

Iron(II)-Catalyzed Intramolecular Olefin Aminofluorination

Deng-Fu Lu, Guan-Sai Liu, Cheng-Liang Zhu, Bo Yuan, and Hao Xu*

Department of Chemistry, Georgia State University, Atlanta GA 30303

Supporting Material

A. General Information

B. Catalyst Discovery

C. Synthesis of New Ligands and Olefin Substrates

D. General Procedures for the Intramolecular Olefin Aminofluorination and Product Characterization

E. Synthetic Application for the Method Discovery: Synthesis of β -Fluoro Amino Acids

F. Iron-Catalyzed Enantioselective Olefin Aminofluorination

G. ESI-TOF MS Studies of the Catalyst Complex: $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} - \text{L3}$ in the Presence of $\text{Et}_3\text{N} \cdot 3\text{HF}$

H. X-ray Crystallographic Analysis of S19

I. References

J. NMR Spectra

A. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma–Aldrich.

Materials. Commercial reagents were purchased from Sigma Aldrich, Fluka, EM Science, and Lancaster and used as received. All solvents were used after being freshly distilled unless otherwise noted.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker UltraShield-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak (CHCl_3 : δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent (CDCl_3 : δ 77.0). Chemical shifts for fluorine are reported in parts per million downfield and are referenced to the fluorine resonances of CFCl_3 . Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), and integration.

When ^{19}F NMR is used for quantitative purpose, 30 degrees pulse and longer delay time ($d_1 = 5$ s) were employed and the receiver gain was manually set as 32.

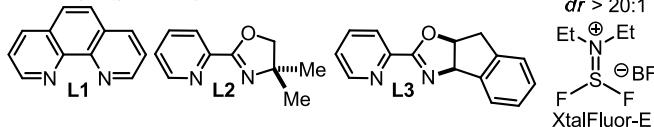
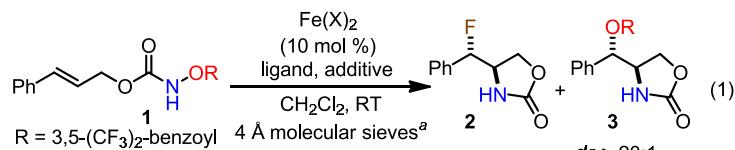
The mass spectroscopic data were obtained at the Georgia State University mass spectrometry facility using a Micromass Platform II single quadrupole instrument. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}).

Abbreviations used: EtOH – ethanol, EtOAc – ethyl acetate, THF – tetrahydrofuran, MeOH – methanol, Et_2O – diethyl ether, DCM – dichloromethane, TEA – triethylamine, MS – molecular sieves, TLC – thin layer chromatography

B. Catalyst Discovery

The General Procedure for Catalyst Discovery

To a flame-dried 5 mL vial (vial **A**) charged with freshly activated 4 Å molecular sieves (equal weight to starting material) and a magnetic stir bar were added the corresponding iron salts (0.01 mmol) and ligands (0.01 or 0.02 mmol). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. The mixture was stirred vigorously at room temperature for 20 min. During this time, to another flame-dried vial (vial **B**) was added Xtalfluor-E (0.12 mmol, 27.5 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. $\text{Et}_3\text{N}\cdot\text{3HF}$ (0.14 mmol, 23 μL) was subsequently added into vial **B** and the solution was stirred for 3 minutes until it becomes clear. The vial **A** was cooled in an ice-water bath and the solution in vial **B** was added into it dropwise. The acyloxyl carbamate **1** (0.1 mmol dissolved in 1 mL of DCM) was then added to vial **A** dropwise at the same temperature. The mixture was stirred at 0 °C for another 10 min and then kept stirring at room temperature until the acyloxyl carbamate was consumed monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution (1 mL), the aqueous layer was separated and extracted by DCM (2 mL \times 3). The combined organic layer was dried with anhydrous Na_2SO_4 and then concentrated *in vacuo*. The residue sample was directly evaluated for *dr* by ^{19}F NMR.



entry ^b	X ^c	ligand (mol %)	additive (equiv)	T (h)	yield (2) ^d	dr (2) ^e	yield (3) ^d
1	BF_4	L1 (20)	none	5.0	9%	1.8	63%
2	BF_4	L1 (20)	$\text{Et}_3\text{N}\cdot\text{3HF}$ (1.4)	5.0	43%	3.1	22%
3	BF_4	L1 (20)	HF-Pyridine (1.4)	5.0	37%	3.0	25%
4	BF_4	L1 (20)	$\text{Et}_3\text{N}\cdot\text{3HF}$ (1.4) XtalFluor-E (1.2)	4.0	61%	3.1	<5%
5	BF_4	L1 (20)	XtalFluor-E (1.2)	5.0	<5%	NA	<5%
6	BF_4	L2 (20)	$\text{Et}_3\text{N}\cdot\text{3HF}$ (1.4) XtalFluor-E (1.2)	4.0	58%	3.7	<5%
7	BF_4	L3 (20)	$\text{Et}_3\text{N}\cdot\text{3HF}$ (1.4) XtalFluor-E (1.2)	1.5	72%	3.9	<5%
8	BF₄	L3 (10)	Et₃N·3HF (1.4) XtalFluor-E (1.2)	1.0	71%	4.2	<5%
9	NTf_2	L3 (20)	$\text{Et}_3\text{N}\cdot\text{3HF}$ (1.6) XtalFluor-E (1.2)	3.5	75%	3.4	<5%

^aReactions were carried out under argon at 23 °C in triplets. ^bFe(BF₄)₂·6H₂O or Fe(NTf₂)₂ was applied as the catalyst. ^cIsolated yield and ^dDr was determined by ¹⁹F NMR analysis. NTf₂ = trifluoromethanesulfonimide.



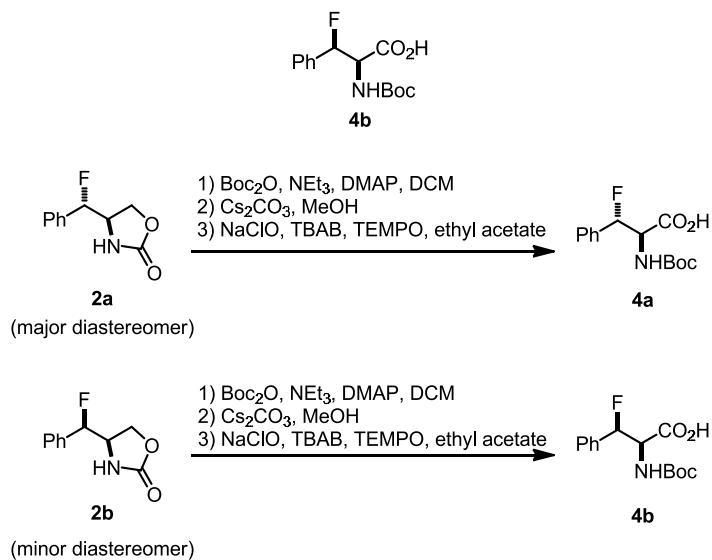
anti-4-(Fluoro(phenyl)methyl)oxazolidin-2-one (2a): The *anti* and *syn* diastereomers can be separated on silica gel column with toluene and THF as the eluent (toluene/THF from 20:1 to 10:1). White solid (m.p. 88–90 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.46–7.44 (m, 3H), 7.36–7.35 (m, 2H), 5.92 (s, 1H), 5.37 (dd, *J* = 46.8, 6.4 Hz, 1H), 4.33–4.21 (m, 2H), 4.17–4.14 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.9, 134.4 (d, *J* = 20.2 Hz), 129.9, 129.8, 126.3 (d, *J* = 6.1 Hz), 94.6 (d, *J* = 177.8 Hz), 65.3 (d, *J* = 7.1 Hz), 56.6 (d, *J* = 25.3 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ -181.6 (dd, *J* = 47.1, 13.6 Hz); IR ν_{max} (neat)/cm⁻¹: 3264 (w), 1753 (s), 1410 (m), 1266 (s), 1236 (s), 1026 (s), 934 (m), 733 (s), 699 (s); HRMS (ESI, m/z): calcd for C₁₀H₁₁NO₂F⁺ [M + H⁺], 196.0774, found 196.0769.

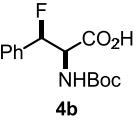
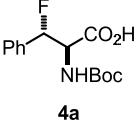
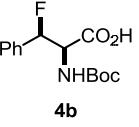


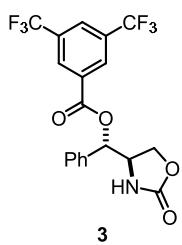
syn-4-(Fluoro(phenyl)methyl)oxazolidin-2-one (2b): White solid (m.p. 82–84 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.44–7.40 (m, 3H), 7.35–7.33 (m, 2H), 5.53 (s, 1H), 5.37 (dd, *J* = 46.4, 6.4 Hz, 1H), 4.50 (d, *J* = 6.4 Hz, 2H), 4.19–4.11 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 159.0, 135.0 (d, *J* = 19.2 Hz), 129.7, 129.1, 126.0 (d, *J* = 7.1 Hz), 93.4 (d, *J* = 179.8 Hz), 66.6 (d, *J* = 3.0 Hz), 56.2 (*J* = 31.3 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ -187.8 (dd, *J* = 46.4, 11.8 Hz); IR ν_{max} (neat)/cm⁻¹: 3271 (w), 1738 (s), 1408 (m), 1231 (s), 1027 (s), 936 (m), 747 (m), 699 (s); HRMS (ESI, m/z): calcd for C₁₀H₁₁NO₂F⁺ [M + H⁺], 196.0774, found 196.0769.

Determination of the Relative Stereochemistry of 2a and 2b

The relative stereochemistry of **2a** and **2b** were determined by comparison of the ¹H NMR spectra of their derivatives with a known compound *syn*-*N*-Boc- β -fluoro phenylalanine **4b**.¹ The acid derived from **2b** (the minor diastereomer) is in accordance with **4b** on ¹H NMR.

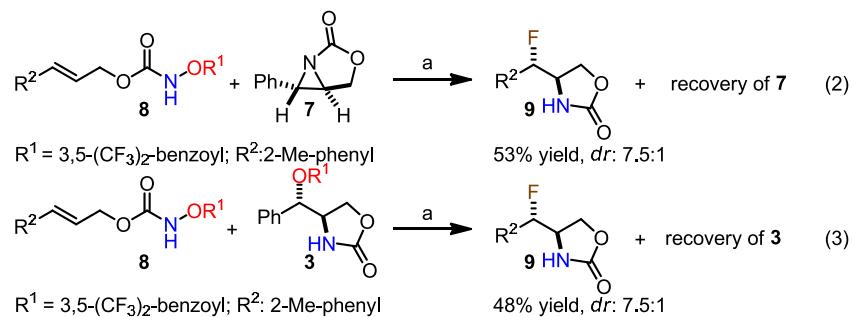


Spectrum	 4b (Literature Data) ¹	 4a	 4b
¹ H NMR	^1H NMR (300 MHz, CDCl_3 , 55 °C): 7.43–7.31 (m, 5H), 5.83 (dd, 1H, J = 45.5, 4.1 Hz), 5.10 (br.d, 1H, J = 8.3 Hz), 4.94–4.76 (m, 1H), 1.42 (s, 9H)	^1H NMR (400 MHz, CDCl_3 , 55 °C): 8.38 (brs, 1H), 7.38 (m, 5H), 6.07 (d, 1H, J = 45.6 Hz), 5.23 (brs, 1H), 4.87–4.81 (m, 1H), 1.32 (s, 9H)	^1H NMR (400 MHz, CDCl_3 , 55 °C): 7.43–7.31 (m, 5H), 5.83 (dd, 1H, J = 45.5, 4.1 Hz), 5.15 (brs, 1H), 4.94–4.76 (m, 1H), 1.43 (s, 9H)



2-Oxooxazolidin-4-yl)(phenyl)methyl 3,5-bis(trifluoromethyl)benzoate (3): ^1H NMR (400 MHz, CDCl_3): δ 8.50 (s, 2H), 8.09 (s, 1H), 7.42 (s, 5H), 6.68 (s, 1H), 5.94 (d, $J = 7.8$ Hz, 1H), 4.42 (td, $J = 8.1, 5.3$ Hz, 1H), 4.30 (t, $J = 9.0$ Hz, 1H), 4.13 (dd, $J = 9.2, 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 159.3, 134.6, 132.3 (q, $J = 35.0$ Hz), 131.6, 129.9, 129.8, 129.4, 127.1, 126.9–126.8 (m), 122.8 (q, $J = 271.0$ Hz), 79.3, 66.2, 56.0; ^{19}F NMR (377 MHz, CDCl_3): δ -62.95 (s); IR ν_{max} (neat)/ cm^{-1} : 3270 (w), 2926 (w), 1760 (s), 1736 (s), 1280 (s), 1137 (s), 1030 (m), 700 (s); HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_4\text{F}_6^+ [\text{M} + \text{H}^+]$, 434.0833, found 434.0827.

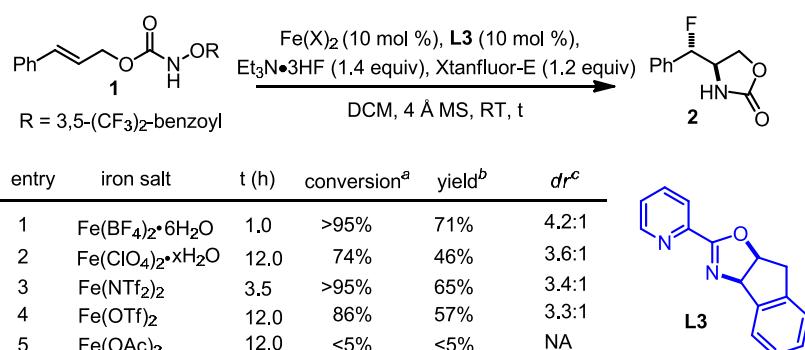
The relative stereochemistry of **3** was determined with a known compound after its hydrolysis.²



^a $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol %), **L3** (10 mol %); $\text{Et}_3\text{N} \cdot 3\text{HF}$ (1.4 equiv), XtanFluor-E (1.2 equiv), CH_2Cl_2 , RT, 4 Å molecular sieves, 24 h.

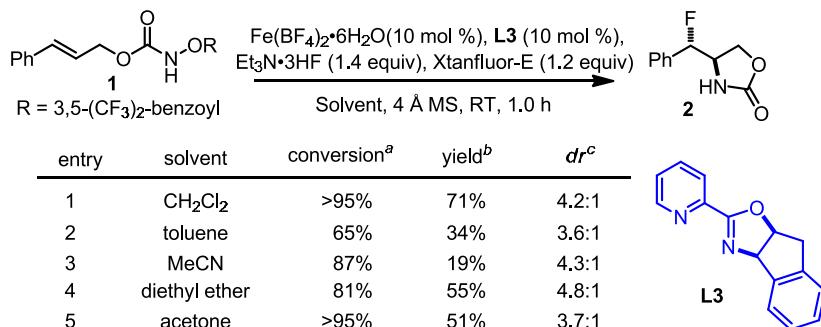
Compounds **7** is a known compound.^{3,4}

a. Iron Salt Optimization



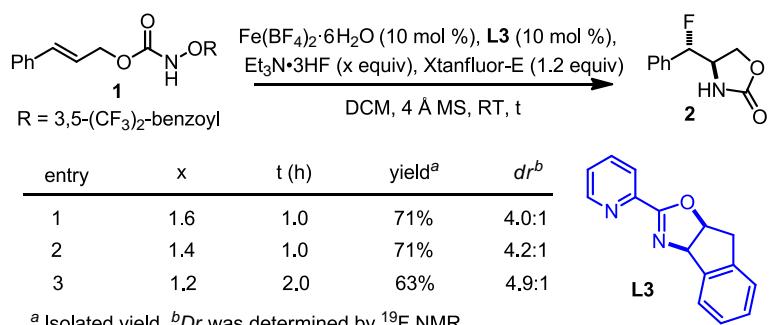
^aConversions were determined by ^{19}F NMR analysis with C_6F_6 as internal standard. ^bIsolated yield. ^cDr was determined by ^{19}F NMR.

b. Solvent Optimization



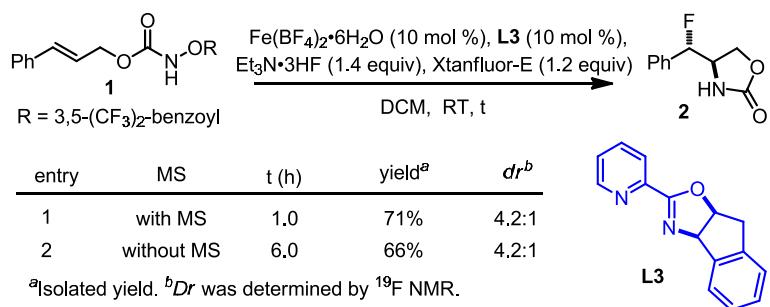
^aConversions were determined by ¹⁹F NMR analysis with C₆F₆ as internal standard. ^bIsolated yield. ^cDr was determined by ¹⁹F NMR.

c. Et₃N·3HF Quantity Optimization



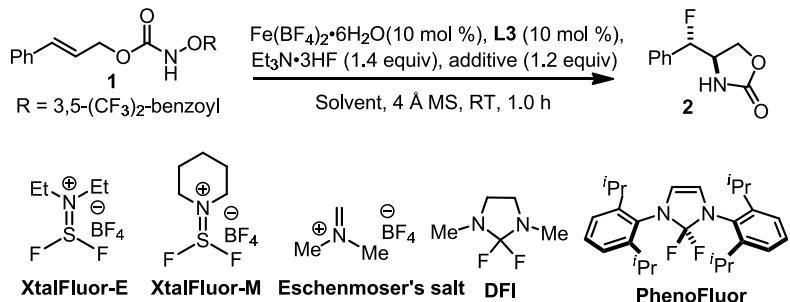
^a Isolated yield. ^bDr was determined by ¹⁹F NMR.

d. The Effect of Molecular Sieves



^a Isolated yield. ^bDr was determined by ¹⁹F NMR.

e. The Effect of Carboxylate Trapping Reagents

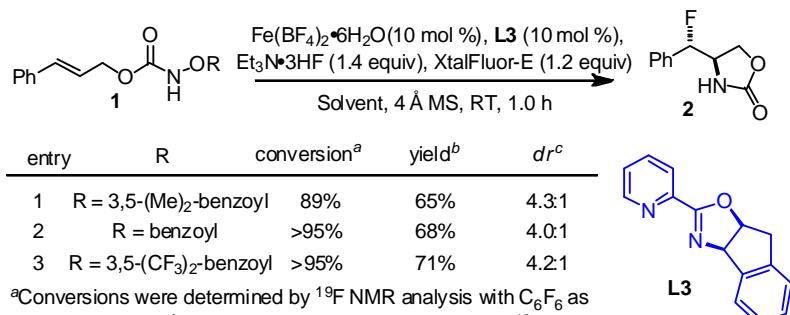


entry	additive	conversion ^a	yield ^b	dr ^c
1	XtalFluor-E	>95%	71%	4.2:1
2	XtalFluor-M	>95%	58%	3.1:1
3	Eschenmoser's salt ^d	56%	15%	3.0:1
4	DFI	>95% decomposition of 1	NA	NA
5	PhenolFluor	>95% decomposition of 1	NA	NA

^aConversions were determined by ¹⁹F NMR analysis with C₆F₆ as internal standard, ^bIsolated yield, ^cDr was determined by ¹⁹F NMR.

^dEschenmoser's BF_4^- salt was generated *insitu* by treating its iodide with AgBF_4 .

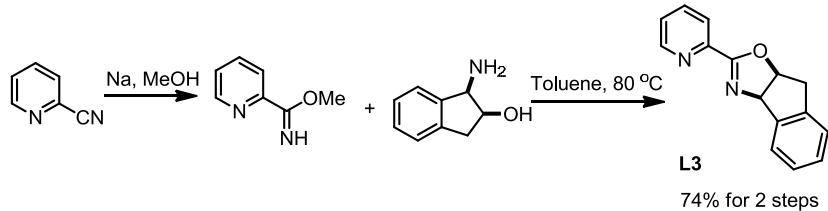
f. Effect of Various Acyl Activating Groups



^aConversions were determined by ¹⁹F NMR analysis with C₆F₆ as internal standard. ^bIsolated yield. ^cDr was determined by ¹⁹F NMR.

C. Synthesis of New Ligands and Olefin Substrates

a. Ligand Synthesis



The synthesis of new ligand **L3** was based on a known procedure for other hybrid pyridine–oxazoline ligand synthesis.⁵

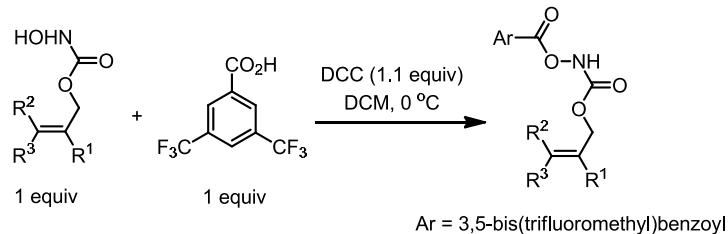
General Procedures:

Sodium methoxide (54 mg, 1 mmol, 0.1 equiv) prepared *in situ* from sodium metal (23 mg, 1 mmol) and anhydrous methanol (3 mL) was added to a solution of 2-cyanopyridine (1.04 g, 10 mmol, 1.0 equiv.) in MeOH (15 mL) and the reaction mixture was stirred at room temperature for 10 h. The reaction was then quenched with glacial acetic acid (57 μ L, 1 mmol) and the mixture was concentrated *in vacuo*. The residue was dissolved in anhydrous toluene (20 mL). Racemic *cis*-1-amino-2,3-dihydro-1H-inden-2-ol (1.49 g, 10 mmol, 1.0 equiv) was then added. The reaction mixture was stirred at 80 °C for 12 h. It was then concentrated *in vacuo* and purified by column flash chromatography on silica gel (dichloromethane–methanol, 10:1), **L3** was isolated as a colorless solid (1.75 g, 74%).

2-(Pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (L3): White solid (m.p. 110–112 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.57 (s, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.57 (s, 1H), 7.32–7.25 (m, 4H), 5.78 (d, J = 7.6 Hz, 1H), 5.57–5.53 (m, 1H), 3.53–3.42 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 149.6, 146.8, 141.6, 139.8, 136.5, 128.6, 127.5, 125.7, 125.5, 125.3, 124.1, 83.9, 77.1, 39.7; IR ν_{max} (neat)/cm⁻¹: 3399 (w), 3057 (w), 2156 (w), 1641 (m), 1475 (m), 1354 (s), 1284 (m), 1114 (s), 1081 (s), 988 (s), 801 (m), 744 (s); HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}^+ [\text{M} + \text{H}^+]$, 237.1028, found 237.1028.

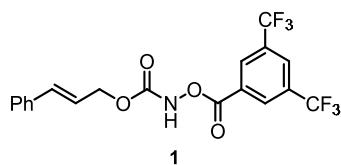
b. Synthesis of the Acyloxy Carbamate Substrates

The synthesis of acyloxy carbamate substrates was based on our previous reported procedure.²

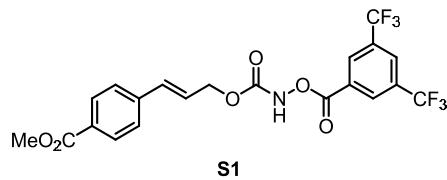


General Procedures:

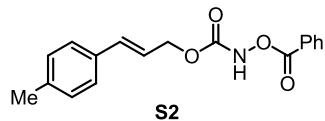
To a 25 mL flame-dried round bottom flask equipped with a magnetic stir bar, a hydroxyl carbamate (1.0 equiv), 3,5-bis(trifluoromethyl) benzoic acid (1.0 equiv) and anhydrous dichloromethane were added. After stirring at 0 °C for 5 min, DCC (1.0 equiv) was added in one portion. The reaction mixture was then stirred at 0 °C for additional 30 min. The solution was diluted with diethyl ether and then filtered to remove the *N,N*'-dicyclohexylurea (DCU). The filtrate was cooled in -20 °C refrigerator for 1 hour and filtered through a short celite pad to remove the rest of DCU. The filtrate was then concentrated *in vacuo* and purified by silica gel flash column chromatography with ethyl acetate/hexane as eluent or recrystallized with hexane and ethyl acetate directly (65–91% yields).



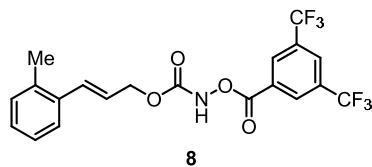
Cinnamyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (1): white solid (87% yield, m.p. 77–79 °C); ¹H NMR (400 MHz, CDCl₃): δ 8.61 (s, 1H), 8.54 (s, 2H), 8.14 (s, 1H), 7.39–7.30 (m, 5H), 6.70 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.8, 6.6 Hz, 1H), 4.90 (d, J = 6.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.3, 156.1, 135.7, 135.5, 132.6 (q, J = 34.4 Hz), 130.2–129.8 (m), 128.9, 128.6, 128.4, 127.6 (dt, J = 7.2, 3.6 Hz), 126.7, 122.6 (q, J = 273.1 Hz), 121.7, 67.7; ¹⁹F NMR (377 MHz, CDCl₃): δ -63.1 (s); IR ν_{max} (neat)/cm⁻¹: 3043 (w), 2956 (w), 1758 (m), 1281 (s), 1264 (s), 1210 (s), 1144 (s), 750 (s), 743 (s); HRMS (ESI, m/z): calcd for C₁₉H₁₂NO₄F₆⁻ [M - H⁺], 432.0671, found 432.0672.



(E)-Methyl-4-((3,5-bis(trifluoromethyl)benzoyl)oxy)carbamoyl)oxy)prop-1-en-1-yl benzoate (S1): White solid (82% yield, m.p. 119–121 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.93 (s, 1H), 8.52 (s, 2H), 8.12 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 15.9 Hz, 1H), 6.36 (dt, J = 15.9, 6.2 Hz, 1H), 4.89 (d, J = 6.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 163.3, 156.1, 140.2, 133.7, 132.6 (q, J = 34.4 Hz), 130.1–130.0 (m), 129.9, 129.6, 129.0, 127.5 (dt, J = 7.3, 3.7 Hz), 126.5, 124.6, 122.5 (q, J = 273.1 Hz), 67.0, 52.1. ^{19}F NMR (377 MHz, CDCl_3): δ -63.1 (s). IR ν_{max} (neat)/ cm^{-1} : 3065 (w), 2956 (w), 1755 (m), 1719 (s), 1265 (s), 1211 (s), 1112 (s), 701 (s), 682 (s). HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{14}\text{NO}_6\text{F}_6^-$ [M - H^+], 490.0725, found 490.0735.

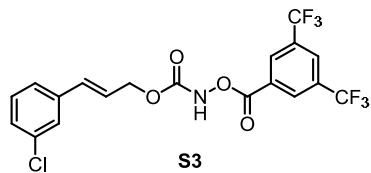


(E)-3-(p-tolyl)allyl benzoyloxycarbamate (S2): S2 is a known compound.²

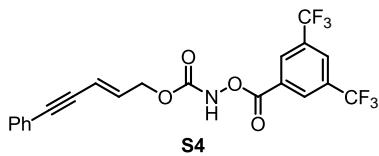


(E)-3-(o-Tolyl)allyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (8): White solid (79% yield, m.p. 97–99 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.55 (s, 2H), 8.42 (s, 1H), 8.15 (s, 1H), 7.44 (d, J = 6.4 Hz, 1H), 7.18–7.13 (m, 3H), 6.93 (d, J = 15.4 Hz, 1H), 6.18 (dt, J = 16.0, 6.4 Hz, 1H), 4.92 (d, J = 6.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 156.1,

135.8, 134.9, 133.4, 132.7 (q, $J = 34.4$ Hz), 130.4, 130.1, 129.0, 128.3, 127.6, 126.2, 125.9, 123.1, 122.6 (q, $J = 273.1$ Hz), 67.9, 19.7; ^{19}F NMR (377 MHz, CDCl_3): δ -63.1 (s); IR ν_{max} (neat)/ cm^{-1} : 3067 (w), 2955 (w), 1758 (m), 1719 (s), 1271 (s), 1213 (s), 705 (s), 683 (s); HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_4\text{F}_6^-$ [M - H^+], 446.0827, found 446.0825.

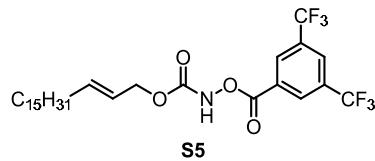


(E)-3-(3-Chlorophenyl)allyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S3): White solid (85% yield, m.p. 81–83 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.57 (s, 2H), 8.48 (s, 1H), 8.17 (s, 1H), 7.39 (s, 1H), 7.27 (s, 3H), 6.66 (d, $J = 15.9$ Hz, 1H), 6.32 (dt, $J = 15.8, 6.4$ Hz, 1H), 4.92 (d, $J = 6.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 155.9, 137.6, 134.6, 133.8, 132.7 (q, $J = 34.3$ Hz), 130.2–130.0 (m), 129.9, 128.9, 128.3, 127.9–127.5 (m), 124.9, 123.4, 122.6 (q, $J = 273.1$ Hz), 67.3; ^{19}F NMR (377 MHz, CDCl_3): δ -63.0 (s); IR ν_{max} (neat)/ cm^{-1} : 3263 (w), 2932 (w), 1755 (m), 1380 (m), 1276 (s), 1211 (s), 1181 (s), 1138 (s), 913 (s), 761 (s), 746 (s); HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{11}\text{NO}_4\text{F}_6\text{Cl}^-$ [M - H^+], 466.0281, found 466.0291.

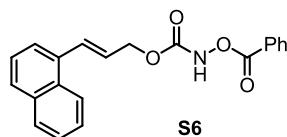


(E)-3-Phenylbut-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S4): white solid (84% yield, m.p. 73–75 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.55 (s, 2H), 8.49 (s, 1H), 8.15 (s, 1H), 7.43 (d, $J = 3.6$ Hz, 2H), 7.33–7.31 (m, 3H), 6.26 (dt, $J = 15.8, 6.2$ Hz, 1H), 6.03 (d, $J = 15.9$ Hz, 1H), 4.83 (d, $J = 5.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.3, 155.8, 134.7, 132.7 (q, $J = 34.4$ Hz), 131.6, 130.09–130.05 (m), 128.9, 128.3, 127.7–127.6 (m), 122.7, 122.6 (q, $J = 273.2$ Hz), 115.0, 91.6, 86.3, 66.6; ^{19}F NMR (377 MHz, CDCl_3): δ -63.0

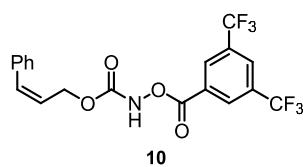
(s); IR ν_{max} (neat)/cm⁻¹: 3247 (w), 2912 (w), 1756 (m), 1382 (m), 1280 (s), 1211 (s), 1140 (s), 914 (s), 733 (s); HRMS (ESI, m/z): calcd for C₂₁H₁₂NO₄F₆⁻ [M - H⁺], 456.0671, found 456.0670.



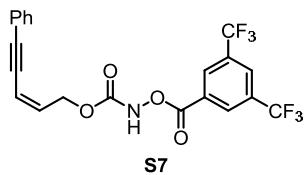
(E)-Octadec-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S5): White solid (65% yield, m.p. 83–85 °C); ¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 2H), 8.34 (s, 1H), 8.17 (s, 1H), 5.91–5.84 (m, 1H), 5.64–5.57 (m, 1H), 4.70 (d, J = 6.4 Hz, 2H), 2.11–2.06 (m, 2H), 1.40–1.28 (m, 26H), 0.90 (t, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 156.1, 138.4, 132.6 (q, J = 34.1 Hz), 130.1–130.0 (m), 129.1, 127.6–127.5 (m), 122.8 (q, J = 273.4 Hz), 122.6, 68.0, 32.2, 31.9, 29.70, 29.68, 29.58, 29.45, 29.36, 29.2, 28.8, 22.7, 14.1; ¹⁹F NMR (377 MHz, CDCl₃): δ -63.1 (s); IR ν_{max} (neat)/cm⁻¹: 3665 (s), 3215 (w), 2982 (s), 2901 (s), 1780 (m), 1724 (m), 1381 (m), 1290 (m), 1218 (s), 1069 (s), 895 (w); HRMS (ESI, m/z): calcd for C₂₈H₃₈NO₄F₆⁻ [M - H⁺], 566.2705, found 566.2714.



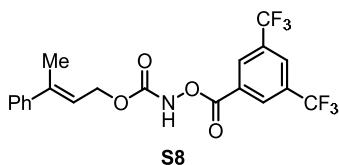
(E)-3-(naphthalen-1-yl)allyl benzoyloxycarbamate (S6): S6 is a known compound.²



(Z)-3-Phenylallyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (10): white solid (76% yield, m.p. 45–47 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.54 (s, 2H), 8.15 (s, 1H), 7.36–7.20 (m, 5H), 6.73 (d, J = 11.7 Hz, 1H), 5.85–5.80 (m, 1H), 5.01 (d, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 156.1, 135.6, 134.2, 132.6 (q, J = 34.4 Hz), 130.3–129.9(m), 128.9, 128.6, 128.4, 127.8, 127.6 (dt, J = 6.9, 3.6 Hz), 124.4, 122.6 (q, J = 273.2 Hz), 63.9; ^{19}F NMR (377 MHz, CDCl_3): δ -63.1 (s); IR ν_{max} (neat)/ cm^{-1} : 3255 (w), 2937 (w), 1749 (m), 1380 (m), 1277 (s), 1215 (s), 1138 (s), 913 (s), 682 (s); HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{12}\text{NO}_4\text{F}_6^-$ ($\text{M} - \text{H}^+$), 432.0671, found 432.0672.

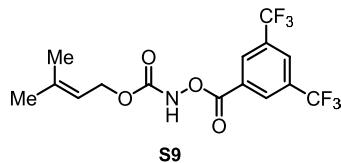


(Z)-3-Phenylbut-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S7): white solid (77% yield, m.p. Mp: 60–62 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.77 (s, 1H), 8.54 (s, 2H), 8.15 (s, 1H), 7.46–7.44 (m, 2H), 7.33–7.32 (m, 3H), 6.13–6.07 (m, 1H), 5.97 (d, J = 10.8 Hz, 1H), 5.11 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.3, 156.2, 134.4, 132.6 (q, J = 34.4 Hz), 131.6, 130.1 (m), 129.0, 128.7, 128.4, 127.6–127.5 (m), 123.2 (q, J = 273.2 Hz), 114.1, 96.6, 84.2, 64.7; ^{19}F NMR (377 MHz, CDCl_3): δ -63.0 (s); IR ν_{max} (neat)/ cm^{-1} : 3263 (w), 2942 (w), 1751 (s), 1382 (m), 1277 (s), 1210 (s), 1179 (s), 930 (s), 732 (s); HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{12}\text{NO}_4\text{F}_6^-$ [$\text{M} - \text{H}^+$], 456.0671, found 456.0673.

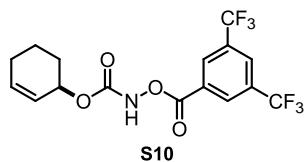


(E)-3-Phenylbut-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S8): White solid (81% yield, m.p. 66–68 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.55 (s, 2H), 8.39 (s, 1H), 8.15 (s, 1H), 7.43–7.28 (m, 5H), 5.92 (t, J = 7.1 Hz, 1H), 4.96 (d, J = 7.1 Hz, 2H), 2.15 (s,

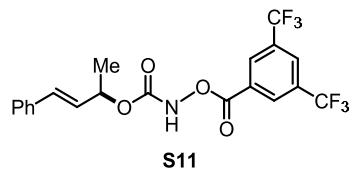
3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 156.2, 142.2, 141.9, 132.7 (q, $J = 34.1$ Hz), 130.2–129.9 (m), 129.0, 128.3, 127.8, 127.7–127.4 (m), 125.9, 122.6 (q, $J = 273.4$ Hz), 119.9, 64.2, 16.3; ^{19}F NMR (377 MHz, CDCl_3): δ -63.0 (s). IR ν_{max} (neat)/ cm^{-1} : 3060 (w), 1751 (m), 1385 (m), 1280 (s), 1211 (s), 1184 (s), 937 (m), 711 (s); HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_4\text{F}_6^-$ [M - H^+], 446.0827, found 446.0823.



3-Methylbut-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S9): White solid (84% yield, m.p. 78–80 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.54 (s, 2H), 8.36 (s, 1H), 8.14 (s, 1H), 5.39–5.36 (m, 1H), 4.74 (d, $J = 7.2$ Hz, 2H), 1.78 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 156.3, 141.0, 132.7 (q, $J = 34.0$ Hz), 130.07–130.04 (m), 129.1, 127.6–127.5 (m), 125.9, 122.6 (q, $J = 264.6$ Hz), 117.5, 64.0, 25.8, 18.1; ^{19}F NMR (377 MHz, CDCl_3): δ -63.1 (s); IR ν_{max} (neat)/ cm^{-1} : 3058 (w), 1757 (m), 1382 (m), 1280 (s), 1210 (s), 1185 (s), 914 (m), 732 (s), 703 (s); HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{12}\text{NO}_4\text{F}_6^-$ (M - H^+), 384.0671, found 384.0676.

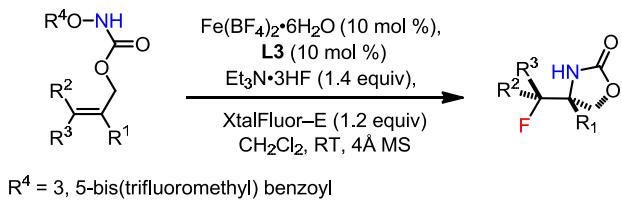


Cyclohex-2-en-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S10): White solid (76% yield, m.p. 94–96 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.55 (s, 3H), 8.15 (s, 1H), 6.03–6.00 (m, 1H), 5.78–5.76 (m, 1H), 5.32 (s, 1H), 2.12–1.66 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.5, 156.1, 133.9, 132.6 (q, $J = 34.4$ Hz), 130.04–130.01 (m), 129.2, 127.52–127.45 (m), 124.5, 122.6 (q, $J = 274.7$), 71.6, 28.2, 24.7, 18.5. ^{19}F NMR (377 MHz, CDCl_3): δ -63.2 (s). IR ν_{max} (neat)/ cm^{-1} : 3055 (w), 1762 (m), 1380 (m), 1277 (s), 1213 (s), 1185 (s), 907 (m), 737 (s). HRMS (ESI, m/z): calcd for $\text{C}_{16}\text{H}_{12}\text{NO}_4\text{F}_6^-$ [M - H^+], 396.0671, found 396.0677.



(E)-4-Phenylbut-3-en-2-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S11): White solid (89% yield, m.p. 72–74 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.61 (s, 1H), 8.56 (s, 2H), 8.16 (s, 1H), 7.40–7.27 (m, 5H), 6.68 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 16.0, 7.2 Hz, 1H), 5.64–5.57 (m, 1H), 1.53 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 155.8, 135.9, 132.9, 132.7 (q, J = 34.1 Hz), 130.1–130.0 (m), 129.1, 128.6, 128.2, 127.6–127.5 (m), 127.4, 126.7, 122.6 (q, J = 273.4 Hz), 74.9, 20.3; ^{19}F NMR (377 MHz, CDCl_3): δ -63.1 (s); IR ν_{max} (neat)/ cm^{-1} : 3063 (w), 1750 (m), 1385 (m), 1271 (s), 1208 (s), 1188 (s), 935 (m), 733 (s); HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_4\text{F}_6^-$ [M - H^+], 446.0827, found 446.0822.

D. Procedures for Iron(II)-Catalyzed Olefin Aminofluorination



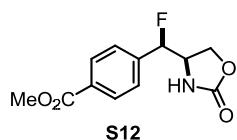
General Procedures:

Procedure A: To a flame-dried 5 mL vial (vial **A**) with freshly activated 4 Å molecular sieves (equal weight to starting material) and a magnetic stir bar were added $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 3.4 mg) and **L3** (0.01 mmol, 2.4 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. The mixture was stirred vigorously at room temperature for 20 minutes. During this time, to another flame-dried vial (vial **B**) was added Xtanfluor-E (0.12 mmol, 27.5 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. $\text{Et}_3\text{N}\cdot 3\text{HF}$ (0.14 mmol, 23 μL) was subsequently added into vial **B** and the solution was stirred for 3 minutes till it became clear. The vial **A** was cooled in an ice-water bath and the solution in vial **B** was added into it dropwise. The acyloxy carbamate (0.1 mmol, dissolved in 1 mL of DCM) was then added to vial **A** dropwise at the same temperature. The mixture was stirred at 0 °C for another 10 min and then kept stirring at room temperature until the acyloxy carbamate was consumed monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution (1 mL), the aqueous layer was separated and extracted by DCM (2 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash columns with 1:1 hexane and ethyl acetate as the eluant to afford β -fluoro oxazolidinone (45–75% yield).

Procedure B: To a flame-dried 5 mL vial (vial **A**) with freshly activated 4 Å molecular sieves (equal weight to starting material) and a magnetic stir bar were added $\text{Fe}(\text{NTf}_2)_2$ (0.01 mmol) and **L3** (0.02 mmol, 4.8 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. The mixture was stirred vigorously at room temperature for 20 minutes. During this time, to another flame-dried vial (vial **B**) was added Xtanfluor-E (0.12 mmol, 27.5 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added.

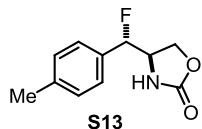
$\text{Et}_3\text{N}\cdot 3\text{HF}$ (0.14 mmol, 23 μL) was subsequently added into vial **B** and the solution was stirred for 3 minutes till it became clear. The vial **A** was cooled in an ice-water bath and the solution in vial **B** was added into it dropwise. The acyloxyl carbamate (0.1 mmol, dissolved in 1 mL of DCM) was then added to vial **A** dropwise at the same temperature. The mixture was stirred at 0 $^{\circ}\text{C}$ for another 10 min and then kept stirring at room temperature until the acyloxyl carbamate was consumed monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution (1 mL), the aqueous layer was separated and extracted by DCM (2 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash columns with 1:1 hexane and ethyl acetate as the eluant to afford the β -fluoro oxazolidinone.

Procedure C: To a flame-dried 5 mL vial (vial **A**) with freshly activated 4 \AA molecular sieves (equal weight to starting material) and a magnetic stir bar were added $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ (0.01 mmol, 3.4 mg) and **L3** (0.01 mmol, 2.4 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. The mixture was stirred vigorously at room temperature for 20 minutes. During this time, to another flame-dried vial (vial **B**) was added Xtanfluor-E (0.18 mmol, 41.3 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. $\text{Et}_3\text{N}\cdot 3\text{HF}$ (0.20 mmol, 33 μL) was subsequently added into vial **B** and the solution was stirred for 3 minutes till it became clear. The vial **A** was cooled in an ice-water bath and the solution in vial **B** was added into it dropwise. The acyloxyl carbamate (0.1 mmol, dissolved in 1 mL of DCM) was then added to vial **A** dropwise at the same temperature. The mixture was stirred at 0 $^{\circ}\text{C}$ for another 10 min and then kept stirring at room temperature until the acyloxyl carbamate was consumed monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution (1 mL), the aqueous layer was separated and extracted by DCM (2 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash columns with 3:1 toluene and ethyl acetate as the eluant to afford the β -fluoro oxazolidinone.



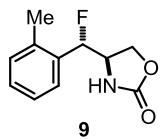
Methyl 4-(fluoro(-2-oxooxazolidin-4-yl)methyl)benzoate (S12):

S12 was synthesized according to the procedure B. White solid (m.p. 101–103 °C); ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 1H, minor diastereomer), 5.89 (s, 1H), 5.49 (dd, *J* = 46.4, 6.0 Hz, 1H), 5.46 (dd, *J* = 46.4, 6.0 Hz, minor diastereomer), 4.49–4.46 (m, 2H), 4.25–4.11 (m, 1H), 4.37–4.11 (m, 3H, minor diastereomer), 3.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 166.25 (minor diastereomer), 159.0, 158.8 (minor diastereomer), 139.7 (d, *J* = 20.0 Hz), 139.1 (d, *J* = 20.0 Hz, minor diastereomer), 131.5 (minor diastereomer), 131.3, 130.32 (minor diastereomer), 130.26, 126.1 (d, *J* = 7.0 Hz, minor diastereomer), 125.9 (d, *J* = 7.0 Hz), 93.6 (d, *J* = 179.0 Hz, minor diastereomer), 92.8 (d, *J* = 179.0 Hz), 66.2 (d, *J* = 4.0 Hz), 65.3 (d, *J* = 7.0 Hz, minor isomer), 56.5 (d, *J* = 24.0 Hz, minor diastereomer), 56.2 (d, *J* = 29.0 Hz), 52.39 (minor diastereomer), 52.37; ¹⁹F NMR (377 MHz, CDCl₃): δ -189.7 (dd, *J* = 46.4, 13.1 Hz), -185.9 (dd, *J* = 46.6, 14.6 Hz, minor diastereomer); IR ν_{max} (neat)/cm⁻¹: 3305 (w), 1756 (s), 1722 (s), 1408 (m), 1284 (s), 1113 (s), 1020 (m), 767 (m), 736 (m); HRMS (ESI, m/z): calcd for C₁₂H₁₃NO₄F⁺ [M + H⁺], 254.0829, found 254.0835.



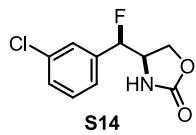
4-(Fluoro(p-tolyl)methyl)oxazolidin-2-one (S13):

S13 was synthesized according to the procedure C. White solid (m.p. 121–123 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.23 (m, 4H), 5.73 (s, 1H), 5.32 (dd, *J* = 46.8, 6.8 Hz, 1H), 4.54–4.52 (m, minor diasteromer), 4.43–4.19 (m, 2H), 4.13–4.09 (m, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 140.0, 131.4 (d, *J* = 20.2 Hz), 129.8, 126.4 (d, *J* = 6.1 Hz), 94.8 (d, *J* = 177.8 Hz), 65.4 (d, *J* = 7.1 Hz), 56.6 (d, *J* = 24.2 Hz), 21.3; ¹⁹F NMR (377 MHz, CDCl₃): δ -179.1 (dd, *J* = 47.3, 12.9 Hz), -185.25 (dd, *J* = 46.1, 10.7 Hz, minor diastereomer); IR ν_{max} (neat)/cm⁻¹: 3269 (w), 1756 (s), 1409 (m), 1236 (s), 1034 (s), 712 (m); HRMS (ESI, m/z): calcd for C₁₁H₁₃NO₂F⁺ [M + H⁺], 210.0930, found 210.0924.



4-(Fluoro(o-tolyl)methyl)oxazolidin-2-one (9):

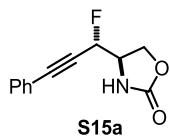
9 was synthesized according to the procedure B. White solid (m.p. 111–113 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.24 (m, 4H), 5.70 (s, 1H), 5.70–5.56 (1H, m, overlap with minor diasteromer), 5.39 (s, minor diasteromer), 4.61–4.51 (m, 2H, minor diastereomer), 4.40–4.21 (m, 2H, overlap with minor diasteromer), 4.14–4.11 (m, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.0, 158.8 (minor diastereomer), 135.5 (d, *J* = 5.1 Hz), 132.5 (d, *J* = 19.2 Hz), 131.3, 131.2 (minor diasteromer), 129.7 (d, *J* = 2.0 Hz), 126.7, 126.4 (d, *J* = 7.1 Hz), 91.6 (d, *J* = 17.8 Hz), 90.6 (d, *J* = 176.8 Hz, minor diasteromer), 66.9 (d, *J* = 2.0 Hz, minor diasteromer), 65.6 (d, *J* = 6.1 Hz), 55.7 (d, *J* = 24.2 Hz), 55.4 (d, *J* = 31.3 Hz, minor diasteromer), 19.3; ¹⁹F NMR (377 MHz, CDCl₃): δ -182.3 (dd, *J* = 46.9, 15.1 Hz), -187.4 (dd, *J* = 46.4, 11.8 Hz, minor diastereomer); IR ν_{max} (neat)/cm⁻¹: 3273 (w), 1753 (s), 1410 (m), 1230 (s), 1035 (m), 755 (m); HRMS (ESI, m/z): calcd for C₁₁H₁₃NO₂F⁺ [M + H⁺], 210.0930, found 210.0922.



4-((3-Chlorophenyl)fluoromethyl)oxazolidin-2-one (S14):

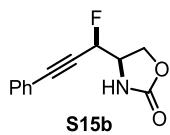
S14 was synthesized according to the procedure A. White solid (m.p. 75–77 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.41–7.37 (m, 3H), 7.25–7.24 (m, 1H), 6.04 (s, 1H, minor diasteromer), 5.91 (s, 1H), 5.38 (dd, *J* = 46.0, 6.2 Hz, 1H), 5.36 (dd, *J* = 46.0, 6.2 Hz, 1H, minor diastereomer), 4.53–4.49 (m, 1H), 4.38–4.34 (m, 1H, minor diastereomer), 4.22–4.11 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 158.9 (minor diastereomer), 137.0 (d, *J* = 20.2 Hz), 136.4 (d, *J* = 20.2 Hz, minor diastereomer), 135.3 (minor diastereomer), 135.2, 130.5 (minor diastereomer), 130.4, 130.0 (minor diastereomer), 129.8, 126.4 (d, *J* = 7.1 Hz, minor

diastereomer), 126.1 (d, $J = 7.1$ Hz), 124.3 (d, $J = 7.1$ Hz, diastereomer), 124.1 (d, $J = 6.1$ Hz), 93.5 (d, $J = 180.8$ Hz, minor diastereomer), 92.6 (d, $J = 181.8$ Hz), 66.3 (d, $J = 3.0$ Hz), 65.3 (d, $J = 6.1$ Hz, minor diastereomer), 56.5 (d, $J = 14.1$ Hz, minor diastereomer), 56.2 (d, $J = 30.3$ Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -184.3 (dd, $J = 46.5, 13.6$ Hz, minor diastereomer), -188.6 (dd, $J = 47.1, 9.4$ Hz); IR ν_{max} (neat)/ cm^{-1} : 3281 (w), 1750 (s), 1411 (m), 1234 (s), 1033 (m), 692 (m); HRMS (ESI, m/z): calcd for $\text{C}_{10}\text{H}_{10}\text{NO}_2\text{FCl}^+ [\text{M} + \text{H}^+]$, 230.0384, found 230.0390.



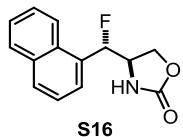
***anti*-4-(1-Fluoro-3-phenylprop-2-yn-1-yl)oxazolidin-2-one (S15a):**

S15a/b were synthesized according to the procedure A. The *anti* and *syn* diastereomers could be separated on silica gel column with toluene and ethyl acetate as eluent (toluene/ethyl acetate: 3:1). White solid (m.p. 121–123 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.50–7.48 (m, 2H), 7.44–7.35 (m, 3H), 5.88 (s, 1H), 5.28 (dd, $J = 48.4, 6.4$ Hz, 1H), 4.57 (t, $J = 9.1$ Hz, 1H), 4.42 (dd, $J = 9.4, 4.5$ Hz, 1H), 4.28–4.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.6, 132.1 (d, $J = 3.0$ Hz), 129.8, 128.5, 120.5 (d, $J = 4.0$ Hz), 90.9 (d, $J = 11.1$ Hz), 83.5 (d, $J = 176.8$ Hz), 80.4 (d, $J = 25.3$ Hz), 65.6 (d, $J = 4.0$ Hz), 55.5 (d, $J = 25.3$ Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -180.8 (dd, $J = 48.4, 11.4$ Hz); IR ν_{max} (neat)/ cm^{-1} : 3275 (w), 2233 (m), 1745 (s), 1407 (m), 1230 (s), 1026 (m), 758 (m); HRMS (ESI, m/z): calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{F}^+ [\text{M} + \text{H}^+]$, 220.0774, found 220.0772.



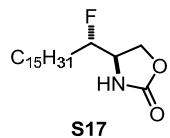
***syn*-4-(1-Fluoro-3-phenylprop-2-yn-1-yl)oxazolidin-2-one (S15b):** White solid (m.p. 92–94 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.50–7.48 (m, 2H), 7.42–7.33 (m, 3H), 5.56 (s, 1H), 5.28 (dd, $J = 48.0, 5.0$ Hz, 1H), 4.58 (t, $J = 8.9$ Hz, 1H), 4.47 (dd, $J = 9.3, 3.9$ Hz, 1H), 4.23 (ddd, J

δ = 13.7, 9.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.6, 132.2 (d, J = 2.0 Hz), 129.8, 128.5, 120.5 (d, J = 5.1 Hz), 91.0 (d, J = 11.1 Hz), 83.1 (d, J = 176.8 Hz), 80.4 (d, J = 28.3 Hz), 65.9 (d, J = 4.0 Hz), 55.2 (d, J = 26.3 Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -181.9 (dd, J = 47.9, 10.6 Hz); IR ν_{max} (neat)/ cm^{-1} : 3264 (w), 2231 (m), 1749 (s), 1409 (m), 1230 (s), 1029 (m), 758 (s); HRMS (ESI, m/z): calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{F}^+$ ($\text{M} + \text{H}^+$), 220.0774, found 220.0772.



4-(Fluoro(naphthalen-1-yl)methyl)oxazolidin-2-one (S16):

S18 was synthesized according to the procedure C. White solid (m.p. 93–95 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.01–7.94 (m, 3H), 7.64–7.53 (m, 4H), 6.12 (dd, J = 46.4, 6.4 Hz), 5.58 (s, 1H), 4.58–4.49 (m, 1H), 4.37 (t, J = 9.0 Hz, 1H), 4.24 (dd, J = 9.0, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.7, 133.9, 130.5 (d, J = 2.0 Hz), 130.0, (d, J = 7.1 Hz), 129.4, 127.2, 126.4, 125.2, 125.0 (d, J = 9.1 Hz), 122.4, 92.5 (d, J = 179.8 Hz), 65.8 (d, J = 6.1 Hz), 55.9 (d, J = 23.2 Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -185.5 (dd, J = 46.4, 15.7 Hz), -190.2 (dd, J = 45.6, 12.0 Hz, minor diastereomer); IR ν_{max} (neat)/ cm^{-1} : 3283 (w), 1752 (s), 1408 (m), 1252 (s), 1033 (m), 749 (s); HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{F}^+$ [$\text{M} + \text{H}^+$], 246.0930, found 246.0927.

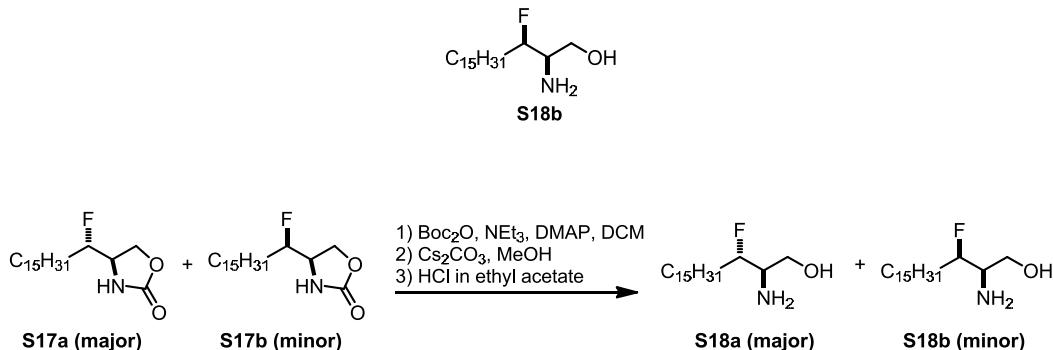


4-(1-Fluorohexadecyl)oxazolidin-2-one (S17):

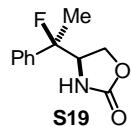
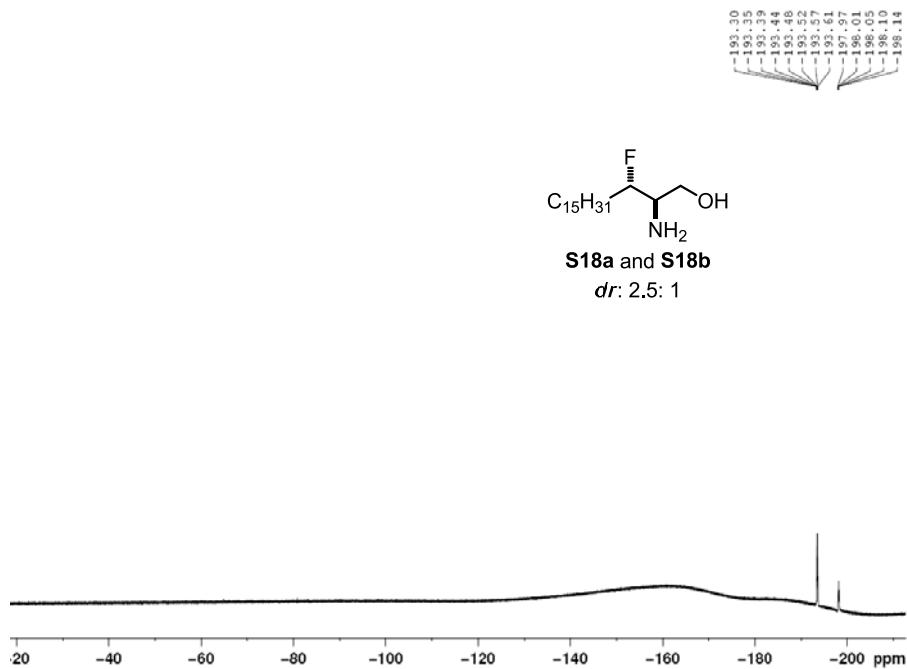
S19 was synthesized according to the procedure A. White solid (m.p. 79–81 °C); ^1H NMR (400 MHz, CDCl_3): δ 6.65–6.55 (m, 1H), 6.41–6.33 (m, 1H, minor isomer), 4.52–3.90 (m, 4H), 1.74–1.27 (m, 27H), 0.90 (t, 3H, J = 6.0 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 160.0, 159.5 (minor diasteromer), 93.7 (d, J = 174.6 Hz, minor diasteromer), 93.5 (d, J = 174.3 Hz),

66.5 (d, $J = 15.4$ Hz), 65.8 (d, $J = 8.6$ Hz, minor diasteromer), 55.3 (d, $J = 22.4$ Hz, minor diasteromer), 54.9 (d, $J = 26.1$ Hz), 31.9, 30.9, 29.71, 29.7, 29.699, 29.691, 29.7, 29.6, 29.5, 29.41, 29.37, 29.3, 24.82 (d, $J = 3.4$ Hz, minor diasteromer), 24.77 (d, $J = 3.0$ Hz), 22.7, 14.1; ^{19}F NMR (377 MHz, CDCl_3): δ -191.9—-192.1 (m, minor diasteromer), -194.0—-194.3 (m); IR ν_{max} (neat)/ cm^{-1} : 3200 (w), 3018 (m), 1761 (s), 1337 (m), 1269 (s), 1017 (m), 742 (s); HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{37}\text{NO}_2\text{F}^+ [\text{M} + \text{H}^+]$, 330.2808, found 330.2810.

Relative Stereochemistry Determination: the relative stereochemistry of **S17** was determined by comparison of ^{19}F NMR spectrum with a known compound **S18b**⁶ after derivatization. The minor diastereomer is in accordance with **S18b** on ^{19}F NMR.

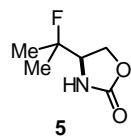
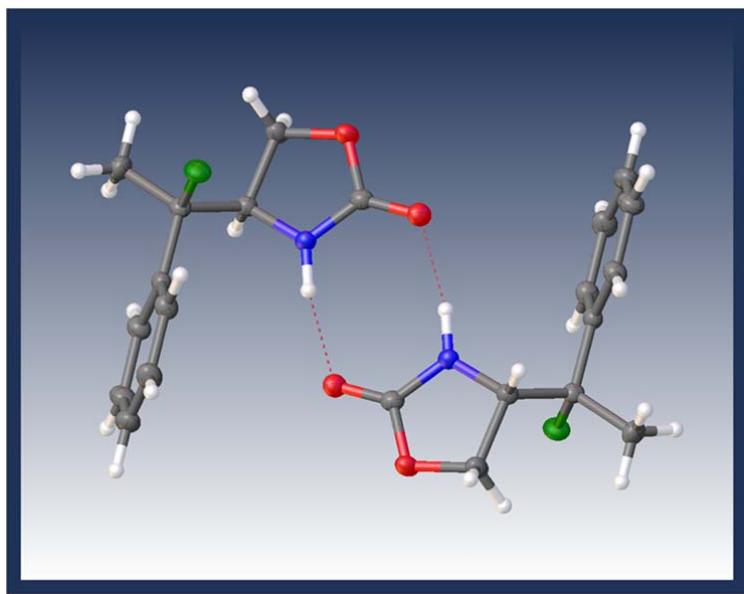


Spectrum	(Literature Data) ⁵	S18a (major)	S18b (minor)
^{19}F NMR	δ ^{19}F (377 MHz, MeOH- d_4): -198.7 (m)	δ ^{19}F (377 MHz, MeOH- d_4): -193.4 (m)	δ ^{19}F (377 MHz, MeOH- d_4): -198.1 (m)



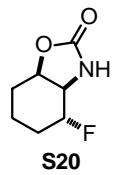
4-(1-Fluoro-1-phenylethyl)oxazolidin-2-one (S19):

S19 was synthesized according to the procedure A. The relative stereochemistry was determined by X-ray crystallographic analysis. White solid (m.p. 97–99 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.47–7.36 (m, 5H), 5.30 (s, 1H), 4.44–4.36 (m, 2H), 4.18 (ddd, J = 17.0, 8.6, 5.5 Hz, 1H), 1.72 (d, J = 22.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 139.7 (d, J = 22.2 Hz), 129.0, 128.8, 124.6 (d, J = 9.1 Hz), 96.3 (d, J = 179.8), 65.3 (d, J = 6.1 Hz), 59.9 (d, J = 26.3 Hz), 21.6 (d, J = 24.2 Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -159.5–159.9 (m); IR ν_{max} (neat)/cm $^{-1}$: 3209 (w), 1751 (s), 1377 (m), 1238 (s), 1033 (s), 949 (m), 741 (s); HRMS (ESI, m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{F}^+ [\text{M} + \text{H}^+]$, 210.0930, found 210.0932.



4-(2-Fluoropropan-2-yl)oxazolidin-2-one (5):

5 was synthesized according to the procedure A. White solid (m.p. 81–83 °C); ¹H NMR (400 MHz, CDCl₃): 7.00 (s, 1H), 4.46–4.42 (m, 1H), 4.30–4.27 (m, 1H), 3.92–3.85 (m, 1H), 1.36 (d, *J* = 22.4 Hz, 3H), 1.35 (d, *J* = 21.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.2, 94.6 (d, *J* = 172.3), 65.8 (d, *J* = 6.1 Hz), 59.1 (d, *J* = 26.3 Hz), 22.5 (d, *J* = 23.2 Hz), 22.3 (d, *J* = 24.2 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ -151.3–151.7 (m); IR ν_{max} (neat)/cm⁻¹: 3207 (w), 1762 (s), 1312 (s), 1213 (m), 737 (s); HRMS (ESI, m/z): calcd for C₆H₁₁NO₂F⁺ [M + H⁺], 148.0774, found 148.0774.



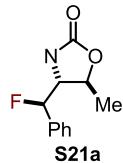
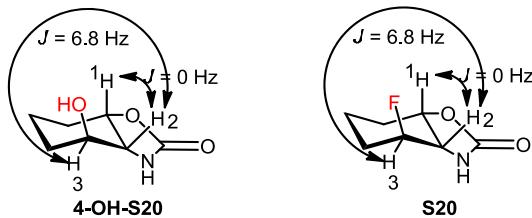
4-Fluorohexahydrobenzo[d]oxazol-2(3H)-one (S20):

S20 was synthesized according to the procedure A. White solid (m.p. 93–95 °C); ¹H NMR (400 MHz, CDCl₃): δ 5.53 (s, 1H), 4.79 (s, 1H), 4.62–4.46 (m, 1H), 3.70–3.63 (dt, *J* = 15.0,

6.8 Hz, 1H), 2.16–2.02 (2H, m), 1.76–1.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.1, 94.3 (d, J = 177.8), 77.2 (d, J = 24.2 Hz), 56.9 (d, J = 25.3 Hz), 27.2 (d, J = 18.2 Hz), 25.9, 16.9 (d, J = 9.1 Hz); ^{19}F NMR (377 MHz, CDCl_3): δ -181.1–181.2 (m); IR ν_{max} (neat)/ cm^{-1} : 3230 (w), 2953 (s), 1754 (s), 1365 (m), 1254 (s), 1103 (m), 737 (s); HRMS (ESI, m/z): calcd for $\text{C}_7\text{H}_{11}\text{NO}_2\text{F}^+ [\text{M} + \text{H}^+]$, 160.0774, found 160.0775.

Relative Stereochemistry Determination:

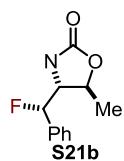
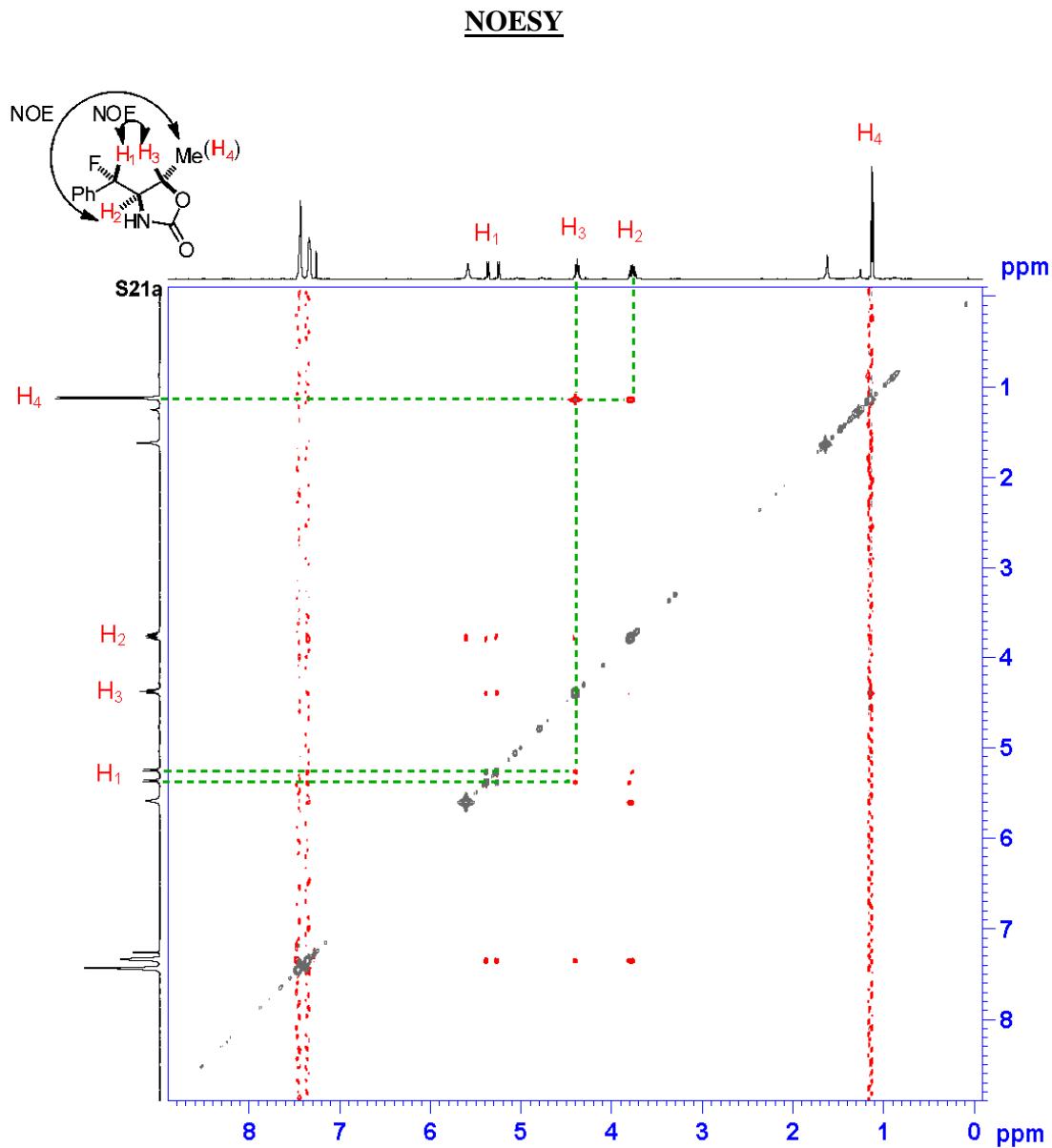
3J of H^1 – H^2 and H^2 – H^3 were compared with ones in an *anti*-hydroxyl oxazolidinone **4-OH S20** (a known compound) shown below.²



4-(Fluoro(phenyl)methyl)-5-methyloxazolidin-2-one (S21a):

S21a/b were synthesized according to the procedure A. Two diastereomers can be separated on silica gel column with hexane and ethyl acetate as the eluent. White solid (m.p. 66–68 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.47–7.46 (m, 3H), 7.36–7.35 (m, 2H), 5.61 (s, 1H), 5.33 (dd, J = 47.0, 7.2 Hz, 1H), 4.38 (p, J = 6.3 Hz, 1H), 3.82–3.76 (m, 1H), 1.15 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 157.9, 134.3 (d, J = 20.2 Hz), 129.9 (d, J = 2.0 Hz), 129.1, 126.4 (d, J = 6.1 Hz), 94.7 (d, J = 177.8 Hz), 73.9 (d, J = 6.1 Hz), 63.5 (d, J = 17.2 Hz), 20.3; ^{19}F NMR (377 MHz, CDCl_3): δ -178.4 (dd, J = 45.2, 15.1 Hz); IR ν_{max} (neat)/ cm^{-1} : 3235 (w), 2955 (s), 1750 (s), 1367 (m), 1200 (s), 1135 (m), 734 (s); HRMS (ESI, m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{F}^+ (\text{M} + \text{H}^+)$, 210.0930, found 210.0938.

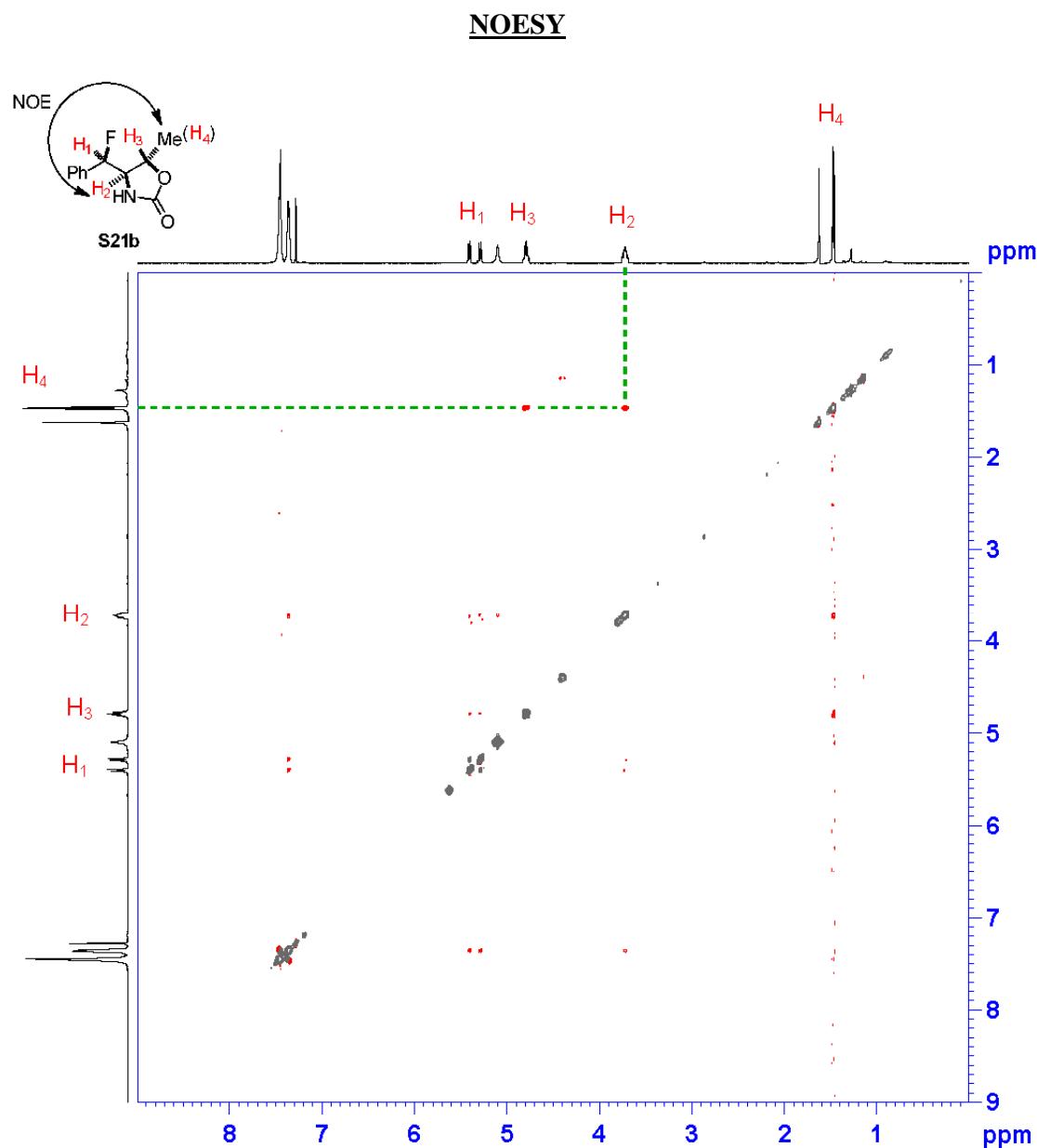
NOE Analysis:



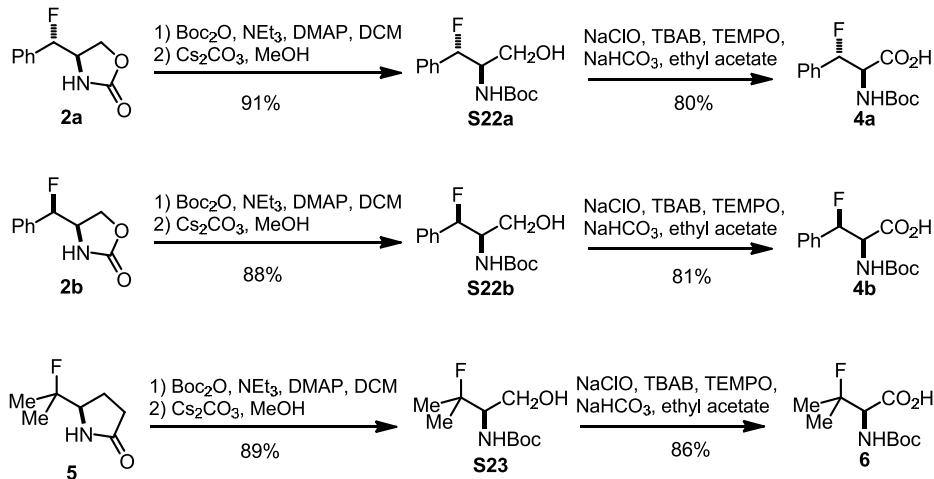
4-(Fluoro(phenyl)methyl)-5-methyloxazolidin-2-one (S21b): White solid (m.p. 92–94 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.45–7.43 (m, 3H), 7.36–7.34 (m, 2H), 5.31 (dd, J = 46.4, 7.4 Hz, 1H), 4.81–4.73 (m, 2H), 3.72–3.67 (m, 1H), 1.47 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100

MHz, CDCl_3): δ 157.8, 135.2 (d, $J = 19.2$ Hz), 129.8 (d, $J = 1.0$ Hz), 129.1, 126.2 (d, $J = 6.1$ Hz), 93.8 (d, $J = 178.8$ Hz), 76.1, 62.8 (d, $J = 32.3$ Hz), 21.0; ^{19}F NMR (377 MHz, CDCl_3): δ -185.4 (dd, $J = 49.0, 9.4$ Hz); IR ν_{max} (neat)/ cm^{-1} : 3201 (w), 2955 (s), 1753 (s), 1366 (m), 1209 (s), 1124 (m), 737 (s); HRMS (ESI, m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{F}^+(\text{M} + \text{H}^+)$, 210.0930, found 210.0934.

NOE Analysis:



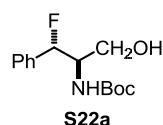
E. Synthetic Application for the Method Discovery: Synthesis of β -Fluoro Amino Acids



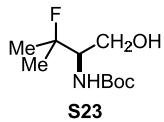
General Procedures: The β -fluoro oxazolidinone (**2** or **5**, 0.1 mmol) was dissolved in 2 mL anhydrous dichloromethane. To the above mentioned solution was added NEt_3 (0.12 mmol), DMAP (0.01 mmol) and Boc_2O (0.15 mmol) at room temperature. The mixture was continued to be stirred at room temperature until all the starting material was consumed (usually within 20 min). After evaporating all the solvent, the obtained mixture was purified by flash chromatography columns (hexane/ethyl acetate = 4/1).

The above obtained Boc protected product (0.1 mmol) was dissolved in 2 mL regular MeOH. Then a catalytic amount of Cs_2CO_3 (0.02 mmol) was added and the mixture was stirred at room temperature until all the starting material was consumed (ca. 2 hours). The reaction was quenched with saturated NH_4Cl solution and after evaporation of methanol, the aqueous phase was extracted by dichloromethane (4 \times 5 mL) and then dried over anhydrous Na_2SO_4 . The product was purified by column chromatography to afford product (91% yield for **S22a**, 88% yield for **S22b** and 89% yield for **S23**).

The *syn* β -fluoro amino alcohol **S22b** is a known compound.¹



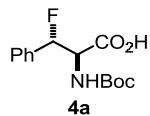
tert-Butyl (1-fluoro-3-hydroxy-1-phenylpropan-2-yl)carbamate (S22a): white solid (m.p. 72–74 °C); ¹H NMR (400 MHz, CDCl₃, 55 °C): δ 7.40–7.33 (m, 5H), 5.71 (d, *J* = 46.4 Hz), 4.98 (s, 1H), 4.05–4.00 (m, 1H), 3.77–3.65 (m, 2H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 136.8, 128.54, 128.48, 125.7 (d, *J* = 8.1 Hz), 92.6 (d, *J* = 174.7 Hz), 80.1, 62.2, 56.6 (d, *J* = 22.2 Hz), 28.2; ¹⁹F NMR (377 MHz, CDCl₃): δ -193.8, -195.8 (minor rotamer); IR ν_{max} (neat)/cm⁻¹: 3426 (w), 2979 (w), 1691 (s), 1367 (m), 1165 (s), 1058 (m), 737 (s); HRMS (ESI, m/z): calcd for C₁₄H₁₉NO₃F⁻ [M - H⁺], 268.1349, found 268.1351.



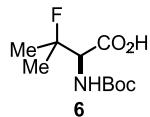
tert-Butyl (3-fluoro-1-hydroxy-3-methylbutan-2-yl)carbamate (S23): white solid (m.p. 83–85 °C); ¹H NMR (400 MHz, CDCl₃): δ 5.09 (s, 1H), 3.88–3.84 (m, 1H), 3.74–3.66 (m, 2H), 2.03 (s, 1H), 1.48 (s, 9H), 1.45 (d, 3H, *J* = 20.8 Hz), 1.43 (d, 3H, *J* = 22.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 156.6, 97.4 (d, *J* = 168.7 Hz), 79.9, 61.9, 58.3 (d, *J* = 21.2 Hz), 28.3, 24.8 (d, *J* = 10.1 Hz), 24.5 (d, *J* = 10.1 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ -149.4–-149.6 (m); IR ν_{max} (neat)/cm⁻¹: 2980 (w), 1720 (s), 1369 (m), 1161 (s), 1029 (m), 701 (s); HRMS (ESI, m/z): calcd for C₁₀H₁₉NO₃F⁻ [M - H⁺], 220.1349, found 220.1347.

The alcohol oxidation was performed by following a known procedure:¹ S22 or S23 (0.2 mmol) was dissolved in ethyl acetate (2 mL), then water (1 mL), TEMPO (1.0 mg), (n-Bu)₄NBr (1.0 mg), and NaHCO₃ (60 mg) were added successively. Commercial bleach (0.5 mL) was added into this mixture (ice bath) dropwise with vigorous stirring, and the solution was stirred for additional 30 min at 0 °C. After the reaction was diluted with EtOAC, the organic phase was extracted with saturated NaHCO₃ aqueous solution. To the combined aqueous phase was added NaHSO₃ (80 mg) slowly, followed by dropwise addition of 10% HCl aq to adjust pH to ca. 3. This cloudy mixture was extracted by ethyl acetate, washed with saturated brine, dried over Na₂SO₄, then evaporated in *vacuo*. The residue was purified on

silica gel column to give the acid as a white solid (80% yield for **4a**, 81% yield for **4b** and 86% for **6**).

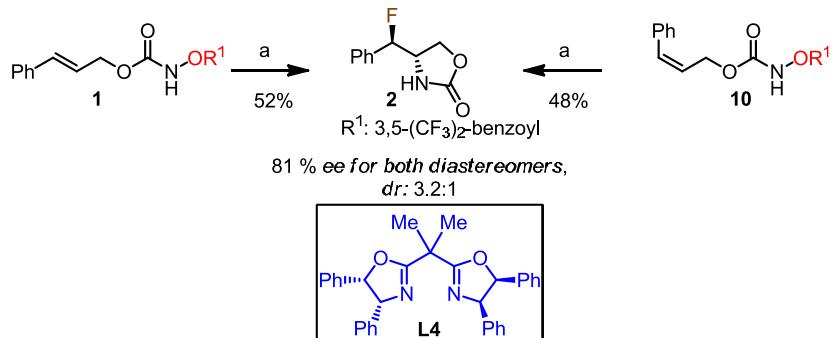


2-((tert-Butoxycarbonyl)amino)-3-fluoro-3-phenylpropanoic acid (4a): white solid (m.p. 96–98 °C); ¹H NMR (400 MHz, CDCl₃, 55 °C): δ 8.38 (brs, 1H), 7.38 (s, 5H), 6.07 (d, *J* = 45.6 Hz), 5.23 (s, 1H), 4.87–4.81 (m, 1H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CD₃OD): δ 172.5, 157.8, 137.9 (d, *J* = 21.0 Hz), 129.5, 129.3, 126.8 (d, *J* = 8.0 Hz), 94.5 (d, *J* = 176.0 Hz), 80.8, 59.7 (d, *J* = 22.0 Hz), 28.6; ¹⁹F NMR (377 MHz, CDCl₃): δ -193.2 (minor rotamer, dd, *J* = 45.2, 26.4 Hz), -195.4 (dd, *J* = 79.2, 33.9 Hz); IR ν_{max} (neat)/cm⁻¹: 3426 (w), 2982 (w), 1694 (s), 1368 (m), 1170 (s), 1057 (m), 739 (s); HRMS (ESI, m/z): calcd for C₁₄H₁₇NO₄F⁻ [M - H⁺], 282.1142, found 282.1136.



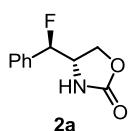
2-((tert-Butoxycarbonyl)amino)-3-fluoro-3-methylbutanoic acid (6): white solid (m.p. 147–149 °C); ¹H NMR (400 MHz, *d*₆-acetone): δ 6.15 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 18.0, 1.6 Hz, 1H), 1.53–1.43 (m, 15H); ¹³C NMR (100 MHz, *d*₆-acetone): δ 170.3 (d, *J* = 3.0 Hz), 155.5, 94.7 (d, *J* = 174.0 Hz), 78.8, 60.3 (d, *J* = 24.0 Hz), 27.6, 24.0 (d, *J* = 24.0 Hz), 23.8 (d, *J* = 23.0 Hz); ¹⁹F NMR (377 MHz, *d*₆-acetone): δ -146.4–146.7 (m). IR ν_{max} (neat)/cm⁻¹: 2984 (w), 1717 (s), 1369 (m), 1159 (s), 1055 (m), 737 (s); HRMS (ESI, m/z): calcd for C₁₀H₁₇NO₄F⁻ [M - H⁺], 234.1142, found 234.1138.

F. Iron-Catalyzed Enantioselective Olefin Aminofluorination

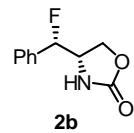


^aFe(BF₄)₂·6H₂O (20 mol %), **L4** (20 mol %); Et₃N·3HF (1.4 equiv), XtalFluor-E (1.2 equiv), CH₂Cl₂, -30 °C, 4 Å molecular sieves, 12 h.

a. **Procedure for the Iron-Catalyzed Asymmetric Olefin Aminofluorination:** To a flame-dried 5 mL vial (vial **A**) with freshly activated 4 Å molecular sieves (equal weight to starting material) and a magnetic stir bar were added Fe(BF₄)₂·6H₂O (0.02 mmol) and **L4** (0.02 mmol). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. The mixture was stirred vigorously at room temperature for 20 minutes. During this time, to another flame-dried vial (vial **B**) was added Xtanfluor-E (0.12 mmol, 27.5 mg). After the vial was evacuated and backfilled with Argon for three times, anhydrous and degassed DCM (1.0 mL) was added. Et₃N·3HF (0.14 mmol, 23 μL) was subsequently added into vial **B** and the solution was stirred for 3 minutes till it became clear. The vial **A** was cooled to -30 °C and the solution in vial **B** was added into it dropwise. The acyloxyl carbamate **1** or **10** (0.1 mmol, dissolved in 1 mL of DCM) was then added to vial **A** dropwise at the same temperature. The mixture was stirred at -30 °C for 12 h until the acyloxyl carbamate was consumed monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution (1 mL), the aqueous layer was separated and extracted by DCM (2 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash columns with 1:1 hexane and ethyl acetate as the eluant to afford β-fluoro oxazolidinone **2a/2b**.



$[\alpha]_D^{20} = +47.3$ (*c* 0.7, CH₂Cl₂, 81% *ee*)

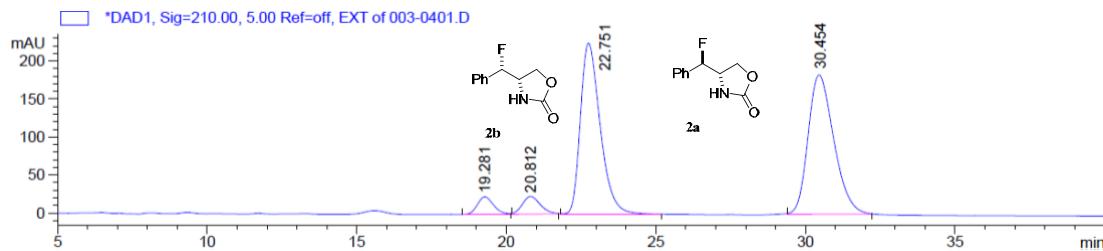


$$[\alpha]_D^{20} = +13.2 \ (c \ 0.3, \text{CH}_2\text{Cl}_2, 81\% \text{ ee})$$

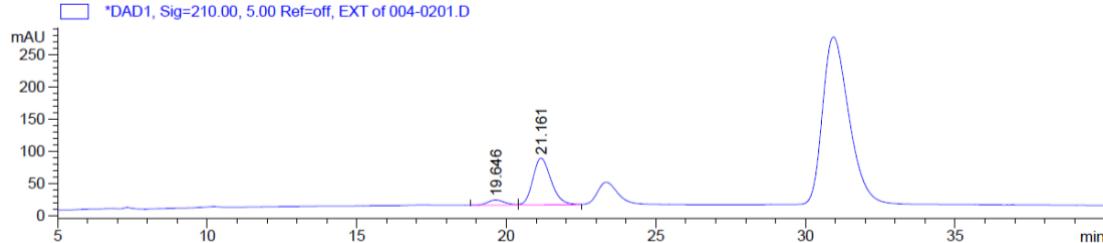
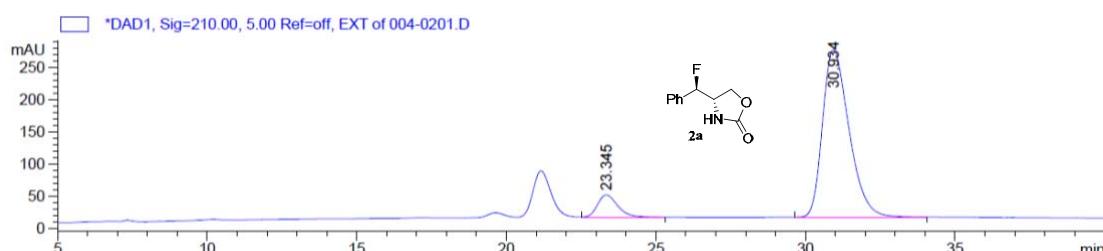
b. HPLC Data:

The samples were analyzed by Chiral HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 210 nm, 20% IPA in hexane)

Racemic sample:

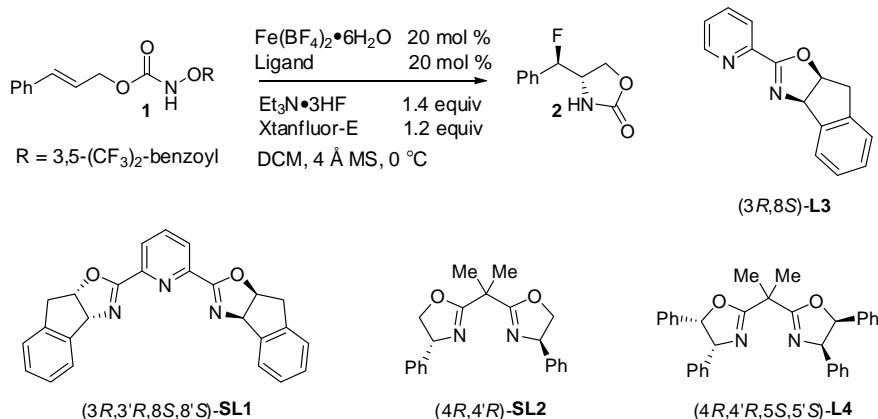


Enantio-enriched sample (81% ee for both diastereomers)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.646	MF	0.6474	300.15857	7.72774	8.9394
2	21.161	FM	0.7034	3057.54443	72.44723	91.0606

c. Structure-Enantioselectivity Relationship of Chiral Catalysts:



ligand	ee of 2
L3	-23%
SL1	5%
SL2	54%
SL3	71%

G. ESI-TOF MS Studies of the Catalyst Complex: $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}-\text{L3}$ in the Presence of $\text{Et}_3\text{N}\cdot 3\text{HF}$

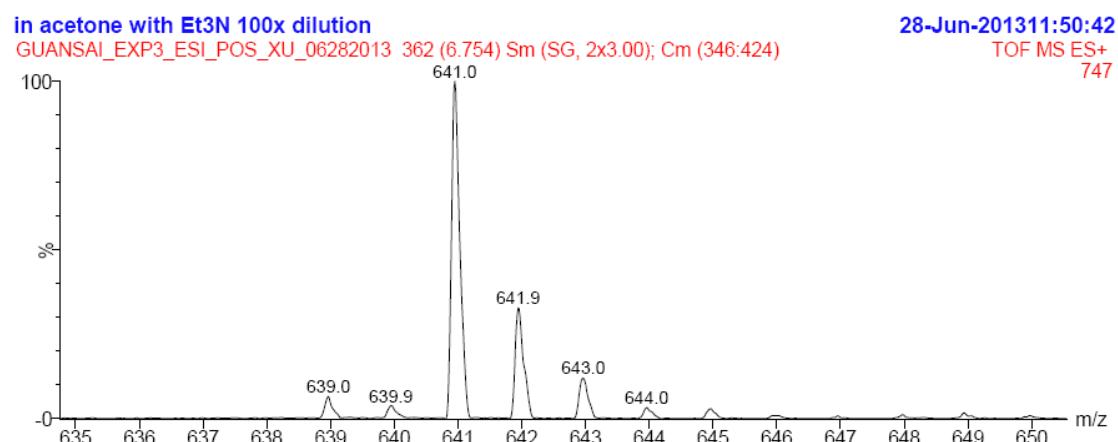
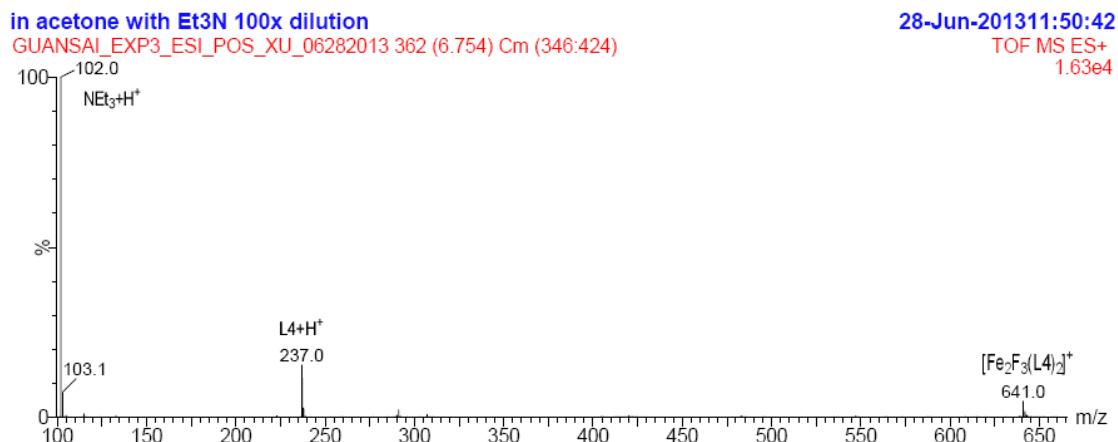
a. Sample Preparation:

To a flame-dried 5 mL vial with activated 4 Å molecular sieves and magnetic stir bar were added $\text{Fe}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ (0.01 mmol, 3.4 mg) and ligand **L3** (0.01 mmol, 2.4 mg). After evacuation upon oil pump and refill with Ar gas three times, anhydrous and degassed acetone (1.0 mL) was added. The obtained solution was stirred vigorously at room temperature for 15 min. $\text{Et}_3\text{N}\cdot 3\text{HF}$ (0.1 mmol) was then added dropwise and the red color gradually disappeared. 0.2 mL supernatant was syringed out and diluted 100 times with anhydrous acetone for MS analysis.

b. MS Analysis:

Mass spectrometry analyses were performed on a Micromass Q-Tof mass spectrometer (Waters, Milford, MA, USA.) equipped with an electrospray ion source. Optimal ESI conditions were capillary voltage of 3200 V, sample cone voltage 60 V, extraction cone voltage 2 V, source temperature 100 °C, Desolvation temperature 150 °C. Nitrogen was used as desolvation gas (500 L/h). Samples were introduced into the mass spectrometer ion source by direct injection at a speed of 5 μ L/min. Mass spectrometer was scanned from m/z 100-1000, at a rate of 1 s per scan. Accurate mass were determined via internal calibration compound, reserpine with m/z 609.2812.

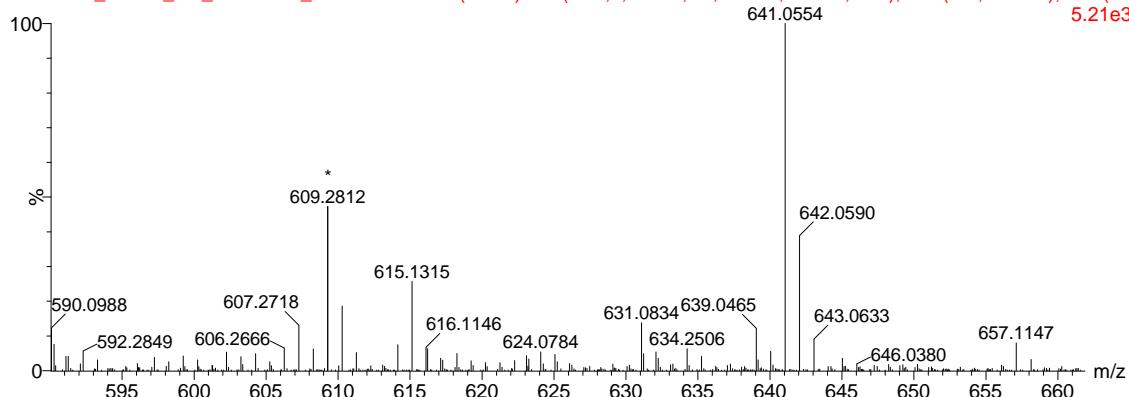
Low resolution ESI-MS:



High resolution ESI-MS:

05-Jul-2013 15:32:48

GUANSAI_GSL-2_XU_07052013_ESI-POS03 268 (4.970) AM (Cen,2, 80.00, Ar,5000.0,609.28,1.00); Sm (SG, 2x3.00); Cm (21: 5.21e3



Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

19500 formula(e) evaluated with 287 results within limits (all results (up to 1000) for each mass)

Elements Used:

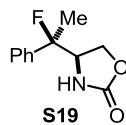
C: 1-150 H: 1-150 N: 1-30 O: 1-60 F: 1-6 Fe: 1-2

Minimum: -1.5

Maximum: 5.0 5.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
641.0554	641.0550	0.4	0.6	19.5	1.5	C ₃₀ H ₂₄ N ₄ O ₂ F ₃ Fe ₂

H. X-ray Crystallographic Analysis of S19:



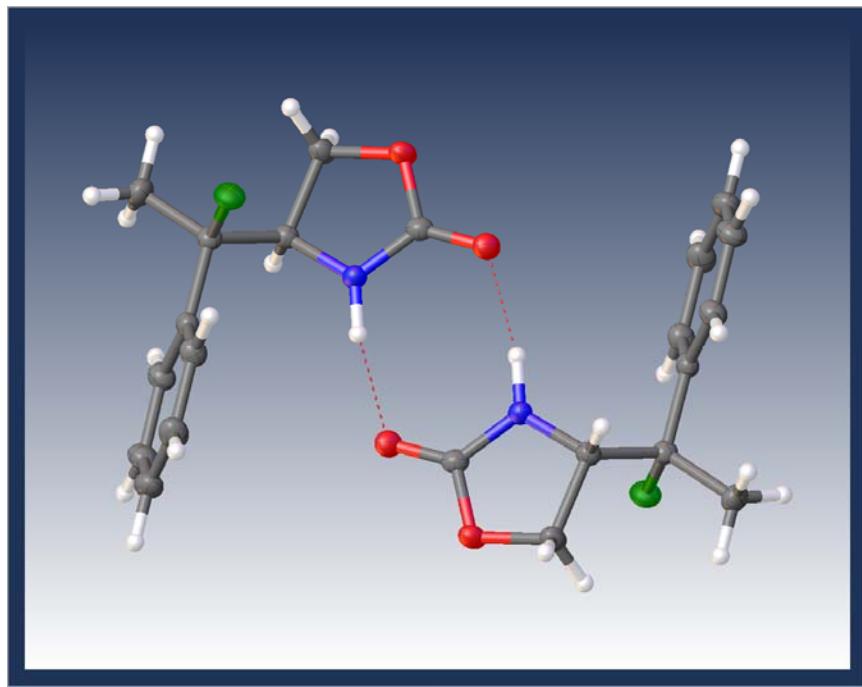


Table 1. Crystal data and structure refinement for gsl.

Identification code	gsl	
Empirical formula	C11 H12 F N O2	
Formula weight	209.22	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	$a = 11.272(2)$ Å	$\beta = 90^\circ$.
	$b = 5.8049(10)$ Å	$\gamma = 108.477(3)^\circ$.
	$c = 16.158(3)$ Å	$\alpha = 90^\circ$.
Volume	$1002.8(3)$ Å ³	
Z	4	
Density (calculated)	1.386 Mg/m ³	
Absorption coefficient	0.108 mm ⁻¹	
F(000)	440	

Crystal size	0.806 x 0.267 x 0.12 mm ³
Theta range for data collection	1.947 to 31.112°
Index ranges	-16<=h<=11, -8<=k<=8, -21<=l<=23
Reflections collected	8274
Independent reflections	3131 [R(int) = 0.0346]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7462 and 0.6507
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3131 / 10 / 184
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1268
R indices (all data)	R1 = 0.0655, wR2 = 0.1401
Extinction coefficient	n/a
Largest diff. peak and hole	0.478 and -0.253 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for gsl. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
F(1)	1395(1)	7799(1)	4863(1)	24(1)
O(1)	2758(1)	6984(2)	3273(1)	25(1)
O(2)	4111(1)	4164(2)	3889(1)	25(1)
N(1)	3807(1)	7293(2)	4676(1)	21(1)
C(3)	3617(1)	5993(2)	3959(1)	19(1)
C(4)	2243(1)	9671(2)	5078(1)	18(1)
C(6)	2998(1)	9491(2)	6036(1)	18(1)
C(2)	3097(1)	9420(2)	4509(1)	18(1)
C(7)	2867(1)	7629(2)	6541(1)	22(1)
C(11)	3867(1)	11213(2)	6420(1)	22(1)
C(1)	2405(1)	9209(2)	3522(1)	22(1)
C(10)	4593(1)	11062(3)	7289(1)	27(1)
C(8)	3594(2)	7495(2)	7420(1)	28(1)
C(9)	4454(1)	9202(3)	7791(1)	28(1)
C(5)	1469(1)	11868(2)	4863(1)	27(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for gsl.

F(1)-C(4)	1.4159(14)
O(1)-C(3)	1.3474(15)
O(1)-C(1)	1.4468(16)
O(2)-C(3)	1.2210(16)

N(1)-C(3)	1.3424(16)
N(1)-C(2)	1.4494(16)
C(4)-C(6)	1.5150(17)
C(4)-C(2)	1.5346(17)
C(4)-C(5)	1.5220(18)
C(6)-C(7)	1.3903(17)
C(6)-C(11)	1.3988(18)
C(2)-C(1)	1.5420(17)
C(7)-C(8)	1.3980(19)
C(11)-C(10)	1.3860(18)
C(10)-C(9)	1.390(2)
C(8)-C(9)	1.384(2)
C(3)-O(1)-C(1)	109.92(10)
C(3)-N(1)-C(2)	112.95(10)
O(2)-C(3)-O(1)	121.68(11)
O(2)-C(3)-N(1)	127.98(12)
N(1)-C(3)-O(1)	110.35(11)
F(1)-C(4)-C(6)	108.38(9)
F(1)-C(4)-C(2)	106.39(9)
F(1)-C(4)-C(5)	107.07(10)
C(6)-C(4)-C(2)	110.48(10)
C(6)-C(4)-C(5)	112.76(10)
C(5)-C(4)-C(2)	111.45(10)
C(7)-C(6)-C(4)	121.56(11)
C(7)-C(6)-C(11)	119.02(12)
C(11)-C(6)-C(4)	119.40(11)
N(1)-C(2)-C(4)	112.56(10)
N(1)-C(2)-C(1)	101.17(9)
C(4)-C(2)-C(1)	114.77(11)
C(6)-C(7)-C(8)	120.14(12)

C(10)-C(11)-C(6)	120.64(12)
O(1)-C(1)-C(2)	105.40(10)
C(11)-C(10)-C(9)	120.09(13)
C(9)-C(8)-C(7)	120.37(13)
C(8)-C(9)-C(10)	119.74(12)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for gsl. The anisotropic displacement factor exponent takes the form: $-2\Box^2 [h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
F(1)	20(1)	26(1)	24(1)	-3(1)	5(1)	-7(1)
O(1)	30(1)	24(1)	17(1)	-2(1)	0(1)	6(1)
O(2)	27(1)	20(1)	24(1)	-3(1)	3(1)	3(1)
N(1)	22(1)	24(1)	16(1)	0(1)	3(1)	6(1)
C(3)	18(1)	20(1)	18(1)	2(1)	4(1)	-2(1)
C(4)	17(1)	17(1)	19(1)	-1(1)	5(1)	-2(1)
C(6)	18(1)	19(1)	17(1)	-1(1)	7(1)	1(1)
C(2)	19(1)	19(1)	16(1)	1(1)	5(1)	-1(1)
C(7)	28(1)	19(1)	22(1)	0(1)	10(1)	-2(1)
C(11)	23(1)	23(1)	21(1)	-2(1)	7(1)	-3(1)
C(1)	28(1)	21(1)	16(1)	1(1)	4(1)	5(1)
C(10)	25(1)	31(1)	22(1)	-5(1)	4(1)	-4(1)
C(8)	37(1)	26(1)	21(1)	5(1)	11(1)	5(1)
C(9)	30(1)	35(1)	18(1)	0(1)	4(1)	6(1)
C(5)	26(1)	26(1)	26(1)	1(1)	6(1)	9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for gsl.

	x	y	z	U(eq)
H(1)	4438(15)	6880(30)	5214(9)	47(5)
H(2)	3664(15)	10720(30)	4635(10)	20(4)
H(1A)	1462(12)	9200(30)	3385(11)	24(4)
H(1B)	2684(17)	10380(30)	3157(11)	33(5)
H(5A)	925(15)	11870(30)	4251(6)	33(4)
H(5B)	2036(15)	13210(20)	4975(12)	39(5)
H(5C)	948(14)	11990(30)	5250(9)	30(4)
H(11)	3956(18)	12560(30)	6075(12)	37(5)
H(10)	5192(17)	12300(30)	7542(12)	39(5)
H(7)	2242(13)	6430(20)	6287(10)	26(4)
H(9)	4970(15)	9110(30)	8410(7)	38(5)
H(8)	3457(18)	6190(20)	7771(11)	39(5)

Table 6. Hydrogen bonds for gsl [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
N(1)-H(1)...O(2)#1	0.964(9)	1.906(10)	2.8541(15)	167.2(19)

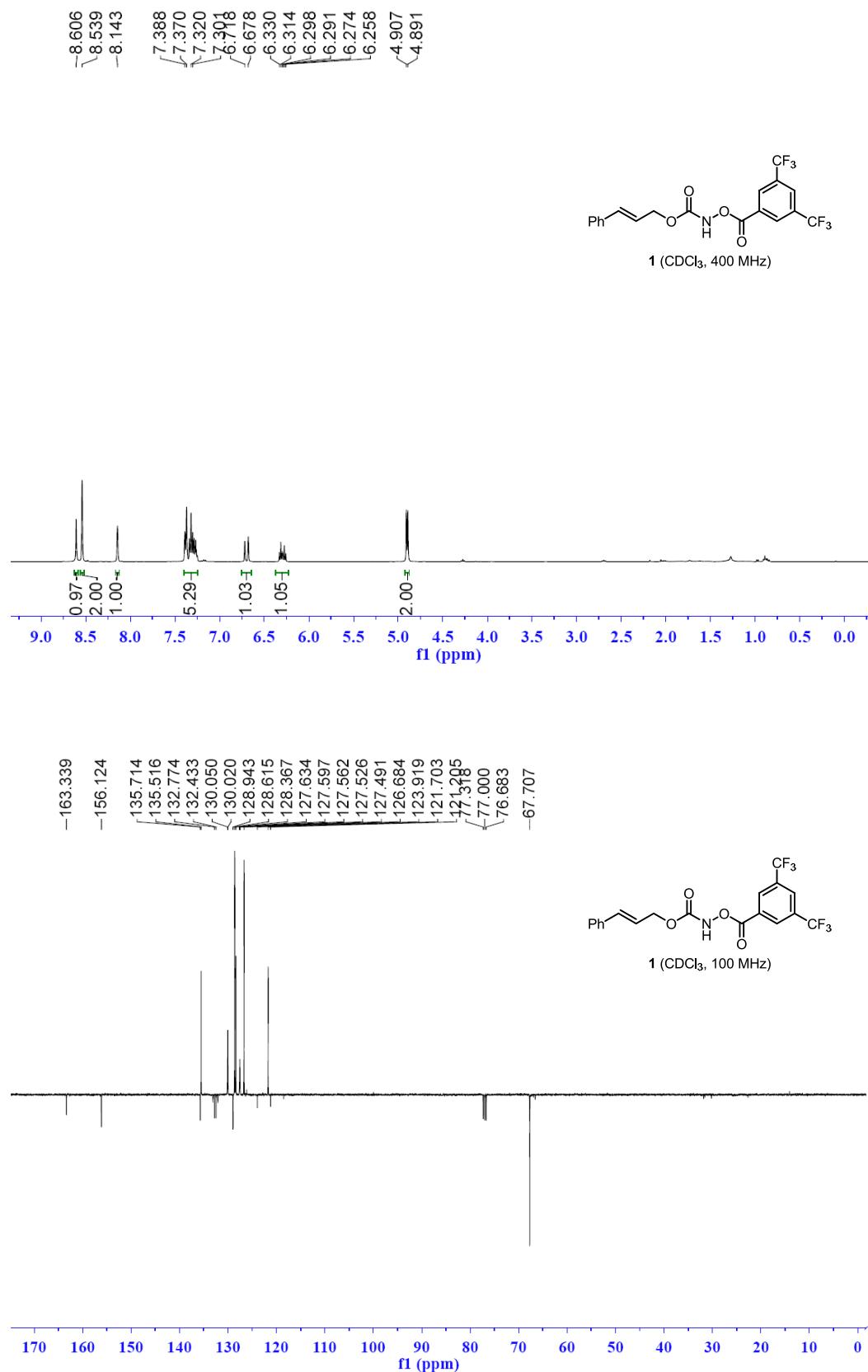
Symmetry transformations used to generate equivalent atoms:

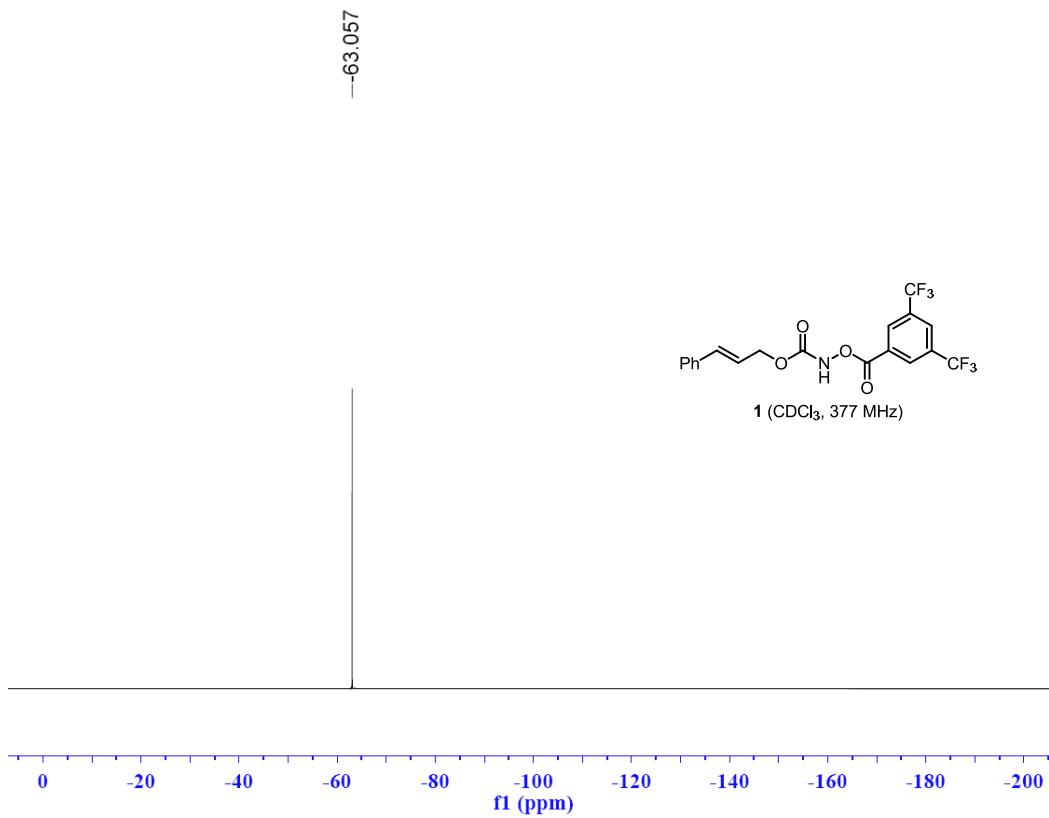
#1 -x+1,-y+1,-z+1

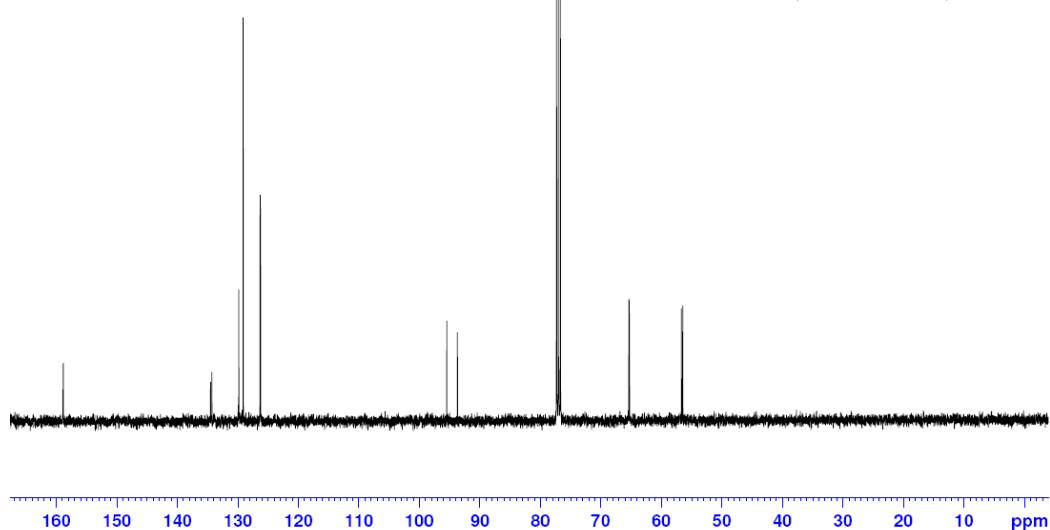
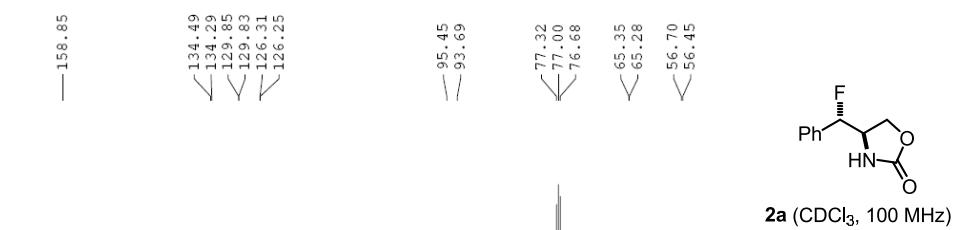
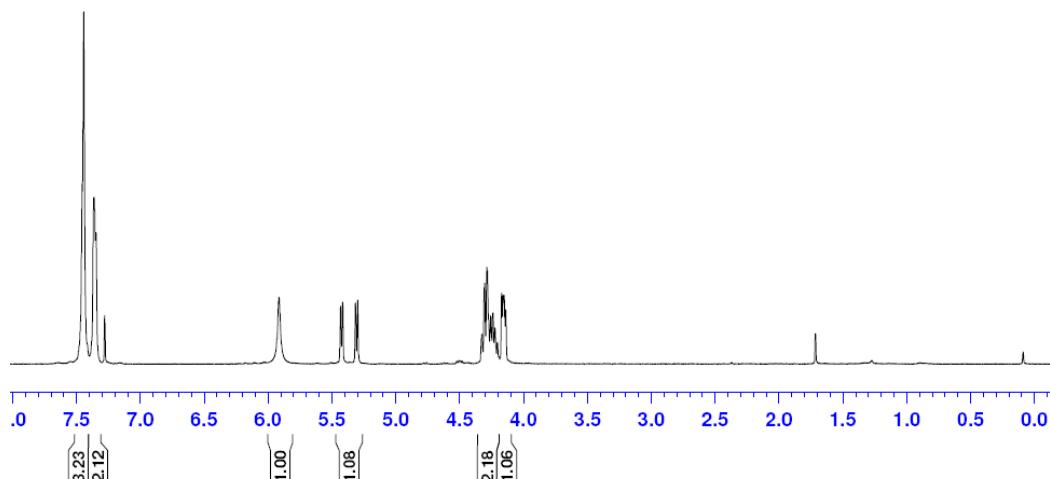
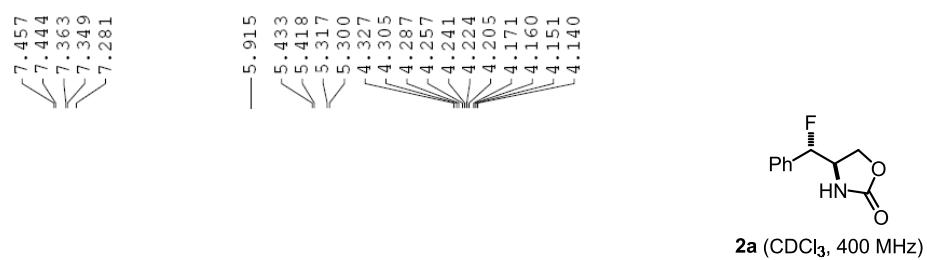
I. References:

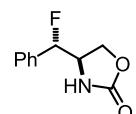
1. Okuda, K.; Hirota, T.; Kingery, D. A.; Nagasawa, H., *J. Org. Chem.* **2009**, *74*, 2609-2612.
2. Liu, G.-S.; Zhang, Y.-Q.; Yuan, Y.-A.; Xu, H., *J. Am. Chem. Soc.* **2013**, *135*, 3343-3346.
3. Lebel, H.; Lectard, S.; Parmentier, M., *Org. Lett.* **2007**, *9*, 4797-4800.
4. Knapp, S.; Kukkola, P. J.; Sharma, S.; Dhar, T. G. M.; Naughton, A. B. J., *J. Org. Chem.* **1990**, *55*, 5700-5710.
5. Davenport, A. J.; Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R., *J. Chem. Soc., Dalton Trans.* **2000**, 4432-4441.
6. Cresswell, A. J.; Davies, S. G.; Lee, J. A.; Morris, M. J.; Roberts, P. M.; Thomson, J. E., *J. Org. Chem.* **2011**, *76*, 4617-4627.

J. NMR Spectra

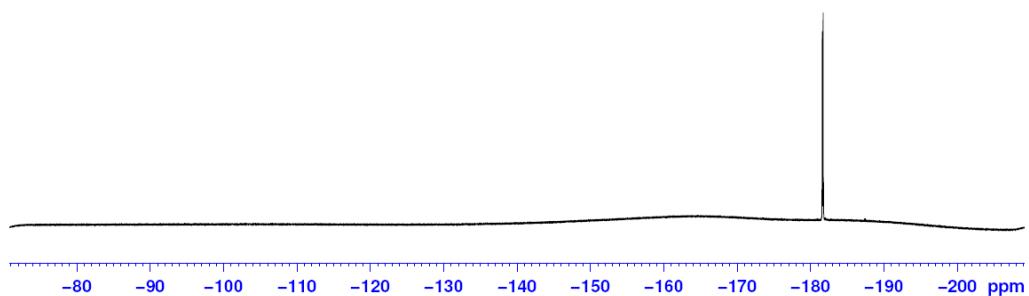


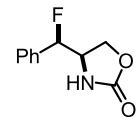
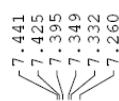




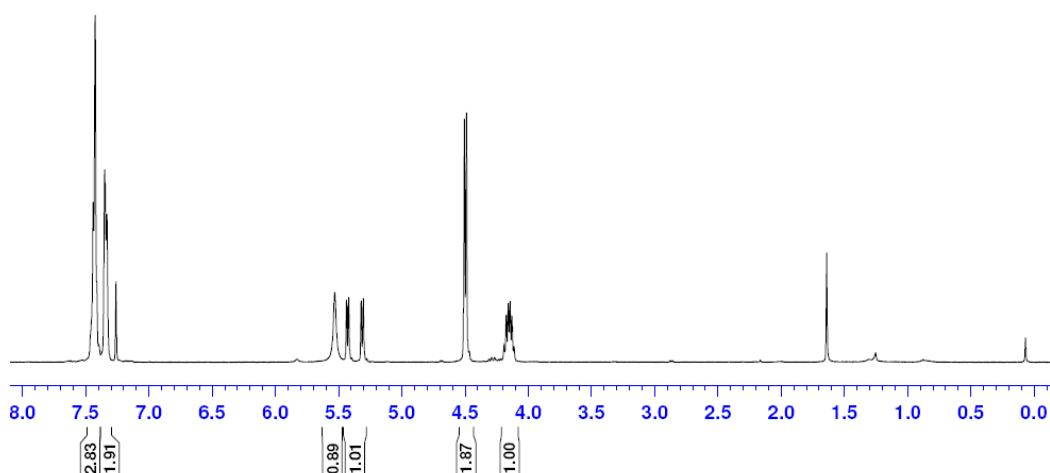


2a (CDCl_3 , 377 MHz)





2b (CDCl_3 , 400 MHz)

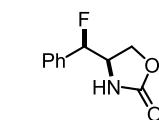


158.95

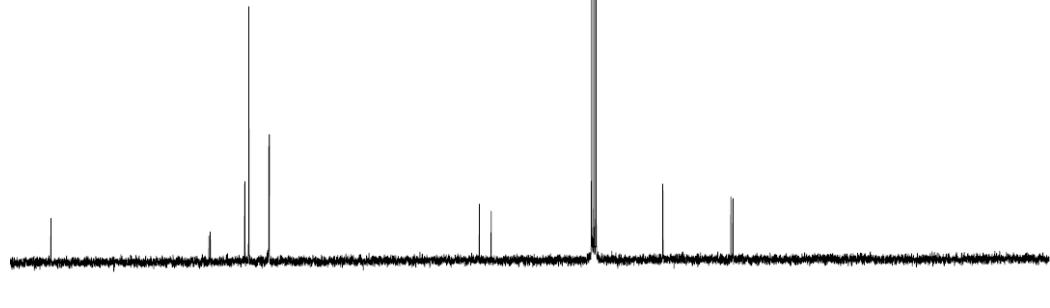
135.10
134.91
129.69
129.09
126.07
126.00

94.29
92.51

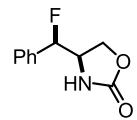
77.35
77.03
76.71
66.62
66.59



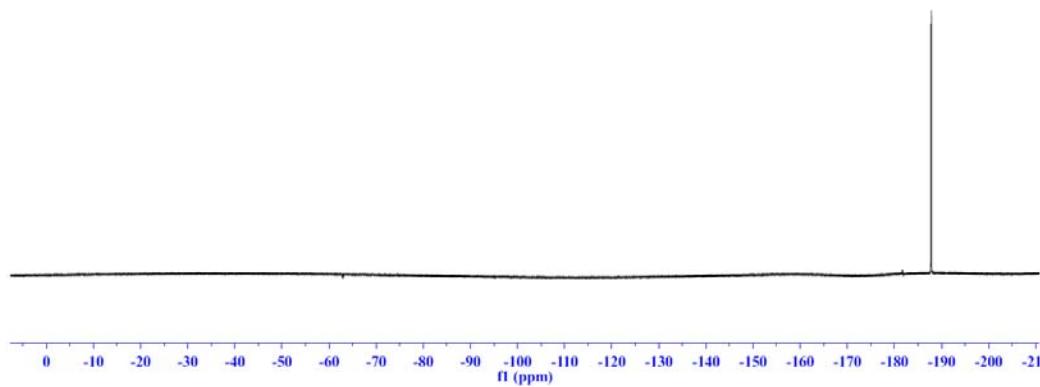
2b (CDCl_3 , 100 MHz)

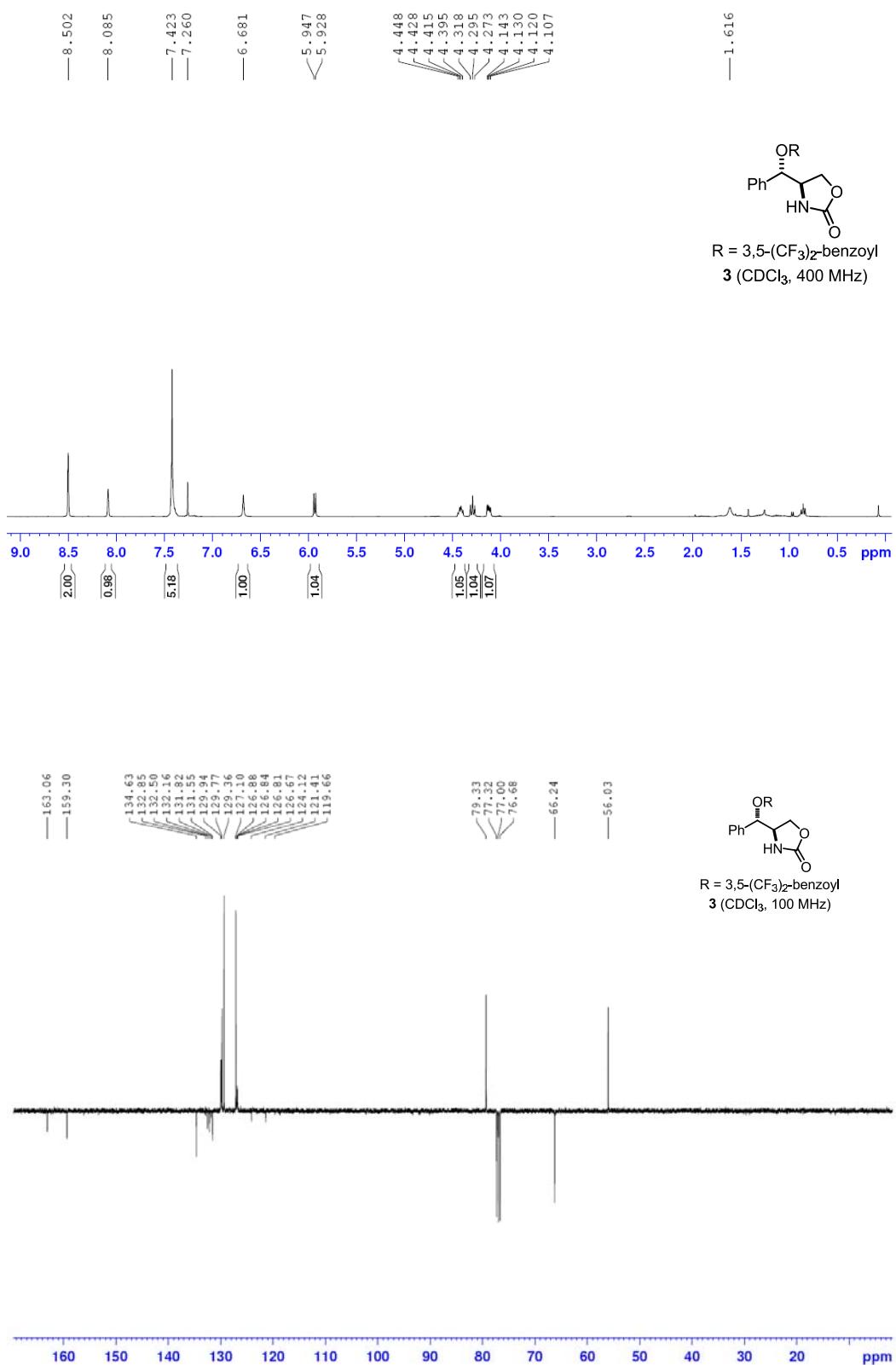


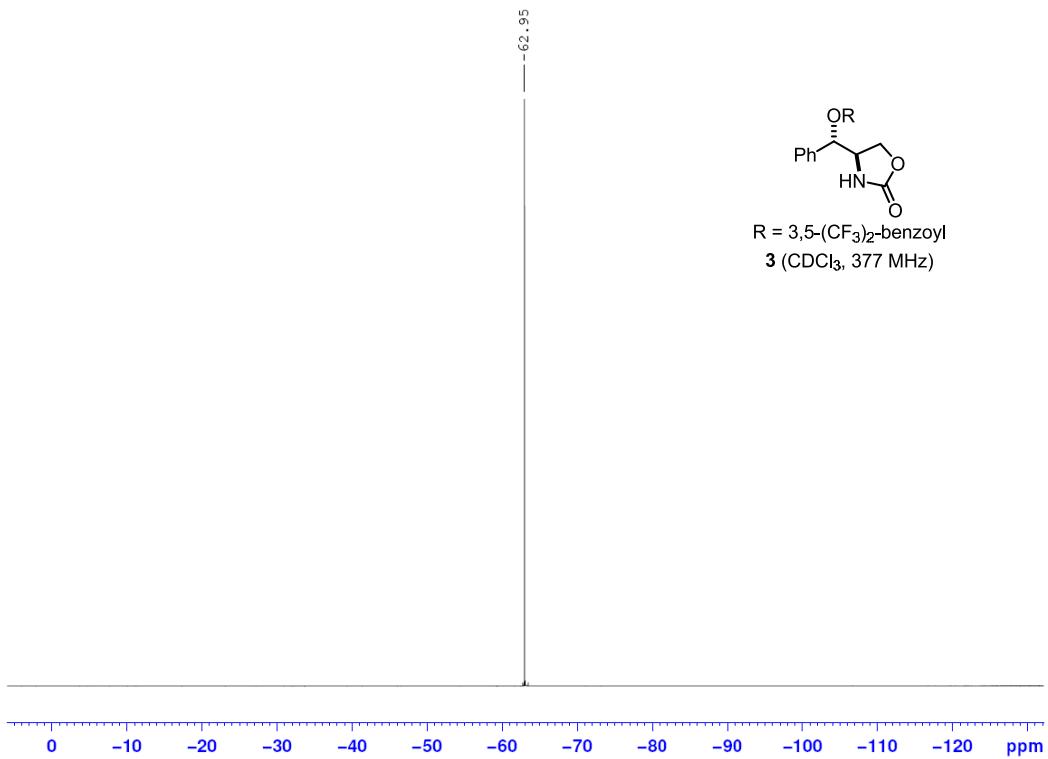
187.731
187.763
187.854
187.886

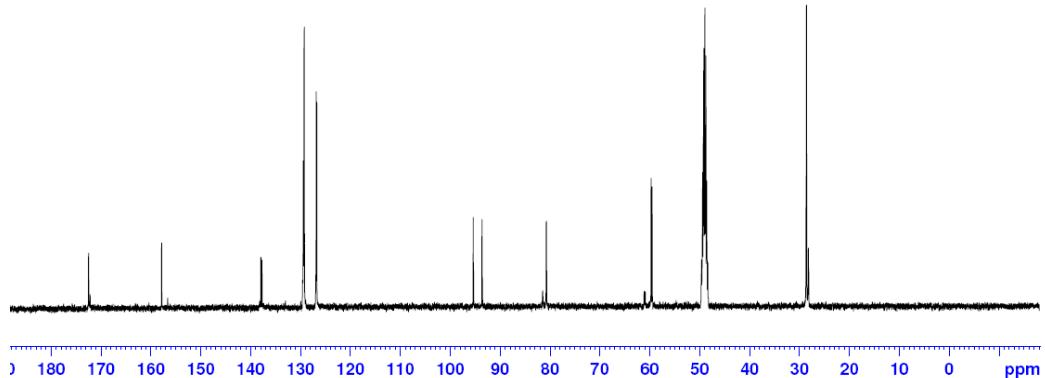
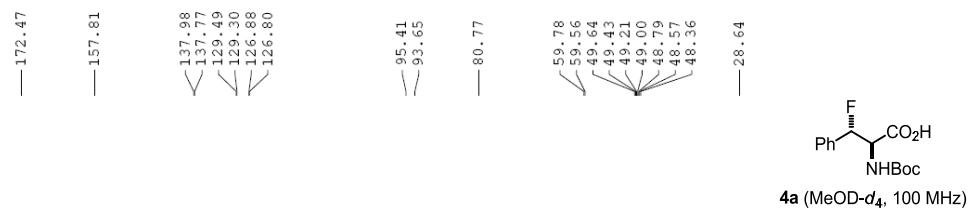
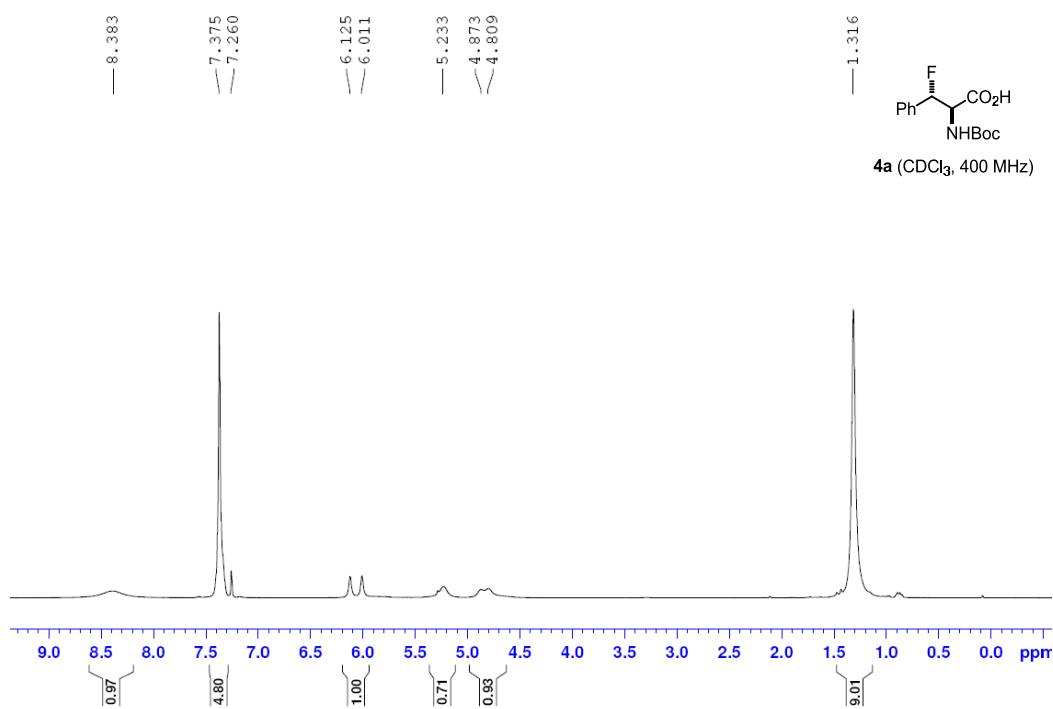


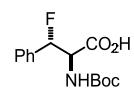
2b (CDCl_3 , 377 MHz)



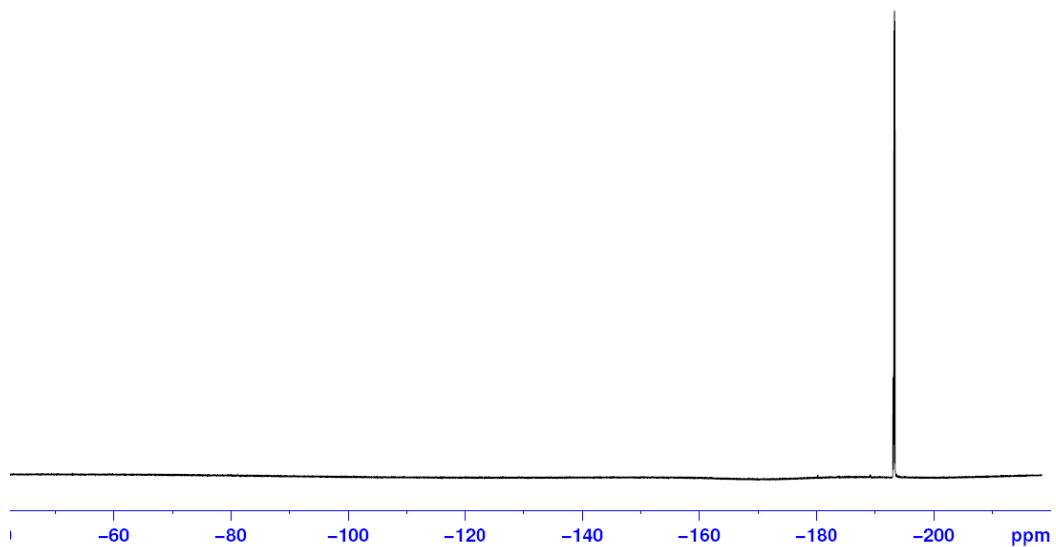


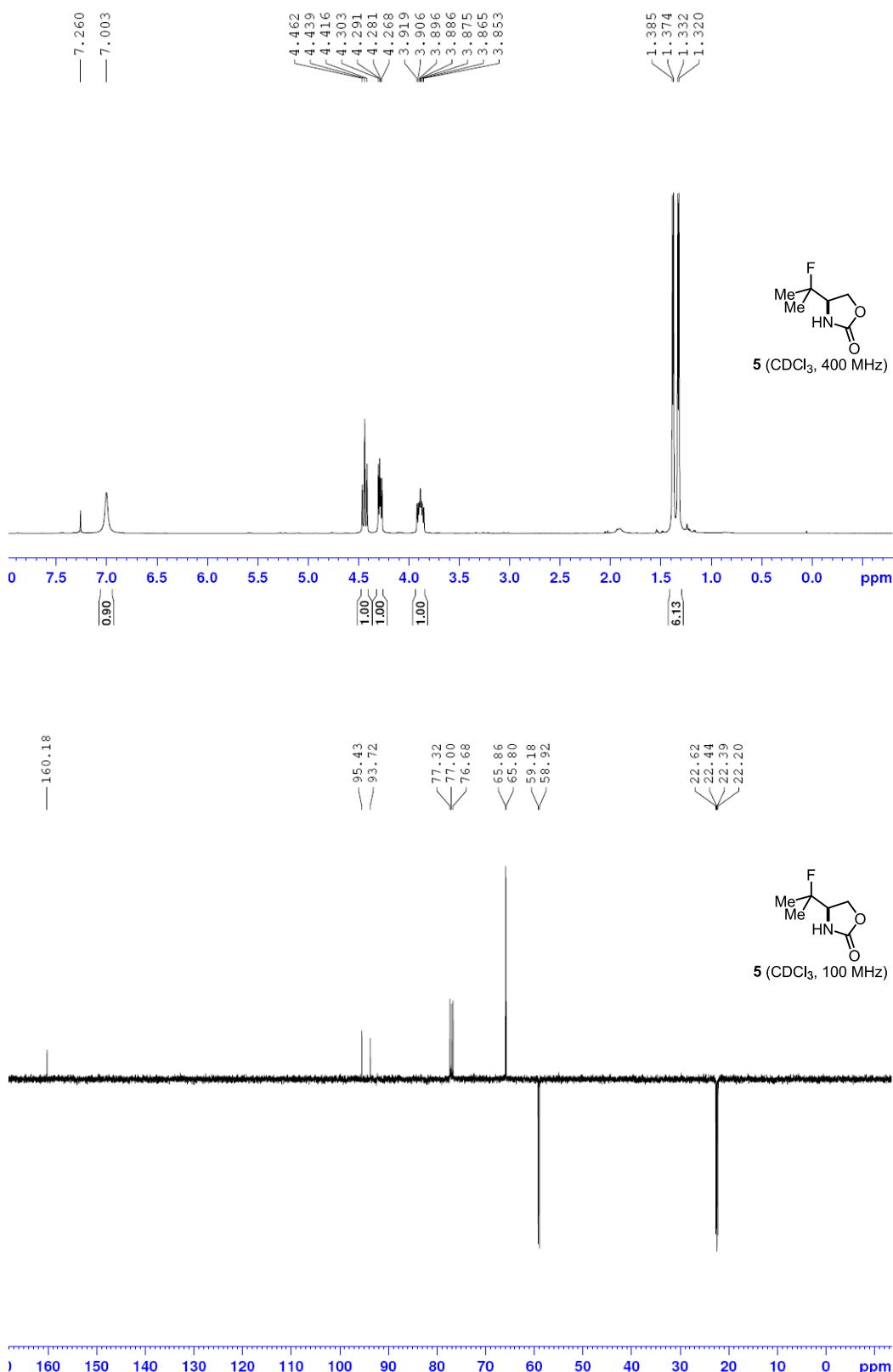






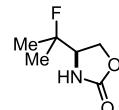
4a (CDCl₃, 377 MHz)



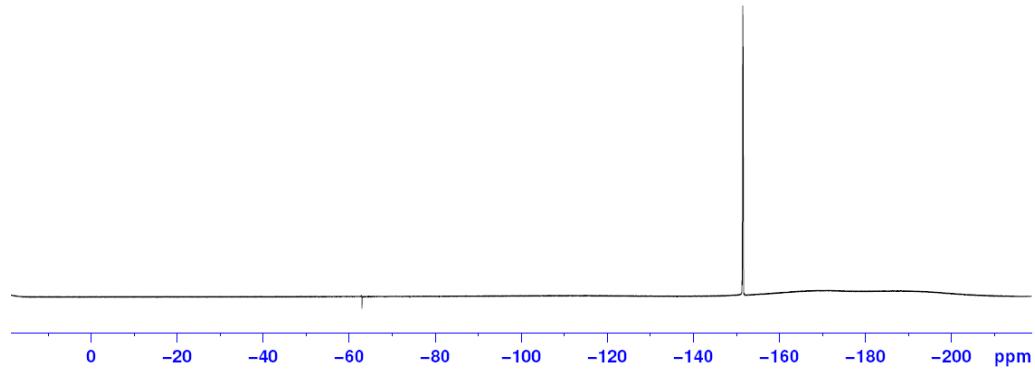


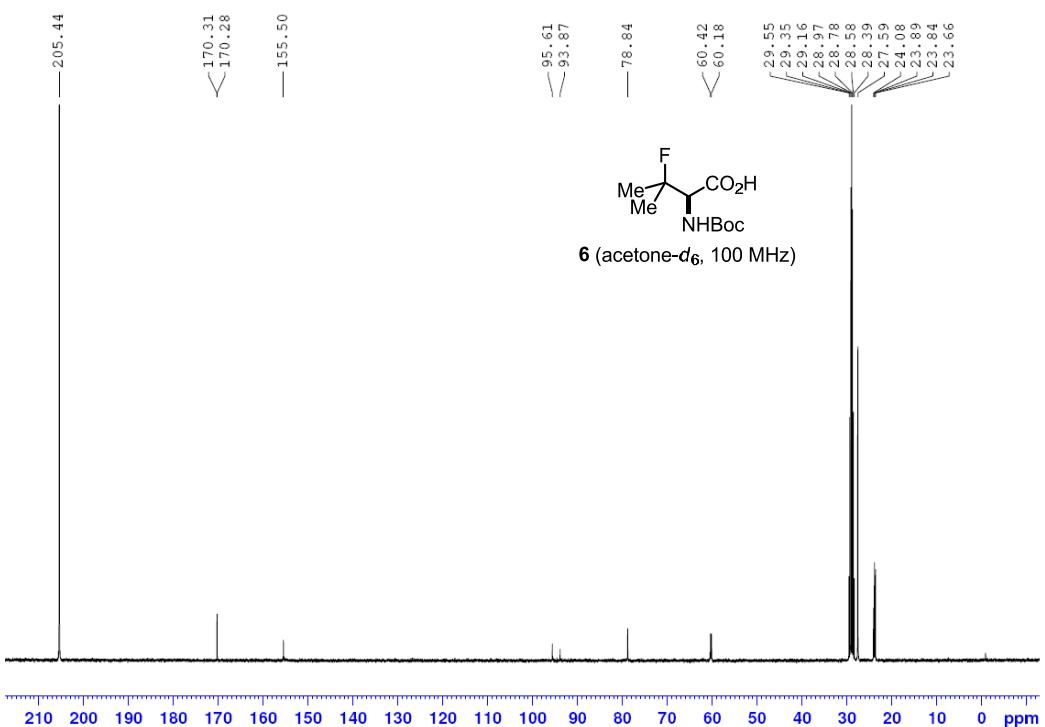
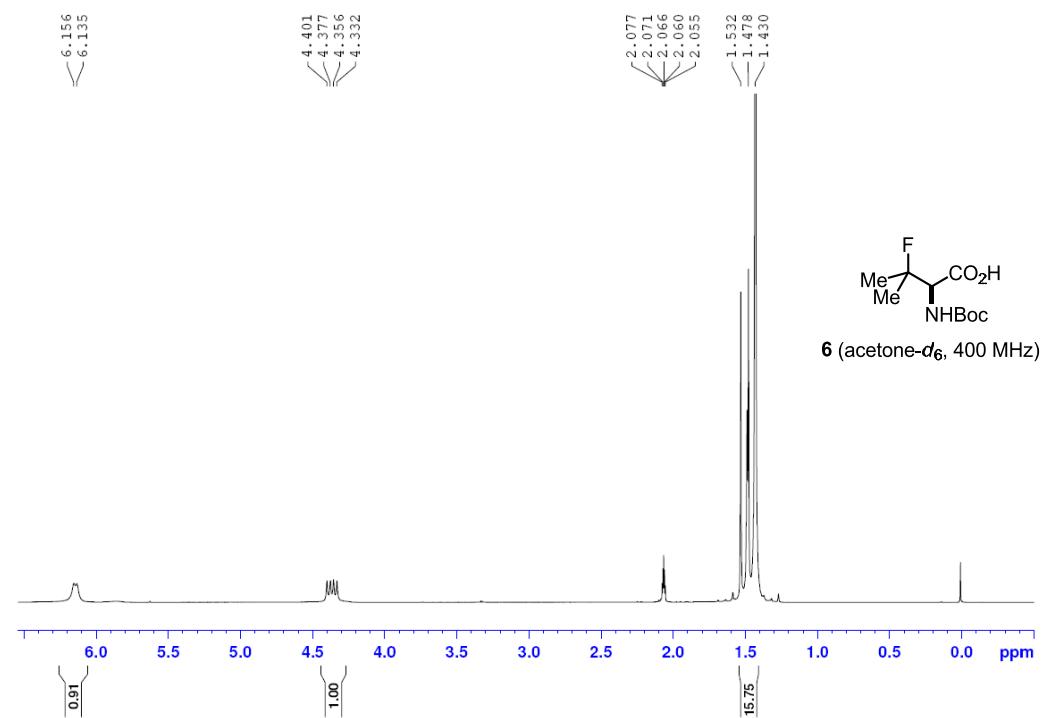
F19

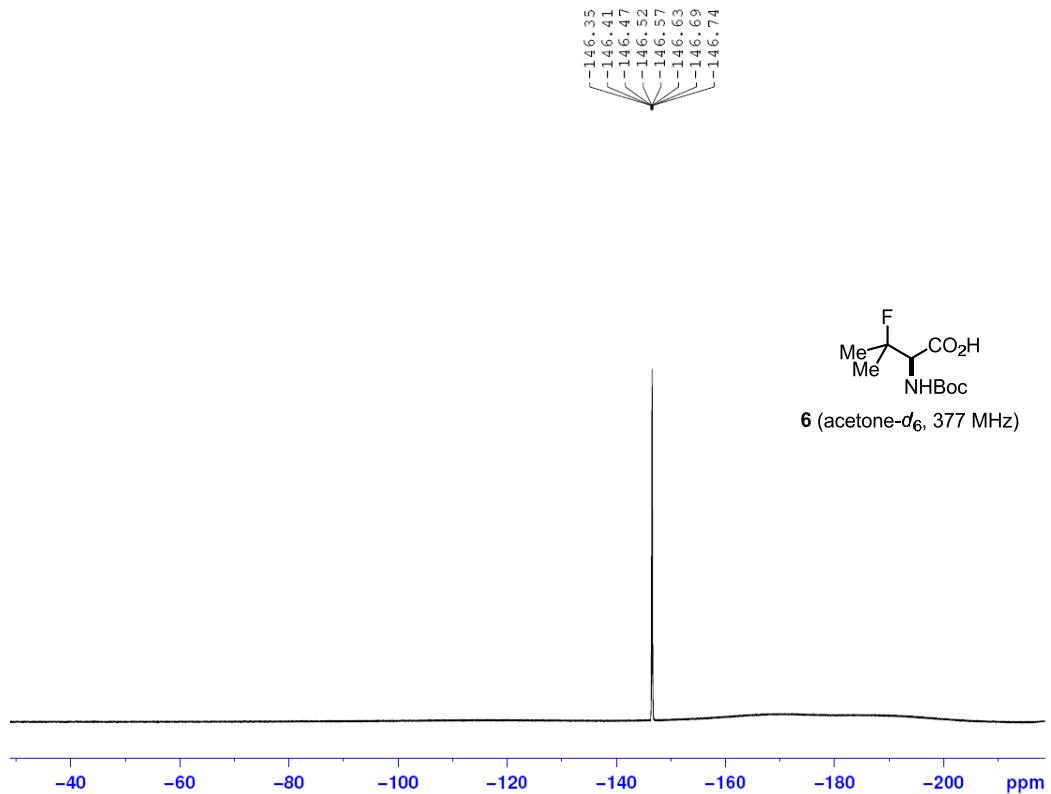
-151.31
-151.37
-151.40
-151.42
-151.45
-151.48
-151.51
-151.54
-151.57
-151.59
-151.62
-151.65
-151.68

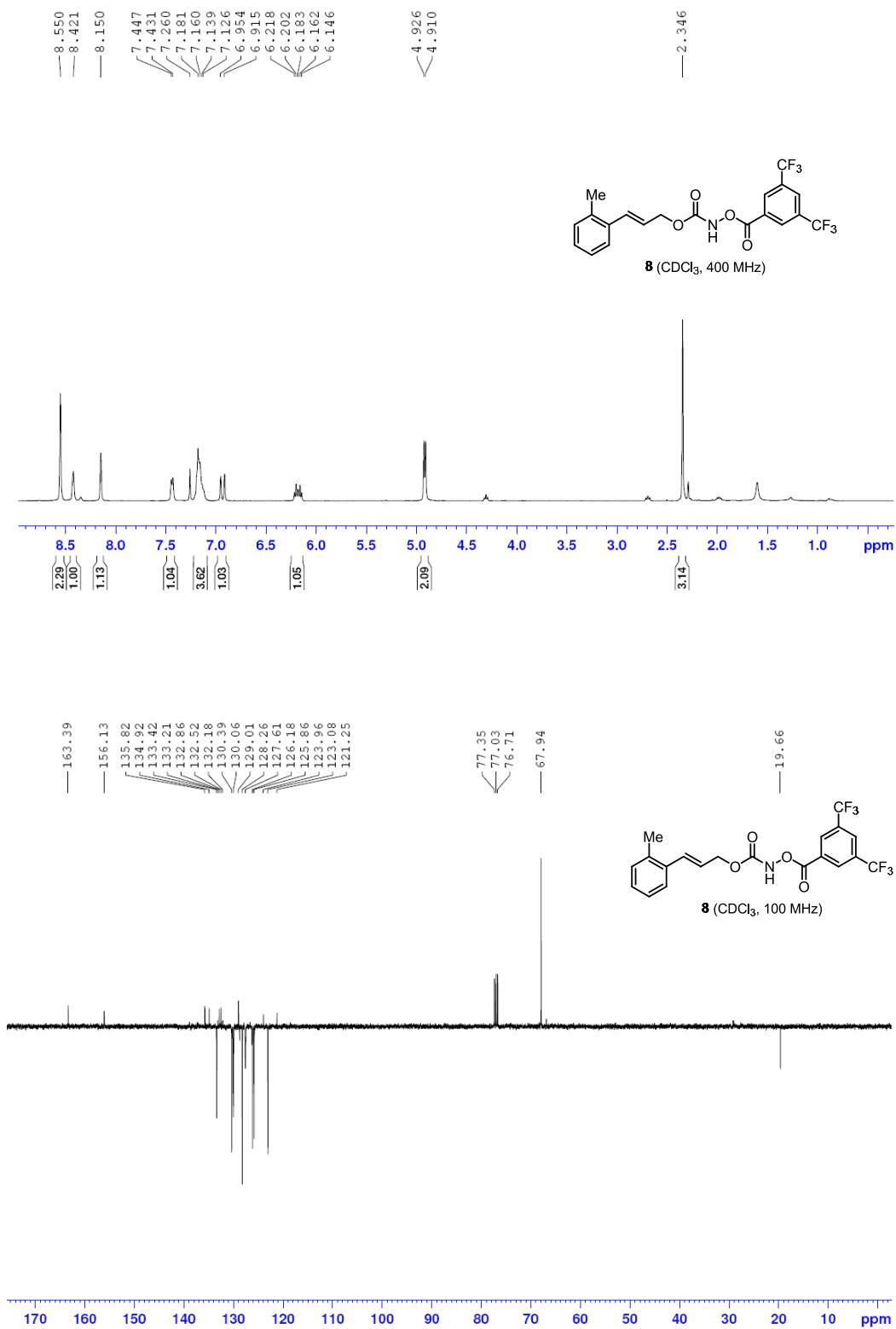


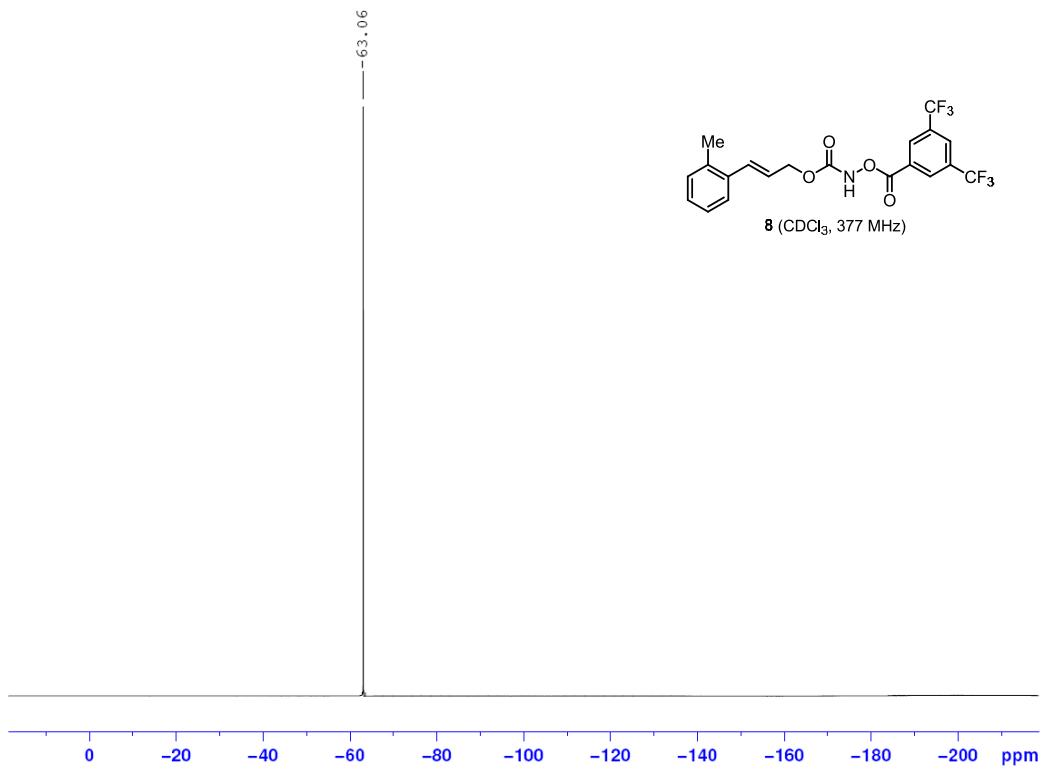
5 (CDCl₃, 377 MHz)

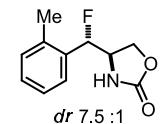
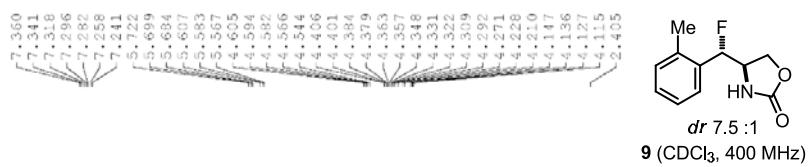




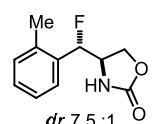
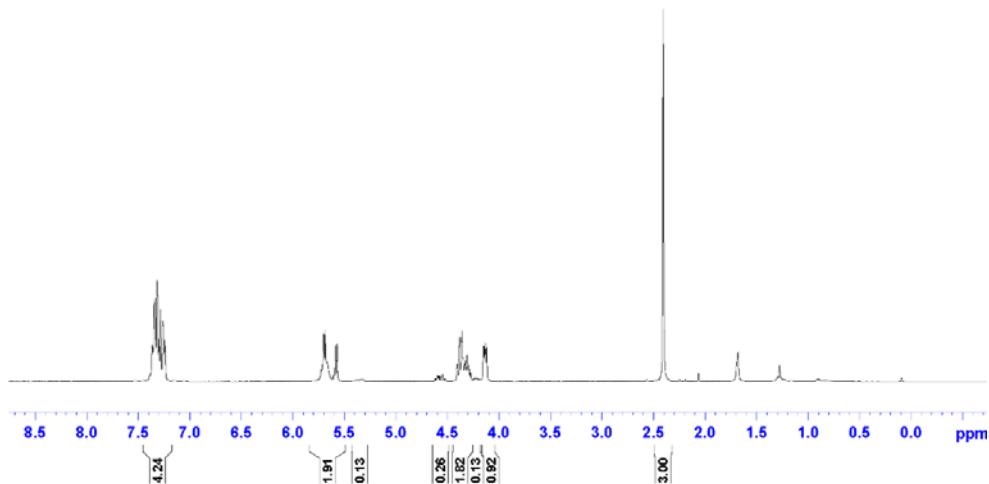




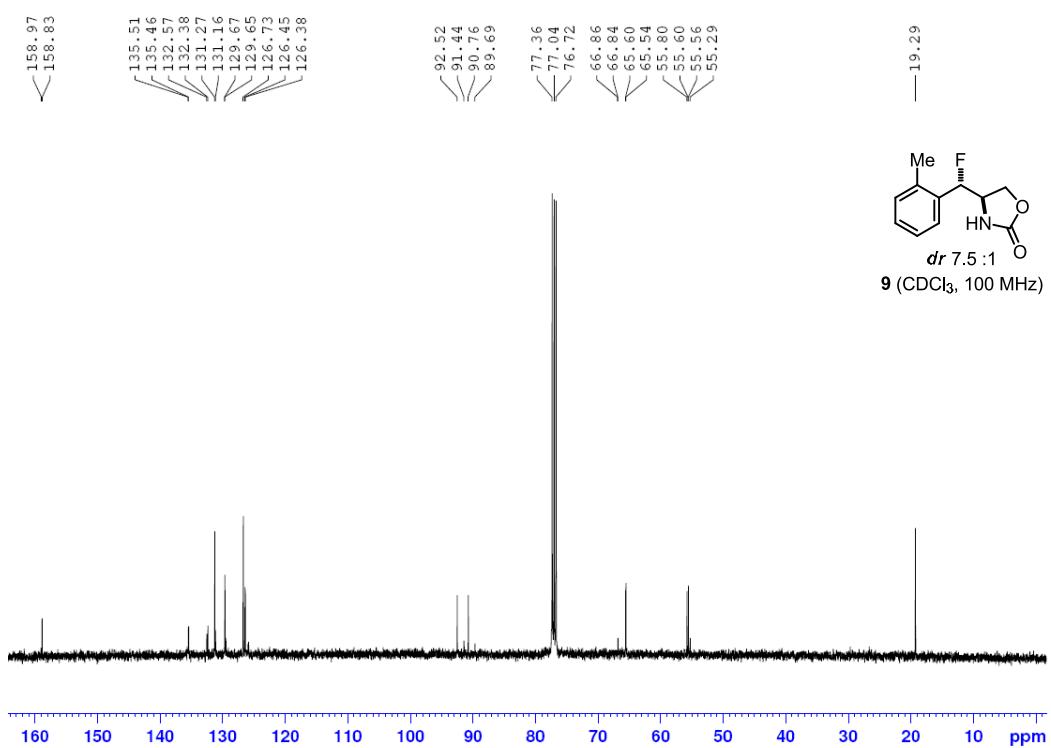


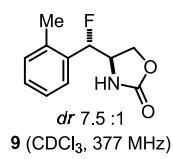


9 (CDCl_3 , 400 MHz)



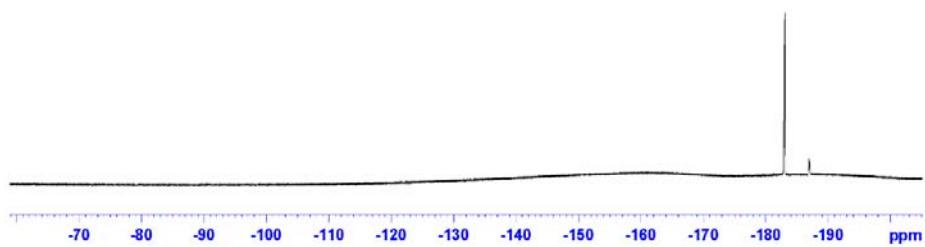
9 (CDCl₃, 100 MHz)

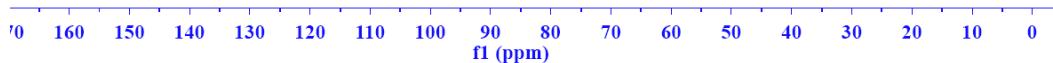
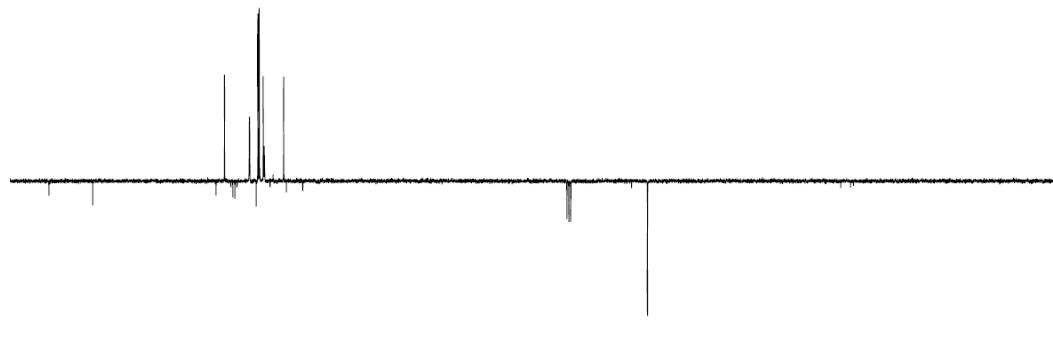
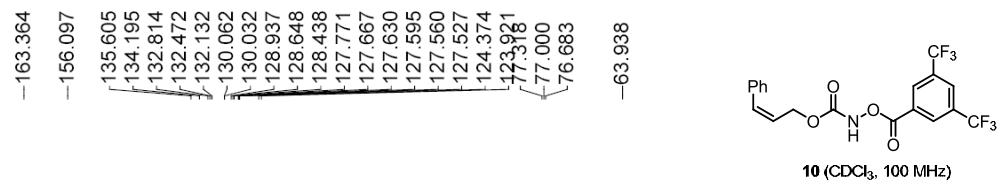
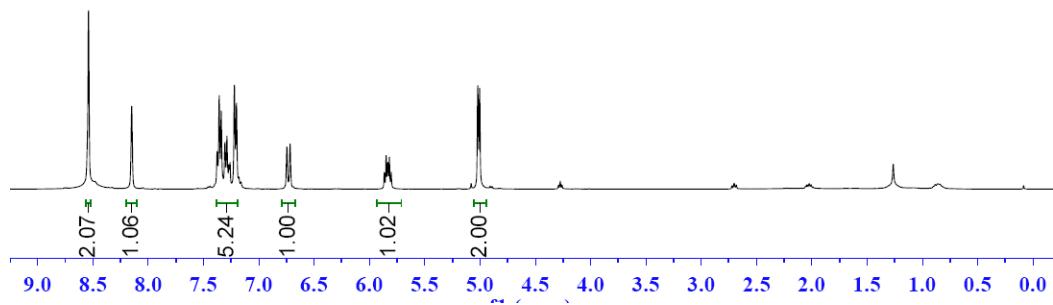
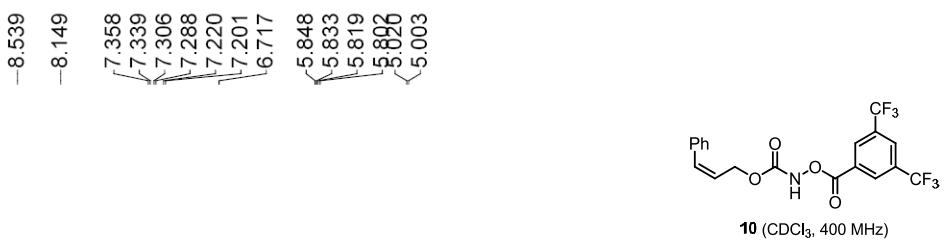


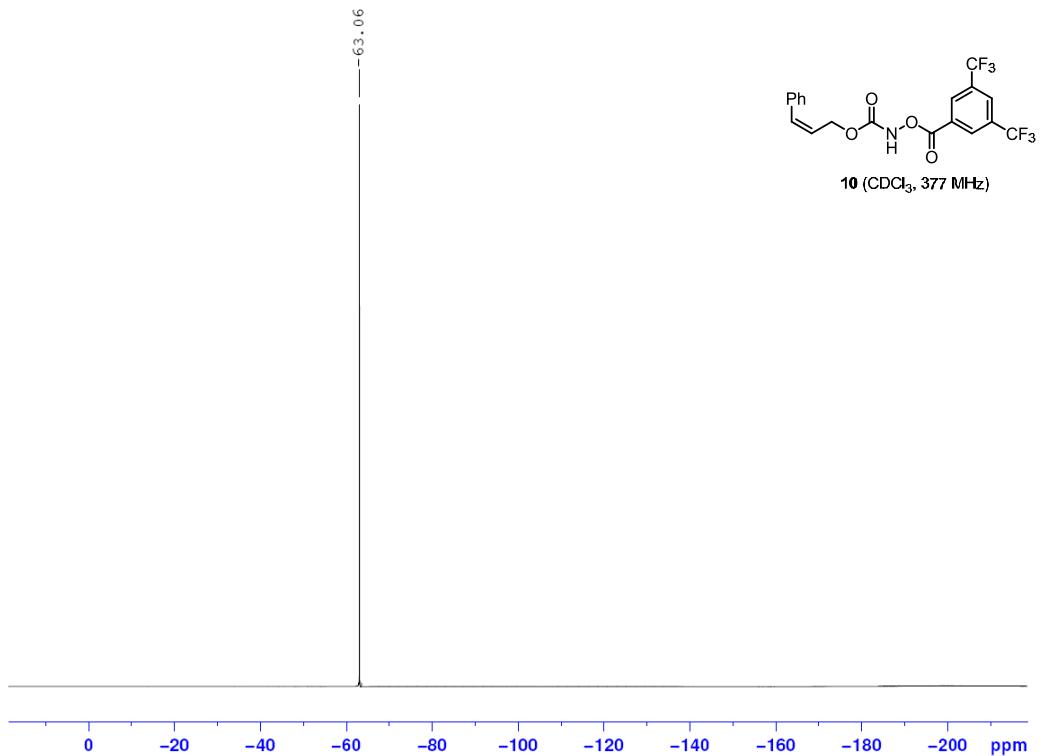


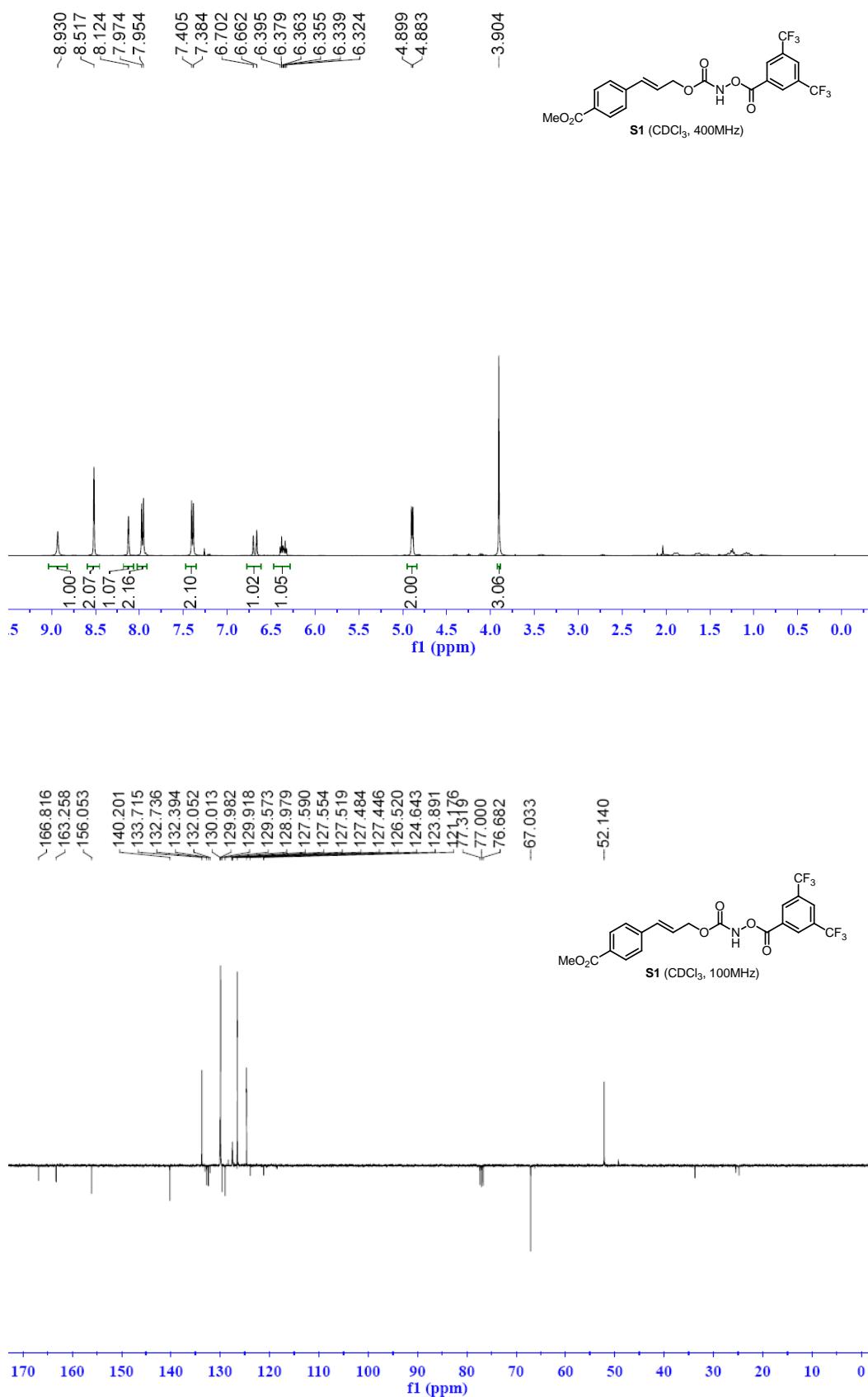
9 (CDCl_3 , 377 MHz)

182.97
183.00
183.10
183.13
186.93
186.96
187.05
187.08

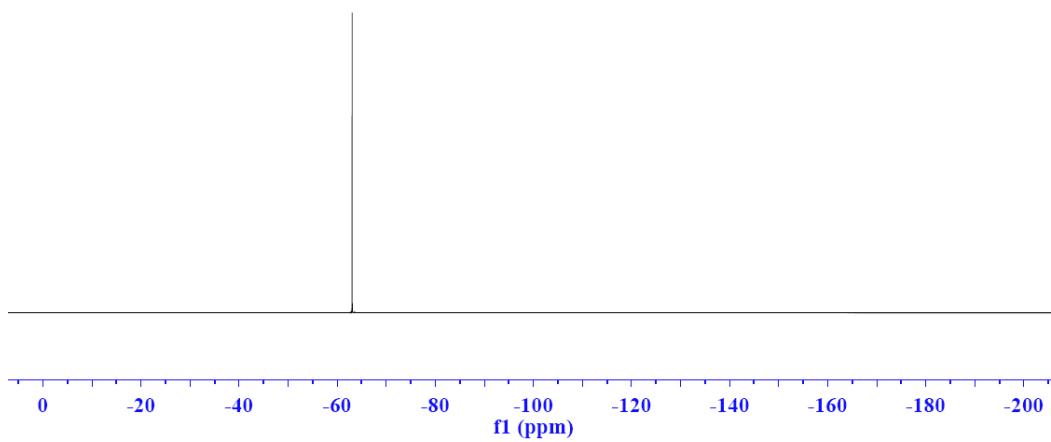
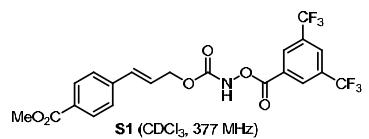


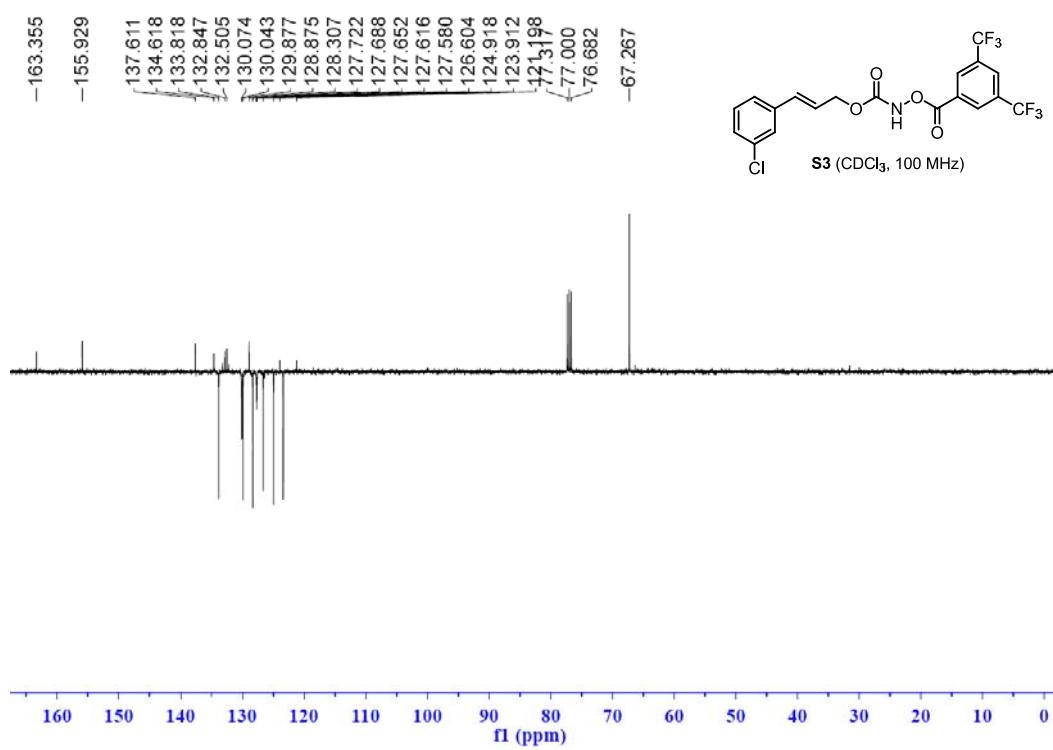
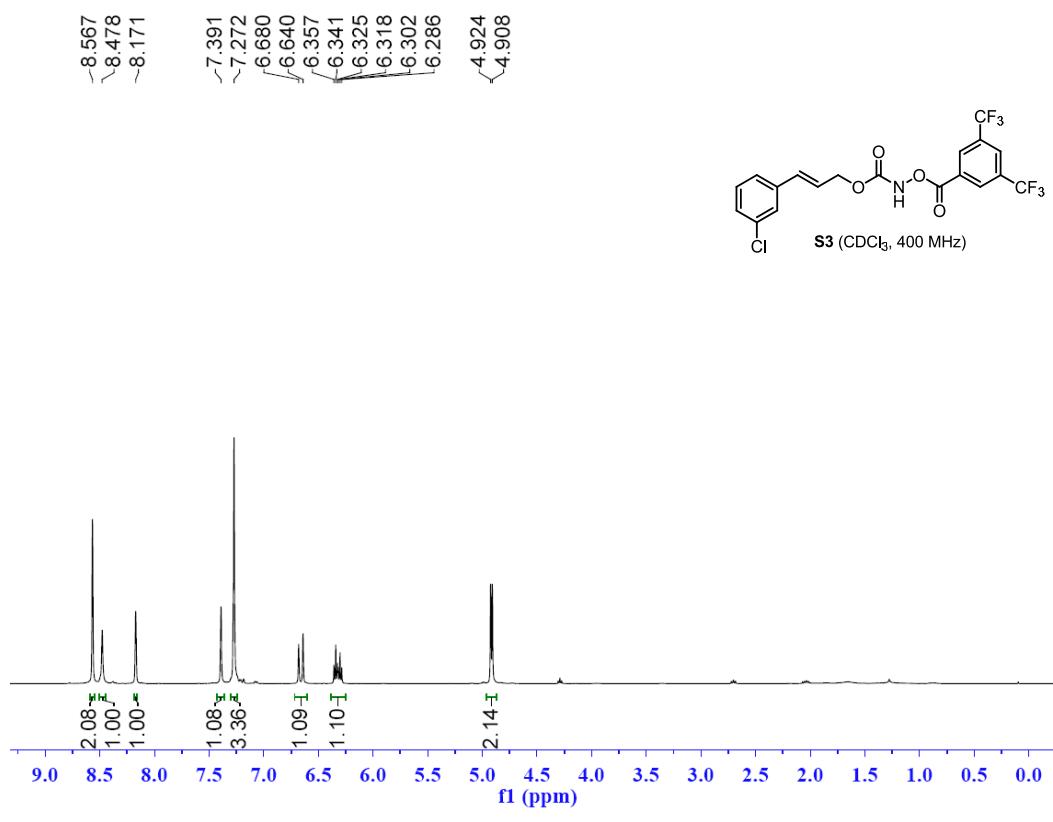




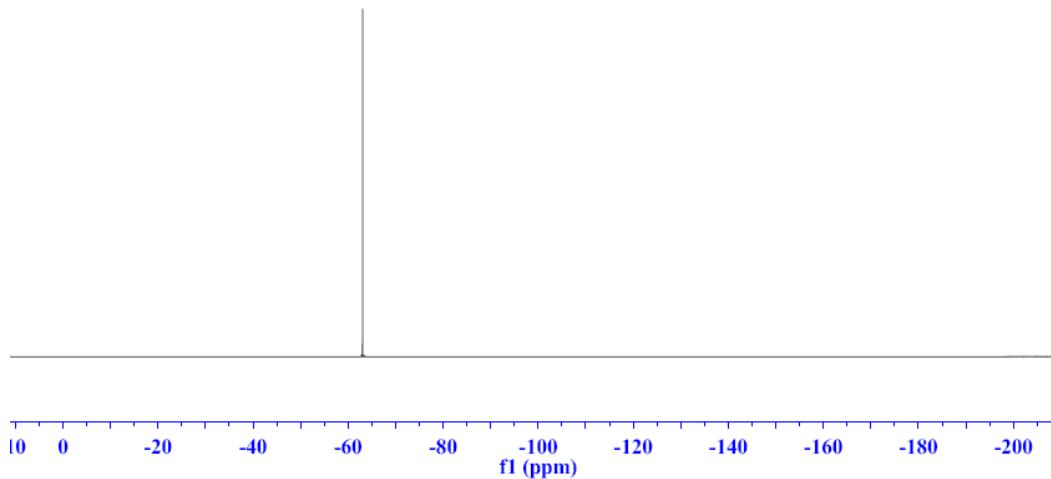
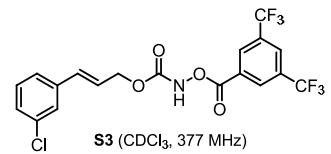


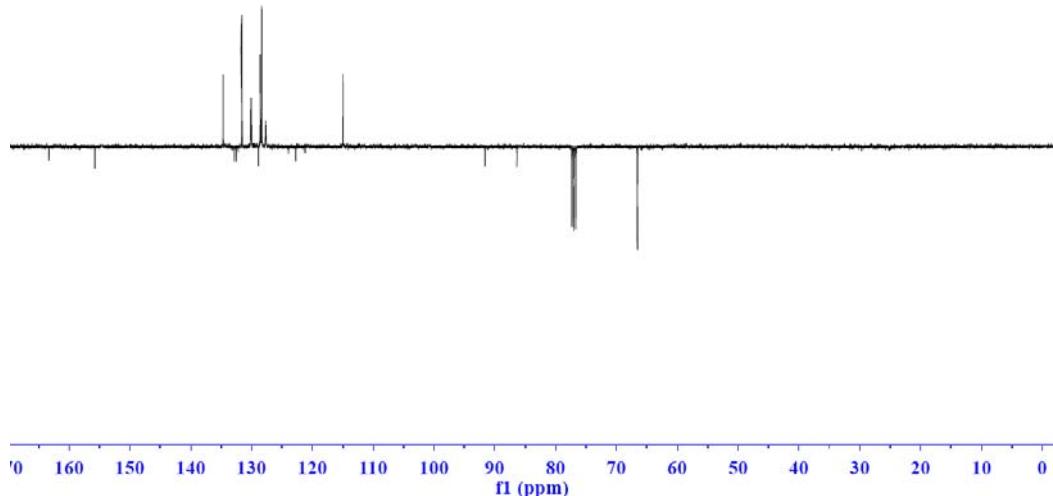
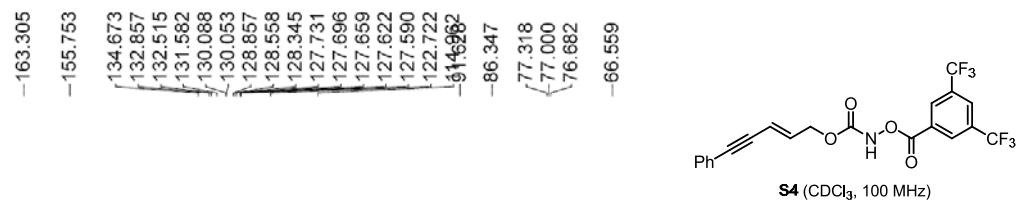
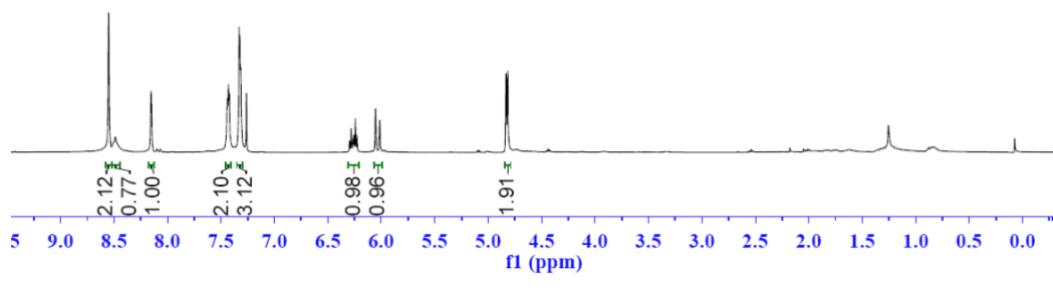
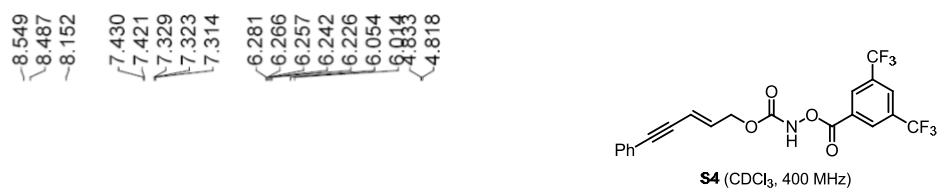
-63.057



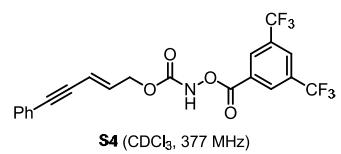


-63.044

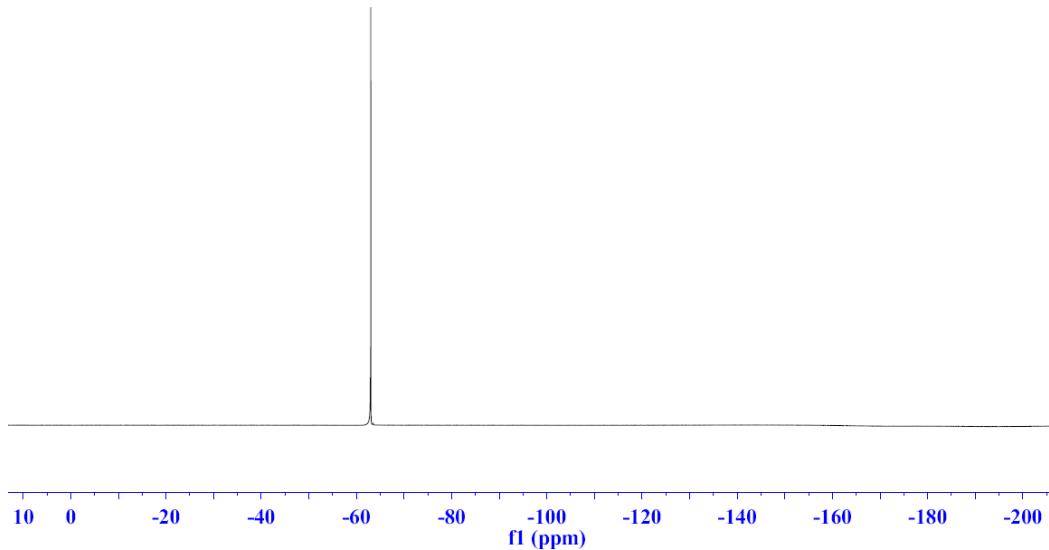


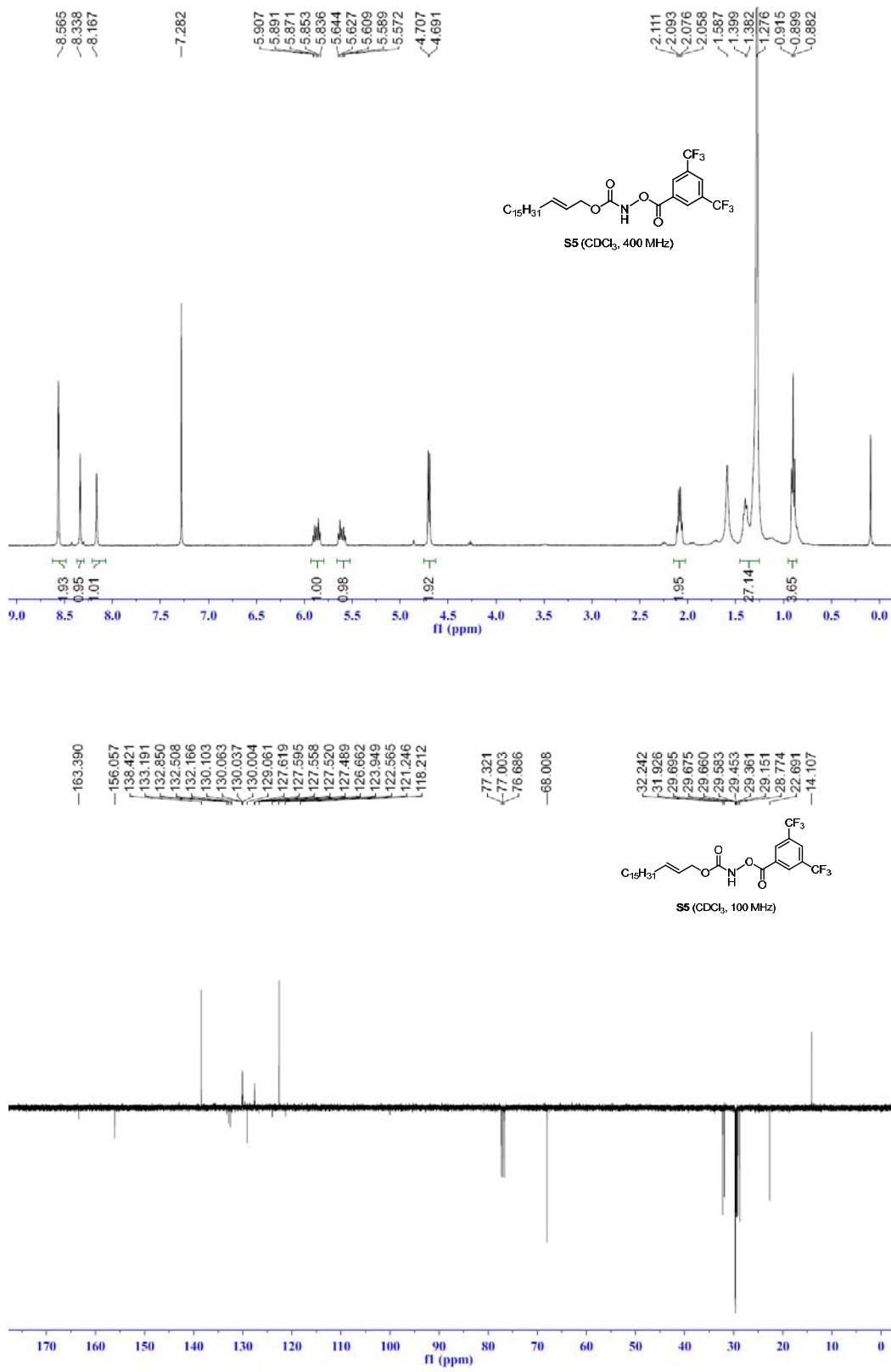


-63.035

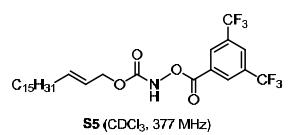


S4 (CDCl₃, 377 MHz)

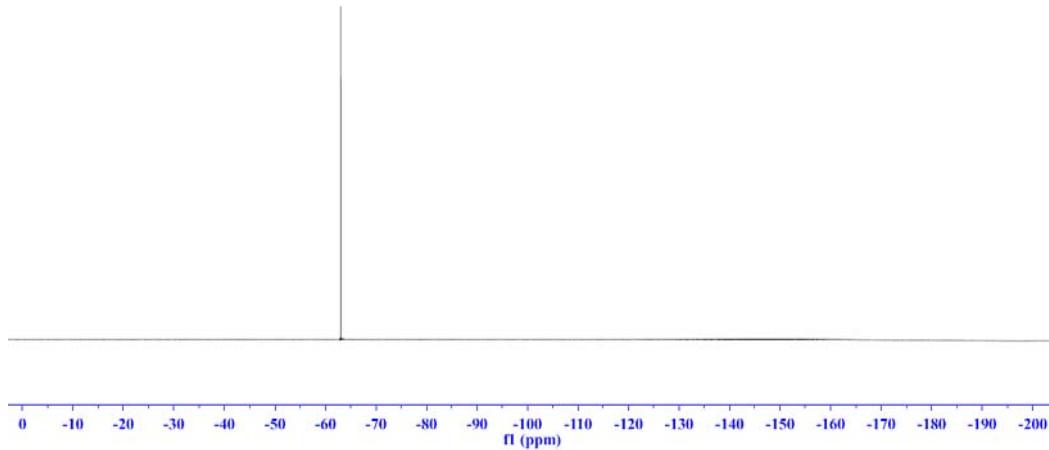


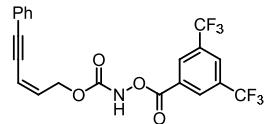


—63.057

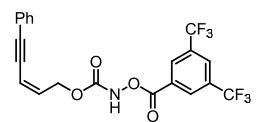
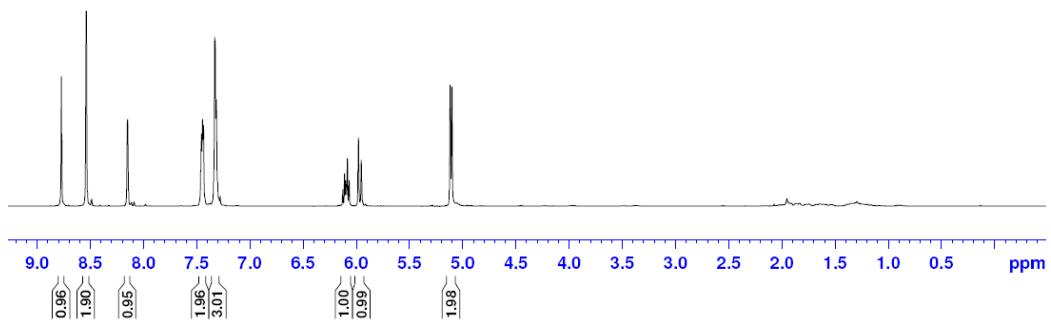


S5 (CDCl_3 , 377 MHz)

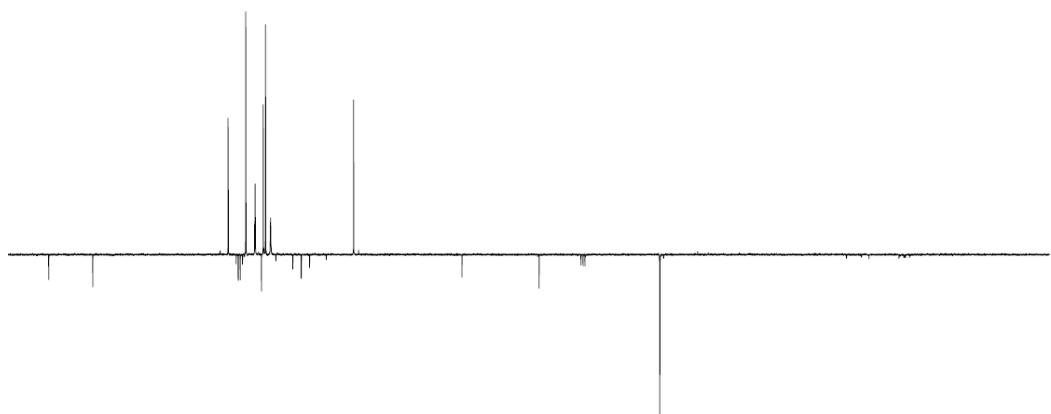


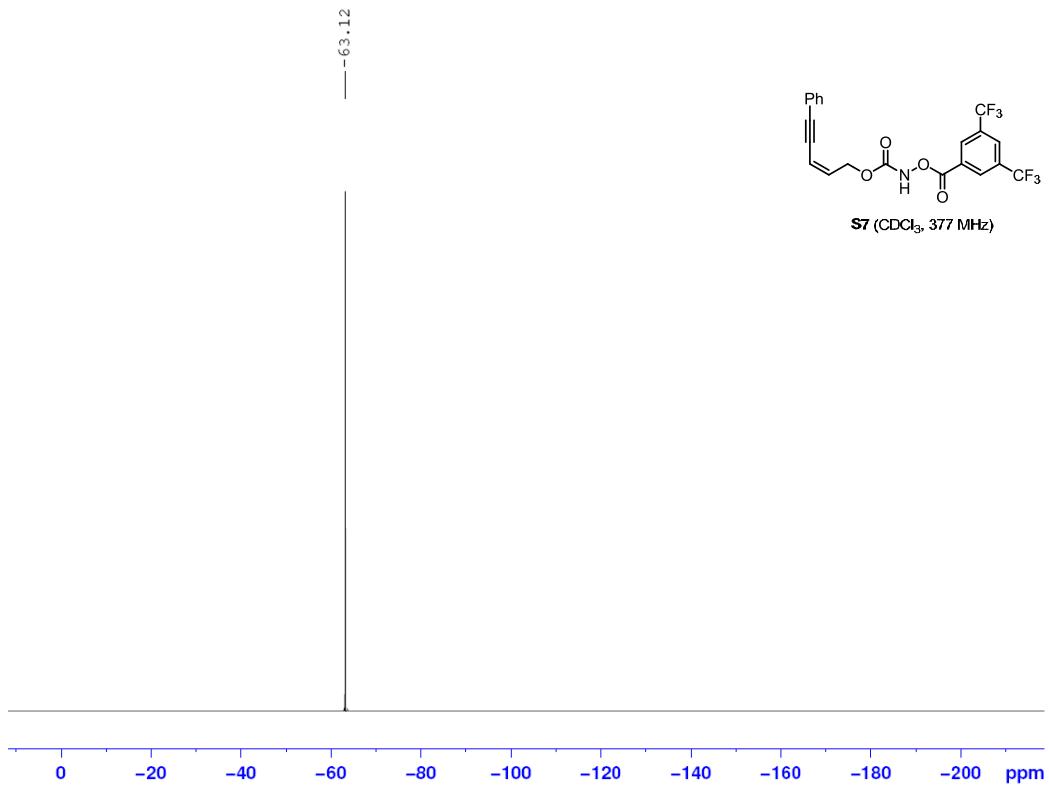


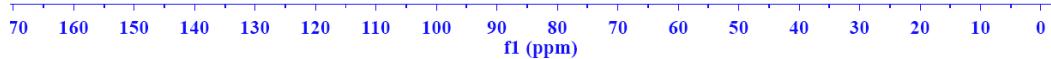
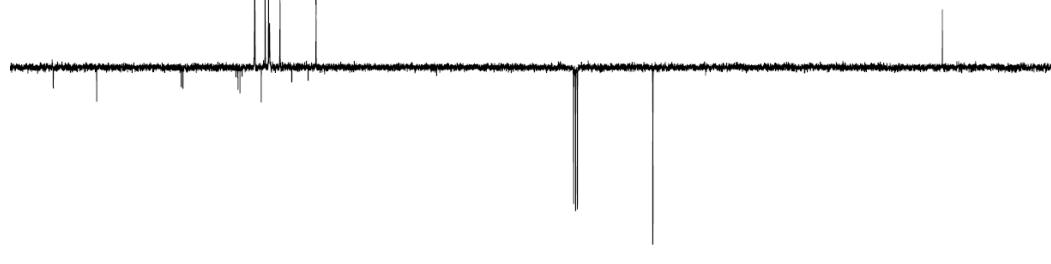
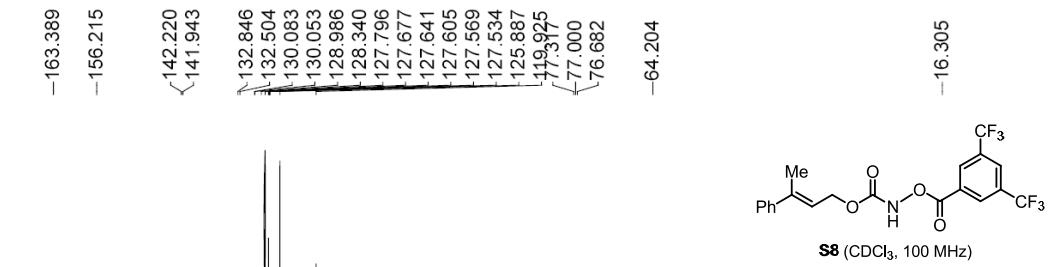
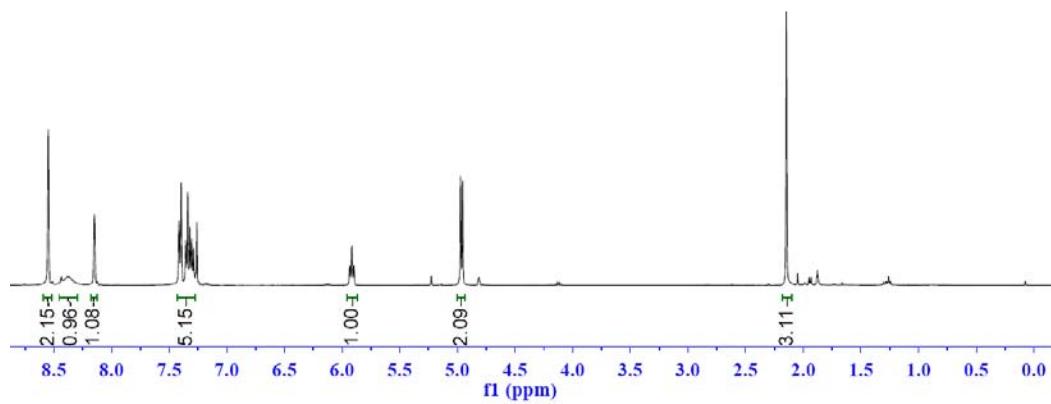
S7 (CDCl_3 , 400 MHz)

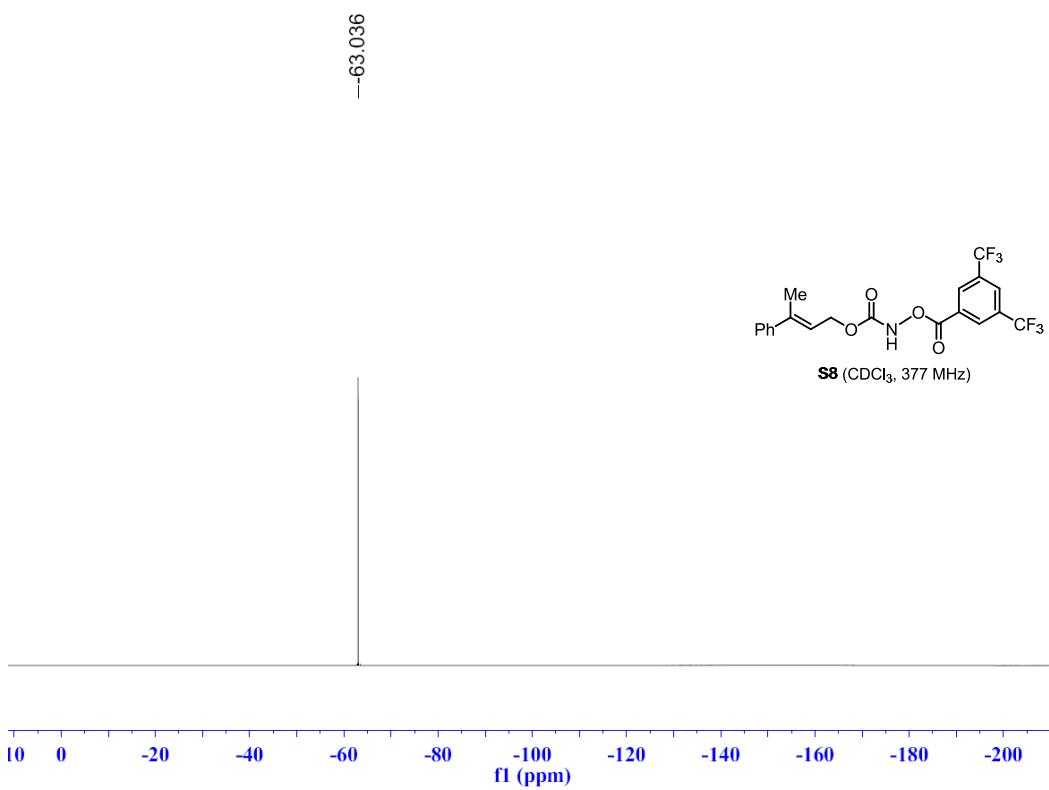


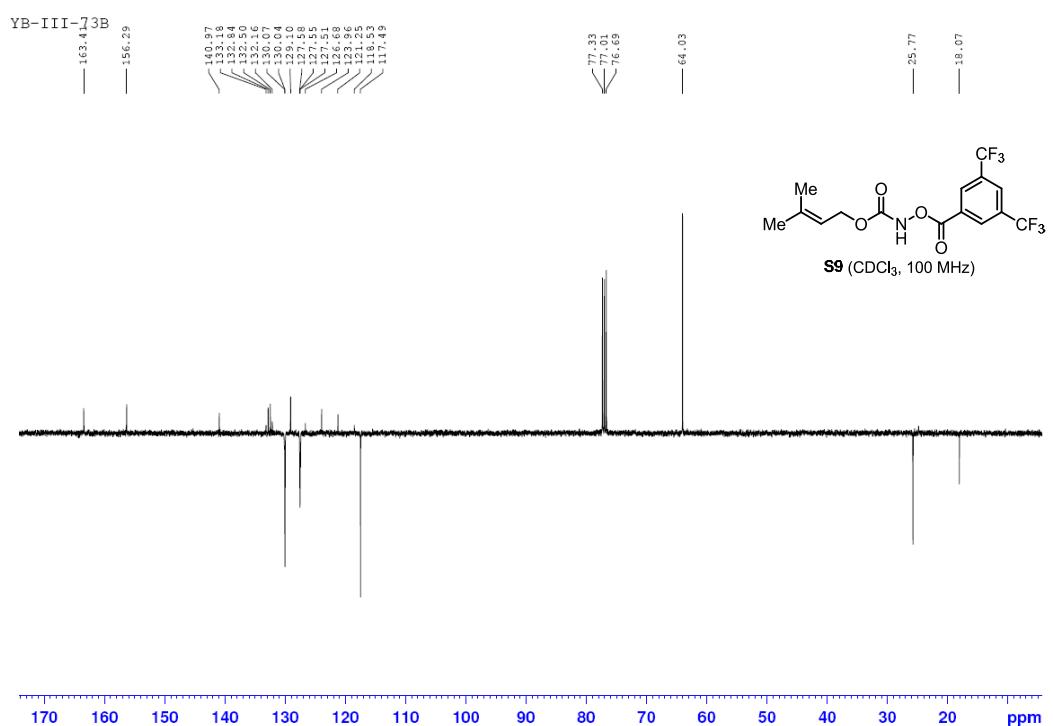
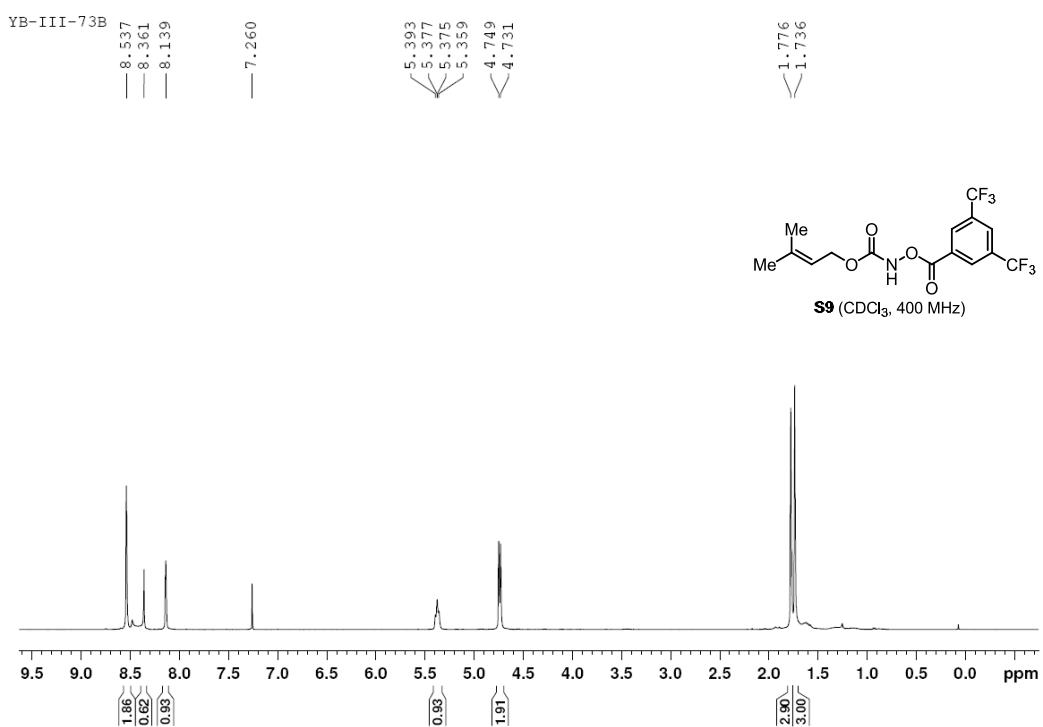
S7 (CDCl₃, 100 MHz)





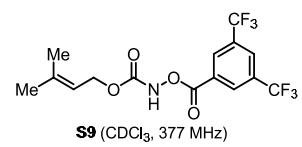






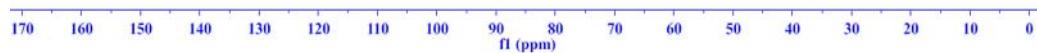
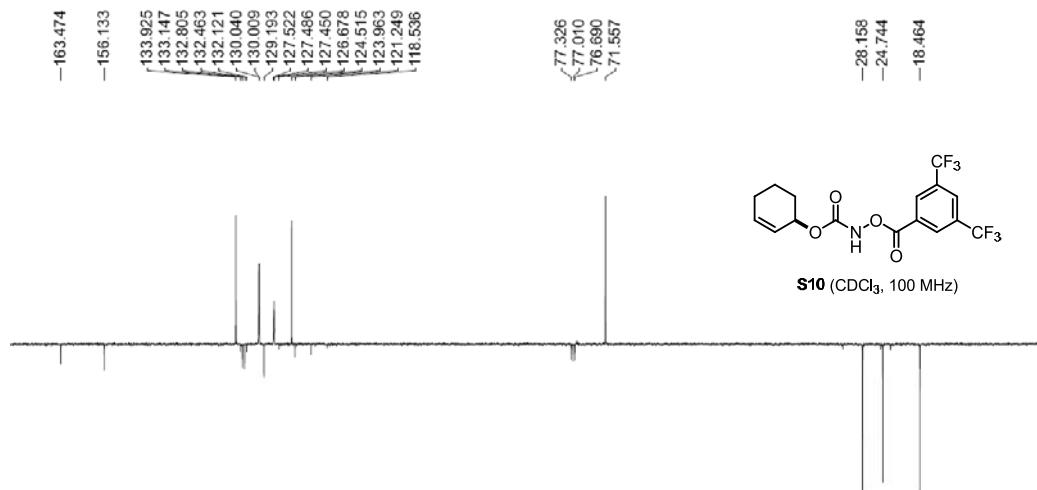
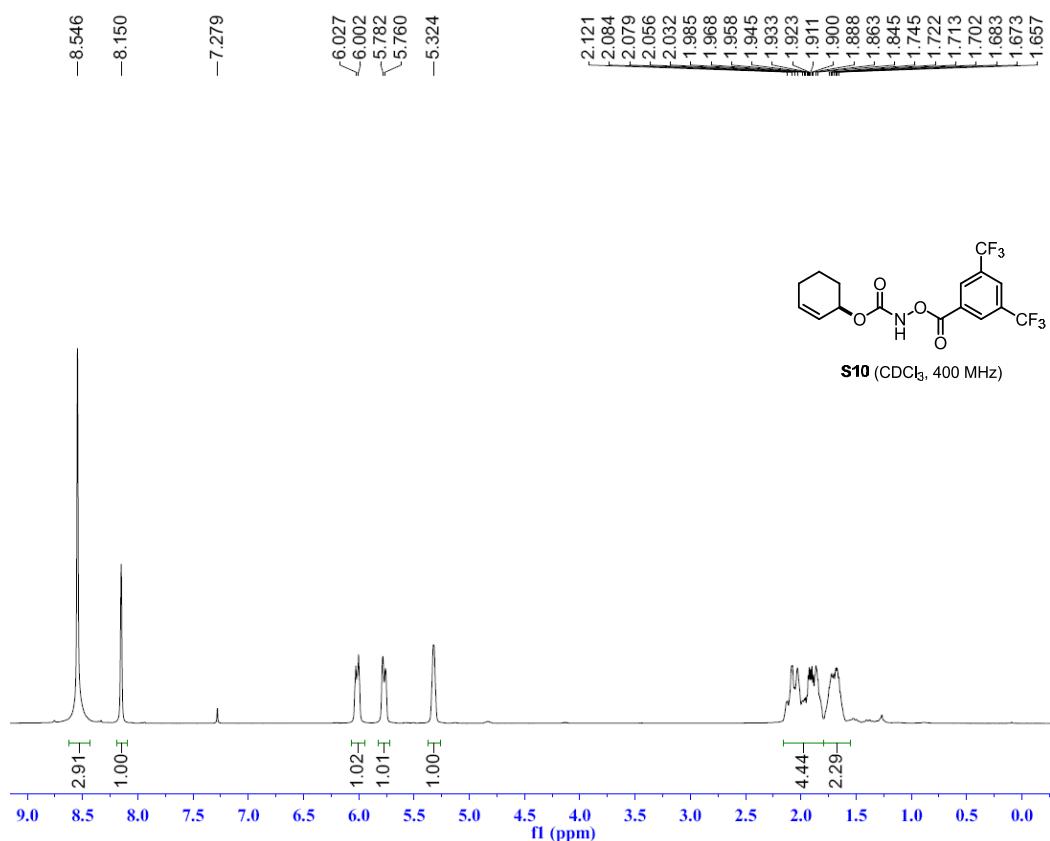
YB-III-73B

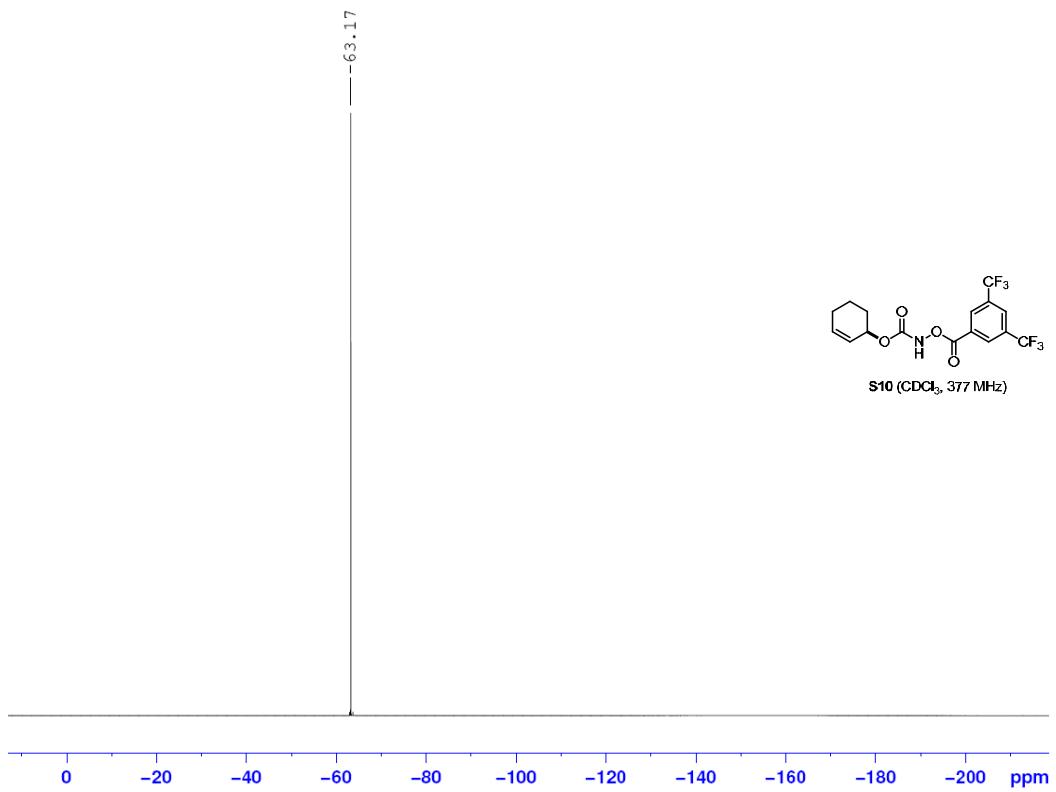
-63.07

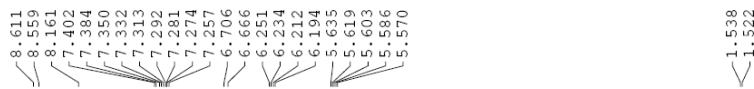


S9 (CDCl_3 , 377 MHz)

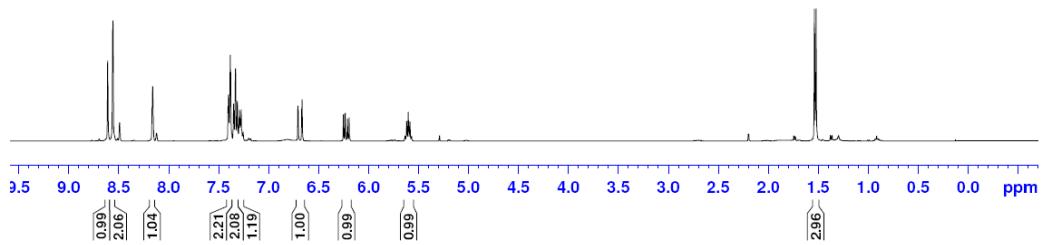
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm







S11 (CDCl_3 , 400 MHz)

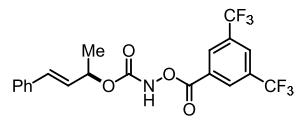


— 163.44

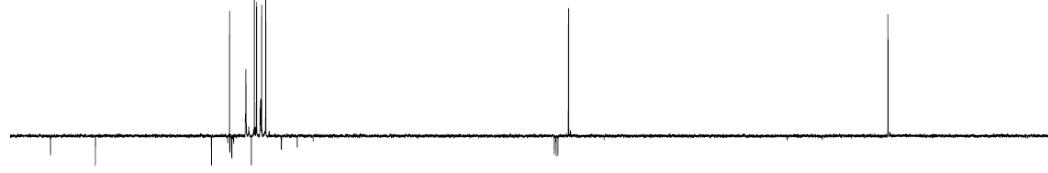
— 155.77
— 135.91
— 133.15
— 132.84
— 132.81
— 132.47
— 132.13
— 130.06
— 130.03
— 129.41
— 128.61
— 128.22
— 127.58
— 127.54
— 127.50
— 127.36
— 127.16
— 126.68
— 123.98
— 121.26

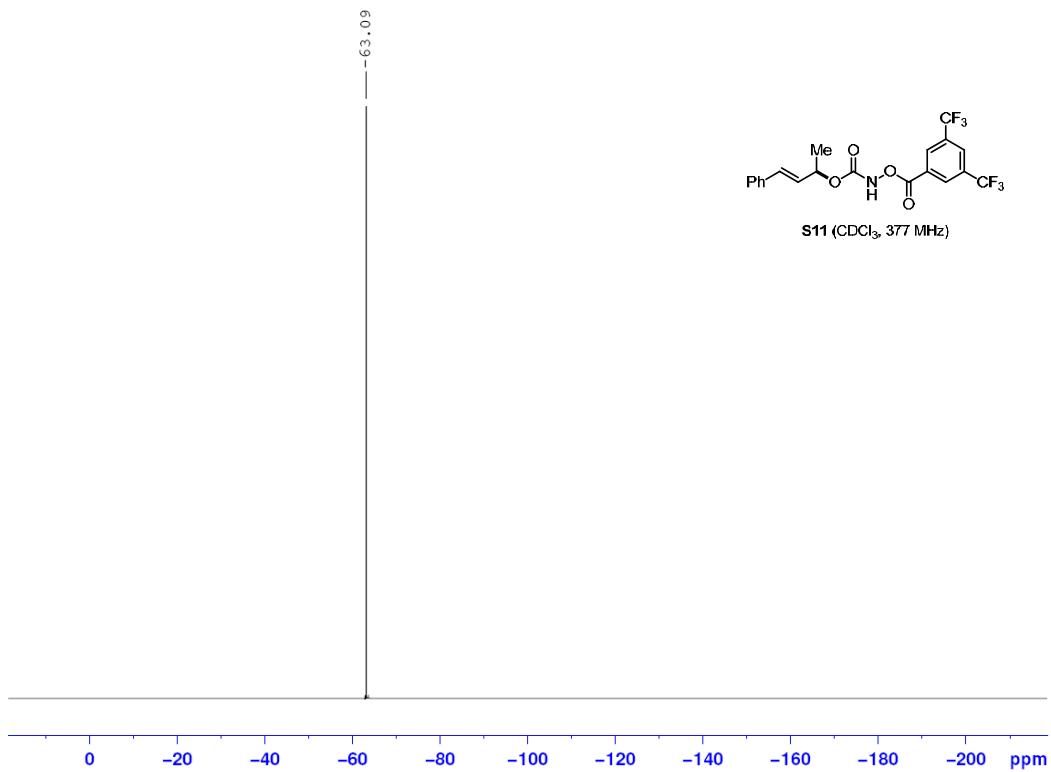
— 118.55

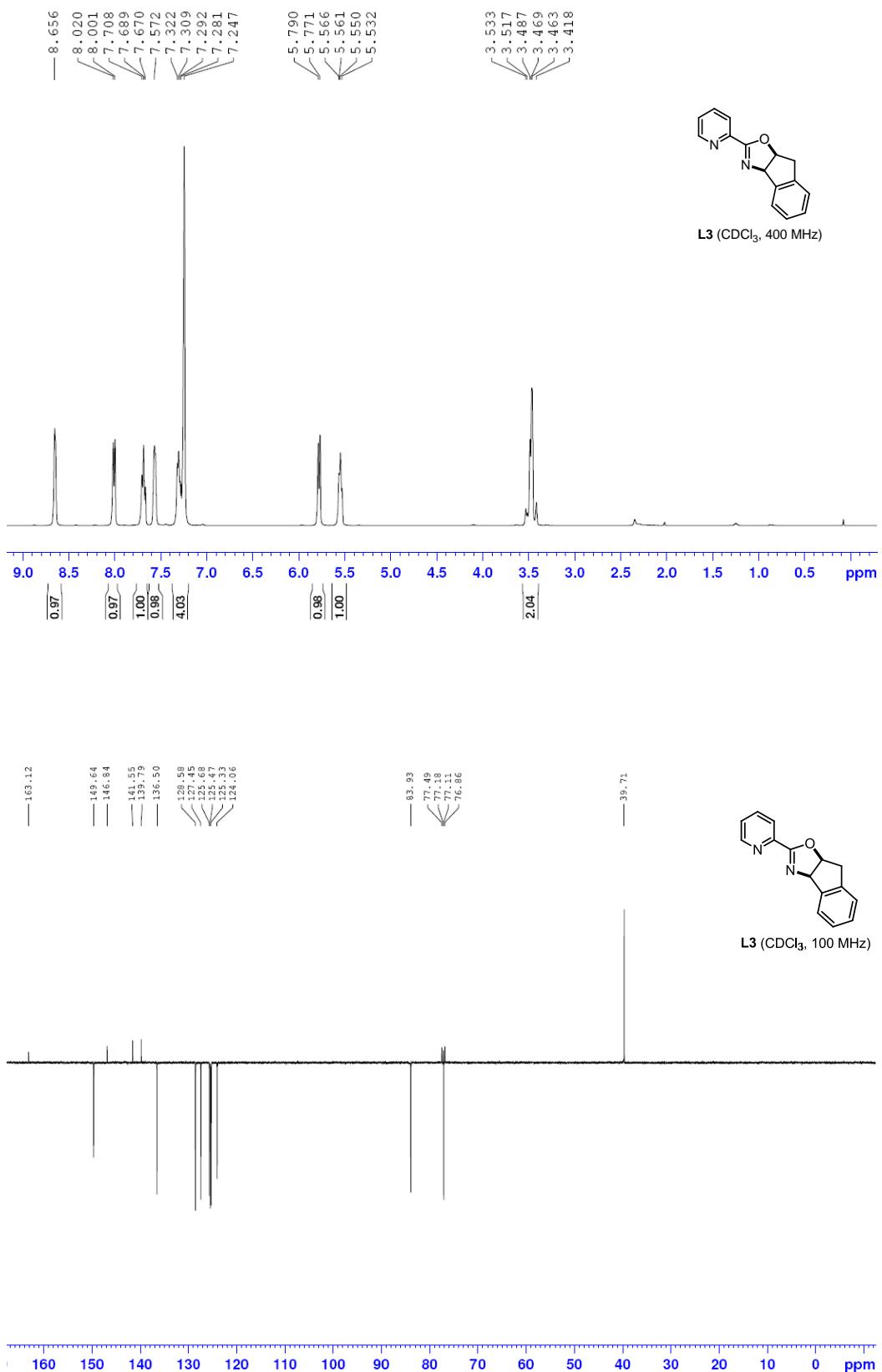
— 20.34

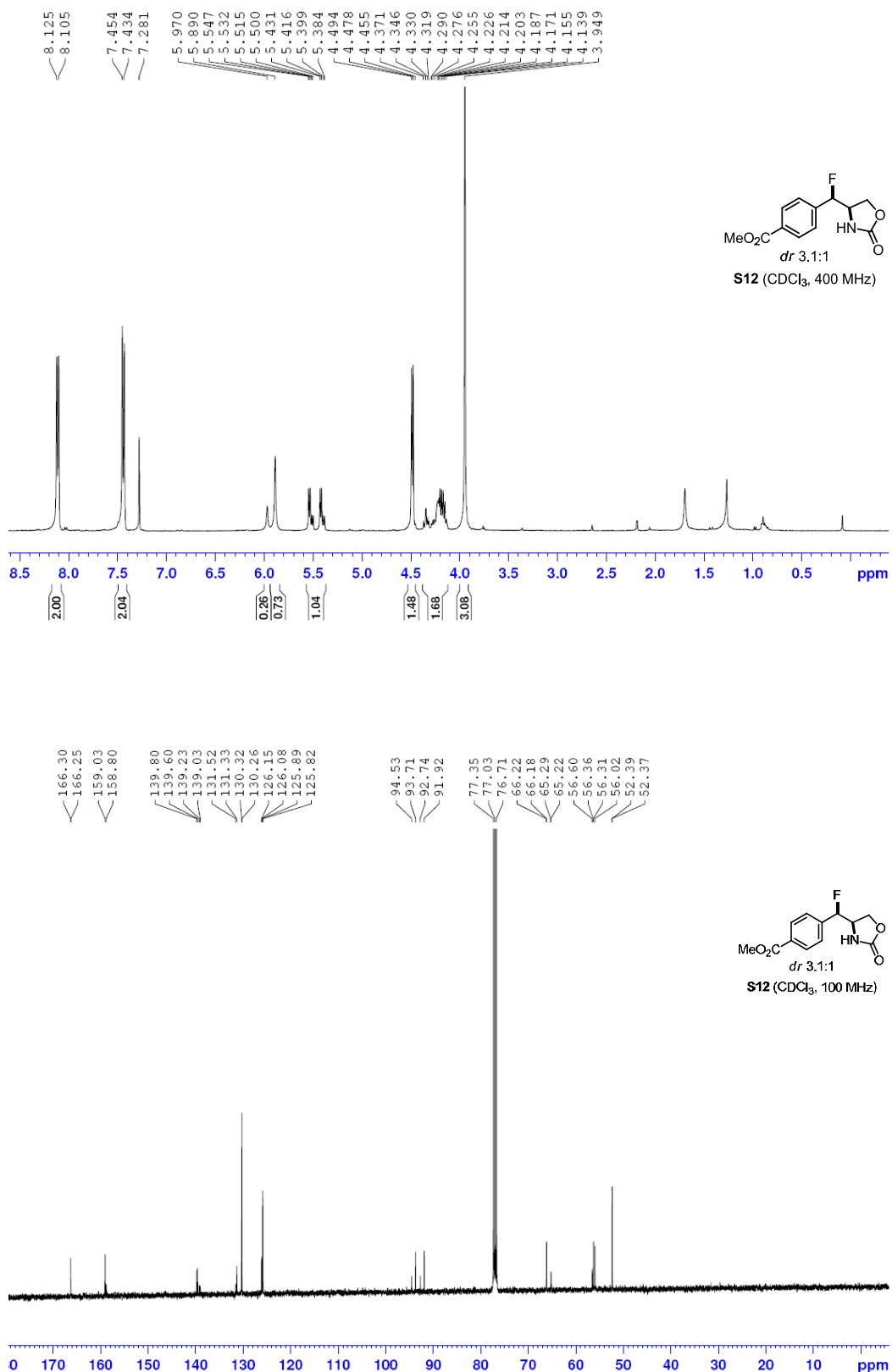


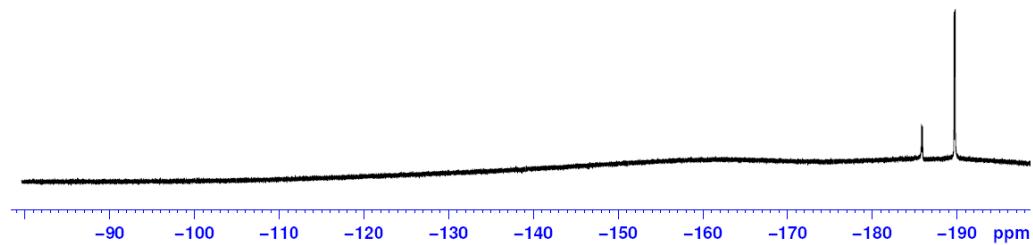
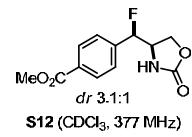
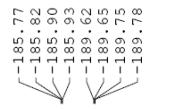
S11 (CDCl_3 , 100 MHz)

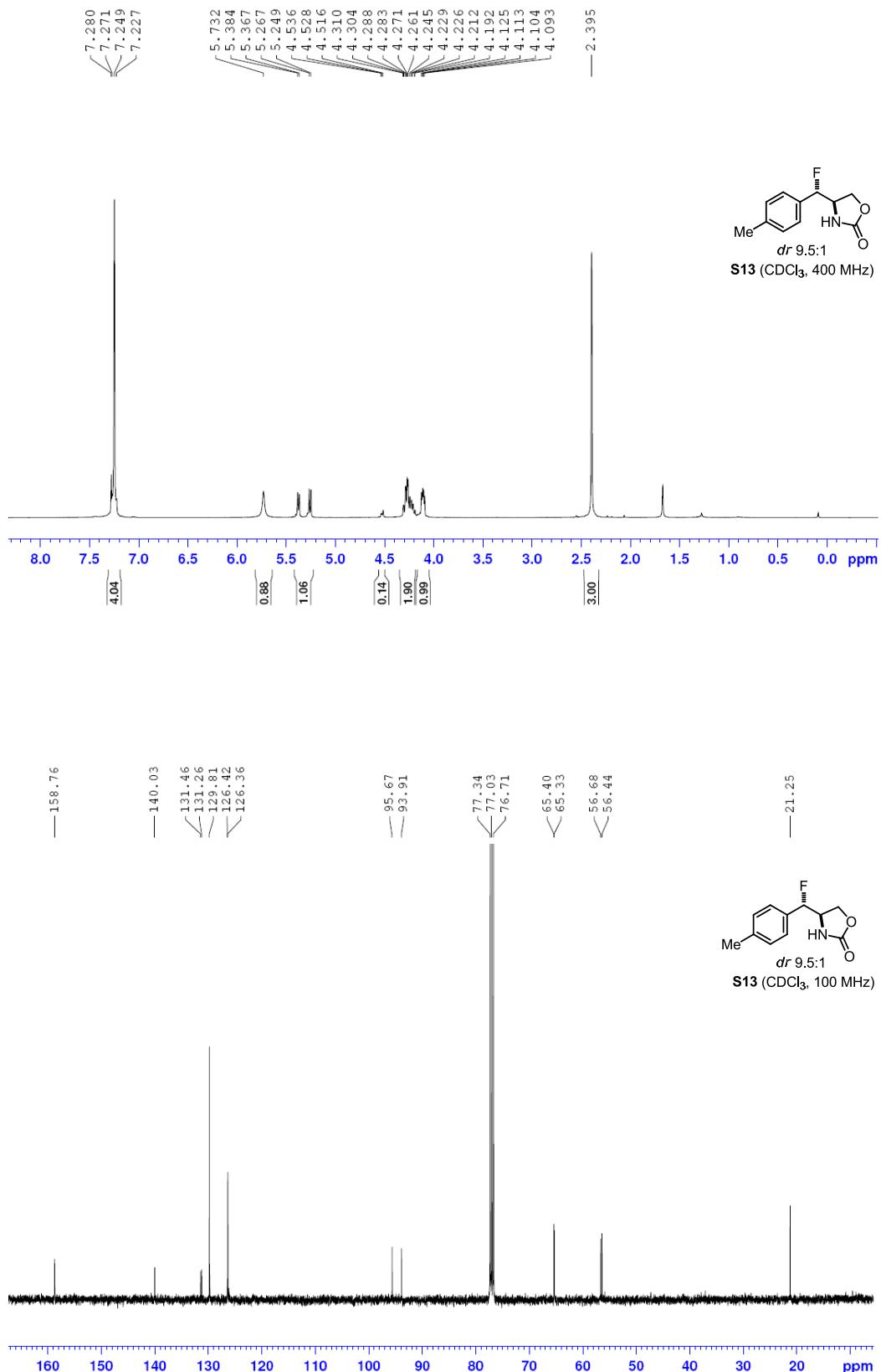




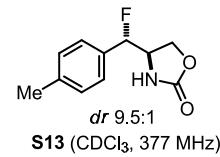




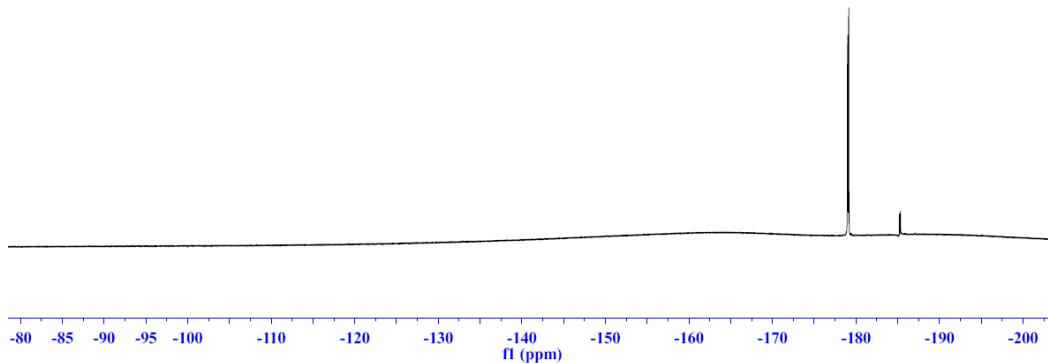


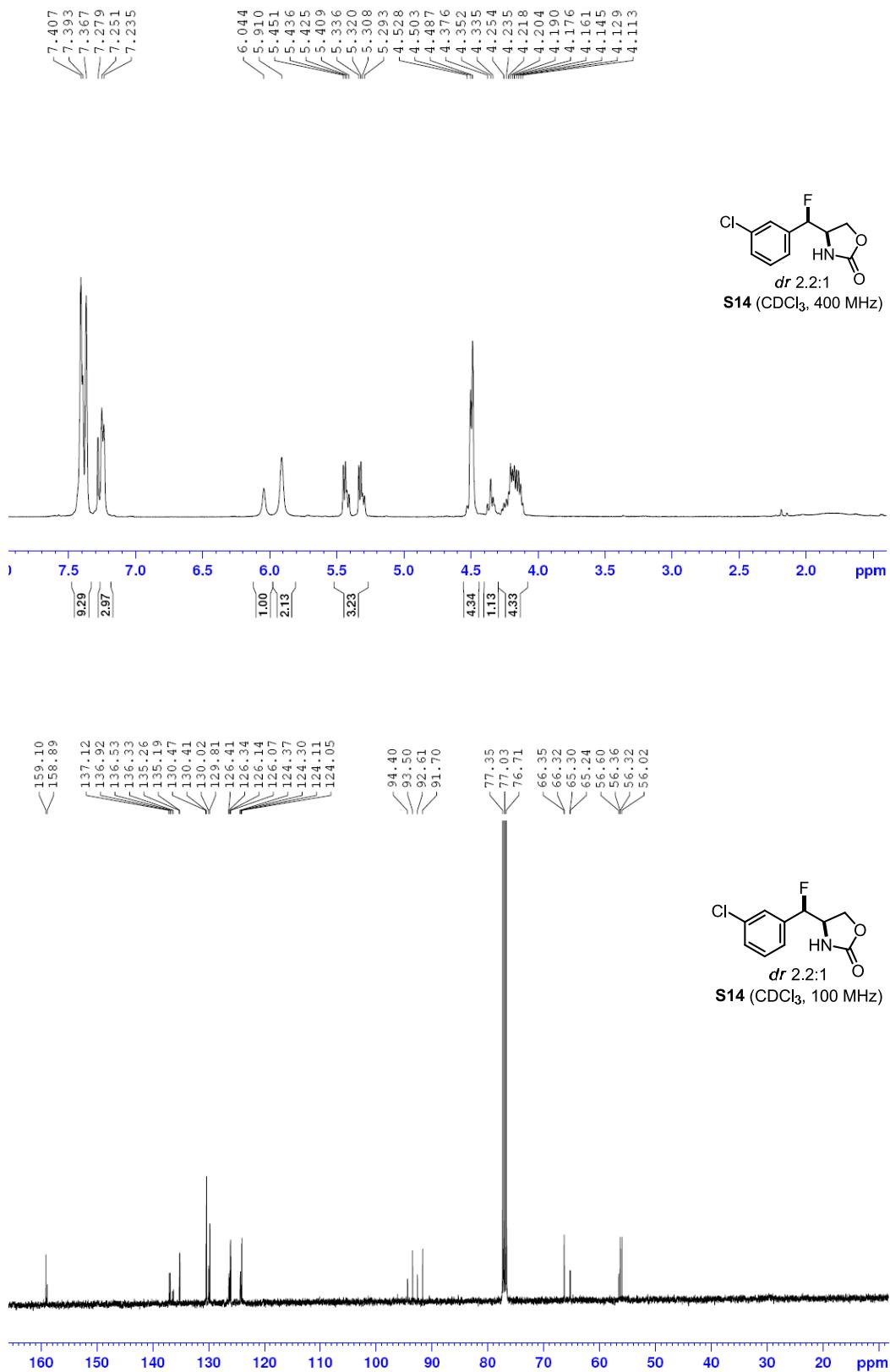


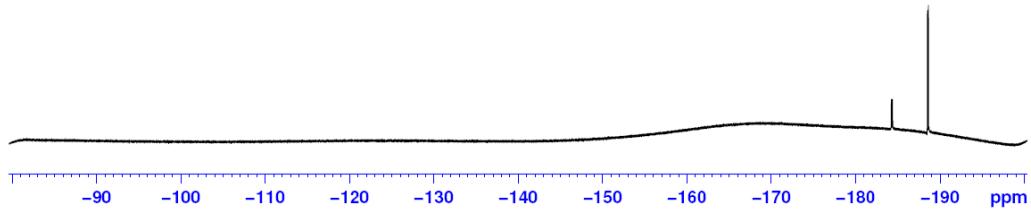
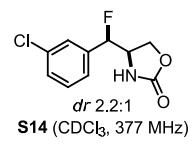
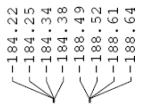
178.981
179.015
179.107
179.141
185.178
185.207
185.301
185.330

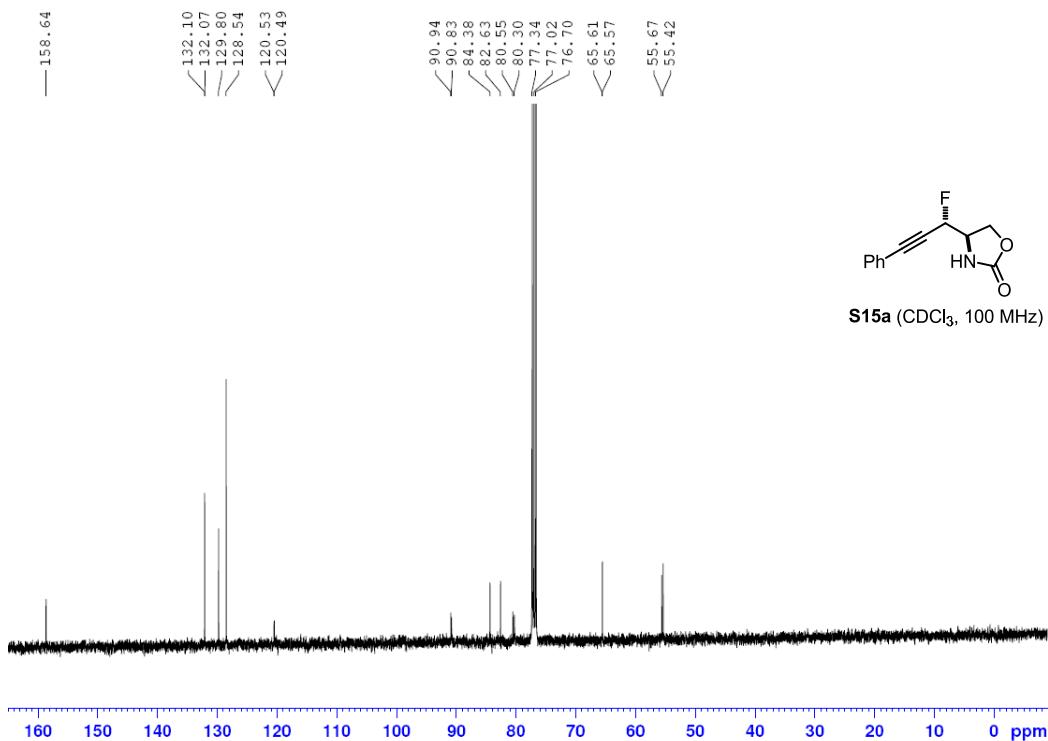
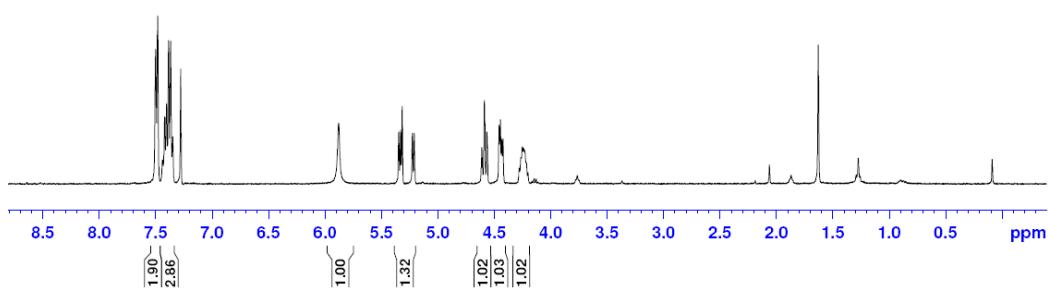
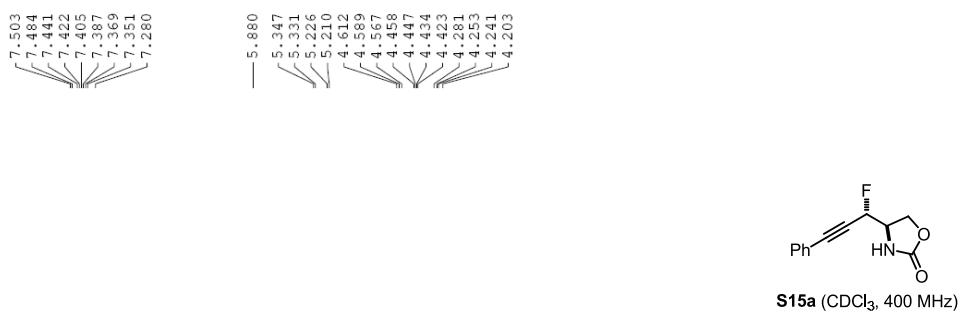


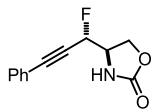
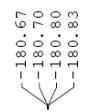
S13 (CDCl_3 , 377 MHz)



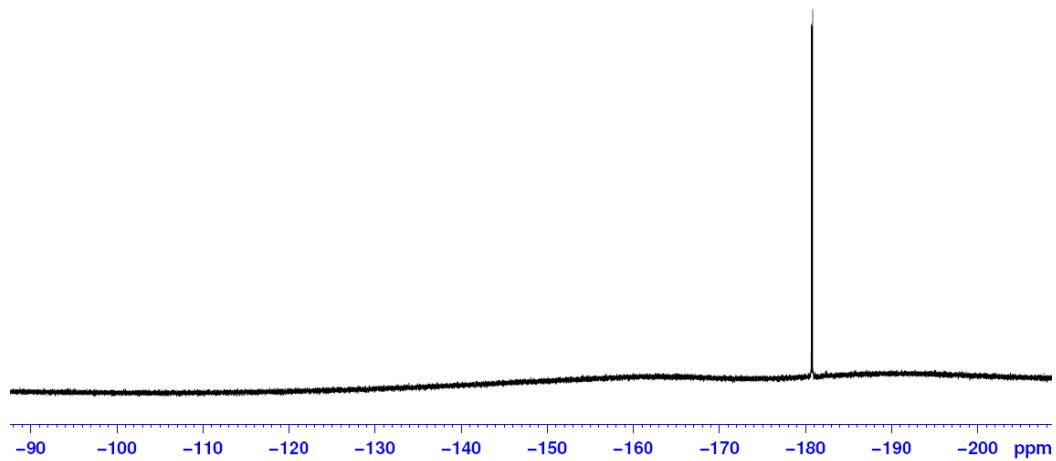


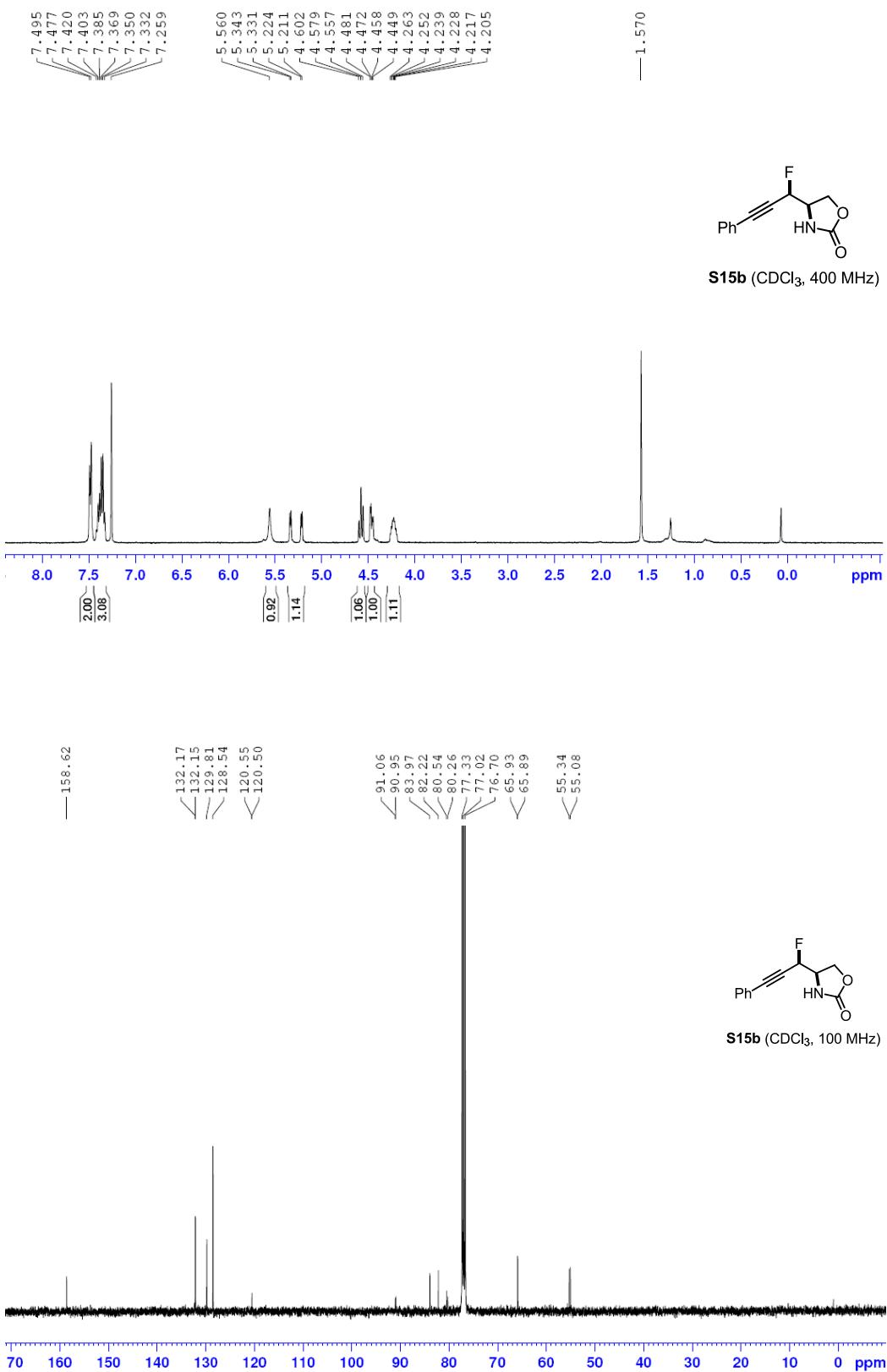




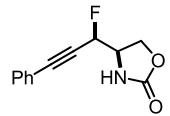


S15a (CDCl_3 , 377 MHz)

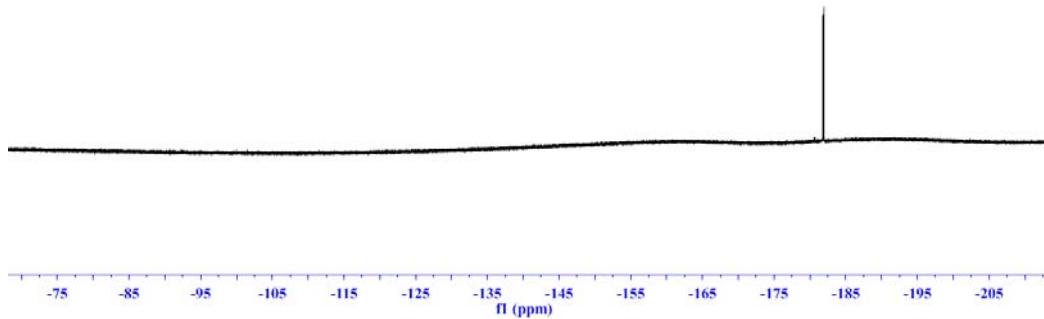


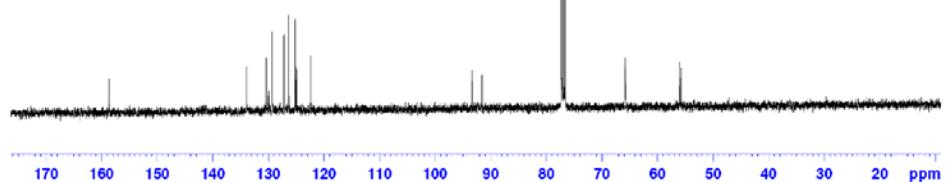
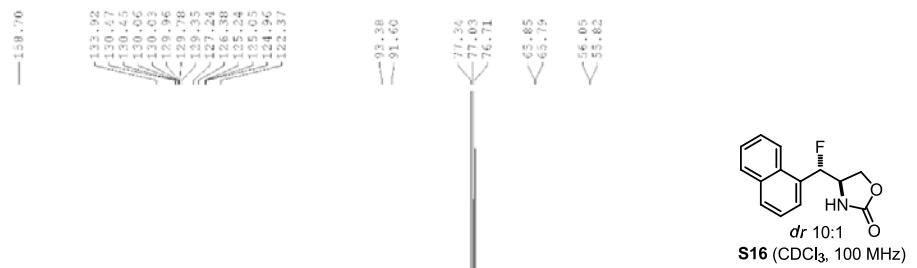
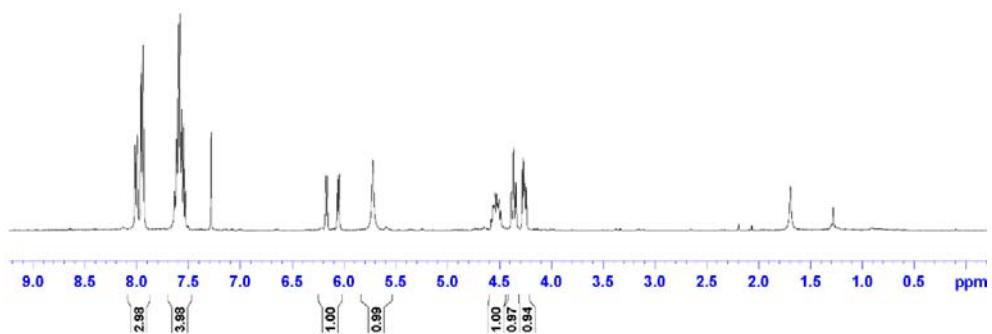
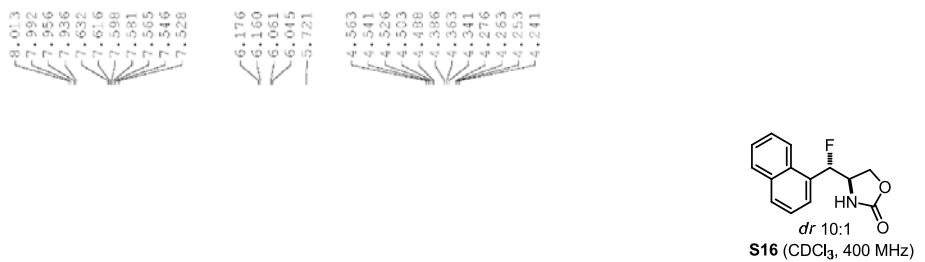


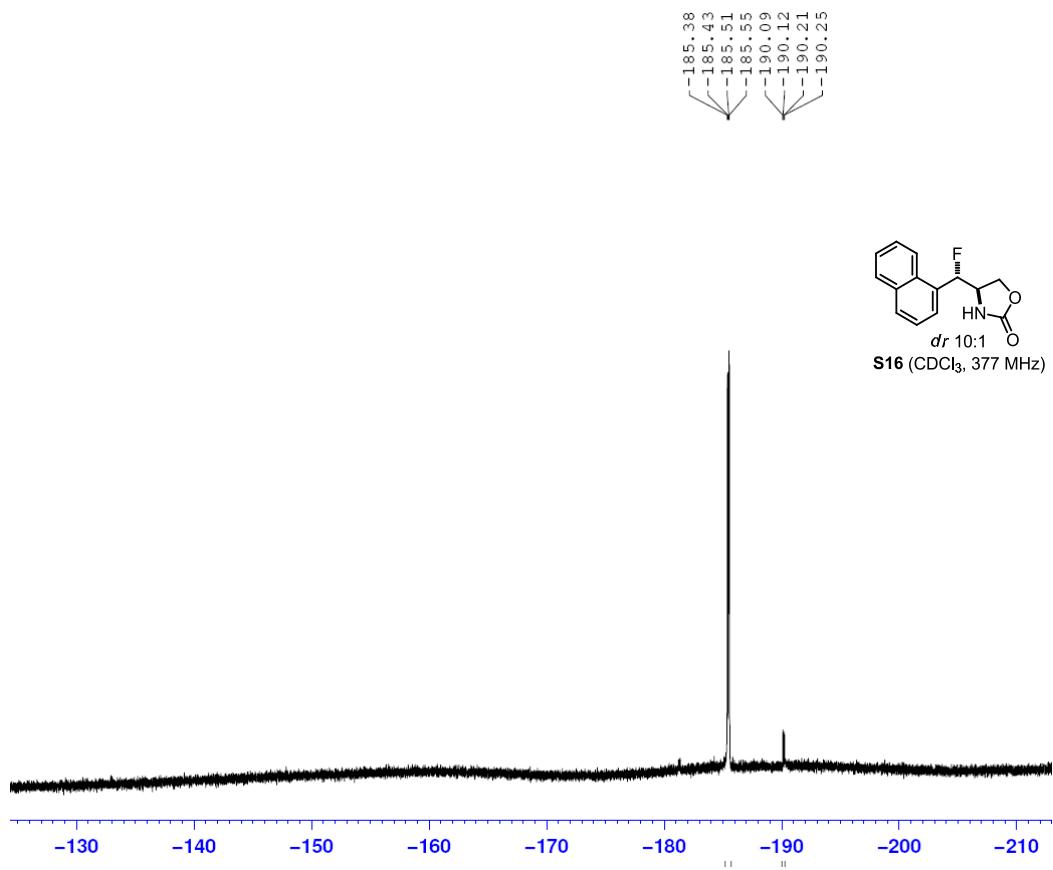
181.808
181.836
181.935
-181.964

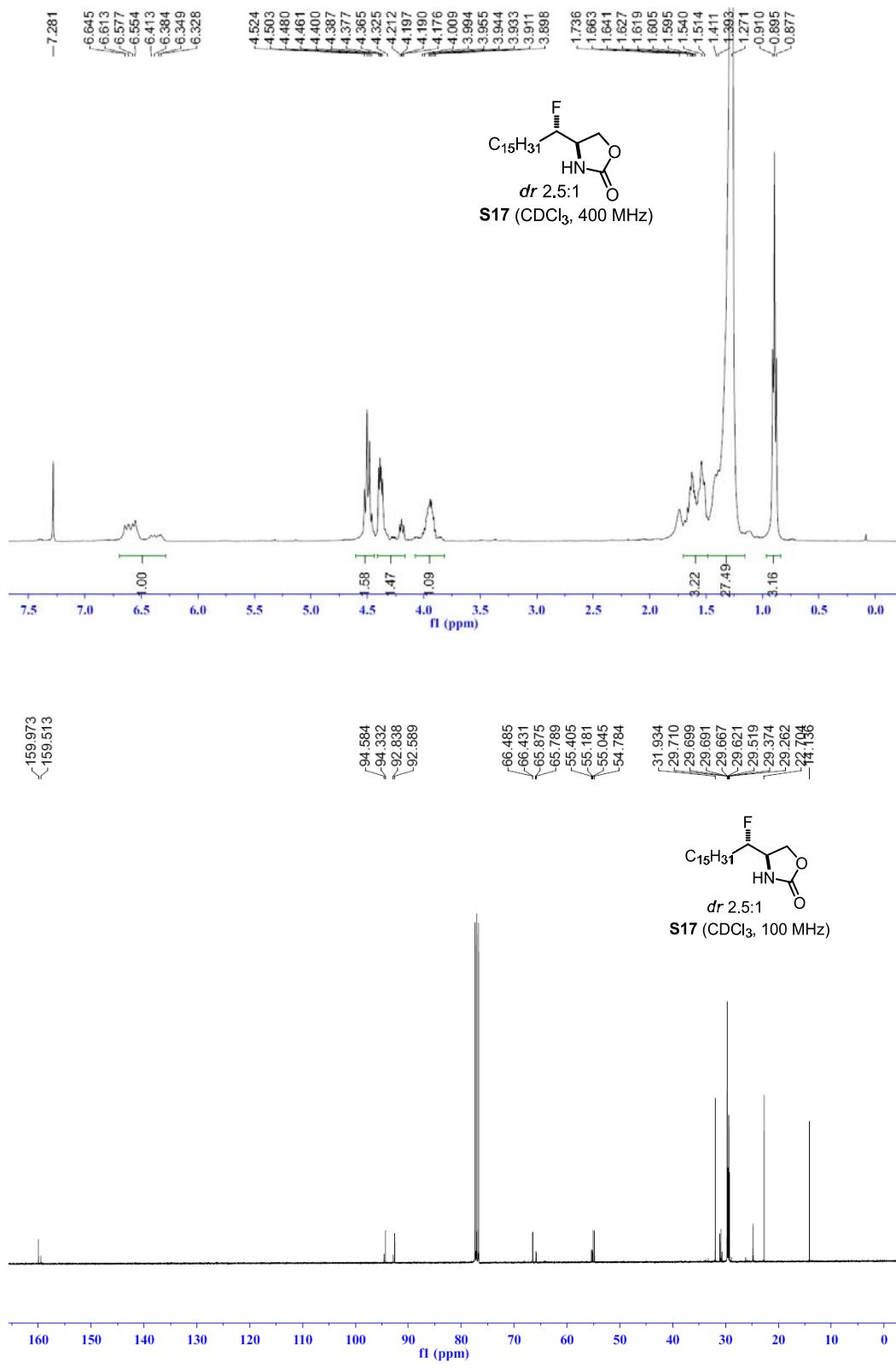


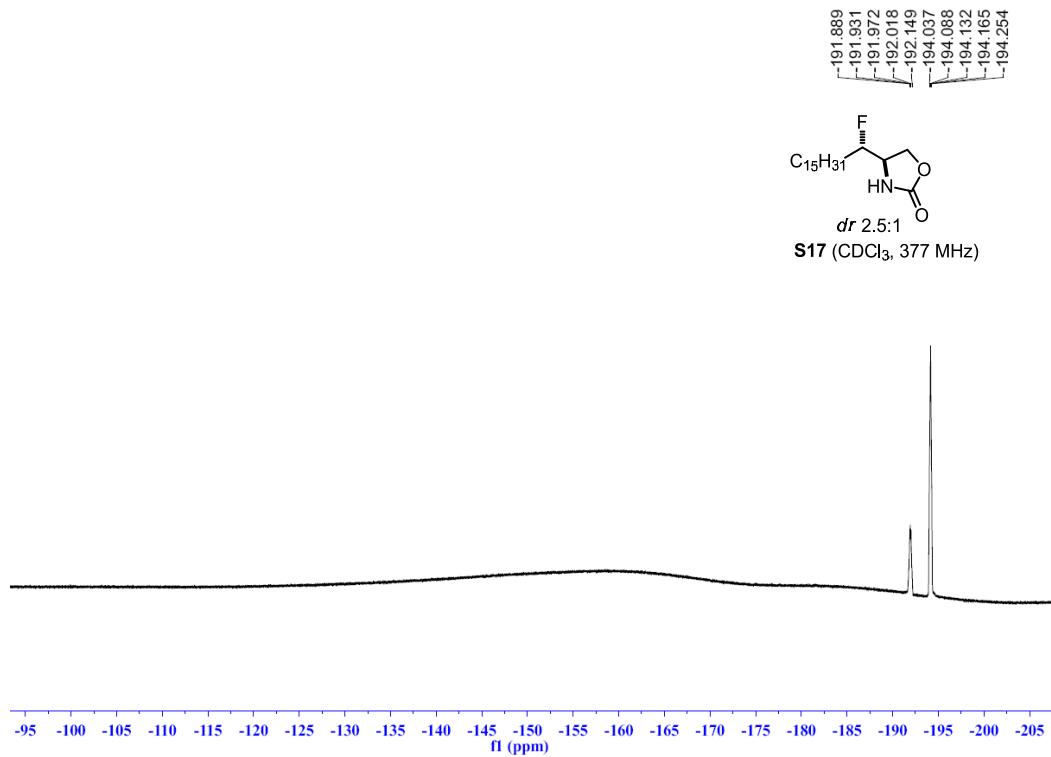
S15b (CDCl_3 , 377 MHz)

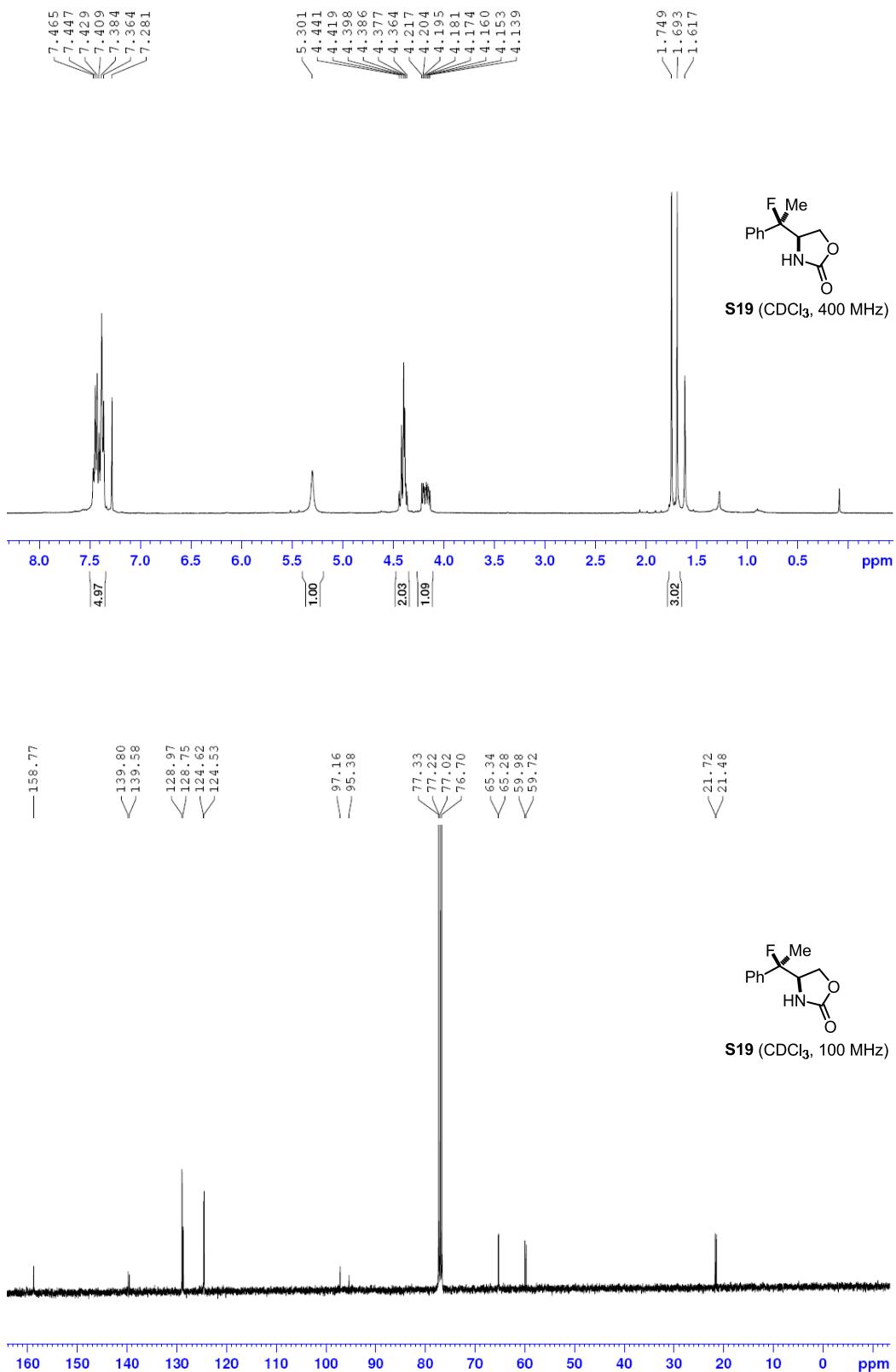




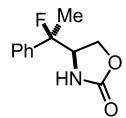




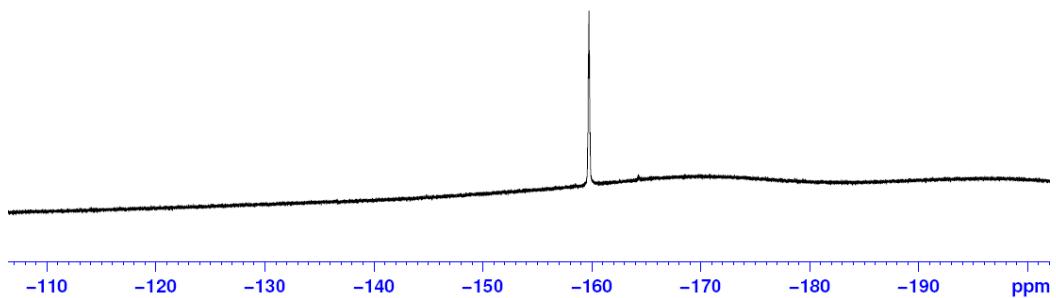


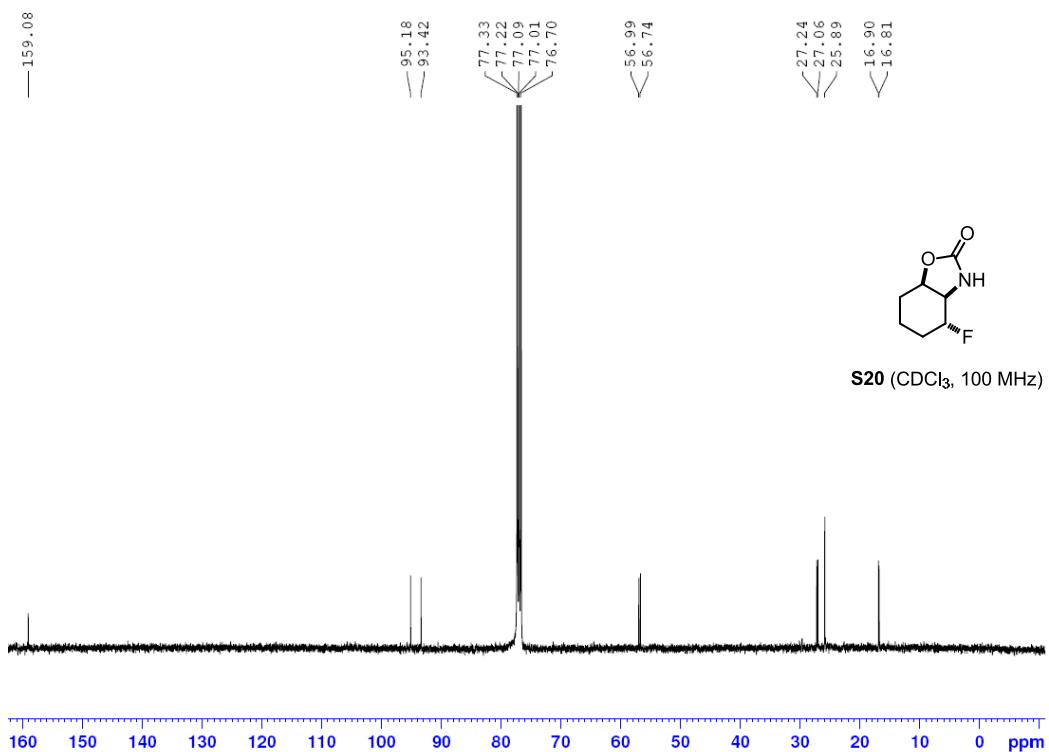
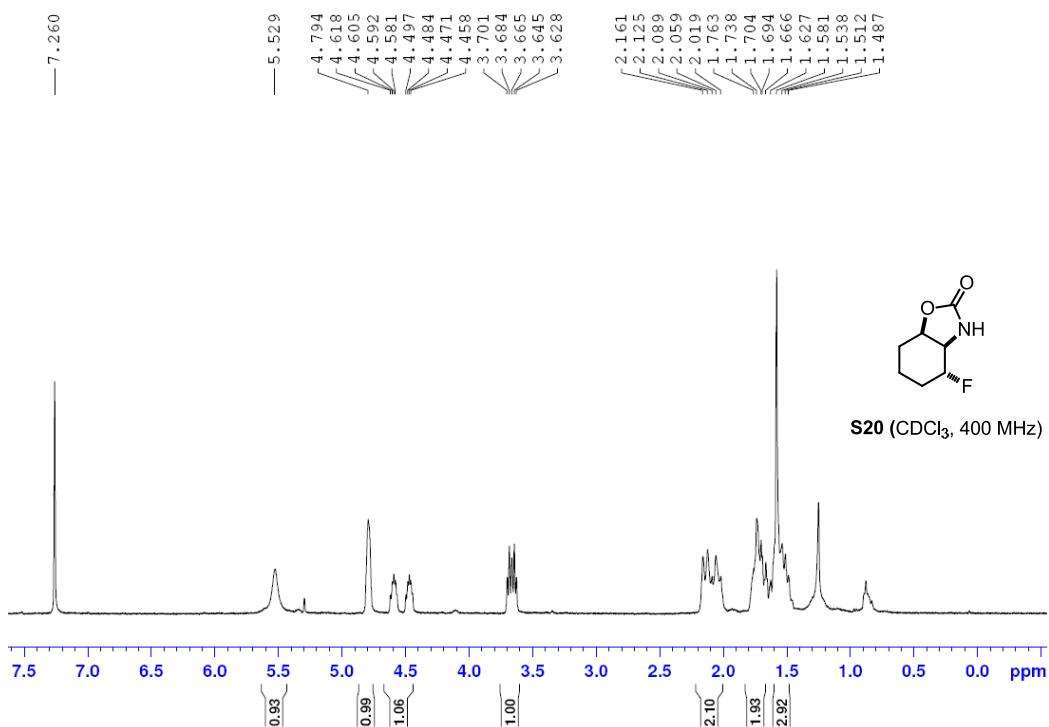


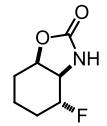
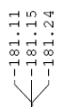
-159.67
-159.72
-159.78
-159.82



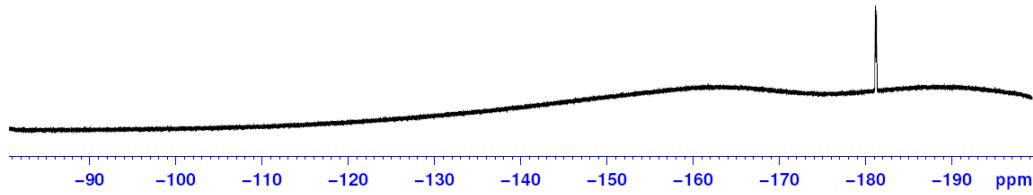
S19 (CDCl_3 , 377 MHz)

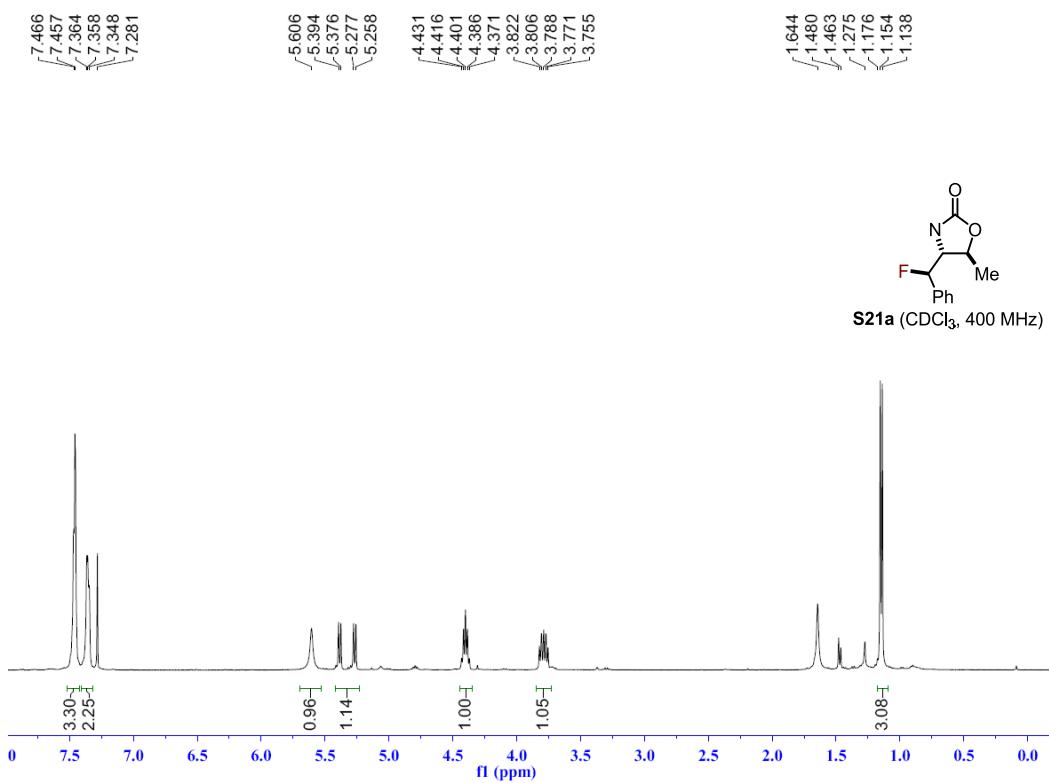


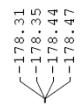




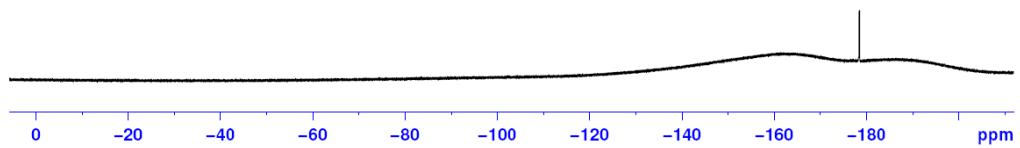
S20 (CDCl_3 , 377 MHz)

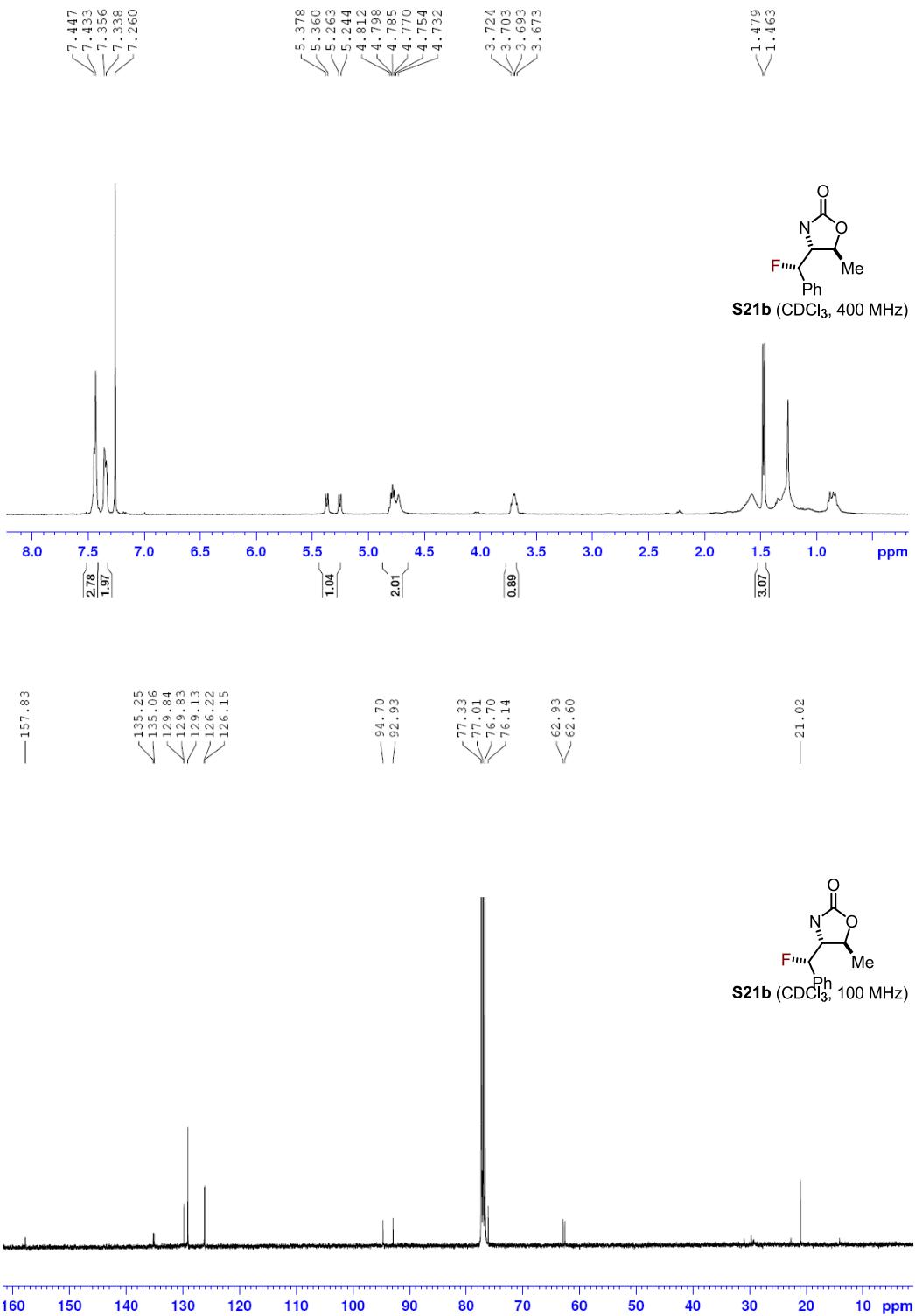


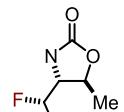
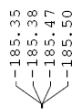




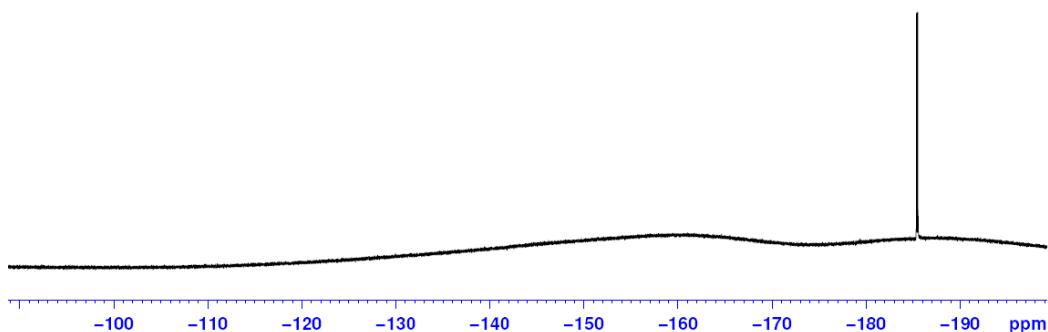
S21a (CDCl_3 , 377 MHz)

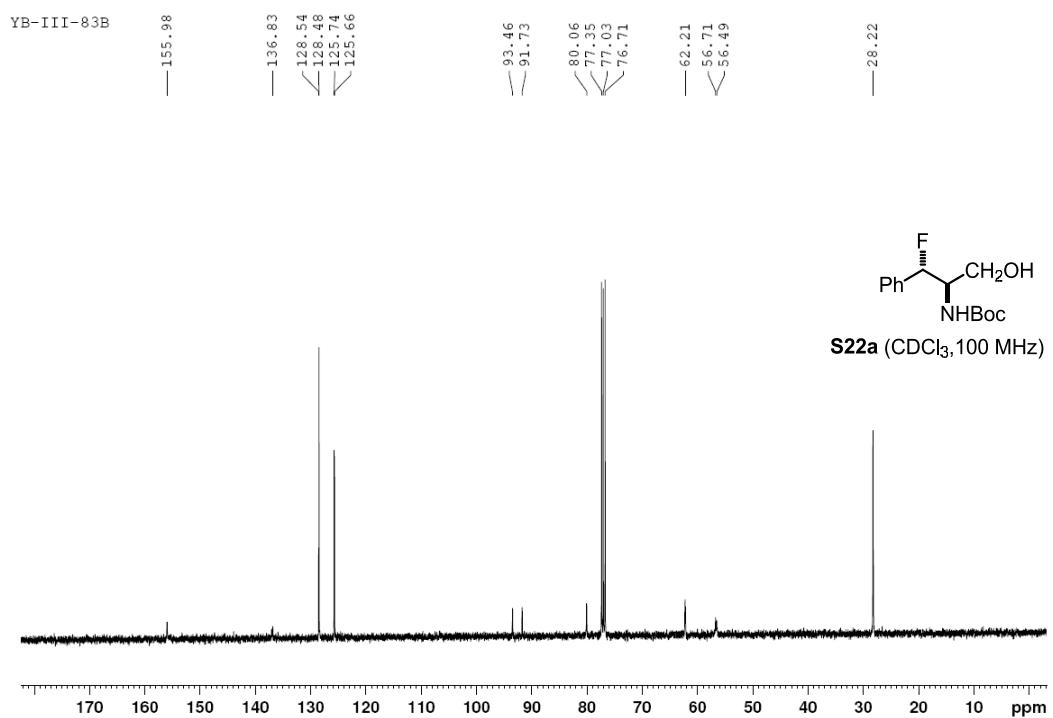
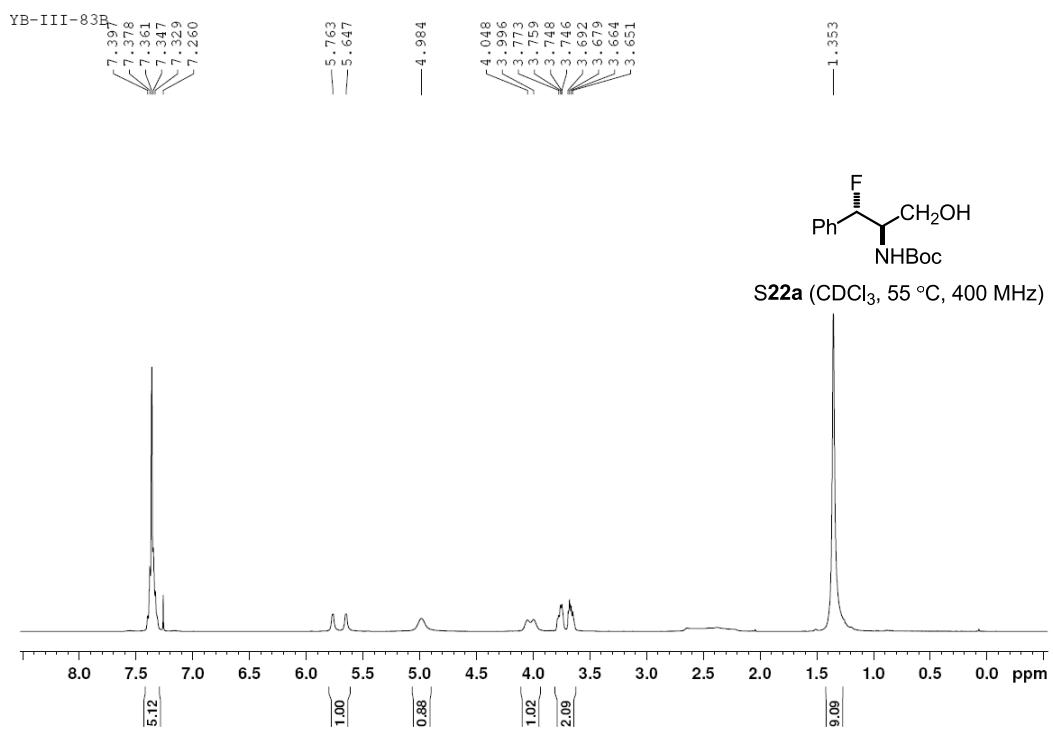




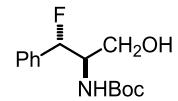


S21b (CDCl_3 , 377 MHz)

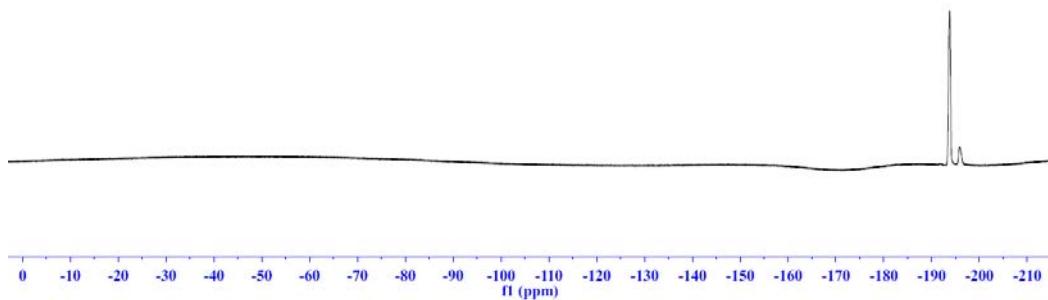


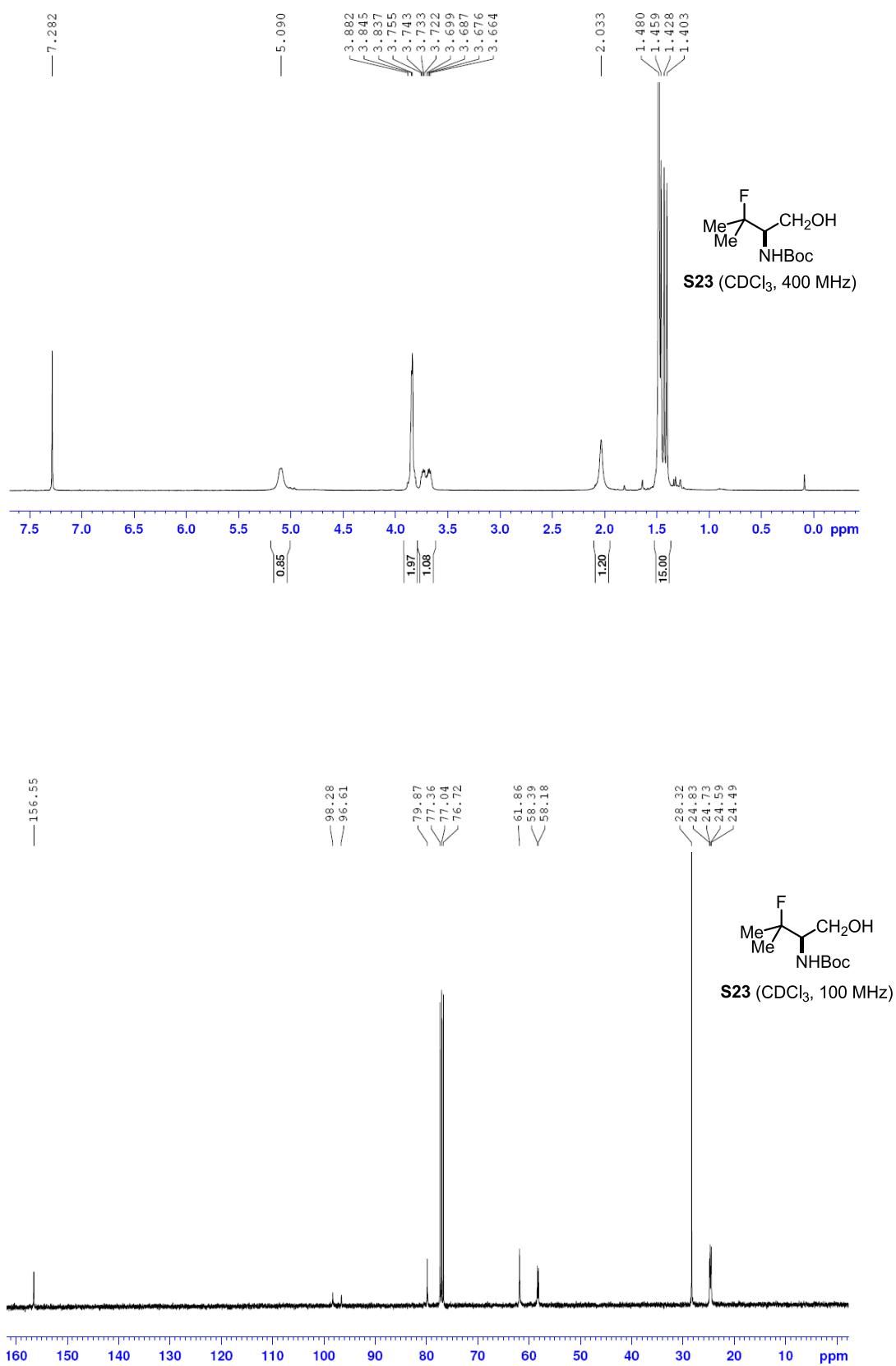


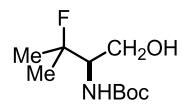
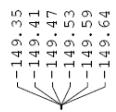
~193.610
~195.626



S22a (CDCl_3 , 377 MHz, with minor rotamer)







S23 (CDCl_3 , 377 MHz)

