Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Access to Enantioenriched Molecules with Diverse Fluorinated Tetrasubstituted Stereocenters Using Hydroxy as Kinetic Resolution Auxiliary Group

Syeda Tazeen Zehra,[a] Shouang Lan,[a] Hao Zhang,[a] Jinggong Liu,*[b] Shuang Yang,[a] and Xinqiang Fang *[a]

[a]State Key Laboratory of Structural Chemistry, and Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.

[b]Orthopedics Department, Guangdong Provincial Hospital of Traditional Chinese Medicine, The Second Affiliated Hospital of Guangzhou University of Chinese Medicine, Guangzhou 510120, China.

∗xqfang@fjirsm.ac.cn
∗liujinggong001@163.com

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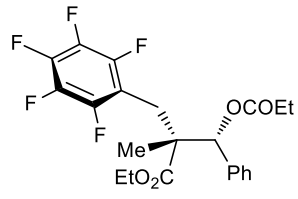
I. General Information.

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using standard procedures. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) or chloroform (δ = 7.26 ppm). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets);

m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific LTQ FT Ultra mass spectrometer. The determination of *e.e.* was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Agilent SuperNova X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 5dm path length on an INESA SGW-1 polarimeter and are reported as follows: $[\alpha]^{rt}_{D}$ (c in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain.

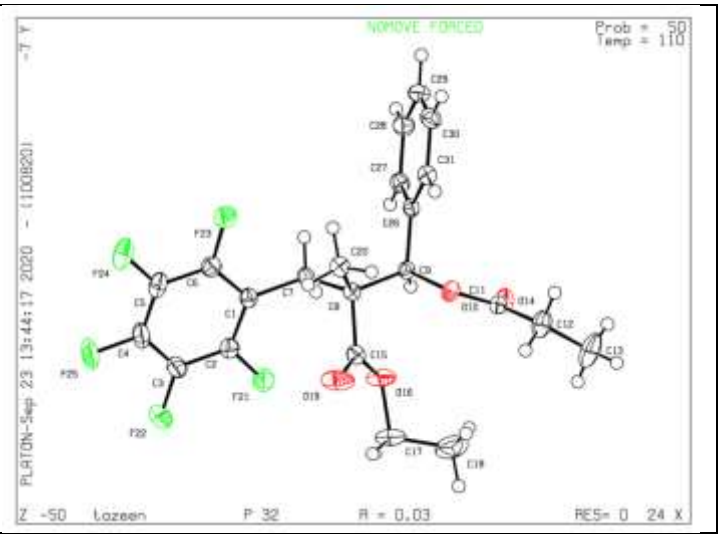
II. X-ray crystallographic analysis

Method for single crystals cultivation: a pure solid sample (10–20 mg) was dissolved in dichloromethane/acetone/THF (2 mL) in a vial at room temperature, and petroleum ether/hexane (0.1 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.



2u

50% probability level



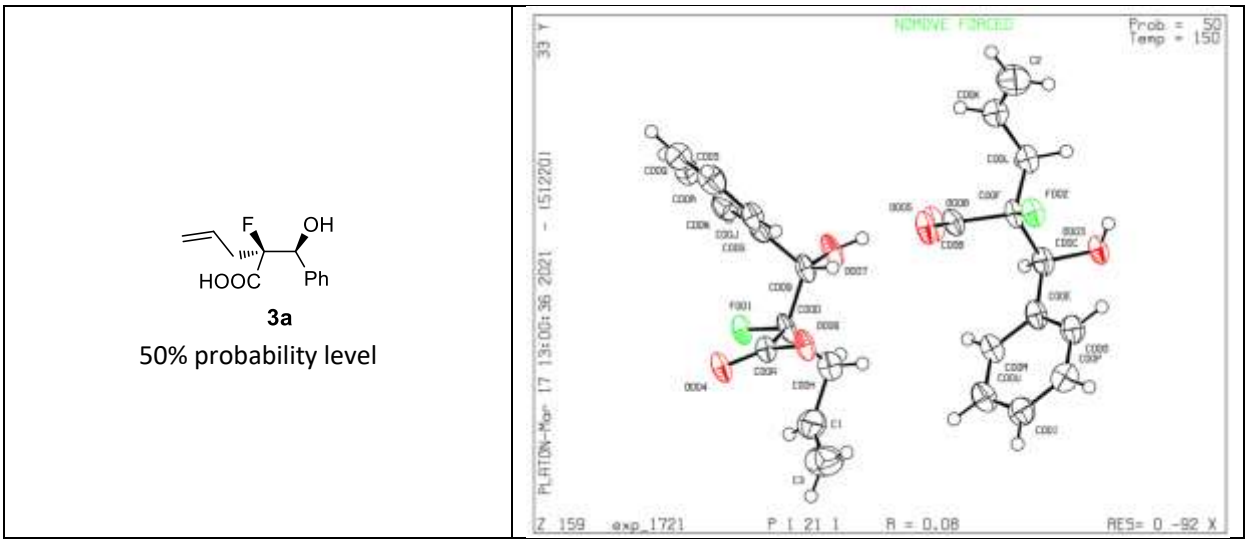


Table 1 Crystal data and structure refinement for 2u.

Identification code	2u
Empirical formula	$C_{22}H_{21}F_5O_4$
Formula weight	444.39
Temperature/K	109.85(16)
Crystal system	trigonal
Space group	$P3_2$
a/Å	17.8769(9)
b/Å	17.8769(9)
c/Å	5.8193(6)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	1610.58(19)
Z	3
ρ_{calc}g/cm^3	1.375
μ/mm^{-1}	0.676
F(000)	690.0
Crystal size/mm^3	0.15 × 0.01 × 0.01
Radiation	Ga Kα (λ = 1.34050)
2Θ range for data collection/°	4.96 to 120.98
Index ranges	$-23 \le h \le 23$, $-22 \le k \le 23$, $-4 \le l \le 7$
Reflections collected	21941
Independent reflections	3736 [R_{int} = 0.0424, R_{sigma} = 0.0271]
Data/restraints/parameters	3736/1/284
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0277, wR_2 = 0.0705

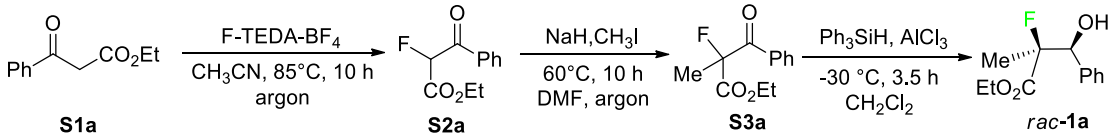
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0713
Largest diff. peak/hole / e Å^{-3}	0.20/-0.17
Flack parameter	0.10(8)

Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{12}H_{12}FO_3$
Formula weight	223.226
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.0078(5)
b/Å	5.8787(2)
c/Å	19.4922(10)
α/°	90
β/°	93.878(5)
γ/°	90
Volume/Å^3	1144.15(9)
Z	4
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.873
F(000)	469.8
Crystal size/mm^3	0.09 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.86 to 156.66
Index ranges	$-11 \le h \le 12$, $-7 \le k \le 7$, $-24 \le l \le 22$
Reflections collected	9609
Independent reflections	4335 [R_{int} = 0.0622, R_{sigma} = 0.0742]
Data/restraints/parameters	4335/1/291
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0821, wR_2 = 0.2301
Final R indexes [all data]	R_1 = 0.0930, wR_2 = 0.2373
Largest diff. peak/hole / e Å^{-3}	0.56/-0.35
Flack parameter	0.2(3)

III. General procedures for the preparation of substrates

1. Typical procedure for the preparation of substrate 1a–1l, and 1t

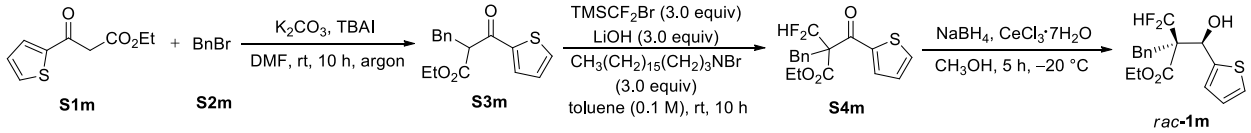


To a stirred suspension of F-TEDA-BF_4 (20 g, 57.2 mmol) in CH_3CN (10 mL), β-ketoester **S1a** (10 g, 52.0 mmol) was introduced at room temperature under argon atmosphere. The reaction mixture was warmed to 85 ℃ and stirred for 10 h. The reaction mixture was filtered. The liquid phase concentrated and the residue was purified by chromatography on silica (petroleum ether/ethyl acetate, v:v = 100:1) to afford **S2a** (10.72 g, 99% yield).

To an oven dried flask sodium hydride (137 mg, 5.7 mmol) in DMF (15 mL) was added under argon at room temperature. After a few minutes stirring, **S2a** (1.0 g, 4.7 mmol) in DMF (5 mL) was added dropwise at the same temperature. After 10 min additional stirring, corresponding methyl iodide (1.35 g, 9.5 mmol) was introduced to the reaction mixture. The reaction mixture was warmed to 60 ˚C and stirred for 10 h. The reaction was quenched with water, and extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give **S3a** as yellow oil (0.76 g, 72% yield).

To the stirring solution of **S3a** (756 mg, 3.4 mmol) in CH_2Cl_2 (15 mL) were added Ph_3SiH (1.17 g, 4.5 mmol) and $AlCl_3$ at –30 ˚C. The reaction mixture was kept at this temperature for 3.5 h. The mixture was then diluted with Et_2O (25 mL), and saturated $NaHCO_3$ was added. Aqueous layer was extracted with Et_2O (2 × 100 mL), and the combine organic layer were washed with water and brine, and dried over Na_2SO_4. Purified by column chromatography (petroleum ether/ethyl acetate, v:v = 10:1) afforded *rac*-**1a** as colorless oil (0.64 g, 85% yield).

2. Typical procedures for the synthesis of substrates 1m–1r, 1u, and 1v



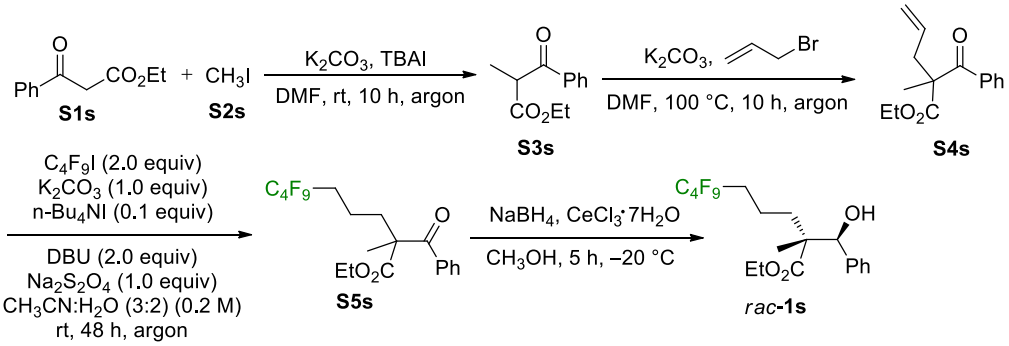
To the stirred suspension of potassium carbonate (1.04 g, 7.5 mmol) and tetra-*n*-butyl ammonium iodide (372 mg, 1.0 mmol) in DMF (10 mL), β-ketoester **S1m** (1.0 g, 5.0 mmol) was introduced at room temperature under argon atmosphere. After an additional 20 min stirring, benzyl bromide **S2m** (1.7 g, 10.1 mmol) was added at the same temperature. After stirring for 10 h, the reaction was quenched with water, and then extracted with ethyl acetate (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The

residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give the product **S3m** as a yellow oil (1.2 g, 85% yield).

The solution of **S3m** (1.2 g, 4.2 mmol), LiOH (0.3 g, 12.5 mmol), $CH_3(CH_2)_{15}(CH_2)_3NBr$ (3.03 g, 8.3 mmol) in 41 mL dry toluene was stirred at room temperature for 10 min. Then $TMSCF_2Br$ (2.53 g, 12.5 mmol) was added slowly, and the reaction mixture was stirred for 10 h at the same temperature. The reaction mixture was diluted with ethyl acetate, and washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. Crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to give **S4m** as a yellow oil (704 mg, 50% yield).

To the solution of **S4m** (704 mg, 1.8 mmol) in 3.5 mL methanol was added $CeCl_3.7H_2O$ (1.01 g, 2.7 mmol) and the mixture was stirred at –20˚C for 10 min. Then $NaBH_4$ (75 mg, 1.99 mmol) was added in two batches. After stirring for 5 h, the reaction mixture was quenched with water and extracted with ethyl acetate (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 10:1) to give the product *rac*-**1m** as a yellow oil (510 mg, 83% yield).

3. Typical procedures for the synthesis of substrate 1s

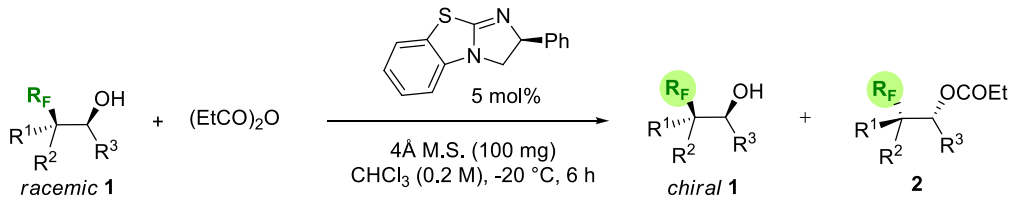


S3s was synthesized by the procedure of **S3m.** In an oven dried flask potassium carbonate (1.0 g, 7.2 mmol) and DMF (10 mL) was taken, then **S3s** (1.0 g, 4.8 mmol) was introduced to this suspension at room temperature under argon atmosphere. After an additional 20 min stirring, allyl bromide (0.7 g, 5.8 mmol) was added at the same temperature. The temperature was slowly rose up to 100 ˚C and continued stirring at this temperature for 10 h. Then the reaction was quenched with water, and extracted with ethyl acetate (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give the product **S4s** as light brown oil (1.05 g, 88% yield).

In a sealed tube **S4s** (1.0 g, 4.06 mmol), C_4F_9I (2.8 g, 8.12 mmol), DBU (1.2 g, 8.12 mmol), K_2CO_3 (0.56 g, 4.06 mmol), $Na_2S_2O_4$ (0.76 g, 4.06 mmol), and tetra-*n*-butyl ammonium iodide

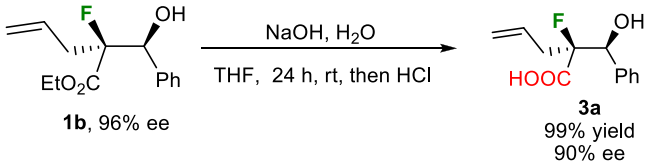
(0.14 g, 0.406 mmol) was added to the mixture of 0.2 M solution of (3:2) acetonitrile and water. After stirring for 48 h at room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate (2 × 20 mL) and washed with brine. The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give the product **S5u** as dark brown (466 mg, 25% yield). Reduction procedure was same as **1m**.

IV. Typical procedures for the kinetic resolution.

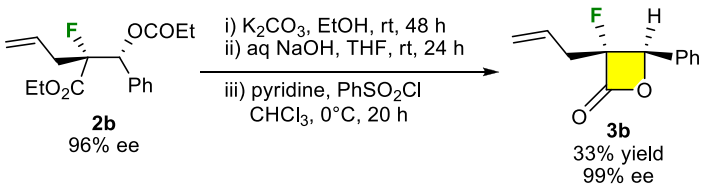


Under argon atmosphere, to a 50 mL Schlenk tube was taken substrate **1a** (452.5 mg, 2.0 mmol), 4 Å M.S (1000 mg) and catalyst (25.3 mg, 0.1 mmol). To this mixture 10 mL of $CHCl_3$ was added and then propionic anhydride (0.13 mg, 1.0 mmol) was added dropwise via syringe and the resulting mixture was stirred for 6 h at –20 ˚C. After 6 h stirring the solvent was removed under reduced pressure and the residue was purified by flash chromatography with petroleum ether/ethyl acetate (v:v = 10:1) as eluent to afford the product **2a** (279 mg, 49% yield) and recovered chiral starting material **1a** (221 mg, 49% yield).

V. Procedures for the derivatizations.



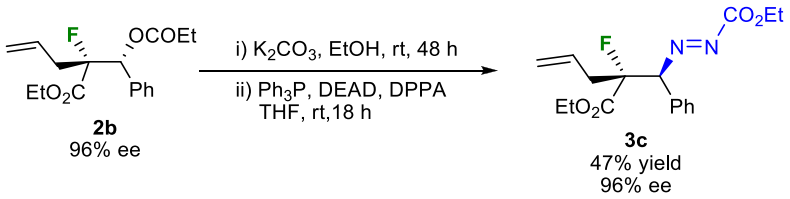
To the solution of **1b** (50.4 mg, 0.2 mmol) in alcohol and THF (0.4 mL), 1 M aqueous solution of NaOH was added to the reaction mixture. The reaction mixture was continued stirring for 24 h. After 24 h, the reaction was acidified with 2M HCl and extracted with CH_2Cl_2. The combine organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduce pressure to get **3a** (44.8 mg, 99% yield).



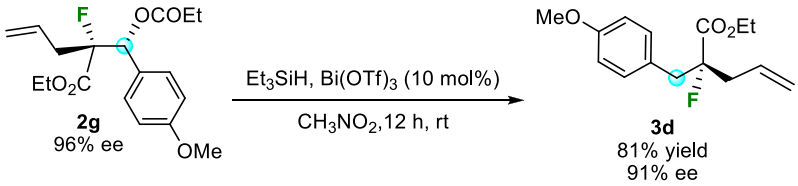
To the solution of **2b** (61.6 mg, 0.2 mmol) in EtOH (1 mL), K_2CO_3 (138 mg, 1.0 mmol) was introduced at rt. After 48h, the solution was evaporated and the crude product was purified by flash chromatography with petroleum ether/ethyl acetate (v:v = 10:1) as eluent to afford the product (50.2 mg, 99% yield).

To the solution of *β*-hydroxy ester (50.2 mg, 0.2 mmol) in alcohol and THF (0.4 mL), 1M aqueous solution of NaOH was added to the reaction mixture. The reaction mixture was continued stirring for 24 h. After 24 h, the reaction was acidified with 2 M HCl and extracted with CH_2Cl_2. The combine organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduce pressure to get *β*-hydroxy acid (44.8 mg, 100% yield).

To the stirred solution of *β*-hydroxy acid **5b** (40.3 mg, 0.18 mmol) and pyridine (28.4 mg, 0.36 mmol) in CH_2Cl_2 (0.2 M) at 0˚C was slowly added benzenesulfonyl chloride (31.7 mg, 0.18 mmol). After 20 h, the mixture was evaporated and residue was extracted with hexane. Evaporation of hexane followed by recrystallization of impure lactone from hexane gave **3b** (12.5 mg, 33% yield).

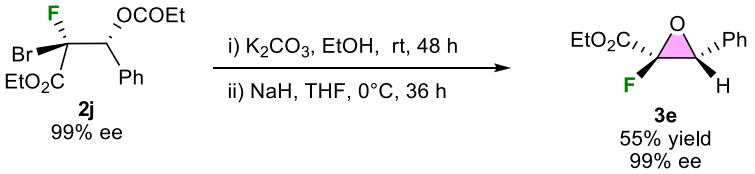


To the solution of **2b** (61.6 mg, 0.2 mmol) in EtOH (1 mL), K_2CO_3 (138 mg, 1.0 mmol) was introduced at room temperature. After 48h, the solution was evaporated. The crude product was purified by flash chromatography with petroleum ether/ethyl acetate (v:v = 10:1) as eluent to afford the *β*-hydroxy ester (50.2 mg, 99% yield). *β*-Hydroxy ester (50.2 mg, 0.2 mmol) was dissolved in THF (0.5 mL). To this solution PPh_3 (86.5 mg, 0.33 mmol), DEAD (870 mg, 5.0 mmol) and DPPA (715 mg, 2.6 mmol) was successively added in this order. After stirring for 48 h at room temperature, the reaction was quenched by saturated NH_4Cl and stirred for additional 5 min. The aqueous layer were extracted with Et_2O and combine organic layer was dried over Na_2SO_4. After removal of solvent, the crude product was purified over column chromatography by using petroleum ether/ethyl acetate (v:v = 20:1) to give title compound **3c** (32.1 mg, 47% yield).



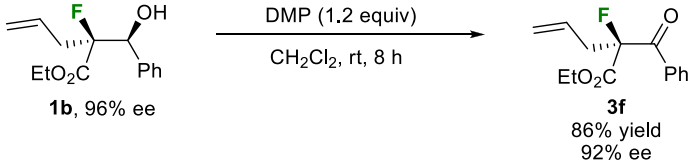
2g (169 mg, 0.5 mmol) and Et_3SiH (580 mg, 5.0 mmol) were dissolved in nitromethane (2 mL). At ambient temperature $Bi(OTf)_3$ (32.8 mg, 0.05 mmol) was added in one portion and the

solution was stirred for the indicated time. After 12 h, the reaction was quenched by the addition of EtOAc/water (10:10 mL) and aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combine organic layers were washed with water and brine, dried crude product over Na_2SO_4 and solvent was remover under reduce pressure. The crude product was purified by flash column chromatography (cyclohexane/ethyl acteate 40:1) to get pure product **3d** (108 mg, 81% yield).



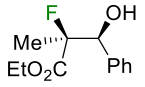
To the solution of **2j** (39.4 mg, 0.114 mmol) in EtOH (1 mL), K_2CO_3 (138 mg, 1.0 mmol) was introduced at rt. After 48h, the solution was evaporated. The crude product was purified by flash chromatography with petroleum ether/ethyl acetate (v:v = 10:1) as eluent to afford the intermediate product (22.6 mg, 68.5% yield).

THF (1 mL) was added to NaH (1.6 mg, 0.065 mmol) at 0˚C under argon atmosphere. *β*-Hydroxy ester (18.9 mg, 0.065 mmol) was dissolved in THF (0.9 mL) and added to the reaction flask. The reaction mixture was continued stirring for 36 h at the same temperature. After 36 h, the crude was directly subjected to the column chromatography by using petroleum ether/ethyl acetate (v:v = 20:1) to get pure epoxide **3e** (7.5 mg, 55% yield).



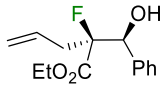
To the stirred solution of chiral **1b** (25.2 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL), Dess-Martin periodinane (50.4 mg, 0.12 mmol) was added at room temperature. After stirring for 8 h at room temperature, the reaction mixture was quenched with saturated $Na_2S_2O_3$ and extracted with CH_2Cl_2 (20 mL × 3). The combine organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give product **3f** as a colorless oil (21.3 mg, 86% yield).

VI. Characterizations of new compounds.



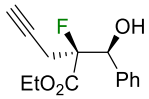
1a

ethyl (2*S*,3*S*)-2-fluoro-3-hydroxy-2-methyl-3-phenylpropanoate (1a): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 221 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44–7.30 (m, 5H), 4.96 (dd, *J* = 15.9, 5.0 Hz, 1H), 4.19–4.12 (m, 2H), 2.79 (d, *J* = 5.1 Hz, 1H), 1.61 (d, *J* = 22.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (d, *J* = 23.9 Hz), 137.8, 128.7, 128.3, 127.7 (d, *J* = 1.6 Hz), 96.2 (d, *J* = 190.9 Hz), 76.4 (d, *J* = 22.8 Hz), 61.9, 19.5 (d, *J* = 23.7 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -165.3 (qd, *J* = 22.2, 15.9 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}O_3FNa$ 249.0897; Found 249.0895. $[\alpha]_D^{29}$: –382.6 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 15.4 min, R_t (minor) = 18.0 min. IR (KBr thin film, cm^{-1}): ν 3478, 2990, 2337, 1743, 1449, 1321, 1055, 699.



1b

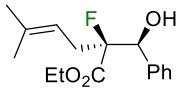
ethyl (*S*)-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)pent-4-enoate (1b): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 255 mg, 51% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.35–7.31 (m, 3H), 5.83–5.75 (m, 1H), 5.19–5.13 (m, 2H), 4.94 (d, *J* = 18.7 Hz, 1H), 4.12–4.05 (m, 2H), 2.91–2.84 (m, 1H), 2.80–2.64 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (d, *J* = 24.5 Hz), 137.7, 130.7 (d, *J* = 4.0 Hz), 128.7, 128.4, 127.7, 120.0, 98.5 (d, *J* = 196.7 Hz), 76.3 (d, *J* = 21.4 Hz), 61.7, 38.3 (d, *J* = 21.8 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.5 (ddd, *J* = 34.4, 18.8, 11.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}O_3FNa$ 275.1054; Found 275.1053. $[\alpha]_D^{29}$: –333.5 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 13.0 min, R_t (minor) = 17.1 min. IR (KBr thin film, cm^{-1}): ν 3692, 2921, 2351, 2351, 1739, 1460, 1218, 1017, 696, 606.



1c

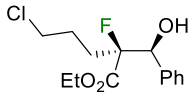
ethyl (*S*)-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)pent-4-ynoate (1c): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 262 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 5.00 (dd, *J* = 17.8, 2.0 Hz, 1H), 4.23–4.07 (m, 2H), 3.11–2.88 (m, 3H), 2.09 (d, *J* = 2.2 Hz, 1H), 1.14 (td, *J* = 7.1, 1.5 Hz, 3H); ^{13}C

NMR (151 MHz, $CDCl_3$) δ 168.6 (d, *J* = 24.0 Hz), 137.1, 128.9, 128.5, 127.6, 96.9 (d, *J* = 200.5 Hz), 77.3 (d, *J* = 4.4 Hz), 75.7 (d, *J* = 20.8 Hz), 72.0, 62.2, 24.7 (d, *J* = 24.2 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.3 – -176.4 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{15}O_3FNa$ 273.0897; Found 273.0895. $[\alpha]_D^{29}$: –286.2 (c 1.0, $CHCl_3$); HPLC analysis: 91% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 13.4 min, R_t (minor) = 20.3 min. IR (KBr thin film, cm^{-1}): ν 3647, 3305, 2987, 2323, 1736, 1335, 1221, 1035, 696.



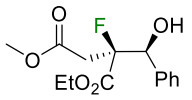
1d

ethyl (*S*)-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)-5-methylhex-4-enoate (1d): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 232 mg, 41% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 7.41–7.29 (m, 5H), 5.25 (t, *J* = 7.2 Hz, 1H), 4.95 (dd, *J* = 18.5, 4.8 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.82–2.70 (m, 3H), 1.70 (s, 3H), 1.61 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9 (d, *J* = 24.5 Hz), 137.9, 136.8, 128.7, 128.4, 127.8, 115.9 (d, *J* = 3.5 Hz), 98.9 (d, *J* = 196.3 Hz), 76.4 (d, *J* = 21.5 Hz), 61.7, 32.7 (d, *J* = 21.8 Hz), 26.1, 18.1, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.2 – -176.5 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{21}O_3FNa$ 303.1367; Found 303.1365. $[\alpha]_D^{29}$: –345.9 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.4 min, R_t (minor) = 5.2 min. IR (KBr thin film, cm^{-1}): ν 3650, 2925, 2966, 2361, 1743, 1466, 1048, 710, 572.



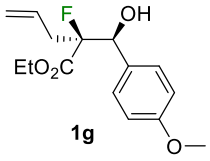
1e

ethyl (*S*)-5-chloro-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)pentanoate (1e): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 58–60 ˚C, 273 mg, 48% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 4.92 (dd, *J* = 19.1, 5.6 Hz, 1H), 4.20–4.05 (m, 2H), 3.60–3.46 (m, 2H), 2.64 (d, *J* = 5.3 Hz, 1H), 2.33–2.09 (m, 2H), 2.06–1.92 (m, 1H), 1.79–1.66 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 (d, *J* = 24.5 Hz), 137.7, 128.9, 128.4, 127.7 (d, *J* = 7.3 Hz), 98.8 (d, *J* = 196.1 Hz), 76.6 (d, *J* = 21.1 Hz), 61.9, 44.6, 31.3 (d, *J* = 22.1 Hz), 26.7 (d, *J* = 3.5 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -177.2 (ddd, *J* = 35.1, 19.1, 9.7 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_3ClFNa$ 311.0821; Found 311.0820. $[\alpha]_D^{29}$: –668.7 (c 1.0, $CHCl_3$); HPLC analysis: 92% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 7.0 min, R_t (minor) = 6.0 min. IR (KBr thin film, cm^{-1}): ν 3668, 3301, 3142, 2973, 2368, 1746, 1536, 1266, 734, 706.



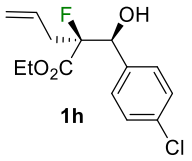
1f

1-ethyl 4-methyl (*S*)-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)succinate (1f): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 120–122 ˚C, 275 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 4.93 (dd, *J* = 17.6, 5.1 Hz, 1H), 4.15 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.68 (s, 3H), 3.21–3.05 (m, 2H), 3.02 (s, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 169.4 (d, *J* = 26.1 Hz), 137.0, 129.0, 128.4, 127.6, 95.8 (d, *J* = 199.1 Hz), 76.1 (d, *J* = 20.1 Hz), 62.2, 52.3, 38.6 (d, *J* = 23.6 Hz), 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.3 (ddd, *J* = 30.5, 17.5, 12.1 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}O_5FNa$ 307.0952; Found 307.0950. $[\alpha]_D^{29}$: –758.1 (c 1.0, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 8.3 min, R_t (minor) = 10.8 min. IR (KBr thin film, cm^{-1}): ν 3650, 3298, 2939, 2361, 1743, 155, 1194, 751.



1g

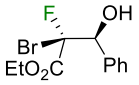
ethyl (*S*)-2-fluoro-2-((*S*)-hydroxy(4-methoxyphenyl)methyl)pent-4-enoate (1g): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 275 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.75–5.63 (m, 1H), 5.15–5.02 (m, 2H), 4.87 (dd, *J* = 21.9, 6.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.00 (d, *J* = 6.8 Hz, 1H), 2.51 (ddd, *J* = 34.9, 14.6, 8.3 Hz, 1H), 2.31–2.18 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2 (d, *J* = 25.8 Hz), 159.8, 130.1 (d, *J* = 3.4 Hz), 129.9, 129.2 (d, *J* = 2.1 Hz), 119.8, 113.7, 98.8 (d, *J* = 197.4 Hz), 76.4 (d, *J* = 20.3 Hz), 61.9, 55.3, 38.9 (d, *J* = 21.3 Hz), 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.5 (ddd, *J* = 34.1, 21.4, 12.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{19}O_4FNa$ 305.1160; Found 305.1154. $[\alpha]_D^{29}$: +233.4 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 10.3 min, R_t (minor) = 13.2 min. R (KBr thin film, cm^{-1}): ν 3671, 2935, 2313, 1736, 1511, 1245, 1038, 748.



1h

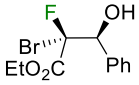
ethyl (S)-2-((S)-(4-chlorophenyl)(hydroxy)methyl)-2-fluoropent-4-enoate (1h): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 275

mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.29 (m, 4H), 5.75–5.64 (m, 1H), 5.15–5.09 (m, 2H), 4.92 (dd, *J* = 19.9, 7.3 Hz, 1H), 4.26 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.90 (dd, *J* = 32.7, 7.3 Hz, 1H), 2.56 (ddd, *J* = 34.1, 14.5, 8.2 Hz, 1H), 2.33–2.24 (m, 1H), 1.27 (td, *J* = 7.2, 1.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0 (d, *J* = 25.2 Hz), 136.2, 134.7, 129.8 (d, *J* = 2.3 Hz), 129.3, 128.7, 120.4, 98.3 (d, *J* = 198.1 Hz), 76.1 (d, *J* = 21.2 Hz), 62.2, 38.9 (d, *J* = 21.5 Hz), 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.4 (ddd, *J* = 32.9, 17.9, 14.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_3ClFNa$ 309.0664; Found 309.0663. $[\alpha]_D^{29}$: +118.7 (c 1.0, $CHCl_3$); HPLC analysis: 93% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 5.6 min, R_t (minor) = 6.2 min. IR (KBr thin film, cm^{-1}): ν 3685, 2980, 2323, 1739, 1487, 1228, 1090, 1010, 737.



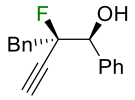
1i

ethyl (2*R*,3*R*)-2-bromo-2-fluoro-3-hydroxy-3-phenylpropanoate (1i): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 80–83 ˚C, 285 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 2H), 7.46–7.37 (m, 3H), 5.29 (dd, *J* = 20.5, 6.4 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.91 (d, *J* = 6.6 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (d, *J* = 27.1 Hz), 135.5, 129.3, 128.8 (d, *J* = 15.7 Hz), 128.3, 98.1 (d, *J* = 275.1 Hz), 78.1 (d, *J* = 20.3 Hz), 63.6, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.8 (d, *J* = 20.6 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}O_3BrFNa$ 312.9846; Found 312.9843. $[\alpha]_D^{29}$: +142.3 (c 1.0, $CHCl_3$); HPLC analysis: 91% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 20.3 min, R_t (minor) = 16.2 min. IR (KBr thin film, cm^{-1}): ν 3671, 3315, 2310, 1760, 1584, 1270, 1031, 751, 692, 589.



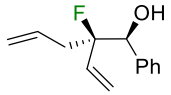
1j

ethyl (2*R*,3*S*)-2-bromo-2-fluoro-3-hydroxy-3-phenylpropanoate (1j): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 289 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.39 (m, 2H), 7.39–7.30 (m, 3H), 5.23 (dd, *J* = 18.9, 3.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 3.0 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4 (d, *J* = 25.3 Hz), 134.8, 129.4, 128.4, 128.3, 100.2 (d, *J* = 275.4 Hz), 77.3 (d, *J* = 19.8 Hz), 63.4, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.1 (d, *J* = 18.9 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}O_3BrFNa$ 312.9846; Found 312.9843. $[\alpha]_D^{29}$: –125.2 (c 1.0, $CHCl_3$); HPLC analysis: 94% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 14.7 min, R_t (minor) = 15.5 min. IR (KBr thin film, cm^{-1}): ν 3671, 3315, 2310, 1760, 1584, 1270, 1031, 751, 692, 589.



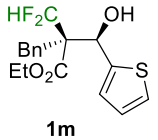
1k

(1*S*,2*R*)-2-benzyl-2-fluoro-1-phenylbut-3-yn-1-ol (1k): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 245 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57–7.48 (m, 2H), 7.42–7.37 (m, 3H), 7.34–7.27 (m, 5H), 4.85 (d, *J* = 13.9 Hz, 1H), 3.15–3.01 (m, 2H), 2.69 (s, 1H), 2.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.6, 134.6, 130.9, 128.8, 128.3, 128.2, 127.2, 94.8 (d, *J* = 178.2 Hz), 79.8 (d, *J* = 9.4 Hz), 79.5 (d, *J* = 29.3 Hz), 77.7 (d, *J* = 24.3 Hz), 41.9 (d, *J* = 23.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.3 – -151.5 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}OFNa$ 277.0999; Found 277.0994. $[\alpha]_D^{29}$: –410.1 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.2 min, R_t (minor) = 7.0 min. IR (KBr thin film, cm^{-1}): ν 3675, 3294, 2379, 1726, 1539, 1263, 1021, 744, 696.



1l

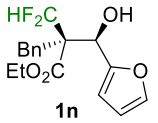
(1*S*,2*R*)-2-fluoro-1-phenyl-2-vinylpent-4-en-1-ol (1l): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 192 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.29 (m, 5H), 5.83–5.67 (m, 2H), 5.41–5.28 (m, 2H), 5.13–5.05 (m, 2H), 4.76 (dd, *J* = 13.0, 2.5 Hz, 1H), 2.70 (ddd, *J* = 14.7, 14.7, 7.1 Hz, 1H), 2.47 (d, *J* = 2.5 Hz, 1H), 2.29 (ddd, *J* = 31.9, 14.7, 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (d, *J* = 3.7 Hz), 136.1 (d, *J* = 20.5 Hz), 132.0 (d, *J* = 4.5 Hz), 128.3, 128.1, 127.9 (d, *J* = 1.4 Hz), 118.8, 116.8 (d, *J* = 11.7 Hz), 98.9 (d, *J* = 182.1 Hz), 78.1 (d, *J* = 25.0 Hz), 38.3 (d, *J* = 21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.0 (ddd, *J* = 31.9, 14.7, 13.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}OFNa$ 229.0999; Found 229.0996. $[\alpha]_D^{29}$: –565.3 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 13.1 min, R_t (minor) = 17.1 min. IR (KBr thin film, cm^{-1}): ν 3654, 3312, 2379, 1695, 1543, 1273, 755.



1m

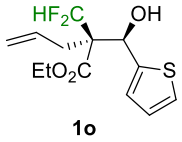
ethyl (2*S*,3*R*)-2-benzyl-2-(difluoromethyl)-3-hydroxy-3-(thiophen-2-yl)propanoate (1m): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 342 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.26–7.22 (m, 3H), 7.17–7.14 (m, 2H), 7.11–7.09 (m, 1H), 7.02–6.99 (m, 1H), 6.08 (t, *J* = 54.4 Hz, 1H), 5.52 (d, *J* = 4.9 Hz, 1H), 4.25–4.15 (m, 2H), 3.37 (dd, *J* = 4.9, 3.5 Hz, 1H), 3.24 (dd, *J* = 13.9,

2.5 Hz, 1H), 2.99 (d, *J* = 14.1 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7 (d, *J* = 5.3 Hz), 142.0, 135.1, 130.4, 128.5, 127.3, 127.1, 126.4, 126.1, 116.9 (dd, *J* = 246.7, 246.7 Hz), 70.6, 62.0, 59.4 (t, *J* = 17.7 Hz), 35.7, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.2 (dd, *J* = 283.3, 55.1 Hz, 1F), -127.2 (dd, *J* = 283.0, 54.2 Hz, 1H). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}F_2O_3SNa$ 363.0837; Found 363.0840. $[\alpha]_D^{29}$: –219.3 (c 1.0, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 29.9 min, R_t (minor) = 33.5 min. IR (KBr thin film, cm^{-1}): ν 3650, 3308, 2935, 2310, 1736, 1543, 1270, 1024, 751.



1n

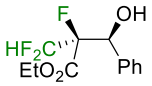
ethyl (2*S*,3*R*)-2-benzyl-2-(difluoromethyl)-3-(furan-2-yl)-3-hydroxypropanoate (1n): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 354 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 6H), 6.97–6.95 (m, 2H), 5.86 (dd, *J* = 54.0, 54.0 Hz, 1H), 5.21 (d, *J* = 6.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 6.5 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 3.35 (d, *J* = 14.0 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 143.2, 135.3, 130.9, 128.4, 127.3, 126.7, 126.4, 125.7, 116.1 (t, *J* = 246.6 Hz), 70.9 (d, *J* = 3.9 Hz), 62.3, 59.3 (t, *J* = 18.2 Hz), 35.8, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.9 (dd, *J* = 285.1, 54.1 Hz, 1F), -127.2 (dd, *J* = 285.0, 54.1 Hz, 1H). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}F_2O_4Na$ 347.3235; Found 347.3236. $[\alpha]_D^{29}$: –464.6 (c 1.0, $CHCl_3$); HPLC analysis: 80% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 21.5 min, R_t (minor) = 23.6 min. IR (KBr thin film, cm^{-1}): ν 3650, 3305, 2925, 2327, 1726, 1539, 1263, 1028, 751, 696.



1o

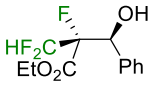
ethyl (*S*)-2-(difluoromethyl)-2-((*R*)-hydroxy(thiophen-2-yl)methyl)pent-4-enoate (1o): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 285 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 5.1 Hz, 1H), 7.05–6.94 (m, 2H), 6.27 (dd, *J* = 55.0, 55.0 Hz, 1H), 5.99–5.82 (m, 1H), 5.33 (d, *J* = 7.1 Hz, 1H), 5.16–5.06 (m, 2H), 4.33–4.19 (m, 2H), 3.41–3.33 (m, 1H), 2.79–2.60 (m, 1H), 2.43 (dd, *J* = 14.7, 8.2 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (d, *J* = 8.5 Hz), 142.1, 132.6, 126.6 (d, *J* = 5.8 Hz), 125.9, 119.3, 117.2 (t, *J* = 247.7 Hz), 71.4, 62.3, 58.4, 33.2, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –125.9 (dd, *J* = 284.4, 55.0 Hz, 1F), -127.7 (dd, *J* = 284.4, 54.8 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_3F_2NaS$ 313.0680; Found 313.0677. $[\alpha]_D^{29}$: –114.8 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90

^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.2 min, R_t (minor) = 6.8 min. IR (KBr thin film, cm^{-1}): ν 3713, 2987, 2379, 1729, 1228, 1041, 696.



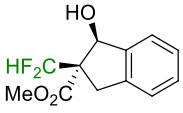
1p

ethyl (2*S*,3*S*)-2-(difluoromethyl)-2-fluoro-3-hydroxy-3-phenylpropanoate (1p): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 251 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 5H), 6.14 (ddd, *J* = 55.6, 52.2, 7.5 Hz, 1H), 5.25 (dd, *J* = 22.6, 2.8 Hz, 1H), 4.24–4.06 (m, 2H), 2.86 (s, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, *J* = 27.1 Hz), 135.9, 129.4, 128.7, 127.8 (d, *J* = 1.4 Hz), 126.1 (d, *J* = 128.6 Hz), 112.8 (td, *J* = 250.0, 34.3 Hz), 95.9 (dt, *J* = 210.0, 21.9 Hz, 1F), 73.8 (d, *J* = 19.3 Hz), 62.7, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δδ -130.0 (ddd, *J* = 294.0, 52.1, 5.3 Hz), -134.7 (ddd, *J* = 294.0, 55.6, 12.7 Hz, 1F), -190.9 – -191.9 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{13}O_3F_3Na$ 285.0709; Found 285.0706. $[\alpha]_D^{29}$: –750.2 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 11.4 min, R_t (minor) = 12.5 min. IR (KBr thin film, cm^{-1}): ν 3498, 2983, 1757, 1294, 1107, 1028, 730, 703.



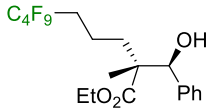
1q

ethyl (2*S*,3*R*)-2-(difluoromethyl)-2-fluoro-3-hydroxy-3-phenylpropanoate (1q): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 253 mg 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.36 (m, 5H), 5.94 (ddd, *J* = 52.8, 52.8, 9.6 Hz, 1H), 5.18 (d, *J* = 17.4 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.87 (s, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, *J* = 27.1 Hz), 136.0, 129.4, 128.7, 127.7 (d, *J* = 1.4 Hz), 126.1 (d, *J* = 128.6 Hz), 112.8 (td, *J* = 250.0, 34.3 Hz), 95.9 (dt, *J* = 203.0, 21.9 Hz), 73.8 (d, *J* = 19.3 Hz), 62.7, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.4 (ddd, *J* = 292.6, 52.8, 10.4 Hz, 1F), -134.7 (ddd, *J* = 292.6, 52.8, 13.4 Hz, 1F), -189.8 – -191.2 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{13}O_3F_3Na$ 285.0709; Found 285.0706. $[\alpha]_D^{29}$: -268.4 (c 1.0, $CHCl_3$); HPLC analysis: 90% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 11.9 min, R_t (minor) = 13.3 min. IR (KBr thin film, cm^{-1}): ν 3498, 2983, 1757, 1294, 1107, 1028, 730, 703.



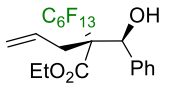
1r

methyl (1*R*,2*S*)-2-(difluoromethyl)-1-hydroxy-2,3-dihydro-1H-indene-2-carboxylate (1r): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 231 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.1 Hz, 1H), 7.32–7.22 (m, 3H), 6.38 (dd, *J* = 55.1, 55.1 Hz, 1H), 5.56 (d, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 3.53 (d, *J* = 17.0 Hz, 1H), 3.43 (d, *J* = 17.0 Hz, 1H), 2.58 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7 (dd, *J* = 8.2, 2.1 Hz), 141.1, 139.8, 129.4, 127.6, 124.6, 124.2, 116.3 (t, *J* = 244.7 Hz), 80.6 (dd, *J* = 4.4, 1.9 Hz), 61.4 (t, *J* = 19.2 Hz), 53.1, 33.1 (t, *J* = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.6 (dd, *J* = 285.9, 55.1 Hz, 1F), -127.4 (dd, *J* = 285.8, 55.1 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{12}O_3F_2Na$ 265.0647; Found 265.0645. $[\alpha]_D^{29}$: –197.3 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.8 min, R_t (minor) = 8.1 min. IR (KBr thin film, cm^{-1}): ν 3654, 3301, 2320, 1729, 1543, 1263, 1059, 755.



1s

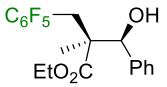
ethyl (*S*)-6,6,7,7,8,8,9,9,9-nonafluoro-2-((*R*)-hydroxy(phenyl)methyl)-2-methylnonanoate (1s): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 445 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 1H), 7.32–7.22 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.12–4.00 (m, 2H), 3.71 (d, *J* = 11.7 Hz, 1H), 3.54–3.44 (m, 1H), 2.72 (ddd, *J* = 23.2, 14.3, 6.8 Hz, 2H), 2.27–2.09 (m, 1H), 1.64–1.55 (m, 2H), 1.51 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 140.5, 136.4, 127.8, 127.2, 127.1, 126.4, 118.7, 75.5, 61.0, 47.3, 40.1 (d, *J* = 2.7 Hz), 39.3, 29.9 (d, *J* = 2.8 Hz), 23.9, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 10.3 Hz, 3F), -110.5 (dd, *J* = 272.2, 43.0 Hz, 1F), -114.5 (dd, *J* = 271.0, 42.5 Hz, 1F), -124.0 – -124.5 (m, 2F), -125.4 – -125.9 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{21}F_9O_3Na$ 491.3596; Found 492.3598. $[\alpha]_D^{29}$: –148.4 (c 1.0, $CHCl_3$); HPLC analysis: 95% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 8.2 min, R_t (minor) = 10.8 min. IR (KBr thin film, cm^{-1}): ν 3675, 3301, 2320, 1736, 1567, 1263, 1017, 765.



1t

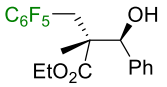
ethyl (*S*)-2-allyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-((*R*)-hydroxy(phenyl)methyl)octanoate (1t): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 528 mg, 48% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 5.83–5.74 (m, 1H), 5.20–5.12 (m, 2H), 4.92 (dd, *J* = 19.1, 0.6 Hz, 1H), 4.13–4.01 (m, 2H), 2.92–2.65 (m, 3H), 1.10 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz,

$CDCl_3$) δ 169.5 (d, *J* = 24.4 Hz), 137.8, 130.6, 129.0 (d, *J* = 4.3 Hz), 128.7 (d, *J* = 9.0 Hz), 128.3 (d, *J* = 3.9 Hz), 128.0, 127.7 (d, *J* = 12.8 Hz), 127.4 (d, *J* = 11.5 Hz), 121.0–118.9 (m), 98.6 (d, *J* = 196.8 Hz), 76.4 (d, *J* = 23.8 Hz), 76.1 (d, *J* = 17.8 Hz), 61.7, 38.3, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.5 – -61.5 (m, 2F), -80.1 – -83.4 (m, 3F), -112.6 – -115.0 (m, 2F), -120.6 – -122.6 (m, 2F), -122.8 – -124.6 (m, 2F), -125.6 – -128.0 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}O_3F_{13}Na$ 575.0862; Found 575.0859. $[\alpha]_D^{29}$: –125.2 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 15.8 min, R_t (minor) = 18.4 min. IR (KBr thin film, cm^{-1}): ν 2977, 2341, 1746, 1449, 1266, 1024, 855, 696.



1u

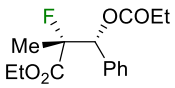
ethyl (2*R*,3*S*)-3-hydroxy-2-methyl-2-((perfluorophenyl)methyl)-3-phenylpropanoate (1u): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 89–91 ˚C, 372 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5H), 4.93 (d, *J* = 6.7 Hz, 1H), 4.24–4.09 (m, 2H), 3.48 (d, *J* = 6.9 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 2.75 (d, *J* = 13.8 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 145.6 (d, *J* = 246.5 Hz), 140.1 (d, *J* = 253.4 Hz), 139.9, 138.3 (t, *J* = 16.4 Hz), 136.6 (t, *J* = 13.4 Hz), 128.2 (d, *J* = 12.9 Hz), 127.9, 111.1 (t, *J* = 18.7 Hz), 79.6, 61.7, 51.8, 30.2, 15.8, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.1 (dd, *J* = 24.5, 9.2 Hz， 2F), -154.9 – -156.6 (m, 1F), -160.9 – -163.2 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}O_3F_5Na$ 411.0990; Found 411.0988. $[\alpha]_D^{29}$: –309.8 (c 1.0, $CHCl_3$); HPLC analysis: 95% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 18.4 min, R_t (minor) = 11.9 min. IR (KBr thin film, cm^{-1}): ν 3509, 2925, 1729, 1525, 1501, 1214, 1100, 990, 699.



1v

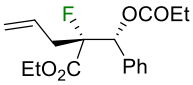
ethyl (2*S*,3*S*)-3-hydroxy-2-methyl-2-((perfluorophenyl)methyl)-3-phenylpropanoate (1v): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 370 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.26 (m, 5H), 5.09 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.39 (d, *J* = 12.9 Hz, 2H), 3.12 (d, *J* = 14.0 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 147.2–146.9 (m), 144.7–144.5 (m), 141.5–141.1 (m), 139.6, 138.9–138.4 (m), 136.3–135.9 (m), 128.2, 128.0 (d, *J* = 12.6 Hz), 111.7 (t, *J* = 15.7 Hz), 77.4, 61.5, 52.0, 27.6, 16.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.2 (dd, *J* = 23.1, 8.6 Hz, 2F), -155.8 – -156.8 (m, 1F), -162.1 – -163.9 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}O_3F_5Na$ 411.0990; Found 411.0981. $[\alpha]_D^{29}$: –215.1 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t

(major) = 9.5 min, R_t (minor) = 10.7 min. IR (KBr thin film, cm-1): ν 3509, 2925, 1729, 1525, 1501, 1214, 1100, 990, 699.



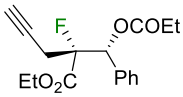
2a

ethyl (2*S*,3*S*)-2-fluoro-2-methyl-3-phenyl-3-(propionyloxy)propanoate (2a): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 279 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.34–7.30 (m, 3H), 6.10 (d, *J* = 22.1 Hz, 1H), 4.20–4.05 (m, 2H), 2.52–2.37 (m, 2H), 1.62 (d, *J* = 21.4 Hz, 3H), 1.20–1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 169.6 (d, *J* = 24.1 Hz), 134.9, 128.9, 128.3, 128.3 (d, *J* = 1.8 Hz), 95.5 (d, *J* = 195.4 Hz), 76.2 (d, *J* = 20.7 Hz), 62.1, 27.7, 20.5 (d, *J* = 24.2 Hz), 14.1, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -166.7 (qd, *J* = 21.6, 21.5 Hz, 3F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{19}O_4FNa$ 305.1160; Found 305.1163. $[\alpha]_D^{29}$: –495.1 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.7 min, R_t (minor) = 5.8 min. IR (KBr thin film, cm^{-1}): ν 3637, 2928, 2845, 2368, 2334, 1657, 1553, 1266, 1017, 751, 668.



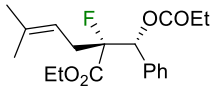
2b

ethyl (*S*)-2-fluoro-2-((*S*)-phenyl(propionyloxy)methyl)pent-4-enoate (2b): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 298 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.34–7.28 (m, 3H), 6.11 (d, *J* = 24.0 Hz, 1H), 5.86–5.71 (m, 1H), 5.20–5.10 (m, 2H), 4.15–4.00 (m, 2H), 2.84–2.59 (m, 2H), 2.54–2.37 (m, 2H), 1.16 (t, *J* = 7.3 Hz, 3H), 1.13 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 168.2 (d, *J* = 24.4 Hz), 134.4, 130.2 (d, *J* = 3.9 Hz), 129.0, 128.4, 128.4, 120.2, 97.8 (d, *J* = 200.7 Hz), 75.9 (d, *J* = 18.9 Hz), 61.8, 38.9 (d, *J* = 22.3 Hz), 27.7, 14.2, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.0 (qd, *J* = 34.2, 24.0, 10.9 Hz, 3F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}O_4FNa$ 331.1316; Found 331.1314. $[\alpha]_D^{29}$: –281.2 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.5 min, R_t (minor) = 5.4 min. IR (KBr thin film, cm^{-1}): ν ν 3671, 3298, 2987, 2945, 2355, 1750, 1543, 1166, 1024, 737, 699.



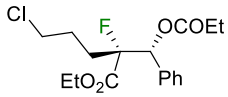
2c

ethyl (*S*)-2-fluoro-2-((*S*)-phenyl(propionyloxy)methyl)pent-4-ynoate (2c): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 290 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.34–7.31 (m, 3H), 6.15 (d, *J* = 22.5 Hz, 1H), 4.29–4.02 (m, 2H), 3.04–2.81 (m, 2H), 2.50–2.34 (m, 2H), 2.09 (t, *J* = 2.6 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 167.5 (d, *J* = 24.4 Hz), 134.3, 129.2, 128.6, 128.5, 128.3 (d, *J* = 1.7 Hz), 96.1 (d, *J* = 203.9 Hz), 76.6 (d, *J* = 4.9 Hz), 75.5 (d, *J* = 19.4 Hz), 72.2, 62.4, 27.7, 25.3 (d, *J* = 25.3 Hz), 14.1, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.3 (ddd, *J* = 27.3, 22.9, 13.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}O_4FNa$ 329.1160; Found 329.1156. $[\alpha]_D^{29}$: +96.5 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 9.5 min, R_t (minor) = 11.4 min. IR (KBr thin film, cm^{-1}): ν 3675, 3294, 2987, 2939, 2348, 1743, 1546, 1169, 1090, 1031, 748, 696.



2d

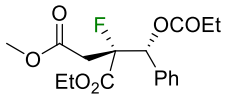
ethyl (*S*)-2-fluoro-5-methyl-2-((*S*)-phenyl(propionyloxy)methyl)hex-4-enoate (2d): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 330 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 2H), 7.33–7.27 (m, 3H), 6.11 (d, *J* = 24.0 Hz, 1H), 5.19–5.09 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.74–2.65 (m, 2H), 2.52–2.37 (m, 2H), 1.60 (s, 3H), 1.57 (s, 3H), 1.16 (t, *J* = 7.4 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 168.6 (d, *J* = 24.6 Hz), 136.9, 135.0, 129.0, 128.4, 128.3, 115.5, 97.9 (d, *J* = 200.4 Hz), 76.2 (d, *J* = 18.8 Hz), 61.8, 33.4 (d, *J* = 22.5 Hz), 27.8, 26.0, 18.1, 14.1, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -175.8 – -176.2 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{19}H_{26}O_4F$ 337.1810; Found 337.1805. $[\alpha]_D^{29}$: –345.9 (c 1.0, $CHCl_3$); HPLC analysis: 90% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.4 min, R_t (minor) = 4.7 min. IR (KBr thin film, cm^{-1}): ν 3654, 2987, 2928, 2368, 1760, 1456, 1162, 1076, 1024, 768, 696.



2e

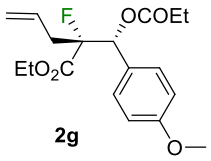
ethyl (*S*)-5-chloro-2-fluoro-2-((*S*)-phenyl(propionyloxy)methyl)pentanoate (2e): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 312 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.28 (m, 5H), 6.08 (d, *J* = 23.6 Hz, 1H), 4.11 (dd, *J* = 9.8, 7.4 Hz, 2H), 3.68–3.46 (m, 2H), 2.56–2.34 (m, 2H), 2.23–2.07 (m, 1H), 2.09–1.93 (m, 1H), 1.71 (dd, *J* = 12.9, 6.8 Hz, 1H), 1.65–1.54 (m, 1H), 1.23–1.06 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 168.5 (d, *J* = 24.8 Hz), 134.7, 129.1, 128.4, 97.9 (d, *J* = 199.7 Hz), 76.2 (d, *J* = 19.2 Hz), 62.1, 44.4, 31.6 (d, *J* = 22.6 Hz), 27.7, 26.6 (d, *J* = 3.1 Hz), 14.1, 9.1; ^{19}F

NMR (376 MHz, $CDCl_3$) δ -176.3 (dd, *J* = 43.2, 23.7 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_4ClFNa$ 367.1083; Found 367.1080; $[\alpha]_D^{29}$: –345.9 (c 1.0, $CHCl_3$). HPLC analysis: 95% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.1 min, R_t (minor) = 3.6 min. IR (KBr thin film, cm^{-1}): ν ν 3664, 3298, 2987, 2932, 2856, 2368, 1750, 1560, 1259, 1166, 1017, 758, 696.



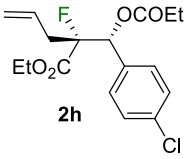
2f

1-ethyl 4-methyl (*S*)-2-fluoro-2-((*S*)-phenyl(propionyloxy)methyl)succinate (2f): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 338 mg, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5H), 6.03 (d, *J* = 21.5 Hz, 1H), 4.18–4.07 (m, 2H), 3.68 (s, 3H), 3.16 (dd, *J* = 36.5, 16.5 Hz, 1H), 2.99 (dd, *J* = 16.5, 8.2 Hz, 1H), 2.54–2.37 (m, 2H), 1.16 (t, *J* = 7.3 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 168.7, 168.2 (d, *J* = 23.3 Hz), 134.0, 129.3, 128.5, 128.3, 94.9 (d, *J* = 203.3 Hz), 75.8 (d, *J* = 20.1 Hz), 62.3, 52.3, 39.1 (d, *J* = 24.1 Hz), 27.7, 13.9, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.9 (ddd, *J* = 37.0, 21.6, 8.8 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}O_6FNa$ 363.1214; Found 363.1210. $[\alpha]_D^{29}$: +91.7 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 8.4 min, R_t (minor) = 11.1 min. IR (KBr thin film, cm^{-1}): ν 3681, 2987, 2939, 2852, 2351, 1746, 1449, 1173, 1010, 703.



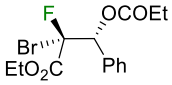
2g

ethyl (*S*)-2-fluoro-2-((*S*)-(4-methoxyphenyl)(propionyloxy)methyl)pent-4-enoate (2g): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 344 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 25.5 Hz, 1H), 5.73–5.60 (m, 1H), 5.13–5.02 (m, 2H), 4.25 (qd, *J* = 7.1, 2.5 Hz, 2H), 3.79 (s, 3H), 2.49 (ddd, *J* = 34.2, 14.5, 8.4 Hz, 1H), 2.37–2.18 (m, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 168.8 (d, *J* = 27.0 Hz), 160.2, 130.2 (d, *J* = 2.1 Hz), 129.7 (d, *J* = 3.8 Hz), 126.4, 120.2, 113.9, 97.6 (d, *J* = 198.9 Hz), 76.7 (d, *J* = 17.3 Hz), 61.9, 55.3, 38.9 (d, *J* = 21.5 Hz), 27.6, 14.4, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.8 (ddd, *J* = 34.9, 25.5, 10.4 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{23}O_5FNa$ 361.1422; Found 361.1419. $[\alpha]_D^{29}$: –333.8 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.0 min, R_t (minor) = 3.5 min. IR (KBr thin film, cm^{-1}): ν 3681, 3315, 2987, 2945, 2838, 2313, 1753, 1605, 1511, 1256, 1176, 1031, 907, 748.



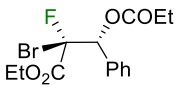
2h

ethyl (*S*)-2-((*S*)-(4-chlorophenyl)(propionyloxy)methyl)-2-fluoropent-4-enoate (2h): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 325 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 4H), 5.97 (d, *J* = 24.9 Hz, 1H), 5.71–5.60 (m, 1H), 5.15–5.03 (m, 2H), 4.32–4.20 (m, 2H), 2.60–2.41 (m, 1H), 2.38–2.28 (m, 2H), 2.27–2.18 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 168.5 (d, *J* = 26.8 Hz), 135.2, 132.8, 130.3 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 3.8 Hz), 128.8, 120.5, 97.2 (d, *J* = 199.5 Hz), 76.4 (d, *J* = 18.4 Hz), 62.1, 38.8 (d, *J* = 21.5 Hz), 27.5, 14.4, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.4 (ddd, *J* = 34.6, 24.9, 10.6 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_4ClFNa$ 365.0926; Found 365.0924. $[\alpha]_D^{29}$: –363.1 (c 1.0, $CHCl_3$); HPLC analysis: 91% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 3.0 min, R_t (minor) = 2.7 min. IR (KBr thin film, cm^{-1}): ν 3685, 3319, 2997, 2317, 1760, 1587, 1491, 1166, 1014, 914, 751.



2i

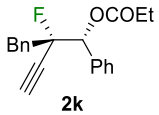
ethyl (2*R*,3*S*)-2-bromo-2-fluoro-3-phenyl-3-(propionyloxy)propanoate (2i): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil. 320 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.43–7.36 (m, 3H), 6.33 (d, *J* = 23.8 Hz, 1H), 4.44–4.28 (m, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 164.8 (d, *J* = 28.3 Hz), 132.5, 129.7 (d, *J* = 1.9 Hz), 129.6 (d, *J* = 1.8 Hz), 128.3, 96.1 (d, *J* = 273.9 Hz), 77.6 (d, *J* = 18.8 Hz), 63.5, 27.5, 14.0, 9.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.5 (d, *J* = 23.8 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_4FBrNa$ 369.0108; Found 369.0109. $[\alpha]_D^{29}$: –249.4 (c 1.0, $CHCl_3$); HPLC analysis: 93% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 12.6 min, R_t (minor) = 11.5 min. IR (KBr thin film, cm^{-1}): ν 3685, 3319, 2997, 2317, 1760, 1587, 1491, 1166, 1014, 914, 751.



2j

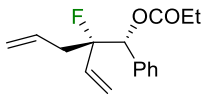
ethyl (2*R*,3*R*)-2-bromo-2-fluoro-3-phenyl-3-(propionyloxy)propanoate (2j): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 320 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.39 (m, 2H), 7.37–7.31 (m, 3H), 6.42 (d, *J* =

23.2 Hz, 1H), 4.21 (qd, *J* = 7.1, 2.4 Hz, 2H), 2.63–2.40 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 164.2 (d, *J* = 25.9 Hz), 132.6, 129.7, 128.9 (d, *J* = 1.8 Hz), 128.7, 96.9 (d, *J* = 275.0 Hz), 76.8 (d, *J* = 17.1 Hz), 63.5, 27.7, 13.8, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.6 (d, *J* = 23.2 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_4FBrNa$ 369.0108; Found 369.0109. $[\alpha]_D^{29}$: –1252.0 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.6 min, R_t (minor) = 7.8 min. IR (KBr thin film, cm^{-1}): ν 3668, 3315, 2980, 2320, 1760, 1598, 1276, 1162, 1031, 744, 692.



2k

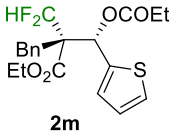
(1*S*,2*R*)-2-benzyl-2-fluoro-1-phenylbut-3-yn-1-yl propionate (2k): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 302 mg, 49% yield. 1H NMR (600 MHz, $CDCl_3$) δ 7.53–7.47 (m, 2H), 7.41–7.33 (m, 3H), 7.32–7.22 (m, 5H), 5.96 (d, *J* = 16.1 Hz, 1H), 3.20 (dd, *J* = 14.1, 11.8 Hz, 1H), 2.98 (dd, *J* = 29.5, 14.1 Hz, 1H), 2.65 (d, *J* = 5.1 Hz, 1H), 2.58–2.41 (m, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 135.1, 134.1, 130.8, 129.0, 128.7, 128.2 (d, *J* = 2.4 Hz), 127.3, 92.7 (d, *J* = 183.3 Hz), 79.7 (d, *J* = 8.9 Hz), 78.9 (d, *J* = 28.8 Hz), 77.4 (d, *J* = 23.7 Hz), 42.6 (d, *J* = 23.6 Hz), 27.9, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.2 – -151.6 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{19}O_2FNa$ 333.1261; Found 333.1258. $[\alpha]_D^{29}$: –512 (c 1.0, $CHCl_3$); HPLC analysis: 95% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 3.7 min, R_t (minor) = 4.2 min. IR (KBr thin film, cm^{-1}): ν 3671, 3294, 3153, 2313, 1753, 1549, 1456, 1266, 1173, 755, 692.



2l

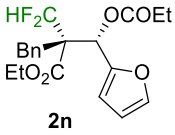
(1*S*,2*R*)-2-fluoro-1-phenyl-2-vinylpent-4-en-1-yl propionate (2l): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 256 mg, 51% yield. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.31–7.27 (m, 3H), 5.82 (d, *J* = 16.8 Hz, 1H), 5.77–5.61 (m, 2H), 5.27 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.22 (dt, *J* = 11.1, 1.3 Hz, 1H), 5.07 (dd, *J* = 10.0, 0.8 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.4 Hz, 1H), 2.47 (td, *J* = 14.3, 6.9 Hz, 1H), 2.43–2.27 (m, 3H), 1.10 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 135.7 (d, *J* = 6.5 Hz), 135.6, 131.4 (d, *J* = 4.5 Hz), 128.6, 128.2, 119.2, 116.8 (d, *J* = 11.5 Hz), 97.3 (d, *J* = 186.1 Hz), 40.0 (d, *J* = 22.3 Hz), 27.8, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.8 – -169.2 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{16}H_{19}O_2FNa$ 285.1261; Found 285.1265. $[\alpha]_D^{29}$: –725.0 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1

mL/min), R_t (major) = 5.5 min, R_t (minor) = 7.6 min. IR (KBr thin film, cm^{-1}): ν 3650, 3326, 3160, 2365, 1708, 1556, 1411, 1266, 1010, 748.



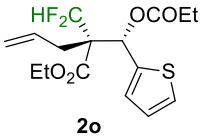
2m

ethyl (2*S*,3*R*)-2-benzyl-2-(difluoromethyl)-3-(propionyloxy)-3-(thiophen-2-yl)propanoate (2m): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 390 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.26–7.20 (m, 5H), 7.11–7.08 (m, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.56 (s, 1H), 5.99 (t, *J* = 53.7 Hz, 1H), 4.26–4.14 (m, 2H), 3.33 (d, *J* = 13.9 Hz, 1H), 3.23 (d, *J* = 13.9 Hz, 1H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 168.8, 138.4, 134.9, 130.7, 128.4, 127.7, 127.3, 126.6, 126.2, 116.4 (dd, *J* = 248.1, 248.1 Hz), 72.0 ,61.9, 59.0 (t, *J* = 18.9 Hz), 35.7, 27.8, 14.1, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.9 (dd, *J* = 283.8, 53.7 Hz, 1F), -127.7 (dd, *J* = 284.0, 54.0 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{22}O_4F_2SNa$ 419.1099; Found 419.1096. $[\alpha]_D^{29}$: –237.0 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 5.8 min, R_t (minor) = 5.2 min. IR (KBr thin film, cm^{-1}): ν 3650, 3315, 3101, 2382, 1736, 1539, 1453, 1380, 1263, 1038, 755.



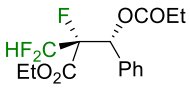
2n

ethyl (2*S*,3*R*)-2-benzyl-2-(difluoromethyl)-3-(furan-2-yl)-3-(propionyloxy)propanoate (2n): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 320 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.3 Hz, 1H), 7.29–7.19 (m, 3H), 7.19–7.12 (m, 2H), 6.47–6.31 (m, 3H), 6.03 (dd, *J* = 54.0, 54.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.08 (s, 2H), 2.35 (dt, *J* = 7.5, 5.9 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 168.7 (d, *J* = 4.3 Hz), 149.7, 142.7, 134.8, 130.4, 128.5, 127.3, 116.0 (dd, *J* = 250.3, 245.8 Hz), 110.6, 110.4, 67.9, 61.7, 58.1 (t, *J* = 17.8 Hz), 36.0, 27.7, 14.1, 9.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.7 (dd, *J* = 279.4, 54.2 Hz, 1F), -128.2 (ddd, *J* = 279.1, 54.1, 1.3 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{22}O_5F_2Na$ 403.1328; Found 403.1324. $[\alpha]_D^{29}$: –372.0 (c 1.0, $CHCl_3$); HPLC analysis: 94% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 16.9 min, R_t (minor) = 20.0 min. IR (KBr thin film, cm^{-1}): ν 3650, 3298, 3149, 2323, 1746, 1539, 1380, 1263, 1024, 758.



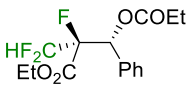
2o

ethyl (*S*)-2-(difluoromethyl)-2-((*R*)-(propionyloxy)(thiophen-2-yl)methyl)pent-4-enoate (2o): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 349 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 1H), 7.07 (d, *J* = 3.4 Hz, 1H), 6.97 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.52 (s, 1H), 6.13 (dd, *J* = 54.6, 54.6 Hz, 1H), 5.90–5.74 (m, 1H), 5.18–5.08 (m, 2H), 4.30–4.20 (m, 2H), 2.66–2.45 (m, 2H), 2.40–2.32 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 168.5, 138.2, 131.9, 127.7, 126.5, 126.3, 119.4, 116.2 (t, *J* = 249.2 Hz), 70.7, 61.8, 57.5 (t, *J* = 18.7 Hz), 33.8, 27.6, 14.1, 8.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.4 (dd, *J* = 284.7, 54.5 Hz, 1F), -128.8 (dd, *J* = 284.7, 54.5 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{16}H_{20}O_4F_2SNa$ 369.0943; Found 369.0940. $[\alpha]_D^{29}$: –273.0 (c 1.0, $CHCl_3$); HPLC analysis: 91% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.9 min, R_t (minor) =6.5 min. IR (KBr thin film, cm^{-1}): ν 3661, 2962, 1748, 1451, 1236, 1088, 1022, 918, 707.



2p

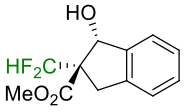
ethyl (2*S*,3*S*)-2-(difluoromethyl)-2-fluoro-3-phenyl-3-(propionyloxy)propanoate (2p): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 301 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 6.34 (d, *J* = 24.6 Hz, 1H), 6.09 (ddd, *J* = 52.5, 52.5, 8.4 Hz, 1H), 4.26–4.12 (m, 2H), 2.51–2.32 (m, 2H), 1.17 (t, *J* = 7.4 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 163.6 (dd, *J* = 24.2, 4.1 Hz), 132.9, 129.7, 128.7, 128.4 (d, *J* = 1.5 Hz), 112.6 (td, *J* = 252.0, 33.0 Hz), 96.2 (d, *J* = 23.0 Hz), 73.6 (dt, *J* = 18.3, 3.4 Hz), 63.0, 27.6, 14.0, 8.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.1 (ddd, *J* = 194.4, 52.4, 4.7 Hz, 1F), -133.5 (dd, *J* = 194.4, 52.4, 11.1 Hz, 1F), -189.8 – 190.0 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{17}O_4F_3Na$ 341.0971; Found 341.0972. $[\alpha]_D^{29}$: –305.0 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 3.1 min, R_t (minor) = 4.8 min. IR (KBr thin film, cm^{-1}): ν 3685, 3319, 2990, 1760, 1567, 1266, 1169, 1093, 1024, 751. 696.



2q

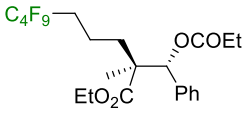
ethyl (2*S*,3*R*)-2-(difluoromethyl)-2-fluoro-3-phenyl-3-(propionyloxy)propanoate (2q): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 312 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.40–7.36

(m, 3H), 6.28 (dd, *J* = 24.0, 2.1 Hz, 1H), 5.59 (ddd, *J* = 52.4, 52.4, 6.8 Hz, 1H), 4.42–4.23 (m, 2H), 2.38 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 164.0 (dd, *J* = 26.4, 3.8 Hz), 133.0, 129.7, 128.9, 128.3 (d, *J* = 1.4 Hz), 112.2 (ddd, *J* = 251.9, 249.9, 32.5 Hz), 94.5 (dt, *J* = 203.2, 23.6 Hz), 73.6 (ddd, *J* = 19.8, 5.2, 1.6 Hz), 63.1, 27.5, 14.1, 9.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.1 (ddd, *J* = 297.8, 52.3, 9.8 Hz, 1F), -134.6 (dd, *J* = 297.8, 52.3, 12.8 Hz, 1F), -187.6 – -188.8 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{17}O_4F_3Na$ 341.0971; Found 341.0970. $[\alpha]_D^{29}$: –118.0 (c 1.0, $CHCl_3$); HPLC analysis: 91% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 5.1 min, R_t (minor) =6.2 min. IR (KBr thin film, cm^{-1}): ν 3685, 3319, 2990, 1760, 1567, 1266, 1169, 1093, 1024, 751. 696.



2r

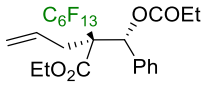
methyl (1*R*,2*S*)-2-(difluoromethyl)-1-(propionyloxy)-2,3-dihydro-1H-indene-2-carboxylate (2r): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 289 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 4H), 6.70 (s, 1H), 6.26 (dd, *J* = 54.9, 54.9 Hz, 1H), 3.79 (s, 3H), 3.60 (d, *J* = 16.7 Hz, 1H), 3.46 (d, *J* = 16.7 Hz, 1H), 2.42 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 170.4 (d, *J* = 6.9 Hz), 140.6, 138.4, 129.8, 127.6, 125.1, 124.6, 115.4 (dd, *J* = 248.8, 245.4 Hz), 79.5, 60.6 (t, *J* = 20.2 Hz), 53.3, 34.1, 27.7, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.3 (dd, *J* = 285.7, 54.9 Hz, 1F), -126.9 (dd, *J* = 285.6, 54.9 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{16}O_4F_2Na$ 321.0909; Found 321.0912. $[\alpha]_D^{29}$: –1096.0 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.2 min, R_t (minor) =5.5 min. IR (KBr thin film, cm^{-1}): ν 3668, 3291, 3118, 2317, 1746, 1539, 1259, 751.



2s

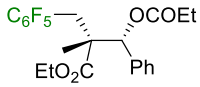
ethyl (*S*)-6,6,7,7,8,8,9,9,9-nonafluoro-2-methyl-2-((*R*)-phenyl(propionyloxy)methyl)nonanoate (2s): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 514 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.30–7.16 (m, 3H), 6.10 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.62 (d, *J* = 7.0 Hz, 1H), 2.83 (dd, *J* = 14.5, 7.4 Hz, 1H), 2.76–2.57 (m, 1H), 2.49–2.26 (m, 3H), 1.83 (dd, *J* = 14.5, 6.2 Hz, 1H), 1.62–1.58 (m, 1H), 1.24 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 168.5 (d, *J* = 24.7 Hz), 134.7, 129.1, 128.4 (d, *J* = 2.4 Hz), 119.0–118.3 (m), 116.2–115.4 (m), 108.6–107.4 (m), 97.9 (d, *J* = 199.6 Hz), 96.4, 93.6–92.7 (m), 90.5–89.5 (m), 76.2 (d, *J* = 19.0 Hz), 62.1, 44.4, 31.6 (d, *J* = 22.6 Hz), 27.7, 26.6, 14.1,

9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 9.6 Hz, 3F), -111.8 (dd, *J* = 267.9, 36.6 Hz, 1F), -114.4 (dd, *J* = 267.1, 34.1 Hz, 1F), -124.2 – -124.5 (m, 2F), -125.7 – -125.9 (m). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{25}O_4F_9Na$ 547.4237; Found 547.4238. $[\alpha]_D^{29}$: –140.5 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 3.5 min, R_t (minor) = 3.0 min. IR (KBr thin film, cm-1): ν 3688, 3318, 3166, 2308, 1745, 1579, 1261, 1015, 752.



2t

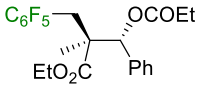
ethyl (*S*)-2-allyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-((*R*)-phenyl(propionyloxy)methyl)octanoate (2t): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 595 mg, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.33–7.30 (m, 3H), 6.11 (d, *J* = 23.9 Hz, 1H), 5.83–5.73 (m, 1H), 5.19–5.13 (m, 2H), 4.14–3.98 (m, 2H), 2.83–2.76 (m, 1H), 2.73–2.62 (m, 1H), 2.50–2.37 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 168.2 (d, *J* = 24.7 Hz), 134.8, 130.2 (d, *J* = 3.2 Hz), 129.1, 128.5 (d, *J* = 8.4 Hz), 120.2, 118.2 (t, *J* = 33.1 Hz), 116.3 (t, *J* = 33.3 Hz), 110.0 (t, *J* = 31.4 Hz), 108.5–107.4 (m), 106.5 (t, *J* = 31.5 Hz), 97.8 (d, *J* = 200.6 Hz), 95.3 (t, *J* = 41.9 Hz), 93.2 (t, *J* = 41.6 Hz), 91.1 (t, *J* = 41.7 Hz), 76.0 (d, *J* = 18.9 Hz), 61.9, 39.1 (d, *J* = 36.4 Hz), 27.8, 14.2, 9.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.5 – -69.5 (m, 2F), -84.8 – -86.2 (m, 3F), -121.6 – -122.7 (m, 2F), -125.4 – -126.7 (m, 2F), -127.0 – -128.2 (m, 2F), -130.3 – -131.5 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{21}F_{13}O_4Na$ 631.1124; Found 631.1120. $[\alpha]_D^{29}$: –150.8 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.6 min, R_t (minor) = 7.7 min. IR (KBr thin film, cm^{-1}): ν 3674, 2986, 1755, 1458, 1257, 1160, 1074, 756, 696.



2u

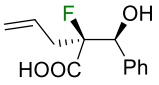
ethyl (2*R*,3*S*)-2-methyl-2-((perfluorophenyl)methyl)-3-phenyl-3-(propionyloxy)propanoate (2u): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 422 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 5H), 6.25 (s, 1H), 4.28–4.19 (m, 1H), 4.14–4.05 (m, 1H), 3.19 (d, *J* = 13.6 Hz, 1H), 2.61 (d, *J* = 13.6 Hz, 1H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.7, 146.6–146.3 (m), 144.8–144.6 (m), 138.4–138.1 (m), 136.7–136.3 (m), 136.1, 128.8, 128.3 (d, *J* = 32.0 Hz), 110.1, 78.9, 61.6, 51.3, 29.1, 27.8, 15.0, 14.1, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.2 (dd, *J* = 24.0, 9.2 Hz, 2F), -155.3 (t, *J* = 21.4 Hz, 1F), -160.7 – -163.1 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{21}O_4F_5Na$

467.1252; Found 467.1251. $[\alpha]_D^{29}$: –152.0 (c 1.0, $CHCl_3$); HPLC analysis: 94% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.4 min, R_t (minor) = 4.1 min. IR (KBr thin film, cm^{-1}): ν 3654, 3291, 2986, 1741, 1530, 1506, 1468, 1261, 1167, 1119, 1008, 967, 752, 693.



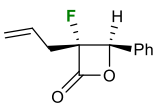
2v

ethyl (2*S*,3*S*)-2-methyl-2-((perfluorophenyl)methyl)-3-phenyl-3-(propionyloxy)propanoate (2v): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 421 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.15 (m, 5H), 6.15 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 13.9 Hz, 1H), 3.00 (d, *J* = 13.9 Hz, 1H), 2.44–2.31 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 172.6, 146.7–146.5 (m), 145.1–144.8 (m), 138.4–138.2 (m), 136.9, 136.8–136.5 (m), 128.5, 128.0 (d, *J* = 40.5 Hz), 110.9 (t, *J* = 15.6 Hz), 77.6, 61.6, 52.1, 29.7 (d, *J* = 40.5 Hz), 28.0, 15.2, 13.9, 9.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.2 (dd, *J* = 23.2, 8.7 Hz, 2F), -155.5 (t, *J* = 21.4 Hz, 1F), -161.0 – -163.7 (m, 2F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{21}O_4F_5Na$ 467.1252; Found 467.1248. $[\alpha]_D^{29}$: –309.7 (c 1.0, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel IA, 02:98 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 7.1 min, R_t (minor) = 3.5 min. IR (KBr thin film, cm^{-1}): ν 3654, 3291, 2986, 1741, 1530, 1506, 1468, 1261, 1167, 1119, 1008, 967, 752, 693.



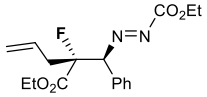
3a

(*S*)-2-fluoro-2-((*S*)-hydroxy(phenyl)methyl)pent-4-enoic acid (3a): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 1:1), white solid, mp 80–82 ˚C, 45 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 5.92–5.60 (m, 3H), 5.13 (s, 1H), 5.09 (d, *J* = 7.2 Hz, 1H), 5.01 (d, *J* = 23.5 Hz, 1H), 2.56 (ddd, *J* = 35.8, 14.6, 8.0 Hz, 1H), 2.30–2.04 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1 (d, *J* = 27.2 Hz), 137.3, 129.9 (d, *J* = 2.9 Hz), 128.7, 128.5, 128.2, 120.3, 98.9 (d, *J* = 196.7 Hz), 76.6 (d, *J* = 18.6 Hz), 38.5 (d, *J* = 21.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.7 – 181.3 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{12}H_{13}O_3FNa$ 247.0741; Found 247.0740. $[\alpha]_D^{29}$: +146.2 (c 1.0, $CHCl_3$); HPLC analysis: 90% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 18.2 min, R_t (minor) = 19.4 min. IR (KBr thin film, cm^{-1}): ν 3692, 2921, 2351, 2351, 1739, 1460, 1017, 696, 606.



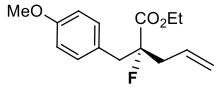
3b

(3*R*,4*S*)-3-allyl-3-fluoro-4-phenyloxetan-2-one (3b): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, 125 mg, 33% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46–7.34 (m, 2H), 7.35–7.26 (m, 3H), 5.83–5.71 (m, 1H), 5.25–5.15 (m, 2H), 5.11 (d, *J* = 25.2 Hz, 1H), 3.15–3.03 (m, 1H), 2.71 (ddd, *J* = 33.3, 14.4, 8.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2 (d, *J* = 26.6 Hz), 135.6 (d, *J* = 8.1 Hz), 129.5 (d, *J* = 4.3 Hz), 129.4, 128.9, 128.6, 121.4–121.1 (m), 98.1 (d, *J* = 201.7 Hz), 64.4–63.7 (m), 40.6–40.2 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.1 – -164.5 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{12}H_{11}O_2FNa$ 229.2163; Found 229.2168. $[\alpha]_D^{29}$: –222.8 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 23.1 min, R_t (minor) = 26.0 min. IR (KBr thin film, cm^{-1}): ν 3692, 3315, 3111, 2319, 1727, 1458, 1274, 756.



3c

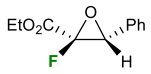
ethyl (*Z*)-2-((1*S*,2*S*)-2-(ethoxycarbonyl)-2-fluoro-1-phenylpent-4-en-1-yl)diazene-1-carboxylate (3c): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), colorless oil, 32.1 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.42–7.35 (m, 3H), 5.86 (d, *J* = 24.3 Hz, 1H), 5.75–5.59 (m, 1H), 5.15–5.04 (m, 2H), 4.37–4.23 (m, 2H), 4.20–4.05 (m, 2H), 2.52 (ddd, *J* = 33.5, 14.4, 8.4 Hz, 1H), 2.31–2.16 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7 (d, *J* = 26.5 Hz), 154.0, 133.7, 129.5 (d, *J* = 3.9 Hz), 129.4, 128.9 (d, *J* = 1.9 Hz), 128.6, 120.5, 97.2 (d, *J* = 200.9 Hz), 80.6 (d, *J* = 18.5 Hz), 77.4, 64.6, 62.1 38.8 (d, *J* = 21.4 Hz), 14.3 (d, *J* = 7.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.8 (ddd, *J* = 33.7, 21.1, 12.7 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{21}O_4FN_2Na$ 337.1378; Found 337.1370. $[\alpha]_D^{29}$: +146.2 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 3.4 min, R_t (minor) = 4.1 min. IR (KBr thin film, cm^{-1}): ν 3678, 3311, 3145, 2160, 1759, 1458, 1261, 749.



3d

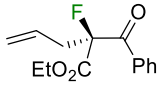
ethyl (*S*)-2-fluoro-2-(4-methoxybenzyl)pent-4-enoate (3d): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), colorless oil, 108 mg, 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.83–6.80 (m, 2H), 5.85–5.77 (m, 1H), 5.18–5.13 (m, 2H), 4.19–4.08 (m, 2H), 3.78 (s, 3H), 3.09 (ddd, *J* = 30.2, 24.4, 14.6 Hz, 2H), 2.74–2.51 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 170.7 (d, *J* = 24.9 Hz), 158.8, 131.4, 130.9 (d, *J* = 3.0 Hz), 126.6, 119.8, 113.4, 97.2 (d, *J* = 191.9 Hz), 61.6, 55.3, 42.2 (d, *J* = 21.5 Hz), 41.5 (d, *J* = 21.5 Hz), 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -164.3 – -164.6 (m, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{19}O_3FNa$ 289.1210; Found 289.1208. $[\alpha]_D^{29}$: +146.2 (c 1.0, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes,

1 mL/min), R_t (major) = 9.5 min, R_t (minor) = 8.0 min. IR (KBr thin film, cm^{-1}): ν 3678, 3304, 2927, 2308, 1727, 1520, 1458, 1257, 1036, 756.



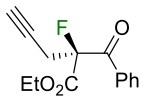
3e

ethyl (2*S*,3*S*)-2-fluoro-3-phenyloxirane-2-carboxylate (33): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), colorless oil, 7.5 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.34 (m, 5H), 4.49 (d, *J* = 1.9 Hz, 1H), 4.19–4.11 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8 (d, *J* = 39.6 Hz), 130.3 (d, *J* = 2.4 Hz), 129.2, 128.4, 126.6, 92.6 (d, *J* = 278.7 Hz), 62.8, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.6 (d, *J* = 1.7 Hz, 1F). HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd. for $C_{11}H_{11}O_3FNa$ 233.0584; Found 233.0585. $[\alpha]_D^{29}$: +146.2 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 15.2 min, R_t (minor) = 18.1 min. IR (KBr thin film, cm^{-1}): ν 3688, 3315, 3135, 2326, 1762, 1458, 1264, 763.



3f

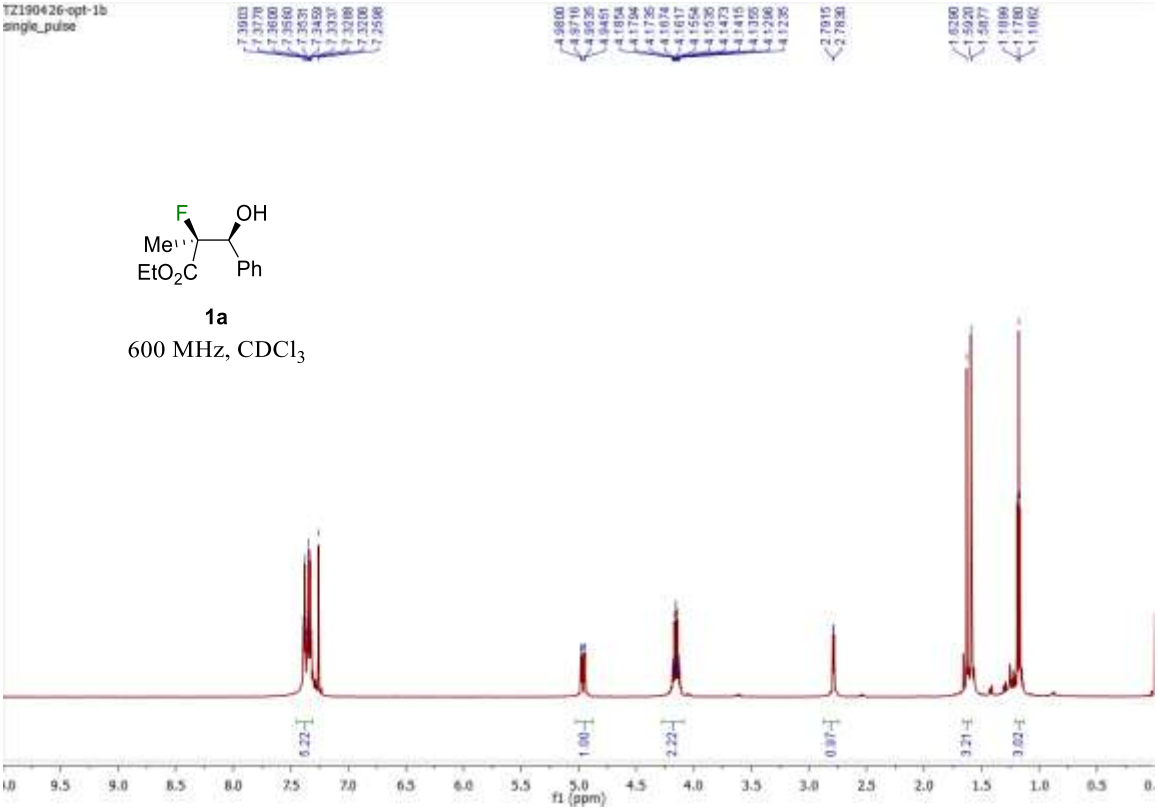
ethyl (*S*)-2-benzoyl-2-fluoropent-4-enoate (3f): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), colorless oil, 21.3 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.89–5.77 (m, 1H), 5.26–5.19 (m, 2H), 4.33–4.17 (m, 2H), 3.13–2.96 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6 (d, *J* = 25.6 Hz), 167.4 (d, *J* = 25.9 Hz), 134.0, 133.8 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 5.6 Hz), 129.8 (d, *J* = 3.4 Hz), 128.7, 120.7, 100.0 (d, *J* = 200.1 Hz), 62.7, 39.0 (d, *J* = 21.4 Hz), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.3 (dd, *J* = 28.9, 20.1 Hz). $[\alpha]_D^{29}$: –883.1 (c 1.0, $CHCl_3$); HPLC analysis: 92% *ee* (Chiralcel OJ-H, 05:95 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 4.1 min, R_t (minor) = 4.8 min.



3g

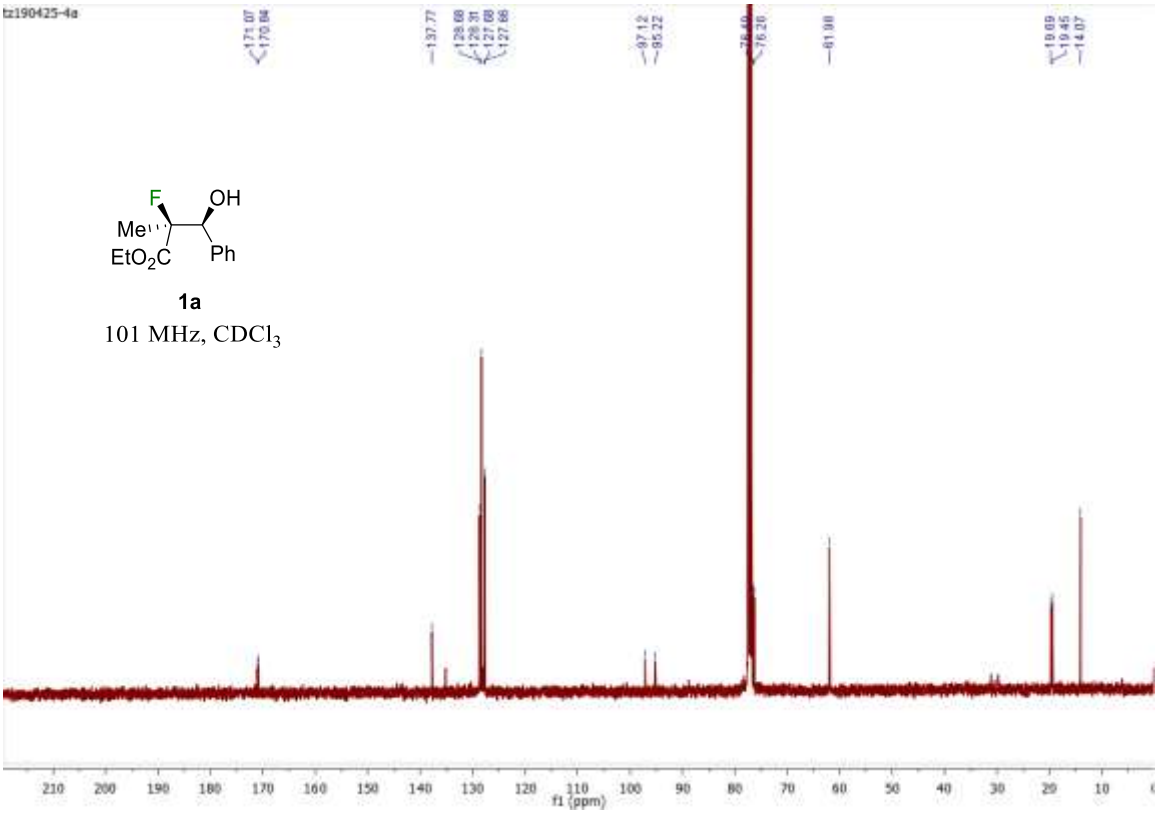
ethyl (*S*)-2-benzoyl-2-fluoropent-4-ynoate (3g): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), colorless oil, 14.8 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.37–4.21 (m, 2H), 3.33 (ddd, *J* = 28.7, 17.5, 2.7 Hz, 1H), 3.13 (td, *J* = 17.3, 2.6 Hz, 1H), 2.12 (t, *J* = 2.6 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3 (d, *J* = 25.0 Hz), 166.3 (d, *J* = 25.8 Hz), 134.4, 133.4 (d, *J* = 3.3 Hz), 130.1 (d, *J* = 5.6 Hz), 128.8, 97.7 (d, *J* = 204.6 Hz), 76.4 (d, *J* = 2.2 Hz), 72.4, 63.2, 25.6 (d, *J* = 22.5 Hz), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.9 (dd, *J* = 28.7, 17.1 Hz). $[\alpha]_D^{29}$: –529.4 (c 1.0, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel OJ-H, 05:95 ^{i}PrOH/Hexanes, 1 mL/min), R_t (major) = 6.8 min, R_t (minor) = 8.1 min.

VII. ^{1}H NMR and ^{13}C NMR spectra of substrates and products.



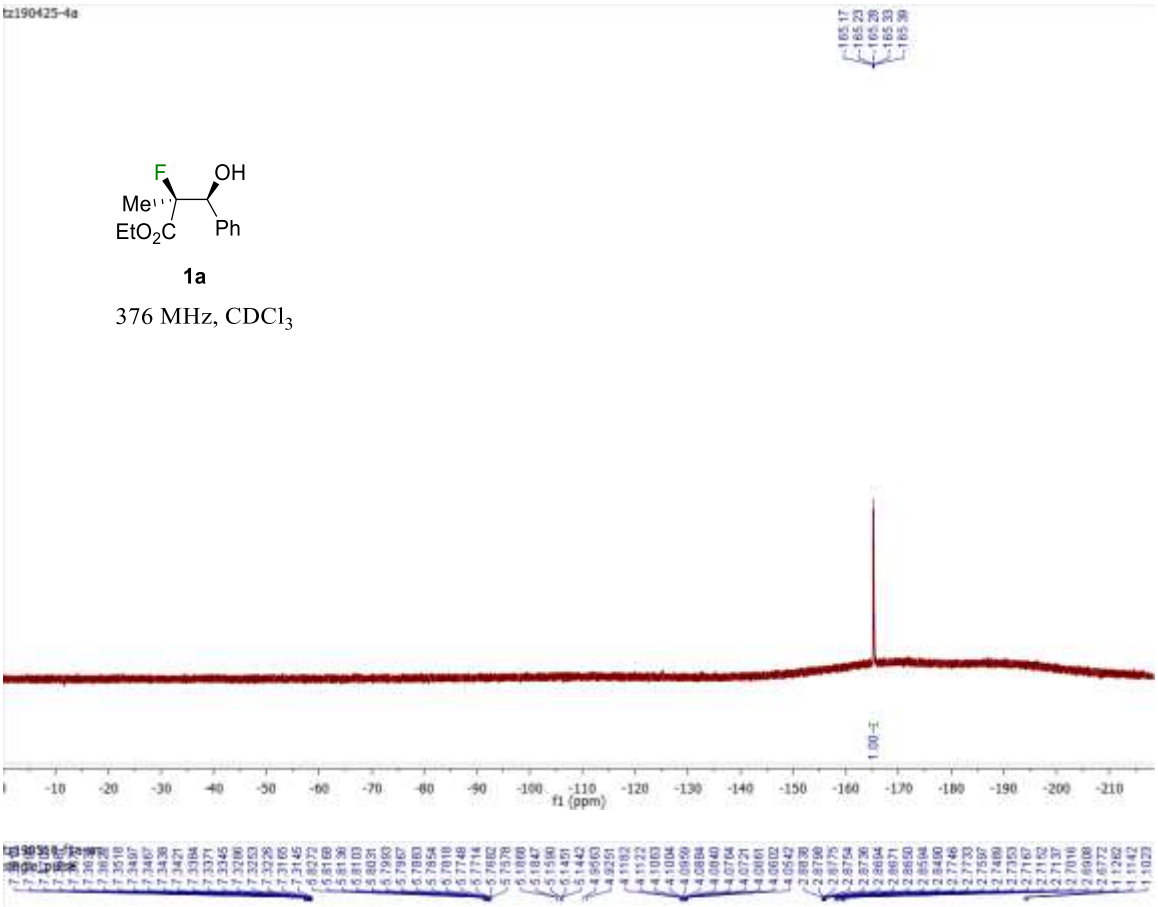
1a

600 MHz, $CDCl_3$



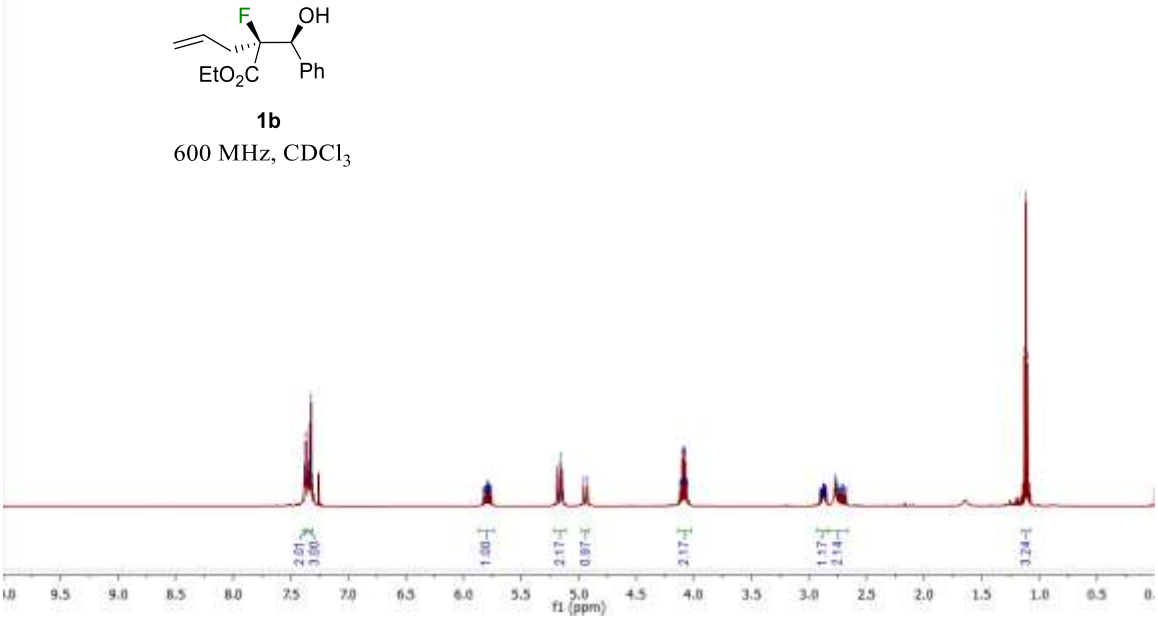
1a

101 MHz, $CDCl_3$



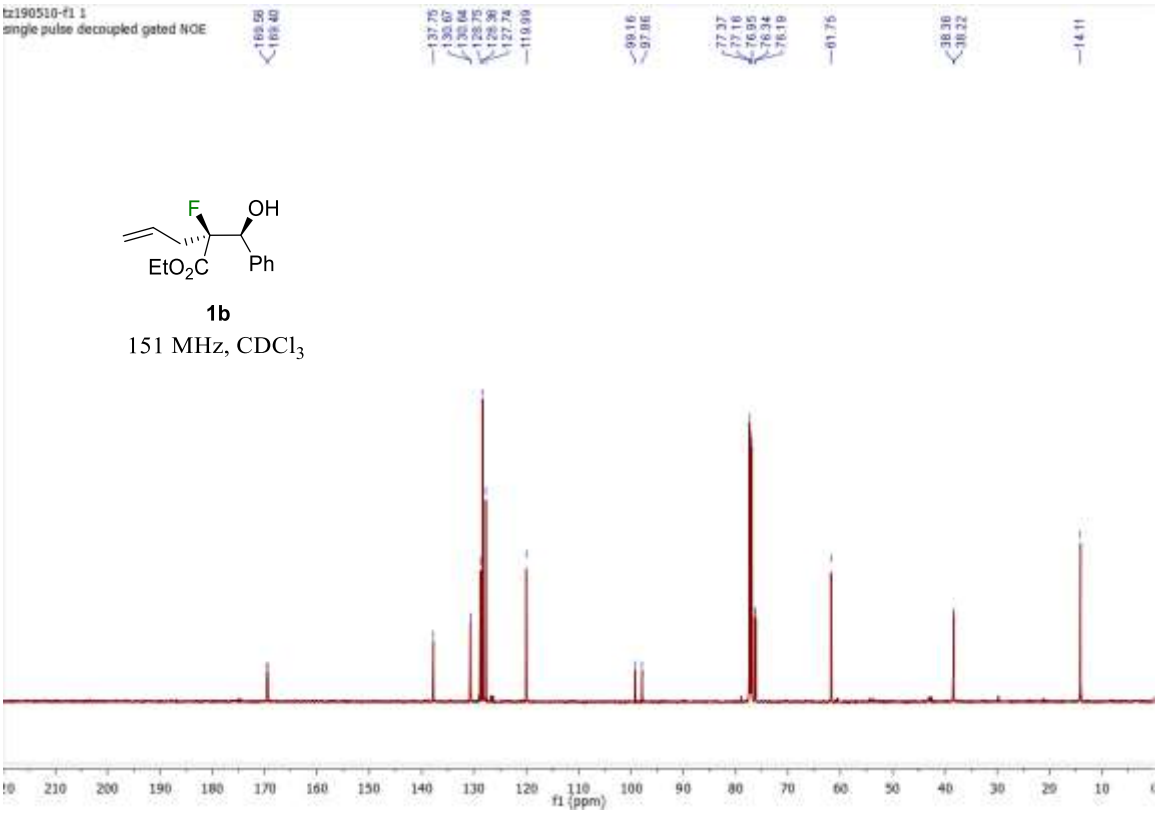
1a

376 MHz, $CDCl_3$



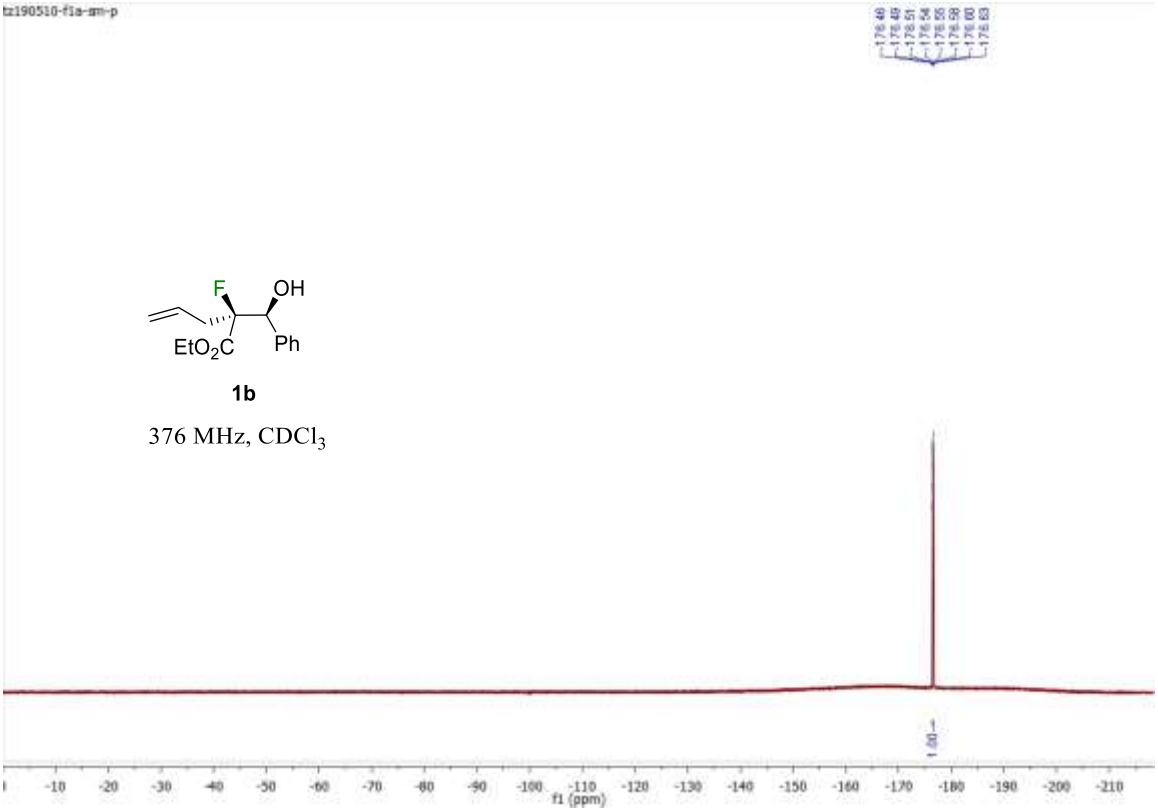
1b

600 MHz, $CDCl_3$



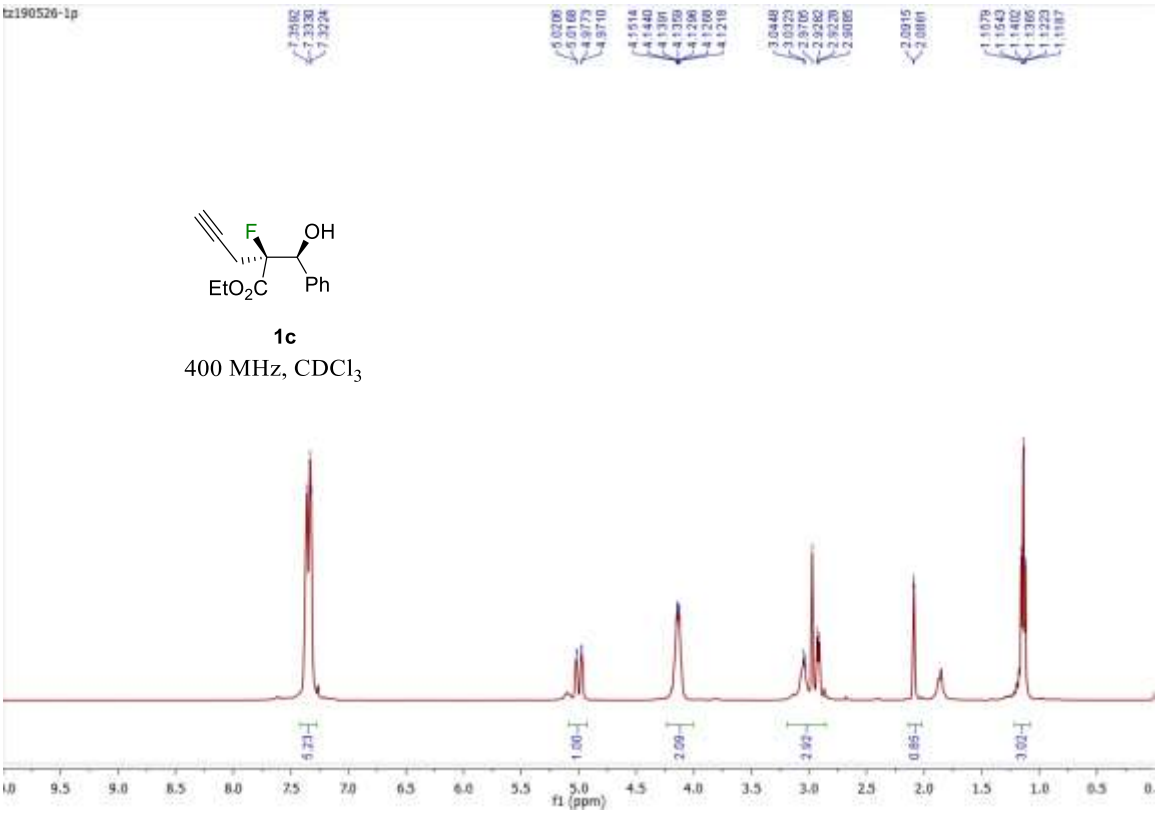
1b

151 MHz, $CDCl_3$



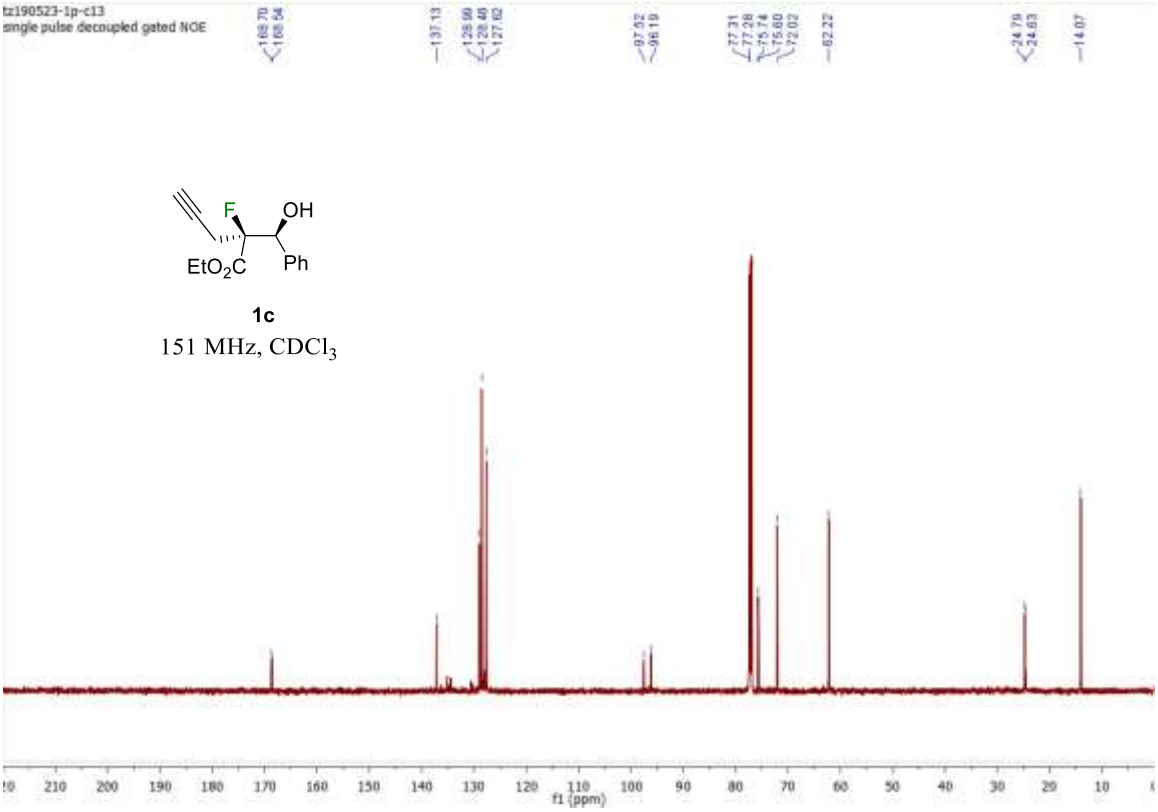
1b

376 MHz, $CDCl_3$



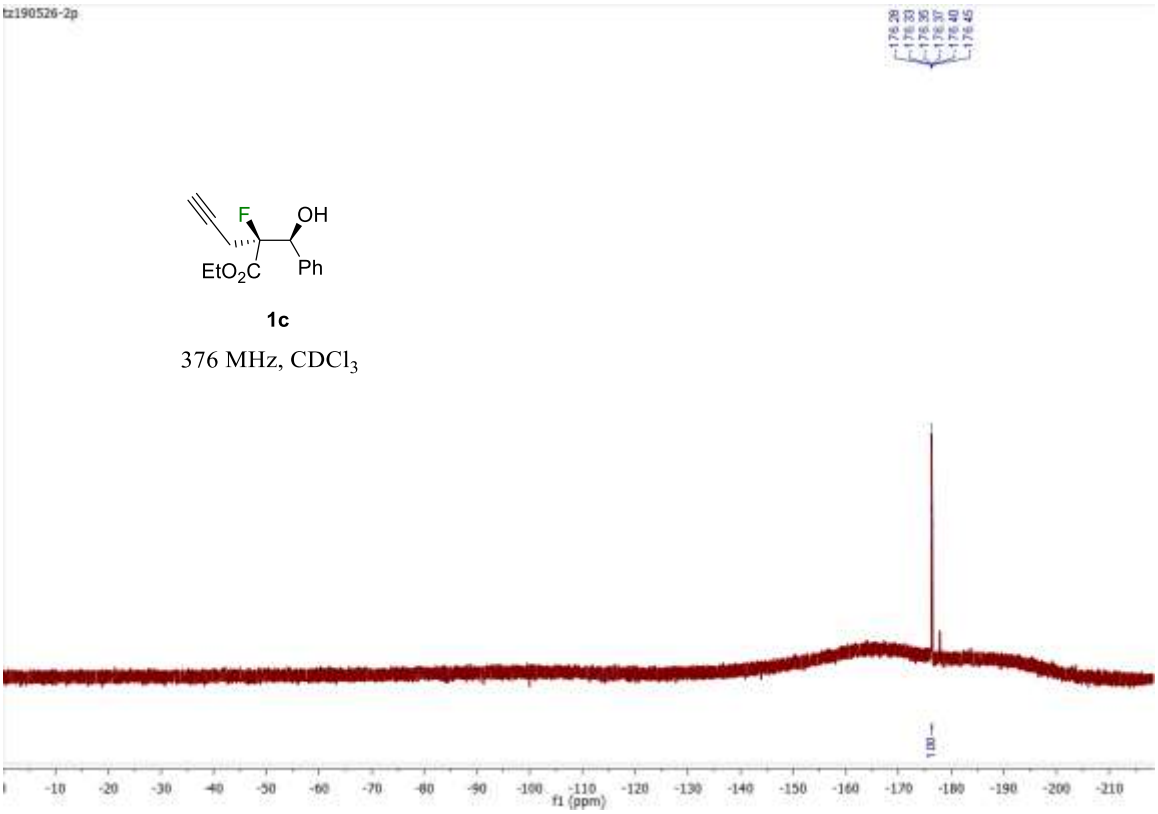
1c

400 MHz, $CDCl_3$



1c

151 MHz, $CDCl_3$



1c

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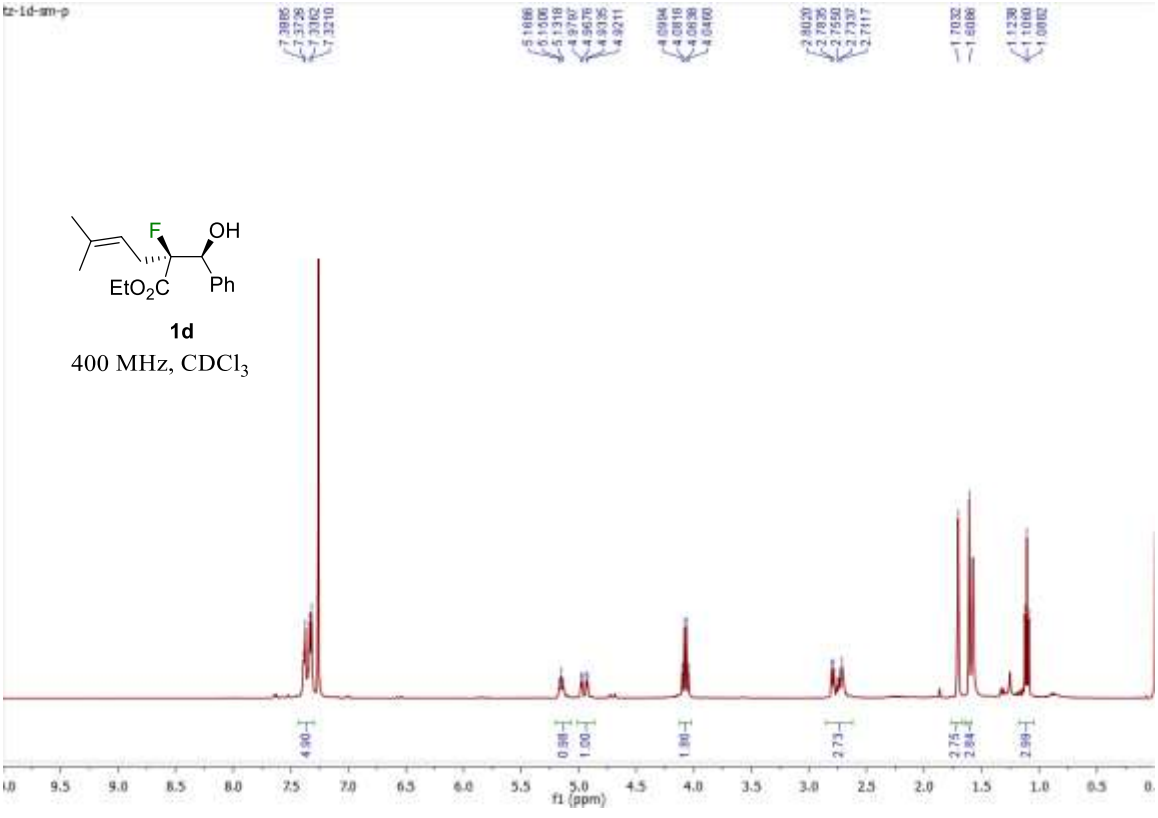
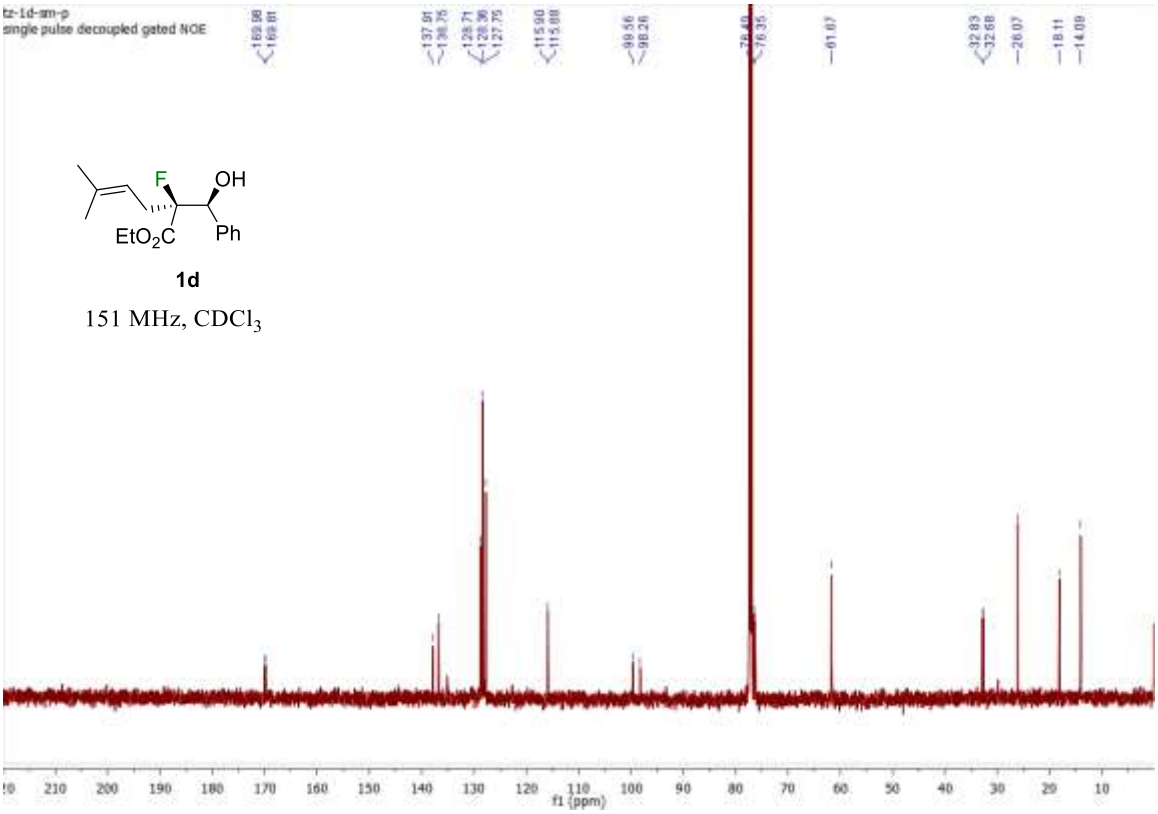


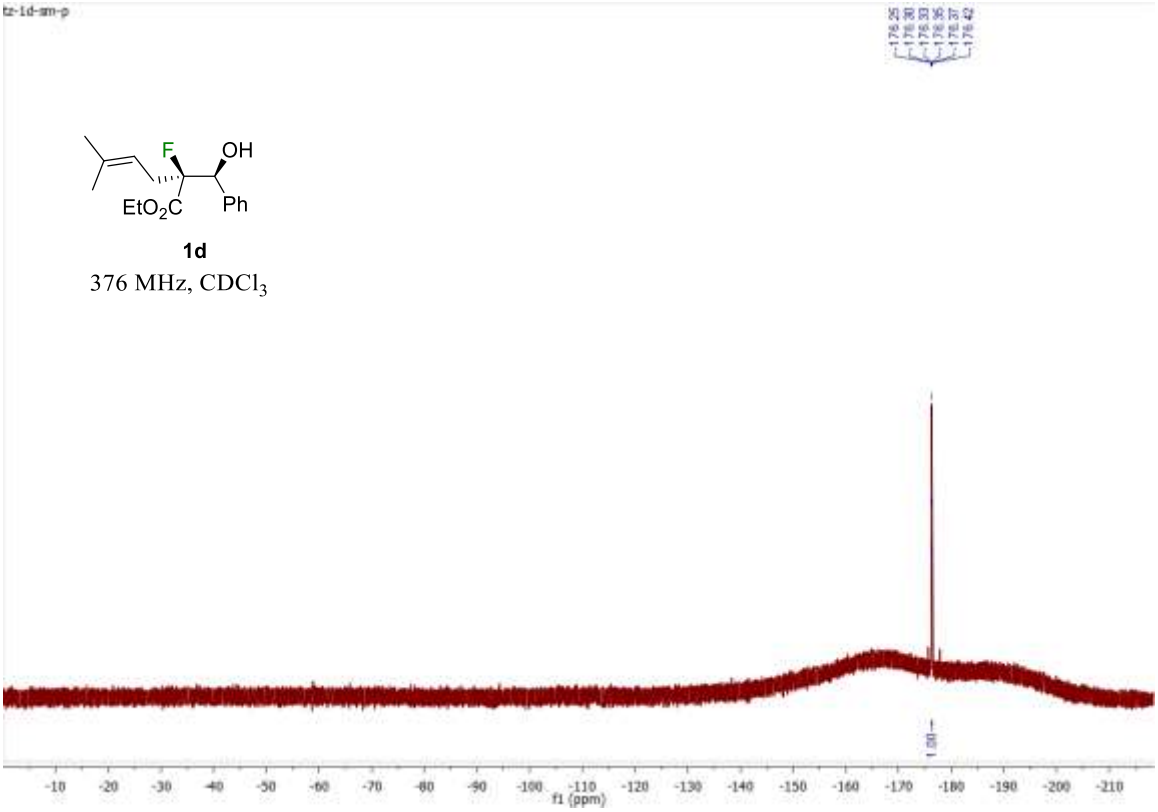
1d

400 MHz, $CDCl_3$



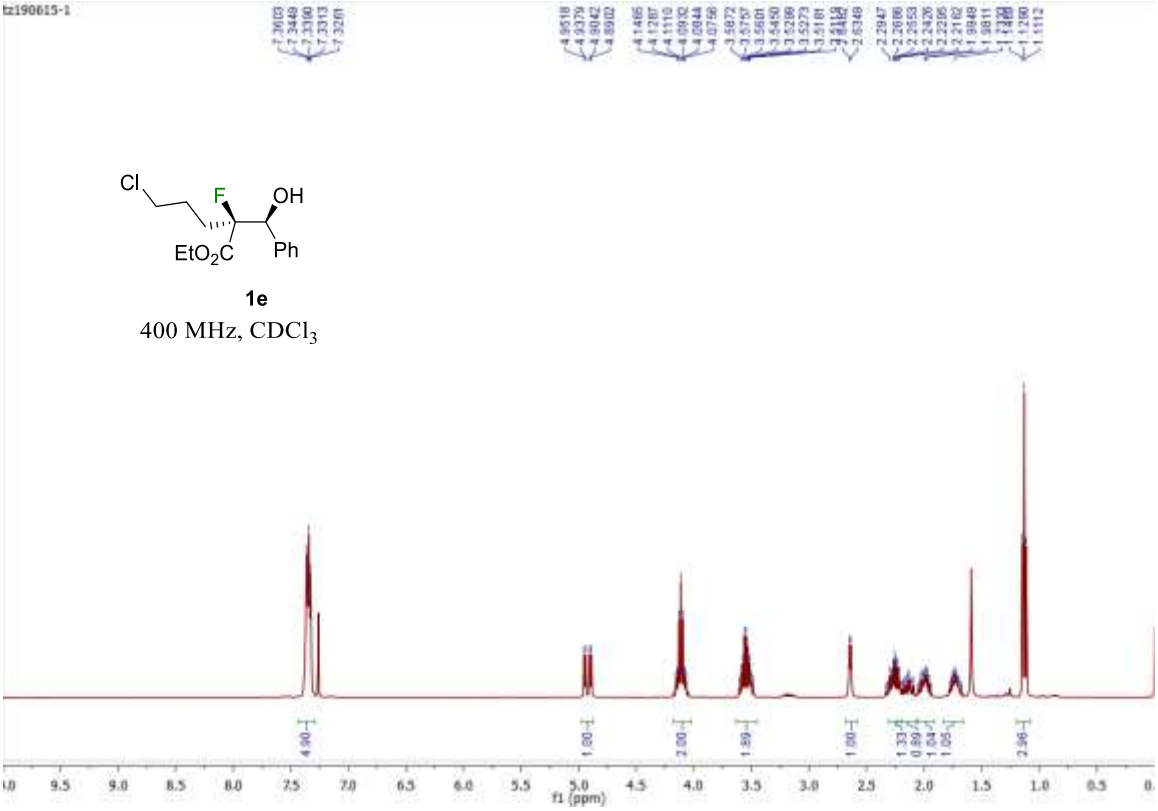
1d

151 MHz, $CDCl_3$



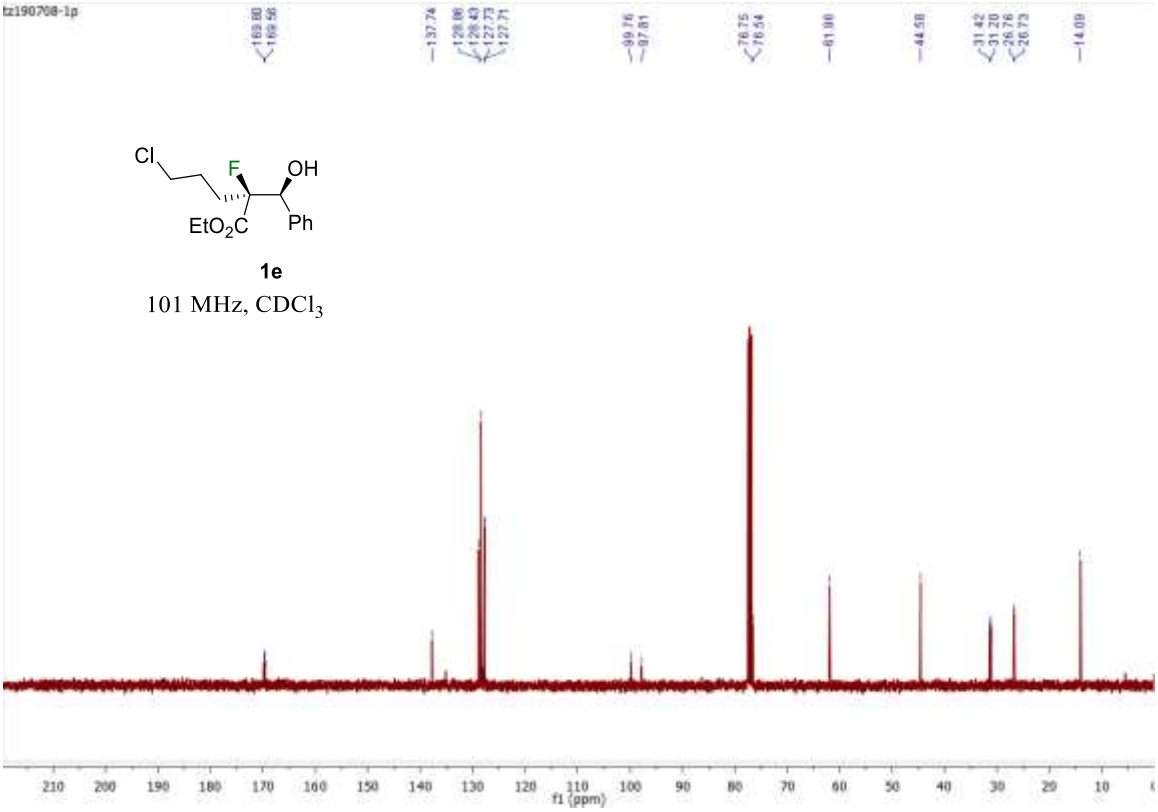
1d

376 MHz, $CDCl_3$



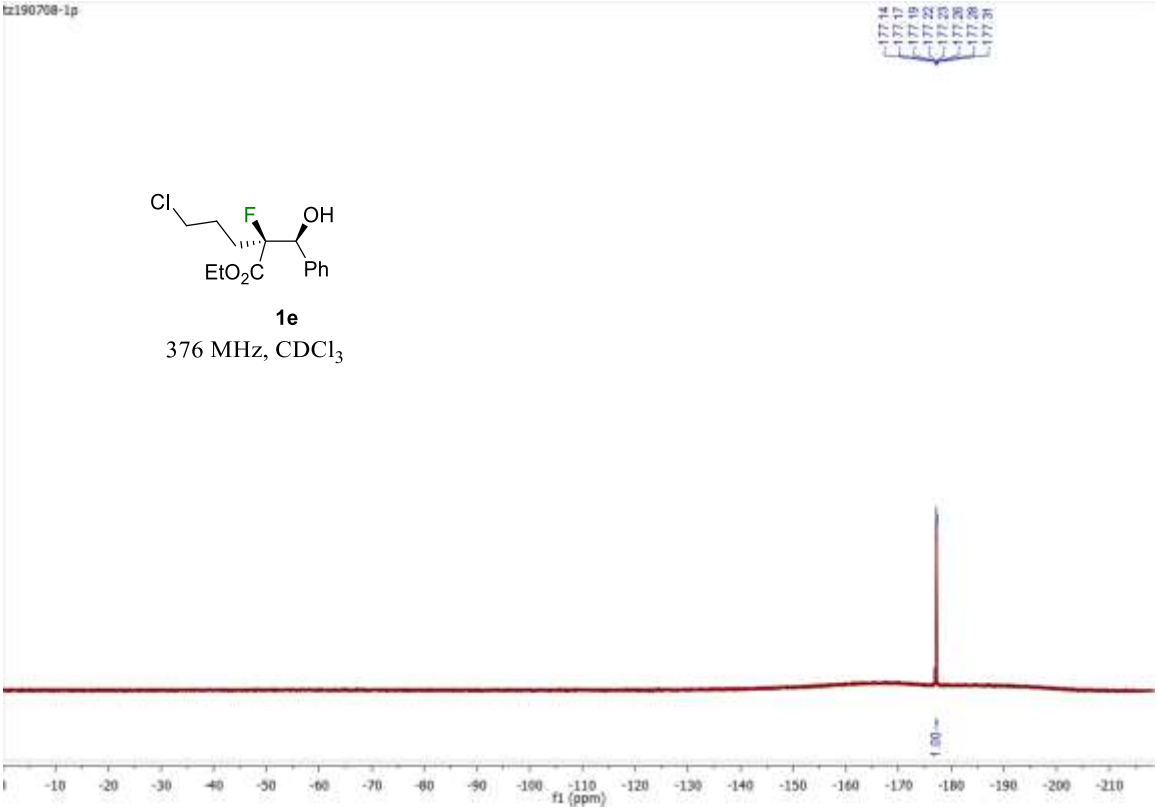
1e

400 MHz, $CDCl_3$



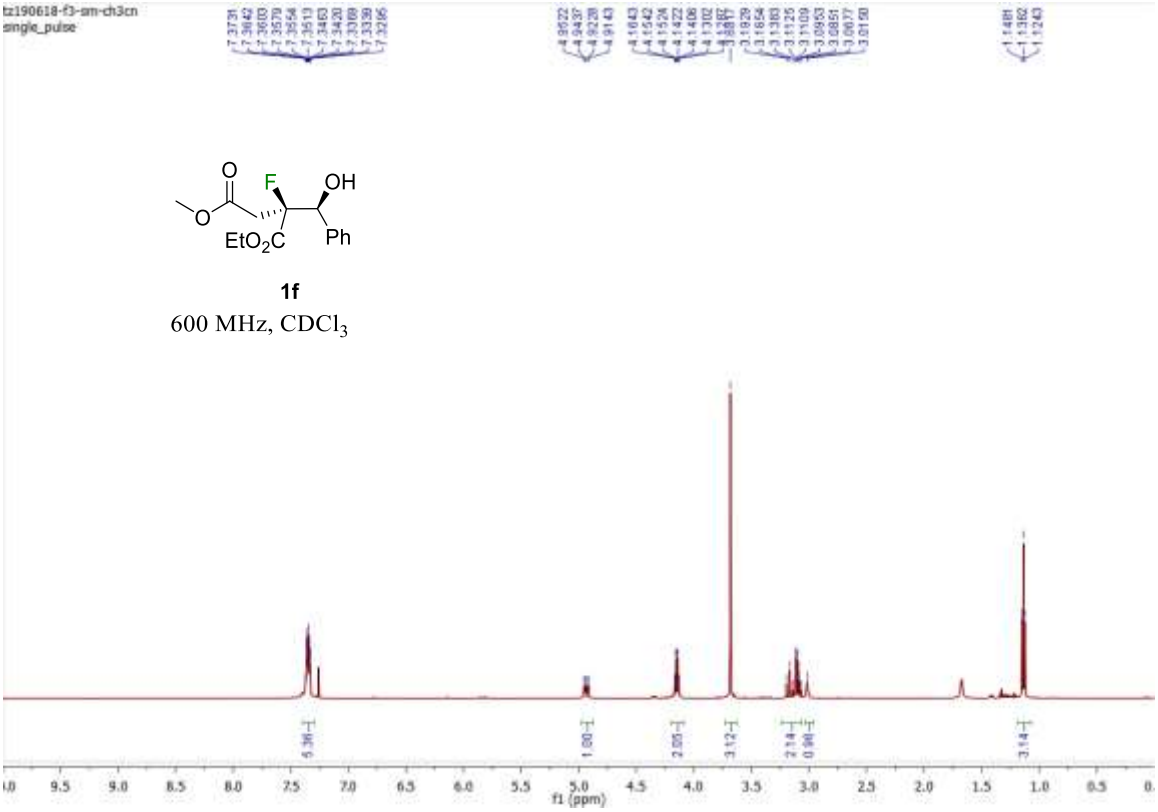
1e

101 MHz, $CDCl_3$



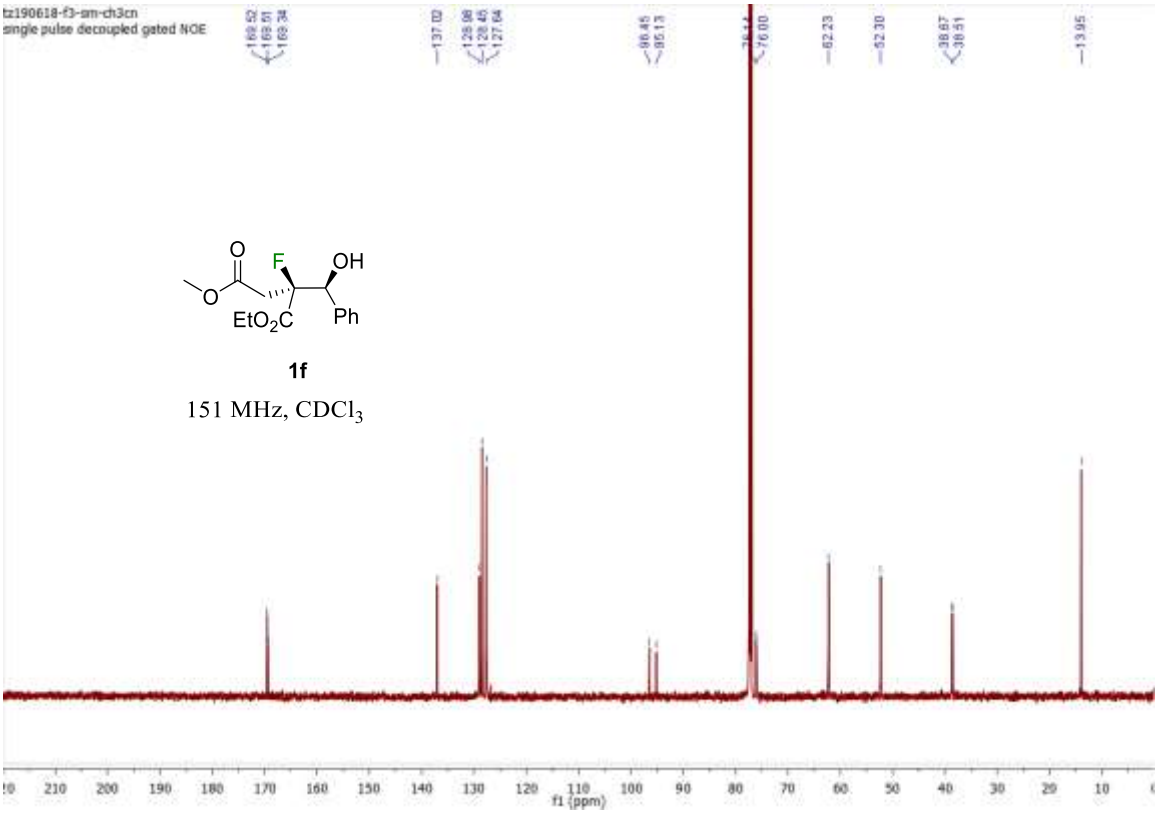
1e

376 MHz, $CDCl_3$



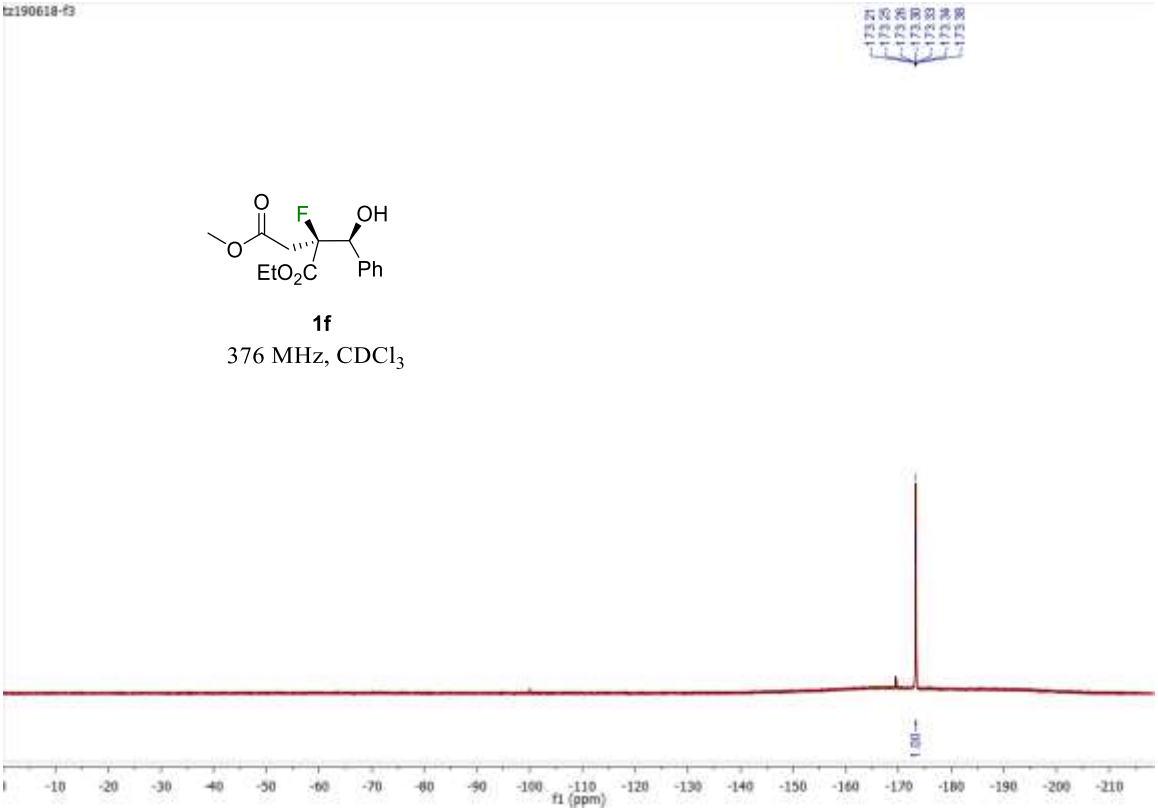
1f

600 MHz, $CDCl_3$



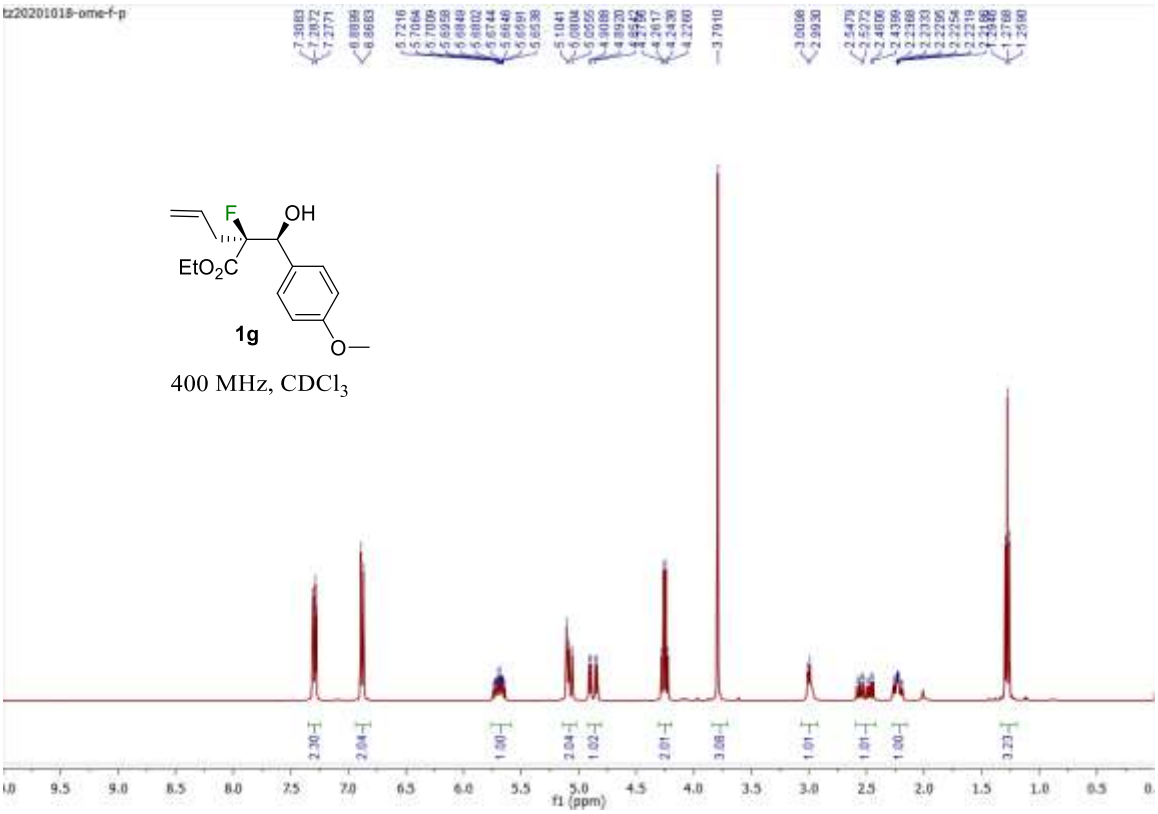
1f

151 MHz, $CDCl_3$

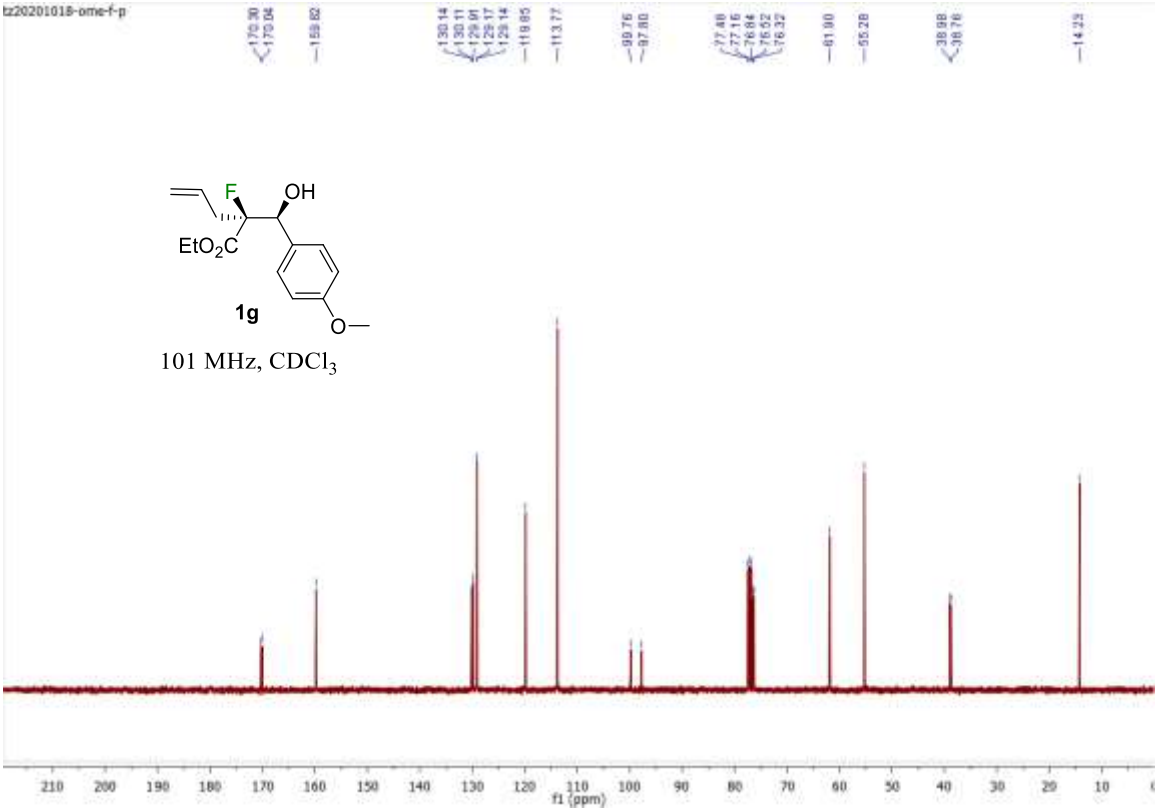


1f

376 MHz, $CDCl_3$



400 MHz, $CDCl_3$



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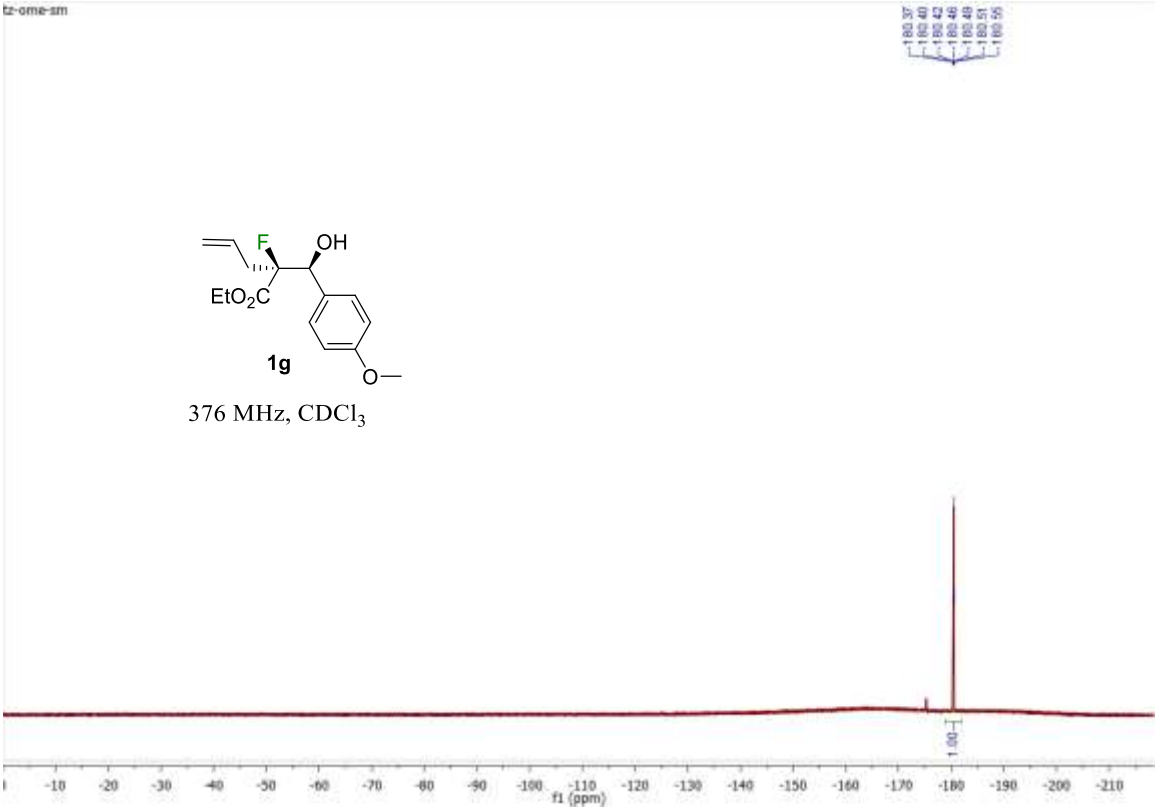

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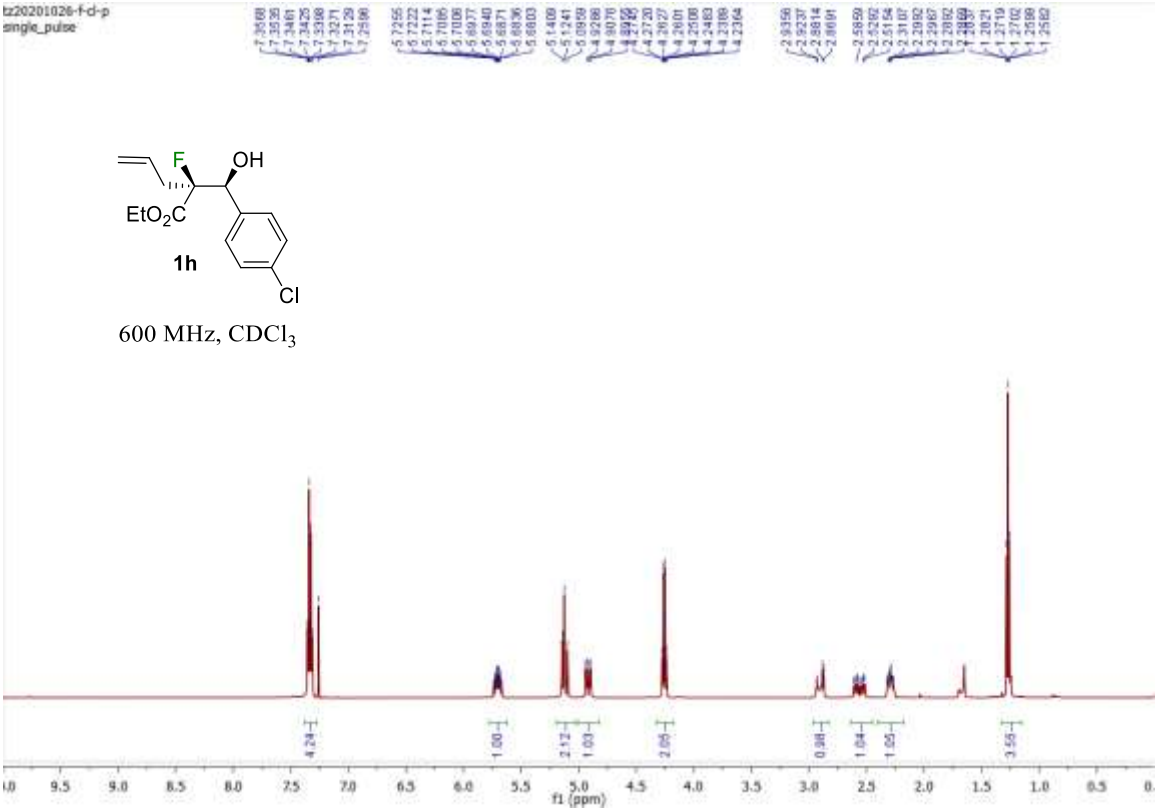
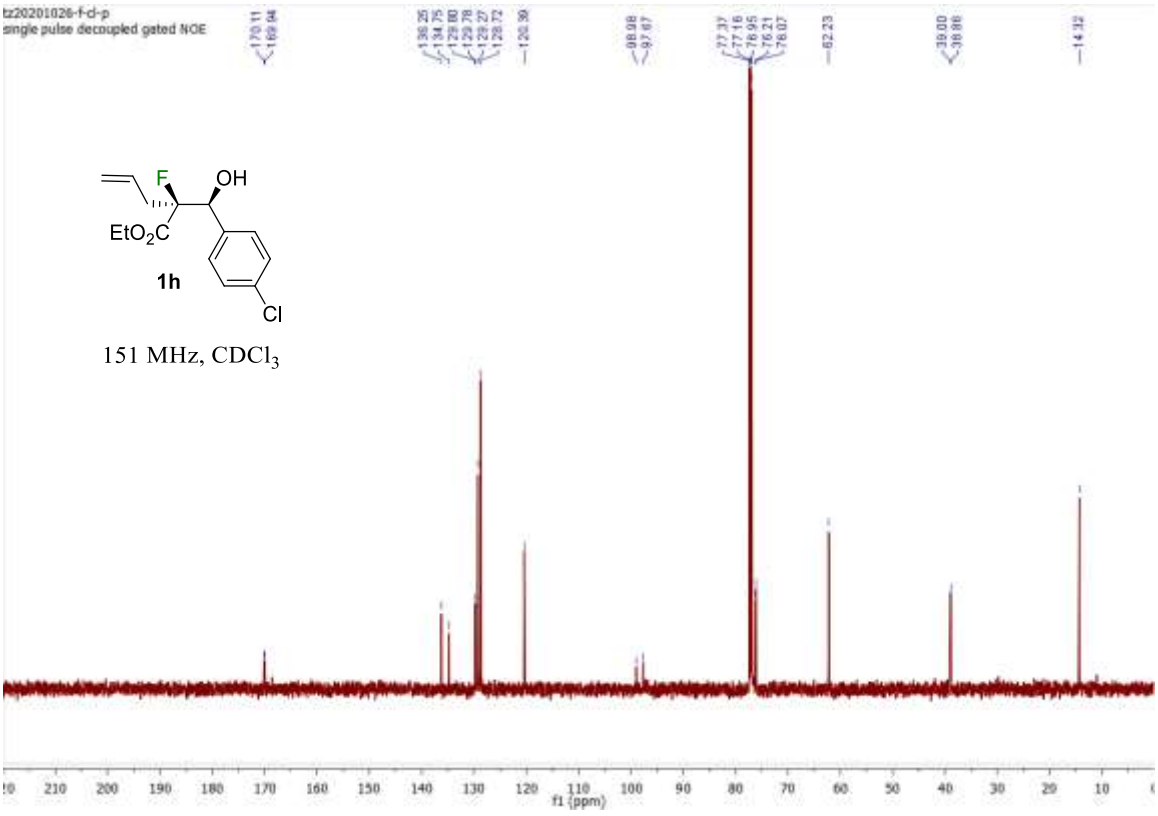
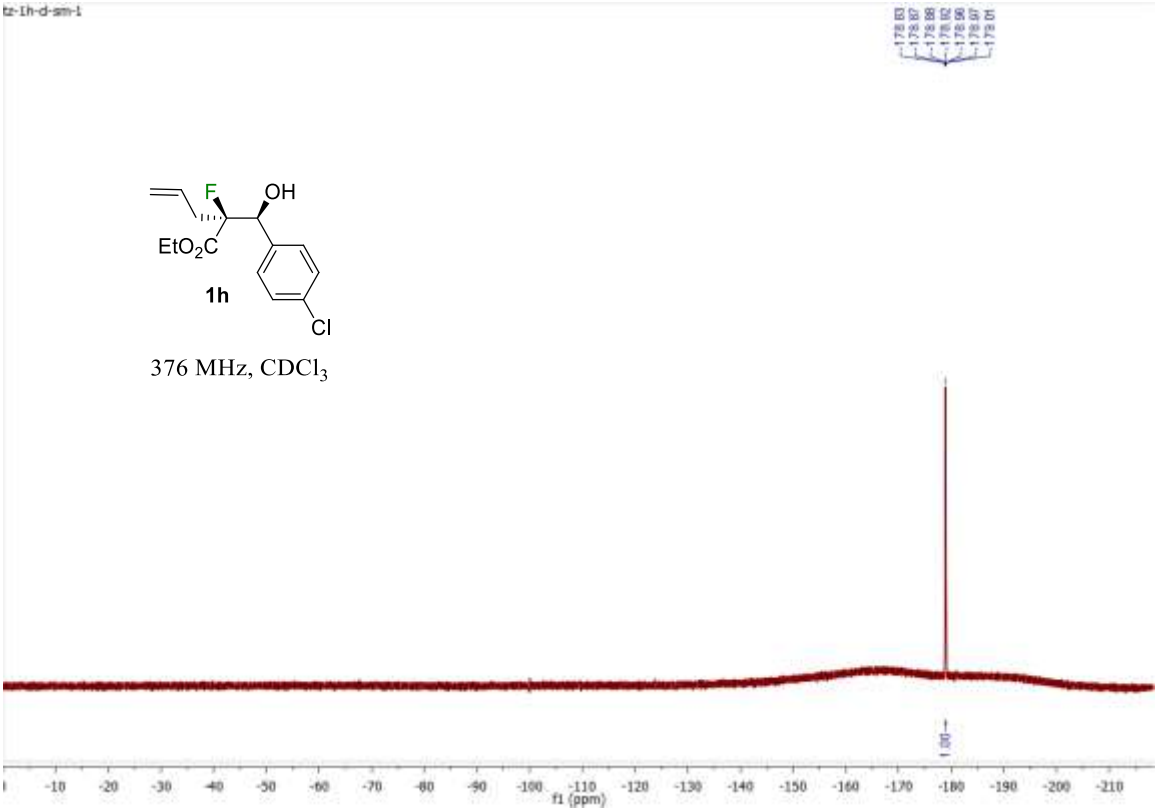


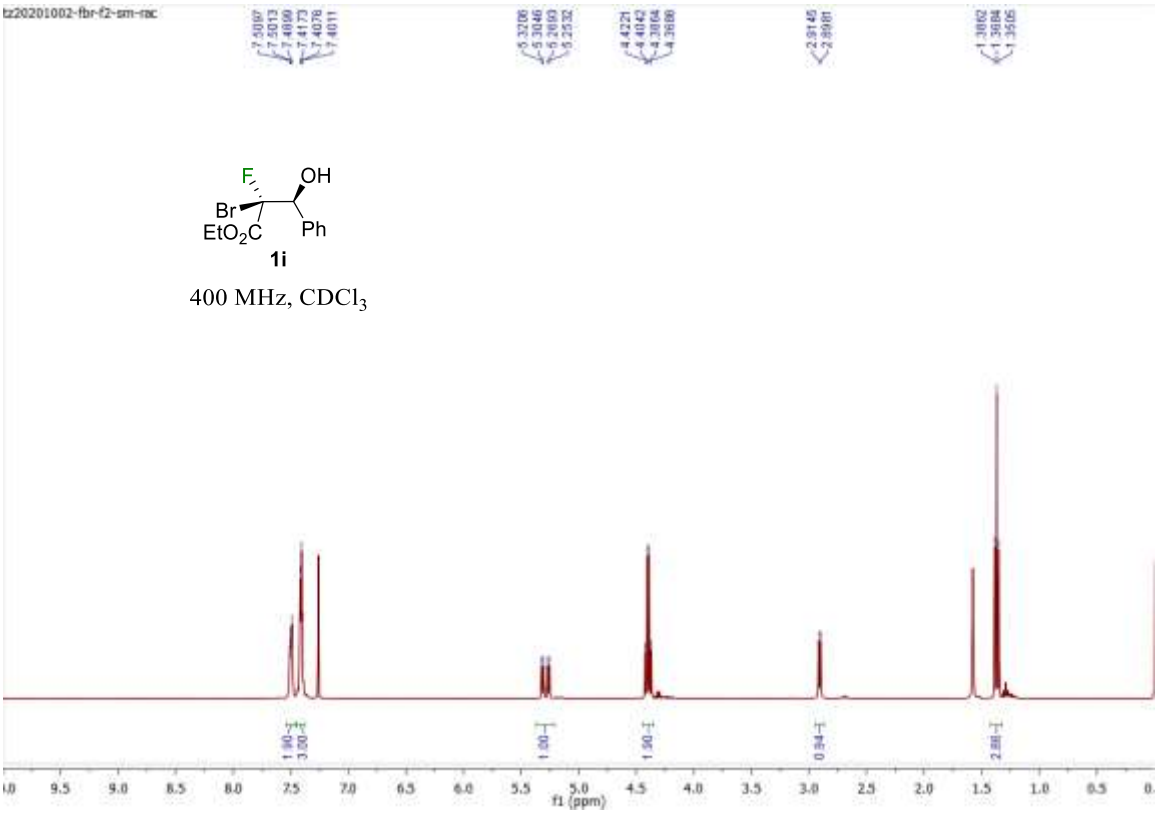
600 MHz, $CDCl_3$



151 MHz, $CDCl_3$



376 MHz, $CDCl_3$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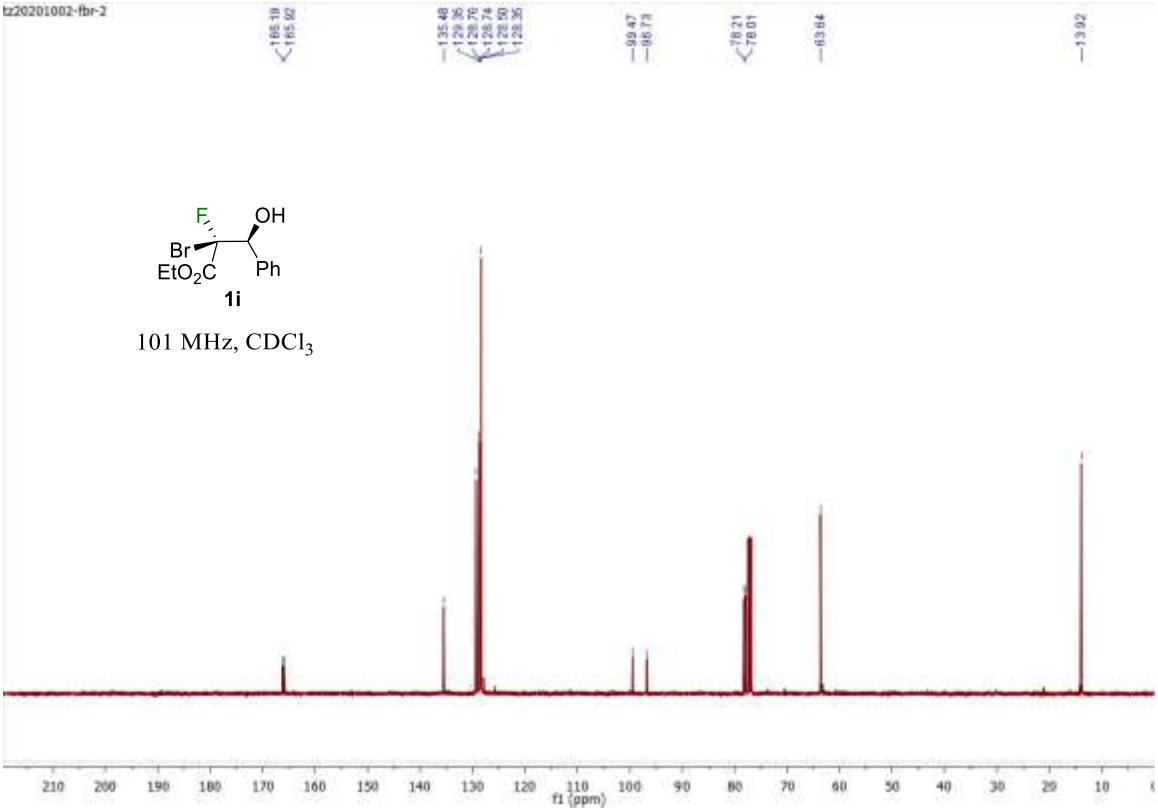
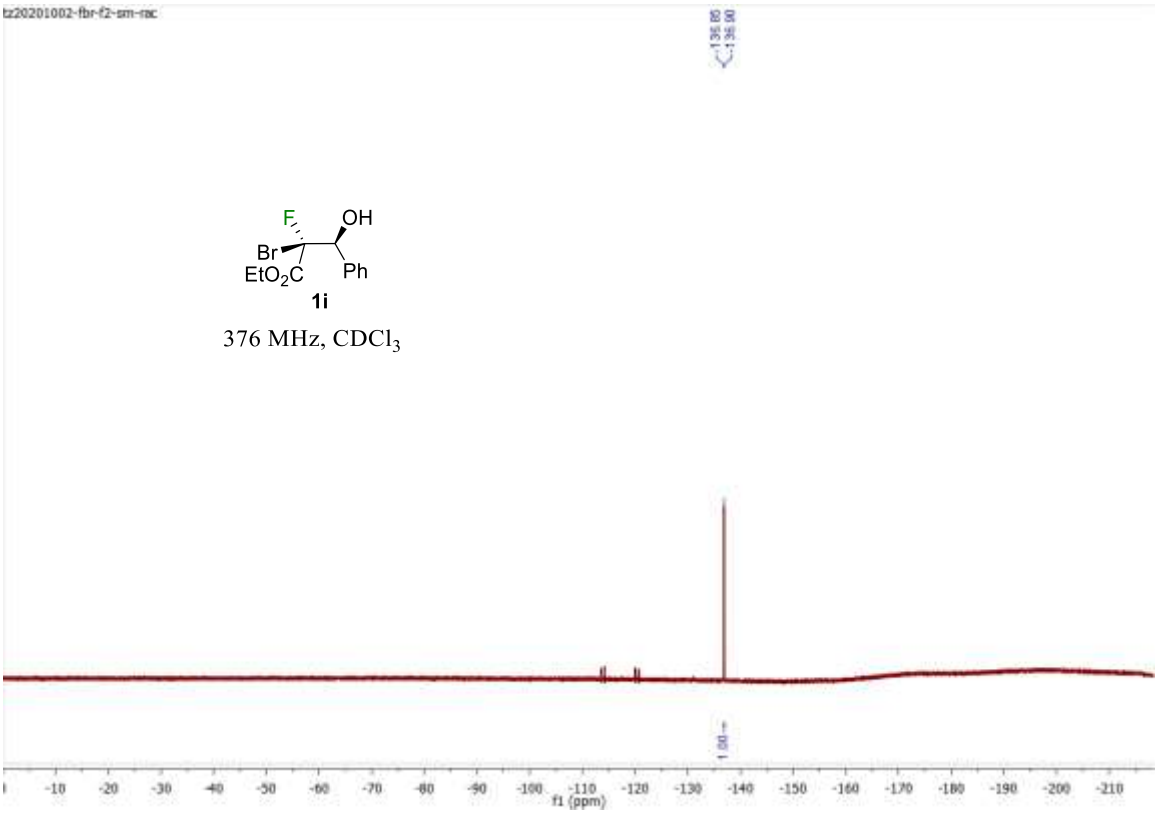
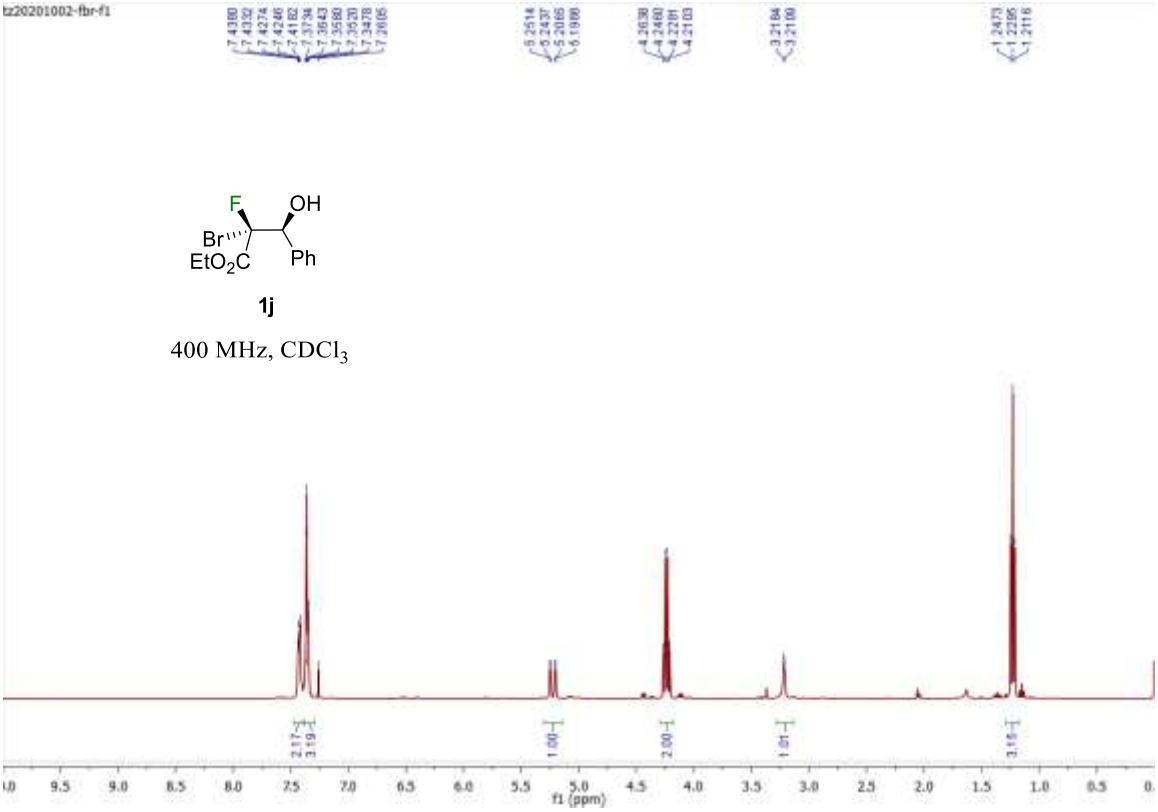
F
OH
Br
EtO2C
Ph
1i
400 MHz, CDCl3
f1 (ppm)


tz20201002-fbr-2
F
OH
Br
EtO2C
Ph
1i
101 MHz, CDCl3
f1 (ppm)



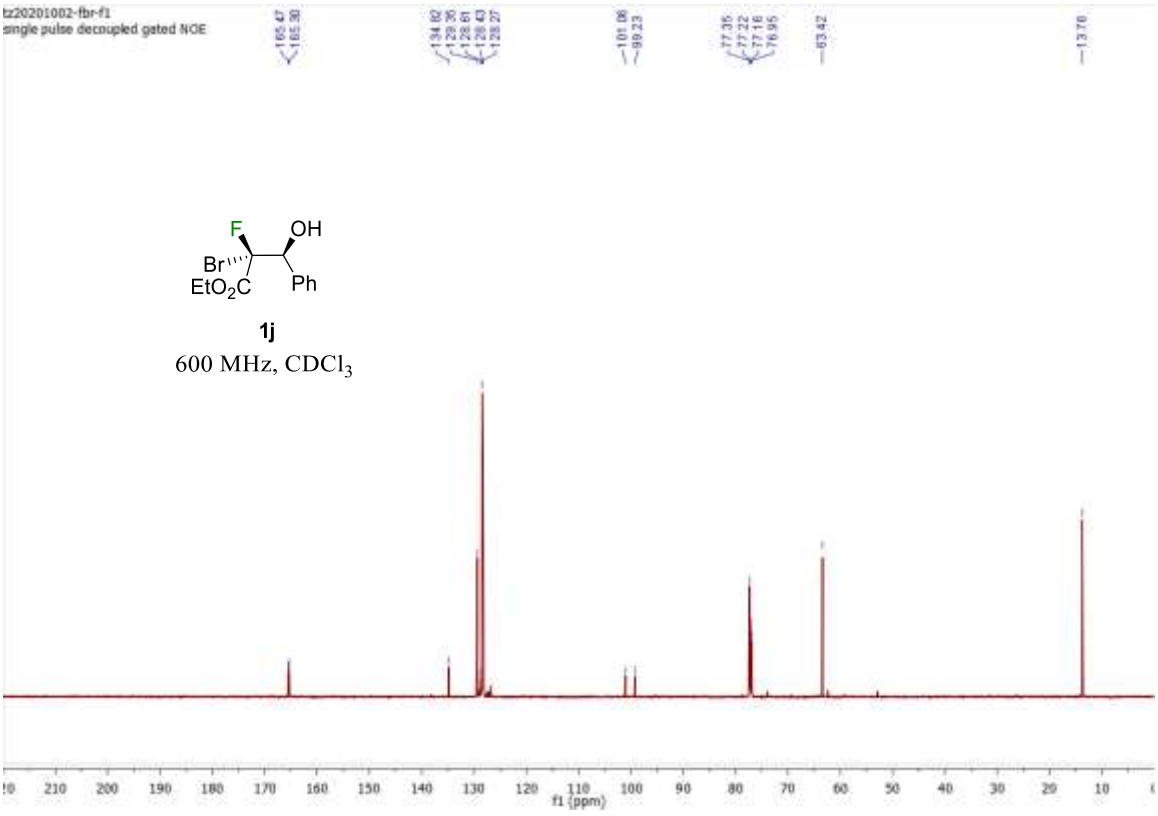
1i

376 MHz, $CDCl_3$



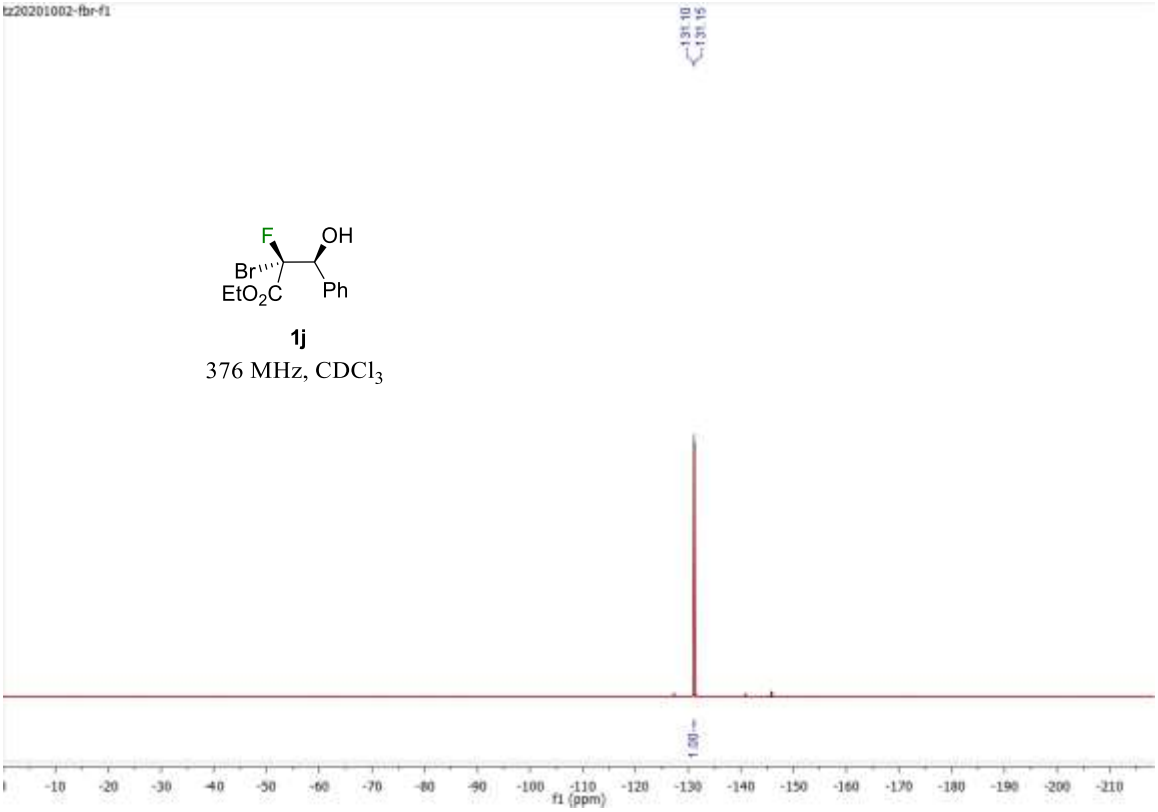
1j

400 MHz, $CDCl_3$



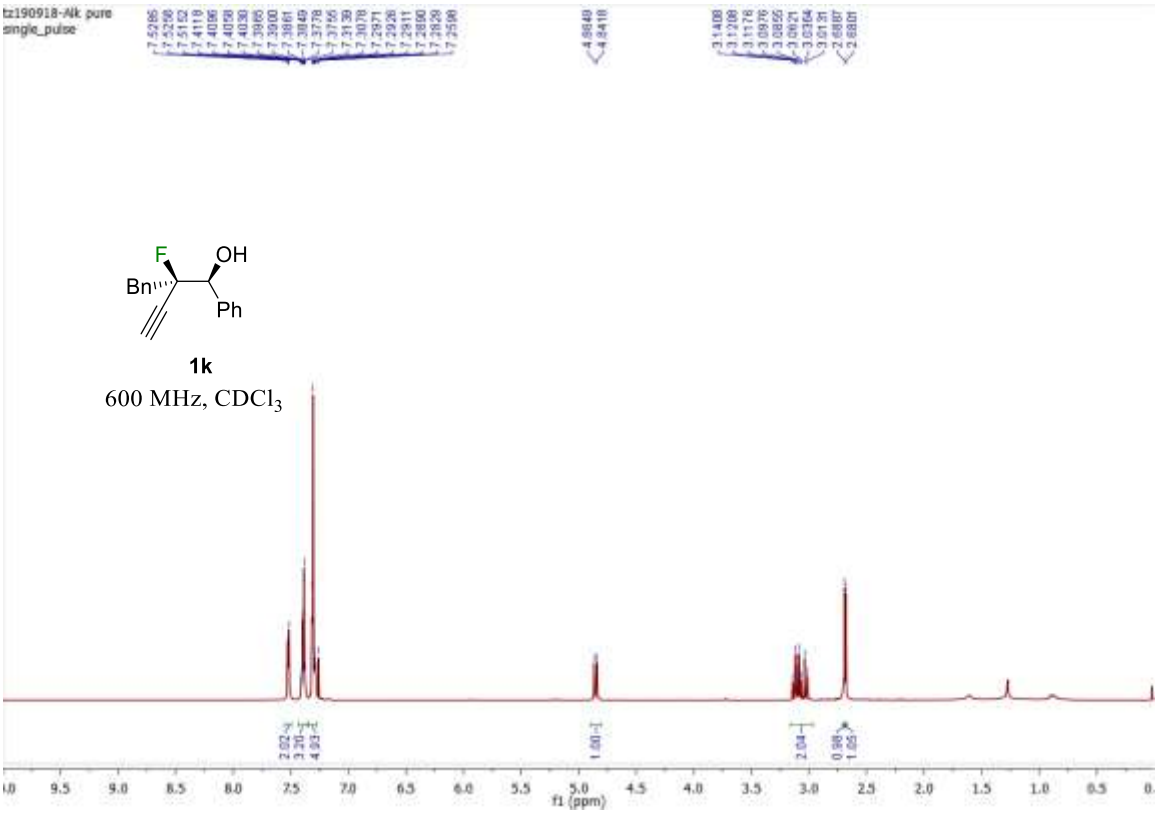
1j

600 MHz, $CDCl_3$



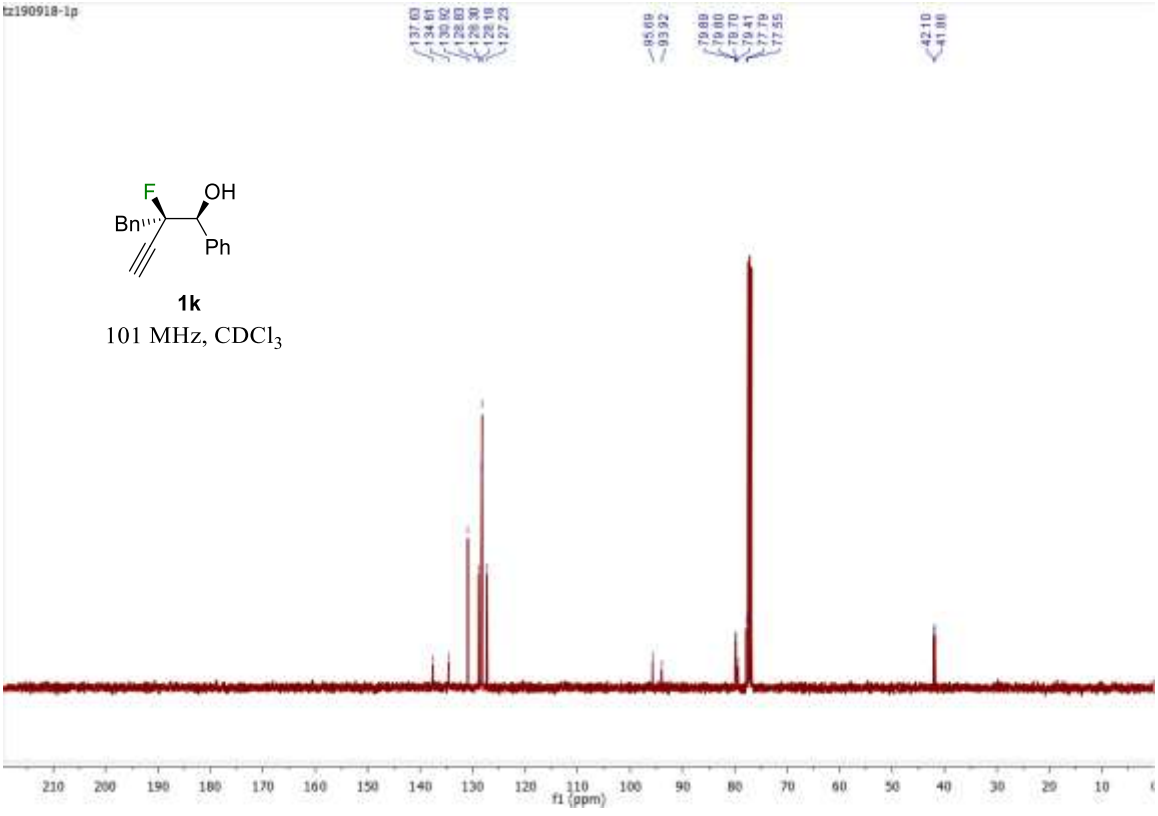
1j

376 MHz, $CDCl_3$



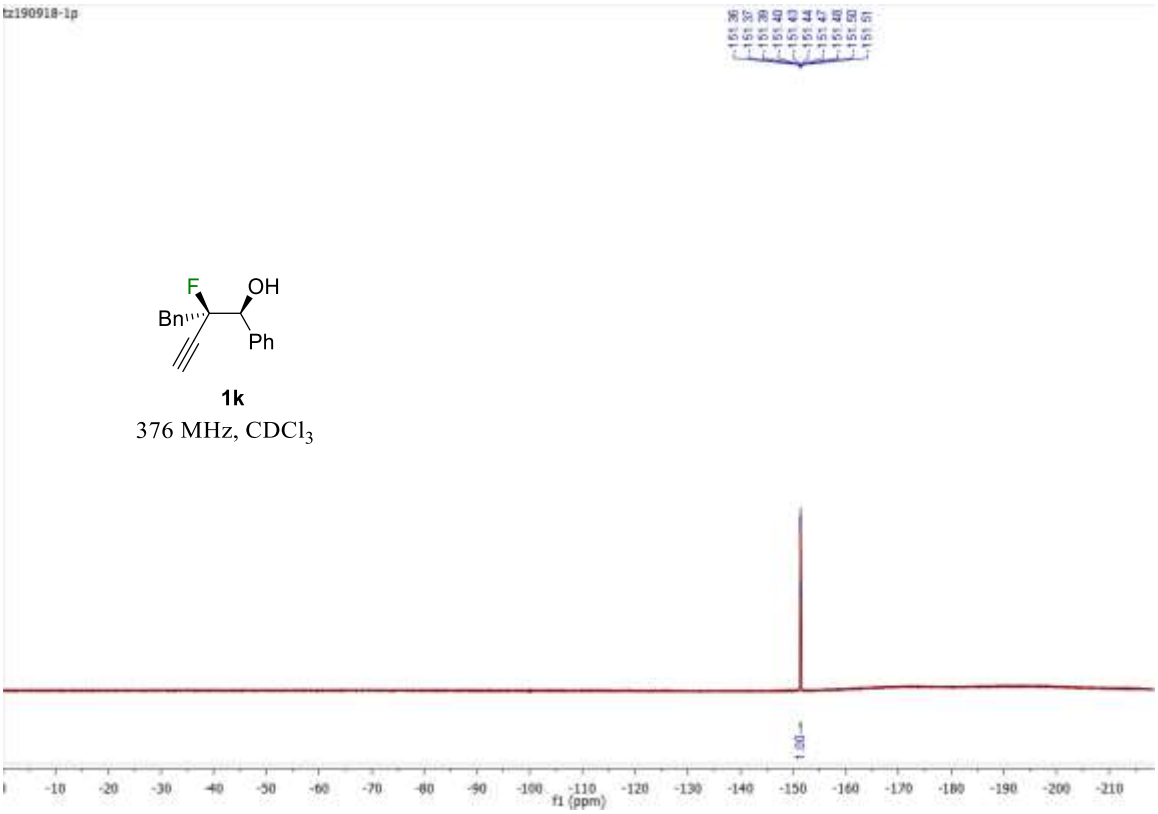
1k

600 MHz, $CDCl_3$



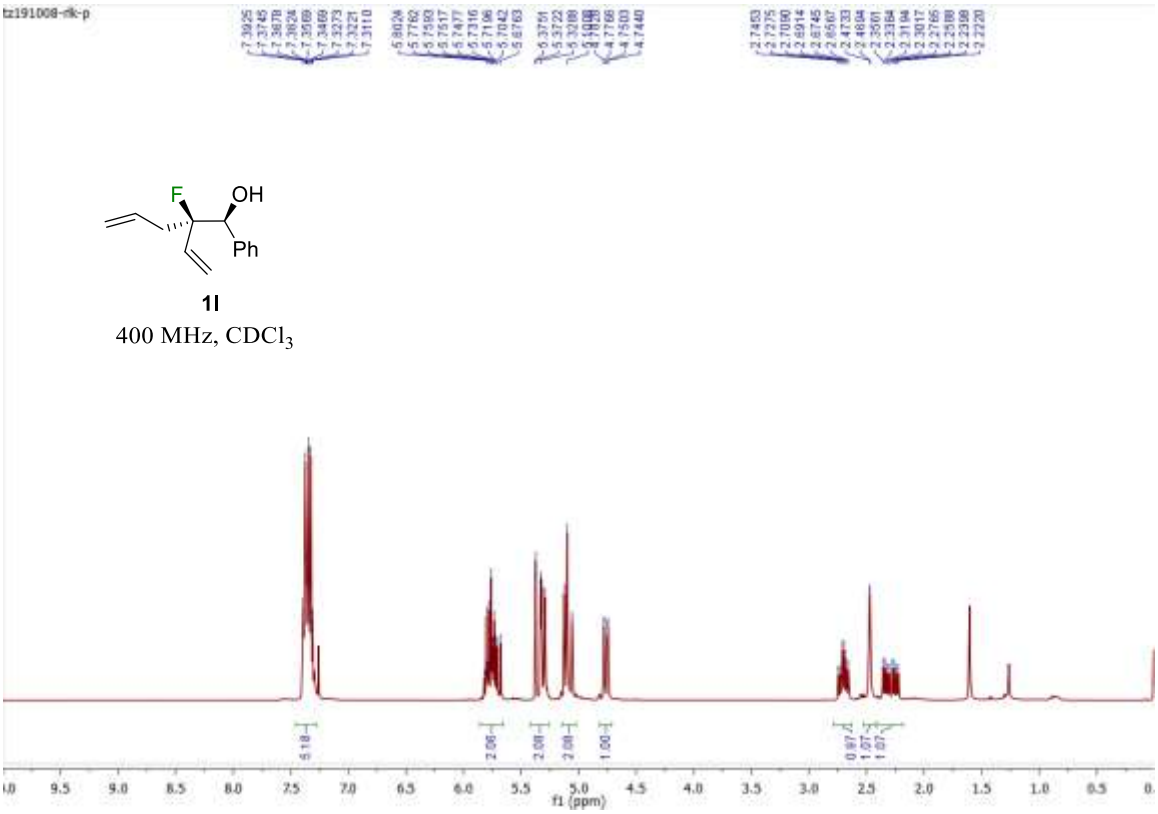
1k

101 MHz, $CDCl_3$



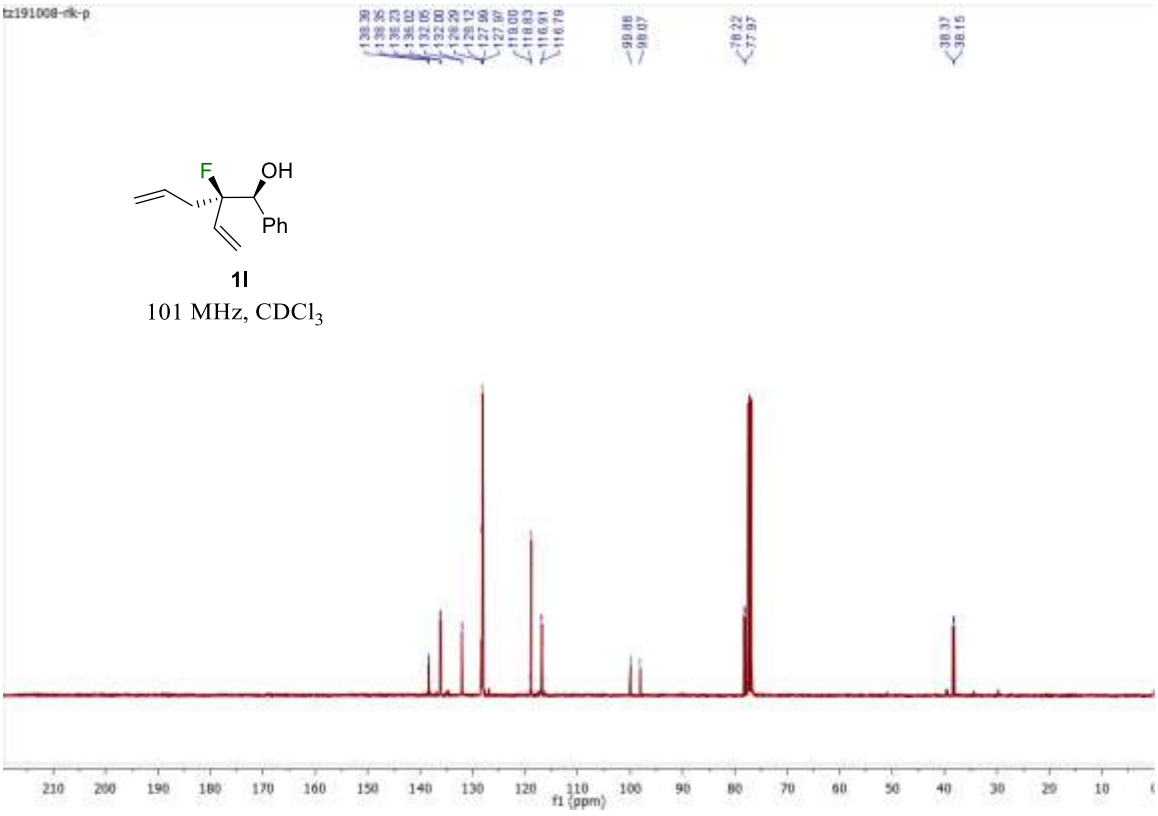
1k

376 MHz, $CDCl_3$



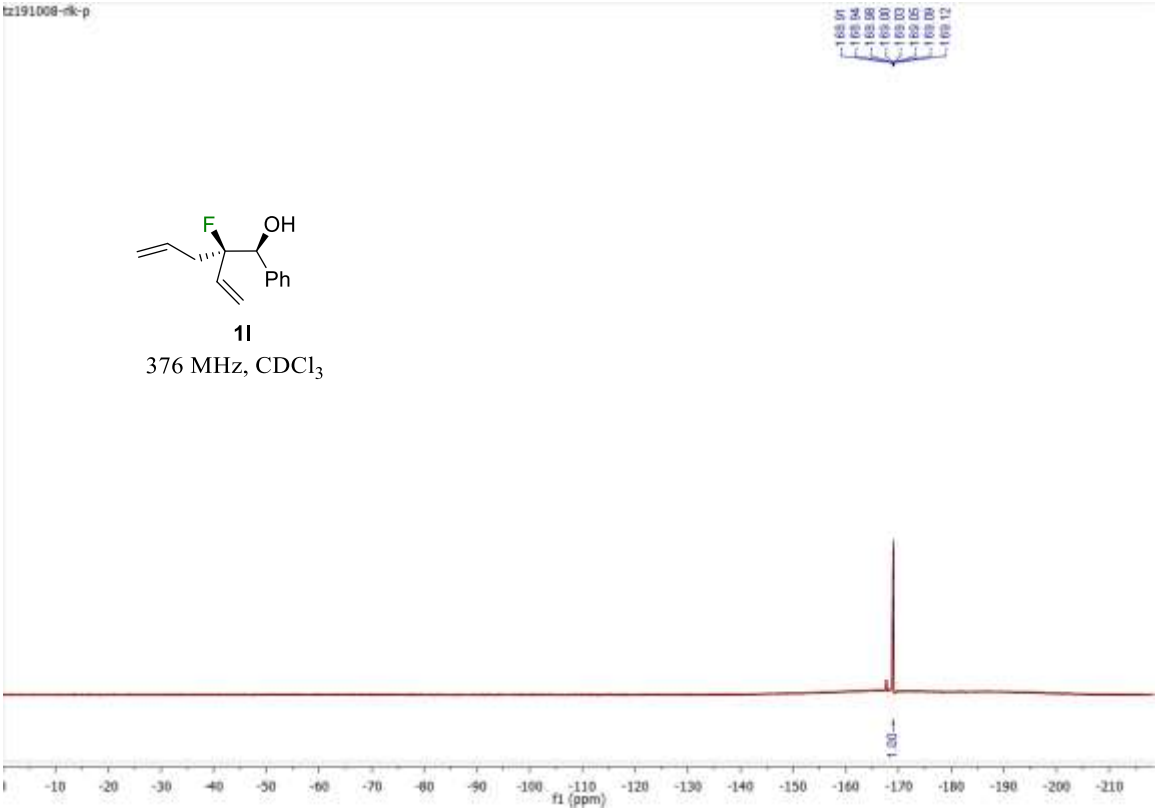
1l

400 MHz, $CDCl_3$



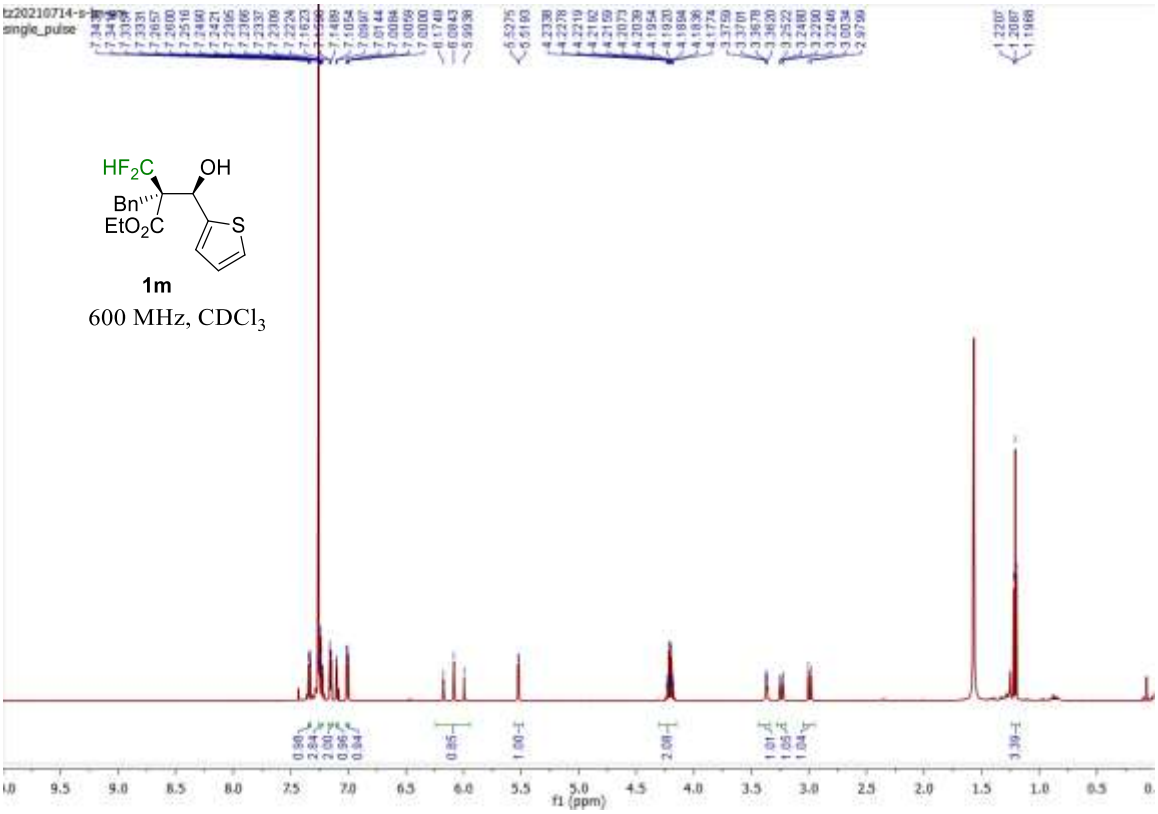
1l

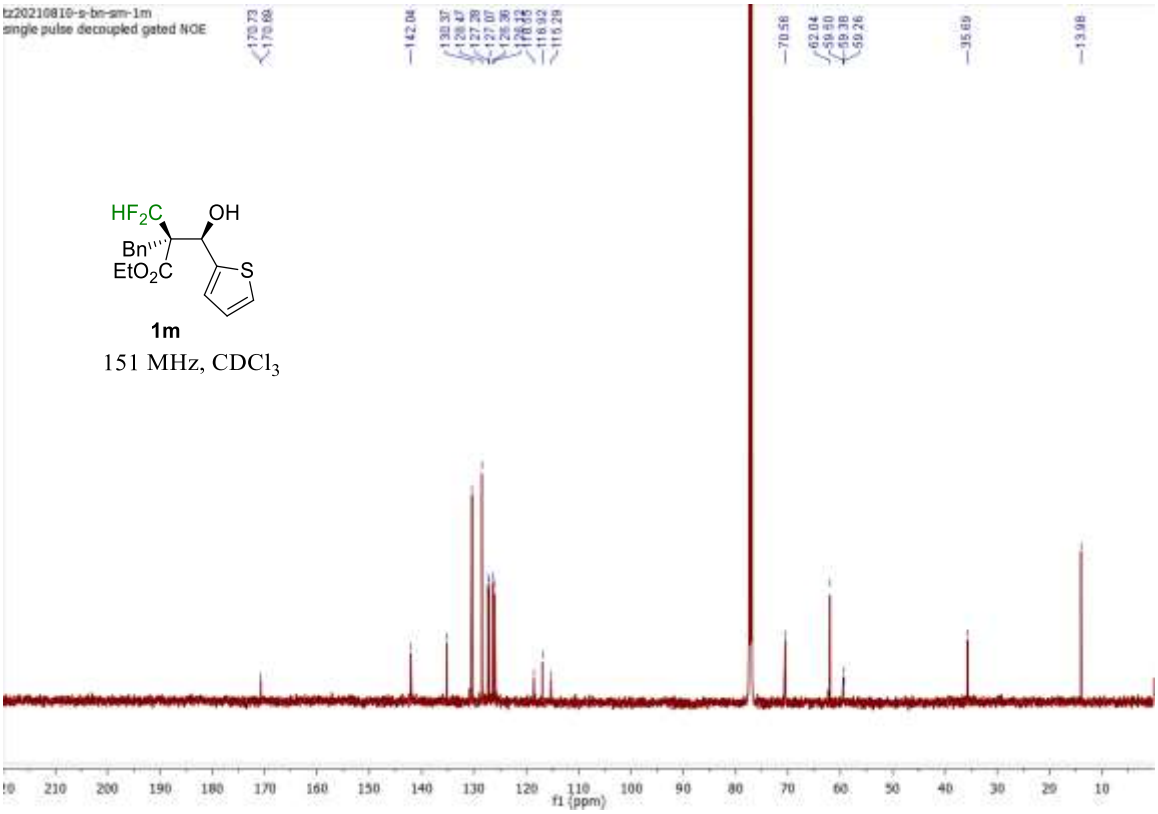
101 MHz, $CDCl_3$

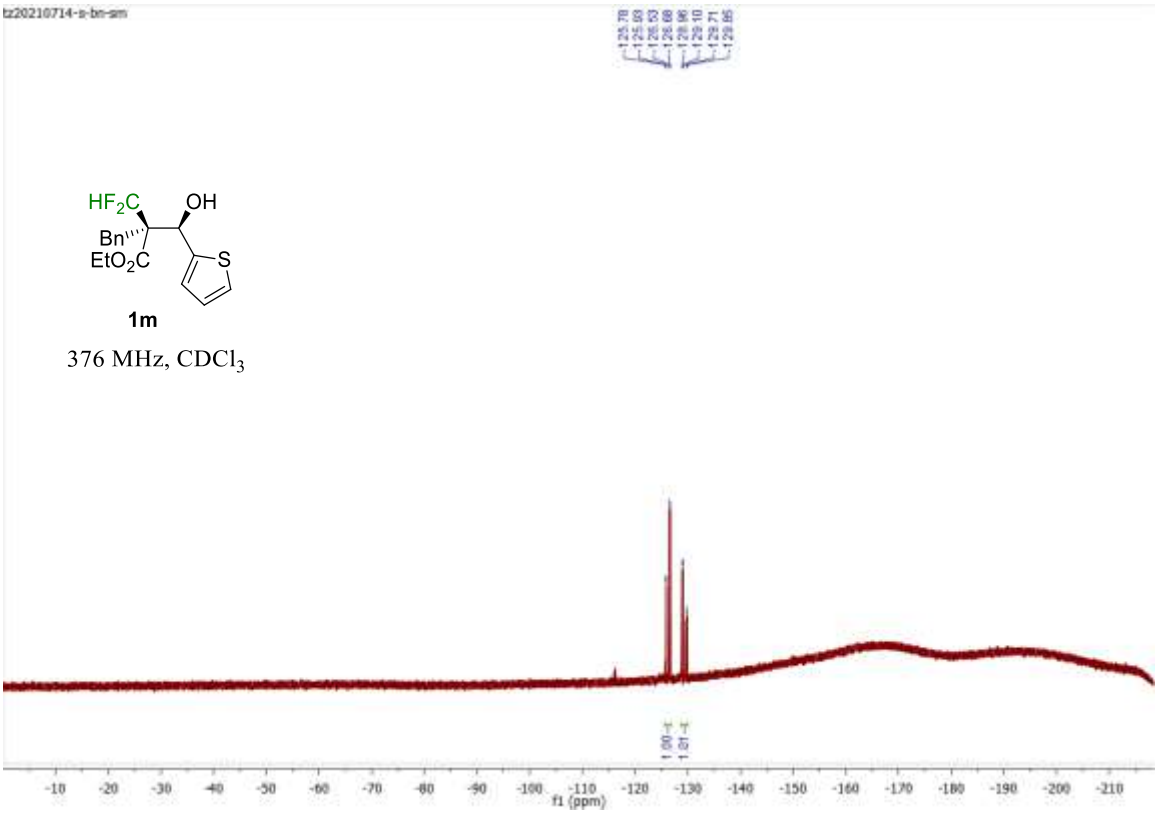


1l

376 MHz, $CDCl_3$

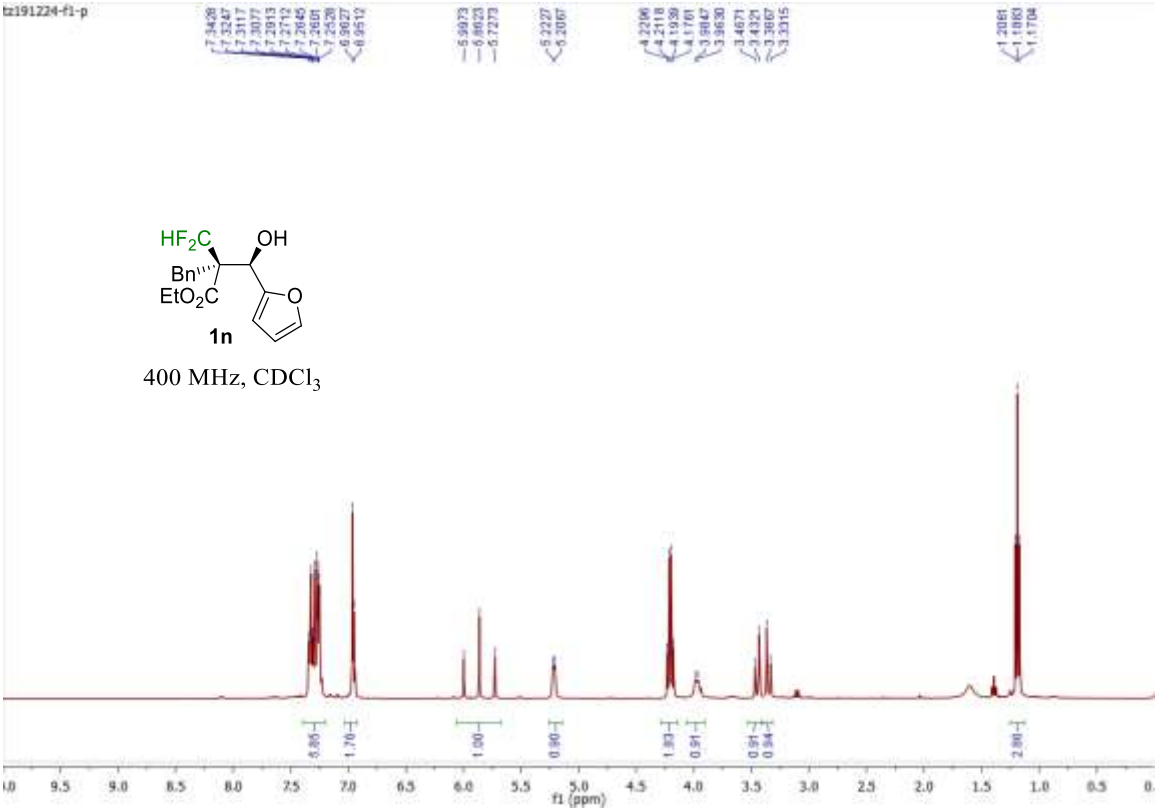

HF2C
OH
Bn
EtO2C
S
1m
600 MHz, CDCl3
f1 (ppm)


HF2C
OH
Bn
EtO2C
S
1m
151 MHz, CDCl3
f1 (ppm)



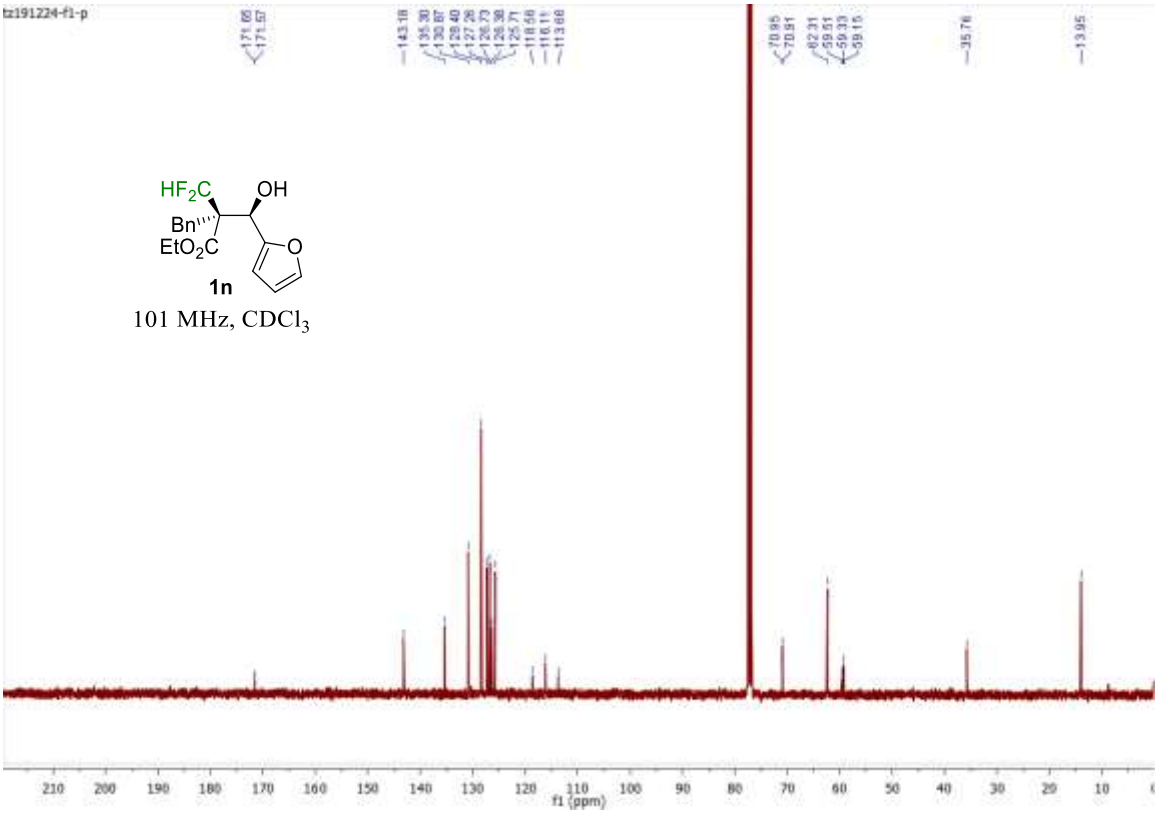
1m

376 MHz, $CDCl_3$



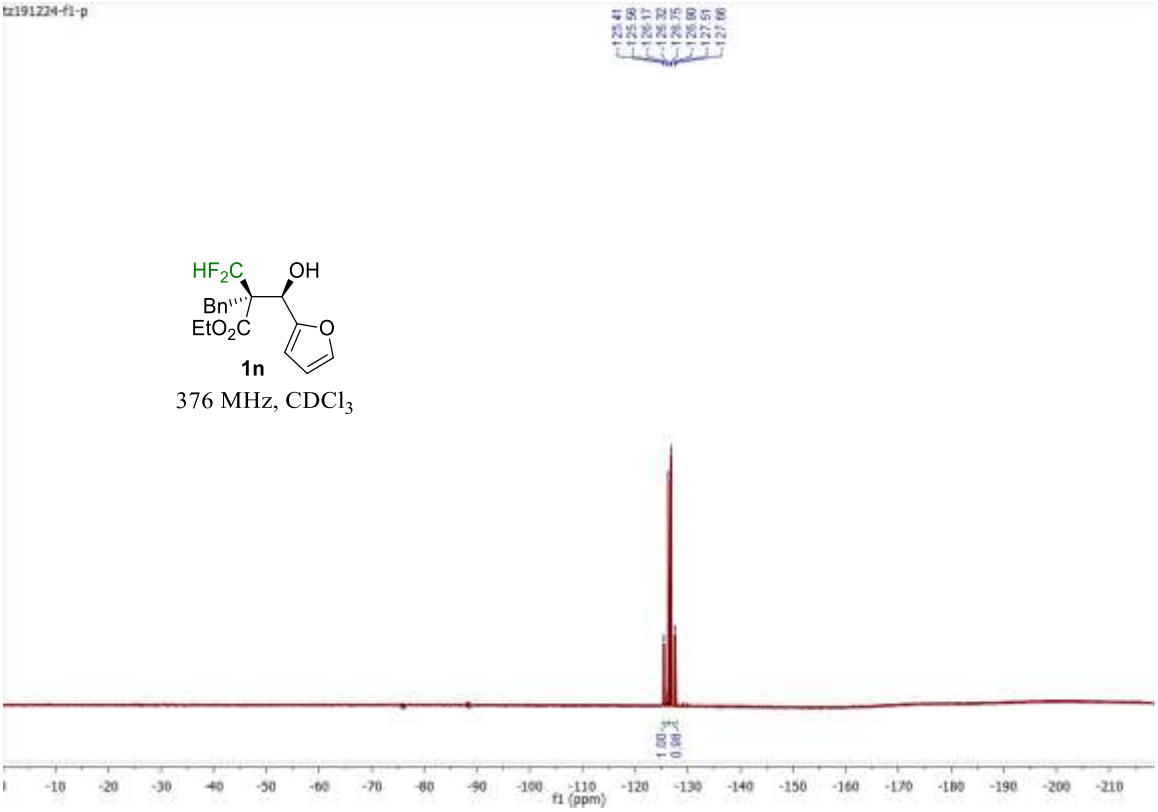
1n

400 MHz, $CDCl_3$



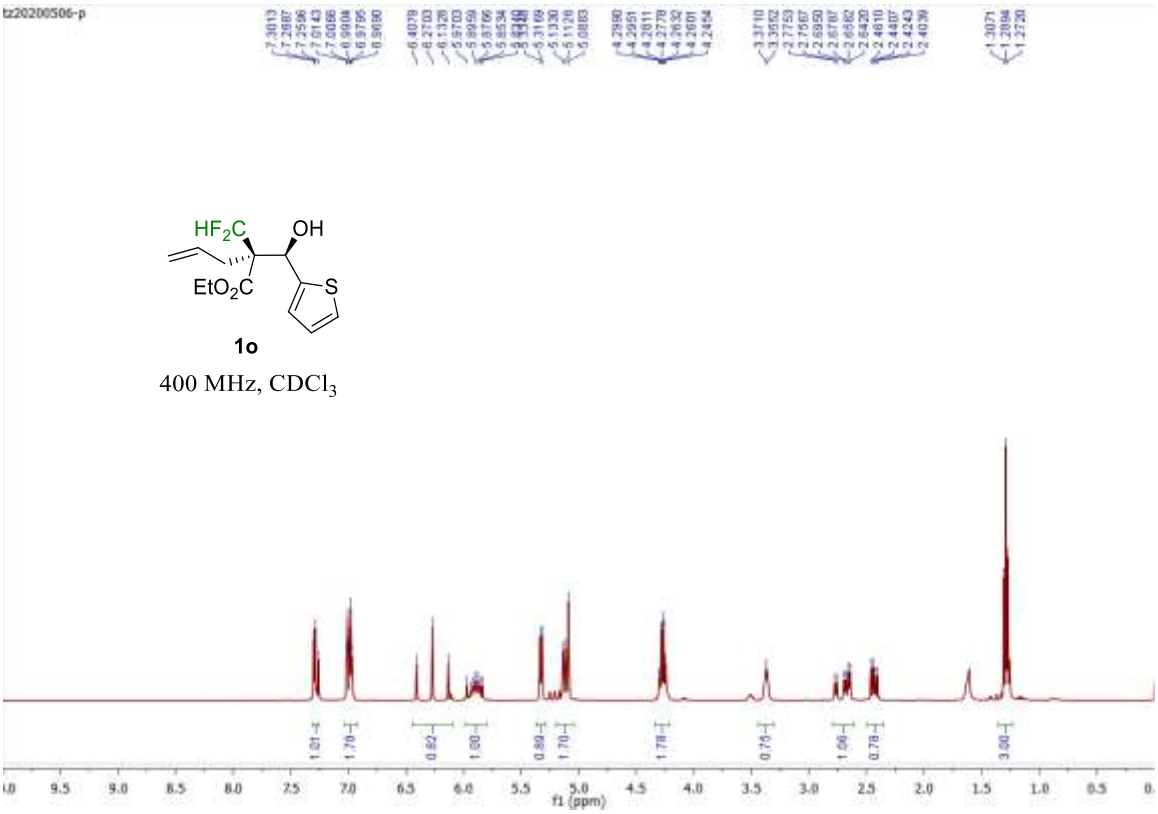
1n

101 MHz, $CDCl_3$



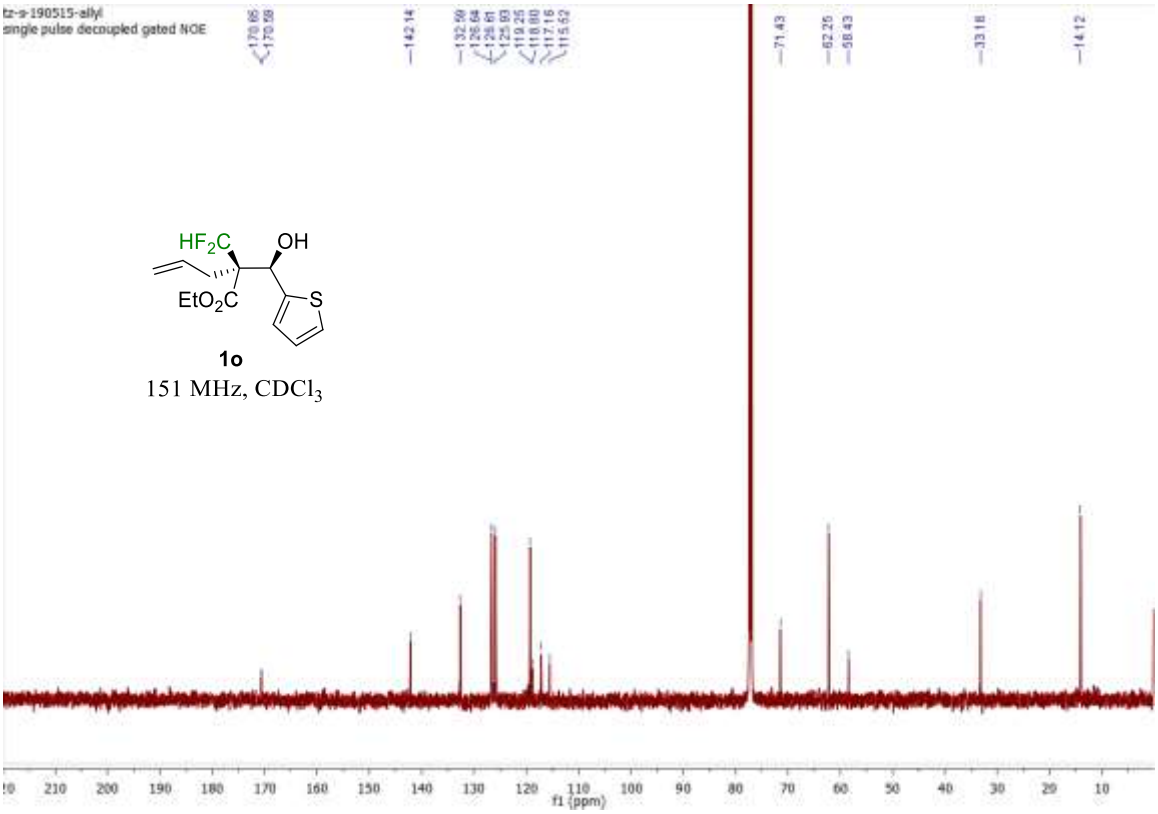
1n

376 MHz, $CDCl_3$



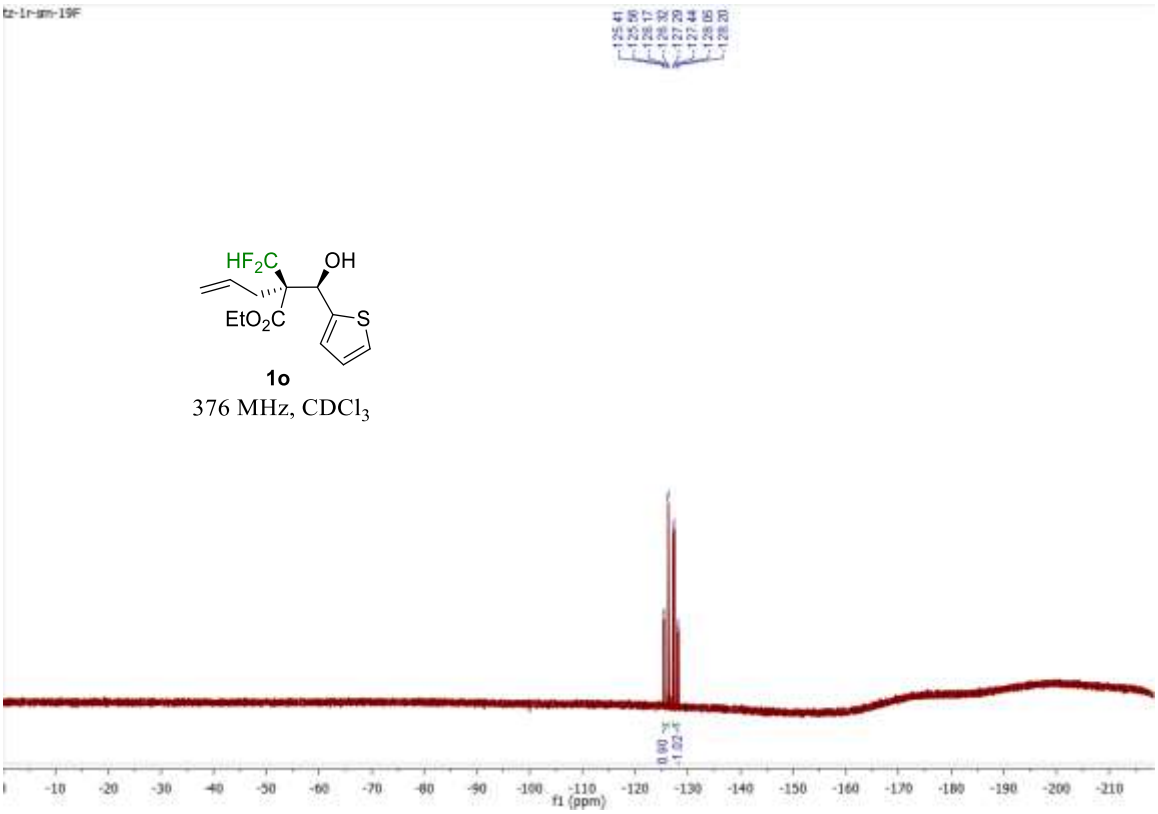
1o

400 MHz, $CDCl_3$



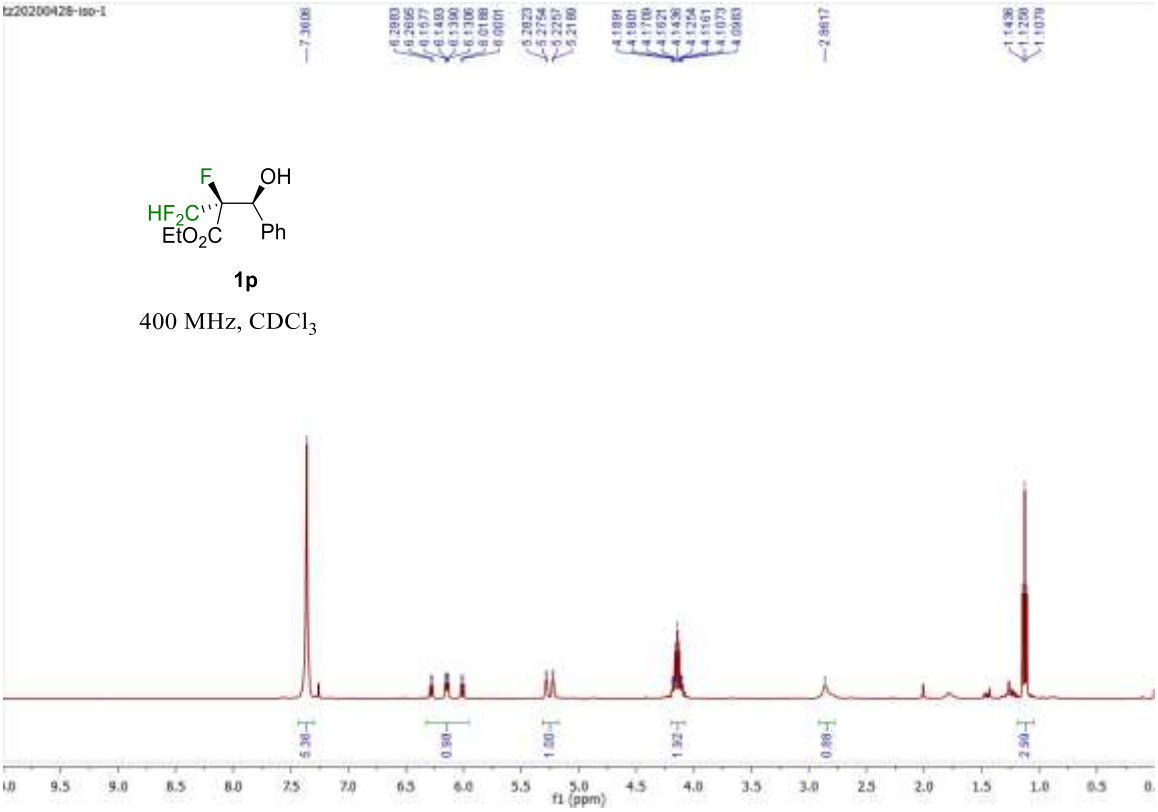
1o

151 MHz, $CDCl_3$



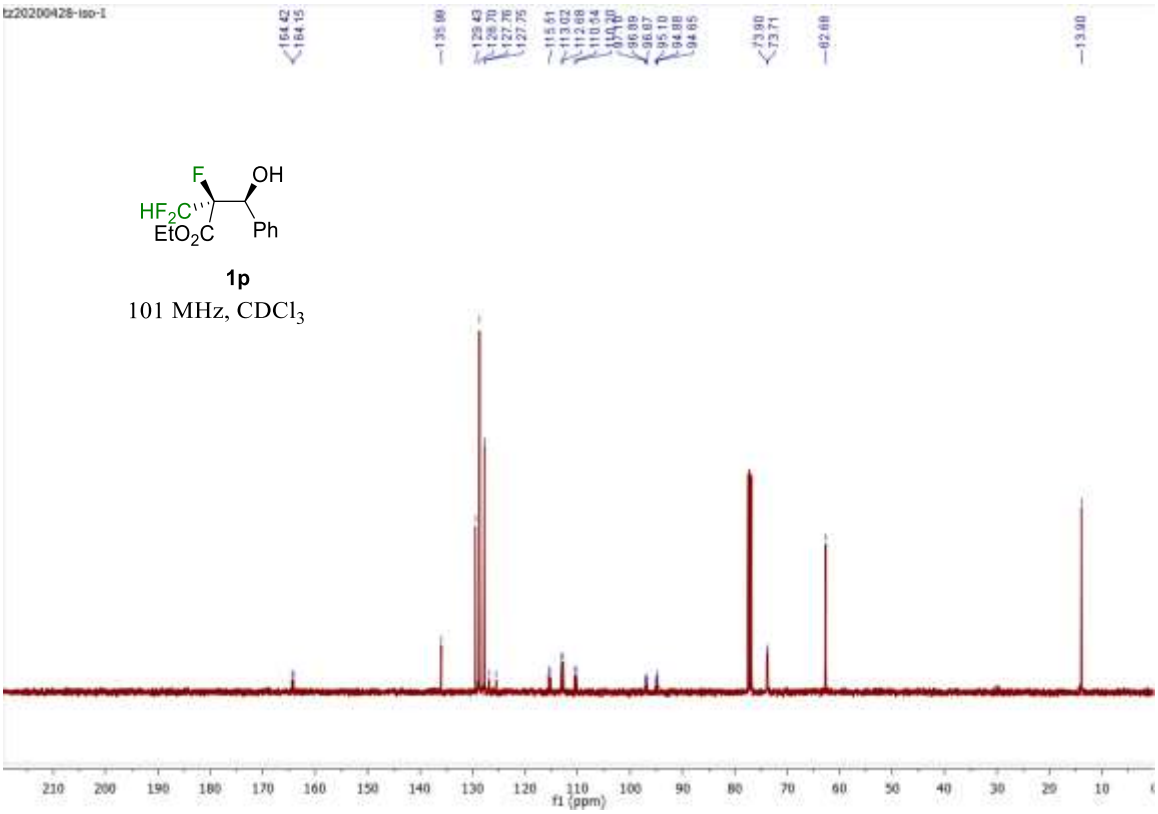
1o

376 MHz, $CDCl_3$



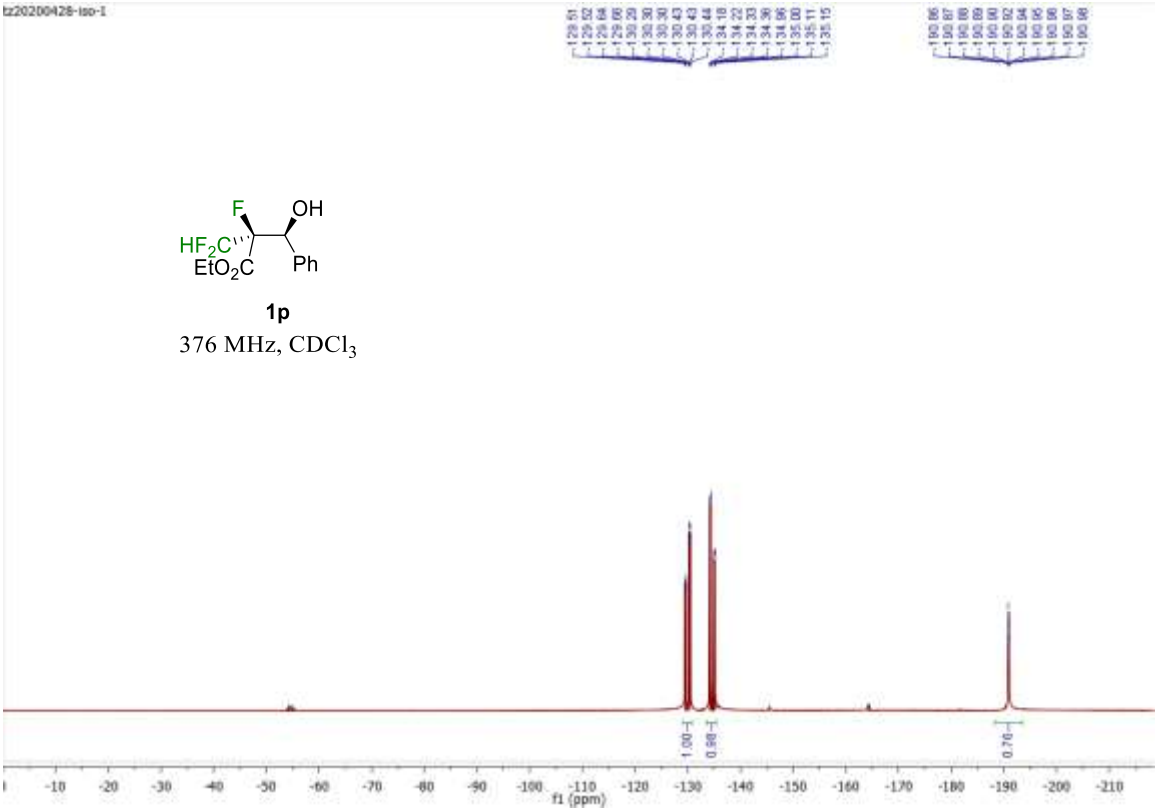
1p

400 MHz, $CDCl_3$



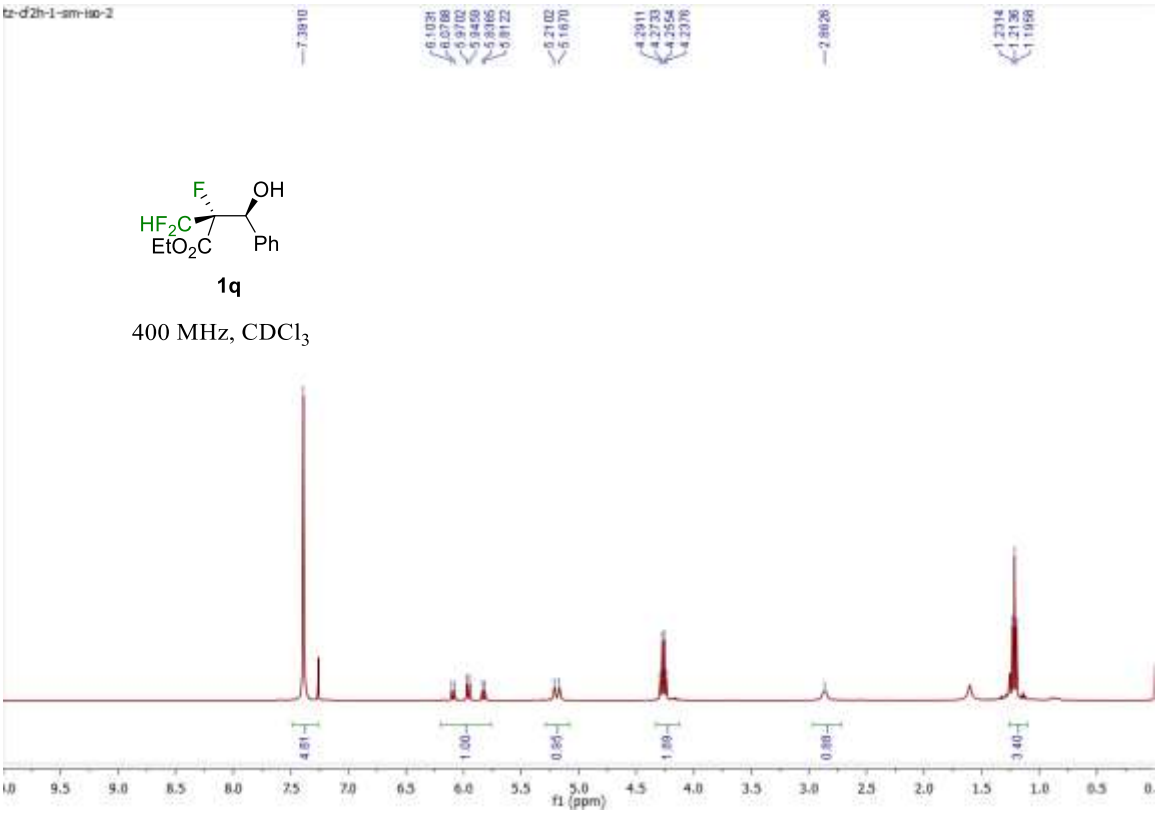
1p

101 MHz, $CDCl_3$



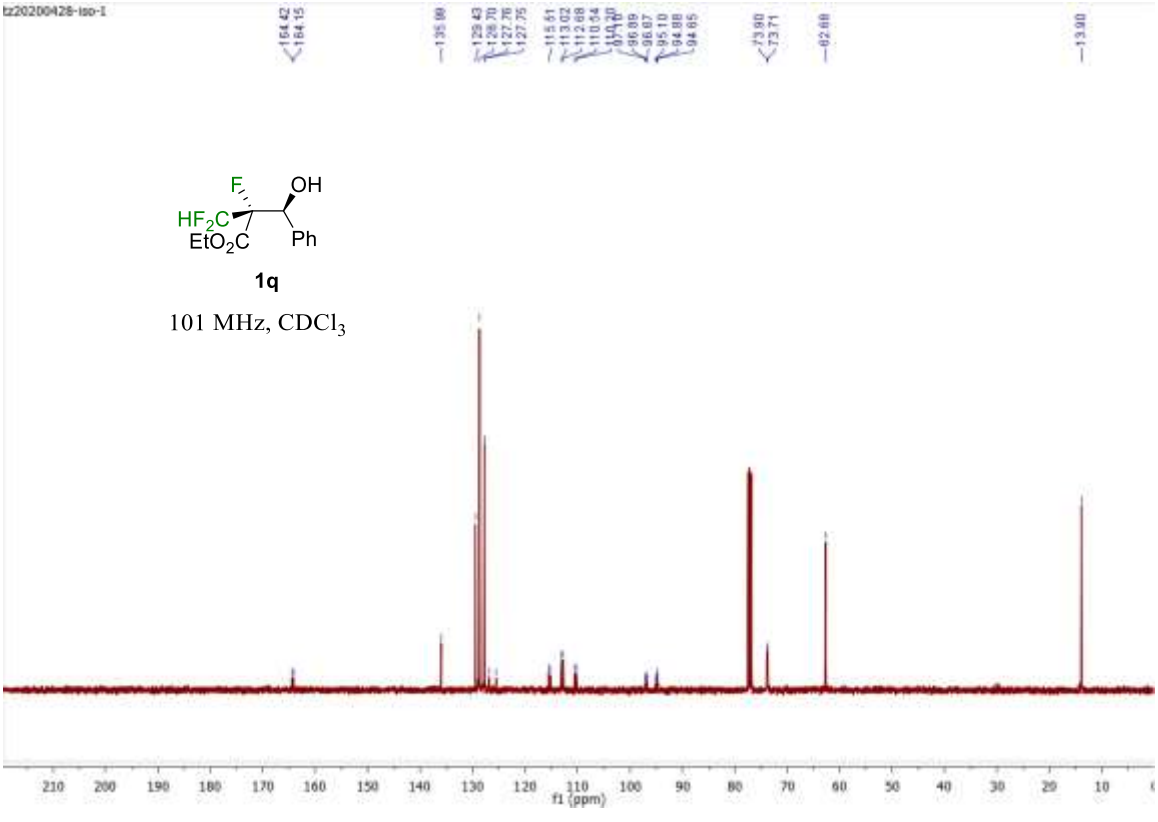
1p

376 MHz, $CDCl_3$



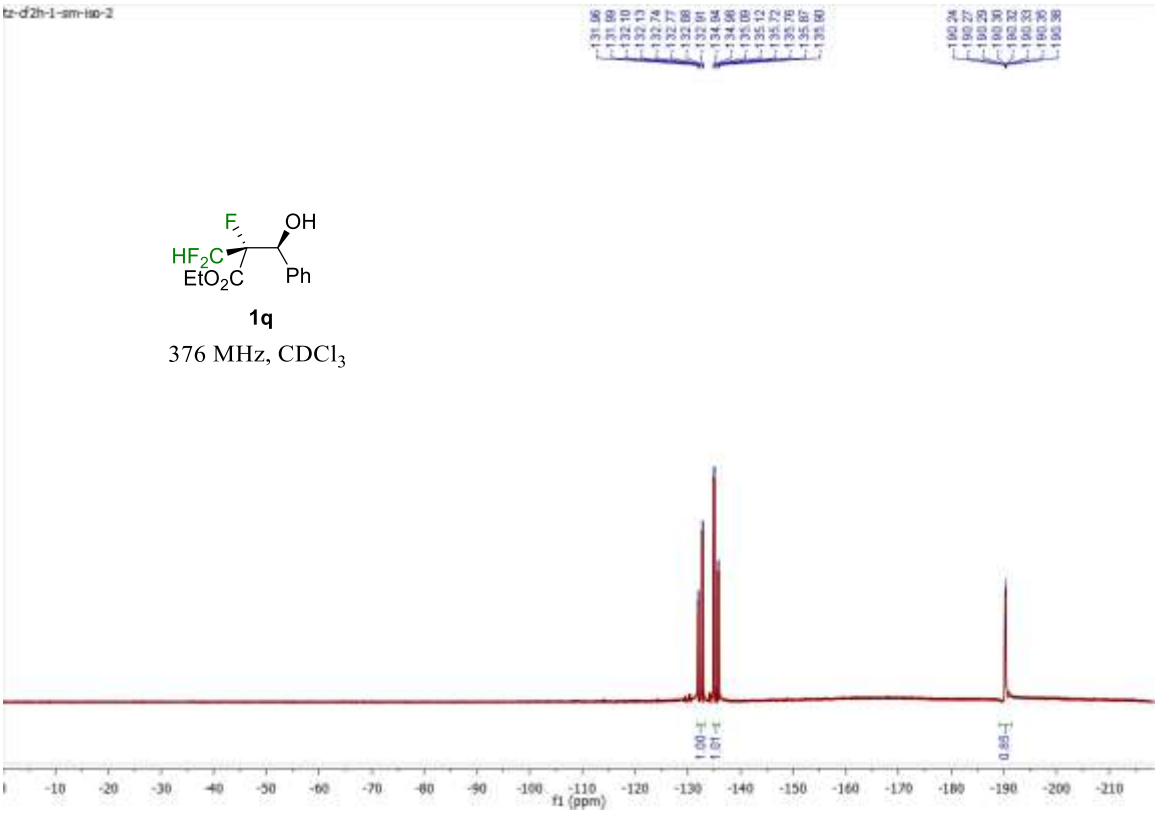
1q

400 MHz, $CDCl_3$



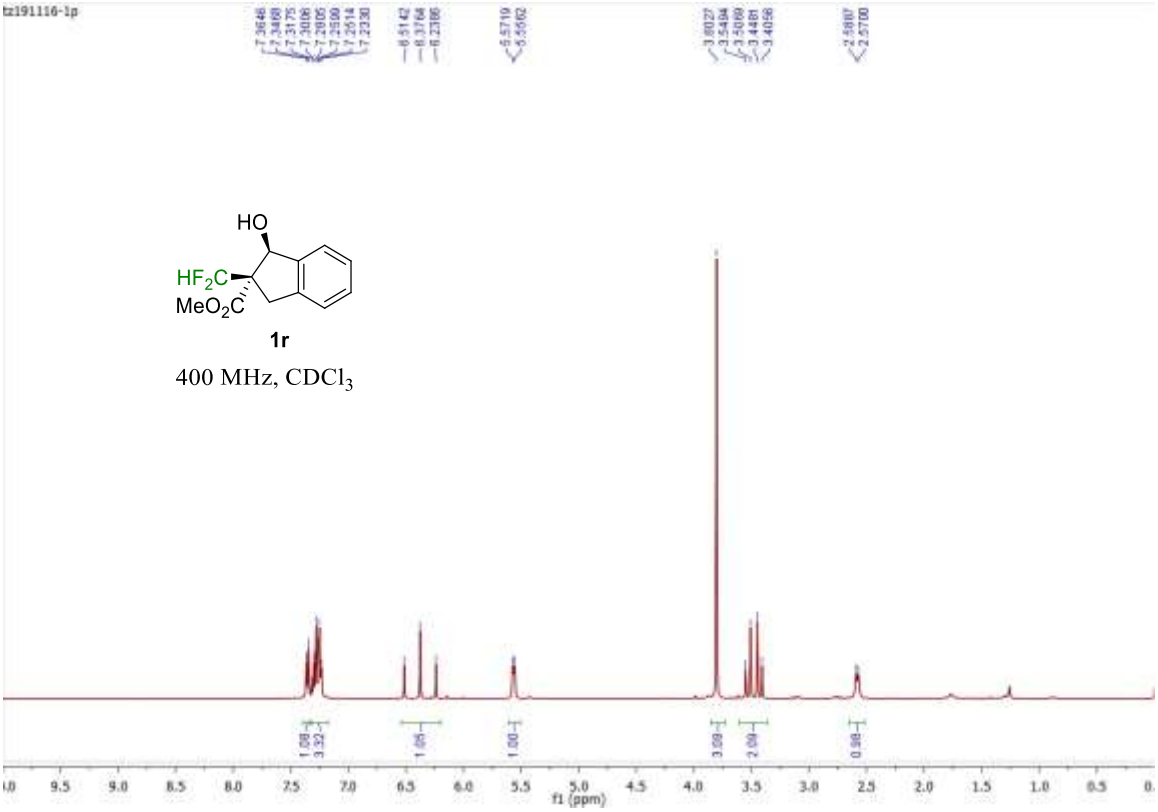
1q

101 MHz, $CDCl_3$



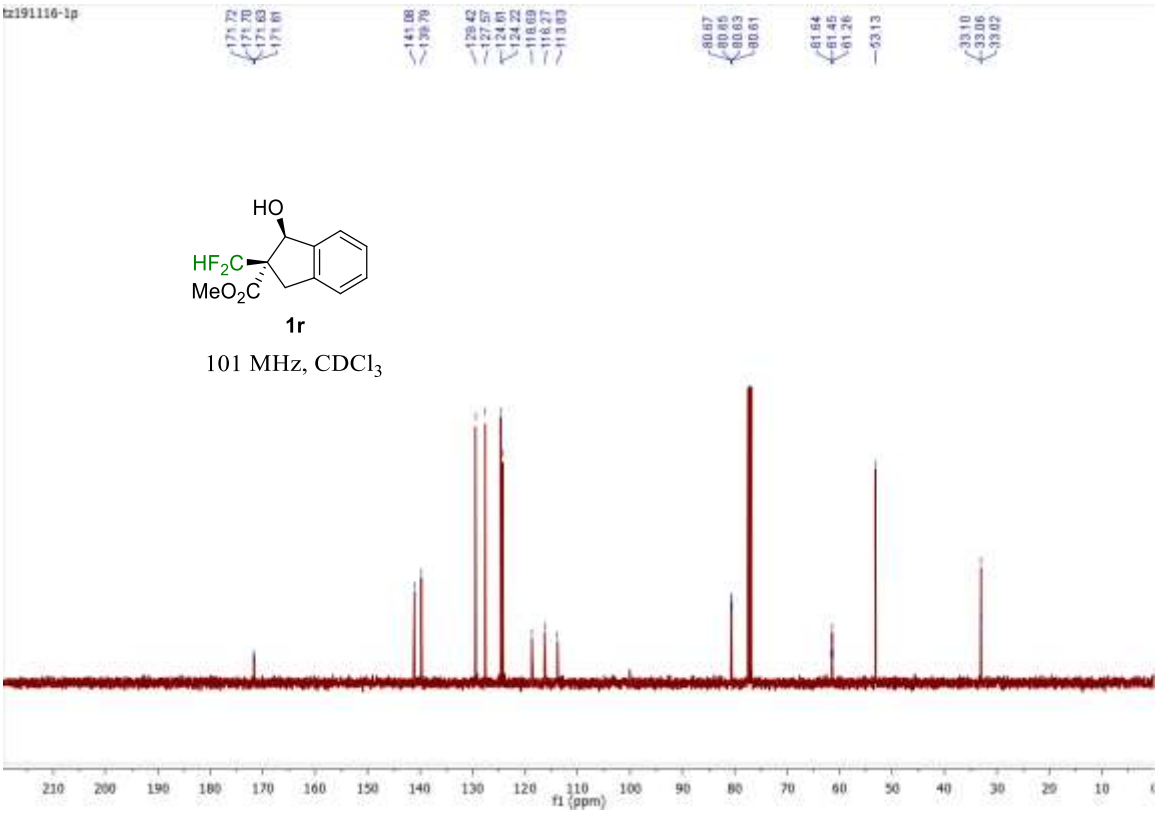
1q

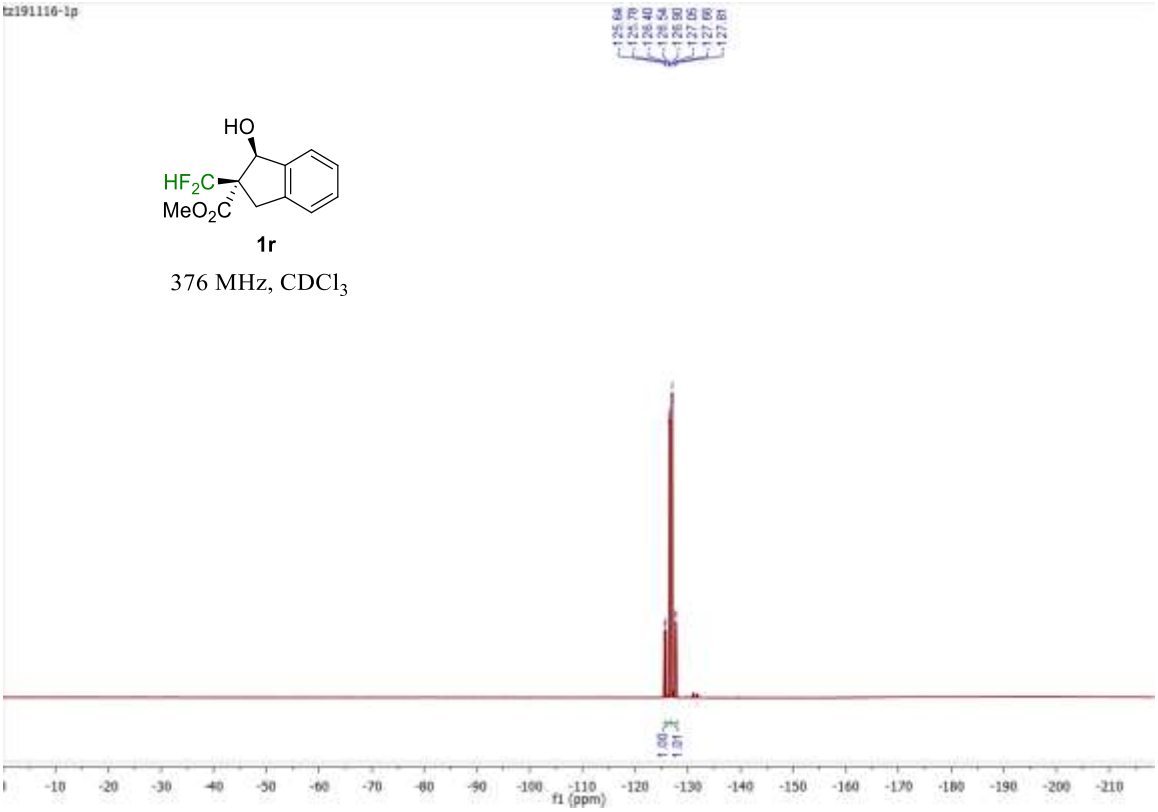
376 MHz, $CDCl_3$

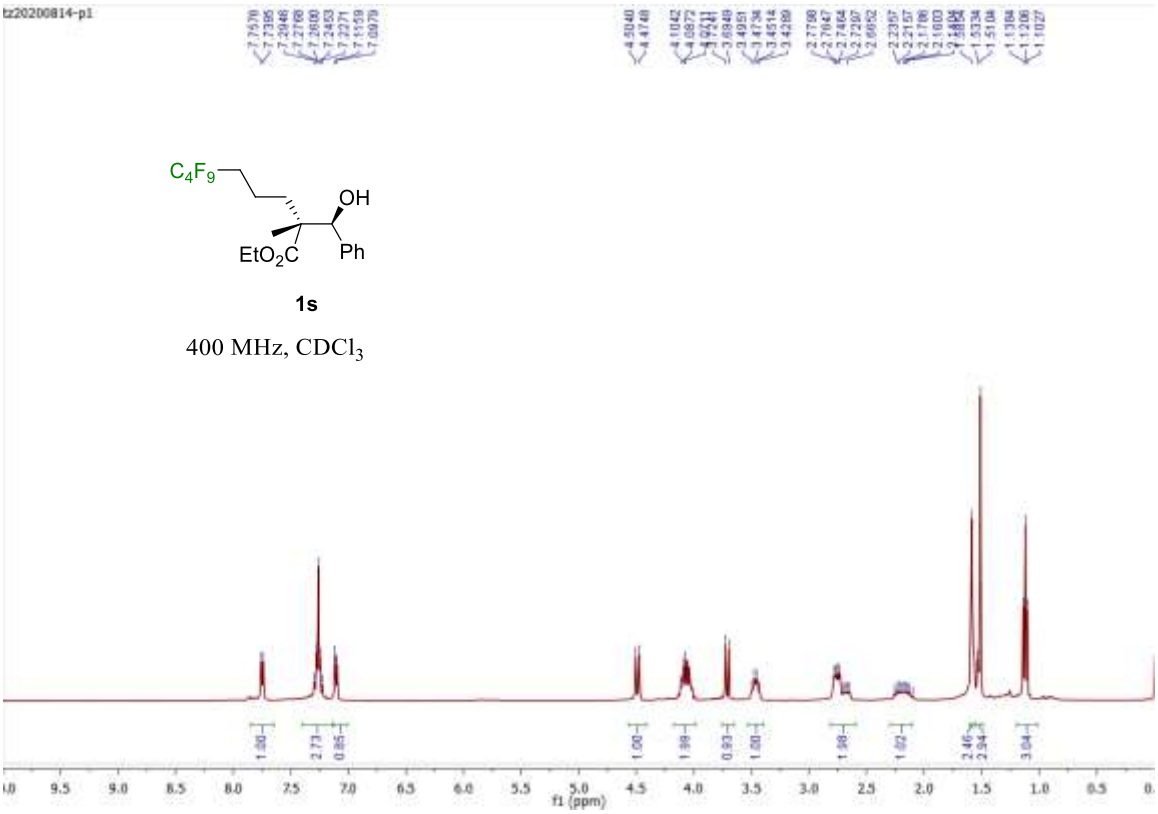


1r

400 MHz, $CDCl_3$

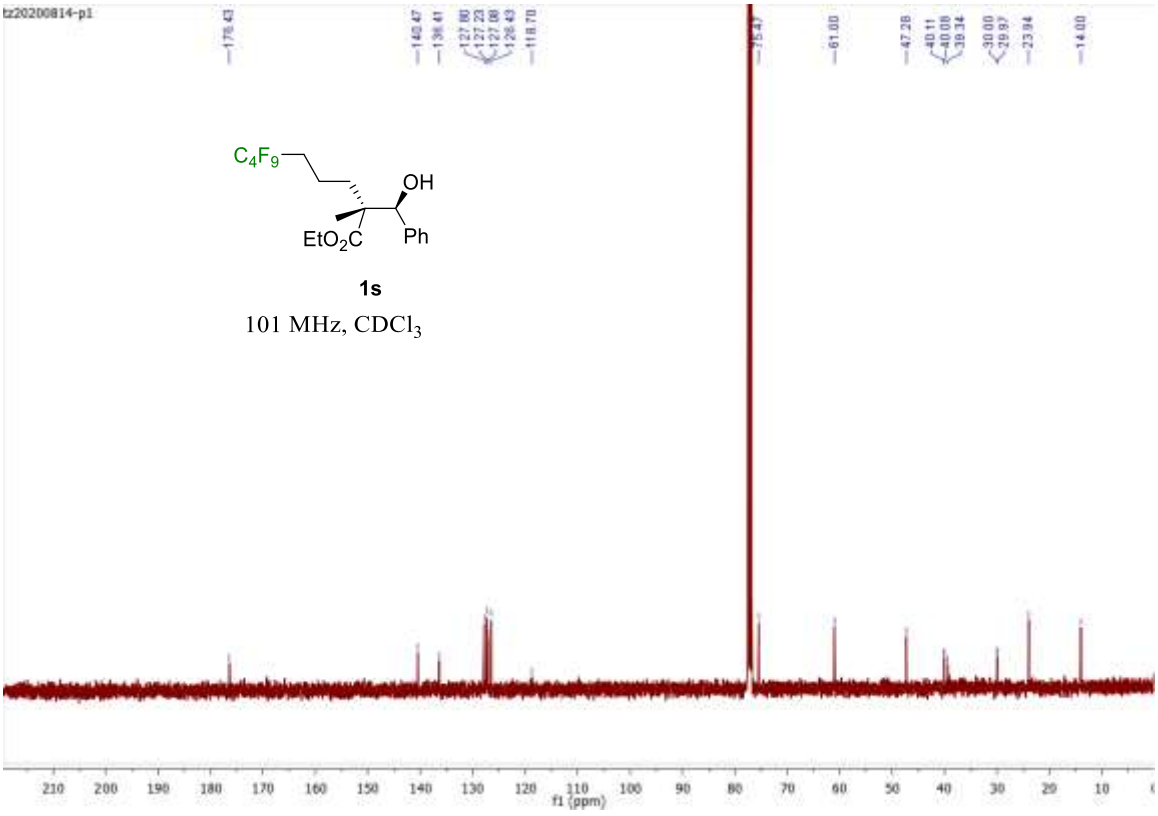

tz191116-1p
HO
HF2C
MeO2C
1r
101 MHz, CDCl3
f1 (ppm)


tz191116-1p
HO
HF2C
MeO2C
1r
376 MHz, CDCl3
f1 (ppm)



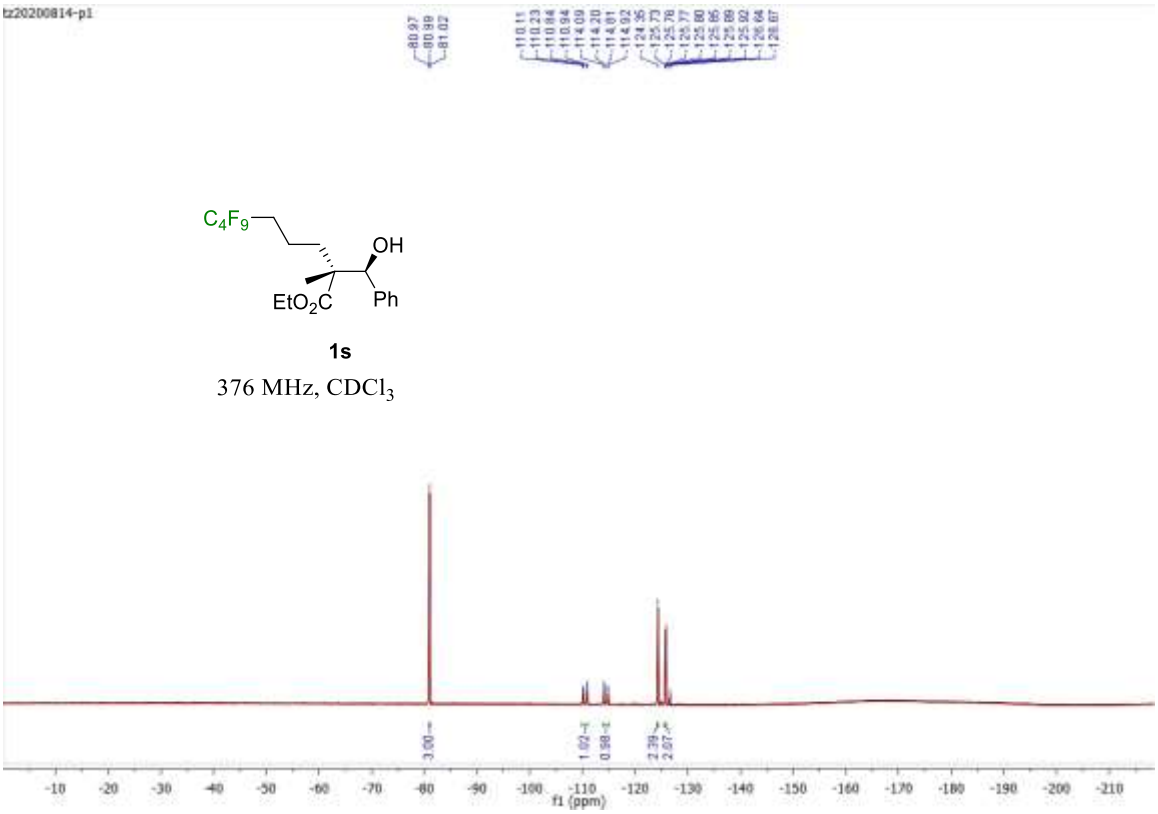
1s

400 MHz, $CDCl_3$



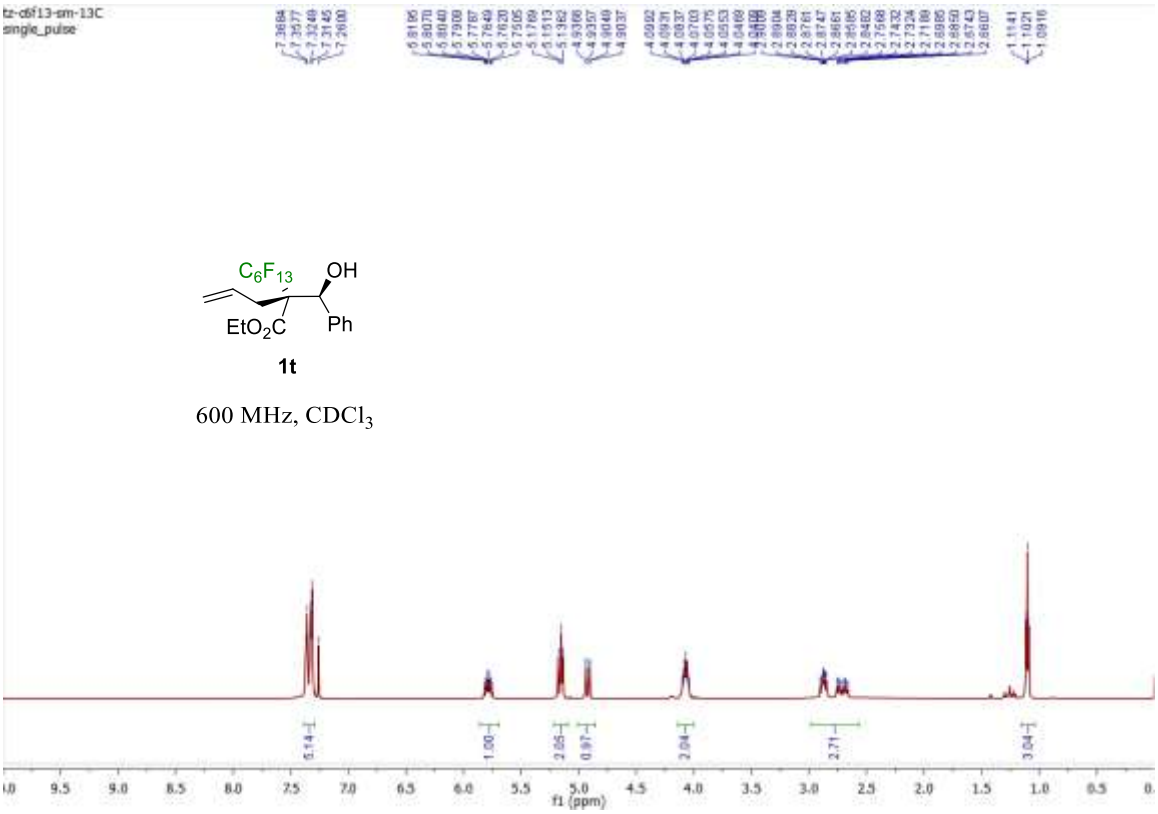
1s

101 MHz, $CDCl_3$



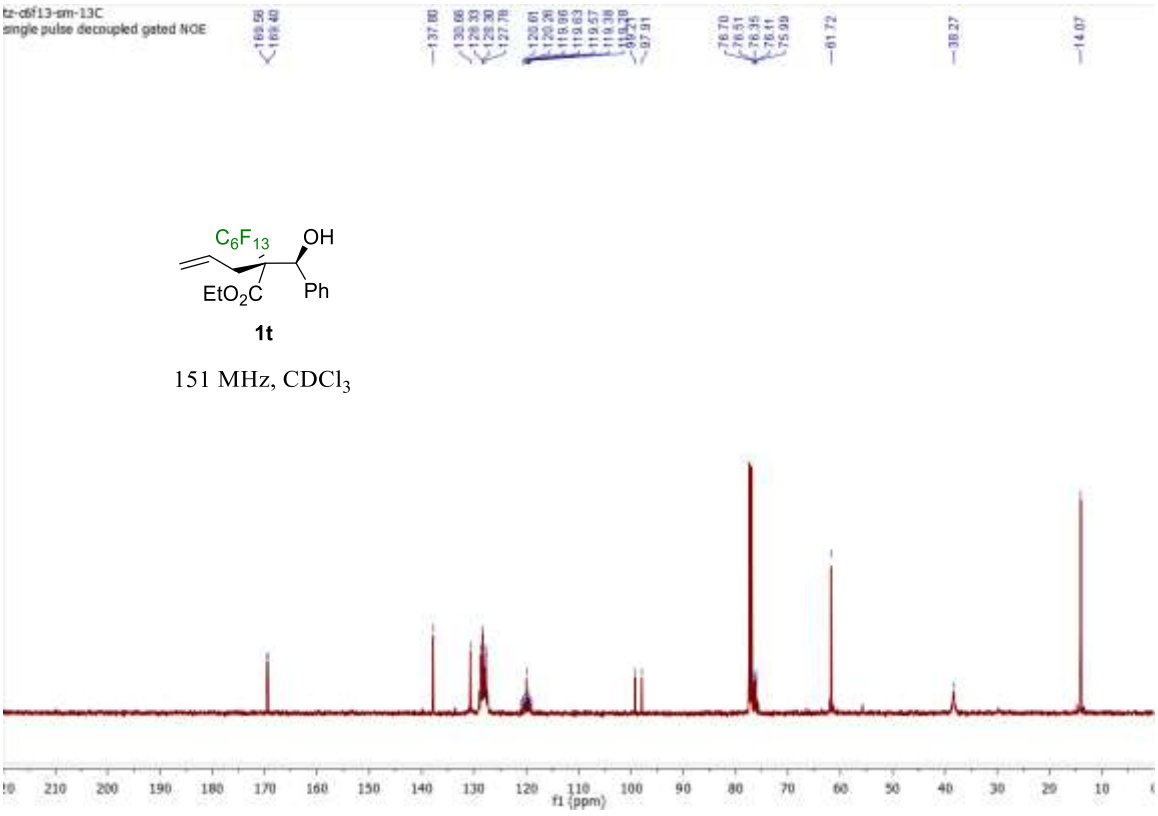
1s

376 MHz, $CDCl_3$



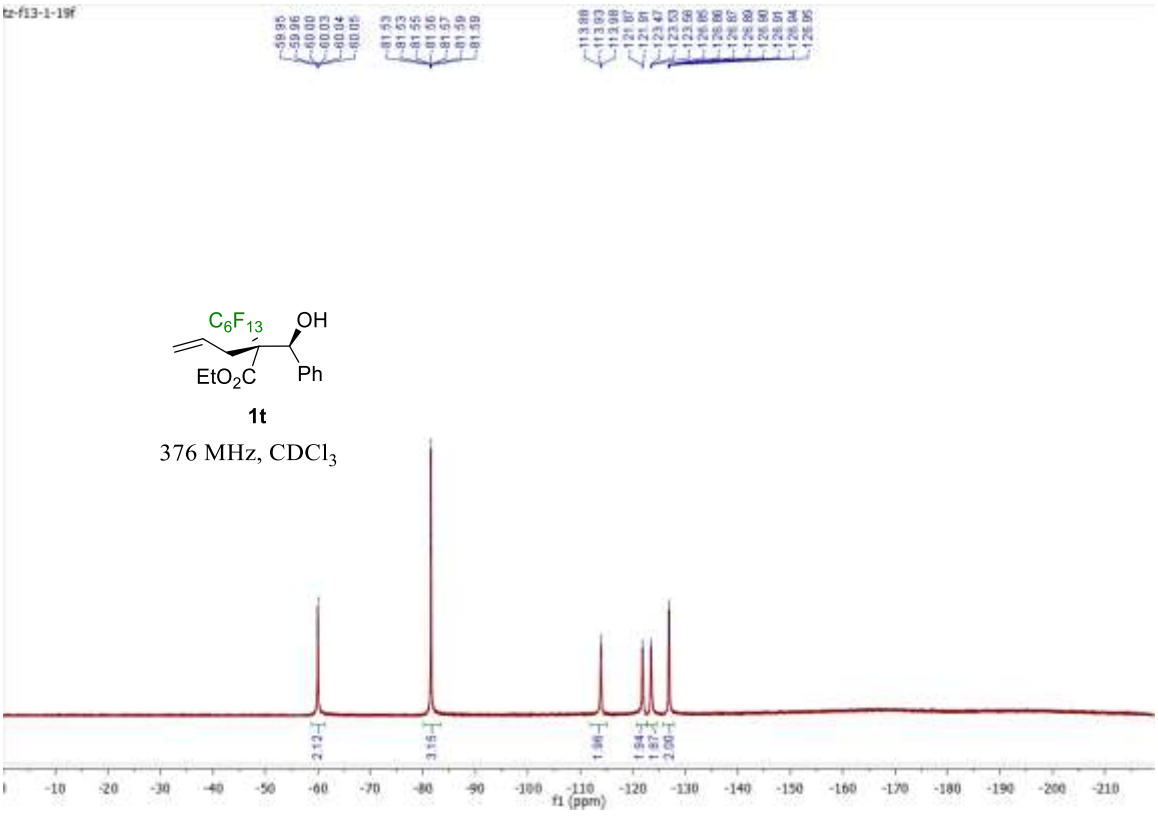
1t

600 MHz, $CDCl_3$



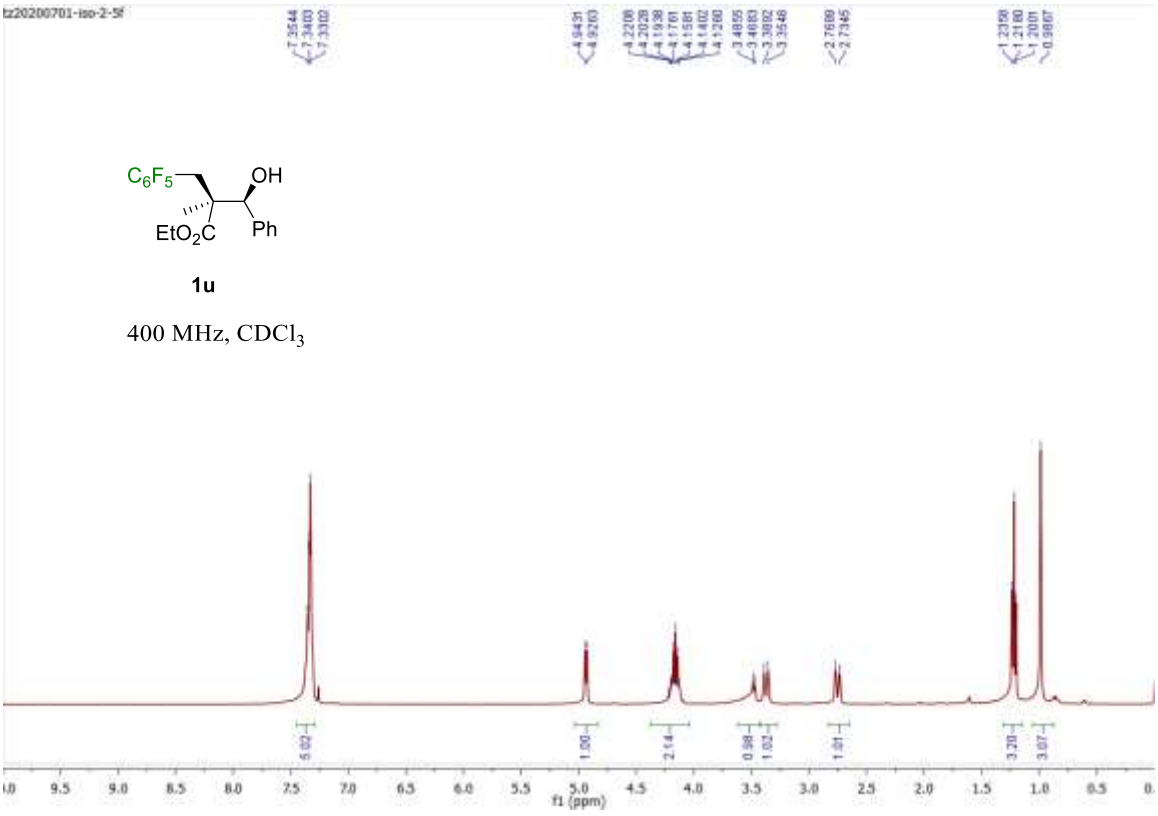
1t

151 MHz, $CDCl_3$



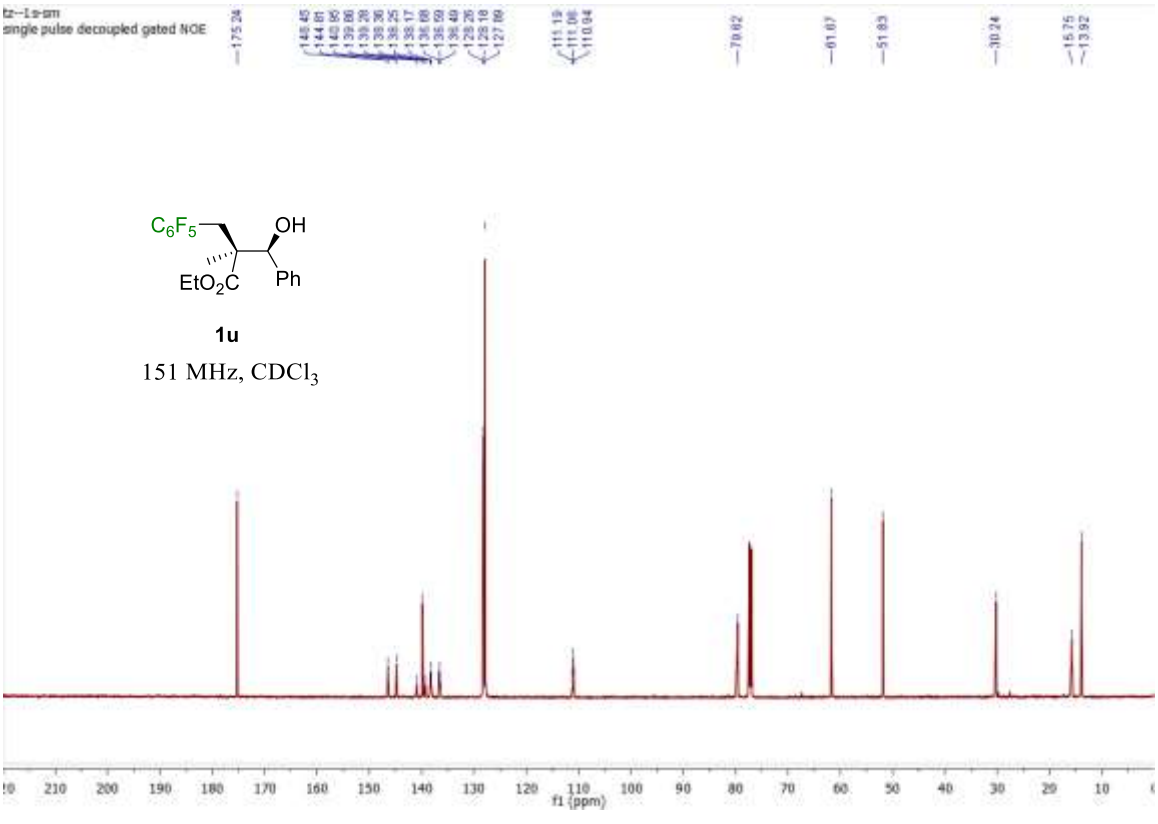
1t

376 MHz, $CDCl_3$



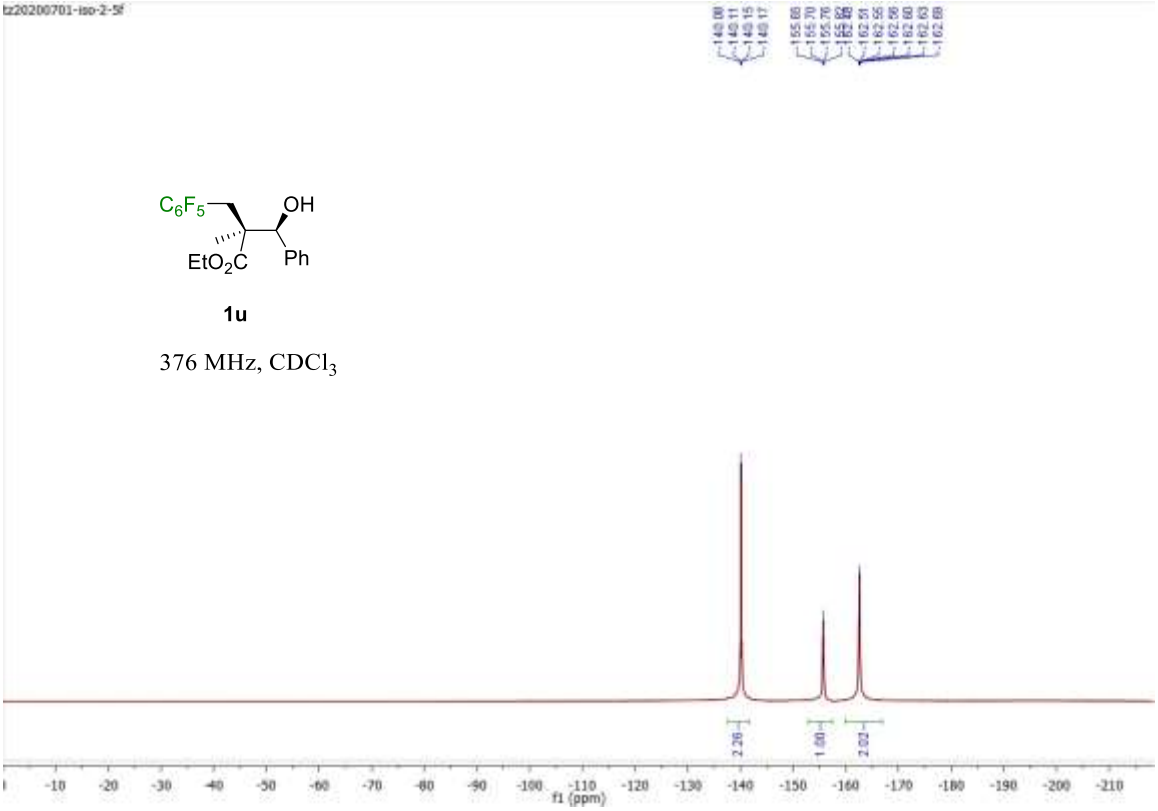
1u

400 MHz, $CDCl_3$



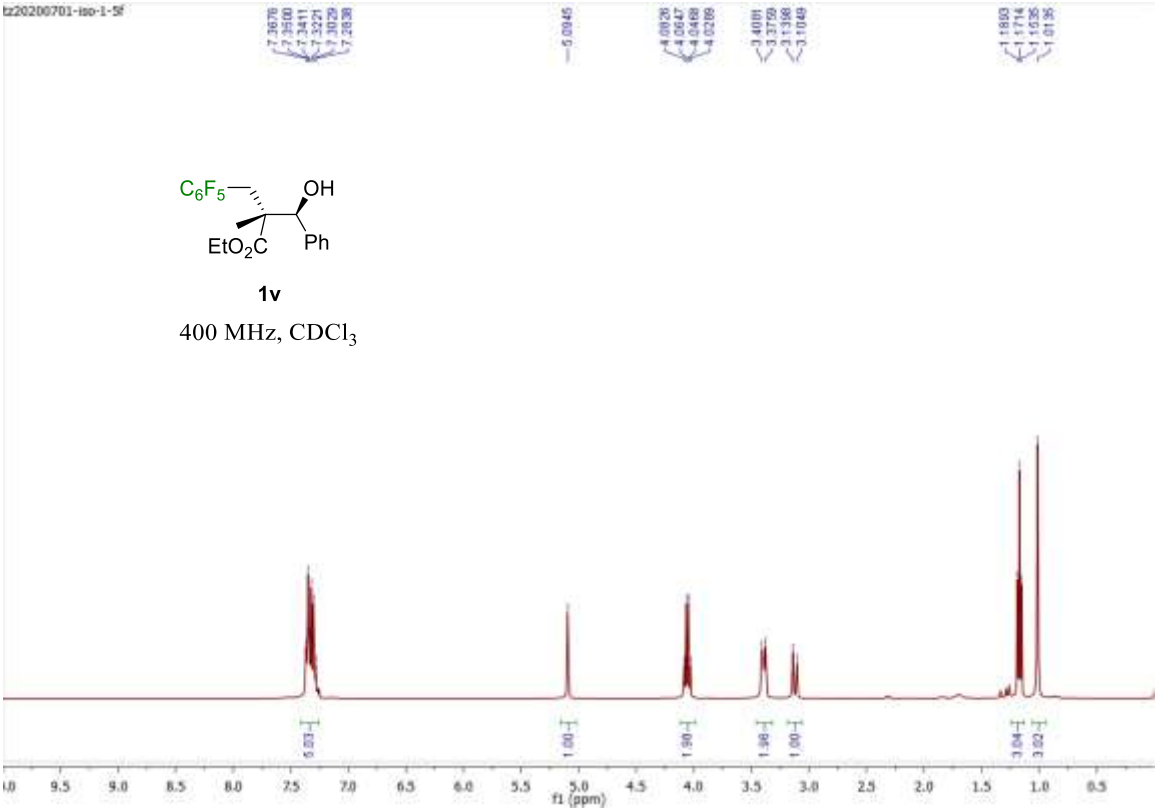
1u

151 MHz, $CDCl_3$



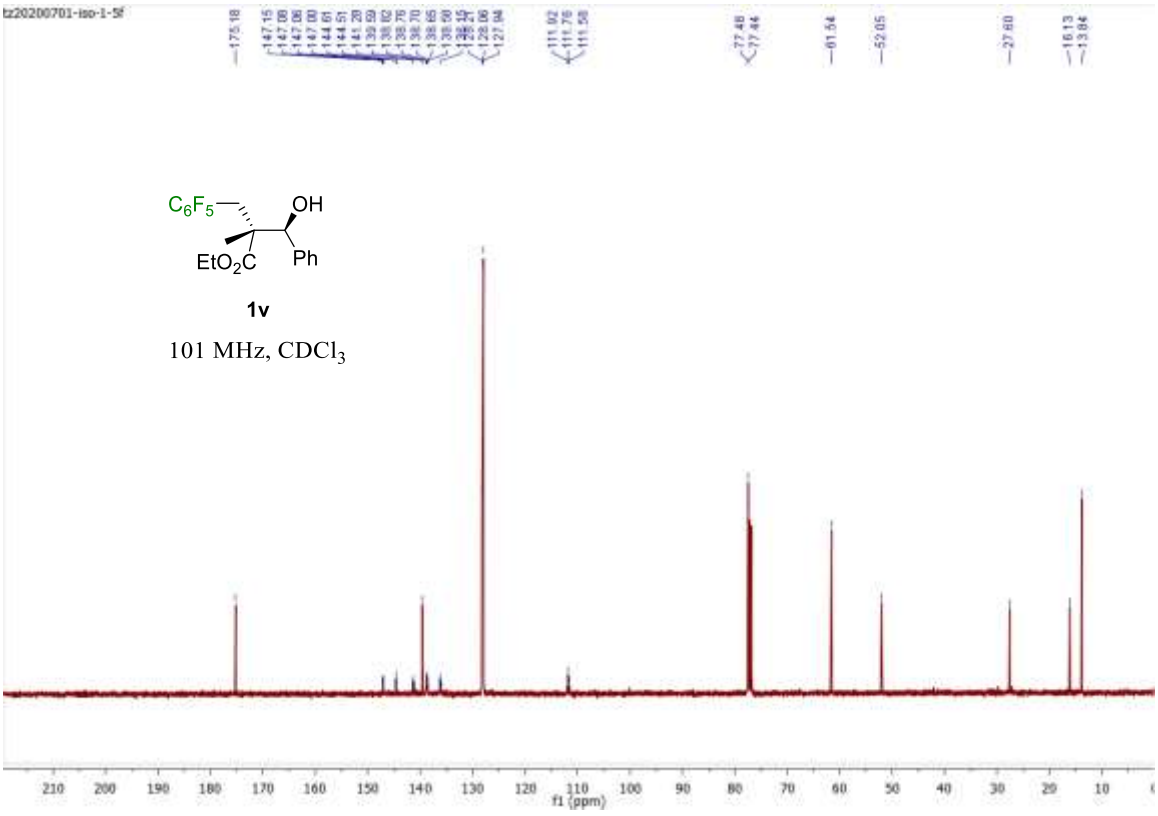
1u

376 MHz, $CDCl_3$



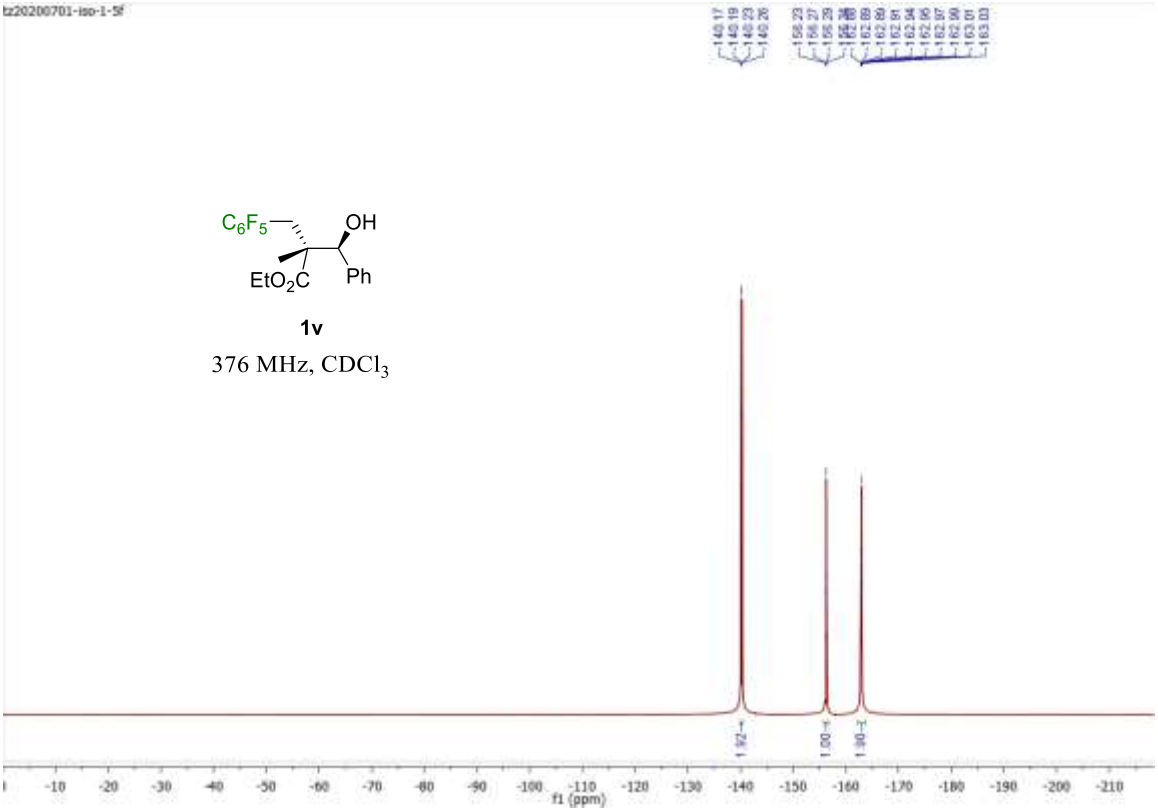
1v

400 MHz, $CDCl_3$



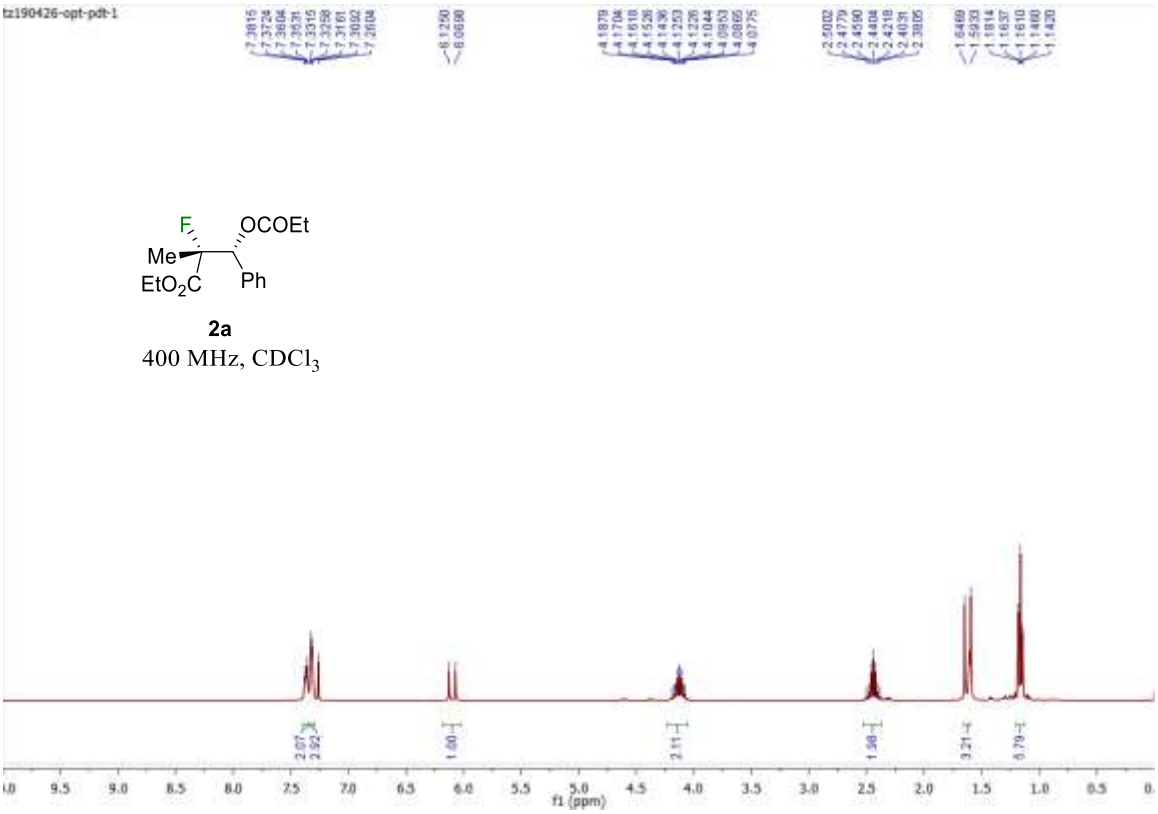
1v

101 MHz, $CDCl_3$



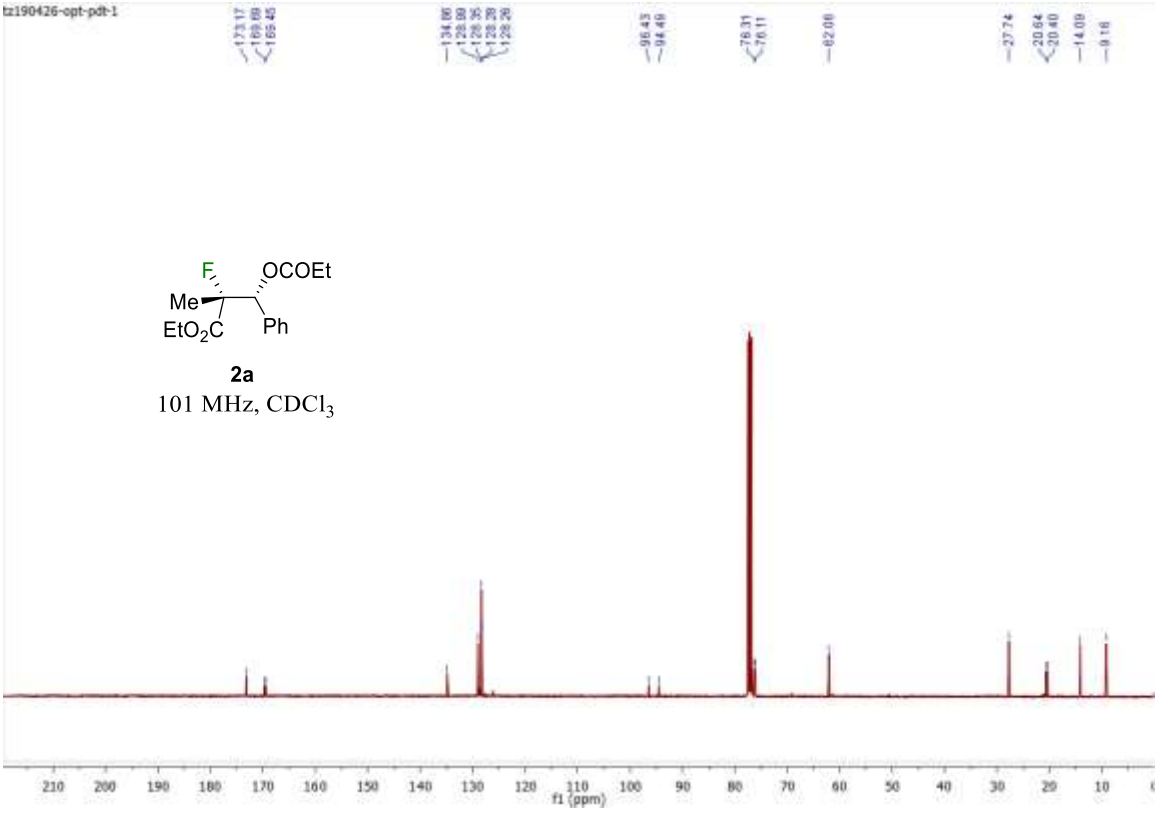
1v

376 MHz, $CDCl_3$



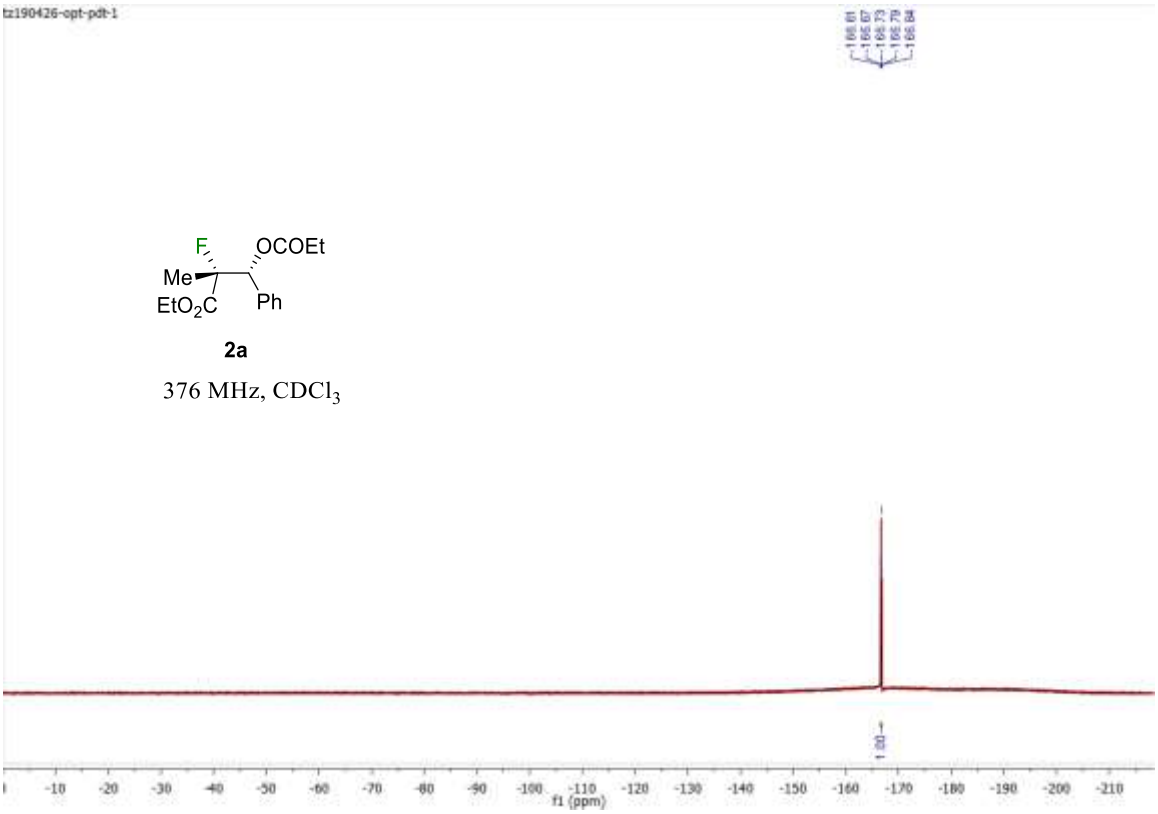
2a

400 MHz, $CDCl_3$



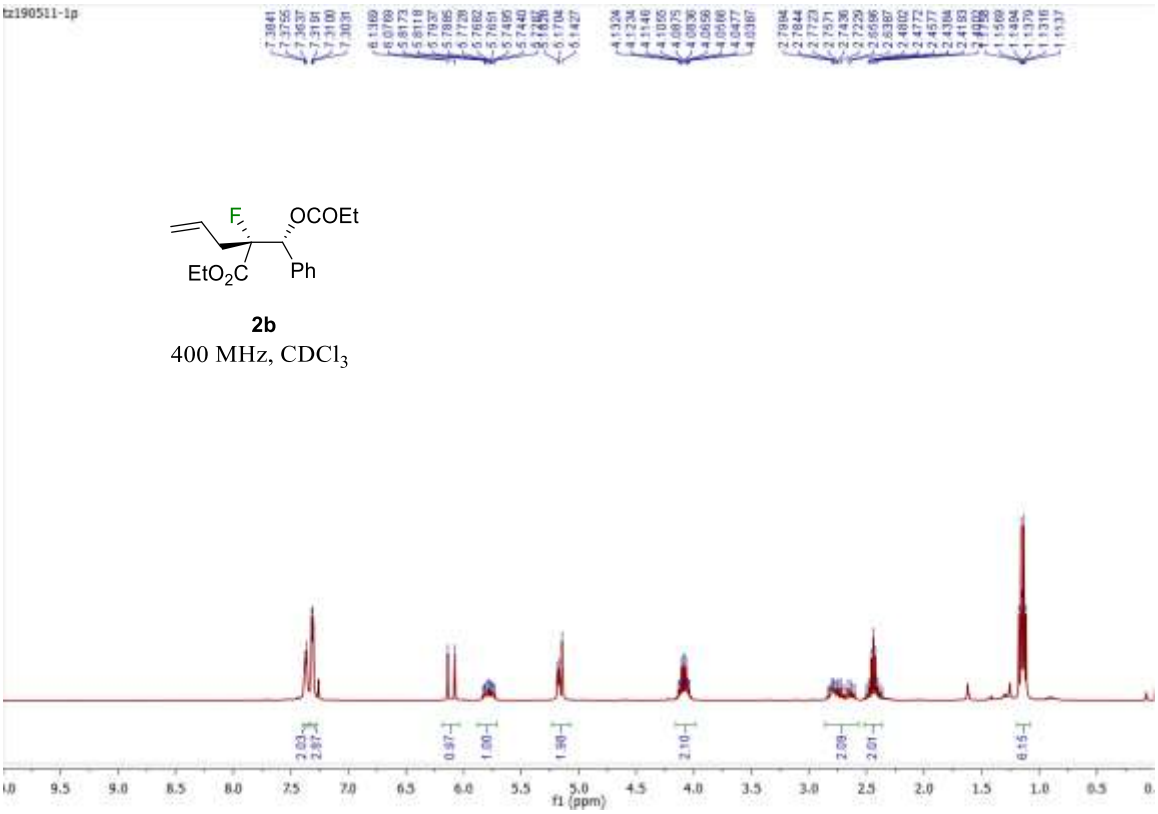
2a

101 MHz, $CDCl_3$



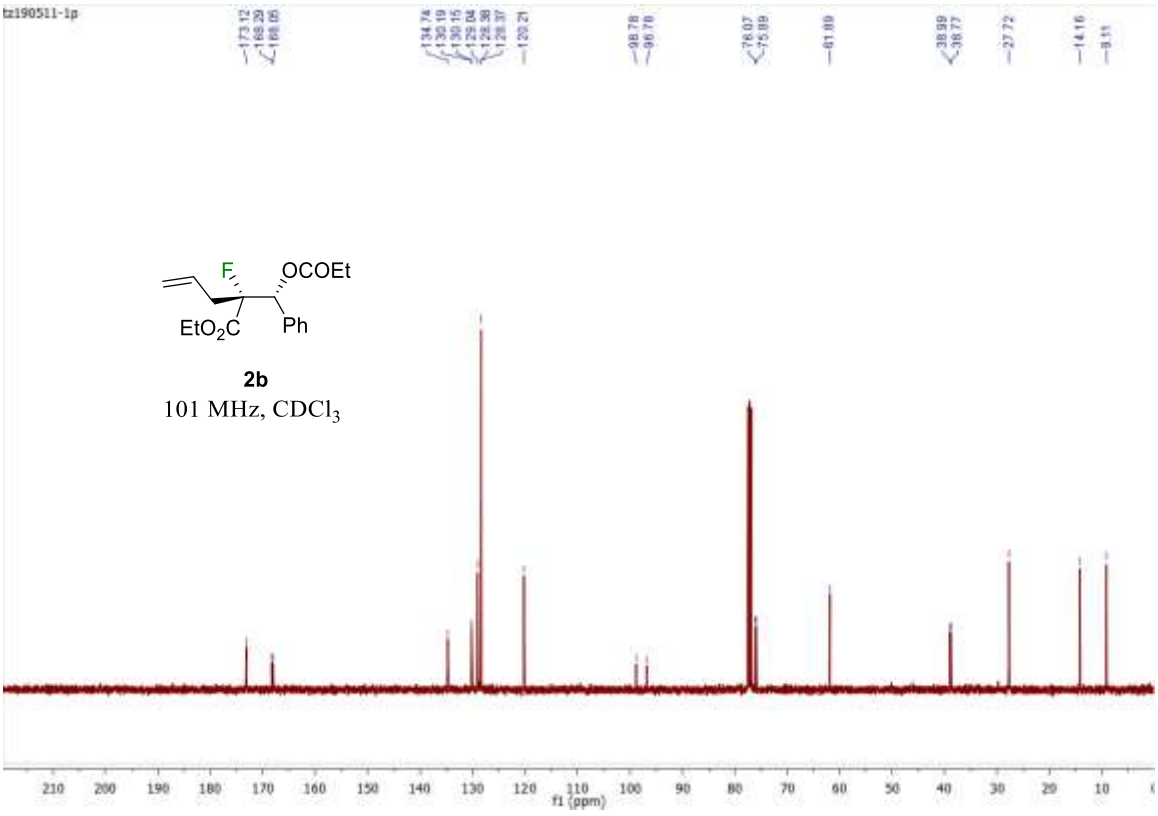
2a

376 MHz, $CDCl_3$



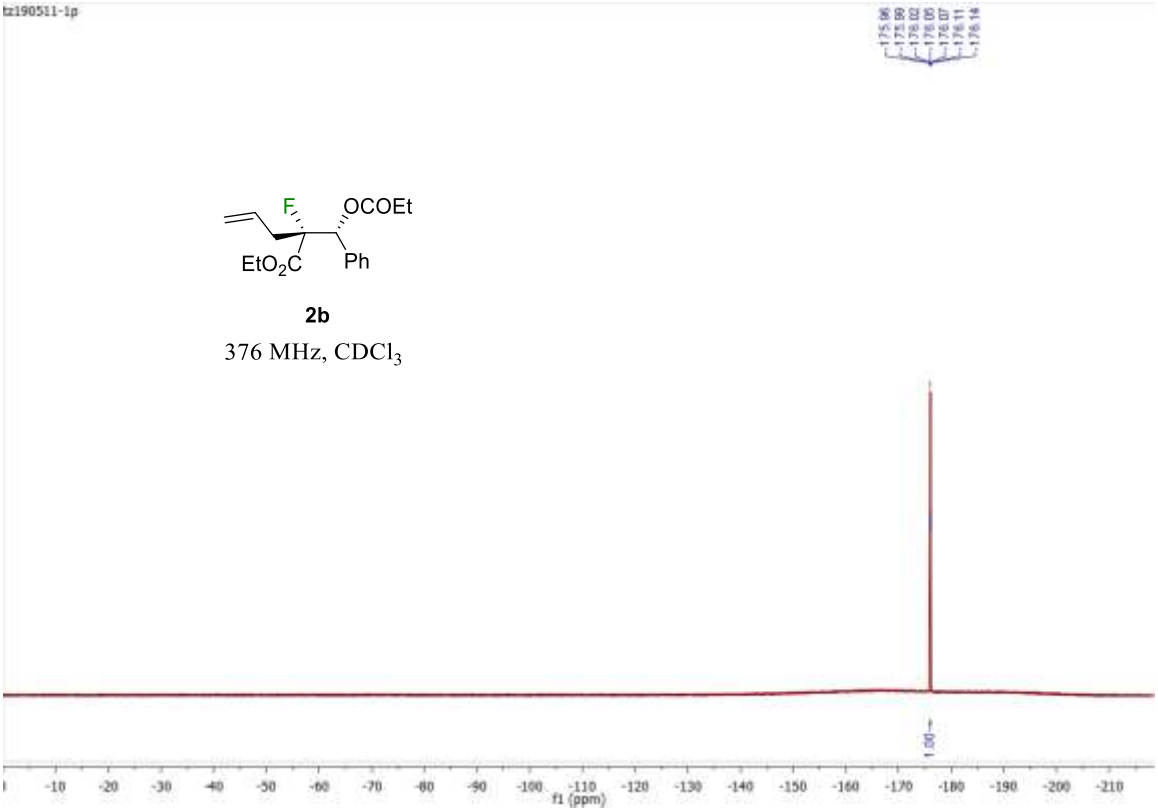
2b

400 MHz, $CDCl_3$



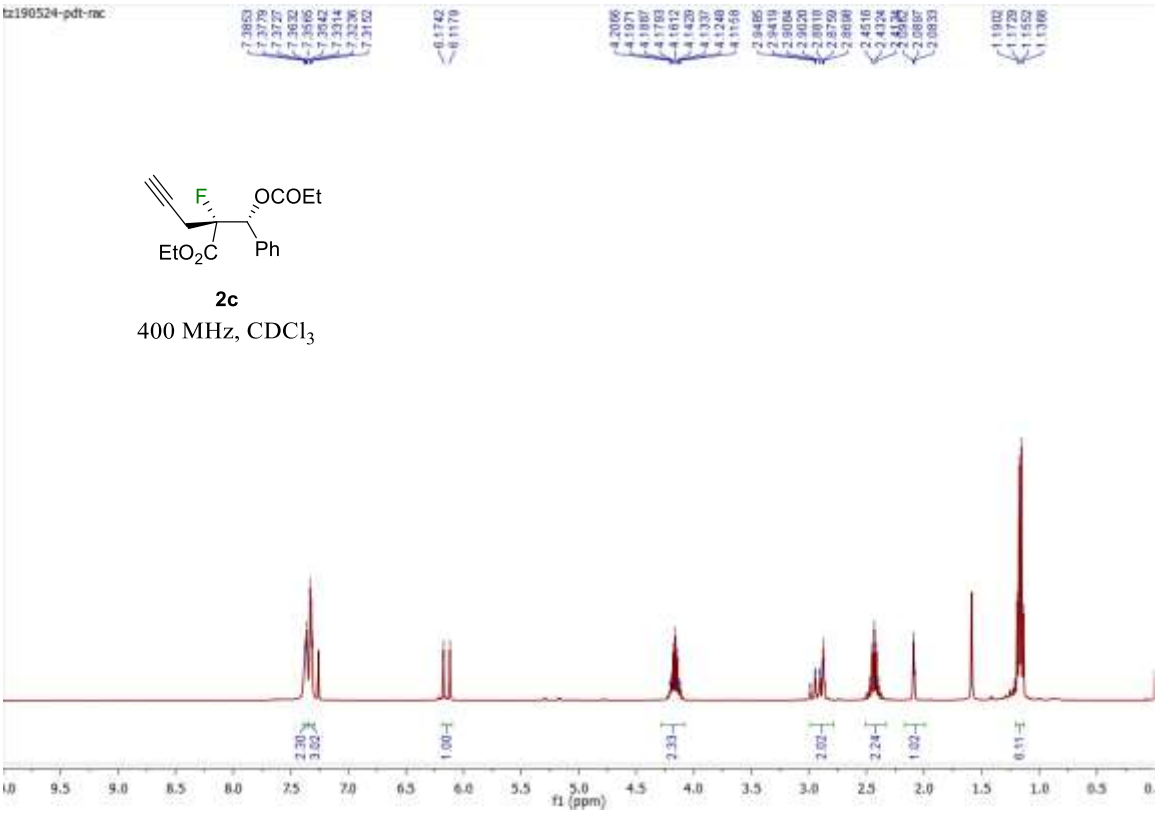
2b

101 MHz, $CDCl_3$



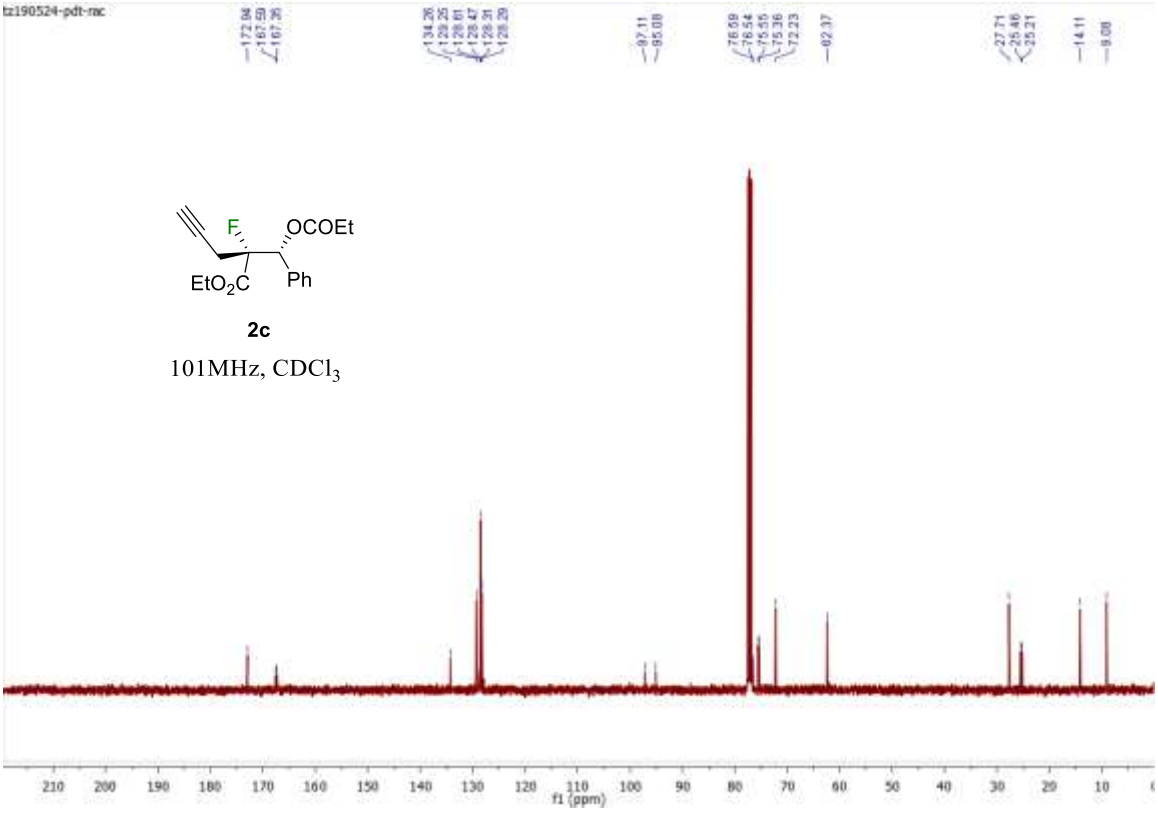
2b

376 MHz, $CDCl_3$



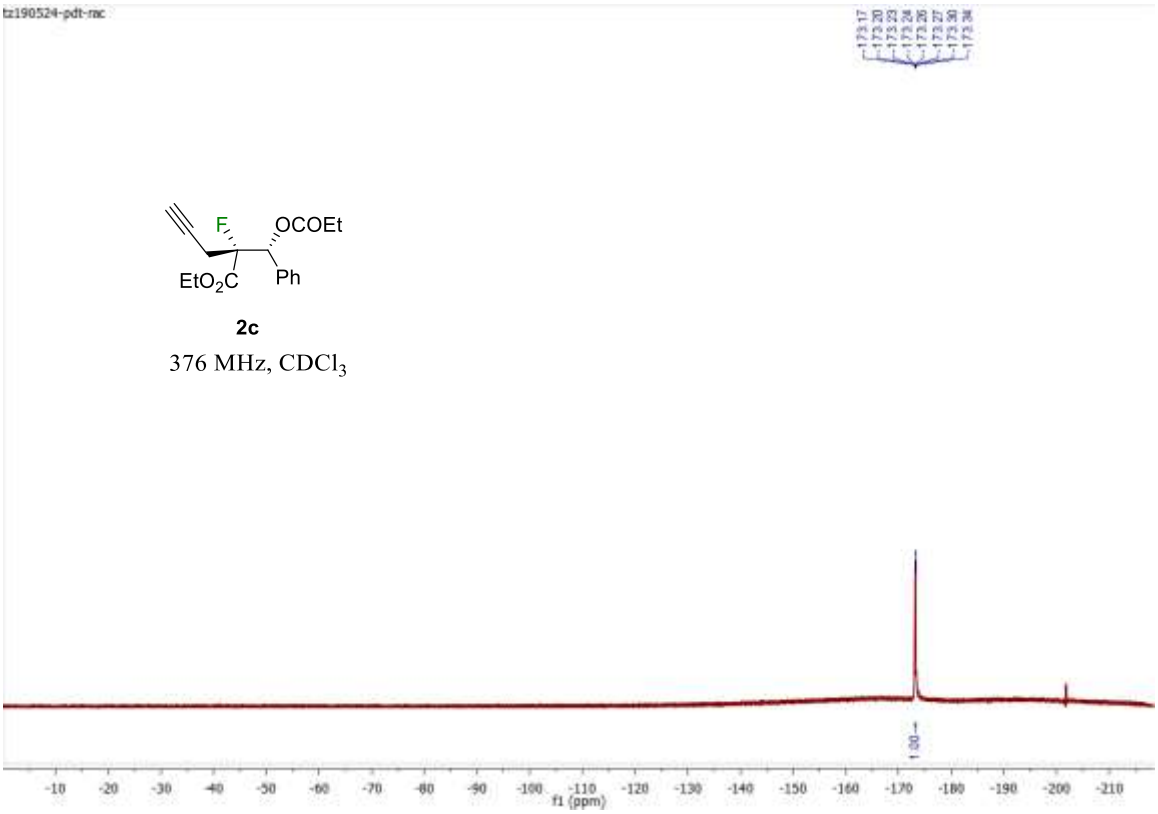
2c

400 MHz, $CDCl_3$



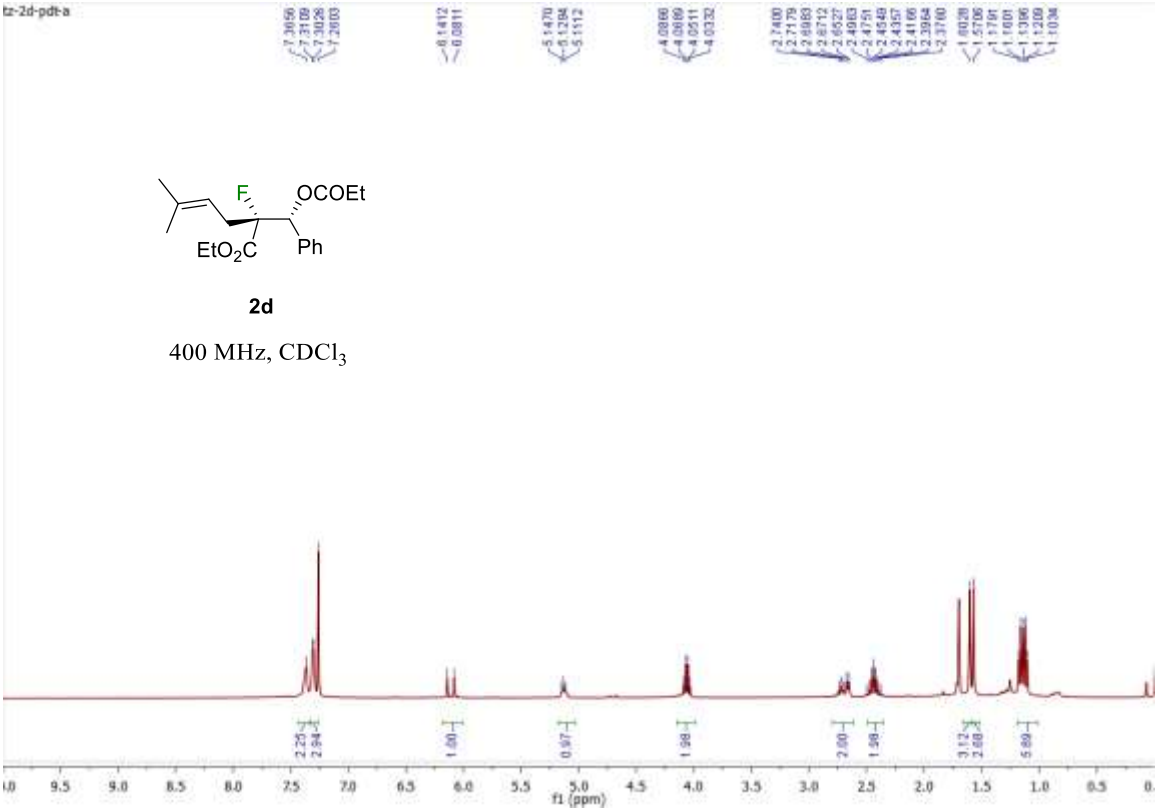
2c

101MHz, $CDCl_3$



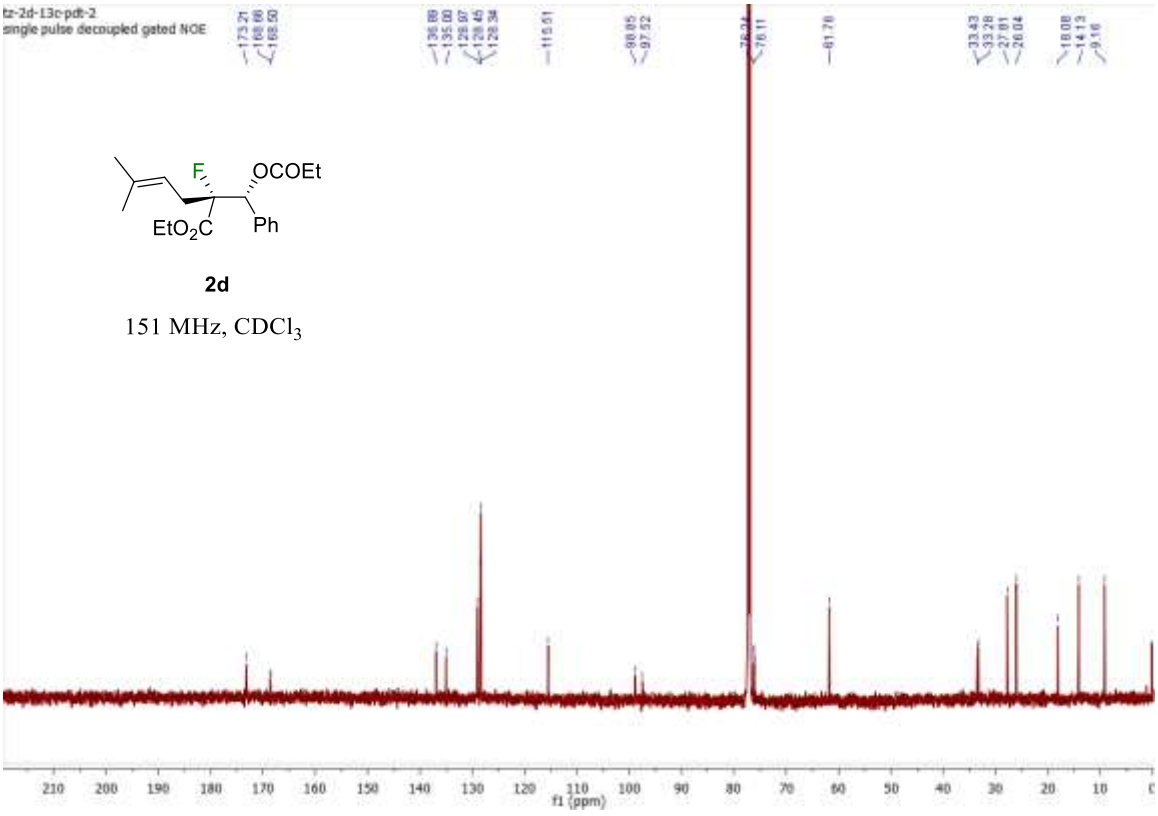
2c

376 MHz, $CDCl_3$



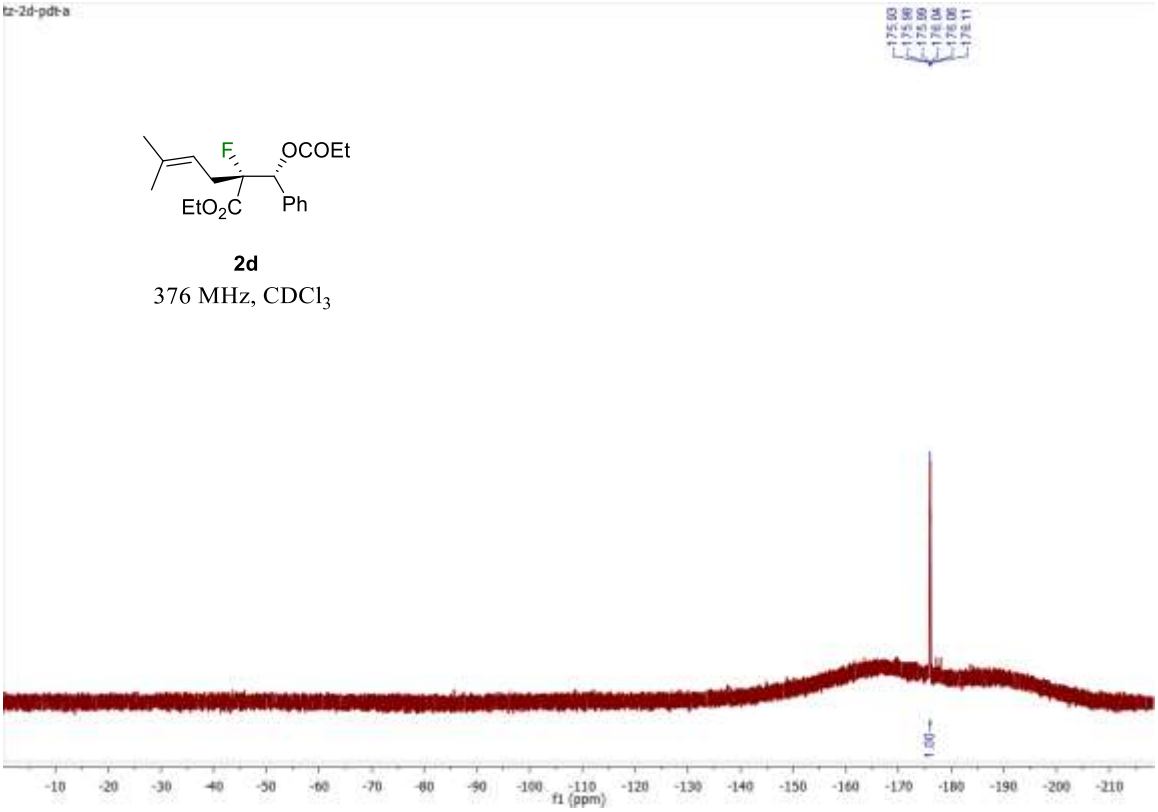
2d

400 MHz, $CDCl_3$



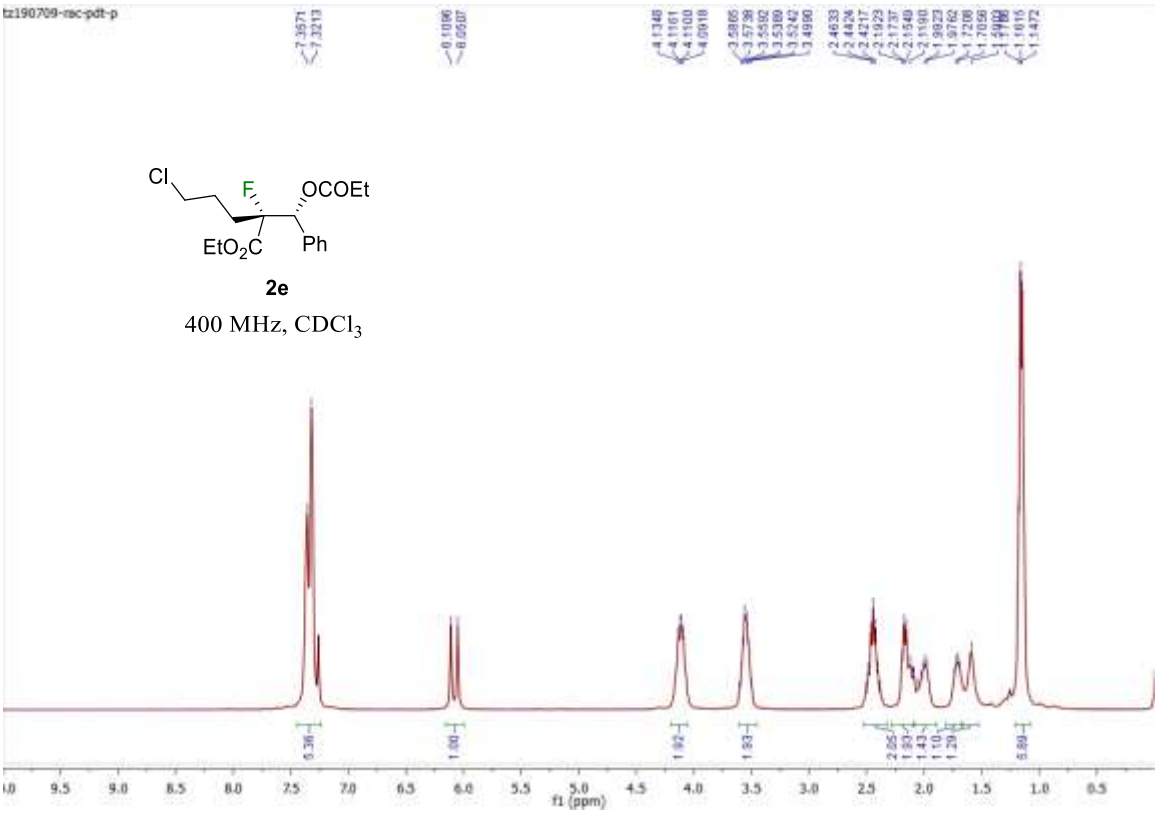
2d

151 MHz, $CDCl_3$



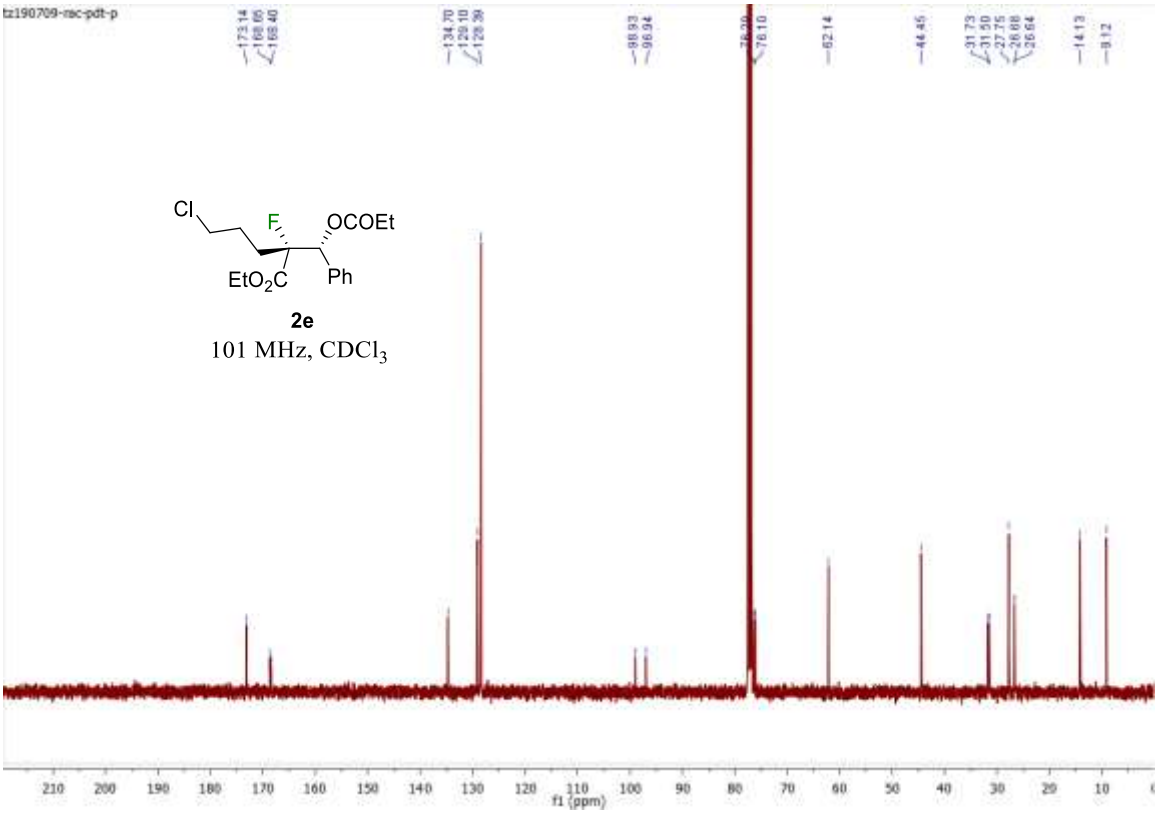
2d

376 MHz, $CDCl_3$



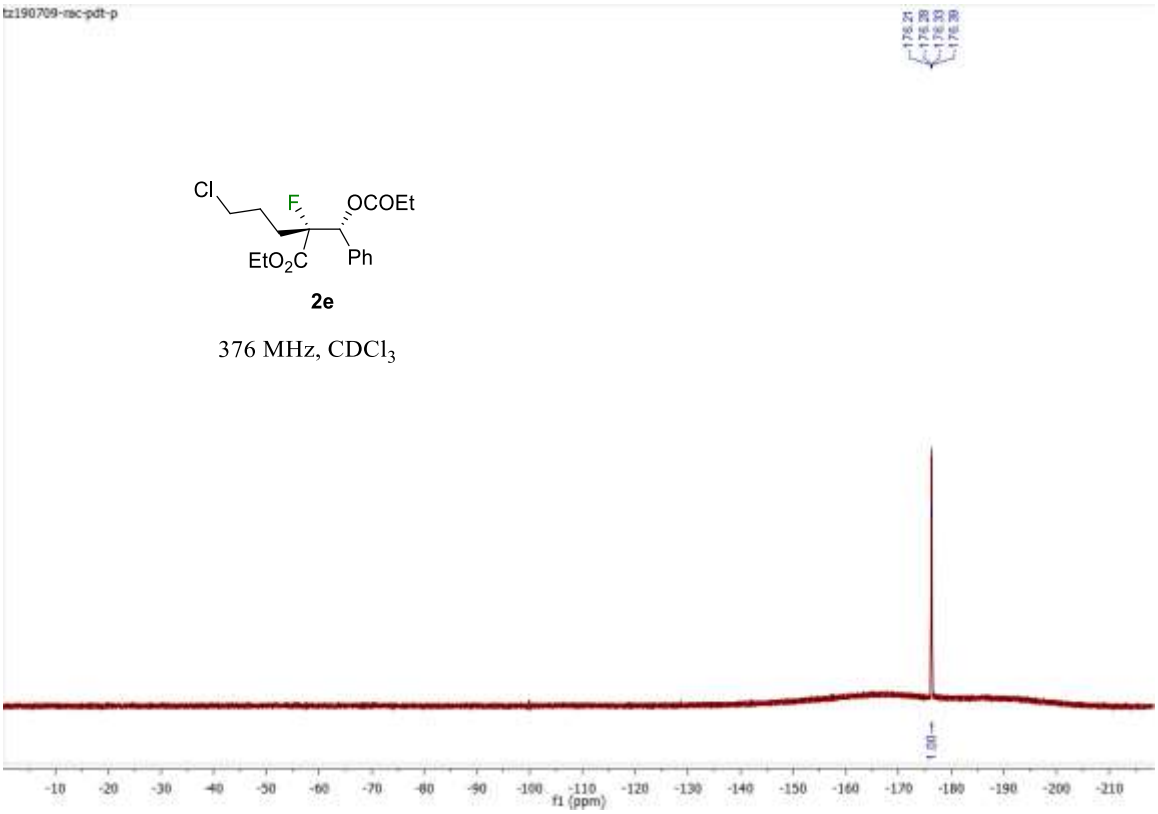
2e

400 MHz, $CDCl_3$



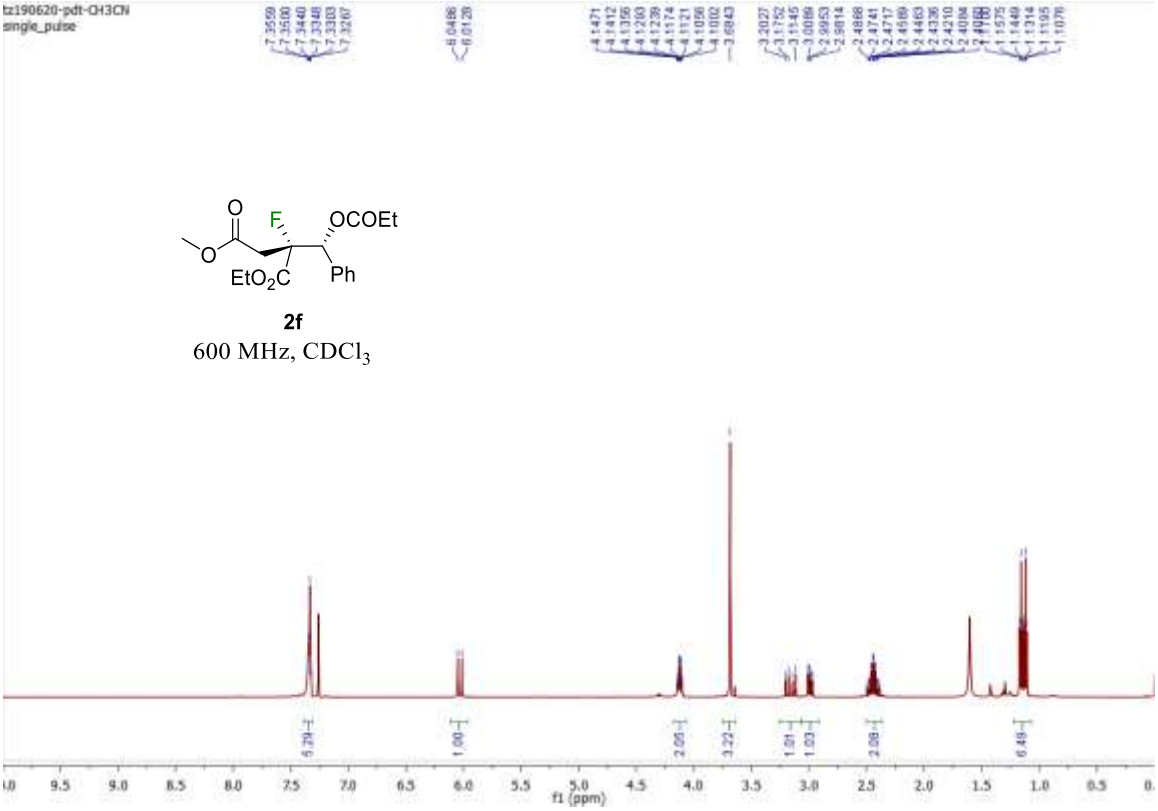
2e

101 MHz, $CDCl_3$



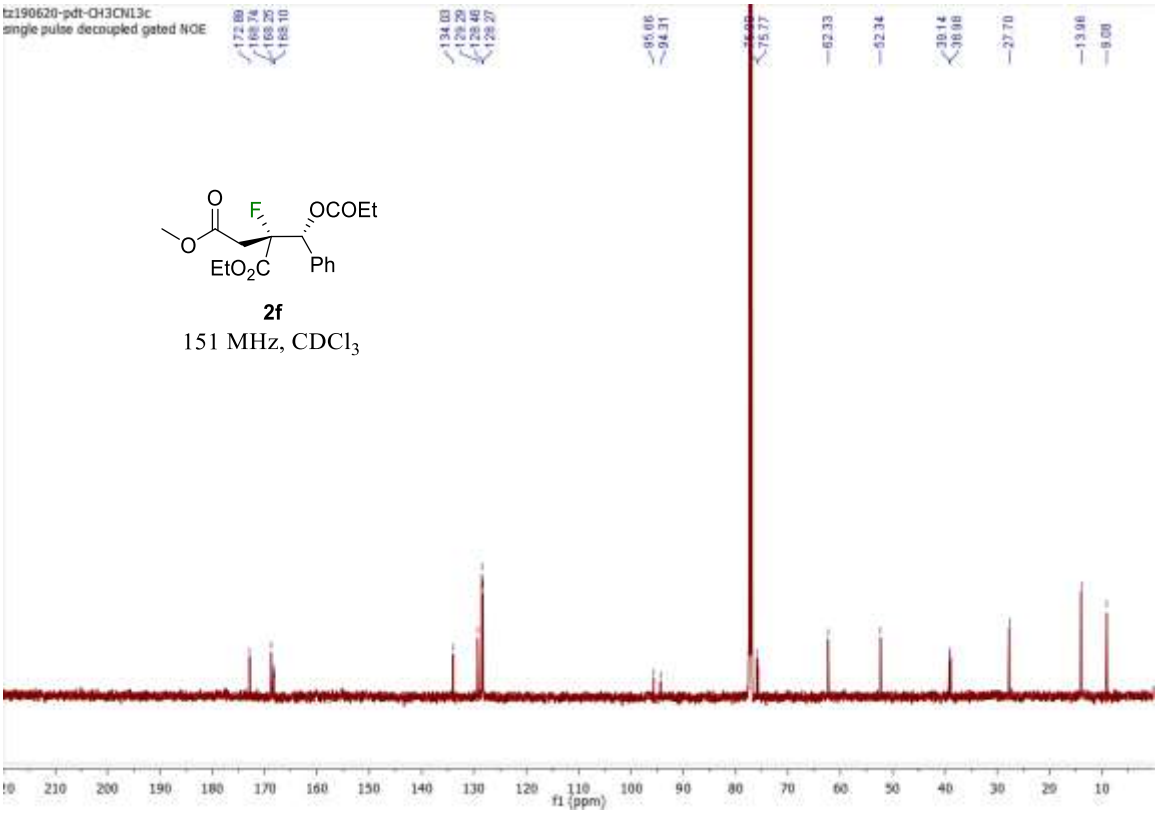
2e

376 MHz, $CDCl_3$



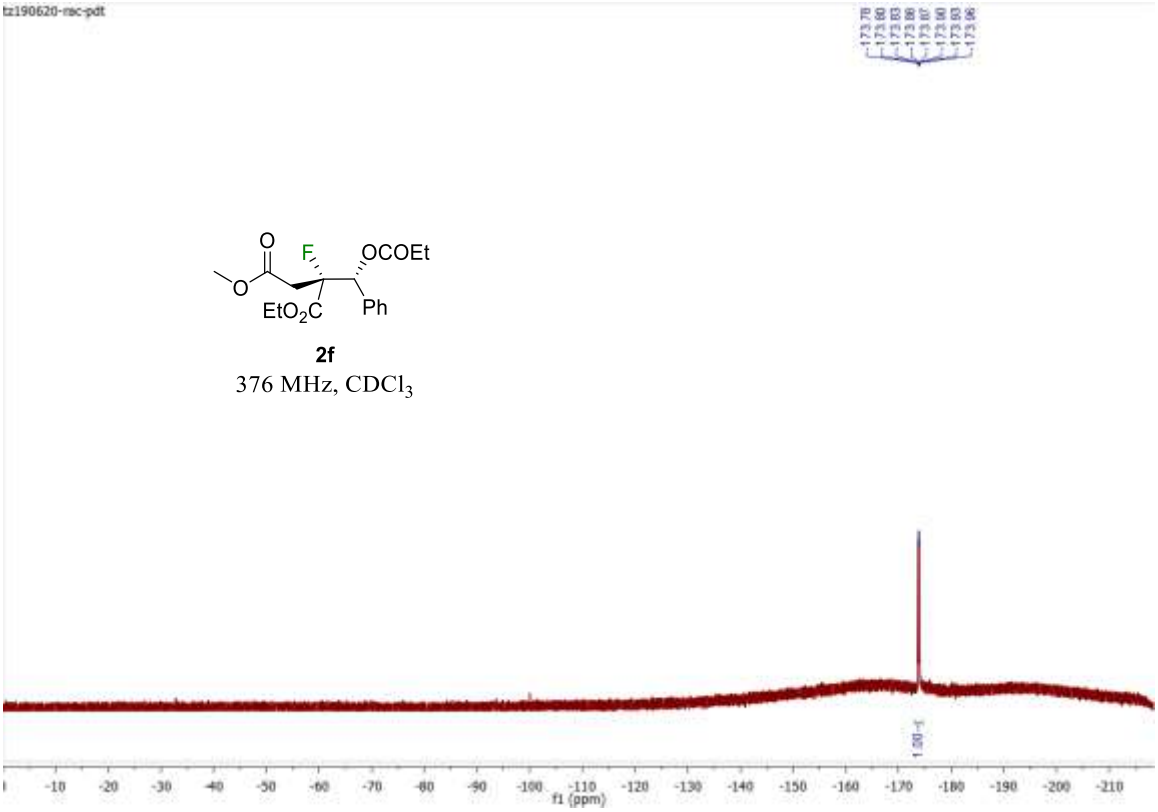
2f

600 MHz, $CDCl_3$



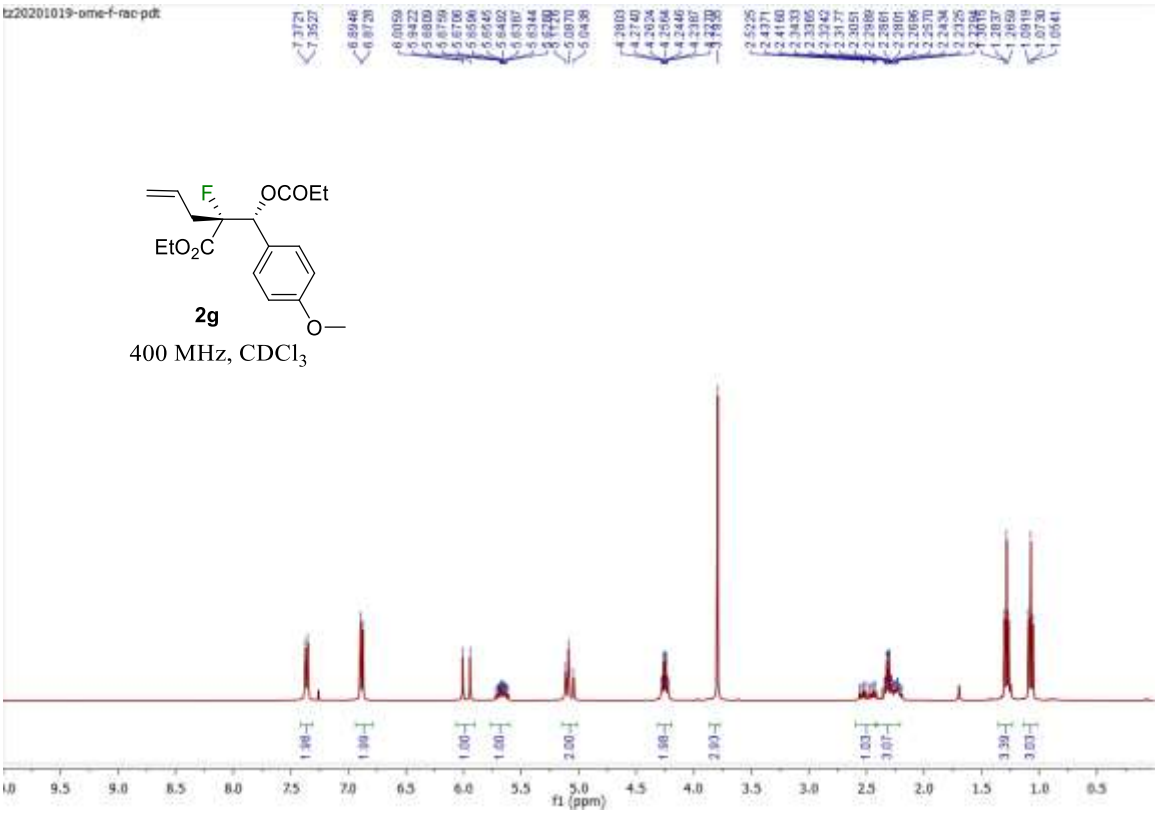
2f

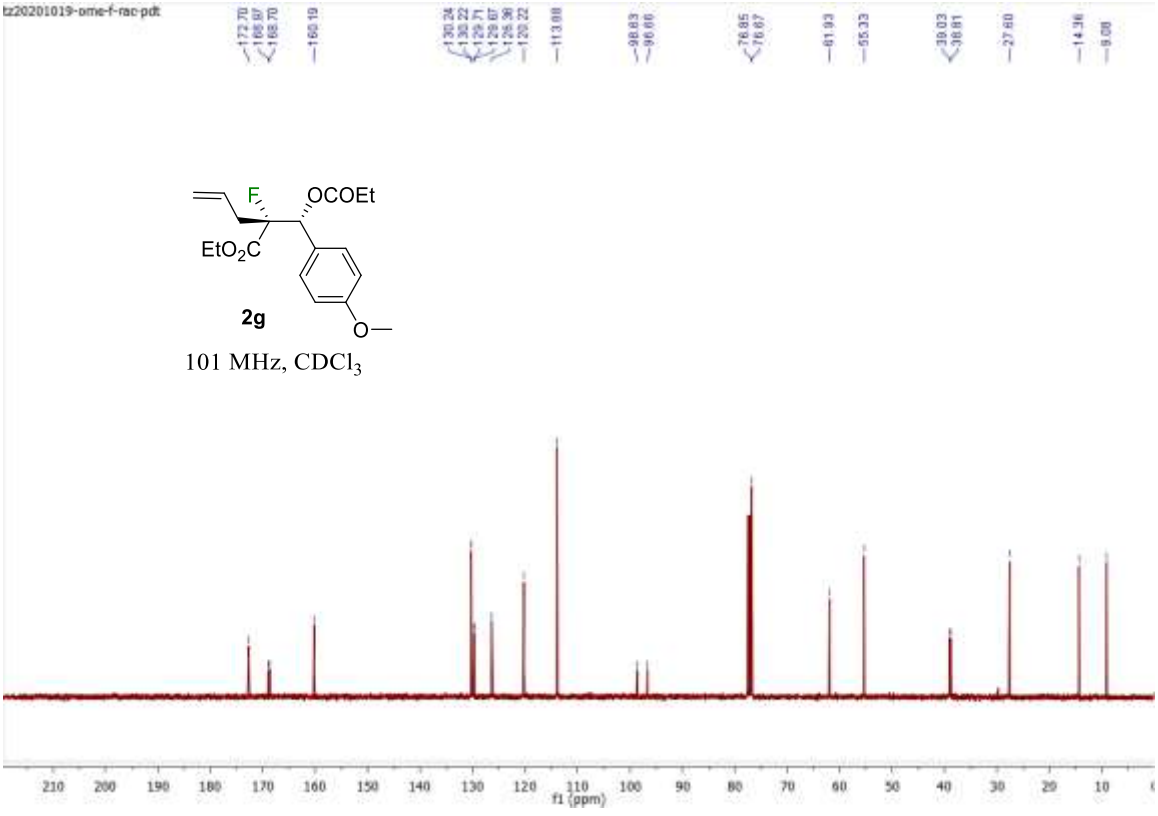
151 MHz, $CDCl_3$

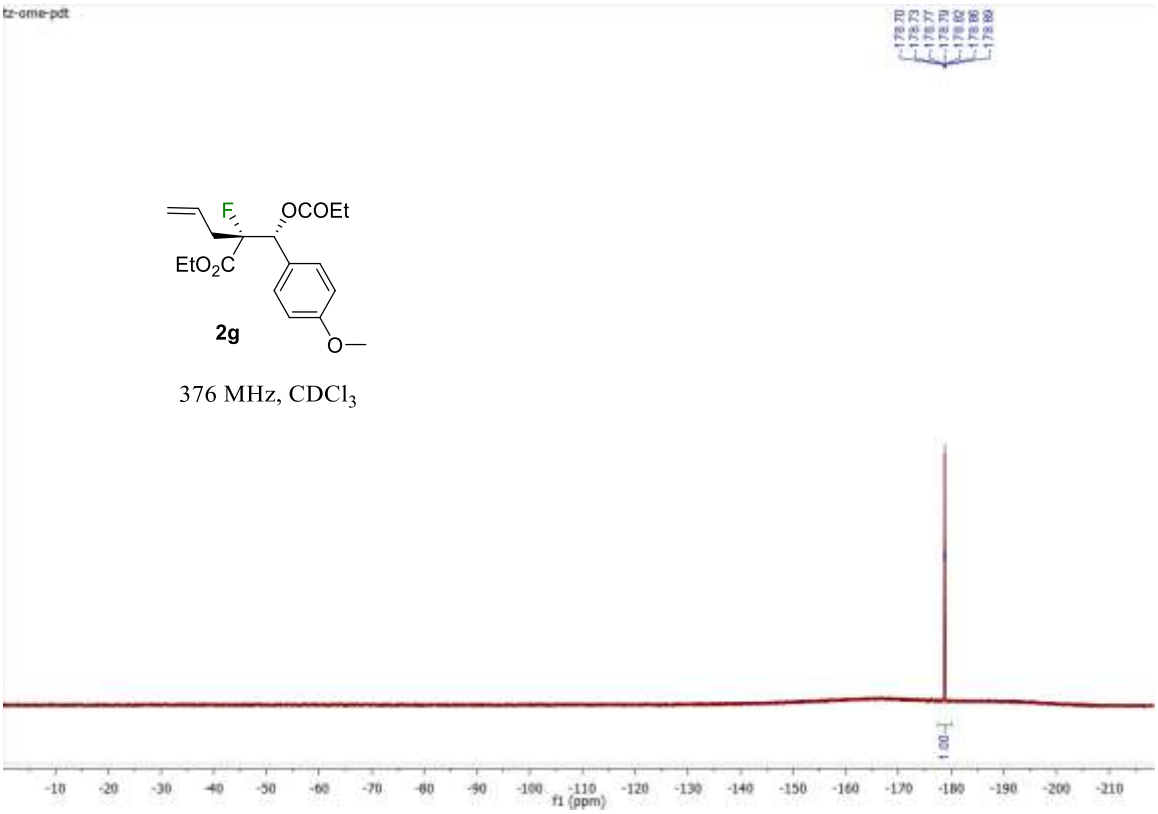


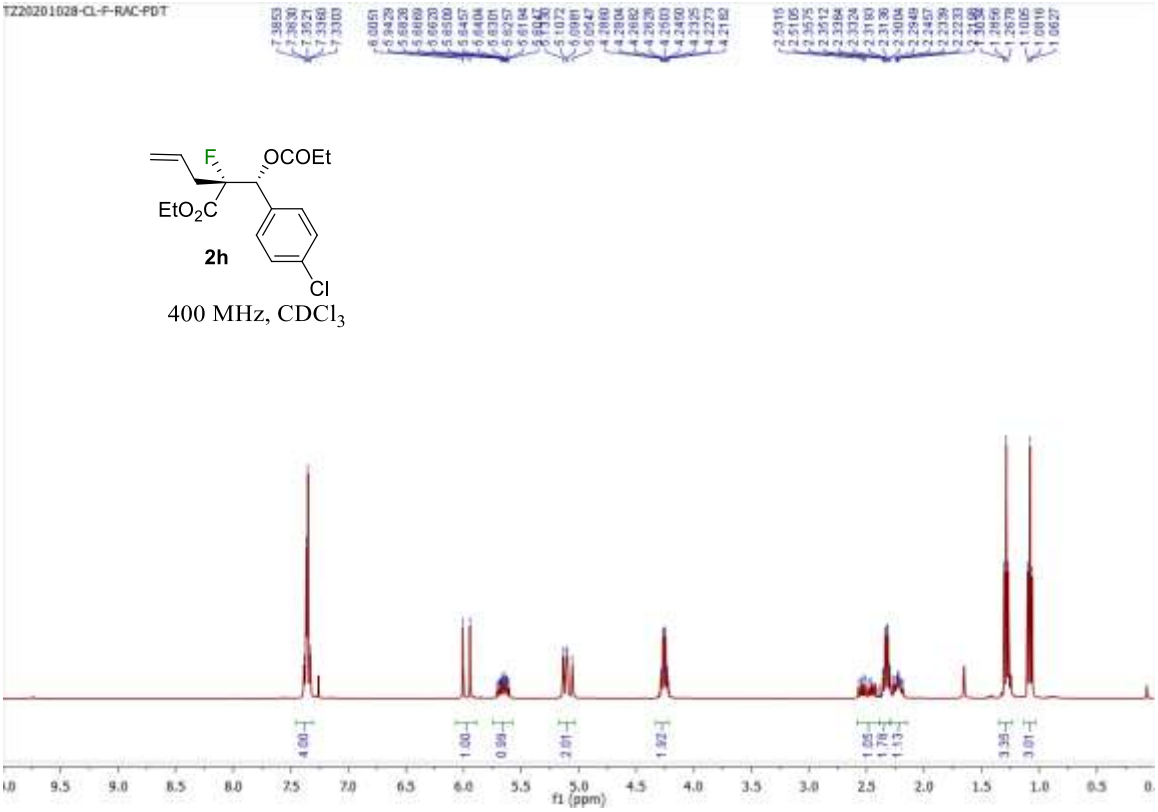
2f

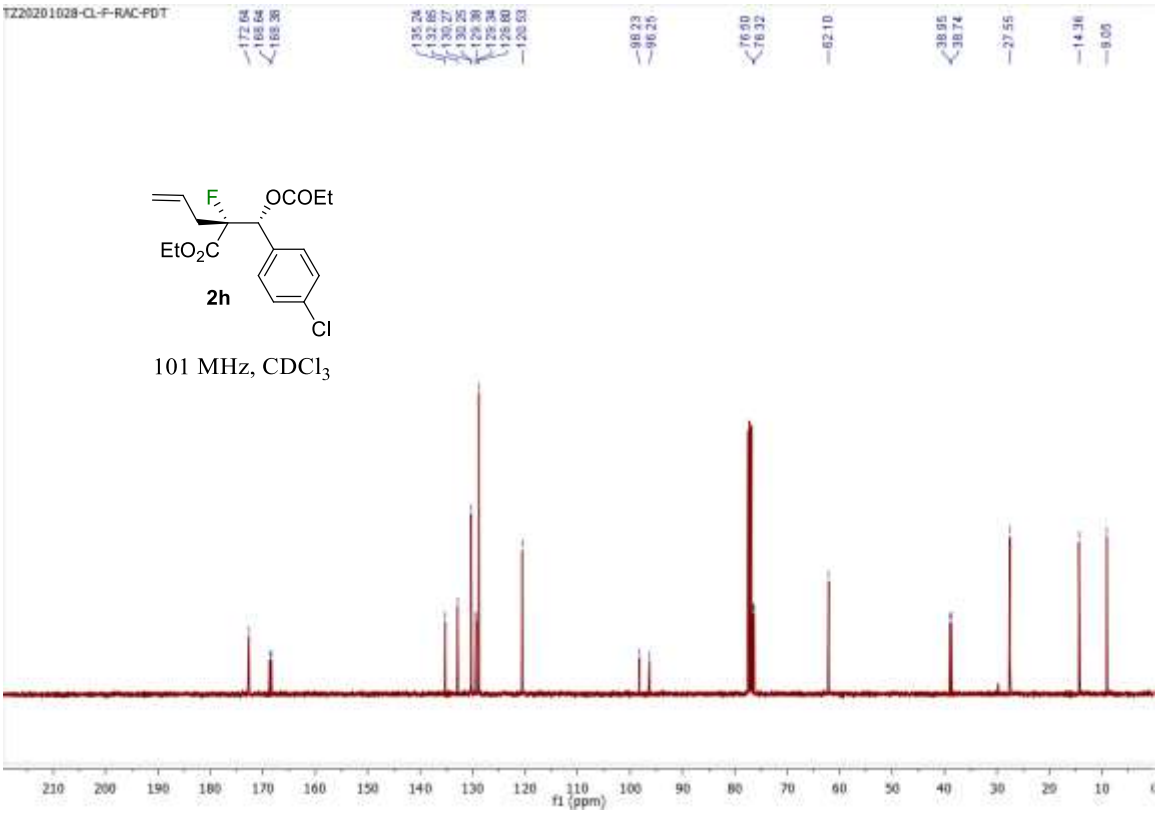
376 MHz, $CDCl_3$


tz20201019-ome-f-rac-pdt
F
OCOEt
EtO2C
O
2g
400 MHz, CDCl3
f1 (ppm)

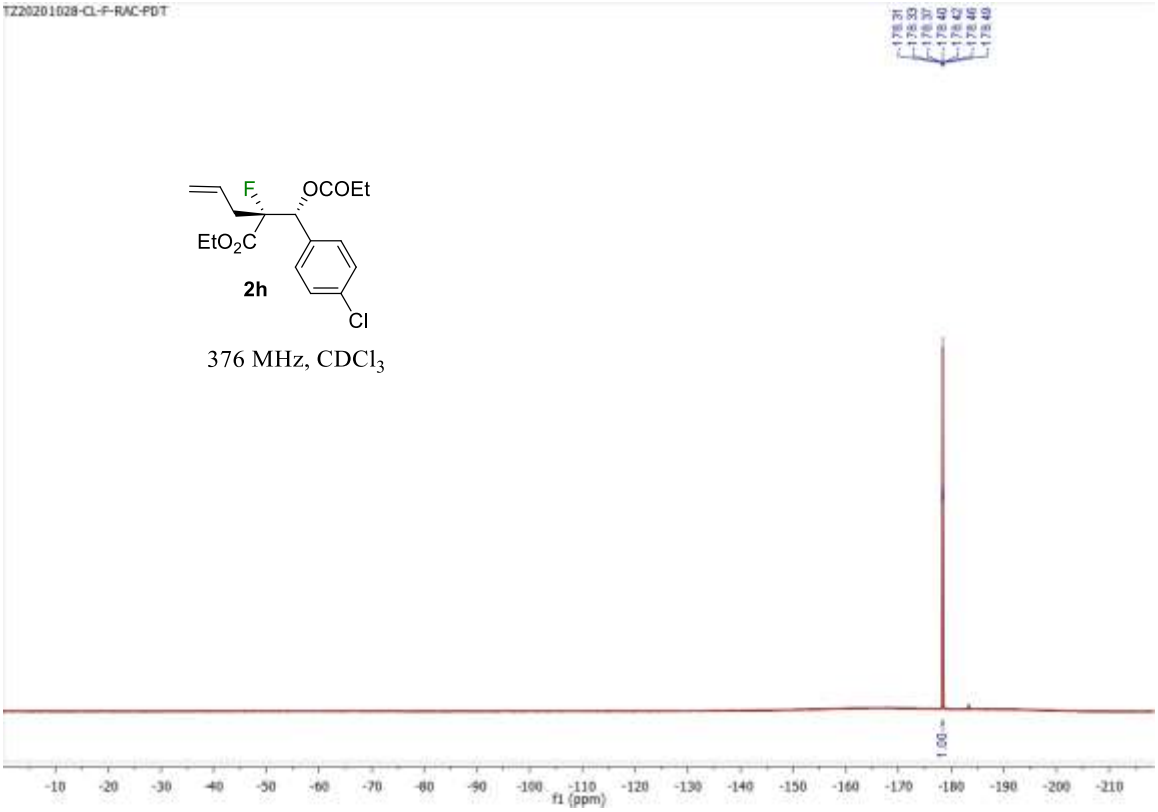

tz20201019-ome-f-rac-pdt
F
OCOEt
EtO2C
O
2g
101 MHz, CDCl3
f1 (ppm)


tz-ome-pdt
F
OCOEt
EtO2C
2g
O
376 MHz, CDCl3
f1 (ppm)

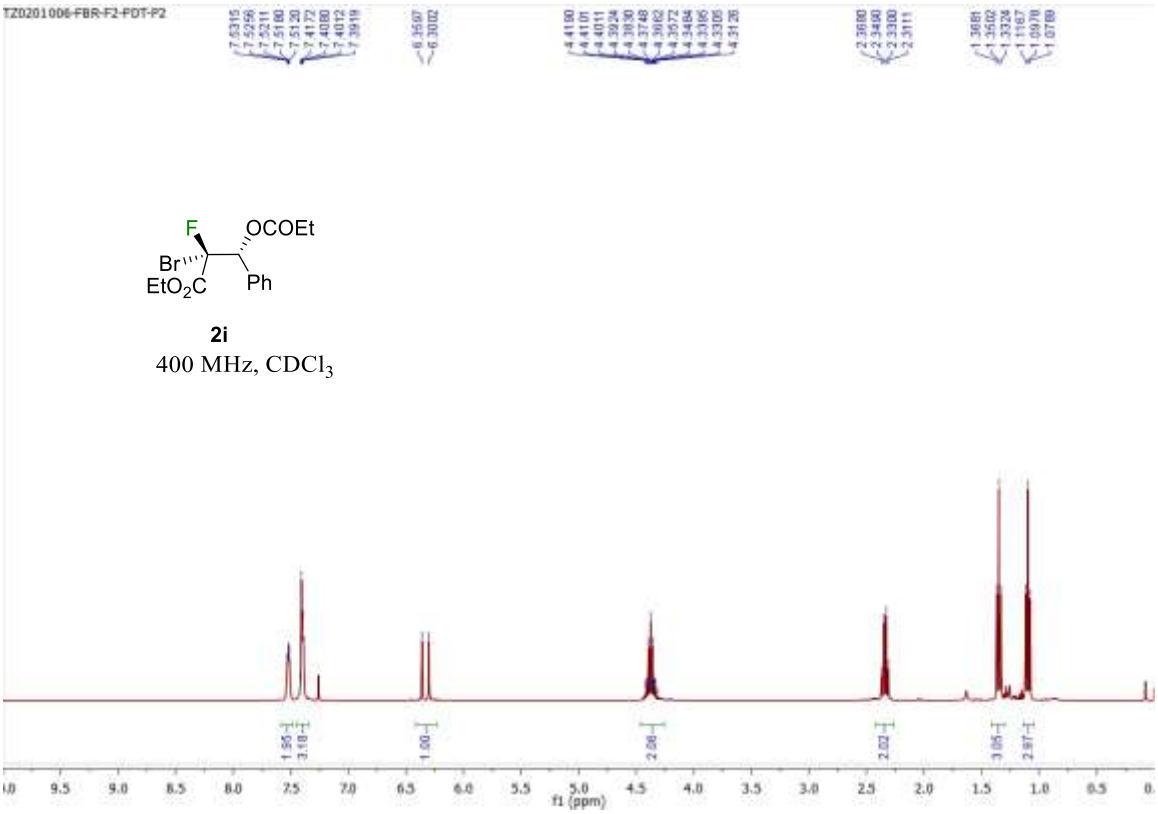

TZ20201028-CL-F-RAC-PDT
F
OCOEt
EtO2C
2h
Cl
400 MHz, CDCl3
f1 (ppm)



101 MHz, $CDCl_3$

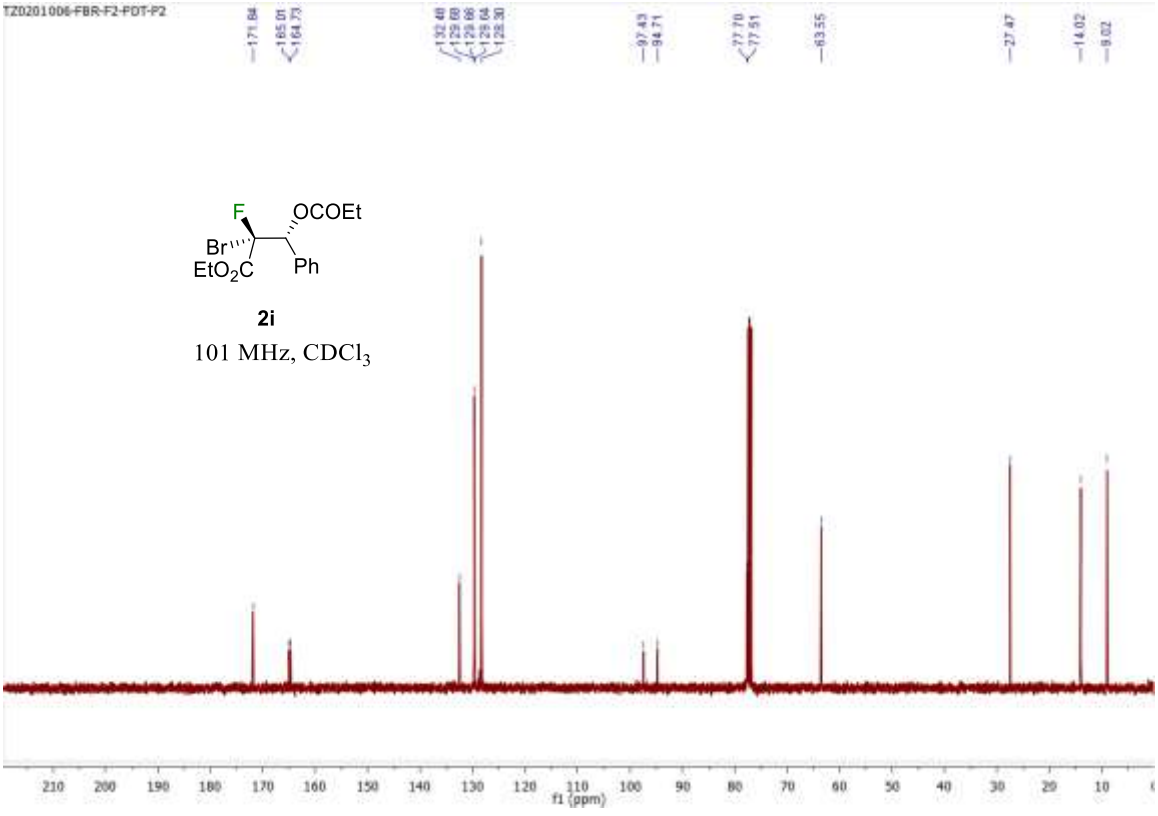


376 MHz, $CDCl_3$



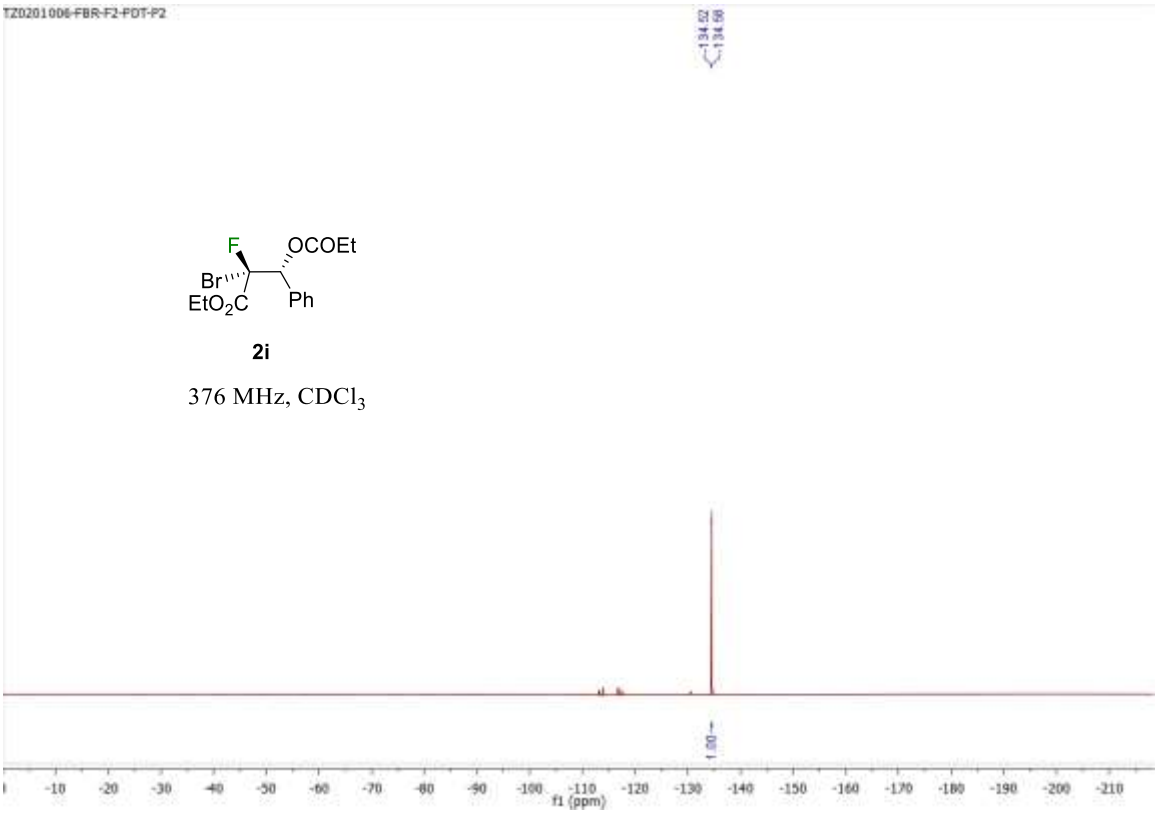
2i

400 MHz, $CDCl_3$



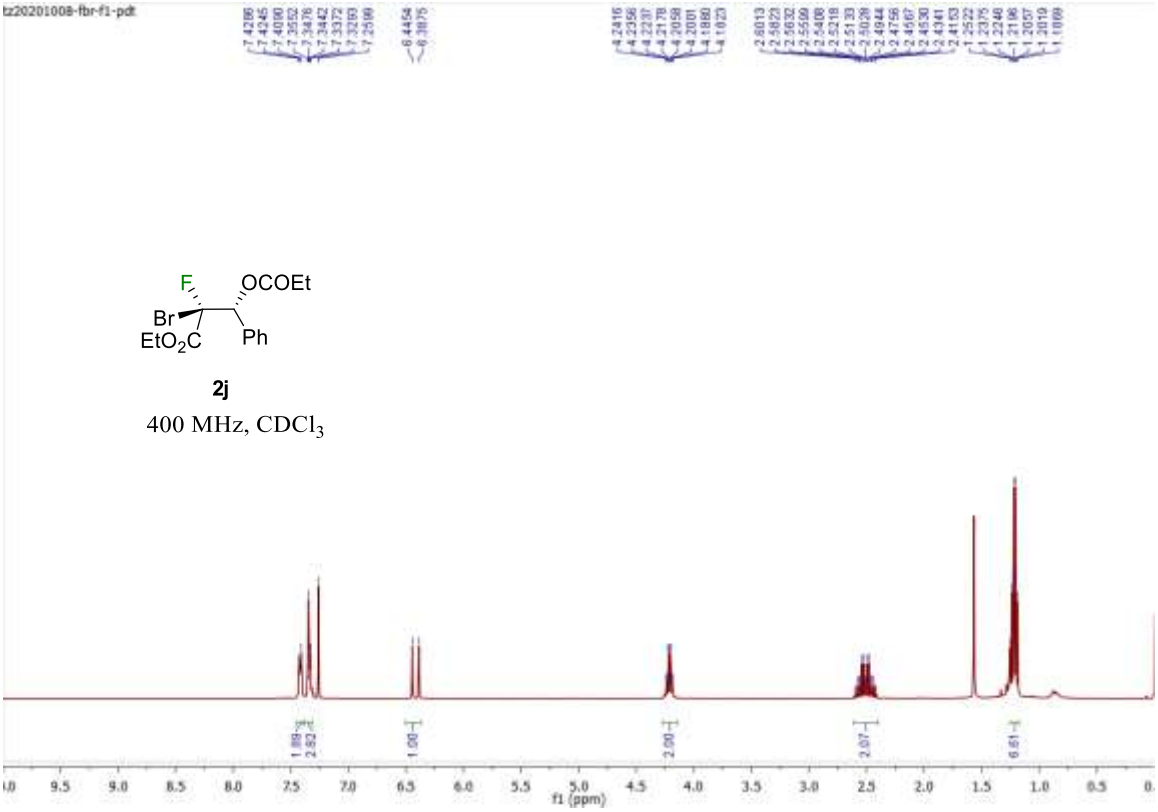
2i

101 MHz, $CDCl_3$



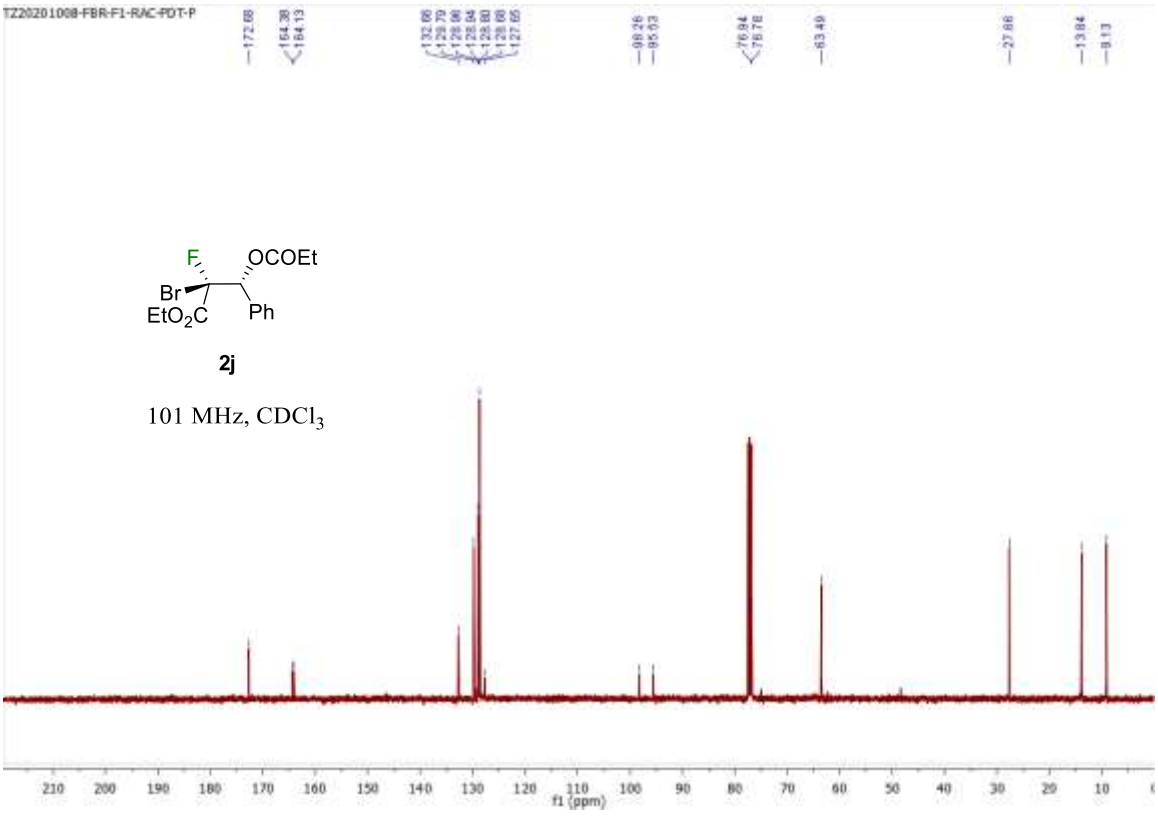
2i

376 MHz, $CDCl_3$



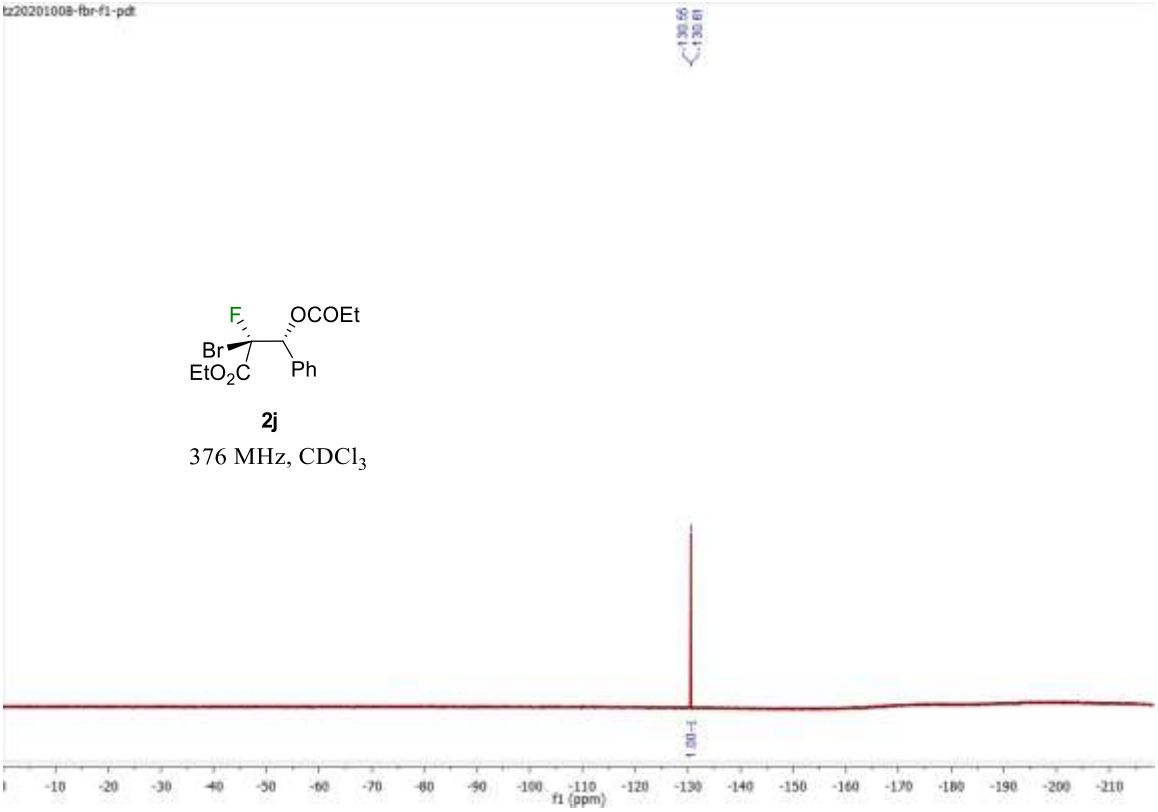
2j

400 MHz, $CDCl_3$



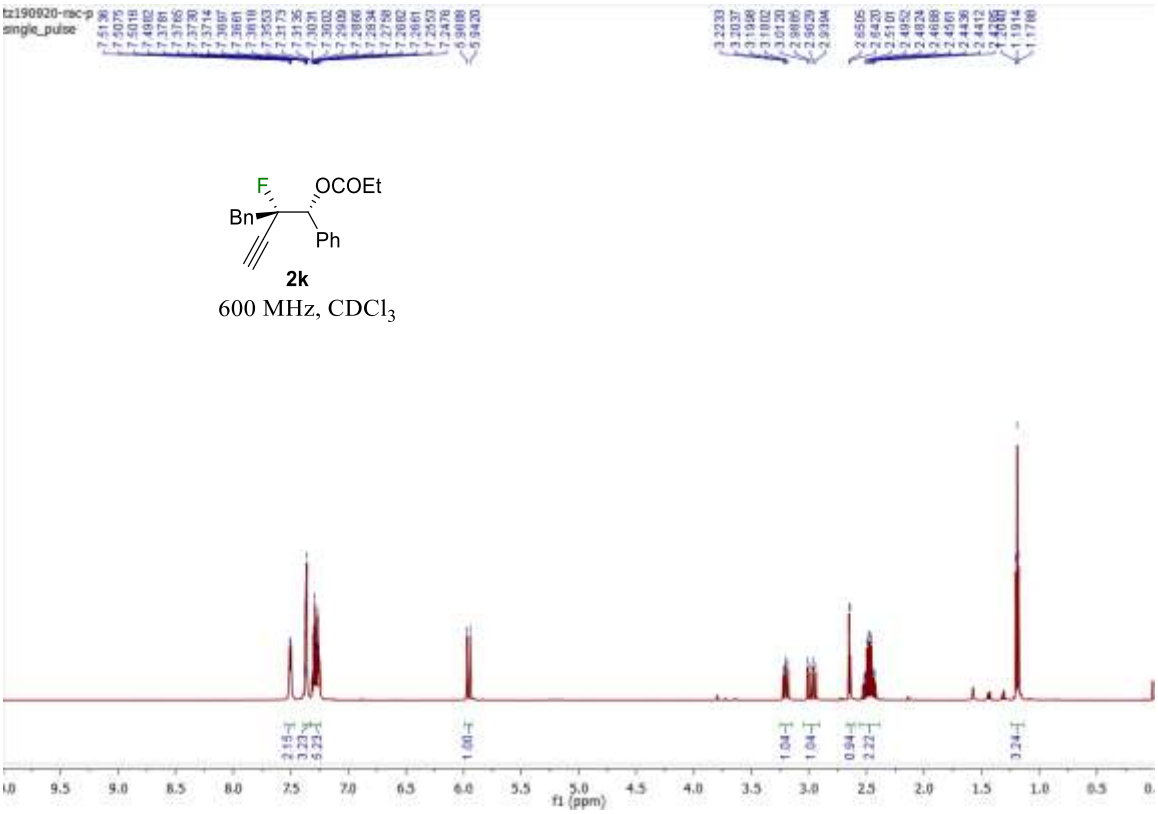
2j

101 MHz, $CDCl_3$



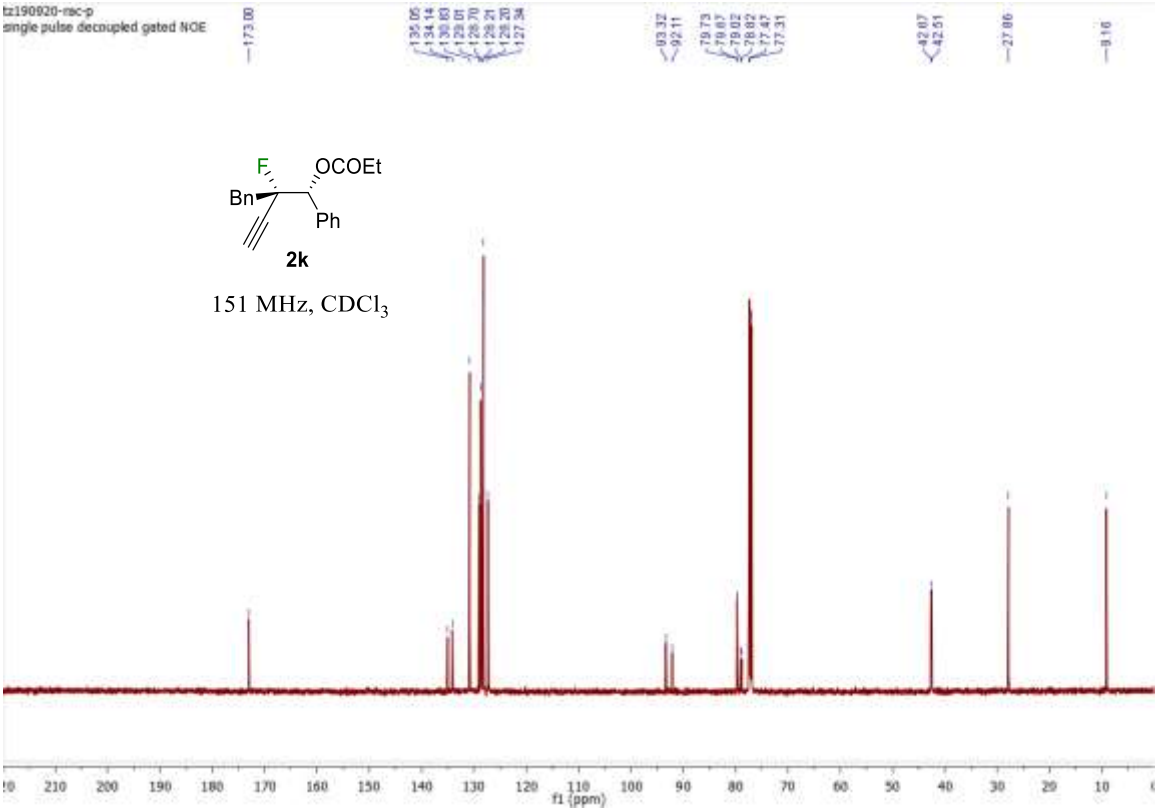
2j

376 MHz, $CDCl_3$



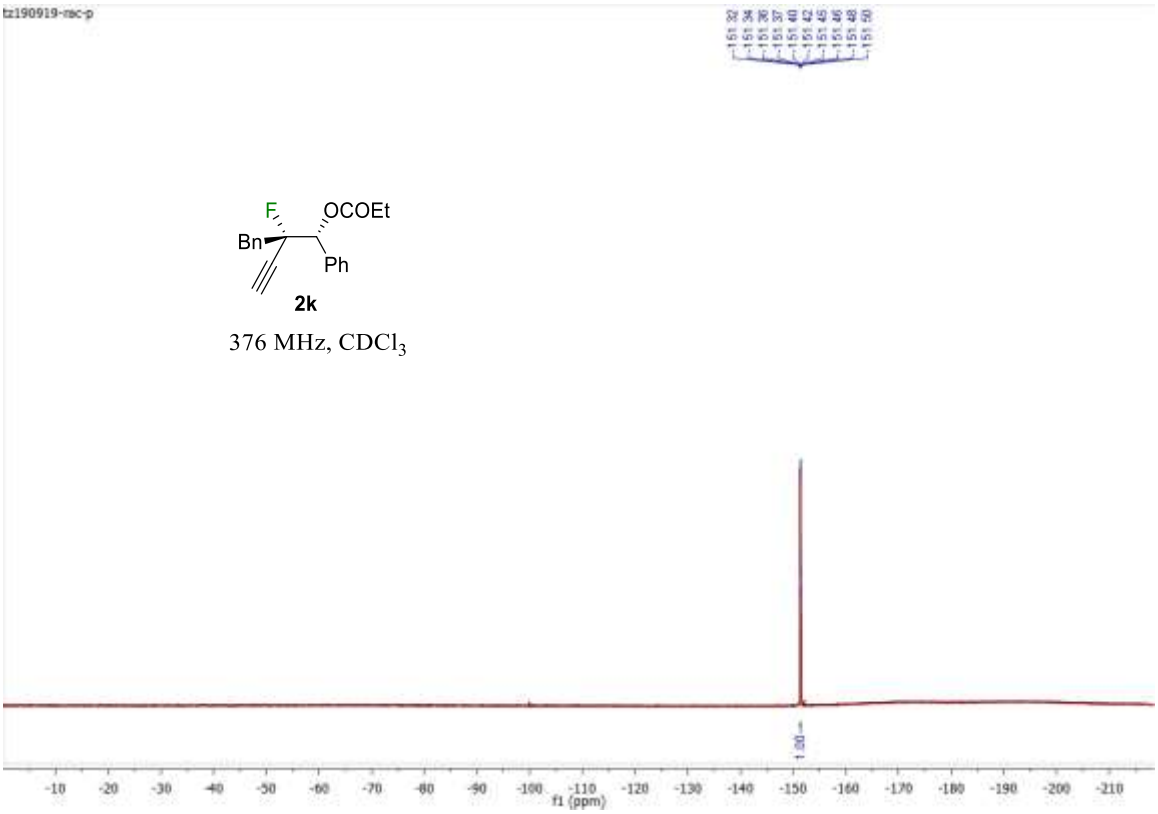
2k

600 MHz, $CDCl_3$



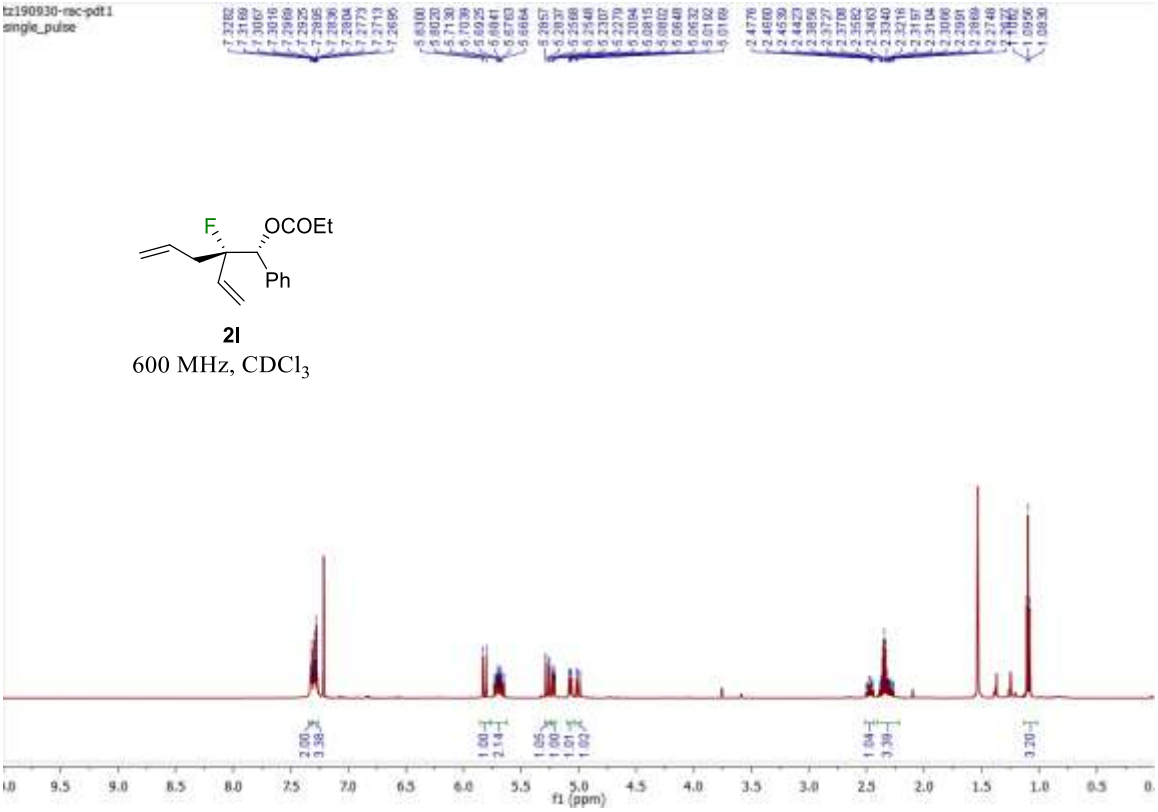
2k

151 MHz, $CDCl_3$



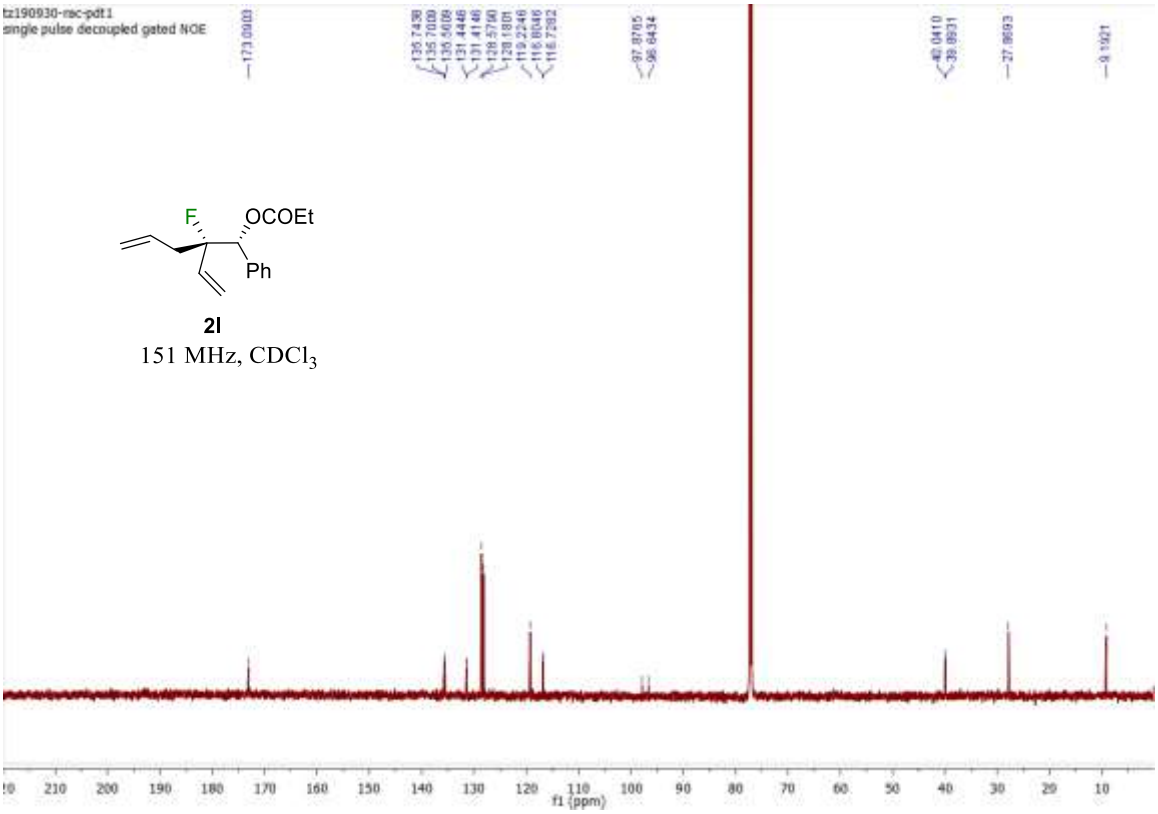
2k

376 MHz, $CDCl_3$



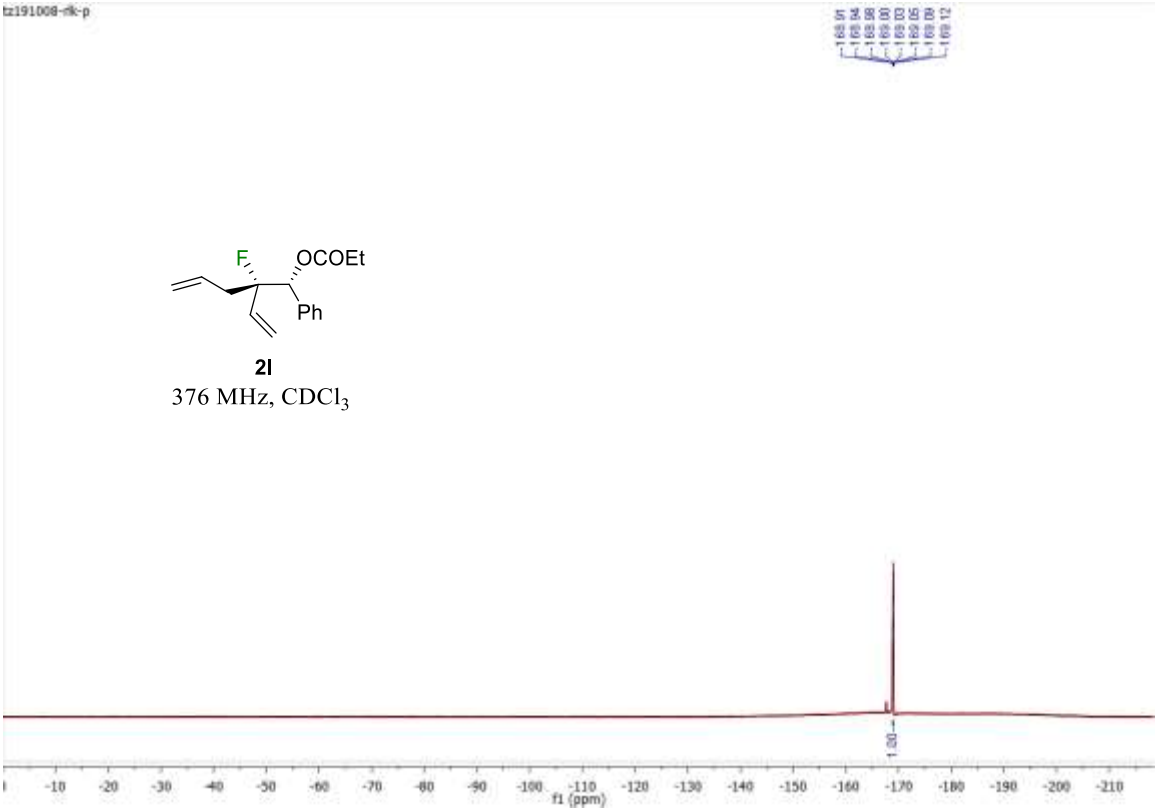
2l

600 MHz, $CDCl_3$



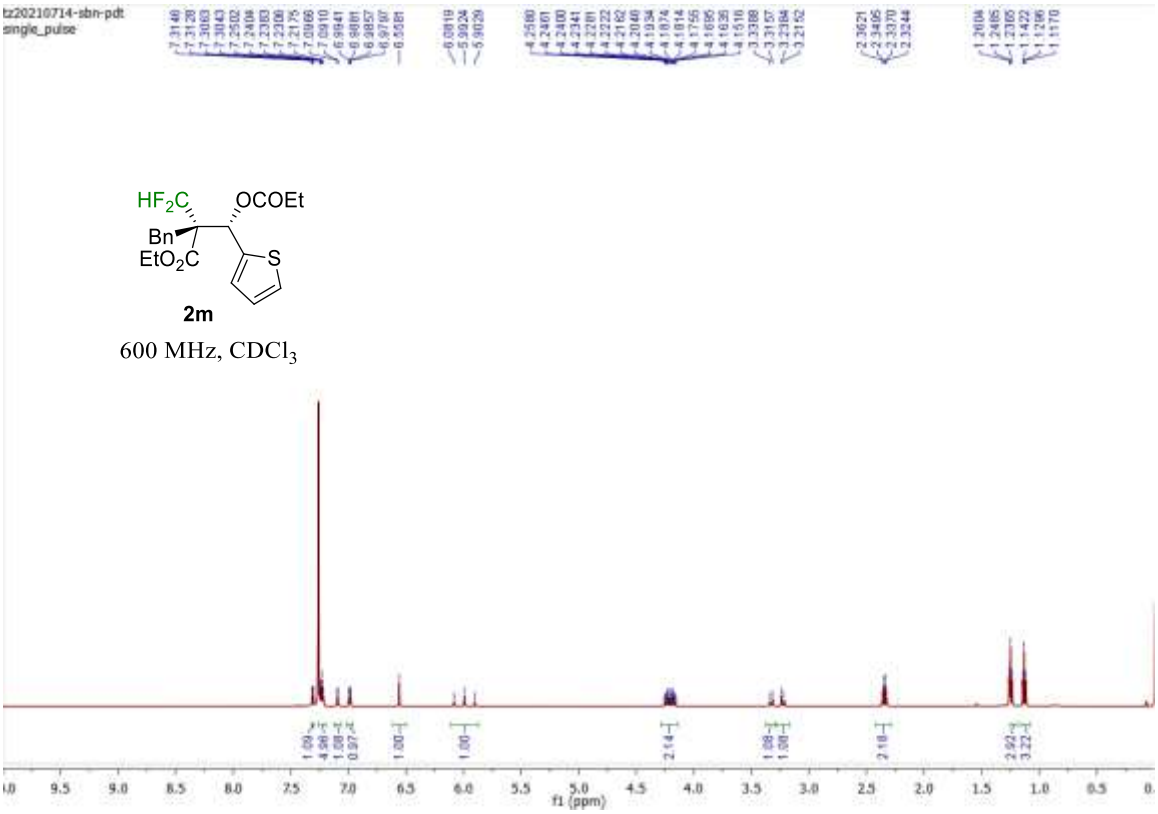
2l

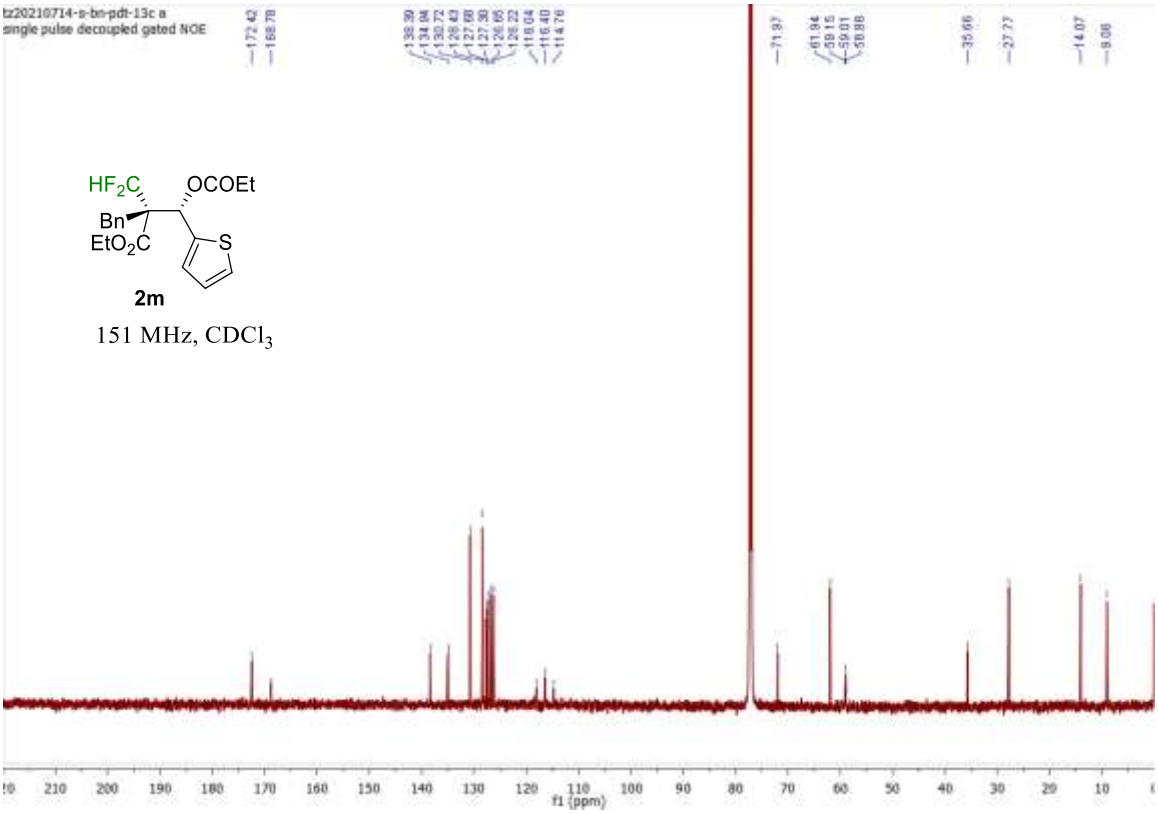
151 MHz, $CDCl_3$

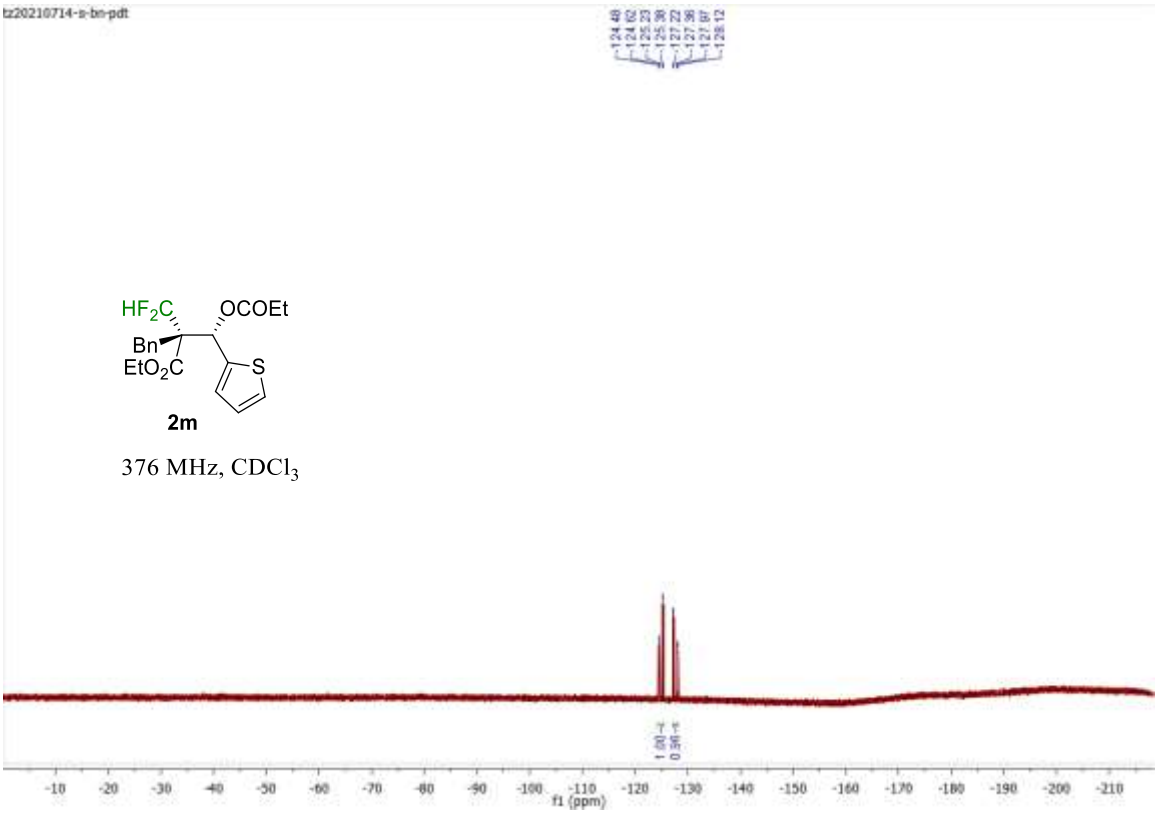


2l

376 MHz, $CDCl_3$

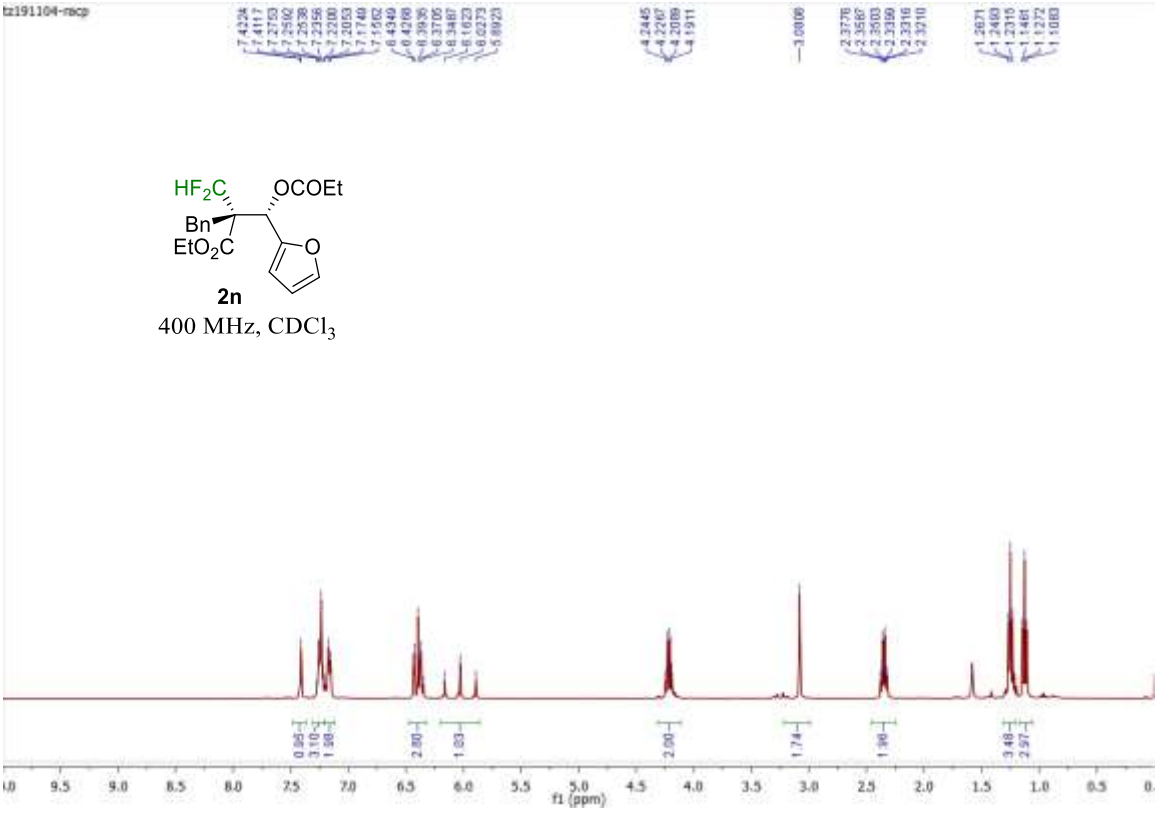

tz20210714-sbn-pdt
single_pulse
HF2C
OCOEt
Bn
EtO2C
S
2m
600 MHz, CDCl3
f1 (ppm)


tz20210714-s-bn-pdt-13c a
single pulse decoupled gated NOE
HF2C
OCOEt
Bn
EtO2C
S
2m
151 MHz, CDCl3
f1 (ppm)



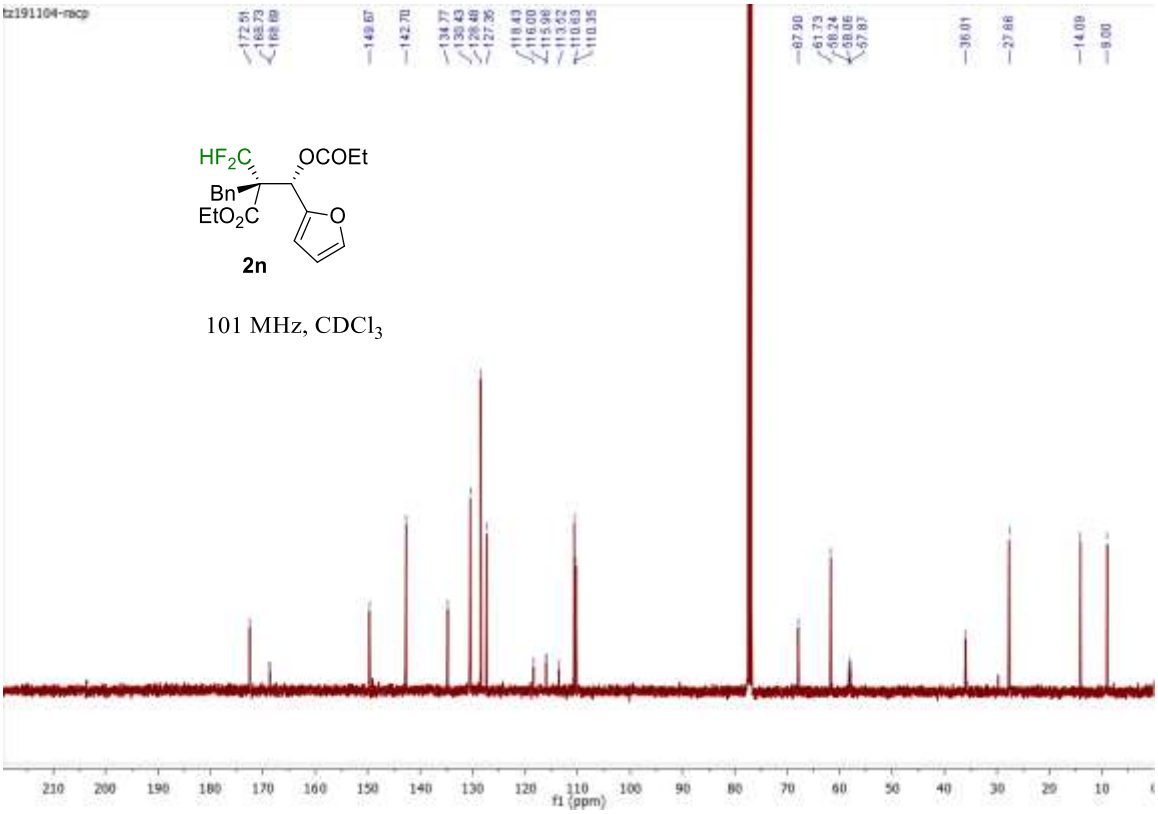
2m

376 MHz, $CDCl_3$



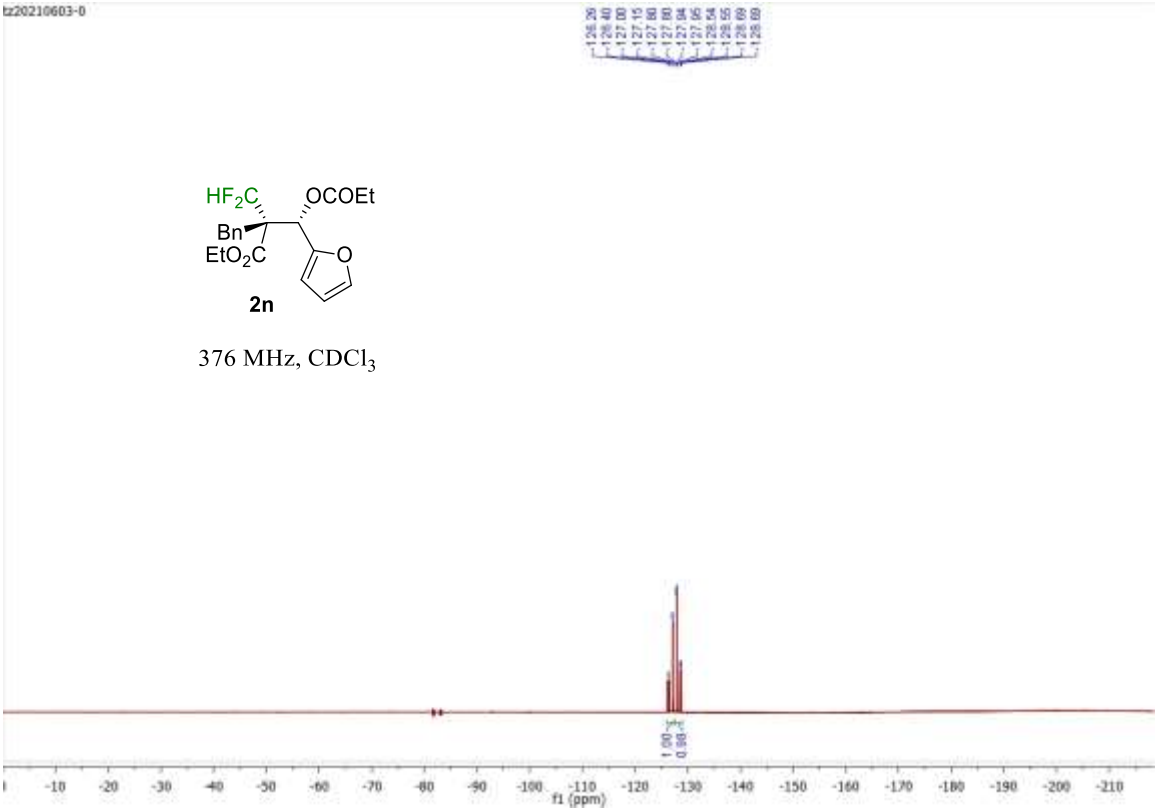
2n

400 MHz, $CDCl_3$



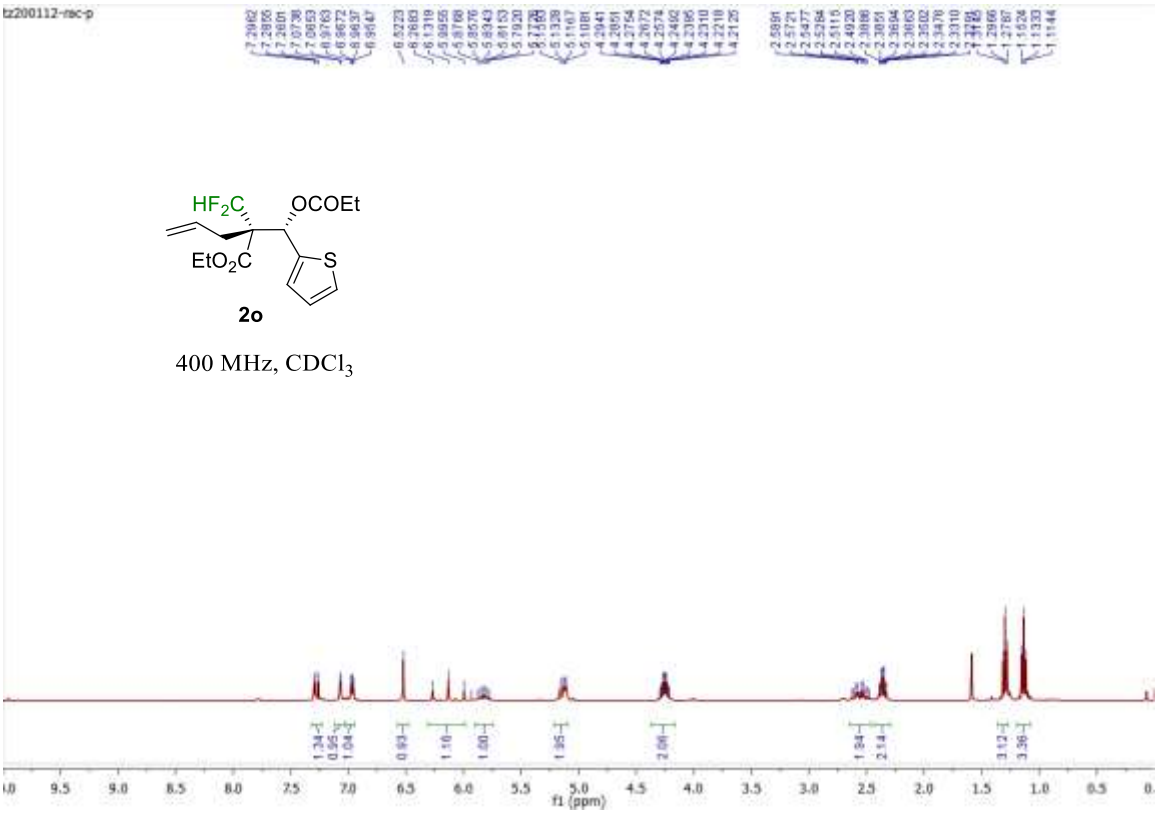
2n

101 MHz, $CDCl_3$



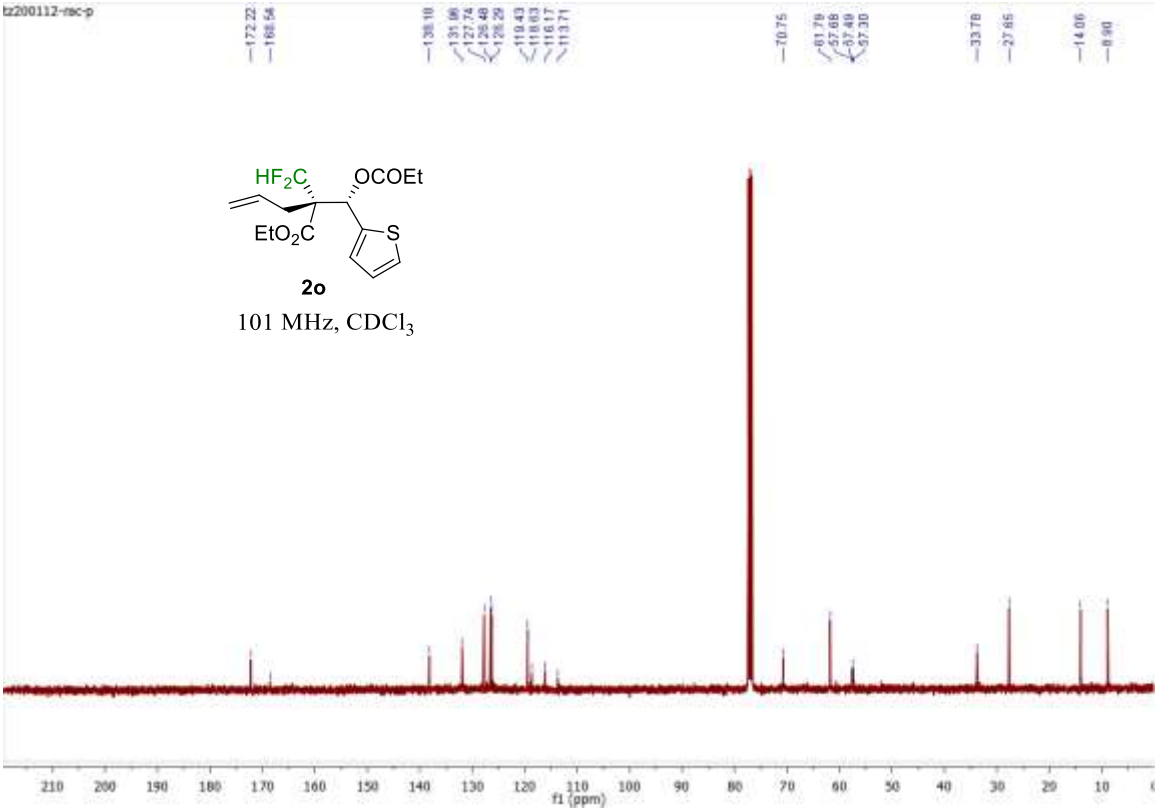
2n

376 MHz, $CDCl_3$



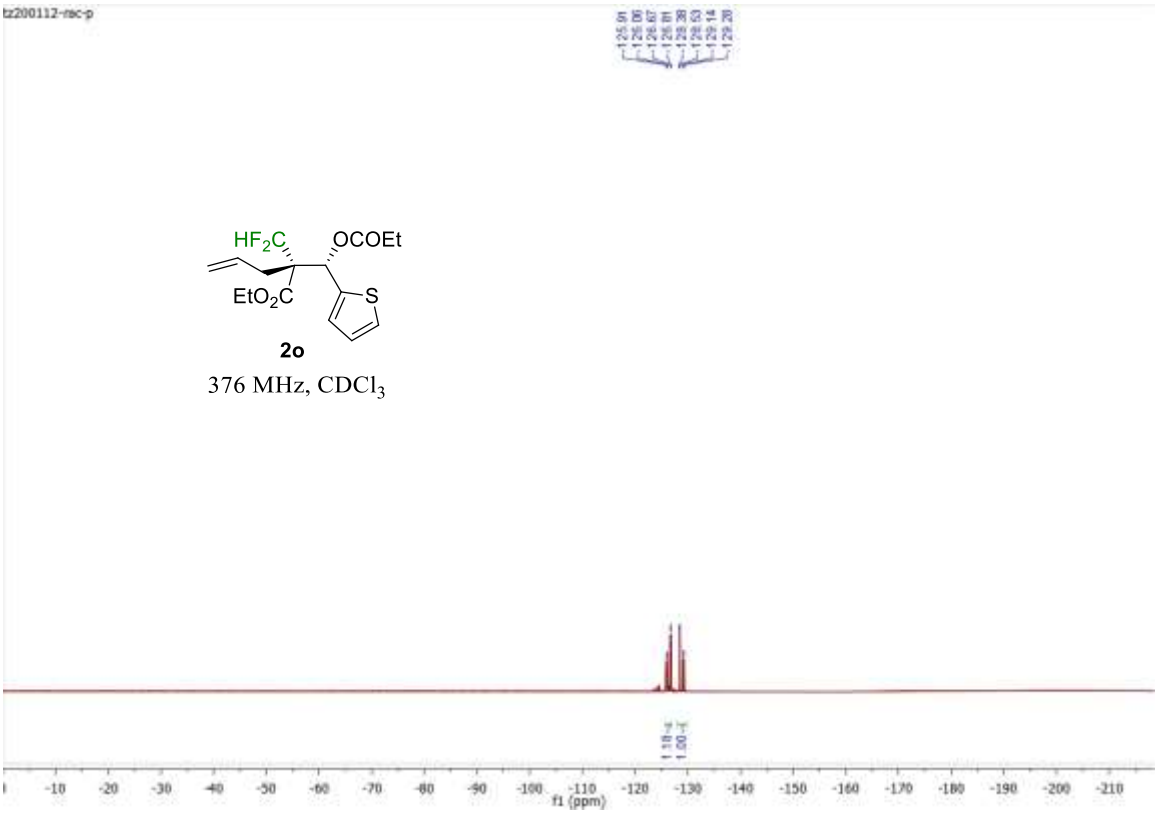
2o

400 MHz, $CDCl_3$



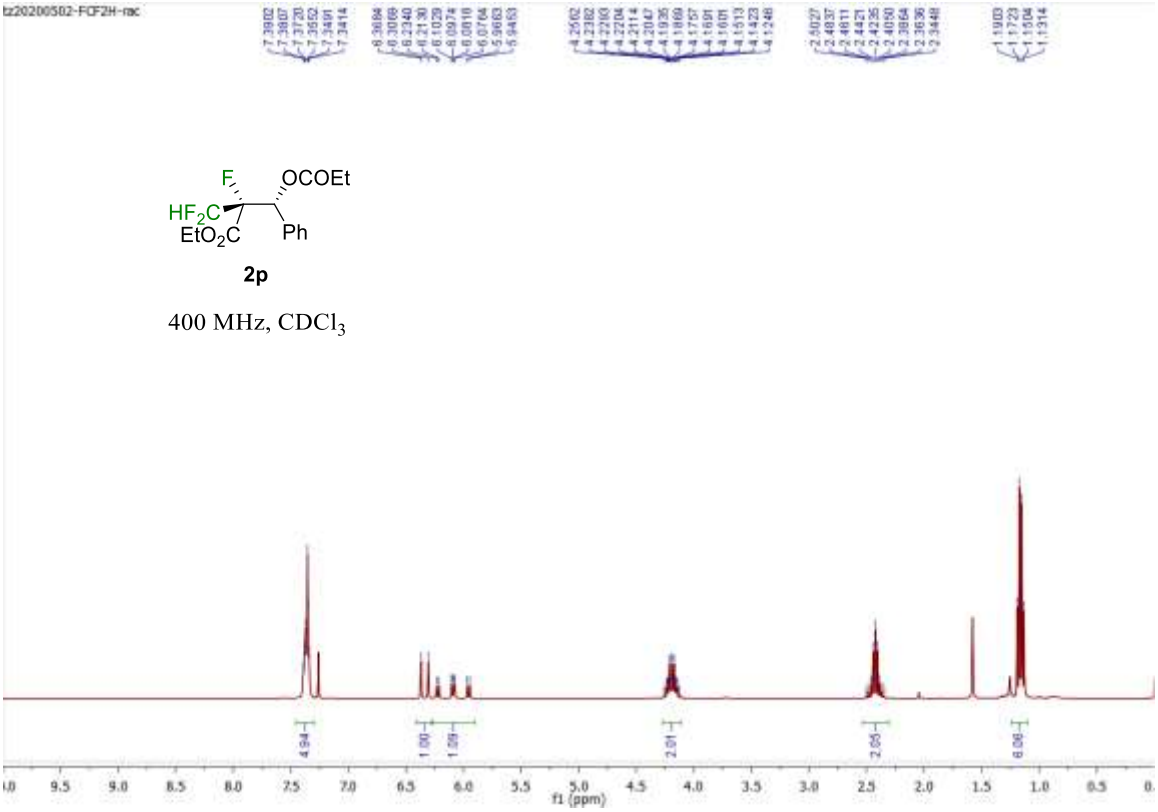
2o

101 MHz, $CDCl_3$



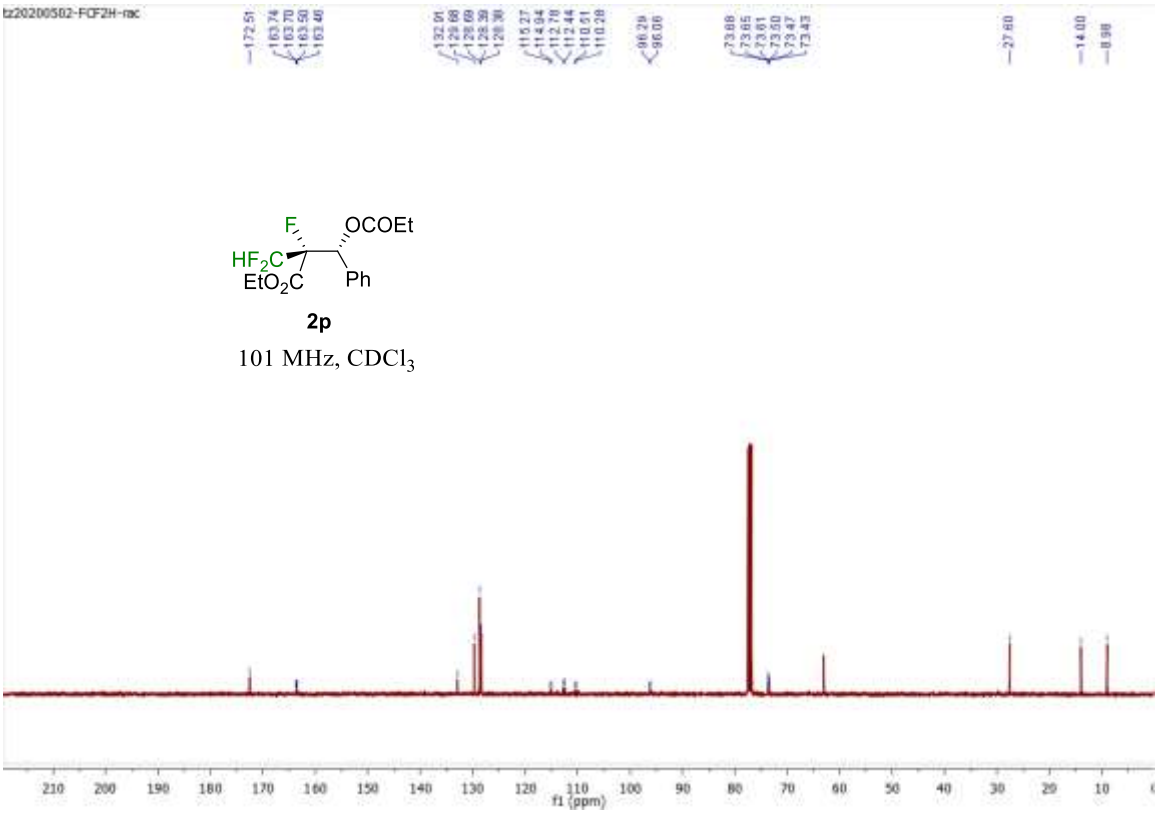
2o

376 MHz, $CDCl_3$



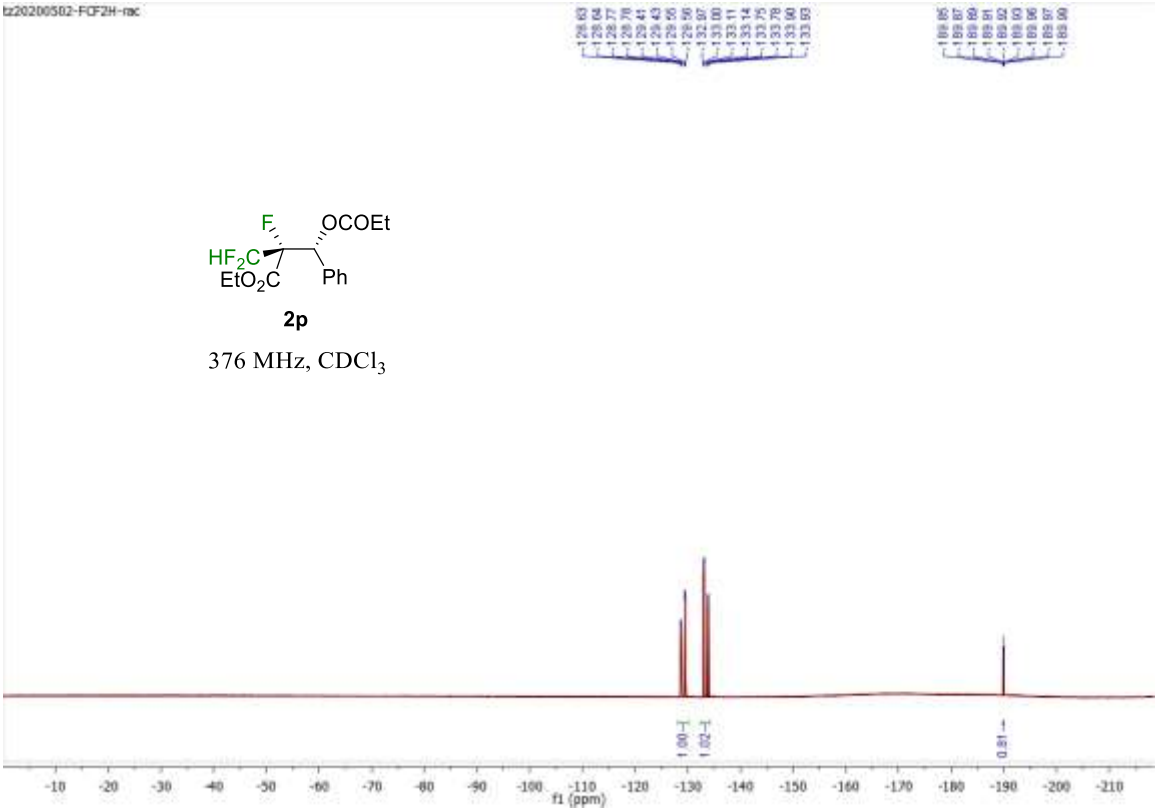
2p

400 MHz, $CDCl_3$



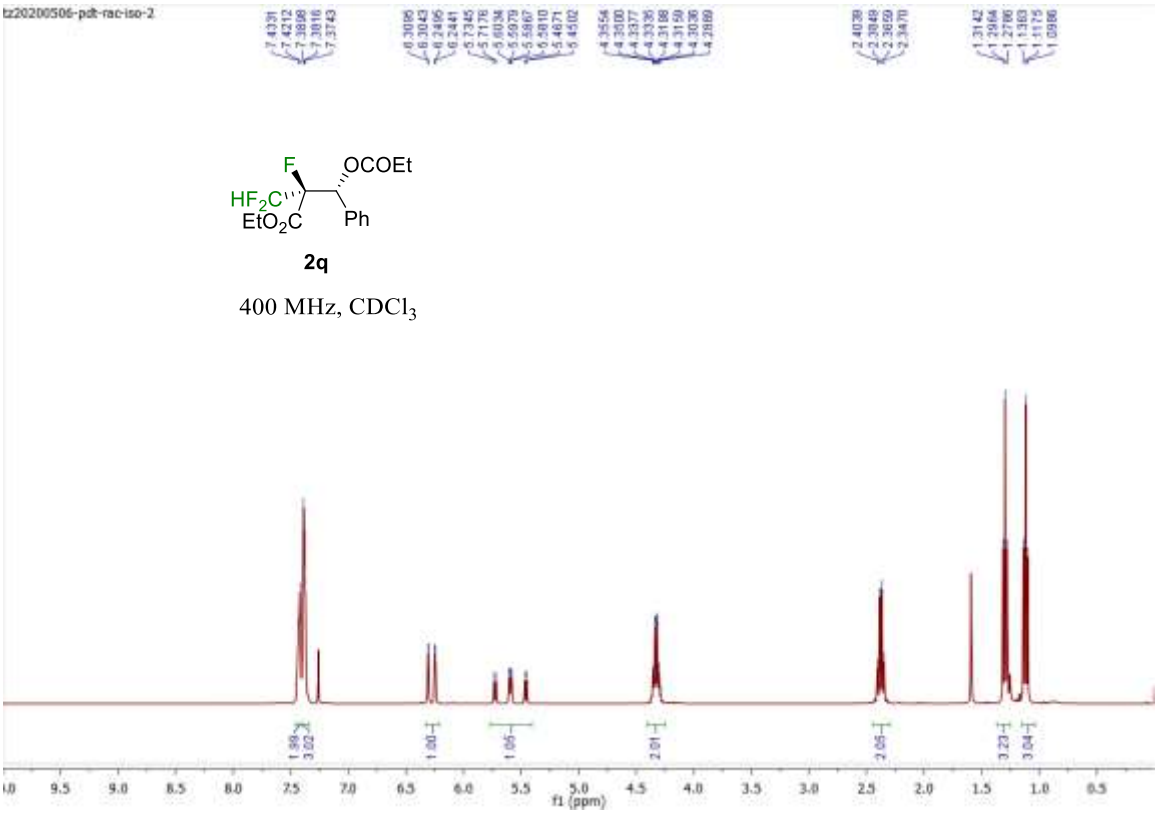
2p

101 MHz, $CDCl_3$



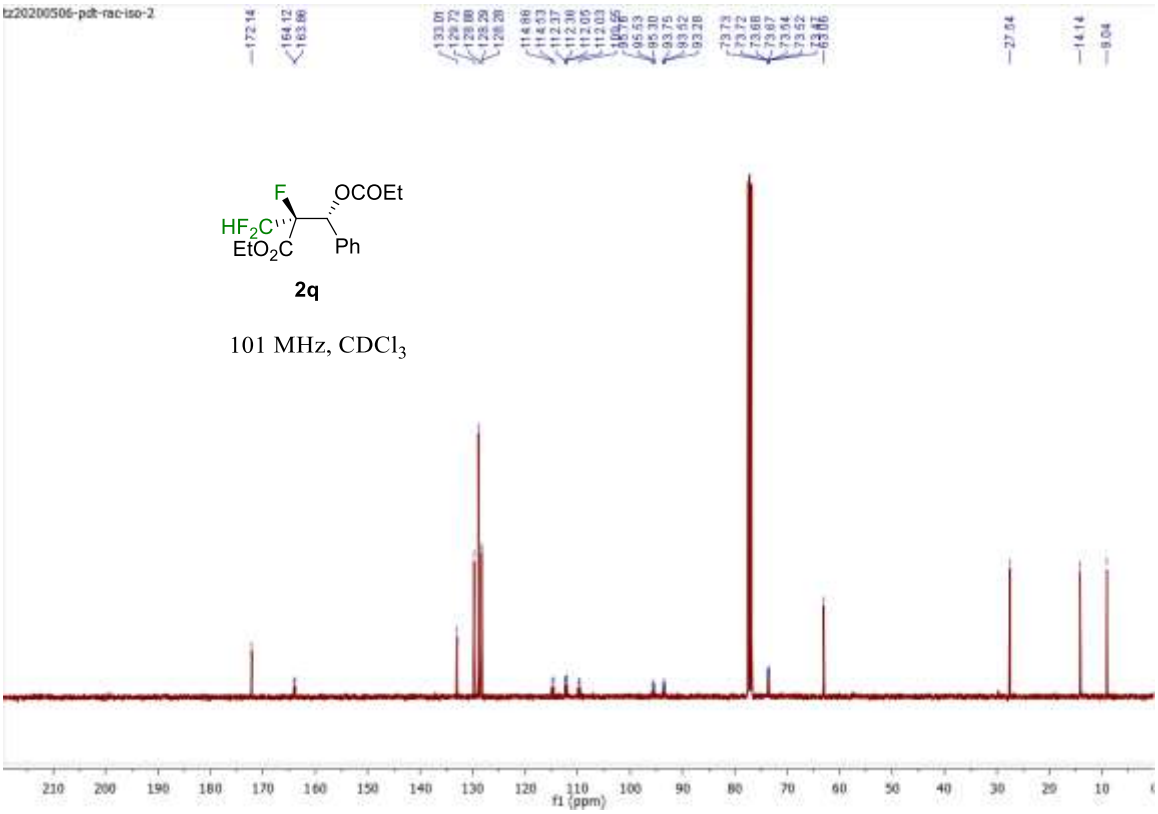
2p

376 MHz, $CDCl_3$



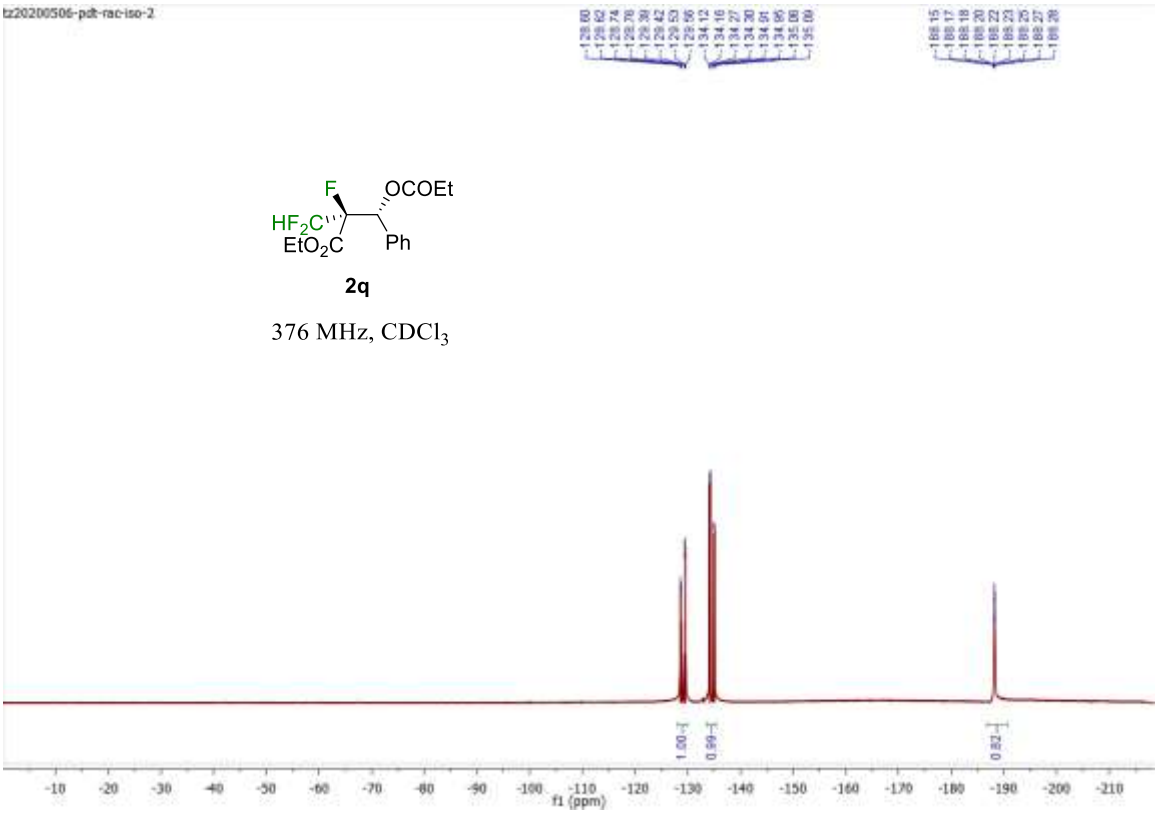
2q

400 MHz, $CDCl_3$



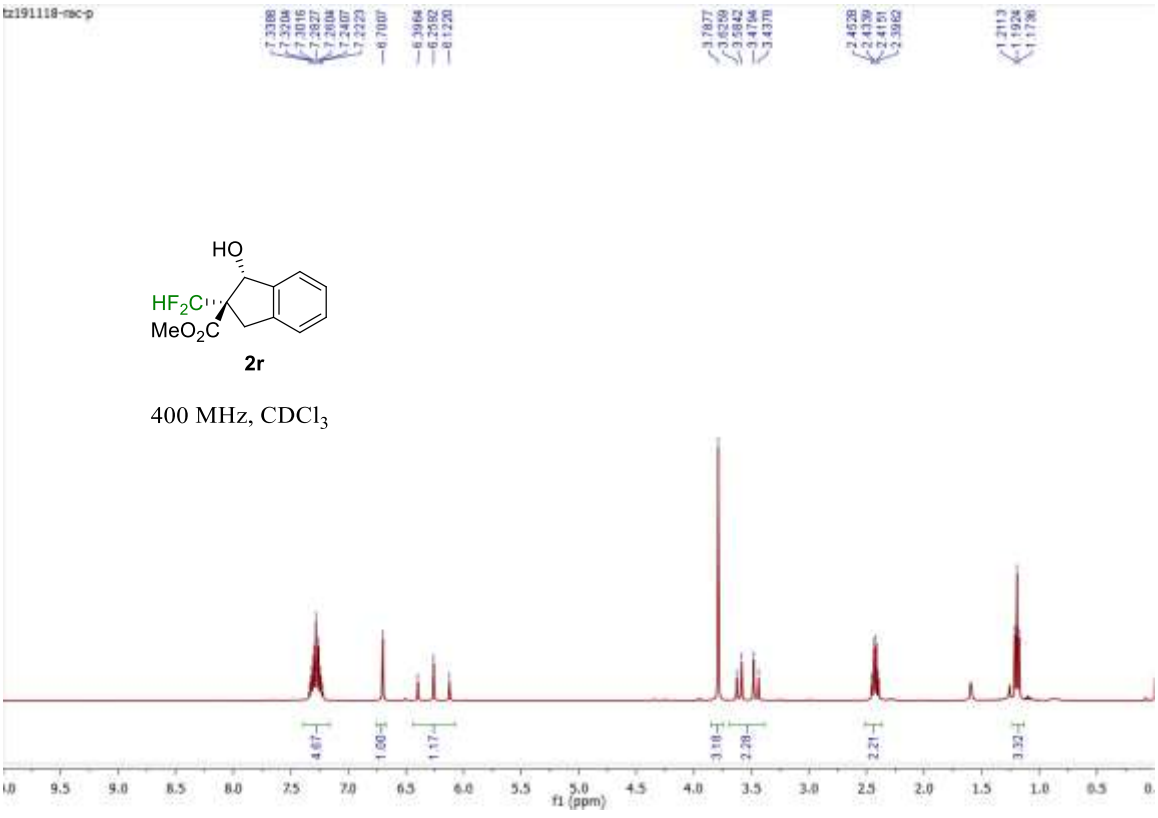
2q

101 MHz, $CDCl_3$



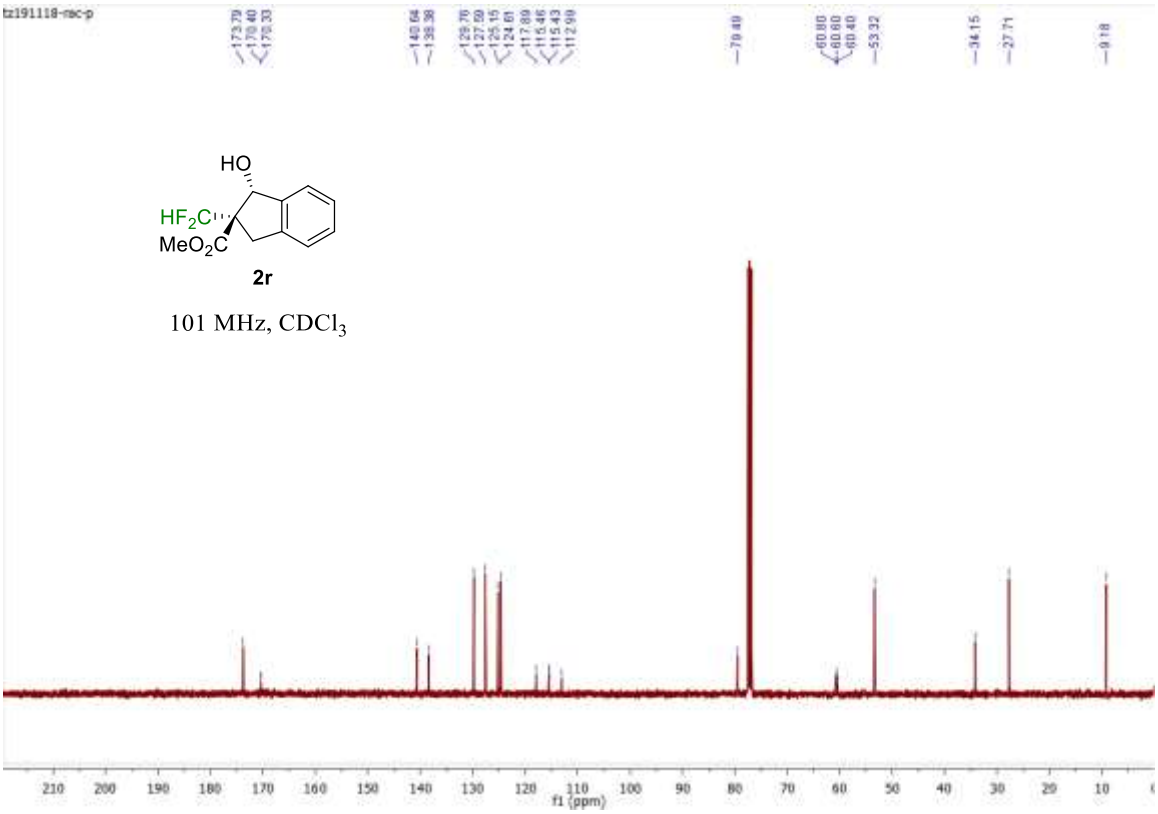
2q

376 MHz, $CDCl_3$



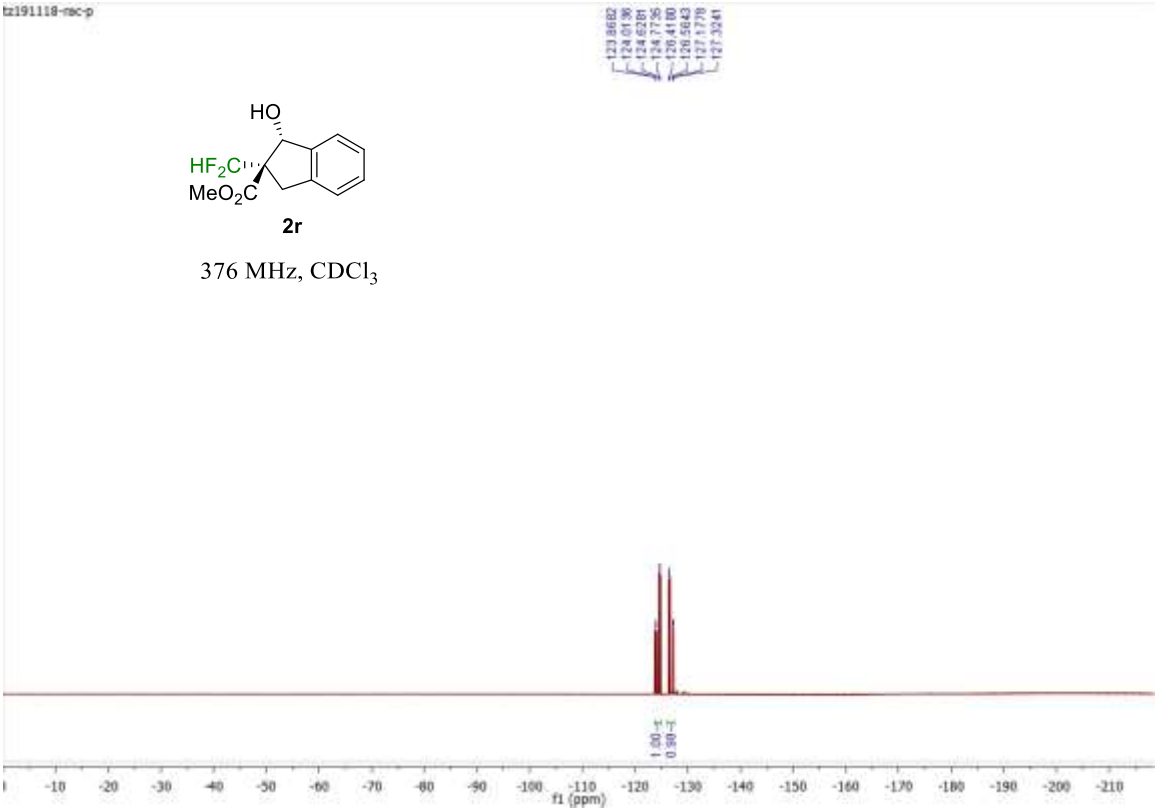
2r

400 MHz, $CDCl_3$



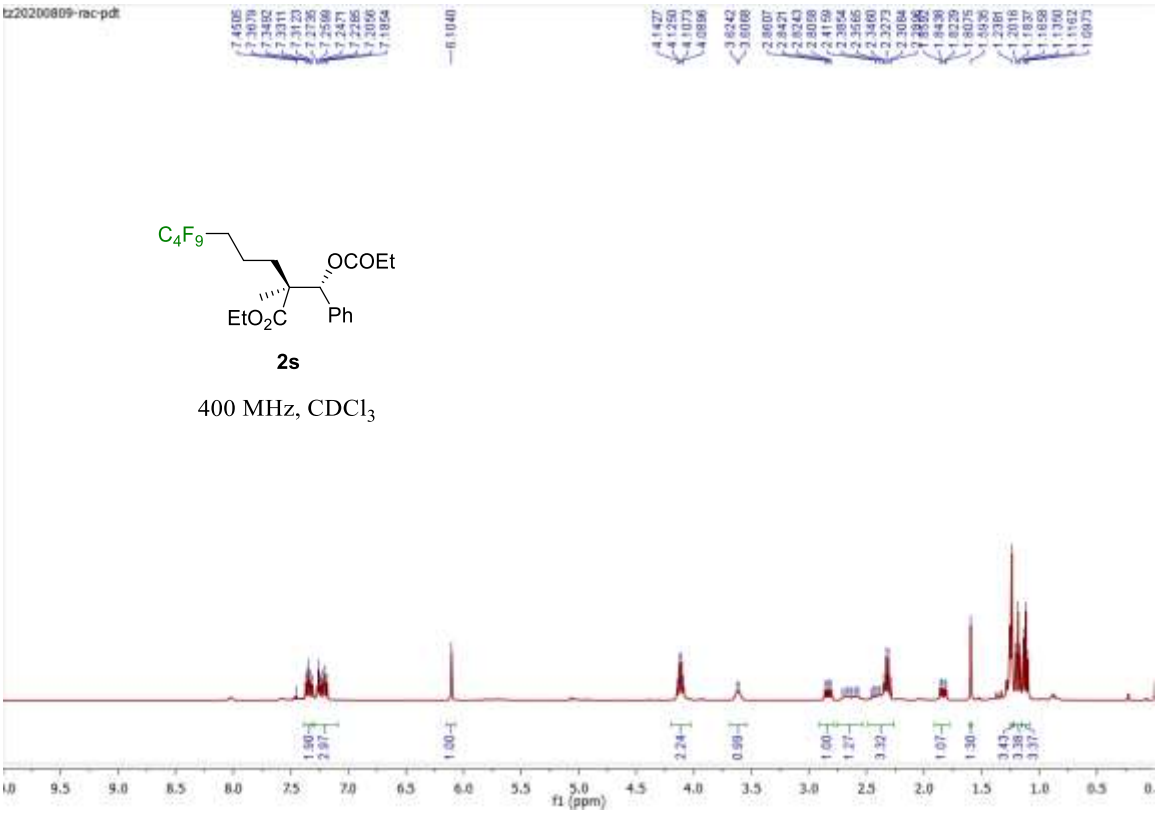
2r

101 MHz, $CDCl_3$



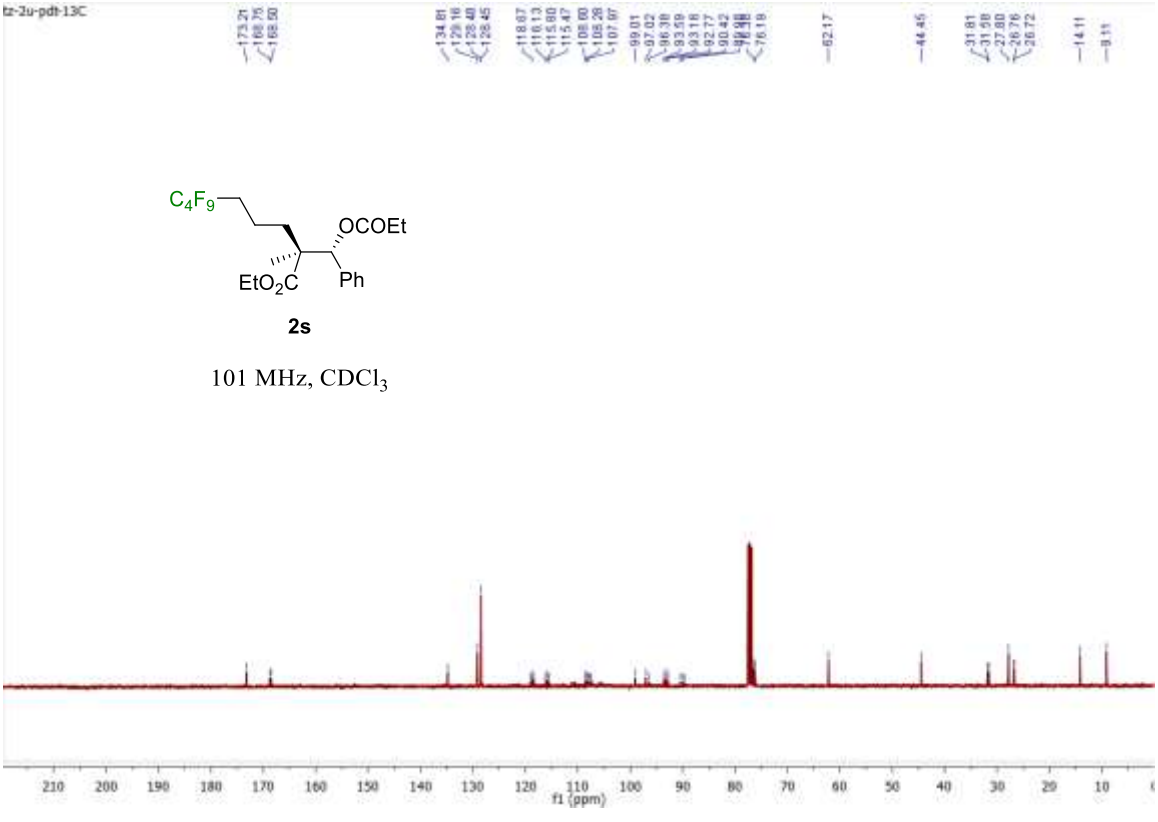
2r

376 MHz, $CDCl_3$



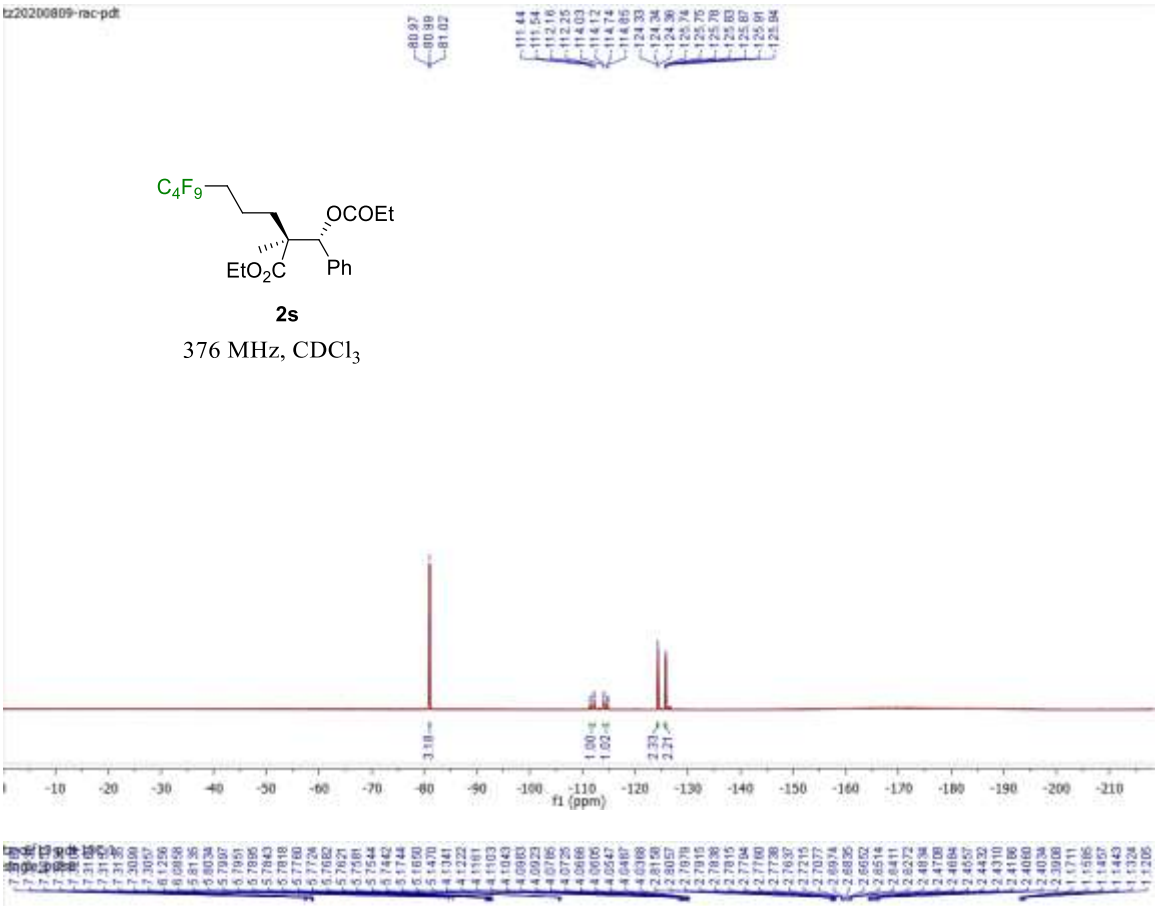
2s

400 MHz, $CDCl_3$



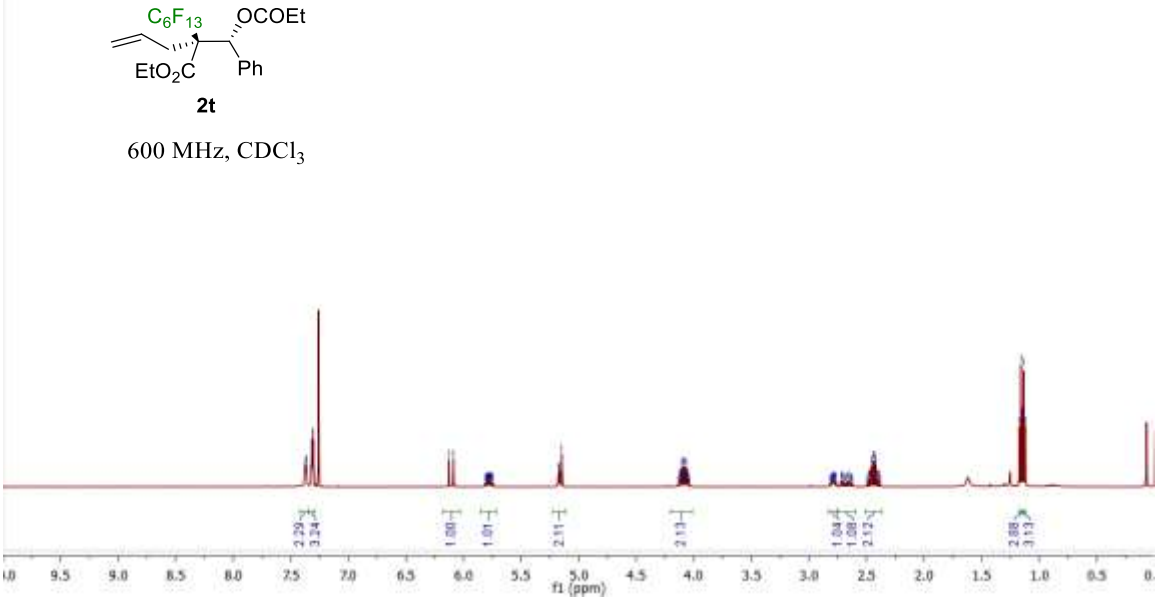
2s

101 MHz, $CDCl_3$



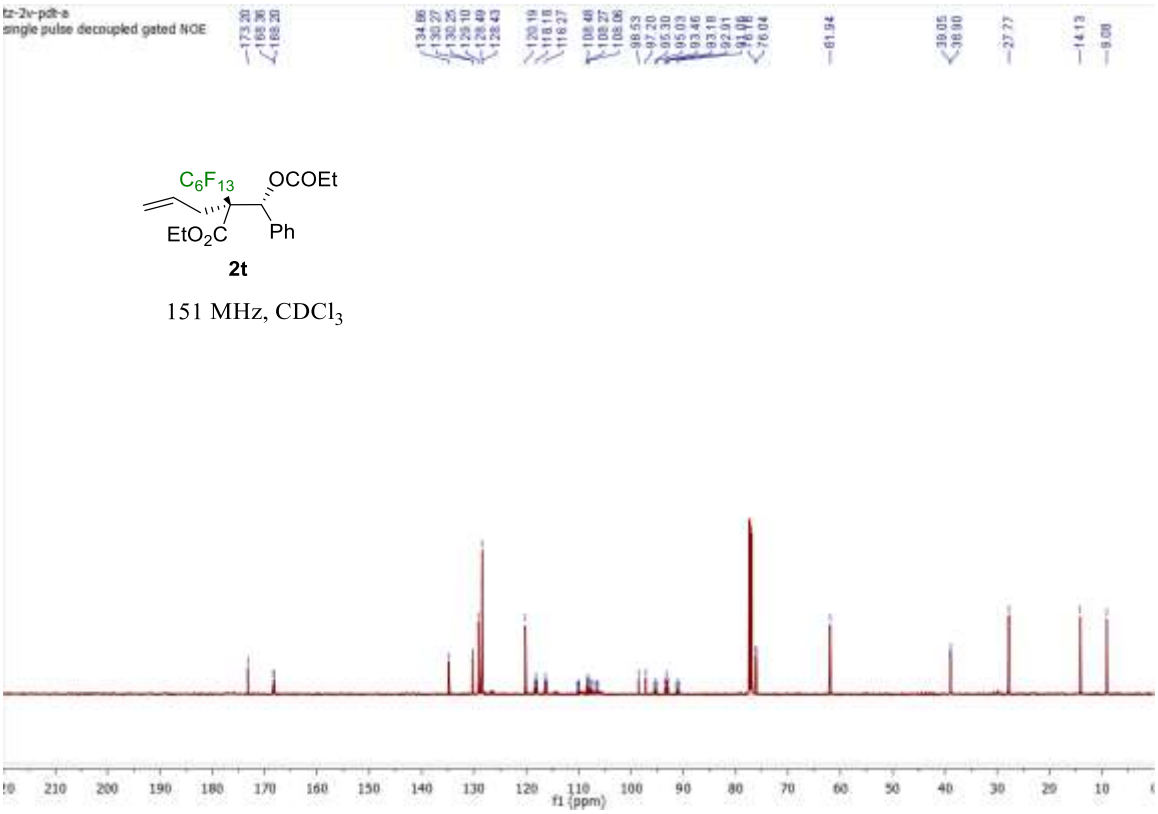
2s

376 MHz, $CDCl_3$



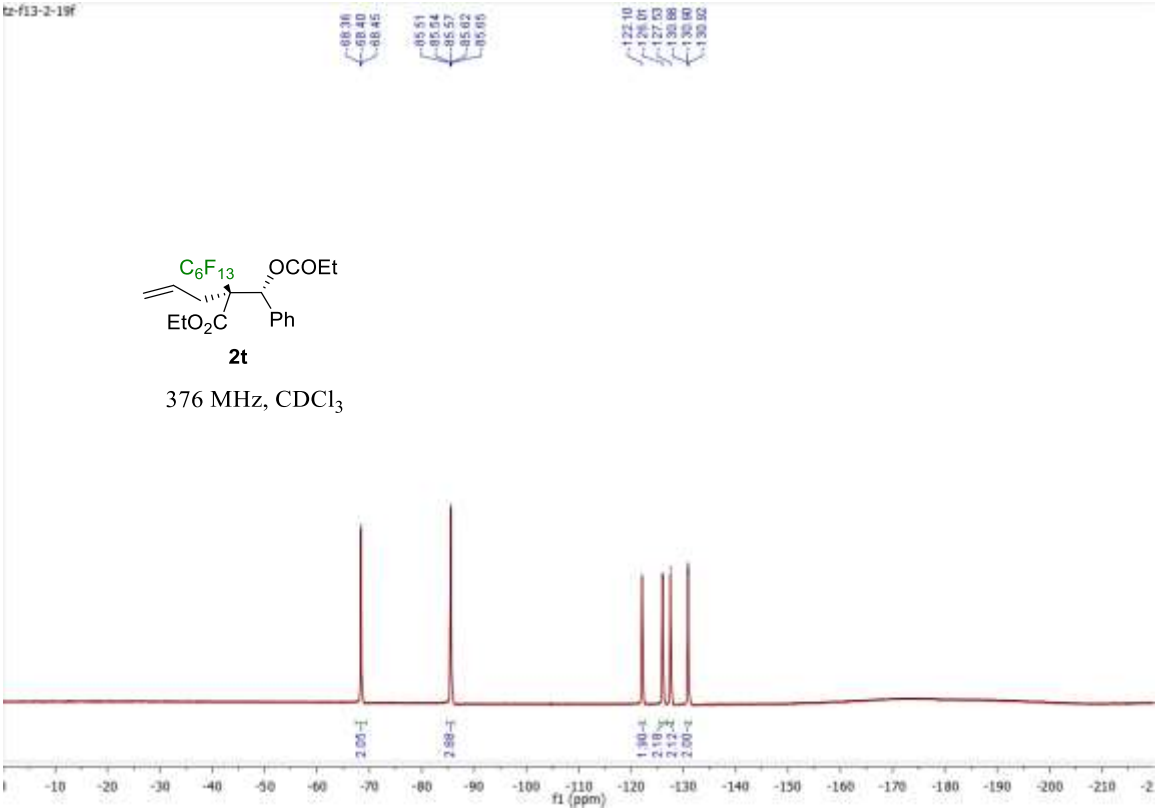
2t

600 MHz, $CDCl_3$



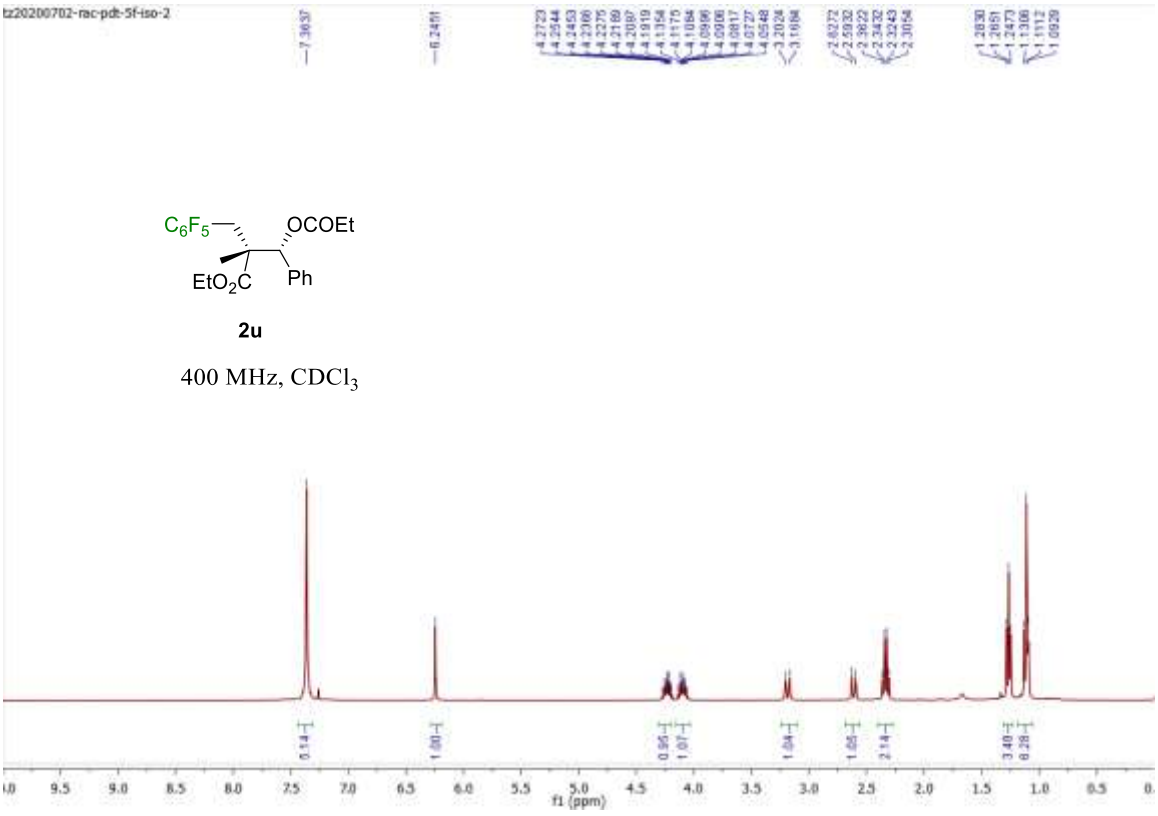
2t

151 MHz, $CDCl_3$



2t

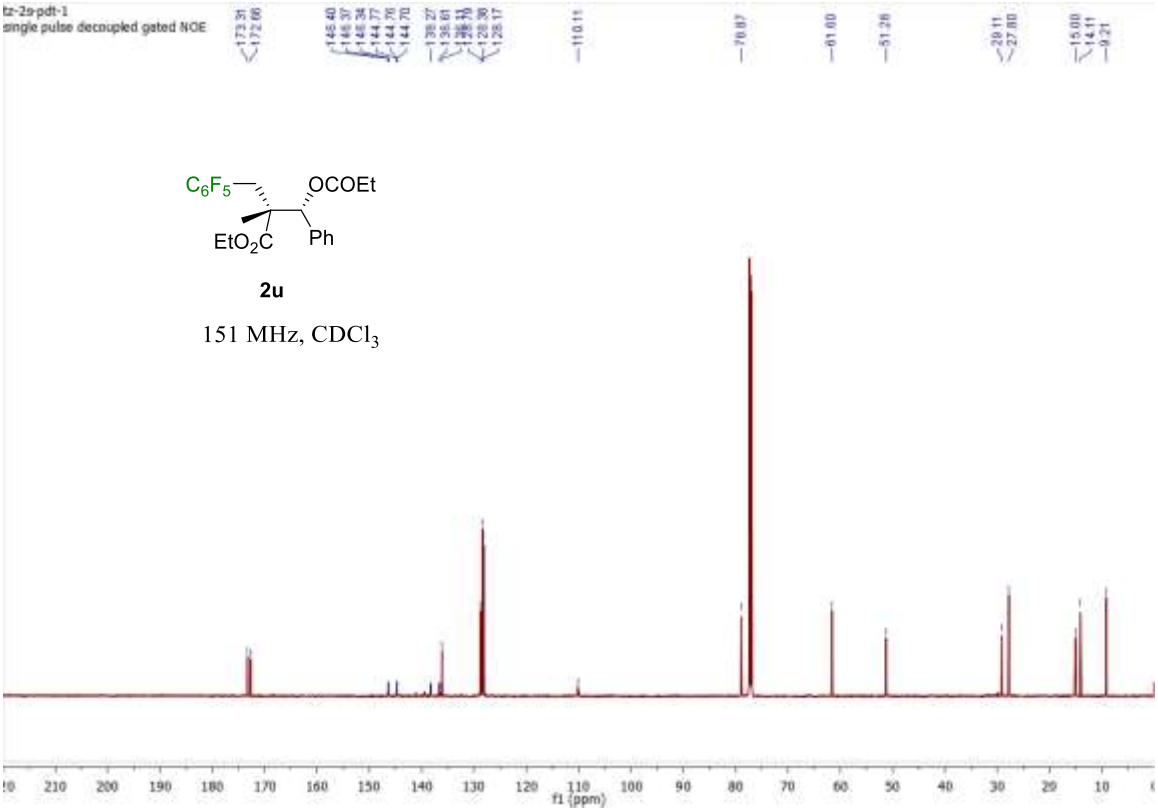
376 MHz, $CDCl_3$



C_6F_5, OCOEt, EtO_2C, Ph

2u

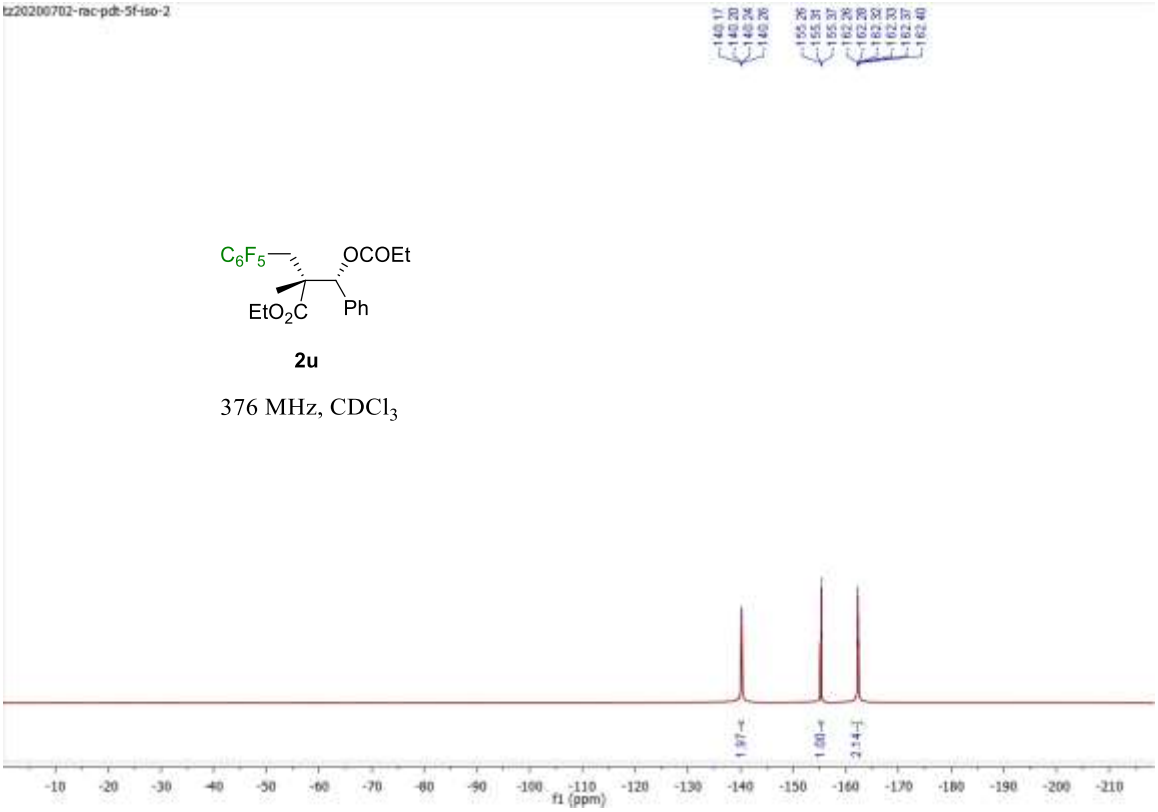
400 MHz, $CDCl_3$



C_6F_5, OCOEt, EtO_2C, Ph

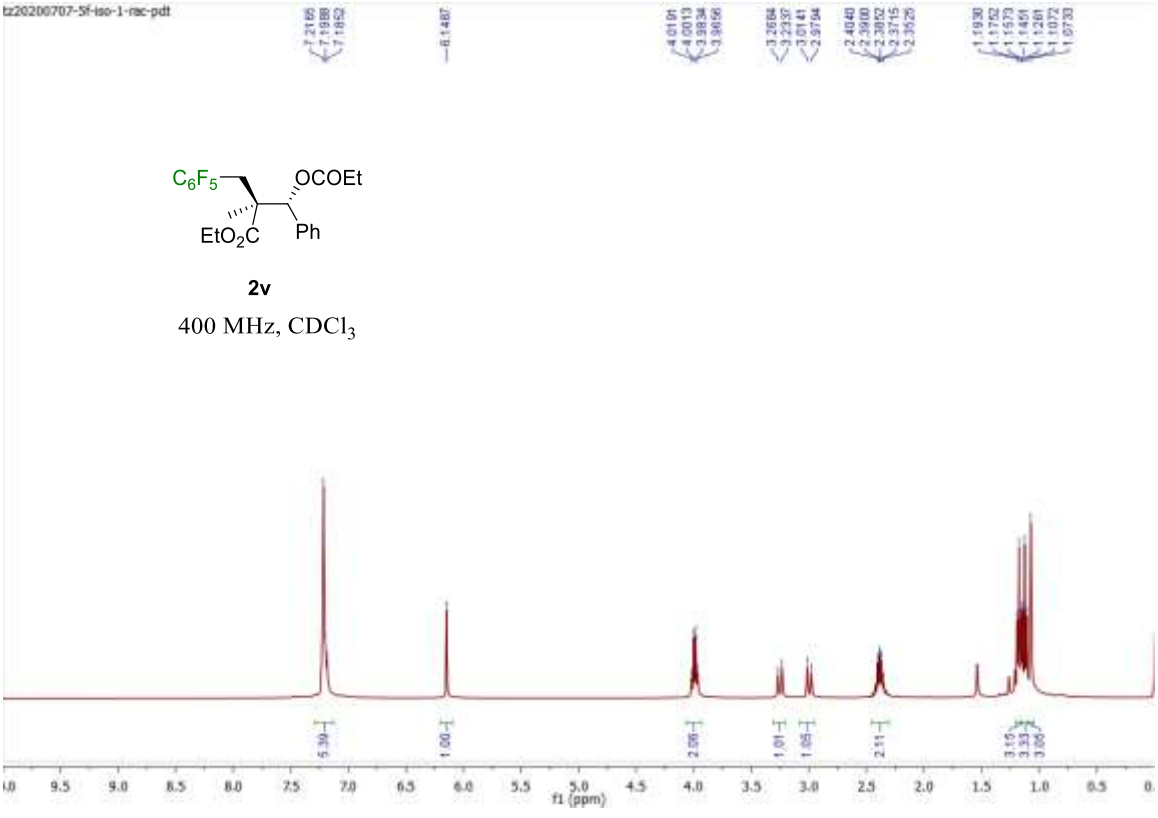
2u

151 MHz, $CDCl_3$



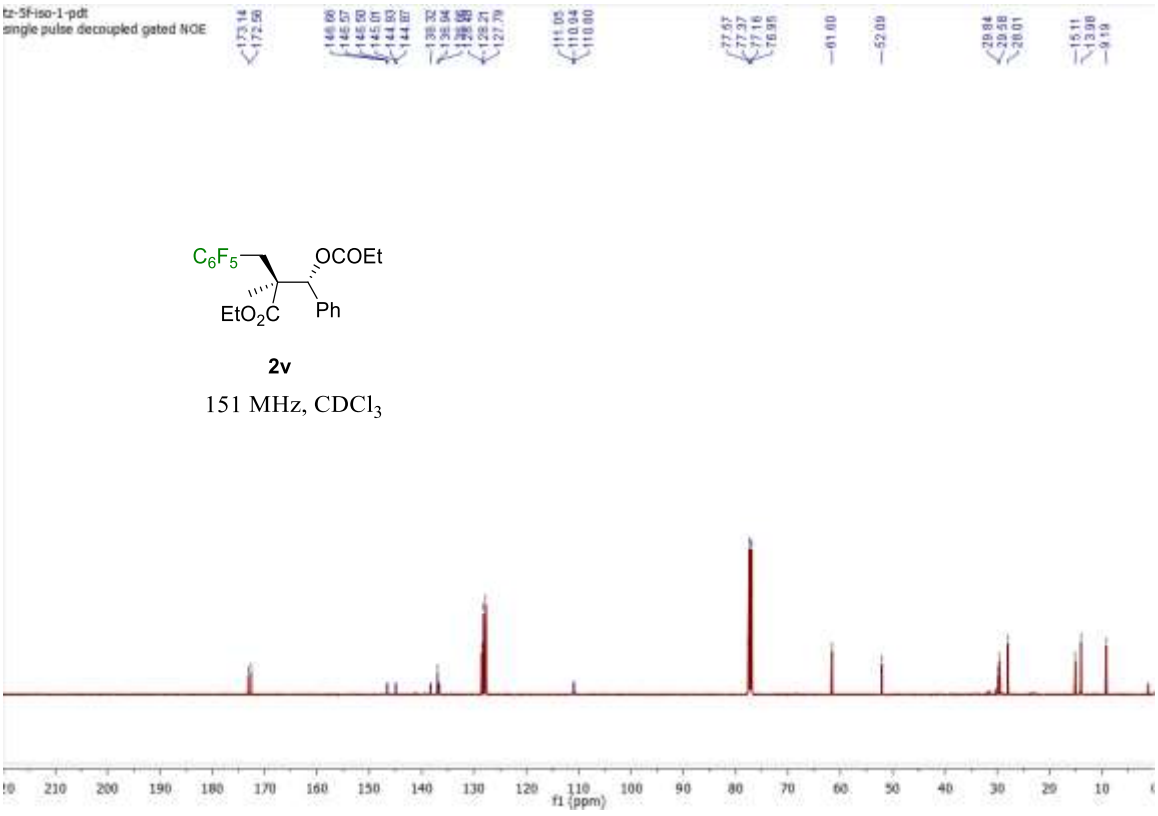
2u

376 MHz, $CDCl_3$



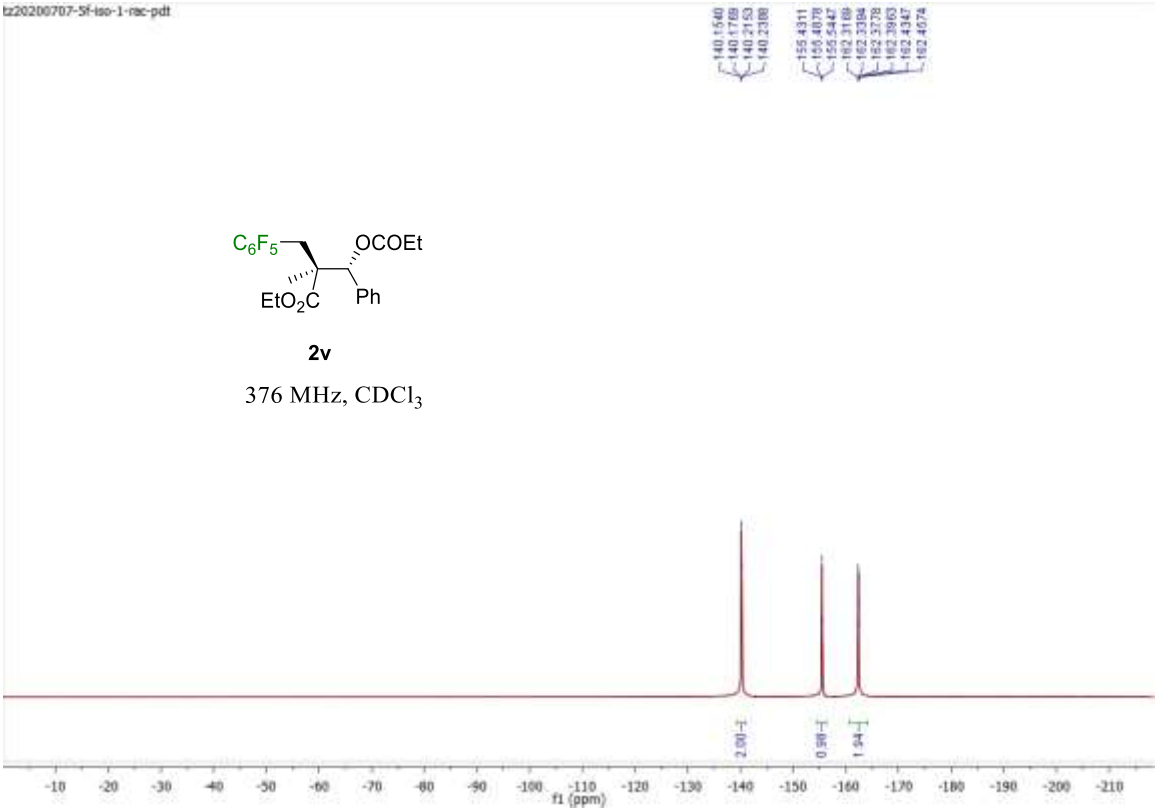
2v

400 MHz, $CDCl_3$



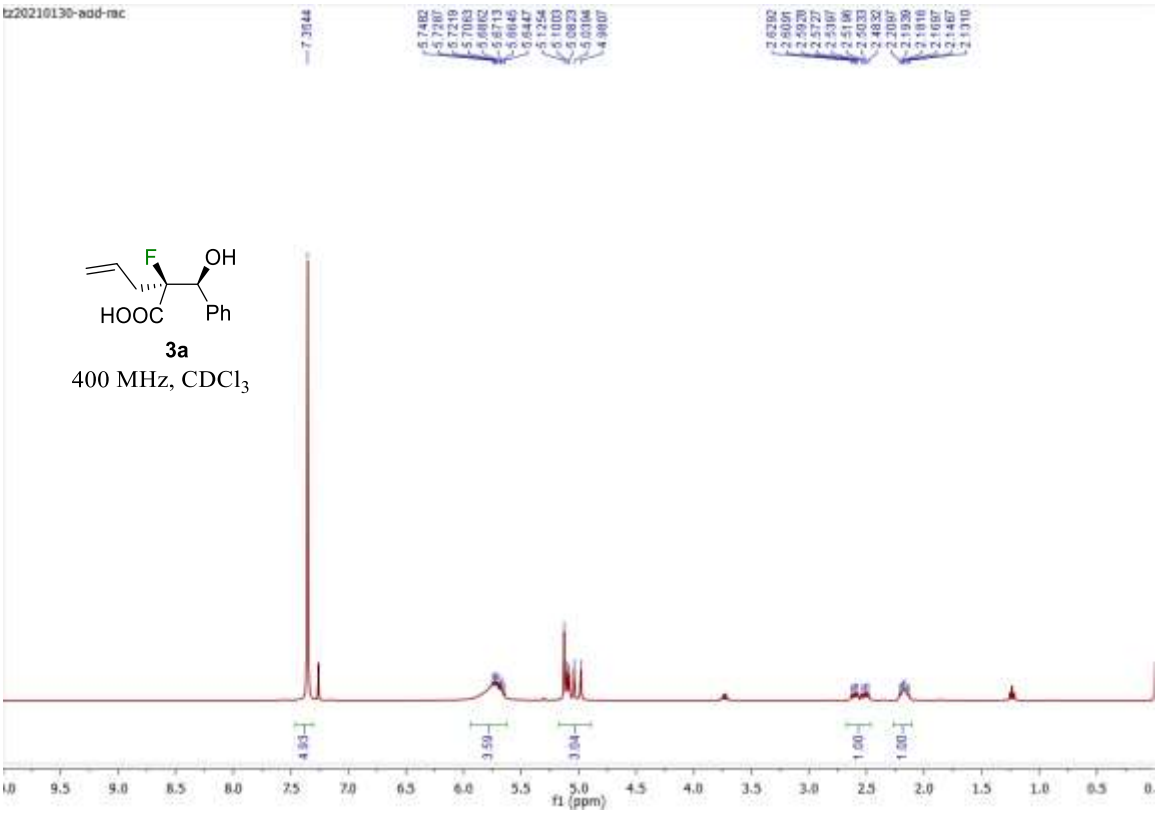
2v

151 MHz, $CDCl_3$



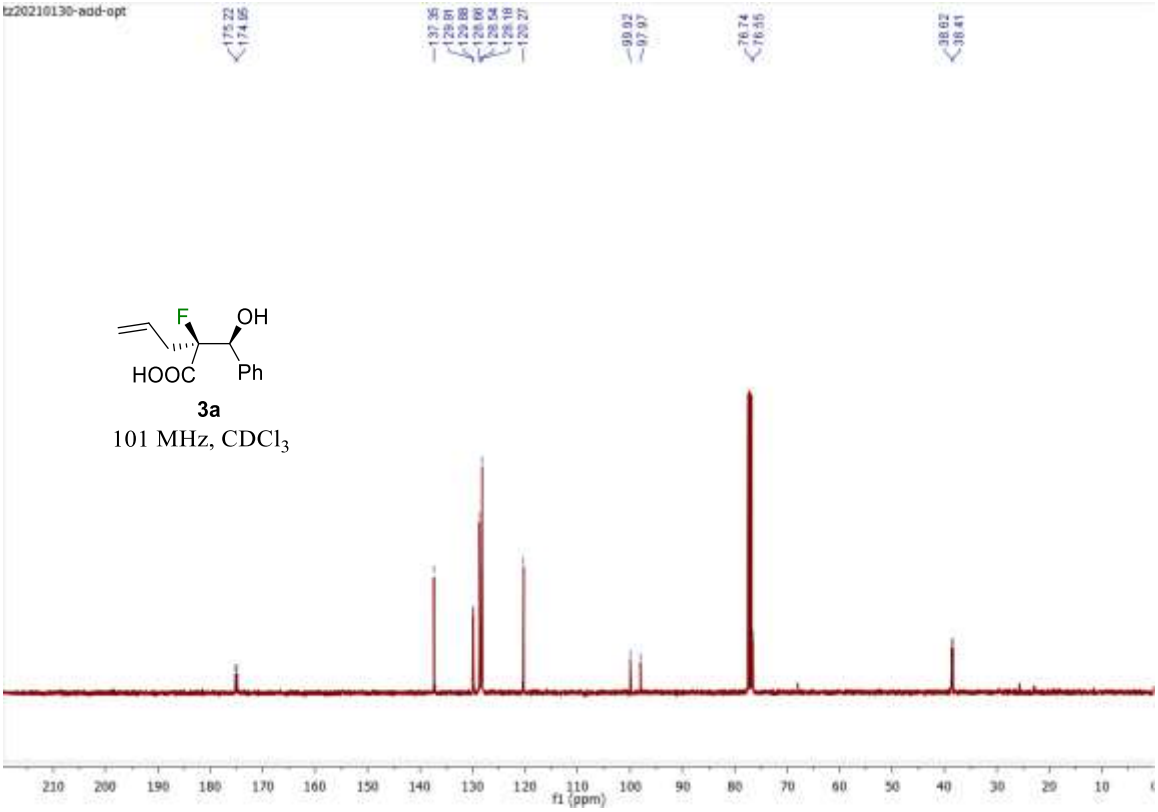
2v

376 MHz, $CDCl_3$



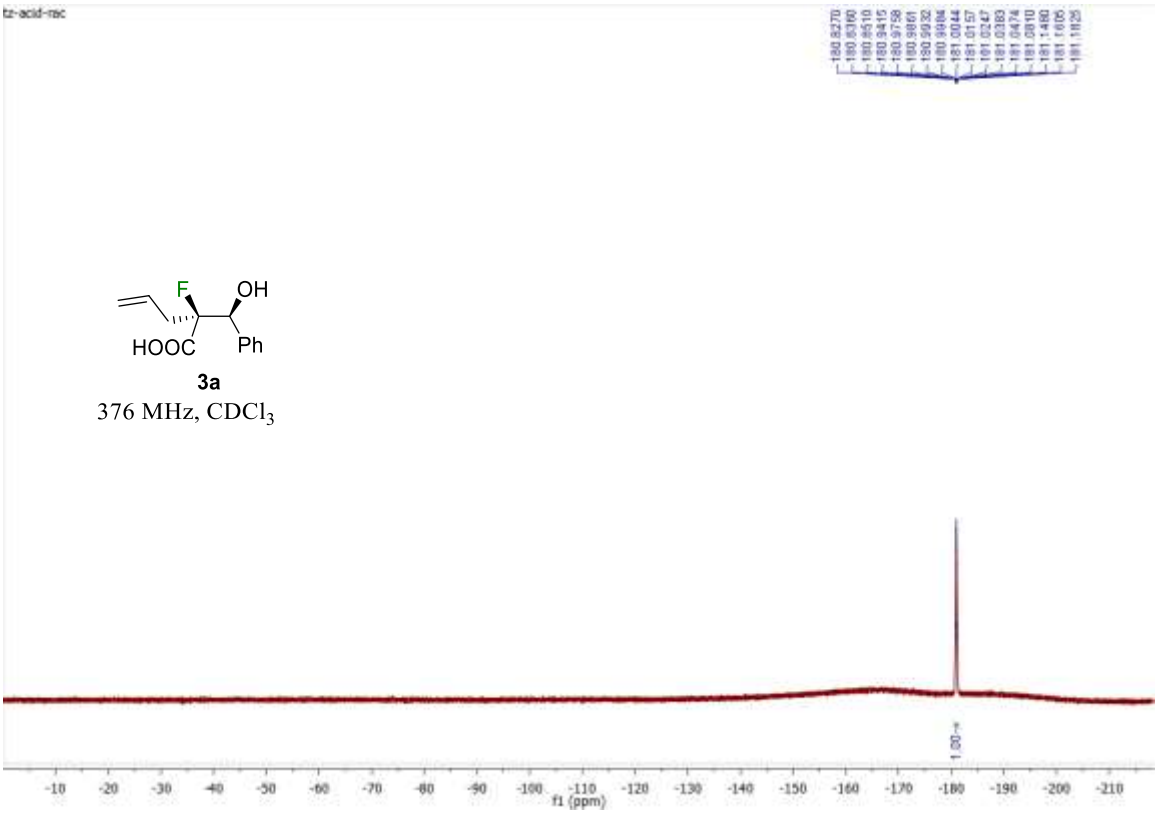
3a

400 MHz, $CDCl_3$



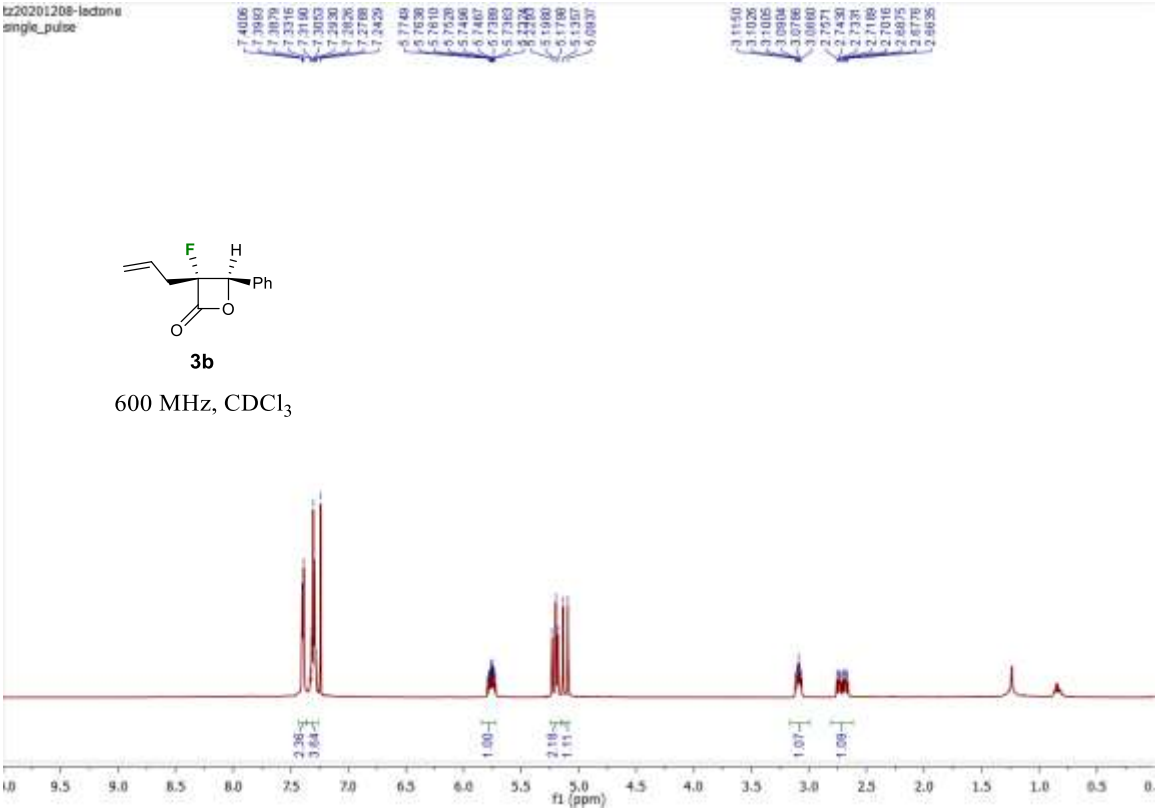
3a

101 MHz, $CDCl_3$



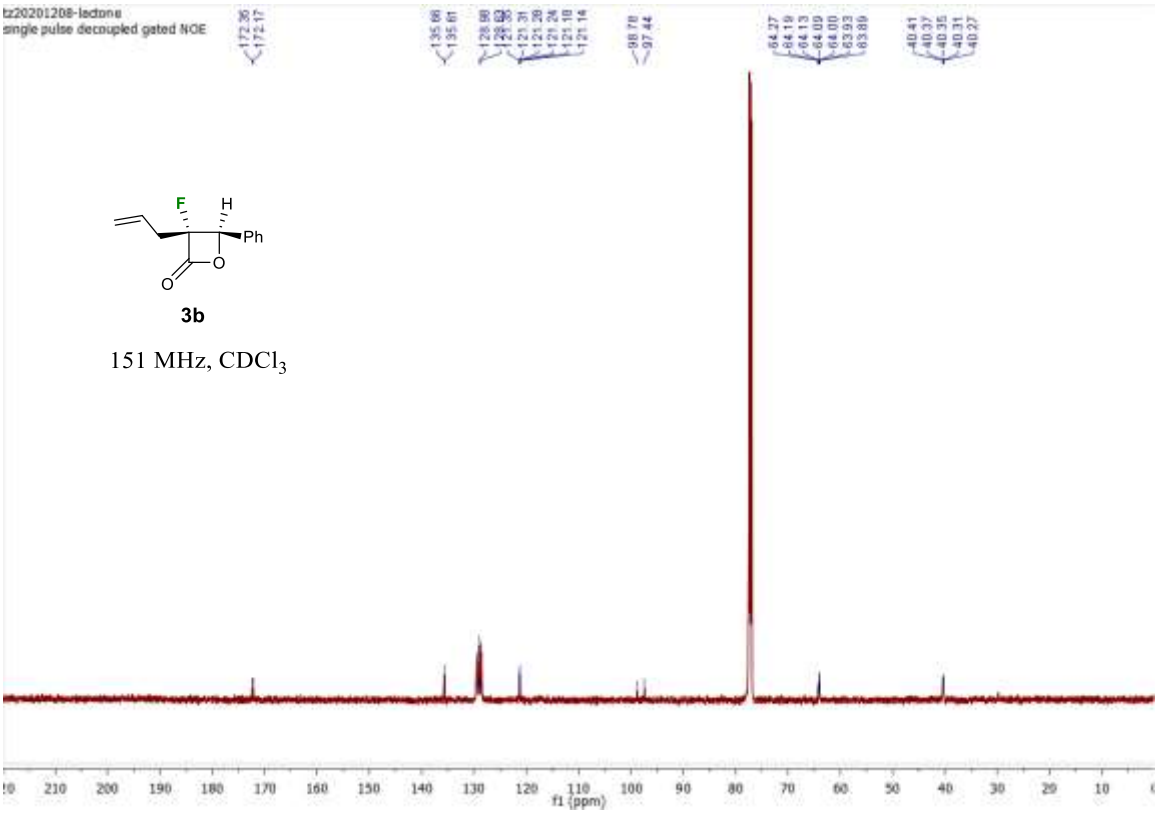
3a

376 MHz, $CDCl_3$



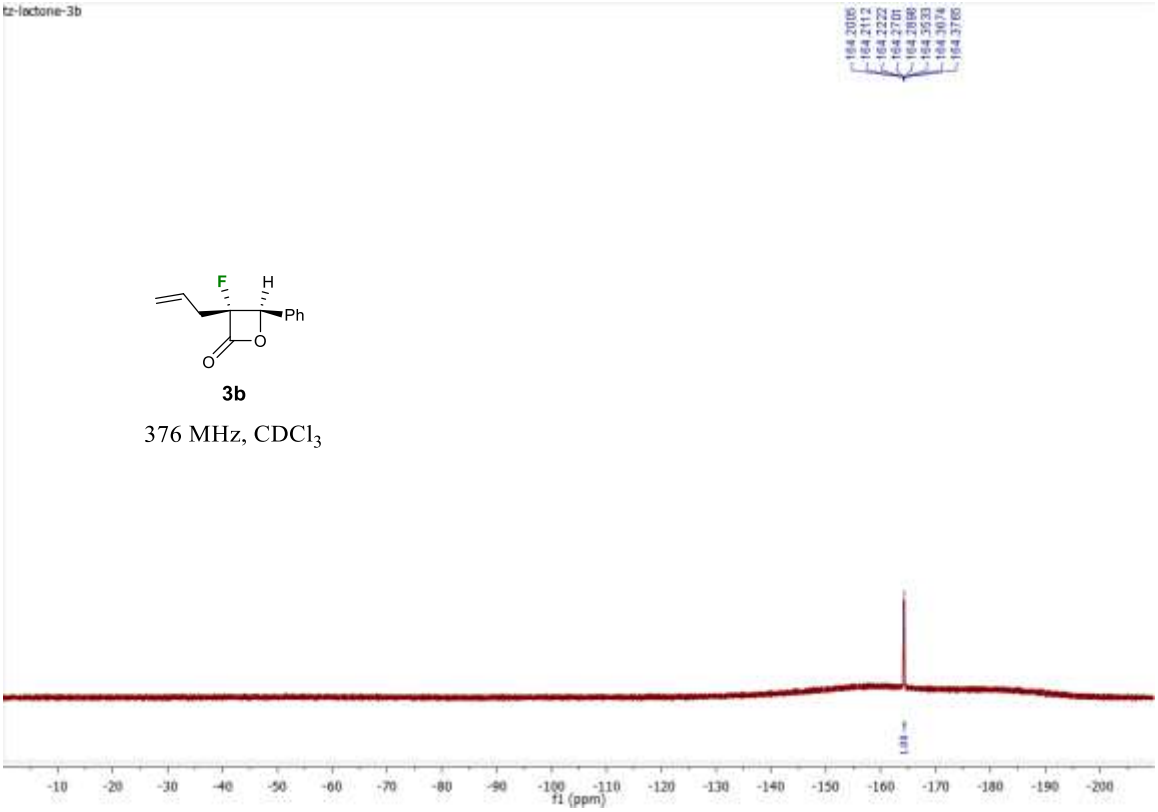
3b

600 MHz, $CDCl_3$



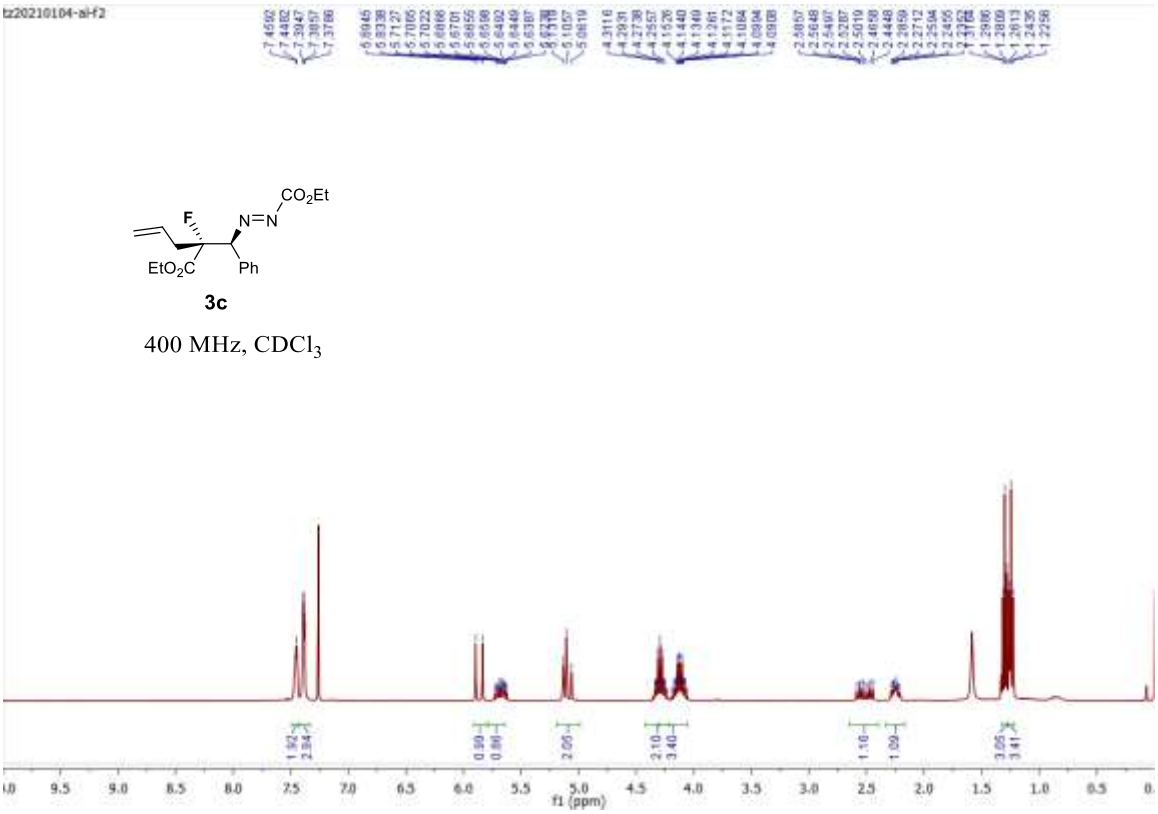
3b

151 MHz, $CDCl_3$



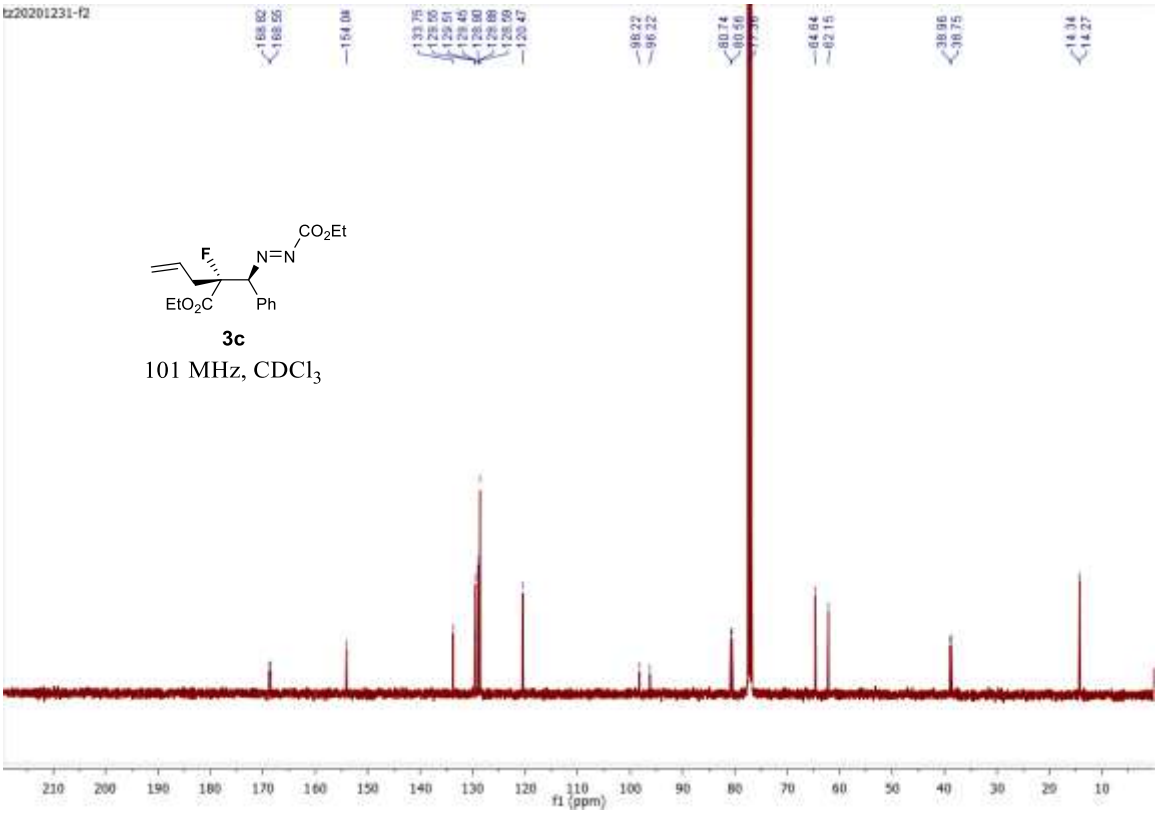
3b

376 MHz, $CDCl_3$



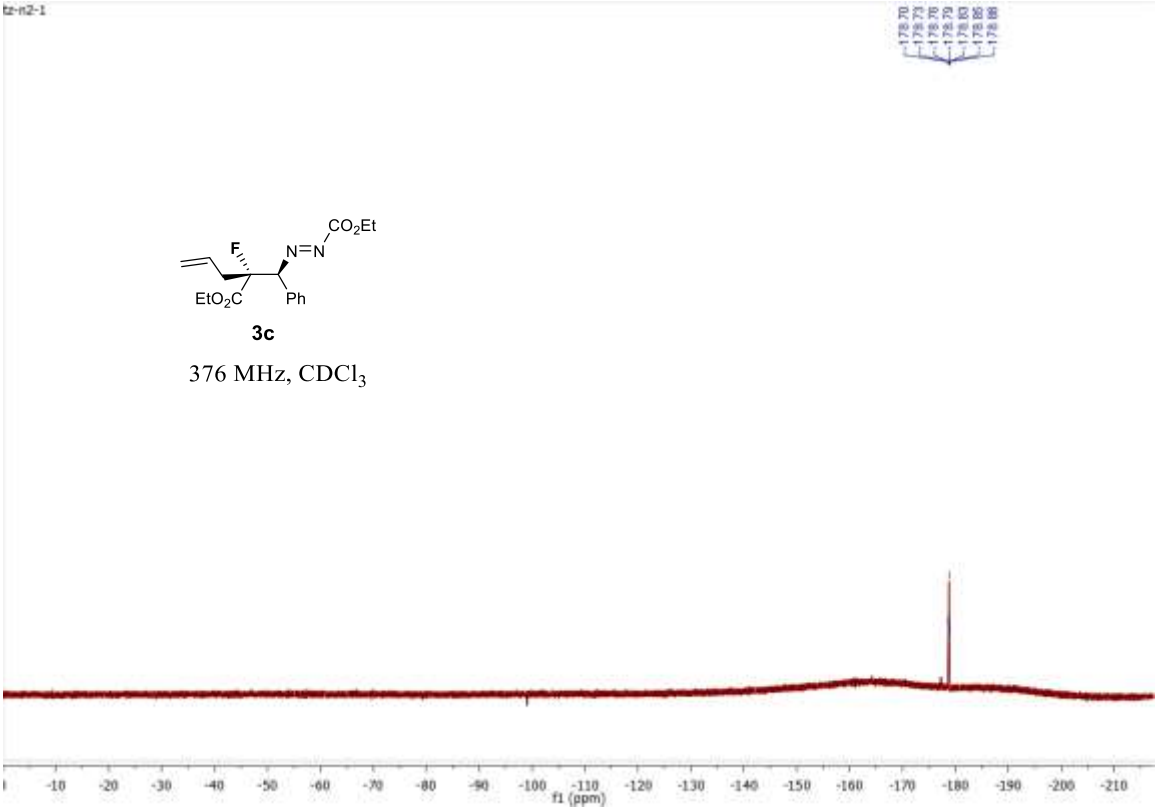
3c

400 MHz, $CDCl_3$



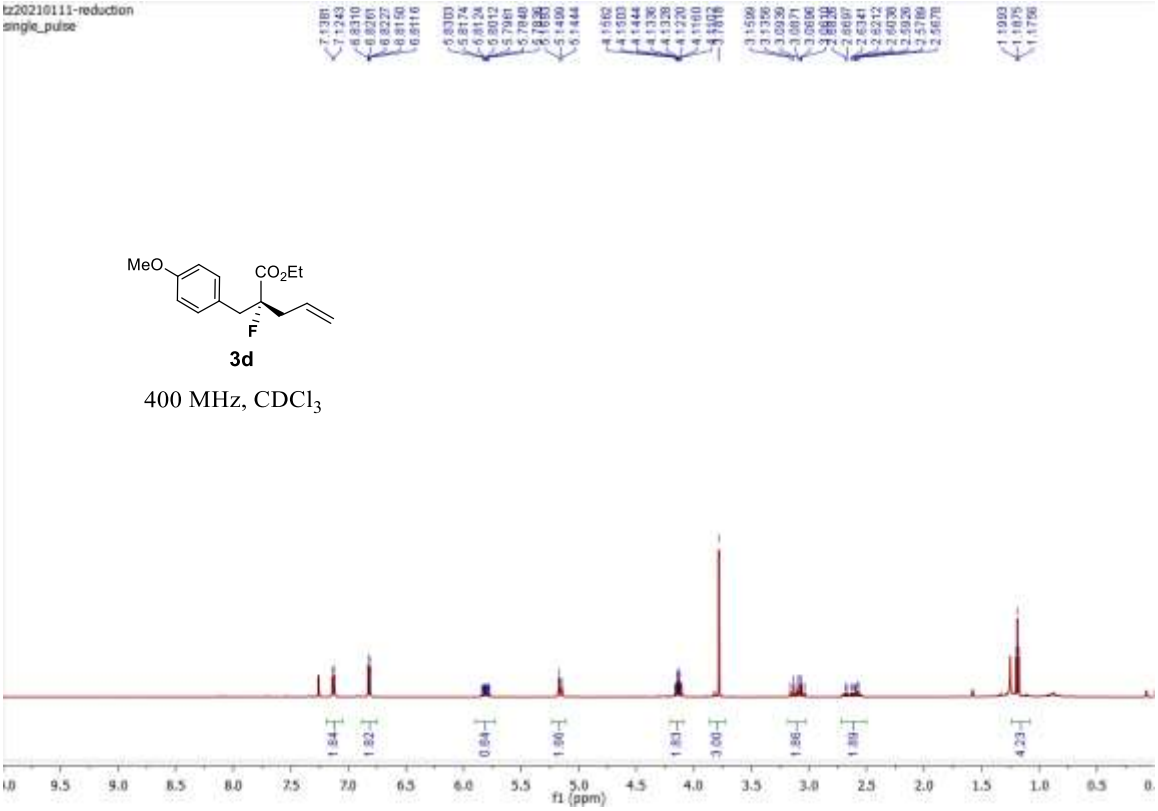
3c

101 MHz, $CDCl_3$



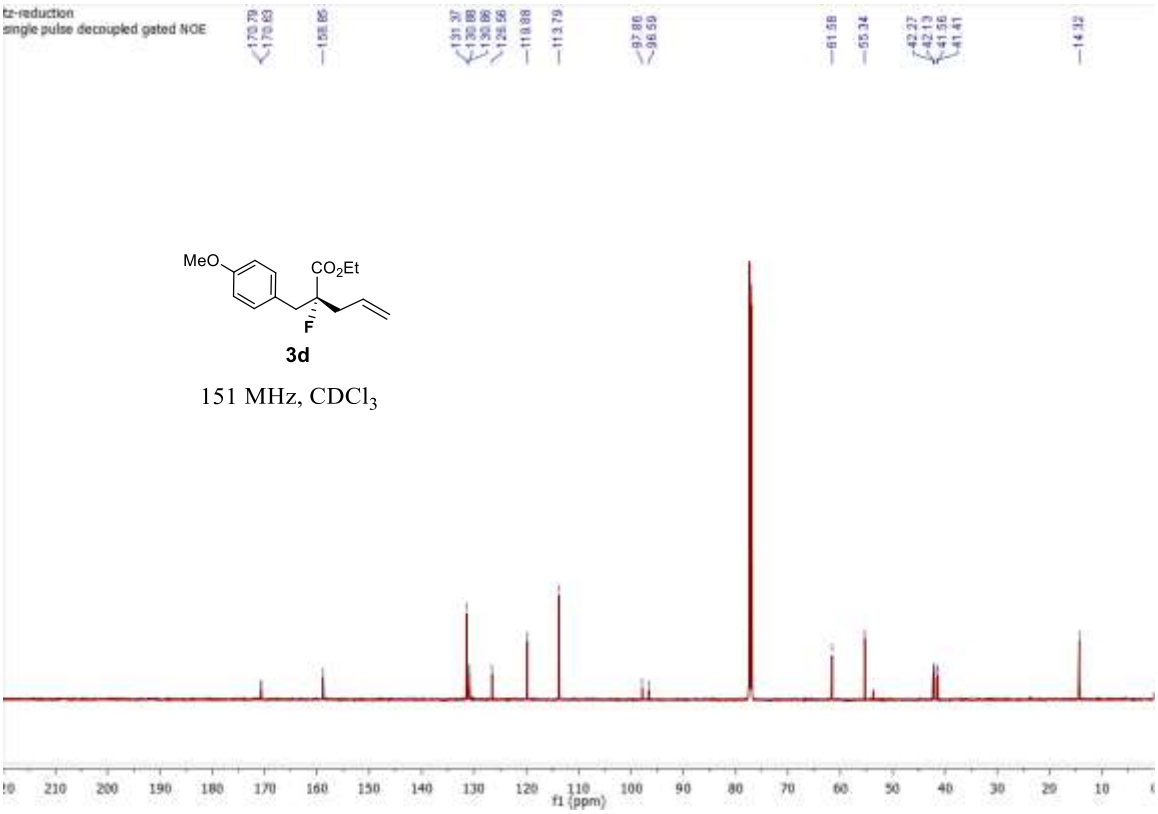
3c

376 MHz, $CDCl_3$



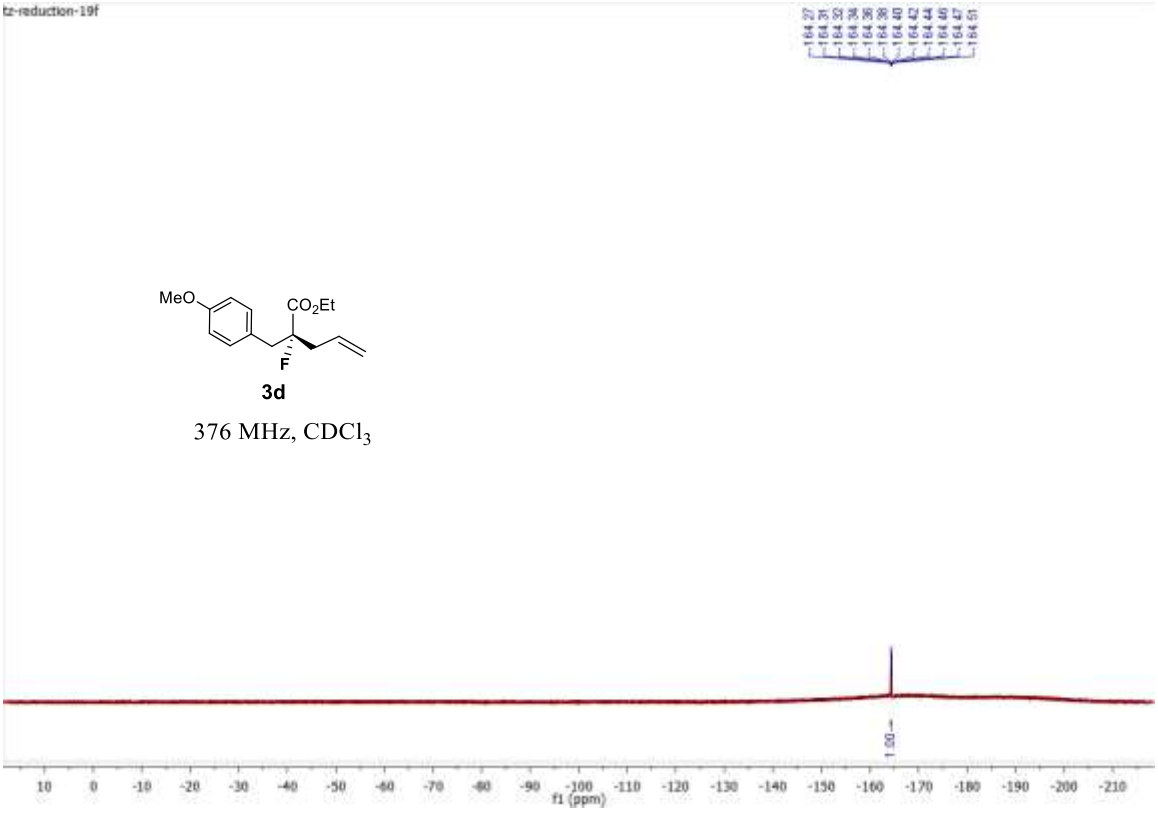
3d

400 MHz, $CDCl_3$



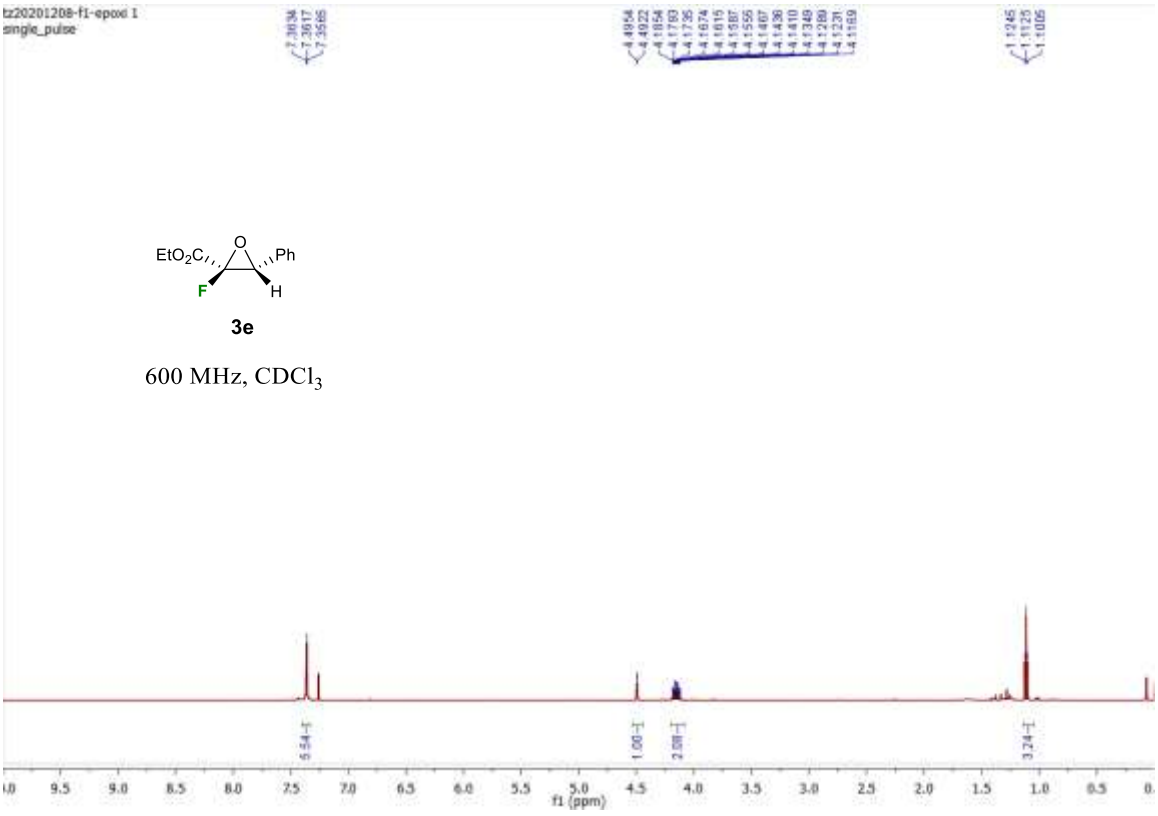
3d

151 MHz, $CDCl_3$



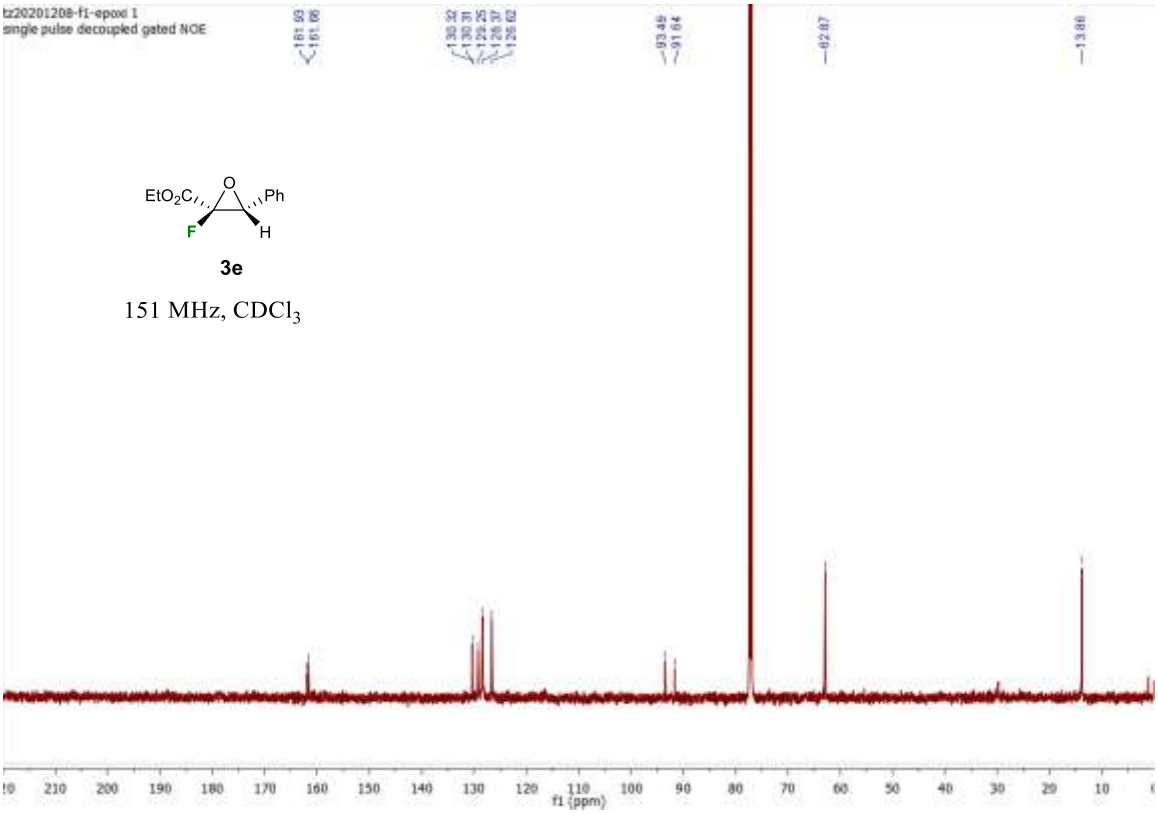
3d

376 MHz, $CDCl_3$



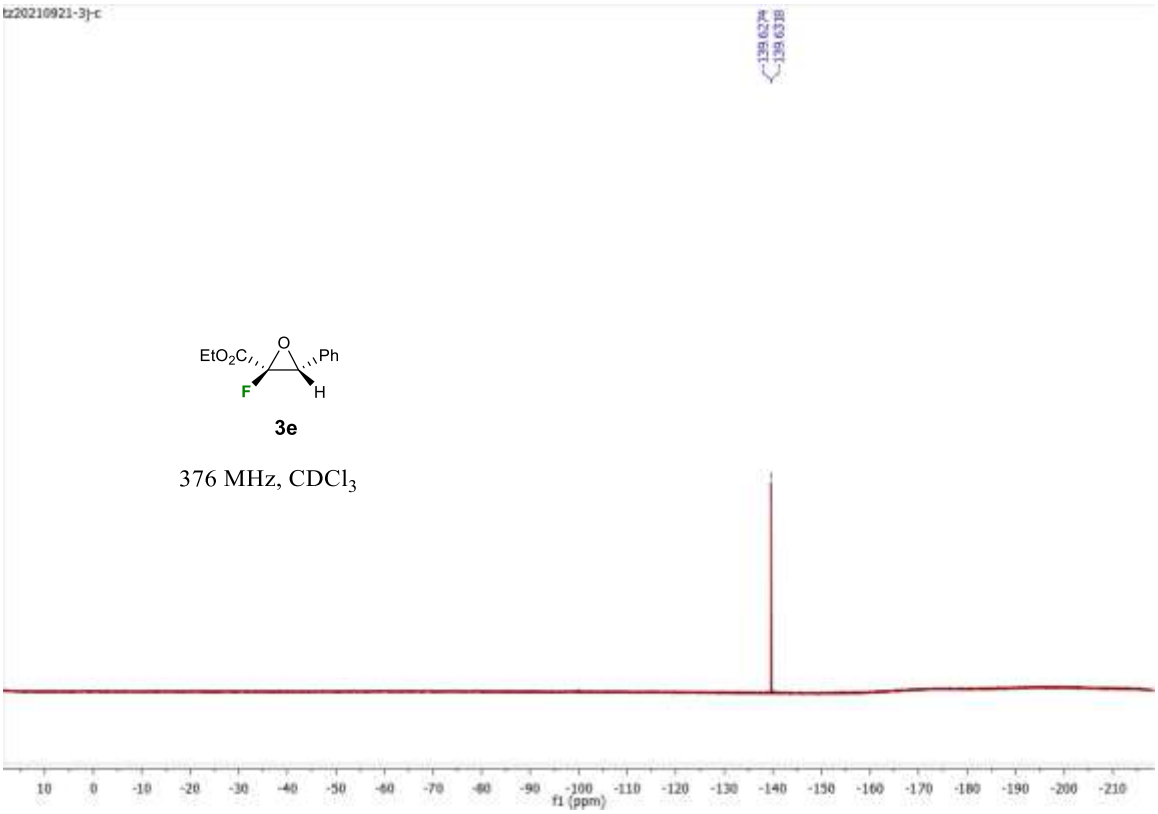
3e

600 MHz, $CDCl_3$



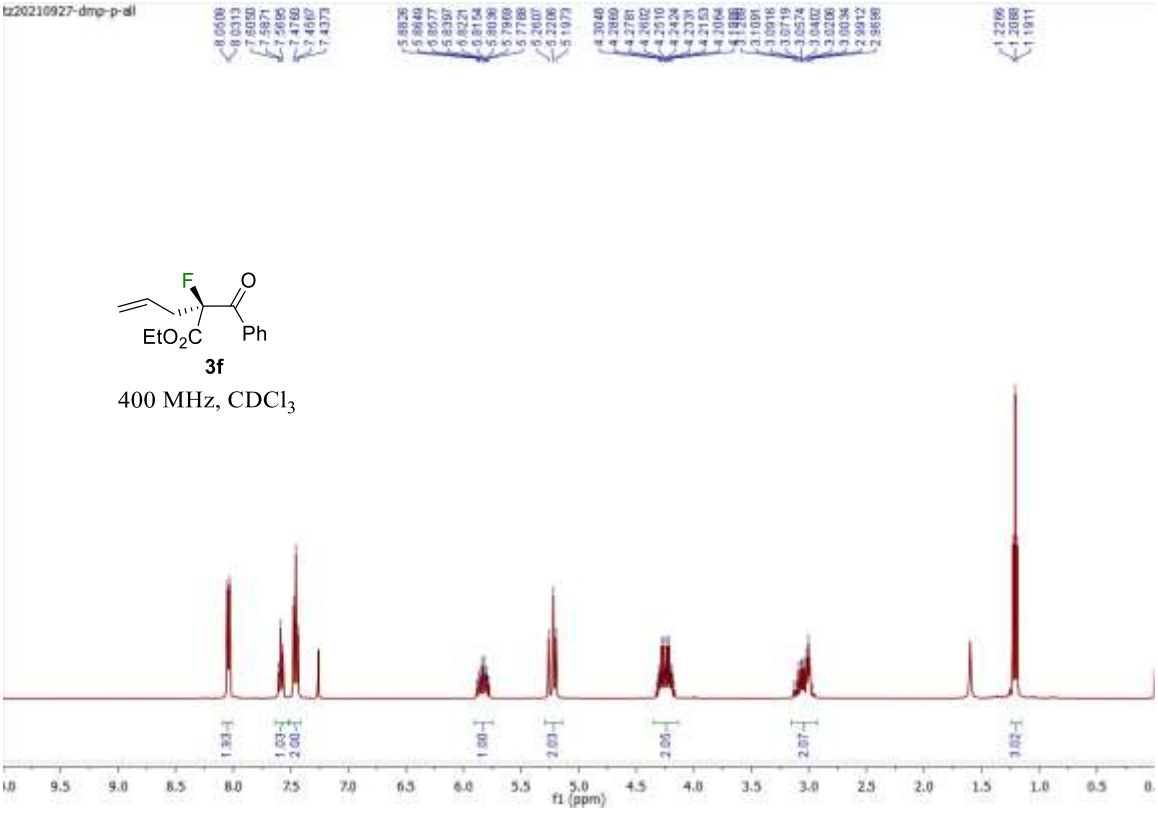
3e

151 MHz, $CDCl_3$



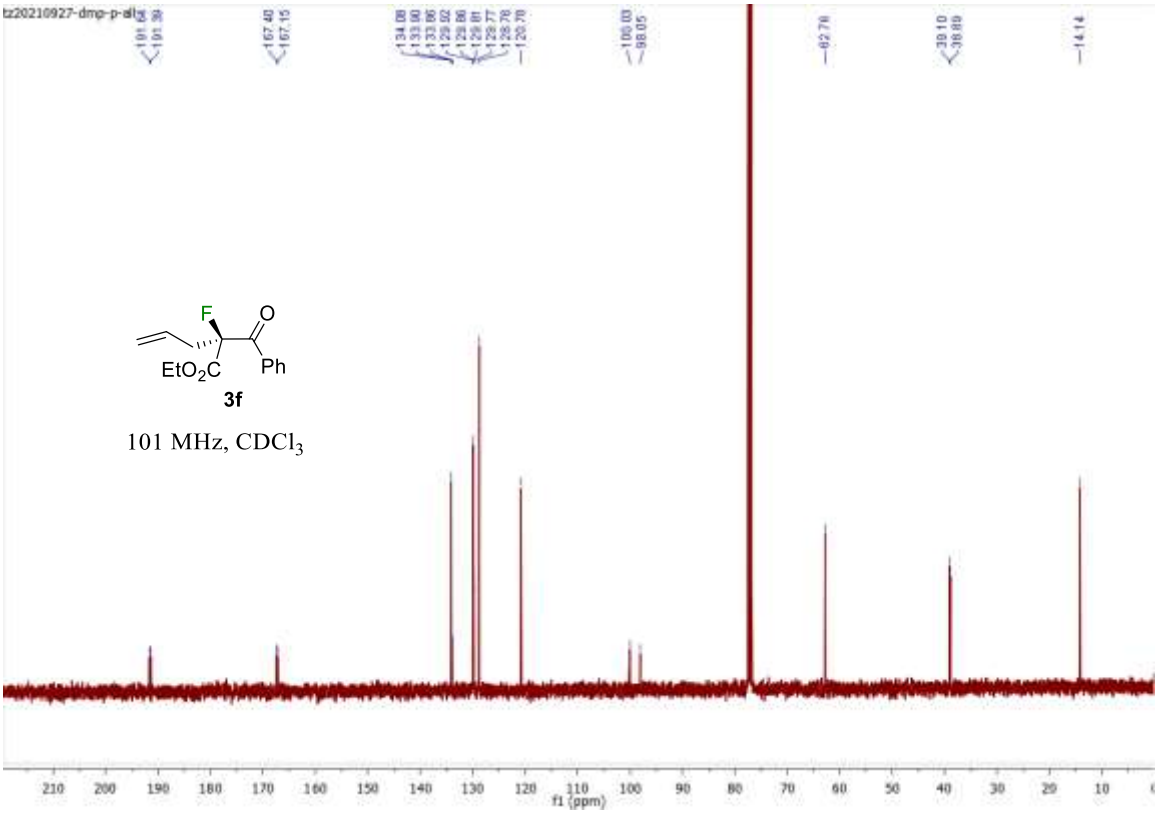
3e

376 MHz, $CDCl_3$

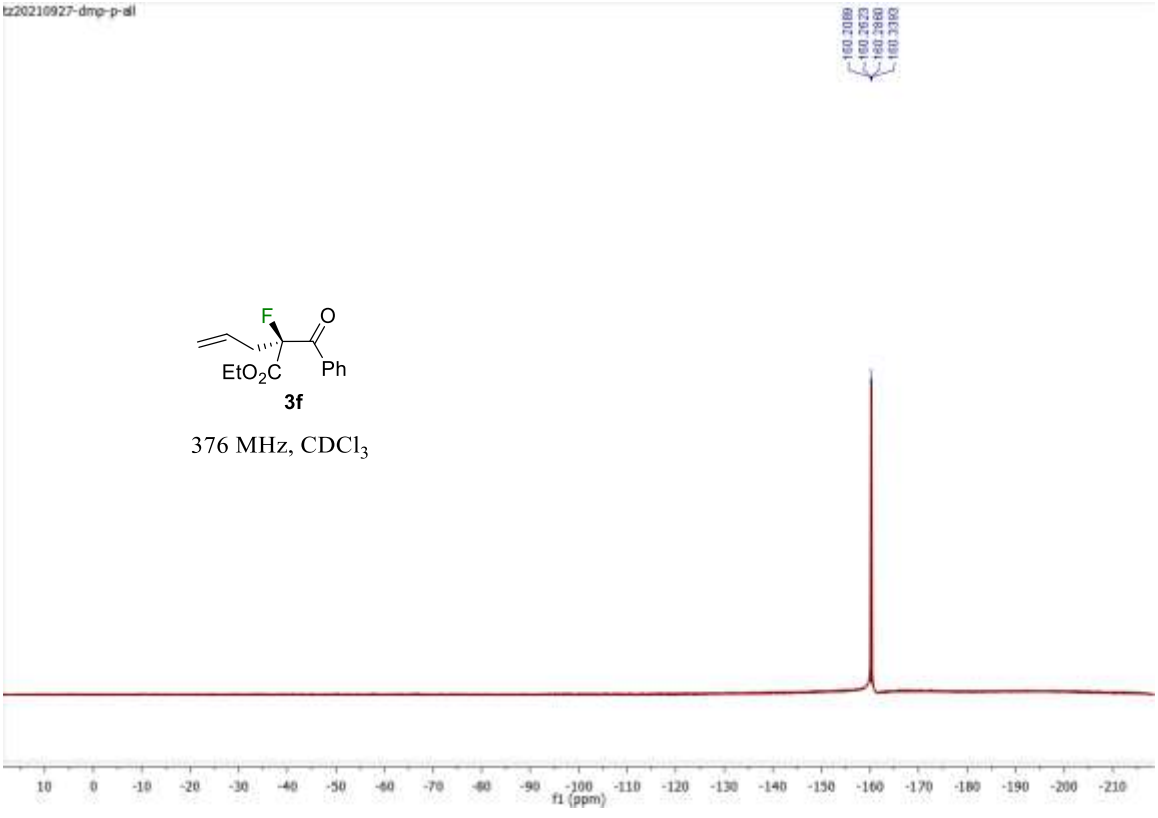


3f

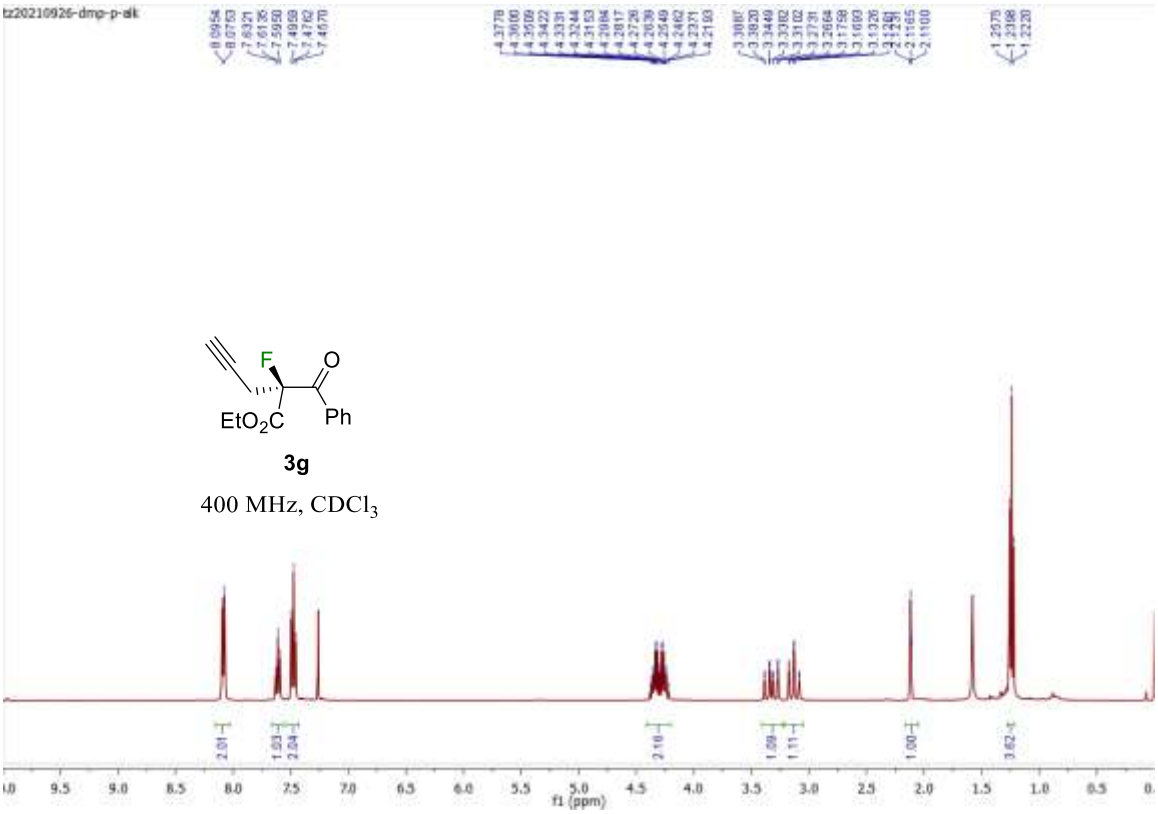
400 MHz, $CDCl_3$



101 MHz, $CDCl_3$

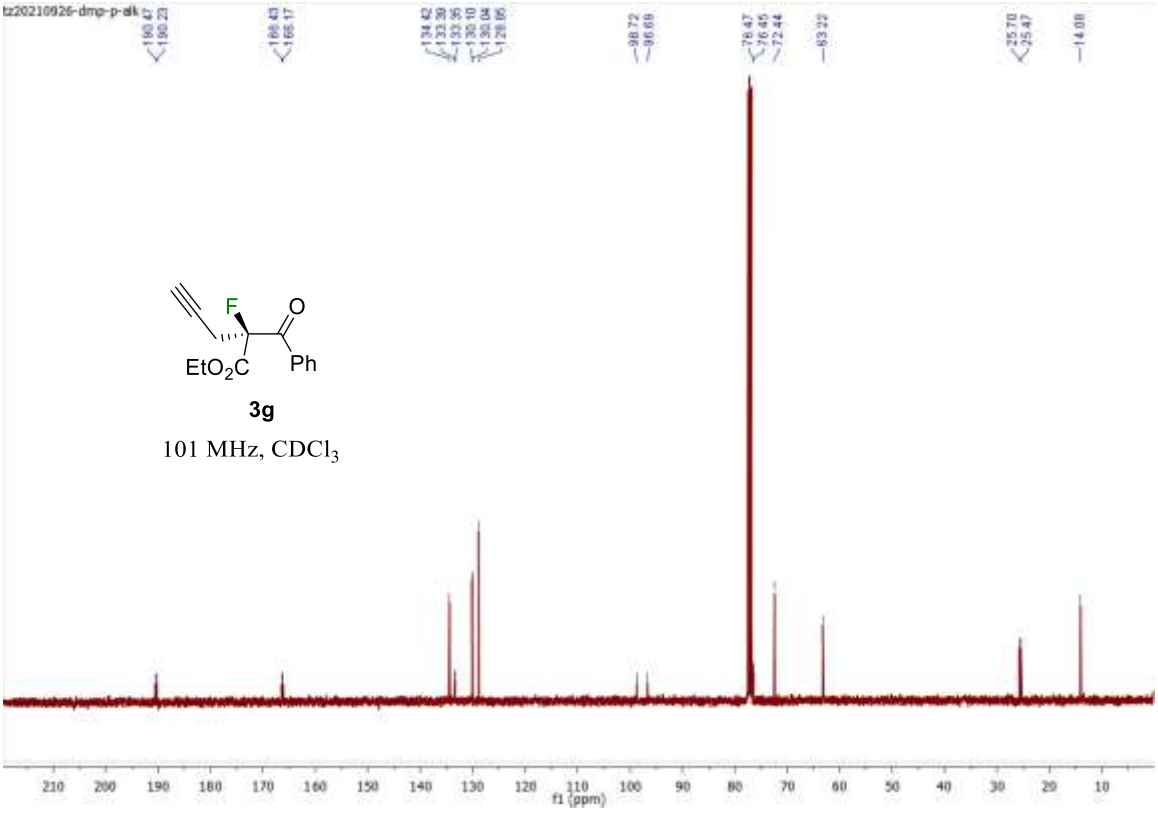


376 MHz, $CDCl_3$



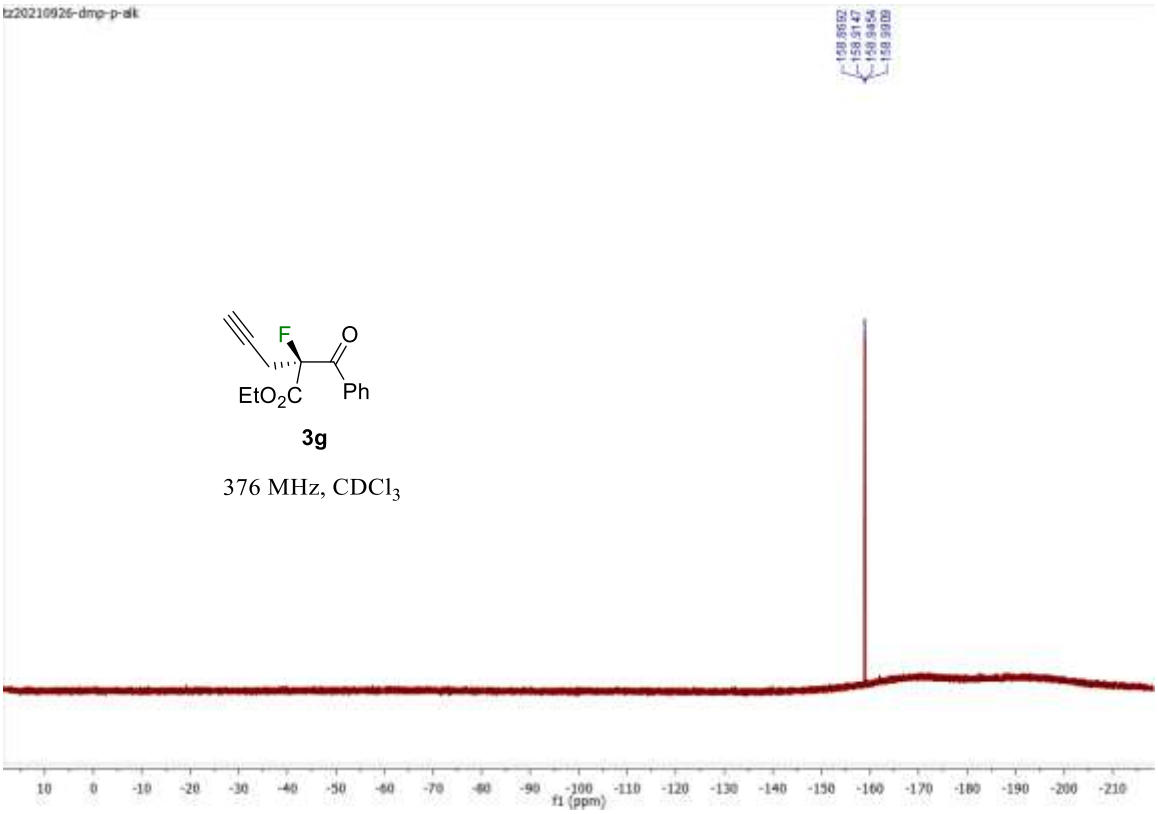
3g

400 MHz, $CDCl_3$



3g

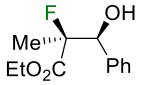
101 MHz, $CDCl_3$



3g

376 MHz, $CDCl_3$

VIII. HPLC spectra for *ee* determination.



1a

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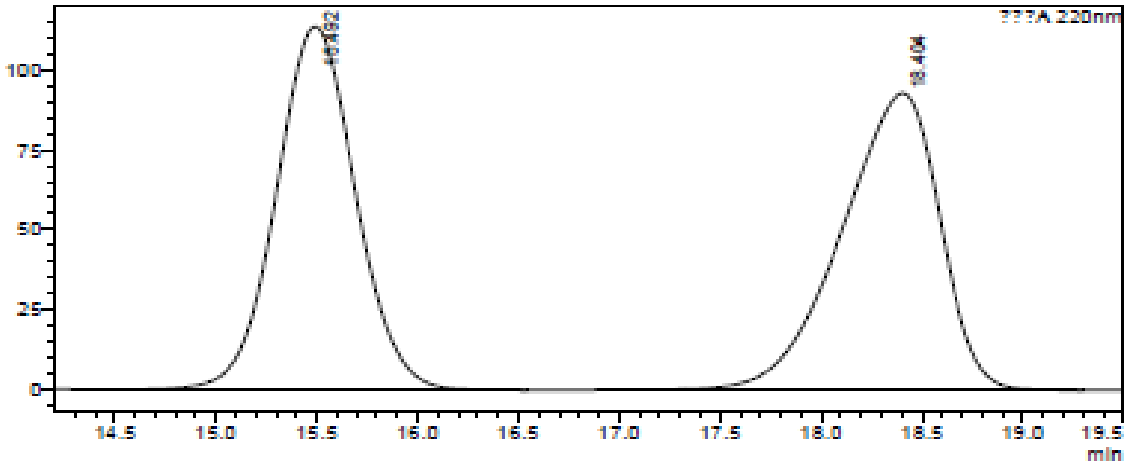
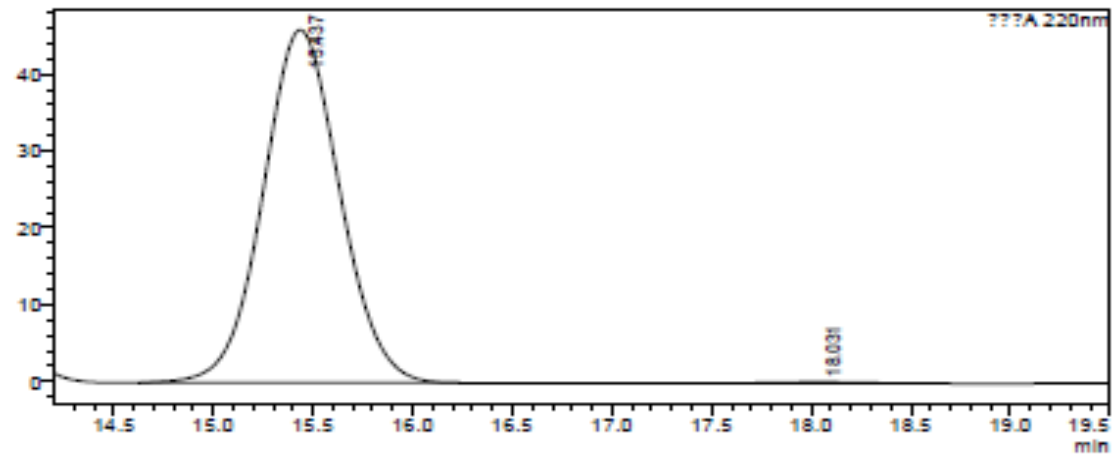


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.492	3115010	113822	49.796			
2	18.404	3140571	92903	50.204			
Total		6255581	206725				

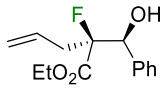
<Chromatogram>



<Peak Table>

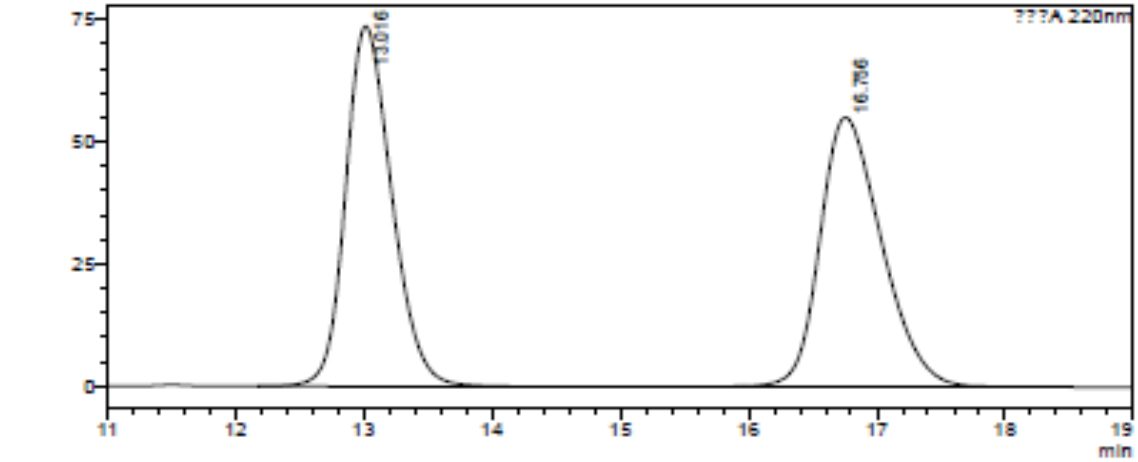
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.437	1228237	45871	99.660		M	
2	18.031	4191	156	0.340			
Total		1232429	46027				



1b

<Chromatogram>

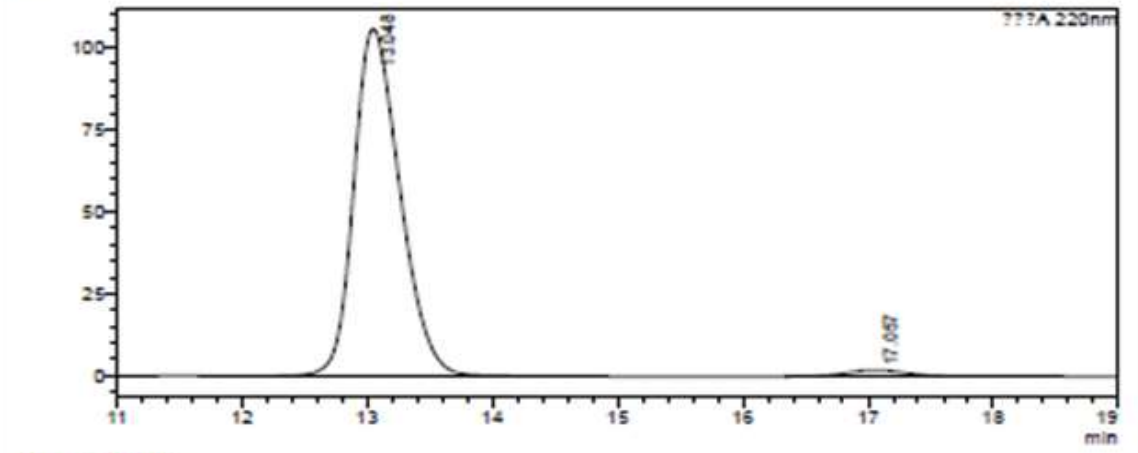


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.016	1848570	73765	50.103			
2	16.756	1840954	55139	49.897			
Total		3689524	128903				

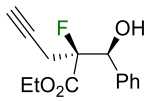
<Chromatogram>



<Peak Table>

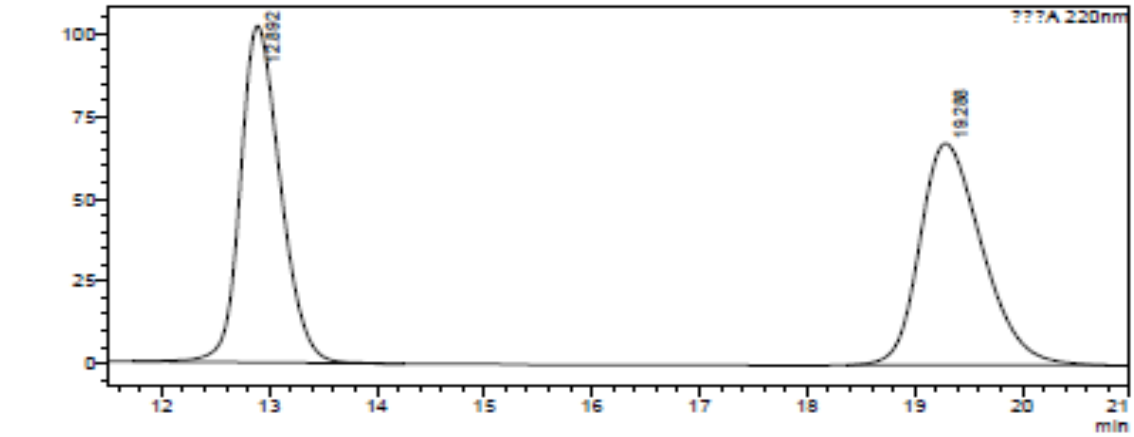
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.048	2707295	105650	97.898			
2	17.057	58142	1889	2.102			
Total		2765437	107540				



1c

<Chromatogram>

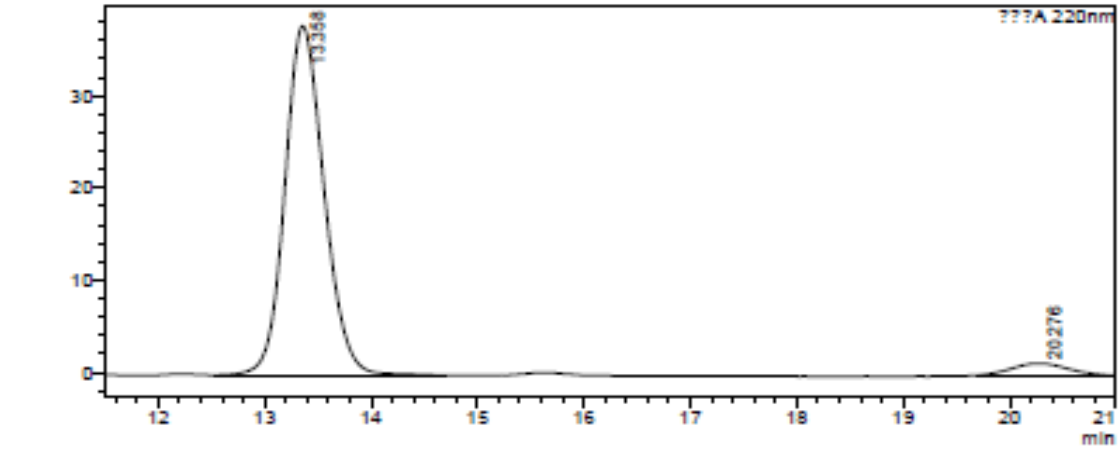


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.892	2643872	102086	49.374			
2	19.288	2710931	67255	50.626		M	
Total		5354804	169341				

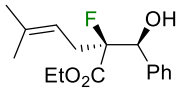
<Chromatogram>



<Peak Table>

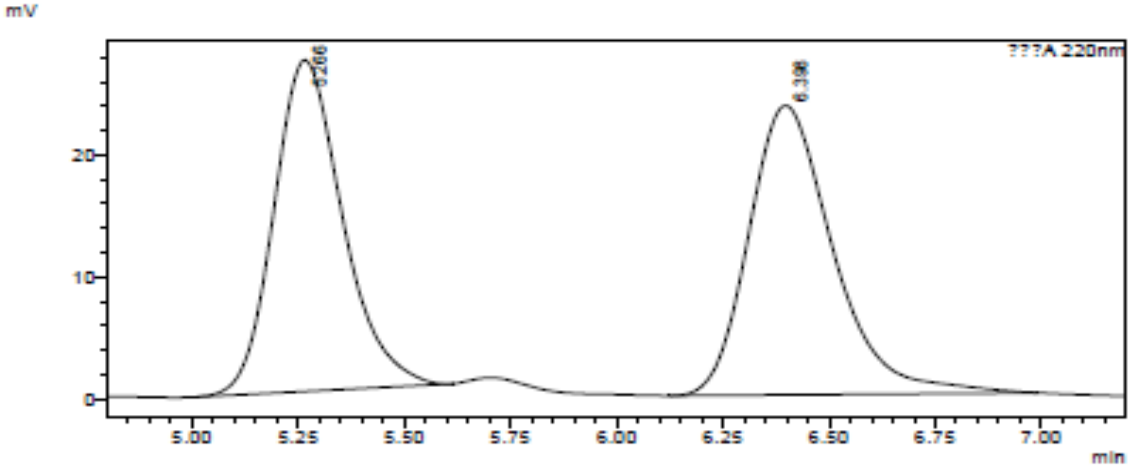
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.358	967935	37844	95.387			
2	20.276	46814	1292	4.613		M	
Total		1014749	39136				



1d

<Chromatogram>

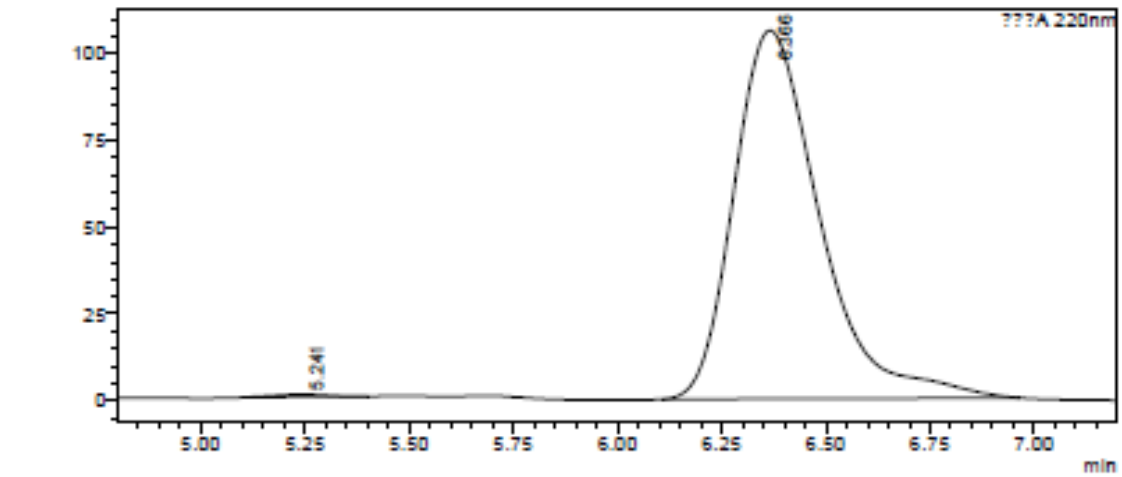


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.266	306412	27210	48.280		M	
2	6.398	328245	23746	51.720		M	
Total		634656	50956				

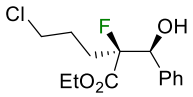
<Chromatogram>



<Peak Table>

???A 220nm

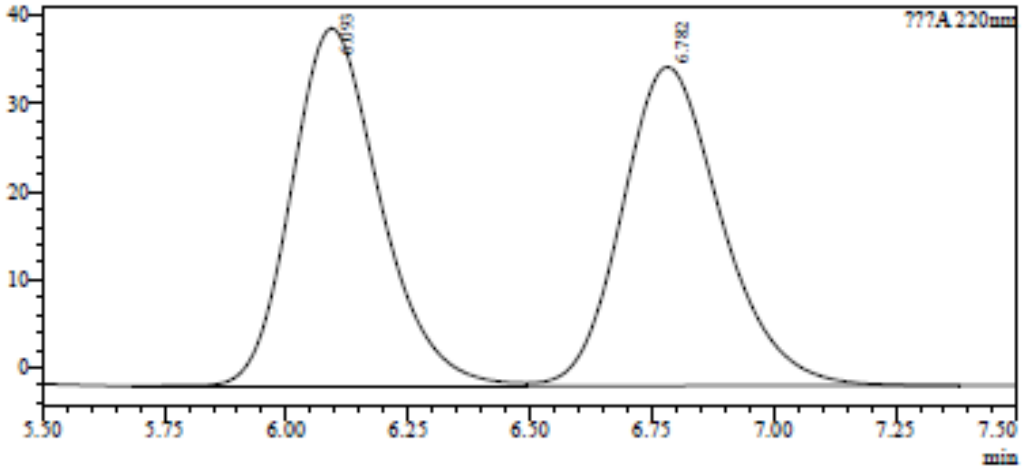
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.241	5418	675	0.354		M	
2	6.366	1523460	106253	99.646			
Total		1528878	106928				



1e

<Chromatogram>

mV



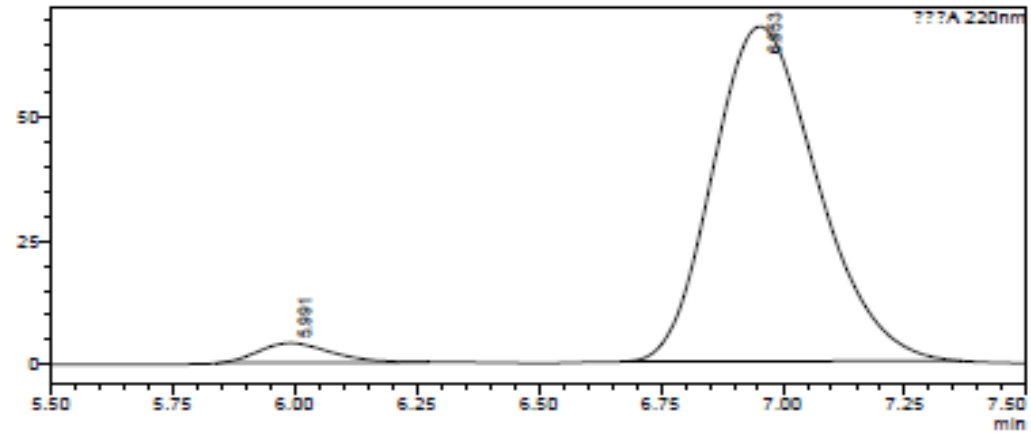
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.093	513689	40652	49.969			
2	6.782	514319	36235	50.031		V	
Total		1028007	76887				

<Chromatogram>

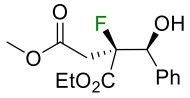
mV



<Peak Table>

???A 220nm

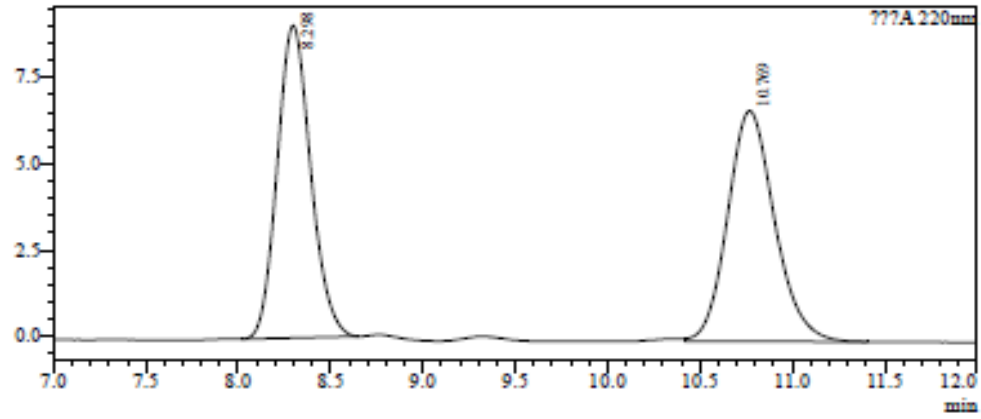
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.991	41215	4002	3.915		M	
2	6.953	1011460	67909	96.085			
Total		1052675	71911				



1f

<Chromatogram>

mV



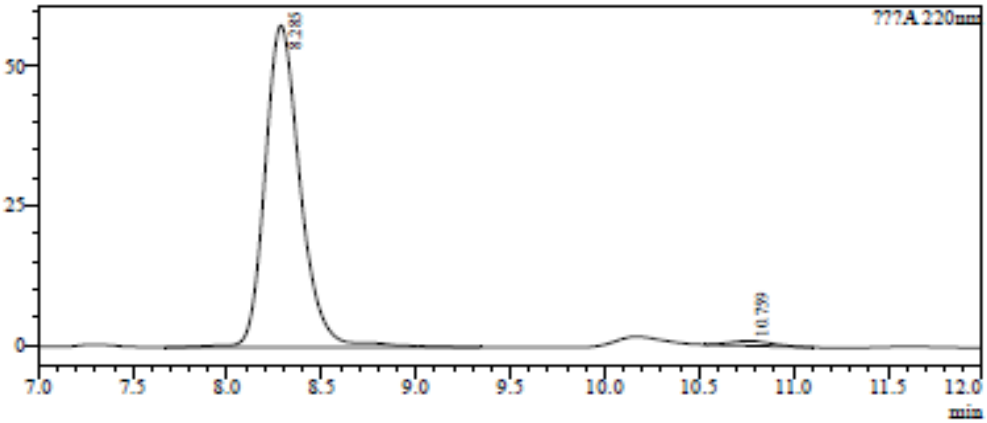
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.298	114495	9052	49.167			
2	10.769	118376	6680	50.833		V	
Total		232871	15732				

<Chromatogram>

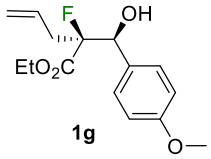
mV



<Peak Table>

???A 220nm

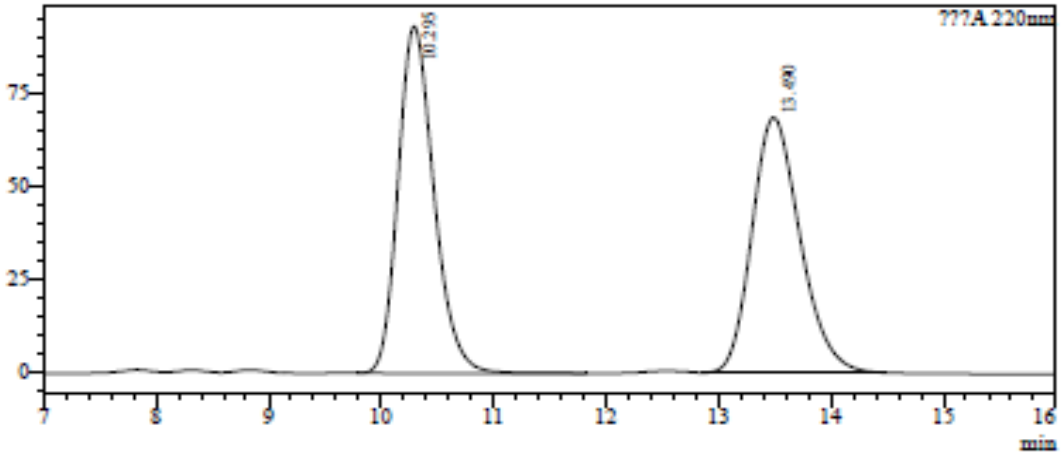
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.285	752890	57693	98.302		S	
2	10.759	13005	869	1.698			
Total		765895	58562				



1g

<Chromatogram>

mV



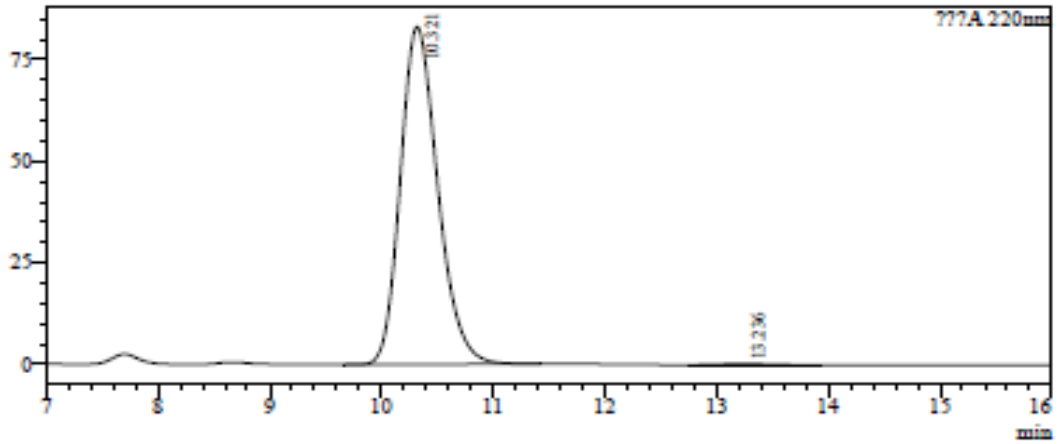
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.295	2055819	92756	50.307			
2	13.490	2030720	68239	49.693		M	
Total		4086539	160995				

<Chromatogram>

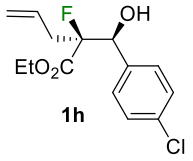
mV



<Peak Table>

???A 220nm

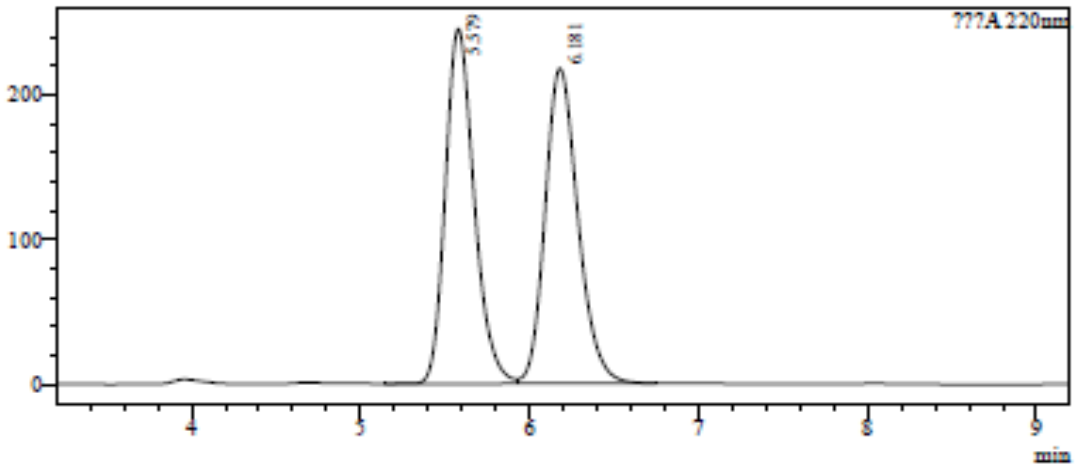
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.321	1931959	82986	99.664			
2	13.236	6520	225	0.336			
Total		1938478	83211				



1h

<Chromatogram>

mV



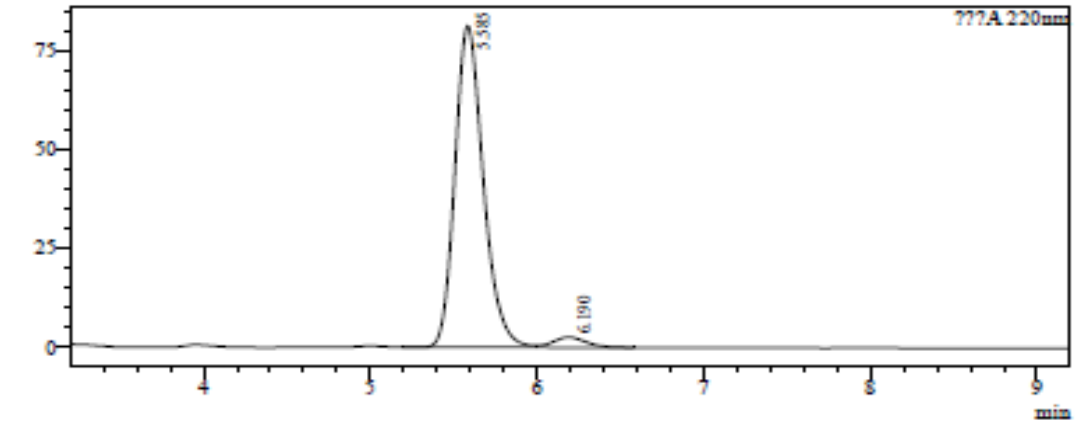
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.579	2922459	244591	49.897			
2	6.181	2934575	217390	50.103		V	
Total		5857034	461980				

<Chromatogram>

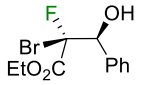
mV



<Peak Table>

???A 220nm

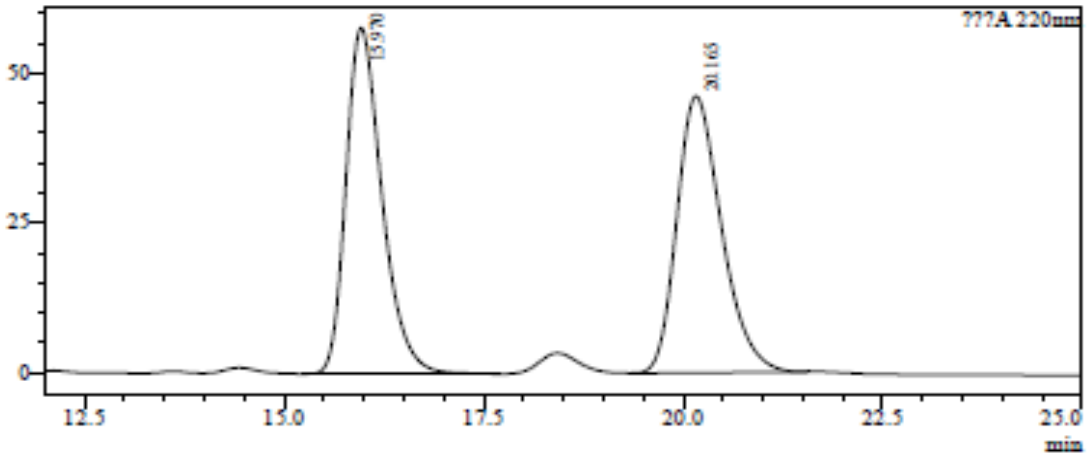
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.585	967821	81386	96.448			
2	6.190	35642	2594	3.552		V	
Total		1003464	83980				



1i

<Chromatogram>

mV



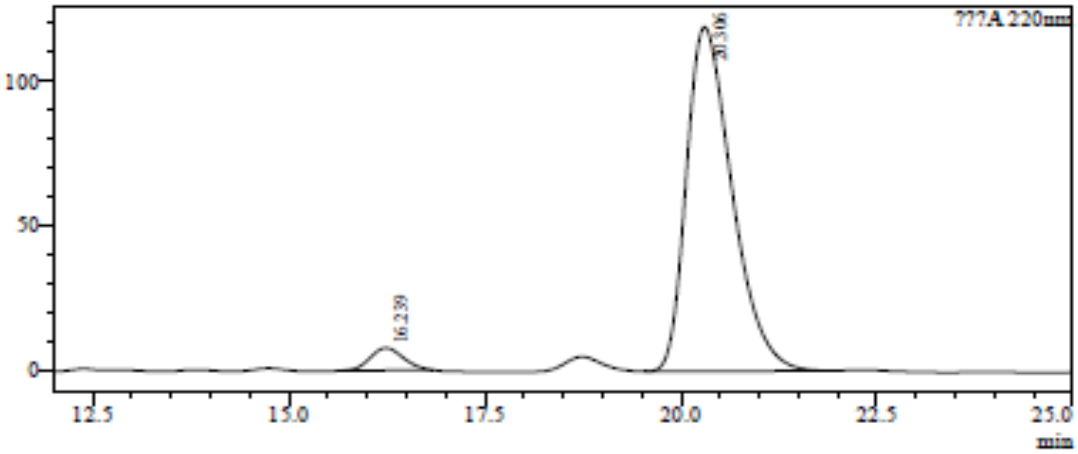
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.970	1815549	57860	50.200			
2	20.165	1801076	46270	49.800			
Total		3616625	104130				

<Chromatogram>

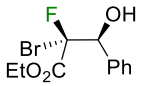
mV



<Peak Table>

???A 220nm

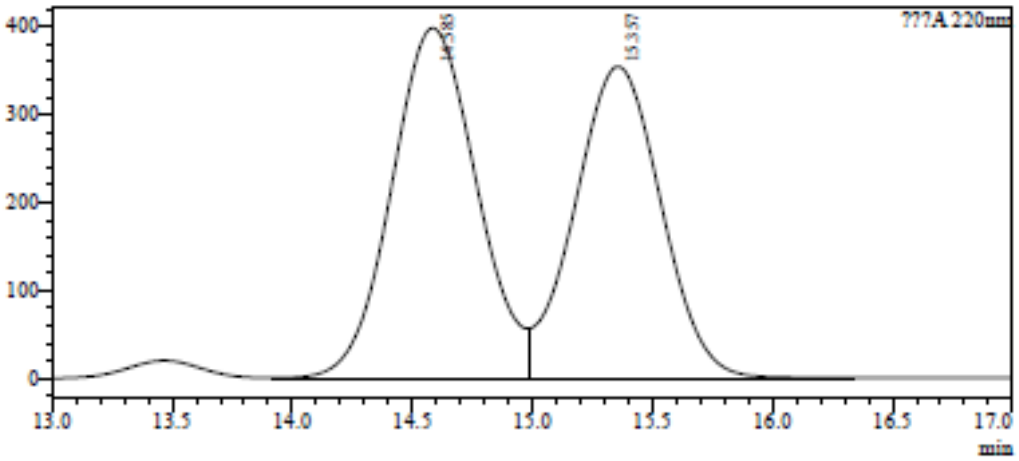
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.239	227182	7734	4.490		M	
2	20.306	4831990	119045	95.510			
Total		5059172	126780				



1j

<Chromatogram>

mV



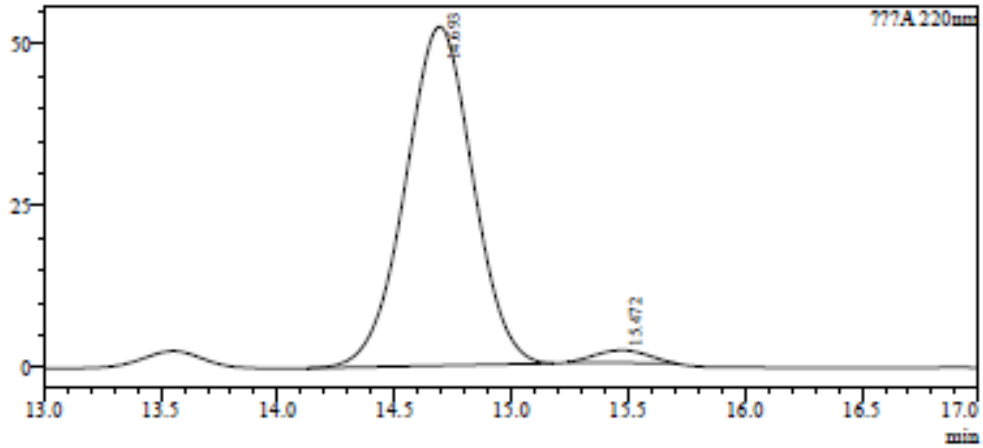
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.585	9788878	398235	52.462			
2	15.357	8869943	354517	47.538		V	
Total		18658821	752751				

<Chromatogram>

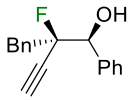
mV



<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.693	1053359	52403	97.242			
2	15.472	29875	1926	2.758		M	
Total		1083234	54328				



1k

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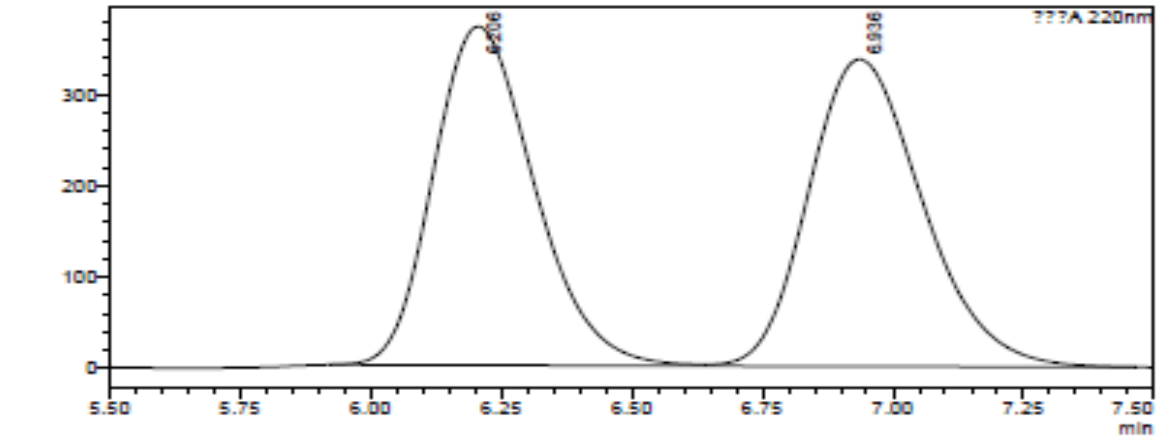
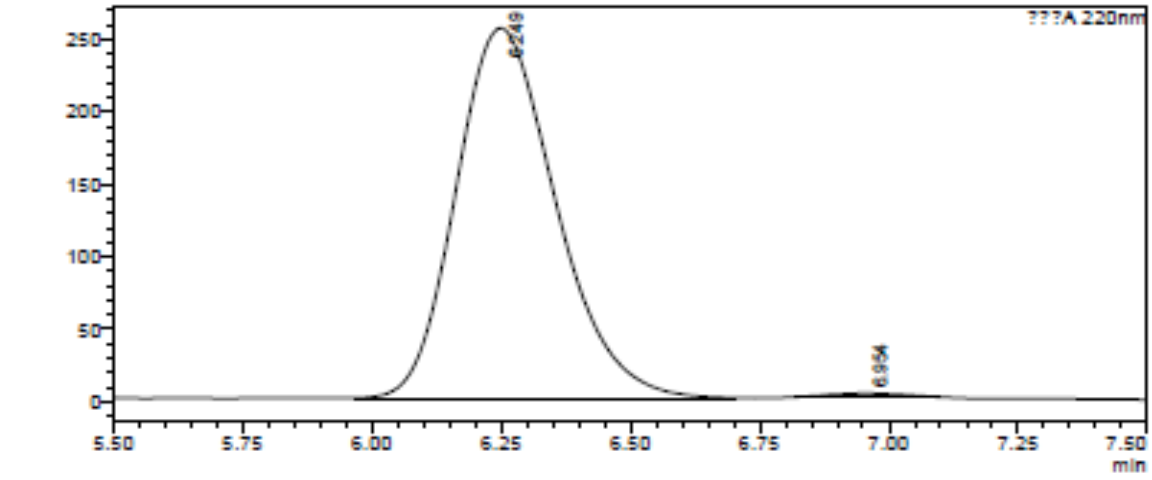


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.206	4970491	370466	49.378			
2	6.936	5095773	335819	50.622		V	
Total		10066264	706285				

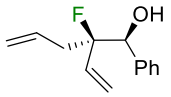
<Chromatogram>



<Peak Table>

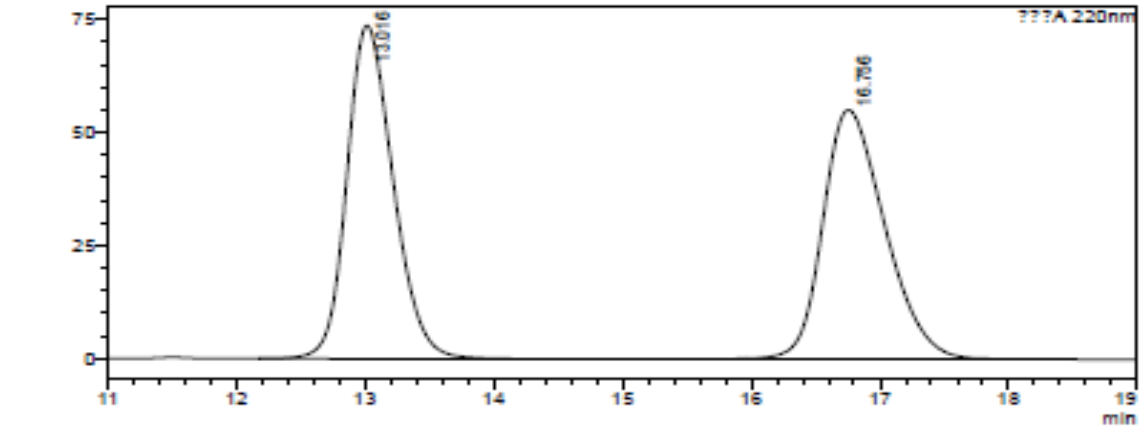
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.249	3419222	255549	99.263			
2	6.954	25393	2556	0.737		M	
Total		3444614	258105				



1l

<Chromatogram>

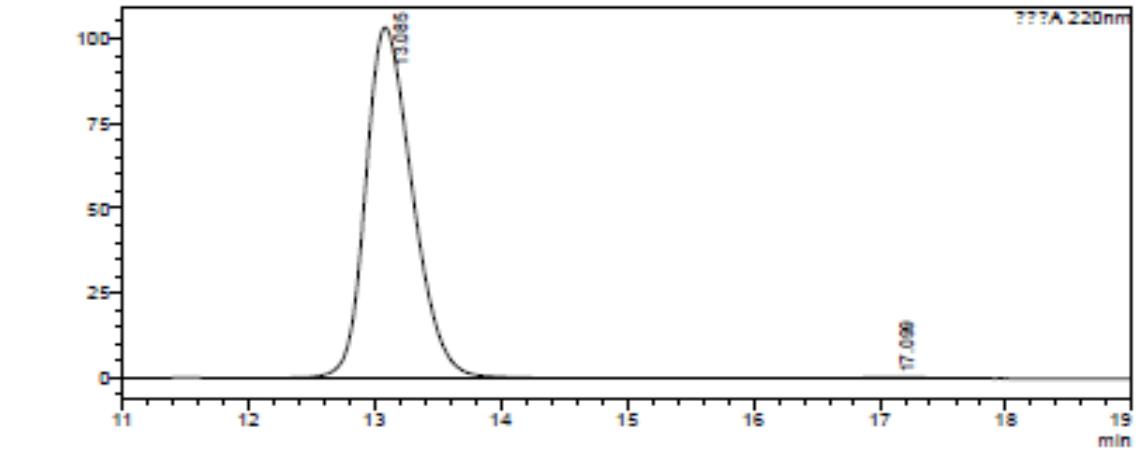


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.016	1848570	73765	50.103			
2	16.756	1840954	55139	49.897			
Total		3689524	128903				

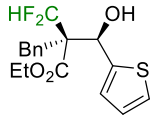
<Chromatogram>



<Peak Table>

???A 220nm

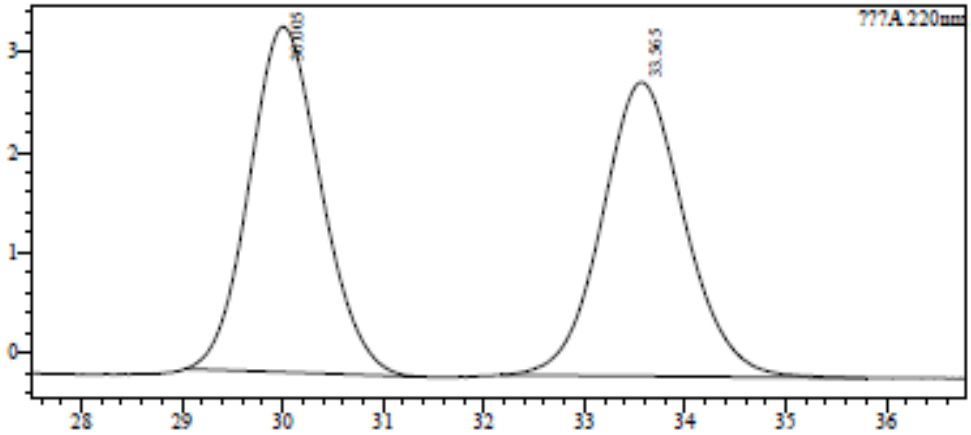
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.085	2660439	103251	99.691			
2	17.099	8233	267	0.309			
Total		2668672	103519				



1m

<Chromatogram>

mV



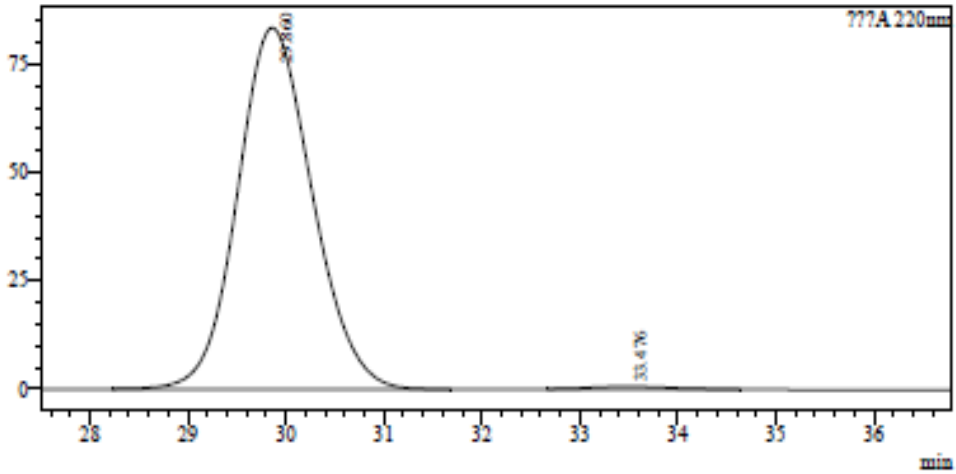
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.005	170160	3441	50.424			
2	33.565	167295	2926	49.576		M	
Total		337455	6367				

<Chromatogram>

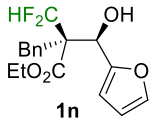
mV



<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.860	4435195	83567	99.241			
2	33.476	33912	648	0.759			
Total		4469106	84215				



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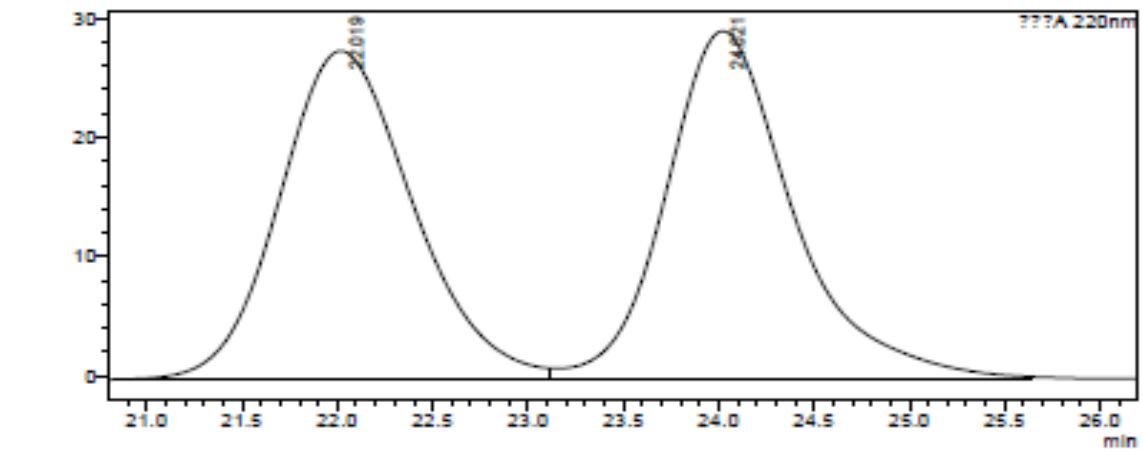
<Chromatogram>

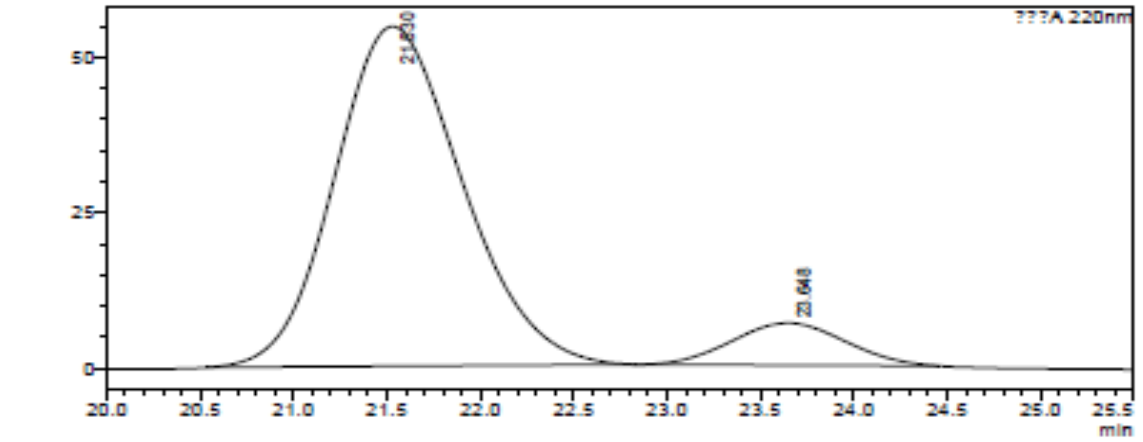


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.019	1337474	27514	49.656		M	
2	24.021	1356032	29171	50.344		V M	
Total		2693506	56685				

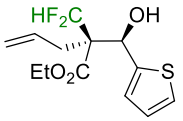
<Chromatogram>



<Peak Table>

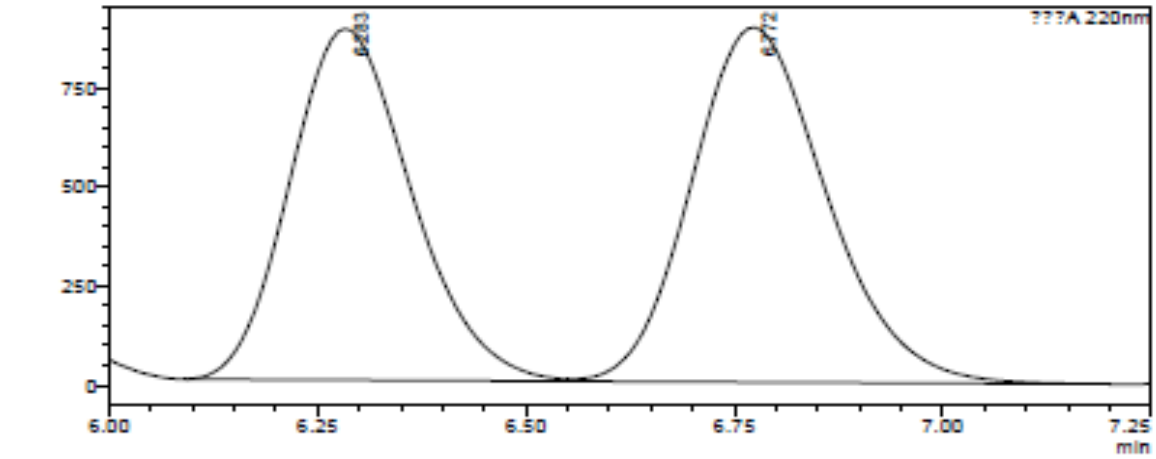
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.530	2593876	54578	90.098		M	
2	23.648	285076	6756	9.902		M	
Total		2878953	61334				



1o

<Chromatogram>

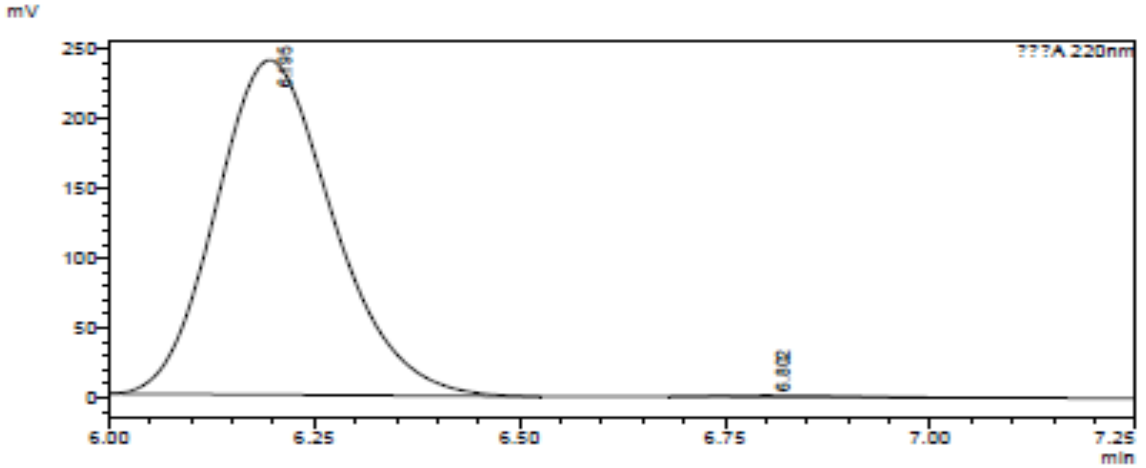


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.283	8955367	885514	47.083			
2	6.772	10065051	893748	52.917		V	
Total		19020418	1779262				

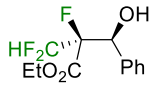
<Chromatogram>



<Peak Table>

???A 220nm

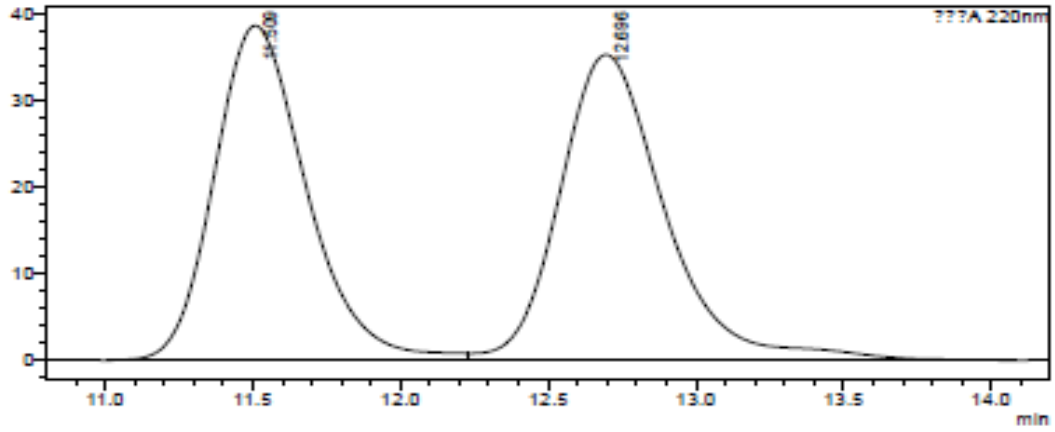
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.195	2381115	239960	99.588			
2	6.802	9856	1022	0.412			
Total		2390971	240962				



1p

<Chromatogram>

mV



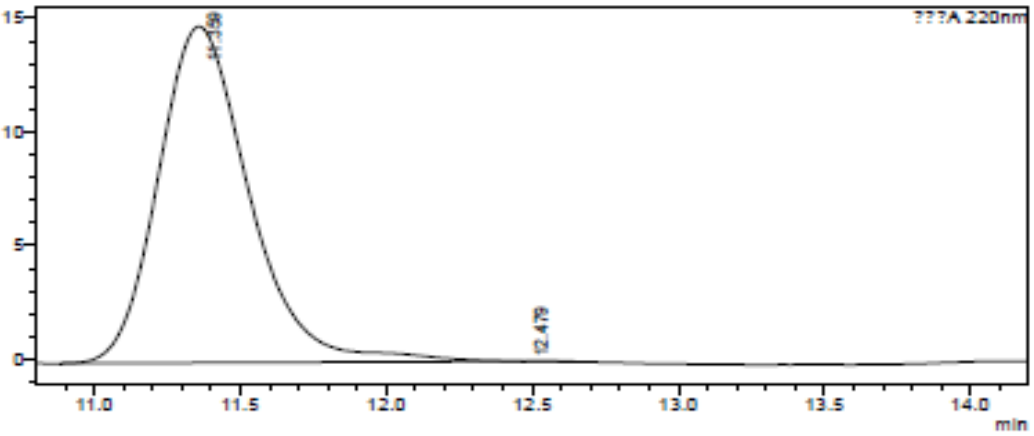
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.509	836960	38578	49.015			
2	12.696	870596	35224	50.985		V	
Total		1707556	73801				

<Chromatogram>

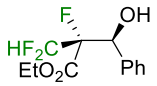
mV



<Peak Table>

???A 220nm

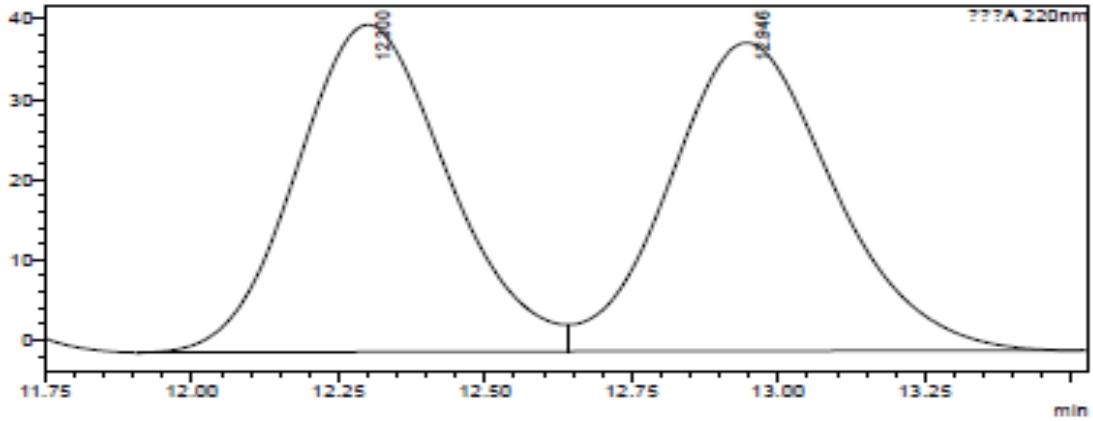
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.359	320901	14792	99.969			
2	12.479	98	1	0.031		M	
Total		321000	14793				



1q

<Chromatogram>

mV



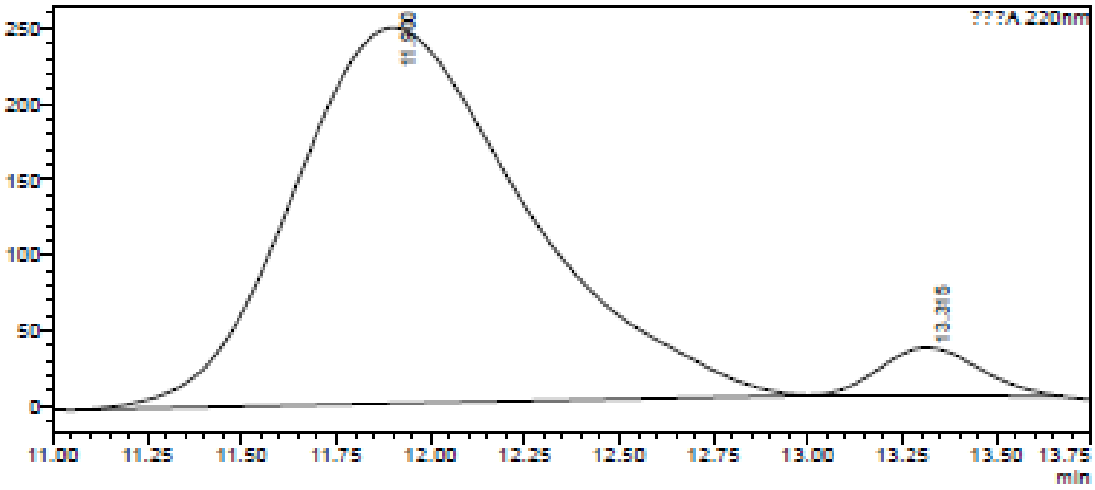
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.300	732411	40777	49.532			
2	12.946	746260	38397	50.468		V	
Total		1478671	79174				

<Chromatogram>

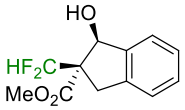
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.900	10657558	248408	94.851			
2	13.315	578494	31784	5.149		M	
Total		11236052	280192				



1r

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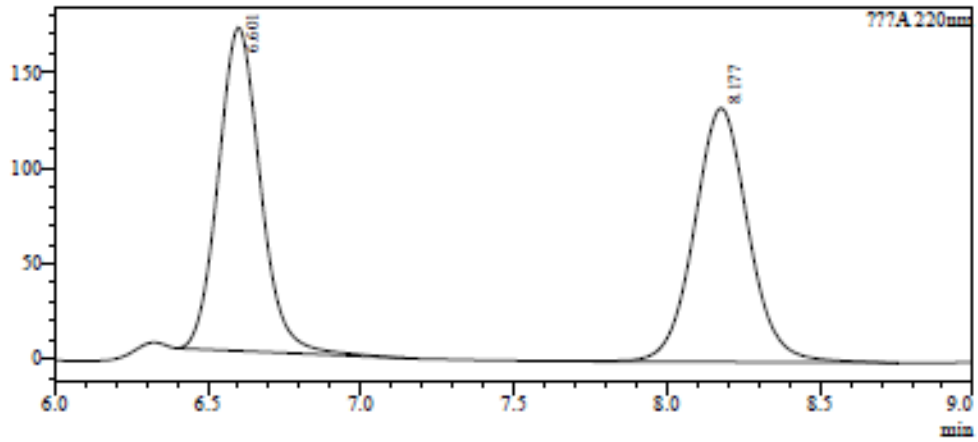
mV



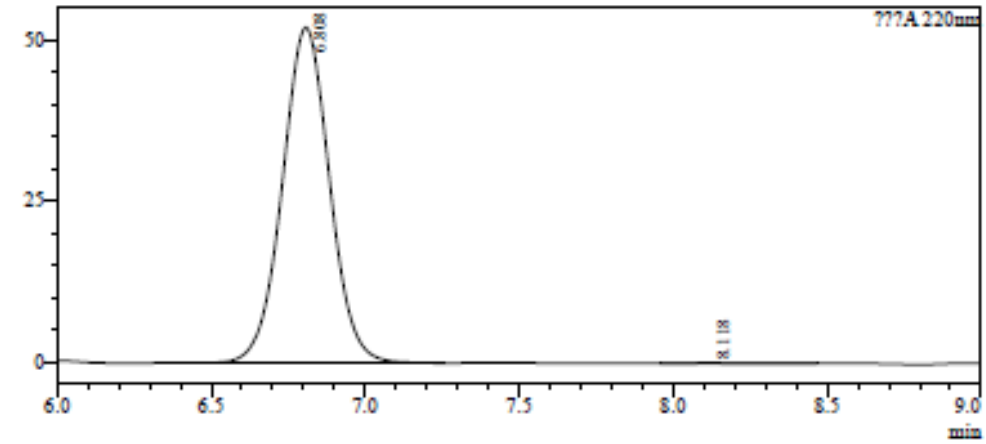
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.601	1623134	169397	49.854			
2	8.177	1632664	132933	50.146			
Total		3255798	302330				

<Chromatogram>

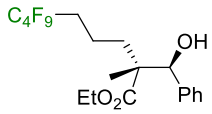
mV



<Peak Table>

???A 220nm

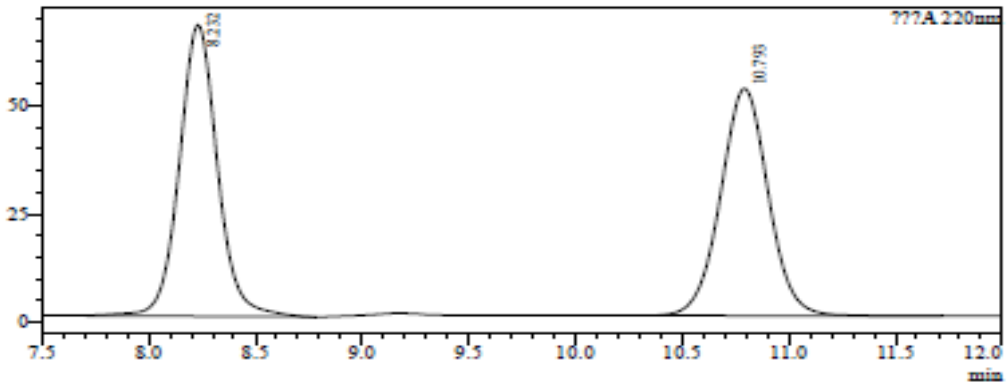
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.808	558770	52304	99.809		V	
2	8.118	1069	90	0.191			
Total		559839	52394				



1s

<Chromatogram>

mV



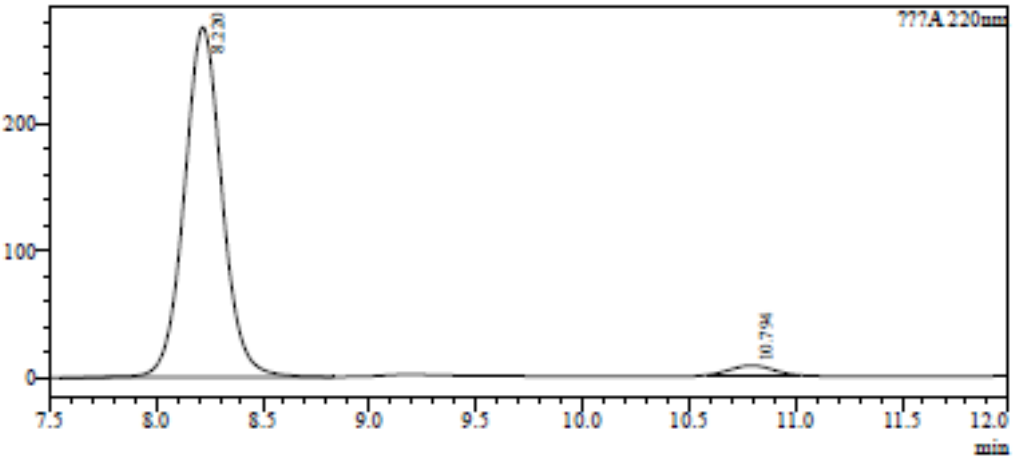
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.232	837867	67161	50.678			
2	10.793	815455	52403	49.322			
Total		1653322	119564				

<Chromatogram>

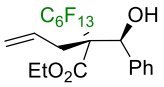
mV



<Peak Table>

???A 220nm

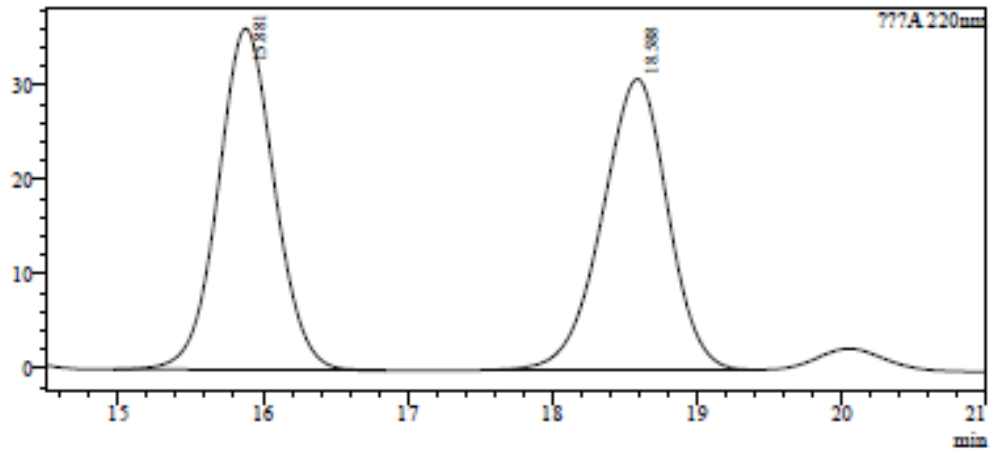
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.220	3403032	275483	97.121			
2	10.794	100895	7629	2.879		M	
Total		3503927	283112				



1t

<Chromatogram>

mV



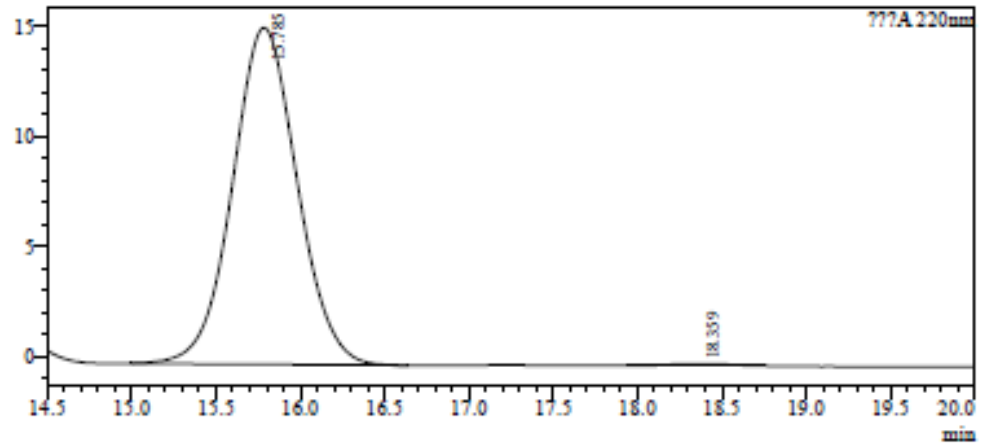
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.881	979692	36175	50.104			
2	18.588	975629	30846	49.896			
Total		1955321	67020				

<Chromatogram>

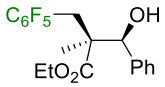
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.785	408550	15310	99.480			
2	18.359	2137	86	0.520		M	
Total		410688	15396				



1u

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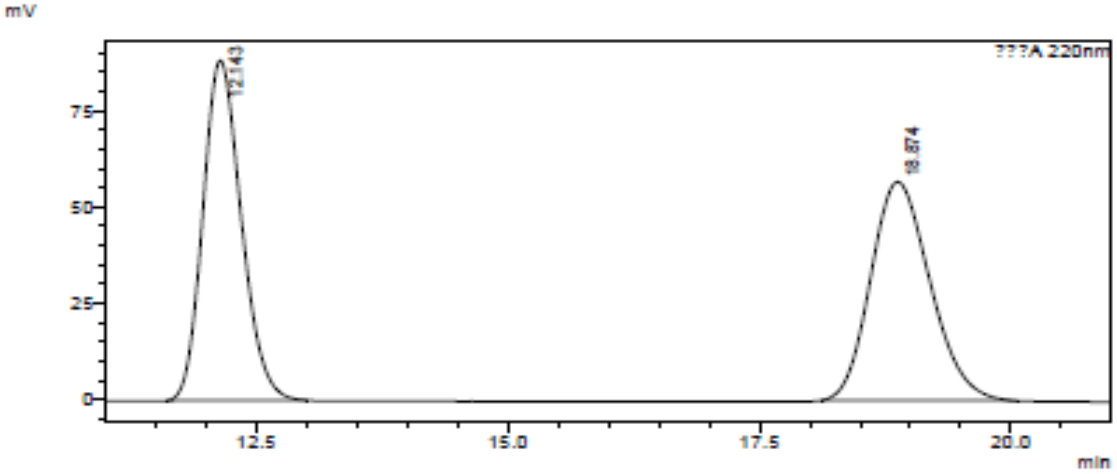
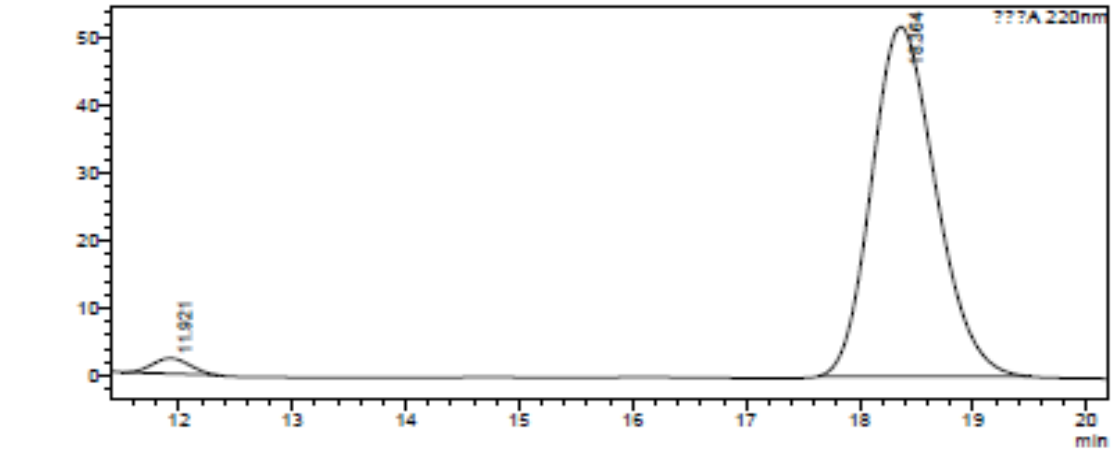


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.143	2343743	88326	50.165			
2	18.874	2328356	56807	49.835			
Total		4672099	145134				

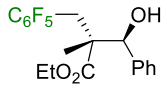
<Chromatogram>



<Peak Table>

???A 220nm

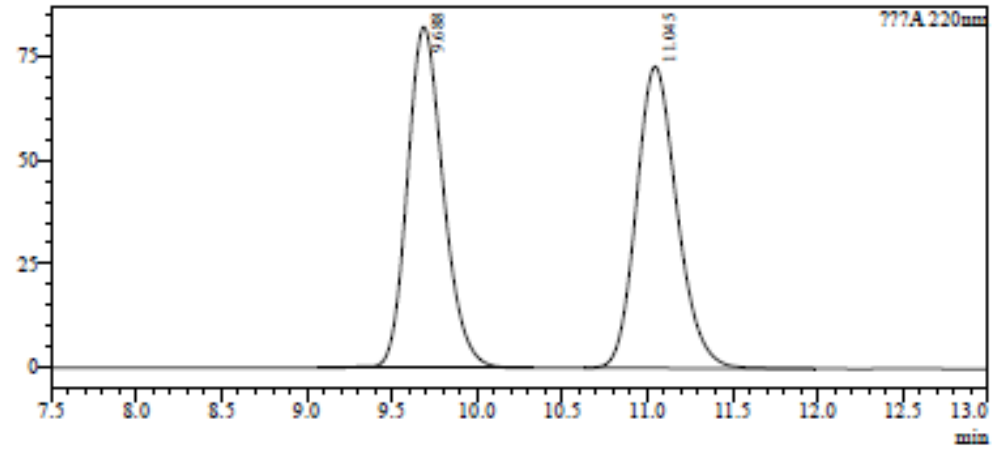
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.921	52192	2280	2.501		M	
2	18.364	2034630	51794	97.499			
Total		2086822	54074				



1v

<Chromatogram>

mV



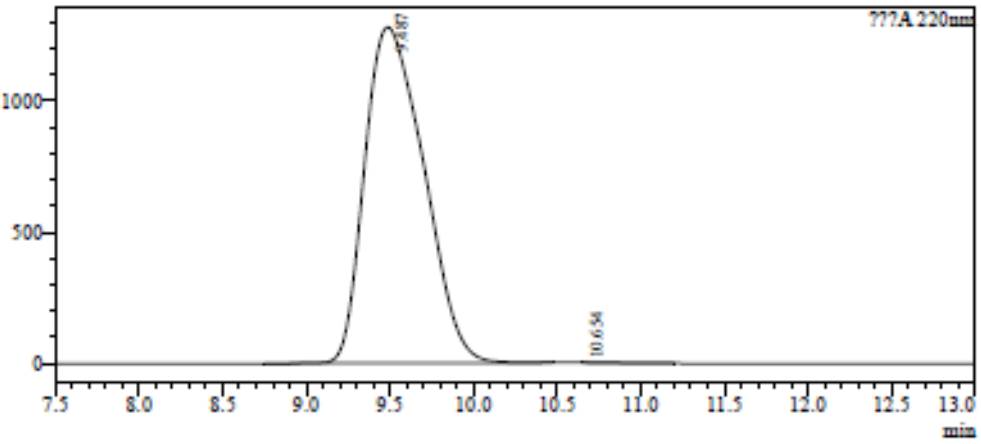
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.688	1207385	81927	50.108			
2	11.045	1202175	72410	49.892			
Total		2409560	154337				

<Chromatogram>

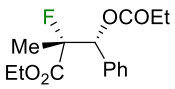
mV



<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.487	31414499	1278637	99.976			
2	10.654	7444	19	0.024		M	
Total		31421943	1278656				



2a

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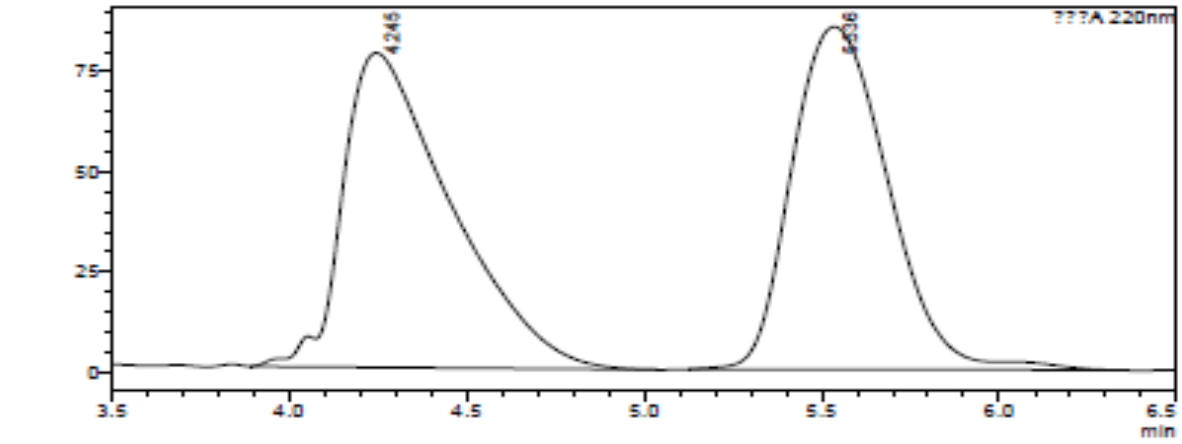
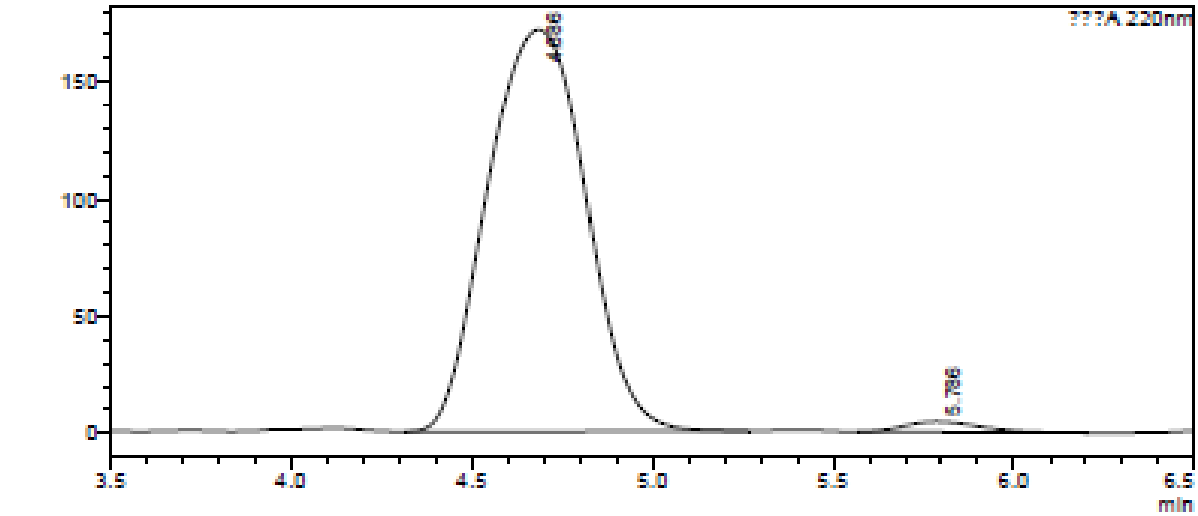


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.245	1661297	78442	50.732			
2	5.536	1613338	85469	49.268		M	
Total		3274635	163911				

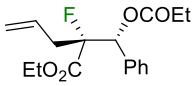
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.686	3255949	171392	98.101			
2	5.786	63018	4425	1.899			
Total		3318968	175817				



2b

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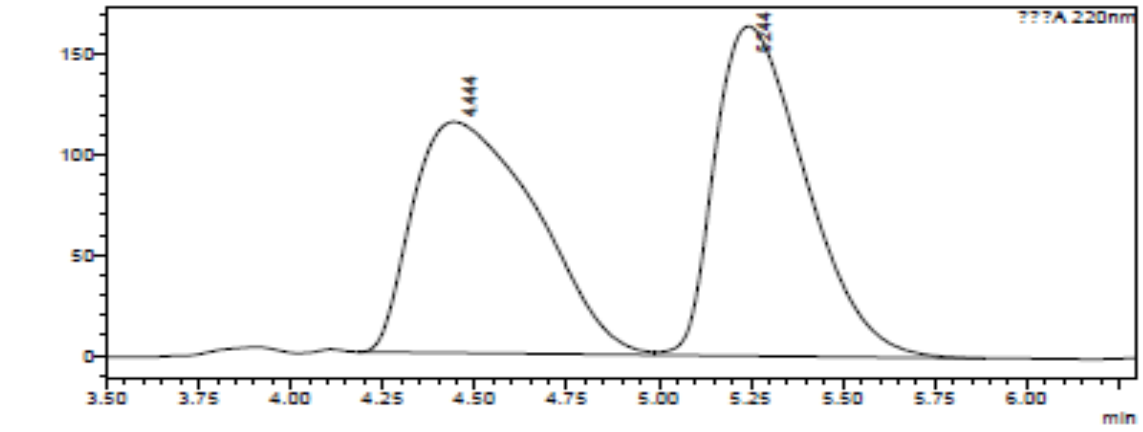

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.444	2703549	115281	48.969			
2	5.244	2817351	164521	51.031		V	
Total		5520900	279801				

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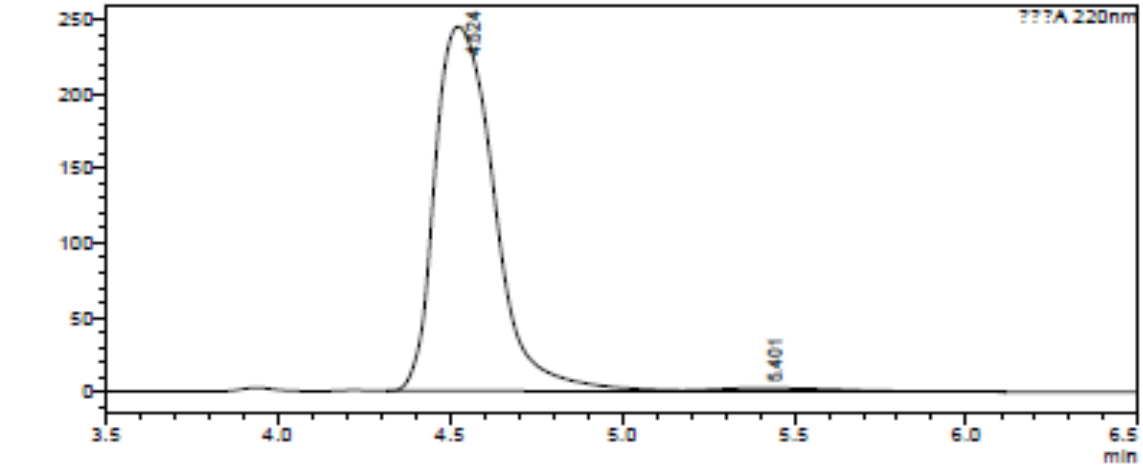
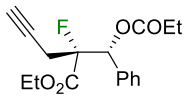


<Peak Table>

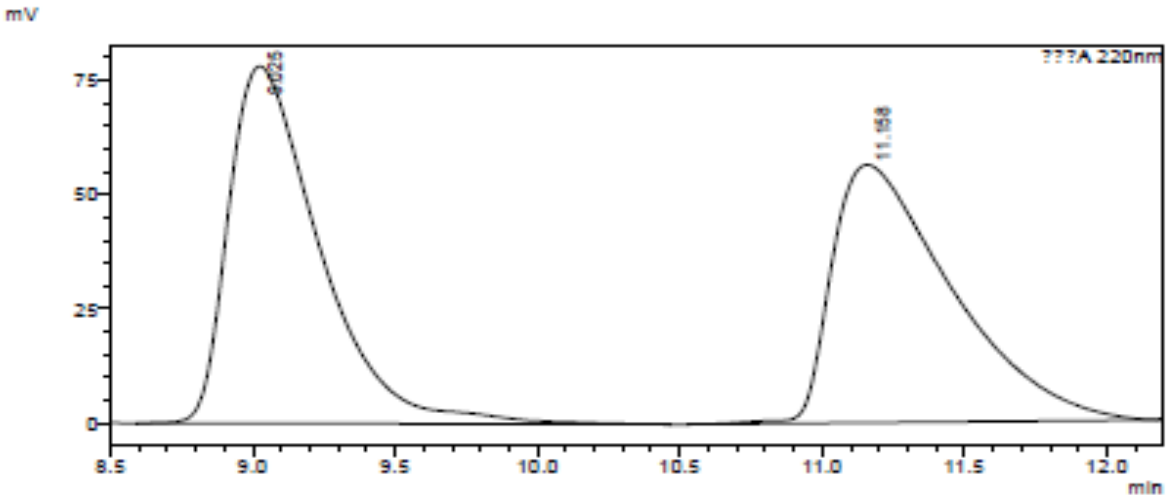
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.524	2944557	244889	98.187			
2	5.401	54364	2230	1.813		V	
Total		2998922	247119				



2c

<Chromatogram>

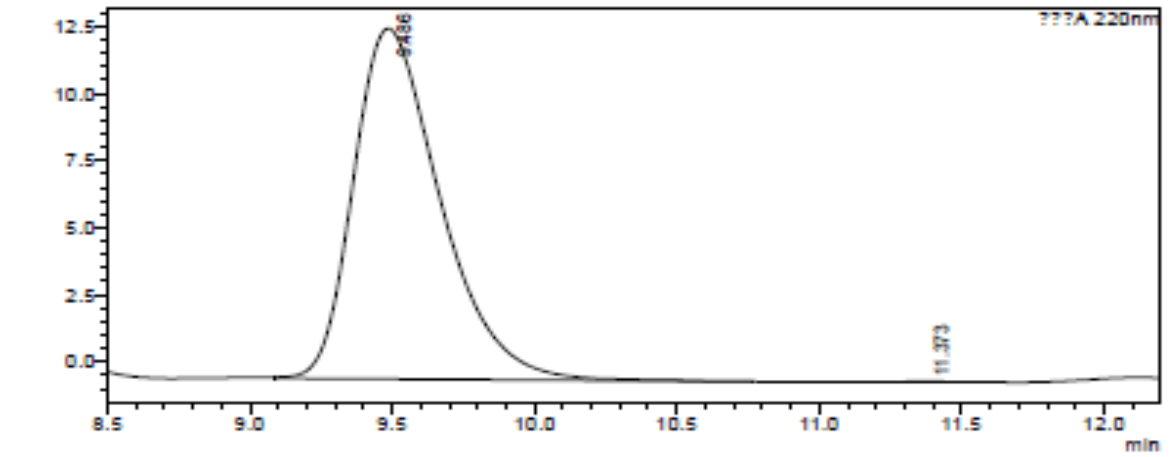


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.025	1740874	78080	51.396			
2	11.158	1646333	56342	48.604			
Total		3387207	134422				

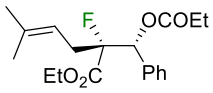
<Chromatogram>



<Peak Table>

???A 220nm

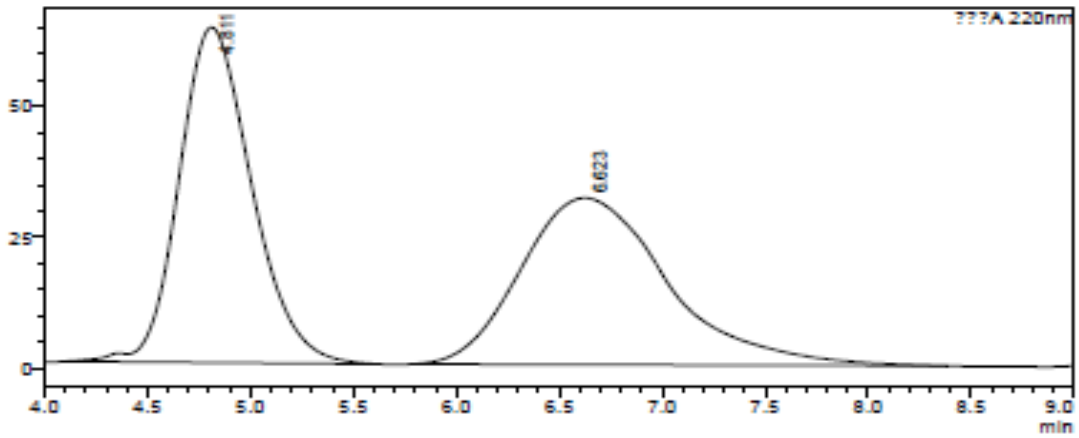
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.486	277361	13065	99.961		V	
2	11.373	108	10	0.039		M	
Total		277470	13075				



2d

<Chromatogram>

mV



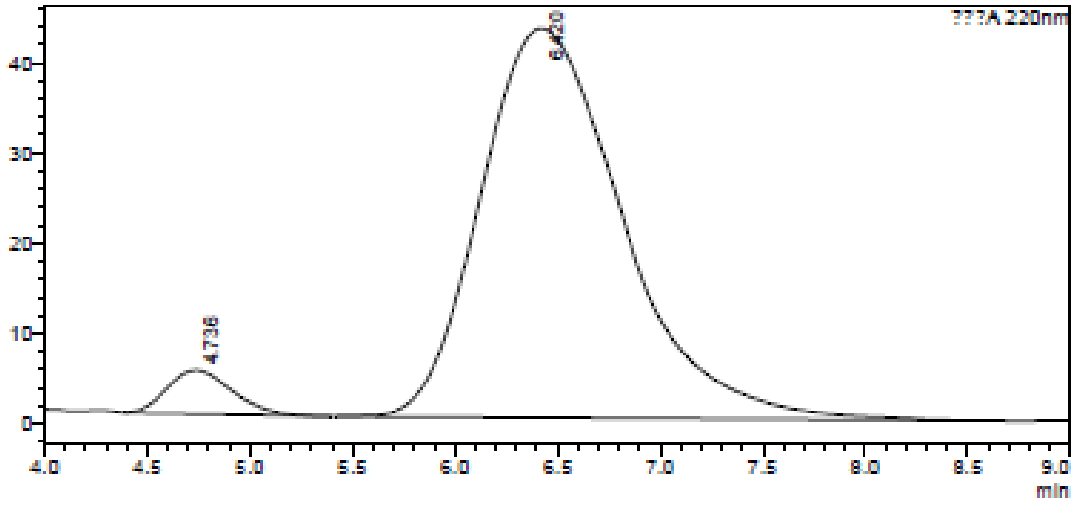
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.811	1574151	64154	49.873		M	
2	6.623	1582196	31911	50.127		M	
Total		3156347	96065				

<Chromatogram>

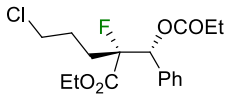
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.736	106131	4843	4.869			
2	6.420	2073387	43138	95.131			
Total		2179518	47981				



2e

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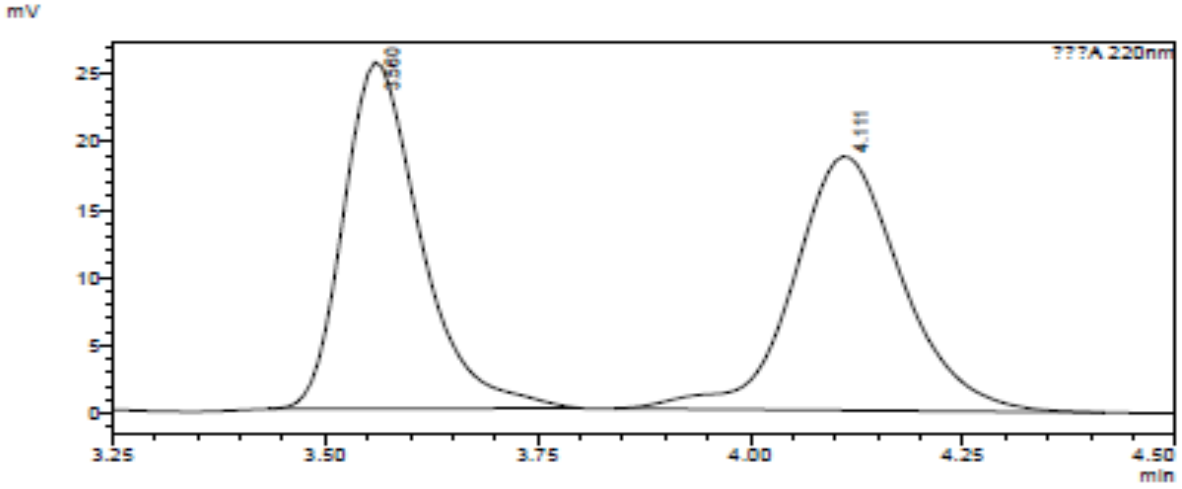
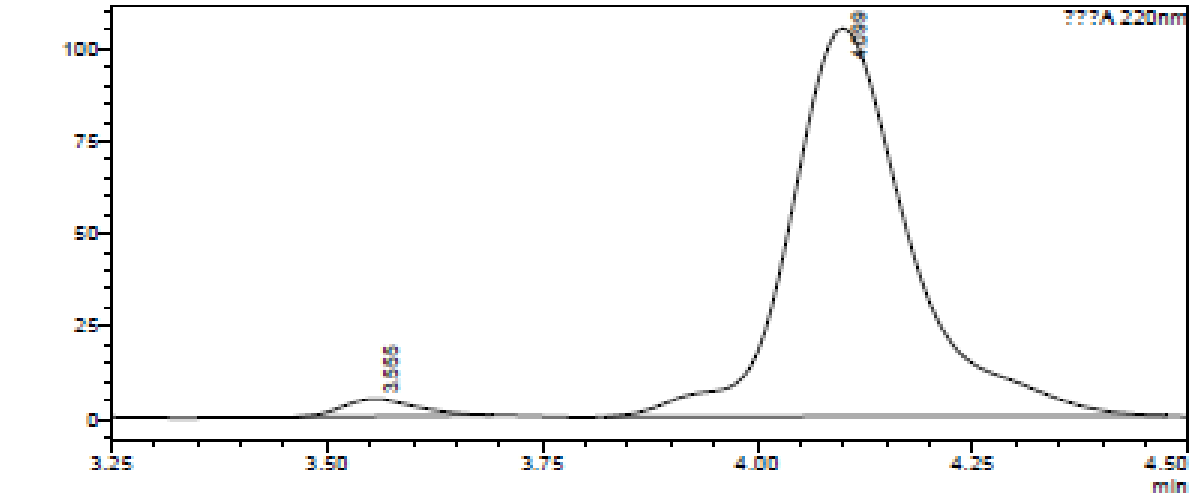


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.560	161013	25542	49.104			
2	4.111	166886	18719	50.896		M	
Tota		327899	44261				

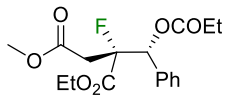
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.555	27577	4637	2.683			
2	4.099	1000386	104856	97.317			
Total		1027964	109494				



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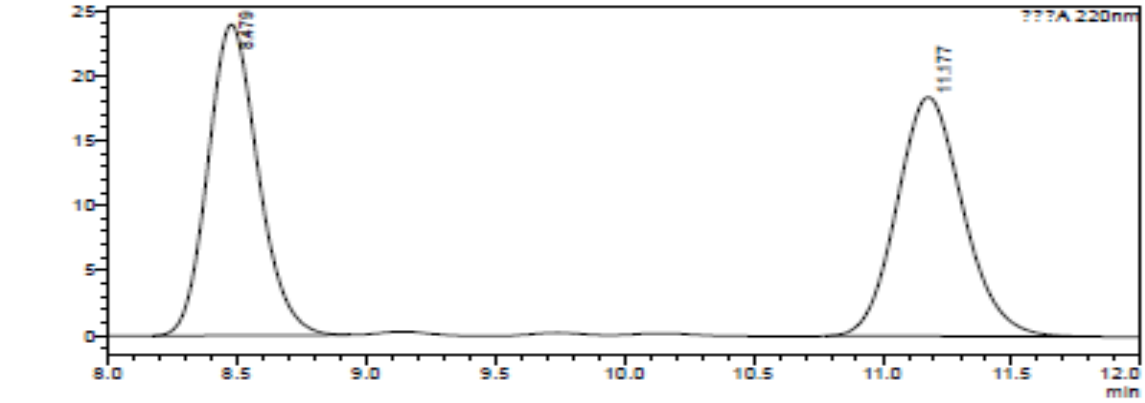
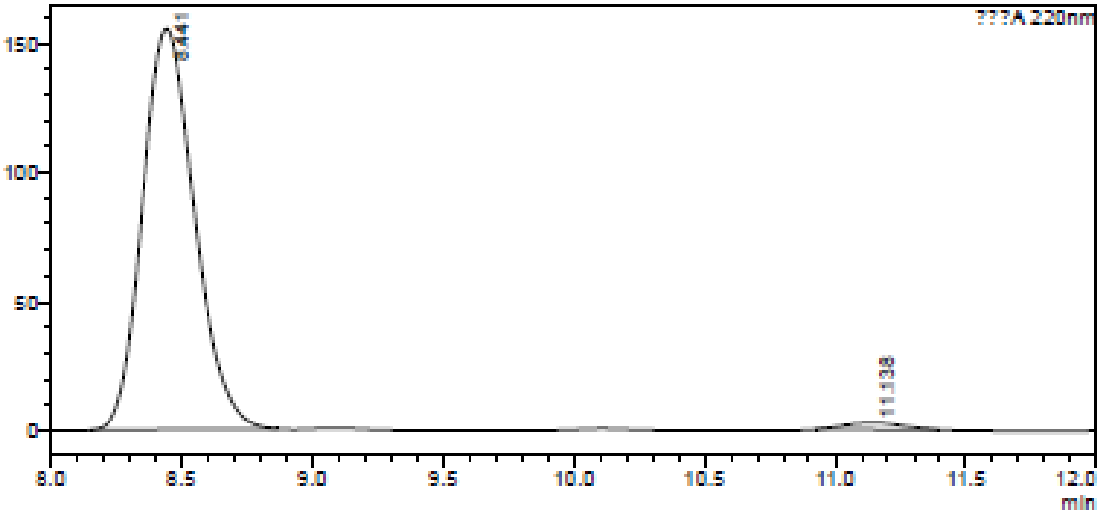


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.479	322918	23914	49.695		M	
2	11.177	326887	18381	50.305		M	
Tota		649805	42295				

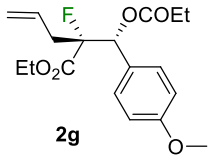
<Chromatogram>



<Peak Table>

???A 220nm

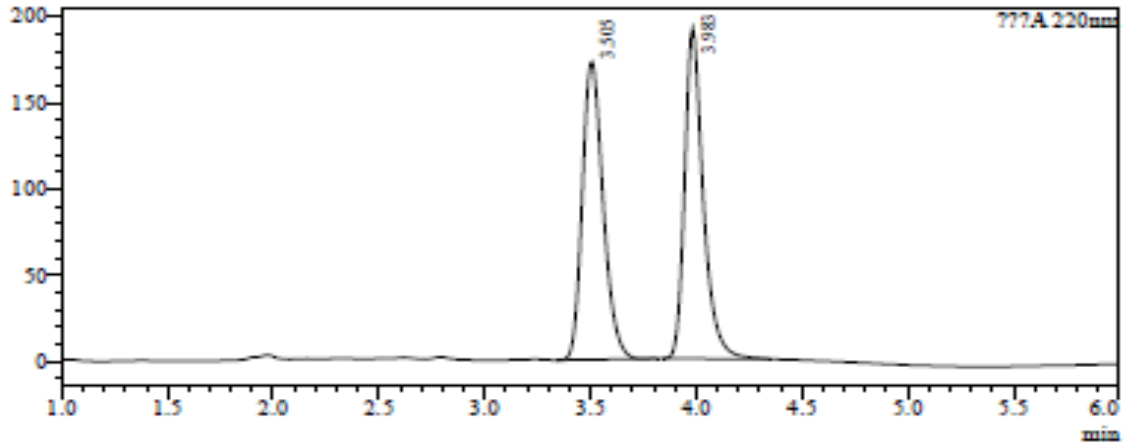
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.441	2160208	155384	98.087			
2	11.138	42135	2833	1.913		M	
Tota		2202343	158217				



2g

<Chromatogram>

mV



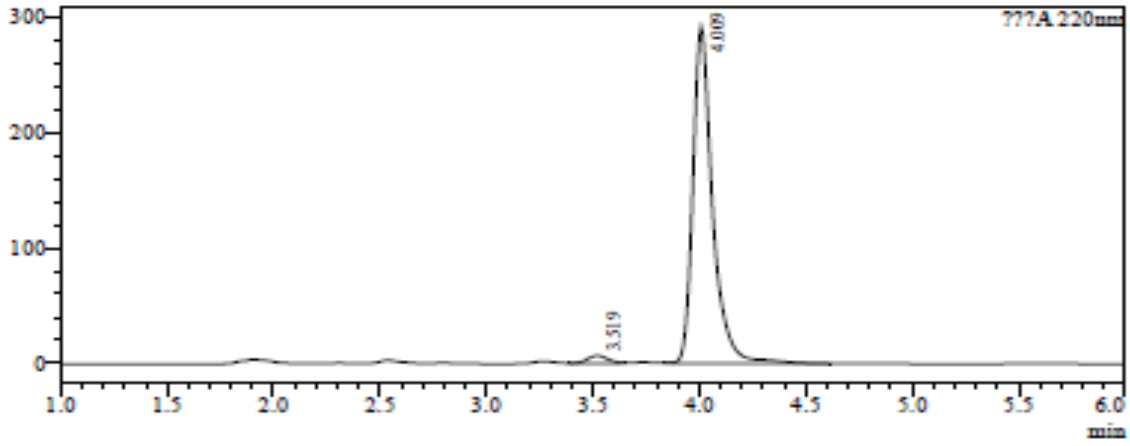
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.505	1175478	172553	50.018			
2	3.983	1174647	191551	49.982		M	
Total		2350125	364103				

<Chromatogram>

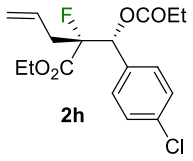
mV



<Peak Table>

777A 220nm

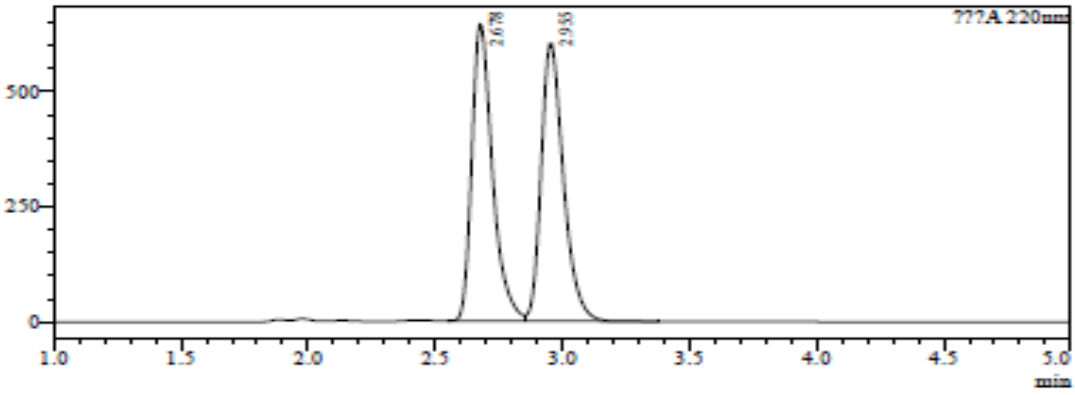
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.519	41757	6562	2.180			
2	4.009	1873749	290848	97.820			
Total		1915506	297410				



2h

<Chromatogram>

mV



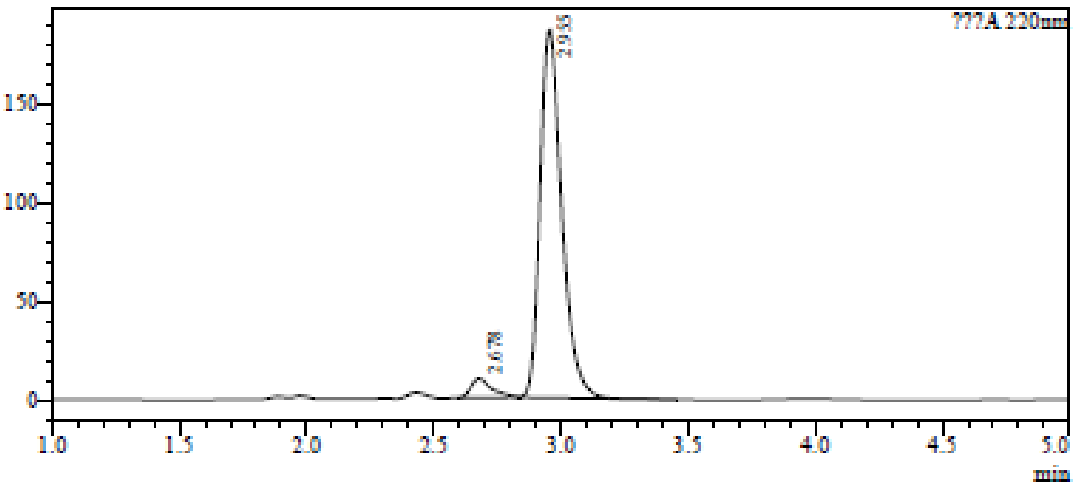
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.678	3644707	644052	49.743			
2	2.955	3682321	602814	50.257		V	
Total		7327029	1246866				

<Chromatogram>

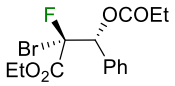
mV



<Peak Table>

777A 220nm

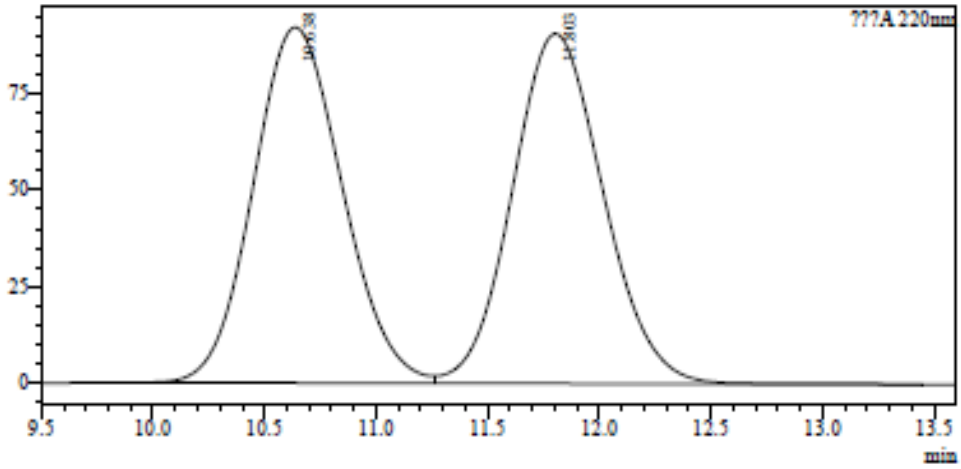
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.678	53664	9567	4.626		M	
2	2.955	1106410	186148	95.374			
Total		1160074	195715				



2i

<Chromatogram>

mV



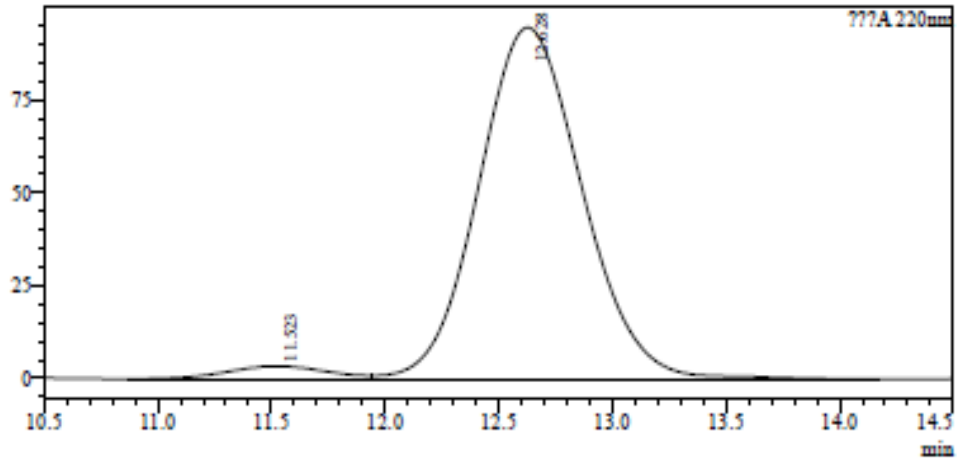
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.638	2551631	91902	49.878			
2	11.803	2564147	90418	50.122		SV	
Total		5115778	182320				

<Chromatogram>

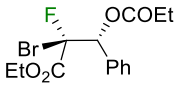
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.523	104201	3438	3.357			
2	12.628	3000239	94787	96.643		V	
Total		3104440	98225				



2j

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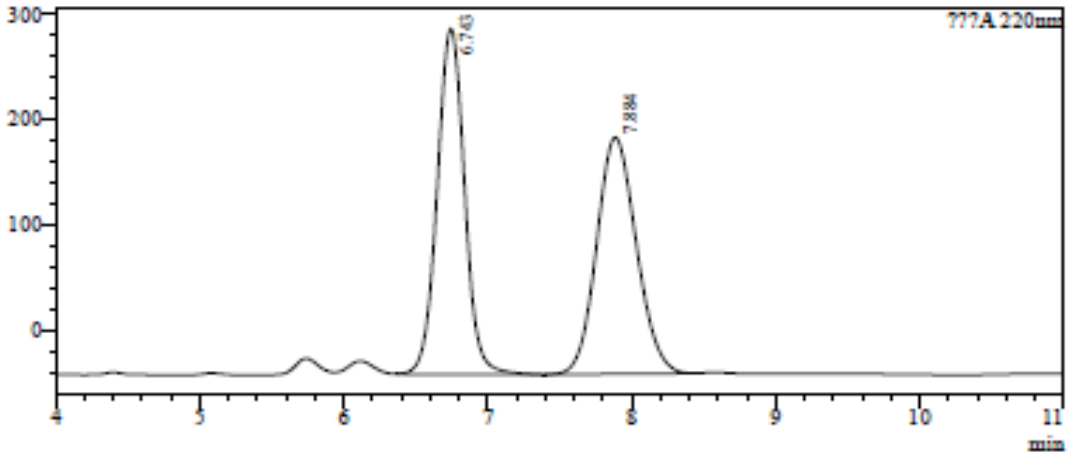
mV



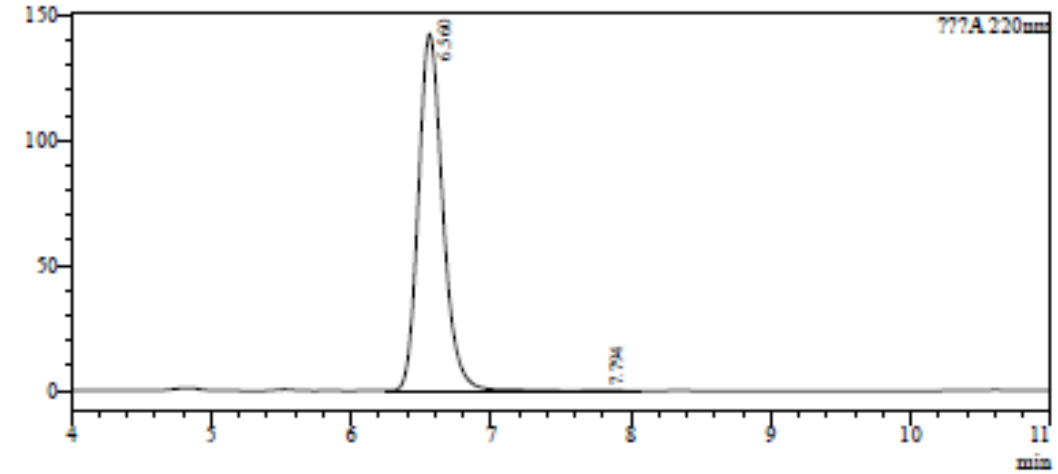
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.743	4326191	327126	50.204			
2	7.884	4291058	224019	49.796			
Total		8617249	551144				

<Chromatogram>

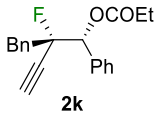
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.560	1725970	142436	99.924		SV	
2	7.794	1319	107	0.076		T	
Total		1727289	142543				



2k

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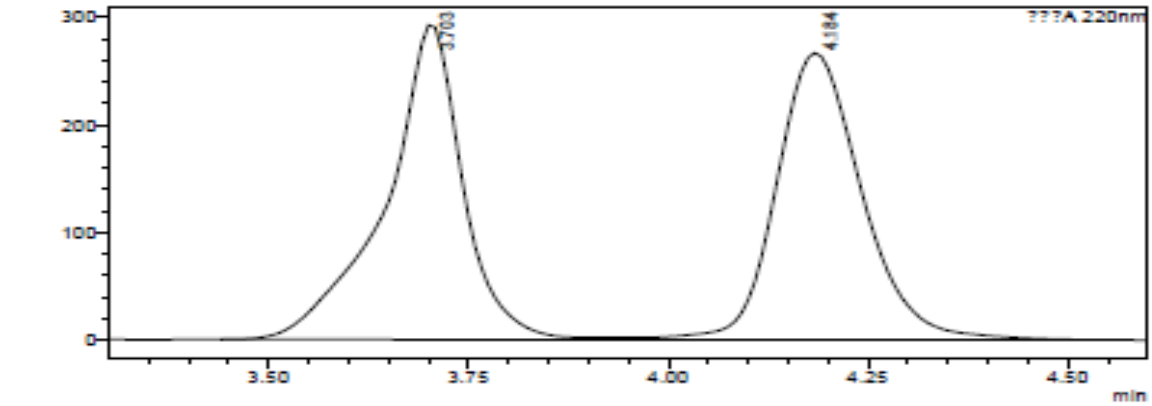
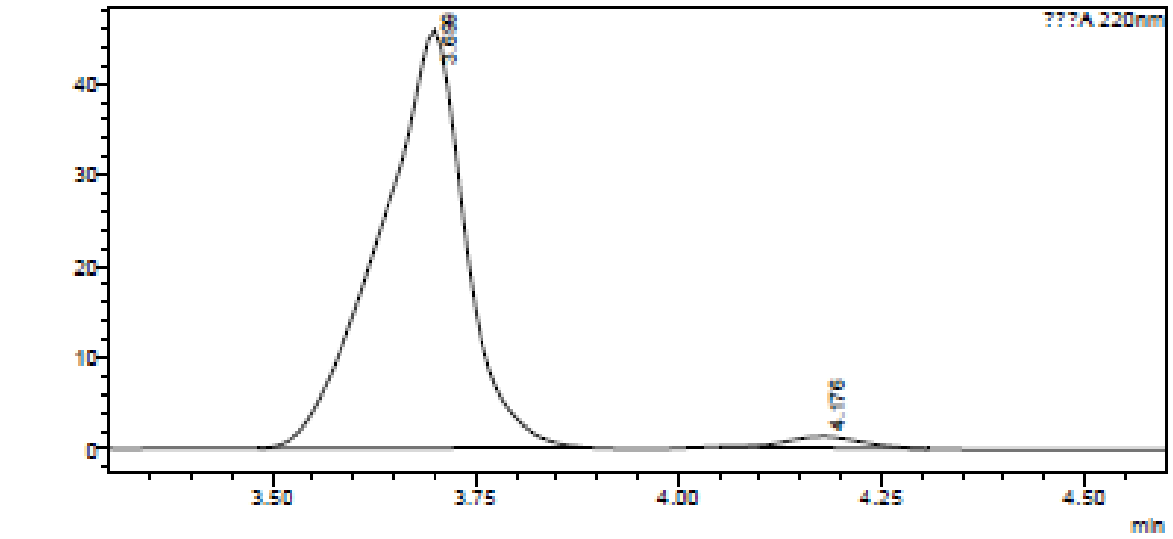


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.703	1962597	291795	49.723			
2	4.184	1984436	266370	50.277		V	
Total		3947032	558165				

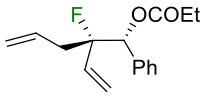
<Chromatogram>



<Peak Table>

???A 220nm

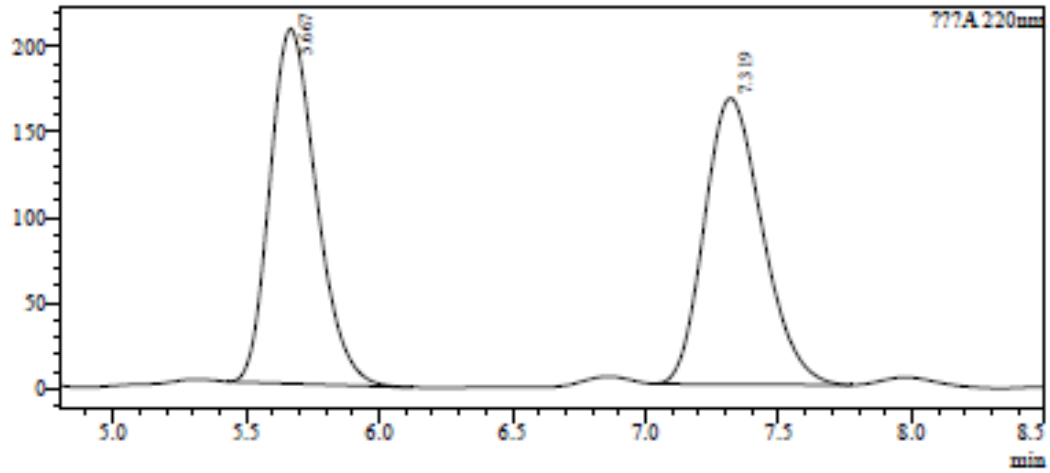
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.699	334403	45817	97.705			
2	4.176	7854	1261	2.295		M	
Total		342257	47078				



2l

<Chromatogram>

mV



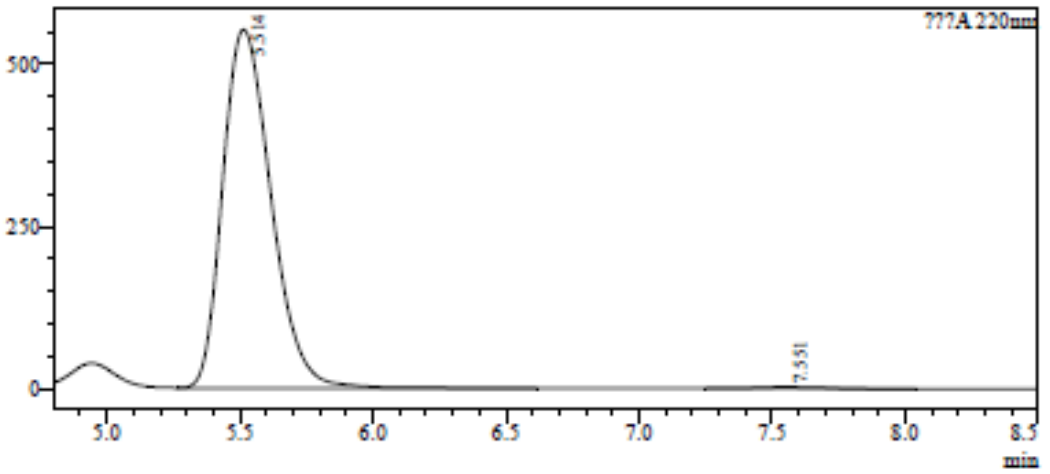
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.667	2526234	207828	49.879			
2	7.319	2538524	167444	50.121			
Total		5064758	375272				

<Chromatogram>

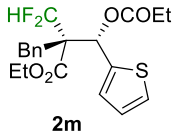
mV



<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.514	6989045	552469	99.460			
2	7.551	37923	2412	0.540			
Total		7026968	554881				



2m

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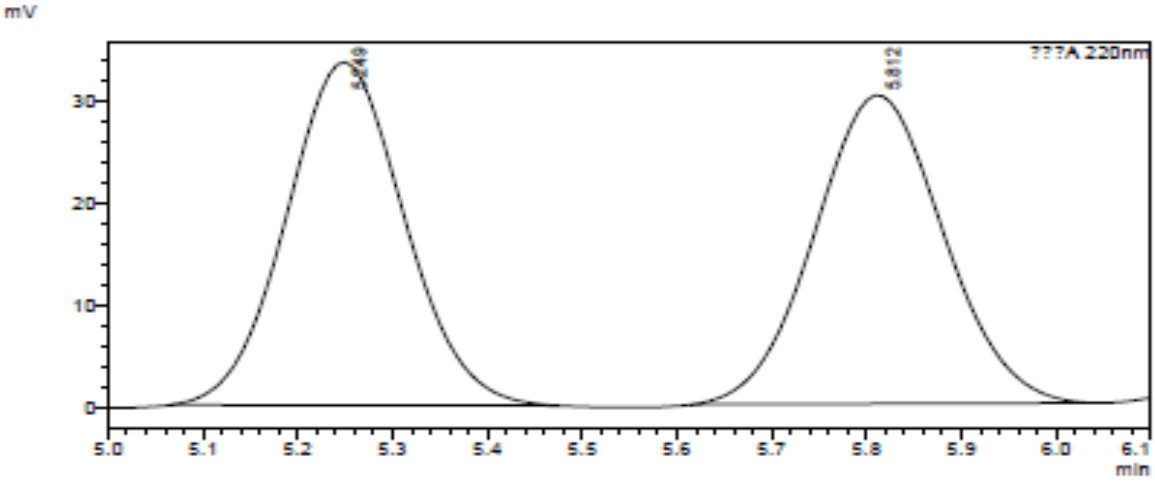
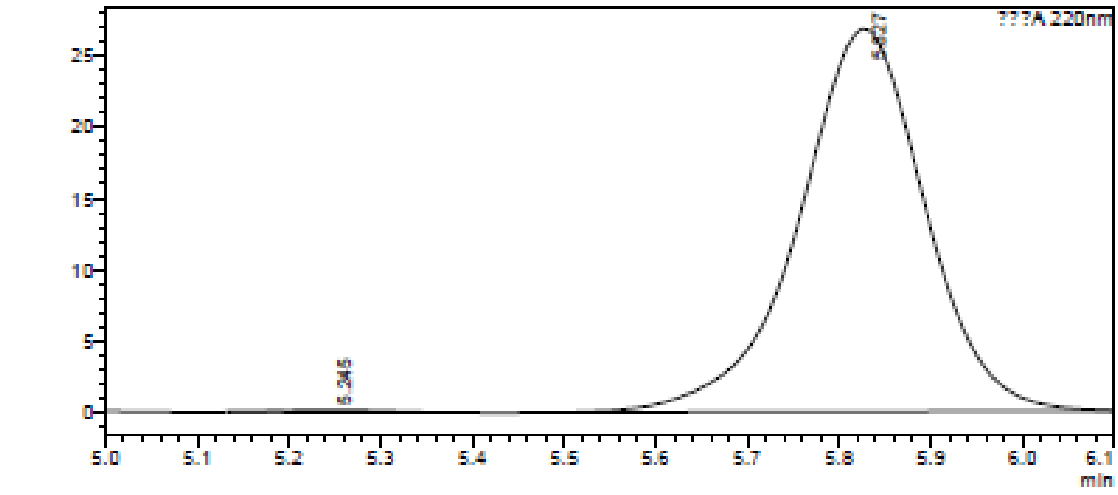


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.249	289330	33472	50.427			
2	5.812	284427	30062	49.573			
Total		573757	63534				

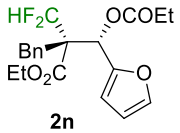
<Chromatogram>



<Peak Table>

???A 220nm

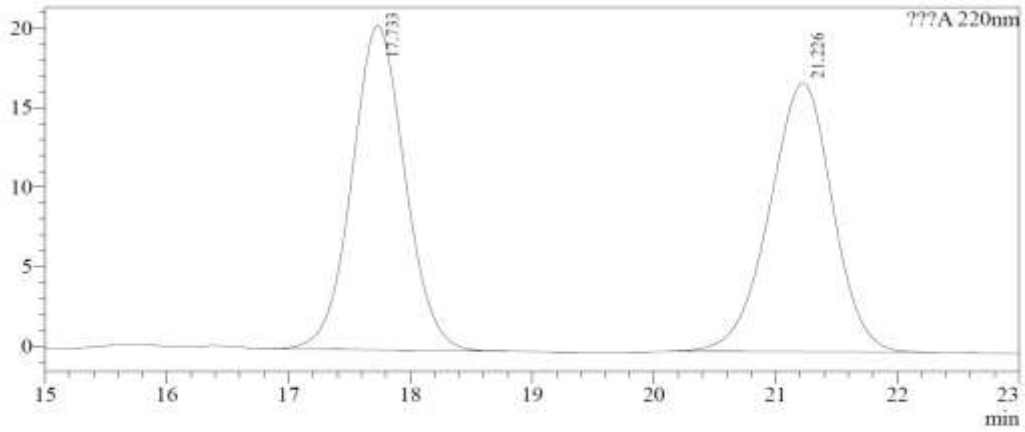
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.245	1139	147	0.444		M	
2	5.827	255139	26684	99.556		M	
Total		256277	26831				



2n

<Chromatogram>

mV



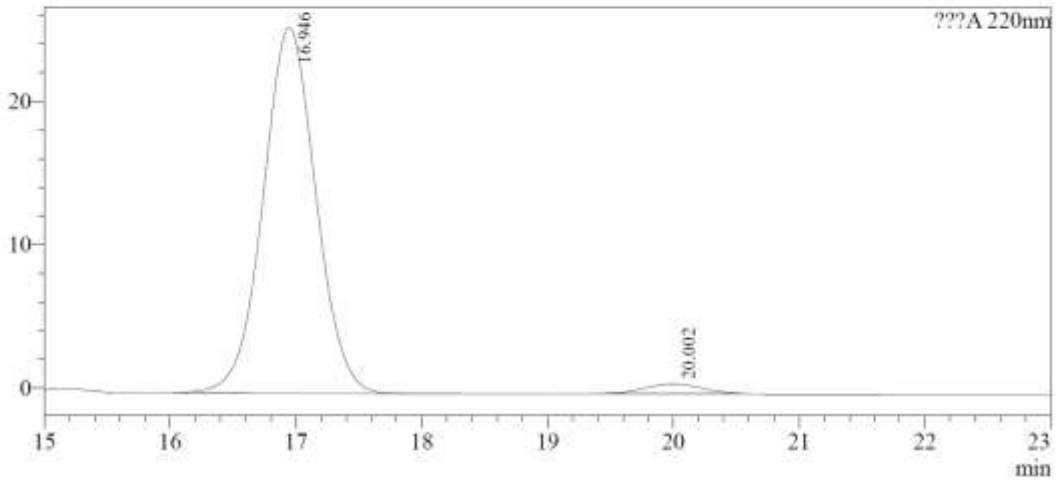
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.733	619123	20398	50.424			
2	21.226	608708	16922	49.576			
Total		1227831	37320				

<Chromatogram>

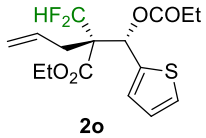
mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.946	744185	25509	97.228			
2	20.002	21220	683	2.772		M	
Total		765404	26191				



2o

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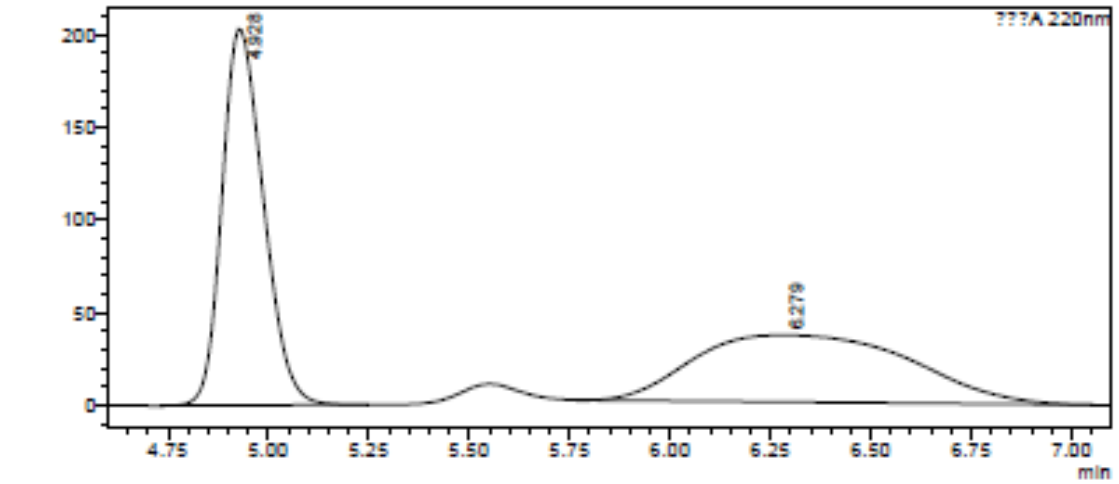
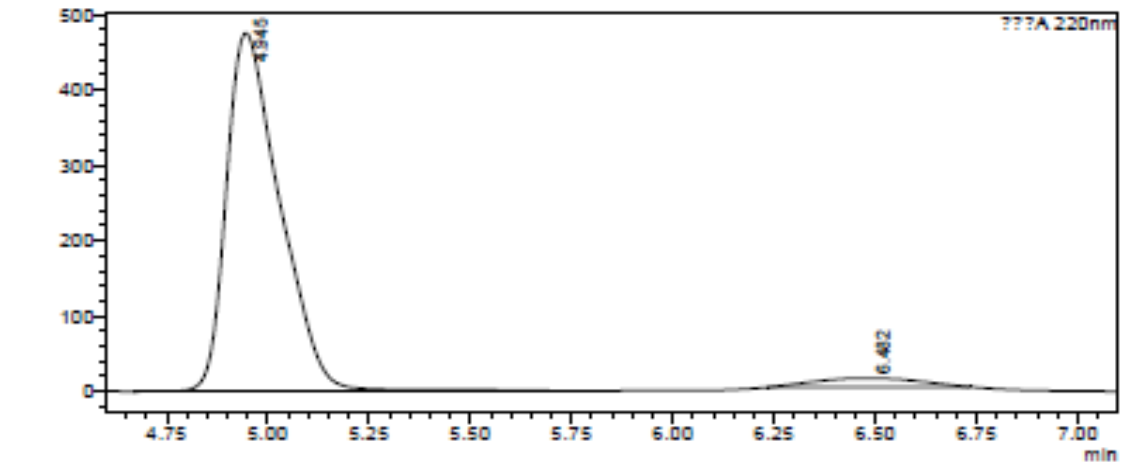


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.928	1454034	202781	51.746			
2	6.279	1355921	36031	48.254		M	
Total		2809955	238812				

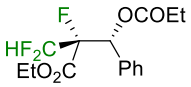
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.945	4371627	474957	95.318			
2	6.482	214750	11841	4.682		M	
Total		4586577	486798				



2p

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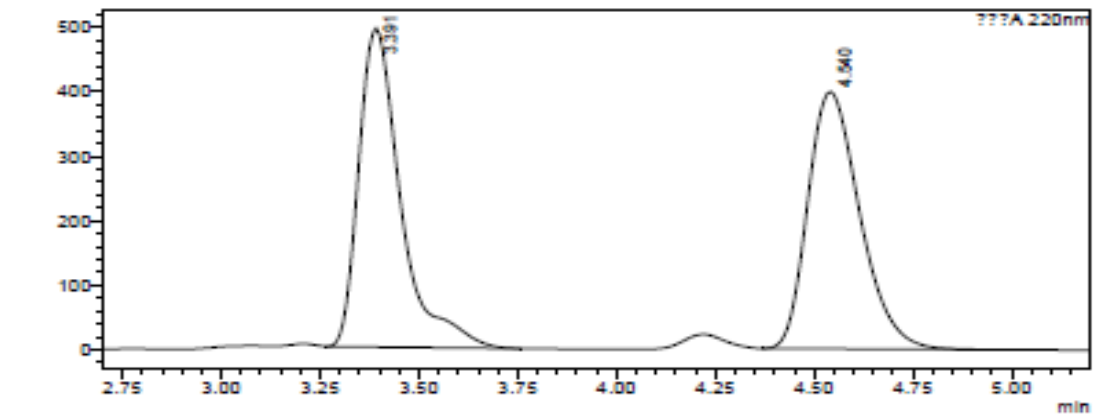
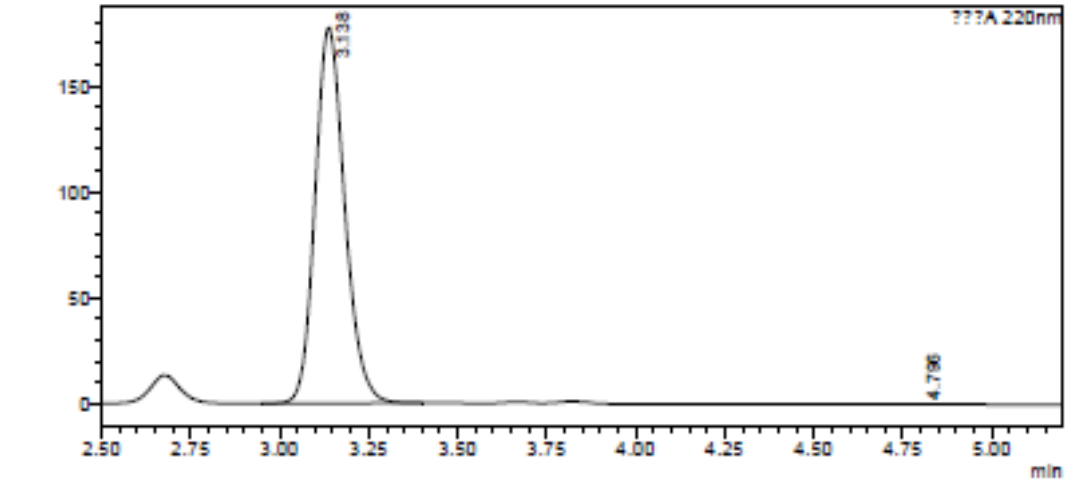


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.391	3644962	494245	50.020			
2	4.540	3642025	398744	49.980			
Total		7286987	892989				

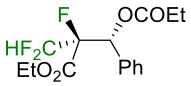
<Chromatogram>



<Peak Table>

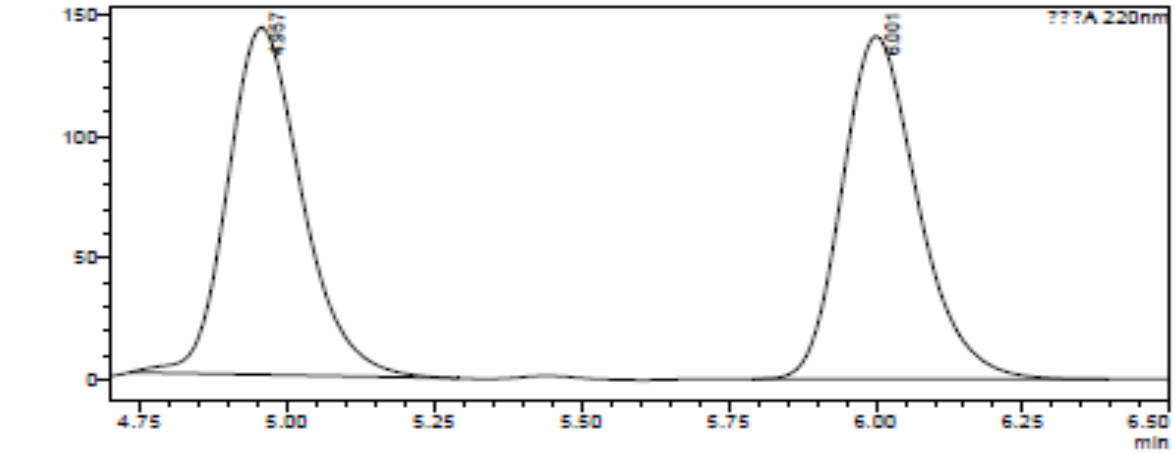
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.138	1025314	176827	99.763			
2	4.796	2440	187	0.237		M	
Total		1027754	177014				



2q

<Chromatogram>

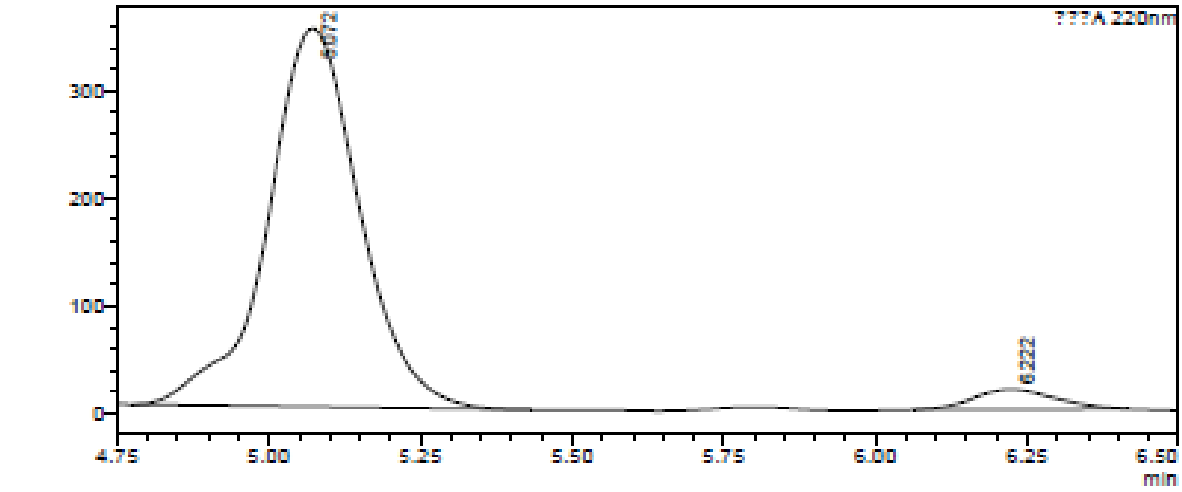


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.957	1254261	142643	49.890		M	
2	6.001	1259811	140792	50.110			
Total		2514073	283435				

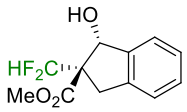
<Chromatogram>



<Peak Table>

???A 220nm

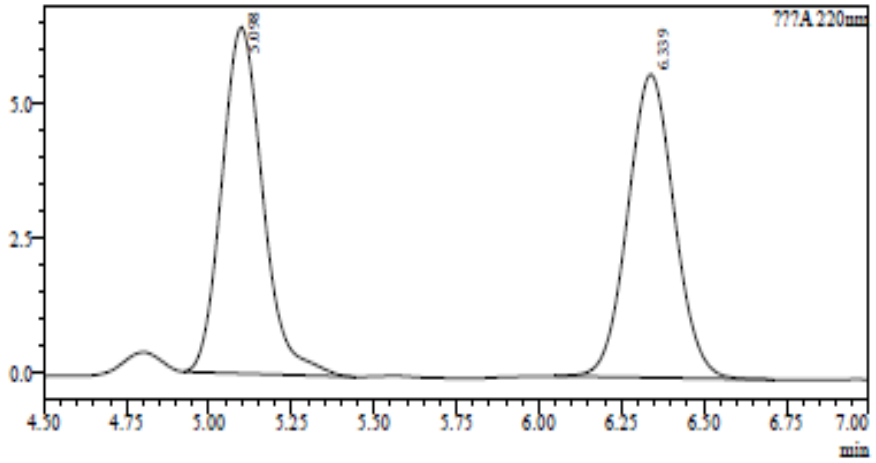
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.072	3713900	351484	95.609			
2	6.222	170567	18271	4.391		M	
Total		3884467	369755				



2r

<Chromatogram>

mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.098	55881	6432	50.302			
2	6.339	55209	5632	49.698			
Total		111091	12065				

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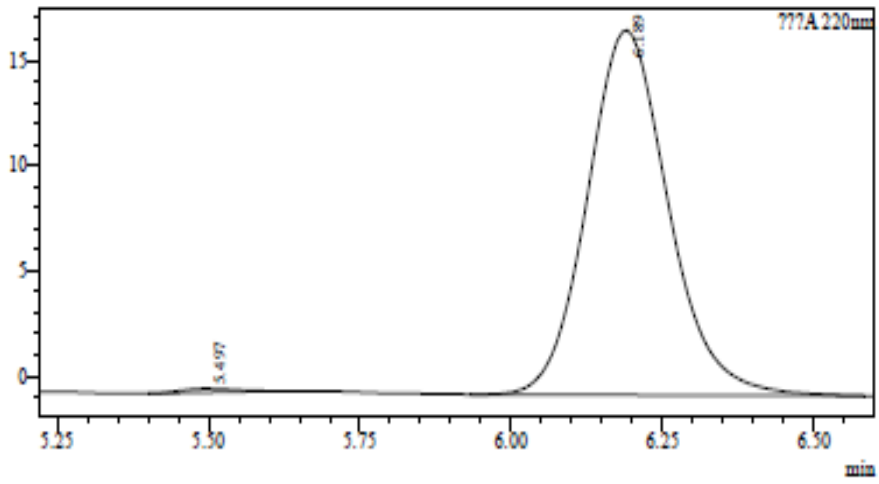
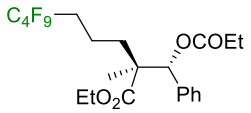
mV



<Peak Table>

???A 220nm

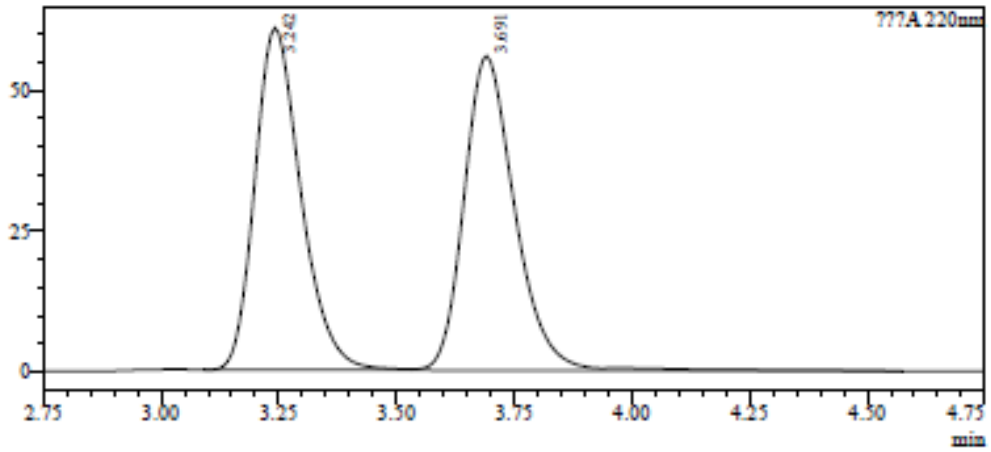
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.497	1146	177	0.704			
2	6.189	161517	17333	99.296		M	
Total		162663	17510				



2s

<Chromatogram>

mV



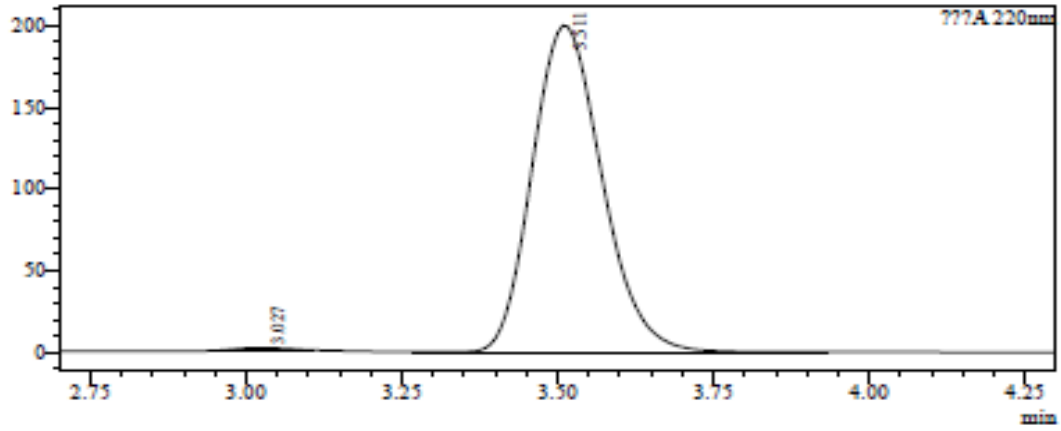
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.242	412978	60642	49.693			
2	3.691	418080	55685	50.307		SV	
Total		831058	116327				

<Chromatogram>

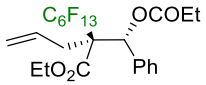
mV



<Peak Table>

777A 220nm

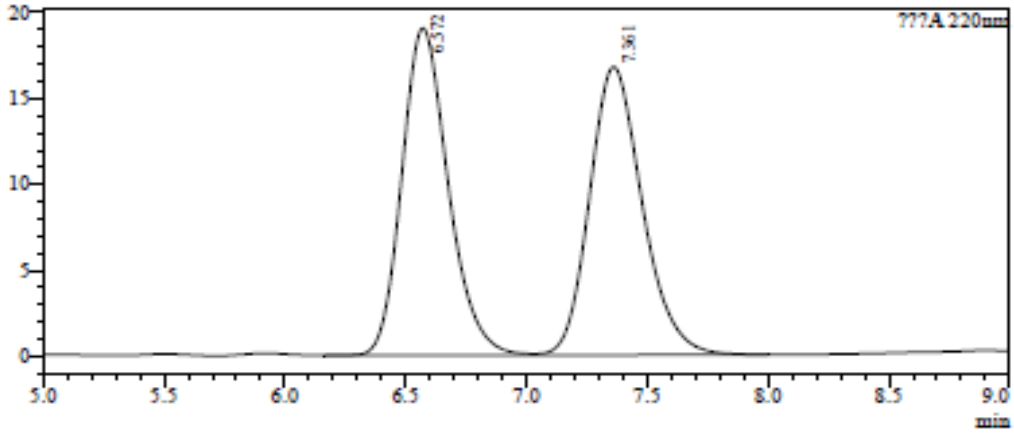
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.027	7531	1413	0.483		M	
2	3.511	1552243	199412	99.517			
Total		1559774	200825				



2t

<Chromatogram>

mV



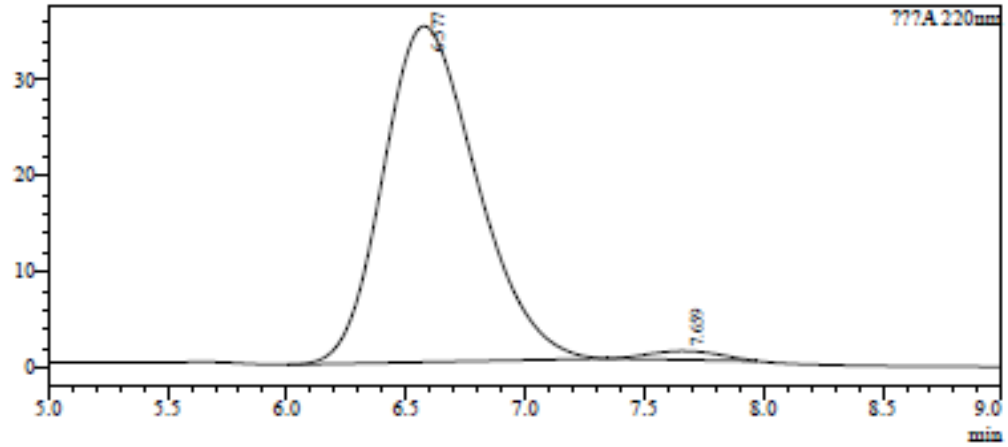
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.572	254105	19016	49.970			
2	7.361	254408	16746	50.030		V	
Total		508513	35762				

<Chromatogram>

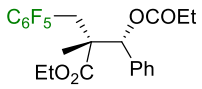
mV



<Peak Table>

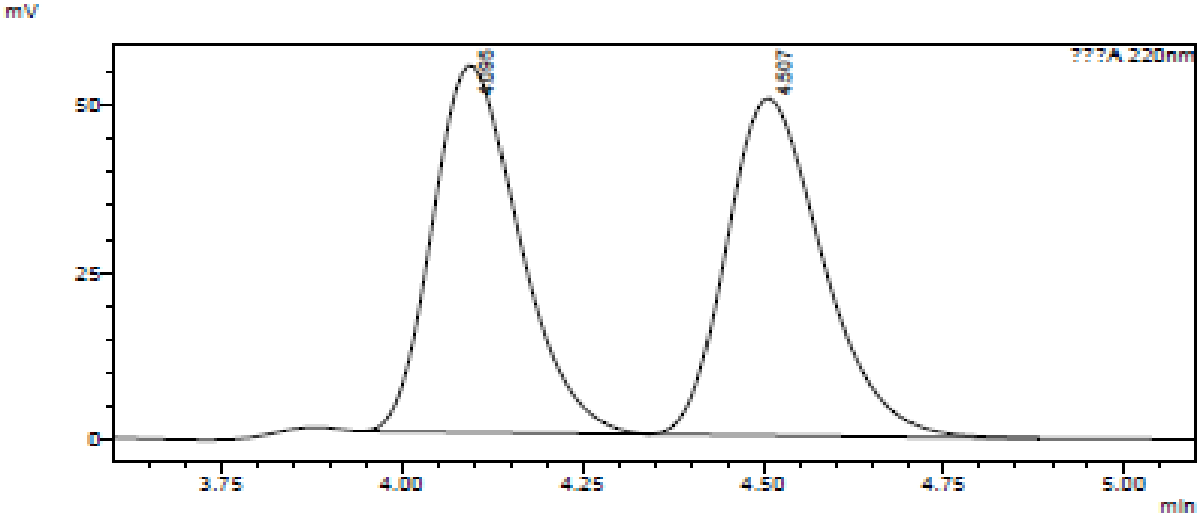
777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.577	955955	34945	98.099			
2	7.659	18524	894	1.901		M	
Total		974479	35839				



2u

<Chromatogram>

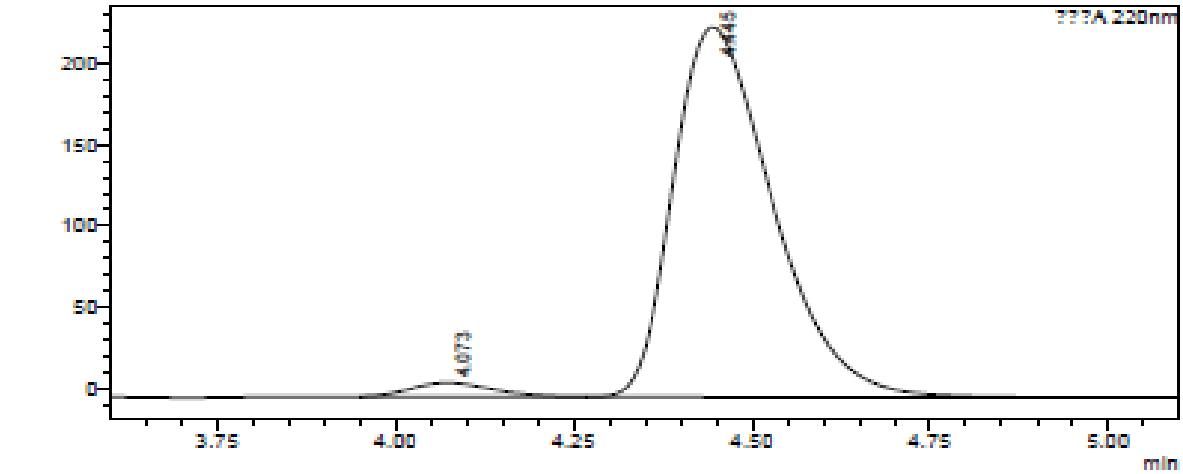


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.095	457175	54910	49.474			
2	4.507	466901	50467	50.526		V	
Total		924075	105377				

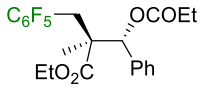
<Chromatogram>



<Peak Table>

???A 220nm

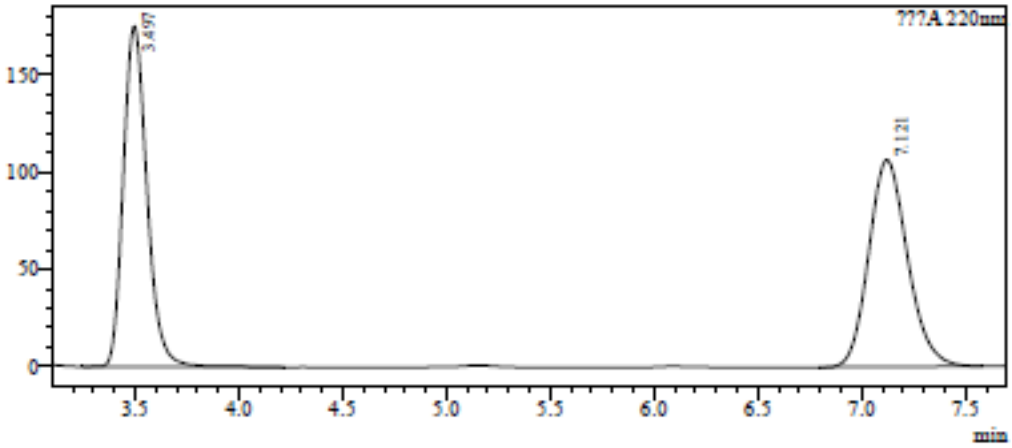
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.073	66100	8448	2.906			
2	4.445	2208902	227874	97.094			
Total		2275003	236322				



2v

<Chromatogram>

mV



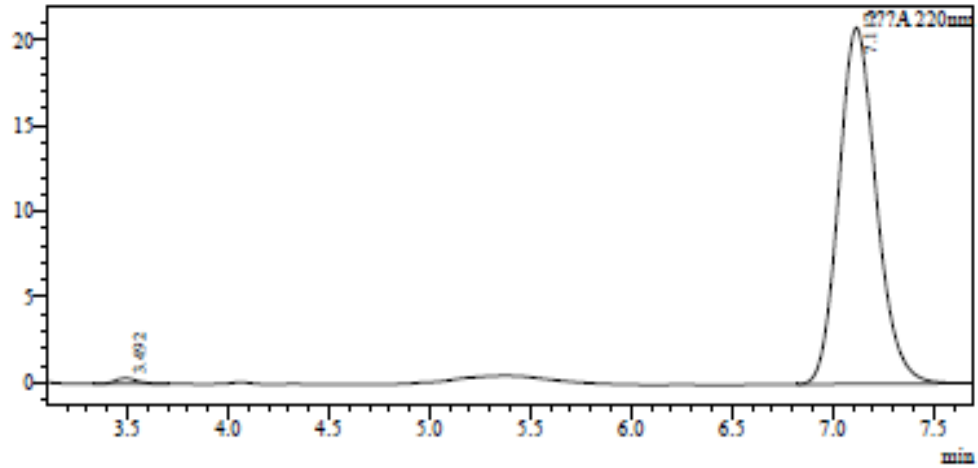
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.497	1388017	175042	50.055		S	
2	7.121	1384980	106342	49.945			
Total		2772998	281384				

<Chromatogram>

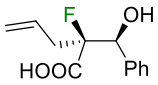
mV



<Peak Table>

777A 220nm

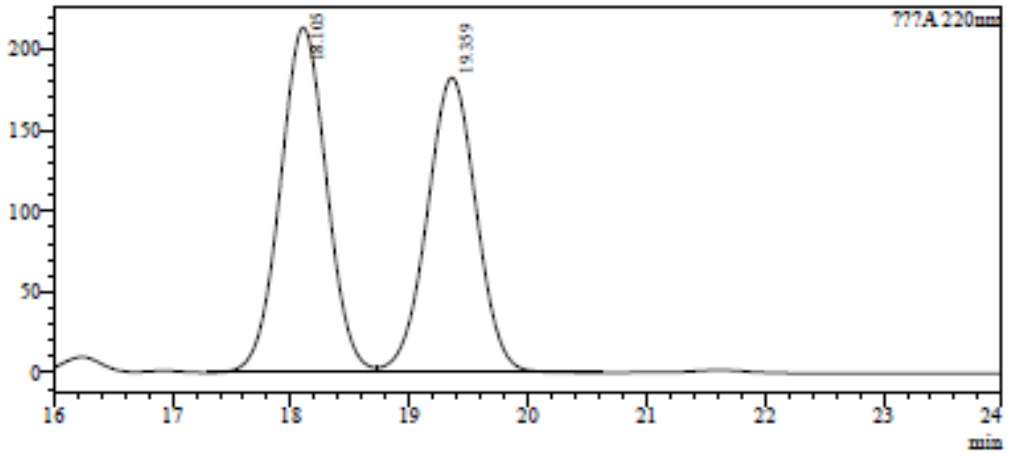
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.492	2502	326	0.920			
2	7.117	269381	20821	99.080		V	
Total		271883	21147				



3a

<Chromatogram>

mV



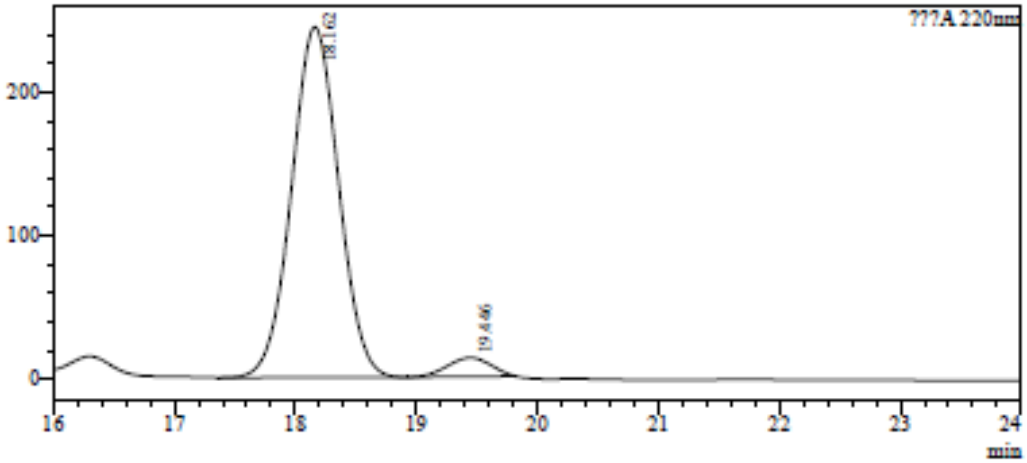
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.105	5823757	213740	52.462			
2	19.359	5277243	182808	47.538		V	
Total		11101000	396547				

<Chromatogram>

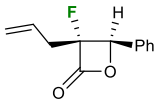
mV



<Peak Table>

777A 220nm

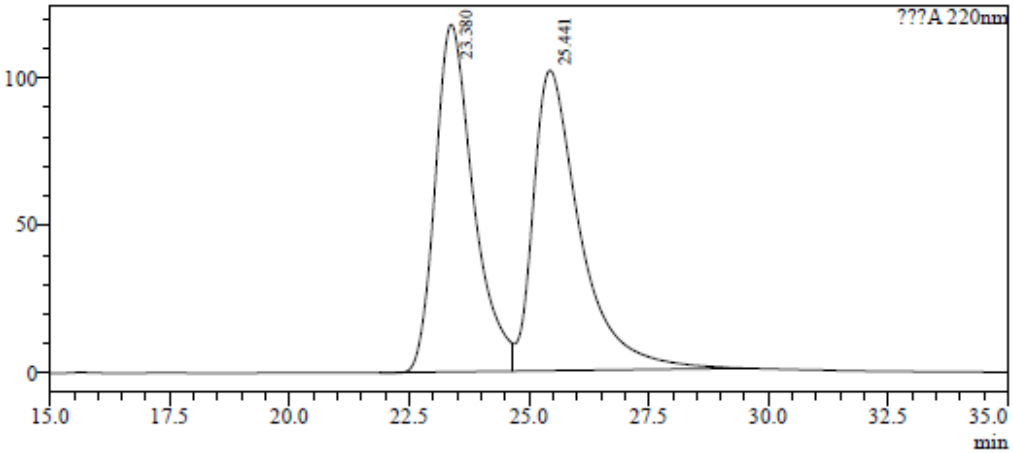
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.162	6603485	244175	95.245			
2	19.446	329677	13122	4.755		M	
Total		6933162	257297				



3b

<Chromatogram>

mV



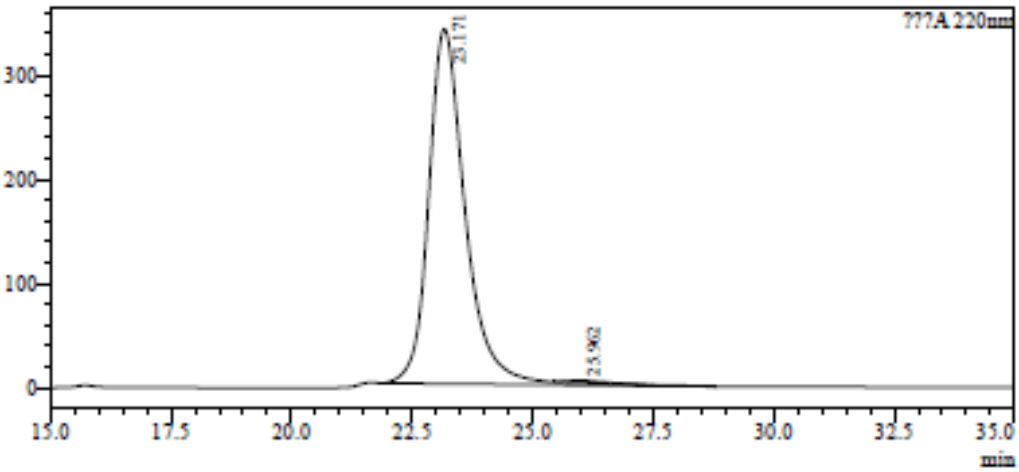
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.380	6534230	117838	48.503		M	
2	25.441	6937677	101860	51.497		V M	
Total		13471907	219698				

<Chromatogram>

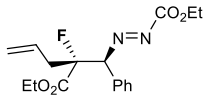
mV



<Peak Table>

???A 220nm

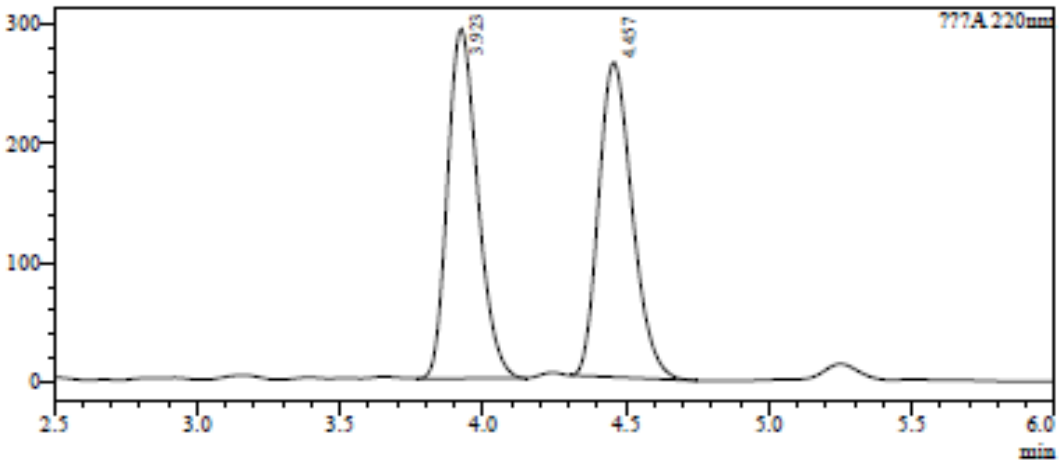
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.171	18068731	340116	99.427		S	
2	25.962	104165	1878	0.573		T	
Total		18172896	341994				



3c

<Chromatogram>

mV



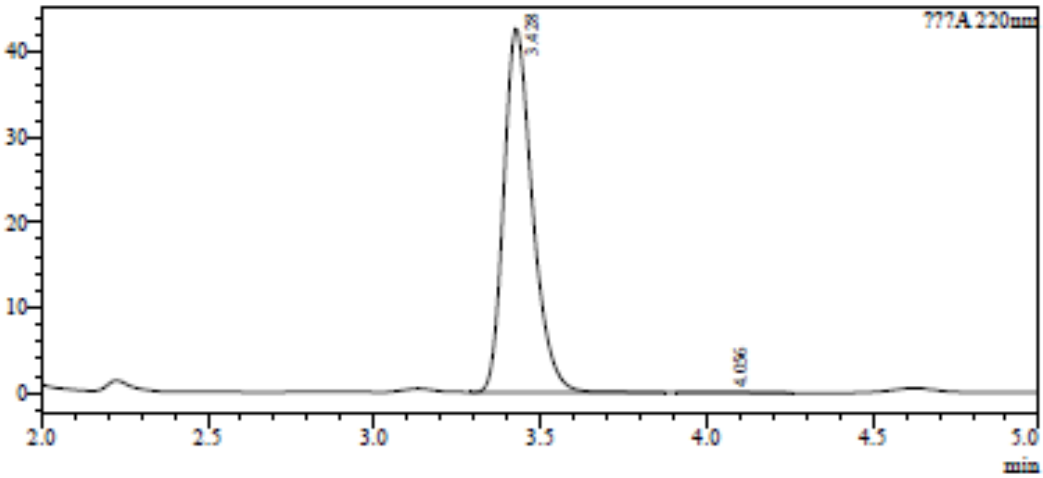
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.923	2146964	293294	49.841			
2	4.457	2160692	264324	50.159			
Total		4307656	557618				

<Chromatogram>

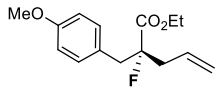
mV



<Peak Table>

???A 220nm

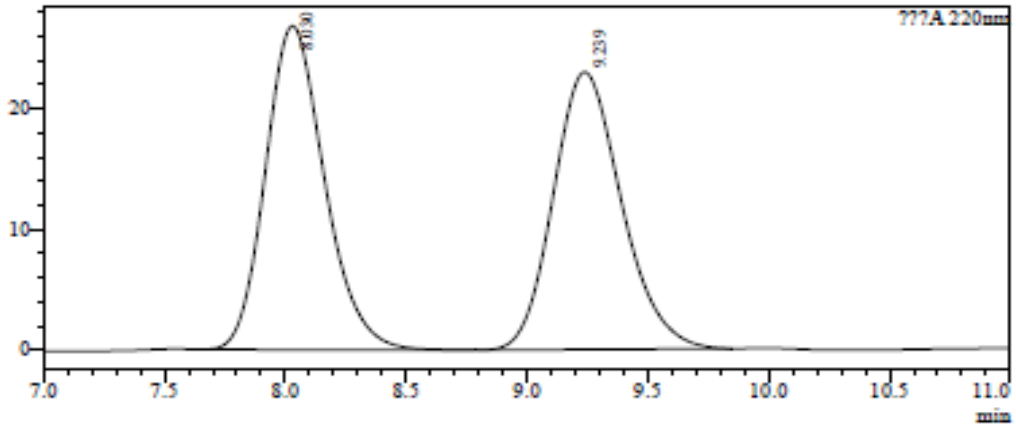
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.428	256201	42588	99.916			
2	4.056	214	18	0.084		M	
Total		256415	42607				



3d

<Chromatogram>

mV



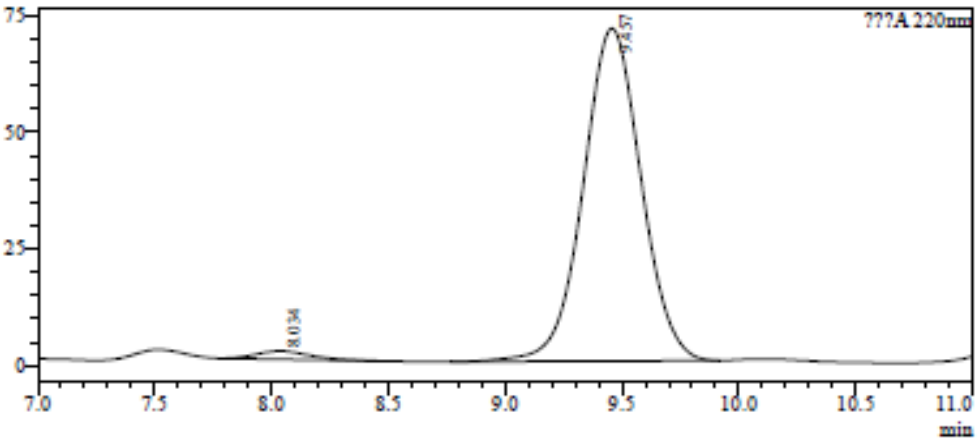
<Peak Table>

777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.030	456923	26856	50.250			
2	9.239	452383	23006	49.750			
Total		909306	49862				

<Chromatogram>

mV



<Peak Table>

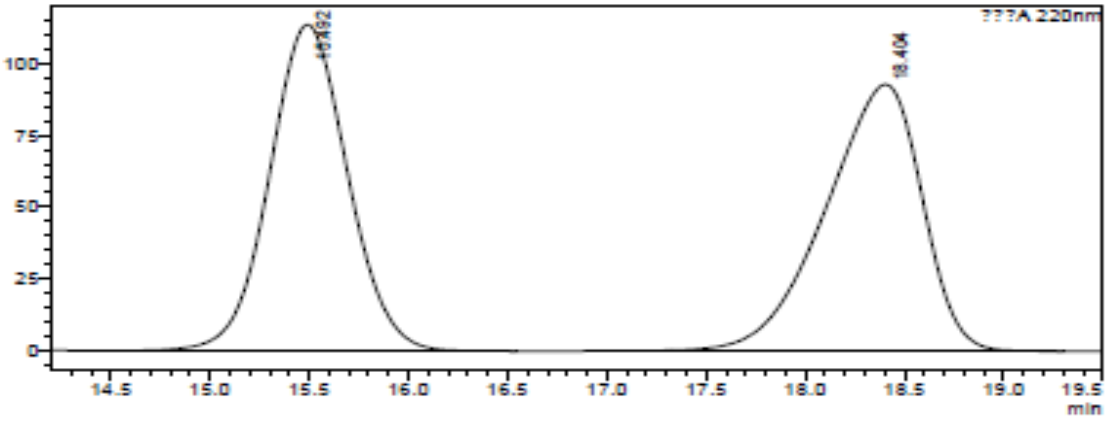
777A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.034	28209	1760	2.242			
2	9.457	1229896	71416	97.758			
Total		1258104	73176				

3e

<Chromatogram>

mV



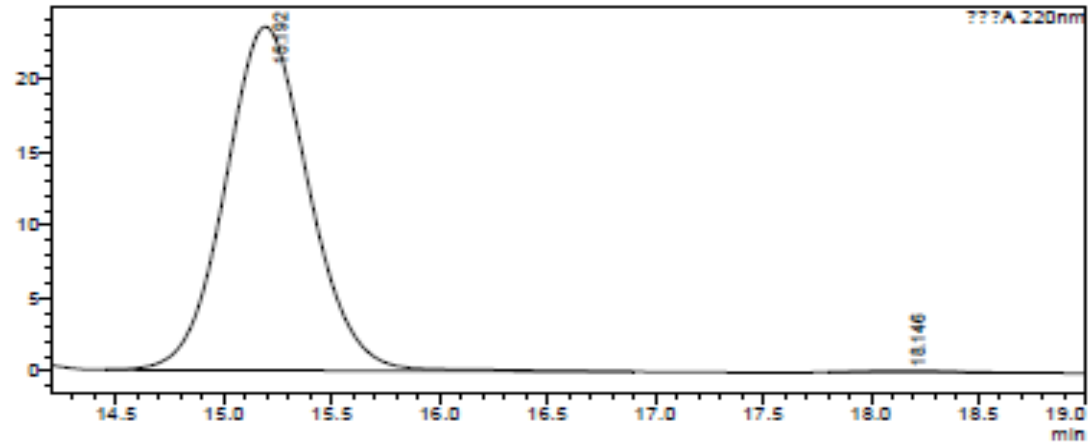
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.492	3115010	113822	49.796			
2	18.404	3140571	92903	50.204			
Total		6255581	206725				

<Chromatogram>

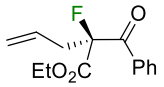
mV



<Peak Table>

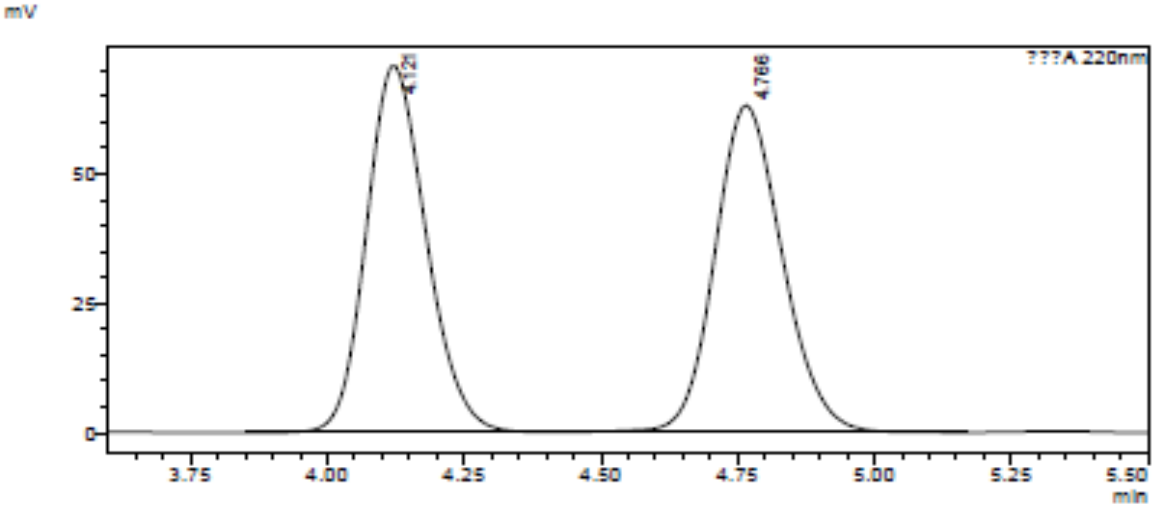
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.192	636023	23566	99.504			
2	18.146	3173	118	0.496			
Total		639196	23684				



3f

<Chromatogram>

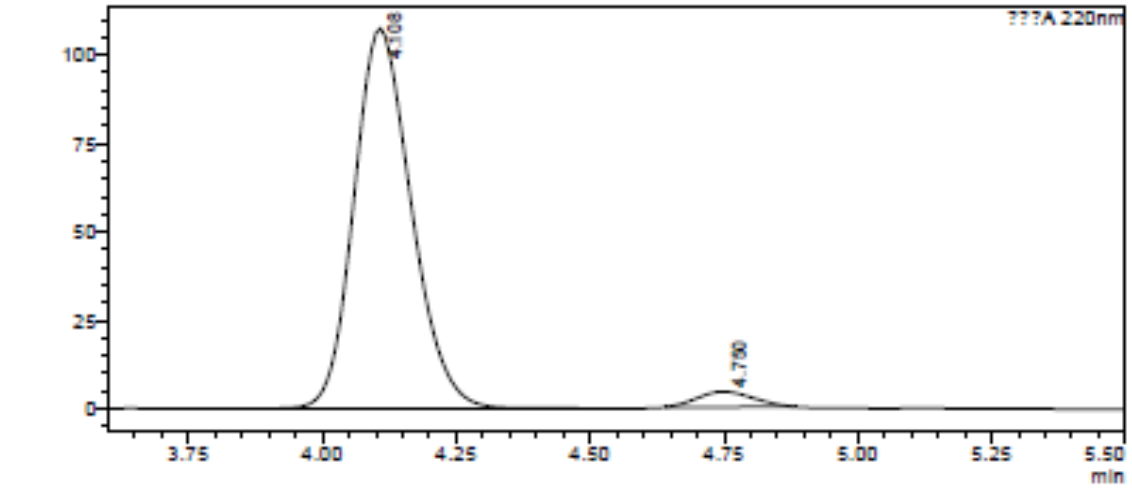


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.121	539869	70797	49.785			
2	4.766	544535	63202	50.215		V	
Total		1084404	133998				

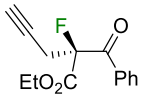
<Chromatogram>



<Peak Table>

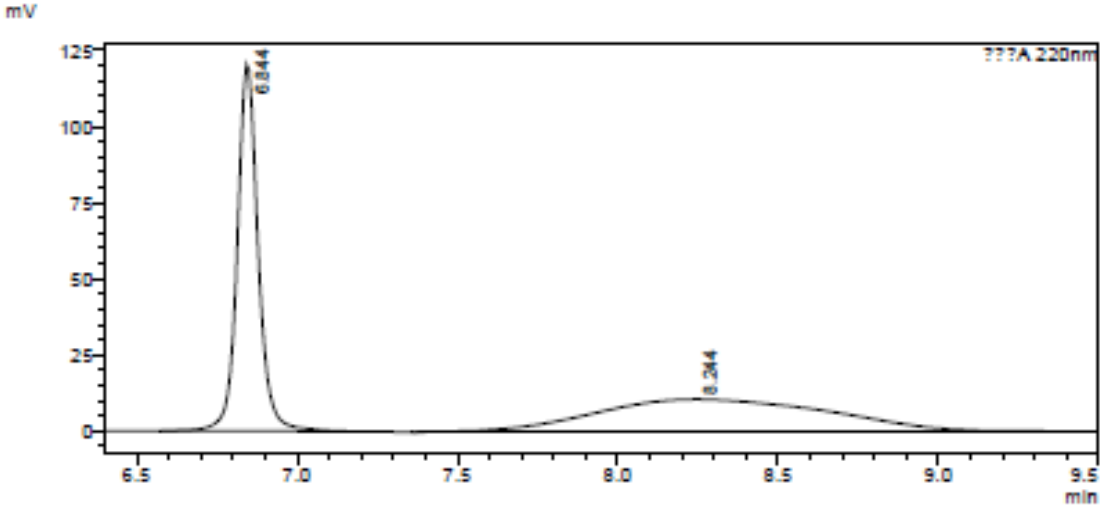
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.108	800948	107483	96.222			
2	4.750	31445	4330	3.778		M	
Total		832393	111813				



3g

<Chromatogram>

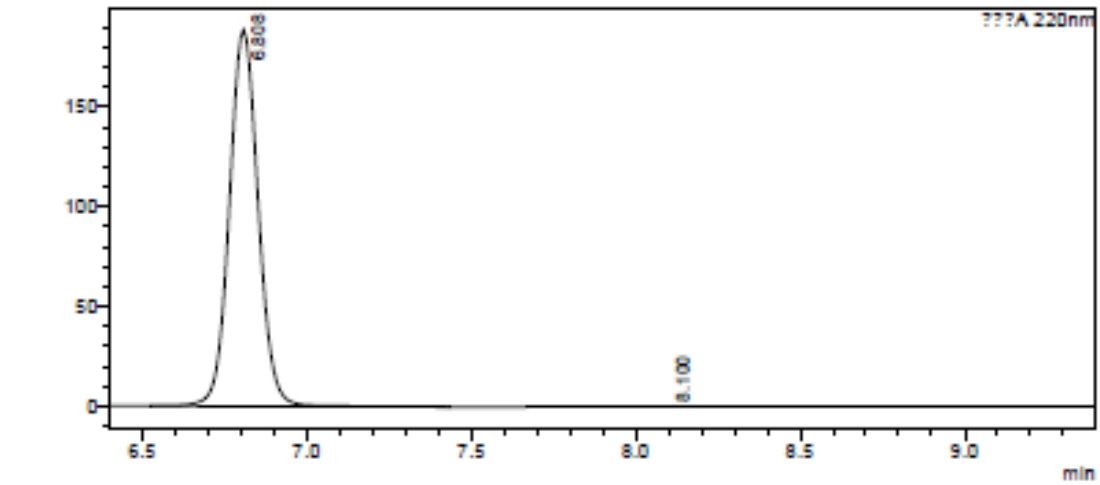


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.844	548679	120348	50.583			
2	8.244	536030	10573	49.417			
Total		1084709	130921				

<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.808	1145250	188510	99.965			
2	8.100	396	31	0.035		M	
Total		1145646	188540				