

Supporting Information

Enantioselective organocatalytic amination of 2-perfluoroalkyl-oxazol-5(2*H*)-ones towards synthesis of chiral *N,O*-aminals with perfluoroalkyl and amino groups

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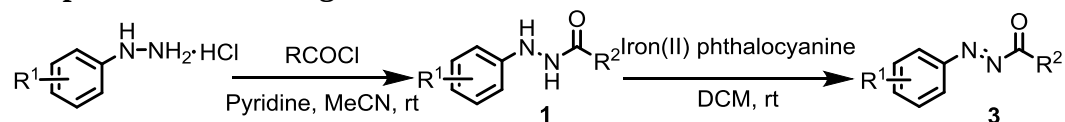
Content

1. General Information	S3
2. Preparation of Starting Materials ^{1,2}	S4
3. Four Ways to Synthesize 6a	S5
4. Gram-Scale Synthesis of 6e	S7
5. Experimental Procedures for Transformations of the Corresponding Products	S8
6. Optimization of Reaction Conditions	S9
7. Characterization of Adducts.....	S11
8. References	S28
9. Copies of NMR Spectra of the Adducts	S29
10. Copies of HPLC Spectra for Racemic and Chiral Adducts	S79

1. General Information

All reactions were carried out under an atmosphere of air. All solvents and reagents were purchased from commercial sources and purified according to established procedures before use. Flash chromatography was carried out using silica gel (100-200 mesh). ^1H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quaternary, m = multiplet), coupling constants (Hz), integration. $^{13}\text{C}\{^1\text{H}\}$ NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. HPLC analysis was performed on a Dionex UltiMate 3000, ThermoScientific. Chiral HPLC data for the products could be obtained using Chiralpak IA, Chiralpak IH, Chiralpak IF and NuAnalytical-FLM NZ_2 column. These chiral columns were purchased from Daicel Chemical Industries Ltd and FLM Scientific Instrument Co. Ltd. Optical rotations were measured on an Insmark polarimeter (IP-digi 300). HRMS was obtained by an ABI/Sciex QStar Mass Spectrometer (ESI). All melting points were conducted on a digital melting point apparatus and were uncorrected. TLC was performed on glass-backed silica plate.

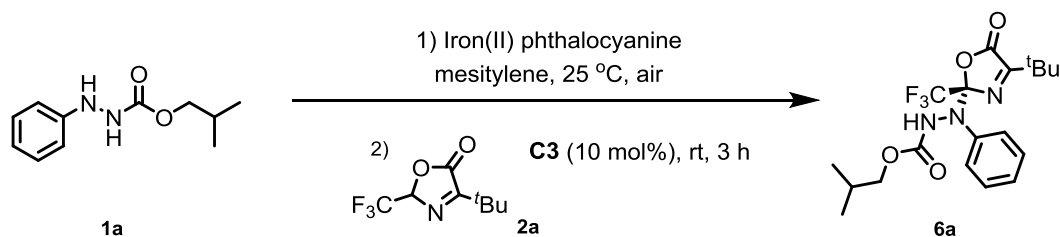
2. Preparation of Starting Materials^{1, 2}



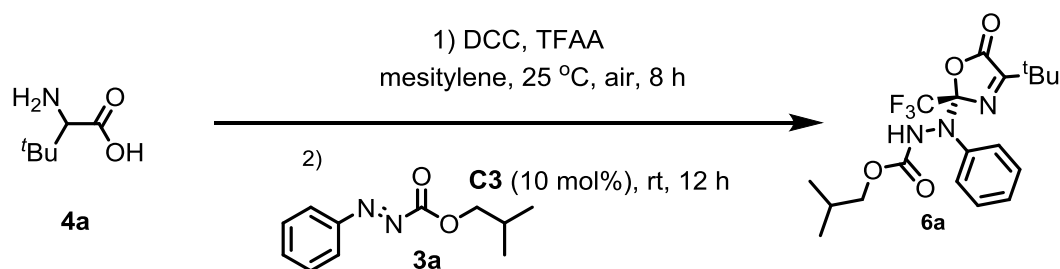
Phenylazocarboxylate **3a-3zc** were prepared following the literature procedure^{3,4,5}. 20ml CH₃CN was added into 100ml round bottom flask. The solution was cooled to 0 °C and the corresponding hydrazine hydrochloride (10 mmol) was dissolved in it. Pyridine (1.71 mL, 21.2 mmol) was added. Then chloroformate (1.04 mL, 11 mmol) was added dropwise under stirring. The reaction mixture was stirred for 30 min at 0 °C and then for 4 h at room temperature. Water (20 mL) was added and the product was extracted with CH₂Cl₂ (50 mL). The combined organic layers were washed with saturated aq. NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄ and the solvent was evaporated to dryness. The crude products were purified by recrystallization with n-Hexane/DCM to afford the corresponding products **1a-1zc** in 60-85% yield.

Iron(II) phthalocyanine (568 mg, 1 mmol) was added to a solution of corresponding hydrazinecarboxylate (10 mmol) in 20 mL DCM. The reaction mixture was stirred for 4 h at room temperature and under an atmosphere of air. The solvent was evaporated to dryness and purified by chromatography on silica gel eluted with PE/EA (10/1-5/1) to afford the corresponding product **3a-3zc** in 75-98% yield.

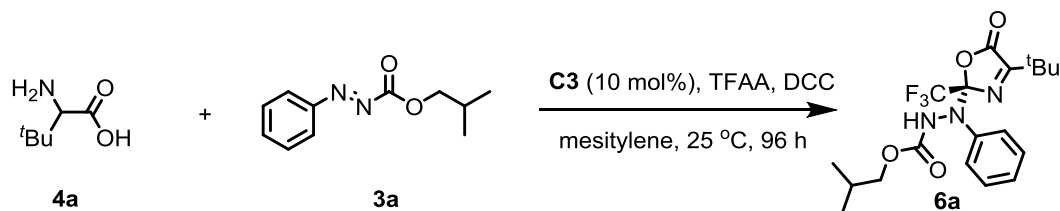
3. Four Ways to Synthesize 6a



Iron(II) phthalocyanine (0.015 mmol, 0.15 equiv) was added to a solution of isobutyl 2-hydrazinecarboxylate **1a** (0.15 mmol, 1.5 equiv) in 1 mL mesitylene. The reaction mixture was stirred for 8 h at room temperature and under an atmosphere of air. Catalyst **C3** (0.01 mmol, 0.1 equiv) and 4-(*tert*-butyl)-2-(trifluoromethyl)oxazol-5(2*H*)-one **2a** (0.10 mmol, 1 equiv) were added in the solvent. The reaction mixture was stirred for 3 h at room temperature. The resulting mixture was monitored by TLC and purified by silica gel column using eluent: PE/EA (10/1-5/1) to afford **6a**.

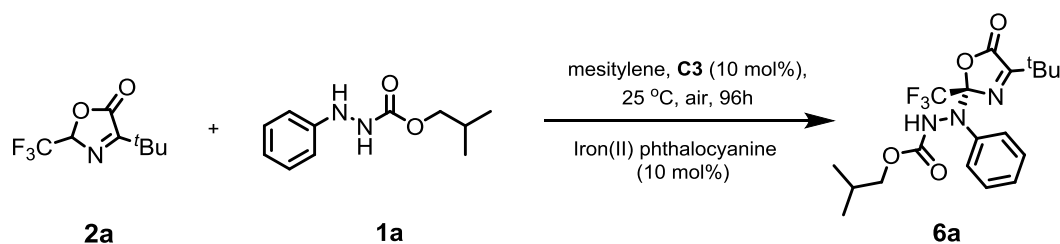


A mixture of tertiary leucine **4a** (0.2 mmol, 2 equiv), Trifluoroacetic anhydride (0.24 mmol, 2.4 equiv) and Dicyclohexylcarbodiimide (DCC) (0.8 mmol, 8 equiv) were dissolved in 1 mL mesitylene and stirred for 8 h at room temperature. Isobutyl 2-phenylazocarboxylate **3a** (0.1 mmol, 1 equiv) and Catalyst **C3** (0.01 mmol, 0.1 equiv) were added in the solvent. The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was monitored by TLC. After suction filtration. Filtrate was evaporated to dryness and purified by silica gel column using eluent: PE/EA (10/1-5/1) to afford **6a**.



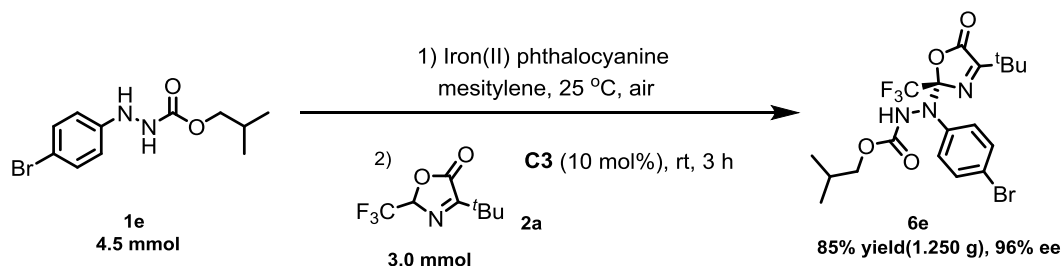
A mixture of tertiary leucine **4a** (0.2 mmol, 2 equiv), Trifluoroacetic anhydride (0.24

mmol, 2.4 equiv), Dicyclohexylcarbodiimide (DCC) (0.8 mmol, 8 equiv), Isobutyl 2-phenylazocarboxylate **3a** (0.1 mmol, 1 equiv) and Catalyst **C3** (0.01 mmol, 0.1 equiv) were dissolved in 1 mL mesitylene and stirred for 96 h at room temperature. The resulting mixture was monitored by TLC. After suction filtration. Filtrate was evaporated to dryness and purified by silica gel column using eluent: PE/EA (10/1-5/1) to afford **6a**.



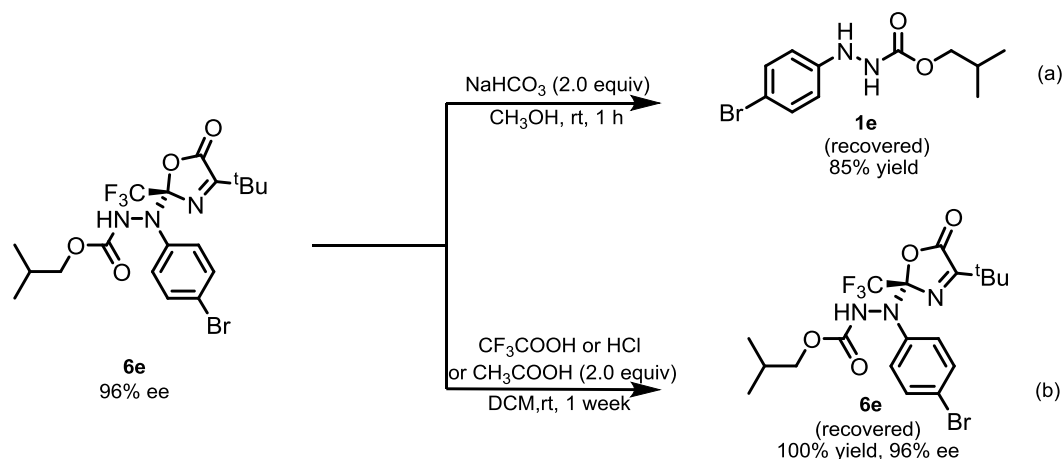
With the presence of Iron(II) phthalocyanine (0.015 mmol, 0.15 equiv), Catalyst **C3** (0.01 mmol, 0.1 equiv), 4-(*tert*-butyl)-2-(trifluoromethyl)oxazol-5(2*H*)-one **2a** (0.1 mmol, 1.0 equiv) and Isobutyl 2-hydrazinecarboxylate **1a** (0.15 mmol, 1.5 equiv) were dissolved in 1 mL mesitylene and stirred for 96 h under an atmosphere of air, at room temperature. The resulting mixture was monitored by TLC and purified by silica gel column using eluent: PE/EA (10/1-5/1) to afford **6a**.

4. Gram-Scale Synthesis of **6e**



Iron(II) phthalocyanine (0.45 mmol, 0.15 equiv) was added to a solution of Isobutyl 2-(4-bromophenyl)hydrazinecarboxylate **1e** (4.5 mmol, 1.5 equiv) in 1 mL mesitylene. The reaction mixture was stirred for 16 h at room temperature and under an atmosphere of air. Catalyst **C3** (0.3 mmol, 0.1 equiv) and 4-(*tert*-butyl)-2-(trifluoromethyl)oxazol-5(2*H*)-one **2a** (3.0 mmol, 1 equiv) were added in the solvent. The reaction mixture was stirred for 10 h at room temperature. The resulting mixture was monitored by TLC and purified by silica gel column using eluent: PE/EA (10/1-5/1) to afford 1.250g **6e** in 85 % yield and 96% ee.

5. Experimental Procedures for Transformations of the Corresponding Products



(a) To a solution of **6e** (0.10 mmol, 1 equiv) in MeOH (1.0 mL), NaHCO_3 (0.20 mmol, 2 equiv) was added. The reaction mixture was stirred for 1 h at room temperature. The excess of solvent were removed under reduced pressure and **1e** was recovered by column chromatography (*silica gel*, PE/EA 5:1–3:1) as white solid in 85% yield. (b) To a solution of **6e** (0.10 mmol, 1 equiv) in CH_2Cl_2 (1.0 mL), HCl (0.50 mmol, 5 equiv) or CF_3COOH (0.50 mmol, 5 equiv) or CH_3COOH (0.50 mmol, 5 equiv) was added respectively. The reaction mixture was stirred for 1 week at room temperature. Structure and enantioselectivity were preserved.

6. Optimization of Reaction Conditions

Table S1. The optimization of the enantioselective organocatalytic amination of 2-(trifluoromethyl)-oxazol-5(2*H*)-one with isobutyl 2-phenylazocarboxylate.

Catalyst structures: Ar = 3,5-(CF₃)₂C₆H₃

C1: X = O
C2: X = S

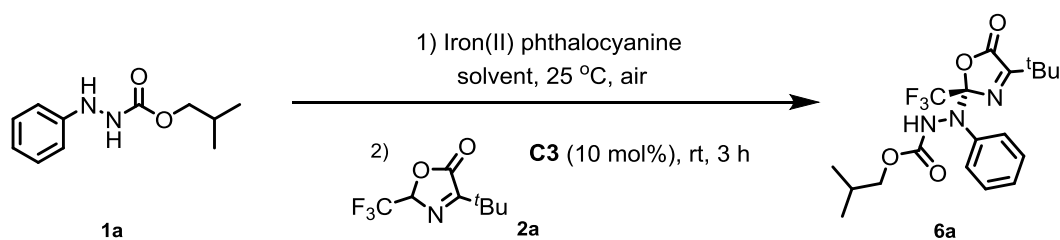
C3

C4

C5: X = O
C6: X = S

Entry ^a	Cat.	Solvent	°C	Time (h)	Yield (%) ^b	Ee (%) ^c
1	C1	toluene	rt	2	91	91
2	C2	toluene	rt	2	81	87
3	C3	toluene	rt	2	92	95
4	C4	toluene	rt	2	90	87
5	C5	toluene	rt	2	73	-95
6	C6	toluene	rt	2	68	-88
7	C3	CH ₂ Cl ₂	rt	2	83	89
8	C3	THF	rt	2	82	74
9	C3	MeCN	rt	2	91	24
10	C3	Et ₂ O	rt	2	86	92
11	C3	C ₆ H ₅ F ₅	rt	2	87	95
12	C3	mesitylene	rt	2	94	96
13	C3	m-xylene	rt	2	91	95
14	C3	PhCl	rt	2	89	93
15	C3	PhCF ₃	rt	2	93	93
16	C3	o-xylene	rt	2	85	93
17	C3	PhBr	rt	2	84	93
18	C3	mesitylene	0	2	62	96
19	C3	mesitylene	35	2	94	93

^aReaction conditions: 1a (0.075 mmol), Cat. (0.005 mmol), 2a (0.05 mmol), solvent (0.5 mL). ^bYield of isolated product. ^cDetermined by HPLC analysis on a chiral stationary phase.

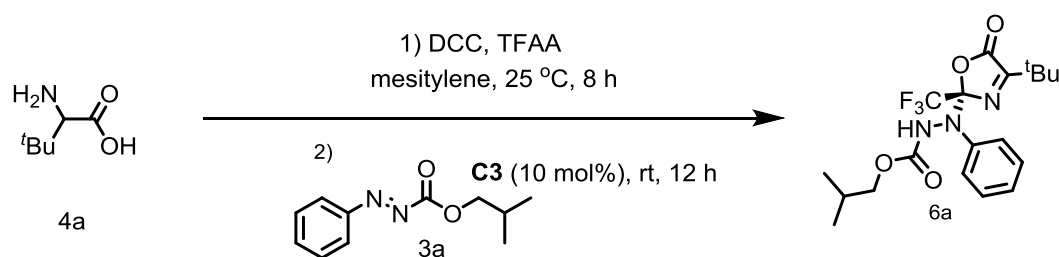
Table S2. The Optimization of the conditions A

Entry ^a	Cat.	Solvent	Time (h) ^c	Yield (%) ^d	Ee (%) ^e
1	Fe(Pc)	CH ₂ Cl ₂	2	83	87
2	Fe(Pc)	THF	2	trance	-
3	Fe(Pc)	MeCN	2	trance	-
4	Fe(Pc)	toluence	2	29	93
5	Fe(Pc)	Et ₂ O	2	27	89
6	Fe(Pc)	mesitylene	2	34	95
7	Fe(Pc)	mesitylene	4	67	95
8	Fe(Pc)	mesitylene	6	78	95
9	Fe(Pc)	mesitylene	8	89	95
10	Fe(Pc) ^b	mesitylene	8	73	95

^aReaction conditions A: step 1) 1a (0.15 mmol), Iron(II) phthalocyanine (0.015 mmol), air, mesitylene (1.0 mL), 25 °C, step 2) 2a (0.10 mmol), C3 (0.01 mmol), 3 h at 25 °C.

^bIron(II) phthalocyanine (0.0075 mmol). ^cTime of step one. ^dYield of isolated product.

^eDetermined by HPLC analysis on a chiral stationary phase. N.A. = not available.

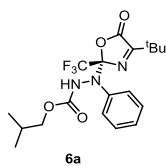
Table S3. The Optimization of the conditions B^a

Entry ^a	4a (eq)	5a (eq)	DCC (eq)	Time (h) ^b	Yield (%) ^c	Ee (%) ^d
1	1.5	1.8	2	1	59	93
2	1.5	1.8	4	1	67	93
3	1.5	1.8	6	1	72	93
4	1.5	1.8	8	1	73	93
5	2	2.4	8	1	82	93
6	2	2.4	8	5	87	93
7	2	2.4	8	8	91	93

^aReaction conditions B: step 1) **4a**, **5a**, DCC, mesitylene (1.0 mL), 8 h at 25 °C, step 2) **C3** (0.01 mmol), **3** (0.10 mmol), 12 h at 25 °C. ^bTime of step one. ^cIsolated yield.

^dDetermined by HPLC analysis on a chiral stationary phase.

7. Characterization of Adducts



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (36.9 mg, 89% yield), 95% ee; Condition B: (37.7 mg, 91% yield), 93% ee; m.p.: 46.2–47.0 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.903 min (minor), 8.313 min (major); 6.990 min (minor), 8.417 min (major);

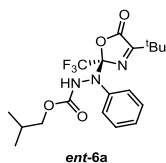
$[\alpha]_{\text{D}}^{18} = -79.2$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.36–7.24 (m, 5H), 7.10 (s, 1H), 4.20–3.66 (m, 2H), 2.15–1.82 (m, 1H), 1.10 (s, 9H), 0.93 (d, J = 6.7 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.2, 161.2, 155.4, 142.5, 129.2, 128.4, 127.0, 120.2 (q, J = 284.5 Hz), 108.0 (d, J = 28.0 Hz), 72.3, 35.1, 28.0, 26.2, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.73.

HRMS (ESI) calcd. for C₁₉H₂₄F₃N₃O₄Na ([M+Na]⁺): 438.1611, found: 438.1607.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (27.8 mg 67% yield), 95% ee; 45.6–46.7 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.890 min (major), 8.433 min (minor);

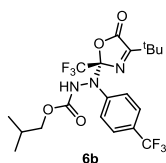
$[\alpha]_{\text{D}}^{20} = 75.4$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.36–7.24 (m, 5H), 7.10 (s, 1H), 4.20–3.66 (m, 2H), 2.15–1.82 (m, 1H), 1.10 (s, 9H), 0.93 (d, J = 6.7 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.2, 161.2, 155.4, 142.5, 129.2, 128.4, 127.0, 120.2 (q, J = 284.5 Hz), 108.0 (d, J = 28.0 Hz), 72.3, 35.1, 28.0, 26.2, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.73.

HRMS (ESI) calcd. for C₁₉H₂₄F₃N₃O₄Na ([M+Na]⁺): 438.1611, found: 438.1607.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (38.6 mg 80% yield), 92% ee; Condition B: (39.6 mg 82% yield), 91% ee; m.p.: 52.2–53.4 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 254 nm, retention time: 5.160 min (minor), 6.043 min (major); 4.970 min (minor), 5.883 min (major);

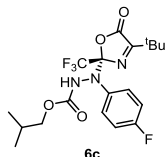
$[\alpha]_D^{21} = -19.5$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.08 (s, 1H), 4.23–3.60 (m, 2H), 2.15–1.75 (m, 1H), 1.17 (s, 9H), 0.90 (dd, J = 6.7, 2.3 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.5, 160.8, 155.1, 145.8, 130.0 (d, J = 32.2 Hz), 126.2 (d, J = 3.8 Hz), 125.8, 123.8 (q, J = 270.3 Hz), 120.3 (q, J = 284.4 Hz), 107.2 (q, J = 32.0 Hz), 72.6, 35.4, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -62.60, -77.01.

HRMS (ESI) calcd. for C₂₀H₂₃F₆N₃O₄Na ([M+Na]⁺): 506.1485, found: 506.1493.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (38.5 mg 89% yield), 95% ee; Condition B: (36.3 mg 84% yield), 92% ee; m.p.: 42.1–43.4 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.787 min (minor), 7.157 min (major); 5.950 min (minor), 7.450 min (major);

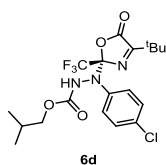
$[\alpha]_D^{21} = -60.0$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.31 (s, 2H), 7.14 (brs, 1H), 7.00 (t, J = 8.4 Hz, 2H), 4.24–3.60 (m, 2H), 1.92 (s, 1H), 1.14 (s, 9H), 0.91 (d, J = 6.8 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.5, 163.0, 161.2 (d, J = 23.6 Hz), 155.4, 138.6, 129.2, 120.2 (q, J = 285.3 Hz), 116.0 (d, J = 22.3 Hz), 108.0 (d, J = 34.4 Hz), 72.4, 35.2, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.76, -112.37.

HRMS (ESI) calcd. for C₁₉H₂₃F₄N₃O₄Na ([M+Na]⁺): 456.1517, found: 456.1498.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (37.7 mg 84% yield), 95% ee; Condition B: (39.0 mg 87% yield), 92% ee; m.p.: 40.1–41.7 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.867 min (minor), 7.240 min (major); 5.933 min (minor), 7.310 min (major);

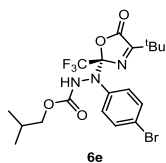
$[\alpha]_D^{22} = -12.6$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.33–7.26 (m, 3H), 7.25 (brs, 1H), 6.94 (s, 1H), 4.07–3.71 (m, 2H), 1.91 (s, 1H), 1.15 (s, 9H), 0.91 (dd, J = 6.9, 2.9 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.5, 161.0, 155.2, 141.1, 134.1, 129.3, 128.3, 120.2 (q, J = 285.0 Hz), 107.7 (d, J = 28.1 Hz), 72.4, 35.3, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.80.

HRMS (ESI) calcd. for C₁₉H₂₃ClF₃N₃O₄Na ([M+Na]⁺): 472.1221, found: 472.1204.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (42.9 mg 87% yield), 94% ee; Condition B: (40.9 mg 83% yield), 91% ee; m.p.: 56.1–57.2 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.170 min (minor), 7.717 min (major); 6.403 min (minor), 8.043 min (major);

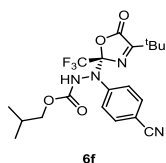
$[\alpha]_D^{22} = -6.3$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.48–7.42 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.89 (s, 1H), 4.20–3.47 (m, 2H), 2.08–1.81 (m, 1H), 1.16 (s, 9H), 0.91 (dd, J = 6.7, 1.8 Hz, 6H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.5, 161.0, 155.4, 141.7, 132.3, 128.5, 121.9, 120.2 (q, J = 284.0 Hz), 107.6 (d, J = 33.0 Hz), 72.5, 35.3, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.79.

HRMS (ESI) calcd. for C₁₉H₂₃BrF₃N₃O₄Na ([M+Na]⁺): 516.0716, found: 516.0702.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; Condition A: (38.7 mg 88% yield), 92% ee; Condition B: (36.1 mg 82% yield), 89% ee;

HPLC CHIRALPAK IF, n-Hexane/2-propanol = 90/10, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.320 min (major), 6.790 min (minor); 6.297 min (major), 6.803 min (minor);

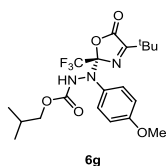
$[\alpha]_D^{19} = -63.1$ (c 1.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 7.61 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.37–7.07 (m, 1H), 3.88 (dd, J = 18.7, 5.6 Hz, 2H), 1.98–1.79 (m, 1H), 1.23 (s, 9H), 0.89 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.5, 160.5, 155.5, 146.9, 133.0, 124.0, 120.4 (d, J = 289.2 Hz), 118.4, 109.8, 106.6 (d, J = 31.2 Hz), 72.7, 35.5, 28.0, 26.4, 19.0, 18.9.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -77.39.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{23}\text{F}_3\text{N}_4\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 463.1564, found: 463.1547.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; Condition A: (23.6 mg 53% yield), 90% ee; Condition B: (27.6 mg 62% yield), 89% ee;

HPLC HPLC CHIRALPAK NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 10.710 min (minor), 13.727 min (major); 11.143 min (minor), 14.240 min (major);

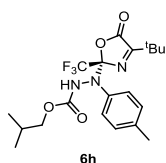
$[\alpha]_D^{22} = -21.2$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, J = 8.3 Hz, 2H), 6.89 (s, 1H), 6.86–6.75 (m, 2H), 4.01–3.81 (m, 2H), 3.77 (s, 3H), 2.04–1.82 (m, 1H), 1.13 (s, 9H), 0.92 (d, J = 6.7 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.2, 161.4, 159.5, 155.3, 135.4, 128.7, 120.2 (q, J = 284.4 Hz), 108.4 (d, J = 24.2 Hz), 72.2, 55.6, 35.1, 28.0, 26.3, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.55.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 468.1717, found: 468.1694.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (32.6 mg 76% yield), 94% ee; Condition B: (35.6 mg 83% yield), 91% ee; m.p.: 43.4–44.7 °C;

HPLC CHIRALPAK IG, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.900 min (minor), 9.183 min (major); 7.883 min (minor), 9.210 min (major);

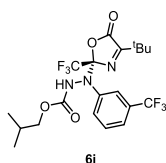
$[\alpha]_D^{21} = -14.4$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.16 (s, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.84 (s, 1H), 4.25–3.56 (m, 2H), 2.30 (s, 3H), 1.92 (s, 1H), 1.10 (s, 9H), 0.92 (d, J = 6.5 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.2, 161.3, 155.2, 140.0, 138.5, 129.7, 127.0, 120.2 (q, J = 284.4 Hz), 108.2 (d, J = 35.1 Hz), 72.3, 35.1, 28.0, 26.3, 21.1, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.61.

HRMS (ESI) calcd. for C₂₀H₂₆F₃N₃O₄Na ([M+Na]⁺): 452.1768, found: 452.1747.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (39.6 mg 82% yield), 95% ee; Condition B: (42.0 mg 87% yield), 93% ee;

HPLC CHIRALPAK IH, n-Hexane/2-propanol = 95/5, flow rate = 1 mL/min, λ = 220 nm, retention time: 4.513 min (minor), 5.610 min (major); 4.320 min (minor), 5.438 min (major);

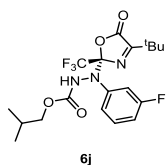
$[\alpha]_D^{23} = -62.8$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1H), 7.52 (d, J = 7.8 Hz, 2 H), 7.48–7.42 (m, 1H), 7.05 (s, 1H), 4.10–3.70 (m, 2H), 2.05–1.82 (m, 1H), 1.14 (s, 9H), 0.91 (dd, J = 6.7, 2.4 Hz, 6H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.7, 160.8, 155.8, 143.2, 131.7 (q, J = 33.0 Hz), 129.8, 129.5, 124.6 (d, J = 3.9 Hz), 123.8, 123.6 (d, J = 270.8 Hz), 120.2 (d, J = 285.0 Hz), 107.4 (d, J = 32.3 Hz), 72.6, 35.3, 28.0, 26.2, 19.0, 18.9.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -62.84, -76.92.

HRMS (ESI) calcd. for C₂₀H₂₃F₆N₃O₄Na ([M+Na]⁺): 506.1485, found: 506.1465.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (36.3 mg 84% yield), 95% ee; Condition B: (37.2 mg 86% yield), 91% ee; m.p.: 38.6–41.1 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.327 min (minor), 6.037 min (major); 5.407 min (minor), 6.163 min (major);

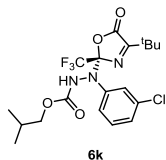
$[\alpha]_{\text{D}}^{19} = -37.5$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.34–7.24 (m, 1H), 7.23–7.02 (m, 3H), 6.98 (td, J = 8.3, 2.5 Hz, 1H), 4.01–3.80 (m, 2H), 2.05–1.86 (m, 1H), 1.16 (s, 9H), 0.92 (dd, J = 6.7, 2.0 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.4, 163.5, 161.9, 161.0, 155.3, 144.1 (d, J = 9.2 Hz), 130.2 (d, J = 8.8 Hz), 122.0, 120.2 (q, J = 285.2 Hz), 115.1 (d, J = 20.8 Hz), 114.2 (d, J = 22.9 Hz), 107.5 (d, J = 32.3 Hz), 72.5, 35.3, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.99, -111.00.

HRMS (ESI) calcd. for C₁₉H₂₃F₄N₃O₄Na ([M+Na]⁺): 456.1517, found: 456.1506.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (38.1 mg 85% yield), 95% ee; Condition B: (36.8 mg 82% yield), 91% ee; m.p.: 65.1–66.2 °C;

HPLC CHIRALPAK IA, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 4.990 min (minor), 5.567 min (major); 4.833 min (minor), 5.397 min (major);

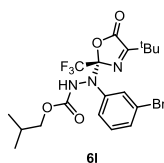
$[\alpha]_{\text{D}}^{20} = -79.4$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.28–7.10 (m, 4H), 4.30–3.60 (m, 2H), 2.20–1.83 (m, 1H), 1.14 (s, 9H), 0.92 (d, J = 6.8 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.5, 161.0, 155.7, 143.7, 134.6, 130.1, 128.2, 127.2, 124.5, 120.2 (q, J = 284.6 Hz), 108.0 (d, J = 33.6 Hz), 72.5, 35.3, 28.0, 26.3, 19.0, 18.9.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.87.

HRMS (ESI) calcd. for C₁₉H₂₃ClF₃N₃O₄Na ([M+Na]⁺): 472.1221, found: 472.1208.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (40.9 mg 83% yield), 94% ee; Condition B: (41.9 mg 85% yield), 93% ee; m.p.: 49.3–52.5 °C;

HPLC CHIRALPAK IA, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.047 min (minor), 5.670 min (major); 4.967 min (minor), 5.583 min (major);

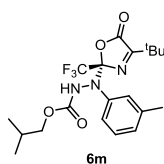
$[\alpha]_D^{22} = -47.8$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.43–7.36 (m, 1H), 7.31–7.01 (m, 3H), 4.05–3.67 (m, 2H), 2.08–1.80 (m, 1H), 1.15 (s, 9H), 0.92 (d, J = 6.1 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.5, 161.0, 155.2, 143.8, 131.2, 130.4, 130.1, 125.0, 122.4, 120.2 (q, J = 284.6 Hz), 107.5 (d, J = 32.2 Hz), 72.5, 35.3, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.85.

HRMS (ESI) calcd. for C₁₉H₂₃BrF₃N₃O₄Na ([M+Na]⁺): 516.0716, found: 516.0711.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (31.3 mg 73% yield), 94% ee; Condition B: (34.3 mg 80% yield), 90% ee; m.p.: 45.7–46.7 °C;

HPLC CHIRALPAK IG, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.727 min (major), 8.920 min (minor); 7.160 min (major), 8.193 min (minor);

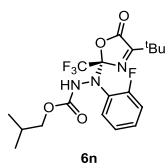
$[\alpha]_D^{22} = -15.0$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.18 (t, J = 7.7 Hz, 1H), 7.15–6.99 (m, 3H), 6.94 (s, 1H), 4.19–3.57 (m, 2H), 2.30 (s, 3H), 1.93 (s, 1H), 1.08 (s, 9H), 0.92 (d, J = 6.7 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.1, 161.3, 155.0, 142.4, 139.2, 129.1, 129.0, 127.8, 123.6, 120.2 (q, J = 284.4 Hz), 108.1 (d, J = 27.7 Hz), 72.3, 35.1, 28.0, 26.2, 21.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.69.

HRMS (ESI) calcd. for C₂₀H₂₆F₃N₃O₄Na ([M+Na]⁺): 452.1768, found: 452.1762.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (34.2 mg 79% yield), 99% ee;
Condition B: (37.2 mg 86% yield), 92% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.170 min (minor), 7.523 min (major); 6.447 min (minor), 7.957 min (major);

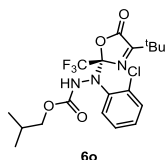
$[\alpha]_{\text{D}}^{20} = -44.0$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 1H), 7.35–7.27 (m, 1H), 7.13 (td, J = 7.7, 1.4 Hz, 1H), 7.10–7.00 (m, 1H), 6.97 (brs, 1H), 4.02–3.73 (m, 2H), 1.93 (s, 1H), 1.14 (s, 9H), 0.93 (d, J = 6.7 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.2, 161.2, 159.0 (d, J = 248.2 Hz), 155.3, 132.1, 130.6 (d, J = 8.5 Hz), 129.9, 124.8, 120.3 (q, J = 284.8 Hz), 116.3 (d, J = 20.7 Hz), 107.1 (d, J = 32.2 Hz), 72.3, 35.2, 28.0, 26.3, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -78.21, -120.04.

HRMS (ESI) calcd. for C₁₉H₂₃F₄N₃O₄Na ([M+Na]⁺): 456.1517, found: 456.1506.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (33.6 mg 75% yield), 98% ee;
Condition B: (37.7 mg 84% yield), 95% ee;

HPLC CHIRALPAK NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.987 min (minor), 7.087 min (major); 6.073 min (minor), 7.187 min (major);

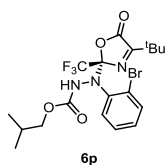
$[\alpha]_{\text{D}}^{17} = -81.6$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.72 (s, 1H), 7.41–7.31 (m, 1H), 7.30–7.26 (m, 1H), 7.12 (brs, 2H), 4.21–3.53 (m, 2H), 1.91 (s, 1H), 1.15 (s, 9H), 0.91 (s, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.0, 161.5, 155.6, 139.7, 133.0, 130.0, 127.6, 120.3 (q, J = 285.2 Hz), 107.2 (d, J = 33.9 Hz), 72.3, 35.2, 28.0, 26.4, 19.1, 19.0.

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -79.13.

HRMS (ESI) calcd. for C₁₉H₂₃ClF₃N₃O₄Na ([M+Na]⁺): 472.1221, found: 472.1206.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (41.4 mg 84% yield), 98% ee;

Condition B: (42.4 mg 86% yield), 96% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 5.993 min (minor), 7.003 min (major); 6.170 min (minor), 7.263 min (major);

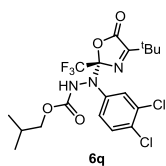
$[\alpha]_{\text{D}}^{21} = -55.6$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.37–7.28 (m, 1H), 7.25–7.06 (m, 2H), 4.05–3.71 (m, 2H), 1.92 (s, 1H), 1.17 (s, 9H), 0.91 (d, J = 6.8 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.1, 161.5, 155.6, 141.1, 133.3, 130.2, 128.2, 120.3 (q, J = 285.3 Hz), 107.2 (d, J = 31.2 Hz), 72.3, 35.2, 28.0, 26.4, 19.0 (two peaks).

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -78.89.

HRMS (ESI) calcd. for C₁₉H₂₃BrF₃N₃O₄Na ([M+Na]⁺): 516.0716, found: 516.0692.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (40.1 mg 83% yield), 95% ee;

Condition B: (41.5 mg 86% yield), 94% ee;

HPLC CHIRALPAK IH, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 4.310 min (minor), 6.513 min (major); 4.337 min (minor), 6.533 min (major);

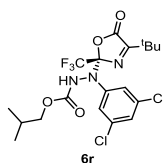
$[\alpha]_{\text{D}}^{21} = -30.3$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.46 (s, 1H), 7.39 (d, J = 8.7 Hz, 1H), 7.21 (s, 1H), 7.04 (s, 1H), 4.04–3.80 (m, 2H), 2.03–1.82 (m, 1H), 1.20 (s, 9H), 0.91 (dd, J = 6.8, 2.7 Hz, 6H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.7, 160.8, 155.3, 142.0, 133.0, 132.1, 130.7, 128.6, 125.6, 120.2 (q, J = 285.2 Hz), 107.3 (d, J = 32.9 Hz), 72.6, 35.4, 28.0, 26.4, 19.0 (two peaks).

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.97.

HRMS (ESI) calcd. for C₁₉H₂₂Cl₂F₃N₃O₄Na ([M+Na]⁺): 506.0832, found: 506.0827.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (41.0 mg 85% yield), 94% ee;

Condition B: (42.5 mg 88% yield), 94% ee;

HPLC CHIRALPAK IH, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 3.710 min (minor), 4.447 min (major); 3.733 min (minor), 4.513 min (major);

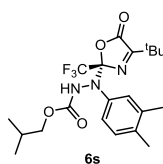
$[\alpha]_D^{23} = -17.7$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.28 (s, 1H), 7.26 (s, 2H), 7.07 (s, 1H), 4.00–3.85 (m, 2H), 2.05–1.85 (m, 1H), 1.24 (s, 9H), 0.94 (dd, $J = 6.8, 1.9$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.7, 160.7, 155.0, 144.5, 135.3, 127.7, 124.4, 120.2 (d, $J = 283.9$ Hz), 107.0 (d, $J = 33.0$ Hz), 72.7, 35.5, 28.0, 26.4, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -77.08.

HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 506.0832, found: 506.0827.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (34.5 mg 78% yield), 96% ee;

Condition B: (35.0 mg 79% yield), 94% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 6.247 min (minor), 7.213 min (major); 6.143 min (minor), 7.127 min (major);

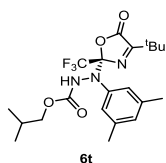
$[\alpha]_D^{21} = -23.1$ (c 1.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 7.05 (d, $J = 8.0$ Hz, 2H), 6.98 (s, 1H), 6.83 (s, 1H), 4.06–3.69 (m, 2H), 2.20 (s, 6H), 1.92 (s, 1H), 1.09 (s, 9H), 0.92 (d, $J = 6.7$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.1, 161.4, 155.5, 140.1, 137.6, 137.1, 130.2, 128.3, 124.0, 120.2 (q, $J = 284.4$ Hz), 108.3 (d, $J = 31.0$ Hz), 72.2, 35.1, 28.0, 26.2, 19.8, 19.5, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.58.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 466.1924, found: 466.1915.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (33.7 mg 76% yield), 95% ee; Condition B: (35.9 mg 81% yield), 91% ee;

HPLC CHIRALPAK IH, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 4.063 min (minor), 5.247 min (major); 4.013 min (minor), 5.173 min (major);

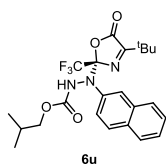
$[\alpha]_{\text{D}}^{23} = -11.8$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.02–6.60 (m, 4H), 4.05–3.74 (m, 2H), 2.26 (s, 6H), 2.02–1.85 (m, 1H), 1.09 (s, 9H), 0.92 (d, J = 5.8 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 176.0, 161.4, 155.5, 142.3, 139.0, 129.9, 124.5, 120.3 (d, J = 284.5 Hz), 108.2 (d, J = 32.4 Hz), 72.2, 35.1, 28.0, 26.2, 21.2, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -76.71.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 466.1924, found: 466.1903.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; Condition A: (37.4 mg 82% yield), 96% ee; Condition B: (39.2 mg 86% yield), 93% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.807 min (minor), 9.443 min (major); 7.670 min (minor), 9.283 min (major);

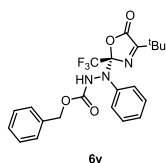
$[\alpha]_{\text{D}}^{18} = -14.0$ (c 1.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 8.00–7.63 (m, 4H), 7.55–7.47 (m, 2H), 7.38 (s, 1H), 6.96 (s, 1H), 4.17–3.62 (m, 2H), 1.93 (s, 1H), 1.02 (s, 9H), 0.92 (d, J = 6.4 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.3, 161.2, 155.4, 139.8, 133.2, 132.7, 129.1, 128.2, 127.7, 126.9, 125.7, 124.6, 120.3 (q, J = 284.9 Hz), 108.1 (d, J = 34.4 Hz), 72.3, 35.1, 28.0, 26.2, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.73.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 488.1768, found: 488.1756.



Eluent: PE/EA (5/1-3/1); Colorless oil; Condition A: (37.7 mg 84% yield), 95% ee;

Condition B: (39.9 mg 89% yield), 91% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 210 nm, retention time: 10.557 min (minor), 12.090 min (major); 11.320 min (minor), 12.647 min (major);

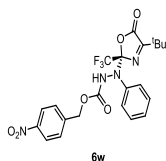
$[\alpha]_{\text{D}}^{24} = -75.1$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.37–7.23 (m, 10H), 7.13 (s, 1H), 5.15 (s, 2H), 1.09 (s, 9H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.3, 161.2, 155.0, 142.4, 135.8, 129.2, 128.6, 128.4, 128.2, 127.0, 120.3 (q, J = 284.6 Hz), 108.0 (d, J = 32.3 Hz), 67.9, 35.1, 26.2.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.64.

HRMS (ESI) calcd. for C₂₂H₂₂F₃N₃O₄Na ([M+Na]⁺): 472.1455, found: 472.1440.



Eluent: PE/EA (5/1-2/1); Colorless oil; Condition A: (45.4 mg 92% yield), 97% ee;

Condition B: (43.9 mg 89% yield), 93% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm, retention time: 8.457 min (minor), 10.987 min (major); 8.148 min (minor), 10.515 min (major);

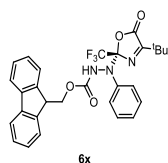
$[\alpha]_{\text{D}}^{18} = -66.8$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 8.29–8.10 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.36–7.23 (m, 6H), 7.15 (s, 1H), 5.60–4.81 (m, 2H), 1.07 (s, 9H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.5, 161.0, 154.7, 147.9, 143.1, 142.3, 129.3, 128.6, 128.3, 126.9, 123.9, 120.2 (q, J = 284.6 Hz), 107.7 (d, J = 30.7 Hz), 66.3, 35.2, 26.2.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.74.

HRMS (ESI) calcd. for C₂₂H₂₁F₃N₄O₆Na ([M+Na]⁺): 517.1305, found: 517.1300.



Eluent: PE/EA (5/1-2/1); Colorless oil; Condition A: (46.7 mg 87% yield), 94% ee;
Condition B: (45.6 mg 85% yield), 93% ee;

HPLC CHIRALPAK IH, n-Hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm, retention time: 4.887 min (minor), 7.373 min (major); 4.787 min (minor), 7.220 min (major);

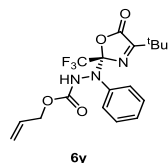
$[\alpha]_D^{20} = -53.8$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 6.9 Hz, 2H), 7.39 (td, J = 7.5, 3.2 Hz, 2H), 7.36–7.27 (m, 6H), 6.96 (s, 1H), 4.60–4.29 (m, 2H), 4.22 (t, J = 7.0 Hz, 1H), 1.10 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 176.3, 161.1, 155.2, 143.7, 142.4, 141.5, 129.2, 128.4, 127.9, 127.2, 126.9, 125.2, 120.3 (q, J = 284.5 Hz), 120.1, 108.0 (d, J = 30.0 Hz), 68.0, 47.2, 35.2, 26.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.63.

HRMS (ESI) calcd. for $\text{C}_{29}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 560.1768, found: 560.1768.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (35.5 mg 89% yield), 95% ee;
Condition B: (35.9 mg 90% yield), 95% ee; m.p.: 47.5–50.1 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.543 min (minor), 8.347 min (major); 7.577 min (minor), 8.270 min (major);

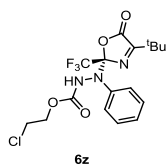
$[\alpha]_D^{21} = -21.8$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.42–7.19 (m, 5H), 7.03 (s, 1H), 6.07–5.72 (m, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.22 (dd, J = 10.4, 1.5 Hz, 1H), 4.90–4.37 (m, 2H), 1.09 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 176.3, 161.2, 154.5, 142.4, 132.1, 129.2, 128.5, 127.0, 120.2 (q, J = 285.1 Hz), 118.5, 108.0 (d, J = 31.9 Hz), 66.7, 35.2, 26.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.67.

HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 422.1298, found: 422.1288.



Eluent: PE/EA (10/1-5/1); Colorless oil; Condition A: (34.9 mg 83% yield), 94% ee;

Condition B: (34.1 mg 81% yield), 90% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 8.247 min (minor), 9.480 min (major); 8.047 min (minor), 9.340 min (major);

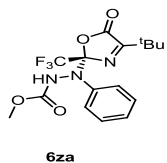
$[\alpha]_{\text{D}}^{22} = -62.4$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.29–7.19 (m, 5H), 7.09 (s, 1H), 4.30 (s, 2H), 3.60 (t, J = 5.7 Hz, 2H), 1.03 (s, 9H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 176.4, 161.1, 154.5, 142.3, 129.3, 128.6, 127.1, 120.2 (q, J = 284.6 Hz), 107.9 (q, J = 32.2 Hz), 65.6, 41.7, 35.2, 26.2.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.67.

HRMS (ESI) calcd. for C₁₇H₁₉F₃N₃O₄Na ([M+Na]⁺): 444.0908, found: 444.0888.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (32.4 mg 87% yield), 94% ee;

Condition B: (28.3 mg 76% yield), 92% ee; m.p.: 50.1–52.2 °C;

HPLC CHIRALPAK IG, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 9.320 min (major), 10.677 min (minor); 8.873 min (major), 10.157 min (minor);

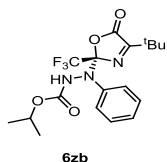
$[\alpha]_{\text{D}}^{19} = -65.8$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.35–7.22 (m, 5H), 7.08 (s, 1H), 3.73 (s, 3H), 1.09 (s, 9H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.3, 161.2, 155.6, 142.4, 129.2, 128.4, 127.0, 120.2 (q, J = 285.1 Hz), 108.0 (d, J = 33.9 Hz), 53.2, 35.1, 26.2.

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.72.

HRMS (ESI) calcd. for C₁₆H₁₈F₃N₃O₄Na ([M+Na]⁺): 396.1142, found: 396.1132.



Eluent: PE/EA (10/1-5/1); White solid; Conditions A: (30.4 mg 76% yield), 96% ee; Conditions B: (31.3 mg 78% yield), 94% ee; m.p.: 38.6–41.1 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.660 min (minor), 9.893 min (major); 7.543 min (minor), 9.790 min (major);

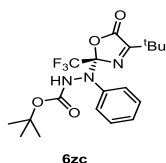
$[\alpha]_D^{22} = -9.6$ (c 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.34–7.23 (m, 5H), 6.84 (s, 1H), 5.04–4.80 (m, 1H), 1.23 (d, J = 6.3 Hz, 6H), 1.09 (s, 9H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.2, 161.3, 154.6, 142.6, 129.2, 128.3, 127.0, 120.2 (q, J = 284.4 Hz), 108.1 (d, J = 31.4 Hz), 70.0, 35.1, 26.2, 22.1, 22.0.

¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -76.68.

HRMS (ESI) calcd. for C₁₈H₂₂F₃N₃O₄Na ([M+Na]⁺): 424.1455, found: 444.1442.



Eluent: PE/EA (10/1-5/1); White solid; Condition A: (14.5 mg 35% yield), 94% ee; Condition B: (19.5 mg 47% yield), 91% ee; m.p.: 46.1–48.1 °C;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 7.410 min (minor), 10.263 min (major); 7.547 min (minor), 10.543 min (major);

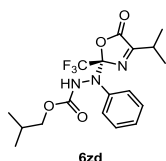
$[\alpha]_D^{22} = -21.3$ (c 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.37–7.17 (m, 5H), 6.72 (s, 1H), 1.44 (s, 9H), 1.09 (s, 9H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 176.1, 161.3, 153.8, 142.7, 129.1, 128.2, 126.9, 120.3 (q, J = 284.9 Hz), 108.1 (d, J = 29.5 Hz), 81.7, 35.1, 28.3, 26.3.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -76.69.

HRMS (ESI) calcd. for C₁₉H₂₄F₃N₃O₄Na ([M+Na]⁺): 438.1611, found: 438.1609.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; (14.4 mg 36% yield), 90% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 8.727 min (minor), 10.347 min (major);

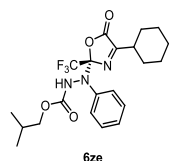
$[\alpha]_{\text{D}}^{18} = -64.5$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.38–7.21 (m, 5H), 7.10 (s, 1H), 4.13–3.64 (m, 2H), 2.84 (s, 1H), 1.92 (s, 1H), 1.12 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 175.0, 162.3, 155.4, 142.5, 129.2, 128.4, 127.0, 120.2 (q, $J = 284.6$ Hz), 109.3 (d, $J = 31.5$ Hz), 72.3, 28.4, 28.0, 19.0 (two peaks), 18.5.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.55.

HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 424.1455, found: 444.1447.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; (18.0 mg 41% yield), 90% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, $\lambda = 220$ nm, retention time: 9.767 min (minor), 10.487 min (major);

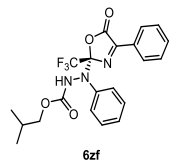
$[\alpha]_{\text{D}}^{19} = -60.4$ (c 1.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.47–6.97 (m, 6H), 4.13–3.56 (m, 2H), 2.78–3.60 (m, 1H), 2.00–1.05 (m, 11H), 0.91 (d, $J = 6.8$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.9, 162.5, 155.8, 142.6, 129.2, 128.3, 127.0, 120.2 (q, $J = 284.7$ Hz), 109.4 (q, $J = 32.7$ Hz), 72.3, 37.3, 28.8, 28.7, 28.0, 25.5, 25.2, 25.1, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.56.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 464.1768, found: 464.1745.



Eluent: PE/EA (10/1-5/1); Pale yellow oil; (20.4 mg 47% yield), 20% ee;

HPLC NuAnalytical-FLM NZ₂, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, $\lambda = 254$ nm, retention time: 11.273 min (major), 12.020 min (minor);

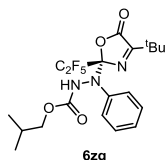
$[\alpha]_{\text{D}}^{21} = -37.5$ (c 1.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 8.25 (s, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.38 (s, 2H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 6.94 (s, 1H), 4.14–3.66 (m, 2H), 1.90 (s, 1H), 0.89 (d, $J = 9.2$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 162.2, 162.0, 155.4, 142.7, 134.5, 129.6, 129.3, 129.1, 128.3, 127.0, 126.8, 120.4 (q, J = 285.5 Hz), 108.6 (d, J = 38.9 Hz), 72.3, 28.0, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -76.21.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 458.1298, found: 458.1298.



Eluent: PE/EA (10/1-5/1); White solid; (40.4 mg 87% yield), 96% ee; m.p.: 44.9–46.8 °C;

HPLC CHIRALPAK IA, n-Hexane/2-propanol = 94/6, flow rate = 1 mL/min, λ = 220 nm, retention time: 4.817 min (minor), 7.733 min (major);

$[\alpha]_{\text{D}}^{23}$ = -26.8 (c 1.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 7.35–7.23 (m, 5H), 6.97 (s, 1H), 4.26–3.63 (m, 2H), 1.92 (s, 1H), 1.08 (s, 9H), 0.92 (d, J = 6.6 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 176.3, 161.2, 155.3, 142.5, 129.2, 128.7 (d, J = 87.4 Hz), 128.4, 127.0, 120.2 (q, J = 284.5 Hz), 108.0 (d, J = 31.4 Hz), 72.3, 35.2, 28.1, 26.3, 19.0 (two peaks).

$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -76.71, -79.33.

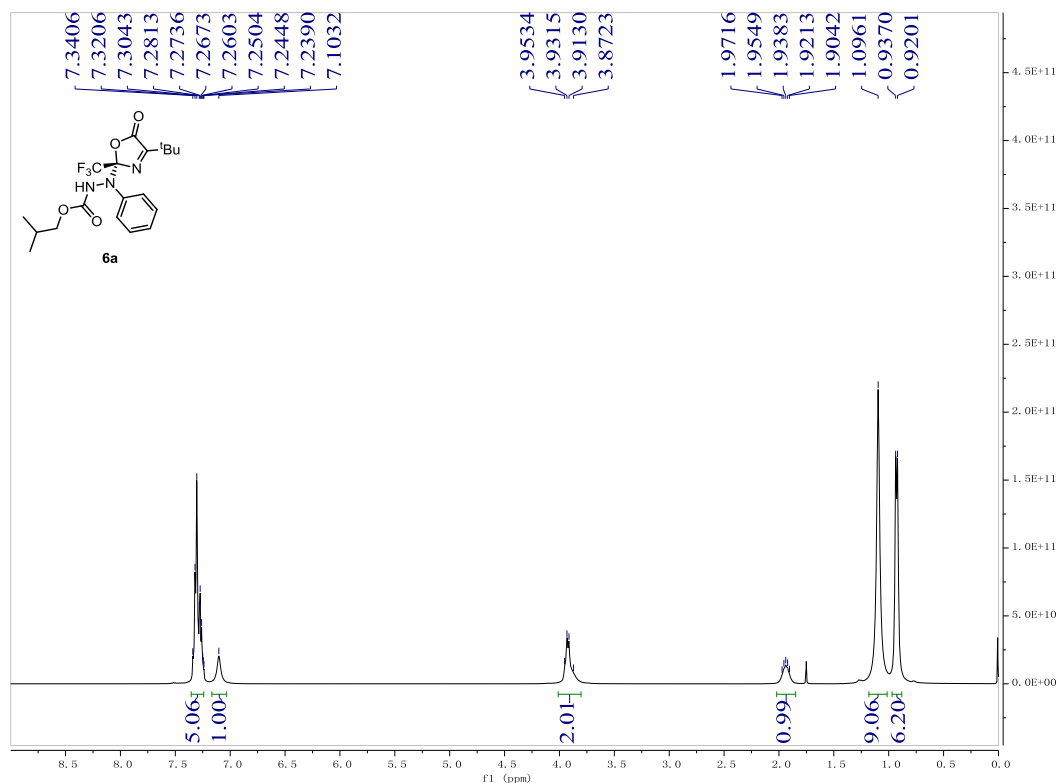
HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{24}\text{F}_5\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 488.1579, found: 488.1591.

8. References

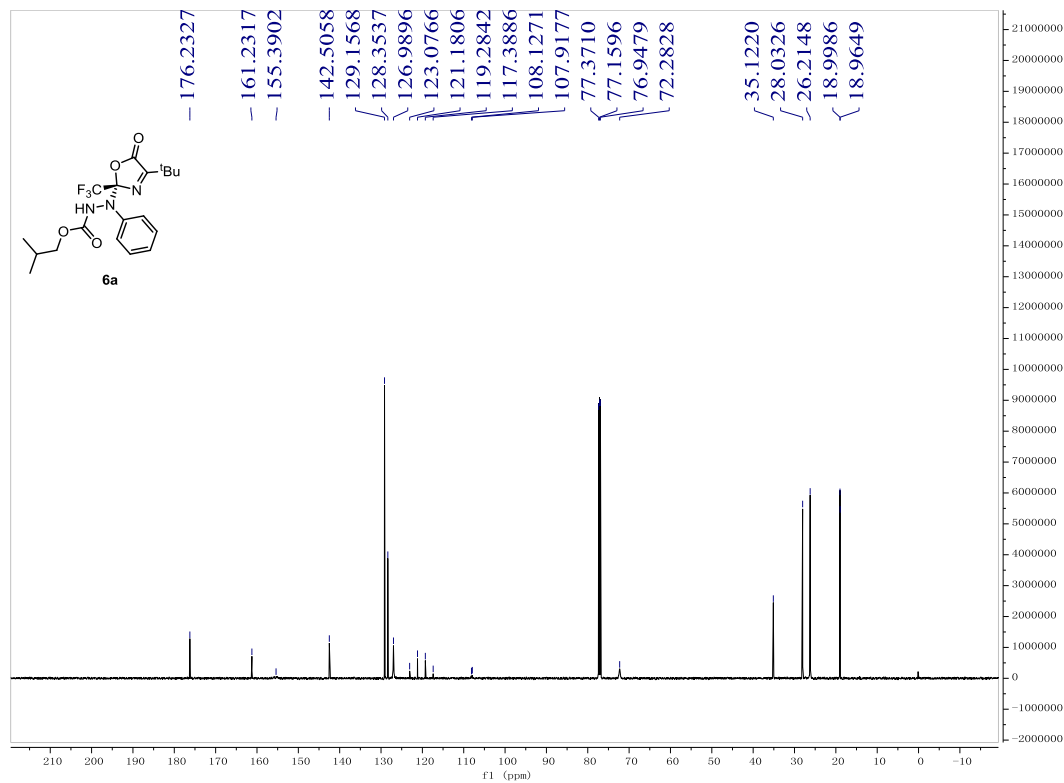
1. L. Li, T. Yang, T. Zhang, B. Zhu and J. Chang, Organocatalytic asymmetric tandem cyclization/michael addition via oxazol-5(2*H*)-one formation: access to perfluoroalkyl-containing *N,O*-acetal derivatives. *J. Org. Chem.*, 2020, **85**, 12294.
2. L. Li, B. Zhu, H. Fan and Z. Jiang, Direct organocatalytic asymmetric michael reaction of fluorine hemiaminal-type nucleophile to 4-nitro-5-styrylisoxazoles. *Org. Chem. Front.*, 2020, **7**, 1343.
3. T. Hashimoto, D. Hirose and T. Taniguchi, Catalytic aerobic oxidation of arylhydrazides with Iron phthalocyanine. *Adv. Synth. Catal.*, 2015, **357**, 14.
4. W. Li, H. Yuan, Y. Li and X. Li, Asymmetric synthesis of atropisomeric pyrazole via an enantioselective reaction of azonaphthalene with pyrazolone. *Chem. Commun.*, 2019, **55**, 84.
5. L. W. Qi, J. H. Mao, Z. Jian and B. Tan, Organocatalytic asymmetric arylation of indoles enabled by azo groups. *Nat. Chem.*, 2018, **10**, 58.

9. Copies of NMR Spectra of the Adducts

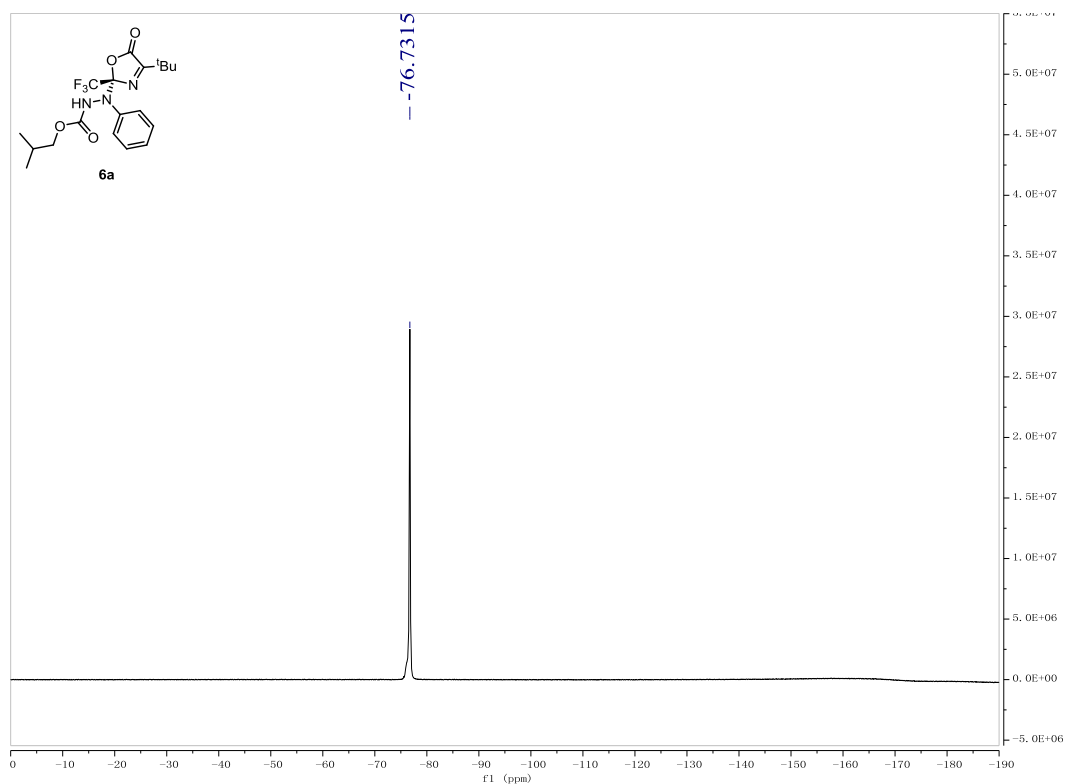
^1H NMR of 6a (400 MHz, CDCl_3)



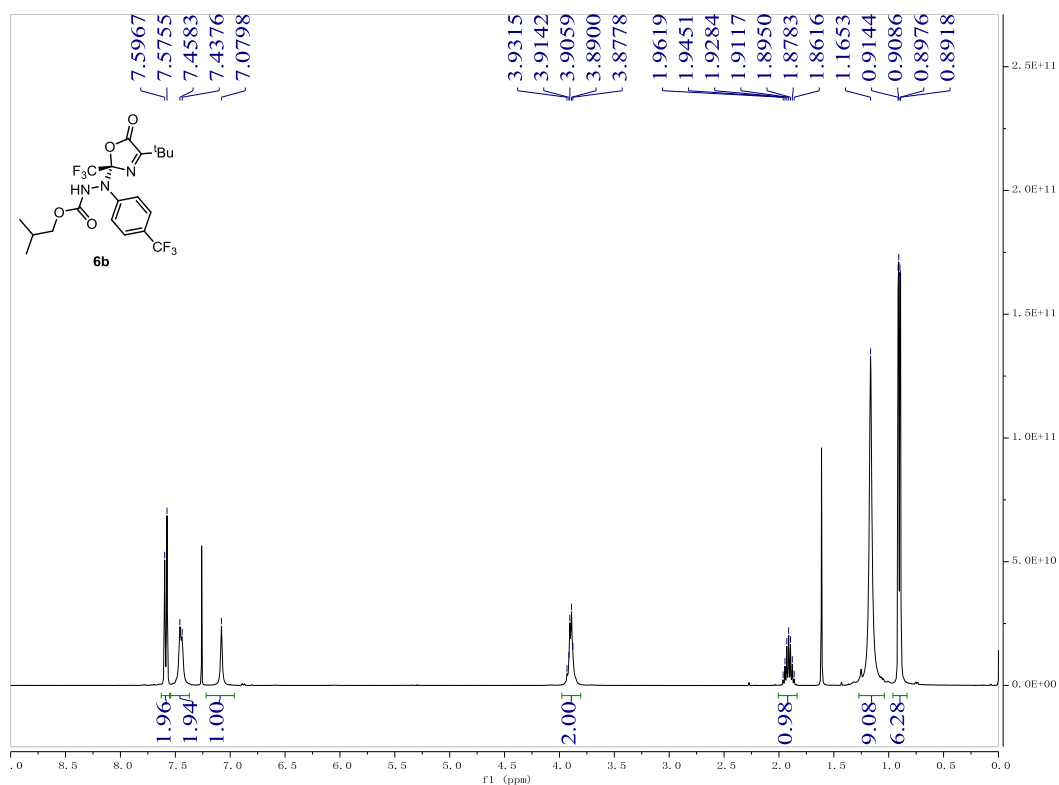
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6a (150 MHz, CDCl_3)



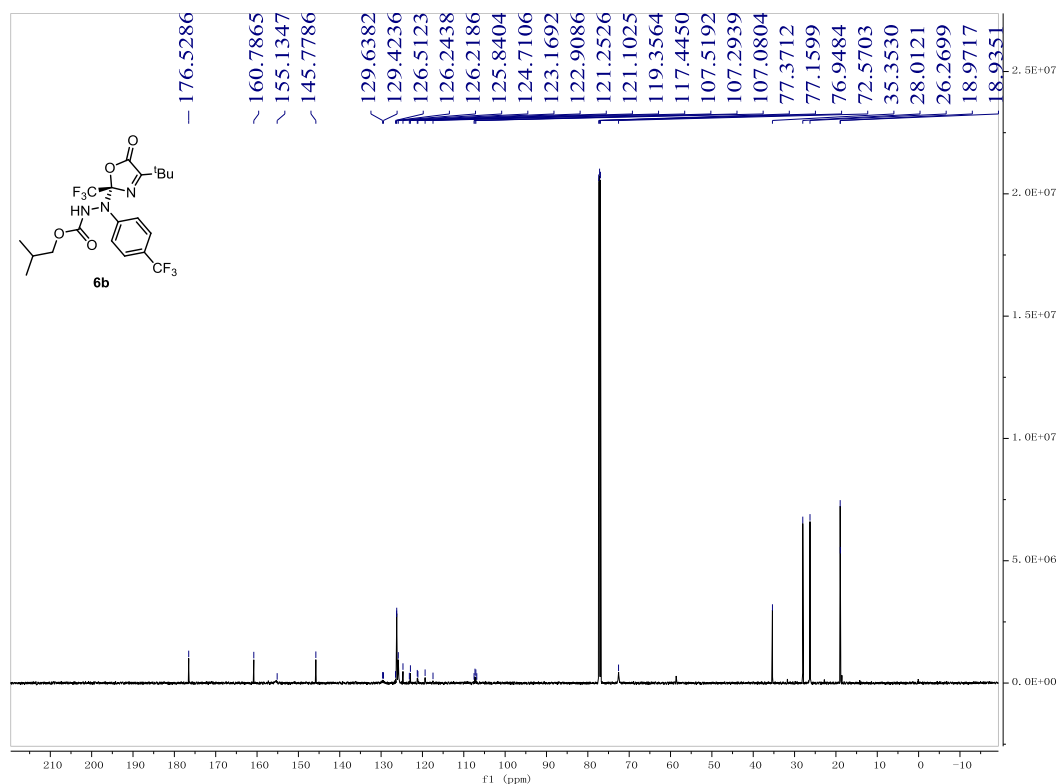
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6a (564 MHz, CDCl_3)



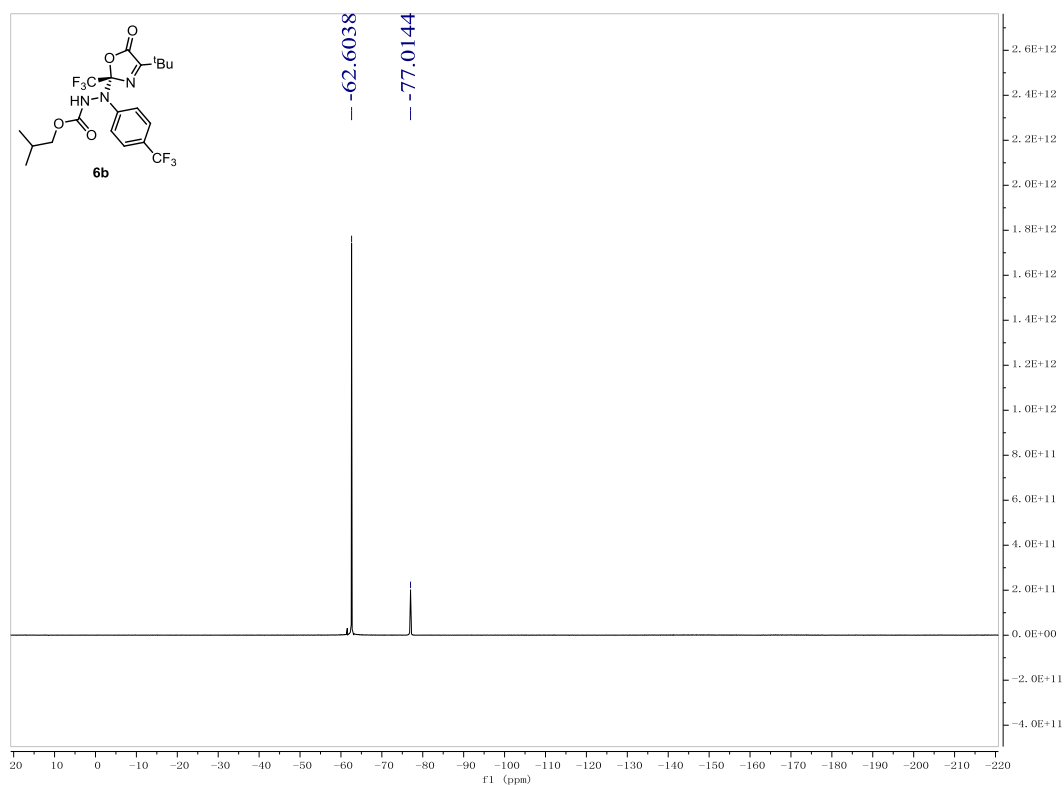
^1H NMR of 6b (400 MHz, CDCl_3)



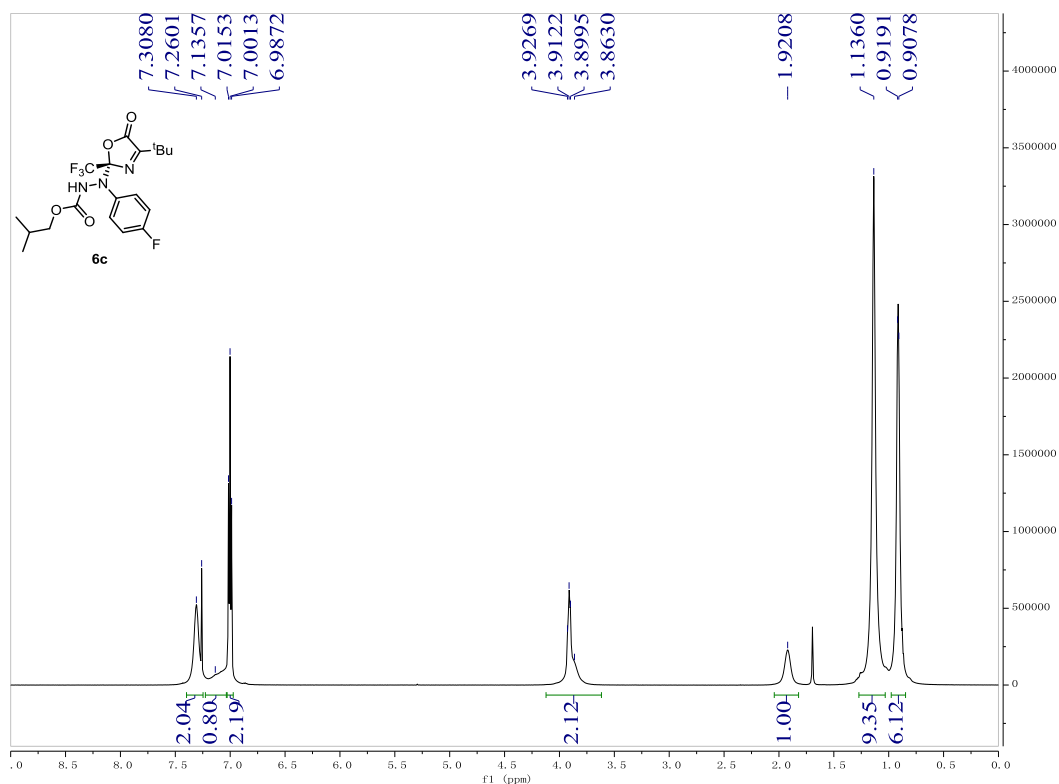
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6b (150 MHz, CDCl_3)



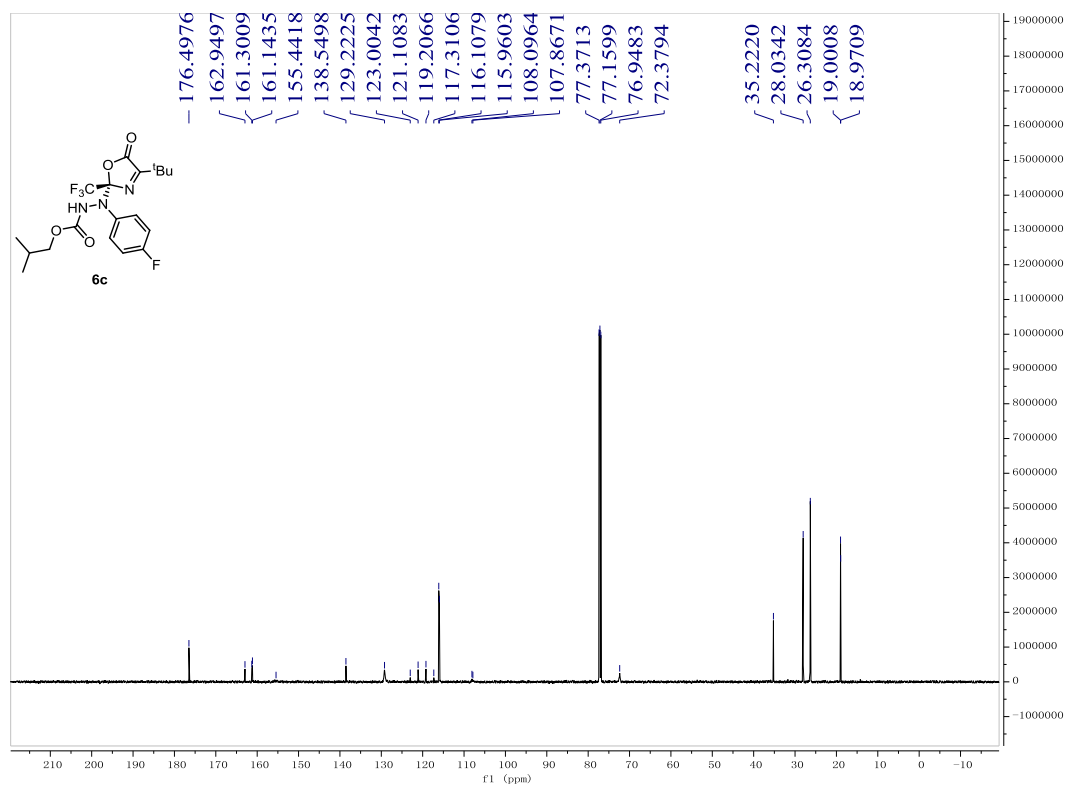
¹⁹F{¹H} NMR of 6b (376 MHz, CDCl₃)



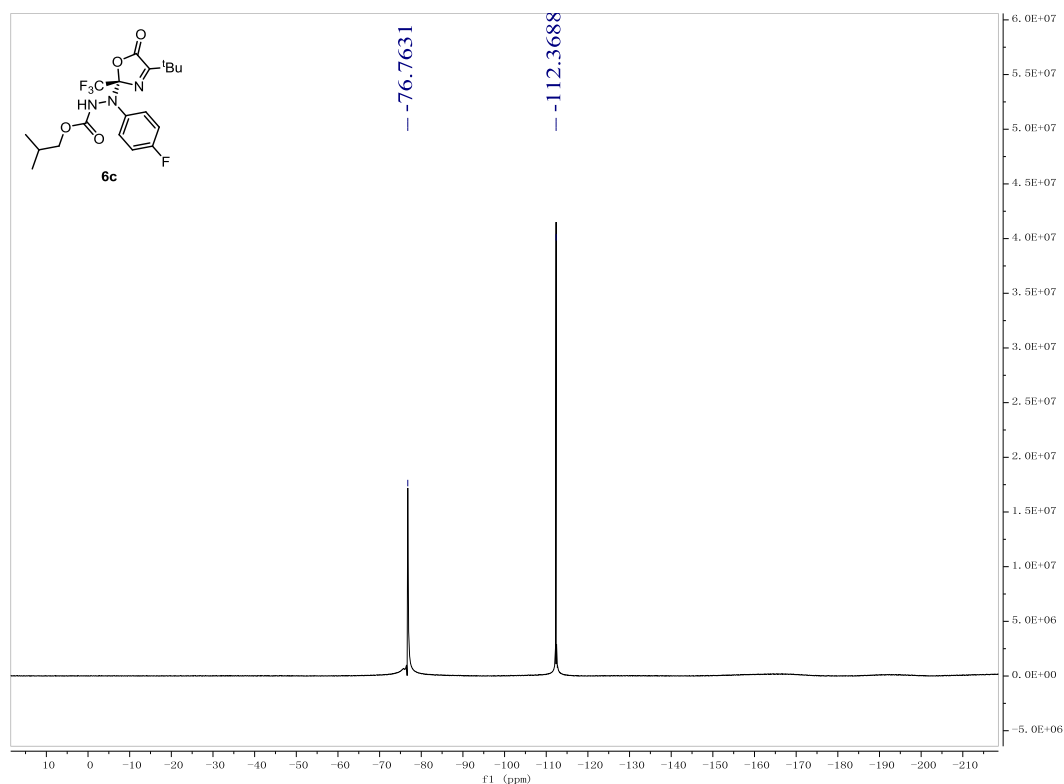
¹H NMR of 6c (600 MHz, CDCl₃)



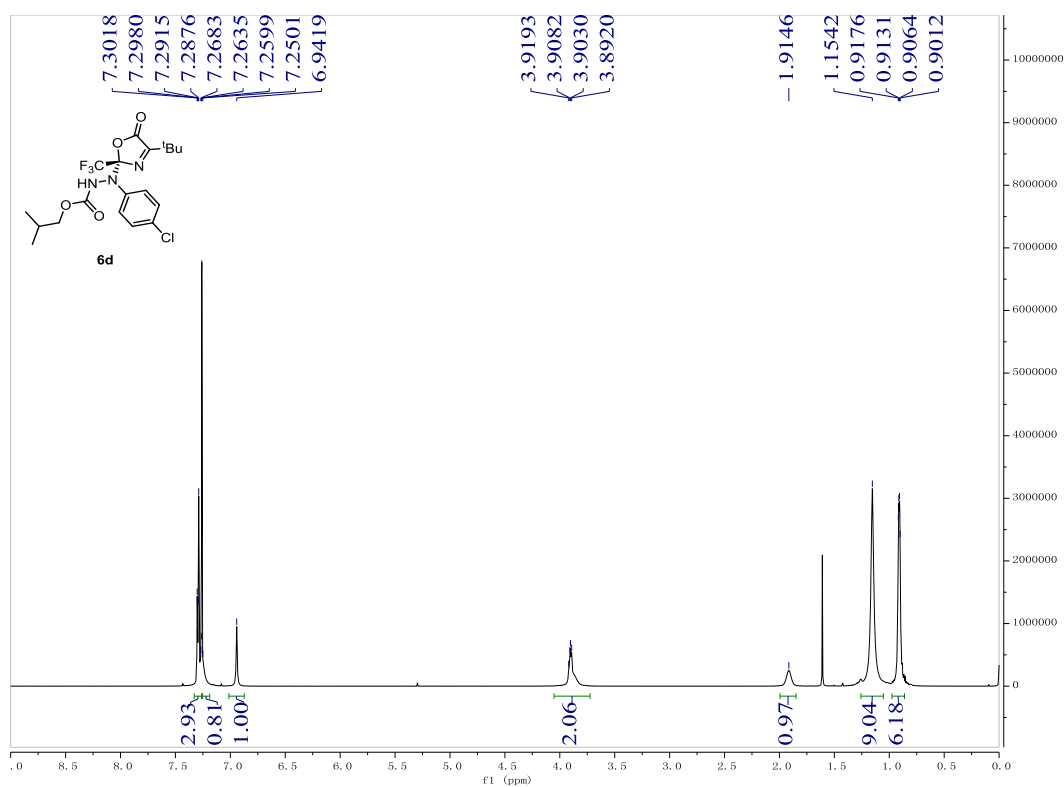
¹³C{¹H} NMR of 6c (150 MHz, CDCl₃)



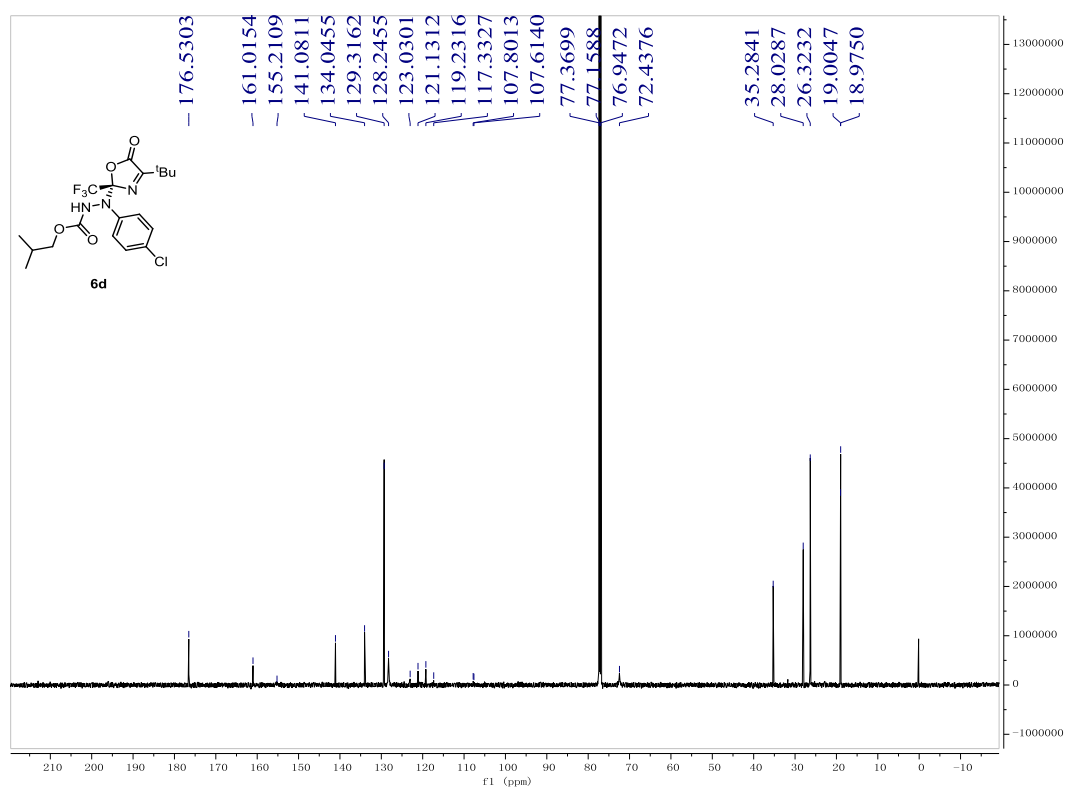
¹⁹F{¹H} NMR of 6c (564 MHz, CDCl₃)



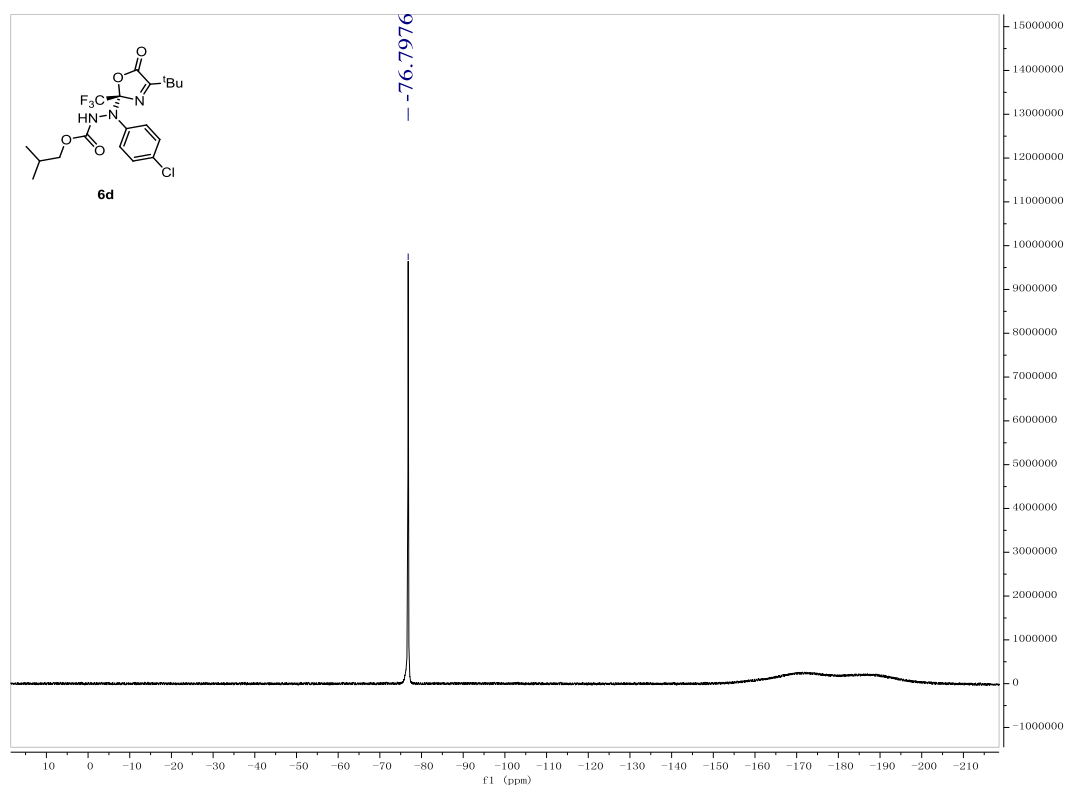
¹H NMR of 6d (600 MHz, CDCl₃)



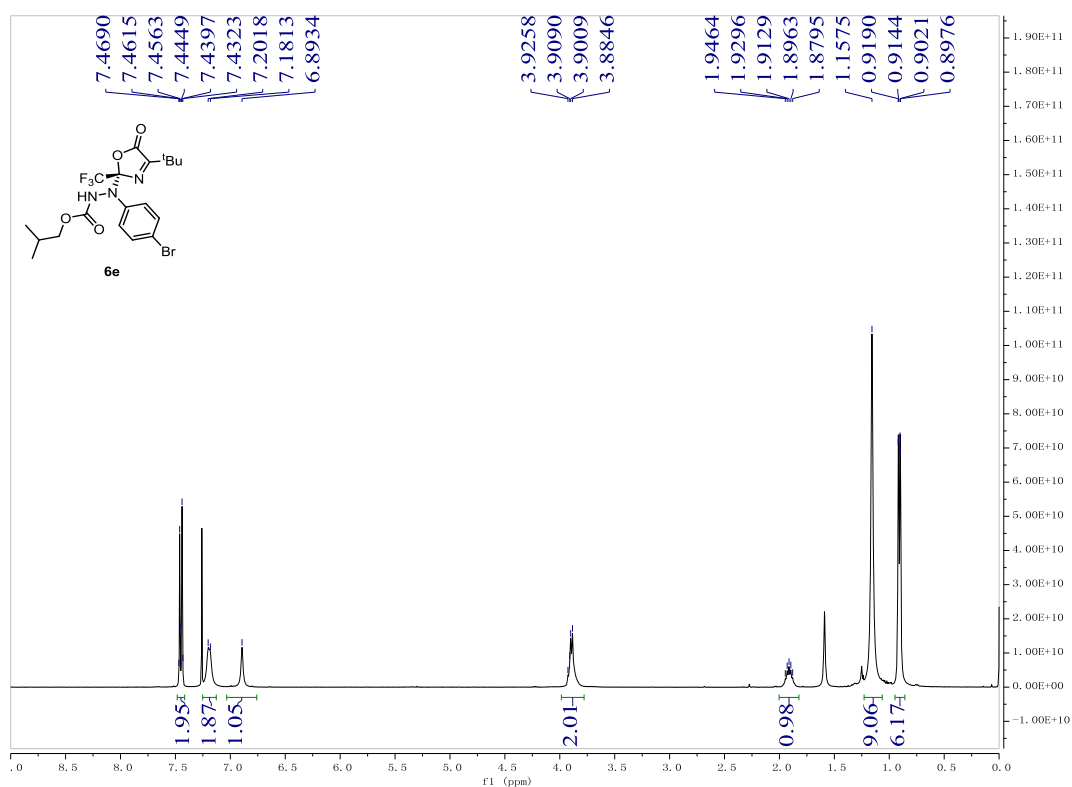
¹³C{¹H} NMR of 6d (150 MHz, CDCl₃)



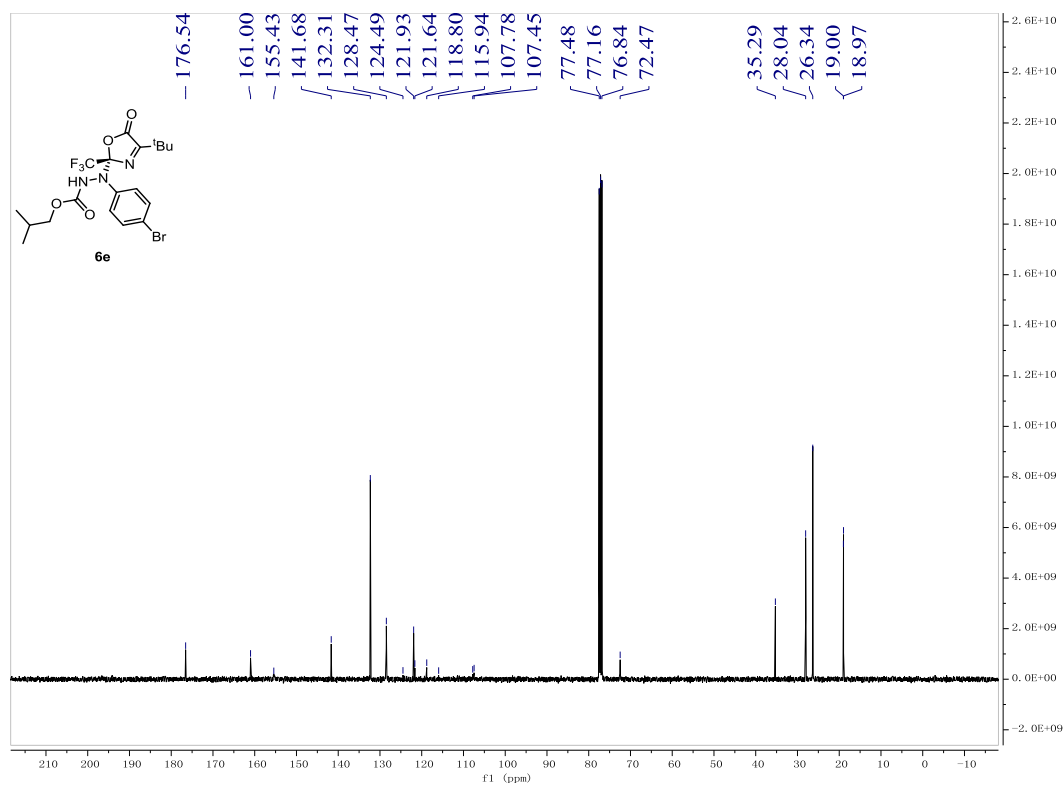
¹⁹F{¹H} NMR of 6d (564 MHz, CDCl₃)



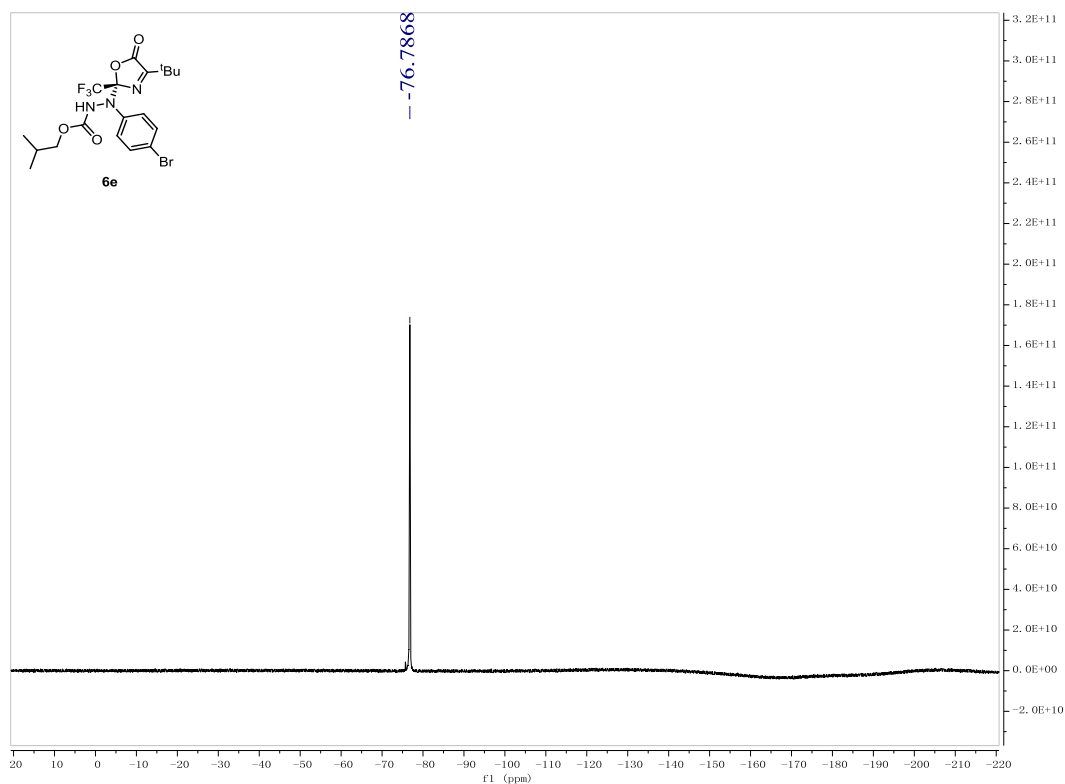
¹H NMR of 6e (400 MHz, CDCl₃)



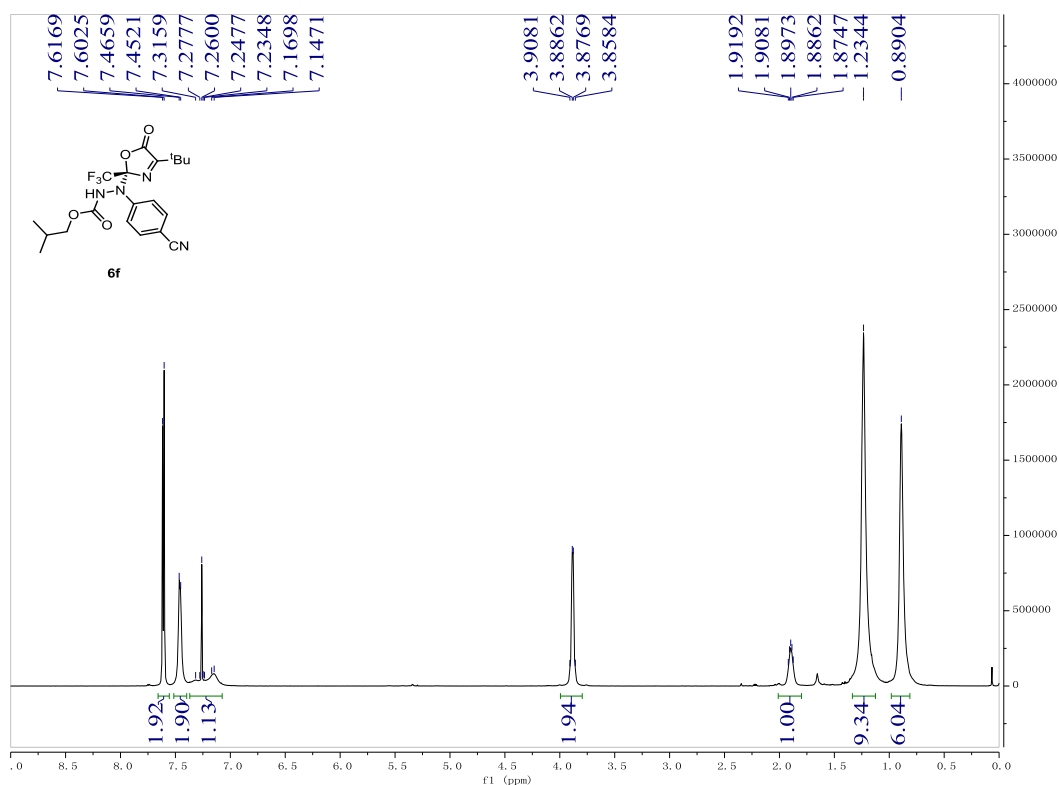
¹³C{¹H} NMR of 6e (100 MHz, CDCl₃)



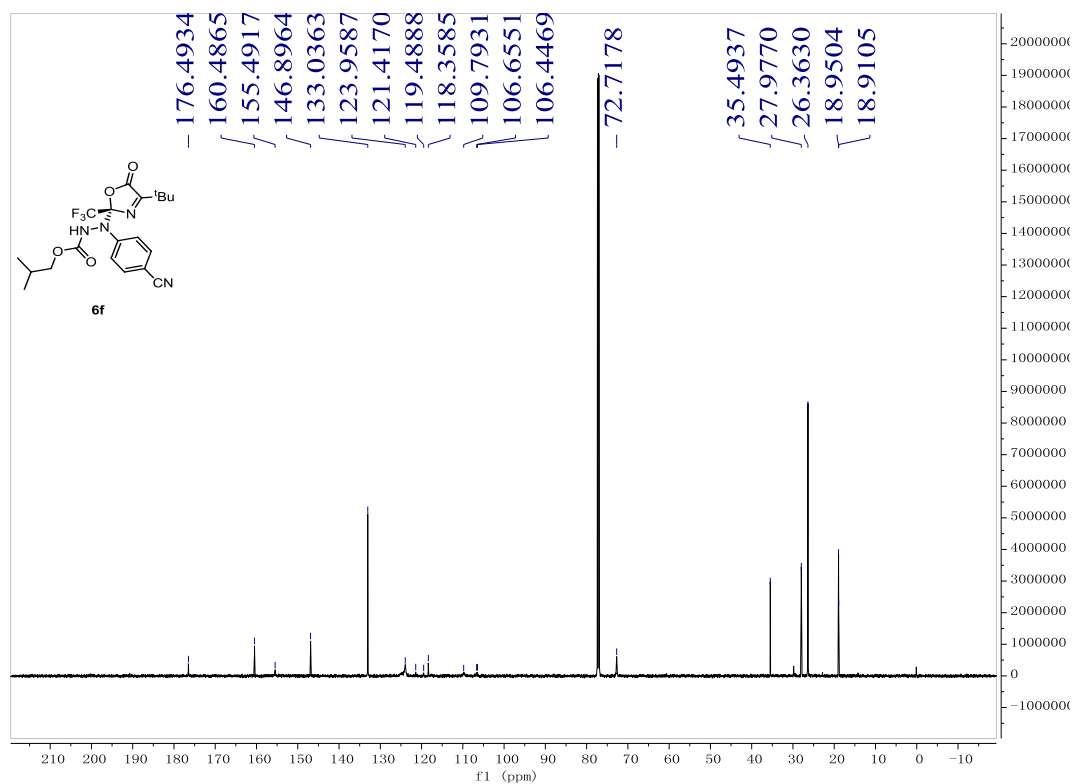
¹⁹F{¹H} NMR of 6e (376 MHz, CDCl₃)



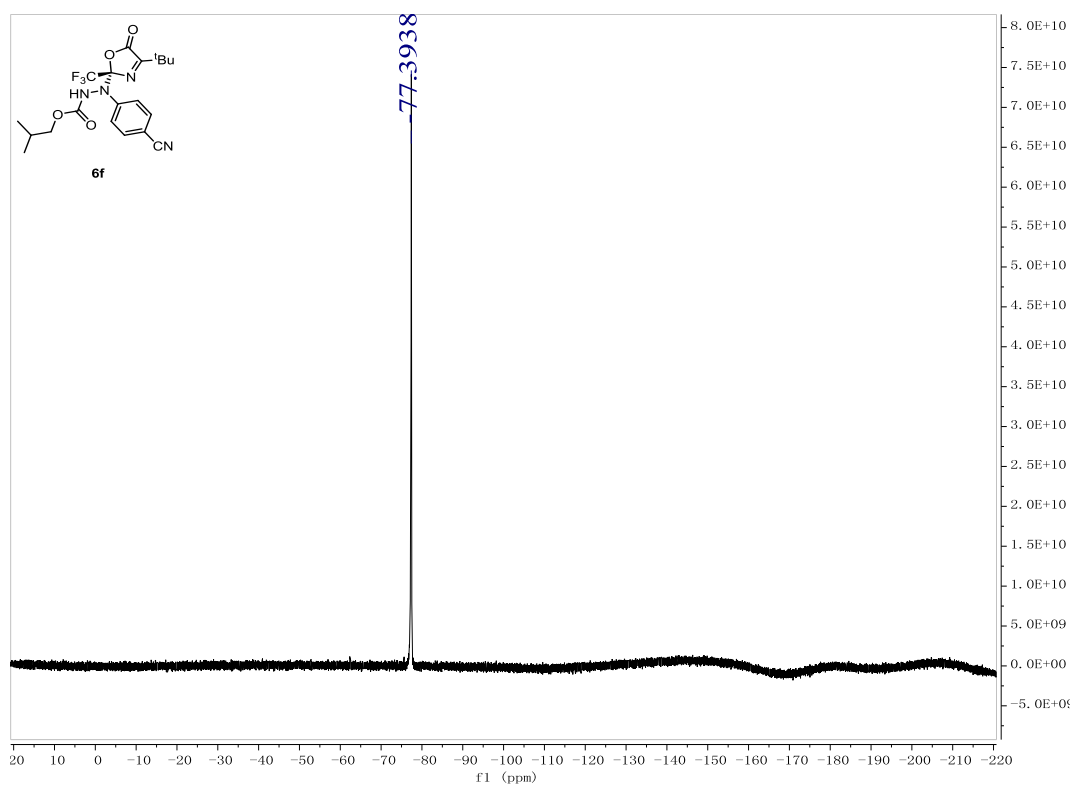
^1H NMR of 6f(600 MHz, CDCl_3)



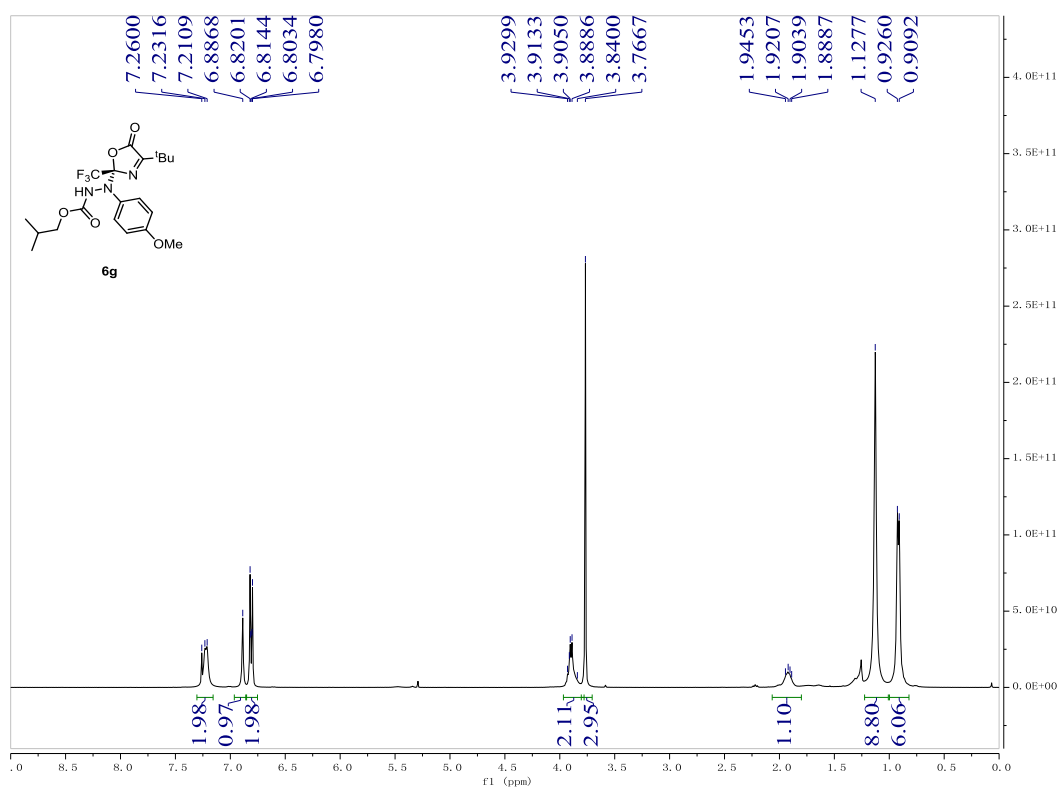
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6f (150 MHz, CDCl_3)



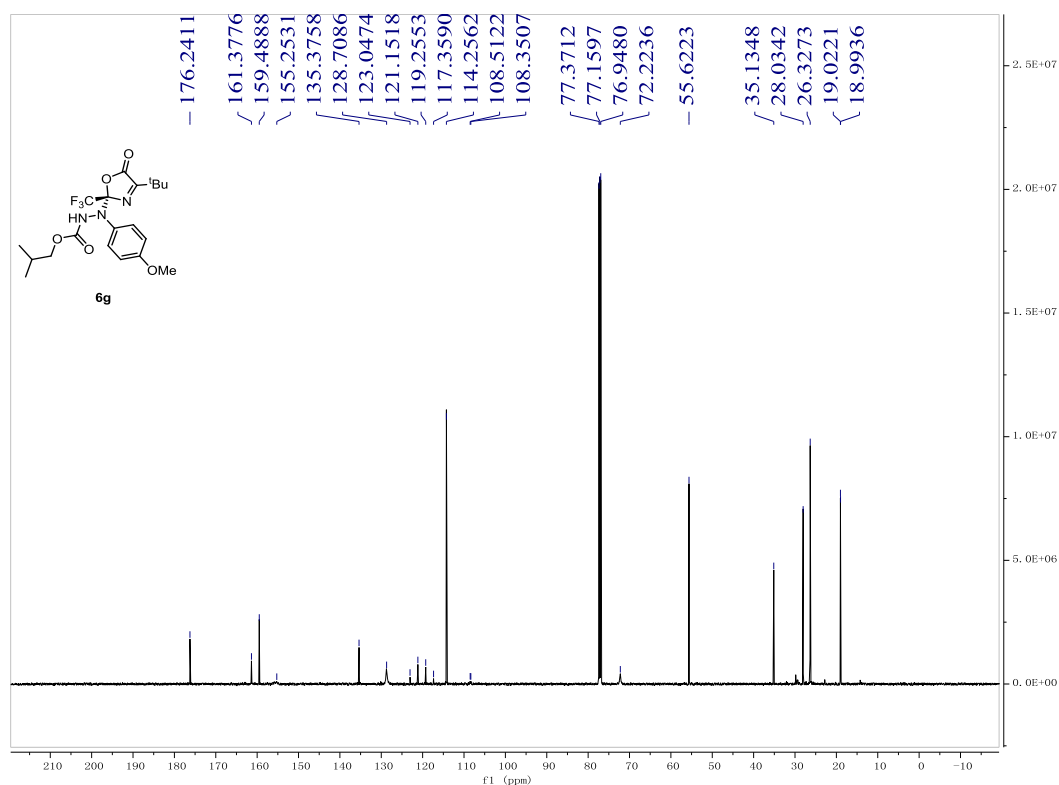
¹⁹F{¹H} NMR of 6f (376 MHz, CDCl₃)



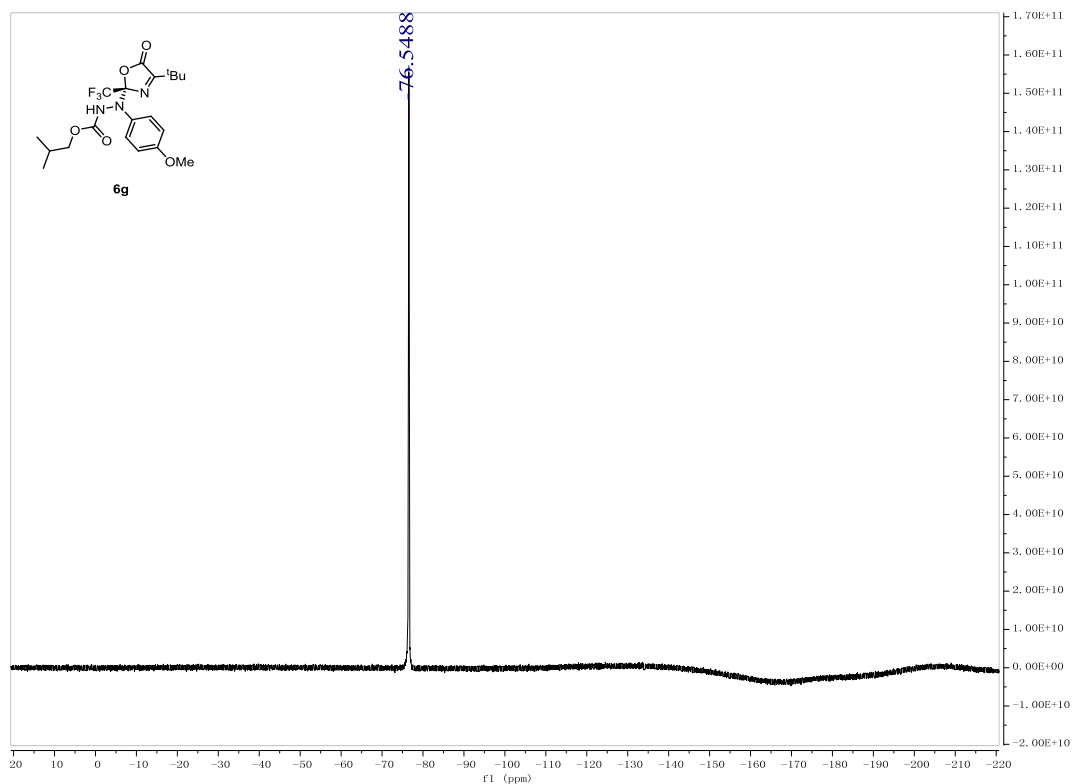
¹H NMR of 6g (400 MHz, CDCl₃)



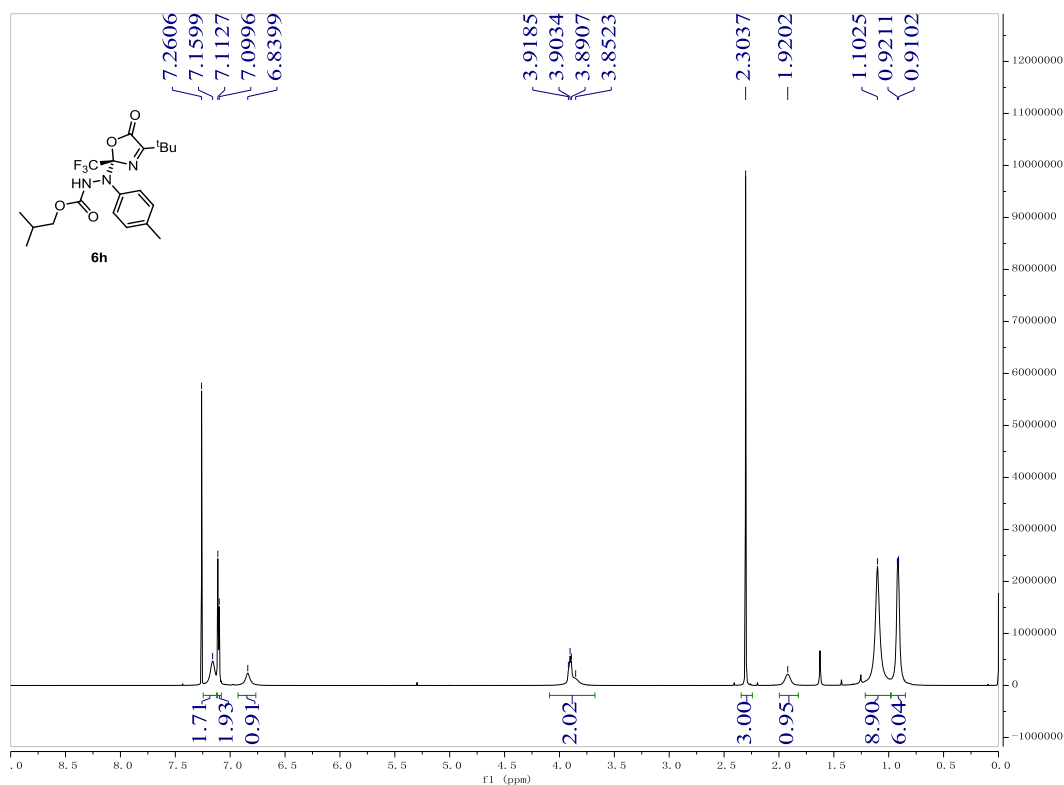
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6g (150 MHz, CDCl_3)



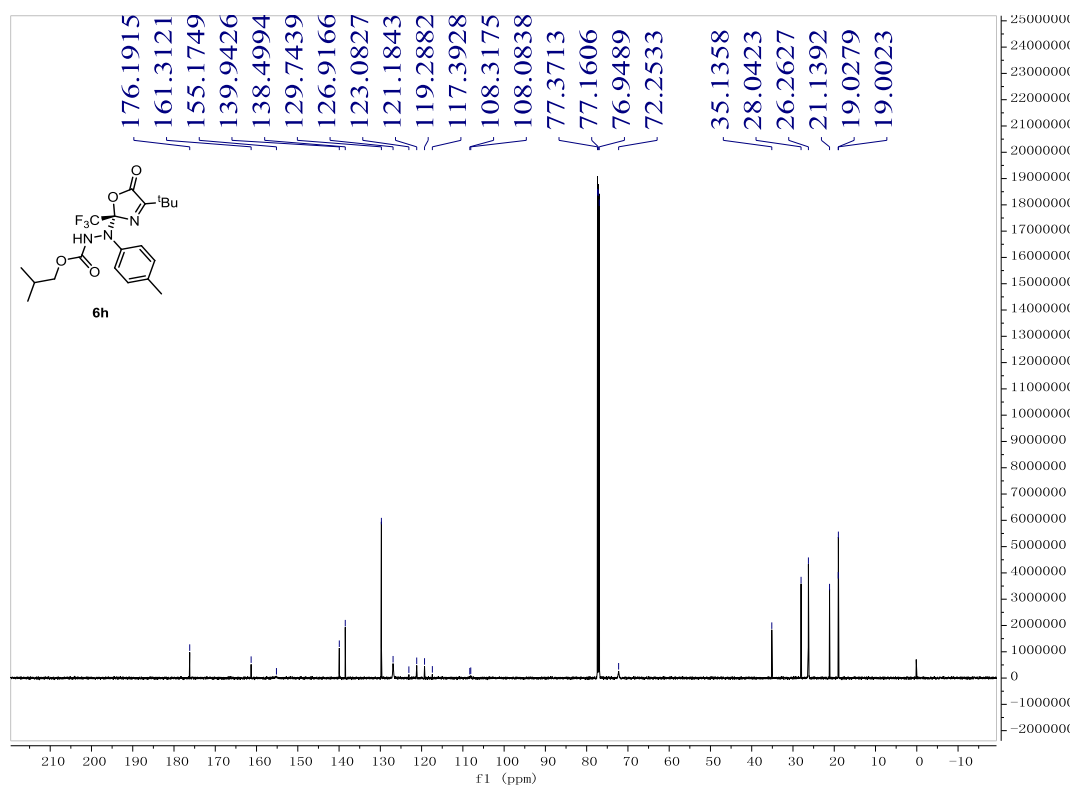
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6g (376 MHz, CDCl_3)



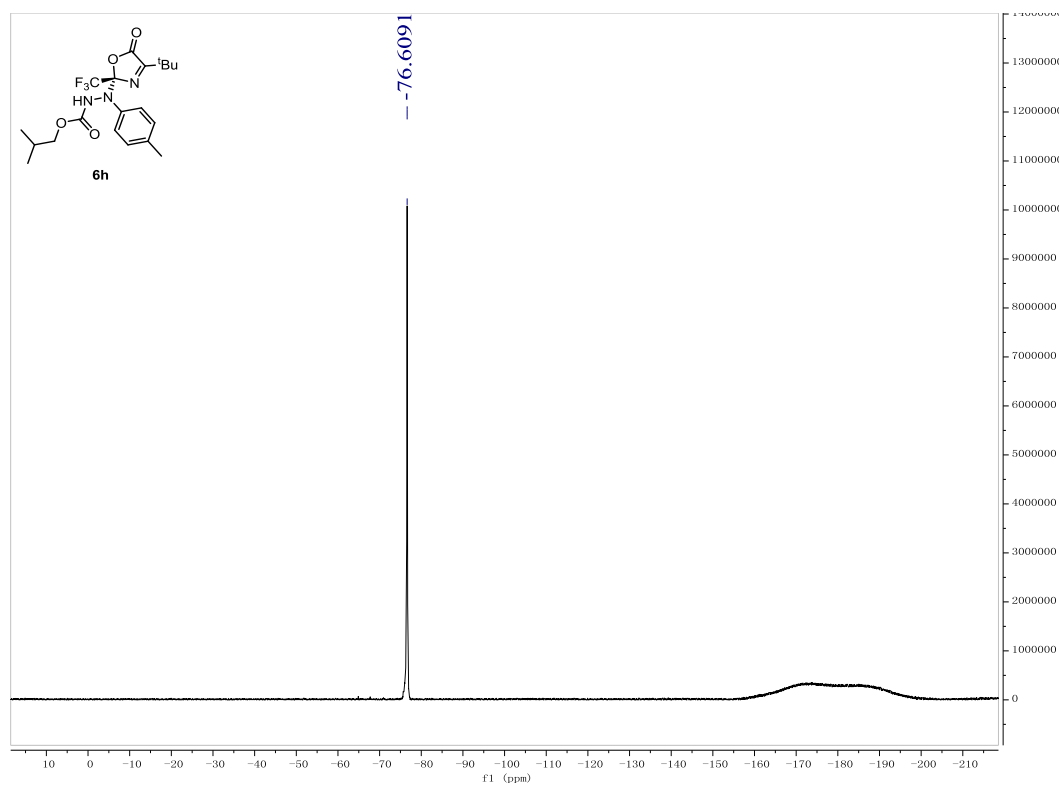
¹H NMR of 6h (600 MHz, CDCl₃)



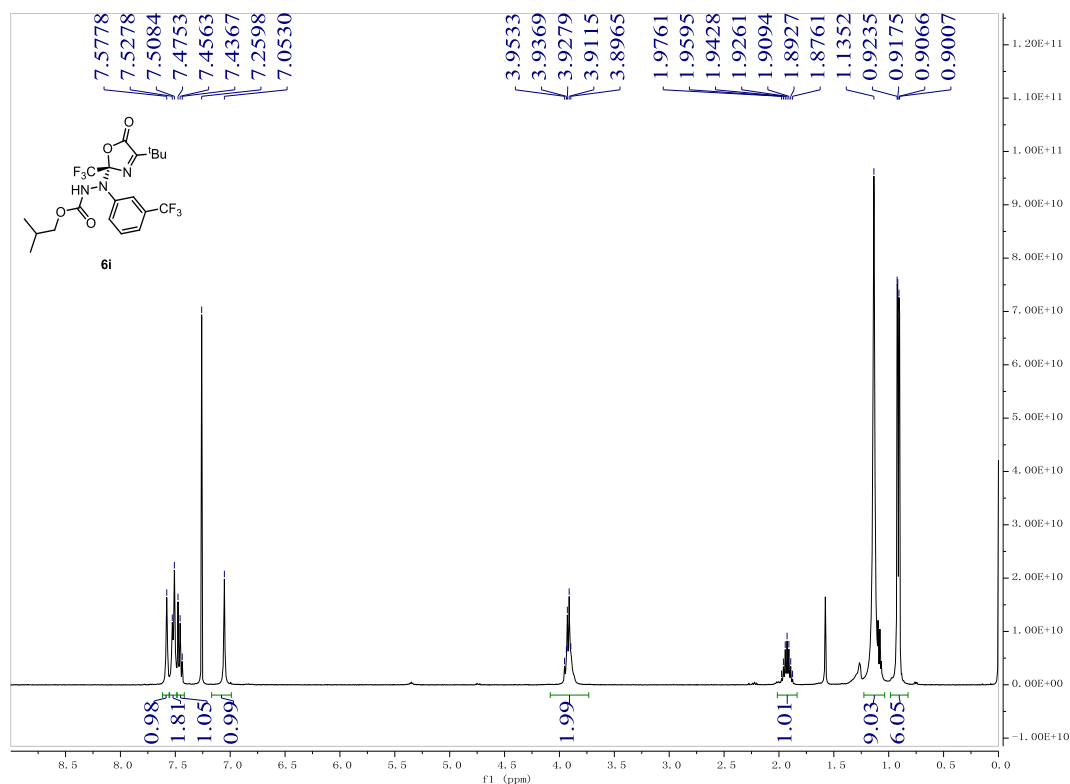
¹³C{¹H} NMR of 6h (150 MHz, CDCl₃)



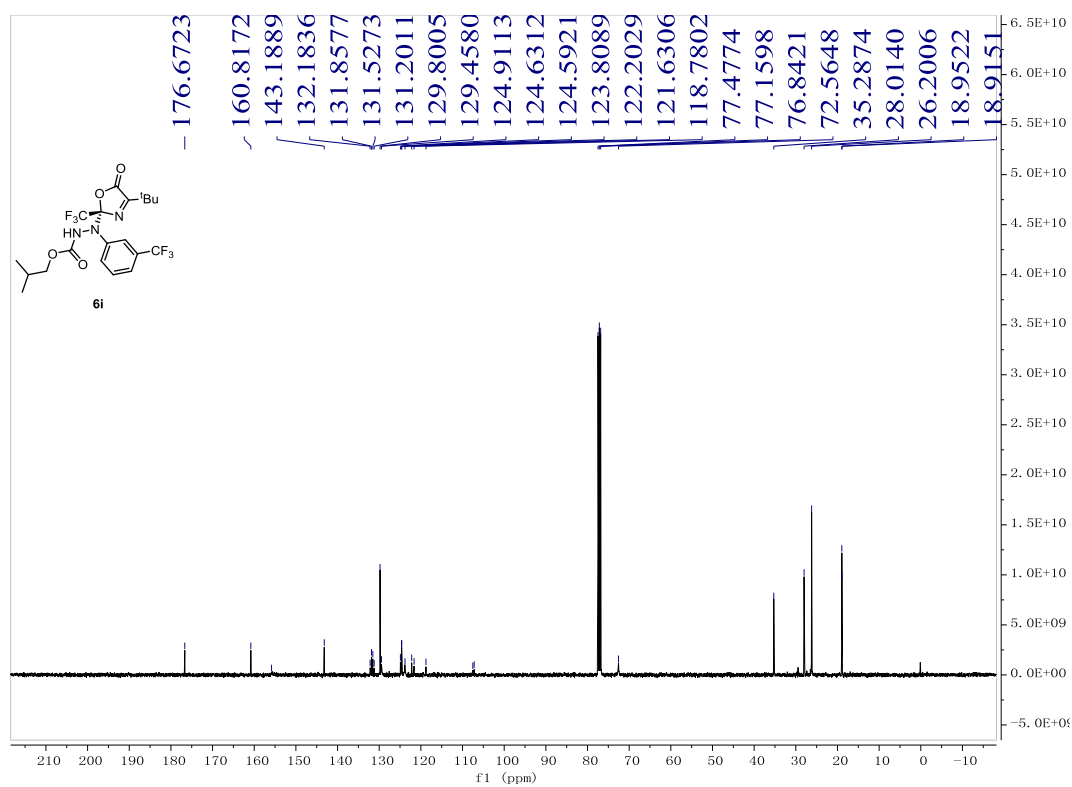
¹⁹F{¹H} NMR of 6h (564 MHz, CDCl₃)



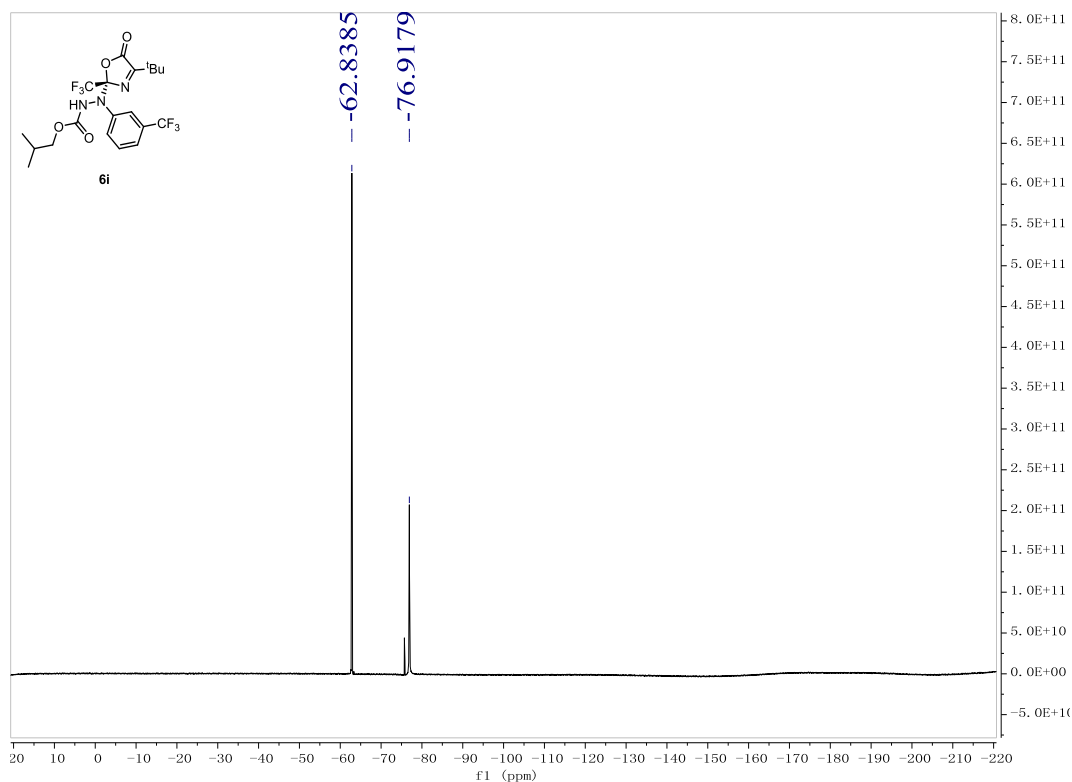
¹H NMR of 6i (400 MHz, CDCl₃)



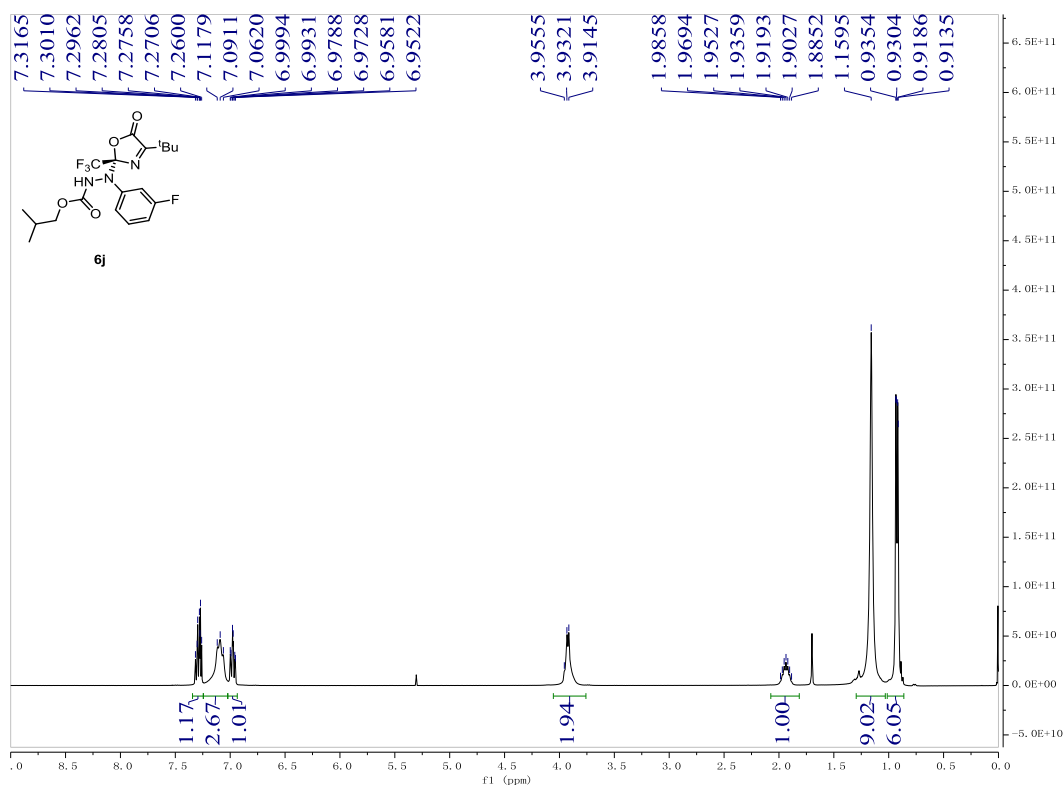
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6i (100 MHz, CDCl_3)



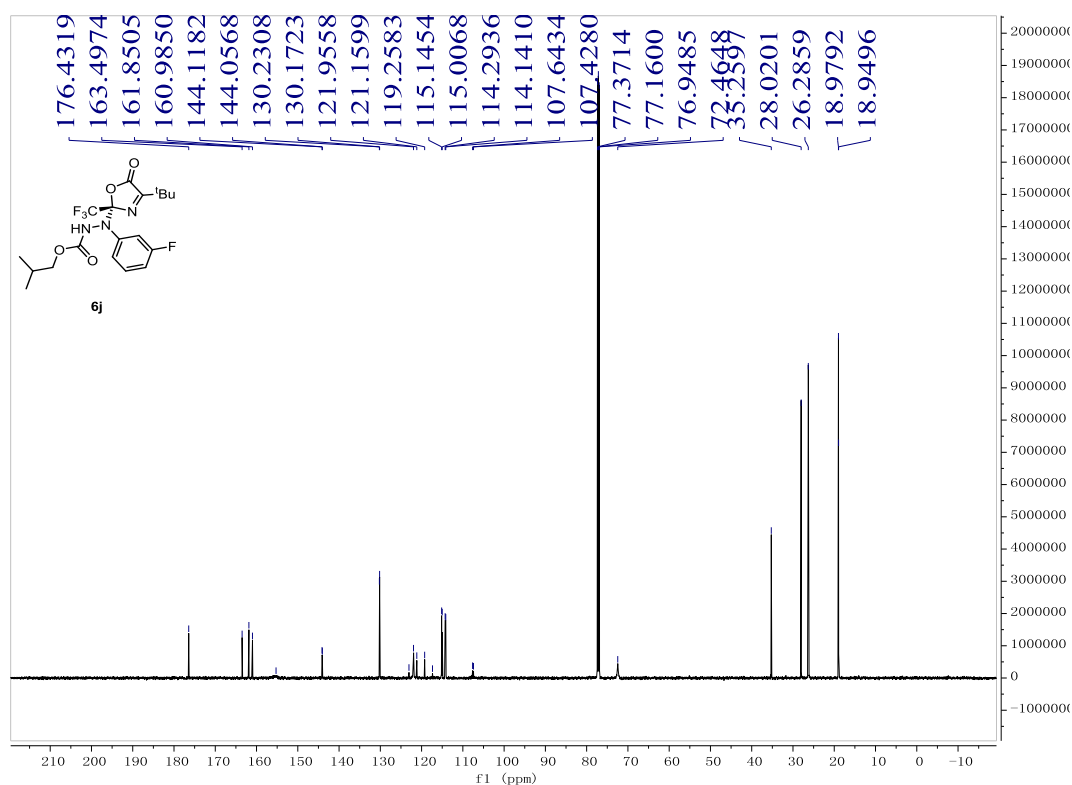
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6i (376 MHz, CDCl_3)



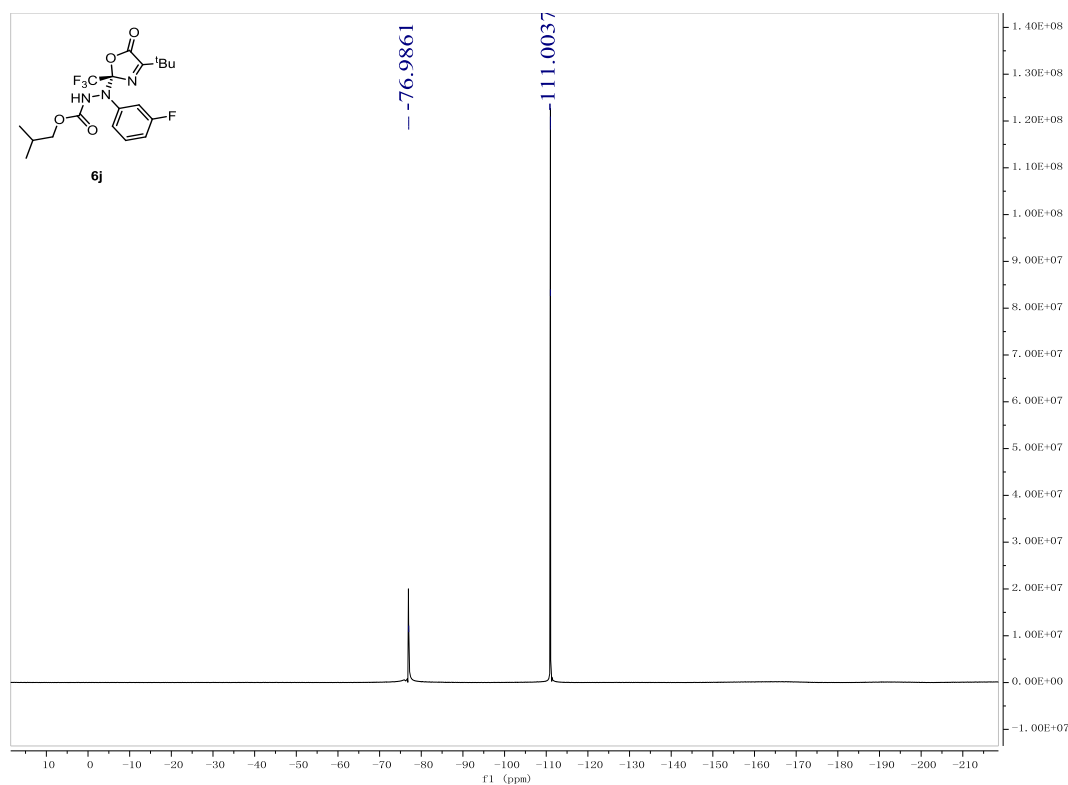
^1H NMR of **6j (400 MHz, CDCl_3)**



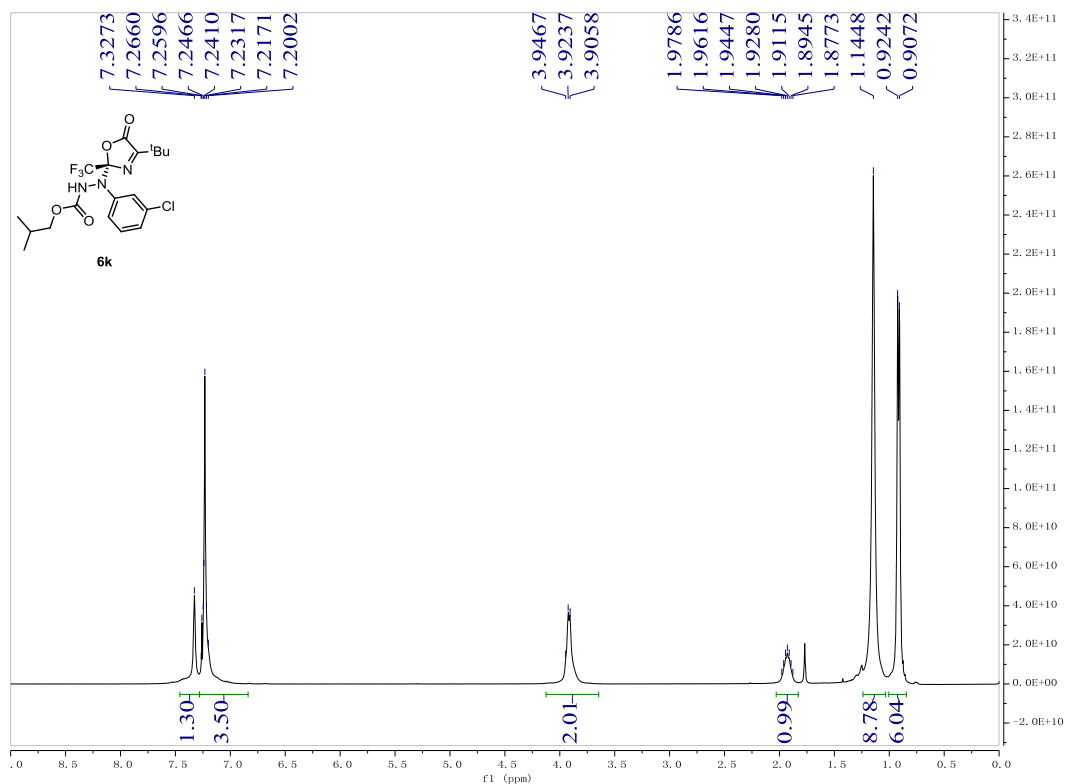
$^{13}\text{C}\{^1\text{H}\}$ NMR of **6j (150 MHz, CDCl_3)**



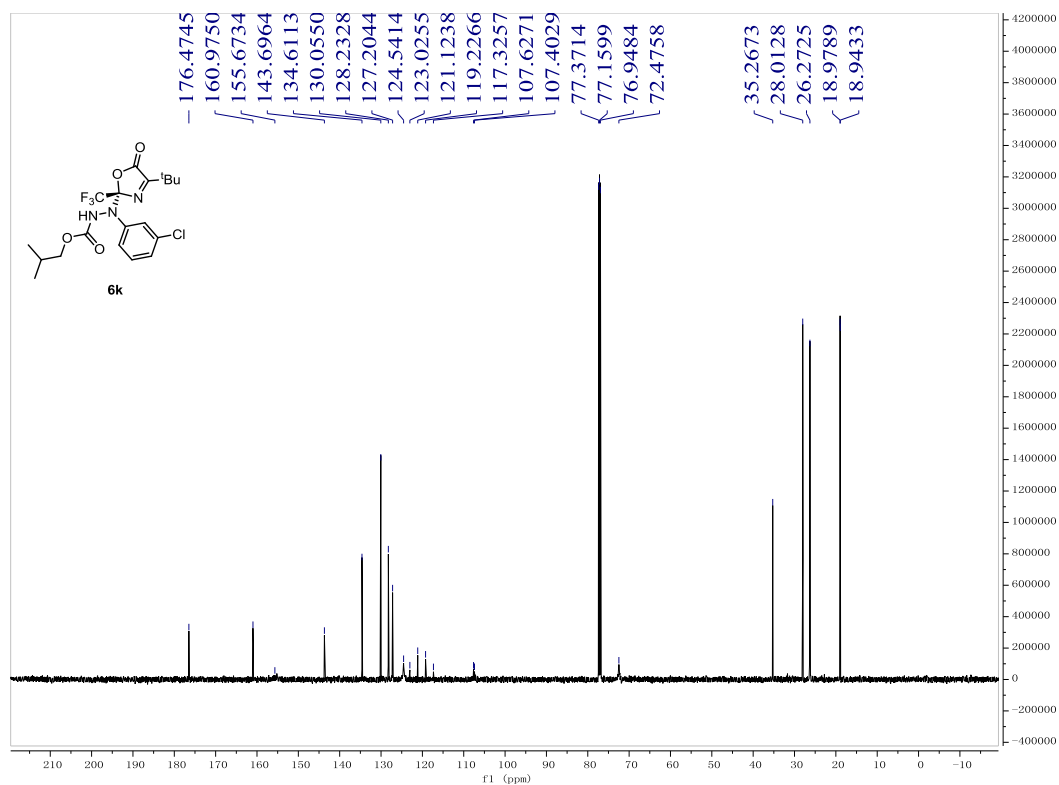
¹⁹F{¹H} NMR of 6j (564 MHz, CDCl₃)



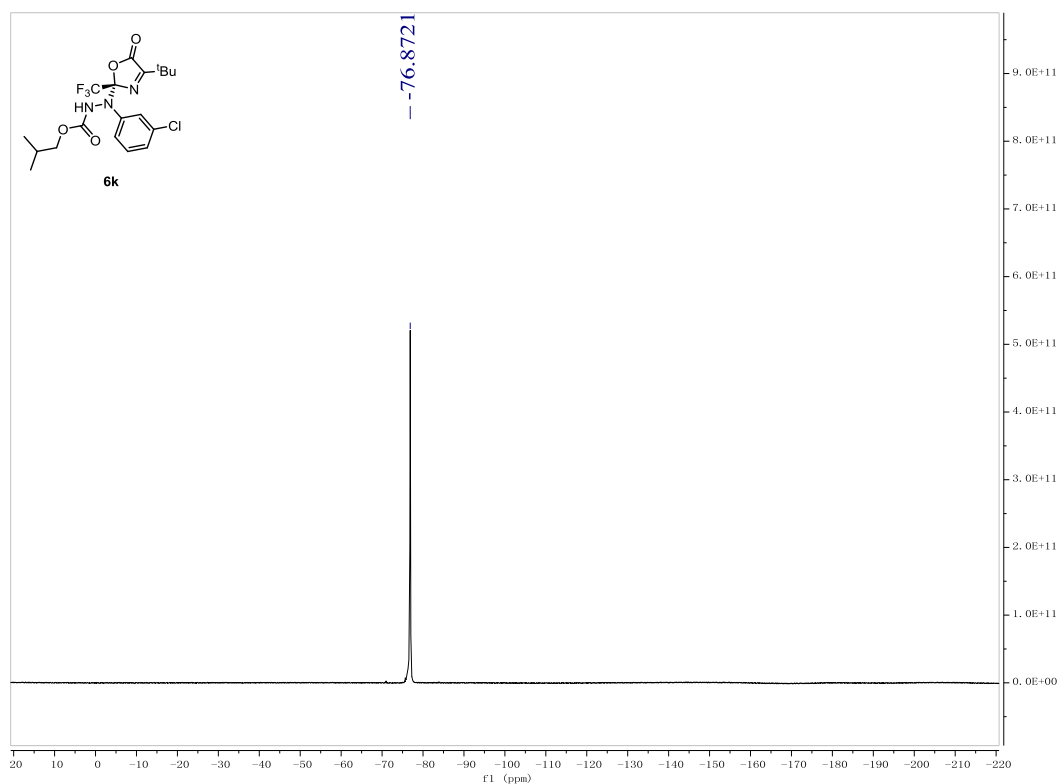
¹H NMR of 6k (400 MHz, CDCl₃)



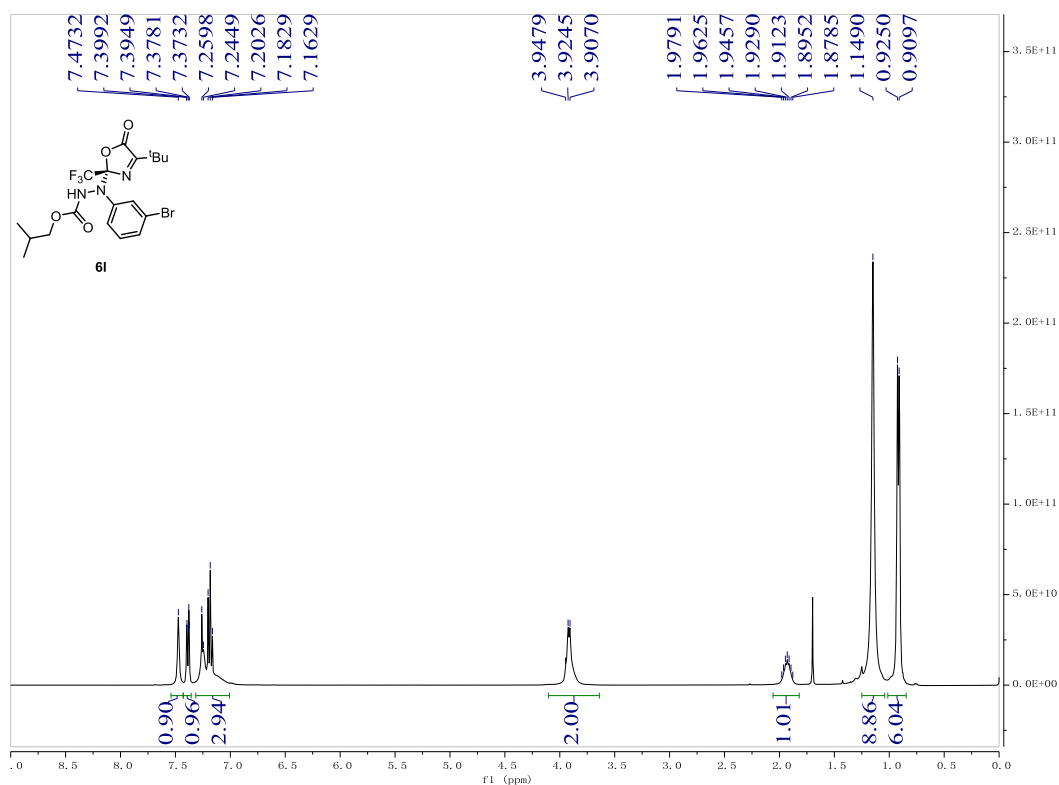
¹³C{¹H} NMR of 6k (150 MHz, CDCl₃)



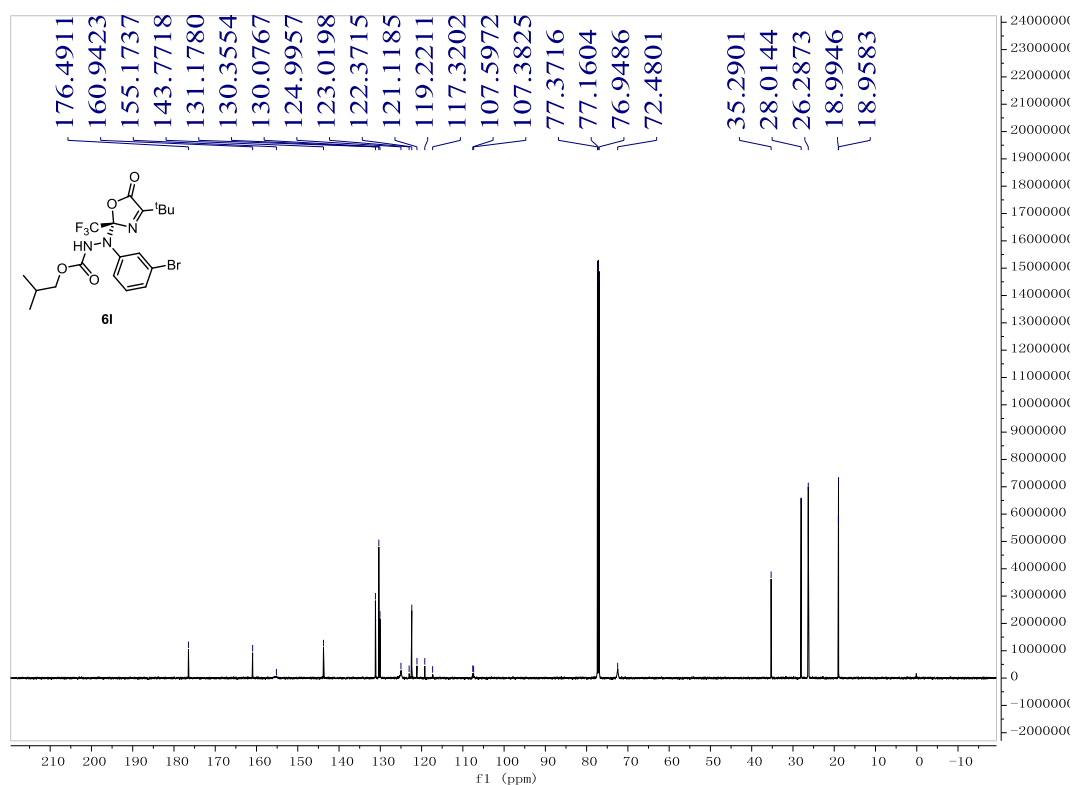
¹⁹F{¹H} NMR of 6k (376 MHz, CDCl₃)



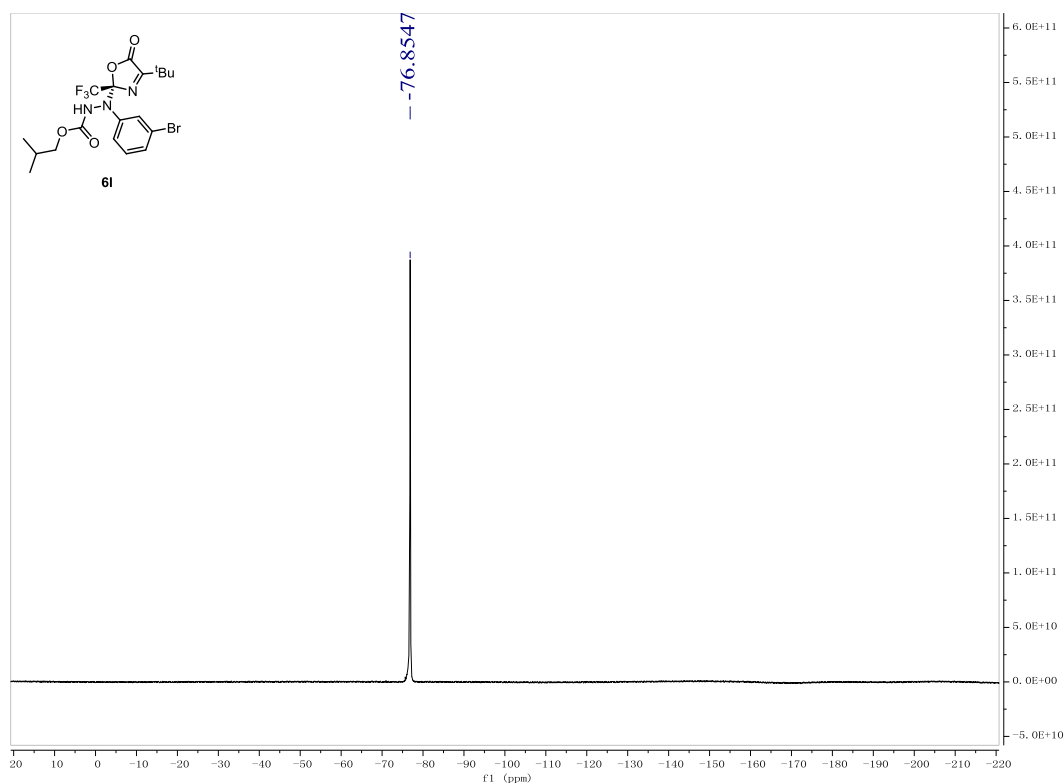
^1H NMR of 6l (400 MHz, CDCl_3)



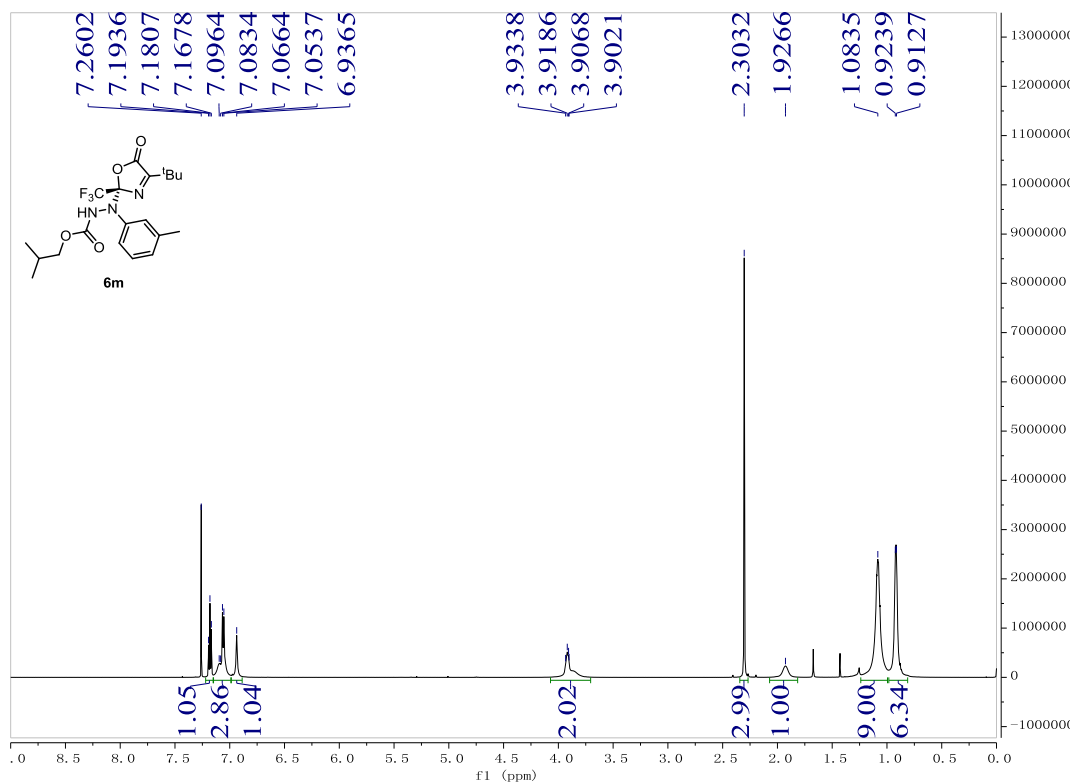
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6l (150 MHz, CDCl_3)



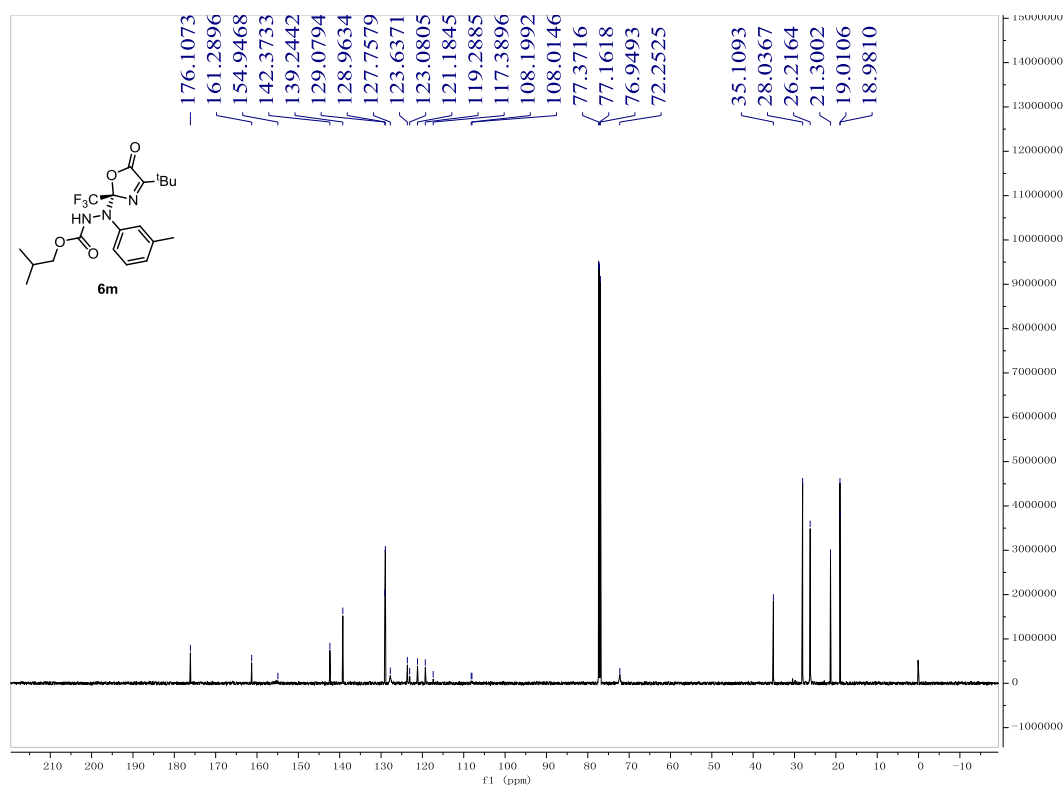
¹⁹F{¹H} NMR of 6l (376 MHz, CDCl₃)



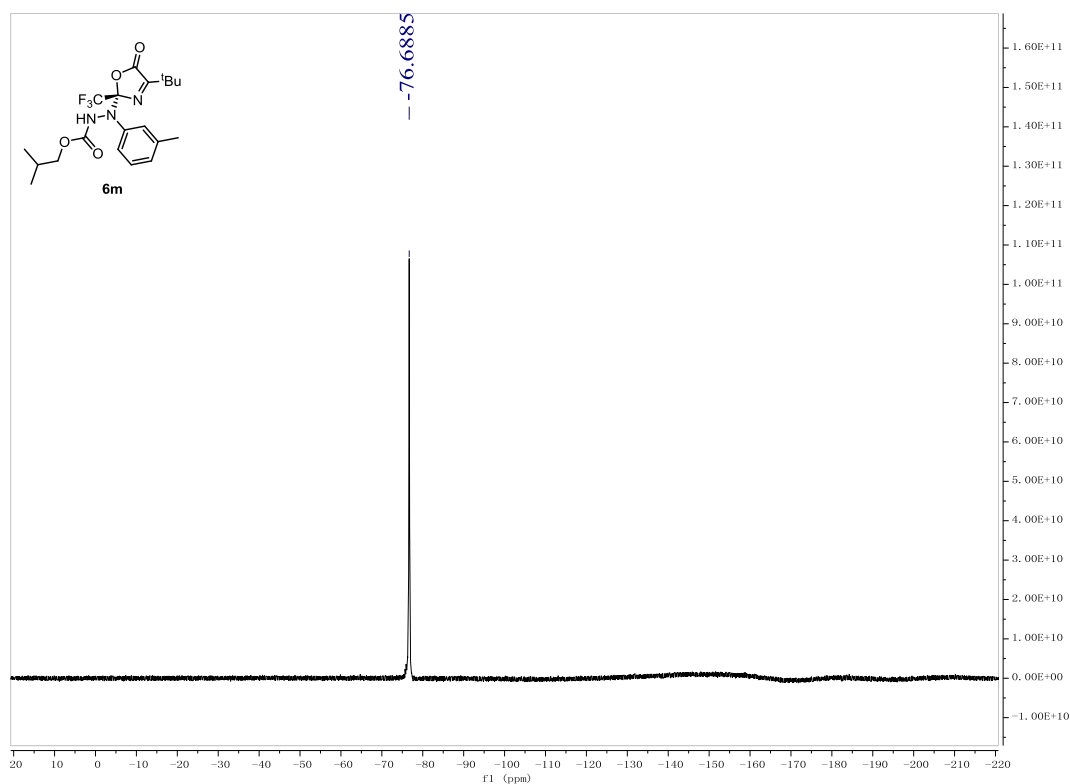
¹H NMR of 6m (600 MHz, CDCl₃)



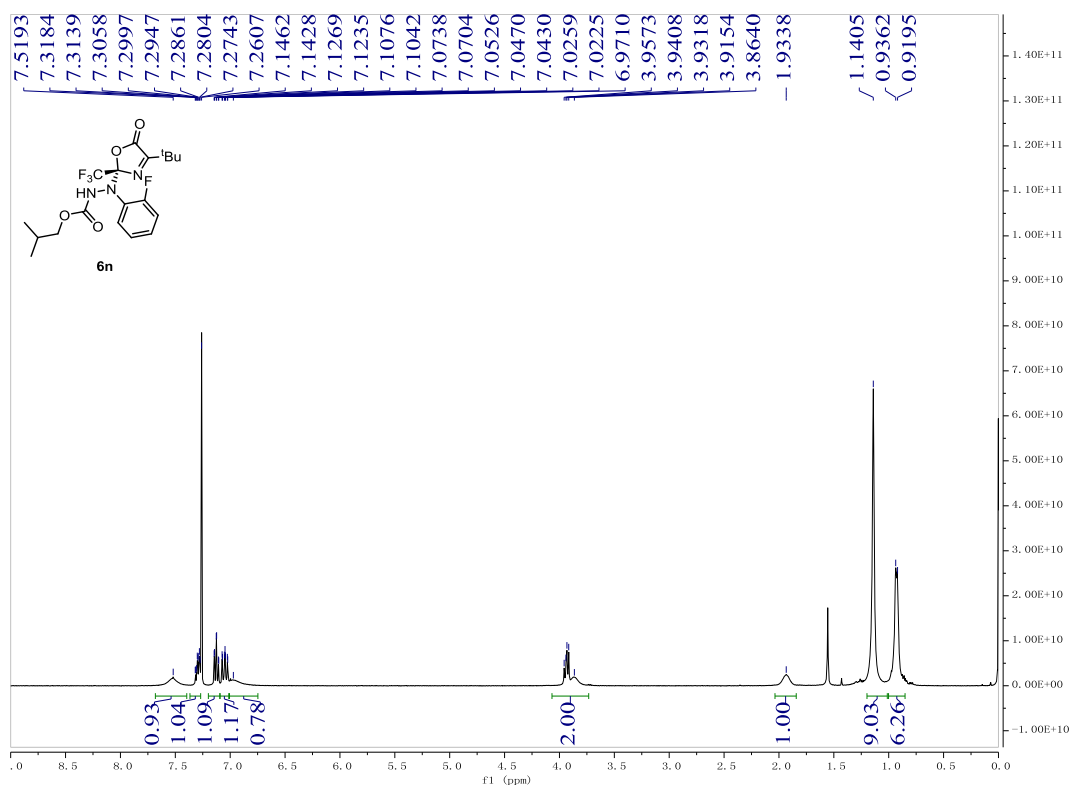
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6m (150 MHz, CDCl_3)



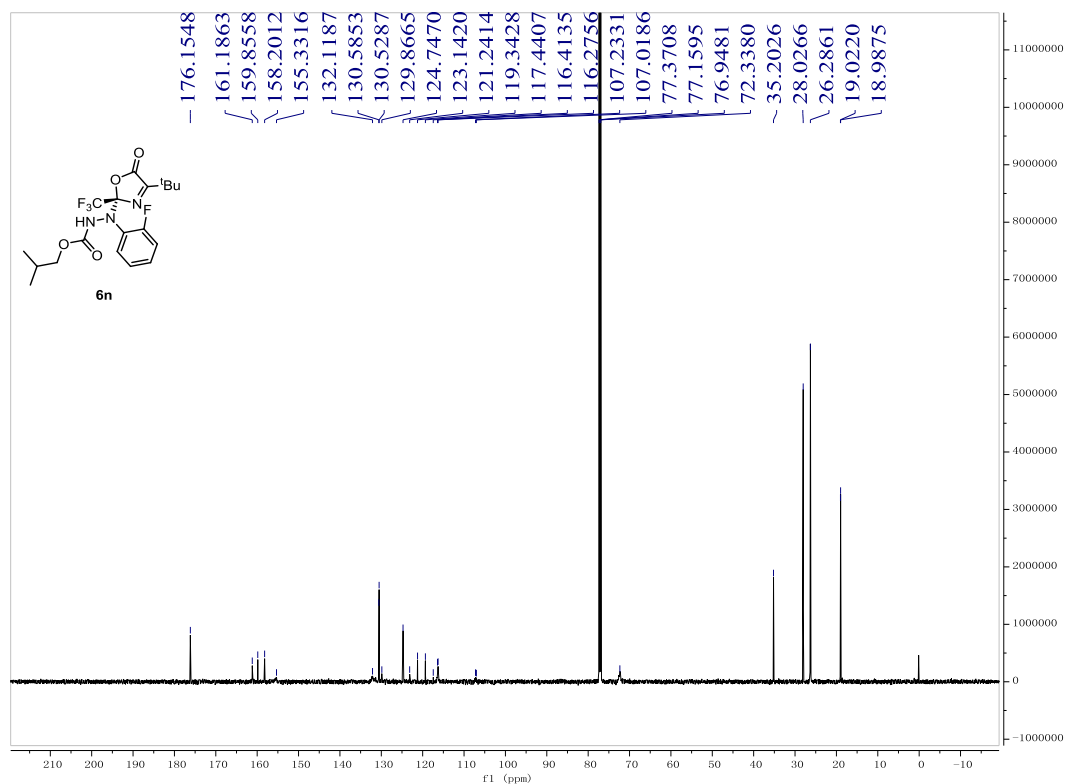
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6m (376 MHz, CDCl_3)



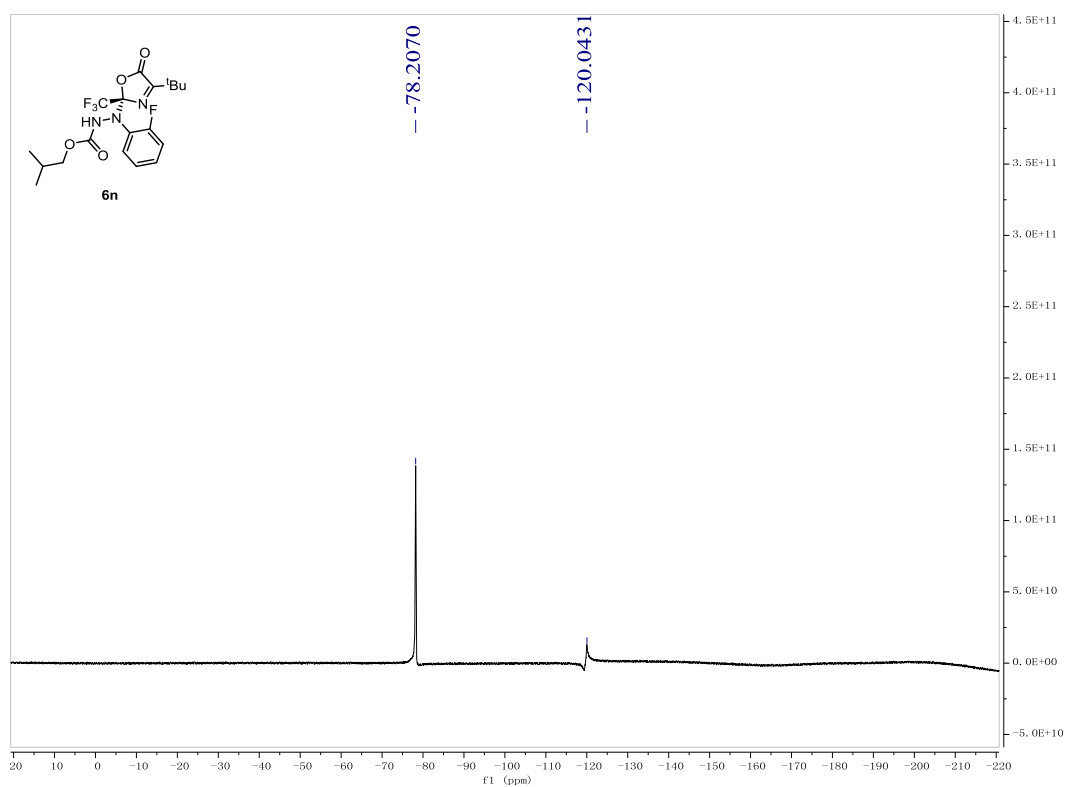
^1H NMR of 6n (400 MHz, CDCl_3)



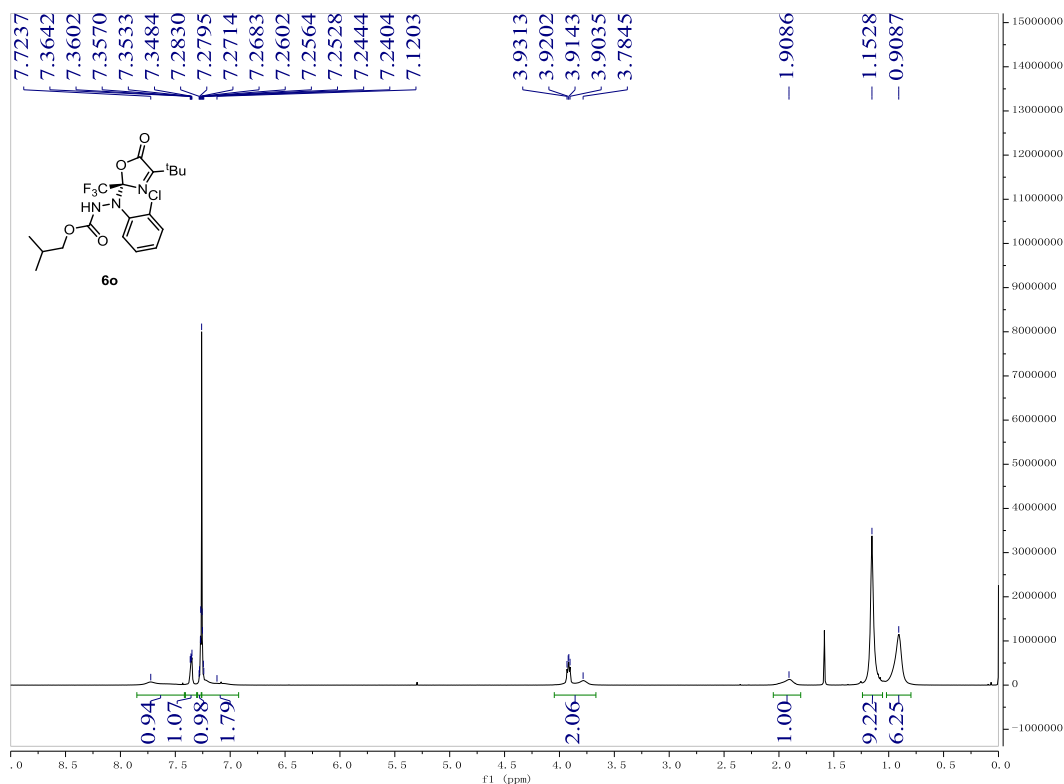
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6n (150 MHz, CDCl_3)



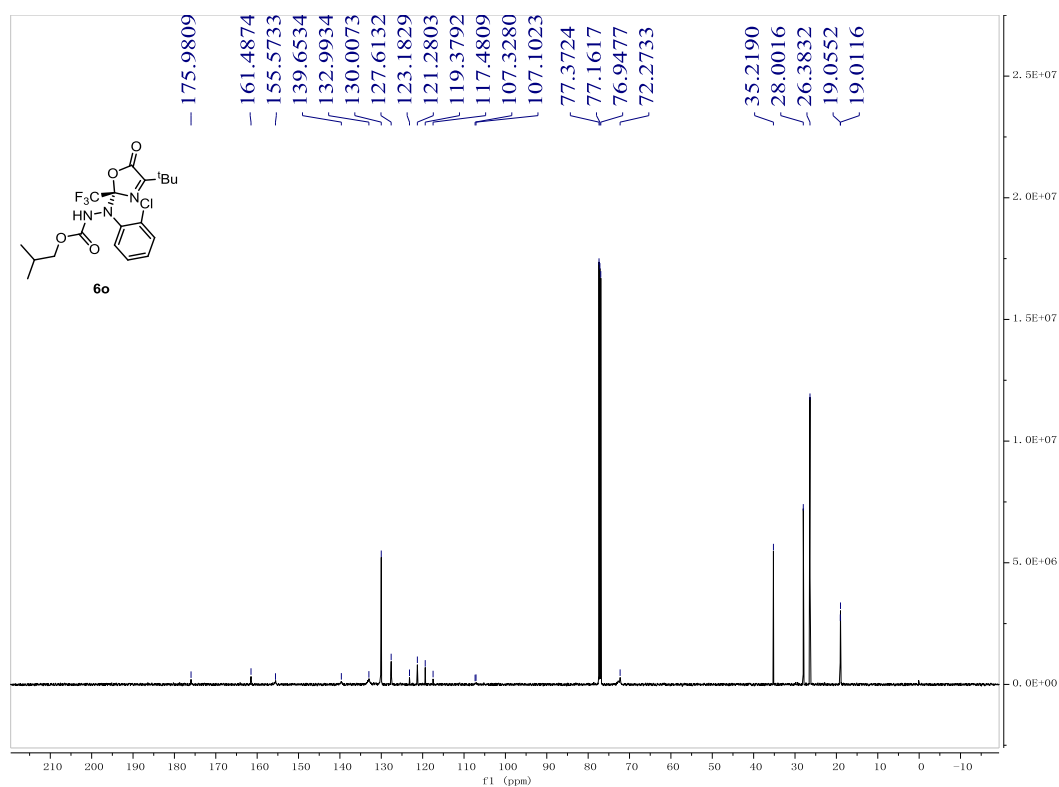
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6n (376 MHz, CDCl_3)



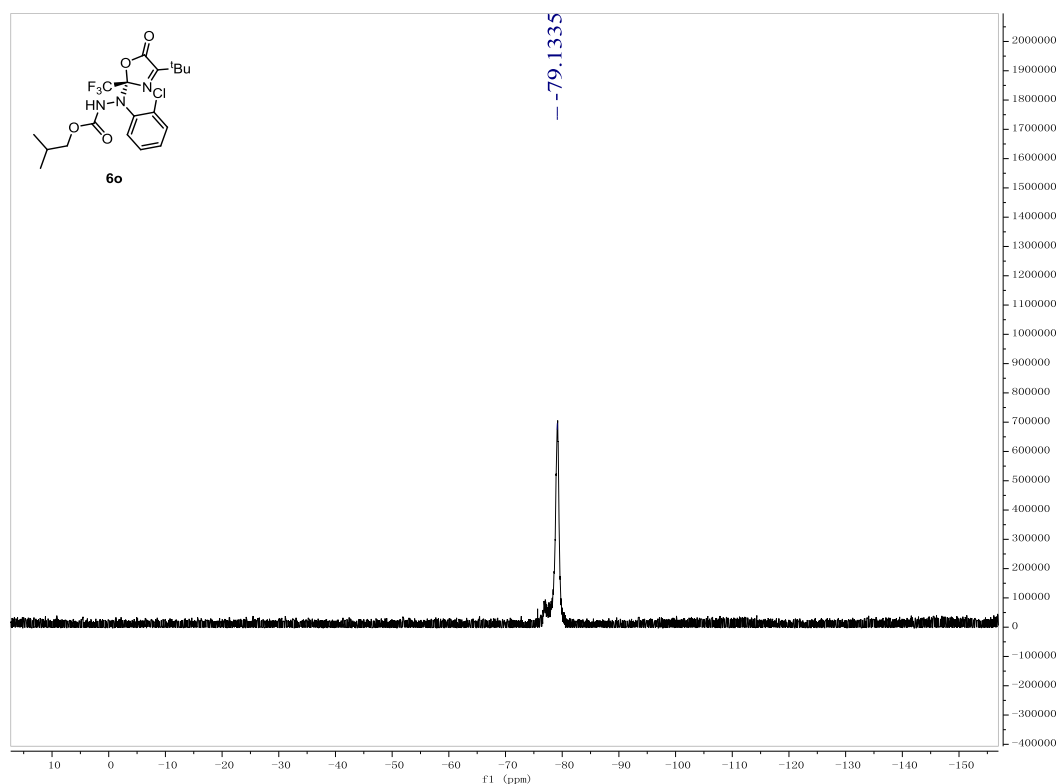
^1H NMR of 6o (600 MHz, CDCl_3)



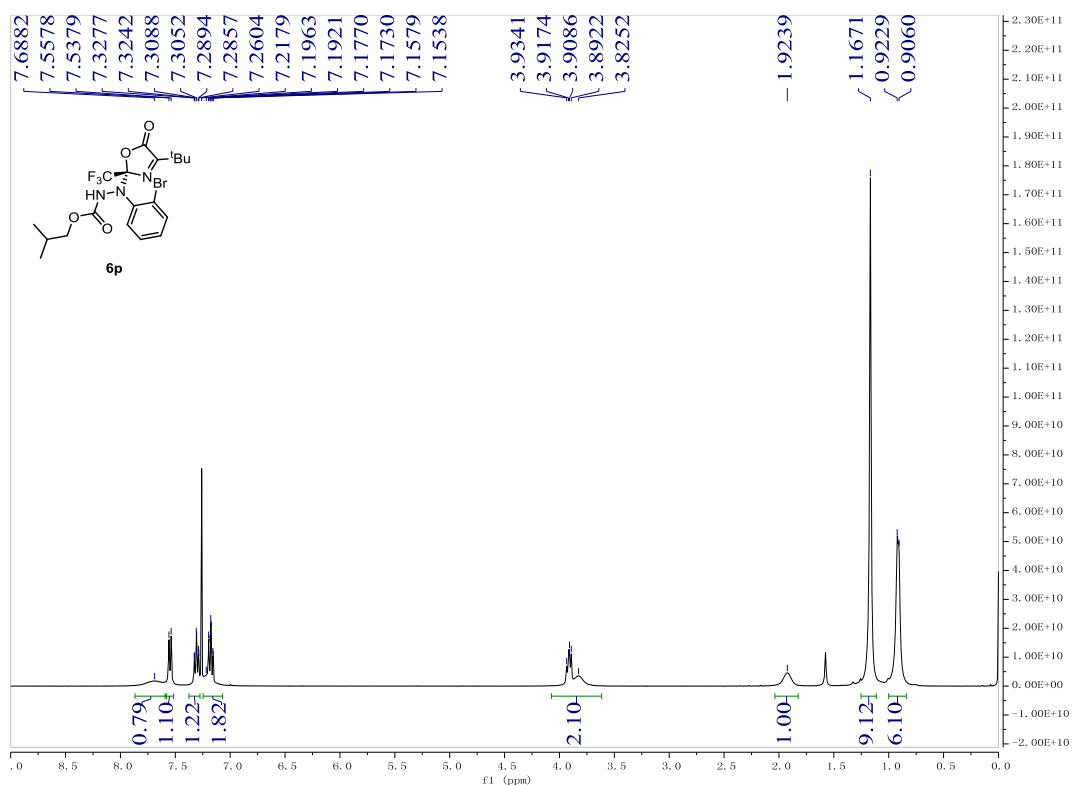
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6o (150 MHz, CDCl_3)



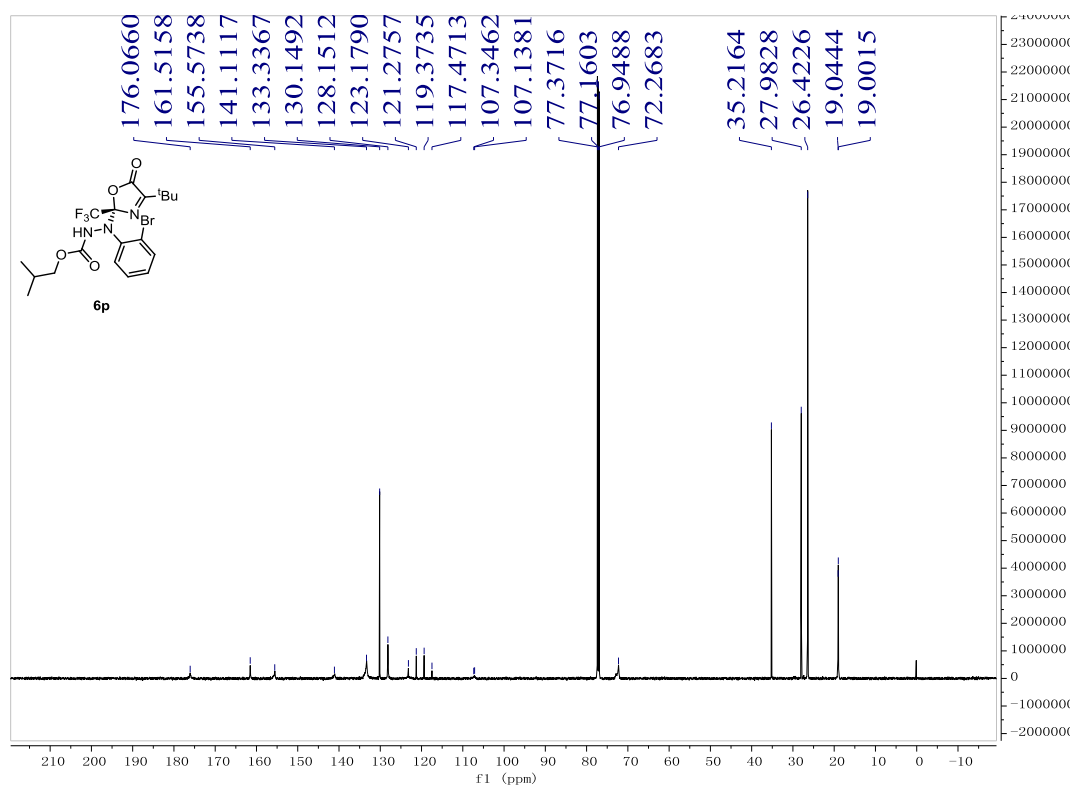
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6o (564 MHz, CDCl_3)



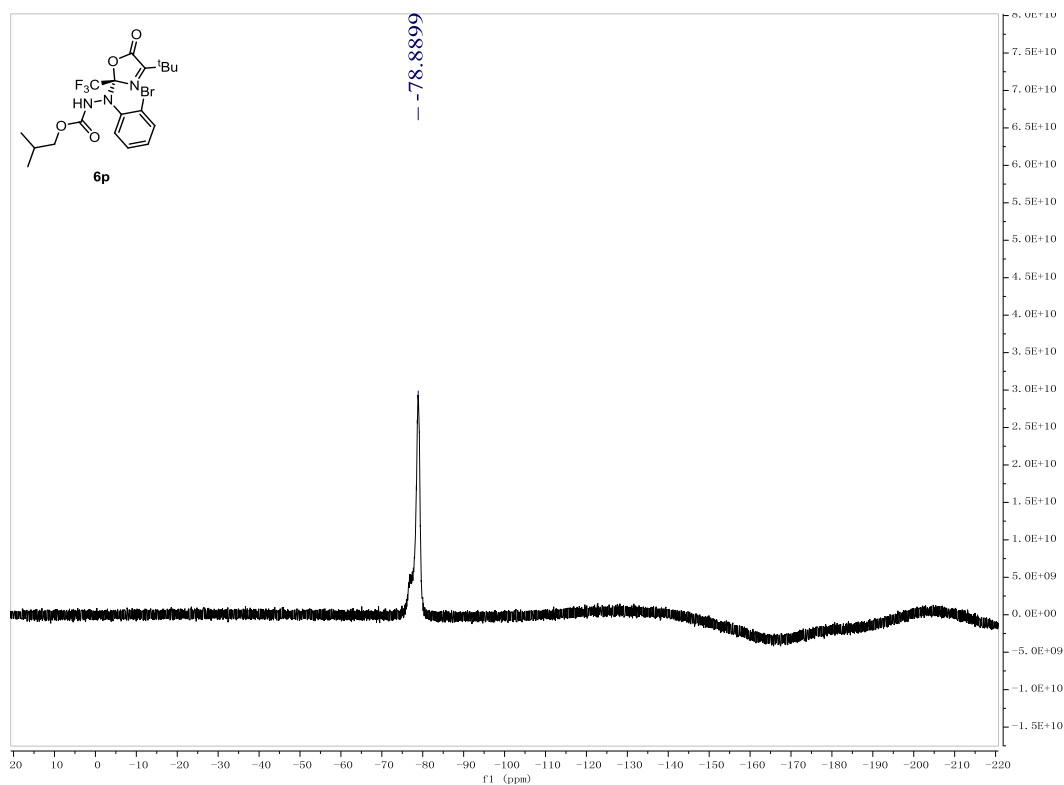
^1H NMR of 6p (400 MHz, CDCl_3)



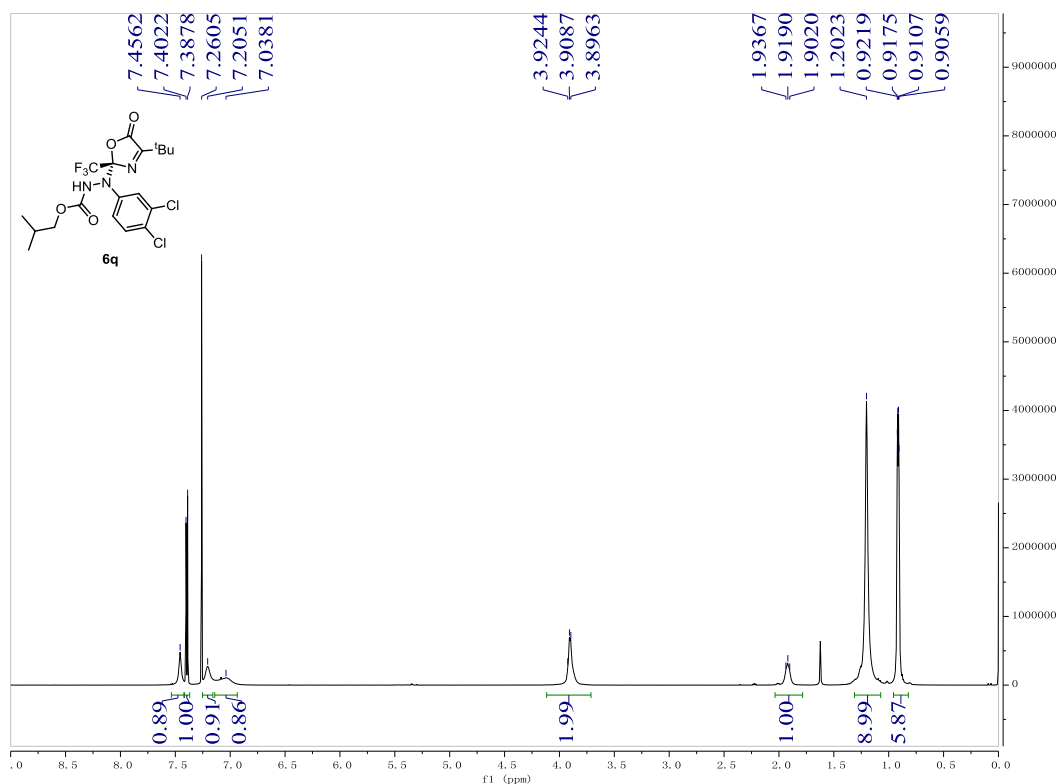
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6p (150 MHz, CDCl_3)



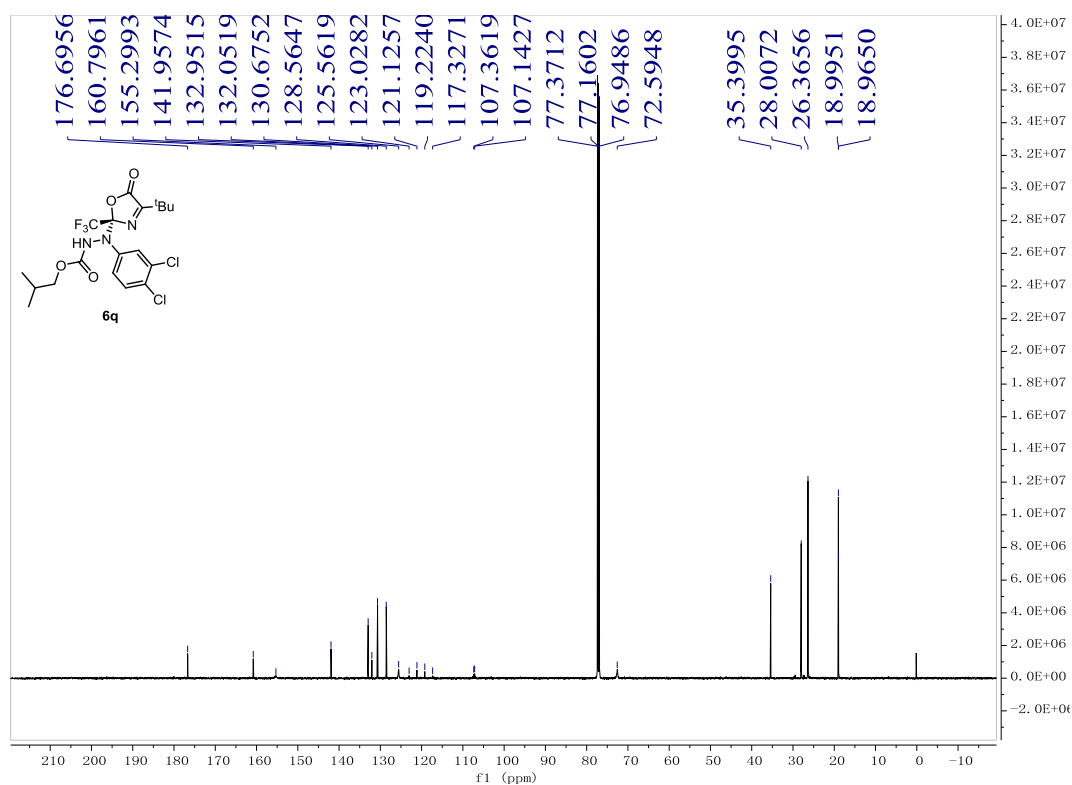
¹⁹F{¹H} NMR of 6p (376 MHz, CDCl₃)



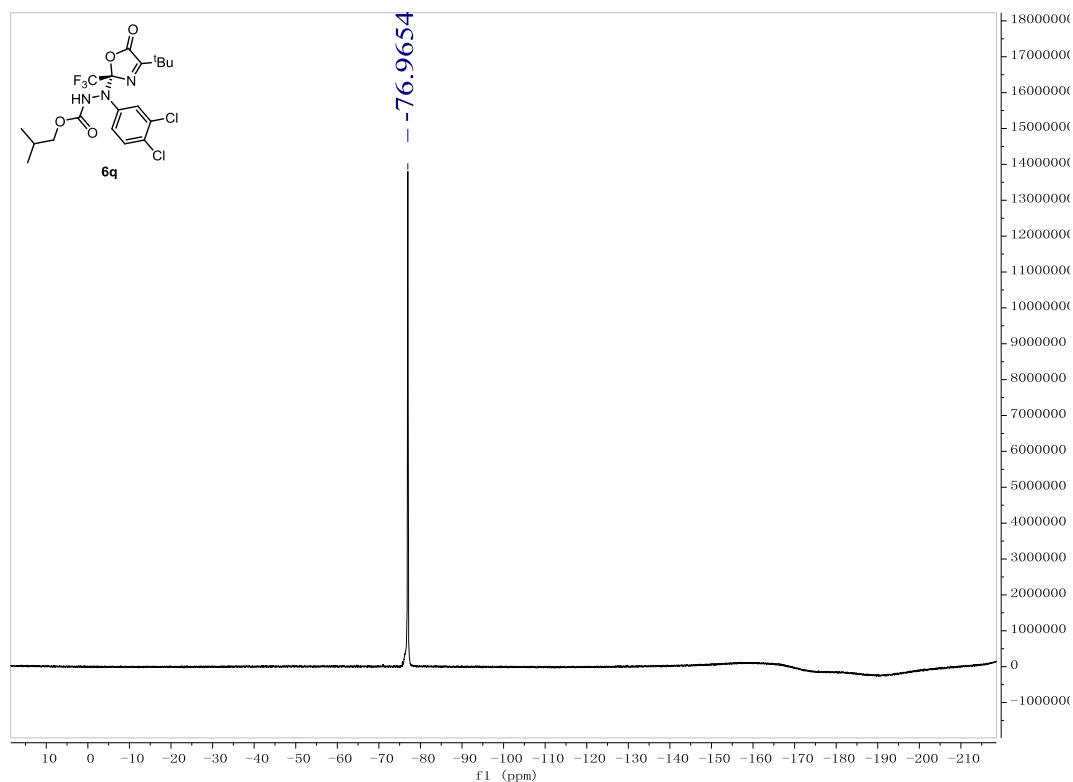
¹H NMR of 6q (600 MHz, CDCl₃)



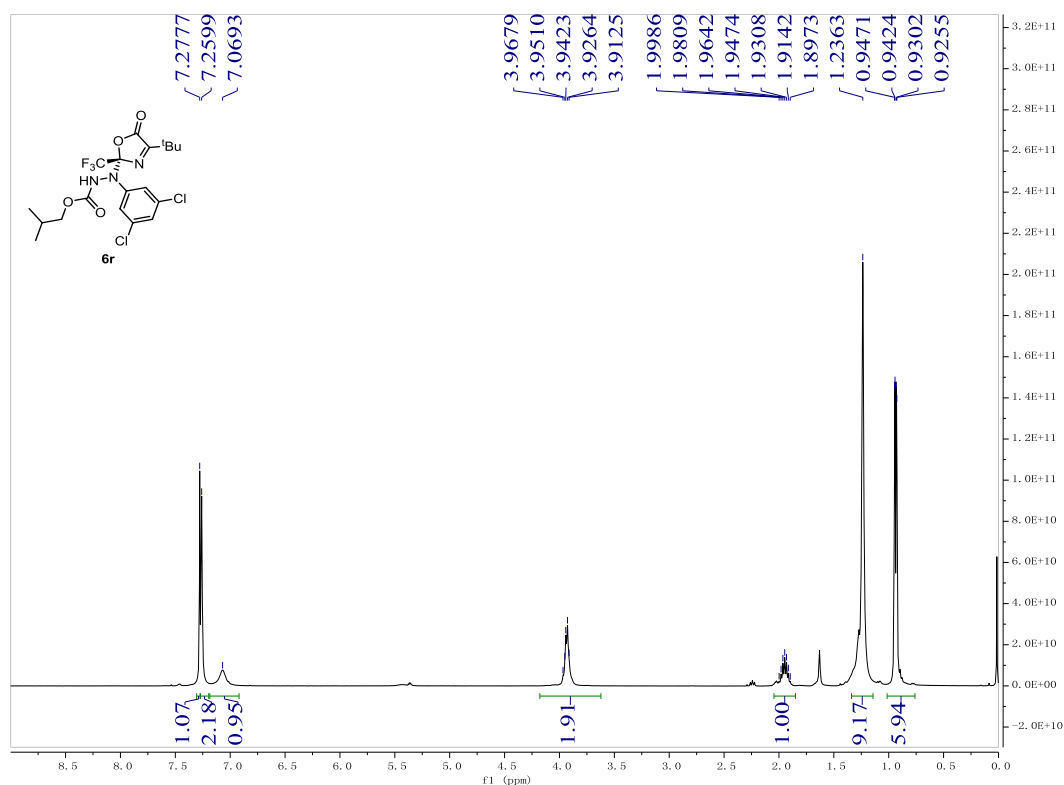
¹³C{¹H} NMR of 6q (150 MHz, CDCl₃)



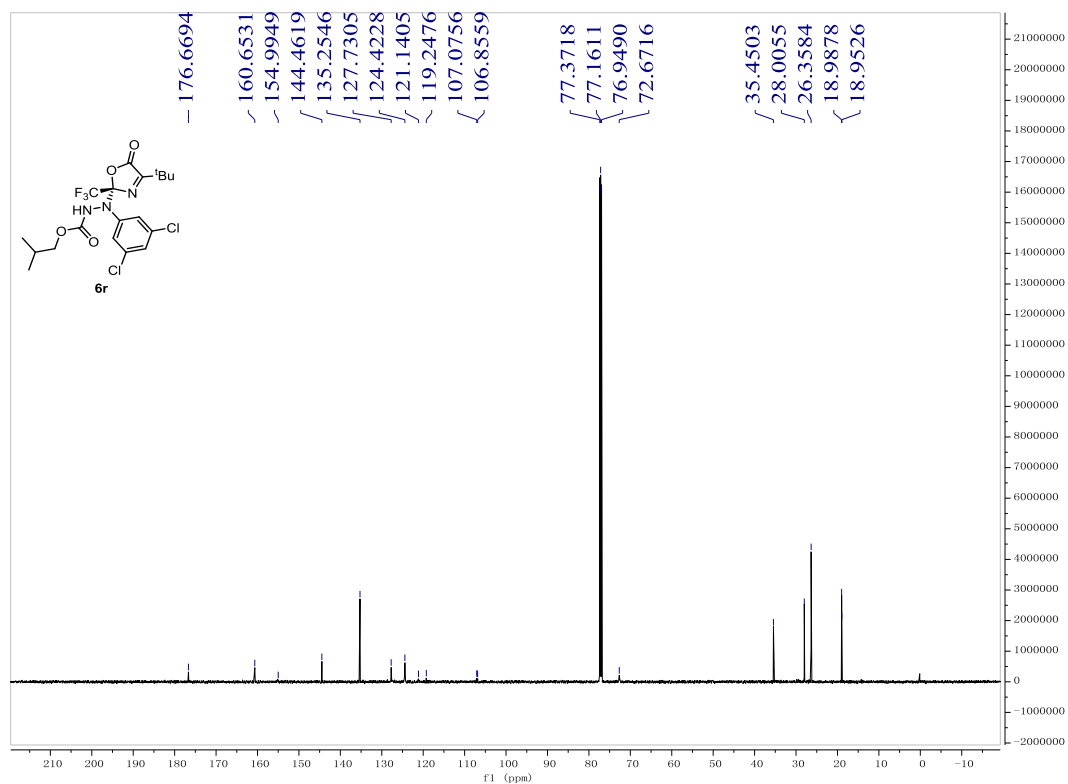
¹⁹F{¹H} NMR of 6q (564 MHz, CDCl₃)



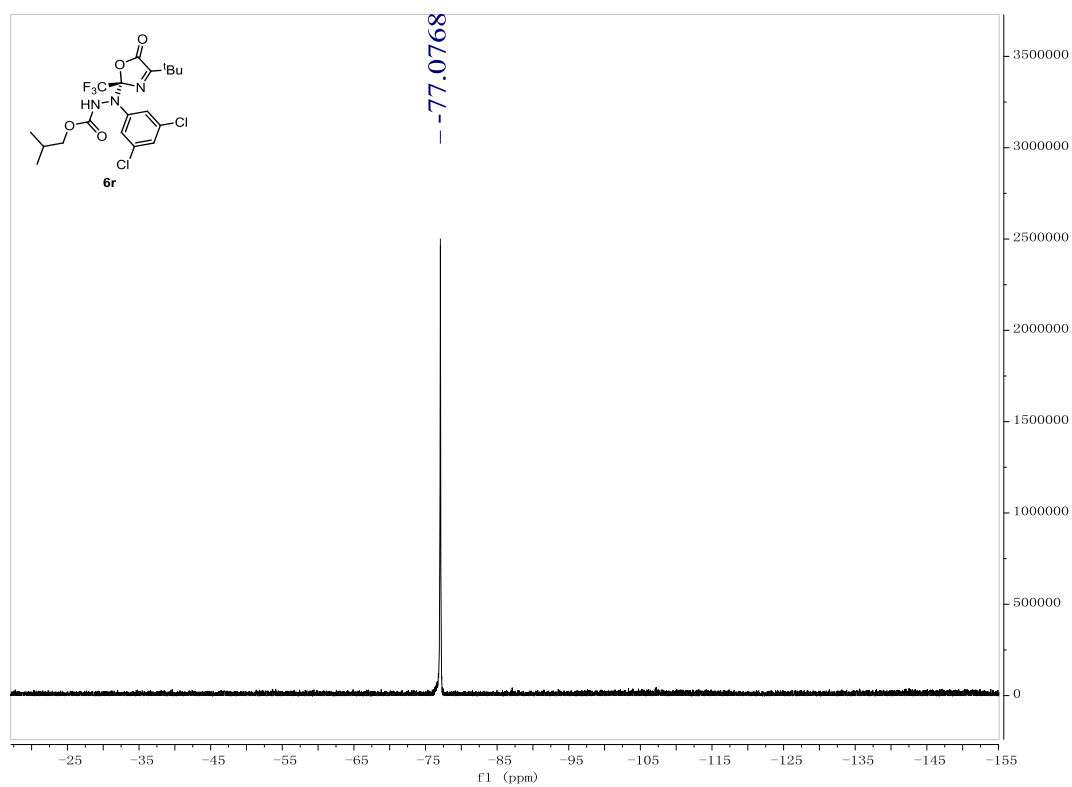
^1H NMR of 6r (400 MHz, CDCl_3)



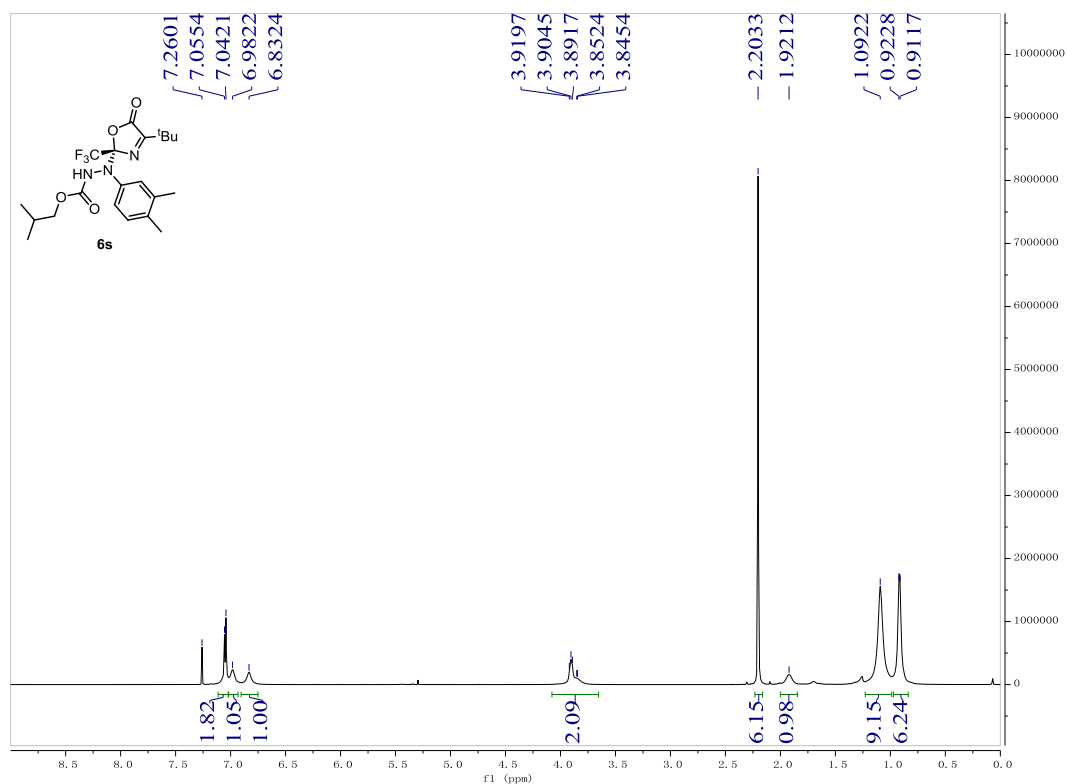
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6r (150 MHz, CDCl_3)



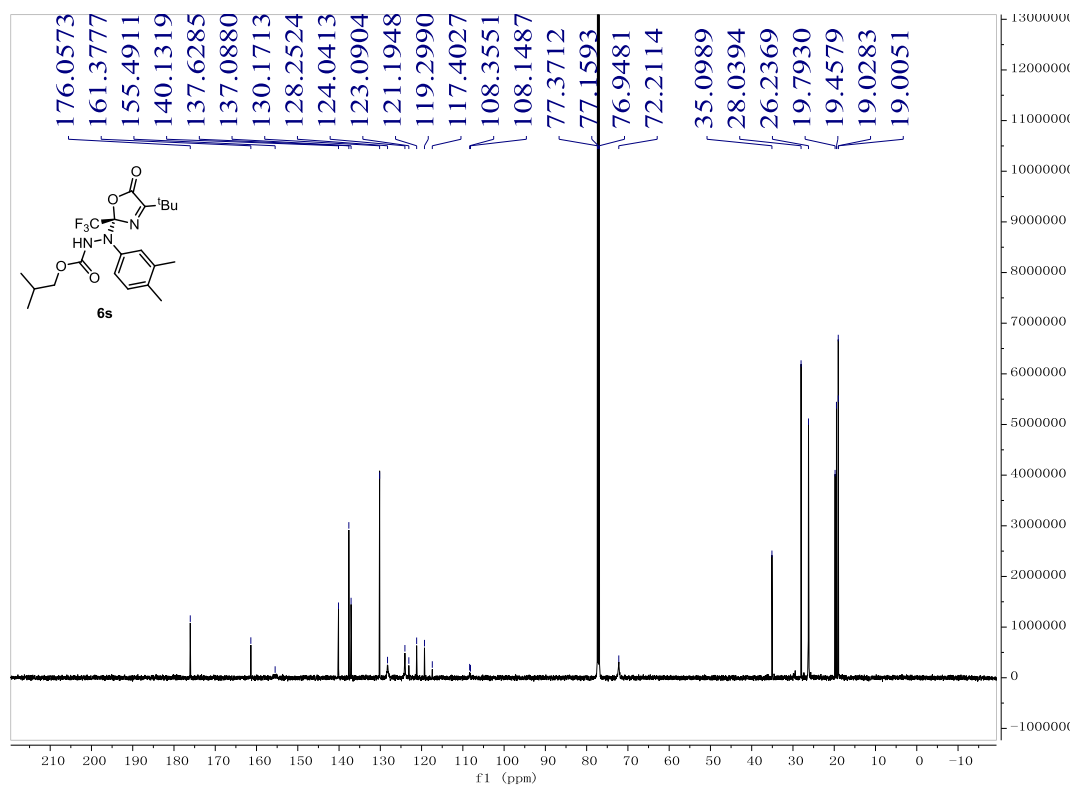
$^{19}\text{F}\{^1\text{H}\}$ NMR of **6r (564 MHz, CDCl_3)**



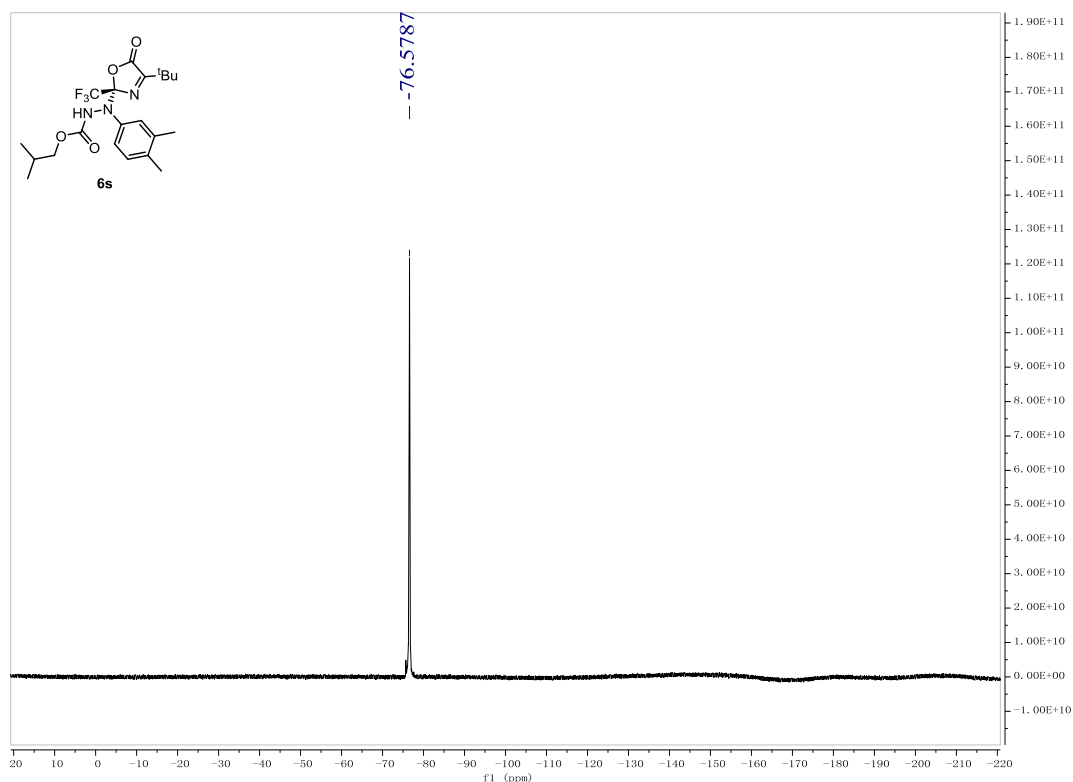
^1H NMR of **6s (600 MHz, CDCl_3)**



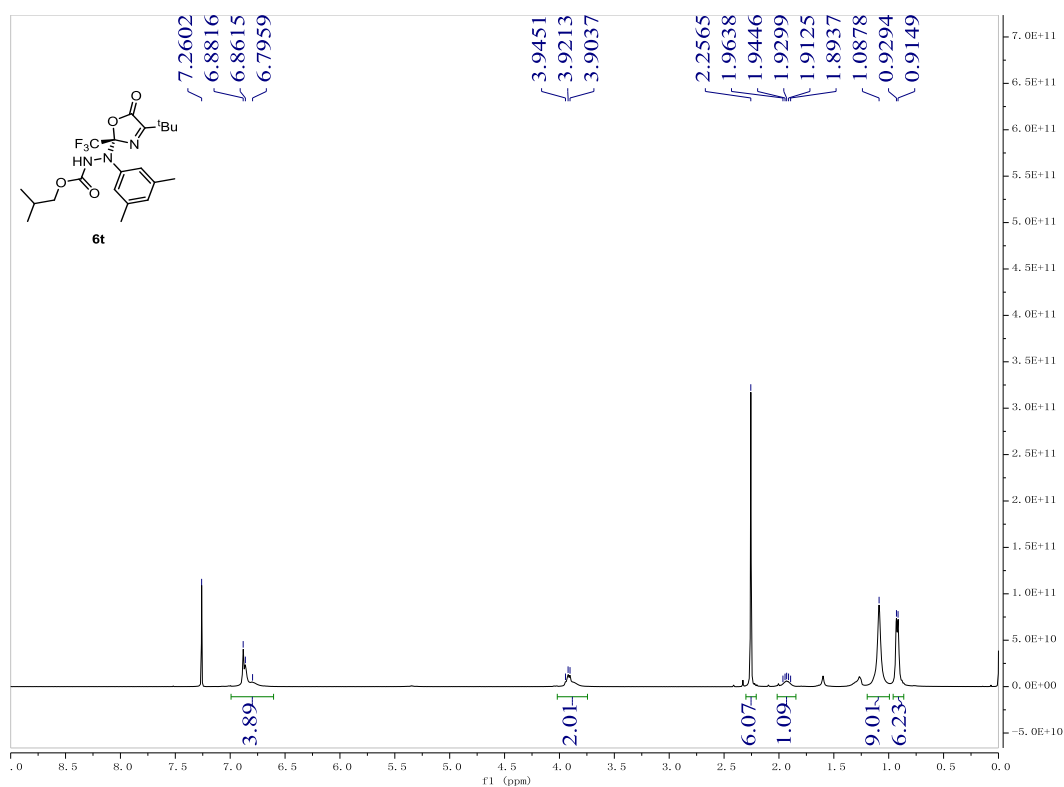
¹³C{¹H} NMR of 6s (150 MHz, CDCl₃)



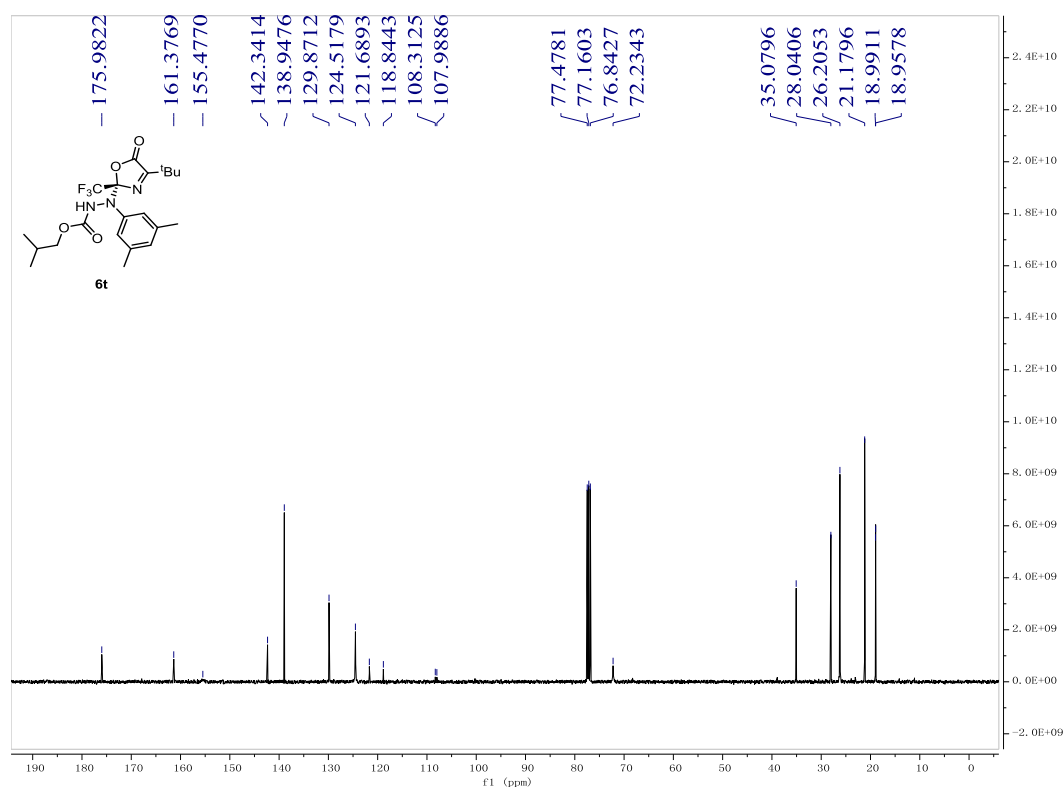
¹⁹F{¹H} NMR of 6s (376 MHz, CDCl₃)



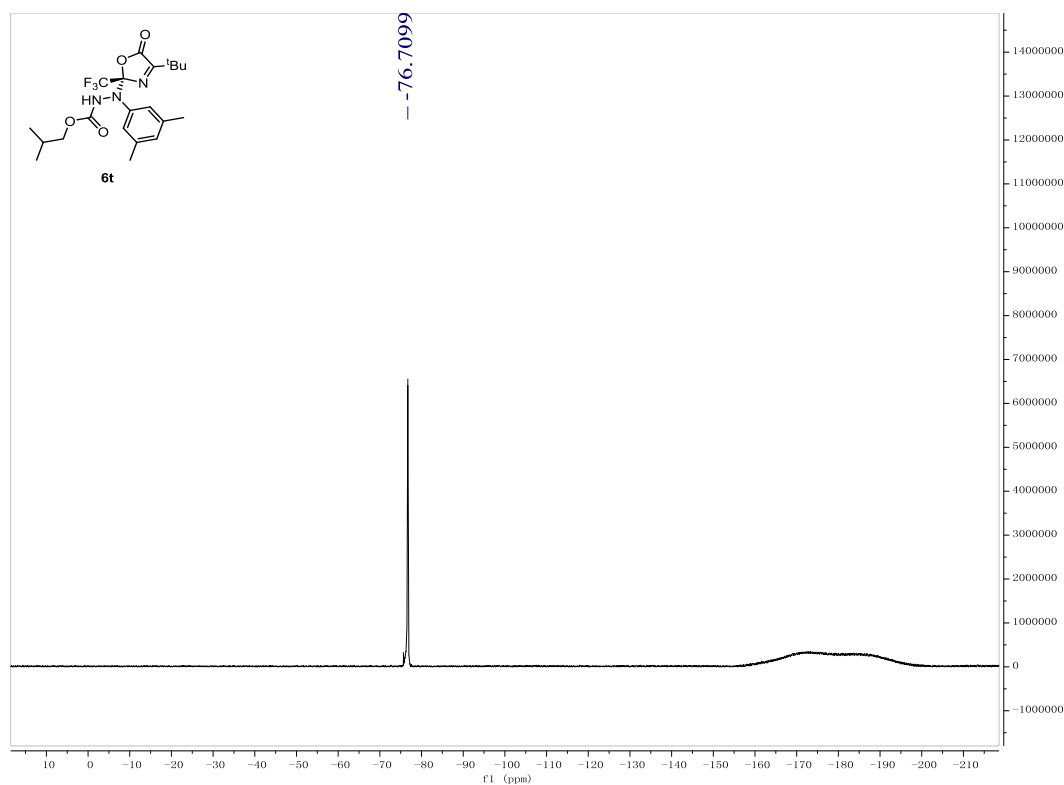
^1H NMR of 6t (400 MHz, CDCl_3)



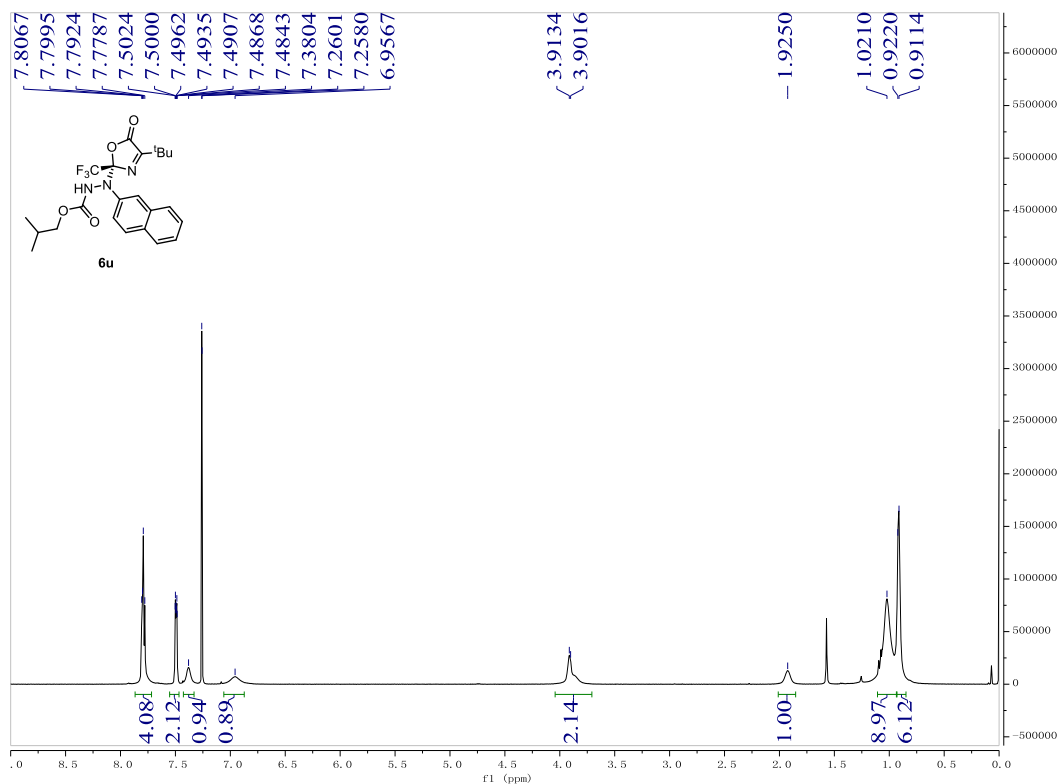
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6t (100 MHz, CDCl_3)



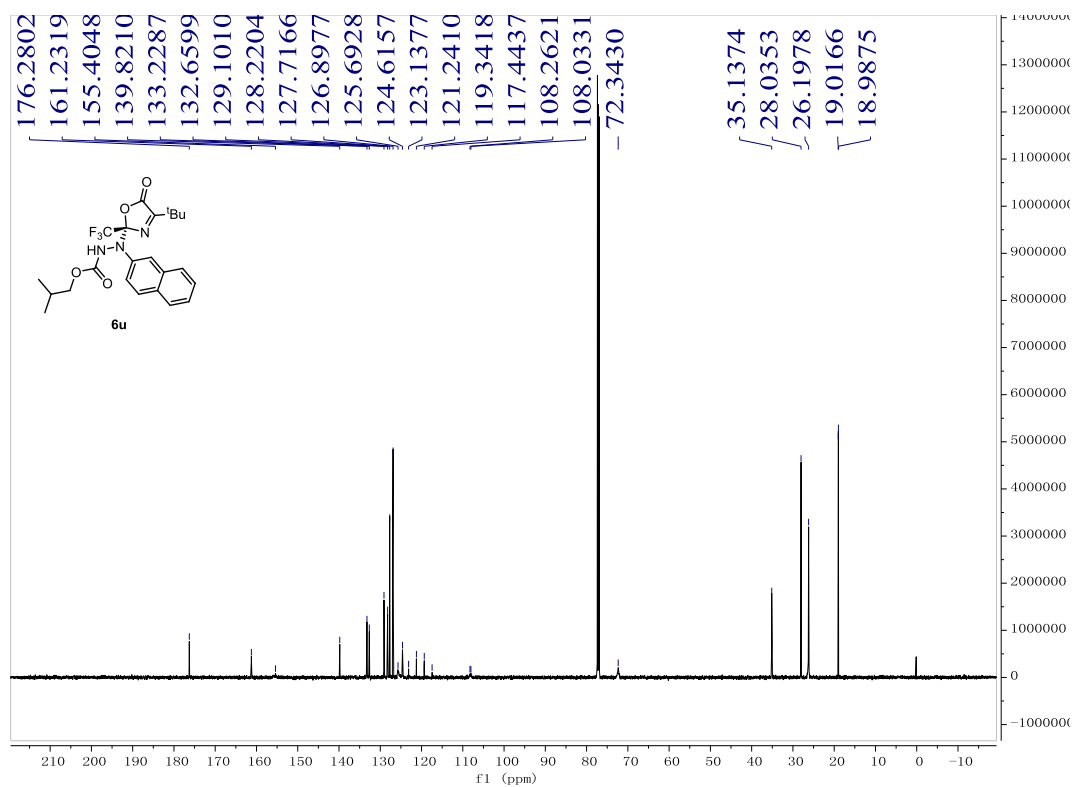
$^{19}\text{F}\{^1\text{H}\}$ NMR of 6t (564 MHz, CDCl_3)



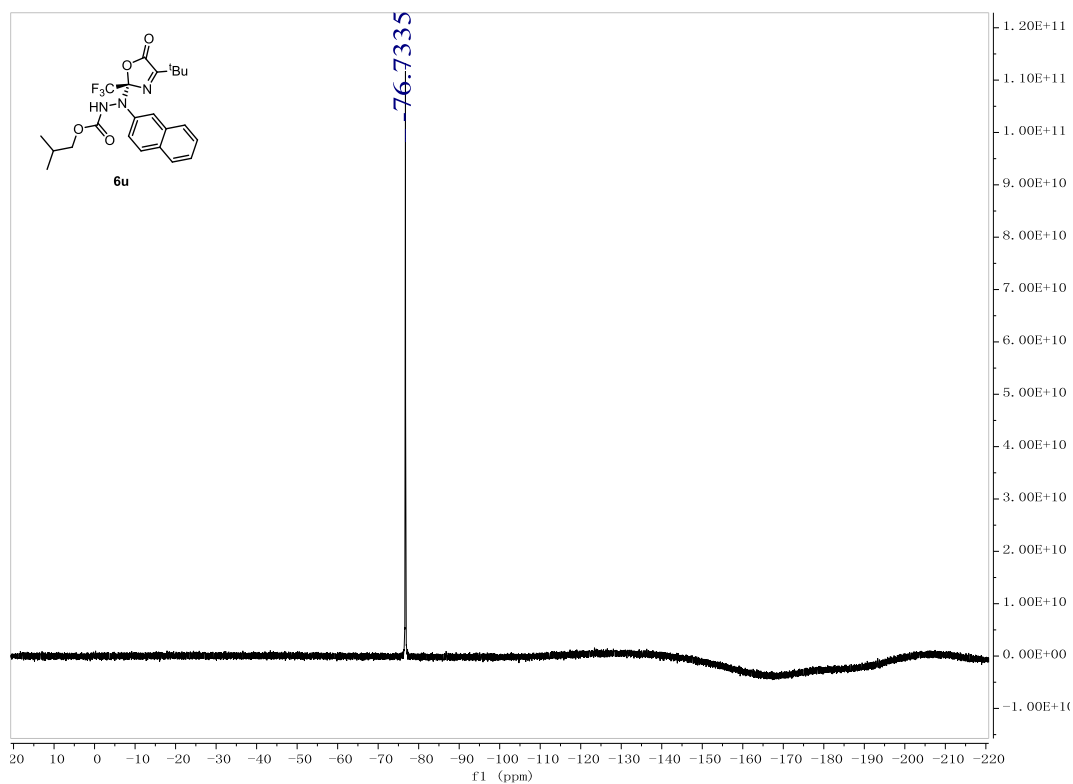
^1H NMR of 6u (600 MHz, CDCl_3)



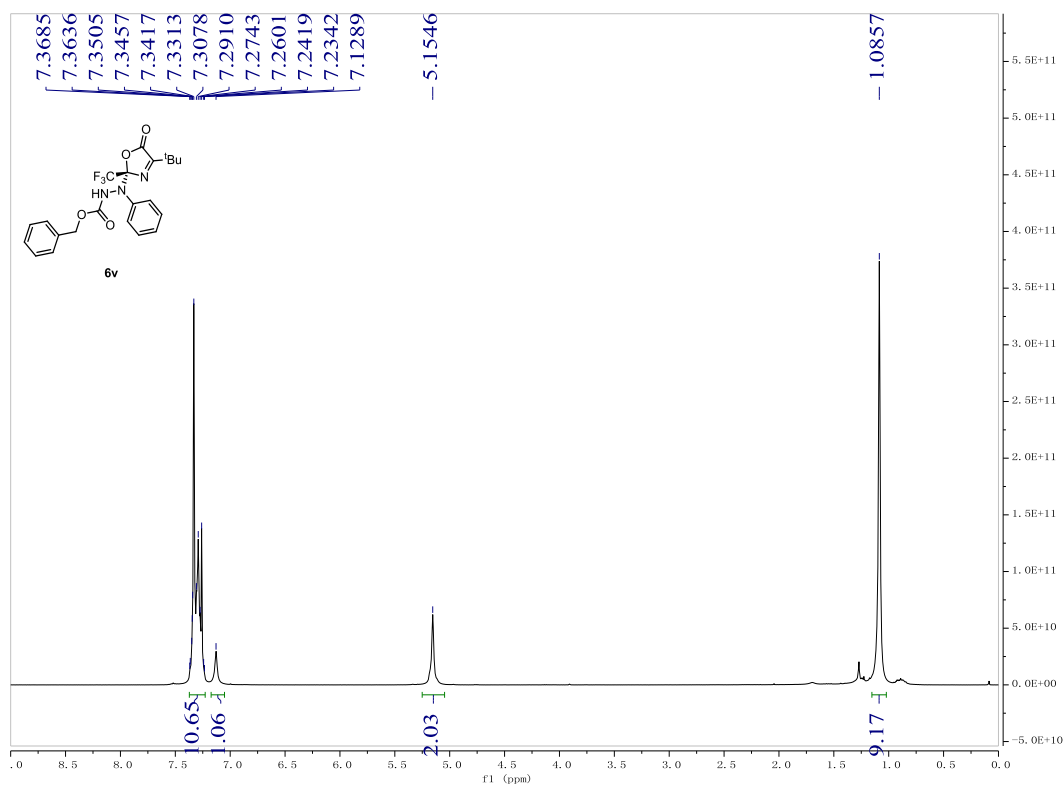
¹³C{¹H} NMR of 6u (150 MHz, CDCl₃)



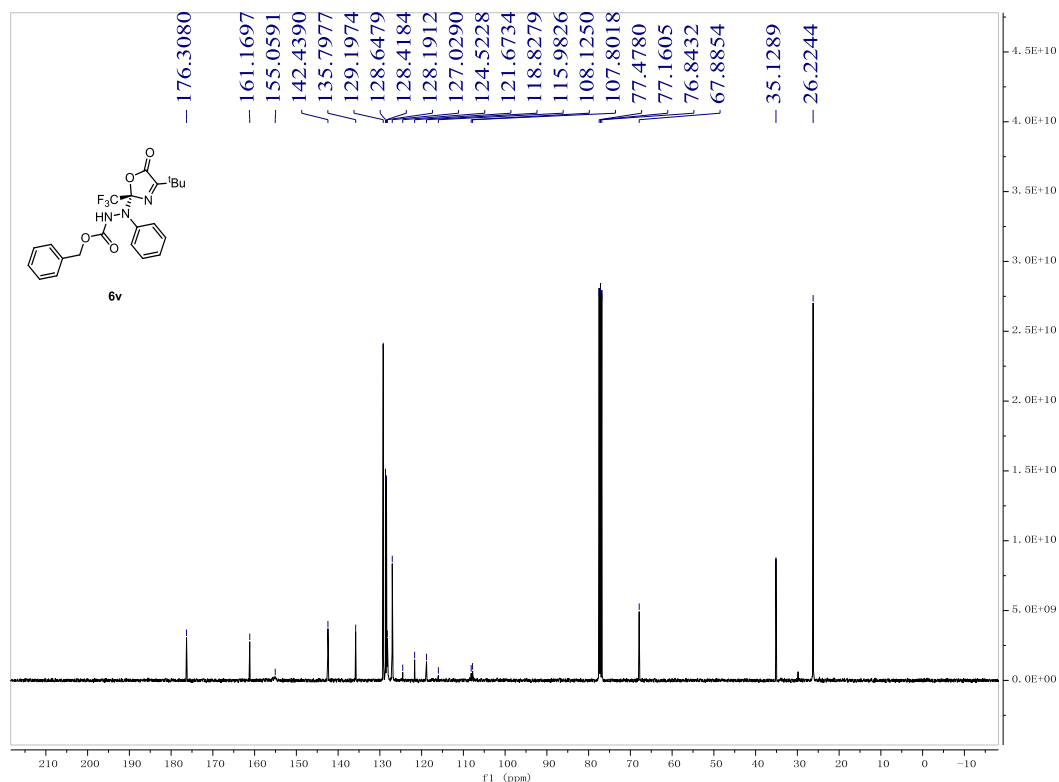
¹⁹F{¹H} NMR of 6u (376 MHz, CDCl₃)



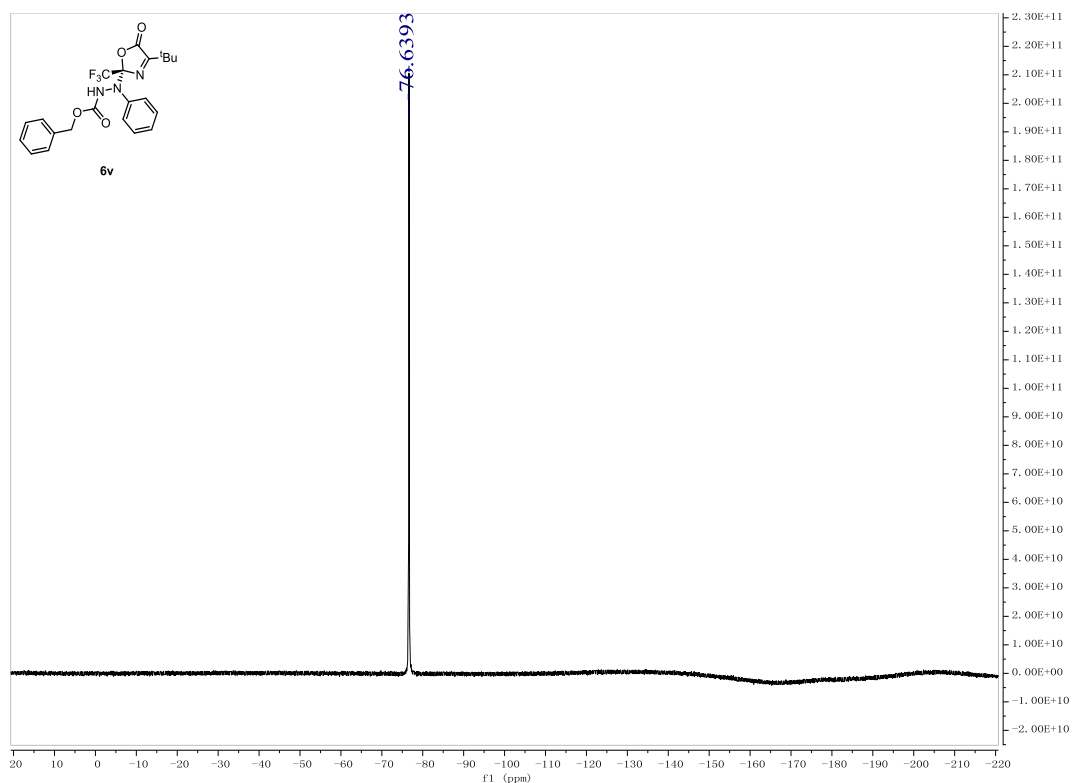
¹H NMR of 6v (400 MHz, CDCl₃)



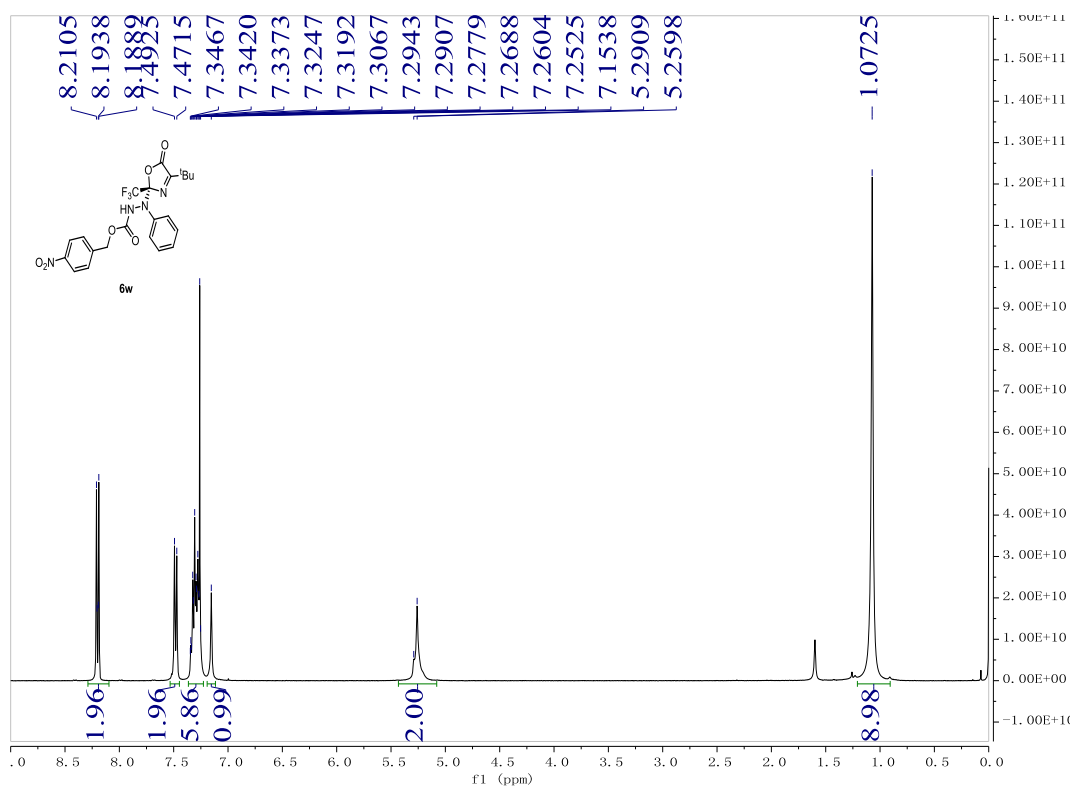
¹³C{¹H} NMR of 6v (150 MHz, CDCl₃)



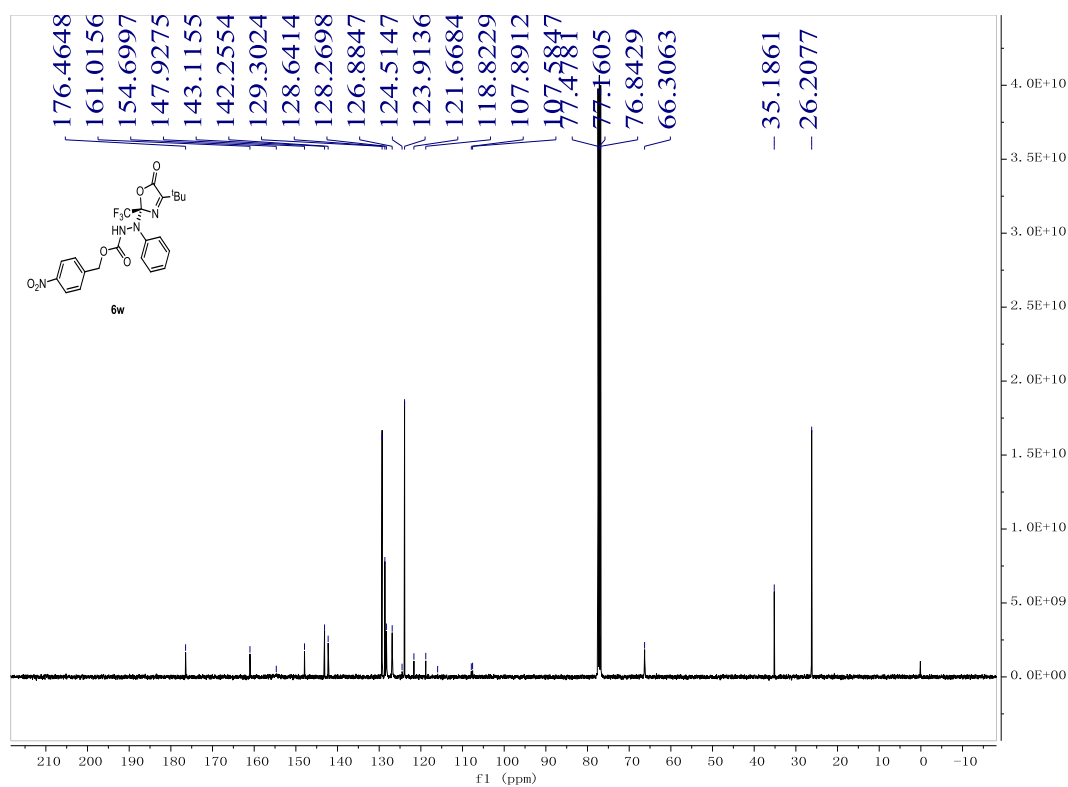
¹⁹F{¹H} NMR of 6v (376 MHz, CDCl₃)



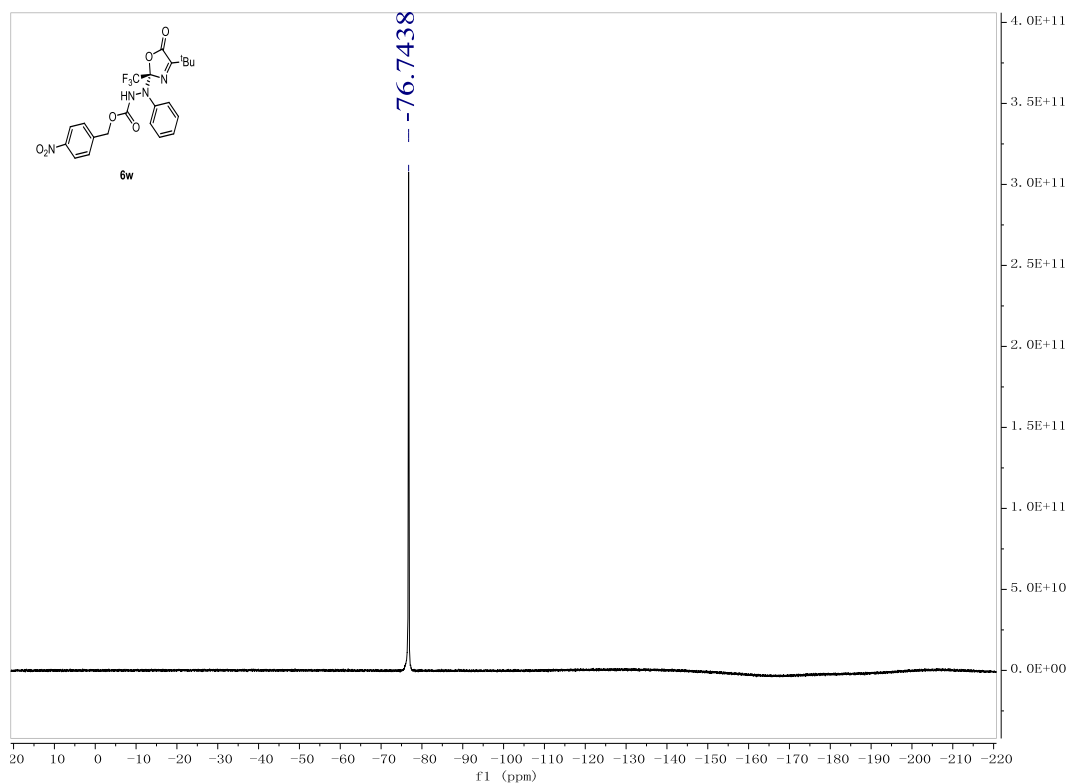
¹H NMR of 6w (400 MHz, CDCl₃)



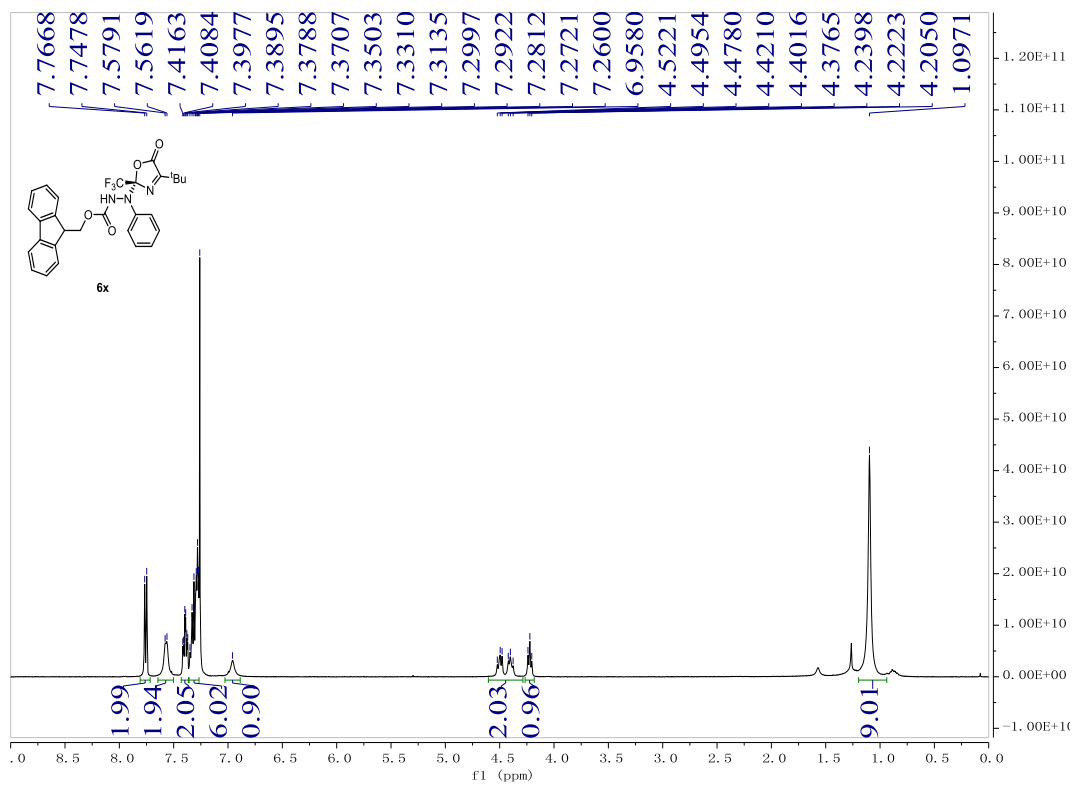
¹³C{¹H} NMR of 6w (100 MHz, CDCl₃)



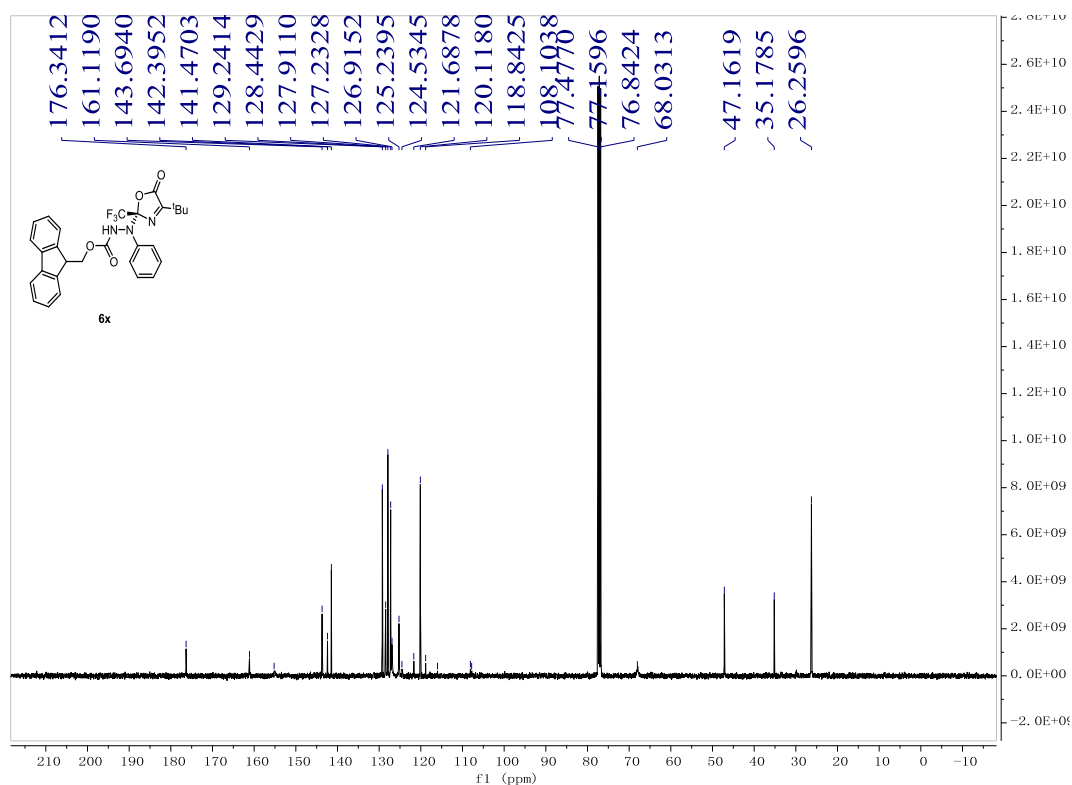
¹⁹F{¹H} NMR of 6w (376 MHz, CDCl₃)



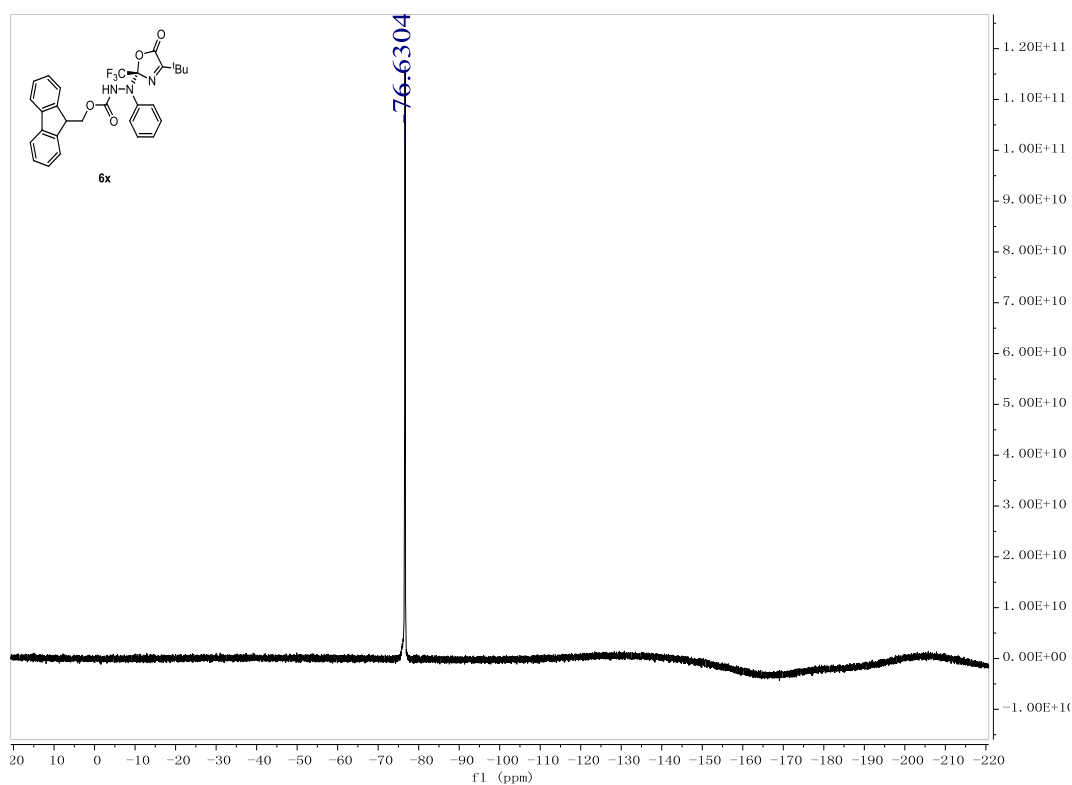
¹H NMR of 6x (400 MHz, CDCl₃)



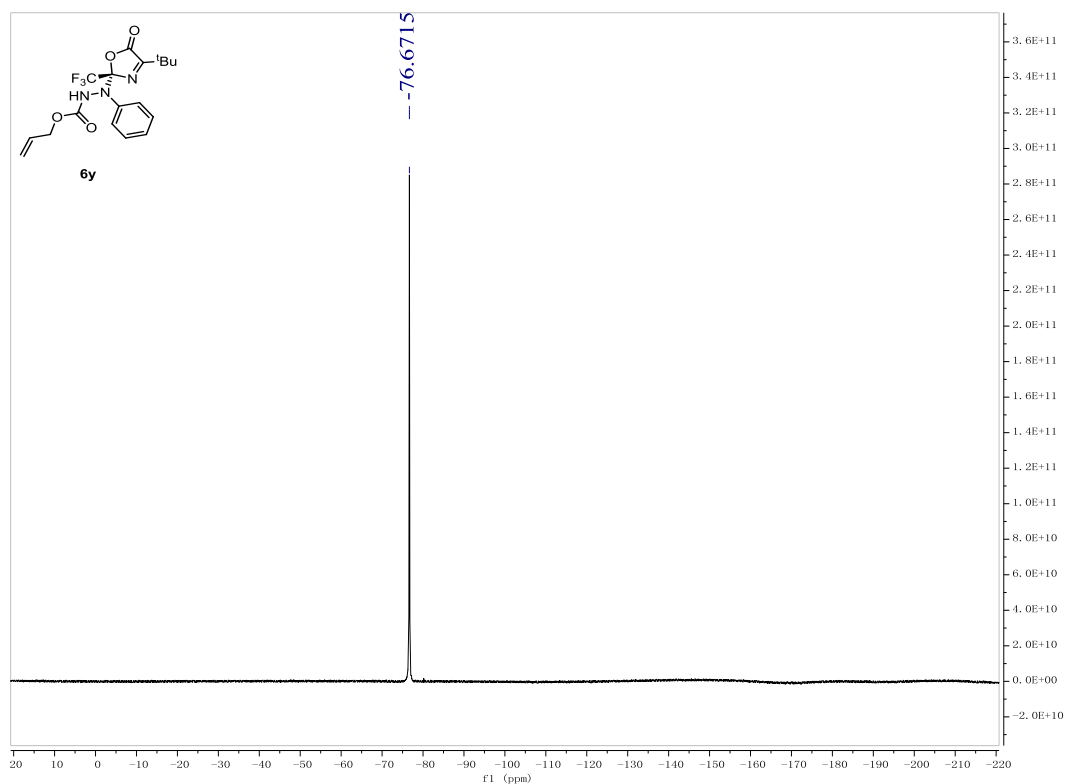
¹³C{¹H} NMR of 6x (100 MHz, CDCl₃)



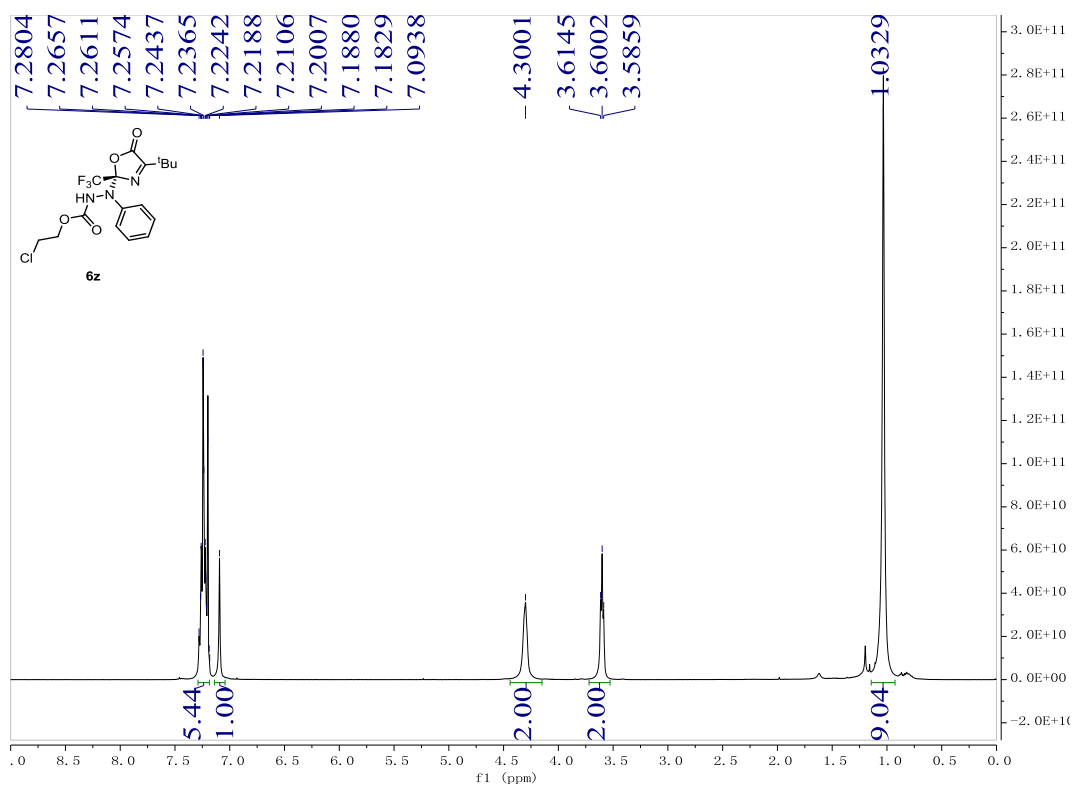
¹⁹F{¹H} NMR of 6x (376 MHz, CDCl₃)



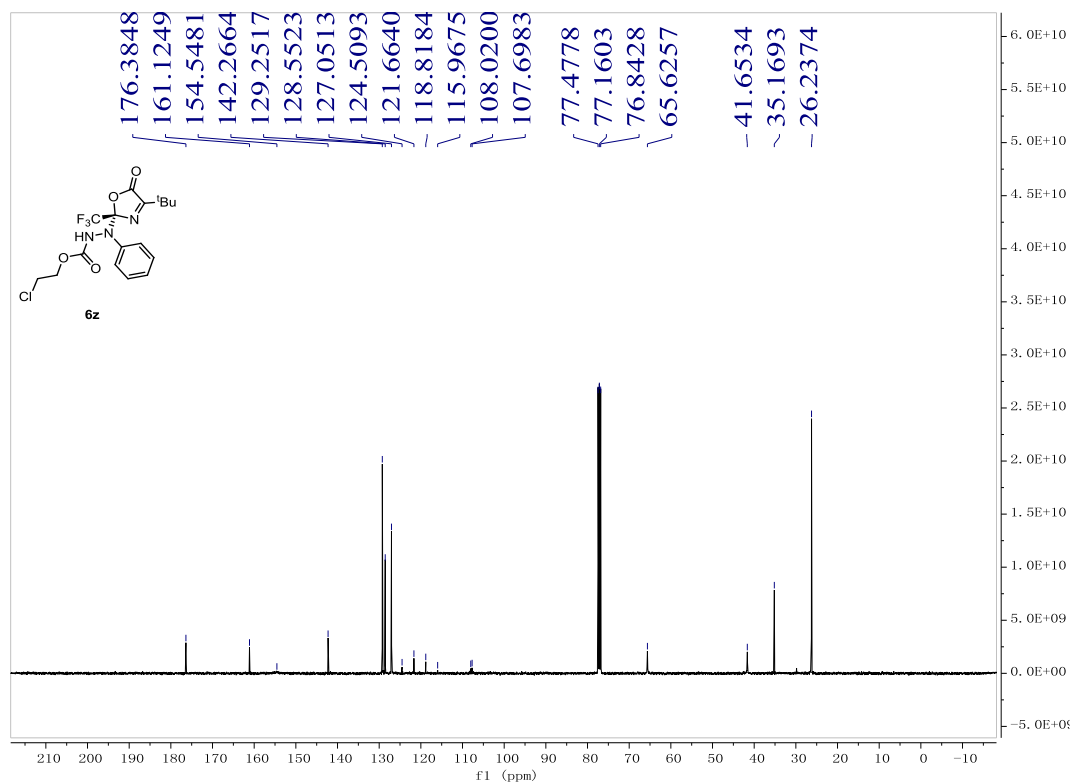
¹H NMR of 6y (400 MHz, CDCl₃)



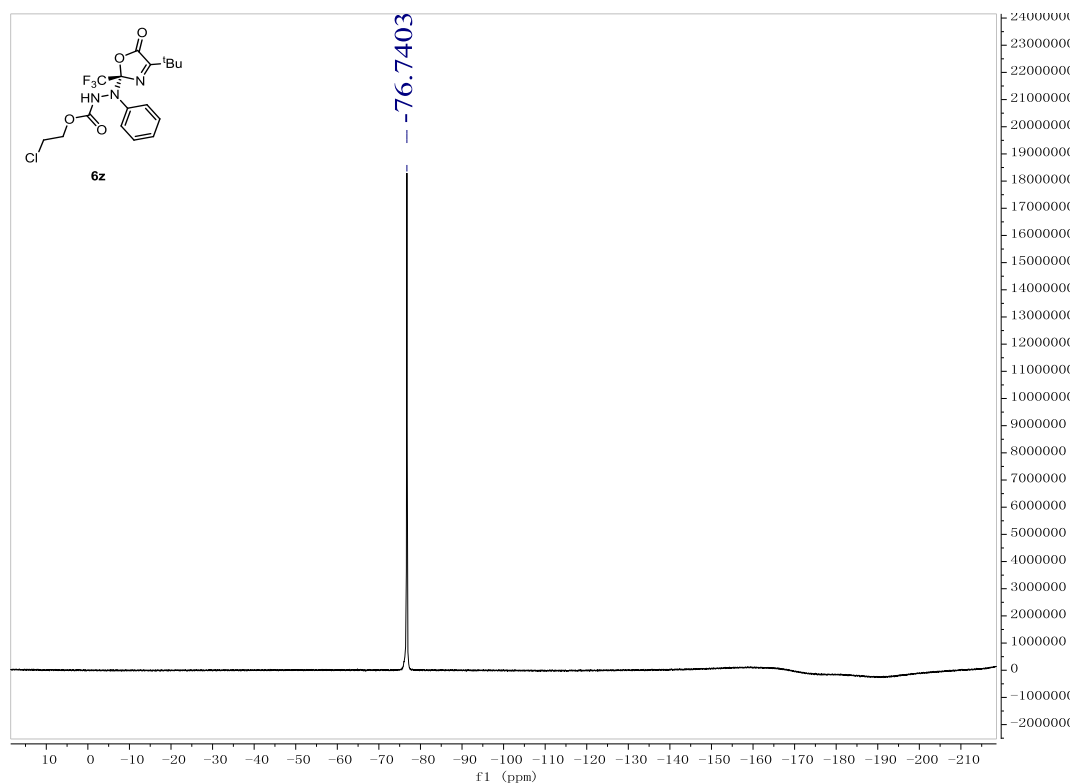
^1H NMR of 6z (400 MHz, CDCl_3)



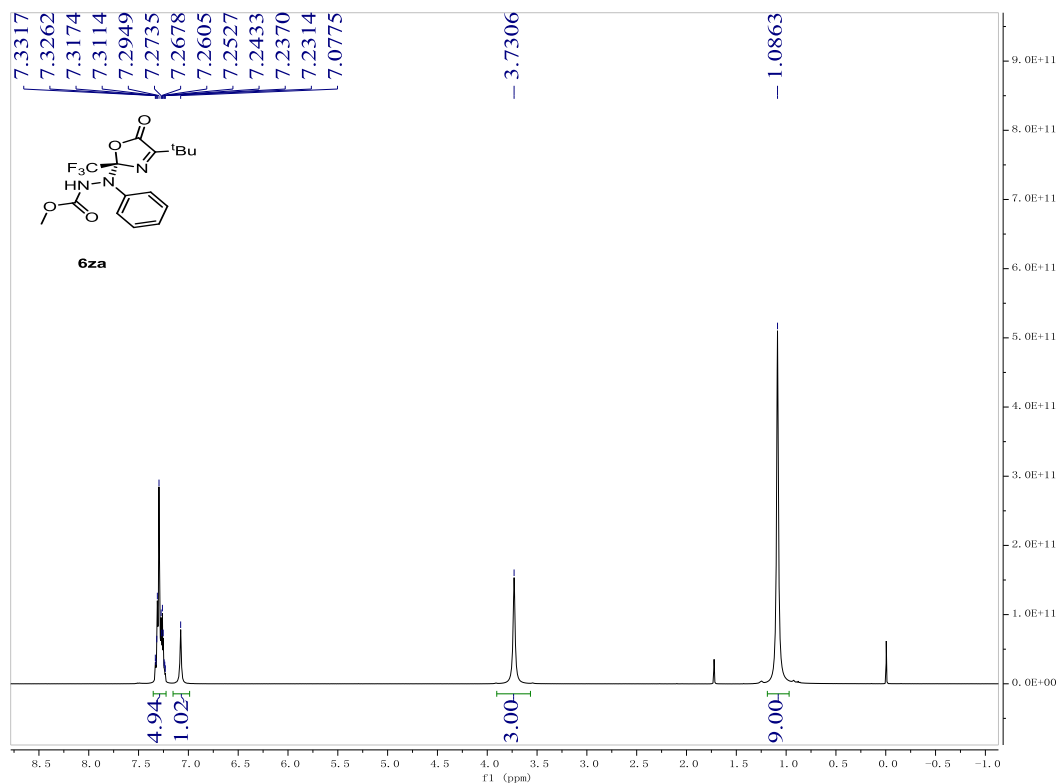
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6z (100 MHz, CDCl_3)



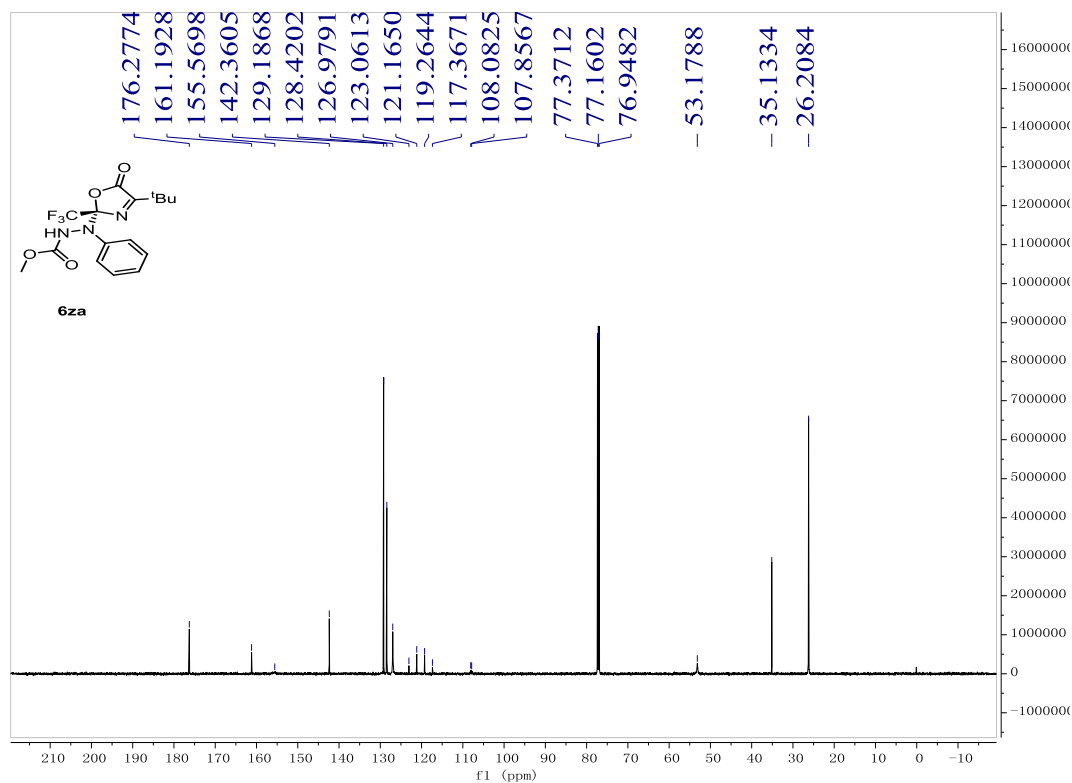
¹⁹F{¹H} NMR of 6z (564 MHz, CDCl₃)



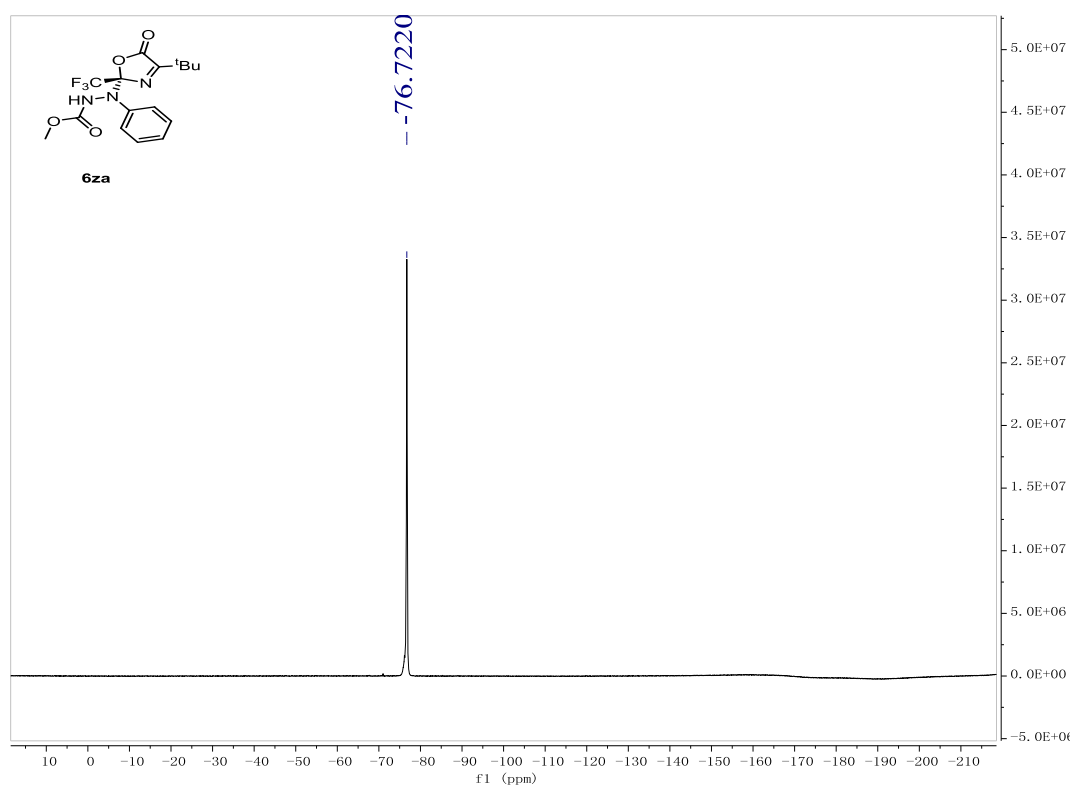
¹H NMR of 6za (400 MHz, CDCl₃)



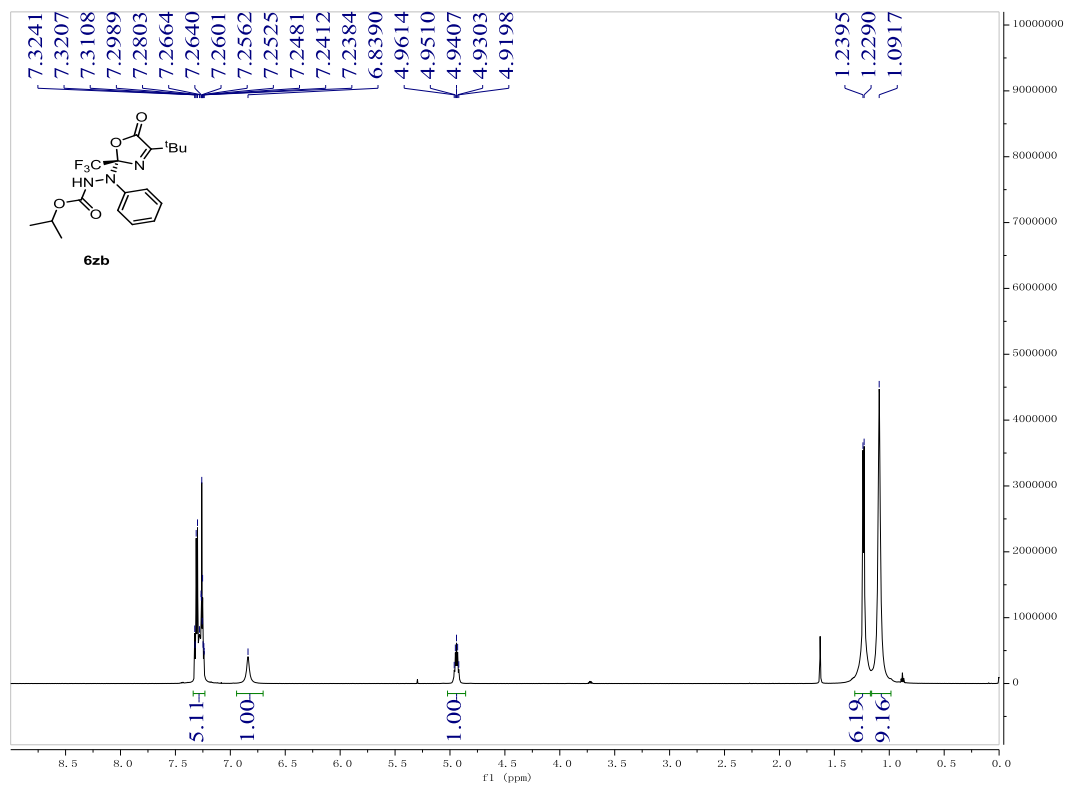
¹³C{¹H} NMR of 6za (150 MHz, CDCl₃)



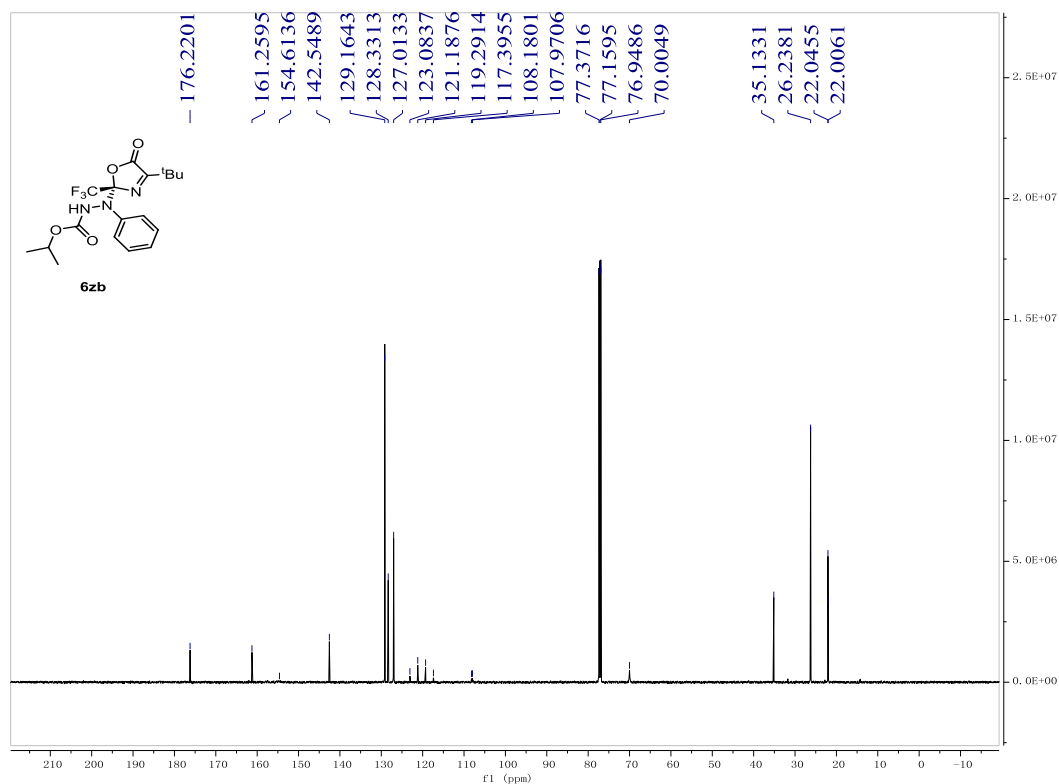
¹⁹F{¹H} NMR of 6za (564 MHz, CDCl₃)



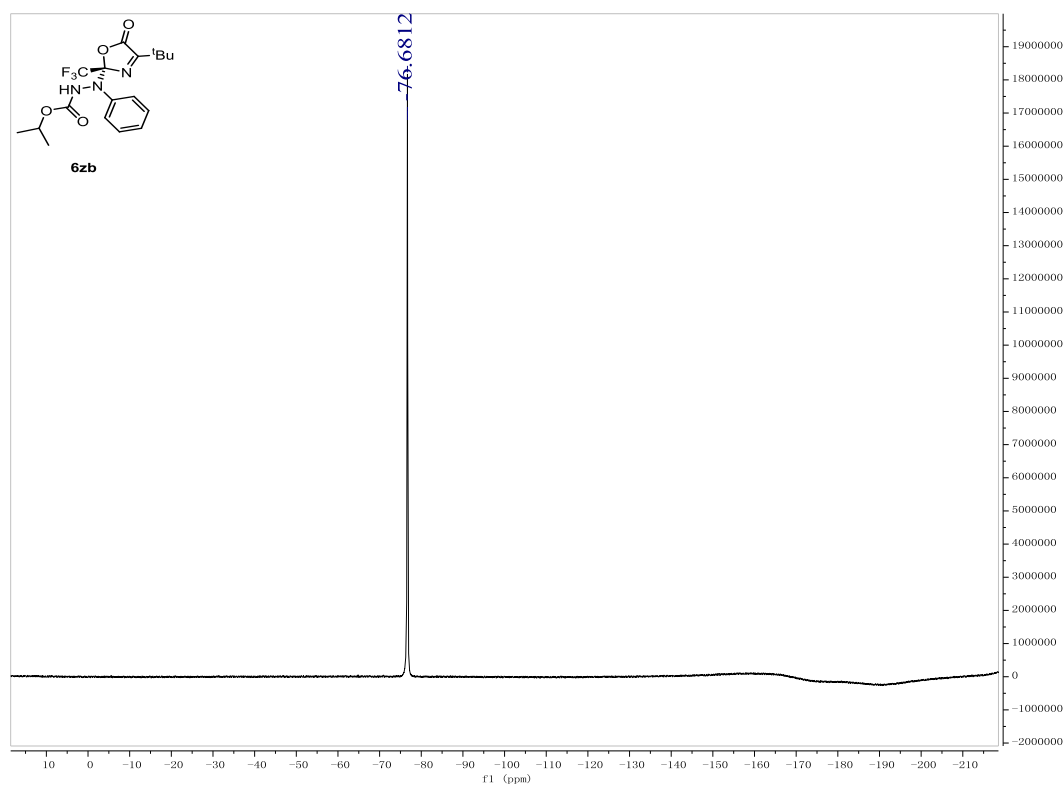
^1H NMR of 6zb (600 MHz, CDCl_3)



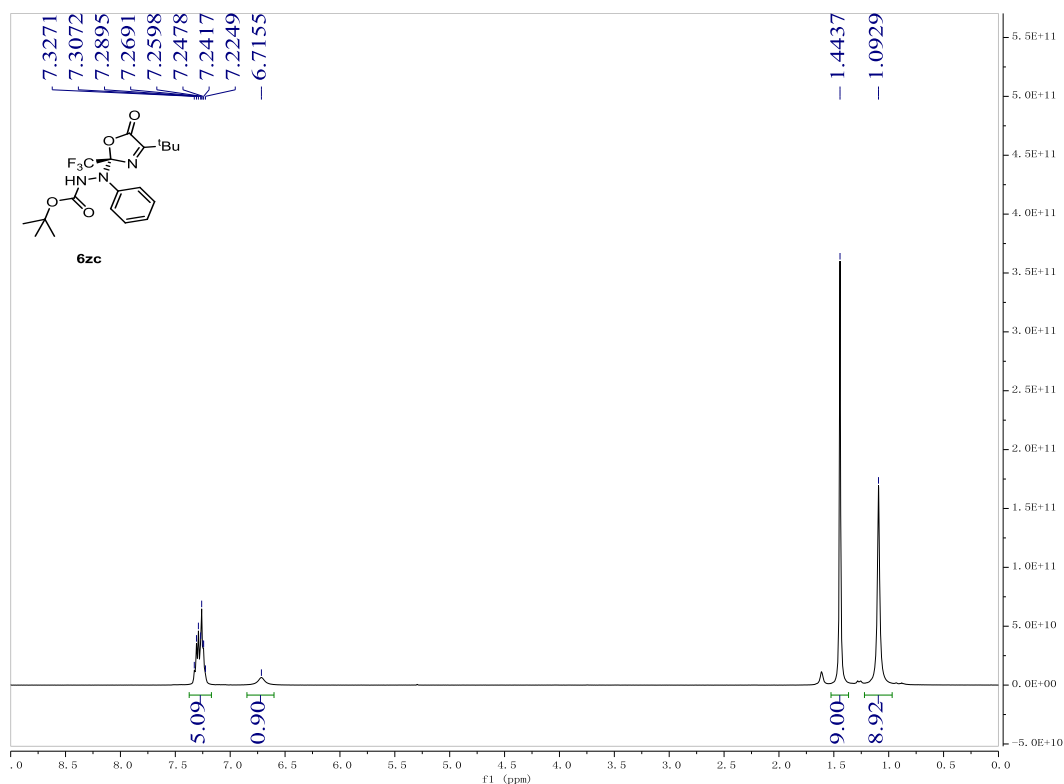
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6zb (150 MHz, CDCl_3)



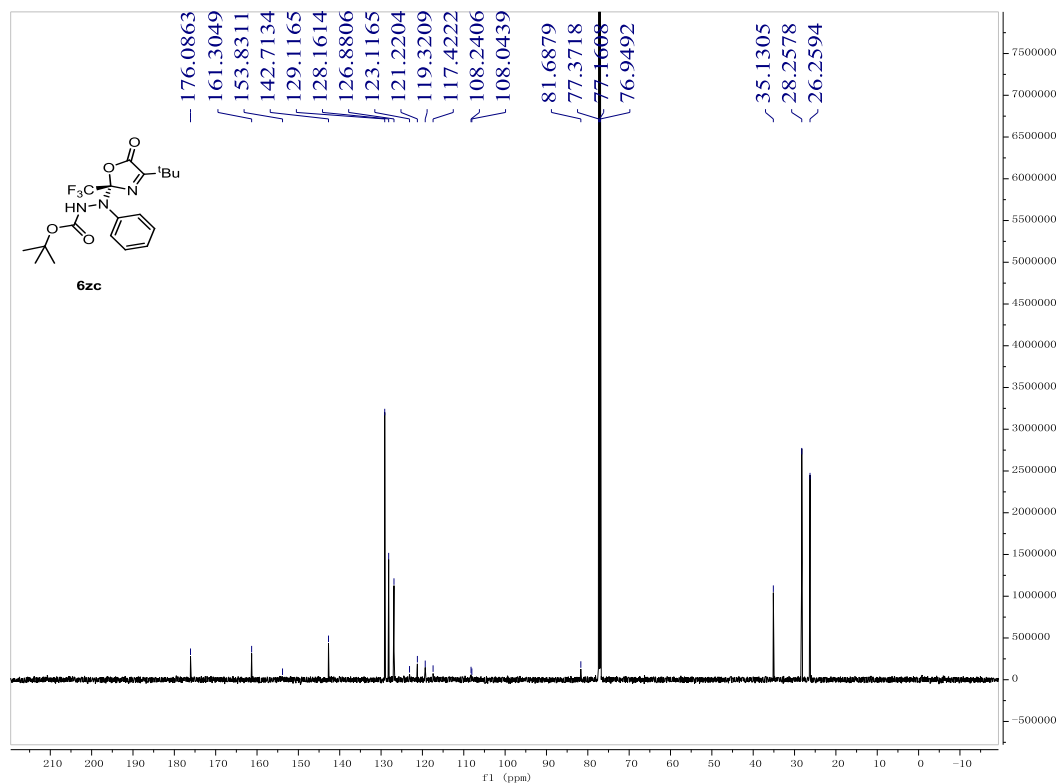
¹⁹F{¹H} NMR of 6zb (564 MHz, CDCl₃)



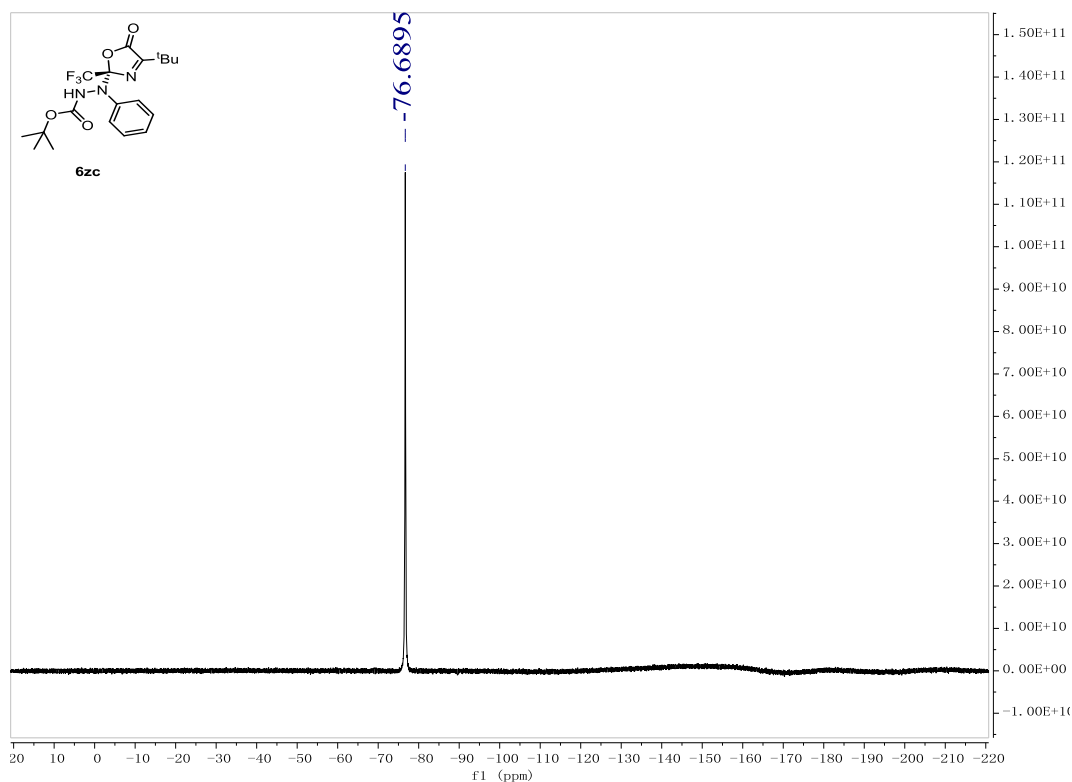
¹H NMR of 6zc (400 MHz, CDCl₃)



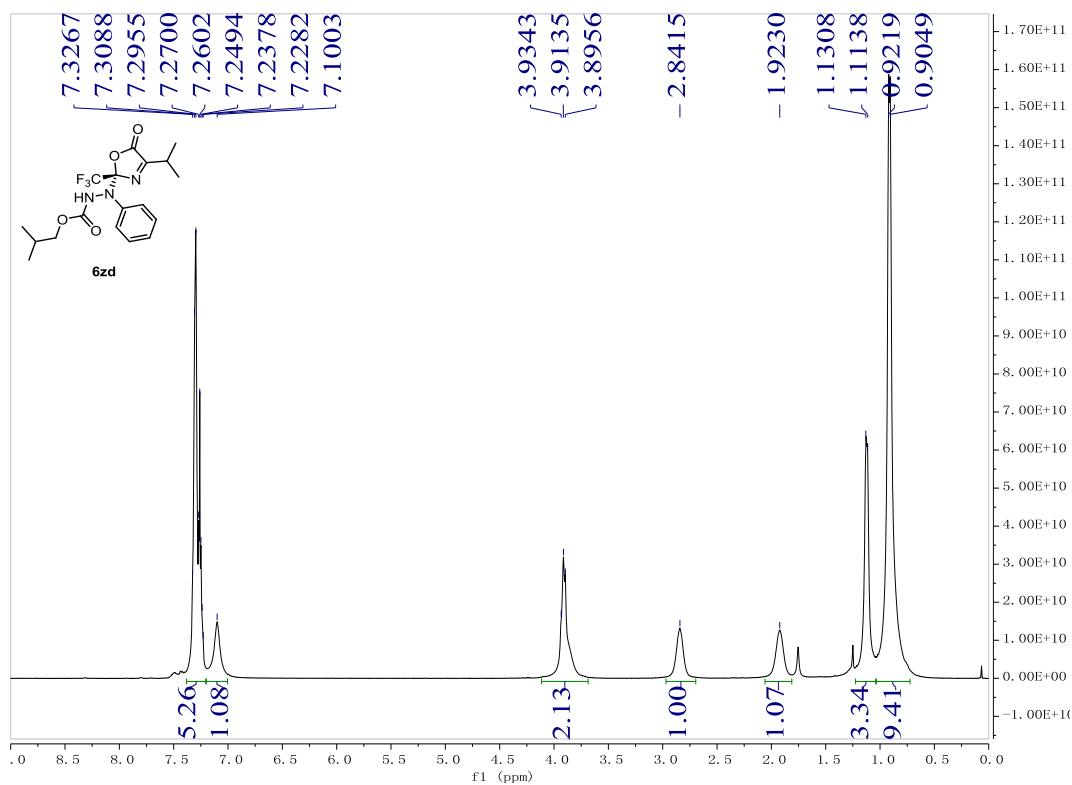
¹³C{¹H} NMR of 6zc (150 MHz, CDCl₃)



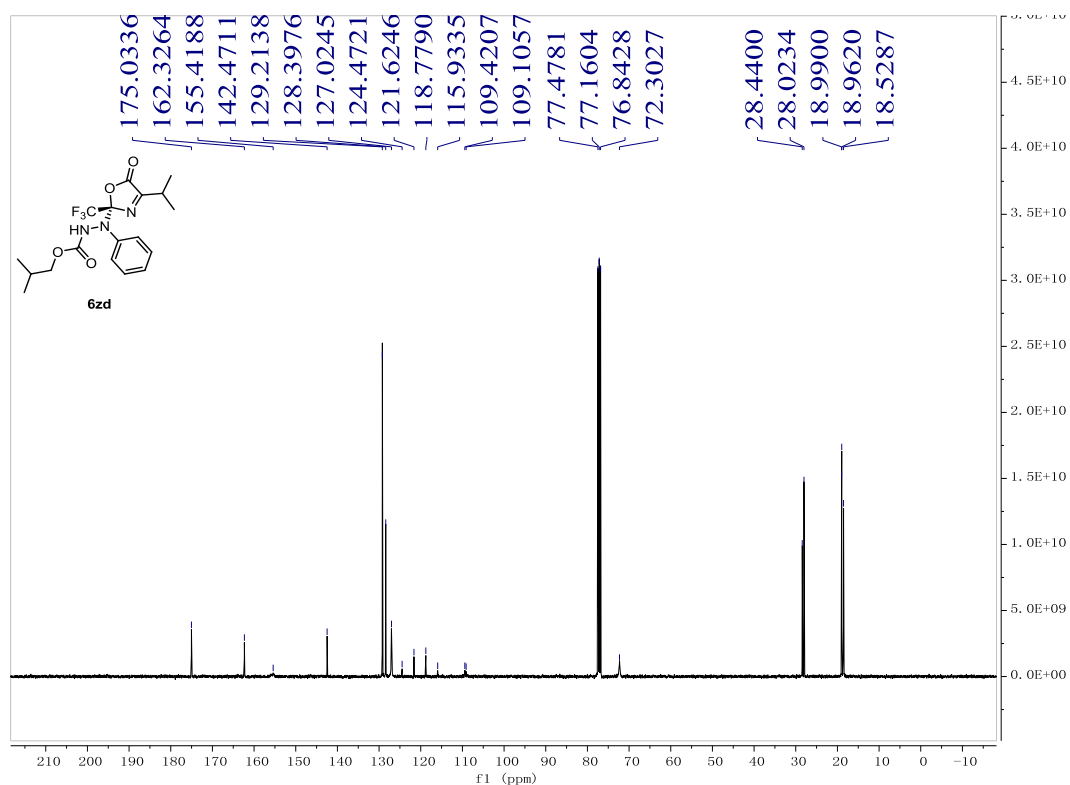
¹⁹F{¹H} NMR of 6zc (376 MHz, CDCl₃)



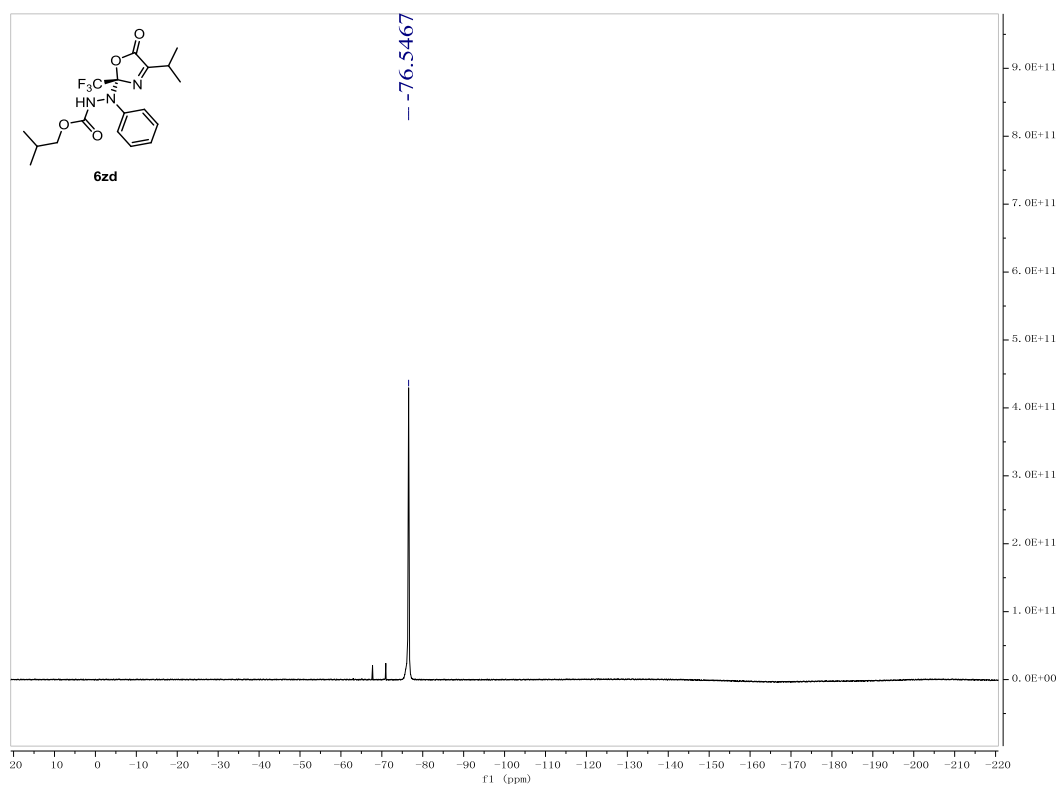
^1H NMR of 6zd (400 MHz, CDCl_3)



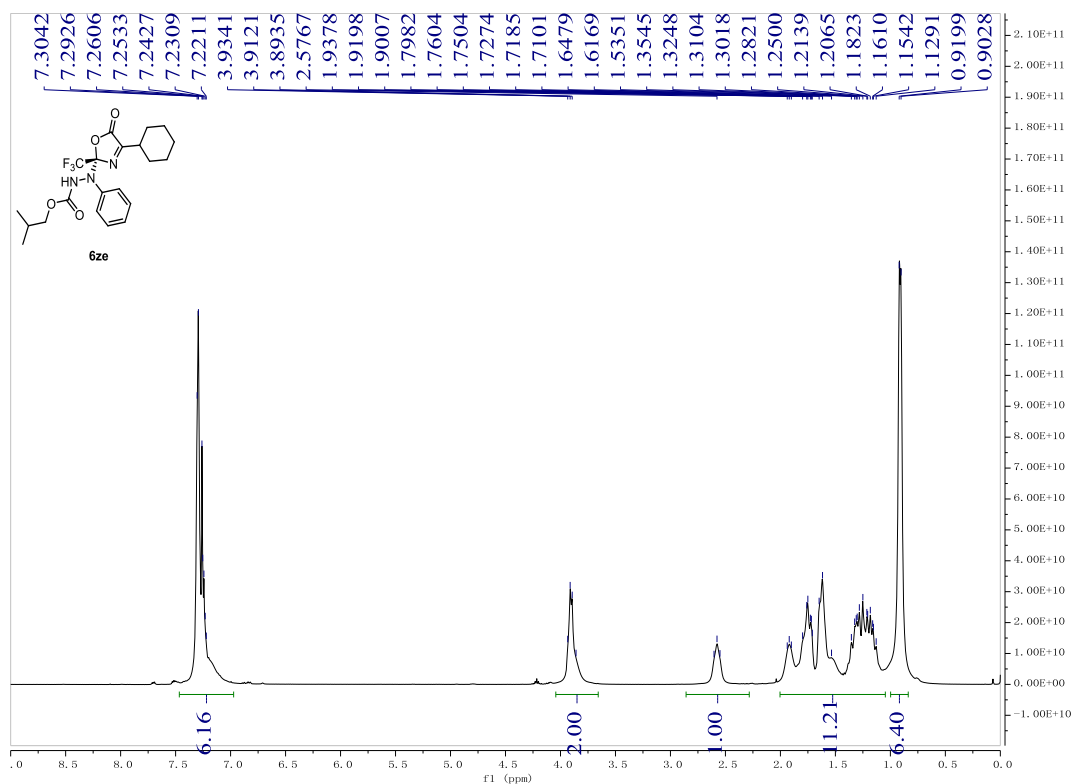
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6zd (100 MHz, CDCl_3)



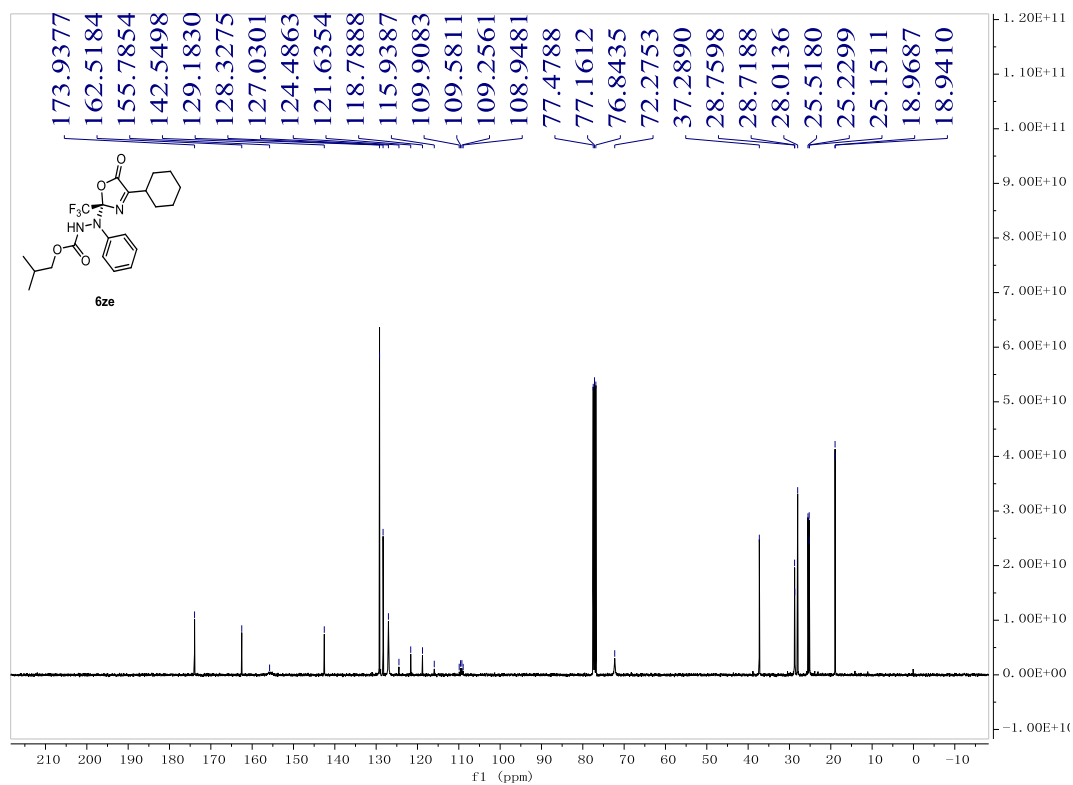
¹⁹F{¹H} NMR of 6zd (376 MHz, CDCl₃)



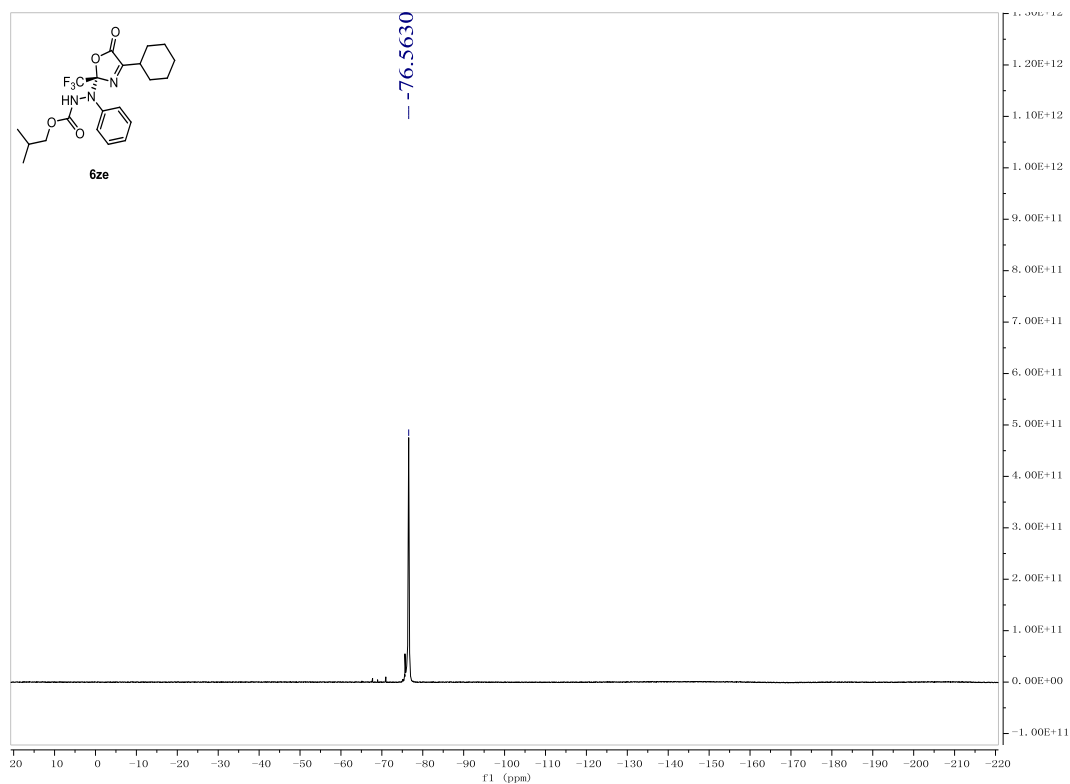
¹H NMR of 6ze (400 MHz, CDCl₃)



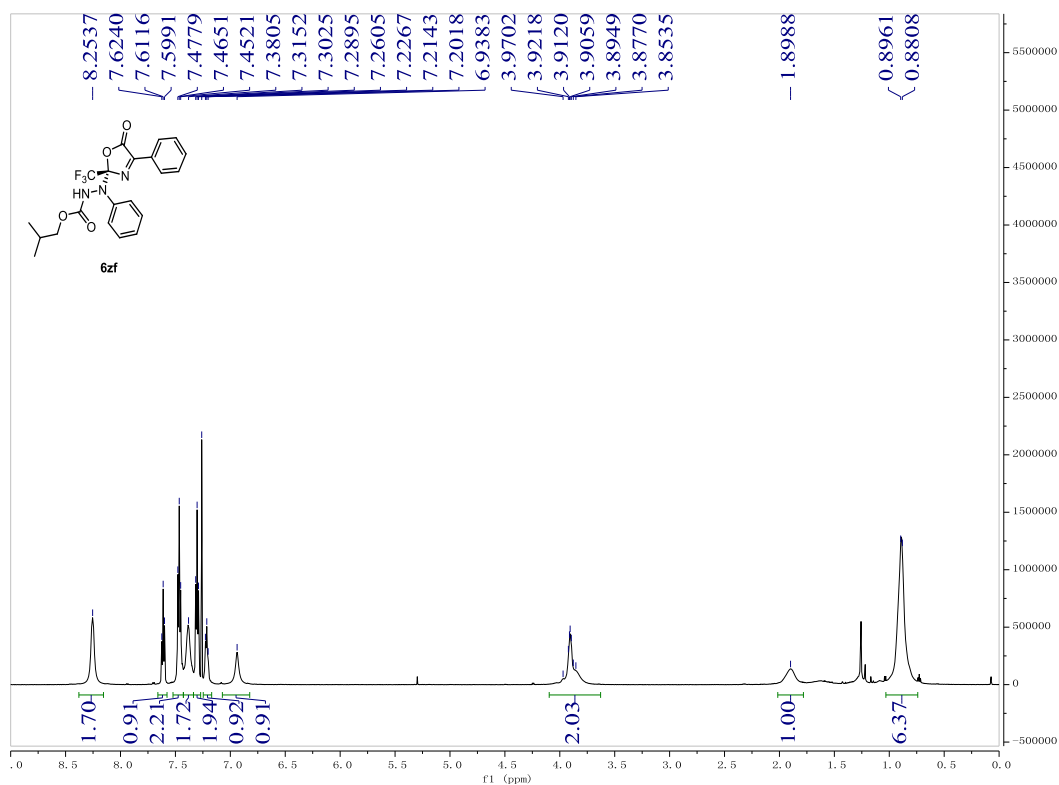
¹³C{¹H} NMR of 6ze (100 MHz, CDCl₃)



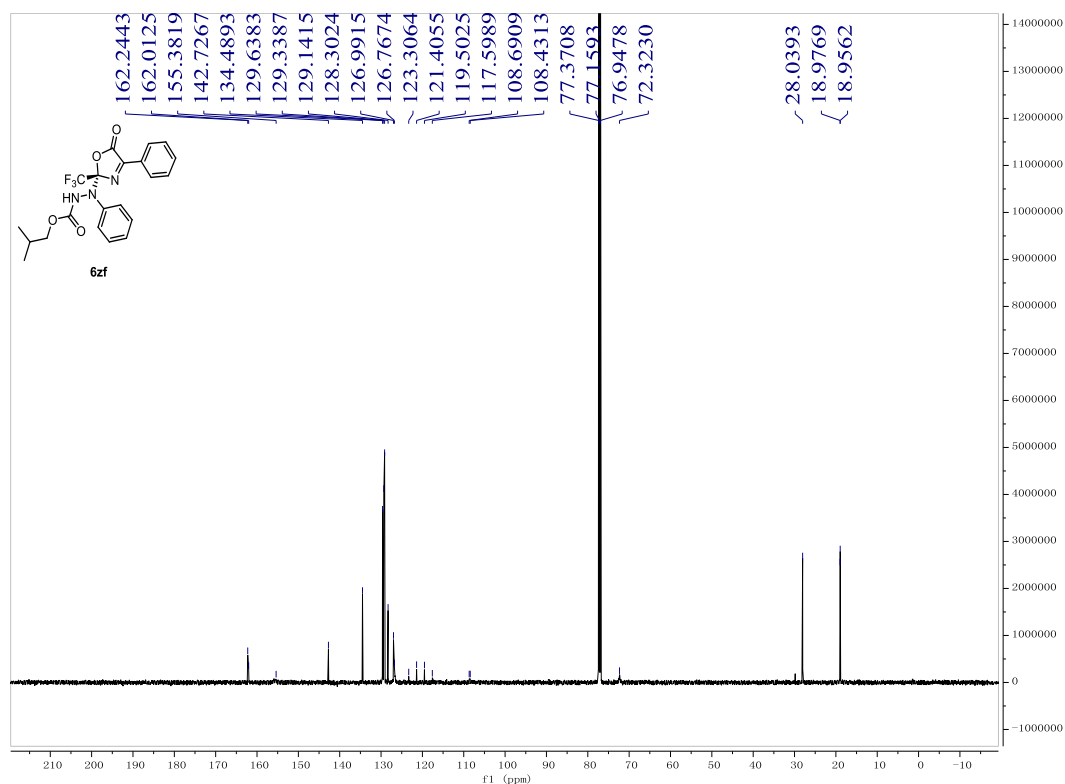
¹⁹F{¹H} NMR of 6ze (376 MHz, CDCl₃)



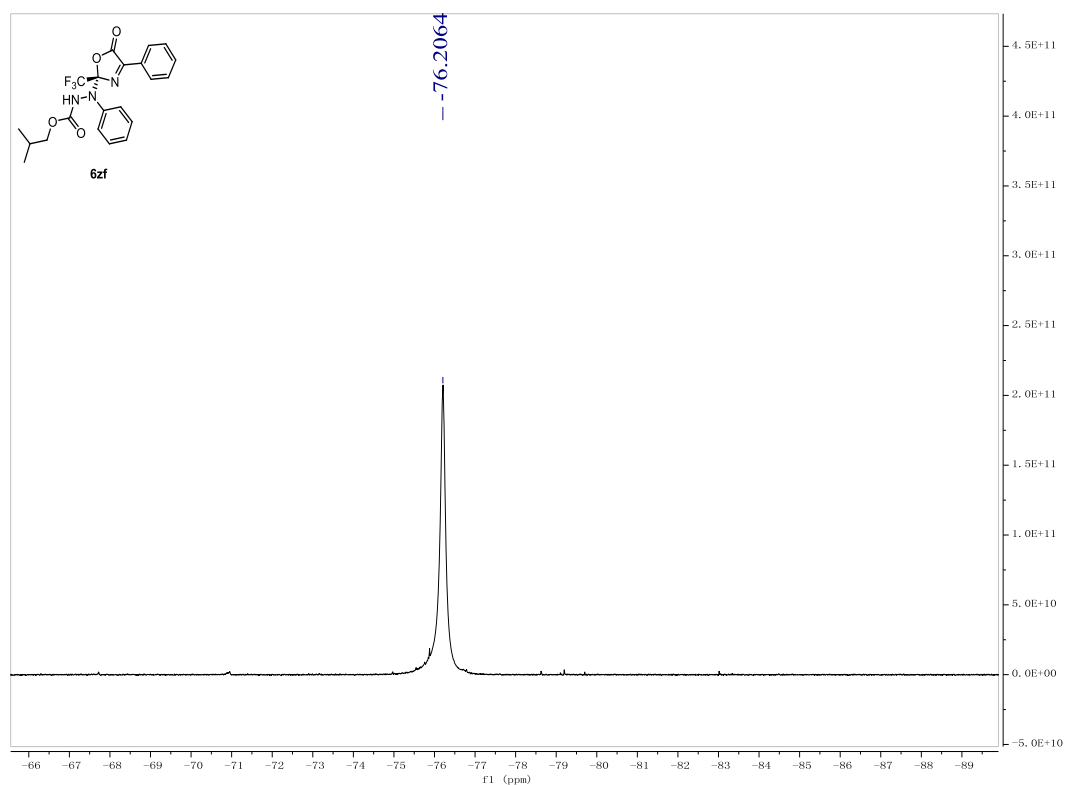
^1H NMR of 6zf (600 MHz, CDCl_3)



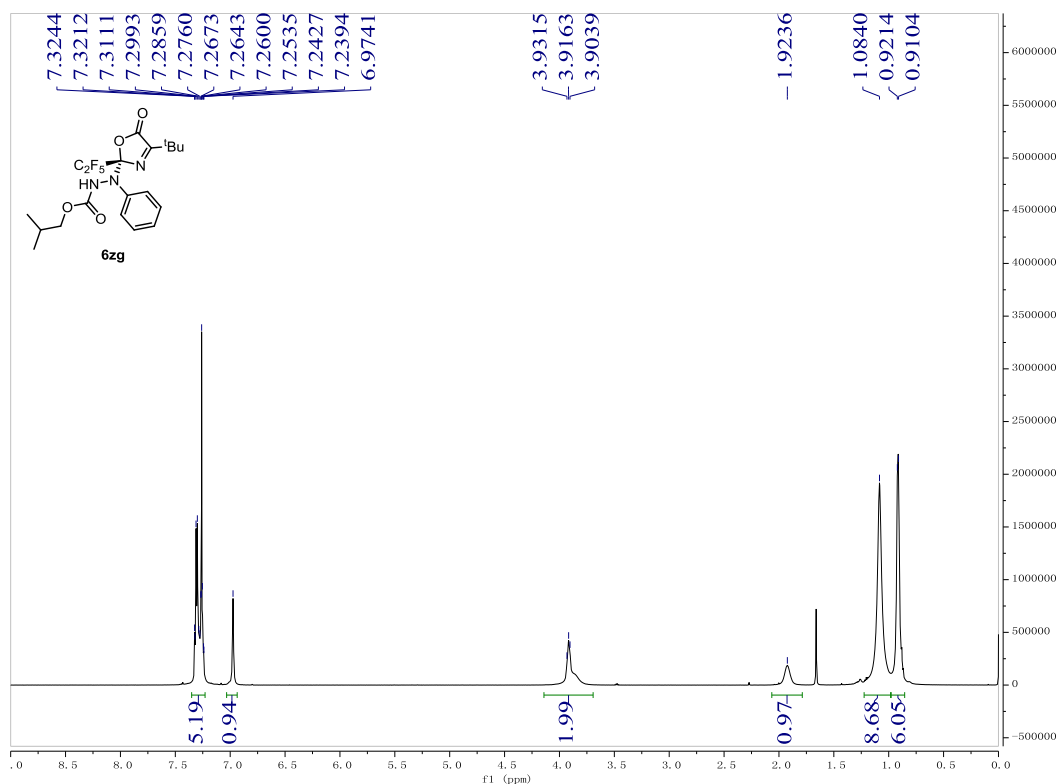
$^{13}\text{C}\{^1\text{H}\}$ NMR of 6zf (150 MHz, CDCl_3)



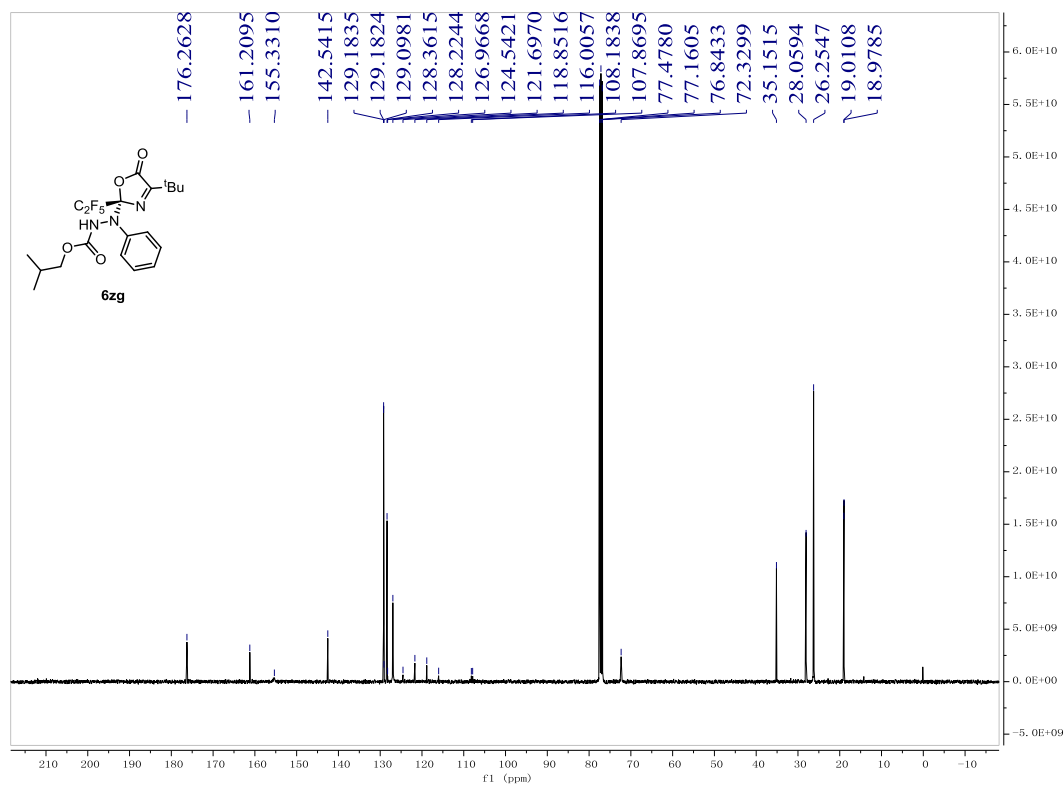
¹⁹F{¹H} NMR of **6zf (376 MHz, CDCl₃)**



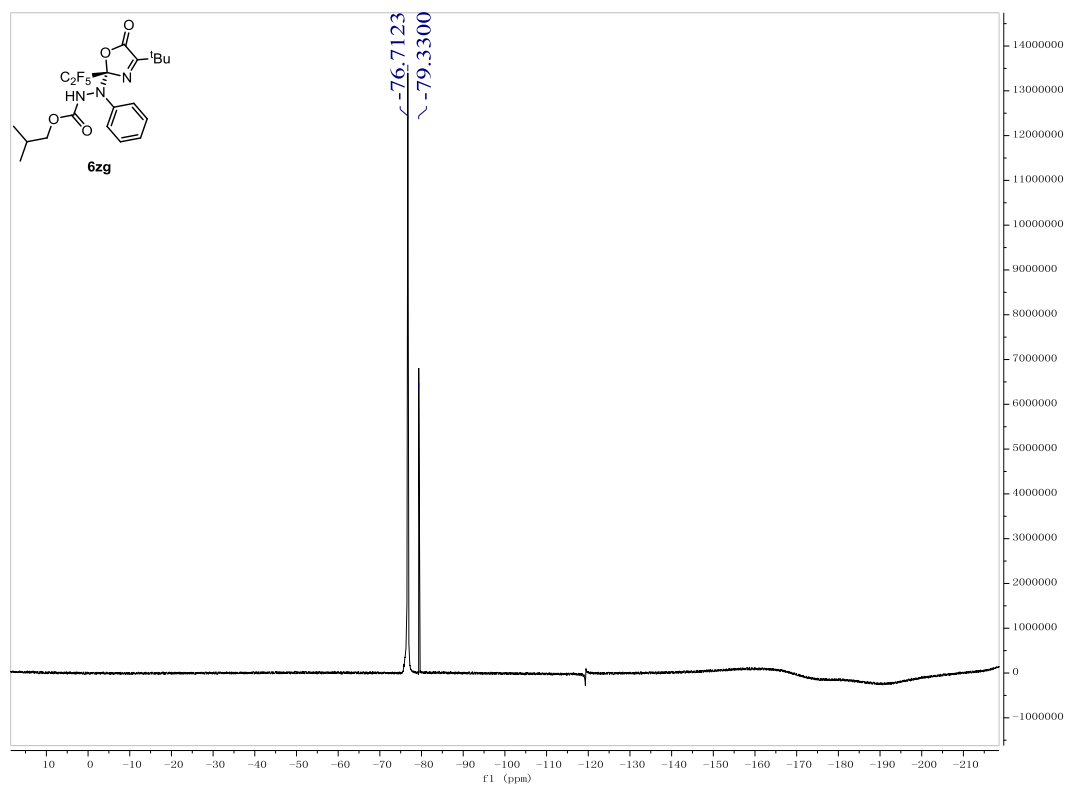
¹H NMR of **6zg (600 MHz, CDCl₃)**



¹³C{¹H} NMR of 6zg (100 MHz, CDCl₃)



¹⁹F{¹H} NMR of 6zg (564 MHz, CDCl₃)



10. Copies of HPLC Spectra for Racemic and Chiral Adducts

