0 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.44 – 7.37 (m, 5H), 7.30 (q, *J* = 7.1 Hz, 2H), 5.89 (d, *J* = 10.4 Hz, 1H), 5.65 (d, *J* = 10.3 Hz, 1H), 4.59 (dd, *J* = 10.9, 6.8 Hz, 1H), 4.38 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.7, 141.4, 134.8, 129.44, 129.39, 128.4, 127.9, 127.2, 125.2, 120.2, 101.7, 69.2, 67.5, 47.3. HRMS (ESI) calcd for $C_{23}H_{18}Cl_3NO_2Na^+$: 468.0295, found 468.0304.

Optical rotation: $[\alpha]_D^{25}$ = 0.53 [c = 0.06, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column OD-3, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm, (*S*)-**3a**: t_R = 15.7 min for the major isomer, t_R = 21.8 min for the minor isomer; (*R*)-**3a**: t_R = 21.5 min for the major isomer, t_R = 15.8 min for the minor isomer.



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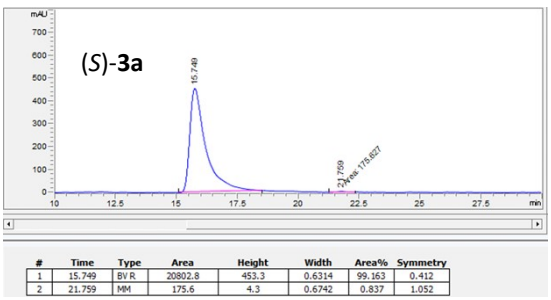
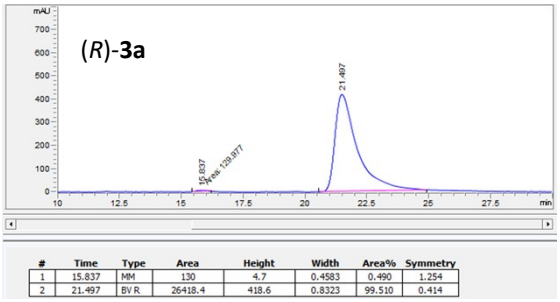


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.749	BV R	20802.8	453.3	0.6314	99.163	0.412
2	21.759	MM	175.6	4.3	0.6742	0.837	1.052



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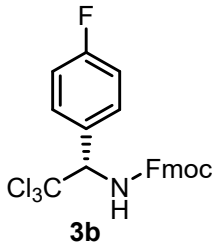
1	15.837	MM	130	4.7	0.4583	0.490	1.254
2	21.497	BV R	26418.4	418.6	0.8323	99.510	0.414

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-fluorophenyl)ethyl)carbamate (3b)

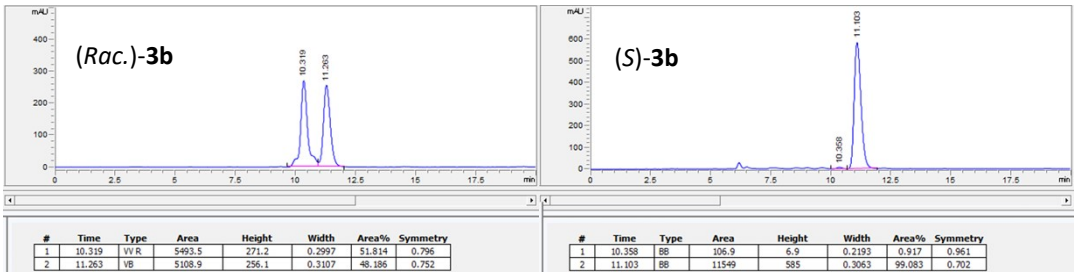


3b

The title compound was isolated [(*S*)-**3b**: 36.2 mg, 78%, 98% *ee*; (*R*)-**3b**: 34.8 mg, 75%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 6.7 Hz, 2H), 7.48 (dd, *J* = 8.5, 5.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 5.85 (d, *J* = 10.2 Hz, 1H), 5.63 (d, *J* = 10.0 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.40 (dd, *J* = 11.0, 6.5 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2 (d, *J* = 249.0 Hz), 155.4, 143.6, 141.5, 131.2 (d, *J* = 8.6 Hz), 130.8, 127.9, 127.2, 125.1, 120.2, 115.4 (d, *J* = 21.8 Hz), 101.5, 68.6, 67.5, 47.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.02. HRMS (ESI) calcd for $C_{23}H_{17}Cl_3FNO_2Na^+$: 486.0201, found 486.0203.

Optical rotation: $[\alpha]_D^{25}$ = 0.83 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3b**: t_R = 11.1 min for the major isomer, t_R = 10.4 min for the minor isomer; (*R*)-**3b**: t_R = 10.3 min for the major isomer, t_R = 11.2 min for the minor isomer.



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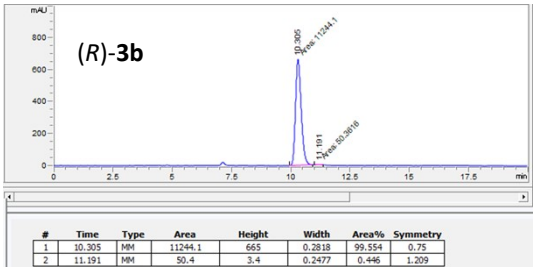
1	10.319	VV R	5493.5	271.2	0.2997	51.814	0.796
2	11.263	VB	5108.9	256.1	0.3107	48.186	0.752

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.358	BB	106.9	6.9	0.2193	0.917	0.961
2	11.103	BB	11549	585	0.3063	99.083	0.702



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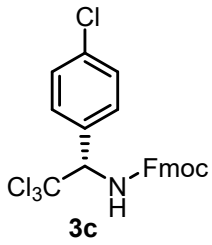
1	10.305	MM	11244.1	665	0.2818	99.554	0.75
2	11.191	MM	50.4	3.4	0.2477	0.446	1.209

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-chlorophenyl)ethyl)carbamate (3c)

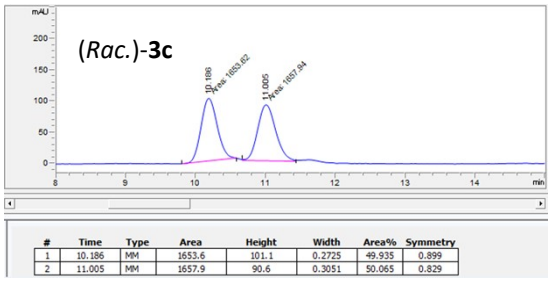


3c

The title compound was isolated [(*S*)-**3c**: 32.2 mg, 67%, 96% *ee*; (*R*)-**3c**: 32.7 mg, 68%, 96% *ee*] as a buff solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 5.96 (d, *J* = 10.1 Hz, 1H), 5.64 (d, *J* = 10.2 Hz, 1H), 4.61 (dd, *J* = 10.8, 6.5 Hz, 1H), 4.42 (dd, *J* = 10.8, 6.7 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.6, 141.4, 135.4, 133.3, 130.7, 128.6, 127.9, 127.2, 125.1, 120.2, 101.2, 68.6, 67.4, 47.2. HRMS (ESI) calcd for $C_{23}H_{17}Cl_4NO_2Na^+$: 501.9906, found 501.9908.

Optical rotation: $[\alpha]_D^{25}$ = 0.60 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3c**: t_R = 11.9 min for the major isomer, t_R = 10.8 min for the minor isomer; (*R*)-**3c**: t_R = 10.9 min for the major isomer, t_R = 12.2 min for the minor isomer.



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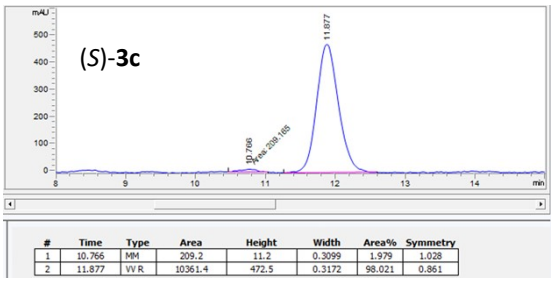
1	10.186	MM	1653.6	101.1	0.2725	49.935	0.899
2	11.005	MM	1657.9	90.6	0.3051	50.065	0.829



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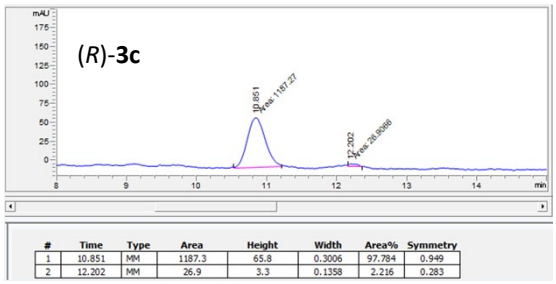
1	10.766	MM	209.2	11.2	0.3099	1.979	1.028
2	11.877	VV R	10361.4	472.5	0.3172	98.021	0.861



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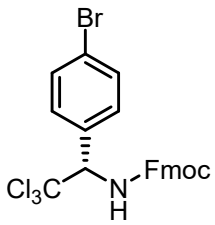
1	10.851	MM	1187.3	65.8	0.3006	97.784	0.949
2	12.202	MM	26.9	3.3	0.1358	2.216	0.283

(9*H*-fluoren-9-yl)methyl-(*S*)-(1-(4-bromophenyl)-2,2,2-trichloroethyl)carbamate (3d)

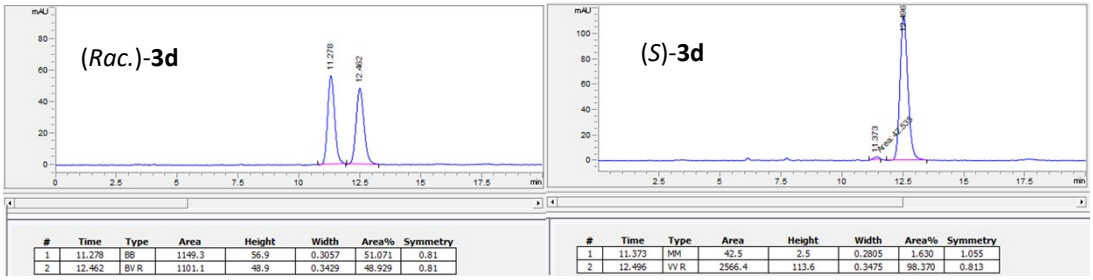


3d

The title compound was isolated [(*S*)-**3d**: 26.2 mg, 50%, 97% *ee*; (*R*)-**3d**: 26.7 mg, 51%, 97% *ee*] as a yellow solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.47 (m, 4H), 7.45 – 7.34 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 5.87 (d, *J* = 10.2 Hz, 1H), 5.61 (d, *J* = 10.2 Hz, 1H), 4.65 – 4.53 (m, 1H), 4.48 – 4.34 (m, 1H), 4.22 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 143.6, 141.5, 133.9, 131.5, 131.0, 127.9, 127.2, 125.1, 123.7, 120.2, 101.1, 68.7, 67.4, 47.3. HRMS (ESI) calcd for $C_{23}H_{17}Cl_3BrNO_2Na^+$: 545.9400, found 545.9405.

Optical rotation: $[\alpha]_D^{25}$ = 0.61 [c = 0.08, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3d**: t_R = 12.5 min for the major isomer, t_R = 11.4 min for the minor isomer; (*R*)-**3d**: t_R = 11.3 min for the major isomer, t_R = 12.6 min for the minor isomer.



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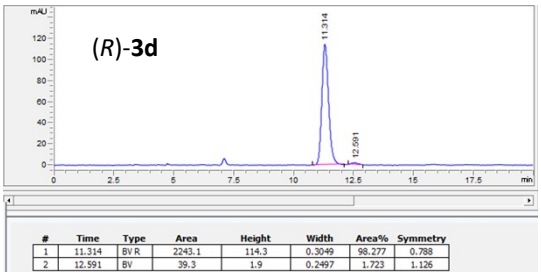
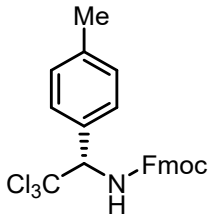
2	12.462	BV R	1101.1	48.9	0.3429	48.929	0.81

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.373	MM	42.5	2.5	0.2805	1.630	1.055
2	12.496	VV R	2566.4	113.6	0.3475	98.370	0.813



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.314	BV R	2243.1	114.3	0.3049	98.277	0.788
2	12.591	BV	39.3	1.9	0.2497	1.723	1.126

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(p-tolyl)ethyl)carbamate (3e)

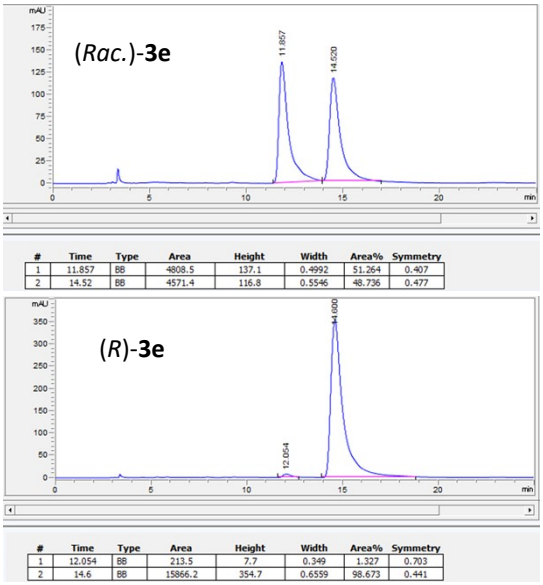


3e

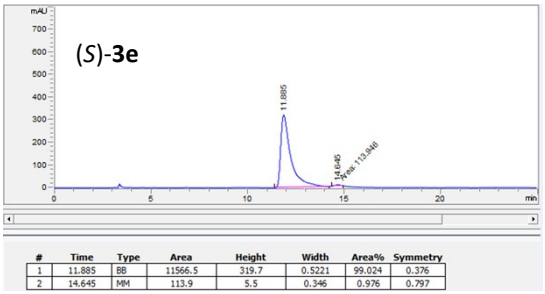
The title compound was isolated [(*S*)-**3e**: 35.9 mg, 78%, 98% *ee*; (*R*)-**3e**: 34.5 mg, 75%, 97% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 6.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 4H), 7.31 (q, *J* = 7.3 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 5.96 (d, *J* = 10.4 Hz, 1H), 5.65 (d, *J* = 10.3 Hz, 1H), 4.59 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.38 (dd, *J* = 10.8, 7.0 Hz, 1H), 4.24 (t, *J* = 6.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.7, 141.4, 139.4, 131.9, 129.3, 129.0, 127.9, 127.2, 125.2, 120.1. 102.0, 69.0, 67.4, 47.2, 21.2. HRMS (ESI) calcd for $C_{24}H_{20}Cl_3NO_2Na^+$: 482.0452, found 482.0457.

Optical rotation: $[\alpha]_D^{25}$ = 0.51 [c = 0.14, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column OD-3, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3e**: t_R = 11.9 min for the major isomer, t_R = 14.7 min for the minor isomer; (*R*)-**3e**: t_R = 14.6 min for the major isomer, t_R = 12.1 min for the minor isomer.



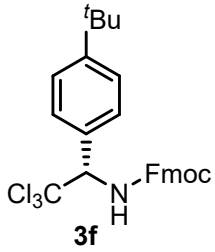
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.857	BB	4808.5	137.1	0.4992	51.264	0.407
2	14.52	BB	4571.4	116.8	0.5546	48.736	0.477



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.885	BB	11566.5	319.7	0.5221	99.024	0.376
2	14.645	MM	113.9	5.5	0.346	0.976	0.797

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.054	BB	213.5	7.7	0.349	1.327	0.703
2	14.6	BB	15866.2	354.7	0.6559	98.673	0.441

(9*H*-fluoren-9-yl)methyl-(*S*)-(1-(4-(tert-butyl)phenyl)-2,2,2-trichloroethyl)carbamate (3f)

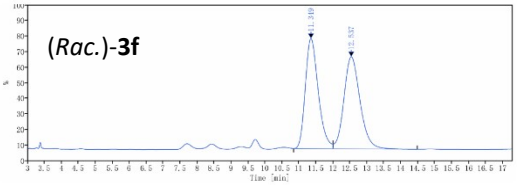


3f

The title compound was isolated [(*S*)-**3f**: 28.2 mg, 56%, 94% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (dd, *J* = 7.7, 2.8 Hz, 2H), 7.41 (p, *J* = 7.8 Hz, 6H), 7.30 (q, *J* = 7.4 Hz, 2H), 5.89 (d, *J* = 10.4 Hz, 1H), 5.64 (d, *J* = 10.4 Hz, 1H), 4.58 (dd, *J* = 10.8, 6.9 Hz, 1H), 4.35 (dd, *J* = 10.9, 7.0 Hz, 1H), 4.24 (t, *J* = 6.9 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 152.4, 143.7, 141.4, 131.8, 129.1, 127.9, 127.2, 125.3, 125.2, 120.2, 102.0, 68.9, 67.5, 47.3, 34.8, 31.4. HRMS (ESI) calcd for $C_{27}H_{27}Cl_3NO_2^+$: 502.1102, found 502.1101.

Optical rotation: $[\alpha]_D^{25}$ = 0.36 [c = 0.07, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3f**: t_R = 12.5 min for the major isomer, t_R = 11.4 min for the minor isomer.



Signal VWD1A, Wavelength=254 nm

Retention Time	Type	Area	Area%
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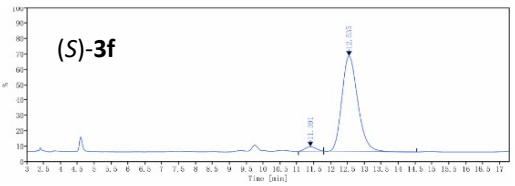
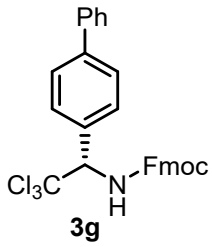
12.537	VB	5768.13	51.09



Signal VWD1A, Wavelength=254 nm

Retention Time	Type	Area	Area%
11.391	MM n	262.09	3.18
12.535	MB n	7972.53	96.82

(9*H*-fluoren-9-yl)methyl-(*S*)-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trichloroethyl)carbamate (3g)

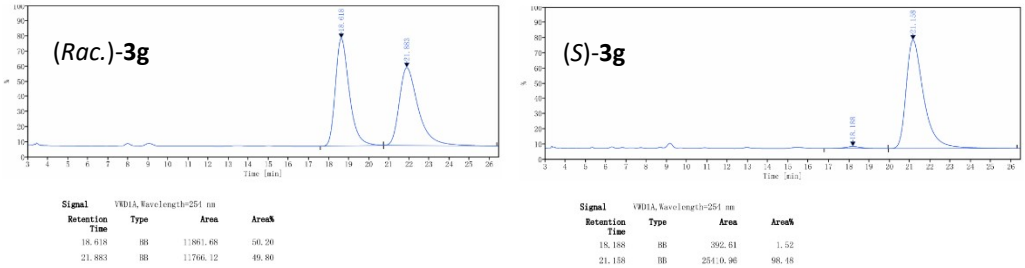


3g

The title compound was isolated [(*S*)-**3g**: 27.1 mg, 52%, 97% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (p, *J* = 8.7, 8.1 Hz, 8H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 (q, *J* = 6.5, 5.2 Hz, 3H), 7.31 (dt, *J* = 10.6, 4.9 Hz, 2H), 5.93 (d, *J* = 10.3 Hz, 1H), 5.70 (d, *J* = 10.3 Hz, 1H), 4.61 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.40 (dd, *J* = 10.8, 6.9 Hz, 1H), 4.25 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.7, 142.2, 141.5, 140.3, 133.8, 129.8, 129.0, 127.93, 127.86, 127.3, 127.2, 127.0, 125.1, 120.2, 101.7, 69.0, 67.5, 47.3. HRMS (ESI) calcd for $C_{29}H_{22}Cl_3NO_2Na^+$: 544.0608, found 544.0612.

Optical rotation: $[\alpha]_D^{25}$ = 1.08 [c = 0.05, CH_2Cl_2 (*S*)].

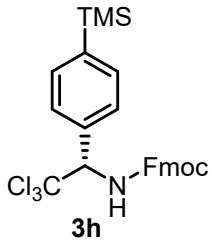
HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3g**: t_R = 21.2 min for the major isomer, t_R =18.2 min for the minor isomer.



Signal	VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	Area%
18.618	BB	11861.68	50.20
21.883	BB	11766.12	49.80

Signal	VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	Area%
18.188	BB	392.61	1.52
21.158	BB	25410.96	98.48

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-(trimethylsilyl)phenyl)ethyl)carbamate (3h)

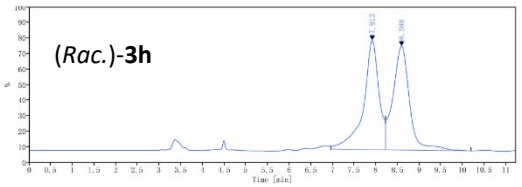


3h

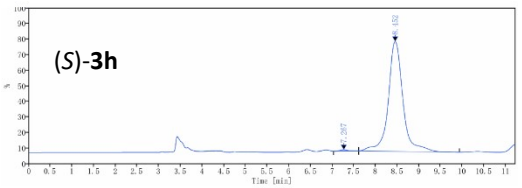
The title compound was isolated [(*S*)-**3h**: 35.2 mg, 68%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 30:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.58 (dd, *J* = 7.5, 2.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.40 (dd, *J* = 8.7, 6.5 Hz, 2H), 7.30 (q, *J* = 7.3 Hz, 2H), 5.90 (d, *J* = 10.3 Hz, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 4.58 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.37 (dd, *J* = 10.8, 6.9 Hz, 1H), 4.24 (t, *J* = 6.8 Hz, 1H), 0.29 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.7, 142.1, 141.5, 135.2, 133.3, 128.7, 127.9, 127.2, 125.2, 120.2, 101.8, 69.3, 67.5, 47.3, -1.1. HRMS (ESI) calcd for $C_{26}H_{26}Cl_3NO_2SiNa^+$: 518.0871, found 518.0867.

Optical rotation: $[\alpha]_D^{25}$ = 0.40 [c = 0.04, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3h**: t_R = 8.5 min for the major isomer, t_R = 7.3 min for the minor isomer.

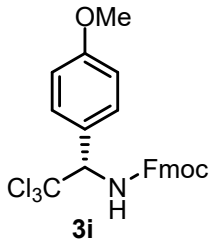


Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
7.913	VV	11575.88	49.72
8.588	VB	11704.12	50.28



Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
7.267	MM m	338.35	0.63
8.452	MB m	53450.56	99.37

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)carbamate (3i)

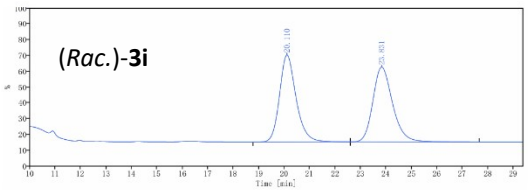


3i

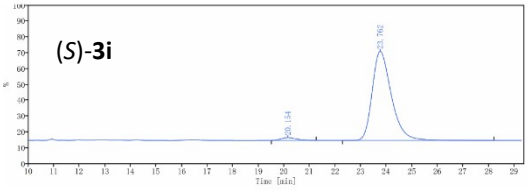
The title compound was isolated [(*S*)-**3i**: 24.3 mg, 51%, 95% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 15:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.58 (s, 2H), 7.41 (dt, *J* = 15.0, 7.8 Hz, 4H), 7.30 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 5.87 (d, *J* = 10.3 Hz, 1H), 5.60 (d, *J* = 10.2 Hz, 1H), 4.58 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.37 (dd, *J* = 10.7, 6.8 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 155.4, 143.7, 141.5, 130.6, 127.9, 127.2, 127.0, 125.2, 120.2, 113.7, 102.2, 68.8, 67.5, 55.4, 47.3. HRMS (ESI) calcd for $C_{24}H_{20}Cl_3NO_3Na^+$: 498.0401, found 498.0405.

Optical rotation: $[\alpha]_D^{25}$ = 1.13 [c = 0.04, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3i**: t_R = 23.8 min for the major isomer, t_R =20.2 min for the minor isomer.

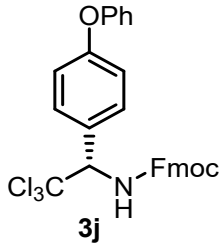


VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	% Area
20.110	BB	2494.45	49.44
23.831	BB	2550.85	50.56



VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	% Area
20.154	MM m	192.81	2.41
23.762	BB	7811.58	97.59

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-phenoxyphenyl)ethyl)carbamate (3j)



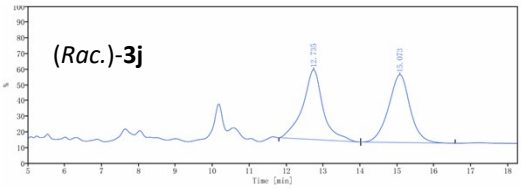
3j

The title compound was isolated [(*S*)-**3j**: 30.1 mg, 57%, 96% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 6.5 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.39 (dt, *J* = 18.0, 7.6 Hz, 4H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 5.86 (d, *J* = 10.3 Hz, 1H), 5.62 (d, *J* = 10.2 Hz, 1H), 4.60 (dd, *J* = 10.9, 6.8 Hz, 1H), 4.39 (dd, *J* = 10.8, 7.0 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 156.3, 155.4, 143.7, 141.5, 130.9, 130.0, 129.2, 127.9, 127.2,

125.2, 124.1, 120.2, 119.8, 117.9, 101.9, 68.7, 67.5, 47.3. HRMS (ESI) calcd for $C_{29}H_{22}Cl_3NO_3Na^+$: 560.0557, found 560.0561.

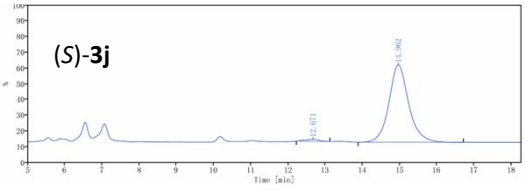
Optical rotation: $[\alpha]_D^{25}$ = 1.05 [c = 0.04, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3j**: t_R = 15.0 min for the major isomer, t_R = 12.7 min for the minor isomer.



VWD1A, Wavelength=254 nm

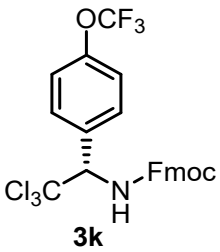
Retention Time	Type	Area	% Area
12.735	MB m	538.71	49.38
15.073	BB	552.21	50.62



VWD1A, Wavelength=254 nm

Retention Time	Type	Area	% Area
12.671	MB m	129.32	1.76
14.962	BB	7203.91	98.24

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-(trifluoromethoxy)phenyl)ethyl)carbamate (3k)

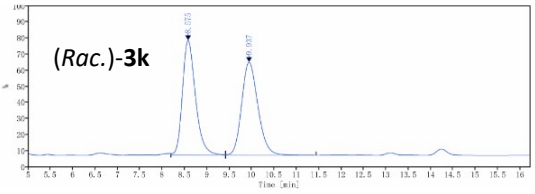


3k

The title compound was isolated [(*S*)-**3k**: 32.3 mg, 61%, 96% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.3 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.43 – 7.37 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.21 (m, 3H), 5.86 (d, *J* = 10.2 Hz, 1H), 5.66 (d, *J* = 10.1 Hz, 1H), 4.61 (ddd, *J* = 9.9, 6.4, 2.4 Hz, 1H), 4.47 – 4.38 (m, 1H), 4.23 (td, *J* = 6.6, 2.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 149.8, 143.6, 141.5, 133.5, 131.0, 128.0, 127.2, 125.1, 120.6, 120.5 (q, *J* = 257.9 Hz), 120.2, 101.2, 68.6, 67.5, 47.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ -57.96. HRMS (ESI) calcd for $C_{24}H_{17}Cl_3F_3NO_3Na^+$: 552.0118, found 552.0120.

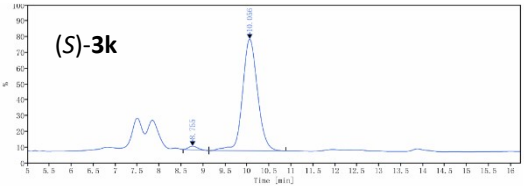
Optical rotation: $[\alpha]_D^{25}$ = 0.43 [c = 0.07, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3k**: t_R = 10.1 min for the major isomer, t_R = 8.8 min for the minor isomer.



Signal VWD1A, Wavelength=254 nm

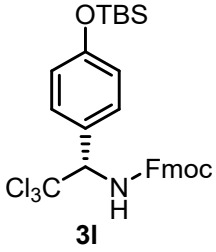
Retention Time	Type	Area	Area%
8.575	VV	11989.82	49.77
9.937	VB	12099.82	50.23



Signal VWD1A, Wavelength=254 nm

Retention Time	Type	Area	Area%
8.755	BB	50.41	2.03
10.056	MB m	2427.39	97.97

(9*H*-fluoren-9-yl)methyl-(*S*)-(1-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2,2,2-trichloroethyl)carbamate (3l)



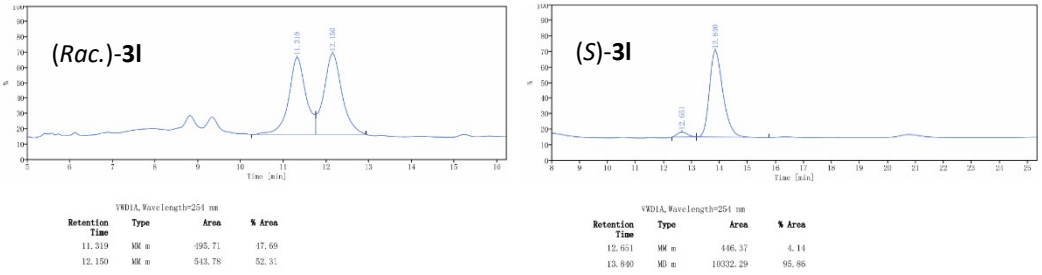
3l

The title compound was isolated [(*S*)-**3l**: 30.5 mg, 53%, 92% *ee*] as a white solid

flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 5.9 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 (q, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 5.85 – 5.76 (m, 1H), 5.58 (d, *J* = 10.3 Hz, 1H), 4.59 (dd, *J* = 10.5, 6.8 Hz, 1H), 4.39 – 4.33 (m, 1H), 4.24 (t, *J* = 6.7 Hz, 1H), 0.99 (s, 9H), 0.22 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 155.4, 143.8, 141.5, 130.6, 127.9, 127.5, 127.2, 125.2, 120.2, 119.8, 102.4, 68.8, 67.5, 47.3, 25.8, 18.3, -4.2. HRMS (ESI) calcd for $C_{29}H_{32}Cl_3NO_3SiNa^+$: 598.1109, found 598.1115.

Optical rotation: $[\alpha]_D^{25}$ = 1.17 [c = 0.07, CH_2Cl_2 (*S*)].

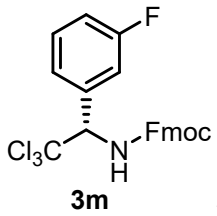
HPLC condition: Chiral column OD, n-hexane/i-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3l**: t_R = 13.8 min for the major isomer, t_R = 12.7 min for the minor isomer.



Retention Time	Type	Area	% Area
11.319	MM m	495.71	47.69
12.150	MM m	543.78	52.31

Retention Time	Type	Area	% Area
12.651	MM m	446.37	4.14
13.840	MM m	10332.29	95.86

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(3-fluorophenyl)ethyl)carbamate (3m)

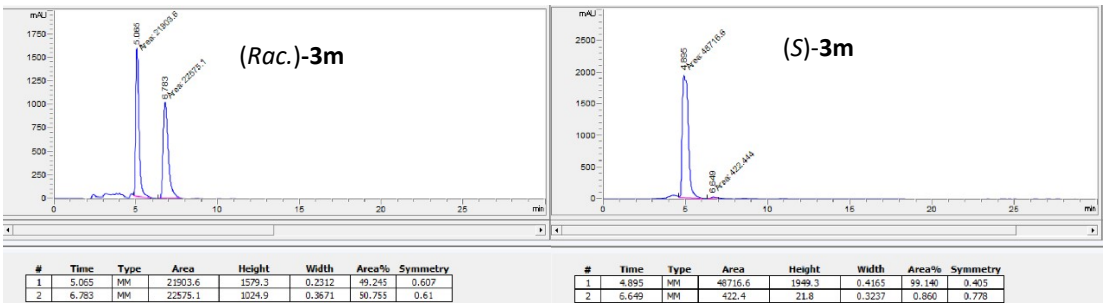


3m

The title compound was isolated [(*S*)-**3m**: 30.2 mg, 65%, 98% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.29 (t, *J* = 7.9 Hz, 3H), 7.22 (d, *J* = 9.7 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.84 (d, *J* = 10.2 Hz, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 4.60 (dd, *J* = 10.8, 6.5 Hz, 1H), 4.41 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.4 Hz), 155.3, 143.7, 143.6, 141.5, 137.3 (d, *J* = 7.0 Hz), 129.9 (d, *J* = 7.8 Hz), 128.0, 127.2, 125.4, 125.0, 120.2, 116.4 (d, *J* = 21.2 Hz), 101.1, 68.8, 67.6, 47.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.07. HRMS (ESI) calcd for $C_{23}H_{17}Cl_3FNO_2Na^+$: 486.0201, found 486.0204.

Optical rotation: $[\alpha]_D^{25}$ = 0.80 [c = 0.03, CH_2Cl_2 (*S*)].

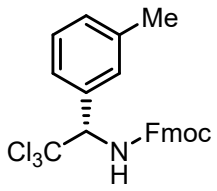
HPLC condition: Chiral column AD-3, n-hexane/i-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 210 nm, t_R = 4.9 min for the major isomer, t_R = 6.6 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.065	MM	21903.6	1579.3	0.2312	49.245	0.607
2	6.783	MM	22575.1	1024.9	0.3671	50.755	0.61

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.895	MM	46716.6	1949.3	0.4165	99.140	0.405
2	6.649	MM	422.4	21.8	0.3237	0.860	0.778

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(m-tolyl)ethyl)carbamate (3n)

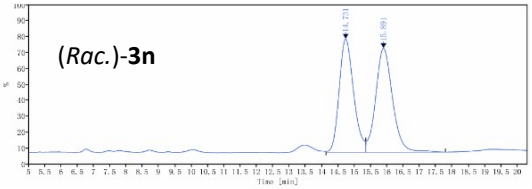


3n

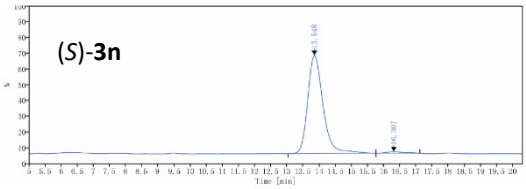
The title compound was isolated [(*S*)-**3n**: 34.0 mg, 74%, 97% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 19.4 Hz, 5H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.94 (d, *J* = 10.2 Hz, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.42 – 4.34 (m, 1H), 4.25 (t, *J* = 6.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.7, 141.4, 138.0, 134.8, 130.2, 130.1, 128.2, 127.9, 127.2, 126.4, 125.2, 120.1, 101.8, 69.2, 67.4, 47.2, 21.6. HRMS (ESI) calcd for $C_{24}H_{20}Cl_3NO_2Na^+$: 482.0452, found 482.0456.

Optical rotation: $[\alpha]_D^{25}$ = 0.95 [c = 0.04, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3n**: t_R = 13.8 min for the major isomer, t_R = 16.3 min for the minor isomer.

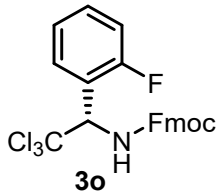


Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
14.731	VV	1512.99	48.27
15.891	VB	1621.28	51.73



Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
13.848	BB	3888.09	98.23
16.307	BM m	70.21	1.77

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(2-fluorophenyl)ethyl)carbamate (3o)

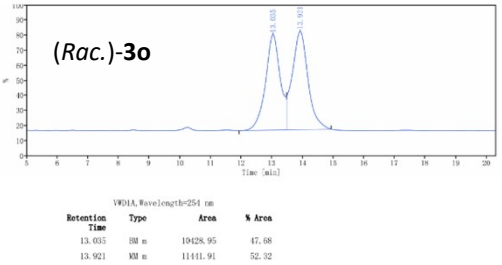


3o

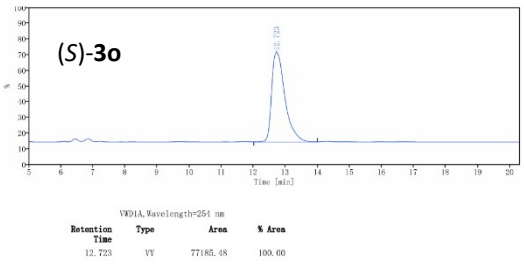
The title compound was isolated [(*S*)-**3o**: 18.6 mg, 40%, >99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (td, *J* = 7.5, 3.5 Hz, 3H), 7.34 – 7.26 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 10.7, 8.3 Hz, 1H), 6.06 – 5.99 (m, 1H), 5.83 (s, 1H), 4.60 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.39 (dd, *J* = 10.8, 7.0 Hz, 1H), 4.25 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9 (d, *J* = 249.0 Hz), 155.4, 143.7, 141.5, 131.3(d, *J* = 8.8 Hz), 130.6, 127.9, 127.2, 125.1 (d, *J* = 19.1 Hz), 124.2, 122.4 (d, *J* = 12.3 Hz), 120.2, 116.3 (d, *J* = 23.0 Hz), 101.5, 67.6, 64.2, 47.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.29. HRMS (ESI) calcd for $C_{23}H_{17}Cl_3FNO_2Na^+$: 486.0201, found 486.0205.

Optical rotation: $[\alpha]_D^{25}$ = 0.40 [c = 0.02, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3o**: t_R = 12.7 min for the major isomer, t_R = 13.9 min for the minor isomer.

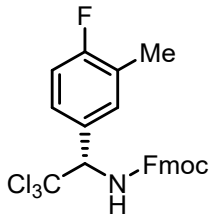


Retention Time	Type	Area	% Area
13.035	BM m	10428.95	47.68
13.921	MM m	11441.91	52.32



Retention Time	Type	Area	% Area
12.723	VV	77185.48	100.00

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-fluoro-3-methylphenyl)ethyl)carbamate (3p)

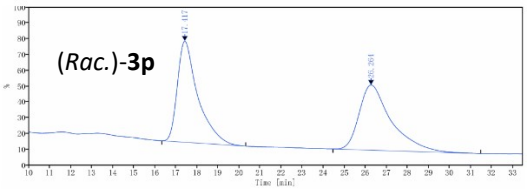


3p

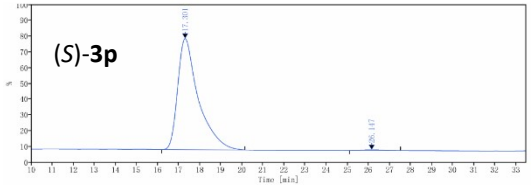
The title compound was isolated [(*S*)-**3p**: 30.1 mg, 63%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 6.2 Hz, 2H), 7.40 (td, *J* = 7.5, 3.1 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 4H), 7.02 (t, *J* = 8.8 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 4.60 (dd, *J* = 10.9, 6.7 Hz, 1H), 4.39 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8 (d, *J* = 247.9 Hz), 155.4, 143.7, 141.5, 132.7, 130.5 (d, *J* = 3.5 Hz), 128.4 (d, *J* = 8.4 Hz), 127.9, 127.2, 125.1, 125.0, 120.2, 115.0 (d, *J* = 22.6 Hz), 101.9, 68.7, 67.5, 47.3, 14.8 (d, *J* = 3.5 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ -116.10. HRMS (ESI) calcd for $C_{24}H_{19}Cl_3FNO_2Na^+$: 500.0358, found 500.0361.

Optical rotation: $[\alpha]_D^{25}$ = 0.80 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3p**: t_R = 17.3 min for the major isomer, t_R = 26.1 min for the minor isomer.

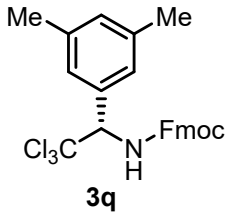


Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
17.417	BB	1468.84	49.75
26.264	BB	1483.42	50.25



Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
17.301	BB	1563.67	99.06
26.147	MM m	24.79	0.54

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(3,5-dimethylphenyl)ethyl)carbamate (3q)



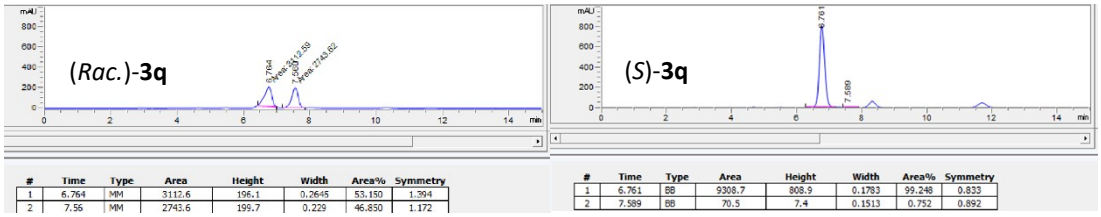
3q

The title compound was isolated [(*S*)-**3q**: 31.3 mg, 66%, 98% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 30:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 4.9 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.31 (q, *J* = 6.8 Hz, 2H), 7.13 (s, 2H), 7.05 (s, 1H), 5.89 (d, *J* = 10.4 Hz, 1H), 5.59 (d, *J* = 10.3 Hz, 1H), 4.60 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.37 (dd, *J* = 10.8, 6.9 Hz, 1H), 4.25 (t, *J* = 7.0 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 143.8, 143.7, 141.5, 137.9, 134.8, 131.0, 127.9, 127.2, 125.2, 120.2, 101.8, 69.3, 67.5, 47.3, 21.5. HRMS (ESI) calcd for

$C_{25}H_{22}Cl_3NO_2Na^+$: 496.0608, found 496.0616.

Optical rotation: $[\alpha]_D^{25}$ = 0.80 [c = 0.07, CH_2Cl_2 (*S*)].

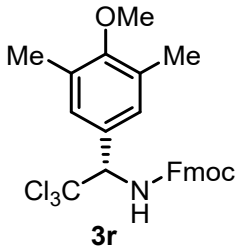
HPLC condition: Chiral column IA, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3q**: t_R = 6.8 min for the major isomer, t_R = 7.6 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.764	MM	3112.6	196.1	0.2645	53.150	1.394
2	7.56	MM	2743.6	199.7	0.229	46.850	1.172

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.761	BB	9308.7	808.9	0.1783	99.248	0.833
2	7.589	BB	70.5	7.4	0.1513	0.752	0.892

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(4-methoxy-3,5-dimethylphenyl)ethyl)carbamate (3r)

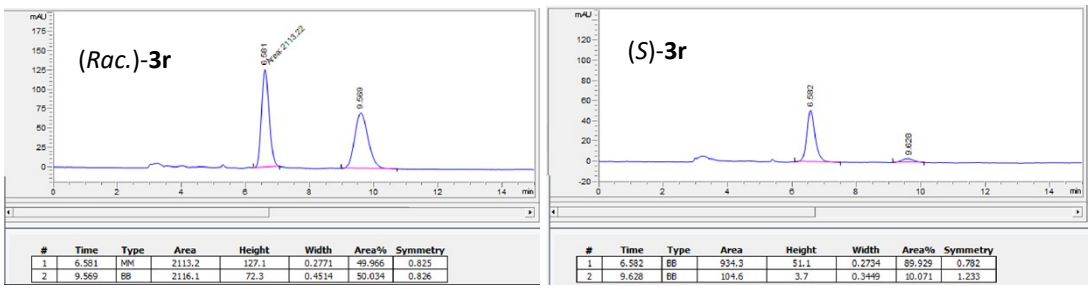


3r

The title compound was isolated [(*S*)-**3r**: 34.8 mg, 69%, 80% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 30:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 4.7 Hz, 2H), 7.58 (d, *J* = 4.7 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.15 (s, 2H), 5.86 (d, *J* = 10.4 Hz, 1H), 5.54 (d, *J* = 10.5 Hz, 1H), 4.59 (q, *J* = 4.0, 3.5 Hz, 1H), 4.35 (t, *J* = 5.6 Hz, 1H), 4.29 – 4.16 (m, 1H), 3.73 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 155.4, 143.8, 141.5, 130.9, 130.2, 129.8, 127.9, 127.2, 125.1, 120.2, 102.0, 68.9, 67.5, 59.8, 47.3, 16.4. HRMS (ESI) calcd for $C_{26}H_{25}Cl_3NO^+$: 504.0895, found 504.0901.

Optical rotation: $[\alpha]_D^{25}$ = 0.83 [c = 0.07, CH_2Cl_2 (*S*)].

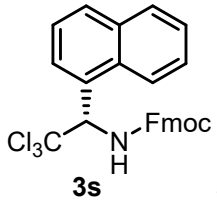
HPLC condition: Chiral column OD-H, n-hexane/i-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 220 nm, (*S*)-**3r**: t_R = 6.6 min for the major isomer, t_R = 9.6 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.581	MM	2113.2	127.1	0.2771	49.966	0.825
2	9.569	BB	2116.1	72.3	0.4514	50.034	0.826

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.582	BB	934.3	51.1	0.2734	89.929	0.782
2	9.628	BB	104.6	3.7	0.3449	10.071	1.233

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(naphthalen-1-yl)ethyl)carbamate (3s)



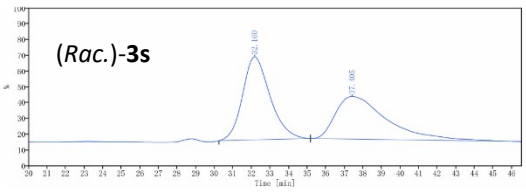
3s

The title compound was isolated [(*S*)-**3s**: 22.3 mg, 45%, 98% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 3H), 7.52 (dd, *J* = 15.1, 7.7 Hz, 4H), 7.42 (dt, *J* = 19.4, 7.5 Hz, 4H), 7.31 (s, 1H), 5.95 (d, *J* = 10.3 Hz, 1H), 5.75 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 8.7 Hz, 1H), 4.43 (t, *J* = 8.9 Hz, 1H), 4.28 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 143.8, 141.9,

141.5, 139.4, 133.9, 131.5, 130.0, 129.4, 128.5, 128.2, 127.9, 127.2, 126.4, 125.5, 125.1, 120.2, 101.8, 69.2, 67.6, 47.3. HRMS (ESI) calcd for $C_{27}H_{21}Cl_3NO_2^+$: 496.0632, found 496.0635.

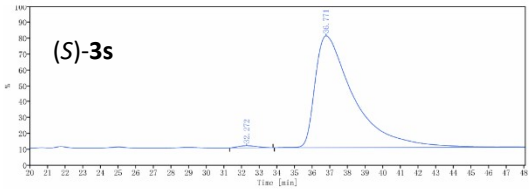
Optical rotation: $[\alpha]_D^{25}$ = 0.53 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 99:1, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3s**: t_R = 36.8 min for the major isomer, t_R = 32.3 min for the minor isomer.



VWD1A, Wavelength=254 nm

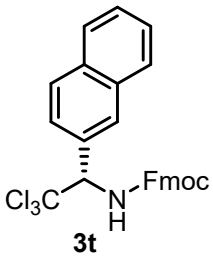
Retention Time	Type	Area	% Area
32.160	MM m	5296.91	50.91
37.405	BB	5107.86	49.09



VWD1A, Wavelength=250 nm

Retention Time	Type	Area	% Area
32.272	MB m	165.27	0.86
36.771	BM m	19059.28	99.14

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(naphthalen-2-yl)ethyl)carbamate (3t)

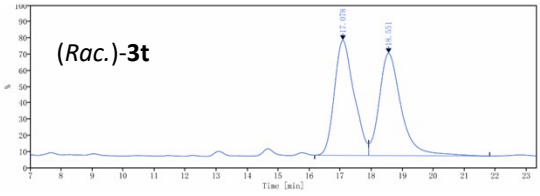


3t

The title compound was isolated [(*S*)-**3t**: 32.7 mg, 66%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 3H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 21.2 Hz, 3H), 7.55 (s, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.29 (s, 2H), 6.02 (d, *J* = 10.2 Hz, 1H), 5.84 (d, *J* = 10.4 Hz, 1H), 4.61 (t, *J* = 9.1 Hz, 1H), 4.47 – 4.35 (m, 1H), 4.24 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 143.7, 141.4, 133.5, 132.8, 132.3, 129.5, 128.4, 128.1, 127.9, 127.8, 127.2, 127.1, 126.7, 126.2, 125.1, 120.2, 101.8, 69.4, 67.5, 47.3. HRMS (ESI) calcd for $C_{27}H_{21}Cl_3NO_2^+$: 496.0632, found 496.0638.

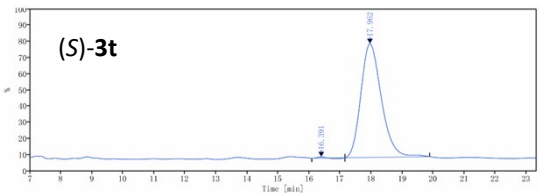
Optical rotation: $[\alpha]_D^{25}$ = 0.63 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3t**: t_R = 18.0 min for the major isomer, t_R = 16.4 min for the minor isomer.



Signal VWD1A, Wavelength=254 nm

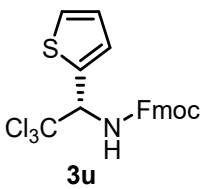
Retention Time	Type	Area	Area%
17.078	BV	3037.13	49.99
18.551	VB	3038.36	50.01



Signal VWD1A, Wavelength=254 nm

Retention Time	Type	Area	Area%
16.391	MM m	0.71	0.02
17.962	MM m	4056.51	99.98

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(thiophen-2-yl)ethyl)carbamate (3u)



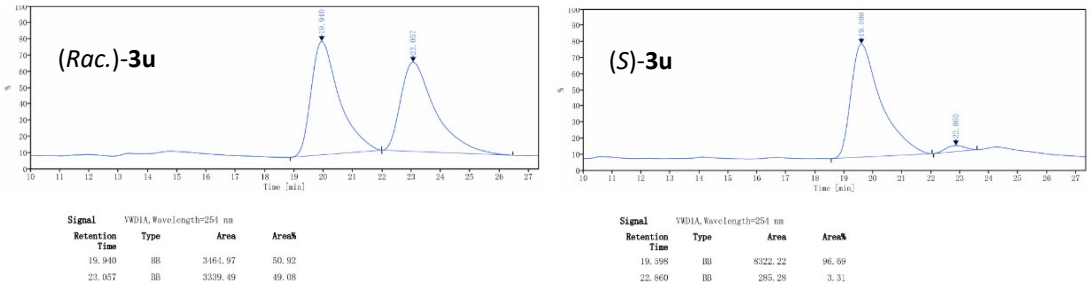
3u

The title compound was isolated [(*S*)-**3u**: 19.8 mg, 44%, 93% *ee*] as a yellow solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.33 – 7.29 (m, 2H),

7.27 (d, *J* = 3.4 Hz, 1H), 7.03 (t, *J* = 4.5 Hz, 1H), 5.96 (d, *J* = 10.2 Hz, 1H), 5.74 (d, *J* = 10.4 Hz, 1H), 4.59 (dd, *J* = 10.8, 6.7 Hz, 1H), 4.41 (dd, *J* = 10.8, 7.0 Hz, 1H), 4.25 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 143.6, 141.4, 137.1, 129.5, 127.9, 127.2, 126.9, 126.7, 125.2, 120.2, 101.3, 67.6, 65.9, 47.2. HRMS (ESI) calcd for $C_{21}H_{16}Cl_3NO_2SNa^+$: 473.9860, found 473.9865.

Optical rotation: $[\alpha]_D^{25}$ = 0.37 [c = 0.03, CH_2Cl_2 (*S*)].

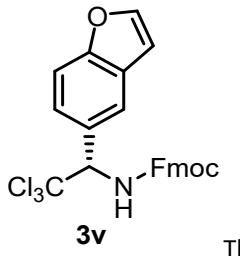
HPLC condition: Chiral column OD, n-hexane/i-PrOH = 88:12, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3u**: t_R = 19.6 min for the major isomer, t_R = 22.9 min for the minor isomer.



Signal	VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	Area%	
19.940	BB	3464.97	50.92	
23.057	BB	3339.49	49.08	

Signal	VWD1A, Wavelength=254 nm			
Retention Time	Type	Area	Area%	
19.598	BB	8322.22	96.69	
22.860	BB	285.28	3.31	

(9*H*-fluoren-9-yl)methyl-(*S*)-(1-(benzofuran-5-yl)-2,2,2-trichloroethyl)carbamate (3v)

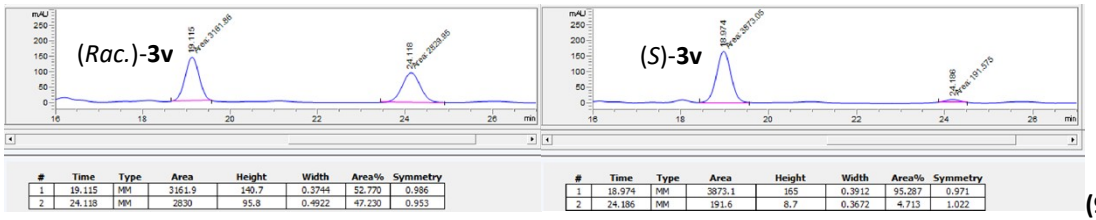


3v

The title compound was isolated [(*S*)-**3v**: 21.1 mg, 43%, 91% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.3 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.30 (d, *J* = 9.4 Hz, 2H), 7.28 (s, 1H), 6.92 (s, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 5.90 (d, *J* = 10.3 Hz, 1H), 4.62 (dd, *J* = 10.8, 6.7 Hz, 1H), 4.44 (dd, *J* = 10.8, 6.9 Hz, 1H), 4.26 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 154.8, 149.5, 146.5, 143.6, 141.5, 127.9, 127.2, 125.4, 125.2, 123.5, 121.7, 120.2, 111.6, 108.4, 100.1, 67.7, 64.5, 47.3. HRMS (ESI) calcd for $C_{25}H_{18}Cl_3NO_3Na^+$: 508.0244, found 508.0249.

Optical rotation: $[\alpha]_D^{25}$ = 0.11 [c = 0.03, CH_2Cl_2 (*S*)].

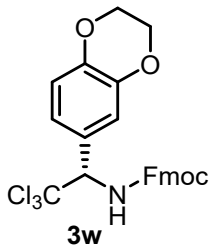
HPLC condition: Chiral column IA, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, (*S*)-**3v**: t_R = 19.0 min for the major isomer, t_R = 24.2 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.115	MM	3161.9	140.7	0.3744	52.770	0.986
2	24.118	MM	2830	95.8	0.4922	47.230	0.953

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.974	MM	3873.1	165	0.3912	95.287	0.971
2	24.186	MM	191.6	8.7	0.3672	4.713	1.022

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trichloro-1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethyl)carbamate (3w)

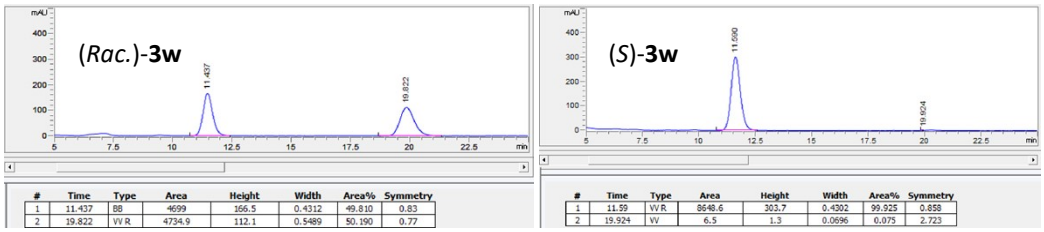


3w

The title compound was isolated [(*S*)-**3w**: 26.2 mg, 52%, 99% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 5.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.30 (td, *J* = 7.9, 4.0 Hz, 2H), 7.04 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.84 (d, *J* = 10.2 Hz, 1H), 5.54 (d, *J* = 10.2 Hz, 1H), 4.57 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.37 (dd, *J* = 10.8, 7.1 Hz, 1H), 4.26 (s, 4H), 4.23 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 144.5, 143.7, 143.2, 141.4, 128.0, 127.9, 127.2, 125.2, 122.7, 120.1, 118.3, 117.1, 102.0, 68.8, 67.5, 64.5, 64.4, 47.3. HRMS (ESI) calcd for $C_{25}H_{20}Cl_3NO_4Na^+$: 526.0350, found 526.0356.

Optical rotation: $[\alpha]_D^{25}$ = [c = 0.03, CH_2Cl_2 (*S*)].

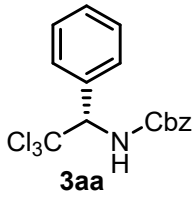
HPLC condition: Chiral column AD-H, n-hexane/i-PrOH = 70:30 flow rate = 1.0 mL/min, wavelength = 210 nm, (*S*)-**3w**: t_R = 11.6 min for the major isomer, t_R = 20.0 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.437	BB	4699	166.5	0.4312	49.810	0.83
2	19.822	VV R	4734.9	112.1	0.5489	50.190	0.77

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.59	VV R	8648.6	303.7	0.4302	99.925	0.858
2	19.924	VV	6.5	1.3	0.0696	0.075	2.723

Benzyl (*S*)-(2,2,2-trichloro-1-phenylethyl) carbamate (3aa)

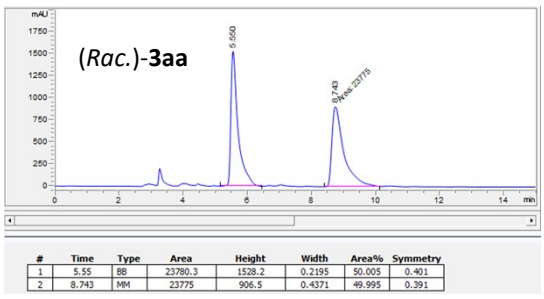


3aa

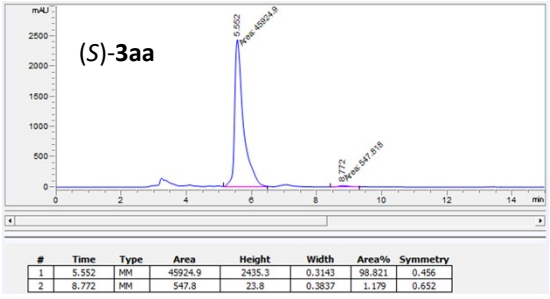
The title compound was isolated [(*S*)-**3aa**: 23.6 mg, 66%, 98% *ee*; (*R*)-**3aa**: 24.3 mg, 68%, 97% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 30:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.7 Hz, 2H), 7.39 (d, *J* = 6.3 Hz, 3H), 7.36 (s, 5H), 5.92 (d, *J* = 10.3 Hz, 1H), 5.67 (d, *J* = 10.2 Hz, 1H), 5.21 – 5.09 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 135.8, 134.9, 129.5, 129.4, 128.7, 128.6, 128.5, 128.4, 101.8, 69.3, 67.8. HRMS (ESI) calcd for $C_{16}H_{14}Cl_3NO_2Na^+$: 379.9982, found 379.9980.

Optical rotation: $[\alpha]_D^{25}$ = 0.87 [c = 0.09, CH_2Cl_2 (*S*)].

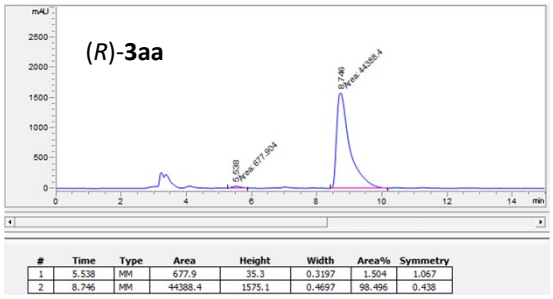
HPLC condition: Chiral column AD-3, n-hexane/i-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 210 nm, (*S*)-**3aa**: t_R = 5.6 min for the major isomer, t_R = 8.8 min for the minor isomer; (*R*)-**3aa**: t_R = 8.7 min for the major isomer, t_R = 5.5 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.55	BB	23780.3	1528.2	0.2195	50.005	0.401
2	8.743	MM	23775	906.5	0.4371	49.995	0.391

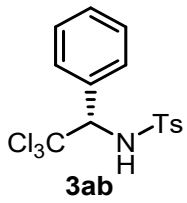


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.552	MM	45924.9	2435.3	0.3143	98.821	0.456
2	8.772	MM	547.8	23.8	0.3837	1.179	0.652



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.538	MM	677.9	35.3	0.3197	1.504	1.067
2	8.746	MM	44388.4	1575.1	0.4697	98.496	0.438

(*S*)-4-methyl-N-(2,2,2-trichloro-1-phenylethyl) benzenesulfonamide (3ab)

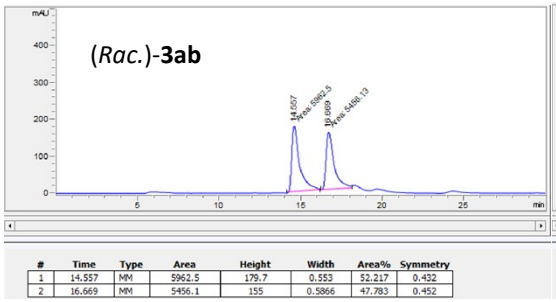


3ab

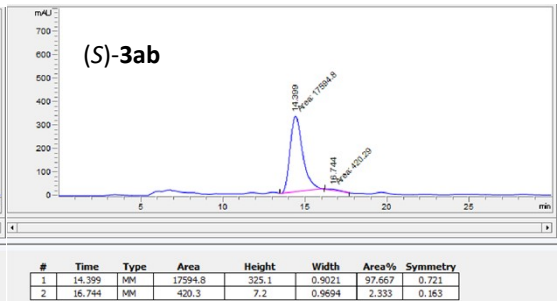
The title compound was isolated [(*S*)-**3ab**: 23.1 mg, 61%, 95% *ee*; (*R*)-**3ab**: 22.7 mg, 60%, 96% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 15:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 9.7 Hz, 1H), 5.11 (d, *J* = 9.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.2, 134.0, 129.5, 129.4, 129.2, 128.2, 127.2, 102.4, 72.0, 21.6. HRMS (ESI) calcd for $C_{15}H_{14}Cl_3NO_2SNa^+$: 399.9703, found 399.9700.

Optical rotation: $[\alpha]_D^{25}$ = 0.36 [c = 0.05, CH_2Cl_2 (*S*)].

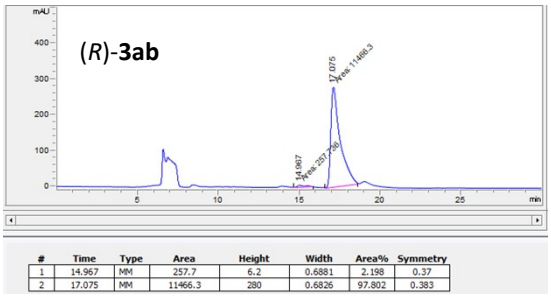
HPLC condition: Chiral column AD-3, n-hexane/i-PrOH = 80:20, flow rate = 0.5 mL/min, wavelength = 220 nm, (*S*)-**3ab**: t_R = 14.4 min for the major isomer, t_R = 16.7 min for the minor isomer; (*R*)-**3ab**: t_R = 17.1 min for the major isomer, t_R = 15.0 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.557	MM	5962.5	179.7	0.553	52.217	0.432
2	16.669	MM	5456.1	155	0.5866	47.783	0.452

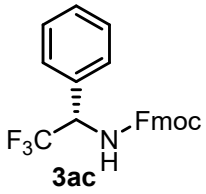


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.399	MM	17594.8	325.1	0.9021	97.667	0.721
2	16.744	MM	420.3	7.2	0.9694	2.333	0.163



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.967	MM	257.7	6.2	0.6881	2.198	0.37
2	17.075	MM	11466.3	280	0.6826	97.802	0.383

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2,2-trifluoro-1-phenylethyl)carbamate (3ac)

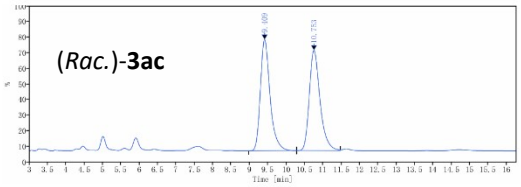


3ac

The title compound was isolated [(*S*)-**3ac**: 23.4 mg, 59%, 95% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 18.0, 7.0 Hz, 6H), 7.30 (t, *J* = 7.6 Hz, 2H), 5.53 (d, *J* = 9.8 Hz, 1H), 5.40 (t, *J* = 8.5 Hz, 1H), 4.52 (dd, *J* = 10.7, 6.8 Hz, 1H), 4.44 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.22 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 143.70, 143.66, 141.5, 132.9, 129.5, 129.2, 128.0, 127.9, 127.3 (d, *J* = 2.1 Hz), 125.0, 120.2, 67.6, 56.7, 47.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -74.23. HRMS (ESI) calcd for $C_{23}H_{18}F_3NO_2Na^+$: 420.1182, found 420.1181.

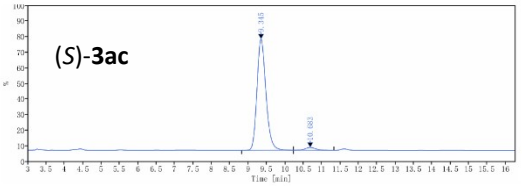
Optical rotation: $[\alpha]_D^{25}$ = 0.40 [c = 0.03, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3ac**: t_R = 9.3 min for the major isomer, t_R = 10.7 min for the minor isomer.



Signal VWD1A, Wavelength=254 nm

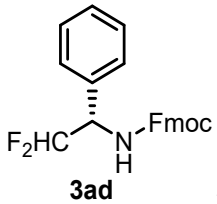
Retention Time	Type	Area	Area%
9.409	BB	3846.53	49.98
10.753	BV	3849.41	50.02



Signal VWD1A, Wavelength=254 nm

Retention Time	Type	Area	Area%
9.345	BB	4423.83	97.28
10.683	BB	123.82	2.72

(9*H*-fluoren-9-yl)methyl-(*S*)-(2,2-difluoro-1-phenylethyl)carbamate (3ad)

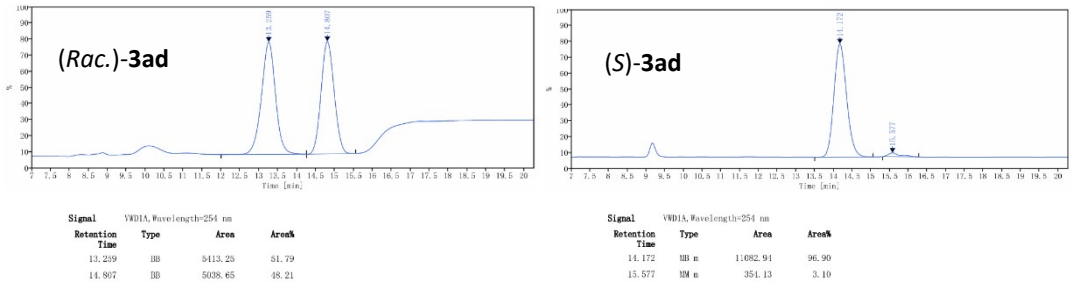


3ad

The title compound was isolated [(*S*)-**3ad**: 21.8 mg, 57%, 94% *ee*] as a white solid flash chromatography on silica gel (Hexane/EtOAc = 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.40 (q, *J* = 6.5, 5.2 Hz, 4H), 7.32 (q, *J* = 7.6 Hz, 4H), 6.02 (t, *J* = 55.4 Hz, 1H), 5.49 (d, *J* = 8.9 Hz, 1H), 5.13 (q, *J* = 13.2, 12.3 Hz, 1H), 4.47 (qd, *J* = 10.7, 6.8 Hz, 2H), 4.23 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 143.8, 141.4, 134.2, 129.1, 129.0, 127.9, 127.8, 127.2 (d, *J* = 1.7 Hz), 125.1, 120.2, 114.8, 67.4, 56.8, 47.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.95 (dd, *J* = 55.9, 15.4 Hz), -125.70 (dd, *J* = 55.9, 15.4 Hz), -127.14 (dd, *J* = 54.9, 14.3 Hz), -127.89 (dd, *J* = 54.4, 14.7 Hz). HRMS (ESI) calcd for $C_{23}H_{19}F_2NO_2Na^+$: 402.1276, found 402.1269.

Optical rotation: $[\alpha]_D^{25}$ = 0.20 [c = 0.04, CH_2Cl_2 (*S*)].

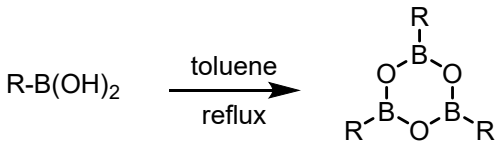
HPLC condition: Chiral column IC, n-hexane/i-PrOH = 97:3, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**3ad**: t_R = 14.2 min for the major isomer, t_R = 15.6 min for the minor isomer.



Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
13.239	BB	5413.25	51.79
14.807	BB	5038.65	48.21

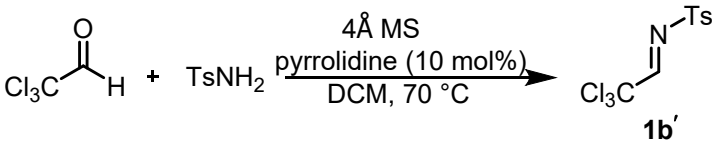
Signal	VWD1A, Wavelength=254 nm		
Retention Time	Type	Area	Area%
14.172	BB m	11682.91	96.90
15.577	BM m	354.13	3.10

General procedure for synthesis of boroxines

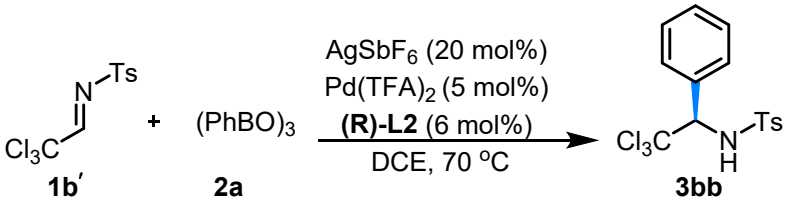


In a flame dried round bottom flask, a mixture of the boronic acid (1.0 g) in toluene (30 mL) was refluxed for 8 h with a Dean-Stark trap. The reaction solution was concentrated under vacuum at 80 °C to yield the corresponding boroxine. This boroxine was directly used in the next step without further purification.

Preparation of trichloromethyl imine and asymmetric arylation reaction



1b′



1b′ **2a** **3bb**

Prepare compound **1b′** according to previously reported procedures[3], a dried schlenk flask was charged with trichloroacetaldehyde (500 mg, 3.4 mmol), $TsNH_2$ (550 mg, 2.3 mmol), activated 4Å molecular sieve and DCM. The reaction mixture was stirred at 70 °C for 24 h. Then the mixture was filtered through Celite and recrystallized in cold hexane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 143.8, 139.1, 129.9, 126.6, 85.4, 21.7.

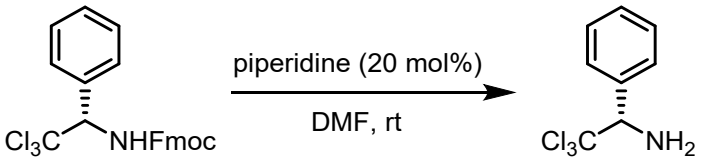
In a flame dried round bottom flask, the solution of Pd $(TFA)_2$ (3.3 mg, 0.01 mmol), (*R*)-^{t}Bu-PyOX **L2** (2.4 mg, 0.012 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), **1b′** (60.1 mg, 0.20 mmol), **2a** (124.4 mg, 0.40 mmol) and DCE (2 mL) were added. The reaction mixture was stirred at 70 °C for 12 h and the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1:15) as eluent, yielding **3bb** (32% yield, 96% *ee*) as white solid.

Gram-scale reaction

In a flame dried round bottom flask, the solution of Pd $(TFA)_2$ (34 mg, 0.10 mmol), (*S*)-^{t}Bu-PyOX (25 mg, 0.12 mmol), $AgSbF_6$ (134 mg, 0.40 mmol), **1a** (0.86 g, 2.01 mmol), boroxine (1.24 g, 0.40 mmol)

and DCE (20 mL) were added. The reaction mixture was stirred at 70 °C for 20 h and the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1:20) as eluent, yielding **3a** (0.72 g, 80% yield, 98% *ee*) as white solid.

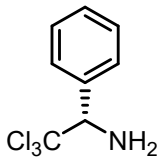
Transformation of α-aryl trichloroethylamines



3a **4**

Prepared according to a previous reported procedure,[4] in a 4 mL screw-capped vial, **3a** (89.2 mg, 0.2 mmol), pieperidine (3.4 mg, 0.06 mmol), DMF (1.0 mL) and a magnetic stirring bar were added under nitrogen. The mixture was stirred at room temperature 1 h. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1:15) as eluent, yielding **4** (88% yield, 99% *ee*) as white solid.

(*S*)-2,2,2-trichloro-1-phenylethan-1-amine (4)

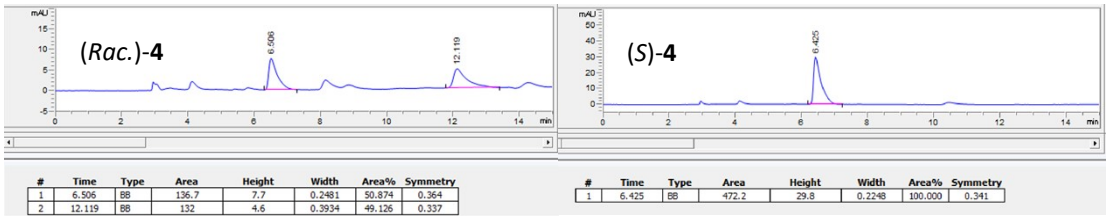


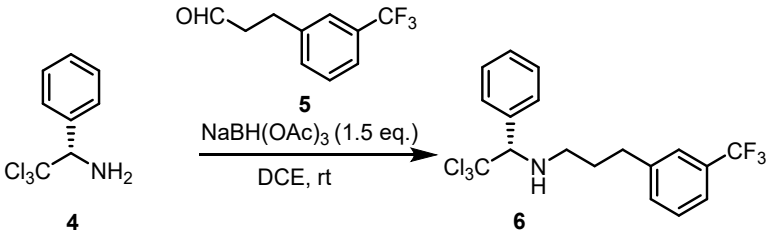
4

The title compound was isolated [(*S*)-**4**: 39.4 mg, 88%, 99% *ee*] as a colorless oil flash chromatography on silica gel (Hexane/EtOAc = 15:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.41 – 7.34 (m, 3H), 4.63 (s, 1H), 2.30 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 129.3, 129.1, 128.1, 105.6, 72.0. HRMS (ESI) calcd for $C_8H_9Cl_3N^+$: 223.9795, found 223.9793.

Optical rotation: $[\alpha]_D^{25}$ = 1.62 [c = 0.05, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column AD-3, n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, (*S*)-**4**: t_R = 6.4 min for the major isomer, t_R = 12.1 min for the minor isomer.



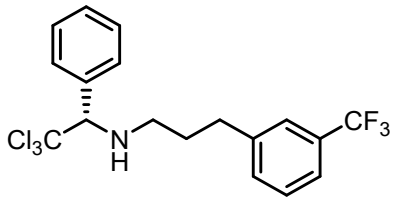


4 **6**

Prepared according to a previous reported method,[5] in a 4 mL screw-capped vial, **4** (22.4 mg, 0.10 mmol), **5** (23.8 mg, 0.11 mmol), $NaBH(OAc)_3$ (29.7 mg, 0.14 mmol), DCE (1.0 mL) and a magnetic stirring bar were added under nitrogen. The mixture was stirred at room temperature 1 h. The resulting solution was added 10 mL H_2O. The crude reaction mixture was then extracted with ethyl

acetate (10 mL × 3). The combined organic layers were then dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash column chromatography to give **6** (62% yield, 99% *ee*) as a colorless oil.

(*S*)-N-(2,2,2-trichloro-1-phenylethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (6)

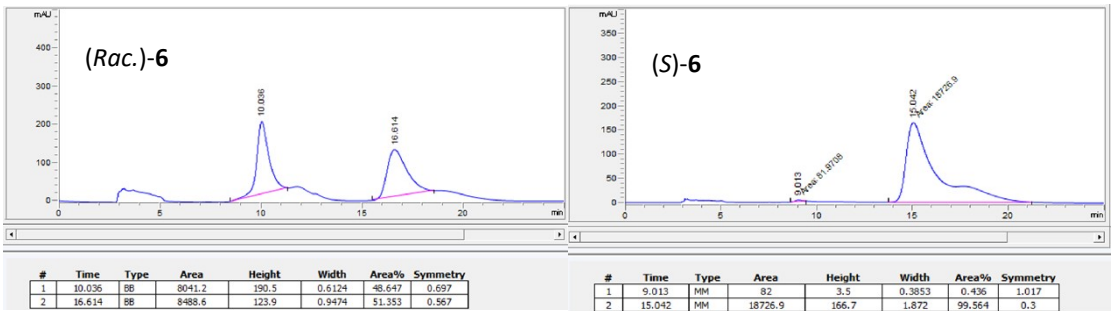


6

The title compound was isolated [(*S*)-**6**: 38.1 mg, 62%, 99% *ee*] as a colorless oil flash chromatography on silica gel (Hexane/EtOAc = 40:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.34 (m, 5H), 7.32 (d, *J* = 7.7 Hz, 1H), 4.32 (s, 1H), 2.75 (dt, *J* = 15.0, 7.7 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.62 (q, *J* = 6.8 Hz, 2H), 2.06 (s, 1H), 1.82 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 136.4, 132.0, 130.8 (d, *J* = 32.0 Hz), 130.0, 129.1, 128.9, 128.2, 125.2 (q, *J* = 7.0, 3.1 Hz), 123.5, 122.9 (q, *J* = 3.8 Hz), 103.1, 77.9, 47.3, 33.1, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52. HRMS (ESI) calcd for $C_{18}H_{18}Cl_3F_3N^+$: 410.0451, found 410.0448.

Optical rotation: $[\alpha]_D^{25}$ = 1.70 [c = 0.10, CH_2Cl_2 (*S*)].

HPLC condition: Chiral column AS-3, n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, (*S*)-**6**: t_R = 15.0 min for the major isomer, t_R = 9.0 min for the minor isomer.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.036	BB	8041.2	190.5	0.6124	48.647	0.697
2	16.614	BB	8488.6	123.9	0.9474	51.353	0.567

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.013	MM	82	3.5	0.3853	0.436	1.017
2	15.042	MM	18726.9	166.7	1.872	99.564	0.3

Mechanism study

In a flame dried round bottom flask, Pd $(TFA)_2$ (1.7 mg, 0.005 mmol), (*S*)-^{t}Bu-PyOX (1.2 mg, 0.006 mmol), $AgSbF_6$ (6.7 mg, 0.02 mmol), *N*,*O*-acetal (0.10 mmol), boroxine (62.2 mg, 0.20 mmol) and DCE (1 mL) were added under air. The reaction mixture was stirred at 70 °C for 5 h. We found that the *N*-Fmoc-CCl_3 imine intermediate could be formed in the presence of Pd catalyst and the Lewis acid additive $AgSbF_6$, which could be detected by HRMS analysis as shown below.

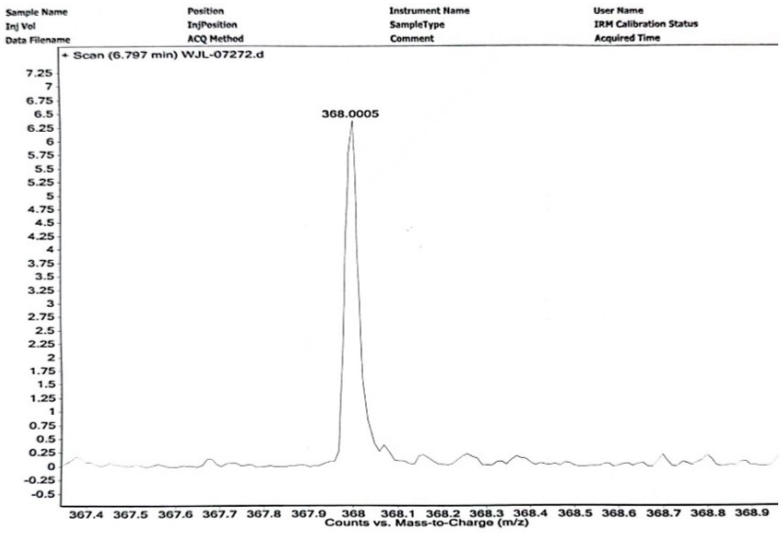


Figure SI-1: HRMS of *N*-Fmoc CCl_3 imine intermediate

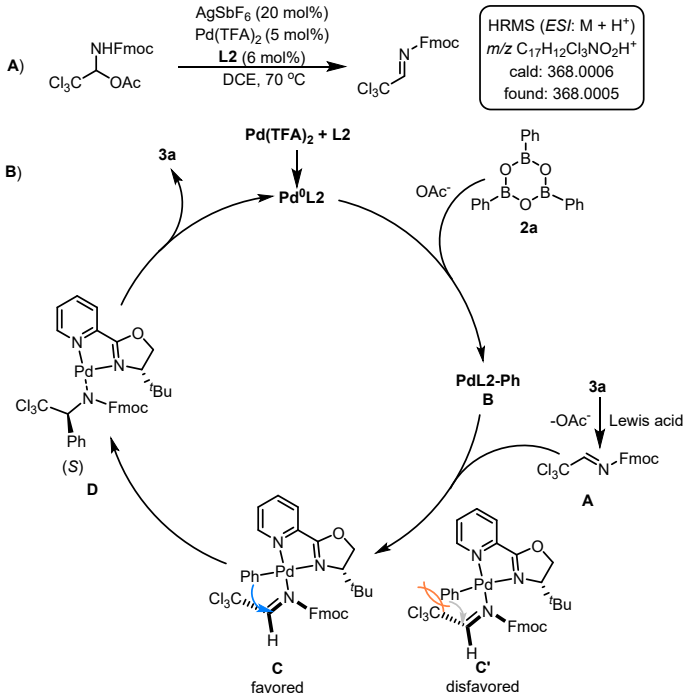


Figure SI-2. Imine intermediate detection and proposed mechanism

Crystal structure of 3a

Single crystal of product **3a** was obtained through slow evaporation of a mix solution in n-hexane and dichloromethane at glove box. X-ray data was collected with a Bruker APEX-II CCD diffractometer.

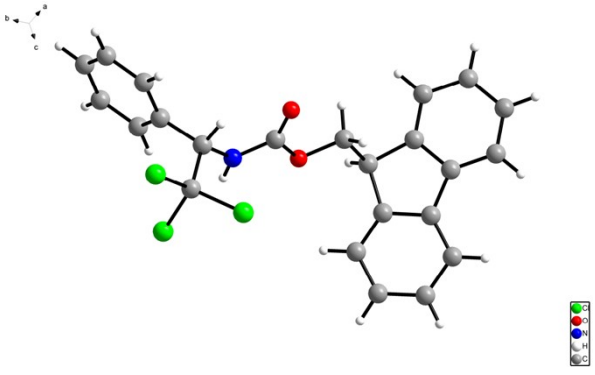


Figure SI-3: X-Ray structure of compound **3a**

Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{23}H_{18}Cl_3NO_2$
Formula weight	446.73
Temperature/K	193.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.5787(5)
b/Å	13.2751(9)
c/Å	27.4431(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2032.4(3)
Z	4
ρ_{calc}g/cm^3	1.460
μ/mm^{-1}	0.471
F(000)	920.0
Crystal size/mm^3	0.120 × 0.110 × 0.080
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.408 to 55.04
Index ranges	-6 ≤ h ≤ 7, -16 ≤ k ≤ 17, -35 ≤ l ≤ 35
Reflections collected	19100
Independent reflections	4684 [R_{int} = 0.0531, R_{sigma} = 0.0487]
Data/restraints/parameters	4684/0/262
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.0711
Final R indexes [all data]	R_1 = 0.0527, wR_2 = 0.0775
Largest diff. peak/hole / e Å^{-3}	0.24/-0.31
Flack parameter	0.04(3)

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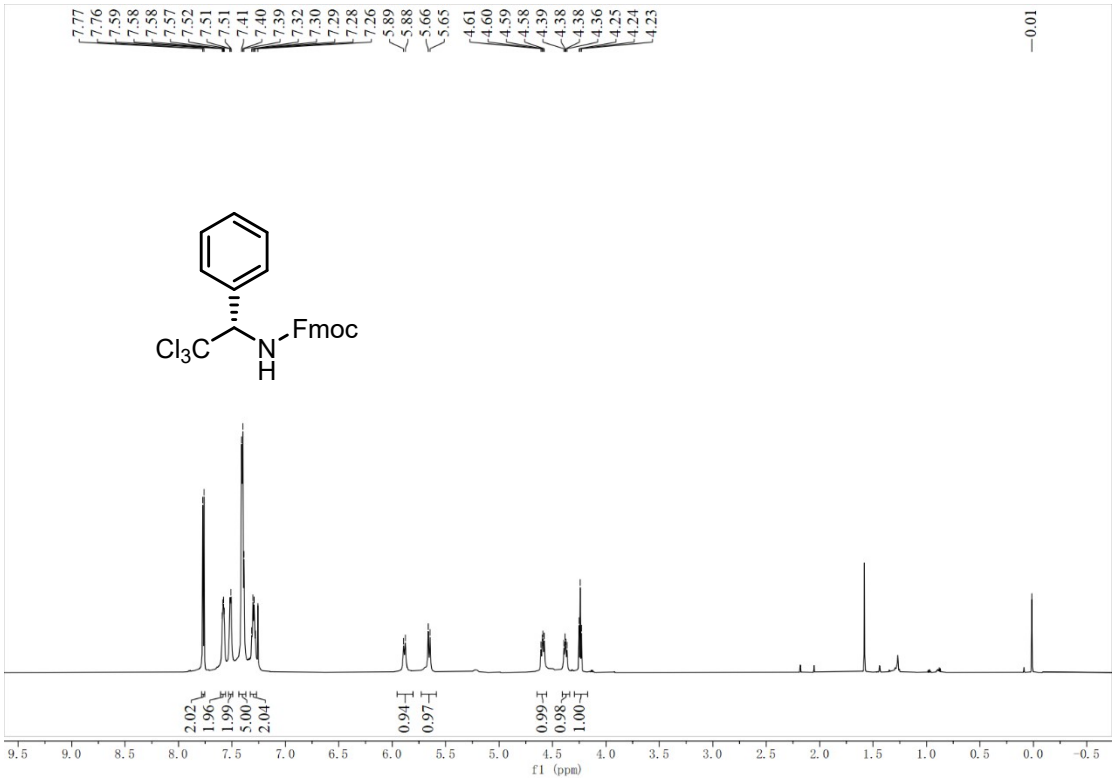
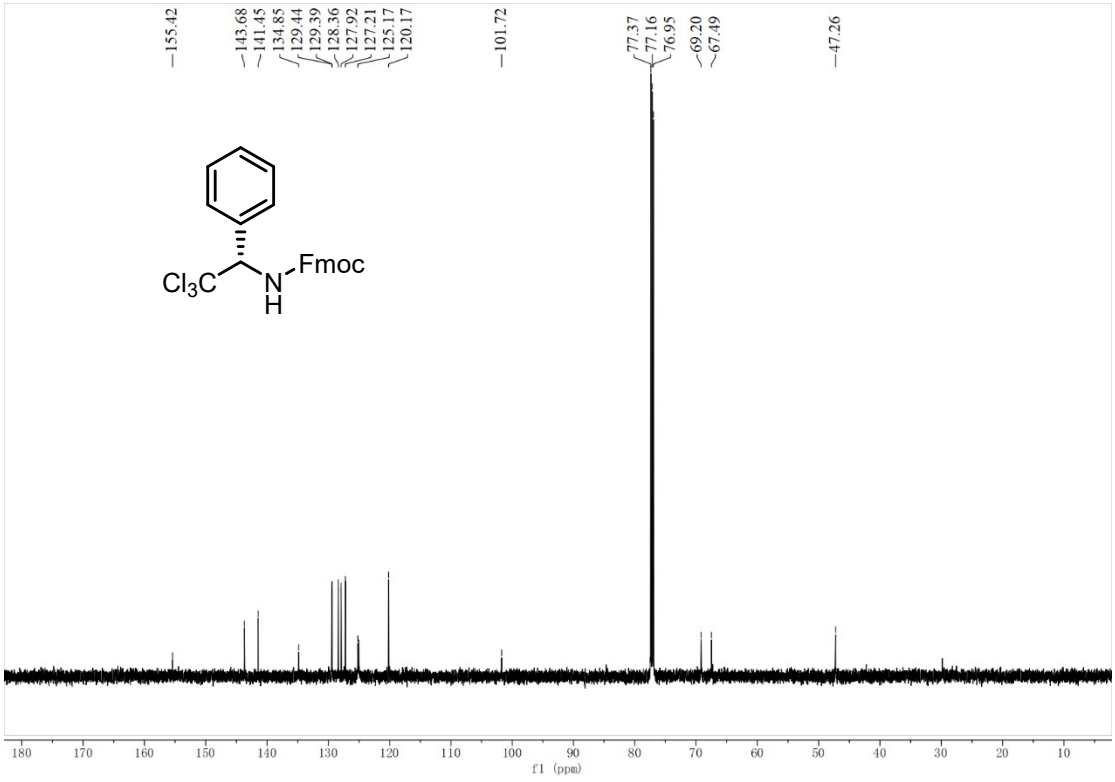
NMR spectra

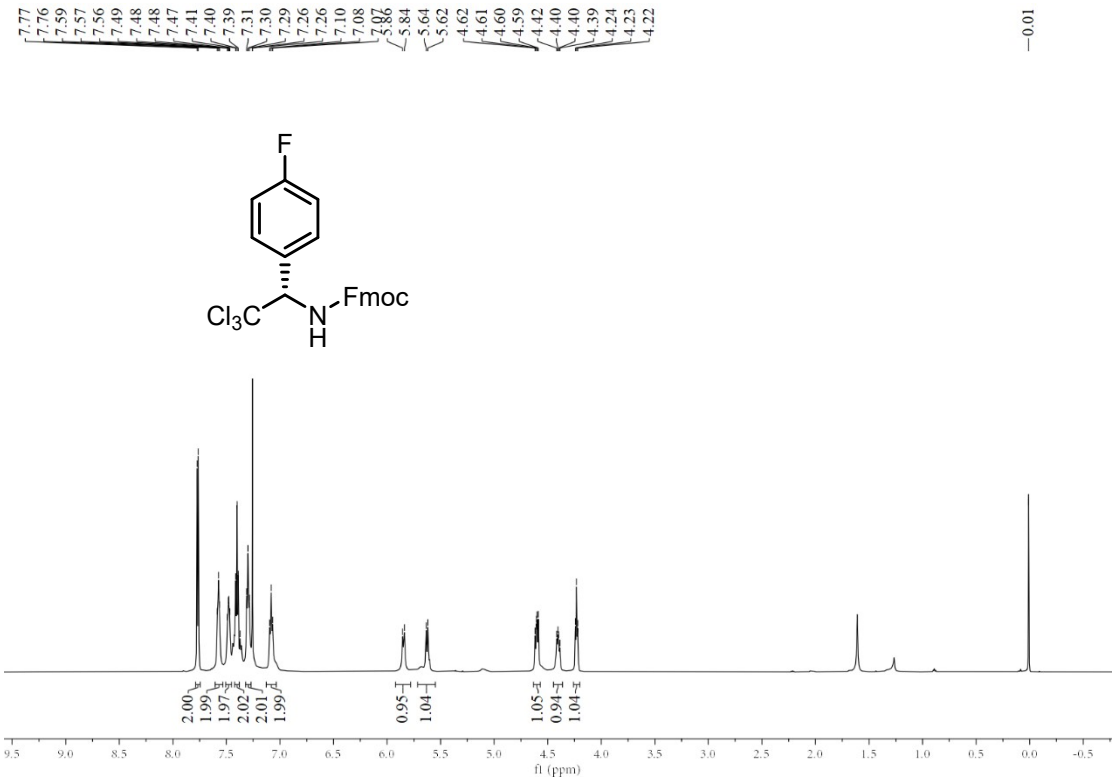
^{1}H NMR of **3a** (600 MHz, $CDCl_3$)



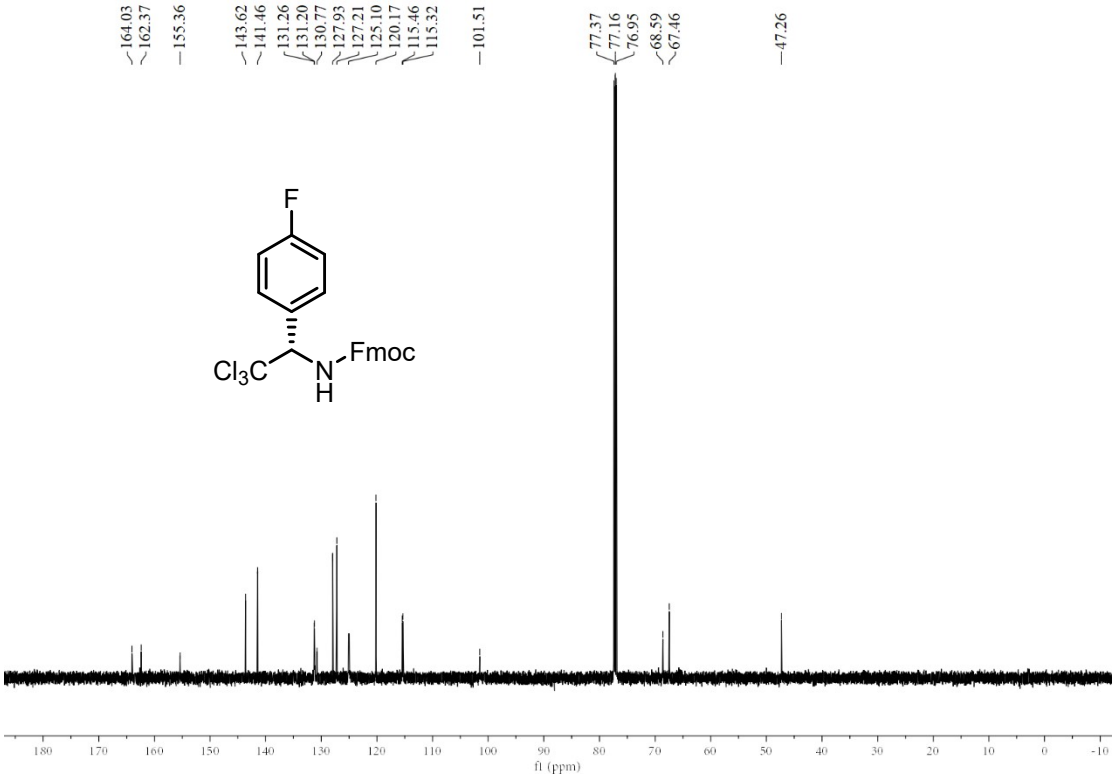
^{13}C NMR of **3a** (151 MHz, $CDCl_3$)



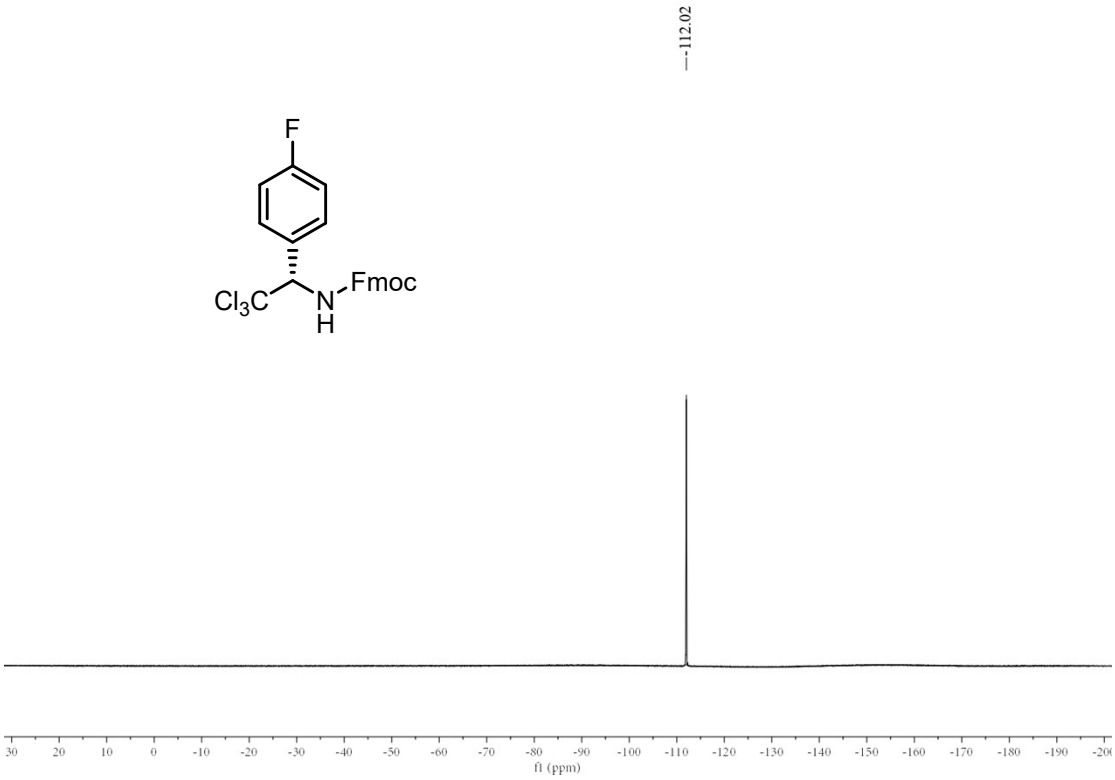
^{1}H NMR of **3b** (600 MHz, $CDCl_3$)



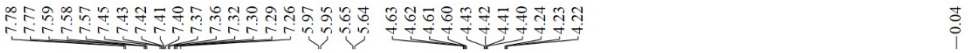
^{13}C NMR of **3b** (151 MHz, $CDCl_3$)

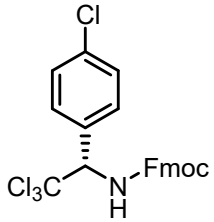


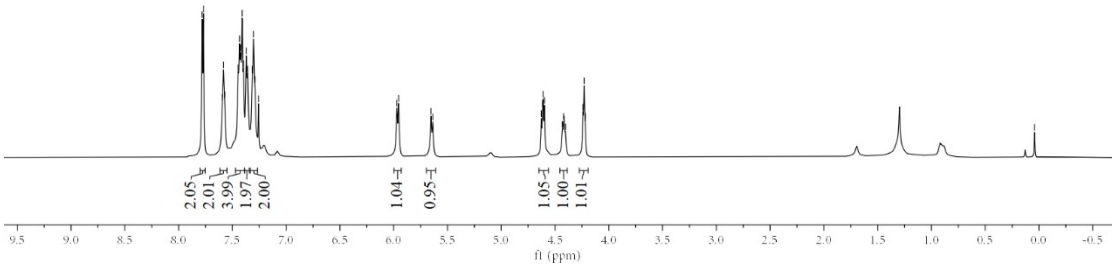
^{19}F NMR of **3b** (564 MHz, $CDCl_3$)



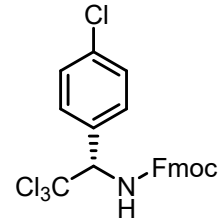
^{1}H NMR of **3c** (600 MHz, $CDCl_3$)

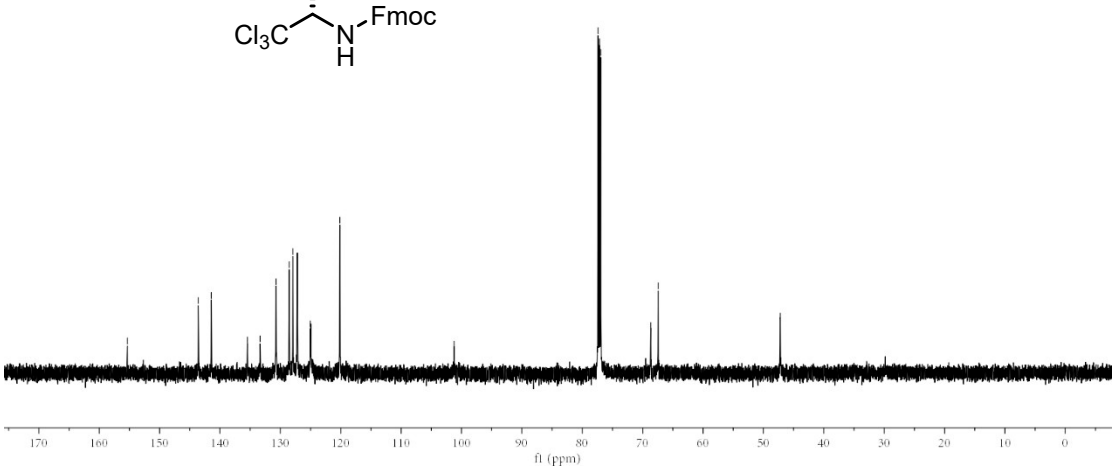




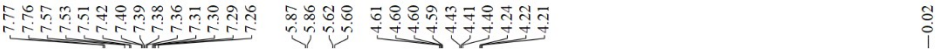


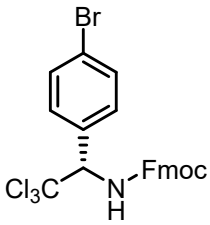
^{13}C NMR of **3c** (151 MHz, $CDCl_3$)

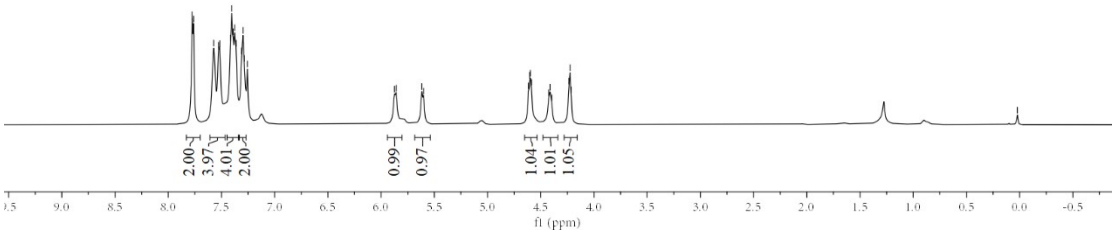




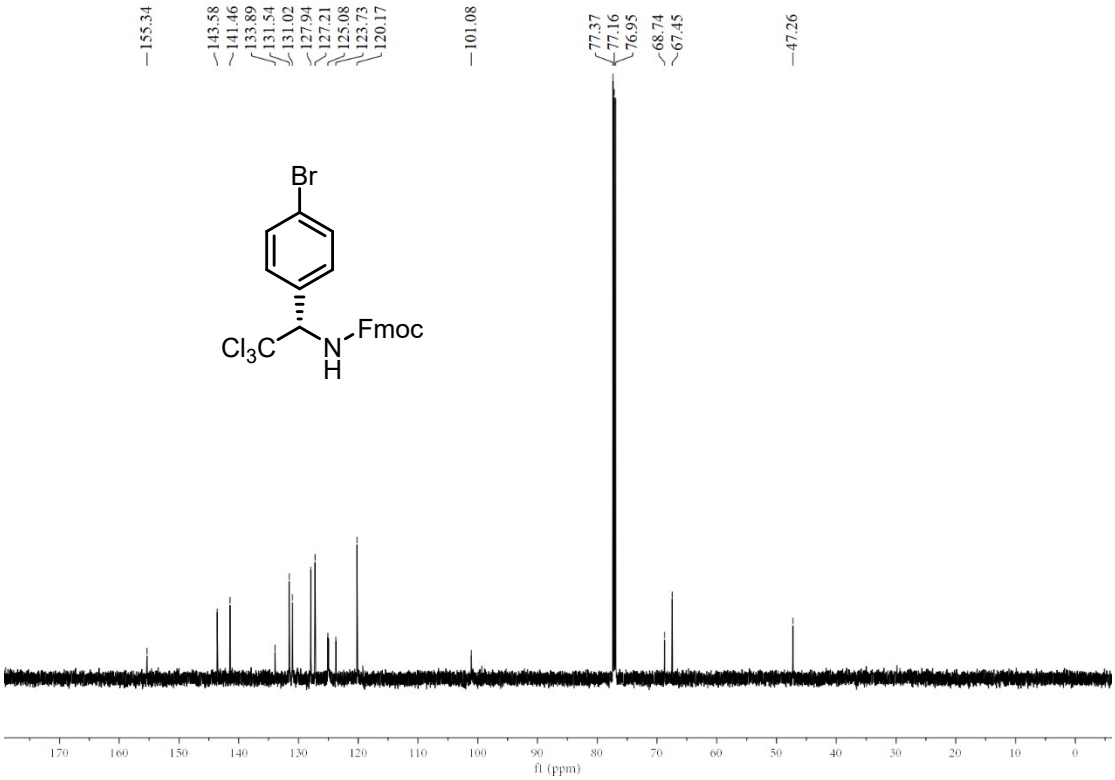
^{1}H NMR of **3d** (600 MHz, $CDCl_3$)



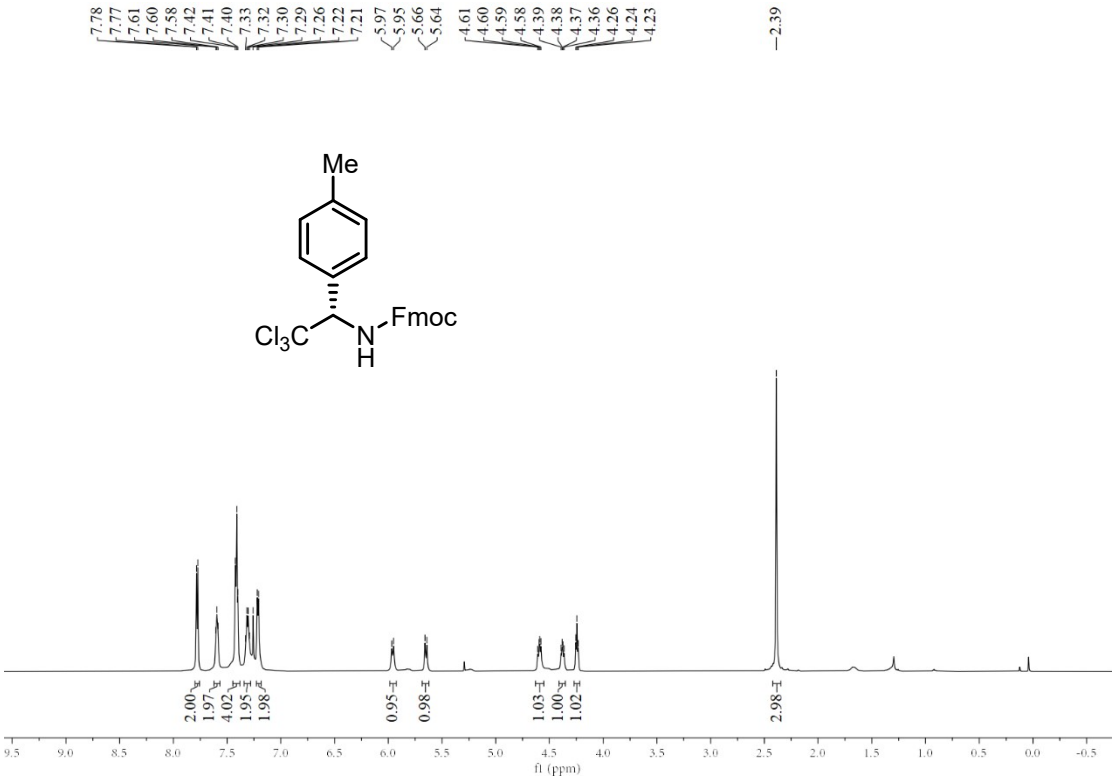




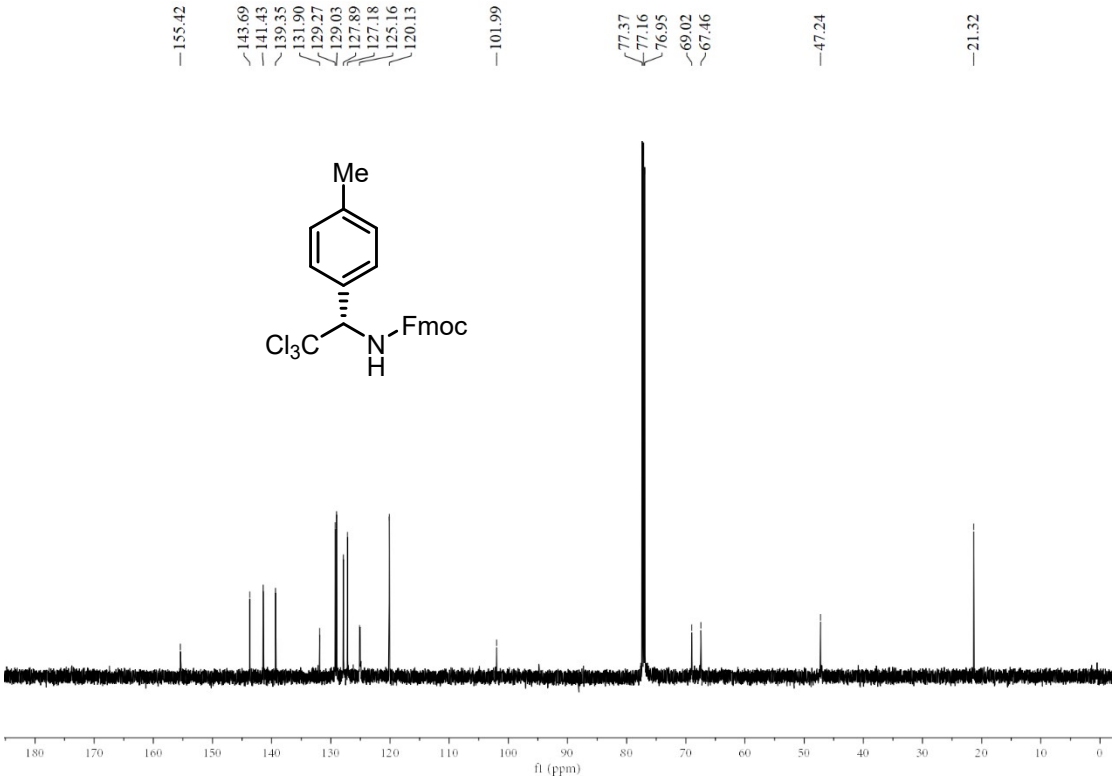
^{13}C NMR of **3d** (151 MHz, $CDCl_3$)



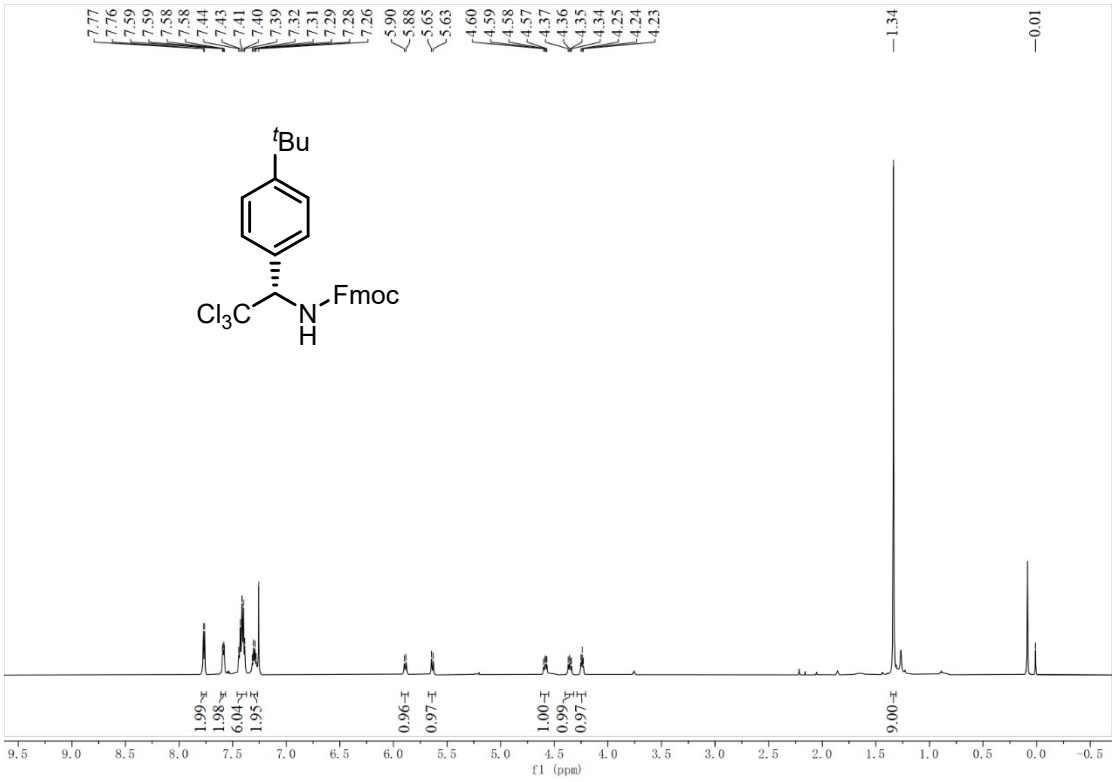
^{1}H NMR of **3e** (600 MHz, $CDCl_3$)



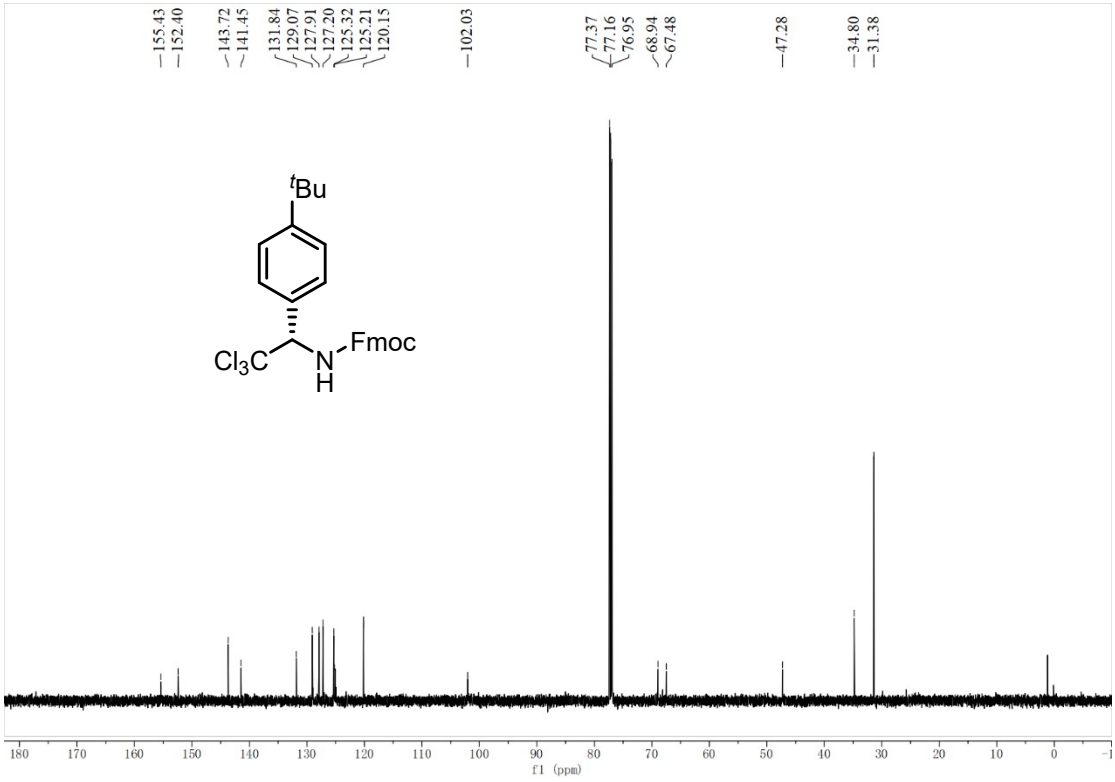
^{13}C NMR of **3e** (151 MHz, $CDCl_3$)



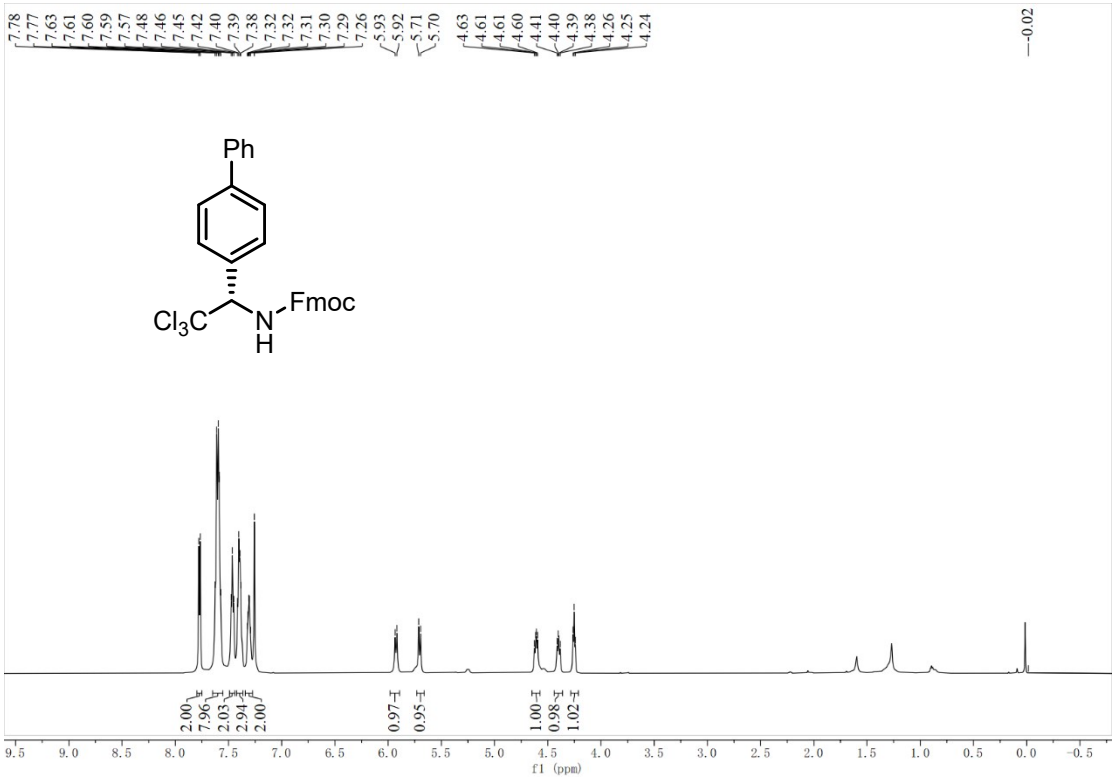
^{1}H NMR of **3f** (600 MHz, $CDCl_3$)



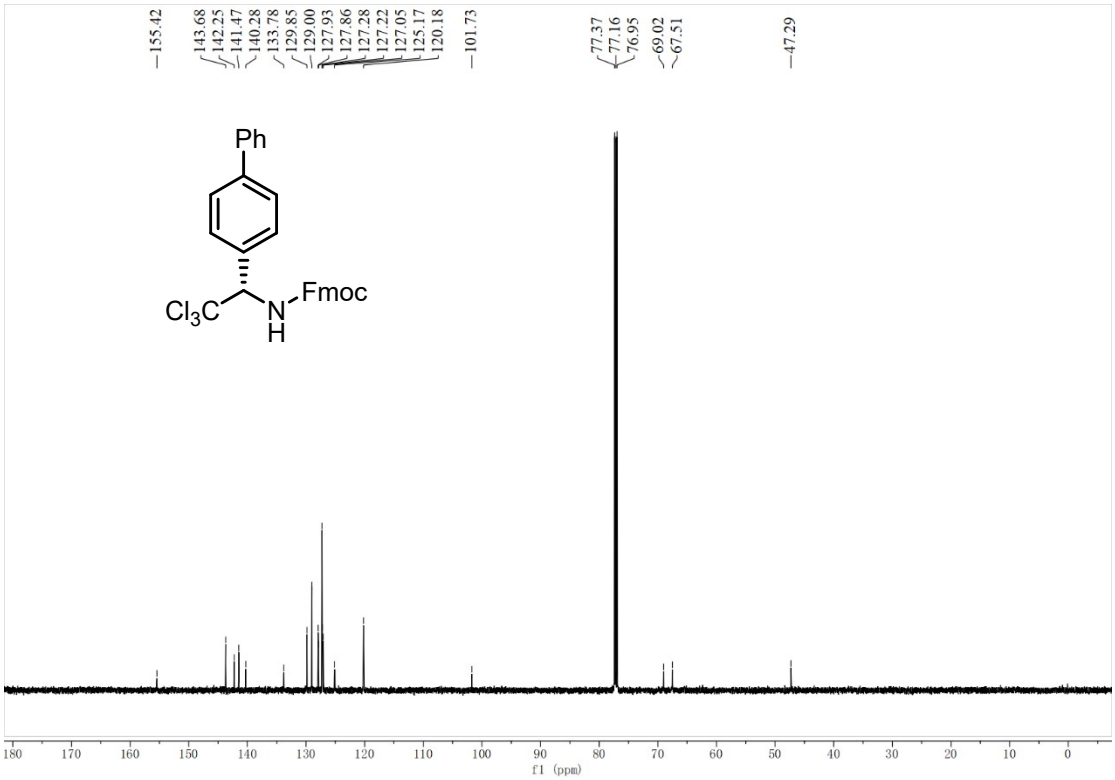
^{13}C NMR of **3f** (151 MHz, $CDCl_3$)



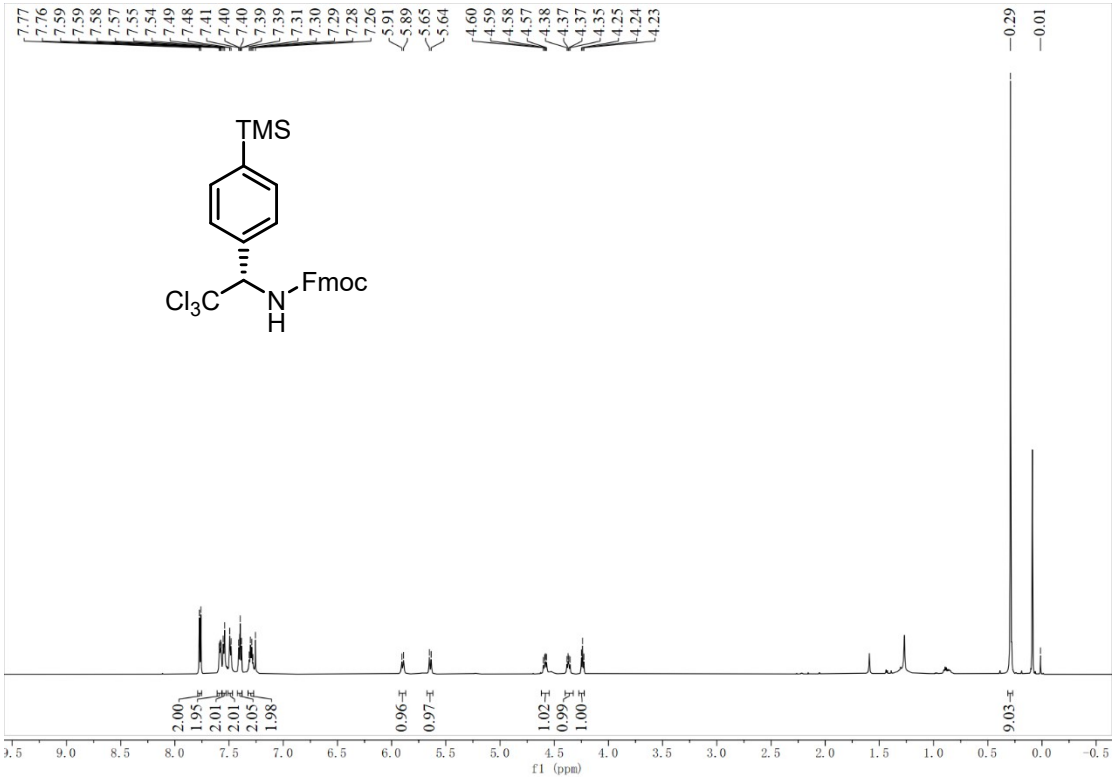
^{1}H NMR of **3g** (600 MHz, $CDCl_3$)



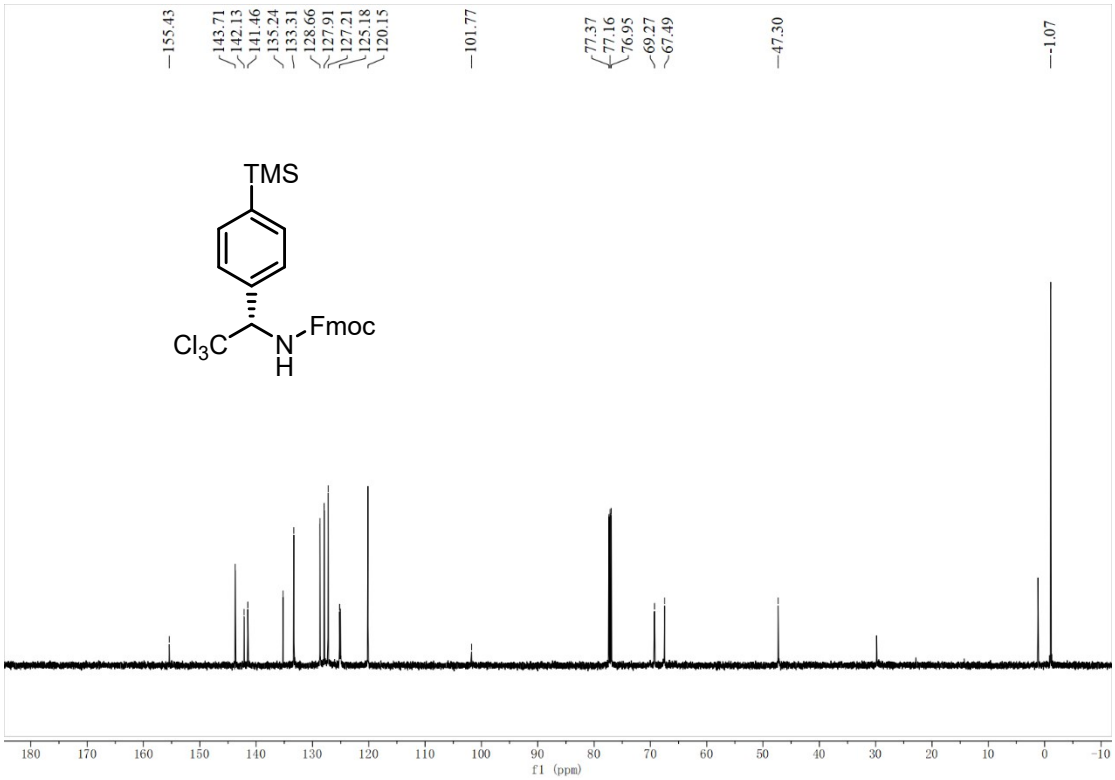
^{13}C NMR of **3g** (151 MHz, $CDCl_3$)



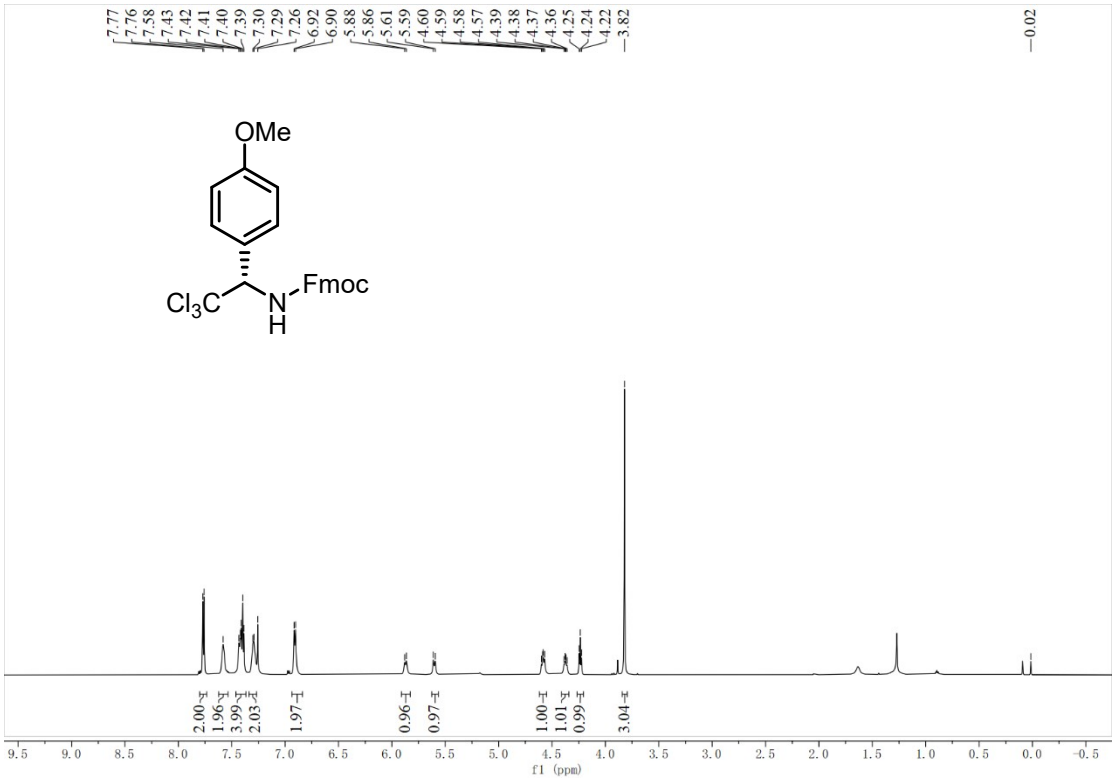
^{1}H NMR of **3h** (600 MHz, $CDCl_3$)



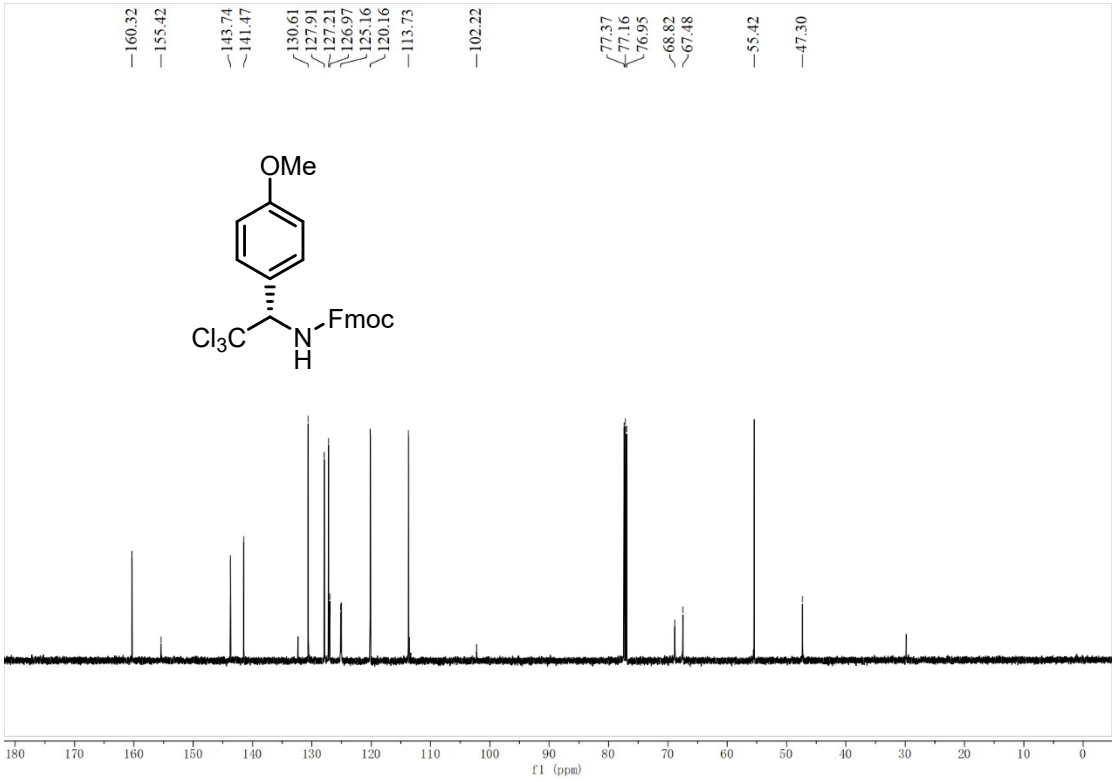
^{13}C NMR of **3h** (151 MHz, $CDCl_3$)



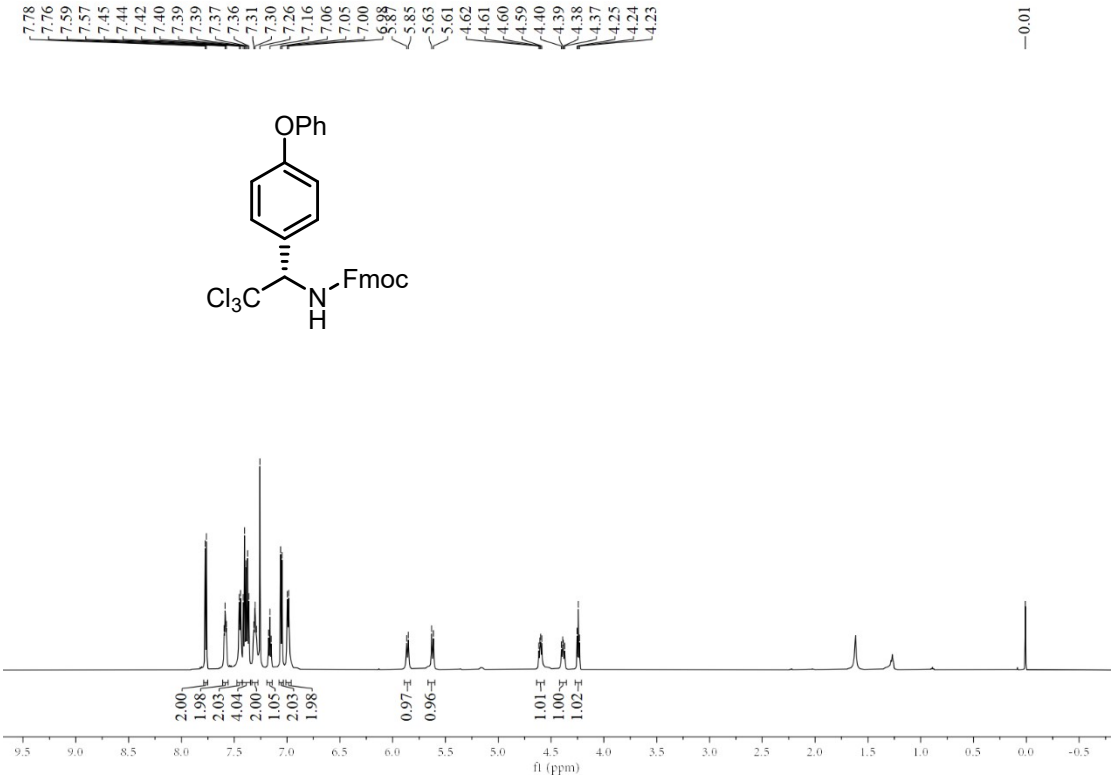
^{1}H NMR of **3i** (600 MHz, $CDCl_3$)



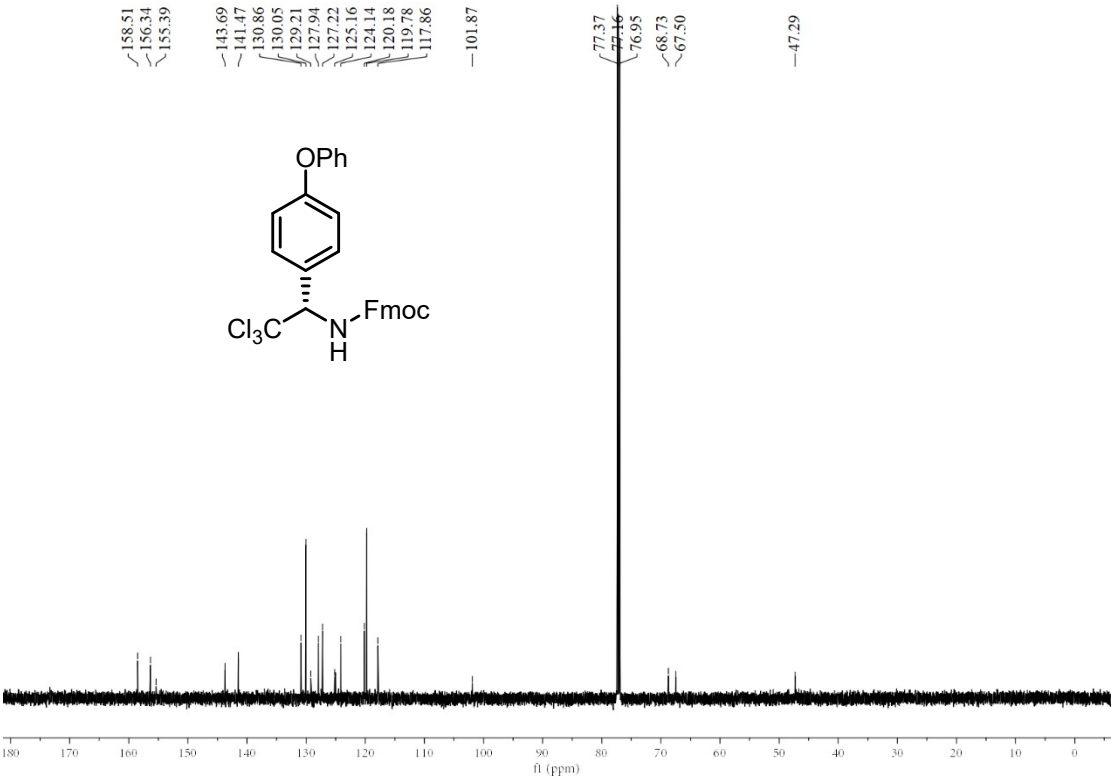
^{13}C NMR of **3i** (151 MHz, $CDCl_3$)



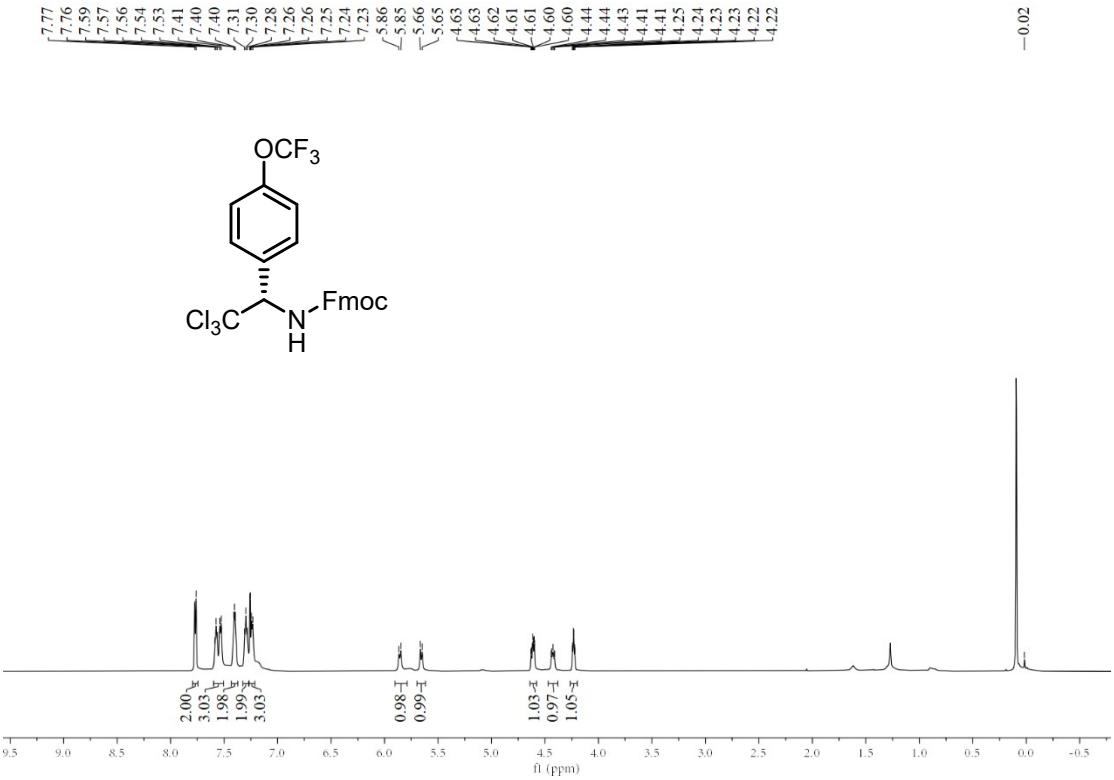
^{1}H NMR of **3j** (600 MHz, $CDCl_3$)



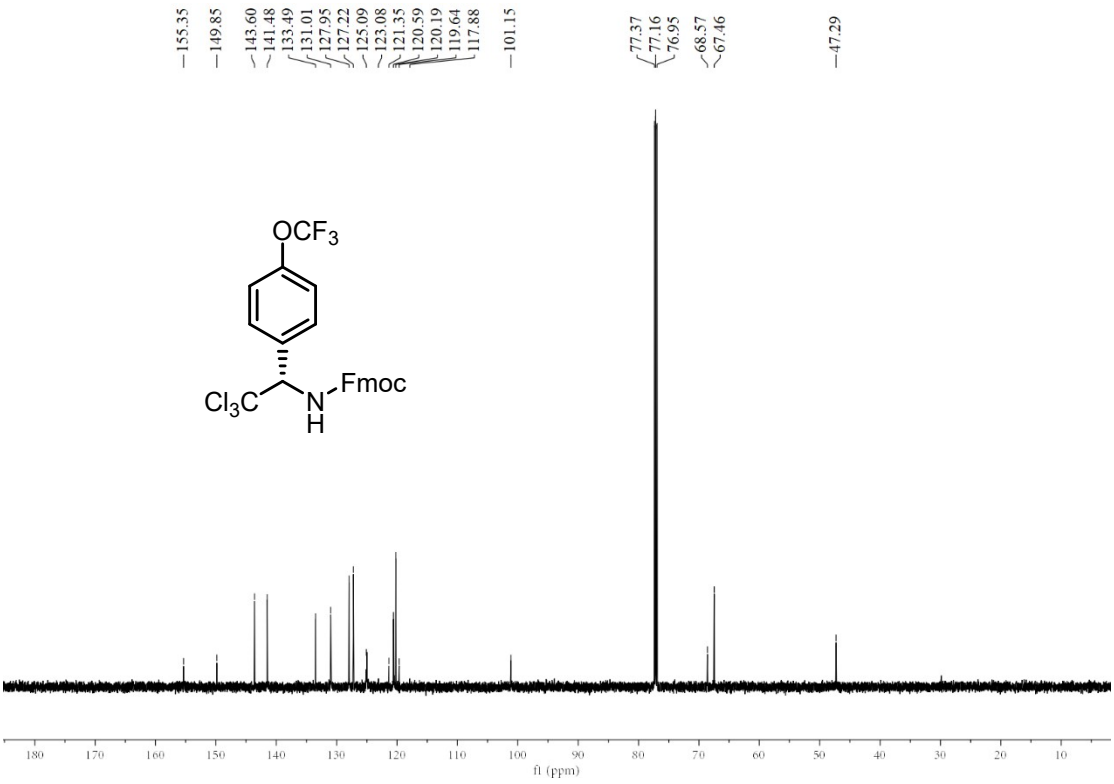
^{13}C NMR of **3j** (151 MHz, $CDCl_3$)



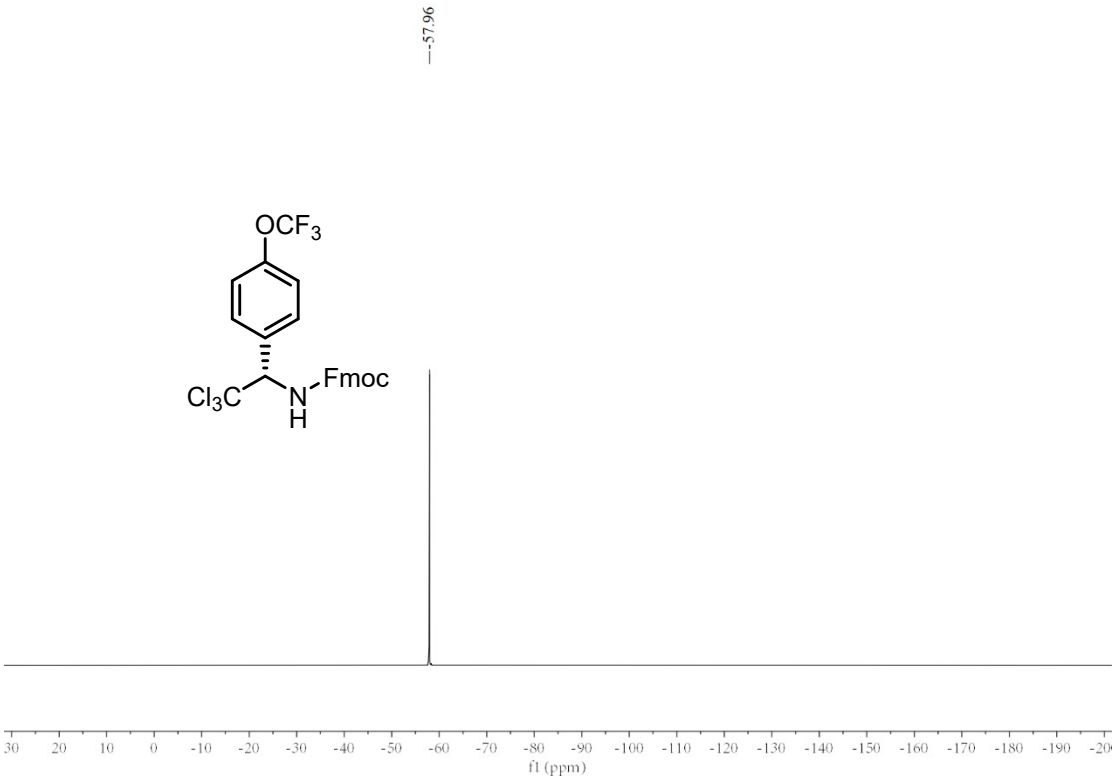
^{1}H NMR of **3k** (600 MHz, $CDCl_3$)



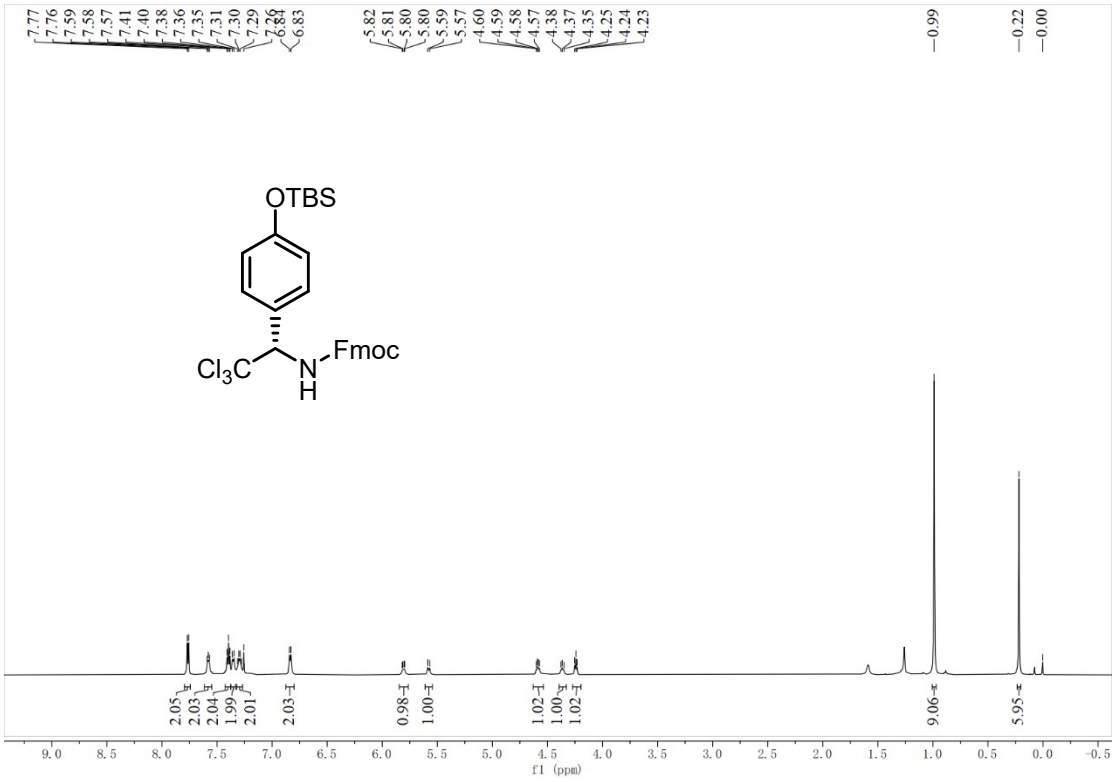
^{13}C NMR of **3k** (151 MHz, $CDCl_3$)



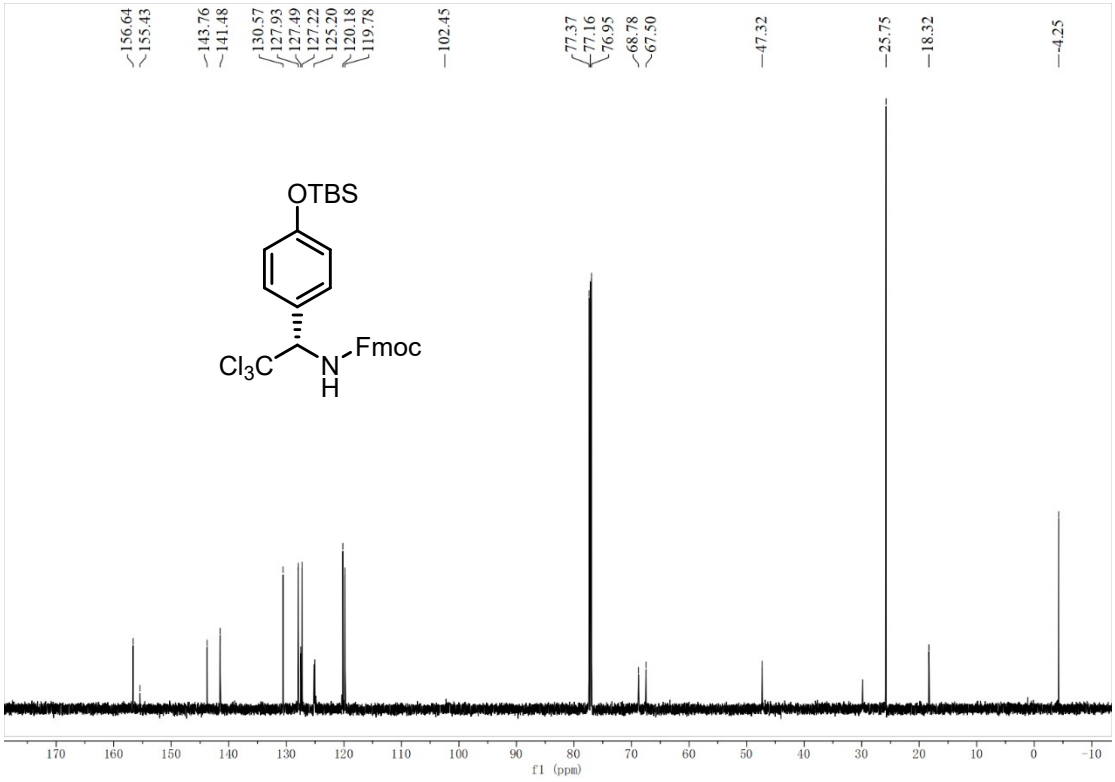
^{19}F NMR of **3k** (564 MHz, $CDCl_3$)



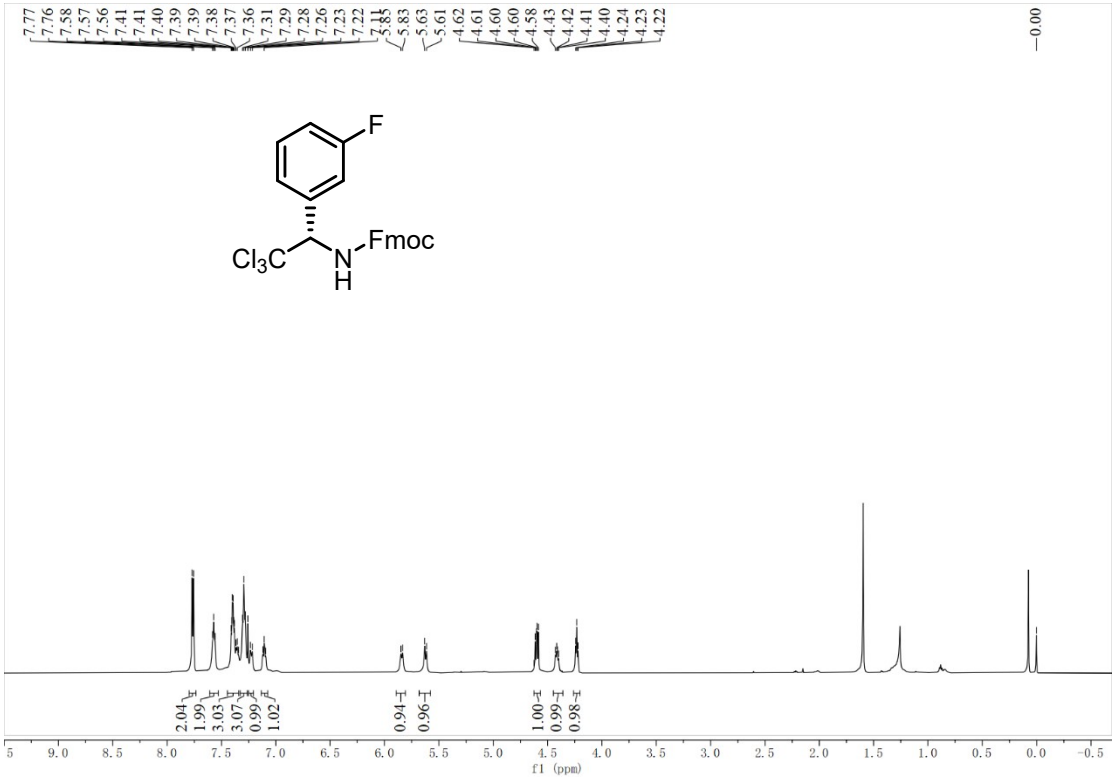
^{1}H NMR of **3l** (600 MHz, $CDCl_3$)



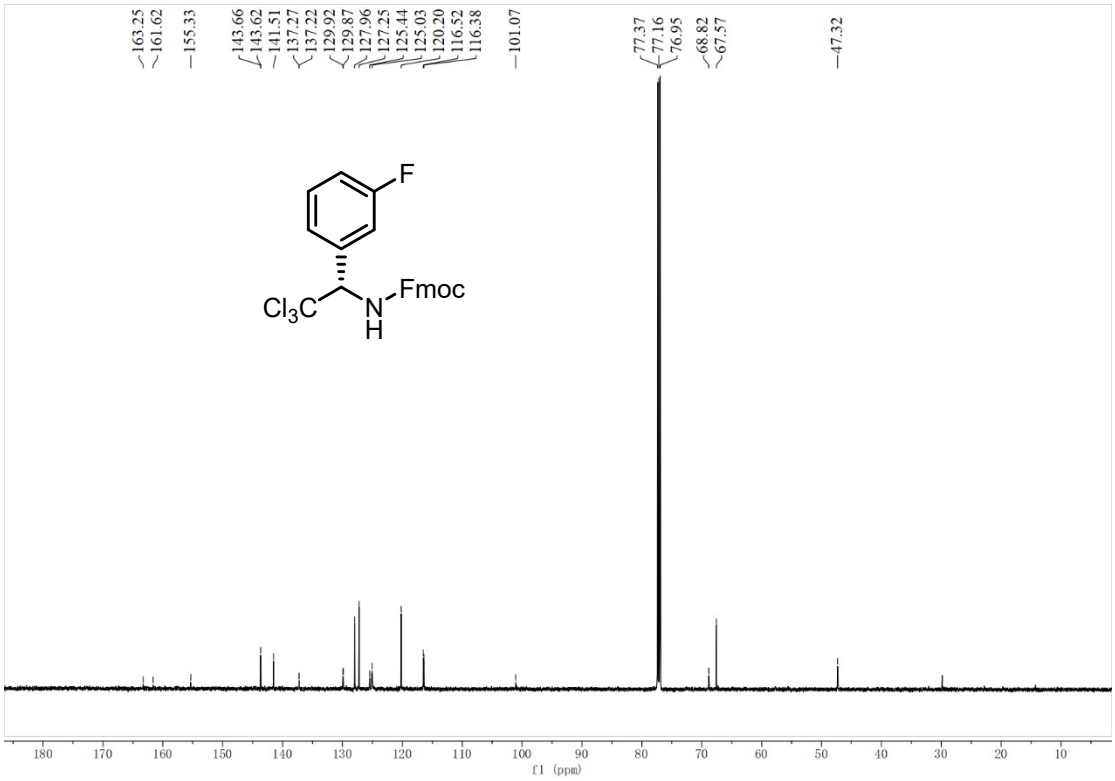
^{13}C NMR of **3l** (151 MHz, $CDCl_3$)



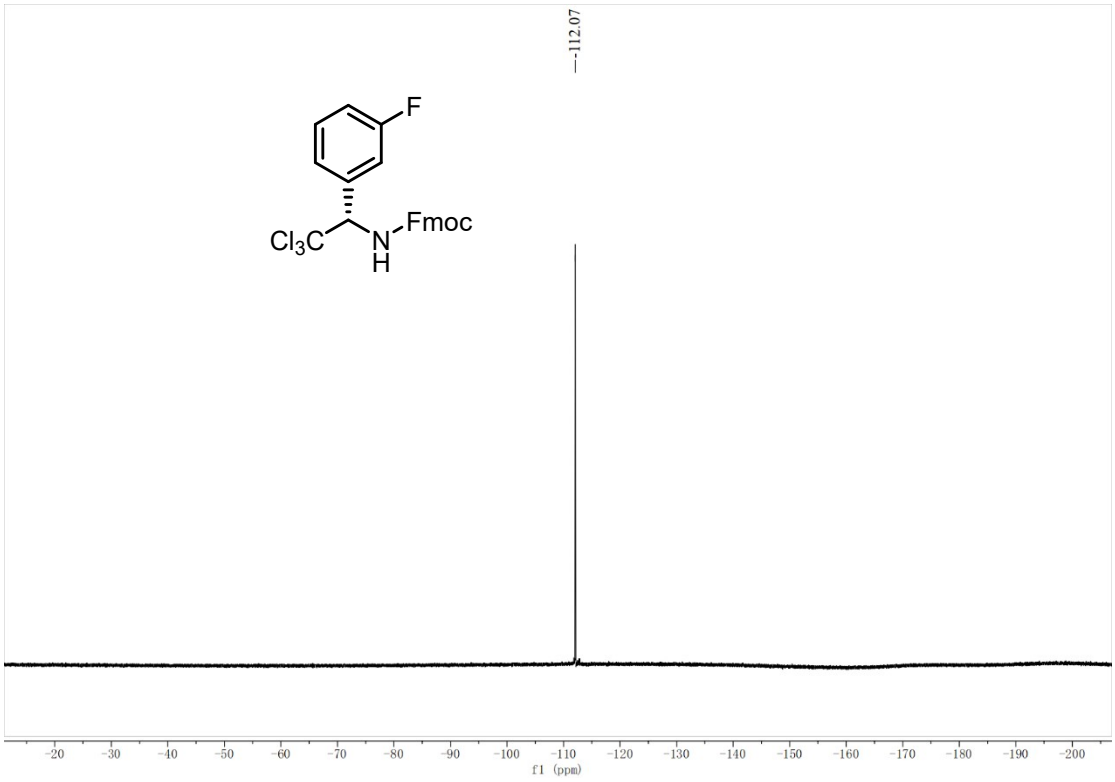
^{1}H NMR of **3m** (600 MHz, $CDCl_3$)



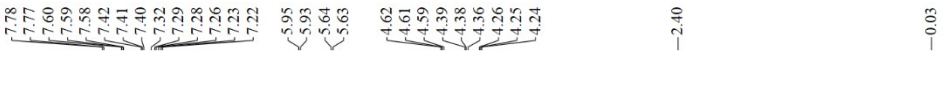
^{13}C NMR of **3m** (151 MHz, $CDCl_3$)

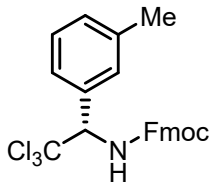


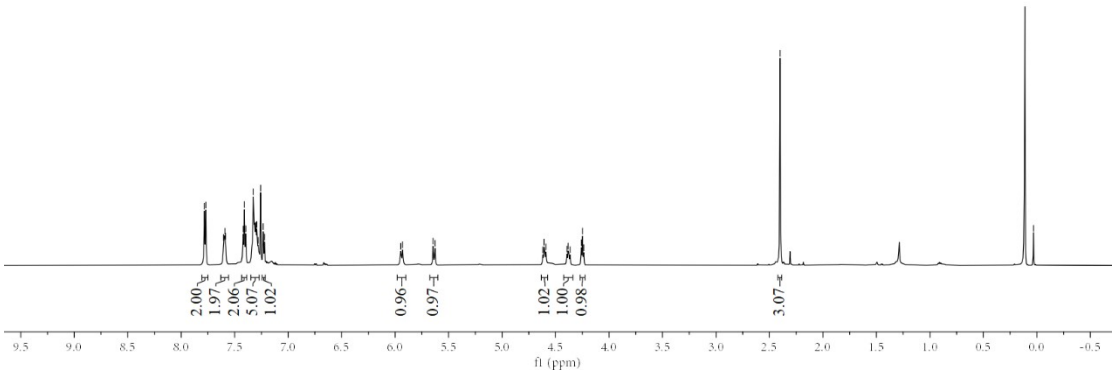
^{19}F NMR of **3m** (377 MHz, $CDCl_3$)



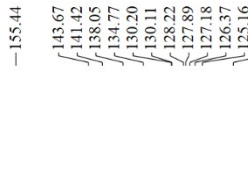
^{1}H NMR of **3n** (600 MHz, $CDCl_3$)

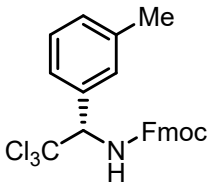




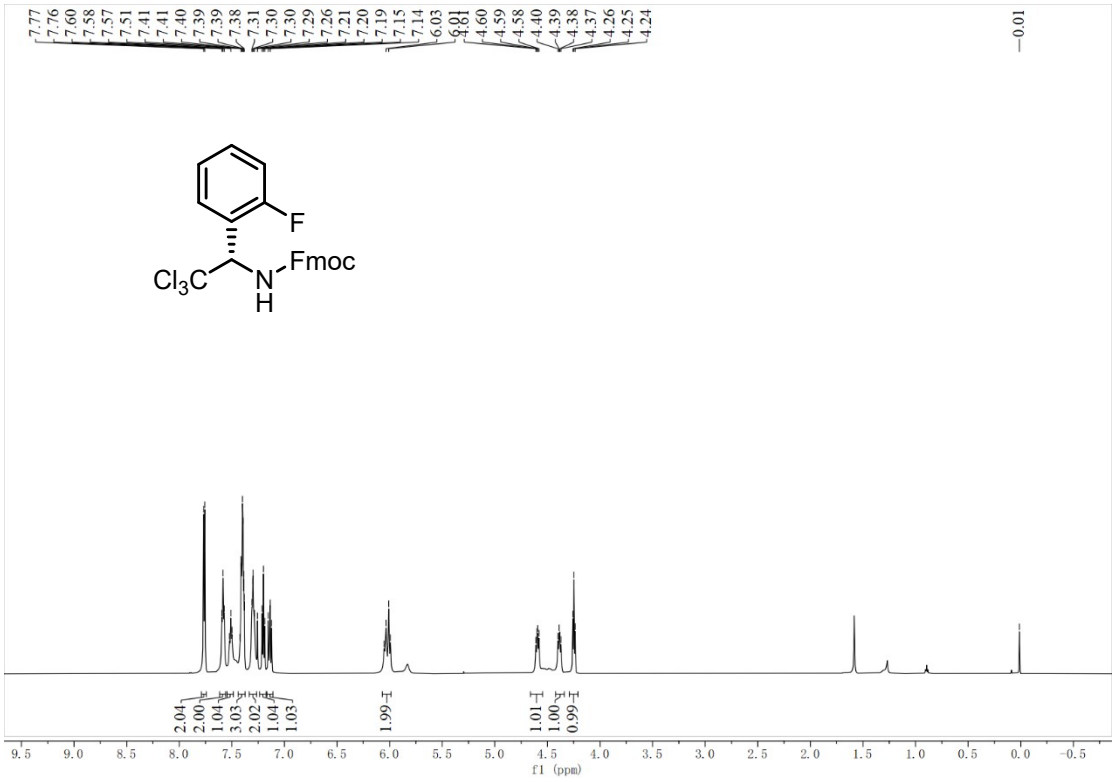


^{13}C NMR of **3n** (151 MHz, $CDCl_3$)

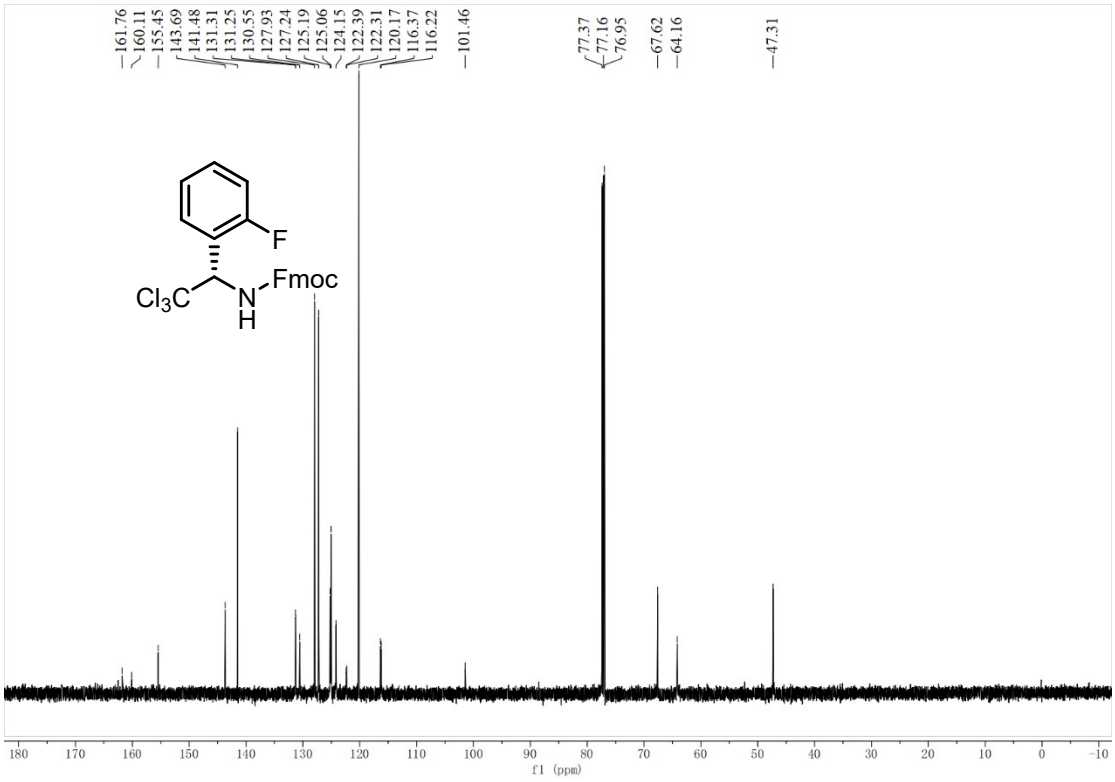




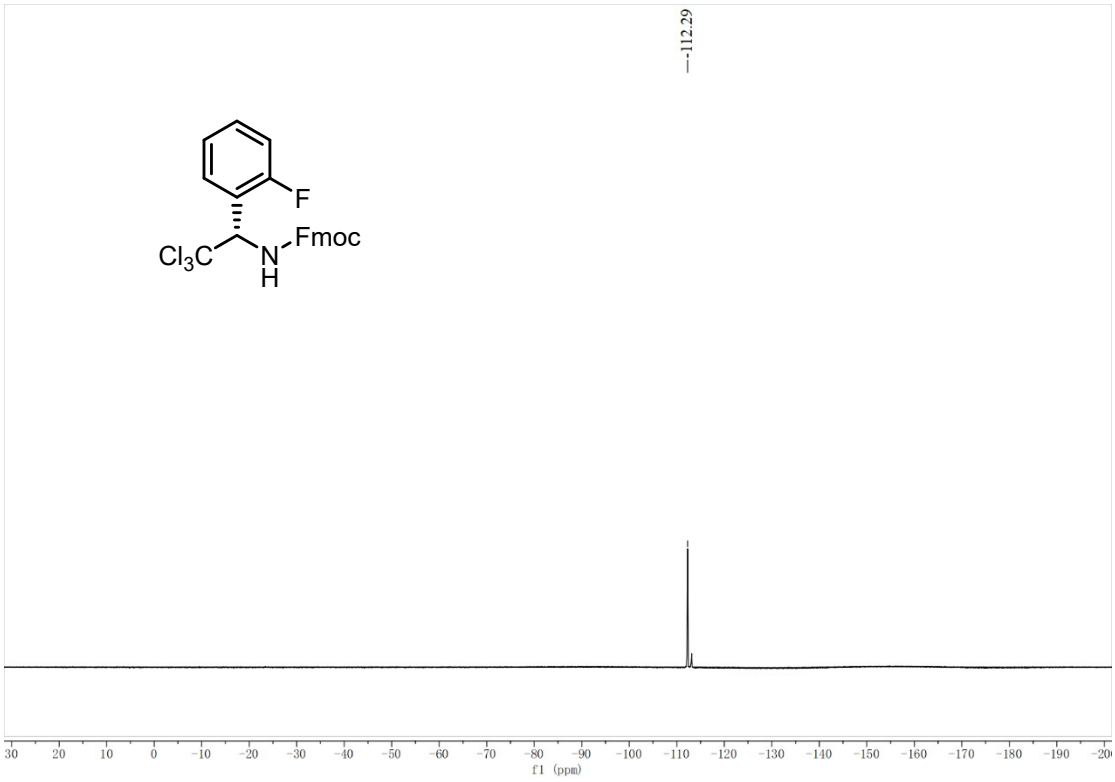
^{1}H NMR of **3o** (600 MHz, $CDCl_3$)



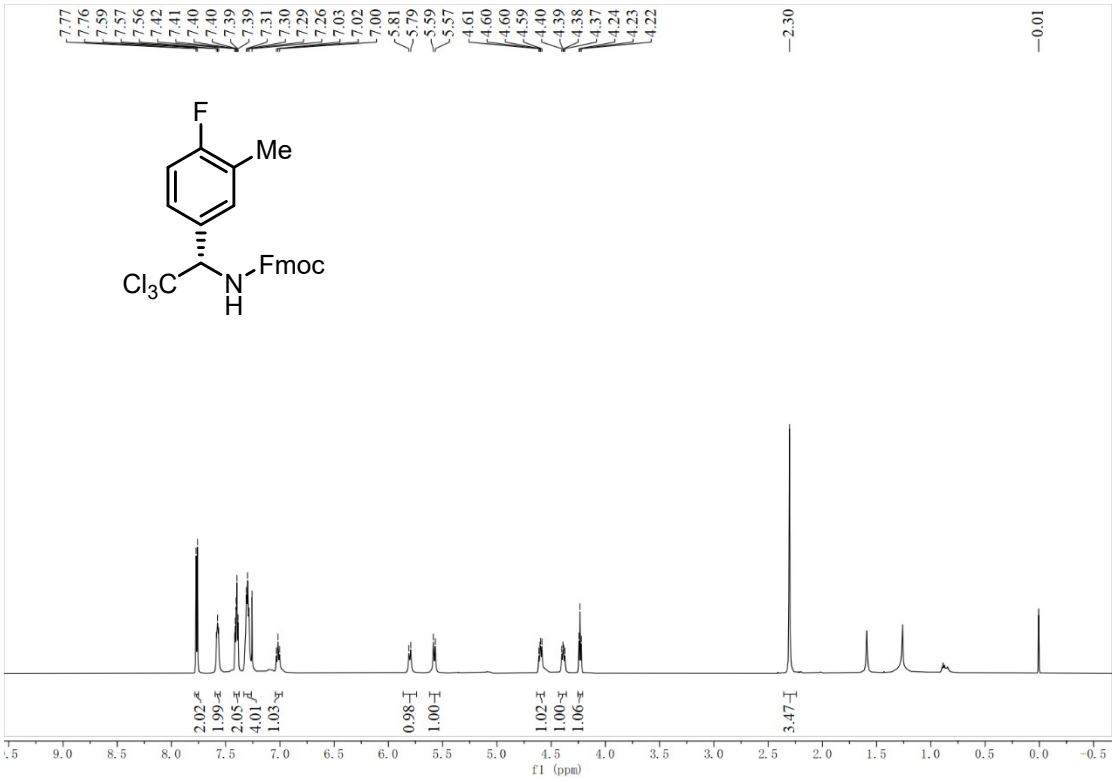
^{13}C NMR of **3o** (151 MHz, $CDCl_3$)



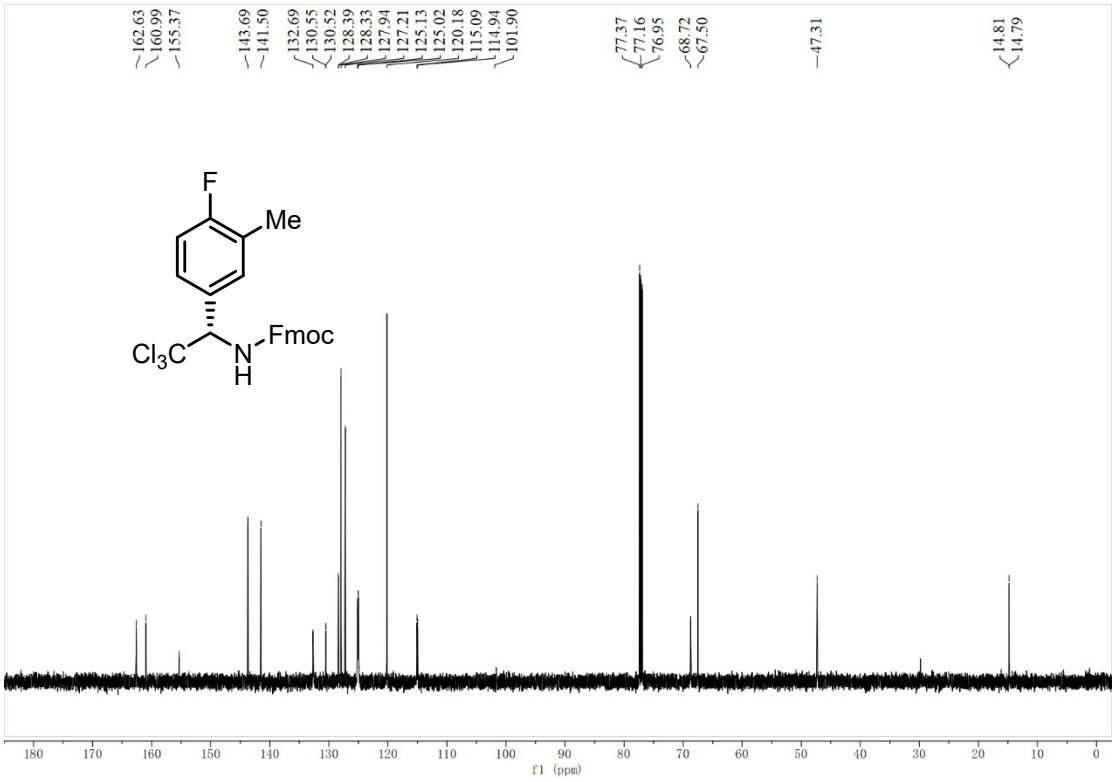
^{19}F NMR of **3o** (564 MHz, $CDCl_3$)



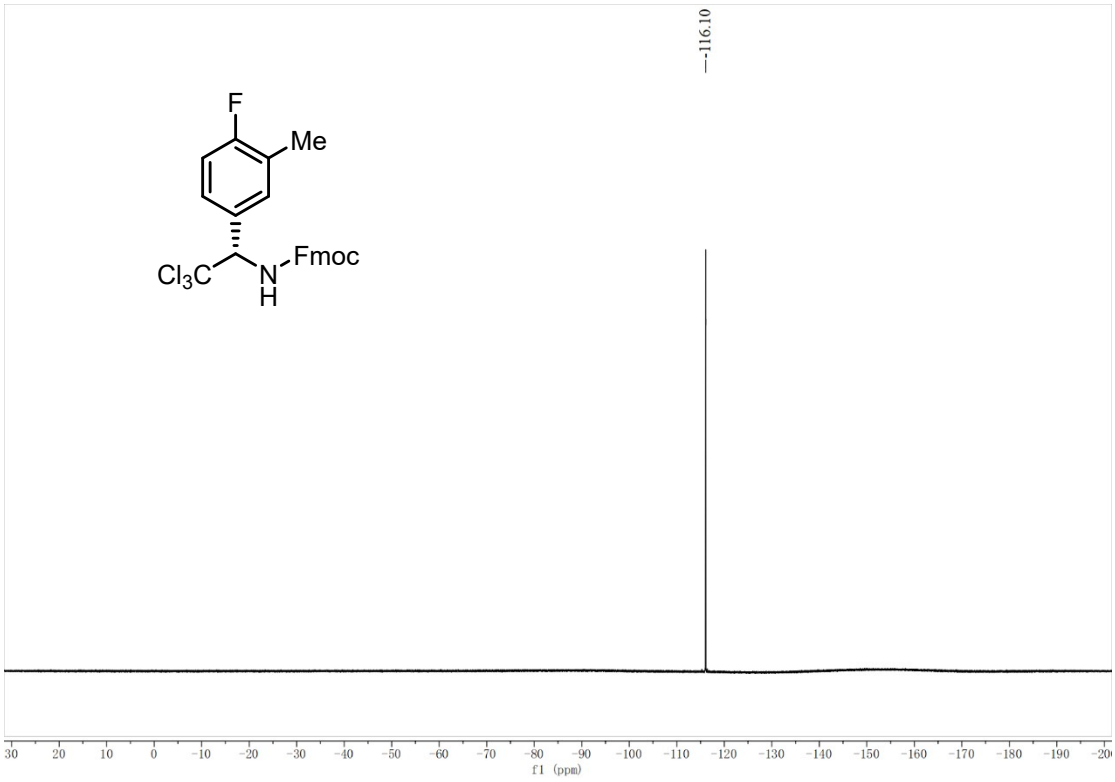
^{1}H NMR of **3p** (600 MHz, $CDCl_3$)



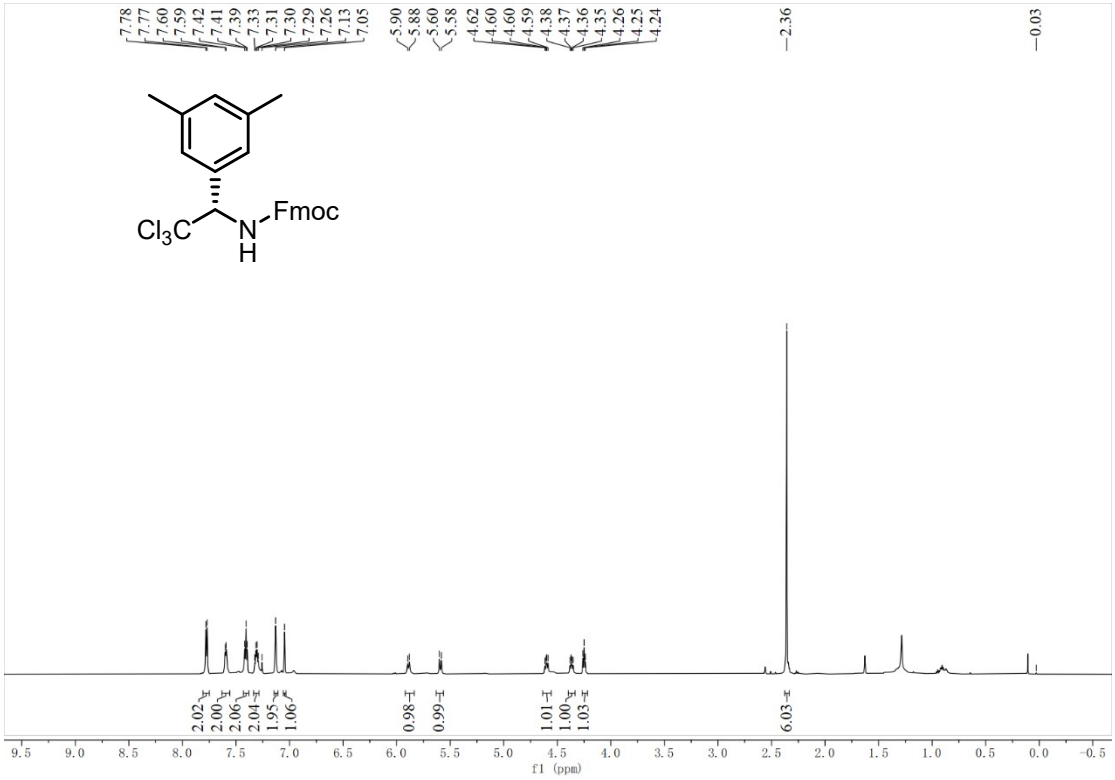
^{13}C NMR of **3p** (151 MHz, $CDCl_3$)



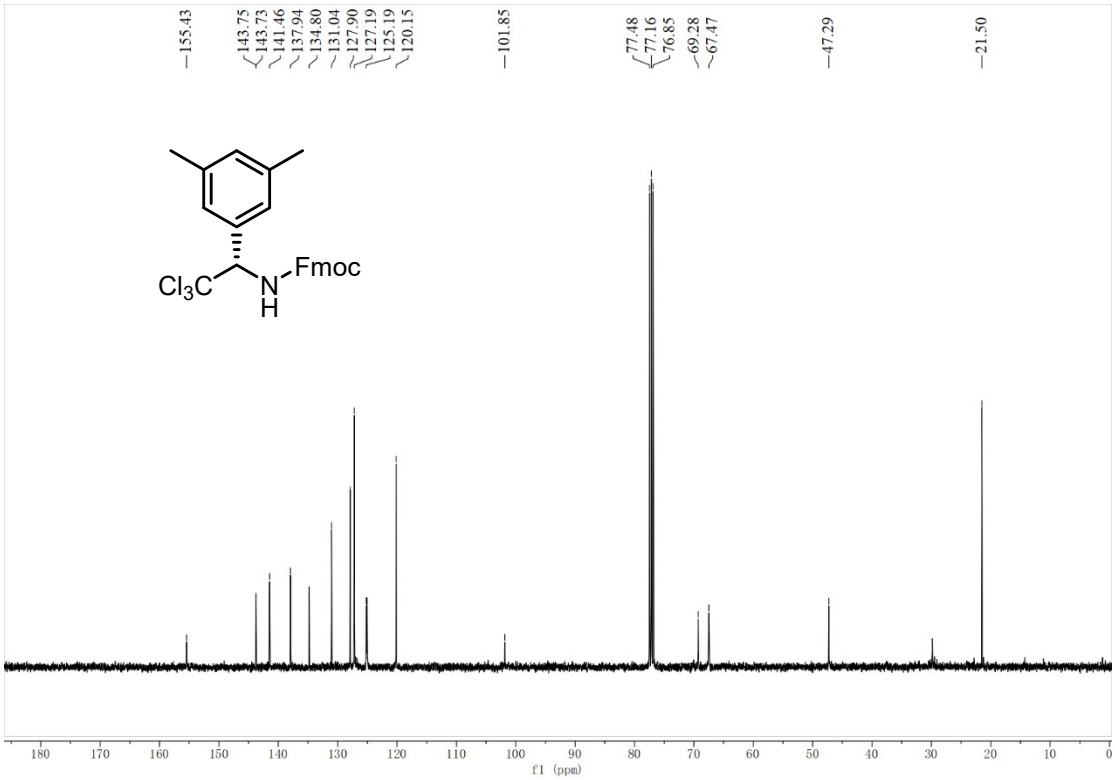
^{19}F NMR of **3p** (564 MHz, $CDCl_3$)



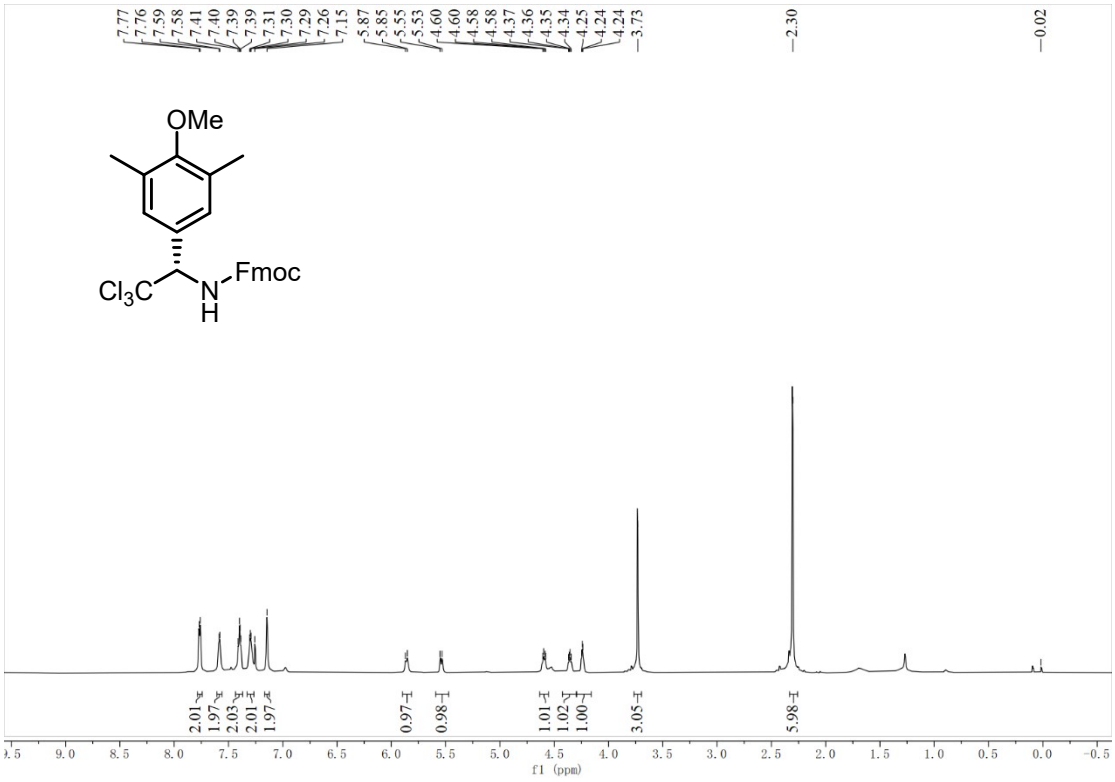
^{1}H NMR of **3q** (600 MHz, $CDCl_3$)



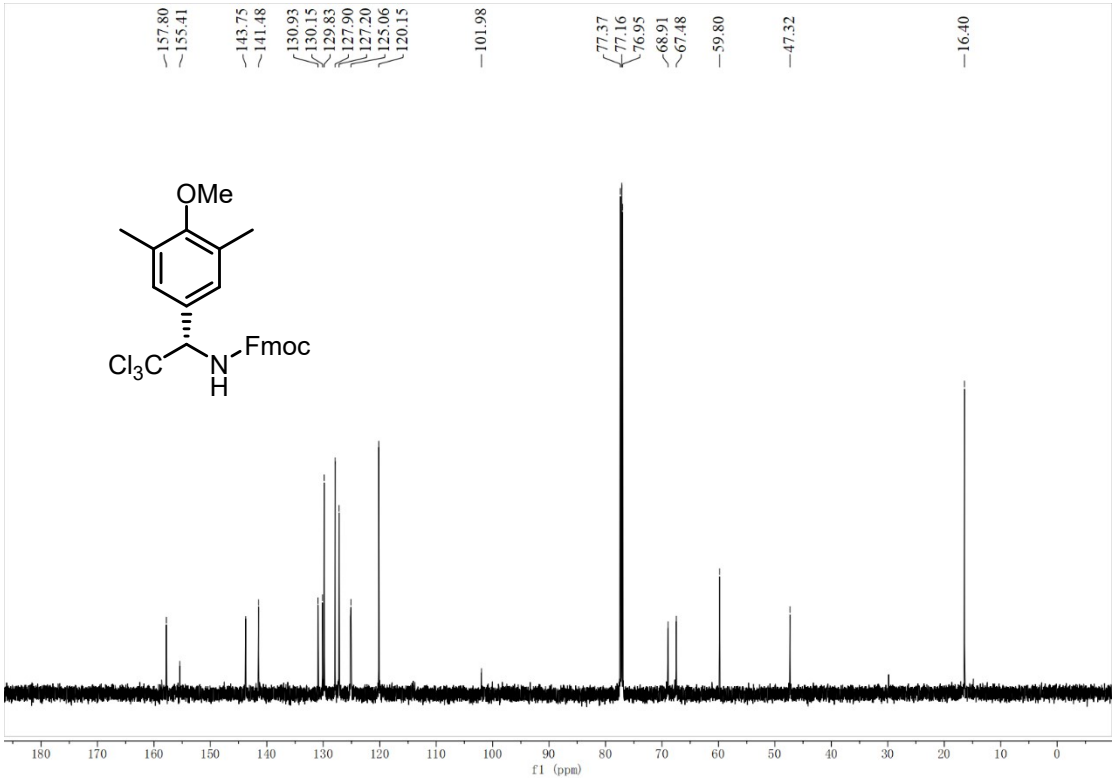
^{13}C NMR of **3q** (101 MHz, $CDCl_3$)



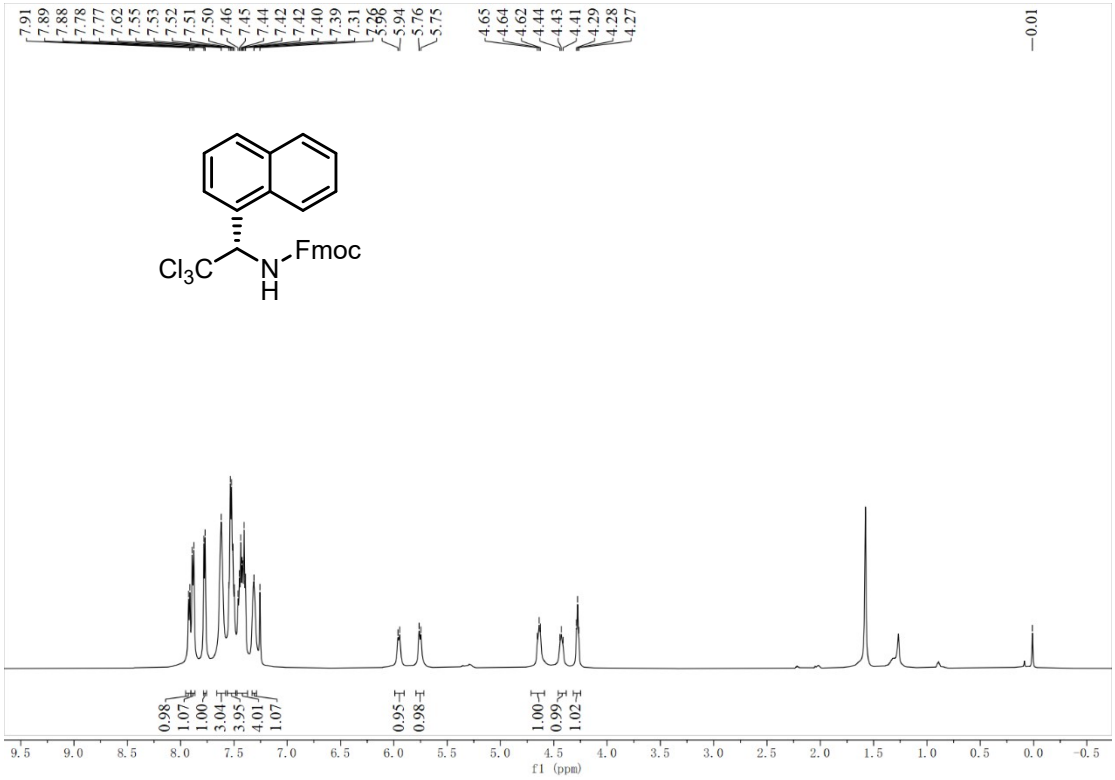
^{1}H NMR of **3r** (600 MHz, $CDCl_3$)



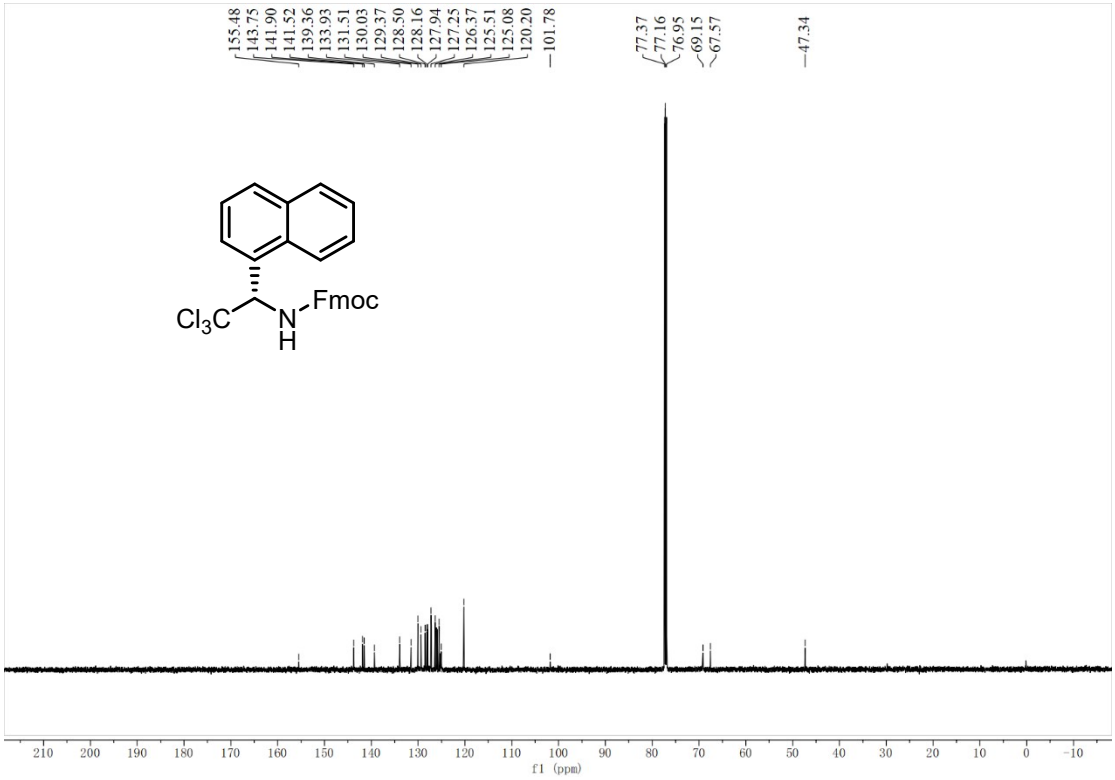
^{13}C NMR of **3r** (101 MHz, $CDCl_3$)



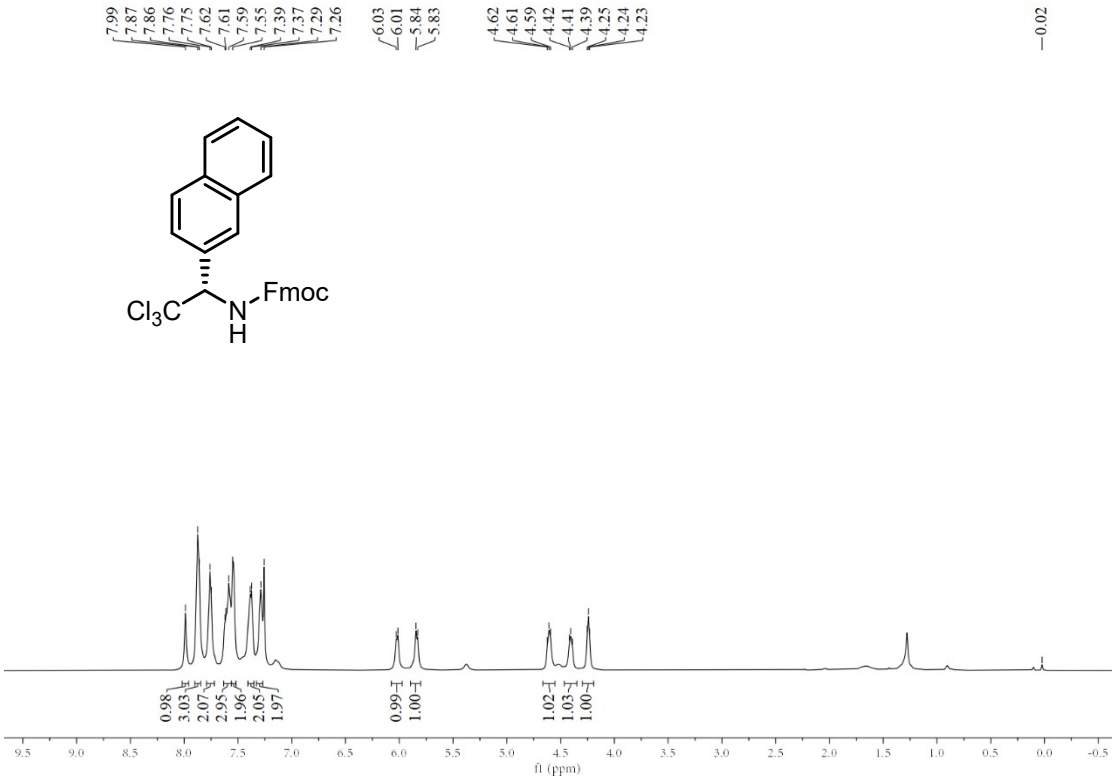
^{1}H NMR of **3s** (600 MHz, $CDCl_3$)



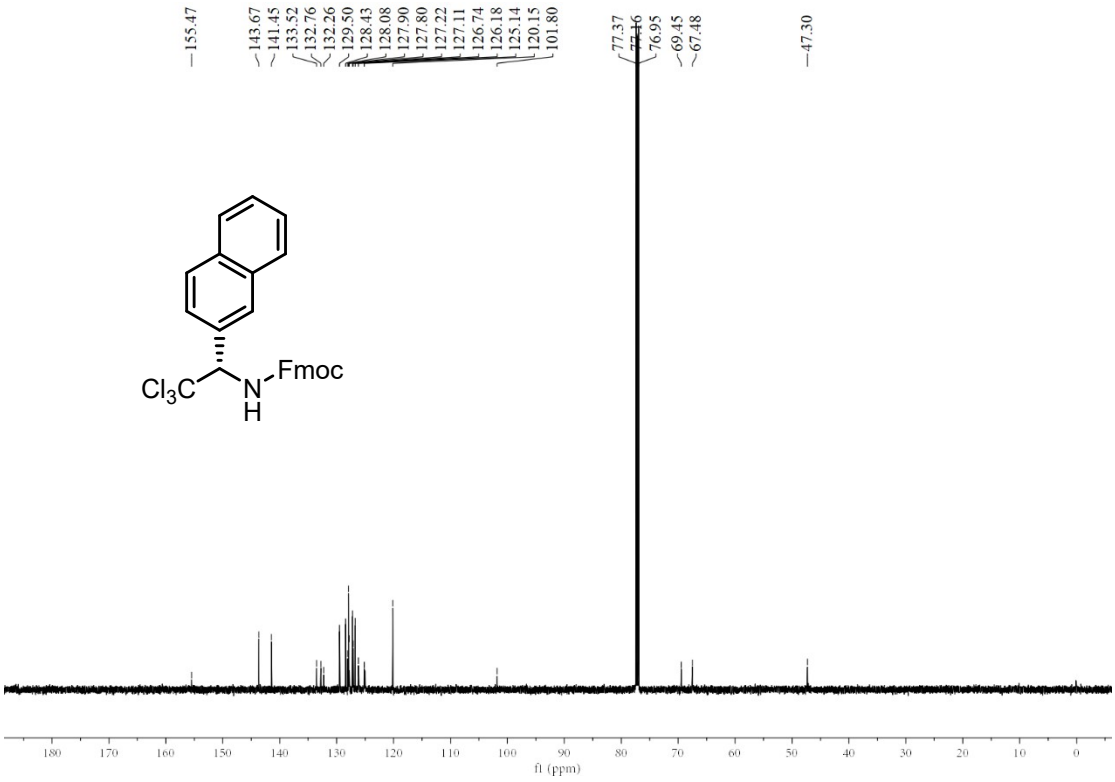
^{13}C NMR of **3s** (151 MHz, $CDCl_3$)



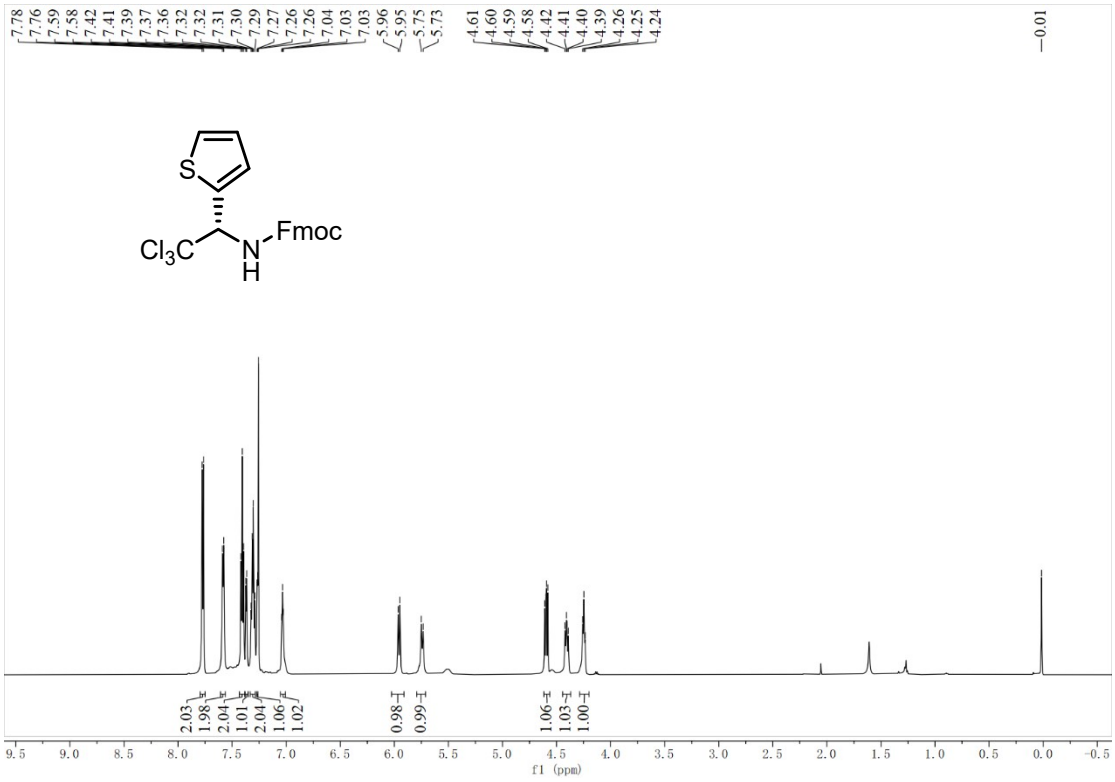
^{1}H NMR of **3t** (600 MHz, $CDCl_3$)



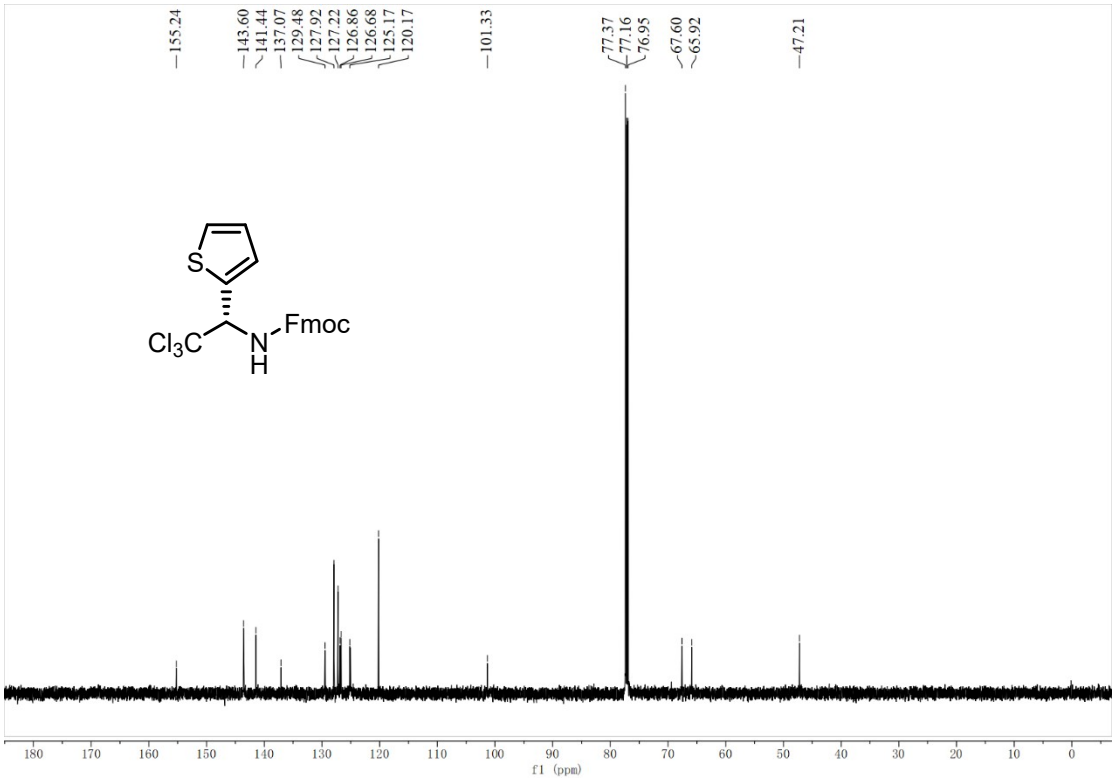
^{13}C NMR of **3t** (151 MHz, $CDCl_3$)



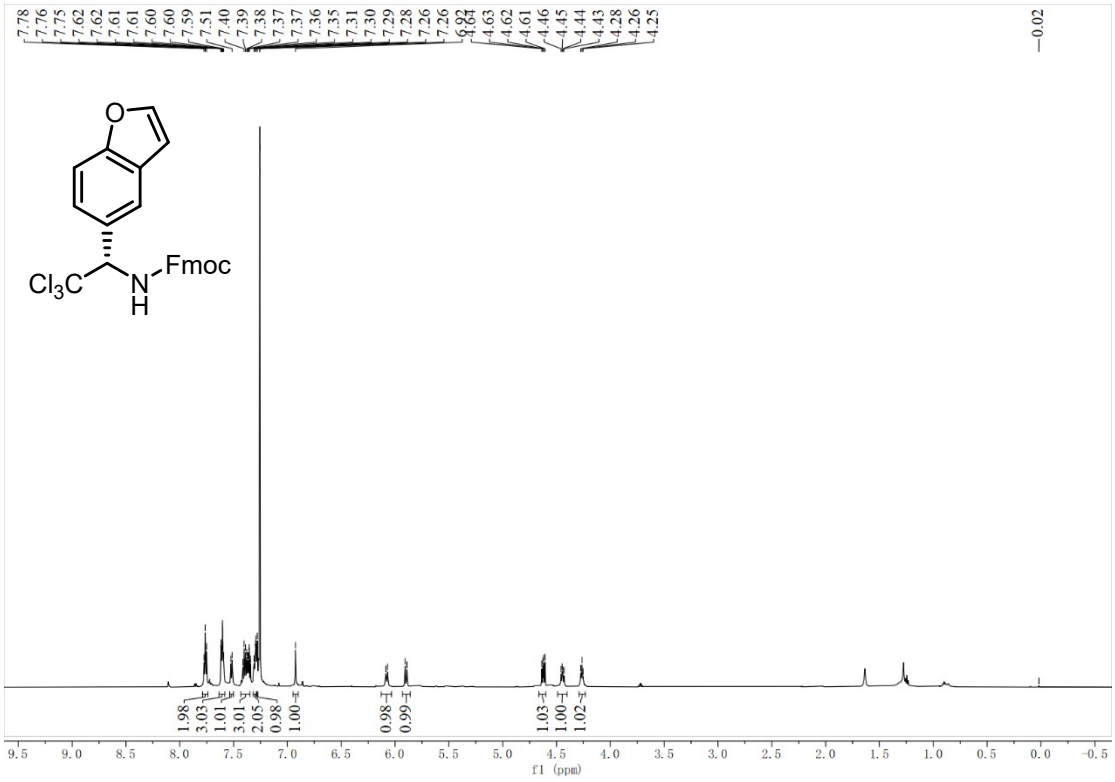
^{1}H NMR of **3u** (600 MHz, $CDCl_3$)



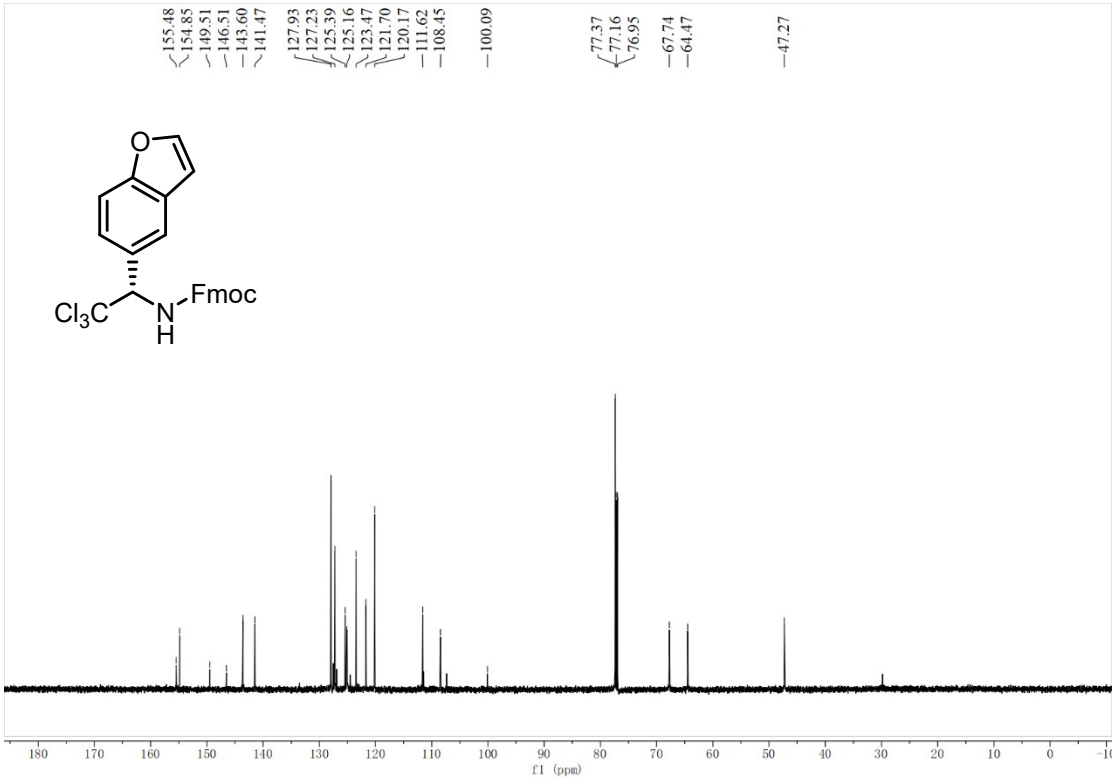
^{13}C NMR of **3u** (151 MHz, $CDCl_3$)



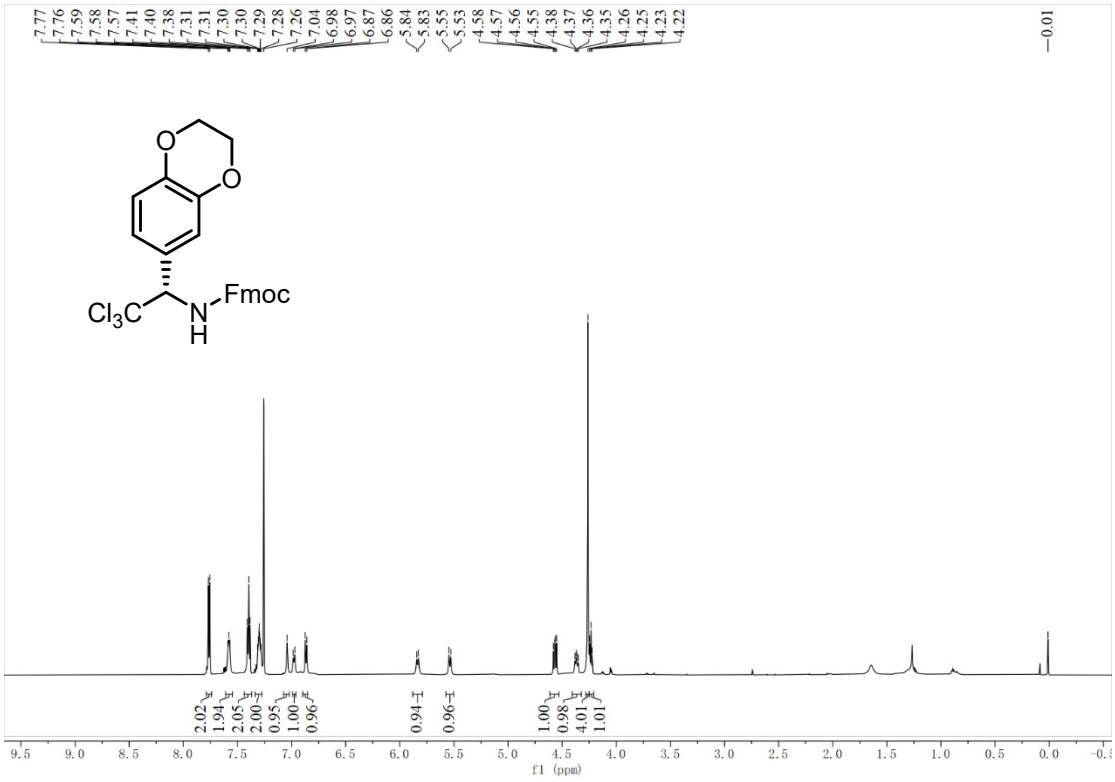
^{1}H NMR of **3v** (600 MHz, $CDCl_3$)



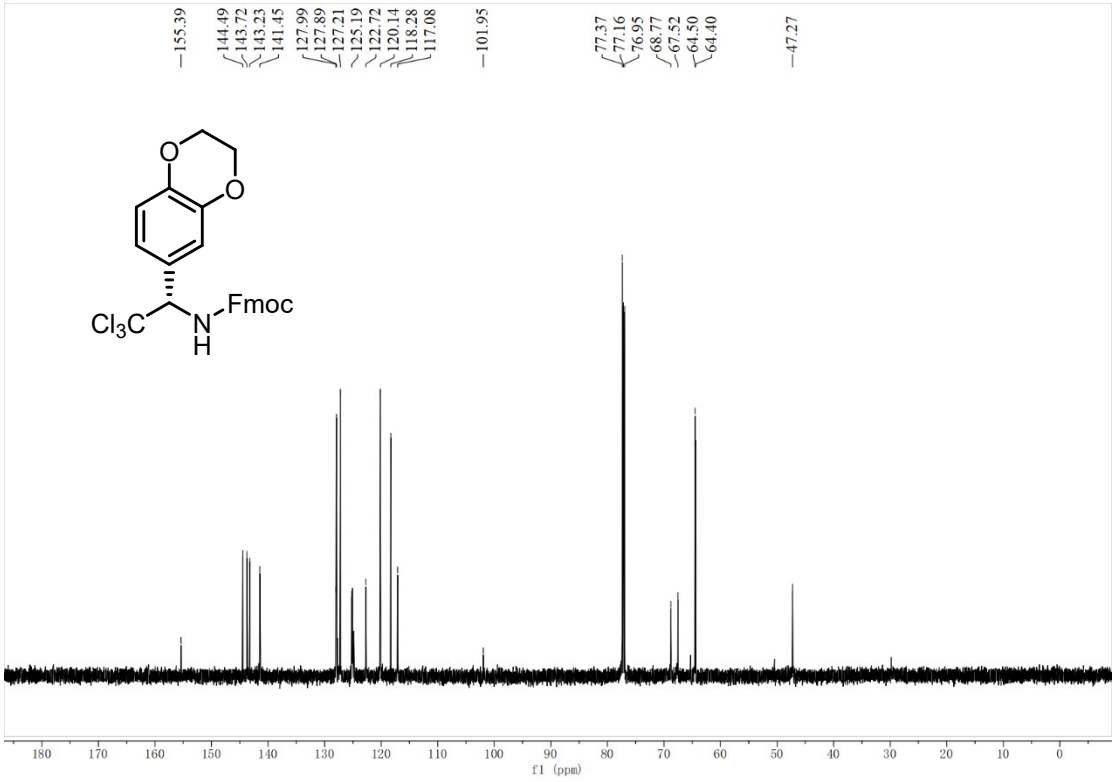
^{13}C NMR of **3v** (151 MHz, $CDCl_3$)



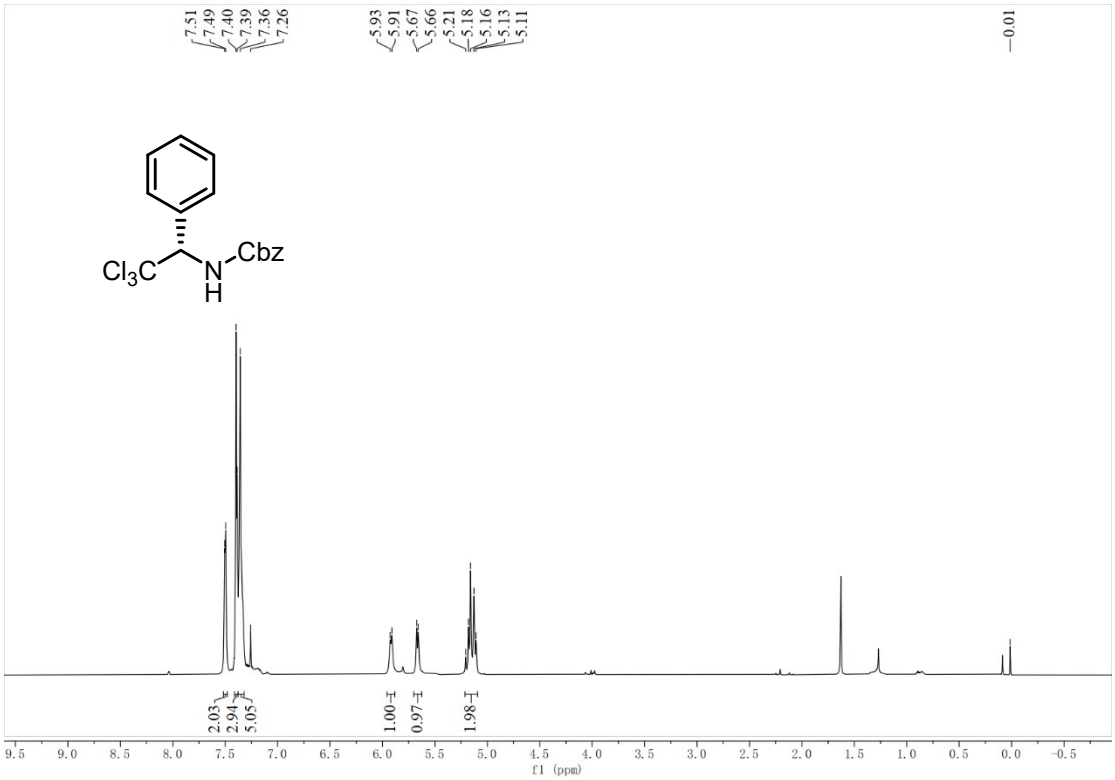
^{1}H NMR of **3w** (600 MHz, $CDCl_3$)



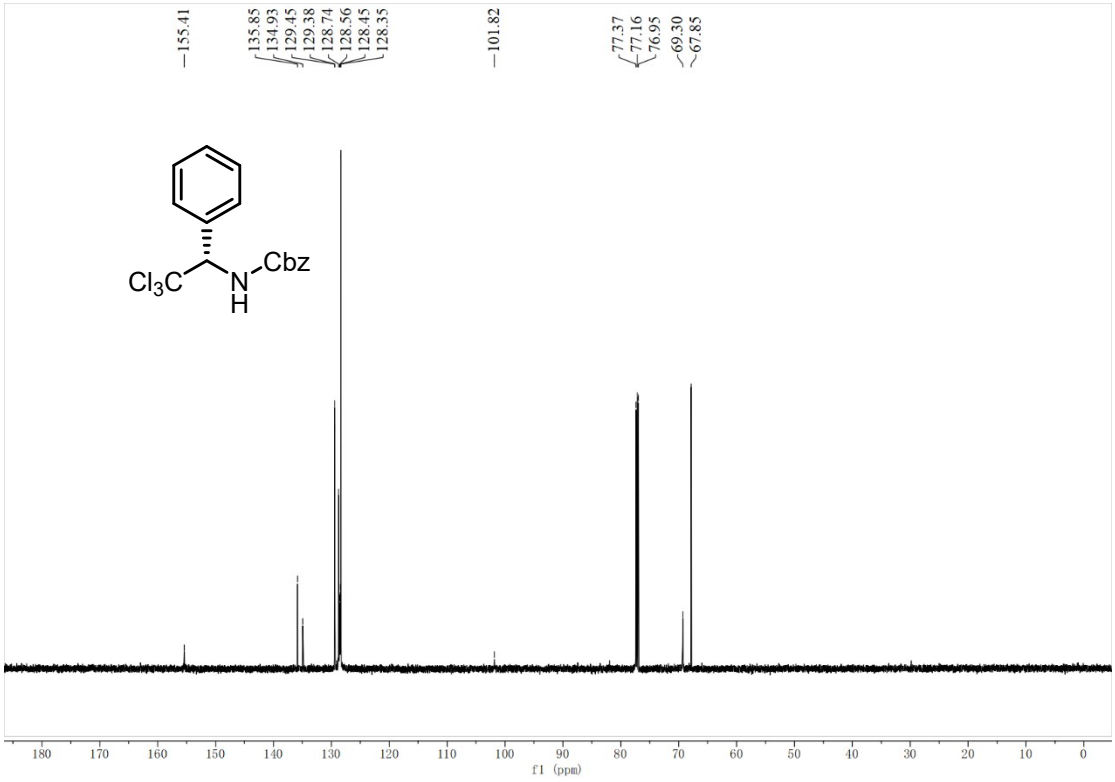
^{13}C NMR of **3w** (151 MHz, $CDCl_3$)



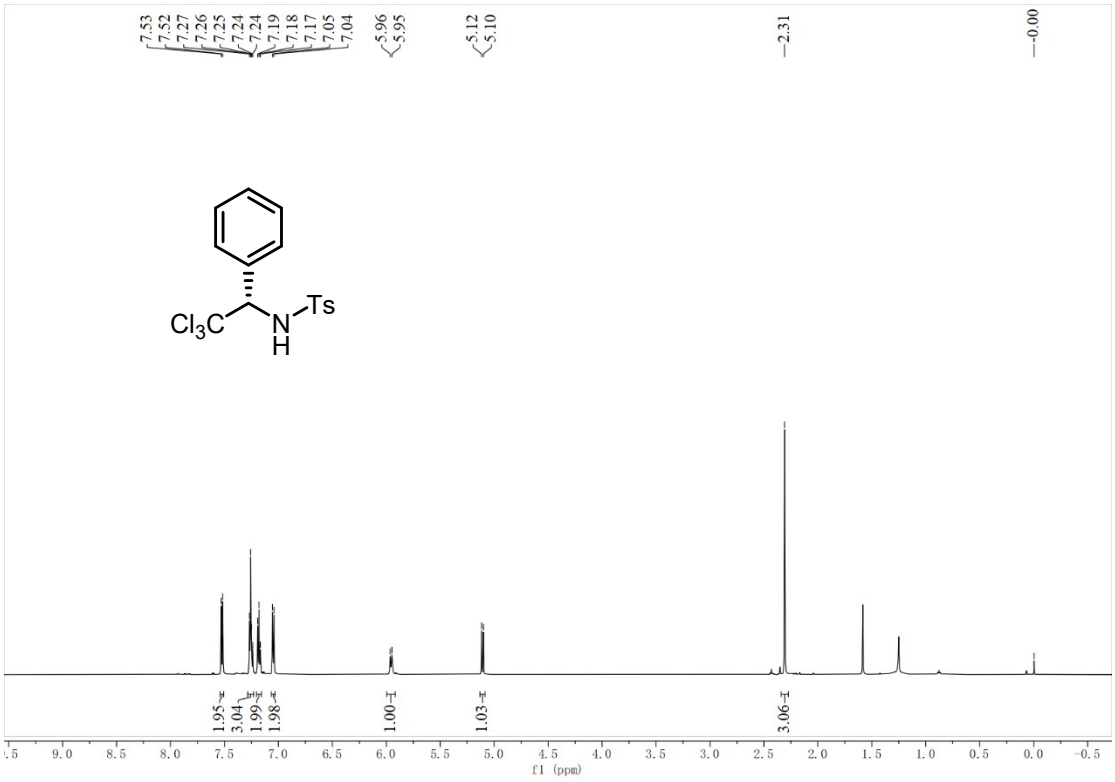
^{1}H NMR of **3aa** (600 MHz, $CDCl_3$)



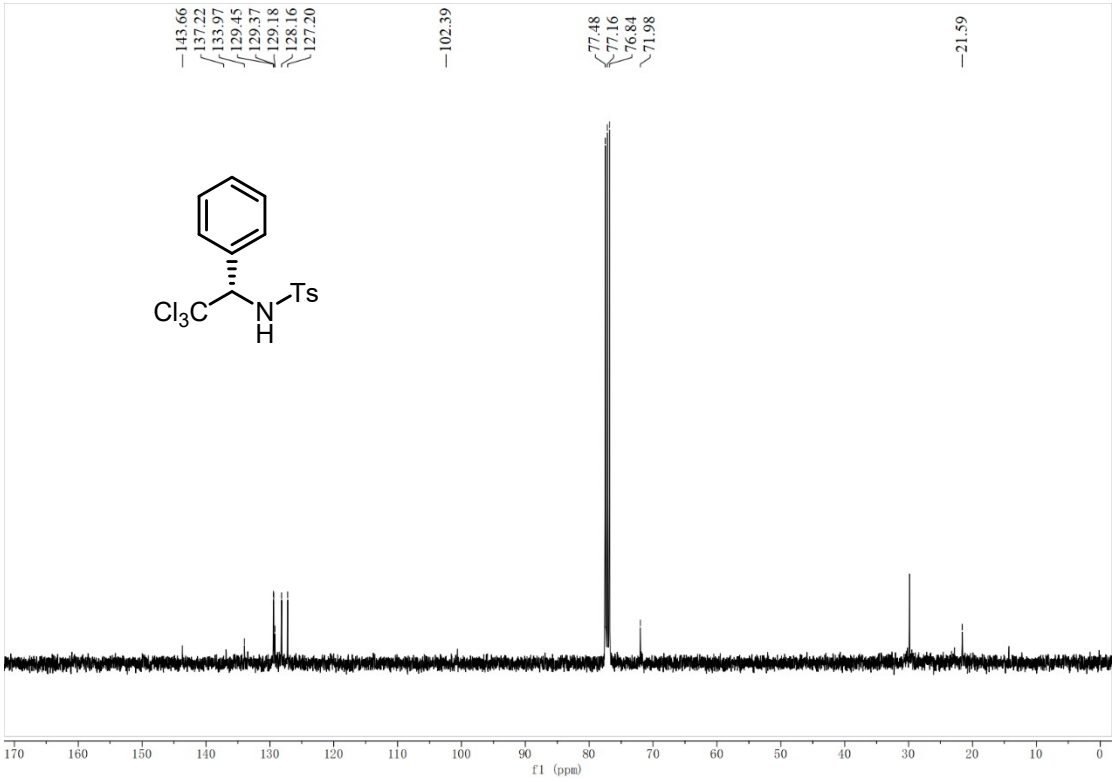
^{13}C NMR of **3aa** (151 MHz, $CDCl_3$)



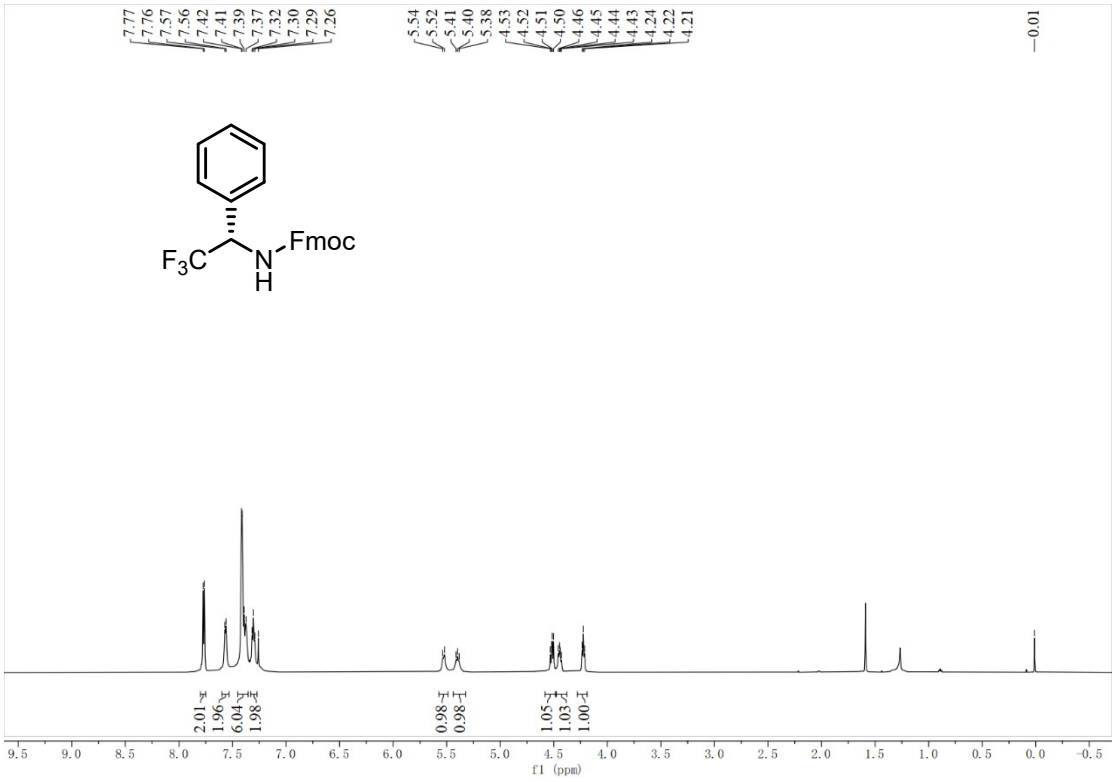
^{1}H NMR of **3ab** (600 MHz, $CDCl_3$)



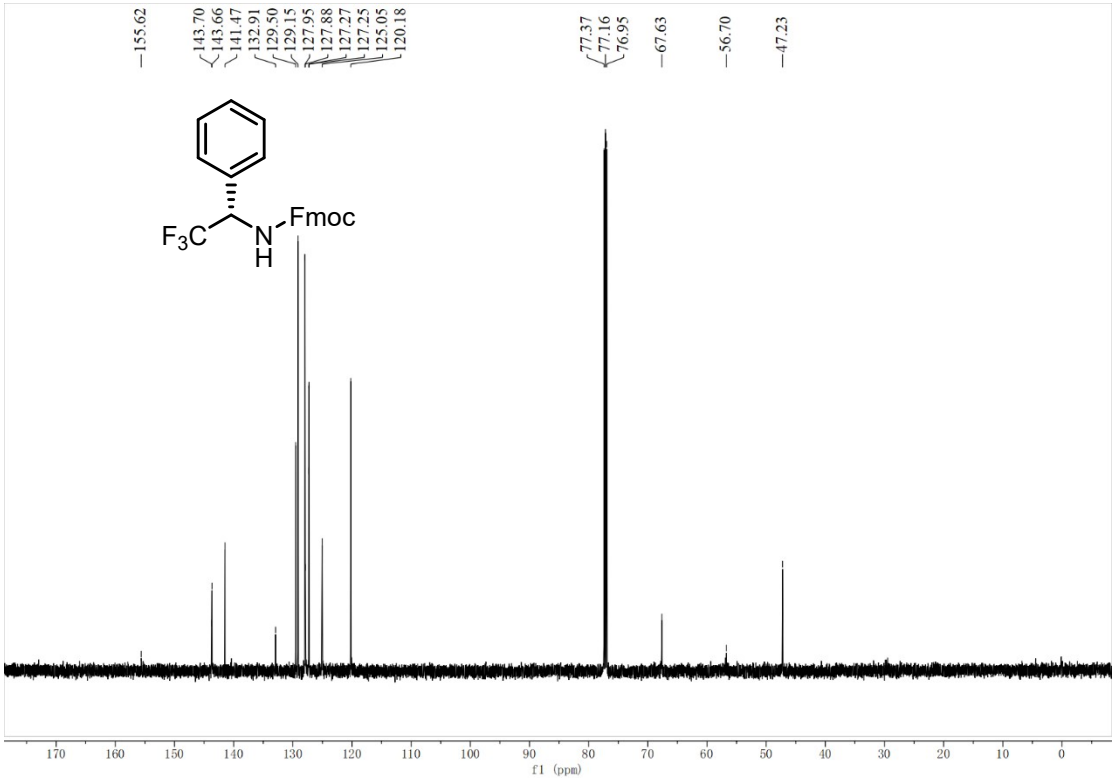
^{13}C NMR of **3ab** (101 MHz, $CDCl_3$)



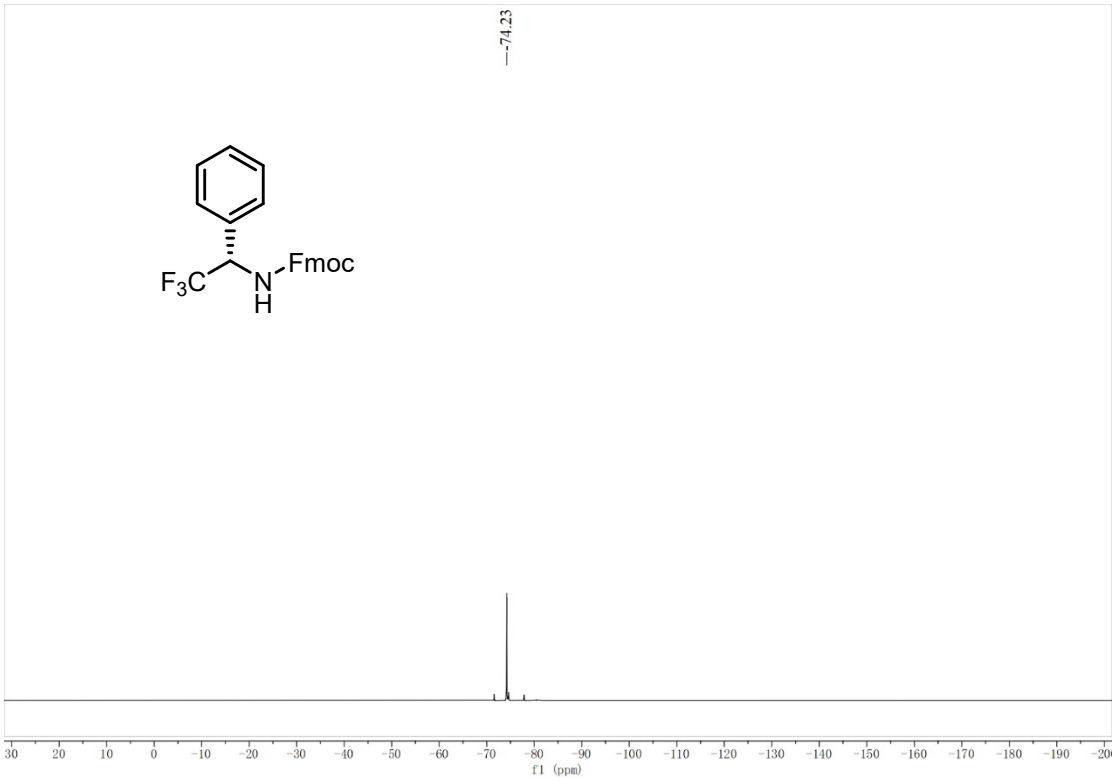
^{1}H NMR of **3ac** (600 MHz, $CDCl_3$)



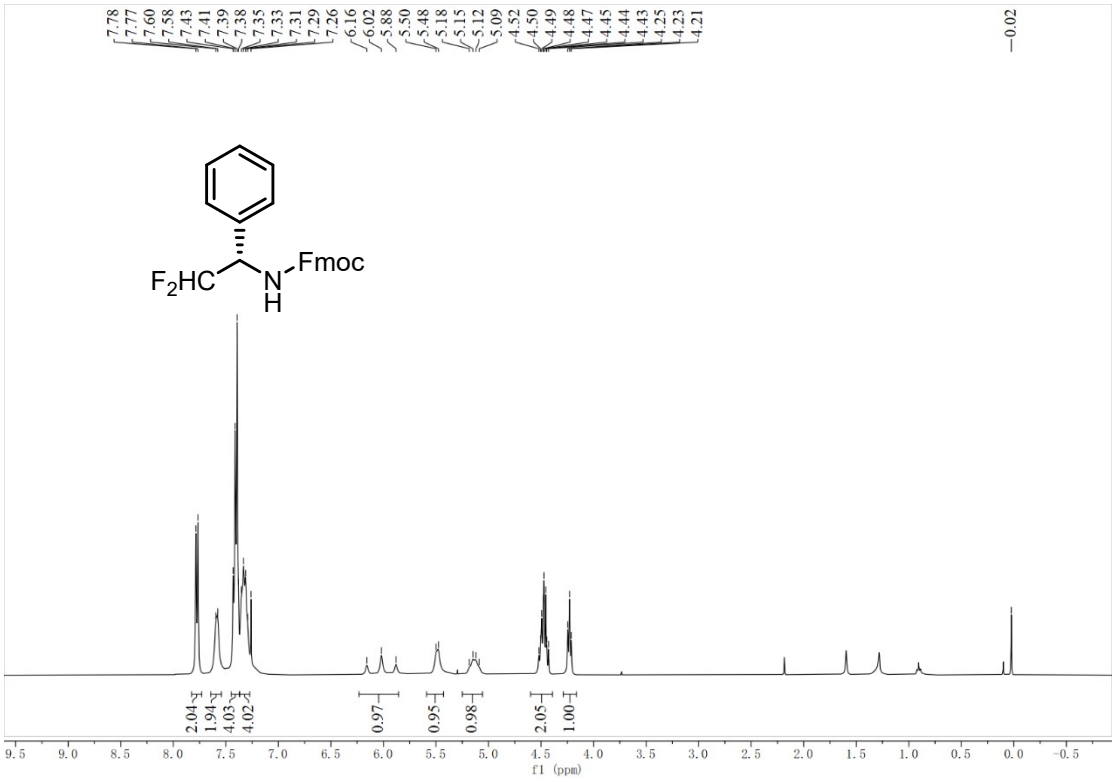
^{13}C NMR of **3ac** (151 MHz, $CDCl_3$)



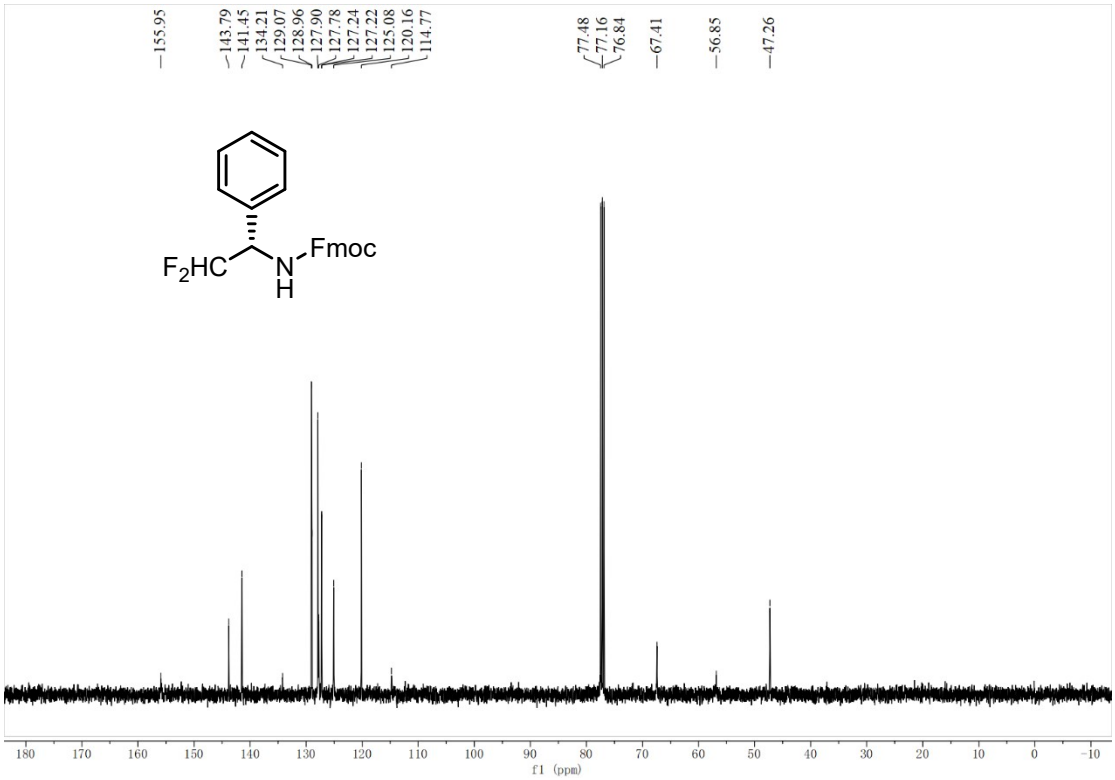
^{19}F NMR of **3ac** (564 MHz, $CDCl_3$)



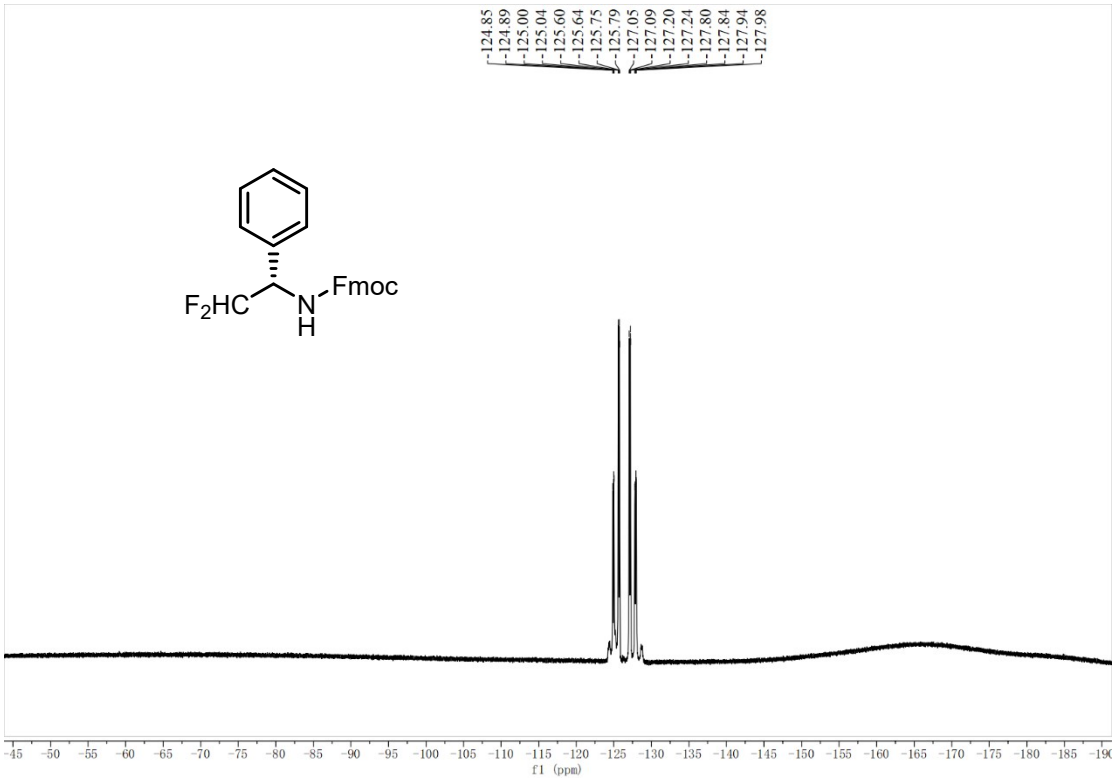
^{1}H NMR of **3ad** (600 MHz, $CDCl_3$)



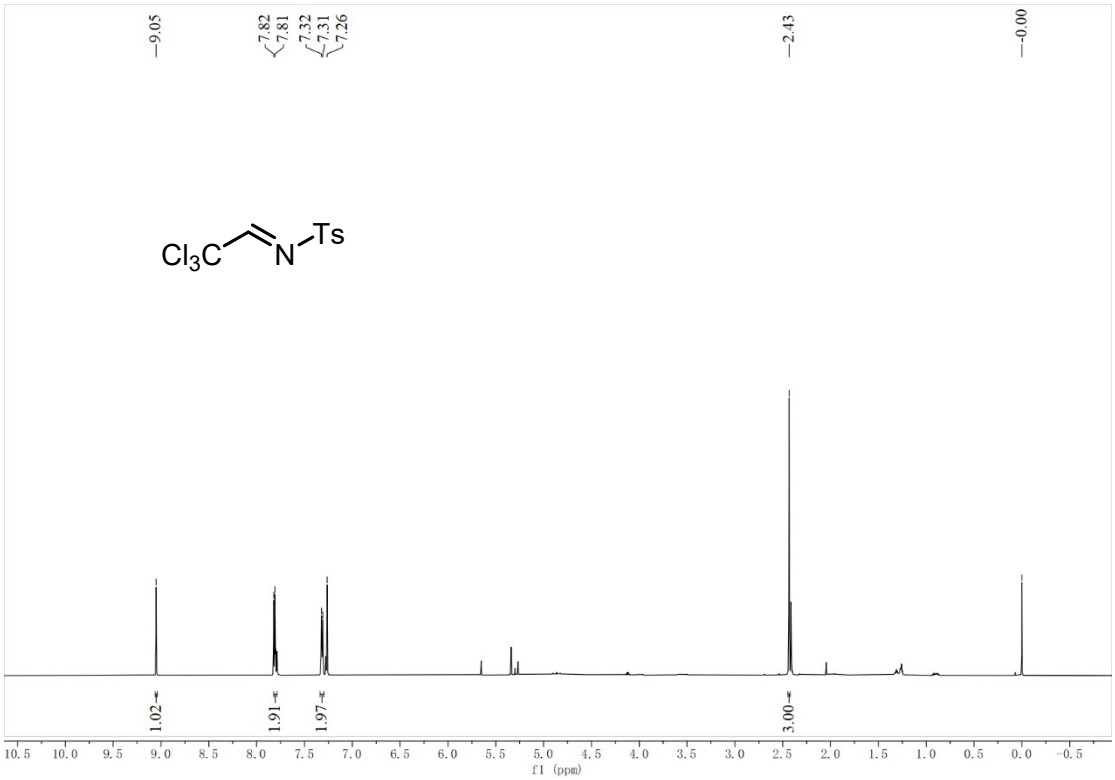
^{13}C NMR of **3ad** (151 MHz, $CDCl_3$)



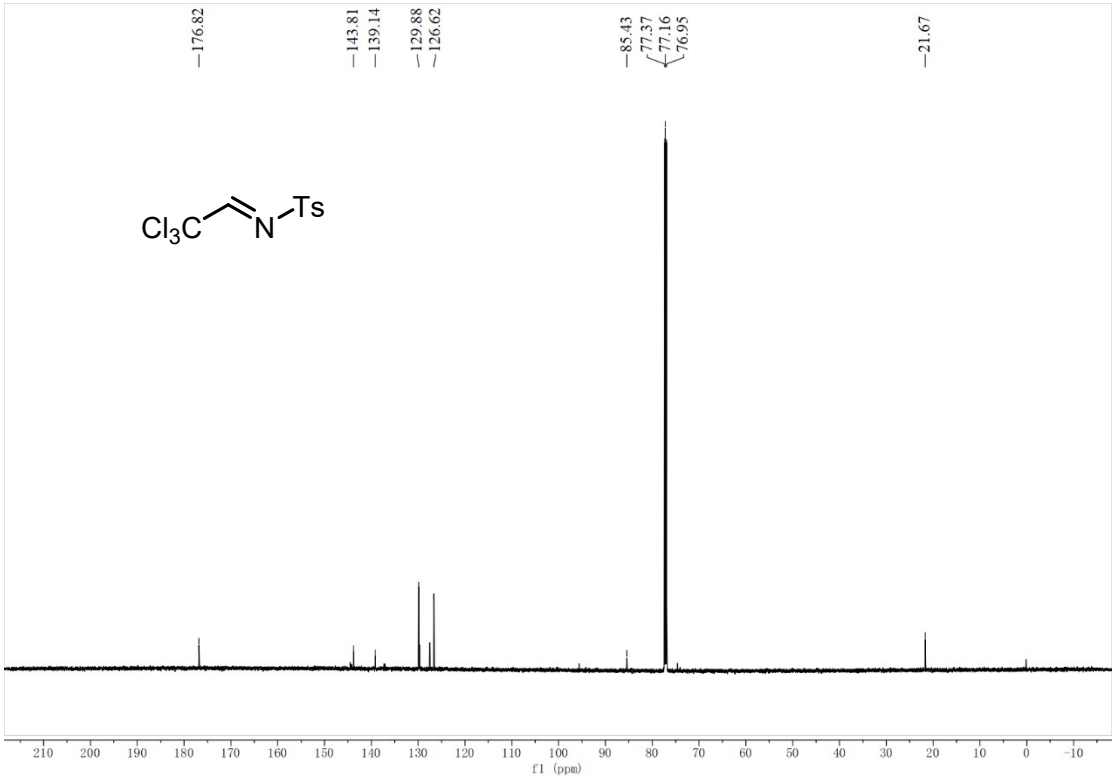
^{19}F NMR of **3ad** (376 MHz, $CDCl_3$)



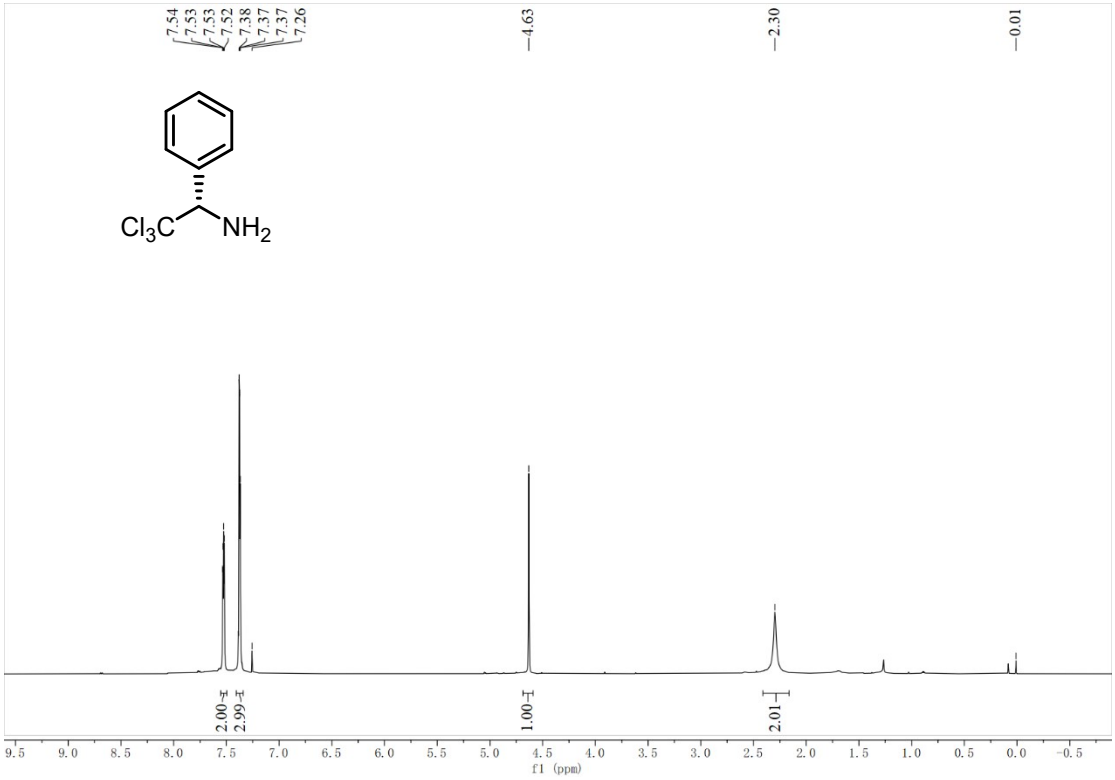
^{1}H NMR of **1b'** (600 MHz, $CDCl_3$)



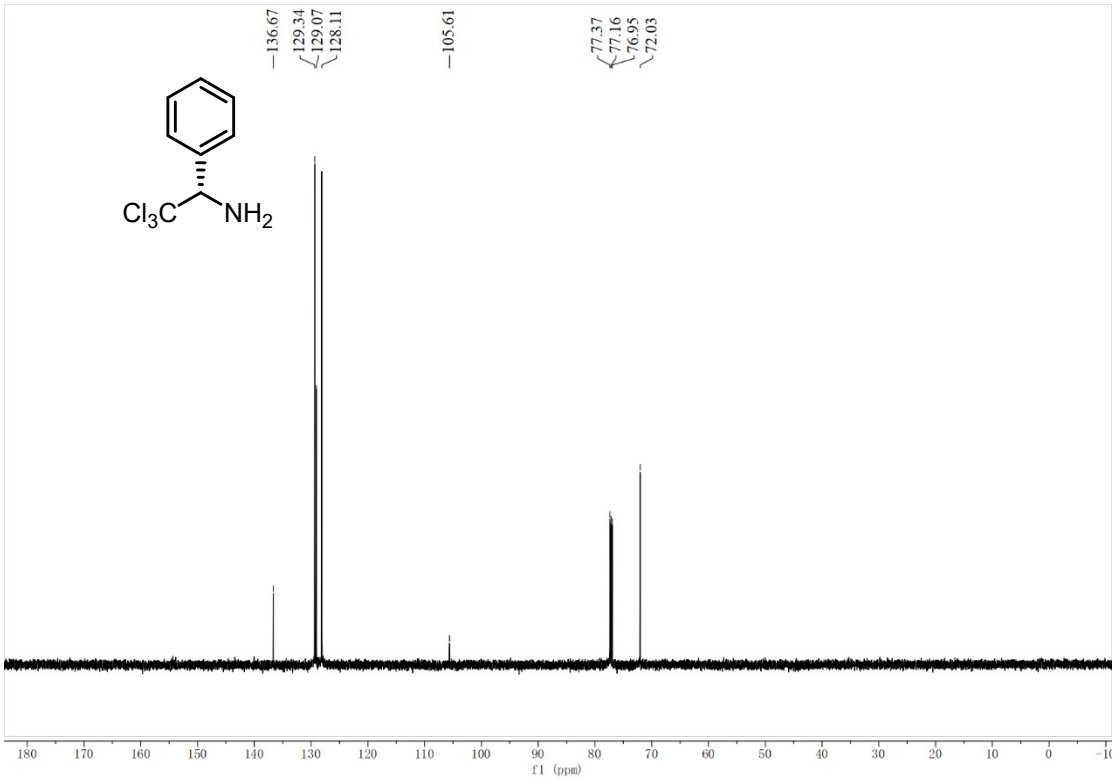
^{13}C NMR of **1b'** (151 MHz, $CDCl_3$)



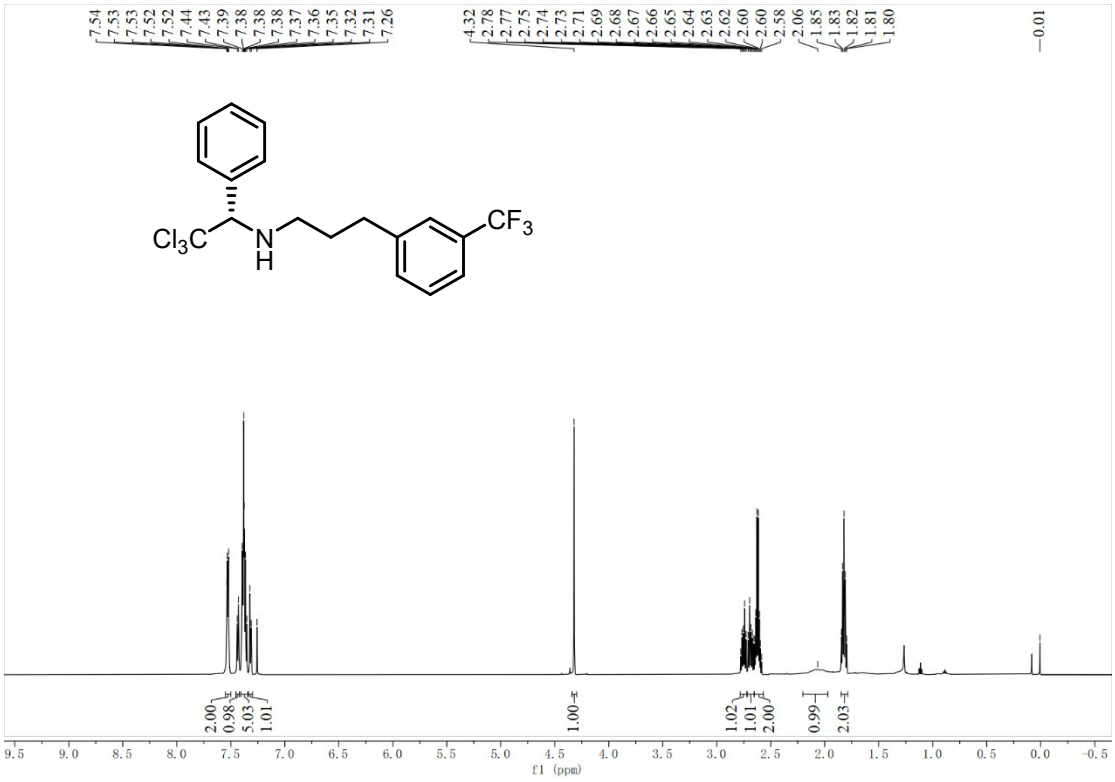
^{1}H NMR of **4** (600 MHz, $CDCl_3$)



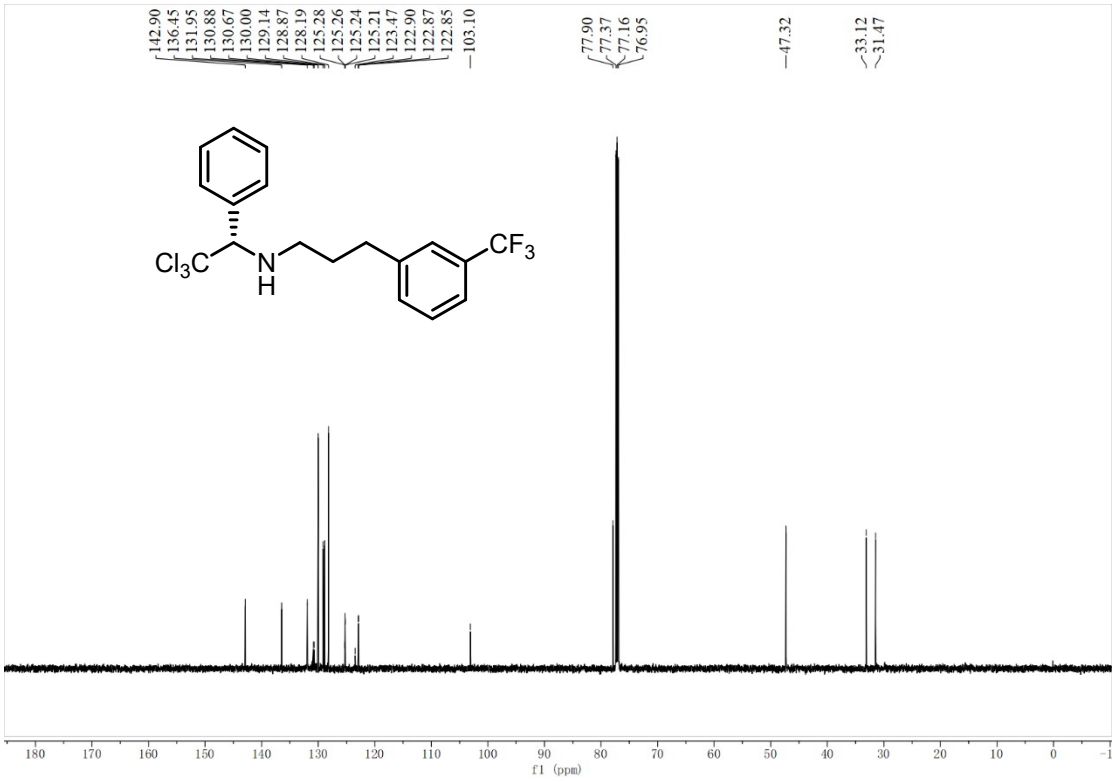
^{13}C NMR of **4** (151 MHz, $CDCl_3$)



^{1}H NMR of **6** (600 MHz, $CDCl_3$)



^{13}C NMR of **6** (151 MHz, $CDCl_3$)



^{19}F NMR of **6** (376 MHz, $CDCl_3$)