

Supporting Information

Diastereoselective Johnson-Corey-Chaykovsky Trifluoroethylidenation

Yaya Duan, Bin Zhou, Jin-Hong Lin and Ji-Chang Xiao^[a]

^a Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

Prof. Ji-Chang Xiao Fax: (+86) 21-6416-6128; Tel: (+86)21-5492-5340; E-mail: jchxiao@sioc.ac.cn.

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1. General Information

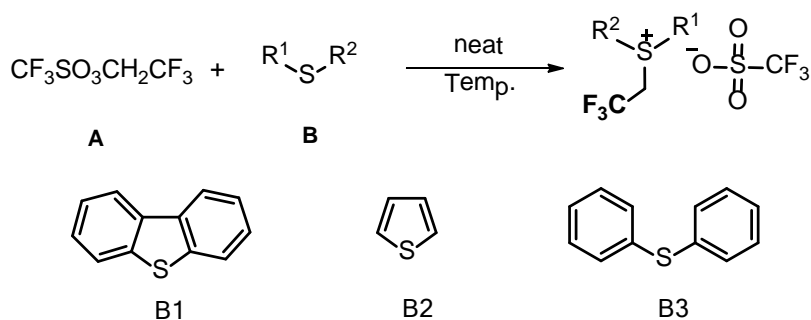
^1H , ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on GC-MS or LC-MS (ESI). High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

Reagents such as 2,2,2-trifluoroethyl triflate, diphenyl sulfide, TBAF, TBAT and extra dry dichloromethane are commercially available.

2. Screening Reaction Conditions for the Synthesis of Salt 1

2.1 Screening reaction conditions for the synthesis of salt 1

Table S2.1. Screening reaction conditions for the synthesis of salt 1

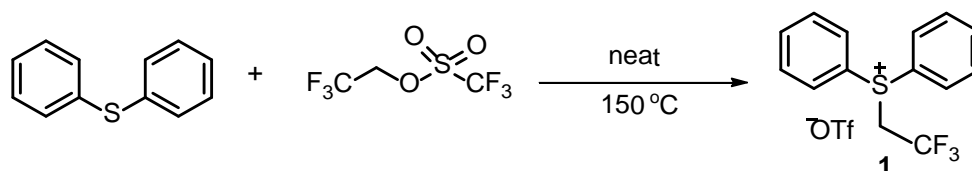


Entry	B	A:B ^a	Temp. (°C)	Yield (%) ^b
1	B1	5 : 1	120 °C	N.R.
2	B1	10 : 1	200 °C	N.R.
3	B2	10 : 1	120 °C	N.R.
4	B3	10 : 1	120 °C	3%
5	B3	1 : 5	100 °C	N.R.
6	B3	1 : 5	200 °C	82%
7	B3	1 : 5	150 °C	80%
8	B3	1 : 5	120 °C	32%

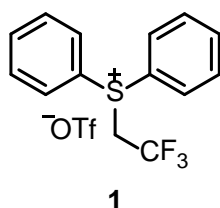
9	B3	1:2	150 °C	50%
10	B3	1:1.5	150 °C	41%

^aMolar ratio; ^bIsolated yields.

2.2 Typical Procedure for the Synthesis of **1**



The mixture of 2,2,2-trifluoroethyl triflate (4.64 g, 20 mmol, 1.0 equiv.) and diphenyl sulfide (18.6 g, 100 mmol, 5.0 equiv.) in a sealed tube was stirred at 150 °C for 30 hours. After the reaction mixture was cooled to room temperature, diethyl ether (10 mL) was added to precipitate the crude product, which was then washed by dry diethyl ether to give the final product **1** (5.9 g, yield 70%).



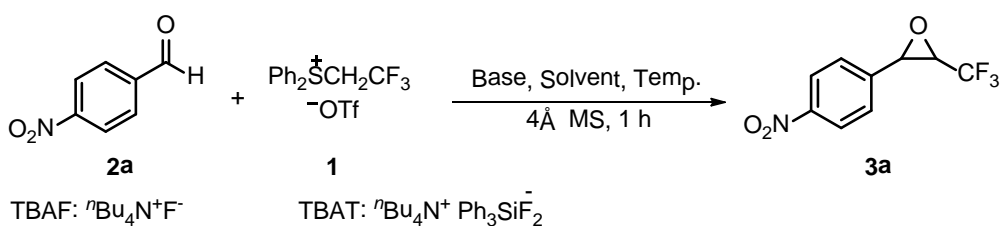
Diphenyl(2,2,2-trifluoroethyl)sulfonium triflate (**1**): White solid. M.P.: 136.6 - 137.8 °C; ¹H NMR (400 MHz, acetone-d₆) δ 8.35 (d, *J* = 7.7 Hz, 4H), 7.98 - 7.90 (m, 2H), 7.89 - 7.80 (m, 4H), 5.75 (q, *J* = 8.8 Hz, 2H); ¹⁹F NMR (376 MHz, acetone-d₆) δ -61.20 (t, *J* = 8.8 Hz, 3F), -78.95 (s, 3F); ¹³C NMR (101 MHz, acetone-d₆) δ 135.44 (s), 131.67 (s), 131.07 (s), 124.25 (s), 122.58 (q, *J* = 278.2 Hz), 121.35 (q, *J* = 321.4 Hz), 45.04 (q, *J* = 33.9 Hz); IR (neat) ν = 3096, 3067, 2999, 2937, 1484, 1450, 1415, 1342, 1244, 1155, 1110, 1029, 761, 740, 690, 679, 639, 541, 517, 507, 467 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₁₂F₃S⁺ [M - OTf]⁺: 269.0606, Found: 269.0604; Calcd for CF₃O₃S⁻ [OTf]⁻: 148.9526, Found: 148.9522.

3. Screening Reaction Conditions for Exoxidation, Cyclopropanation and Airdination

3.1 Screening reaction conditions for epoxidation

Screening bases for the epoxidation of **2a** (4-nitrobenzaldehyde) with reagent **1** in DCM suggested that TBAT was a suitable base (entries 1-7, Table S3.1). The reaction was sensitive to the solvent, and DCM seemed to be a good choice (entries 8-12 vs Entry 5). Lowering the reaction temperature led to a dramatic decrease in the yield (entry 13, Table S3.1), and elevating the temperature improved the yield slightly to 68% (entry 14). The use of excess aldehyde (2 equiv.) was necessary to efficiently trap the unstable ylide intermediate generated in situ, as evidenced by the observation that decreasing the loading of aldehyde resulted in lower yield (entry 15). Increasing the reaction scale and shortening the time had no negative effect on this transformation (entry 16). Under these optimal reaction conditions (entry 16), the substrate scope of epoxidation was investigated.

Table S3.1. Screening reaction conditions for epoxidation^a



Entry	Base	Solvent	Temp. (°C)	Yield (%) ^b
1	NaF	DCM	r.t.	NR
2	CsF	DCM	r.t.	NR
3 ^c	CsF	DCM	r.t.	27
4	TBAF	DCM	r.t.	35
5	TBAT	DCM	r.t.	64
6 ^d	<i>i</i> Pr ₂ NH	DCM	r.t.	14
7	Cs ₂ CO ₃	DCM	r.t.	30
8	TBAT	DMF	r.t.	16
9	TBAT	CH ₃ CN	r.t.	30
10	TBAT	THF	r.t.	13
11	TBAT	Toluene	r.t.	11
12	TBAT	DCE	r.t.	48
13	TBAT	DCM	0 °C	43

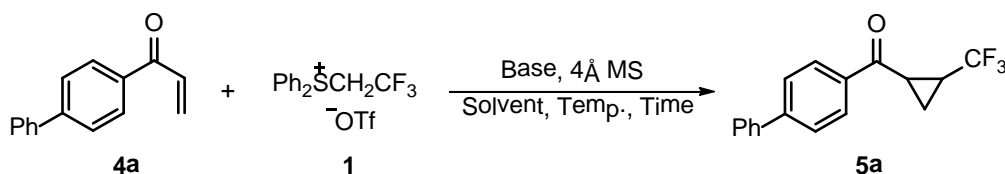
14	TBAT	DCM	Reflux	68
15 ^e	TBAT	DCM	r.t.	39
16 ^f	TBAT	DCM	Reflux	68

^aReaction conditions: **1** (0.1 mmol), **2a** (2 equiv.), base (1.5 equiv.) and 4Å MS (80 mg) in solvent (2 mL) for 1 h. NR: no reaction; ^bDetermined by ¹⁹F NMR with the use of trifluoromethyl benzene as an internal standard; ^c18-crown-6 (1.5 equiv.) was used as additive; ^dThe reaction was run for 4 h; ^eMolar ratio: **1** : **2a** : base = 1: 1.5 :1; ^fReaction conditions: **1** (0.5 mmol), **2a** (1 mmol), base (0.75 mmol) and 4Å MS (400 mg) in DCM (10 mL) for 20 minutes.

3.2 Screening reaction conditions for cyclopropanation

The investigation of the base (entries 1-10, Table S3.2) for the cyclopropanation of 4'-phenyl-phenyl vinyl ketone **4a** with reagent **1** showed that TBAF or TBAT was suitable (entries 9 and 10). This transformation was not sensitive to the reaction solvent (entries 11-16). Considering the price of the base and the operational convenience of the solvent, TBAF and DCM were chosen as the base and the solvent respectively (entry 9).

Table S3.2. Screening reaction conditions for cyclopropanation^a



Entry	Base	Solvent	Time	Ratio ^b	Yield ^c
1	Cs ₂ CO ₃	DCM	1 h	2 : 1 : 1.5	49
2	Na ₂ CO ₃	DCM	1 h	2 : 1 : 1.5	N.R.
3	DBU	DCM	1 h	2 : 1 : 1.5	29
4	Et ₃ N	DCM	1 h	2 : 1 : 1.5	14
5	KF	DCM	1 h	2 : 1 : 1.5	N.R.
6 ^d	KF	DCM	1 h	2 : 1 : 1.5	58
7	CsF	DCM	1 h	2 : 1 : 1.5	10
8	TBAF	DCM	1 h	2 : 1 : 1.5	90
9	TBAF	DCM	2 h	2 : 1 : 1.5	100
10	TBAT	DCM	2 h	2 : 1 : 1.5	100
11	TBAF	DCM	2 h	1 : 1.5 : 1.5	92

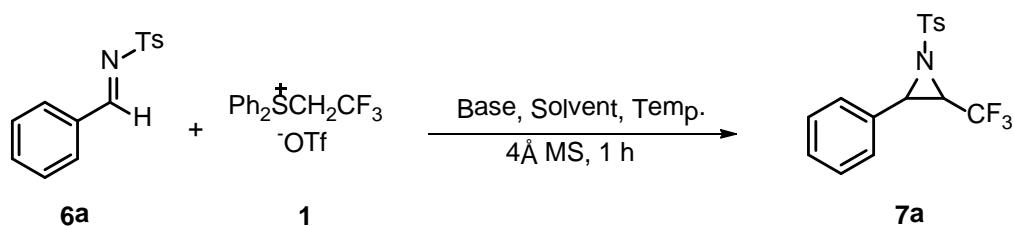
12	TBAF	CH ₃ CN	2 h	2 : 1 : 1.5	89
13	TBAF	NMP	2 h	2 : 1 : 1.5	83
14	TBAF	DMF	2 h	2 : 1 : 1.5	98
15	TBAF	DMA	2 h	2 : 1 : 1.5	100
16	TBAF	THF	2 h	2 : 1 : 1.5	96
17	TBAF	Dioxane	2 h	2 : 1 : 1.5	98

Notes: ^a Reaction conditions: **1** (0.1 mmol), **4a** (2 equiv.), base (1.5 equiv.) and 4Å MS (80 mg) in solvent (2 mL); ^b Molar ratio: **1** : **4a** : base = 1 : 2 : 1.5; ^c Determined by ¹⁹F NMR with the use of trifluoromethyl benzene as an internal standard. ^d 18-crown-6 (1.5 equiv.) was used as additive.

3.3 Screening reaction conditions for aziridination

Various reaction conditions, including base, solvent and temperature, were examined for aziridination of compound **6a** with reagent **1**. The optimal reaction conditions (entry 1, Table S3.3) were similar with that for cyclopropanation.

Table S3.3. Screening reactions conditions for aziridination^a



Entry	Base	Solvent	Ratio ^b	Yield ^c
1	DCM	TBAF	rt.	100%
2	DCM	TBAT	rt.	100%
3	DCM	Et ₃ N	rt.	89%
4	DCM	DBU	rt.	78%
5	DCM	Cs ₂ CO ₃	rt.	90%
6	DCM	CsF	rt.	62%
7 ^d	DCM	KF	rt.	76%
8	THF	TBAF	rt.	95%
9	CH ₃ CN	TBAF	rt.	76%
10	Dioxane	TBAF	rt.	100%
11	DMF	TBAF	rt.	72%
12	DMSO	TBAF	rt.	84%
13	DMA	TBAF	rt.	76%
14	NMP	TBAF	rt.	86%

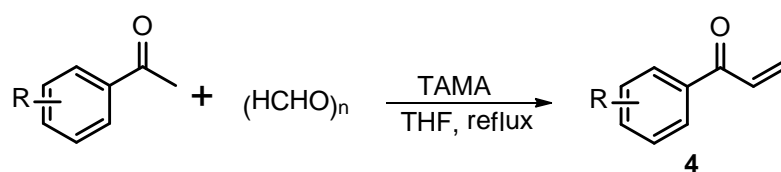
15	DCM	TBAF	0 °C	100%
16	DCM	TBAF	reflux	94%

^aReaction conditions: **1** (0.1 mmol), **6a** (2 equiv.), base (1.5 equiv.) and 4Å MS (80 mg) in solvent (2 mL); ^bMolar ratio: **1** : **6a** : base = 1 : 2 : 1.5; ^cDetermined by ¹⁹F NMR with the use of trifluoromethyl benzene as an internal standard. ^d18-crown-6 (1.5 equiv.) was used as additive.

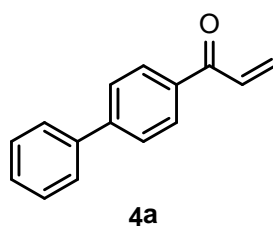
4. Typical Procedure for the Preparation of **4**, **6**

4.1 Procedure for the Preparation of **4**

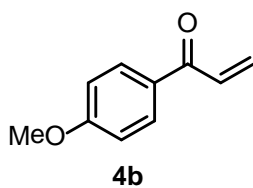
4 were synthesized according to the procedure reported in literature.^[1]



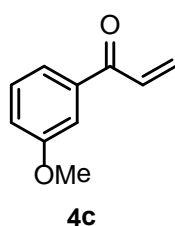
Into the solution of paraformaldehyde (7.5g, 250/n mmol, 5.0 equiv.) and *N*-methylanilinium trifluoroacetate (TAMA, 11.05 g, 50 mmol, 1.0 equiv.) in THF (50 mL) was added aryl methyl ketone (50 mmol, 1.0 equiv.) under N₂ atmosphere. The mixture was refluxed for 10 h. After being cooled to room temperature, the solvent was removed by concentration under vacuum. The residue was dissolved in ethyl acetate (100 mL). The organic phase was washed with H₂O (100 mL × 2), HCl solution (1M) and H₂O (100 mL), and then dried over Na₂SO₄. After filtration and concentration, the residue was subjected to flash column chromatography with hexane/ethyl acetate to afford the product **4**.



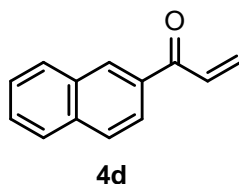
1-([1,1'-Biphenyl]-4-yl)prop-2-en-1-one (**4a**)^[2]: 56%; ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 17.1, 10.5 Hz, 1H), 6.48 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.96 (dd, *J* = 10.5, 1.5 Hz, 1H).



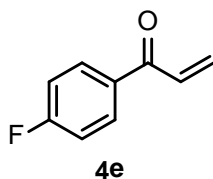
1-(4-Methoxyphenyl)prop-2-en-1-one (**4b**)^[1]: 40%; ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.18 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 17.1 Hz, 1H), 5.88 (d, *J* = 10.6 Hz, 1H), 3.88 (s, 3H).



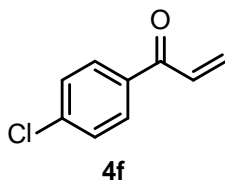
1-(3-Methoxyphenyl)prop-2-en-1-one (**4c**)^[1]: 26%; ¹H NMR (400 MHz, CDCl₃) δ 7.50 - 7.39 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.16 - 7.01 (m, 2H), 6.38 (d, *J* = 17.1 Hz, 1H), 5.85 (d, *J* = 10.5 Hz, 1H), 3.78 (s, 3H).



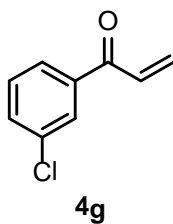
1-(Naphthalen-2-yl)prop-2-en-1-one (**4d**)^[1]: 45%; ¹H NMR (300 MHz, CDCl₃) δ 8.47 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 8.00 - 7.85 (m, 3H), 7.67 - 7.51 (m, 2H), 7.33 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.51 (d, *J* = 17.1 Hz, 1H), 5.98 (d, *J* = 10.6 Hz, 1H).



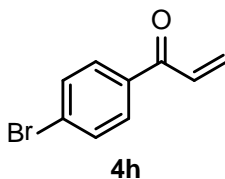
1-(4-Fluorophenyl)prop-2-en-1-one (**4e**)^[1]: 37%; ¹H NMR (300 MHz, CDCl₃) δ 8.09 - 7.87 (m, 2H), 7.22 - 7.04 (m, 3H), 6.44 (d, *J* = 17.1 Hz, 1H), 5.94 (d, *J* = 10.6 Hz, 1H); ¹⁹F NMR (282 MHz, CDCl₃) δ -105.06 - -105.56 (m, 1F).



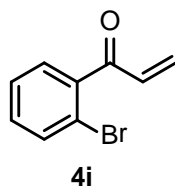
1-(4-Chlorophenyl)prop-2-en-1-one (**4g**)^[1]: 72%; ¹H NMR (300 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.12 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.45 (d, *J* = 17.1 Hz, 1H), 5.96 (d, *J* = 10.6 Hz, 1H).



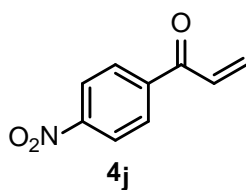
1-(3-Chlorophenyl)prop-2-en-1-one (**4g**)^[1]: 44%; ¹H NMR (300 MHz, CDCl₃) δ 7.79 (s, 1H), 7.73 - 7.66 (m, 1H), 7.46 - 7.38 (m, 1H), 7.36 - 7.26 (m, 1H), 7.00 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.34 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.85 (dd, *J* = 10.6, 1.3 Hz, 1H).



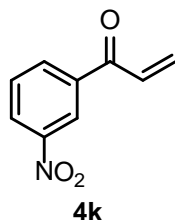
1-(4-Bromophenyl)prop-2-en-1-one (**4h**)^[1]: 59%; Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.12 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.45 (dd, *J* = 17.1 Hz, 1.5 Hz, 1H), 5.96 (dd, *J* = 10.6 Hz, 1.5 Hz, 1H).



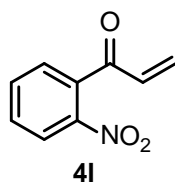
1-(2-Bromophenyl)prop-2-en-1-one (**4i**)^[2]: 31%; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.3 Hz, 1H), 7.41 - 7.27 (m, 3H), 6.71 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.09 (d, *J* = 17.5 Hz, 1H), 6.06 (d, *J* = 10.5 Hz, 1H).



1-(4-Nitrophenyl)prop-2-en-1-one (**4j**)^[1]: 27%; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.06 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.41 (d, *J* = 17.1 Hz, 1H), 6.00 (d, *J* = 10.6 Hz, 1H).

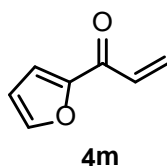


1-(3-Nitrophenyl)prop-2-en-1-one (**4k**)^[3]: 31%; ¹H NMR (300 MHz, CDCl₃) δ 8.77 (s, 1H), 8.45 (d, *J* = 7.4 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.18 (dd, *J* = 17.1, 9.7 Hz, 1H), 6.53 (d, *J* = 17.1 Hz, 1H), 6.08 (d, *J* = 9.7 Hz, 1H).

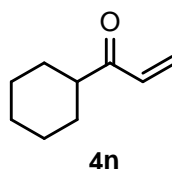


1-(2-Nitrophenyl)prop-2-en-1-one (**4l**)^[4]: 52%; ¹H NMR (400 MHz, CDCl₃) δ 7.91 - 7.79 (m, 2H), 7.45 - 7.34 (m, 2H), 7.07 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.40 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.90

(dd, $J = 10.6, 1.6$ Hz, 1H).



1-(Furan-2-yl)prop-2-en-1-one (**4m**)^[5]: 29%; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, $J = 0.9$ Hz, 1H), 7.32 - 7.20 (m, 1H), 7.04 (dd, $J = 17.2, 10.5$ Hz, 1H), 6.60 - 6.43 (m, 2H), 5.84 (dd, $J = 10.5, 1.6$ Hz, 1H).

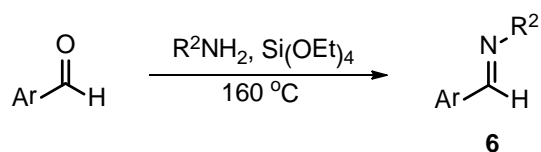


1-Cyclohexylprop-2-en-1-one (**4n**)^[5]: 23%; ¹H NMR (400 MHz, CDCl₃) δ 6.43 (dd, $J = 17.5, 10.5$ Hz, 1H), 6.25 (dd, $J = 17.5, 1.2$ Hz, 1H), 5.75 (dd, $J = 10.5, 1.2$ Hz, 1H), 2.62 (ddd, $J = 11.0, 8.7, 2.3$ Hz, 1H), 1.86 - 1.78 (m, 4H), 1.69 (d, $J = 11.6$ Hz, 1H), 1.40 - 1.25 (m, 5H).

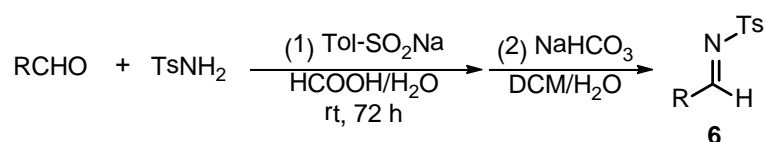
4.2 Procedure for the Synthesis of **6**

6 were synthesized according to the procedure reported in literature^[6].

Method A:



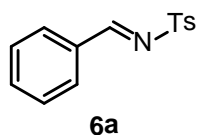
Method B:



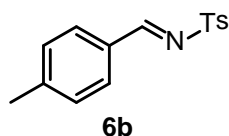
Method A^[6b, 6c]: Aldehyde (31.5 mmol, 1.05 equiv), sulfonamide (30.0 mmol, 1.0 equiv) and tetraethyl orthosilicate (120 mmol, 25 g, 4.0 equiv) were combined in a flask equipped with a still head and the mixture was stirred at 160°C until no ethanol was produced. After the reaction

system was cooled to room temperature, ethyl acetate/n-hexane (1:3) was added to precipitate the crude product. After filtration, the solid was washed by ethyl acetate/n-hexane(1:3) followed by ethanol to give the pure product **6a-j, l-m**.

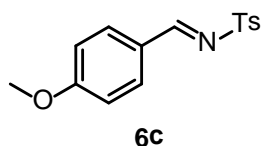
Method B^[6a]: Aldehyde (30.0 mmol, 1.0 equiv), sodium *p*-tolylsulfinate (30.0 mmol, 1.0 equiv) and sulfonamide (30 mmol, 1.0 equiv) were mixed in formic acid/H₂O (1:1, 100 mL) and stirred for 72 h at room temperature. The resulting white precipitate was filtered off, washed with H₂O (2 x 30 mL), then pentane (30 mL), and dissolved in CH₂Cl₂ (150 mL). Sat. aq NaHCO₃ was added and the solution was well stirred overnight at room temperature. The organic phase was decanted, then washed with brine and dried over Na₂SO₄. Filtered off and the solvent removed under vacuum to yield the corresponding product **6k**.



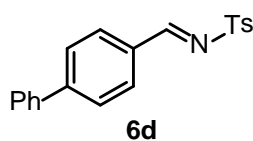
(*E*)-*N*-Benzylidene-4-methylbenzenesulfonamide (**6a**)^[7]: ¹H NMR (300 MHz, CDCl₃) δ 9.03 (s, 1H), 7.95 - 7.86 (m, 4H), 7.65 - 7.58 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).



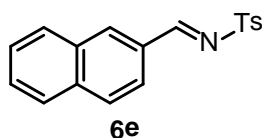
(*E*)-4-Methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (**6b**)^[7]: ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 6H).



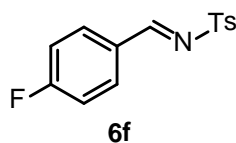
(*E*)-*N*-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (**6c**)^[7]: ¹H NMR (300 MHz, CDCl₃) δ 8.94 (s, 1H), 7.94 - 7.83 (m, 4H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H).



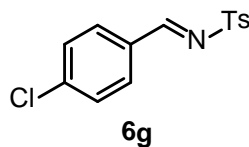
(*E*)-*N*-([1,1'-Biphenyl]-4-ylmethylene)-4-methylbenzenesulfonamide (**6d**)^[8]: ¹H NMR (400 MHz, CDCl₃) δ 9.05 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.50 - 7.37 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).



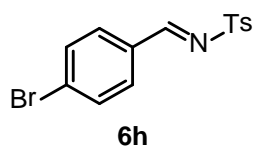
(*E*)-4-Methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide (**6e**)^[9]: ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.32 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.96 - 7.84 (m, 5H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H).



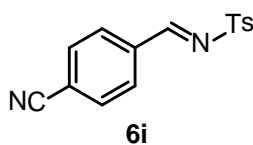
(*E*)-*N*-(4-Fluorobenzylidene)-4-methylbenzenesulfonamide (**6f**)^[9]: ¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.94 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 2.42 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -101.03 - -101.13 (m, 1F).



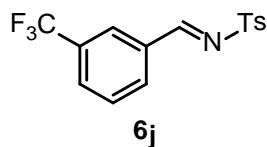
(*E*)-*N*-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide (**6g**)^[10]: ¹H NMR (300 MHz, CDCl₃) δ 8.99 (s, 1H), 7.94 - 7.81 (m, 4H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 2.44 (s, 3H).



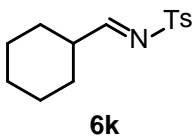
(*E*)-*N*-(4-Bromobenzylidene)-4-methylbenzenesulfonamide (**6h**)^[10]: ¹H NMR (400 MHz, CDCl₃) δ 8.95 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H).



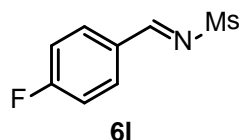
(*E*)-*N*-(4-Cyanobenzylidene)-4-methylbenzenesulfonamide (**6i**)^[7]: ¹H NMR (400 MHz, CDCl₃) δ 9.04 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H).



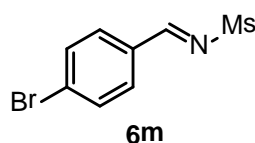
(*E*)-4-Methyl-*N*-(3-(trifluoromethyl)benzylidene)benzenesulfonamide (**6j**)^[11]: ¹H NMR (300 MHz, CDCl₃) δ 9.08 (s, 1H), 8.20 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.04 (s, 3F).



(*E*)-*N*-(Cyclohexylmethylene)-4-methylbenzenesulfonamide (**6k**)^[9]: ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 4.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.48 - 2.36 (br s, 4H), 1.91 - 1.80 (m, 5H), 1.76 - 1.70 (m, 2H), 1.68 - 1.62 (m, 1H), 1.36 - 1.12 (m, 5H).



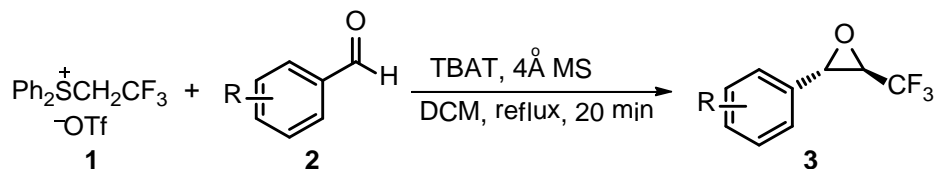
(*E*)-*N*-(4-Fluorobenzylidene)methanesulfonamide (**6l**)^[12]: ¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.98 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.20 (t, *J* = 8.3 Hz, 2H), 3.12 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -99.07 - -101.73 (m).



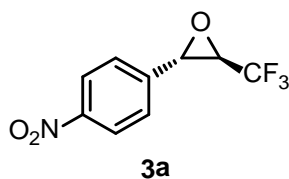
(*E*)-*N*-(4-Bromobenzylidene)methanesulfonamide (**6m**)^[13]: ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 3.12 (s, 3H).

5. Procedure for the Synthesis of 3, 5, 7

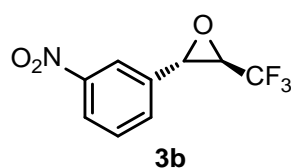
5.1 Procedure for the Synthesis of 3



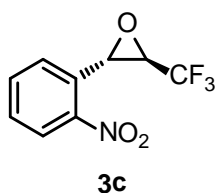
Into the mixture of diphenyl(2,2,2-trifluoroethyl)sulfonium triflate **1** (0.5 mmol, 0.2092 g, 1.0 equiv.), aldehyde **2** (1.0 mmol, 2.0 equiv.), TBAT (0.75 mmol, 0.4048 g, 1.5 equiv.) and 4Å MS (0.4 g) was added dichloromethane (8 mL) under N₂ atmosphere. The resulting mixture was refluxed for 20 min. After filtration, the solvent was removed by concentration under vacuum and the residue was subjected to flash column chromatography with hexane/ethyl acetate (100:1-20:1) as the eluent to afford the final product.



(2*SR*,3*RS*)-2-(4-Nitrophenyl)-3-(trifluoromethyl)oxirane (**3a**): 61%; White solid. M.P. 55.0-56.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.25 (s, 1H), 3.57 - 3.44 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.01 (d, *J* = 4.6 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 148.44 (s), 140.65 (s), 126.72 (s), 123.97 (s), 121.71 (q, *J* = 276.3 Hz), 57.06 (q, *J* = 41.3 Hz), 53.95 (q, *J* = 2.8 Hz); IR (neat) ν = 3087, 2973, 1936, 1608, 1525, 1465, 1351, 1285, 1159, 872, 698 cm⁻¹; HRMS (EI) Calcd for C₉H₆NO₃F₃ [M]⁺: 233.0300, Found: 233.0298.

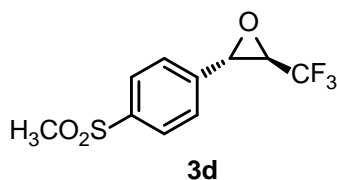


(2*SR*,3*RS*)-2-(3-Nitrophenyl)-3-(trifluoromethyl)oxirane (**3b**): 50%; Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 7.9 Hz, 1H), 8.20 (s, 1H), 7.73 - 7.58 (m, 2H), 4.29 (s, 1H), 3.56 (dq, *J* = 4.6, 1.3 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.01 (d, *J* = 4.6 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 148.63 (s), 135.88 (s), 131.74 (s), 130.06 (s), 124.24 (s), 121.74 (q, *J* = 276.2 Hz), 120.92 (s), 57.02 (q, *J* = 41.3 Hz), 53.96 (q, *J* = 2.8 Hz); IR (neat) ν = 3095, 1587, 1537, 1488, 1465, 1441, 1354, 1286, 1250, 1207, 1161, 1113, 1097, 1077, 938, 902, 839, 812, 737, 689, 672, 624 cm⁻¹; HRMS (EI): calcd. for C₉H₆F₃NO₃ [M]⁺: 233.0300, Found: 233.0297.

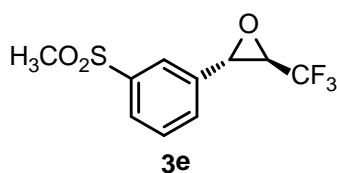


(2*SR*,3*RS*)-2-(2-Nitrophenyl)-3-(trifluoromethyl)oxirane (**3c**): 62%; Light yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.78 - 7.68 (m, 1H), 7.64 - 7.52 (m, 2H), 4.75 (d, *J* = 1.9 Hz, 1H), 3.37 (qd, *J* = 4.7, 1.9 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.36 (d, *J* = 4.7 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 147.26 (s), 134.63 (s), 130.64 (s), 129.76 (s), 127.19 (s), 125.02 (s), 121.85 (q, *J* = 276.1 Hz), 56.21 (q, *J* = 41.4 Hz), 53.79 (q, *J* = 3.3 Hz); IR (neat) ν = 3091, 2864, 1621, 1579, 1533, 1489, 1459, 1445, 1347, 1313, 1282, 1247, 1199, 1166, 1093,

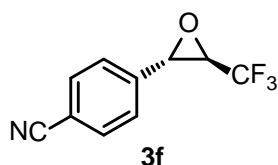
973, 932, 890, 875, 861, 844, 794, 739, 702, 685, 675, 629, 571, 503 cm^{-1} ; HRMS (EI): calcd. for $\text{C}_9\text{H}_6\text{F}_3\text{NO}_3$ $[\text{M}]^+$: 233.0300, Found: 233.0298.



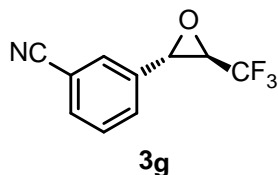
(2*SR*,3*RS*)-2-(4-(Methylsulfonyl)phenyl)-3-(trifluoromethyl)oxirane (**3d**): 56%; White solid. M.P. 103.5-104.8 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 4.22 (d, $J = 1.7$ Hz, 1H), 3.49 (qd, $J = 4.6, 1.7$ Hz, 1H), 3.04 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -74.02 (d, $J = 4.6$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 141.52 (s), 139.75 (s), 127.99 (s), 126.80 (s), 121.76 (q, $J = 276.2$ Hz), 57.09 (q, $J = 41.3$ Hz), 54.10 (q, $J = 2.8$ Hz), 44.43 (s); IR (neat) $\nu = 3033, 2943, 1607, 1466, 1413, 1354, 1304, 1290, 1252, 1203, 1155, 1119, 1086, 968, 926, 867, 836, 799, 767, 722, 675, 558, 544, 535$ cm^{-1} ; HRMS (EI): calcd. for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_3\text{S}$ $[\text{M}]^+$: 266.0224, Found: 266.0225.



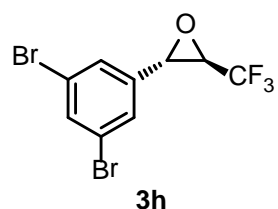
(2*SR*,3*RS*)-2-(3-(Methylsulfonyl)phenyl)-3-(trifluoromethyl)oxirane (**3e**): 49%; White solid. M.P. 68.1-69.3 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dt, $J = 7.0, 1.8$ Hz, 1H), 7.91 (s, 1H), 7.70 - 7.58 (m, 2H), 4.26 (d, $J = 1.5$ Hz, 1H), 3.56 (qd, $J = 4.6, 1.5$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -74.02 (d, $J = 4.6$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 141.58 (s), 135.64 (s), 131.00 (s), 130.09 (s), 128.20 (s), 124.83 (s), 121.78 (q, $J = 276.2$ Hz), 56.99 (q, $J = 41.3$ Hz), 54.16 (q, $J = 2.8$ Hz), 44.39 (s); IR (neat) $\nu = 3070, 3039, 2941, 1721, 1473, 1426, 1345, 1320, 1299, 1250, 1211, 1146, 1088, 998, 971, 961, 926, 905, 891, 860, 792, 767, 691, 680, 633, 588, 542, 533, 490$ cm^{-1} ; HRMS (EI): calcd. for $\text{C}_{10}\text{H}_6\text{F}_3\text{NO}$ $[\text{M}]^+$: 213.0224, Found: 213.0220.



4-((2*SR*,3*RS*)-3-(Trifluoromethyl)oxiran-2-yl)benzonitrile (**3f**): 56%; White solid. M.P. 53.8 - 54.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.19 (s, 1H), 3.47 (qd, *J* = 4.7, 1.7 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.03 (d, *J* = 4.7 Hz, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 138.76 (s), 132.61 (s), 126.51 (s), 121.74 (q, *J* = 276.2 Hz), 118.11 (s), 113.25 (s), 57.06 (q, *J* = 41.2 Hz), 54.13 (q, *J* = 2.8 Hz); IR (neat) ν = 3048, 2230, 1615, 1511, 1465, 1352, 1285, 1155, 925, 869, 680 cm⁻¹; HRMS (EI) Calcd for C₉H₆NO₂F₃ [M]⁺: 213.0401, Found: 213.0403.

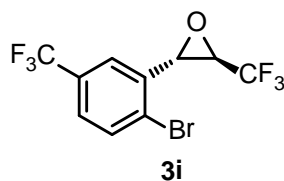


3-((2*SR*,3*RS*)-3-(Trifluoromethyl)oxiran-2-yl)benzonitrile (**3g**): 50%; White solid. M.P. 49.8-50.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 6.7 Hz, 1H), 7.60 (s, 1H), 7.57 - 7.45 (m, 2H), 4.18 (d, 1.5 Hz, 1H), 3.47 (qd, *J* = 4.6, 1.5 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.03 (d, *J* = 4.6 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 135.29 (s), 132.86 (s), 130.05 (s), 129.75 (s), 129.33 (s), 121.70 (q, *J* = 276.2 Hz), 117.94 (s), 113.29 (s), 56.94 (q, *J* = 41.3 Hz), 53.90 (q, *J* = 2.8 Hz); IR (neat) ν = 3093, 2231, 1614, 1588, 1485, 1474, 1425, 1341, 1291, 1252, 1233, 1176, 1142, 1110, 1087, 934, 914, 894, 862, 815, 795, 745, 694, 680, 641, 606, 549, 543, 479 cm⁻¹; HRMS (EI): calcd. for C₁₀H₆F₃NO [M]⁺: 213.0401, Found: 213.0397.

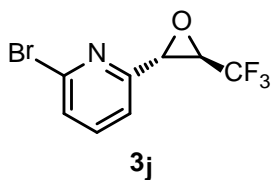


(2*SR*,3*RS*)-2-(3,5-Dibromophenyl)-3-(trifluoromethyl)oxirane (**3h**): 59%; White solid. M.P. 69.2-70.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (t, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 1.4 Hz, 2H),

4.07 (d, $J = 1.6$ Hz, 1H), 3.44 (qd, $J = 4.6, 1.6$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -74.04 (d, $J = 4.6$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 137.53 (s), 135.03 (s), 127.64 (s), 123.52 (s), 121.71 (q, $J = 276.3$ Hz), 56.90 (q, $J = 41.3$ Hz), 53.50 (q, $J = 2.8$ Hz); IR (neat) $\nu = 3068, 1590, 1560, 1466, 1428, 1414, 1341, 1288, 1202, 1153, 1103, 1078, 991, 930, 914, 890, 884, 867, 857, 816, 745, 696, 670, 650, 528$ cm^{-1} ; HRMS (EI): calcd. for $\text{C}_9\text{H}_5\text{Br}_2\text{F}_3\text{O}$ $[\text{M}]^+$: 343.8659, Found: 343.8664.



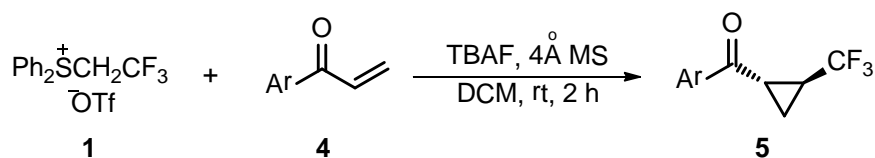
(2*SR*,3*RS*)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-3-(trifluoromethyl)oxirane (**3i**): 60%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, 1H), 7.59 - 7.39 (m, 2H), 4.42 (d, $J = 1.5$ Hz, 1H), 3.38 (qd, $J = 4.6, 1.5$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -62.98 (s, 3F), -74.17 (d, $J = 4.6$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 134.82 (s), 133.24 (s), 130.66 (q, $J = 33.4$ Hz), 127.01 (q, $J = 3.6$ Hz), 126.18 (d, $J = 1.5$ Hz), 123.45 (q, $J = 3.8$ Hz), 123.41 (q, $J = 272.4$ Hz), 121.76 (q, $J = 276.1$ Hz), 56.46 (q, $J = 41.5$ Hz), 54.63 (q, $J = 3.0$ Hz); IR (neat) $\nu = 3040, 2920, 1611, 1584, 1484, 1458, 1418, 1347, 1327, 1287, 1264, 1246, 1163, 1135, 1079, 1033, 934, 922, 908, 871, 831, 756, 725, 688, 642, 626$ cm^{-1} ; HRMS (EI): calcd. for $\text{C}_{10}\text{H}_5\text{BrF}_6\text{O}$ $[\text{M}]^+$: 333.9428, Found: 333.9427.



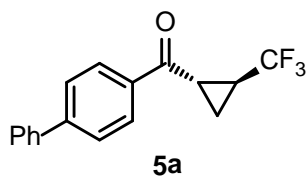
2-Bromo-6-((2*SR*,3*RS*)-3-(trifluoromethyl)oxiran-2-yl)pyridine (**3j**): 56%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.63 - 7.54 (m, 1H), 7.52 - 7.45 (m, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 4.22 (d, $J = 1.4$ Hz, 1H), 3.79 (qd, $J = 4.8, 1.4$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -73.90 (d, $J = 4.8$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 154.25 (s), 142.36 (s), 139.22 (s), 128.79 (s), 121.90 (q, $J = 276.1$ Hz), 120.07 (s), 55.75 (q, $J = 41.4$ Hz), 54.49 (q, $J = 2.6$ Hz); IR (neat) $\nu =$

3050, 2923, 1581, 1557, 1476, 1442, 1405, 1349, 1329, 1275, 1238, 1161, 1124, 1112, 1085, 1071, 988, 927, 892, 860, 820, 793, 736, 699, 682, 632, 598, 536 cm⁻¹; HRMS (EI): calcd. for C₈H₅BrF₃NO [M]⁺: 266.9507, Found: 266.9506.

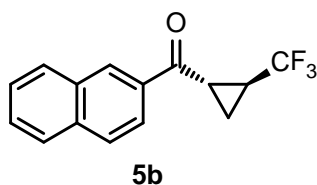
5.2 The Procedure for the Synthesis of 5



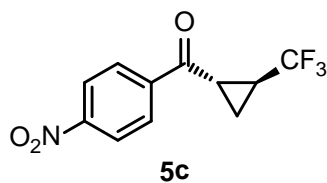
Into the mixture of diphenyl(2,2,2-trifluoroethyl)sulfonium triflate **1** (0.2 mmol, 83.7 mg, 1.0 equiv.), compound **4** (0.4 mmol, 2.0 equiv.) and 4Å MS (160 mg) in dichloromethane (2 mL) was added TBAF (0.3 mmol, 0.3 mL, 1.5 equiv.) dropwise under N₂ atmosphere. The reaction mixture was stirred at room temperature for 2 h. After concentration, the residue was subjected to flash column chromatography with hexane/ethyl acetate (100:1-20:1) as the eluent to afford the final product **5**.



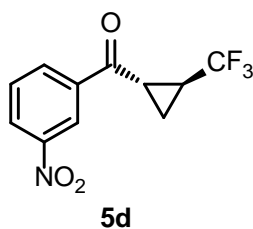
[1,1'-Biphenyl]-4-yl((1*S*,2*S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5a**): 90%; White solid. M.P.: 108.7-110.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.41 (t, *J* = 7.1 Hz, 1H), 3.08 - 3.02 (m, 1H), 2.42 - 2.33 (m, 1H), 1.58 - 1.51 (m, 1H), 1.47 - 1.41 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.65 (d, *J* = 6.2 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 195.79 (s), 146.33 (s), 139.65 (s), 135.39 (s), 128.99 (s), 128.85 (s), 128.39 (s), 127.38 (s), 127.27 (s), 125.24 (q, *J* = 271.1 Hz), 23.82 (q, *J* = 37.8 Hz), 20.08 (q, *J* = 2.0 Hz), 12.50 (q, *J* = 2.6 Hz); IR (neat) ν = 2925, 2361, 1673, 1603, 560, 1509, 1341, 1264, 1150, 1063, 1305, 936, 849, 772, 739 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₃OF₃ [M]⁺: 290.0918, Found: 290.0920.



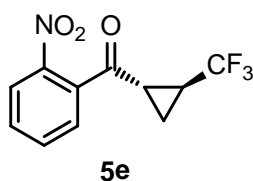
Naphthalen-2-yl((*1SR,2SR*)-2-(trifluoromethyl)cyclopropyl)methanone (**5b**): 89%; Light yellow solid. M.P.: 42.4-44.4°C; ¹H NMR (400 MHz, CDCl₃) δ 8.56 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.66 - 7.55 (m, 2H), 3.22 - 3.14 (m, 1H), 2.49 - 2.37 (m, 1H), 1.63 - 1.54 (m, 1H), 1.53 - 1.45 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.66 (d, *J* = 6.6 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 196.22 (s), 135.78 (s), 134.04 (s), 132.44 (s), 130.23 (s), 129.67 (s), 128.83 (s), 128.72 (s), 127.82 (s), 127.01 (s), 125.24 (q, *J* = 271.1 Hz), 123.69 (s), 23.86 (q, *J* = 37.8 Hz), 20.13 (q, *J* = 1.9 Hz), 12.70 (q, *J* = 2.6 Hz); IR (neat) ν = 3059, 2361, 1673, 1628, 1597, 1471, 1357, 1333, 1107, 756 cm⁻¹; HRMS (EI) Calcd for C₁₅H₁₁OF₃ [M]⁺: 264.0762, Found: 264.0767.



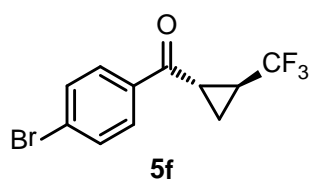
(4-Nitrophenyl)((*1SR, 2SR*)-2-(trifluoromethyl) cyclopropyl) methanone (**5c**): 97%; White solid. M.P.: 57.6-59.1°C; ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 7.6 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 3.02 - 2.98 (m, 1H), 2.54 - 2.31 (m, 1H), 1.65 - 1.55 (m, 1H), 1.55 - 1.50 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.91 (d, *J* = 6.4 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 195.11 (s), 150.59 (s), 141.04 (s), 129.26 (s), 124.80 (q, *J* = 271.0 Hz), 123.99 (s), 24.52 (q, *J* = 38.0 Hz), 20.63 (q, *J* = 2.1 Hz), 13.28 (q, *J* = 2.7 Hz); IR (neat) ν = 3113, 1686, 1605, 1529, 1420, 1266, 1221, 1151, 1064, 852, 715, 635 cm⁻¹; HRMS (EI) Calcd for C₁₁H₈NO₃F₃ [M]⁺: 259.0456, Found: 259.0455.



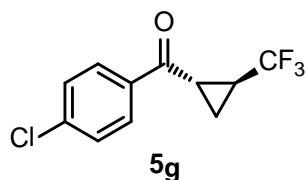
(3-Nitrophenyl)((*1S*, *2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5d**): Quantitative; White solid. M.P.: 29.9-32.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.84 (s, 1H), 8.49 (d, $J = 8.0$ Hz, 1H), 8.35 (d, $J = 8.0$ Hz, 1H), 7.84 - 7.69 (m, 1H), 3.17 - 2.98 (m, 1H), 2.54 - 2.36 (m, 1H), 1.74 - 1.51 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.88 (d, $J = 6.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 194.42 (s), 148.50 (s), 137.85(s), 133.70 (s), 130.11 (s), 127.81 (s), 124.84 (q, $J = 271.4$ Hz), 123.30 (s), 24.35 (q, $J = 38.1$ Hz), 20.32 (q, $J = 1.3$ Hz), 13.35 (q, $J = 2.0$ Hz); IR (neat) $\nu = 3089$, 2360, 1687, 1612, 1536, 1340, 1266, 1224, 1151, 1001, 940, 716 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_8\text{NO}_3\text{F}_3$ $[\text{M}]^+$: 259.0456, Found: 259.0461.



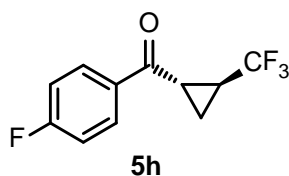
(2-Nitrophenyl)((*1S*, *2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5e**): Quantitative; Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.5$ Hz, 1H), 7.76 (t, $J = 7.5$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 2.54 - 2.51 (m, 1H), 2.49 - 2.38 (m, 1H), 1.72 - 1.61 (m, 1H), 1.51 - 1.46(m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -67.13 (d, $J = 6.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 198.94 (s), 145.93 (s), 137.00 (s), 134.39 (s), 131.25 (s), 127.74 (s), 124.70 (q, $J = 271.5$ Hz), 124.53 (s), 25.18 (q, $J = 38.1$ Hz), 24.30 (q, $J = 2.1$ Hz), 13.78 (q, $J = 2.6$ Hz); IR (neat) $\nu = 3066$, 1701, 1608, 1575, 1477, 1348, 1265, 1152, 945, 753 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_8\text{NOF}_3$ $[\text{M}]^+$: 259.0456, Found: 259.0458.



(4-Bromophenyl)((*ISR*, 2*SR*)-2-(trifluoromethyl)cyclopropyl)methanone (**5f**): Quantitative; White solid. M.P.: 28.8-29.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 2.98 - 2.92 (m, 1H), 2.32 - 2.38 (m, 1H), 1.60 - 1.48(m, 1H), 1.48 - 1.39(m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.83 (d, *J* = 6.5 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 195.34 (s), 135.39 (s), 132.10 (s), 129.70 (s), 129.08 (s), 125.03 (q, *J* = 271.2 Hz), 23.97 (q, *J* = 37.9 Hz), 20.00 (q, *J* = 2.1 Hz), 12.69 (q, *J* = 2.7 Hz); IR (neat) ν = 3059, 1681, 1587, 1506, 1397, 1341, 1263, 1150, 1071, 995, 838, 739 cm⁻¹; HRMS (EI) Calcd for C₁₁H₈OF₃Br [M]⁺: 291.9711, Found: 291.9713.

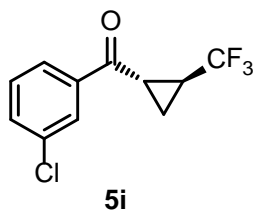


(4-Chlorophenyl)((*ISR*, 2*SR*)-2-(trifluoromethyl)cyclopropyl)methanone (**5g**): Quantitative; White solid. M.P.: 25.7-26.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 2.97 - 2.93 (m, 1H), 2.56 - 2.19 (m, 1H), 1.56 - 1.49 (m, 1H), 1.47 - 1.39 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.82 (d, *J* = 6.5 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 195.19 (s), 140.20 (s), 134.95 (s), 129.64 (s), 129.11 (s), 125.05 (q, *J* = 271.2 Hz), 23.96 (q, *J* = 37.9 Hz), 20.00 (q, *J* = 2.0 Hz), 12.72 (q, *J* = 2.5 Hz); IR (neat) ν = 3061, 2360, 1681, 1592, 1490, 1400, 1344, 1264, 1224, 1151, 1116, 1063, 996, 840, 775 cm⁻¹; HRMS (EI) Calcd for C₁₁H₈OF₃Cl [M]⁺: 248.0216, Found: 248.0214; Anal. Calcd. for C₁₁H₈OF₃Cl [M]⁺: C, 53.14;H, 3.24; Found: C, 52.99; H, 3.43.

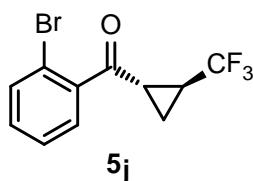


(4-Fluorophenyl)((*ISR*,2*SR*)-2-(trifluoromethyl)cyclopropyl)methanone (**5h**): 65%; Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.06 - 8.02 (m, 2H), 7.23 - 7.10 (m, 2H), 3.04 - 2.87 (m, 1H), 2.43 - 2.25 (m, 1H), 1.54 - 1.50(m, 1H), 1.45 - 1.40(m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ

-66.84 (d, $J = 6.5$ Hz, 3F), -104.15 - -104.22 (m, 1F); ^{13}C NMR (101 MHz, CDCl_3) δ 194.73 (s), 166.08 (d, $J = 255.9$ Hz), 133.13 (d, $J = 3.0$ Hz), 130.91 (d, $J = 9.5$ Hz), 125.09 (q, $J = 271.2$ Hz), 115.94 (d, $J = 22.0$ Hz), 23.84 (q, $J = 37.8$ Hz), 19.96 (q, $J = 2.1$ Hz), 12.53 (q, $J = 2.7$ Hz); IR (neat) $\nu = 3064, 1681, 1600, 1558, 1509, 1420, 1410, 1343, 1264, 1279, 1157, 1032, 847, 796, 597\text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_8\text{OF}_4$ $[\text{M}]^+$: 232.0511, Found: 232.0513.

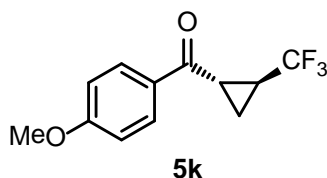


(3-Chlorophenyl)((*1S,2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5i**): 94%; Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 2.99 - 2.94 (m, 1H), 2.59 - 2.14 (m, 1H), 1.57 - 1.49 (m, 1H), 1.49 - 1.40 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.84 (d, $J = 6.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 196.18 (s), 138.18 (s), 135.16 (s), 133.51 (s), 130.08 (s), 128.30 (s), 126.34 (s), 124.99 (q, $J = 271.2$ Hz), 24.03 (q, $J = 37.9$ Hz), 20.16 (q, $J = 2.1$ Hz), 12.87 (q, $J = 2.7$ Hz); IR (neat) $\nu = 3070, 2360, 1683, 1573, 1417, 1340, 1264, 1222, 1150, 1000, 941, 787, 734, 708\text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_8\text{OF}_3\text{Cl}$ $[\text{M}]^+$: 248.0216, Found: 248.0215.

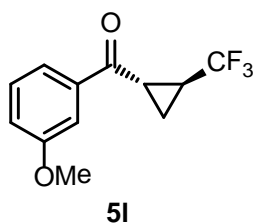


(2-Bromophenyl)((*1S,2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5j**): 82%; Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.0$ Hz, 1H), 7.46 (d, $J = 7.1$ Hz, 1H), 7.39 (t, $J = 7.1$ Hz, 1H), 7.34 (t, $J = 7.0$ Hz, 1H), 2.90 - 2.85 (m, 1H), 2.45 - 2.39 (m, 1H), 1.62 - 1.54 (m, 1H), 1.49 - 1.44 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.76 (d, $J = 6.3$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 200.01 (s), 140.72 (s), 133.80 (s), 132.35 (s), 129.32 (s), 127.54 (s), 124.88 (q, $J = 270.9$ Hz), 119.31 (s), 25.37 (q, $J = 38.2$ Hz), 24.24 (q, $J = 1.4$ Hz), 14.20 (q, $J = 2.3$ Hz); IR

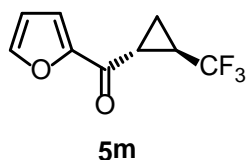
(neat) $\nu = 3059, 1694, 1588, 1565, 1466, 1389, 1263, 1109, 739 \text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_8\text{OF}_3\text{Br} [\text{M}]^+$: 291.9711, Found: 291.9715.



(4-Methoxyphenyl)((*1S,2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5k**): 87%; Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.1$ Hz, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 3.88 (s, 3H), 2.99 - 2.94 (m, 1H), 2.32 - 2.27 (m, 1H), 1.49 (m, 1H), 1.38 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.70 (d, $J = 6.1$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 194.60 (s), 163.95 (s), 130.57 (s), 129.75 (s), 125.27 (q, $J = 271.0$ Hz), 113.93 (s), 55.53 (s), 23.50 (q, $J = 37.8$ Hz), 19.66 (q, $J = 1.8$ Hz), 12.18 (q, $J = 2.7$ Hz); IR (neat) $\nu = 2940, 2843, 1669, 1601, 1576, 1513, 1481, 1345, 1264, 1234, 1149, 1209, 841 \text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{F}_3 [\text{M}]^+$: 244.0711, Found: 244.0715.

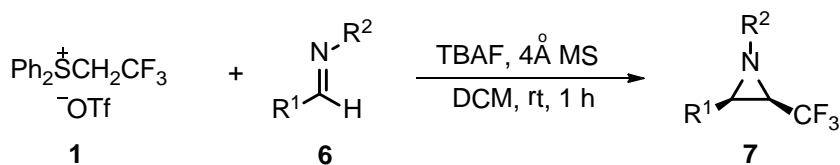


(3-Methoxyphenyl)((*1S,2S*)-2-(trifluoromethyl)cyclopropyl)methanone (**5l**): 88%; Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 1H), 7.49 (s, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 3.85 (s, 3H), 3.12 - 2.80 (m, 1H), 2.37 - 2.31 (m, 1H), 1.52 - 1.49 (m, 1H), 1.46 - 1.36 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.80 (d, $J = 6.5$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 196.15 (s), 159.91 (s), 138.04 (s), 129.74 (s), 125.15 (q, $J = 271.0$ Hz), 120.90 (s), 120.06 (s), 112.41 (s), 55.42 (s), 23.83 (q, $J = 37.8$ Hz), 20.18 (q, $J = 2.0$ Hz), 12.55 (q, $J = 2.6$ Hz); IR (neat) $\nu = 3058, 2943, 1680, 1598, 1583, 1467, 1432, 1343, 1262, 1151, 1033, 942, 786, 745 \text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{F}_3 [\text{M}]^+$: 244.0711, Found: 244.0707.

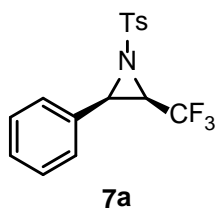


Furan-2-yl((*1R,2R*)-2-(trifluoromethyl)cyclopropyl)methanone (**5m**): 88%; White solid. M.P.: 46.5-48.4°C; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 1.7$ Hz, 1H), 7.31 (d, $J = 3.4$ Hz, 1H), 6.6 (dd, $J = 3.4, 1.7$ Hz, 1H), 3.17 - 2.74 (m, 1H), 2.66 - 2.17 (m, 1H), 1.56 - 1.45 (m, 1H), 1.43 - 1.36 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -66.97 (d, $J = 6.5$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 184.77 (s), 152.36 (s), 147.14 (s), 125.03 (q, $J = 271.1$ Hz), 117.86 (s), 112.59 (s), 23.33 (q, $J = 37.9$ Hz), 19.99 (q, $J = 2.1$ Hz), 12.08 (q, $J = 2.6$ Hz); IR (neat) $\nu = 3138, 2360, 1674, 1572, 1469, 1420, 1345, 1268, 1151, 1086, 1017, 763, 642$ cm^{-1} ; HRMS (EI) Calcd for $\text{C}_9\text{H}_7\text{O}_2\text{F}_3$ $[\text{M}]^+$: 204.0398, Found: 204.0396.

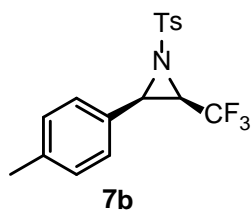
5.3 The Procedure for The Synthesis of 7



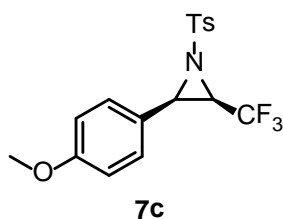
Into the mixture of diphenyl(2,2,2-Trifluoroethyl)sulfonium triflate **1** (1.0 mmol, 0.4184 g, 1.0 equiv.), imine **6** (2.0 mmol, 2.0 equiv.) and 4Å MS (0.8 g) in dichloromethane (10 mL) was added TBAF (1.5 mmol, 1.5 mL, 1.5 equiv.) dropwise under N_2 atmosphere. The reaction mixture was stirred at room temperature for 1 h. After filtration, the solid was washed with DCM (10 mL). The combined organic phase was washed with water, sat. sodium bisulfite and water in sequence and then dried over Na_2SO_4 . The solvent was removed by concentration, and the residue was subjected to flash column chromatography with hexane/ethyl acetate (50:1-20:1) as the eluent to afford the final product **7**.



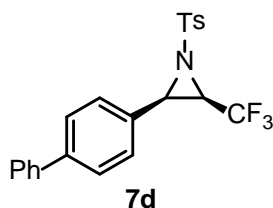
(*2RS,3RS*)-2-Phenyl-1-tosyl-3-(trifluoromethyl)aziridine (**7a**): 86%; White solid. M.P. 69.0 - 70.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 5H), 4.19 (d, *J* = 7.0 Hz, 1H), 3.49 (dq, *J* = 7.0, 5.4 Hz, 1H), 2.45 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.82 (d, *J* = 5.4 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 145.74 (s), 133.55 (s), 130.08 (s), 128.63 (s), 128.43 (s), 128.28 (s), 127.35 (s), 127.35 (s), 122.21 (q, *J* = 275.7 Hz), 43.51 (q, *J* = 1.1 Hz), 42.55 (q, *J* = 40.2 Hz), 21.77 (s); IR (neat) ν = 3064, 3034, 1698, 1597, 1489, 1458, 1442, 1384, 1347, 1299, 1237, 1181, 1085, 1050, 1013, 954, 933, 923, 825, 805, 787, 700, 663, 605, 545 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₅F₃NO₂S [M+H]⁺: 342.0770, Found: 342.0766.



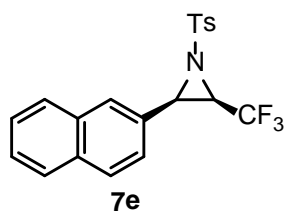
(*2RS,3RS*)-2-(*p*-Tolyl)-1-tosyl-3-(trifluoromethyl)aziridine (**7b**): 88%; White solid. M.P. 90.3 - 91.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 4.19 (d, *J* = 7.0 Hz, 1H), 3.51 (dq, *J* = 7.0, 5.4 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.69 (d, *J* = 5.4 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 145.66 (s), 138.48 (s), 133.64 (s), 130.04 (s), 129.11 (s), 128.26 (s), 127.22 (s), 127.04 (s), 122.26 (q, *J* = 275.7 Hz), 43.50 (q, *J* = 1.2 Hz), 42.53 (q, *J* = 40.0 Hz), 21.75 (s), 21.19 (s); IR (neat) ν = 3037, 2927, 1598, 1519, 1494, 1435, 1377, 1335, 1292, 1187, 1165, 1150, 1091, 1052, 1041, 945, 910, 880, 814, 777, 683, 666, 609, 558, 539 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₇F₃NO₂S [M+H]⁺: 356.0927, Found: 356.0921.



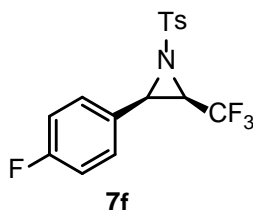
(*2RS,3RS*)-2-(4-Methoxyphenyl)-1-tosyl-3-(trifluoromethyl)aziridine (**7c**): 72%; White solid. M.P.: 104.5 - 106.1 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.14 (d, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 3.45 (dq, *J* = 7.0, 5.5 Hz, 1H), 2.46 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.69 (d, *J* = 5.5 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 159.82 (s), 145.67 (s), 133.67 (s), 130.04 (s), 128.59 (s), 128.24 (s), 122.31 (q, *J* = 276.1 Hz), 121.97 (s), 113.87 (s), 55.21 (s), 43.27 (s), 42.60 (q, *J* = 39.9 Hz), 21.70 (s); IR (neat) ν = 3021, 2968, 2842, 1917, 1614, 1598, 1519, 1495, 1436, 1377, 1339, 1293, 1259, 1188, 1146, 1051, 1032, 936, 877, 838, 806, 778, 681, 665, 577, 549 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₆F₃NNaO₃S [M+Na]⁺: 394.0695, Found: 394.0702.



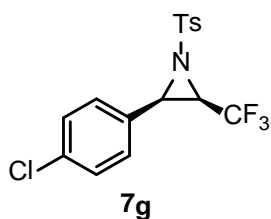
(*2RS,3RS*)-2-([1,1'-Biphenyl]-4-yl)-1-tosyl-3-(trifluoromethyl)aziridine (**7d**): 95%; White solid. M.P. 103.9 - 105.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.63 - 7.50 (m, 4H), 7.49 - 7.32 (m, 7H), 4.25 (d, *J* = 7.0 Hz, 1H), 3.56 (dq, *J* = 7.0, 5.4 Hz, 1H), 2.46 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.62 (d, *J* = 5.4 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 145.77 (s), 141.55 (s), 140.31 (s), 133.62 (s), 130.11 (s), 129.10 (s), 128.85 (s), 128.30 (s), 127.86 (s), 127.63 (s), 127.14 (s), 127.08 (s), 122.30 (q, *J* = 275.7 Hz), 43.42 (q, *J* = 1.8 Hz), 42.70 (q, *J* = 40.1 Hz), 21.74 (s); IR (neat) ν = 3075, 3024, 1597, 1489, 1442, 1353, 1300, 1163, 1087, 1056, 960, 935, 803, 816, 766, 690, 662, 605, 559, 849, 530 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₁₉F₃NO₂S [M+H]⁺: 418.1083, Found: 418.1079.



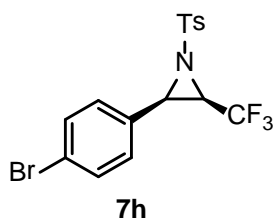
(*2RS,3RS*)-2-(Naphthalen-2-yl)-1-tosyl-3-(trifluoromethyl)aziridine (**7e**): 96%; White solid. M.P. 100.6 - 102.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.87 - 7.78 (m, 4H), 7.55 - 7.49 (m, 2H), 7.46 - 7.40 (m, 3H), 4.39 (d, *J* = 7.0 Hz, 1H), 3.61 (dq, *J* = 7.0, 5.4 Hz, 1H), 2.50 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.62 (d, *J* = 5.4 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 145.80 (s), 133.56 (s), 133.24 (s), 132.90 (s), 130.11 (s), 128.34 (s), 128.31 (s), 127.98 (s), 127.78 (s), 127.51 (s), 126.94 (s), 126.59 (s), 126.53 (s), 124.54 (s), 122.24 (q, *J* = 275.7 Hz), 43.64 (q, *J* = 1.1 Hz), 42.81 (q, *J* = 40.2 Hz), 21.78 (s); IR (neat) ν = 3055, 1599, 1436, 1388, 1338, 1293, 1223, 1171, 1148, 1090, 1055, 974, 941, 906, 842, 820, 776, 761, 684, 661, 559, 544 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₁₇F₃NO₂S [M+H]⁺: 392.0927, Found: 392.0919.



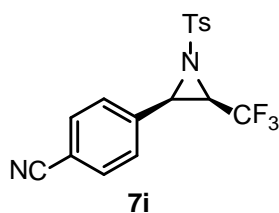
(*2RS,3RS*)-2-(4-Fluorophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (**7f**): Quantitative; White solid. M.P.: 116.2 - 116.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.30 - 7.21 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.14 (d, *J* = 7.0 Hz, 1H), 3.45 (dq, *J* = 7.0, 5.4 Hz, 1H), 2.46 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.80 (d, *J* = 5.4 Hz, 3F), -112.64 - -113.03 (m, 1F); ¹³C NMR (101 MHz, CDCl₃) δ 162.81 (d, *J* = 247.7 Hz), 145.87 (s), 133.42 (s), 130.12 (s), 129.20 (d, *J* = 8.4 Hz), 128.25 (s), 125.92 (d, *J* = 3.2 Hz), 122.15 (q, *J* = 275.6 Hz), 115.53 (d, *J* = 21.9 Hz), 42.75 (s), 42.63 (q, *J* = 40.1 Hz), 21.73 (s); IR (neat) ν = 3037, 1599, 1514, 1452, 1376, 1338, 1282, 1236, 1190, 1170, 1147, 1091, 1058, 952, 905, 885, 831, 817, 784, 750, 703, 682, 669 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₄F₄NO₂S [M+H]⁺: 360.0676, Found: 360.0670.



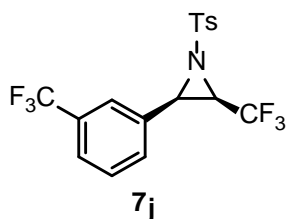
(*2RS,3RS*)-2-(4-Chlorophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (**7g**): 89%; White solid. M.P.: 86.8 - 88.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 4.13 (d, $J = 7.0$ Hz, 1H), 3.48 (dq, $J = 7.0, 5.4$ Hz, 1H), 2.45 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -65.80 (d, $J = 5.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 145.90 (s), 134.69 (s), 133.38 (s), 130.13 (s), 128.77 (s), 128.72 (s), 128.66 (s), 128.26 (s), 122.08 (q, $J = 275.7$ Hz), 42.72 (s), 42.65 (q, $J = 40.2$ Hz), 21.78 (s); IR (neat) $\nu = 3032, 1599, 1495, 1437, 1375, 1341, 1293, 1166, 1091, 1053, 1017, 943, 882, 789, 697, 557, 542$ cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{14}\text{ClF}_3\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 376.0380, Found: 376.0373.



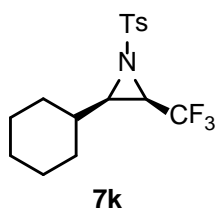
(*2RS,3RS*)-2-(4-Bromophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (**7h**): 92%; White solid. M.P. 80.4 - 83.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 4.11 (d, $J = 7.0$ Hz, 1H), 3.48 (dq, $J = 7.0, 5.4$ Hz, 1H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -65.77 (d, $J = 5.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 145.91 (s), 133.39 (s), 131.66 (s), 130.13 (s), 129.23 (s), 129.07 (s), 128.25 (s), 122.85 (s), 122.09 (q, $J = 275.7$ Hz), 42.80 (s), 42.60 (q, $J = 39.9$ Hz), 21.74 (s); IR (neat) $\nu = 3090, 3030, 1598, 1491, 1437, 1402, 1372, 1335, 1292, 1162, 1090, 1043, 1013, 939, 826, 819, 788, 757, 694, 673, 614, 571, 549, 528$ cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{14}\text{BrF}_3\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 419.9875, Found: 419.9872.



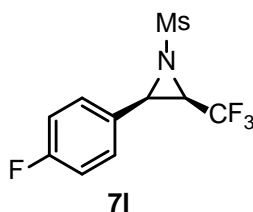
4-((*2RS,3RS*)-1-Tosyl-3-(trifluoromethyl)aziridin-2-yl)benzonitrile (**7i**): 94%; White solid. M.P. 135.9 - 136.4 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 4.21 (d, $J = 6.0$ Hz, 1H), 3.55 (dq, $J = 7.0, 5.4$ Hz, 1H), 2.49 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -65.94 (d, $J = 5.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 146.14 (s), 135.45 (s), 133.16 (s), 132.28 (s), 130.21 (s), 128.30 (s), 128.27 (s), 121.89 (q, $J = 275.7$ Hz), 118.20 (s), 112.82 (s), 42.88 (q, $J = 40.5$ Hz), 42.48 (q, $J = 1.3$ Hz), 21.79 (s); IR (neat) $\nu = 3060, 3042, 2231, 1613, 1598, 1509, 1437, 1374, 1339, 1295, 1190, 1167, 1145, 1089, 1040, 934, 849, 796, 772, 678, 601, 573, 560$ cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 367.0723, Found: 367.0718.



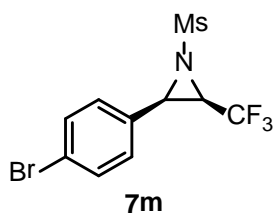
(*2RS,3RS*)-1-Tosyl-2-(trifluoromethyl)-3-(3-(trifluoromethyl)phenyl)aziridine (**7j**): 85%; Colourless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.55 - 7.50 (m, 2H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 2H), 4.23 (d, $J = 6.9$ Hz, 1H), 3.57 (dq, $J = 6.9, 5.4$ Hz, 1H), 2.50 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -62.87 (s, 3F), -65.87 (d, $J = 5.4$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 146.10 (s), 133.20 (s), 131.32 (s), 131.14 (s), 130.81 (s), 130.17 (s), 129.06 (s), 128.30 (s), 125.56 (q, $J = 3.7$ Hz), 124.36 (q, $J = 3.6$ Hz), 123.71 (q, $J = 272.4$ Hz), 122.01 (q, $J = 275.6$ Hz), 42.67 (q, $J = 40.4$ Hz), 42.62 (q, $J = 0.5$ Hz), 21.72 (s); IR (neat) $\nu = 3033, 1598, 1433, 1379, 1329, 1292, 1230, 1166, 1092, 1074, 955, 916, 814, 771, 743, 701, 679, 543$ cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 410.0644, Found: 410.0637.



(*2RS,3RS*)-2-cyclohexyl-1-tosyl-3-(trifluoromethyl)aziridine (**7k**): 83%; White solid. M.P. 62.5 - 64.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.23 (dq, *J* = 6.9, 6.1 Hz, 1H), 2.76 - 2.69 (m, 1H), 2.46 (s, 3H), 1.78 - 1.62 (m, 5H), 1.50 - 1.38 (m, 1H), 1.28 - 0.99 (m, 5H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.45 (d, *J* = 6.0 Hz, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 145.38 (s), 133.70 (s), 129.83 (s), 128.28 (s), 122.97 (q, *J* = 275.1 Hz), 48.05 (s), 41.29 (q, *J* = 40.5 Hz), 35.29 (q, *J* = 1.2 Hz), 31.53 (s), 29.47 (s), 25.89 (s), 25.24 (s), 25.17 (s), 21.68 (s); IR (neat) ν = 3060, 2936, 2852, 1599, 1456, 1408, 1349, 1305, 1283, 1248, 1156, 1119, 1087, 1047, 933, 888, 826, 811, 748, 659, 604, 558, 549, 528 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₂₀F₃NNaO₂S [M+Na]⁺: 370.1059, Found: 370.1058.

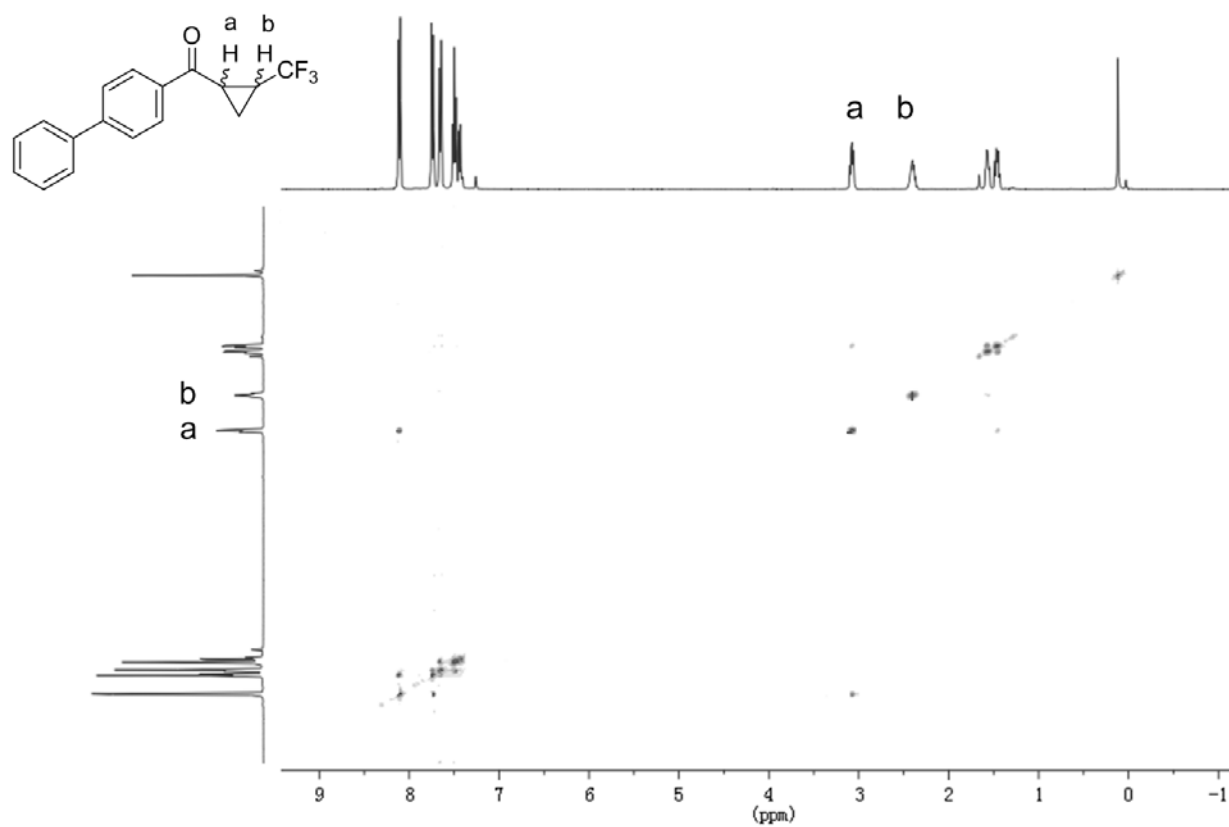


(*2RS,3RS*)-2-(4-fluorophenyl)-1-(methylsulfonyl)-3-(trifluoromethyl)aziridine (**7l**): 90%; White solid. M.P. 76.7 - 78.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.09 - 7.02 (m, 2H), 4.14 (d, *J* = 7.0 Hz, 1H), 3.48 (dq, *J* = 7.0, 5.4 Hz, 1H), 3.23 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.72 (d, *J* = 5.4 Hz, 3F), -111.96 - -113.28 (m, 1F); ¹³C NMR (101 MHz, CDCl₃) δ 162.93 (d, *J* = 247.9 Hz), 129.24 (d, *J* = 8.5 Hz), 125.67 (d, *J* = 3.2 Hz), 122.22 (q, *J* = 275.4 Hz), 115.65 (d, *J* = 22.0 Hz), 42.77 (q, *J* = 40.1 Hz), 41.97 (q, *J* = 0.9 Hz), 39.60 (s); IR (neat) ν = 3032, 2940, 1609, 1516, 1444, 1380, 1340, 1296, 1238, 1156, 1056, 974, 945, 884, 834, 819, 795, 525, 418 cm⁻¹; HRMS (EI) Calcd for C₁₀H₉F₄NO₂S [M]⁺: 283.0290, Found: 283.0294.

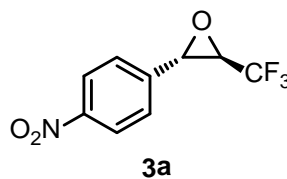
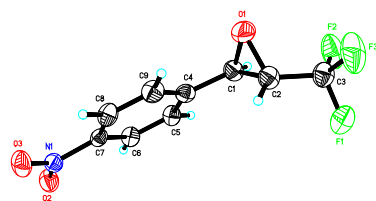


(*2RS,3RS*)-2-(4-bromophenyl)-1-(methylsulfonyl)-3-(trifluoromethyl)aziridine (**7m**): 92%; White solid. M.P. 74.4 - 75.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 4.09 (d, $J = 7.0$ Hz, 1H), 3.47 (dq, $J = 6.8, 5.5$ Hz, 1H), 3.22 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -65.75 (d, $J = 5.5$ Hz, 3F); ^{13}C NMR (101 MHz, CDCl_3) δ 131.80 (s), 129.09 (s), 128.89 (s), 123.10 (s), 122.13 (q, $J = 275.5$ Hz), 42.85 (q, $J = 40.2$ Hz), 41.97 (q, $J = 0.9$ Hz), 39.72 (s); IR (neat) $\nu = 3021, 2945, 1492, 1436, 1408, 1331, 1290, 1236, 1182, 1162, 1143, 1049, 1011, 972, 942, 913, 877, 819, 799, 538, 525$ cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_9\text{BrF}_3\text{NO}_2\text{S}$ $[\text{M}]^+$: 342.9489, Found: 342.9490.

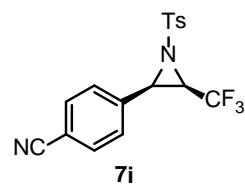
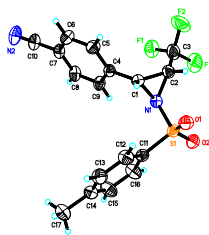
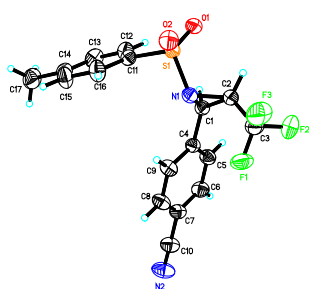
6. NOESY Spectrum and Structure Refinement for 5a



7. X-Ray Diffraction Data and Structure Refinement for 3a, 7i



Empirical formula	C ₉ H ₆ F ₃ N O ₃
Formula weight	233.15
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 4.8359(6) Å alpha = 90 deg. b = 6.4223(8) Å beta = 90 deg. c = 30.645(4) Å gamma = 90 deg.
Volume	951.8(2) Å ³
Z, Calculated density	4, 1.627 Mg/m ³
Absorption coefficient	0.159 mm ⁻¹
F(000)	472
Crystal size	0.311 x 0.167 x 0.086 mm
Theta range for data collection	2.66 to 25.99 deg.
Limiting indices	-5<=h<=5, -7<=k<=5, -35<=l<=37
Reflections collected / unique	5407 / 1850 [R(int) = 0.0309]
Completeness to theta = 25.99	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.14145
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1850 / 6 / 145
Goodness-of-fit on F ²	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1313
R indices (all data)	R1 = 0.0559, wR2 = 0.1383
Absolute structure parameter	0.1(15)
Largest diff. peak and hole	0.278 and -0.281 e. Å ⁻³

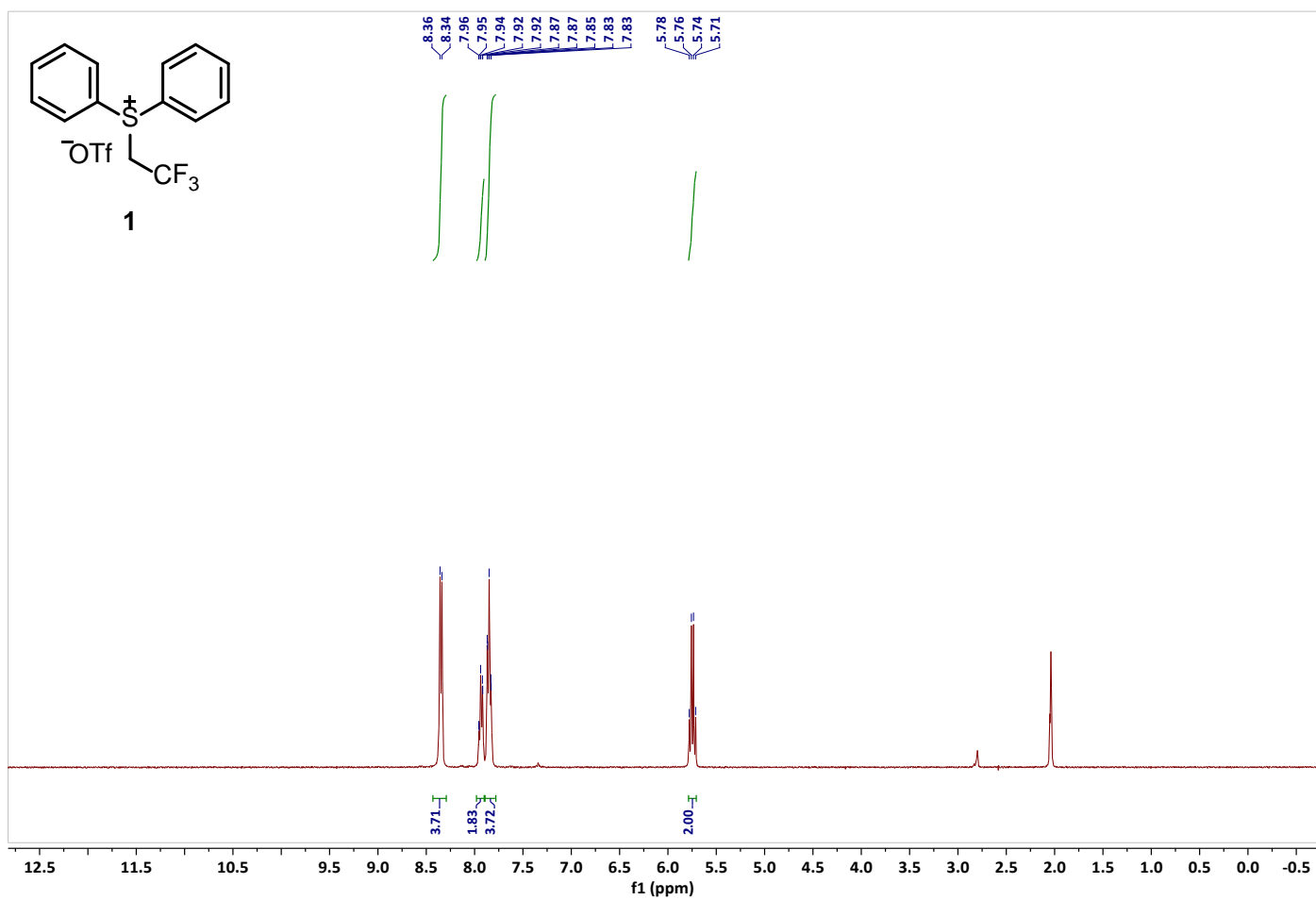


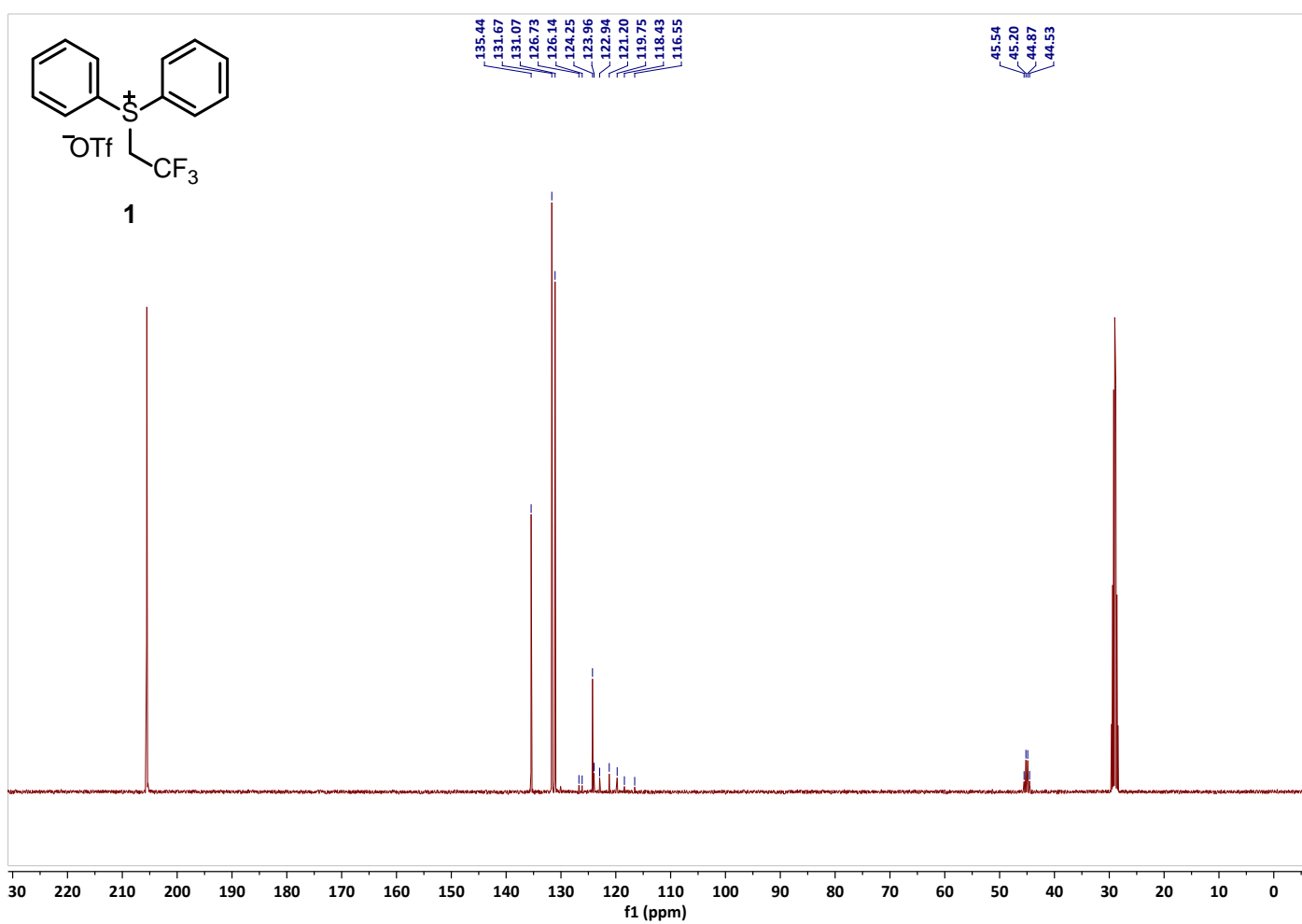
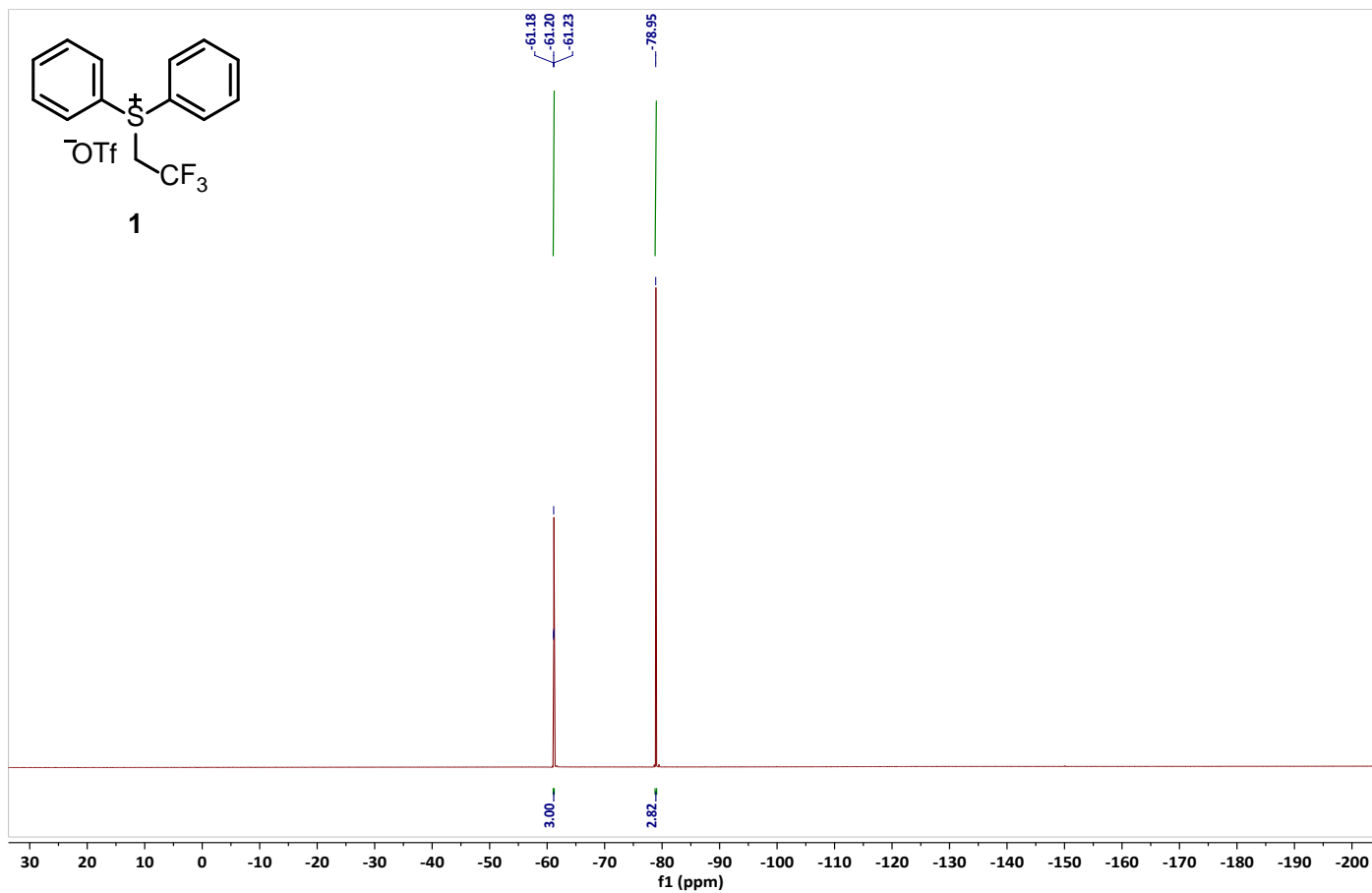
Empirical formula	C17 H13 F3 N2 O2 S
Formula weight	366.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 17.549(4) Å α = 90°. b = 11.355(2) Å β = 111.289(4)°. c = 18.820(4) Å γ = 90°.
Volume	3494.2(12) Å ³
Z	8
Density (calculated)	1.393 Mg/m ³
Absorption coefficient	0.228 mm ⁻¹
F(000)	1504
Crystal size	0.211 x 0.166 x 0.123 mm ³
Theta range for data collection	2.184 to 25.995°.
Index ranges	-21 ≤ h ≤ 21, -14 ≤ k ≤ 12, -23 ≤ l ≤ 20
Reflections collected	10399
Independent reflections	3430 [R(int) = 0.0353]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6295
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3430 / 36 / 255
Goodness-of-fit on F ²	1.058
Final R indices [I > 2σ(I)]	R1 = 0.0465, wR2 = 0.1261
R indices (all data)	R1 = 0.0579, wR2 = 0.1363
Extinction coefficient	0.0041(5)
Largest diff. peak and hole	0.282 and -0.289 e.Å ⁻³

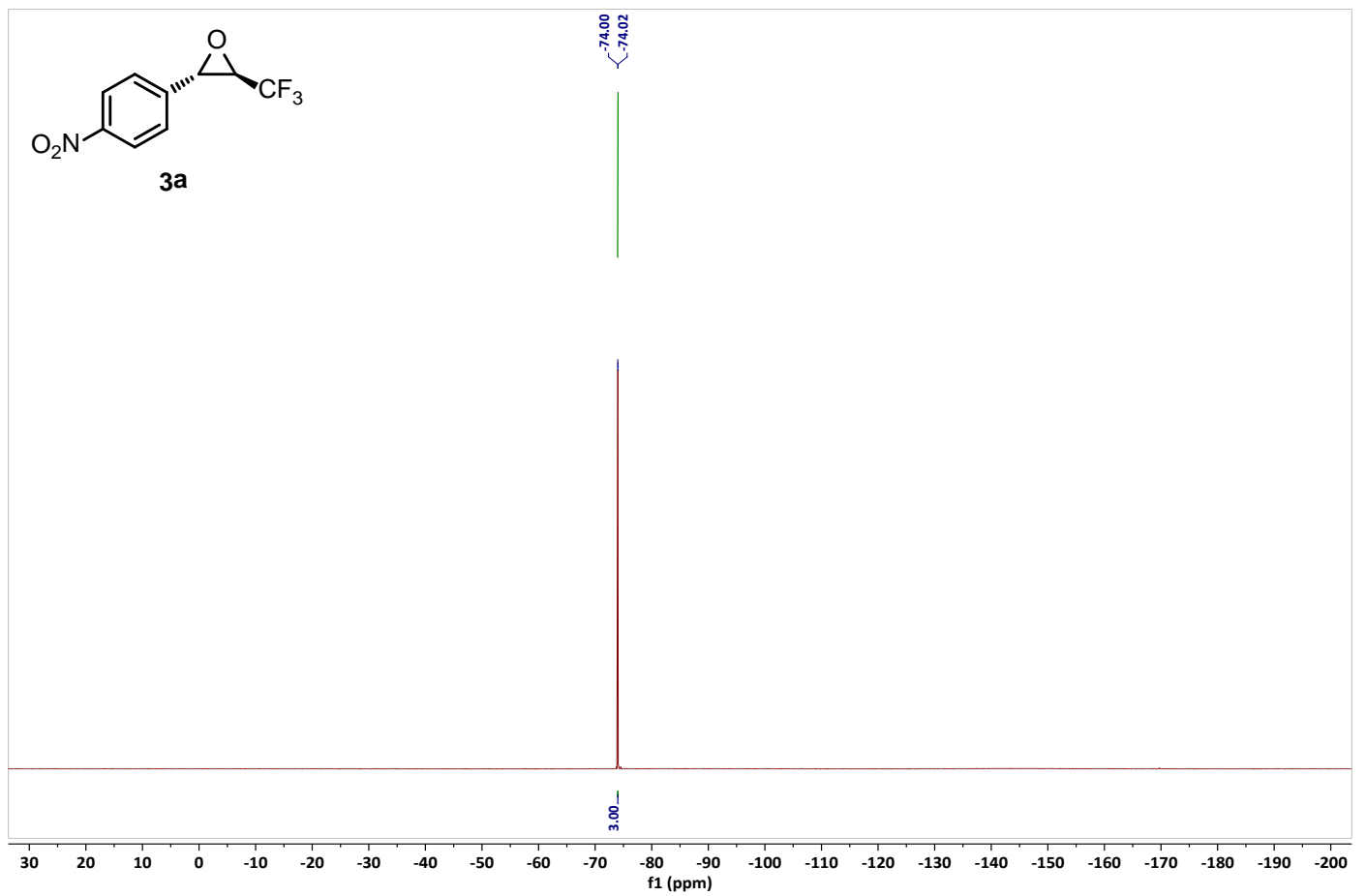
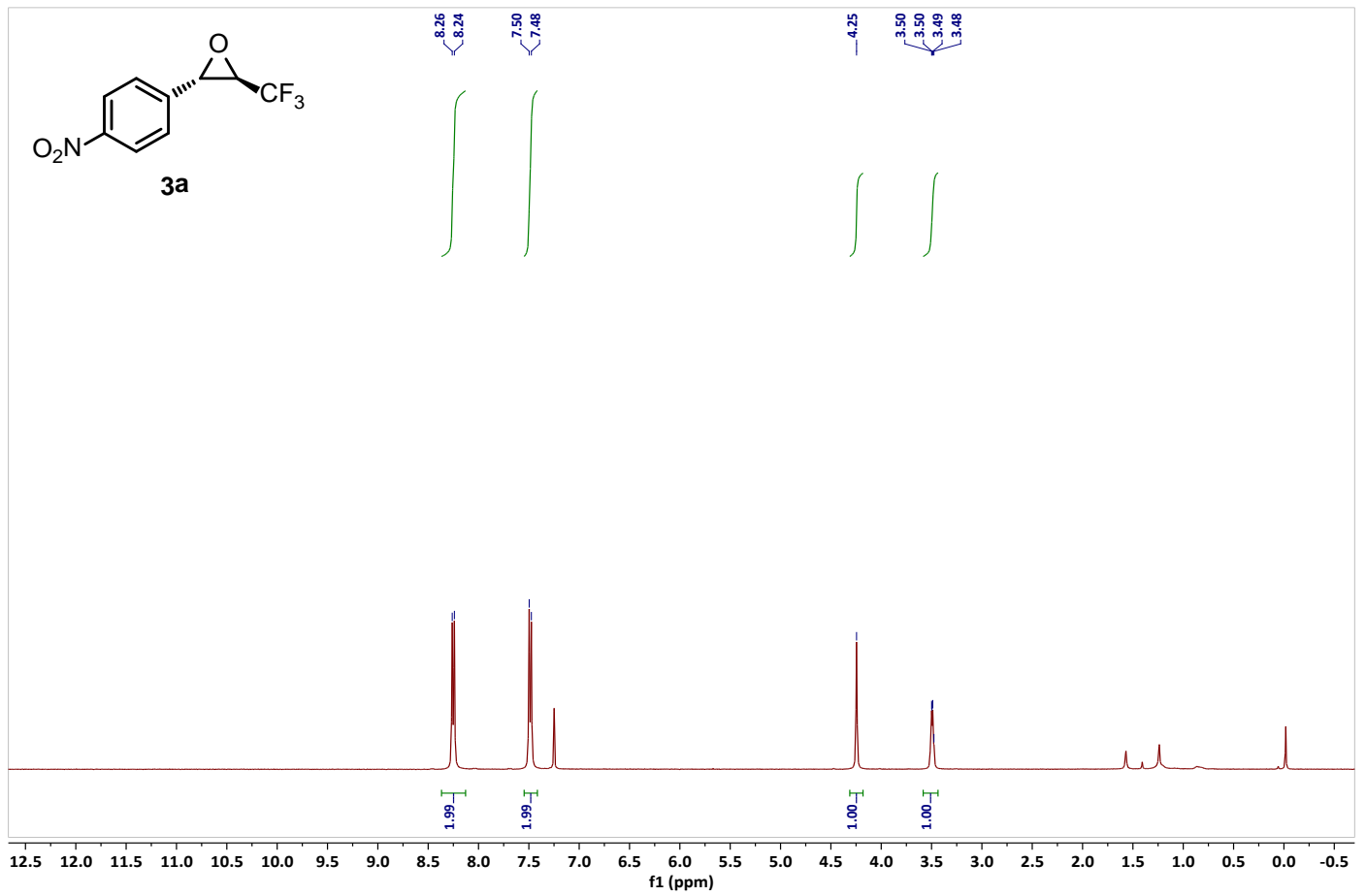
8. References

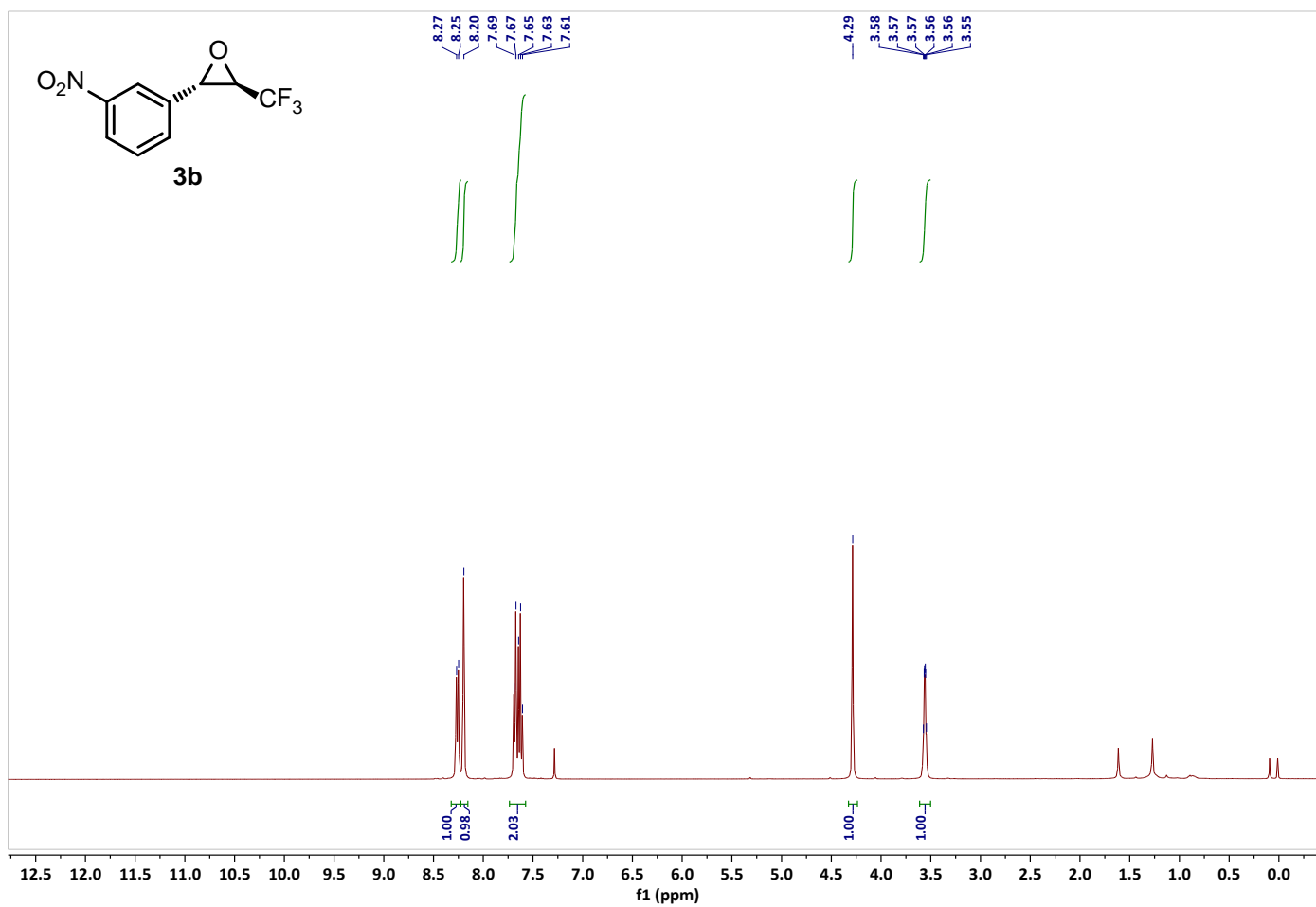
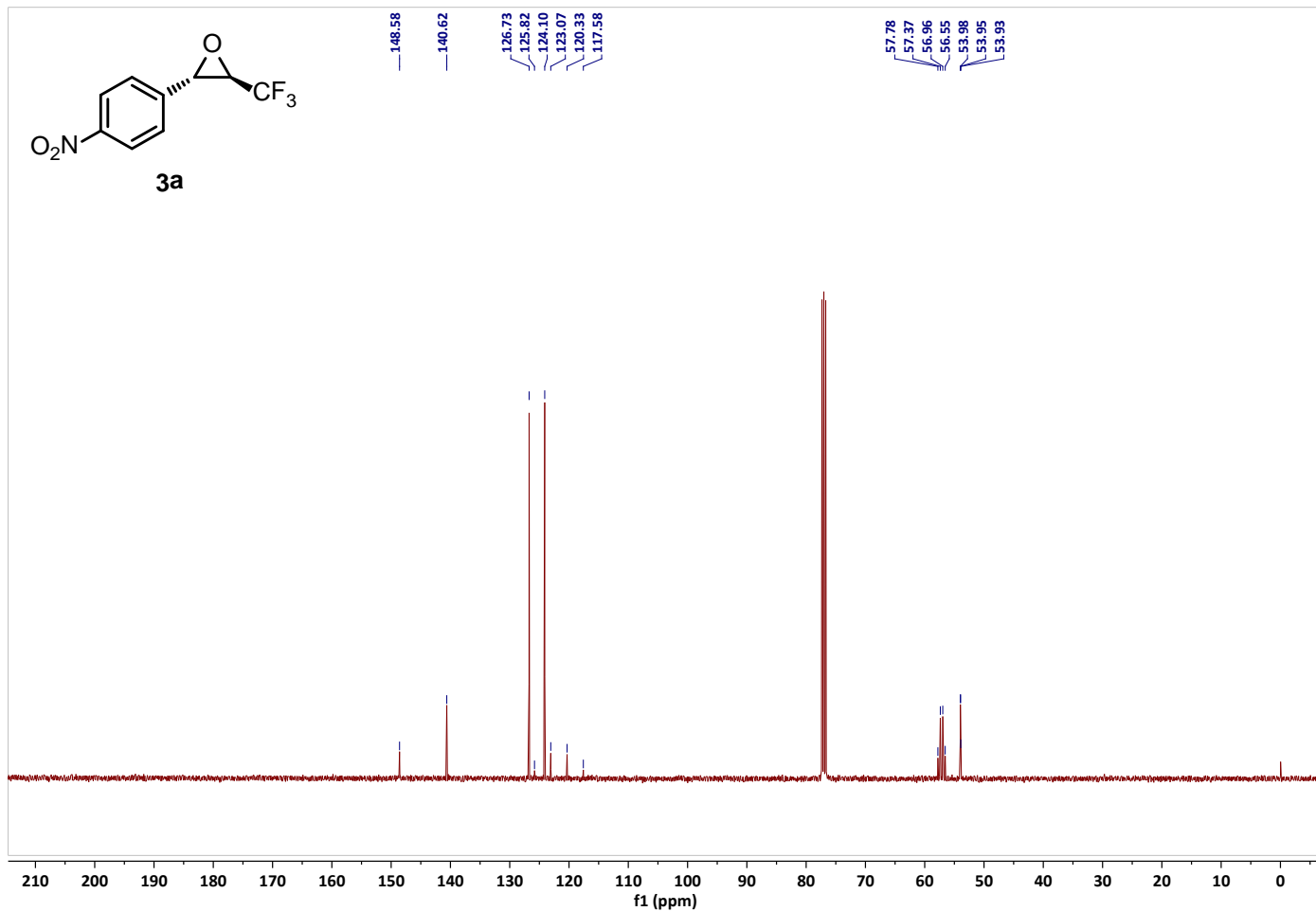
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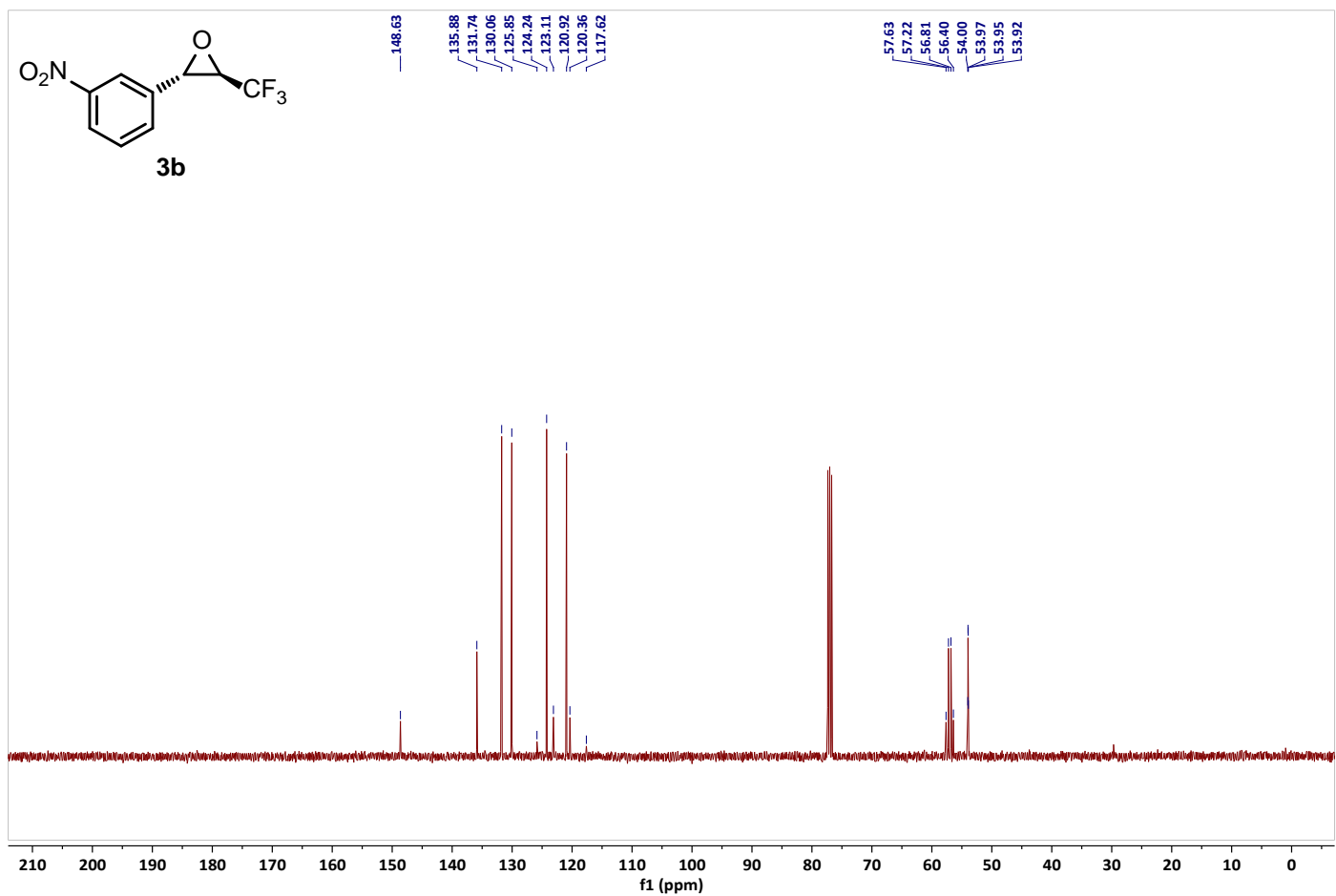
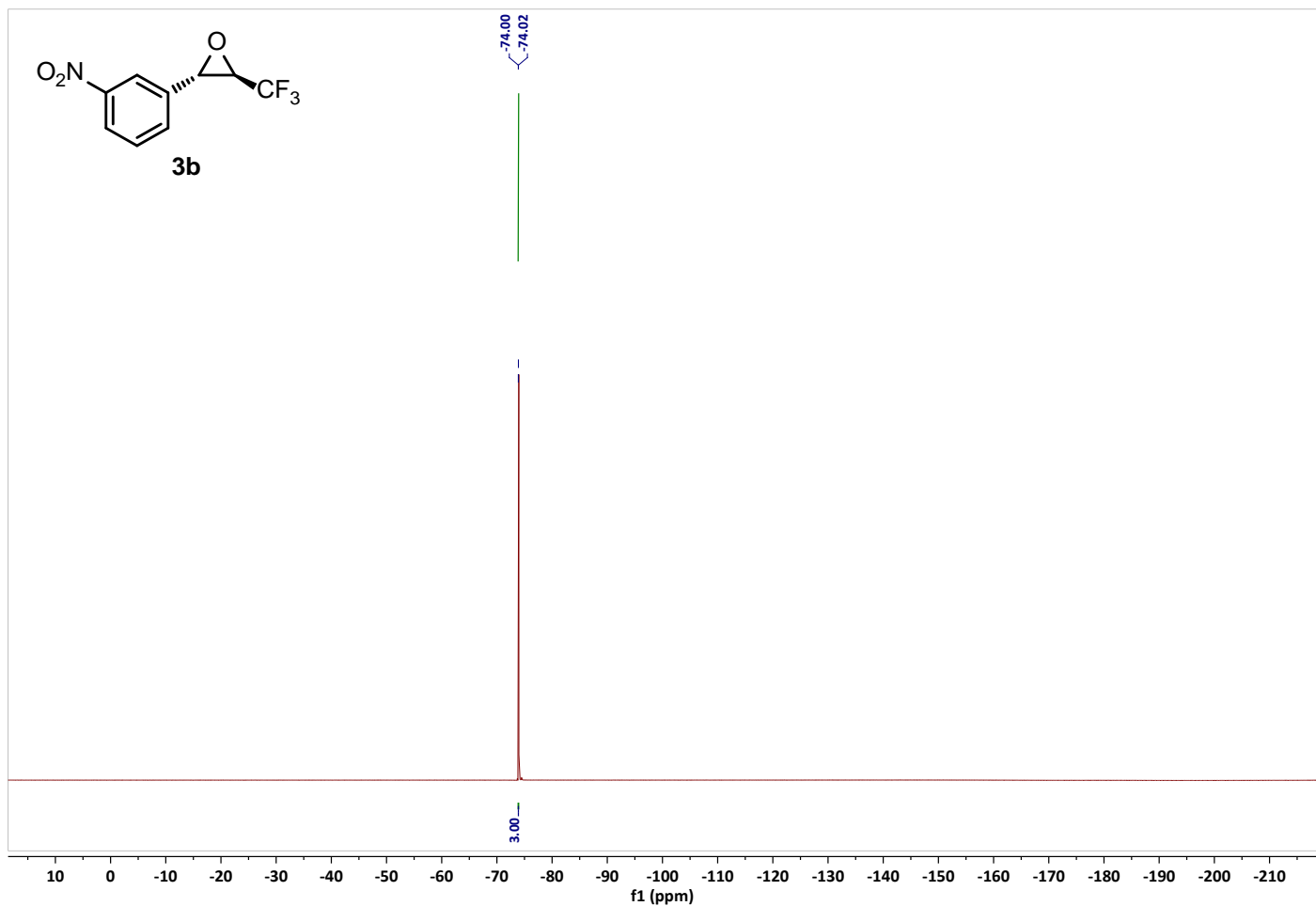
9. Copies of ^1H NMR, ^{19}F NMR and ^{13}C NMR Spectra of 1, 3, 5 and 7

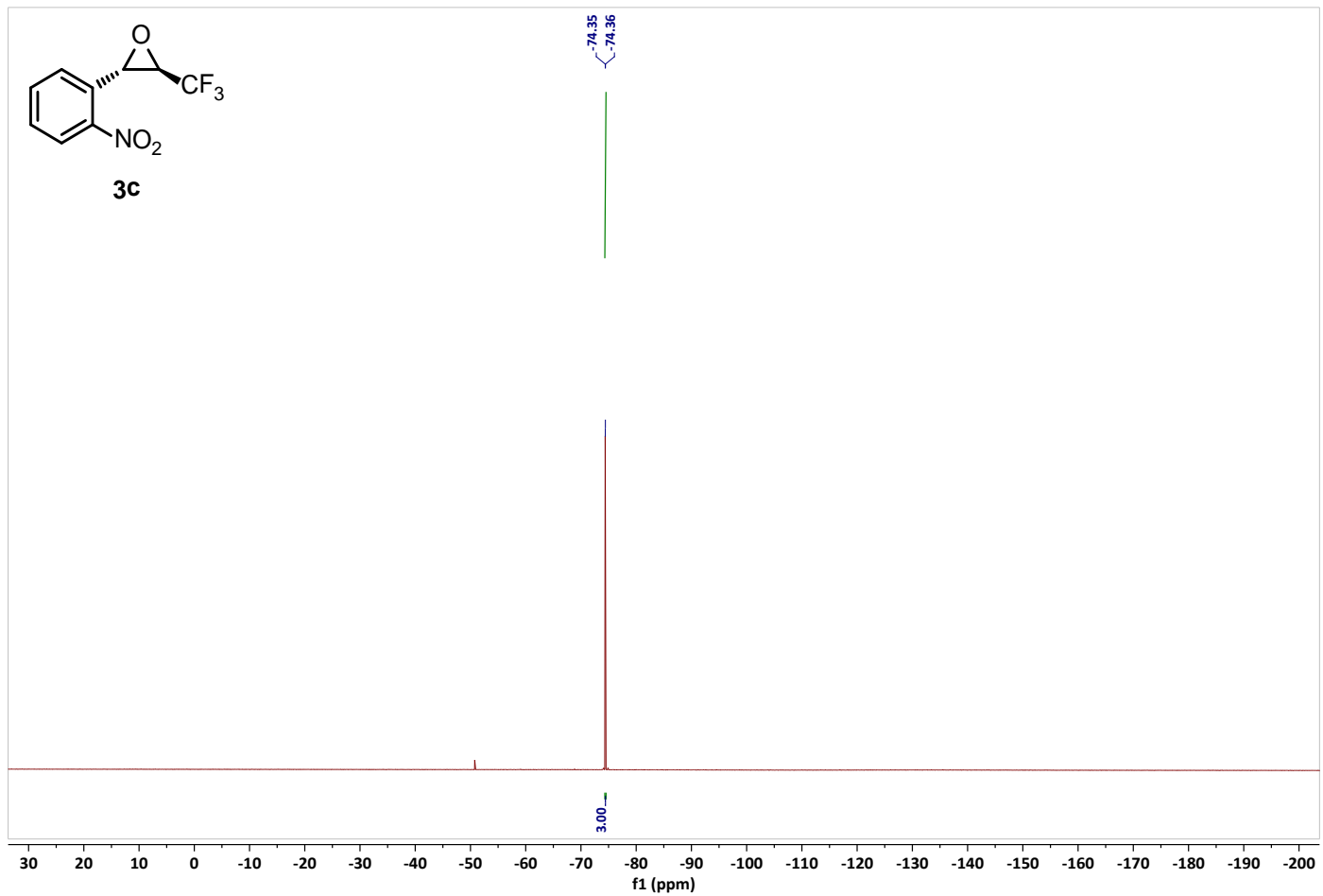
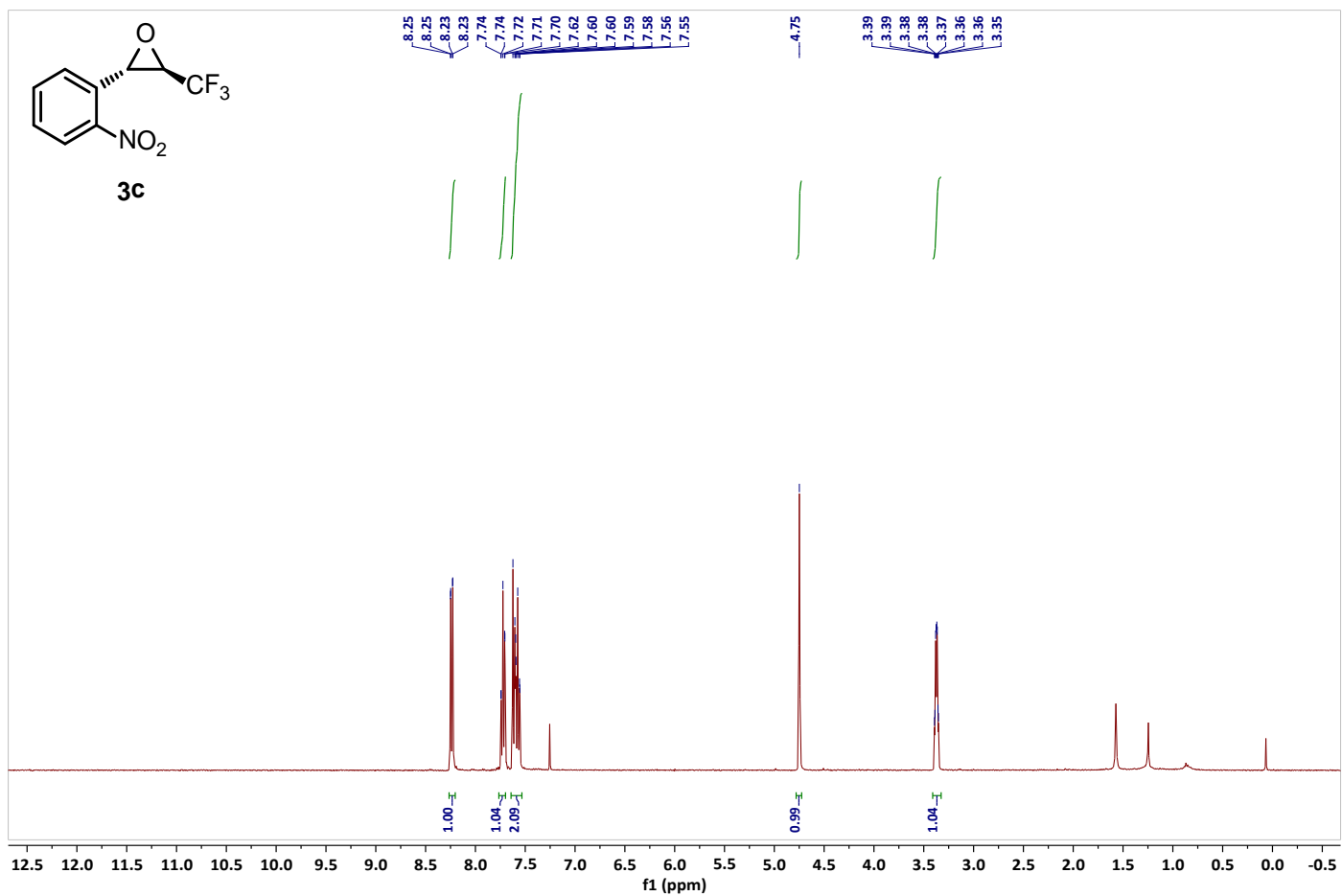


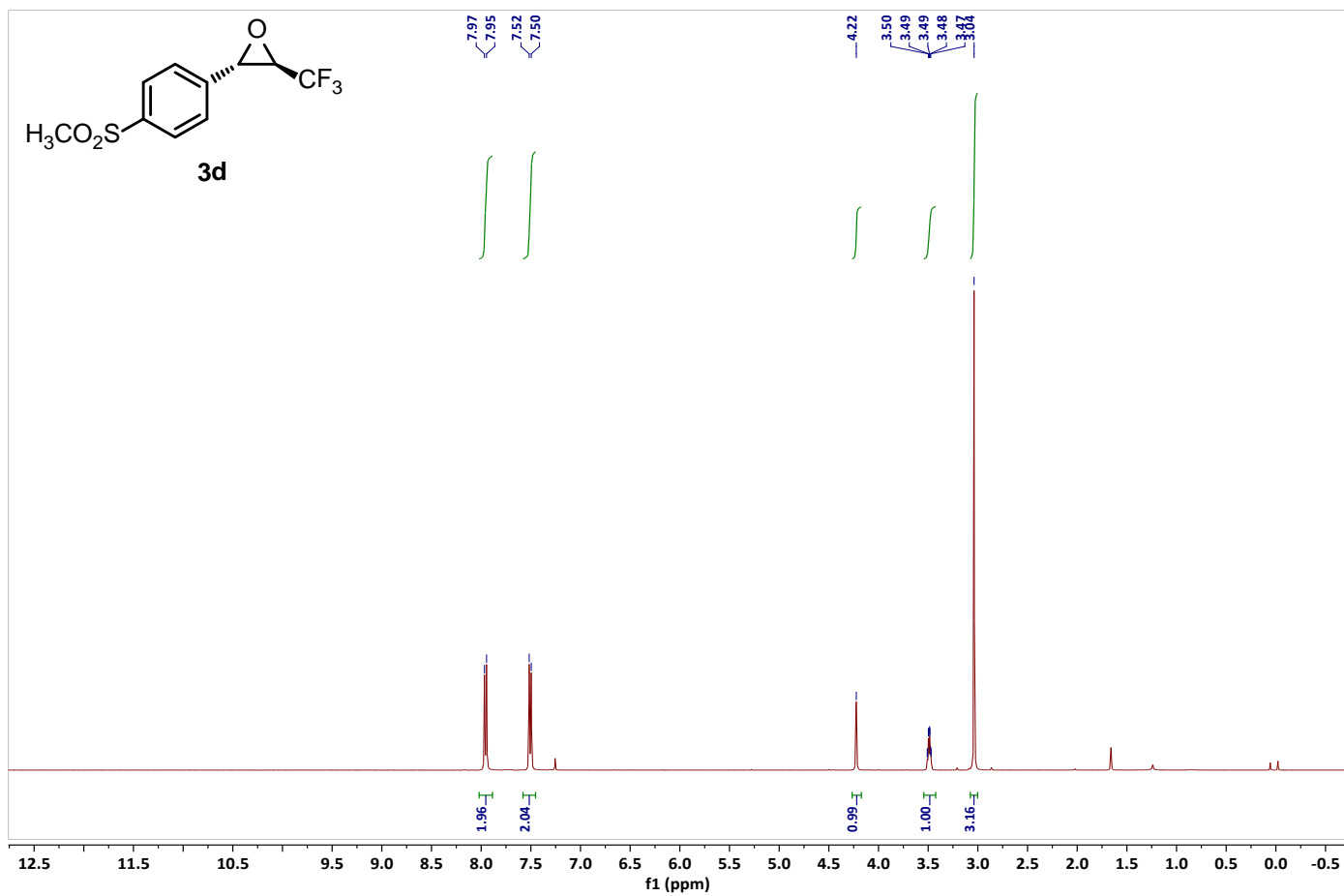
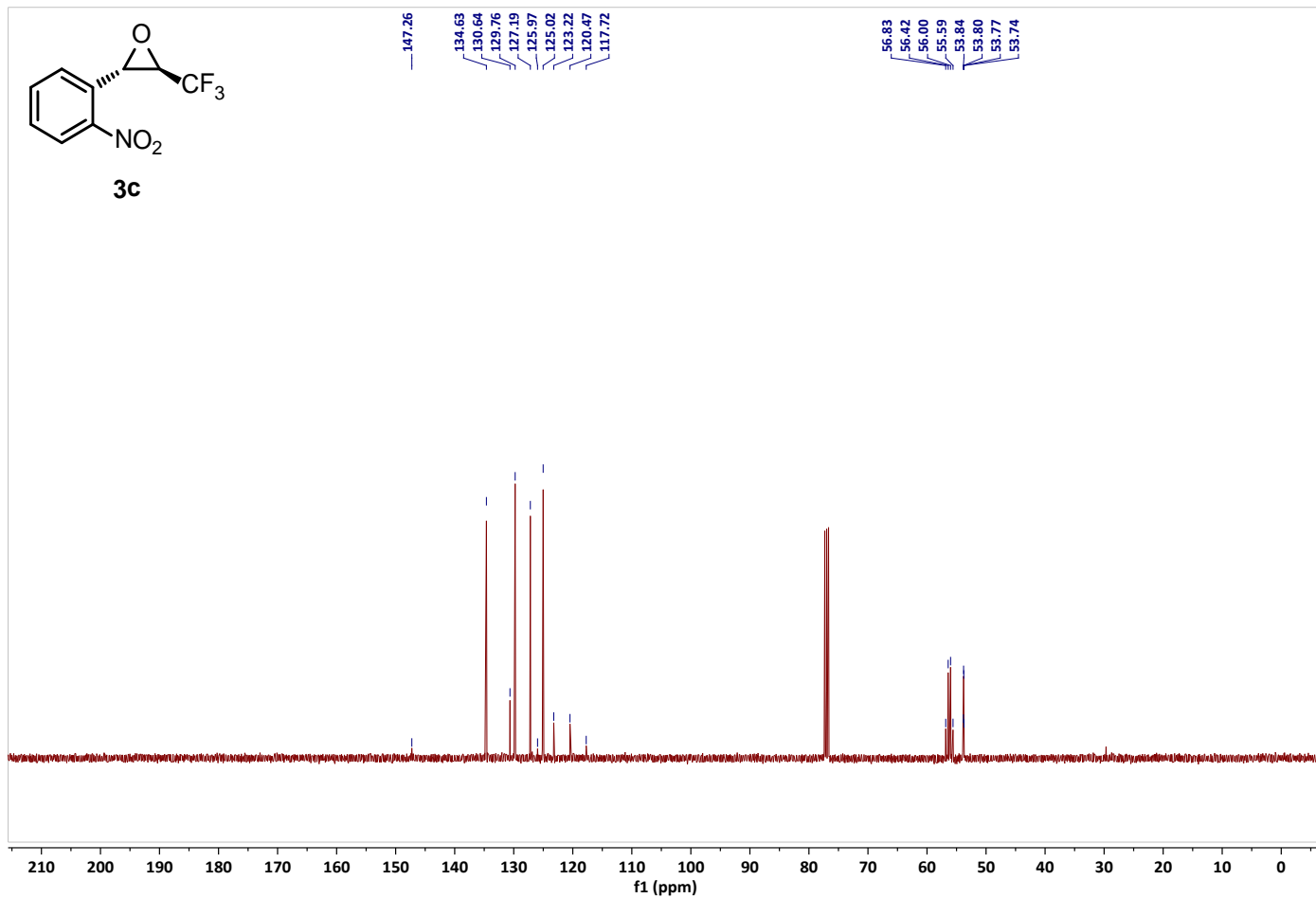


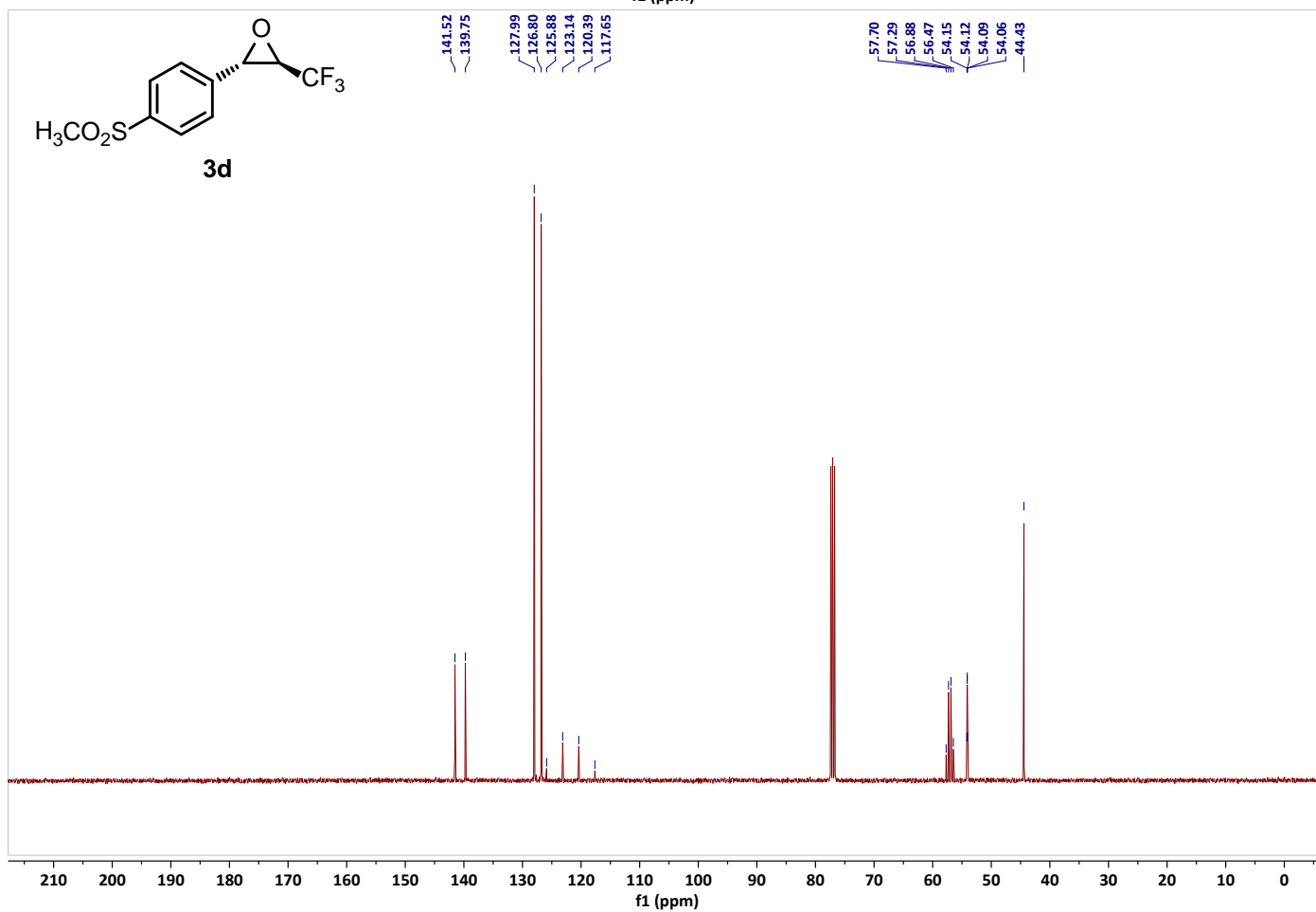
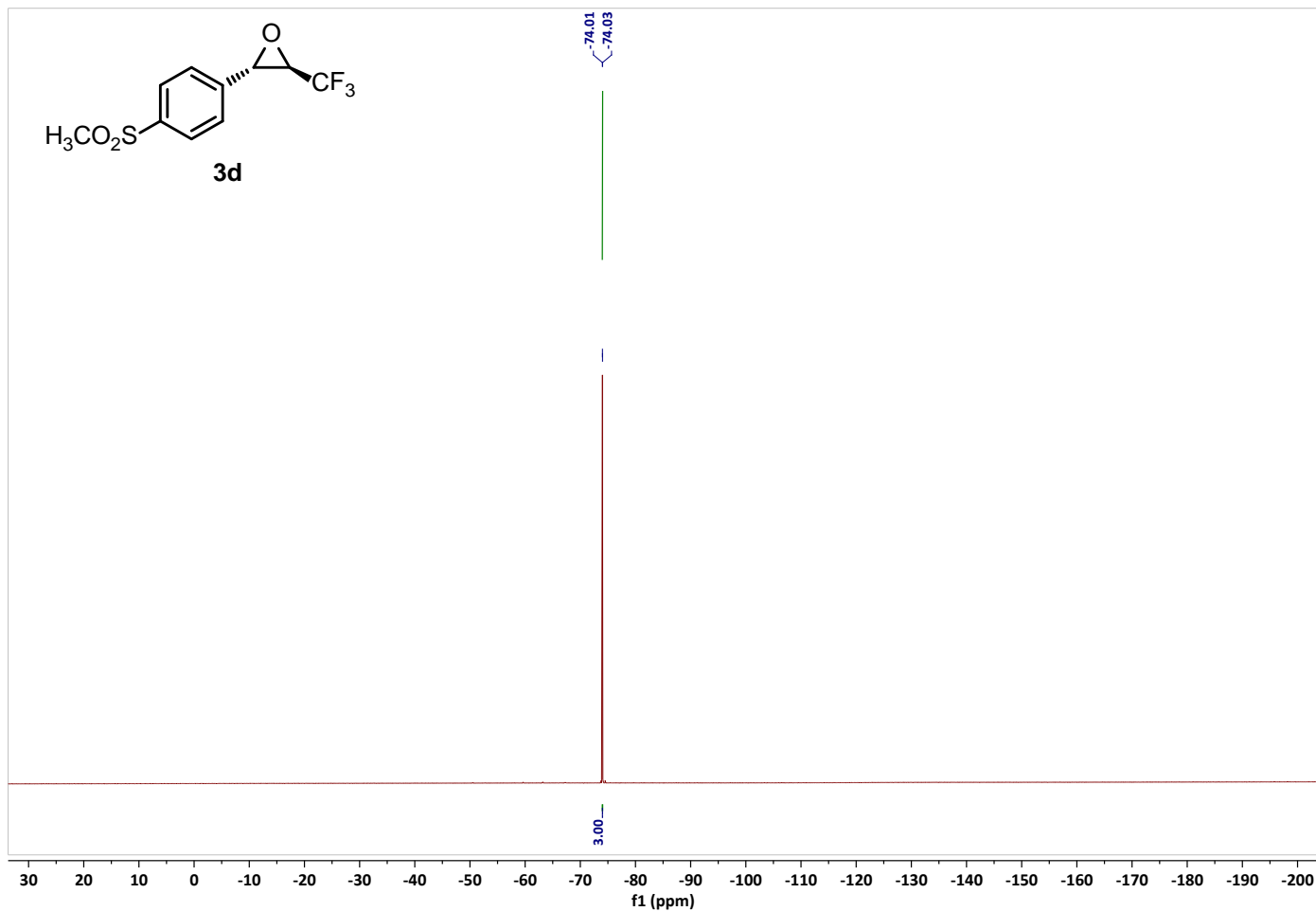


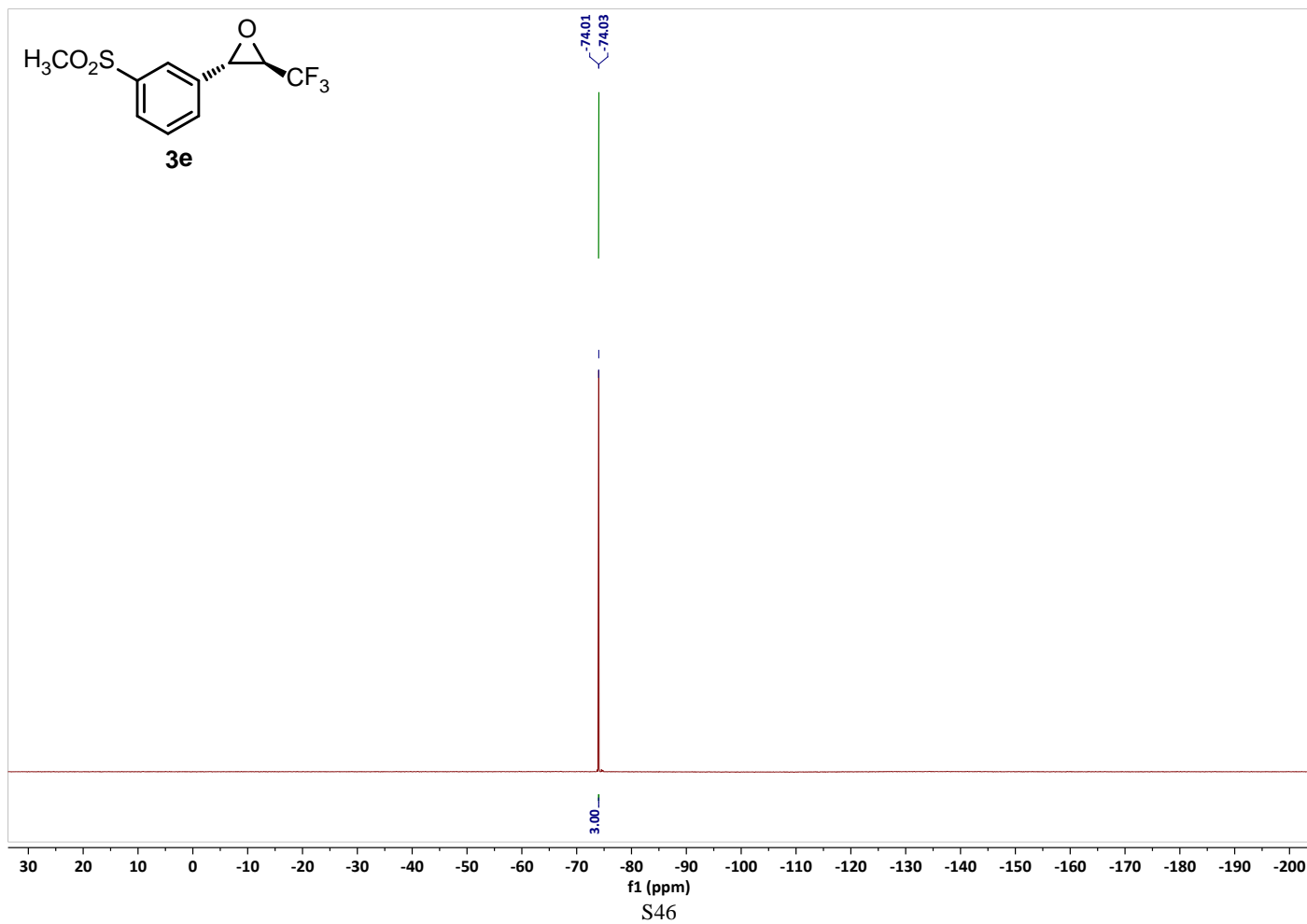
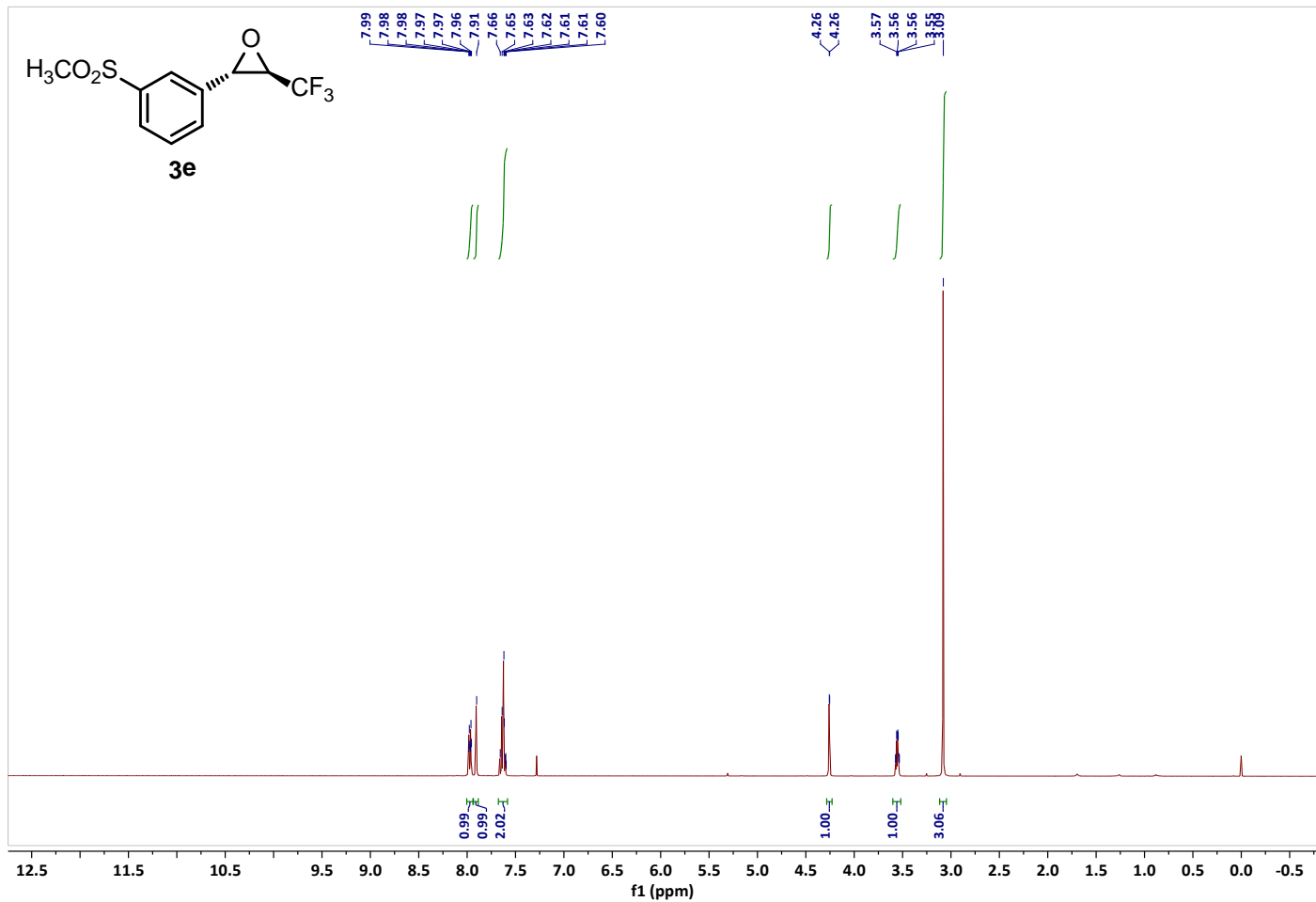


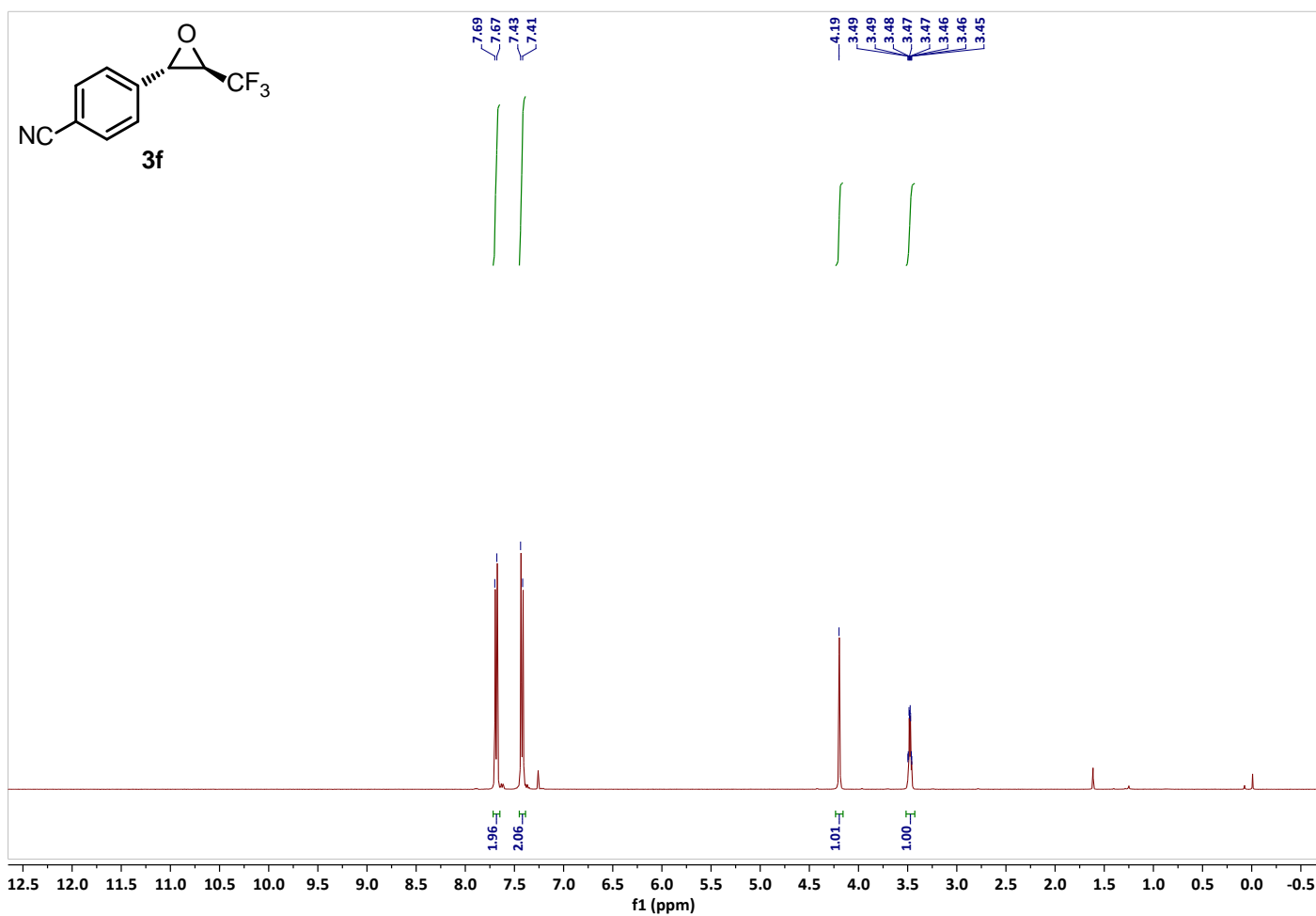
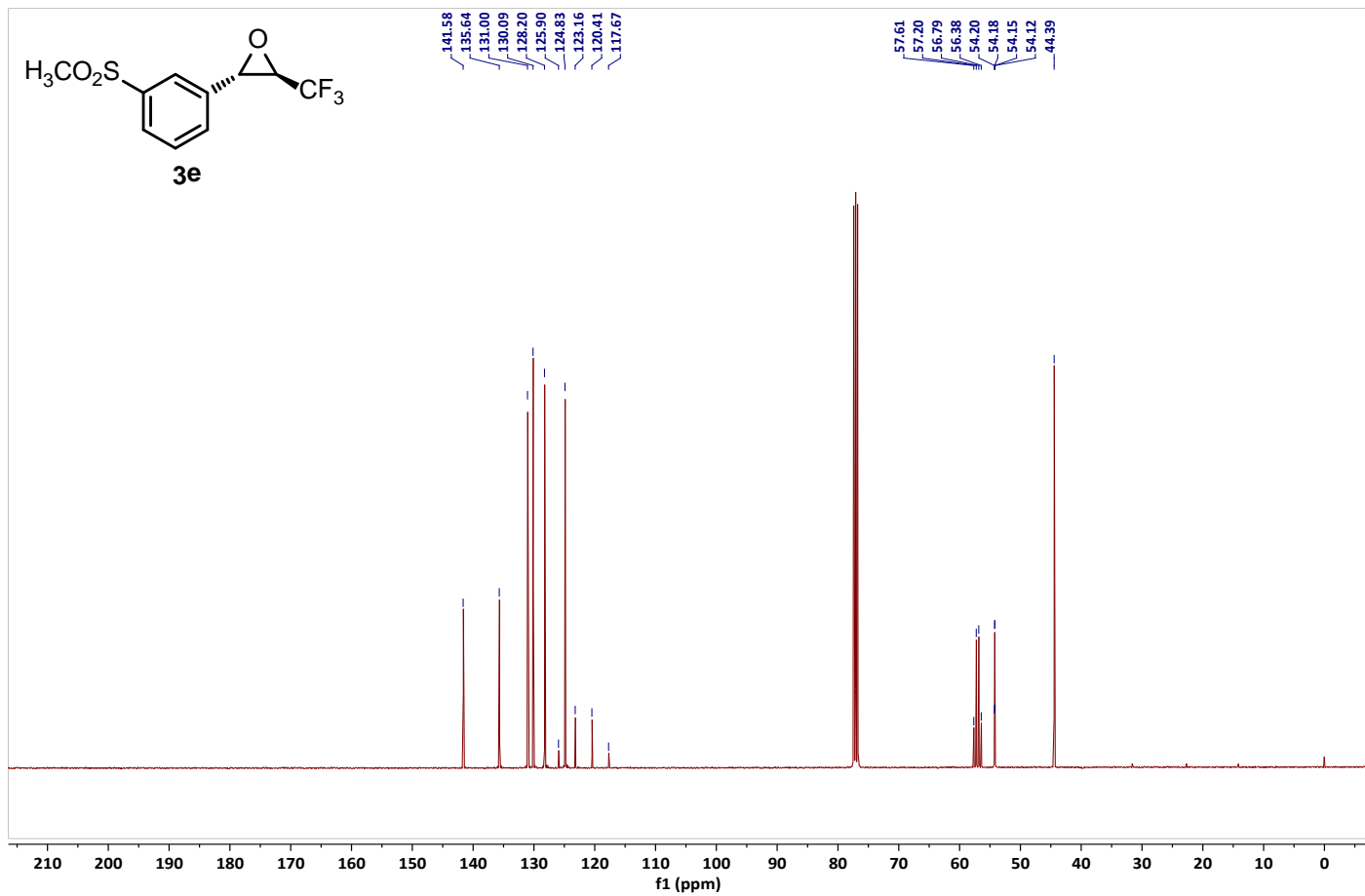


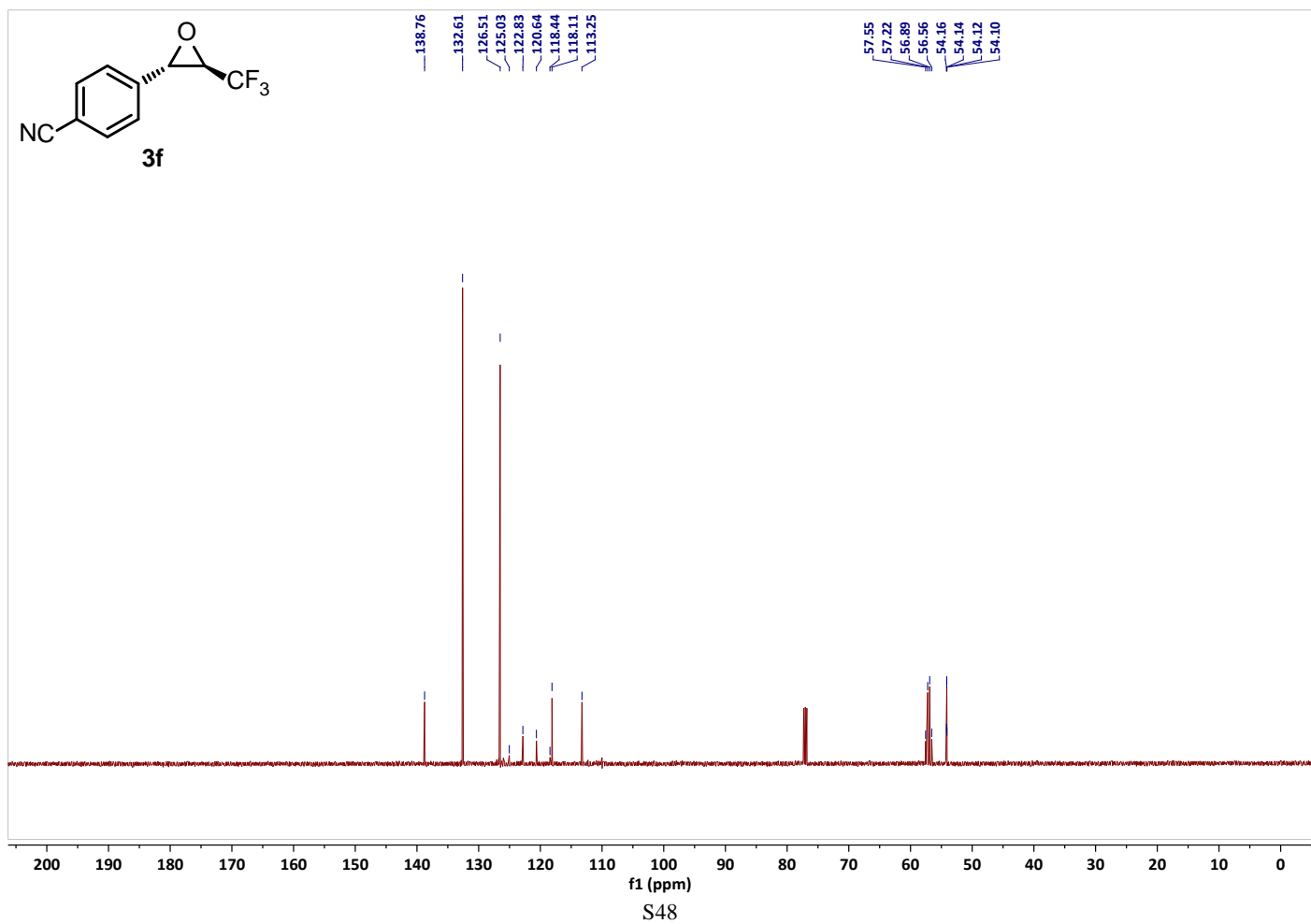
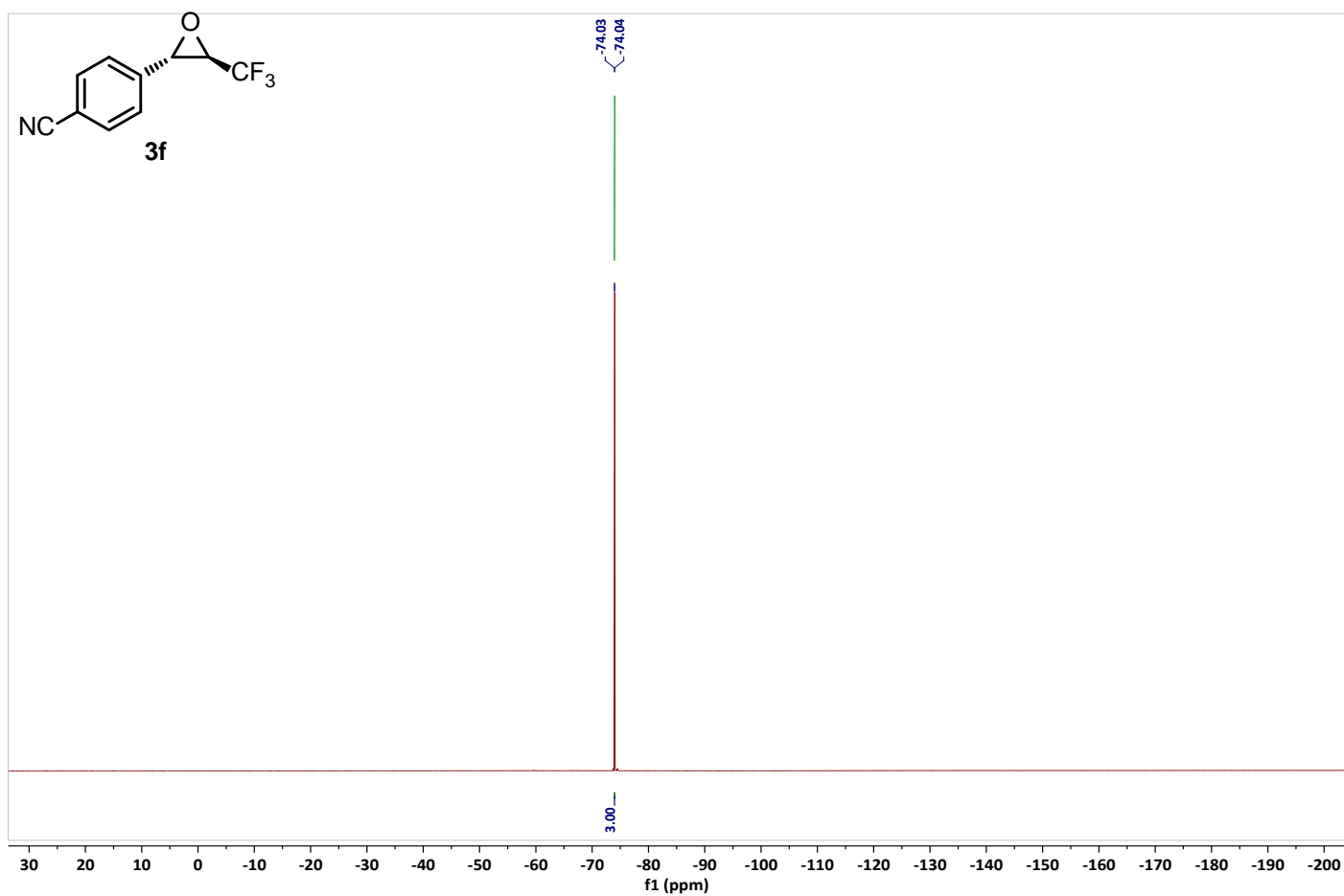


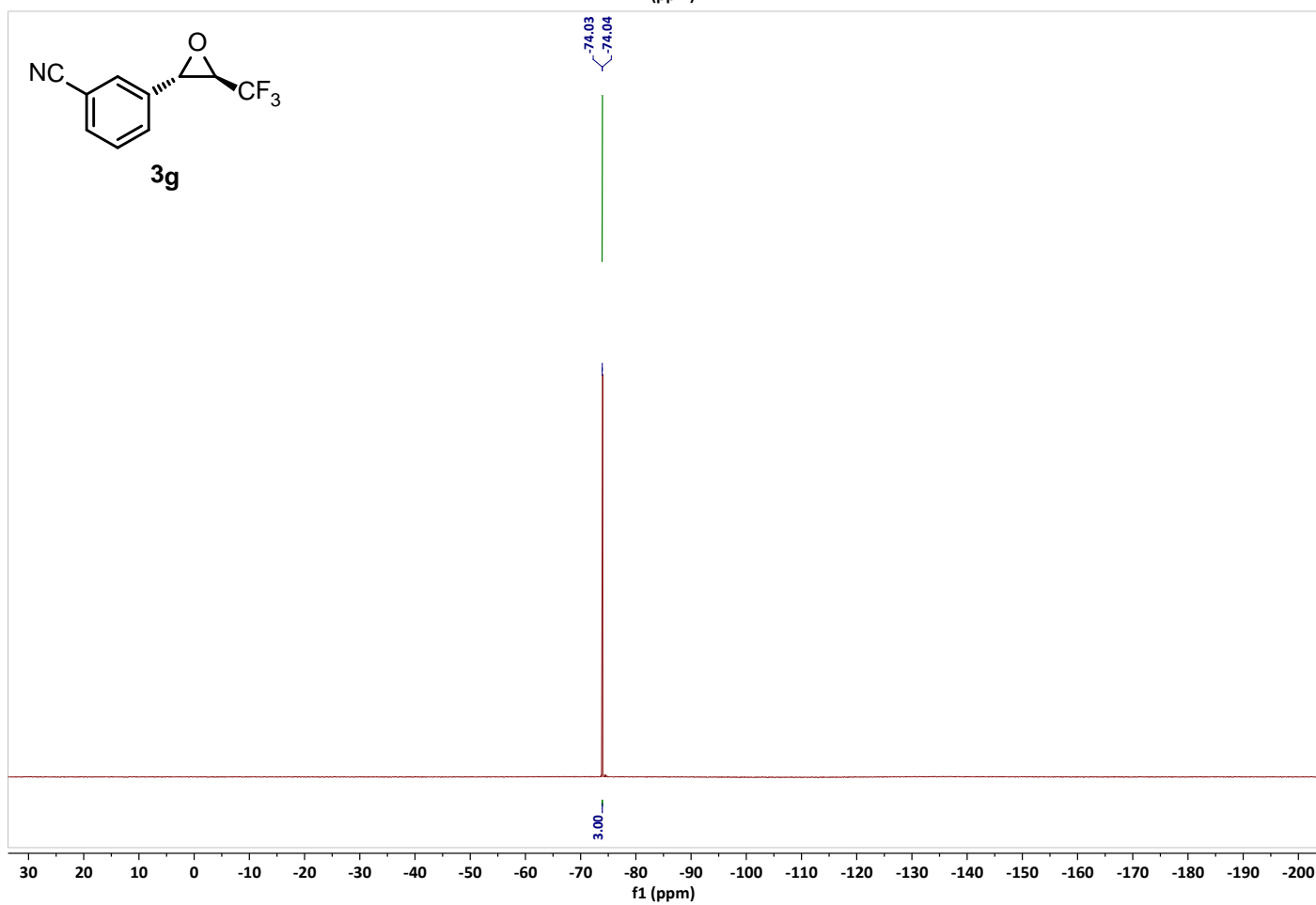
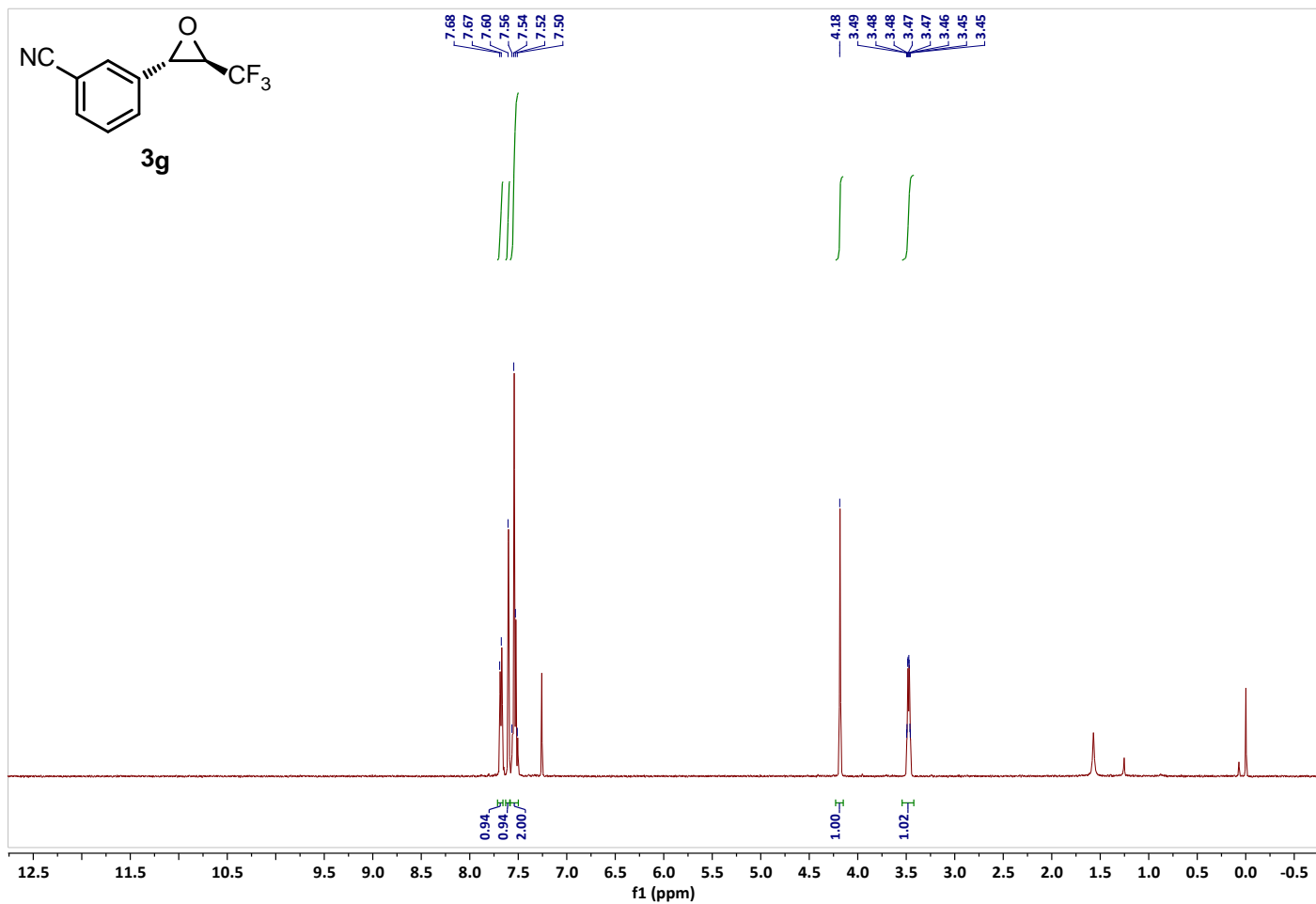


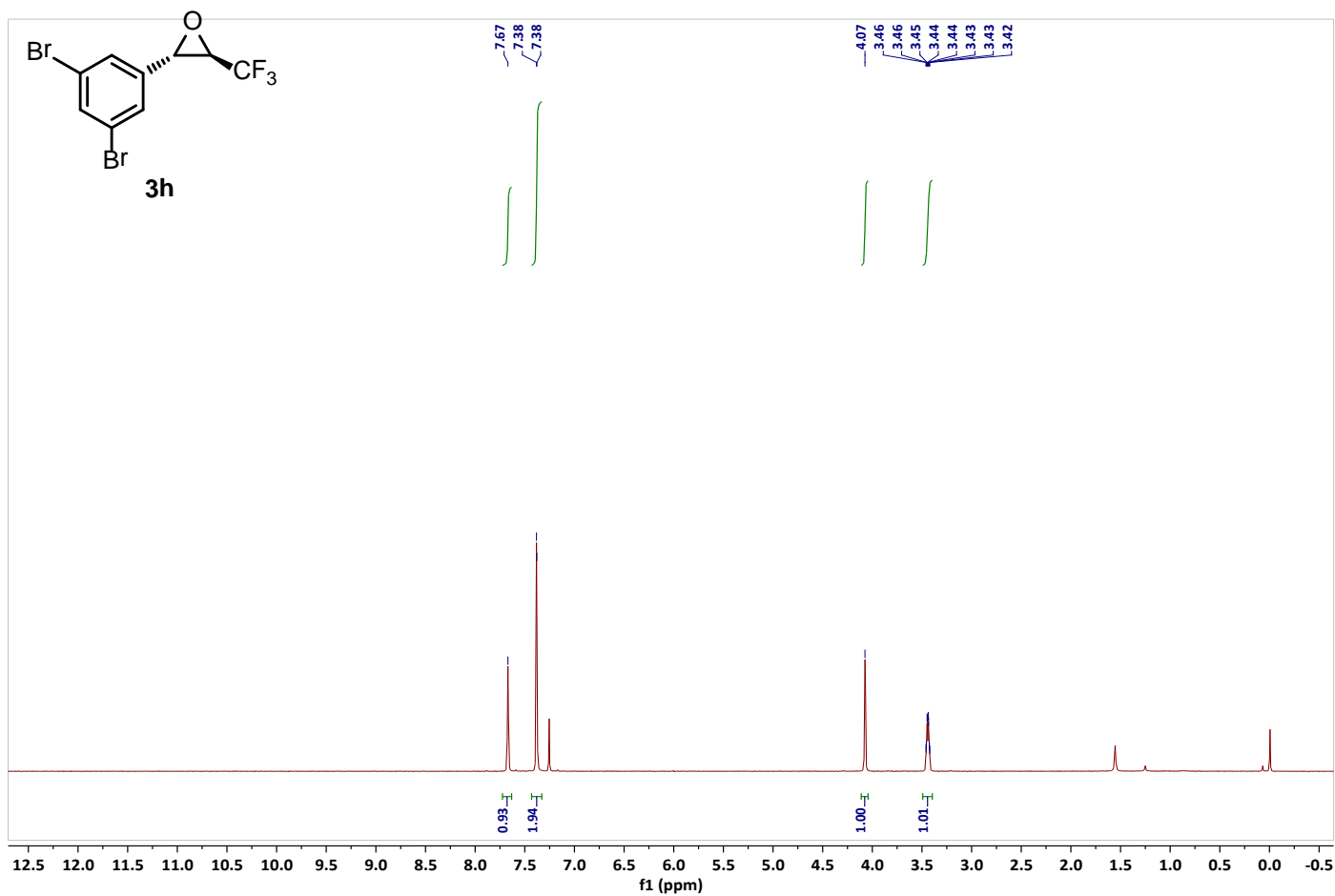
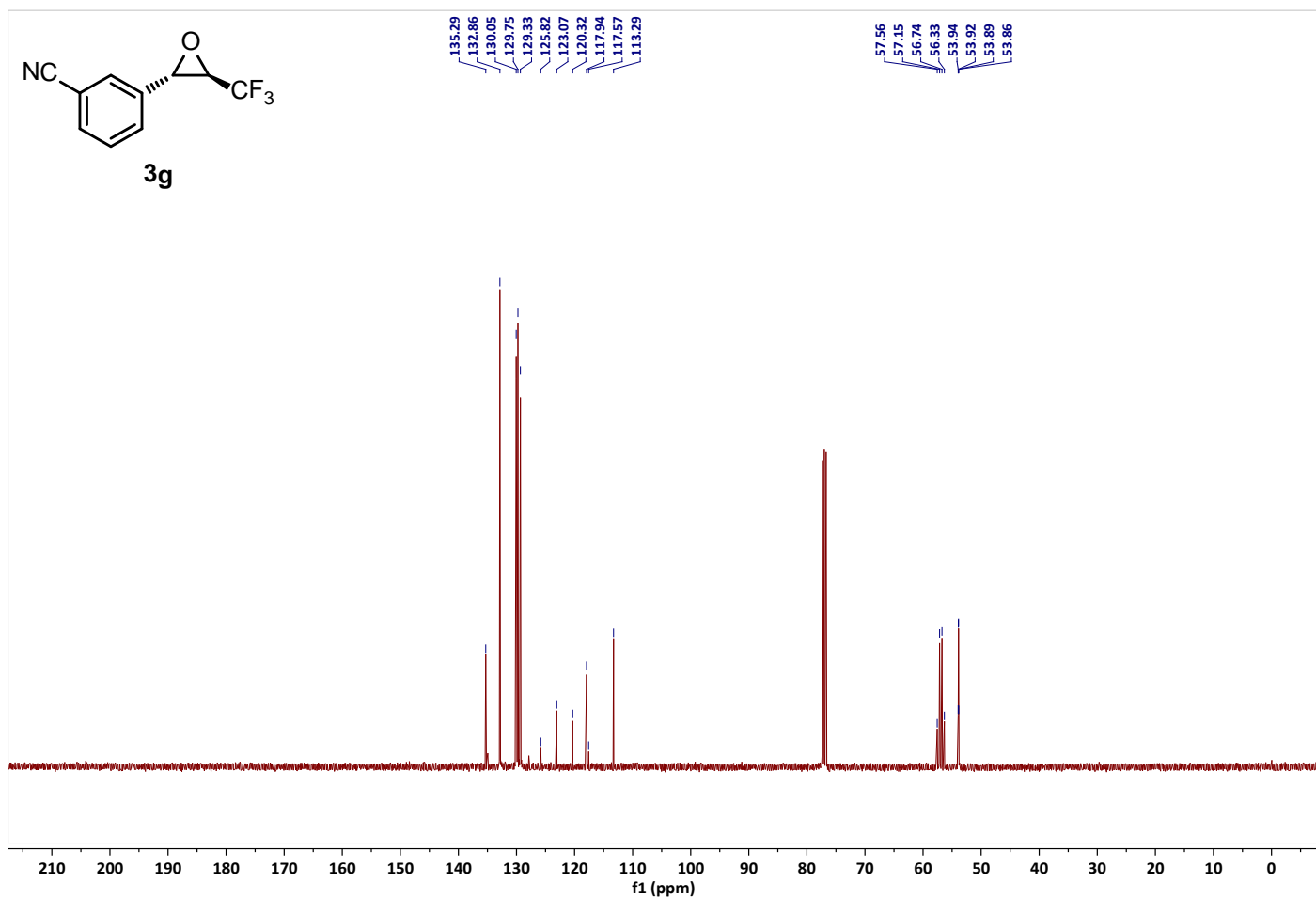


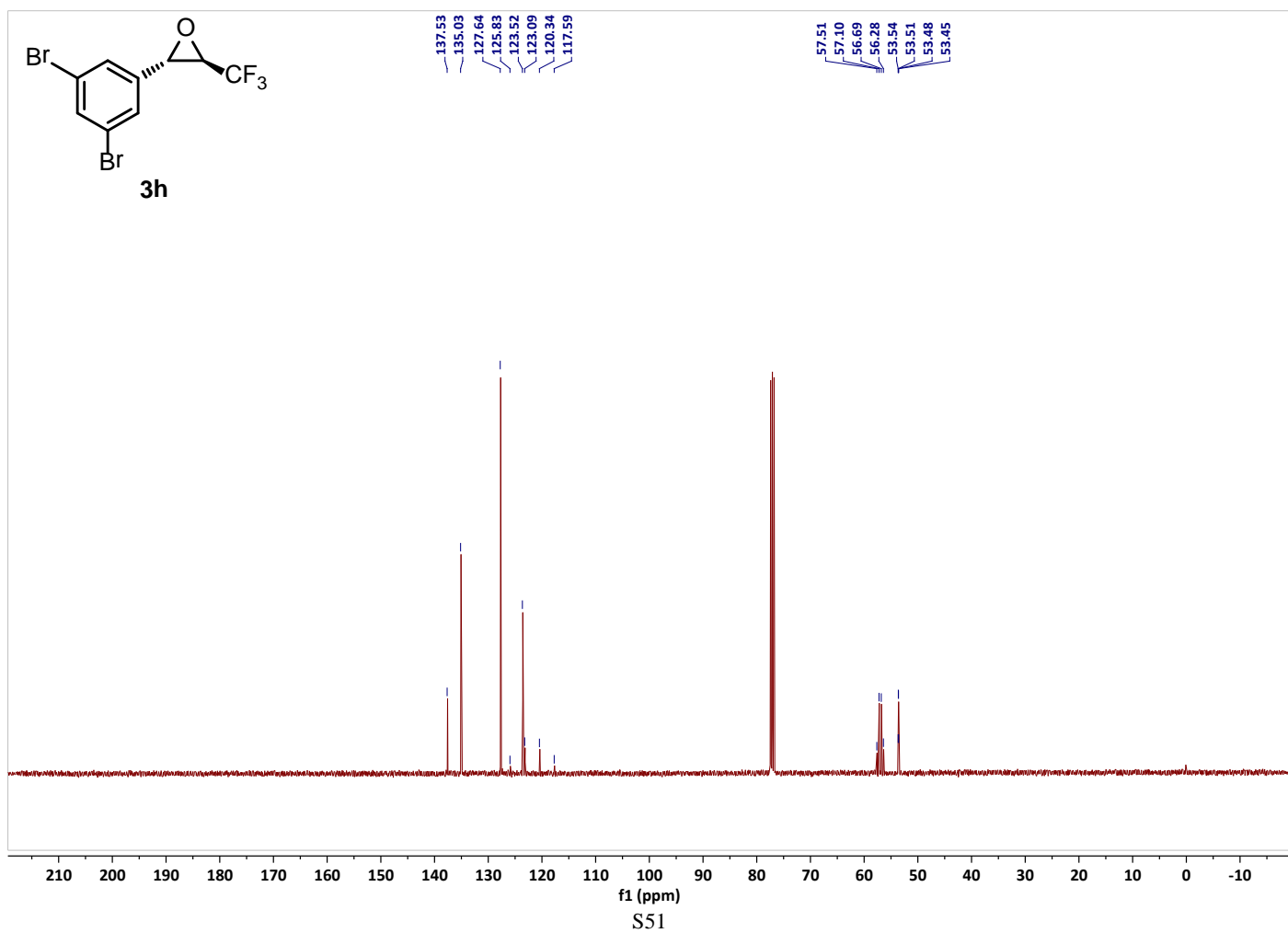
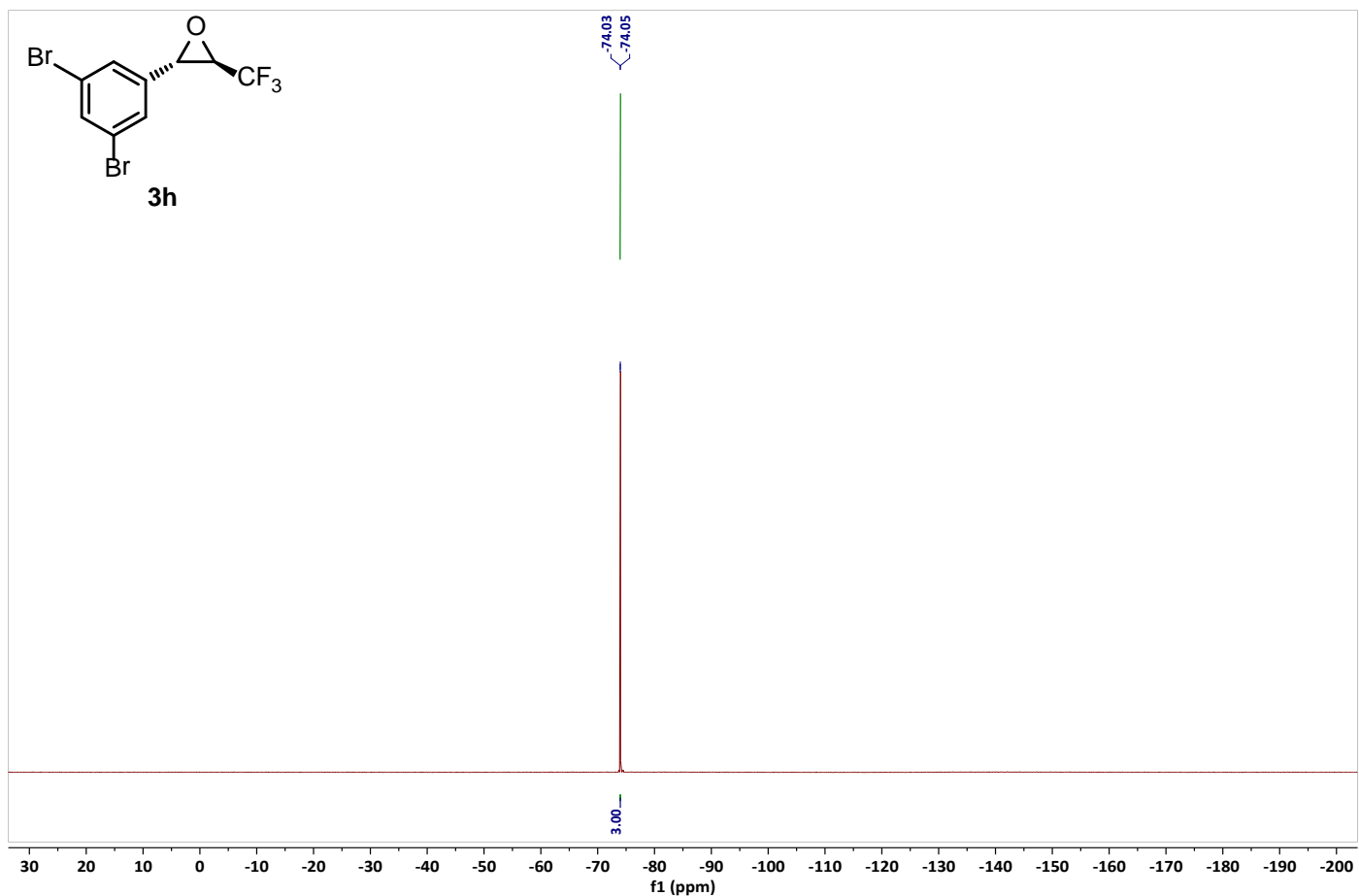


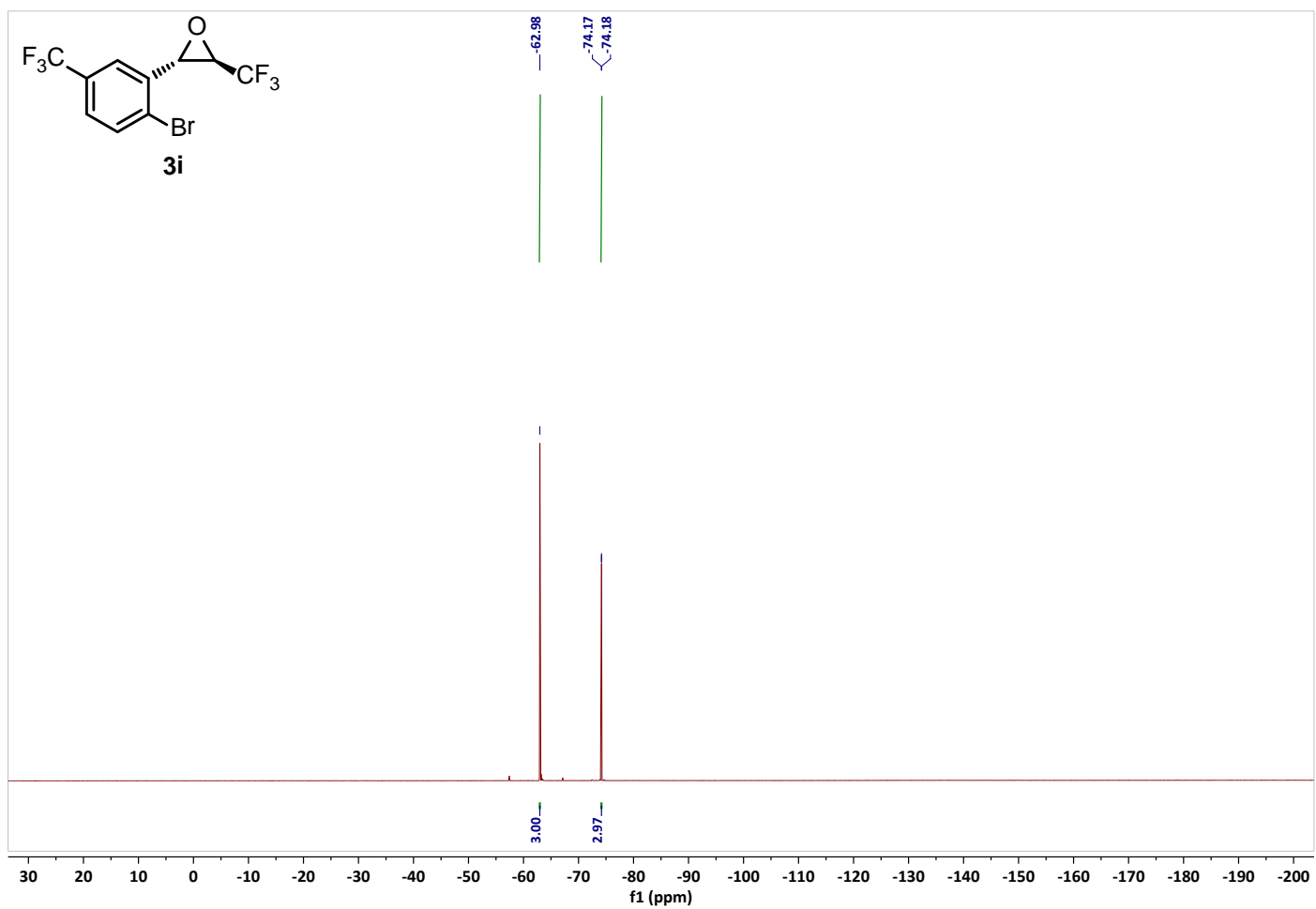
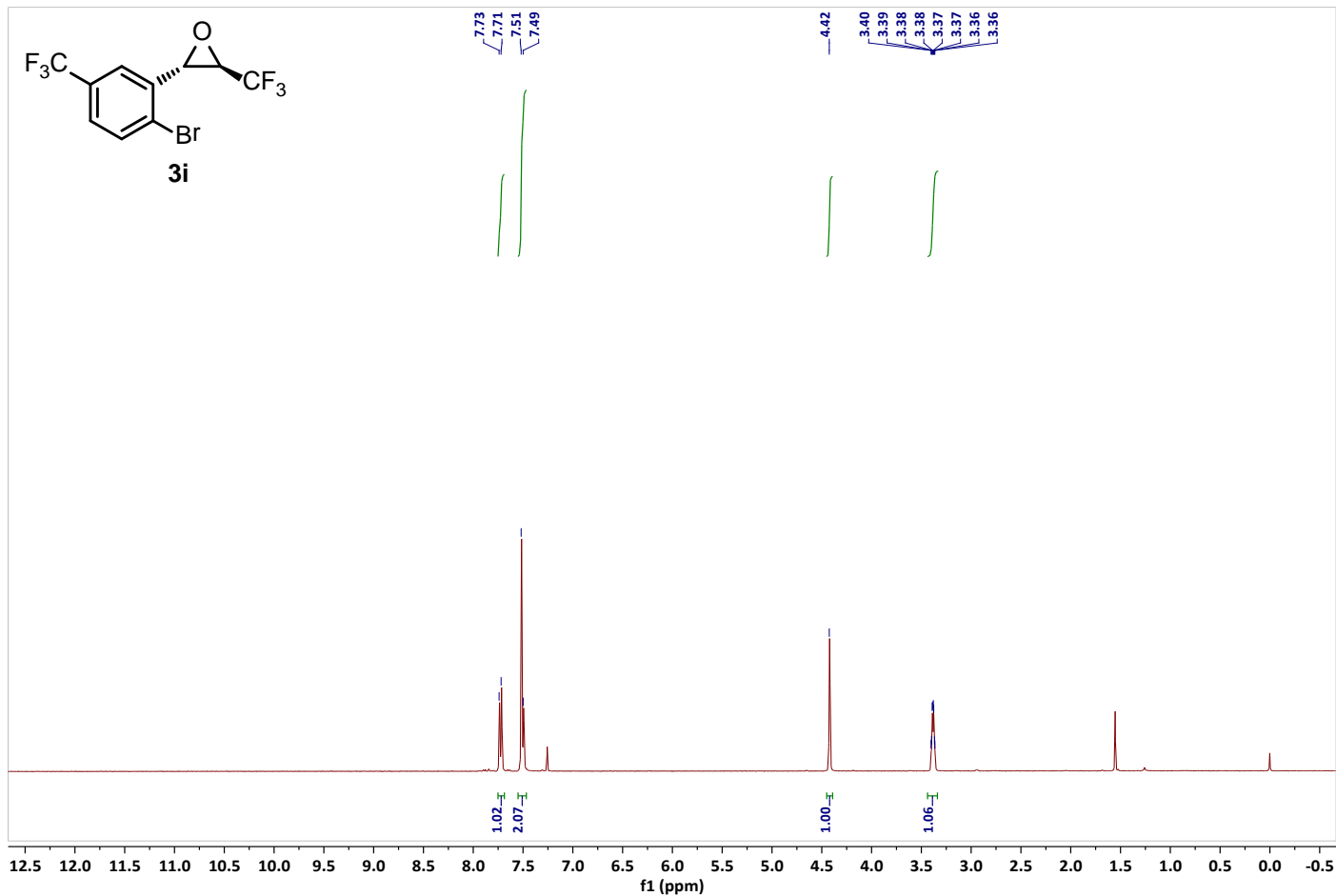


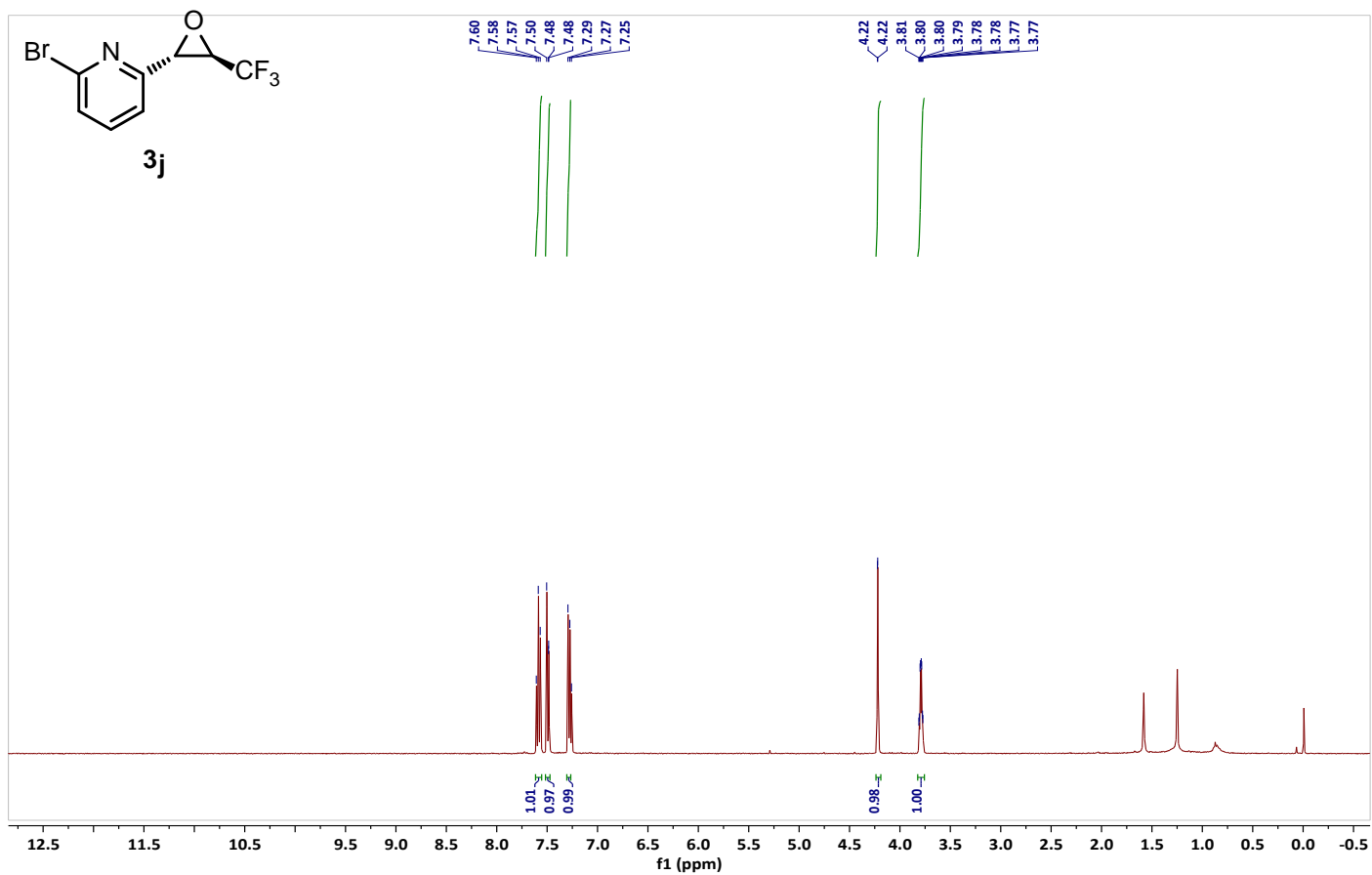
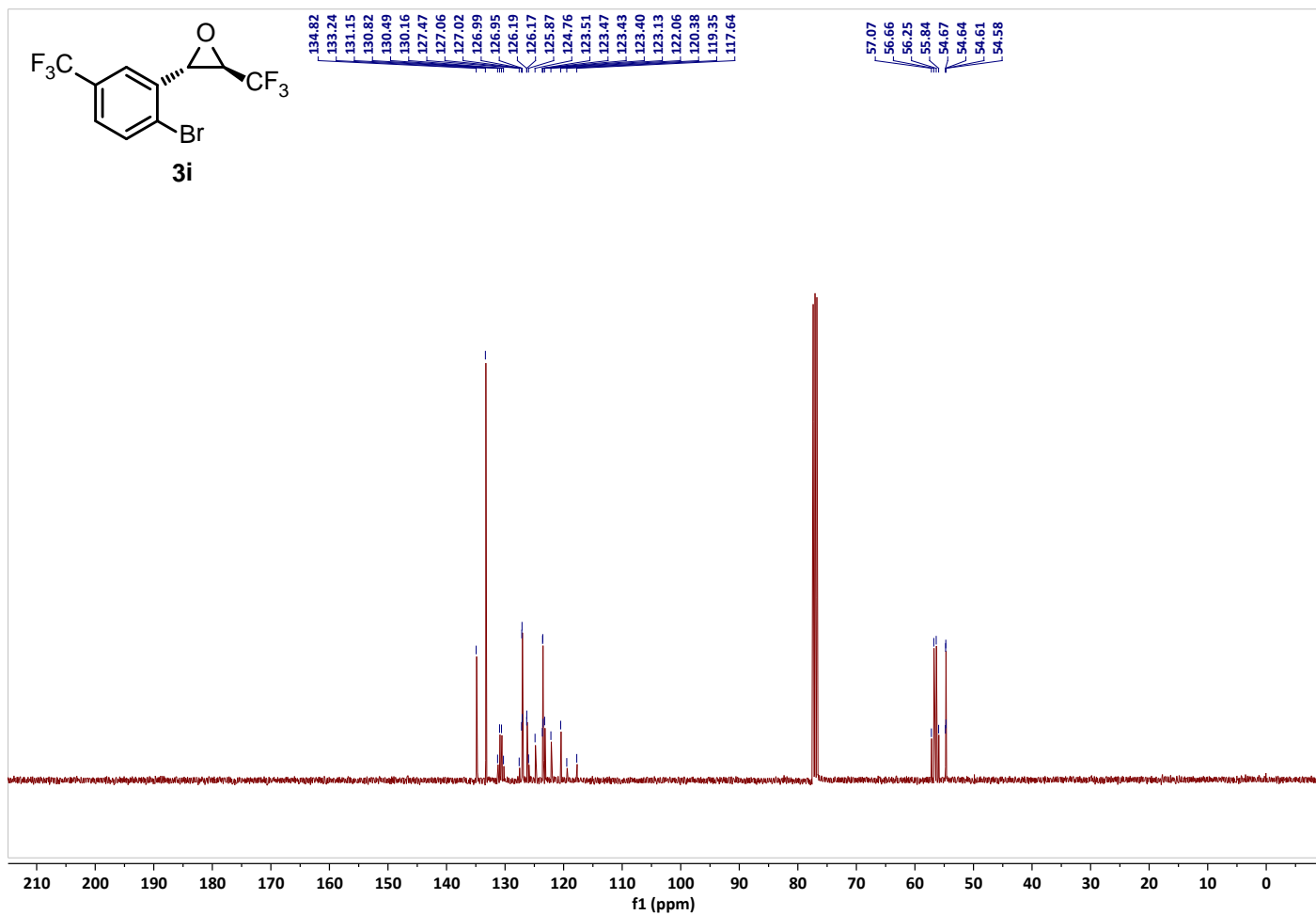


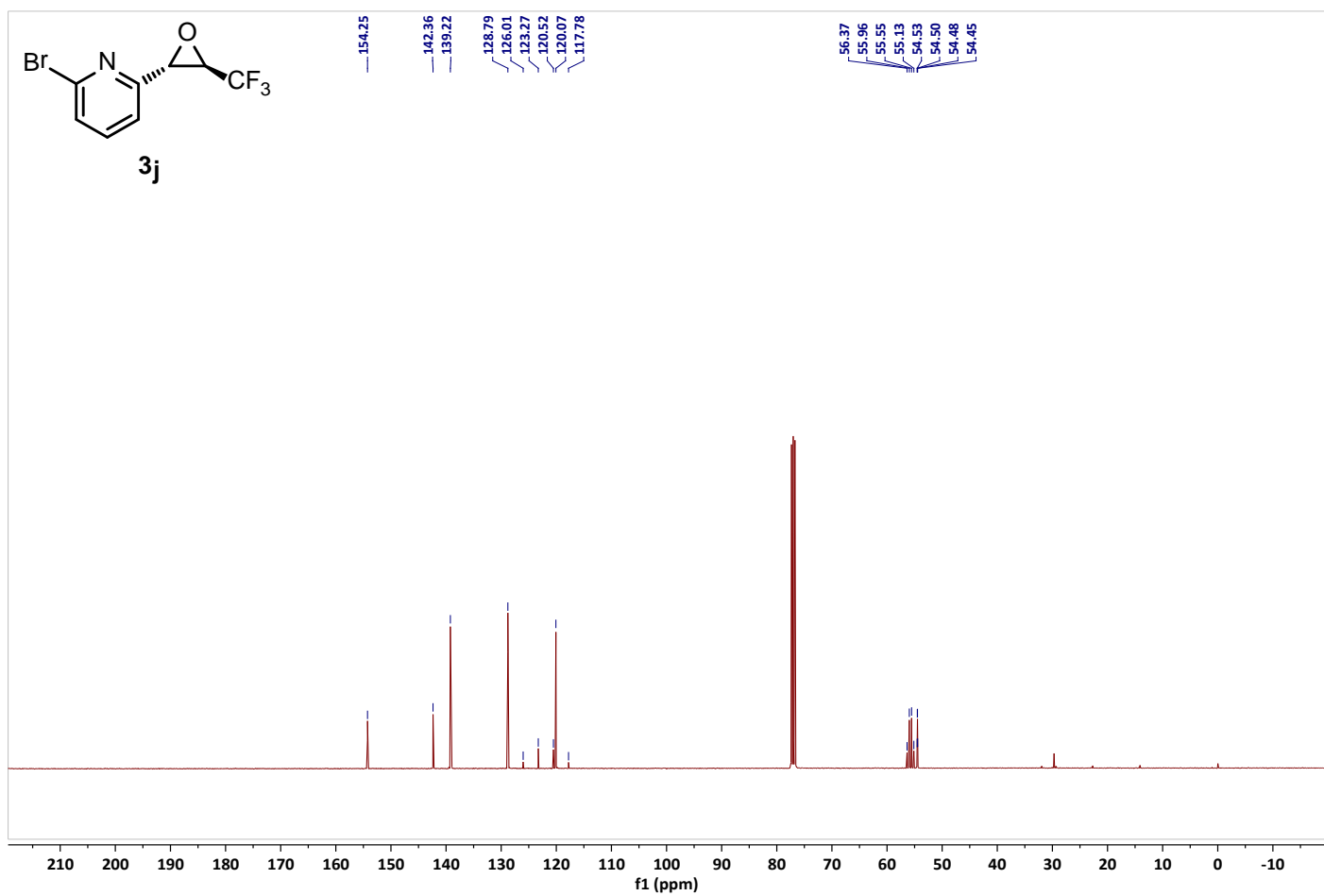
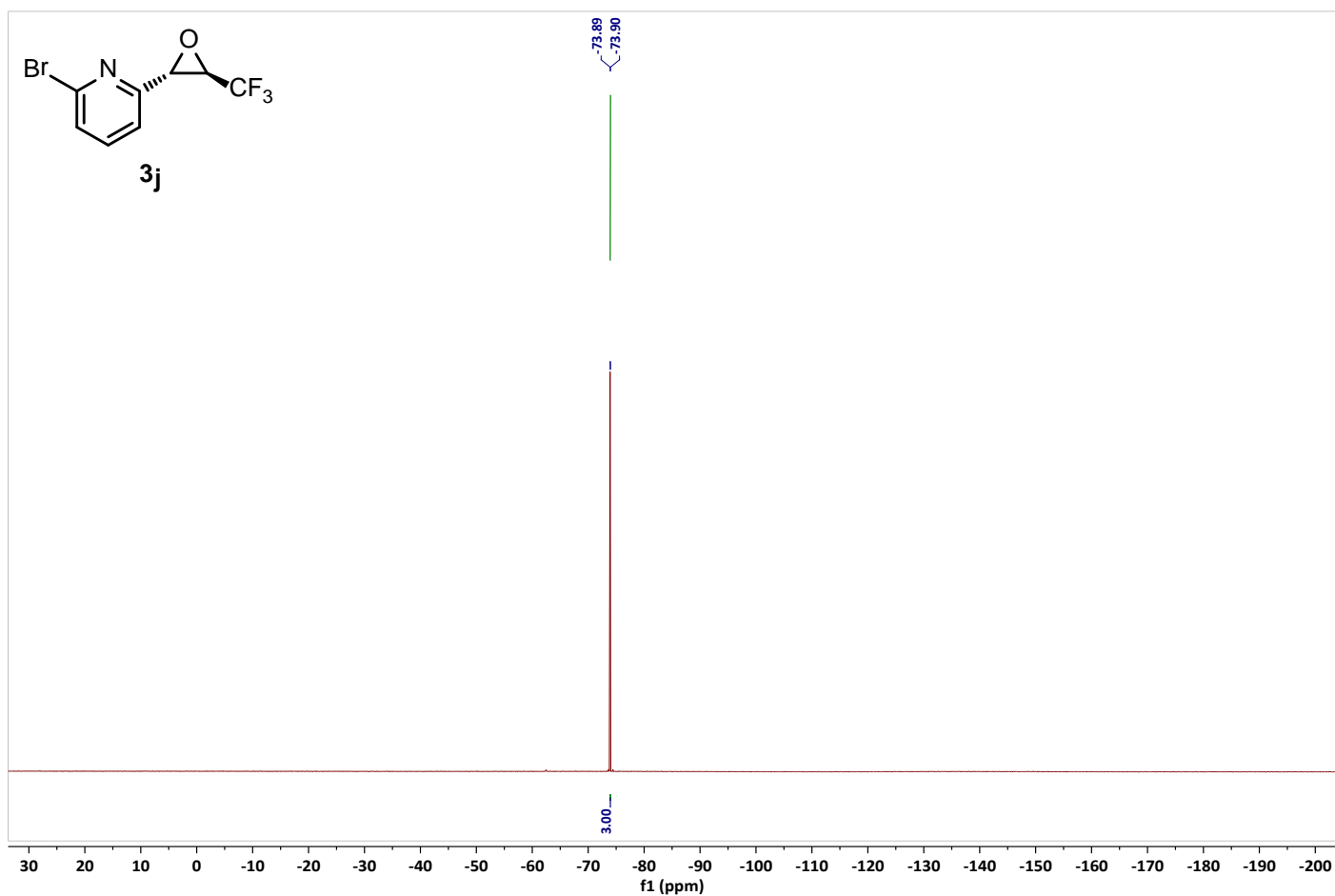


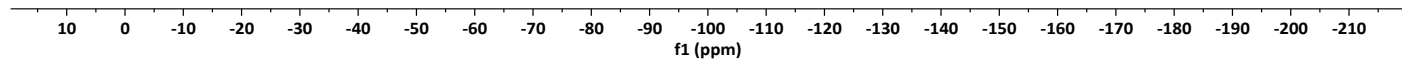
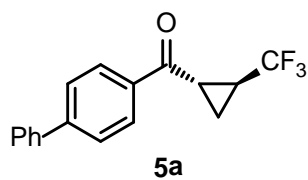
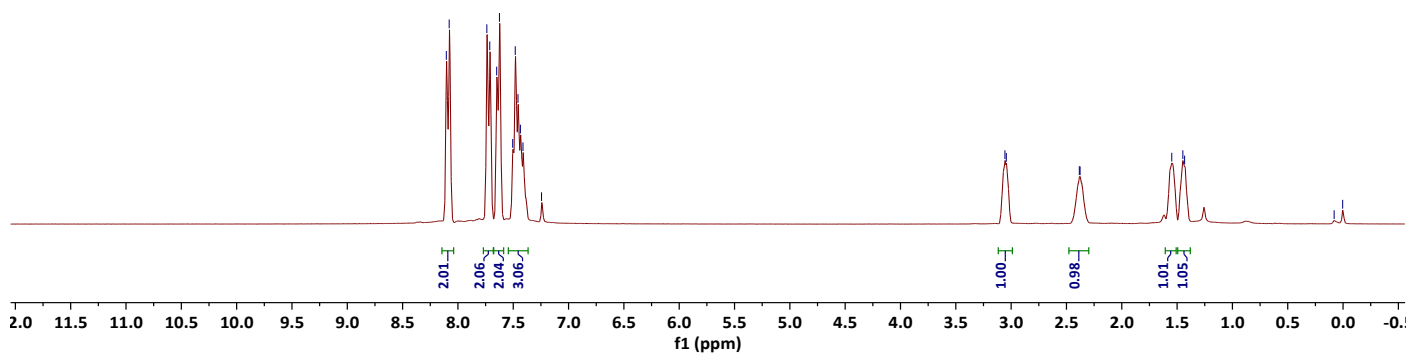
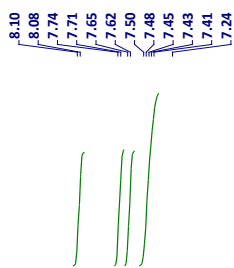
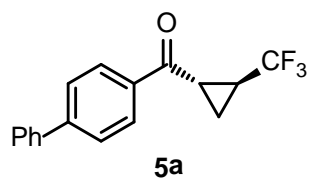


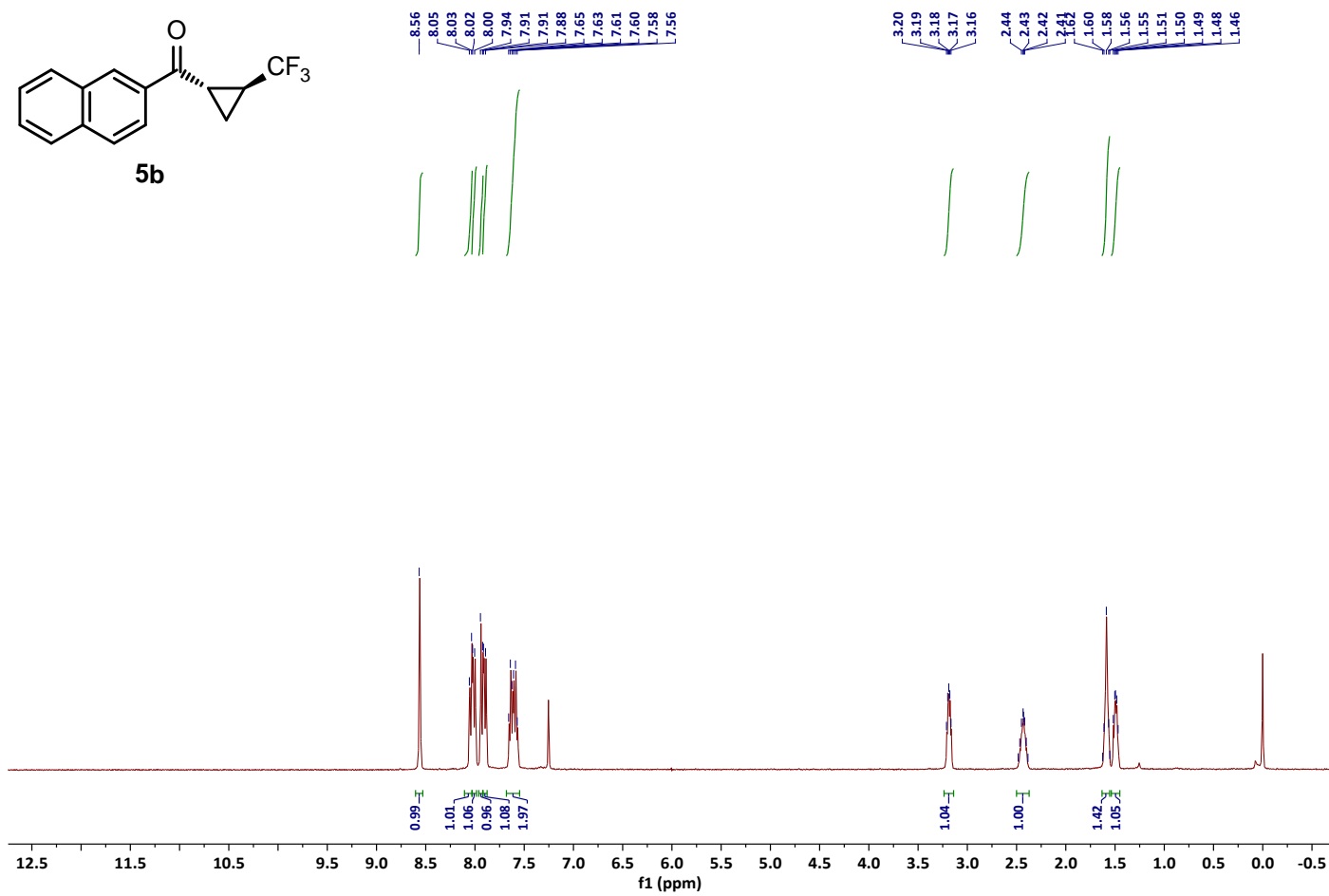
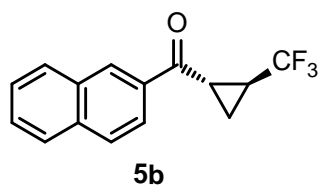
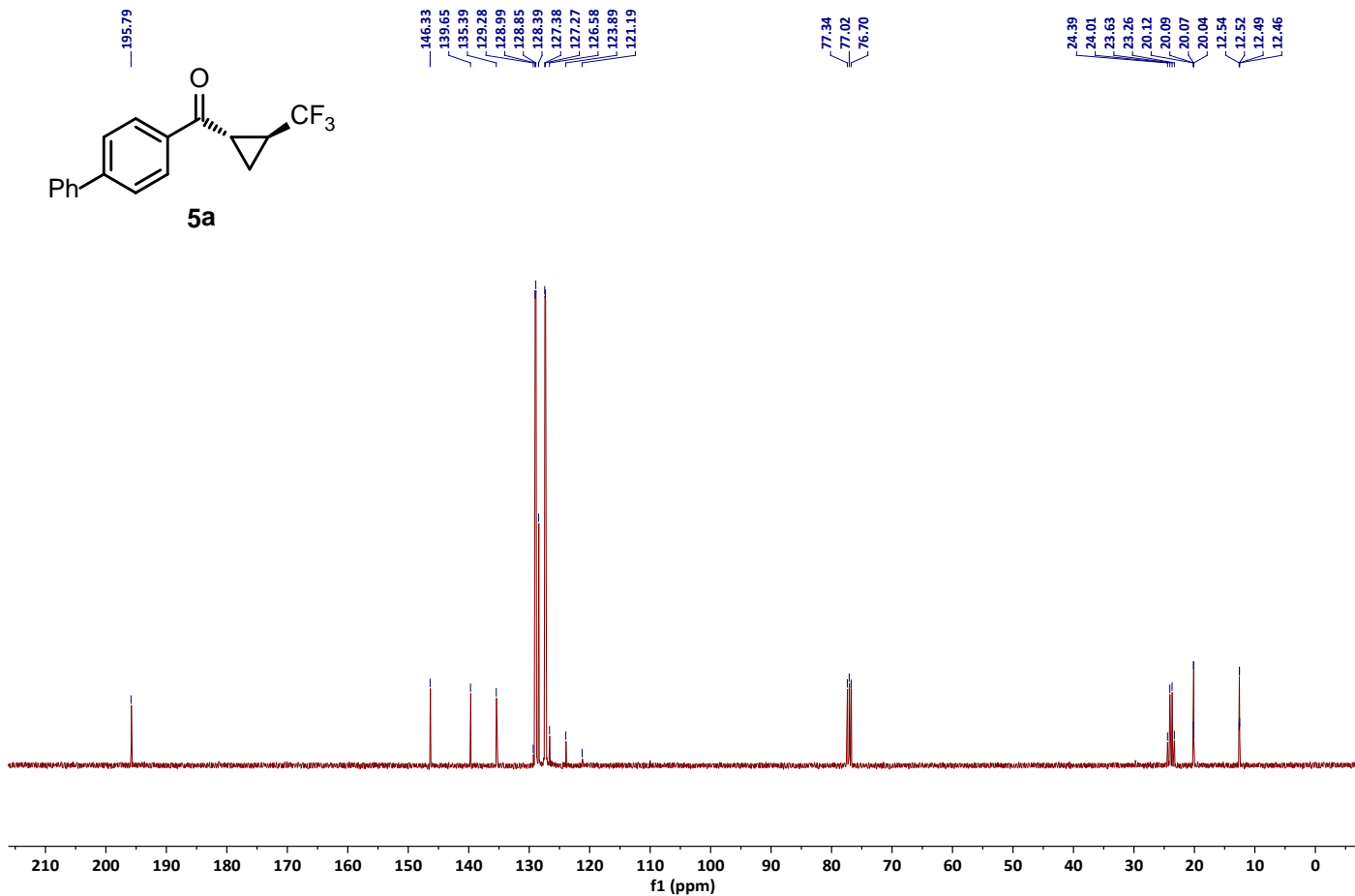
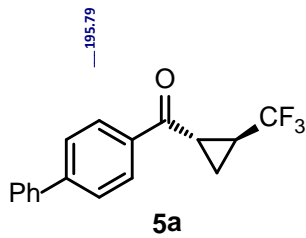


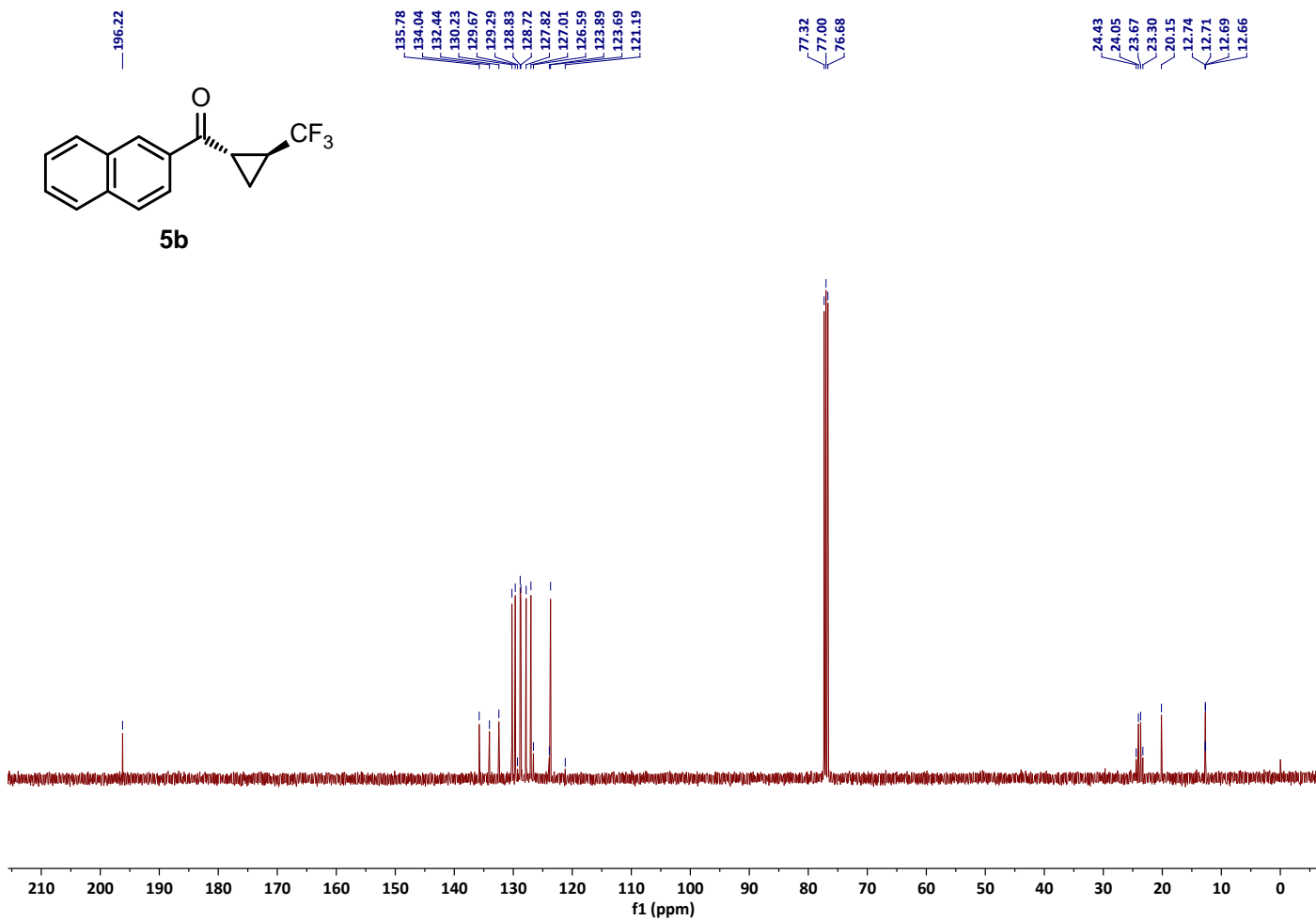
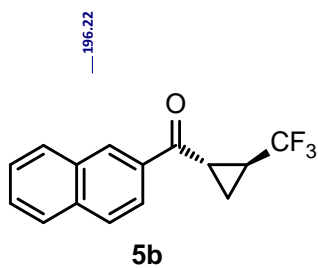
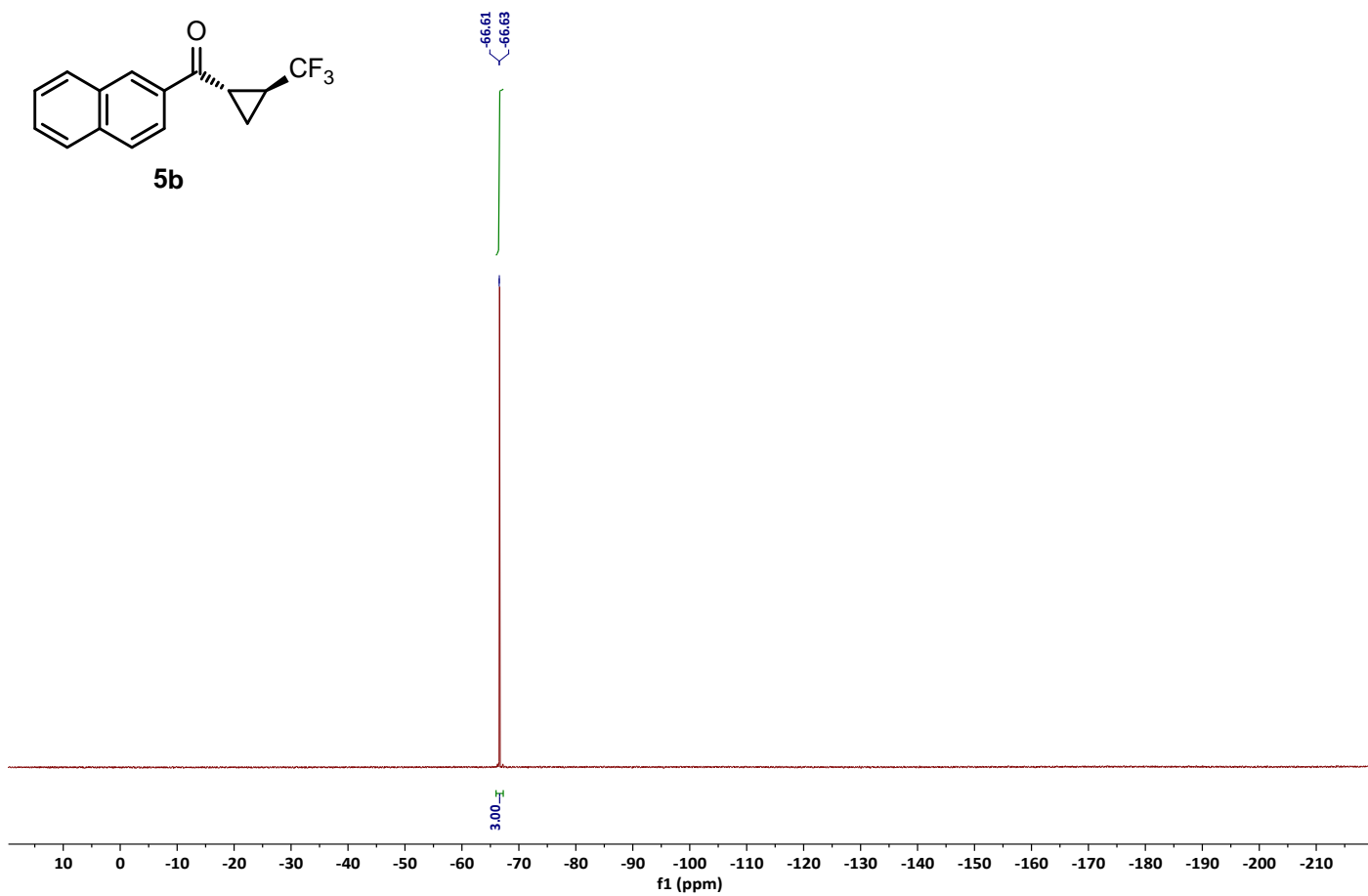
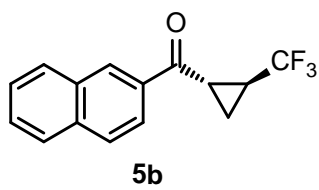


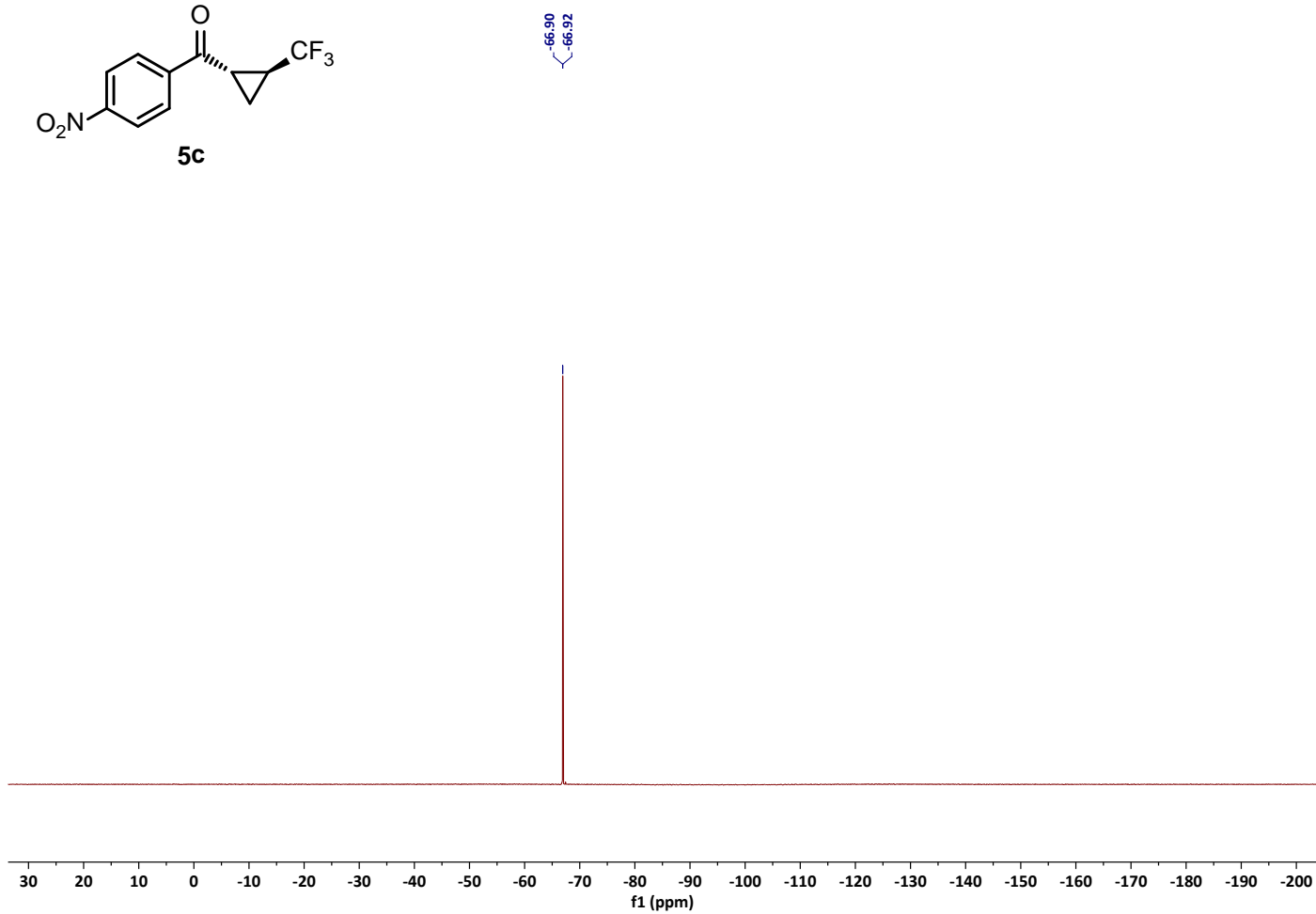
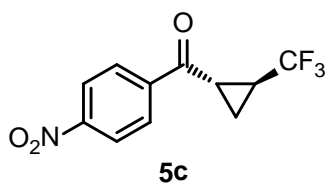
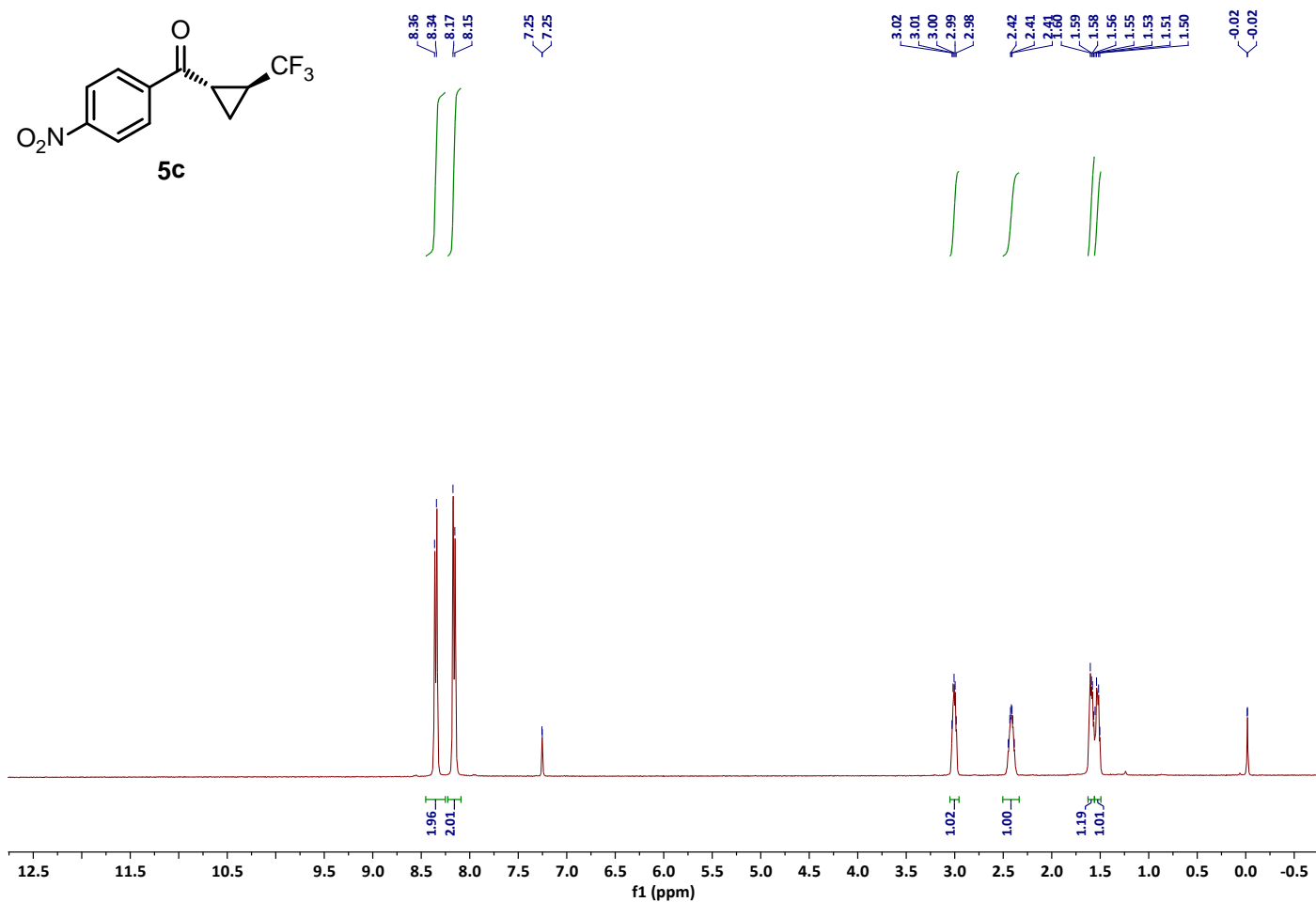
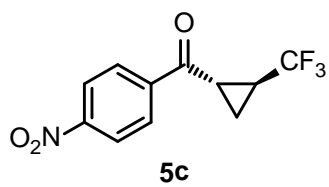


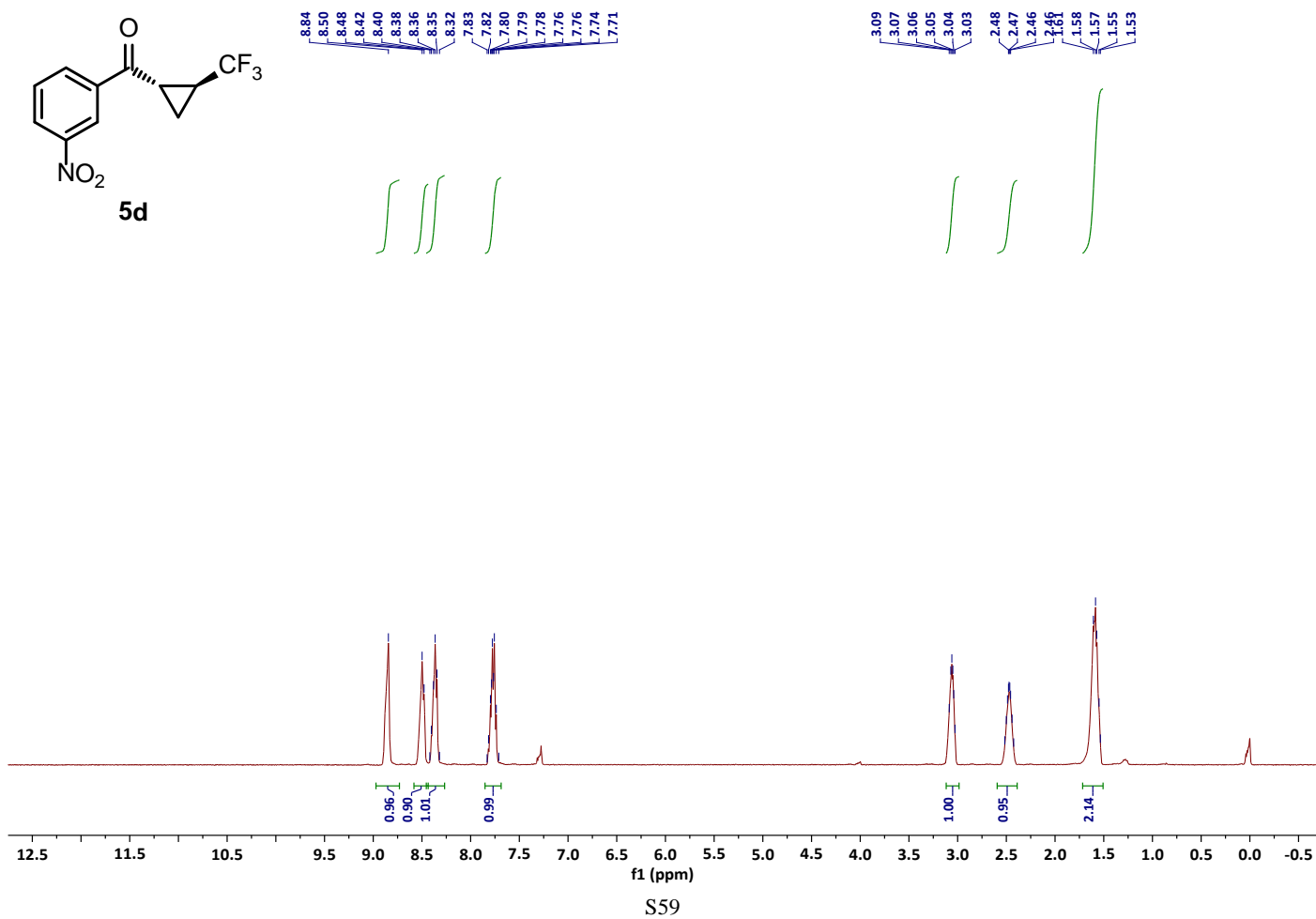
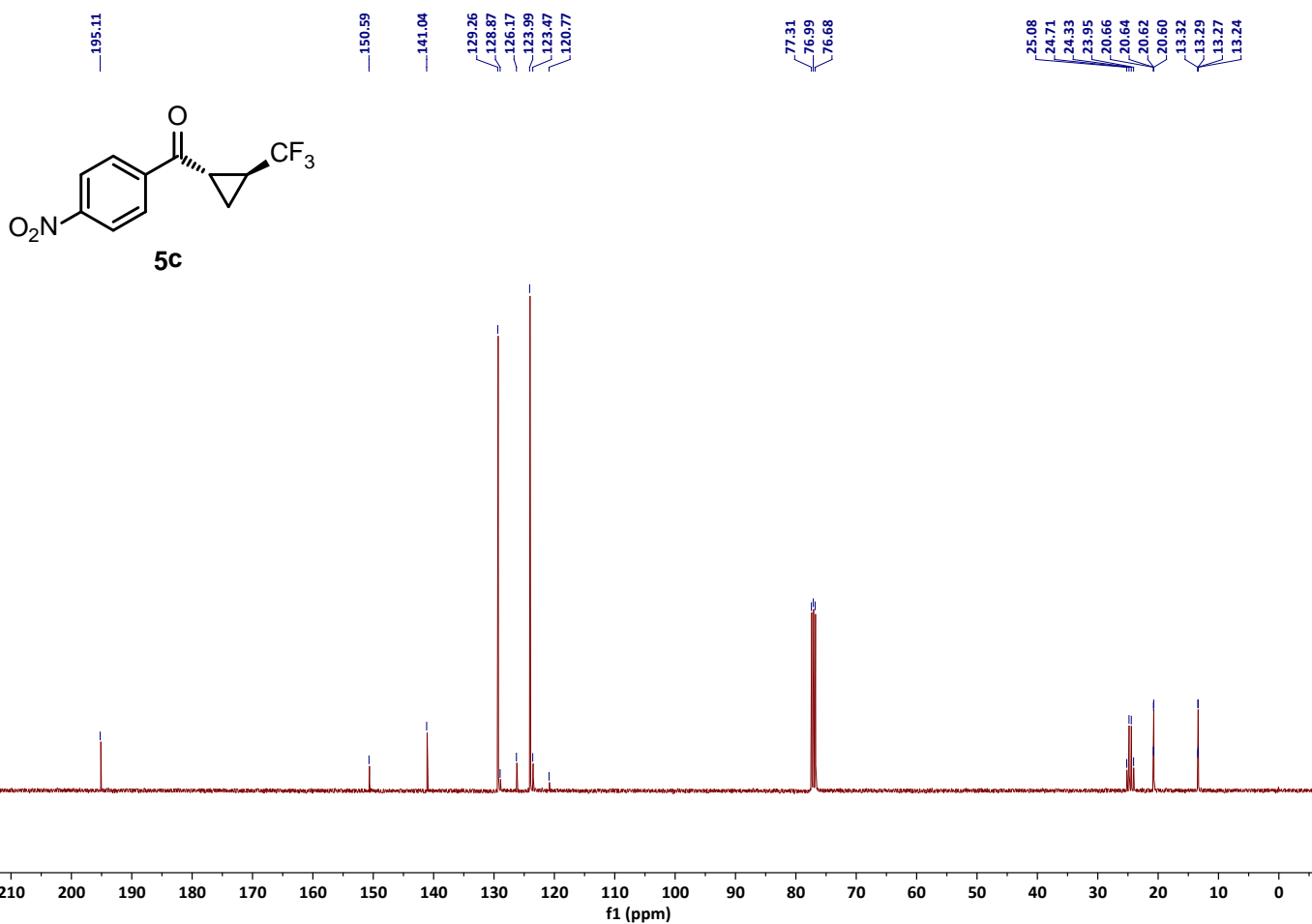


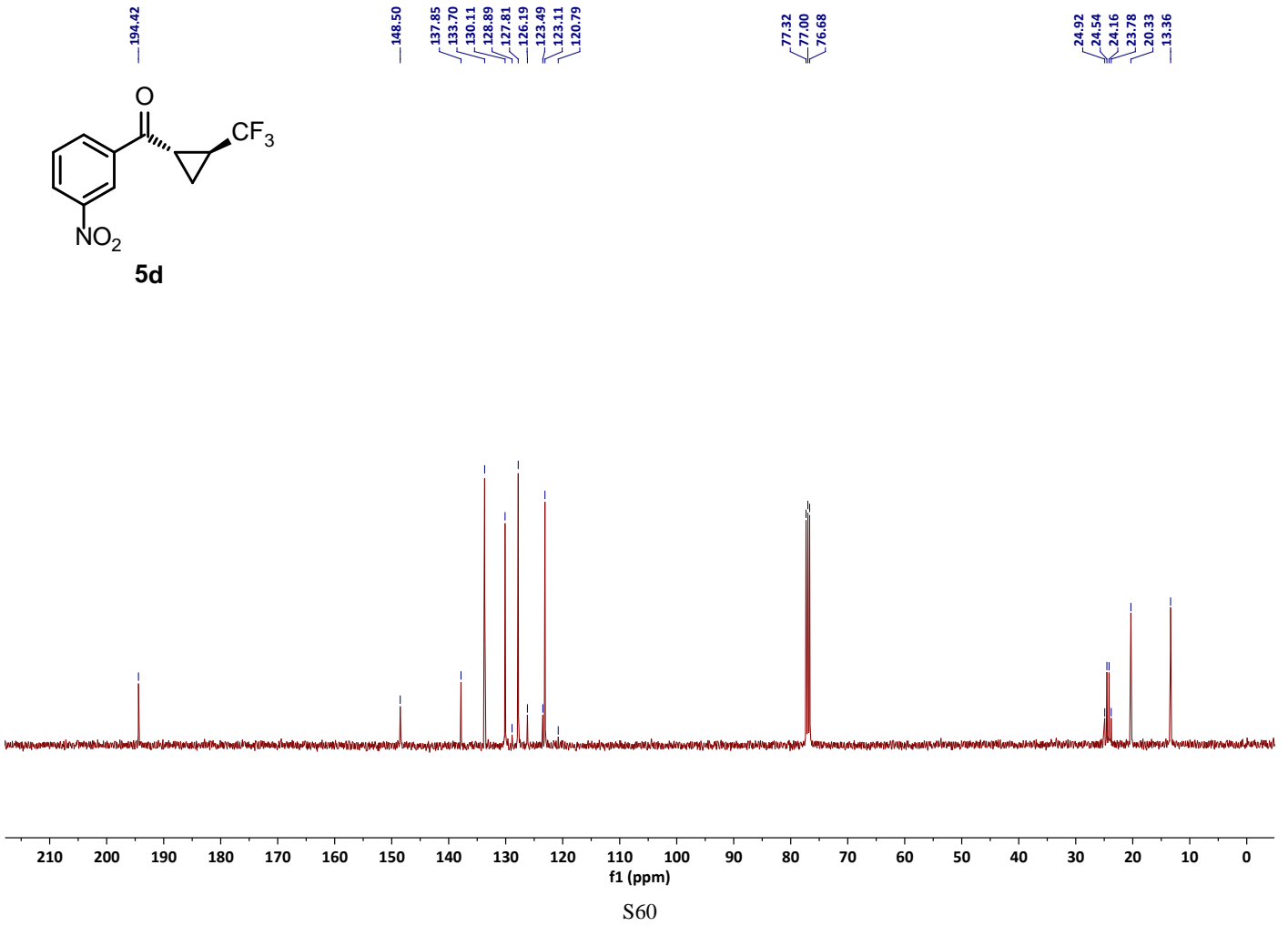
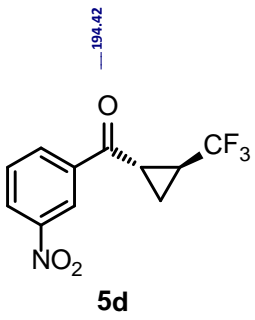
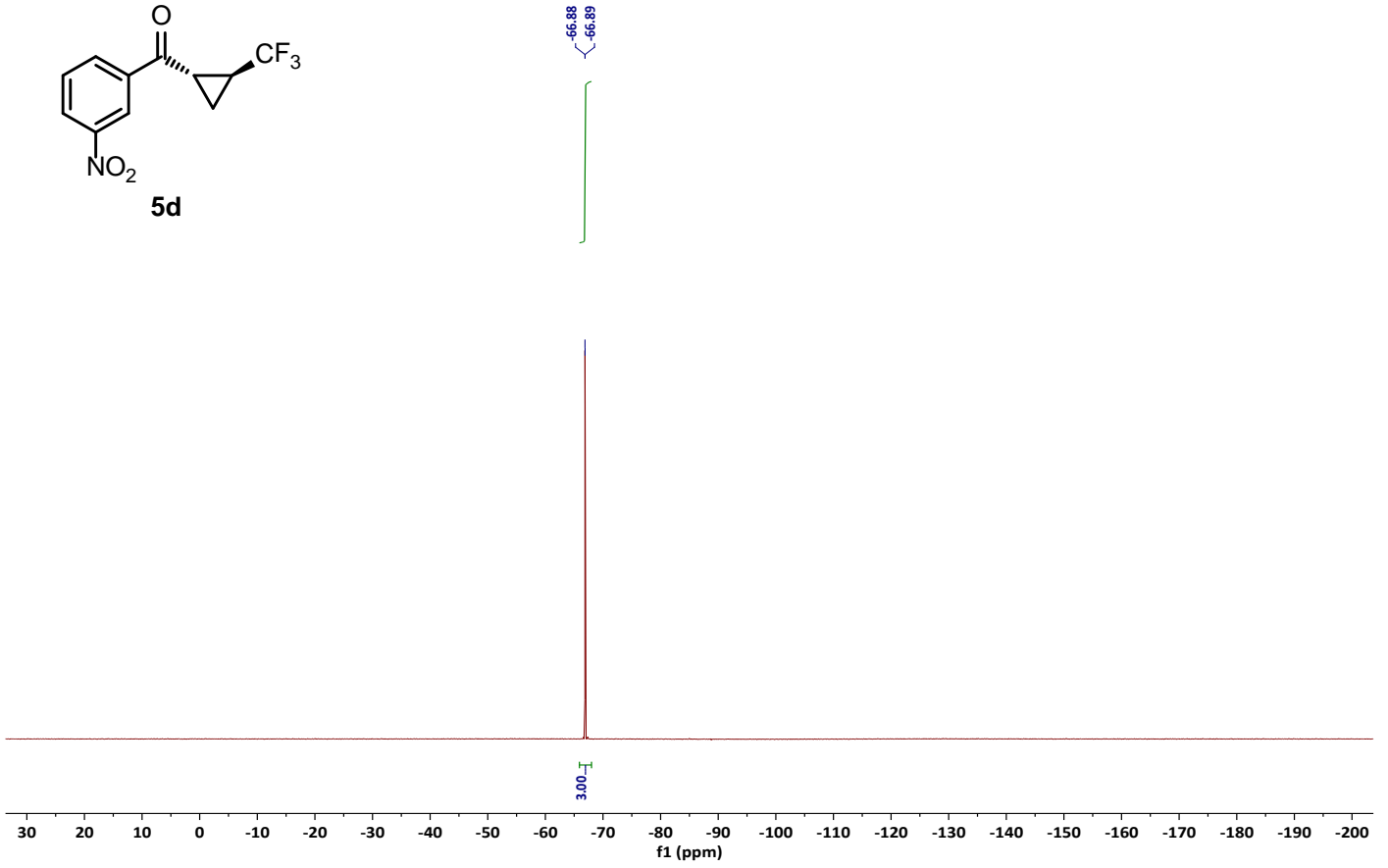
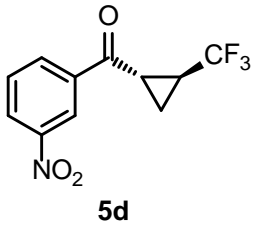


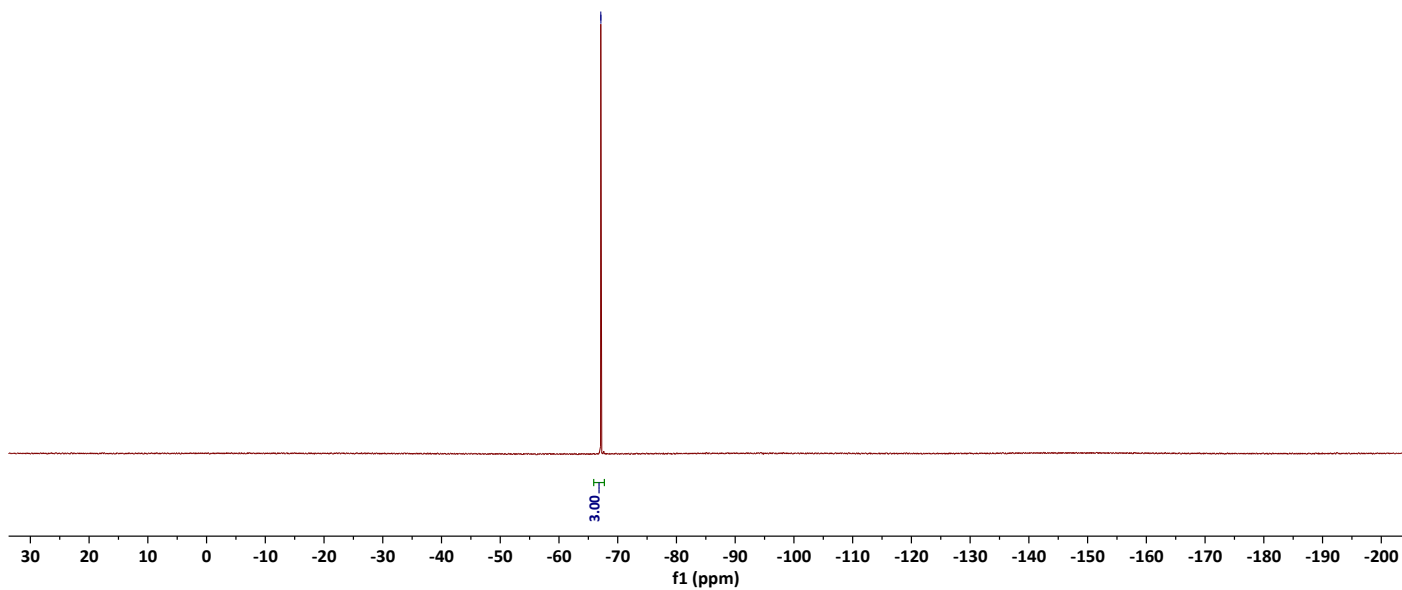
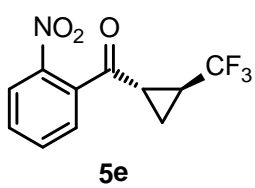
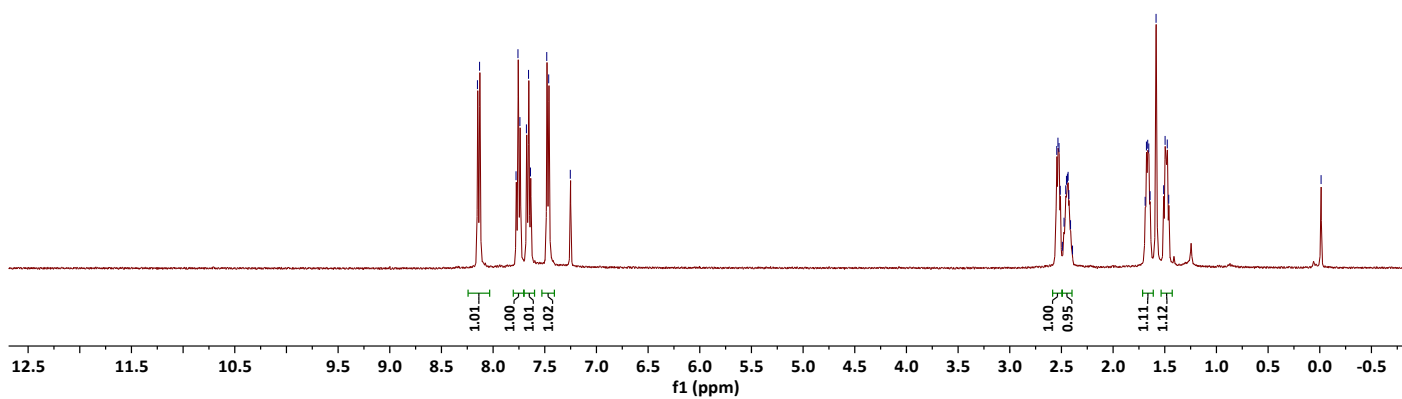
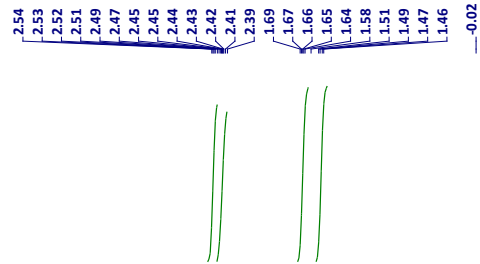
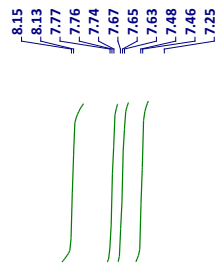
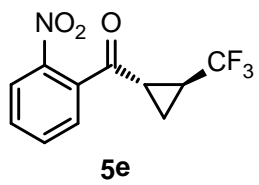


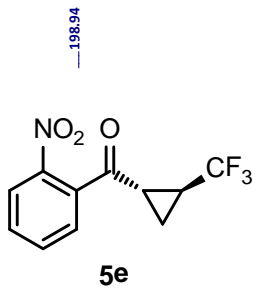








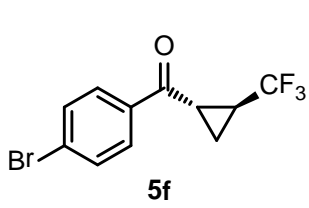
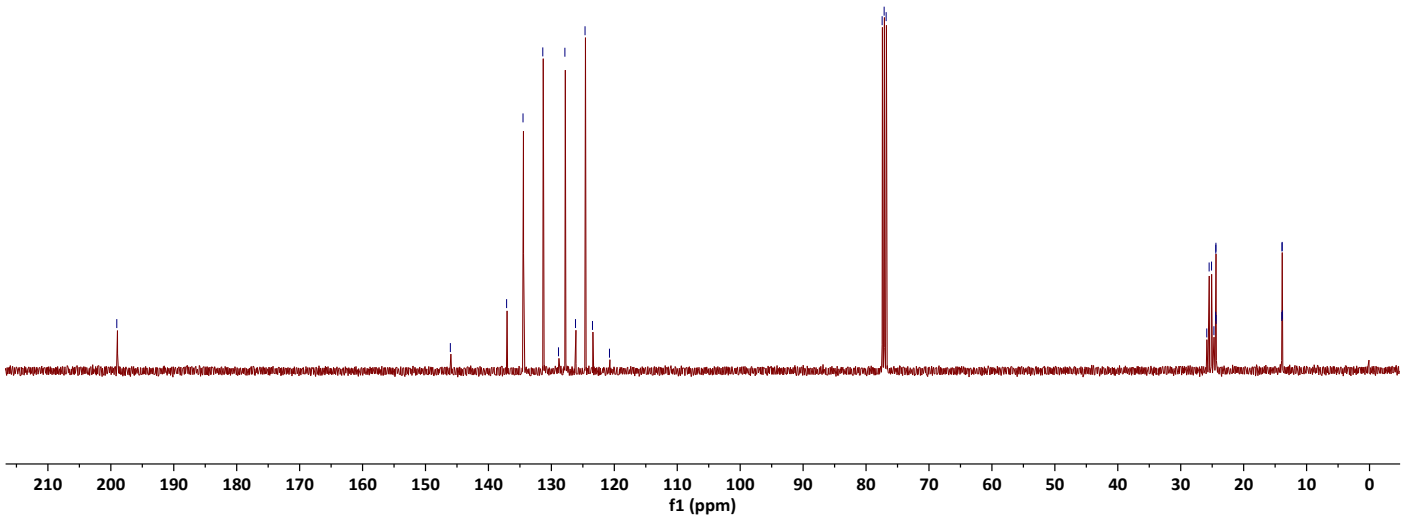




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123.35
120.65

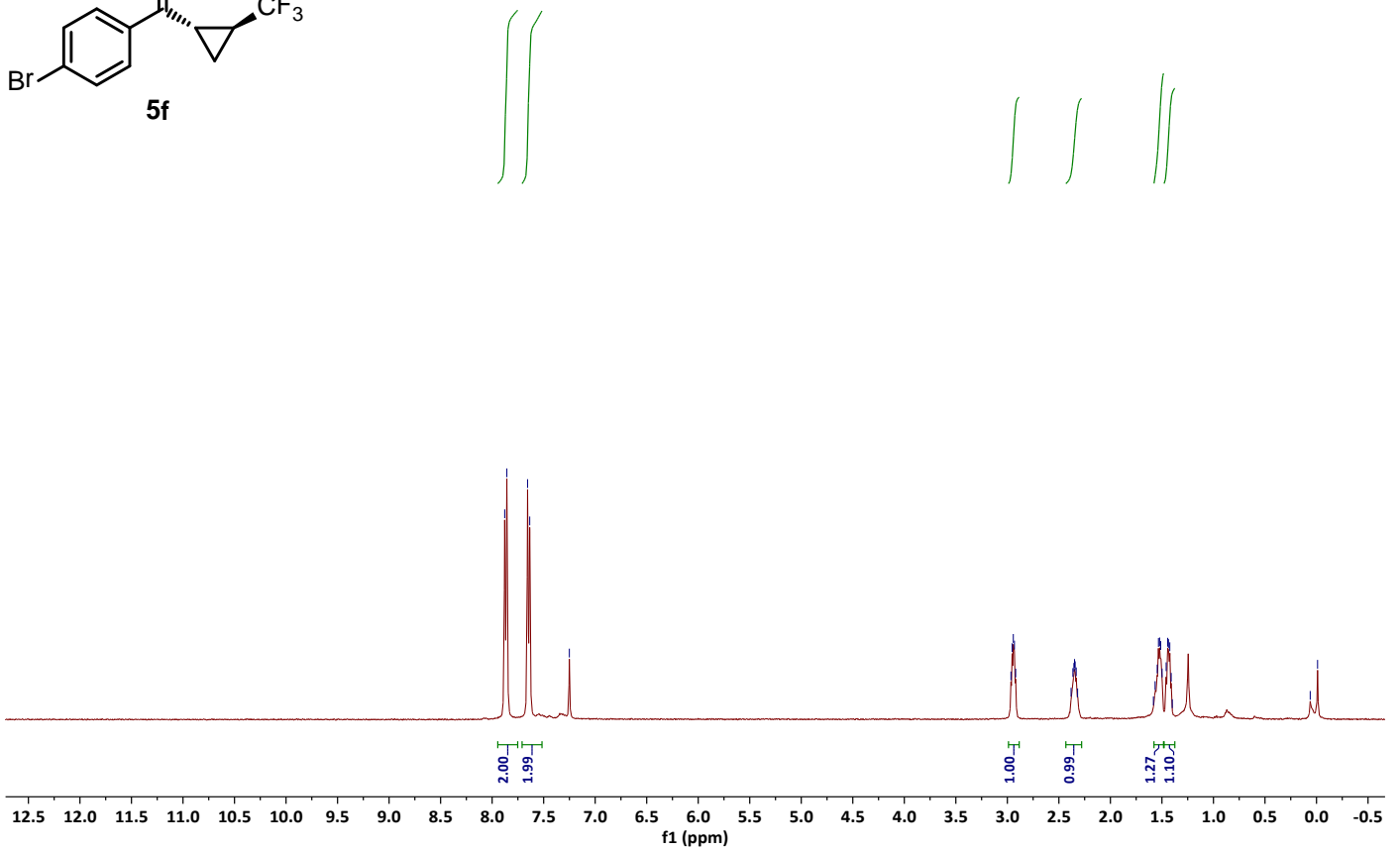
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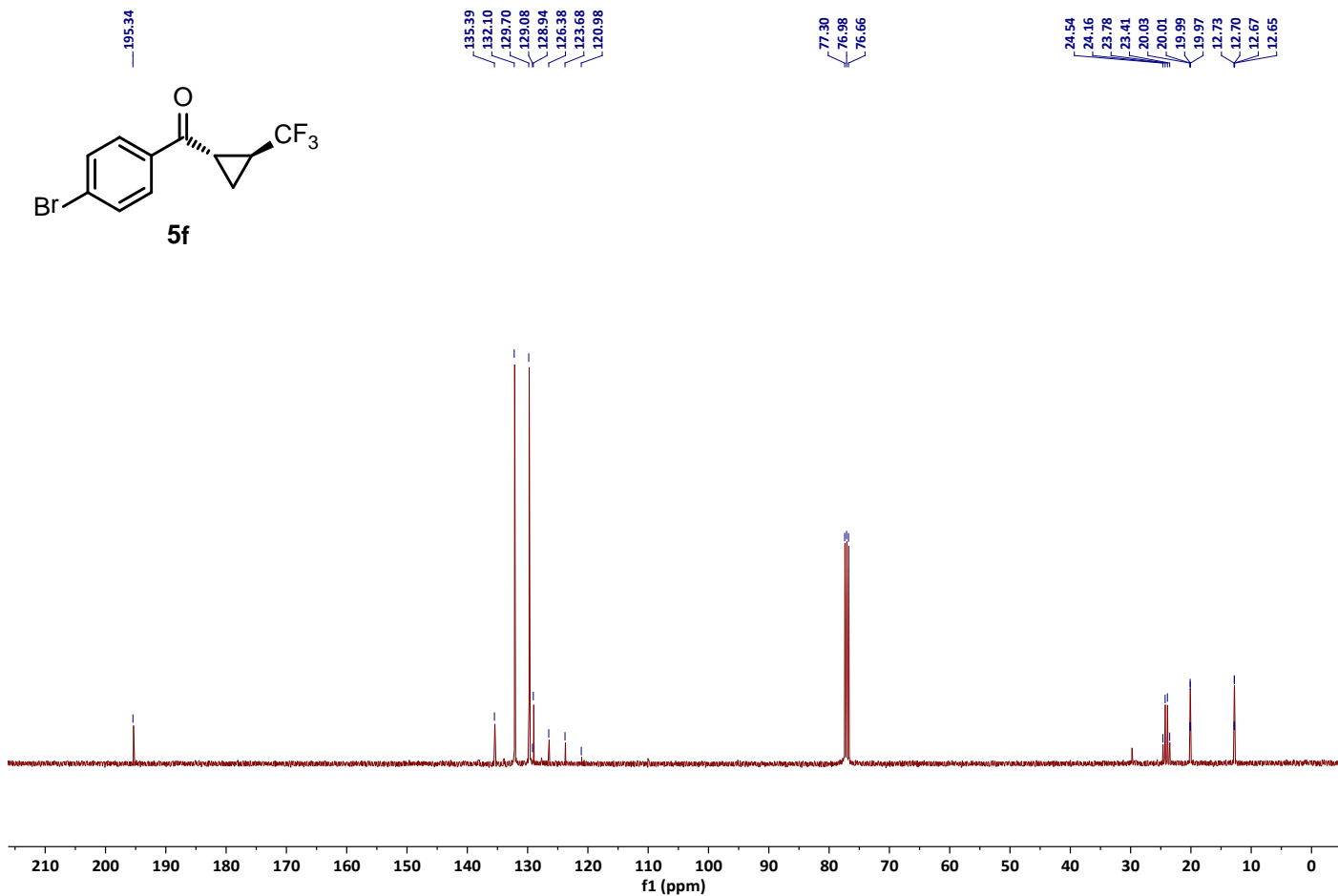
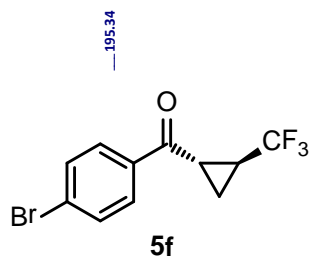
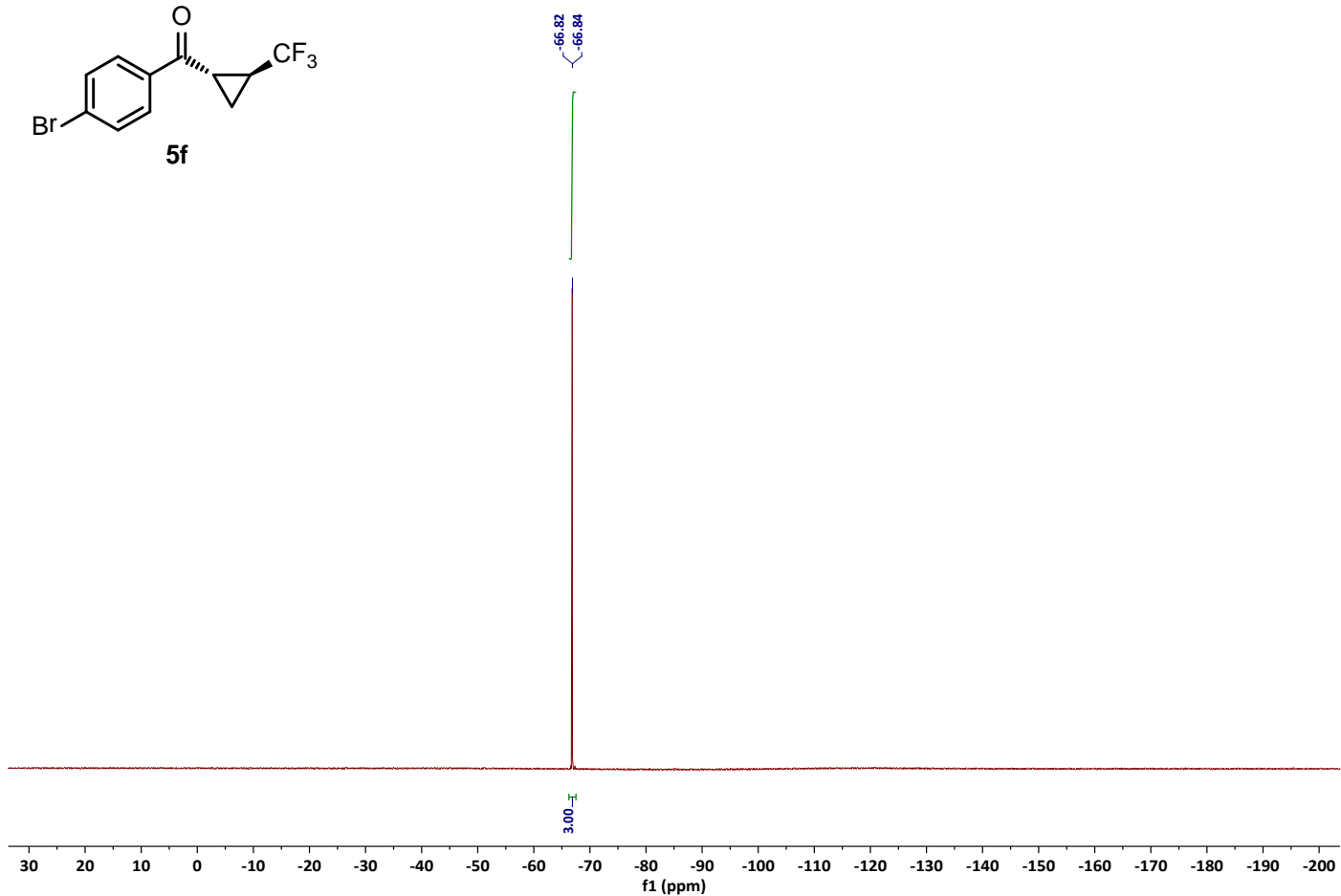
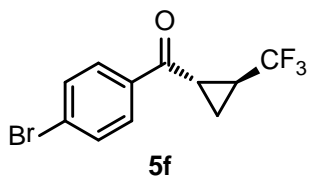


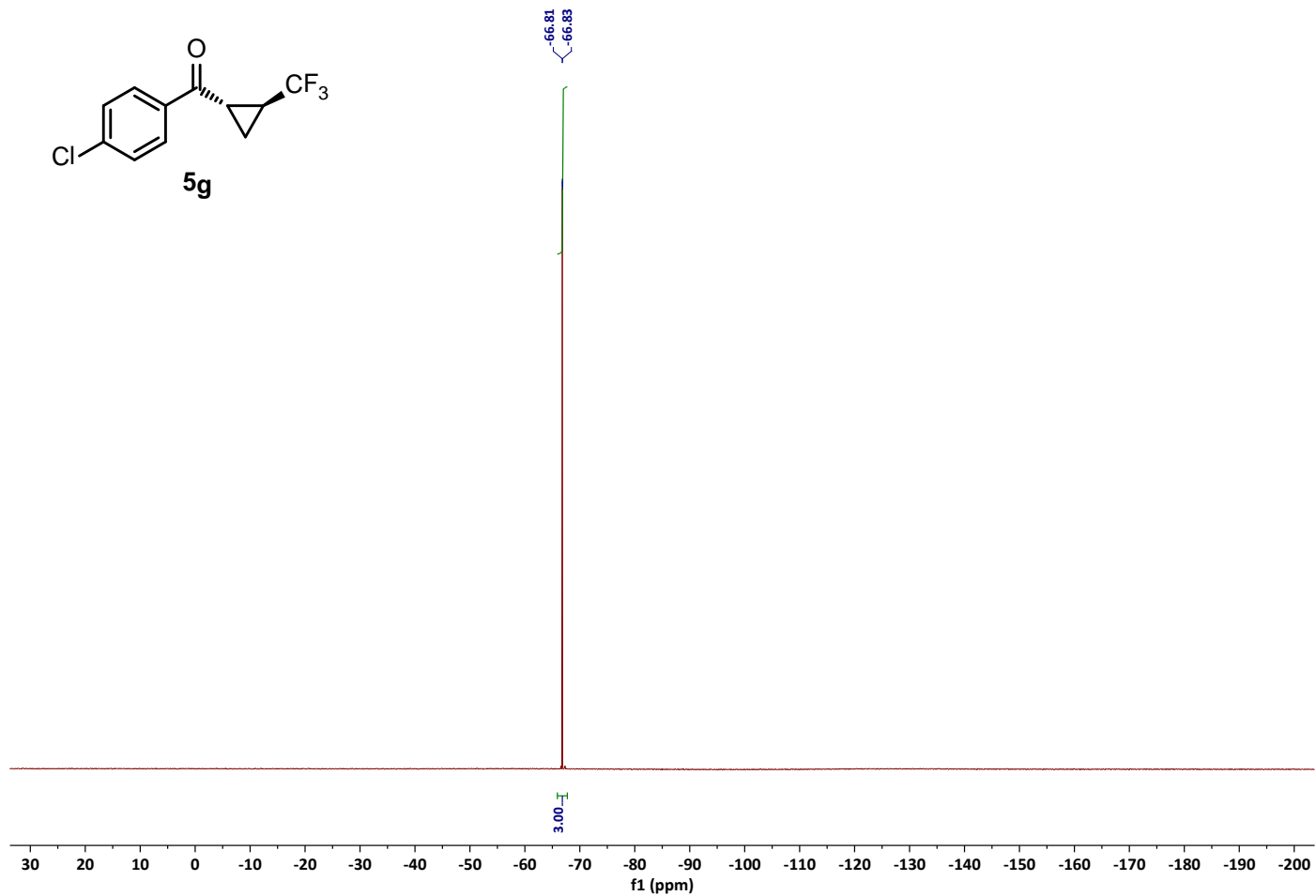
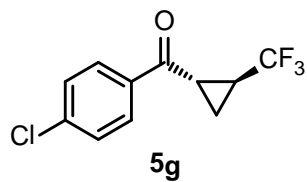
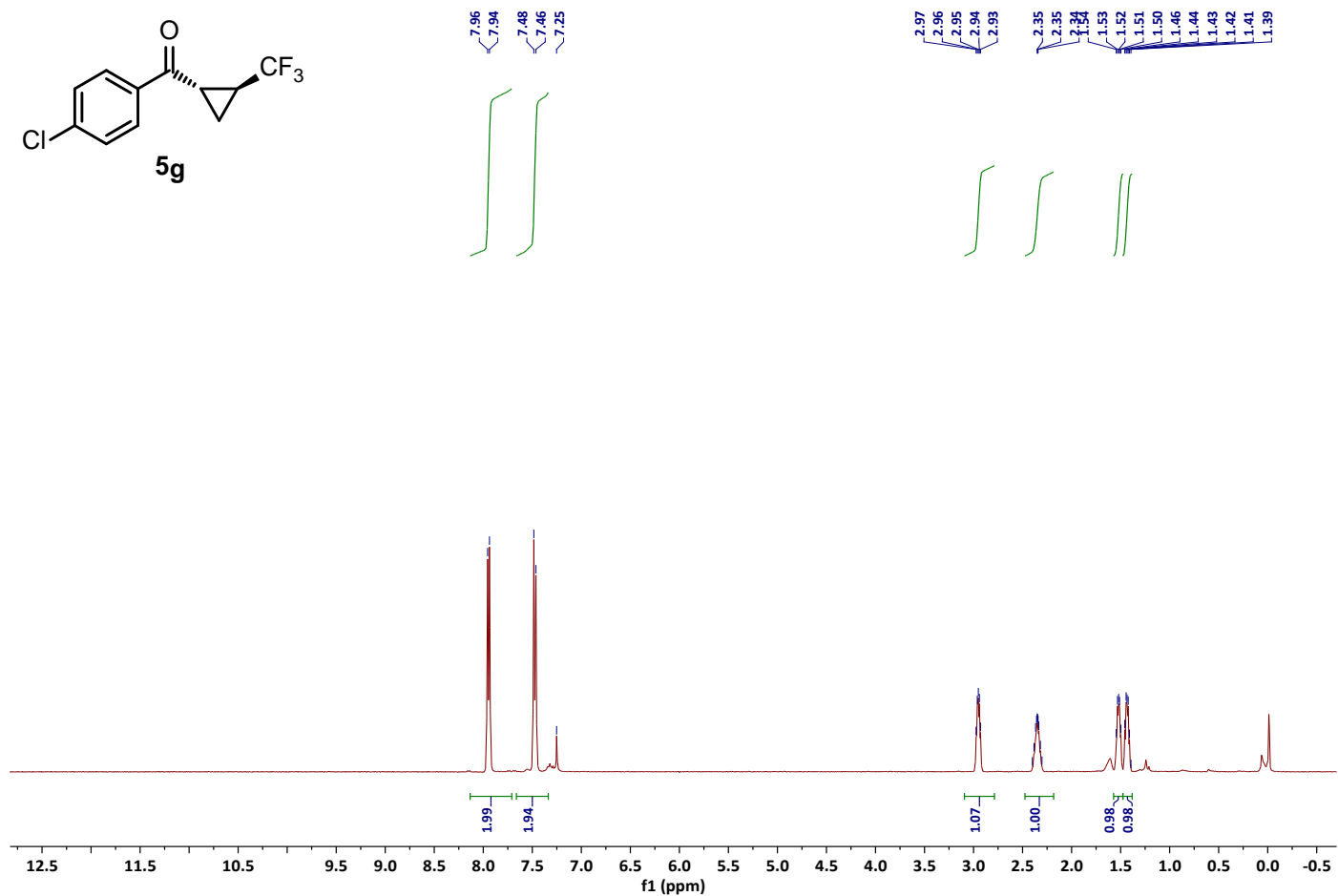
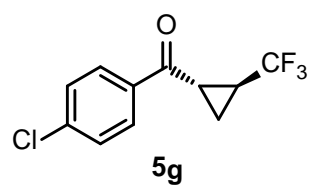
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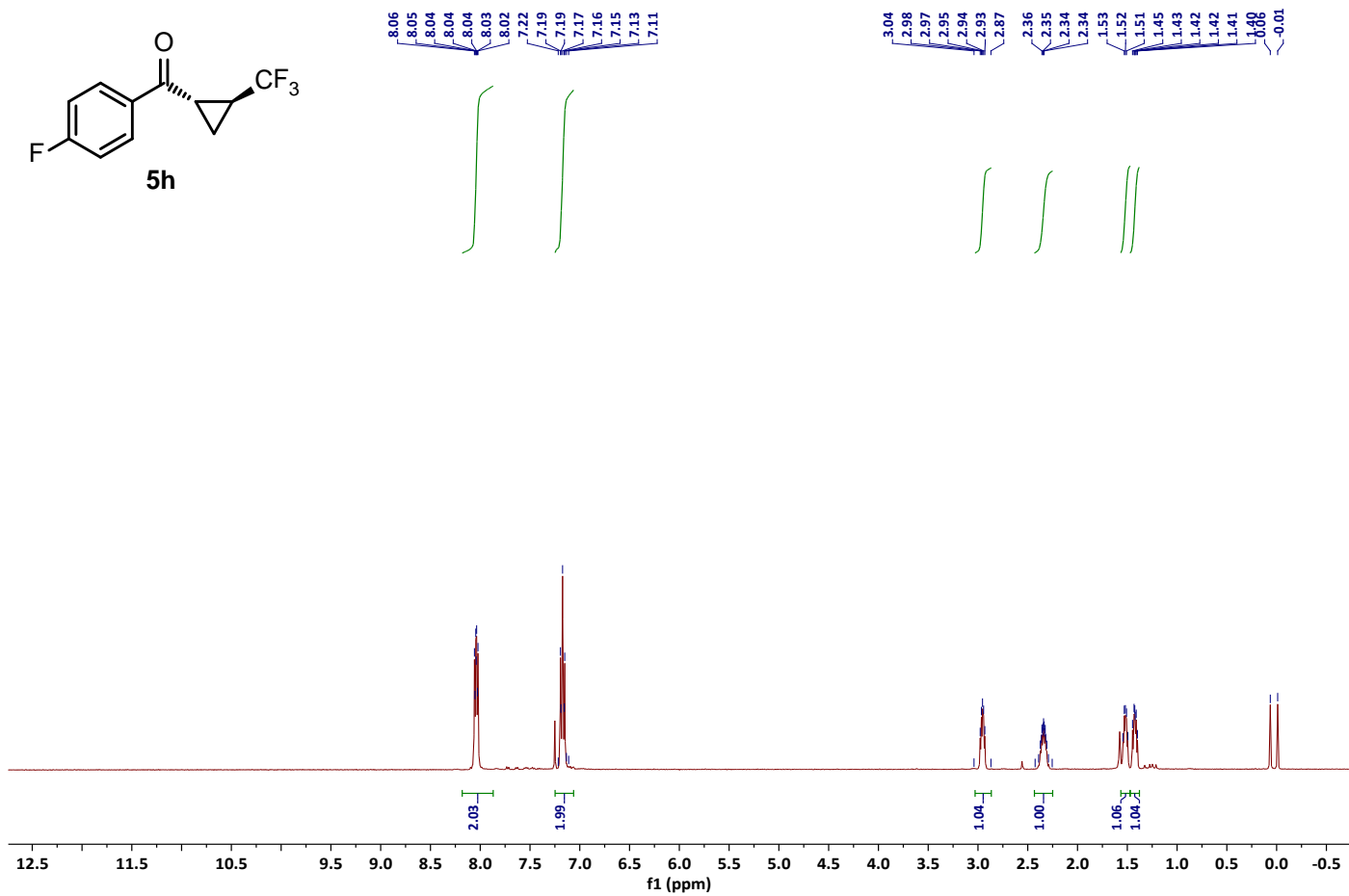
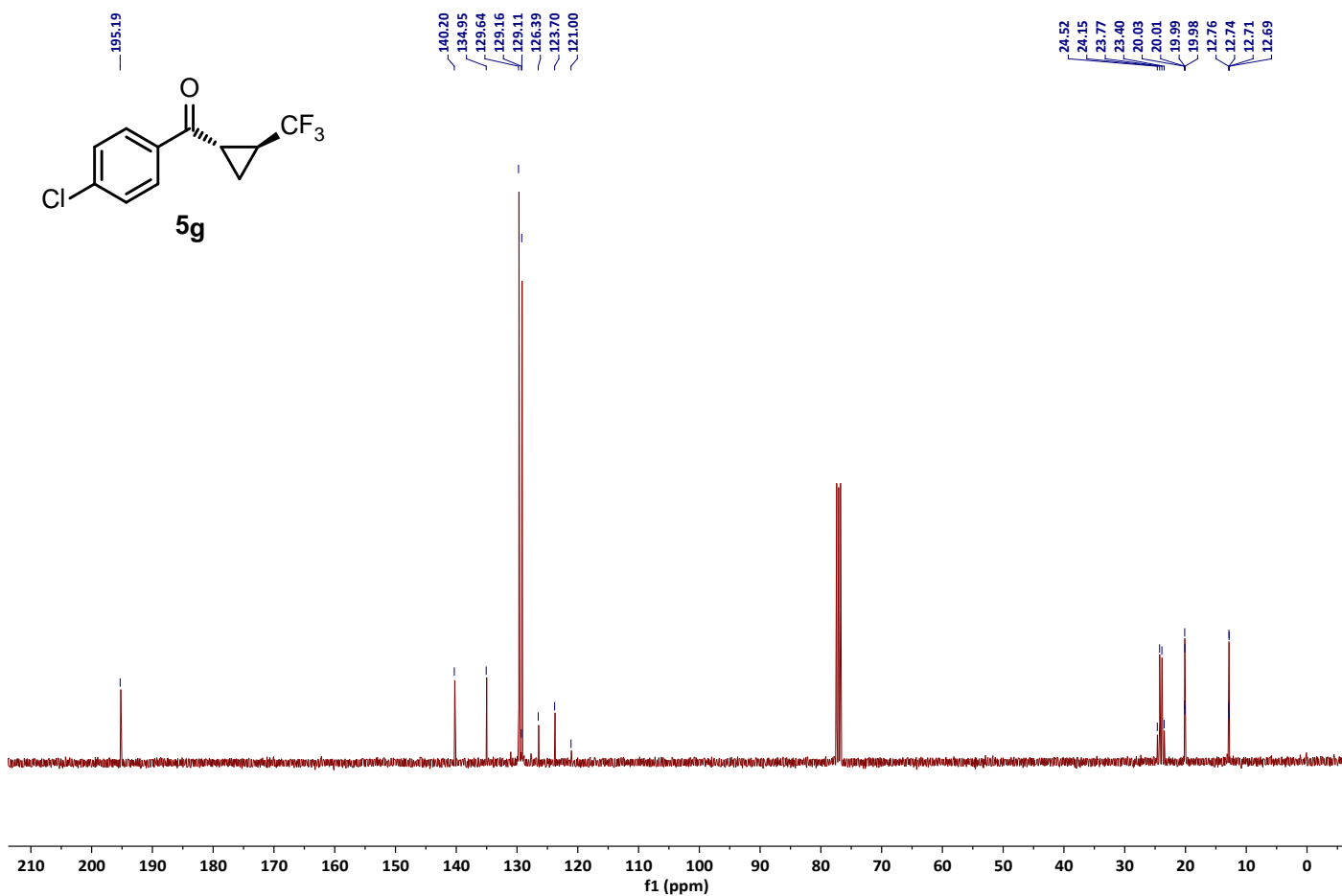
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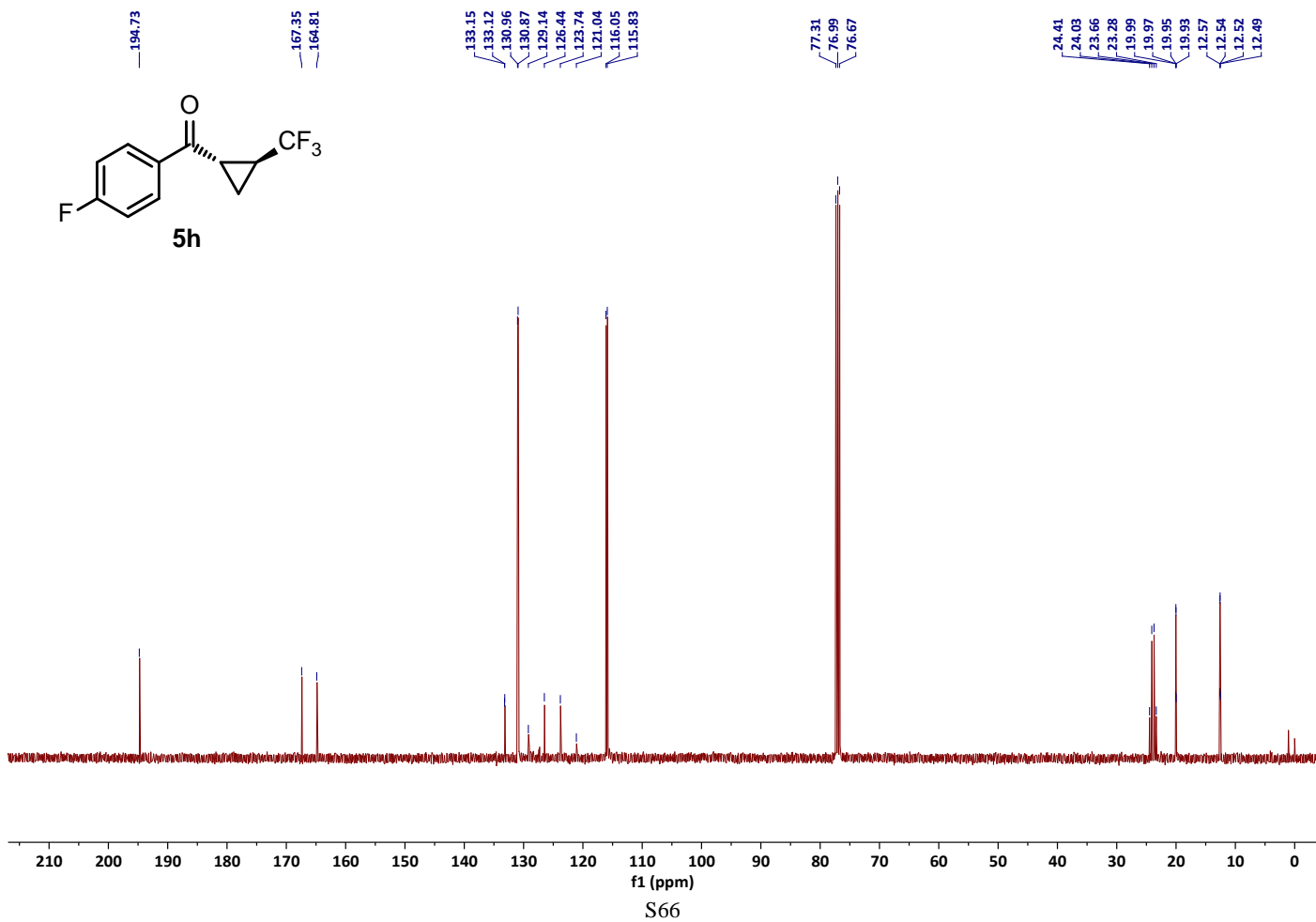
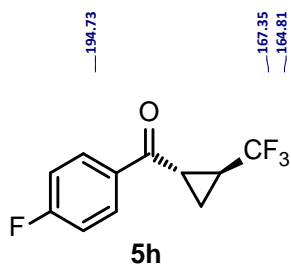
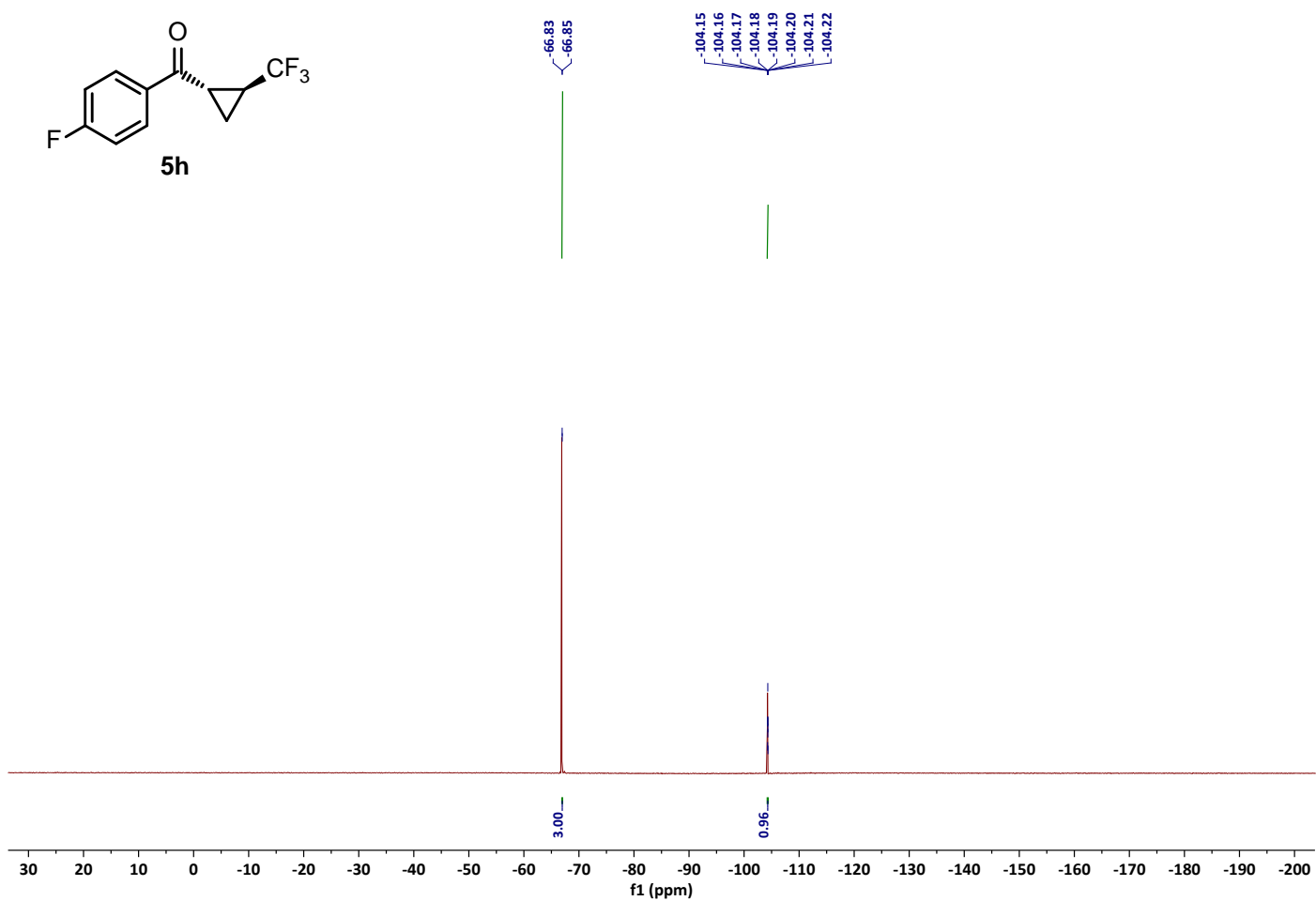
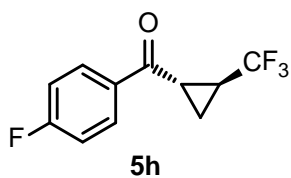


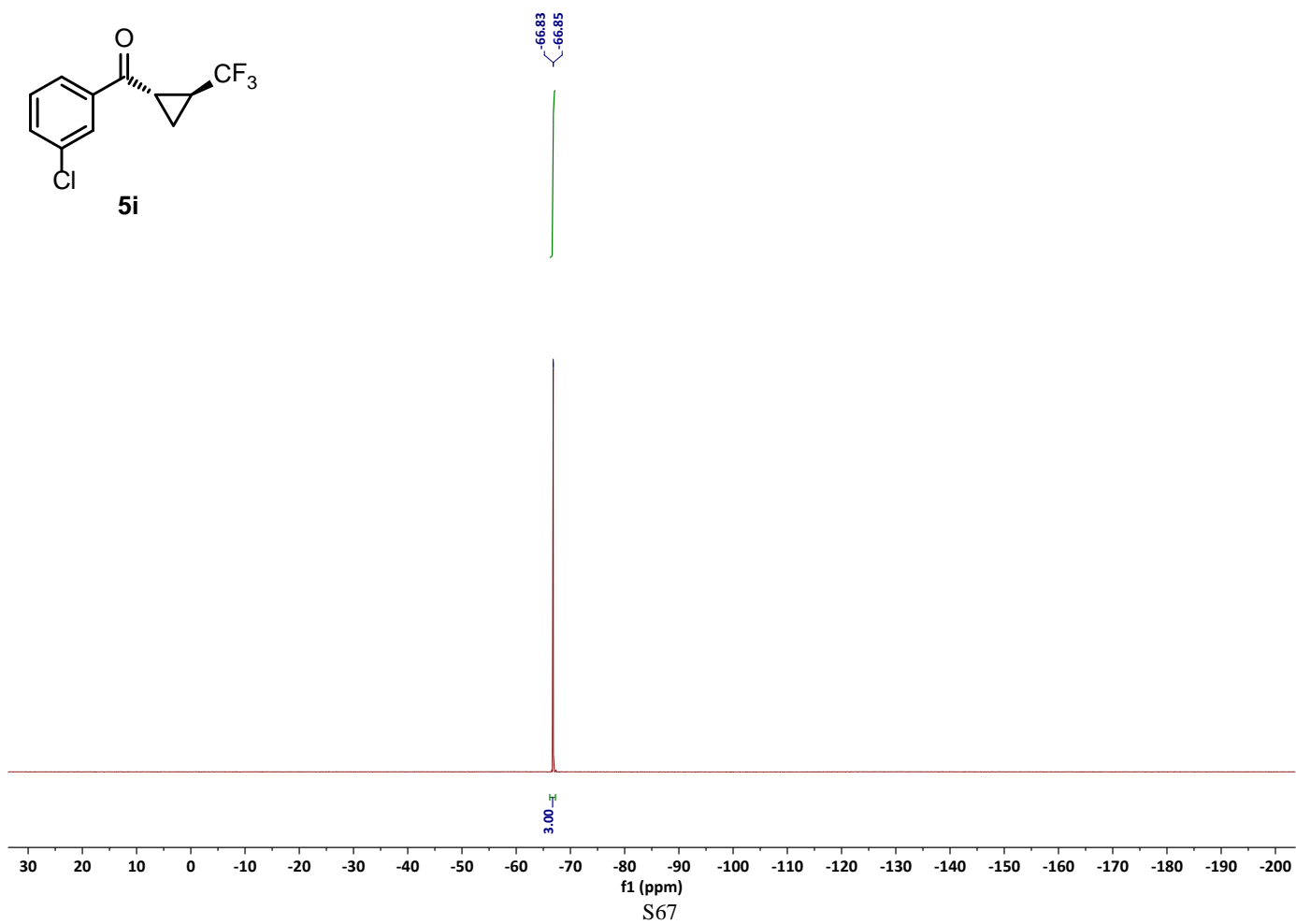
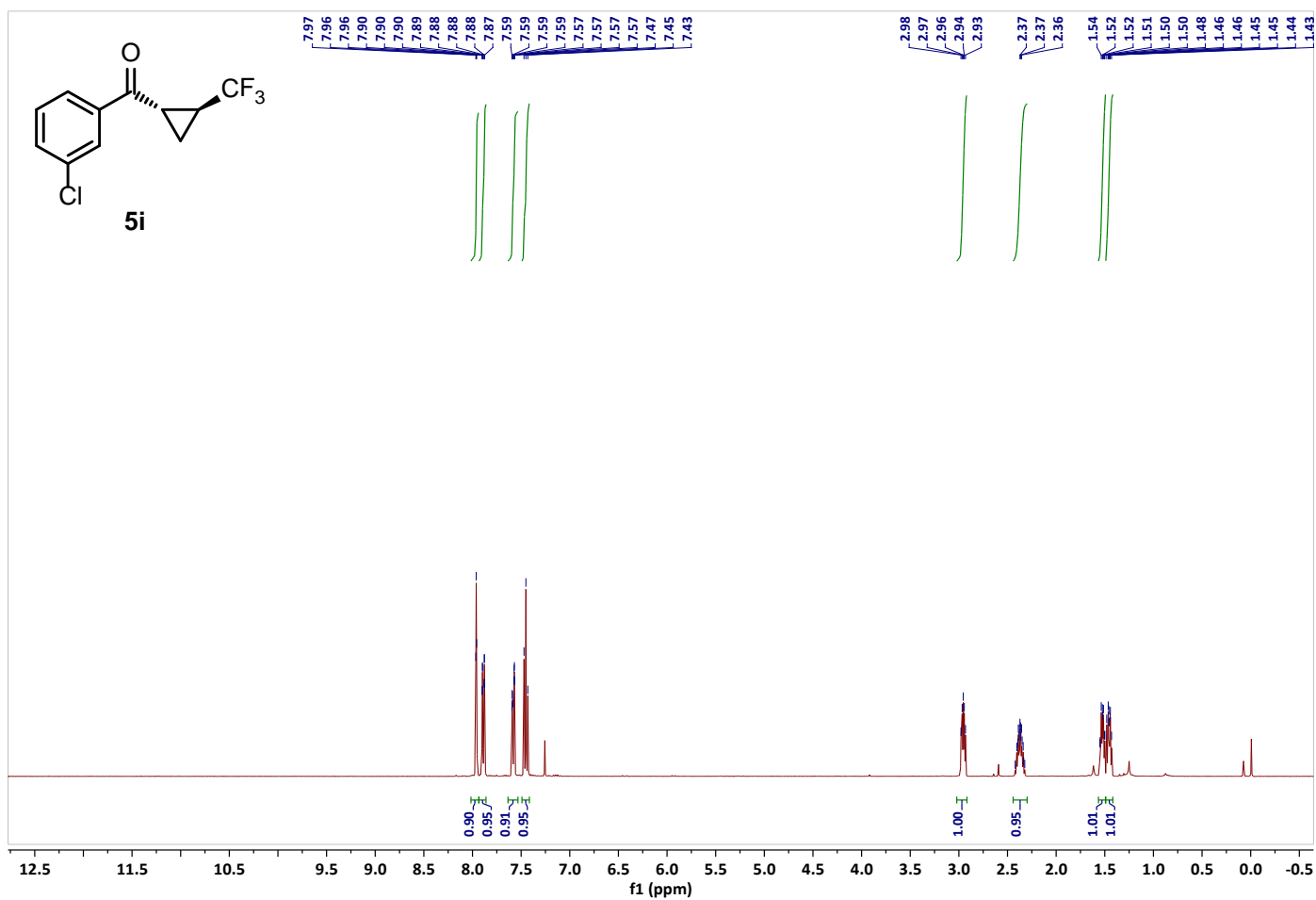
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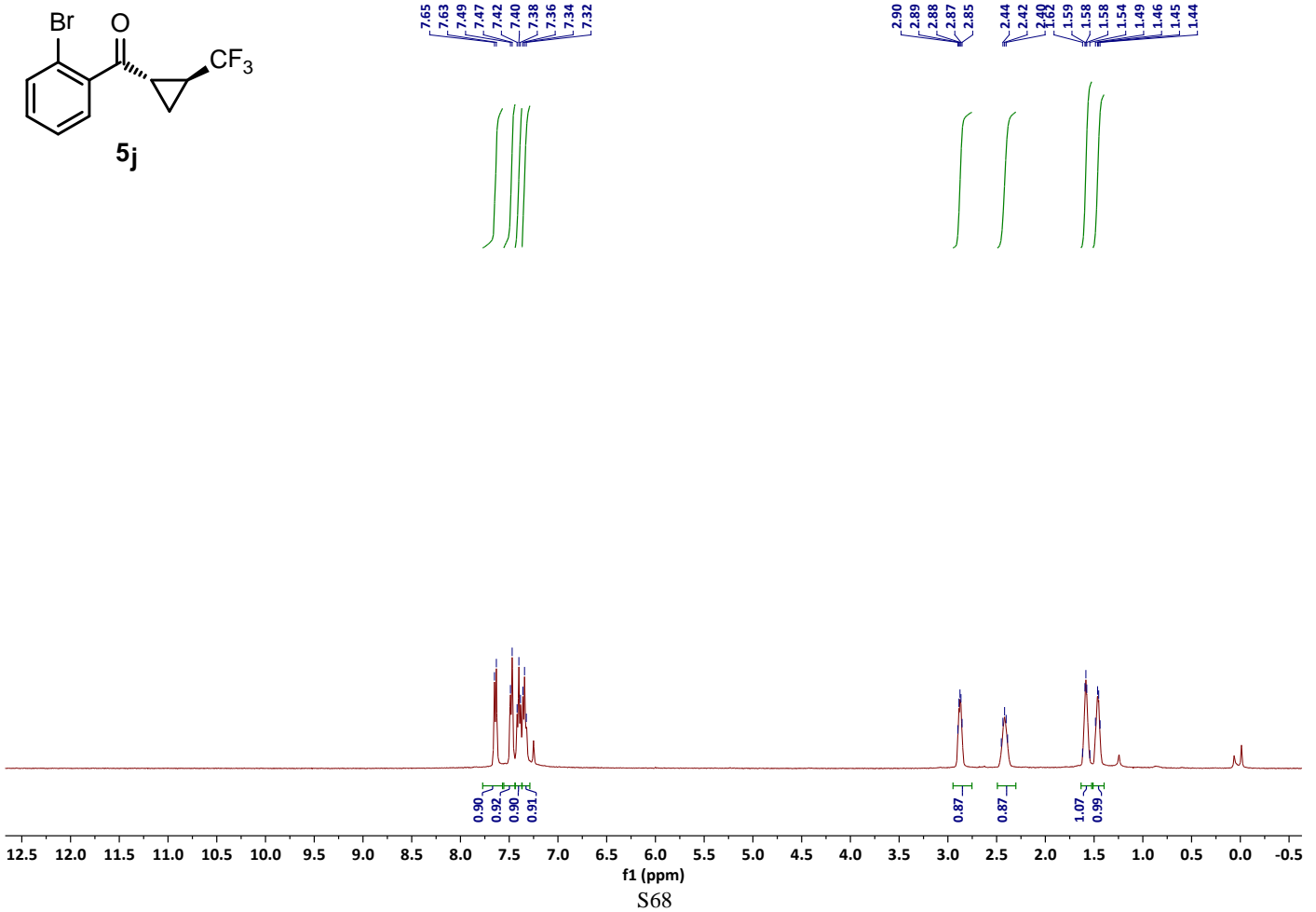
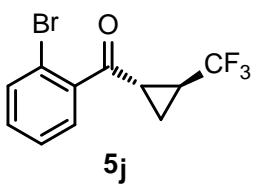
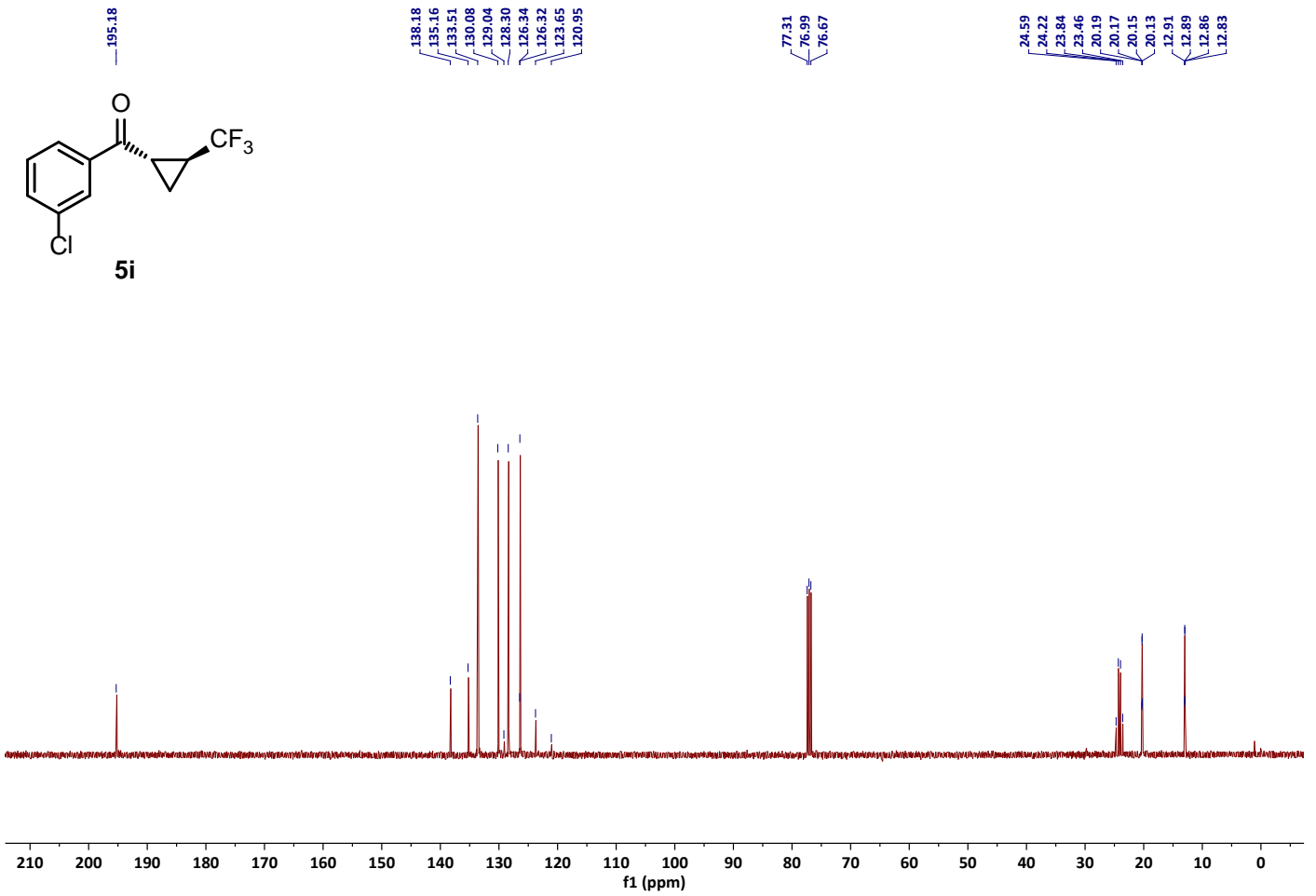
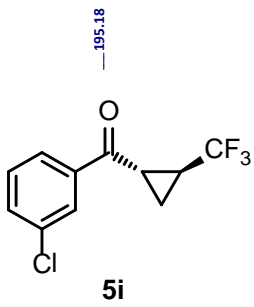


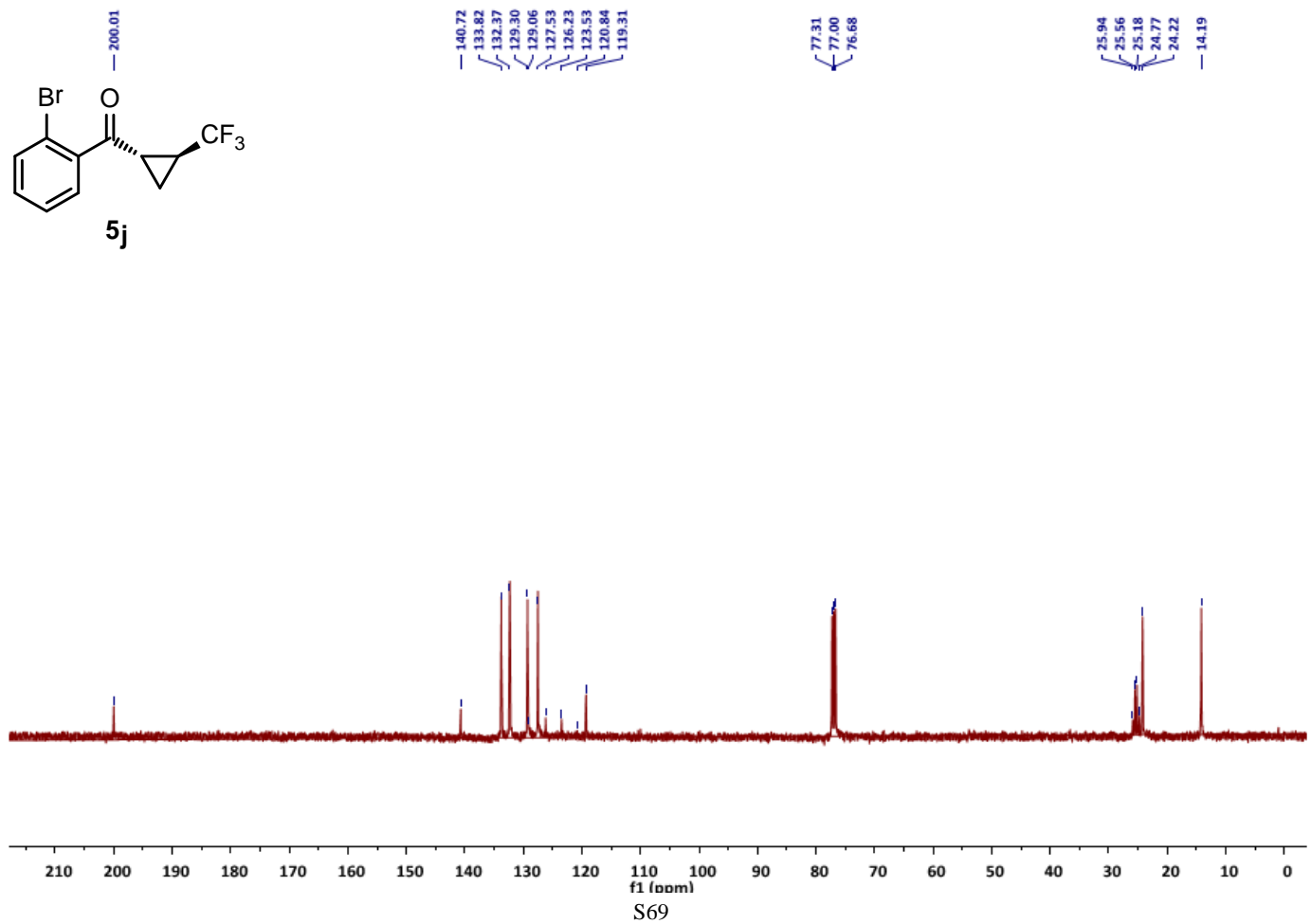
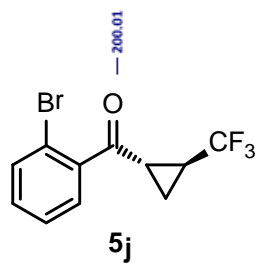
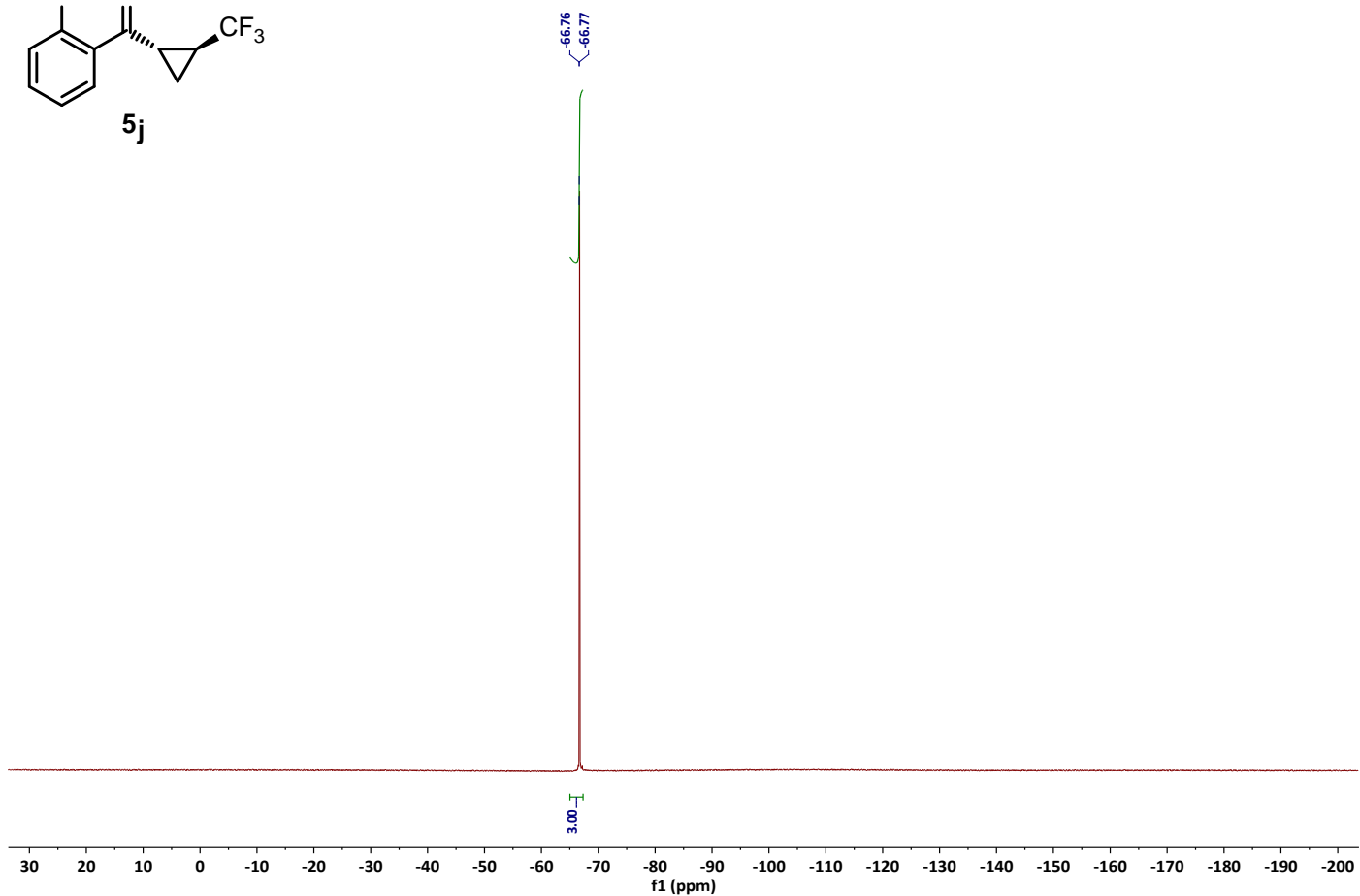
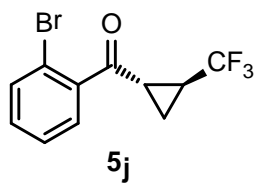


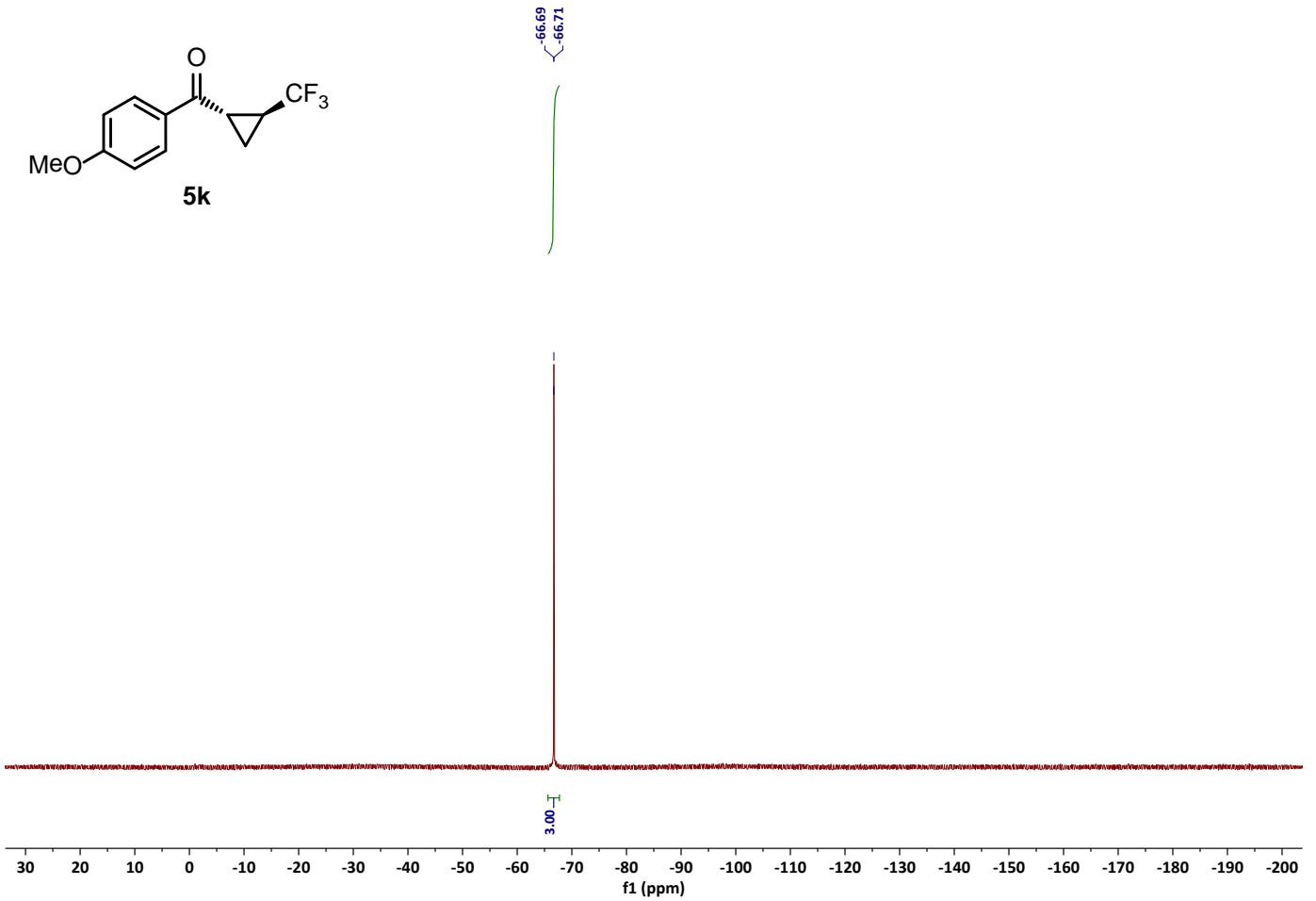
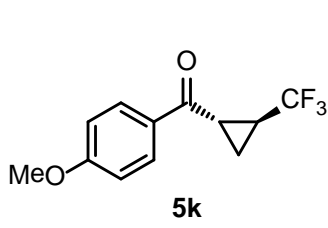
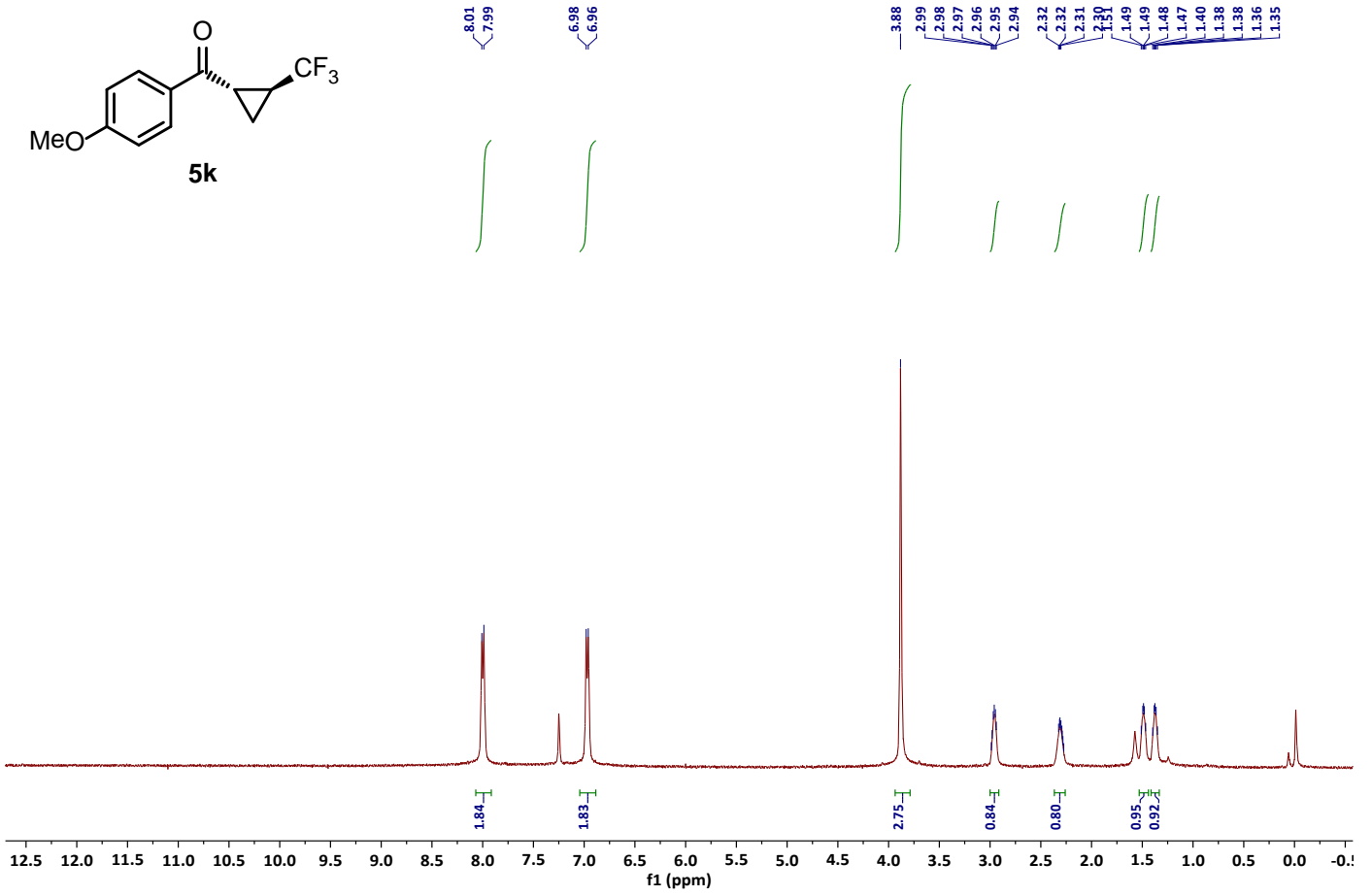
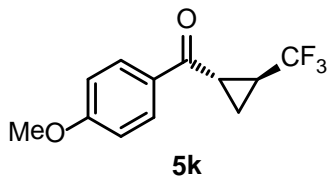


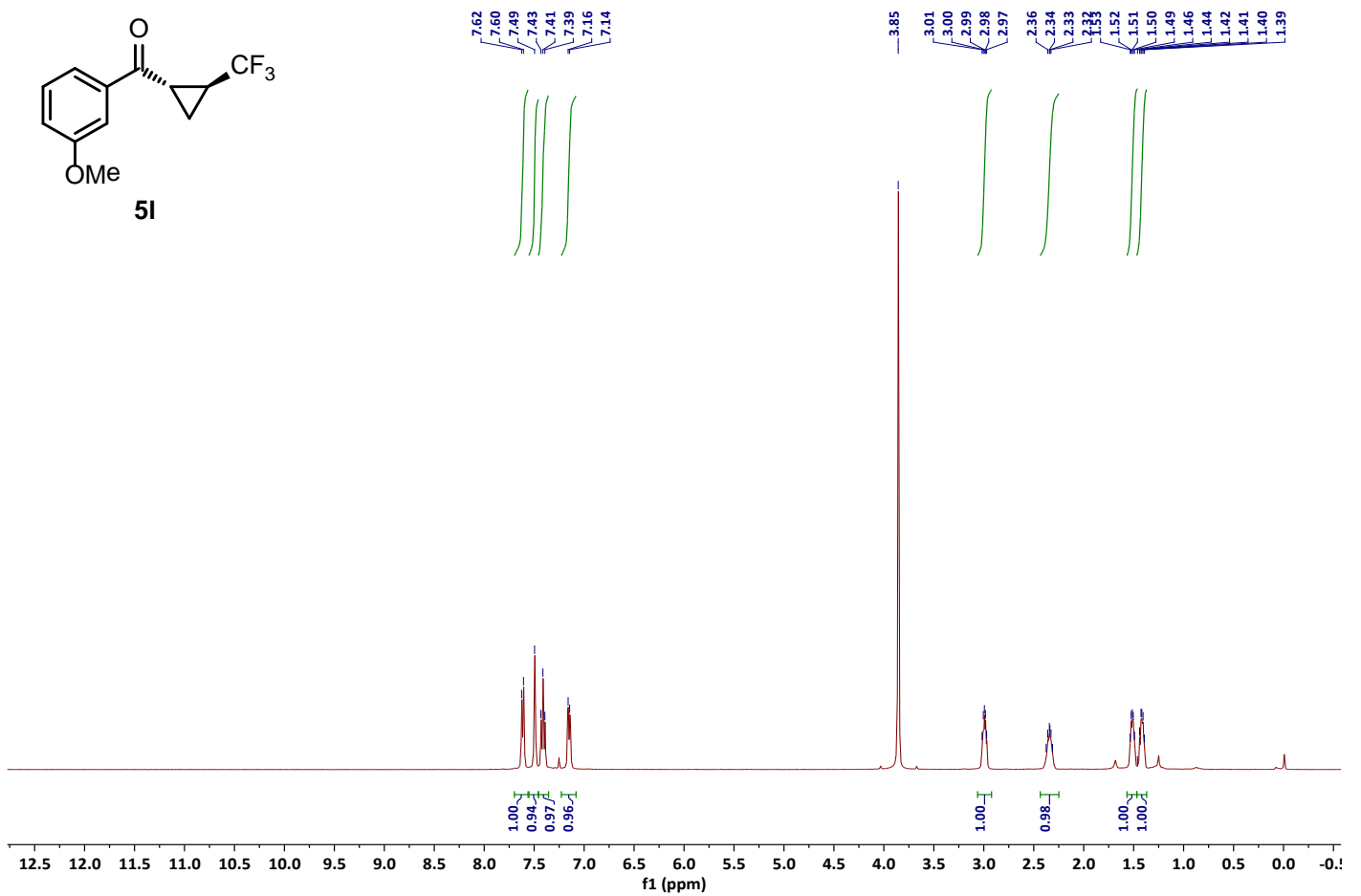
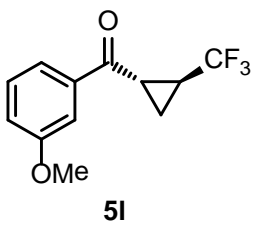
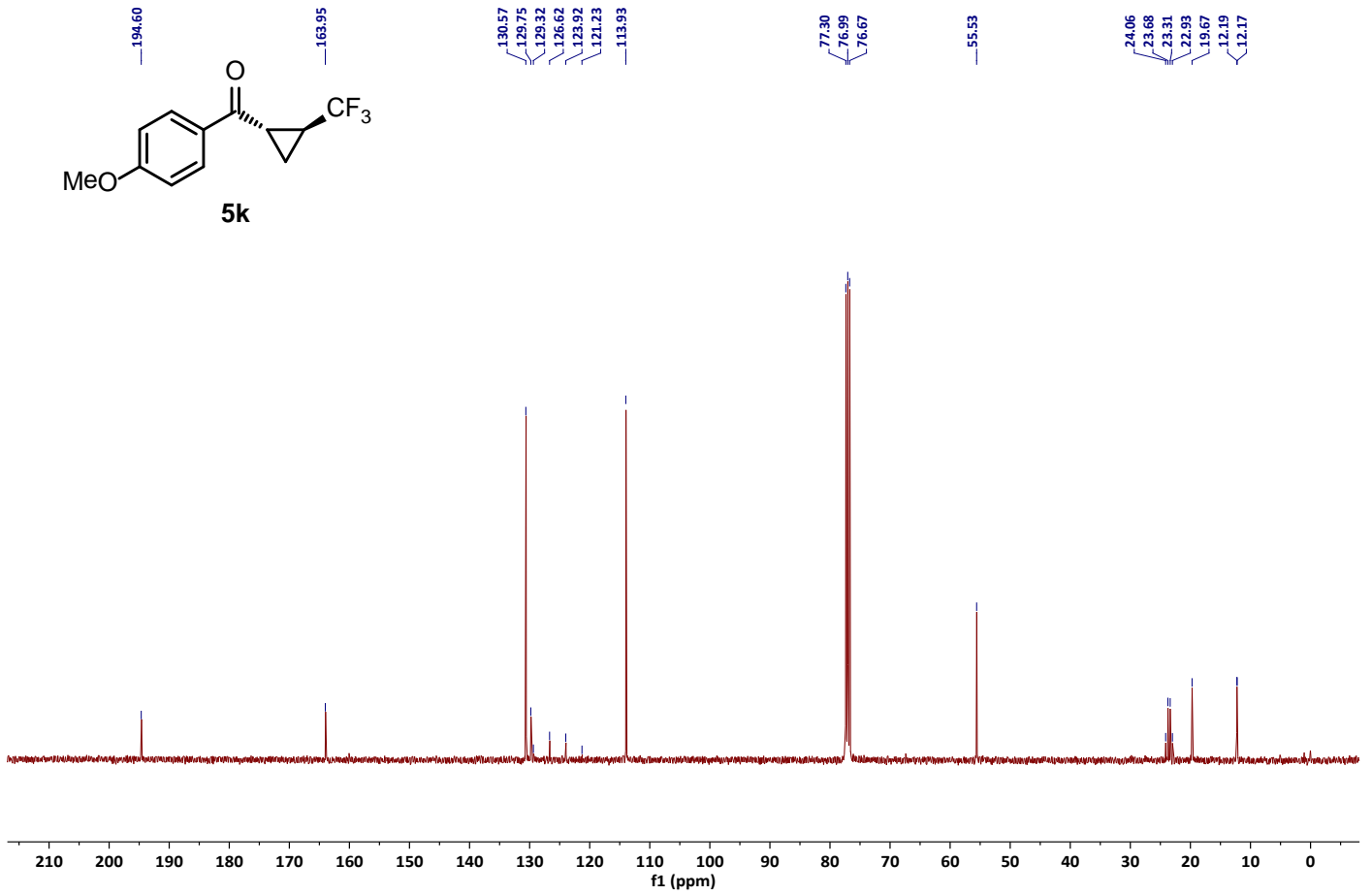
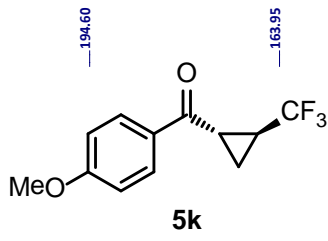


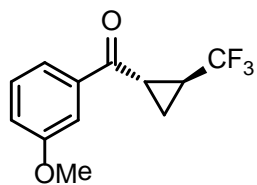




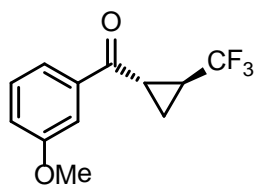
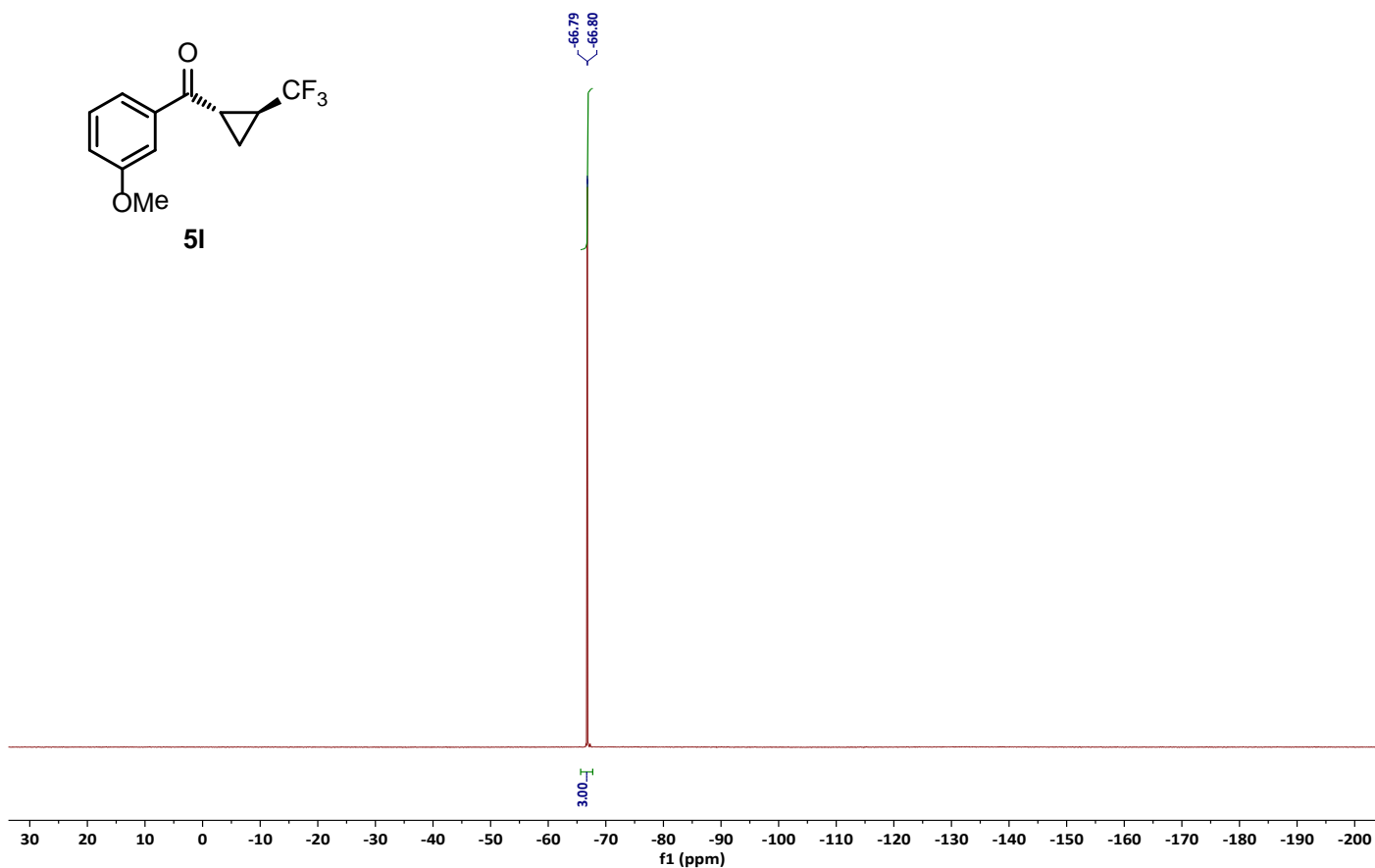








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