Supporting Information for

Chiral Selenide-Catalyzed Enantioselective Synthesis of Trifluoromethylthiolated 2,5-Disubstituted Oxazolines

Tian Qin, Quanbin Jiang, Jieying Ji, Jie Luo and Xiaodan Zhao*

Institute of Organic Chemistry & MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China

E-mail: zhaoxd3@mail.sysu.edu.cn

Contents

1. General considerations

Unless otherwise noted, commercial reagents were purchased from Energy Chemical, Ark, *J & K* or Adamas and used without further purification. The solvents were dried and distilled prior to use by the literature methods. Hexanes and isopropanol for HPLC were purchased from Fisher Scientific and were HPLC grade without a note. All reactions were carried out using oven-dried glassware and all catalytic reactions proceeded without special care. Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light or by staining with potassium permanganate. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Ascend 400MHz spectrometer at ambient temperature. ^{1}H NMR spectra are referred to the TMS signal and ^{13}C NMR spectra are referred to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration. Data for ^{13}C NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (q = quartet), coupling constant (Hz).

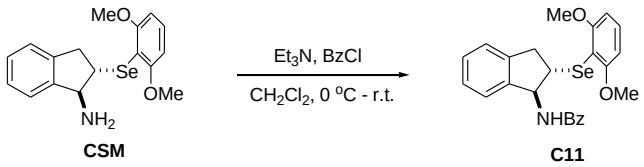
High resolution mass spectra of novel compounds were recorded on LTQ Orbitrap Elite LC/MS (ESI), or MAT 95XP (Thermo, EI) at analytical center of Sun Yat-Sen University. Melting points were determined on WRS-1B melting point apparatus made by Shanghai Precision Instrument Co. Ltd.. Enantiomeric excesses were determined by HPLC analysis on Shimadzu HPLC. The Shimadzu HPLC units including the following instruments: LC-20AT pump, SPD-M20A detector and Daicel Chiralpak IA, OJ-H, OD-H, AD-H and IC columns.

All the racemic products were obtained by using PhSePh as the catalyst at -20 ^{o}C or 0 ^{o}C without note.

2. Experimental procedures, characterization data, and HPLC traces

2.1 Preparation of catalysts

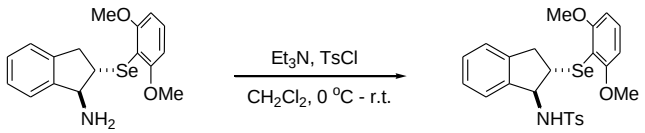
Catalysts **C1-C10** were prepared according to the literature method.[1] All the above compounds are known and were identified by comparison of their NMR data with those reported in the literature. Catalysts **C11**, **C12**, and **C13** were prepared based on the known procedure.[1]



Compound **CSM** was prepared according to the literature method.[2]

To a solution of **CSM** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) were added Et_3N (1.3 mmol, 1.3 equiv) and BzCl (1.2 mmol, 1.2 equiv) at 0 °C. The solution was warmed up to room temperature and then stirred overnight. The resulting mixture was treated with water (5 mL) and extracted with DCM (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (eluent: PE/EtOAc = 5/1, v/v) to afford **C11** as a white solid.

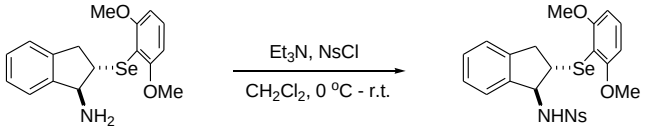
***N*-((1*S*,2*S*)-2-((2,6-Dimethoxyphenyl)selanyl)-2,3-dihydro-1H-inden-1-yl)benzamide (C11):** 0.33 g, 72% yield. $[\alpha]^{25}_D$ = +105.4 (c = 0.2, $CHCl_3$). White solid. mp: 138.5 – 140.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.20 – 7.16 (m, 4H), 6.50 (d, *J* = 8.3 Hz, 2H), 6.22 (d, *J* = 7.9 Hz, 1H), 5.64 (t, *J* = 8.2 Hz, 1H), 4.05 (dd, *J* = 16.9, 8.2 Hz, 1H), 3.81 (s, 6H), 3.32 (dd, *J* = 16.1, 7.9 Hz, 1H), 3.12 – 3.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.19, 161.02, 143.20, 141.61, 134.63, 131.55, 130.34, 128.54, 128.09, 127.21, 127.12, 124.42, 124.24, 105.69, 104.36, 62.28, 56.40, 45.31, 38.40. HR-ESI-MS *m/z* calcd. for $C_{24}H_{22}NO_3Se$ $[M-H]^-$: 452.0765, found: 452.0774.



CSM **C12**

To a solution of **CSM** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) were added Et_3N (1.3 mmol, 1.3 equiv) and TsCl (1.2 mmol, 1.2 equiv) at 0 °C. The solution was warmed up to room temperature and then stirred overnight. The resulting mixture was treated with water (5 mL) and extracted with DCM (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (eluent: PE/EtOAc = 5/1, v/v) to afford **C12** as a white solid.

***N*-((1*S*,2*S*)-2-((2,6-Dimethoxyphenyl)selanyl)-2,3-dihydro-1H-inden-1-yl)-4-methylbenzenesulfonamide (C12):** 0.22 g, 43% yield. $[\alpha]^{25}_D$ = -0.1 (c = 0.2, $CHCl_3$). White solid. mp: 144.1 – 147.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 4.8 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.07 (m, 3H), 6.59 (d, *J* = 8.3 Hz, 2H), 4.82 (d, *J* = 6.4 Hz, 1H), 4.57 (t, *J* = 5.7 Hz, 1H), 4.04 – 3.99 (m, 1H), 3.83 (s, 6H), 3.30 (dd, *J* = 16.8, 7.4 Hz, 1H), 2.84 (dd, *J* = 16.8, 5.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.08, 143.43, 142.14, 141.28, 137.32, 130.46, 129.71, 128.70, 127.66, 127.42, 124.96, 124.78, 106.05, 104.34, 65.12, 56.35, 45.42, 38.22, 21.73. HR-ESI-MS *m/z* calcd. for $C_{24}H_{24}NO_4SSe$ $[M-H]^-$: 502.0591, found: 502.0599.



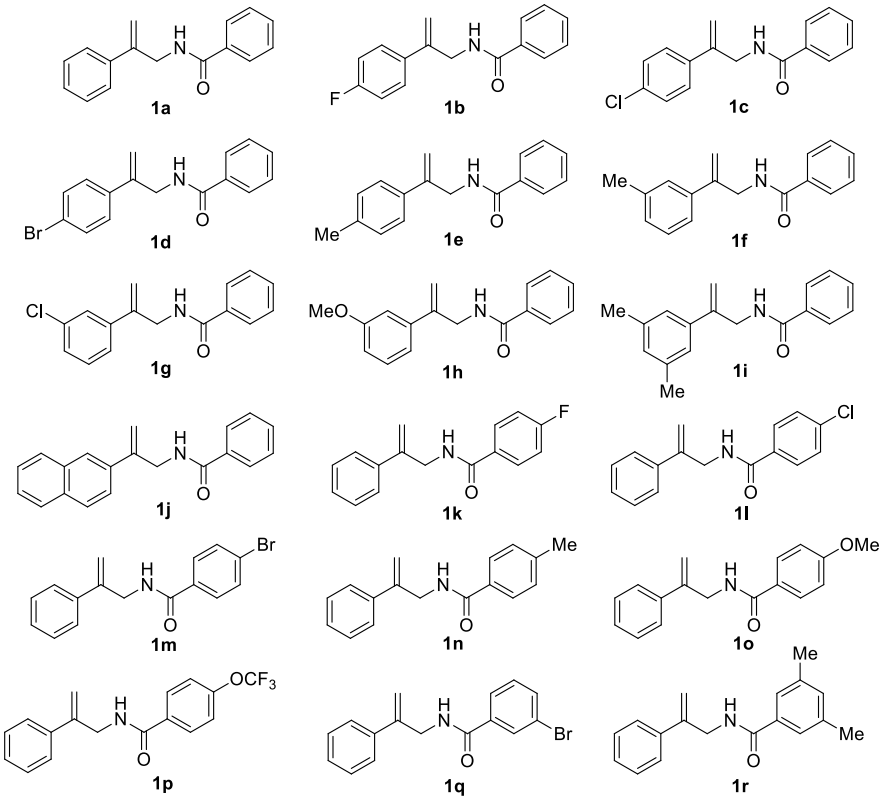
CSM **C13**

To a solution of **a** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) were added Et_3N (1.3 mmol, 1.3 equiv) and NsCl (1.2 mmol, 1.2 equiv) at 0 °C. The solution was warmed up to room temperature and then stirred overnight. The resulting mixture was treated with water (5 mL) and extracted with DCM (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue

was purified by flash column chromatography (eluent: PE/EtOAc = 5/1, v/v) to afford **C13** as a white solid.

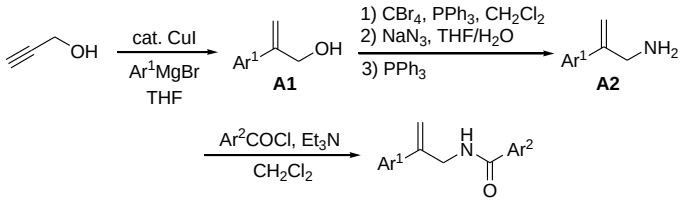
***N*-((1*S*,2*S*)-2-((2,6-Dimethoxyphenyl)selanyl)-2,3-dihydro-1H-inden-1-yl)-4-nitro benzenesulfonamide (C13):** 0.29 g, 52% yield. $[\alpha]^{25}_{D}$ = +25.8 (c = 0.2, $CHCl_3$). Yellow solid. mp: 162.1 – 165.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.25 (m, 2H), 7.93 – 7.91 (m, 2H), 7.34 – 7.27 (m, 2H), 7.21 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 2H), 5.16 (d, *J* = 7.0 Hz, 1H), 4.71 (t, *J* = 6.6 Hz, 1H), 3.95 (dt, J = 7.5, 6.5 Hz, 1H), 3.83 (s, 6H), 3.28 (dd, *J* = 16.7, 7.6 Hz, 1H), 2.85 (dd, *J* = 16.6, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.77, 150.08, 146.20, 141.82, 140.84, 130.47, 128.96, 128.82, 127.62, 124.89, 124.79, 124.27, 105.82, 104.47, 65.78, 56.37, 45.15, 38.20. HR-ESI-MS *m/z* calcd. for $C_{23}H_{21}N_2O_6SSe$ $[M-H]^-$: 533.0286, found: 533.0295.

2.2 Preparation of *N*-allylamide substrates



Substrates **1a**,[3] **1b**,[3] **1c**,[3] **1d**,[3] **1e**,[3] **1g**,[3] **1h**,[3] **1j**,[3] **1m**[4] and **1o**[4] were prepared according to the literature methods. All the above compounds are known and were identified by comparison of their NMR data with those reported in the literature.

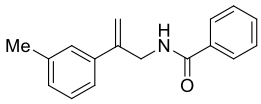
General procedure for the synthesis of compounds **1f**, **1i**, **1k**, **1l**, **1n**, **1p**, **1q** and **1r** based on the known procedure.[3]



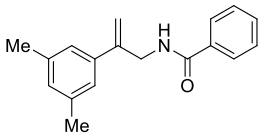
To an oven-dried 100 mL Schlenk flask equipped with a magnetic stir bar was added Ar^1MgBr (1.0 M in THF, 10 mL, 2.5 equiv) under N_2 atmosphere. The cuprous iodide (0.6 mmol, 0.15 equiv) was added at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, after which a solution of propargyl alcohol (4.0 mmol, 1.0 equiv) in dry THF (15 mL) was added slowly at 0 °C. The reaction mixture was heated to reflux and stirred for 24 h. Themixture was cooled to room temperature, saturated NH_4Cl solution was added dropwise carefully. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: PE/EtOAc = 10:1, v/v) to give the target compound **A1**.

To an oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar were added **A1** (2.0 mmol, 1.0 equiv) triphenylphosphine (2.6 mmol, 1.3 equiv) and CH_2Cl_2 (5 mL) at room temperature. After the solution was cooled to 0 °C, CBr_4 (2.4 mmol, 1.2 equiv) was added. The resulting mixture was stirred at 0 °C for 3h. The solvent was concentrated *in vacuo*. The residue was redissolved in THF/H_2O (4/1, v/v, 10 mL) and treated with NaN_3 (2.6 mmol, 1.3 equiv) for 1 h. Then, triphenylphosphine (3.0 mmol, 1.5 equiv) was added. After the mixture was stirred at room temperature for 12 h, the organic solvent of the mixture was *in vacuo*. The residual aqueous layer was basified by adding solid NaOH and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to get crude **A2** without further purification.

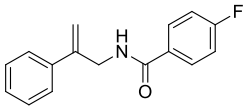
To an oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar were added the obtained **A2** (1.0 mmol, 1.0 equiv) triethylamine and CH_2Cl_2 (5 mL) at 0 ºC. Then, a solution of Ar^2COCl (1.1 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added. The reaction was stirred for 2 h at room temperature and quenched by saturated NH_4Cl solution. The mixture was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by recrystallized from PE/CH_2Cl_2 to afford the desired product.



***N*-(2-(M-tolyl)allyl)benzamide (1f):** 0.38 g, 80% yield. White solid. mp: 92.4 - 94.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.50 – 7.46 (m, 1H), 7.42 – 7.38 (m, 1H), 7.29 – 7.23 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.18 (s, 1H), 5.50 (s, 1H), 5.30 (s, 1H), 4.53 (d, *J* = 5.5 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 144.47, 138.47, 138.34, 134.64, 131.62, 129.05, 128.71, 128.64, 127.02, 126.99, 123.33, 113.99, 43.97, 21.63. HR-ESI-MS *m/z* calcd. for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383, found: 252.1379.

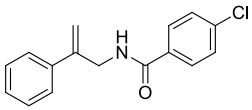


***N*-(2-(3,5-Dimethylphenyl)allyl)benzamide (1i):** 0.19 g, 61% yield. White solid. mp: 96.0–97.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 7.09 (s, 2H), 6.96 (s, 1H), 6.16 (s, 1H), 5.48 (s, 1H), 5.28 (s, 1H), 4.51 (d, *J* = 5.5 Hz, 2H), 2.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.51, 144.50, 138.55, 138.12, 134.63, 131.52, 129.86, 128.62, 127.02, 124.07, 113.53, 43.92, 21.45. HR-ESI-MS *m/z* calcd. for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539, found: 266.1532.

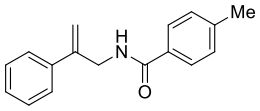


4-Fluoro-*N*-(2-phenylallyl)benzamide (1k): 0.17 g, 72% yield. White solid. mp: 148.4 – 149.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.49 – 7.47 (m,

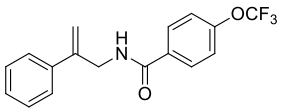
2H), 7.39 – 7.29 (m, 3H), 7.10 – 7.06 (m, 2H), 6.10 (s, 1H), 5.53 (s, 1H), 5.32 (s, 1H), 4.54 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.82 (d, *J* = 251.9 Hz), 163.56, 144.25, 138.37, 130.69 (d, *J* = 3.1 Hz), 129.36 (d, *J* = 8.9 Hz), 128.73, 128.28, 126.17, 115.69 (d, *J* = 21.9 Hz), 114.21, 43.91. HR-ESI-MS *m/z* calcd. for $C_{16}H_{15}FNO$ $[M+H]^+$: 256.1132, found: 256.1127.



4-Chloro-*N*-(2-phenylallyl)benzamide (1l): 0.16 g, 64% yield. White solid. mp: 167.5–167.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.48 – 7.46 (m, 2H), 7.38 – 7.28 (m, 5H), 6.17 (s, 1H), 5.52 (s, 1H), 5.31 (s, 1H), 4.53 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.46, 144.19, 138.33, 137.86, 132.88, 128.92, 128.75, 128.48, 128.31, 126.18, 114.30, 43.93. HR-ESI-MS *m/z* calcd. for $C_{16}H_{15}ClNO$ $[M+H]^+$: 272.0837, found: 272.0831.

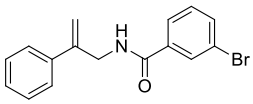


4-Methyl-*N*-(2-phenylallyl)benzamide (1n): 0.22 g, 77% yield. White solid. mp: 153.4 – 153.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.37 – 7.30 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 5.52 (s, 1H), 5.32 (s, 1H), 4.54 (d, *J* = 5.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 144.44, 142.01, 138.51, 131.68, 129.31, 128.68, 128.19, 127.02, 126.19, 114.01, 43.77, 21.53. HR-ESI-MS *m/z* calcd. for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383, found: 252.1379.

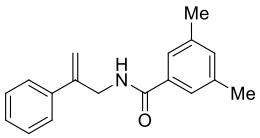


***N*-(2-Phenylallyl)-3-(trifluoromethoxy)benzamide (1p):** 0.19 g, 58% yield. Yellow solid. mp: 126.8 – 127.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.49 – 7.47 (m, 2H), 7.38 – 7.29 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.16 (s, 1H), 5.53 (s, 1H), 5.32 (s, 1H), 4.54 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.28, 151.57, 144.15, 138.33, 132.98, 128.95, 128.74, 128.31, 126.16, 120.71, 120.41 (q, *J*

= 258.3 Hz), 114.27, 114.24, 43.94. HR-ESI-MS *m/z* calcd. for $C_{17}H_{15}F_3NO_2$ $[M+H]^+$: 322.1049, found: 322.1043.



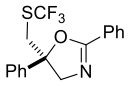
3-Bromo-*N*-(2-phenylallyl)benzamide (1q): 0.23 g, 75% yield. White solid. mp: 119.9 – 120.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 1.8 Hz, 1H), 7.61 (dd, J = 7.8, 1.7 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.39 – 7.28 (m, 4H), 6.12 (s, 1H), 5.54 (s, 1H), 5.32 (s, 1H), 4.54 (d, J = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.08, 144.07, 138.30, 136.50, 134.56, 130.31, 130.21, 128.73, 128.29, 126.16, 125.58, 122.86, 114.30, 43.93. HR-ESI-MS *m/z* calcd. for $C_{16}H_{15}BrNO$ $[M+H]^+$: 316.0332, found: 316.0329.



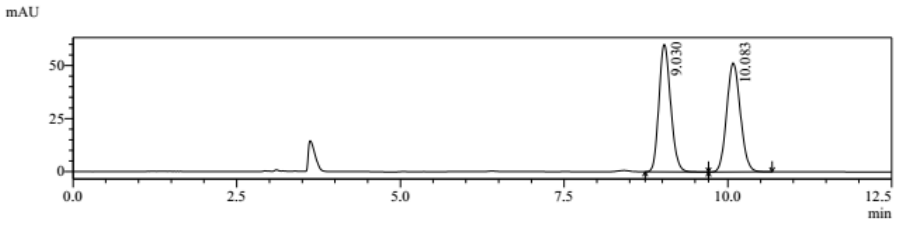
3,5-Dimethyl-*N*-(2-phenylallyl)benzamide (1r): 0.29 g, 68% yield. White solid. mp: 85.6 – 86.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.37 – 7.28 (m, 5H), 7.10 (s, 1H), 6.17 (s, 1H), 5.52 (s, 1H), 5.31 (s, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 2.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.85, 144.45, 138.51, 138.38, 134.57, 133.20, 128.70, 128.21, 126.21, 124.79, 114.06, 43.79, 21.33. HR-ESI-MS *m/z* calcd. for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539, found: 266.1532.

2.3 Chiral selenide catalyzed asymmetric CF_3S cyclization

General Method: To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added **1** (0.1 mmol), **2** (59.6 mg, 0.15 mmol), catalyst **C8** (9.3 mg, 0.02 mmol) and solvent (4.0 mL, CH_2Cl_2/toluene = 1:1, v/v) subsequently. The solution was stirred at the room temperature for 20 min then cooled to -78 °C for another 20 min. $BF_3 \cdot OEt_2$ (18.5 μL, 0.15 mmol) was added at -78 °C. The mixture was stirred at -78 °C for 18 h. The reaction was quenched by Et_3N and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography to afford the corresponding CF_3S product.



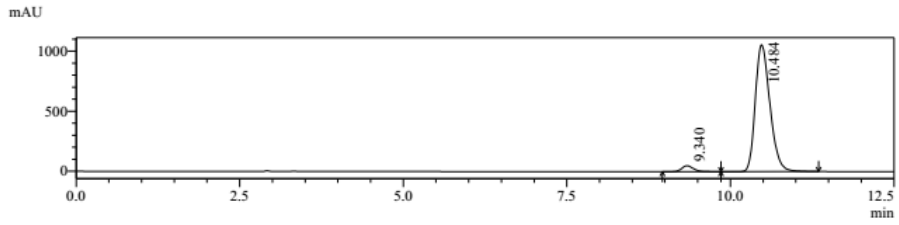
(*R*)-2,5-Diphenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrooxazole (3a): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3a** as a colorless oil. 23.5 mg, 70% yield and 93% ee. $[\alpha]^{25}_D$ = -160.4 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.54 – 7.51 (m, 1H), 7.48 – 7.44 (m, 2H), 7.41 – 7.38 (m, 4H), 7.35 – 7.31 (m, 1H), 4.41 (d, *J* = 15.0 Hz, 1H), 4.27 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 13.6 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.99, 142.26, 131.84, 130.77 (q, *J* = 306.4 Hz), 129.06, 129.02, 128.62, 128.43, 127.30, 124.71, 86.96, 66.92, 40.50. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.89. HR-ESI-MS *m/z* calcd. for $C_{17}H_{15}F_3NOS$ $[M+H]^+$: 338.0821, found: 338.0817. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 240 nm) t_1 = 10.5 min (major), t_2 = 9.3 min (minor).



Peak Table

PDA Ch1 240nm

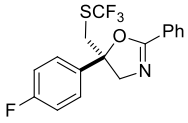
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.030	747008	54647	50.058	53.850
2	10.083	745262	46833	49.942	46.150
Total		1492270	101480	100.000	100.000



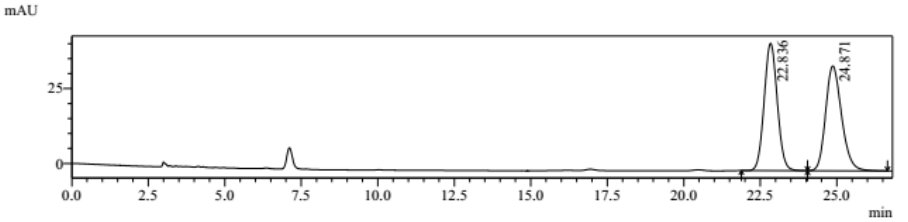
Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.340	589731	42284	3.471	3.995
2	10.484	16401650	1016259	96.529	96.005
Total		16991381	1058544	100.000	100.000



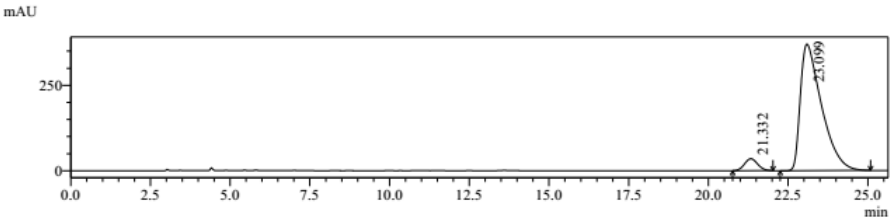
(*R*)-5-(4-Fluorophenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroox azole (3b): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3b** as a colorless oil. 24.2 mg, 68% yield and 89% ee. $[\alpha]^{25}_D$ = -128.3 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.12 – 7.06 (m, 2H), 4.40 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.47 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.86, 162.63 (d, *J* = 247.7 Hz), 138.01 (d, *J* = 3.1 Hz), 131.95, 130.68 (q, *J* = 306.3 Hz), 128.66, 128.42, 127.15, 126.69 (d, *J* = 8.3 Hz), 115.98 (d, *J* = 21.8 Hz), 86.68, 67.00, 40.50. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.90, -113.53. HR-ESI-MS *m/z* calcd. for $C_{17}H_{13}F_4NOS$ $[M+H]^+$: 356.0727, found: 356.0720. HPLC (Daicel Chiralpak IA column, *i*-PrOH/hexane = 0.8/99.2, 1 mL/min, 240 nm) t_1 = 23.1 min (major), t_2 = 21.3 min (minor).



Peak Table

PDA Ch1 240nm

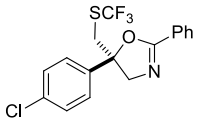
Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.836	1271019	42054	49.954	54.988
2	24.871	1273344	34425	50.046	45.012
Total		2544363	76479	100.000	100.000



Peak Table

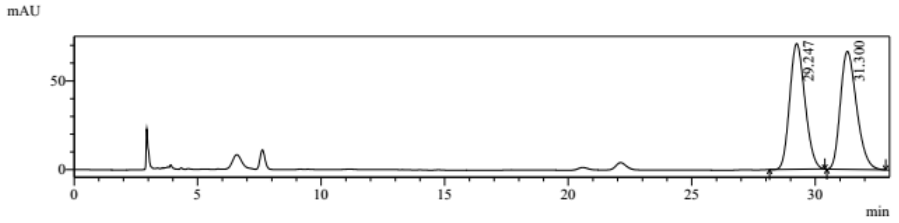
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	21.332	998885	34534	5.503	8.579
2	23.099	17152072	367987	94.497	91.421
Total		18150957	402522	100.000	100.000



(*R*)-5-(4-Chlorophenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroo xazole (3c): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3c** as a colorless oil. 24.6 mg, 66% yield and 89% ee. $[\alpha]^{25}_D$ = -153.4 (c = 0.2, $CHCl_3$).

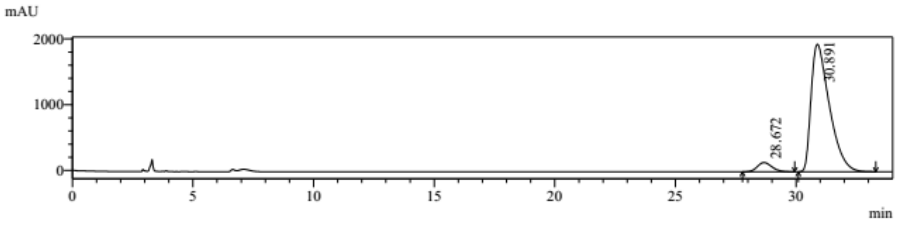
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.44 (m, 2H), 7.39 – 7.32 (m, 4H), 4.39 (d, *J* = 15.0 Hz, 1H), 4.22 (d, *J* = 15.0 Hz, 1H), 3.53 (d, *J* = 13.7 Hz, 1H), 3.46 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.91, 140.71, 134.47, 131.99, 130.64 (q, *J* = 306.4 Hz), 129.23, 128.68, 128.43, 127.09, 126.28, 86.64, 66.99, 40.32. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.84. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}ClF_3NOS$ $[M+H]^+$: 372.0431, found: 372.0439. HPLC (Daicel Chiralpak AD-H column, *i*-PrOH/hexane = 0.8/99.2, 1 mL/min, 224 nm) t_1 = 30.9 min (major), t_2 = 28.7 min (minor).



Peak Table

PDA Ch1 224nm

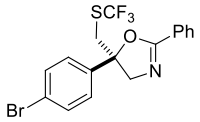
Peak#	Ret. Time	Area	Height	Area%	Height%
1	29.247	3042681	70591	49.943	51.680
2	31.300	3049569	66001	50.057	48.320
Total		6092251	136593	100.000	100.000



Peak Table

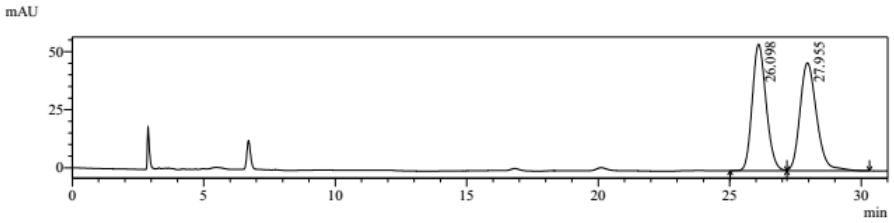
PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.672	5812832	137688	5.369	6.647
2	30.891	102455988	1933632	94.631	93.353
Total		108268820	2071320	100.000	100.000



(*R*)-5-(4-Bromophenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroox azole (3d): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3d** as a colorless oil. 28.1 mg, 67% yield and 90% ee. $[\alpha]^{25}_D$ = -207.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.52 (m, 3H), 7.48 – 7.44 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.39 (d, *J* = 15.0 Hz, 1H), 4.22 (d, *J* = 15.0 Hz, 1H), 3.52 (d, *J* = 13.7 Hz, 1H), 3.46 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.88, 141.23, 132.17, 131.98, 130.64 (q, *J* = 306.3 Hz), 128.67, 128.42, 127.07,

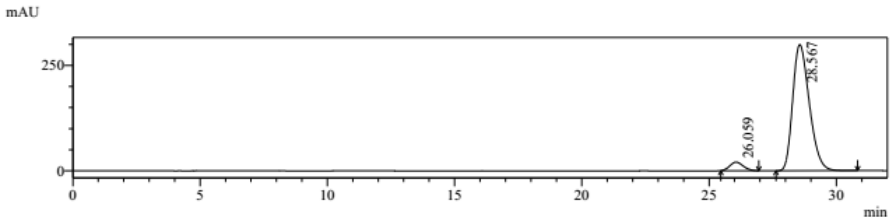
126.57, 122.56, 86.65, 66.95, 40.24. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.85. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}BrF_3NOS$ $[M+H]^+$: 415.9926, found: 415.9929. HPLC (Daicel Chiralpak AD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 231 nm) t_1 = 28.6min (major), t_2 = 26.1 min (minor).



Peak Table

PDA Ch1 231nm

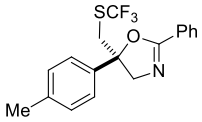
Peak#	Ret. Time	Area	Height	Area%	Height%
1	26.098	2003335	54291	49.509	53.967
2	27.955	2043058	46310	50.491	46.033
Total		4046393	100601	100.000	100.000



Peak Table

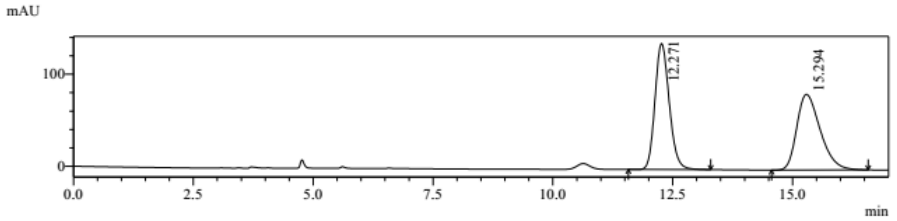
PDA Ch1 231nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	26.059	742420	20035	5.170	6.288
2	28.567	13616570	298600	94.830	93.712
Total		14358990	318636	100.000	100.000



(*R*)-2-Phenyl-5-(p-tolyl)-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrooxazole

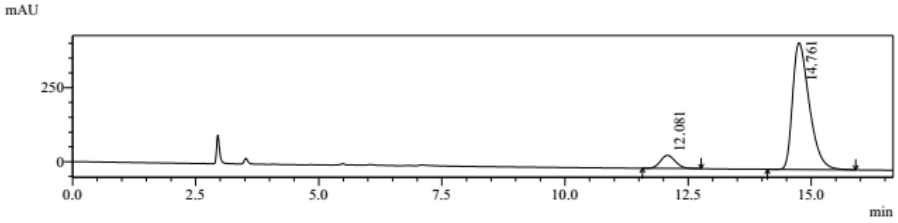
(3e): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3e** as a colorless oil. 24.1 mg, 69% yield and 83% ee. $[\alpha]^{25}_D$ = -193.3 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.47 – 7.43 (m, 2H), 7.29 – 7.24 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 4.38 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.00, 139.26, 138.27, 131.78, 130.81 (q, *J* = 306.2 Hz), 129.66, 128.59, 128.42, 127.40, 124.63, 86.95, 66.92, 40.49, 21.18. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.84. HR-ESI-MS *m/z* calcd. for $C_{18}H_{17}F_3NOS$ $[M+H]^+$:352.0977, found: 352.0971. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 0.5/99.5, 1 mL/min, 225 nm) t_1 = 14.8 min (major), t_2 = 12.1 min (minor).



Peak Table

PDA Ch1 225nm

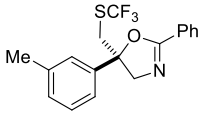
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.271	2836595	133720	50.333	62.139
2	15.294	2799077	81476	49.667	37.861
Total		5635671	215196	100.000	100.000



Peak Table

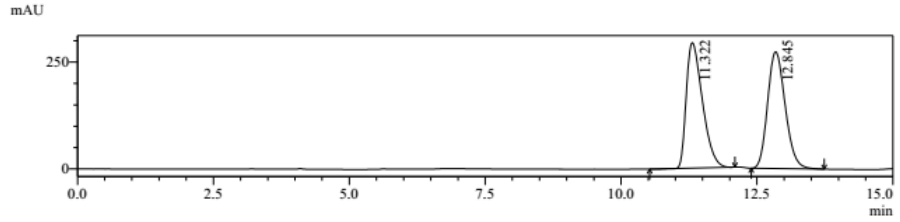
PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.081	927969	43189	8.412	9.254
2	14.761	10103945	423492	91.588	90.746
Total		11031914	466681	100.000	100.000



(*R*)-2-Phenyl-5-(m-tolyl)-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrooxazole

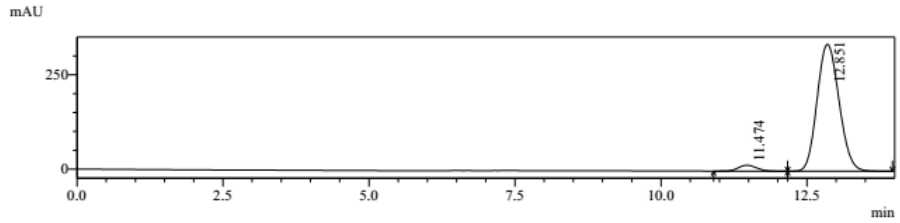
(3f): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3f** as a colorless oil. 23.3 mg, 66% yield and 93% ee. $[\alpha]^{25}_D$ = -111.5 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.44 (m, 1H), 7.31 – 7.27 (m, 1H), 7.19 – 7.14 (m, 3H), 4.39 (d, *J* = 15.0 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.02, 142.24, 138.84, 131.82, 130.82 (q, *J* = 306.4 Hz), 129.19, 128.93, 128.62, 128.45, 127.38, 125.31, 121.77, 86.96, 77.48, 40.55, 21.74. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.90. HR-ESI-MS *m/z* calcd. for $C_{18}H_{17}F_3NOS$ $[M+H]^+$: 352.0977, found: 352.0971. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 0.5/99.5, 1 mL/min, 240 nm) t_1 = 12.9 min (major), t_2 = 11.5 min (minor).



Peak Table

PDA Ch1 240nm

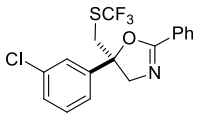
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.322	6066608	289538	49.703	52.393
2	12.845	6139188	263092	50.297	47.607
Total		12205796	552629	100.000	100.000



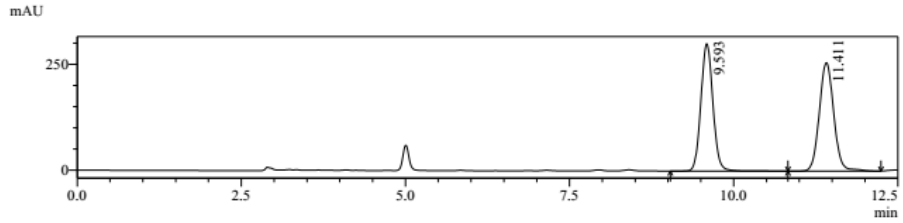
Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.474	337333	15404	3.695	4.488
2	12.851	8791152	327800	96.305	95.512
Total		9128485	343204	100.000	100.000



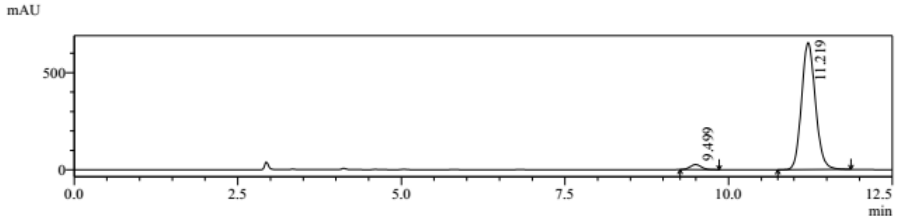
(*R*)-5-(3-Chlorophenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroo xazole (3g): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3g** as a colorless oil. 23.7 mg, 64% yield and 94% ee. $[\alpha]^{25}_D$ = -26.8 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.49 – 7.45 (m, 2H), 7.41 (s, 1H), 7.37 – 7.31 (m, 2H), 7.27 – 7.25 (m, 1H), 4.40 (d, *J* = 15.1 Hz, 1H), 4.24 (d, *J* = 15.1 Hz, 1H), 3.53 (d, *J* = 13.7 Hz, 1H), 3.46 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89, 144.28, 135.11, 131.99, 130.62 (q, *J* = 306.6 Hz), 130.39, 128.68, 128.49, 128.45, 127.02, 125.15, 122.97, 86.51, 66.93, 40.35. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.83. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}ClF_3NOS$ $[M+H]^+$: 372.0431, found: 372.0420. HPLC (Daicel Chiralpak IA column, *i*-PrOH/hexane = 1/99, 1 mL/min, 240 nm) t_1 = 11.2 min (major), t_2 = 9.5 min (minor).



Peak Table

PDA Ch1 240nm

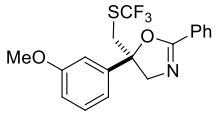
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.593	3835125	289243	49.481	54.135
2	11.411	3915556	245057	50.519	45.865
Total		7750681	534301	100.000	100.000



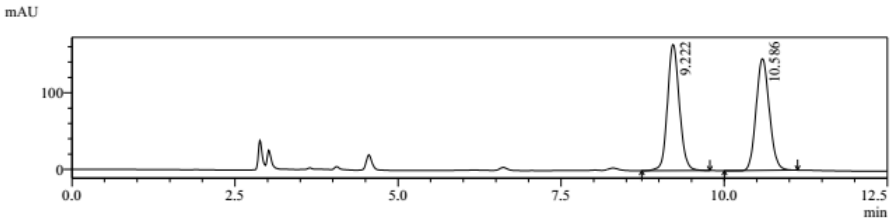
Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.499	313830	23566	3.142	3.692
2	11.219	9675087	614810	96.858	96.308
Total		9988917	638376	100.000	100.000



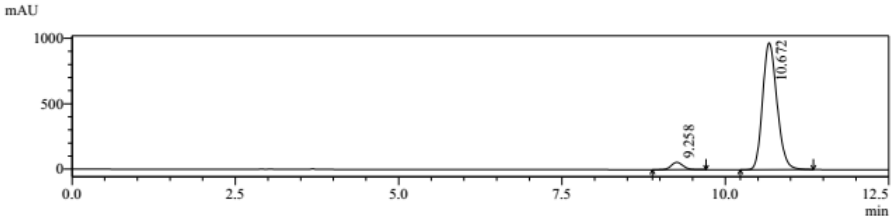
(*R*)-5-(3-Methoxyphenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydro oxazole (3h): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3h** as a colorless oil. 24.6 mg, 68% yield and 91% ee. $[\alpha]^{25}_D$ = -136.9 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.47 – 7.43 (m, 2H), 7.34 – 7.30 (m, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.39 (d, *J* = 15.0 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 3.81 (s, 3H), 3.56 (d, *J* = 13.6 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.95, 160.08, 143.89, 131.81, 131.26 (q, *J* = 306.4 Hz), 130.21, 128.60, 128.50, 128.41, 127.30, 116.90, 113.18, 111.18, 86.86, 66.91, 55.42, 40.41. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.89. HR-ESI-MS *m/z* calcd. for $C_{18}H_{17}F_3NO_2S$ $[M+H]^+$: 368.0027, found: 368.0034. HPLC (Daicel Chiralpak IA column, *i*-PrOH/hexane = 2/98, 1 mL/min, 226 nm) t_1 = 10.7 min (major), t_2 = 9.3 min (minor).



Peak Table

PDA Ch1 226nm

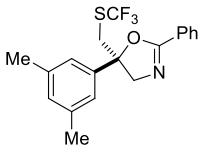
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.222	2093250	158103	50.470	53.055
2	10.586	2054240	139894	49.530	46.945
Total		4147489	297997	100.000	100.000



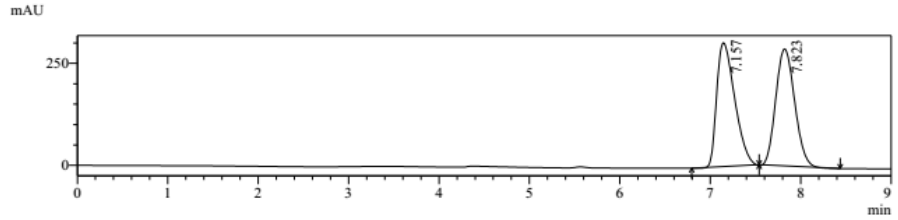
Peak Table

PDA Ch1 226nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.258	707349	50398	4.543	5.232
2	10.672	14861653	912858	95.457	94.768
Total		15569001	963256	100.000	100.000



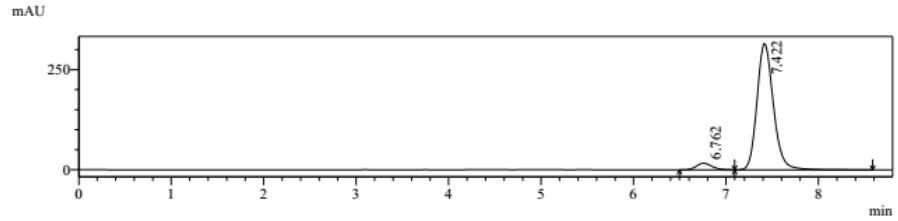
(*R*)-5-(3,5-Dimethylphenyl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrooxazole (3i): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3i** as a colorless oil. 23.1 mg, 63% yield and 90% ee. $[\alpha]^{25}_D$ = -107.2 (c = 0.2, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.45 (m, 2H), 6.98 (s, 3H), 4.38 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.44 (d, *J* = 13.5 Hz, 1H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.04, 142.22, 138.72, 131.79, 130.85 (q, *J* = 306.4 Hz), 130.04, 128.62, 128.46, 127.41, 122.38, 86.95, 66.87, 40.56, 21.61. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.90. HR-ESI-MS *m/z* calcd. for $C_{19}H_{19}F_3NOS$ $[M+H]^+$: 366.1134, found: 366.1131. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 0.5/99.5, 1 mL/min, 239 nm) t_1 = 7.4 min (major), t_2 = 6.8 min (minor).



Peak Table

PDA Ch1 239nm

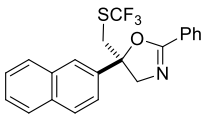
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.157	4168587	291434	50.142	51.300
2	7.823	4145056	276660	49.858	48.700
Total		8313643	568093	100.000	100.000



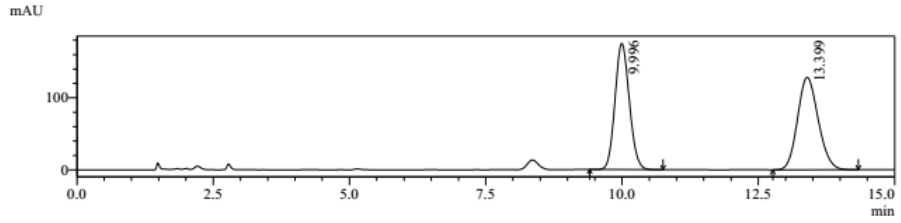
Peak Table

PDA Ch1 239nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.762	197802	15904	4.826	5.070
2	7.422	3900691	297797	95.174	94.930
Total		4098493	313702	100.000	100.000



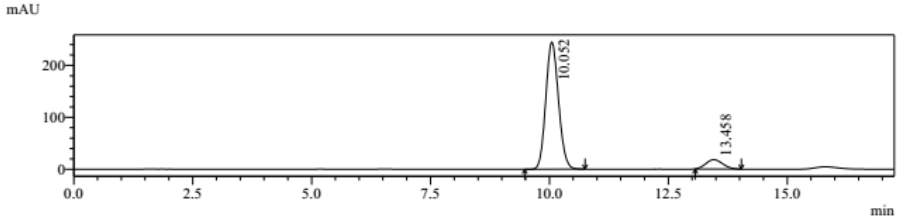
(*R*)-5-(Naphthalen-1-yl)-2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroo xazole (3j): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3j** as a colorless oil. 26.9 mg, 70% yield and 82% ee. $[\alpha]^{25}_D$ = -204.5 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 7.91 – 7.88 (m, 2H), 7.87 – 7.83 (m, 2H), 7.57 – 7.43 (m, 6H), 4.48 (d, *J* = 15.1 Hz, 1H), 4.36 (d, *J* = 15.1 Hz, 1H), 3.67 (d, *J* = 13.6 Hz, 1H), 3.58 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.06, 139.31, 133.10, 133.04, 131.89, 130.56 (q, *J* = 306.5 Hz), 129.22, 128.66, 128.49, 128.36, 127.82, 127.33, 126.88, 126.75, 123.80, 122.42, 87.12, 66.95, 40.39. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.81. HR-ESI-MS *m/z* calcd. for $C_{21}H_{17}F_3NOS$ $[M+H]^+$: 388.0977, found: 388.0965. HPLC (Daicel Chiralpak AD-H column, i-PrOH/hexane = 2/98, 2 mL/min, 226 nm) t_1 = 13.4 min (major), t_2 = 10.1 min (minor).



Peak Table

PDA Ch1 226nm

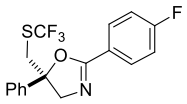
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.996	3205825	169493	48.630	57.160
2	13.399	3386421	127032	51.370	42.840
Total		6592246	296525	100.000	100.000



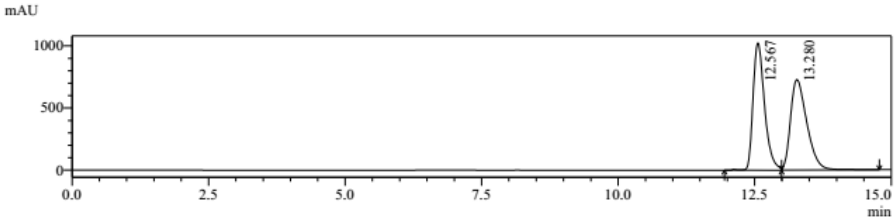
Peak Table

PDA Ch1 226nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.052	4543752	240914	91.063	93.148
2	13.458	445910	17721	8.937	6.852
Total		4989662	258635	100.000	100.000



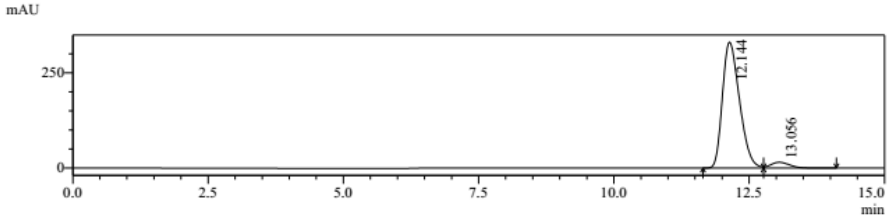
(*R*)-2-(4-Fluorophenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroox azole (3k): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3k** as a colorless oil. 21.1 mg, 59% yield and 91% ee. $[\alpha]^{25}_D$ = -27.5 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 2H), 7.55 – 7.34 (m, 5H), 7.16 – 7.06 (m, 2H), 4.40 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.56 (d, *J* = 13.6 Hz, 1H), 3.47 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06 (d, *J* = 252.4 Hz), 163.81, 142.13, 130.71 (d, *J* = 8.9 Hz), 130.73 (q, *J* = 306.1 Hz), 130.66, 129.06, 128.51, 124.69, 123.54 (d, *J* = 3.1 Hz), 115.82 (d, *J* = 22.0 Hz), 87.21, 66.91, 40.52. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.88, 107.48. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}F_4NOS$ $[M+H]^+$: 356.0727, found: 356.0713. HPLC (Daicel Chiralpak IC column, *i*-PrOH/hexane = 0.8/99.2, 0.5 mL/min, 240 nm) t_1 = 12.1 min (major), t_2 = 13.1 min (minor).



Peak Table

PDA Ch1 240nm

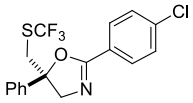
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.567	14987548	963672	49.657	57.514
2	13.280	15194866	711872	50.343	42.486
Total		30182414	1675543	100.000	100.000



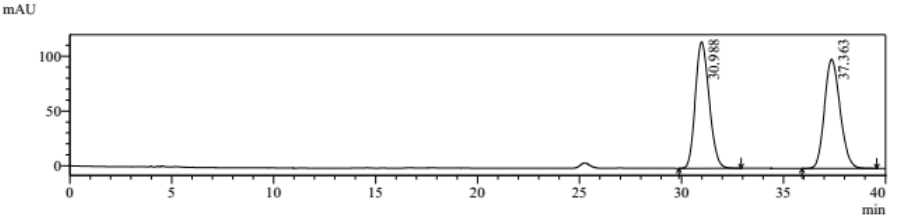
Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.144	7247573	326708	95.258	95.650
2	13.056	360790	14859	4.742	4.350
Total		7608363	341567	100.000	100.000



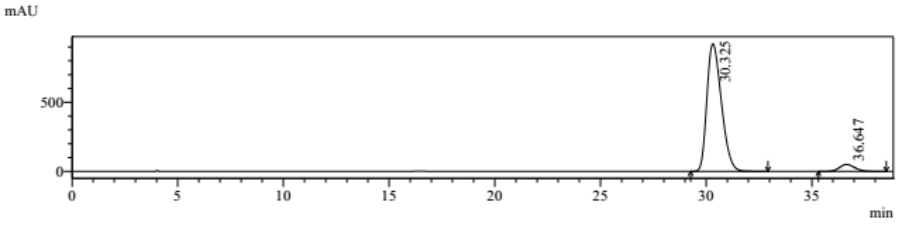
(*R*)-2-(4-Chlorophenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroo xazole (3l): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3l** as a colorless oil. 24.2 mg, 65% yield and 89% ee. $[\alpha]^{25}_D$ = -101.5 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.45 – 7.32 (m, 7H), 4.40 (d, *J* = 15.1 Hz, 1H), 4.26 (d, *J* = 15.1 Hz, 1H), 3.56 (d, *J* = 13.7 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.15, 142.07, 138.12, 130.71 (q, *J* = 306.6 Hz), 129.76, 129.08, 128.98, 128.54, 125.77, 124.67, 87.28, 66.91, 40.51. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.85. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}ClF_3NOS$ $[M+H]^+$: 372.0431, found: 372.0430. HPLC (Daicel Chiralpak AD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 248 nm) t_1 =30.3min (major), t_2 = 36.6 min (minor).



Peak Table

PDA Ch1 248nm

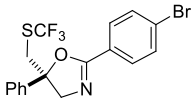
Peak#	Ret. Time	Area	Height	Area%	Height%
1	30.988	5443968	114415	50.627	53.519
2	37.363	5309132	99370	49.373	46.481
Total		10753101	213785	100.000	100.000



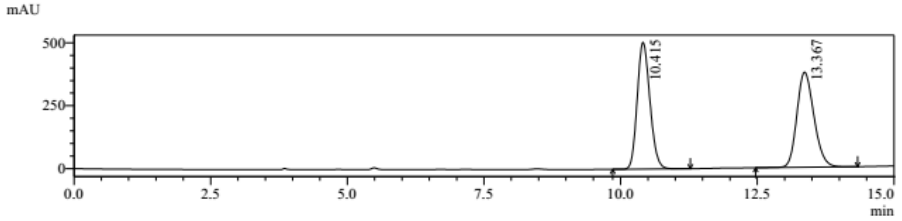
Peak Table

PDA Ch1 248nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	30.325	44063601	915840	94.639	94.866
2	36.647	2495825	49563	5.361	5.134
Total		46559425	965403	100.000	100.000



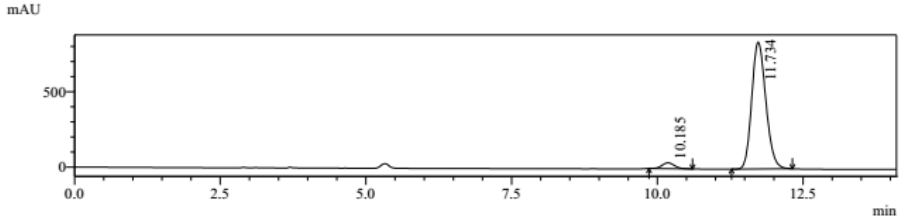
(*R*)-2-(4-Bromophenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroox azole (3m): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3m** as a colorless oil. 30.4 mg, 73% yield and 92% ee. $[\alpha]^{25}_D$ = -243.8 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.58 (m, 2H), 7.43 – 7.31 (m, 5H), 4.39 (d, *J* = 15.1 Hz, 1H), 4.26 (d, *J* = 15.1 Hz, 1H), 3.56 (d, *J* = 13.7 Hz, 1H), 3.46 (d, *J* = 13.7 Hz, 1H). δ 162.24, 142.06, 131.94, 130.71 (q, *J* = 306.3 Hz), 129.93, 129.07, 128.54, 126.61, 126.24, 124.66, 87.29, 66.91, 40.49. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.84. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}BrF_3NOS$ $[M+H]^+$: 415.9932, found: 415.9931. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 250 nm) t_1 = 11.7 min (major), t_2 = 10.2 min (minor).



Peak Table

PDA Ch1 250nm

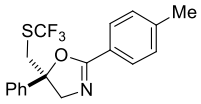
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.415	8134319	490267	49.833	57.481
2	13.367	8188679	362649	50.167	42.519
Total		16322997	852916	100.000	100.000



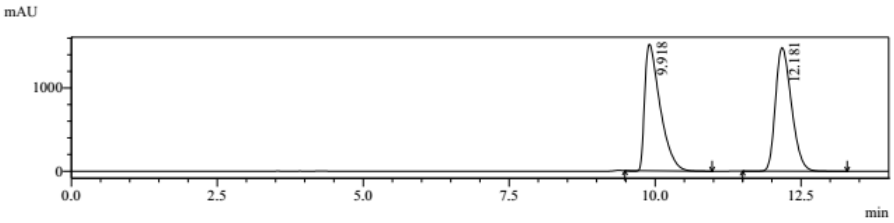
Peak Table

PDA Ch1 250nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.185	574805	37426	3.908	4.520
2	11.734	14134274	790675	96.092	95.480
Total		14709079	828101	100.000	100.000



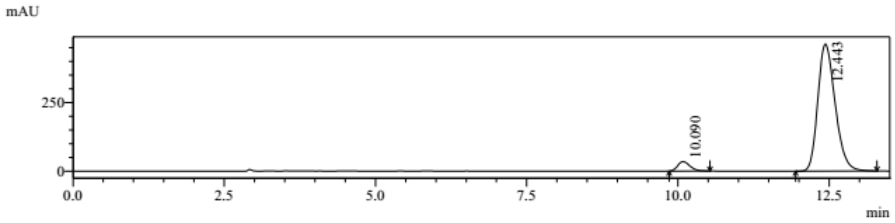
(*R*)-5-Phenyl-2-(p-tolyl)-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrooxazole (3n): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3n** as a colorless oil. 26.7 mg, 76% yield and 90% ee. $[\alpha]^{25}_D$ = -131.5 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 3.5 Hz, 4H), 7.35 – 7.33 (m, 1H), 7.27 (d, *J* = 7.3 Hz, 2H), 4.39 (d, *J* = 14.9 Hz, 1H), 4.25 (d, *J* = 14.9 Hz, 1H), 3.57 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.10, 142.33, 130.78 (q, *J* = 306.6 Hz), 129.35, 129.01, 128.40, 124.74, 124.51, 86.81, 66.91, 40.50, 21.76. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.92. HR-ESI-MS m/z calcd. for $C_{18}H_{17}F_3NOS$ $[M+H]^+$: 352.0977, found: 352.0986. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 246 nm) t_1 = 12.4 min (minor), t_2 = 10.1 min (major).



Peak Table

PDA Ch1 246nm

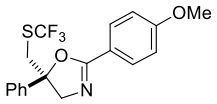
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.918	27853152	1487831	49.607	51.332
2	12.181	28294780	1410614	50.393	48.668
Total		56147933	2898446	100.000	100.000



Peak Table

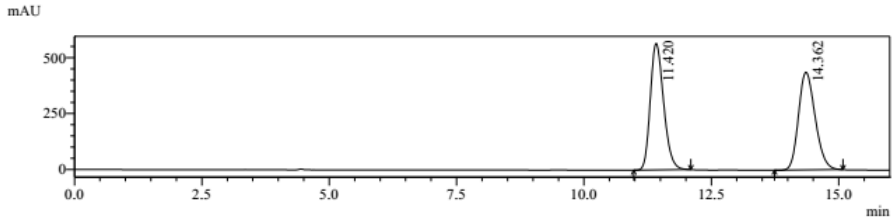
PDA Ch1 246nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.090	481673	31219	4.956	6.395
2	12.443	9237094	456972	95.044	93.605
Total		9718767	488191	100.000	100.000



(*R*)-2-(4-Methoxyphenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydro oxazole (3o): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3o**

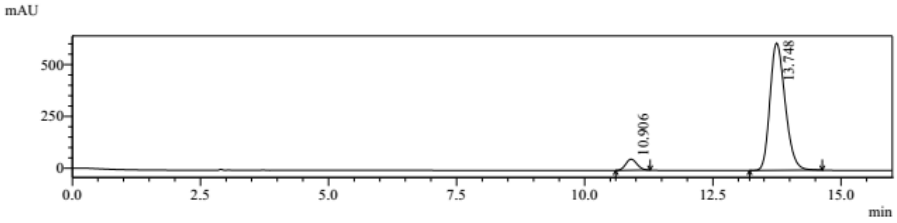
as a colorless oil. 24.9 mg, 68% yield and 88% ee. $[\alpha]^{25}_{D}$ = -128.4 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.39 (s, 4H), 7.35 – 7.33 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.37 (d, *J* = 14.8 Hz, 1H), 4.24 (d, *J* = 14.8 Hz, 1H), 3.86 (s, 3H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.48 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.83, 162.53, 142.35, 130.80 (q, *J* = 306.3 Hz), 130.19, 128.99, 128.39, 124.74, 119.77, 114.01, 86.79, 66.90, 55.54, 40.48. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.91. HR-ESI-MS *m/z* calcd. for $C_{18}H_{17}O_2NF_3S$ $[M+H]^+$: 368.0927, found: 368.0920. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 258 nm) t_1 = 13.7 min (minor), t_2 = 10.9 min (major).



Peak Table

PDA Ch1 258nm

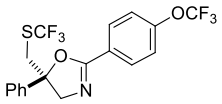
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.420	10280411	541572	50.847	55.859
2	14.362	9937740	427966	49.153	44.141
Total		20218150	969539	100.000	100.000



Peak Table

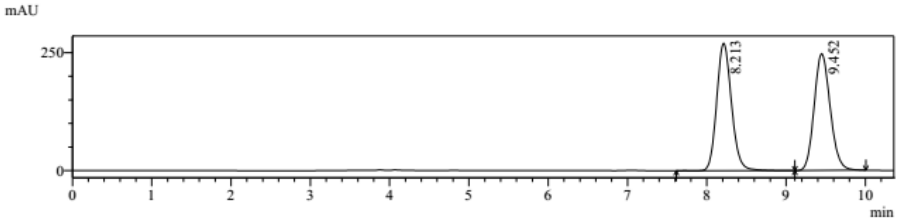
PDA Ch1 258nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.906	815053	49016	6.032	7.704
2	13.748	12697523	587190	93.968	92.296
Total		13512576	636206	100.000	100.000



(*R*)-5-Phenyl-2-(4-(trifluoromethoxy)phenyl)-5-(((trifluoromethyl)thio)methyl)-4, 5-dihydrooxazole (3p): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3p** as a colorless oil. 30.3 mg, 72% yield and 92% ee. $[\alpha]^{25}_{D}$ = -114.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 7.44 – 7.32 (m, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.41 (d, *J* = 15.1 Hz, 1H), 4.28 (d, *J* = 15.1 Hz, 1H), 3.57 (d, *J* = 13.7 Hz, 1H), 3.47 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 151.84, 142.07, 130.73 (q, *J* = 306.6 Hz), 130.26, 129.11, 128.58, 125.86, 124.67,

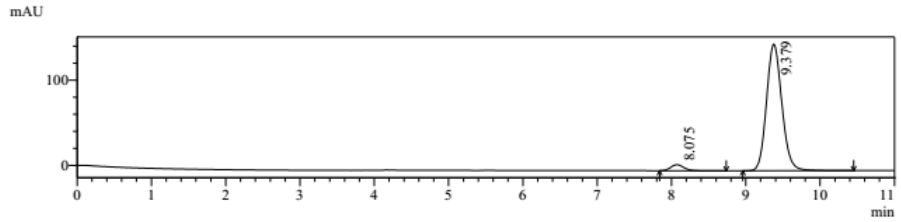
120.78, 120.51 (q, J = 258.2 Hz), 87.38, 66.95, 40.51. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.86, -57.68. HR-ESI-MS *m/z* calcd. for $C_{18}H_{14}NO_2F_6S$ $[M+H]^+$: 422.0644, Found: 422.0652. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 242 nm) t_1 = 9.4 min (major), t_2 = 8.1 min (minor).



Peak Table

PDA Ch1 242nm

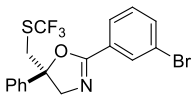
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.213	3513012	243782	50.188	50.298
2	9.452	3486755	240898	49.812	49.702
Total		6999767	484680	100.000	100.000



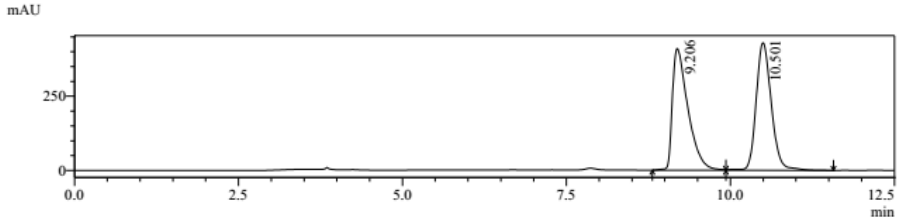
Peak Table

PDA Ch1 242nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.075	86265	6242	3.886	4.132
2	9.379	2133840	144822	96.114	95.868
Total		2220104	151064	100.000	100.000



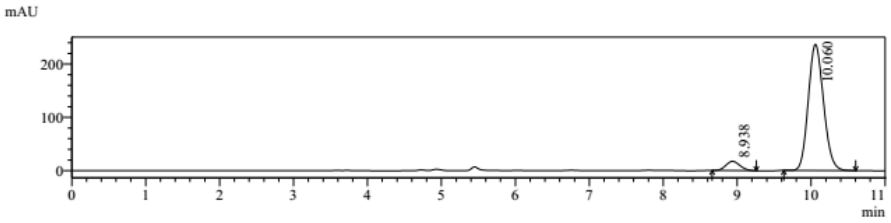
(*R*)-2-(3-Bromophenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydroox azole (3q): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3q** as a colorless oil. 31.7 mg, 76% yield and 87% ee. $[\alpha]^{25}_D$ = -63.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.43 – 7.31 (m, 6H), 4.41 (d, J = 15.2 Hz, 1H), 4.28 (d, J = 15.2 Hz, 1H), 3.57 (d, J = 13.7 Hz, 1H), 3.46 (d, J = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.69, 142.01, 134.81, 131.37, 130.71 (q, J = 306.3 Hz), 130.20, 29.18, 129.09, 128.57, 126.99, 124.66, 122.69, 87.39, 66.79, 40.50. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.85. HR-ESI-MS *m/z* calcd. for $C_{17}H_{14}BrF_3NOS$ $[M+H]^+$: 415.9926, found: 415.9936. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 242 nm) t_1 = 10.1 min (minor), t_2 = 8.9 min (major).



Peak Table

PDA Ch1 242nm

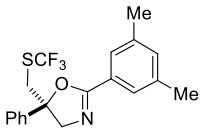
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.206	6799470	382727	49.574	47.670
2	10.501	6916253	420145	50.426	52.330
Total		13715723	802872	100.000	100.000



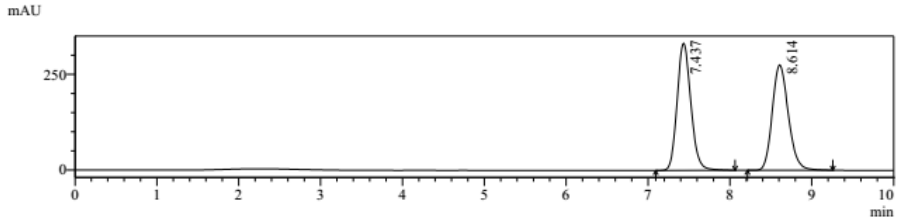
Peak Table

PDA Ch1 242nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.938	228122	16731	6.295	6.803
2	10.060	3395577	229188	93.705	93.197
Total		3623698	245919	100.000	100.000



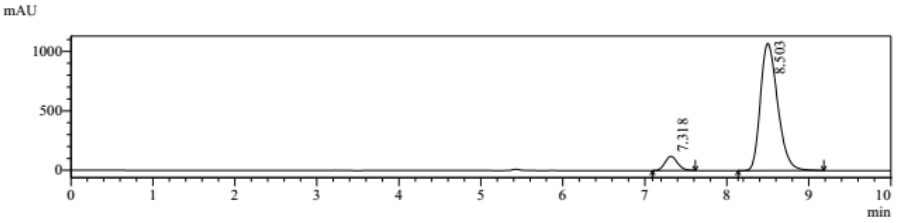
(*R*)-2-(3,5-Dimethylphenyl)-5-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihyd rooxazole (3r): Prepared by general method and purified by flash silica gel column chromatography (eluent: PE/EtOAc = 20:1 to 10:1 with 0.3% Et_3N, v/v) to afford **3r** as a colorless oil. 23.7 mg, 65% yield and 85% ee. $[\alpha]^{25}_D$ = -114.7 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.43 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 7.16 (s, 1H), 4.39 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.36, 142.36, 138.31, 133.57, 130.08 (q, *J* = 306.2 Hz), 129.02, 127.06, 126.15, 124.74, 86.85, 66.80, 40.46, 21.34. ^{19}F NMR (377 MHz, $CDCl_3$) δ -40.95. HR-ESI-MS *m/z* calcd. for $C_{19}H_{19}F_3NOS$ $[M+H]^+$: 366.1134, found: 366.1131. HPLC (Daicel Chiralpak OD-H column, *i*-PrOH/hexane = 1/99, 1 mL/min, 245 nm) t_1 = 8.5 min (minor), t_2 = 7.3 min (major).



Peak Table

PDA Ch1 245nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.437	3869812	319327	50.669	55.011
2	8.614	3767683	261147	49.331	44.989
Total		7637494	580474	100.000	100.000

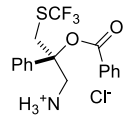


Peak Table

PDA Ch1 245nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.318	1262653	101984	7.464	9.116
2	8.503	15654151	1016763	92.536	90.884
Total		16916804	1118747	100.000	100.000

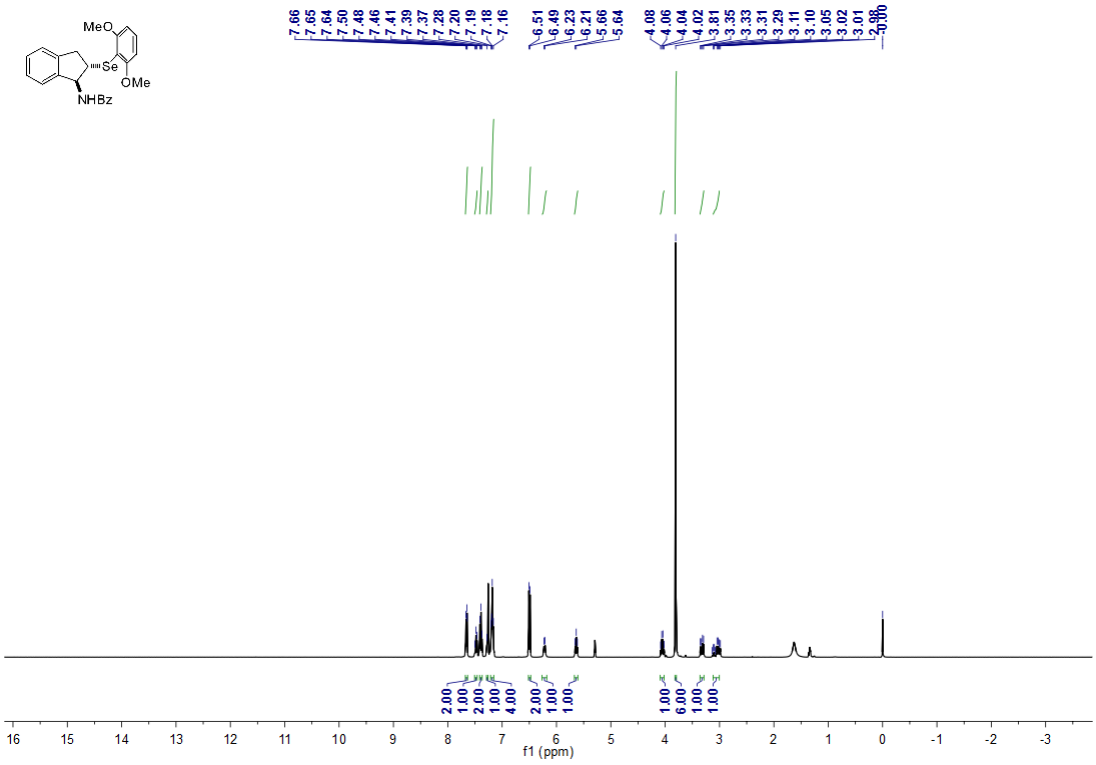
2.4 Transformation of the products

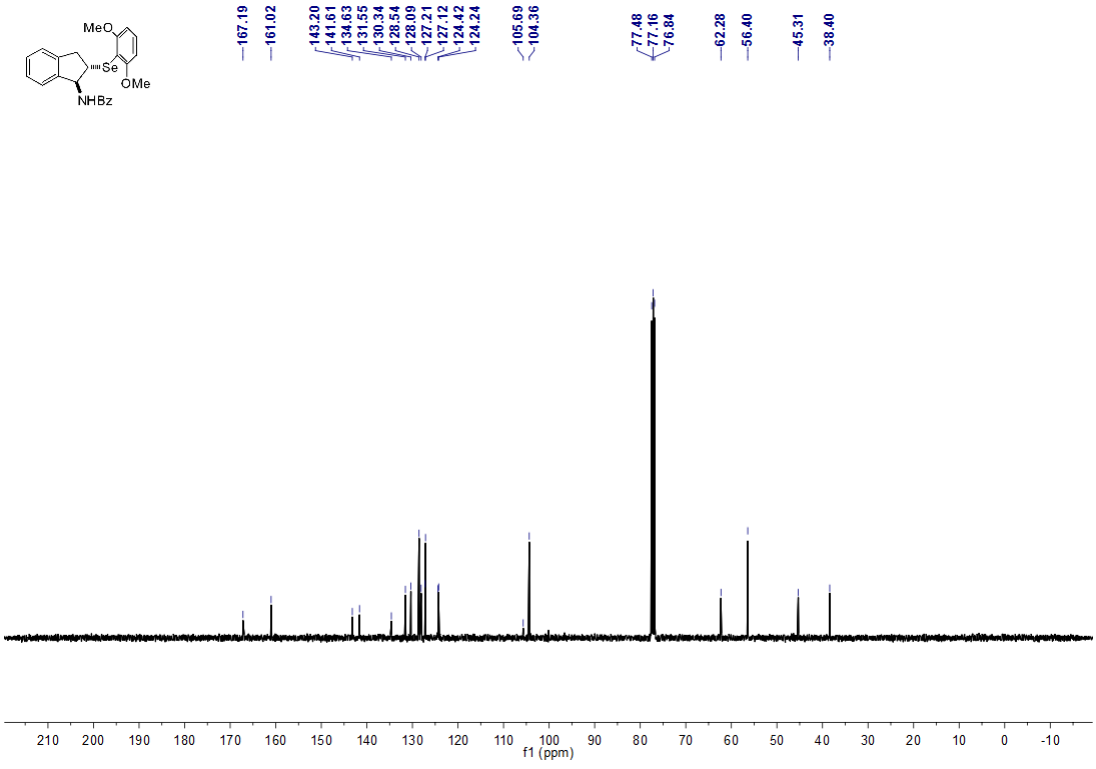


(*R*)-1-Amino-2-phenyl-3-((trifluoromethyl)thio)propan-2-yl benzoate hydrochloride ((*R*)-4): Prepared according to the literature.[5] The residue was recrystallized from hexane/CH_2Cl_2 to afford (*R*)-4. 16.6 mg, 85% yield. $[\alpha]^{25}_D$ = -78.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 3H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (m, 2H), 7.38 (m, 5H), 3.98 (s, 2H), 3.86 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.11, 136.05, 134.20, 130.69 (q, *J* = 306.4 Hz), 130.49, 129.64, 129.50, 129.19, 128.80, 125.50, 82.95, 46.52, 37.75. HR-ESI-MS m/z calcd. for $C_{17}H_{17}F_3NO_2S$ $[M]^+$: 356.0927, found: 356. 0927.

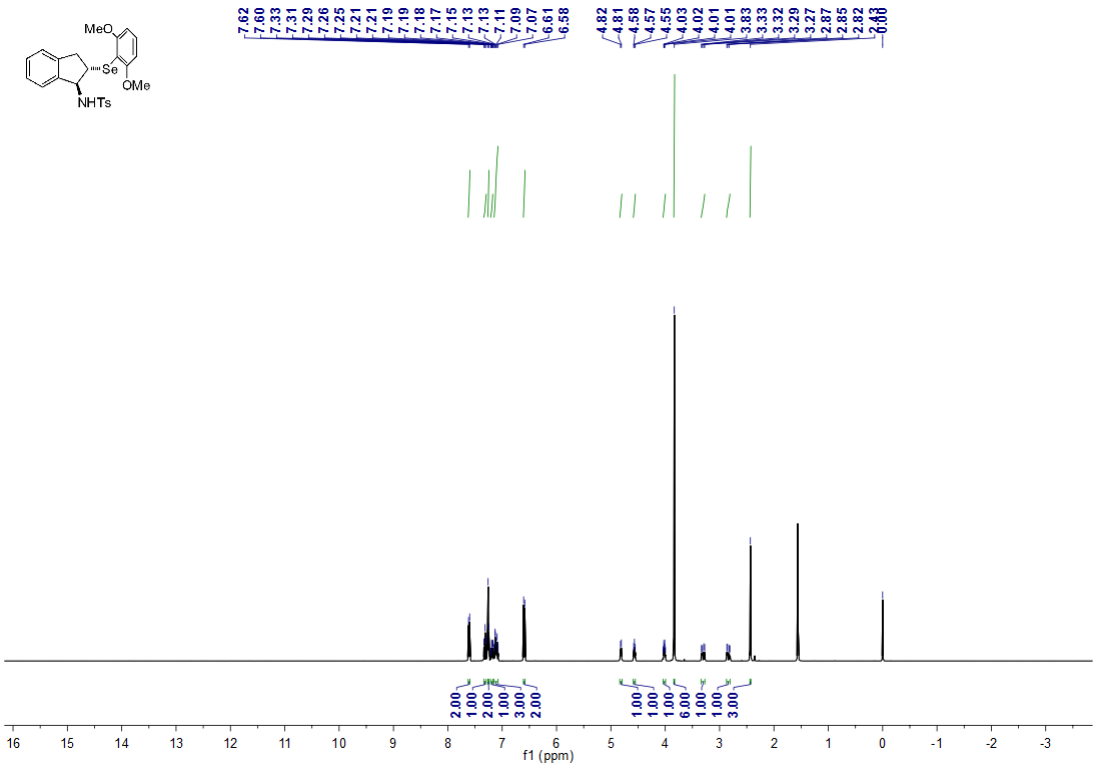
3. NMR spectra for new compounds

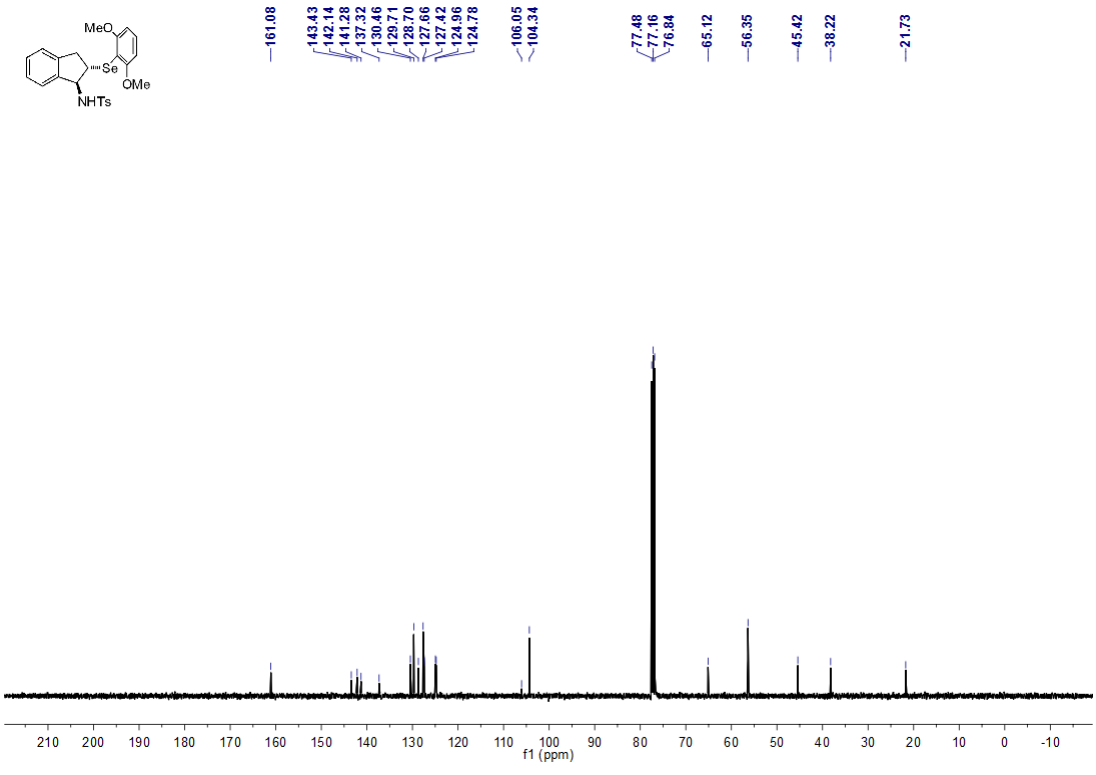
NMR spectra of compound **C11** in $CDCl_3$



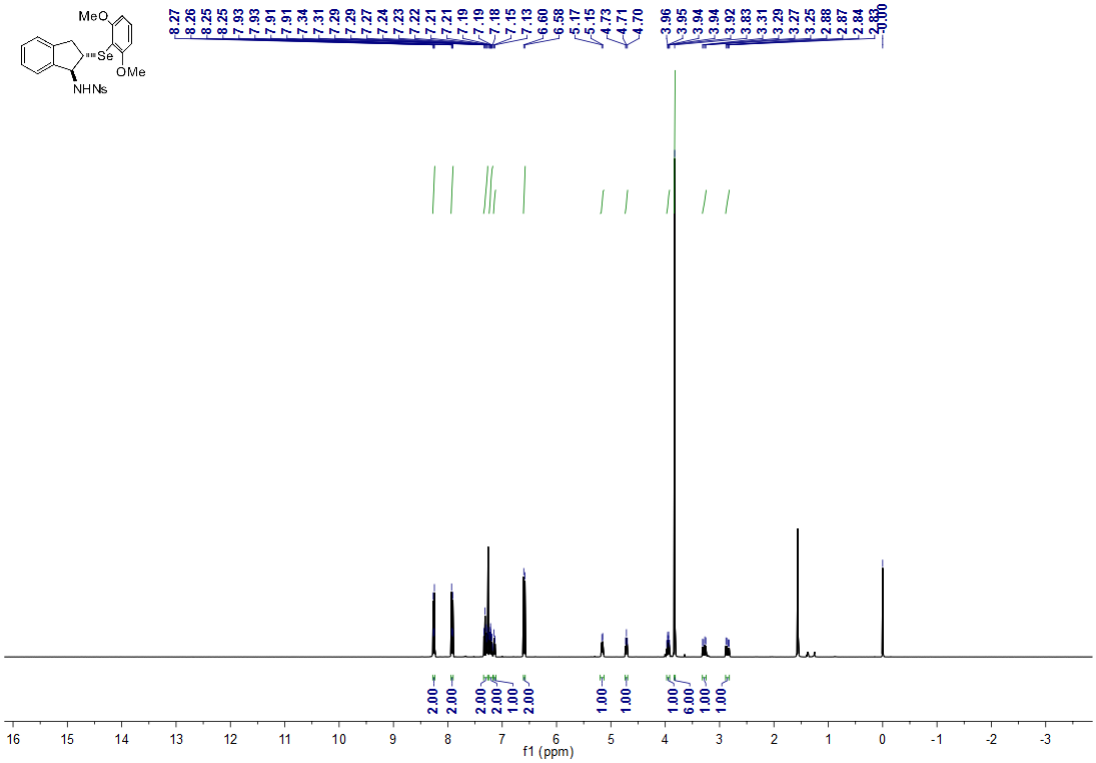


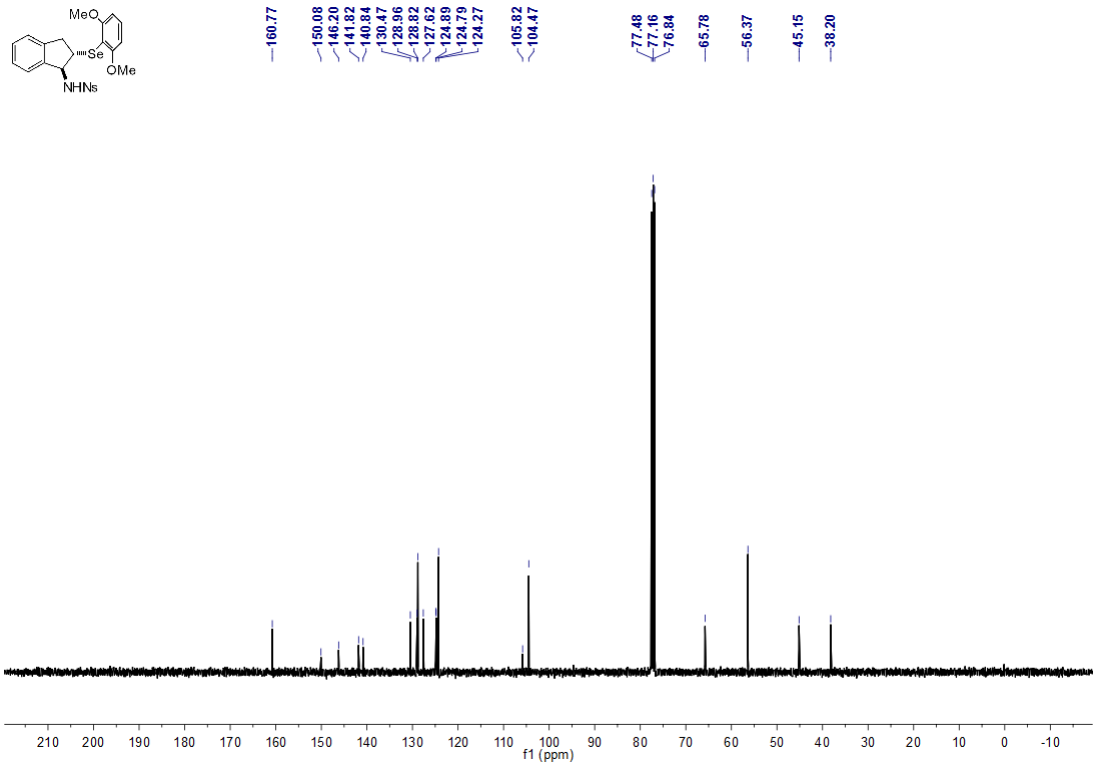
NMR spectra of compound **C12** in $CDCl_3$



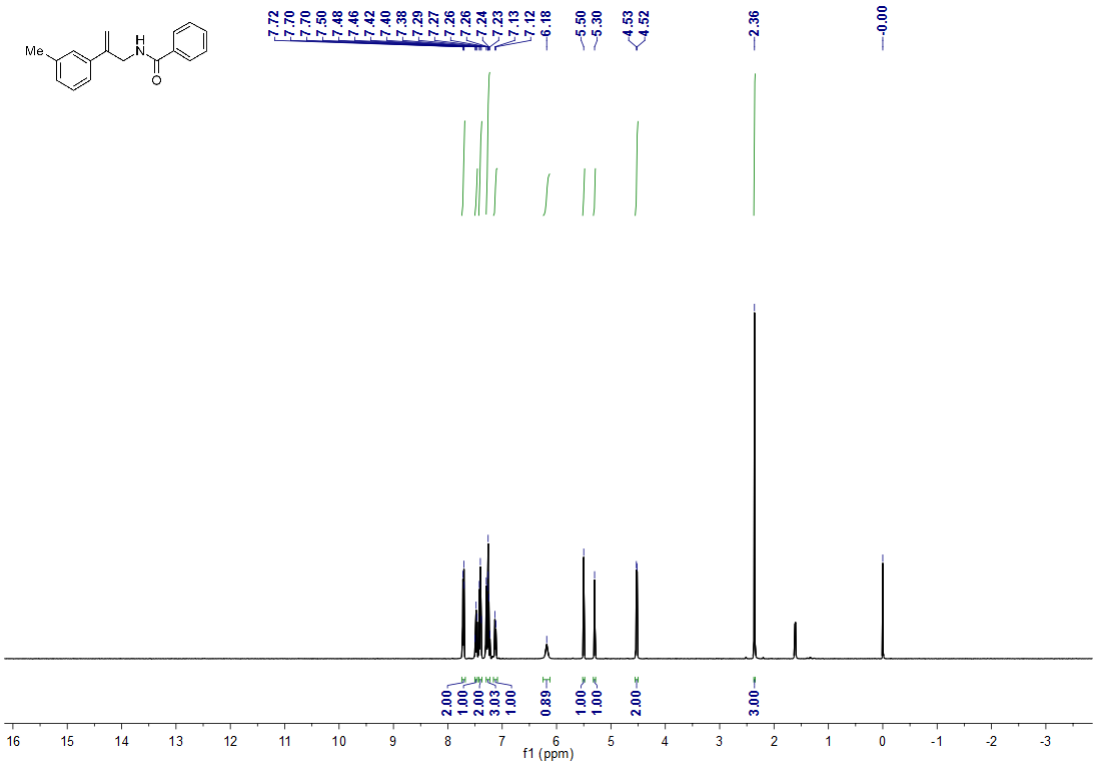


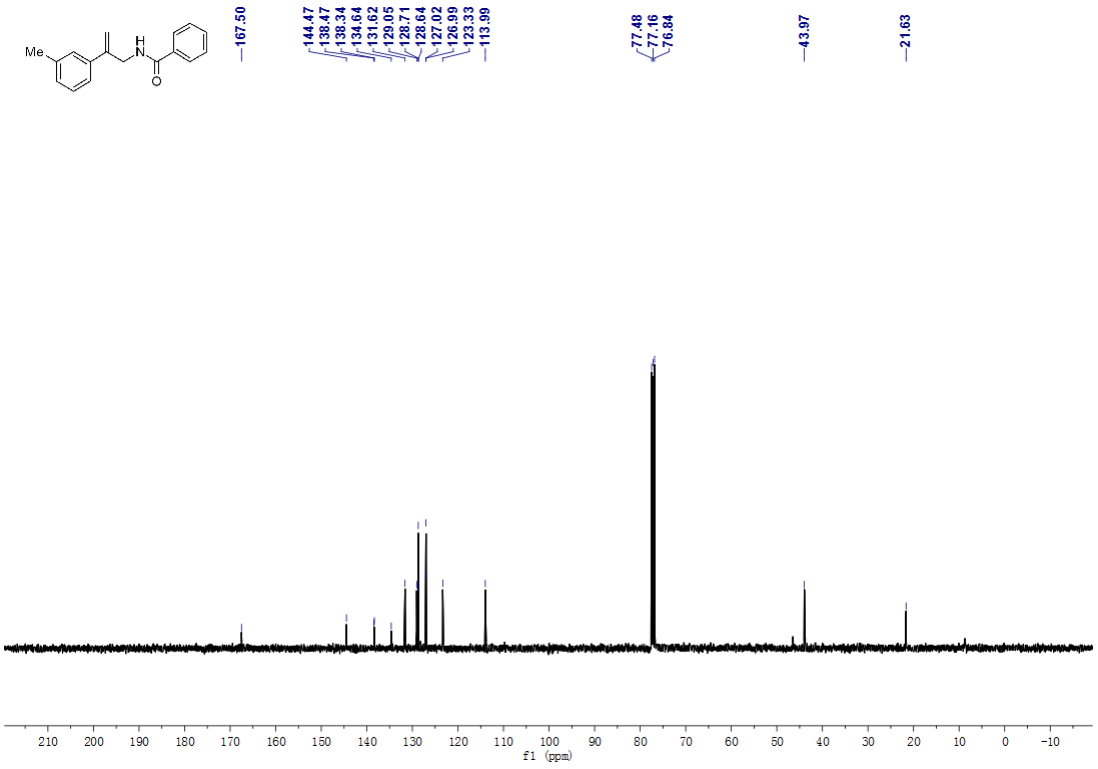
NMR spectra of compound **C13** in $CDCl_3$



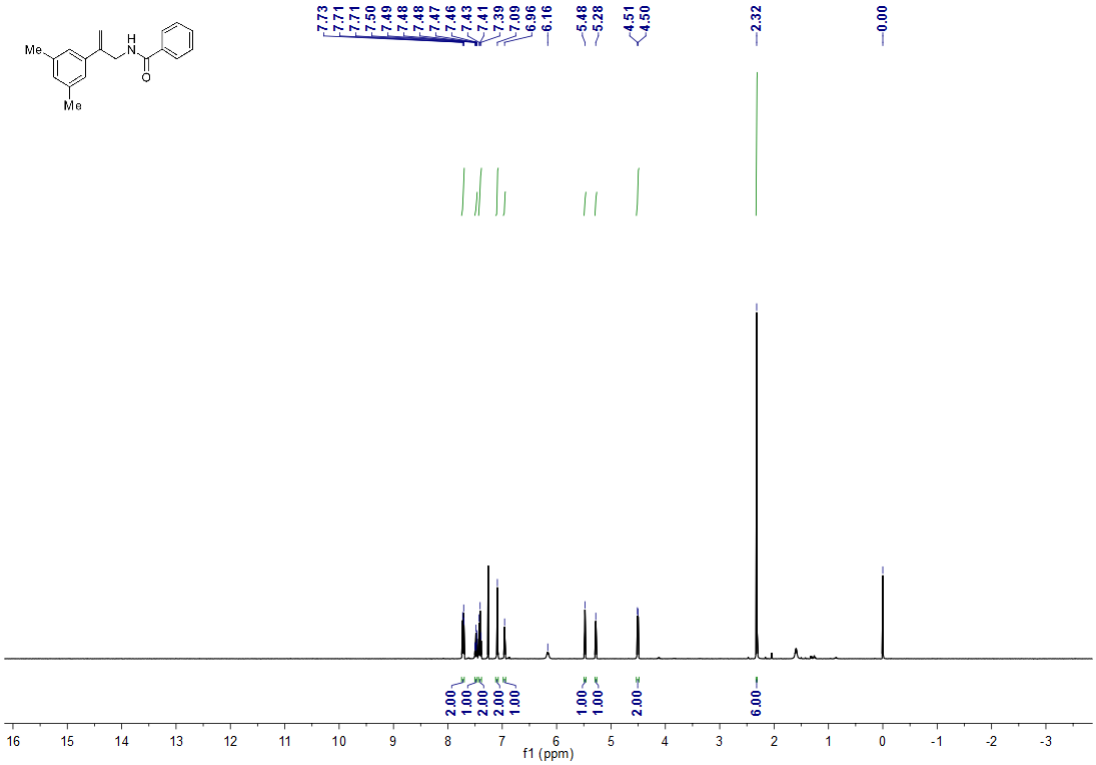


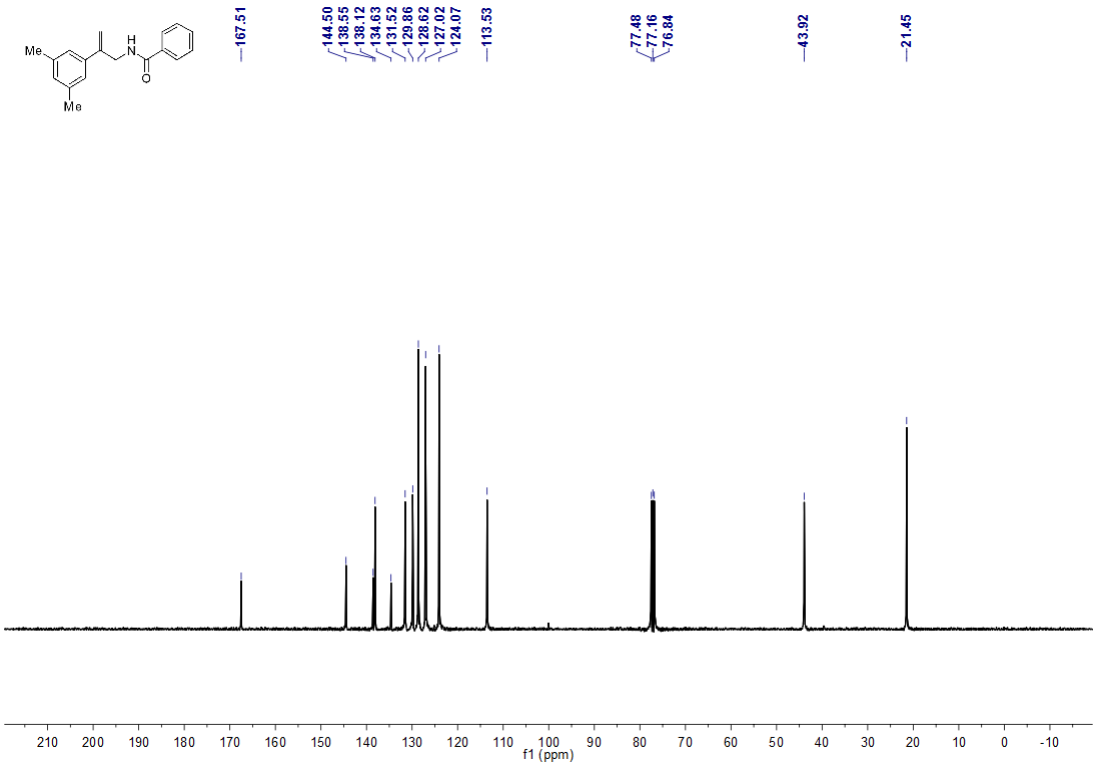
NMR spectra of compound **1f** in $CDCl_3$



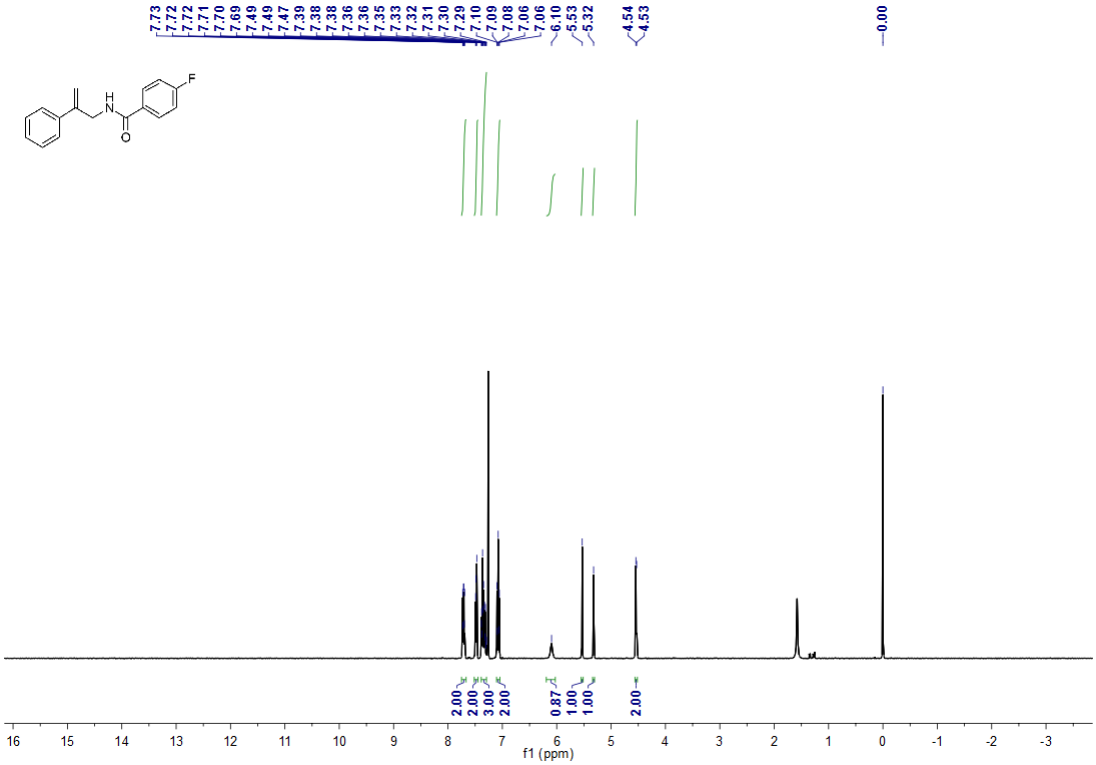


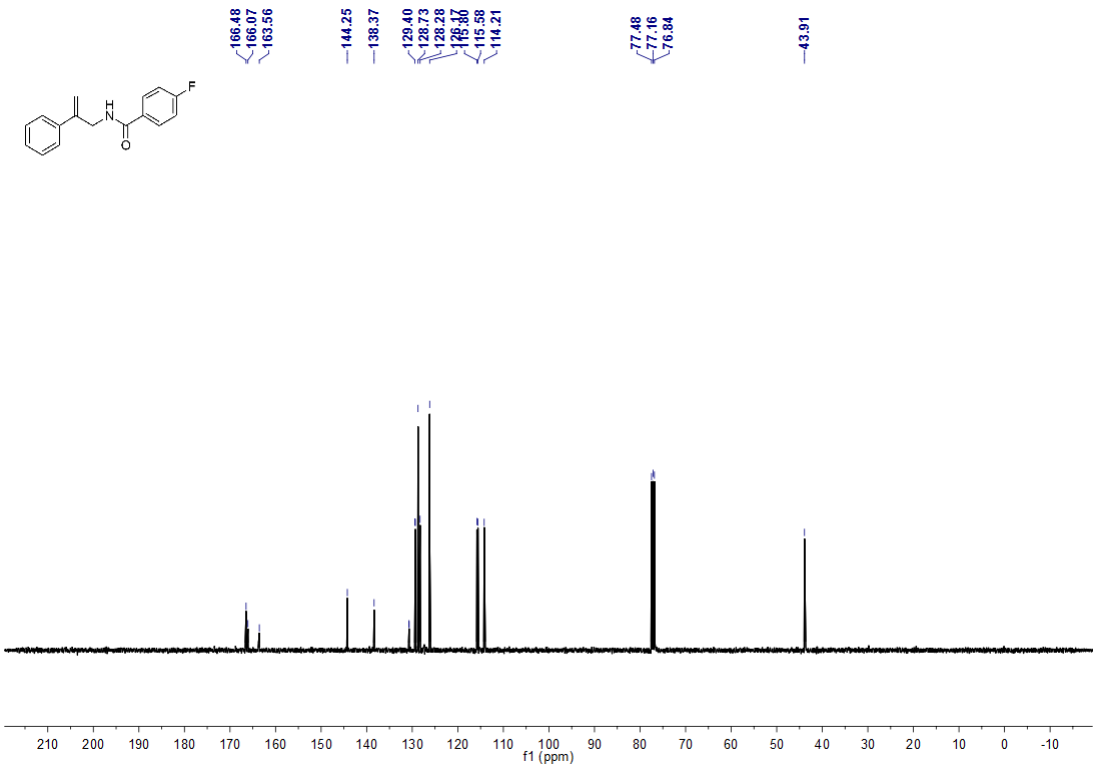
NMR spectra of compound **1i** in $CDCl_3$



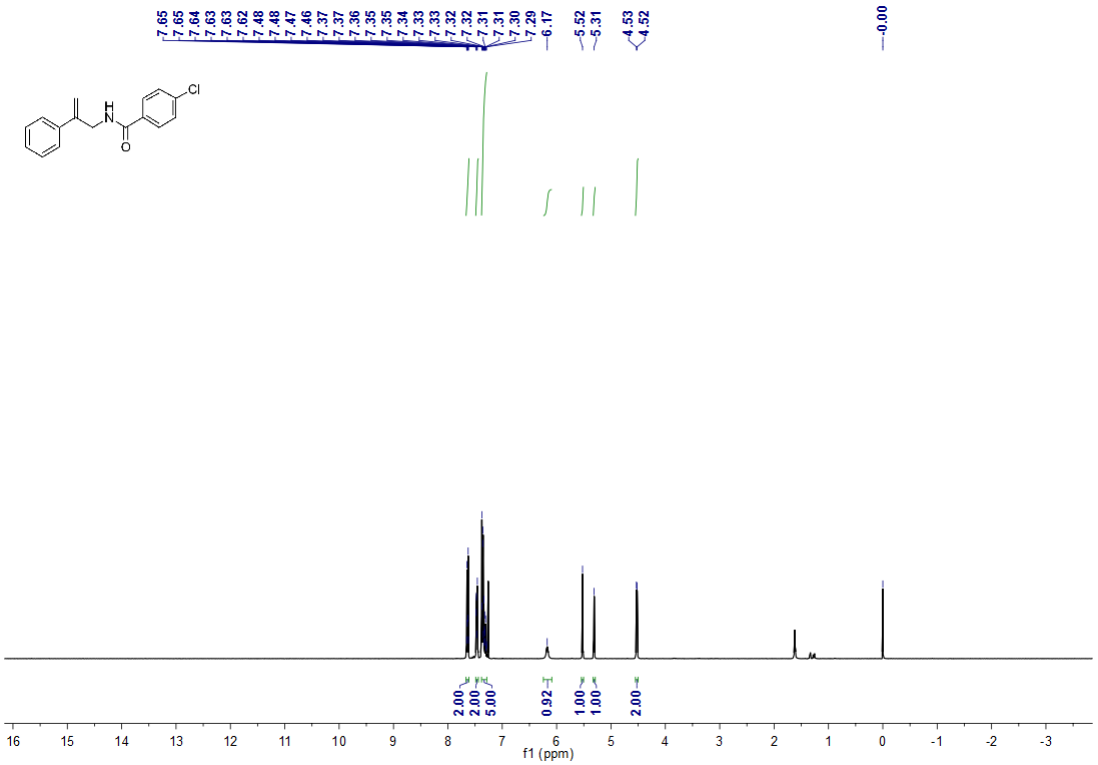


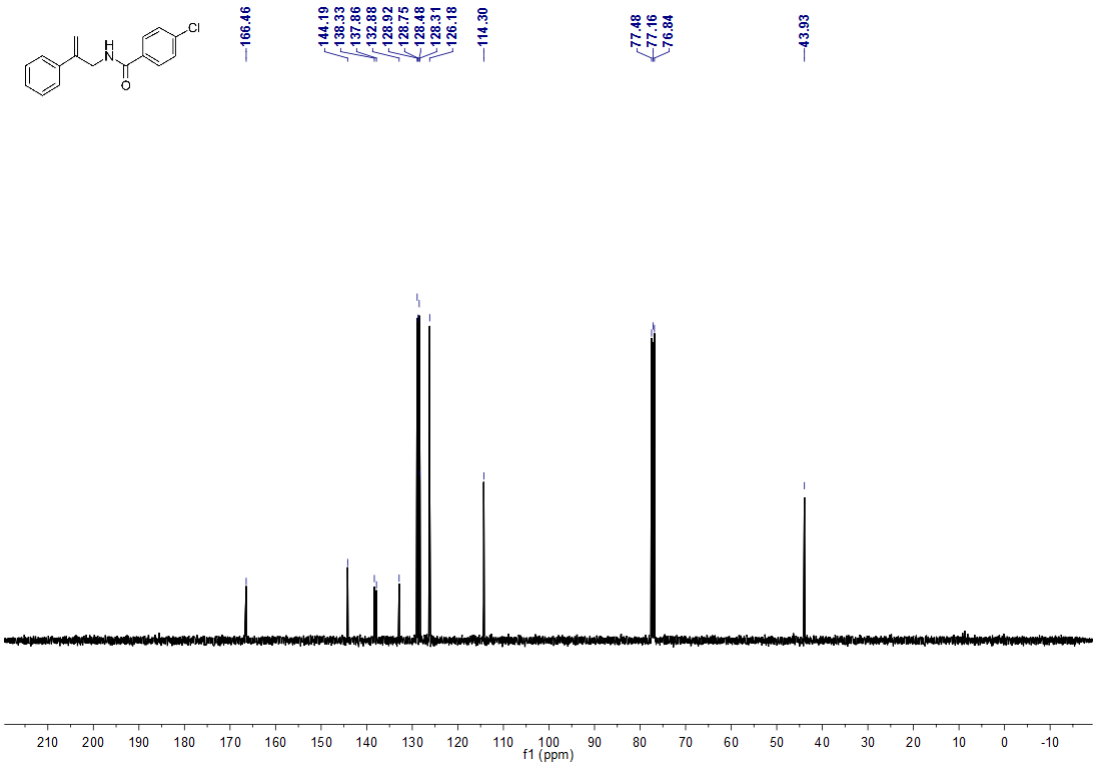
NMR spectra of compound **1k** in $CDCl_3$



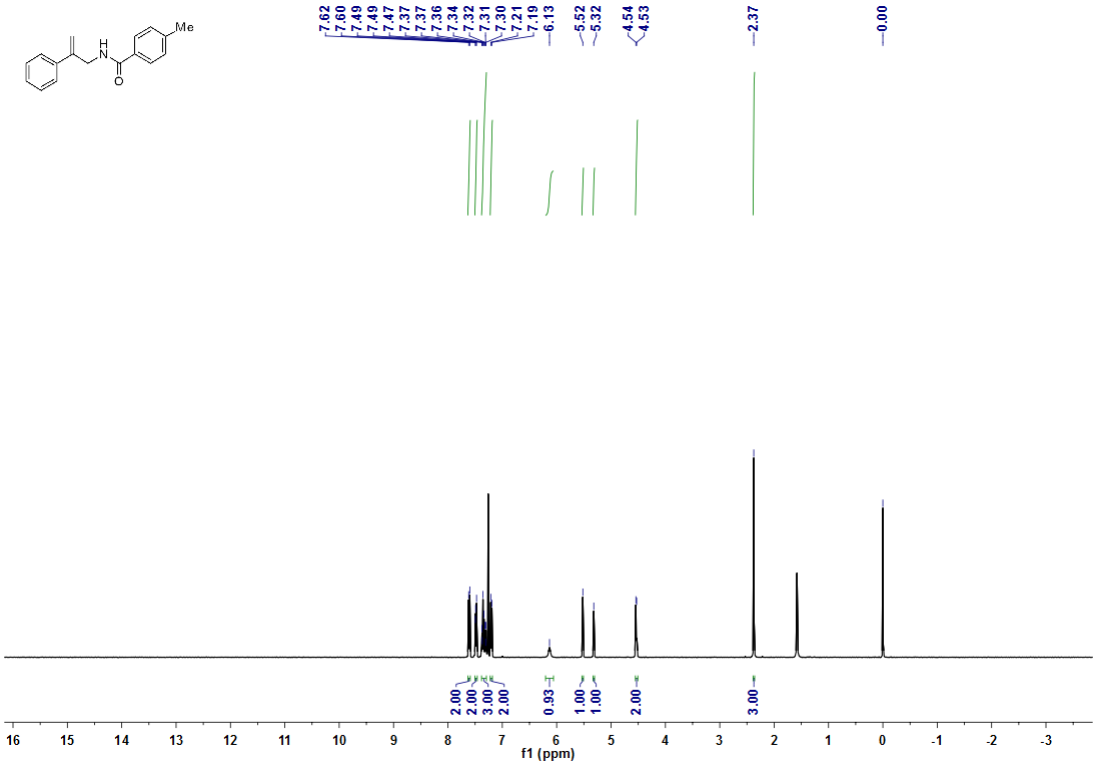


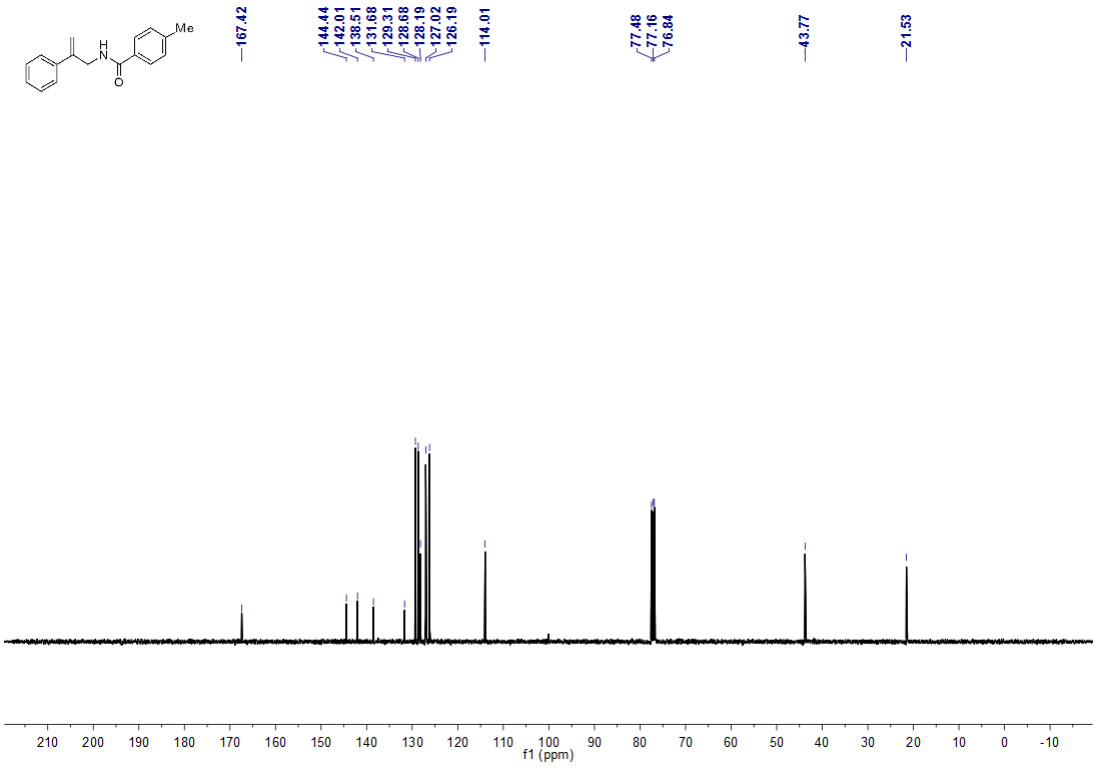
NMR spectra of compound **1l** in $CDCl_3$



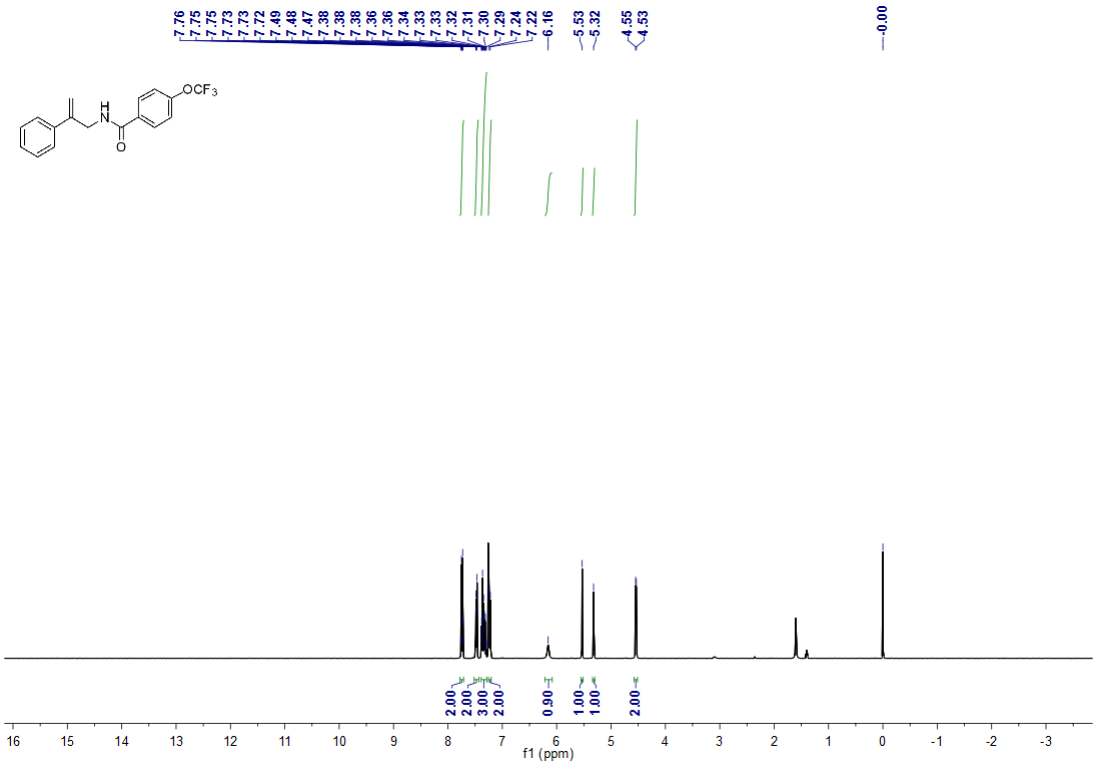


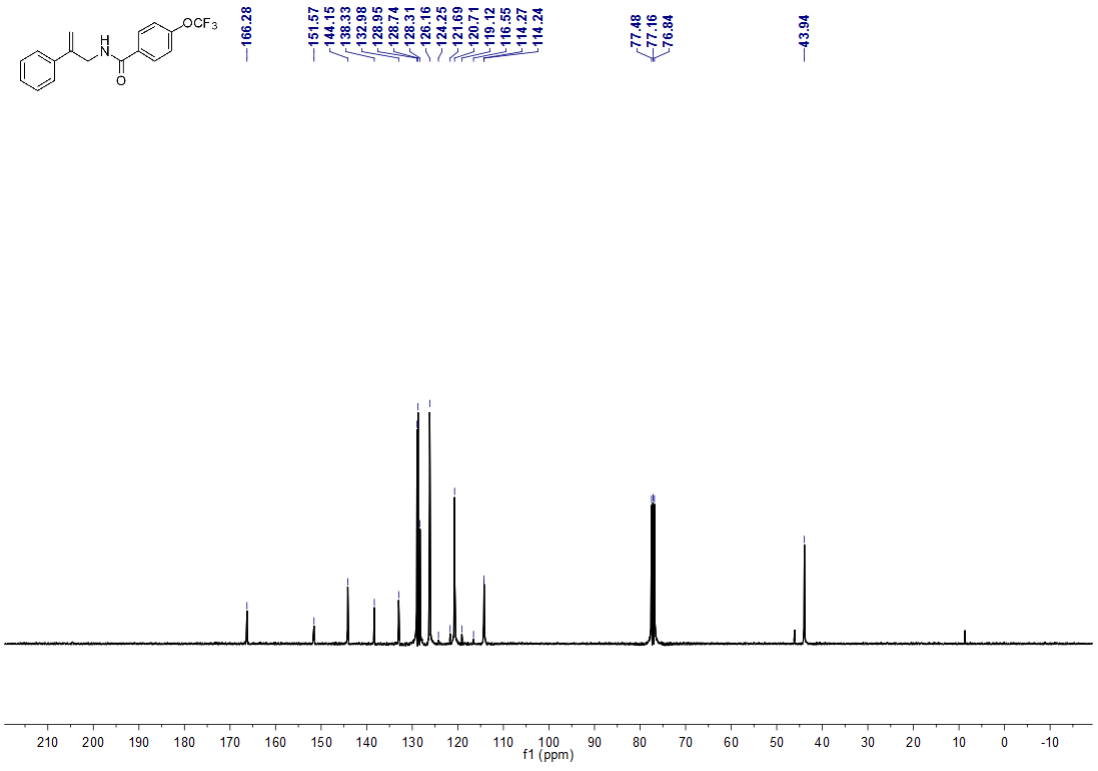
NMR spectra of compound **1n** in $CDCl_3$



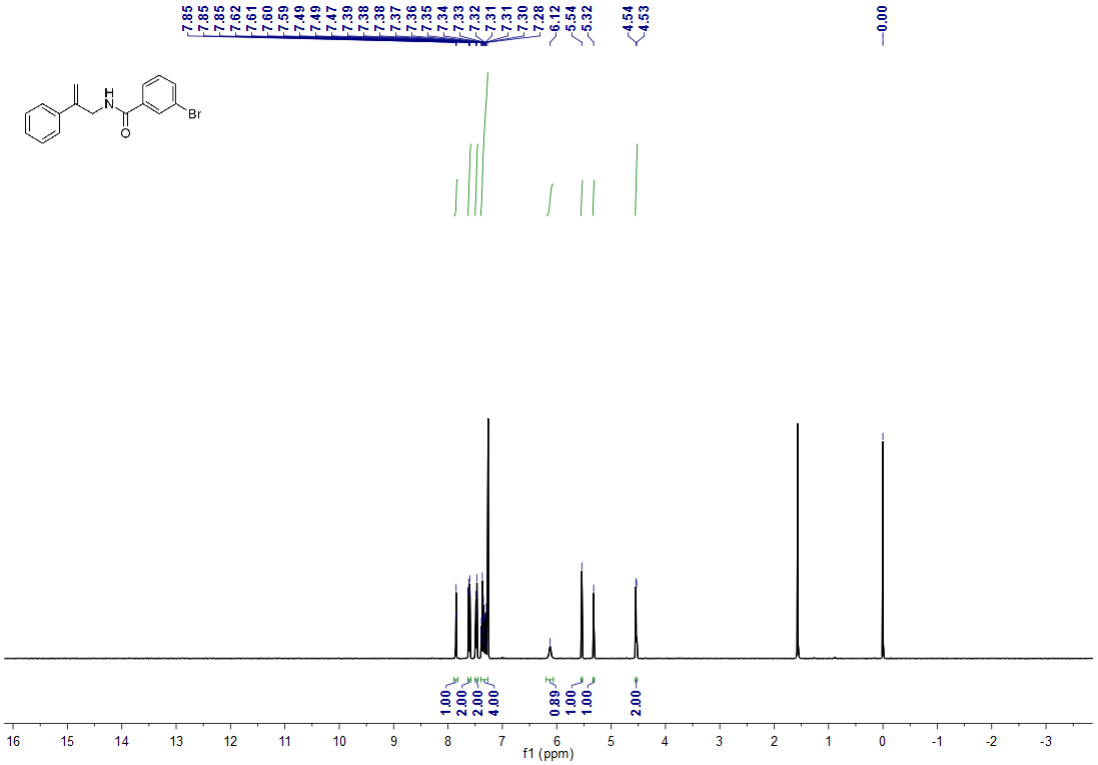


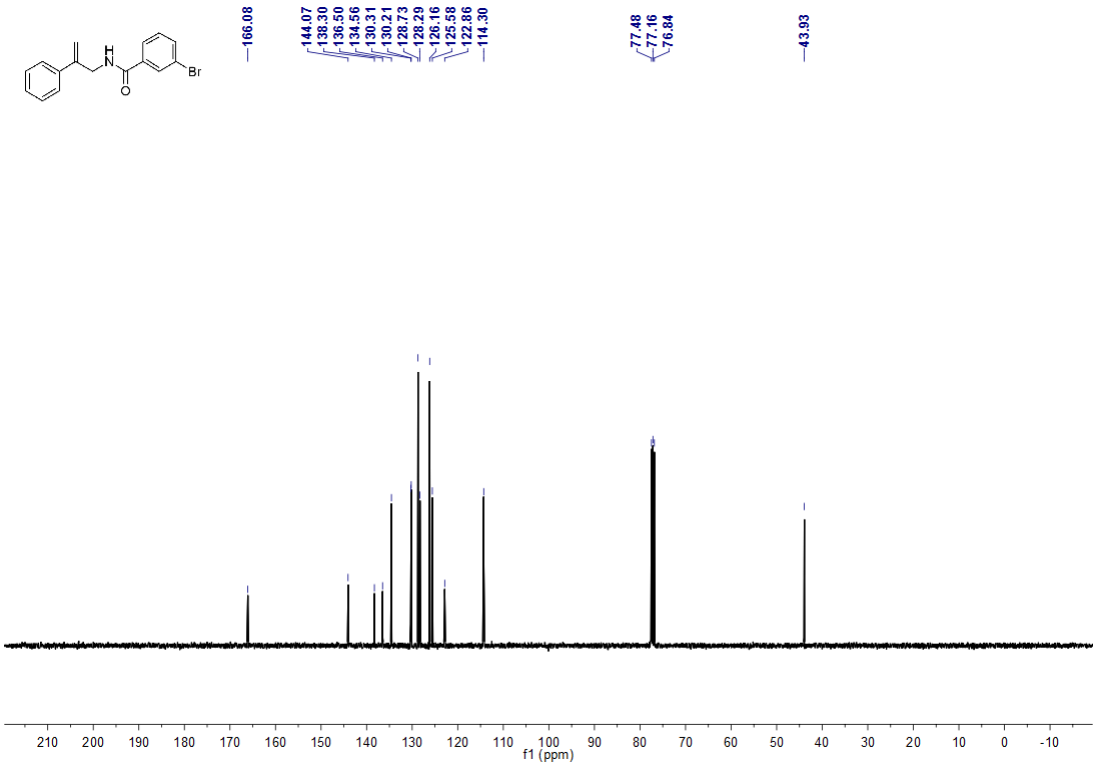
NMR spectra of compound **1p** in $CDCl_3$



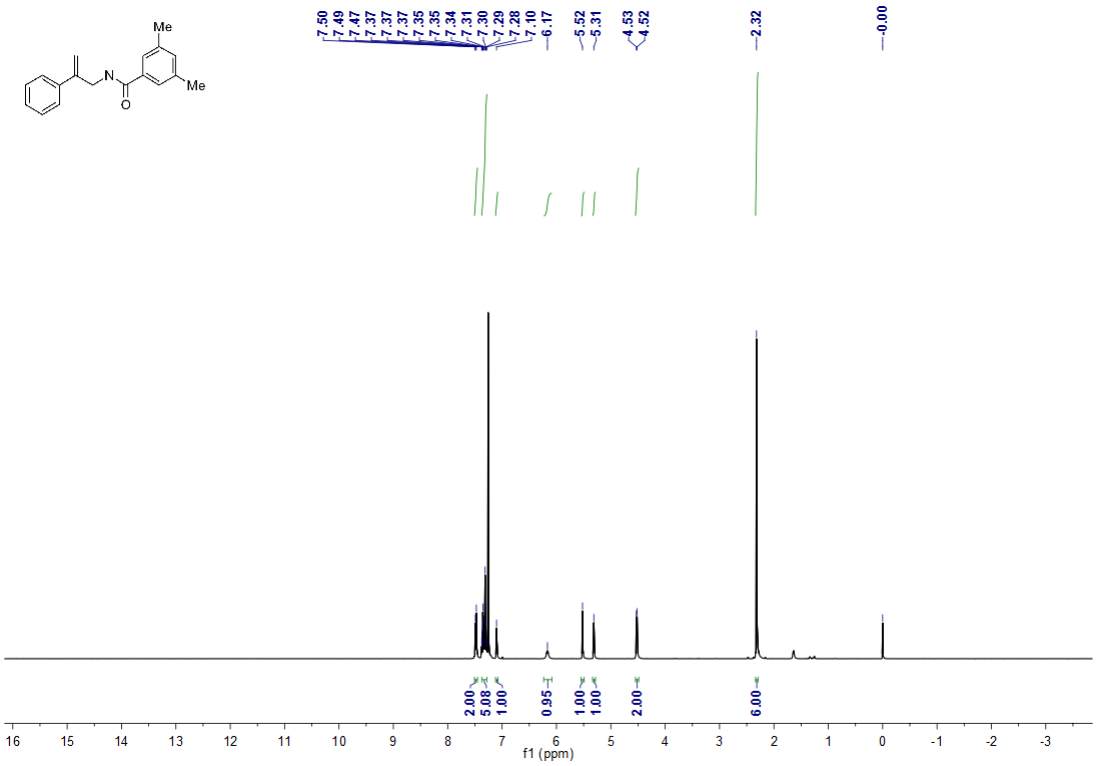


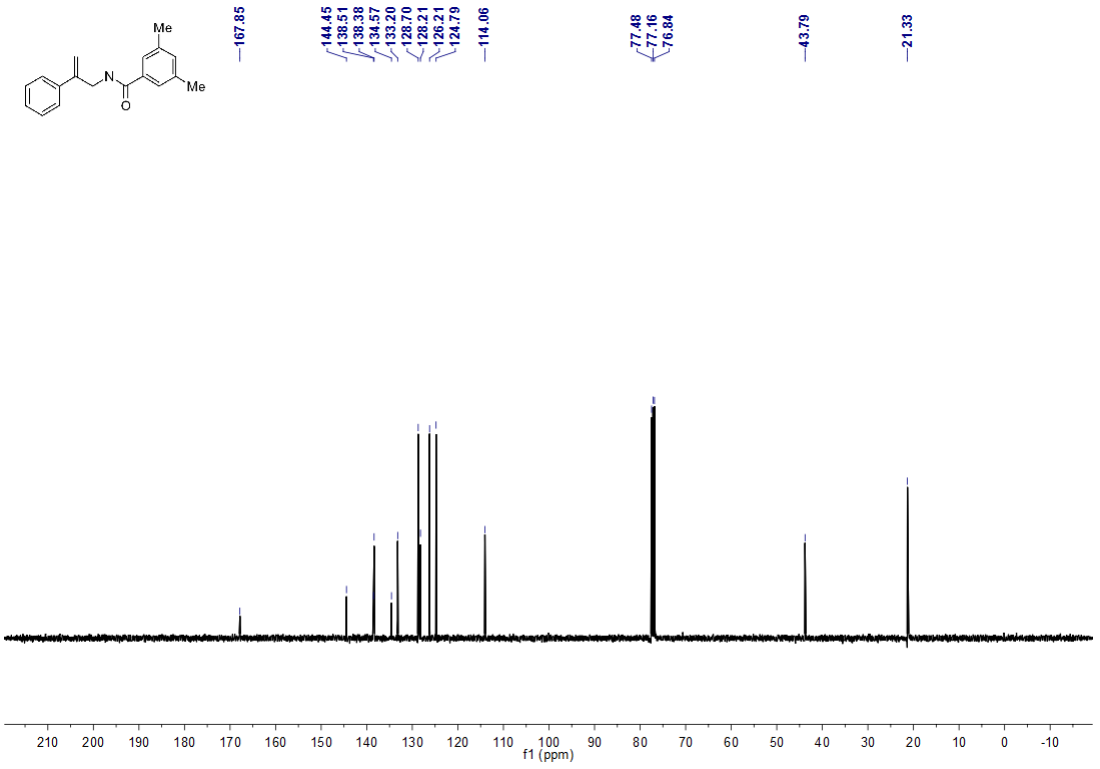
NMR spectra of compound **1q** in $CDCl_3$



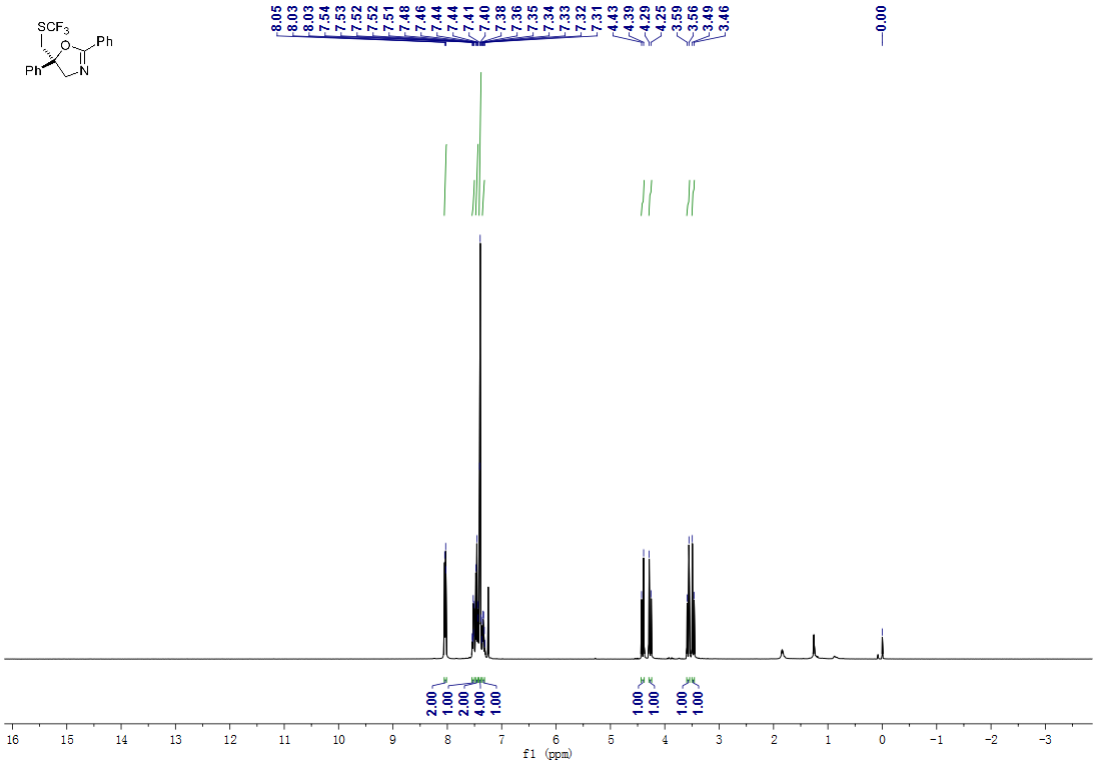


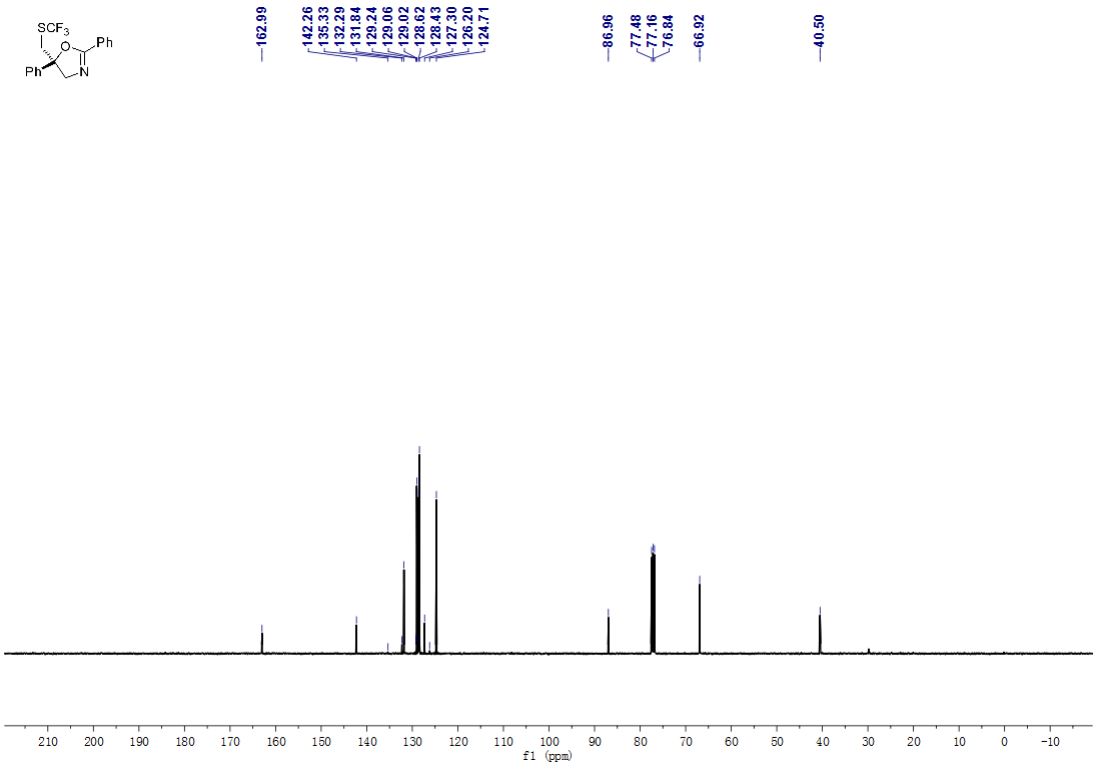
NMR spectra of compound **1r** in $CDCl_3$



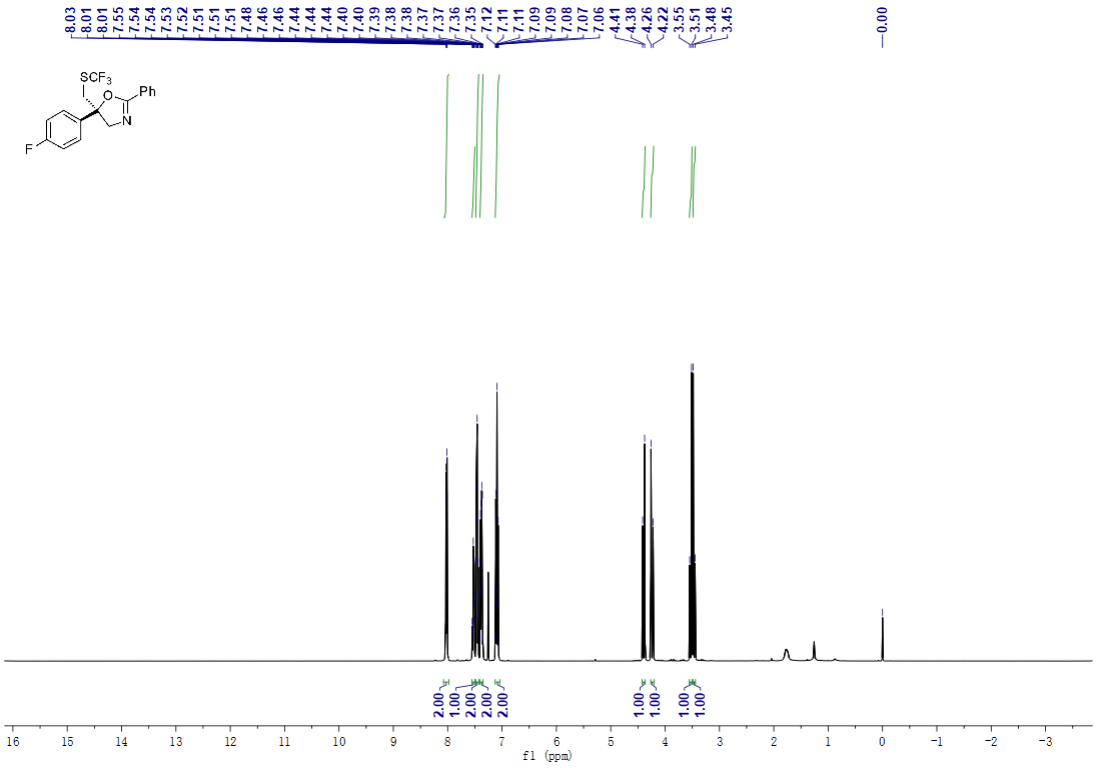


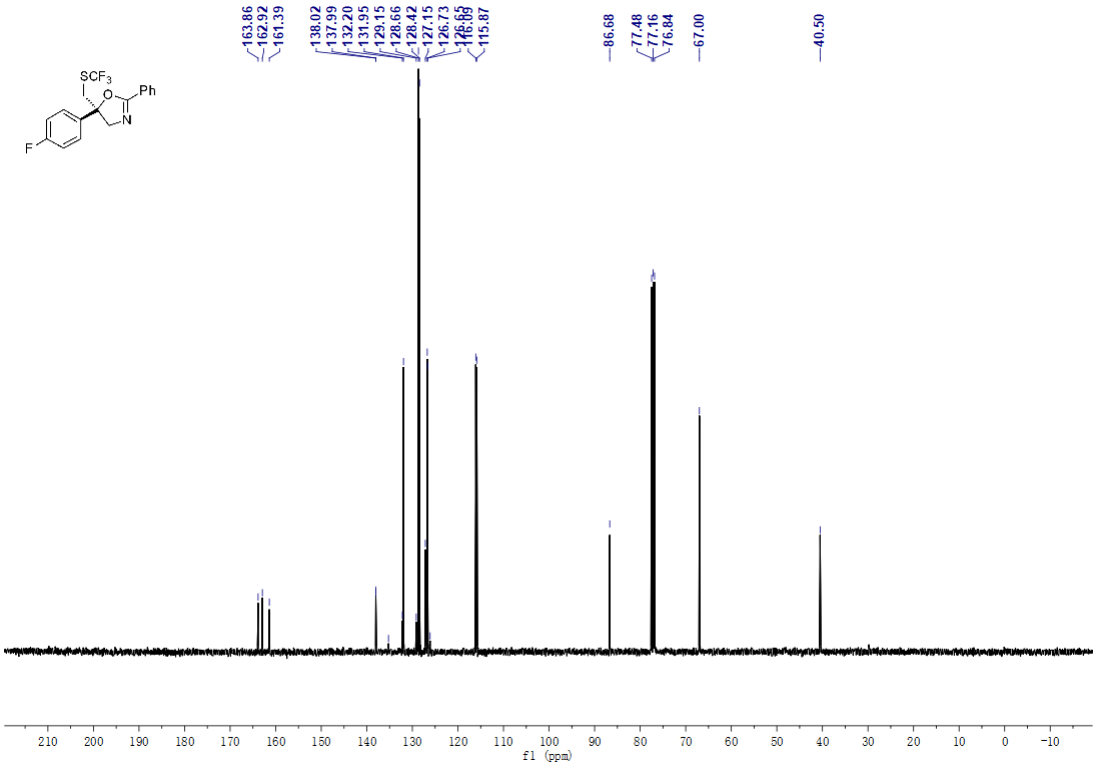
NMR spectra of compound **3a** in $CDCl_3$



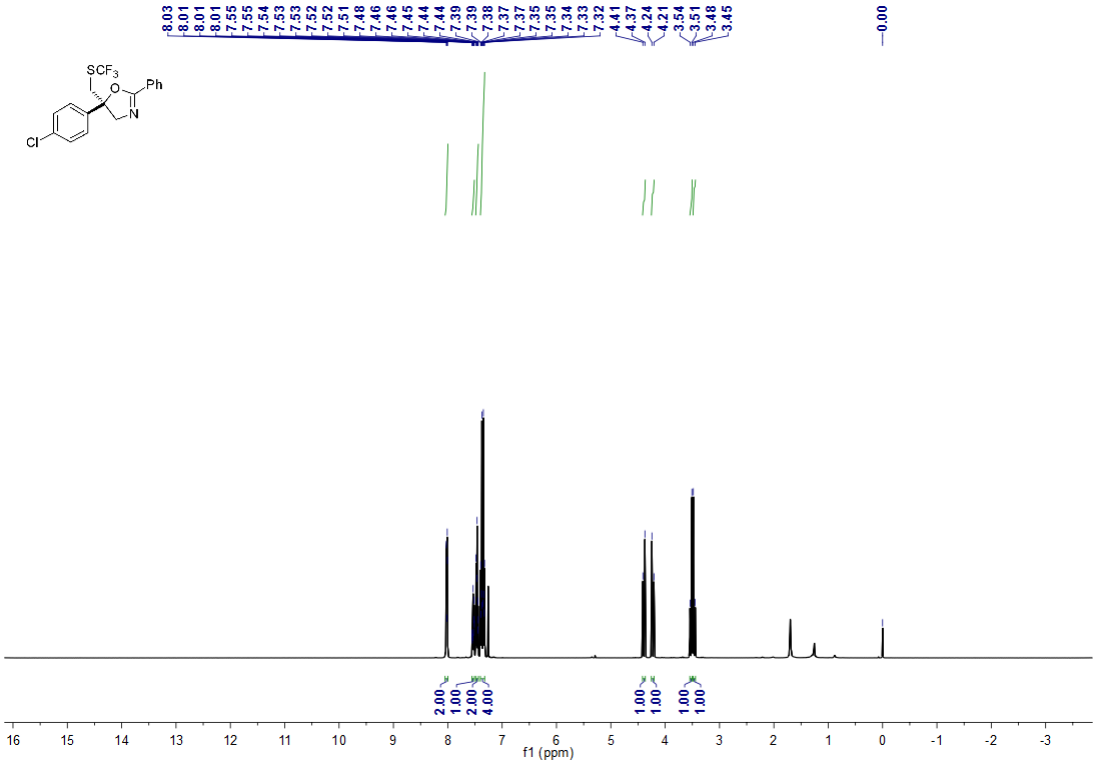


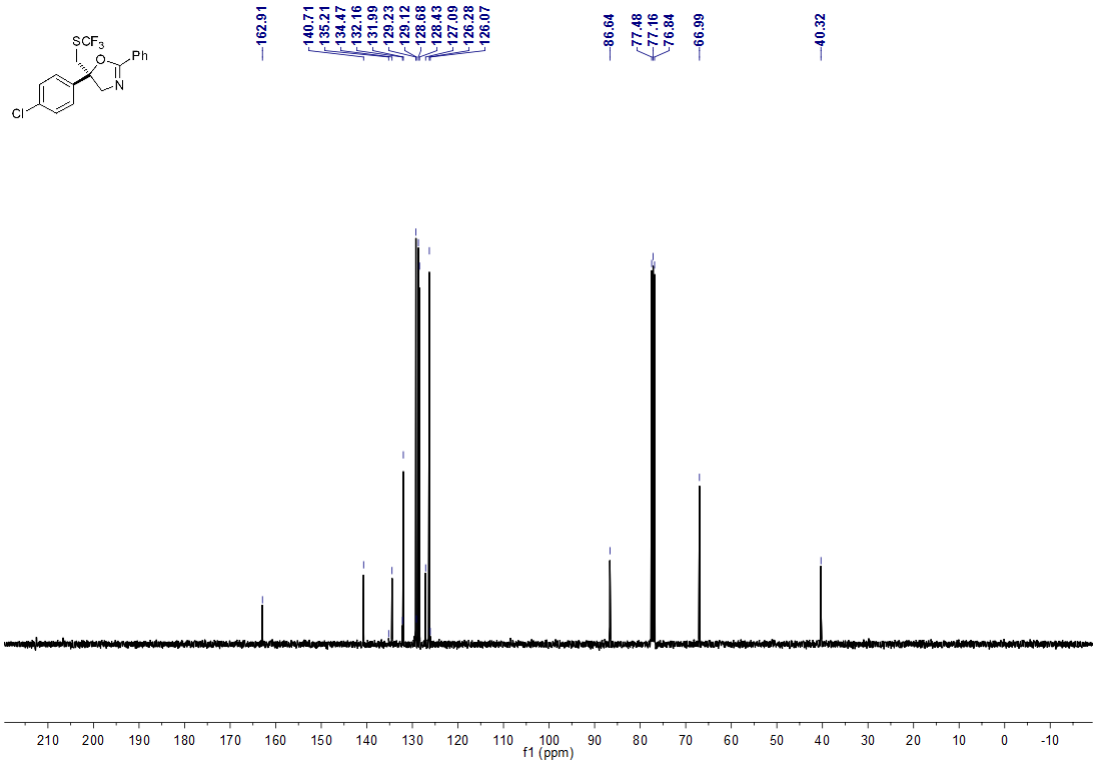
NMR spectra of compound **3b** in $CDCl_3$



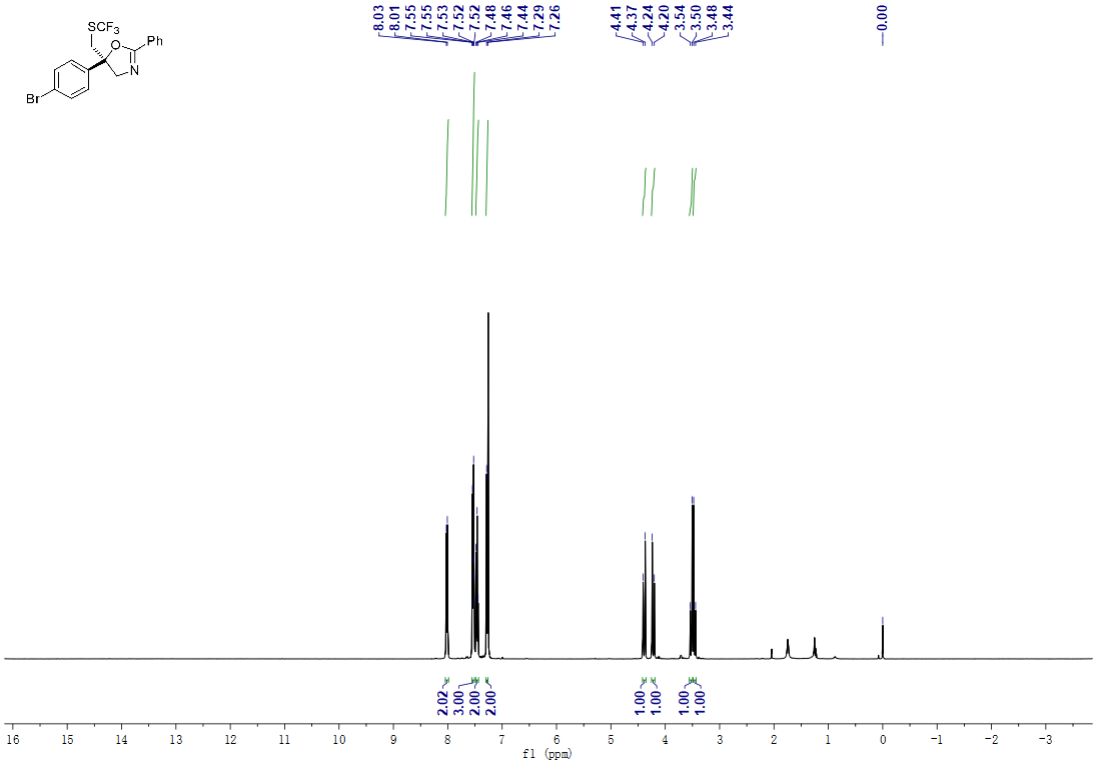


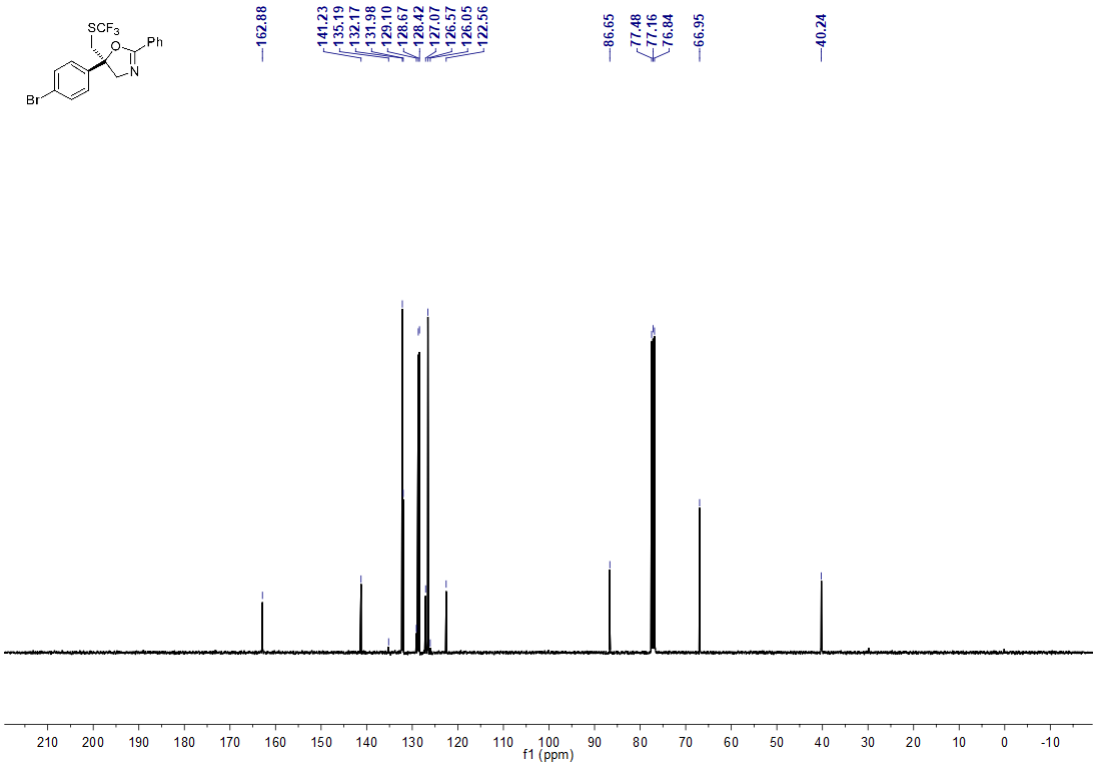
NMR spectra of compound **3c** in $CDCl_3$



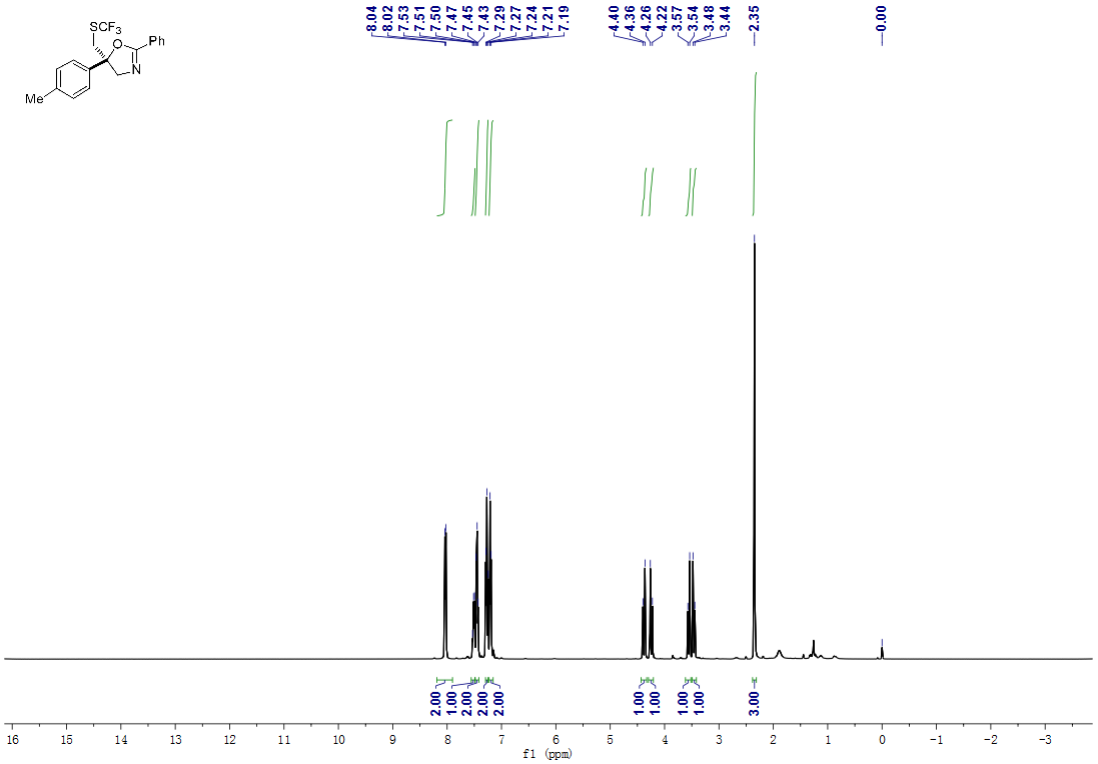


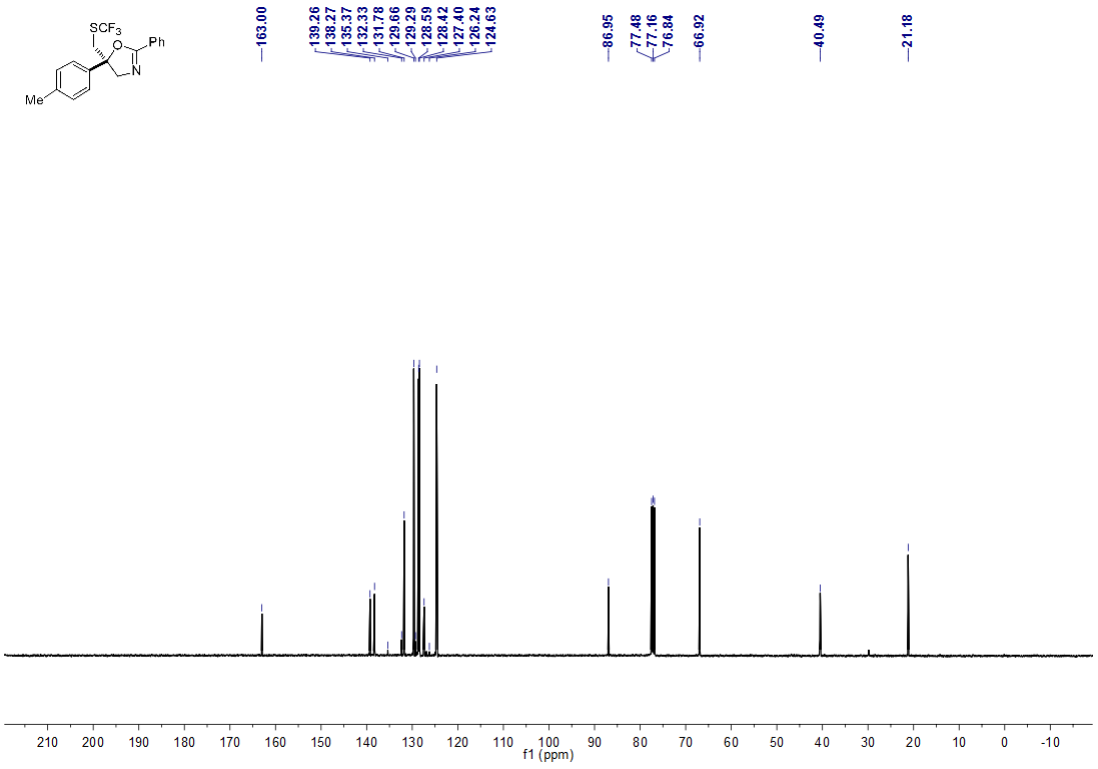
NMR spectra of compound **3d** in $CDCl_3$



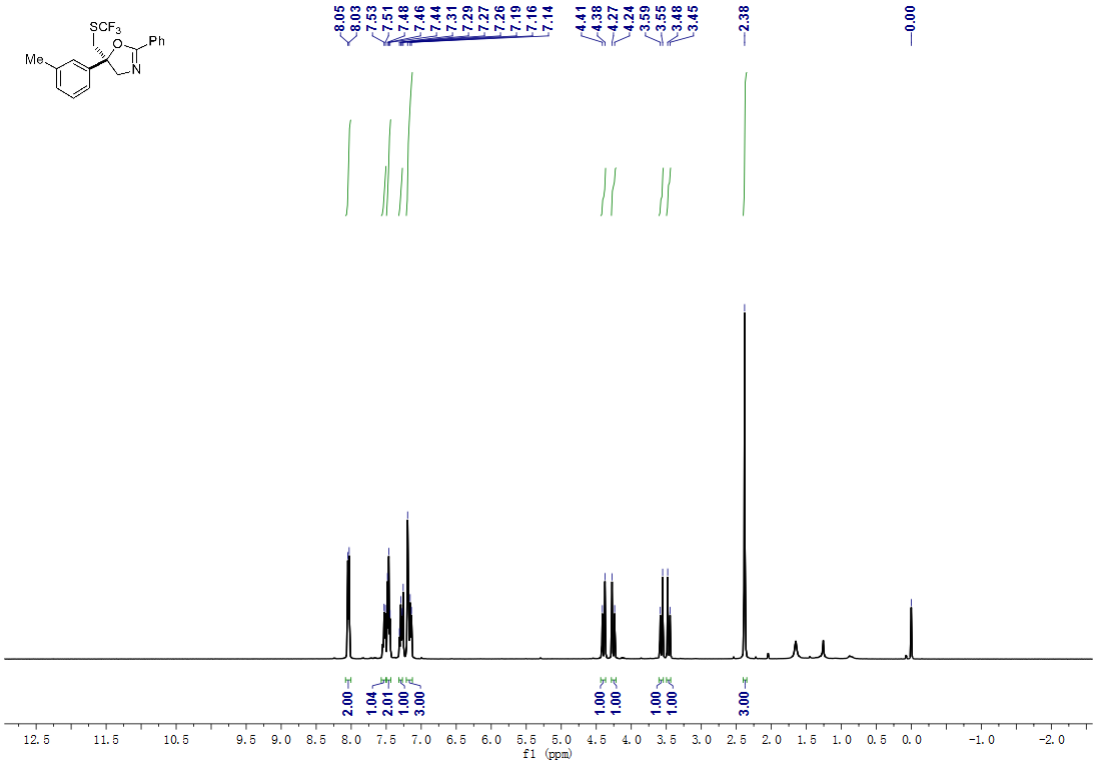


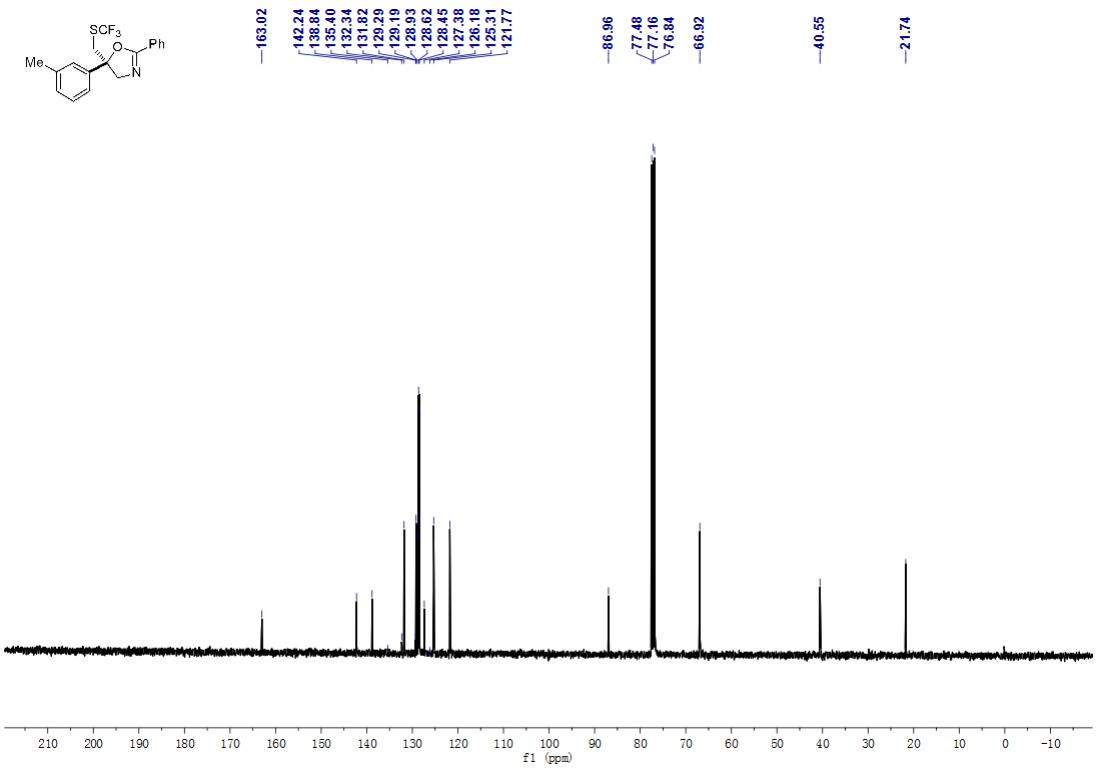
NMR spectra of compound **3e** in $CDCl_3$



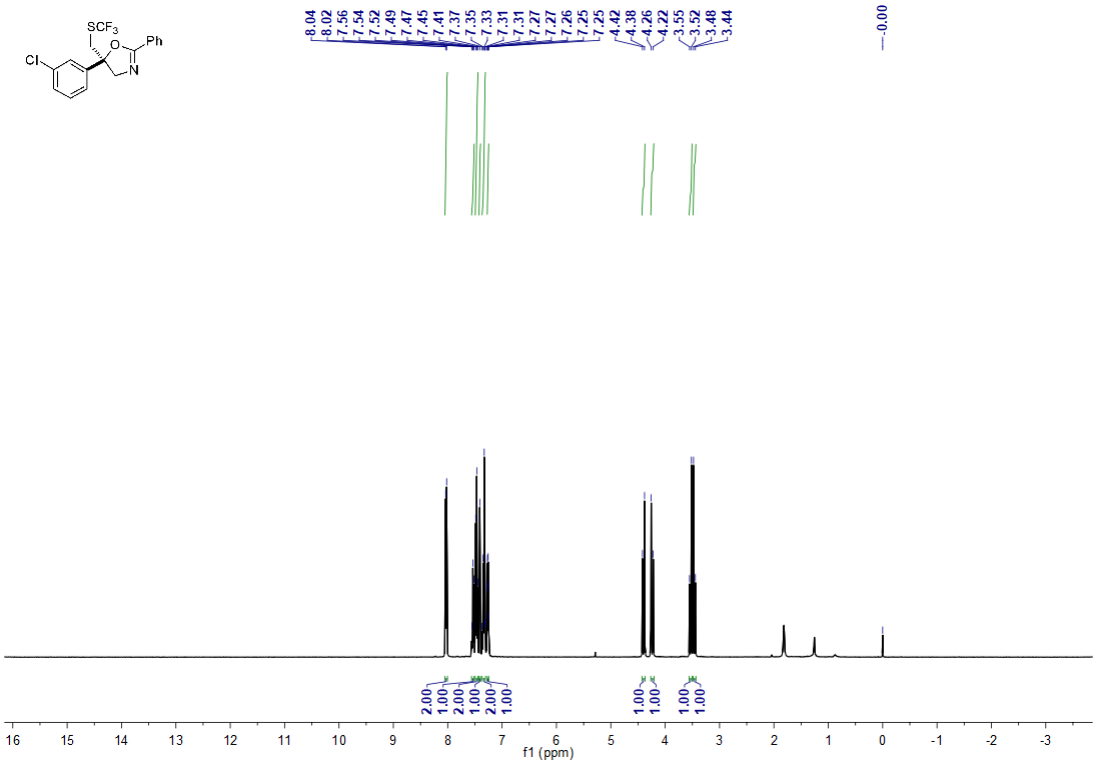


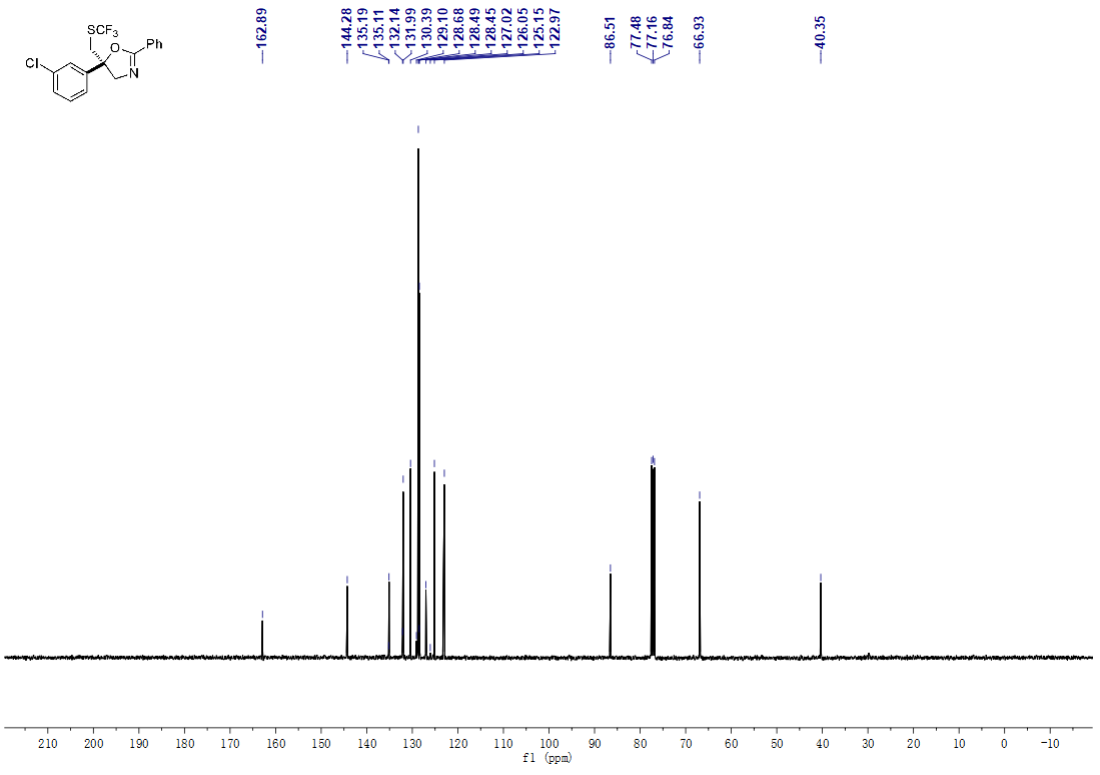
NMR spectra of compound **3f** in $CDCl_3$



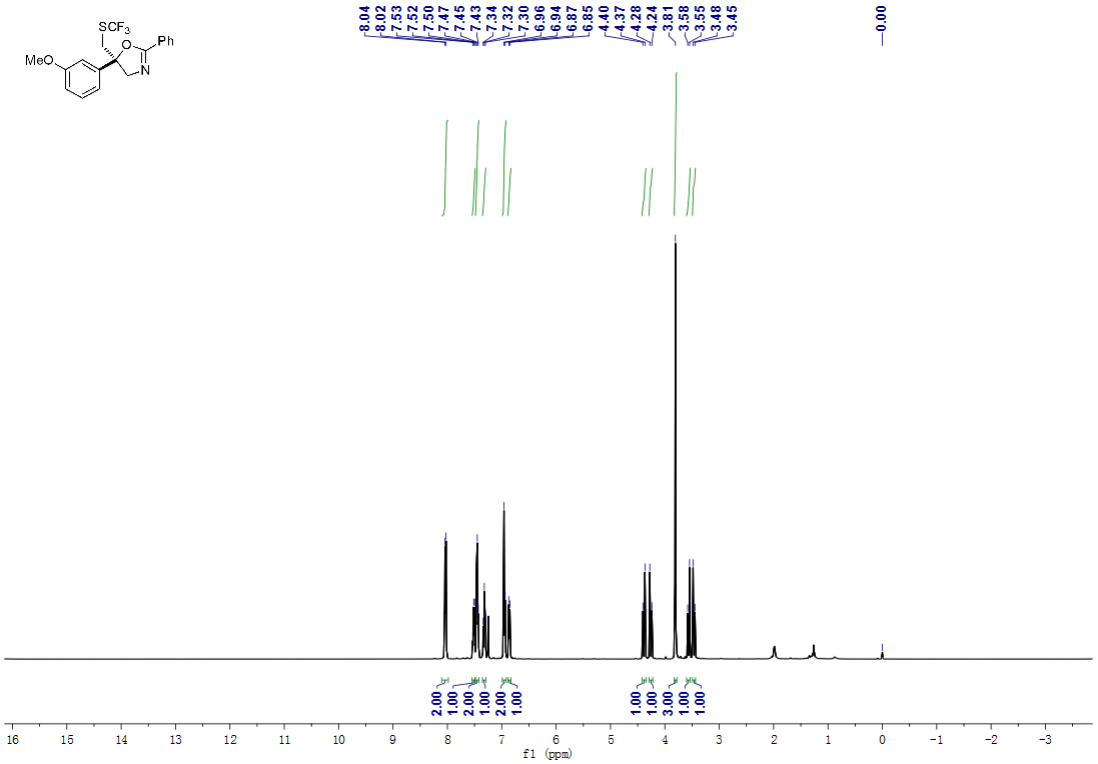


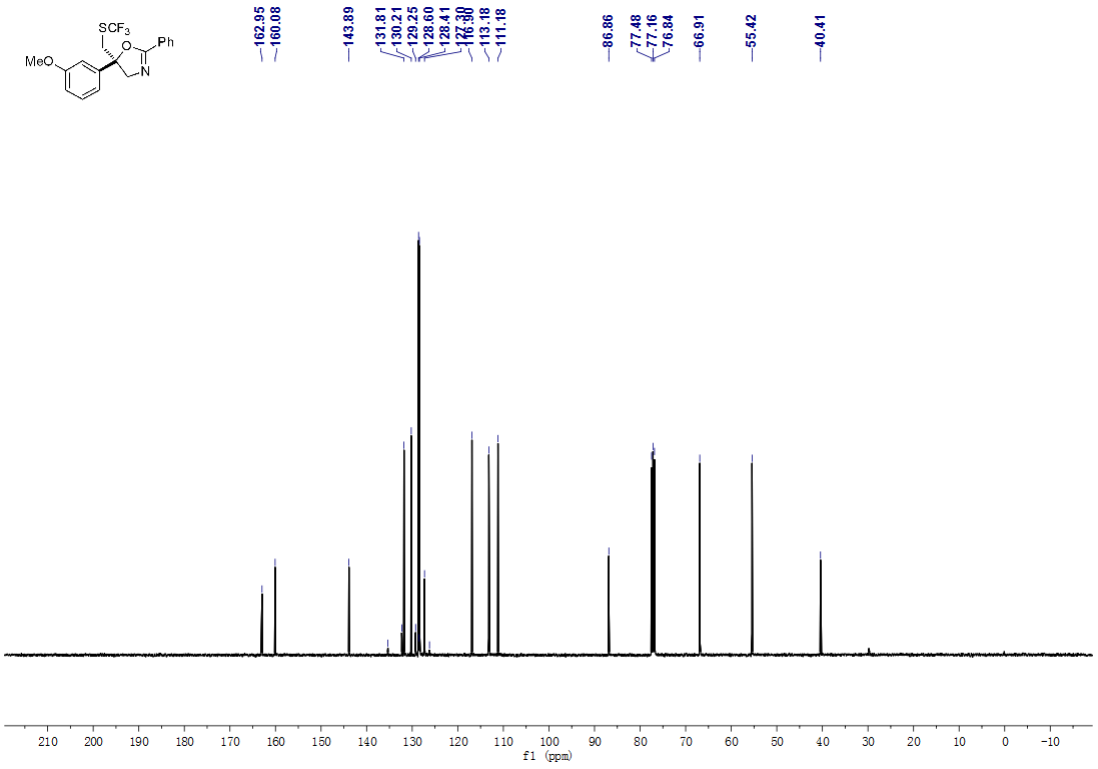
NMR spectra of compound **3g** in $CDCl_3$



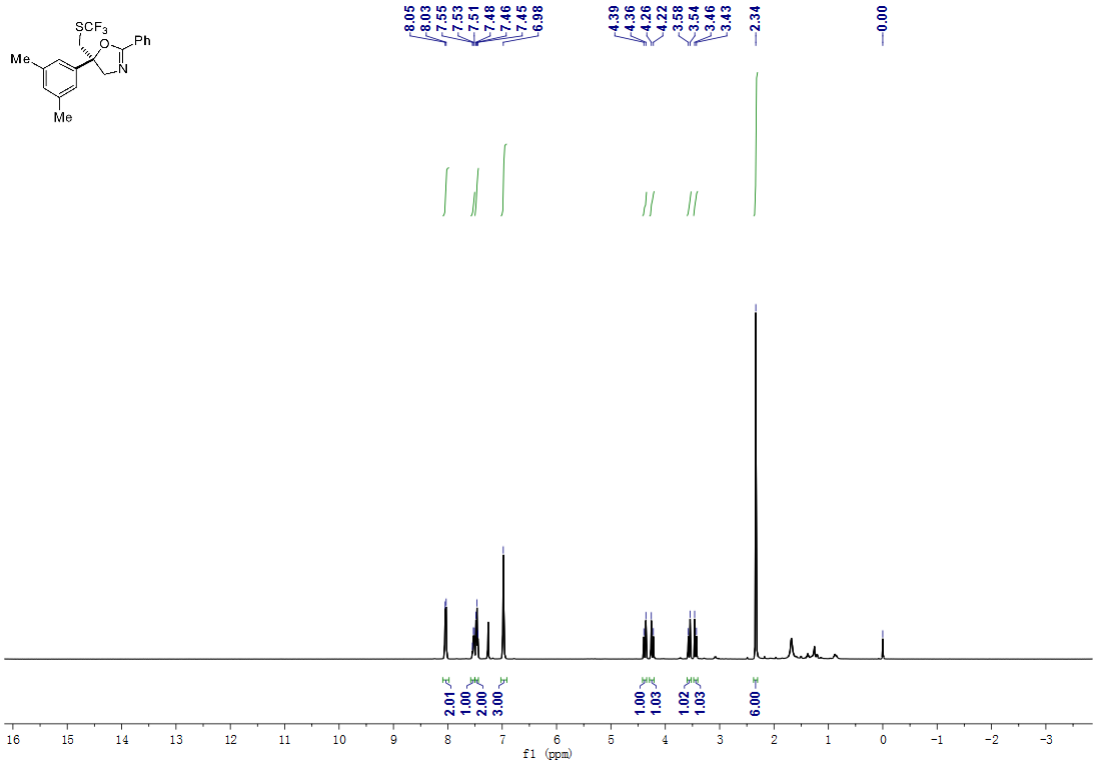


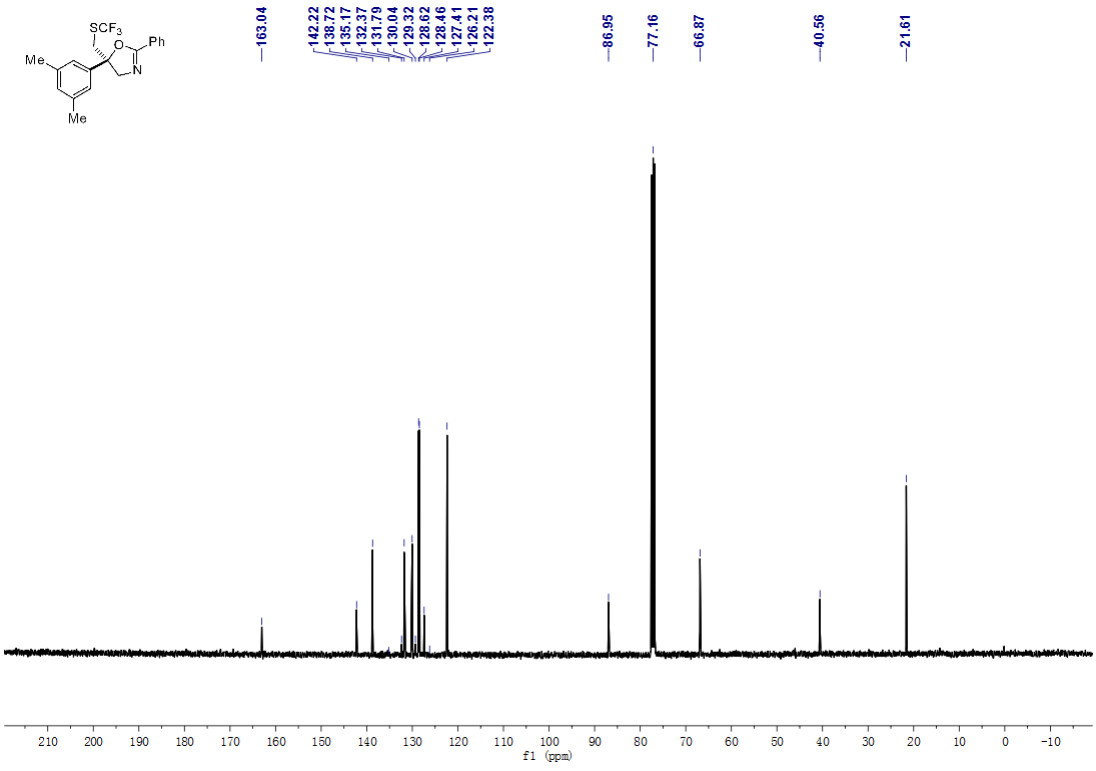
NMR spectra of compound **3h** in $CDCl_3$



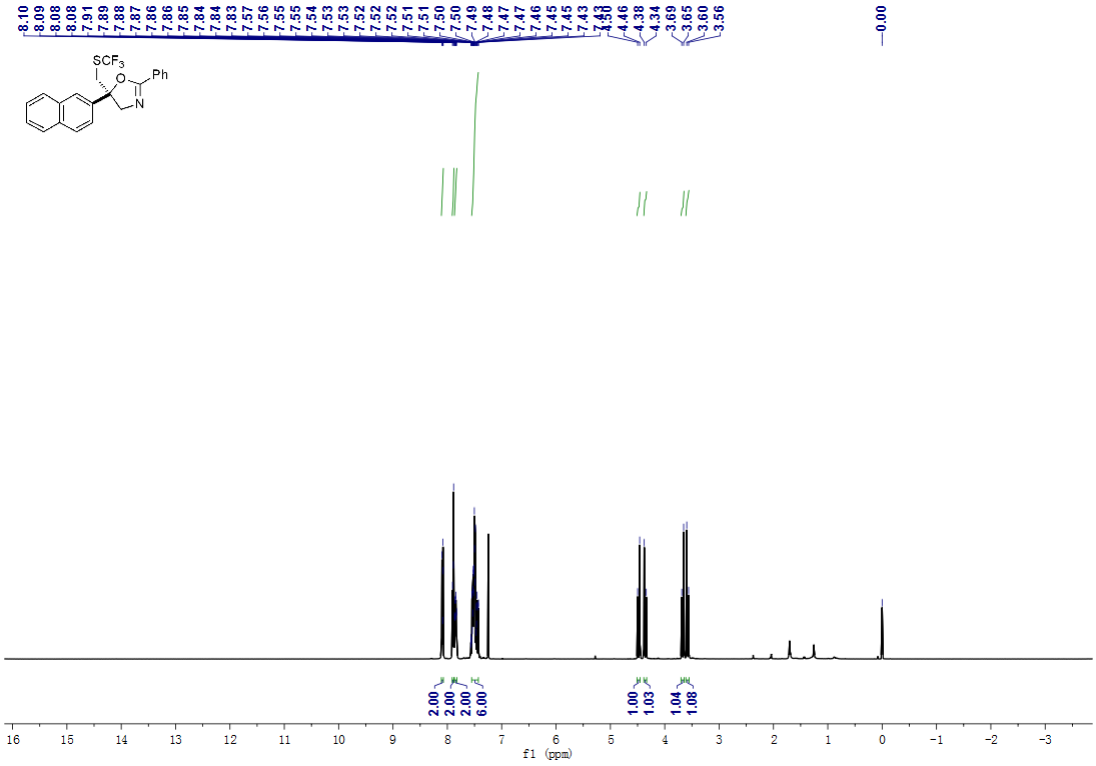


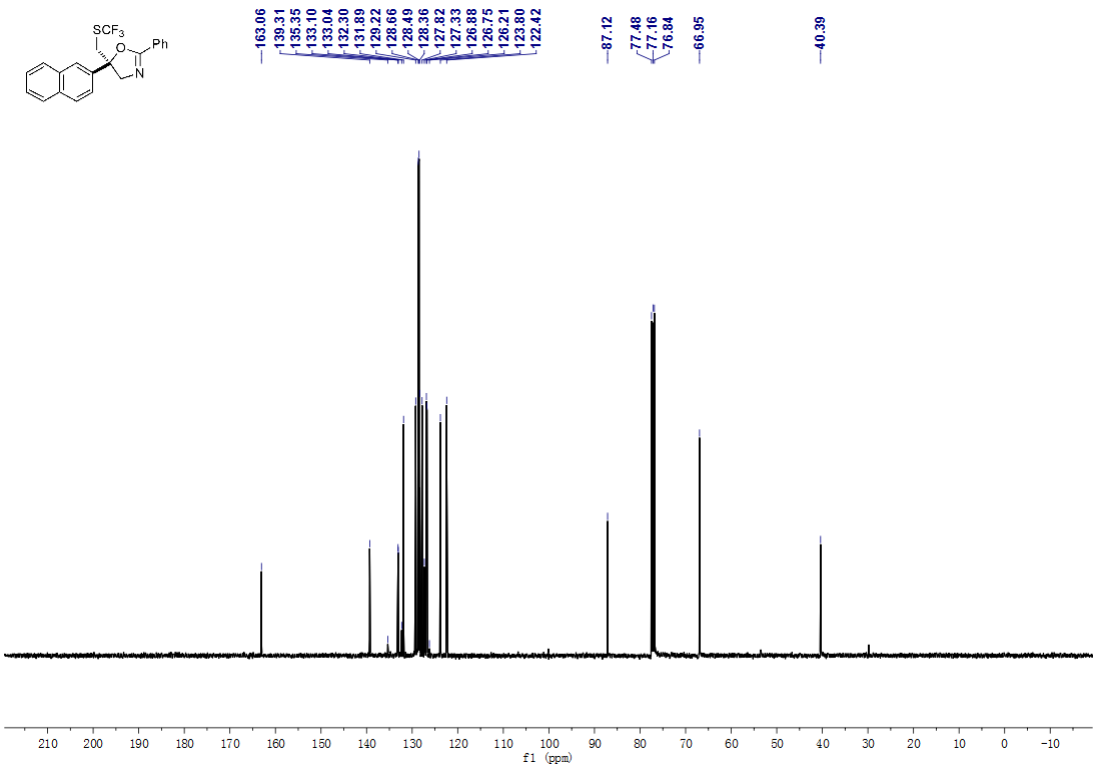
NMR spectra of compound **3i** in $CDCl_3$



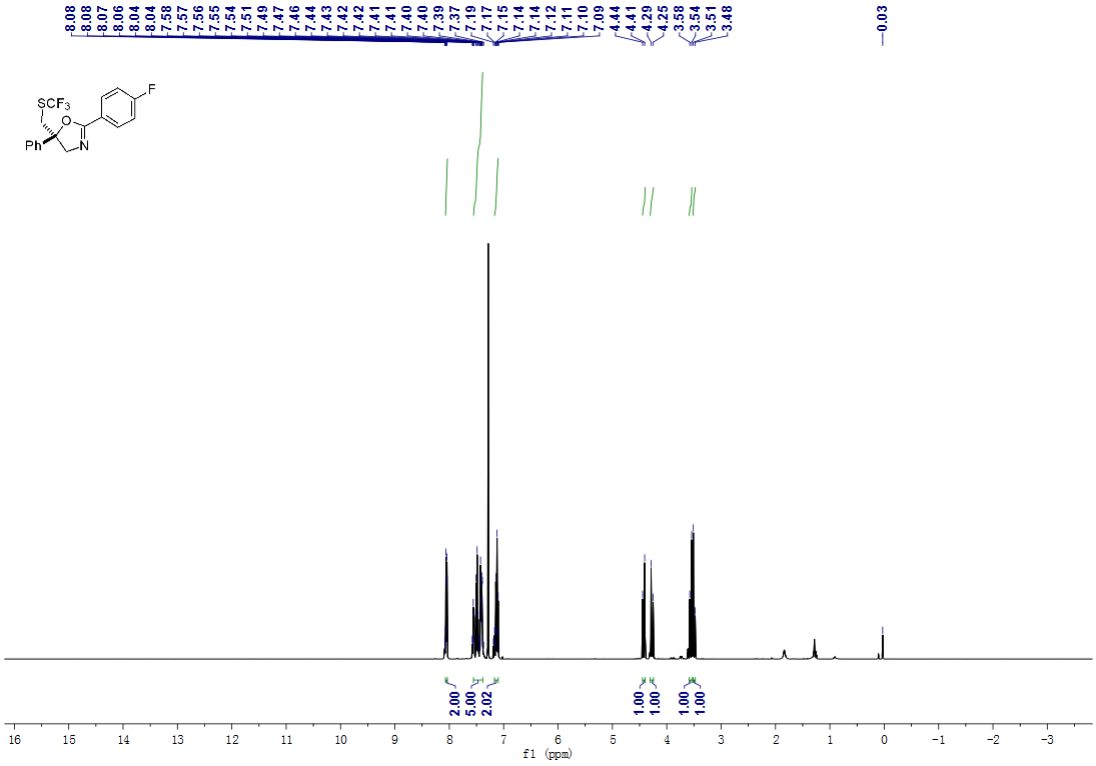


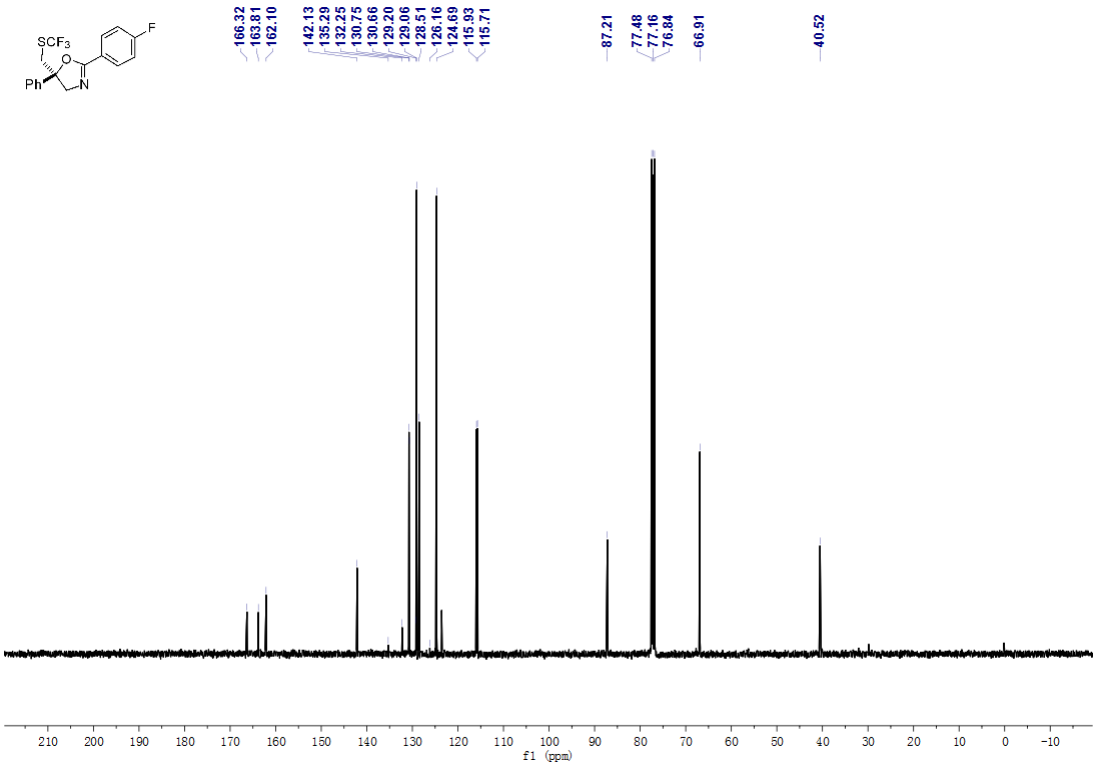
NMR spectra of compound **3j** in $CDCl_3$



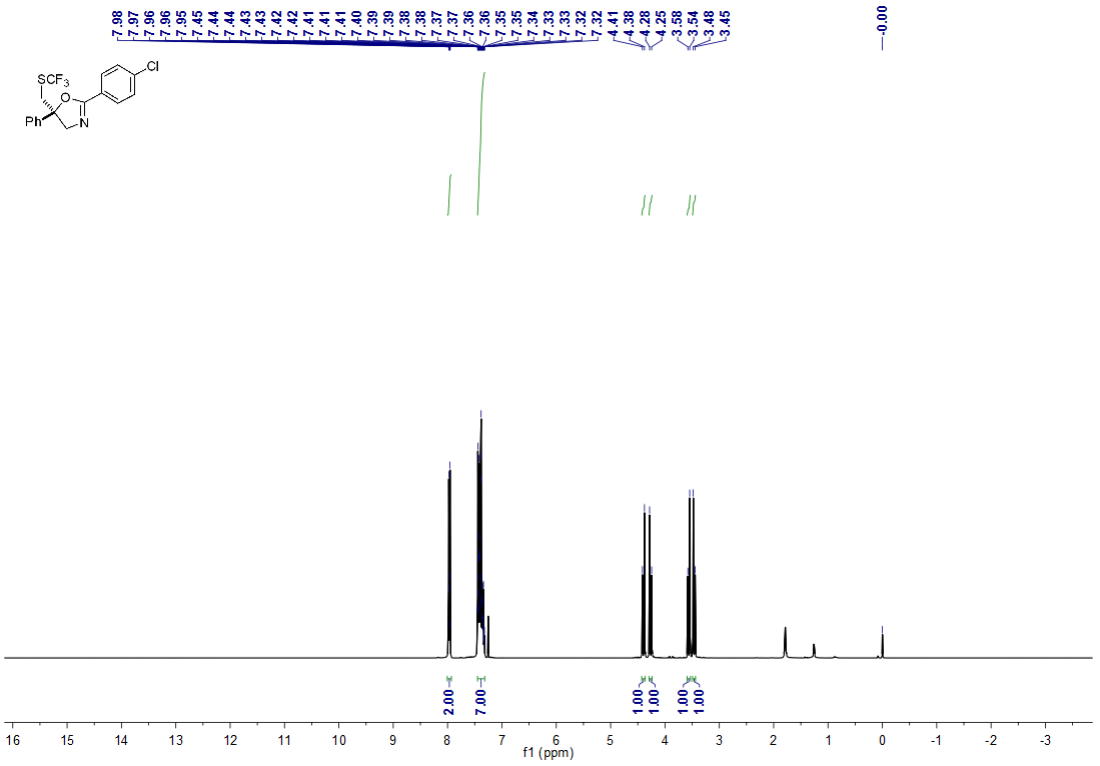


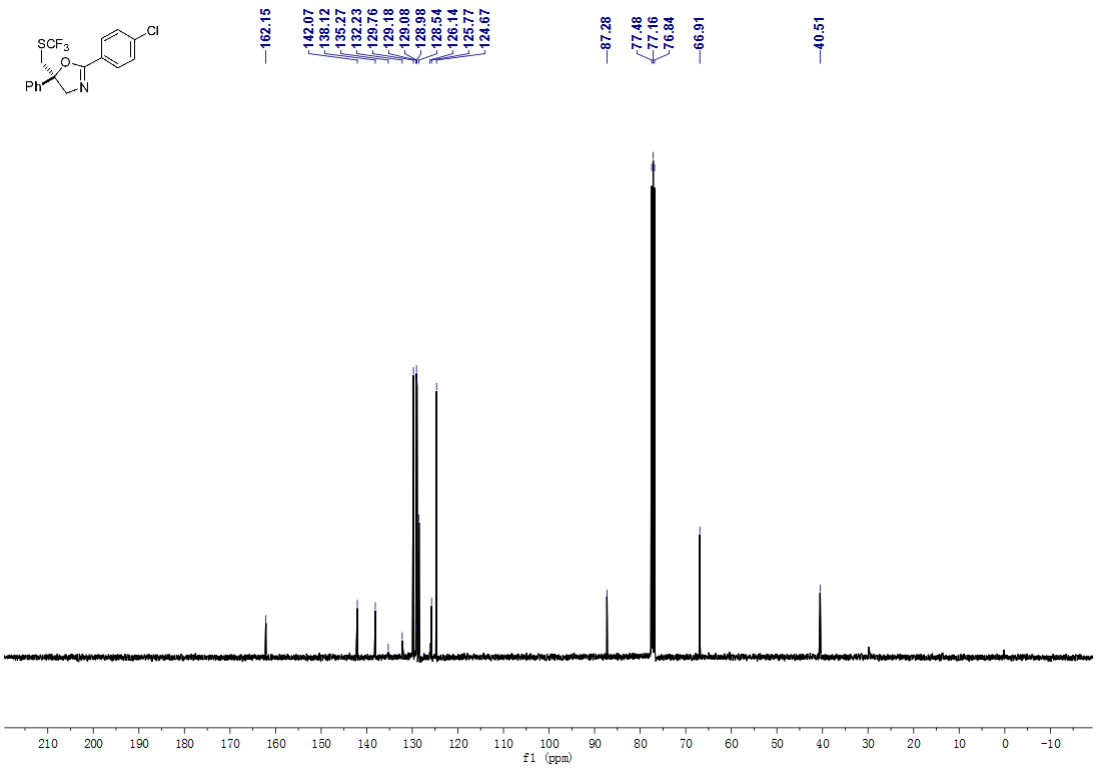
NMR spectra of compound **3k** in $CDCl_3$



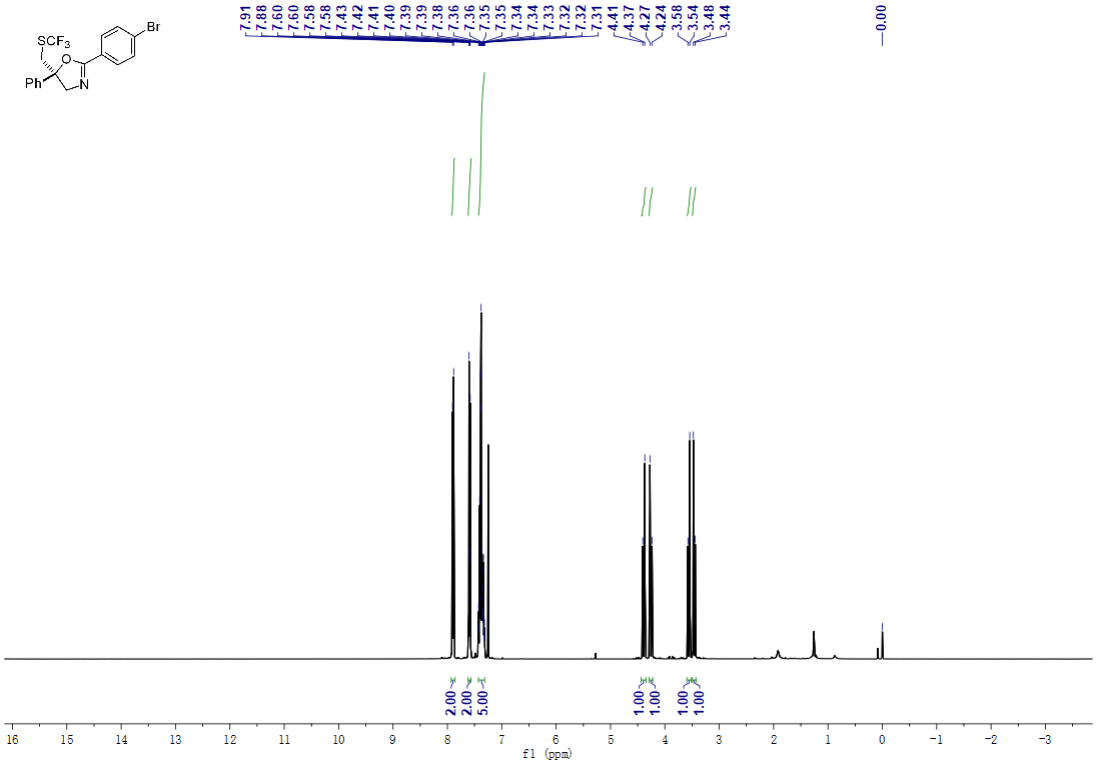


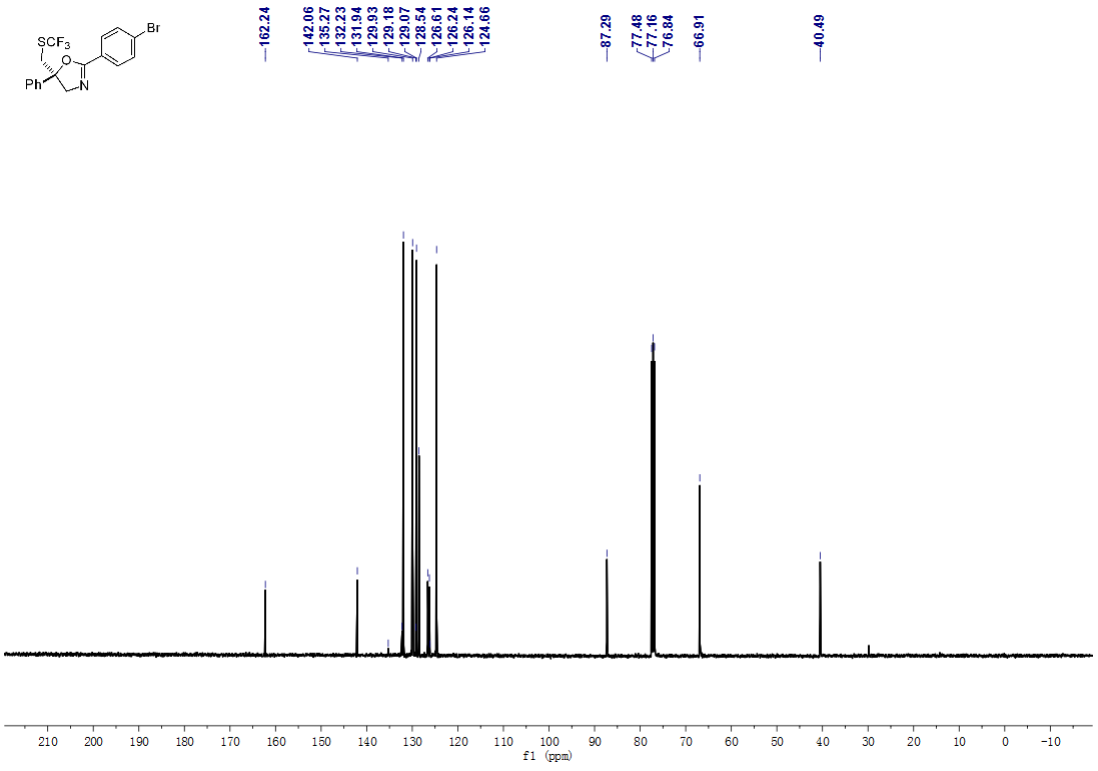
NMR spectra of compound **3l** in $CDCl_3$



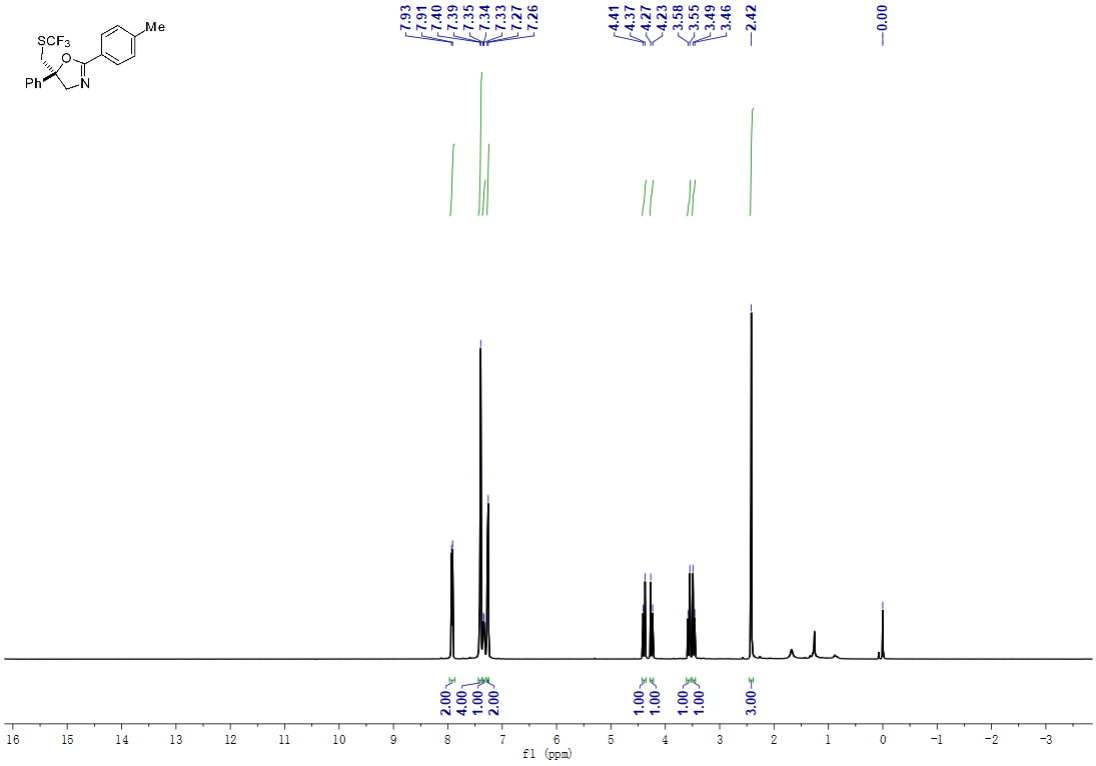


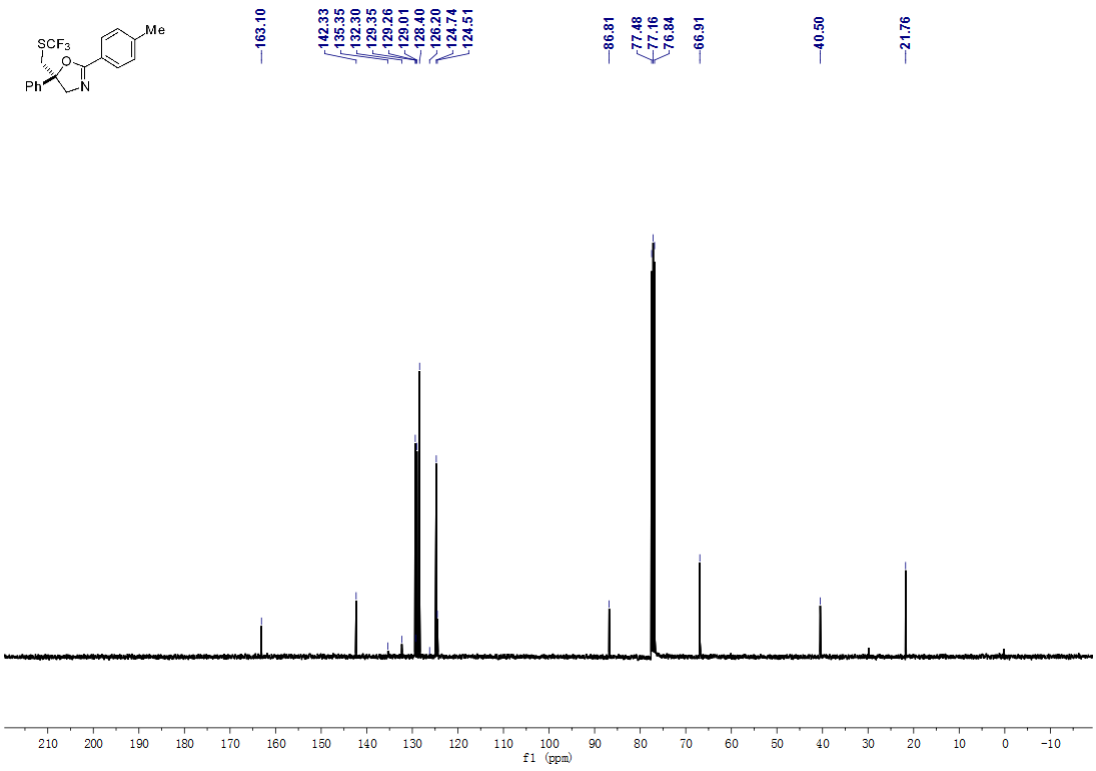
NMR spectra of compound **3m** in $CDCl_3$



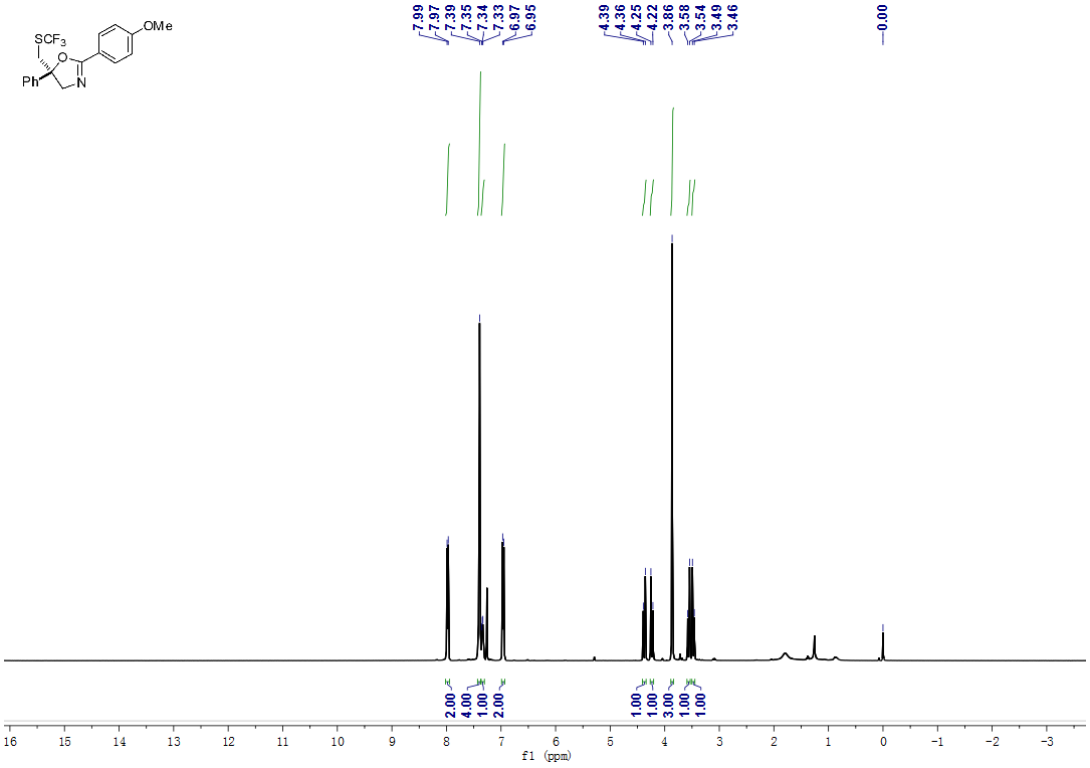


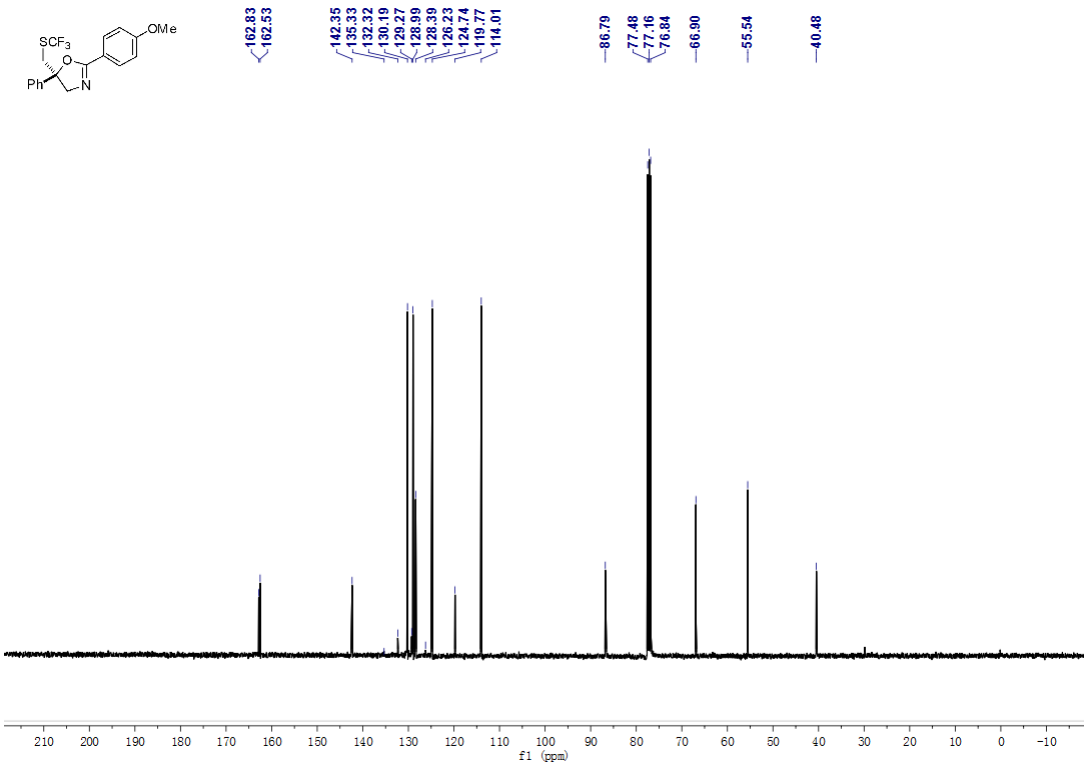
NMR spectra of compound **3n** in $CDCl_3$



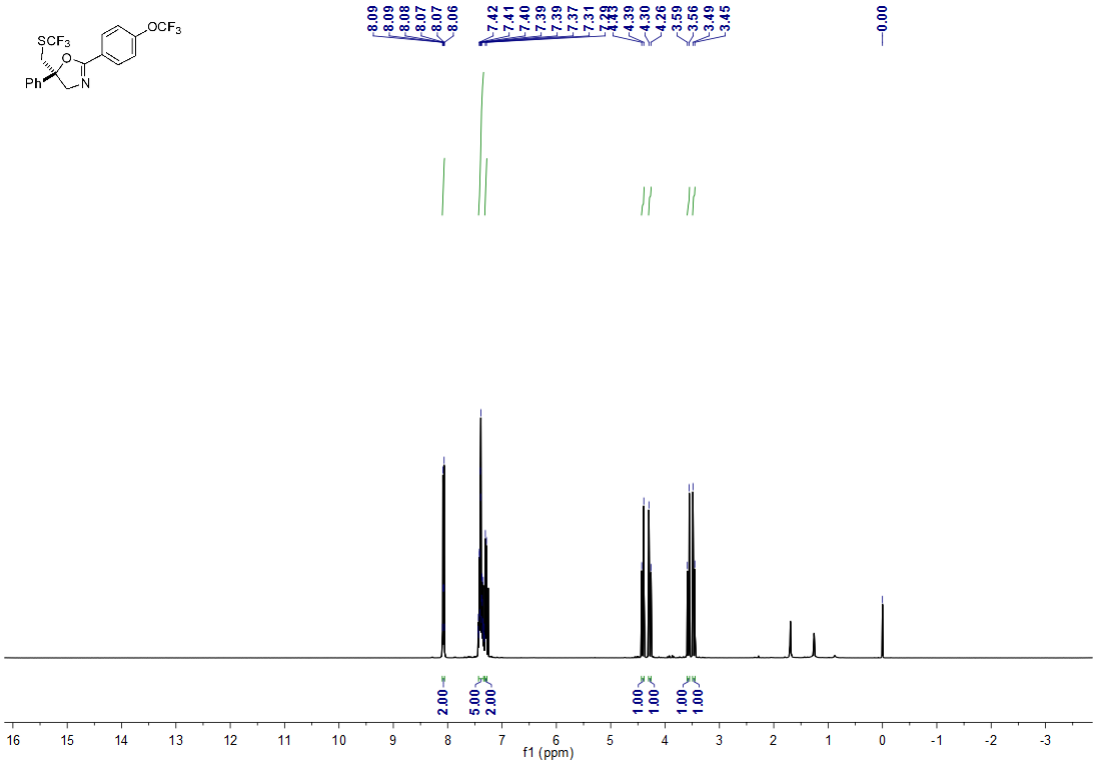


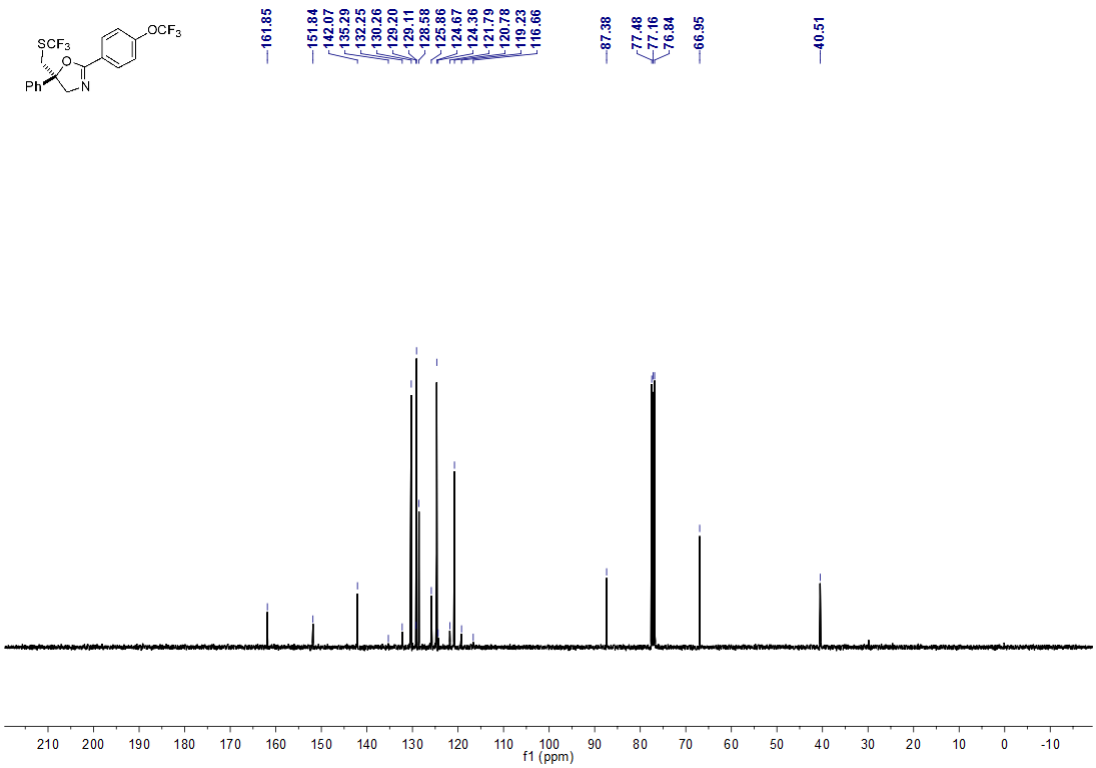
NMR spectra of compound **3o** in $CDCl_3$



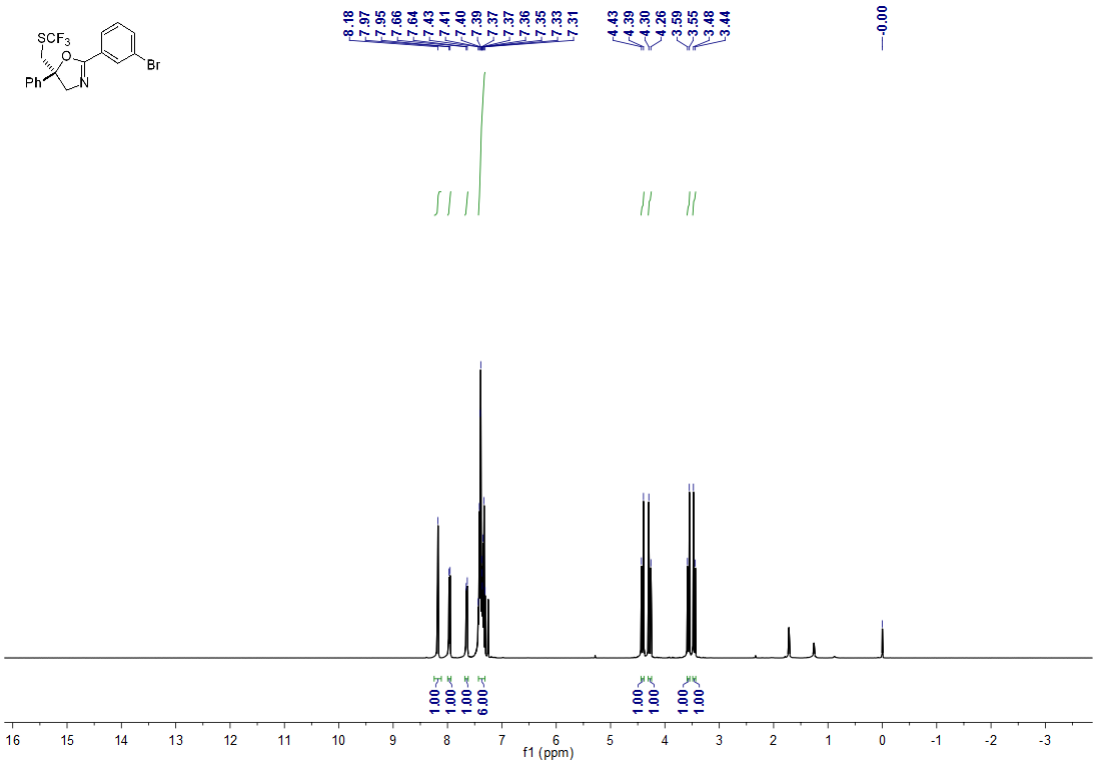


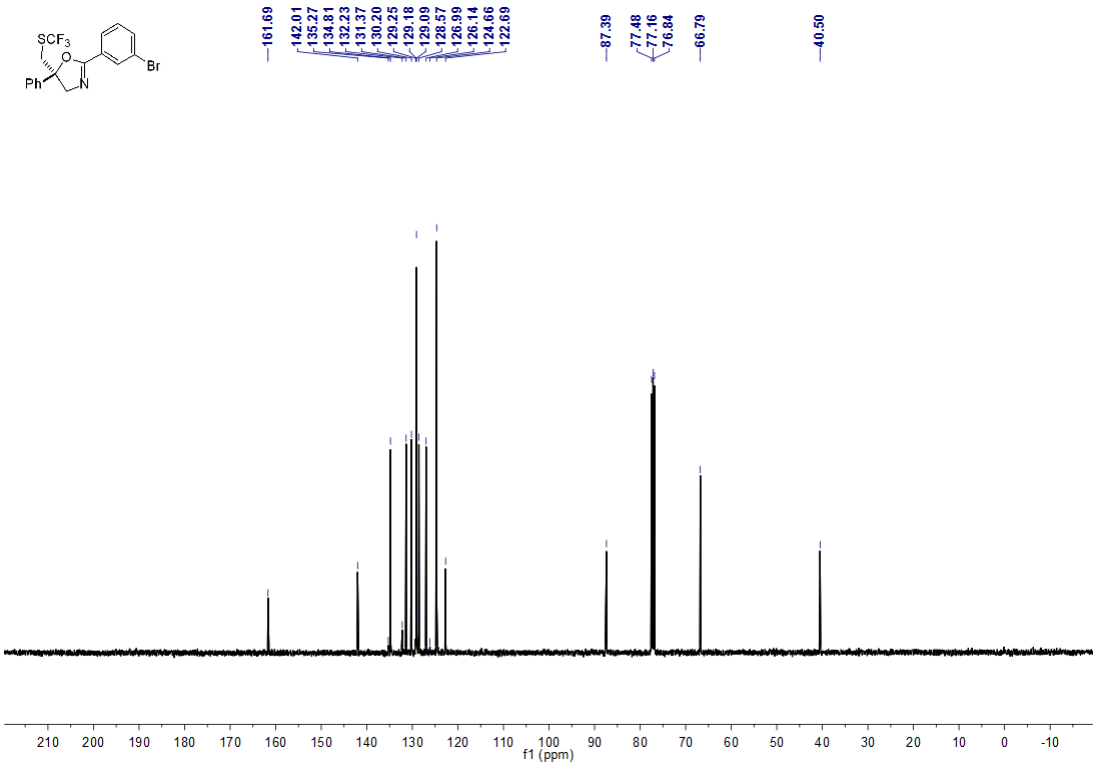
NMR spectra of compound **3p** in $CDCl_3$



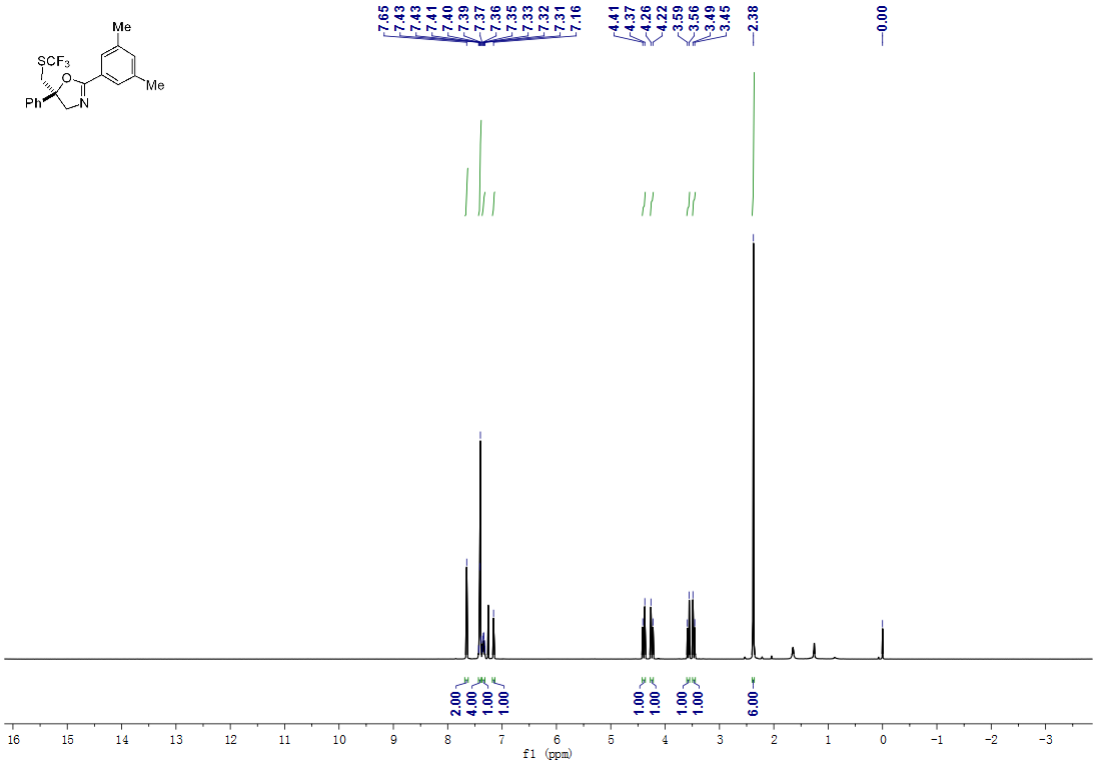


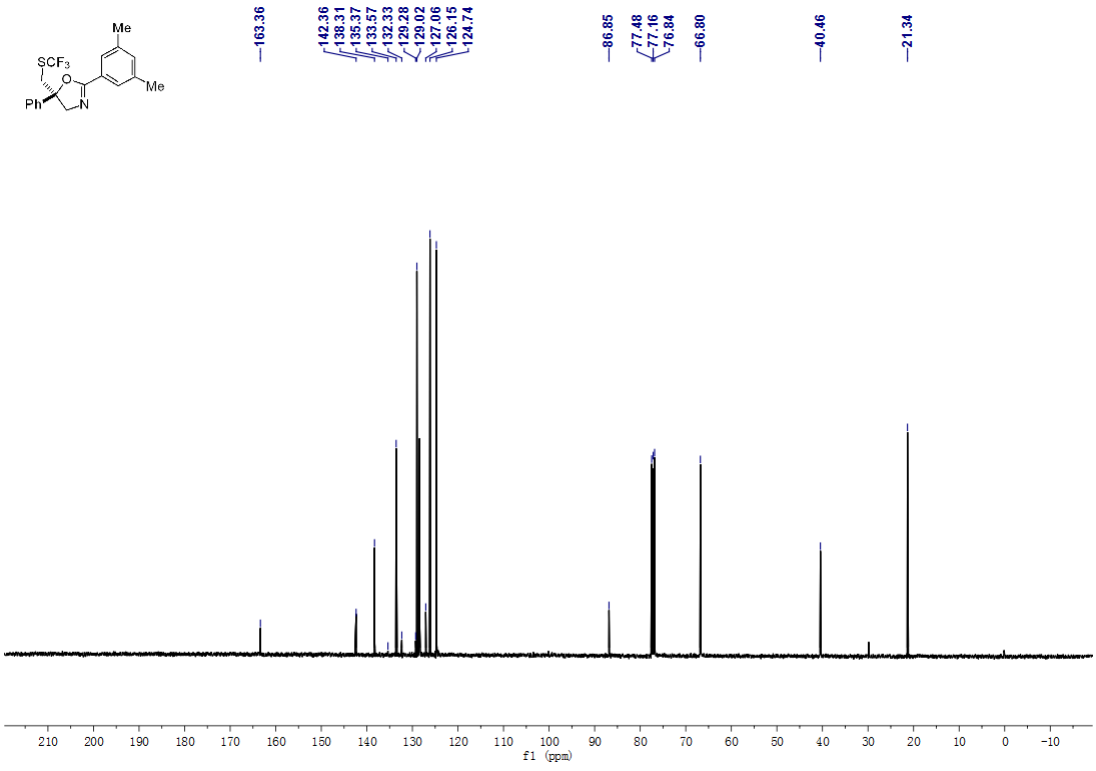
NMR spectra of compound **3q** in $CDCl_3$



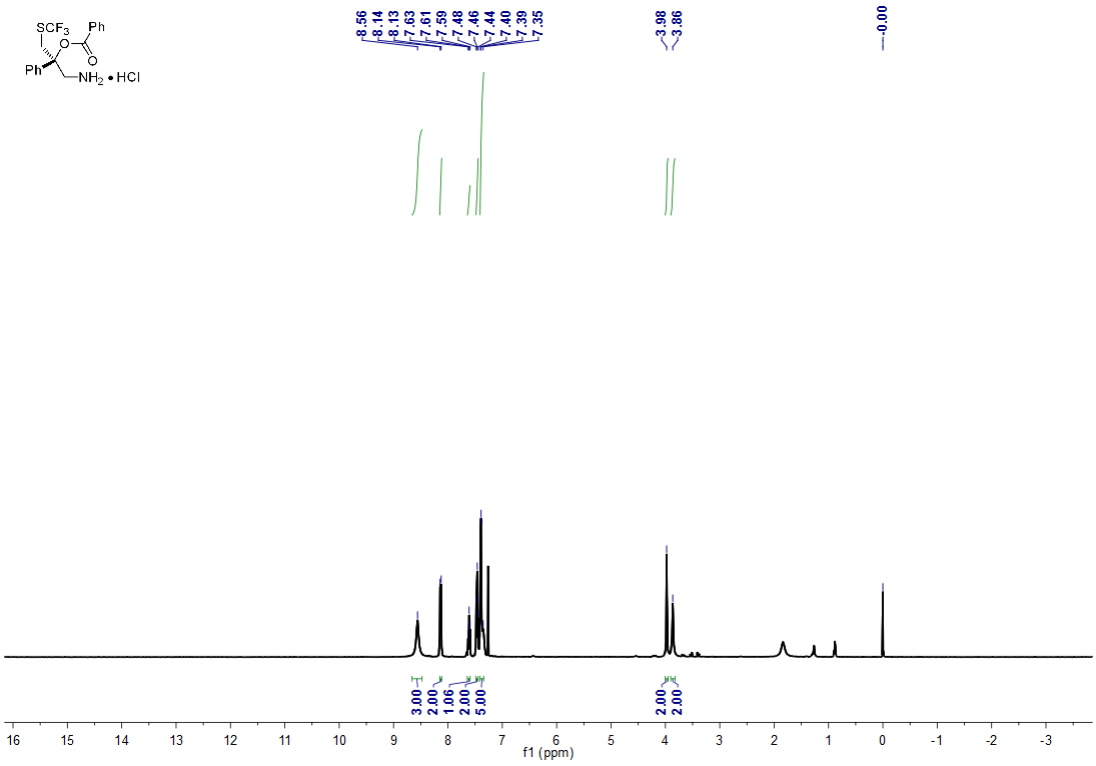


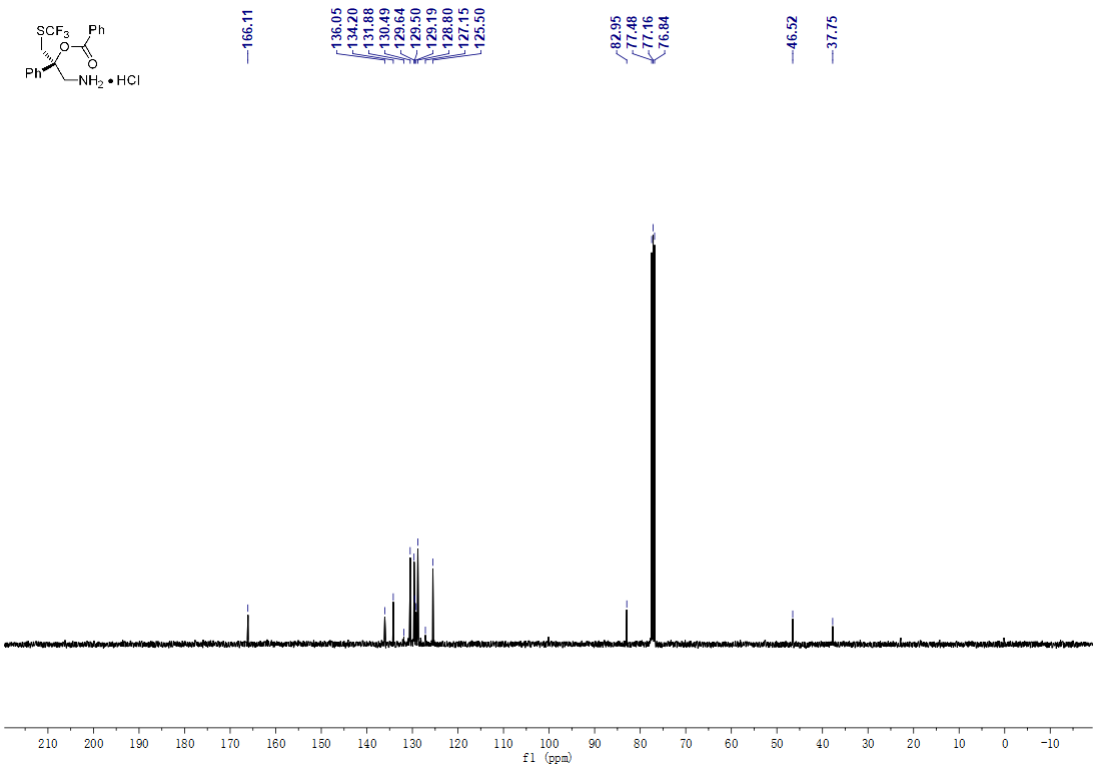
NMR spectra of compound **3r** in $CDCl_3$



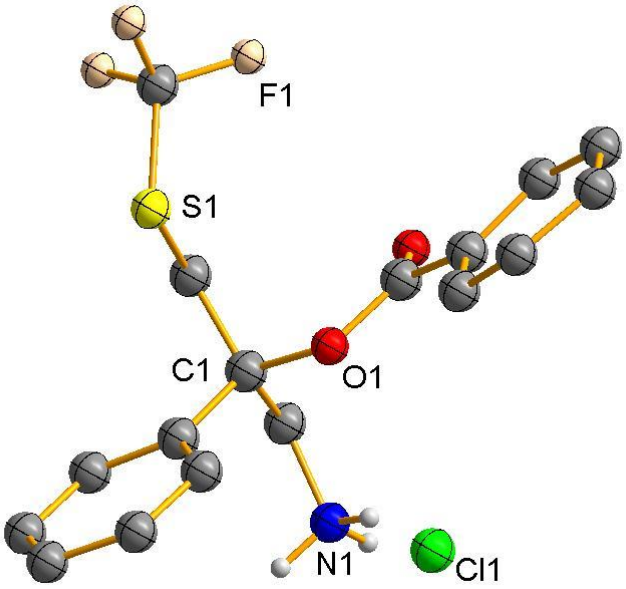


NMR spectra of compound **(*R*)-4** in $CDCl_3$





4. X-ray crystallographic data of (*R*)-4



Single crystals of **(*R*)-4** were grown by slow evaporation of its hexane/ isopropanol solution. The single-crystal collected on Agilent Technologies Gemini A Ultra system, with Cu/Kα 4 radiation (λ = 1.54178 Å). All empirical absorption corrections were applied using the **SCALE3 ABSPACK** program.[6] The structures were solved by direct method and refined by full-matrix least-squares analysis on F^2 using the **SHELX97** program package. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs.[7] Crystallographic data and details of refinements are listed in ***Table S1***, and selected bond distances and angles for are listed in ***Table S2***. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 1873635).

Table S1 Crystal data and structure refinement for **(*R*)-4**.

Empirical formula	$C_{17}H_{17}ClF_3NO_2S$
Formula weight	1567.30
Temperature/K	150.02(10)
Crystal system	orthorhombic
Space group	P212121
a/Å	15.1112(4)
b/Å	15.5876(5)

c/Å	31.4003(9)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å3	7396.3(4)
Z	4
ρcalcg/cm3	1.408
μ/mm-1	3.250
F(000)	3232.0
Crystal size/mm3	0.30 × 0.20 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.62 to 134.58
Index ranges	-8 ≤ h ≤ 17, -17 ≤ k ≤ 18, -37 ≤ l ≤ 36
Reflections collected	21018
Independent reflections	11812 [Rint = 0.0675, Rsigma = N/A]
Data/restraints/parameters	11812/29/1119
Goodness-of-fit on F2	1.018
Final R indexes [I>=2σ (I)]	R1 = 0.0566, wR2 = 0.1316
Final R indexes [all data]	R1 = 0.0805, wR2 = 0.1466
Largest diff. peak/hole / e Å-3	0.74/-0.59
Flack parameter	-0.012(16)

Table S2 Bond Lengths for **(*R*)-4.**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
N1	C2	1.464(6)	N3	C36	1.481(6)
O1	C11	1.328(8)	O5	C45	1.358(6)
O1	C1	1.452(7)	O5	C35	1.450(6)
O2	C11	1.213(9)	O6	C45	1.209(7)
C1	C4	1.504(8)	C44	F9	1.304(9)
C1	C3	1.545(8)	C44	F7	1.307(9)
C1	C2	1.547(7)	C44	F8	1.319(9)
C3	S1	1.802(8)	C44	S3	1.772(9)
S1	C10	1.766(8)	S3	C37	1.802(9)
C10	F2	1.313(8)	C37	C35	1.540(9)
C10	F1	1.317(8)	C35	C36	1.523(7)
C10	F3	1.325(8)	C35	C38	1.543(7)
C4	C9	1.378(8)	C38	C39	1.377(7)
C4	C5	1.398(9)	C38	C43	1.388(7)

C5	C6	1.384(13)		C39	C40	1.382(8)	

Table S3 Bond Angles for **(*R*)-4.**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C11	O1	C1	122.6(5)	C45	O5	C35	122.6(4)
O1	C1	C4	109.8(4)	F9	C44	F7	108.8(9)
O1	C1	C3	111.4(6)	F9	C44	F8	106.0(8)
C4	C1	C3	100.0(6)	F7	C44	F8	106.1(8)
O1	C1	C2	111.3(5)	F9	C44	S3	111.7(11)
C4	C1	C2	116.5(4)	F7	C44	S3	109.0(8)
C3	C1	C2	107.3(5)	F8	C44	S3	115.0(8)
O1	C1	C3'	91.0(6)	C44	S3	C37	96.8(5)
C4	C1	C3'	122.9(7)	C35	C37	S3	112.4(7)
C3	C1	C3'	25.6(5)	O5	C35	C36	113.1(4)
C2	C1	C3'	102.5(5)	O5	C35	C37'	114.9(8)
C1	C3	S1	114.2(6)	C36	C35	C37'	104.8(5)
C10	S1	C3	98.8(5)	O5	C35	C37	103.9(8)
F2	C10	F1	106.2(7)	C36	C35	C37	110.9(5)
F2	C10	F3	105.8(7)	O5	C35	C38	104.0(4)
F1	C10	F3	106.0(7)	C36	C35	C38	109.3(4)
F2	C10	S1	114.3(6)	C37	C35	C38	115.4(9)
F1	C10	S1	114.9(6)	N3	C36	C35	113.2(4)
F3	C10	S1	108.9(7)	C39	C38	C43	119.3(5)
N1	C2	C1	116.5(4)	C39	C38	C35	121.3(4)
C9	C4	C5	117.9(6)	C43	C38	C35	119.1(4)
C9	C4	C1	123.1(5)	C38	C39	C40	120.1(5)
C5	C4	C1	118.6(6)	C41	C40	C39	120.7(5)

5. References

(1) J. Luo, Y. Liu and X. Zhao, *Org. Lett.*, 2017, **19**, 3434.

(2) X. Liu, R. An, X. Zhang, J. Luo and X. Zhao, *Angew. Chem., Int. Ed.*, 2016, **55**, 5846;

(3) Y. Kawato, A. Kubota, H. Ono, H. Egami and Y. Hamashima, *Org Lett.*, 2015, **17**, 1244.

(4) A. Jaganathan, A. Garzan, D. C. Whitehead, R. J. Staples and B. Borhan, *Angew. Chem., Int. Ed*., 2011, **50**, 2593.

(5) H. Aït- Haddou, O. Hoarau, D. Cramailére, F. Pezet, C. J. Daran and G. G. A. Balavoine, *Chem. - Eur. J*., 2004, **10**, 699.

(6) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

(7) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59.