Supporting Information for

Access to Fluorinated Dienes through Hydrofluorination of 2-En-4-ynoates

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Contents

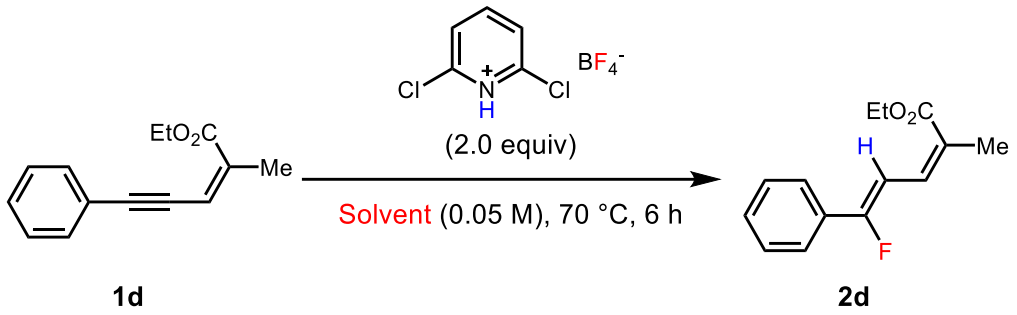
General information

General reagent information: Anhydrous chloroform, 1,2-dichloroethane, dichloromethane, and toluene were purchased from Acros (AcroSeal packaging), Sigma Aldrich (Sure/Seal packaging), and Frontier Scientific (J&KSeal packaging), respectively, and were transferred into an argon-filled glovebox and used as received. Other dry solvents were obtained by distillation and storage over 3Å or 4Å molecular sieves. All other reagents were purchased from Oakwood, Acros, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle SiliaFlash® F60 silica gel and preparative thin-layer chromatography (TLC) using Silicycle 1000 μm silica gel plates, unless otherwise indicated.

General analytical information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Copies of the ^{1}H NMR and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 500 MHz instruments. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$). All ^{19}F NMR spectra are reported in ppm relative to internal standard signal at –161.64 ppm (C_6F_6). Thin-layer chromatography (TLC) was performed on Silicycle 250 μm (analytical) or 1000 μm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with potassium permanganate, or cerium molybdate stain (Hanessian's stain). Yields refer to isolated compounds, unless otherwise indicated. High resolution mass spectra were recorded on a Thermo Scientific Q-Exactive mass spectrometer. NMR yield was determined by using 1,3-dinitrobenzene as internal standard for ^{1}H spectroscopy.

Optimization of reaction conditions

1. Optimization of solvent.

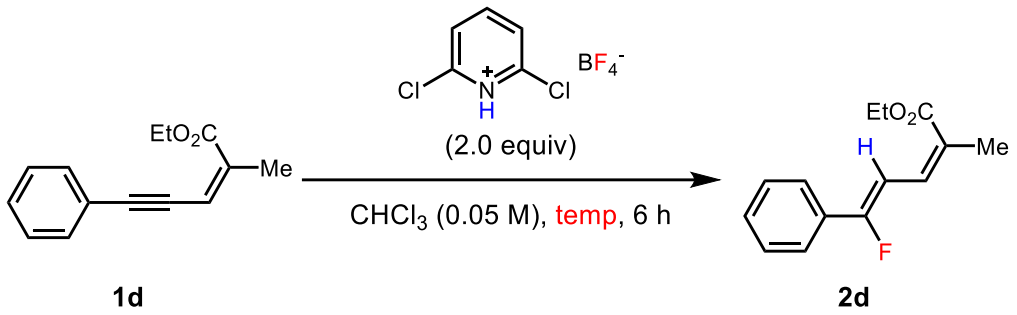


1d **2d**

Entry	Base	NMR Yield (%) [a]
1	Toluene	21
2	Chloroform	50
3	Chlorobenzene	34
4	Trifluorotoluene	25
5	1,2-Dichloroethane	0

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

2. Optimization of temperature.



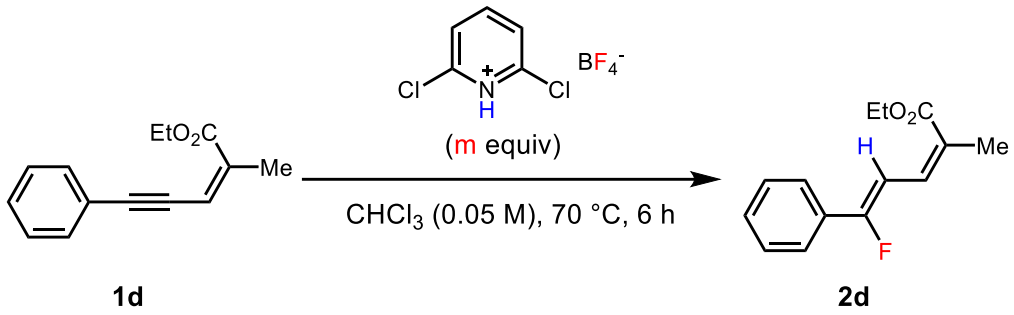
1d **2d**

Entry	Temperature (°C)	NMR Yield (%) [a]
1	20	trace
2	30	12
3	40	16
4	50	29

5	60	39
6	70	50
7	80	45

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

3. Optimization of reagent ratio.

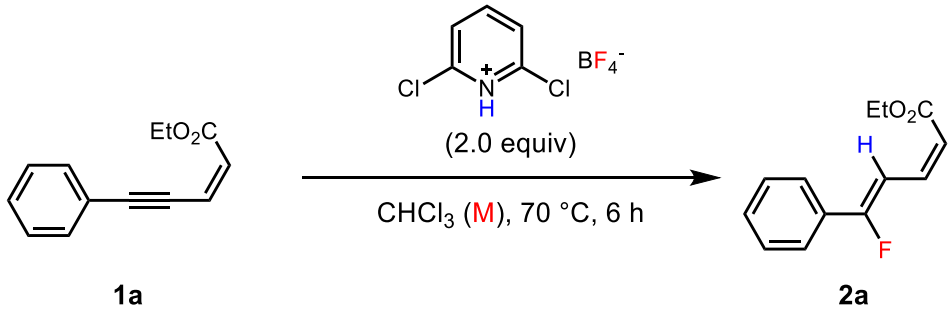


1d **2d**

Entry	Equiv. of pyridinium salt	NMR Yield (%) [a]
1	1.0	45
2	2.0	50
3	3.0	41
4	4.0	39

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

4. Optimization of reagent concentration.



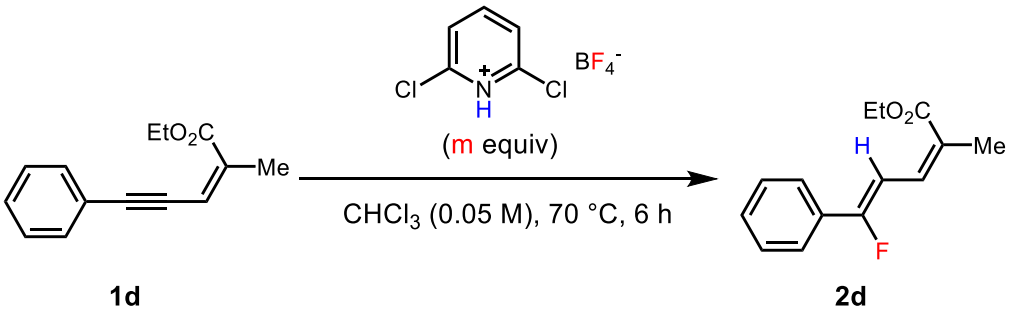
1a **2a**

Entry	Concentration of enyne	NMR Yield (%) [a]
1	0.05	40
2	0.10	33

3	0.20	26

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

5. Optimization of additives.

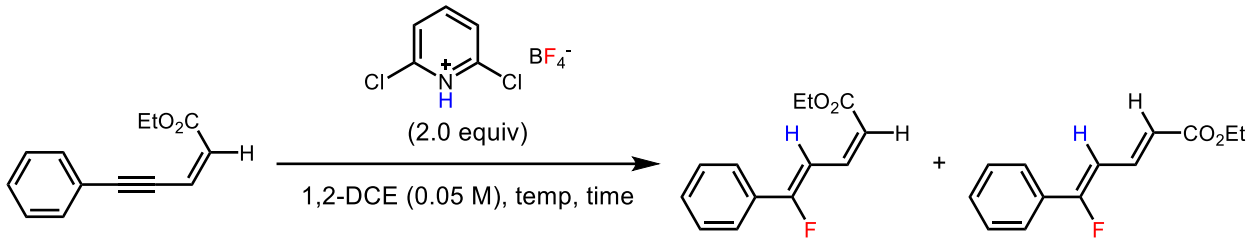


1d **2d**

Entry	Additive	Equiv. of additive	NMR Yield (%) [a]
1	N/A	N/A	50
2	$LiBF_4$	3.0	53
3	BHT	0.05	50
4	MEHQ	0.05	51
5	Ascorbic acid	0.05	48
6	$Et_2O{\cdot}HBF_4/LiBF_4$	2.0/0.25	19
7	$Et_2O{\cdot}HBF_4/LiBF_4$	2.0/0.50	22
8	$Et_2O{\cdot}HBF_4/LiBF_4$	2.0/1.0	21
9	2,6-Cl_2Py	2.0	24
10	PPh_3	2.0	0
11	Me_2S	5.0	39
12	Ph_2S	5.0	53

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard. BHT = butylated hydroxytoluene. MEHQ = mequinol.

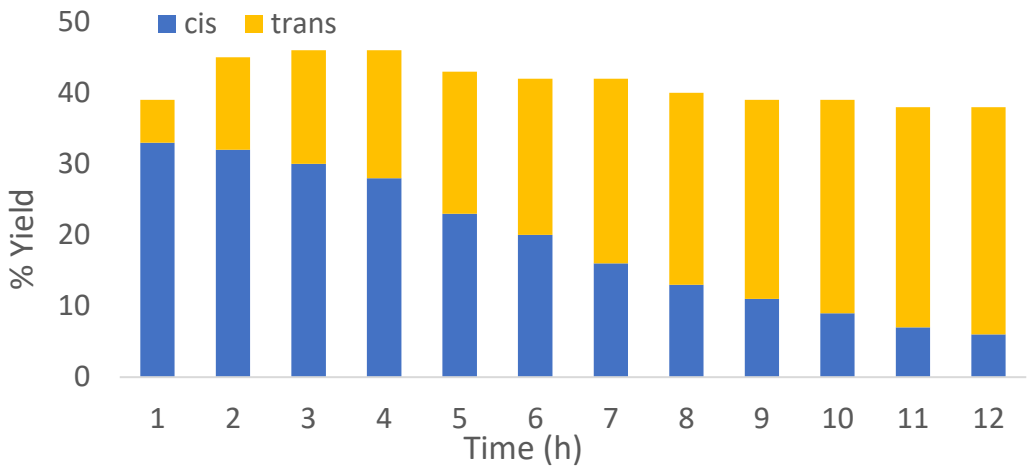
Stereoselectivity study on the hydrofluorination of C2-unsubstituted enyne



1a **2a (*cis*)** **2a' (*trans*)**

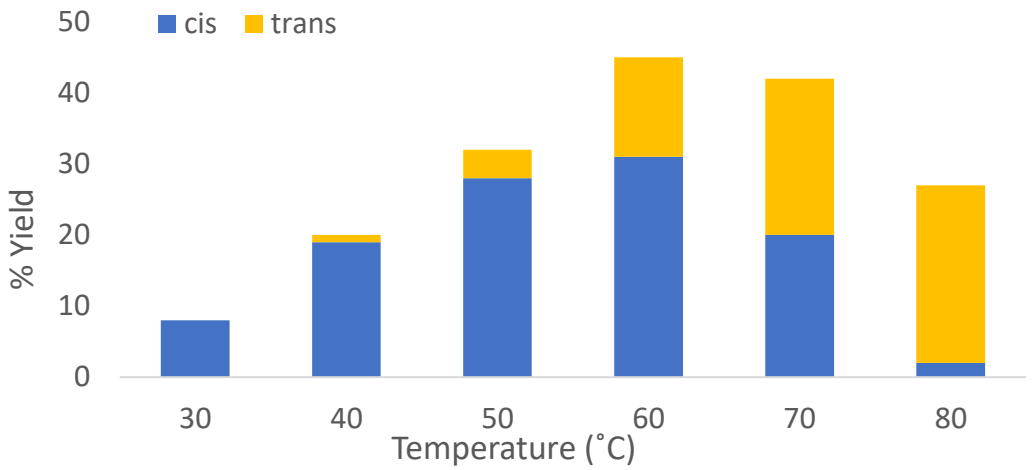
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**, 20.0 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for the given reaction time. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Time (h)	**Temp (˚C)**	***cis*/*trans***	**Yield (%)**	***cis* (%)**	***trans* (%)**
1	70	5.5:1	39	33	6
2	70	2.5:1	45	32	13
3	70	1.8:1	45	29	16
4	70	1.6:1	46	28	18
5	70	1.2:1	43	23	20
6	70	1:1.1	42	20	22
7	70	1:1.6	42	16	26
8	70	1:2.1	40	13	27
9	70	1:2.5	39	11	28
10	70	1:3.3	39	9	30
11	70	1:4.4	38	7	31
12	70	1:5.3	38	6	32

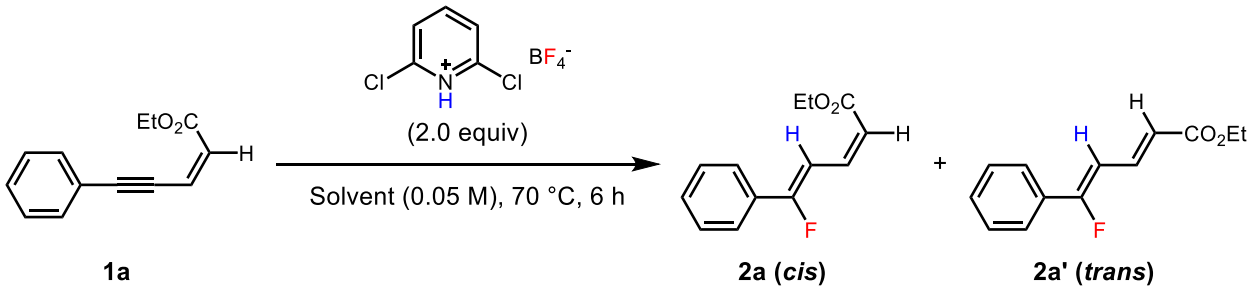


A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**, 20.0 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox. After stirring at the given temperature for 6 h, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Time (h)	**Temp (˚C)**	***cis*/*trans***	**Yield (%)**	***cis* (%)**	***trans* (%)**
6	30	*cis* only	8	8	0
6	40	19.0:1	20	19	1
6	50	7.0:1	32	28	4
6	60	2.2:1	45	31	14
6	70	1:1.1	42	20	22
6	80	1:12.5	27	2	25



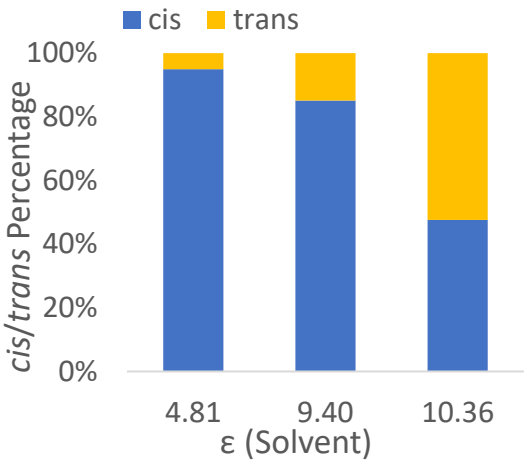
Dielectric constant study on the hydrofluorination of C2-unsubstituted enyne



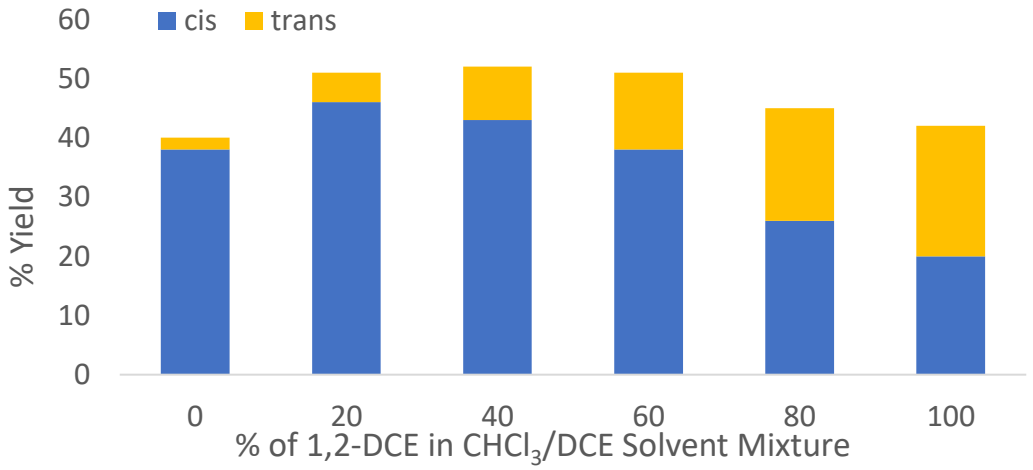
1a **2a (*cis*)** **2a' (*trans*)**

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in corresponding dry solvent (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**, 20.0 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for 6 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

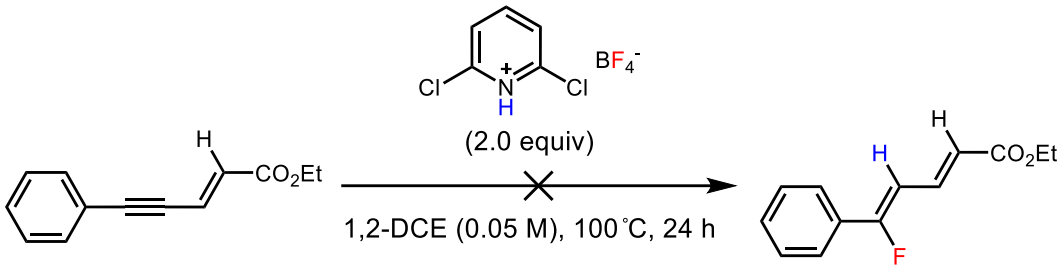
Solvent	**ε**	***cis*/*trans***
$CHCl_3$	4.81	19.0:1
$PhCF_3$	9.40	5.7:1
1,2-DCE	10.36	1:1.1



Solvent	*cis*/*trans*	Yield (%)	*cis* (%)	*trans* (%)
$CHCl_3$	19.0:1	40	38	2
20% 1,2-DCE in $CHCl_3$	9.2:1	51	46	5
40% 1,2-DCE in $CHCl_3$	4.8:1	52	43	9
60% 1,2-DCE in $CHCl_3$	2.9:1	51	38	13
80% 1,2-DCE in $CHCl_3$	1:4.1	45	26	19
1,2-DCE	1:1.1	42	20	22

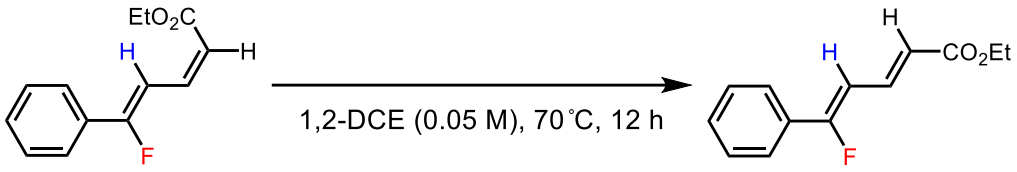


Isomerization of fluorinated diene



1a' ***No reaction, 100% SM recovered*** **2a' (*trans*)**

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added ethyl (*E*)-5-phenylpent-2-en-4-ynoate (**1a'**, 20.0 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 100 °C, where it was stirred for 24 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

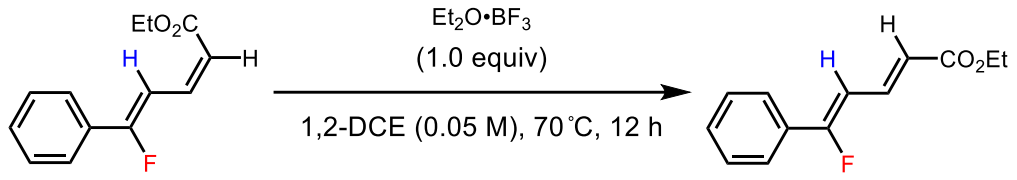


2a **2a'**

0%

74% SM Residue

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, ethyl (2*Z*,4*Z*)-5-fluoro-5-phenylpenta-2,4-dienoate (**2a**, 22.0 mg, 0.10 mmol) was dissolved in dry 1,2-dichloroethane (2.0 mL). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for 12 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

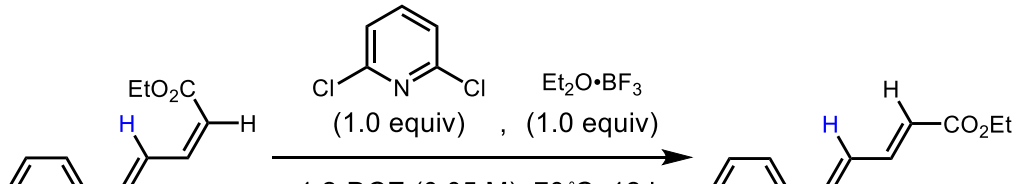


2a **2a'**

12%

53% SM Residue

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, to the solution of ethyl (2*Z*,4*Z*)-5-fluoro-5-phenylpenta-2,4-dienoate (**2a**, 22.0 mg, 0.10 mmol, 1.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added boron trifluoride etherate (14.2 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for 12 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.



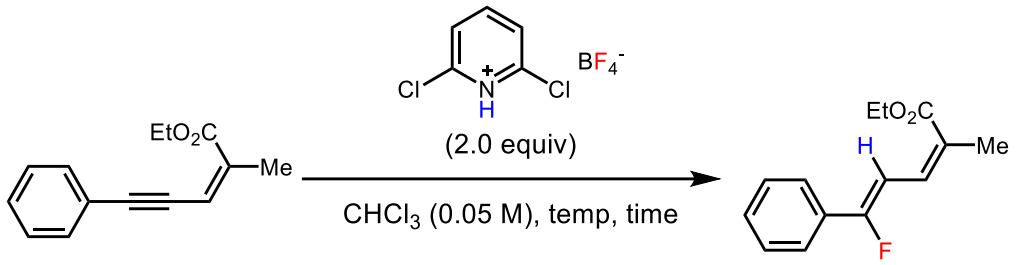
2a **2a'**

32%

47% SM Residue

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, to the solution of ethyl (2*Z*,4*Z*)-5-fluoro-5-phenylpenta-2,4-dienoate (**2a**, 22.0 mg, 0.10 mmol, 1.0 equiv) and 2,6-dichloropyridine (14.8 mg, 0.10 mmol, 1.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added boron trifluoride etherate (14.2 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for 12 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

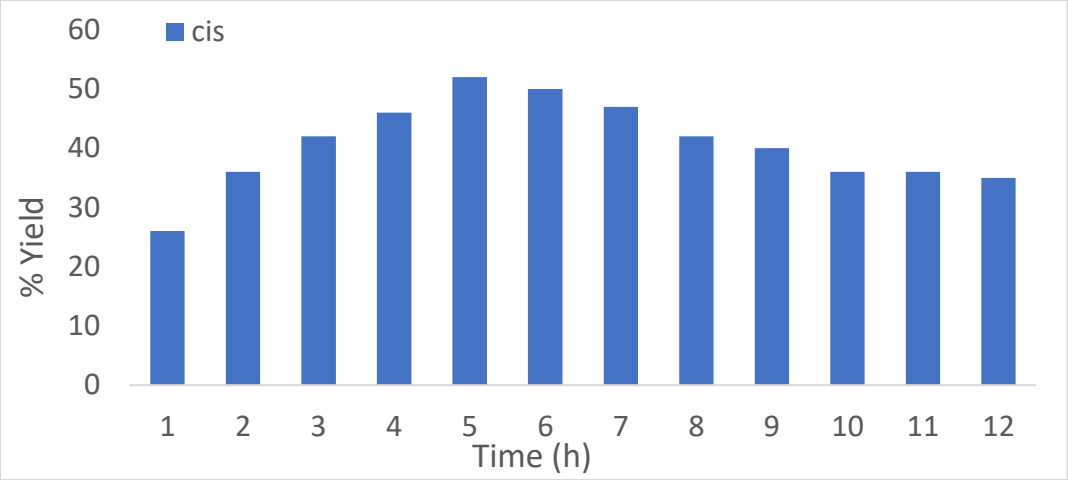
Stereoselectivity study on the hydrofluorination of C2-substituted enyne



1d **2d**

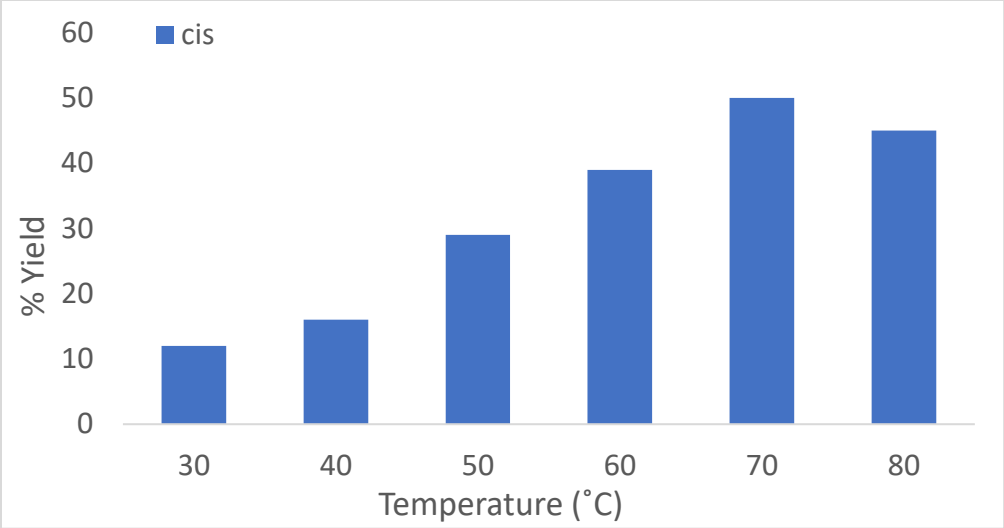
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1d**, 21.4 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for the given reaction time. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Time (h)	**Temp (˚C)**	***cis*/*trans***	**Yield (%)**	***cis* (%)**	***trans* (%)**
1	70	*cis* only	26	26	0
2	70	*cis* only	36	36	0
3	70	*cis* only	42	42	0
4	70	*cis* only	45	45	0
5	70	*cis* only	52	52	0
6	70	*cis* only	50	50	0
7	70	*cis* only	47	47	0
8	70	*cis* only	42	42	0
9	70	*cis* only	40	40	0
10	70	*cis* only	36	36	0
11	70	*cis* only	36	36	0
12	70	*cis* only	35	35	0

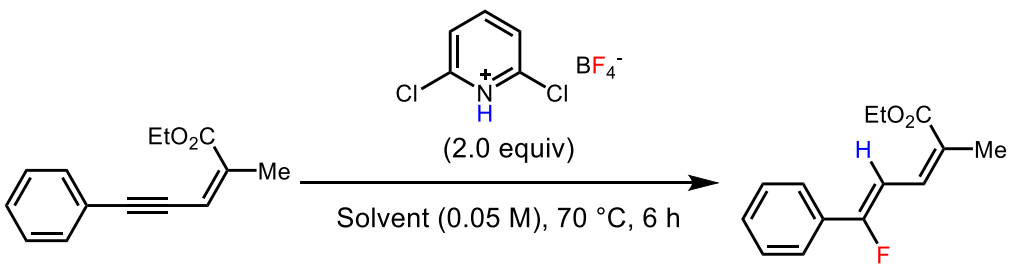


A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in dry 1,2-dichloroethane (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1d**, 21.4 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox. After stirring at the given temperature for 6 h, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Time (h)	**Temp (˚C)**	***cis*/*trans***	**Yield (%)**	***cis* (%)**	***trans* (%)**
6	30	*cis* only	12	12	0
6	40	*cis* only	16	16	0
6	50	*cis* only	29	29	0
6	60	*cis* only	39	39	0
6	70	*cis* only	50	50	0
6	80	*cis* only	45	45	0



Dielectric constant study on the hydrofluorination of C2-substituted enyne

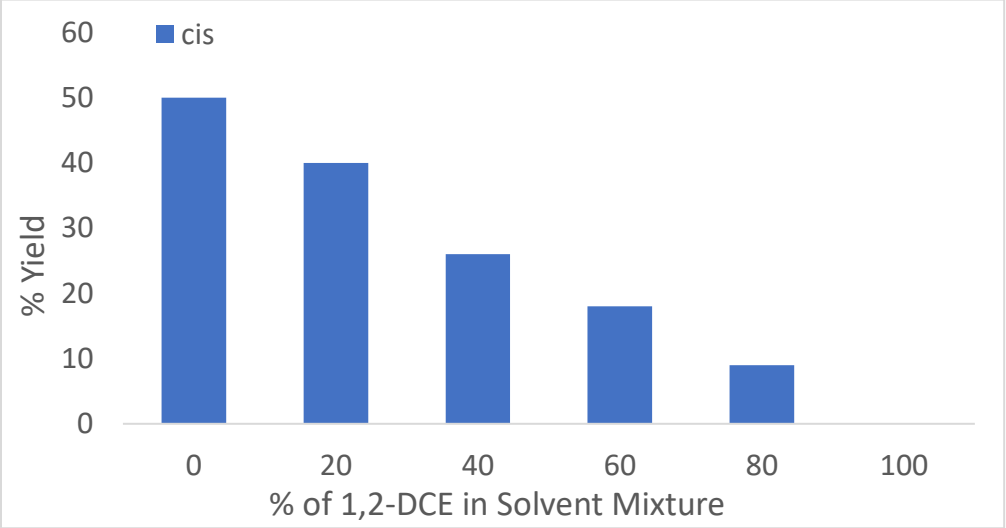


1d **2d**

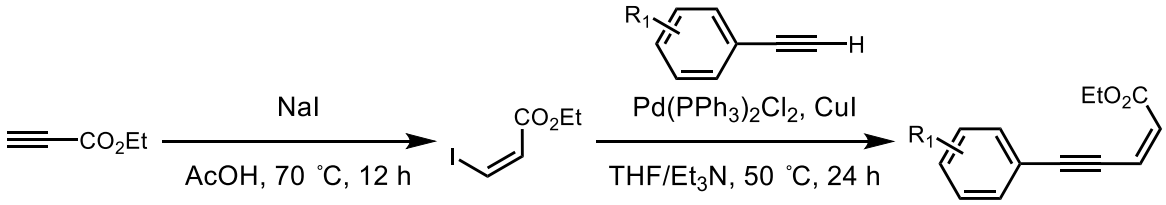
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of 2,6-dichloropyridinium tetrafluoroborate (47.2 mg, 0.20 mmol, 2.0 equiv) in corresponding dry solvent (2.0 mL) was added ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1d**, 21.4 mg, 0.10 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for 6 h. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel, then concentrated *in vacuo*. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Solvent	***cis*/*trans***	**Yield (%)**	***cis* (%)**	***trans* (%)**
$CHCl_3$	*cis* only	50	50	0
20% 1,2-DCE in $CHCl_3$	*cis* only	40	40	0
40% 1,2-DCE in $CHCl_3$	*cis* only	26	26	0
60% 1,2-DCE in $CHCl_3$	*cis* only	18	18	0

80% 1,2-DCE in $CHCl_3$	*cis* only	9	9	0
1,2-DCE	-	0	0	0



General procedure A for synthesis of C2-unsubstituted enynes



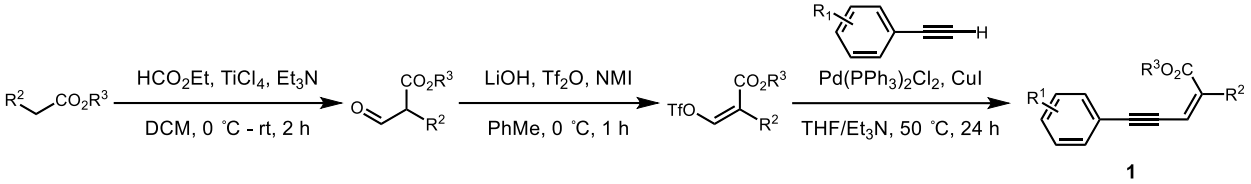
1

To a 10 mL round bottom flask was sequentially added NaI (1.12 g, 7.5 mmol, 1.5 equiv), glacial acetic acid (3.0 mL) and ethyl propiolate (0.49 g, 5.0 mmol, 1.0 equiv). The reaction mixture was stirred at 70 °C for 12 h, then quenched upon pouring into saturated aqueous sodium bicarbonate (30 mL). The aqueous layer was extracted with ethyl acetate (4 × 15 mL). The combined extracts were washed with saturated aqueous sodium thiosulfate and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude ethyl (*Z*)-3-iodoacrylate was used for the next step without further purification.

In an argon-filled glovebox, a 50 mL round bottom flask was sequentially added $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 1 mol %), CuI (28.6 mg, 0.15 mmol, 3 mol %), tetrahydrofuran (10.0 mL), triethylamine (10.0 mL), ethyl (*Z*)-3-iodoacrylate (1.13 g, 5.0 mmol, 1.0 equiv) and alkyne (5.5 mmol, 1.1 equiv). The reaction mixture was stirred at 50 °C for 24 h, then quenched upon pouring into saturated aqueous ammonium chloride (30 mL). The aqueous layer was extracted with ethyl acetate (5 × 20 mL). The combined extracts were washed with brine, dried over anhydrous sodium

sulfate, and concentrated *in vacuo*. The crude mixture was purified via flash column chromatography to provide the desired product **1**.

General procedure B for synthesis of C2-substituted enynes

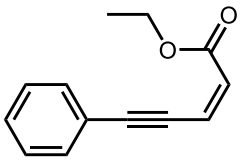


To a nitrogen-flushed 100 mL round bottom flask containing a solution of ester (15.0 mmol, 1.0 equiv) and ethyl formate (3.33 g, 45.0 mmol, 3.0 equiv) in dry dichloromethane (30 mL) at 0 °C was sequentially added $TiCl_4$ (5.69 g, 30.0 mmol, 2.0 equiv) and triethylamine (3.64 g, 36.0 mmol, 2.4 equiv). The reaction mixture was stirred at 0 °C for 1 h, then allowed to warm to rt over 1 h. The reaction was quenched upon adding water (60 mL). The aqueous layer was extracted with dichloromethane (4 × 30 mL). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude ethyl formylacetate intermediate was used for the next step without further purification.

To a nitrogen-flushed 100 mL round bottom flask containing a suspension of lithium hydroxide (0.43 g, 18.0 mmol, 1.2 equiv) in dry toluene (15 mL) at 0 °C was slowly added the solution of crude ethyl formylacetate (15.0 mmol, 1.0 equiv) in dry toluene (15 mL) (Note: rigorously dry toluene was needed for high levels of (*Z*)-selectivity). The reaction mixture was stirred at 0 °C for 5 min, then sequentially added Tf_2O (5.08 g, 18.0 mmol, 1.2 equiv) and *N*-methylimidazole (1.48 g, 18.0 mmol, 1.2 equiv). The reaction mixture was stirred at 0 °C for 1 h, then quenched upon adding water (60 mL). The aqueous layer was extracted with ethyl acetate (4 × 30 mL). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude vinyl triflate intermediate was used for the next step without further purification.

In an argon-filled glovebox, a 100 mL round bottom flask was sequentially added $Pd(PPh_3)_2Cl_2$ (105.3 mg, 0.15 mmol, 1 mol %), CuI (85.7 mg, 0.45 mmol, 3 mol %), tetrahydrofuran (15.0 mL), triethylamine (15.0 mL), vinyl triflate intermediate (15.0 mmol, 1.0 equiv) and alkyne (16.5 mmol, 1.1 equiv). The reaction mixture was stirred at 50 °C for 24 h, then quenched upon pouring into saturated aqueous ammonium chloride (50 mL). The aqueous layer was extracted with ethyl acetate (5 × 30 mL). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude mixture was purified via flash column chromatography to provide the desired product **1**.

Characterization data for enynes 1



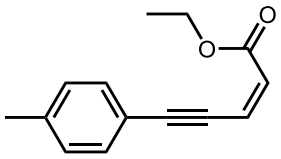
1a

Ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (1a): Prepared following general procedure A, using ethyl propiolate (0.49 g, 5.0 mmol, 1.0 equiv) and phenylacetylene (0.56 g, 5.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1a** as a yellow oil (0.65 g, 65% yield, 2 steps) with spectral properties identical to those reported in the literature.[1]

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.55-7.51 (m, 2H), 7.38-7.31 (m, 3H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.14 (d, *J* = 11.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 165.0, 132.2, 129.3, 128.5, 128.4, 123.0, 122.8, 101.3, 86.5, 60.6, 14.4.

HRMS: (ESI) calcd. for $C_{13}H_{13}O_2$ $[M+H]^+$: 201.0910, found: 201.0909.



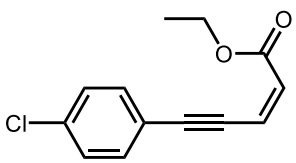
1b

Ethyl (*Z*)-5-(*p*-tolyl)pent-2-en-4-ynoate (1b): Prepared following general procedure A, using ethyl propiolate (0.49 g, 5.0 mmol, 1.0 equiv) and 4-ethynyltoluene (0.64 g, 5.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1b** as a yellow oil (0.76 g, 71% yield, 2 steps) with spectral properties identical to those reported in the literature.[1]

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.43 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 6.36 (d, *J* = 11.5 Hz, 1H), 6.10 (t, *J* = 11.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

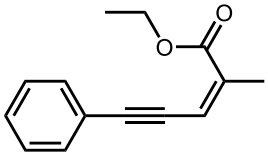
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 165.1, 139.7, 132.2, 129.3, 127.9, 123.2, 119.7, 101.8, 86.1, 60.5, 21.7, 14.5.

HRMS: (ESI) calcd. for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.1067, found: 215.1069.



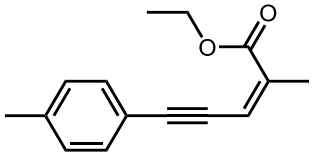
1c

Ethyl (*Z*)-5-(4-chlorophenyl)pent-2-en-4-ynoate (1c): Prepared following general procedure A, using ethyl propiolate (0.49 g, 5.0 mmol, 1.0 equiv) and 1-chloro-4-ethynylbenzene (0.75 g, 5.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1c** as a yellow oil (0.78 g, 66% yield, 2 steps).[2]
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.46 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 11.4 Hz, 1H), 6.15 (d, *J* = 11.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 164.9, 135.5, 133.4, 128.9, 128.8, 122.7, 121.3, 100.0, 87.4, 60.7, 14.4.
HRMS: (ESI) calcd. for $C_{13}H_{12}ClO_2$ $[M+H]^+$: 235.0520, found: 235.0526.



1d

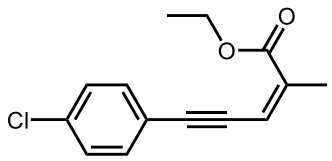
Ethyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (1d): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1d** as a yellow oil (1.38 g, 43% yield, 3 steps) with spectral properties identical to those reported in the literature.[3]
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.50-7.45 (m, 2H), 7.35-7.30 (m, 3H), 6.19 (q, *J* = 1.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.06 (d, *J* = 1.6 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.6, 138.2, 131.8, 128.8, 128.5, 123.4, 117.5, 97.4, 87.1, 60.9, 20.2, 14.5.
HRMS: (ESI) calcd. for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.1067, found: 215.1065.



1e

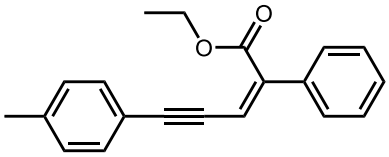
Ethyl (*Z*)-2-methyl-5-(*p*-tolyl)pent-2-en-4-ynoate (1e): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 4-ethynyltoluene (1.92 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1e** as a white resin (1.27 g, 37% yield, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.37 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.19 (d, *J* = 1.5 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.05 (d, *J* = 1.6 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.7, 139.0, 137.6, 131.8, 129.3, 120.3, 117.7, 97.8, 86.6, 60.9, 21.7, 20.2, 14.5.

HRMS: (ESI) calcd. for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1223, found: 229.1227.



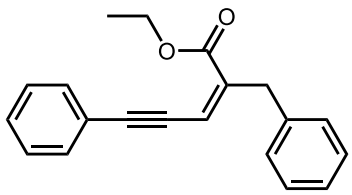
1f

Ethyl (*Z*)-2-methyl-5-(4-chlorophenyl)pent-2-en-4-ynoate (1f): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 1-chloro-4-ethynylbenzene (2.25 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1f** as a yellow resin (1.31 g, 35% yield, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.39 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.16 (d, *J* = 1.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.06 (d, *J* = 1.6 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.4, 138.7, 134.8, 133.0, 128.9, 121.9, 117.2, 96.1, 88.0, 60.9, 20.2, 14.5.
HRMS: (ESI) calcd. for $C_{14}H_{14}ClO_2$ $[M+H]^+$: 249.0677, found: 249.0683.



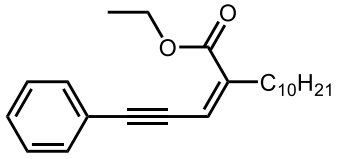
1g

Ethyl (*Z*)-2-phenyl-5-(*p*-tolyl)pent-2-en-4-ynoate (1g): Prepared following general procedure B, using ethyl phenylacetate (2.46 g, 15.0 mmol, 1.0 equiv) and 4-ethynyltoluene (1.92 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1g** as a yellow oil (0.96 g, 22% yield, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.43 (dt, *J* = 8.5, 2.2 Hz, 2H), 7.40-7.34 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.42 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.3, 143.2, 139.3, 136.0, 131.8, 129.3, 128.9, 128.7, 127.1, 120.0, 114.1, 98.9, 86.2, 61.4, 21.7, 14.5.
HRMS: (ESI) calcd. for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found: 291.1380.



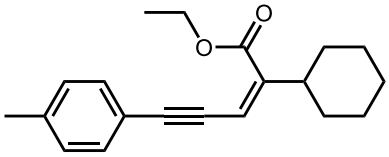
1h

Ethyl (*Z*)-2-benzyl-5-phenylpent-2-en-4-ynoate (1h): Prepared following general procedure B, using ethyl 3-phenylpropionate (2.67 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1h** as a yellow oil (1.52 g, 35%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.47-7.43 (m, 2H), 7.34-7.29 (m, 5H), 7.25-7.20 (m, 3H), 6.08 (t, *J* = 1.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.2, 141.8, 138.3, 131.8, 129.3, 128.9, 128.7, 128.5, 126.8, 123.3, 118.4, 98.7, 86.9, 61.0, 39.7, 14.4.
HRMS: (ESI) calcd. for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found: 2911.1387.



1i

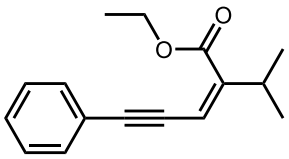
Ethyl (*Z*)-2-(3-phenylprop-2-yn-1-ylidene)dodecanoate (1i): Prepared following general procedure B, using ethyl dodecanoate (3.43 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1i** as a yellow oil (1.92 g, 38%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.49-7.43 (m, 2H), 7.35-7.30 (m, 3H), 6.12 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.41-2.36 (m, 2H), 1.52-1.45 (m, 2H), 1.35 (t, *J* = 7.1, 3H, partially obscured by multiplet at 1.34-1.22), 1.34-1.22 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.8, 143.3, 131.8, 128.7, 128.5, 123.4, 116.2, 97.2, 87.0, 60.9, 34.1, 32.1, 29.7, 29.7, 29.5, 29.5, 29.3, 28.9, 22.8, 14.5, 14.3.
HRMS: (ESI) calcd. for $C_{23}H_{33}O_2$ $[M+H]^+$: 341.2475, found: 341.2484.



1j

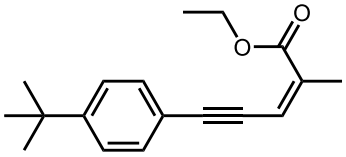
Ethyl (*Z*)-2-cyclohexyl-5-(*p*-tolyl)pent-2-en-4-ynoate (1j): Prepared following general procedure B, using ethyl 2-cyclohexylacetate (2.55 g, 15.0 mmol, 1.0 equiv) and 4-ethynyltoluene (1.92 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1j** as a white solid (1.05 g, 24%, 3 steps).
m.p.: 50.9-53.7 °C.
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.33 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.99 (d, *J* = 1.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.56-2.46 (m, 1H), 2.35 (s, 3H), 1.87-1.77 (m, 4H), 1.75-

1.67 (m, 1H), 1.39-1.29 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H, partially obscured by multiplet at 1.39-1.29), 1.24-1.13 (m, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.7, 148.8, 138.8, 131.6, 129.3 120.4, 112.8, 97.2, 86.2, 60.9, 41.3, 32.4, 26.6, 26.2, 21.7, 14.5.
HRMS: (ESI) calcd. for $C_{20}H_{25}O_2$ $[M+H]^+$: 297.1849, found: 297.1858.



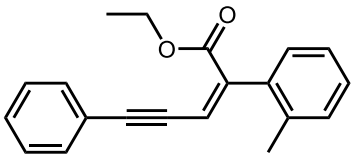
1k

Ethyl (*Z*)-2-isopropyl-5-phenylpent-2-en-4-ynoate (1k): Prepared following general procedure B, using ethyl isovalerate (1.95 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1k** as a pale yellow oil (0.99 g, 27%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.48-7.40 (m, 2H), 7.36-7.26 (m, 3H), 6.04 (d, *J* = 1.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.88 (septd, *J* = 6.8, 1.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.4, 149.8, 131.7, 128.6, 128.5, 123.4, 112.6, 96.9, 86.7, 60.9, 31.6, 21.7, 14.5.
HRMS: (ESI) calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1390.



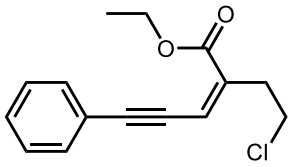
1l

Ethyl (*Z*)-5-(4-(*tert*-butyl)phenyl)-2-methylpent-2-en-4-ynoate (1l): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 1-(tert-butyl)-4-ethynylbenzene (2.61 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1l** as a colorless oil (1.04 g, 26%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.42-7.38 (m, 2H), 7.36-7.32 (m, 2H), 6.19 (d, *J* = 1.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.05 (d, *J* = 1.6 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.32 (s, 9H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.7, 152.1, 137.7, 131.6, 125.5, 120.4, 117.7, 97.8, 86.6, 60.9, 35.0, 31.3, 20.2, 14.5.
HRMS: (ESI) calcd. for $C_{18}H_{23}O_2$ $[M+H]^+$: 271.1693, found: 271.1701.



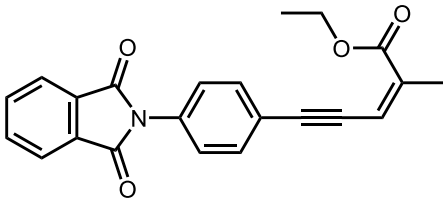
1m

Ethyl (*Z*)-5-phenyl-2-(*o*-tolyl)pent-2-en-4-ynoate (1m): Prepared following general procedure B, using ethyl *o*-tolylacetate (2.67 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1m** as a yellow oil (0.96 g, 22%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.56-7.51 (m, 2H), 7.39-7.34 (m, 3H), 7.29-7.24 (m, 1H), 7.23-7.18 (m, 3H), 6.29 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.1, 143.3, 137.6, 136.5, 132.0, 130.3, 129.6, 129.1, 128.7, 128.6, 126.0, 123.1, 119.7, 99.6, 86.8, 61.2, 20.1, 14.4.
HRMS: (ESI) calcd. for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found: 291.1388.



1n

Ethyl (*Z*)-2-(2-chloroethyl)-5-phenylpent-2-en-4-ynoate (1n): Prepared following general procedure B, using ethyl 4-chlorobutyrate (2.26 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1n** as a colorless oil (1.30 g, 33%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.51-7.46 (m, 2H), 7.37-7.31 (m, 3H), 6.33 (s, 1H), 4.31 (q, *J* = 7.1, 2H), 3.69 (t, *J* = 6.8 Hz, 2H), 2.84 (td, *J* = 6.8, 0.9 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 165.7, 137.3, 131.9, 129.1,128.6, 123.1, 120.9, 99.6, 86.7, 61.2, 43.2, 37.4, 14.5
HRMS: (ESI) calcd. for $C_{15}H_{16}ClO_2$ $[M+H]^+$: 263.0833, found: 263.0842.



1o

Ethyl (*Z*)-5-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-2-methylpent-2-en-4-ynoate (1o): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 2-(4-

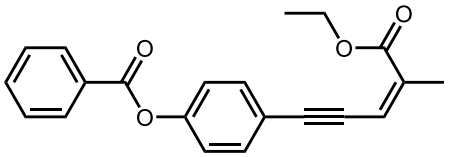
ethynylphenyl)isoindoline-1,3-dione (4.08 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (4:1 hexanes: ethyl acetate) to afford the product **1o** as a white solid (1.16 g, 19%, 3 steps).

m.p.: 135.7-137.5 °C.

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 8.00-7.94 (m, 2H), 7.84-7.78 (m, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 6.20 (d, *J* = 1.6 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.07 (d, *J* = 1.5 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.1, 166.6, 138.8, 134.7, 132.5, 132.0, 131.8, 126.3, 124.0, 123.1, 117.2, 96.5, 87.9, 61.0, 20.3, 14.5

HRMS: (ESI) calcd. for $C_{22}H_{18}NO_4$ $[M+H]^+$: 360.1230, found: 360.1229.



1p

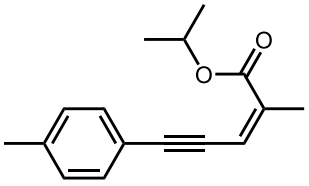
(*Z*)-4-(5-Ethoxy-4-methyl-5-oxopent-3-en-1-yn-1-yl)phenyl benzoate (1p): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 4-ethynylphenyl benzoate (3.67 g, 16.5 mmol, 1.1 equiv. The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1p** as a white solid (1.20 g, 21%, 3 steps).

m.p.: 62.5-64.5 °C.

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 8.22-8.17 (m, 2H), 7.68-7.62 (m, 1H), 7.57-7.49 (m, 4H), 7.24-7.18 (m, 2H), 6.19 (d, *J* = 1.6 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.07 (d, *J* = 1.6 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.5, 164.9, 151.2, 138.4, 133.9, 133.1, 130.3, 129.4, 128.8, 122.0, 121.1, 117.4, 96.6, 87.2, 60.9, 20.2, 14.5.

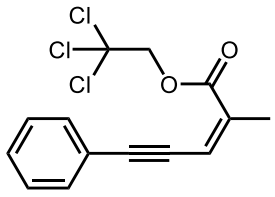
HRMS: (ESI) calcd. for $C_{21}H_{19}O_4$ $[M+H]^+$: 335.1280, found: 335.1276.



1q

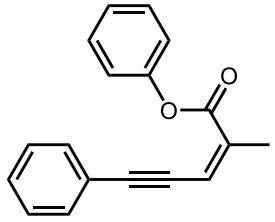
Isopropyl (*Z*)-2-methyl-5-(*p*-tolyl)pent-2-en-4-ynoate (1q): Prepared following general procedure B, using isopropyl propionate (1.74 g, 15.0 mmol, 1.0 equiv) and 4-ethynyltoluene (1.92

g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1q** as a colorless oil (1.24 g, 34%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.36 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.17 (d, *J* = 1.5 Hz, 1H), 5.15 (sept, *J* = 6.3 Hz 1H), 2.35 (s, 3H), 2.04 (d, *J* = 1.6 Hz, 3H), 1.32 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.3, 138.9, 138.1, 131.7, 129.3, 120.4, 117.2, 97.5, 86.5 68.4, 22.2, 21.7, 20.2.
HRMS: (ESI) calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1379.



1r

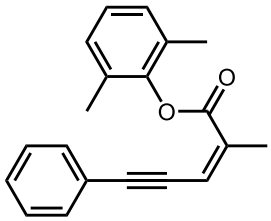
2,2,2-Trichloroethyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (1r): Prepared following general procedure B, using 2,2,2-trichloroethyl propionate (3.08 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1r** as a colorless oil (1.32 g, 28%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.52-7.47 (m, 2H), 7.36-7.31 (m, 3H), 6.34 (d, *J* = 1.6 Hz, 1H), 4.89 (s, 2H), 2.15 (d, *J* = 1.6 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 164.4, 135.9, 132.0, 129.1, 128.5, 123.1, 120.6, 99.6, 95.1, 86.8, 74.5, 20.0.
HRMS: (ESI) calcd. for $C_{14}H_{12}Cl_3O_2$ $[M+H]^+$: 316.9897, found: 316.9897.



1s

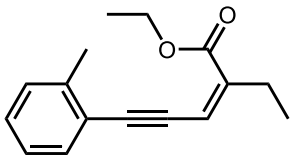
Phenyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (1s): Prepared following general procedure B, using phenyl propionate (2.25 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1s** as a white solid (1.17 g, 30%, 3 steps).
m.p.: 66.8-69.6 °C.
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.44-7.38 (m, 4H), 7.33-7.23 (m, 4H), 7.22-7.18 (m, 2H), 6.37 (d, *J* = 1.6 Hz, 1H), 2.20 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 164.9, 150.9, 137.1, 132.1, 129.6, 129.0, 128.5, 126.0, 123.1, 121.8, 119.7, 99.1, 87.0, 20.3.
HRMS: (ESI) calcd. for $C_{18}H_{15}O_2$ $[M+H]^+$: 263.1067, found: 263.1066.



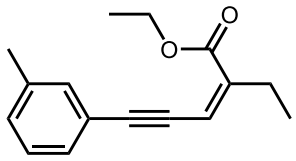
1t

2,6-Dimethylphenyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (1t): Prepared following general procedure B, using 2,6-dimethylphenyl propionate (2.67 g, 15.0 mmol, 1.0 equiv) and phenylacetylene (1.69 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: ethyl acetate) to afford the product **1t** as a white solid (0.95 g, 22%, 3 steps).
m.p.: 80.4-83.4 °C.
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.41-7.38 (m, 2H), 7.32-7.24 (m, 3H), 7.12-7.04 (m, 3H), 6.37 (d, *J* = 1.6 Hz, 1H), 2.23 (d, *J* = 1.6 Hz, 3H), 2.21 (s, 6H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 164.1, 148.4, 137.0, 132.0, 130.3, 128.9, 128.7, 128.5, 126.0, 123.2, 119.3, 98.8, 87.1, 20.4, 16.6
HRMS: (ESI) calcd. for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found: 291.1379.



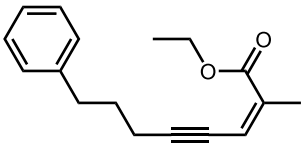
1u

Ethyl (Z)-2-ethyl-5-(o-tolyl)pent-2-en-4-ynoate (1u): Prepared following general procedure B, using ethyl butyrate (1.74 g, 15.0 mmol, 1.0 equiv) and 2-ethynyltoluene (1.92 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **1u** as a yellow oil (0.51 g, 14%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.43 (d, *J* = 7.6 Hz, 1H), 7.25-7.18 (m, 2H), 7.17-7.11 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 2.44 (qd, *J* = 7.4, 1.3 Hz), 1.33 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.8, 144.0, 140.6, 132.3, 129.6, 128.8, 125.7, 123.2, 115.6, 96.4, 90.6, 60.8, 27.2, 20.8, 114.5, 13.3.
HRMS: (ESI) calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1412.



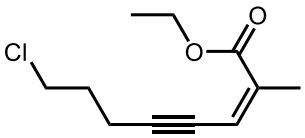
1v

Ethyl (Z)-2-ethyl-5-(m-tolyl)pent-2-en-4-ynoate (1v): Prepared following general procedure B, using ethyl butyrate (1.74 g, 15.0 mmol, 1.0 equiv) and 3-ethynyltoluene (1.92 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **1v** as a yellow oil (0.61 g, 17%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.30-7.26 (m, 2H), 7.21 (t, *J* = 7.6, 1H), 7.14 (d, *J* = 7.6, 1H), 6.13 (t, *J* = 1.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.43 (qd, *J* = 7.4, 1.4 Hz, 2H), 2.33 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.7, 144.2, 138.1, 132.4, 129.7, 128.9, 128.4, 123.2, 115.8, 97.7, 86.7, 60.8, 27.1, 21.3, 14.5, 13.3.
HRMS: (ESI) calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1411.



1w

Ethyl (Z)-2-methyl-8-phenyloct-2-en-4-ynoate (1w): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 5-phenyl-1-pentyne (2.38 g, 16.5 mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **1w** as a yellow oil (0.86 g, 23%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.28 (t, *J* = 7.5 Hz, 2H), 7.22-7.16 (m, 3H), 5.98 (d, *J* = 1.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.41 (td, *J* = 7.0, 2.1 Hz, 2H), 1.99 (d, *J* = 0.7 Hz, 3H), 1.89 (p, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.7, 141.7, 137.2, 128.7, 128.5, 126.0, 118.3, 99.1, 78.7, 60.7, 35.0, 30.3, 20.0, 19.5, 14.4.
HRMS: (ESI) calcd. for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1536, found: 257.1540.

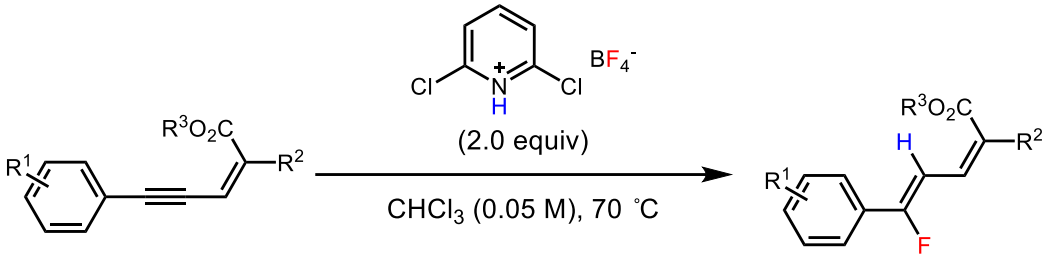


1x

Ethyl (Z)-8-chloro-2-methyloct-2-en-4-ynoate (1x): Prepared following general procedure B, using ethyl propionate (1.53 g, 15.0 mmol, 1.0 equiv) and 5-chloro-1-pentyne (1.69 g, 16.5

mmol, 1.1 equiv). The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **1x** as a yellow oil (0.57 g, 18%, 3 steps).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 5.93 (dd, *J* = 3.9, 2.3 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.59 (td, *J* = 6.7, 2.2 Hz, 2H), 2.01 (p, *J* = 6.6 Hz, 2H, partially obscured by d at 1.98), 1.98 (d, *J* = 0.7 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.6, 137.7, 117.9, 97.1, 79.1, 60.8, 43.8, 31.4, 20.2, 17.5, 14.4.
HRMS: (ESI) calcd. for $C_{11}H_{16}O_2Cl$ $[M+H]^+$: 215.0833, found: 215.0838.

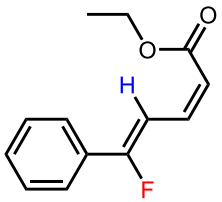
General procedure C for hydrofluorination of C2-substituted enynes



1 **2**

A reaction tube (20 mm × 125 mm, Fisherbrand, part # 14-959-37A) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # B7995-18) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, to a suspension of 2,6-dichloropyridinium tetrafluoroborate (117.9 mg, 0.50 mmol, 2.0 equiv) in dry chloroform (5.0 mL) was added enyne (**1**, 0.25 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for a specific time. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel with dichloromethane or ethyl acetate, then concentrated *in vacuo*. The crude mixture was purified via flash column chromatography to provide the desired product **2**.

Characterization data for product 2



2a

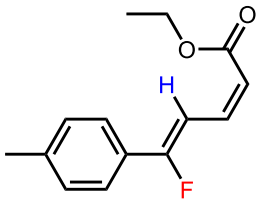
Ethyl (2*Z*,4*Z*)-5-fluoro-5-phenylpenta-2,4-dienoate (2a): Prepared following general procedure C, using ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**, 50.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2a** as a clear oil (23.1 mg, 42% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.66 (ddd, J = 11.7, 0.7 Hz, $J_{H–F}$ = 35.1 Hz, 1H), 7.41-7.39 (m, 3H), 7.14 (t, J = 11.5 Hz, 1H), 5.75 (d, J = 11.3 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9 (s), 161.9 (d, $J_{C–F}$ = 265.9 Hz), 135.9 (d, $J_{C–F}$ = 8.5 Hz), 131.4 (d, $J_{C–F}$ = 27.2 Hz), 130.4 (s), 128.8 (d, $J_{C–F}$ = 2.4 Hz), 125.2 (d, $J_{C–F}$ = 7.7 Hz), 117.6 (d, $J_{C–F}$ = 5.3 Hz), 102.6 (d, $J_{C–F}$ = 9.0 Hz), 60.2 (s), 14.5 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ –111.5 (d, $J_{H–F}$ = 35.1 Hz), *E*-isomer: –87.0 (d, $J_{H–F}$ = 19.1 Hz).

HRMS (ESI) calcd. for $C_{13}H_{14}FO_2$ $[M+H]^+$: 221.0972, found: 221.0966.



2b

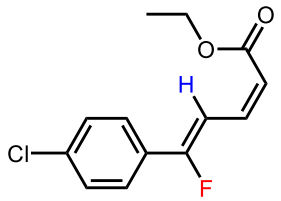
Ethyl (2*Z*,4*Z*)-5-fluoro-5-(*p*-tolyl)penta-2,4-dienoate (2b): Prepared following general procedure C, using ethyl (*Z*)-5-(*p*-tolyl)pent-2-en-4-ynoate (**1b**, 53.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 1 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2b** as a clear oil (26.3 mg, 45% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.60 (dd, J = 11.9 Hz, $J_{H–F}$ = 35.3 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.14 (t, J = 11.5 Hz, 1H), 5.72 (d, J = 11.3 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.0 (s), 162.2 (d, $J_{C–F}$ = 265.5 Hz), 140.8 (s), 136.1 (d, $J_{C–F}$ = 8.6 Hz), 129.5 (d, $J_{C–F}$ = 2.2 Hz), 128.6 (d, $J_{C–F}$ = 27.3 Hz), 125.2 (d, $J_{C–F}$ = 7.7 Hz), 117.0 (d, $J_{C–F}$ = 5.3 Hz), 101.8 (d, $J_{C–F}$ = 9.0 Hz), 60.1 (s), 21.6 (s), 14.5 (s).

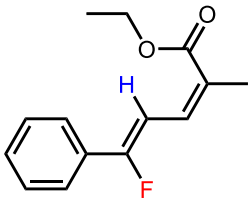
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –111.3 (d, $J_{H–F}$ = 35.2 Hz), *E*-isomer: –86.7 (d, $J_{H–F}$ = 19.1 Hz).

HRMS: (ESI) calcd. for $C_{14}H_{16}FO_2$ $[M+H]^+$: 235.1129, found: 235.1127.



2c

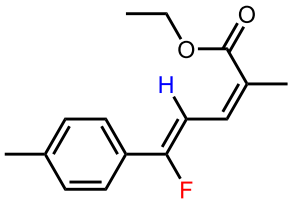
Ethyl (2*Z*,4*Z*)-5-(4-chlorophenyl)-5-fluoropenta-2,4-dienoate (2c): Prepared following general procedure C, using ethyl (*Z*)-5-(4-chlorophenyl)pent-2-en-4-ynoate (**1c**, 58.7 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 18 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2c** as a clear oil (26.2 mg, 41% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.64 (dd, J = 11.7 Hz, $J_{H–F}$ = 35.0 Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.11 (t, J = 11.5 Hz, 1H), 5.77 (d, J = 11.3Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.8 (s), 160.8 (d, $J_{C–F}$ = 265.2 Hz), 136.4 (s), 135.5 (d, $J_{C–F}$ = 8.3 Hz), 129.9 (d, $J_{C–F}$ = 28.0 Hz), 129.1 (d, $J_{C–F}$ = 2.2 Hz), 126.4 (d, $J_{C–F}$ = 7.6 Hz), 118.1 (d, $J_{C–F}$ = 5.4 Hz), 103.0 (d, $J_{C–F}$ = 9.0 Hz), 60.3 (s), 14.4 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –111.9 (d, $J_{H–F}$ = 35.0 Hz), *E*-isomer: –88.1 (d, $J_{H–F}$ = 19.1 Hz).
HRMS: (ESI) calcd. for $C_{13}H_{13}ClFO_2$ $[M+H]^+$: 255.0583, found: 255.0583.



2d

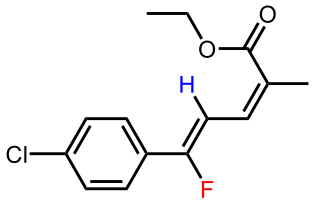
Ethyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-phenylpenta-2,4-dienoate (2d): Prepared following general procedure C, using ethyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (**1d**, 53.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2d** as a clear oil (28.7 mg, 49% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.62 (dd, J = 4.3, 2.3 Hz, 2H), 7.43 (dd, J = 11.7 Hz, $J_{H–F}$ = 35.2 Hz, 1H), 7.40-7.34 (m, 3H), 6.98 (dd, J = 11.7, 1.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.06 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 159.9 (d, $J_{C–F}$ = 262.5 Hz), 131.9 (d, $J_{C–F}$ = 27.5 Hz), 131.5 (d, $J_{C–F}$ = 7.7 Hz), 129.8 (s), 128.7 (d, $J_{C–F}$ = 2.3 Hz), 126.7 (d, $J_{C–F}$ = 5.4 Hz), 124.8 (d, $J_{C–F}$ = 7.6 Hz), 103.4 (d, $J_{C–F}$ = 8.8 Hz), 60.5 (s), 21.2 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.5(d, $J_{H–F}$ = 35.1 Hz).

HRMS: (ESI) calcd. for $C_{14}H_{16}FO_2$ $[M+H]^+$: 235.1129, found: 235.1128.



2e

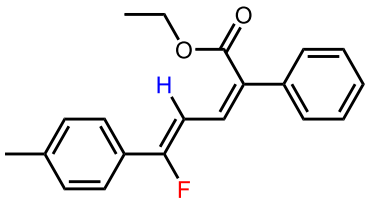
Ethyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-(*p*-tolyl)penta-2,4-dienoate (2e): Prepared following general procedure C, using ethyl (*Z*)-2-methyl-5-(*p*-tolyl)pent-2-en-4-ynoate (**1e**, 57.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 45 min. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2e** as a white resin (40.4 mg, 65% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 8.3 Hz, 2H), 7.38 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 35.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.97 (dd, *J* = 11.7, 1.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.05 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.9 (s), 160.2 (d, $J_{C–F}$ = 262.3 Hz), 140.1 (s), 131.8 (d, $J_{C–F}$ = 7.9 Hz), 129.5 (d, $J_{C–F}$ = 2.2 Hz), 129.1 (d, $J_{C–F}$ = 27.6 Hz), 126.1 (d, $J_{C–F}$ = 5.3 Hz), 124.8 (d, $J_{C–F}$ = 7.6 Hz), 102.6 (d, $J_{C–F}$ = 8.8 Hz), 60.4 (s), 21.5 (s), 21.2 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.3 (d, $J_{H–F}$ = 35.4 Hz), *E*-isomer: –91.4 (d, $J_{H–F}$ = 19.9 Hz).
HRMS: (ESI) calcd. for $C_{15}H_{18}FO_2$ $[M+H]^+$: 249.1285, found: 249.1285.



2f

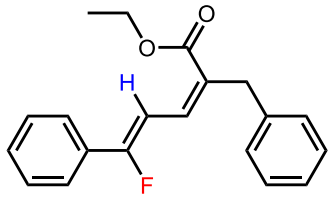
Ethyl (2*Z*,4*Z*)-5-(4-chlorophenyl)-5-fluoro-2-methylpenta-2,4-dienoate (2f): Prepared following general procedure C, using ethyl (*Z*)-5-(4-chlorophenyl)-2-methylpent-2-en-4-ynoate (**1f**, 62.2 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 15 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2f** as a white resin (29.6 mg, 44% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 8.7 Hz, 2H), 7.43 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 35.2 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.94 (dd, *J* = 11.7, 1.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.7 (s), 158.9 (d, $J_{C–F}$ = 261.9 Hz), 135.7 (s), 131.2 (d, $J_{C–F}$ = 7.6 Hz), 130.4 (d, $J_{C–F}$ = 28.2 Hz), 129.0 (d, $J_{C–F}$ = 2.2 Hz), 127.3 (d, $J_{C–F}$ = 5.4 Hz), 126.0 (d, $J_{C–F}$ = 7.5 Hz), 103.8 (d, $J_{C–F}$ = 8.7 Hz), 60.5 (s), 21.2 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.9 (d, $J_{H–F}$ = 35.2 Hz), *E*-isomer: –93.0 (d, $J_{H–F}$ = 19.7 Hz).
HRMS: (ESI) calcd. for $C_{14}H_{15}ClFO_2$ $[M+H]^+$: 269.0739, found: 269.0744.



2g

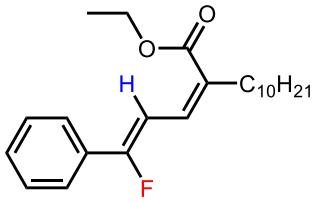
Ethyl (2*Z*,4*Z*)-5-fluoro-2-phenyl-5-(*p*-tolyl)penta-2,4-dienoate (2g): Prepared following general procedure C, using ethyl (*Z*)-2-phenyl-5-(p-tolyl)pent-2-en-4-ynoate (**1g**, 57.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2g** as a yellow oil (26.3 mg, 34% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 8.3 Hz, 2H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 2H), 7.33-7.29 (m, 1H), 7.23 (d, *J* = 11.6 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 11.8 Hz, $J_{H–F}$ = 33.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.39 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.9 (s), 161.4 (d, $J_{C–F}$ = 263.8 Hz), 140.5 (s), 138.6 (s), 132.2 (d, $J_{C–F}$ = 5.0 Hz), 130.2 (d, $J_{C–F}$ = 7.5 Hz), 129.6 (d, $J_{C–F}$ = 2.1 Hz), 128.9 (d, $J_{C–F}$ = 27.2 Hz), 128.3 (s), 128.1 (s), 127.9 (s), 124.9 (d, $J_{C–F}$ = 7.6 Hz), 102.7 (d, $J_{C–F}$ = 9.9 Hz), 61.0 (s), 21.6 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –111.9 (d, $J_{H–F}$ = 33.9 Hz).
HRMS: (ESI) calcd. for $C_{20}H_{20}FO_2$ $[M+H]^+$: 311.1442, found: 311.1437.



2h

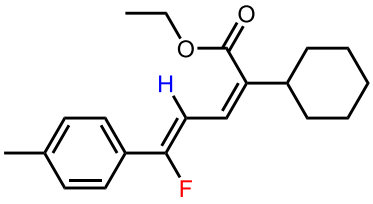
Ethyl (2*Z*,4*Z*)-2-benzyl-5-fluoro-5-phenylpenta-2,4-dienoate (2h): Prepared following general procedure C, using ethyl (*Z*)-2-benzyl-5-phenylpent-2-en-4-ynoate (**1h**, 72.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2h** as a yellow oil (31.9 mg, 41%, > 20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.65-7.61 (m, 2H), 7.43 (dd, J = 11.7 Hz, $J_{H–F}$ = 34.9 Hz, 1H, partially obscured by multiplet at 7.41-7.35), 7.41-7.35 (m, 3H), 7.32-7.28 (m, 2H), 7.26-7.18 (m, 3H), 7.02 (d, J = 11.7 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.74 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.2 (s), 160.6 (d, $J_{C–F}$ = 263.5 Hz), 139.6 (s), 132.3 (d, $J_{C–F}$ = 7.9 Hz), 131.8 (d, $J_{C–F}$ = 27.4 Hz), 130.3 (d, $J_{C–F}$ = 5.2 Hz), 129.9 (s), 129.0 (s), 128.8 (d, $J_{C–F}$ = 2.3 Hz), 128.5 (s), 126.4 (s), 124.9 (d, $J_{C–F}$ = 7.6 Hz), 103.3 (d, $J_{C–F}$ = 8.8 Hz), 60.5 (s), 40.9 (s), 14.3 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –113.2 (d, $J_{H–F}$ = 35.0 Hz), *E*-isomer: –91.1 (d, $J_{H–F}$ = 19.7 Hz).
HRMS: (ESI) calcd. For $C_{20}H_{20}FO_2$ $[M+H]^+$: 311.1442, found: 311.1428.



2i

Ethyl (*Z*)-2-((*Z*)-3-fluoro-3-phenylallylidene)dodecanoate (2i): Prepared following general procedure C, using ethyl (*Z*)-2-(3-phenylprop-2-yn-1-ylidene)dodecanoate (**1i**, 85.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2i** as a yellow oil (38.1 mg, 42%, > 20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.64-7.59 (m, 2H), 7.41-7.33 (m, 3H), 7.33 (dd, J = 11.7 Hz, $J_{H–F}$ = 35.2 Hz, 1H, partially obscured by multiplet at 7.41-7.33), 6.92 (d, J = 11.7 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.41-35 (m, 2H), 1.52-1.45 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H) 1.34-1.21 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 159.8 (d, $J_{C–F}$ = 262.1 Hz), 132.0 (d, $J_{C–F}$ = 26.6 Hz), 132.0 (s), 130.5 (d, $J_{C–F}$ = 7.7 Hz), 129.7 (s), 128.7 (d, $J_{C–F}$ = 2.3 Hz), 124.8 (d, $J_{C–F}$ = 7.5 Hz), 103.5 (d, $J_{C–F}$ = 8.9 Hz), 60.4 (s), 35.0 (s), 32.1 (s), 29.8 (s), 29.7 (s), 29.7 (s), 29.6 (s), 29.5 (s), 29.4 (s), 22.8 (s), 14.5 (s), 14.3 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.5 (d, $J_{H–F}$ = 35.1 Hz).
HRMS: (ESI) calcd. for $C_{23}H_{34}FO_2$ $[M+H]^+$: 361.2537, found: 361.2523.



2j

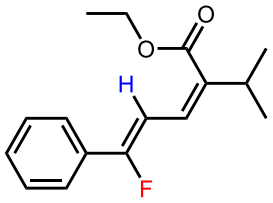
Ethyl (2*Z*,4*Z*)-2-cyclohexyl-5-fluoro-5-(*p*-tolyl)penta-2,4-dienoate (2j): Prepared following general procedure C, using ethyl (*Z*)-2-cyclohexyl-5-(*p*-tolyl)pent-2-en-4-ynoate (**1j**, 74.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 1 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2j** as a colorless oil (24.1 mg, 30% yield, 17:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 8.2 Hz, 2H), 7.118 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 11.6 Hz, $J_{H–F}$ = 34.8 Hz, 1H), 6.83 (d, *J* = 11.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 11.4 Hz, 1H), 2.37 (s, 3H), 1.88-1.68 (m, 5H), 1.37 (t, *J* = 7.1 Hz, 3H, partially obscured by multiplet at 1.39-1.15), 1.39-1.15 (m, 5H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 168.5 (s), 159.9 (d, $J_{C–F}$ = 261.1 Hz), 139.9 (s), 137.4 (d, $J_{C–F}$ = 4.9 Hz), 129.5 (d, $J_{C–F}$ = 2.1 Hz), 129.3 (d, $J_{C–F}$ = 27.6 Hz), 126.6 (d, $J_{C–F}$ = 7.7 Hz), 124.7 (d, $J_{C–F}$ = 7.5 Hz), 102.8 (d, $J_{C–F}$ = 9.4 Hz), 60.5 (s), 41.6 (s), 32.9 (s), 26.9 (s), 26.3 (s), 21.5 (s), 14.6 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.5 (d, $J_{H–F}$ = 34.8 Hz), *E*-isomer: –93.0 (d, $J_{H–F}$ = 20.0 Hz).

HRMS: (ESI) calcd. for $C_{20}H_{26}FO_2$ $[M+H]^+$: 317.1911, found: 317.1900.



2k

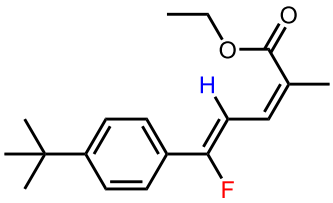
Ethyl (2*Z*,4*Z*)-5-fluoro-2-isopropyl-5-phenylpenta-2,4-dienoate (2k): Prepared following general procedure C, using ethyl (*Z*)-2-isopropyl-5-phenylpent-2-en-4-ynoate (**1k**, 68.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2k** as a yellow oil (21.7 mg, 33% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.63-7.57 (m, 2H), 7.41-7.33 (m, 3H), 7.14 (dd, *J* = 11.6 Hz, $J_{H–F}$ = 34.8 Hz, 1H), 6.87 (d, *J* = 11.6 Hz, 1H) 4.30 (q, *J* = 7.1 Hz, 2H), 2.90 (sept, *J* = 6.8 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 168.3 (s), 159.6 (d, $J_{C–F}$ = 261.2 Hz), 138.7 (s), 132.1 (d, $J_{C–F}$ = 27.6 Hz), 129.7 (s), 128.7 (d, $J_{C–F}$ = 2.3 Hz), 126.2 (d, $J_{C–F}$ = 7.6 Hz), 124.7 (d, $J_{C–F}$ = 7.5 Hz), 103.5 (s), 60.5 (s), 31.7 (s), 22.2 (s), 14.5 (s).

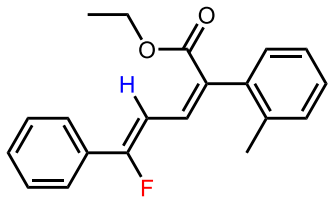
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.6 (d, $J_{H–F}$ = 34.8 Hz), *E*-isomer: –93.2 (d, $J_{H–F}$ = 19.5 Hz).

HRMS: (ESI) calcd. for $C_{16}H_{20}FO_2$ $[M+H]^+$: 263.1442, found: 263.1445.



2l

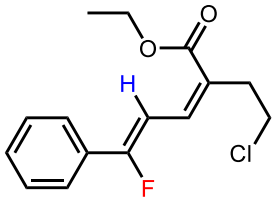
Ethyl (2*Z*,4*Z*)-5-(4-(*tert*-butyl)phenyl)-5-fluoro-2-methylpenta-2,4-dienoate (2l): Prepared following general procedure C, using ethyl (*Z*)-5-(4-(*tert*-butyl)phenyl)-2-methylpent-2-en-4-ynoate (**1l**, 67.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 1 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2l** as a yellow oil (41.9 mg, 58% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.56 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.37 (dd, J = 11.7 Hz, $J_{H–F}$ = 35.0 Hz, 1H, partially obscured by doublet at 7.40), 6.97 (dd, *J* = 11.7, 1.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.33 (s, 9H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.9 (s), 160.2 (d, $J_{C–F}$ = 262.3 Hz), 153.3 (s), 131.7 (d, $J_{C–F}$ = 7.8 Hz), 129.1 (d, $J_{C–F}$ = 27.7 Hz), 126.2 (d, $J_{C–F}$ = 5.1 Hz), 125.7 (d, $J_{C–F}$ = 2.2 Hz), 124.7 (d, $J_{C–F}$ = 7.5 Hz), 102.8 (s), 60.4 (s), 35.0 (s), 31.3 (s), 21.2 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.3 (d, $J_{H–F}$ = 35.3 Hz), *E*-isomer: –91.7 (d, $J_{H–F}$ = 19.9 Hz).
HRMS: (ESI) calcd. for $C_{18}H_{24}FO_2$ $[M+H]^+$: 291.1755, found: 291.1769.



2m

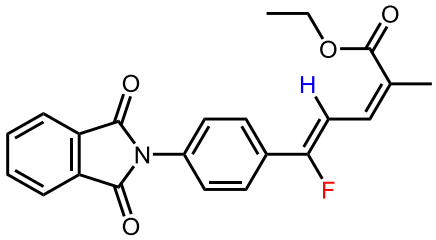
Ethyl (2*Z*,4*Z*)-5-fluoro-5-phenyl-2-(*o*-tolyl)penta-2,4-dienoate (2m): Prepared following general procedure C, using ethyl (*Z*)-5-phenyl-2-(*o*-tolyl)pent-2-en-4-ynoate (**1m**, 72.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2m** as a yellow oil (26.4 mg, 34% yield, 12:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.69-7.65 (m, 2H), 7.50 (dd, *J* = 11.8 Hz, $J_{H–F}$ = 34.6 Hz, 1H), 7.43-7.38 (m, 3H), 7.25-7.15 (m, 4H), 7.07 (d, *J* = 11.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.2 (s), 161.6 (d, $J_{C–F}$ = 264.8 Hz), 139.5 (s), 136.6 (s), 133.9 (d, $J_{C–F}$ = 7.7 Hz), 132.1 (d, $J_{C–F}$ = 5.4 Hz), 131.7 (d, $J_{C–F}$ = 27.2 Hz), 130.2 (s), 130.0 (d, $J_{C–F}$ = 2.6 Hz), 128.8 (d, $J_{C–F}$ = 2.3 Hz), 128.7 (s), 128.0 (s), 125.9 (s), 125.1 (d, $J_{C–F}$ =2.3 Hz), 103.3(d, $J_{C–F}$ = 9.0 Hz), 60.8 (s), 20.1 (s), 14.4 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –111.9 (d, $J_{H–F}$ = 34.6 Hz), *E*-isomer: –88.3 (d, $J_{H–F}$ = 19.6 Hz).
HRMS: (ESI) calcd. for $C_{20}H_{20}FO_2$ $[M+H]^+$: 311.1442, found: 311.1457.



2n

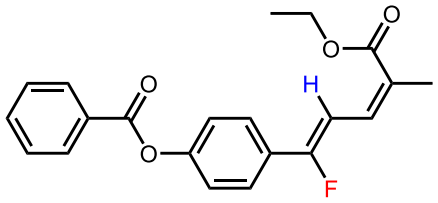
Ethyl (2*Z*,4*Z*)-2-(2-chloroethyl)-5-fluoro-5-phenylpenta-2,4-dienoate (2n): Prepared following general procedure C, using ethyl (*Z*)-2-(2-chloroethyl)-5-phenylpent-2-en-4-ynoate (**1n**, 65.7 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 6 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2n** as a colorless oil (16.4 mg, 23% yield, 20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.67-7.62 (m, 2H), 7.44 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 34.7 Hz, 1H, partially obscured by multiplet at 7.41-7.37), 7.41-7.37 (m, 3H), 7.08 (d, *J* = 11.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.68 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.8 (s), 161.3 (d, $J_{C–F}$ = 265.0 Hz), 134.6 (d, $J_{C–F}$ = 8.0 Hz), 131.6 (d, $J_{C–F}$ = 27.2 Hz), 130.2 (s), 128.2 (d, $J_{C–F}$ = 2.3 Hz), 126.3 (d, $J_{C–F}$ = 5.3 Hz), 125.0 (d, $J_{C–F}$ = 7.7 Hz), 103.1 (d, $J_{C–F}$ = 8.5 Hz), 60.8 (s), 43.9 (s), 38.4 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –111.8 (d, $J_{H–F}$ = 34.6 Hz), *E*-isomer: –88.9 (d, $J_{H–F}$ = 19.3 Hz).
HRMS: (ESI) calcd. for $C_{15}H_{17}ClFO_2$ $[M+H]^+$: 283.0896, found: 283.0887.



2o

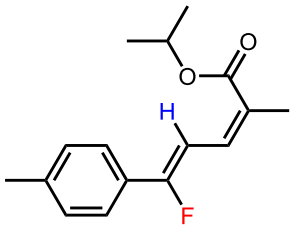
Ethyl (2*Z*,4*Z*)-5-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-5-fluoro-2-methylpenta-2,4-dienoate (2o): Prepared following general procedure C, using ethyl (*Z*)-5-(4-(1,3-dioxoisoindolin-2-yl)phenyl)-2-methylpent-2-en-4-ynoate (**1o**, 89.8 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 12 h. The crude mixture was purified via column chromatography on silica gel (4:1 hexanes: ethyl acetate) to afford the product **2o** as a white solid (33.7 mg, 36% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
m.p.: 121.0-124.3 °C.

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 8.00-7.95 (m, 2H), 7.84-7.79 (m, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 35.1 Hz, 1H, partially obscured by doublet at 7.52), 6.98 (dd, *J* = 11.7, 1.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.07 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.7 (s), 167.1 (s), 159.0 (d, $J_{C–F}$ = 262.1 Hz), 134.7 (s), 132.1 (s), 131.8 (s), 131.4 (d, $J_{C–F}$ = 28.1 Hz), 131.2 (d, $J_{C–F}$ = 7.6 Hz), 127.5 (d, $J_{C–F}$ = 5.4 Hz), 126.5 (d, $J_{C–F}$ = 2.0 Hz), 125.5 (d, $J_{C–F}$ = 7.5 Hz), 124.0 (s), 104.2 (s), 60.6 (s), 21.3 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.9 (d, $J_{H–F}$ = 35.0 Hz), *E*-isomer: –93.0 (d, $J_{H–F}$ = 20.0 Hz).
HRMS: (ESI) calcd. for $C_{22}H_{19}FNO_4$ $[M+H]^+$: 380.1293, found: 380.1275.



2p

4-((1*Z*,3*Z*)-5-Ethoxy-1-fluoro-4-methyl-5-oxopenta-1,3-dien-1-yl)phenyl benzoate (2p): Prepared following general procedure C, using (*Z*)-4-(5-ethoxy-4-methyl-5-oxopent-3-en-1-yn-1-yl)phenyl benzoate (**1p**, 87.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 4 h. The crude mixture was purified via column chromatography on silica gel (19:1 hexanes: diethyl ether) to afford the product **2p** as a white solid (39.8 mg, 45% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
m.p.: 87.7-90.1 °C.
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 8.24-8.18 (m, 2H), 7.69 (d, *J* = 8.8, 2H), 7.65 (t, *J* = 7.5, 1H), 7.53 (t, *J* = 7.8 Hz, 2 H), 7.42 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 35.2 Hz), 7.28-7.24 (m, 2H), 6.97 (dd, *J* = 11.7, 1.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.06 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 165.0 (s), 159.3 (d, $J_{C–F}$ = 262.1 Hz), 152.1 (s), 133.9 (s), 131.4 (d, $J_{C–F}$ = 7.6 Hz), 130.4 (s), 129.7 (d, $J_{C–F}$ = 28.1 Hz), 129.4 (s), 128.8 (s), 127.0 (d, $J_{C–F}$ = 7.6 Hz), 126.1 (d, $J_{C–F}$ = 7.5 Hz), 122.2 (s), 103.6 (s), 60.5 (s), 21.2 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.3 (d, $J_{H–F}$ = 35.2 Hz), *E*-isomer: –92.1 (d, $J_{H–F}$ = 20.2 Hz).
HRMS: (ESI) calcd. for $C_{21}H_{20}FO_4$ $[M+H]^+$: 355.1340, found: 355.1338.



2q

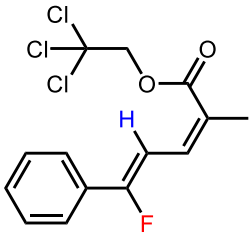
Isopropyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-(*p*-tolyl)penta-2,4-dienoate (2q): Prepared following general procedure C, using isopropyl (*Z*)-2-methyl-5-(*p*-tolyl)pent-2-en-4-ynoate (**1q**, 60.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 15 min. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2q** as a colorless oil (24.6 mg, 38% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.51 (d, J = 8.3 Hz, 2H), 7.36 (dd, J = 11.7 Hz, , $J_{H–F}$ = 35.4 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 6.95 (dd, J = 11.7, 1.3 Hz, 1H), 5.13 (sept, J = 6.3 Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H), 1.33 (d, J = 6.3 Hz, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.4 (s), 160.1 (d, $J_{C–F}$ = 262.0 Hz), 140.0 (s), 131.4 (d, $J_{C–F}$ = 7.8 Hz), 129.5 (d, $J_{C–F}$ = 2.2 Hz), 129.2 (d, $J_{C–F}$ = 27.6 Hz), 126.6 (d, $J_{C–F}$ = 5.3 Hz), 124.75 (d, $J_{C–F}$ = 7.5 Hz), 102.7 (d, $J_{C–F}$ = 8.9 Hz), 67.2 (s), 22.2 (s), 21.5 (s), 21.2 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.6 (d, $J_{H–F}$ = 35.4 Hz), *E*-isomer: –91.7 (d, $J_{H–F}$ = 19.9 Hz).

HRMS: (ESI) calcd. for $C_{16}H_{20}FO_2$ $[M+H]^+$: 263.1442, found: 263.1443.

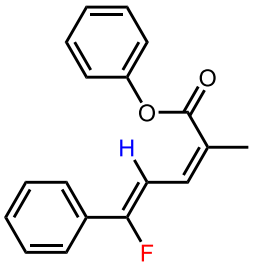


2r

2,2,2-Trichloroethyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-phenylpenta-2,4-dienoate (2r): Prepared following general procedure C, using 2,2,2-trichloroethyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (**1r**, 79.4 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 24 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2r** as a colorless oil (23.7 mg, 28% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

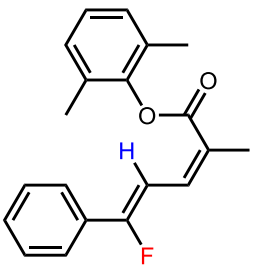
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.68-7.63 (m, 2H), 7.44 (dd, J = 11.8 Hz, $J_{H–F}$ = 34.2 Hz, 1H, partially obscured by miltuplet at 7.41-7.37), 7.41-7.37 (m, 3H), 7.14 (dd, J = 11.8, 1.3 Hz, 1H), 4.87 (s, 2H), 2.14 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 165.8 (s), 161.0 (d, $J_{C–F}$ = 264.7 Hz), 134.0 (d, $J_{C–F}$ = 8.1 Hz), 131.6 (d, $J_{C–F}$ = 27.3 Hz), 130.2 (s), 128.8 (d, $J_{C–F}$ = 2.3 Hz), 125.1 (d, $J_{C–F}$ = 7.7 Hz), 124.6 (d, $J_{C–F}$ = 5.3 Hz), 103.3 (d, $J_{C–F}$ = 8.7 Hz), 95.3 (s), 74.5 (s), 21.1 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –112.2 (d, $J_{H–F}$ = 34.3 Hz), *E*-isomer: –89.1 (d, $J_{H–F}$ = 18.4 Hz).
HRMS: (ESI) calcd. for $C_{14}H_{13}Cl_3FO_2$ $[M+H]^+$: 336.9960, found: 336.9958.



2s

Phenyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-phenylpenta-2,4-dienoate (2s): Prepared following general procedure C, using phenyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (**1s**, 65.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 7 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2s** as a white solid (30.0 mg, 43% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
m.p.: 61.7-64.7 °C.
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.65-7.06 (m, 2H), 7.52 (dd, *J* = 11.8 Hz, $J_{H–F}$ = 34.9 Hz, 1H), .45-7.40 (m, 2H), 7.39-7.34 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19-7.13 (m, 3H), 2.23 (s, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.2 (s), 160.8 (d, $J_{C–F}$ = 264.3 Hz), 150.9 (s), 134.2 (d, $J_{C–F}$ = 7.9 Hz), 131.7 (d, $J_{C–F}$ =27.3 Hz), 130.1 (s), 129.6 (s), 128.8 (d, $J_{C–F}$ = 2.3 Hz), 126.0 (s), 125.3 (d, $J_{C–F}$ = 5.4 Hz), 125.0 (d, $J_{C–F}$ =7.7 Hz), 121.9 (s), 103.3 (s), 21.2 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –113.0 (d, $J_{H–F}$ = 34.9 Hz), *E*-isomer: –89.6 (d, $J_{H–F}$ = 19.9 Hz).
HRMS: (ESI) calcd. for $C_{18}H_{16}FO_2$ $[M+H]^+$: 283.1129, found: 283.1128.



2t

2,6-Dimethylphenyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-phenylpenta-2,4-dienoate (2t): Prepared following general procedure C, using 2,6-dimethylphenyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (**1t**, 72.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 8 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2t** as a colorless glassy solid (26.3 mg, 34% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

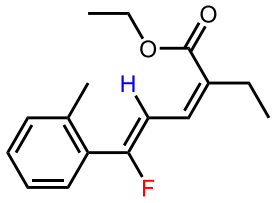
m.p.: 66.6-70.0 °C

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.64-7.59 (m, 2H), 7.53 (dd, *J* = 11.7 Hz, $J_{H–F}$ = 35.0 Hz, 1H), 7.39-7.34 (m, 3H), 7.17 (dd, J = 11.7, 1.3 Hz, 1H), 7.12-7.05 (m, 3H), 2.27 (s, 3H), 2.19 (s, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 165.4 (s), 160.8 (d, $J_{C–F}$ = 264.1 Hz), 148.4 (s), 134.0 (d, $J_{C–F}$ = 7.8 Hz), 131.7 (d, $J_{C–F}$ = 27.3 Hz), 130.3 (s), 130.0 (s), 128.8 (s), 126.0 (s), 125.2 (d, $J_{C–F}$ = 5.5 Hz), 125.0 (d, $J_{C–F}$ = 7.6 Hz), 123.0 (s), 103.3 (d, $J_{C–F}$ = 8.6 Hz), 21.3 (s), 16.6 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –113.1 (d, $J_{H–F}$ = 35.0 Hz), *E*-isomer: –89.6 (d, $J_{H–F}$ = 19.5 Hz).

HRMS: (ESI) calcd. for $C_{20}H_{20}FO_2$ $[M+H]^+$: 311.1442, found: 311.1428.



2u

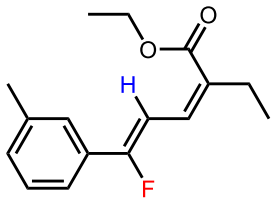
Ethyl (2Z,4Z)-2-ethyl-5-fluoro-5-(o-tolyl)penta-2,4-dienoate (2u): Prepared following general procedure C, using ethyl (Z)-2-ethyl-5-(o-tolyl)pent-2-en-4-ynoate (**1u**, 60.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 1 h. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2u** as a yellow oil (34.0 mg, 52% yield, 11:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.45 (d, J = 7.5 Hz, 1H), 7.31-7.26 (m 1H), 7.23-7.18 (m, 2H), 6.95 (dd, *J* = 11.6 Hz, $J_{H–F}$ = 31.9 Hz, 1H), 6.91 (s, 1H, partially obscured by dd at 6.95), 4.24 (q, J = 7.1 Hz, 2H), 2.45 (d, J = 3.3 Hz, 3H), 2.43 (q, J = 7.4 Hz, 2H, partially obscured by d at 2.45), 1.32 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.4 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 161.4 (d, $J_{C–F}$ = 266.8 Hz), 136.8 (s), 133.2 (d, $J_{C–F}$ = 5.1 Hz), 132.2 (d, $J_{C–F}$ = 24.8 Hz), 131.2 (s), 129.8 (s), 129.5 (d, $J_{C–F}$ = 7.1 Hz), 128.7 (d, $J_{C–F}$ = 6.2 Hz), 126.0 (s), 107.6 (d, $J_{C–F}$ = 9.6 Hz), 60.4 (s), 28.0 (s), 21.2 (s), 14.5 (s), 14.0 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –98.2 (m), *E*-isomer: –83.5 (d, $J_{H–F}$ = 18.2 Hz).

HRMS: (ESI) calcd. for $C_{16}H_{20}FO_2$ $[M+H]^+$: 263.1442, found: 263.1777.



2v

Ethyl (2Z,4Z)-2-ethyl-5-fluoro-5-(m-tolyl)penta-2,4-dienoate (1v): Prepared following general procedure C, using ethyl (Z)-2-ethyl-5-(m-tolyl)pent-2-en-4-ynoate (**1v**, 60.6 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for 1 h. The crude mixture was purified via column chromatography -on silica gel (39:1 hexanes: diethyl ether) to afford the product **2v** as a yellow oil (18.2 mg, 28% yield, 17:1 *Z*:*E* determined by ^{19}F NMR upon isolation).

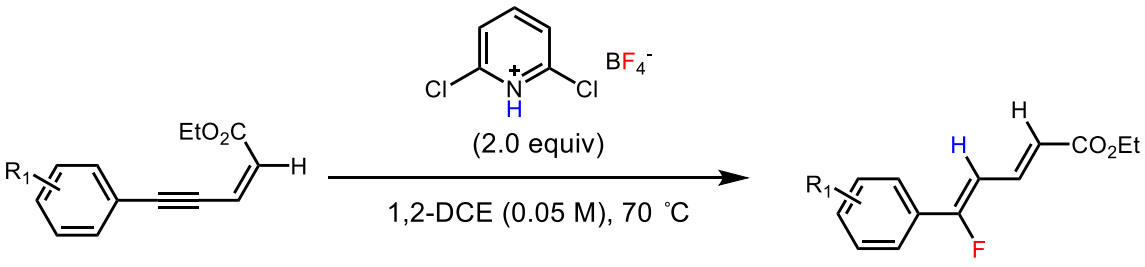
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.46-7.41(m, 2H), 7.34 (dd, J = 11.7 Hz, $J_{H–F}$ = 35.2 Hz, 1H), 7.29-7.24 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 11.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.43 (q, J = 7.5 2H), 2.37 (s, 3H), 1.36 (t, J = 7.1, 3H), 1.13 (t, J = 7.4 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 160.2 (d, $J_{C–F}$ = 262.4 Hz), 138.4 (d, $J_{C–F}$ = 2.4 Hz), 133.0 (d, $J_{C–F}$ = 5.2 Hz), 131.9 (d, $J_{C–F}$ = 27.2 Hz), 130.6 (s), 130.0 (d, $J_{C–F}$ = 7.8 Hz), 128.6 (d, $J_{C–F}$ = 2.2 Hz), 125.4 (d, $J_{C–F}$ = 7.4 Hz), 122.0 (d, $J_{C–F}$ = 7.6 Hz), 103.3 (d, $J_{C–F}$ = 8.9 Hz), 60.4 (s), 28.0 (s), 21.6 (s), 14.5 (s), 14.1 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.2 (d, $J_{H–F}$ = 35.2 Hz), *E*-isomer: –91.8 (d, $J_{H–F}$ = 19.9 Hz).

HRMS: (ESI) calcd. for $C_{16}H_{20}FO_2$ $[M+H]^+$: 263.1442, found: 263.1476.

General procedure D for hydrofluorination of C2-unsubstituted enynes

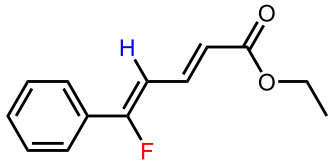


1 **2'**

A reaction tube (20 mm × 125 mm, Fisherbrand, part # 14-959-37A) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # B7995-18) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, to a suspension of 2,6-dichloropyridinium tetrafluoroborate (117.9 mg, 0.50 mmol, 2.0 equiv) in dry 1,2-dichloroethane (5.0 mL) was added

enyne (**1**, 0.25 mmol, 1.0 equiv). The reaction tube was capped and removed from the glovebox, placed in an oil bath preheated to 70 °C, where it was stirred for a specific time. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel with dichloromethane or ethyl acetate, then concentrated *in vacuo*. The crude mixture was purified via flash column chromatography to provide the desired product **2′**.

Characterization data for product 2′



2a'

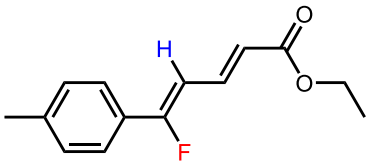
Ethyl (2*E*,4*Z*)-5-fluoro-5-phenylpenta-2,4-dienoate (2a′): Prepared following general procedure D, using ethyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**, 50.1 mg, 0.25 mmol, 1.0 equiv) in 1,2-dichloroethane (5.0 mL) for 9 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2a′** as a clear oil (14.3 mg, 26% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation) (Crude isomer ratio of C2–C3 double bond 2.5:1 *E*:*Z*.)

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.77 (dd, J = 15.5, 11.5 Hz, 1H), 7.63-7.61 (m, 2H), 7.42-7.40 (m, 3H), 6.23 (dd, J = 11.5 Hz, $J_{H–F}$ = 33.2 Hz, 1H), 5.99 (d, J = 15.5 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.9 (s), 161.5 (d, $J_{C–F}$ = 264.9 Hz), 136.4 (d, $J_{C–F}$ = 6.7 Hz), 131.1 (d, $J_{C–F}$ = 26.8 Hz), 130.5 (s), 128.9 (d, $J_{C–F}$ = 2.3 Hz), 125.0 (d, $J_{C–F}$ = 7.6 Hz), 121.2 (d, $J_{C–F}$ = 3.7 Hz), 104.5 (d, $J_{C–F}$ = 13.2 Hz), 60.6 (s), 14.5 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –108.5 (d, $J_{H–F}$ = 33.0 Hz).

HRMS: (ESI) calcd. for $C_{13}H_{14}FO_2$ $[M+H]^+$: 221.0972, found: 221.0969.

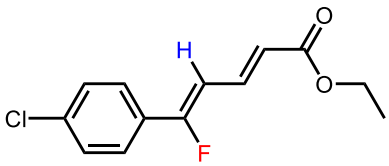


2b'

Ethyl (2*E*,4*Z*)-5-fluoro-5-(*p*-tolyl)penta-2,4-dienoate (2b′): Prepared following general procedure D, using ethyl (*Z*)-5-(*p*-tolyl)pent-2-en-4-ynoate (**1b**, 53.6 mg, 0.25 mmol, 1.0 equiv) in 1,2-dichloroethane (5.0 mL) for 2 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2b′** as a

yellow resin (10.6 mg, 18% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation). (Crude isomer ratio of C2–C3 double bond 12:1 *E*:*Z*.)

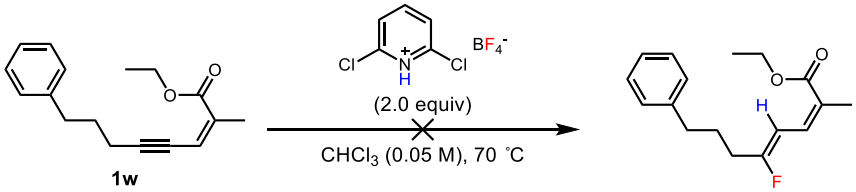
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.77 (dd, *J* = 15.5, 11.5 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.18 (dd, *J* = 11.5 Hz, $J_{H–F}$ = 33.4 Hz, 1H), 5.96 (d, *J* = 15.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 167.1 (s), 161.8 (d, $J_{C–F}$ = 264.6 Hz), 140.9 (s), 136.6 (d, $J_{C–F}$ = 6.8 Hz), 129.6 (d, $J_{C–F}$ = 2.2 Hz), 128.3 (d, $J_{C–F}$ = 26.9 Hz), 125.0 (d, $J_{C–F}$ = 7.6 Hz), 120.6 (d, $J_{C–F}$ = 3.7 Hz), 103.7 (d, $J_{C–F}$ = 13.2 Hz), 60.5 (s), 21.6 (s), 14.5 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –108.3 (d, $J_{H–F}$ = 33.4 Hz).
HRMS: (ESI) calcd. for $C_{14}H_{16}FO_2$ $[M+H]^+$: 235.1129, found: 235.1132.



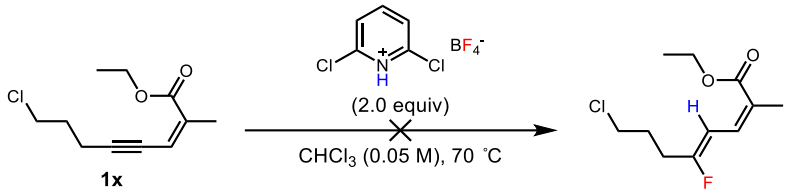
2c'

Ethyl (2*E*,4*Z*)-5-(4-chlorophenyl)-5-fluoropenta-2,4-dienoate (2c′): Prepared following general procedure D, using ethyl (*Z*)-5-(4-chlorophenyl)pent-2-en-4-ynoate (**1c**, 58.7 mg, 0.25 mmol, 1.0 equiv) in 1,2-dichloroethane (5.0 mL) for 24 h. The crude mixture was purified via column chromatography on silica gel (gradient from 49:1 to 19:1 hexanes: ethyl acetate) to afford the product **2c′** as a yellow resin (9.0 mg, 14% yield, >20:1 *Z*:*E* determined by ^{19}F NMR upon isolation).
^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.73 (dd, *J* = 15.5, 11.4 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.20 (dd, *J* = 11.4 Hz, $J_{H–F}$ = 33.1 Hz, 1H), 5.99 (d, *J* = 15.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 166.8 (s), 160.4 (d, $J_{C–F}$ = 264.3 Hz), 136.5 (s), 136.0 (d, $J_{C–F}$ = 6.5 Hz), 129.6 (d, $J_{C–F}$ = 27.5 Hz), 129.2 (d, $J_{C–F}$ = 2.2 Hz), 126.2 (d, $J_{C–F}$ = 7.5 Hz), 121.7 (d, $J_{C–F}$ = 3.8 Hz), 104.9 (d, $J_{C–F}$ = 13.1 Hz), 60.6 (s), 14.4 (s).
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –108.9 (d, $J_{H–F}$ = 33.1 Hz).
HRMS: (ESI) calcd. for $C_{13}H_{13}ClFO_2$ $[M+H]^+$: 255.0583, found: 255.0589.

Unsuccessful Hydrofluorination Substrates

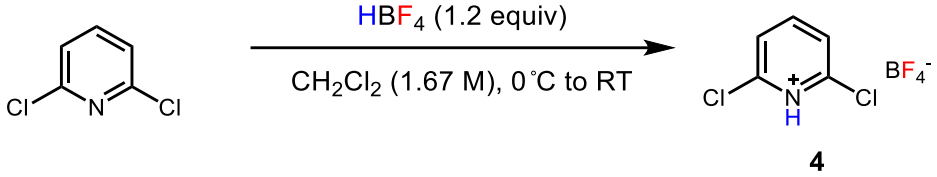


Reaction with ethyl (Z)-2-methyl-8-phenyloct-2-en-4-ynoate (1w): Attempted following general procedure C, using ethyl (Z)-2-methyl-8-phenyloct-2-en-4-ynoate (**1w**, 64.1 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for various times. No product was detected via crude NMR. No unreacted **1w** was detected via crude NMR, indicating decomposition of the starting material.



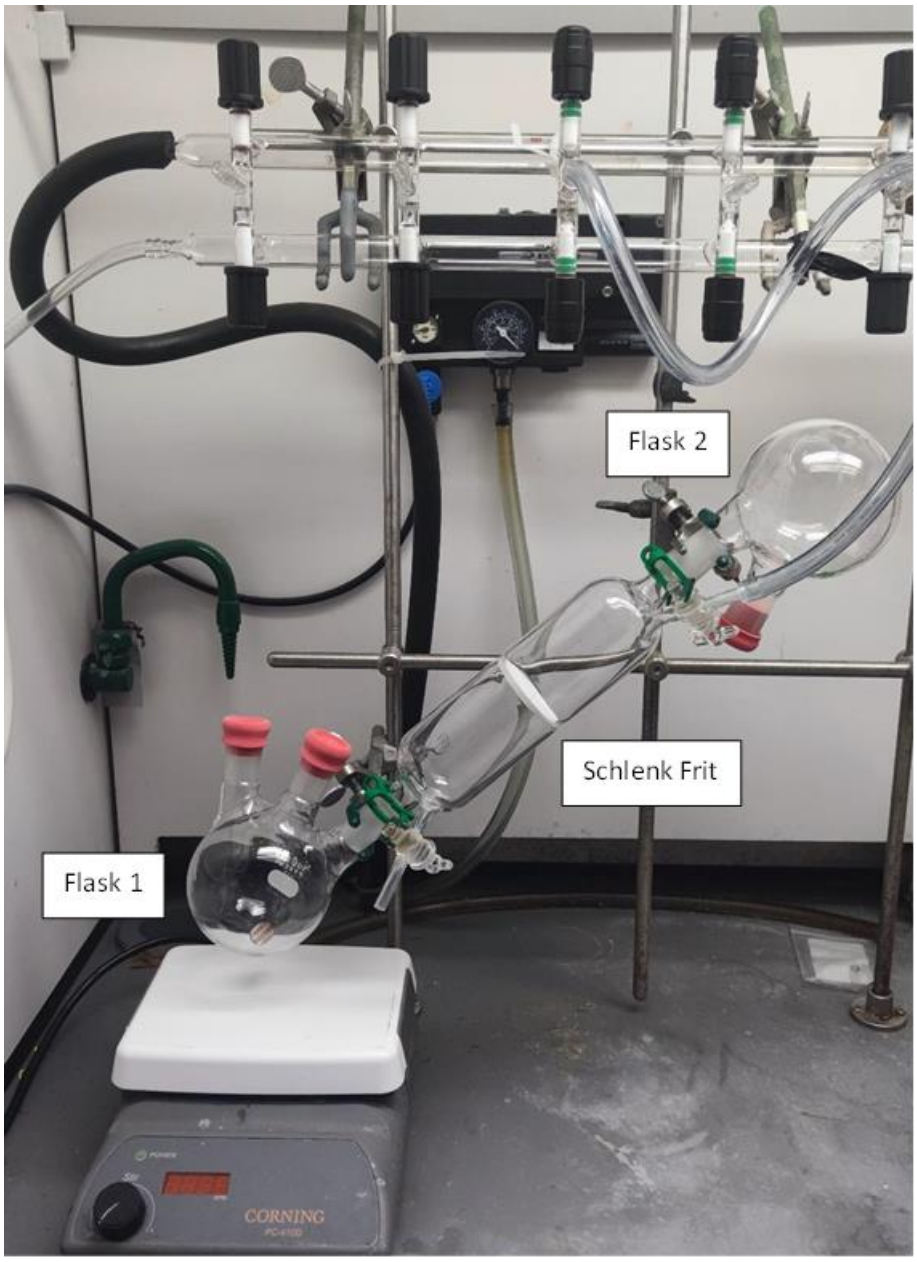
Reaction with ethyl (Z)-8-chloro-2-methyloct-2-en-4-ynoate (1x): Attempted following general procedure C, using ethyl (Z)-8-chloro-2-methyloct-2-en-4-ynoate (**1x**, 53.7 mg, 0.25 mmol, 1.0 equiv) in chloroform (5.0 mL) for various times. No product was detected via crude NMR. No unreacted **1x** was detected via crude NMR, indicating decomposition of the starting material.

Large scale procedure E for 2,6-dichloropyridinium tetrafluoroborate salt

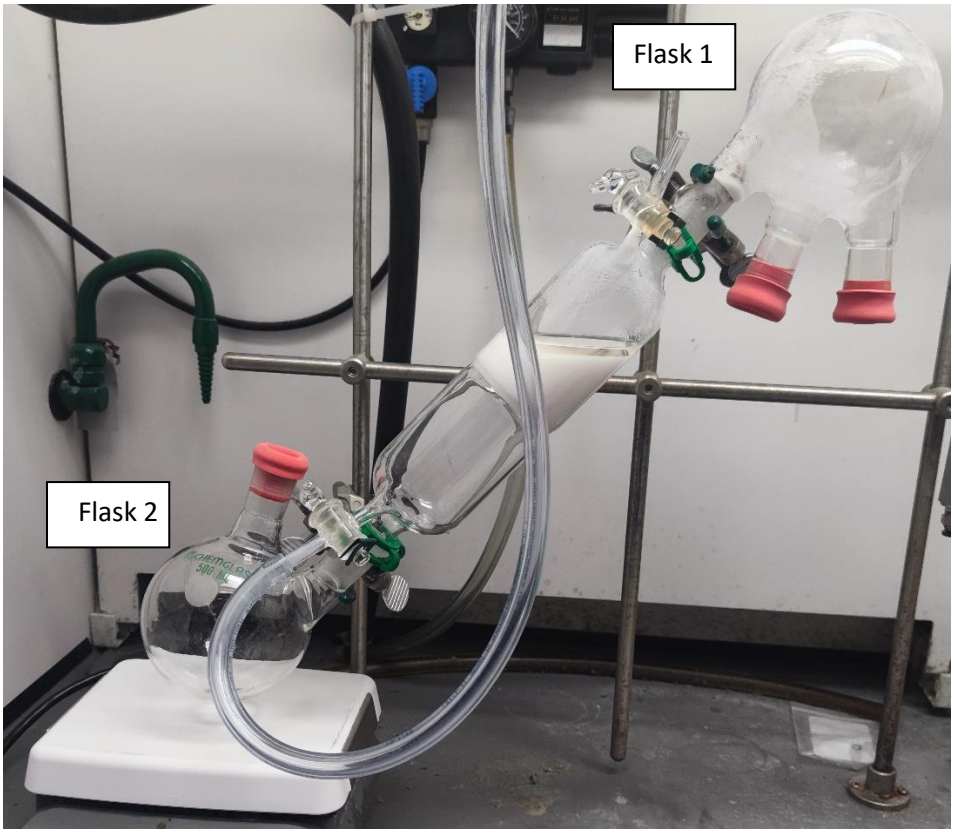


4

A 500 mL, three necked round- bottom flask fitted with a magnetic stir bar (egg shaped, 1 1/4 in × 5/8 in, Chemglass Life Sciences, part # CG200512) was oven dried and the right neck is attached to a Schlenk frit. The left and center necks were fitted with rubber stoppers. To the other side of the Schlenk frit was connected another 500 mL round-bottom flask, with the center and right joints fitted with rubber stoppers. The upper valve of the Schlenk frit was connected to Schlenk line, and the entire apparatus was purged with dry nitrogen after removing the air on vacuum. The "vacuum-then-nitrogen-purge" process was repeated 2 more times, then allowed to cool to room temperature under a gentle flow of nitrogen. Once at room temperature, the left stopper of flask 1 was removed and to the flask was added 2,6-dichloropyridine (22.20 g, 150.0 mmol, 1.0 equiv) under a gentle counterflow of nitrogen. The stopper was returned to the left neck, and the apparatus is vacuum purged and refilled with dry nitrogen for three times. To the flask, dichloromethane (90 mL) was added *via* syringe and the solution was stirred at 400 rpm to allow full dissolution. Once fully dissolved, the round-bottom flask was placed in an ice bath and allowed to cool to 0 °C.

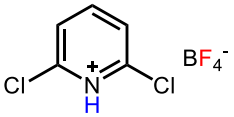


Tetrafluoroboric acid etherate complex (24.5 mL, 180 mmol, 1.2 equiv) was added dropwise *via* syringe, steadily over about 5 minutes. Once the addition is complete, the ice bath was removed, and the reaction was left to stir for 1 hour. While stirring, if the heterogeneous mixture became thick and does not stir well, the stir rate could be increased as needed to ensure proper stirring. After one hour, the entire Schlenk frit apparatus was flipped, allowing the suspension to be filtered from the excess dichloromethane and tetrafluoroboric acid mixture. A light vacuum could be pulled on the apparatus to aid in the filtration.



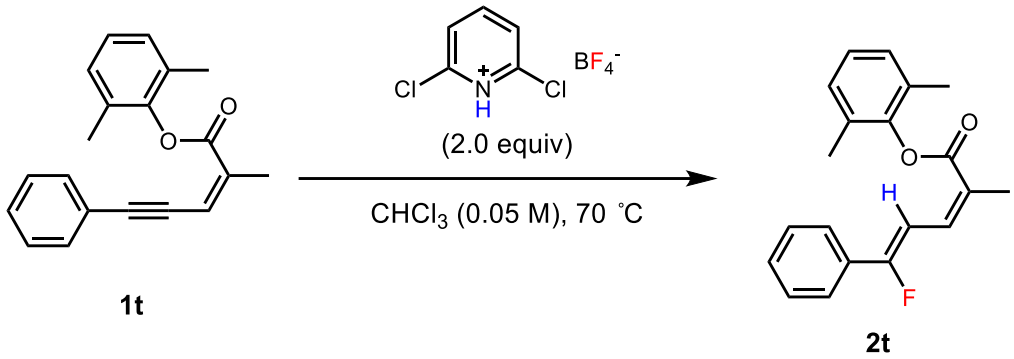
Once flipped, the filtrate was removed from flask 2 via syringe. Then, the apparatus was flipped to its original position. The product would likely stay caked onto the frit. Dichloromethane (45 mL) was then added to flask 1 and the apparatus was flipped, allowing added dichloromethane to fully rinse the solid. A light vacuum can be pulled to enable proper filtration and removal of solvent from the wet solid. Upon completion of filtration, the filtrate was removed through a rubber stopper on flask 2 via syringe and this washing process was repeated 4 more times. Upon completion, the apparatus was vacuumed for 48 hours before transferred into a sealed container within a glove box and stored under an inert atmosphere. The pyridinium tetrafluoroborate was afforded as a white crystalline powder (31.147 g, 88% yield).

Characterization data for 2,6-dichloropyridinium tetrafluoroborate salt



2,6-Dichloropyridinium tetrafluoroborate: Prepared following general procedure F to afford the hydrofluorinating reagent as a white solid (31.15 g, 88%).
^{1}H NMR: (500 MHz, $(CD_3)_2CO$) δ (ppm) 7.91 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 7.9 Hz, 2H).
^{13}C NMR: (125 MHz, $(CD_3)_2CO$) δ (ppm) 150.9, 143.0, 124.2.
^{19}F NMR: (470 MHz, $(CD_3)_2CO$) δ (ppm) –150.0 (s, 4F).
^{11}B NMR: (160 MHz, $(CD_3)_2CO$) δ (ppm) –0.65 (s, 1B).

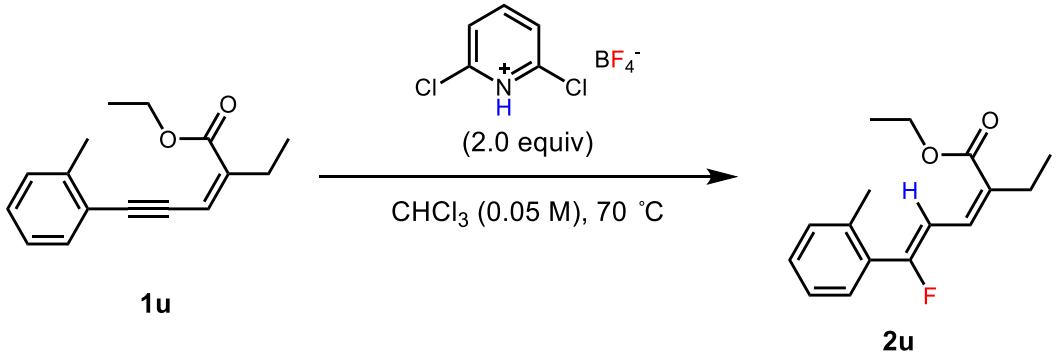
Scale-up synthesis and derivatizations of products



1t 2t

Large scale synthesis of 2,6-dimethylphenyl (2*Z*,4*Z*)-5-fluoro-2-methyl-5-phenylpenta-2,4-dienoate (2t):

A pressure vessel (150 mL, Synthware) equipped with a magnetic stir bar was flame dried and cooled in the vacuum chamber of an argon-filled glovebox. In the glovebox, to a suspension of 2,6-dichloropyridinium tetrafluoroborate (1.179 g, 5.0 mmol, 2.0 equiv) in dry chloroform (50.0 mL) was added 2,6-dimethylphenyl (*Z*)-2-methyl-5-phenylpent-2-en-4-ynoate (**1t**, 726.0 mg, 2.5 mmol, 1.0 equiv). The pressure vessel was capped with a Teflon bushing equipped with an O-ring and removed from the glovebox, placed in an oil bath preheated to 70 °C, and was stirred for eight hours. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel with ethyl acetate, then concentrated *in vacuo*. The crude mixture was purified via column chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2t** as a colorless glassy solid (271.8 mg, 35%).

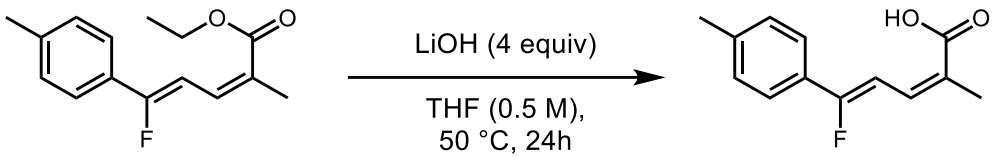


1u 2u

Large scale synthesis of Ethyl (2Z,4Z)-2-ethyl-5-fluoro-5-(o-tolyl)penta-2,4-dienoate (2u):

A pressure vessel (150 mL, Synthware) equipped with a magnetic stir bar was flame dried and cooled in the vacuum chamber of an argon-filled glovebox. In the glovebox, to a suspension of 2,6-dichloropyridinium tetrafluoroborate (589.5 mg, 2.5 mmol, 2.0 equiv) in dry chloroform (25.0 mL) was added ethyl (Z)-2-ethyl-5-(o-tolyl)pent-2-en-4-ynoate (**1u**, 303.0 mg, 1.25 mmol, 1.0 equiv). The pressure vessel was capped with a Teflon bushing equipped with an O-ring and removed from the glovebox, placed in an oil bath preheated to 70 °C, and was stirred for 45 minutes. Upon completion, the reaction mixture was cooled to room temperature, filtered through silica gel with ethyl acetate, then concentrated *in vacuo*. The crude mixture was purified via column

chromatography on silica gel (39:1 hexanes: diethyl ether) to afford the product **2t** as a yellow oil. (161.3 mg, 49%).



2e **3**

Synthesis of (2*Z*,4*Z*)-5-fluoro-2-methyl-5-(*p*-tolyl)penta-2,4-dienoic acid (3): To a 10 mL round bottom flask was added **2e** (49.7 mg, 0.2 mmol, 1 equiv), lithium hydroxide (19.2 mg, 0.8 mmol, 4 equiv), and THF (0.4 mL). The reaction was stirred at 50 °C for 24 hours, then quenched with the dropwise addition of 1 M HCl until the solution turned acidic. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated in *vacuo.* The crude product was purified with flash column chromatography (1% acetic acid in 9:1 hexanes: ethyl acetate) to provide compound **3** as a white solid (28.1 mg, 64 %).

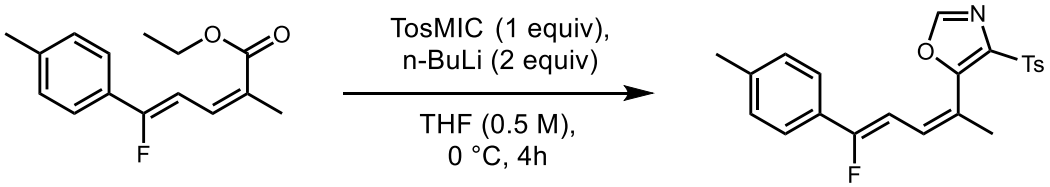
Temp. Decomp.: 120 °C

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 8.2 Hz), 7.37 (dd, J = 11.9 Hz, $J_{H–F}$ = 34.5 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 11.8 Hz, 1H), 2.39 (s, 3H), 2.09 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 172.9 (s), 161.2 (d, $J_{C–F}$ = 264.0 Hz), 140.5 (s), 134.4 (d, $J_{C–F}$ = 8.2 Hz), 129.5 (s), 128.9 (d, $J_{C–F}$ = 27.3 Hz), 125.1 (d, $J_{C–F}$ = 7.6 Hz), 124.7 (d, $J_{C–F}$ = 5.2 Hz), 102.7 (d, $J_{C–F}$ = 8.5 Hz), 21.6 (s), 21.1 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –112.3 (d, $J_{H–F}$ = 34.5 Hz).

HRMS: (ESI) calcd. for $C_{13}H_{12}FO_2$ $[M\text{-}H]^-$: 219.0816, found: 219.0822



2e **4**

Synthesis of 5-((2*Z*,4*Z*)-5-fluoro-5-(*p*-tolyl)penta-2,4-dien-2-yl)-4-tosyloxazole (4): To a flame dried 10 mL round bottom flask flushed with N_2 was added toluenesulfonylmethyl isocyanide (TosMIC, 39.0 mg, 0.2 mmol, 1 equiv) and THF (0.2 mL), and cooled to 0 °C. *n*-Butyllithium solution (2.5 M, 0.16 mL, 0.4 mmol, 2 equiv) was added dropwise, and the mixture was stirred at 0 °C for 1 hour. Then a solution of **2e** (49.7 mg, 0.2 mmol, 1 equiv) in THF (0.2 mL) was added dropwise and the mixture was stirred for 3 hours at 0 °C, then quenched with water. The aqueous

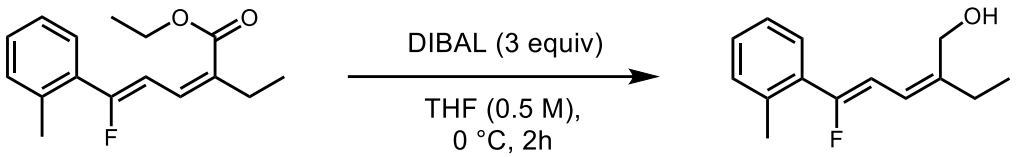
layer was extracted with ethyl acetate (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated in *vacuo.* The crude product was purified with flash column chromatography (4:1 hexanes: ethyl acetate) to provide compound **4** as a yellow oil (45.2 mg, 57 %).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.89 (d, *J* = 8.3 Hz, 2H), 7.87 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.93 (dd, *J* = 11.6, 1.4 Hz, 1H), 5.72 (dd, *J* = 11.6 Hz, $J_{H–F}$ = 33.5 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.24 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 158.8 (d, $J_{C–F}$ = 260.0 Hz), 152.7 (s), 150.3 (s), 145.0 (s), 139.9 (s), 137.3 (s), 137.0 (s), 129.9 (s), 129.4 (d, $J_{C–F}$ = 2.1 Hz), 128.8 (d, $J_{C–F}$ = 6.3 Hz), 128.8 (d, $J_{C–F}$ = 27.2 Hz), 128.4 (s), 124.6 (d, $J_{C–F}$ = 7.4), 121.6 (d, $J_{C–F}$ = 4.6 Hz), 102.1 (d, $J_{C–F}$ = 12.5 Hz), 23.3 (s), 21.7 (s), 21.5 (s).

^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –114.0 (d, $J_{H–F}$ = 33.5 Hz).

HRMS: (ESI) calcd. for $C_{22}H_{21}FNO_3S$ $[M+H]^+$: 398.1221, found: 398.1202



2u **5**

Synthesis of (2Z,4Z)-2-Ethyl-5-fluoro-5-(o-tolyl)penta-2,4-dien-1-ol (5): To a flame dried 10 mL round bottom flask flushed with N_2 was added **2u** (62.1 mg, 0.25 mmol, 1 equiv) and THF (0.5 mL), and cooled to 0 °C. Diisobutylaluminum hydride solution (1.2 M in toluene, 0.63 mL, 0.75 mmol, 3 equiv) was added dropwise, and the solution was stirred at 0 °C for 2 hours. To quench the reaction, Glauber's Salt was added portion-wise until the solution no longer bubbled, then the salt was filtered out, and the solution was dried over anhydrous sodium sulfate and concentrated in *vacuo.* The crude product was purified with flash column chromatography (4:1 hexanes: ethyl acetate) to provide compound **5** as a colorless oil (23.8 mg, 43.2%).

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) 7.39 (d, J = 7.6 Hz, 1H), 7.32-7.25 (m, 1H), 7.24-7.16 (m, 1H), 6.39 (d, J = 6.39 Hz, 1H), 6.07 (dd, *J* = 11.4 Hz, $J_{H–F}$ = 34.1 Hz, 1H), 4.27 (s, 2H), 2.42 (d, J = 3.4 Hz, 3H), 2.29 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.5 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ (ppm) 158.4 (d, $J_{C–F}$ = 259.2 Hz), 144.2 (d, $J_{C–F}$ = 4.4 Hz), 136.9 (s), 133.0 (d, $J_{C–F}$ = 25.0 Hz), 131.3 (s), 129.6 (s), 128.7 (d, $J_{C–F}$ = 5.6 Hz), 126.1 (s), 118.0 (d, $J_{C–F}$ = 5.3 Hz), 106.4 (d, $J_{C–F}$ = 13.1 Hz), 61.0 (s), 28.8 (s), 21.0 (d, $J_{C–F}$ = 4.0 Hz), 12.9 (s).

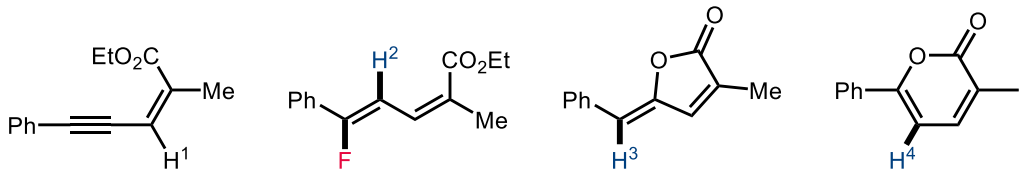
^{19}F NMR: (470 MHz, $CDCl_3$) δ (ppm) –103.2 (d, $J_{H–F}$ = 34.4 Hz).

HRMS: (ESI) calcd. for $C_{14}H_{16}FO$ $[M–H]^+$: 219.1180, found: 219.1184.

Side Product Identification

A crude NMR spectrum was obtained for the following reaction conducted, and components counted toward a total of 78% of the mass balance could be characterized. The characteristic 1H NMR signal of fluorinated diene product, starting enyne, and side products were identified and

labeled on the NMR spectrum. The spectrum of cyclized product **2d-C$_5$** was consistent with literature data.[4] The spectra of cyclized product **2d-C$_6$** was consistent with literature data.[5]



1d 14%

2d 47%

2d-C$_5$ 15%

2d-C$_6$ 2%

Notes and references

1. C. G. Bates, P. Saejueng, and D. Venkataraman, Copper-Catalyzed Synthesis of 1,3-Enynes, *Org. Lett.* 2004, **6**, 1441-1444.
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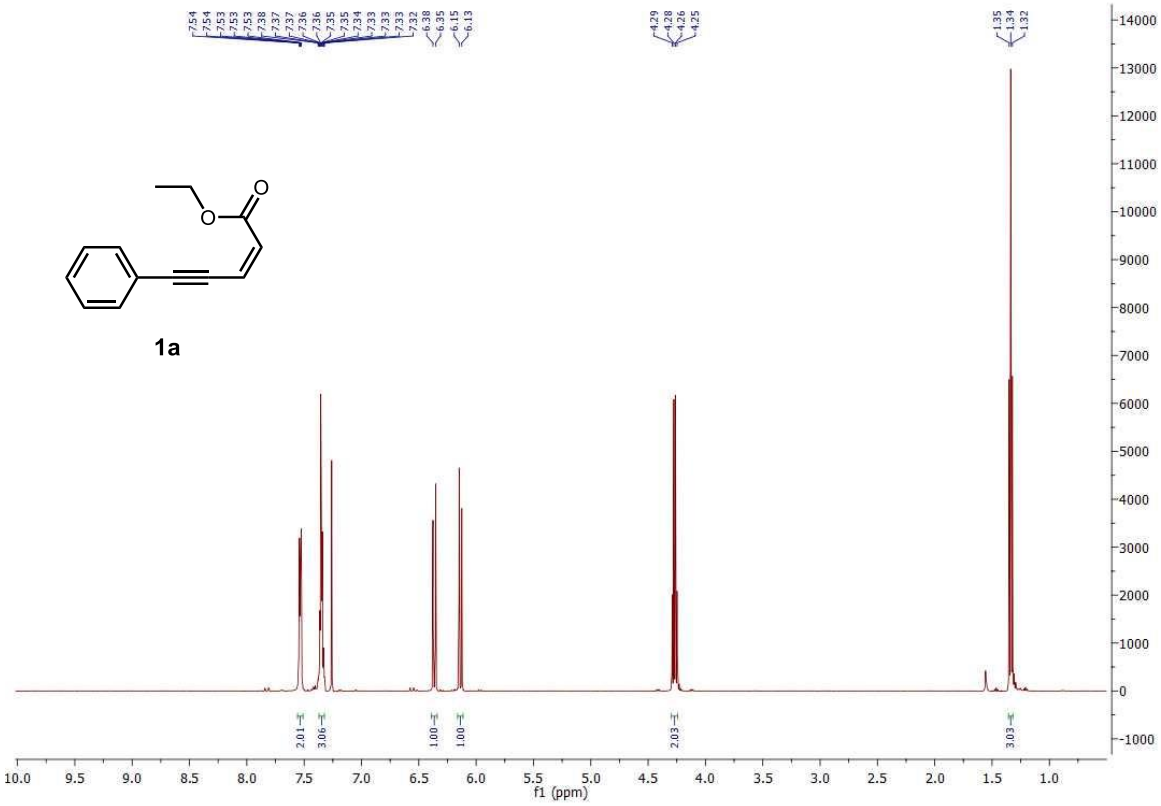
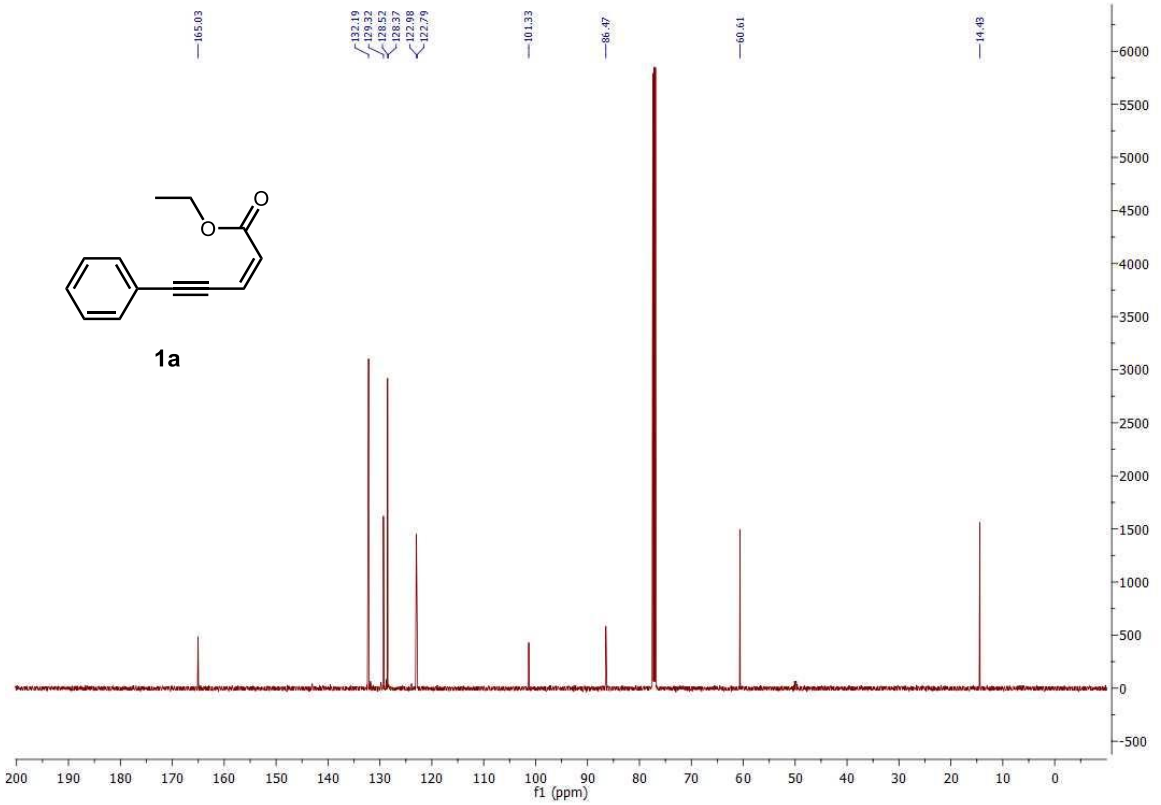
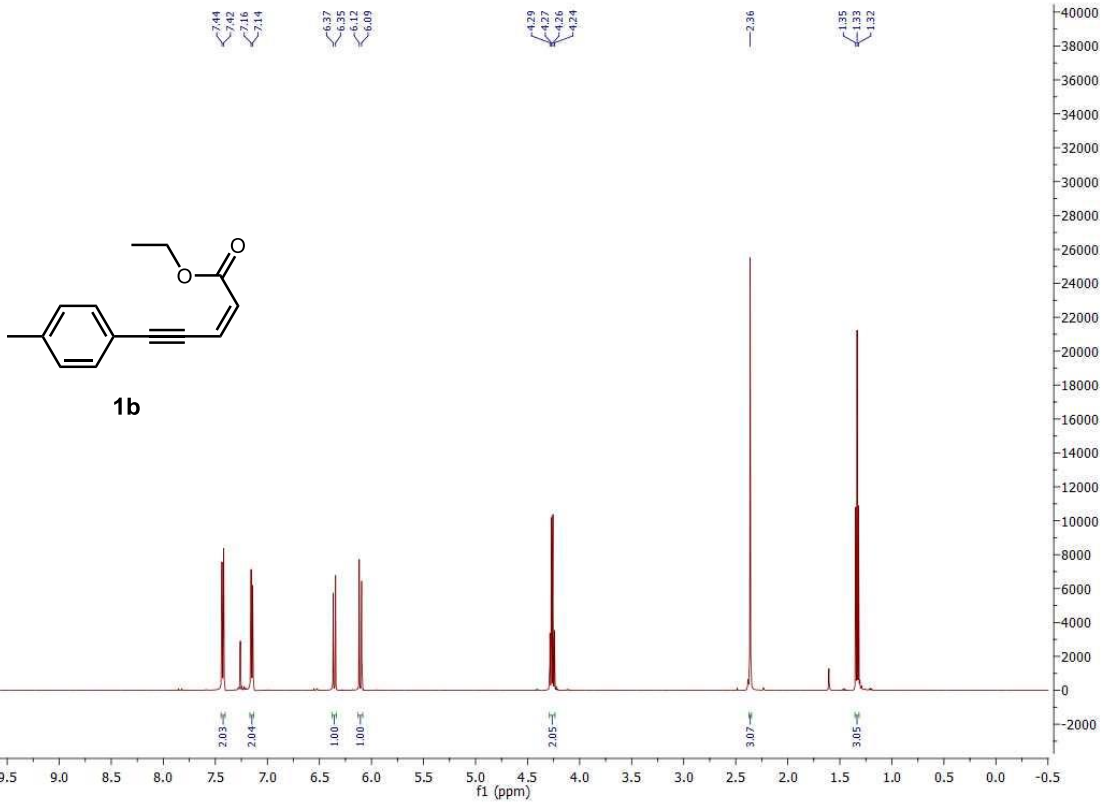
Copies of NMR spectra for starting materials



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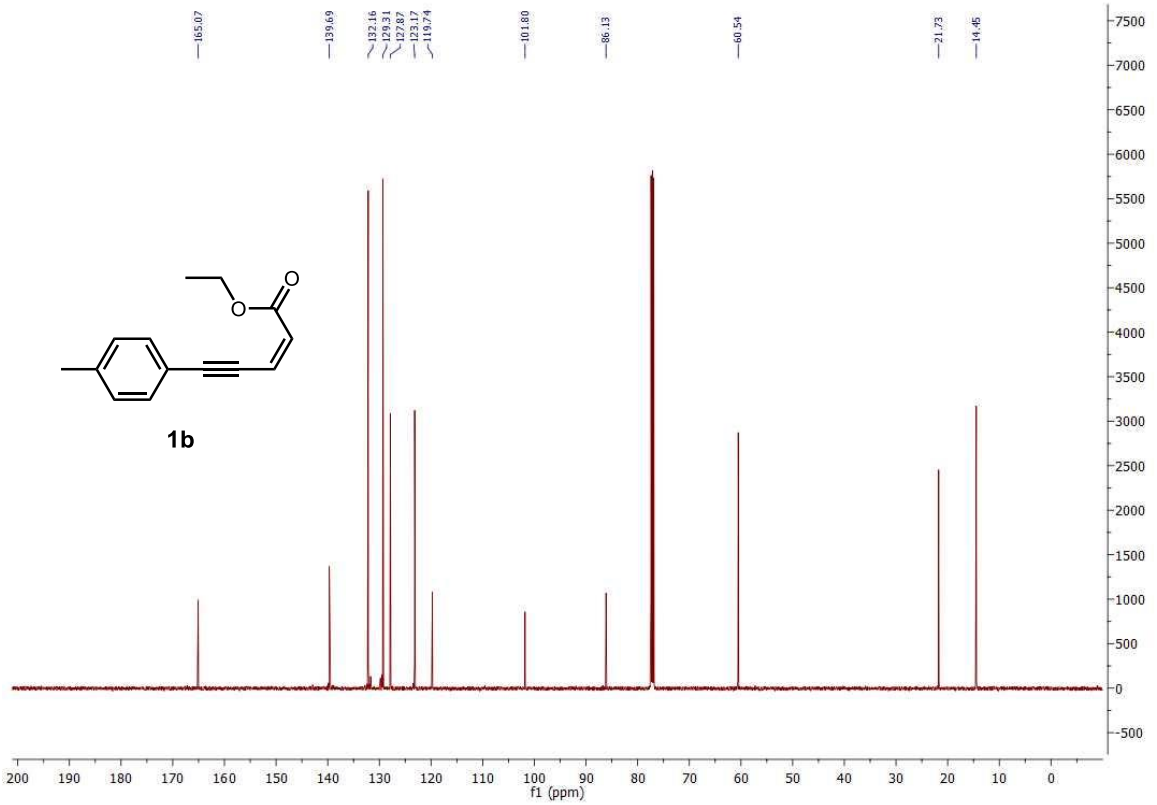
3.05
f1 (ppm)

1b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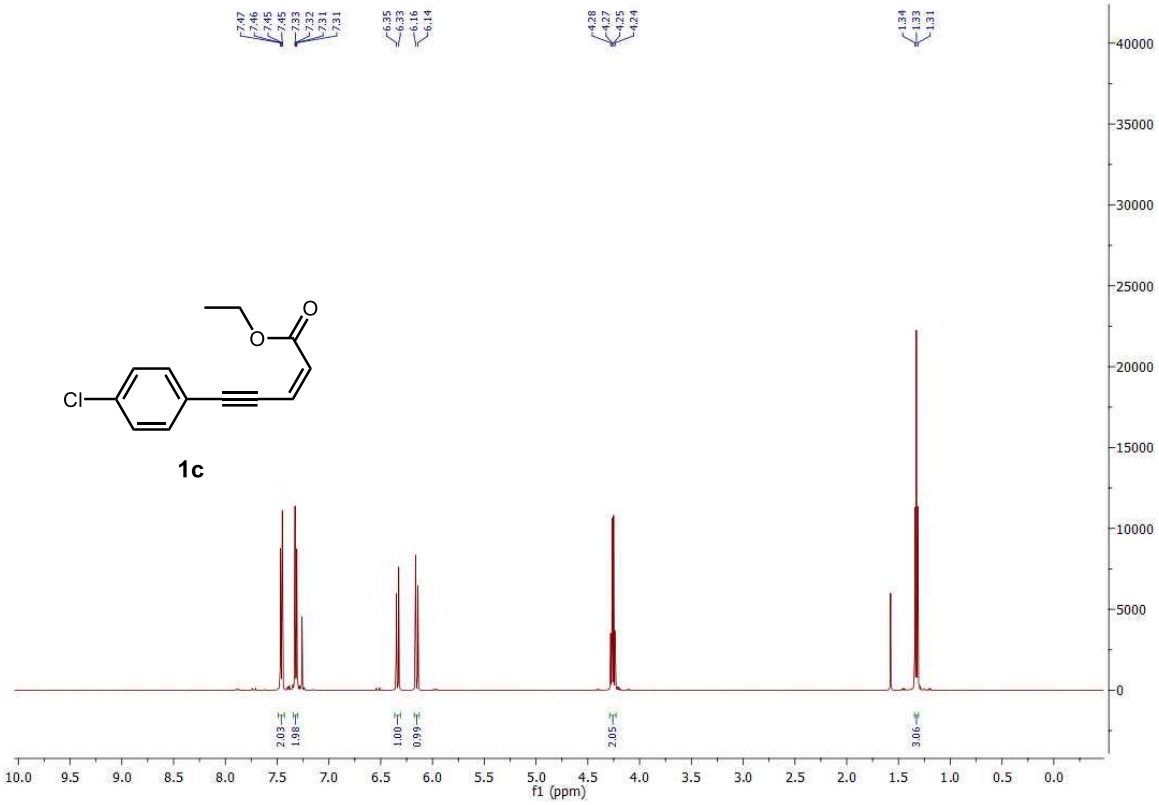
1b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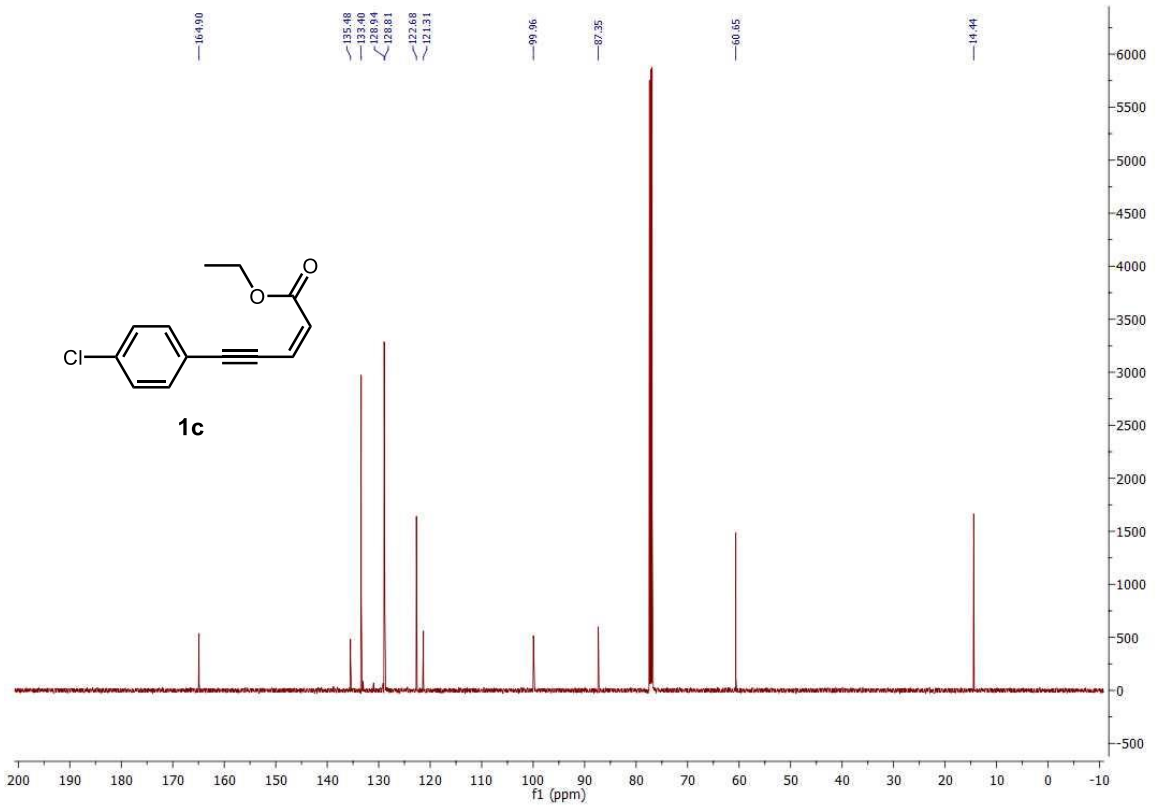
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1c
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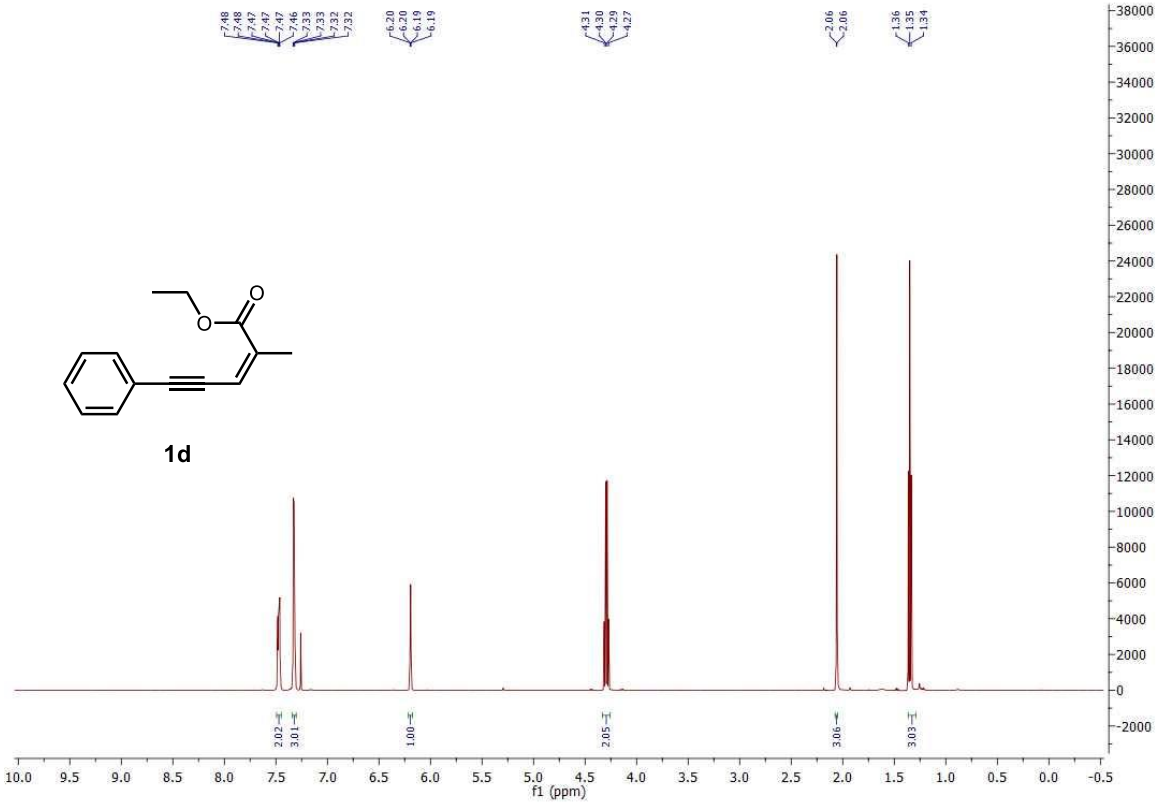
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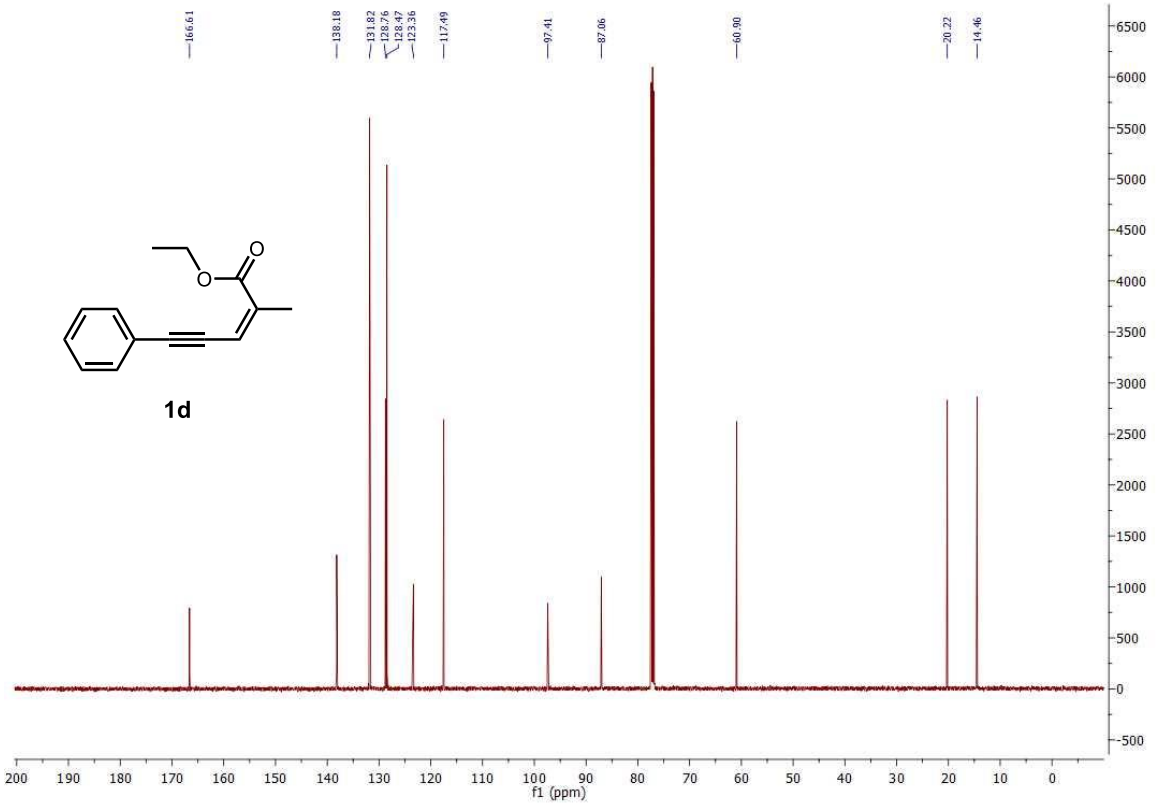
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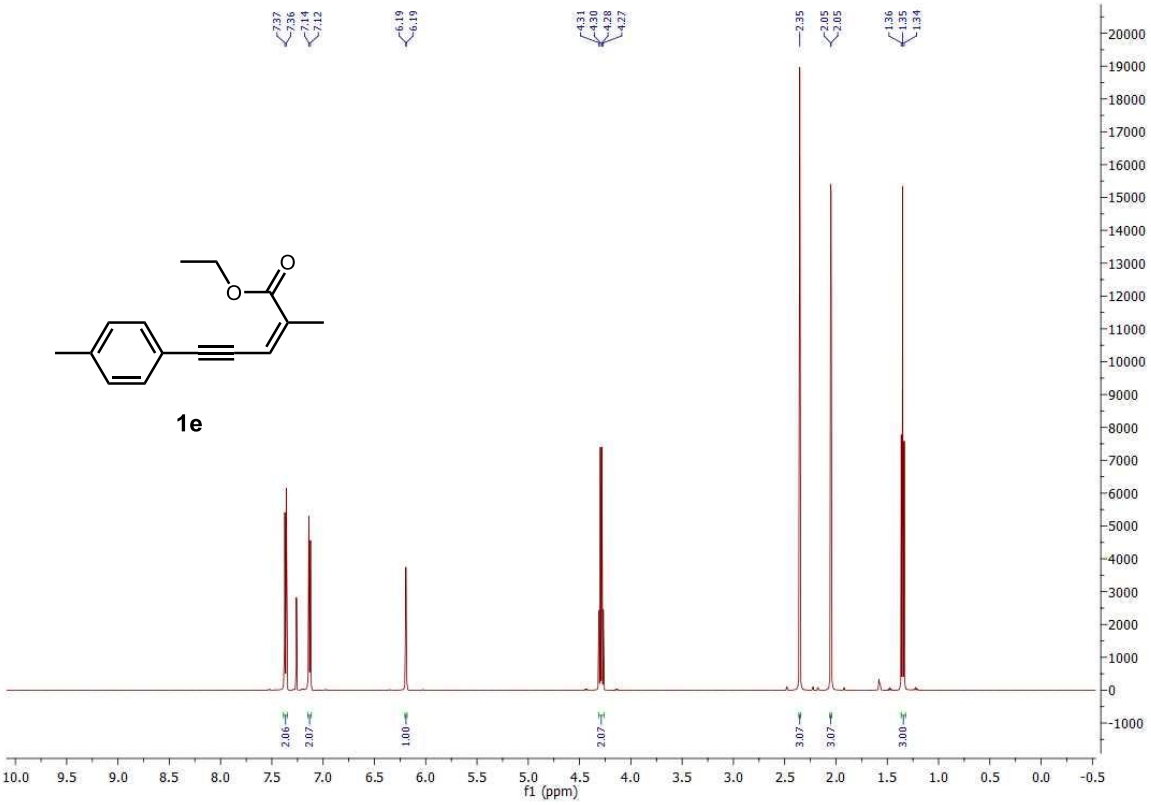
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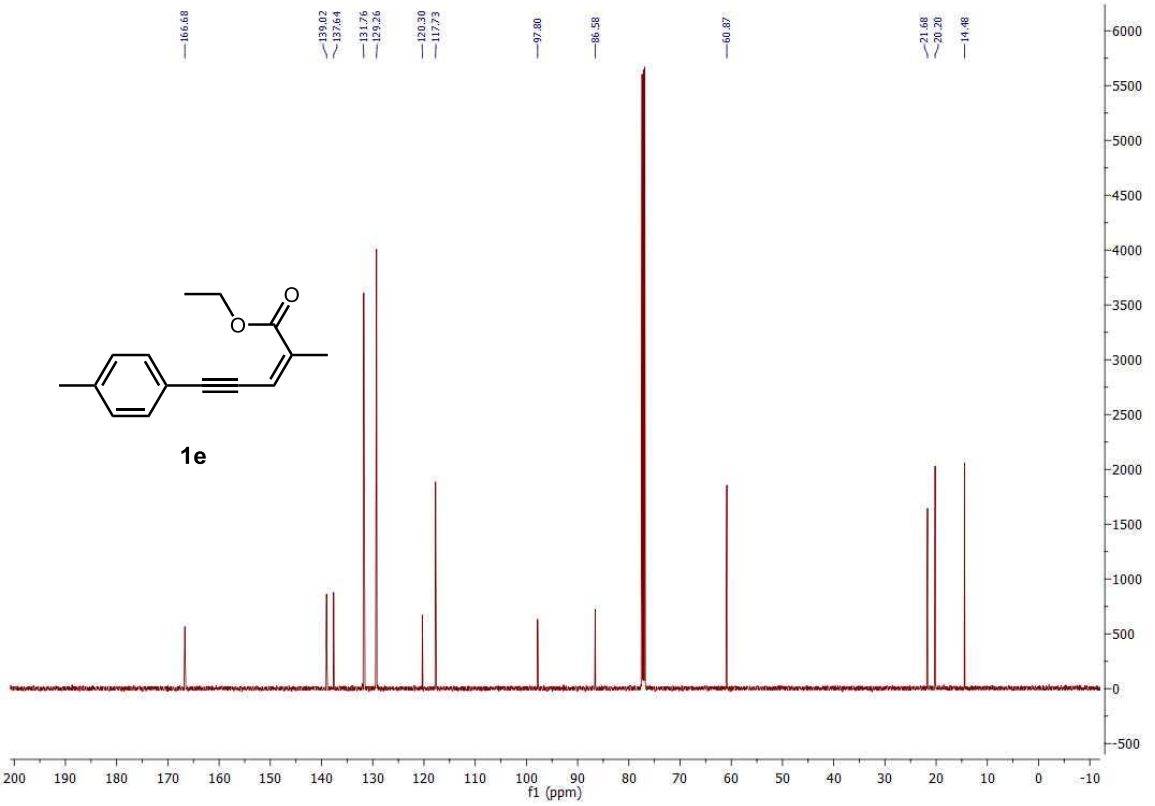
f1 (ppm)

1e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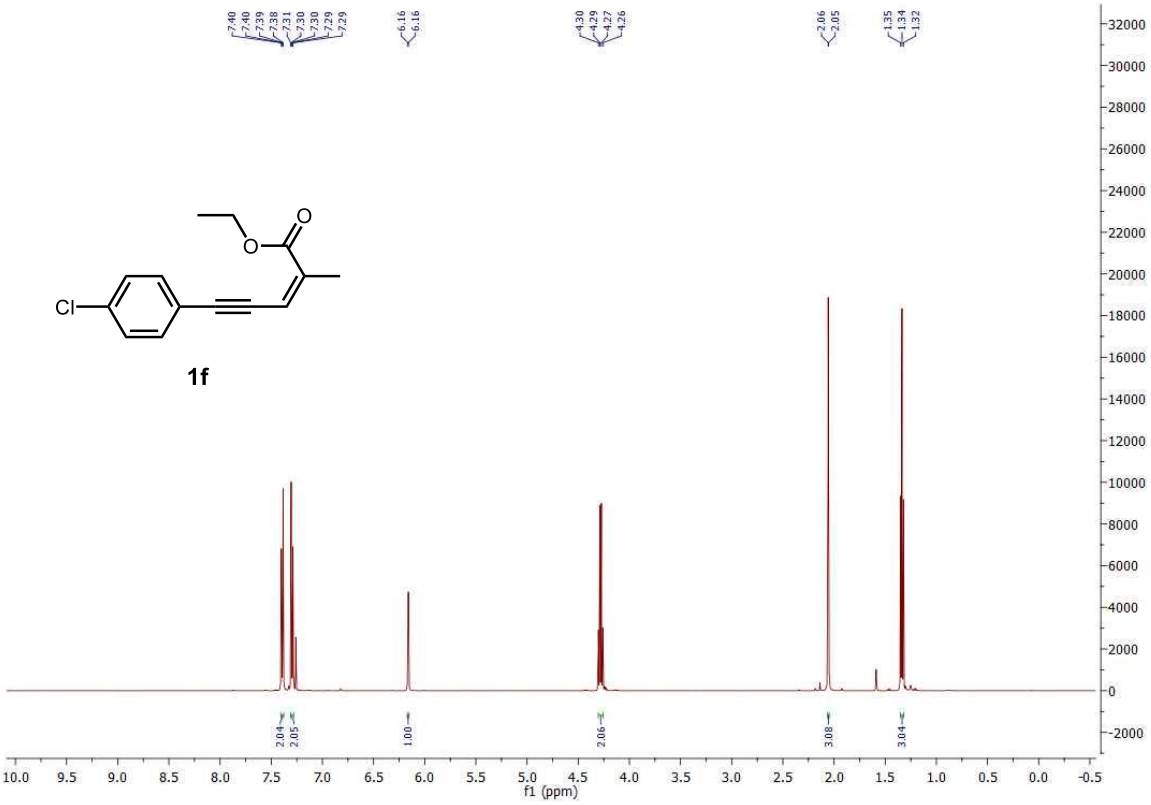
1e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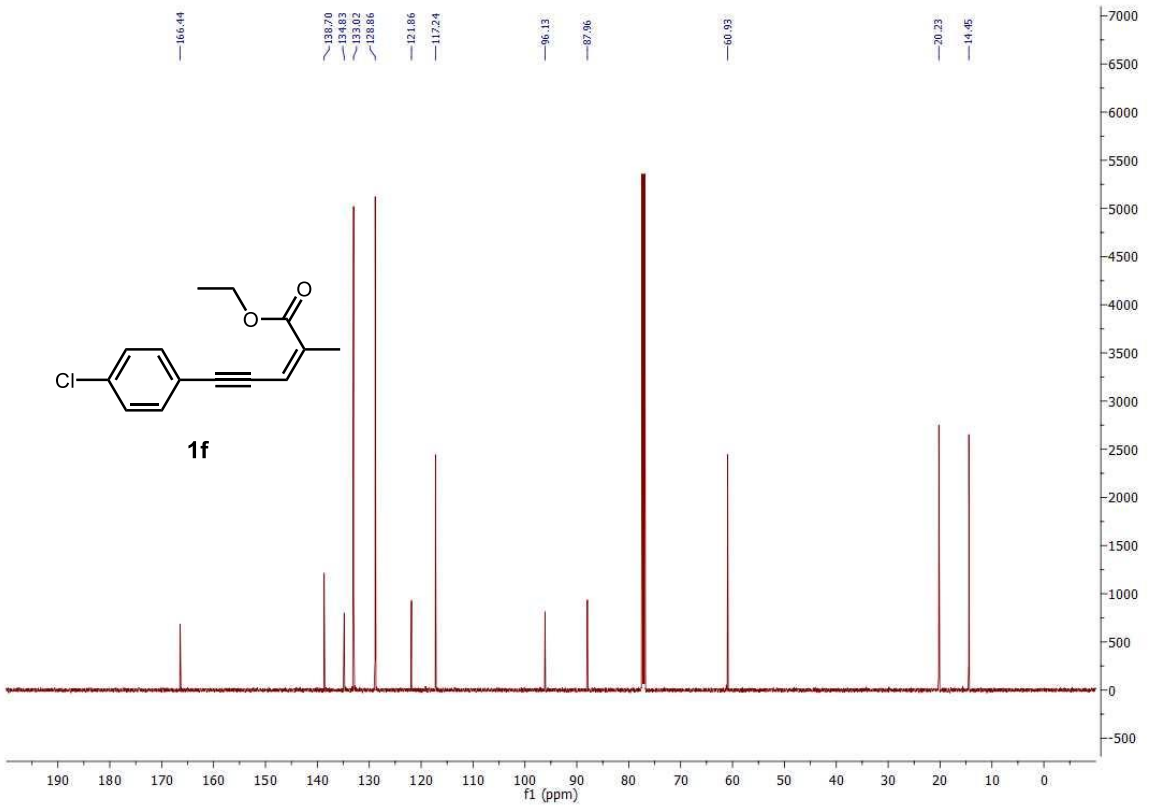
f1 (ppm)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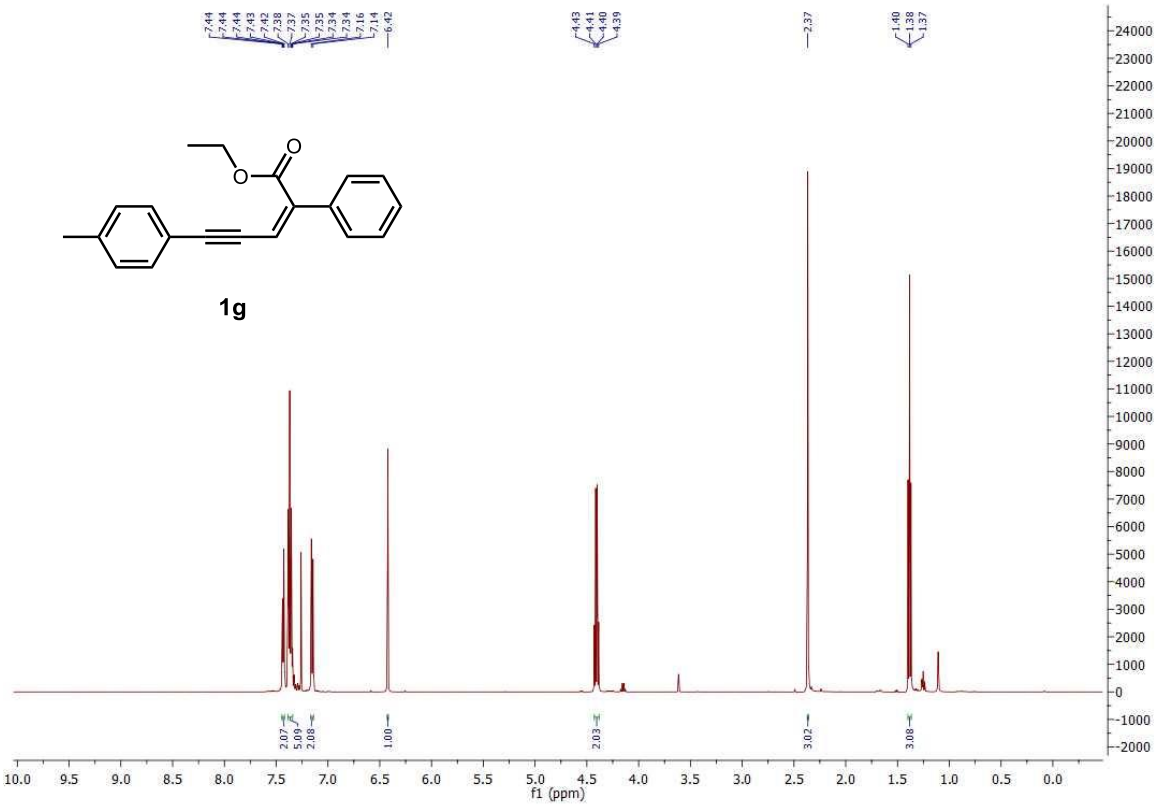
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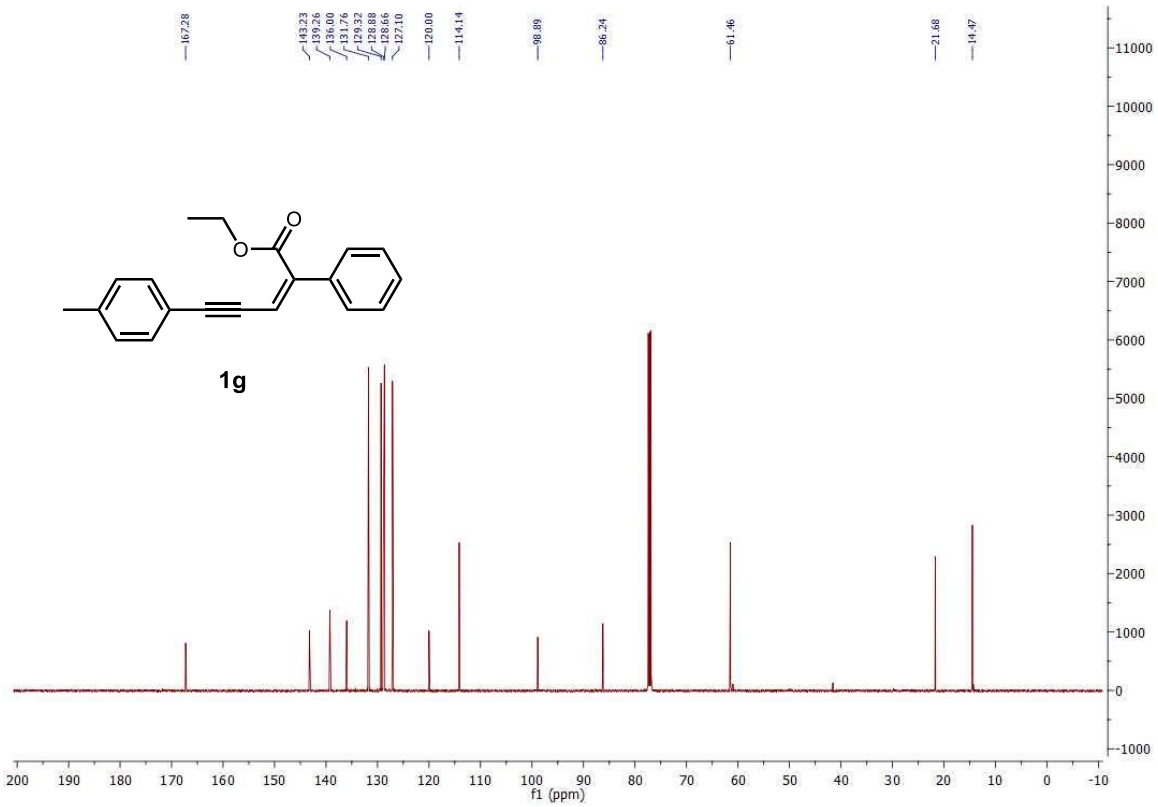
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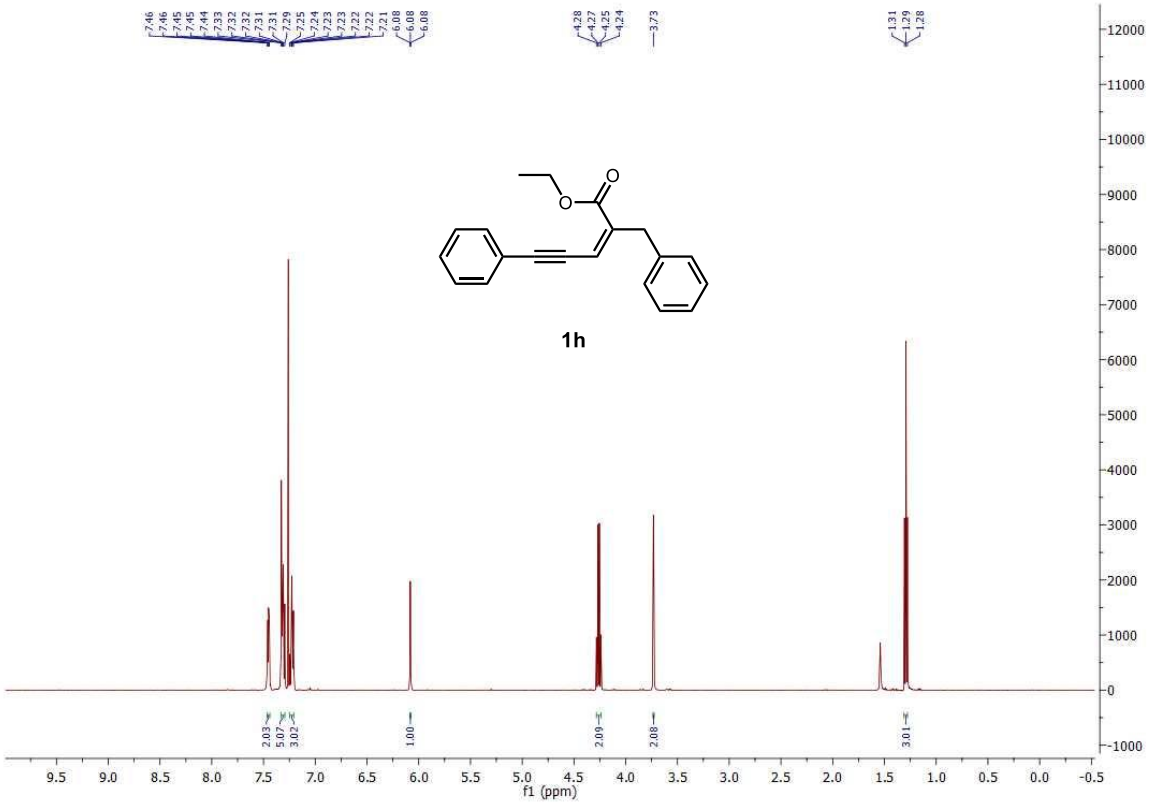
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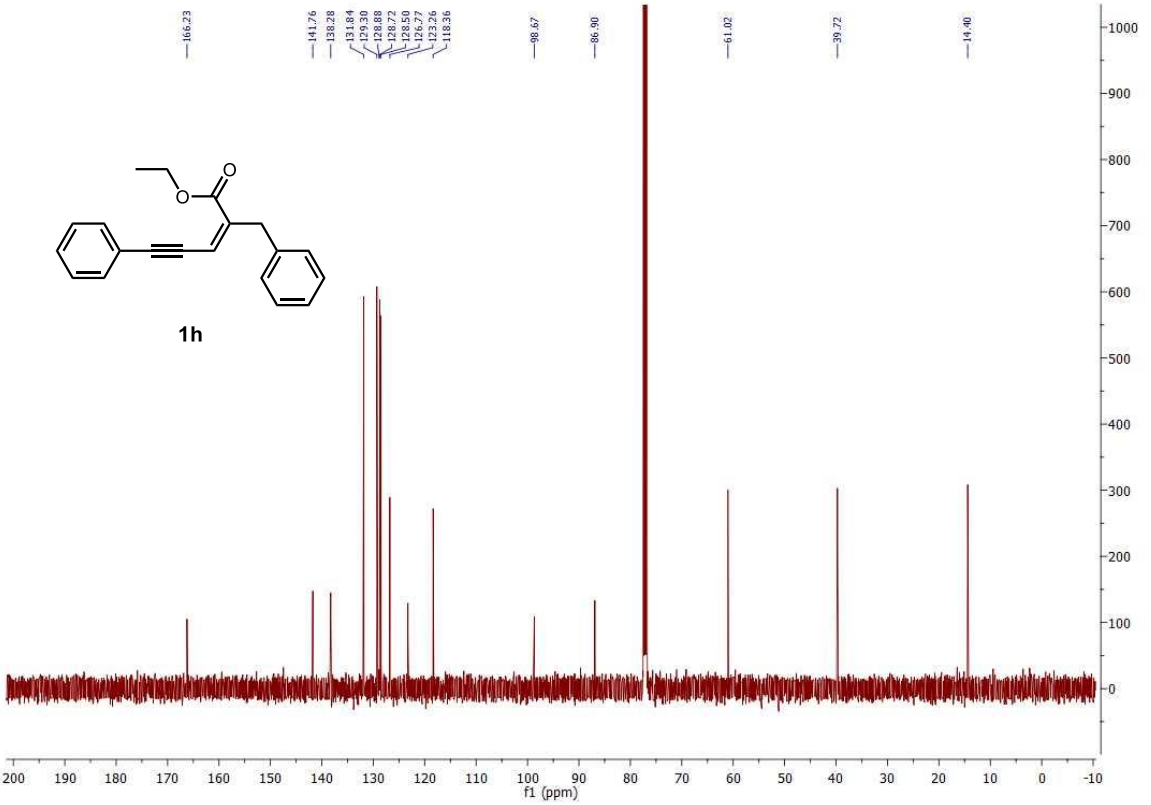
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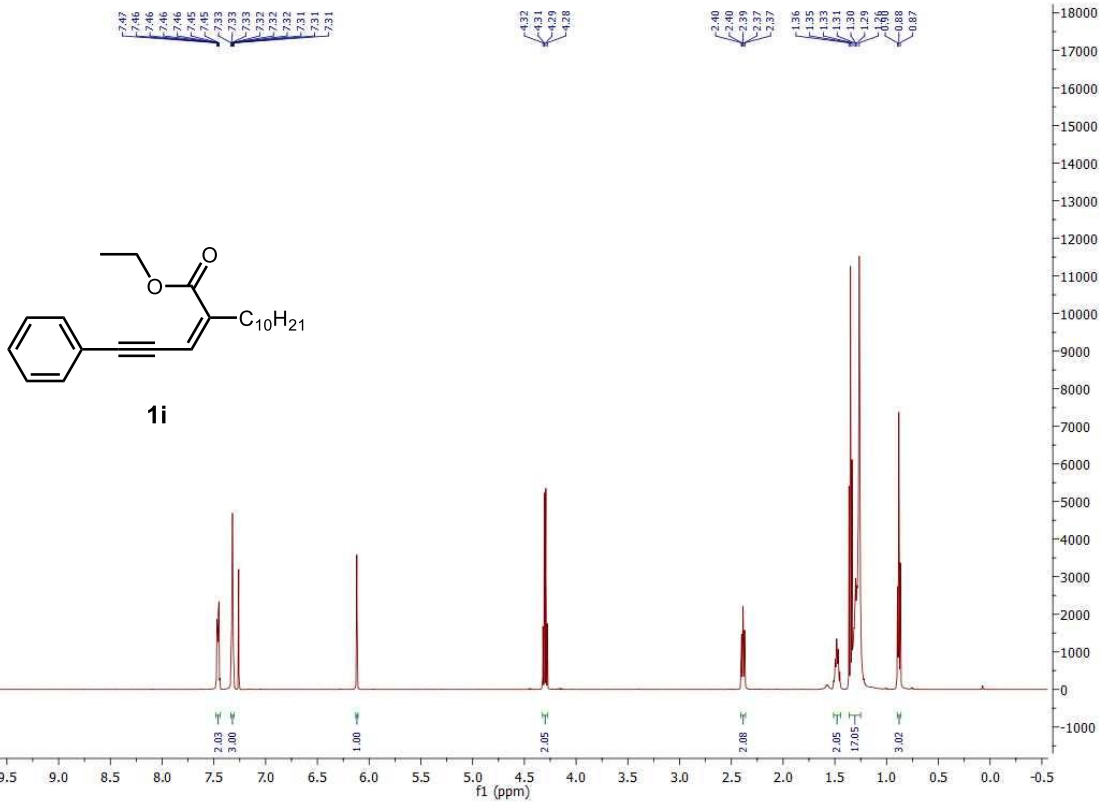
1h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1.35
1.33
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1.30
1.29
0.90
0.88
0.87
O
O
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2.05
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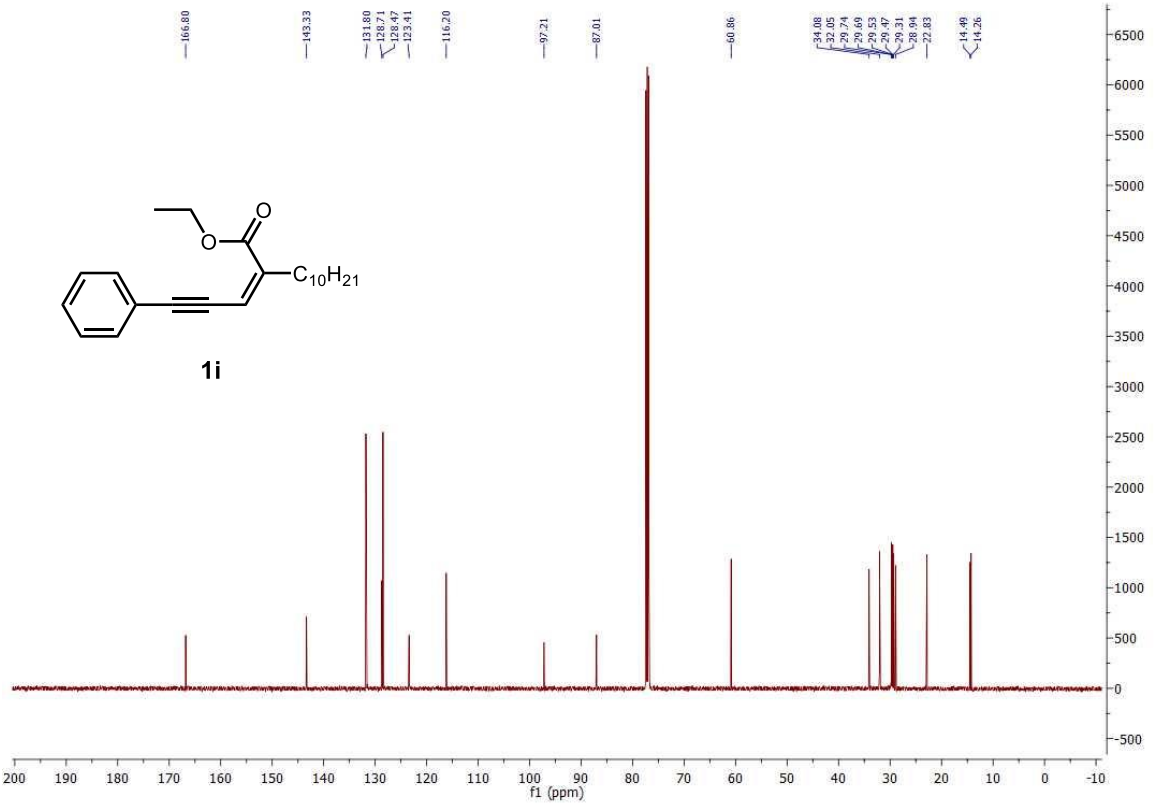
2.05
17.05
3.02
f1 (ppm)

1i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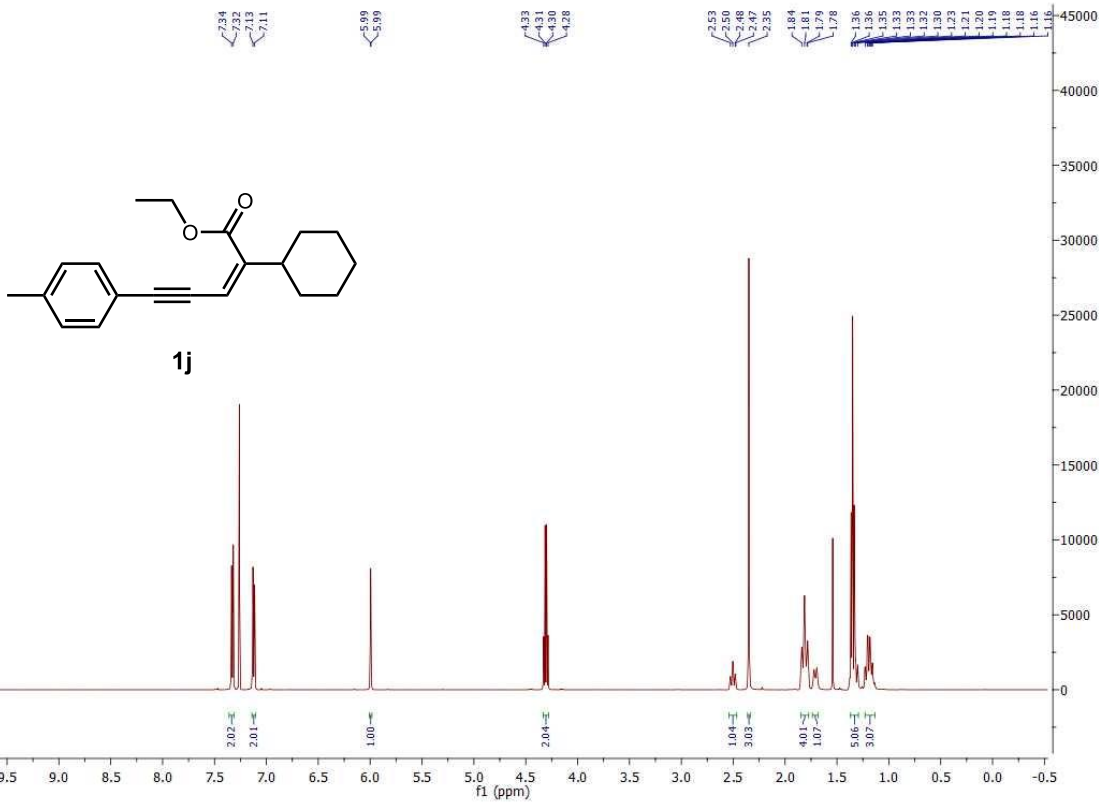
O
$C_{10}H_{21}$
f1 (ppm)

1i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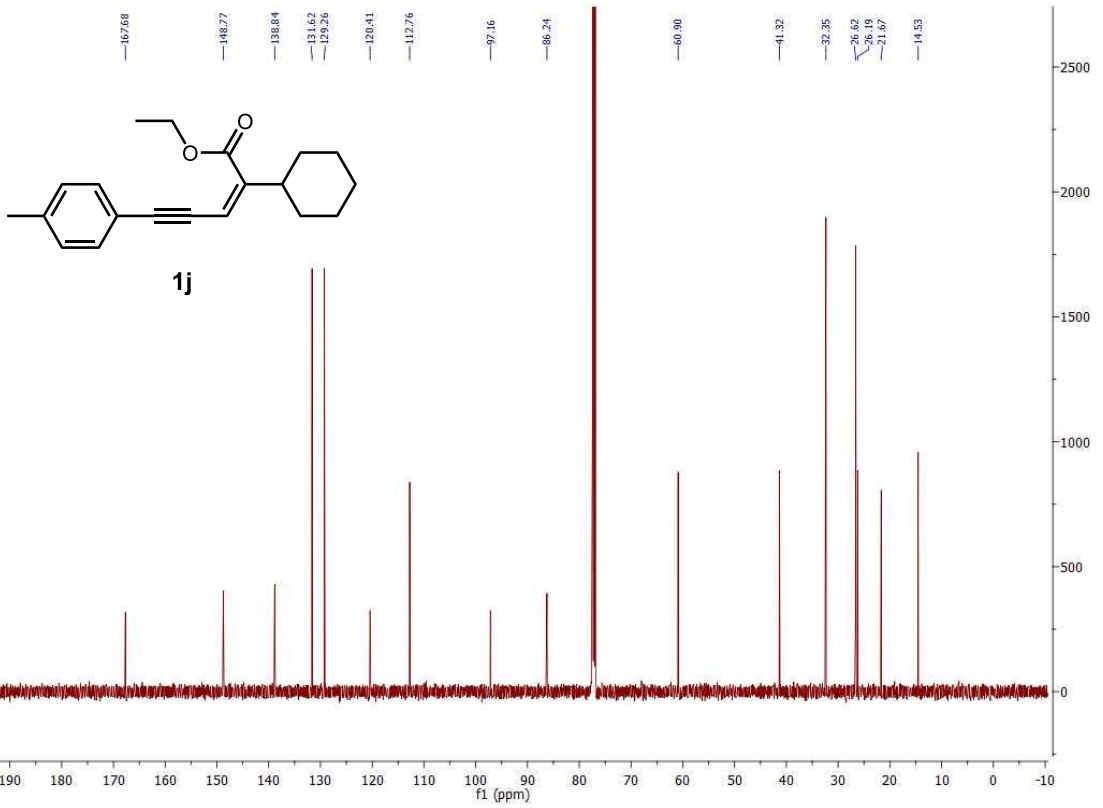
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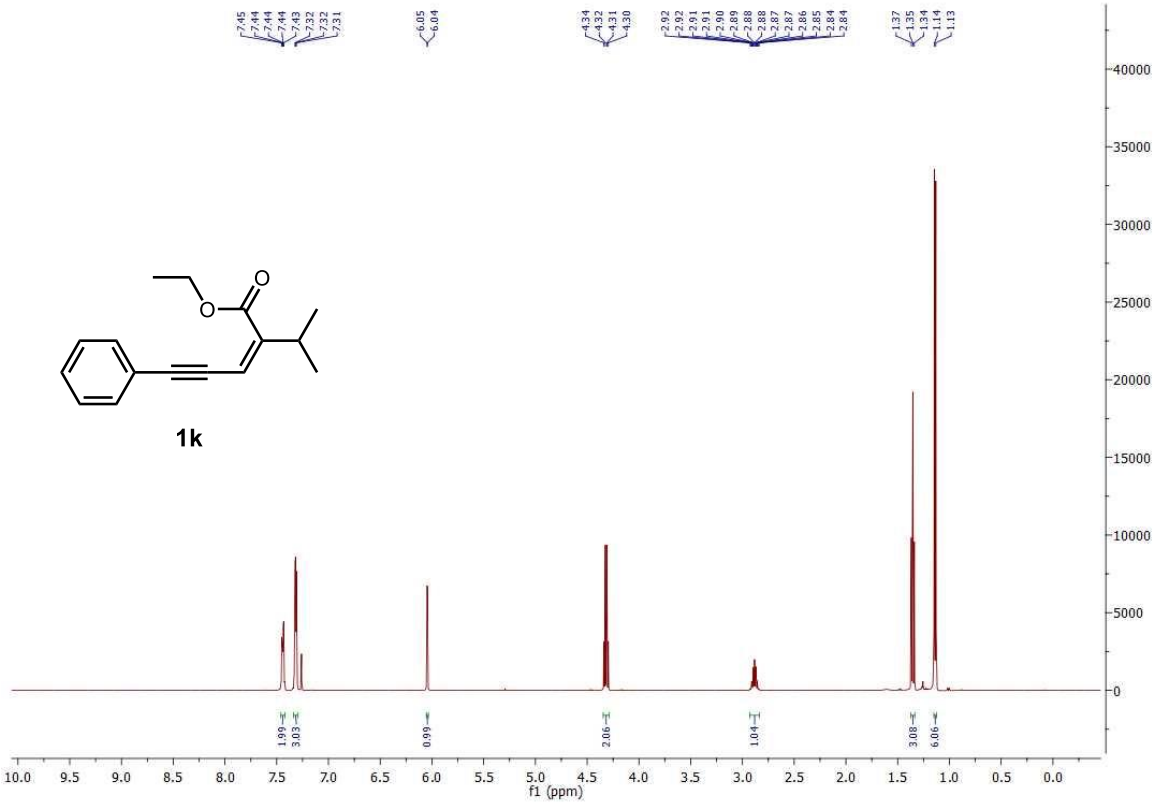
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2.91
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2.90
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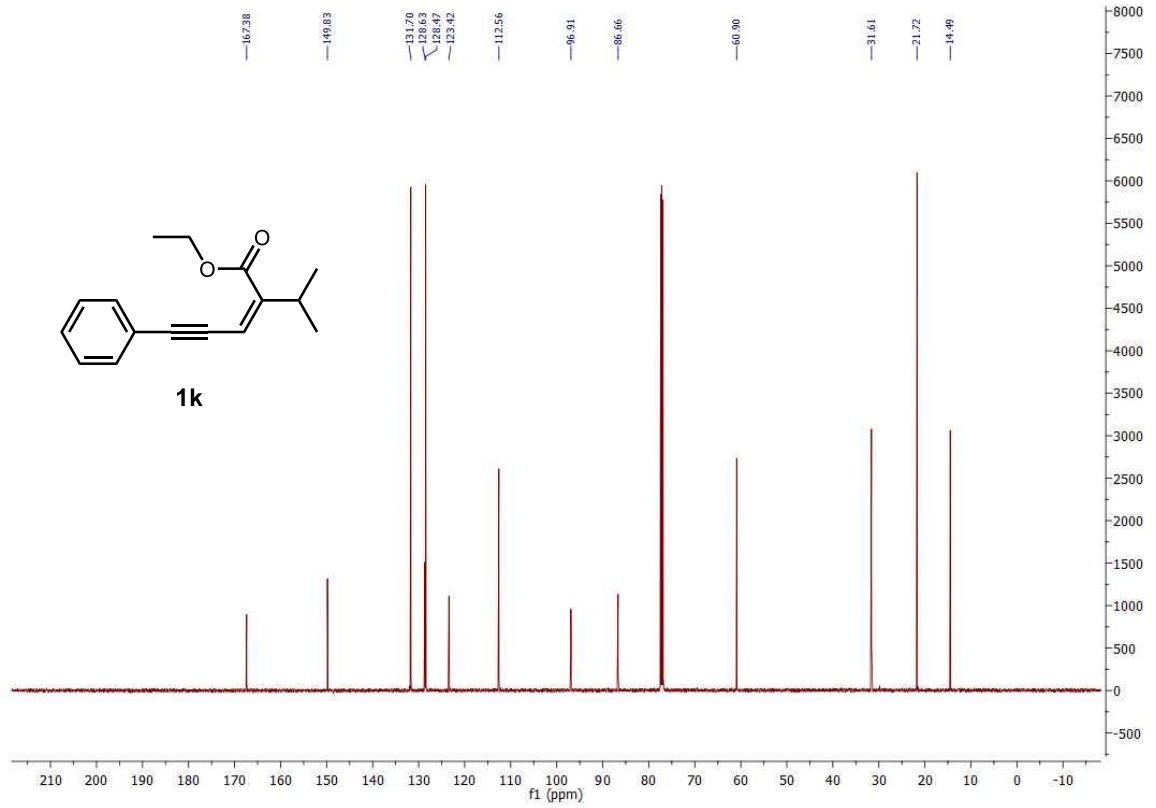
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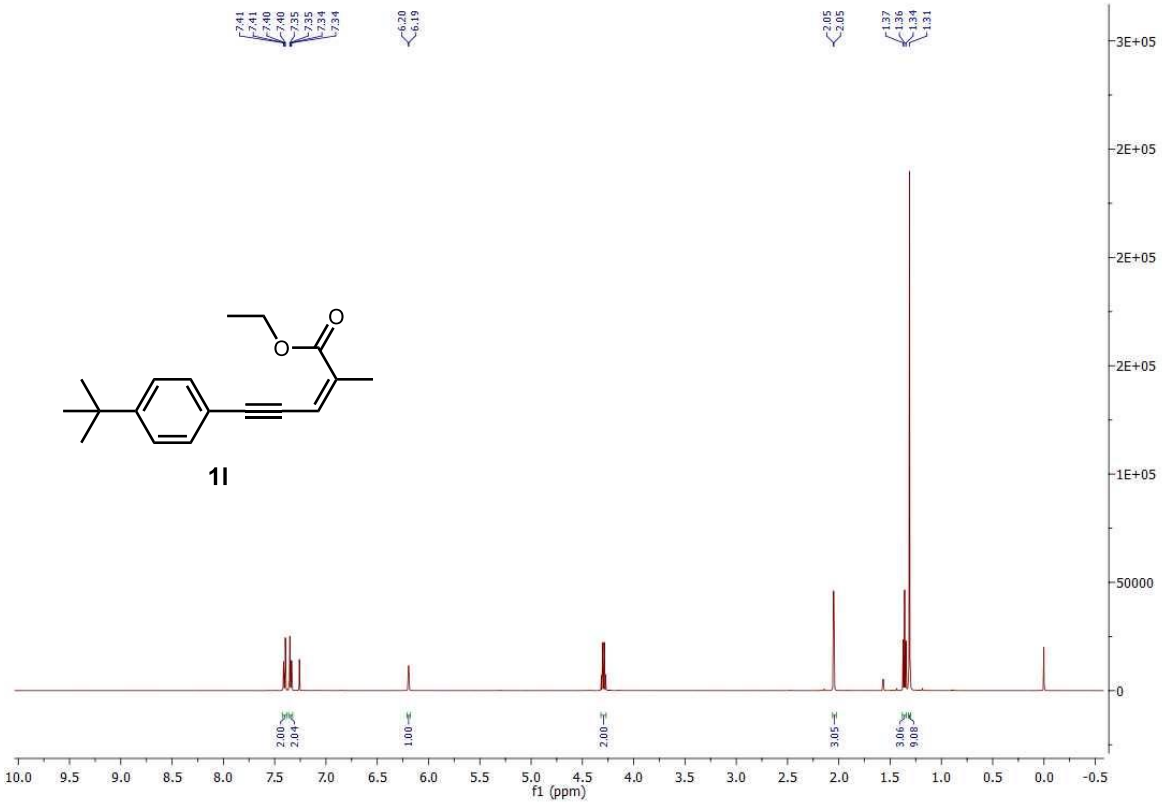
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3.06
9.08
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O
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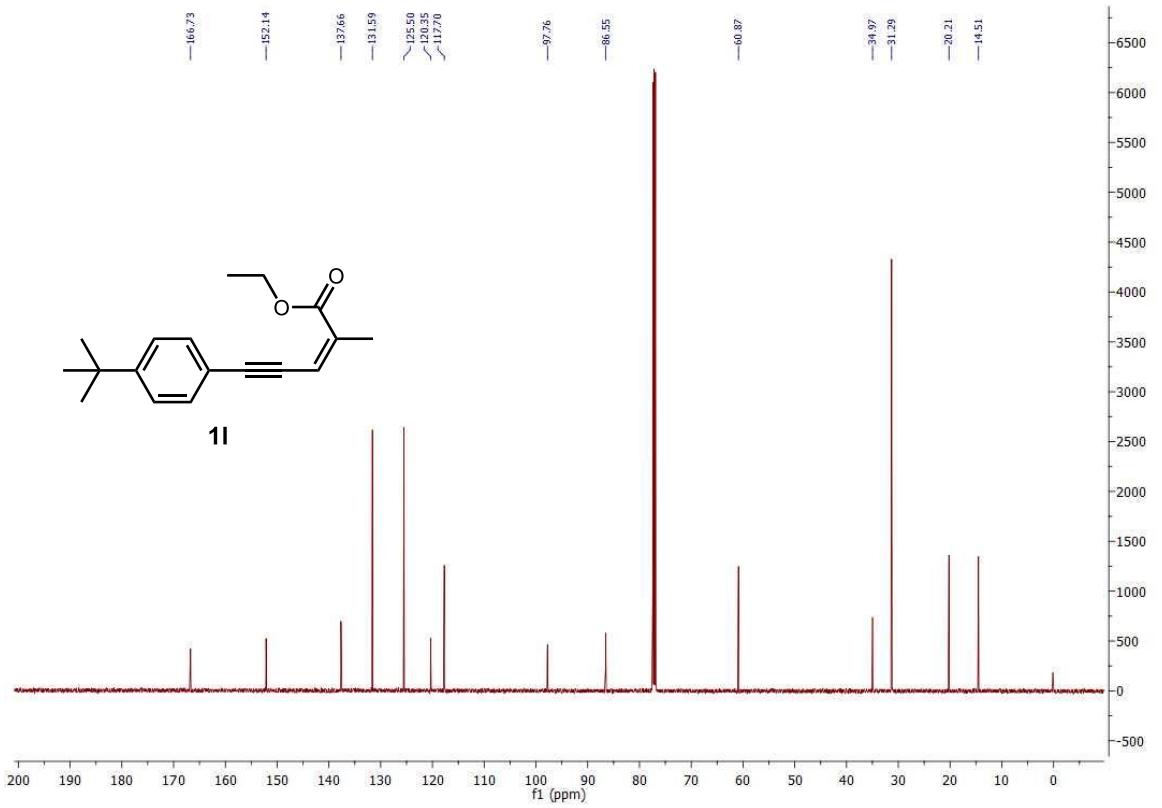
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3000
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O
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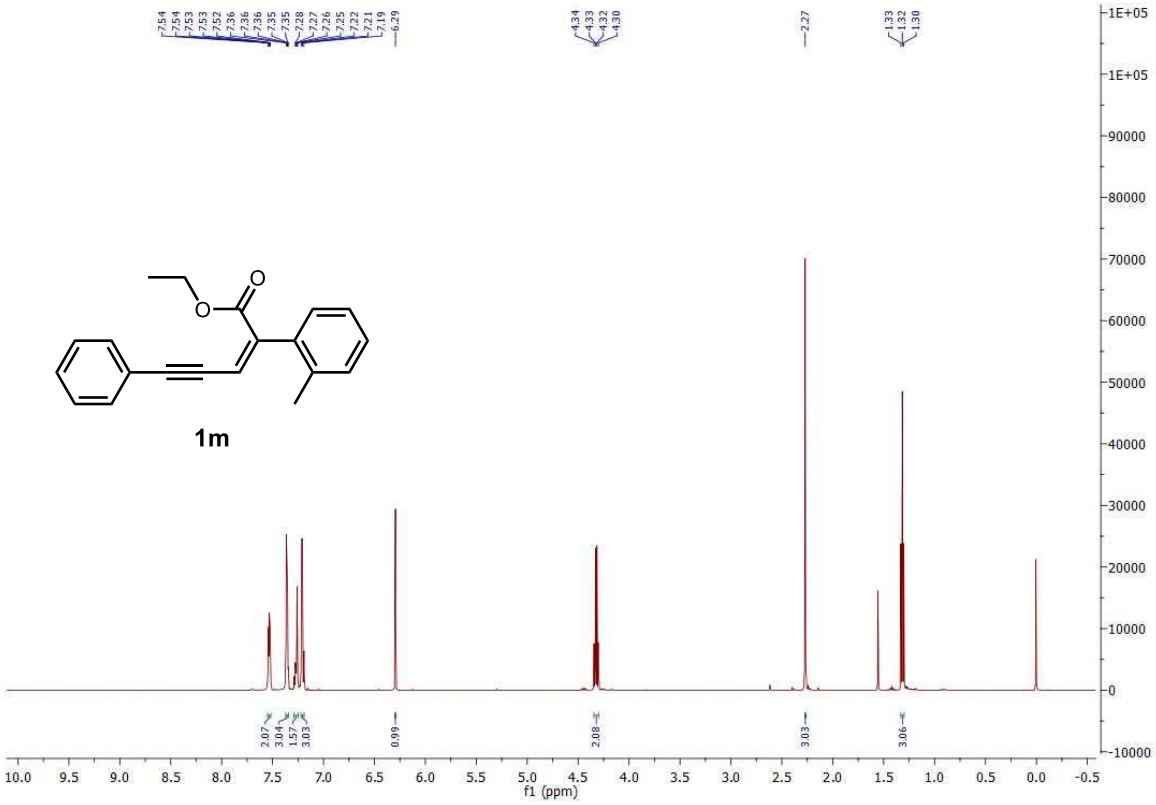
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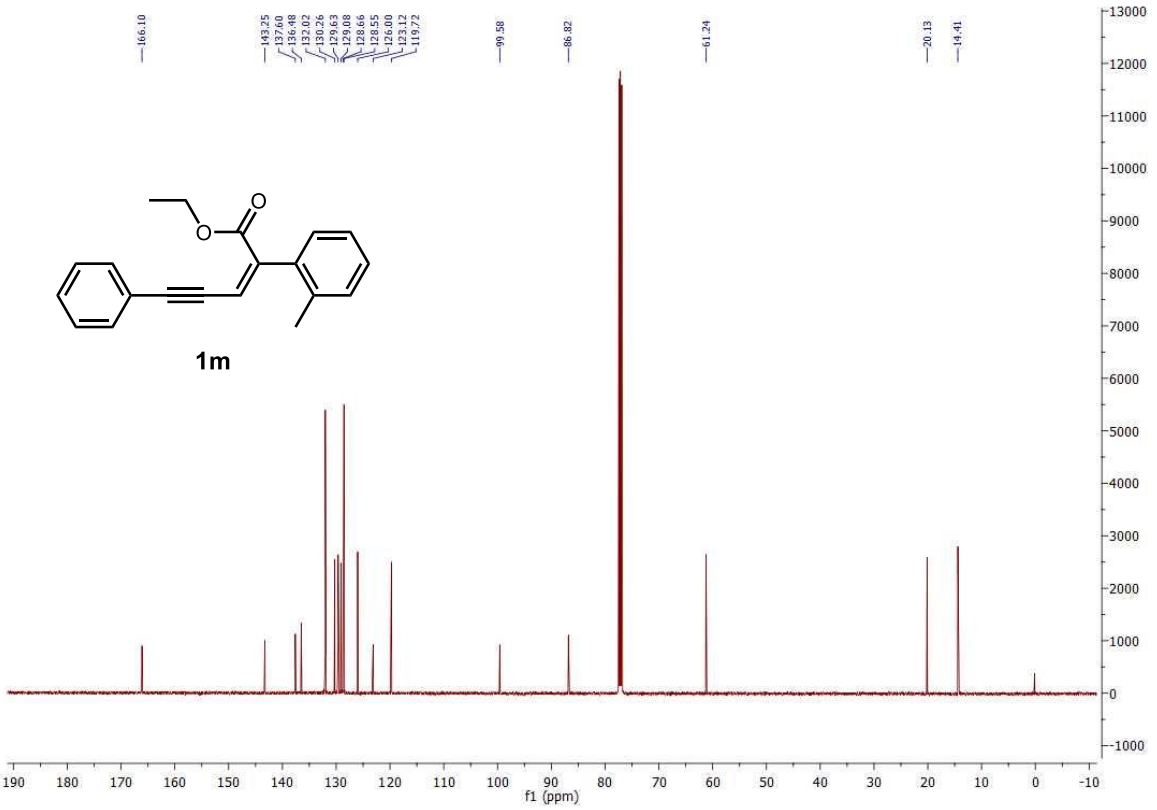
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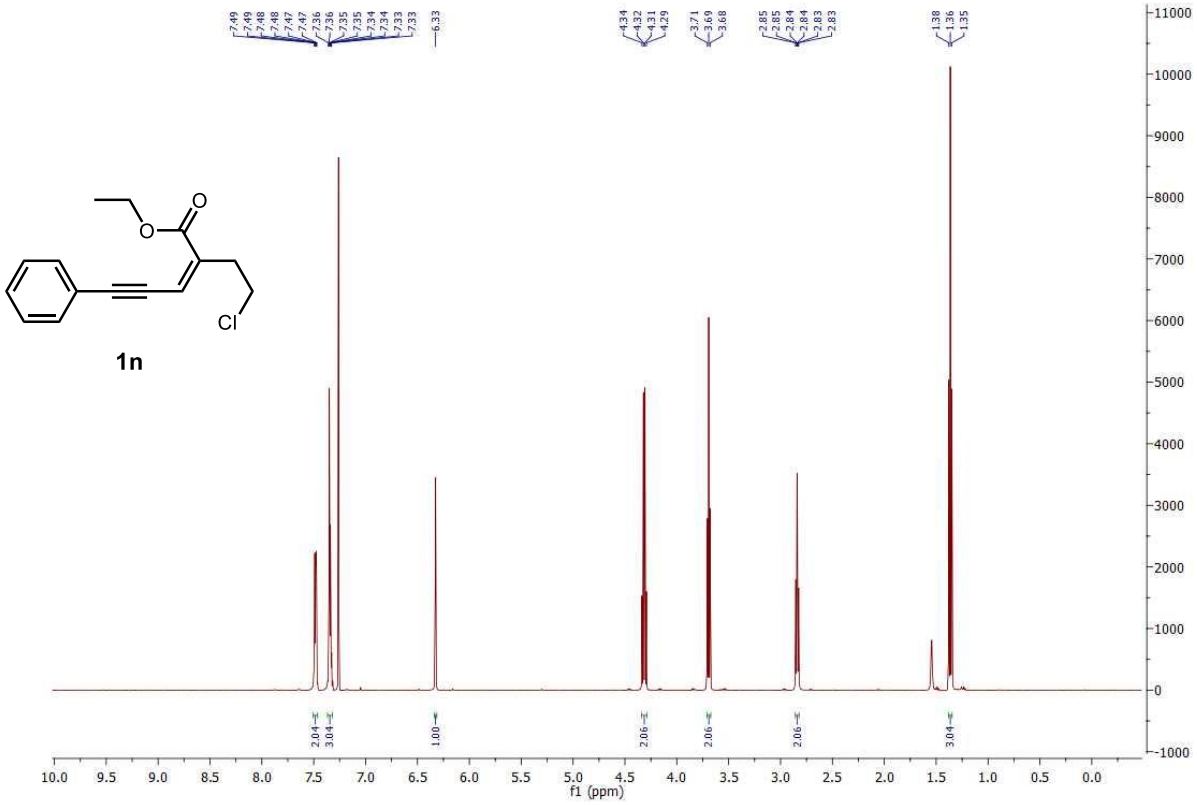
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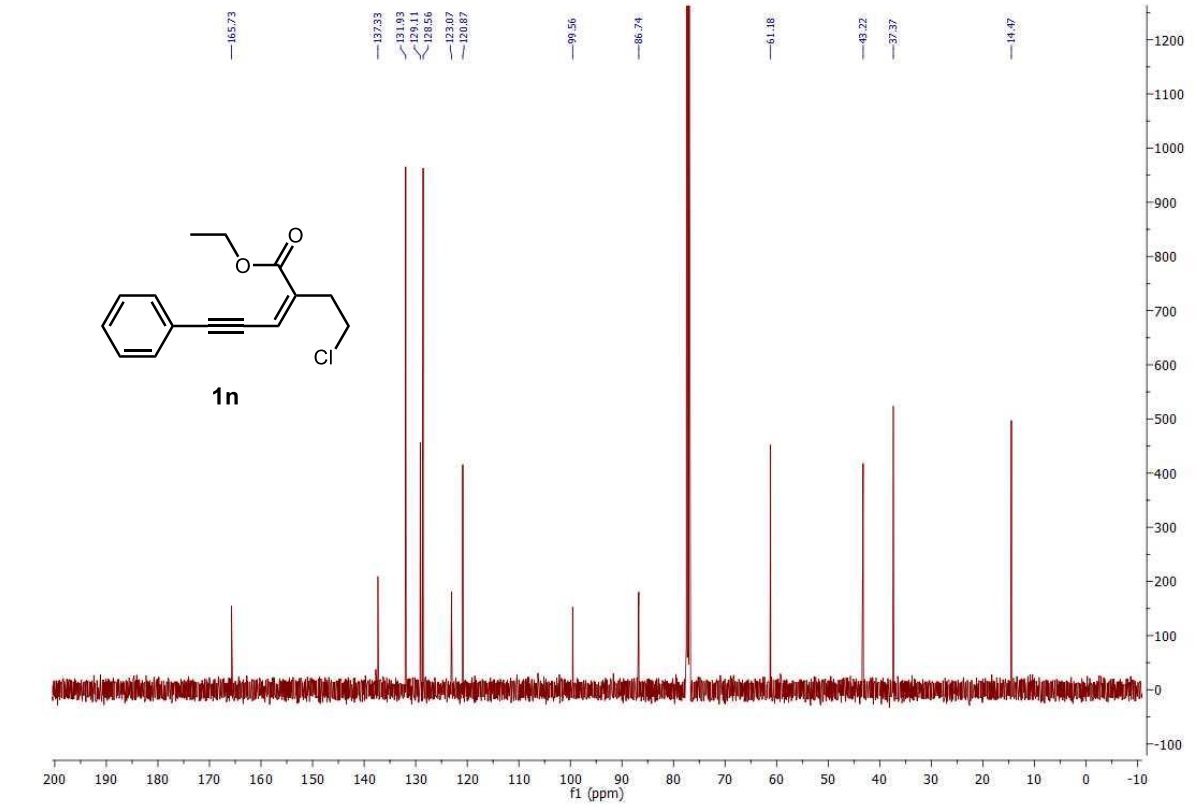
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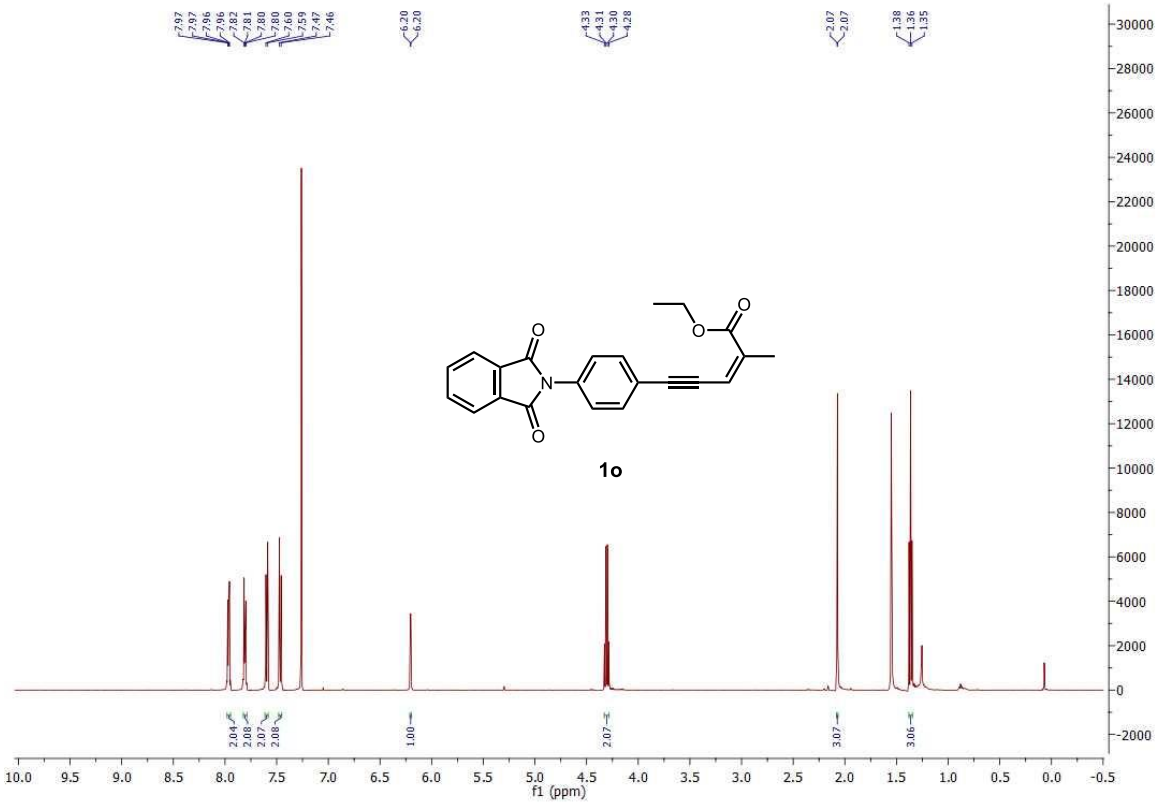
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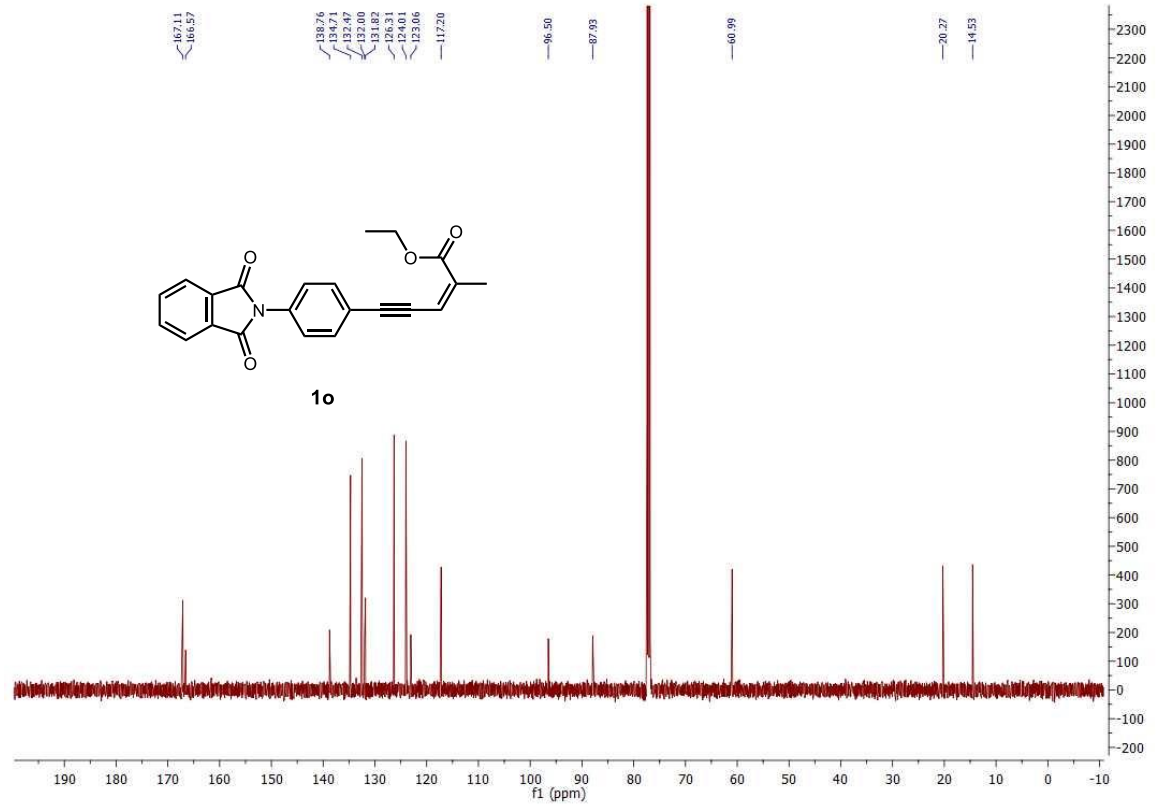
1o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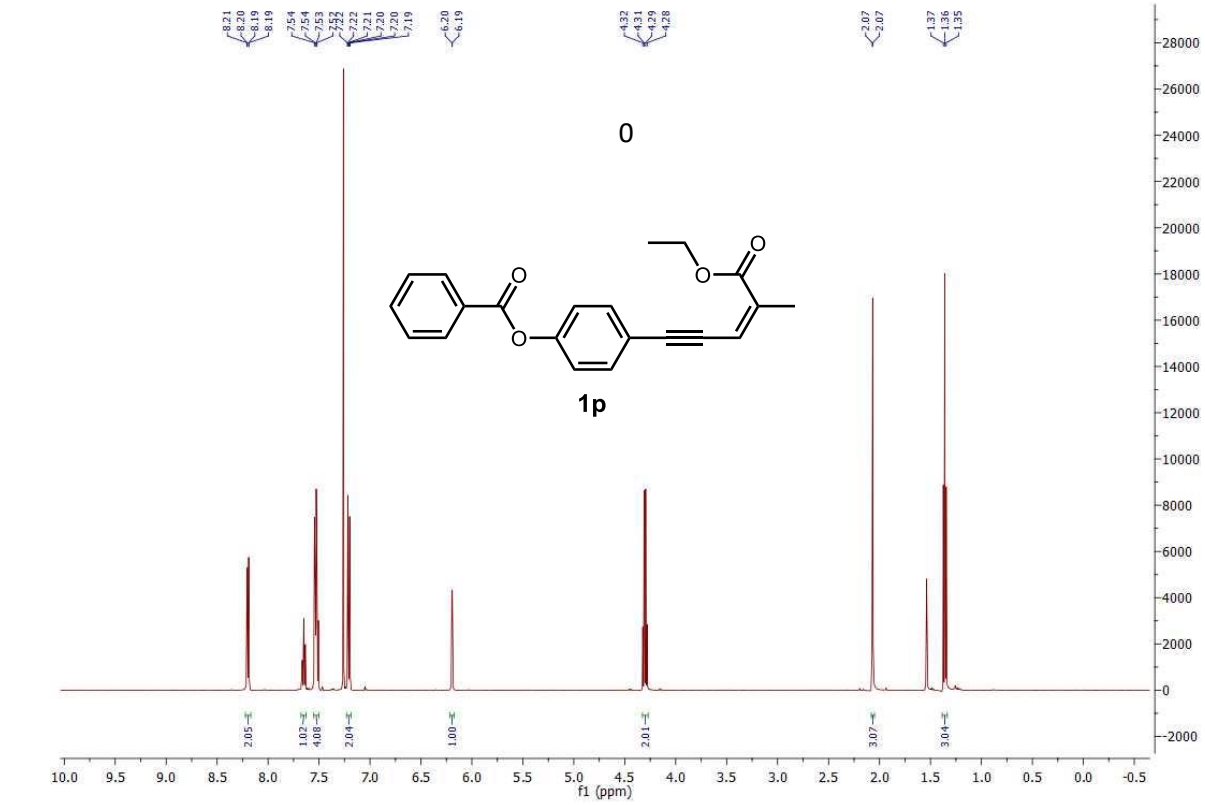
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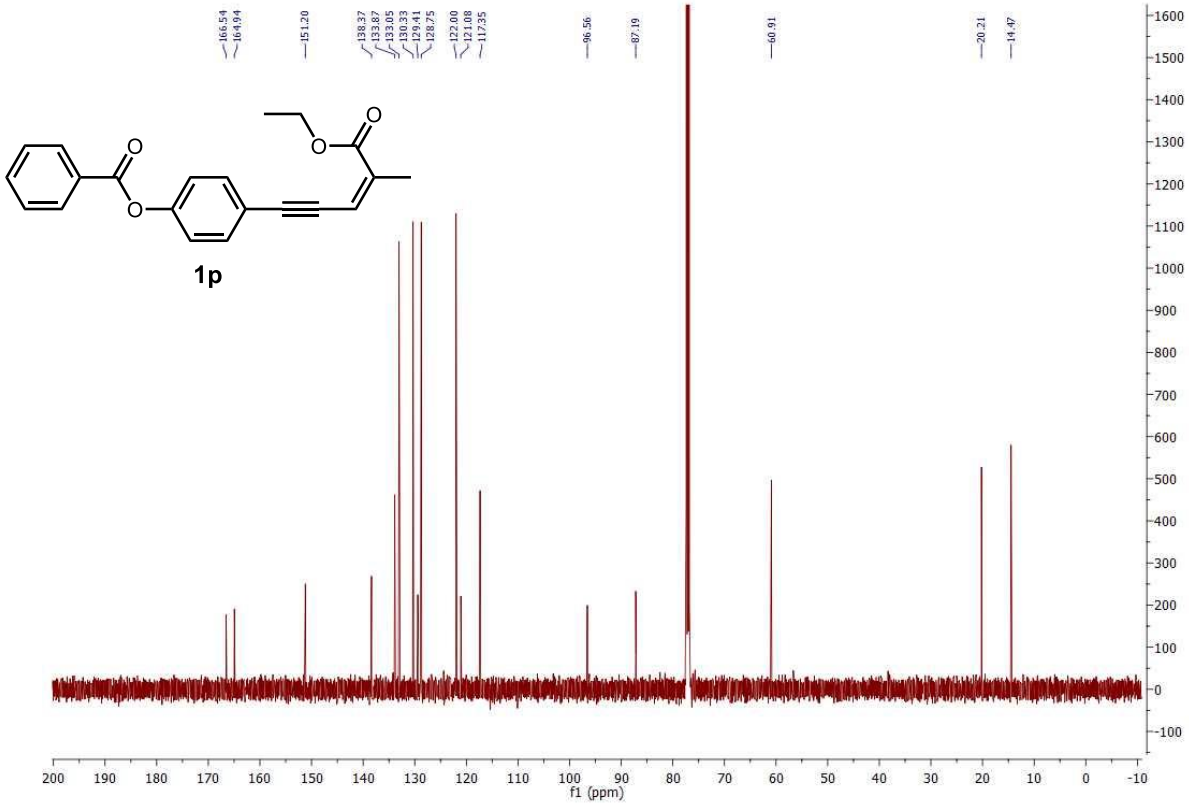
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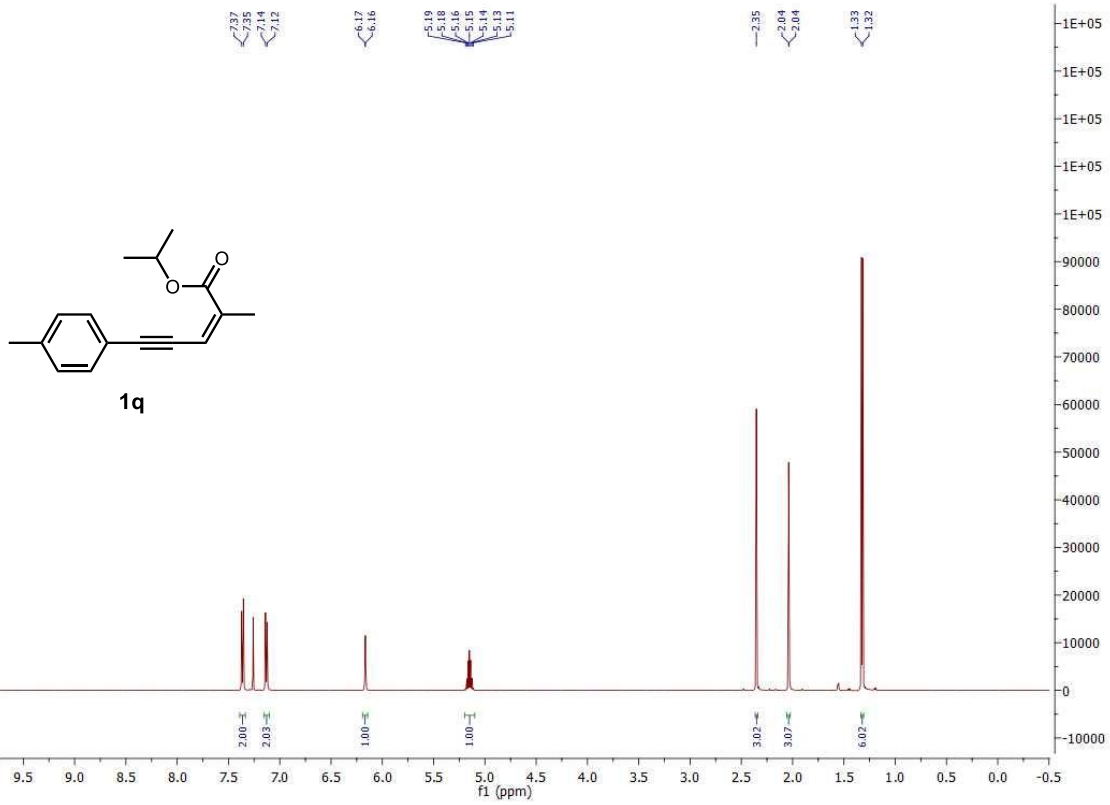
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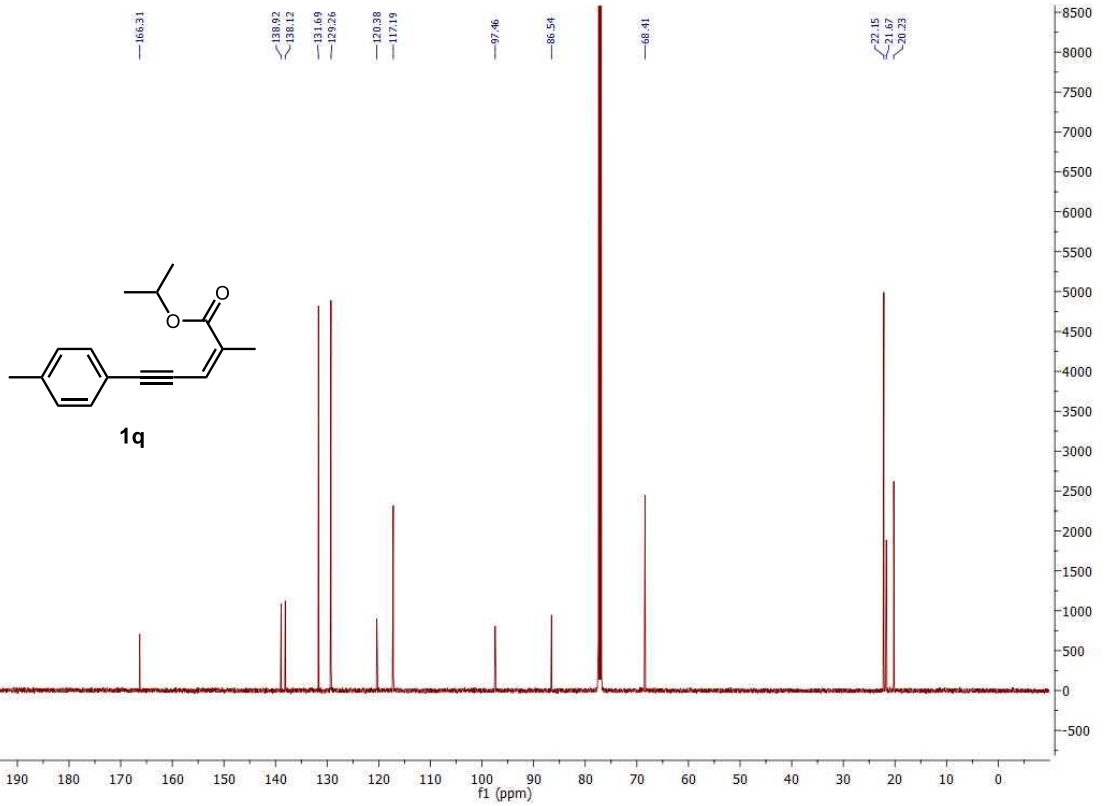
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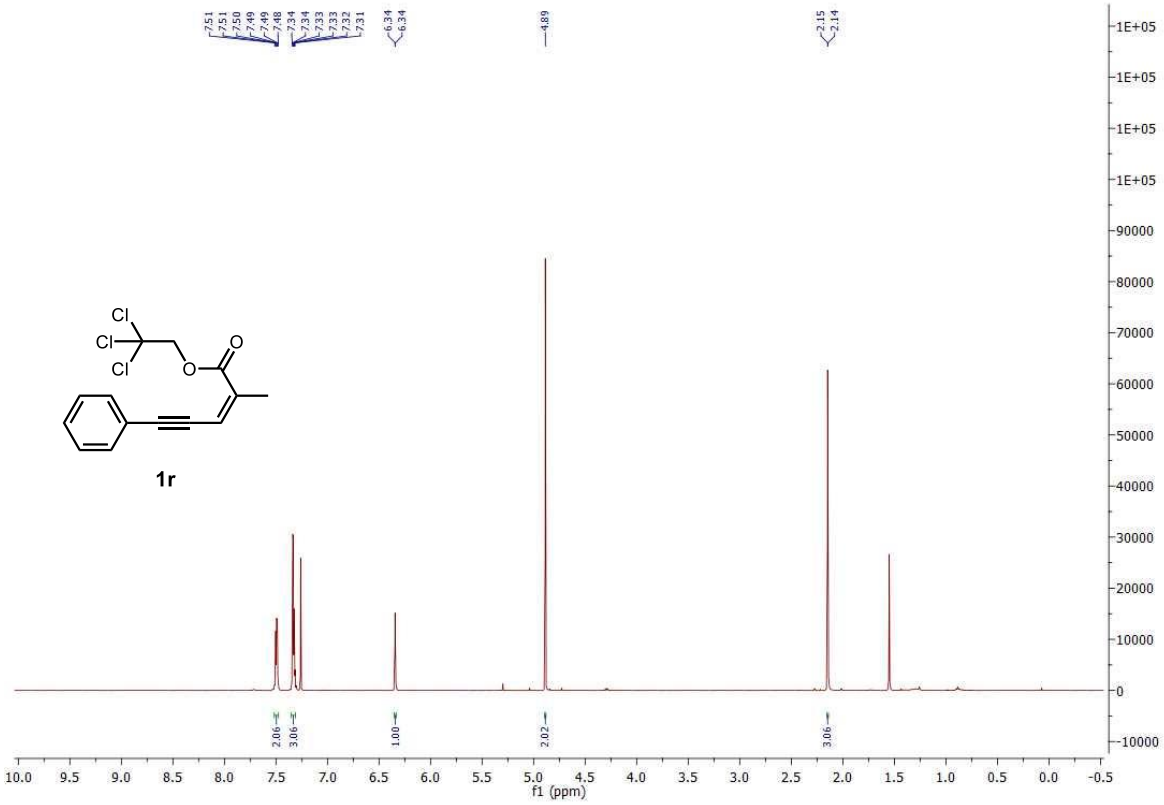
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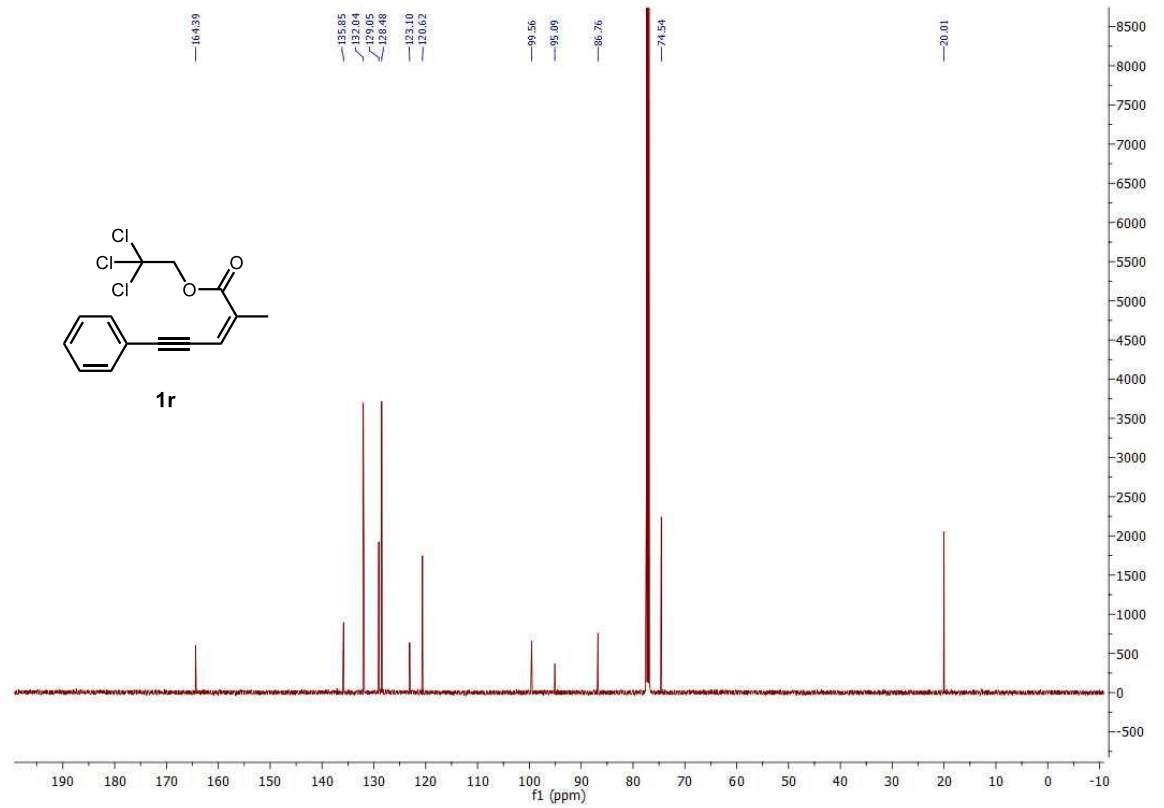
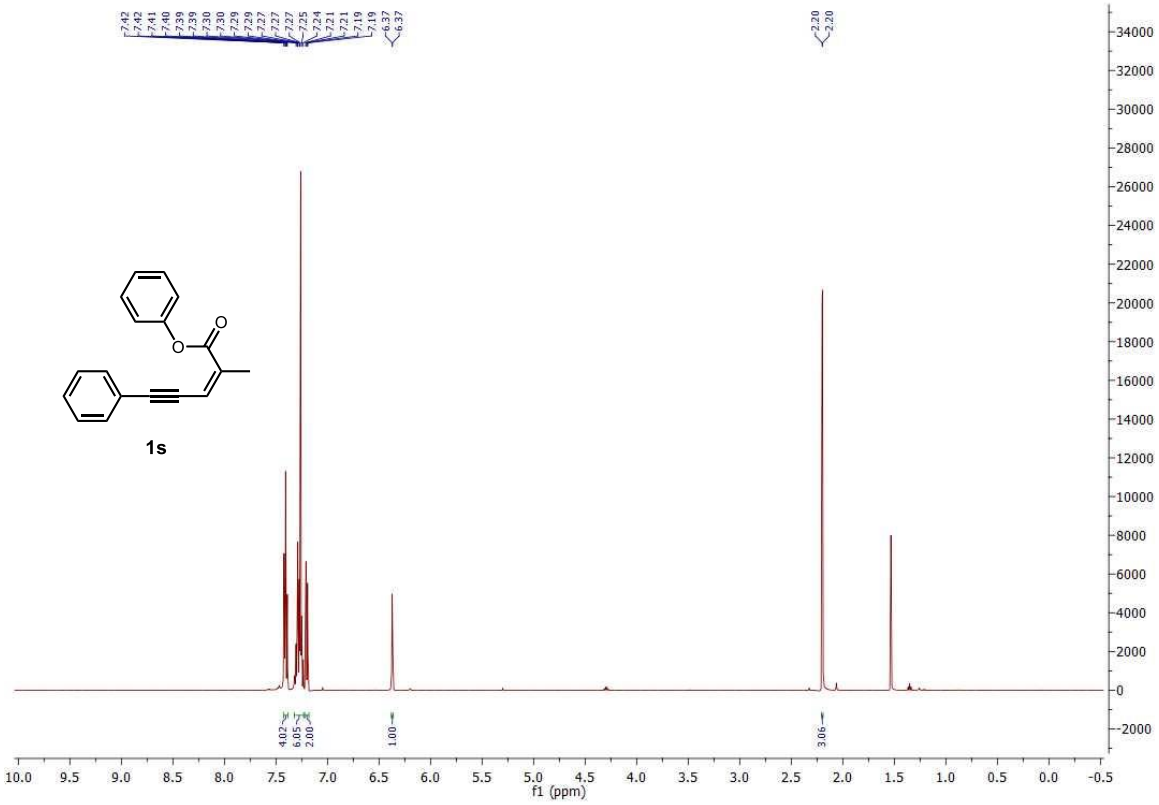
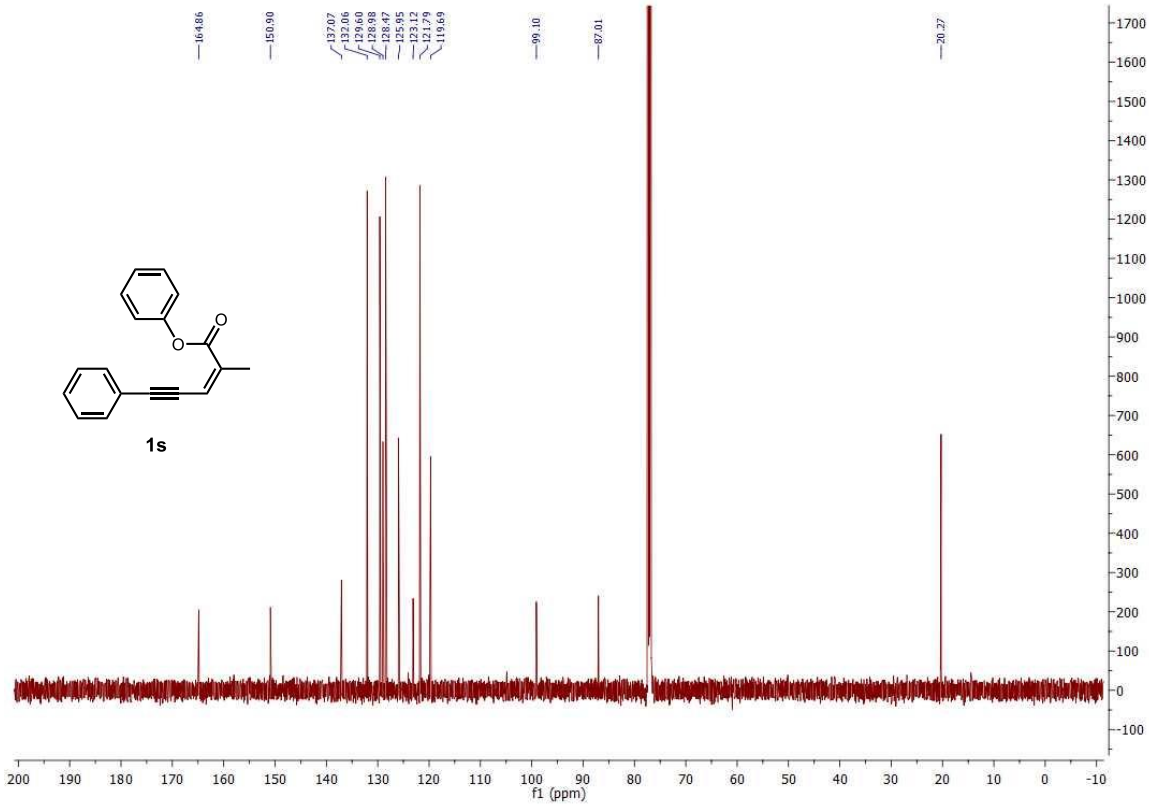
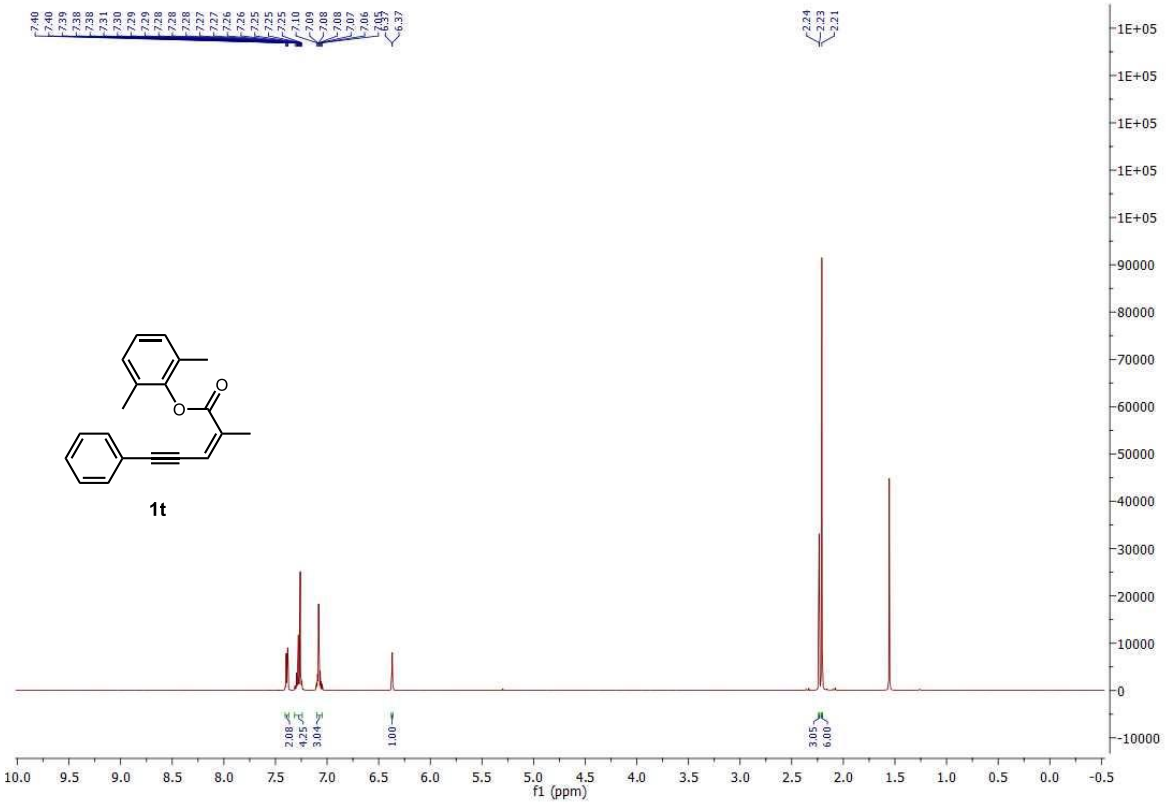
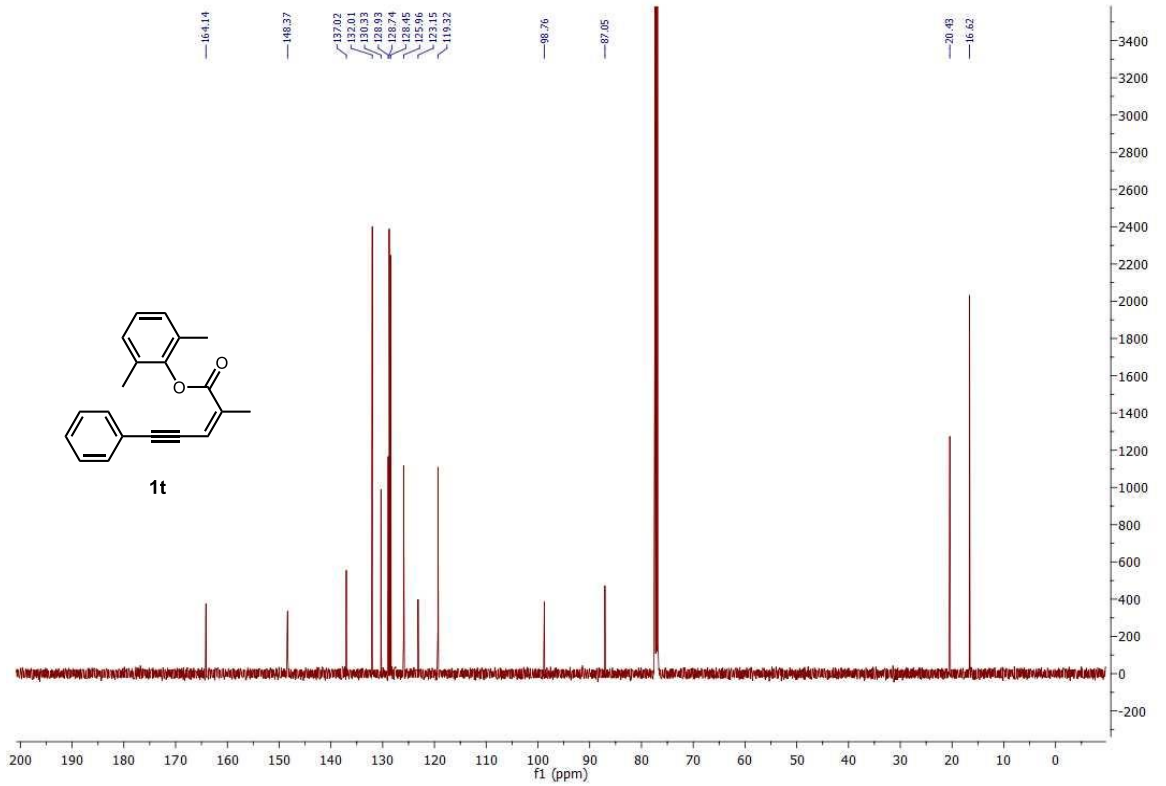
1.00
2.02
3.06
f1 (ppm)

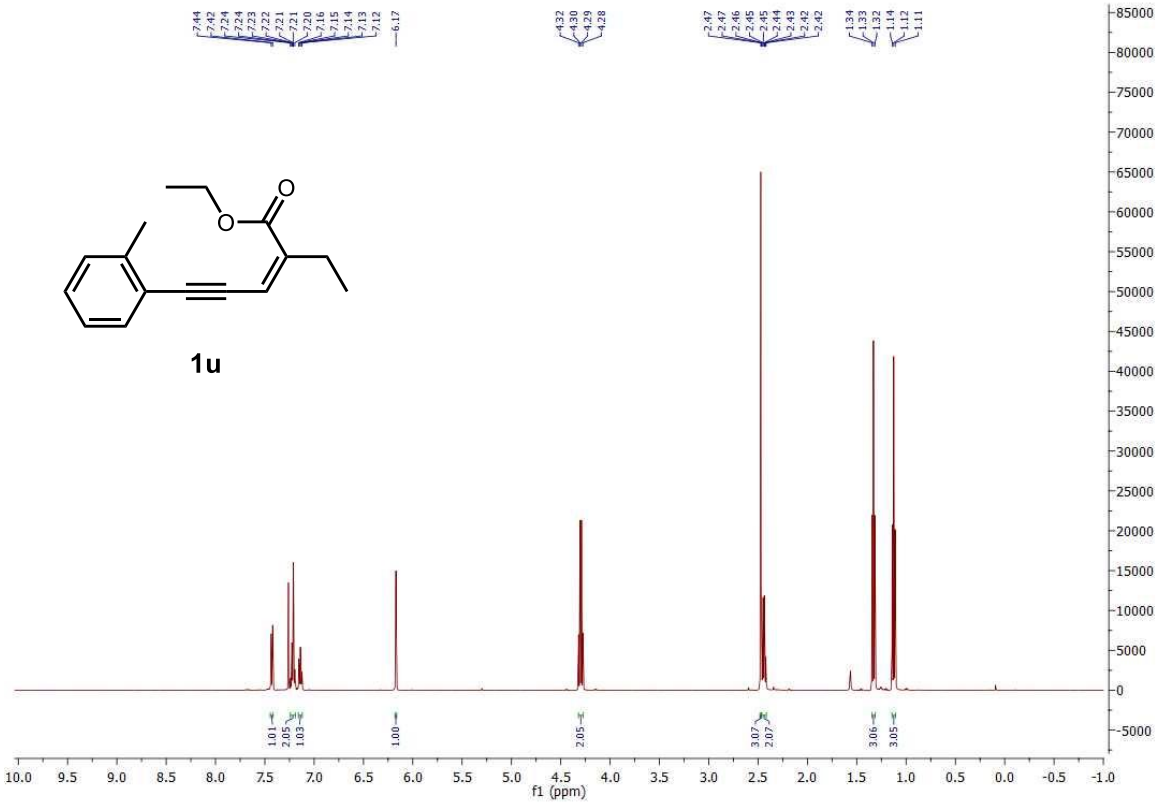

164.39
135.85
132.04
129.05
128.48
123.10
120.62
99.56
95.09
86.76
74.54
20.01
Cl
Cl
Cl
O
O
1r
f1 (ppm)

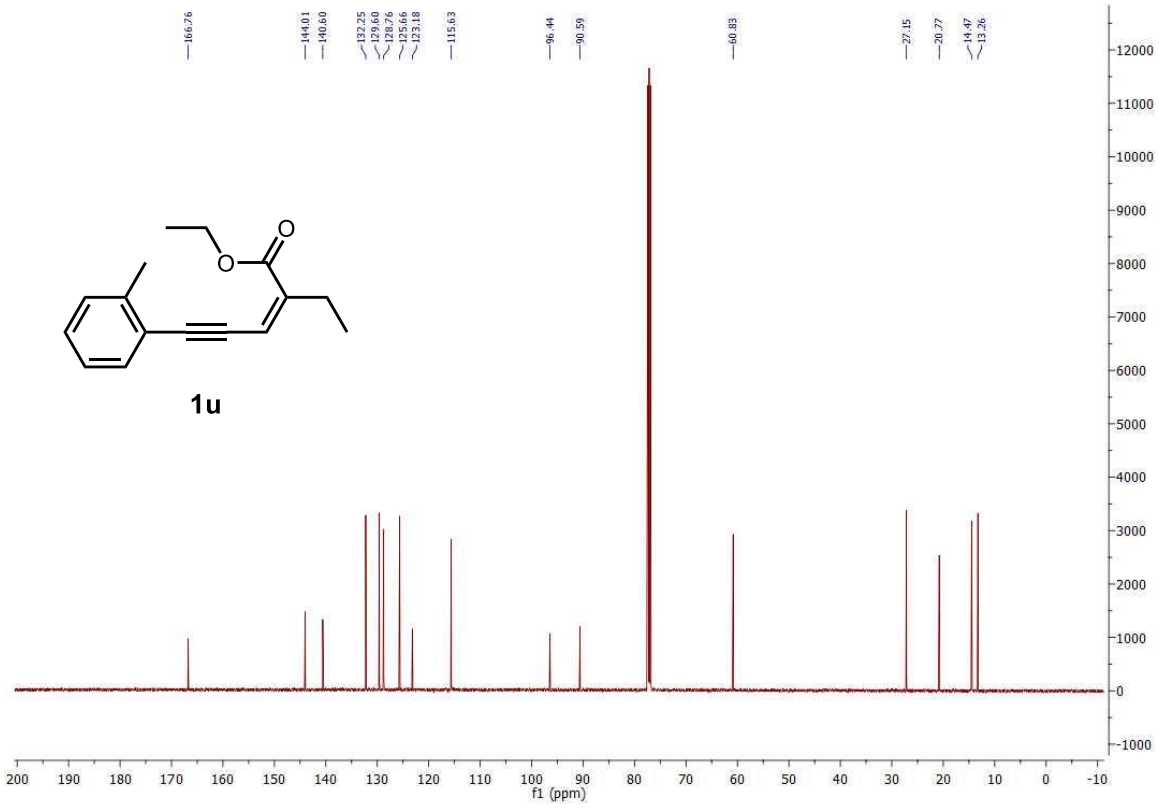

1s
f1 (ppm)

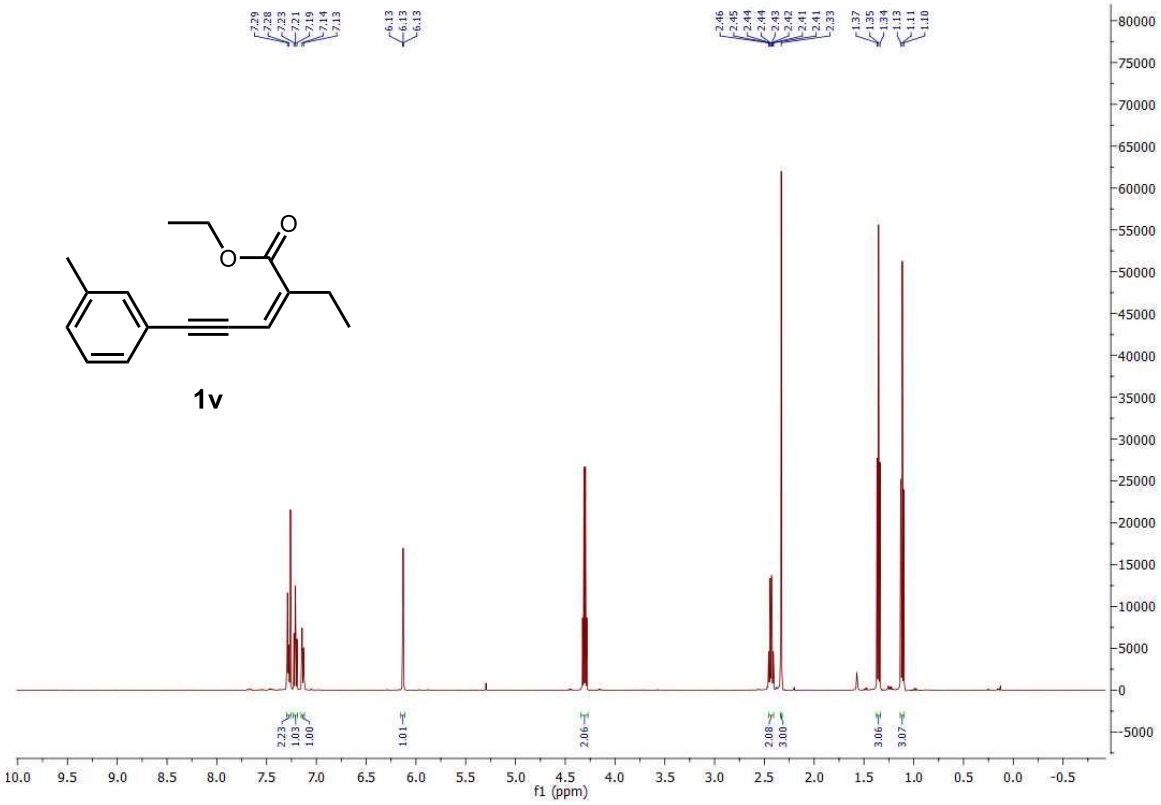

1s
f1 (ppm)

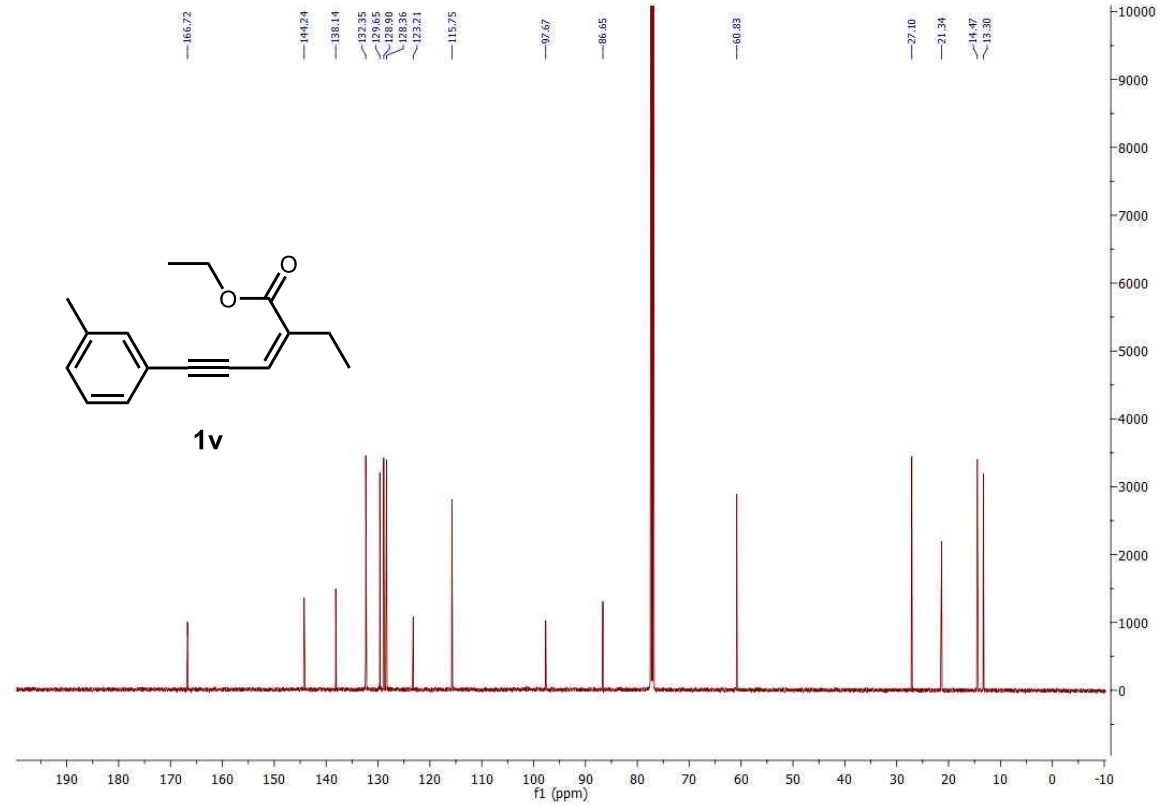

1t
f1 (ppm)

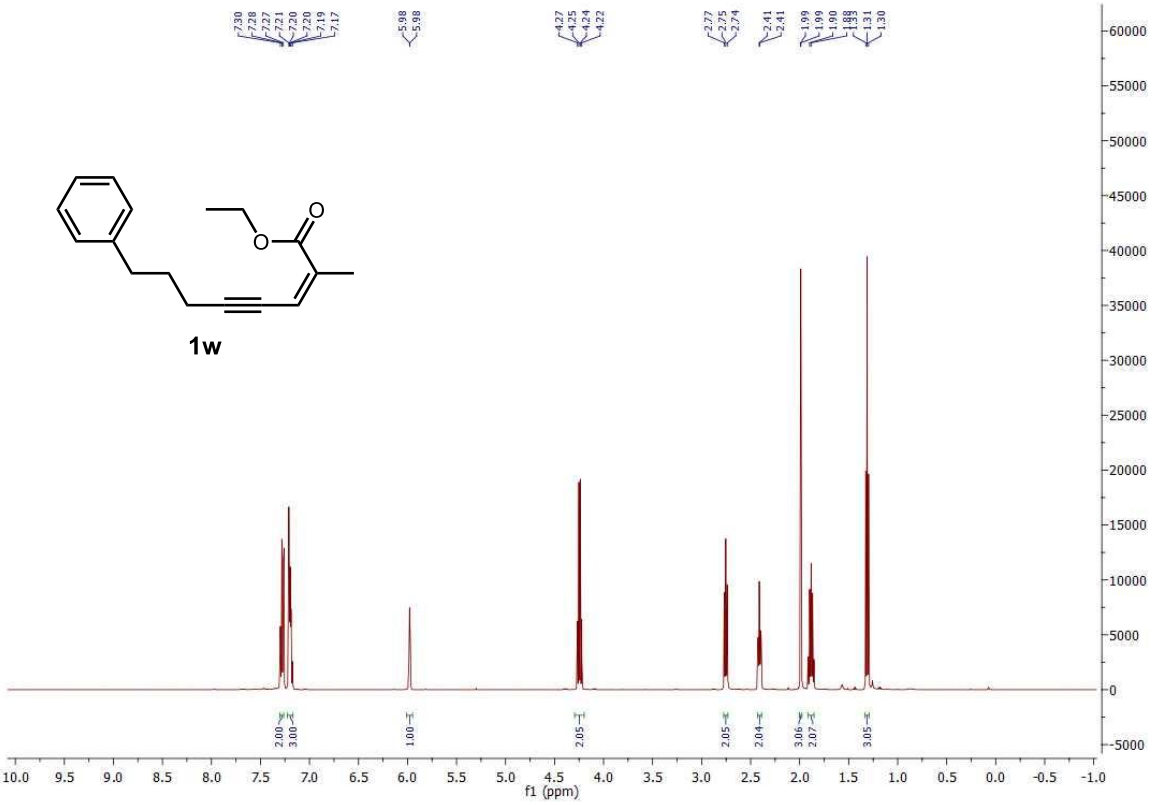

1t
f1 (ppm)

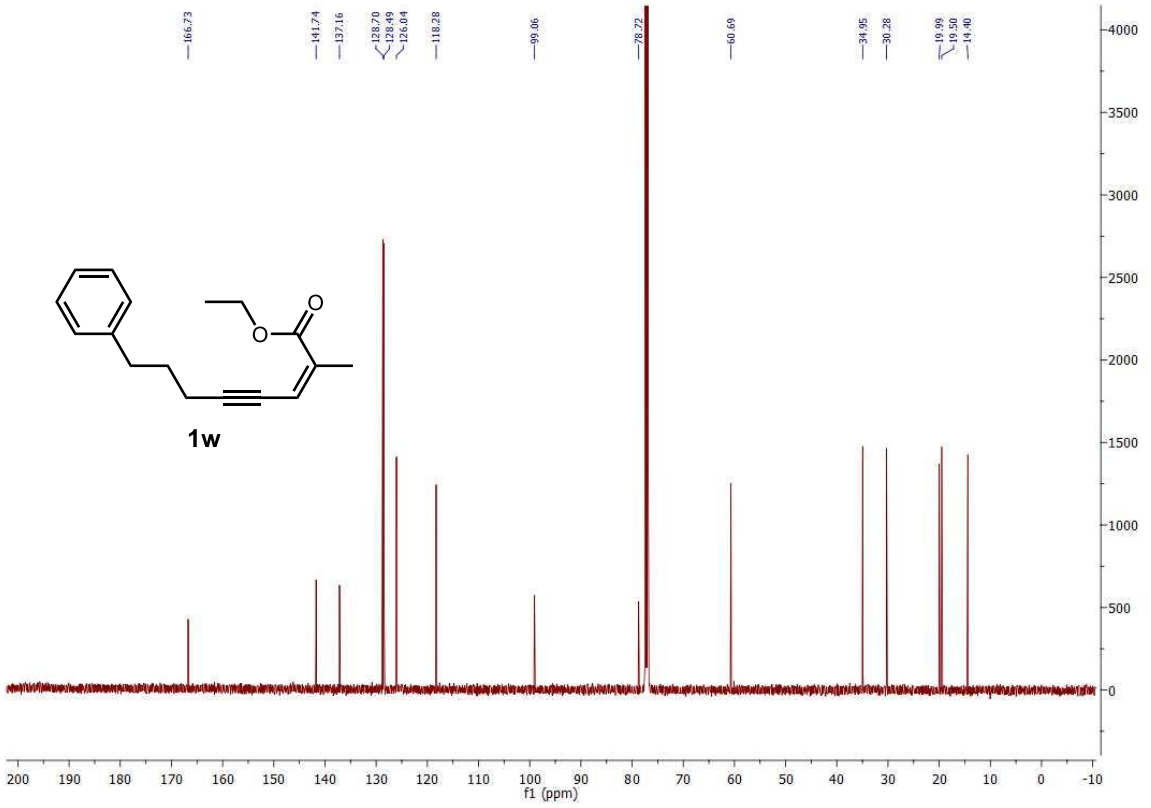

1u
f1 (ppm)

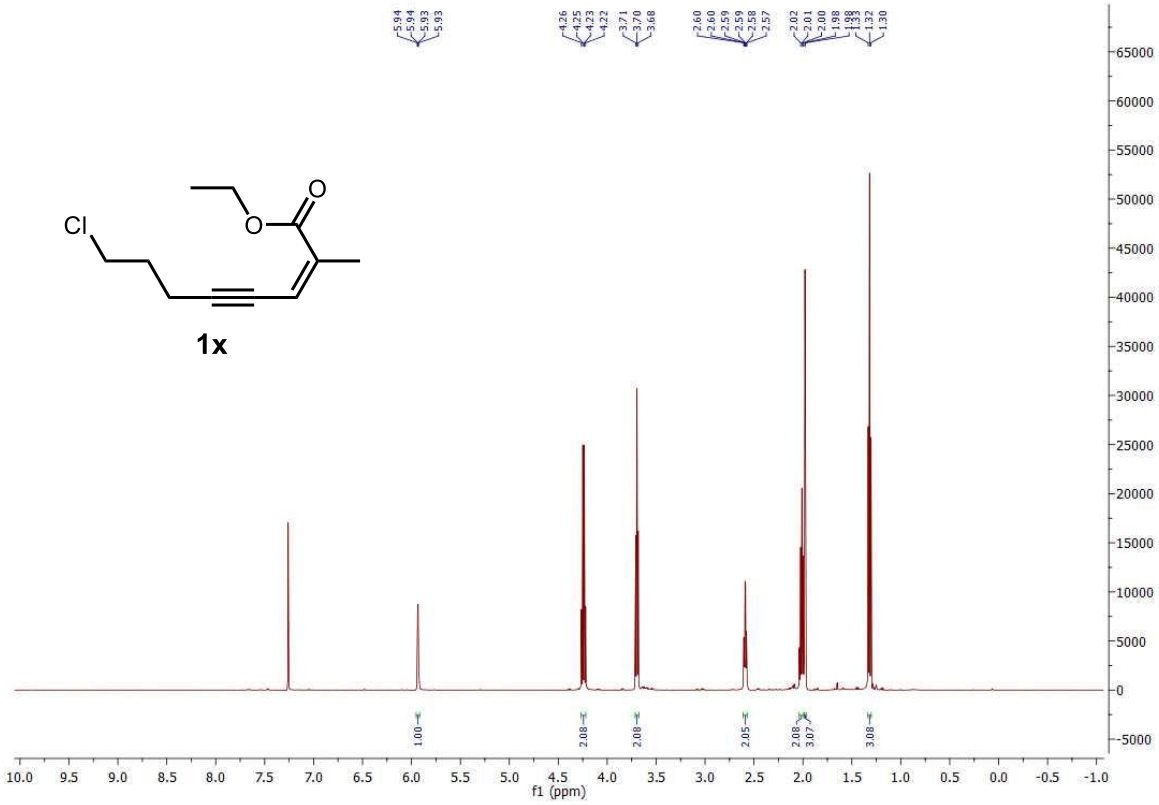

1u
f1 (ppm)

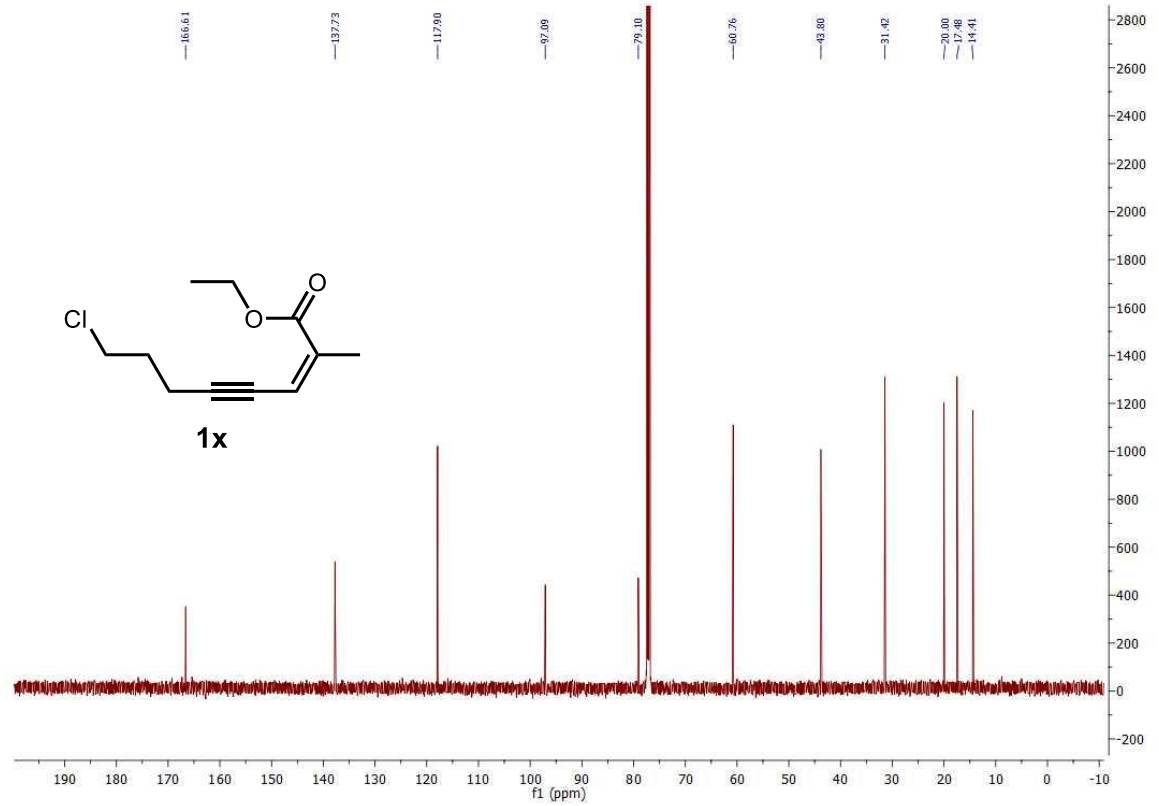

7.29
7.28
7.23
7.21
7.19
7.14
7.13
6.13
6.13
6.13
2.46
2.45
2.44
2.44
2.43
2.42
2.41
2.41
2.33
1.37
1.35
1.34
1.13
1.11
1.10
O
O
1v
2.23
1.03
1.00
1.01
2.06
2.08
3.00
3.06
3.07
f1 (ppm)


166.72
144.24
138.14
132.35
129.65
128.90
128.36
123.21
115.75
97.67
86.65
60.83
27.10
21.34
14.47
13.30
O
O
1v
f1 (ppm)

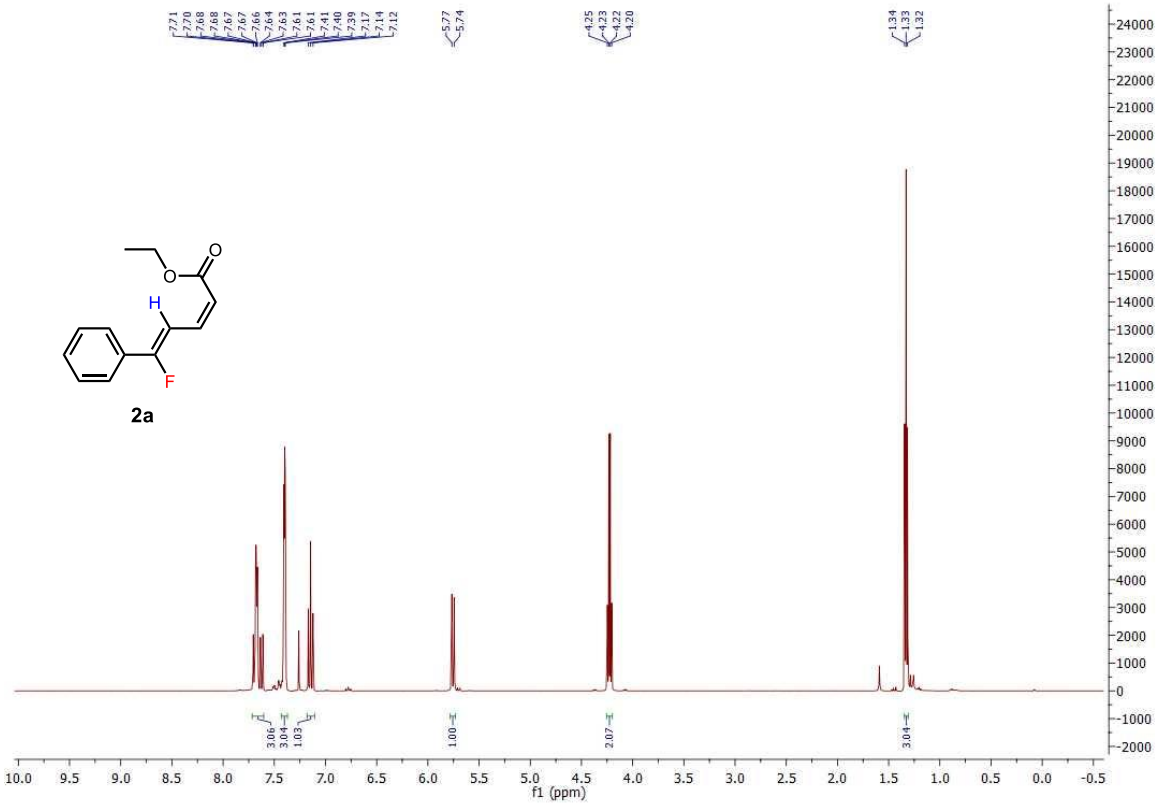

1w
f1 (ppm)

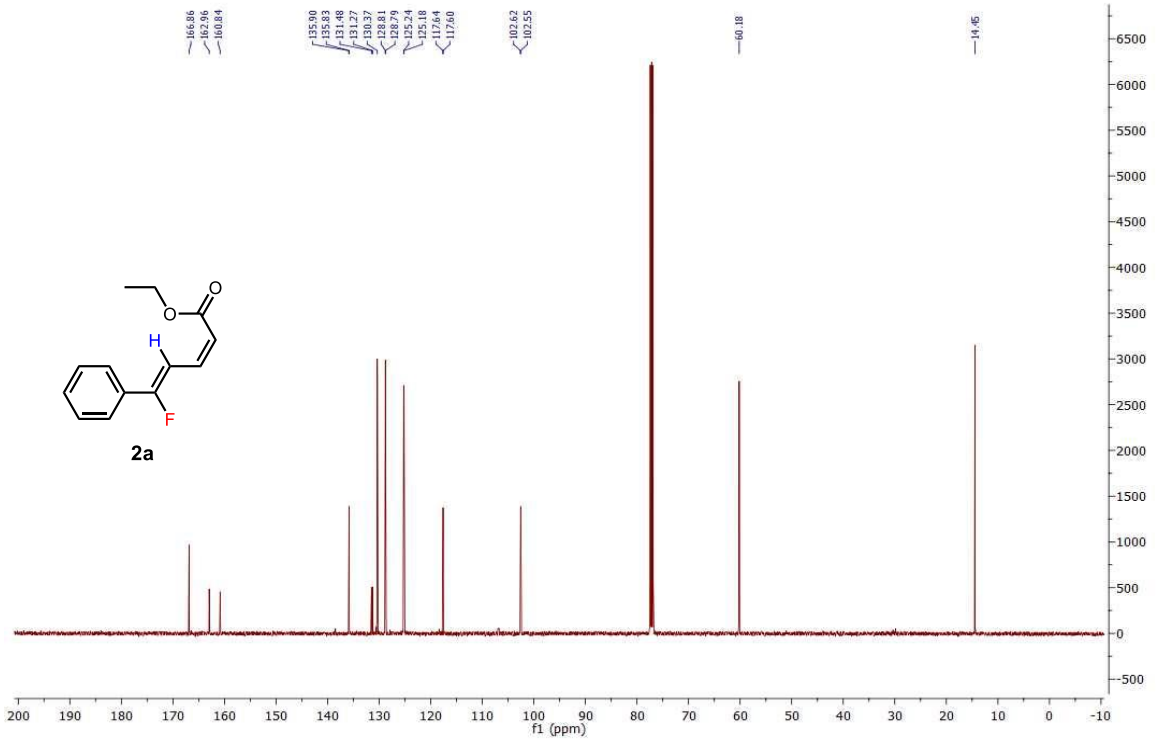

1w
f1 (ppm)

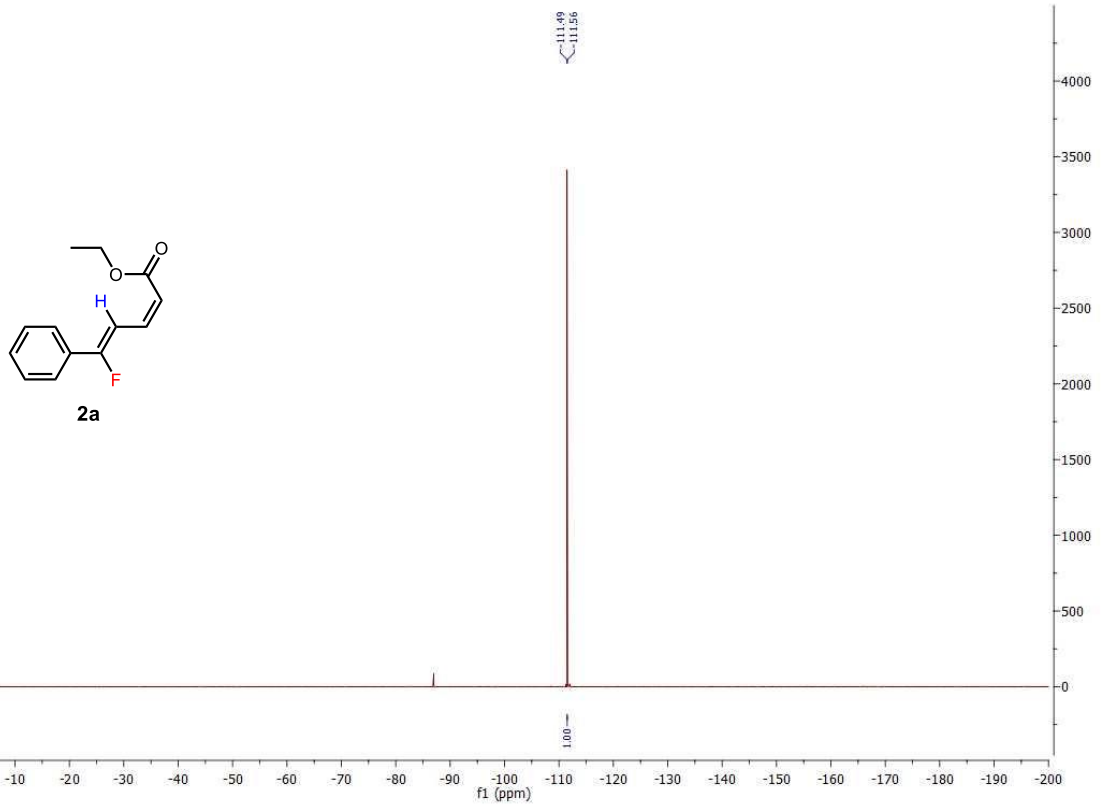

Cl
O
O
1x
f1 (ppm)

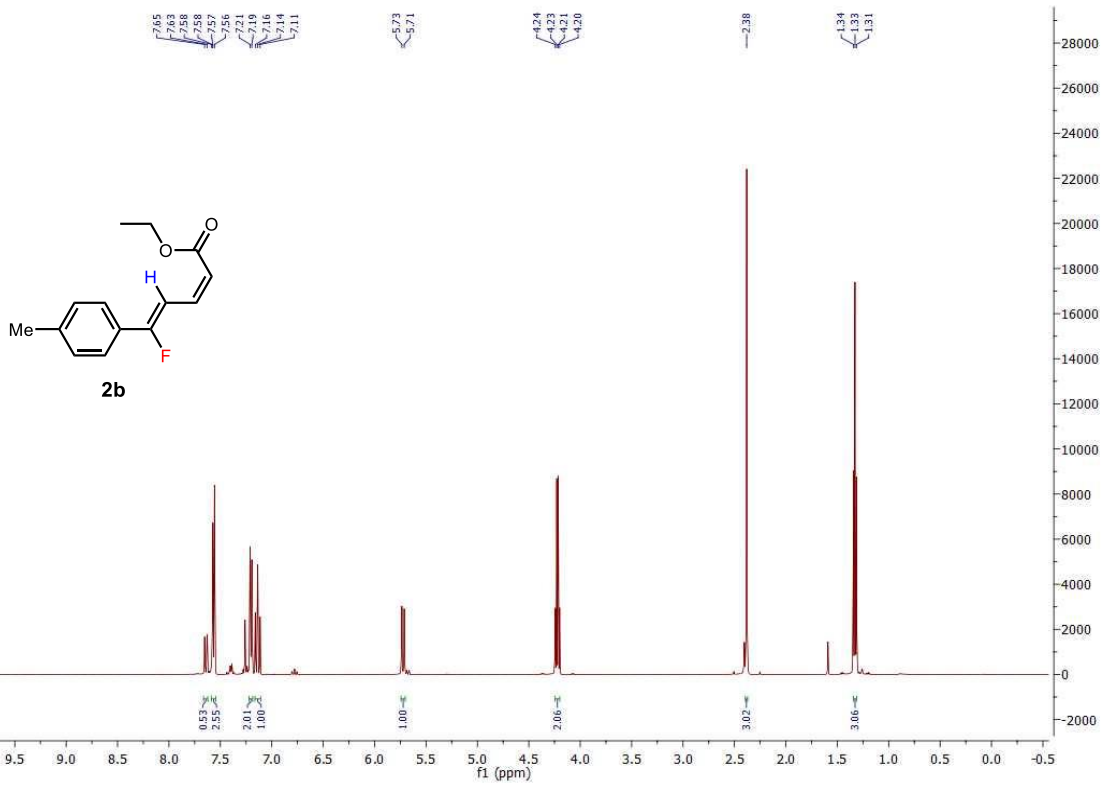

Cl
O
O
1x
f1 (ppm)

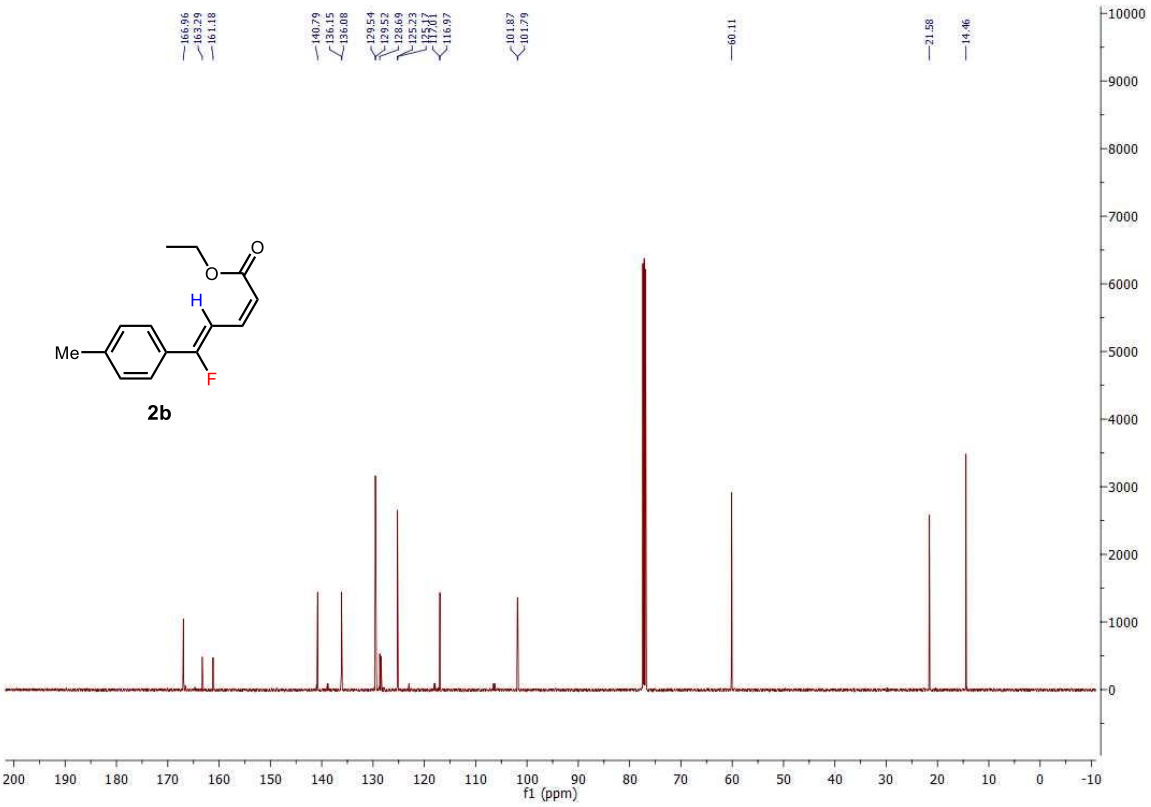
Copies of NMR spectra for (*Z*) products






O
O
H
F
2a
-111.49
-111.56
1.00
f1 (ppm)


7.65
7.63
7.58
7.58
7.57
7.56
7.21
7.19
7.16
7.14
7.11
5.73
5.71
4.24
4.23
4.21
4.20
2.38
1.34
1.33
1.31
O
O
H
Me
F
2b
0.53
2.55
2.01
1.00
1.00
2.06
3.02
3.06
f1 (ppm)


166.96
165.29
161.18
140.79
136.15
136.08
129.54
129.52
128.69
125.23
117.17
116.97
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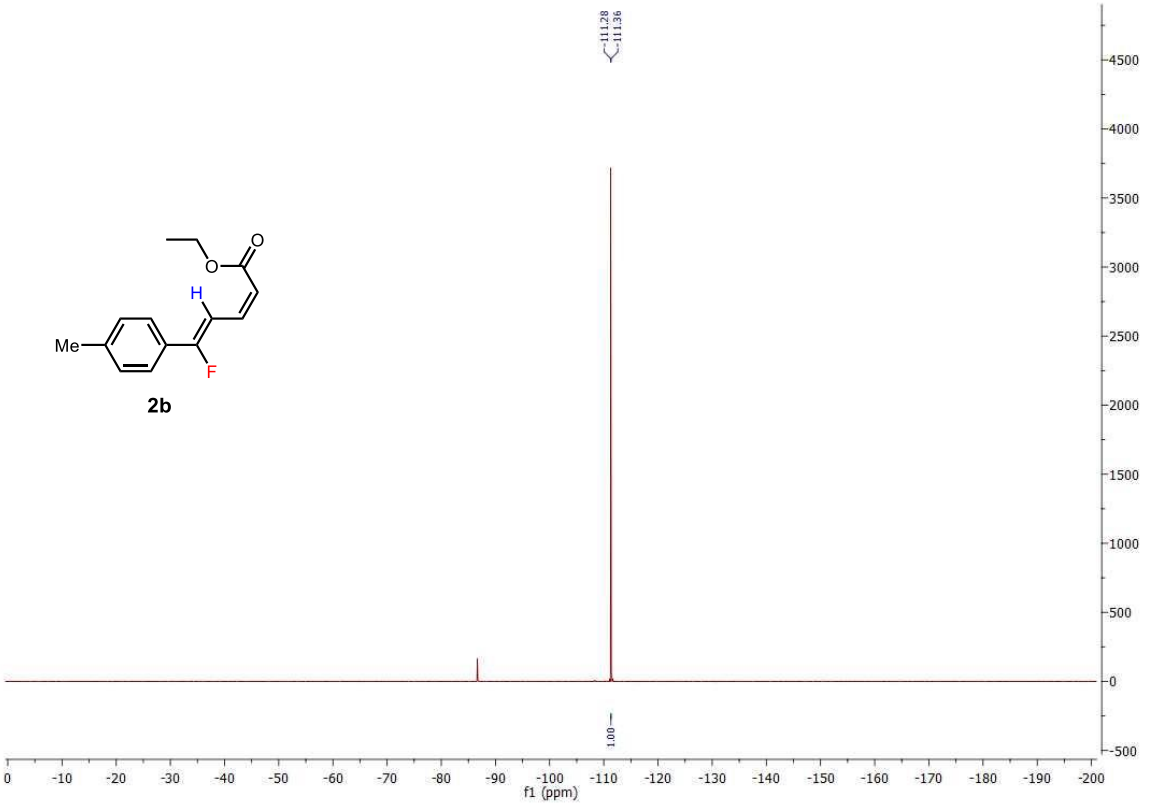
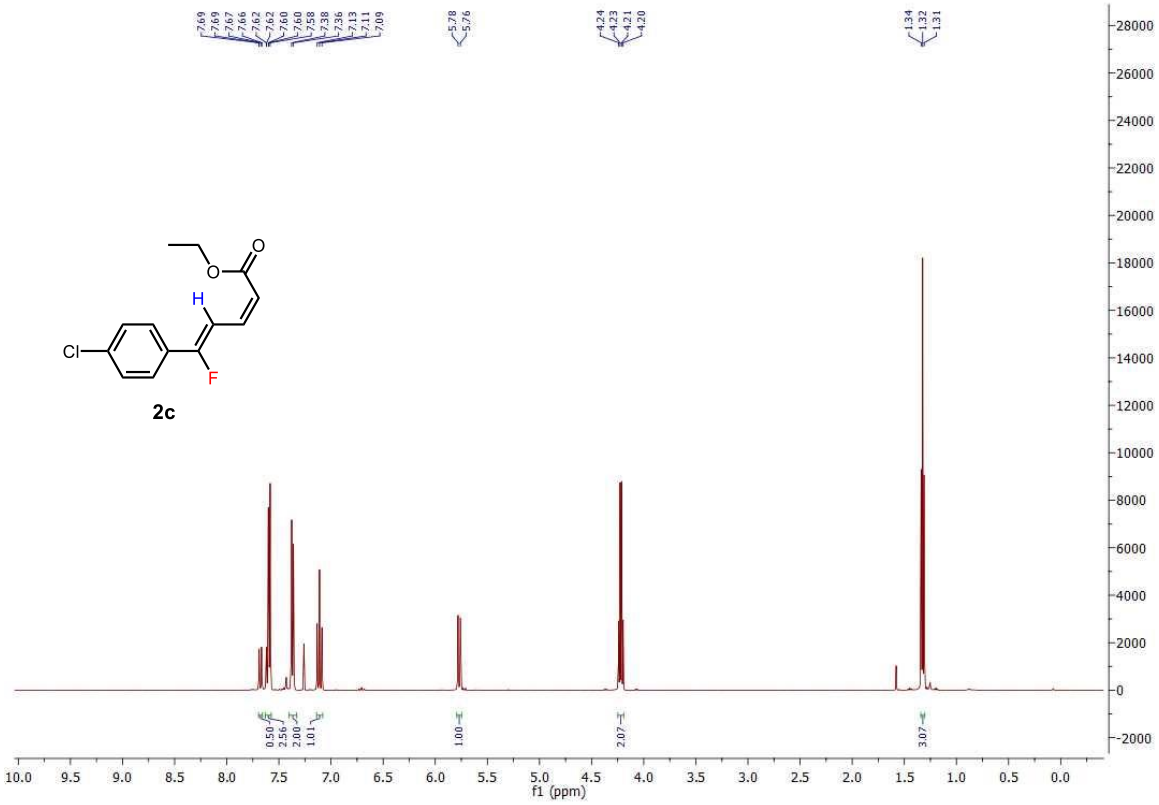
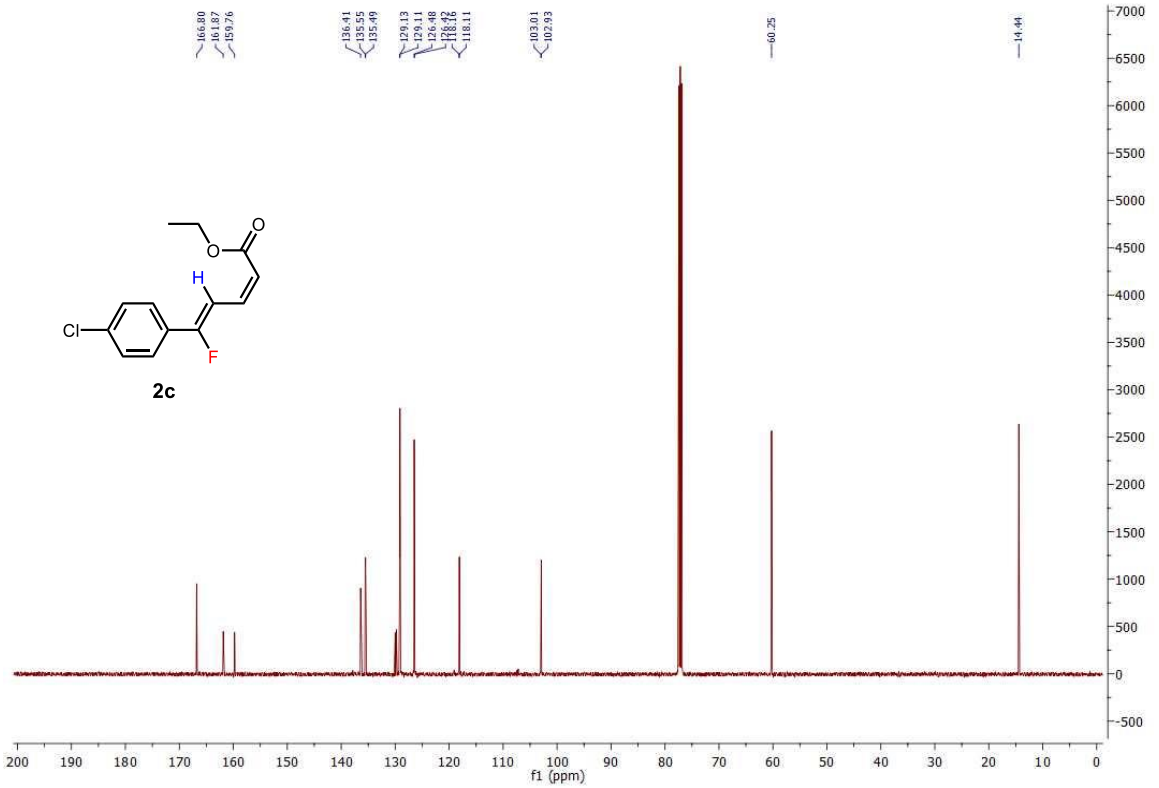
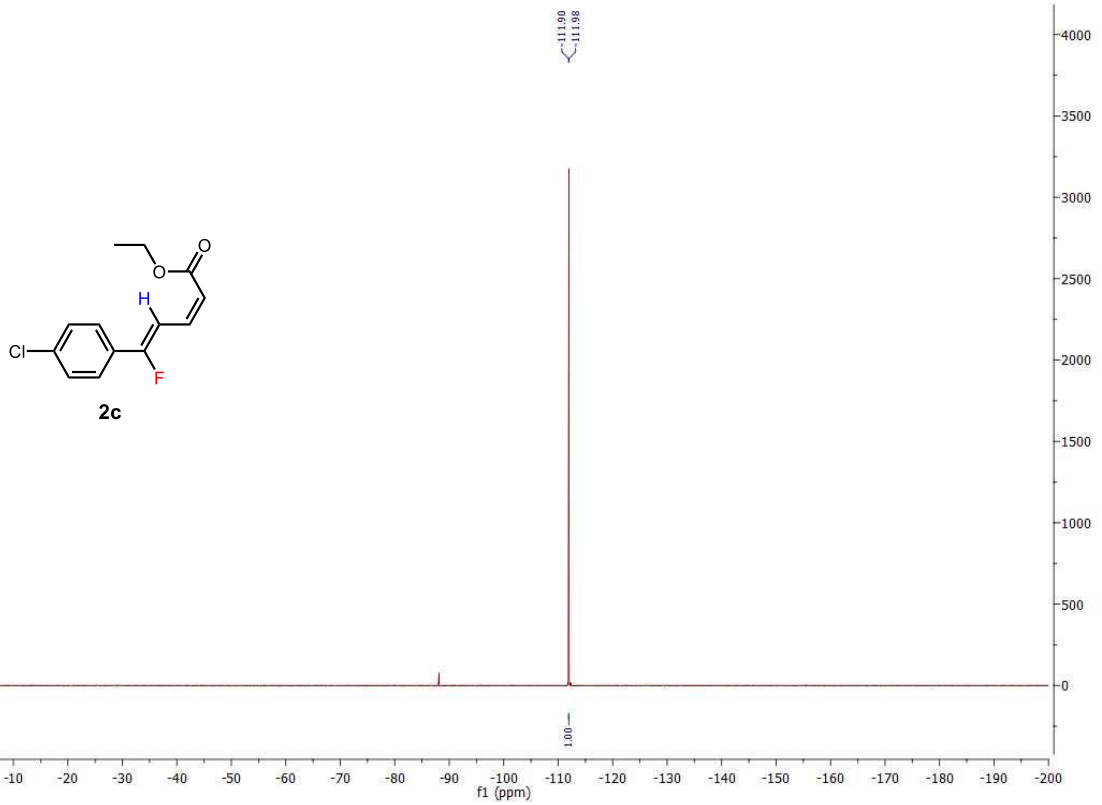
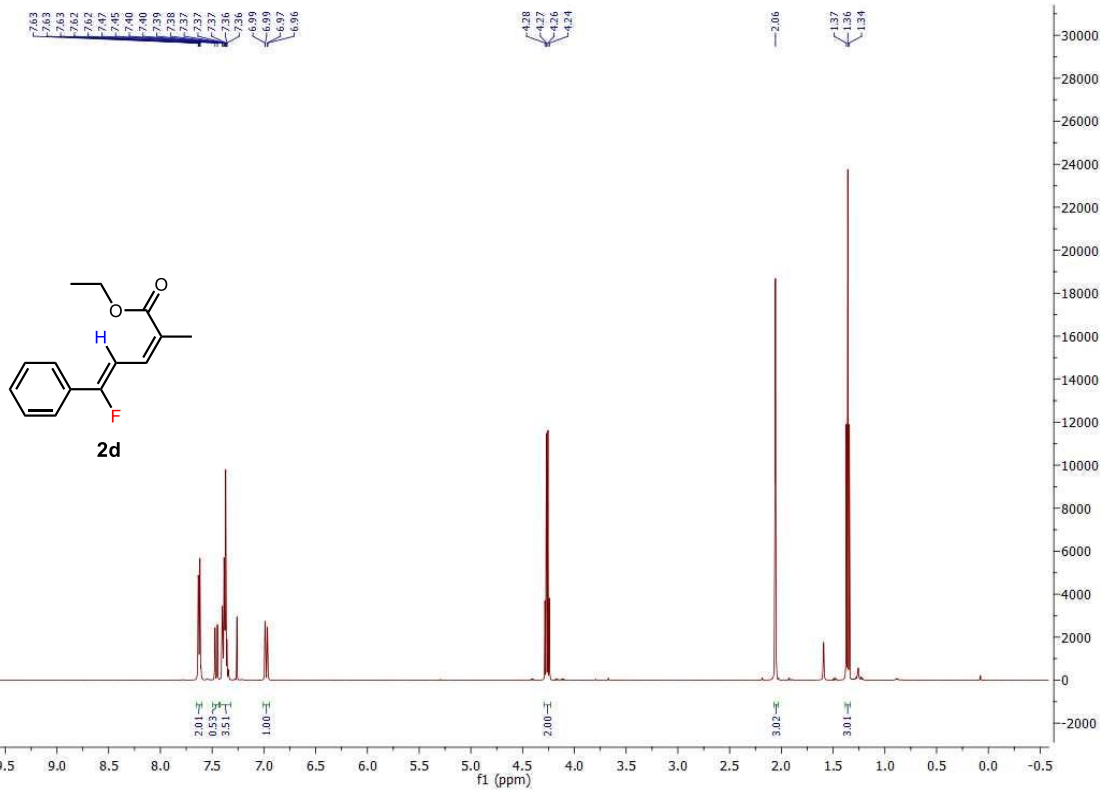
101.79
60.11
21.58
14.46
Me
F
H
O
O
2b
f1 (ppm)

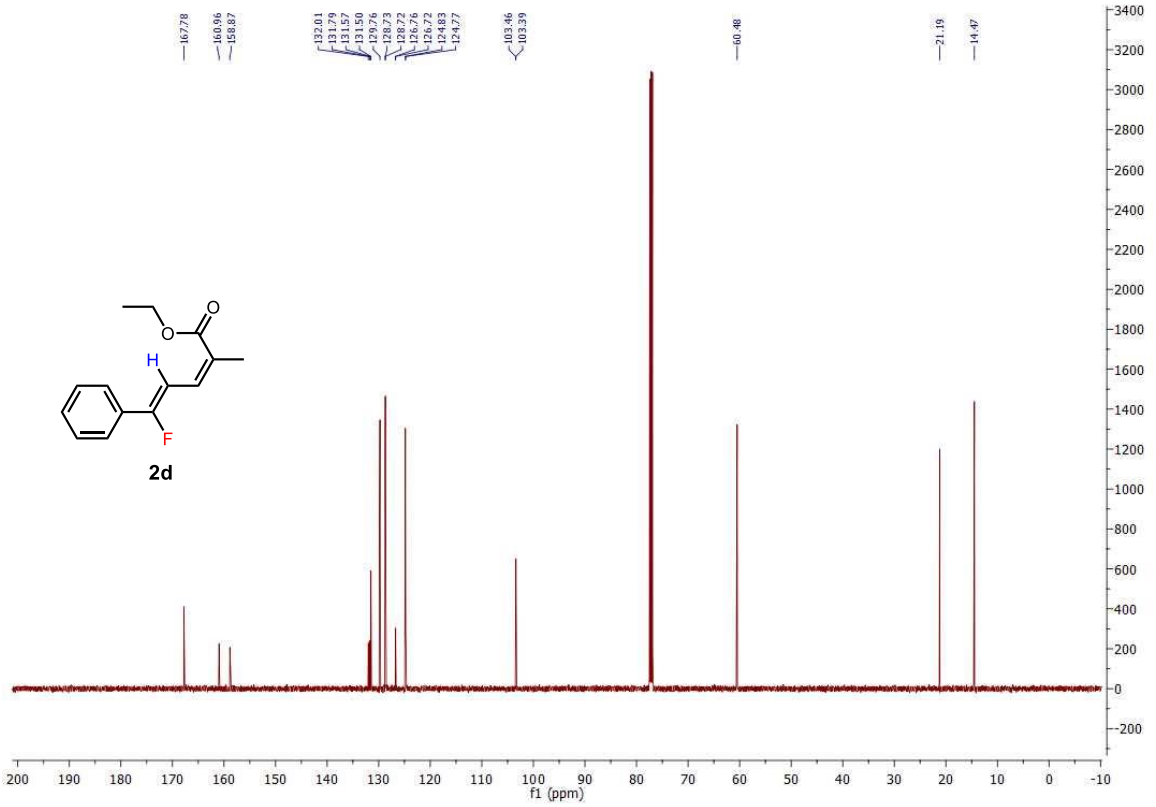

111.28
111.36
1.00
Me
F
H
O
O
2b
f1 (ppm)

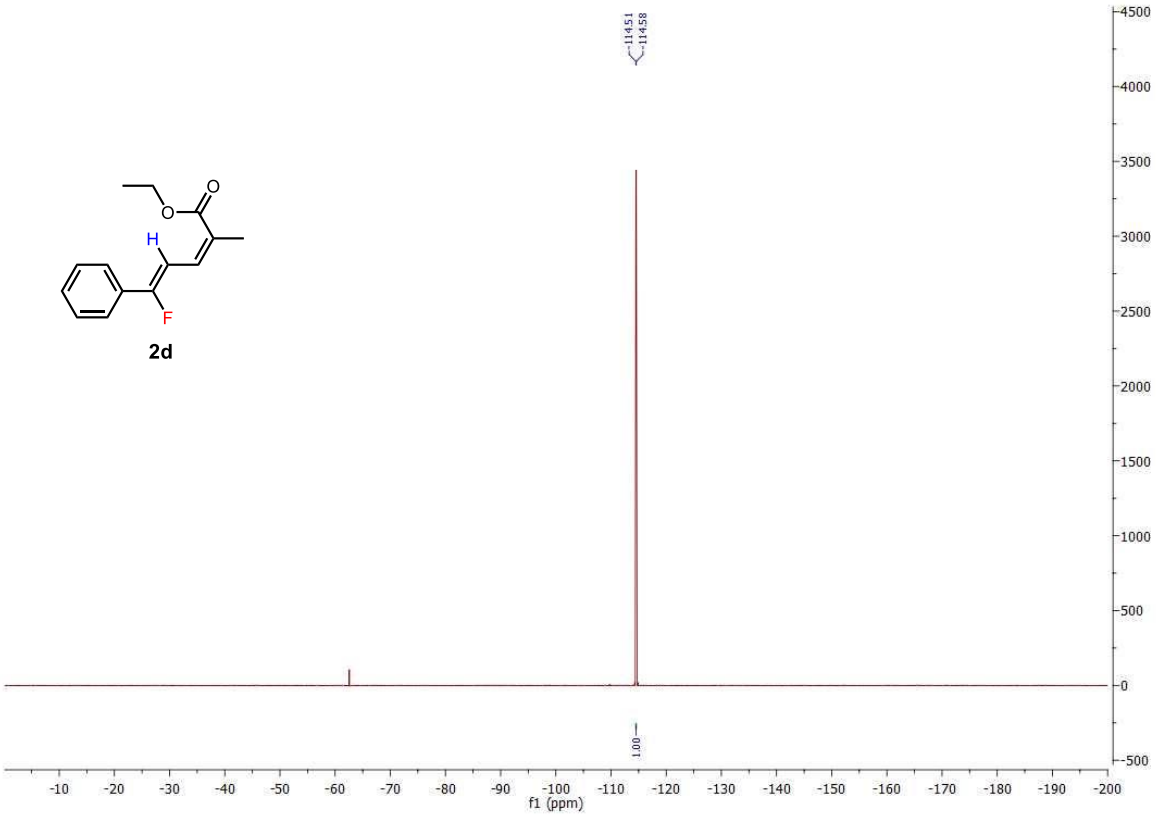

7.69
7.69
7.67
7.66
7.62
7.62
7.60
7.60
7.58
7.38
7.36
7.13
7.11
7.09
5.78
5.76
4.24
4.23
4.21
4.20
1.34
1.32
1.31
O
O
H
Cl
F
2c
0.50
2.56
2.00
1.01
1.00
2.07
3.07
f1 (ppm)

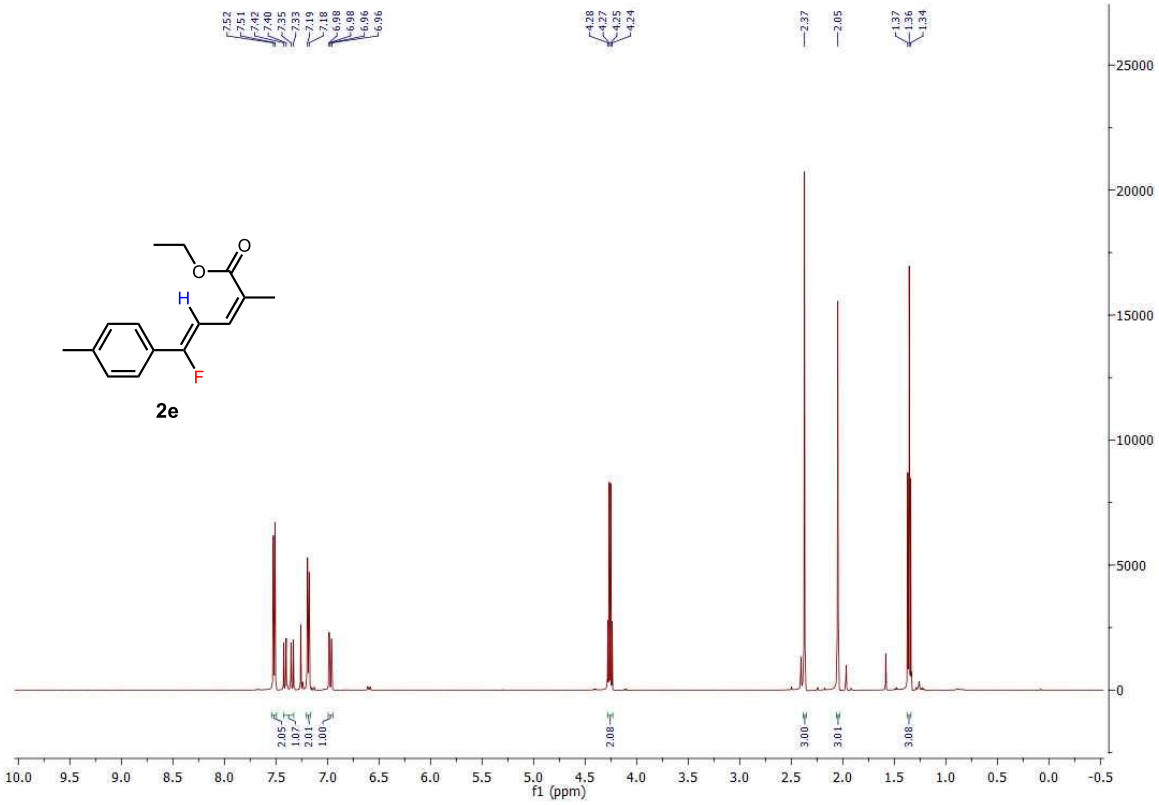

166.80
161.87
159.76
136.41
135.55
135.49
129.13
129.11
126.48
118.42
118.11
103.01
102.93
60.25
14.44
O
O
H
Cl
F
2c
f1 (ppm)

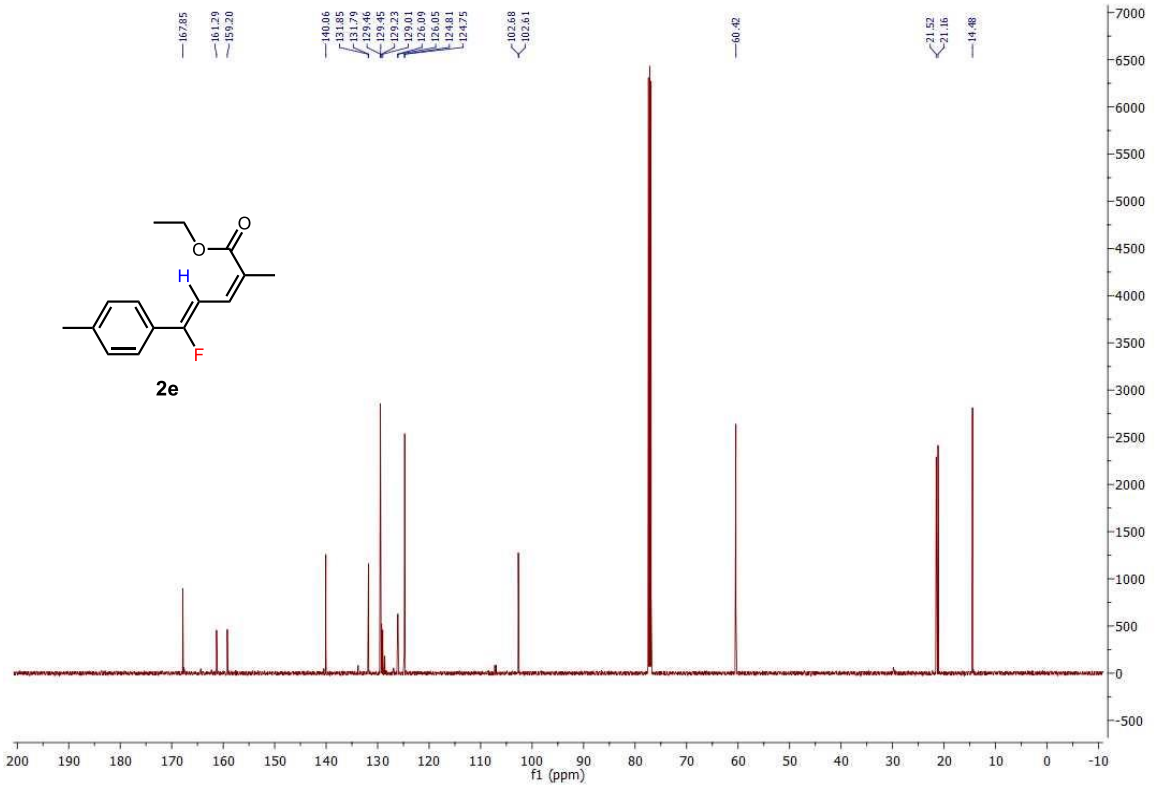

-111.90
-111.98
Cl
O
O
H
F
2c
1.00
f1 (ppm)

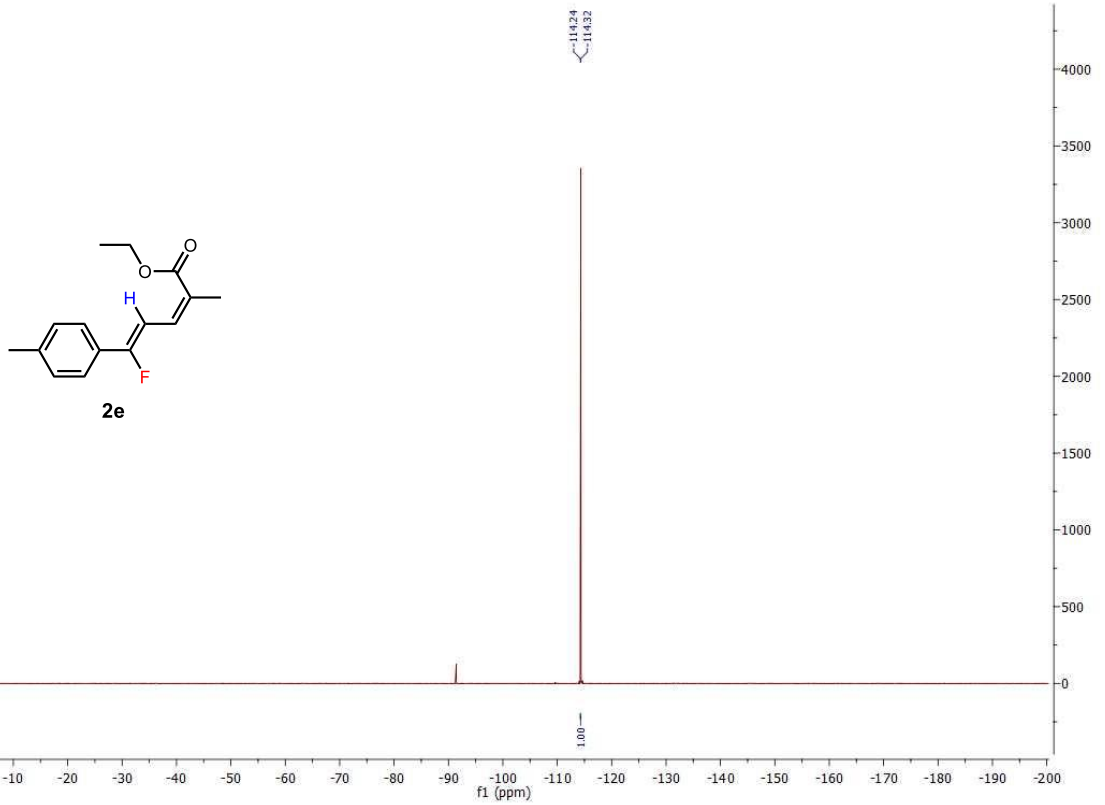

7.63
7.63
7.63
7.62
7.62
7.47
7.45
7.40
7.40
7.39
7.38
7.37
7.37
7.37
7.36
7.36
6.99
6.99
6.97
6.96
4.28
4.27
4.26
4.24
2.06
1.37
1.36
1.34
O
O
H
F
2d
2.01
0.53
3.51
1.00
2.00
3.02
3.01
f1 (ppm)


167.78
160.96
158.87
132.01
131.79
131.57
131.50
129.76
128.73
128.72
126.76
126.72
124.83
124.77
103.46
103.39
60.48
21.19
14.47
O
O
H
F
2d
f1 (ppm)

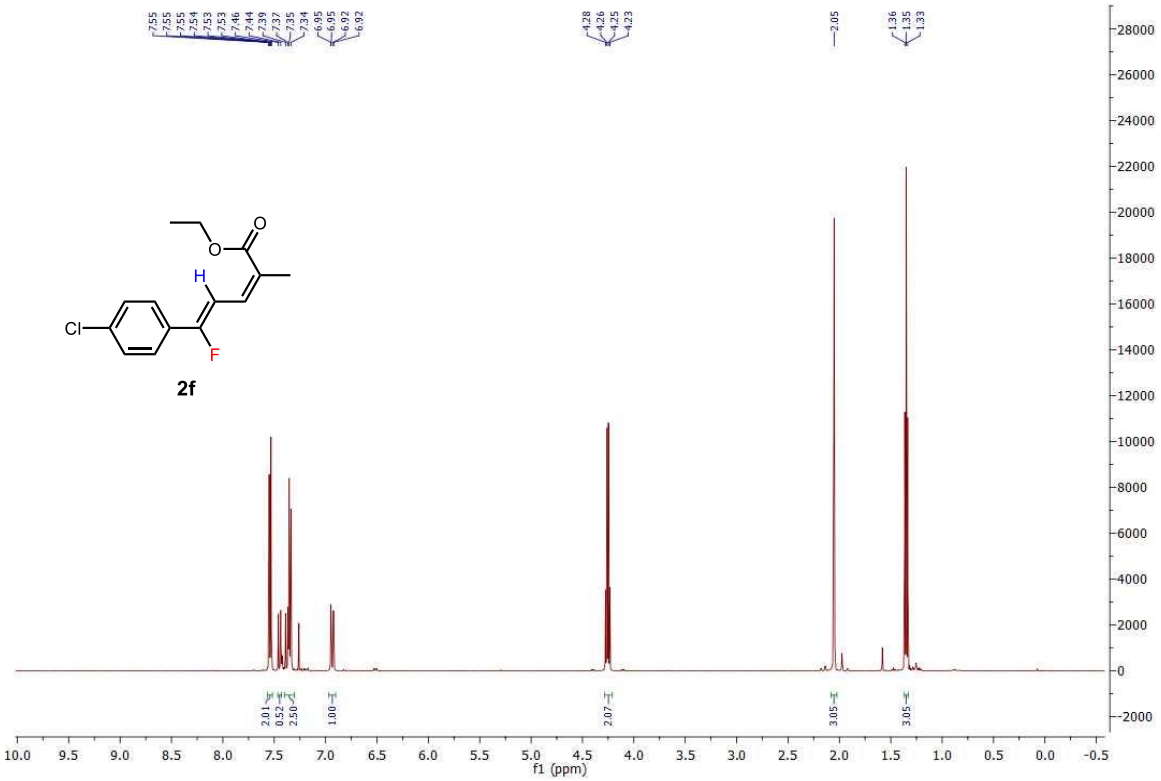

114.51
114.58
O
O
H
F
2d
1.00
f1 (ppm)


7.52
7.51
7.42
7.40
7.35
7.33
7.19
7.18
6.98
6.98
6.96
6.96
4.28
4.27
4.25
4.24
2.37
2.05
1.37
1.36
1.34
O
O
H
F
2e
2.05
1.07
2.01
1.00
2.08
3.00
3.01
3.08
f1 (ppm)

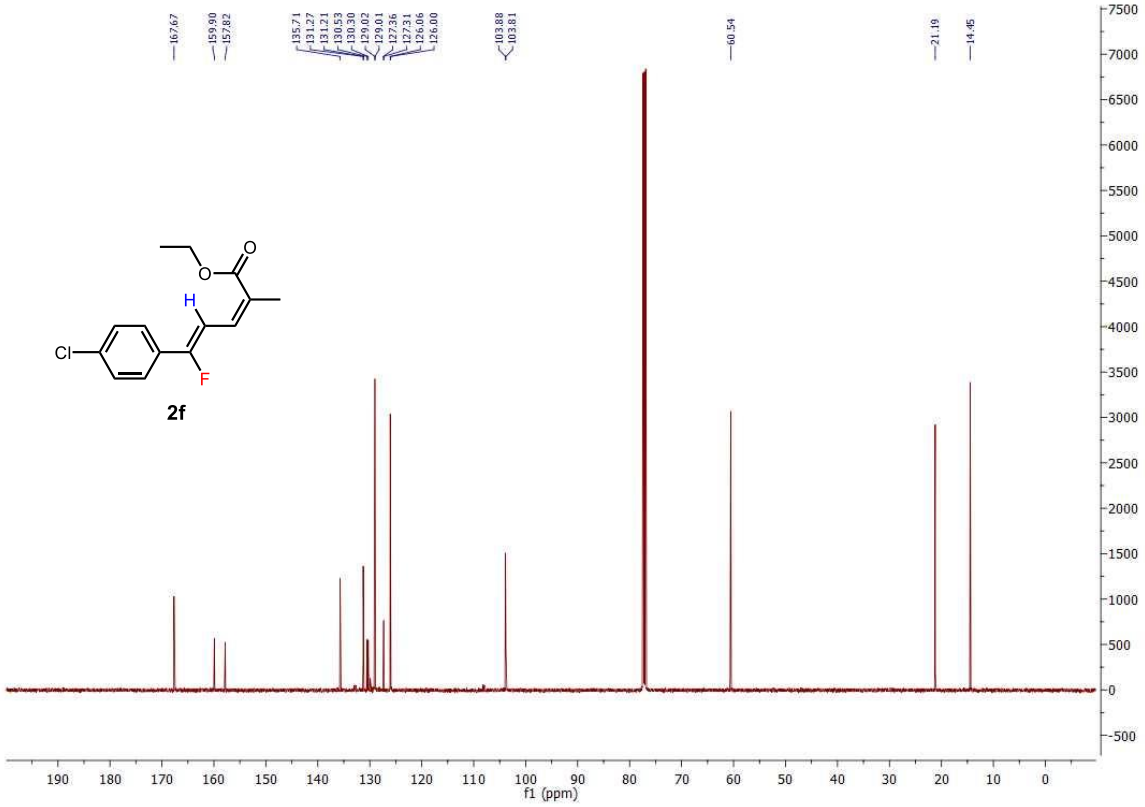

167.85
161.29
159.20
140.06
131.85
131.79
129.46
129.45
129.23
129.01
126.09
126.05
124.81
124.75
102.68
102.61
60.42
21.52
21.16
14.48
O
O
H
F
2e
f1 (ppm)


-114.24
-114.32
1.00
f1 (ppm)

2e


7.55
7.55
7.55
7.54
7.53
7.53
7.46
7.44
7.39
7.37
7.35
7.34
6.95
6.92
6.92
4.28
4.26
4.25
4.23
2.05
1.36
1.35
1.33
2.01
0.52
2.50
1.00
2.07
3.05
3.05
f1 (ppm)

2f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157.82
135.71
131.27
131.21
130.55
130.30
129.02
129.01
127.36
127.31
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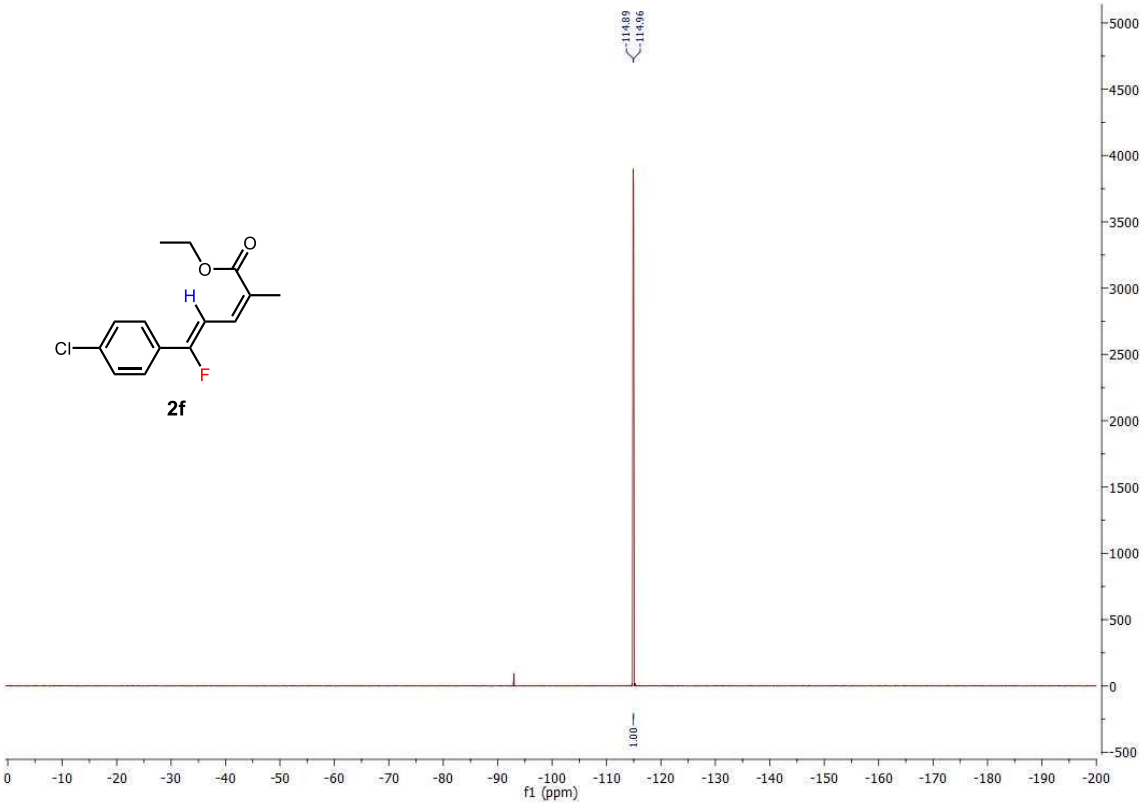
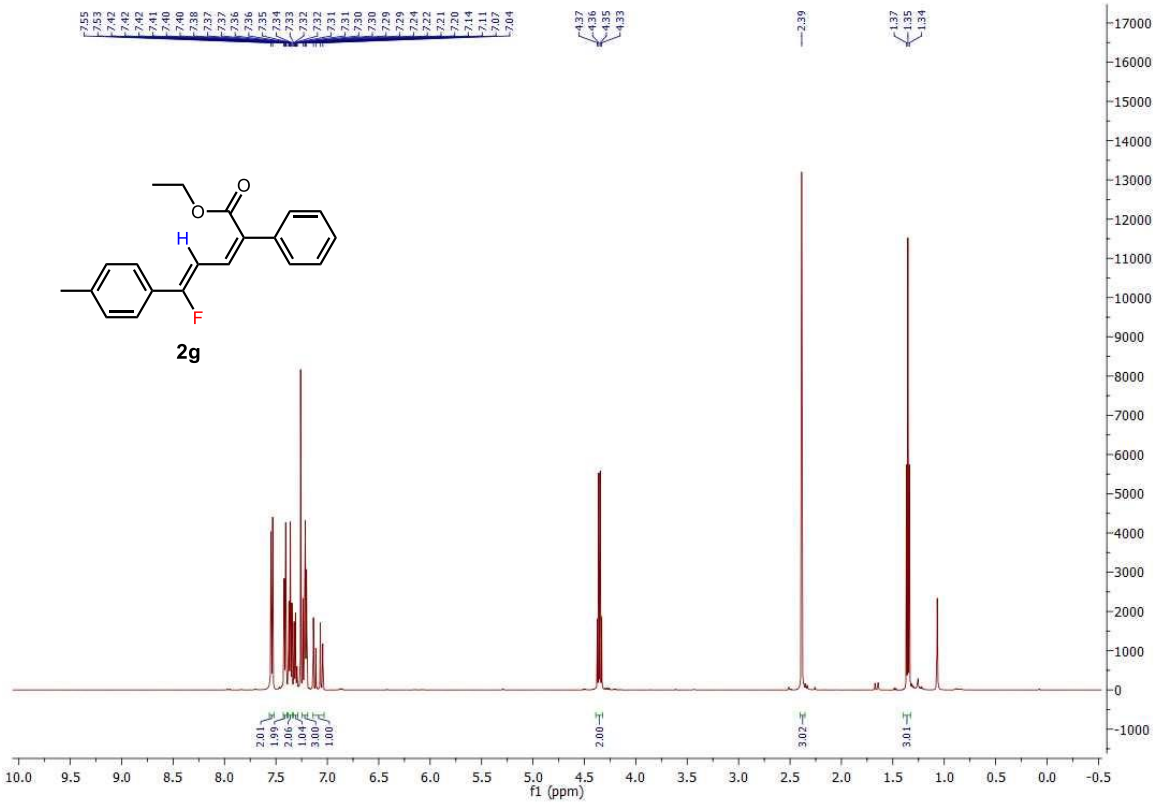
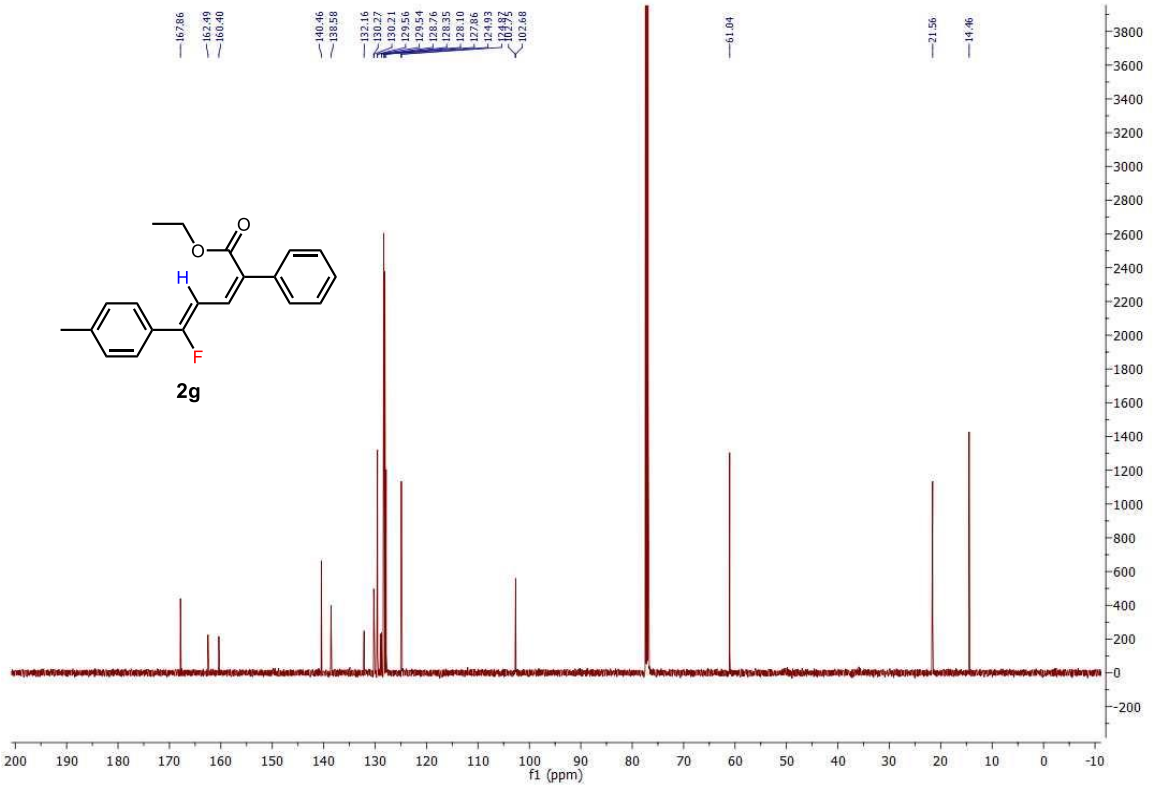
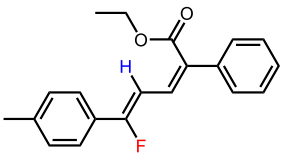
103.81
60.54
21.19
14.45
O
O
H
Cl
F
2f
f1 (ppm)


114.89
114.96
1.00
O
O
H
Cl
F
2f
f1 (ppm)

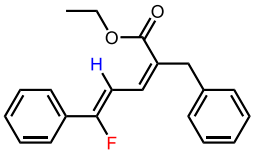

O
O
H
F
2g
f1 (ppm)


O
O
H
F
2g
f1 (ppm)



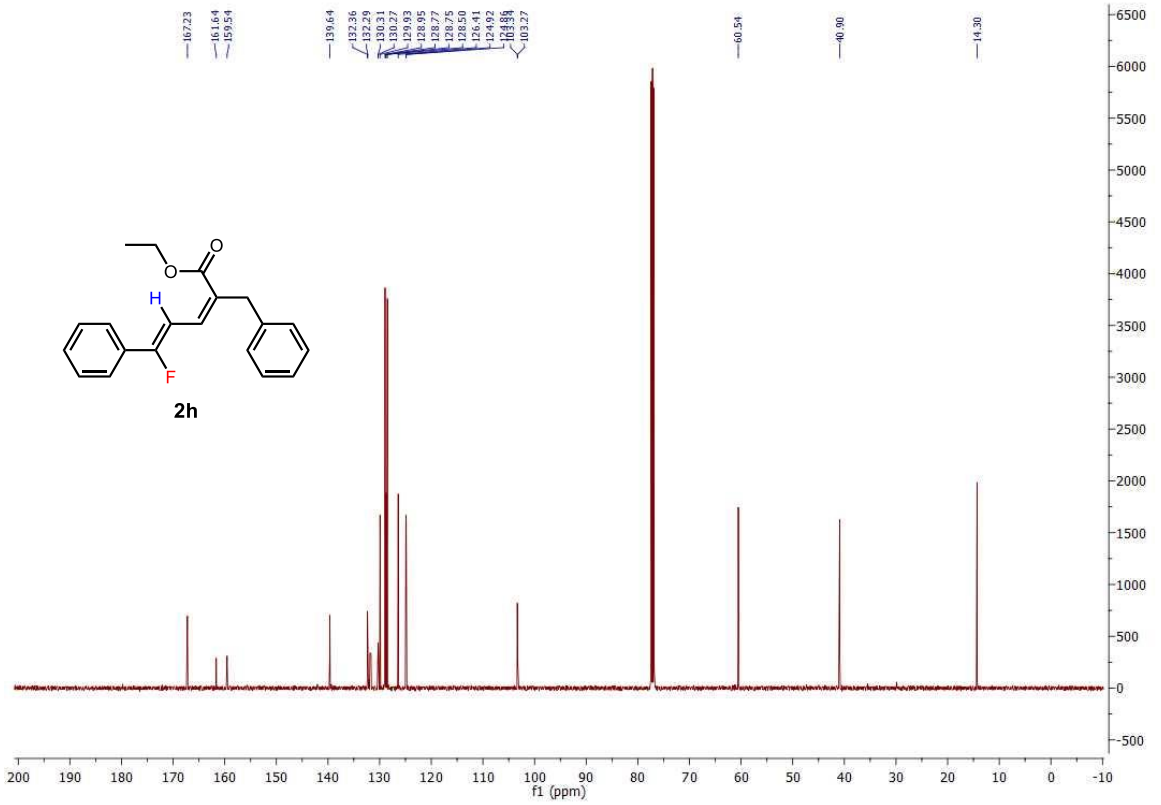
2g

-111.84
-111.91
1.00
f1 (ppm)



2h

7.54
7.54
7.53
7.53
7.53
7.52
7.38
7.36
7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.21
7.21
7.20
7.19
7.18
7.15
7.13
7.13
7.11
7.10
7.10
6.93
6.91
4.12
4.10
4.09
4.07
3.64
1.17
1.16
1.14
2.00
0.51
3.52
2.05
3.04
1.00
2.08
2.01
3.07
f1 (ppm)


167.23
161.64
159.54
139.64
132.36
132.29
130.31
130.27
129.93
128.95
128.77
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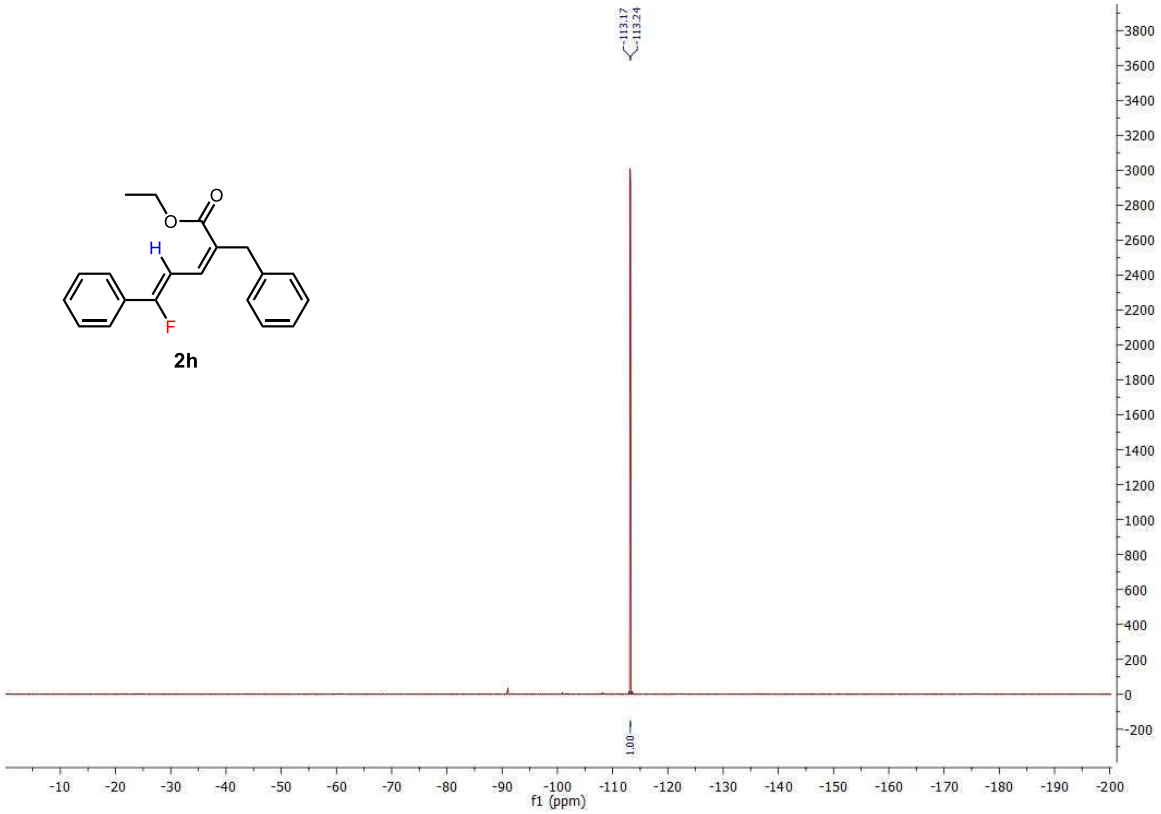
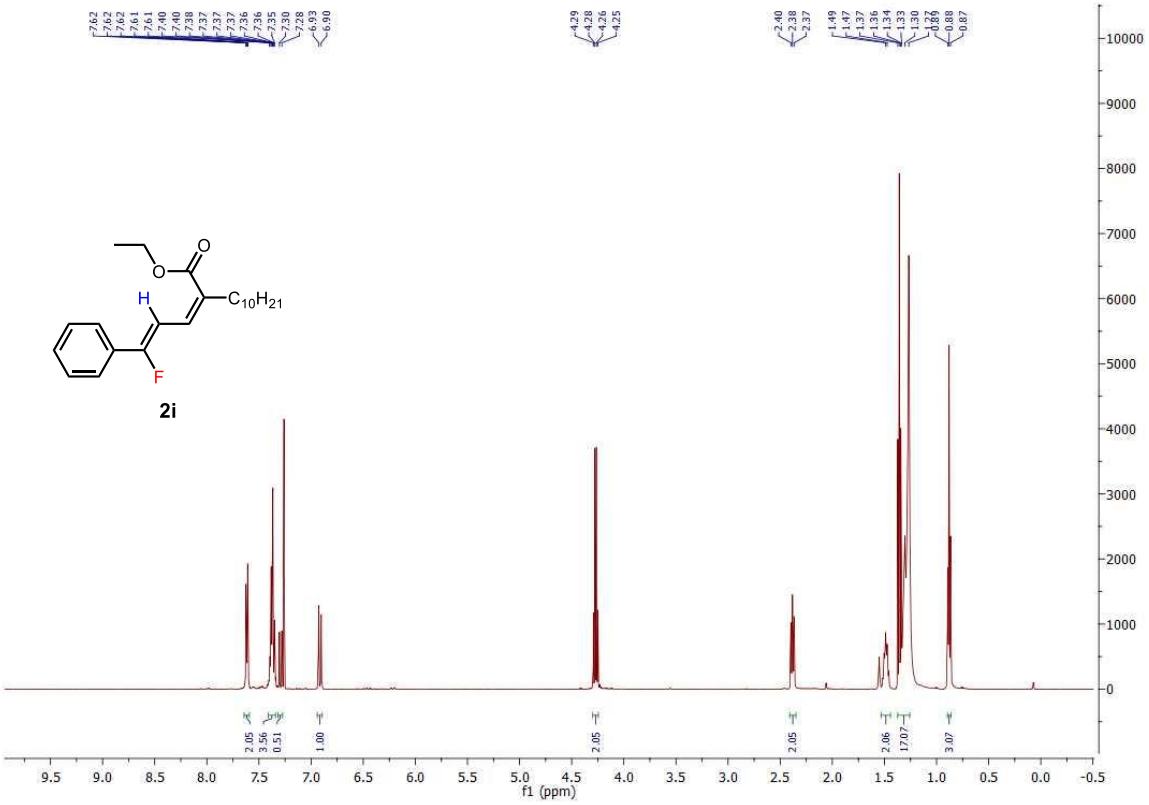
128.50
126.41
124.92
103.27
60.54
40.90
14.30
f1 (ppm)

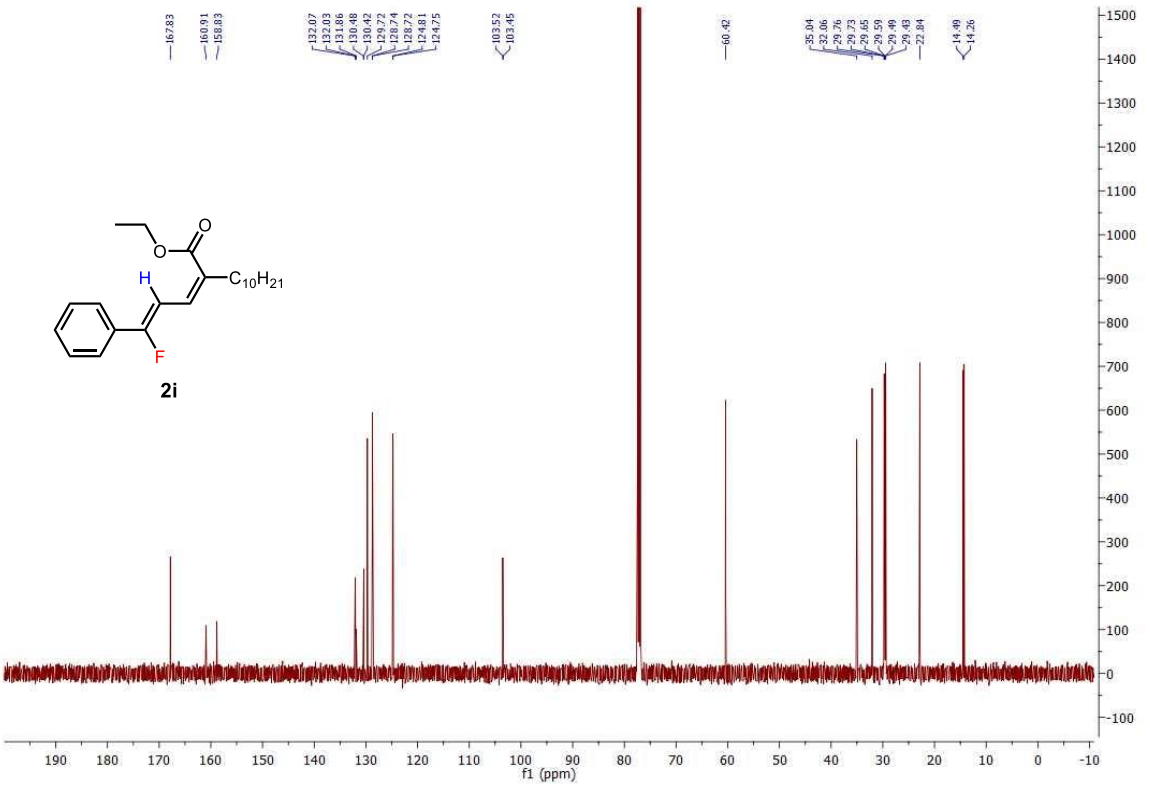
2h


113.17
113.24
1.00
f1 (ppm)

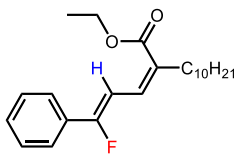
2h



2i

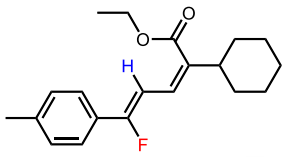


2i


O
O
H
$C_{10}H_{21}$
F

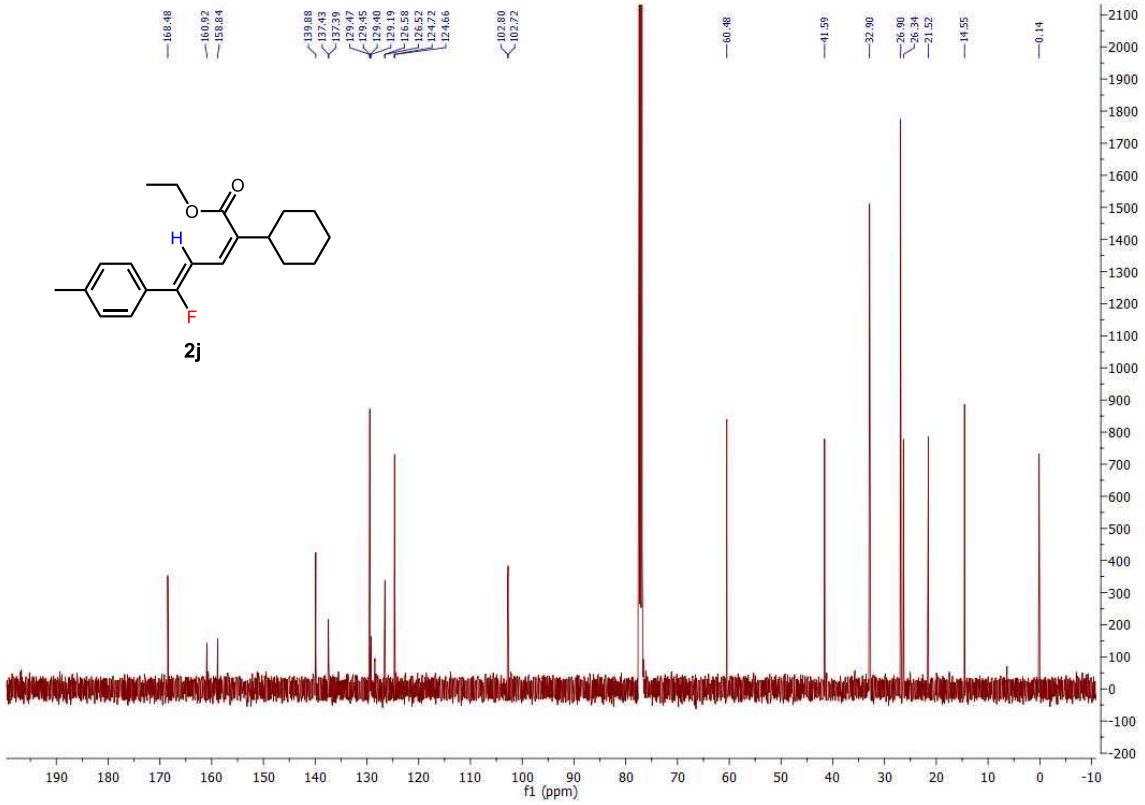
2i

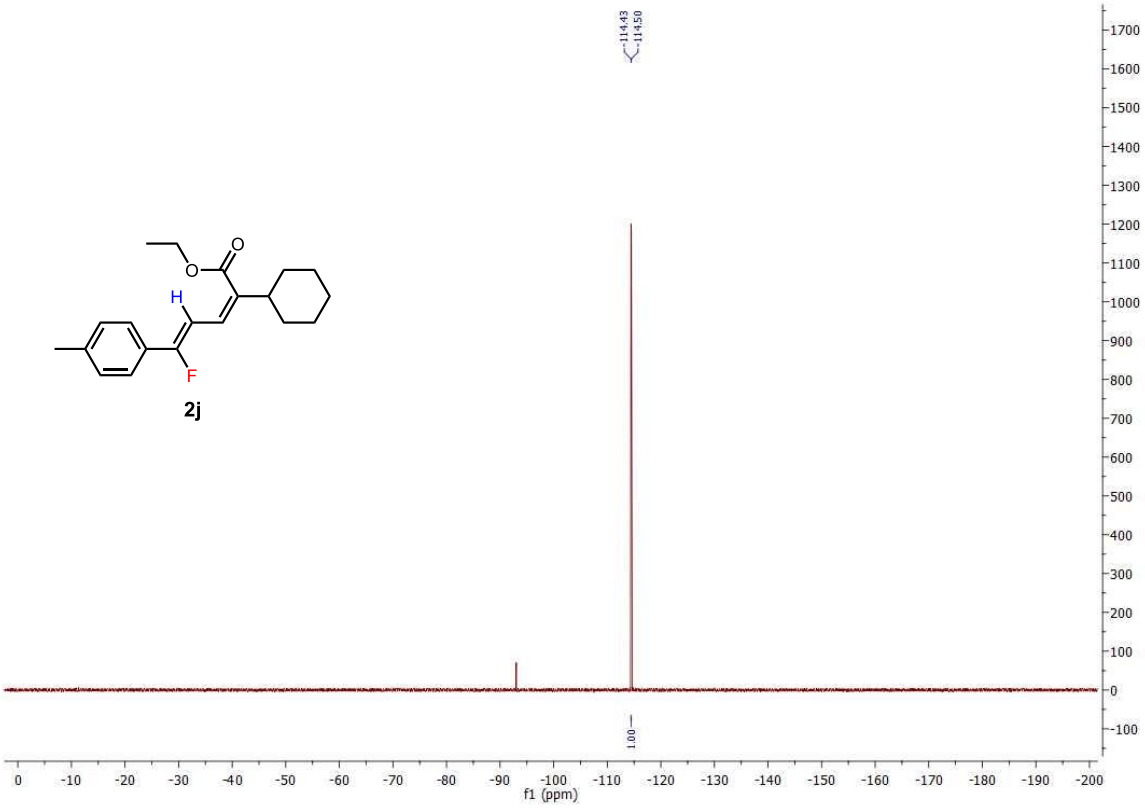
114.48
114.55
1.00
f1 (ppm)

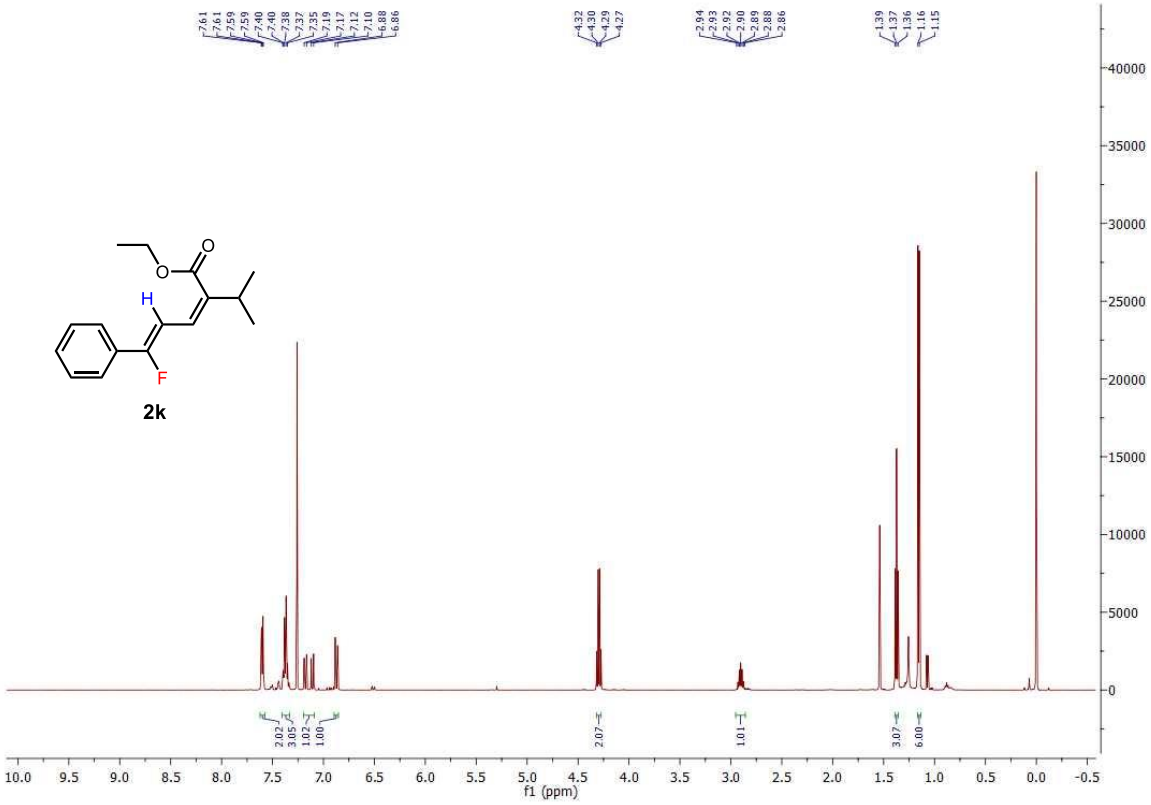

O
O
H
F

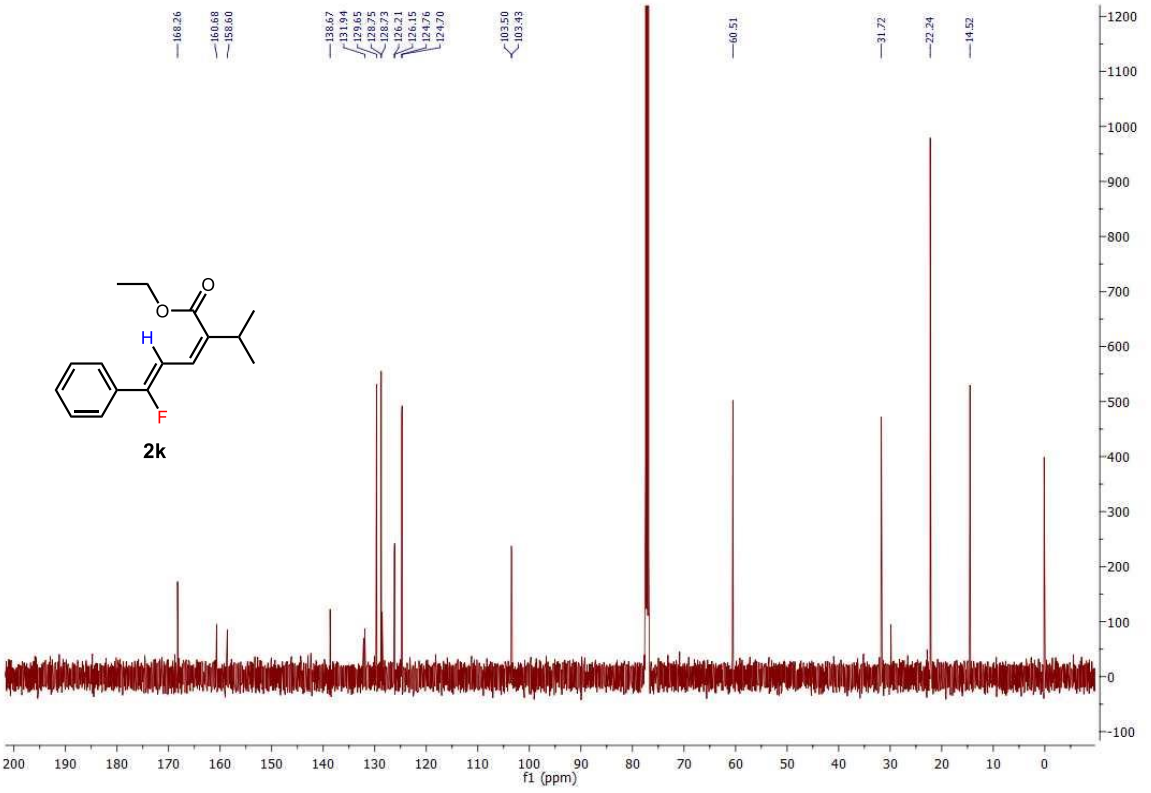
2j

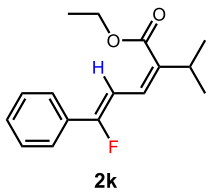
7.49
7.47
7.19
7.17
7.11
7.09
7.04
7.02
6.84
6.81
4.31
4.29
4.28
4.26
2.54
2.51
2.49
2.37
1.84
1.82
1.80
1.79
1.54
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.29
1.27
1.26
1.24
1.24
1.21
2.04
2.00
1.00
1.01
2.08
1.03
3.02
5.07
8.07
f1 (ppm)


168.48
160.92
158.84
139.88
137.43
137.39
129.47
129.45
129.40
129.19
126.58
126.52
124.72
124.66
102.80
102.72
60.48
41.59
32.90
26.90
26.34
21.52
14.55
0.14
O
O
H
F
2j
f1 (ppm)


114.43
114.50
1.00
O
O
H
F
2j
f1 (ppm)

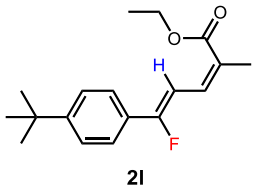

7.61
7.61
7.59
7.59
7.40
7.40
7.38
7.37
7.35
7.19
7.17
7.12
7.10
6.88
6.86
4.32
4.30
4.29
4.27
2.94
2.93
2.92
2.90
2.89
2.88
2.86
1.39
1.37
1.36
1.16
1.15
O
O
H
F
2k
2.02
3.05
1.02
1.00
2.07
1.01
3.07
6.00
f1 (ppm)


168.26
160.68
158.60
138.67
131.94
129.65
128.75
128.73
126.21
126.15
124.76
124.70
103.50
103.43
60.51
31.72
22.24
14.52
O
O
H
F
2k
f1 (ppm)



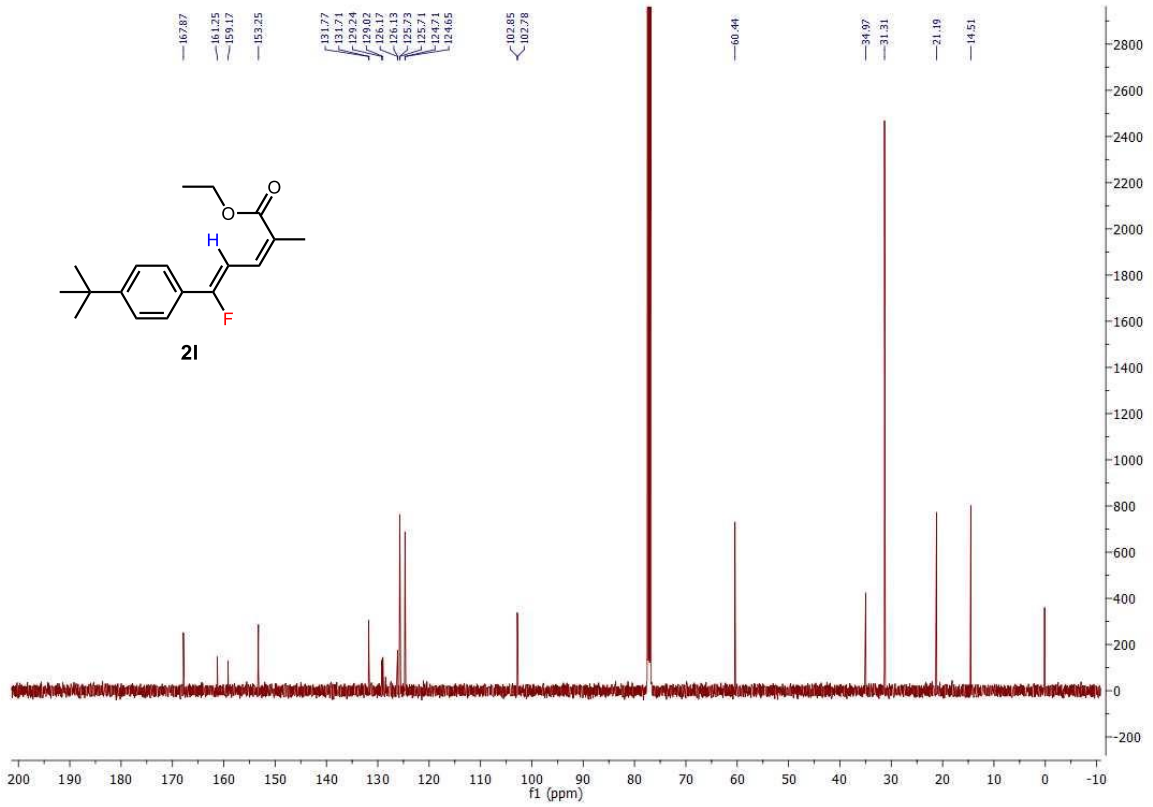
2k

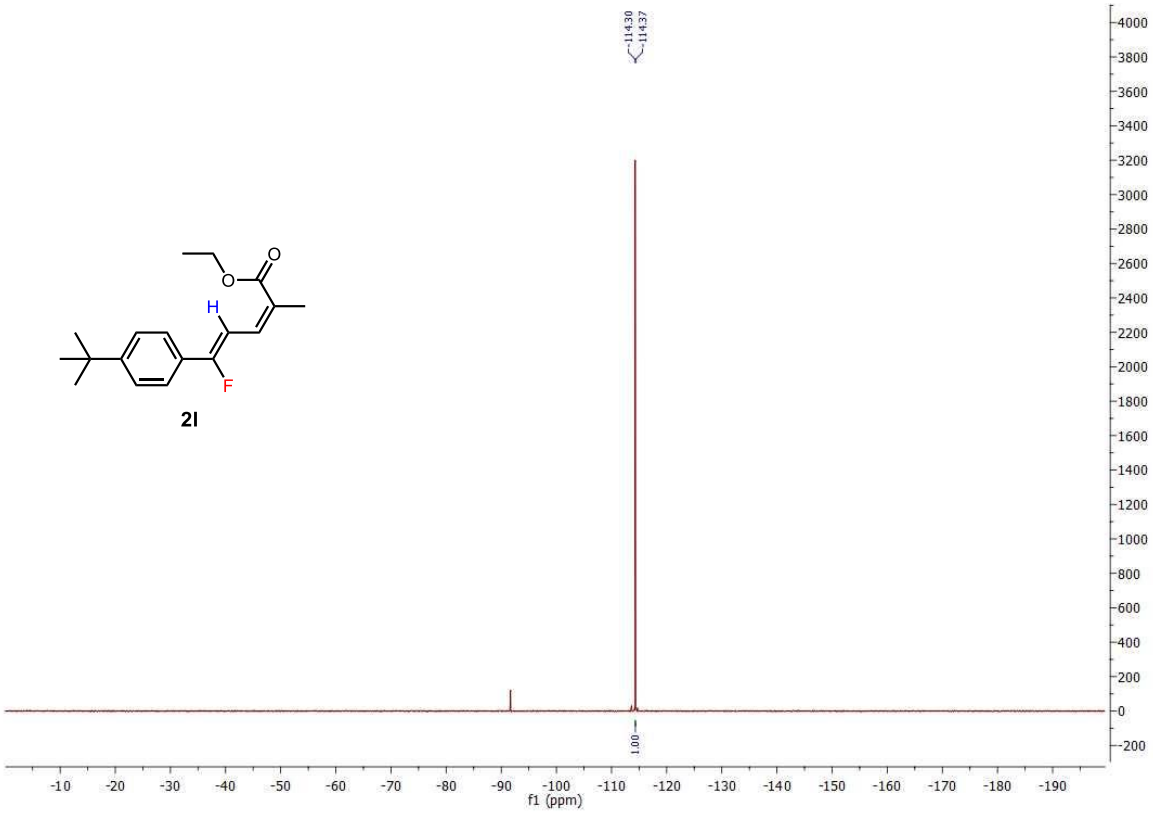
-114.59
-114.67
1.00
f1 (ppm)

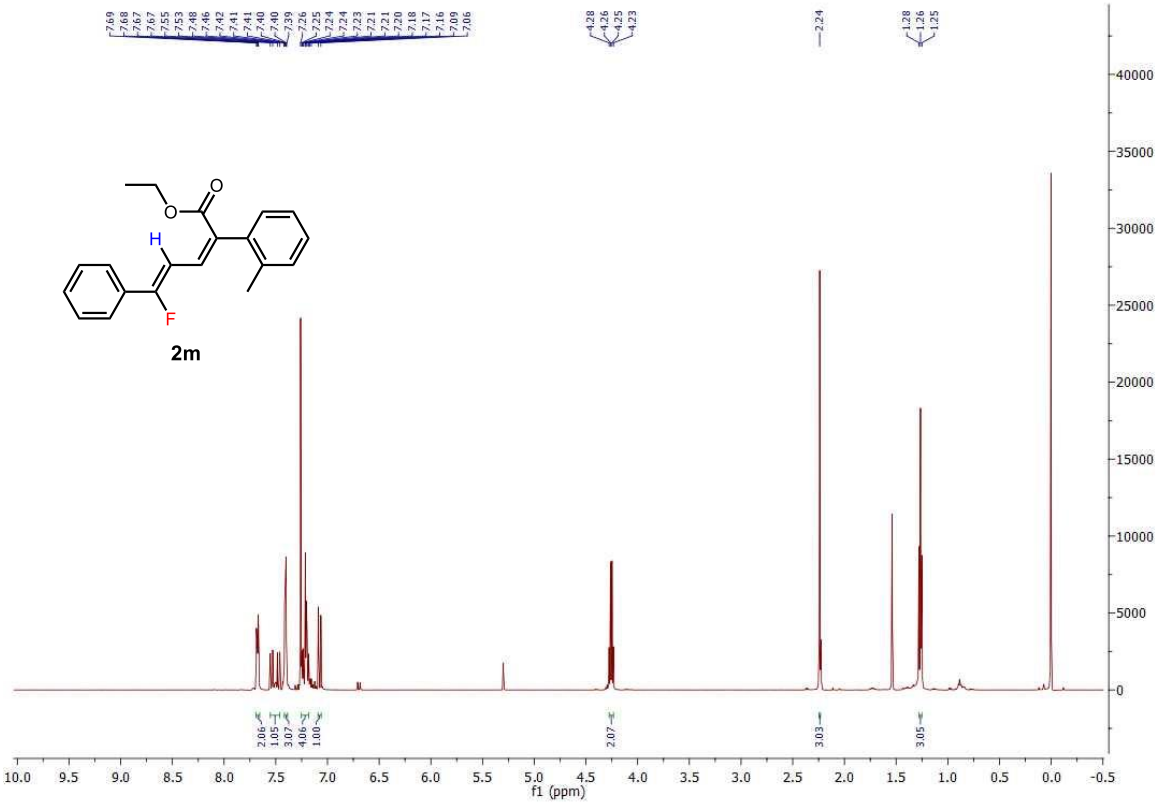


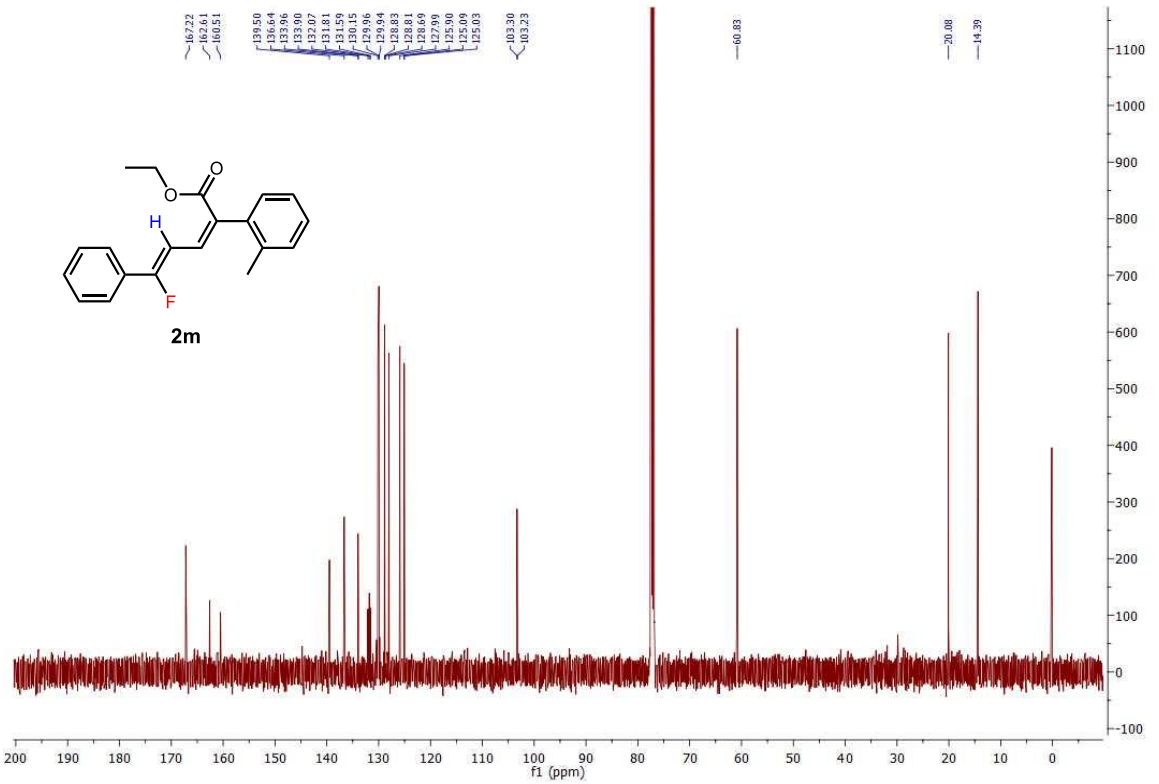
2l

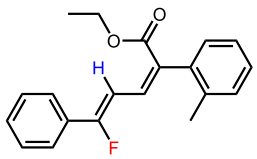
7.57
7.55
7.41
7.41
7.39
7.34
7.32
6.99
6.98
6.96
6.96
4.28
4.27
4.25
4.24
2.05
1.37
1.36
1.35
1.33
2.00
2.50
0.50
1.00
2.05
3.03
3.08
9.02
f1 (ppm)


167.87
161.25
159.17
153.25
131.77
131.71
129.24
129.02
126.17
126.13
125.73
125.71
124.71
124.65
102.85
102.78
60.44
34.97
31.31
21.19
14.51
O
O
H
F
2l
f1 (ppm)


114.30
114.37
1.00
O
O
H
F
2l
f1 (ppm)

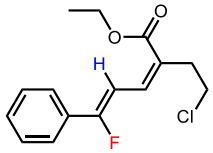

2m
f1 (ppm)


2m
f1 (ppm)



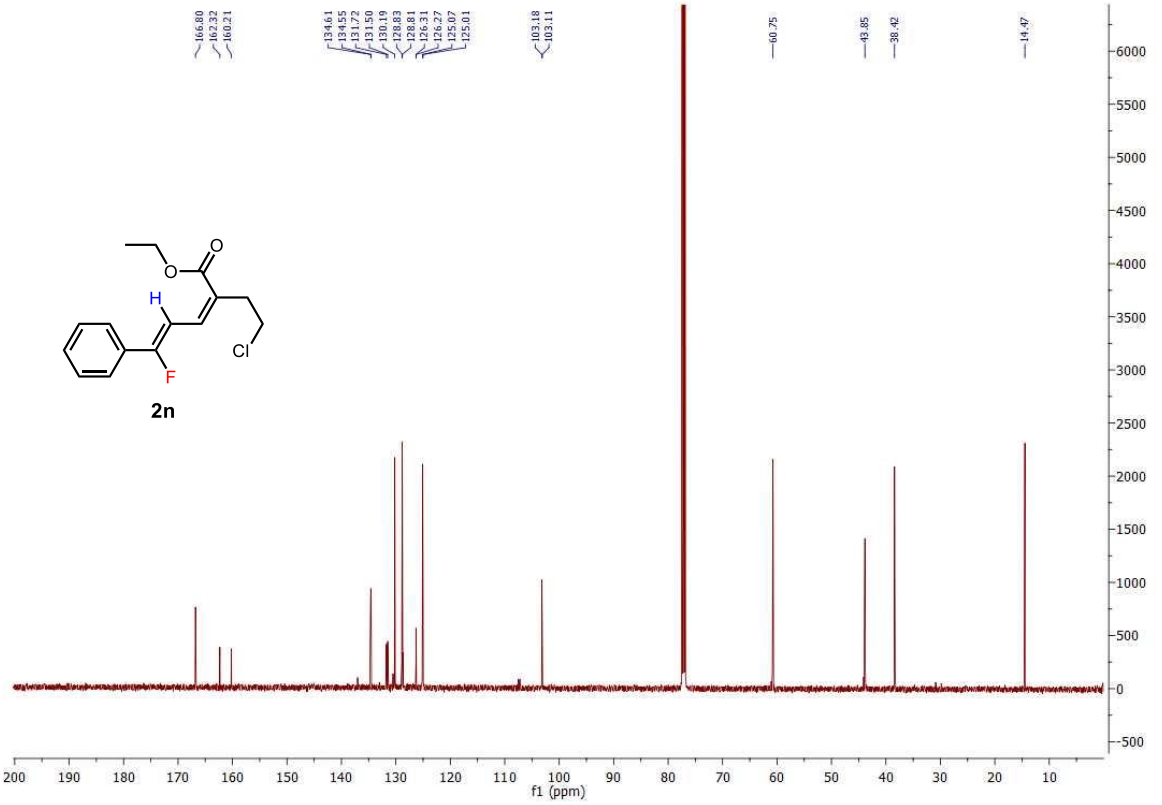
2m

111.91
111.98
1.00
f1 (ppm)



2n

7.65
7.64
7.63
7.63
7.49
7.47
7.42
7.41
7.40
7.39
7.09
7.07
4.31
4.30
4.28
4.27
3.70
3.68
3.67
2.86
2.84
2.83
1.38
1.37
1.36
2.00
0.56
3.50
1.00
2.06
2.06
2.01
3.05
f1 (ppm)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160.21
134.61
134.55
131.72
131.50
130.19
128.83
128.81
126.31
126.27
125.07
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60.75
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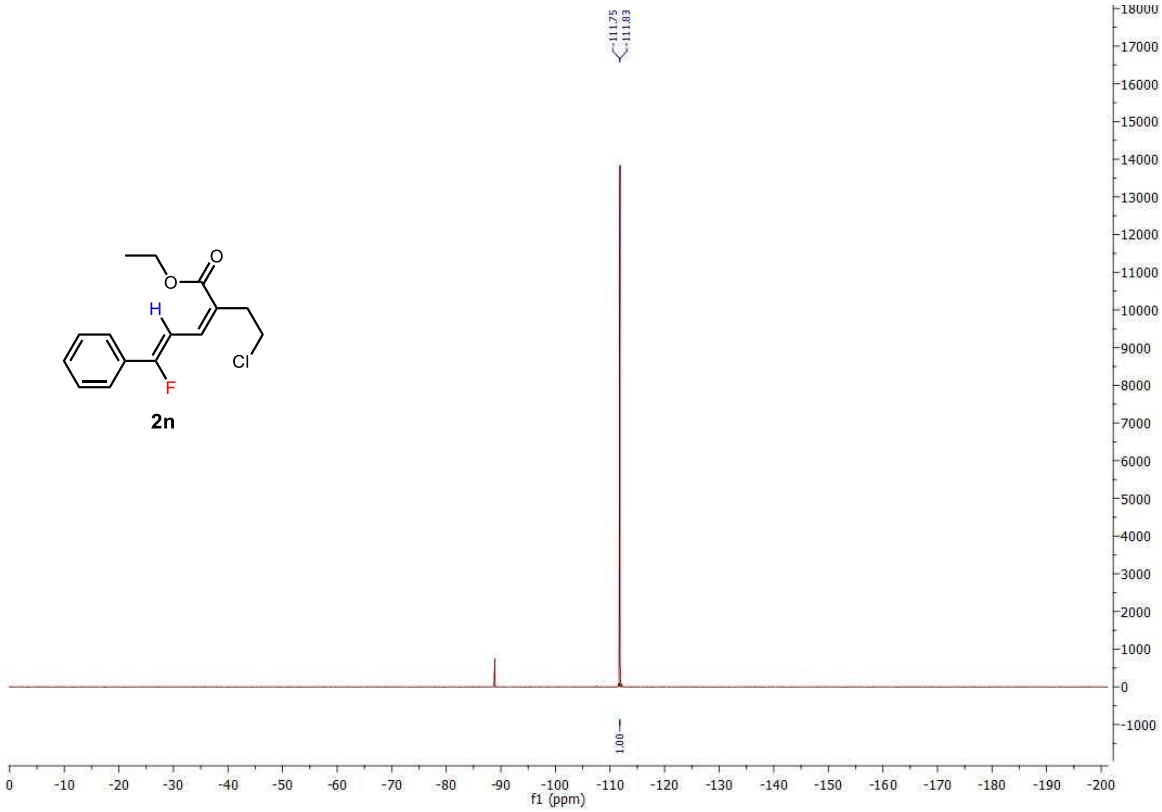
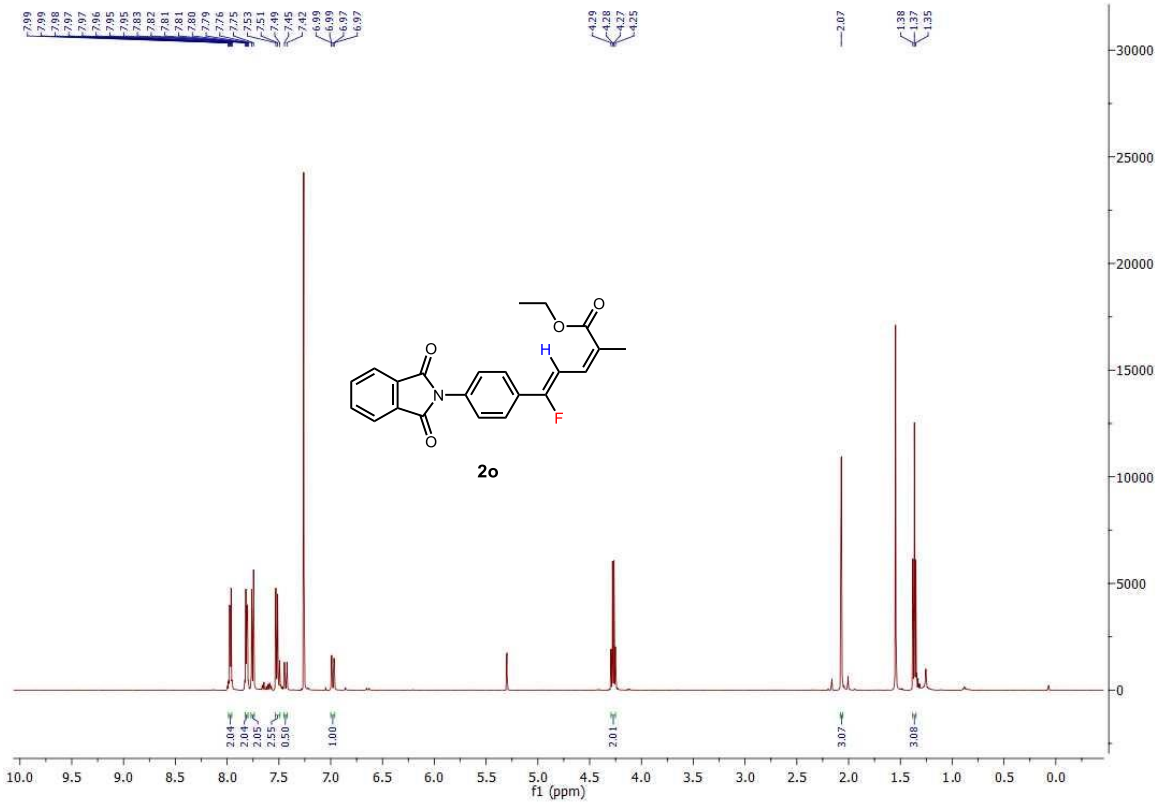
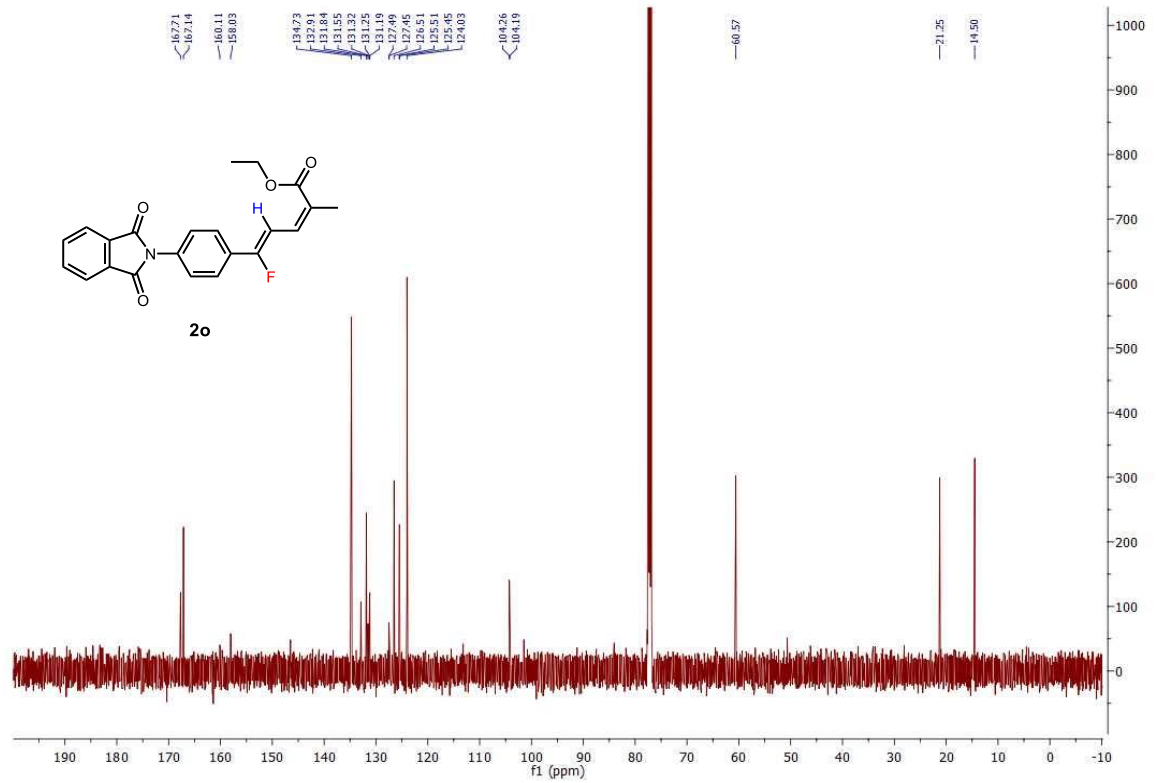
38.42
14.47
O
O
H
Cl
F
2n
f1 (ppm)

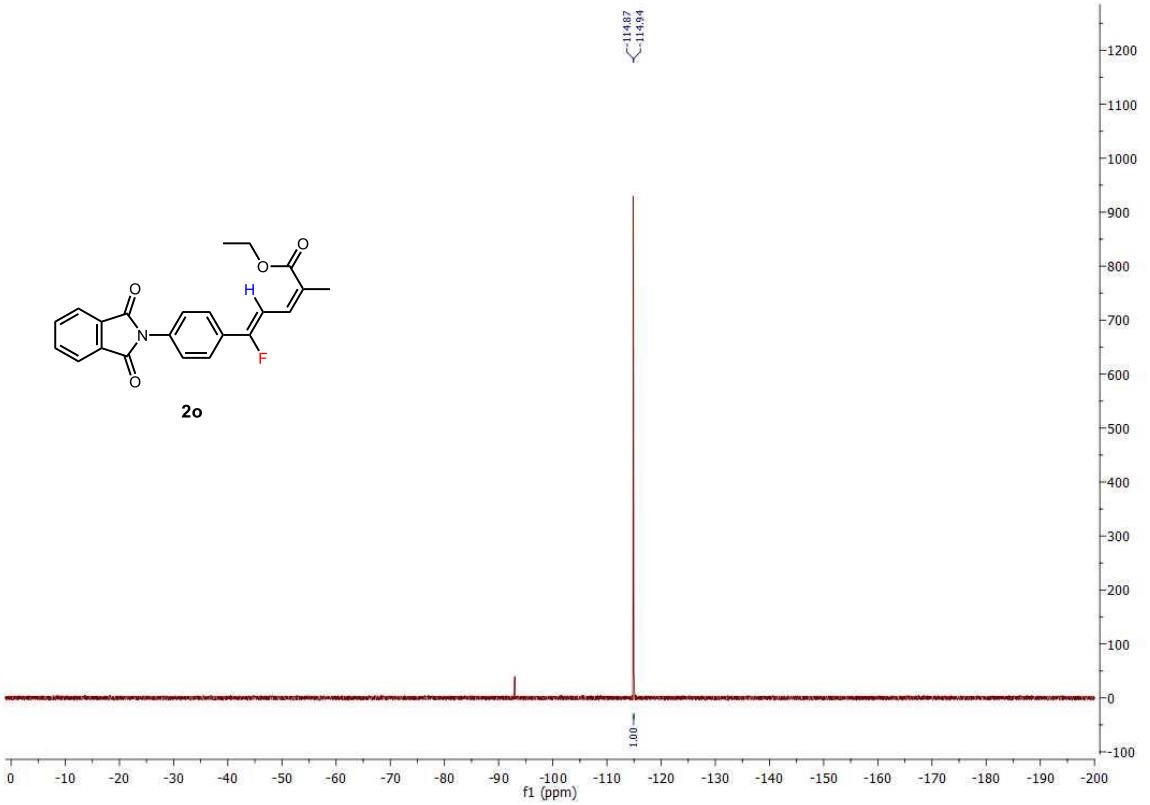

-111.75
-111.83
1.00
O
O
H
Cl
F
2n
f1 (ppm)


7.99
7.99
7.98
7.97
7.97
7.96
7.95
7.95
7.83
7.82
7.81
7.81
7.80
7.80
7.79
7.76
7.75
7.53
7.51
7.49
7.45
7.42
6.99
6.99
6.97
6.97
4.29
4.28
4.27
4.25
2.07
1.38
1.37
1.35
2.04
2.04
2.05
2.55
0.50
1.00
2.01
3.07
3.08
f1 (ppm)

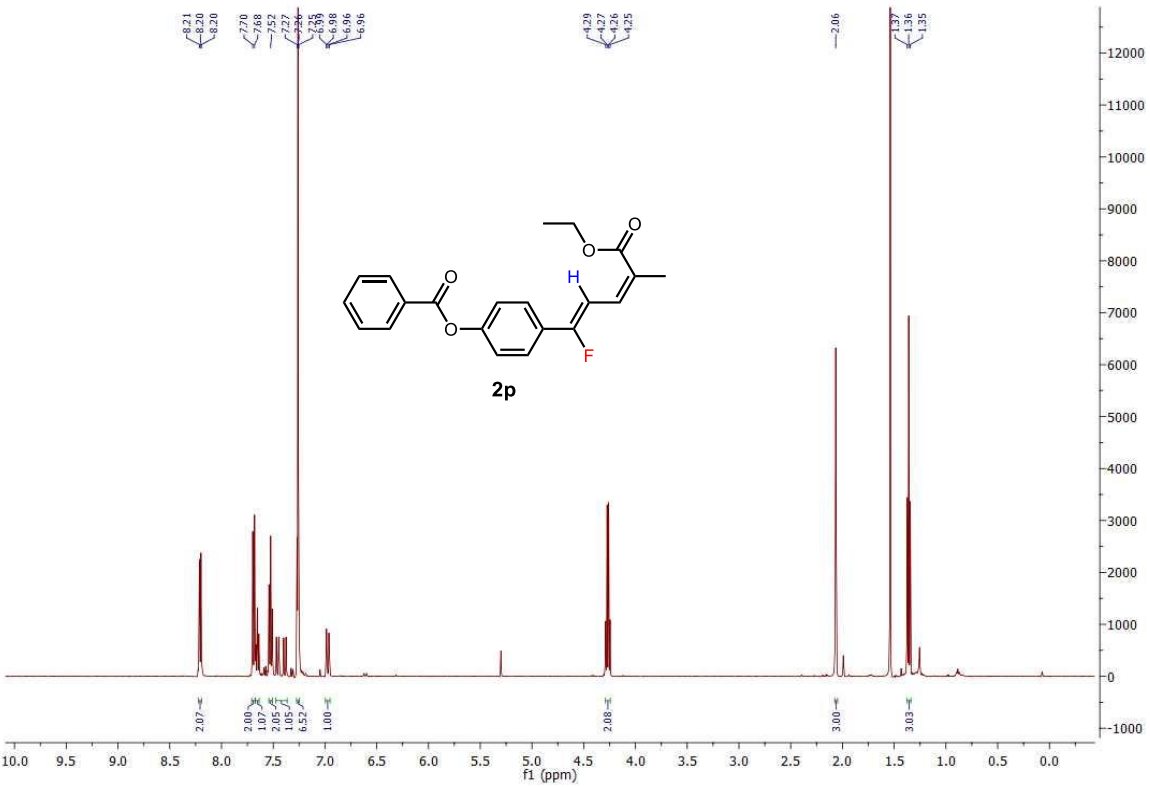
2o


167.1
167.14
160.11
158.03
134.73
132.91
131.84
131.55
131.32
131.25
131.19
127.49
127.45
126.51
125.51
125.45
124.03
104.26
104.19
60.57
21.25
14.50
f1 (ppm)

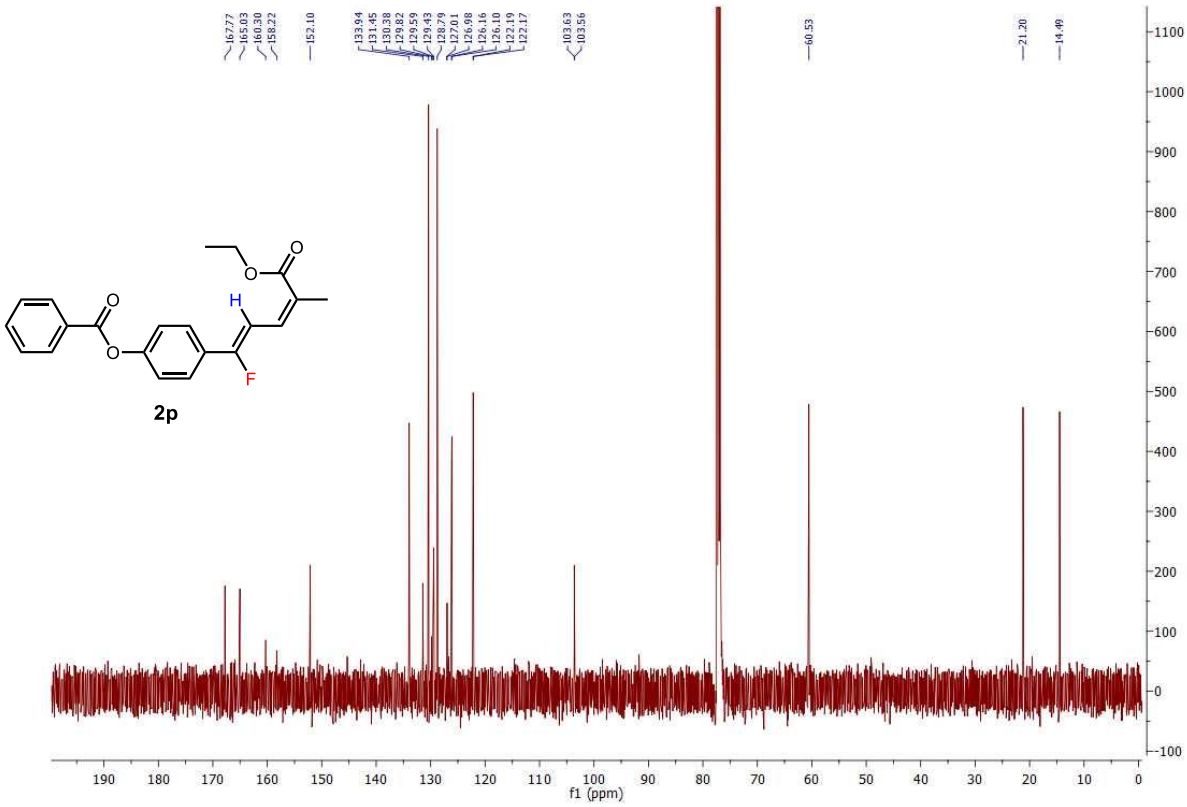
2o


-114.87
-114.94
1.00
f1 (ppm)

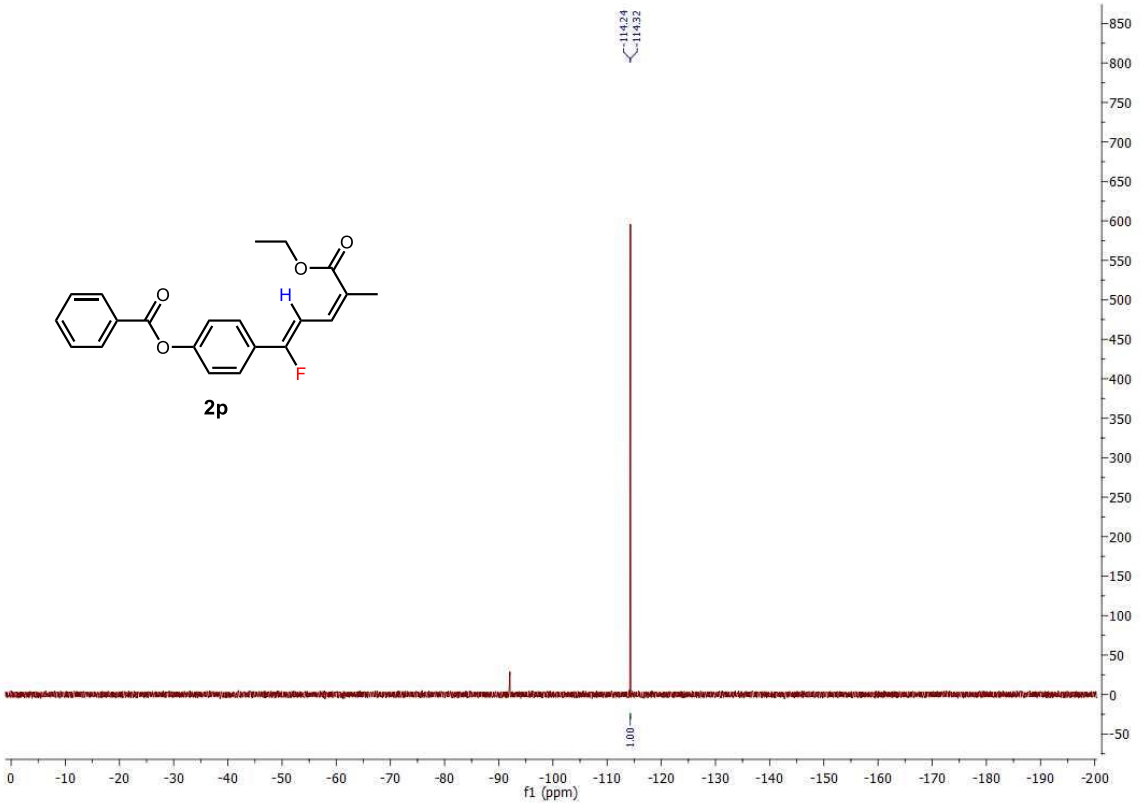
2o


8.21
8.20
8.20
7.70
7.68
7.52
7.27
7.26
6.98
6.96
6.96
4.29
4.27
4.26
4.25
2.06
1.37
1.36
1.35
2.07
2.00
1.07
2.05
1.05
6.52
1.00
2.08
3.00
3.03
f1 (ppm)

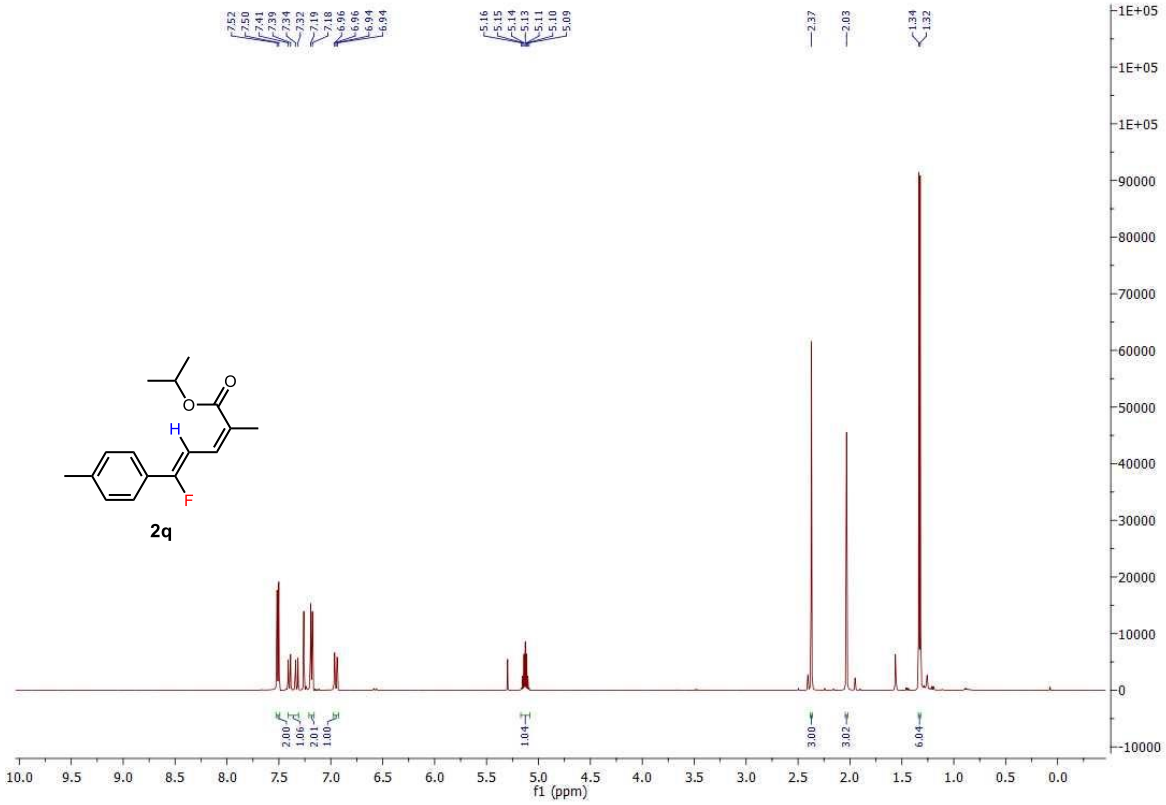
2p


167.77
165.03
160.30
158.22
152.10
133.94
131.45
130.38
129.82
129.59
129.43
128.79
127.01
126.98
126.16
126.10
123.19
122.17
103.63
103.56
60.53
21.20
14.49
f1 (ppm)

2p


114.24
114.32
1.00
f1 (ppm)

2p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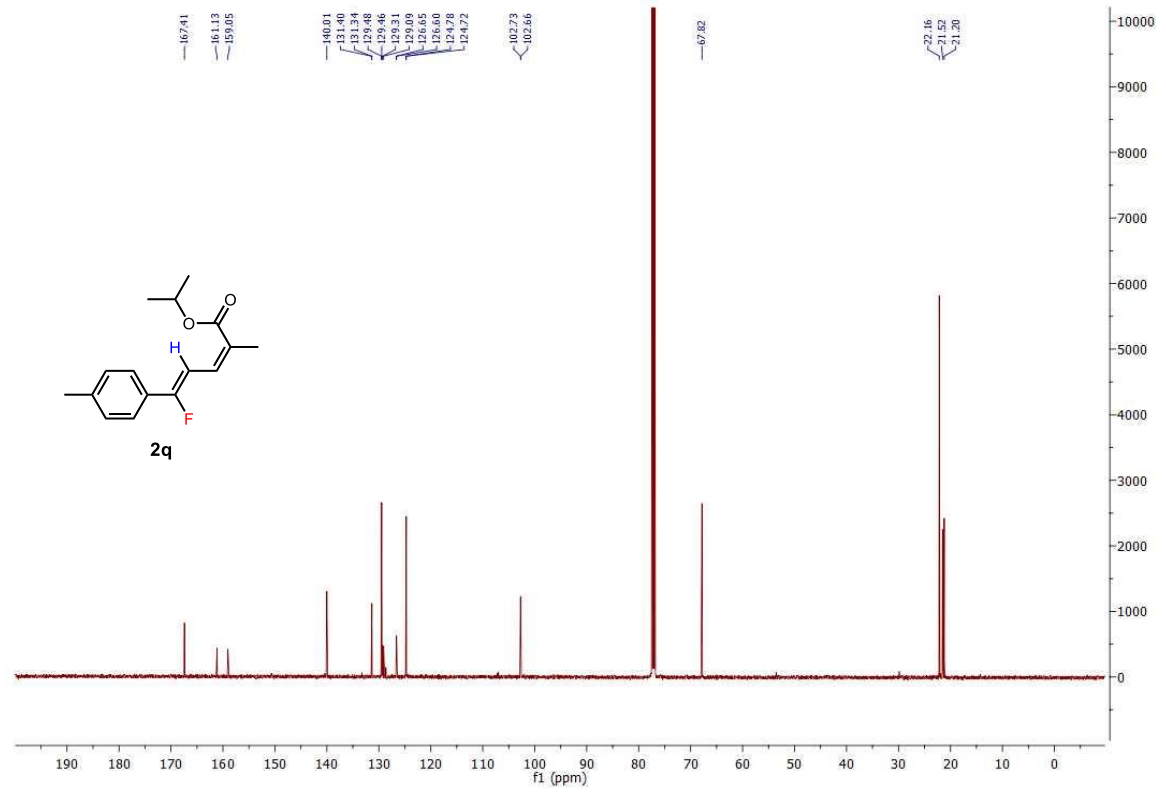
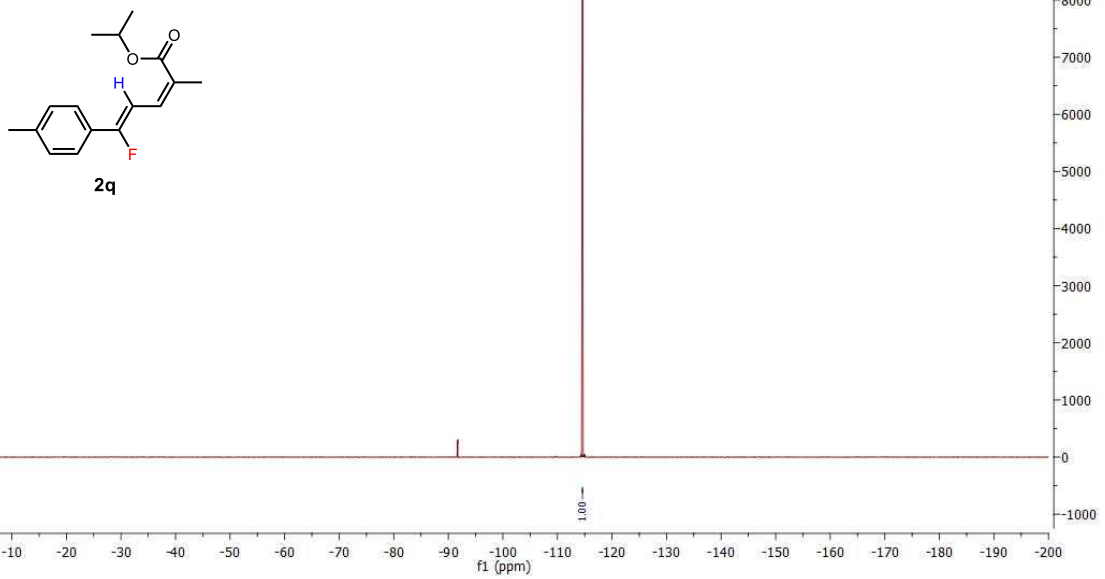
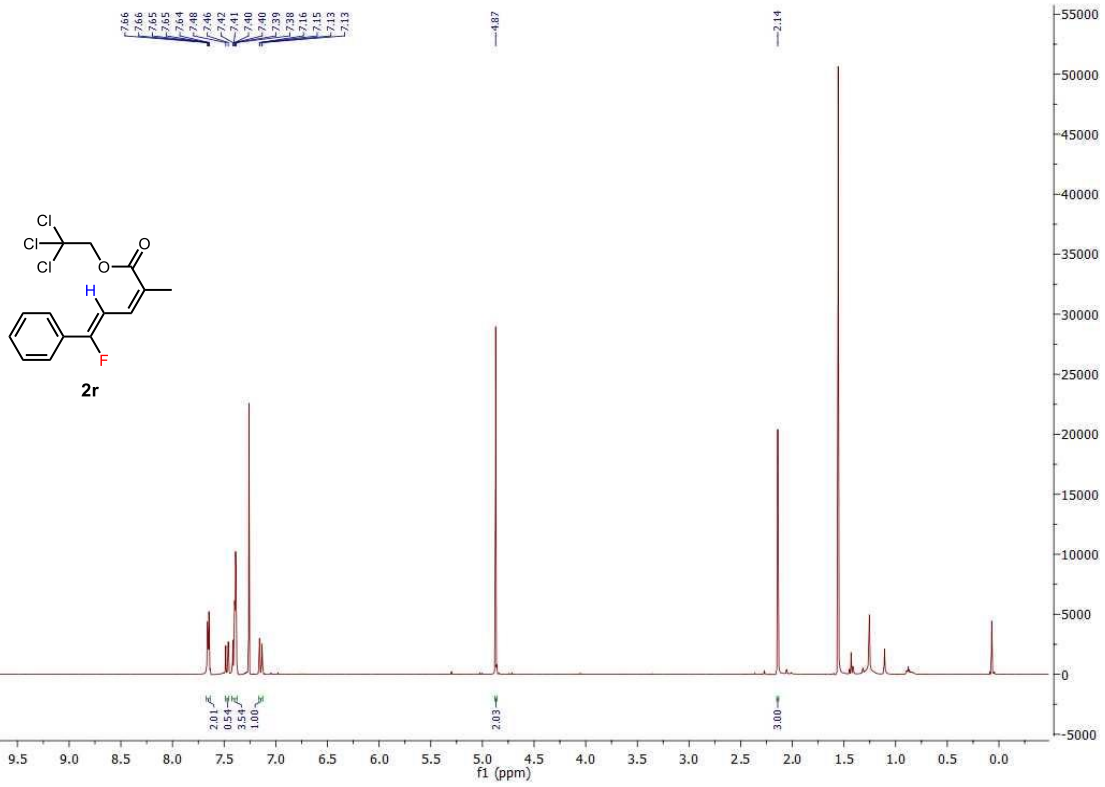
7.39
7.34
7.32
7.19
7.18
6.96
6.96
6.94
6.94
5.16
5.15
5.14
5.13
5.11
5.10
5.09
2.37
2.03
1.34
1.32
O
O
H
F
2q
2.00
1.06
2.01
1.00
1.04
3.00
3.02
6.04
f1 (ppm)


167.41
161.13
159.05
140.01
131.40
131.34
129.48
129.46
129.31
129.09
126.65
126.60
124.78
124.72
102.73
102.66
67.82
22.16
21.52
21.20
O
O
H
F
2q
f1 (ppm)


-114.55
-114.62
1.00
f1 (ppm)

2q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7.66
7.65
7.65
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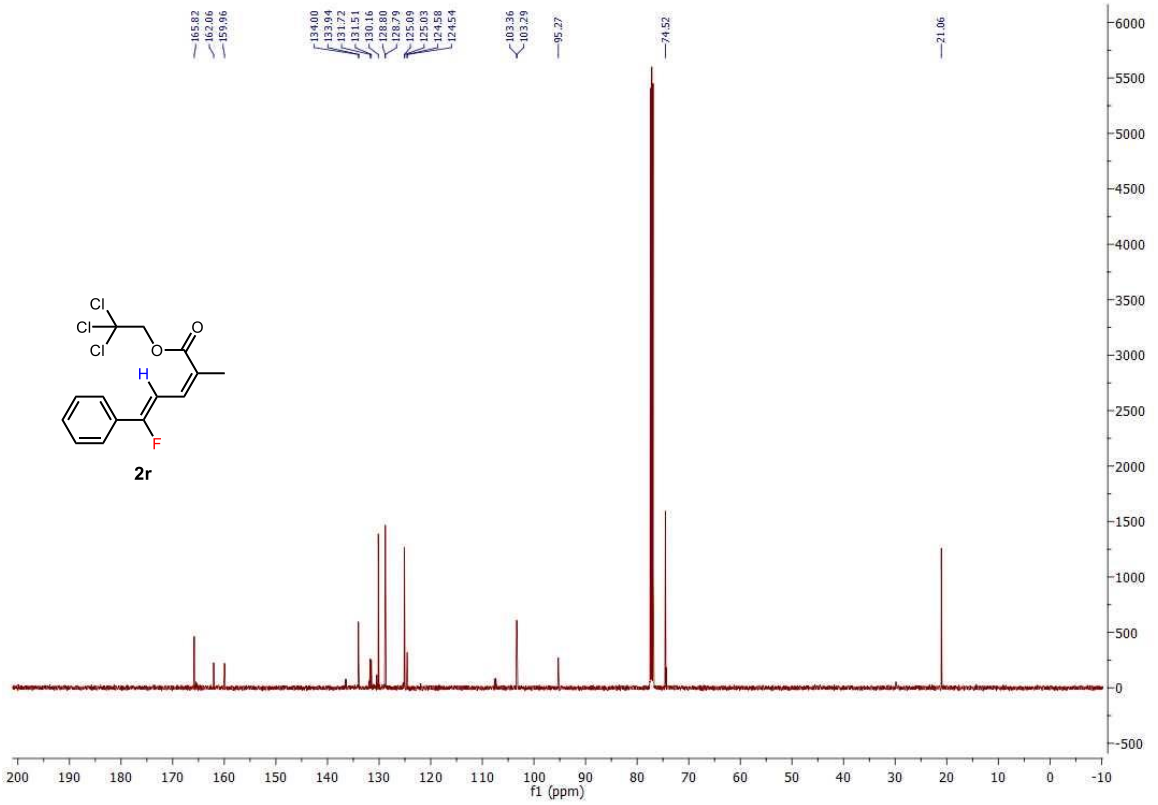
7.64
7.46
7.42
7.41
7.40
7.40
7.39
7.38
7.16
7.15
7.13
7.13
4.87
2.14
2.01
0.54
3.54
1.00
2.03
3.00
f1 (ppm)

2r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162.06
159.96
134.00
133.94
131.72
131.51
130.16
128.80
128.79
125.09
125.03
124.58
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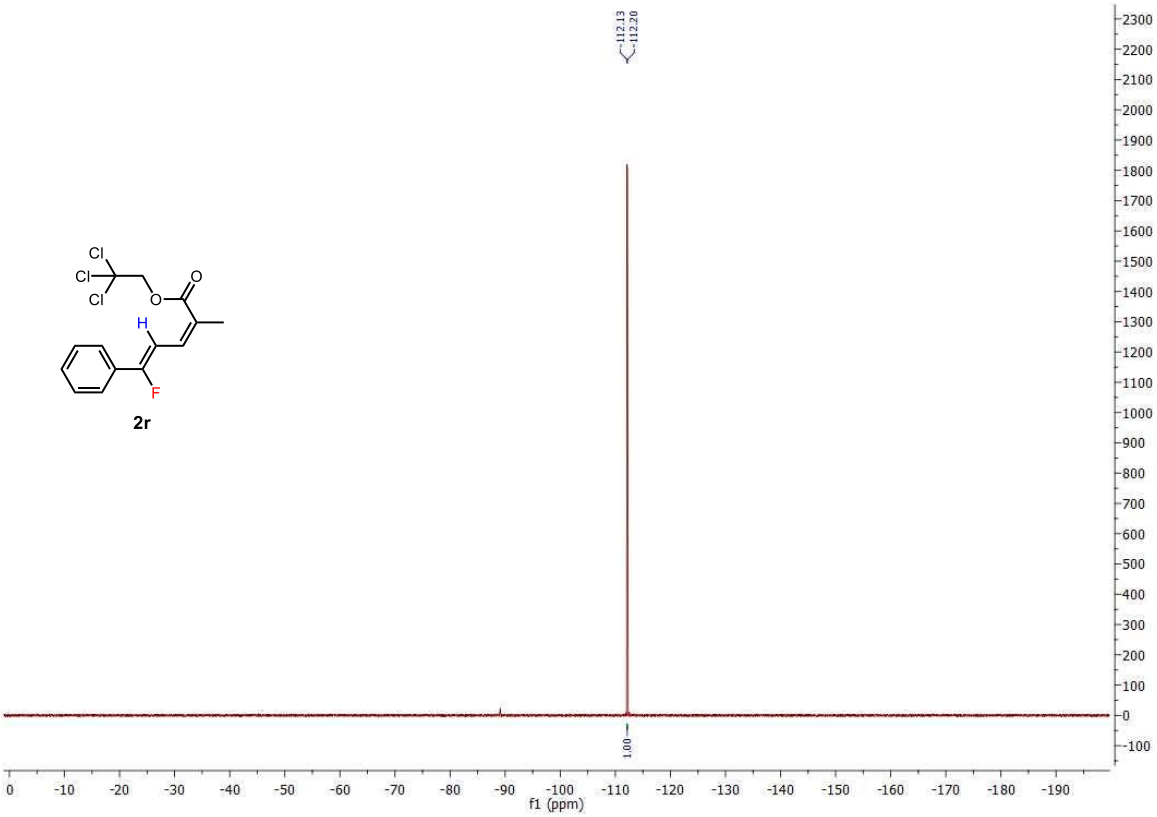
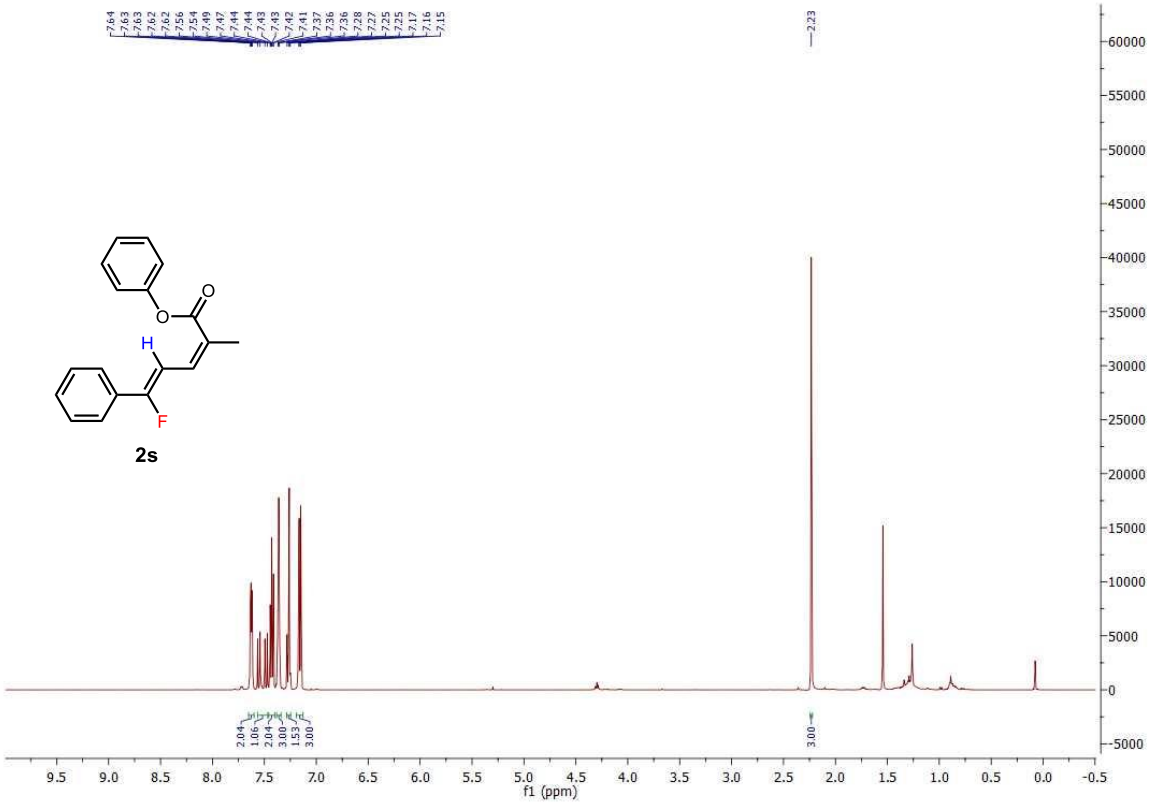
95.27
74.52
21.06
Cl
Cl
Cl
O
O
H
F
2r
f1 (ppm)


112.13
112.20
1.00
Cl
Cl
Cl
O
O
H
F
2r
f1 (ppm)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7.63
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7.62
7.62
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7.54
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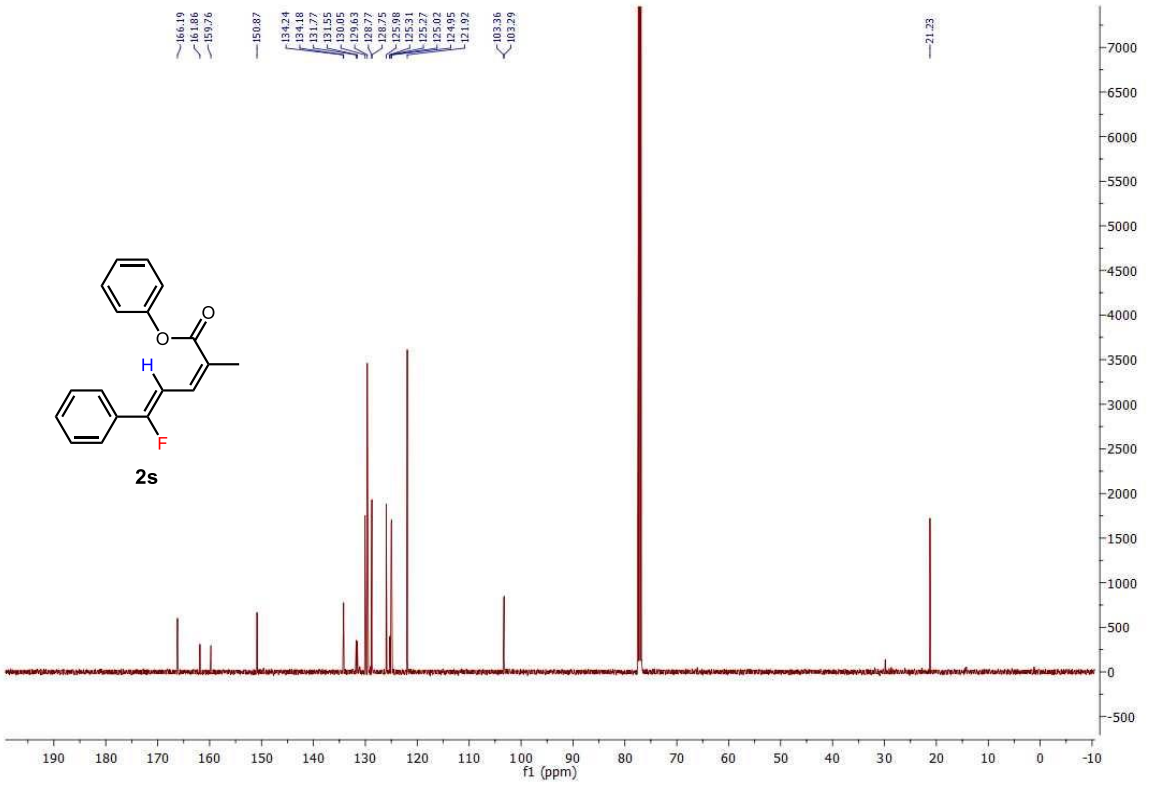
7.44
7.43
7.43
7.42
7.41
7.37
7.36
7.36
7.28
7.27
7.25
7.25
7.17
7.16
7.15
2.23
O
O
H
F
2s
2.04
1.06
2.04
3.00
1.57
3.00
3.00
f1 (ppm)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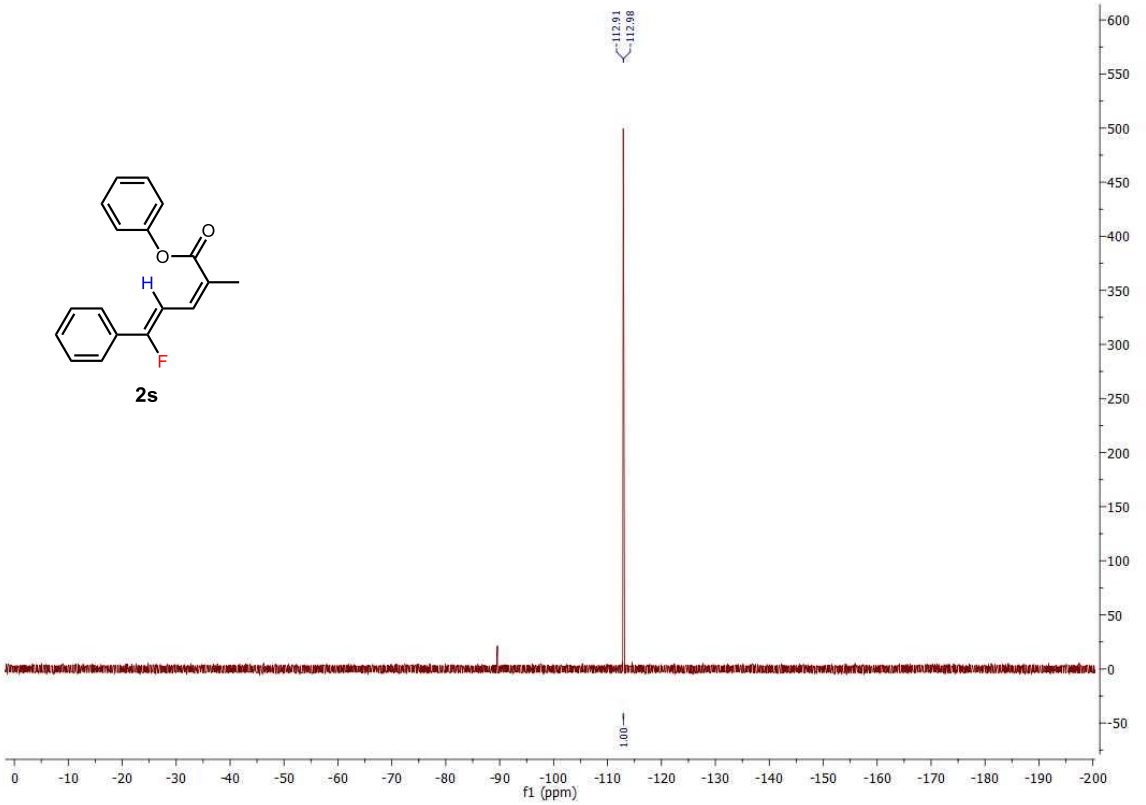
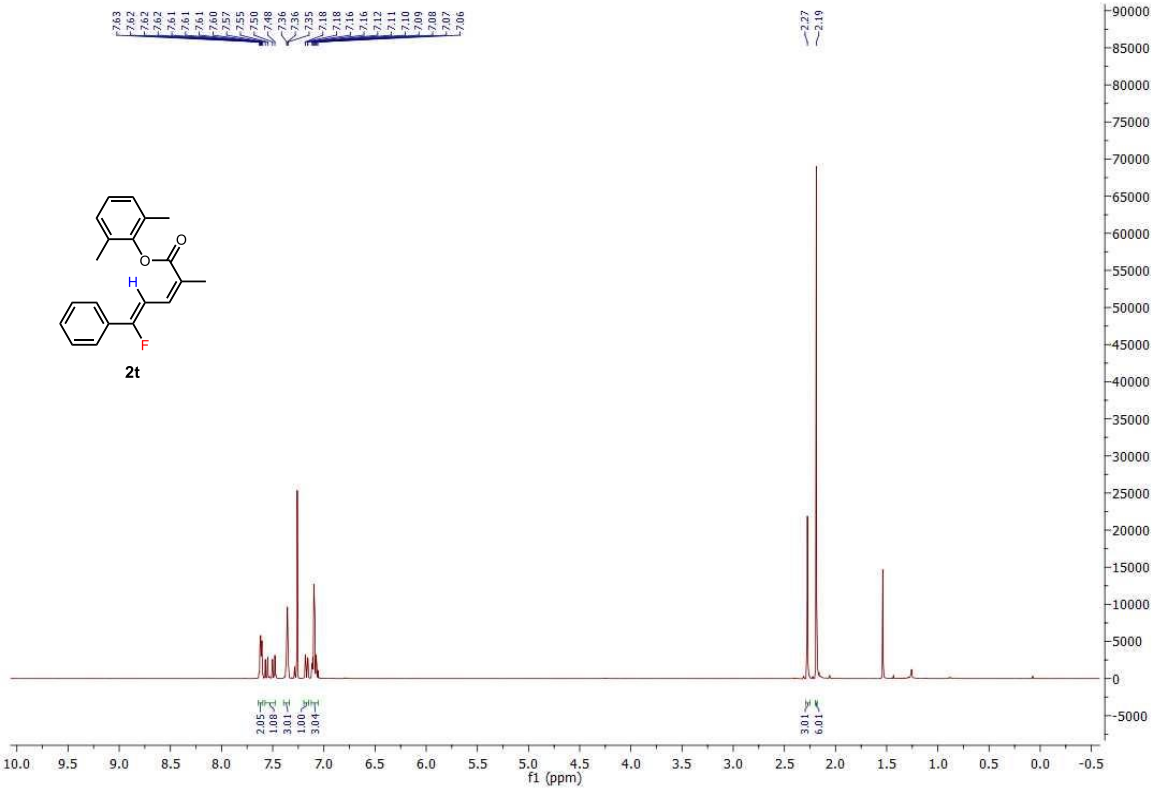
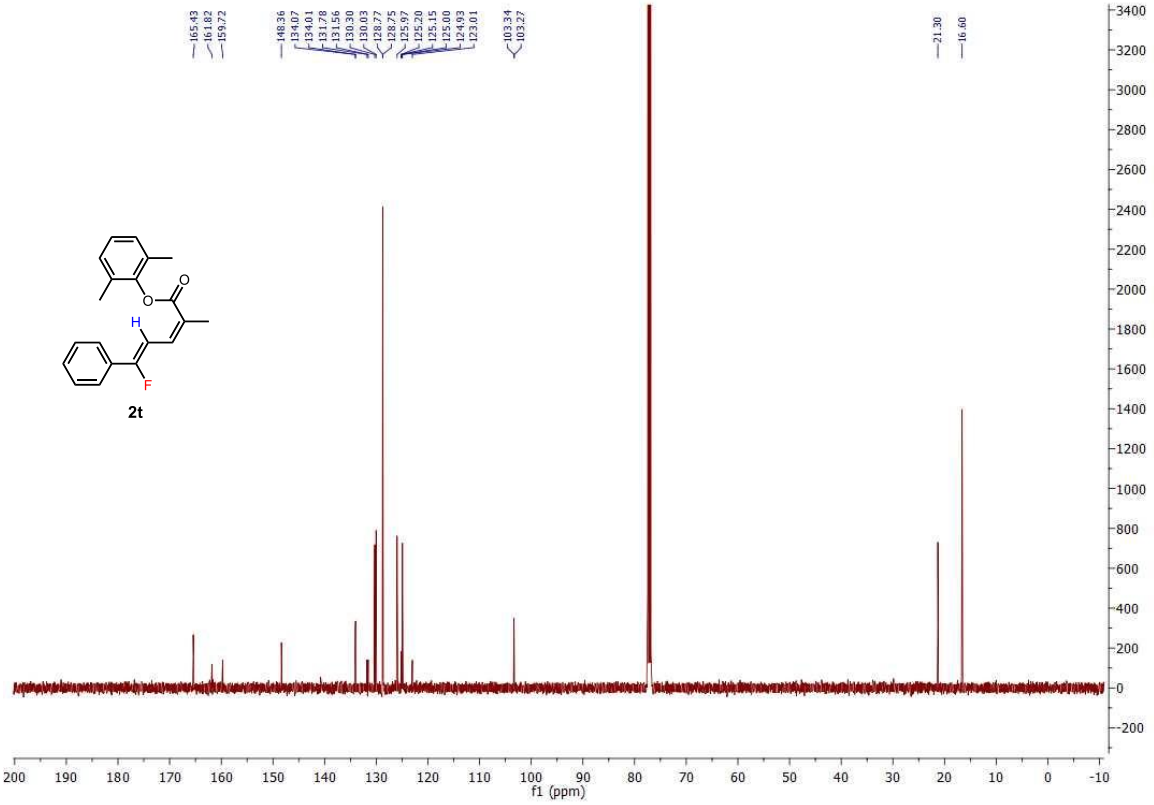
130.05
129.63
128.77
128.75
125.98
125.31
125.27
125.02
124.95
121.92
103.36
103.29
21.23
O
O
H
F
2s
f1 (ppm)

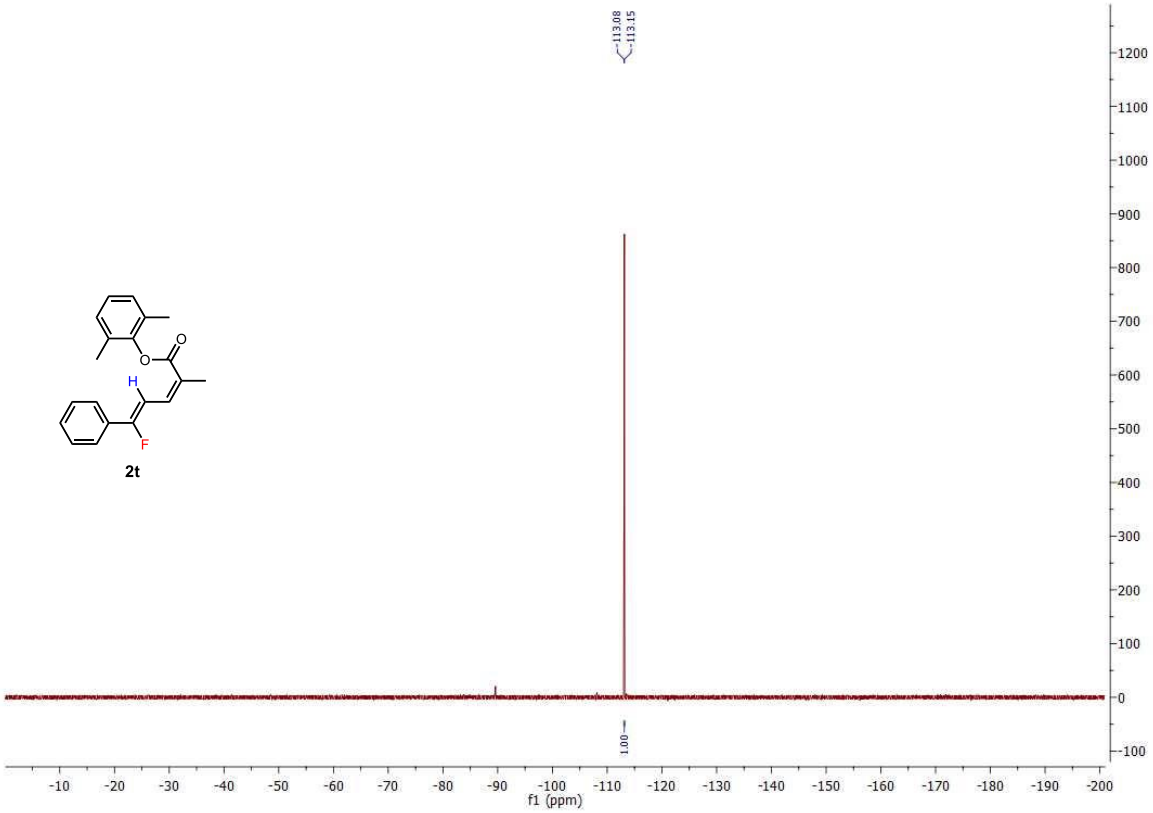

112.91
112.98
1.00
f1 (ppm)

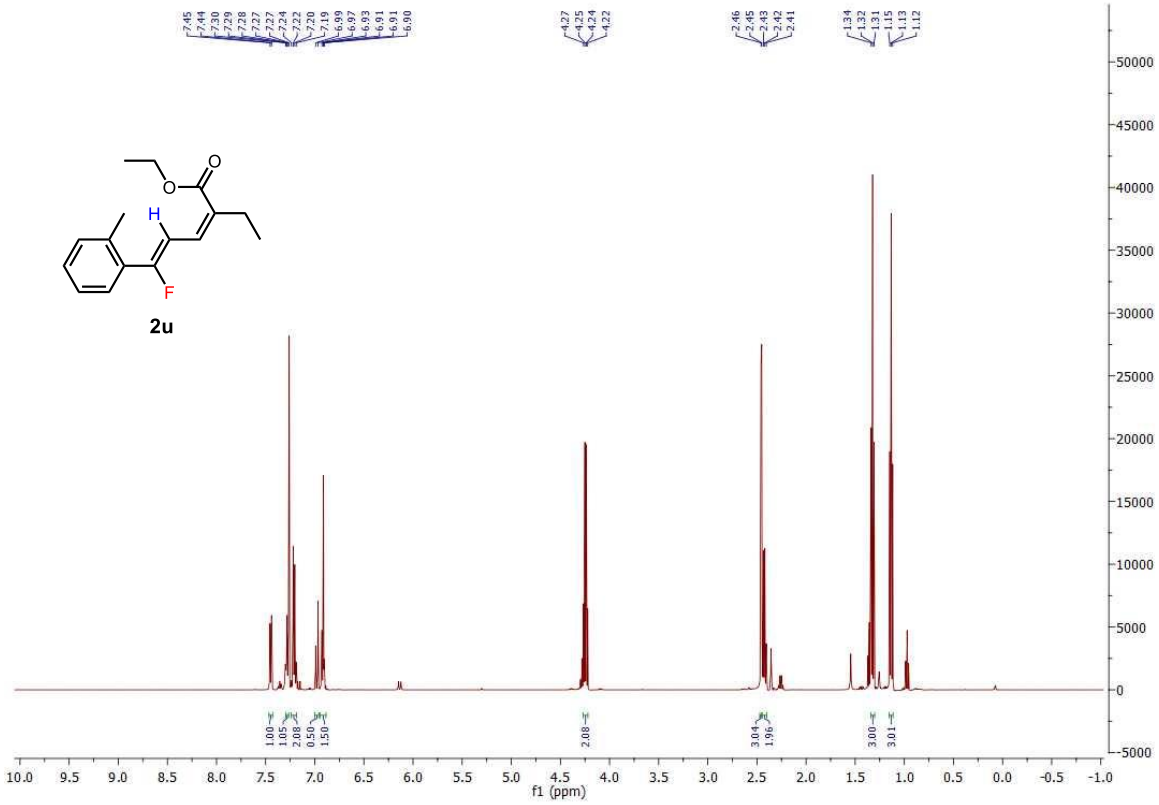
2s

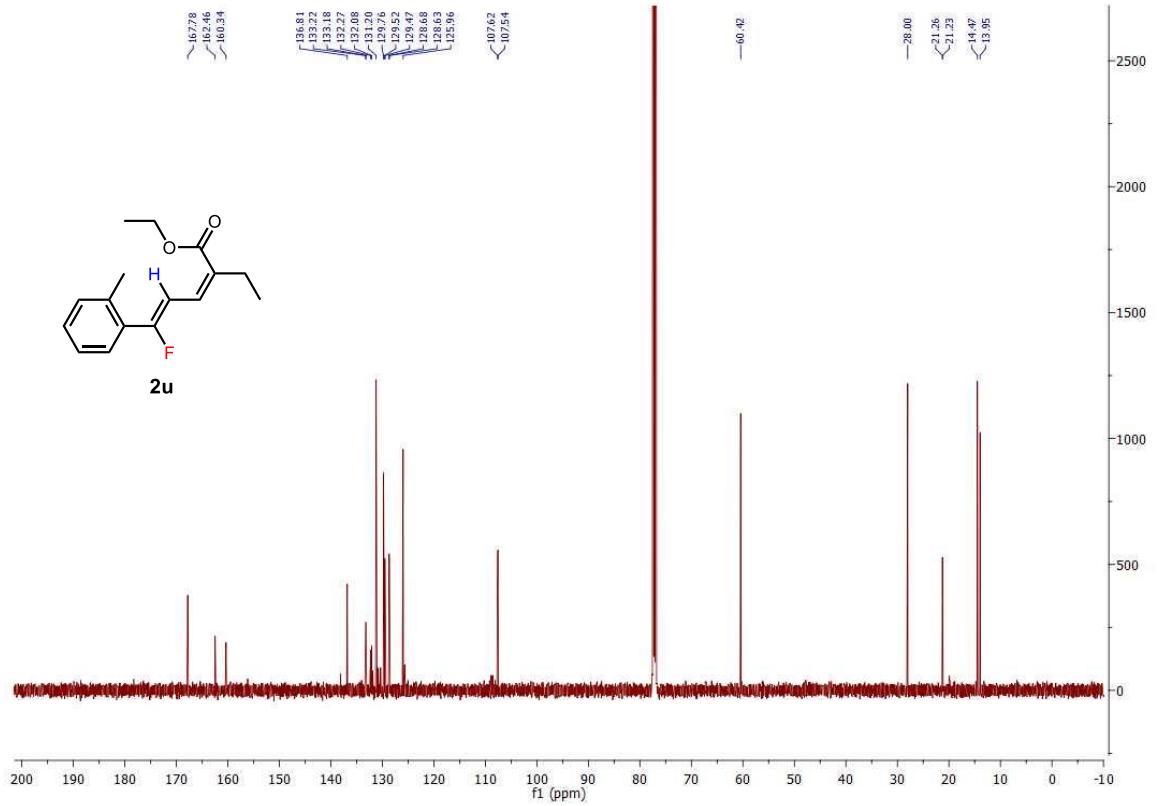

7.63
7.62
7.62
7.62
7.61
7.61
7.61
7.60
7.57
7.55
7.50
7.48
7.36
7.36
7.35
7.18
7.16
7.16
7.12
7.11
7.10
7.09
7.08
7.07
7.06
2.27
2.19
2.05
1.08
3.01
1.00
3.04
3.01
6.01
f1 (ppm)

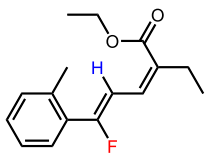
2t


165.43
161.82
159.72
148.36
134.07
134.01
131.78
131.56
130.30
130.03
128.77
128.75
125.97
125.20
125.15
125.00
124.93
123.01
103.34
103.27
21.30
16.60
O
O
H
F
2t
f1 (ppm)


113.08
113.15
O
O
H
F
2t
1.00
f1 (ppm)

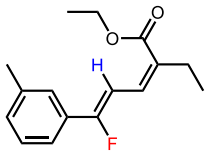

O
O
H
F
2u
f1 (ppm)


O
O
H
F
2u
f1 (ppm)



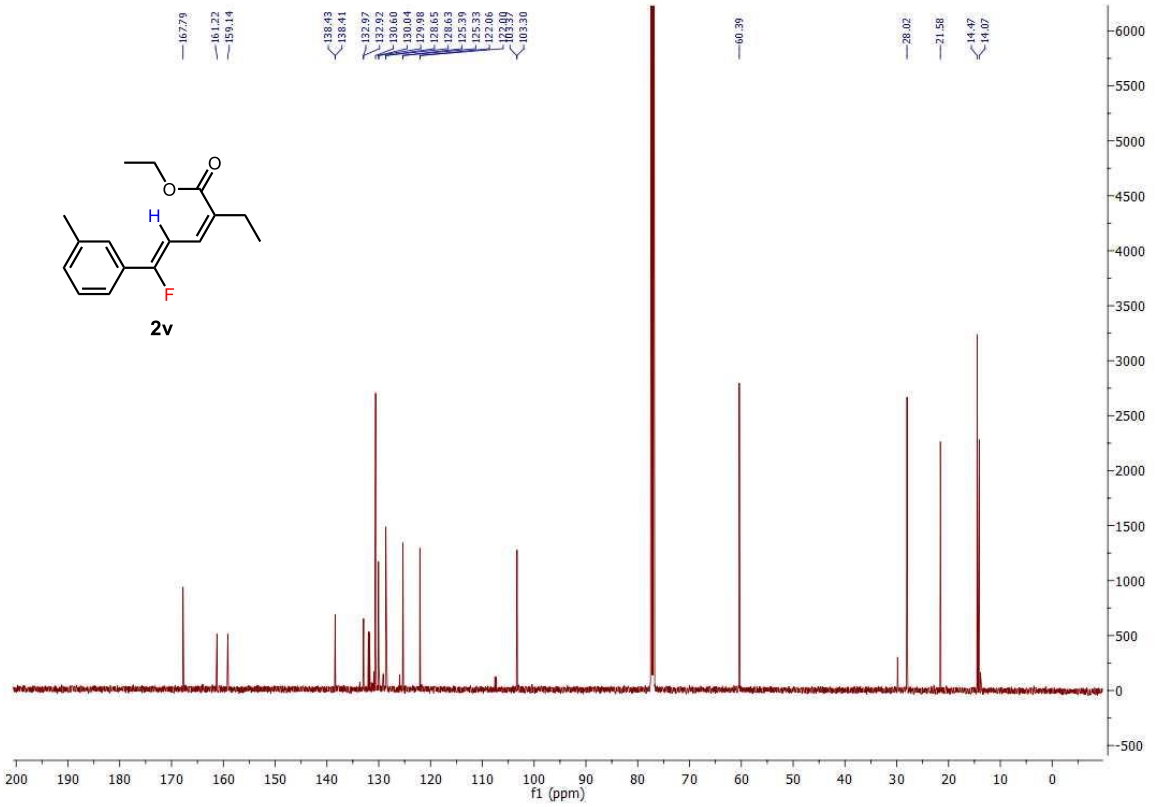
2u

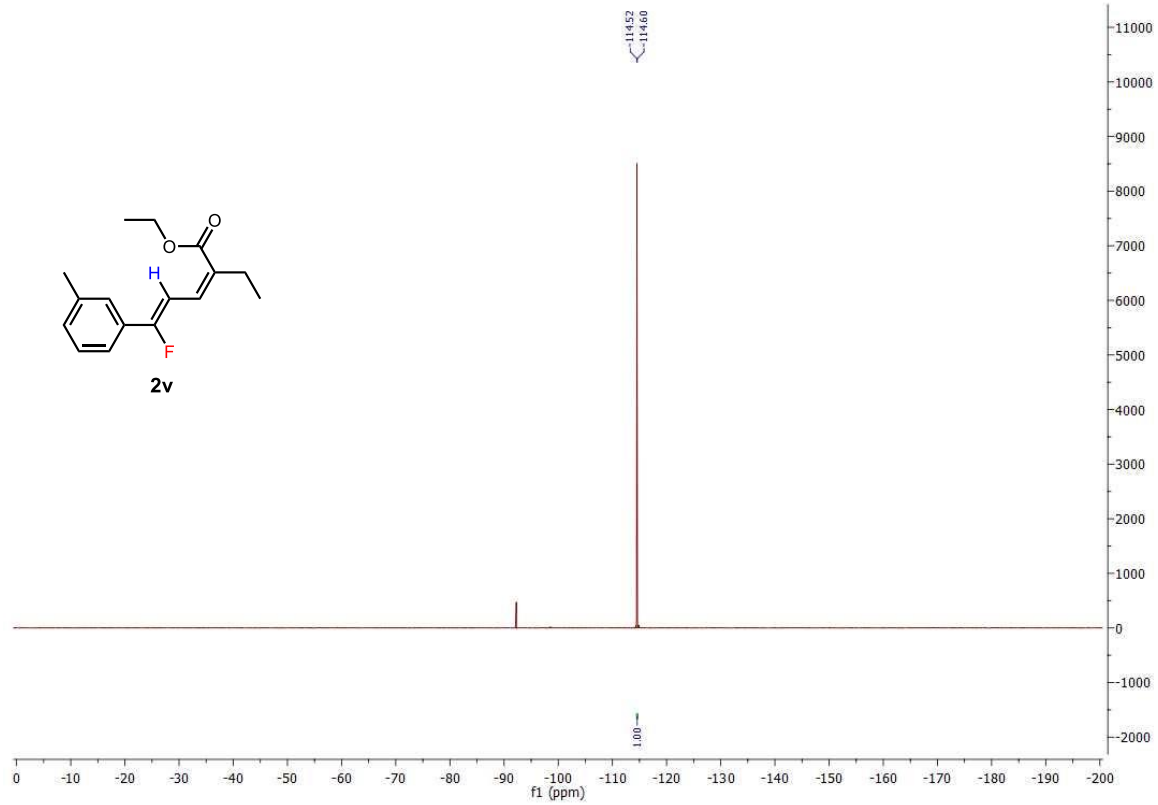
-98.06
-98.12
-98.14
-98.14
1.00
f1 (ppm)



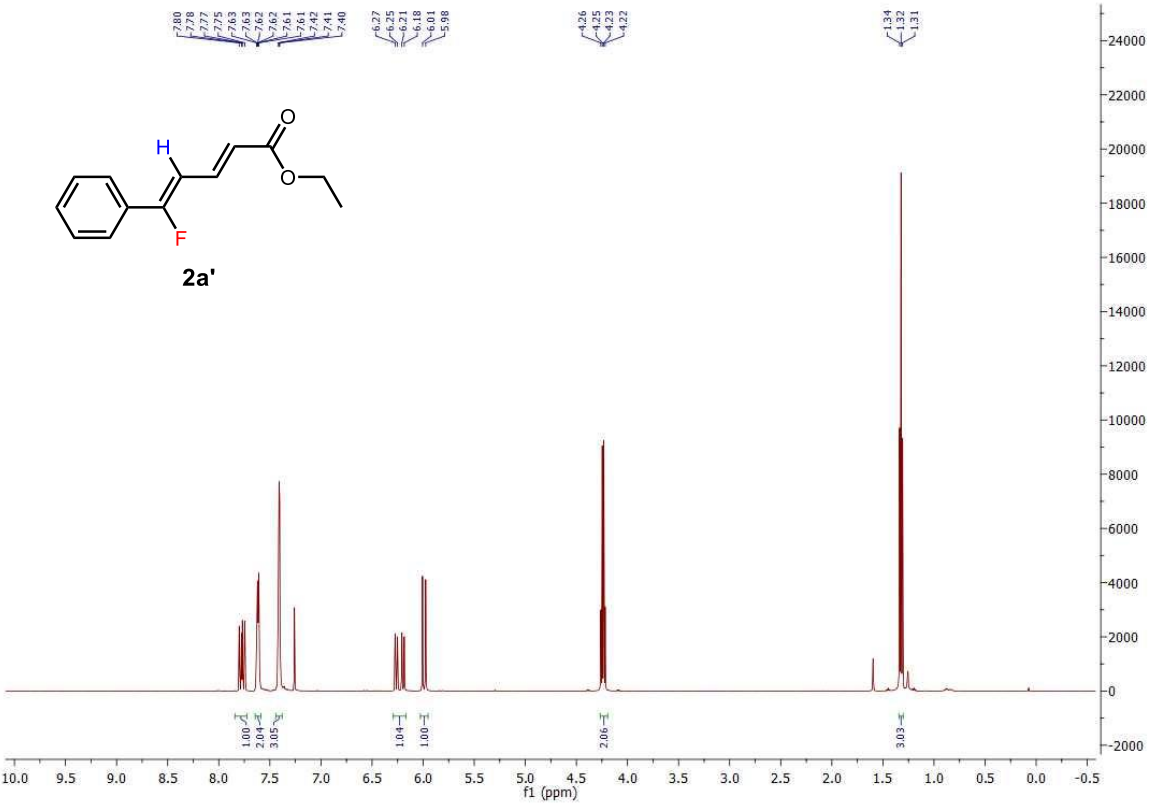
2v

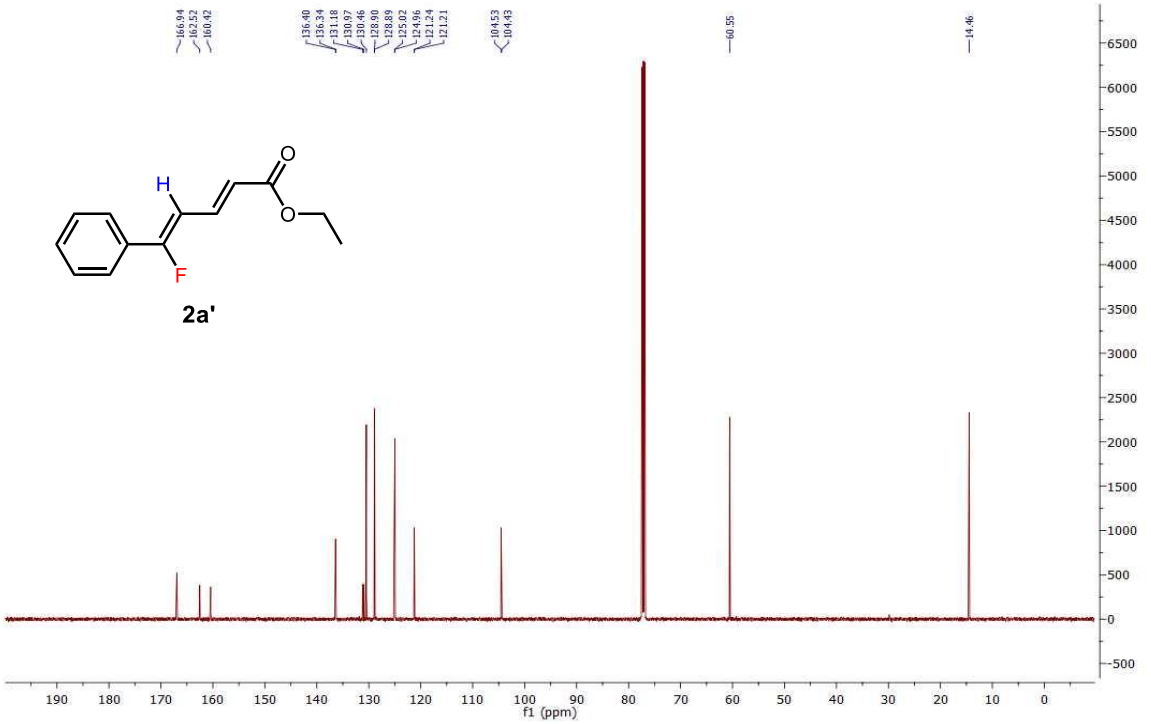
7.43
7.42
7.39
7.36
7.32
7.29
7.28
7.27
7.25
7.18
7.17
6.95
6.92
4.30
4.29
4.27
4.26
2.45
2.43
2.42
2.40
2.37
1.38
1.36
1.35
1.14
1.13
1.11
2.02
0.50
0.56
1.42
1.00
1.00
2.05
3.06
3.02
3.04
3.07
f1 (ppm)

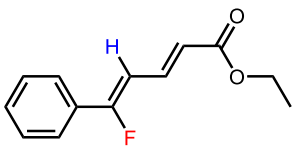

167.79
161.22
159.14
138.43
138.41
132.97
132.92
130.60
130.04
129.98
128.65
128.63
125.39
125.33
122.06
103.39
103.30
60.39
28.02
21.58
14.47
14.07
O
O
H
F
2v
f1 (ppm)


114.52
114.60
1.00
O
O
H
F
2v
f1 (ppm)

Copies of NMR spectra for (*E*) products

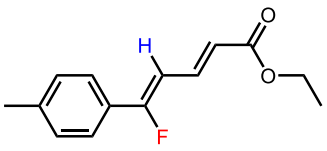





H
O
O
F

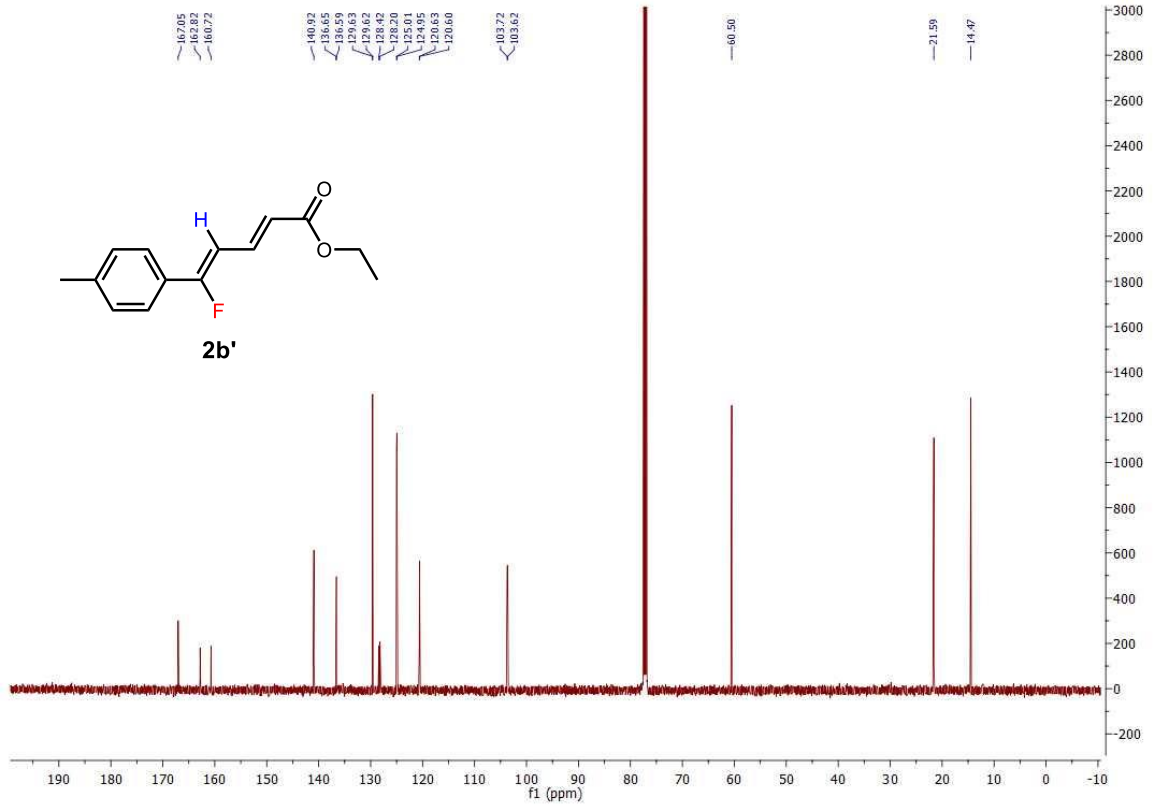
2a'

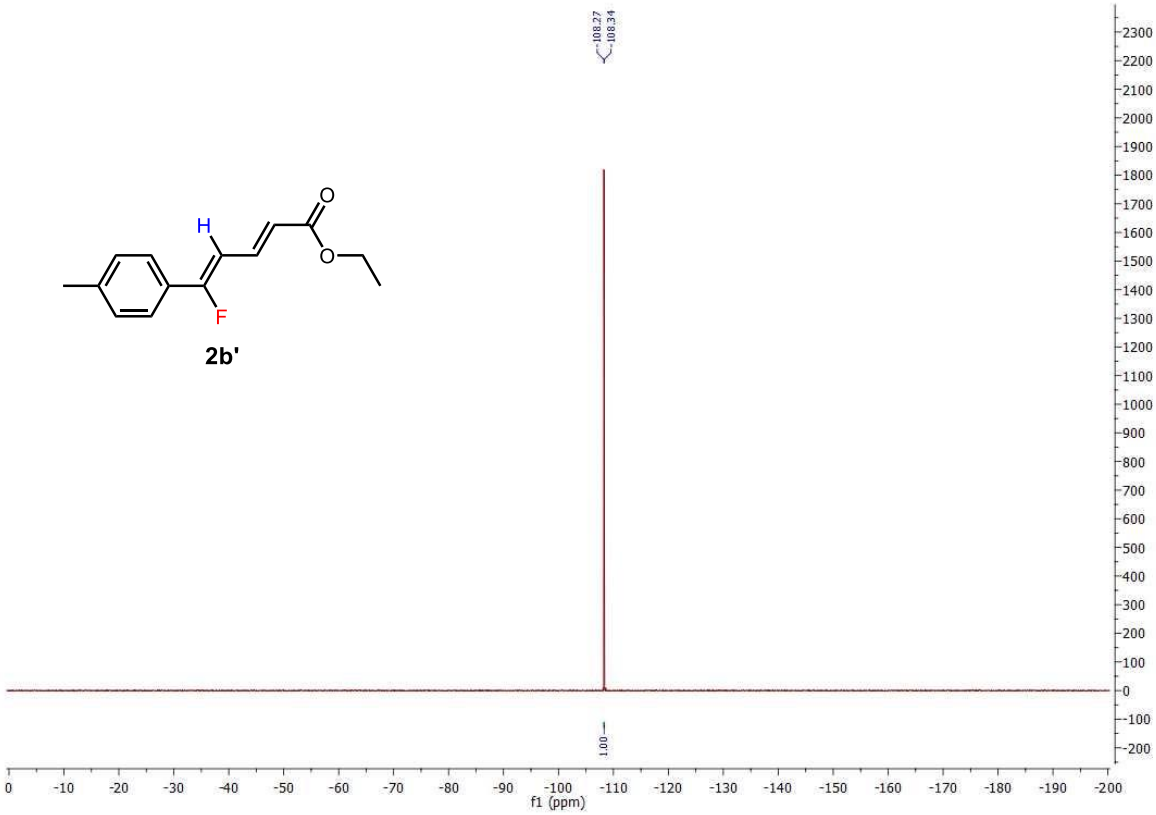
-108.46
-108.53
1.00
f1 (ppm)

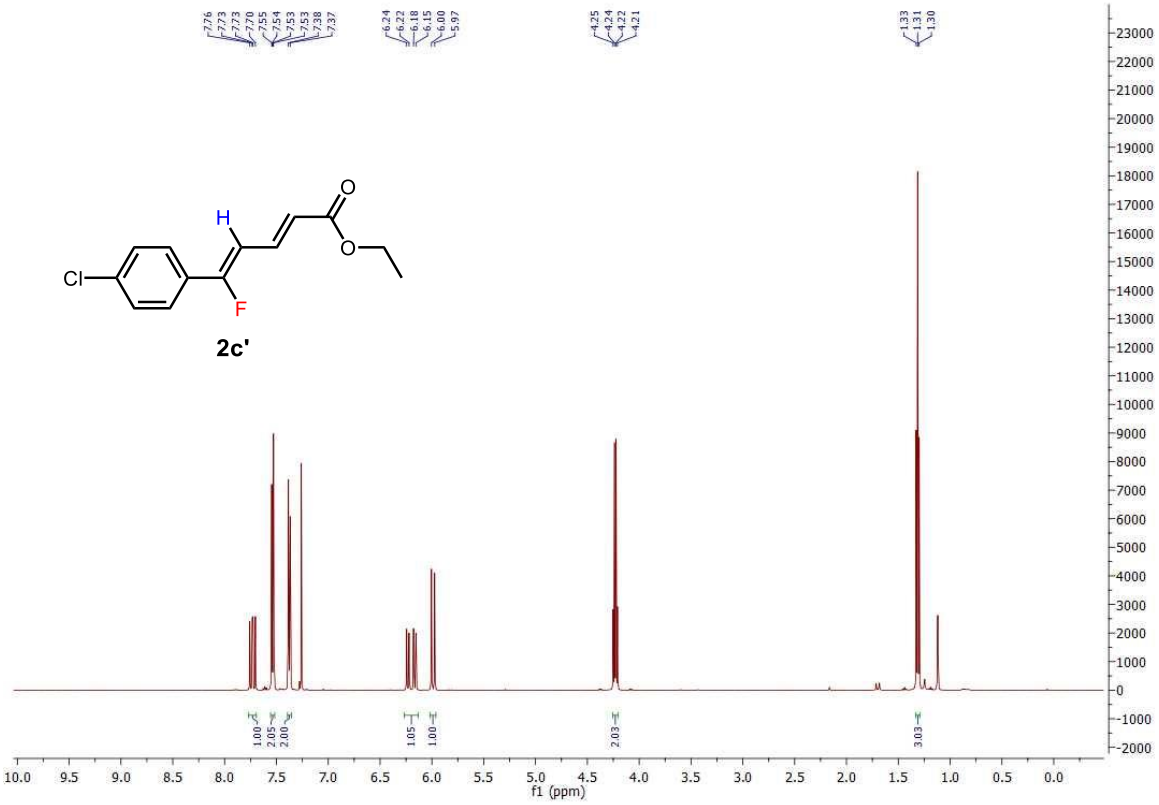

H
O
O
F

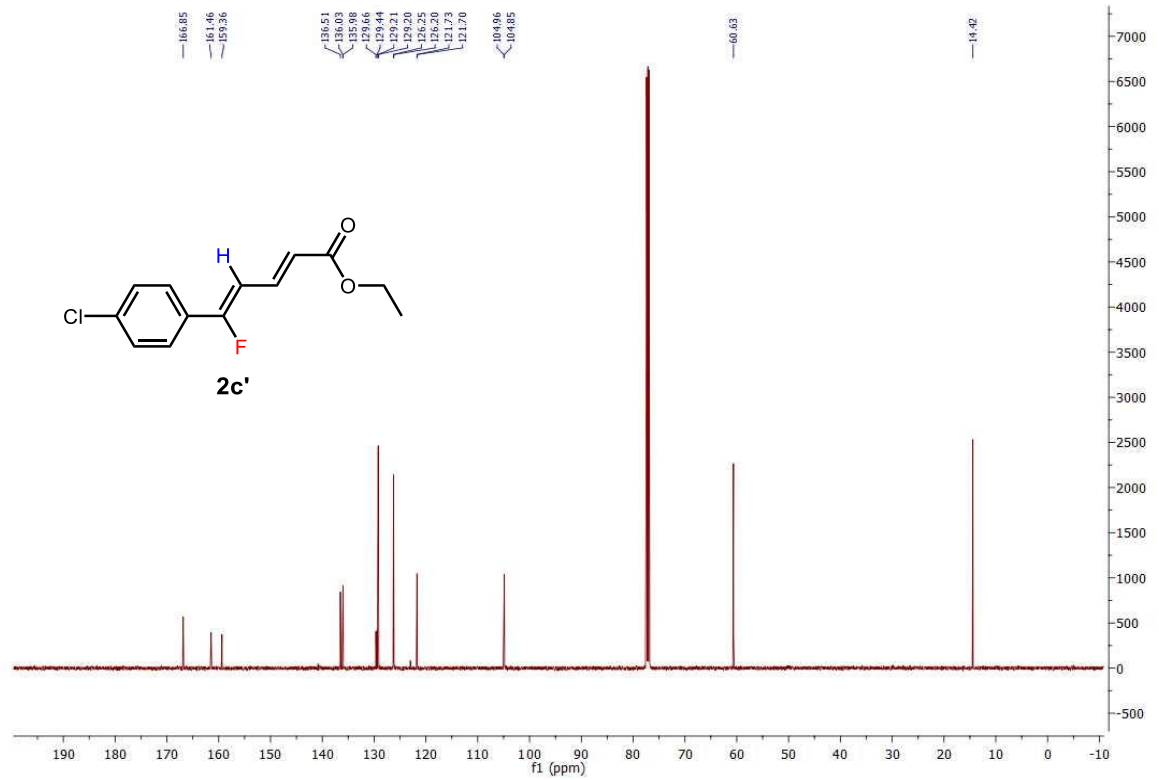
2b'

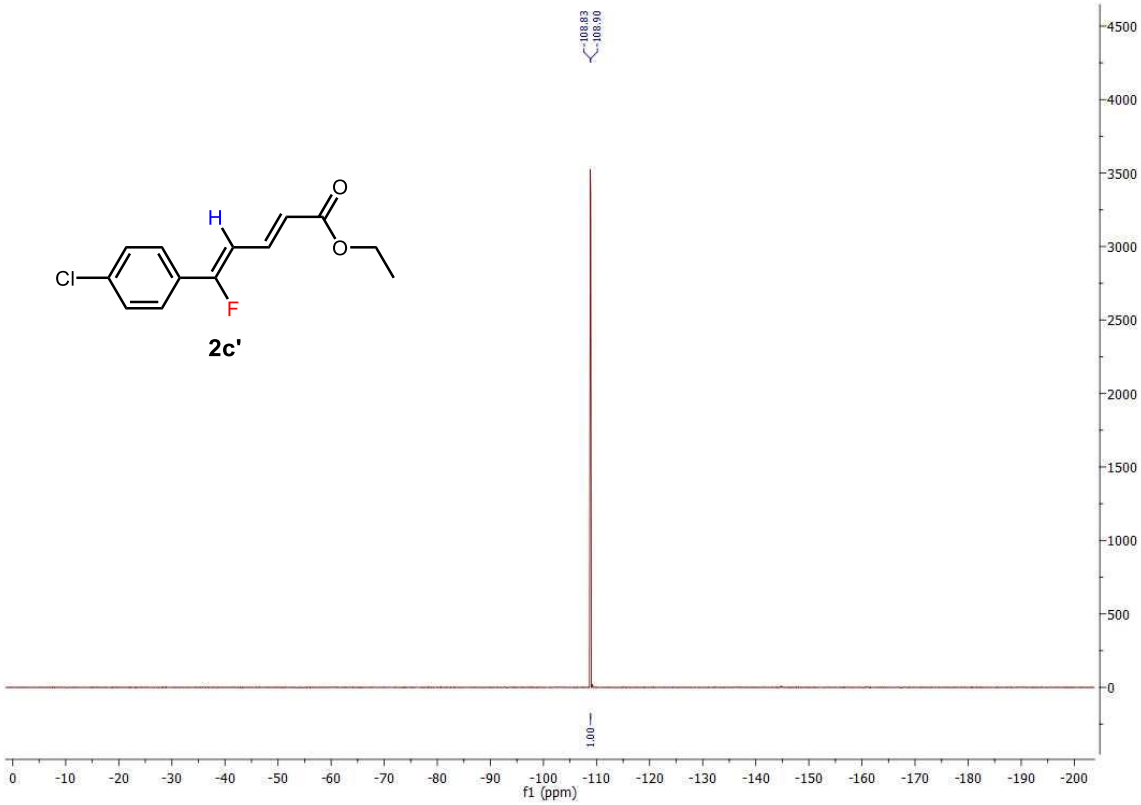
7.79
7.77
7.76
7.74
7.52
7.50
7.22
7.20
6.22
6.20
6.16
6.13
5.97
5.94
4.26
4.24
4.23
4.21
2.39
1.33
1.32
1.30
1.00
2.05
2.02
1.04
1.00
2.06
3.08
3.03
f1 (ppm)


166.05
162.82
160.72
140.92
136.65
136.59
129.63
129.62
128.42
128.20
125.01
124.95
120.63
120.60
103.72
103.62
60.50
21.59
14.47
H
O
O
F
2b'
f1 (ppm)


108.27
108.34
H
O
O
F
2b'
1.00
f1 (ppm)

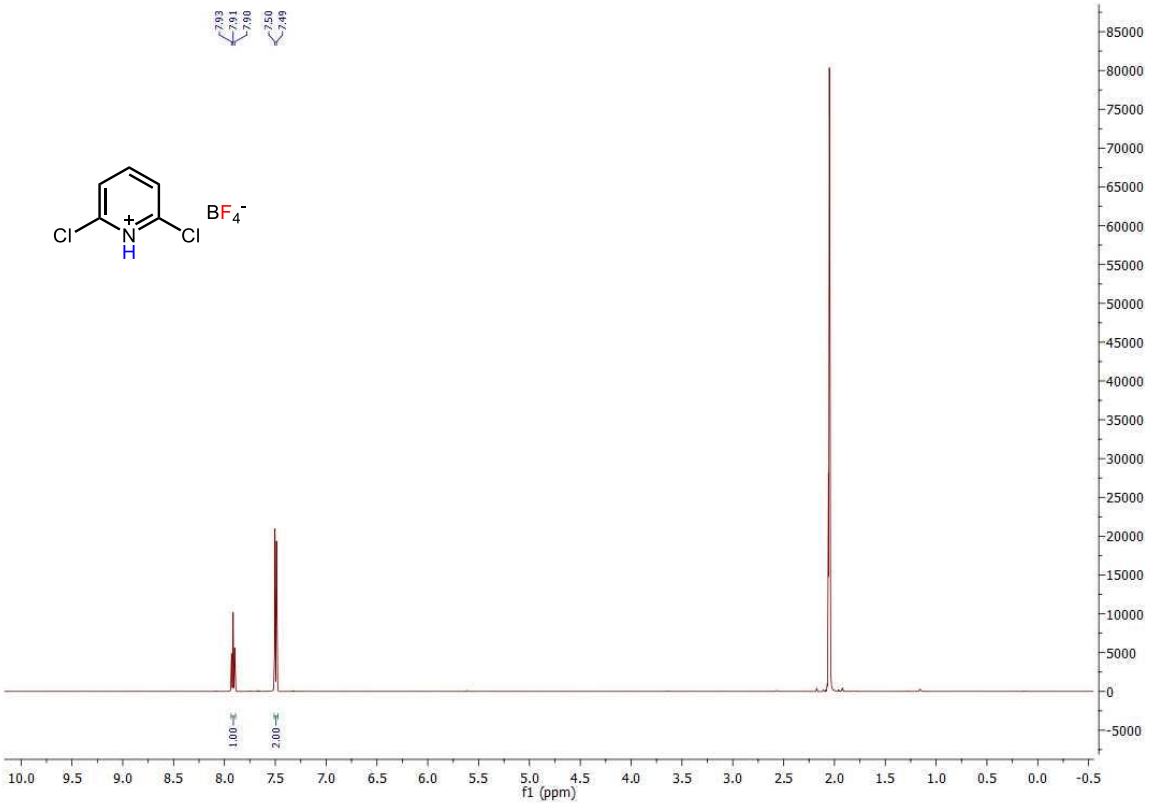

7.76
7.73
7.73
7.70
7.55
7.54
7.53
7.53
7.38
7.37
6.24
6.22
6.18
6.15
6.00
5.97
4.25
4.24
4.22
4.21
1.33
1.31
1.30
H
O
O
Cl
F
2c'
1.00
2.05
2.00
1.05
1.00
2.03
3.03
f1 (ppm)

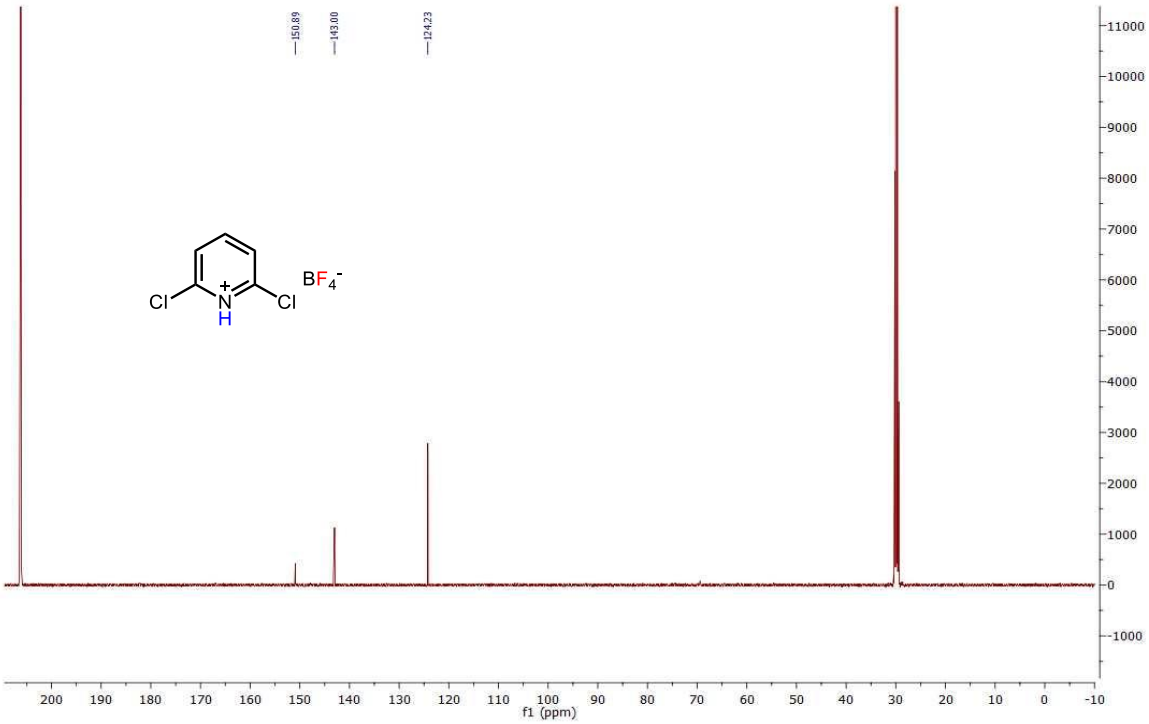

166.85
161.46
159.36
136.51
136.03
135.98
129.66
129.44
129.21
129.20
126.25
126.20
121.73
121.70
104.96
104.85
60.63
14.42
H
O
O
Cl
F
2c'
f1 (ppm)

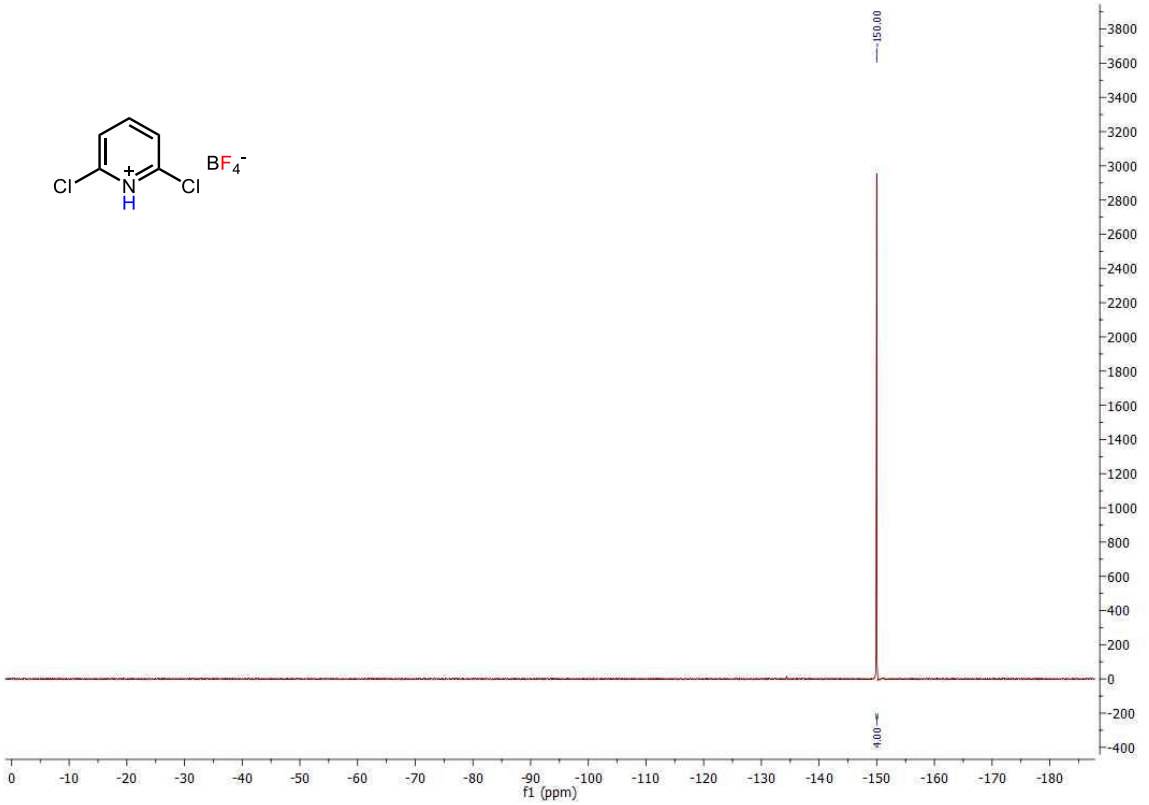

-108.83
-108.90
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)
H
O
O
Cl
F

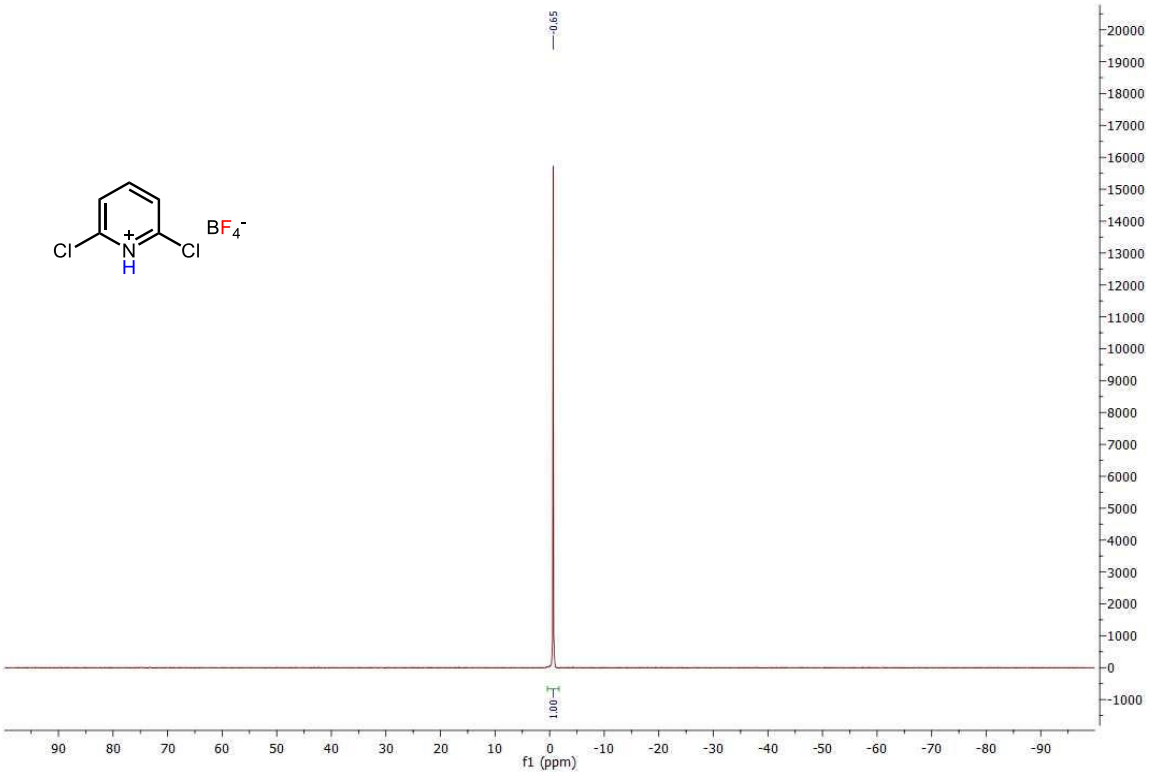
2c'

Copies of NMR spectra for 2,6-dichloropyridinium tetrafluoroborate

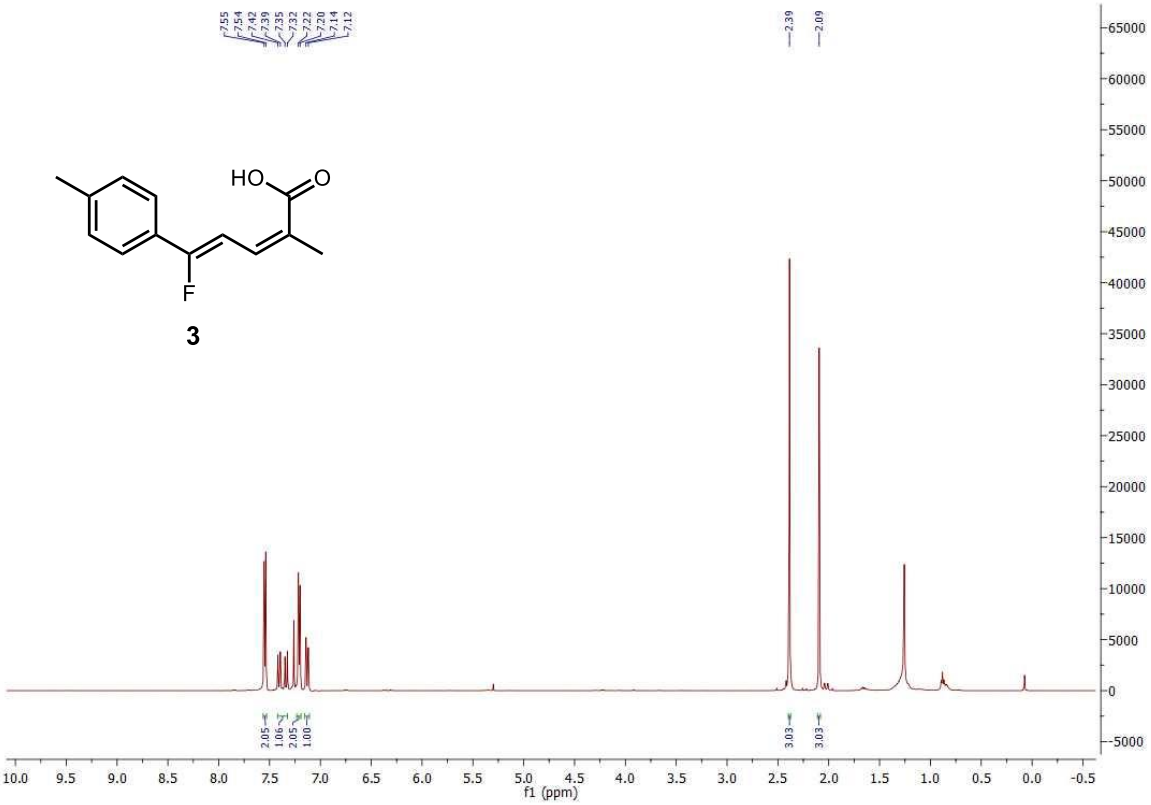


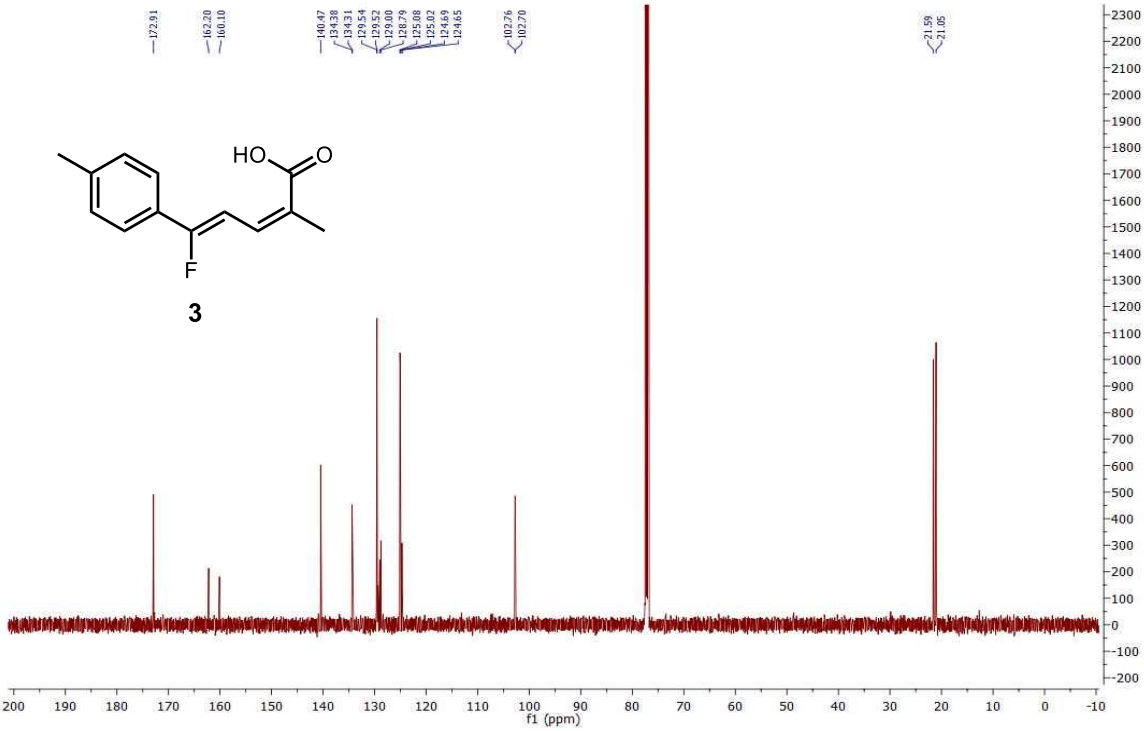


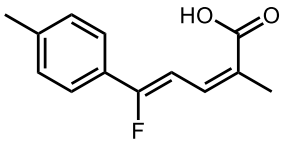

Cl
N
H
Cl
BF4-
-150.00
4.00
f1 (ppm)


Cl
N
H
Cl
BF4-
-0.65
1.00
f1 (ppm)

Copies of NMR spectra for derivatization products

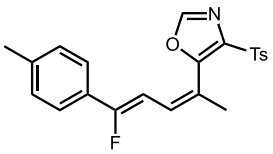





HO
O
F

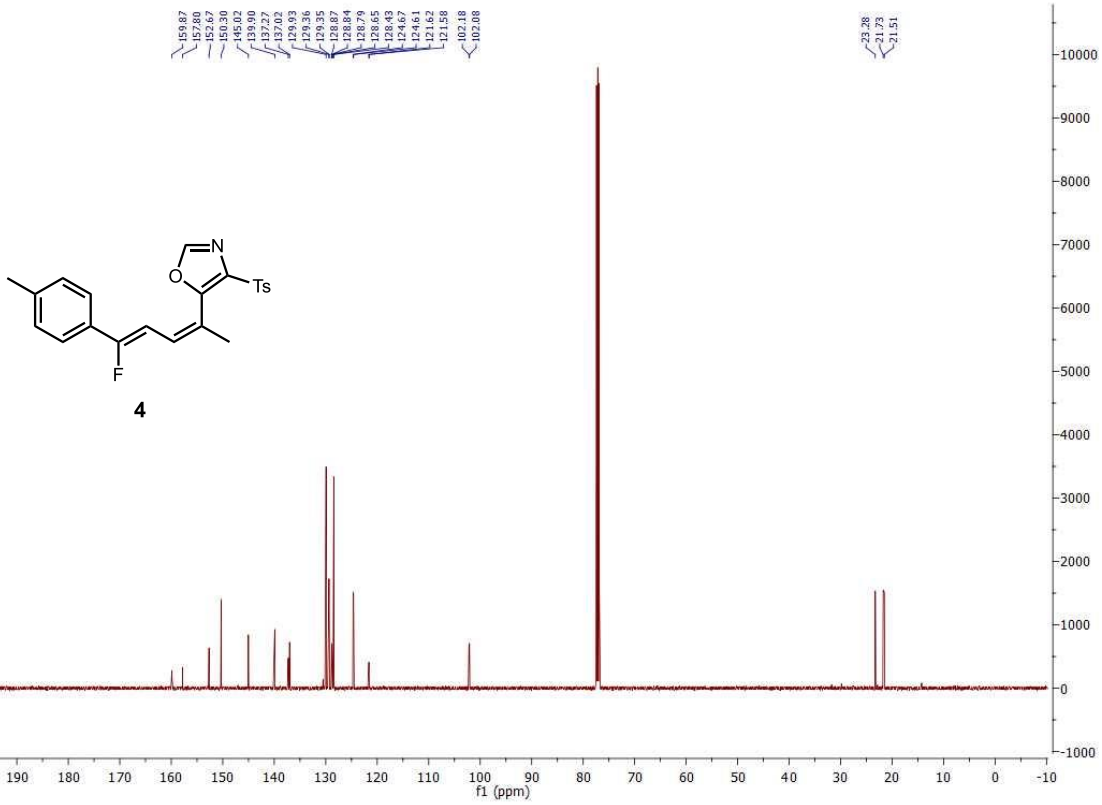
3

112.30
112.38
1.00
f1 (ppm)

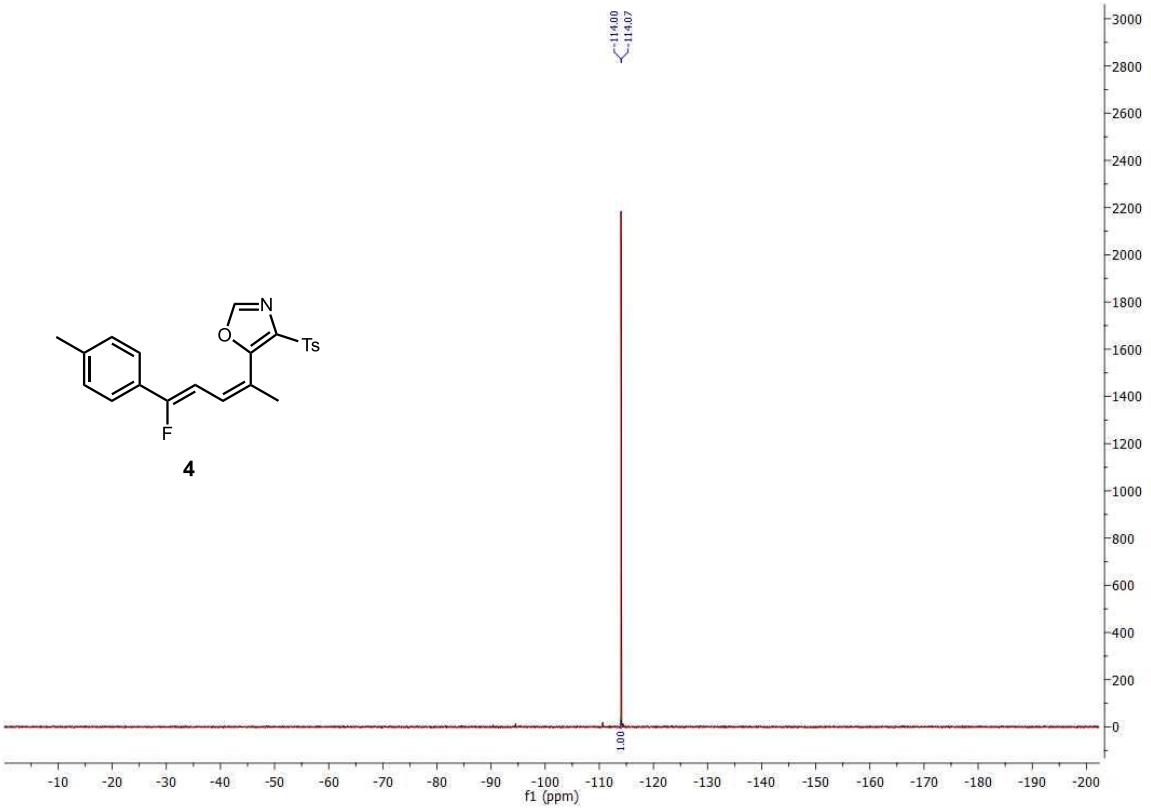

N
O
Ts
F

4

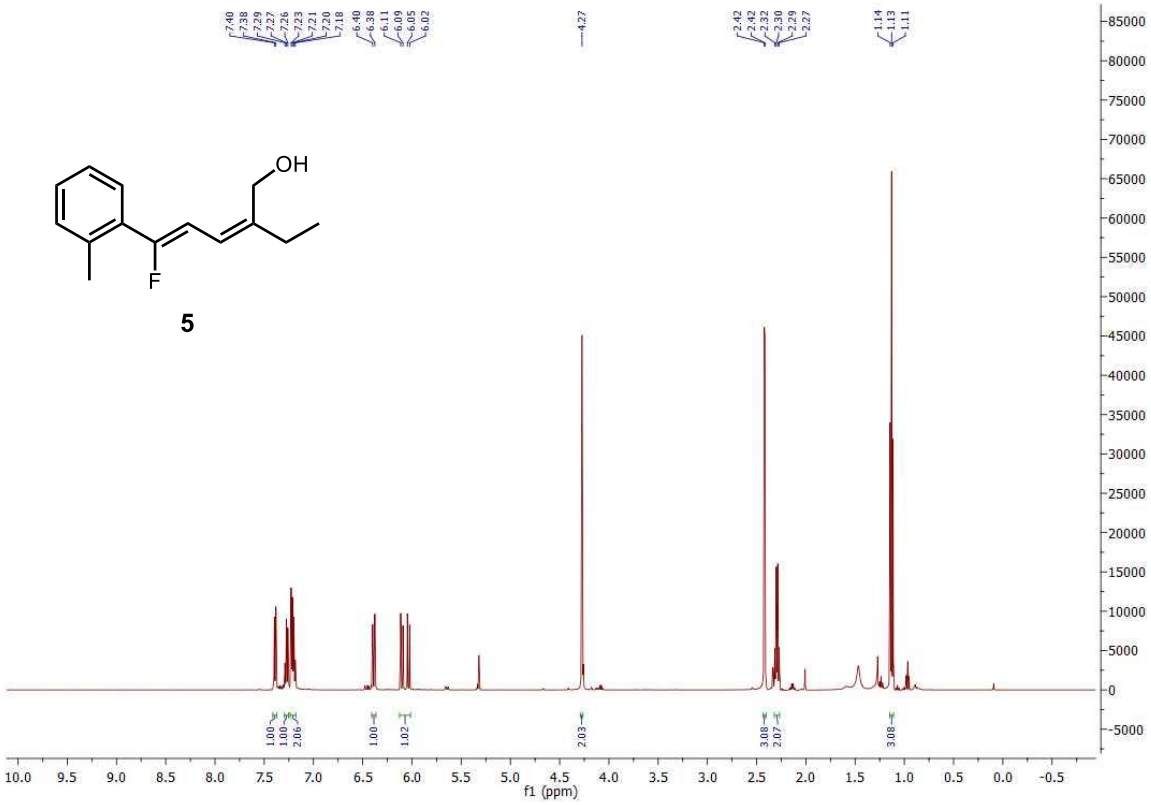
7.90
7.89
7.87
7.29
7.27
7.21
7.19
7.13
7.11
6.94
6.94
6.92
6.91
5.77
5.74
5.70
5.68
2.36
2.33
2.24
2.00
1.03
2.01
2.00
2.01
1.00
1.00
3.01
3.03
3.00
f1 (ppm)

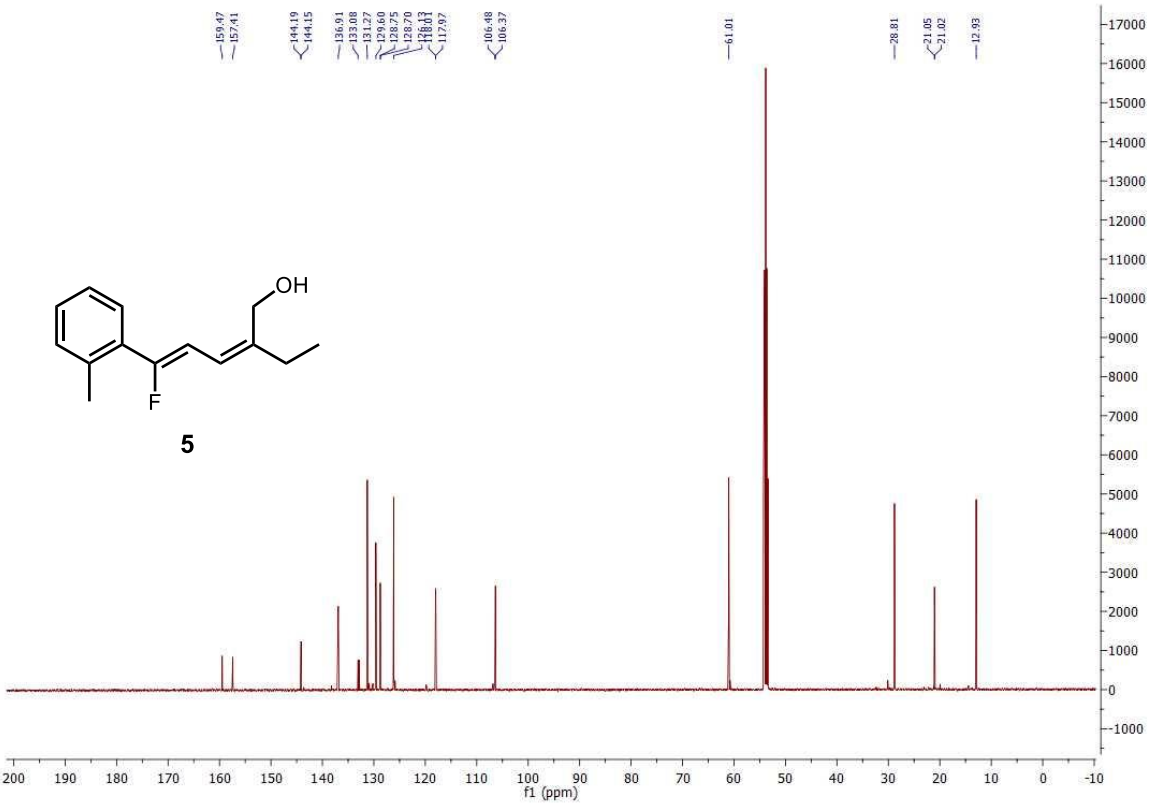

159.87
157.80
152.67
150.30
145.02
139.90
137.27
137.02
129.93
129.36
129.35
128.87
128.84
128.79
128.65
128.43
124.67
124.61
121.62
121.58
102.18
102.08
23.28
21.73
21.51
N
O
Ts
F
f1 (ppm)

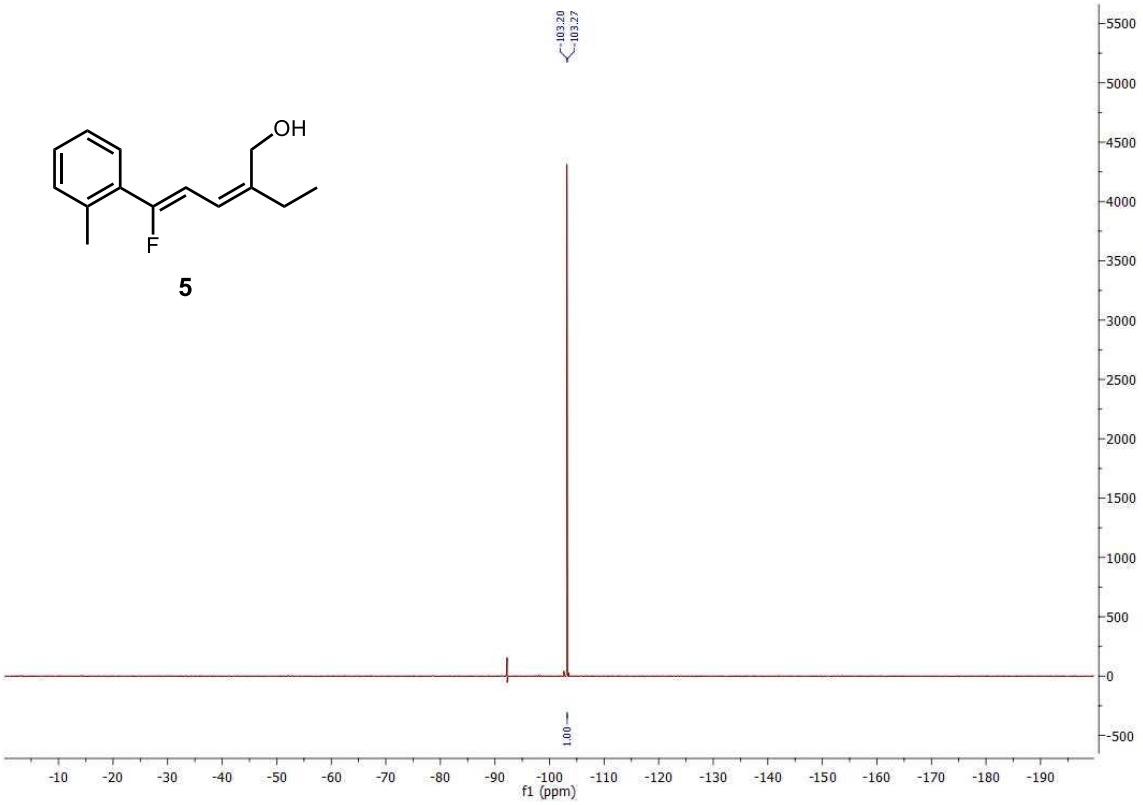
4


114.00
114.07
1.00
N
O
Ts
F
f1 (ppm)

4


OH
F
5
f1 (ppm)


OH
F
5
f1 (ppm)


OH
F
-103.20
-103.27
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)
5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

5

Copy of Crude NMR spectrum for side product determination