Synthesis of Remote Fluoroalkylated Alkenes by Palladium-Catalyzed Relay Heck-Type Reaction

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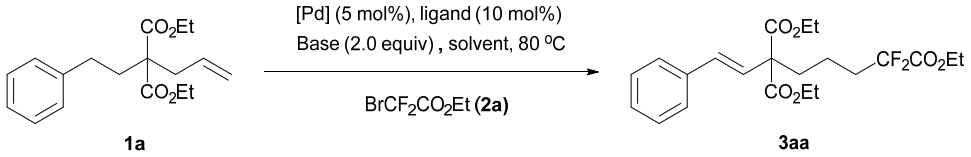
Contents

1. General information

NMR Spectra was recorded on a JNM-ECZ00R/S3 (^{1}H NMR 600 MHz, ^{13}C NMR 150 MHz, ^{19}F NMR 564 MHz). Chemical shift are given in ppm. The spectra are calibrated to residual ^{1}H and ^{13}C singals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a MicroMass Waters Xevo G2-XS QTof.

Materials and Methods: Unless otherwise stated, starting materials were purchased from Energy and Aldrich. Conversion was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ehanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh). Unless otherwise stated. Starting materials were according to previously reported procedures.

2. Optimization of the reaction conditions[a]



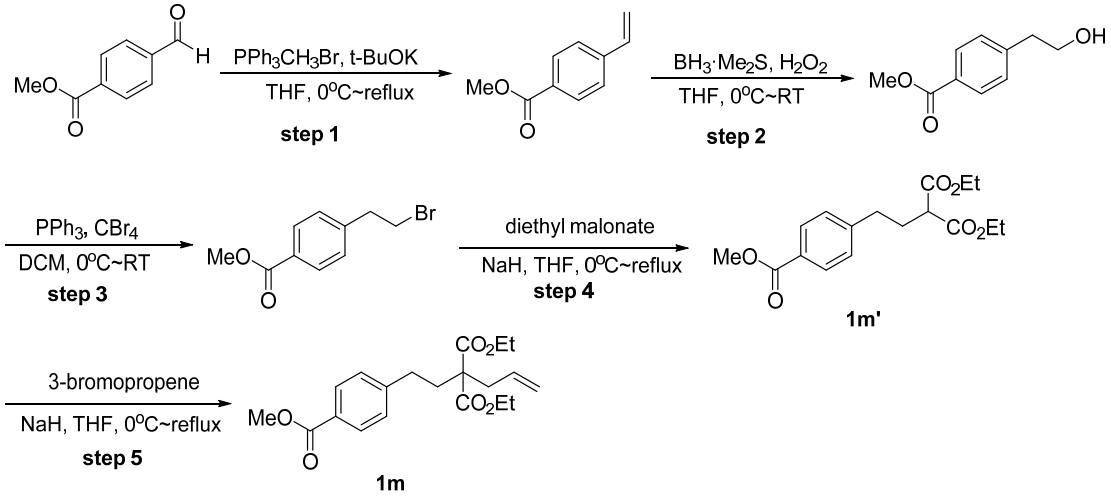
1a **3aa**

Entry	[Pd]	Ligand	Base	Solvent	Yield(%)[b]
1	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	DCM	48
2	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	DCE	33
3	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	THF	37
4	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	Dioxane	39
5	**$Pd(PPh_3)_2Cl_2$**	**Xantphos**	**K_2CO_3**	**CH_3CN**	**72**
6	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	$PhCH_3$	33
7	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	MeOH	NR[c]
8	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	DMF	trace
9	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	DMSO	trace
10	$Pd(CH_3CN)_2Cl_2$	Xantphos	K_2CO_3	CH_3CN	37
11	$Pd_2(dba)_3$	Xantphos	K_2CO_3	CH_3CN	30
12	$[Pd(allyl)Cl]_2$	Xantphos	K_2CO_3	CH_3CN	20
13	$Pd(TFA)_2$	Xantphos	K_2CO_3	CH_3CN	25
14	$Pd(PPh_3)_4$	Xantphos	K_2CO_3	CH_3CN	42
15	$Pd(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	CH_3CN	45
16	$Pd(PPh_3)_2Cl_2$	Xantphos	KH_2PO_4	CH_3CN	15
17	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2HPO_4	CH_3CN	52
18	$Pd(PPh_3)_2Cl_2$	Xantphos	Na_3PO_4	CH_3CN	trace
19	$Pd(PPh_3)_2Cl_2$	Xantphos	Li_3PO_4	CH_3CN	trace
20	$Pd(PPh_3)_2Cl_2$	Xantphos	Cs_2CO_3	CH_3CN	28
21	$Pd(PPh_3)_2Cl_2$	Xantphos	Na_2CO_3	CH_3CN	25
22	$Pd(PPh_3)_2Cl_2$	Xantphos	KOAc	CH_3CN	44
23	$Pd(PPh_3)_2Cl_2$	Xantphos	NEt_3	CH_3CN	NR
24	$Pd(PPh_3)_2Cl_2$	DPPE	K_2CO_3	CH_3CN	NR
25	$Pd(PPh_3)_2Cl_2$	DPPP	K_2CO_3	CH_3CN	NR
26	$Pd(PPh_3)_2Cl_2$	DPPB	K_2CO_3	CH_3CN	NR
27	$Pd(PPh_3)_2Cl_2$	DPPF	K_2CO_3	CH_3CN	NR
28	$Pd(PPh_3)_2Cl_2$	DPEphos	K_2CO_3	CH_3CN	22
29	$Pd(PPh_3)_2Cl_2$	BINAP	K_2CO_3	CH_3CN	NR
30[d]	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	CH_3CN	trace
31[e]	$Pd(PPh_3)_2Cl_2$	Xantphos	K_2CO_3	CH_3CN	trace

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.2 mmol), [Pd] (5 mol %), ligand (10 mol%), Base (0.2 mmol),solvent (1.0 mL), under N_2, 80°C, 24h. [b] Yield determined by ^{19}F NMP using $PhCF_3$ as an internal standard. [c] NR = no reaction [d] at 25 °C. [e] Blue LED.

3. General procedures

3.1 General procedures for unknownsubstances



Step 2: In an 500 mL oven-dried Schlenk flask containing a magnetic stir bar under inert atmosphere, potassium tert-butylate (60 mmol, 6.72 g) was added into the solution of methy 4-formylbenzoate (50 mmol, 8.2 g) in THF (250 mL) under ice bath. After the mixture was stirred for one hour, methyltriphenylphosphonium bromide (60 mmol, 21.42 g) was added the reaction mixture under ice bath. The resulting mixture was stirred overnight at room temperature. After the reaction completed, saturated NaCl solution (200 mL) was added to quench the reaction and extracted with hexane (50 mL x3), the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane) to give the pure alkene (8.09 g, 99%).

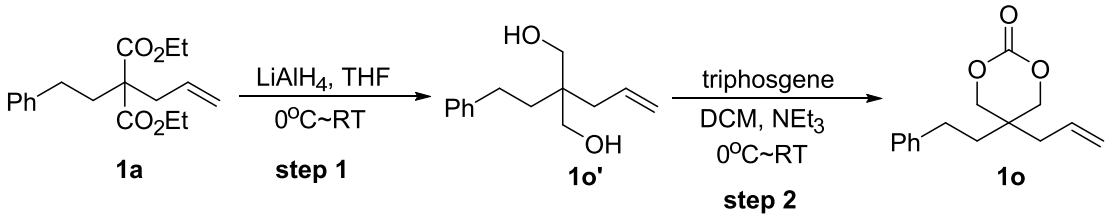
Step 2: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, BH_3•Me_2S (2 M in THF, 8.74 mL) was added into the solution of the obtained alkene (8.4 g, 51.7 mmol) in THF (50 mL) under ice bath. After the reaction mixture was stirred for two hours at room temperature, water (20 mL), aqueous NaOH solution (3 M, 18 mL), aqueous H_2O_2 solution (30% w/w, 34 mL) was added into the reaction mixture subsequently under ice bath, then the resulting mixture was stirred for two hours at room temperature. The reaction was quenched by DCM (25 mL), the mixture was extracted with DCM (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 3/1) to give the pure alcohol (4.75 g, 51%). The experimental data are in agreement with the literature report (*J. Am. Chem.***2006**, *128*, 16020-16021).

Step 3: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, PPh_3 (12.5 mmol, 3.3 g), CBr_4 (12.5 mmol, 4.13 g) was added into the solution of the obtained alcohol (10 mmol, 1.8 g) in DCM (30 mL) under ice bath. After the reaction mixture was stirred overnight at room temperature, the reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with DCM (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 10/1) to give the pure homobenzylic

bromide (2.2 g, 92%). The experimental data are in agreement with the literature report (*Chem.-Eur. J.* **2019**, *38*, 9001-9005).

Step 4: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, NaH (11 mmol, 440 mg) was added into the solution of diethyl malonate (9.9 mmol, 1.6 g) in THF (100 mL) under ice bath. After the reaction mixture was stirred for one hour at room temperature, the obtained homobenzylic bromide (9 mmol, 2.2 g) was added, and then the reaction mixture was stirred under 70 ^{o}C overnight. The reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 5/1) to give the pure product diethyl 2-(4-(methoxycarbonyl)phenethyl)malonate**1m'** (2.09 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 5.5 Hz, 2H), 4.22 -4.18 (m, 4H), 3.90 (s, 3H), 3.33 (t, *J* = 7.3 Hz, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.25 - 2.21 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.15, 167.03, 146.12, 129.82, 128.56, 128.22, 61.48, 52.03, 51.16, 33.31, 29.92, 14.07; HRMS (ESI) m/z calcd for $C_{17}H_{22}O_6Na$ [M+Na^+] 345.1309, found 345.1325.

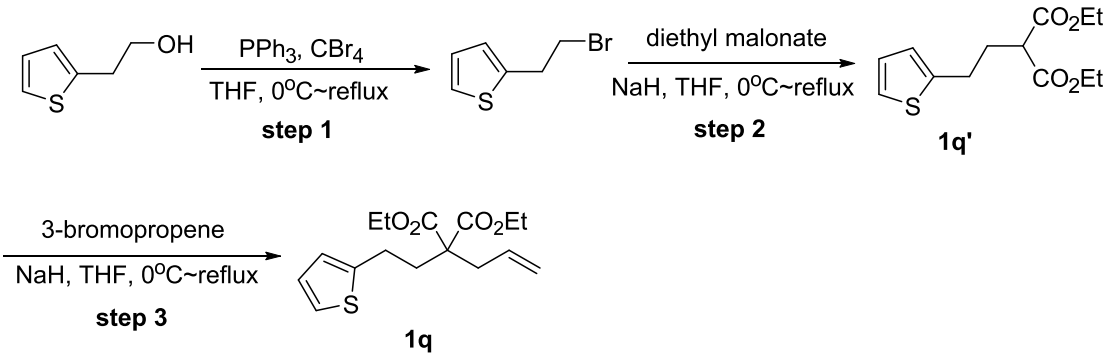
Step 5: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, NaH (7.4 mmol, 297 mg) was added into the solution of the obtained diethyl 2-(4-(methoxycarbonyl)phenethyl)malonate (6 mmol, 2.0 g) in THF (50 mL) under ice bath. After the reaction mixture was stirred for one hour at room temperature, the obtained 3-bromopropene (12 mmol, 1.1 mL) was added, and then the reaction mixture was stirred under 70 ^{o}C overnight. The reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 3/1) to give the pure product **1m** (1.77 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 8.2 Hz, 2H), 5.71 - 5.64 (m, 1H), 5.17 - 5.12 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 2.74 (d, *J* = 7.5 Hz, 2H), 2.59 - 2.56 (m, 2H), 2.17-2.15 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.94, 167.04, 146.91, 132.24, 129.76, 128.39, 128.04, 119.19, 61.34, 57.14, 52.00, 37.21, 33.89, 30.54, 14.1; HRMS (ESI) m/z calcd for $C_{20}H_{26}O_6Na$ [M+Na^+] 385.1622, found 385.1633.



Step 1: To an oven-dried 200 mL Schlenk flask was added 50 mL THF, $LiAlH_4$ (1.2equiv), and **1a** (3 mmol, 912 mg) at 0^{o}C, the resulting mixture was stirred overnight under room temperature. After the reaction was completed, aqueous HCl soulution (1N, 20 mL) was added into the reaction mixture slowly under ice bath and extracted with ethyl acetate (30 mL x3), the combined organic layers was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane/ethyl acetate = 5/1) to afford the pure product **1o'** (528 mg, 80%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 - 7.27 (m, 2H), 7.20 - 7.17 (m,3H), 5.90 - 5.83 (m, 1H), 5.19 - 5.13 (m, 2H), 3.65 (s, 4H), 2.62 -

2.59 (m, 2H), 2.23(br, 2H), 2.19 (d, J = 7.4 Hz, 2H), 1.63 - 1.60 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.62, 133.83, 128.41, 128.25, 125.83, 118.13, 68.68, 41.80, 35.82, 33.45, 29.44; HRMS (ESI) m/z calcd for $C_{14}H_{19}O_2$ [M-H$^+$] 219.1391, found 219.1369.

Step 2: To an oven-dried 50 mL Schlenk flash was added **1o'** (0.5 mmol, 110 mg), DCM (10 mL), triphosgene (0.5 mmol, 148.4 mg) and NEt_3 (1.0 mmol, 101.2 mg) subsequently under ice bath. The resulting mixture was stirred overnight under room temperature. After the reaction was completed, the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane/ethyl acetate = 10/1) to give the pure product **1o** (80 mg, 65%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.3 Hz, 2H), 5.82 -5.75 (m, 1H), 5.28 - 5.24 (m, 2H), 4.21 - 4.16 (m, 4H), 2.65 - 2.62 (m, 2H), 2.32 (d, J = 7.4 Hz, 2H), 1.74 - 1.71 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.21, 140.59, 130.58, 128.68, 128.11, 126.43, 120.70, 74.71, 35.04, 33.96, 33.14, 29.21; HRMS (ESI) m/z calcd for $C_{15}H_{18}O_3$ [M+Na$^+$] 269.1148, found 269.1150.



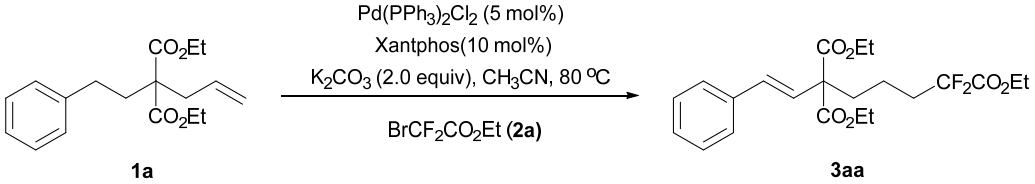
Step 1: In an 500 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, PPh_3 (40.0 mmol, 10.5 g), CBr_4 (40.0 mmol, 13.08 g) was added into the solution of the alcohol (11 mmol, 5.6 g) in THF (200 mL) under ice bath. After the reaction mixture was stirred overnight at room temperature, the reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 100/1) to give the pure 2-(2-bromoethyl)thiophene (7.1 g, 94%). The experimental data are in agreement with the literature report(*Chem.-Eur. J.* **2019**, *38*, 9001-9005).

Step 2: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, NaH (15 mmol, 600 mg) was added into the solution of diethyl malonate (10.0 mmol, 1.6 g) in THF (50 mL) under ice bath. After the reaction mixture was stirred for one hour at room temperature, 2-(2-bromoethyl)thiophene (10 mmol, 1.89 g) was added, and then the reaction mixture was stirred under 70 °C overnight. The reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 100/1) to give the pure product diethyl 2-(2-(thiophen-2-yl)ethyl)malonate**1q'** (810 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (dd, J_1= 5.3 Hz, J_2= 1.0 Hz, 1H), 6.93 – 6.91 (m, 1H), 6.81 – 6.80 (m, 1H), 4.22 (dq, J_1 = 7.4 Hz, J_2 = 1.8 Hz, 4H), 3.40 (t, J = 7.4 Hz, 1H), 2.74 (t, J = 7.7 Hz, 2H), 2.28 (q, J

= 7.6 Hz, 2H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.16, 143.09, 126.81, 124.85, 123.49, 61.43, 50.89, 30.51, 27.32, 14.05; HRMS (ESI) m/z calcd for $C_{13}H_{18}O_4SNa$ [M+Na^+] 293.0818, found 293.0826.

Step 3: In an 250 mL oven-dried Schlenk flask containing a magnetic bar under inertatmosphere, NaH (2.6 mmol, 106 mg) was added into the solution of the obtained diethyl 2-(2-(thiophen-2-yl)ethyl)malonate (2.2 mmol , 600 mg) in THF (50 mL) under ice bath. After the reaction mixture was stirred for one hour at room temperature, the obtained 3-bromopropene (4.2 mmol, 0.36 mL) was added, and then the reaction mixture was stirred under 70 °C overnight. The reaction was quenched by saturated NaCl solution (25 mL), the mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layers was dried by $NaSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ ethyl acetate = 3/1) to give the pure product **1q** (401 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 - 7.11 (m, 1H), 6.92 (dd, J_1= 5.2 Hz, J_2= 3.4 Hz, 1H), 6.80 (d, J = 3.4 Hz, 1H), 5.71 - 5.64 (m, 1H), 5.16 - 5.11 (m, 2H), 4.22 (q, J = 7.0 Hz, 4H), 2.78 - 2.75 (m, 2H), 2.72 (d, J = 7.4 Hz, 2H), 2.27 - 2.24 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.88, 144.03, 132.16, 126.71, 124.22, 123.18, 119.22, 61.32, 57.06, 37.15, 34.21, 24.60, 14.10; HRMS (ESI) m/z calcd for $C_{16}H_{22}O_4SNa$ [M+Na^+] 333.1131, found 333.1129.

3.2 General procedures for relay Heck-type reaction



1a **3aa**

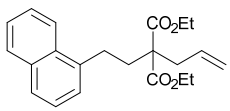
To an oven-dried 10 mL Schlenk tube was added $Pd(PPh_3)_2Cl_2$ (5 mol%), Xantphos (10 mol%), and K_2CO_3 (2.0 equiv). The tube was evacuated and back-filled with nitrogen (this process was repeated three times), **1a** (0.2 mmol, 29.2 mg), **2a** (0.4 mmol, 80.4 mg) and CH_3CN (2.0 mL) was added subsequently via syring. The resulting mixture was stirred under 80 °C until the reaction completion (about 24 hours). The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel with PE/EA (20:1 to 5:1) as eluent to give **3aa** (61.3 mg, 72% yield).

Procedure for Gram-scale reaction:

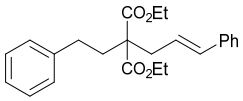
To an oven-dried 100 mL Schlenk round flask was added $Pd(PPh_3)_2Cl_2$ (5 mol%), Xantphos (10 mol%), and K_2CO_3 (2.0 equiv). The tube was evacuated and back-filled with nitrogen (this process was repeated three times), **1a** (3.0 mmol, 730.0 mg), **2a** (6.0 mmol, 1.21 g) and CH_3CN (20.0 mL) was added subsequently via syring. The resulting mixture was stirred at 80 °C until the reaction completion about 36 hours. The mixture was filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel with PE/EA (20:1 to 5:1) as eluent to give **3aa** (852.2 mg, 67% yield).

3.3 Problematic substrates

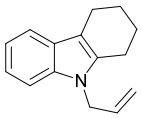
Alkenes in Scheme 2



S-1

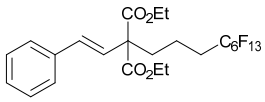


S-2

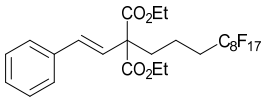


S-3

Fluoroalkyl Bromides in Scheme 3



3ai

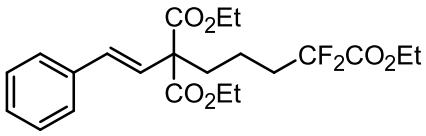


3aj

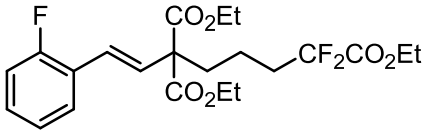
These substrates (**S-1**, **S-2**, **S-3**) in above figure are not suitable for the relay Heck-type reaction. When **S-1** acted as substrate, only trace product was obtained. No reaction occurred when **S-2** acted as substrate due to the steric effect. When analogues of *N*-allylic substrate (**S-3**) acted as substrate, no reaction occurred.

The desired products **3ai** and **3aj** was obtained combined with the corresponding start material. Because the two compounds can separate hardly, the yield was detected by ^{19}F spectrum using $PhCF_3$ as internal standard.

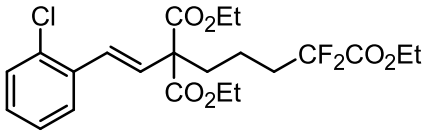
4. Characterization of new compounds



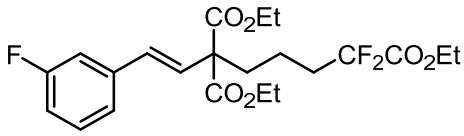
triethyl (E)-1,1-difluoro-7-phenylhept-6-ene-1,5,5-tricarboxylate (3aa):
Colorless oil, 60.5 mg, (71% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 16.6 Hz, 1H), 6.49 (d, *J* = 16.6 Hz, 1H), 4.29 - 4.21 (m, 6H), 2.20 (t, *J* = 8.5 Hz, 2H), 2.13 - 2.04 (m, 2H), 1.49 - 1.43 (m, 2H), 1.30 - 1.25 (m, 9H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.86 (t, *J* = 16.9 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.18, 164.08 (t, *J* = 32.9 Hz), 136.30, 131.56, 128.55, 127.99, 126.52, 125.73, 115.87 (t, *J* = 249.1 Hz), 62.79, 61.70, 59.21, 34.95, 34.49 (t, *J* = 23.1 Hz), 16.64, 13.98, 13.85; HRMS (ESI) m/z calcd for $C_{22}H_{29}F_2O_6$ [M+H$^+$] 427.1927, found 427.1920.



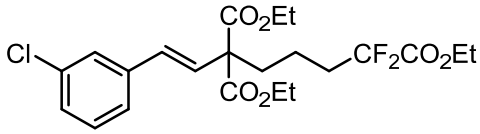
triethyl (E)-1,1-difluoro-7-(2-fluorophenyl)hept-6-ene-1,5,5-tricarboxylate (3ba):
Colorless oil, 63.9 mg, (72% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dt, J_1= 7.7 Hz, J_2= 1.7 Hz, 1H), 7.25 - 7.21 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04-7.01 (m, 1H), 6.79 (d, *J* = 17.0 Hz, 1H), 6.66 (d, *J* = 16.9 Hz, 1H), 4.30 - 4.22 (m, 6H), 2.20 (t, *J* = 8.4 Hz, 2H), 2.12 - 2.06 (m, 2H), 1.50 - 1.44 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.91 (t, *J* = 16.7 Hz, 2F), -117.96 (t, *J* = 13.1 Hz, 1F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.03, 164.09 (t, *J* = 32.5 Hz), 160.95 (d, *J* = 248.2 Hz), 129.37 (d, *J* = 8.4 Hz), 128.21 (d, *J* = 3.8 Hz), 127.20 (d, *J* = 2.6 Hz), 124.19, 124.11 (d, *J* = 1.7 Hz), 124.06 (d, *J* = 3.3 Hz), 115.85 (d, *J* = 248.7 Hz), 115.77 (d, *J* = 221.7 Hz), 62.81, 61.79, 59.54, 34.89, 34.52 (t, *J* = 23.2 Hz), 16.66, 13.98, 13.86; HRMS (ESI) m/z calcd for $C_{22}H_{28}F_3O_6$ [M+H$^+$] 445.1832, found 445.1825.



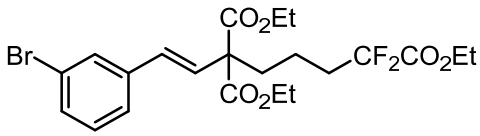
triethyl (E)-7-(2-chlorophenyl)-1,1-difluorohept-6-ene-1,5,5-tricarboxylate (3ca):
Colorless oil, 60.7 mg, (66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, J_1= 7.6 Hz, J_2= 1.3 Hz, 1H), 7.35 (dd, J_1= 7.6 Hz, J_2= 1.0 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.21 (dt, J_1= 7.6 Hz, J_2= 1.4 Hz, 1H), 6.89 (d, *J* = 16.6 Hz, 1H), 6.69 (d, *J* = 16.6 Hz, 1H), 4.30 (q, *J* = 7.3 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 4H), 2.22 (t, *J* = 8.3 Hz, 2H), 2.14 - 2.06 (m, 2H), 1.52 - 1.46 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.96 (t, *J* = 17.4 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.99, 164.10 (t, *J* = 32.4 Hz), 134.62, 133.27, 129.60, 129.01, 128.69, 128.21, 126.97, 126.89, , 115.84 (t, *J* = 248.3 Hz), 62.82, 61.82, 59.55, 34.88, 34.56 (t, *J* = 23.1 Hz), 16.68, 14.02, 13.89; HRMS (ESI) m/z calcd for $C_{22}H_{28}{}^{35}ClF_2O_6$ [M+H$^+$] 461.1531, found 461.1537.



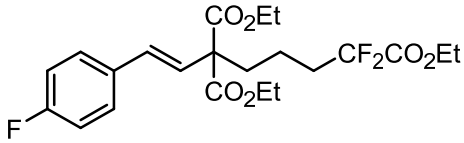
triethyl (E)-1,1-difluoro-7-(3-fluorophenyl)hept-6-ene-1,5,5-tricarboxylate (3da):
Colorless oil, 62.1 mg, (70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 - 7.27 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 - 7.10 (m, 1H), 6.97 (dt, J_1= 8.3 Hz, J_2= 2.0 Hz, 1H), 6.73 (d, *J* = 16.6 Hz, 1H), 6.46 (d, *J* = 16.6 Hz, 1H), 4.29 - 4.22 (m, 6H), 2.19 (t, *J* = 8.5 Hz, 2H), 2.13 - 2.04 (m, 2H), 1.48 - 1.42 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.85 (t, *J* = 15.0 Hz, 2F), -113.25 (q, *J* = 8.2 Hz, 1F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.99, 164.07 (t, *J* = 32.5 Hz), 163.83 (d, *J* = 24.4 Hz), 138.65 (d, *J* = 7.5 Hz), 130.56 (d, *J* = 1.8 Hz), 130.05 (d, *J* = 8.0 Hz), 127.25, 122.47, 115.85 (d, *J* = 249.2 Hz), 114.88 (d, *J* = 21.0 Hz), 113.06 (d, *J* = 21.7 Hz), 62.82, 61.81, 59.22, 34.88, 34.45 (t, *J* = 23.5 Hz), 16.65, 13.99, 13.87; HRMS (ESI) m/z calcd for $C_{22}H_{28}F_3O_6$ [M+H$^+$] 445.1832, found 445.1827.



triethyl (E)-7-(3-chlorophenyl)-1,1-difluorohept-6-ene-1,5,5-tricarboxylate (3ea):
Colorless oil, 61.6 mg, (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.27 - 7.22 (m, 3H), 6.74 (d, *J* = 16.8 Hz, 1H), 6.43 (d, *J* = 16.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 4H), 2.19 (t, *J* = 8.4 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.46 - 1.43 (m, 2H), 1.29 (t, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.86 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.96, 164.06 (t, *J* = 32.4 Hz), 138.15, 134.54, 130.35, 129.79, 127.93, 127.37, 126.42, 124.79, 115.85 (t, *J* = 248.8 Hz), 62.83, 61.82, 59.23, 34.88, 34.45 (t, *J* = 23.1 Hz), 16.65, 13.99, 13.88; HRMS (ESI) m/z calcd for $C_{22}H_{28}{}^{35}ClF_2O_6$ [M+H$^+$] 461.1537, found 461.1523.

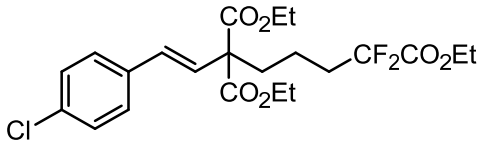


triethyl (E)-7-(3-bromophenyl)-1,1-difluorohept-6-ene-1,5,5-tricarboxylate (3fa):
Colorless oil, 65.5 mg, (65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 16.6 Hz, 1H), 6.42 (t, *J* = 16.7 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.3 Hz, 4H), 2.18 (t, *J* = 6.0 Hz, 2H), 2.11 - 2.05 (m, 2H), 1.47 - 1.41 (m, 2H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.84 (t, *J* = 17.1 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.94, 164.04 (t, *J* = 32.5 Hz), 138.40, 130.83, 130.23, 130.06, 129.32, 127.39, 125.39, 125.23, 122.73, 115.84 (t, *J* = 248.9 Hz), 62.81, 61.81, 59.21, 34.86, 34.43 (t, *J* = 23.4 Hz), 16.64, 13.98, 13.87; HRMS (ESI) m/z calcd for $C_{22}H_{28}{}^{79}BrF_2O_6$ [M+H$^+$] 505.1032, found 505.1025.



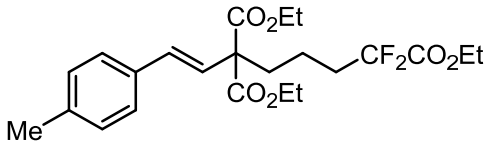
triethyl (E)-1,1-difluoro-7-(4-fluorophenyl)hept-6-ene-1,5,5-tricarboxylate (3ga):

Colorless oil, 64.8 mg, (73% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 - 7.36 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 16.6 Hz, 1H), 6.44 (d, *J* = 16.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.25 - 4.21 (m,4H), 2.18 (t, *J* = 8.3 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.47 - 1.42 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.89 (t, *J* = 17.3 Hz, 2F) -113.66 (s, 1F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.14, 164.08 (t, *J* = 32.8 Hz), 163.34 (d, *J* = 246.1 Hz), 132.49 (d, *J* = 2.6 Hz), 130.43, 128.13 (d, *J* = 7.8 Hz), 125.48, 115.87 (t, *J* = 248.7 Hz), 115.56 (d, *J* = 21.5 Hz), 62.81, 61.75, 59.18, 34.90, 34.47 (t, *J* = 23.1 Hz), 16.64, 13.99, 13.87; HRMS (ESI) m/z calcd for $C_{22}H_{28}F_3O_6$ [M+H$^+$] 445.1832, found 445.1813.



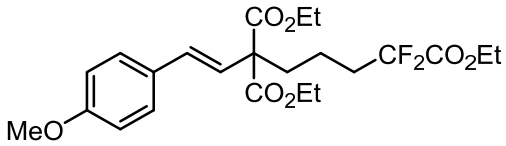
ethyl 5-(2-(4-chlorobenzoyl)phenyl)-2,2-difluoropentanoate (3ha):

Colorless oil, 69.9 mg, (76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 - 7.32 (m, 2H), 7.29 - 7.27 (m, 2H), 6.70 (d, *J* = 16.8 Hz, 1H), 6.43 (d, *J* = 16.6 Hz, 1H), 4.28 - 4.21 (m, 6H), 2.18 (t, *J* = 8.3 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.46 - 1.41 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.88 (t, *J* = 17.2 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.01, 164.04 (t, *J* = 32.4 Hz), 134.78, 133.63, 130.39, 128.69, 127.73, 126.43, 115.84 (t, *J* = 248.7 Hz), 62.79, 61.76, 59.20, 34.85, 34.43 (t, *J* = 23.1 Hz), 16.63, 13.96, 13.85; HRMS (ESI) m/z calcd for $C_{22}H_{27}{}^{35}ClF_2O_6Na$ [M+Na$^+$] 483.1356, found 483.1364.



triethyl (E)-1,1-difluoro-7-(p-tolyl)hept-6-ene-1,5,5-tricarboxylate (3ia):

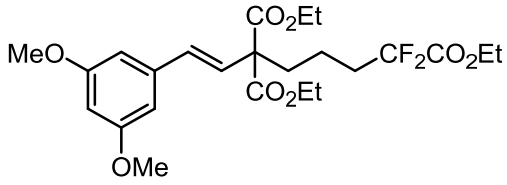
Colorless oil, 72.1 mg, (82% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 16.7 Hz, 1H), 6.45 (d, *J* = 16.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.24 - 4.20 (m, 4H), 2.34 (s, 3H), 2.19 (t, *J* = 8.4 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.48 - 1.42 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.87 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.26, 164.08 (t, *J* = 32.8 Hz), 137.88, 133.54, 131.39, 129.22, 126.42, 124.62, 115.87 (t, *J* = 248.8 Hz), 62.77, 61.64, 59.17, 34.95, 34.50 (t, *J* = 23.1 Hz), 21.16, 16.62, 13.97, 13.86; HRMS (ESI) m/z calcd for $C_{23}H_{31}F_2O_6$ [M+H$^+$] 441.2083, found 441.2084.



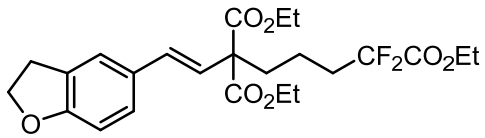
triethyl (E)-1,1-difluoro-7-(4-methoxyphenyl)hept-6-ene-1,5,5-tricarboxylate (3ja):

Colorless oil, 71.1 mg, (78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 16.6 Hz, 1H), 6.42 (d, *J* = 16.6 Hz, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 4.24 – 4.20 (m, 4H), 3.81 (s, 3H), 2.18 (t, *J* = 8.5 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.47 - 1.42 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.87 (t, *J* = 15.9 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.34, 164.10 (t, *J* = 32.9 Hz), 159.48, 130.96,

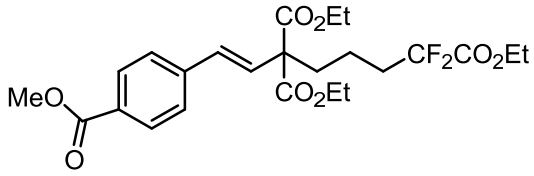
129.11, 127.75, 123.36, 115.90 (t, J = 248.9Hz), 113.94, 62.79, 61.65, 59.15, 55.29, 34.95, 34.51 (t, J = 23.0 Hz), 16.63, 14.00, 13.87; HRMS (ESI) m/z calcd for $C_{23}H_{31}F_2O_7$ [M+H$^+$] 457.2032, found 457.2030.



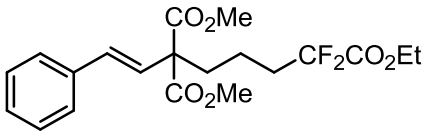
triethyl (E)-7-(3,5-dimethoxyphenyl)-1,1-difluorohept-6-ene-1,5,5-tricarboxylate (3ka): Colorless oil, 68.0 mg, (70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J = 1.9 Hz, 1H), 6.93 (dd, J_1 = 8.2 Hz, J_1 = 1.9 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.59 (d, J = 16.6 Hz, 1H), 6.41 (d, J = 16.6 Hz, 1H), 4.28 - 4.20 (m, 6H), 3.91 (s, 3H), 3.87 (s, 3H), 2.19 (t, J = 8.4 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.46 - 1.43 (m, 2H), 1.28 (t, J = 7.3 Hz, 3H), 1.25 (t, J = 7.1 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.87 (t, J = 17.2 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.31, 164.07 (t, J = 32.0 Hz), 149.06, 148.96, 131.29, 129.34, 123.45, 119.90, 115.87 (t, J = 248.8 Hz), 110.89, 108.60, 62.78, 61.67, 59.08, 55.88, 55.83, 34.96, 34.47 (t, J= 23.0 Hz), 16.61, 13.98, 13.85; HRMS (ESI) m/z calcd for $C_{24}H_{33}F_2O_8$ [M+H$^+$] 487.2138, found 487.2117.



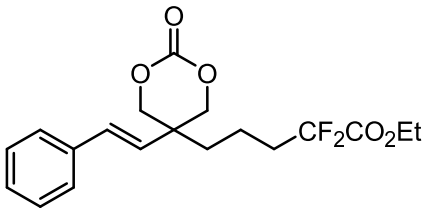
triethyl (E)-7-(2,3-dihydrobenzofuran-5-yl)-1,1-difluorohept-6-ene-1,5,5-tricarboxylate (3la): Colorless oil, 67.4 mg, (72% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.13 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 16.6 Hz, 1H), 6.40 (d, J = 16.6 Hz, 1H), 4.57 (t, J = 8.6 Hz, 2H), 4.29 (q, J = 7.3 Hz, 2H), 4.23 (q, J = 7.2 Hz, 4H), 3.19 (t, J = 8.7 Hz, 2H), 2.17 (t, J = 8.4 Hz, 2H), 2.12 - 2.03 (m, 2H), 1.47 - 1.41 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.1 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.90 (t, J = 16.8 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.36, 164.09 (t, J = 32.8 Hz), 160.12, 131.30, 129.17, 127.51, 127.19, 122.67, 122.64, 115.88 (t, J = 248.9 Hz), 109.14, 71.46, 62.77, 61.60, 59.09, 34.95, 34.50 (t, J = 23.1 Hz), 29.46, 16.60, 13.98, 13.87; HRMS (ESI) m/z calcd for $C_{24}H_{31}F_2O_7$ [M+H$^+$] 469.2032, found 469.2022.



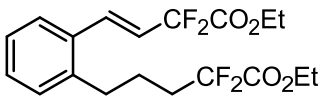
triethyl (E)-1,1-difluoro-7-(4-(methoxycarbonyl)phenyl)hept-6-ene-1,5,5-tricarboxylate(3ma): Colorless oil, 66.0 mg, (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 16.6 Hz, 1H), 6.52 (d, J = 16.6 Hz, 1H), 4.28 - 4.20 (m, 6H), 3.90 (s, 3H), 2.21 (t, J = 17.0 Hz, 2H), 2.12 - 2.04 (m, 2H), 1.47 - 1.42 (m, 2H), 1.28 - 1.24 (m, 9H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.84 (t, J = 14.7 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.89, 166.72, 164.24 (t, J = 32.8 Hz), 140.68, 130.73, 129.87, 129.36, 128.50, 125.42, 117.48 (t, J = 249.3 Hz), 62.80, 61.83, 59.33, 52.07, 34.84, 34.56 (t, J = 23.1 Hz), 16.65, 13.96, 13.84; HRMS (ESI) m/z calcd for $C_{24}H_{30}F_2O_8Na$ [M+Na$^+$] 507.1801, found 507.1811.



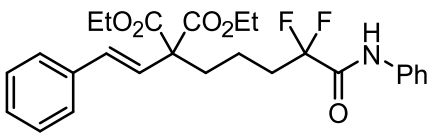
1-ethyl 5,5-dimethyl (E)-1,1-difluoro-7-phenylhept-6-ene-1,5,5-tricarboxylate (3na):
Colorless oil, 54.9 mg, (69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 - 7.40 (m, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 5.6 Hz, 1H), 6.71 (d, *J* = 16.6 Hz, 1H), 6.48 (d, *J* = 16.7 Hz, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 3.77 (s, 6H), 2.20 (t, *J* = 8.5 Hz, 2H), 2.11 - 2.04 (m, 2H), 1.47 - 1.42 (m, 2H), 1.29 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.83 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.65, 164.08 (t, *J* = 25.9 Hz), 136.14, 131.76, 128.59, 128.10, 126.57, 125.43, 115.86 (t, *J* = 249.1 Hz), 62.82, 59.27, 52.90, 34.96, 34.45 (t, *J* = 23.2 Hz), 16.69, 13.88; HRMS (ESI) m/z calcd for $C_{20}H_{25}F_2O_6$ [M+H$^+$] 399.1614, found 399.1604.



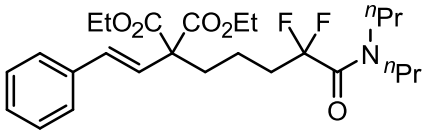
ethyl (E)-2,2-difluoro-5-(2-oxo-5-styryl-1,3-dioxan-5-yl)pentanoate (3oa):
Colorless oil, 49.3 mg, (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 - 7.33 (m, 4H), 7.30 - 7.28 (m, 1H), 6.57 (d, *J* = 16.6 Hz, 1H), 5.97 (d, *J* = 16.6 Hz, 1H), 4.43 (d, *J* = 10.9 Hz, 2H), 4.30 - 4.27 (m, 4H), 2.12 - 2.04 (m, 2H), 1.65 - 1.62 (m, 2H), 1.56 - 1.51 (m, 2H) 1.30 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.73 (t, *J* = 17.4 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.93 (t, *J* = 32.1 Hz), 147.68, 135.55, 133.16, 128.72, 128.46, 126.40, 125.85, 115.69 (t, *J* = 249.0 Hz), 73.98, 62.99, 37.25, 34.35 (t, *J* = 23.4 Hz), 32.78, 15.80, 13.88; HRMS (ESI) m/z calcd for $C_{19}H_{22}F_2O_5Na$ [M+Na$^+$] 391.1328, found 391.1316.



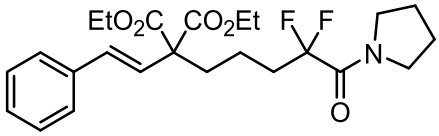
ethyl (E)-5-(2-(4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)phenyl)-2,2-difluoropentanoate (3pa): Colorless oil, 48.4 mg, (62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.35 - 7.31 (m, 2H), 7.26 - 7.23 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 6.25 (dt, J_1 = 22.7 Hz, J_2 = 11.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.13 - 2.07 (m, 2H), 1.78 - 1.74 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -106.19 (d, *J* = 12.3 Hz, 2F), -105.84 (t, *J* = 14.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.14 (t, *J* = 32.9 Hz), 163.84 (t, *J* = 34.8 Hz), 139.63, 134.12 (t, *J* = 9.5 Hz), 132.86, 129.81, 129.59, 126.91, 126.59, 120.80 (t, *J* = 24.8 Hz), 116.04 (t, *J* = 248.6 Hz), 112.58 (t, *J* = 248.0 Hz), 63.18, 62.85, 33.84 (t, *J* = 23.2 Hz), 22.79, 13.93, 13.92; HRMS (ESI) m/z calcd for $C_{19}H_{22}F_4O_4Na$ [M+Na$^+$] 413.1346, found 413.1333.



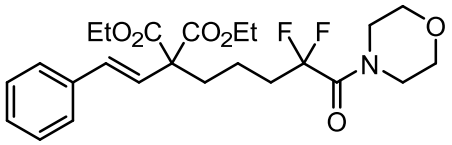
diethyl (E)-2-(4,4-difluoro-5-oxo-5-(phenylamino)pentyl)-2-styrylmalonate (3ab):
Colorless oil, 42.3 mg, (45% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (br, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.36 - 7.30(m, 4H), 7.27 - 7.26 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 16.6 Hz, 1H), 6.49 (d, *J* = 16.6 Hz, 1H), 4.24 - 4.20 (m, 4H), 2.25 - 2.18 (m, 4H), 1.54 - 1.49 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.43 (d, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.24, 161.84 (t, *J* = 28.1 Hz), 136.32, 135.84, 131.63, 129.18, 128.58, 127.99, 126.58, 125.76, 125.56, 120.18, 118.00 (t, *J* = 252.3 Hz), 61.74, 59.26, 34.96, 33.73 (t, *J* = 23.0 Hz), 16.76, 14.01; HRMS (ESI) m/z calcd for $C_{26}H_{30}F_2NO_5$ [M+H$^+$] 474.2087, found 474.2073.



diethyl (E)-2-(5-(dipropylamino)-4,4-difluoro-5-oxopentyl)-2-styrylmalonate (3ac):
Colorless oil, 52.9 mg, (55% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 16.6 Hz, 1H), 6.50 (d, *J* = 16.6 Hz, 1H), 4.26 - 4.20 (m, 4H), 3.34 (t, *J* = 7.9 Hz, 2H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.22 (t, *J* = 8.5 Hz, 2H), 2.17 - 2.13 (m, 2H), 1.60 - 1.52 (m, 4H), 1.51 - 1.47 (m, 2H), 1.26 (t, *J* = 7.3 Hz, 6H), 0.88 - 0.85 (m, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -99.92 (t, *J* = 18.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.33, 162.95 (t, *J* = 28.8 Hz), 136.46, 131.45, 128.50, 127.86, 126.55, 125.91, 119.34 (t, *J* = 253.1 Hz), 61.60, 59.35, 49.08, 48.47, 35.12, 34.86 (t, *J* = 23.5 Hz), 22.11, 20.18, 16.66, 13.98, 11.22, 10.93; HRMS (ESI) m/z calcd for $C_{26}H_{38}F_2NO_5$ [M+H$^+$] 482.2713, found 482.2709.

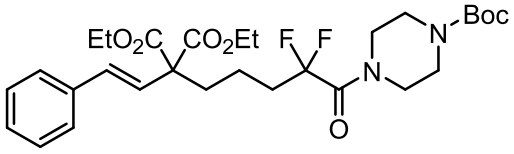


diethyl (E)-2-(4,4-difluoro-5-oxo-5-(pyrrolidin-1-yl)pentyl)-2-styrylmalonate (3ad):
Colorless oil, 55.9 mg, (62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 5.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 - 7.24 (m, 1H), 6.74 (d, *J* = 16.6 Hz, 1H), 6.50 (d, *J* = 16.6 Hz, 1H), 4.26 - 4.20 (m, 4H), 3.64 (t, *J* = 6.7 Hz, 2H), 3.47 (t, *J* = 7.0 Hz, 2H), 2.22 (t, *J* = 8.5 Hz, 2H), 2.16 - 2.12 (m, 2H), 1.94 - 1.90 (m, 2H), 1.84 - 1.81 (m, 2H), 1.52 - 1.46 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.43 (t, *J* = 18.7 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.32, 162.04 (t, *J* = 29.8 Hz), 136.44, 131.47,128.51, 127.88, 126.55, 125.91, 118.77 (t, *J* = 251.6 Hz), 61.62, 59.35, 47.28, 46.51, 35.10, 34.24 (t, *J* = 23.0 Hz), 26.44, 23.22, 16.61, 13.99; HRMS (ESI) m/z calcd for $C_{24}H_{32}F_2NO_5$ [M+H$^+$] 452.2243, found 452.2244.



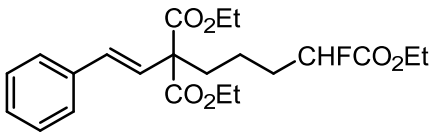
diethyl (E)-2-(4,4-difluoro-5-morpholino-5-oxopentyl)-2-styrylmalonate (3ae):
Colorless oil, 55.1 mg, (59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 - 7.24 (m, 1H), 6.75 (d, *J* = 16.6 Hz, 1H), 6.50 (d, *J* = 16.6 Hz, 1H), 4.25 - 4.20 (m, 4H), 3.70 - 3.66 (m, 6H), 3.61 (t, *J* = 4.9 Hz, 2H), 2.22 (t, *J* = 8.5 Hz, 2H), 2.17 - 2.12 (m, 2H), 1.54 - 1.48 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -99.53 (t, *J* = 9.7

Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.31, 161.80 (t, *J* = 29.5 Hz), 136.44, 131.51, 128.54, 127.92, 126.56, 125.90, 119.22 (t, *J* = 252.7 Hz), 66.75, 66.68, 61.65, 59.35, 46.44, 43.25, 35.13, 34.61 (t, *J* = 22.9 Hz), 16.62, 14.01; HRMS (ESI) m/z calcd for $C_{24}H_{32}F_2NO_6$ [M+H$^+$] 468.2192, found 468.2191.



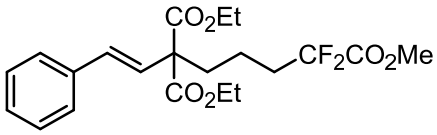
diethyl (E)-2-(5-(4-(tert-butoxycarbonyl)piperazin-1-yl)-4,4-difluoro-5-oxopentyl)-2-styrylmalonate (3af):

Colorless oil, 63.3 mg, (56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.26 - 7.24 (m, 1H), 6.74 (d, *J* = 16.6 Hz, 1H), 6.50 (d, *J* = 16.6 Hz, 1H), 4.26 - 4.20 (m, 4H), 3.64 (s, 2H), 3.56 (s, 2H), 3.43 (s, 4H), 2.22 (d, *J* = 5.1 Hz, 2H), 2.17 - 2.13 (m, 2H), 1.51 - 1.48 (m, 2H), 1.46 (s, 9H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -99.39 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.30, 161.89 (t, *J* = 28.5 Hz), 154.40, 136.42, 131.50, 128.53, 127.91, 126.54, 125.88, 119.20 (t, *J* = 253.1 Hz), 80.37, 61.64, 59.33, 45.60, 42.87, 35.11, 34.60 (t, *J* = 22.8 Hz), 28.31, 16.61, 14.00; HRMS (ESI) m/z calcd for $C_{29}H_{41}F_2N_2O_7$ [M+H$^+$] 567.2876, found 567.2877.



triethyl (E)-1-fluoro-7-phenylhept-6-ene-1,5,5-tricarboxylate (3ag):

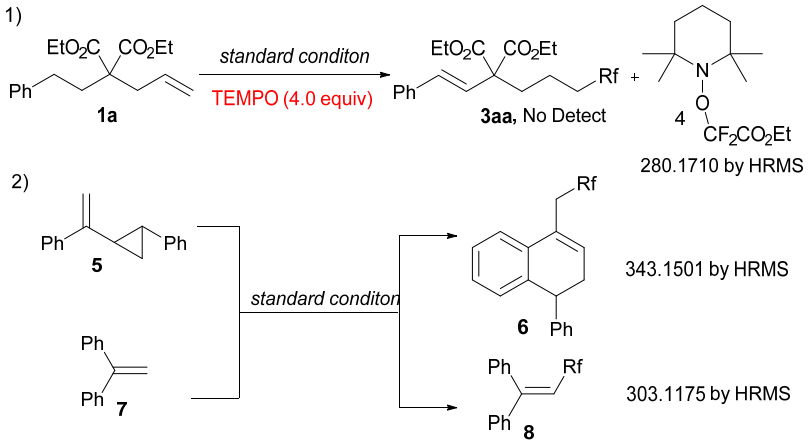
Colorless oil, 35.1 mg, (43% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.27 - 7.25 (m, 1H), 6.75 (d, *J* = 16.6 Hz, 1H), 6.49 (d, *J* = 16.6 Hz, 1H), 4.92 - 4.81 (m, 1H), 3.24 - 4.21 (m, 6H), 2.22 - 2.16 (m, 2H), 1.94 - 1.87 (m, 2H), 1.47 - 1.42 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 9H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -199.13 - -192.31 (m, 1F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.33 (d, *J* = 2.1 Hz), 169.83 (d, *J* = 23.5 Hz), 136.37, 131.44, 128.56, 127.96, 126.54, 125.94, 89.07 (t, *J* = 183.3 Hz), 61.67, 61.48, 59.25, 34.97, 32.58 (t, *J* = 21.2 Hz), 19.47, 14.10, 14.02; HRMS (ESI) m/z calcd for $C_{22}H_{30}FO_6$ [M+H$^+$] 409.2021, found 409.2007.



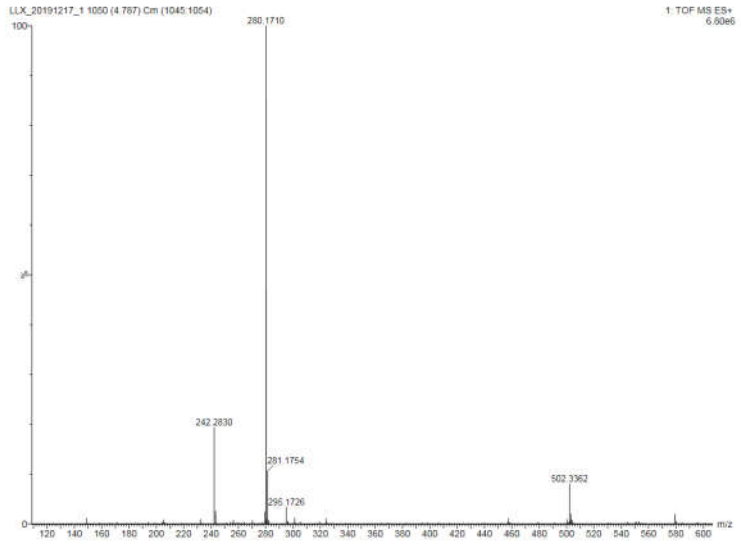
5,5-diethyl 1-methyl (E)-1,1-difluoro-7-phenylhept-6-ene-1,5,5-tricarboxylate (3ah):

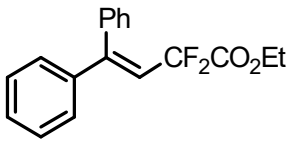
Colorless oil, 62.6 mg, (76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.28 - 7.25 (m, 1H), 6.73 (d, *J* = 16.7 Hz, 1H), 6.49 (d, *J* = 16.7 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 4H), 3.82 (s, 3H), 2.20 (t, *J* = 8.3 Hz, 2H), 2.13 - 2.05 (s, 2H), 1.48 - 1.45 (m, 2H), 1.26 (t, *J* = 7.3 Hz, 6H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -105.60 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.18, 164.57 (t, *J* = 32.8 Hz), 136.30, 131.58, 128.57, 128.00, 126.54, 125.71, 115.92 (t, *J* = 249.2 Hz), 61.72, 59.21, 53.28, 34.90, 34.49 (t, *J* = 23.1 Hz), 16.60, 13.99; HRMS (ESI) m/z calcd for $C_{21}H_{27}F_2O_6$ [M+H$^+$] 413.1770, found 413.1766.

5. Control experiments



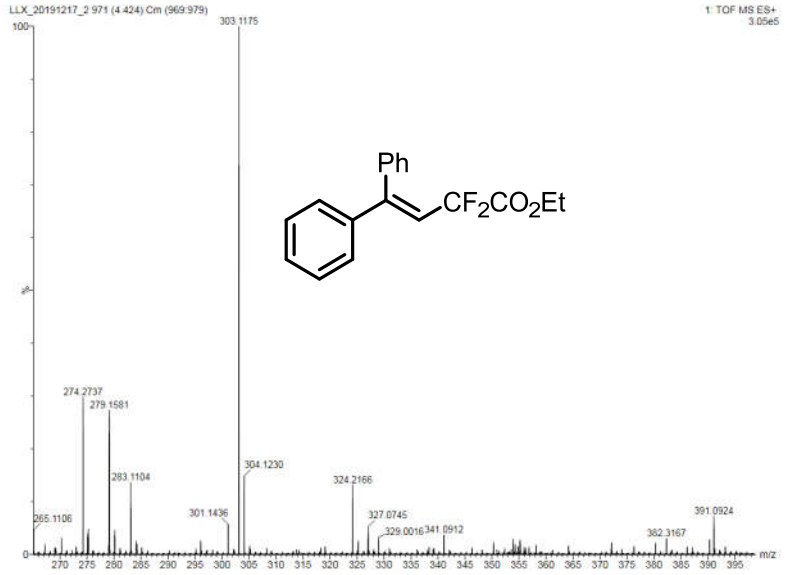
To an oven-dried 10 mL Schlenk tube was added $Pd(PPh_3)_2Cl_2$(5 mol%) and Xantphos (10mol%), and K_2CO_3 (2.0 equiv). The tube was evacuated and back-filled with nitrogen (this process was repeated three times), alkene (0.2 mmol), alkyl bromide (0.3 mmol), Tempo (1.2 mmol) and CH_3CN (2.0 mL) was added subsequently via syring. The resulting mixture was stirred at 80 ^oC for 24 hours. The mixture was determined by HRMS. HRMS (ESI) m/z calcd for $C_{13}H_{24}F_2NO_3$ $[M+H^+]$ 280.1723, found 280.1710.





ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate (5):

Colorless oil.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.36 (m, 6H), 7.33 – 7.31 (m, 2H), 7.25 – 7.19 (m, 2H), 6.26 (t, J = 11.9 Hz, 1H), 3.91 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -90.78 (d, J = 12.1 Hz, 2F); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.42 (t, J = 33.3 Hz), 150.95 (t, J = 37.0 Hz), 140.42, 137.02, 128.36, 127.97, 127.87, 119.45 (t, J = 28.3 Hz), 112.51 (t, J = 243.7 Hz), 62.73, 13.65. HRMS (ESI) m/z calcd for $C_{18}H_{27}F_2NO_2$ $[M+H^+]$ 303.1191, found 303.1175.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Ph
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279.1581
283.1104
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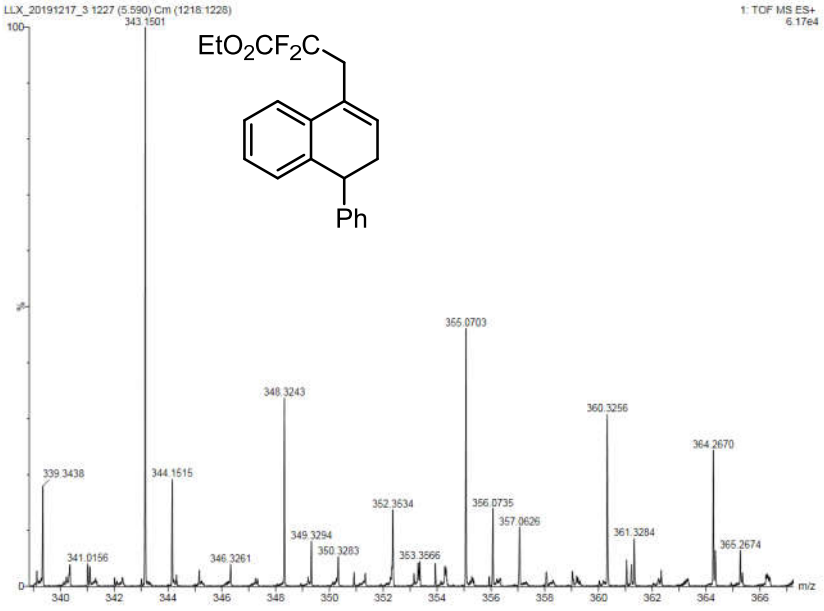
391.0924
m/z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350.3283
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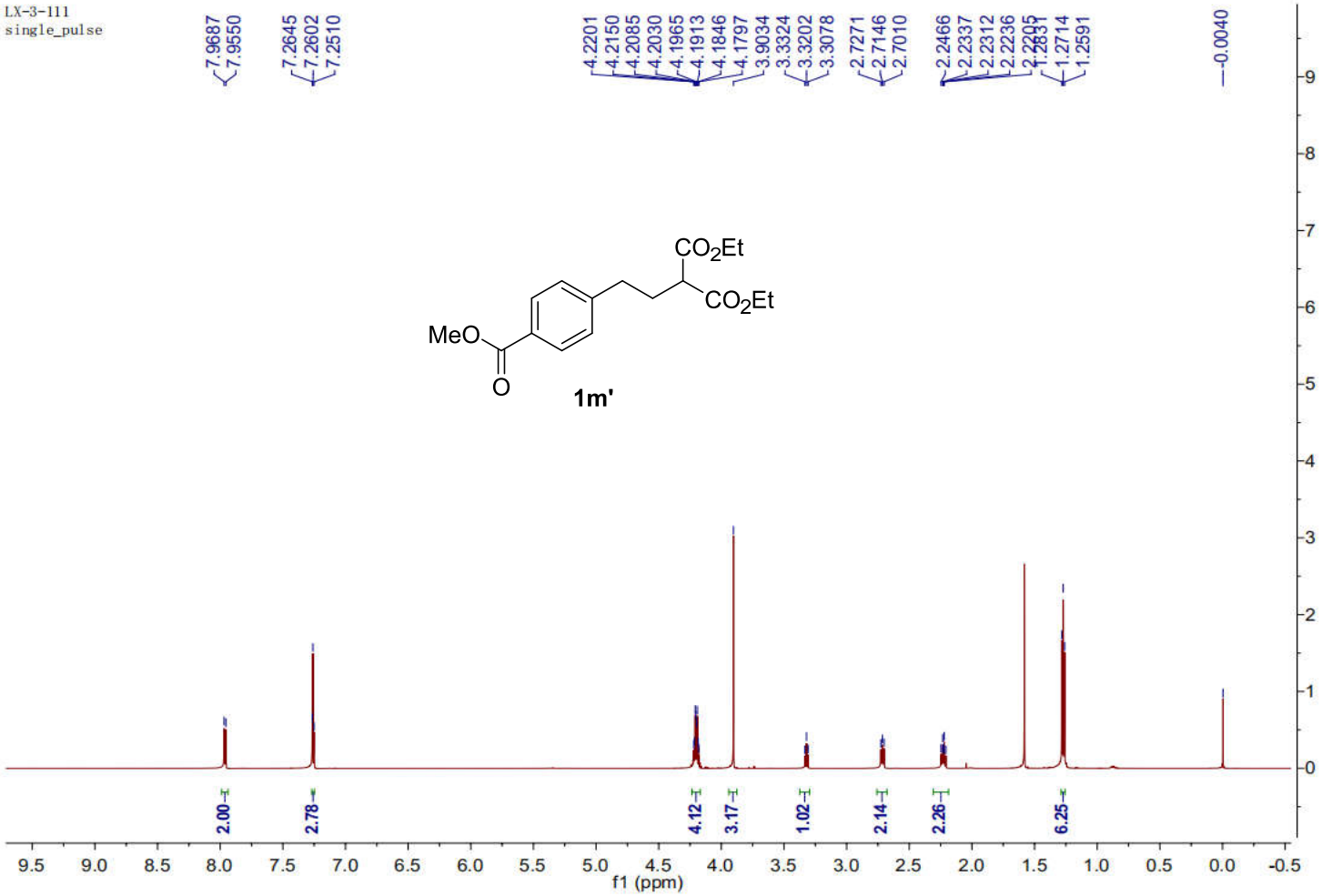
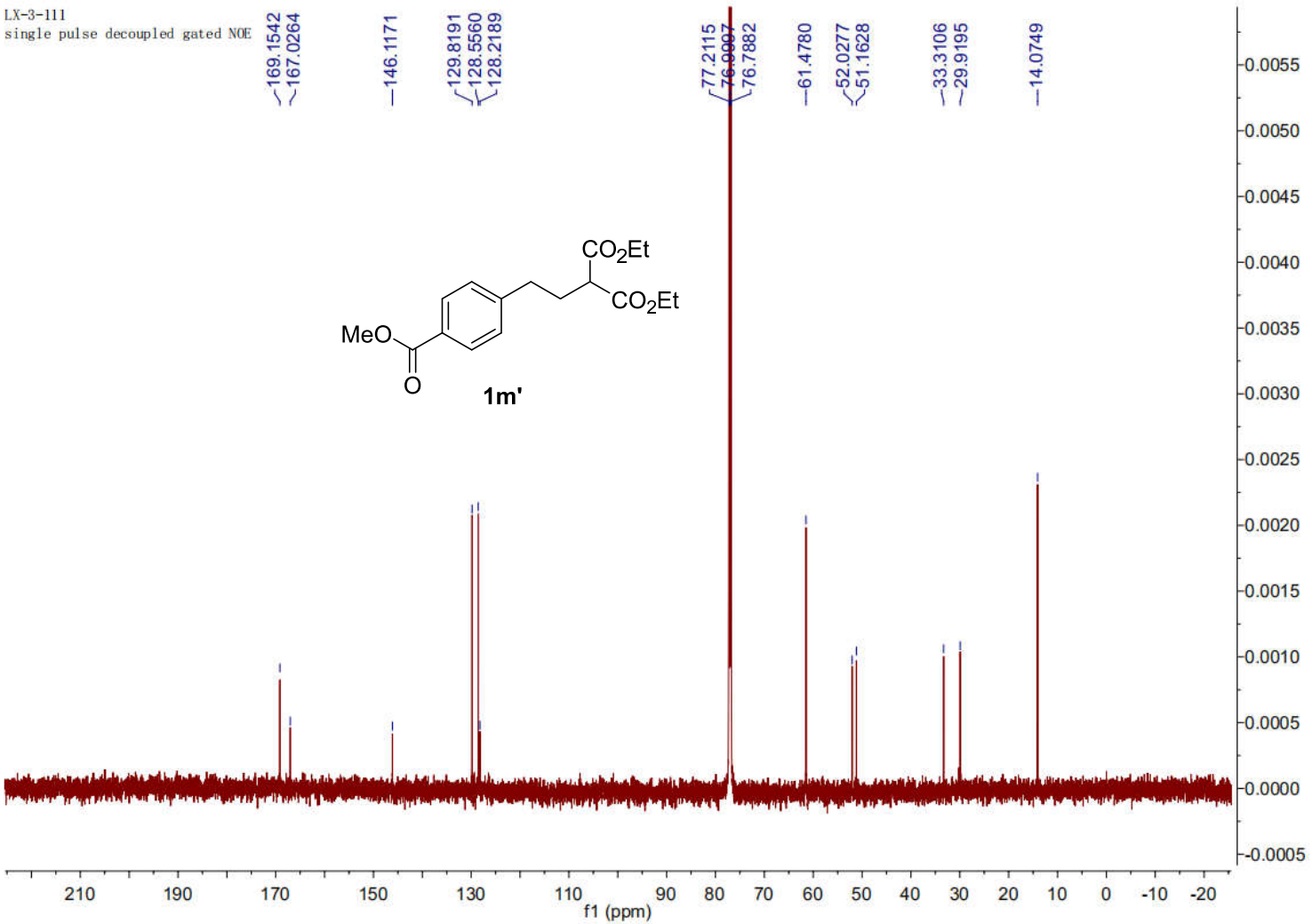
346.3261
353.3566
365.2674
m/z

6. Spectra of new compounds

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52.0277
51.1628
33.3106
29.9195
14.0749
CO2Et
CO2Et
MeO
O
1m'
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0.0050
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0.0040
0.0035
0.0030
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0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
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70
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20
10
0
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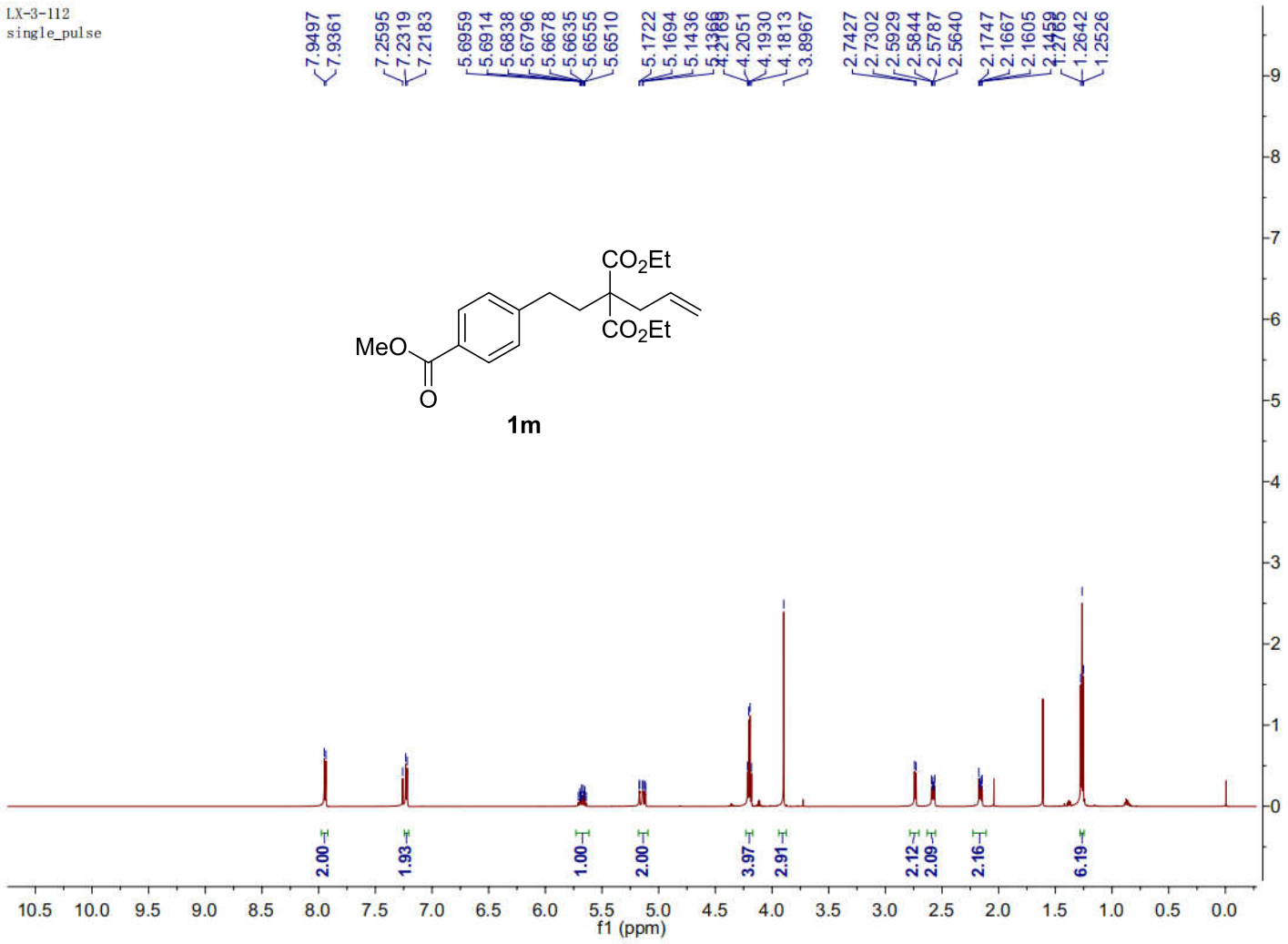
-20
f1 (ppm)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CO2Et
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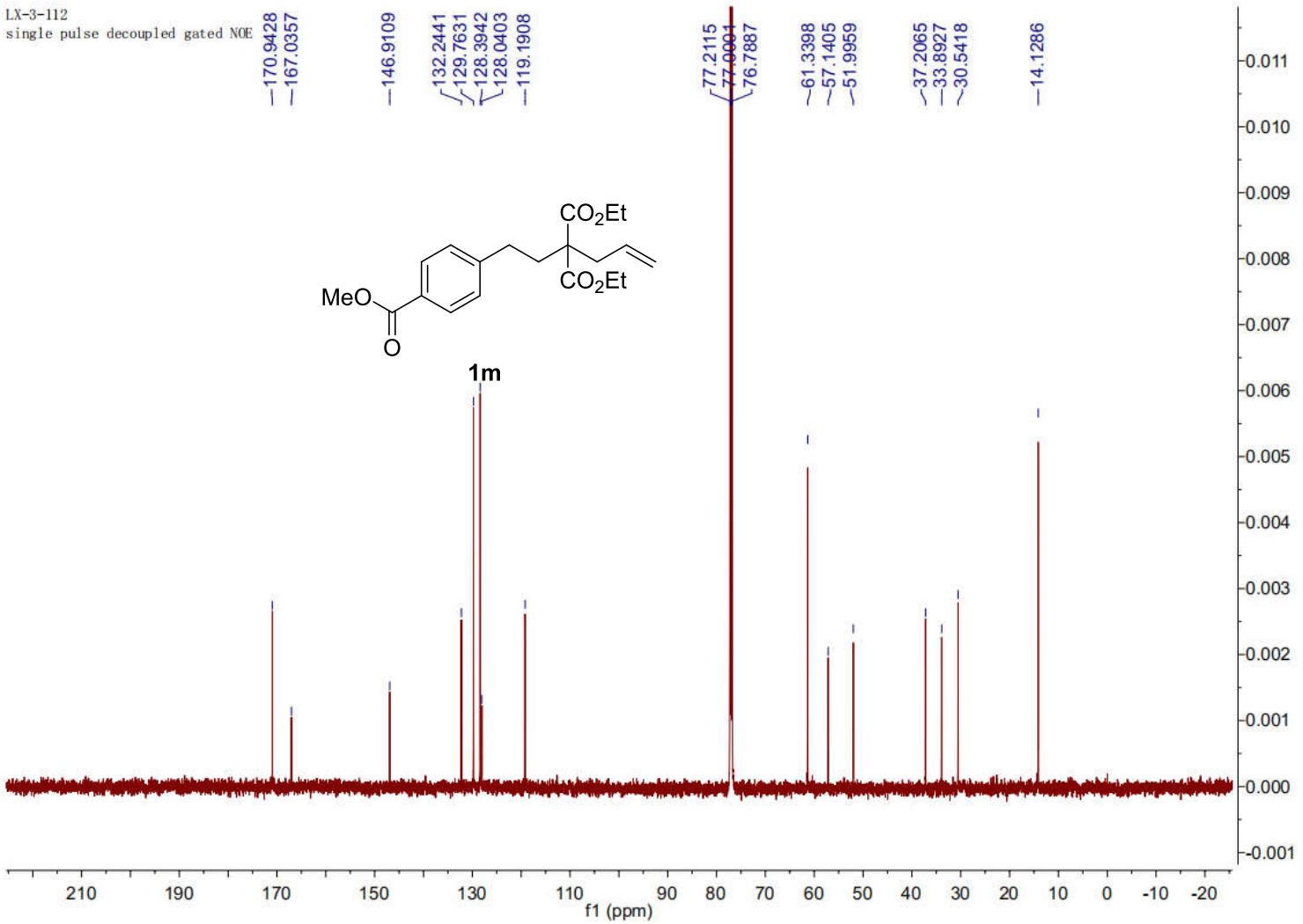
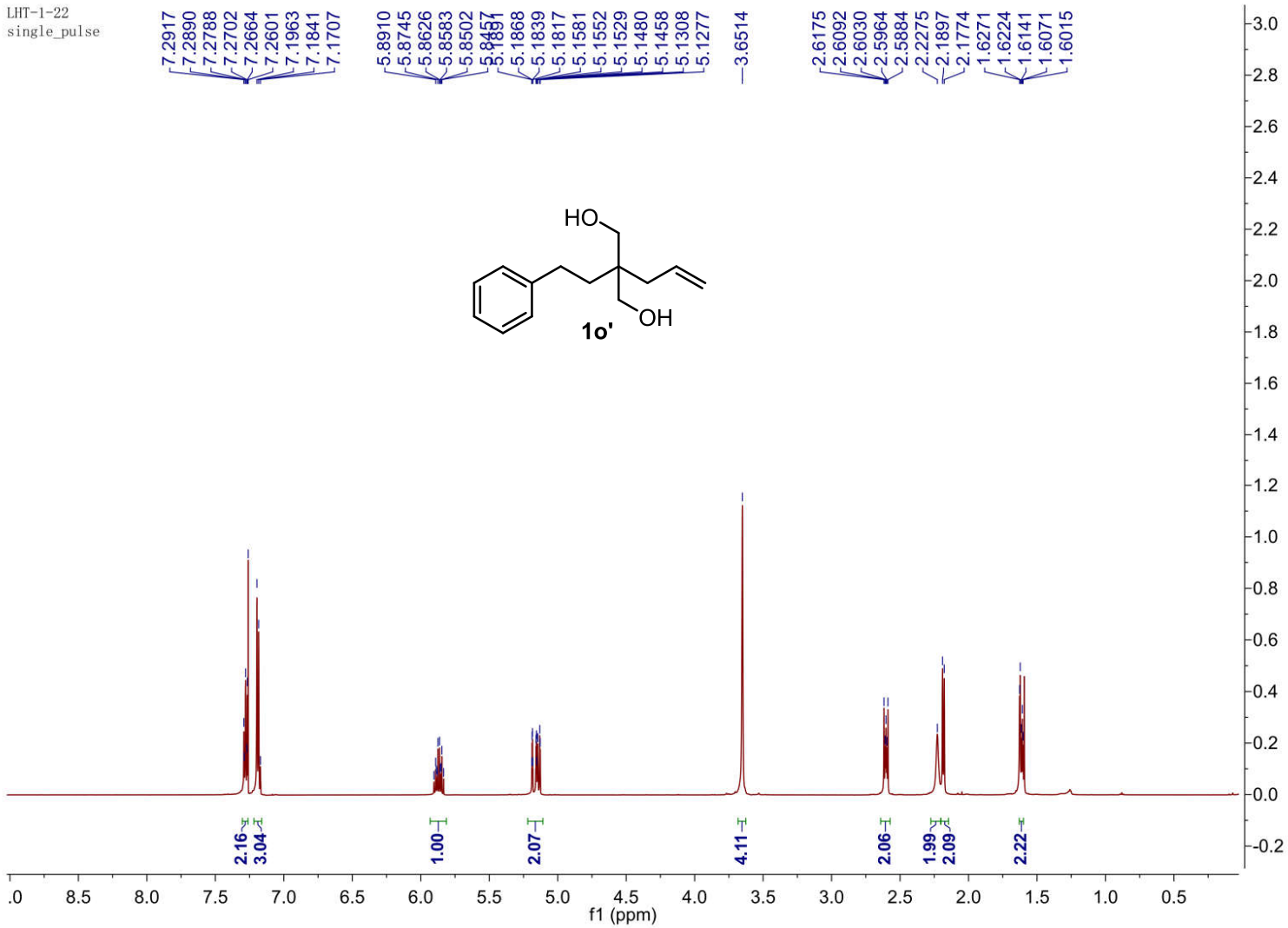
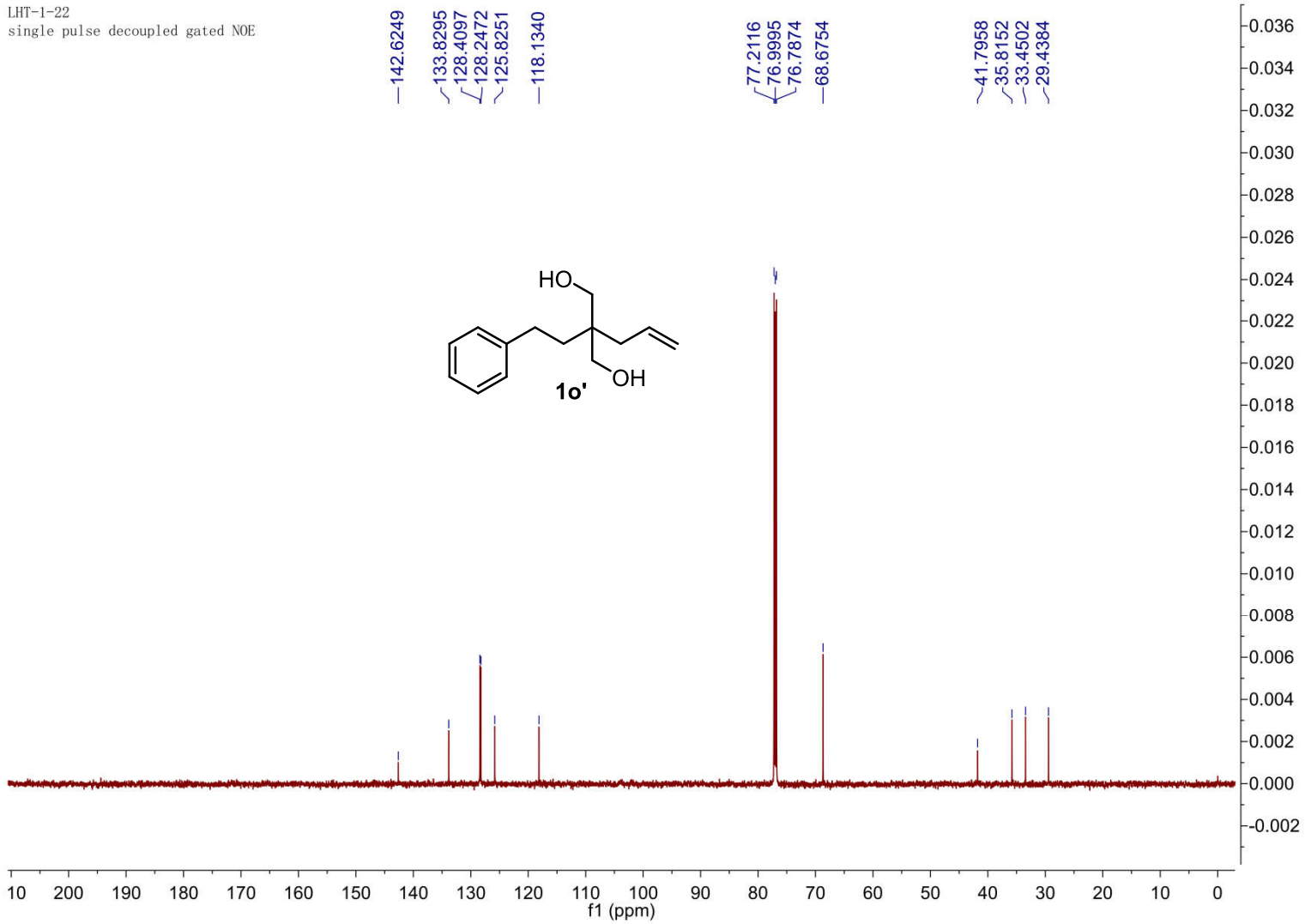
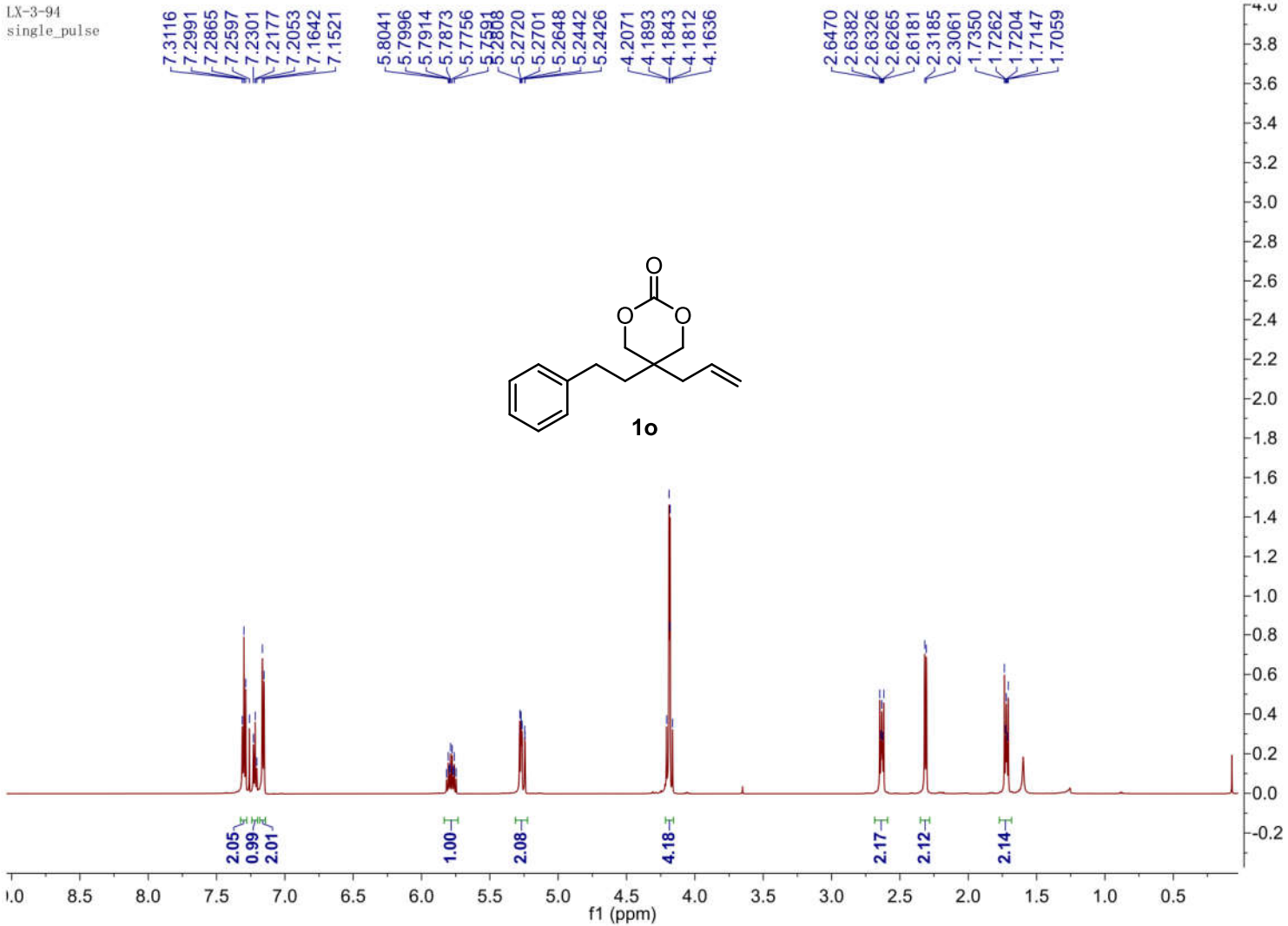
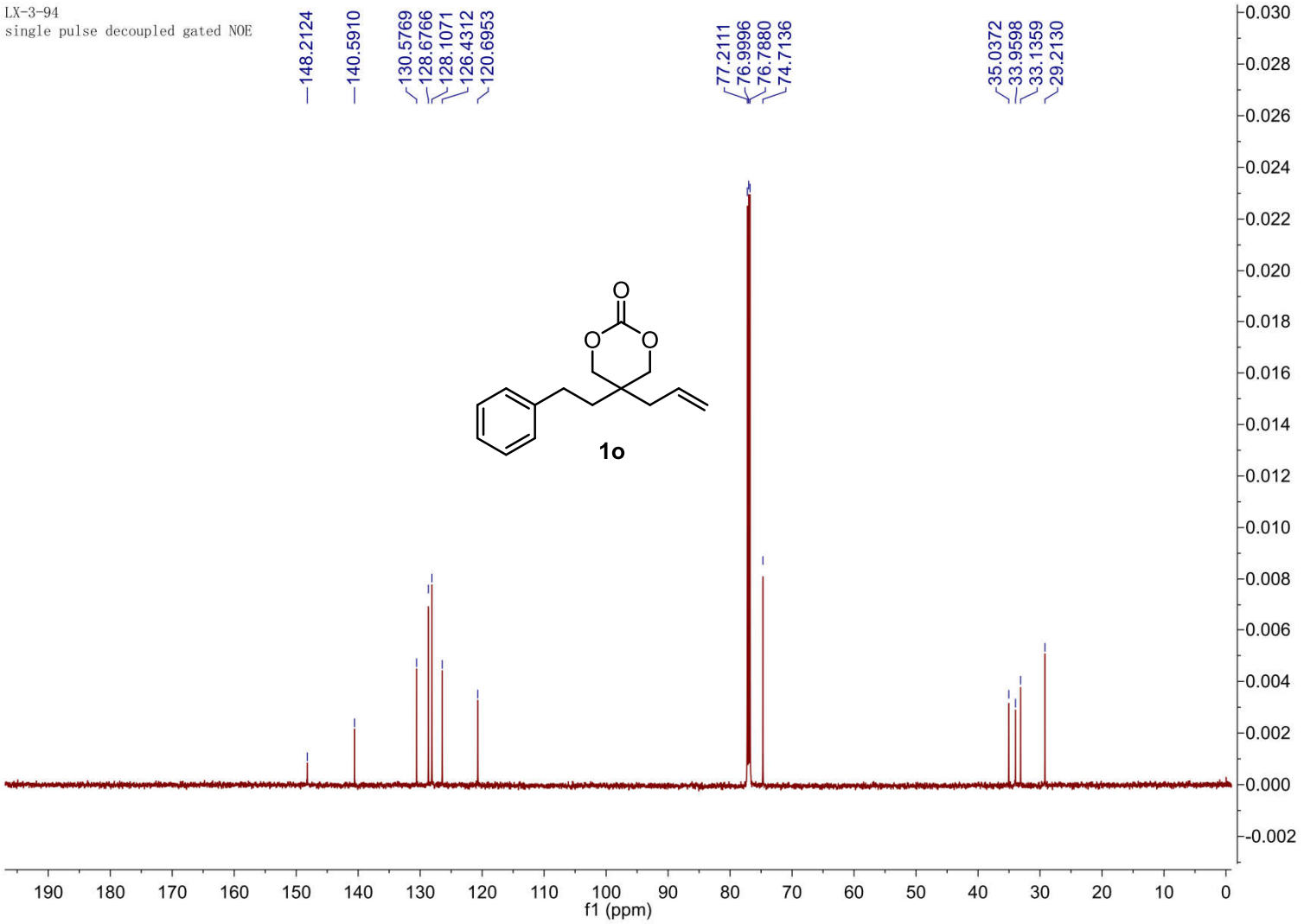
1.00
2.00
3.97
2.91
2.12
2.09
2.16
6.19
f1 (ppm)

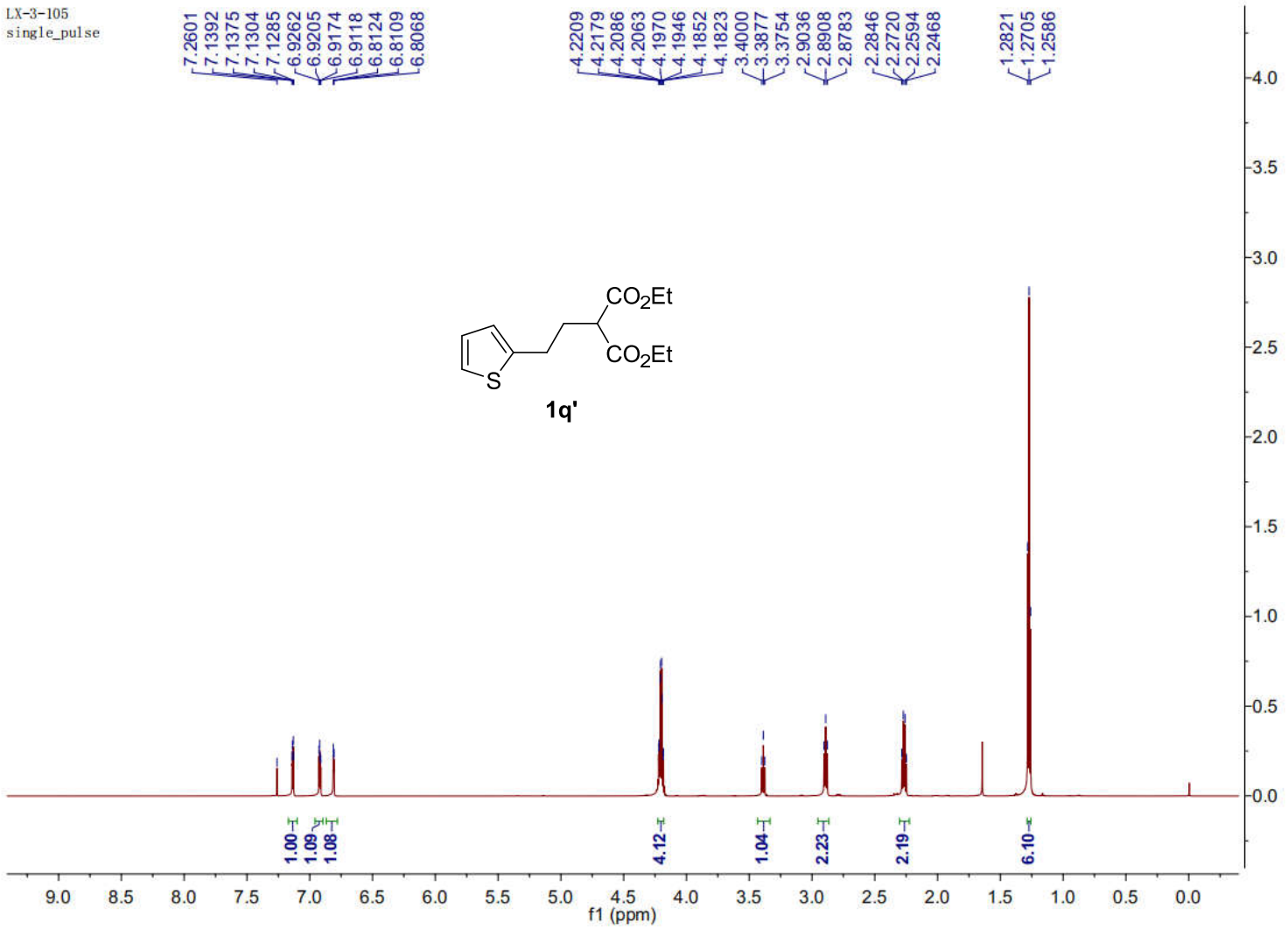

LX-3-112
single pulse decoupled gated NOE
170.9428
167.0357
146.9109
132.2441
129.7631
128.3942
128.0403
119.1908
77.2115
77.0001
76.7887
61.3398
57.1405
51.9959
37.2065
33.8927
30.5418
14.1286
CO2Et
CO2Et
MeO
O
1m
f1 (ppm)

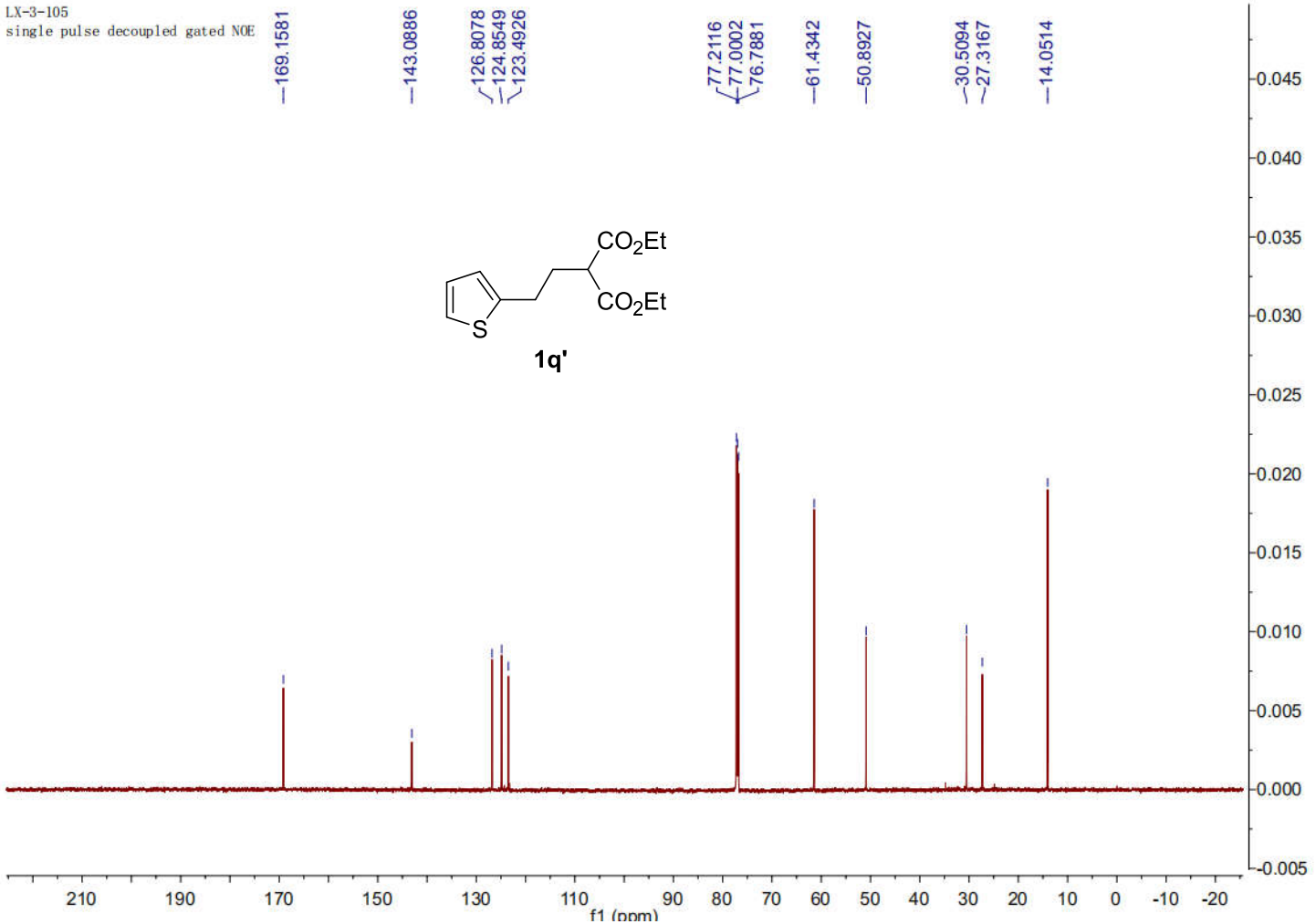

LHT-1-22
single_pulse
7.2917
7.2890
7.2788
7.2702
7.2664
7.2601
7.1963
7.1841
7.1707
5.8910
5.8745
5.8626
5.8583
5.8502
5.8457
5.1891
5.1868
5.1839
5.1817
5.1581
5.1552
5.1529
5.1480
5.1458
5.1308
5.1277
3.6514
2.6175
2.6092
2.6030
2.5964
2.5884
2.2275
2.1897
2.1774
1.6271
1.6224
1.6141
1.6071
1.6015
HO
OH
1o'
2.16
3.04
1.00
2.07
4.11
2.06
1.99
2.09
2.22
f1 (ppm)

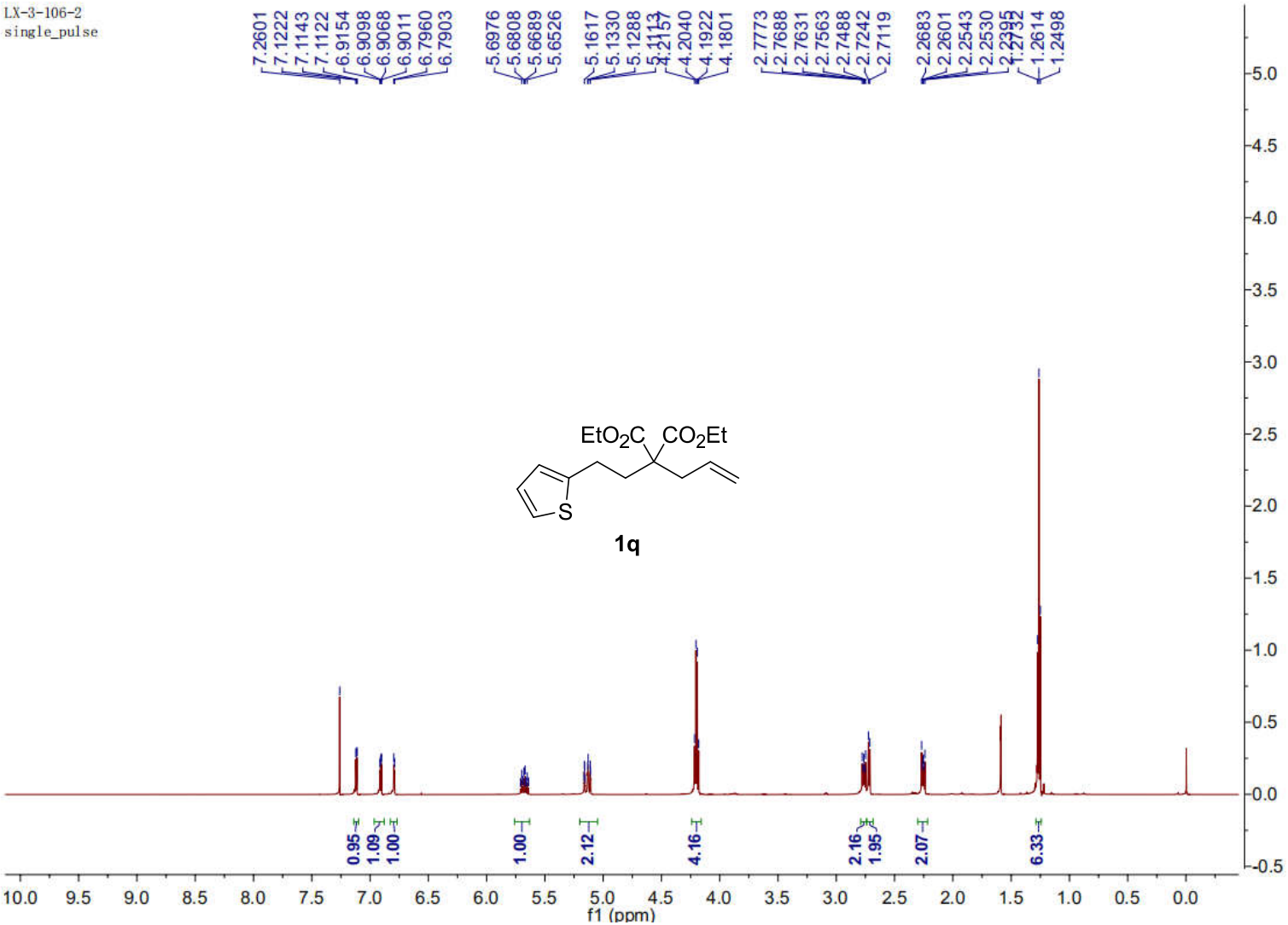

LHT-1-22
single pulse decoupled gated NOE
142.6249
133.8295
128.4097
128.2472
125.8251
118.1340
77.2116
76.9995
76.7874
68.6754
41.7958
35.8152
33.4502
29.4384
HO
OH
1o'
f1 (ppm)

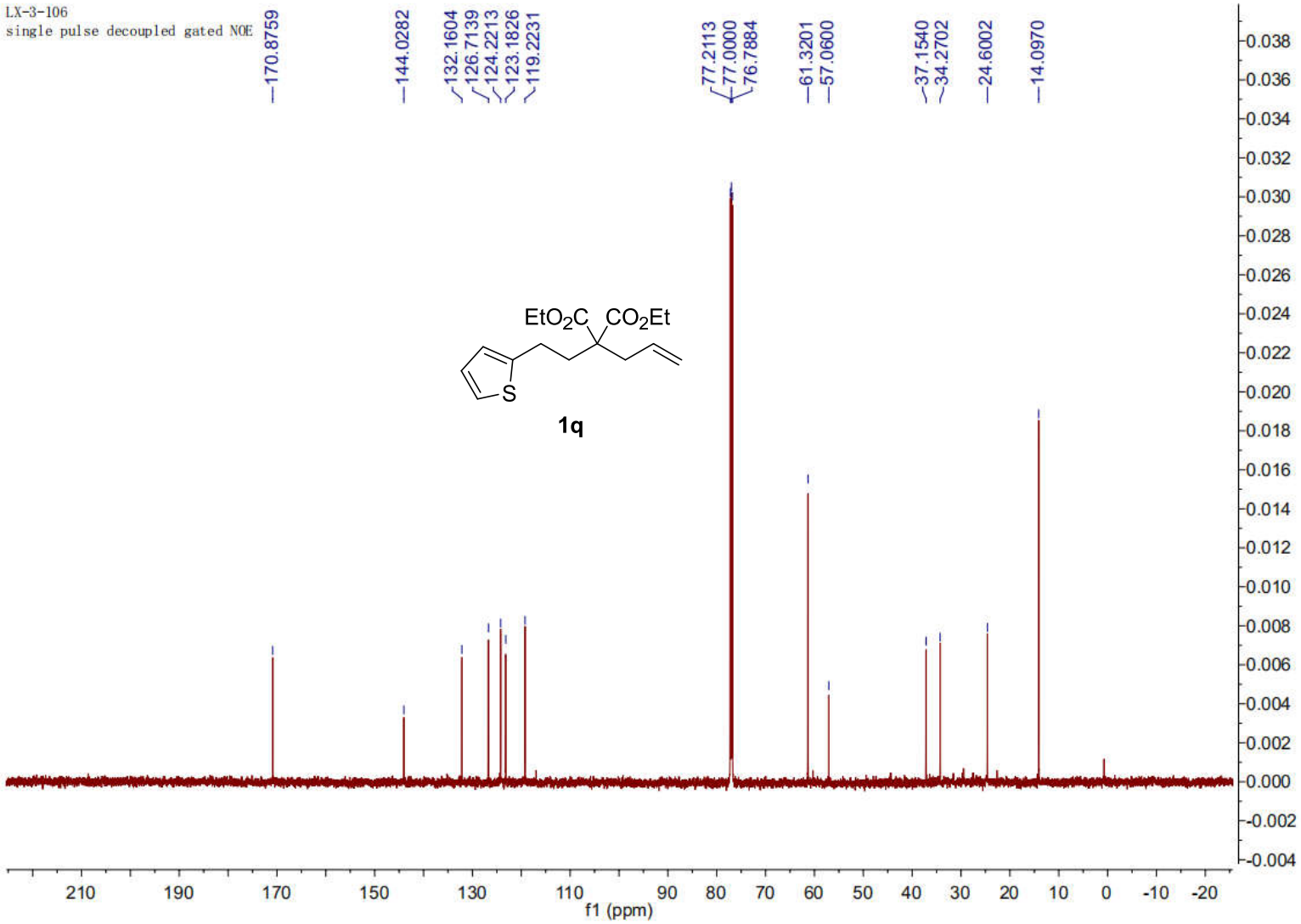

LX-3-94
single_pulse
7.3116
7.2991
7.2865
7.2597
7.2301
7.2177
7.2053
7.1642
7.1521
5.8041
5.7996
5.7914
5.7873
5.7756
5.2720
5.2701
5.2648
5.2442
5.2426
4.2071
4.1893
4.1843
4.1812
4.1636
2.6470
2.6382
2.6326
2.6265
2.6181
2.3185
2.3061
1.7350
1.7262
1.7204
1.7147
1.7059
1o
2.05
0.99
2.01
1.00
2.08
4.18
2.17
2.12
2.14
f1 (ppm)

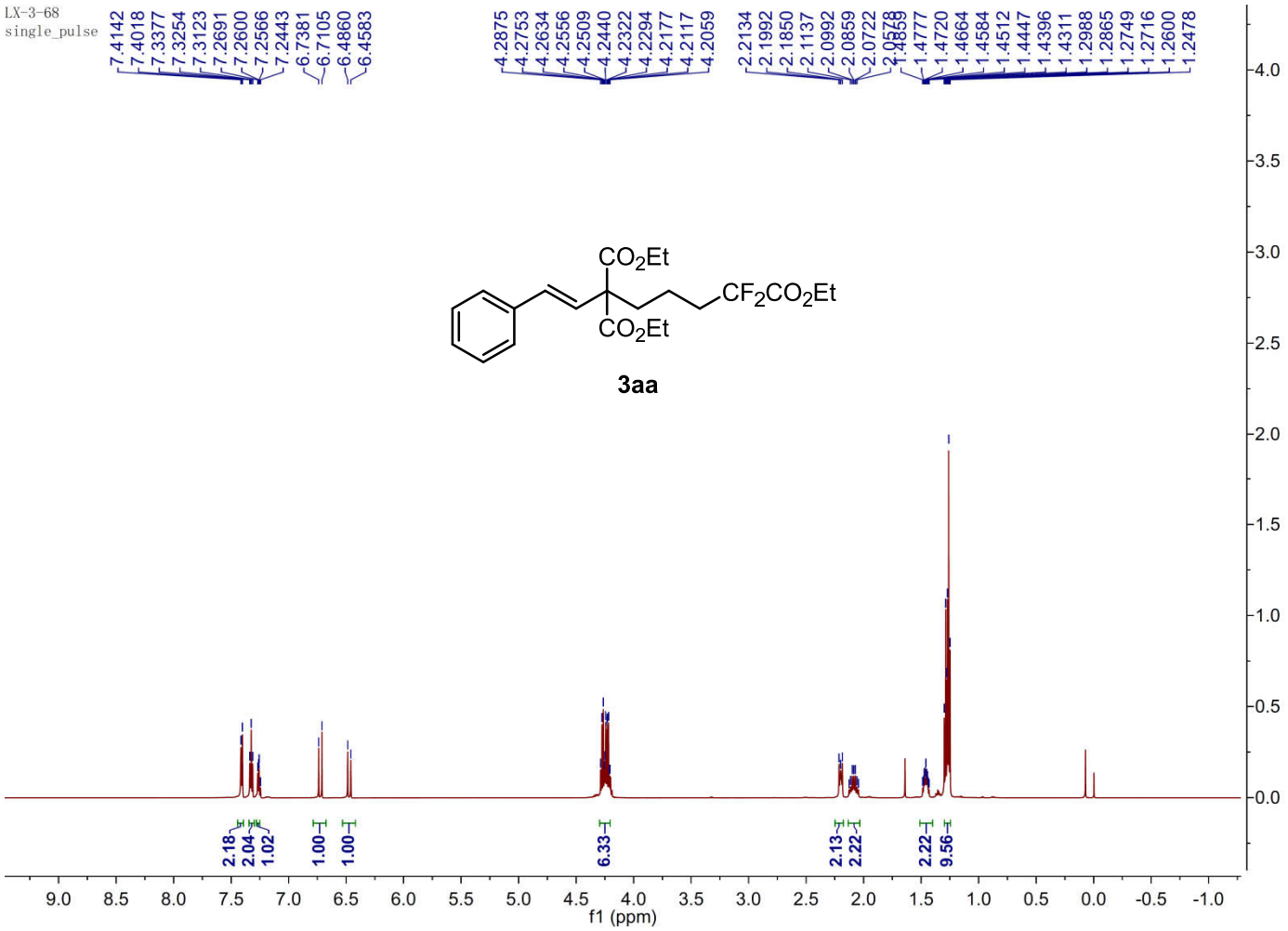

LX-3-94
single pulse decoupled gated NOE
148.2124
140.5910
130.5769
128.6766
128.1071
126.4312
120.6953
77.2111
76.9996
76.7880
74.7136
35.0372
33.9598
33.1359
29.2130
1o
f1 (ppm)

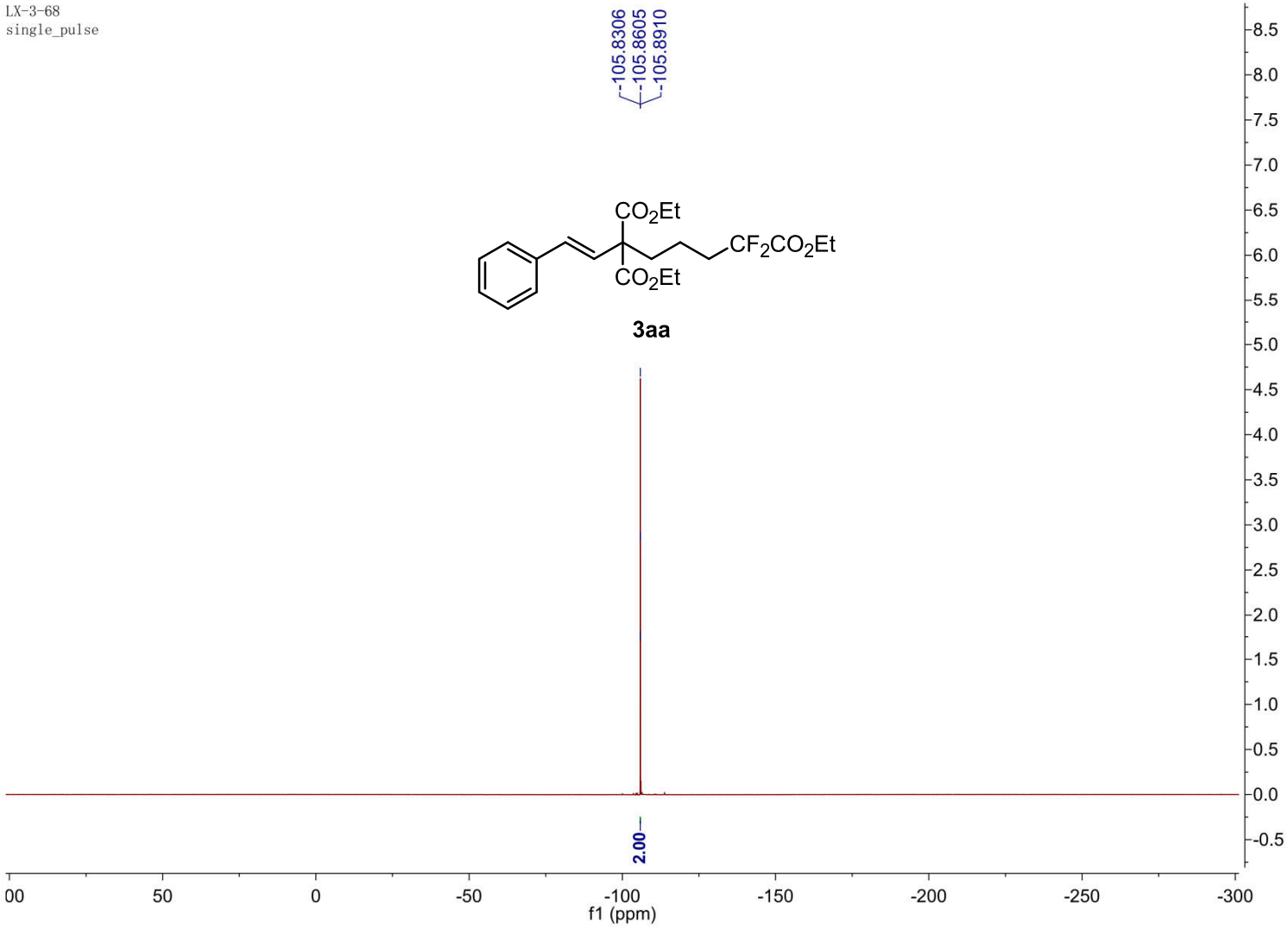

LX-3-105
single_pulse
7.2601
7.1392
7.1375
7.1304
7.1285
6.9262
6.9205
6.9174
6.9118
6.8124
6.8109
6.8068
4.2209
4.2179
4.2086
4.2063
4.1970
4.1946
4.1852
4.1823
3.4000
3.3877
3.3754
2.9036
2.8908
2.8783
2.2846
2.2720
2.2594
2.2468
1.2821
1.2705
1.2586
CO2Et
CO2Et
S
1q'
1.00
1.09
1.08
4.12
1.04
2.23
2.19
6.10
f1 (ppm)

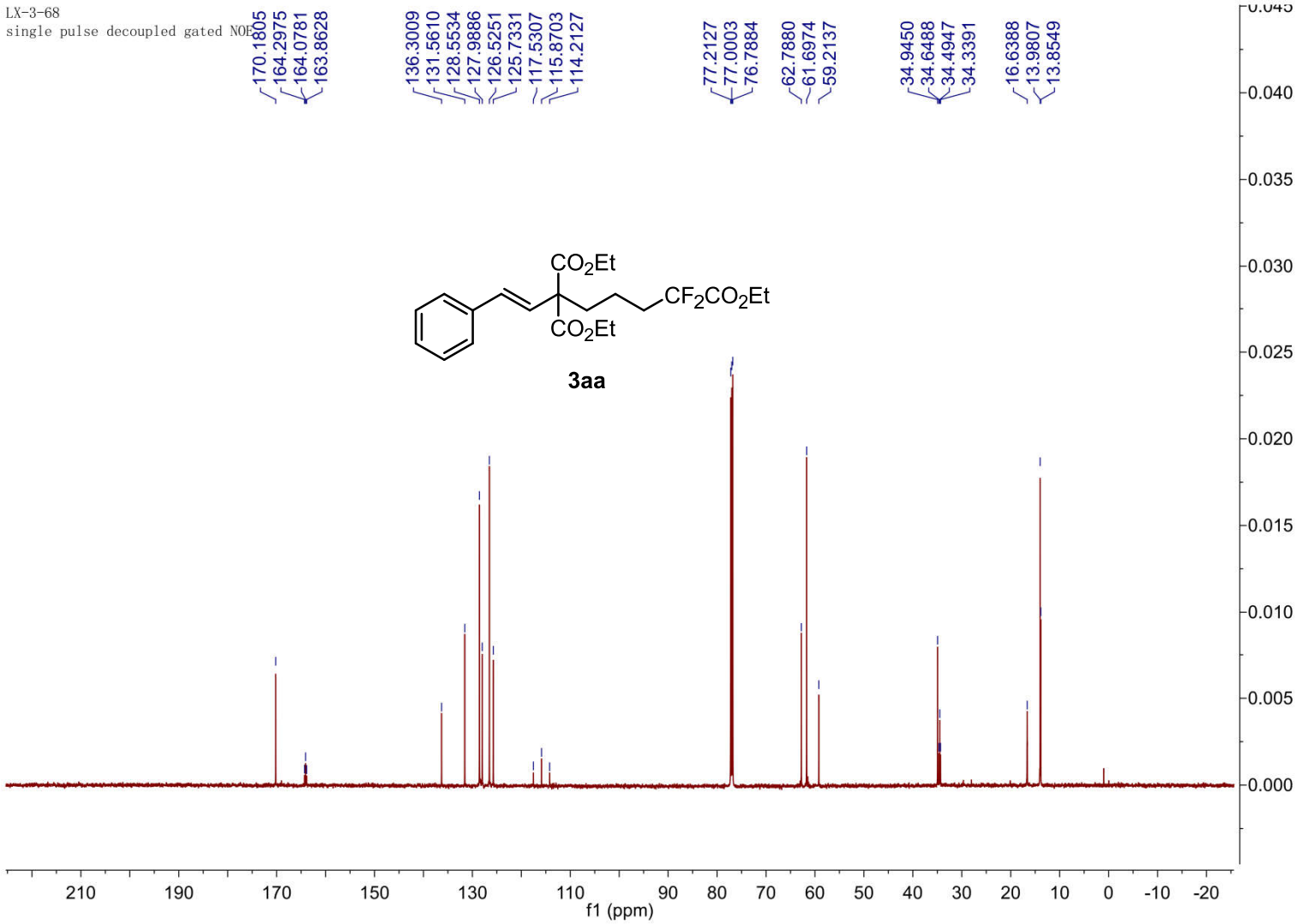

LX-3-105
single pulse decoupled gated NOE
169.1581
143.0886
126.8078
124.8549
123.4926
77.2116
77.0002
76.7881
61.4342
50.8927
30.5094
27.3167
14.0514
CO2Et
CO2Et
S
1q'
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

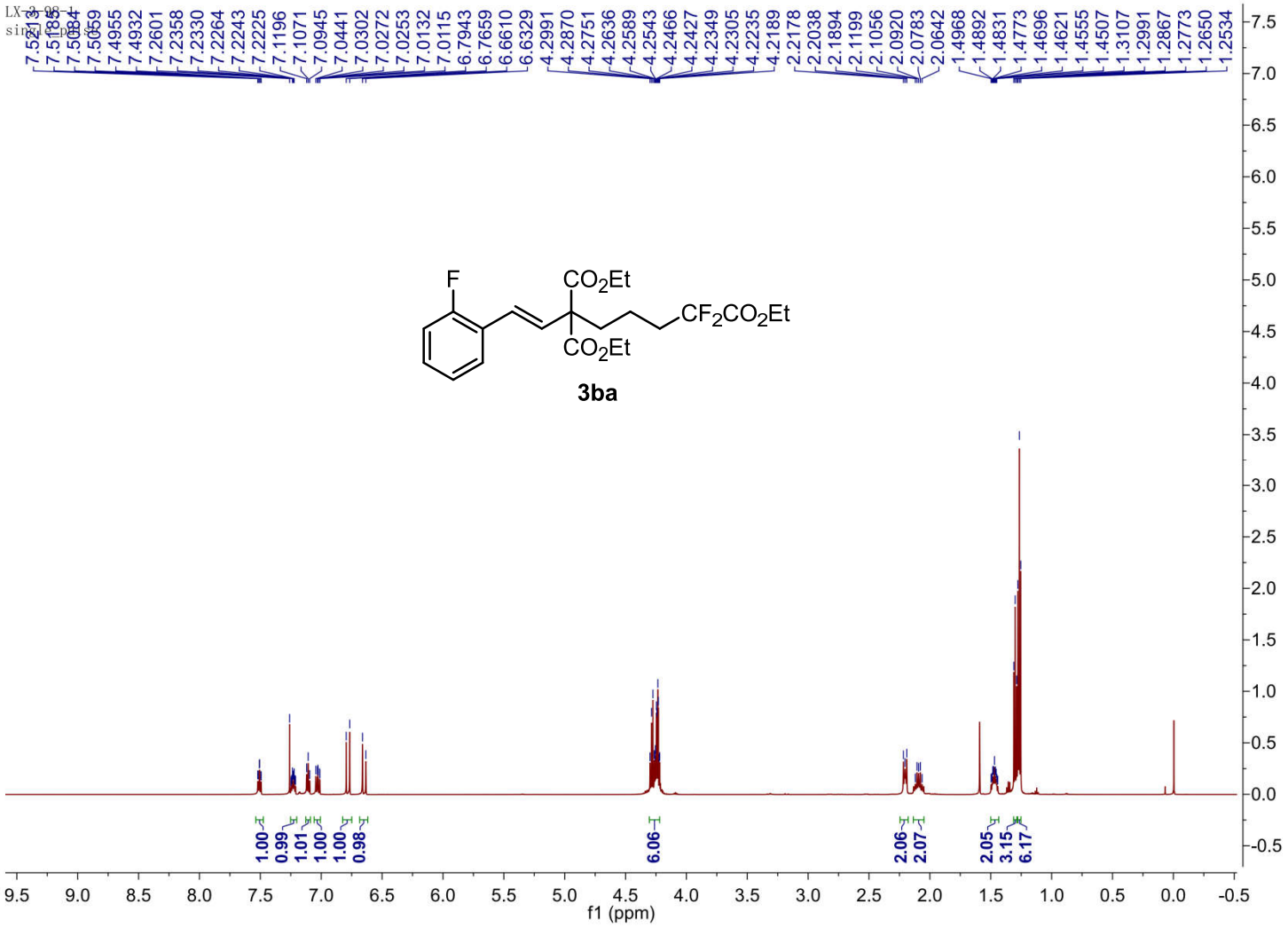

LX-3-106-2
single_pulse
7.2601
7.1222
7.1143
7.1122
6.9154
6.9098
6.9068
6.9011
6.7960
6.7903
5.6976
5.6808
5.6689
5.6526
5.1617
5.1330
5.1288
5.1113
4.2157
4.2040
4.1922
4.1801
2.7773
2.7688
2.7631
2.7563
2.7488
2.7242
2.7119
2.2683
2.2601
2.2543
2.2530
2.2395
1.2732
1.2614
1.2498
EtO2C CO2Et
S
1q
0.95
1.09
1.00
1.00
2.12
4.16
2.16
1.95
2.07
6.33
f1 (ppm)

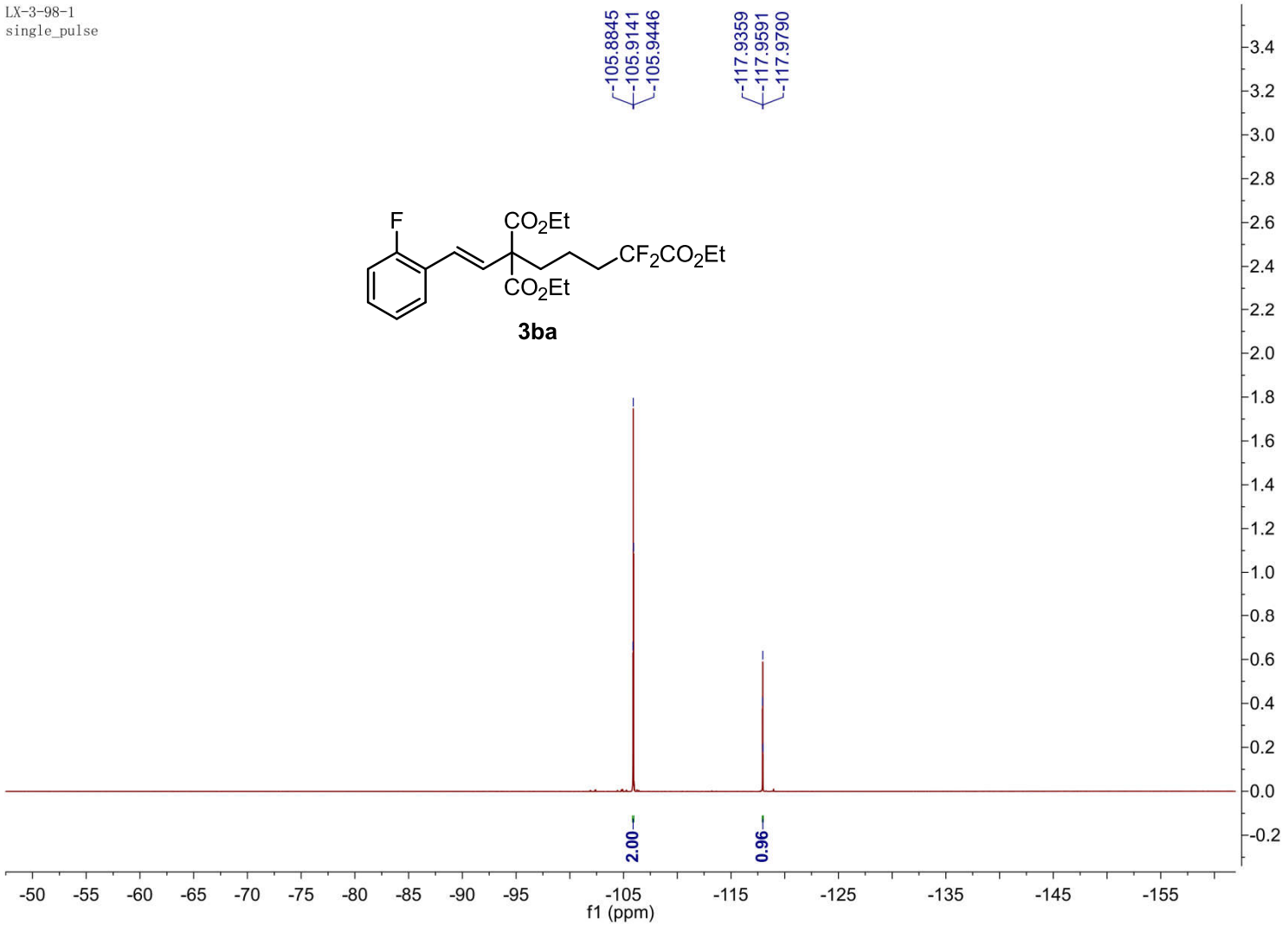

LX-3-106
single pulse decoupled gated NOE
170.8759
144.0282
132.1604
126.7139
124.2213
123.1826
119.2231
77.2113
77.0000
76.7884
61.3201
57.0600
37.1540
34.2702
24.6002
14.0970
EtO2C CO2Et
S
1q
f1 (ppm)

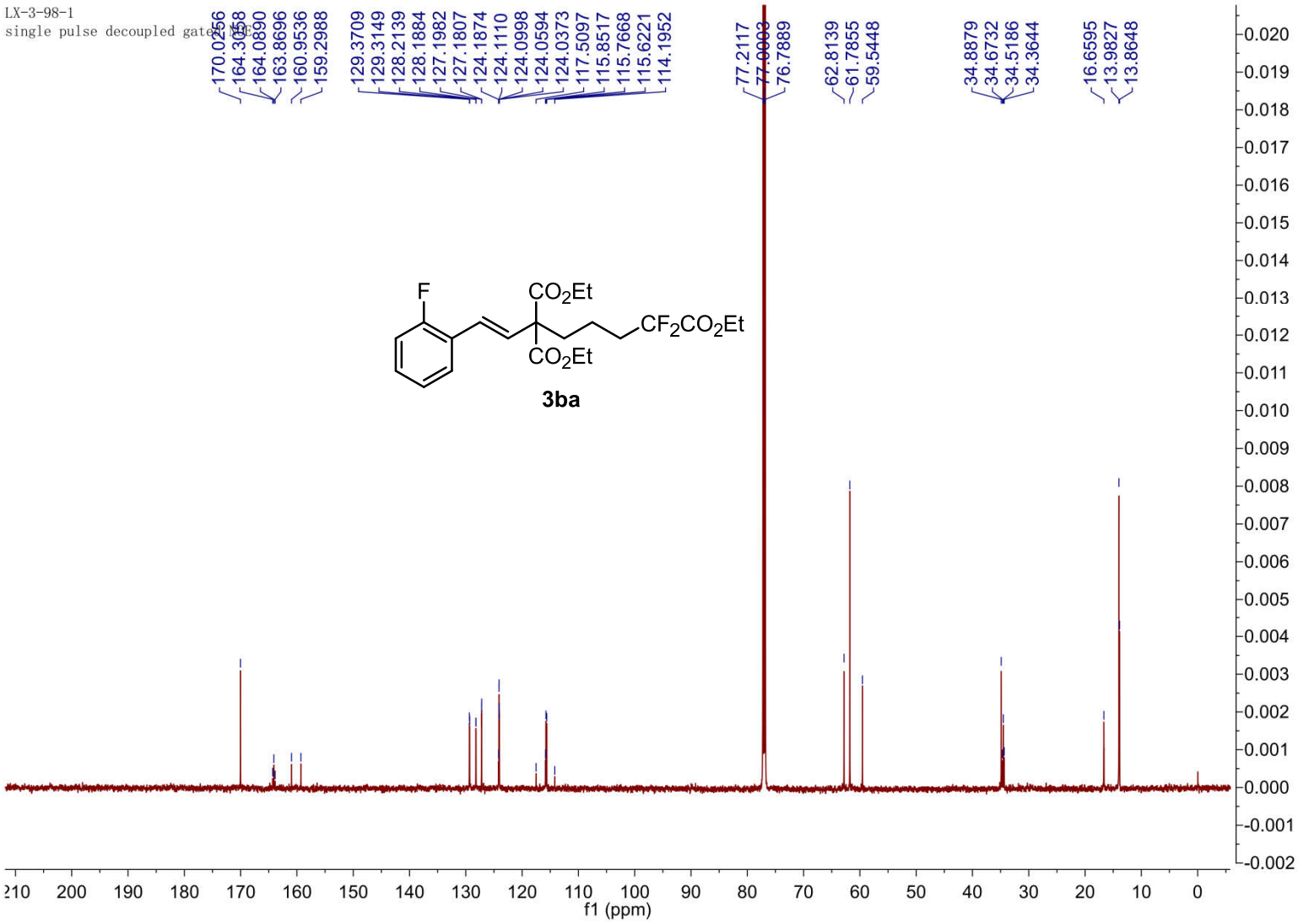

LX-3-68
single_pulse
7.4142
7.4018
7.3377
7.3254
7.3123
7.2691
7.2600
7.2566
7.2443
6.7381
6.7105
6.4860
6.4583
4.2875
4.2753
4.2634
4.2556
4.2509
4.2440
4.2322
4.2294
4.2177
4.2117
4.2059
2.2134
2.1992
2.1850
2.1137
2.0992
2.0859
2.0722
1.4777
1.4720
1.4664
1.4584
1.4512
1.4447
1.4396
1.4311
1.2988
1.2865
1.2749
1.2716
1.2600
1.2478
CO2Et
CF2CO2Et
CO2Et
3aa
2.18
2.04
1.02
1.00
1.00
6.33
2.13
2.22
2.22
9.56
f1 (ppm)

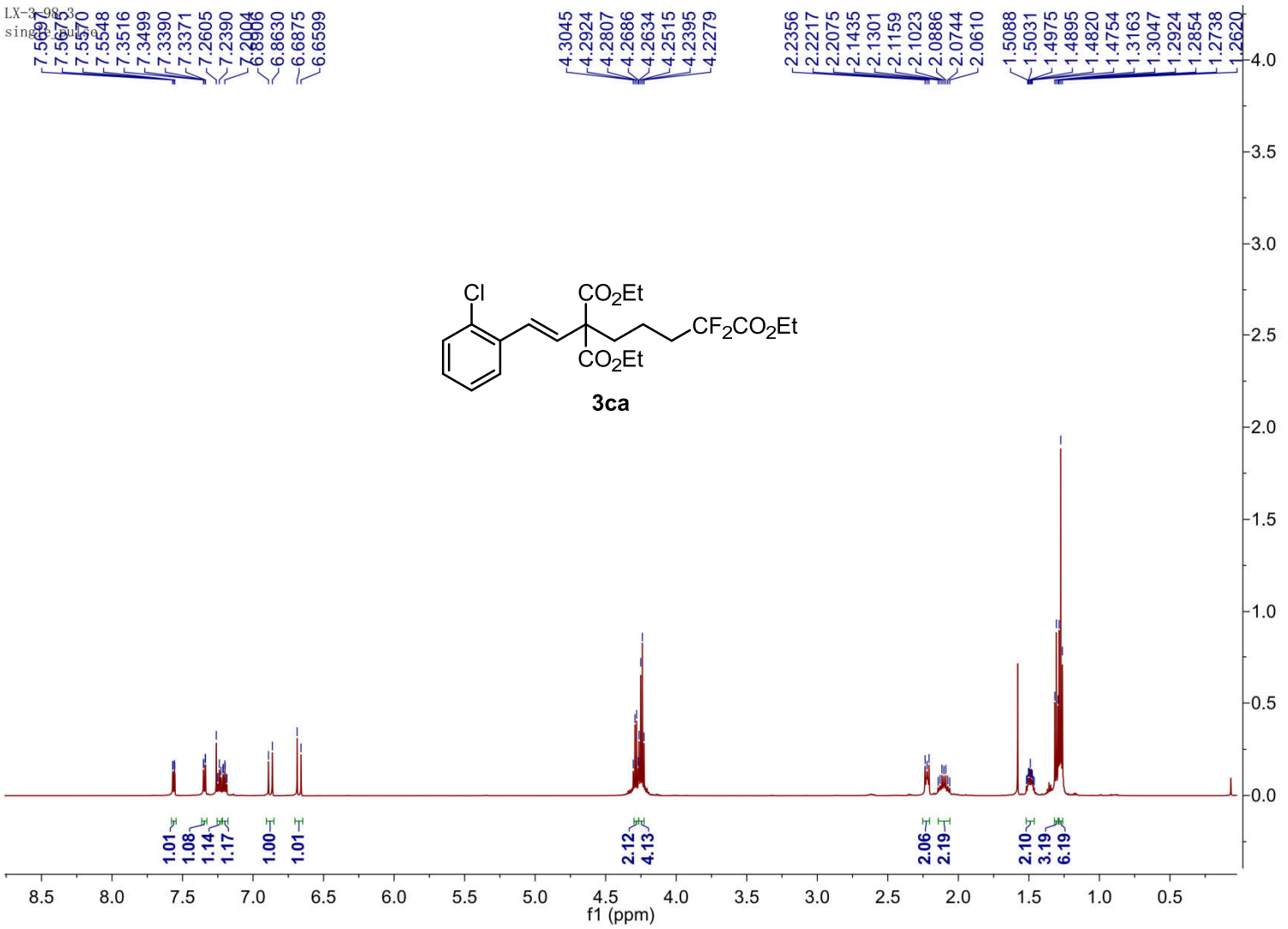

LX-3-68
single_pulse
-105.8306
-105.8605
-105.8910
CO2Et
CF2CO2Et
CO2Et
3aa
2.00
f1 (ppm)

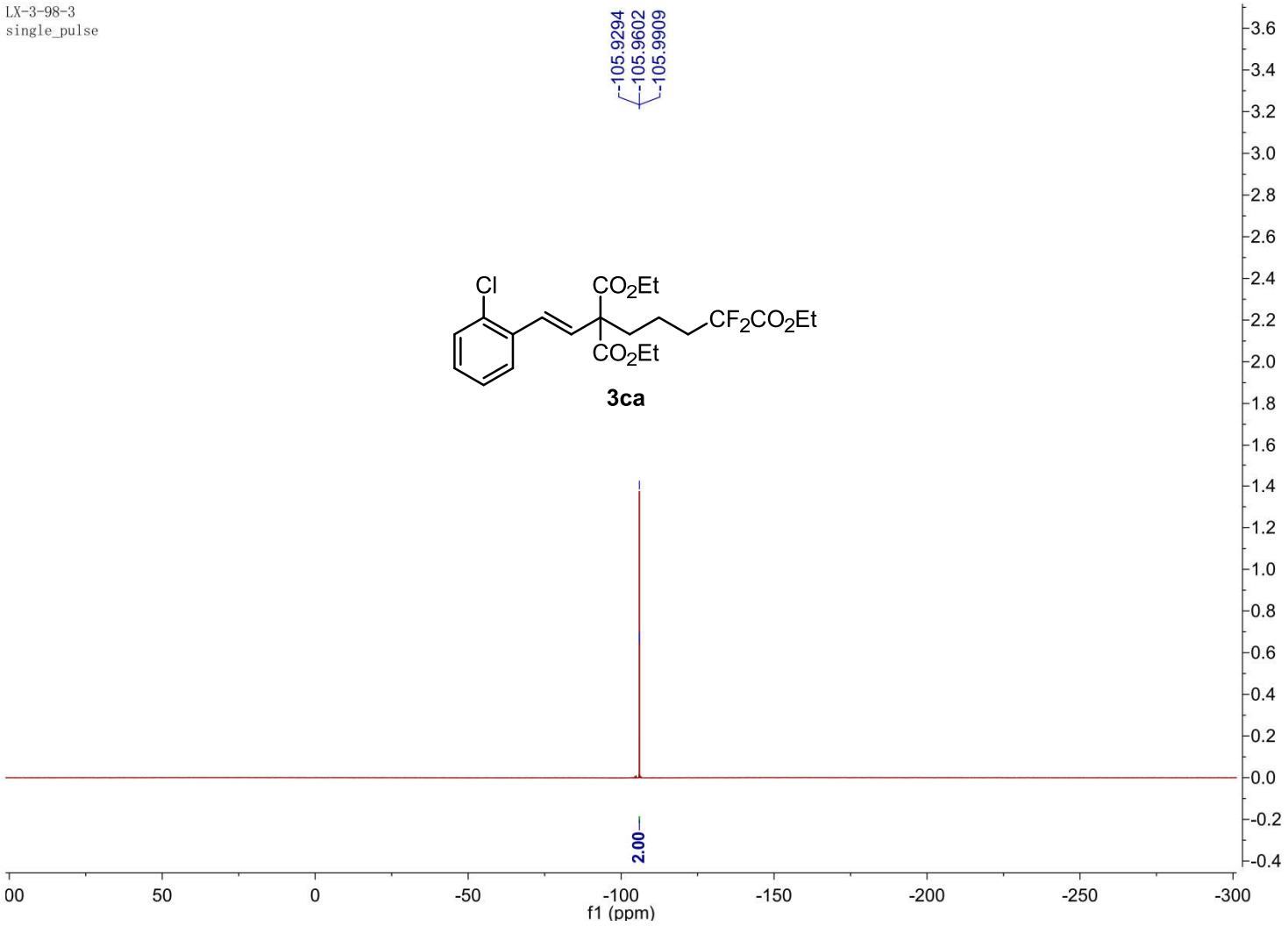

LX-3-68
single pulse decoupled gated NOE
170.1805
164.2975
164.0781
163.8628
136.3009
131.5610
128.5534
127.9886
126.5251
125.7331
117.5307
115.8703
114.2127
77.2127
77.0003
76.7884
62.7880
61.6974
59.2137
34.9450
34.6488
34.4947
34.3391
16.6388
13.9807
13.8549
CO2Et
CF2CO2Et
CO2Et
3aa
f1 (ppm)

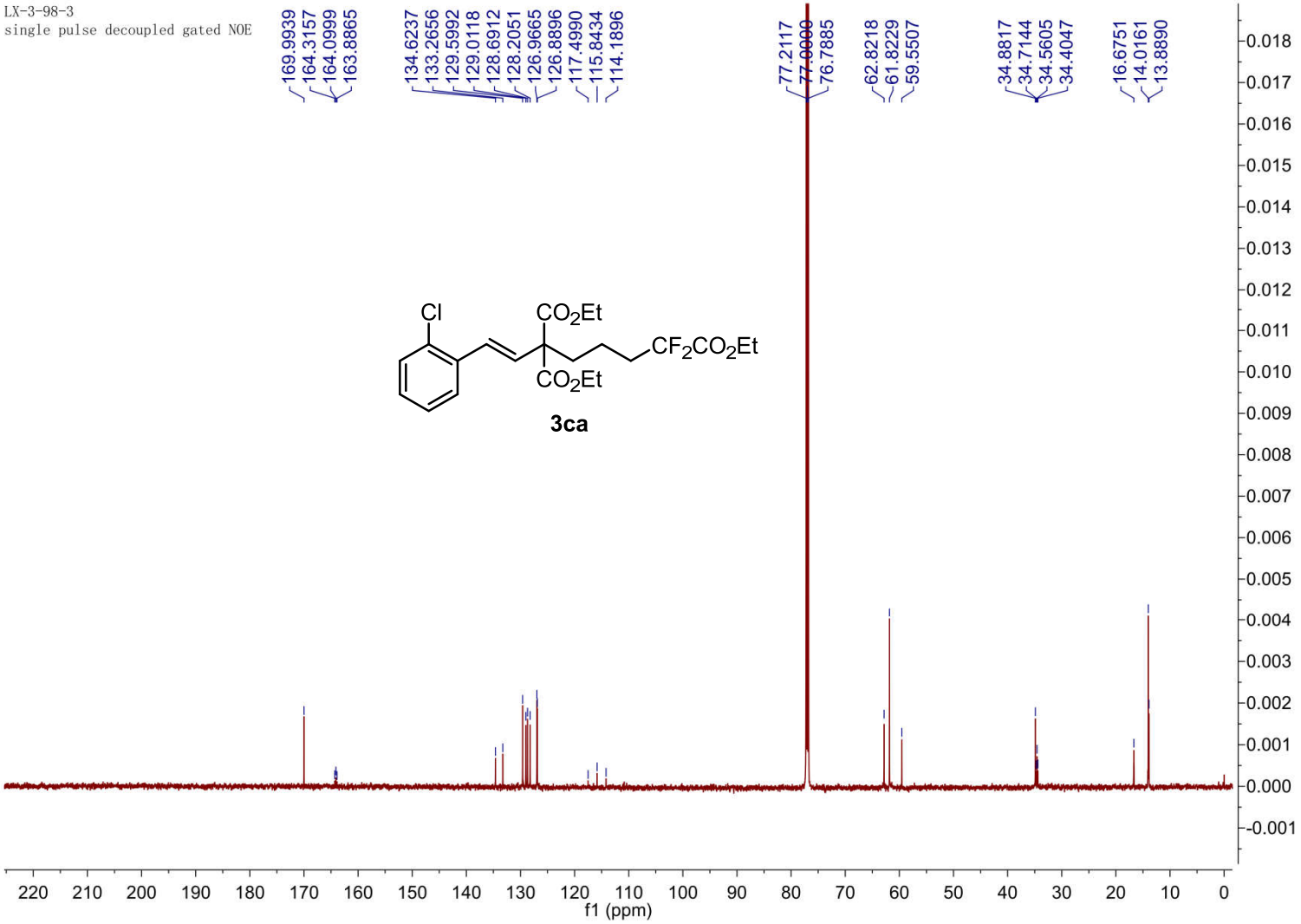

F
CO2Et
CF2CO2Et
CO2Et
3ba
f1 (ppm)

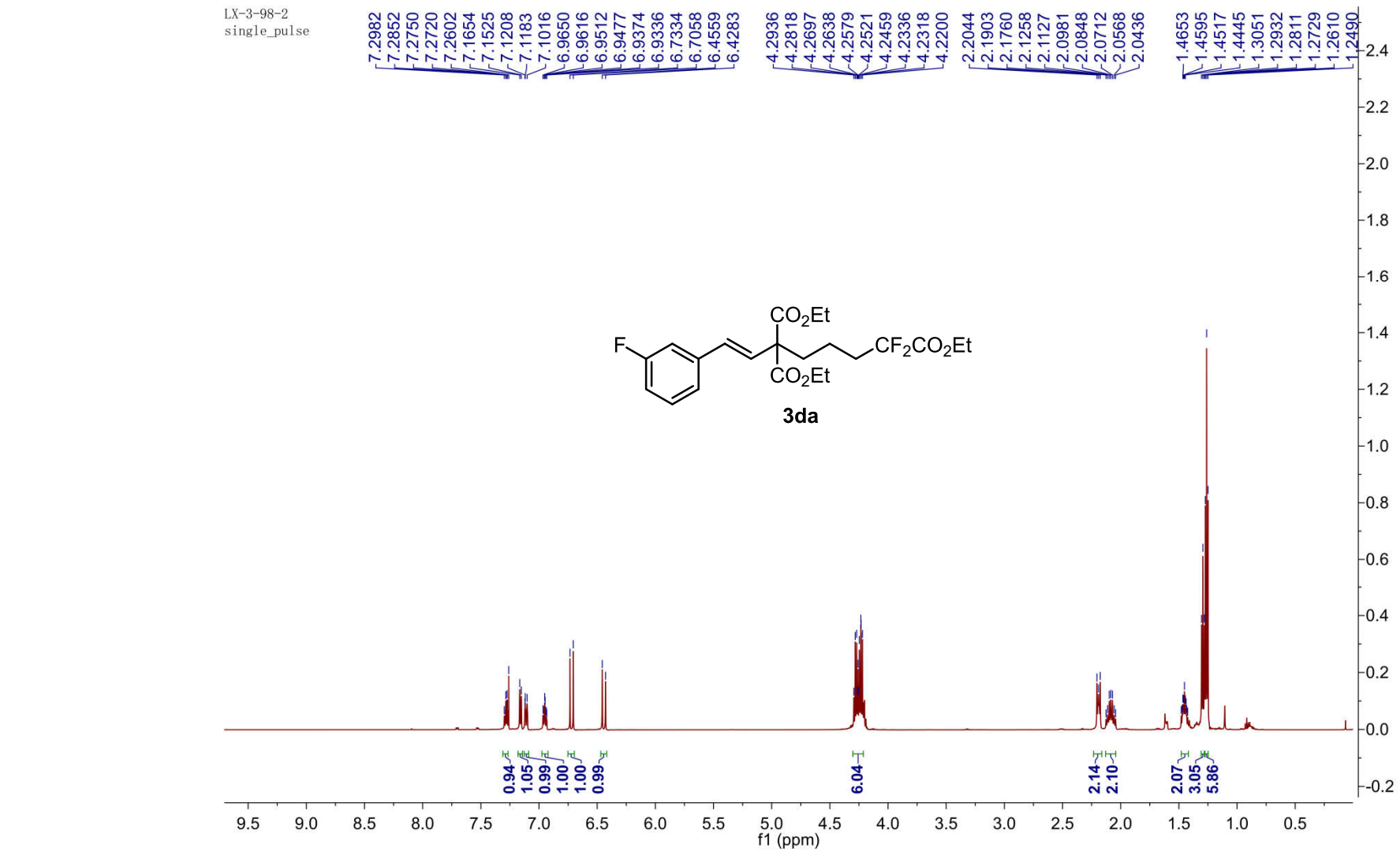

LX-3-98-1
single_pulse
-105.8845
-105.9141
-105.9446
-117.9359
-117.9591
-117.9790
F
CO2Et
CO2Et
CF2CO2Et
3ba
2.00
0.96
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
f1 (ppm)
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2

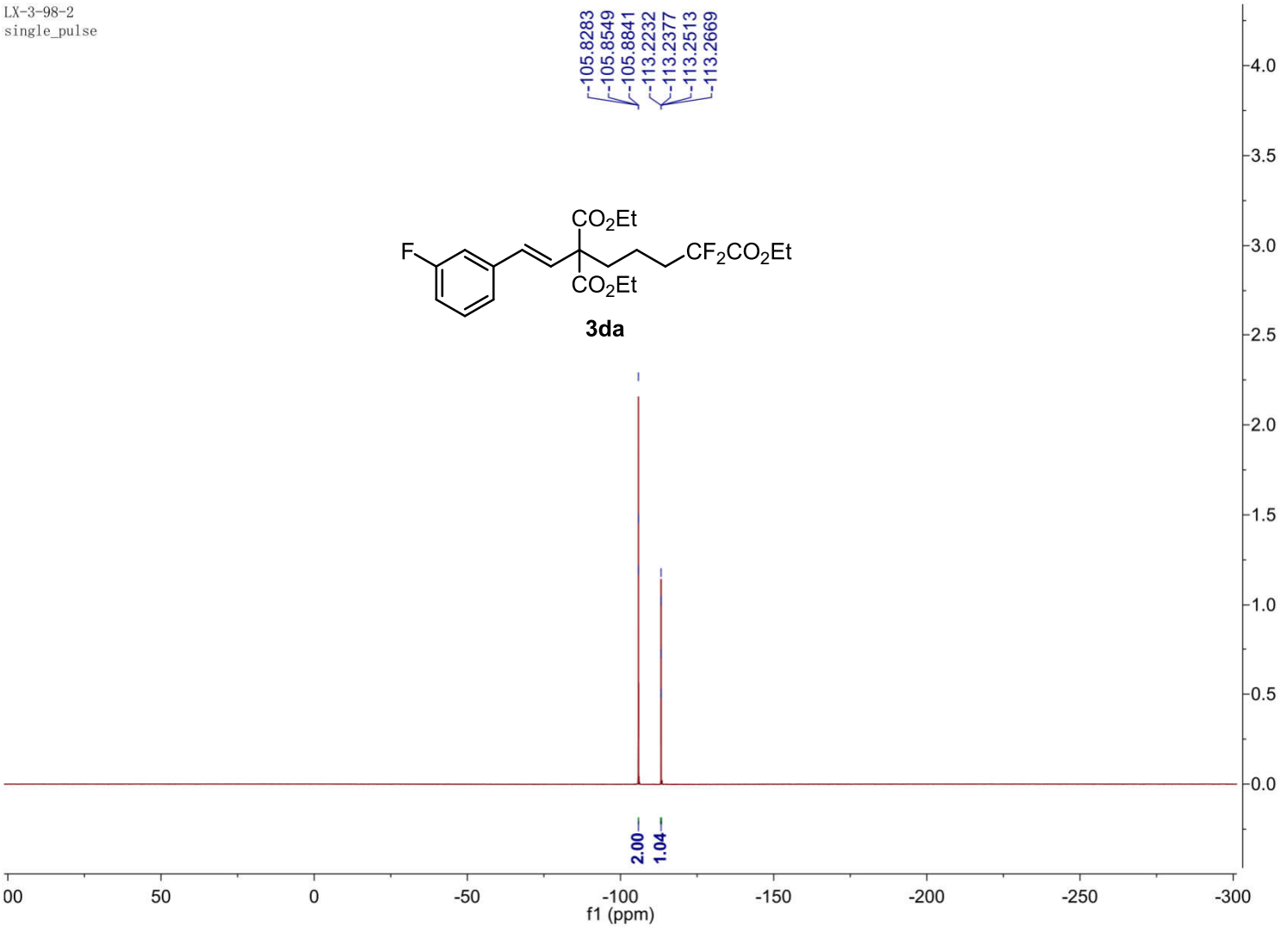

LX-3-98-1
single pulse decoupled gated DE
170.0256
164.3058
164.0890
163.8696
160.9536
159.2988
129.3709
129.3149
128.2139
128.1884
127.1982
127.1807
124.1874
124.1110
124.0998
124.0594
124.0373
117.5097
115.8517
115.7668
115.6221
114.1952
77.2117
77.0003
76.7889
62.8139
61.7855
59.5448
34.8879
34.6732
34.5186
34.3644
16.6595
13.9827
13.8648
F
CO2Et
CO2Et
CF2CO2Et
3ba
f1 (ppm)

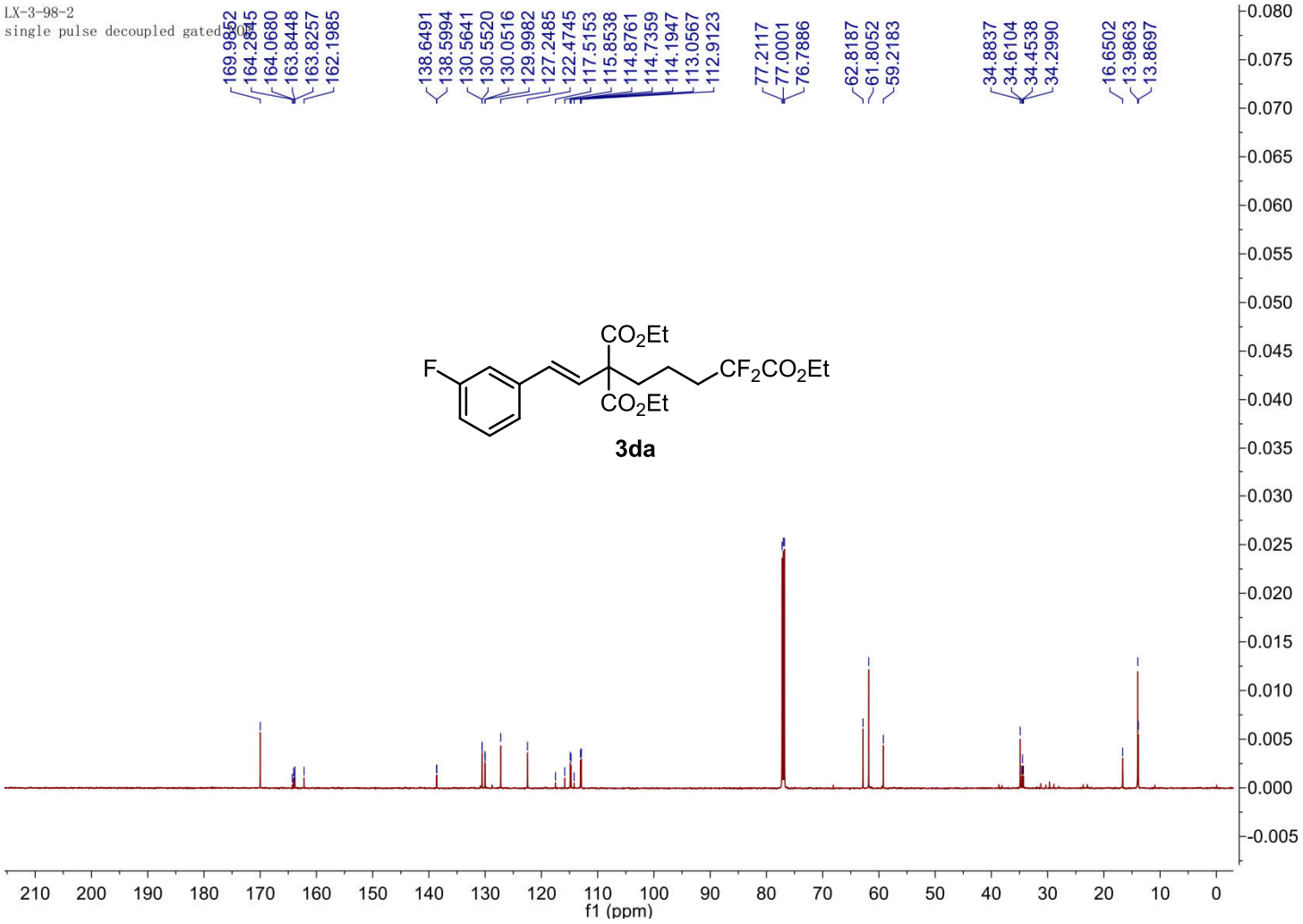

LX-3-98-3
single pulse
7.5997
7.5775
7.5570
7.5548
7.3516
7.3499
7.3390
7.3371
7.2605
7.2390
7.2004
6.8806
6.8630
6.6875
6.6599
4.3045
4.2924
4.2807
4.2686
4.2634
4.2515
4.2395
4.2279
2.2356
2.2217
2.2075
2.1435
2.1301
2.1159
2.1023
2.0886
2.0744
2.0610
1.5088
1.5031
1.4975
1.4895
1.4820
1.4754
1.3163
1.3047
1.2924
1.2854
1.2738
1.2620
Cl
CO2Et
CO2Et
CF2CO2Et
3ca
1.01
1.08
1.14
1.17
1.00
1.01
2.12
4.13
2.06
2.19
2.10
3.19
6.19
f1 (ppm)

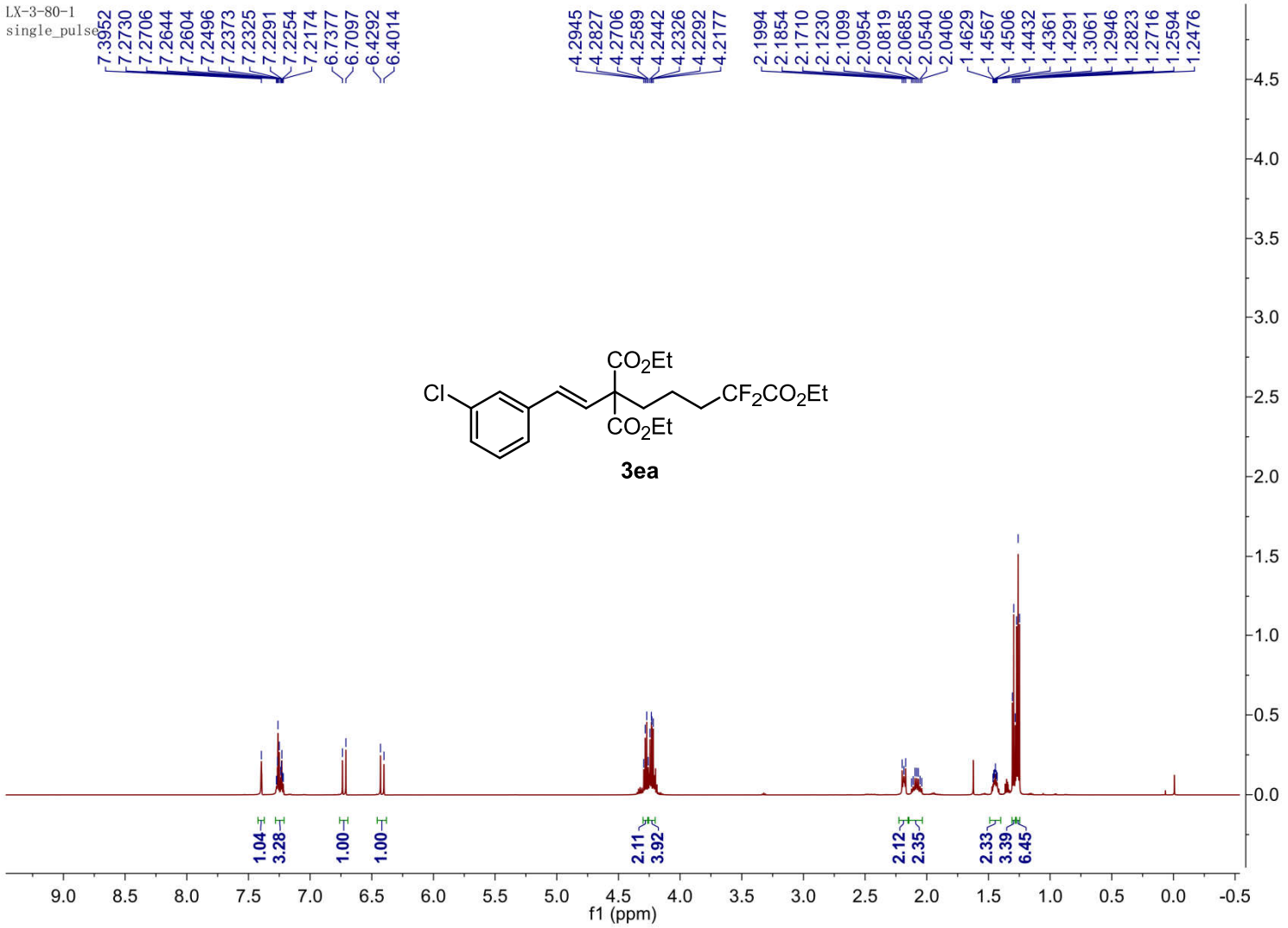

LX-3-98-3
single_pulse
-105.9294
-105.9602
-105.9909
Cl
CO2Et
CF2CO2Et
CO2Et
3ca
2.00
f1 (ppm)

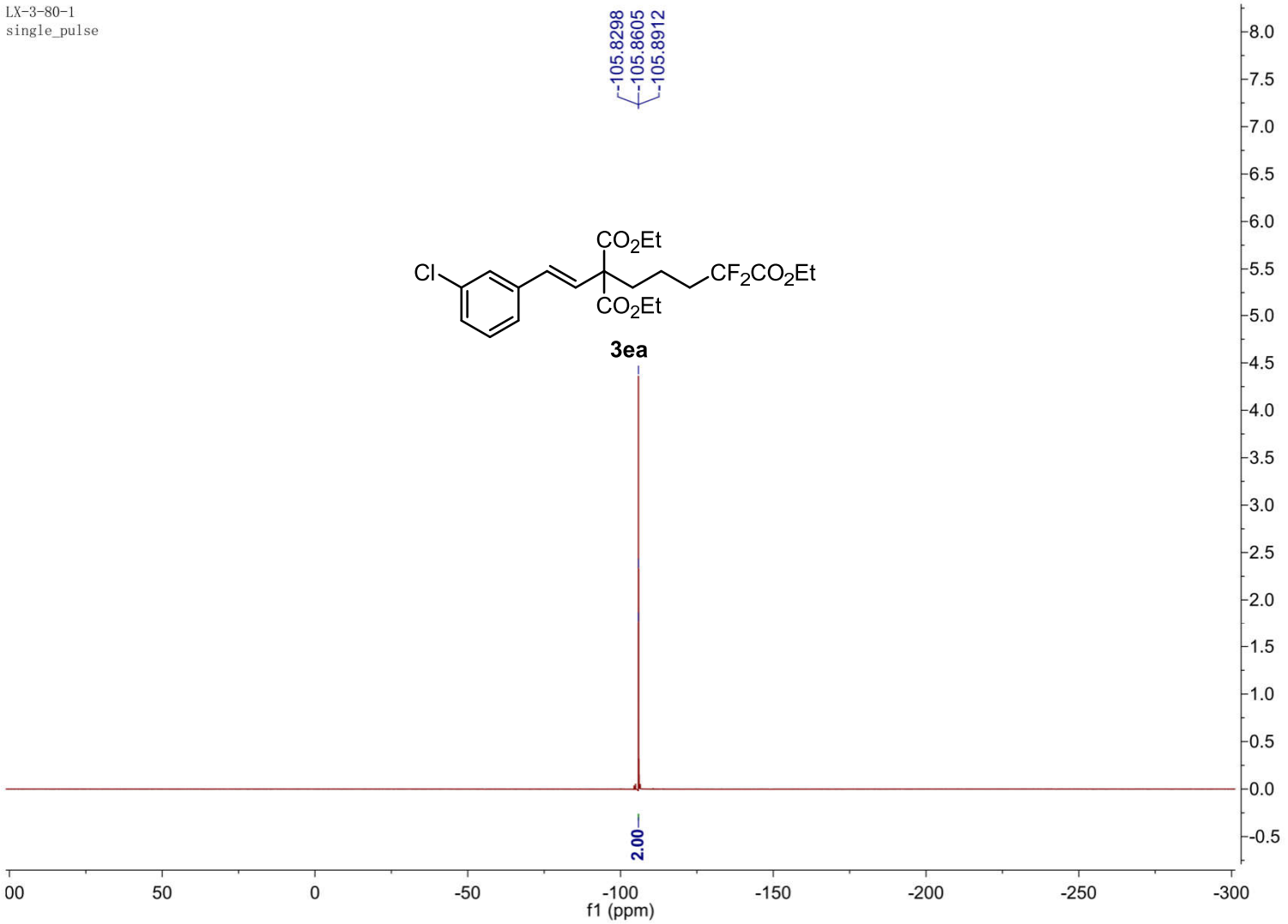

LX-3-98-3
single pulse decoupled gated NOE
169.9939
164.3157
164.0999
163.8865
134.6237
133.2656
129.5992
129.0118
128.6912
128.2051
126.9665
126.8896
117.4990
115.8434
114.1896
77.2117
77.0000
76.7885
62.8218
61.8229
59.5507
34.8817
34.7144
34.5605
34.4047
16.6751
14.0161
13.8890
Cl
CO2Et
CO2Et
CF2CO2Et
3ca
f1 (ppm)

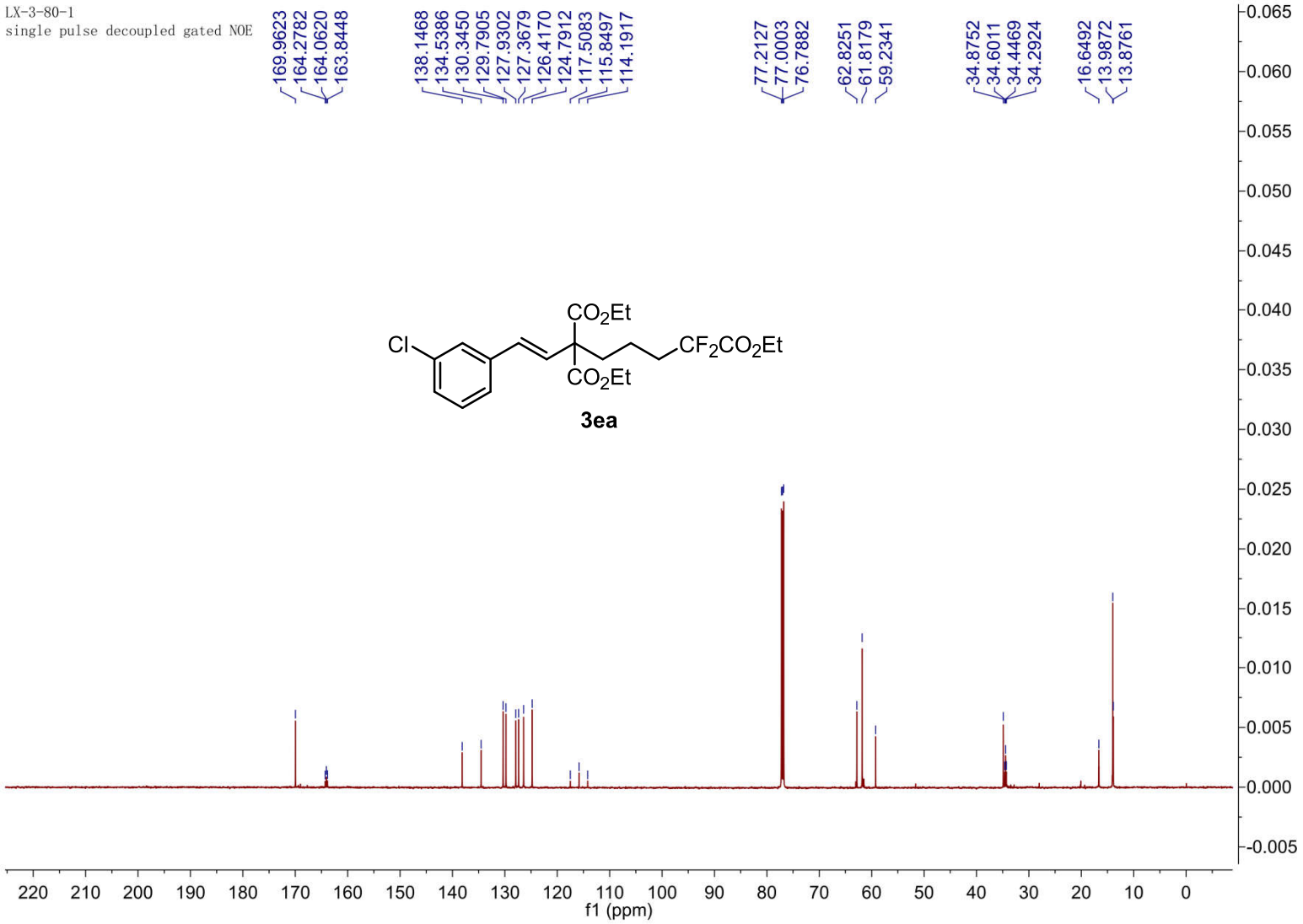

LX-3-98-2
single_pulse
7.2982
7.2852
7.2750
7.2720
7.2602
7.1654
7.1525
7.1208
7.1183
7.1016
6.9650
6.9616
6.9512
6.9477
6.9374
6.9336
6.7334
6.7058
6.4559
6.4283
4.2936
4.2818
4.2697
4.2638
4.2579
4.2521
4.2459
4.2336
4.2318
4.2200
2.2044
2.1903
2.1760
2.1258
2.1127
2.0981
2.0848
2.0712
2.0568
2.0436
1.4653
1.4595
1.4517
1.4445
1.3051
1.2932
1.2811
1.2729
1.2610
1.2490
CO2Et
F
CF2CO2Et
CO2Et
3da
0.94
1.05
0.99
1.00
1.00
0.99
6.04
2.14
2.10
2.07
3.05
5.86
f1 (ppm)

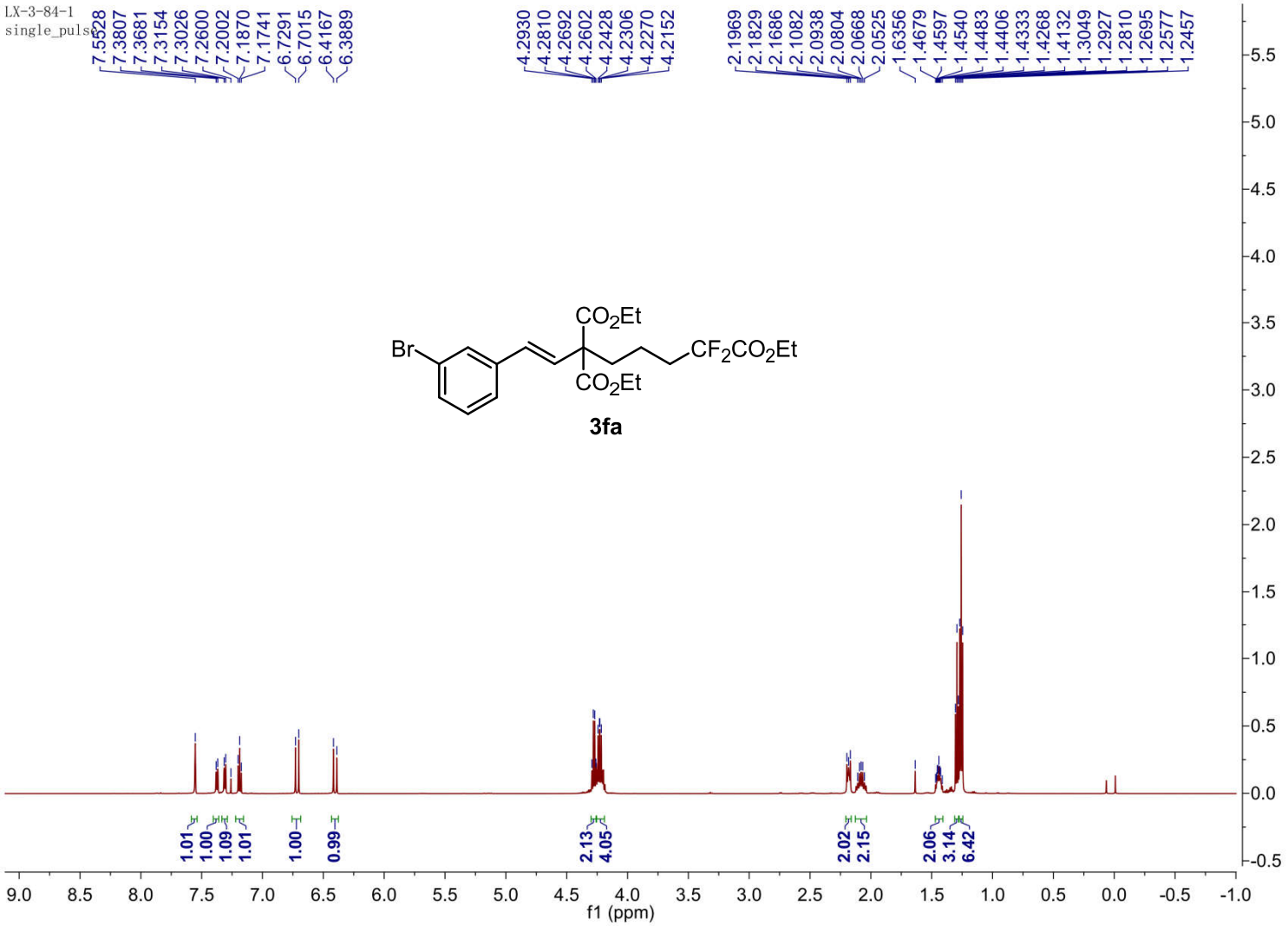

LX-3-98-2
single_pulse
-105.8283
-105.8549
-105.8841
-113.2232
-113.2377
-113.2513
-113.2669
CO2Et
F
CF2CO2Et
CO2Et
3da
2.00
1.04
f1 (ppm)

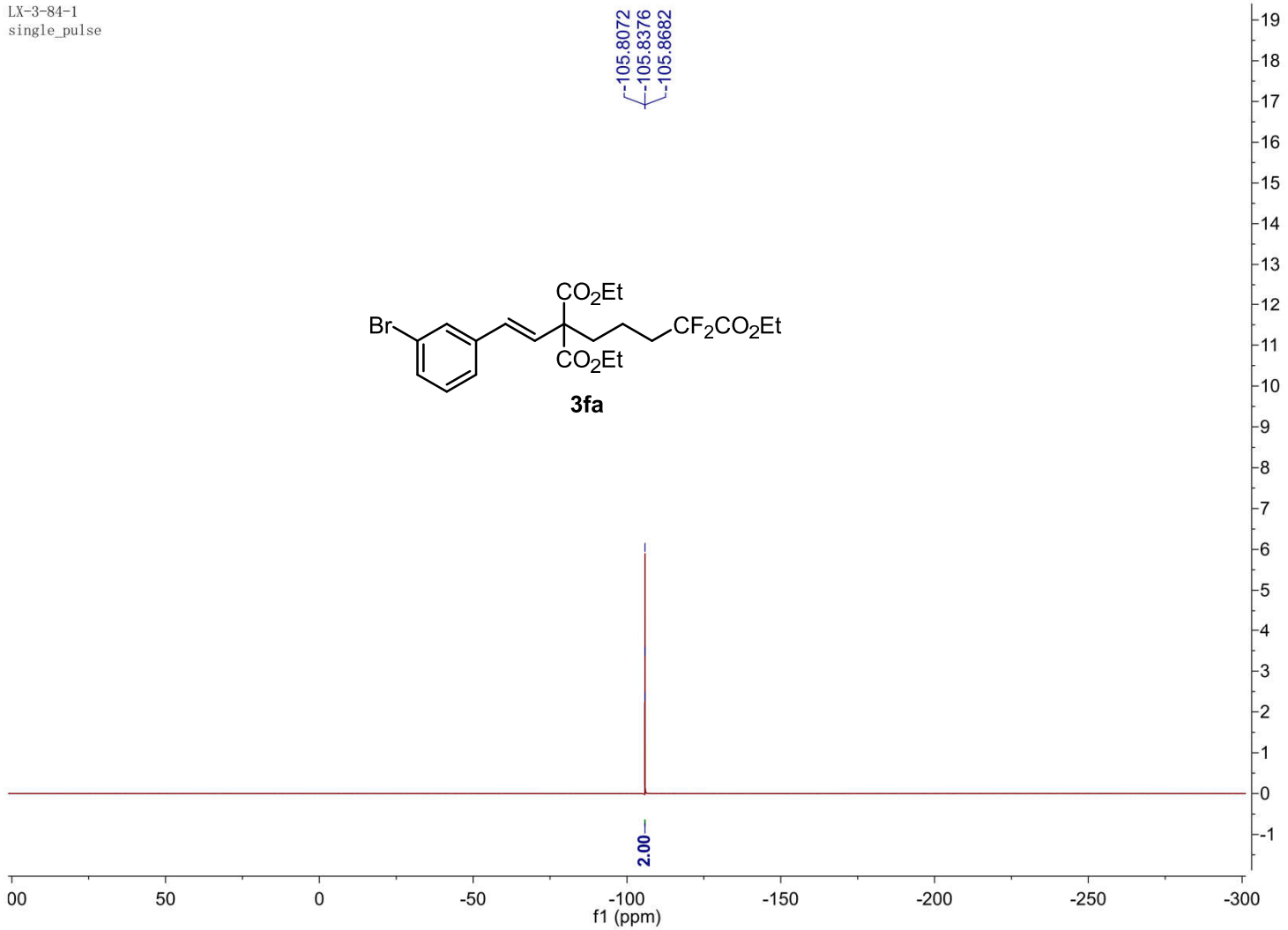

LX-3-98-2
single pulse decoupled gated 13C
169.9852
164.2845
164.0680
163.8448
163.8257
162.1985
138.6491
138.5994
130.5641
130.5520
130.0516
129.9982
127.2485
122.4745
117.5153
115.8538
114.8761
114.7359
114.1947
113.0567
112.9123
77.2117
77.0001
76.7886
62.8187
61.8052
59.2183
34.8837
34.6104
34.4538
34.2990
16.6502
13.9863
13.8697
CO2Et
F
CF2CO2Et
CO2Et
3da
f1 (ppm)

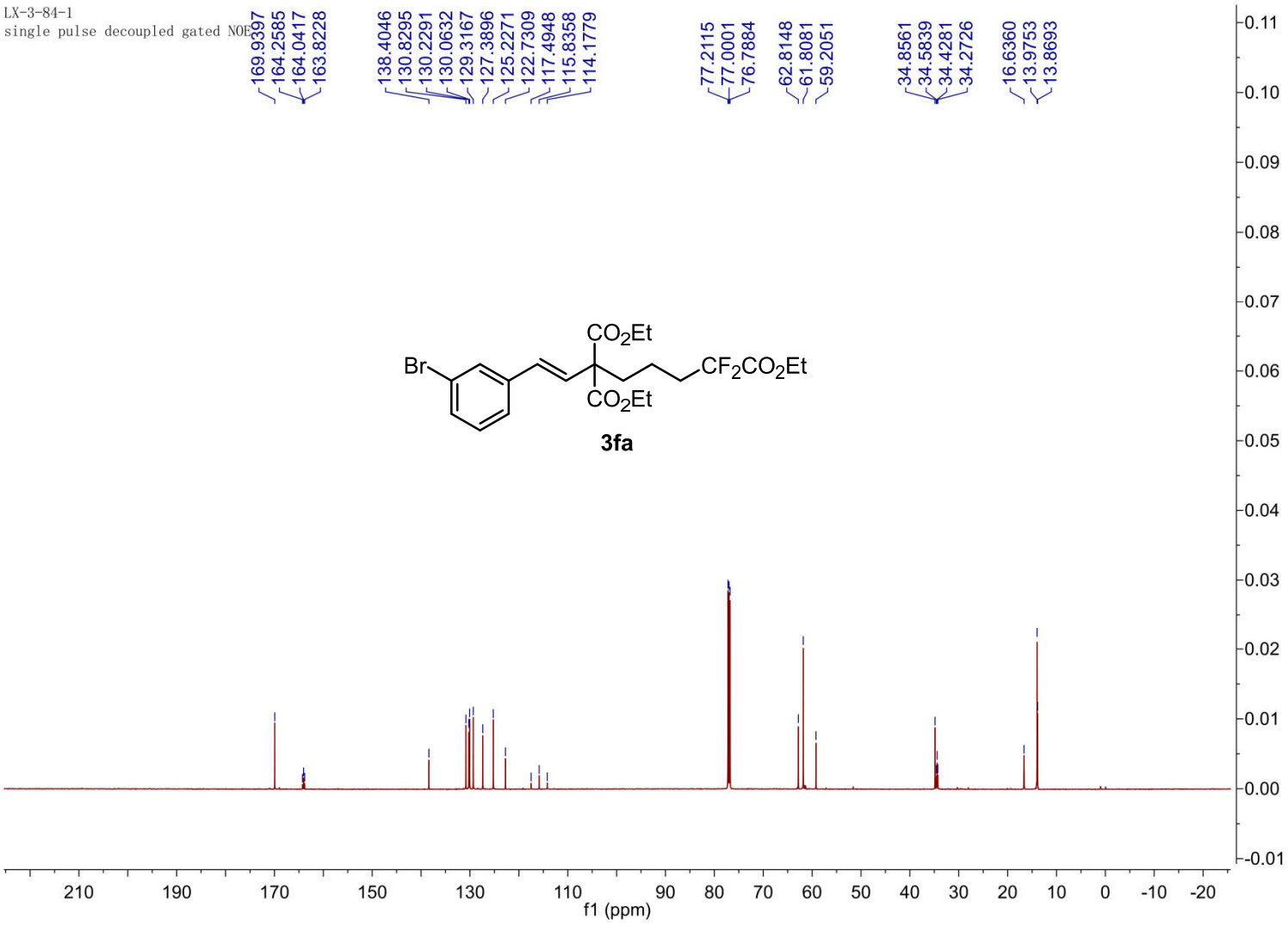

LX-3-80-1
single_pulse
7.3952
7.2730
7.2706
7.2644
7.2604
7.2496
7.2373
7.2325
7.2291
7.2254
7.2174
6.7377
6.7097
6.4292
6.4014
4.2945
4.2827
4.2706
4.2589
4.2442
4.2326
4.2292
4.2177
2.1994
2.1854
2.1710
2.1230
2.1099
2.0954
2.0819
2.0685
2.0540
2.0406
1.4629
1.4567
1.4506
1.4432
1.4361
1.4291
1.3061
1.2946
1.2823
1.2716
1.2594
1.2476
Cl
CO2Et
CO2Et
CF2CO2Et
3ea
1.04
3.28
1.00
1.00
2.11
3.92
2.12
2.35
2.33
3.39
6.45
f1 (ppm)

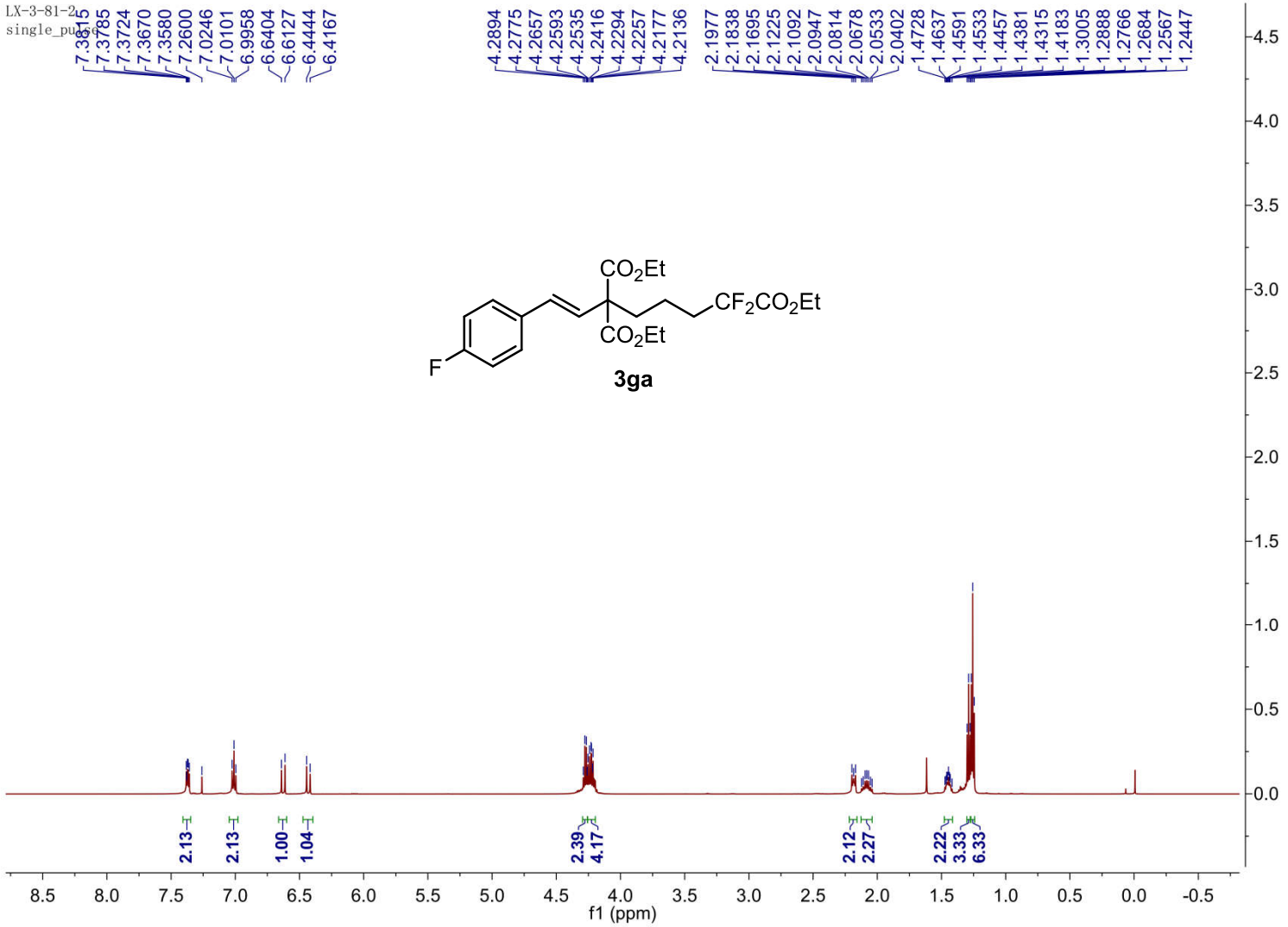

LX-3-80-1
single_pulse
-105.8298
-105.8605
-105.8912
Cl
CO2Et
CO2Et
CF2CO2Et
3ea
2.00
f1 (ppm)

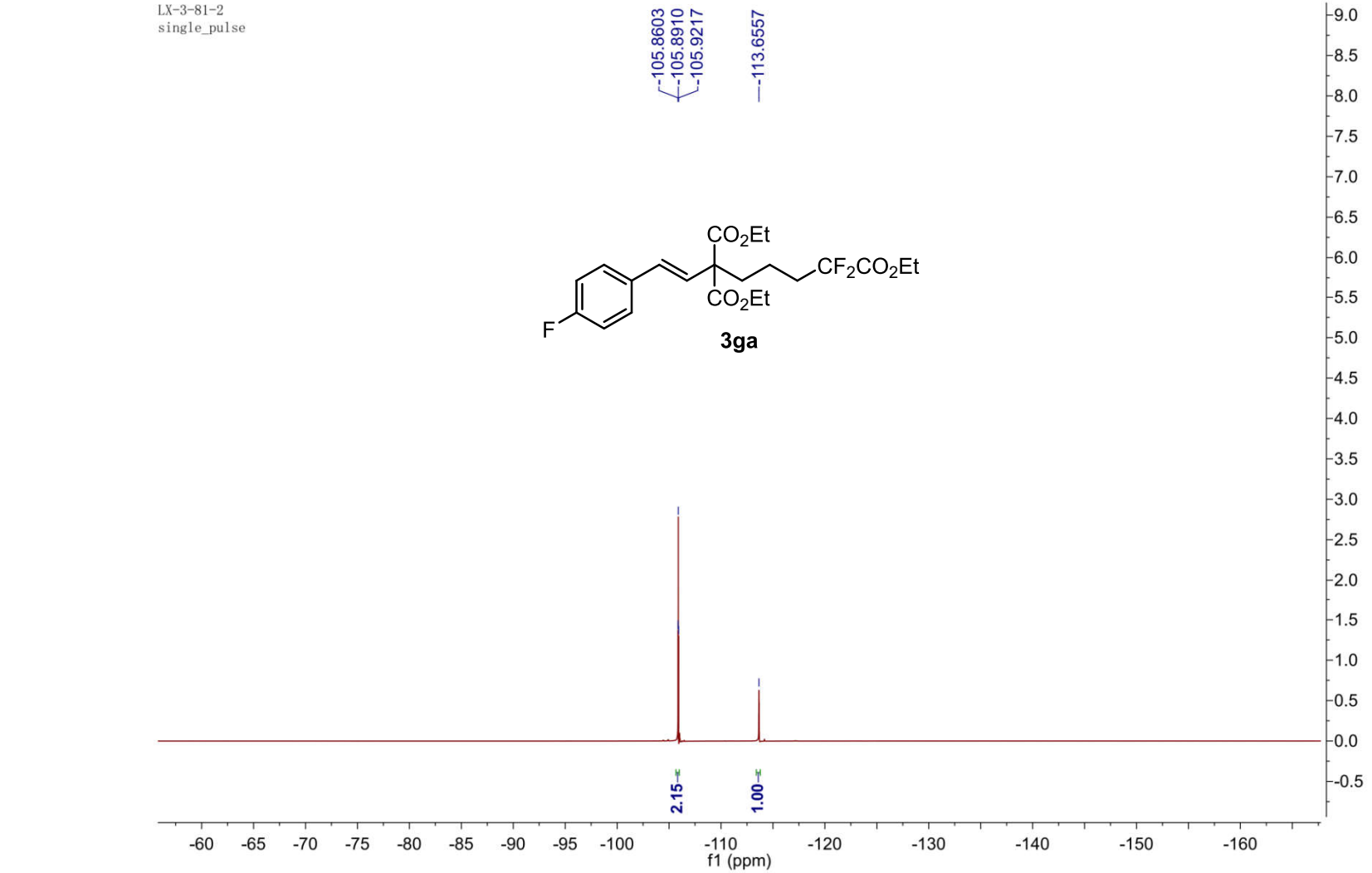

LX-3-80-1
single pulse decoupled gated NOE
169.9623
164.2782
164.0620
163.8448
138.1468
134.5386
130.3450
129.7905
127.9302
127.3679
126.4170
124.7912
117.5083
115.8497
114.1917
77.2127
77.0003
76.7882
62.8251
61.8179
59.2341
34.8752
34.6011
34.4469
34.2924
16.6492
13.9872
13.8761
CO2Et
Cl
CF2CO2Et
CO2Et
3ea
f1 (ppm)

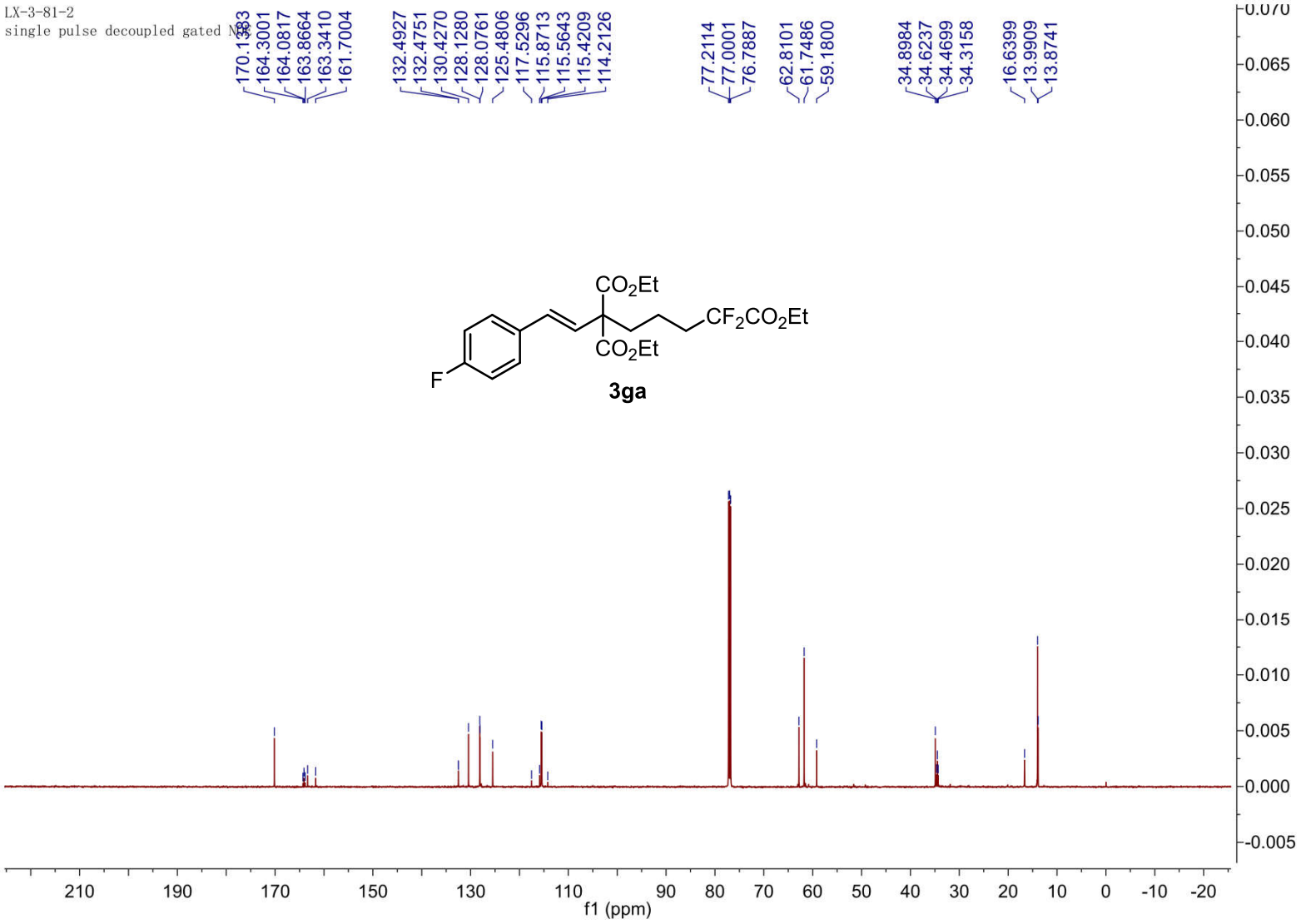

LX-3-84-1
single_puls
7.5528
7.3807
7.3681
7.3154
7.3026
7.2600
7.2002
7.1870
7.1741
6.7291
6.7015
6.4167
6.3889
4.2930
4.2810
4.2692
4.2602
4.2428
4.2306
4.2270
4.2152
2.1969
2.1829
2.1686
2.1082
2.0938
2.0804
2.0668
2.0525
1.6356
1.4679
1.4597
1.4540
1.4483
1.4406
1.4333
1.4268
1.4132
1.3049
1.2927
1.2810
1.2695
1.2577
1.2457
Br
CO2Et
CO2Et
CF2CO2Et
3fa
1.01
1.00
1.09
1.01
1.00
0.99
2.13
4.05
2.02
2.15
2.06
3.14
6.42
f1 (ppm)

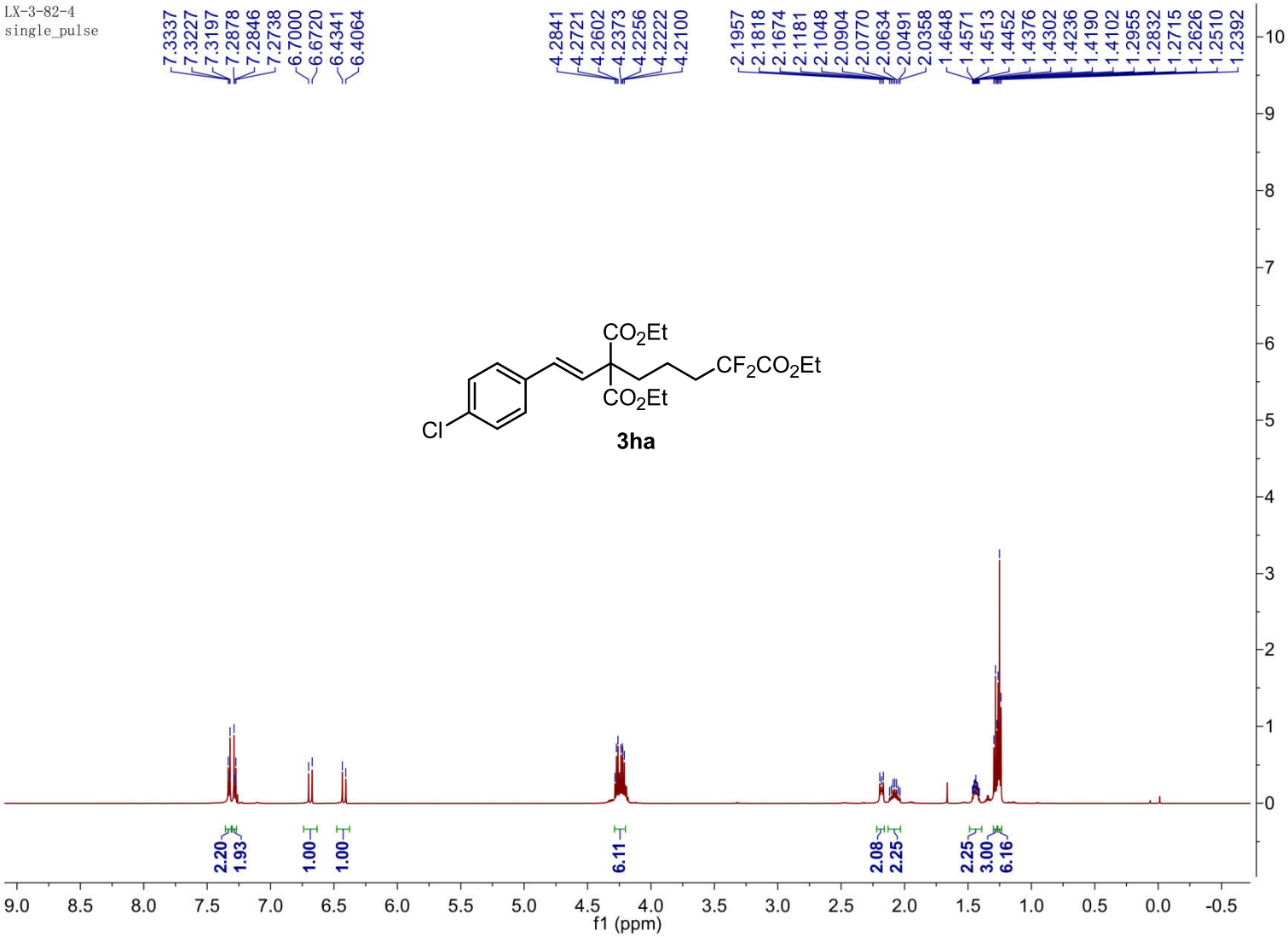

LX-3-84-1
single_pulse
-105.8072
-105.8376
-105.8682
CO2Et
Br
CF2CO2Et
CO2Et
3fa
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

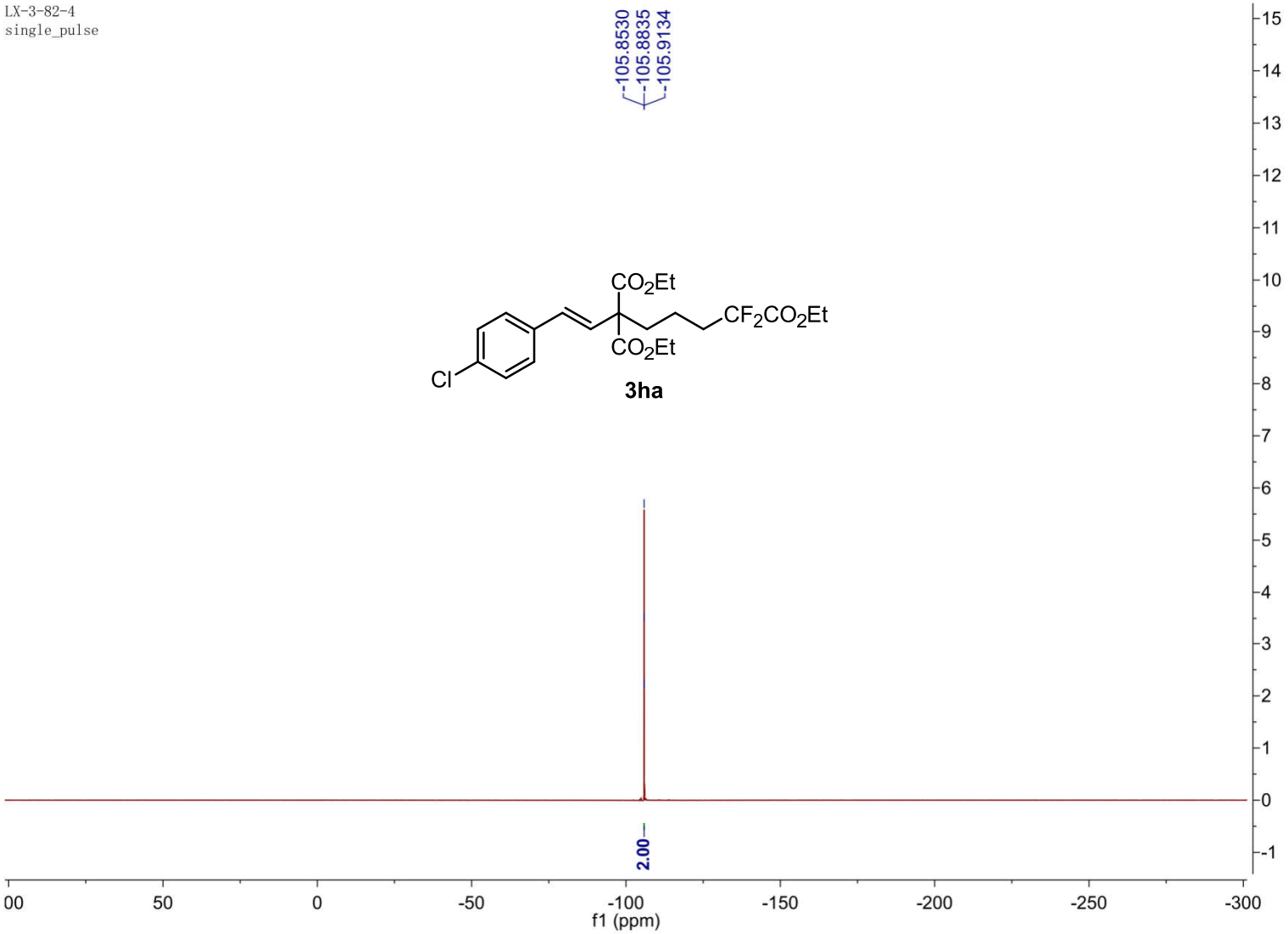

LX-3-84-1
single pulse decoupled gated NOE
169.9397
164.2585
164.0417
163.8228
138.4046
130.8295
130.2291
130.0632
129.3167
127.3896
125.2271
122.7309
117.4948
115.8358
114.1779
77.2115
77.0001
76.7884
62.8148
61.8081
59.2051
34.8561
34.5839
34.4281
34.2726
16.6360
13.9753
13.8693
Br
CO2Et
CO2Et
CF2CO2Et
3fa
f1 (ppm)

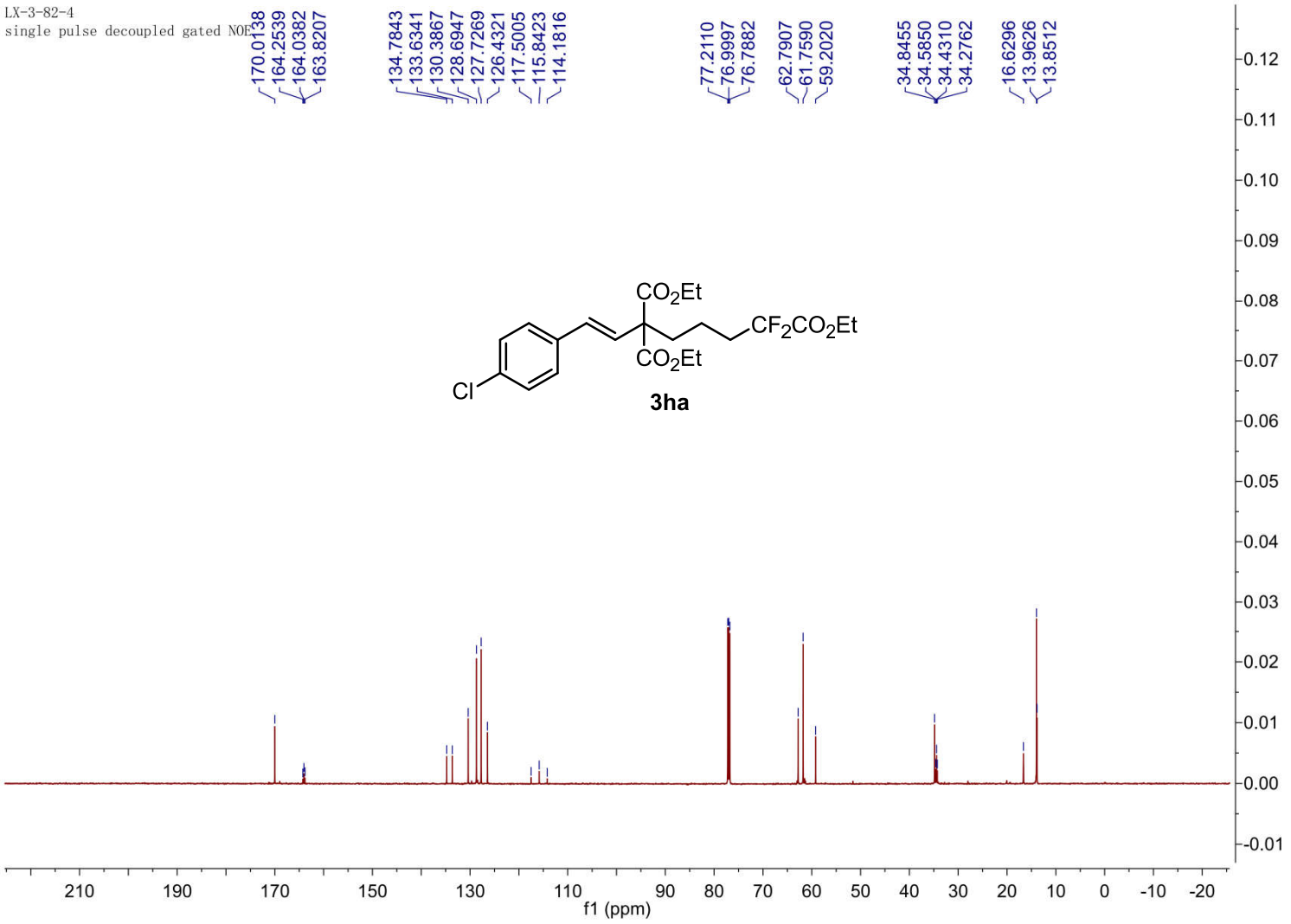

LX-3-81-2
single_pulse
7.3815
7.3785
7.3724
7.3670
7.3580
7.2600
7.0246
7.0101
6.9958
6.6404
6.6127
6.4444
6.4167
4.2894
4.2775
4.2657
4.2593
4.2535
4.2416
4.2294
4.2257
4.2177
4.2136
2.1977
2.1838
2.1695
2.1225
2.1092
2.0947
2.0814
2.0678
2.0533
2.0402
1.4728
1.4637
1.4591
1.4533
1.4457
1.4381
1.4315
1.4183
1.3005
1.2888
1.2766
1.2684
1.2567
1.2447
CO2Et
CF2CO2Et
CO2Et
F
3ga
2.13
2.13
1.00
1.04
2.39
4.17
2.12
2.27
2.22
3.33
6.33
f1 (ppm)

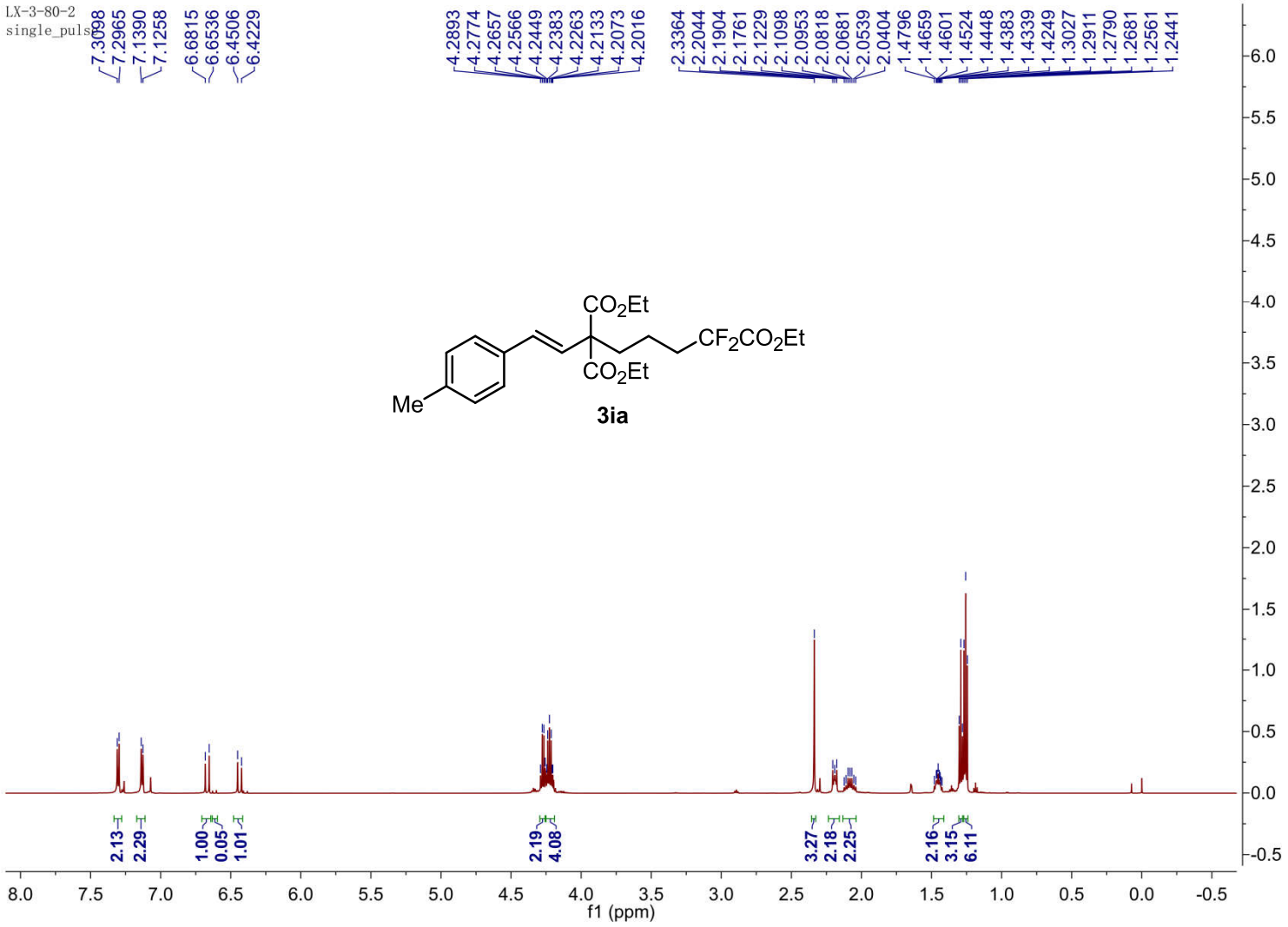

LX-3-81-2
single_pulse
-105.8603
-105.8910
-105.9217
-113.6557
CO2Et
CF2CO2Et
CO2Et
F
3ga
2.15
1.00
-60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

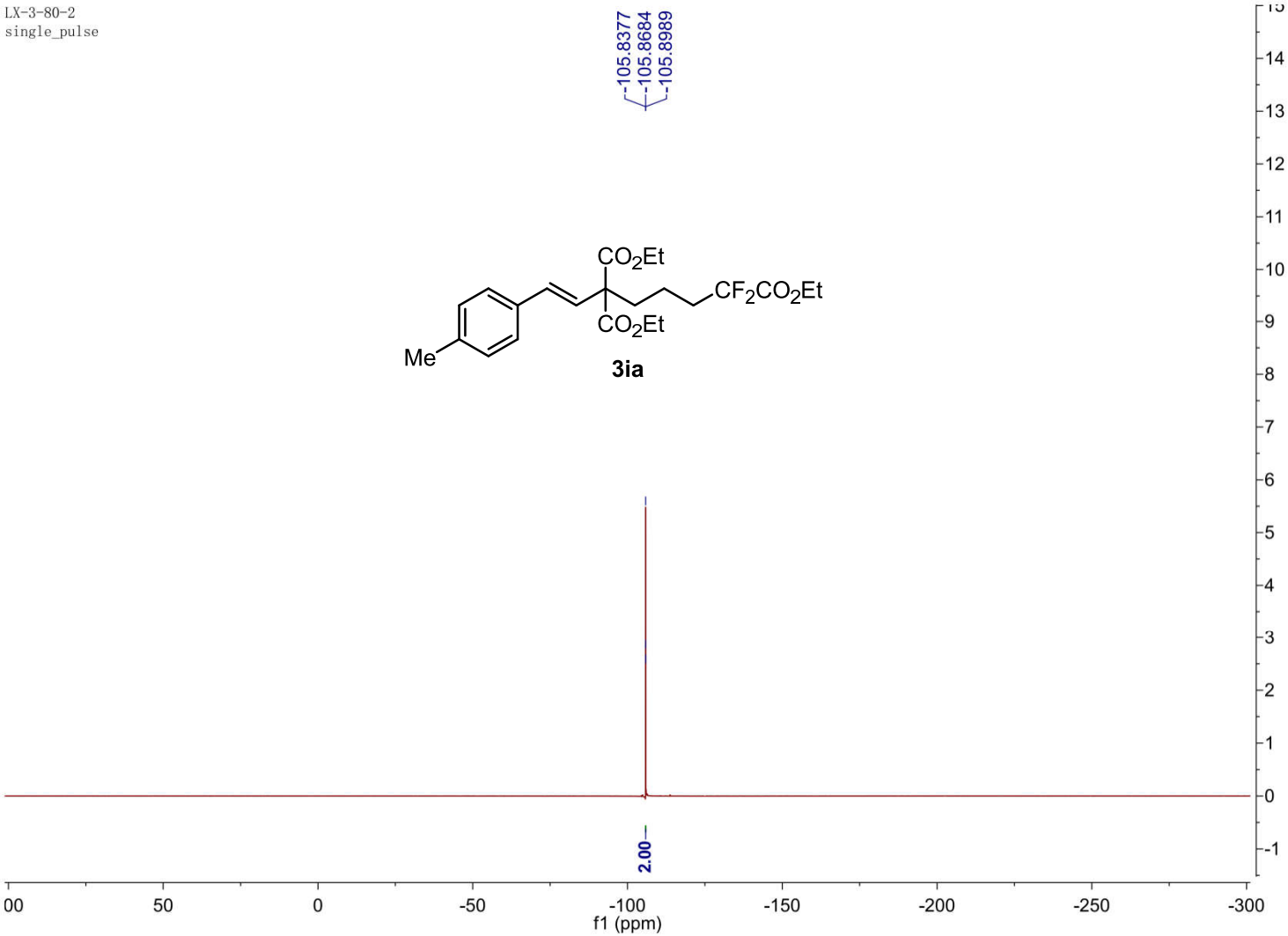

LX-3-81-2
single pulse decoupled gated NMR
170.1393
164.3001
164.0817
163.8664
163.3410
161.7004
132.4927
132.4751
130.4270
128.1280
128.0761
125.4806
117.5296
115.8713
115.5643
115.4209
114.2126
77.2114
77.0001
76.7887
62.8101
61.7486
59.1800
34.8984
34.6237
34.4699
34.3158
16.6399
13.9909
13.8741
CO2Et
CF2CO2Et
CO2Et
F
3ga
f1 (ppm)

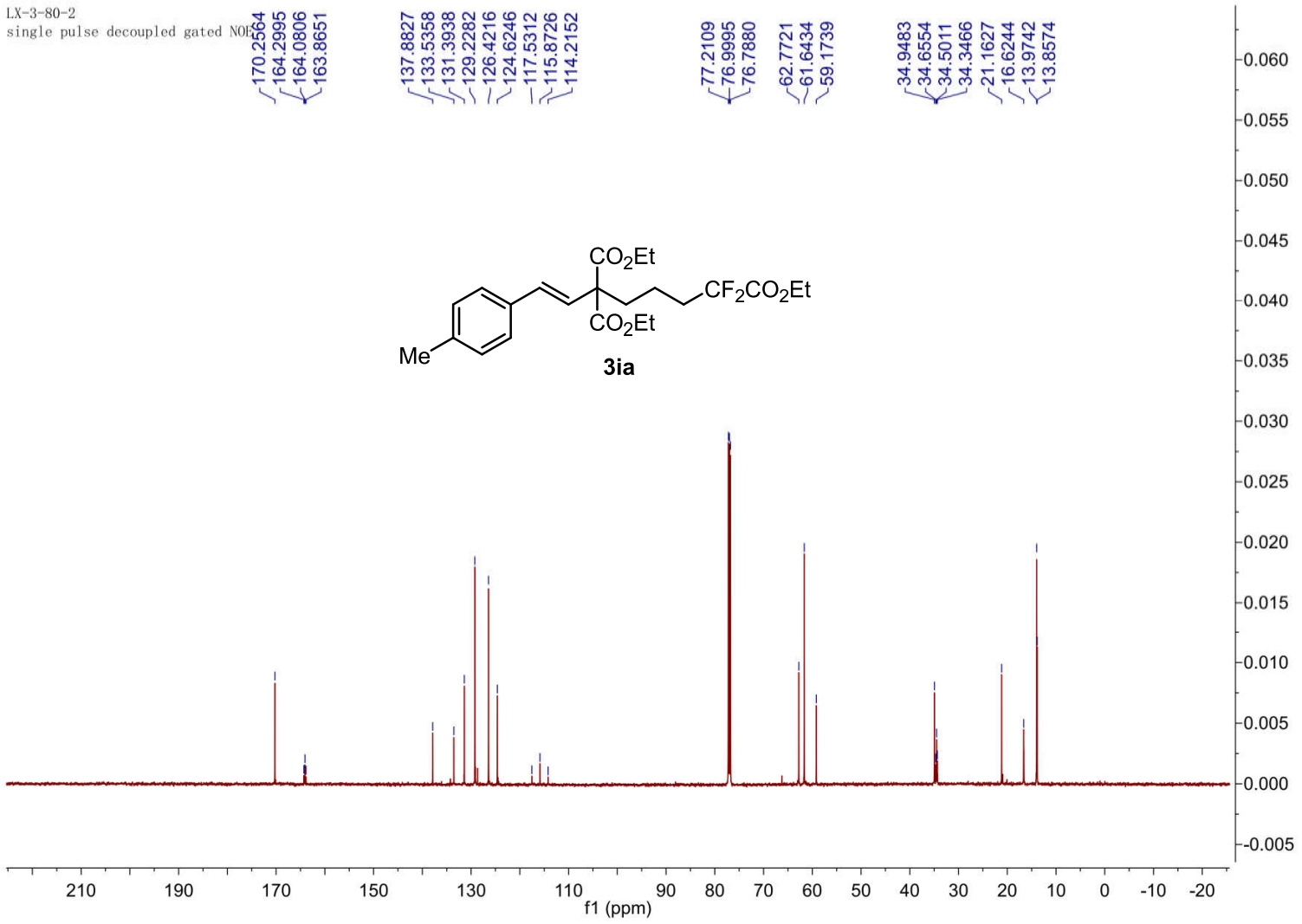

LX-3-82-4
single_pulse
7.3337
7.3227
7.3197
7.2878
7.2846
7.2738
6.7000
6.6720
6.4341
6.4064
4.2841
4.2721
4.2602
4.2373
4.2256
4.2222
4.2100
2.1957
2.1818
2.1674
2.1181
2.1048
2.0904
2.0770
2.0634
2.0491
2.0358
1.4648
1.4571
1.4513
1.4452
1.4376
1.4302
1.4236
1.4190
1.4102
1.2955
1.2832
1.2715
1.2626
1.2510
1.2392
CO2Et
CF2CO2Et
CO2Et
Cl
3ha
2.20
1.93
1.00
1.00
6.11
2.08
2.25
2.25
3.00
6.16
f1 (ppm)

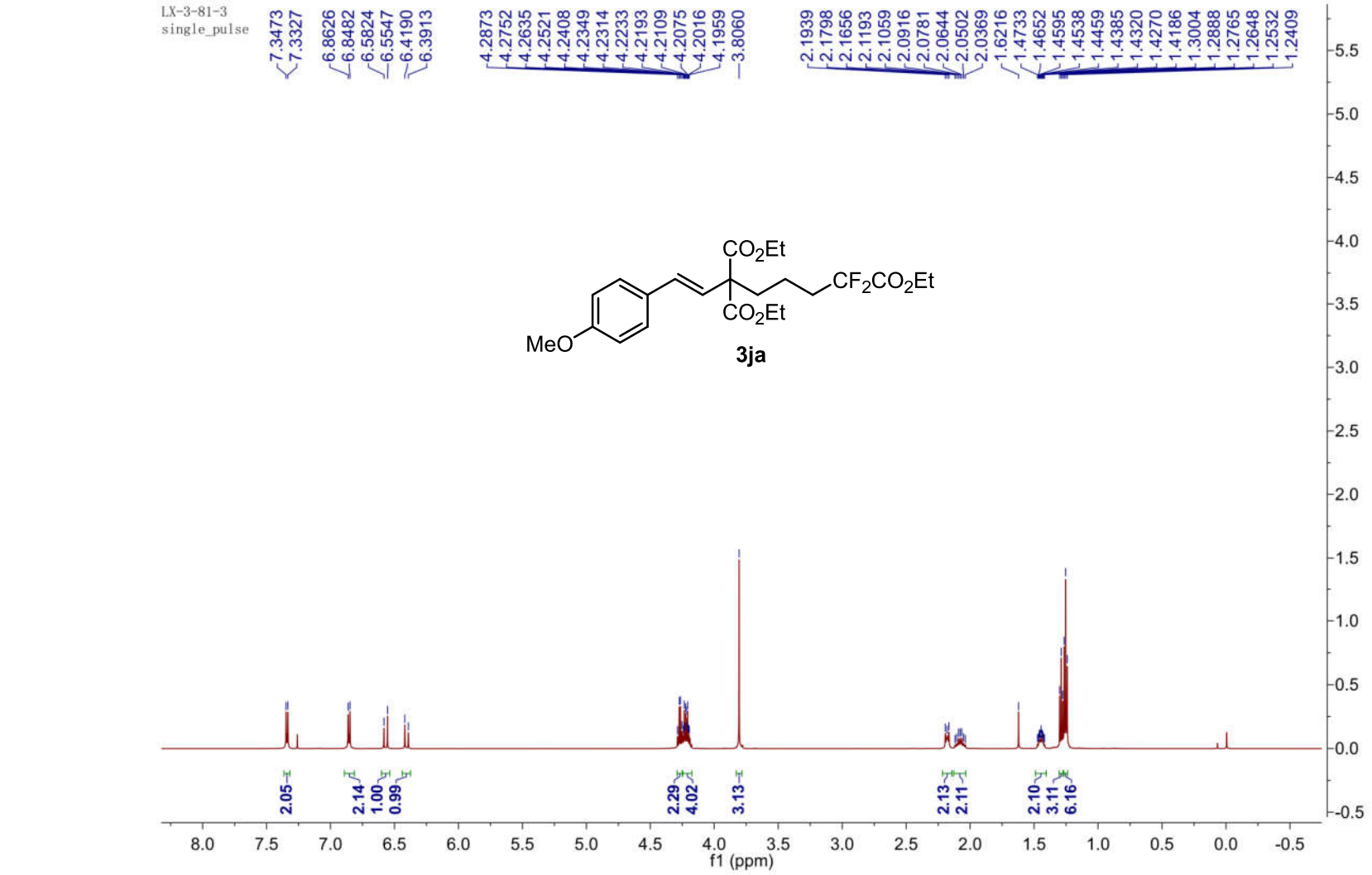

LX-3-82-4
single_pulse
-105.8530
-105.8835
-105.9134
CO2Et
CF2CO2Et
CO2Et
Cl
3ha
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

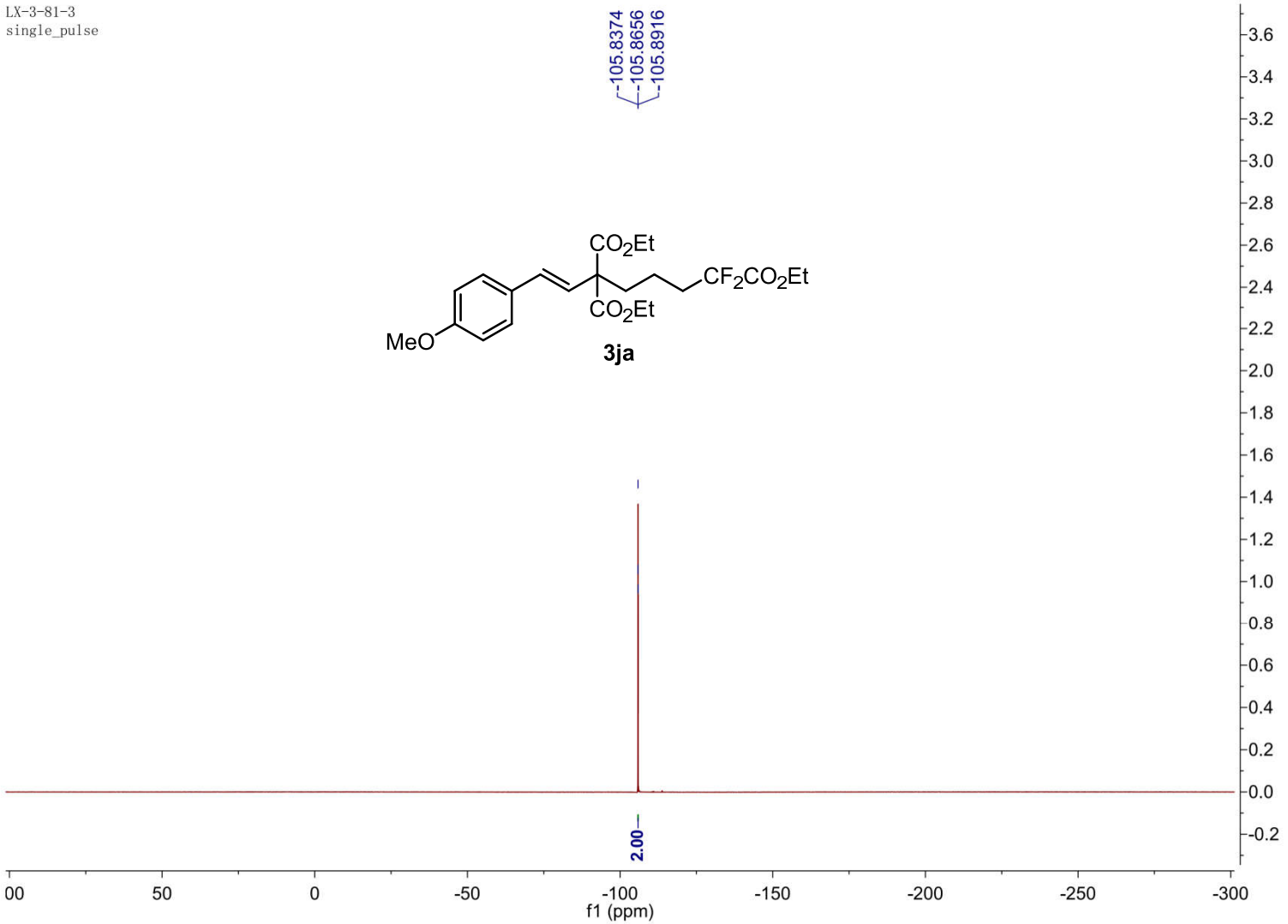

LX-3-82-4
single pulse decoupled gated NOE
170.0138
164.2539
164.0382
163.8207
134.7843
133.6341
130.3867
128.6947
127.7269
126.4321
117.5005
115.8423
114.1816
77.2110
76.9997
76.7882
62.7907
61.7590
59.2020
34.8455
34.5850
34.4310
34.2762
16.6296
13.9626
13.8512
CO2Et
CO2Et
CF2CO2Et
Cl
3ha
f1 (ppm)

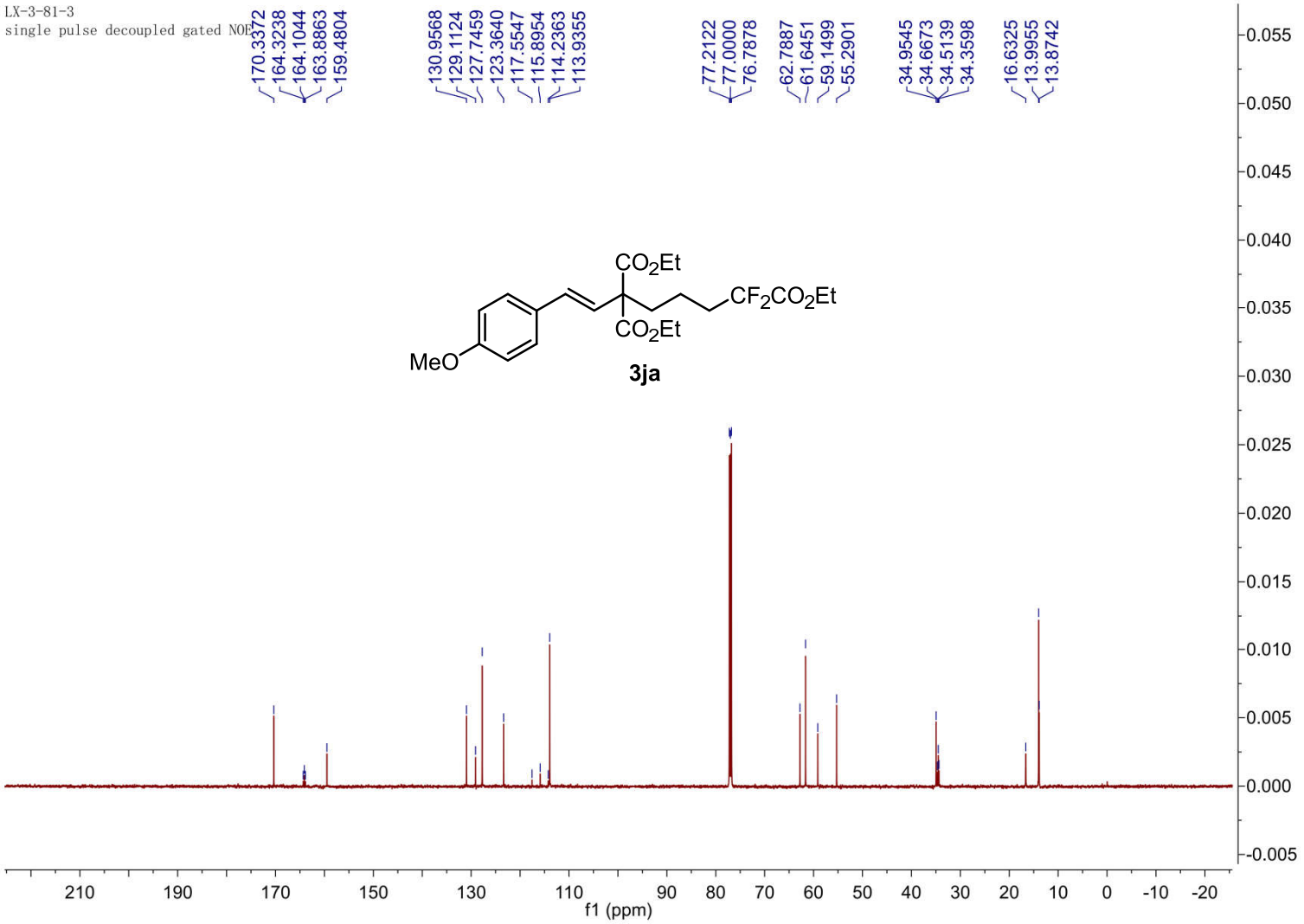

LX-3-80-2
single_puls
7.3098
7.2965
7.1390
7.1258
6.6815
6.6536
6.4506
6.4229
4.2893
4.2774
4.2657
4.2566
4.2449
4.2383
4.2263
4.2133
4.2073
4.2016
2.3364
2.2044
2.1904
2.1761
2.1229
2.1098
2.0953
2.0818
2.0681
2.0539
2.0404
1.4796
1.4659
1.4601
1.4524
1.4448
1.4383
1.4339
1.4249
1.3027
1.2911
1.2790
1.2681
1.2561
1.2441
CO2Et
CF2CO2Et
CO2Et
Me
3ia
2.13
2.29
1.00
0.05
1.01
2.19
4.08
3.27
2.18
2.25
2.16
3.15
6.11
f1 (ppm)

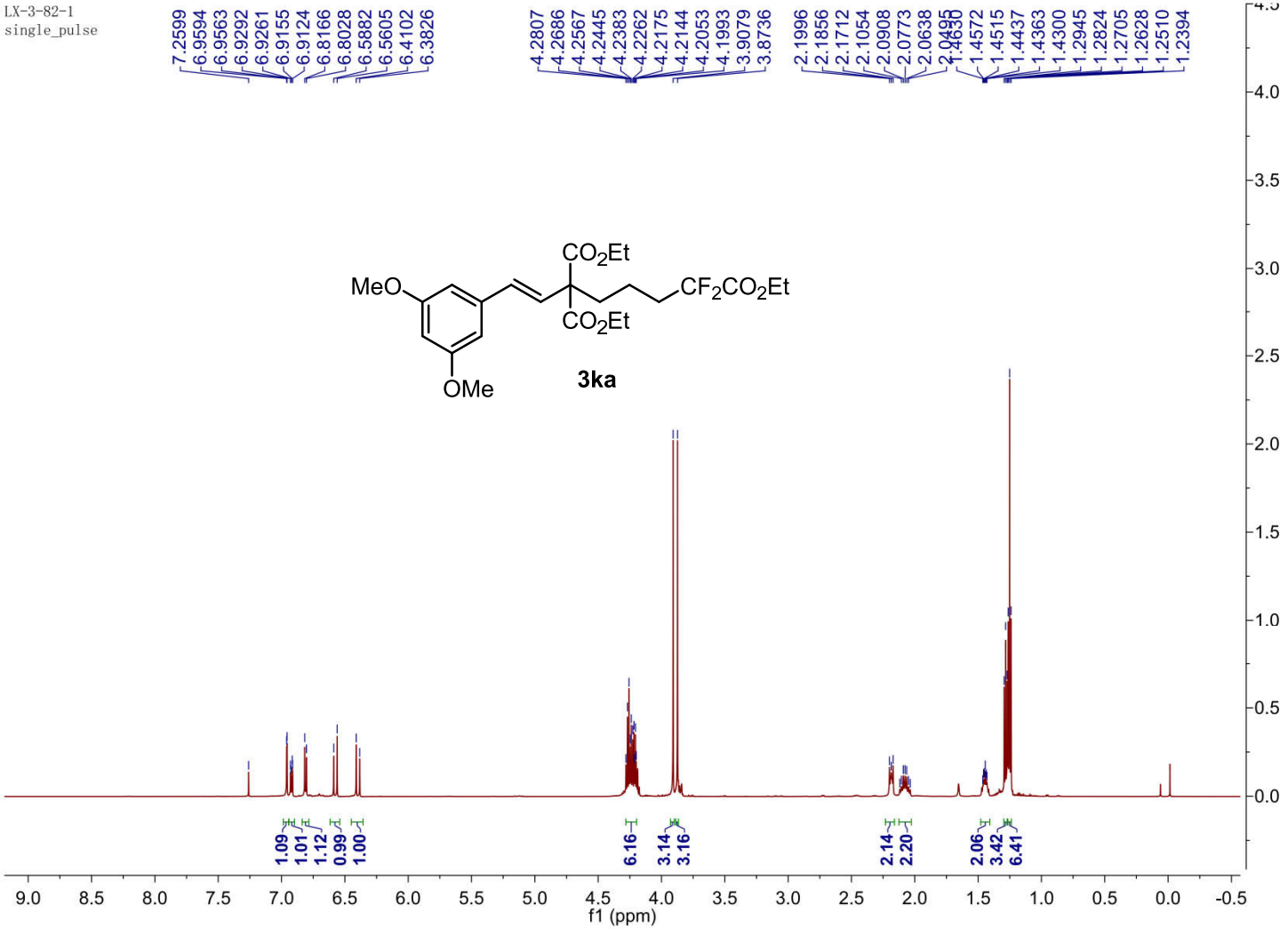

LX-3-80-2
single_pulse
-105.8377
-105.8684
-105.8989
CO2Et
CF2CO2Et
CO2Et
Me
3ia
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

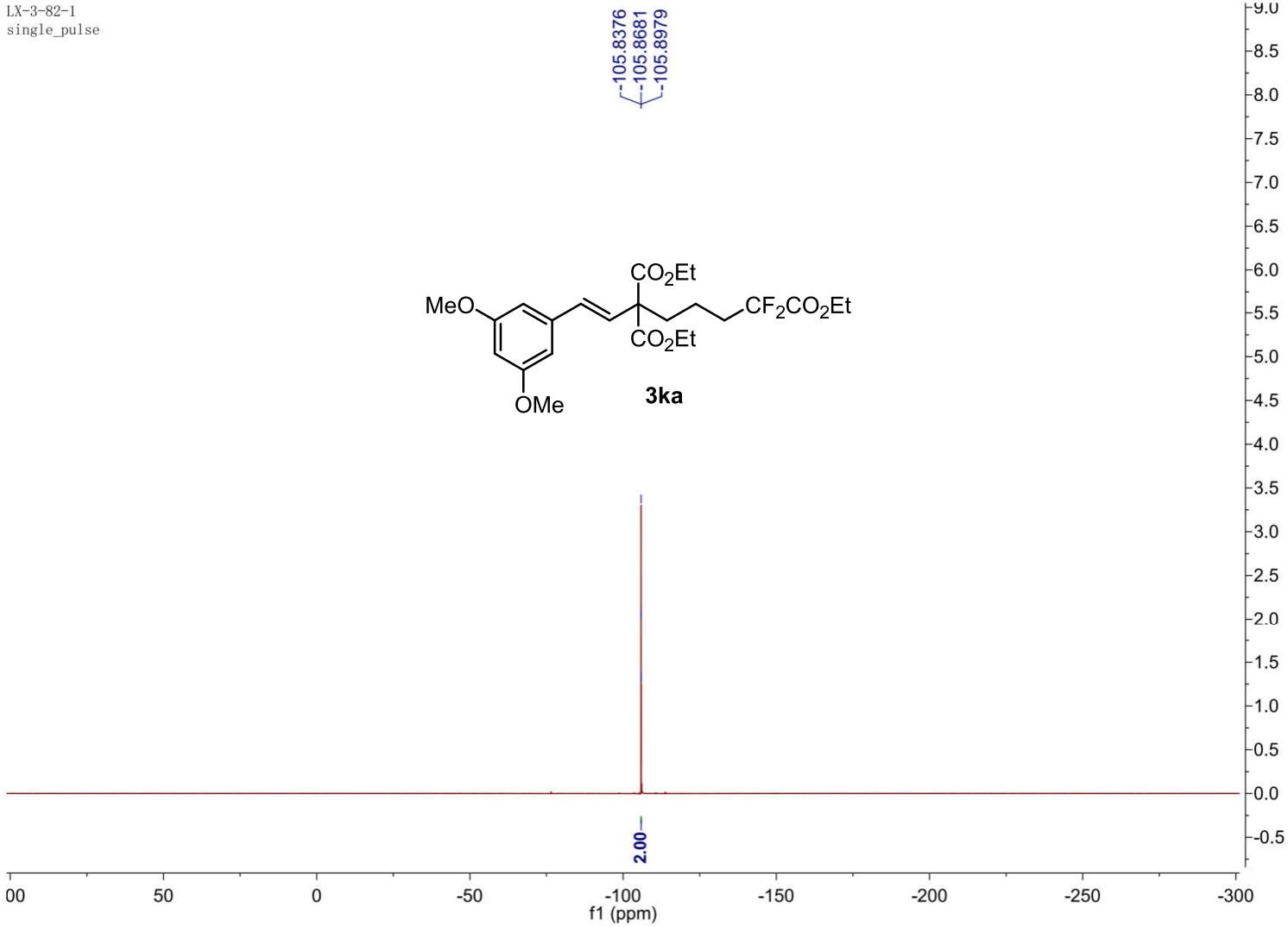

LX-3-80-2
single pulse decoupled gated NOE
170.2564
164.2995
164.0806
163.8651
137.8827
133.5358
131.3938
129.2282
126.4216
124.6246
117.5312
115.8726
114.2152
77.2109
76.9995
76.7880
62.7721
61.6434
59.1739
34.9483
34.6554
34.5011
34.3466
21.1627
16.6244
13.9742
13.8574
CO2Et
CF2CO2Et
CO2Et
Me
3ia
f1 (ppm)

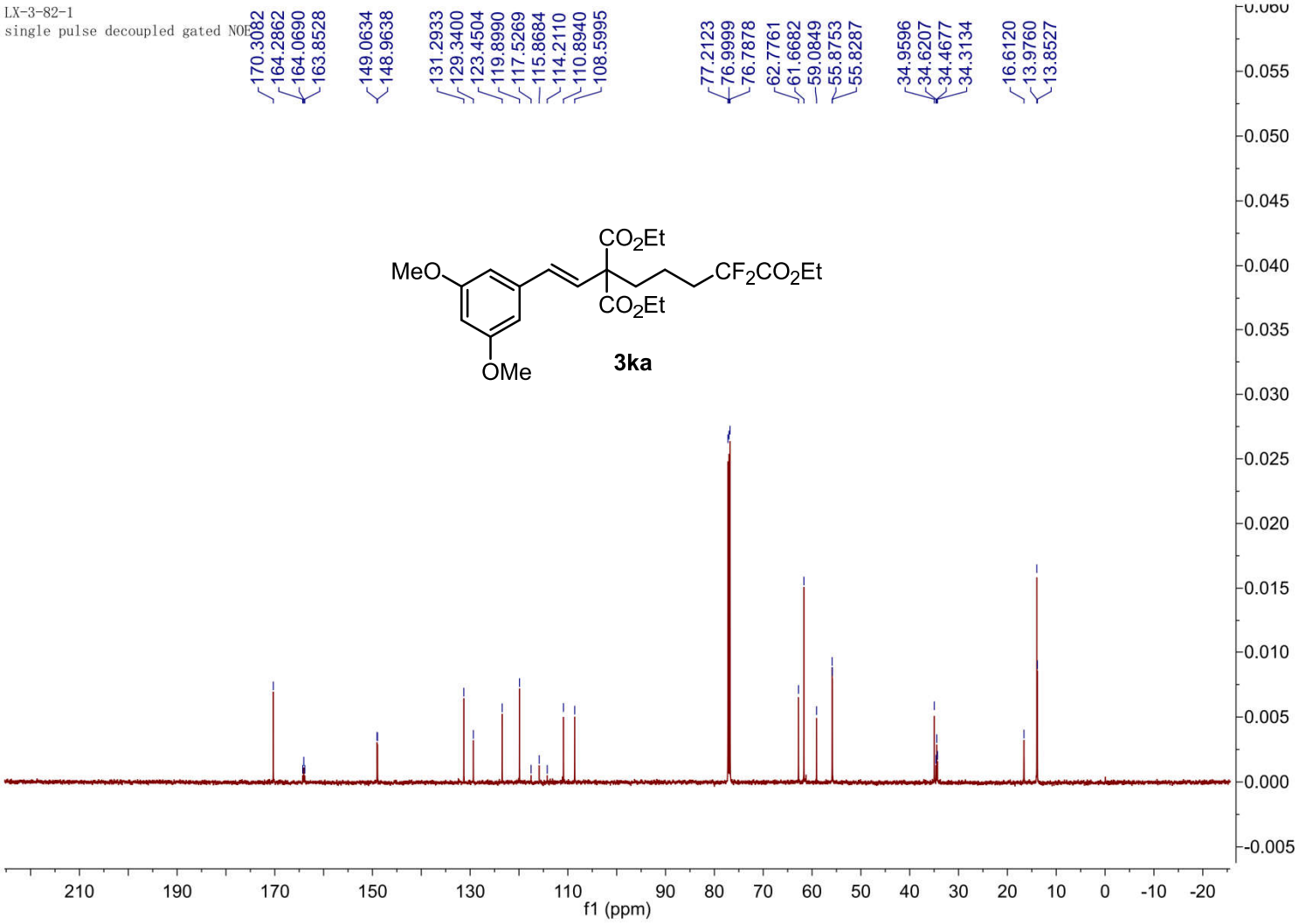

LX-3-81-3
single_pulse
7.3473
7.3327
6.8626
6.8482
6.5824
6.5547
6.4190
6.3913
4.2873
4.2752
4.2635
4.2521
4.2408
4.2349
4.2314
4.2233
4.2193
4.2109
4.2075
4.2016
4.1959
3.8060
2.1939
2.1798
2.1656
2.1193
2.1059
2.0916
2.0781
2.0644
2.0502
2.0369
1.6216
1.4733
1.4652
1.4595
1.4538
1.4459
1.4385
1.4320
1.4270
1.4186
1.3004
1.2888
1.2765
1.2648
1.2532
1.2409
CO2Et
CF2CO2Et
CO2Et
MeO
3ja
2.05
2.14
1.00
0.99
2.29
4.02
3.13
2.13
2.11
2.10
3.11
6.16
f1 (ppm)

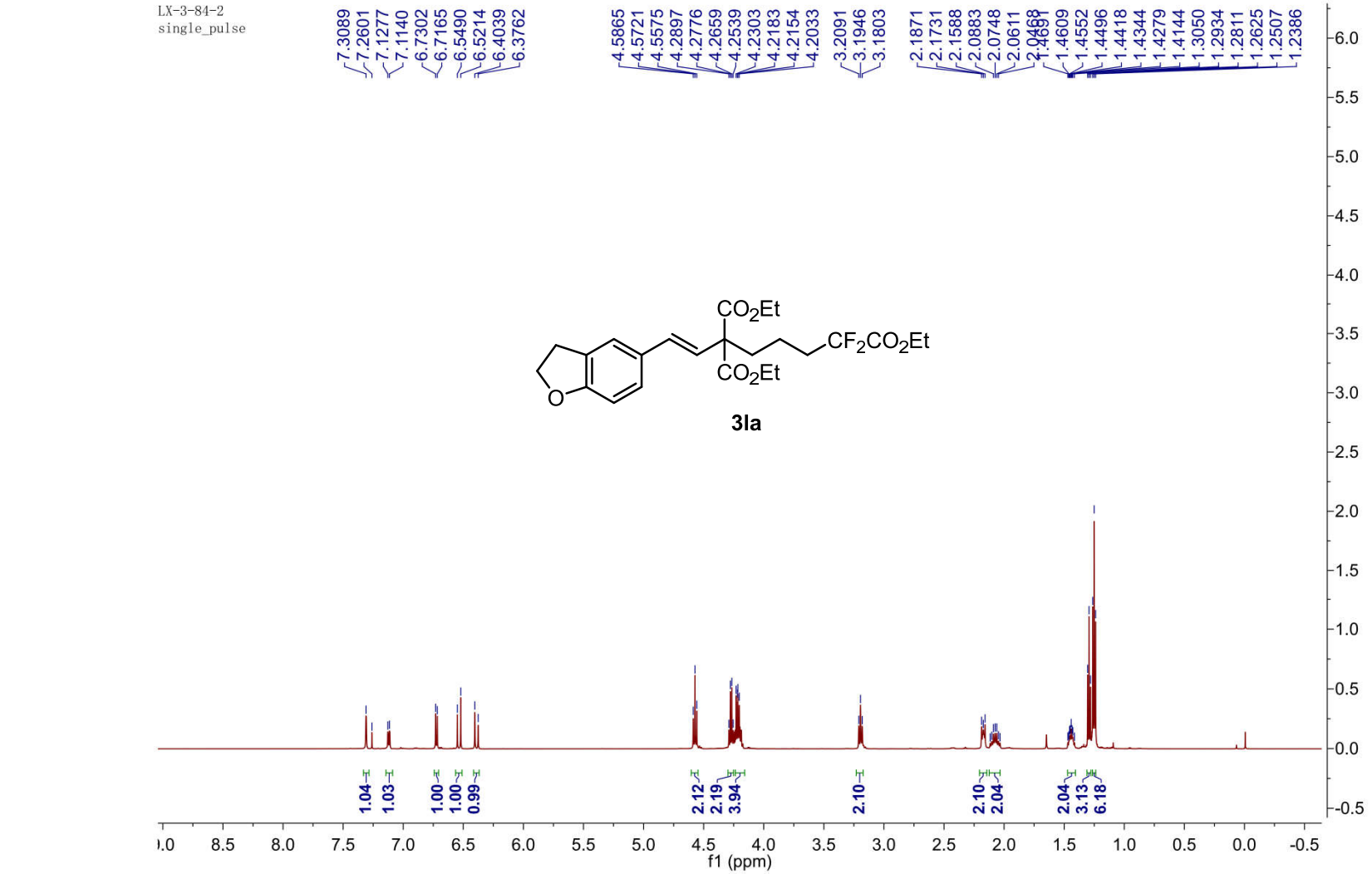

LX-3-81-3
single_pulse
-105.8374
-105.8656
-105.8916
CO2Et
CF2CO2Et
CO2Et
MeO
3ja
2.00
f1 (ppm)

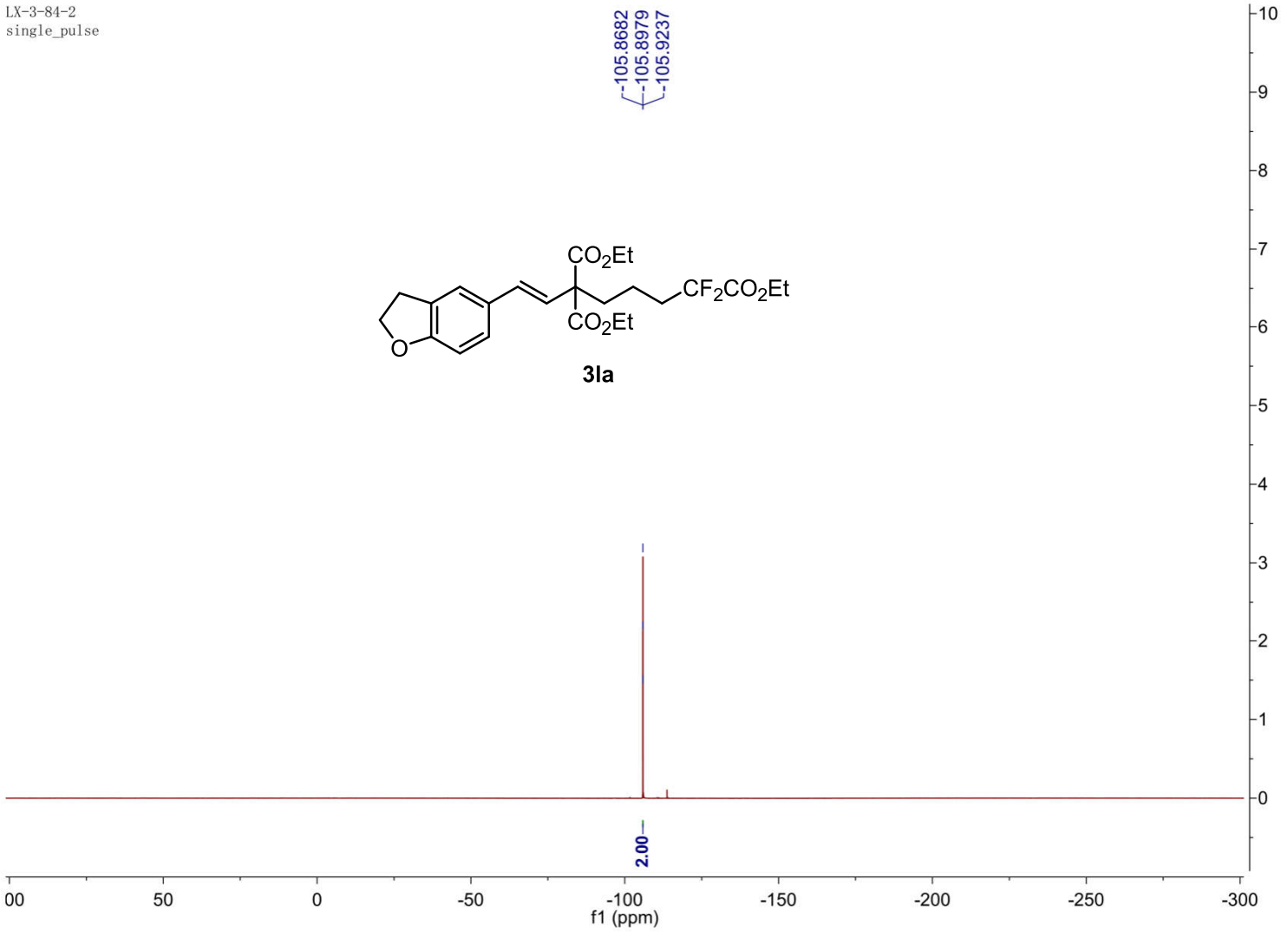

LX-3-81-3
single pulse decoupled gated NOE
170.3372
164.3238
164.1044
163.8863
159.4804
130.9568
129.1124
127.7459
123.3640
117.5547
115.8954
114.2363
113.9355
77.2122
77.0000
76.7878
62.7887
61.6451
59.1499
55.2901
34.9545
34.6673
34.5139
34.3598
16.6325
13.9955
13.8742
CO2Et
CF2CO2Et
CO2Et
MeO
3ja
f1 (ppm)

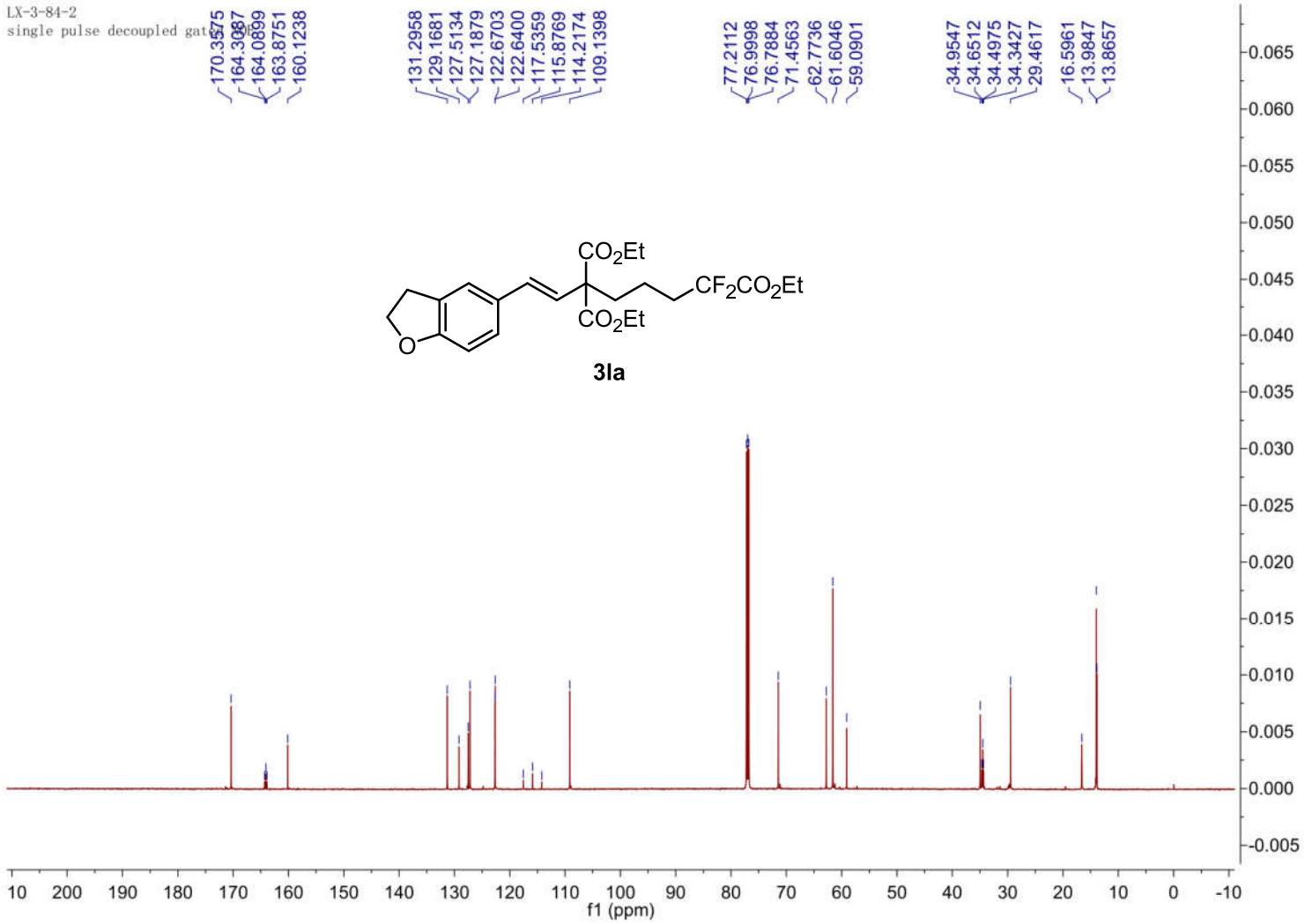

LX-3-82-1
single_pulse
7.2599
6.9594
6.9563
6.9292
6.9261
6.9155
6.9124
6.8166
6.8028
6.5882
6.5605
6.4102
6.3826
4.2807
4.2686
4.2567
4.2445
4.2383
4.2262
4.2175
4.2144
4.2053
4.1993
3.9079
3.8736
2.1996
2.1856
2.1712
2.1054
2.0908
2.0773
2.0638
1.4572
1.4515
1.4437
1.4363
1.4300
1.2945
1.2824
1.2705
1.2628
1.2510
1.2394
MeO
CO2Et
CO2Et
CF2CO2Et
OMe
3ka
1.09
1.01
1.12
0.99
1.00
6.16
3.14
3.16
2.14
2.20
2.06
3.42
6.41
f1 (ppm)

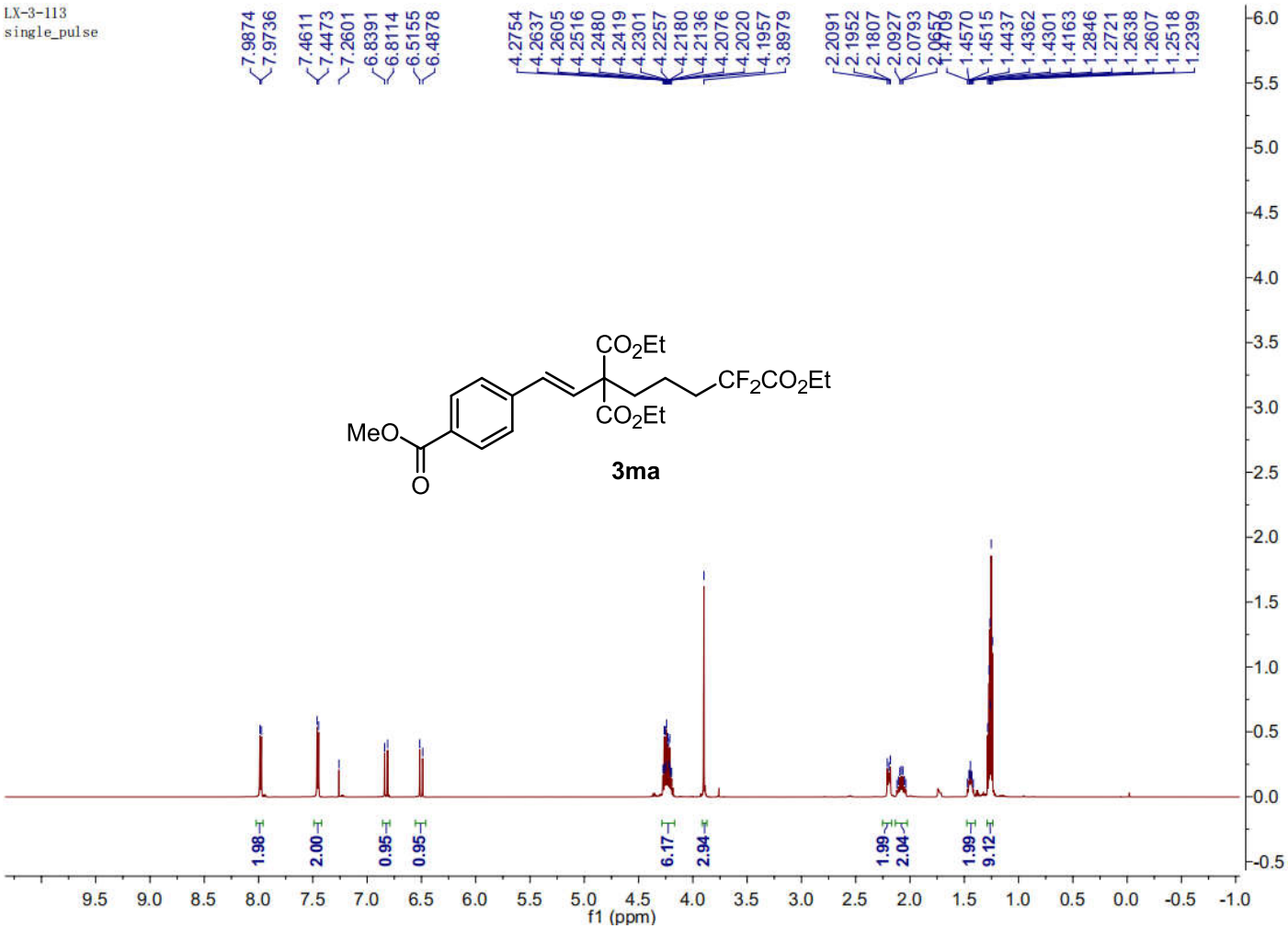

LX-3-82-1
single_pulse
-105.8376
-105.8681
-105.8979
MeO
CO2Et
CO2Et
CF2CO2Et
OMe
3ka
2.00
f1 (ppm)

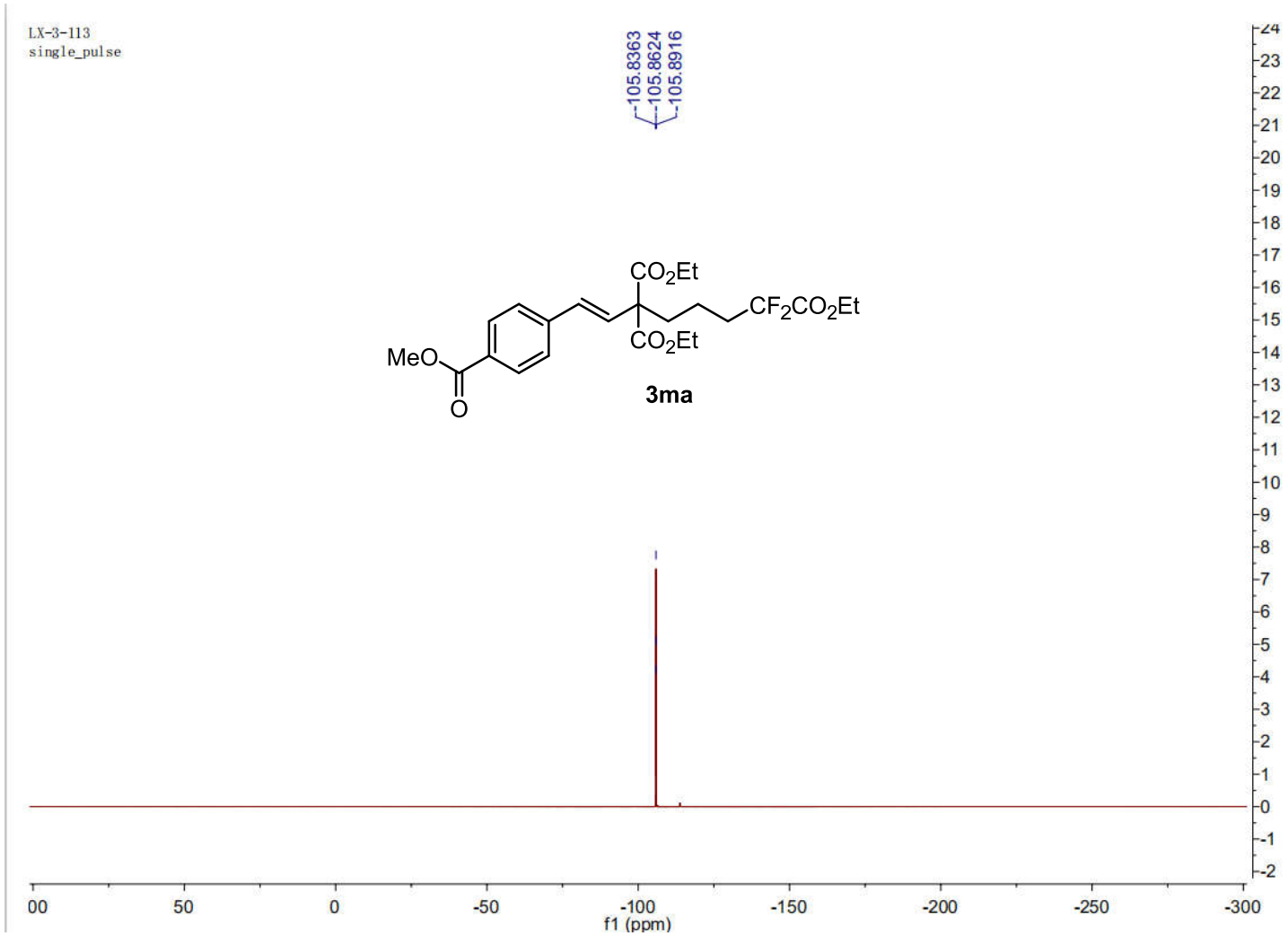

LX-3-82-1
single pulse decoupled gated NOE
170.3082
164.2862
164.0690
163.8528
149.0634
148.9638
131.2933
129.3400
123.4504
119.8990
117.5269
115.8684
114.2110
110.8940
108.5995
77.2123
76.9999
76.7878
62.7761
61.6682
59.0849
55.8753
55.8287
34.9596
34.6207
34.4677
34.3134
16.6120
13.9760
13.8527
MeO
CO2Et
CO2Et
CF2CO2Et
OMe
3ka
f1 (ppm)

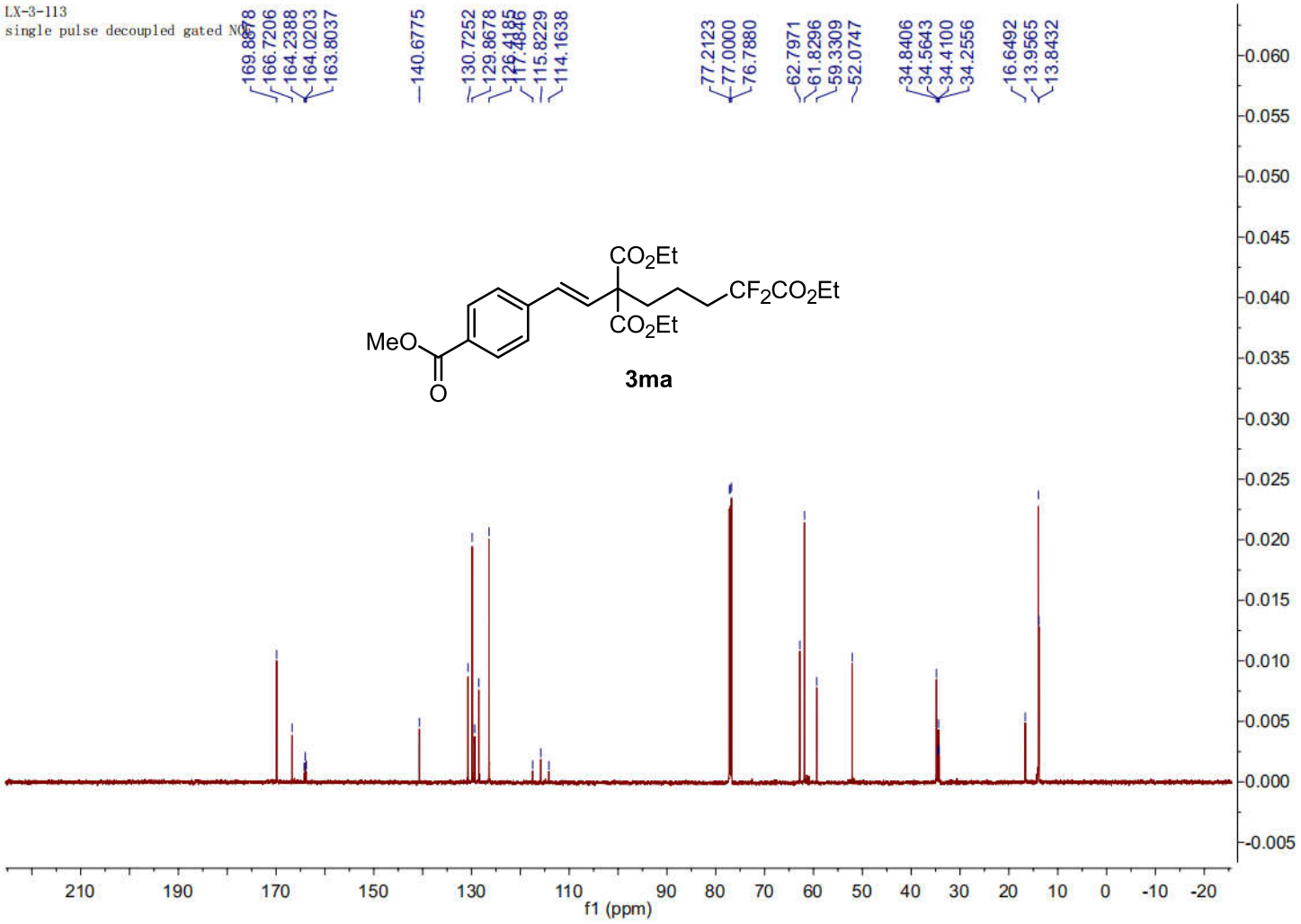

LX-3-84-2
single_pulse
7.3089
7.2601
7.1277
7.1140
6.7302
6.7165
6.5490
6.5214
6.4039
6.3762
4.5865
4.5721
4.5575
4.2897
4.2776
4.2659
4.2539
4.2303
4.2183
4.2154
4.2033
3.2091
3.1946
3.1803
2.1871
2.1731
2.1588
2.0883
2.0748
2.0611
1.4609
1.4552
1.4496
1.4418
1.4344
1.4279
1.4144
1.3050
1.2934
1.2811
1.2625
1.2507
1.2386
CO2Et
CF2CO2Et
CO2Et
O
3Ia
1.04
1.03
1.00
1.00
0.99
2.12
2.19
3.94
2.10
2.10
2.04
2.04
3.13
6.18
f1 (ppm)

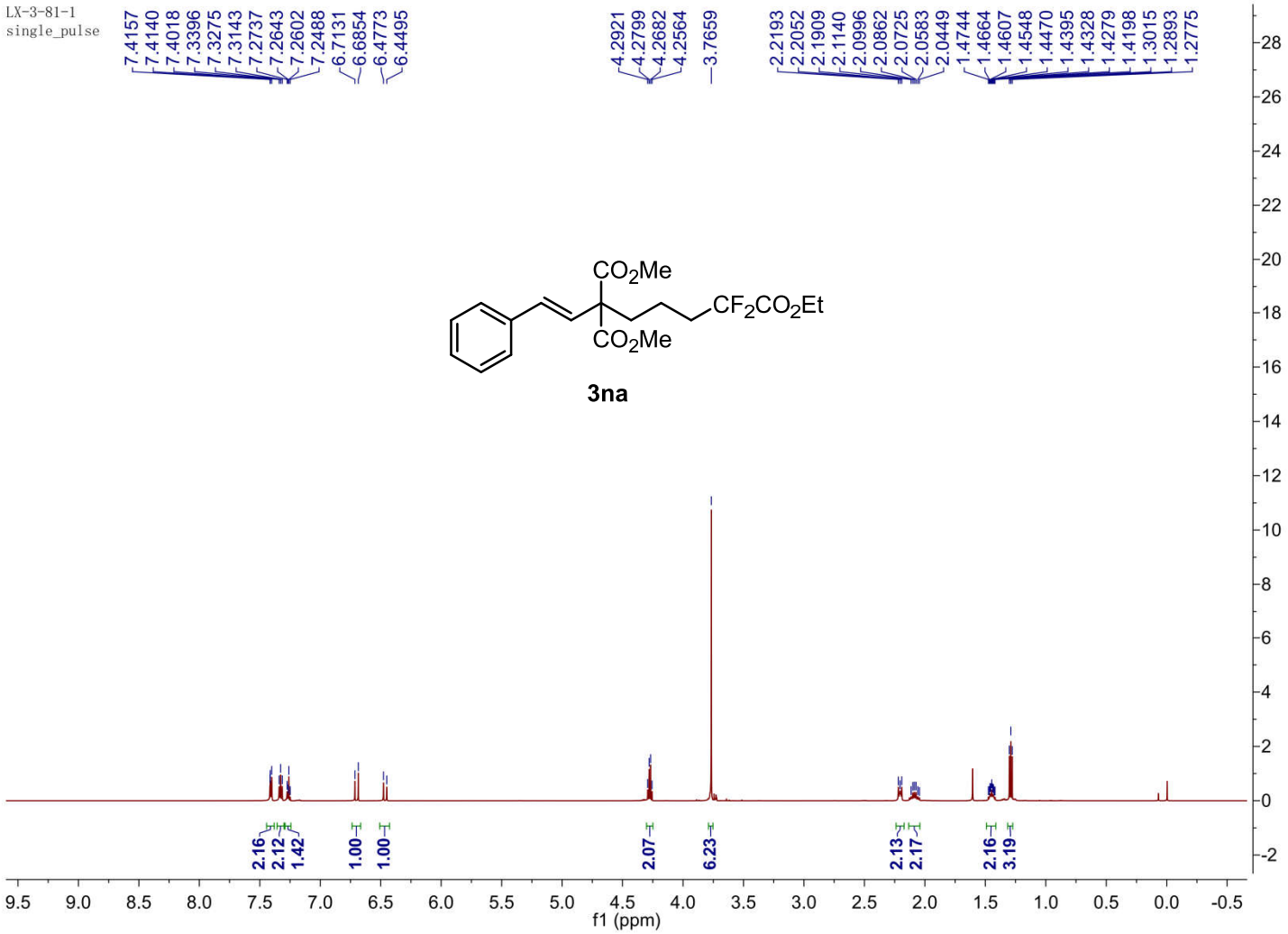

LX-3-84-2
single_pulse
-105.8682
-105.8979
-105.9237
CO2Et
CF2CO2Et
CO2Et
O
3Ia
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
10
9
8
7
6
5
4
3
2
1
0

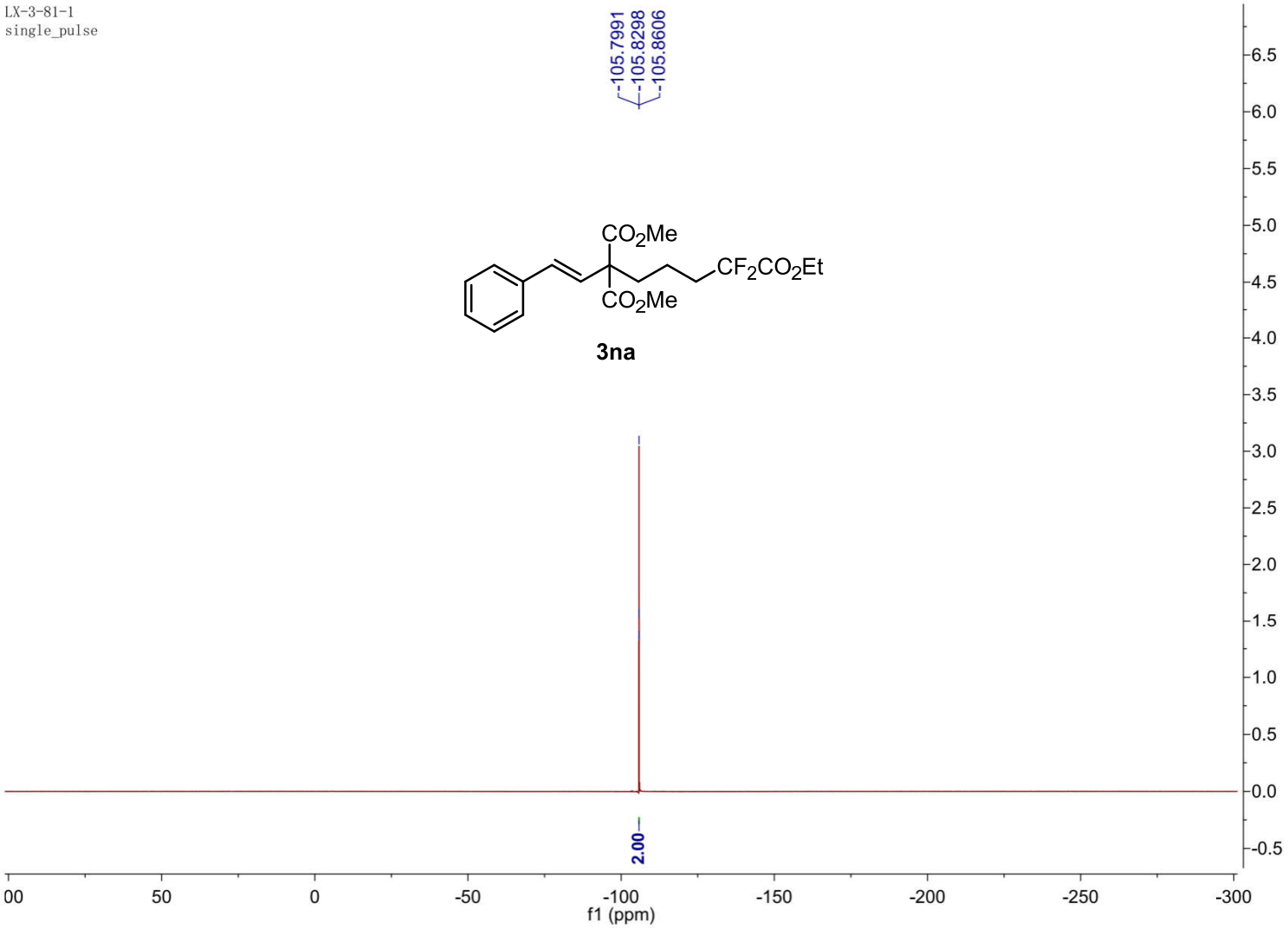

LX-3-84-2
single pulse decoupled gated DEPT
170.3375
164.3087
164.0899
163.8751
160.1238
131.2958
129.1681
127.5134
127.1879
122.6703
122.6400
117.5359
115.8769
114.2174
109.1398
77.2112
76.9998
76.7884
71.4563
62.7736
61.6046
59.0901
34.9547
34.6512
34.4975
34.3427
29.4617
16.5961
13.9847
13.8657
CO2Et
CF2CO2Et
CO2Et
O
3la
f1 (ppm)

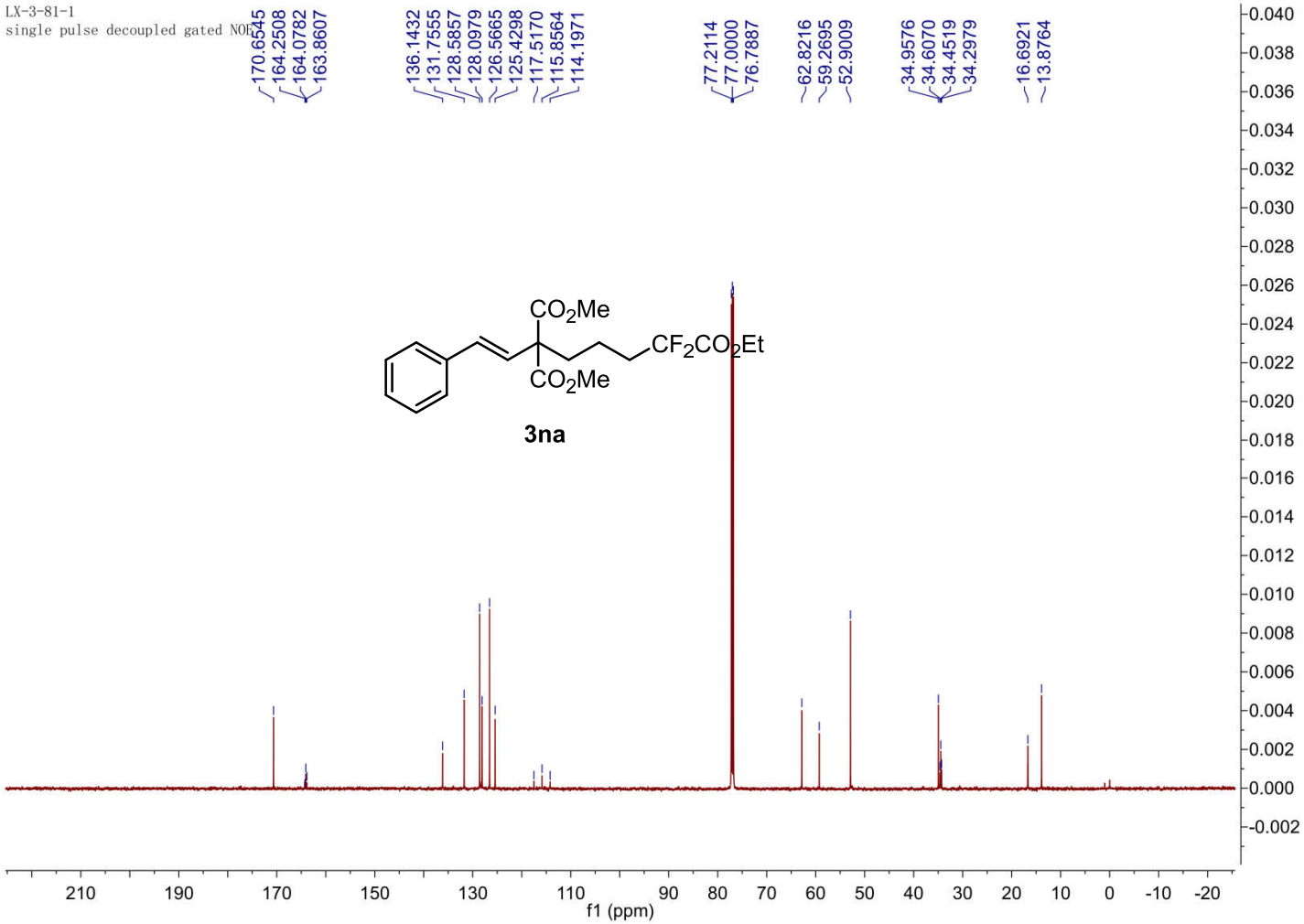

LX-3-113
single_pulse
7.9874
7.9736
7.4611
7.4473
7.2601
6.8391
6.8114
6.5155
6.4878
4.2754
4.2637
4.2605
4.2516
4.2480
4.2419
4.2301
4.2257
4.2180
4.2136
4.2076
4.2020
4.1957
3.8979
2.2091
2.1952
2.1807
2.0927
2.0793
1.4570
1.4515
1.4437
1.4362
1.4301
1.4163
1.2846
1.2721
1.2638
1.2607
1.2518
1.2399
CO2Et
CF2CO2Et
CO2Et
MeO
O
3ma
1.98
2.00
0.95
0.95
6.17
2.94
1.99
2.04
1.99
9.12
f1 (ppm)

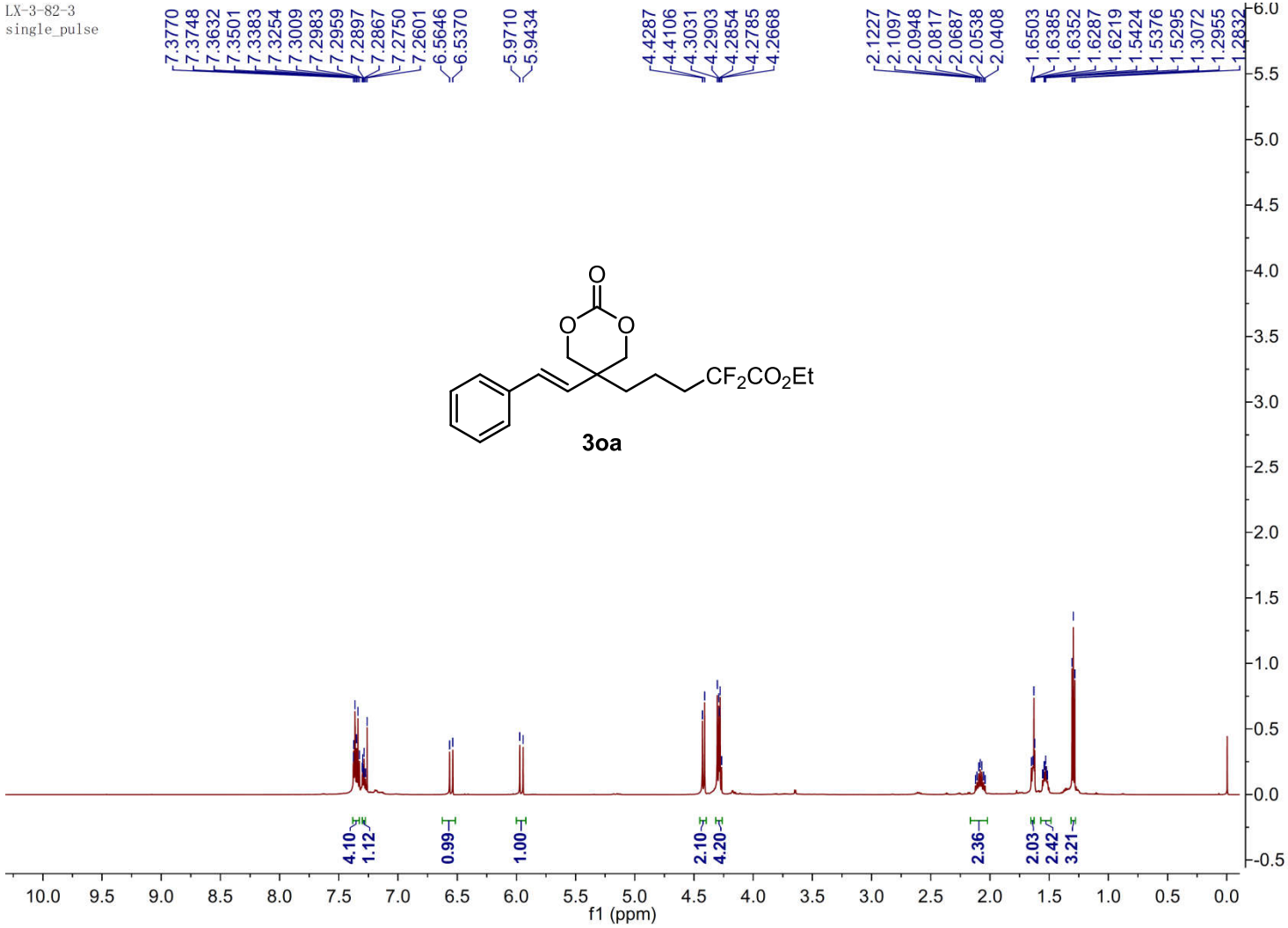

LX-3-113
single_pulse
-105.8363
-105.8624
-105.8916
CO2Et
CF2CO2Et
CO2Et
MeO
O
3ma
f1 (ppm)

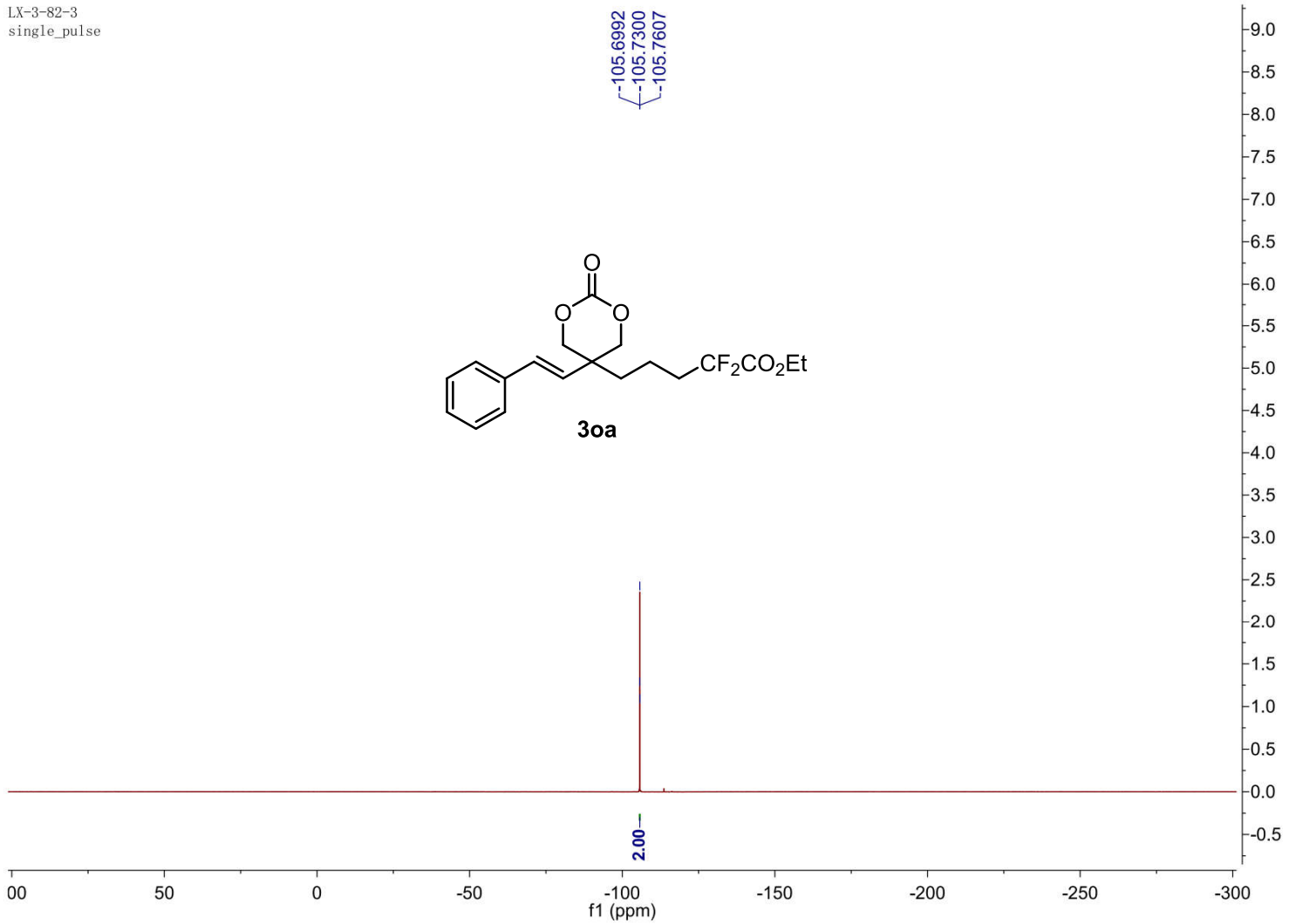

LX-3-113
single pulse decoupled gated NOE
169.8678
166.7206
164.2388
164.0203
163.8037
140.6775
130.7252
129.8678
126.4185
117.4846
115.8229
114.1638
77.2123
77.0000
76.7880
62.7971
61.8296
59.3309
52.0747
34.8406
34.5643
34.4100
34.2556
16.6492
13.9565
13.8432
CO2Et
CF2CO2Et
CO2Et
MeO
O
3ma
f1 (ppm)

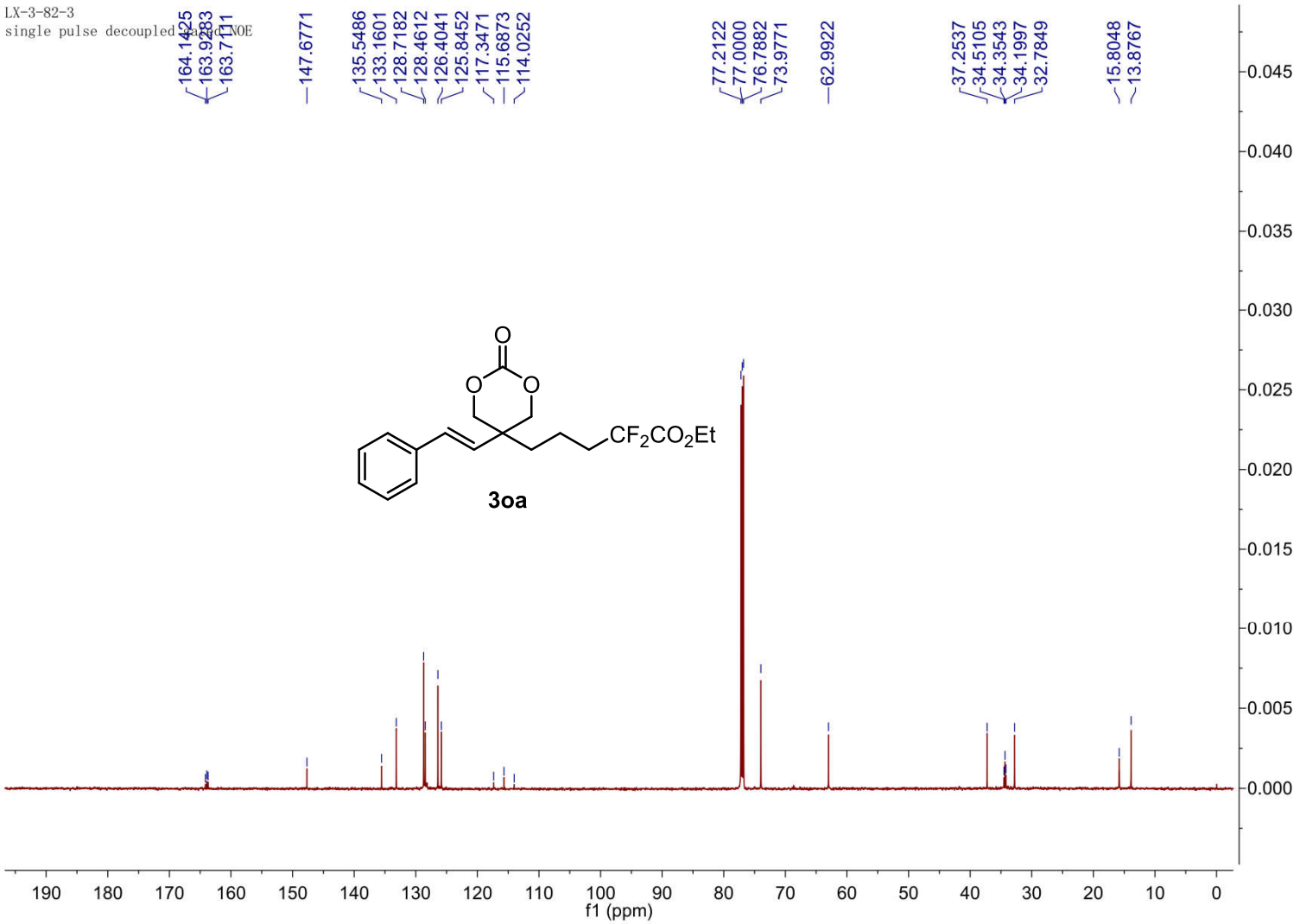

LX-3-81-1
single_pulse
7.4157
7.4140
7.4018
7.3396
7.3275
7.3143
7.2737
7.2643
7.2602
7.2488
6.7131
6.6854
6.4773
6.4495
4.2921
4.2799
4.2682
4.2564
3.7659
2.2193
2.2052
2.1909
2.1140
2.0996
2.0862
2.0725
2.0583
2.0449
1.4744
1.4664
1.4607
1.4548
1.4470
1.4395
1.4328
1.4279
1.4198
1.3015
1.2893
1.2775
CO2Me
CF2CO2Et
CO2Me
3na
2.16
2.12
1.42
1.00
1.00
2.07
6.23
2.13
2.17
2.16
3.19
f1 (ppm)

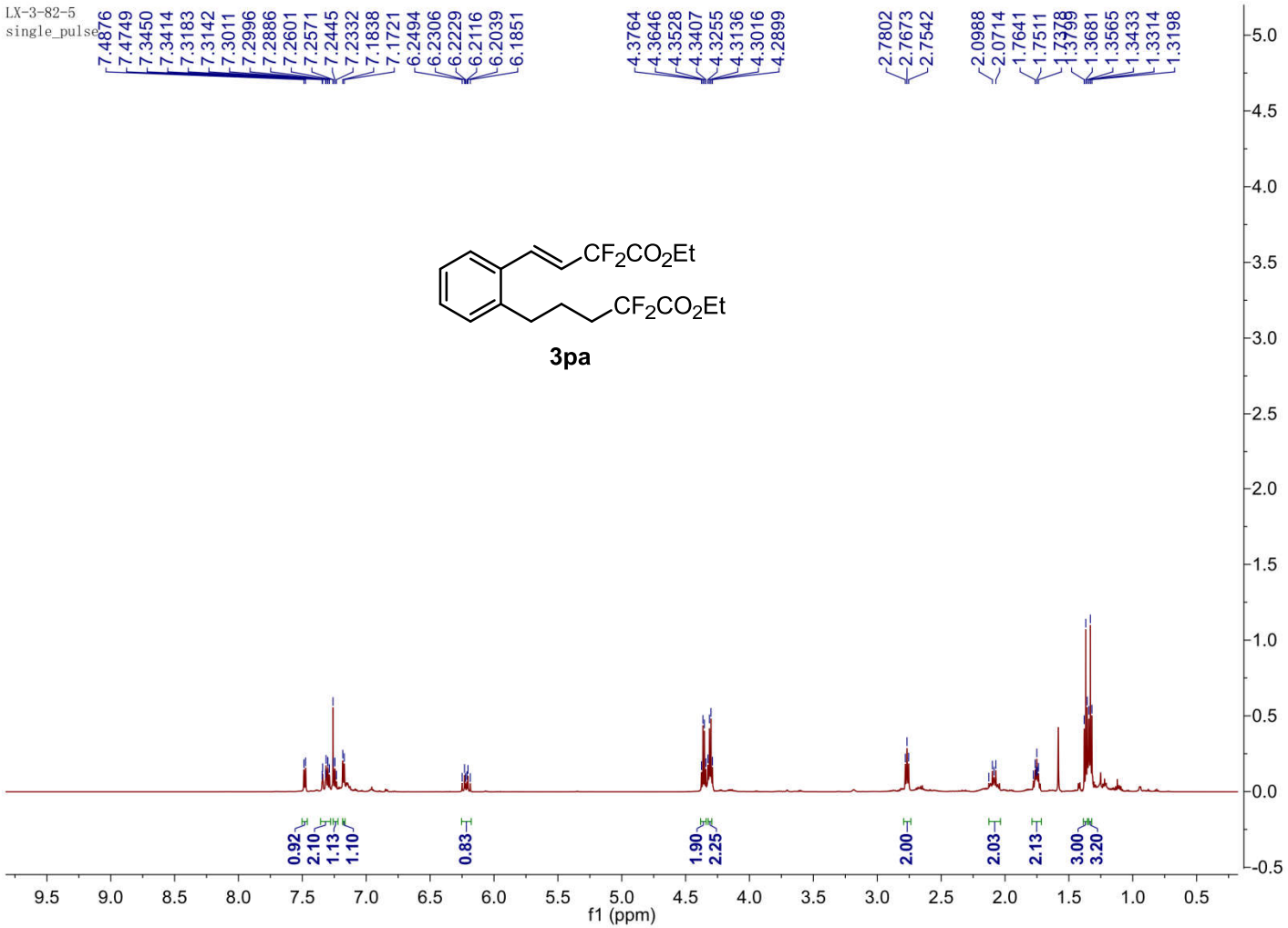

LX-3-81-1
single_pulse
-105.7991
-105.8298
-105.8606
CO2Me
CF2CO2Et
CO2Me
3na
2.00
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

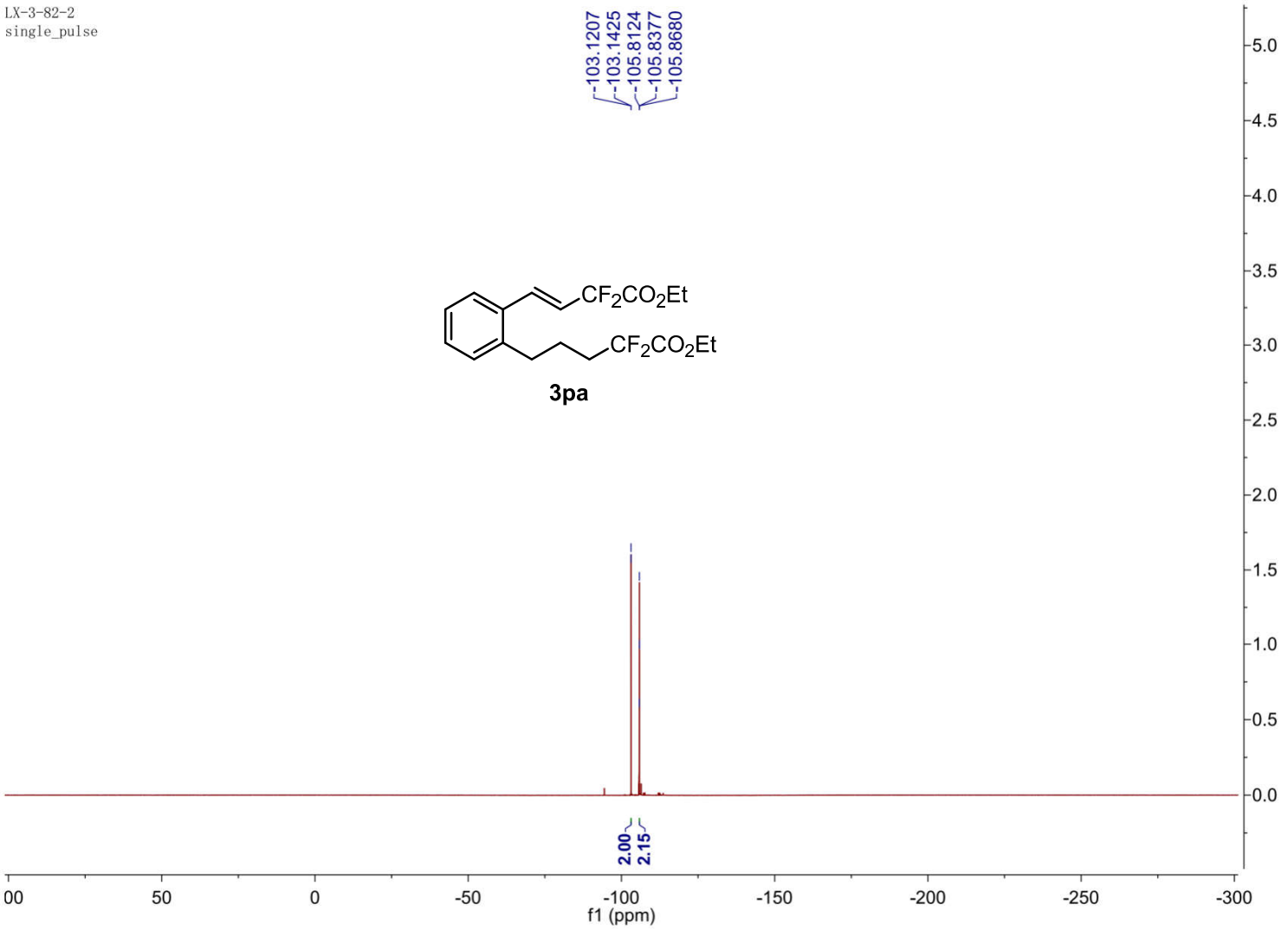

LX-3-81-1
single pulse decoupled gated NOE
170.6545
164.2508
164.0782
163.8607
136.1432
131.7555
128.5857
128.0979
126.5665
125.4298
117.5170
115.8564
114.1971
77.2114
77.0000
76.7887
62.8216
59.2695
52.9009
34.9576
34.6070
34.4519
34.2979
16.6921
13.8764
CO2Me
CF2CO2Et
CO2Me
3na
f1 (ppm)

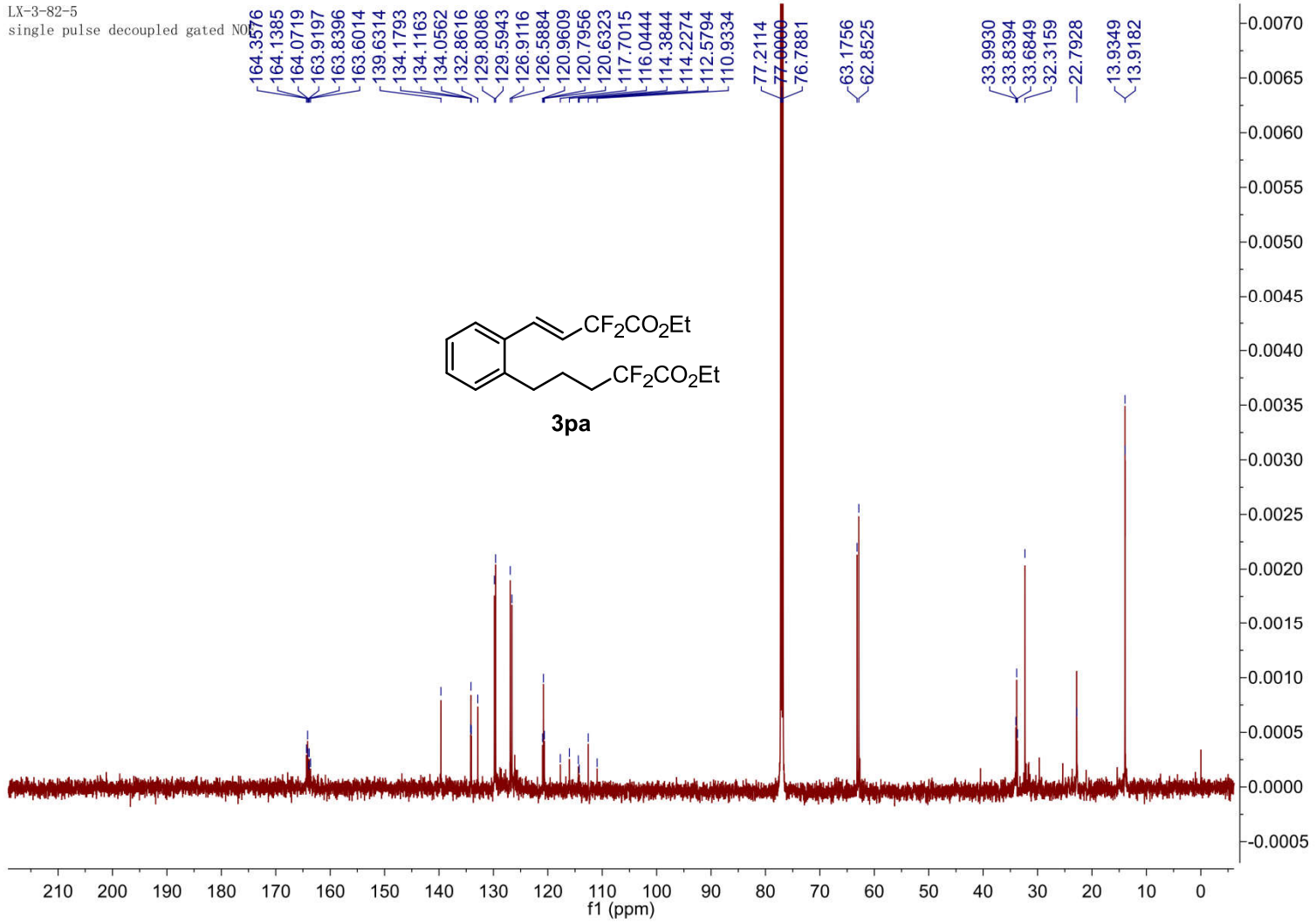

LX-3-82-3
single_pulse
7.3770
7.3748
7.3632
7.3501
7.3383
7.3254
7.3009
7.2983
7.2959
7.2897
7.2867
7.2750
7.2601
6.5646
6.5370
5.9710
5.9434
4.4287
4.4106
4.3031
4.2903
4.2854
4.2785
4.2668
2.1227
2.1097
2.0948
2.0817
2.0687
2.0538
2.0408
1.6503
1.6385
1.6352
1.6287
1.6219
1.5424
1.5376
1.5295
1.3072
1.2955
1.2832
O
O
O
CF2CO2Et
3oa
4.10
1.12
0.99
1.00
2.10
4.20
2.36
2.03
2.42
3.21
f1 (ppm)

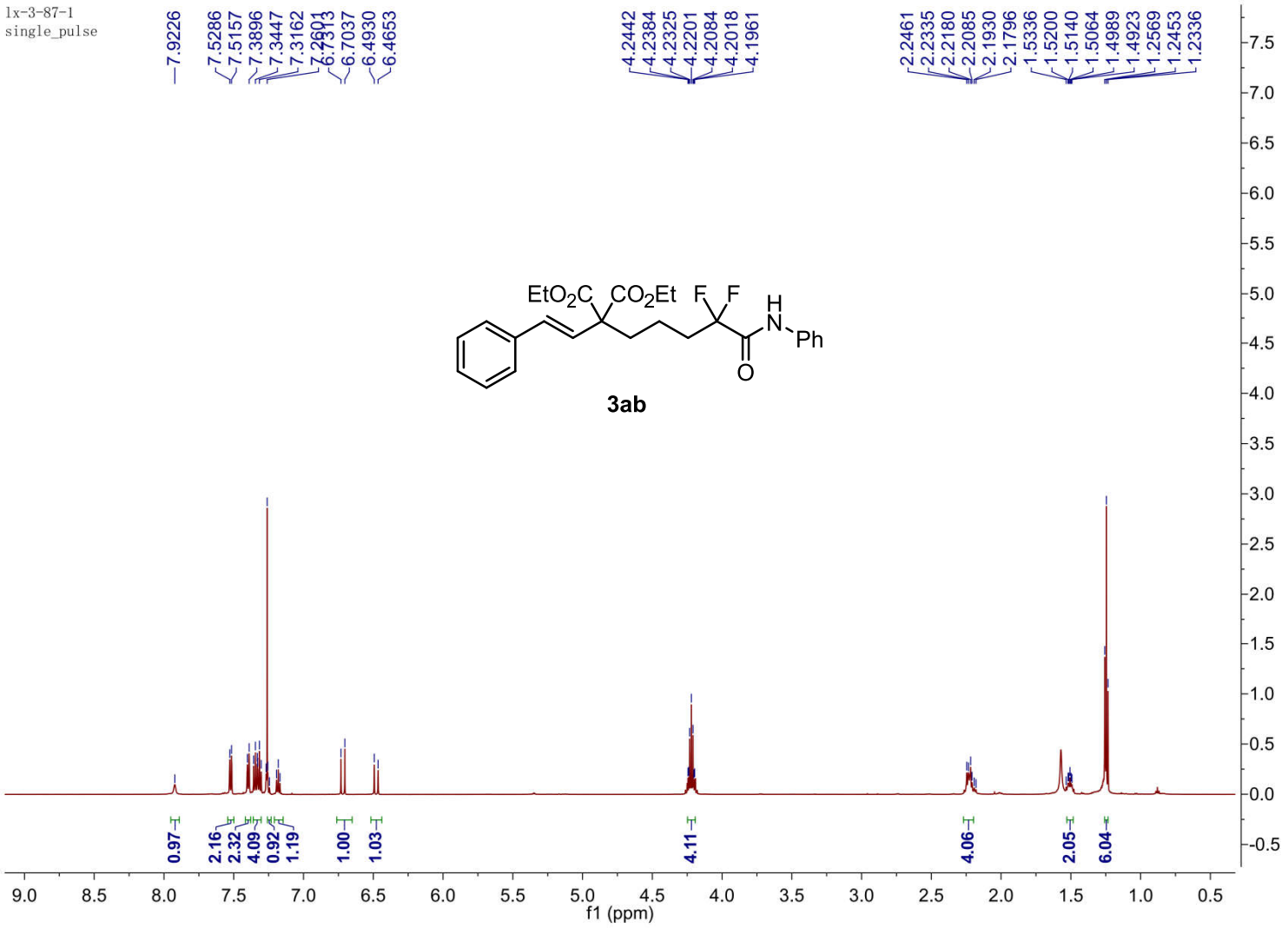

LX-3-82-3
single_pulse
-105.6992
-105.7300
-105.7607
O
O
O
CF2CO2Et
3oa
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

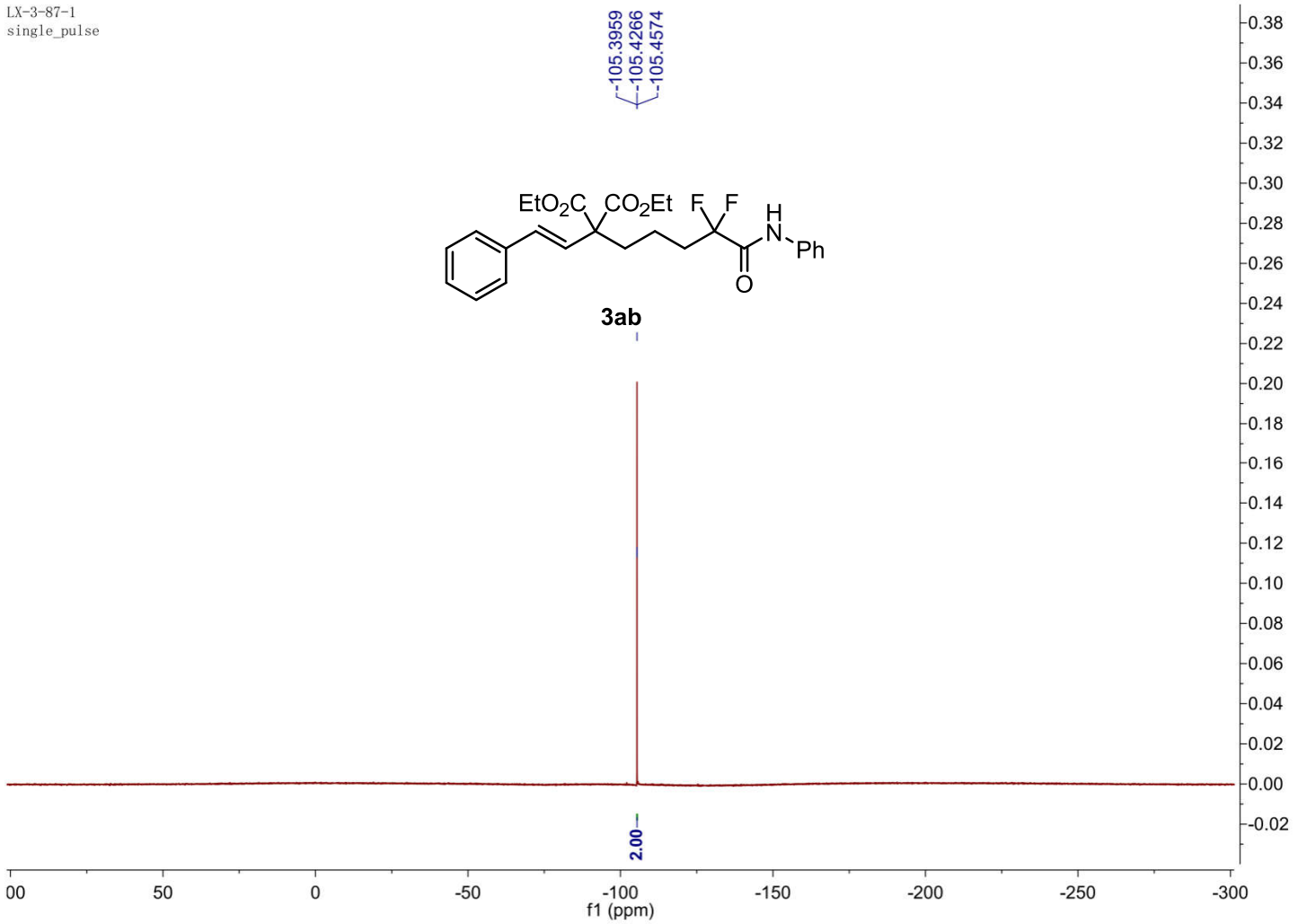

LX-3-82-3
single pulse decoupled gated NOE
164.1425
163.9263
163.7711
147.6771
135.5486
133.1601
128.7182
128.4612
126.4041
125.8452
117.3471
115.6873
114.0252
77.2122
77.0000
76.7882
73.9771
62.9922
37.2537
34.5105
34.3543
34.1997
32.7849
15.8048
13.8767
O
O
O
O
CF2CO2Et
3oa
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

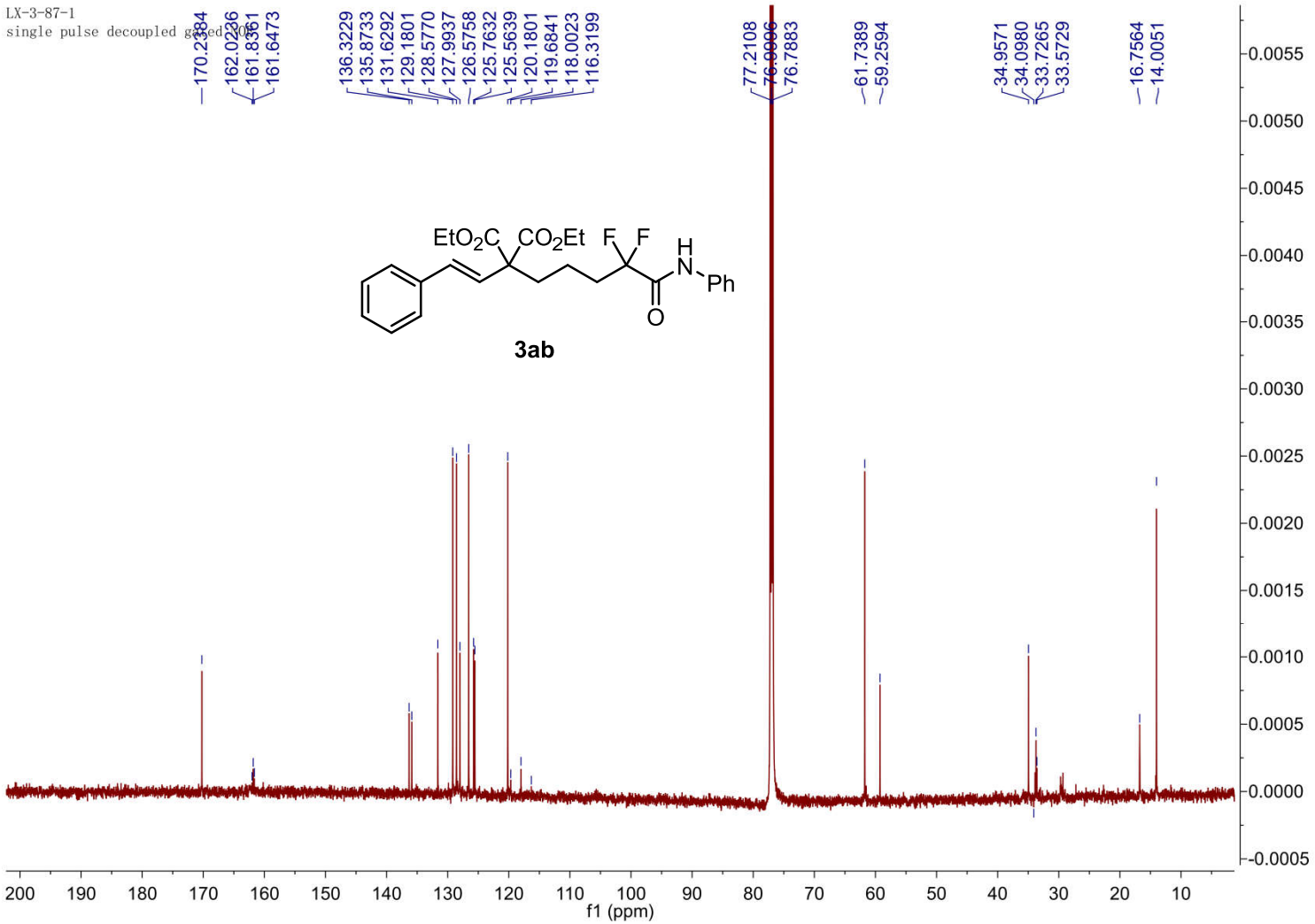

LX-3-82-5
single_pulse
7.4876
7.4749
7.3450
7.3414
7.3183
7.3142
7.3011
7.2996
7.2886
7.2601
7.2571
7.2445
7.2332
7.1838
7.1721
6.2494
6.2306
6.2229
6.2116
6.2039
6.1851
4.3764
4.3646
4.3528
4.3407
4.3255
4.3136
4.3016
4.2899
2.7802
2.7673
2.7542
2.0988
2.0714
1.7641
1.7511
1.3799
1.3681
1.3565
1.3433
1.3314
1.3198
CF2CO2Et
CF2CO2Et
3pa
0.92
2.10
1.13
1.10
0.83
1.90
2.25
2.00
2.03
2.13
3.00
3.20
f1 (ppm)

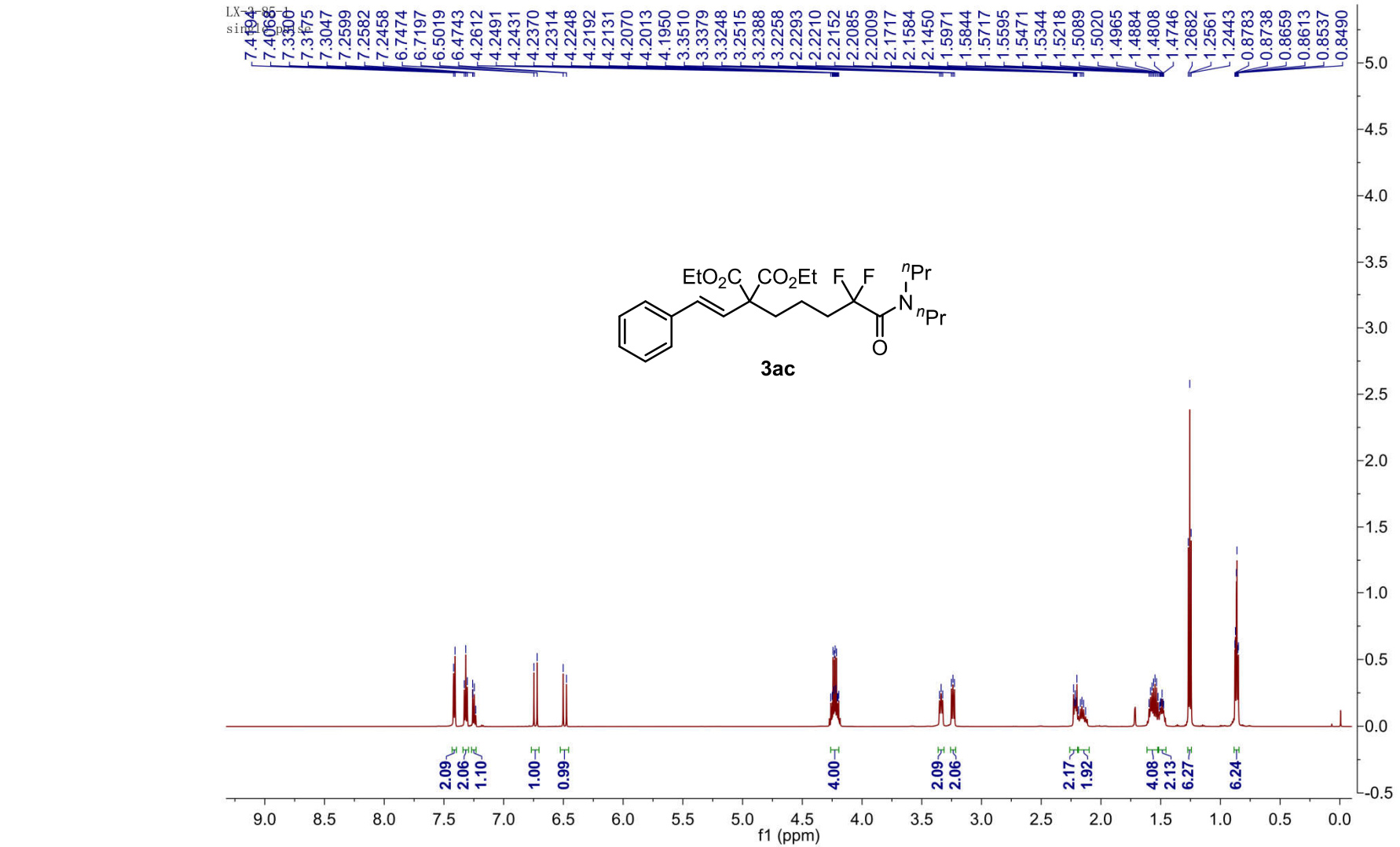

LX-3-82-2
single_pulse
-103.1207
-103.1425
-105.8124
-105.8377
-105.8680
CF2CO2Et
CF2CO2Et
3pa
2.00
2.15
f1 (ppm)

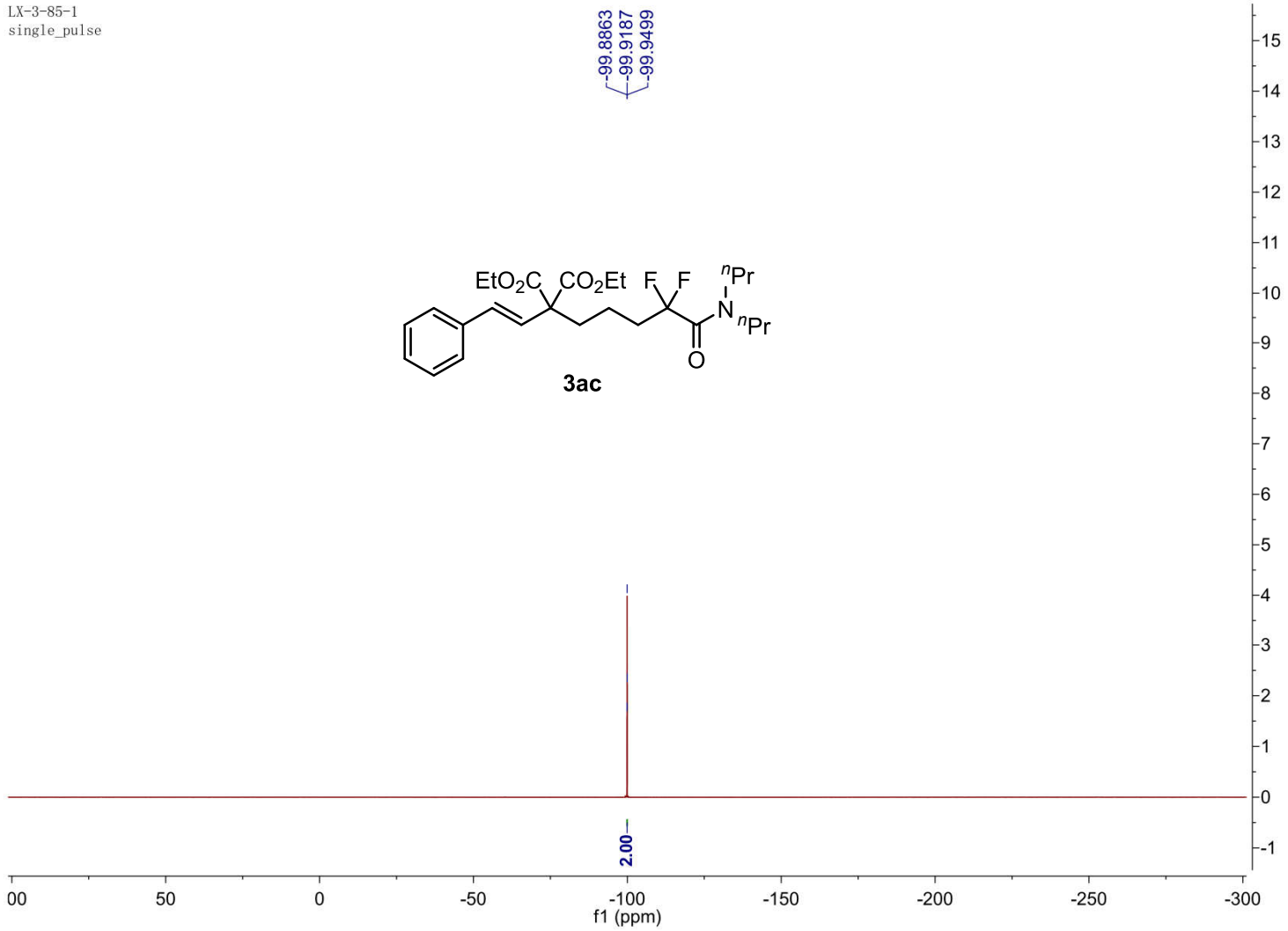

LX-3-82-5
single pulse decoupled gated NOE
164.3576
164.1385
164.0719
163.9197
163.8396
163.6014
139.6314
134.1793
134.1163
134.0562
132.8616
129.8086
129.5943
126.9116
126.5884
120.9609
120.7956
120.6323
117.7015
116.0444
114.3844
114.2274
112.5794
110.9334
77.2114
77.0000
76.7881
63.1756
62.8525
33.9930
33.8394
33.6849
32.3159
22.7928
13.9349
13.9182
CF2CO2Et
CF2CO2Et
3pa
f1 (ppm)

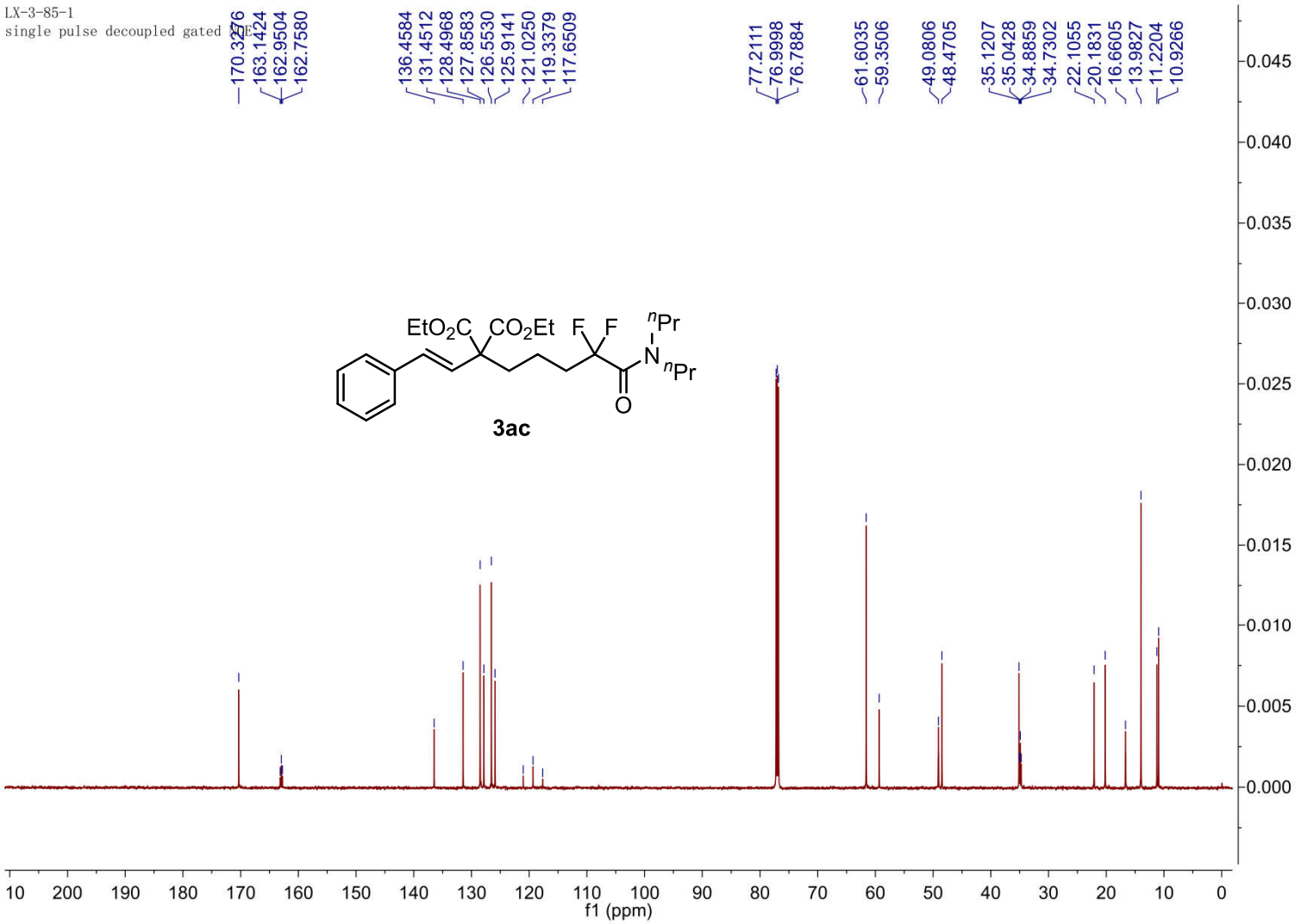

1x-3-87-1
single_pulse
7.9226
7.5286
7.5157
7.3896
7.3447
7.3162
7.2601
7.1313
6.7037
6.4930
6.4653
4.2442
4.2384
4.2325
4.2201
4.2084
4.2018
4.1961
2.2461
2.2335
2.2180
2.2085
2.1930
2.1796
1.5336
1.5200
1.5140
1.5064
1.4989
1.4923
1.2569
1.2453
1.2336
EtO2C
CO2Et
F
F
H
N
Ph
O
3ab
0.97
2.16
2.32
4.09
0.92
1.19
1.00
1.03
4.11
4.06
2.05
6.04
f1 (ppm)

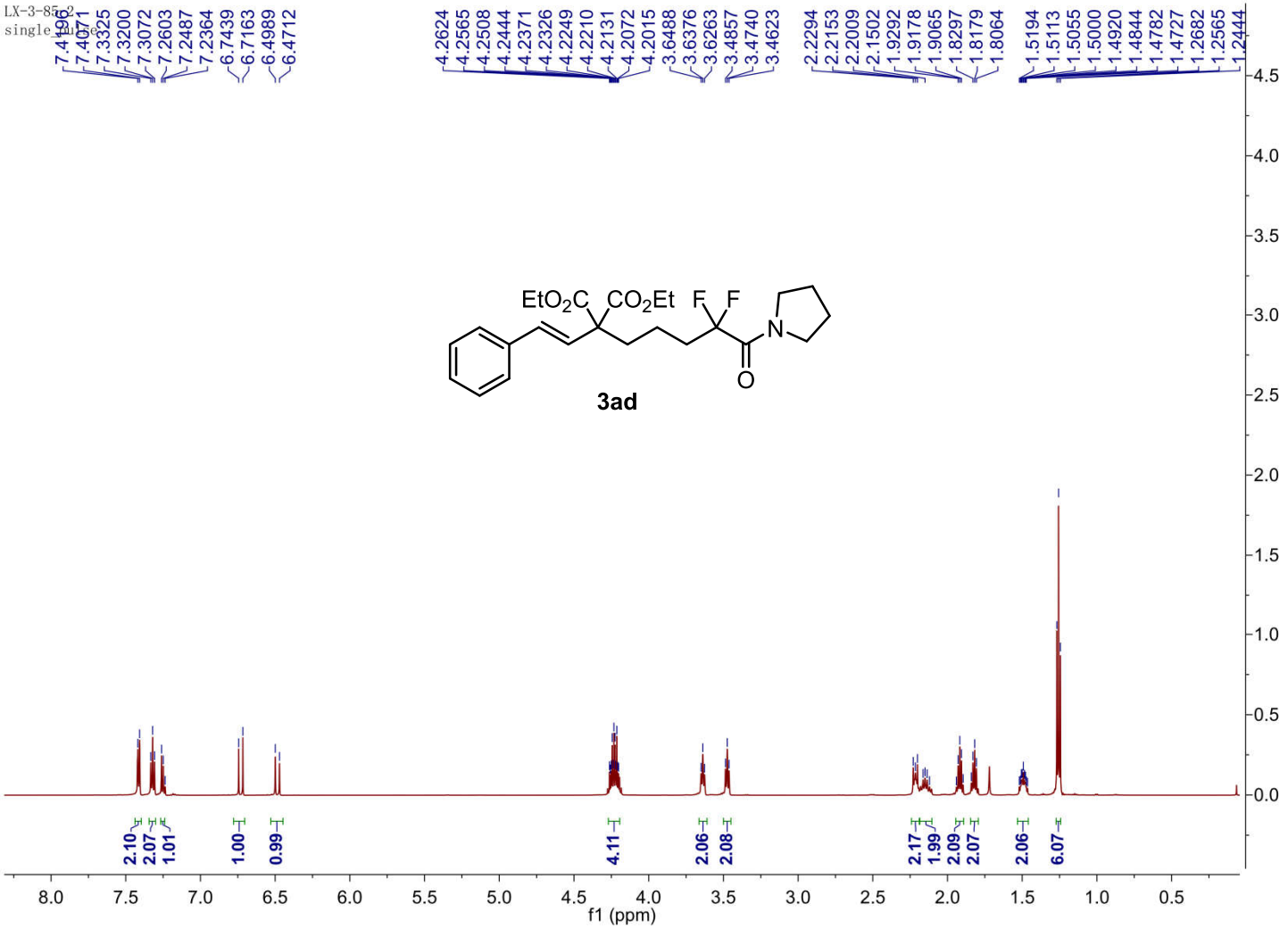

LX-3-87-1
single_pulse
-105.3959
-105.4266
-105.4574
EtO2C
CO2Et
F
F
H
N
Ph
O
3ab
2.00
f1 (ppm)

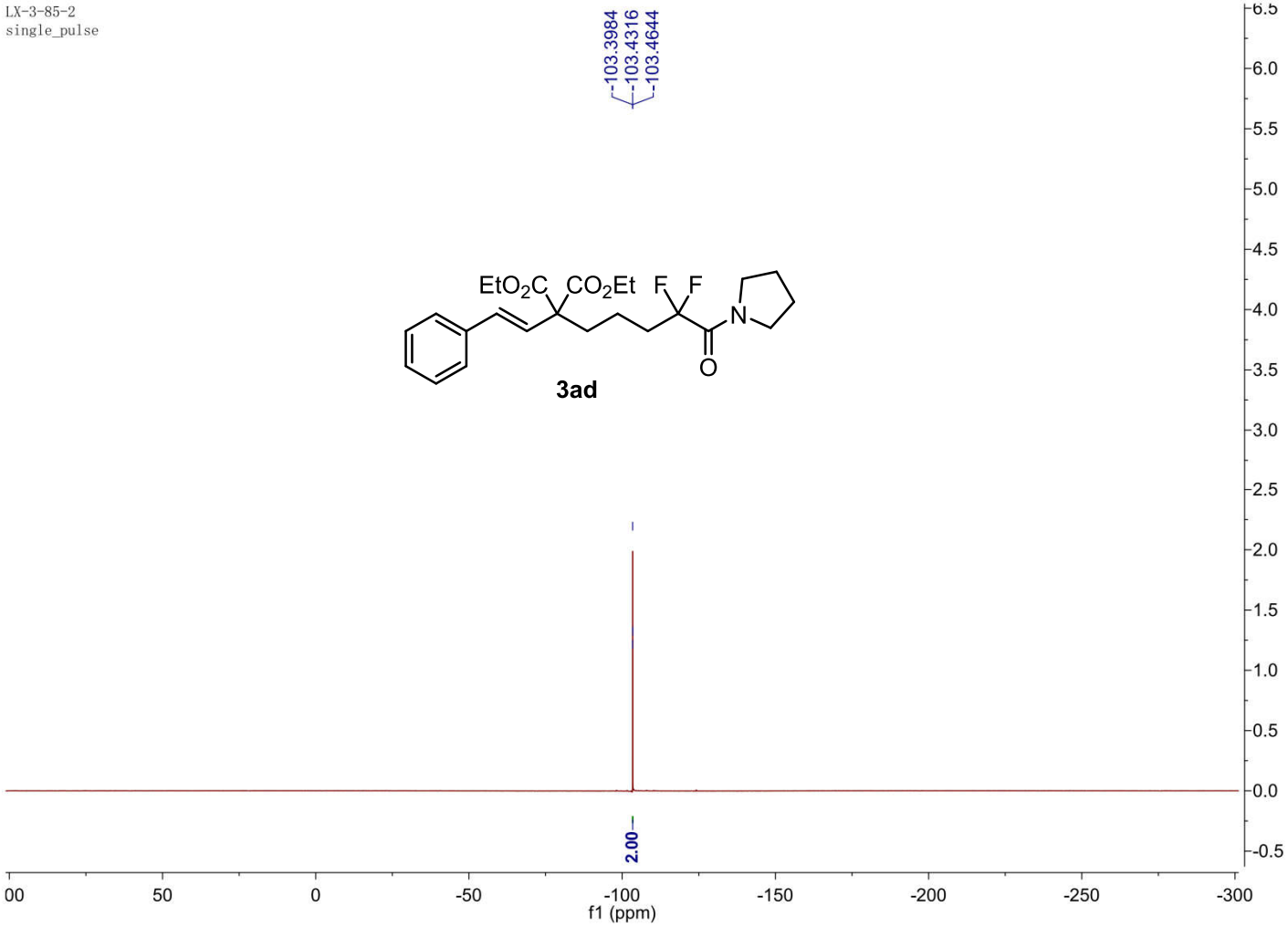

LX-3-87-1
single pulse decoupled gated 20
170.2384
162.0236
161.8361
161.6473
136.3229
135.8733
131.6292
129.1801
128.5770
127.9937
126.5758
125.7632
125.5639
120.1801
119.6841
118.0023
116.3199
77.2108
76.0000
76.7883
61.7389
59.2594
34.9571
34.0980
33.7265
33.5729
16.7564
14.0051
EtO2C
CO2Et
F
F
H
N
Ph
O
3ab
f1 (ppm)

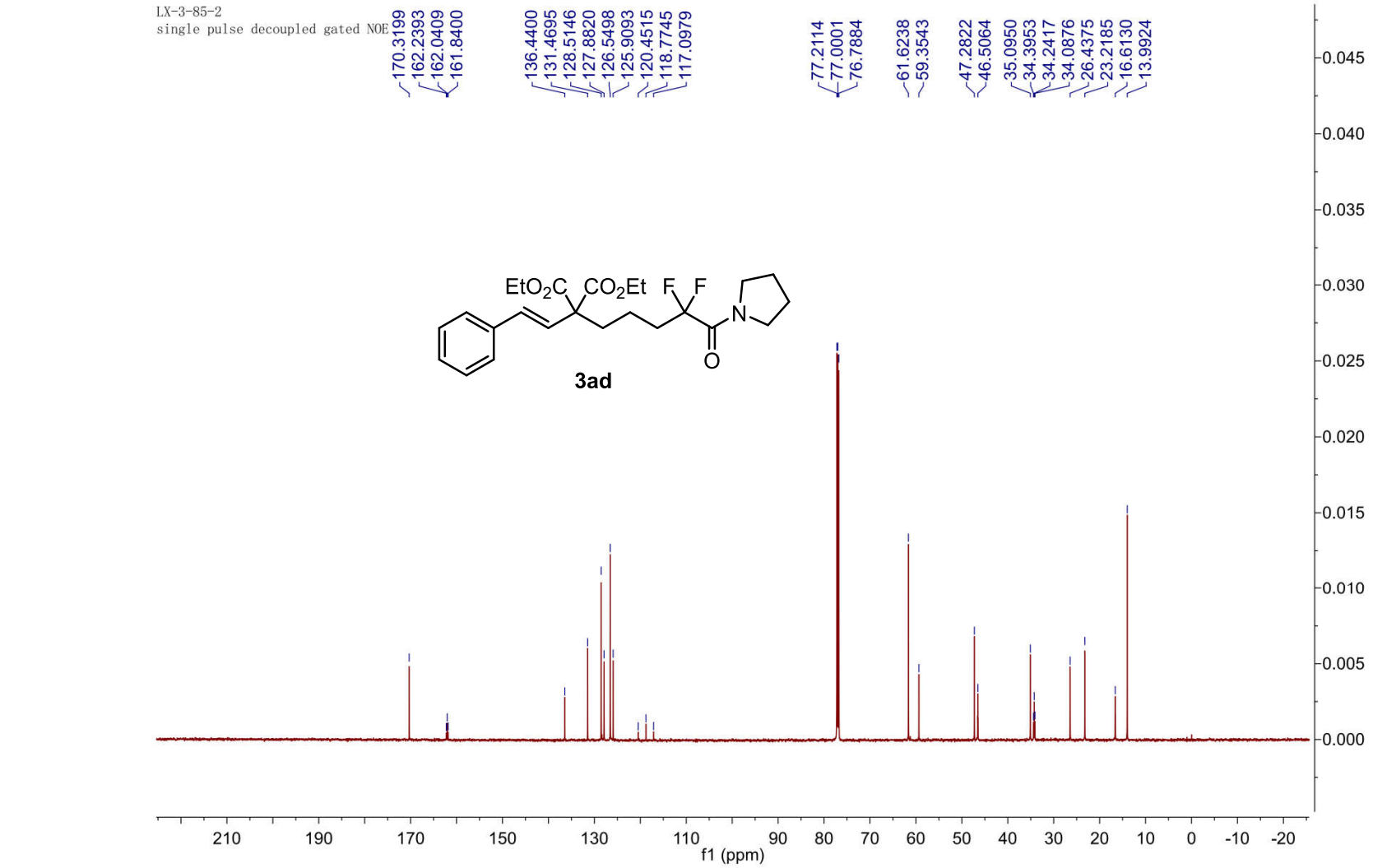

LX-3-85
single_pulse
7.4194
7.4068
7.3600
7.3175
7.3047
7.2599
7.2582
7.2458
6.7474
6.7197
6.5019
6.4743
4.2612
4.2491
4.2431
4.2370
4.2314
4.2248
4.2192
4.2131
4.2070
4.2013
4.1950
3.3510
3.3379
3.3248
3.2515
3.2388
3.2258
3.2293
2.2210
2.2152
2.2085
2.2009
2.1717
2.1584
2.1450
1.5971
1.5844
1.5717
1.5595
1.5471
1.5344
1.5218
1.5089
1.5020
1.4965
1.4884
1.4808
1.4746
1.2682
1.2561
1.2443
0.8783
0.8738
0.8659
0.8613
0.8537
0.8490
EtO2C
CO2Et
F
F
nPr
N
nPr
O
3ac
2.09
2.06
1.10
1.00
0.99
4.00
2.09
2.06
2.17
1.92
4.08
2.13
6.27
6.24
f1 (ppm)

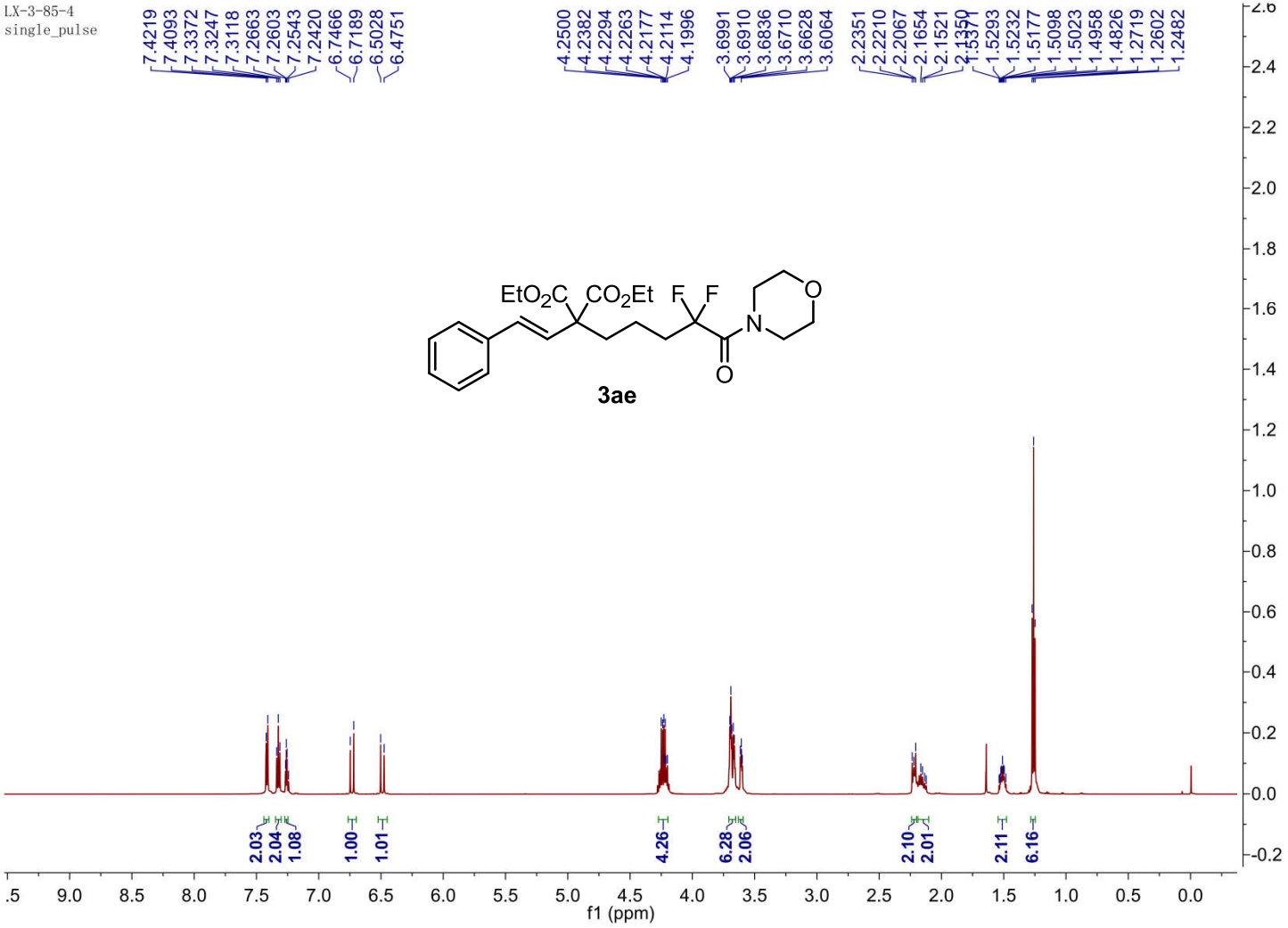

LX-3-85-1
single_pulse
-99.8863
-99.9187
-99.9499
EtO2C
CO2Et
F
F
nPr
N
nPr
O
3ac
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

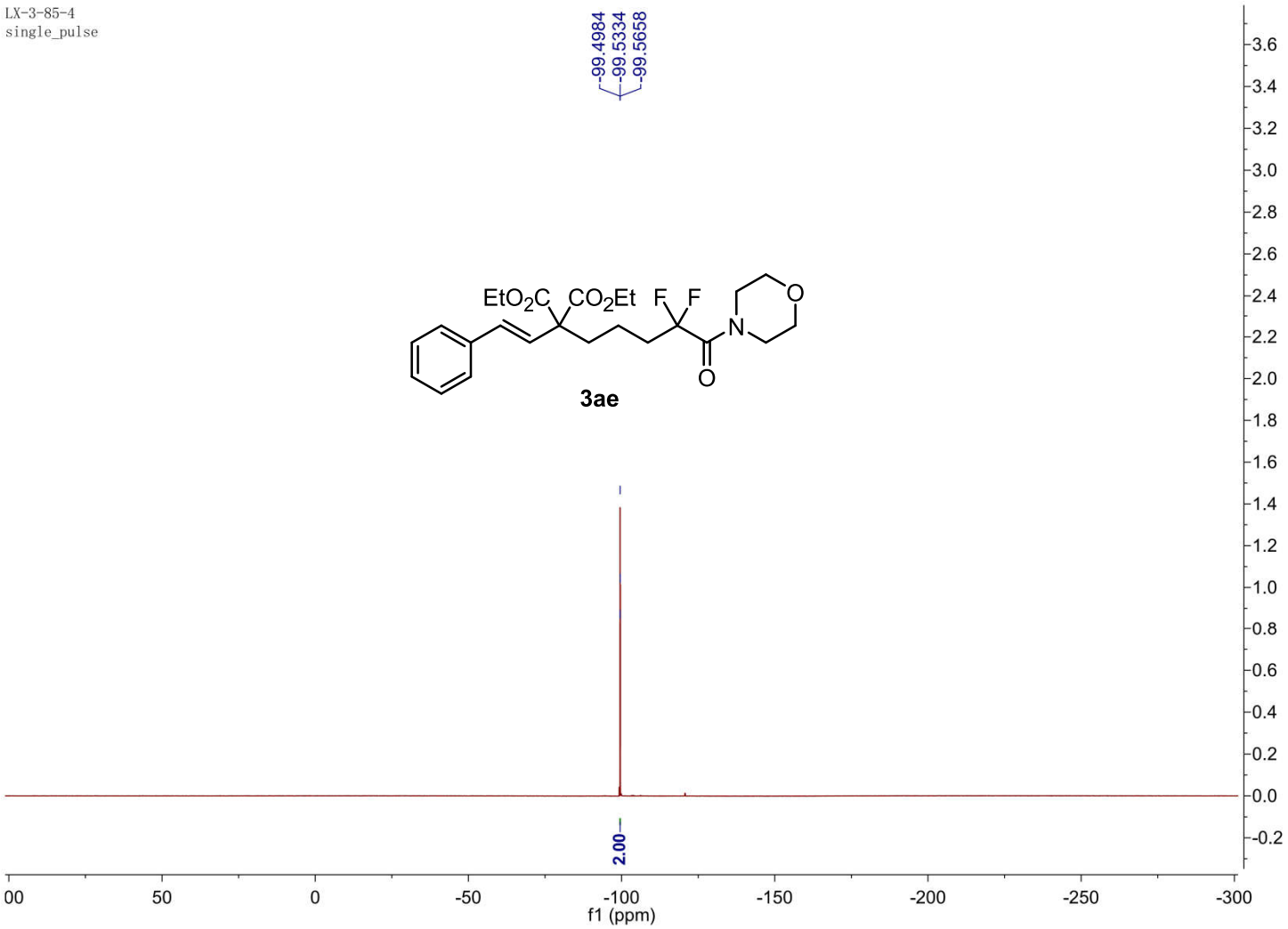

LX-3-85-1
single pulse decoupled gated 13C
170.3276
163.1424
162.9504
162.7580
136.4584
131.4512
128.4968
127.8583
126.5530
125.9141
121.0250
119.3379
117.6509
77.2111
76.9998
76.7884
61.6035
59.3506
49.0806
48.4705
35.1207
35.0428
34.8859
34.7302
22.1055
20.1831
16.6605
13.9827
11.2204
10.9266
EtO2C
CO2Et
F
F
nPr
N
nPr
O
3ac
f1 (ppm)

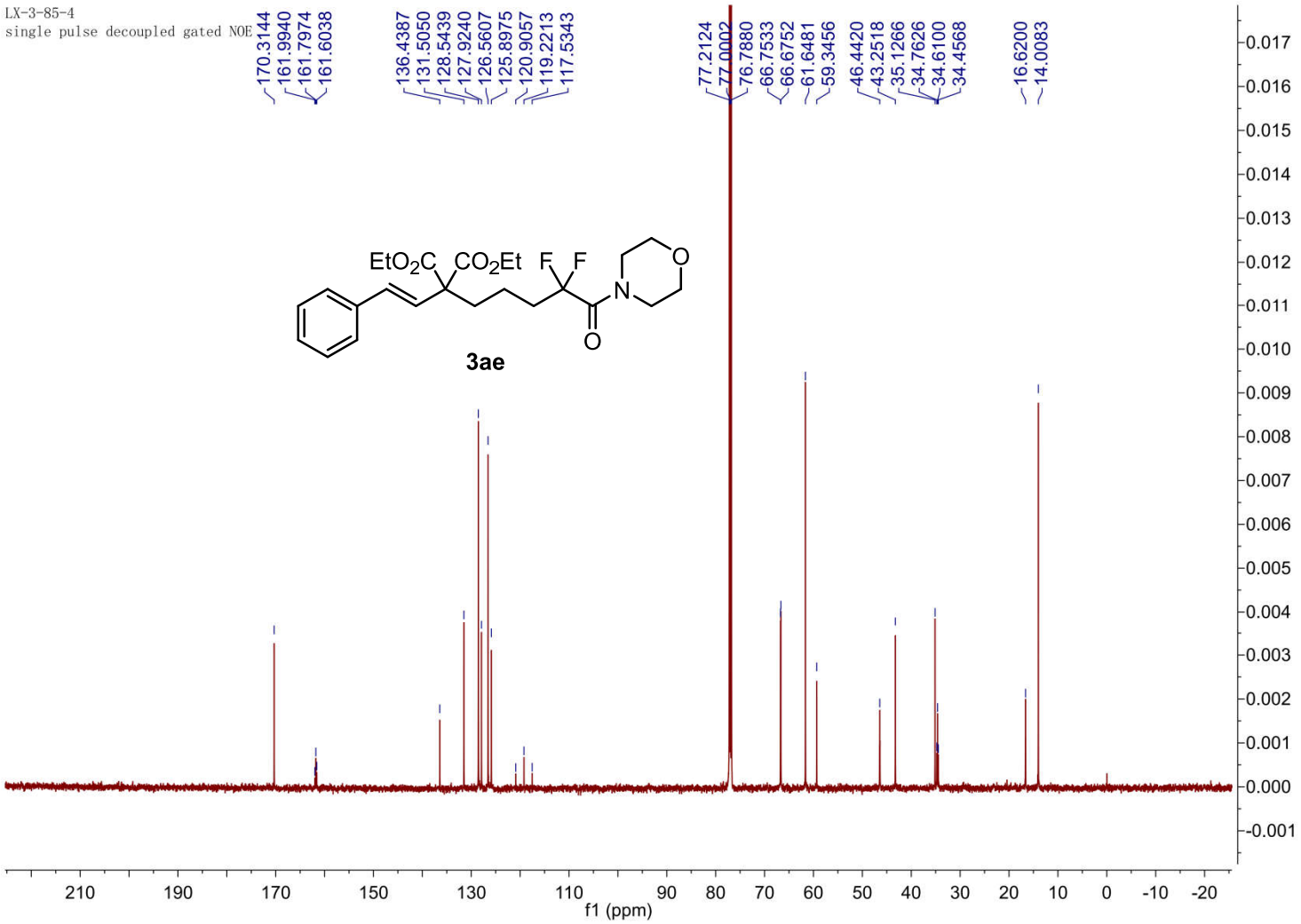

LX-3-85-2
single Pulse
7.4196
7.4071
7.3325
7.3200
7.3072
7.2603
7.2487
7.2364
6.7439
6.7163
6.4989
6.4712
4.2624
4.2565
4.2508
4.2444
4.2371
4.2326
4.2249
4.2210
4.2131
4.2072
4.2015
3.6488
3.6376
3.6263
3.4857
3.4740
3.4623
2.2294
2.2153
2.2009
2.1502
1.9292
1.9178
1.9065
1.8297
1.8179
1.8064
1.5194
1.5113
1.5055
1.5000
1.4920
1.4844
1.4782
1.4727
1.2682
1.2565
1.2444
EtO2C
CO2Et
F
F
N
O
3ad
2.10
2.07
1.01
1.00
0.99
4.11
2.06
2.08
2.17
1.99
2.09
2.07
2.06
6.07
f1 (ppm)

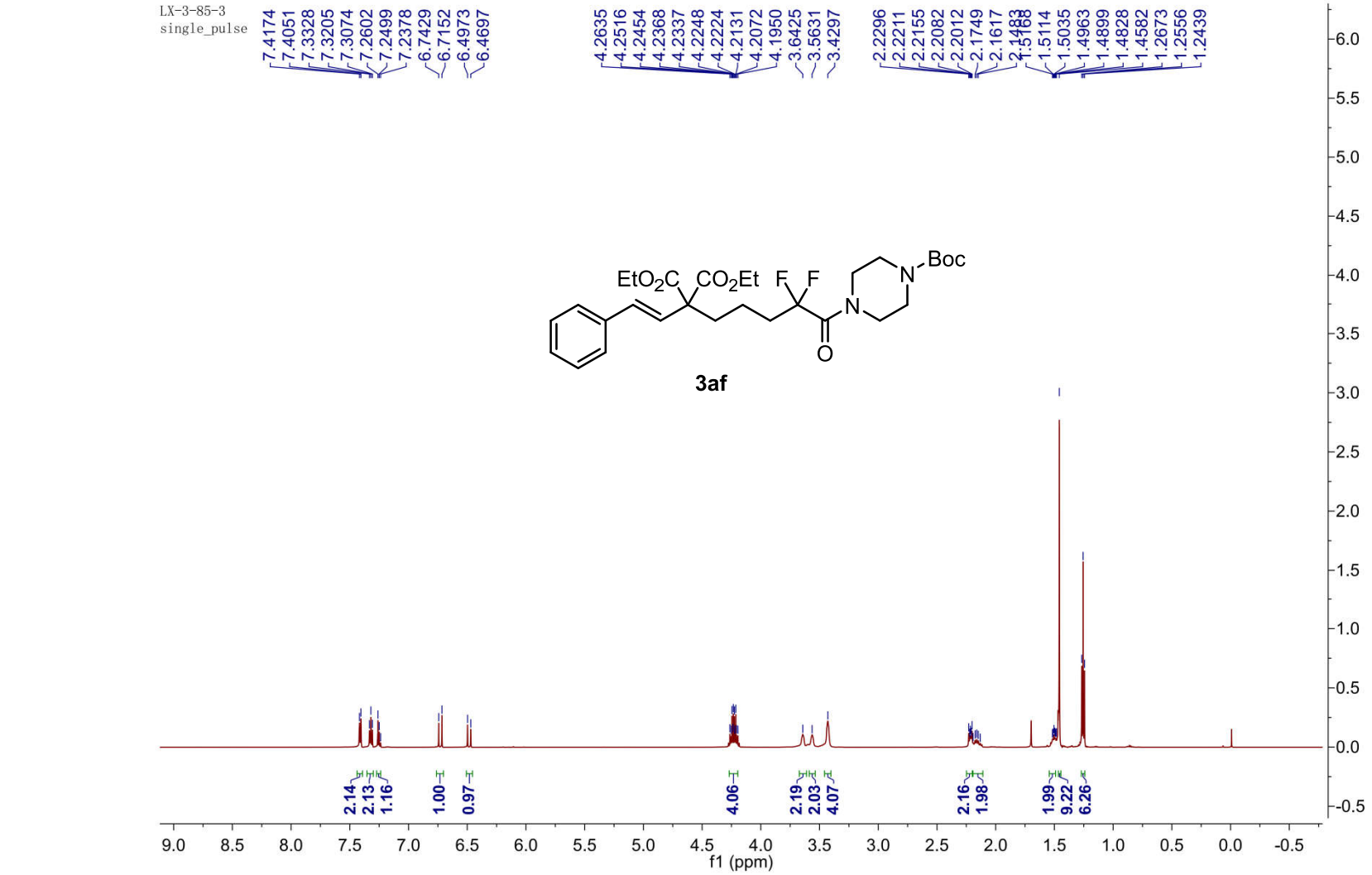

LX-3-85-2
single_pulse
-103.3984
-103.4316
-103.4644
EtO2C
CO2Et
F
F
N
O
3ad
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

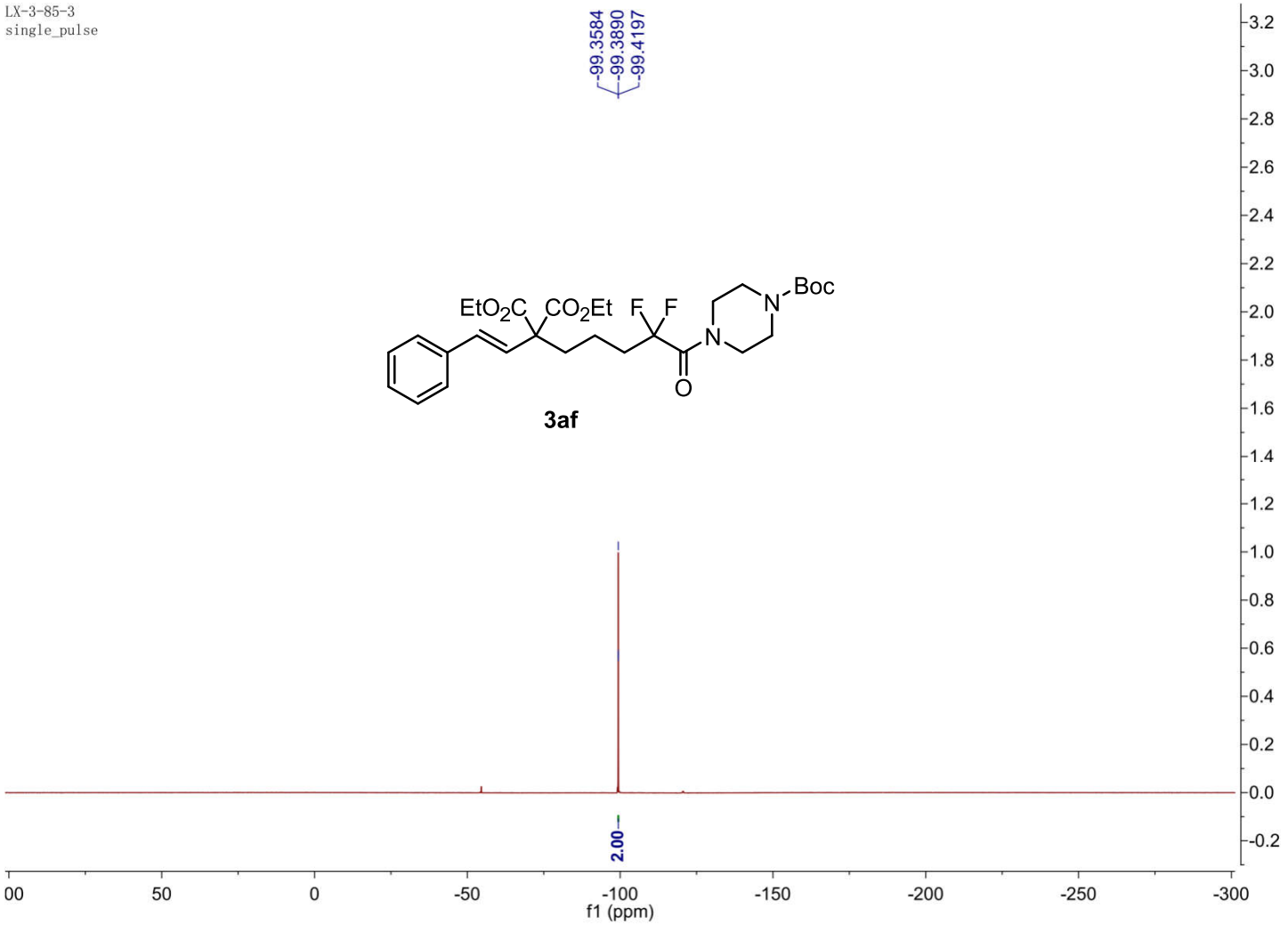

LX-3-85-2
single pulse decoupled gated NOE
170.3199
162.2393
162.0409
161.8400
136.4400
131.4695
128.5146
127.8820
126.5498
125.9093
120.4515
118.7745
117.0979
77.2114
77.0001
76.7884
61.6238
59.3543
47.2822
46.5064
35.0950
34.3953
34.2417
34.0876
26.4375
23.2185
16.6130
13.9924
EtO2C
CO2Et
F
F
N
O
3ad
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

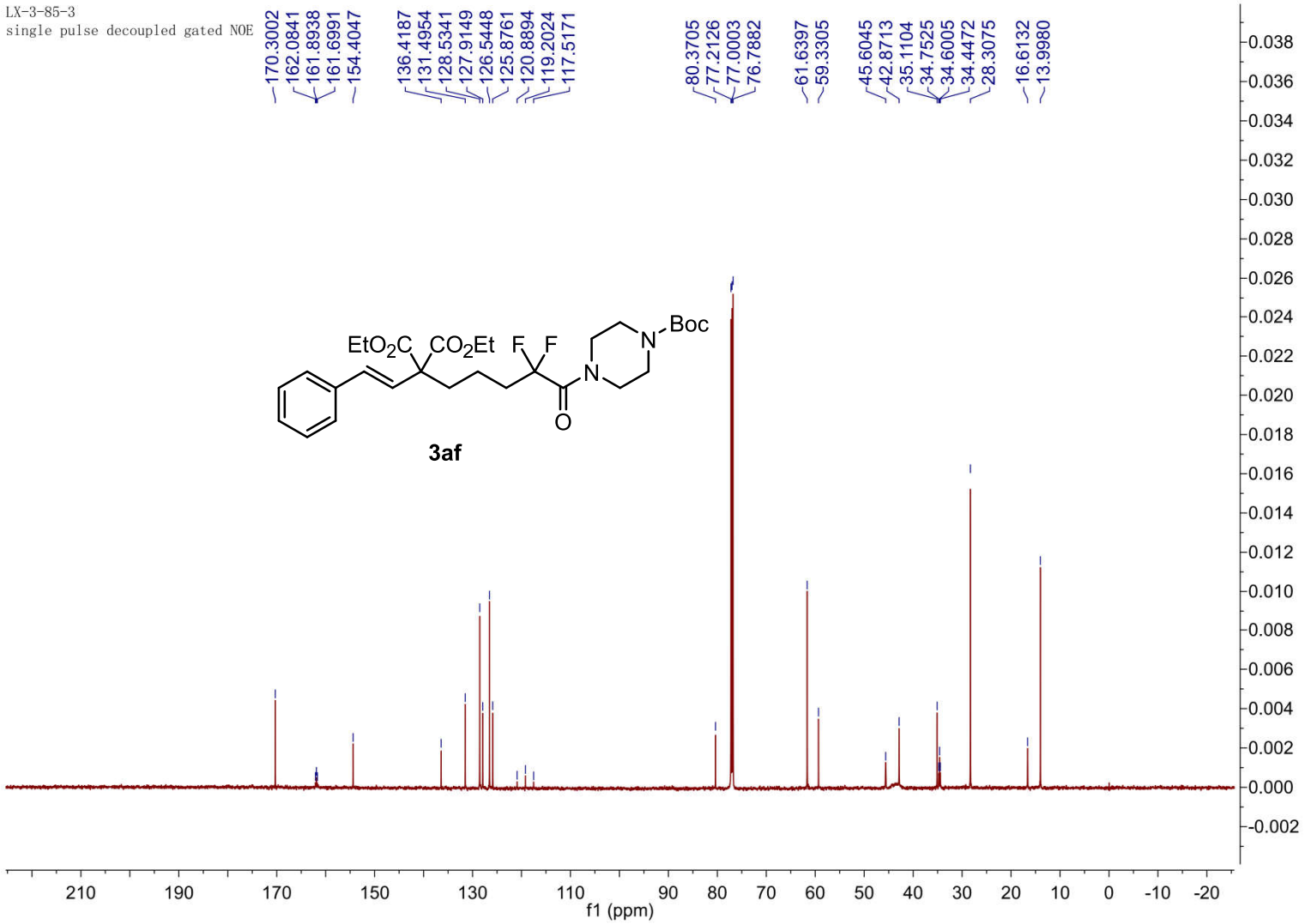

LX-3-85-4
single_pulse
7.4219
7.4093
7.3372
7.3247
7.3118
7.2663
7.2603
7.2543
7.2420
6.7466
6.7189
6.5028
6.4751
4.2500
4.2382
4.2294
4.2263
4.2177
4.2114
4.1996
3.6991
3.6910
3.6836
3.6710
3.6628
3.6064
2.2351
2.2210
2.2067
2.1654
2.1521
2.1350
1.5371
1.5293
1.5232
1.5177
1.5098
1.5023
1.4958
1.4826
1.2719
1.2602
1.2482
EtO2C
CO2Et
F
F
O
N
O
3ae
2.03
2.04
1.08
1.00
1.01
4.26
6.28
2.06
2.10
2.01
2.11
6.16
f1 (ppm)

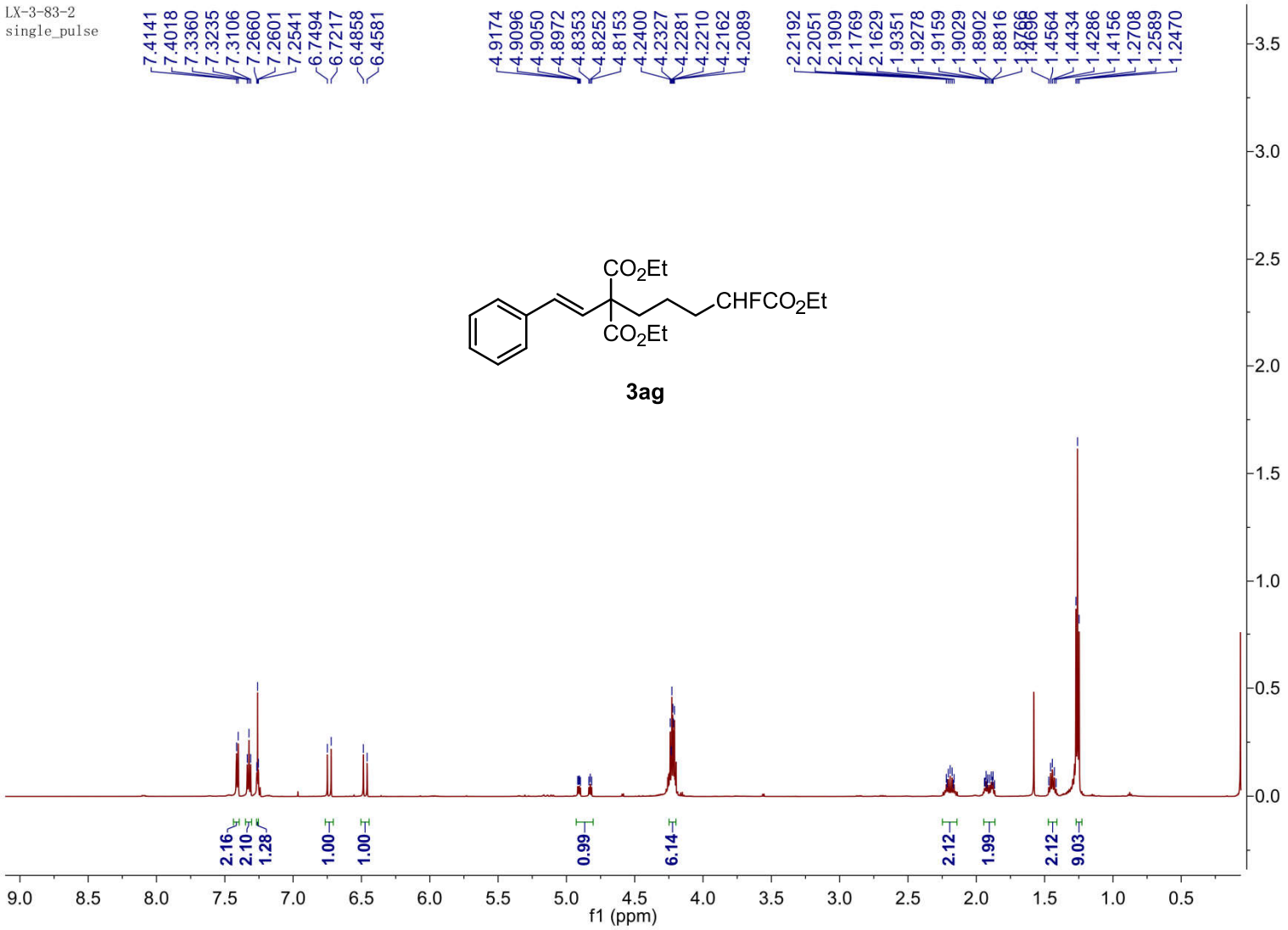

LX-3-85-4
single_pulse
-99.4984
-99.5334
-99.5658
EtO2C
CO2Et
F
F
O
N
O
3ae
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2

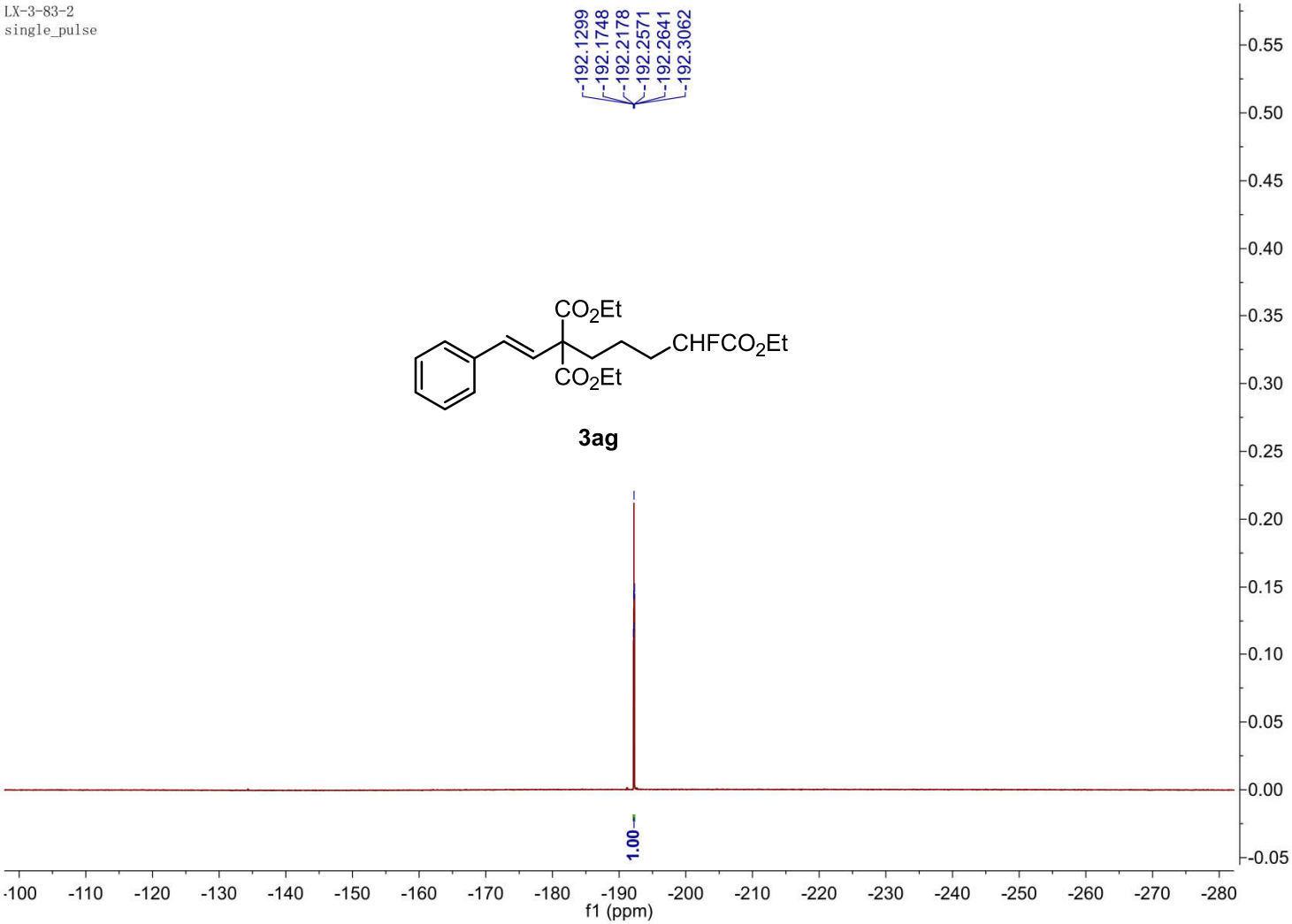

LX-3-85-4
single pulse decoupled gated NOE
170.3144
161.9940
161.7974
161.6038
136.4387
131.5050
128.5439
127.9240
126.5607
125.8975
120.9057
119.2213
117.5343
77.2124
77.0002
76.7880
66.7533
66.6752
61.6481
59.3456
46.4420
43.2518
35.1266
34.7626
34.6100
34.4568
16.6200
14.0083
EtO2C
CO2Et
F
F
N
O
O
3ae
f1 (ppm)

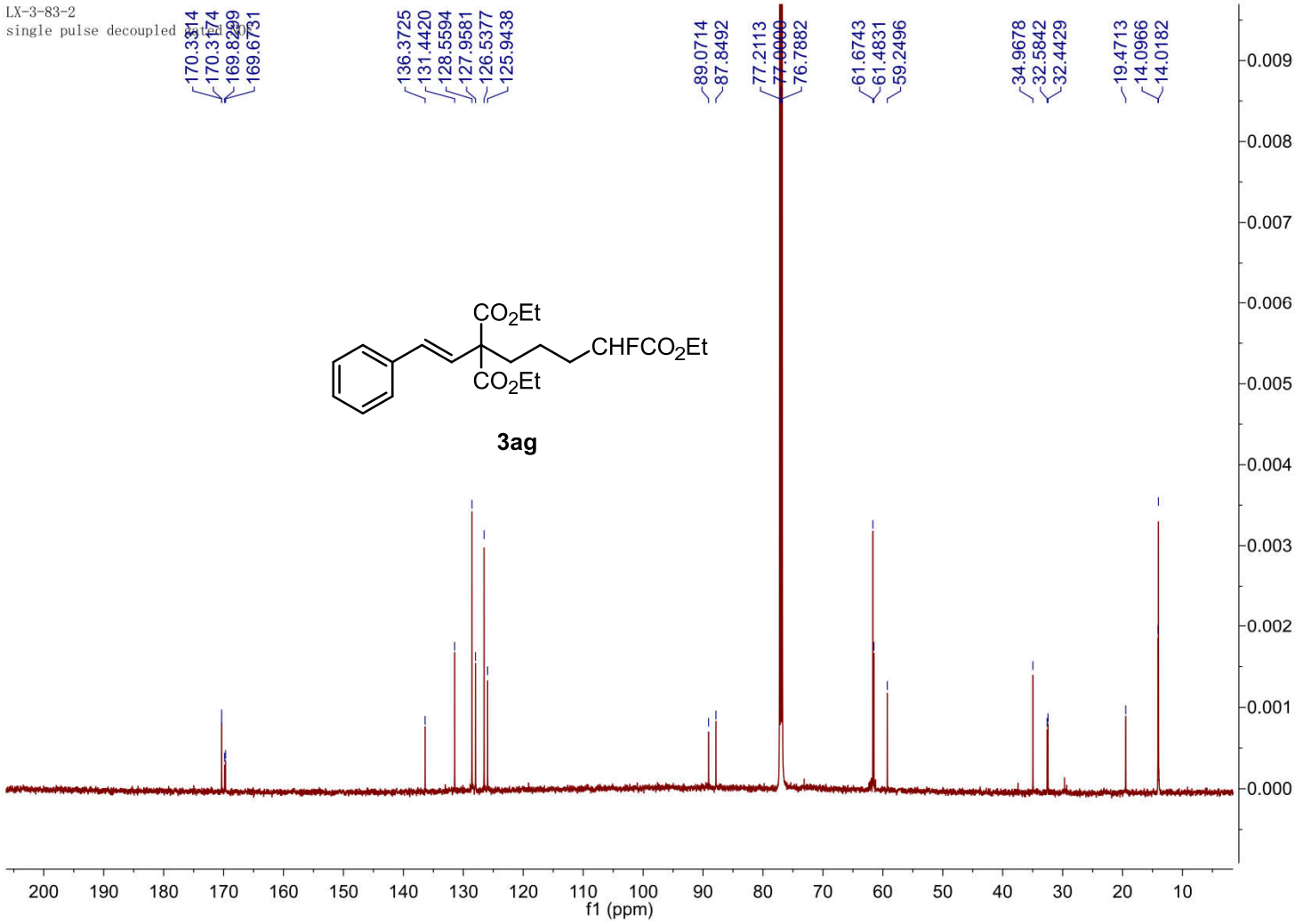

LX-3-85-3
single_pulse
7.4174
7.4051
7.3328
7.3205
7.3074
7.2602
7.2499
7.2378
6.7429
6.7152
6.4973
6.4697
4.2635
4.2516
4.2454
4.2368
4.2337
4.2248
4.2224
4.2131
4.2072
4.1950
3.6425
3.5631
3.4297
2.2296
2.2211
2.2155
2.2082
2.2012
2.1749
2.1617
1.5114
1.5035
1.4963
1.4899
1.4828
1.4582
1.2673
1.2556
1.2439
EtO2C
CO2Et
F
F
N
Boc
N
O
3af
2.14
2.13
1.16
1.00
0.97
4.06
2.19
2.03
4.07
2.16
1.98
1.99
9.22
6.26
f1 (ppm)

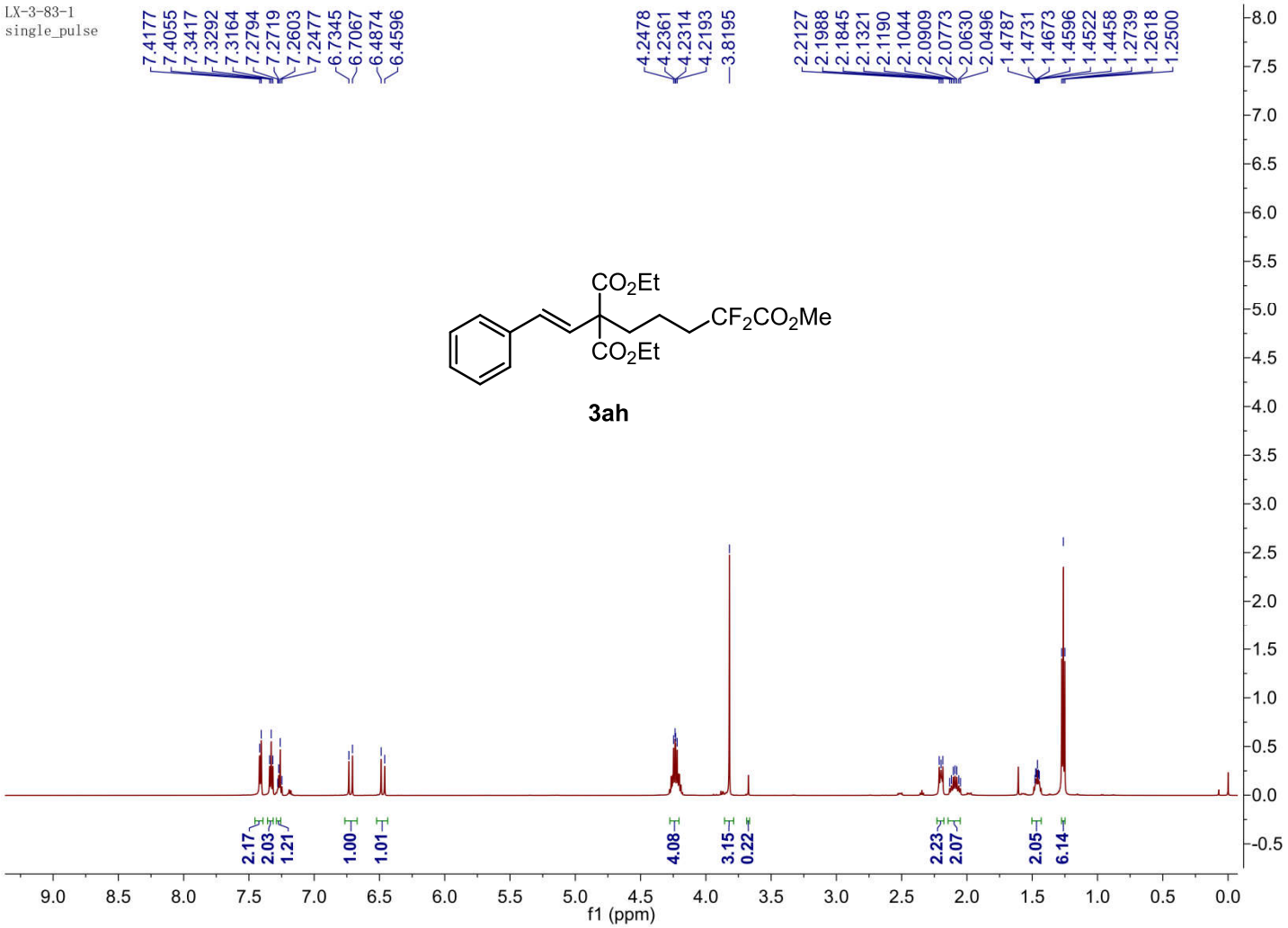

LX-3-85-3
single_pulse
-99.3584
-99.3890
-99.4197
EtO2C
CO2Et
F
F
N
Boc
N
O
3af
2.00
f1 (ppm)


LX-3-85-3
single pulse decoupled gated NOE
170.3002
162.0841
161.8938
161.6991
154.4047
136.4187
131.4954
128.5341
127.9149
126.5448
125.8761
120.8894
119.2024
117.5171
80.3705
77.2126
77.0003
76.7882
61.6397
59.3305
45.6045
42.8713
35.1104
34.7525
34.6005
34.4472
28.3075
16.6132
13.9980
EtO2C
CO2Et
F
F
N
Boc
N
O
3af
f1 (ppm)

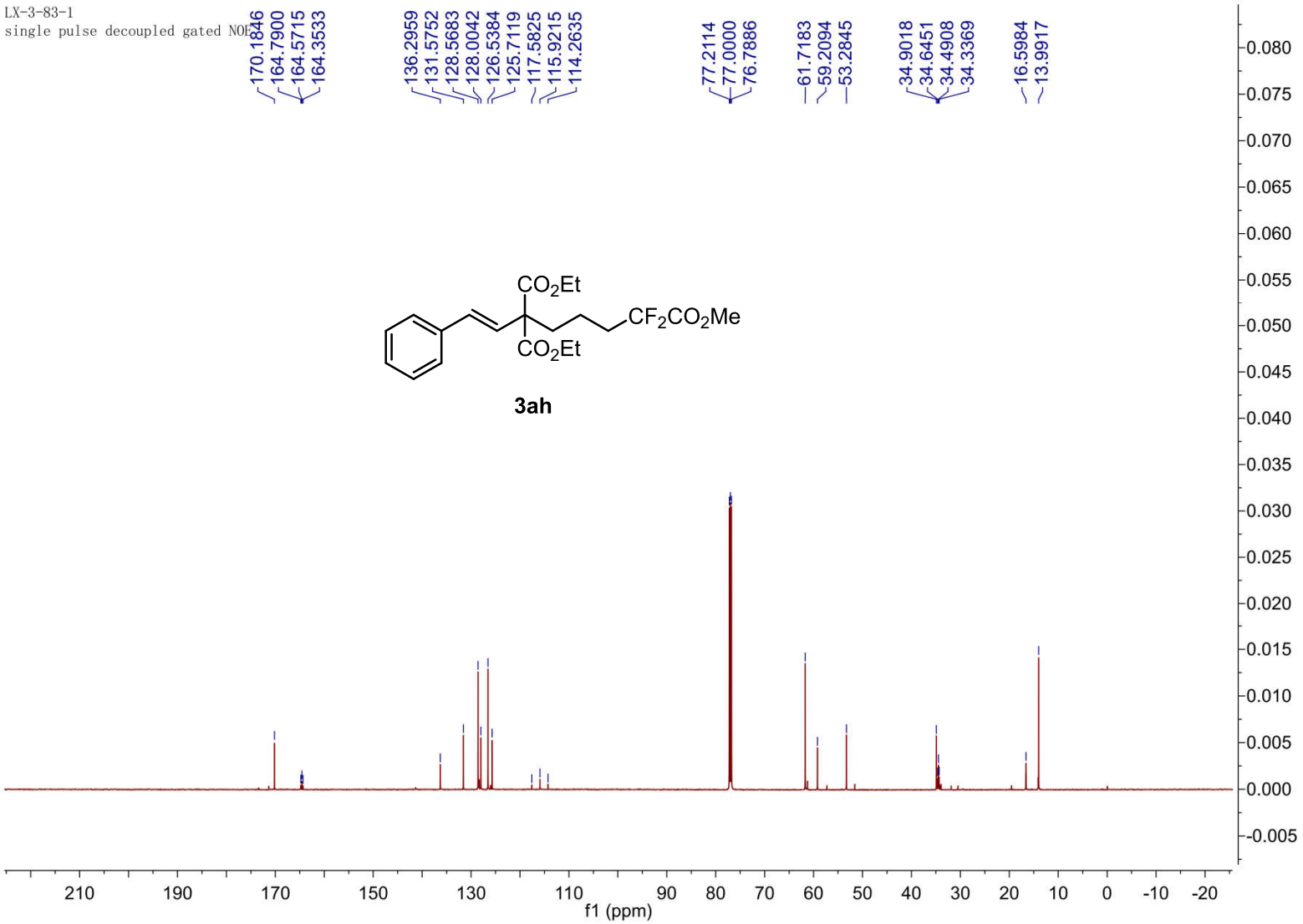

LX-3-83-2
single_pulse
7.4141
7.4018
7.3360
7.3235
7.3106
7.2660
7.2601
7.2541
6.7494
6.7217
6.4858
6.4581
4.9174
4.9096
4.9050
4.8972
4.8353
4.8252
4.8153
4.2400
4.2327
4.2281
4.2210
4.2162
4.2089
2.2192
2.2051
2.1909
2.1769
2.1629
1.9351
1.9278
1.9159
1.9029
1.8902
1.8816
1.4564
1.4434
1.4286
1.4156
1.2708
1.2589
1.2470
CO2Et
CHFCO2Et
CO2Et
3ag
2.16
2.10
1.28
1.00
1.00
0.99
6.14
2.12
1.99
2.12
9.03
f1 (ppm)


LX-3-83-2
single_pulse
-192.1299
-192.1748
-192.2178
-192.2571
-192.2641
-192.3062
CO2Et
CHFCO2Et
CO2Et
3ag
1.00
f1 (ppm)


LX-3-83-2
single pulse decoupled 13C
170.3314
170.3174
169.8299
169.6731
136.3725
131.4420
128.5594
127.9581
126.5377
125.9438
89.0714
87.8492
77.2113
77.0000
76.7882
61.6743
61.4831
59.2496
34.9678
32.5842
32.4429
19.4713
14.0966
14.0182
CO2Et
CHFCO2Et
CO2Et
3ag
f1 (ppm)


LX-3-83-1
single_pulse
7.4177
7.4055
7.3417
7.3292
7.3164
7.2794
7.2719
7.2603
7.2477
6.7345
6.7067
6.4874
6.4596
4.2478
4.2361
4.2314
4.2193
3.8195
2.2127
2.1988
2.1845
2.1321
2.1190
2.1044
2.0909
2.0773
2.0630
2.0496
1.4787
1.4731
1.4673
1.4596
1.4522
1.4458
1.2739
1.2618
1.2500
CO2Et
CF2CO2Me
CO2Et
3ah
2.17
2.03
1.21
1.00
1.01
4.08
3.15
0.22
2.23
2.07
2.05
6.14
f1 (ppm)


LX-3-83-1
single_pulse
-105.5689
-105.5995
-105.6302
CO2Et
CF2CO2Me
CO2Et
3ah
2.00
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
-1


LX-3-83-1
single pulse decoupled gated NOE
170.1846
164.7900
164.5715
164.3533
136.2959
131.5752
128.5683
128.0042
126.5384
125.7119
117.5825
115.9215
114.2635
77.2114
77.0000
76.7886
61.7183
59.2094
53.2845
34.9018
34.6451
34.4908
34.3369
16.5984
13.9917
CO2Et
CF2CO2Me
CO2Et
3ah
f1 (ppm)