Supporting Information

Nickel-Catalyzed Stereo-controlled C–F Activation for the Synthesis of Monofluoroalkenyl *C*-Glycosides

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Content

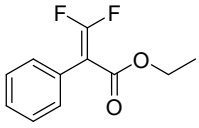
1. General Information

Reagents: All commercial materials were used as received unless otherwise noted. Solvents were purchased from commercial sources (J & K, Bidepharm, Sinopharm, Adamas-beta, etc.) and used without further purification. TLC were performed on silica gel $HSGF_{254}$ plates of Leyan and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 or 365 nm). Flash chromatography was performed using silica gel (200 − 400 mesh) purchased from Qingdao Haiyang.

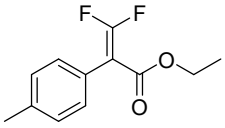
Instruments: All products were characterized by nuclear magnetic resonance (NMR) spectrum and mass spectrum (MS). ^{1}H-, ^{13}C- and ^{19}F-NMR spectrum were recorded in chloroform-*d* ($CDCl_3$) on Bruker 400, 500, 600 and 800 MHz instruments. All NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks (chloroform-*d* (δ = 7.26 ppm) or TMS (δ = 0.00 ppm) for ^{1}H NMR, chloroform-*d* (δ = 77.16 ppm) for ^{13}C NMR, and $C_6H_5CF_3$ (δ = -63.80 ppm) for ^{19}F NMR) as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, ddt = doublet of doublet of triplets, etc. High resolution ESI mass experiments were operated on a Varian instrument. All of the heating reactions are carried out in oil bath.

2. Synthesis and Characterization of Substrates

2.1. Synthesis of *gem*-Difluoroalkyl Acceptor Substrates



1a



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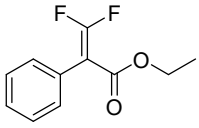

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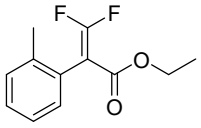

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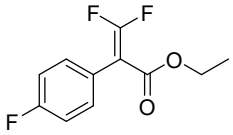

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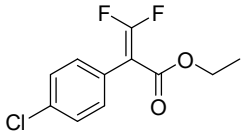

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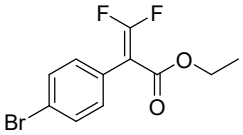

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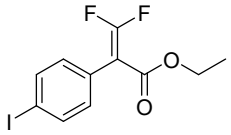

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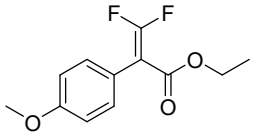

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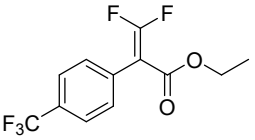

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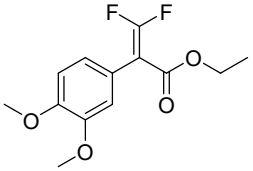

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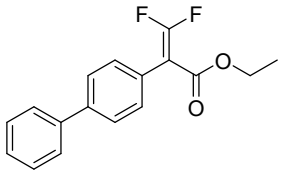

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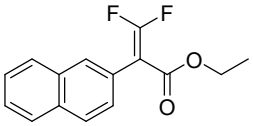

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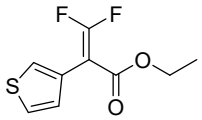

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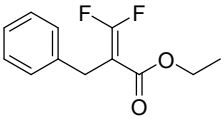

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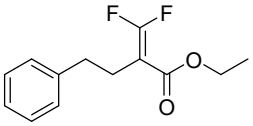

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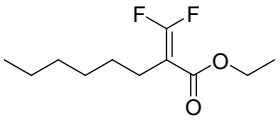

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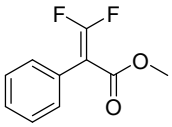

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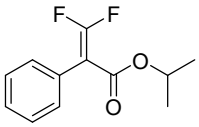

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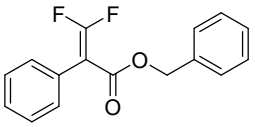

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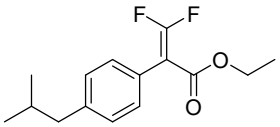

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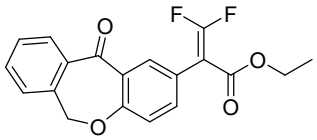
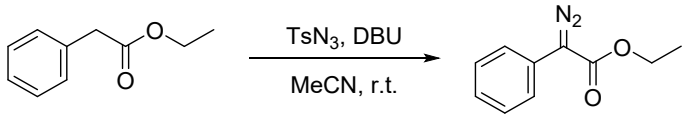


1v

Compounds **1a -1v** were prepared according to procedures from literature [1, 2] with minor changes, and all the substrates were reported compounds.

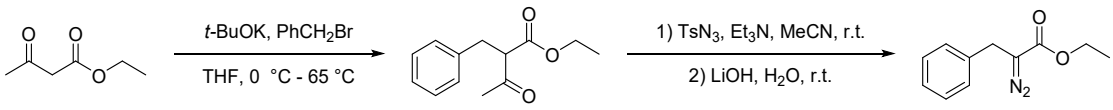
2.1.1. Typical procedure (I-1) for the synthesis of *α*-diazo esters 1j – 1n, 1r – 1v (take S1a as an example)



S1a

To a 100 mL flask, **ethyl 2-phenylacetate** (1.64 g, 10.00 mmol) and **4-methylbenzenesulfonyl azide** (2.96 g, 15.00 mmol) were dissolved in anhydrous MeCN (20 mL). Then, **DBU** (2.28 g, 15.00 mmol) was added dropwise. After being stirred at room temperature for 12 hours, the mixture was quenched with saturated NH_4Cl solution (50 mL), and extracted with DCM (50 mL). Next, the organic layer was washed with brine (25 mL*3), and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 100/1) to obtain desired ***α*-diazoester** (1.85 g, 97.3%) as orange liquid.

2.1.2. Typical procedure (I-2) for the synthesis of *α*-diazo esters 1o – 1q (take S1o as an example)



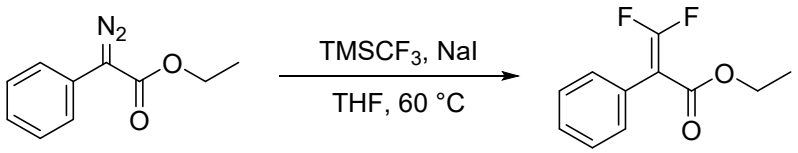
S1o

To a 250 mL flask, **ethyl 3-oxobutanoate** (2.60 g, 20.00 mmol) was dissolved in anhydrous THF (40 mL) and cooled to 0 °C. Then, ***t*-BuOK** (2.47 g, 22.00mmol) was added slowly. After being stirred at 0 °C for 30 minutes, **benzyl bromide** (10.26, 60.00 mmol) in THF (10 mL) was added slowly. After being stirred and refluxed for 3 hours, the mixture was quenched with saturated NH_4Cl solution (50 mL), and extracted with DCM (100 mL). Next, the organic layer was washed with brine (50 mL*3), and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 100/1) to obtain desired **benzyl product** (3.98 g, 90.3%) as yellow oil.

To a 100 mL flask, the previous **benzyl product** (1.10 g, 5.00 mmol) and **4-**

methylbenzenesulfonyl azide (1.48 g, 7.50 mmol) dissolved in anhydrous MeCN (20 mL). Then, **TEA** (758.95 mg, 7.50 mmol) was added dropwise. After being stirred at room temperature for 12 hours, **LiOH** (0.60 g, 25.00 mmol) solution in water (20 mL) was added. After being stirred at room temperature for another 12 hours, the mixture extracted with DCM (50 mL). Next, the organic layer was washed with brine (25 mL*3), and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 100/1) to obtain desired ***α*-diazoester** (758 mg, 97.3%) as orange liquid.

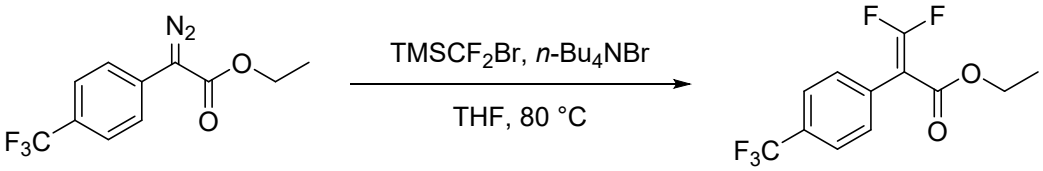
2.1.3. Typical procedure (II-1) for the synthesis of *gem*-difluoroalkenes 1a – 1i, 1k - 1v (take 1a as an example)



1a

To a 100 mL flask, **NaI** (1.50 g, 10.00 mmol) was heated at 60 °C in vacuo for 30 minutes to dry, and then cooled to room temperature, followed by addition of ***α*-diazoester S1a** (951.01 mg, 5.00 mmol) and **$TMSCF_3$** (1.56 g, 11.00 mmol) dissolved in anhydrous THF (20 mL). After being stirred at 60 °C for 5 hours, the mixture was quenched with $Na_2S_2O_3$ solution (50 mL), and extracted with **EA** (50 mL). Next, the organic layer was washed with brine (50 mL*3), and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 100/1) to obtain desired **benzyl product** (650 mg, 61.3%) as colorless oil.

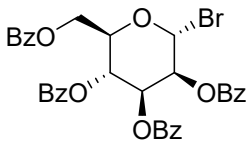
2.1.4. Procedure for the synthesis of *gem*-difluoroalkenes 1j



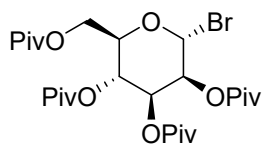
1j

To a 100 mL flask, ***α*-diazoester S1j** (1.29 g, 5.00 mmol), **$TMSCF_2Br$** (1.52g, 7.50 mmol) and ***n*-Bu_4NBr** (64.48 mg, 4.0 mol%) were dissolved in THF (20 mL). After being stirred at 80 ºC for 24 hours under argon protection, the mixture was evaporated to remove solvent, and purified by silica gel chromatography (PE/EA = 100/1) to obtain desired product **1j** (750 mg, 53.53%) as colorless oil.

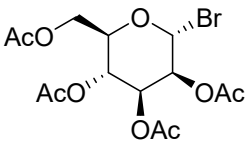
2.2. Synthesis of Bromide Glycosyl Donor Substrates



2a



2b



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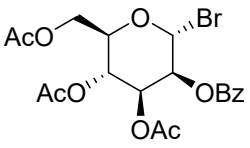
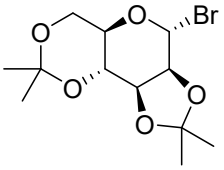


2d



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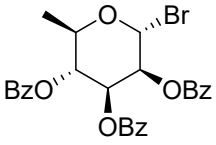

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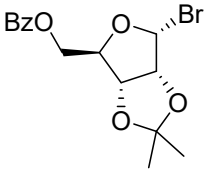
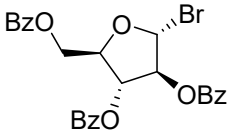


2g



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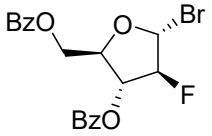
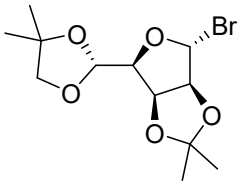


2i



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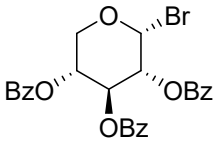
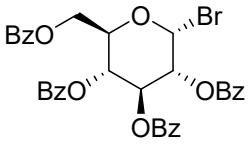
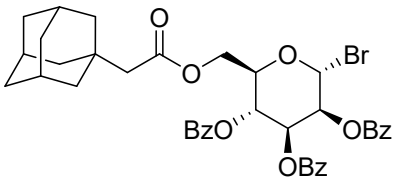


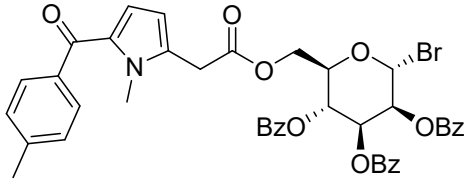
2k



2l



2x



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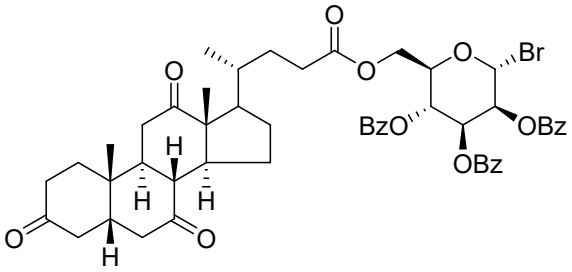
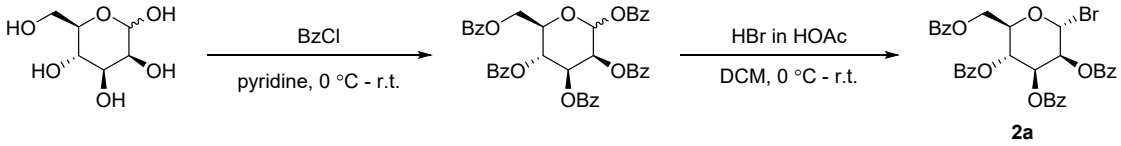


2z

All the substrates were reported compounds and compounds **2a** – **2g**, **2j**, **2k**, **2x** – **2z** were prepared according to procedures from literatures [3-6]with minor changes, while **2h**, **2i**, **2l** were acquired from commercial resources.

2.2.1 Typical procedure (III) for the synthesis of glycosyl substrates 2a – 2d, 2f, and 2k (take 2a as an example)

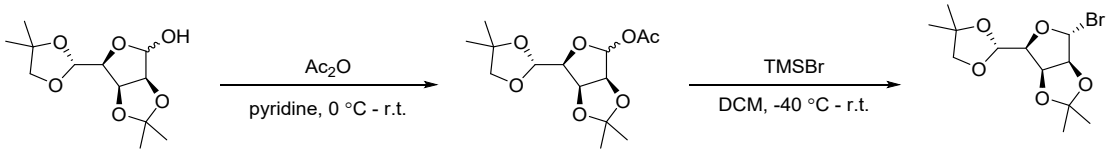


2a

To a 250 mL flask, **mannose** (1.80 g, 10.00 mmol) was dissolved in pyridine (50 mL) and cooled to 0 °C. Then, **benzoyl chloride**(16.87 g, 120.00 mmol) was added dropwise. After being stirred at room temperature for 12 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL) extracted by DCM (100 mL). Next, the organic layer was neutralized by 1 *M* HCl solution (100 mL), washed by brine (50 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 4/1) to obtain **desired ester** as a white solid (5.80 g, 82.8%).

To another 250 mL flask, the **previous ester** (3.5 g, 5.00 mmol) was dissolved in DCM (25 mL) and cooled to 0 °C. Then, **hydrogen bromide** (3.68 g, 15.00 mmol, dissolved in acetic acid with 33%WT) was added dropwise. After being stirred at room temperature for 3 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL), and extracted by DCM (100 mL). Next, the organic layer was washed with brine (50 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was evaporated to remove solvent and obtain **desired bromide** (3.30 g, 54.6 %) as a white solid.

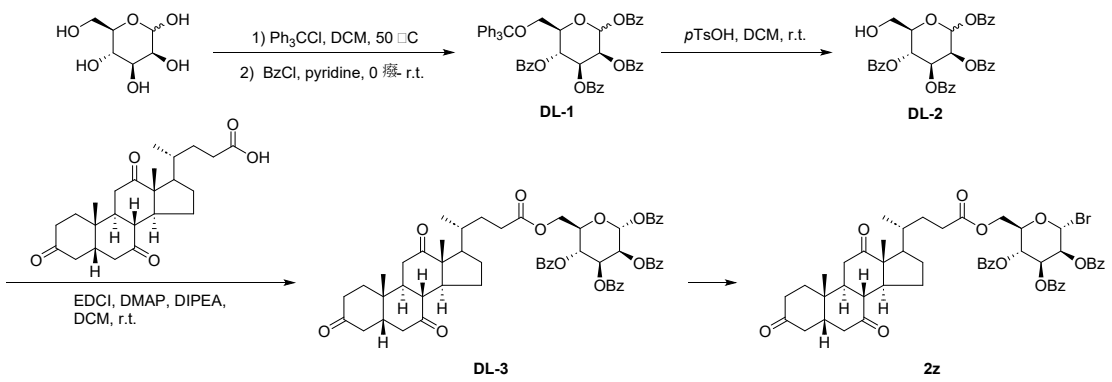
2.2.2. Typical procedure (IV) for the synthesis of glycosyl substrates 2e, 2g, and 2j (take 2j as an example)



To a 250 mL flask, **protected mannofuranose** (2.60 g, 10.00 mmol) was dissolved in pyridine (50 mL) and cooled to 0 °C. Then, **acetic anhydride** (2.04 g, 20.00 mmol) was added dropwise. After being stirred at room temperature for 12 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL) extracted by DCM (100 mL). Next, the organic layer was neutralized by 1 *M* HCl solution (100 mL), washed by brine (50 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 4/1) to obtain **desired ester** as a white solid (2.88 g, 95.3%).

To another 250 mL flask, the **previous ester** (1.51 g, 5.00 mmol) was dissolved in DCM (25 mL) and cooled to -40 °C. Then, **trimethylsilyl bromide** (1.53 g, 10.00 mmol) was added dropwise. After being stirred at -40 °C for 30 minutes and room temperature for 2 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL), and extracted by DCM (100 mL). Next, the organic layer was washed with brine (50 mL) for three times, and dried over anhydrous Na_2SO_4. The residue was evaporated to remove solvent and obtain **desired bromide** (840 mg, 52.0 %) as a white solid.

2.2.3. Typical procedure (III) for the synthesis of drug-like glycosyl substrates 2x – 2z (take 2z as an example)

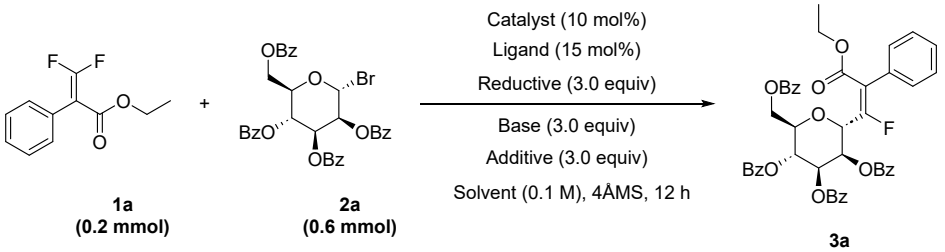


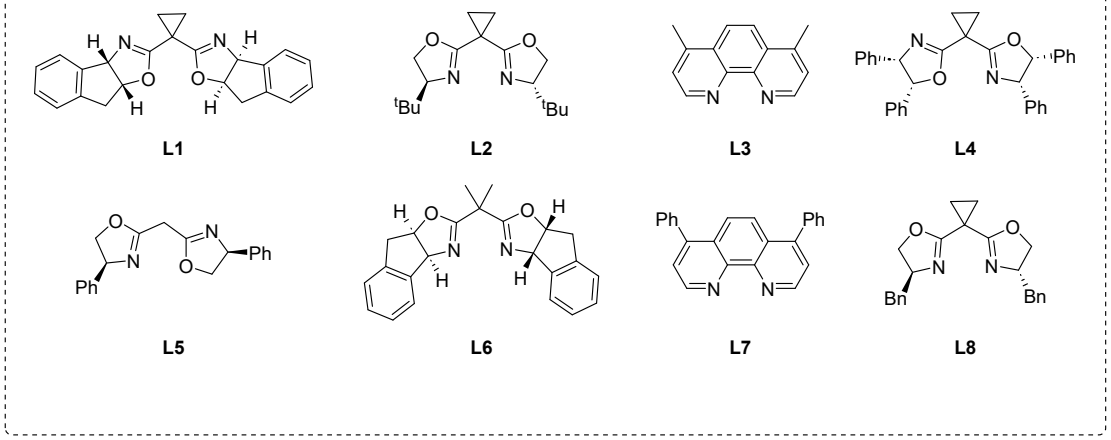
To a 250 mL flask, **mannose** (3.60 g, 20.00 mmol) and **triphenylmethyl chloride** (6.13 g, 22.00 mmol) were dissolved in DCM (50 mL). After being stirred at 50 °C for 12 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL) extracted by DCM (100 mL). Next, the organic layer was washed by brine (50 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 2/1) to obtain **desired easer** as a white solid. The secondary reaction with **benzoyl chloride** was referred to **Procedure (**III**)**, and desired product **DL-1** (10.5 g, 62.6% in two steps) was white solid.

To another 250 mL flask, **DL-1** (4.19 g, 5.00 mmol) and **4-methylbenzenesulfonic acid** (10 mol%, 8.61 mg) was dissolved in DCM (50 mL). After being stirred at room temperature for 12 hours, the mixture was quenched by saturated $NaHCO_3$ solution (50 mL) extracted by DCM (100 mL). Next, the organic layer was washed by brine (50 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 4/1) to obtain **DL-2** (2.7 g, 90.5%) as a white solid.

To a 100 mL flask, **DL-2** (1.19 g, 2.00 mmol), **steroid fatty acid** (966.07 mg, 2.40 mmol), **DMAP** (73.30 mg, 0.60 mmol) and **DIPEA** (465.29 mg, 3.60 mmol) were dissolved in DCM (20 mL). Then, **EDCI** (342.70 mg, 3.00 mmol) was added slowly. After being stirred at room temperature for 12 hours, the mixture was quenched by saturated $NaHCO_3$ solution (20 mL) extracted by DCM (50 mL). Next, the organic layer was washed by brine (25 mL*3) for three times, and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (PE/EA = 6/1) to obtain **DL-3** as a white solid. The final reaction with **hydrogen bromide** was referred to **Procedure (**III**)**, and desired product **2z** (798 mg, 41.8% in two steps) was yellow solid.

3. Reaction Condition Optimization[a,b,c]





No.	[cat]	[L]	[Red]	[Add]	[Base]	[Sc]	[T]	Yield[b]	α : β[c]
1	(4,4′-dMeObpy) $NiCl_2$	**L1**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	74% (72%)	α
2	(4,4′-dMeObpy) $NiCl_2$	**L2**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	50%	α
3	(4,4′-dMeObpy) $NiCl_2$	**L3**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	7%	α
4	(4,4′-dMeObpy) $NiCl_2$	**L4**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	41%	α
5	(4,4′-dMeObpy) $NiCl_2$	**L5**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	19%	α
6	(4,4′-dMeObpy) $NiCl_2$	**L6**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	33%	α
7	(4,4′-dMeObpy) $NiCl_2$	**L7**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	40%	α

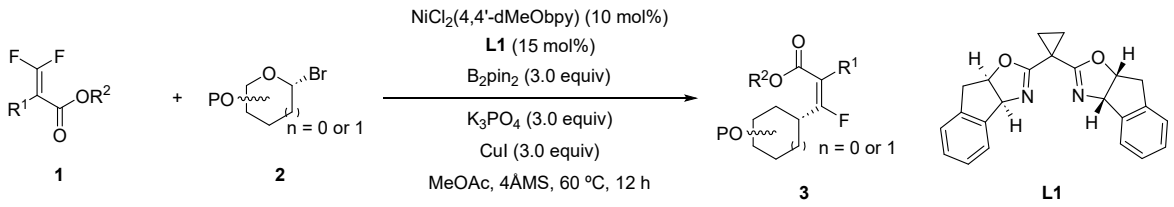
No.	[cat]	[L]	[Red]	[Add]	[Base]	[Sc]	[T]	Yield[b]	α : β[c]
8	(4,4′-dMeObpy) $NiCl_2$	**L8**	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	23%	α
9	**$NiCl_2$(dppf)**	L2	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	42%	α
10	**$NiCl_2$(dme)**	L2	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	33%	α
11	**$NiCl_2$(tbpy)**	L2	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	10%	α
12	**$NiCl_2$(dppe)**	L2	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	26%	α
13	**$NiCl_2(NH_3)_6$**	L2	B_2pin_2	CuI	K_2CO_3	MeOAc	60 °C	10%	α
14	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**Toluene**	60 °C	Trace	--
15	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**Acetone**	60 °C	32%	α
16	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**MeCN**	60 °C	20%	α
17	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**DCM**	60 °C	Trace	--
18	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**MeOH**	60 °C	4%	α
19	$NiCl_2$(dme)	L2	B_2pin_2	CuI	K_2CO_3	**Xylene**	60 °C	Trace	--
20	$NiCl_2$(dme)	L2	B_2pin_2	**NaI**	K_2CO_3	MeCN	60 °C	12%	α
21	$NiCl_2$(dme)	L2	B_2pin_2	**KI**	K_2CO_3	MeCN	60 °C	8%	α
22	$NiCl_2$(dme)	L2	B_2pin_2	**CuCl**	K_2CO_3	MeCN	60 °C	8%	α
23	$NiCl_2$(dme)	L2	B_2pin_2	**NaI**	K_2CO_3	MeCN	**70 °C**	10%	α
24	$NiCl_2$(dme)	L2	B_2pin_2	**NaI**	K_2CO_3	MeCN	**50 °C**	9%	α
25	$NiCl_2$(dme)	L2	B_2pin_2	**NaI**	K_2CO_3	MeCN	**40 °C**	8%	α
26	(4,4′-dMeObpy) $NiCl_2$	L1	**B_2nep_2**	CuI	K_2CO_3	MeOAc	60 °C	41%	α
27	$NiCl_2$(dme)	L2	**Mn**	NaI	K_2CO_3	MeCN	60 °C	Trace	--
28	$NiCl_2$(dme)	L2	**Zn**	NaI	K_2CO_3	MeCN	60 °C	Trace	--
29	$NiCl_2$(dme)	L2	B_2pin_2	CuI	**KOAc**	MeCN	60 °C	1%	α
30	$NiCl_2$(dme)	L2	B_2pin_2	CuI	**DIPEA**	MeCN	60 °C	7%	α
31	$NiCl_2$(dme)	L2	B_2pin_2	CuI	**TEA**	MeCN	60 °C	Trace	--
32	$NiCl_2$(dme)	L2	B_2pin_2	CuI	**DBU**	MeCN	60 °C	4%	α

No.	[cat]	[L]	[Red]	[Add]	[Base]	[Sc]	[T]	Yield[b]	α : β[c]
33	--	L1	B_2pin_2	CuI	K_2CO_3	MAc	60 °C	Trace	--
34	(4,4′-dMeObpy) $NiCl_2$	--	B_2pin_2	CuI	K_2CO_3	MAc	60 °C	Trace	--
35	(4,4′-dMeObpy) $NiCl_2$	L1	--	CuI	K_2CO_3	MAc	60 °C	Trace	--
36	(4,4′-dMeObpy) $NiCl_2$	L1	B_2pin_2	CuI	K_2CO_3	MAc	60 °C	Trace **w.o 4ÅMS**	--

[a]Reaction reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Catalyst (10 mol%, 0.1 equiv), Ligand (15 mol%, 0.15 equiv), Base (0.4 mmol, 2.0 equiv), Additive (0.6 mmol, 3.0 equiv), Reductive (0.6 mmol, 3.0 equiv) and 4Å Molecule Sieves (100 mg) in solvent (0.1 M, 1.0 mL) under argon. [b]Yields were determined by ^{19}F-NMR using trifluoromethyl benzene as the internal standard, and the number in parentheses is isolated yield. [c]The α : β ratio was determined by ^{1}H-NMR.

4. Synthesis and Characterization of Products

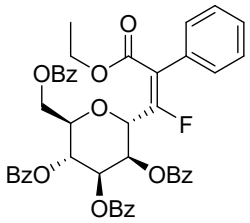
4.1. General Procedures for the Synthesis of *mono*-Fluoroalkyl Glycosides



To a 10 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, ***gem*-difluoroalkene 1** (0.2 mmol), **glycosyl bromide 2** (0.6 mmol), **$NiCl_2$(4,4'-*d*MeObpy)** (6.92 mg, 10 mol%), **L1** (10.69 mg, 15 mol%), **B_2pin_2** (152.36 mg, 0.6 mmol), **CuI** (114.27 mg, 0.6 mmol), **K_2CO_3** (127.36 mg, 0.6 mmol) and **4Å MS** (100 mg) were added subsequently, followed by addition of anhydrous methyl acetate (1.0 mL). After being sealed and stirred at 60 °C for 12 hours, the mixture was cooled to room temperature and filtered over a pad of Celite with EA (2 mL). The crude residue was concentrated under reduced pressure and purified by flash column chromatography to give the desired product.

4.2. Characterization of Products

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3a)

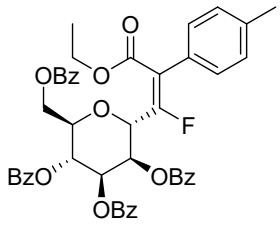


Chemical Formula: $C_{45}H_{37}FO_{11}$
Molecular Weight: 772.78

Compound **3a** was obtained following the general procedure in 72% yield (111 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 – 8.10 (m, 2H), 8.06 – 8.01 (m, 2H), 8.00 – 7.96 (m, 2H), 7.90 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.41 (m, 5H), 7.40 (s, 3H), 7.39 – 7.36 (m, 4H), 7.33 (t, *J* = 7.8 Hz, 3H), 6.13 – 6.08 (m, 2H), 5.89 (ddd, *J* = 8.6, 3.3, 1.1 Hz, 1H), 5.84 (dd, *J* = 23.1, 3.7 Hz, 1H), 4.75 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.60 (ddd, *J* = 14.0, 11.3, 3.5 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.71, 165.34 (d, *J* = 15.6

Hz), 165.03, 164.88, 164.74, 159.91 (d, J = 278.3 Hz), 133.16, 133.09, 132.99, 132.69, 130.32, 129.51, 129.47, 129.44, 129.40, 128.89, 128.87, 128.81, 128.52, 128.49, 128.49 (d, J = 46.2 Hz), 128.16, 128.11, 128.06, 128.05, 127.91, 119.92 (d, J = 15.9 Hz), 73.60 (d, J = 3.2 Hz), 71.16 (d, J = 22.5 Hz), 70.03 (d, J = 3.2 Hz), 66.46, 61.93, 61.61, 13.51. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.52 (d, J = 21.2 Hz). **HRMS m/z (ESI):** calcd for $C_{45}H_{41}FNO_{11}$ $(M + NH_4)^+$ 790.2658, found 790.2660.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(*p*-tolyl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3b)

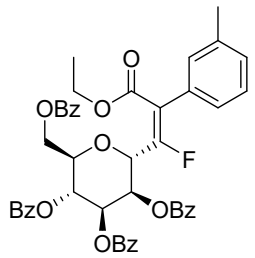


Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

Compound **3b** was obtained following the general procedure in 76% yield (120 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (800 MHz, $CDCl_3$)** δ 8.13 (dd, J = 8.4, 1.2 Hz, 2H), 8.03 (dd, J = 8.2, 1.4 Hz, 2H), 7.98 (dd, J = 8.4, 1.4 Hz, 2H), 7.90 (dd, J = 8.4, 1.3 Hz, 2H), 7.58 (qt, J = 7.4, 1.3 Hz, 2H), 7.52 (tt, J = 7.3, 1.3 Hz, 1H), 7.48 (tt, J = 7.3, 1.3 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.40 – 7.38 (m, 2H), 7.37 – 7.35 (m, 2H), 7.34 – 7.31 (m, 2H), 7.31 – 7.29 (m, 2H), 7.21 (d, J = 7.9 Hz, 2H), 6.13 – 6.08 (m, 2H), 5.89 (dd, J = 8.7, 3.3 Hz, 1H), 5.80 (dd, J = 22.9, 3.7 Hz, 1H), 4.75 (dd, J = 12.0, 3.0 Hz, 1H), 4.60 (dd, J = 12.0, 4.6 Hz, 1H), 4.57 (dt, J = 8.0, 2.3 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 166.14, 165.96 (d, J = 15.5 Hz), 165.44, 165.31, 165.16, 159.80 (d, J = 277.2 Hz), 138.57, 133.55, 133.47, 133.38, 133.08, 129.92, 129.88, 129.85, 129.81, 129.45, 129.25, 129.14, 129.13, 129.05, 128.96, 128.93, 128.90, 128.56, 128.51, 128.47, 128.45, 127.74, 120.29 (d, J = 15.8 Hz), 73.94 (d, J = 2.7 Hz), 71.68 (d, J = 22.9 Hz), 70.48 (d, J = 3.1 Hz), 69.04, 66.90, 62.37, 61.98, 21.34, 13.93. **^{19}F NMR (753 MHz, $CDCl_3$)** δ -103.55. **HRMS m/z (ESI):** calcd for $C_{46}H_{43}FNO_{11}$ $(M + NH_4)^+$ 804.2815, found 804.2813.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(*m*-

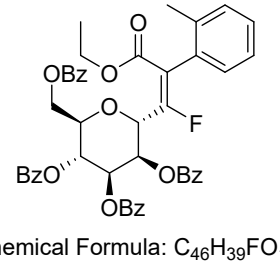
tolyl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3c)



Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

Compound **3c** was obtained following the general procedure in 80% yield (126 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.07 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.02 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.94 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.55 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.51 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 4H), 7.37 – 7.31 (m, 3H), 7.23 (dd, *J* = 14.3, 6.9 Hz, 3H), 6.18 – 6.13 (m, 2H), 5.93 (ddd, *J* = 8.7, 3.3, 1.2 Hz, 1H), 5.85 (dd, *J* = 22.9, 3.5 Hz, 1H), 4.79 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.67 – 4.63 (m, 1H), 4.63 – 4.59 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.71, 165.45 (d, *J* = 15.6 Hz), 165.04, 164.89, 164.74, 159.55 (d, *J* = 277.7 Hz), 137.59, 133.15, 133.08, 132.98, 132.68, 130.16, 129.51, 129.47, 129.44, 129.40, 128.98, 128.83, 128.53, 128.51, 128.16, 128.10, 128.06, 128.04, 127.82, 125.89, 125.87, 120.03 (d, *J* = 16.2 Hz), 73.55 (d, *J* = 2.6 Hz), 71.29 (d, *J* = 22.8 Hz), 70.08 (d, *J* = 3.2 Hz), 68.63, 66.45, 61.94, 61.60, 21.06, 13.52. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -103.10. **HRMS m/z (ESI):** calcd for $C_{46}H_{43}FNO_{11}$ $(M + NH_4)^+$ 804.2815, found 804.2816.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(*o*-tolyl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3d)

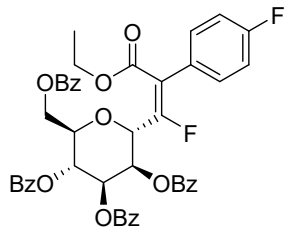


Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

Compound **3d** was obtained following the general procedure in 59% yield (93 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 (dd, *J* = 6.8, 1.6 Hz, 2H), 8.03 (dd, *J* = 6.9, 1.4 Hz, 2H), 7.98 (dd, *J* = 6.9, 1.4 Hz, 2H), 7.90 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.53 – 7.50 (m, 1H), 7.47 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.43 (td, *J* = 8.0, 1.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.33 (d, *J* = 8.2 Hz,

2H), 7.30 – 7.27 (m, 1H), 7.19 (dd, *J* = 14.8, 6.9 Hz, 3H), 6.14 – 6.08 (m, 2H), 5.90 (dd, *J* = 8.1, 3.9 Hz, 1H), 5.81 (dd, *J* = 22.9, 3.8 Hz, 1H), 4.76 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.64 – 4.55 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.13, 165.87 (d, *J* = 15.7 Hz), 165.45, 165.31, 165.16, 159.97 (d, *J* = 277.5 Hz), 138.01, 133.56, 133.50, 133.39, 133.10, 130.59, 129.93, 129.89, 129.86, 129.82, 129.40, 129.26, 128.96, 128.94, 128.58, 128.52, 128.48, 128.23, 126.31, 126.29, 120.47 (d, *J* = 15.7 Hz), 73.97, 71.69 (d, *J* = 22.9 Hz), 70.50 (d, *J* = 3.3 Hz), 69.04, 66.90, 62.37, 62.00, 21.47, 13.94. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.98 (d, *J* = 22.7 Hz). **HRMS m/z (ESI):** calcd for $C_{46}H_{43}FNO_{11}$ $(M + NH_4)^+$ 804.2815, found 804.2818.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-2-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3e)

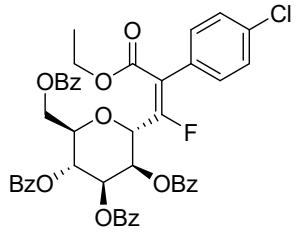


Chemical Formula: $C_{45}H_{36}F_2O_{11}$
Molecular Weight: 790.77

Compound **3e** was obtained following the general procedure in 73% yield (116 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.05 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.02 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.94 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.63 – 7.61 (m, 1H), 7.61 – 7.59 (m, 1H), 7.57 – 7.54 (m, 1H), 7.54 – 7.50 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.40 (d, *J* = 1.2 Hz, 3H), 7.36 (dd, *J* = 8.4, 7.6 Hz, 3H), 7.15 – 7.09 (m, 2H), 6.14 – 6.09 (m, 2H), 5.94 – 5.85 (m, 2H), 4.77 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.67 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.60 (qt, *J* = 4.9, 2.5 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.71, 165.13 (d, *J* = 15.3 Hz), 165.04, 164.87, 164.73, 162.25 (d, *J* = 248.5 Hz), 160.32 (d, *J* = 278.6 Hz), 133.18, 133.12, 133.04, 132.71, 130.85 (d, *J* = 3.5 Hz), 130.80 (d, *J* = 3.2 Hz), 129.49, 129.47, 129.43, 129.40, 128.74, 128.48, 128.46, 128.16, 128.12, 128.06, 126.24 (d, *J* = 3.5 Hz), 118.96 (d, *J* = 15.9 Hz), 115.06, 114.91, 73.69 (d, *J* = 2.9 Hz), 70.91 (d, *J* = 22.3 Hz), 69.92 (d, *J* =

2.9 Hz), 68.45, 66.49, 61.85, 61.69, 13.48. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.12, -112.58 (dd, *J* = 9.6, 5.0 Hz). **HRMS m/z (ESI):** calcd for $C_{45}H_{40}F_2NO_{11}$ $(M + NH_4)^+$ 808.2564, found 808.2563.

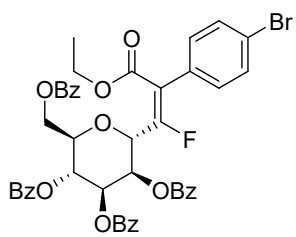
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-(4-chlorophenyl)-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3f)



Chemical Formula: $C_{45}H_{36}ClFO_{11}$
Molecular Weight: 807.22

Compound **3f** was obtained following the general procedure in 72% yield (118 mg) as colorless crystalline. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). m.p. < 50 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.06 – 8.04 (m, 2H), 8.03 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.95 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.61 (dt, *J* = 7.0, 1.5 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.52 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 2H), 7.40 (d, *J* = 3.1 Hz, 2H), 7.39 – 7.37 (m, 2H), 7.36 – 7.33 (m, 2H), 7.32 (d, *J* = 1.1 Hz, 1H), 6.13 – 6.08 (m, 2H), 5.94 – 5.87 (m, 2H), 4.78 (dd, *J* = 12.2, 3.4 Hz, 1H), 4.69 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.61 (dq, *J* = 4.6, 2.5 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.71, 165.31 (d, *J* = 102.3 Hz), 165.03, 164.87, 164.72, 160.62 (d, *J* = 279.2 Hz), 134.17, 133.20, 133.14, 133.06, 132.73, 130.59 (d), 130.33, 130.31, 129.87, 129.51, 129.50, 129.48, 129.43, 129.41, 129.27, 128.77, 128.72, 128.53, 128.48, 128.46, 128.29, 128.16, 128.13, 128.09, 128.07, 128.05, 127.93, 118.89 (d, *J* = 15.6 Hz), 73.74 (d, *J* = 2.9 Hz), 70.79 (d, *J* = 22.5 Hz), 69.88 (d, *J* = 2.9 Hz), 68.38, 66.51, 61.82, 61.74, 13.49. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.29. **HRMS m/z (ESI):** calcd for $C_{45}H_{40}ClFNO_{11}$ $(M + NH_4)^+$ 824.2268, found 824.2262.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-(4-bromophenyl)-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3g)

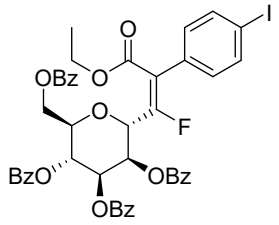


Chemical Formula: $C_{45}H_{36}BrFO_{11}$
Molecular Weight: 851.67

Compound **3g** was obtained following the general procedure in 72% yield (123 mg) as colorless oil. (Rf =

0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.00 (td, *J* = 8.2, 1.3 Hz, 4H), 7.92 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.54 – 7.52 (m, 2H), 7.49 (dd, *J* = 6.0, 1.5 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.39 (m, 3H), 7.38 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.10 – 6.04 (m, 2H), 5.90 – 5.81 (m, 2H), 4.74 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.65 (dd, *J* = 12.2, 4.9 Hz, 1H), 4.57 (d, *J* = 6.3 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.66, 164.97, 164.82, 164.78 (d, *J* = 15.4 Hz), 164.67, 160.61 (d, *J* = 279.4 Hz), 133.14, 133.07, 132.99, 132.66, 131.06, 130.55, 130.52, 129.52 (d, *J* = 74.9 Hz), 129.44, 129.43, 129.37, 129.36, 128.43, 128.42, 128.27 (d, *J* = 101.1 Hz), 128.11, 128.07, 128.03, 128.00, 122.36, 118.89 (d, *J* = 16.6 Hz), 73.85 – 73.44 (m), 70.68 (d, *J* = 21.2 Hz), 69.81 (d, *J* = 2.5 Hz), 68.30, 66.50, 61.78, 61.68, 13.43. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.09. **HRMS m/z (ESI):** calcd for $C_{45}H_{37}BrFNO_{11}$ $(M + H)^+$ 851.1498, found 851.1501.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-2-(4-iodophenyl)-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3h)

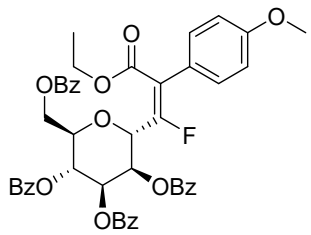


Chemical Formula: $C_{45}H_{36}FIO_{11}$
Molecular Weight: 898.67

Compound **3h** was obtained following the general procedure in 53% yield (96 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 – 8.12 (m, 2H), 8.02 (td, *J* = 8.3, 1.4 Hz, 4H), 7.96 – 7.93 (m, 2H), 7.63 – 7.58 (m, 2H), 7.57 – 7.53 (m, 3H), 7.51 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.42 – 7.37 (m, 4H), 7.37 – 7.35 (m, 1H), 7.28 – 7.26 (m, 2H), 6.11 – 6.06 (m, 2H), 5.92 – 5.85 (m, 2H), 4.76 (dd, *J* = 12.2, 3.4 Hz, 1H), 4.67 (dd, *J* = 12.2, 4.9 Hz, 1H), 4.61 – 4.56 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.11, 165.55 (d, *J* = 97.1 Hz), 165.43, 165.28, 165.12, 158.97 (d, *J* = 807.8 Hz), 133.60, 133.53, 133.45, 133.12, 131.52, 131.01, 130.98, 129.90, 129.89, 129.83, 129.82, 129.14, 128.89, 128.88, 128.57, 128.53, 128.49, 128.47, 122.82, 74.16 (d, *J* = 2.5 Hz), 71.15 (d, *J* = 22.8 Hz), 70.27 (d, *J* = 2.2 Hz), 68.77, 66.95, 62.24, 62.14, 13.89. **^{19}F NMR (471 MHz, $CDCl_3$)**

δ -100.86 (d, *J* = 22.3 Hz). **HRMS m/z (ESI):** calcd for $C_{45}H_{37}FIO_{11}$ $(M + H)^+$ 899.1359, found 899.1353.

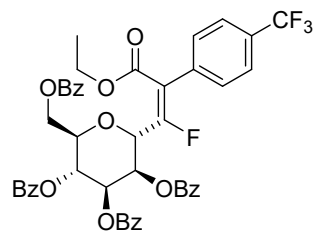
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-2-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3i)



Chemical Formula: $C_{46}H_{39}FO_{12}$
Molecular Weight: 802.80

Compound **3i** was obtained following the general procedure in 75% yield (120 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 – 8.12 (m, 2H), 8.05 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.03 – 7.98 (m, 2H), 7.93 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.60 (tdd, *J* = 7.2, 4.4, 1.3 Hz, 2H), 7.55 (td, *J* = 7.4, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.37 (m, 5H), 7.37 – 7.33 (m, 2H), 7.00 – 6.93 (m, 2H), 6.17 – 6.08 (m, 2H), 5.92 (ddd, *J* = 8.7, 3.3, 1.2 Hz, 1H), 5.79 (dd, *J* = 22.5, 3.6 Hz, 1H), 4.78 (dd, *J* = 11.3, 2.3 Hz, 1H), 4.66 – 4.56 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.72, 165.69 (d, *J* = 15.2 Hz), 165.04, 164.89, 164.75, 159.27, 158.80 (d, *J* = 276.6 Hz), 133.14, 133.07, 132.97, 132.67, 130.19, 130.17, 129.50, 129.46, 129.43, 129.39, 128.82, 128.52, 128.50, 128.15, 128.09, 128.05, 128.03, 122.46, 119.51 (d, *J* = 15.6 Hz), 113.38, 73.44 (d, *J* = 2.1 Hz), 71.38 (d, *J* = 23.1 Hz), 70.08 (d, *J* = 2.1 Hz), 68.64, 66.43, 61.93, 61.59, 54.91, 13.52. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -104.97 (d, *J* = 22.2 Hz). **HRMS m/z (ESI):** calcd for $C_{46}H_{43}FNO_{12}$ $(M + NH_4)^+$ 820.2764, found 820.2765.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3j)

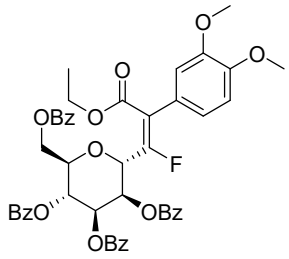


α : β = 6 : 5
Chemical Formula: $C_{46}H_{36}F_4O_{11}$
Molecular Weight: 840.78

Compound **3h** was obtained following the general procedure in 58% yield (93 mg) as colorless oil, *α* : *β* = 6 : 5. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz,**

$CDCl_3$) δ 8.13 (dd, *J* = 14.1, 7.7 Hz, 2H), 8.08 – 8.01 (m, 3H), 7.98 – 7.81 (m, 3H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 15.0, 7.8 Hz, 3H), 7.56 – 7.36 (m, 11H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.12 – 5.90 (m, 3H), 4.87 – 4.37 (m, 4H), 4.28 (dq, *J* = 41.1, 7.1 Hz, 2H), 1.27 (dt, *J* = 79.9, 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.12, 165.99, 165.42, 165.30, 165.27, 165.23, 165.12, 164.99, 164.01, 162.03 (d, *J* = 280.6 Hz), 159.53 (d, *J* = 283.8 Hz), 134.85 (d, *J* = 5.4 Hz), 133.68, 133.66, 133.63, 133.57, 133.50, 133.25, 133.15, 130.78 (dd, *J* = 57.3, 32.7 Hz), 130.16, 130.14, 129.92, 129.90, 129.86, 129.83, 129.80, 129.76, 129.66, 128.59, 128.55, 128.52, 128.48, 125.63, 125.60, 125.25, 125.22, 123.89 (dd, *J* = 272.3, 15.4 Hz), 119.63 (dd, *J* = 100.5, 14.5 Hz), 74.46 – 73.86 (m), 70.72 (dd, *J* = 34.4, 22.8 Hz), 70.18, 70.16, , 70.05 – 69.41 (m) 68.66, 68.42, 67.20, 67.01, 62.23, 62.19, 62.13, 62.10, 14.13, 13.88. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.76, -99.66, -100.22. **HRMS m/z (ESI):** calcd for $C_{46}H_{40}F_4NO_{11}$ $(M + NH_4)^+$ 858.2532, found 858.2538.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-(3,4-dimethoxyphenyl)-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3k)

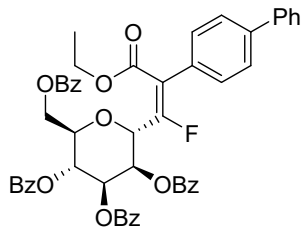


Chemical Formula: $C_{47}H_{41}FO_{13}$
Molecular Weight: 832.83

Compound **3k** was obtained following the general procedure in 51% yield (85 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.05 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.01 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.93 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.62 – 7.59 (m, 2H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.43 – 7.39 (m, 4H), 7.37 – 7.34 (m, 2H), 7.01 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.12 (q, *J* = 4.0 Hz, 2H), 5.94 – 5.74 (m, 2H), 4.78 (dd, *J* = 12.1, 3.1 Hz, 1H), 4.64 (dd, *J* = 12.1, 4.7 Hz, 1H), 4.61 – 4.57 (m, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.11, 165.77 (d, *J* = 69.9 Hz), 165.43,

165.29, 165.16, 159.20 (d, *J* = 276.6 Hz), 149.28, 148.65, 133.56, 133.49, 133.40, 133.08, 129.91, 129.88, 129.85, 129.81, 129.48 (d, *J* = 61.9 Hz), 128.77 (d, *J* = 42.0 Hz), 128.56, 128.51, 128.46, 123.03, 122.07 (d, *J* = 2.9 Hz), 112.36 (d, *J* = 4.1 Hz), 110.82, 73.92 (d, *J* = 2.3 Hz), 71.62 (d, *J* = 23.2 Hz), 70.65 – 70.00 (m), 68.95, 66.95, 62.27, 62.01, 55.97, 55.92, 13.95. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -105.00 (d, *J* = 20.7 Hz). **HRMS m/z (ESI):** calcd for $C_{47}H_{45}FNO_{13}$ $(M + NH_4)^+$ 850.2869, found 850.2872.

(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((*E*)-2-([1,1'-biphenyl]-4-yl)-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)-6-((benzoyloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3l)

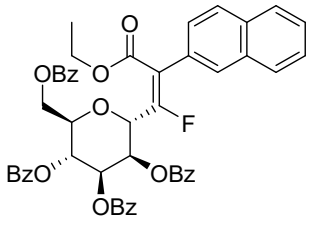


Chemical Formula: $C_{51}H_{41}FO_{11}$
Molecular Weight: 848.88

Compound **3l** was obtained following the general procedure in 82% yield (140 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.06 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.03 – 8.00 (m, 2H), 7.94 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.67 – 7.66 (m, 1H), 7.66 – 7.64 (m, 2H), 7.62 – 7.59 (m, 2H), 7.55 (tt, *J* = 7.6, 1.4 Hz, 2H), 7.52 – 7.49 (m, 4H), 7.47 – 7.44 (m, 3H), 7.43 – 7.41 (m, 3H), 7.40 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 6.16 – 6.12 (m, 2H), 5.94 (ddd, *J* = 8.6, 3.0, 1.1 Hz, 1H), 5.86 (dd, *J* = 22.8, 3.7 Hz, 1H), 4.79 (dd, *J* = 11.9, 2.8 Hz, 1H), 4.65 (dd, *J* = 12.0, 4.7 Hz, 1H), 4.63 – 4.58 (m, 1H), 4.29 (t, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.72, 165.38 (d, *J* = 15.3 Hz), 165.04, 164.88, 164.75, 159.81 (d, *J* = 278.3 Hz), 141.00, 140.07, 133.49 (d, *J* = 61.8 Hz), 133.16, 133.09, 133.00, 132.69, 129.51, 129.47, 129.44, 129.40, 129.38, 129.32, 129.29, 129.00 (d, *J* = 61.3 Hz), 128.50 (d, *J* = 4.3 Hz), 128.44, 128.16, 128.10, 128.06, 128.05, 127.21, 126.76, 126.62, 119.60 (d, *J* = 15.5 Hz), 71.23 (d, *J* = 22.6 Hz)., 70.03, 68.57, 66.45, 61.91, 61.71, 13.53. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.77 (d, *J* = 19.6 Hz). **HRMS m/z (ESI):** calcd for $C_{51}H_{45}FNO_{11}$ $(M + NH_4)^+$ 866.2971, found 866.2971.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-2-

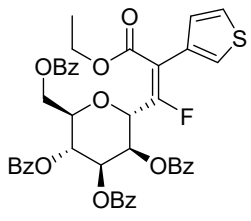
(naphthalen-2-yl)-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3m)



dr = 9 : 4
Chemical Formula: $C_{49}H_{39}FO_{11}$
Molecular Weight: 822.84

Compound **3m** was obtained following the general procedure in 70% yield (115 mg) as colorless oil, *dr* = 9:4. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.20 (ddd, *J* = 32.1, 8.3, 1.4 Hz, 2H), 8.13 – 8.06 (m, 3H), 8.01 (ddd, *J* = 14.4, 8.4, 1.4 Hz, 2H), 7.96 – 7.86 (m, 4H), 7.73 – 7.63 (m, 1H), 7.62 – 7.49 (m, 6H), 7.49 – 7.39 (m, 7H), 7.34 (dt, *J* = 22.0, 8.1 Hz, 2H), 6.69 – 5.89 (m, 4H), 4.92 – 3.91 (m, 5H), 1.25 (dt, *J* = 37.0, 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.65, 165.39 (d, *J* = 102.3 Hz), 165.30, 164.89, 164.75, 163.44, 160.15 (d, *J* = 278.3 Hz), 133.69, 133.29, 133.17, 133.15, 133.05 (d, *J* = 14.7 Hz), 133.02, 132.69, 132.68, 132.59 (d, *J* = 5.5 Hz), 129.77, 129.57, 129.53, 129.48, 129.45, 129.43, 129.41, 129.38, 128.70 (d, *J* = 33.8 Hz), 128.44, 128.39, 128.28, 128.16, 128.10, 128.09, 128.06, 128.05, 128.02, 127.91, 127.50, 127.26, 126.32, 126.25 (d, *J* = 3.2 Hz), 125.96, 119.97 (d, *J* = 15.9 Hz), 73.65 (d, *J* = 2.4 Hz), 71.16 (d, *J* = 22.8 Hz), 90.97, 70.78, 70.05 (d, *J* = 2.9 Hz), 69.60, 69.03, 65.74, 61.93, 61.67, 13.81, 13.52. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.54. **HRMS m/z (ESI):** calcd for $C_{49}H_{43}FNO_{11}$ $(M + NH_4)^+$ 840.2815, found 840.2818.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(thiophen-3-yl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3n)

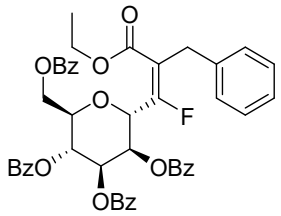


Chemical Formula: $C_{43}H_{35}FO_{11}S$
Molecular Weight: 778.80

Compound **3n** was obtained following the general procedure in 62% yield (96 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.18 – 8.12 (m, 2H), 8.05 (dd, *J* = 8.5, 1.2 Hz, 2H), 8.02 – 7.97 (m, 2H), 7.94 – 7.88 (m, 2H), 7.63 – 7.58 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.43 – 7.35 (m, 6H), 7.35 – 7.32 (m, 2H), 6.18 (t, *J* = 8.7 Hz, 1H), 6.14 (t, *J* = 3.0 Hz, 1H), 5.87 (dd, *J* = 8.8,

3.2 Hz, 1H), 5.62 (dd, *J* = 18.3, 3.3 Hz, 1H), 4.77 (dd, *J* = 12.1, 2.8 Hz, 1H), 4.58 – 4.48 (m, 2H), 4.34 (qd, *J* = 7.1, 2.4 Hz, 2H), 1.28 – 1.27 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.61, 165.43 (d, *J* = 16.3 Hz), 165.01, 164.83, 164.74, 153.54 (d, *J* = 546.9 Hz), 133.09, 133.04, 132.93, 132.61, 129.53, 129.45, 129.42, 129.40, 129.35, 128.77, 128.12, 128.04, 128.01, 127.98, 127.59 (d, *J* = 5.0 Hz), 125.57 (d, *J* = 6.8 Hz), 124.91, 115.32 (d, *J* = 14.1 Hz), 73.03, 70.15 (d), 68.48, 66.18, 61.81, 61.69, 29.26, 13.44. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -105.91 (d, *J* = 17.9 Hz). **HRMS m/z (ESI):** calcd for $C_{43}H_{36}FNO_{11}S$ $(M + H)^+$ 779.1957, found 779.1959.

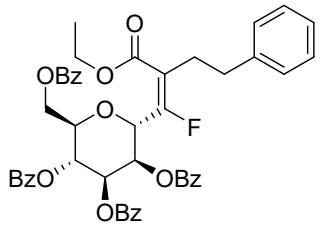
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-benzyl-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3o)



Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

Compound **3o** was obtained following the general procedure in 78% yield (122 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.04 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.96 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.94 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.56 (qd, *J* = 6.6, 1.4 Hz, 3H), 7.52 – 7.48 (m, 1H), 7.42 (td, *J* = 7.9, 4.4 Hz, 4H), 7.35 (t, *J* = 7.9 Hz, 4H), 7.19 – 7.12 (m, 5H), 6.05 (dd, *J* = 20.7, 3.6 Hz, 2H), 5.96 (d, *J* = 4.1 Hz, 2H), 4.75 (dd, *J* = 12.1, 5.9 Hz, 1H), 4.67 (dd, *J* = 12.1, 3.6 Hz, 1H), 4.61 (dq, *J* = 4.6, 3.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (dd, *J* = 14.6, 3.1 Hz, 1H), 3.73 (dd, *J* = 14.6, 4.3 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.15, 165.53 (d, *J* = 17.6 Hz), 165.40, 165.32, 165.06, 163.05 (d, *J* = 274.7 Hz), 137.97, 133.61, 133.43, 133.08, 129.94, 129.90, 129.83, 129.82, 129.18, 128.97, 128.55, 128.50, 128.46, 128.43, 126.43, 118.71 (d, *J* = 18.6 Hz), 74.35 (d, *J* = 3.3 Hz), 70.07 (d, *J* = 2.9 Hz), 69.93 (d, *J* = 22.2 Hz), 68.60, 67.45, 62.31, 61.52, 31.56 (d, *J* = 6.7 Hz), 13.87. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -100.87. **HRMS m/z (ESI):** calcd for $C_{46}H_{40}FO_{11}$ $(M + H)^+$ 787.2549, found 787.2549.

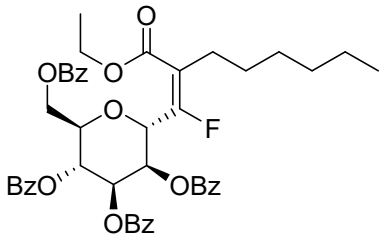
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-(ethoxycarbonyl)-1-fluoro-4-phenylbut-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3p)



Chemical Formula: $C_{47}H_{41}FO_{11}$
Molecular Weight: 800.83

Compound **3p** was obtained following the general procedure in 75% yield (120 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 – 8.14 (m, 2H), 8.05 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.61 (tdd, *J* = 7.3, 2.7, 1.4 Hz, 2H), 7.56 (dt, *J* = 7.0, 1.6 Hz, 1H), 7.51 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.44 – 7.39 (m, 4H), 7.38 – 7.31 (m, 4H), 7.26 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.08 (td, *J* = 8.2, 1.4 Hz, 1H), 6.01 – 5.89 (m, 3H), 4.74 – 4.65 (m, 2H), 4.45 (qd, *J* = 4.9, 2.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.87 – 2.77 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.17, 165.88 (d, *J* = 17.6 Hz), 165.46, 165.34, 165.10, 163.21 (d, *J* = 274.7 Hz), 140.84, 133.58, 133.48, 133.40, 133.12, 129.91, 129.84, 129.82, 129.31, 129.02, 128.65, 128.57, 128.54, 128.47, 128.43, 126.24, 118.62 (d, *J* = 18.8 Hz), 74.03 (d, *J* = 3.3 Hz), 70.92 (d, *J* = 22.4 Hz), 70.41 (d, *J* = 3.8 Hz), 69.05, 67.14, 62.54, 61.52, 34.77, 27.97 (d, *J* = 5.7 Hz), 14.03. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -99.00. **HRMS m/z (ESI):** calcd for $C_{47}H_{42}FO_{11}$ $(M + H)^+$ 801.2706, found 801.2705.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3q)

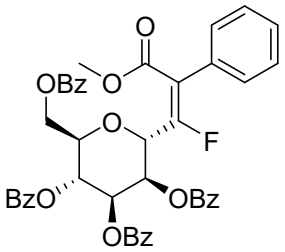


Chemical Formula: $C_{45}H_{45}FO_{11}$
Molecular Weight: 780.84

Compound **3q** was obtained following the general procedure in 75% yield (117 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.04 (td, *J* = 8.4, 1.3 Hz, 4H), 7.95 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.62 – 7.54 (m, 3H), 7.51 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.47 – 7.34 (m, 8H), 6.08 – 6.01 (m, 2H), 5.99 – 5.88 (m, 2H), 4.76 – 4.67 (m, 2H), 4.63 – 4.58 (m,

1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.36 (m, 2H), 1.46 (p, *J* = 7.2 Hz, 2H), 1.38 – 1.27 (m, 6H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.94 – 0.85 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.24 (d, *J* = 17.6 Hz), 166.15, 165.45, 165.34, 165.10, 162.15 (d, *J* = 272.8 Hz), 133.57, 133.43, 133.39, 133.08, 129.91, 129.89, 129.86, 129.82, 129.28, 129.00, 128.99, 128.52, 128.46, 128.44, 119.85 (d, *J* = 19.1 Hz), 74.13 (d, *J* = 3.3 Hz), 70.70 (d, *J* = 22.4 Hz), 70.35 (d, *J* = 3.3 Hz), 68.96, 67.26, 62.49, 61.40, 31.50, 28.92, 28.43, 25.94 (d, *J* = 5.7 Hz), 22.51, 14.10, 14.01. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.87. **HRMS m/z (ESI):** calcd for $C_{45}H_{45}FNaO_{11}$ $(M + Na)^+$ 803.2838, found 803.2840.

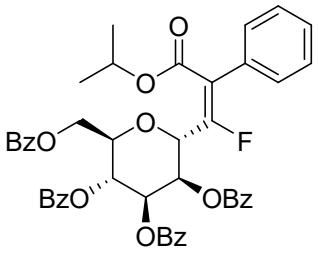
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-1-fluoro-3-methoxy-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3r)



Chemical Formula: $C_{44}H_{35}FO_{11}$
Molecular Weight: 758.75

Compound **3r** was obtained following the general procedure in 71% yield (107 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.07 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.03 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.98 – 7.94 (m, 2H), 7.64 – 7.59 (m, 2H), 7.58 – 7.54 (m, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.46 (m, 2H), 7.45 (q, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 2.7 Hz, 3H), 7.42 (d, *J* = 1.9 Hz, 2H), 7.40 (dd, *J* = 2.1, 0.9 Hz, 2H), 7.37 (dd, *J* = 8.3, 7.4 Hz, 3H), 6.19 – 6.10 (m, 2H), 5.98 – 5.86 (m, 2H), 4.79 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.69 (dd, *J* = 12.2, 4.8 Hz, 1H), 4.62 (ddt, *J* = 8.1, 5.9, 2.3 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.81 (d, *J* = 15.7 Hz), 165.69, 164.99, 164.87, 164.71, 160.18 (d, *J* = 278.5 Hz), 133.15, 133.07, 132.99, 132.68, 129.49, 129.47 (d, *J* = 179.8 Hz), 129.44, 129.42, 129.38, 128.85, 128.82, 128.49, 128.46, 128.21, 128.13, 128.09, 128.04, 127.94, 119.65 (d, *J* = 16.7 Hz), 73.64 (d, *J* = 2.9 Hz), 70.99 (d, *J* = 22.9 Hz), 69.95 (d, *J* = 2.9 Hz), 68.48, 66.48, 61.79, 52.45. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.77. **HRMS m/z (ESI):** calcd for $C_{45}H_{41}FNO_{11}$ $(M + H)^+$ 759.2236, found 759.2235.

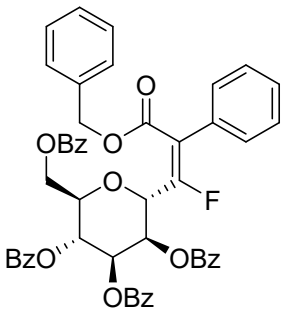
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-1-fluoro-3-isopropoxy-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3s)



Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

Compound **3s** was obtained following the general procedure in 70% yield (110 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.06 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.01 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.94 – 7.92 (m, 2H), 7.61 (td, *J* = 7.4, 1.3 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.48 – 7.44 (m, 2H), 7.43 (d, *J* = 4.6 Hz, 3H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.40 (dd, *J* = 2.2, 1.4 Hz, 3H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.37 – 7.33 (m, 2H), 6.17 – 6.11 (m, 2H), 5.94 (ddd, *J* = 8.5, 3.2, 1.2 Hz, 1H), 5.84 (dd, *J* = 24.0, 3.7 Hz, 1H), 5.14 (dq, *J* = 11.8, 6.0 Hz, 1H), 4.86 – 4.77 (m, 1H), 4.65 – 4.60 (m, 2H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.68, 165.02, 164.85, 164.83 (d, *J* = 15.3 Hz), 164.72, 159.64 (d, *J* = 278.0 Hz), 133.10, 133.04, 132.93, 132.64, 130.41, 129.56 (d, *J* = 69.6 Hz), 129.46, 129.43, 129.40, 129.36, 128.86, 128.83, 128.51, 128.48, 128.13, 128.06, 128.02, 127.99, 127.82, 120.20 (d, *J* = 15.7 Hz), 73.53 (d, *J* = 3.3 Hz), 71.21 (d, *J* = 22.4 Hz), 70.04 (d, *J* = 3.3 Hz), 69.42, 68.60, 66.48, 62.04, 21.17, 20.90. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -103.26 (d, *J* = 23.9 Hz). **HRMS m/z (ESI):** calcd for $C_{46}H_{40}FO_{11}$ $(M + H)^+$ 787.2549, found 787.2550.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-(benzyloxy)-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3t)

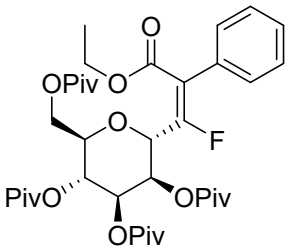


Chemical Formula: $C_{50}H_{39}FO_{11}$
Molecular Weight: 834.85

Compound **3t** was obtained following the general procedure in 75% yield (125 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.8 Hz, 2H), 8.01 (t, *J* = 8.2 Hz, 4H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H),

7.42 (d, *J* = 2.9 Hz, 4H), 7.41 – 7.39 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.24 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.19 – 7.17 (m, 2H), 6.16 – 6.09 (m, 2H), 5.92 – 5.77 (m, 2H), 5.27 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.3 Hz, 1H), 4.79 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.60 (dd, *J* = 12.1, 4.5 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.69 (d, *J* = 114.0 Hz), 166.09, 165.59 (d, *J* = 15.7 Hz), 165.44, 165.29, 165.07, 160.46 (d, *J* = 279.4 Hz), 149.85, 135.58 (d, *J* = 111.1 Hz), 135.02, 133.55, 133.47, 133.38, 133.09, 130.51, 129.93, 129.87, 129.83, 129.29, 129.27, 129.21, 129.08, 128.94, 128.91, 128.77, 128.66, 128.62, 128.54, 128.51, 128.48, 128.45, 128.40, 128.34, 128.33, 128.29, 123.77, 120.08 (d, *J* = 16.2 Hz), 73.89 (d, *J* = 2.1 Hz), 71.73 (d, *J* = 22.9 Hz), 70.51 (d, *J* = 3.3 Hz), 68.89, 67.67, 66.80, 62.25. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.57 (d, *J* = 21.9 Hz). **HRMS m/z (ESI):** calcd for $C_{50}H_{39}FNaO_{11}$ $(M + Na)^+$ 857.2369, found 857.2367.

(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)-6-((pivaloyloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (4a)



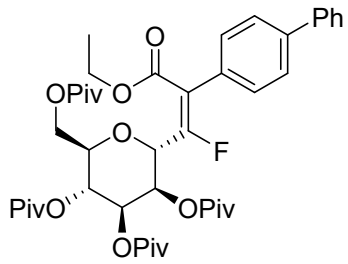
Chemical Formula: $C_{37}H_{53}FO_{11}$
Molecular Weight: 692.82

Compound **4a** was obtained following the general procedure in 60% yield (83 mg) as colorless oil. (Rf = 0.4, PE/EA = 16 : 1 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 5H), 5.61 (dd, *J* = 4.9, 2.8 Hz, 1H), 5.49 (dd, *J* = 23.8, 4.8 Hz, 1H), 5.40 (td, *J* = 9.0, 4.7 Hz, 2H), 4.44 (dd, *J* = 13.0, 6.1 Hz, 1H), 4.26 (dd, *J* = 15.9, 7.1 Hz, 2H), 4.21 – 4.16 (m, 2H), 1.27 (d, *J* = 5.0 Hz, 18H), 1.25 (t, 3H), 1.21 (d, *J* = 4.1 Hz, 18H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 177.68, 176.57, 176.36, 176.30, 165.25 (d, *J* = 15.6 Hz), 159.90 (d, *J* = 278.3 Hz), 130.39, 129.63 (d, *J* = 23.7 Hz), 128.79, 128.76, 128.40 (d, *J* = 13.0 Hz), 128.05, 127.83, 119.78 (d, *J* = 16.2 Hz), 73.56 (d, *J* = 2.2 Hz), 69.96 (d, *J* = 21.0 Hz), 68.81, 67.15, 65.51, 61.38, 60.89, 38.49, 38.47, 38.42, 26.73, 26.69, 26.63. **^{19}F NMR (471**

MHz, $CDCl_3$) δ -103.86. **HRMS m/z (ESI):** calcd for $C_{37}H_{54}FO_{11}$ $(M + H)^+$ 693.3645, found 693.3647.

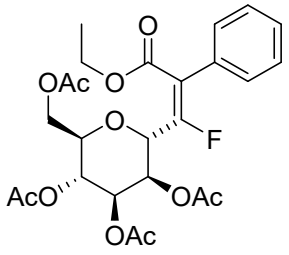
(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((*E*)-2-([1,1'-biphenyl]-4-yl)-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)-6-((pivaloyloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (4b)



Chemical Formula: $C_{43}H_{57}FO_{11}$
Molecular Weight: 768.92

Compound **4b** was obtained following the general procedure in 67% yield (103 mg) as colorless oil. (Rf = 0.4, PE/EA = 16 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (dd, *J* = 8.6, 2.2 Hz, 4H), 7.50 – 7.41 (m, 4H), 7.41 – 7.36 (m, 1H), 5.63 (dd, *J* = 4.9, 2.8 Hz, 1H), 5.49 (dd, *J* = 23.5, 4.8 Hz, 1H), 5.45 – 5.36 (m, 2H), 4.45 (dd, *J* = 12.9, 6.0 Hz, 1H), 4.37 – 4.23 (m, 2H), 4.23 – 4.17 (m, 2H), 1.31 – 1.28 (m, 12H), 1.27 (s, 9H), 1.22 (d, *J* = 4.6 Hz, 18H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.10, 176.99, 176.79, 176.71, 165.71 (d, *J* = 15.3 Hz), 160.24 (d, *J* = 278.3 Hz), 141.32, 140.46, 129.72, 129.64, 129.61, 128.83, 127.59, 127.14, 126.97, 119.90 (d, *J* = 15.7 Hz), 73.98, 70.50 (d, *J* = 20.5 Hz), 69.25, 67.56, 65.93, 61.89, 61.30, 38.92, 38.90, 38.85, 27.16, 27.12, 27.06, 13.97. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -103.97. **HRMS m/z (ESI):** calcd for $C_{43}H_{57}FNaO_{11}$ $(M + Na)^+$ 791.3777, found 791.3778.

(2*R*,3*R*,4*S*,5*S*)-2-(acetoxymethyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4c)

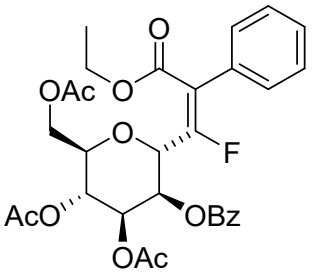


α : β = 6 : 5
Chemical Formula: $C_{25}H_{29}FO_{11}$
Molecular Weight: 524.49

Compound **4c** was obtained following the general procedure in 71% yield (111 mg) as colorless oil, *α* : *β* = 6 : 5. (Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 – 7.32 (m, 5H), 5.63 – 5.48 (m, 1H), 5.41 (dddd, *J* = 50.6, 8.0, 3.4, 1.1 Hz, 1H), 5.23 (dtd, *J* = 39.9, 7.7, 1.2 Hz, 1H), 4.60 – 4.35 (m, 1H),

4.35 – 3.97 (m, 5H), 2.18 – 2.10 (m, 6H), 2.09 – 1.99 (m, 6H), 1.30 (dt, *J* = 23.0, 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.18, 170.05, 169.18, 169.12, 165.21 (d, *J* = 15.8 Hz), 169.05, 169.00, 164.34 – 156.03 (m), 130.59 (d, *J* = 5.9 Hz), 130.20, 128.94, 128.91, 128.75, 128.72, 128.43, 128.11, 128.05, 127.78, 121.08 – 118.92 (m), 73.28 (dd, *J* = 15.1, 2.2 Hz), 70.21 (dd, *J* = 37.3, 23.3 Hz), 68.59 (dd, *J* = 24.4, 3.8 Hz), 67.21, 67.14, 65.99, 65.95, 61.51, 61.39, 61.33, 61.31, 20.32, 20.29, 20.27, 20.23, 20.17, 20.06, 13.62, 13.48. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.72, -103.37. **HRMS m/z (ESI):** calcd for $C_{25}H_{29}FNaO_{11}$ $(M + Na)^+$ 547.1586, found 547.1589.

(2*R*,3*R*,4*S*,5*S*)-2-(acetoxymethyl)-5-(benzoyloxy)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (4d)

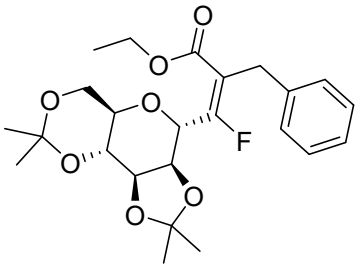


α : β = 11 : 10
Chemical Formula: $C_{30}H_{31}FO_{11}$
Molecular Weight: 586.57

Compound **4d** was obtained following the general procedure in 72% yield (85 mg) as colorless oil, *α* : *β* = 11 : 10. (Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 – 8.09 (m, 1H), 8.02 – 7.98 (m, 1H), 7.70 – 7.28 (m, 8H), 5.81 (dt, *J* = 47.2, 3.7 Hz, 1H), 5.73 – 4.66 (m, 3H), 4.45 – 4.08 (m, 5H), 2.19 – 2.08 (m, 6H), 2.00 (d, *J* = 49.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 170.67, 170.55, 169.72, 169.63, 169.61, 169.60, 165.69 (d, *J* = 15.5 Hz), 165.16, 165.05, 164.65, 161.39 – 157.17 (m), 133.62, 133.61, 131.05 (d, *J* = 5.7 Hz), 130.72, 129.91, 129.84, 129.44, 129.43, 129.27, 129.25, 129.08, 128.95, 128.65, 128.58, 128.55, 128.26, 120.71 (dd, *J* = 163.8, 14.6 Hz), 74.05 – 73.43 (m), 70.91, 70.79, 69.30 (dd, *J* = 15.0, 3.7 Hz), 68.43, 68.39, 66.47, 62.03, 61.90, 61.82, 24.86, 20.78, 20.76, 20.69, 20.57, 14.12, 13.94. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.83 (d, *J* = 22.6 Hz), -102.97 (d, *J* = 27.0 Hz). **HRMS m/z (ESI):** calcd for $C_{30}H_{32}FO_{11}$ $(M + H)^+$ 587.1923, found 587.1927.

Ethyl (*E*)-3-fluoro-2-phenyl-3-((3a*S*,4*S*,5a*R*,9a*R*,9b*S*)-2,2,8,8-

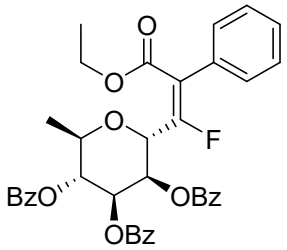
tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-d][1,3]dioxin-4-yl)acrylate (4e)



Chemical Formula: $C_{24}H_{31}FO_7$
Molecular Weight: 450.50

Compound **4e** was obtained following the general procedure in 72% yield (65 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.24 – 7.19 (m, 3H), 5.66 (d, *J* = 32.2 Hz, 1H), 4.91 (d, *J* = 1.9 Hz, 2H), 4.41 (ddd, *J* = 12.0, 5.9, 1.1 Hz, 1H), 4.20 (qq, *J* = 7.0, 3.7 Hz, 2H), 4.16 – 4.08 (m, 3H), 3.75 (dd, *J* = 14.6, 3.1 Hz, 1H), 3.67 (dd, *J* = 14.6, 4.3 Hz, 1H), 1.56 (s, 3H), 1.49 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.41, 166.22, 166.02, 165.87, 138.59, 138.58, 128.80 (d, *J* = 68.2 Hz), 128.46, 126.40, 115.64 (d, *J* = 18.6 Hz), 113.27, 109.25, 85.02, 83.91 (d, *J* = 3.9 Hz), 81.28, 80.78 (d, *J* = 20.1 Hz), 73.55, 66.94, 61.39, 31.10 (d, *J* = 6.8 Hz), 26.95, 26.29, 25.21, 24.82, 14.00. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.25 (dd, *J* = 32.2, 3.9 Hz). **HRMS m/z (ESI):** calcd for $C_{24}H_{35}FNO_7$ $(M + NH_4)^+$ 468.2392, found 468.2393.

(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-phenylprop-1-en-1-yl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (4f)

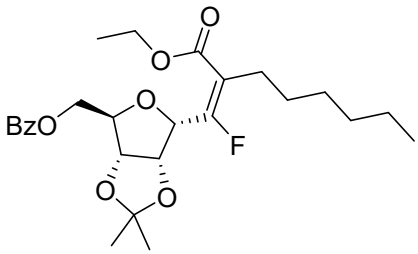


Chemical Formula: $C_{38}H_{33}FO_9$
Molecular Weight: 652.67

Compound **4f** was obtained following the general procedure in 73% yield (95 mg) as colorless oil. (Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 7.9 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 15.9, 7.4 Hz, 4H), 7.44 – 7.41 (m, 5H), 7.41 – 7.38 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 6.06 (t, *J* = 3.8 Hz, 1H), 5.86 (dd, *J* = 8.2, 3.5 Hz, 1H), 5.80 (dd, *J* = 22.4, 4.1 Hz, 1H), 5.65 (t, *J* = 7.8 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.24 (t, *J* = 7.1

Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.99 (d, *J* = 15.3 Hz), 165.62, 165.41, 165.32, 160.39 (d, *J* = 278.9 Hz), 133.49, 133.46, 133.32, 130.87, 129.94, 129.85, 129.78, 129.32, 129.23, 129.21, 129.14, 128.56, 128.50, 128.43, 128.30, 120.07 (d, *J* = 16.2 Hz), 71.97, 71.68, 70.72 (d, *J* = 22.9 Hz), 70.38 (d, *J* = 2.9 Hz), 68.94, 61.83, 17.66, 13.95. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.60 (d, *J* = 22.3 Hz). **HRMS m/z (ESI):** calcd for $C_{38}H_{34}FO_9$ $(M + H)^+$ 653.2181, found 653.2182.

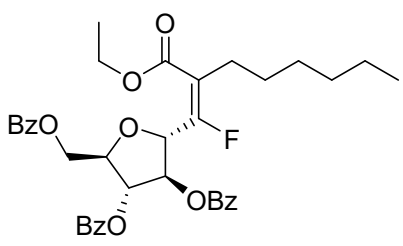
((3a*R*,4*R*,6*S*,6a*R*)-6-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl benzoate (4g)



Chemical Formula: $C_{26}H_{35}FO_7$
Molecular Weight: 478.56

Compound **4g** was obtained following the general procedure in 61% yield (58 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 – 8.06 (m, 2H), 7.62 – 7.56 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.61 (dd, *J* = 29.9, 3.6 Hz, 1H), 4.88 (dd, *J* = 6.4, 3.7 Hz, 1H), 4.75 (dd, *J* = 6.4, 4.0 Hz, 1H), 4.53 (dd, *J* = 11.7, 4.6 Hz, 1H), 4.46 (dd, *J* = 11.7, 5.1 Hz, 1H), 4.41 (q, *J* = 4.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.43 – 2.30 (m, 2H), 1.61 (s, 3H), 1.47 – 1.40 (m, 2H), 1.39 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.32 – 1.23 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.53 (d, *J* = 18.1 Hz), 166.31, 162.69 (d, *J* = 268.0 Hz), 133.12, 129.81, 129.77, 128.39, 118.64 (d, *J* = 19.9 Hz), 114.50, 82.99, 82.77, 82.75, 82.41, 80.13 (d, *J* = 23.2 Hz), 64.38 (d, *J* = 2.4 Hz), 61.19, 31.47, 28.97, 28.46, 27.48, 25.81 (d, *J* = 5.8 Hz), 25.59, 22.53, 14.15, 14.06. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -108.40 (dd, *J* = 29.8, 3.8 Hz). **HRMS m/z (ESI):** calcd for $C_{26}H_{36}FO_7$ $(M + H)^+$ 479.2440, found 479.2444.

(2*R*,3*R*,4*S*,5*S*)-2-((benzoyloxy)methyl)-5-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)tetrahydrofuran-3,4-diyl dibenzoate (4h)

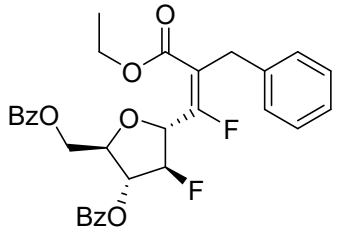


Chemical Formula: $C_{37}H_{39}FO_9$
Molecular Weight: 646.71

Compound **4h** was obtained following the general

procedure in 66% yield (86 mg) as colorless oil. (Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.12 – 8.04 (m, 6H), 7.64 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 (dt, *J* = 15.5, 7.8 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 2H), 5.96 – 5.86 (m, 2H), 5.77 (dd, *J* = 4.2, 2.7 Hz, 1H), 4.76 – 4.70 (m, 3H), 4.14 (qd, *J* = 7.0, 0.9 Hz, 2H), 2.44 (td, *J* = 7.9, 3.4 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.37 – 1.28 (m, 6H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.94 – 0.84 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.41 (d, *J* = 18.1 Hz), 166.25, 165.65, 165.33, 163.19 (d, *J* = 270.8 Hz), 133.60, 133.54, 133.11, 129.95, 129.93, 129.86, 129.67, 129.04 (d, *J* = 4.3 Hz), 128.54, 128.51, 128.36, 118.23 (d, *J* = 19.4 Hz), 82.57, 80.26, 79.11 (d, *J* = 23.4 Hz), 78.96, 64.33, 61.10, 31.53, 28.96, 28.50, 25.80 (d, *J* = 5.7 Hz), 22.54, 14.09, 14.04. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -106.65 (d, *J* = 27.6 Hz). **HRMS m/z (ESI):** calcd for $C_{37}H_{40}FO_9$ $(M + H)^+$ 647.2651, found 647.2655.

((2*R*,3*R*,4*S*,5*S*)-3-(benzoyloxy)-5-((*E*)-2-benzyl-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)-4-fluorotetrahydrofuran-2-yl)methyl benzoate (4i)

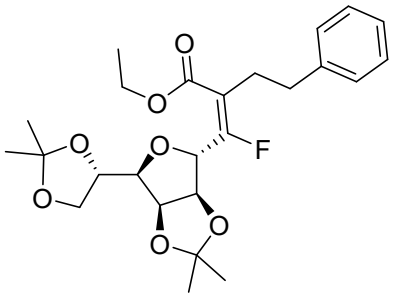


Chemical Formula: $C_{31}H_{28}F_2O_7$
Molecular Weight: 550.55

Compound **4i** was obtained following the general procedure in 65% yield (72 mg) as colorless oil. (Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.08 (td, *J* = 7.9, 1.4 Hz, 4H), 7.67 – 7.61 (m, 1H), 7.60 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.28 – 7.18 (m, 5H), 5.73 (ddd, *J* = 19.1, 3.5, 2.1 Hz, 1H), 5.53 (ddd, *J* = 51.5, 3.2, 2.1 Hz, 1H), 5.35 (ddd, *J* = 24.7, 21.0, 3.3 Hz, 1H), 4.75 – 4.61 (m, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.83 – 3.66 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 166.18, 165.60, 165.06, 158.26 (dd, *J* = 276.6, 9.2 Hz), 137.39 (d, *J* = 2.7 Hz), 133.82, 133.25, 129.97, 129.80, 129.13 (d, *J* = 167.1 Hz), 128.63, 128.61, 128.45, 128.23, 126.78, 116.08 (d, *J* = 7.2 Hz), 97.45 (d, *J* = 189.2 Hz), 82.63 (d, *J* = 3.4 Hz), 79.01 (dd, *J* = 30.1, 25.9 Hz), 78.67 (d, *J* = 28.9 Hz), 63.60, 61.29, 32.76, 14.06. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -107.70 (d, *J* = 24.9 Hz), -186.04 (dt, *J* = 51.4, 20.1 Hz). **HRMS m/z (ESI):** calcd for $C_{31}H_{29}F_2O_7$ $(M + H)^+$

551.1876, found 551.1876.

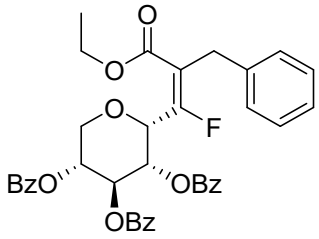
Ethyl (*E*)-2-(((3a*S*,4*S*,6*R*,6a*S*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)fluoromethylene)-4-phenylbutanoate (4j)



Chemical Formula: $C_{25}H_{33}FO_7$
Molecular Weight: 464.53

Compound **4j** was obtained following the general procedure in 69% yield (64 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.19 (dd, *J* = 8.0, 1.5 Hz, 2H), 5.55 (d, *J* = 31.7 Hz, 1H), 4.80 (dd, *J* = 6.1, 3.9 Hz, 1H), 4.69 (d, *J* = 6.0 Hz, 1H), 4.37 (dt, *J* = 7.1, 5.1 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.13 – 4.05 (m, 2H), 4.00 (dt, *J* = 7.6, 3.7 Hz, 1H), 2.83 – 2.70 (m, 2H), 2.69 – 2.59 (m, 2H), 1.54 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.19 (d, *J* = 275.1 Hz), 166.23 (d, *J* = 18.6 Hz), 141.03, 128.64, 128.31, 128.48 (d, *J* = 4.8 Hz), 126.10, 115.38 (d, *J* = 19.1 Hz), 113.12, 109.22, 84.96, 83.74 (d, *J* = 3.8 Hz), 81.15, 80.63 (d, *J* = 20.5 Hz), 73.52, 66.91, 61.28, 34.84, 29.72, 27.48 (d, *J* = 5.7 Hz), 26.94, 26.22, 25.22, 24.74, 14.16. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -100.90 (dd, *J* = 31.5, 3.8 Hz). **HRMS m/z (ESI):** calcd for $C_{25}H_{33}FNaO_7$ $(M + Na)^+$ 487.2103, found 487.2105.

(2*S*,3*R*,4*S*,5*R*)-2-((*E*)-2-benzyl-3-ethoxy-1-fluoro-3-oxoprop-1-en-1-yl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (4k)

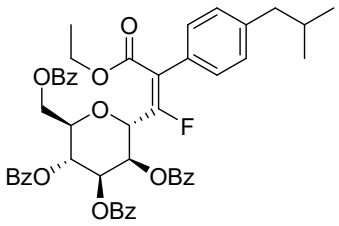


Chemical Formula: $C_{38}H_{33}FO_9$
Molecular Weight: 652.67

Compound **4k** was observed trace following the general procedure via LC-MS. **HRMS m/z (ESI):** calcd for $C_{38}H_{37}FNO_9$ $(M + NH_4)^+$ 670.2447, found 670.2452.

4.3. Characterization of Further Transformations

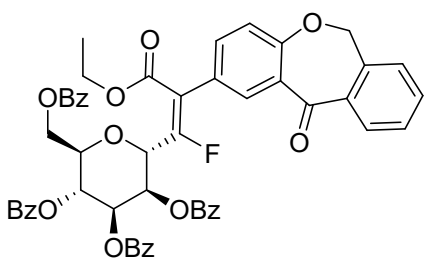
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-2-(4-isobutylphenyl)-3-oxoprop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (5a)



Chemical Formula: $C_{49}H_{45}FO_{11}$
Molecular Weight: 828.89

Compound **5a** was obtained following the general procedure in 76% yield (126 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.09 – 8.06 (m, 2H), 8.04 – 8.00 (m, 2H), 7.94 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.33 (m, 8H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.21 – 6.13 (m, 2H), 5.98 – 5.90 (m, 1H), 5.81 (dd, *J* = 22.2, 3.5 Hz, 1H), 4.83 – 4.77 (m, 1H), 4.66 – 4.59 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.54 (d, *J* = 7.2 Hz, 2H), 1.93 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.69, 165.60 (d, *J* = 15.7 Hz), 165.01, 164.86, 164.74, 158.96 (d, *J* = 277.5 Hz), 141.92, 133.10, 133.04, 132.94, 132.64, 129.48, 129.43, 129.42, 129.37, 128.82, 128.65, 128.53, 128.52, 128.50, 128.13, 128.07, 128.03, 128.00, 127.50, 119.88 (d, *J* = 15.7 Hz), 73.43 (d, *J* = 2.9 Hz), 71.44 (d, *J* = 22.9 Hz), 70.10 (d, *J* = 3.3 Hz), 68.65, 66.40, 61.92, 61.56, 44.79, 29.74, 21.98, 13.48. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -104.18 (d, *J* = 22.2 Hz). **HRMS m/z (ESI):** calcd for $C_{46}H_{43}FNO_{11}$ $(M + H)^+$ 829.3019, found 829.3020.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((benzoyloxy)methyl)-6-((*E*)-3-ethoxy-1-fluoro-3-oxo-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (5b)

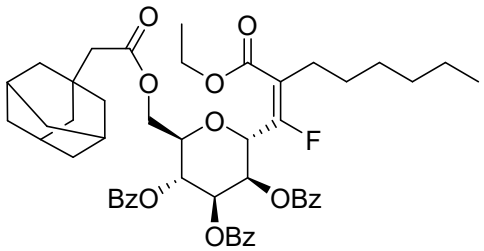


Chemical Formula: $C_{53}H_{41}FO_{13}$
Molecular Weight: 904.90

Compound **5b** was obtained following the general procedure in 36% yield (122 mg) as colorless oil.

(Rf = 0.4, PE/EA = 4 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 2.4 Hz, 1H), 8.18 – 8.13 (m, 2H), 8.04 (ddd, *J* = 15.4, 8.4, 1.3 Hz, 4H), 7.94 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.55 – 7.51 (m, 3H), 7.49 – 7.45 (m, 2H), 7.42 (d, *J* = 7.3 Hz, 4H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.11 (q, *J* = 3.7 Hz, 2H), 5.95 – 5.86 (m, 2H), 5.27 (s, 2H), 4.77 (dd, *J* = 12.1, 3.1 Hz, 1H), 4.70 – 4.60 (m, 2H), 4.26 (qd, *J* = 7.0, 0.8 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.57, 166.13, 165.64 (d, *J* = 53.2 Hz), 165.40, 165.29, 165.13, 161.18, 140.54, 136.22 (d), 135.28, 133.54, 133.48, 133.21 (d, *J* = 26.5 Hz), 133.08, 132.85, 129.93, 129.90, 129.86, 129.82, 129.53, 129.40, 128.93 (d, *J* = 4.3 Hz), 128.56, 128.50, 128.47, 128.45, 127.89, 124.90 (d, *J* = 38.1 Hz), 120.85, 74.10 (d), 73.62, 70.40 (d), 70.36, 68.88, 66.93, 62.31, 62.14, 29.71, 13.93. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.65 (d, *J* = 21.5 Hz). **HRMS m/z (ESI):** calcd for $C_{53}H_{42}FO_{13}$ $(M + H)^+$ 905.2604, found 905.2604.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-((2-(adamantan-1-yl)acetoxy)methyl)-6-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (5c)

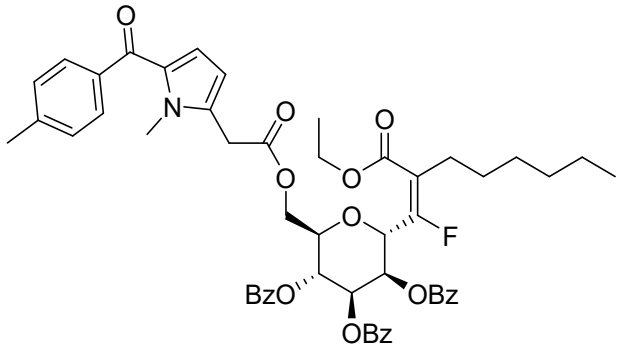


Chemical Formula: $C_{50}H_{57}FO_{11}$
Molecular Weight: 852.99

Compound **5c** was obtained following the general procedure in 62% yield (106 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (ddd, *J* = 15.3, 8.3, 1.4 Hz, 4H), 7.98 – 7.94 (m, 2H), 7.62 – 7.56 (m, 2H), 7.53 (td, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.38 (t, *J* = 7.8 Hz, 2H), 5.97 – 5.88 (m, 3H), 5.79 (t, *J* = 7.0 Hz, 1H), 4.61 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.46 (q, *J* = 6.3 Hz, 1H), 4.32 (dd, *J* = 12.1, 3.7 Hz, 1H), 4.24 (qq, *J* = 7.0, 3.7 Hz, 2H), 2.42 (dddd, *J* = 25.1, 13.2, 6.5, 3.7 Hz, 2H), 2.12 (s, 2H), 1.95 – 1.91 (m, 3H), 1.68 (d, *J* = 11.8 Hz, 3H), 1.60 (s, 5H), 1.60 (s, 3H), 1.40 (q, *J* = 7.4 Hz, 2H), 1.33 – 1.20 (m, 10H), 0.90 – 0.84 (m, 3H). **^{13}C NMR (151**

MHz, $CDCl_3$) δ 171.32, 166.16 (d, *J* = 17.8 Hz), 165.33, 165.27, 165.07, 162.01 (d, *J* = 273.1 Hz), 133.56, 133.44, 133.41, 129.93, 129.89, 129.83, 129.27, 129.03, 129.00, 128.53, 128.49, 128.46, 119.82 (d, *J* = 19.1 Hz), 74.08 (d, *J* = 2.3 Hz), 70.02 – 69.86 (m), 69.61 (d, *J* = 22.2 Hz), 68.53, 67.66, 61.59, 61.31, 48.70, 42.25, 36.66, 32.75, 31.49, 28.90, 28.58, 28.39, 25.88 (d, *J* = 5.9 Hz)., 22.47, 14.07, 14.04. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.99. **HRMS m/z (ESI):** calcd for $C_{50}H_{57}FNaO_{11}$ $(M + Na)^+$ 875.3777, found 875.3776.

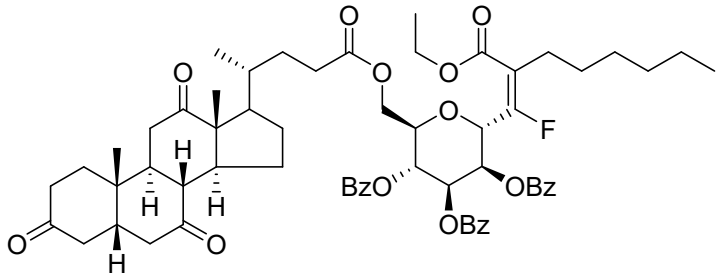
(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)-6-((2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetoxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (5d)



Chemical Formula: $C_{53}H_{54}FNO_{12}$
Molecular Weight: 916.01

Compound **5d** was obtained following the general procedure in 54% yield (99 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.57 – 7.45 (m, 7H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.13 (d, *J* = 4.0 Hz, 1H), 6.11 – 6.03 (m, 2H), 5.94 (d, *J* = 1.9 Hz, 1H), 5.92 (t, *J* = 2.5 Hz, 1H), 4.73 (ddd, *J* = 9.4, 4.6, 2.6 Hz, 1H), 4.47 (dd, *J* = 12.4, 4.7 Hz, 1H), 4.42 – 4.34 (m, 3H), 3.93 (s, 3H), 3.85 – 3.72 (m, 2H), 2.44 (s, 3H), 2.37 – 2.28 (m, 2H), 1.50 – 1.47 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.36 – 1.28 (m, 7H), 0.90 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 185.94, 170.91, 169.02, 166.11 (d, *J* = 14.9 Hz), 165.54, 165.28, 165.13, 159.34 (d, *J* = 292.3 Hz), 141.89, 137.33, 133.92, 133.90, 133.73, 133.35, 131.49, 130.20, 129.93, 129.82, 129.80, 129.77, 129.75, 129.46, 129.24, 128.85, 128.73, 128.69, 128.66, 128.60, 128.53, 128.50, 128.38, 122.24, 109.56, 70.97, 97.21 (d, *J* = 3.6 Hz), 95.93 (d, *J* = 30.1 Hz), 69.59 (d, *J* = 66.9 Hz), 69.25, 68.98, 66.15, 63.02, 61.03, 33.12, 32.36, 31.57, 29.01, 28.83, 25.39, 22.61, 21.54, 14.51, 14.09. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -75.37 (t, *J* = 3.2 Hz). **HRMS m/z (ESI):** calcd for $C_{53}H_{55}FNO_{12}$ $(M + H)^+$ 916.3703, found 916.3705.

(2*S*,3*R*,4*S*,5*S*,6*R*)-2-((*E*)-2-(ethoxycarbonyl)-1-fluorooct-1-en-1-yl)-6-((((*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-10,13,17-trimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (5e)

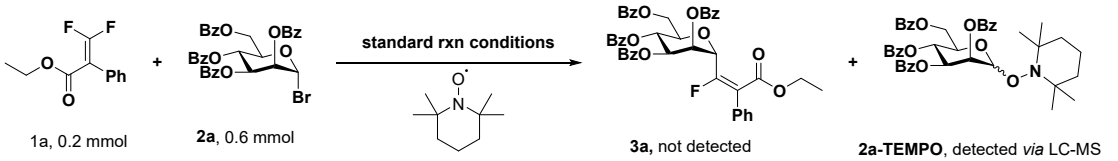


Chemical Formula: $C_{62}H_{73}FO_{14}$
Molecular Weight: 1061.25

Compound **5e** was obtained following the general procedure in 42% yield (89 mg) as colorless oil. (Rf = 0.4, PE/EA = 8 : 1 (v/v)). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.7 Hz, 4H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.53 (t, *J* = 6.9 Hz, 2H), 7.45 (td, *J* = 7.8, 3.6 Hz, 4H), 7.37 (t, *J* = 7.9 Hz, 2H), 5.98 – 5.94 (m, 1H), 5.93 – 5.85 (m, 2H), 5.81 (t, *J* = 7.5 Hz, 1H), 4.55 (dd, *J* = 11.9, 6.0 Hz, 1H), 4.44 (qd, *J* = 5.5, 2.8 Hz, 1H), 4.34 (dd, *J* = 11.8, 3.7 Hz, 1H), 4.24 (td, *J* = 7.2, 2.1 Hz, 2H), 2.96 – 2.83 (m, 4H), 2.47 – 2.40 (m, 3H), 2.39 – 2.30 (m, 6H), 2.29 – 2.22 (m, 4H), 2.16 (d, *J* = 12.8 Hz, 2H), 2.04 (d, *J* = 2.4 Hz, 1H), 2.02 – 1.97 (m, 3H), 1.88 – 1.83 (m, 2H), 1.42 (s, 3H), 1.27 (d, *J* = 5.2 Hz, 6H), 1.26 – 1.24 (m, 6H), 1.07 (s, 3H), 0.88 – 0.84 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 211.89, 209.05, 208.68, 173.64, 169.84 (d, *J* = 930.6 Hz), 165.35, 165.28, 165.06, 161.97 (d, *J* = 272.7 Hz), 133.57, 133.49, 133.40, 129.89, 129.80, 129.74, 129.61 (d, *J* = 87.7 Hz), 129.00, 128.53, 128.50, 128.47, 119.88 (d, *J* = 19.3 Hz), 74.01 (d), 70.02 (d), 68.65, 67.50, 62.16, 61.35, 56.90, 51.73, 49.01, 46.87, 45.68, 45.55, 45.00, 42.81, 38.64, 36.51, 36.03, 35.43, 35.31, 31.48, 31.22, 30.68 (d, *J* = 120.1 Hz), 30.27, 29.72, 28.90, 28.39, 27.53, 25.92 (d, *J* = 5.6 Hz), 25.14, 22.49, 21.93, 18.63, 14.29 (d, *J* = 6.8 Hz), 14.08, 14.05, 11.84. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.66. **HRMS m/z (ESI):** calcd for $C_{62}H_{74}FO_{14}$ $(M + H)^+$ 1061.5057, found 1061.5062.

5. Mechanism Study Experiment

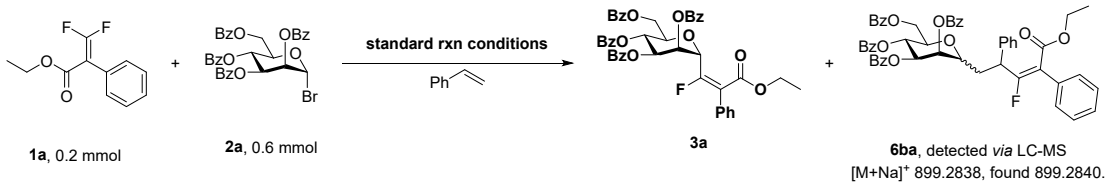
5.1. Radical trap experiment



To a 10 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, ***gem*-difluoroalkene 1a** (0.2 mmol), **glycosyl bromide 2a** (0.6 mmol), **$NiCl_2$(4,4'-*d*MeObpy)** (6.92 mg, 10 mol%), **L1** (10.69 mg, 15 mol%), **B_2pin_2** (152.36 mg, 0.6 mmol), **CuI** (114.27 mg, 0.6 mmol), **K_2CO_3** (127.36 mg, 0.6 mmol), **4 Å MS** (100 mg) and **TEMPO** (0.6 mmol, 3.0 equiv.) were added subsequently, followed by addition of anhydrous methyl acetate (1.0 mL). After being sealed and stirred at 60 °C for 12 hours, the mixture was cooled to room temperature and filtered over a pad of Celite with EA (2 mL). The crude residue was concentrated under reduced pressure and detected by LC-MS, showing only **2a-TEMPO** complex without desired **3a**.

2a-TEMPO: HRMS m/z (ESI): calcd for $C_{43}H_{46}NO_{10}$ $(M + H)^+$ 736.3116, found 736.3119.

5.2. Radical relay experiment

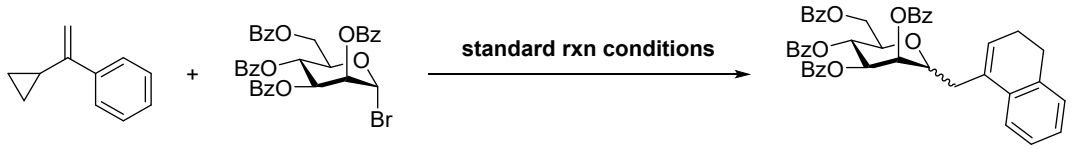


To a 10 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, ***gem*-difluoroalkene 1a** (0.2 mmol), **glycosyl bromide 2a** (0.6 mmol), **$NiCl_2$(4,4'-*d*MeObpy)** (6.92 mg, 10 mol%), **L1** (10.69 mg, 15 mol%), **B_2pin_2** (152.36 mg, 0.6 mmol), **CuI** (114.27 mg, 0.6 mmol), **K_2CO_3** (127.36 mg, 0.6 mmol), **4 Å MS** (100 mg) and **styrene** (0.2 mmol, 3.0 equiv.) were added subsequently, followed by addition of anhydrous methyl acetate (1.0 mL). After being sealed and stirred at 60 °C for 12 hours,

the mixture was cooled to room temperature and filtered over a pad of Celite with EA (2 mL). The crude residue was concentrated under reduced pressure and purified by flash column chromatography to give the product **3a** (26.3 mg, 15%) and **6ba** (30.9 mg, 20%).

6ba: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 7.95 (m, 6H), 7.88 – 7.82 (m, 2H), 7.64 – 7.30 (m, 21H), 7.27 – 7.23 (m, 1H), 6.15 – 6.09 (m, 1H), 5.89 – 5.79 (m, 1H), 5.78 – 5.68 (m, 1H), 5.26 – 5.14 (m, 1H), 4.76 – 4.45 (m, 3H), 4.29 – 4.16 (m, 3H), 2.86 – 2.41 (m, 2H), 1.24 – 1.17 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.44 – 165.26 (m), 133.58, 133.52, 133.45, 133.16, 133.11, 130.21, 130.03, 129.98, 129.95, 129.89, 129.83, 129.68, 129.22, 129.09, 129.03, 128.77, 128.69, 128.65, 128.59, 128.53, 128.44, 128.32, 128.13, 128.09, 127.85, 127.76, 73.99, 72.07 – 71.73 (m), 70.72, 70.51 – 70.23 (m), 67.55, 63.17, 61.57 – 61.37 (m), 42.45 – 41.80 (m), 31.37, 31.22, 29.85, 14.44 – 13.98 (m), 14.25, 14.18. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -93.27 (d, *J* = 34.9 Hz), -97.16 (d, *J* = 33.9 Hz). HRMS m/z (ESI): calcd for $C_{53}H_{45}FNaO_{11}$ $(M + Na)^+$ 899.2838, found 899.2840.

5.3. Radical clock experiment



6a, 0.2 mmol **2a**, 0.6 mmol **6aa**, detected *via* LC-MS $[M+Na]^+$ 745.2408, found 745.2402.

To a 10 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, **(1-cyclopropylvinyl)benzene 6a** (0.2 mmol), **glycosyl bromide 2a** (0.6 mmol), **$NiCl_2$(4,4'-*d*MeObpy)** (6.92 mg, 10 mol%), **L1** (10.69 mg, 15 mol%), **B_2pin_2** (152.36 mg, 0.6 mmol), **CuI** (114.27 mg, 0.6 mmol), **K_2CO_3** (127.36 mg, 0.6 mmol) and **4 Å MS** (100 mg) were added subsequently, followed by addition of anhydrous methyl acetate (1.0 mL). After being sealed and stirred at 60 °C for 12 hours, the mixture was cooled to room temperature and filtered over a pad of Celite with EA (2 mL). The crude

residue was concentrated under reduced pressure and detected by LC-MS, showing desired product **6aa** was afforded.

6aa: HRMS m/z (ESI): calcd for $C_{45}H_{38}NaO_9$ $(M + Na)^+$ 745.2408, found 745.2402.

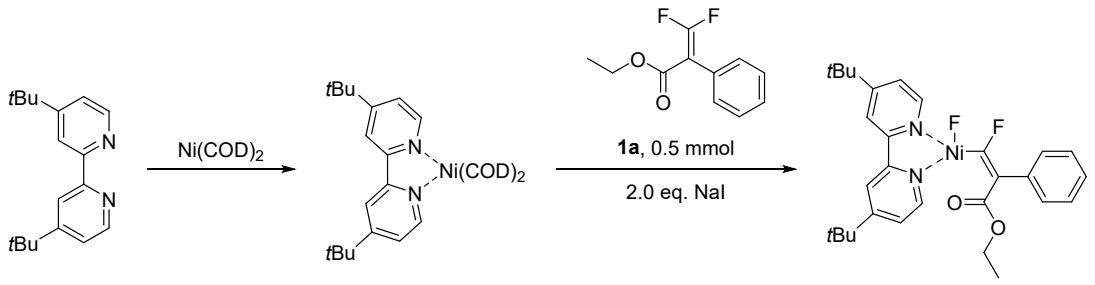
5.4. Control experiment

1v, 0.2 mmol **2a**, 0.6 mmol

1u, 0.2 mmol **2a**, 0.6 mmol

To a 10 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, **(2,2-difluorovinyl)benzene 1v** or **2,2-difluoro-1-phenylvinyl 4-methylbenzenesulfonate 1u** (0.2 mmol), **glycosyl bromide 2a** (0.6 mmol), **$NiCl_2$(4,4'-*d*MeObpy)** (6.92 mg, 10 mol%), **L1** (10.69 mg, 15 mol%), **B_2pin_2** (152.36 mg, 0.6 mmol), **CuI** (114.27 mg, 0.6 mmol), **K_2CO_3** (127.36 mg, 0.6 mmol) and **4 Å MS** (100 mg) were added subsequently, followed by addition of anhydrous methyl acetate (1.0 mL). After being sealed and stirred at 60 °C for 12 hours, the mixture was cooled to room temperature and filtered over a pad of Celite with EA (2 mL). The crude residue was concentrated under reduced pressure and detected by TLC, showing no desired product was afforded.

5.5. Characterization of nickel intermediates



Ni-1a-dtbppy detected via GC-MS
[M] 538.1936 found 538.1941

To a 25 mL Schlenk tube with a magnetic stirring bar in glove box charged with argon, **Ni(COD)$_2$** (138.0 mg, 0.5 mmol) and **4,4'-di-*tert*-butyl-2,2'-bipyridine** (134.0 mg, 0.5 mmol) were added, followed by addition of anhydrous THF (5.0 mL). After being sealed and stirred at room temperature for 24 hours, the mixture turned into purple solution. Then, ***gem*-difluoroalkene 1a** (125.6 mg, 0.5 mmol) and **NaI** (150 mg, 1.0 mmol) were added. After being sealed and stirred at 60 °C for another 9 hours, the mixture was cooled to room temperature and evaporated to remove solvent without further purification, and the desired intermediate **Ni-1a-dtbbpy** was detected by GC-MS.

Ni-1a-dtbbpy: HRMS m/z (GC): calcd for $C_{29}H_{34}N_2O_2F_2Ni$ (M) 538.1936, found 538.1941.

6. References

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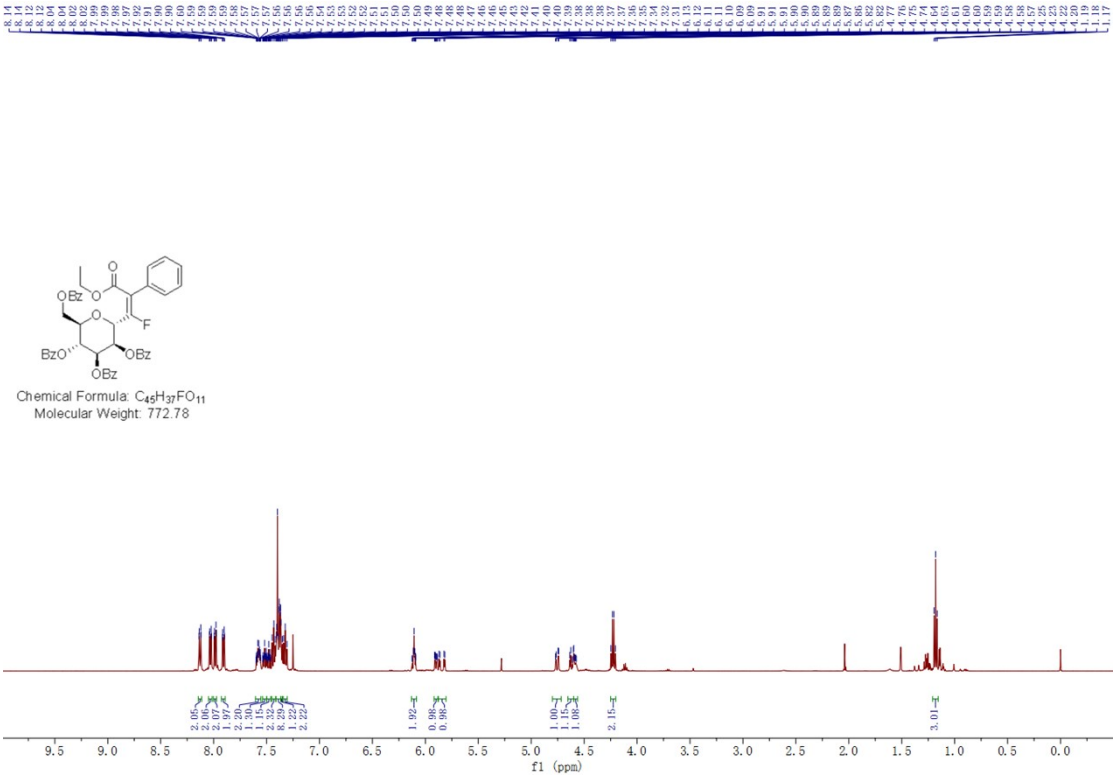
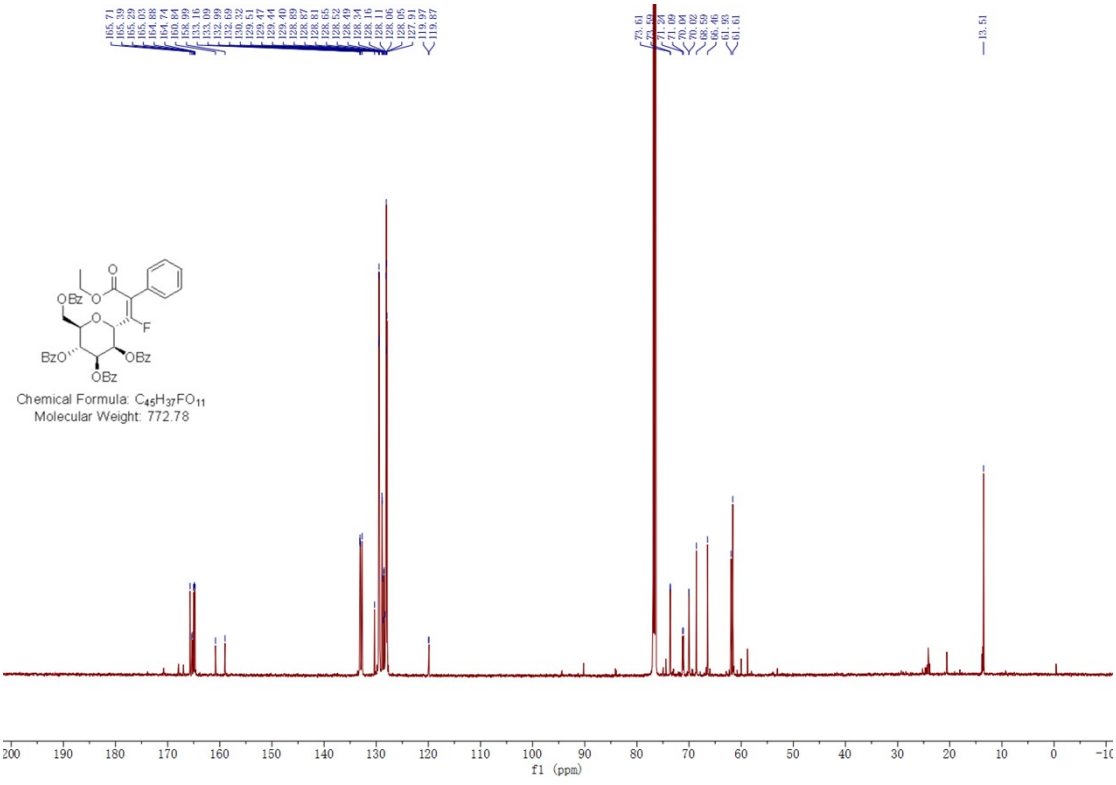
7. NMR Spectra

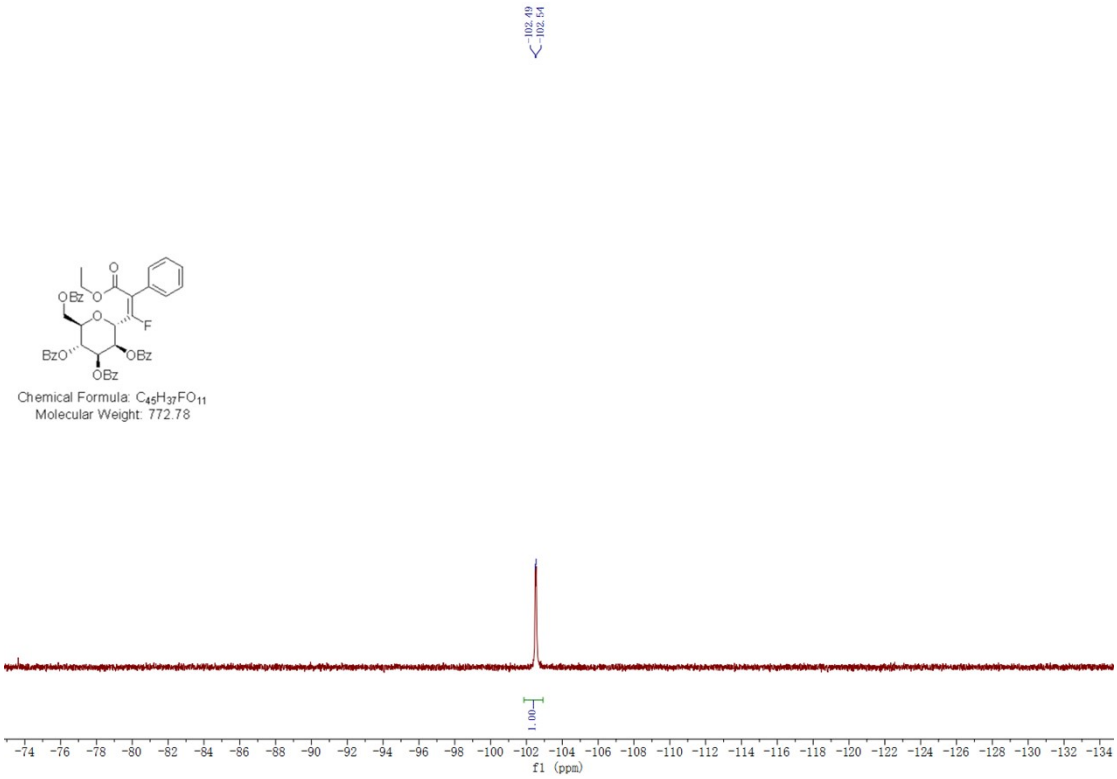
^{1}H NMR (500 MHz, Chloroform-*d*) of **3a**



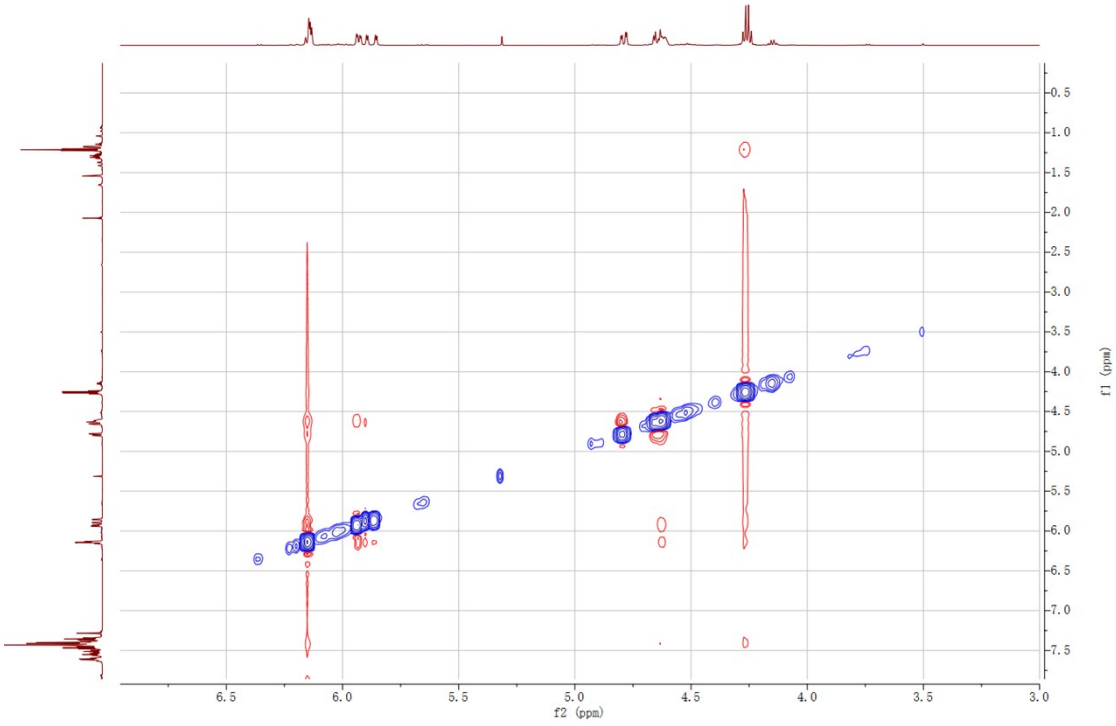
^{13}C NMR (151 MHz, Chloroform-*d*) of **3a**



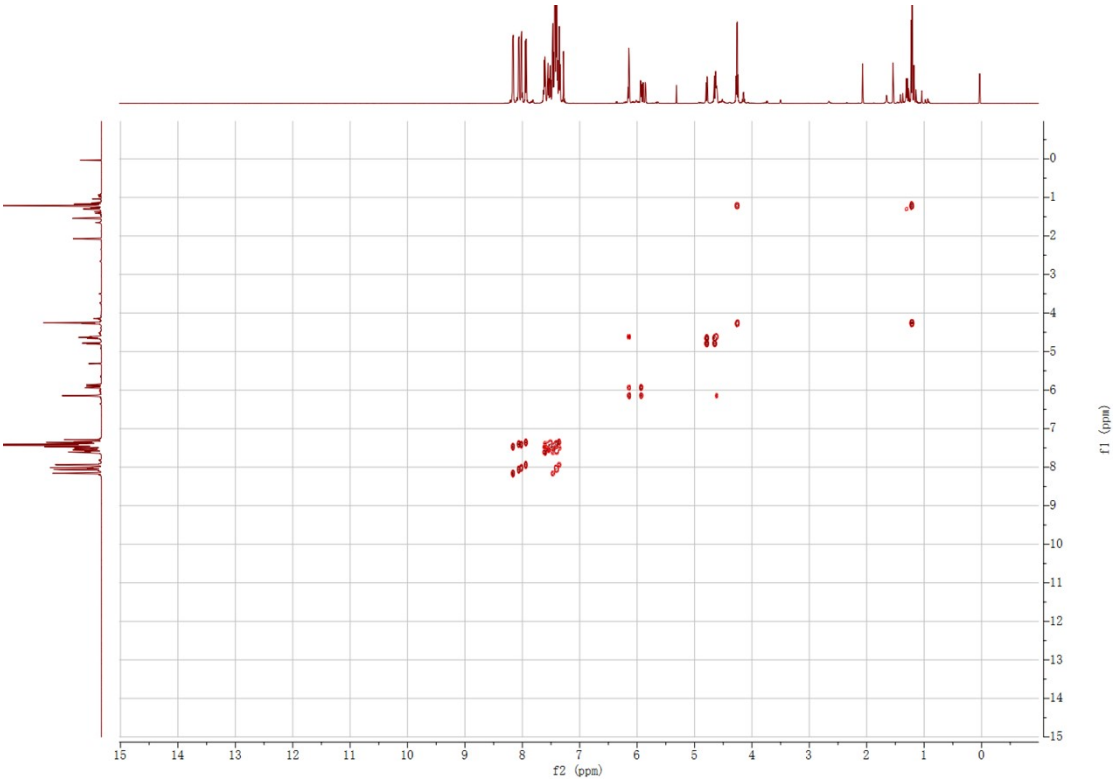
^{19}F NMR (471 MHz, Chloroform-*d*) of **3a**



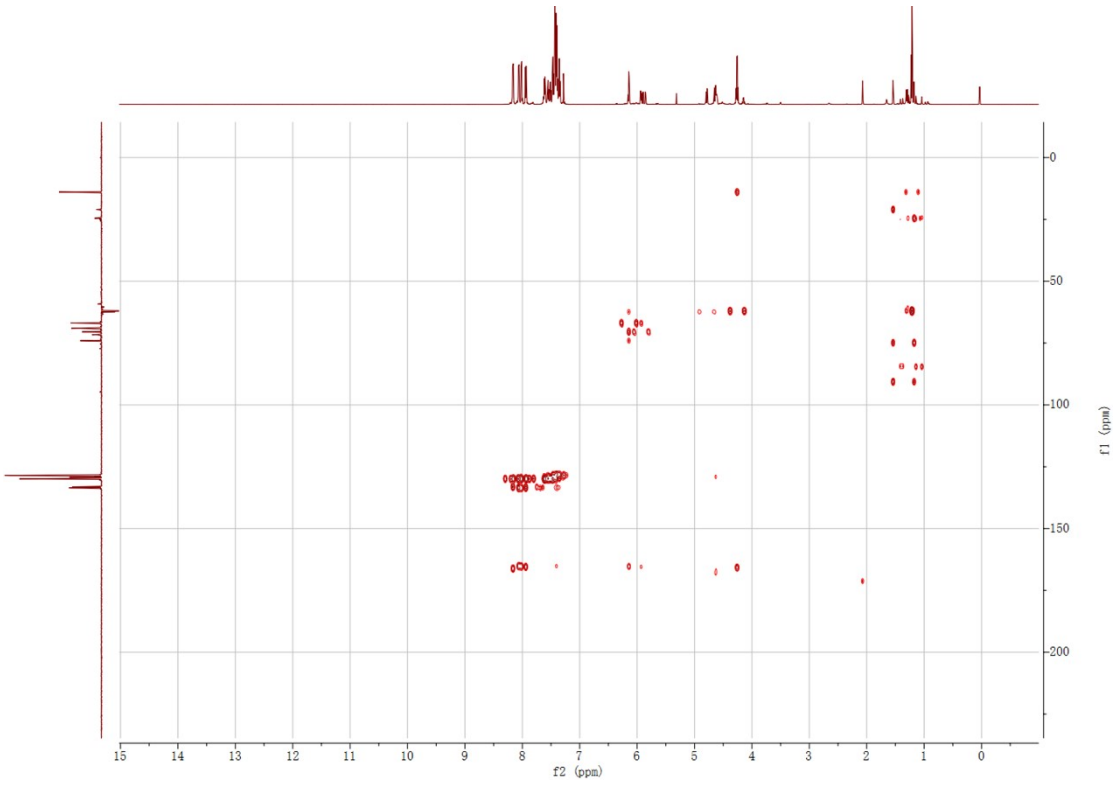
^{1}H-^{1}H NOESY of **3a**



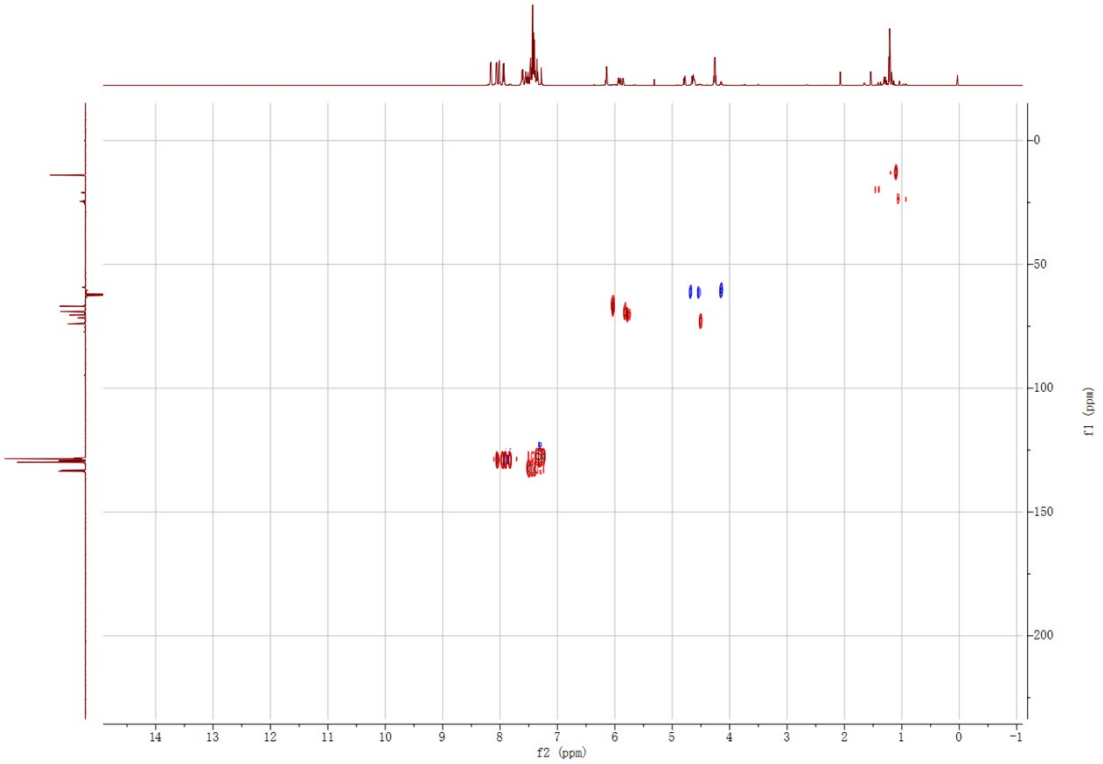
^{1}H-^{1}H COSY of **3a**



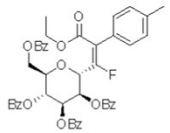
^{1}H-^{13}C HMBC of **3a**



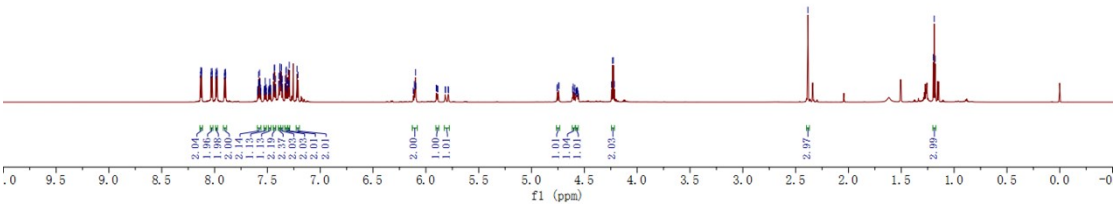
^{1}H-^{13}C HSQC of **3a**



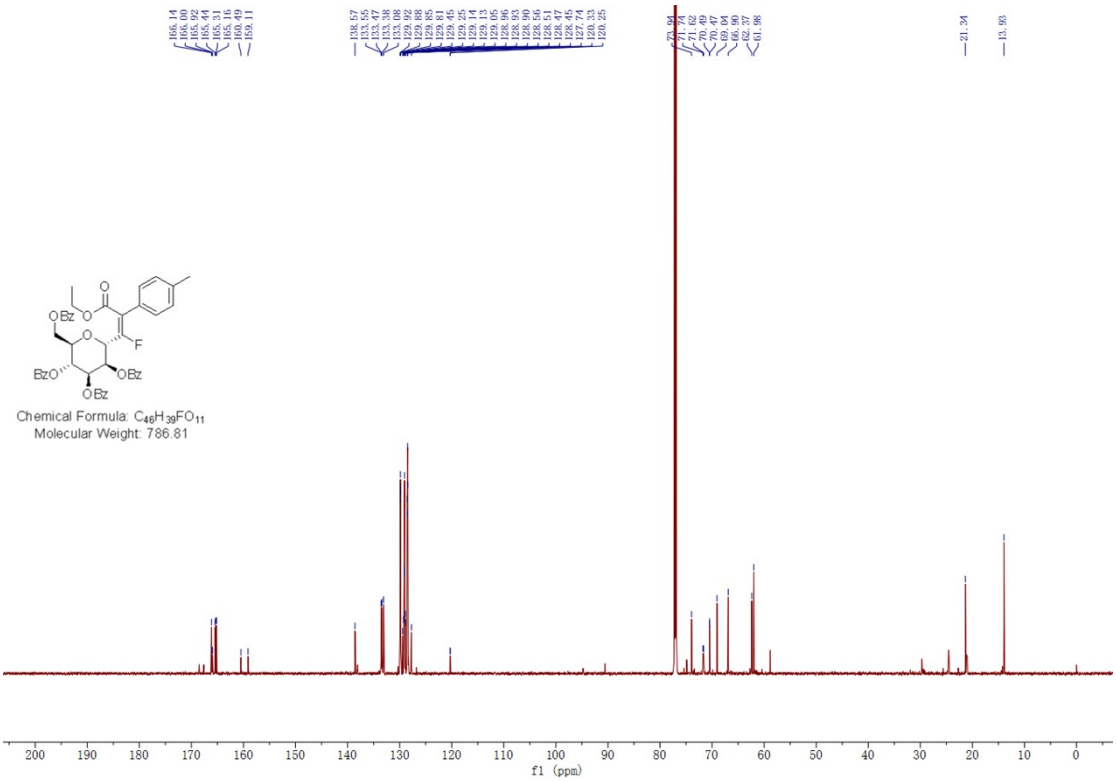
^{1}H NMR (800 MHz, Chloroform-*d*) of **3b**



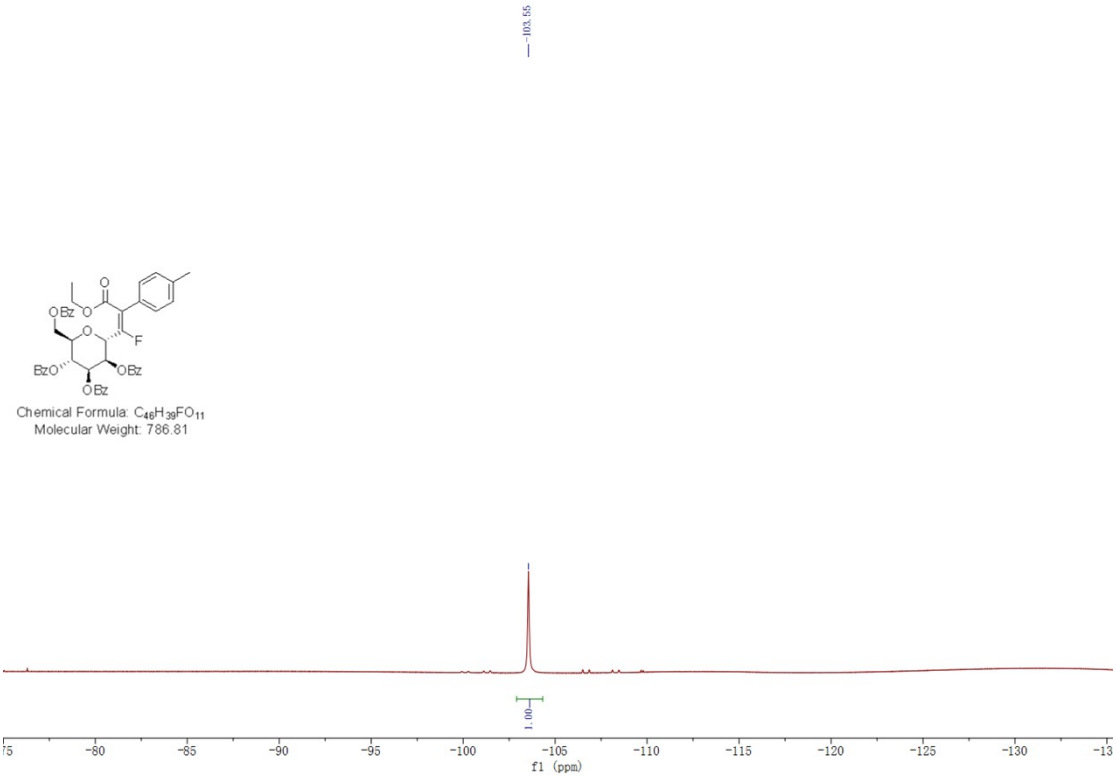
Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81



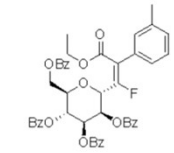
^{13}C NMR (201 MHz, Chloroform-*d*) of **3b**



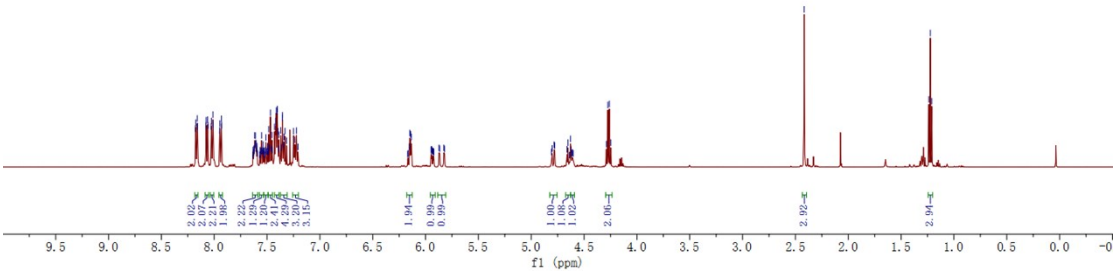
^{19}F NMR (753 MHz, Chloroform-*d*) of **3b**



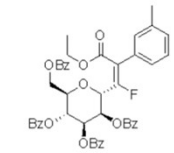
^{1}H NMR (500 MHz, Chloroform-*d*) of **3c**



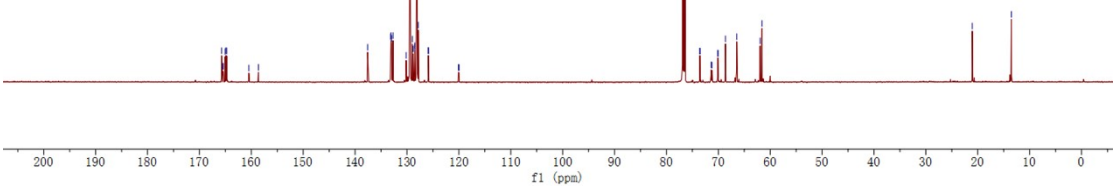
Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81



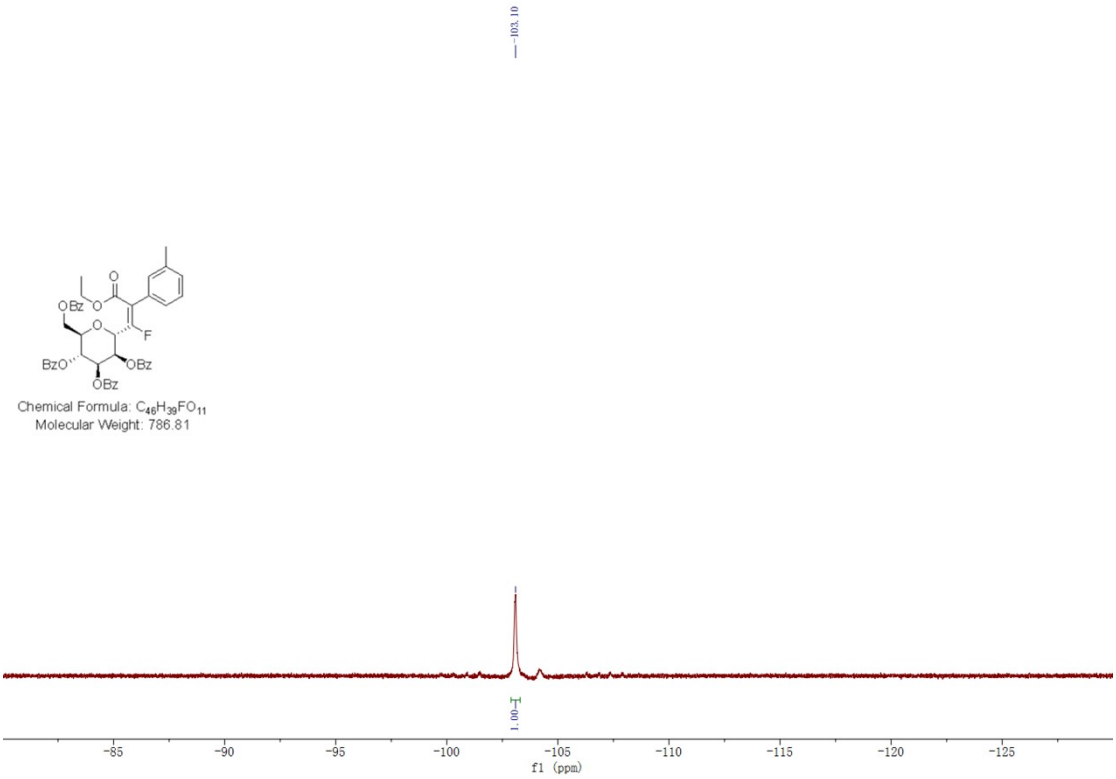
^{13}C NMR (151 MHz, Chloroform-*d*) of **3c**



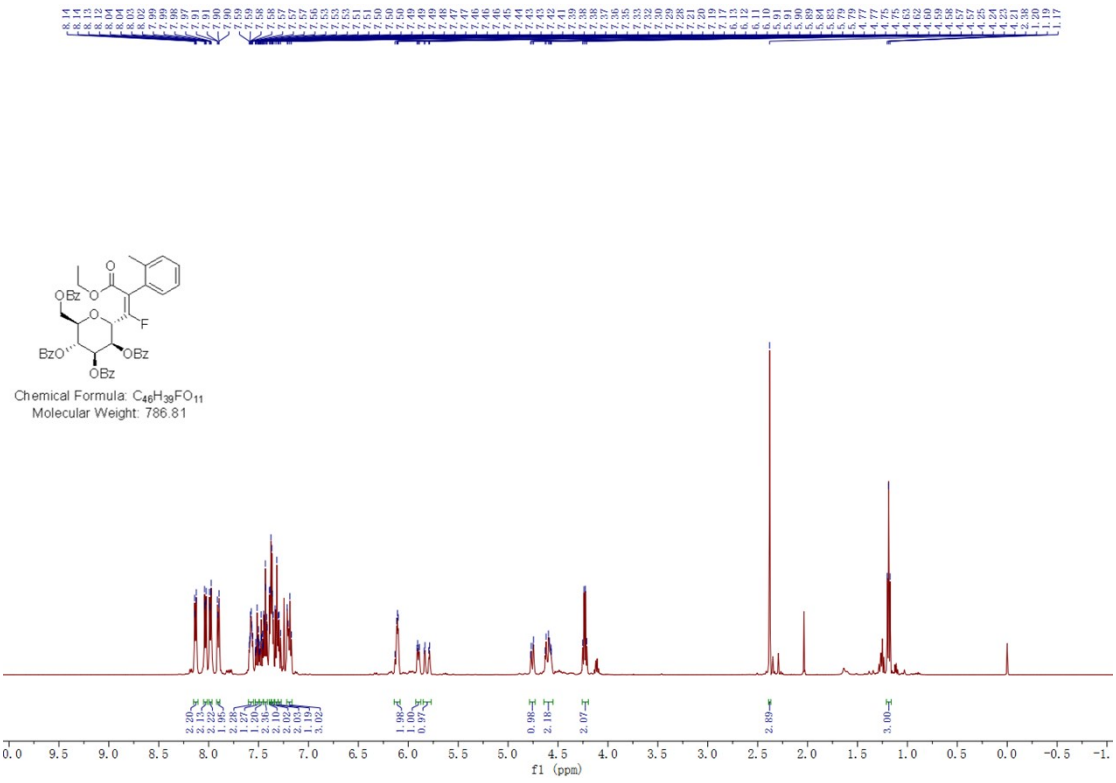
Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81



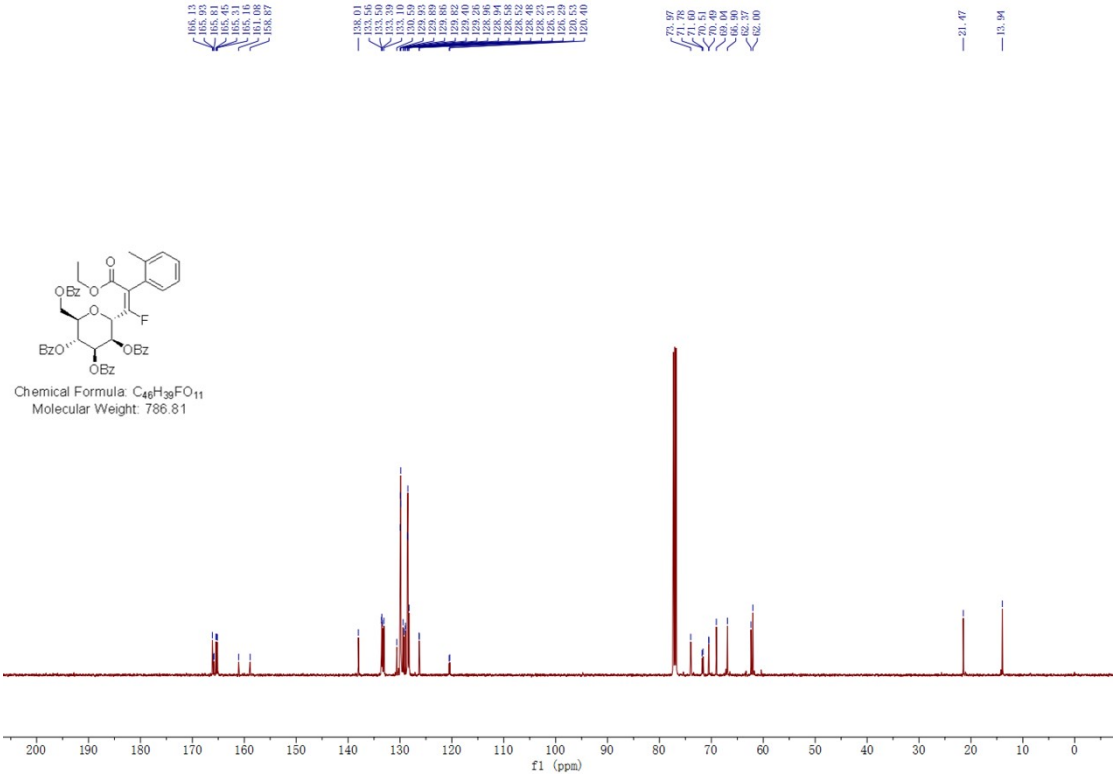
^{19}F NMR (471 MHz, Chloroform-*d*) of **3c**



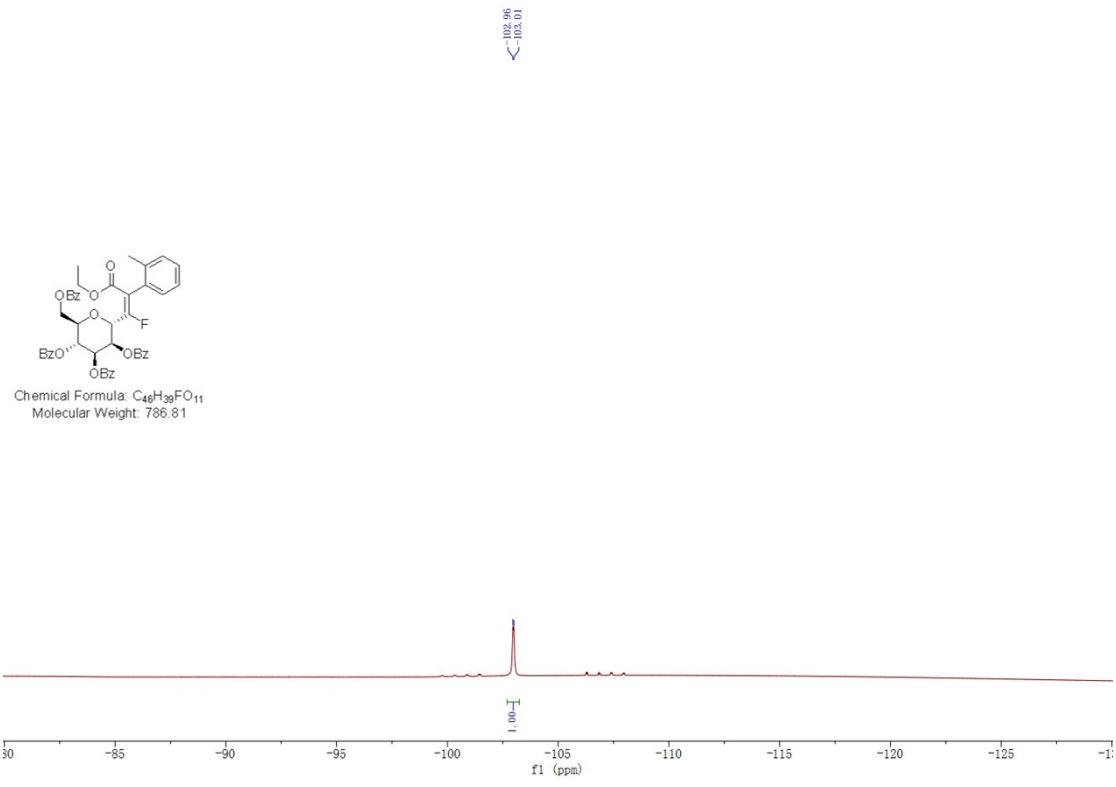
^{1}H NMR (500 MHz, Chloroform-*d*) of **3d**



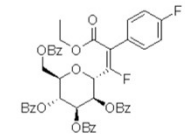
^{13}C NMR (126 MHz, Chloroform-*d*) of **3d**



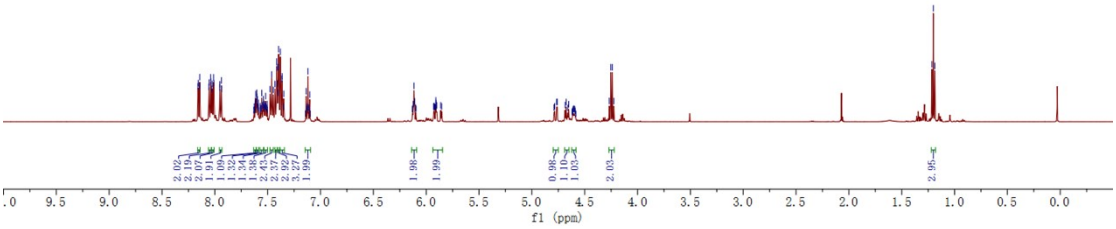
^{19}F NMR (471 MHz, Chloroform-*d*) of **3d**



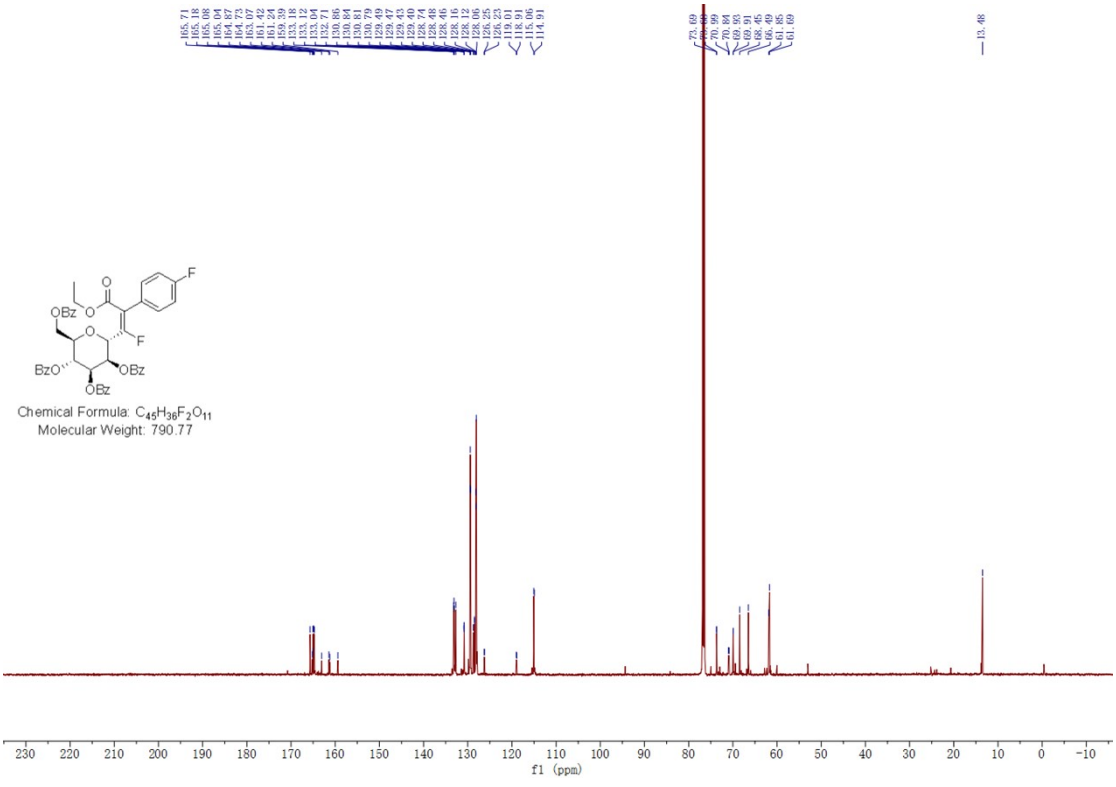
[1]H NMR (500 MHz, Chloroform-*d*) of **3e**



Chemical Formula: $C_{45}H_{36}F_2O_{11}$
Molecular Weight: 790.77

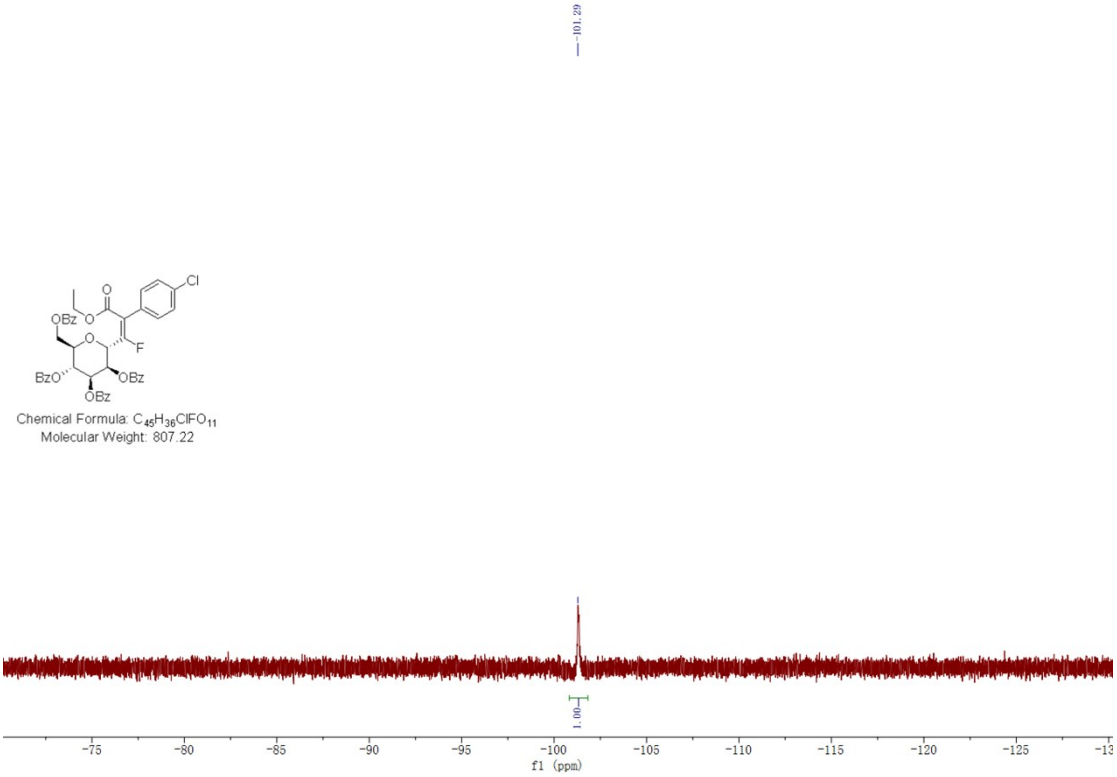


[13]C NMR (151 MHz, Chloroform-*d*) of **3e**

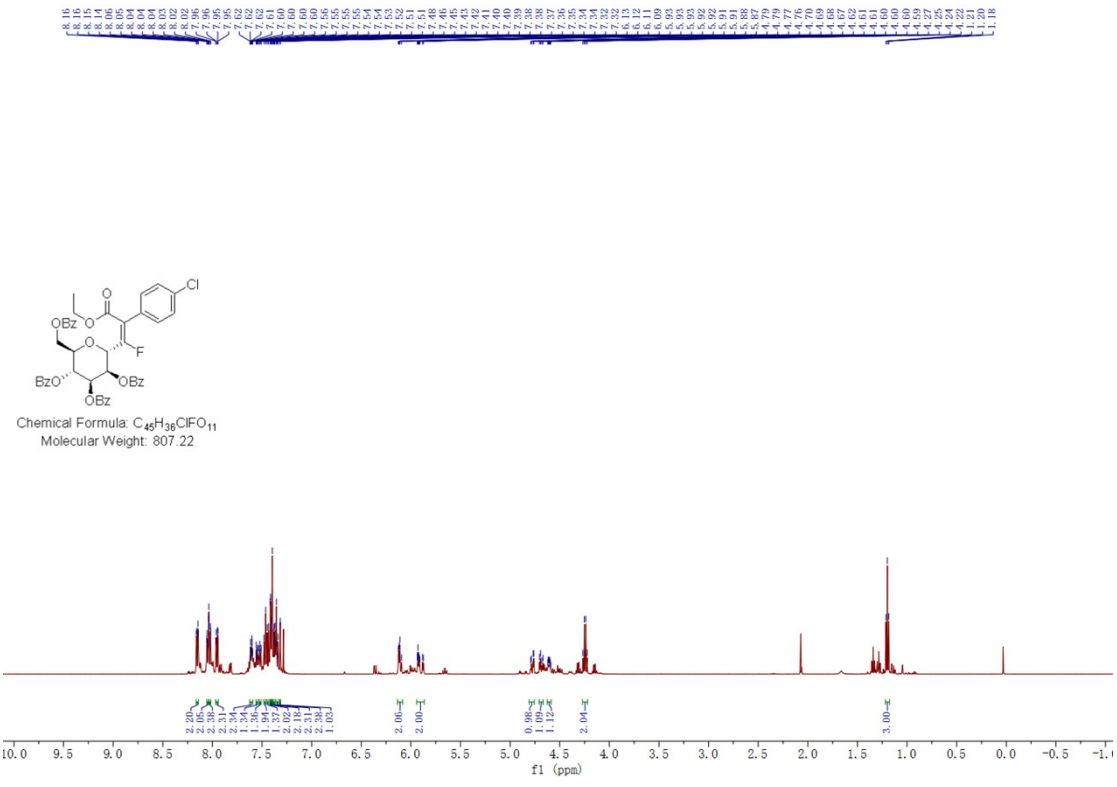


Chemical Formula: $C_{45}H_{36}F_2O_{11}$
Molecular Weight: 790.77

^{19}F NMR (471 MHz, Chloroform-*d*) of **3e**



^{1}H NMR (500 MHz, Chloroform-*d*) of **3f**



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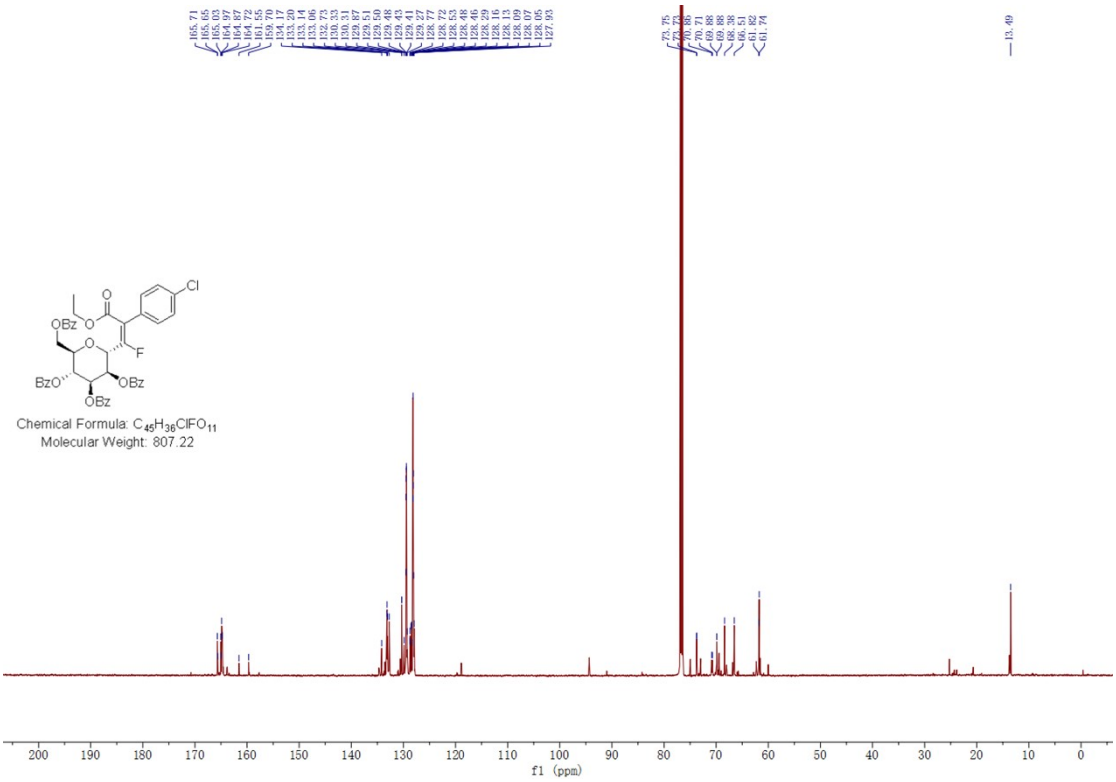
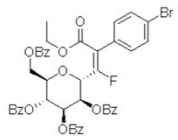
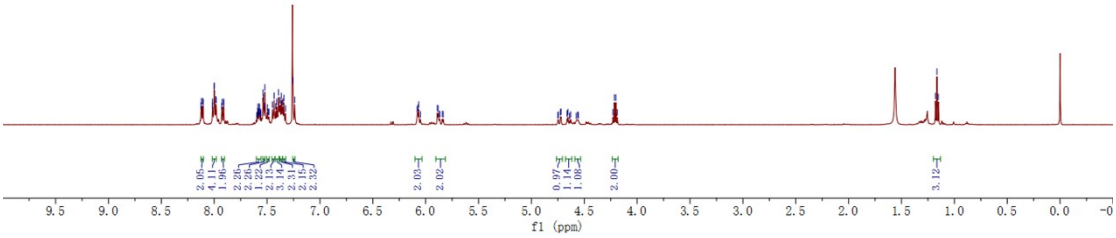


^{19}F NMR (471 MHz, Chloroform-*d*) of **3f**

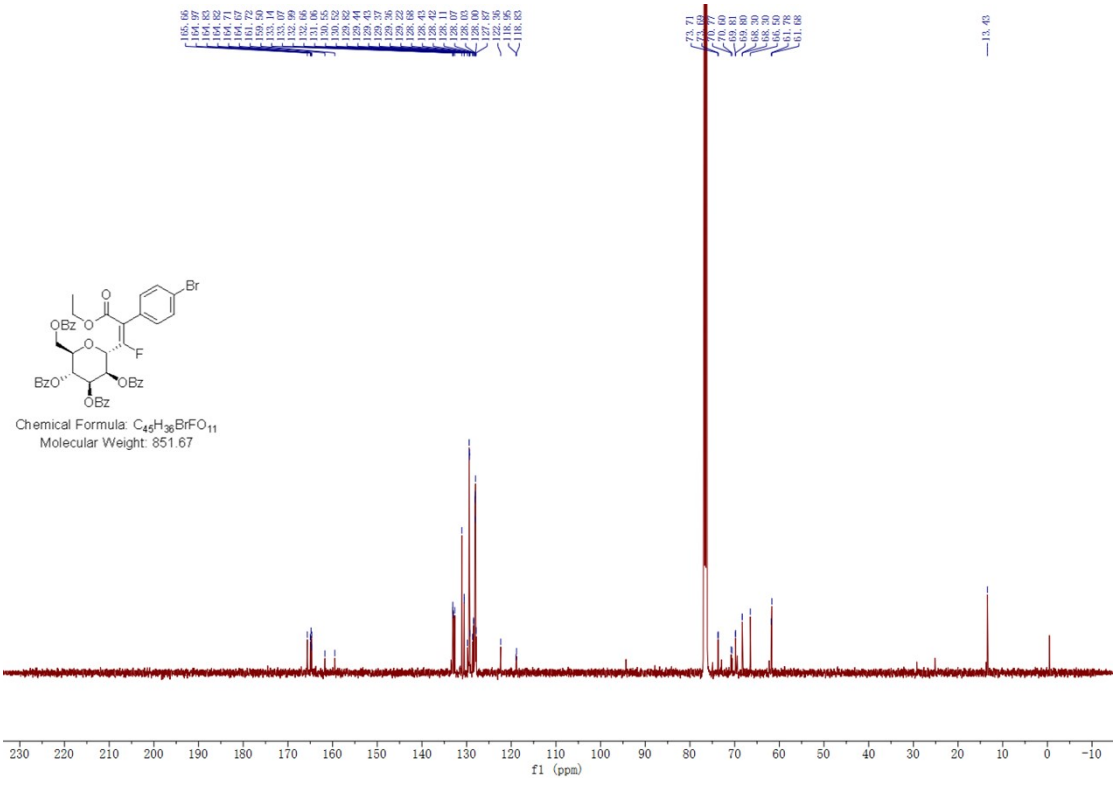
^{1}H NMR (500 MHz, Chloroform-*d*) of **3g**



Chemical Formula: $C_{45}H_{36}BrFO_{11}$
Molecular Weight: 851.67

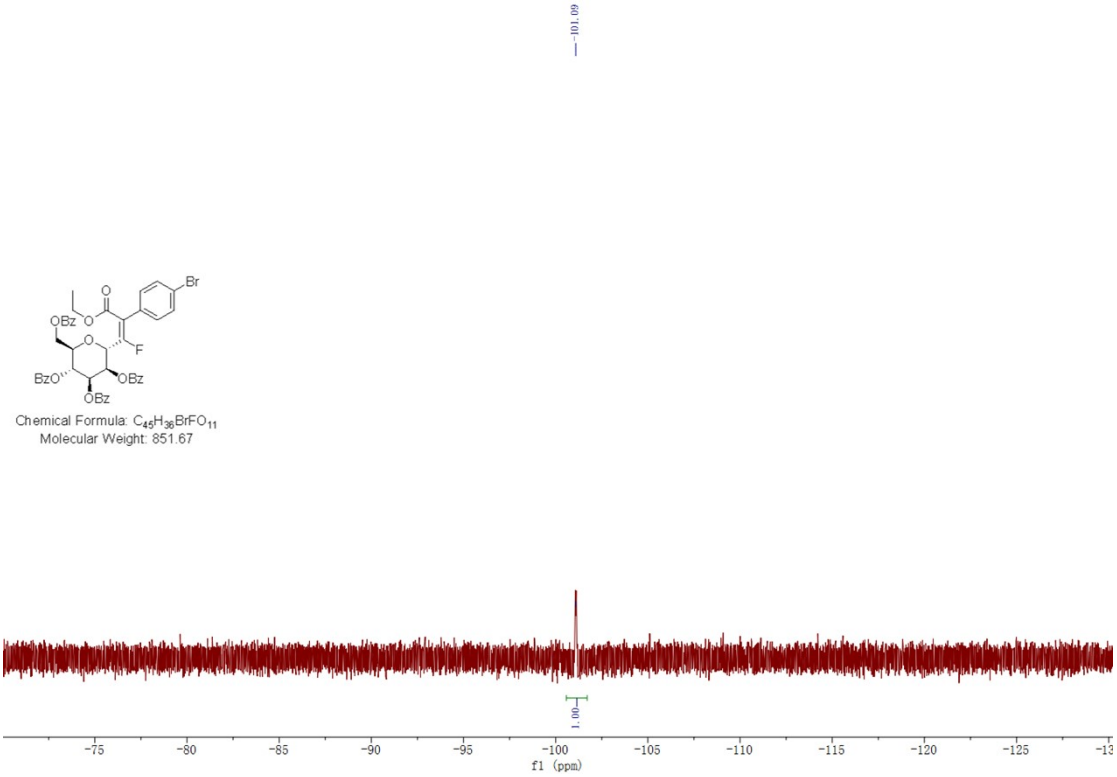


^{13}C NMR (126 MHz, Chloroform-*d*) of **3g**

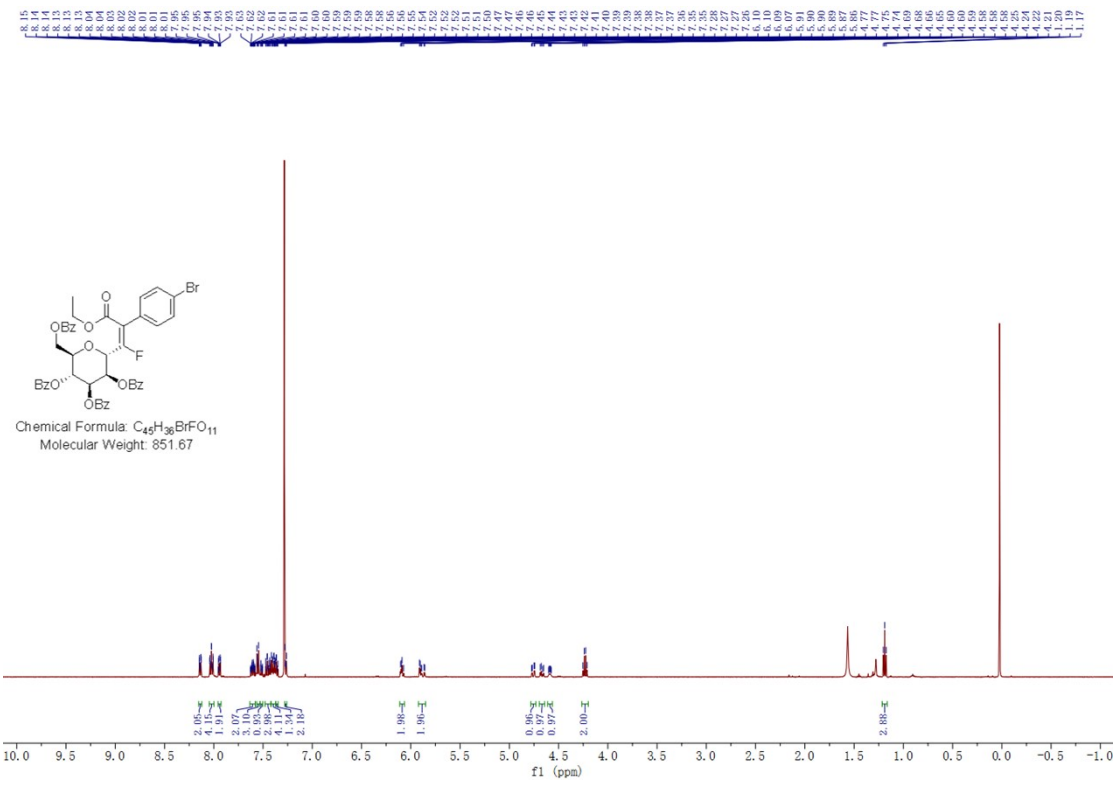


Chemical Formula: $C_{45}H_{36}BrFO_{11}$
Molecular Weight: 851.67

^{19}F NMR (471 MHz, Chloroform-*d*) of **3g**



^{1}H NMR (500 MHz, Chloroform-*d*) of **3h**



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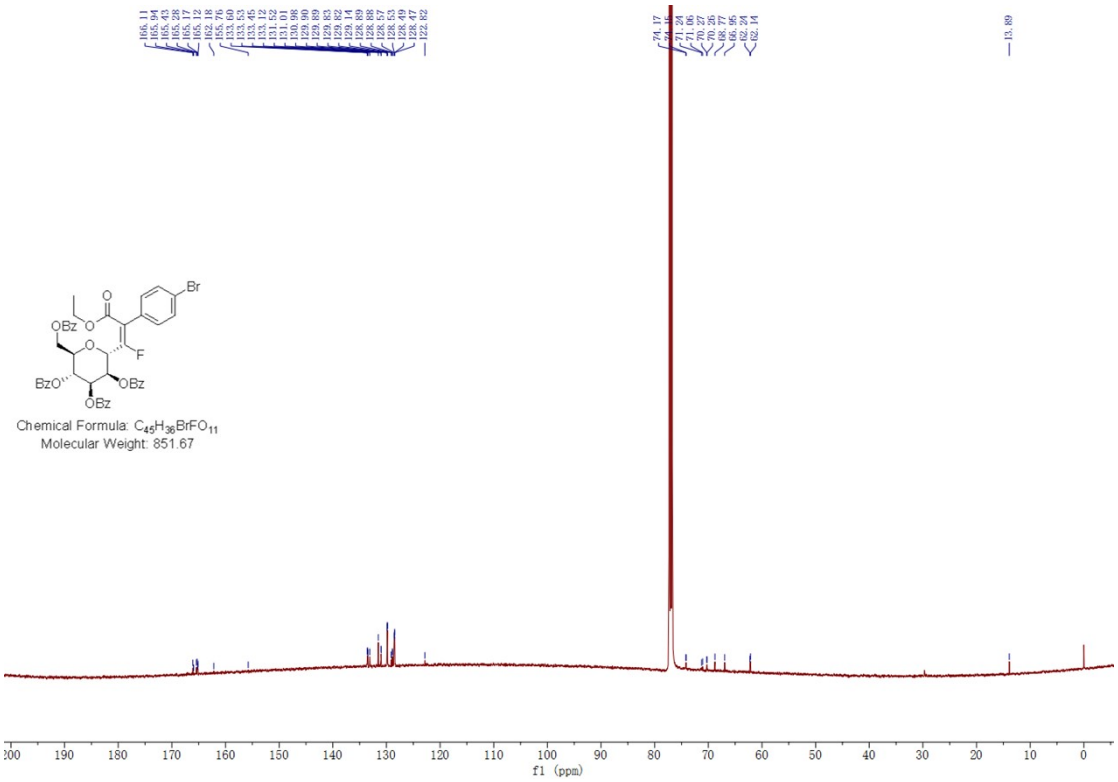
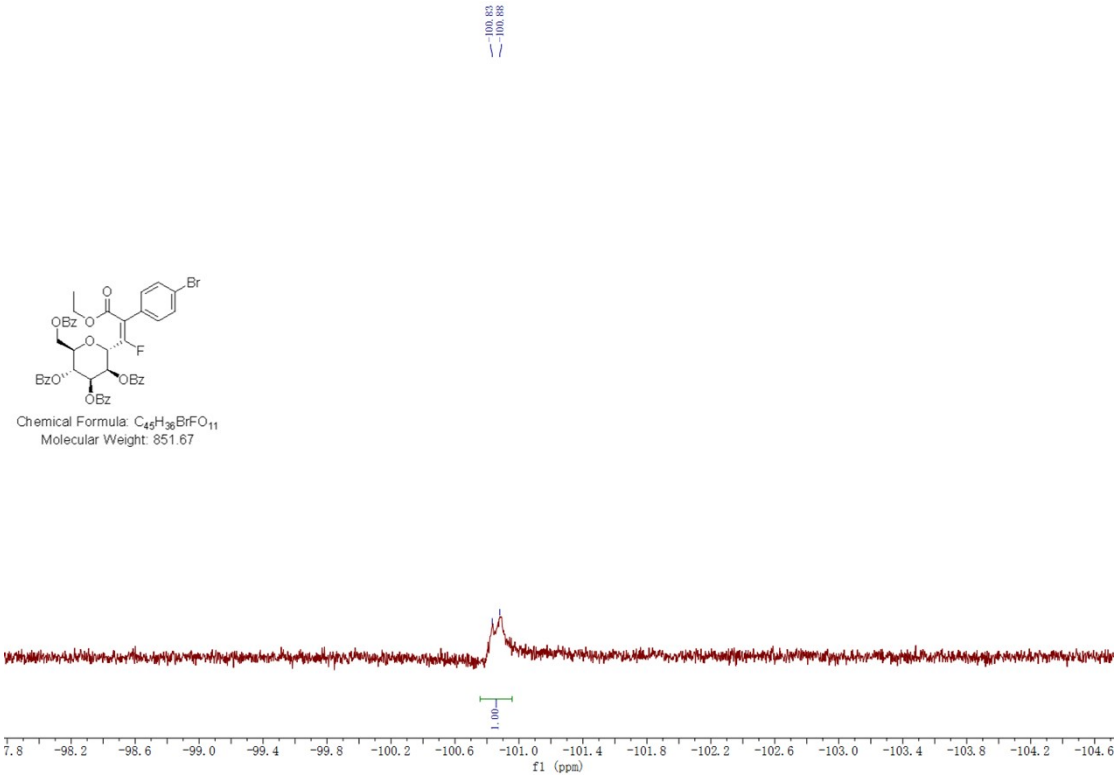
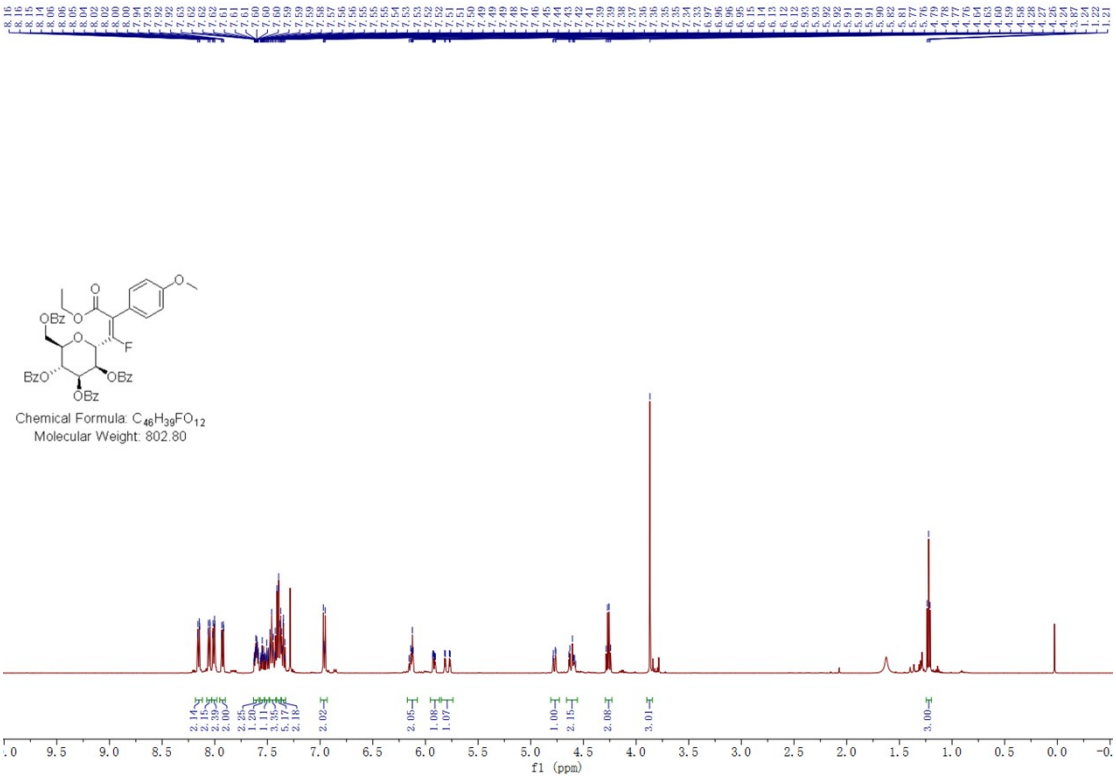


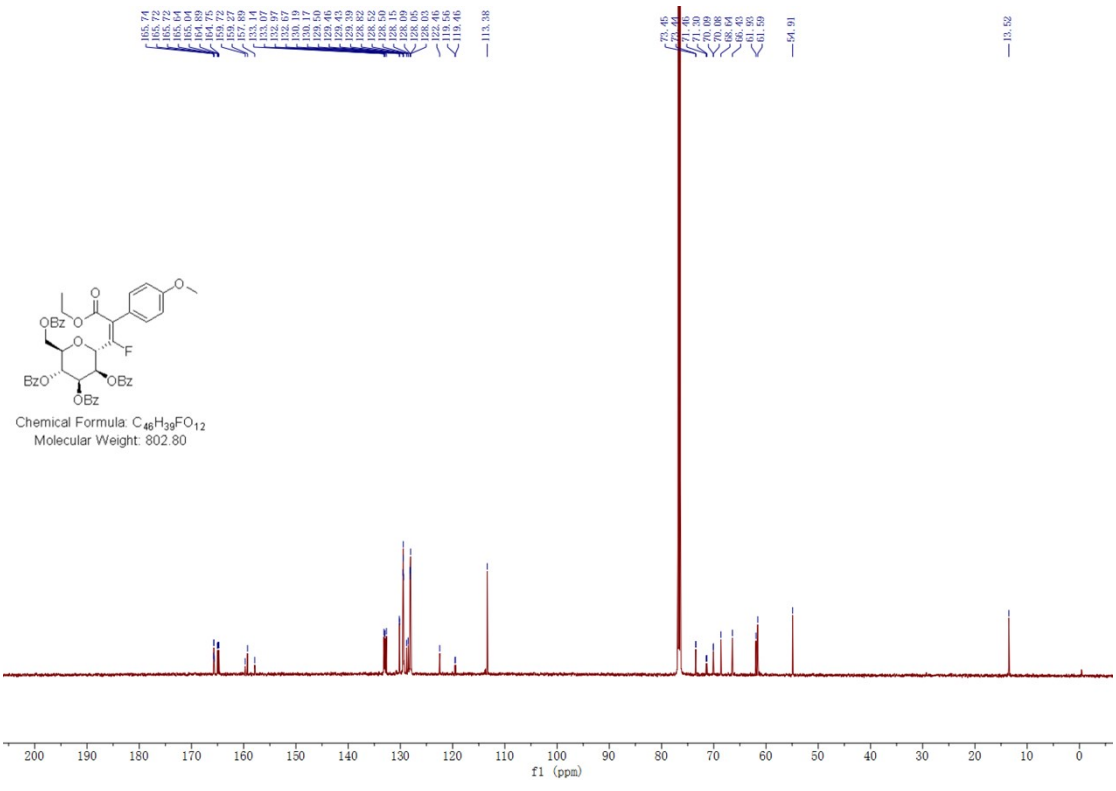
^{19}F NMR (471 MHz, Chloroform-*d*) of **3h**



^{1}H NMR (500 MHz, Chloroform-*d*) of **3i**



^{13}C NMR (151 MHz, Chloroform-*d*) of **3i**



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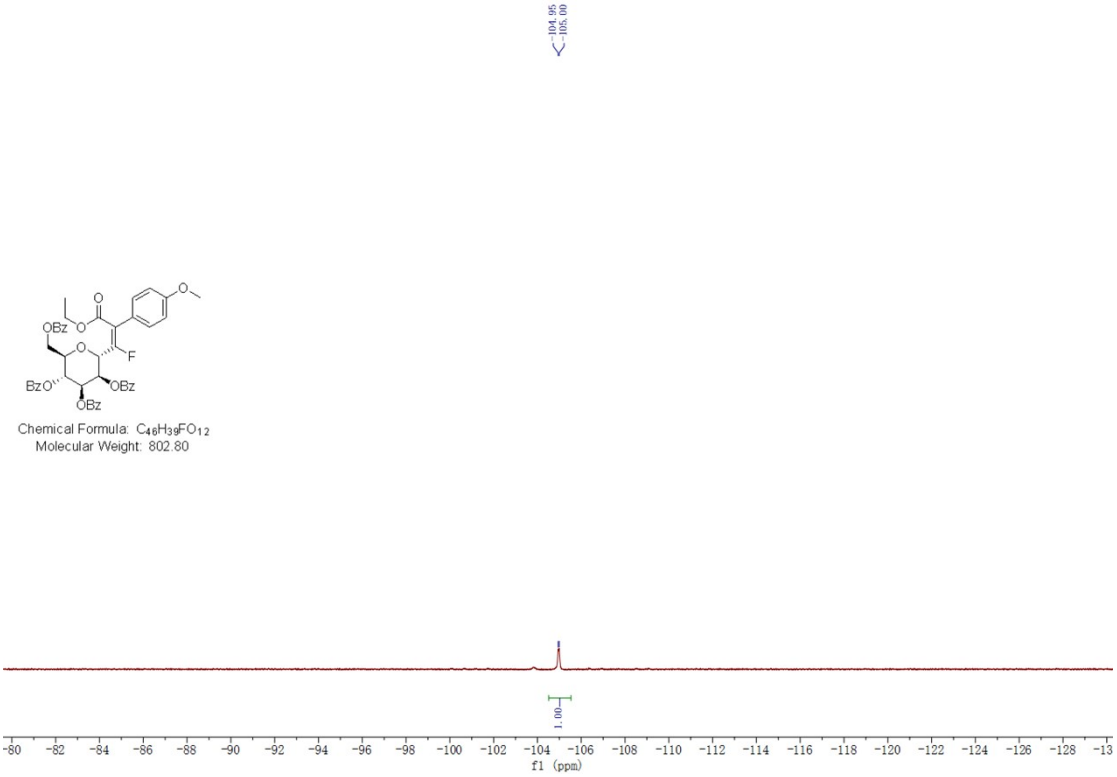

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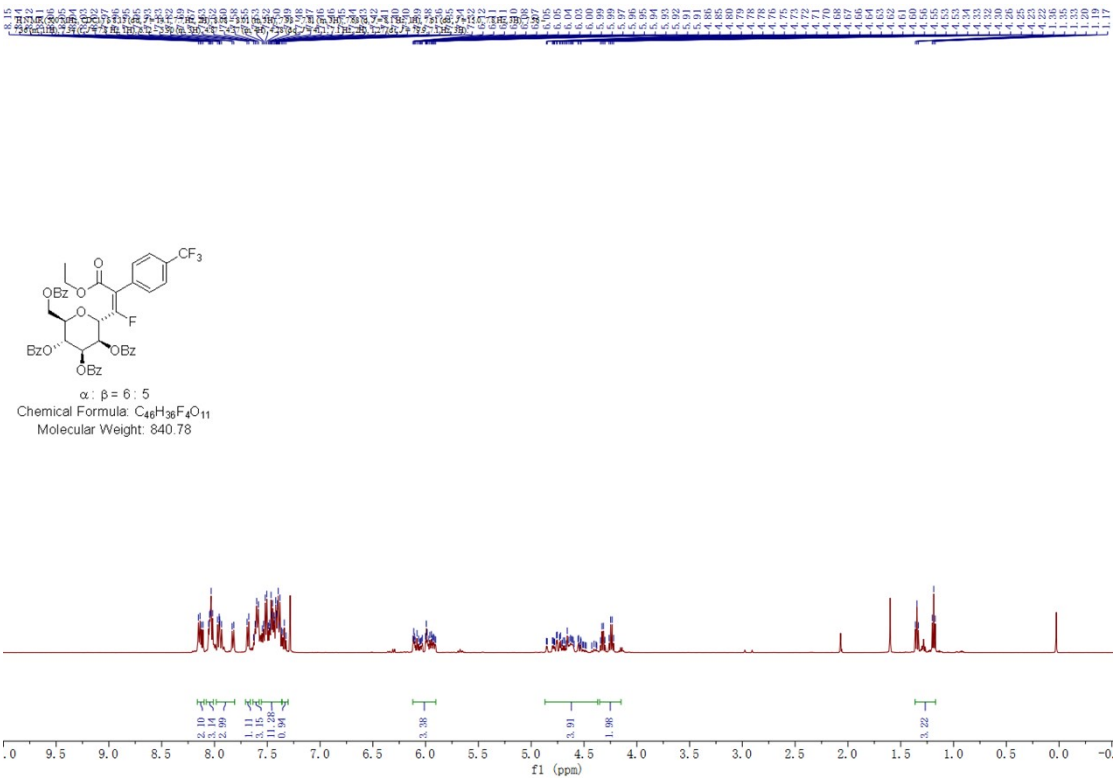
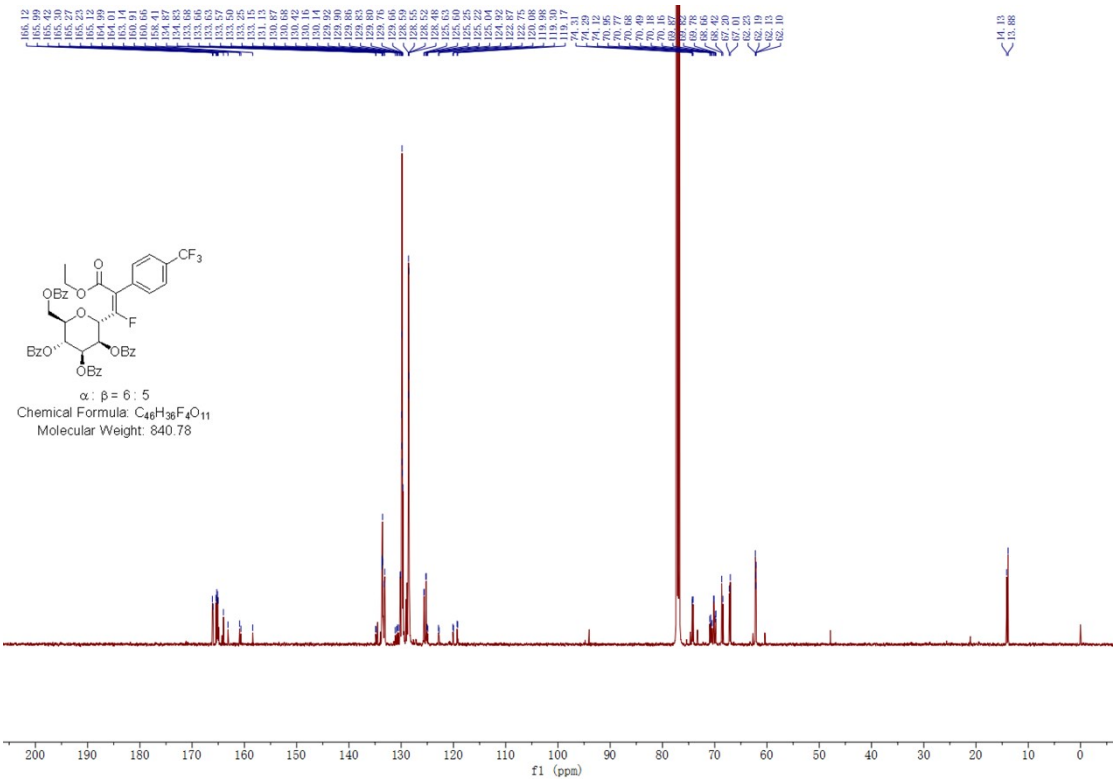


^{13}C NMR (126 MHz, Chloroform-*d*) of **3j**



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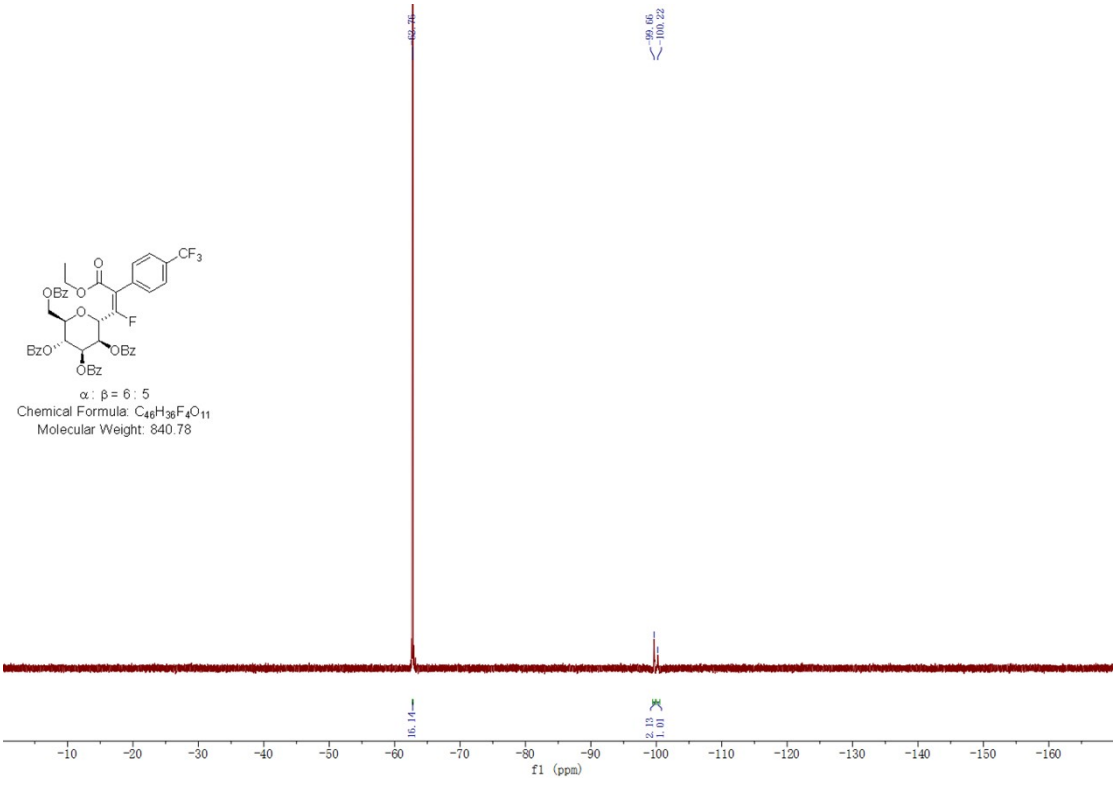

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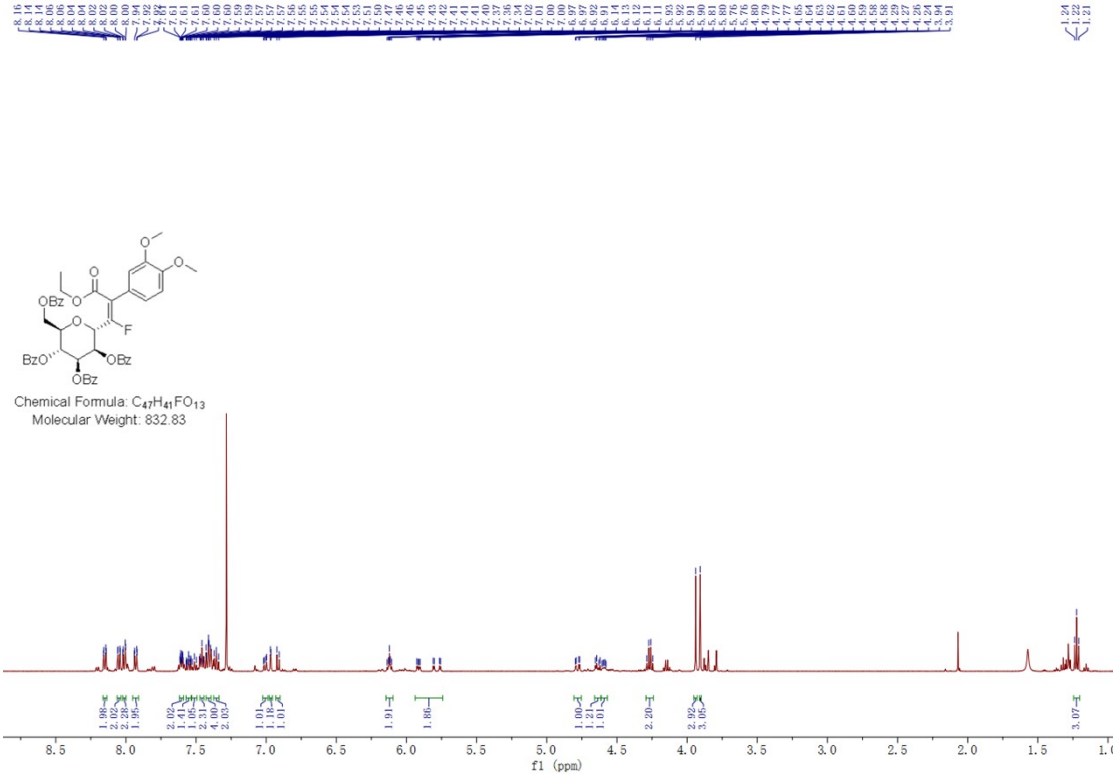
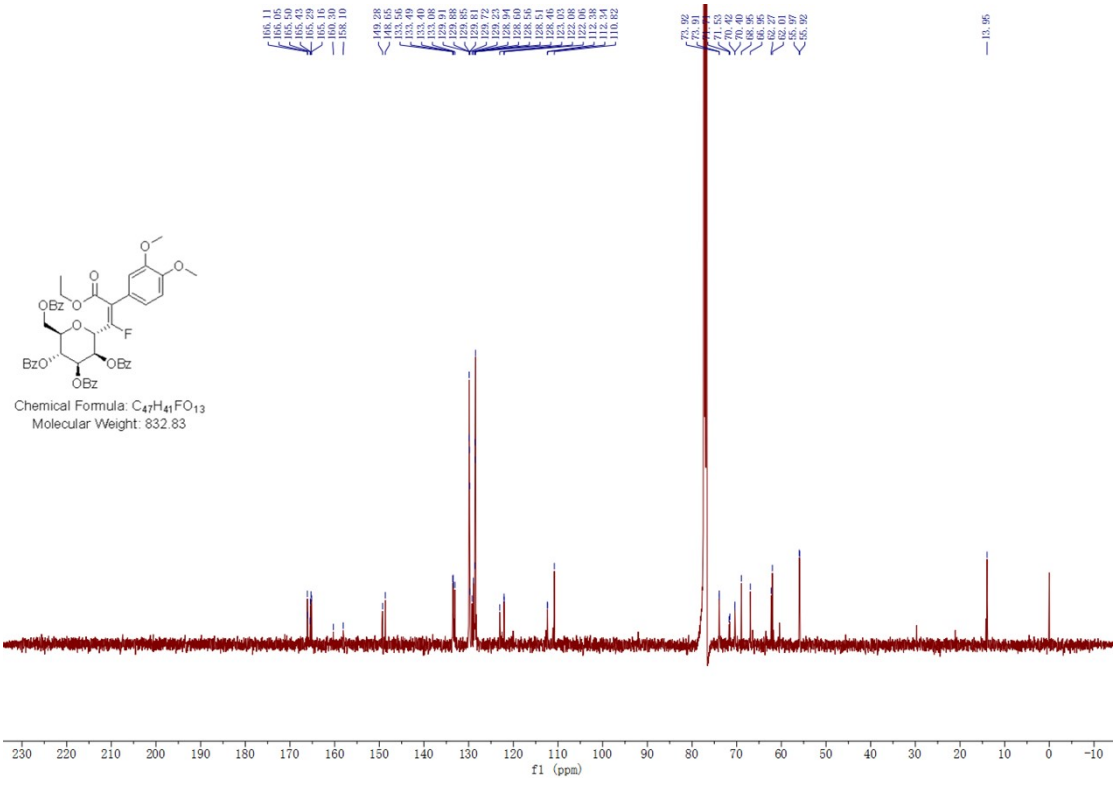


^{13}C NMR (126 MHz, Chloroform-*d*) of **3k**



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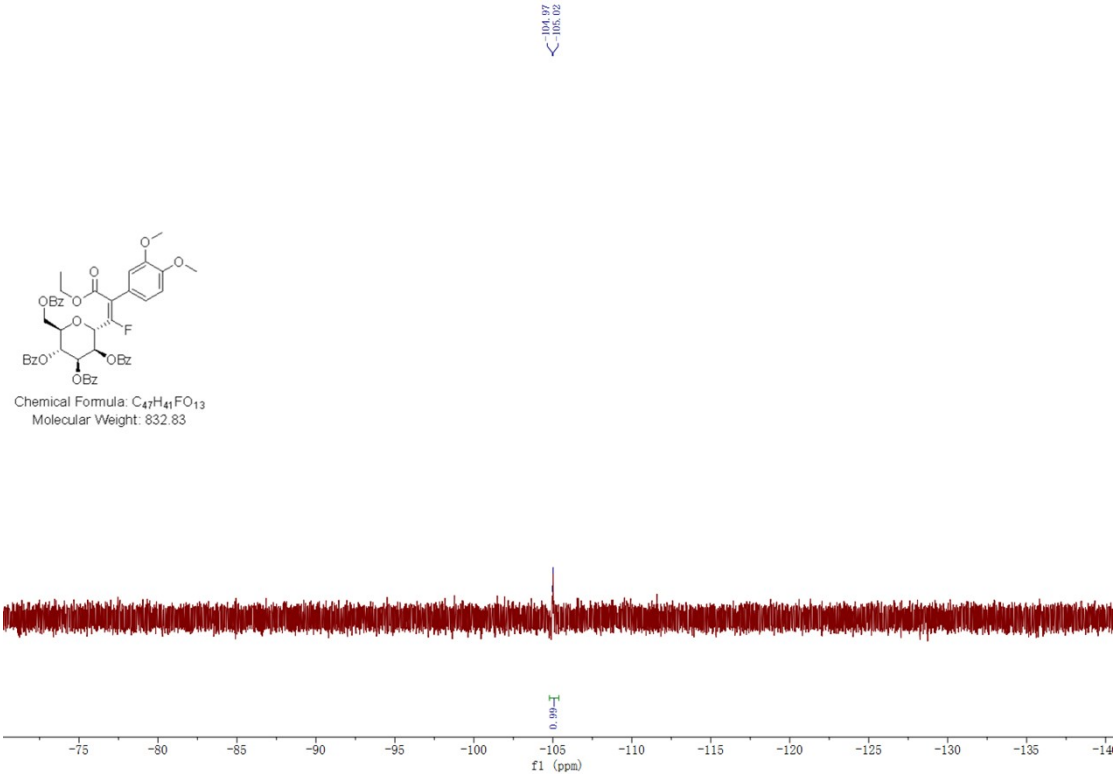

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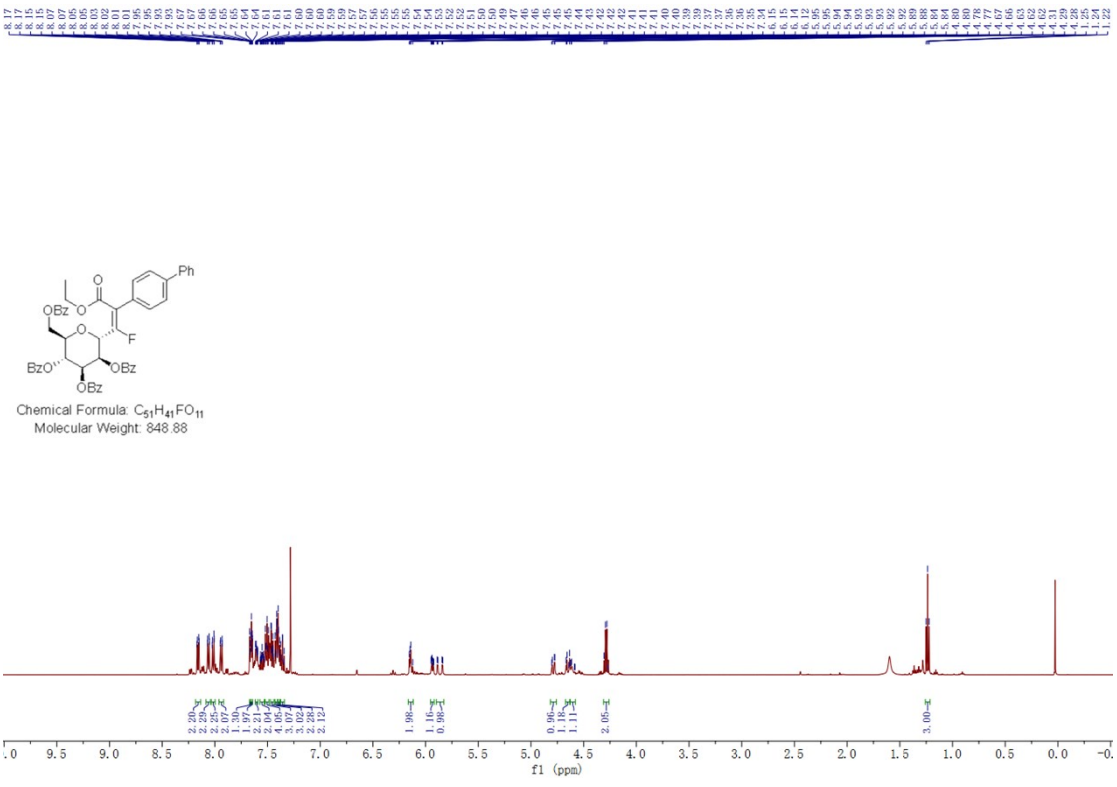
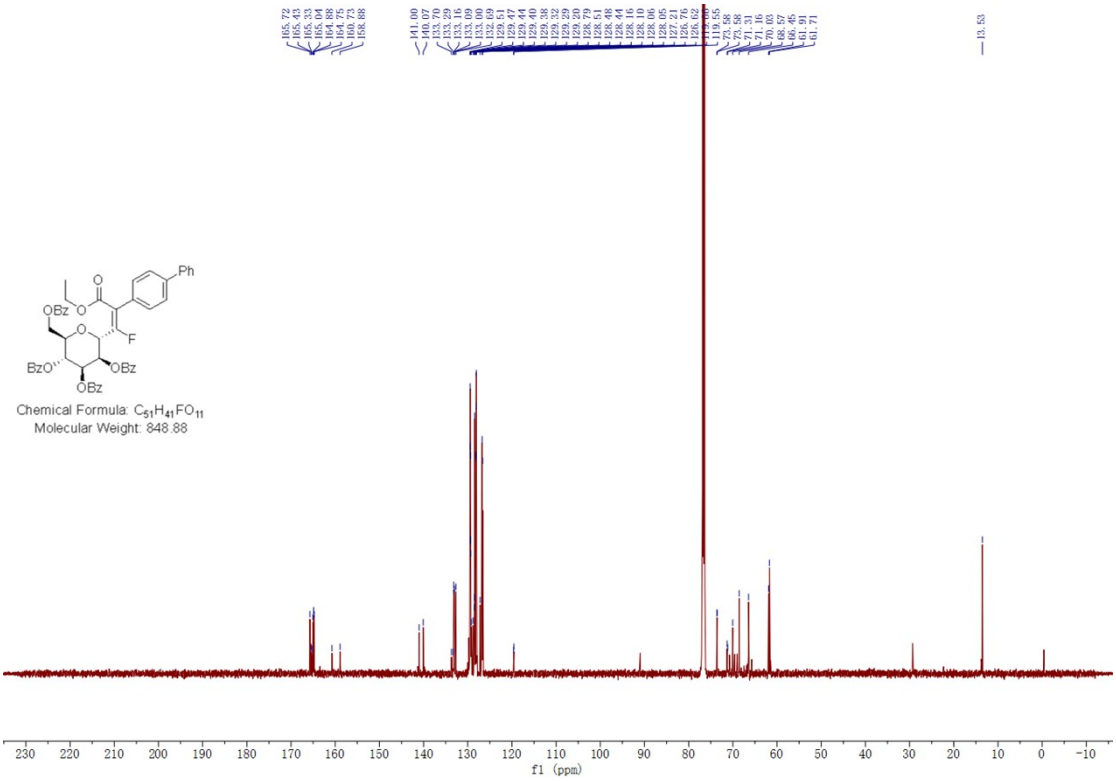
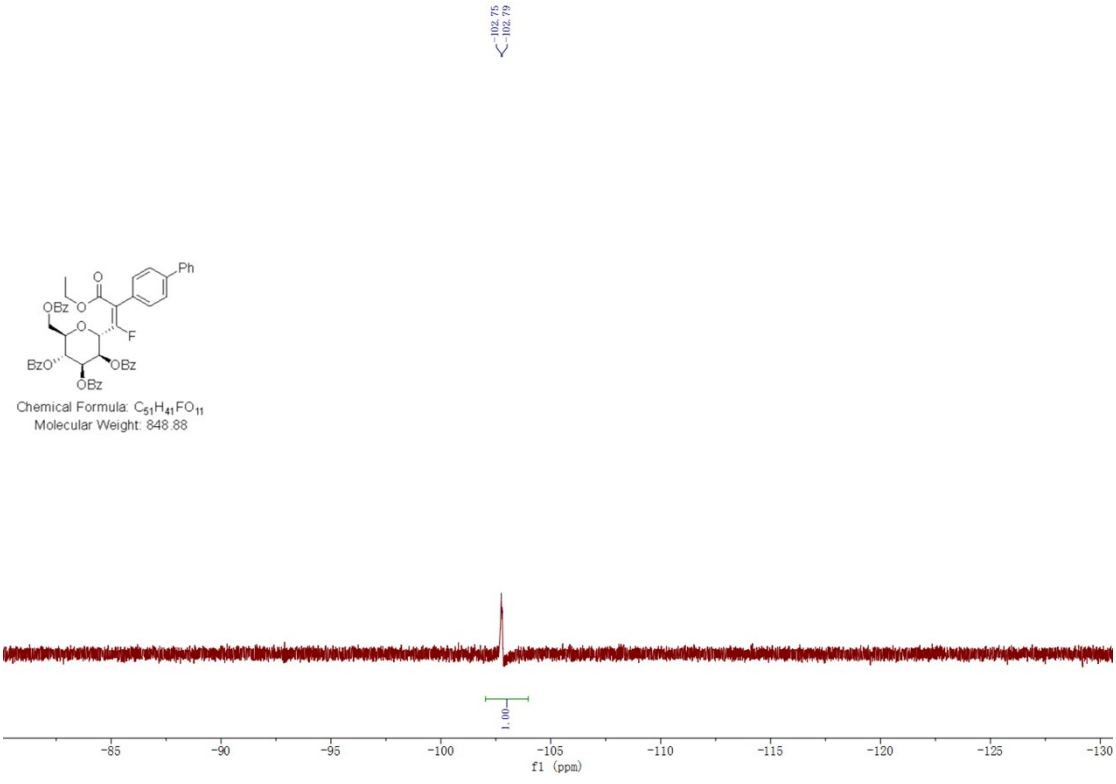


^{13}C NMR (151 MHz, Chloroform-*d*) of **3l**



^{19}F NMR (471 MHz, Chloroform-*d*) of **3l**



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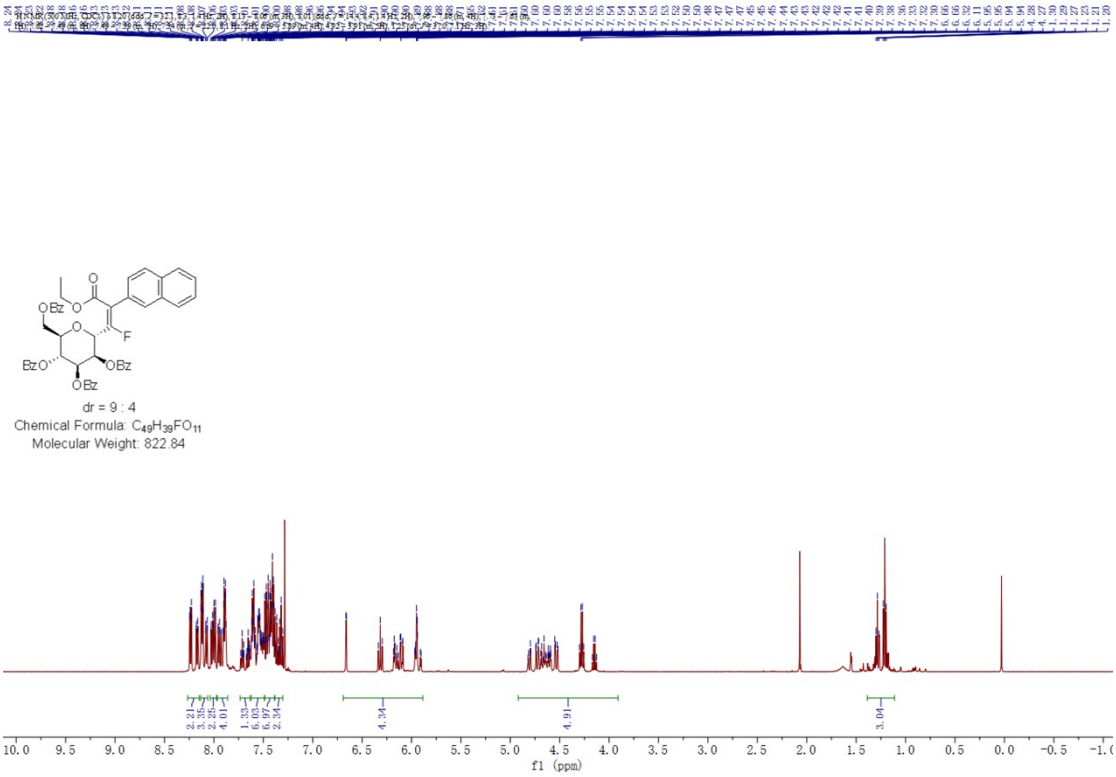

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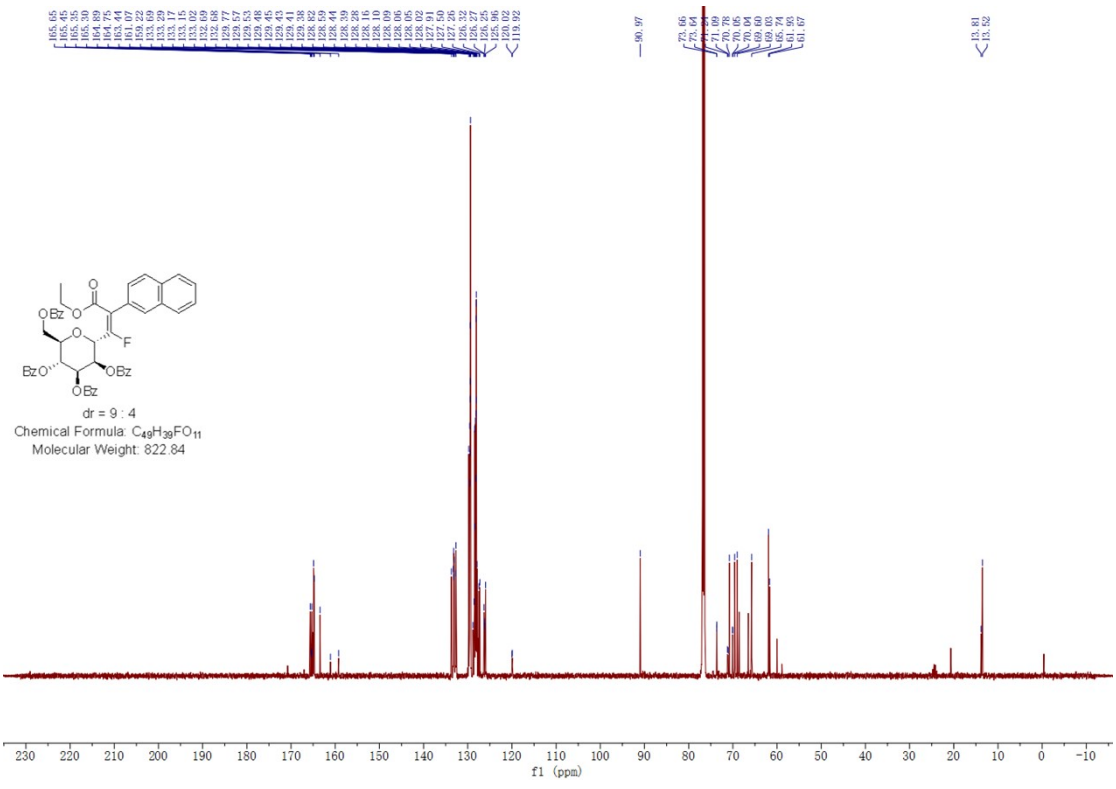

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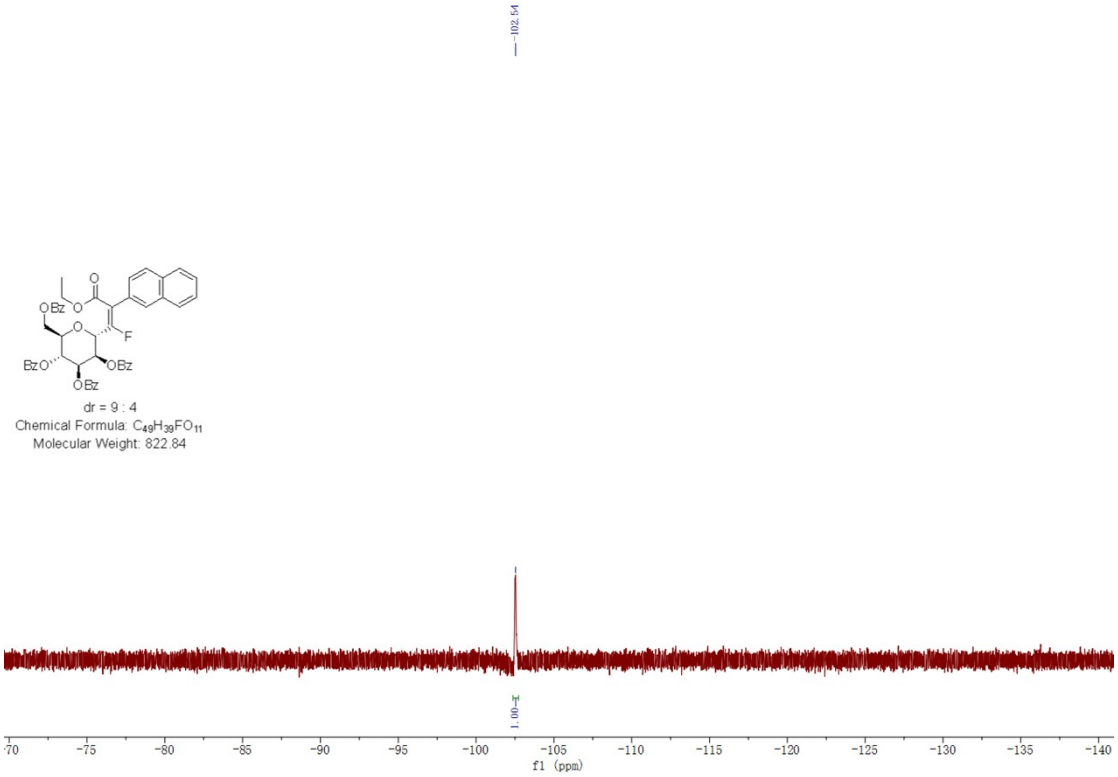

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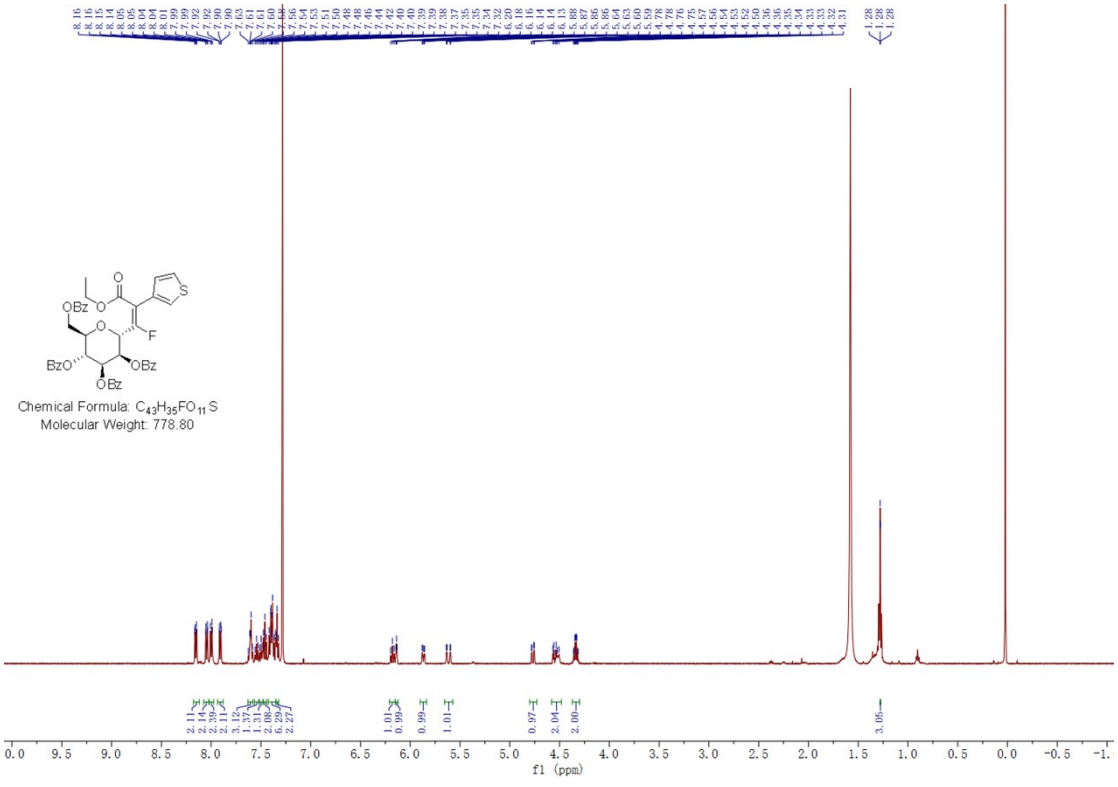
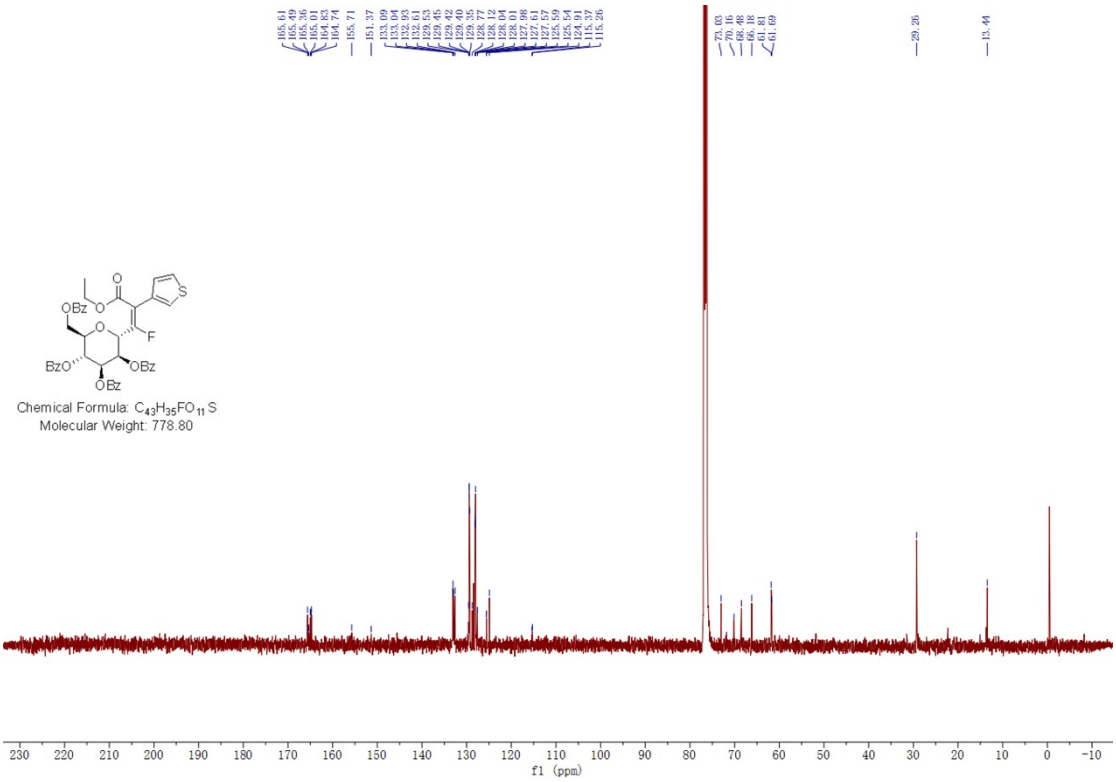


^{13}C NMR (126 MHz, Chloroform-*d*) of **3n**



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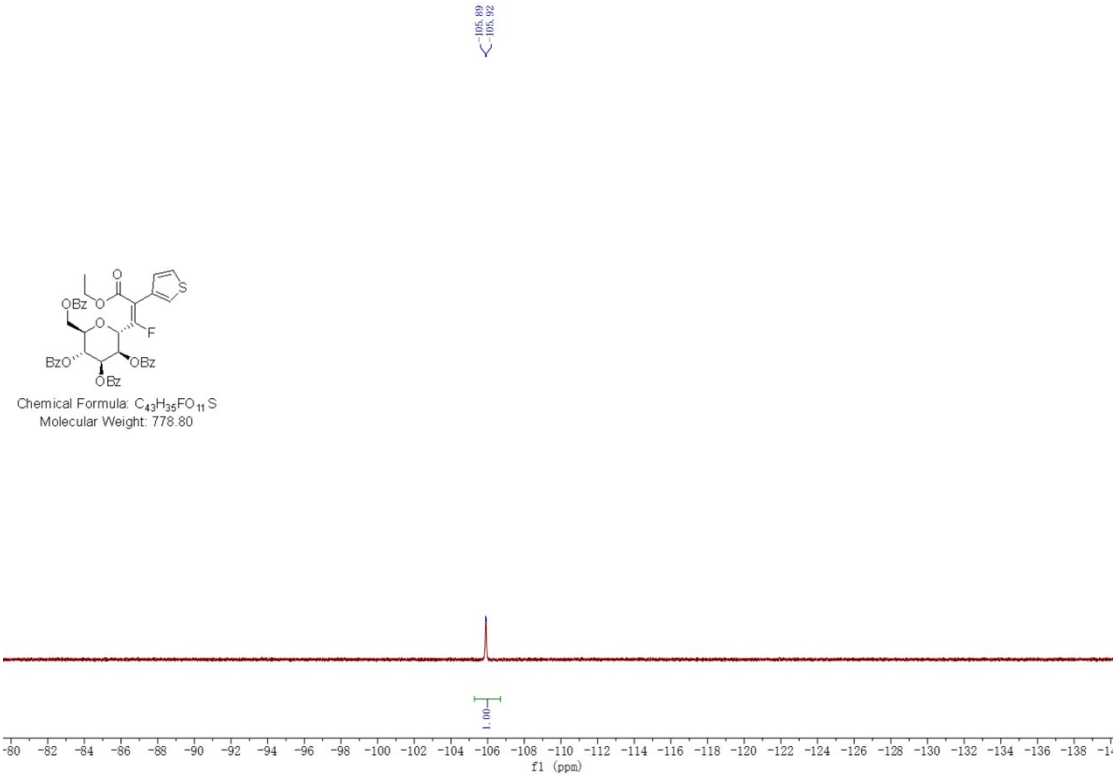
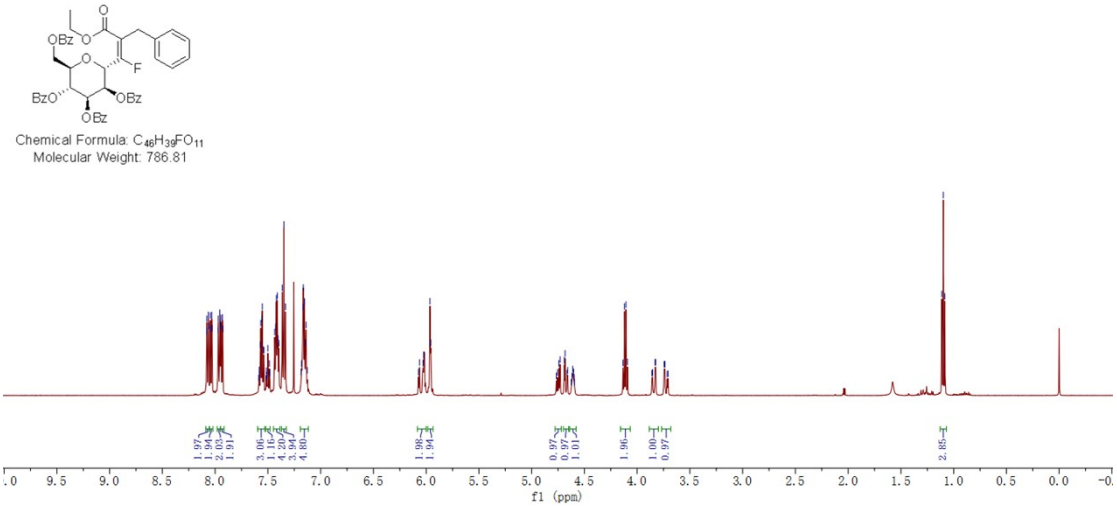
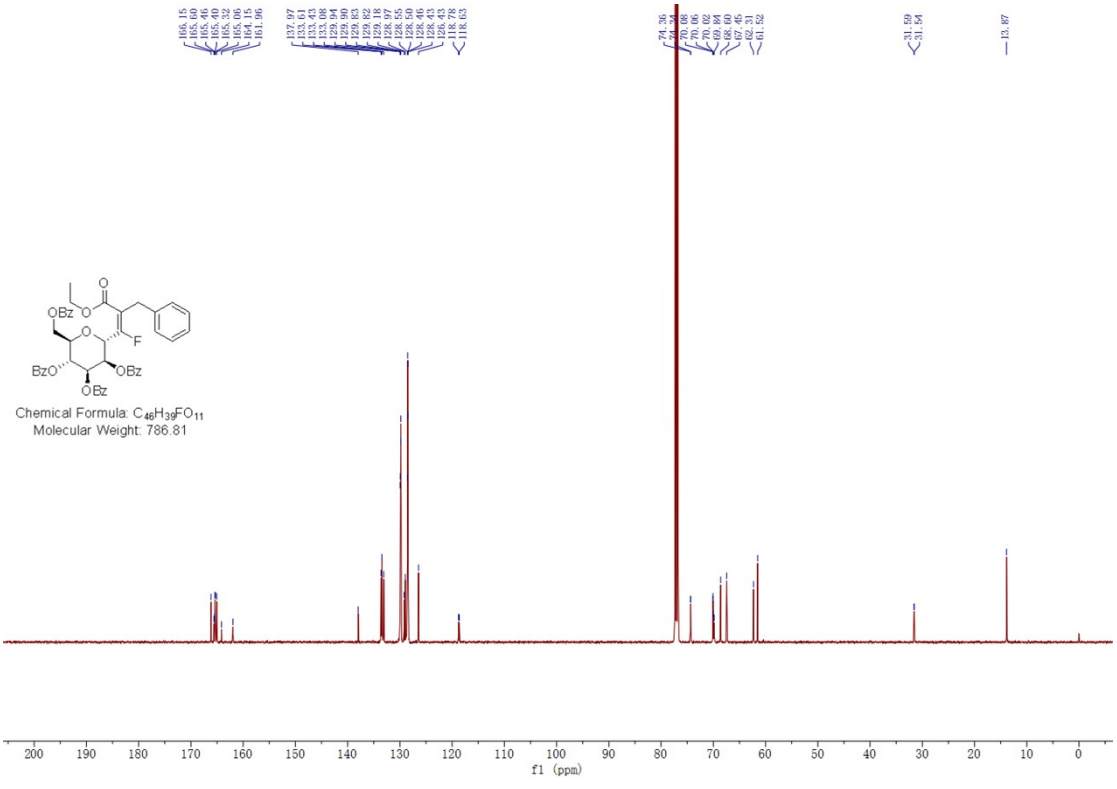


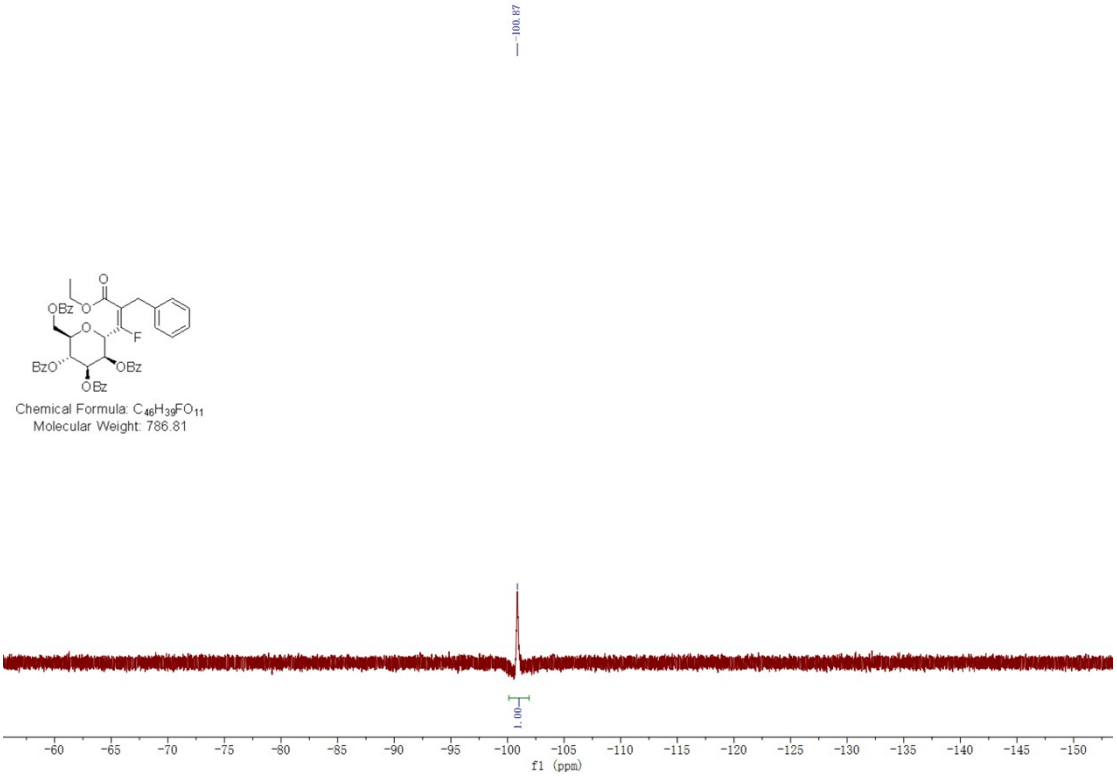
^{1}H NMR (500 MHz, Chloroform-*d*) of **3o**



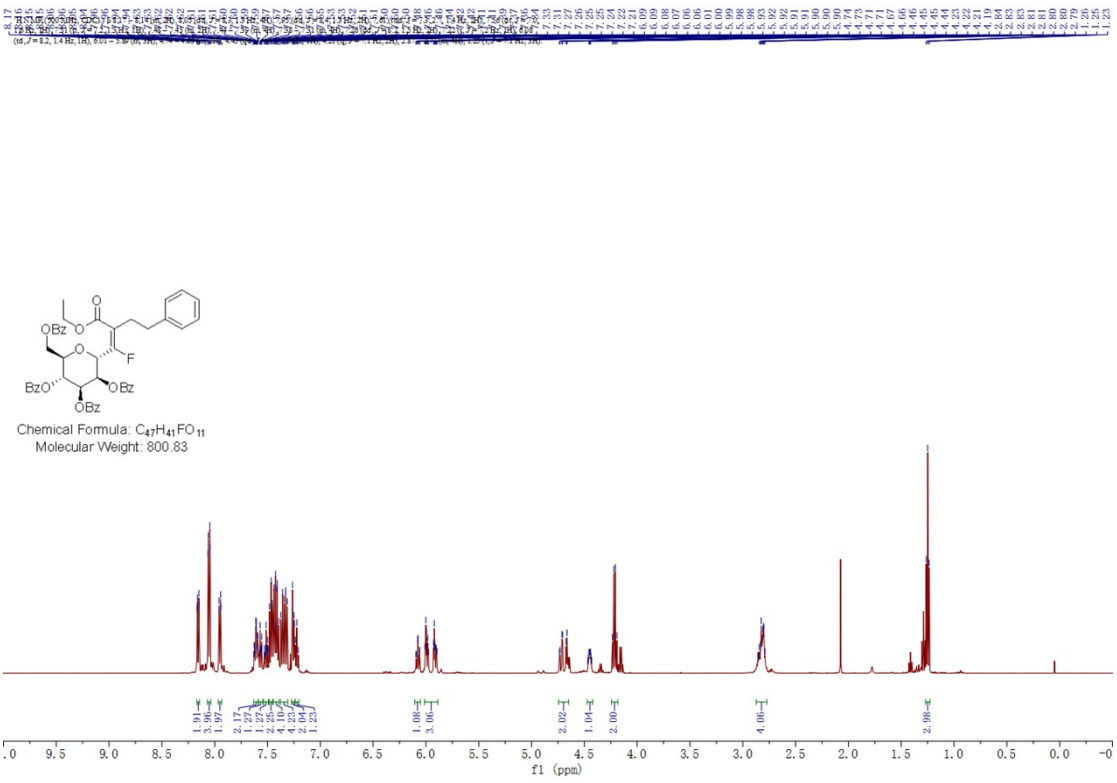
^{13}C NMR (126 MHz, Chloroform-*d*) of **3o**



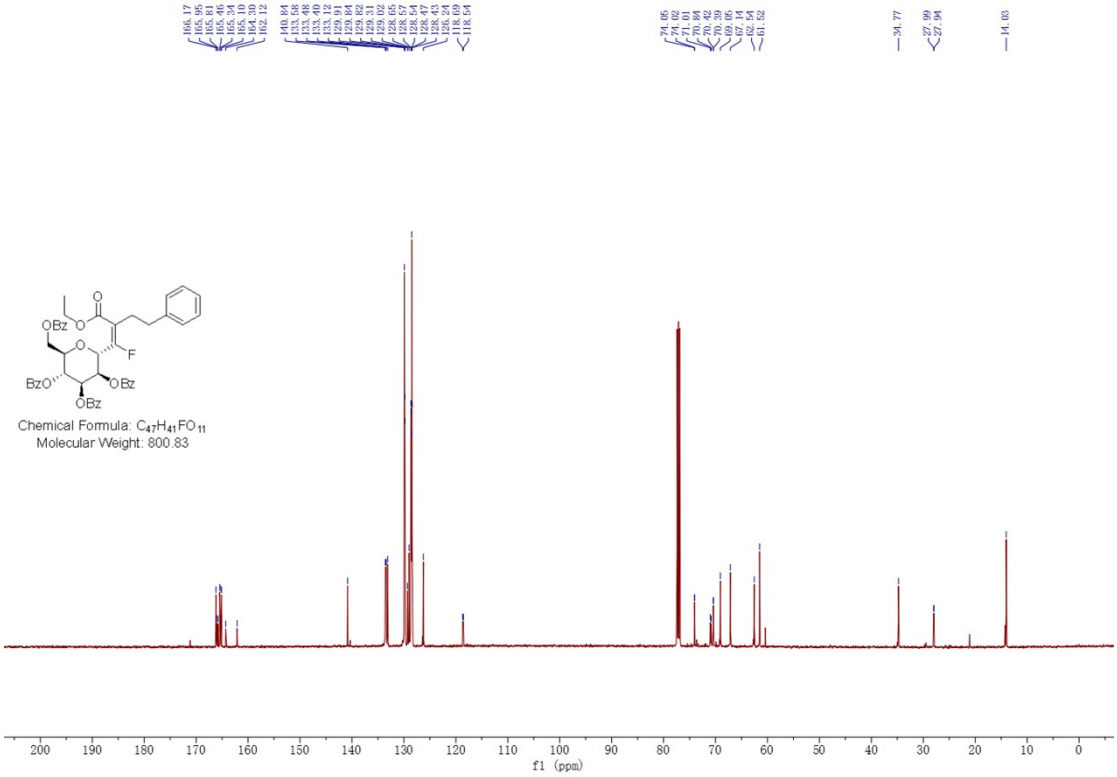
^{19}F NMR (471 MHz, Chloroform-*d*) of **3o**



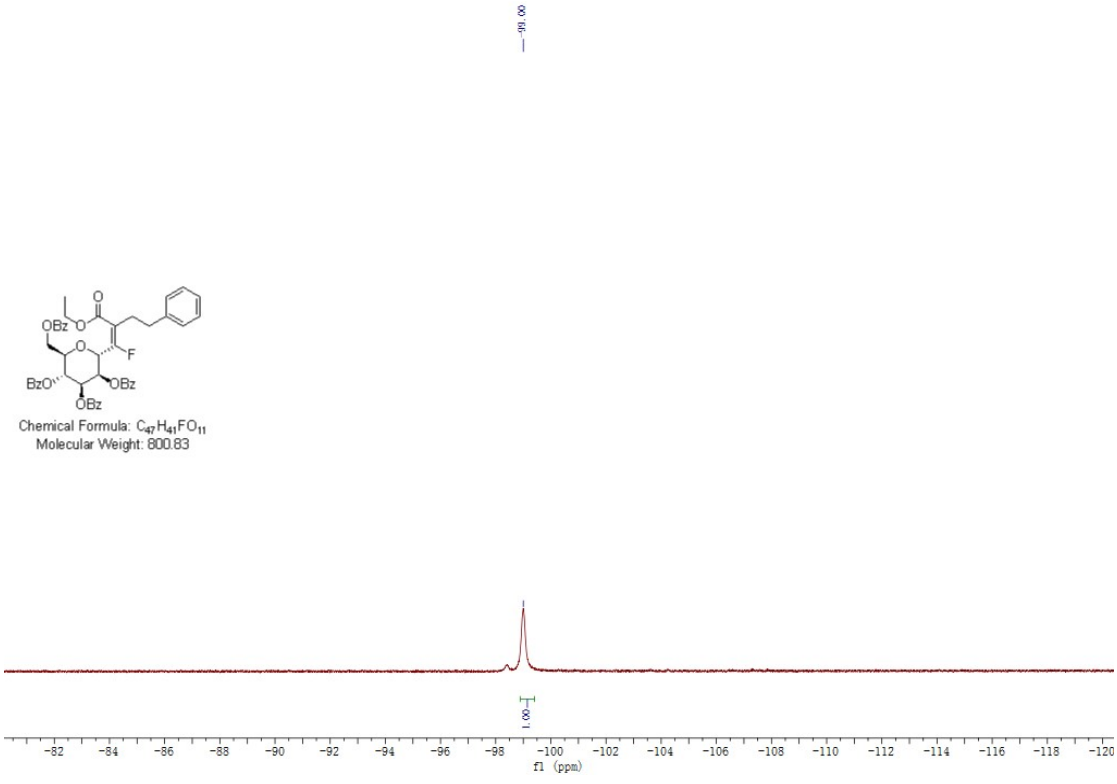
^{1}H NMR (500 MHz, Chloroform-*d*) of **3p**



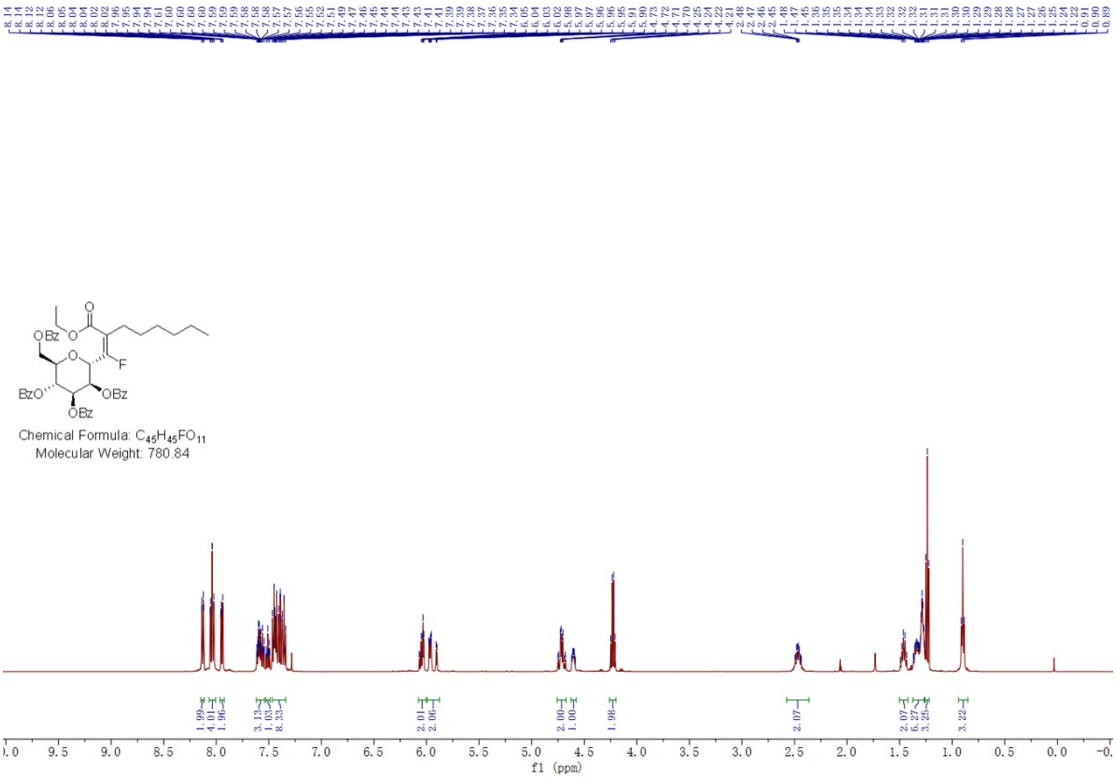
^{13}C NMR (126 MHz, Chloroform-*d*) of **3p**



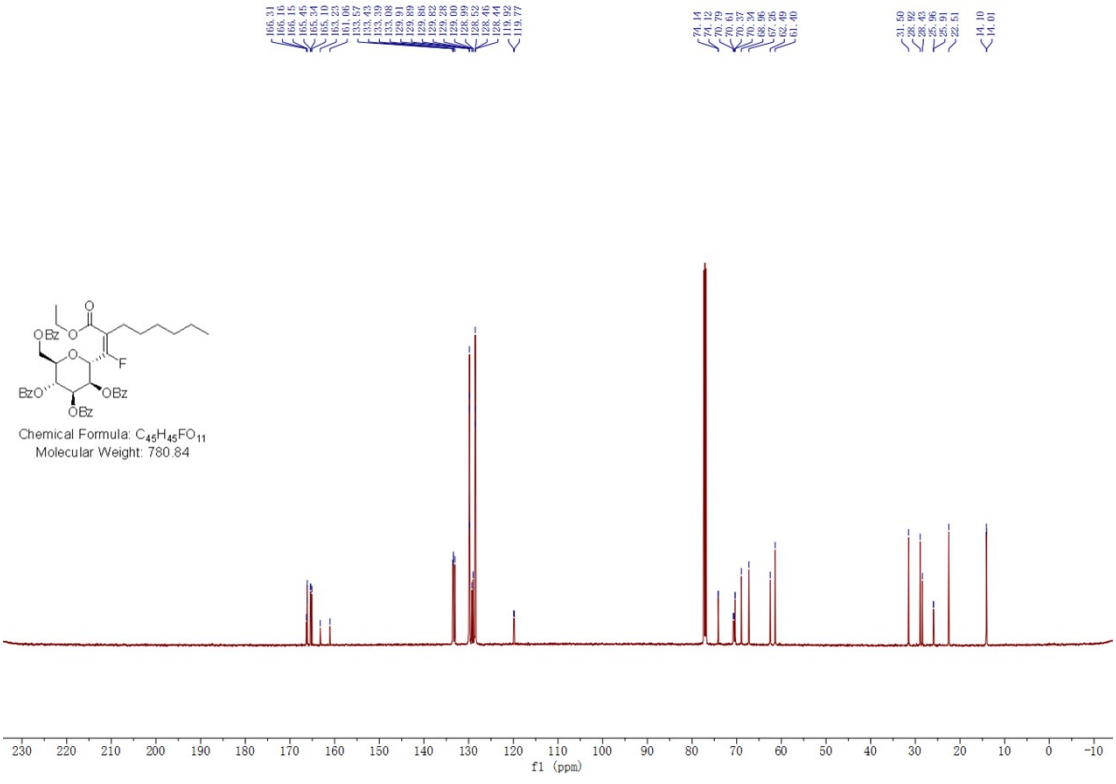
^{19}F NMR (471 MHz, Chloroform-*d*) of **3p**



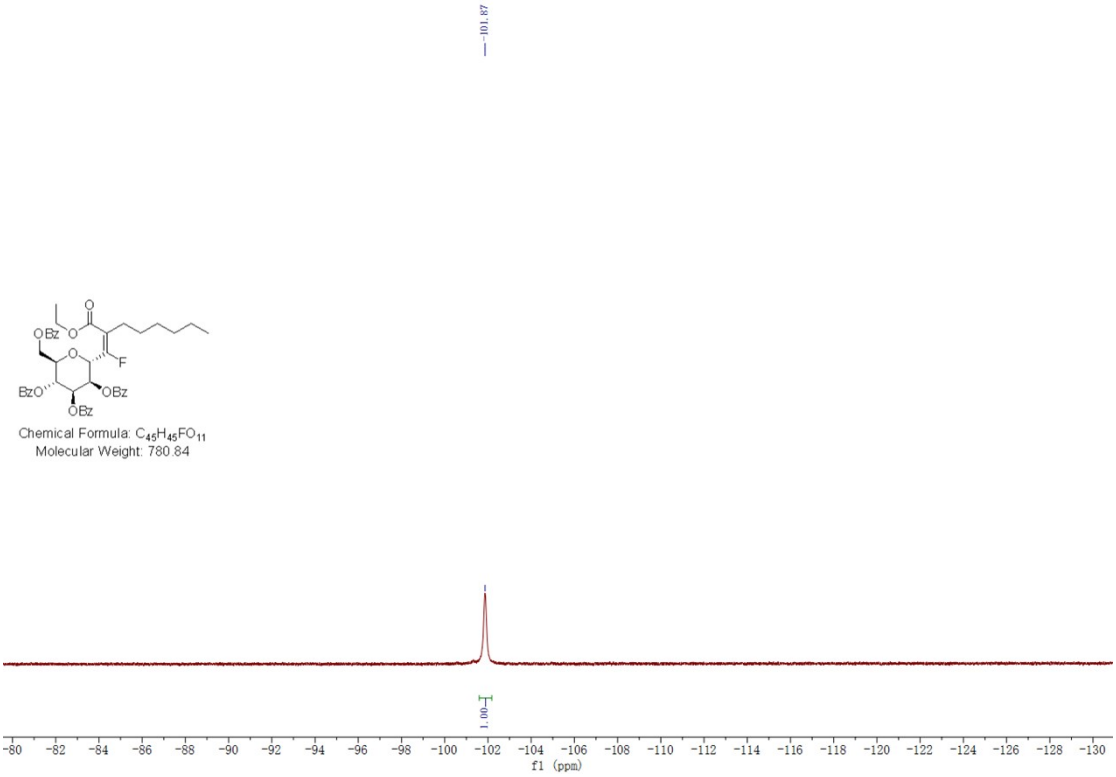
^{1}H NMR (500 MHz, Chloroform-*d*) of **3q**



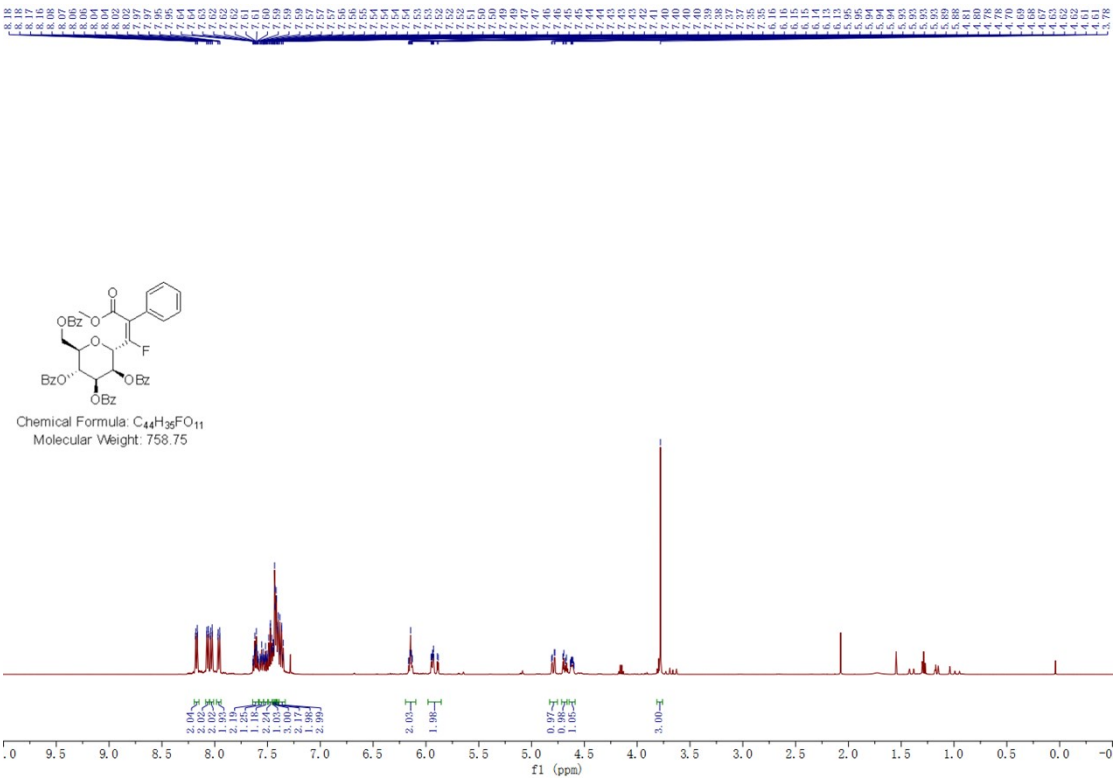
^{13}C NMR (126 MHz, Chloroform-*d*) of **3q**



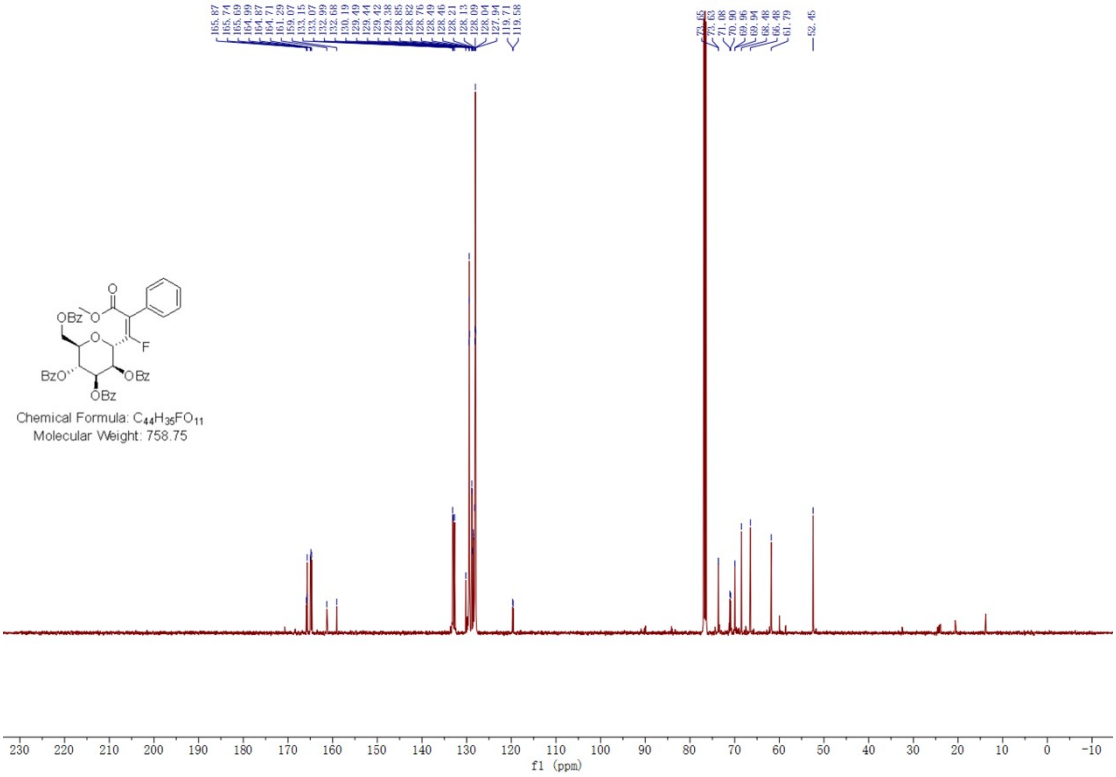
^{19}F NMR (471 MHz, Chloroform-*d*) of **3q**



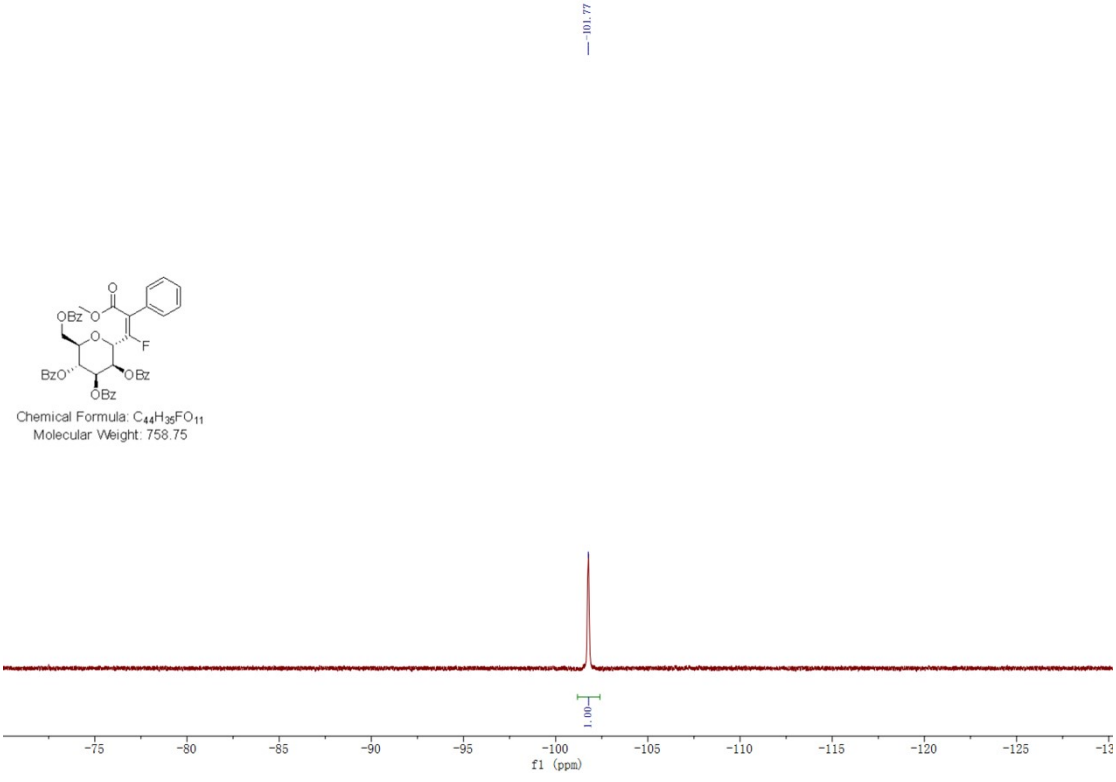
^{1}H NMR (500 MHz, Chloroform-*d*) of **3r**



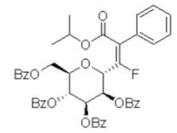
^{13}C NMR (126 MHz, Chloroform-*d*) of **3r**



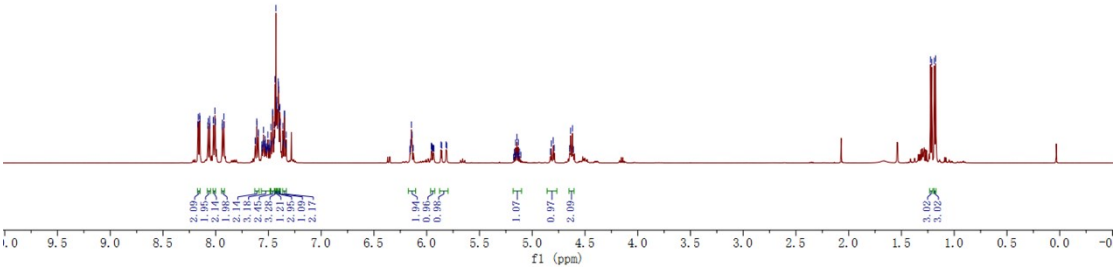
^{19}F NMR (471 MHz, Chloroform-*d*) of **3r**



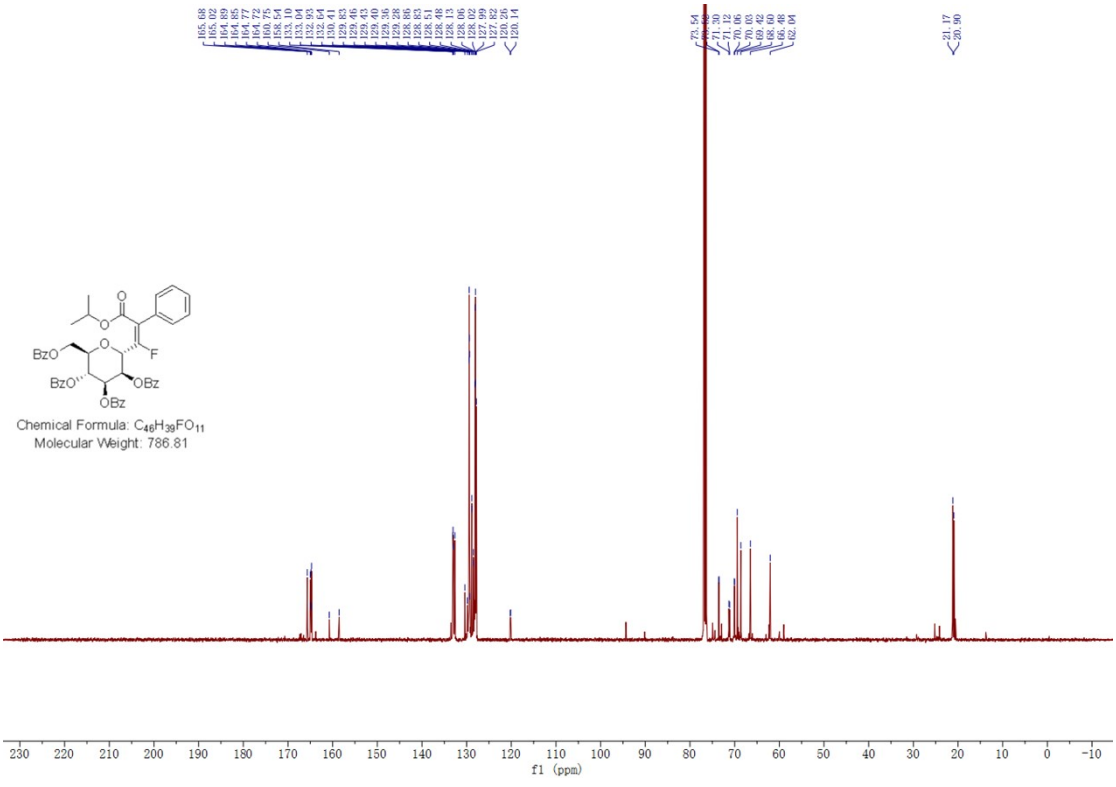
^{1}H NMR (500 MHz, Chloroform-*d*) of **3s**



Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

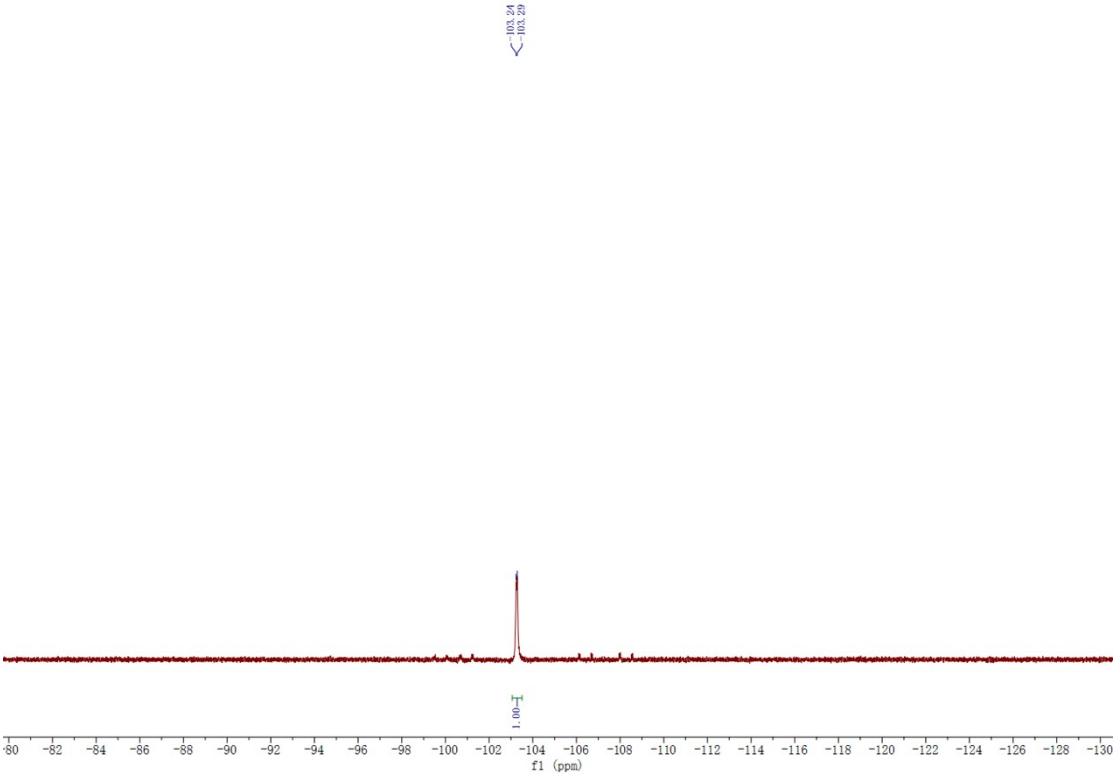


^{13}C NMR (126 MHz, Chloroform-*d*) of **3s**

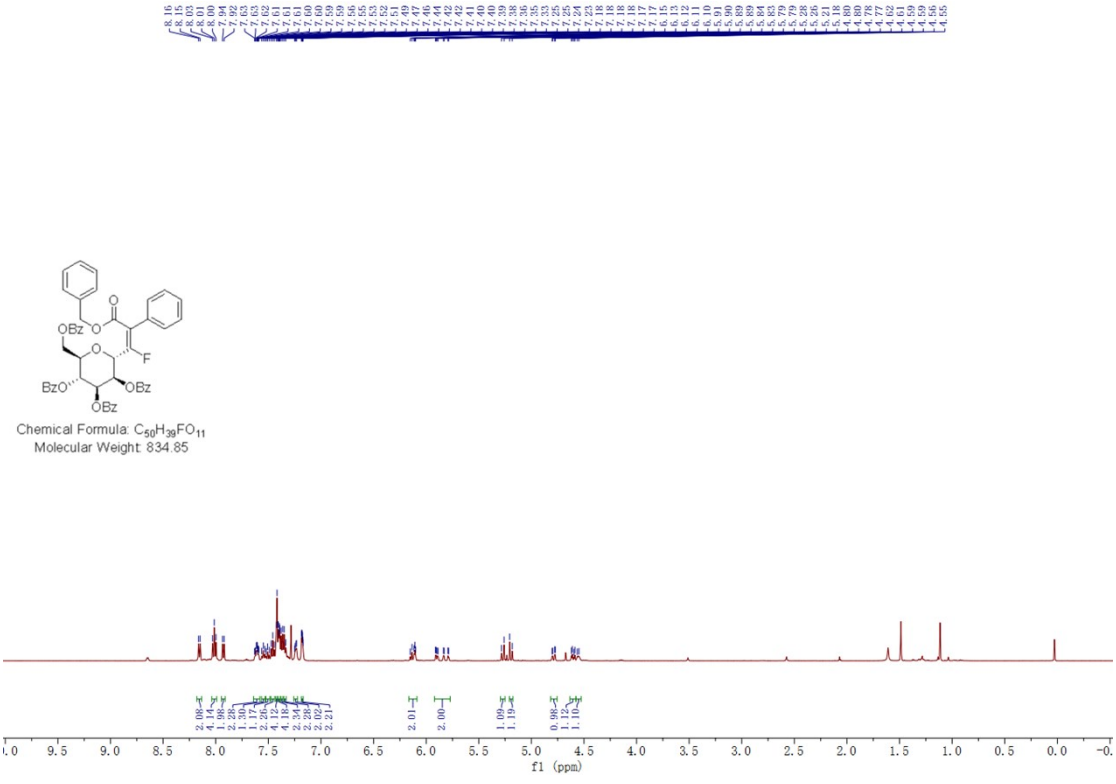


Chemical Formula: $C_{46}H_{39}FO_{11}$
Molecular Weight: 786.81

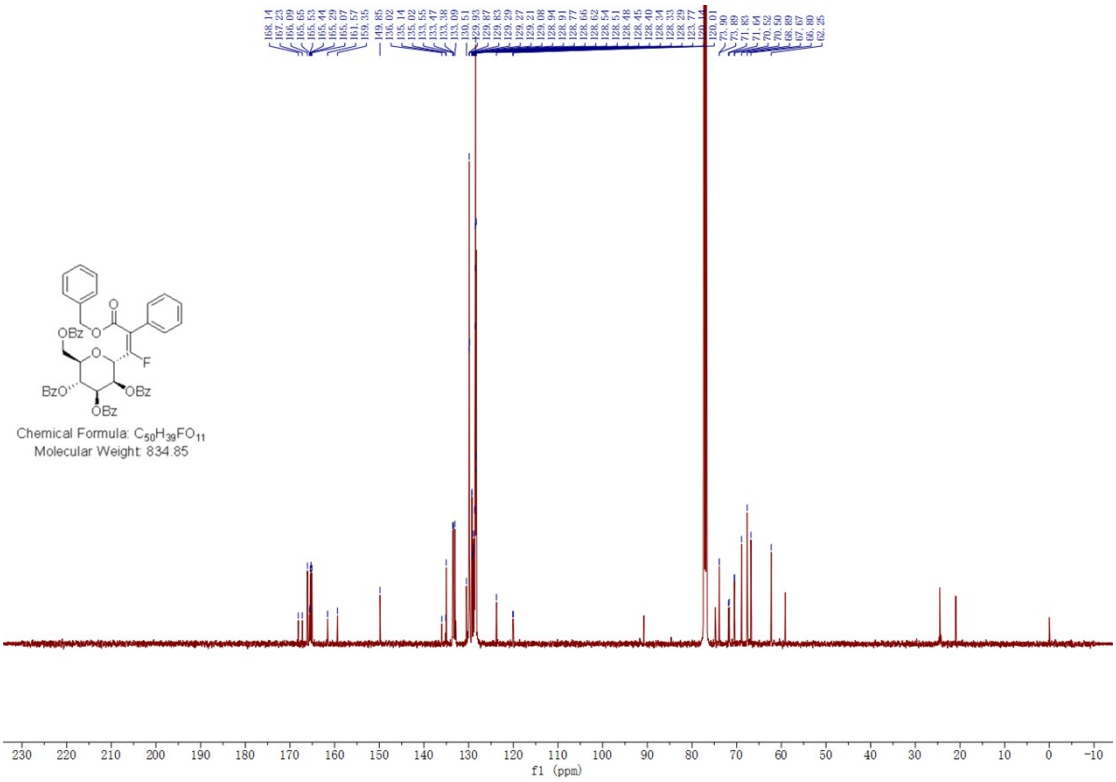
^{19}F NMR (471 MHz, Chloroform-*d*) of **3s**



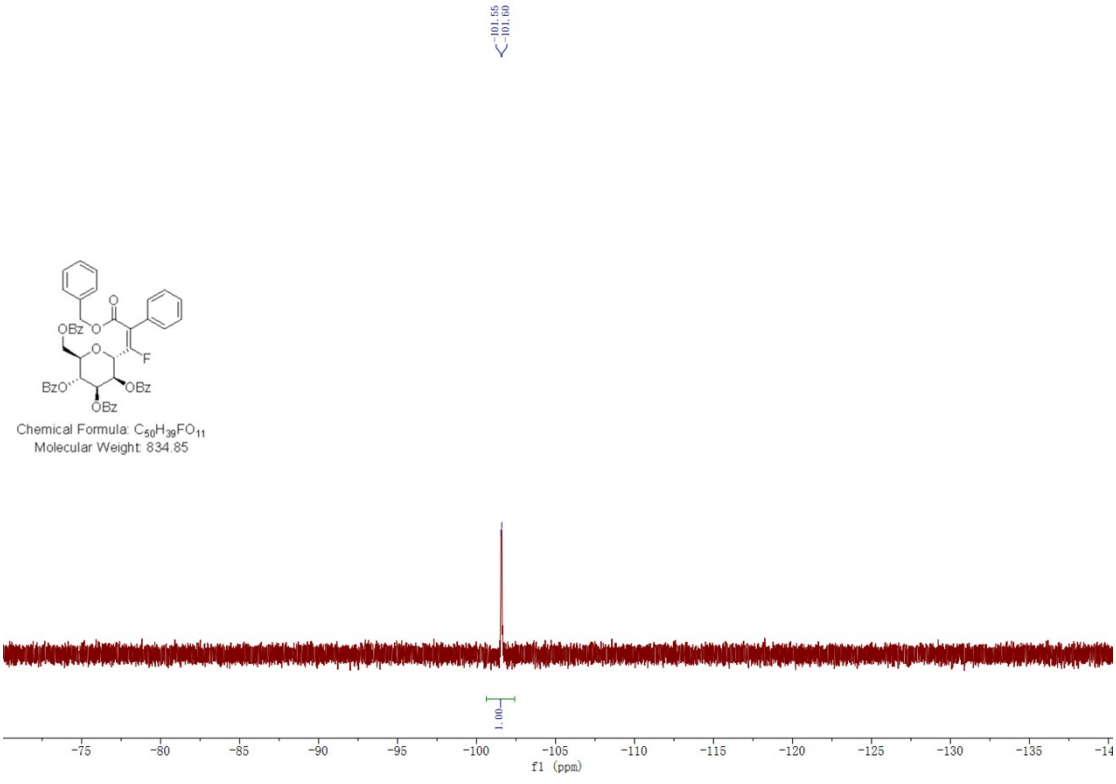
^{1}H NMR (500 MHz, Chloroform-*d*) of **3t**



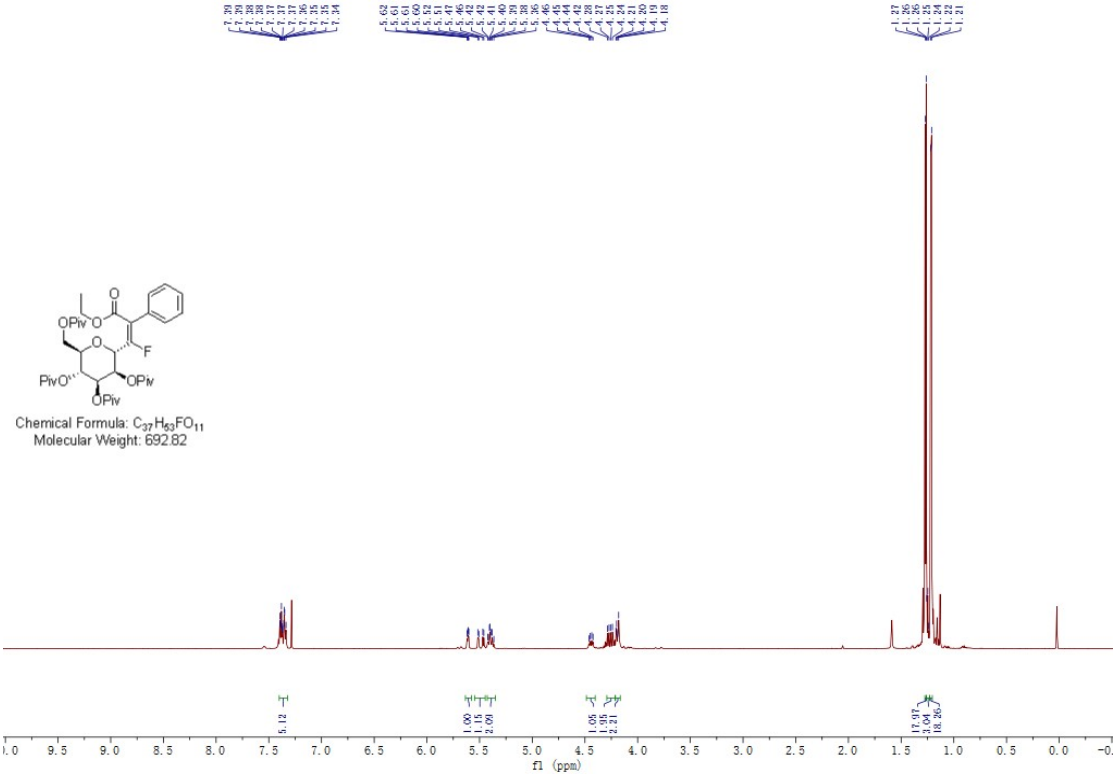
^{13}C NMR (126 MHz, Chloroform-*d*) of **3t**



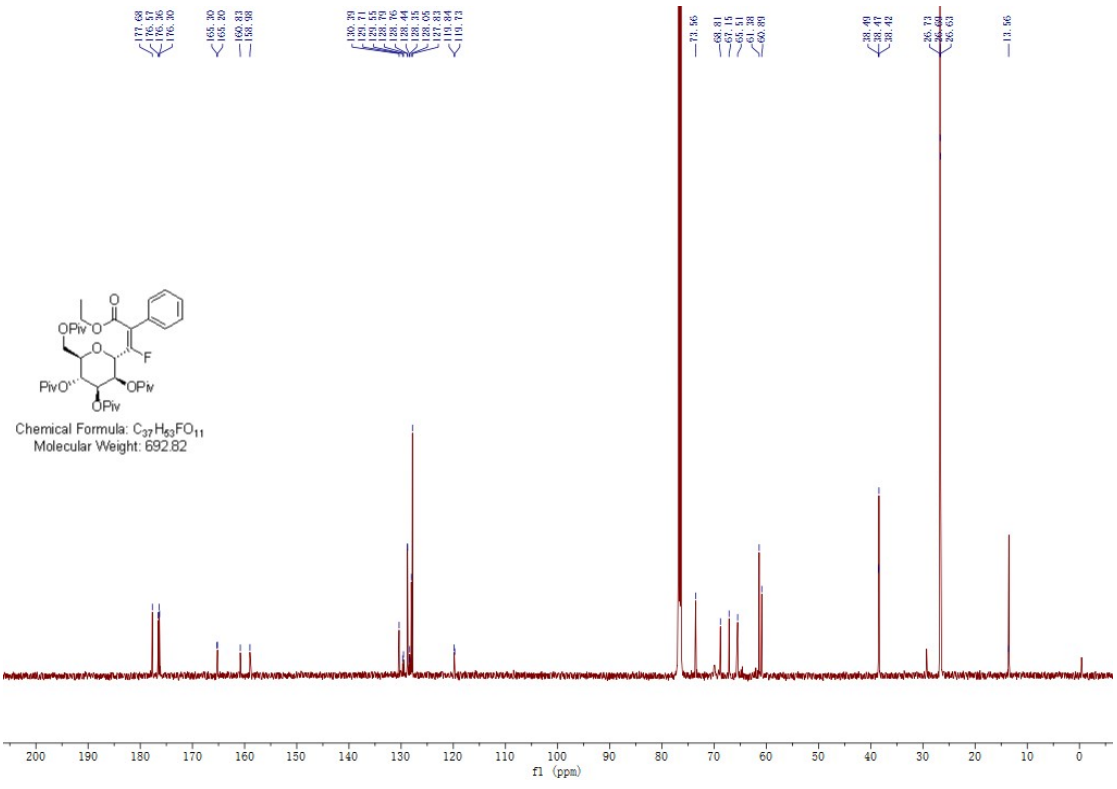
^{19}F NMR (471 MHz, Chloroform-*d*) of **3t**



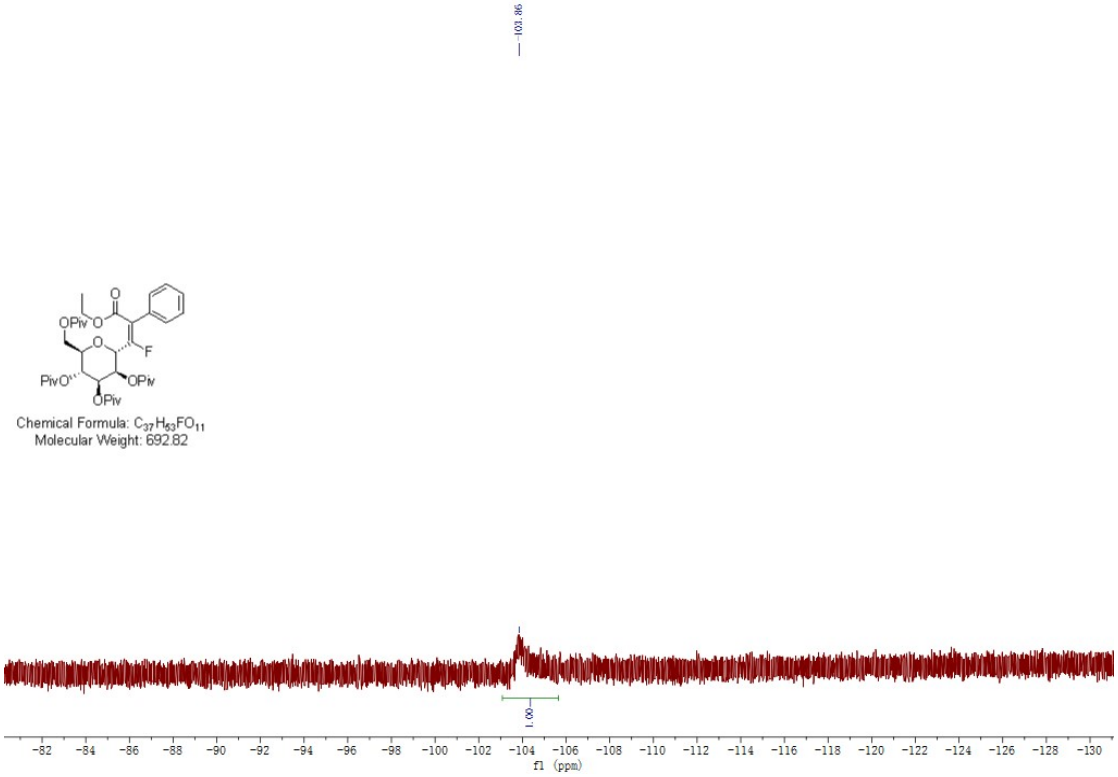
^{1}H NMR (500 MHz, Chloroform-*d*) of **4a**



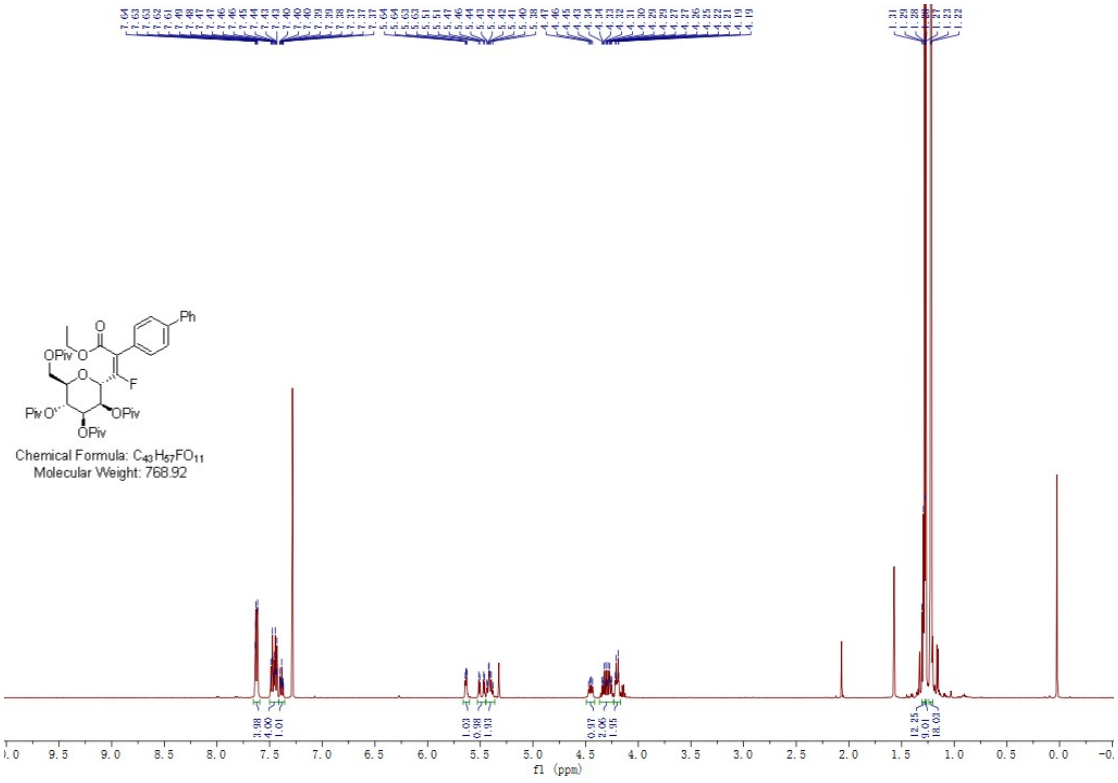
^{13}C NMR (151 MHz, Chloroform-*d*) of **4a**



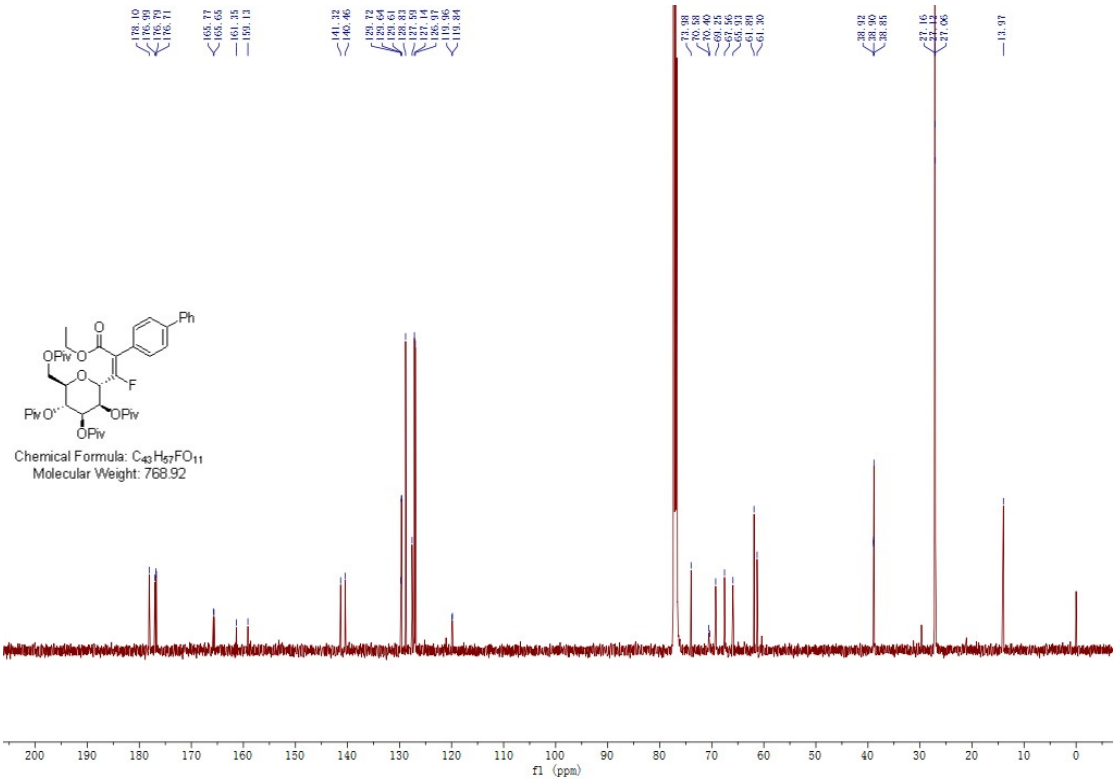
^{19}F NMR (471 MHz, Chloroform-*d*) of **4a**



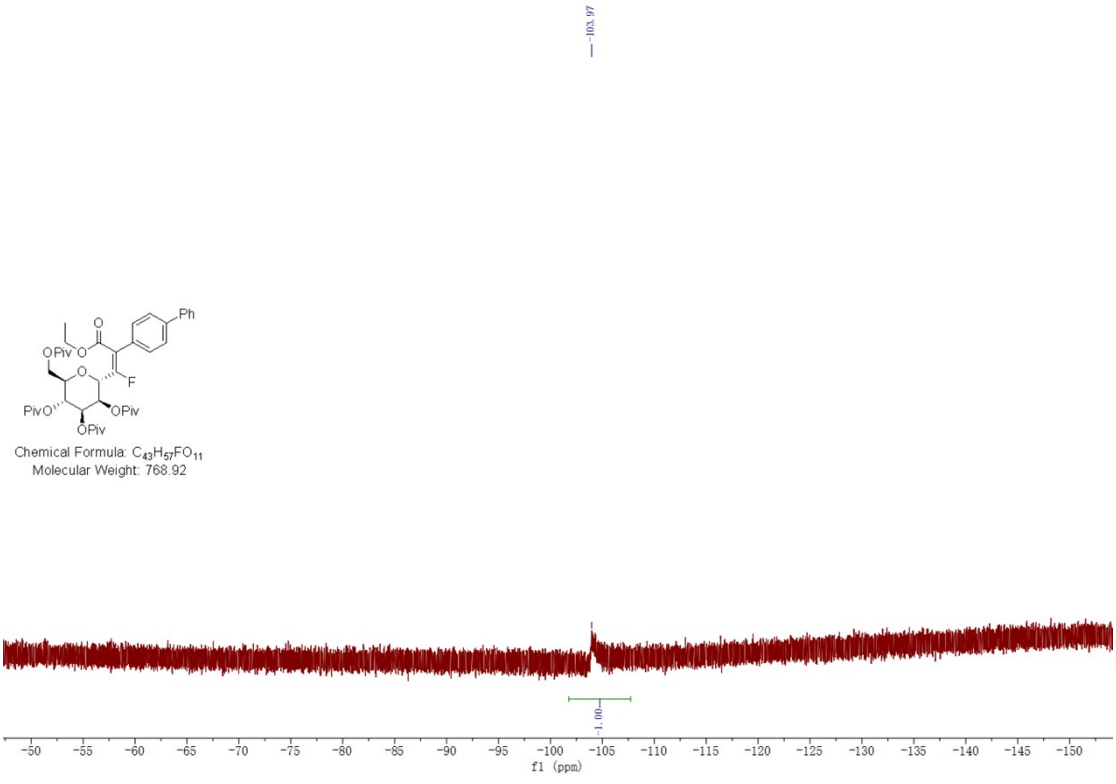
^{1}H NMR (500 MHz, Chloroform-*d*) of **4b**



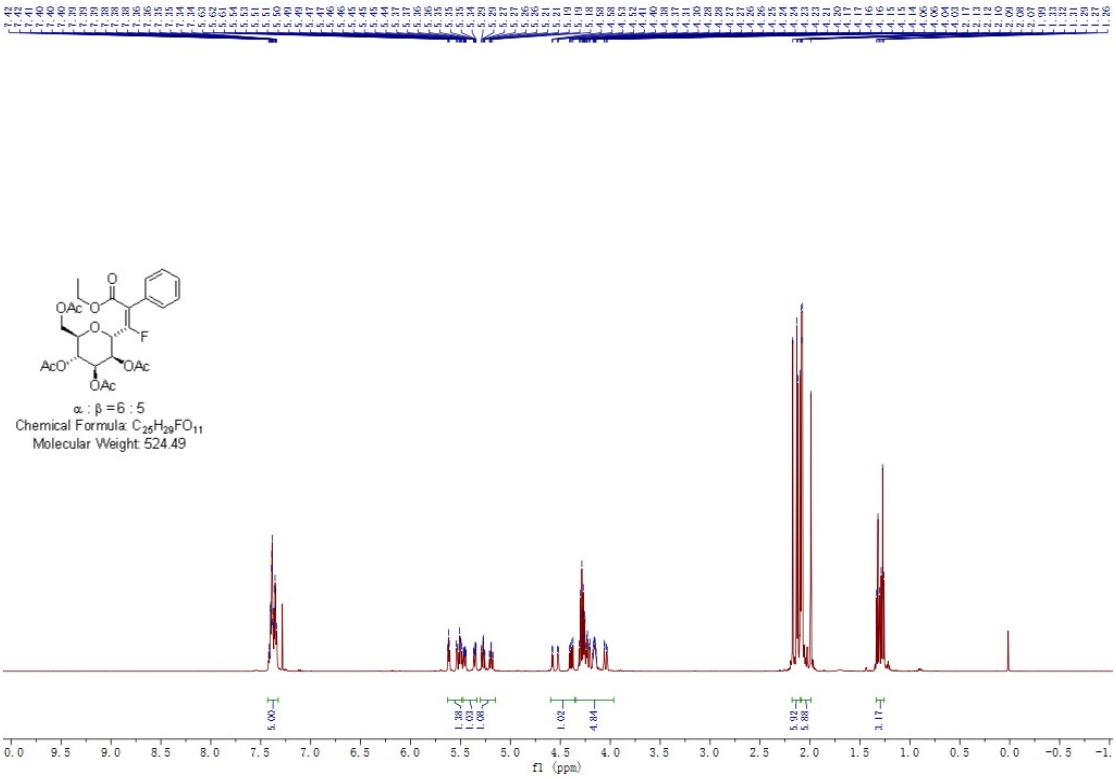
^{13}C NMR (126 MHz, Chloroform-*d*) of **4b**



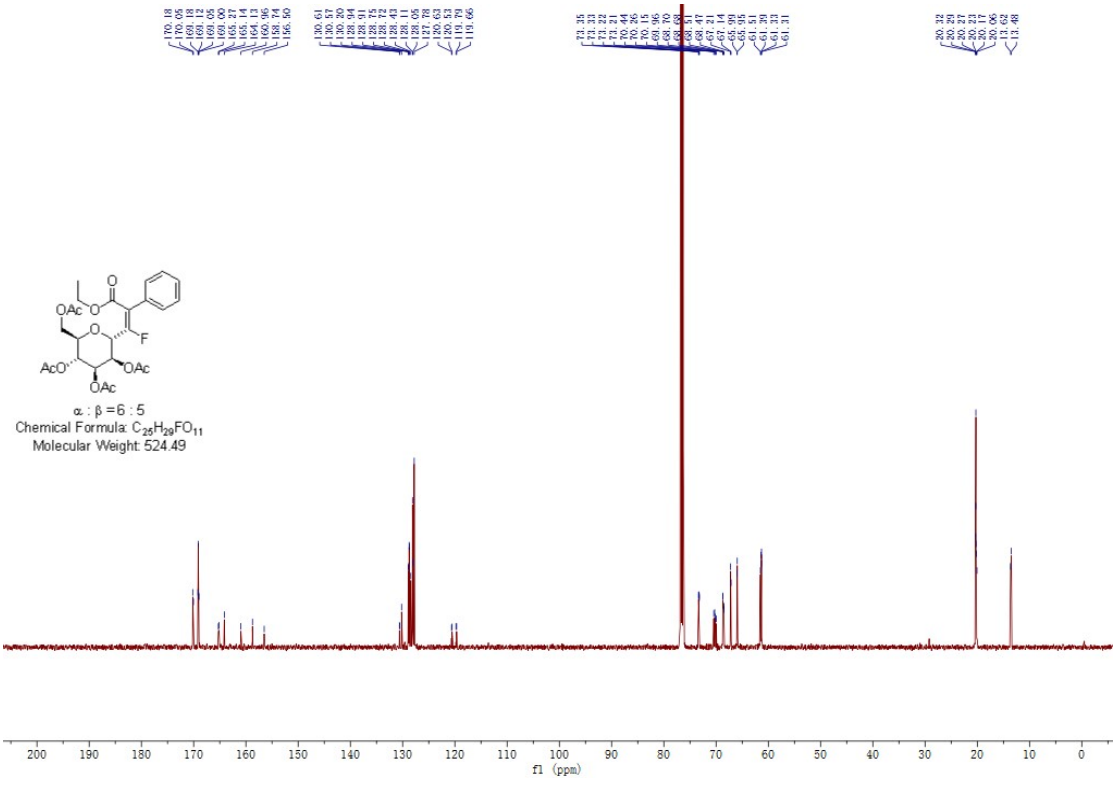
^{19}F NMR (471 MHz, Chloroform-*d*) of **4b**



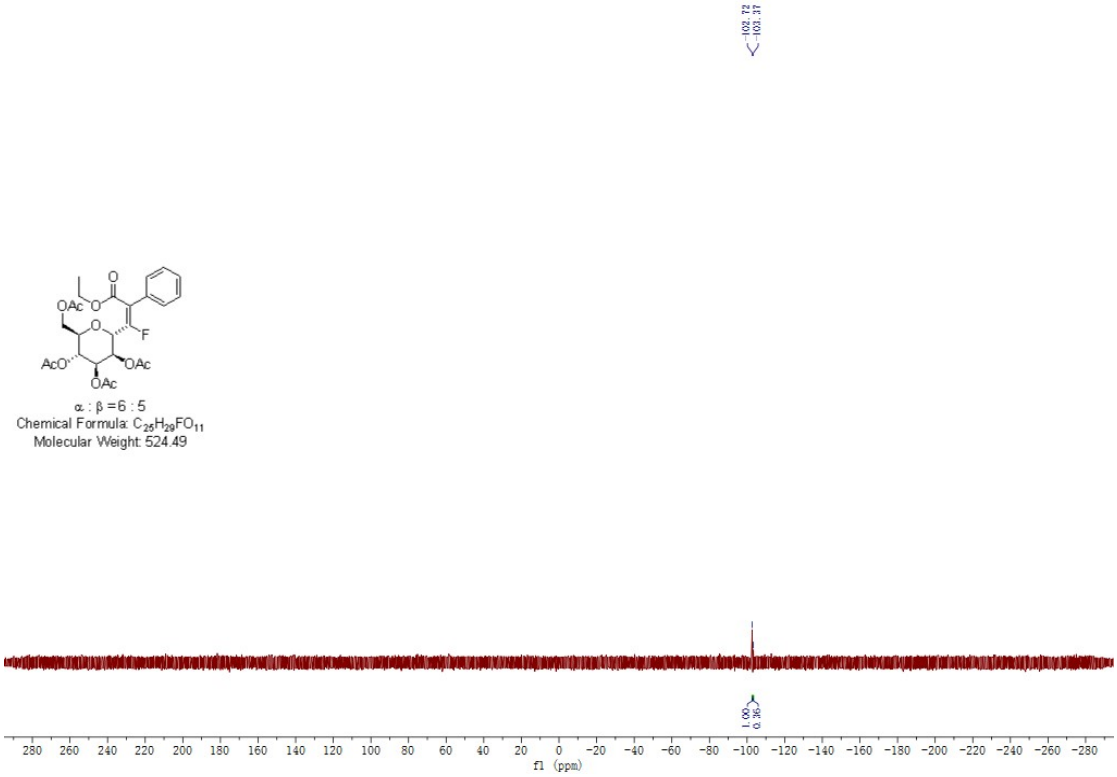
^{1}H NMR (500 MHz, Chloroform-*d*) of **4c**



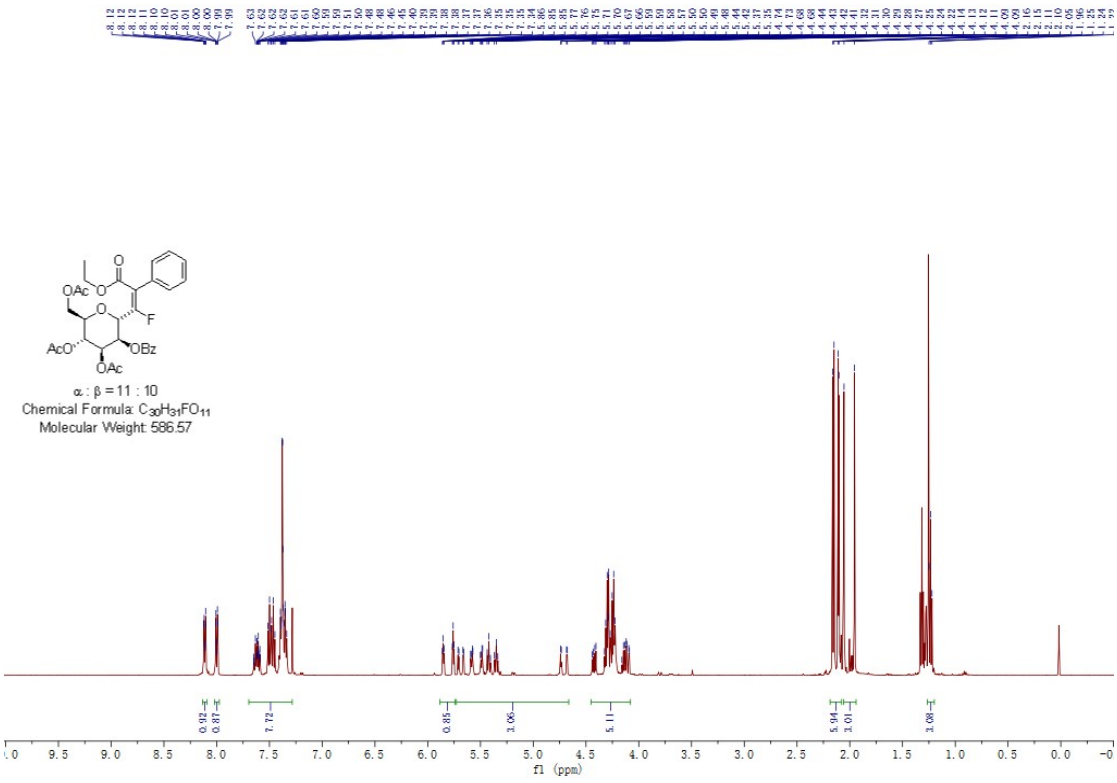
^{13}C NMR (126 MHz, Chloroform-*d*) of **4c**



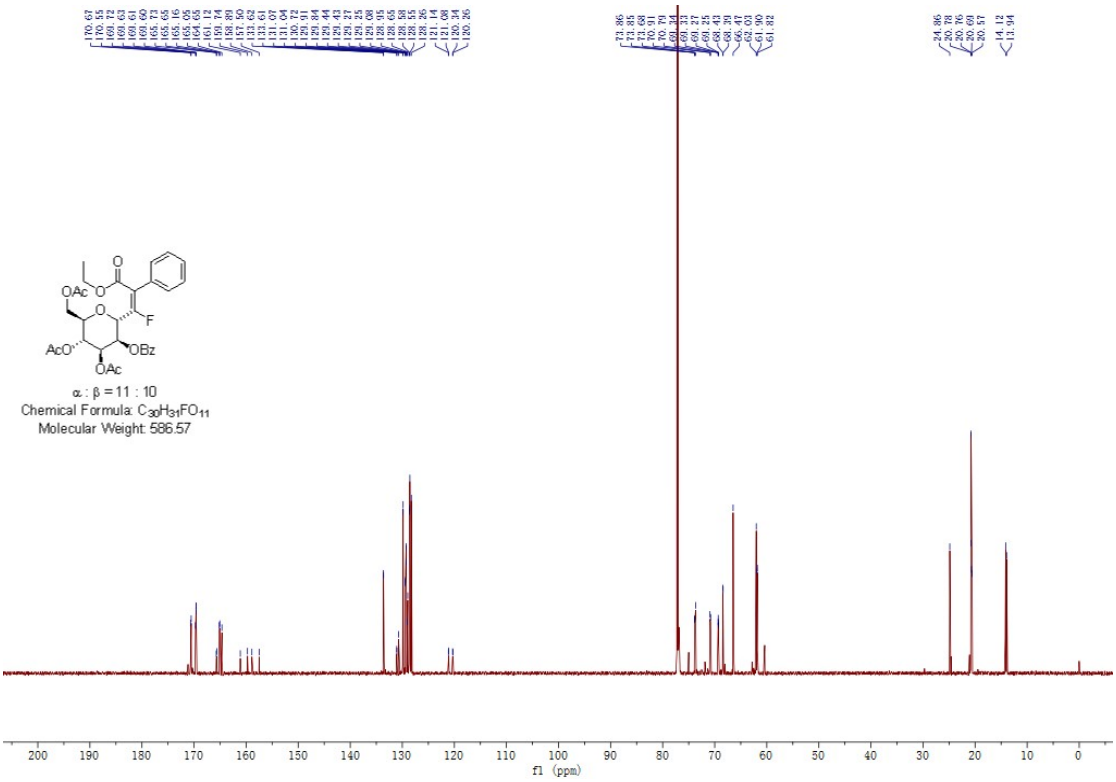
^{19}F NMR (471 MHz, Chloroform-*d*) of **4c**



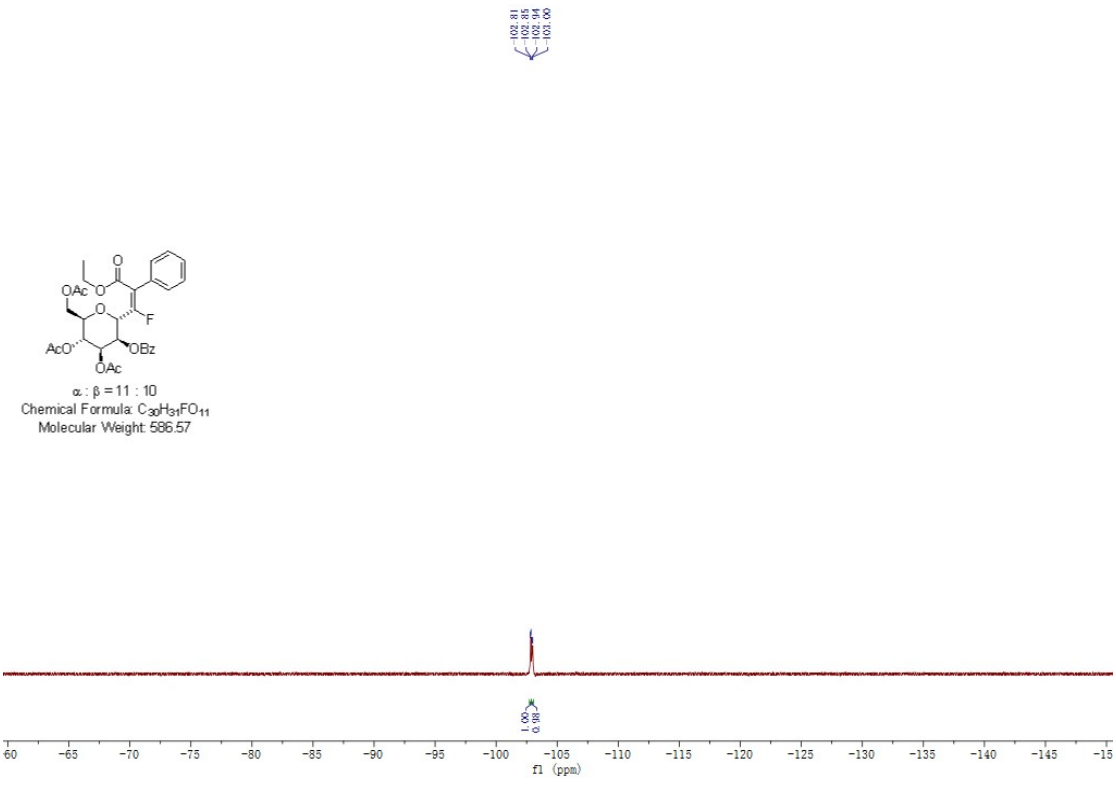
^{1}H NMR (500 MHz, Chloroform-*d*) of **4d**



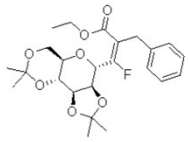
^{13}C NMR (201 MHz, Chloroform-*d*) of **4d**



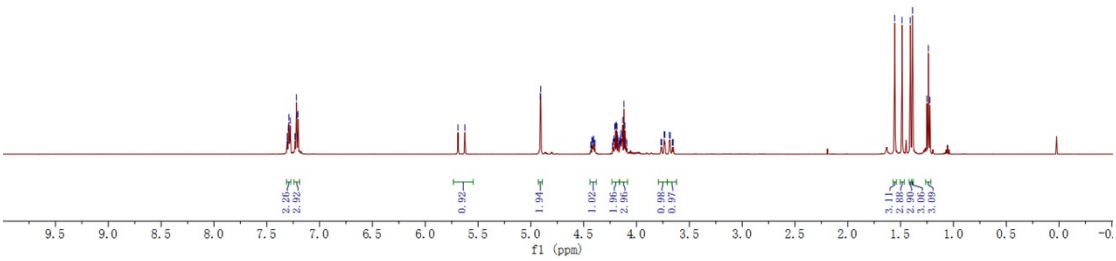
^{19}F NMR (471 MHz, Chloroform-*d*) of **4d**



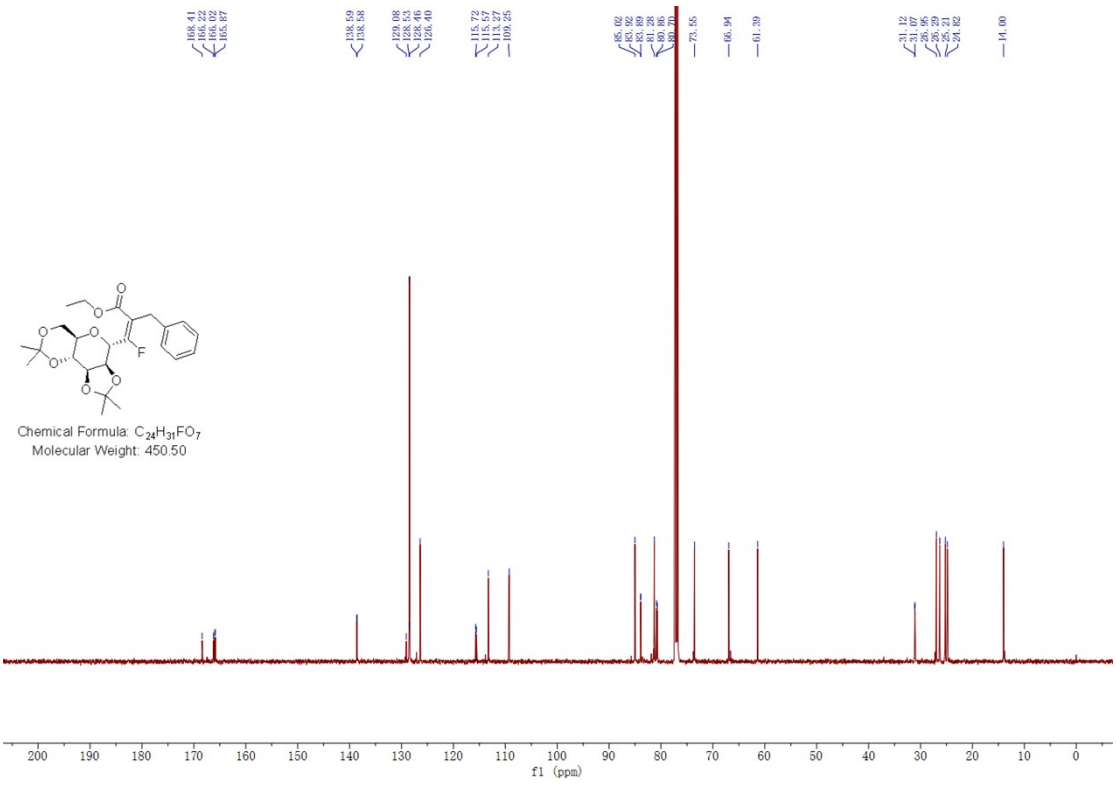
^{1}H NMR (500 MHz, Chloroform-*d*) of **4e**



Chemical Formula: $C_{24}H_{31}FO_7$
Molecular Weight: 450.50

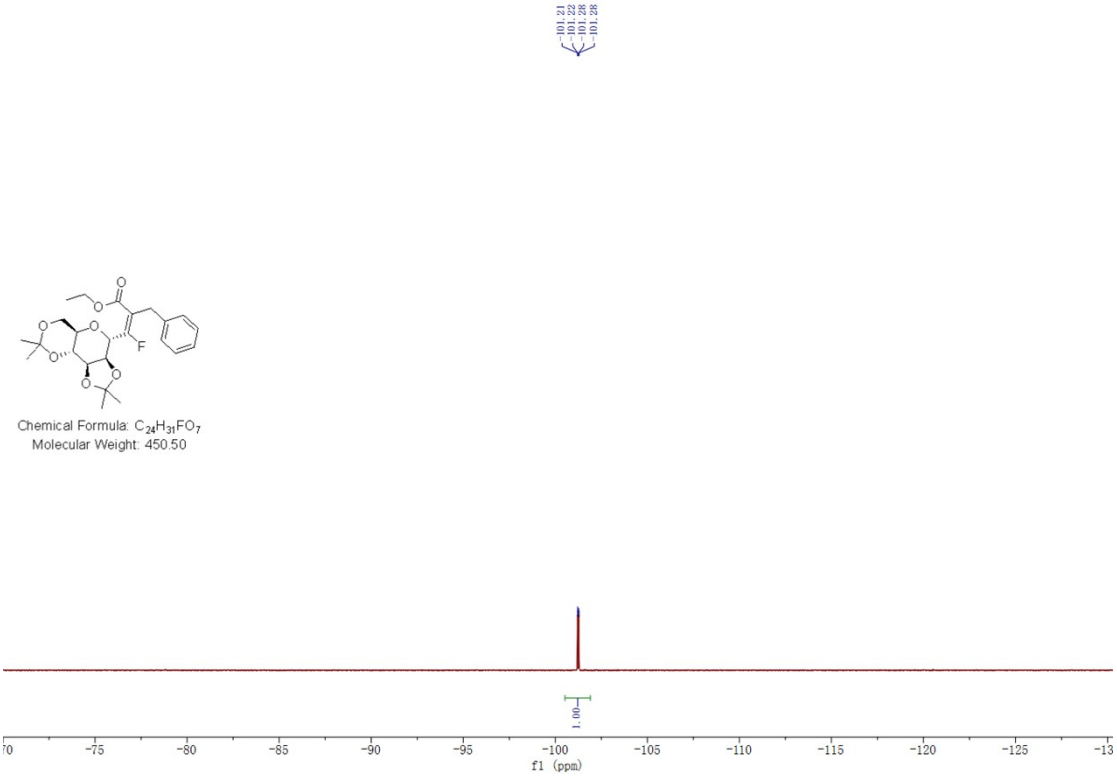


^{13}C NMR (201 MHz, Chloroform-*d*) of **4e**

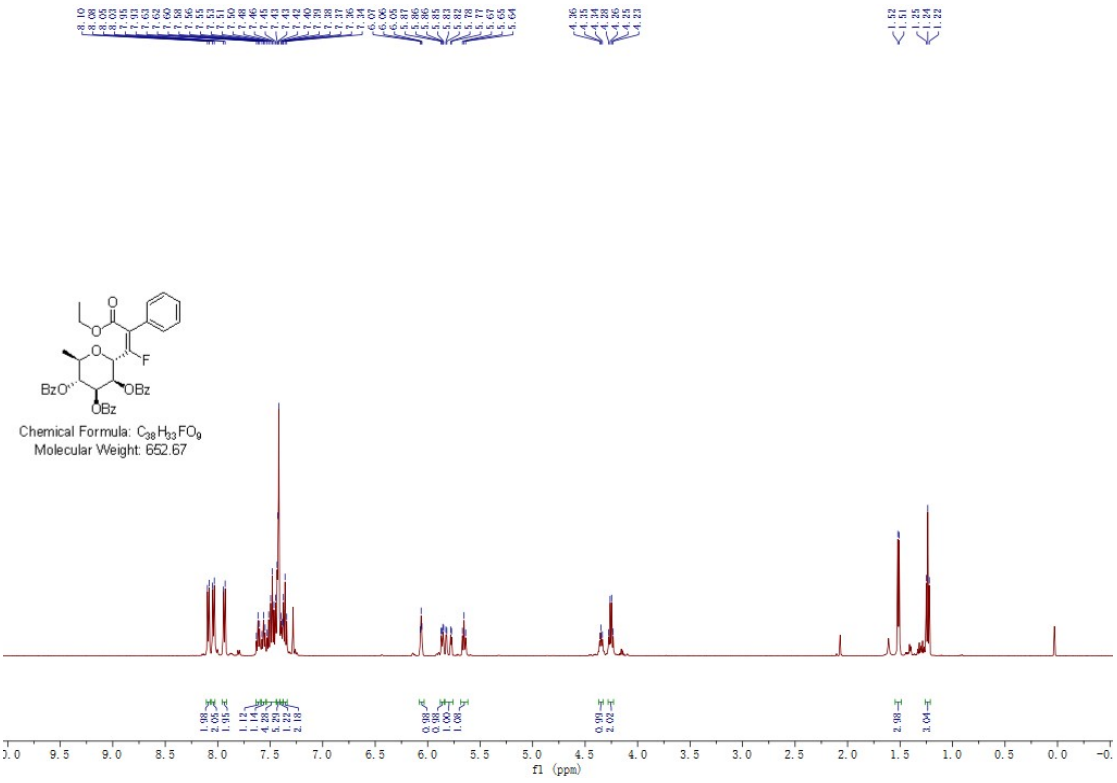


Chemical Formula: $C_{24}H_{31}FO_7$
Molecular Weight: 450.50

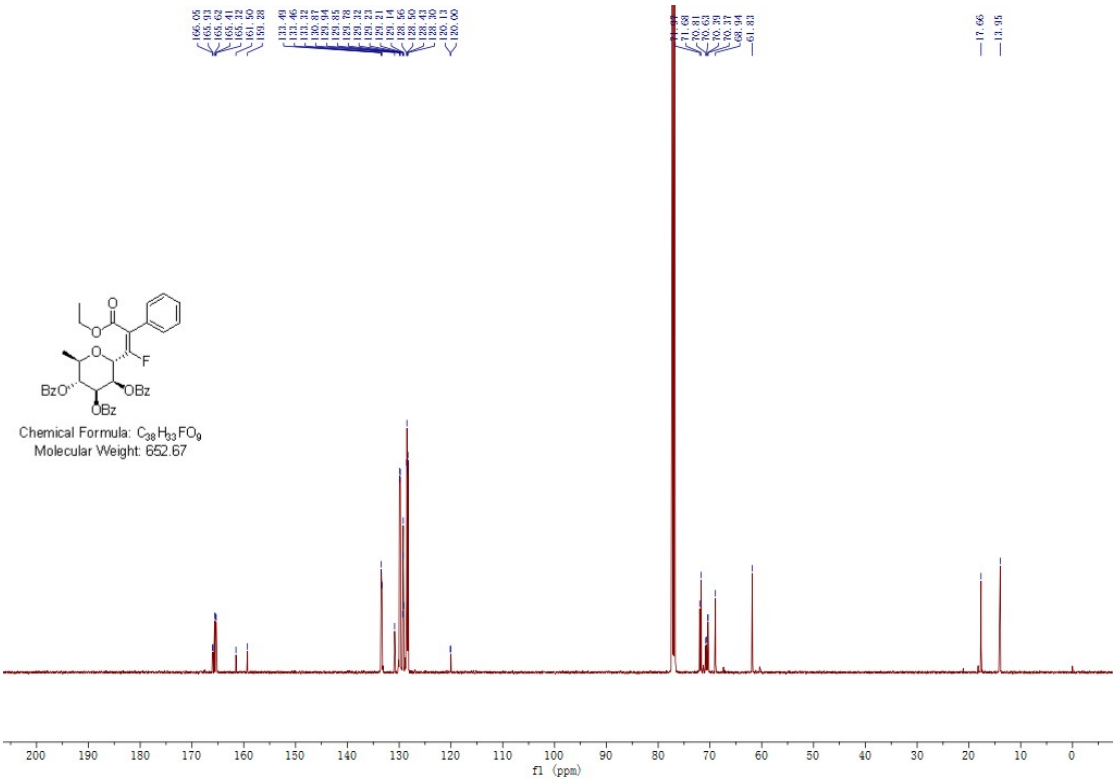
^{19}F NMR (471 MHz, Chloroform-*d*) of **4e**



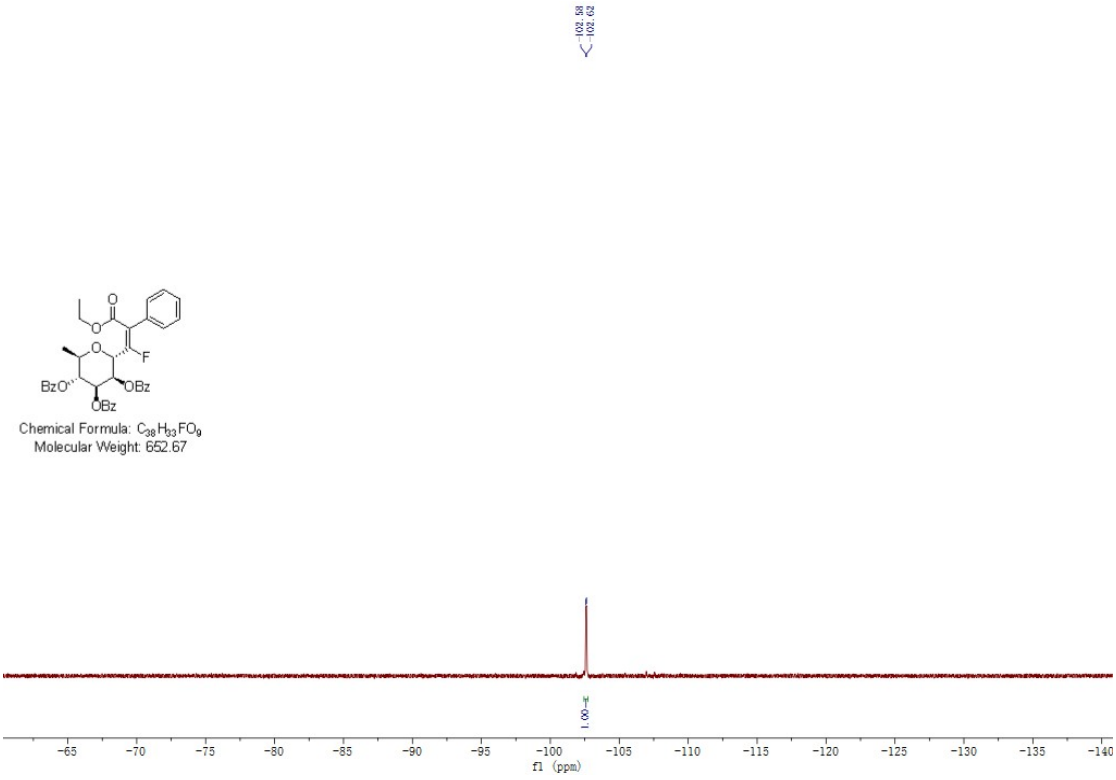
^{1}H NMR (500 MHz, Chloroform-*d*) of **4f**



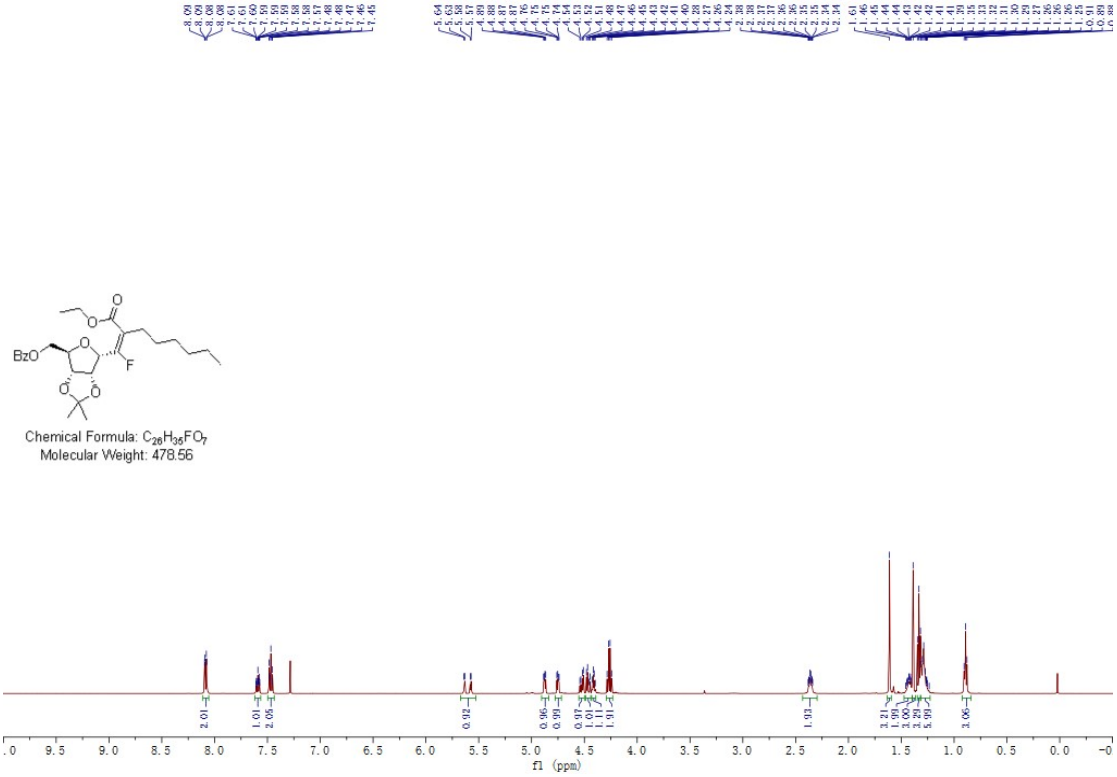
^{13}C NMR (126 MHz, Chloroform-*d*) of **4f**



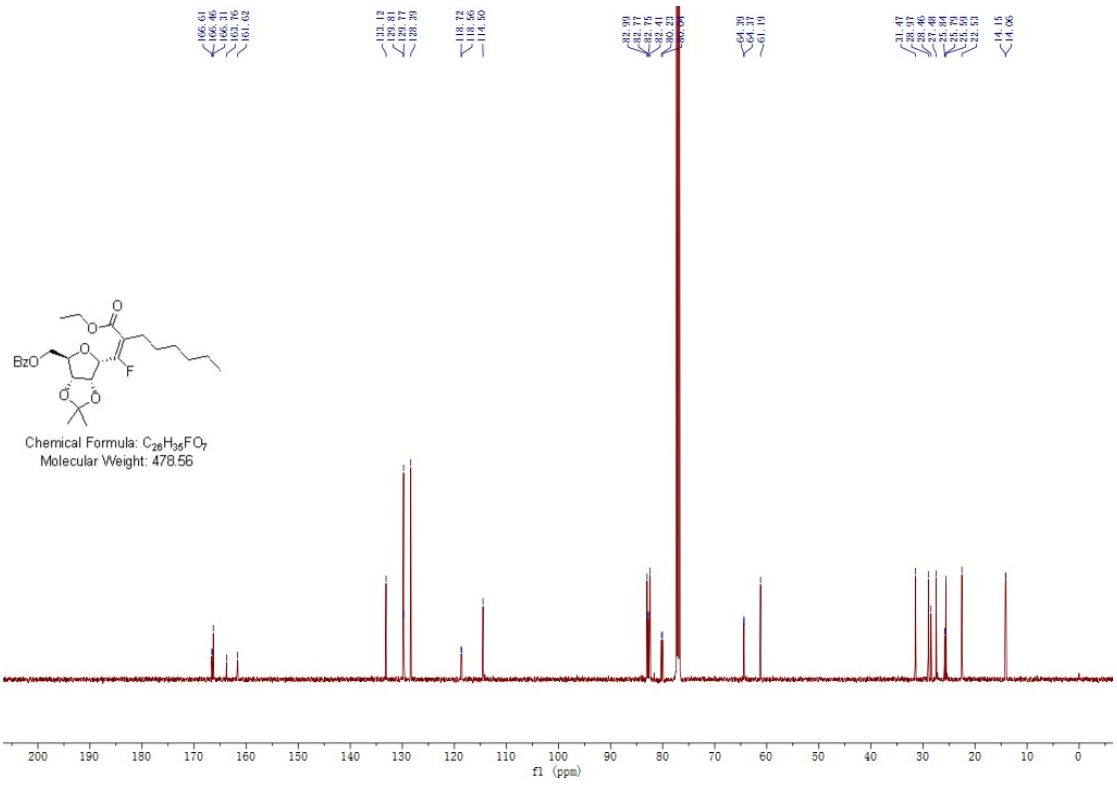
^{19}F NMR (471 MHz, Chloroform-*d*) of **4f**



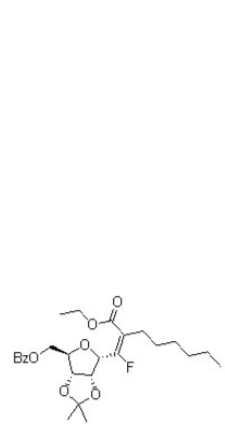
^{1}H NMR (500 MHz, Chloroform-*d*) of **4g**



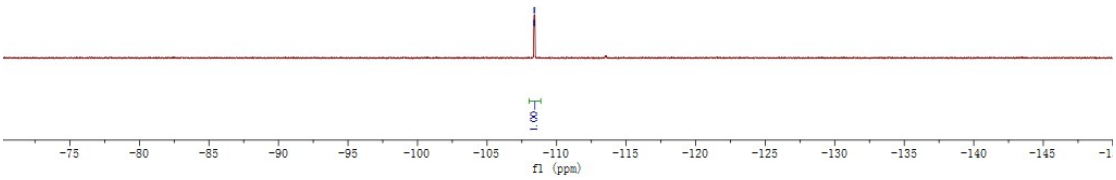
^{13}C NMR (126 MHz, Chloroform-*d*) of **4g**



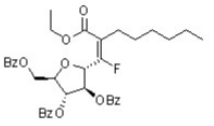
^{19}F NMR (471 MHz, Chloroform-*d*) of **4g**



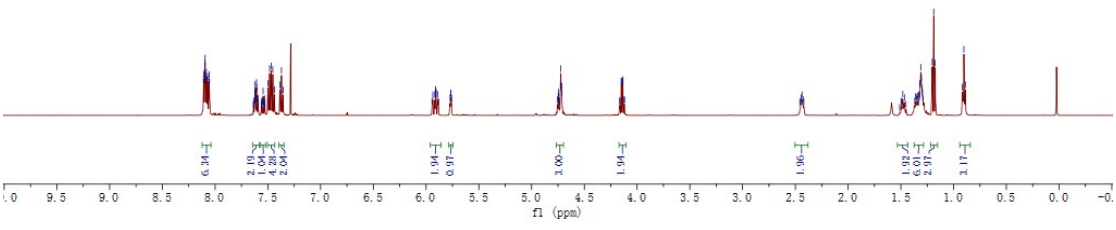
Chemical Formula: $C_{28}H_{35}FO_7$
Molecular Weight: 478.56



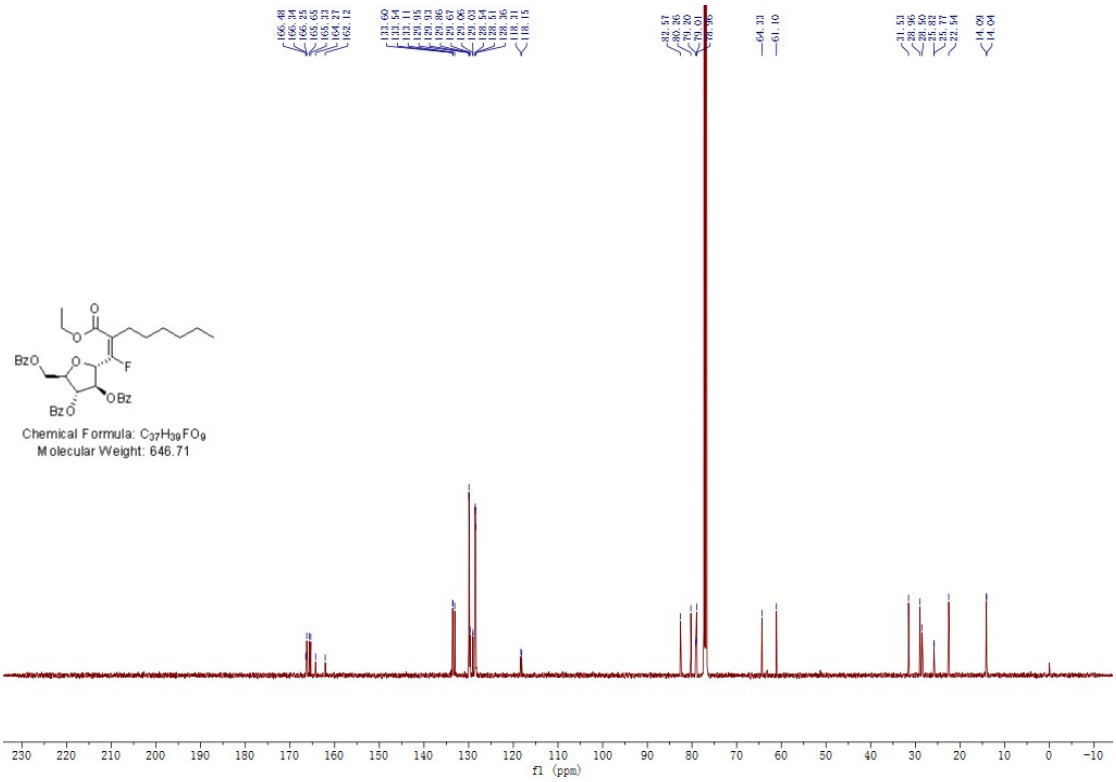
^{1}H NMR (500 MHz, Chloroform-*d*) of **4h**



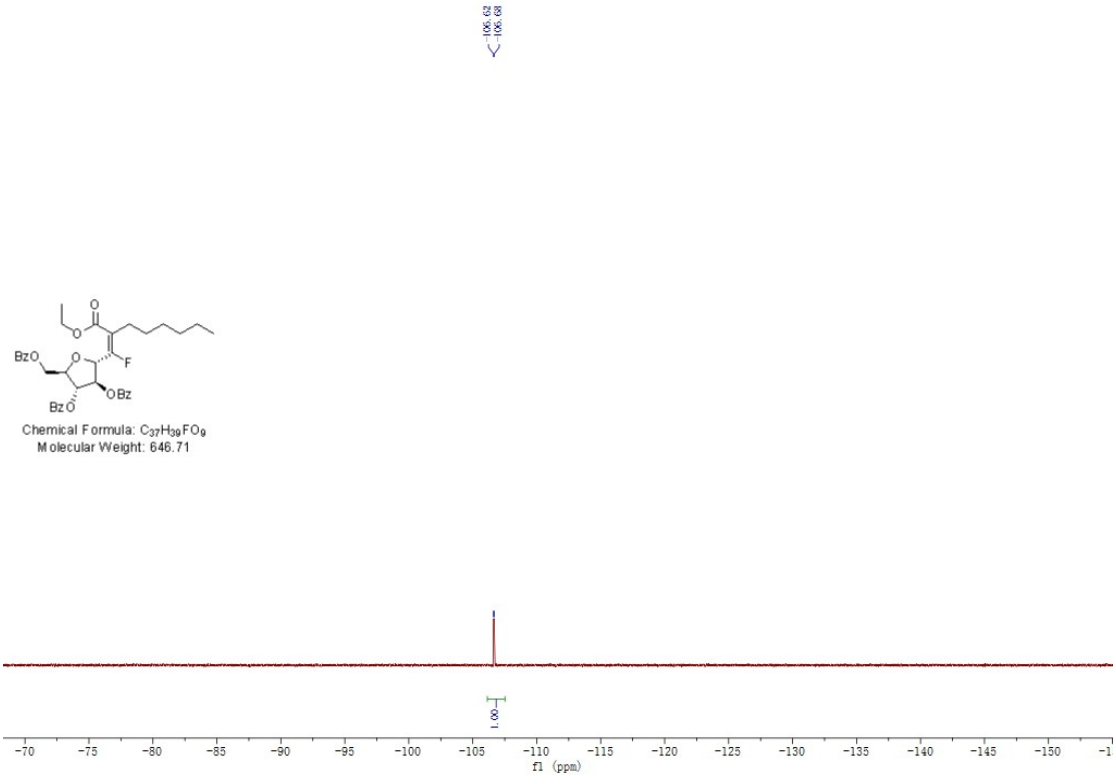
Chemical Formula: $C_{37}H_{39}FO_9$
Molecular Weight: 646.71



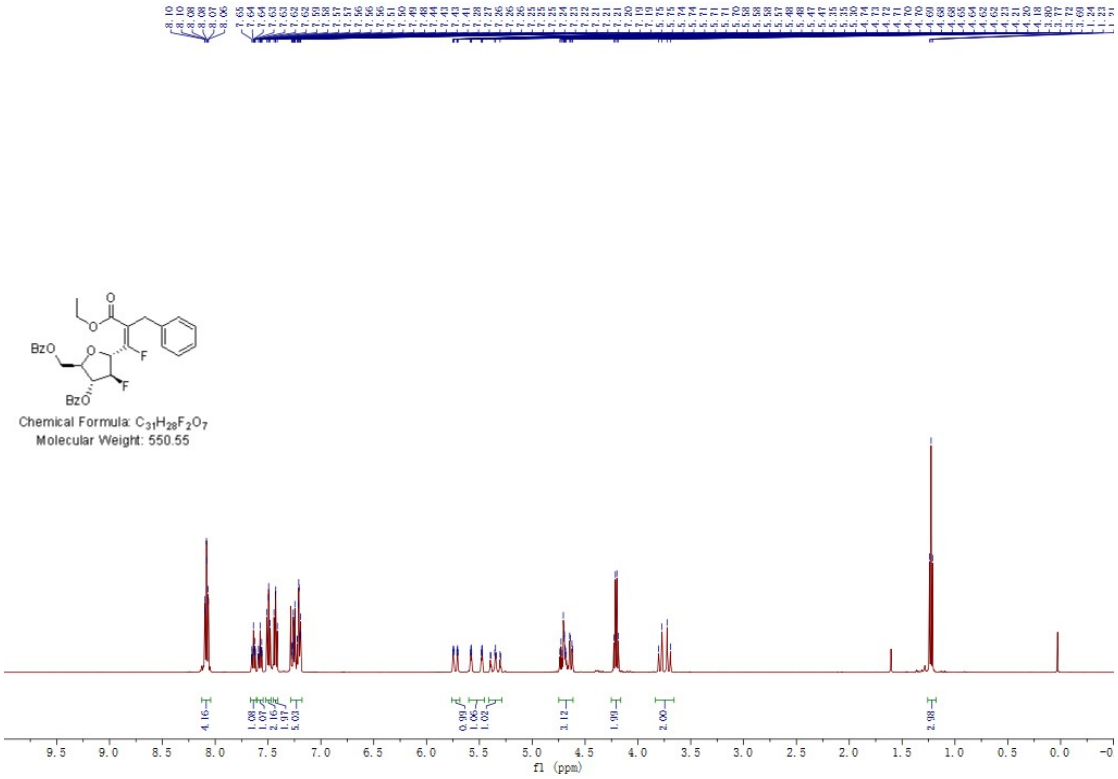
^{13}C NMR (126 MHz, Chloroform-*d*) of **4h**



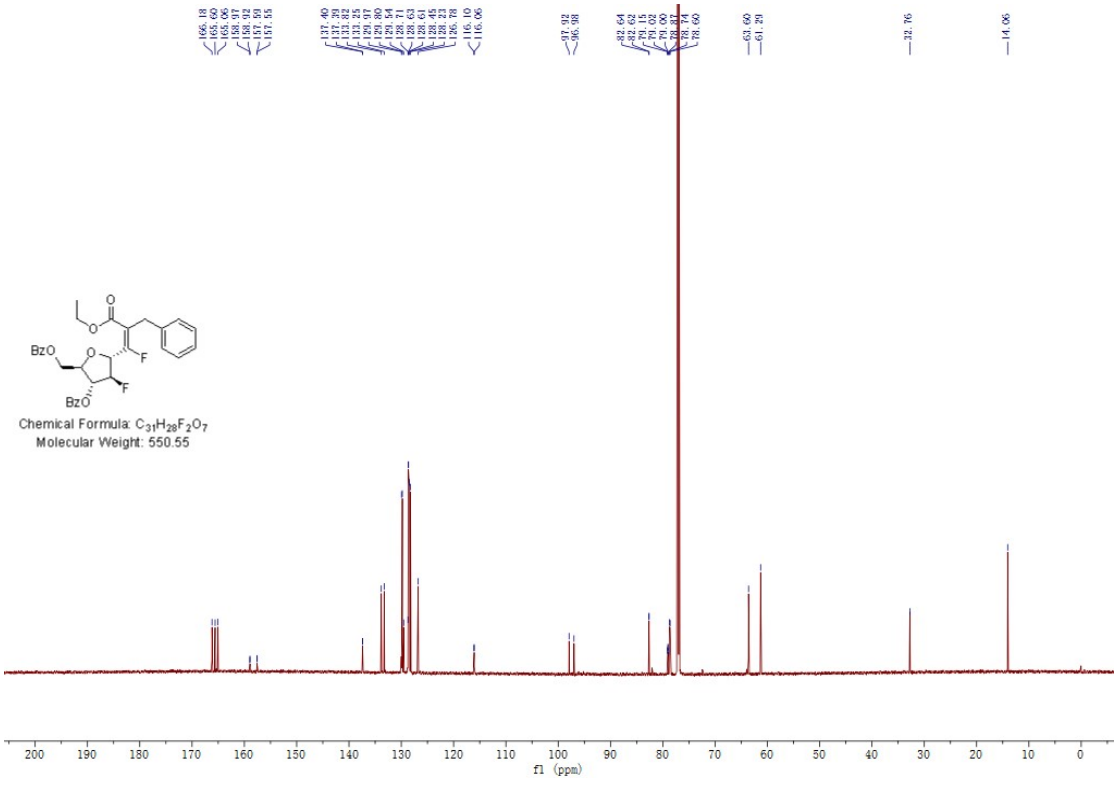
^{19}F NMR (471 MHz, Chloroform-*d*) of **4h**



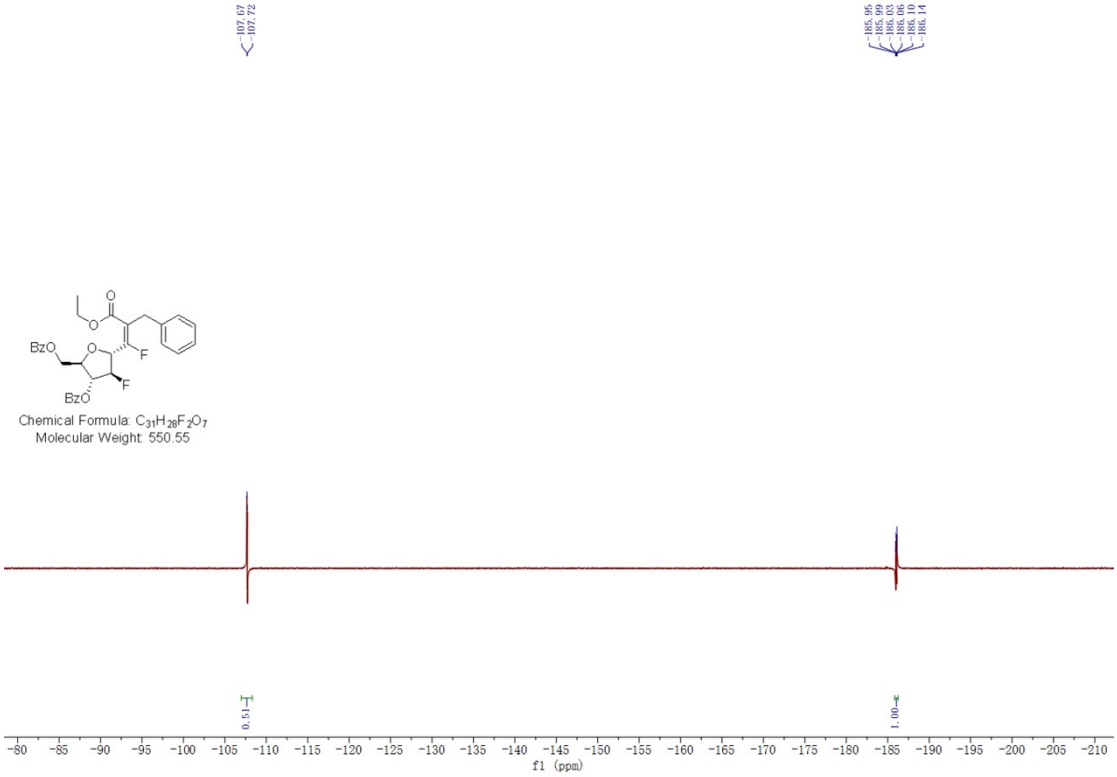
^{1}H NMR (500 MHz, Chloroform-*d*) of **4i**



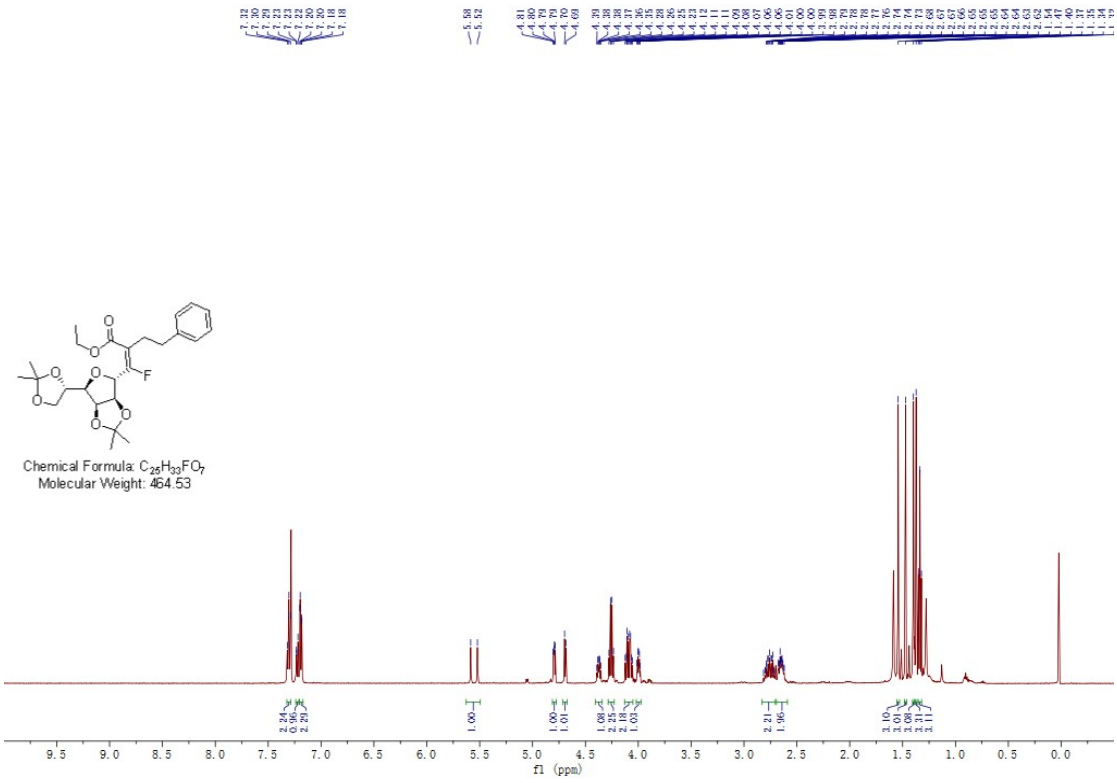
^{13}C NMR (201 MHz, Chloroform-*d*) of **4i**



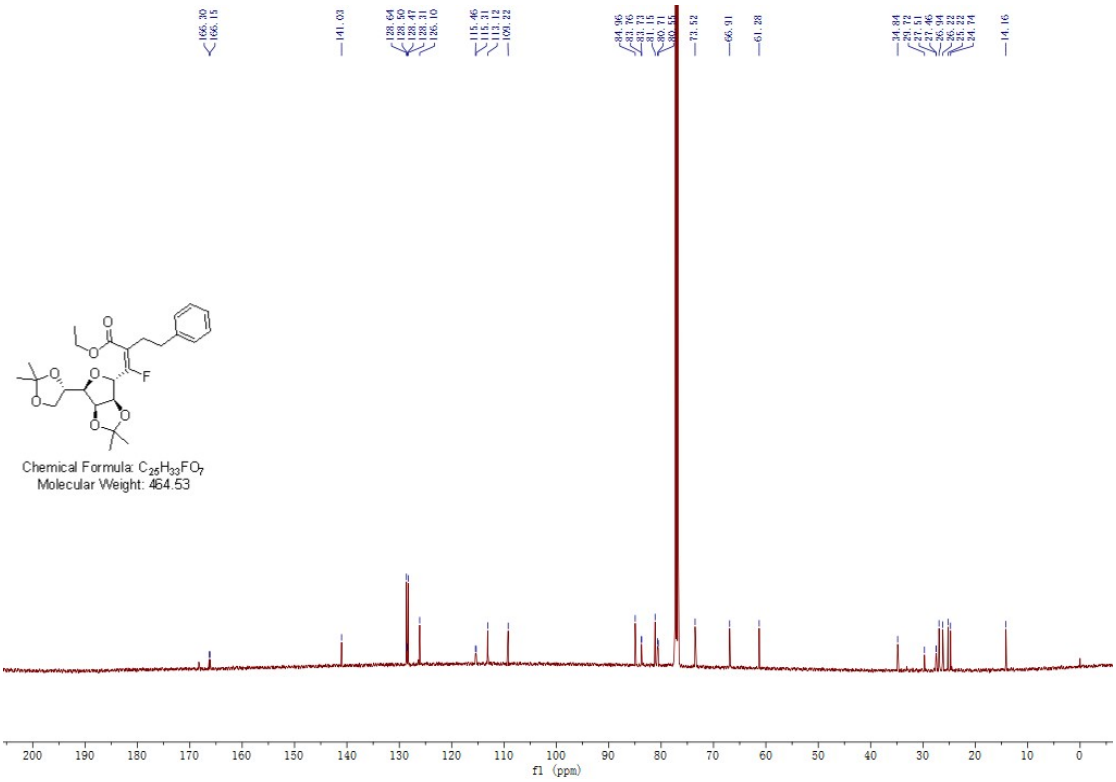
^{19}F NMR (471 MHz, Chloroform-*d*) of **4i**



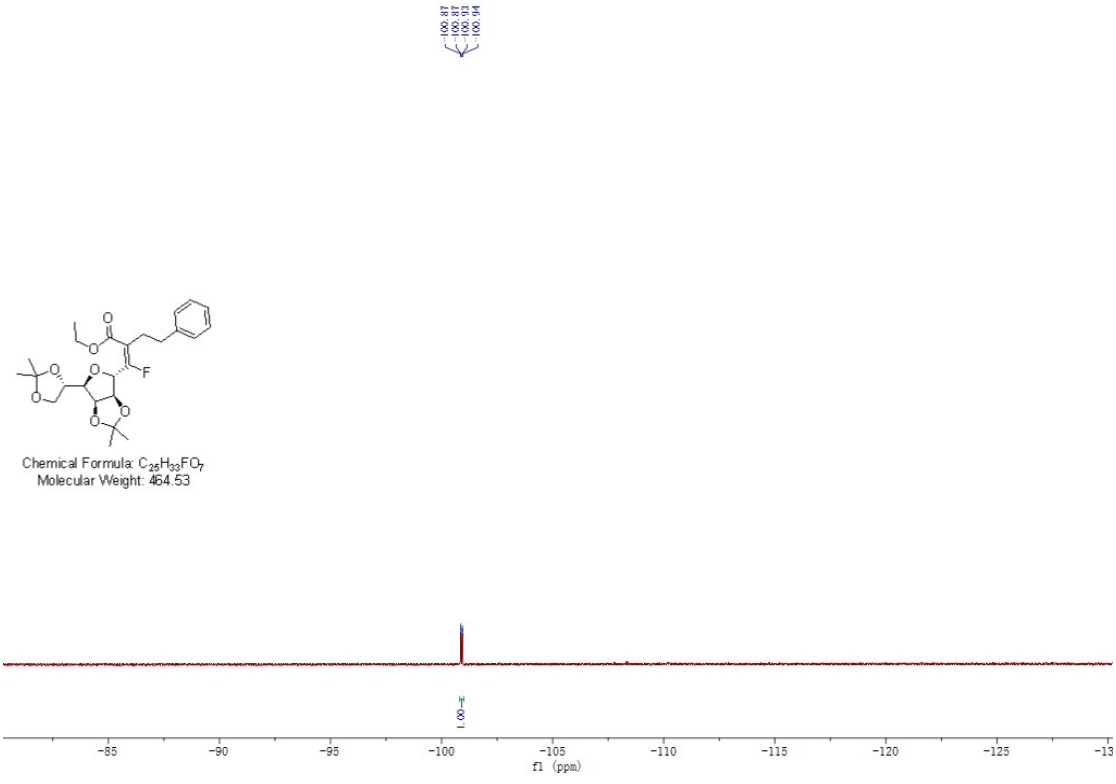
^{1}H NMR (500 MHz, Chloroform-*d*) of **4j**



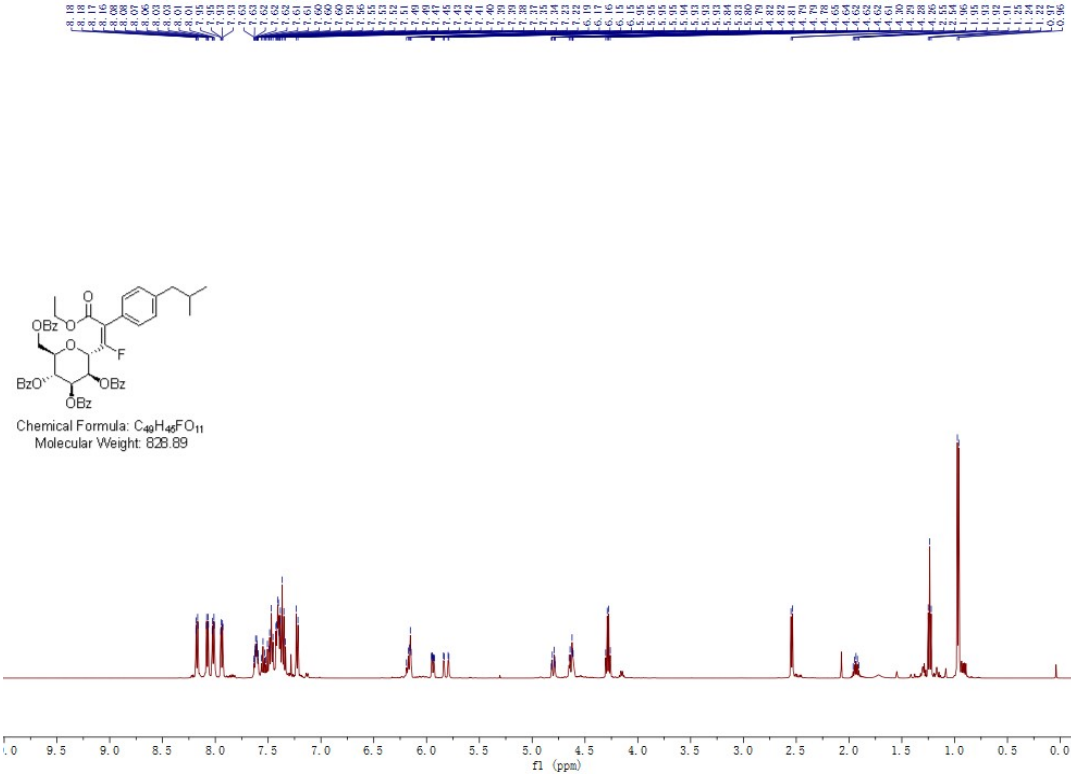
^{13}C NMR (126 MHz, Chloroform-*d*) of **4j**



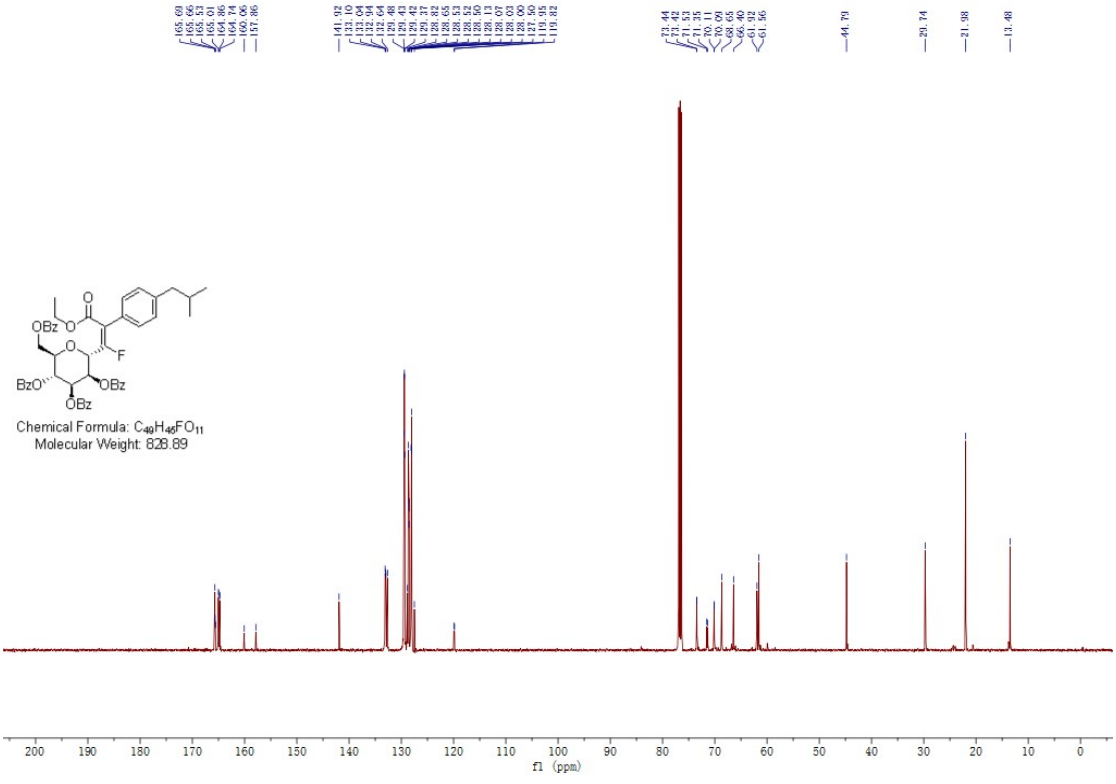
^{19}F NMR (471 MHz, Chloroform-*d*) of **4j**



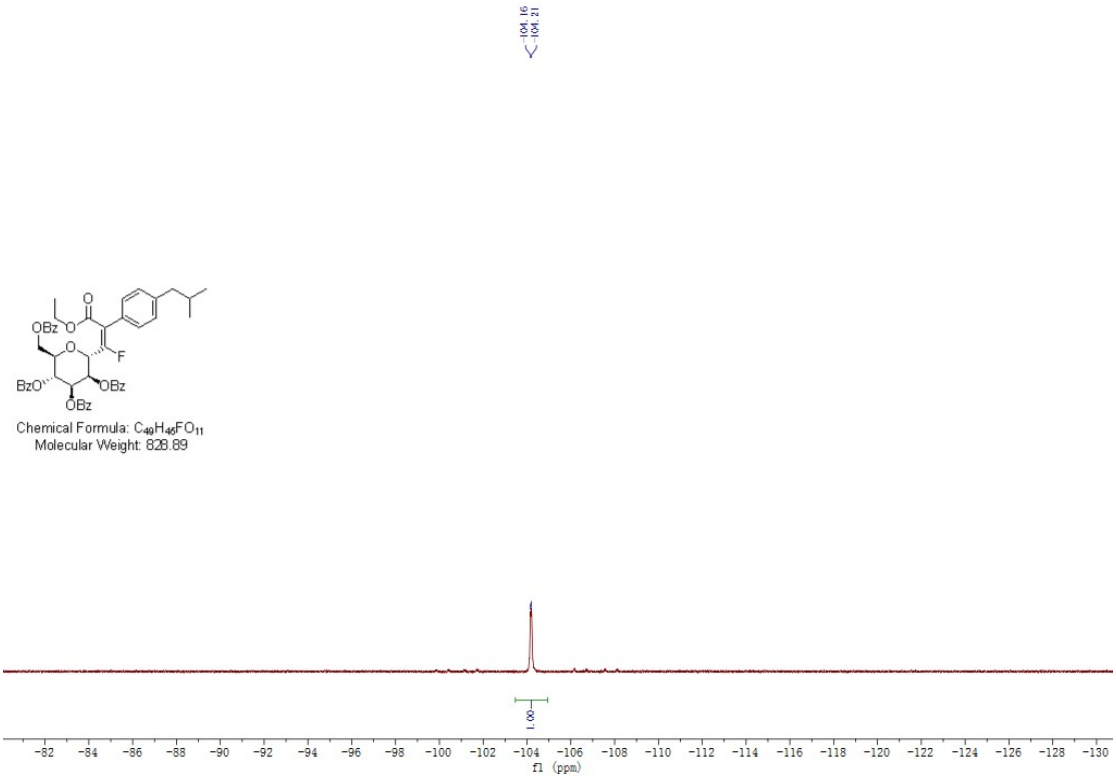
^{1}H NMR (500 MHz, Chloroform-*d*) of **app1**



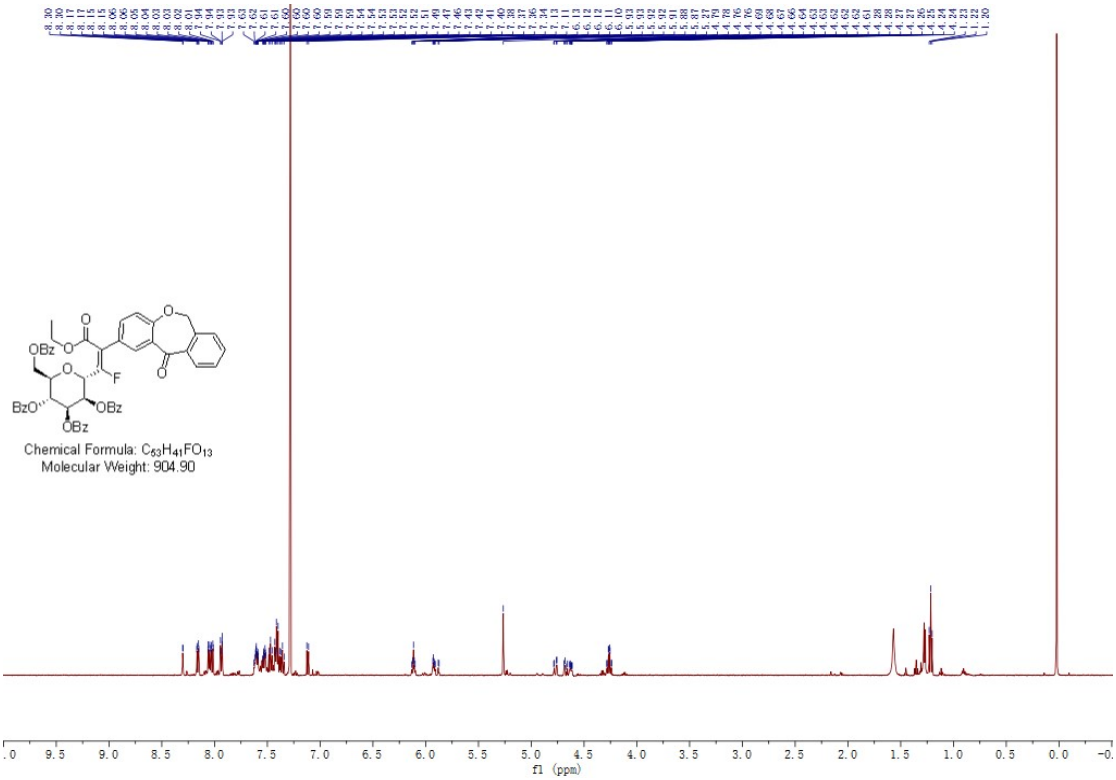
^{13}C NMR (126 MHz, Chloroform-*d*) of **app1**



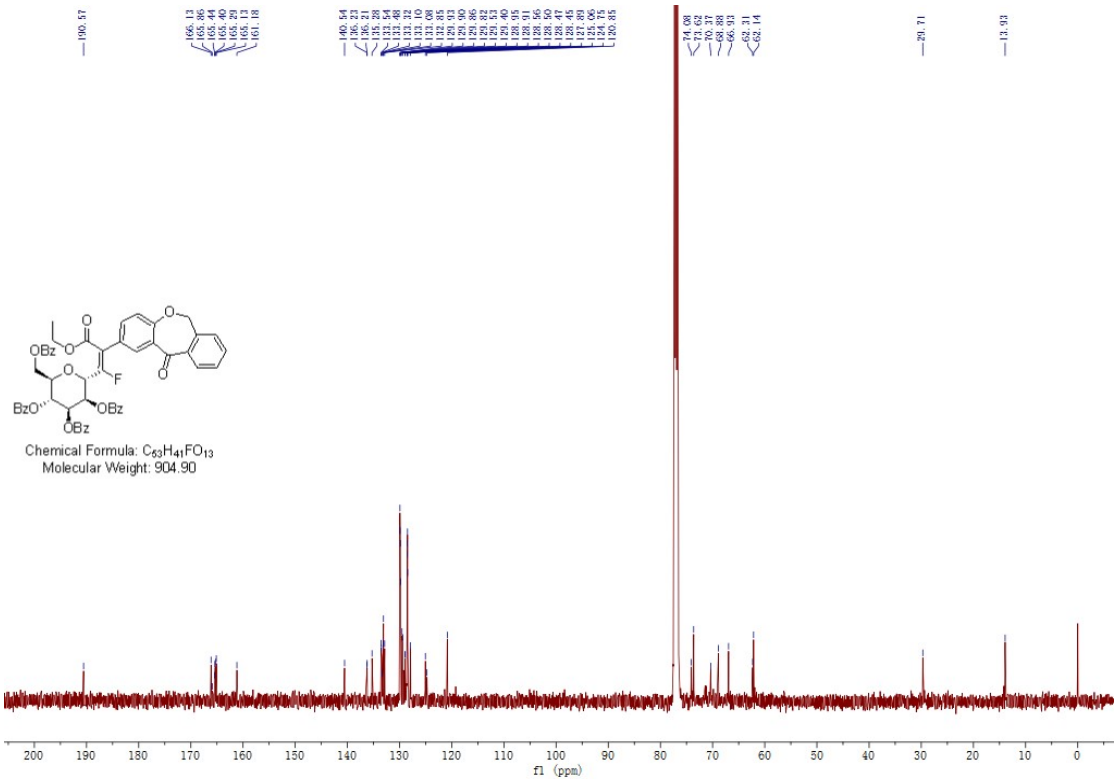
^{19}F NMR (471 MHz, Chloroform-*d*) of **app1**



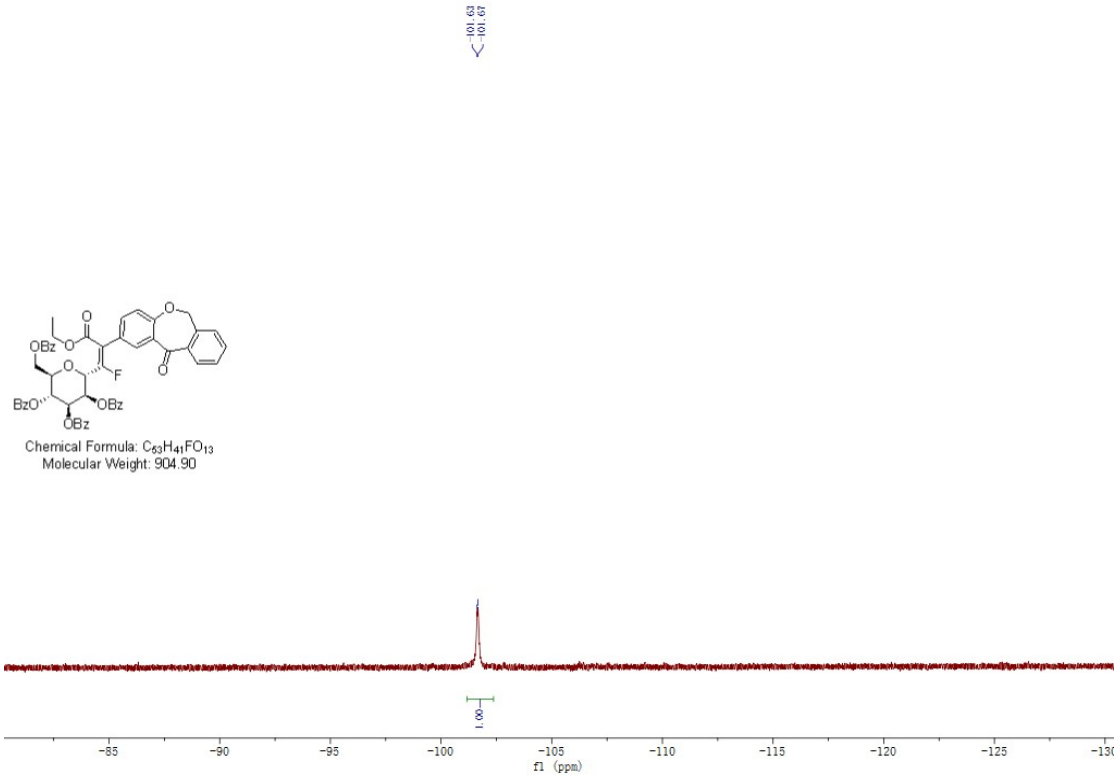
^{1}H NMR (500 MHz, Chloroform-*d*) of **app2**



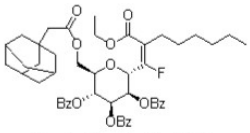
^{13}C NMR (126 MHz, Chloroform-*d*) of **app2**



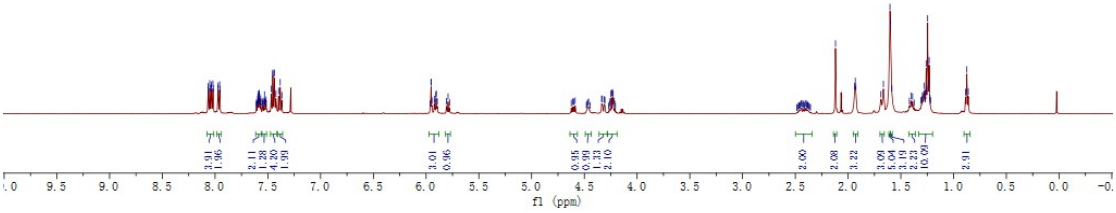
^{19}F NMR (471 MHz, Chloroform-*d*) of **app2**



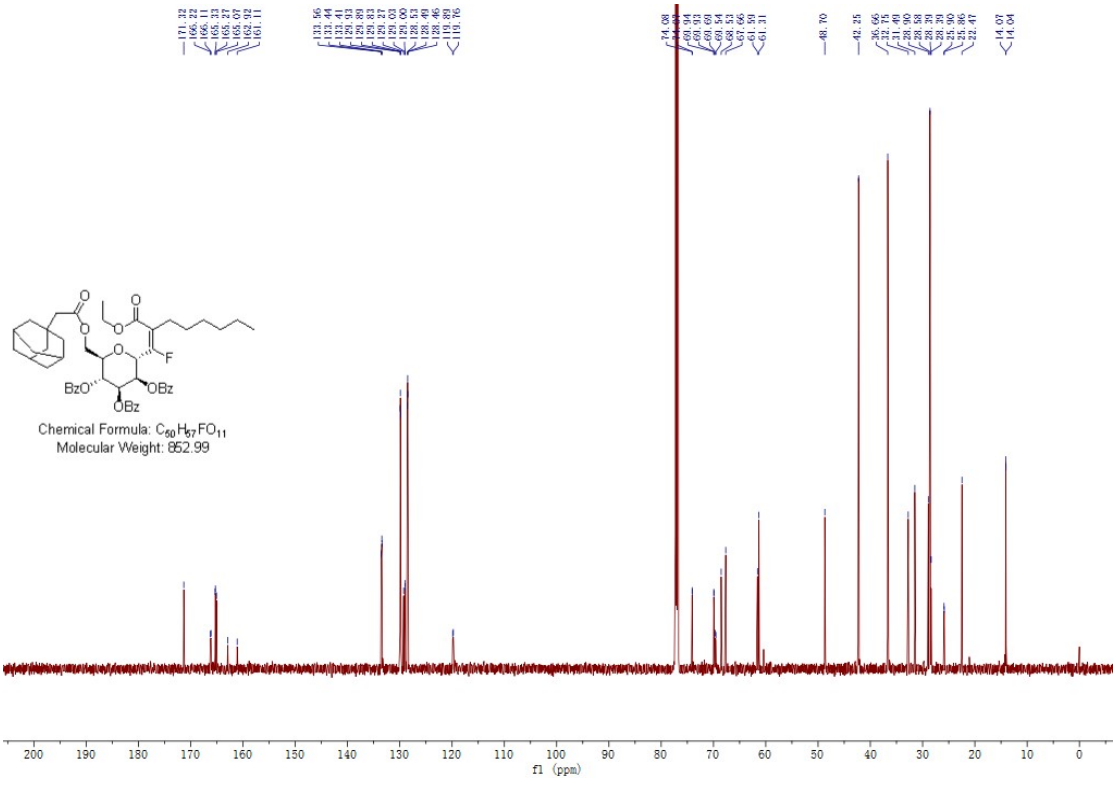
^{1}H NMR (500 MHz, Chloroform-*d*) of **app3**



Chemical Formula: $C_{50}H_{67}FO_{11}$
Molecular Weight: 852.99

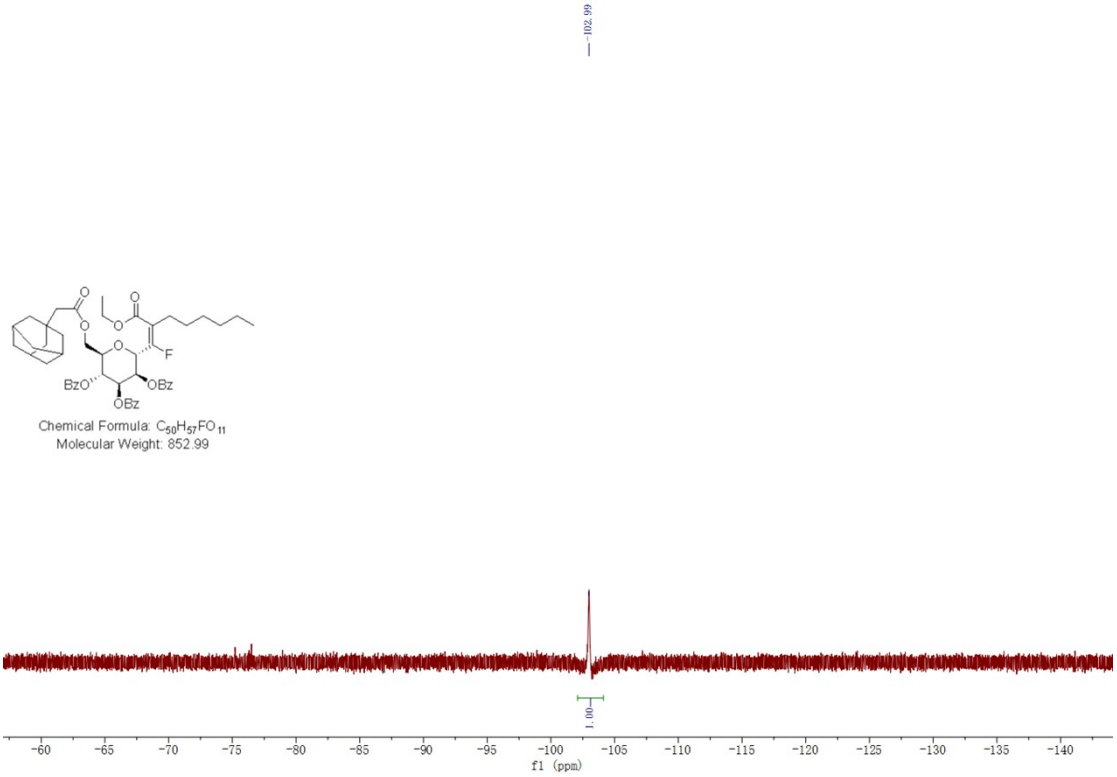


^{13}C NMR (151 MHz, Chloroform-*d*) of **app3**

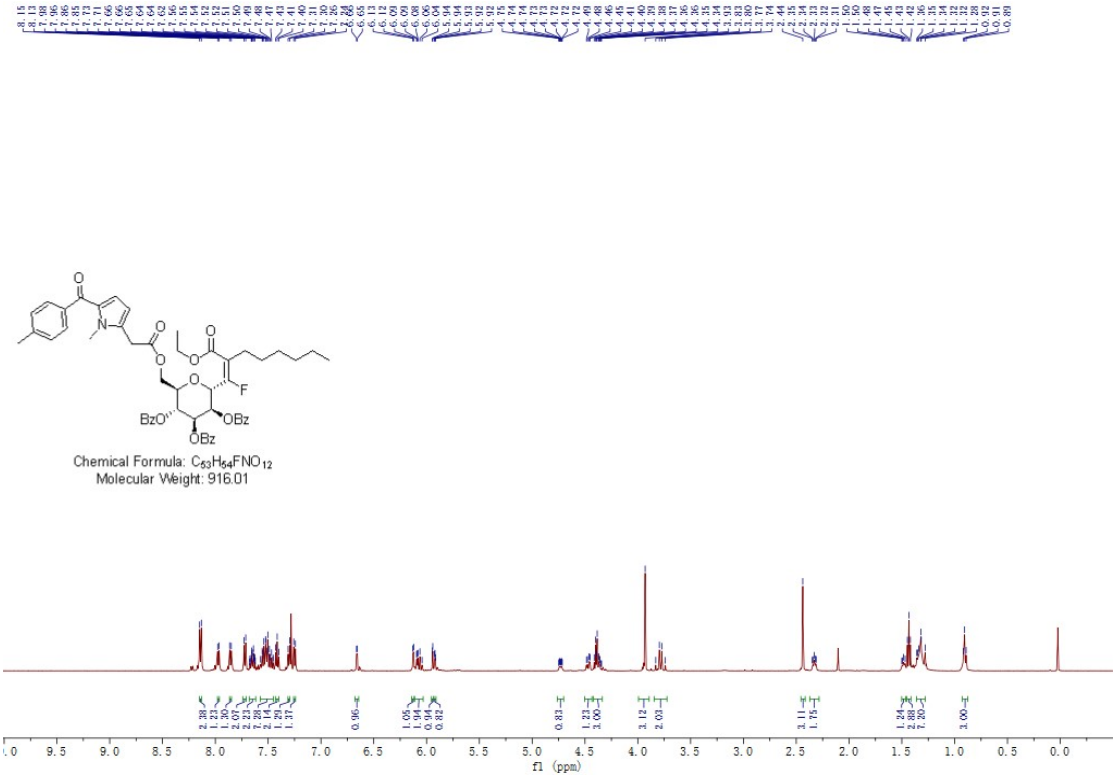


Chemical Formula: $C_{50}H_{67}FO_{11}$
Molecular Weight: 852.99

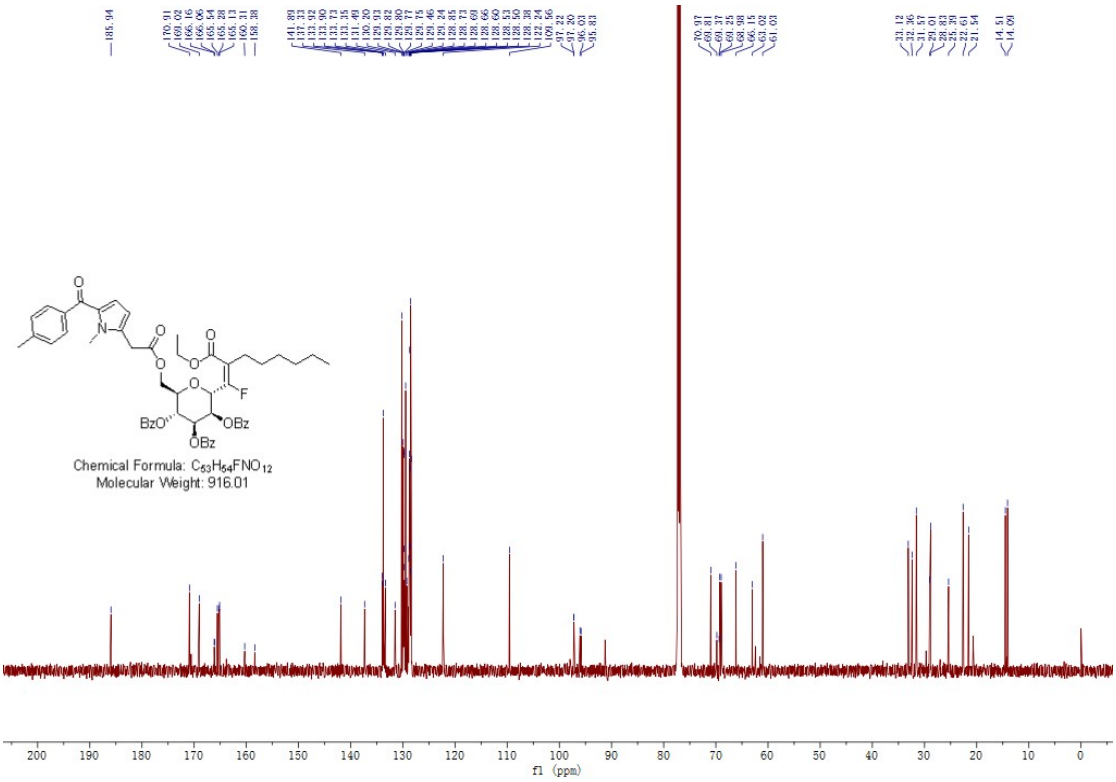
^{19}F NMR (471 MHz, Chloroform-*d*) of **app3**



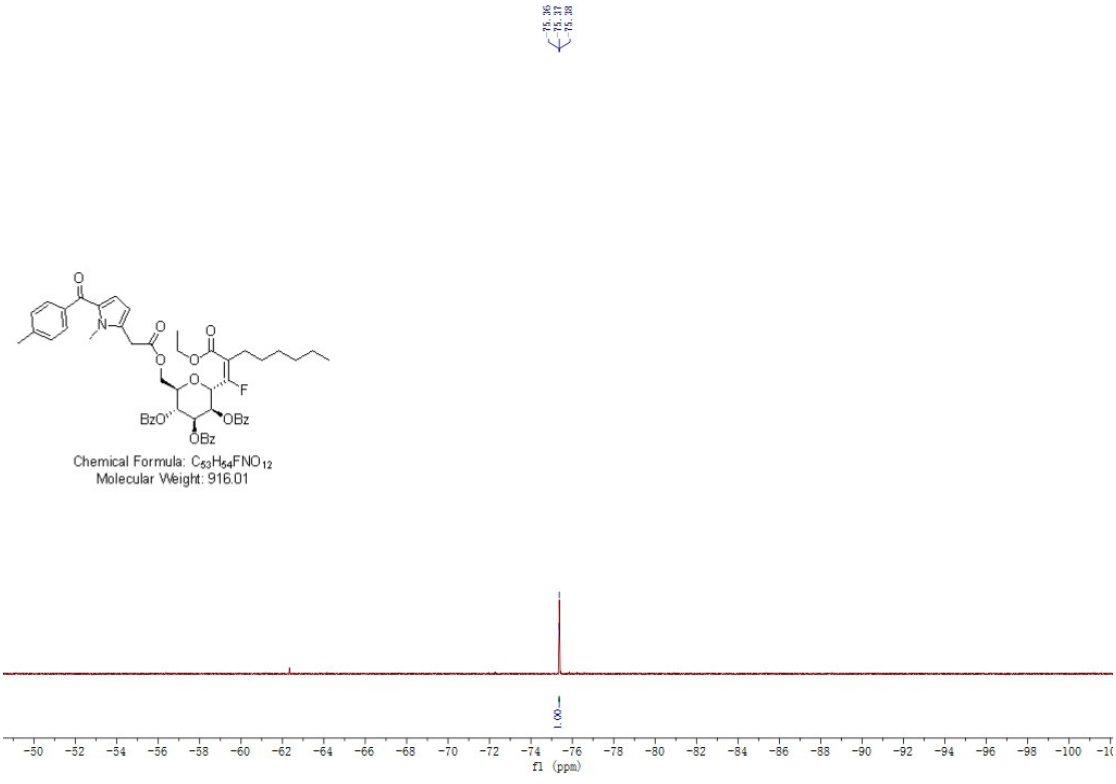
^{1}H NMR (500 MHz, Chloroform-*d*) of **app4**



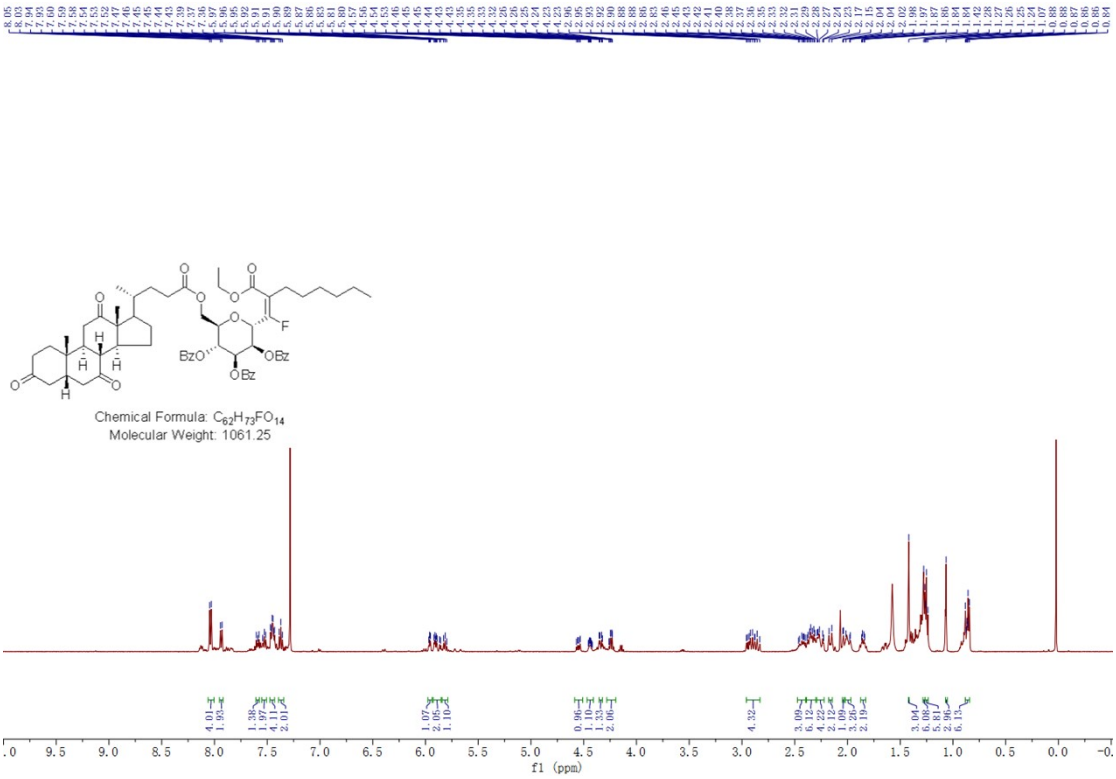
^{13}C NMR (151 MHz, Chloroform-*d*) of **app4**



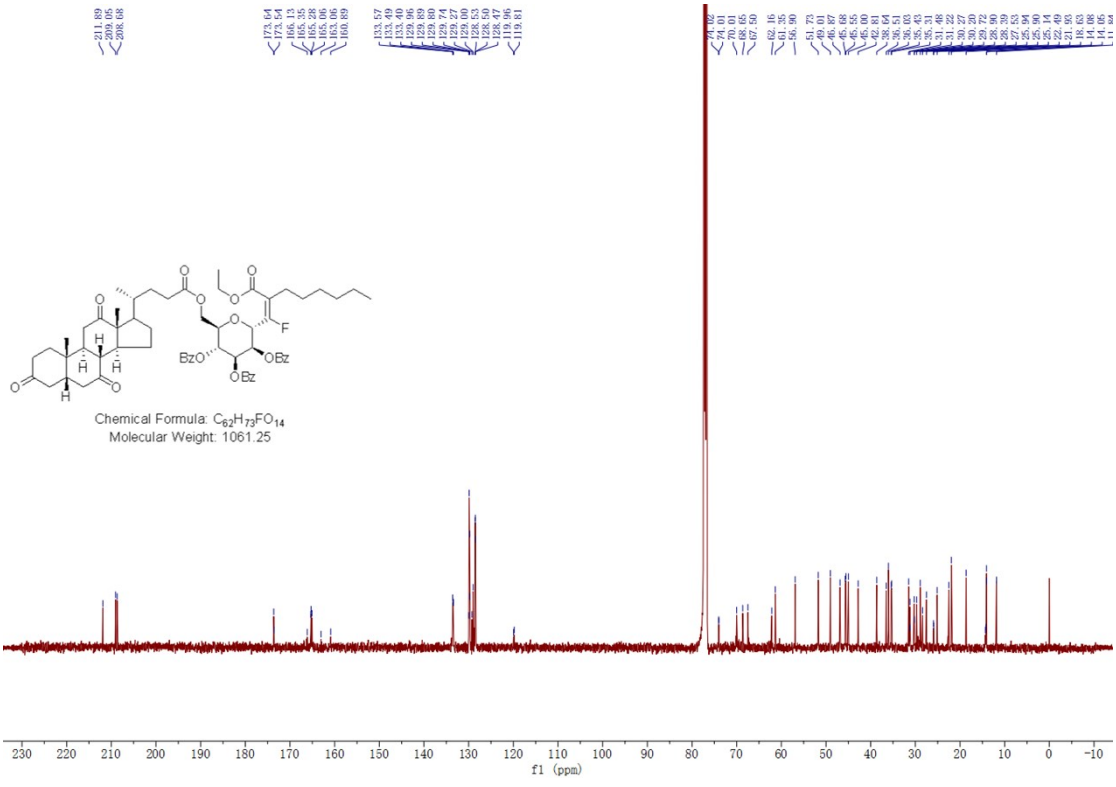
^{19}F NMR (471 MHz, Chloroform-*d*) of **app4**



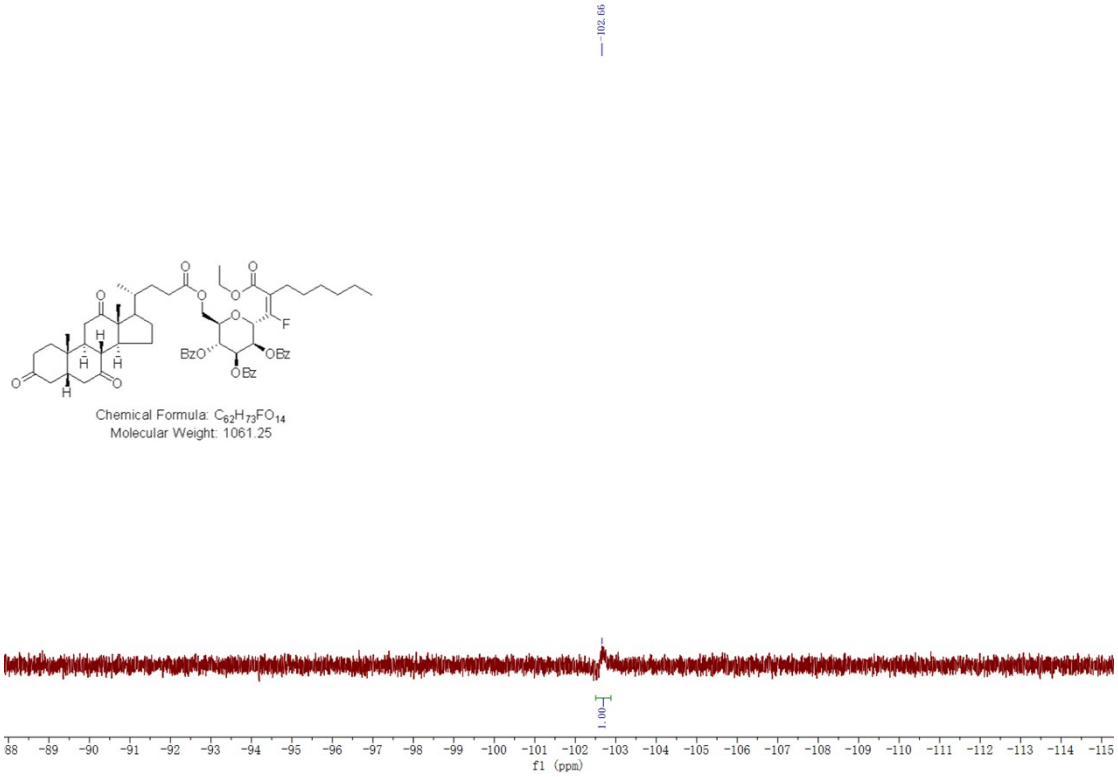
^{1}H NMR (500 MHz, Chloroform-*d*) of **app5**



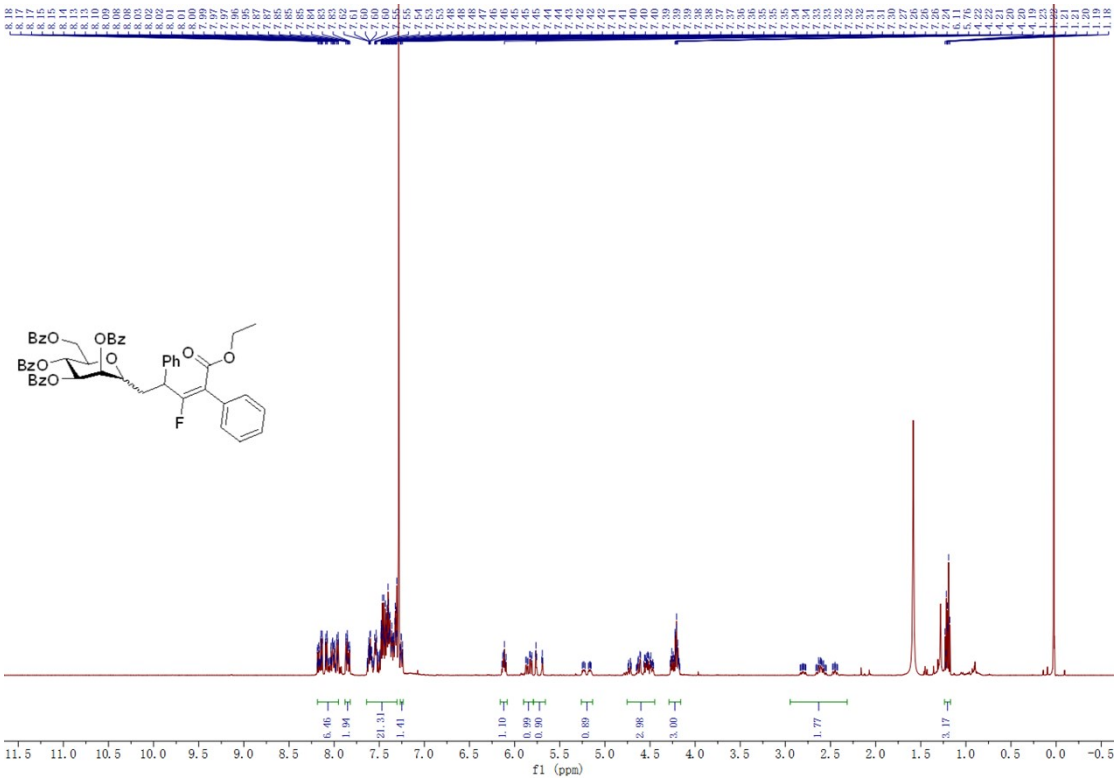
^{13}C NMR (151 MHz, Chloroform-*d*) of **app5**



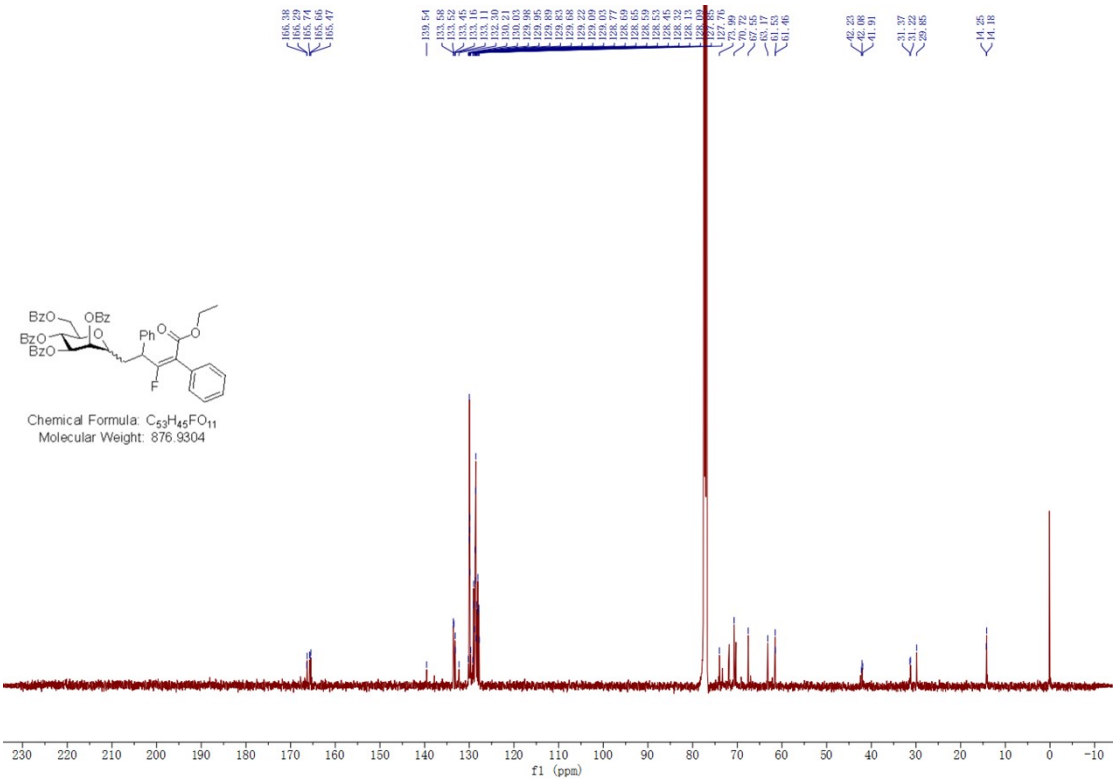
^{19}F NMR (471 MHz, Chloroform-*d*) of **app5**



^{1}H NMR (500 MHz, Chloroform-*d*) of **6ba**



^{13}C NMR (151 MHz, Chloroform-*d*) of **6ba**



^{19}F NMR (471 MHz, Chloroform-*d*) of **6ba**