Supporting Information

Gold-Catalyzed Hydrofluorination of Electron-Deficient Alkynes: Stereoselective Synthesis of *β*-Fluoro Michael Acceptors

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Table of Contents

General Experimental Details

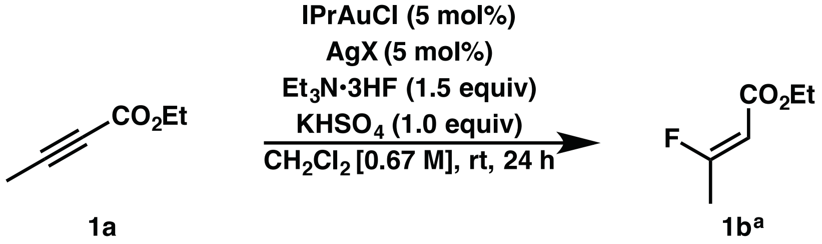
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Vessels used in air-free reactions were oven-dried prior to use. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed using ICN SiliTech 32-63D 60Å silica gel. Commercial grade solvents were used without further purification except as indicated below. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), toluene (PhMe), diethyl ether (Et_2O), dimethyl formamide (DMF), triethylamine (Et_3N) and tetrahydrofuran (THF) were dried by passing commerically available pre-dried, oxygen-free formulations through activated alumina columns under argon. Thin layer chromatography analysis was performed using Merck 60 pre-coated silica gel plates with F254 indicator. Visualization was accomplished by iodine, p-anisaldehyde, potassium permanganate, Dragendorff-Munier, and/or UV light (254 nm). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AVQ-400, DRX-500 and AV-600 instruments with 400, 500 and 600 MHz frequencies. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker DRX-500 and AV-600 instruments with a ^{13}C operating frequency of 126 and 150 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded on Bruker AVQ-400, DRX-500 and AV-600 instruments with 376, 471, and 565 MHz frequencies. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$, δ 5.32 for CH_2Cl_2) was used as an internal reference for ^{1}H spectra. For ^{13}C spectra, chemical shifts are reported relative to the δ 77.16 resonance of $CDCl_3$ and relative to the δ 53.84 for CD_2Cl_2. For ^{19}F spectra, chemical shifts are reported in relative to the δ -113.15 resonance of PhF. Coupling constants are reported in Hz. Mass spectral data were obtained from either the UC-Berkeley Catalysis Center operated by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI (or APCI) mode or the QB3/Chemistry Mass Spectrometry Facility at UC-Berkeley. FTIR measurements were recorded on a Bruker Vertex 80 FTIR spectrometer in the Catalysis Center at UC-Berkeley and are reported in frequency of absorption (cm^{-1}). Alkynes (11a),[1-2] (13a),[3] (18a, 20a, 23a),[4] (17a),[5] (19a, 21a),[6] (22a),[7-8] (24a),[9] (25a),[10] (26a),[1] (29a),[11] 5-phenylpent-2-yn-1-ol,[12] 1-methyl-4-(prop-1-ynylsulfonyl)benzene,[13] and 1-methyl-4-(phenylethynylsulfonyl)benzene[13] could be prepared according to previously reported procedures; the spectral data were in agreement.

Gold complexes were synthesized according to the procedure outlined in Mauleon et al[14] and their spectra match those reported in the literature.[14-17] JohnPhosAuNTf$_2$ was prepared as described by Gagosz and coworkers.[18]

Investigation of Reaction Conditions

In a nitrogen-filled glove-box, solvent was added to a 4 mL glass vial charged with LAuCl (0.01 mmol, 5 mol%) and AgX (0.01 mmol, 5 mol%). After 4–5 minutes of mixing with a syringe in the absence of light, the resulting mixture was filtered through a glass fiber pad (packed into the neck of 9" pipette) into a 2 mL screw-lid plastic centrifuge tube containing specified additive. Alkyne **1a** (23 µL, 0.20 mmol, 1 equiv) was added and the centrifuge tube sealed and brought outside the glove-box. In the absence of light, the plastic centrifuge tube was opened (exposed to air) and the fluorination reagent added. The reaction was sealed and placed on a IKA KS 130 basic shaker table (560 revolutions/min) under protection from light. After the designated time, the reaction was diluted with an appropriate solvent (500 µL total), charged with 2,4-dinitrofluorobenzene (25 µL, 0.20 mmol, 1 equiv), filtered into an NMR tube, and analyzed by ^{1}H and ^{19}F NMR spectroscopy.

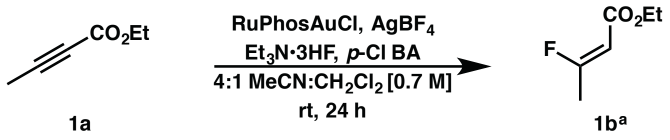
Table S1. Effect of the silver salt on the hydrofluorination of **1a**.



Entry	AgX	Yield [%] (*Z:E*)^b
1	BF_4	50 (66:34)
2	SbF_6	43 (70:30)
3	OTf	26 (69:31)
4	OMs	NR
5	CF_3CO_2	31 (70:30)

^{a} General reaction conditions: 0.2 mmol **1a**, plastic vial. ^{b} Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

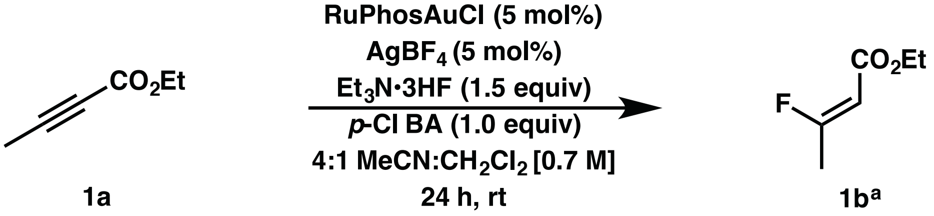
Table S2. Control studies for the hydrofluorination of **1a**.



Entry	Au [mol%]	Ag [mol%]	RuPhos [mol%]	HF [equiv]	*p*-Cl BA [equiv]	Yield [%] (*Z:E*)[b]
1	5	5	0	1.5	1.0	76 (96:4)
2	0	5	0	1.5	1.0	NR
3	0	5	5	1.5	1.0	NR
4	0	0	5	1.5	1.0	NR
5	5	5	0	1.5	0	65 (96:4)

[a] General reaction conditions: 0.2 mmol **1a**, plastic vial. [b] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

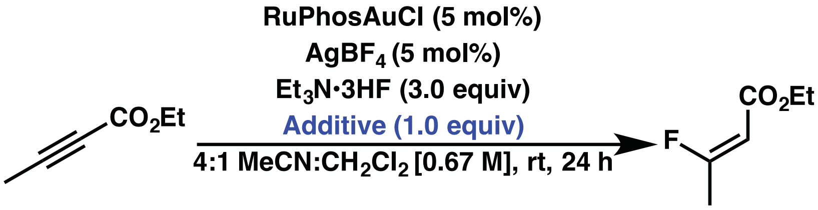
Table S3. Effect of reaction vessel, HF source, and temperature on the hydrofluorination of **1a**.



Entry	Deviation from Standard Conditions	Yield [%] (*Z:E*)[b]
1	None	76 (96:4)
2	Et_3N•2HF	5 (>98:2)
3	Et_3N•1HF	<2
4	pyridine•HF(30:70)	NR
5	Glass Vial	74 (97:3)
6	50 °C, Glass vial	78 (62:38)

[a] General reaction conditions: 0.2 mmol **1a**, 1.5 equiv HF source, plastic vial.
[b] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with 2,4-dinitrofluorobenzene as an internal standard.

Table S4. Effect of the additive on the hydrofluorination of **1a**.



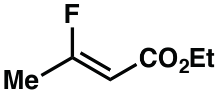
1a **1b**[a]

Entry	Additive	Yield [%] (*Z:E*)[b]
1	*p*-CN benzoic acid	48 (>98:2)
2	*p*-Cl benzoic acid	80 (96:4)
3	benzoic acid	62 (97:3)
4	*p*-Et benzoic acid	71 (97:3)
5	*p*-OMe benzoic acid	73 (97:3)
6	TsOH	65 (97:3)
7	Cl_3CCO_2H	31 (>98:2)
8	$HNTf_2$	34 (>98:2)

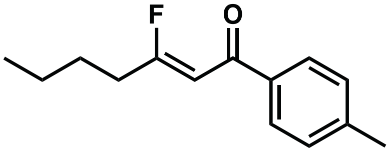
[a] General reaction conditions: 0.2 mmol **1a**, plastic vial. [b] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with PhF as an internal standard.

Table S5. Comparison of hydrofluorination conditions.

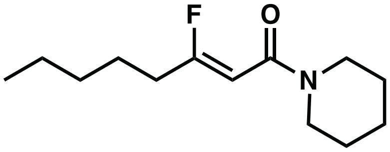
NMR yield; *Z:E* [c]



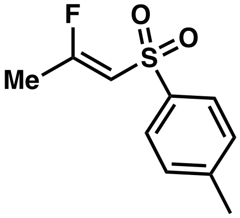
80%; 96:4
29%; >98:2



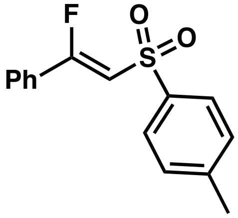
75%; 90:10
0%[d]



59%; >98:2[e]
0%



7%;>98:2
63%; >98:2[f]



13%; >98:2
81%; >98:2[g]

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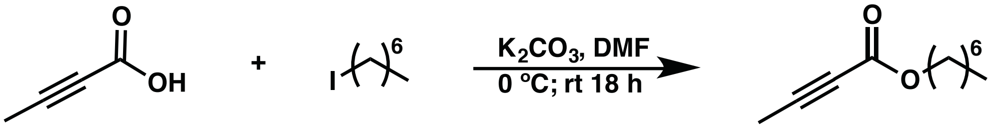
[a] Conditions A: 0.5 mmol alkyne, 3.0 equiv Et_3N•3HF, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 MeCN:CH_2Cl_2 [0.7 M], rt, 24 h, plastic vial. [b] Conditions B: 0.2 mmol alkyne, 4.0 equiv pyridine•HF (70% HF), 2.5 mol% JohnPhosAuNTf$_2$, $PhCF_3$ [0.4 M], rt, 8 h, plastic vial. [c] Yields and *Z:E* ratios were determined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d] Only 19% of the difluoro *β*-ketone was detected by ^{19}F NMR spectroscopy and GC-MS analysis. [e] Modified Conditions A: 4.0 equiv Et_3N•3HF, 4:1 MeCN:CH_2Cl_2 [1.25 M], 48 h. [f] Literature value: 64% *Z*. [g] Literature value: 90% *Z*.

Synthesis of Alkynes

heptyl but-2-ynoate **(2a)**



Prepared according to a published procedure.[19] To a stirring solution of but-2-ynoic acid (1.26 g, 15.0 mmol, 1 equiv) in dimethyl formamide (12.6 mL) at 0 ºC was added potassium carbonate 5.18 g, 37.5 mmol, 2.5 equiv) under a flow of nitrogen. After heptyl iodide (3.7 mL, 22.5 mmol, 1.5 equiv) was added dropwise and the resultant reaction mixture was stirred at RT. After completion of the reaction (by TLC), the reaction mixture was diluted with water (50 mL) and ethyl acetate (100 mL). The separated organic phase was washed with ice cold, deionized water (dH$_2$O) (3 x 80 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated. The crude reside was purified by silica gel column chromatography (10:1 hexanes:ethyl acetate).

Colorless oil (24%, 656 mg):

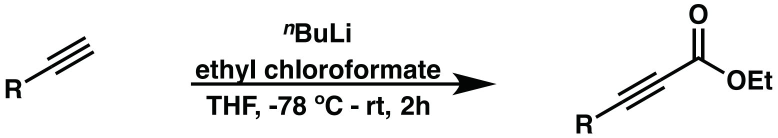
^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 4.10 (t, *J* = 6.8 Hz, 2H), 1.97 (s, 3H), 1.66 – 1.60 (m, 2H), 1.37 – 1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, CD$_2$Cl$_2$) δ = 154.1, 85.4, 72.8, 66.2, 32.1, 29.3, 28.9, 26.2, 23.0, 14.2, 3.9.

HRMS (ESI+) calc'd for $C_{11}H_{19}O_2^+$ [M+H]$^+$: 183.1380, found: 183.1380.

IR (neat) 2927, 2243, 1707 cm^{-1}.

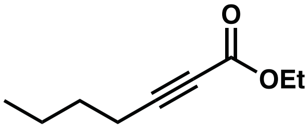
Synthesis of alkynes **3a, 4a, 5a, 6a** and **8a.**



Prepared according to a published procedure.[20] To a solution of terminal alkyne (18.0 mmol, 1 equiv) at -78 ºC was added ^{n}BuLi (7.2 mL, 2.5 M in hexanes, 18.0 mmol, 1 equiv), and the reaction was stirred for 30 minutes at -78 ºC. Ethyl chloroformate (1.71 mL, 18.0 mmol, 1 equiv) was added dropwise, and then the reaction warmed to room temperature and stirred for 2 h. The reaction was quenched with ice cold, deionized water (125 mL) and extracted with Et$_2$O (3 x 150 mL). The combined organic layers were washed with brine (200 mL), dried over

$MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexanes:ethyl acetate).

ethyl hept-2-ynoate **(3a)**

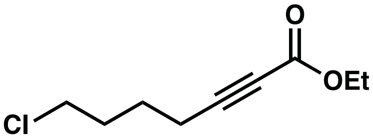


Light yellow oil (48%, 1.33 g):

In accordance with previously reported spectra.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 7.1 Hz, 2H), 1.53 (p, *J* = 7.2 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

ethyl 7-chlorohept-2-ynoate **(4a)**



Colorless oil (70%, 2.38 g):

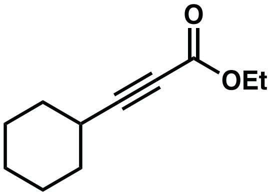
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.1, 2H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.36 (t, *J* = 6.9 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.77 – 1.69 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 88.2, 73.8, 61.9, 44.2, 31.4, 24.8, 18.1, 14.1.

HRMS (ESI+) calc'd for $C_9H_{14}ClO_2^+$ $[M+H]^+$: 189.0677, found: 189.0677.

IR (neat) 2984, 2236, 1704, 1246, 1072, 730 cm^{-1}.

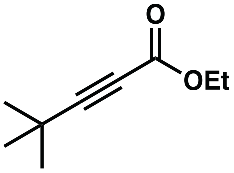
ethyl 3-cyclohexylpropiolate **(5a)**



Colorless oil (81%, 2.64g):

In accordance with previously reported spectra.[21]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.18 (q, *J* = 7.2 Hz, 2H), 2.51 – 2.45 (m, 1H), 1.87 – 1.76 (m, 2H), 1.73 – 1.64 (m, 2H), 1.54 – 1.45 (m, 3H), 1.34 – 1.23 (m, 6H) ethyl 4,4-dimethylpent-2-ynaote **(6a)**

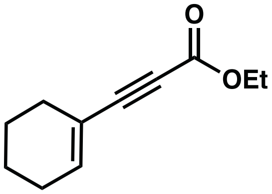


Colorless oil (81%, 2.25 g):

In accordance with previously reported spectra.[21]

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.23 (s, 9H).

ethyl 3-(cyclohex-1-en-1-yl)propiolate **(8a)**

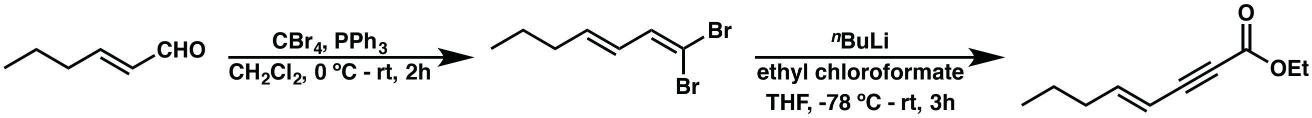


light yellow oil (67%, 2.15 g):

In accordance with previously reported spectra.[21]

^{1}H NMR (600 MHz, CDCl$_3$) δ 6.44 – 6.36 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.15 – 2.06 (m, 4H), 1.64 – 1.58 (m, 2H), 1.58 – 1.54 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

ethyl-(*E*)-oct-4-en-2-ynoate **(7a)**



Prepared according to a modified literature procedure.[22] To a CH$_2$Cl$_2$ (59 mL) solution of carbon tetrabromide (5.8 g, 17.5 mmol, 2 equiv) was added a CH$_2$Cl$_2$ solution of triphenylphosphine (9.2 g, 35.0 mmol, 4 equiv) at 0 ºC dropwise. The reaction mixture was warmed to rt and stirred for 30 minutes before a CH$_2$Cl$_2$ (4 mL) solution of (*E*)-hex-2-enal (8.75 mmol, 1.04 mL, 1.0 equiv) was slowly added. The resulting mixture was stirred at rt for 2 h before the addition of dH$_2$O (50 mL) to partition the organic layer. The mixture was extracted with CH$_2$Cl$_2$ (3 x 20 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. To this residue was added Et$_2$O (40 mL) and the resulting suspension filtered. The ethereal filtrate is concentrated and chromatographed through a silica gel column (hexanes) to afford (*E*)-1,1-dibromo-hepta-1,3-diene as a light yellow oil whose ^{1}H and ^{13}C spectra matched reported values.[23]

To a THF solution (28 mL) of (*E*)-1,1-dibromo-hepta-1,3-diene (1.08 g, 4.25 mmol, 1.0 equiv) at -78 ºC was added ^{n}BuLi (3.57 mL, 2.5 M in hexanes, 8.93 mmol, 2.1 equiv) dropwise. The resulting solution was stirred at -78 ºC for 30 min before ethyl chloroformate (0.41 mL, 4.72 mmol, 1.0 equiv) was added dropwise. After the dropwise addition, the reaction mixture was stirred at -78 ºC for 30 min and then stirred at rt for 2 h. To this solution was added saturated NH_4Cl (50 mL). The aqueous layer was separated, extracted with Et_2O (3 x 25 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel column chromatography (Et_2O:hexanes 1:9) to afford ethyl-(*E*)-oct-4-en-2-ynoate (7a) as a yellow oil (25% from (*E*)-hex-2-enal, 304 mg).

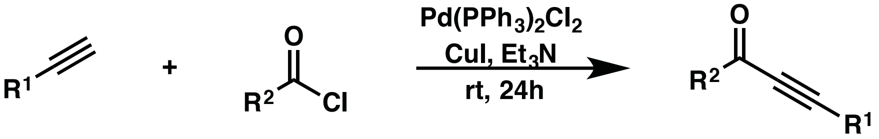
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (dt, *J* = 14.6, 7.1 Hz, 1H), 5.53 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.41 (p, *J* = 7.3 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 152.4, 107.2, 85.6, 79.5, 61.9, 35.5, 21.5, 14.1,

HRMS (ESI+) calc'd for $C_{10}H_{15}O_2^+$ $[M+H]^+$: 167.1067, found: 167.1065.

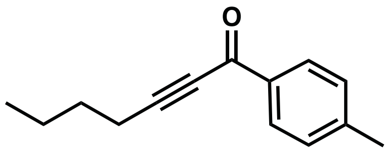
IR (neat) 2962, 2933, 2874, 2212, 1704, 1626, 1245, 1096 cm^{-1}.

Synthesis of alkynes **9a** and **10a**



Prepared from a modified procedure.[24] To a solution of Et_3N (20 mL) was added terminal alkyne (12.5 mmol, 1.25 equiv), acyl chloride (10.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.5 mol%), and CuI (2.5 mol%). After 24 h of stirring at rt, MeOH (10 mL) was added, the solvent evaporated and Et_2O (150 mL) was added. The mixture was filtered, washed with 3 M HCl (75 mL), dH_2O (75 mL), brine (75 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (EtOAc:hexanes) to afford **9a** or **10a**.

1-(4-methylphenyl)hept-2-yn-1-one **(9a)**

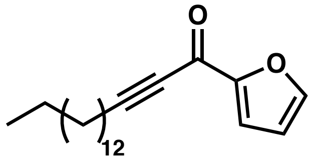


tan/yellow oil (50%, 1.00 g):

In accordance with previously reported spectra.[25]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.73 – 1.59 (m, 2H), 1.56 – 1.44 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

1-(furan-2-yl)heptadec-2-yn-1-one **(10a)**



orange solid (48%, 1.51 g):

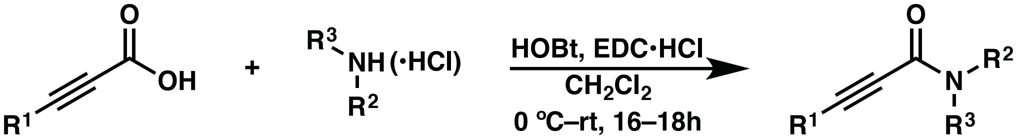
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.30 (d, *J* = 3.5 Hz, 1H), 6.56 – 6.54 (m, 1H), 2.44 (t, *J* = 7.1 Hz, 1H), 1.63 (p, *J* = 7.2 Hz, 2H), 1.44 (p, *J* = 7.1 Hz, 2H), 1.33 – 1.21 (m, 20H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 153.4, 147.8, 120.7, 112.6, 112.6, 95.7, 79.1, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.0, 27.8, 22.8, 19.3, 14.2, 14.2.

HRMS (ESI+) calc'd for $C_{21}H_{33}O_2^+$ $[M+H]^+$: 317.2475, found: 317.2471.

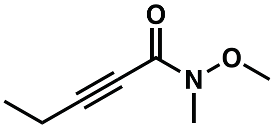
IR (neat) 2919, 2849, 2210, 1626, 1458, 794 cm^{-1}.

Synthesis of alkynes **12a, 14a, 28a, 30a** and **31a.**



Prepared according to a modified literature procedure.[26] To an ice-cold solution of acid (10.7 mmol, 1.0 equiv) in CH_2Cl_2 (71 mL), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC•HCl) (11.8 mmol, 1.1 equiv) and 1-hydroxybenzotriazole (HOBt) (13.91 mmol, 1.3 equiv; concentrated twice with distilled benzene) were added and the mixture stirred for 5 min. The amine (13.91 mmol 1.3 equiv; if HCl salt of amine added 1.3 equiv Et_3N) was then added and the reaction was allowed to reach rt overnight. After 16–19 h the solvent was evaporated and the residue dissolved in EtOAc (150 mL). The organic phase was washed with 1 M HCl (100 mL), saturated $NaHCO_3$ (100 mL), brine (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (EtOAc:hexanes) to afford pure **12a, 14a, 28a, 30a** and **31a**.

N-methoxy-*N*-methylpent-2-ynamide (**12a**)



colorless oil (68%, 1.55 g, 16.2 mmol scale, employed HCl salt of amine):

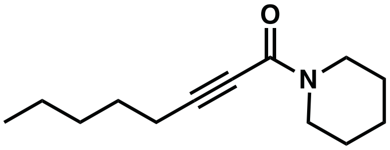
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.33 – 3.01 (m, 3H), 2.28 (q, *J* = 7.5 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 94.4, 72.4, 61.9, 32.2, 12.7, 12.5.

HRMS (ESI+) calc'd for $C_7H_{12}NO_2^+$ $[M+H]^+$: 142.0863, found: 142.0860.

IR (neat) 2980, 2939, 2235, 1636, 1412, 1378, 988, 722 cm^{-1}.

1-(piperidin-1-yl)oct-2-yn-1-one (**14a**)



orange oil (88%, 1.95 g, 10.7 mmol scale):

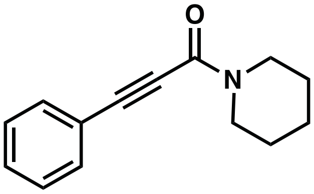
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.55 (t, *J* = 5.6 Hz, 2H), 3.42 (t, *J* = 5.5 Hz, 2H), 2.21 (t, *J* = 7.2 Hz, 2H), 1.54 – 1.49 (m, 2H), 1.48 – 1.43 (m, 4H), 1.42 – 1.37 (m, 2H), 1.28 – 1.15 (m, 4H), 0.76 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 92.8, 73.7, 47.8, 41.9, 30.8, 27.3, 26.2, 25.2, 24.3, 21.9, 18.7, 13.7.

HRMS (APCI+) calc'd for $C_{13}H_{22}NO^+$ $[M+H]^+$: 208.1696, found: 208.1691.

IR (neat) 2933, 2857, 2244, 2222, 1622, 1428, 1266, 1234, 731 cm^{-1}.

3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-one (**28a**)

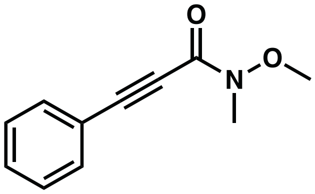


white solid (75%, 963 mg, 6.0 mmol scale)

In accordance with previously reported spectra.[27]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.33 (m, 2H), 3.77 (t, *J* = 5.7, 5.1 Hz, 2H), 3.62 (t, *J* = 5.6 Hz, 2H), 1.70 – 1.62 (m, 4H), 1.58 (p, *J* = 5.7 Hz, 2H).

N-methoxy-*N*-methyl-3-phenylpropiolamide (**30a**)

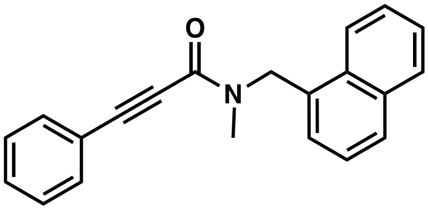


colorless oil (62%, 2.13 g, 18 mmol scale, employed HCl salt of amine)

In accordance with previously reported spectra.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 2H), 3.82 (s, 3H), 3.26 (bs, 3H).

N-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylpropiolamide (**31a**)



opaque, colorless oil (98%, 1.85 g, 6.3 mmol scale):

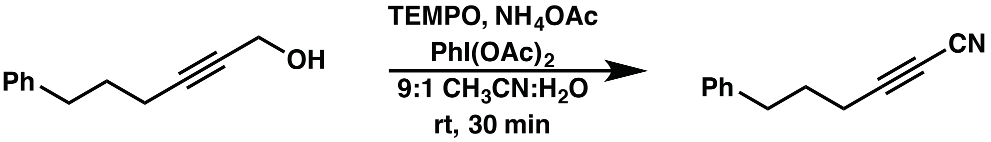
^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers ca. 59:41) δ 8.15 (d, *J* = 8.4 Hz, 1H, major rotamer), 8.09 (d, *J* = 8.3 Hz, 0.7H, minor rotamer), 7.92 – 7.81 (m, 3.4H), 7.60 – 7.38 (m, 11.4H), 7.36 – 7.25 (m, 5.2H), 5.34 (s, 1.4H, minor rotamer), 5.14 (s, 2H, major rotamer), 3.11 (s, 3H, major rotamer), 2.98 (s, 2.2H minor rotamer).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 154.5, 133.8, 133.8, 132.4, 132.3, 131.6, 131.5, 131.4, 131.2, 130.0, 129.0, 128.8, 128.6, 128.6, 128.5, 128.4, 127.3, 126.7, 126.6, 126.1, 126.0, 125.4, 125.3, 125.1, 123.8, 122.5, 120.4, 120.2, 90.7, 90.5, 81.7, 52.5, 47.7, 35.5, 32.2.

HRMS (APCI+) calc'd for $C_{21}H_{18}NO^+$ $[M+H]^+$: 300.1383, found: 300.1381.

IR (neat) 3060, 2926, 2855, 2213, 1740, 1665, 1619, 1398, 1244, 1109, 908, 760, 728, 689 cm^{-1}.

6-phenylhex-2-ynenitrile **(15a)**



Prepared according to a modified literature report.[29] To a solution of 9:1 CH_3CN:dH_2O was added (under a positive flow of N_2) 5-phenylpent-2-yn-1-ol (1.22 g, 7.0 mmol, 1.0 equiv) followed by TEMPO (55mg, 5 mol%), NH_4OAc (2.09 g, 27.2 mmol, 3.88 equiv) and $PhI(OAc)_2$ (4.94 g, 15.33, 2.19 equiv). The suspension was stirred at rt for 30 min, concentrated and diluted with dH_2O (40 mL) and Et_2O (80 mL). The layers were separated and the aqueous layer extracted with Et_2O (2 x 80 mL). The organics were collected and washed with brine (200 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (1:15 Et_2O:hexanes) to afford **15a** as a colorless oil (1.04 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.4 Hz, 2H), 2.74 (t, J = 7.4 Hz, 2H), 2.36 (t, J = 7.1 Hz, 2H), 1.94 (p, J = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 128.7, 128.6, 126.5, 105.4, 87.1, 55.8, 34.6, 28.7, 18.2.

HRMS (ESI+) calc'd for $C_{11}H_{11}NNa^+$ $[M+Na]^+$: 192.0784, found: 192.0780.

IR (neat) 3028, 2939, 2314, 2259, 1496, 1454, 743, 608, 500 cm^{-1}.

General Procedures for Gold-Catalyzed Alkyne Hydrofluorination

Attention: Hydrogen fluoride amine complexes are hazardous and should be handled with care. In case of skin contact, calcium gluconate gel should be applied to the affected area and medical attention sought. Although some hydrogen fluoride amine complexes are known to etch normal laboratory glassware, the catalytic hydrofluorination reactions disclosed in this communication can be contacted in glass vials without a significant decrease in yield. However, plastic, screw-lid centrifuge tubes are recommended.

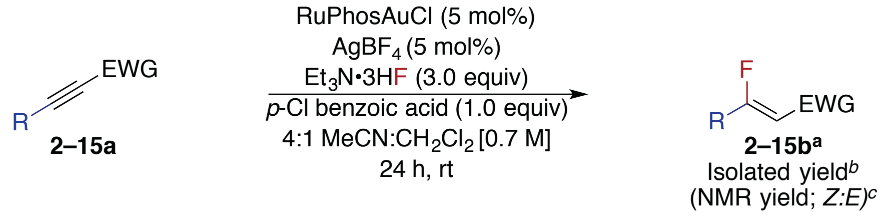
Notes:

- Before each experiment (1–24 h), RuPhosAuCl (white solid) was dissolved in dry dichloromethane, filtered through a plug of basic alumina (1-inch of basic alumina layered on a glass fiber pad in a Kimble 5-3/4” Monster Pipette) into a 20-mL vial that had been rinsed with dry dichloromethane (1 mL), and concentrated.
- Glass vials, stir bars, and heating blocks were utilized for reactions conducted at elevated temperatures. Only a slight decrease in the NMR yield (1–3%) of **1b** was observed upon switching from plastic to glass reaction vessels. Reactions at room temperature were conducted in plastic, screw-lid centrifuge tubes that were heated at 70 ºC for 5–7 days before being pumped in a nitrogen-filled glovebox.
- Presence of water results in competitive hydration of the alkyne.
- See substrate tables for variations on the standard procedures below.

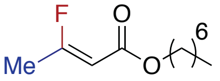
Standard Procedure for 0.5 mmol scale

In a nitrogen-filled glove-box (in the absence of light) solvent (700 μL) was added to a 4-mL glass vial charged with RuPhosAuCl (17.5 mg, 0.025 mmol, 5 mol%) and $AgBF_4$ (5 mg, 0.025 mmol, 5 mol%). After 8–10 minutes of mixing with a syringe, the white slurry was filtered through a glass fiber pad (packed into the neck of 9” pipette) into a 2-mL screw-lid plastic centrifuge tube containing *p*-chlorobenzoic acid (87 mg, 0.5 mmol, 1 equiv). Alkyne (**2-30a**) was quickly added to the reaction mixture. Outside the glove-box, in the absence of light, the plastic centrifuge tube was opened (briefly exposed to air) and $Et_3N•3HF$ (250 μL, 1.50 mmol, 3 equiv) added. The reaction was sealed and placed on a IKA KS 130 basic shaker table (560 revolutions/min) under the protection from light. After 24 hours, the reaction mixture was transferred to a round bottom flask (50 mL) with dichloromethane (15 mL) and treated with a 10% Na_2CO_3 solution (15 mL). After stirring for 20–30 minutes, the biphasic solution was transferred to a separatory funnel with dichloromethane (20 mL) and additional 10% Na_2CO_3 (10 mL) added. The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 30 mL). Dichloromethane was added to the organic fractions until the total volume reached 200 mL. Then the organics were washed with brine (1 x 150 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was chromatographed (hexanes:Et_2O) to afford **2–30b**.

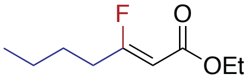
Table S6. Scope of β-alkyl, β-fluoro Michael Acceptors.



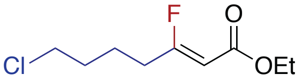
2–15b[a]
Isolated yield[b]
(NMR yield; *Z:E*)[c]



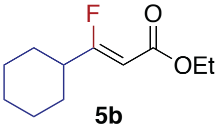
2b
71%
(80%; 95:5)



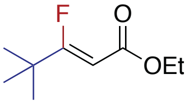
3b
73%[d]
(78%; 97:3)



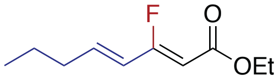
4b
69%
(73%; >98:2)



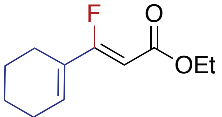
5b
74%[e]
(76%; >98:2)



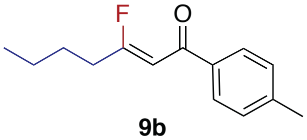
6b
71%[f]
(86%; >98:2)



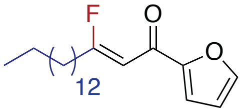
7b
69%
(82%; >98:2)



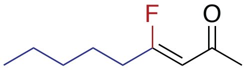
8b
64%
(78%; >98:2)



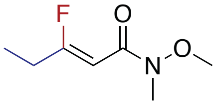
9b
62%
(75%; 90:10)



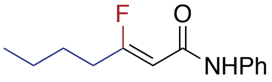
10b
61%
(-)[g]



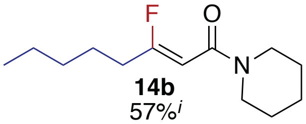
11b
60%; 99:1
(73%; >82:18)



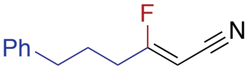
12b
72%[h]
(78%; >98:2)



13b
56%[i]
(64%; 98:2)



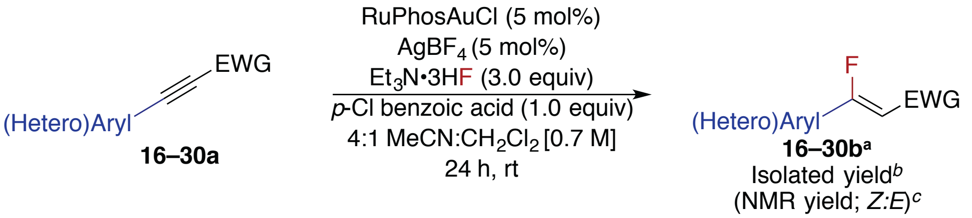
14b
57%[i]
(59%;) >98:2

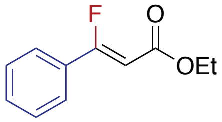


15b
49%[j]
(51% 98:2)

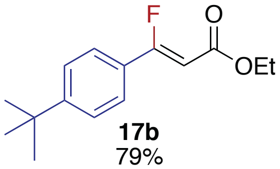
[a] Standard reaction conditions: 0.5 mmol **2–15a**, 3.0 equiv Et_3N•3HF, 1.0 equiv *p*-Cl BA, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 MeCN:CH_2Cl_2 [0.7 M], rt, 24 h. [b] **2–15b** isolated as a single isomer except **11b**. [c] Determined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d] 6.0 mmol scale. [e] 5.0 mmol scale. [f] 55 °C. [g] insoluble product. [h] 1.25 M, 4.0 equiv Et_3N•3HF. [i] 1.25 M, 4.0 equiv Et_3N•3HF, 48h. [j] 1.43 M, 4.5 equiv Et_3N•3HF, 50 °C.

Table S7. Scope of *β*-aryl, *β*-fluoro Michael Acceptors.

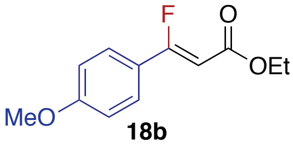




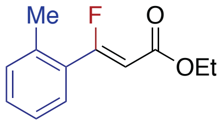
16b
65%
(79%; >98:2)



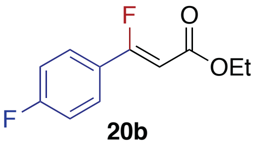
17b
79%
(88%; >98:2)



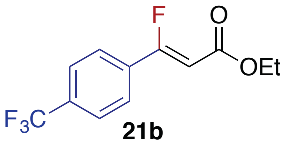
18b
79%
(86%; >98:2)



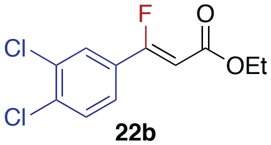
19b
53%[d]
(63%; >98:2)



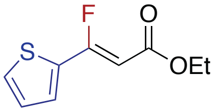
20b
77%
(87%; >98:2)



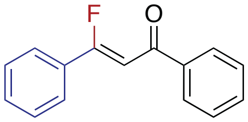
21b
73%[e]
(84%; >98:2)



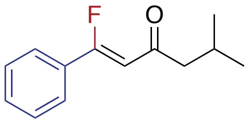
22b
71%[e]
(86%; >98:2)



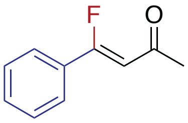
23b
80%
(88%; >98:2)



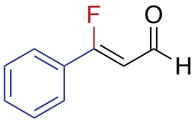
24b
66%[e]
(85%; 96:4)



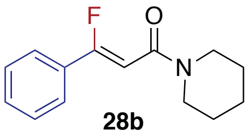
25b
54%[e]
(60%; >98:2)



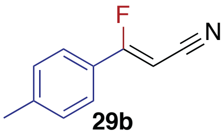
26b
60%
(65%; >98:2)



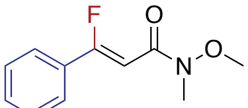
27b
63%[f]
(70%; >98:2)



28b
64%[g]
(74%; >98:2)



29b
68%[h]
(75%; >98:2)

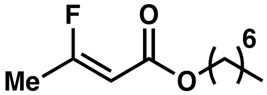


30b
71%[e]
(73%; >98:2)

---

[a] Standard reaction conditions: 0.5 mmol **16–30a**, 3.0 equiv Et_3N•3HF, 1.0 equiv *p*-Cl BA, 5 mol% RuPhosAuCl, 5 mol% $AgBF_4$, 4:1 MeCN:CH_2Cl_2 [0.7 M], rt, 24 h. [b] **16–30b** isolated as a single isomer. [c] Determined by ^{19}F NMR spectroscopy with PhF as an internal standard. [d] 1.43 M, 45 ºC. [e] 45 ºC. [f] 4.5 mmol. [g] 1.25 M, 55 ºC, 4.0 equiv Et_3N•3HF. [h] 45 ºC, 48 h, 4.0 equiv Et_3N•3HF.

heptyl (*Z*)-3-fluorobut-2-enoate (**2b**)



Column chromatography (SiO_2, eluting with 1:30→1:20 Et_2O:hexanes) afforded the desired product as a colorless oil (71.8 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.16 (d, *J* = 32.6 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.00 (d, *J* = 16.6 Hz, 3H), 1.61 (p, *J* = 6.7 Hz, 2H), 1.37 – 1.20 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H).

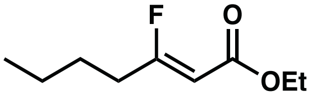
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8 (d, *J* = 283.8 Hz), 163.9 (d, *J* = 2.1 Hz), 131.7, 129.0, 99.7 (d, *J* = 5.0 Hz), 64.4, 31.8, 29.0, 28.7, 26.0, 22.7, 19.2 (d, *J* = 26.5 Hz), 14.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.6 (dq, *J* = 32.7, 16.4 Hz).

HRMS (APCI+) calc'd for $C_{11}H_{20}FO_2^+$ $[M+H]^+$: 203.1442, found: 203.1443.

IR (neat) 2956, 2928, 2858, 1716, 1687, 1219, 1136, 1037 cm^{-1}.

ethyl (*Z*)-3-fluorohept-2-enoate (**3b**)



Column chromatography (SiO_2, eluting with 1:30→1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (763.4 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.15 (d, *J* = 33.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.25 (dt, *J* = 17.0, 7.5 Hz, 2H), 1.53 (p, *J* = 7.5 Hz, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

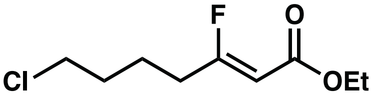
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3 (d, *J* = 286.4 Hz), 163.9 (d, *J* = 1.6 Hz), 131.7, 129.0, 98.9 (d, *J* = 5.3 Hz), 60.2, 32.8 (d, *J* = 23.8 Hz), 27.7 (d, *J* = 1.9 Hz), 22.0, 14.3, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -80.0 (dt, *J* = 33.8, 17.2 Hz).

HRMS (APCI+) calc'd for $C_9H_{16}FO_2^+$ $[M+H]^+$: 175.1129, found: 175.1121.

IR (neat) 2961, 2936, 2875, 1727, 1715, 1681, 1215, 1133, 1037, 907, 836 cm^{-1}.

ethyl (*Z*)-7-chloro-3-fluorohept-2-enoate (**4b**)



Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a colorless oil (72.0 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (d, *J* = 33.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.29 (dt, *J* = 16.9, 7.4 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.66 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

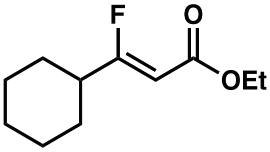
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2 (d, *J* = 286.1 Hz), 163.7 (d, *J* = 1.8 Hz), 99.4 (d, *J* = 5.0 Hz), 60.3, 44.3, 32.3 (d, *J* = 24.2 Hz), 31.5, 23.0 (d, *J* = 1.9 Hz), 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -80.6 (dt, *J* = 33.7, 17.0 Hz).

HRMS (APCI+) calc'd for $C_9H_{15}ClFO_2^+$ $[M+H]^+$: 209.0739, found: 209.0736.

IR (neat) 2960, 2874, 1722, 1681, 1271, 1214, 1133, 1037, 839 cm^{-1}.

ethyl (*Z*)-3-cyclohexyl-3-fluoroacrylate (**5b**)



Column chromatography (SiO_2, eluting with 1:24 Et_2O:hexanes) afforded the desired product as a colorless oil (740.0 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (d, *J* = 34.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.21 – 2.12 (m, 1H), 1.91 – 1.87 (m, 2H), 1.81 – 1.78 (m, 2H), 1.71 – 1.67 (m, 1H), 1.29 – 1.25 (m, 7H), 1.21 – 1.16 (m, 1H).

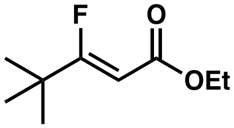
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8 (d, *J* = 287.7 Hz), 164.3, 97.0 (d, *J* = 5.4 Hz), 60.2, 41.7 (d, *J* = 22.2 Hz), 29.4 (d, *J* = 2.2 Hz), 25.8, 25.7, 14.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -85.3 (dd, *J* = 34.3, 14.9 Hz).

HRMS (APCI+) calc'd for $C_{11}H_{18}FO_2^+$ $[M+H]^+$: 201.1285, found: 201.1288.

IR (neat) 2981, 2932, 2858, 1728, 1712, 1675, 1199, 1140, 1041, 910 cm^{-1}.

ethyl (*Z*)-3-fluoro-4,4-dimethylpent-2-enoate (**6b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (62.0 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.20 (d, *J* = 34.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 9H).

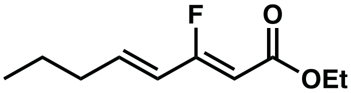
^{13}C NMR (151 MHz, $CDCl_3$) δ 178.7 (d, *J* = 289.4 Hz), 164.4, 95.8 (d, *J* = 6.1 Hz), 60.2, 36.0 (d, *J* = 21.5 Hz), 26.9 (d, *J* = 2.8 Hz), 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -89.8 (d, *J* = 34.2 Hz).

HRMS (APCI+) calc'd for $C_9H_{16}FO_2^+$ $[M+H]^+$: 175.1129, found: 175.1124.

IR (neat) 2974, 2876, 1730, 1711, 1672, 1278, 1175, 1099, 1038 cm^{-1}.

ethyl (2*Z*, 4*E*)-3-fluoroocta-2,4-dienoate (**7b**)



Column chromatography (SiO_2, eluting with 1:24 Et_2O:hexanes) afforded the desired product as a light yellow oil (64.0 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.82 (dd, *J* = 24.1, 15.6 Hz, 1H), 5.14 (d, *J* = 32.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.17 – 2.13 (m, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

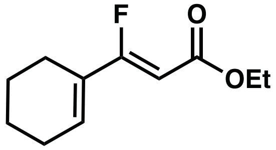
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1 (d, *J* = 277.7 Hz), 164.4 (d, *J* = 2.2 Hz), 141.1 (d, *J* = 5.0 Hz), 121.6 (d, *J* = 20.9 Hz), 98.8 (d, *J* = 6.4 Hz), 60.2, 34.7, 21.8, 14.3, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.1 (dd, *J* = 32.6, 24.1 Hz).

HRMS (APCI+) calc'd for $C_{10}H_{16}FO_2^+$ $[M+H]^+$: 187.1129, found: 187.1121.

IR (neat) 2962, 2934, 2875, 1721, 1704, 1658, 1627, 1229, 1136, 1037, 966 cm^{-1}.

ethyl (*Z*)-3-(cyclohex-1-en-1-yl)-3-fluoroacrylate (**8b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a light yellow oil (63.0 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 – 6.58 (m, 1H), 5.23 (d, *J* = 34.2 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 6H), 2.23 – 2.18 (m, 8H), 2.06 (q, *J* = 4.7, 3.0 Hz, 9H), 1.72 – 1.65 (m, 9H), 1.63 – 1.56 (m, 10H), 1.27 (t, *J* = 7.1 Hz, 8H).

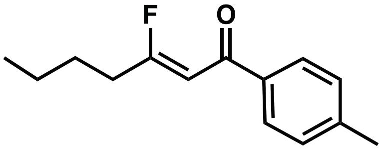
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8 (d, *J* = 277.8 Hz), 164.7, 133.8 (d, *J* = 8.8 Hz), 128.5 (d, *J* = 17.5 Hz), 95.3 (d, *J* = 6.9 Hz), 60.2, 25.8, 23.8 (d, *J* = 2.8 Hz), 22.0, 21.5, 14.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.2 (d, *J* = 34.7 Hz).

HRMS (APCI+) calc'd for $C_{11}H_{16}FO_2^+$ $[M+H]^+$: 199.1129, found: 199.1126.

IR (neat) 2981, 2935, 2864, 1723, 1700, 1642, 1320, 1249,1150, 1044, 731 cm^{-1}.

(*Z*)-3-fluoro-1-(4-methylphenyl)hept-2-en-1-one (**9b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a light yellow oil (68.0 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.04 (d, *J* = 34.3 Hz, 1H), 2.40 (s, 3H), 2.36 (dt, *J* = 17.0, 7.7 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.47 – 1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

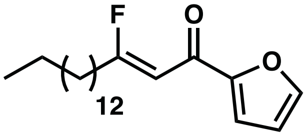
^{13}C NMR (151 MHz, $CDCl_3$) δ 188.5, 170.8 (d, *J* = 286.9 Hz), 143.6, 135.9, 129.3, 128.6, 103.7 (d, *J* = 5.4 Hz), 33.1 (d, *J* = 24.0 Hz), 27.9, 22.2, 21.7, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -81.4 (dt, *J* = 34.3, 17.4 Hz).

HRMS (APCI+) calc'd for $C_{14}H_{18}FO^+$ $[M+H]^+$: 221.1336, found: 221.1333.

IR (neat) 2959, 2932, 2872, 1679, 1629, 1605, 1572, 1237, 1181, 895, 732 cm^{-1}.

(*Z*)-3-fluoro-1-(furan-2-yl)heptadec-2-en-1-one (**10b**)



Column chromatography (SiO_2, eluting with 1:1 CH_2Cl_2:hexanes) afforded the desired product as a white solid (102.0 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.11 (d, *J* = 33.7 Hz, 1H), 2.34 (dt, *J* = 17.3, 7.6 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.42 – 1.21 (m, 23H), 0.87 (t, *J* = 7.0 Hz, 3H).

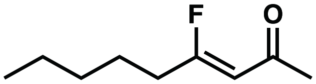
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 172.4 (d, *J* = 291.2 Hz), 153.5, 146.2, 116.9, 112.6, 102.4 (d, *J* = 3.2 Hz), 33.6 (d, *J* = 23.2 Hz), 32.0, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.0, 25.9 (d, *J* = 1.5 Hz), 22.8, 14.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -79.1 (dt, *J* = 34.3, 17.4 Hz).

HRMS (APCI+) calc'd for $C_{21}H_{34}FO_2^+$ $[M+H]^+$: 337.2537, found: 337.2537.

IR (neat) 3123, 3094, 2953, 2914, 2849, 1690, 1628, 1469, 1399, 1276, 1018, 890, 750 cm^{-1}.

(*Z*)-4-fluoronon-3-en-2-one (**11b**)



Column chromatography (SiO_2, eluting with 1:10 Et_2O:hexanes) afforded the desired product as a colorless liquid (47.5 mg, 60%; *Z:E* = 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, *J* = 38.4 Hz, 1H), 2.33 (d, *J* = 3.9 Hz, 3H), 2.31 – 2.22 (m, 2H), 1.58 – 1.50 (m, 2H), 1.33 – 1.29 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

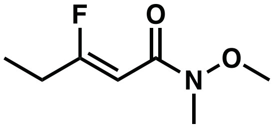
^{13}C (126 MHz, $CDCl_3$) δ 196.7, 171.9 (d, *J* = 283.3 Hz), 109.3 (d, *J* = 8.1 Hz), 32.9 (d, *J* = 25.2 Hz), 31.2 (d, *J* = 6.3 Hz), 31.1, 25.4 (d, *J* = 1.8 Hz), 22.4, 13.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ -80.1 (dtd, *J* = 38.8, 17.5, 4.1 Hz).

HRMS (ESI+) calc'd for $C_9H_{16}FO^+$ $[M+H]^+$: 159.1180, found: 159.1184.

IR (neat) 2959, 2932, 2864, 1667, 1364, 1250, 910, 732 cm^{-1}.

(*Z*)-3-fluoro-*N*-methoxy-*N*-methylpent-2-enamide (**12b**)



Column chromatography (SiO_2, eluting with 1:4→1:2 Et_2O:hexanes) afforded the desired product as a colorless oil (58.0 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 (d, *J* = 33.8 Hz, 1H), 3.65 (s, 3H), 3.17 (s, 3H), 2.29 (dq, *J* = 14.9, 7.5 Hz, 2H), 1.16 – 1.10 (m, 3H).

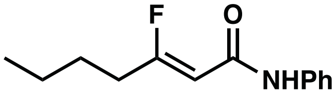
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5 (d, *J* = 284.8 Hz), 164.6, 96.0, 61.5, 32.1, 26.5 (d, *J* = 25.3 Hz), 10.3 (d, *J* = 3.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -85.5 (bs).

HRMS (ESI+) calc'd for $C_7H_{13}FNO_2^+$ $[M+H]^+$: 162.0925, found: 162.0928.

IR (neat) 2977, 2941, 2246, 1686, 1647, 1378, 1181, 1104, 1060, 978, 878, 811, 730 cm^{-1}.

(*Z*)-3-fluoro-*N*-phenylhept-2-enamide (**13b**)



Column chromatography (SiO_2, eluting with 3:7→2:1 Et_2O:hexanes) afforded the desired product as a white solid (61.4 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 11.7 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 38.3 Hz, 1H), 2.30 (dt, *J* = 18.3, 7.5 Hz, 2H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

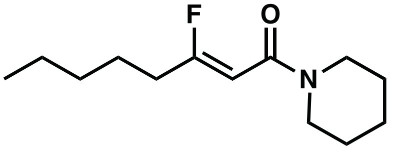
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1 (d, *J* = 273.0 Hz), 161.7, 137.9, 129.0, 124.4, 120.2, 103.7 (d, *J* = 7.1 Hz), 32.3 (d, *J* = 25.9 Hz), 27.7 (d, *J* = 1.9 Hz), 22.0, 13.7 (d, *J* = 2.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -88.6 (dtd, *J* = 37.5, 18.3, 11.8 Hz).

HRMS (ESI+) calc'd for $C_{13}H_{17}FNO_2^+$ $[M+H]^+$: 222.1289, found: 222.1281.

IR (neat) 3274, 3138, 2956, 1689, 1646, 1599, 1550, 1441, 1375, 1310, 1253, 1151, 900, 752, 688 cm^{-1}.

(*Z*)-3-fluoro-1-(piperidin-1-yl)oct-2-en-1one (**14b**)



Column chromatography (SiO_2, eluting with 1:3→4:1 Et_2O:hexanes) afforded the desired product as a colorless oil (65.4 mg, 57%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.18 (d, *J* = 38.5 Hz, 1H), 3.55 (t, *J* = 5.6 Hz, 2H), 3.39 (t, *J* = 5.5 Hz, 2H), 2.20 (dt, *J* = 15.8, 7.6 Hz, 2H), 1.63 – 1.59 (m, 2H), 1.56 – 1.49 (m, 6H), 1.32 – 1.27 (m, 4H), 0.86 (t, *J* = 6.6 Hz, 3H).

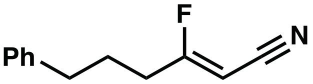
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1 (d, *J* = 269.0 Hz), 163.2, 100.4 (d, *J* = 13.9 Hz), 47.9, 42.4, 32.2 (d, *J* = 25.7 Hz), 31.1, 26.5, 25.5, 25.4 (d, *J* = 1.9 Hz), 24.6, 22.4, 14.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.4 (dt, *J* = 38.4, 16.4 Hz).

HRMS (APCI+) calc'd for $C_{13}H_{23}FNO^+$ $[M+H]^+$: 228.1758, found: 228.1761.

IR (neat) 3067, 2932, 2857, 1690, 1623, 1439, 1254, 1227, 1025, 729 cm^{-1}.

(*Z*)-3-fluoro-6-phenylhex-2-enenitrile (**15b**)



Column chromatography (SiO_2, eluting with 1:3→4:1 Et_2O:hexanes) afforded the desired product as a colorless oil (46.5 mg, 49%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.17 (d, *J* = 6.9 Hz, 2H), 4.77 (d, *J* = 32.6 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.35 (dt, *J* = 15.9, 7.6 Hz, 2H), 1.91 (p, *J* = 7.6 Hz, 2H).

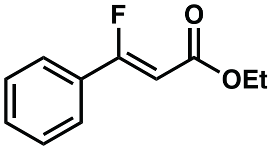
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6 (d, *J* = 285.1 Hz), 140.4, 128.7, 128.5, 126.5, 112.9 (d, *J* = 3.2 Hz), 79.1 (d, *J* = 13.8 Hz), 34.7, 31.6 (d, *J* = 22.0 Hz), 26.8 (d, *J* = 1.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -85.9 (dt, *J* = 33.1, 16.7 Hz).

HRMS (APCI+) calc'd for $C_{21}H_{34}FO_2^+$ $[M+H]^+$: 337.2537, found: 337.2537.

IR (neat) 3085, 2939, 2231, 1669, 1496, 1454, 1333, 1176, 910, 886, 732, 699 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-phenylacrylate (**16b**)



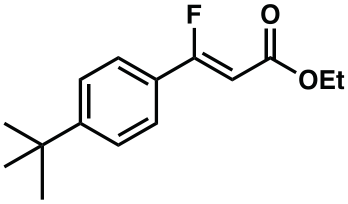
Column chromatography (SiO_2, eluting with 1:30 Et_2O:hexanes) afforded the desired product as a colorless oil (63.0 mg, 65%).

In accordance with previously reported spectra.[30]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.90 (d, *J* = 33.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.1 (d, *J* = 33.3 Hz).

ethyl (*Z*)-3-(4-(*tert*-butyl)phenyl)-3-fluoroacrylate (**17b**)



Column chromatography (SiO_2, eluting with 1:15→1:12 Et_2O:hexanes) afforded the desired product as a light yellow oil (98.5 mg, 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 33.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.34 – 1.31 (m, 12H).

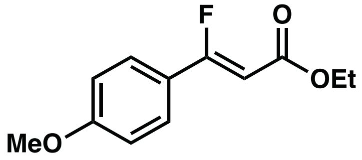
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6 (d, *J* = 277.2 Hz), 164.3 (d, *J* = 2.1 Hz), 155.3, 127.9 (d, *J* = 26.0 Hz), 125.9 (d, *J* = 1.8 Hz), 125.6 (d, *J* = 8.0 Hz), 96.4 (d, *J* = 6.9 Hz), 60.4, 35.1, 31.2, 14.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.0 (d, *J* = 33.2 Hz).

HRMS (APCI+) calc'd for $C_{15}H_{20}FO_2^+$ $[M+H]^+$: 251.1442, found: 251.1443.

IR (neat) 3083, 2964, 1721, 1702, 1653, 1331, 1283, 1269, 1158, 1110, 828, 731 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-methoxyphenyl)acrylate (**18b**)



Column chromatography (SiO_2, eluting with 1:15→1:12 Et_2O:hexanes) afforded the desired product as a colorless oil (89.0 mg, 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 33.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.31 (t, *J* = 7.1, 3H).

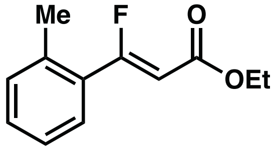
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6 (d, *J* = 276.2 Hz), 164.4 (d, *J* = 2.2 Hz), 162.3, 127.5 (d, *J* = 8.2 Hz), 123.0 (d, *J* = 26.3 Hz), 114.4 (d, *J* = 2.0 Hz), 95.2 (d, *J* = 7.0 Hz), 60.3, 55.5, 14.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.7 (d, *J* = 32.9 Hz).

HRMS (APCI+) calc'd for $C_{12}H_{14}FO_3^+$ $[M+H]^+$: 225.0921, found: 225.0920.

IR (neat) 2980, 2936, 1717, 1648, 1605, 1513, 1287, 1255, 1151, 1023, 826, 729 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(2-methylphenyl)acrylate (**19b**)



Column chromatography (SiO_2, eluting with 1:1:24 CH_2Cl_2:Et_2O:hexanes) afforded the desired product as a colorless oil (55.0 mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 5.57 (d, *J* = 32.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.45 (d, *J* = 3.5 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

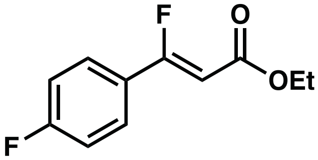
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6 (d, *J* = 283.4 Hz), 164.0 (d, *J* = 2.9 Hz), 137.3, 131.3, 131.0, 129.1 (d, *J* = 5.7 Hz), 126.1, 101.7 (d, *J* = 7.4 Hz), 60.5, 20.7 (d, *J* = 3.9 Hz), 14.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -78.5 (dd, *J* = 31.8, 4.0 Hz).

HRMS (APCI+) calc'd for $C_{12}H_{14}FO_2^+$ $[M+H]^+$: 209.0972, found: 209.0970.

IR (neat) 3087, 2981, 2934, 1724, 1707, 1658, 1324, 1264, 1154, 1045, 1024, 835, 766, 725 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-fluorophenyl)acrylate (**20b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (80.5 mg, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 33.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

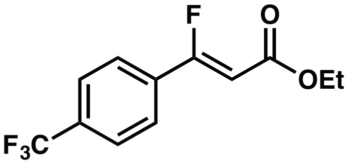
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 165.4 (d, *J* = 277.0 Hz), 164.1 – 163.3 (m), 128.0 (t, *J* = 8.4 Hz), 127.0 (dd, *J* = 26.9, 3.3 Hz), 116.2 (dd, *J* = 22.3, 1.7 Hz), 97.2 (dd, *J* = 6.8, 1.5 Hz), 60.5, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.6 (d, *J* = 33.6 Hz, 1F), -108.3 – -108.4 (m, 1F).

HRMS (APCI+) calc'd for $C_{11}H_{11}F_2O_2^+$ $[M+H]^+$: 213.0722, found: 213.0721.

IR (neat) 3093, 2984, 1720, 1655, 1604, 1510, 1281, 1237, 1157, 1105, 1056, 894, 830 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(4-(trifluoromethyl)phenyl)acrylate (**21b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a colorless oil (96.0 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 5.97 (d, *J* = 32.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

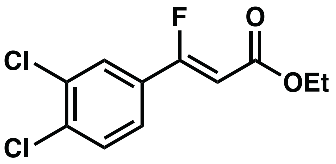
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5 (d, *J* = 277.4 Hz), 163.6 (d, *J* = 2.2 Hz), 134.2 (d, *J* = 26.9 Hz), 133.2 (q, *J* = 33.0 Hz), 126.1 (d, *J* = 7.7 Hz), 126.0 – 126.0 (m), 122.8 (q, *J* = 272.7 Hz), 99.4 (d, *J* = 6.9 Hz), 60.8, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -64.2 (s, 3F), -98.2 (d, *J* = 32.4 Hz, 1F).

HRMS (APCI+) calc'd for $C_{12}H_{11}F_4O_2^+$ $[M+H]^+$: 263.0690, found: 263.0697.

IR (neat) 3089, 2986, 1723, 1659, 1414, 1320, 1279, 1165, 1127, 1114, 1068, 1013, 833 cm^{-1}.

ethyl (*Z*)-3-(3,4-dichlorophenyl)-3-fluoroacrylate (**22b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (93.0 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.88 (d, *J* = 32.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

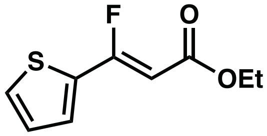
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, *J* = 277.2 Hz), 163.5 (d, *J* = 2.4 Hz), 136.0, 133.6 (d, *J* = 2.1 Hz), 131.1 (d, *J* = 1.9 Hz), 130.7 (d, *J* = 27.6 Hz), 127.5 (d, *J* = 8.2 Hz), 124.7 (d, *J* = 7.6 Hz), 98.8 (d, *J* = 6.6 Hz), 60.8, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.3 (d, *J* = 33.0 Hz).

HRMS (APCI+) calc'd for $C_{11}H_{10}Cl_2FO_2^+$ $[M+H]^+$: 263.0036, found: 263.0038.

IR (neat) 3100, 2990, 2911, 1700, 1656, 1468, 1395, 1330, 1274, 1253, 1024, 847, 816, 764 cm^{-1}.

ethyl (*Z*)-3-fluoro-3-(thiophen-2-yl)acrylate (**23b**)



Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a white solid (80.0 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H), 7.09 – 7.06 (m, 1H), 5.71 (d, *J* = 32.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

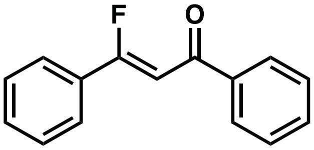
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, *J* = 2.7 Hz), 161.7 (d, *J* = 274.0 Hz), 133.9 (d, *J* = 31.7 Hz), 129.6, 128.7 (d, *J* = 4.9 Hz), 128.3, 96.1 (d, *J* = 6.5 Hz), 60.5, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.0 (d, *J* = 32.7 Hz).

HRMS (APCI+) calc'd for $C_9H_{10}FO_2S^+$ $[M+H]^+$: 201.0380, found: 201.0377.

IR (neat) 3094, 2981, 1715, 1699, 1642, 1368, 1264, 1226, 1150, 1038, 824, 707 cm^{-1}.

(*Z*)-3-fluoro-1,3-diphenylprop-2-en-1-one (**24b**)



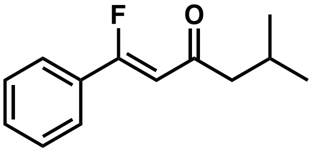
Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a yellow oil (74.0 mg, 66%).

In accordance with previously reported spectra.[31]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.45 (m, 5H), 6.80 (d, *J* = 34.2 Hz, 1H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.3 (d, *J* = 34.2 Hz).

(*Z*)-3-fluoro-1,3-diphenylprop-2-en-1-one (**25b**)



Column chromatography (SiO_2, eluting with 1:12 Et_2O:hexanes) afforded the desired product as a yellow oil (74.0 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.06 (d, *J* = 38.9 Hz, 1H), 2.65 (dd, *J* = 6.9, 2.1 Hz, 2H), 2.26 – 2.18 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

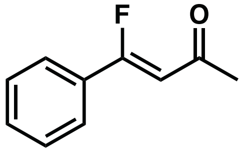
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7 (d, *J* = 2.7 Hz), 164.7 (d, *J* = 274.1 Hz), 131.6, 130.7 (d, *J* = 27.5 Hz), 129.0 (d, *J* = 2.1 Hz), 125.8 (d, *J* = 8.0 Hz), 106.7 (d, *J* = 9.5 Hz), 52.8 (d, *J* = 5.0 Hz), 24.9 (d, *J* = 1.4 Hz), 22.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -128.2 (d, *J* = 38.6 Hz).

HRMS (APCI+) calc'd for $C_{13}H_{16}FO^+$ $[M+H]^+$: 207.1180, found: 207.1185.

IR (neat) 3066, 2957, 2871, 1639, 1619, 1578, 1325, 1286, 1191, 1003, 766, 687 cm^{-1}.

(*Z*)-4-fluoro-4-phenylbut-3-en-2-one (**26b**)



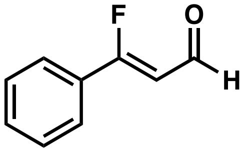
Column chromatography (SiO_2, eluting with 1:10 Et_2O:hexanes) afforded the desired product as a white solid (49.0 mg, 60%).

In accordance with previously reported spectra.[32]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.53 – 7.40 (m, 3H), 6.06 (d, *J* = 38.6 Hz, 1H), 2.48 (d, *J* = 4.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -97.6 (dd, *J* = 38.6, 3.5 Hz).

(*Z*)-3-fluoro-3-phenylacrylaldehyde (**27b**)



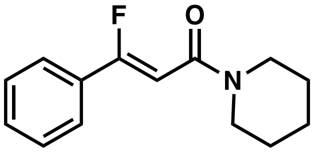
Column chromatography (SiO_2, eluting with 1:15 Et_2O:hexanes) afforded the desired product as a yellow solid (423.0 mg, 63%).

In accordance with previously reported spectra.[31]

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.18 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.09 (dd, *J* = 33.8, 7.6 Hz, 1H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.0 (d, *J* = 33.7 Hz).

(*Z*)-3-fluoro-3-phenyl-1-(piperidin-1-yl)prop-2-en-1-one (**28b**)



Column chromatography (SiO_2, eluting with 3:1→ 9:1 Et_2O:hexanes) afforded the desired product as a white solid (75.0 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.40 – 7.38 (m, 3H), 5.97 (d, *J* = 38.4 Hz, 1H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.49 (t, *J* = 5.5 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.60 (h, *J* = 5.5 Hz, 4H).

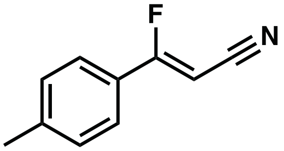
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 159.5 (d, *J* = 260.2 Hz), 131.0 (d, *J* = 28.0 Hz), 130.4, 128.8 (d, *J* = 2.1 Hz), 125.0 (d, *J* = 7.2 Hz), 99.6 (d, *J* = 16.1 Hz), 48.0 (d, *J* = 1.9 Hz), 42.7, 26.7, 25.6, 24.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -107.4 (d, *J* = 39.3 Hz).

HRMS (APCI+) calc'd for $C_{14}H_{17}FNO^+$ $[M+H]^+$: 234.1289, found: 234.1288.

IR (neat) 3062, 2935, 2856, 1663, 1611, 1436, 1246, 1164, 1006, 871, 765 cm^{-1}.

(*Z*)-3-fluoro-3-(4-methylphenyl)acrylonitrile (**29b**)



Column chromatography (SiO_2, eluting with 1:24→1:15 Et_2O:hexanes) afforded the desired product as a white solid (54.6 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 5.36 (d, *J* = 32.9 Hz, 1H), 2.41 (s, 3H).

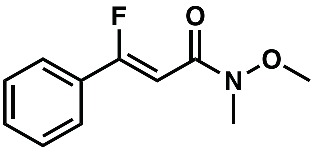
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9 (d, *J* = 274.3 Hz), 143.7, 129.9 (d, *J* = 2.1 Hz), 125.7 (d, *J* = 24.4 Hz), 125.5 (d, *J* = 7.9 Hz), 113.9, 75.5 (d, *J* = 16.0 Hz), 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.0 (d, *J* = 33.0 Hz).

HRMS (APCI+) calc'd for $C_{10}H_9FN^+$ $[M+H]^+$: 162.0714, found: 162.0709.

IR (neat) 3077, 2922, 2218, 1642, 1605, 1514, 1330, 1075, 822, 774 cm^{-1}.

(*Z*)-3-fluoro-*N*-methoxy-*N*-methyl-3-phenylacrylamide (**30b**)



Column chromatography (SiO$_2$, eluting with 1:1→3:1 Et$_2$O:hexanes) afforded the desired product as a yellow oil (74.2 mg, 71%).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 – 7.59 (m, 2H), 7.44 – 7.38 (m, 3H), 6.37 (d, *J* = 33.5 Hz, 1H), 3.71 (s, 3H), 3.24 (s, 3H).

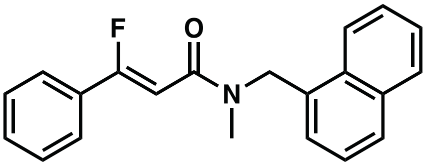
^{13}C NMR (151 MHz, CDCl$_3$) δ 164.9 (d, *J* = 275.1 Hz), 164.4, 131.3 (d, *J* = 26.6 Hz), 131.0, 128.8 (d, *J* = 2.0 Hz), 125.5 (d, *J* = 7.7 Hz), 95.5, 61.7, 32.2.

^{19}F NMR (565 MHz, CDCl$_3$) δ -101.7 (d, *J* = 34.0 Hz).

HRMS (ESI+) calc'd for $C_{11}H_{13}FNO_2^+$ [M+H]$^+$: 210.0925, found: 210.0926.

IR (neat) 3065, 2937, 1667, 1632, 1495, 1376, 1177, 995, 766 cm^{-1}.

(*Z*)-3-fluoro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylacrylamide (**31b**)



Column chromatography (SiO$_2$, eluting with 0:1→1:13 EtOAc:CH$_2$Cl$_2$) afforded the desired product as a yellow oil (344.3 mg, 55%).

^{1}H NMR (mixture of rotamers, 600 MHz, CDCl$_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1.5H), 7.61 – 7.24 (m, 14H), 6.09 (d, *J* = 37.4 Hz, 1H), 6.08 (d, *J* = 35.9 Hz, 0.5H), 5.17 (s, 2H), 5.08 (s, 1H), 3.07 (s, 1.4H), 2.91 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.1, 164.4, 161.8 (d, *J* = 265.5 Hz), 160.6 (d, *J* = 263.1 Hz), 133.8, 133.7, 132.1, 131.6, 131.4, 130.8 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 7.4 Hz), 130.4, 130.4, 128.9, 128.6 (d, *J* = 1.9 Hz), 128.5, 128.4, 128.2, 126.9, 126.5, 125.9, 125.9, 125.5, 125.1, 125.0 (d, *J* = 7.3 Hz), 124.9 (d, *J* = 7.4 Hz), 123.8, 123.6, 122.1, 99.2 (d, *J* = 14.4 Hz), 98.6 (d, *J* = 13.1 Hz), 51.7, 48.1, 34.9 (d, *J* = 2.4 Hz), 33.4.

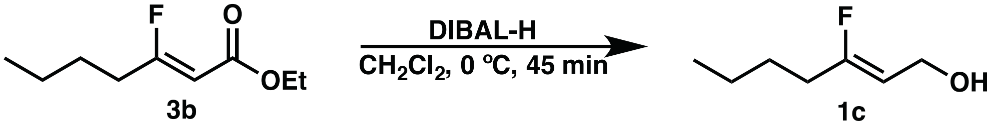
^{19}F NMR (mixture of rotamers, 565 MHz, CDCl$_3$) δ -104.1 (d, *J* = 35.9 Hz, 0.5F), -105.3 (d, *J* = 37.4 Hz, 1F).

HRMS (APCI+) calc'd for $C_{21}H_{19}FNO^+$ [M+H]$^+$: 320.1445, found: 320.1449.

IR (neat) 3059, 2924, 1664, 1610, 1579, 1398, 1115, 1044, 791, 763, 731, 688, 596 cm^{-1}.

Procedures for Derivatizations of Fluorinated Michael Acceptors

Reduction of ester (**3b**):



Prepared according to a modified literature procedure.[33] Ester (**3b**) (405 mg, 2.32 mmol, 1.0 equiv) was added to 25-mL Schlenk flask containing CH_2Cl_2 (4.6 mL, 0.5 M). The reaction vessel was placed in an ice water bath and the reaction mixture was allowed to reach 0 ºC before the dropwise addition (9 minutes) of DIBAL-H (1.0 M in hexanes, 6.17 mL, 6.17 mmol, 2.5 equiv). After stirring for 45 min at 0 ºC, 3.5 M HCl (4 mL) was added dropwise. The reaction was transferred to a separatory funnel and diluted with CH_2Cl_2 (40 mL) and 3.5 M HCl (40 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 40 mL). The organics were dried over Na_2SO_4, filtered, concentrated, and the crude residue purified by silica gel column chromatography (1:1 Et_2O:hexanes) to afford **1c**, (*Z*)-3-fluorohept-2-en-1-ol, as a colorless oil (267.0 mg, 87%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.81 (dt, *J* = 37.2, 7.1 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 2H), 2.39 (bs, 1H), 2.17 (dt, *J* = 17.5, 7.5 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

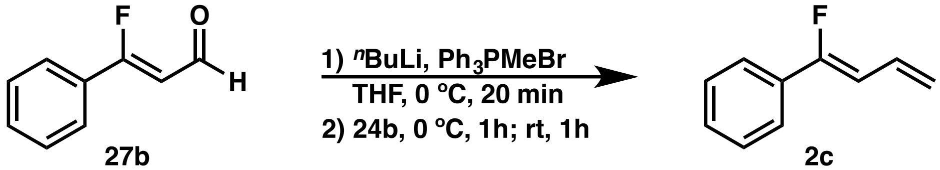
^{13}C NMR (126 MHz, CD_2Cl_2) δ 162.2 (d, *J* = 257.9 Hz), 105.1 (d, *J* = 13.4 Hz), 55.6 (d, *J* = 7.8 Hz), 31.9 (d, *J* = 27.0 Hz), 28.5 (d, *J* = 1.6 Hz), 22.4, 13.9.

^{19}F NMR (470 MHz, CD_2Cl_2) δ -106.1 (dt, *J* = 36.2, 17.6 Hz).

HRMS (ESI+) calc'd for $C_7H_{14}FO^+$ $[M+H]^+$: 133.1023, found: 133.1022.

IR (neat) 3316, 2959, 2933, 2874, 1706, 1159, 1073, 1006, 972 cm^{-1}.

Witting olefination of aldehyde (**27b**):



27b **2c**

Prepared according to a modified literature procedure.[34] To a suspension of methyltriphenylphosphonium bromide (137 mg, 0.375 mmol, 1.25 equiv) in THF (1.9 mL, 0.2 M wrt Ph_3PMeBr) at 0 ºC was added ^{n}BuLi (2.5 M in hexanes, 150 μL, 0.375 mmol, 1.25 equiv) dropwise. The reaction was stirred for 20 min before **27b** (45 mg, 0.3 mmol, 1.0 equiv) in a solution of THF (300 μL, 1.0 M wrt **27b**) was added dropwise (4 min). After stirring at 0 ºC for 1 h, the reaction was warmed to rt and stirred for another hour before the addition of saturated NH_4Cl (1 mL). The reaction mixture was transferred to a separatory funnel and diluted with Et_2O (40 mL) and NH_4Cl (40 mL). The phases were separated and the aqueous layer extracted with Et_2O (3 x 40 mL). The organics were washed with brine (120 mL), dried over Na_2SO_4, filtered, concentrated, and the crude residue purified by silica gel column chromatography (hexanes) to afford **2c**, (*Z*)-(1-fluorobuta-1,3-dien-1-yl)benzene, as a colorless oil (29.0 mg, 65%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (dt, *J* = 17.2, 10.6 Hz, 1H), 6.12 (dd, *J* = 35.1, 10.8 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H).

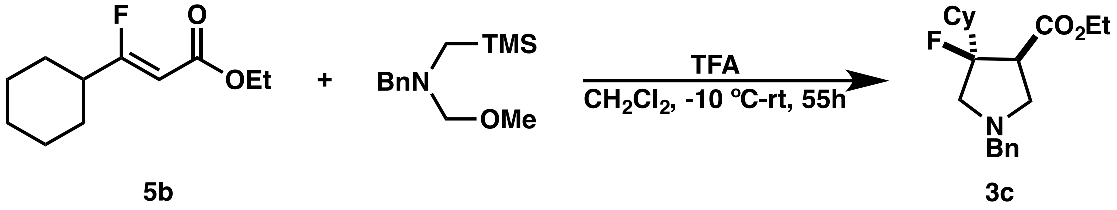
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9 (d, *J* = 255.4 Hz), 132.1 (d, *J* = 27.7 Hz), 129.2, 129.0 (d, *J* = 6.6 Hz), 128.7 (d, *J* = 2.2 Hz), 124.3 (d, *J* = 7.5 Hz), 117.5 (d, *J* = 3.4 Hz), 107.1 (d, *J* = 13.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -118.5 (d, *J* = 35.0 Hz).

HRMS (EI+) calc'd for $C_{10}H_9F$: 148.0688, found: 148.0686.

IR (neat) 3089, 3061, 2925, 1649, 1494, 1449, 1320, 1281, 1009, 992, 901, 760, 603 cm^{-1}.

Cycloaddition of ester (**5b**):



Prepared according to a modified literature procedure.[35] To a solution of **5b** (60 mg, 0.3 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL, 0.3 M) at -10 ºC (ice-acetone slurry) was added trifluoroacetic acid (6 μL, 22 mol%) followed by dropwise addition of ylide[36] (214 mg, 0.9 mmol, 3.0 equiv). The reaction was warmed to rt. Addition ylide and TFA were added after 7 h (0.3 mmol ylide and 11 mol% TFA), 23 h (1.5 mmol ylide and 22 mol% TFA), 32 h (0.6 mmol ylide and 11 mol% TFA), 44 h (500 μL CH_2Cl_2, 2.0 mmol ylide, and 33 mol% TFA), and 53 h (1.5 mmol ylide and 11 mol% TFA). After 55 h, the reaction mixture was transferred to a separatory funnel with CH_2Cl_2 (100 mL), washed with saturated $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (1:7 EtOAc:hexanes) to afford **3c**, ethyl 1-benzyl-4-cyclohexyl-4-fluoropyrrolidine-3-carboxylate, as a colorless oil (61 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 4.26 – 4.11 (m, 2H), 3.73 (d, *J* = 13.1 Hz, 1H), 3.62 (d, *J* = 13.1 Hz, 1H), 3.19 – 3.10 (m, 2H), 2.98 (dd, *J* = 25.8, 11.2 Hz, 1H), 2.84 (tt, *J* = 6.7, 3.2 Hz, 1H), 2.68 (dd, *J* = 28.9, 11.2 Hz, 1H), 1.99 (d, *J* = 12.7 Hz, 1H), 1.92 (dt, *J* = 15.3, 12.3 Hz, 1H), 1.84 – 1.76 (m, 3H), 1.69 (d, *J* = 12.3 Hz, 1H), 1.31 – 0.94 (m, 9H).

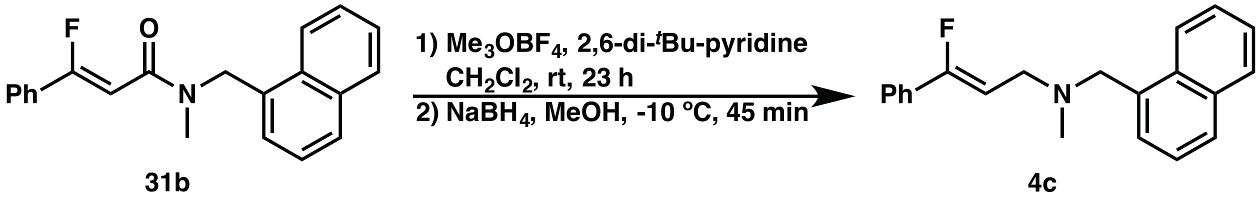
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7 (d, *J* = 7.1 Hz), 138.7, 128.7, 128.4, 127.2, 105.9 (d, *J* = 183.8 Hz), 61.4 (d, *J* = 25.8 Hz), 60.8, 60.1, 54.8, 49.2 (d, *J* = 22.1 Hz), 43.9 (d, *J* = 23.4 Hz), 27.7 (d, *J* = 7.1 Hz), 27.1 (d, *J* = 4.5 Hz), 26.3 (d, *J* = 10.7 Hz), 26.2, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -153.3 (tq, *J* = 25.6, 13.7 Hz).

HRMS (ESI+) calc'd for $C_{20}H_{29}FNO_2^+$: 334.2177, found: 334.2173.

IR (neat) 3063, 3029, 2928, 2854, 2799, 1451, 1371, 1231, 1179, 1027, 911, 732, 699 cm^{-1}.

Reduction of amide (**31b**), generation of fluorine containing analog of Exoderil:



Prepared according to a modified literature procedure.[37] In a nitrogen-filled glovebox, to a solution of **31b** (173.0 mg, 0.54 mmol, 1 equiv) in CH_2Cl_2 (17.2 mL, 0.031 M) was added 2,6-di-*tert*-butylpryidine (362 μL, 1.61 mmol, 2.92 equiv) followed by the portionwise addition (3 min) of trimethyloxonium tetrafluoroborate (216 mg, 1.46 mmol, 2.65 equiv). The reaction mixture was stirred for 23 h at rt, removed from the glovebox, placed under nitrogen from a Schlenk line, and submerged into an ice-acetone slurry (-10 ºC). Anhydrous methanol (5.8 mL) was added dropwise (4 min) and the reaction was stirred for 10 min. Sodium borohydride (219 mg, 5.67 mmol, 10.3 equiv) was added in equal portions over 5 min and the reaction mixture stirred for 45 min at -10 ºC. Saturated $NaHCO_3$ (15 mL) was added dropwise to the chilled reaction mixture. The biphasic mixture was diluted with CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ (50 mL) and the layers separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 70 mL), the organics combined, dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (1:15 EtOAc:hexanes) to afford **4c**, as a yellow oil (93.2 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.53 – 7.47 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 5.66 (dt, *J* = 37.1, 7.3 Hz, 1H), 4.00 (s, 2H), 3.45 (d, *J* = 7.3 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6 (d, *J* = 249.3 Hz), 134.9, 134.0, 132.6, 132.4 (d, *J* = 29.1 Hz), 129.0, 128.6, 128.6, 128.1, 127.6, 126.0, 125.7, 125.3, 124.7, 124.3 (d, *J* = 6.9 Hz), 103.1 (d, *J* = 15.3 Hz), 60.2, 51.5 (d, *J* = 4.4 Hz), 42.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -118.8 (d, *J* = 37.1 Hz).

HRMS (ESI+) calc'd for $C_{21}H_{21}FN^+$: 306.1653, found: 306.1651.

IR (neat) 3058, 3043, 2928, 2837, 2790, 1679, 1447, 1364, 1279, 1016, 980, 791, 774, 760, 689 cm^{-1}.

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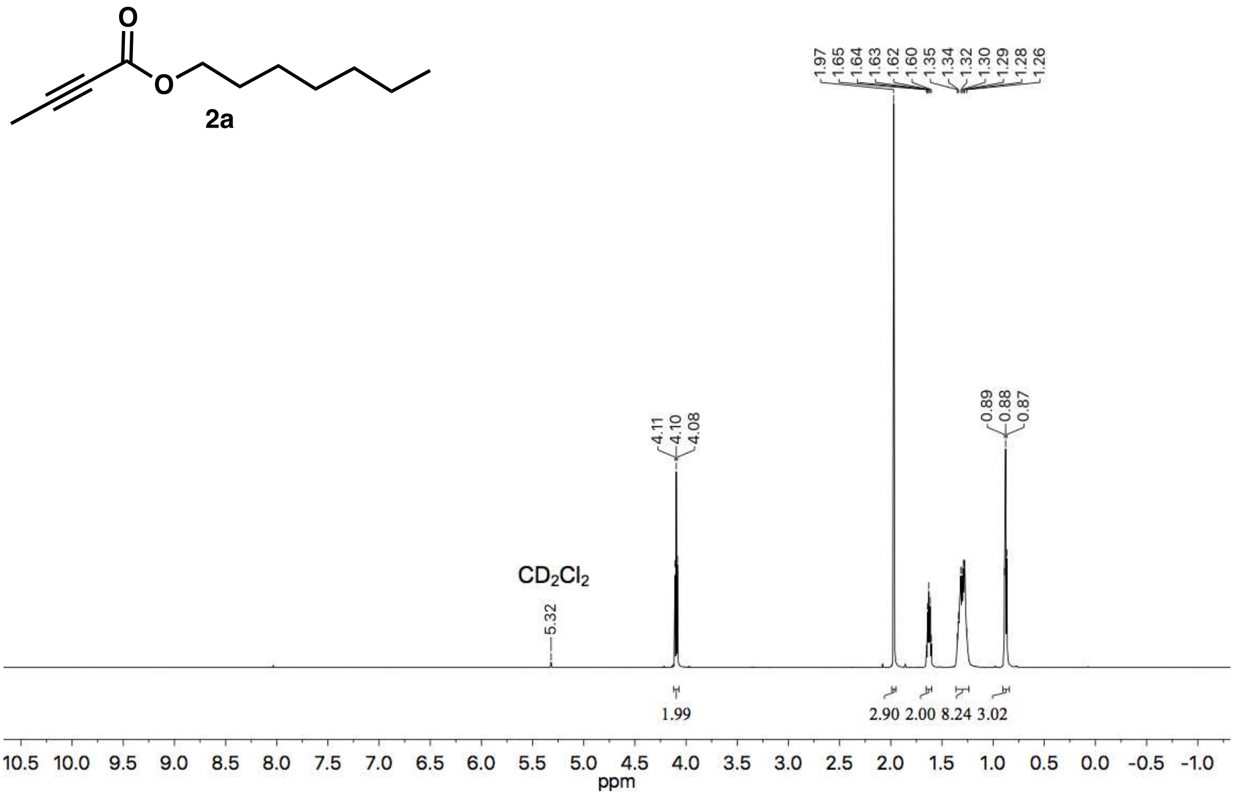
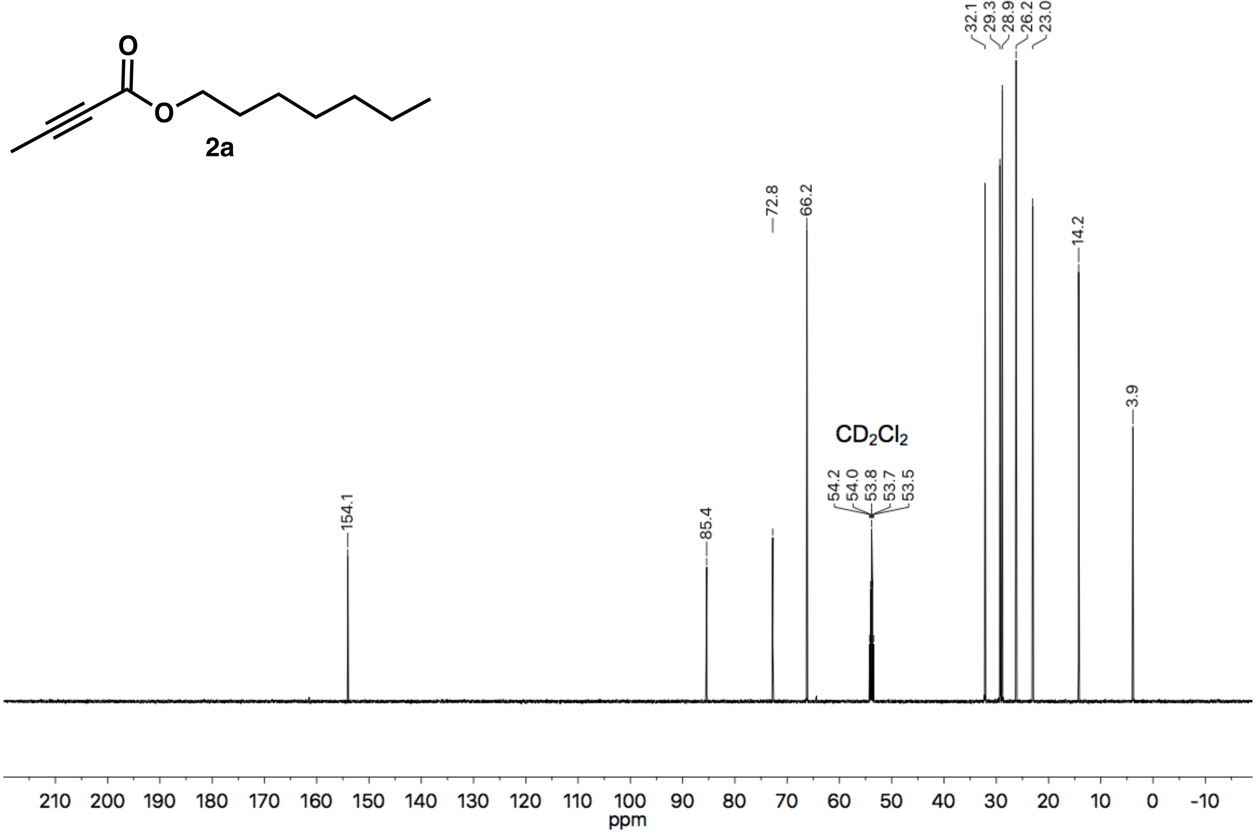
^{1}H NMR (600 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, CD_2Cl_2)



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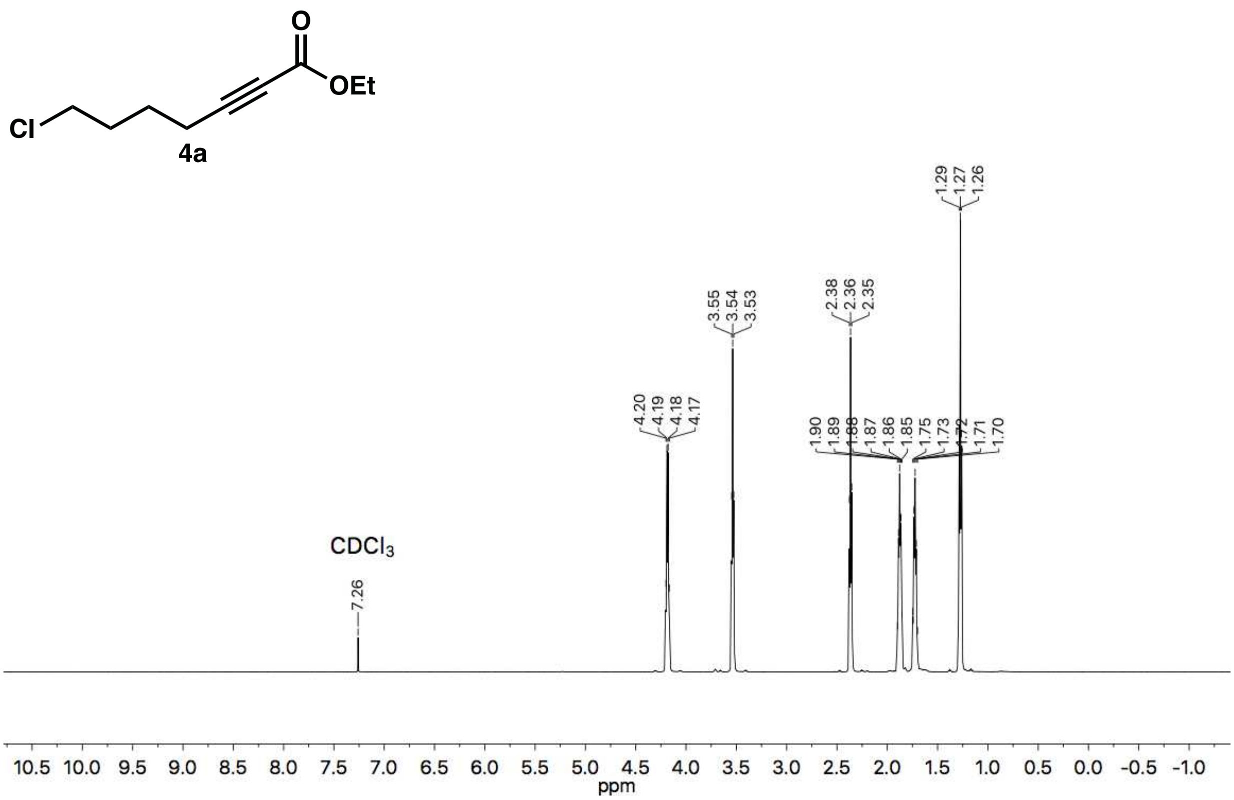

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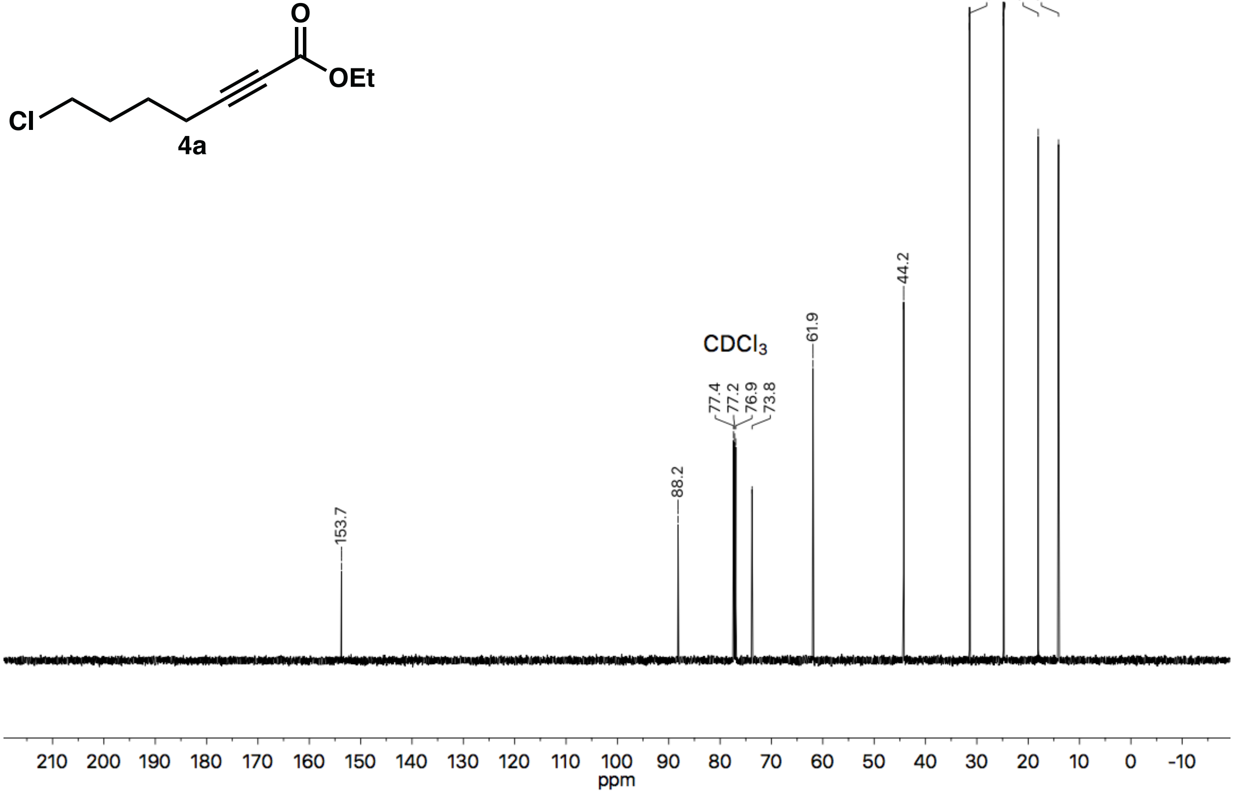

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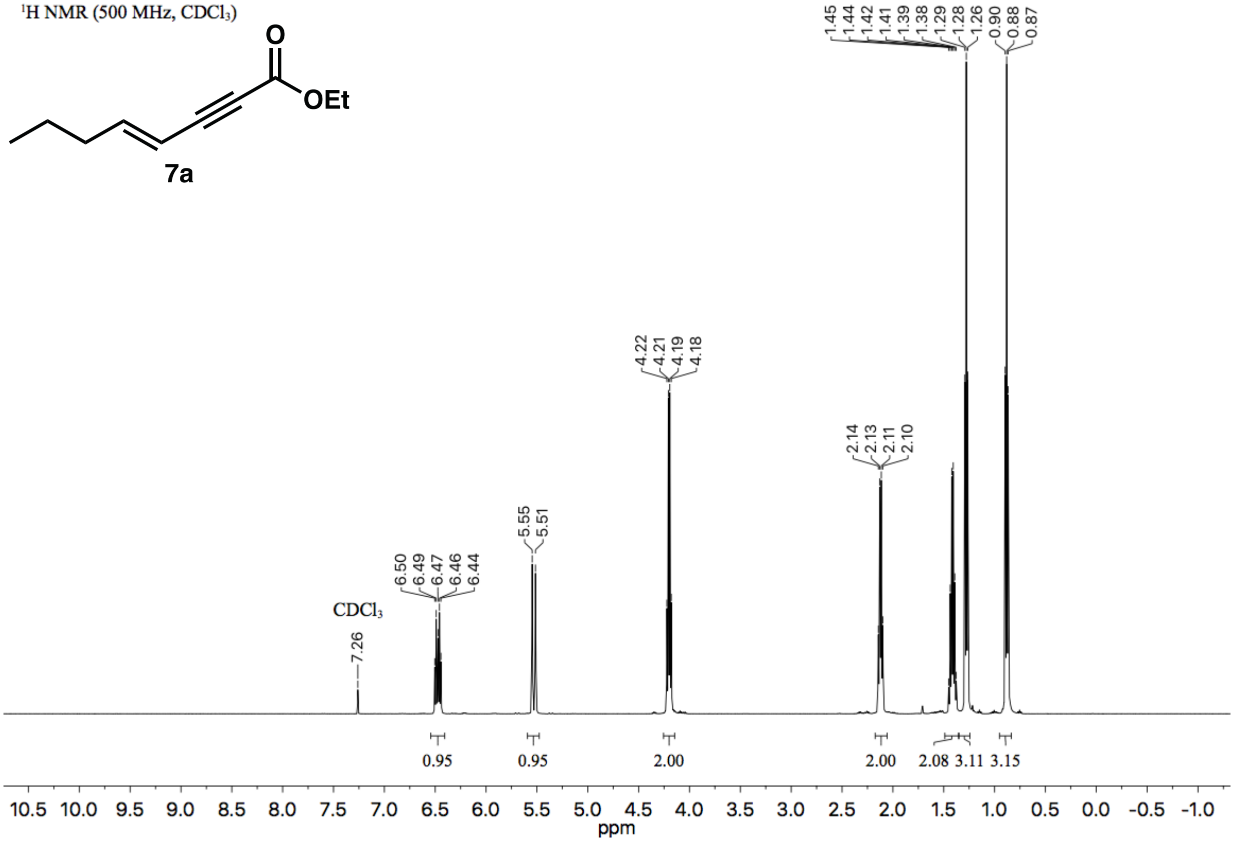
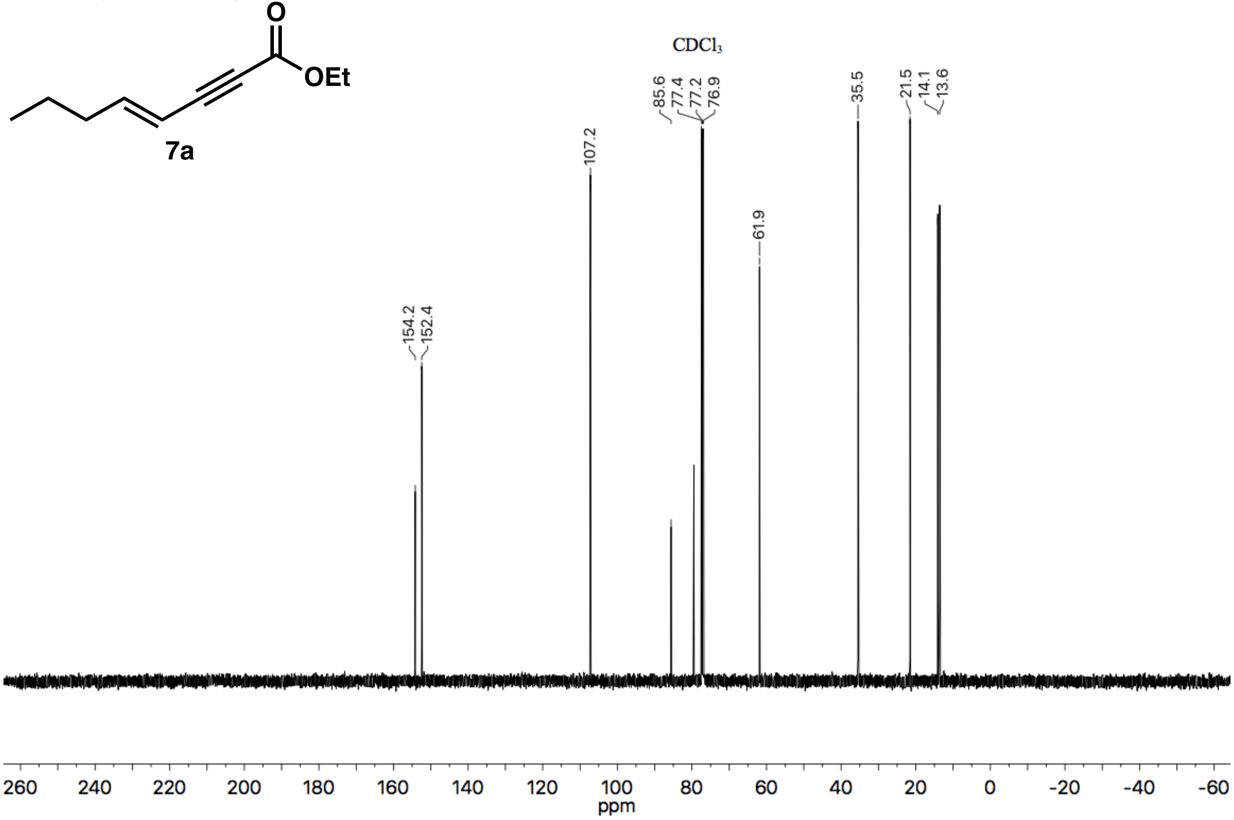
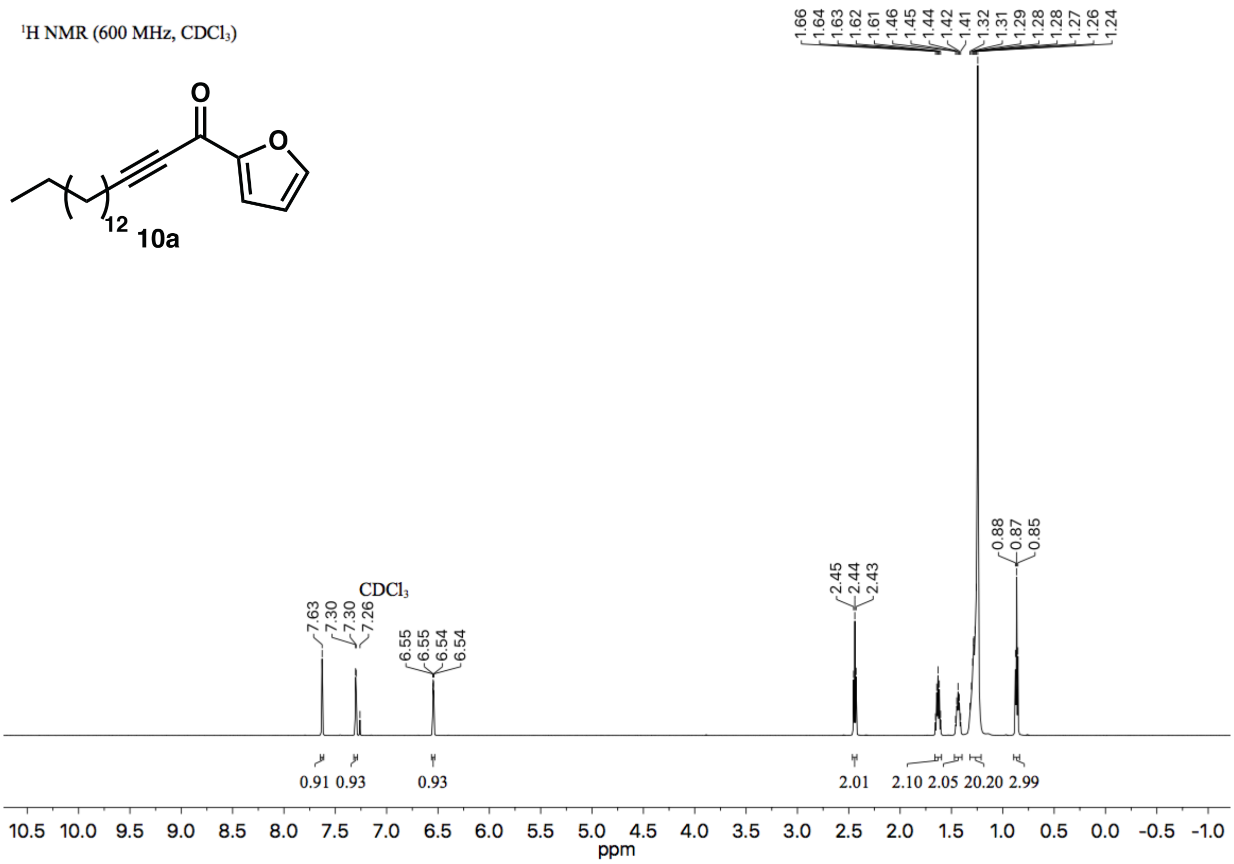


^{13}C NMR (126 MHz, CDCl$_3$)





1H NMR (600 MHz, CDCl3)
10a
12
CDCl3
7.63
7.30
7.30
7.26
6.55
6.55
6.54
6.54
2.45
2.44
2.43
1.66
1.64
1.63
1.62
1.61
1.46
1.45
1.44
1.42
1.41
1.32
1.31
1.29
1.28
1.28
1.27
1.26
1.24
0.88
0.87
0.85
0.91
0.93
0.93
2.01
2.10
2.05
20.20
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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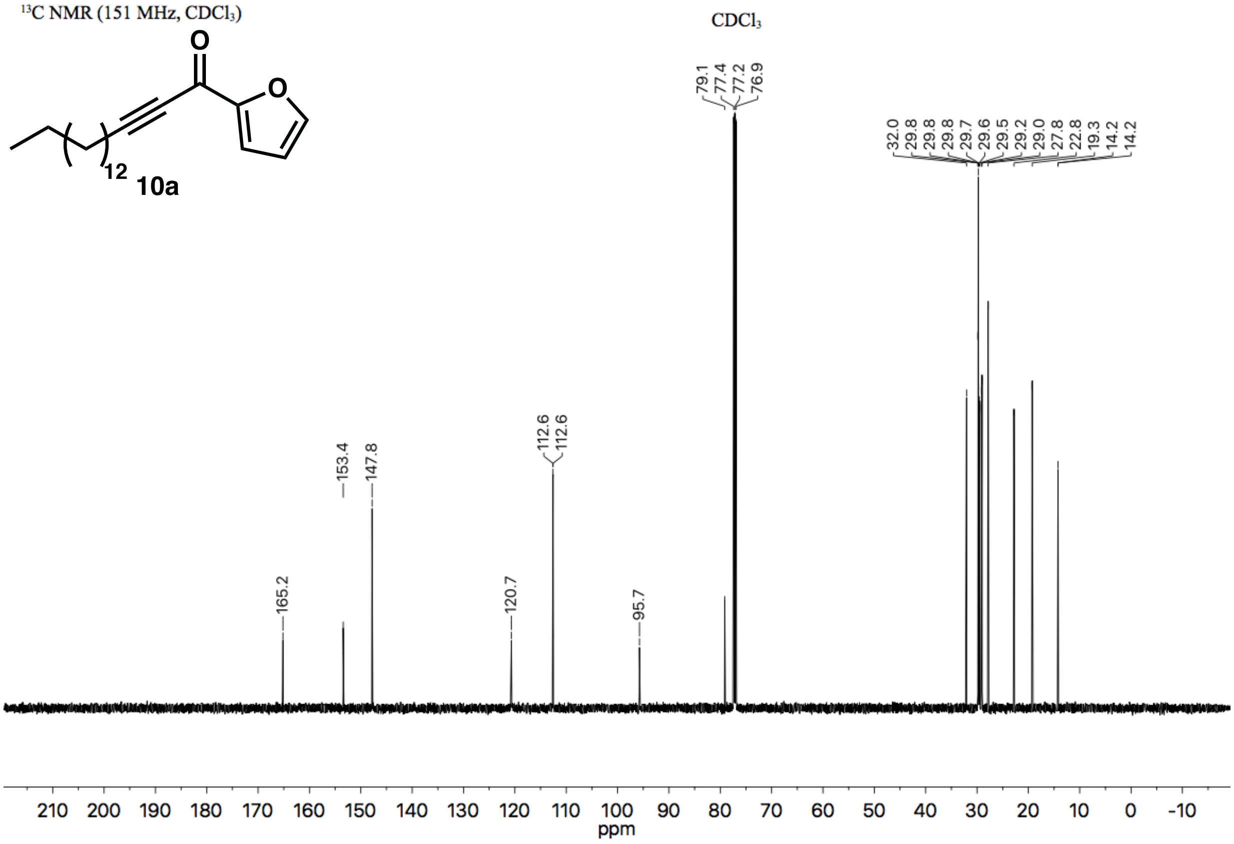
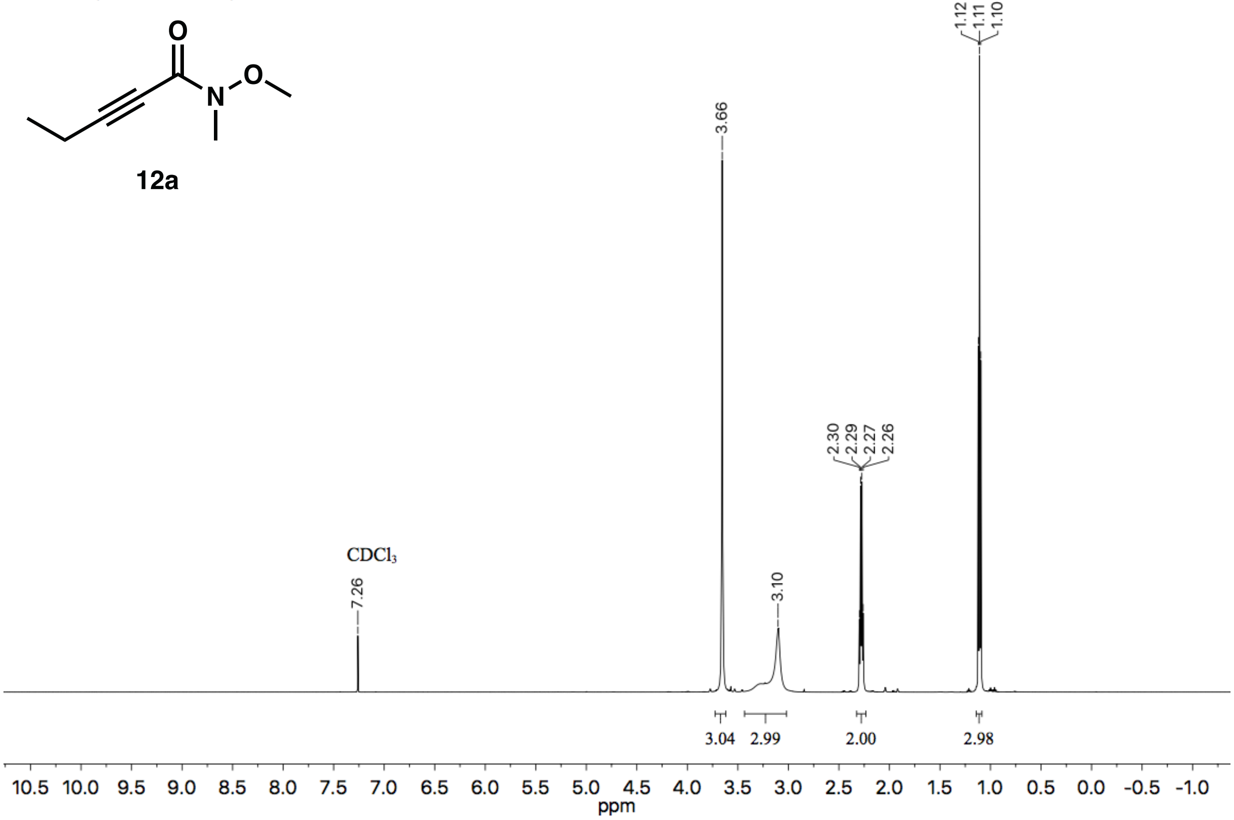
ppm



13C NMR (151 MHz, CDCl3)
10a
12
CDCl3
79.1
77.4
77.2
76.9
32.0
29.8
29.8
29.8
29.7
29.6
29.5
29.2
29.0
27.8
22.8
19.3
14.2
14.2
165.2
153.4
147.8
120.7
112.6
112.6
95.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

^{1}H NMR (600 MHz, $CDCl_3$)



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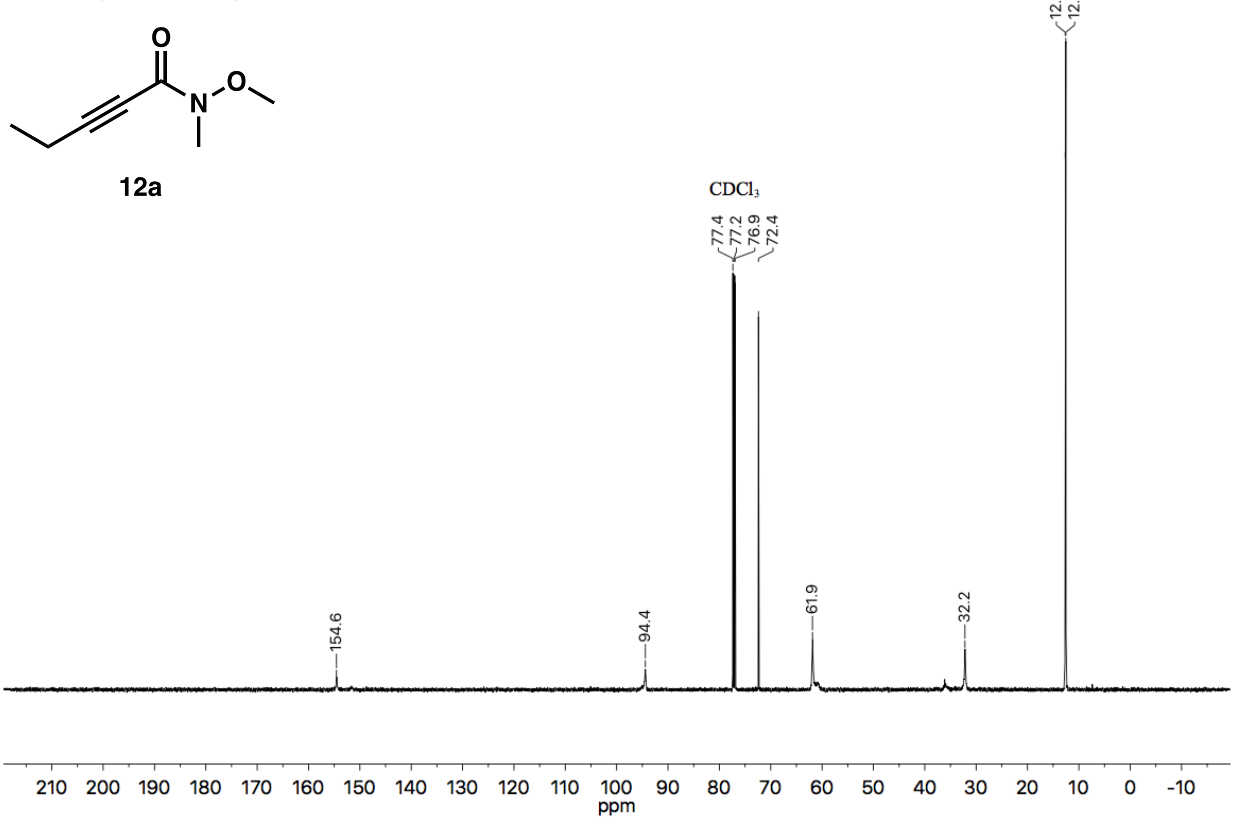
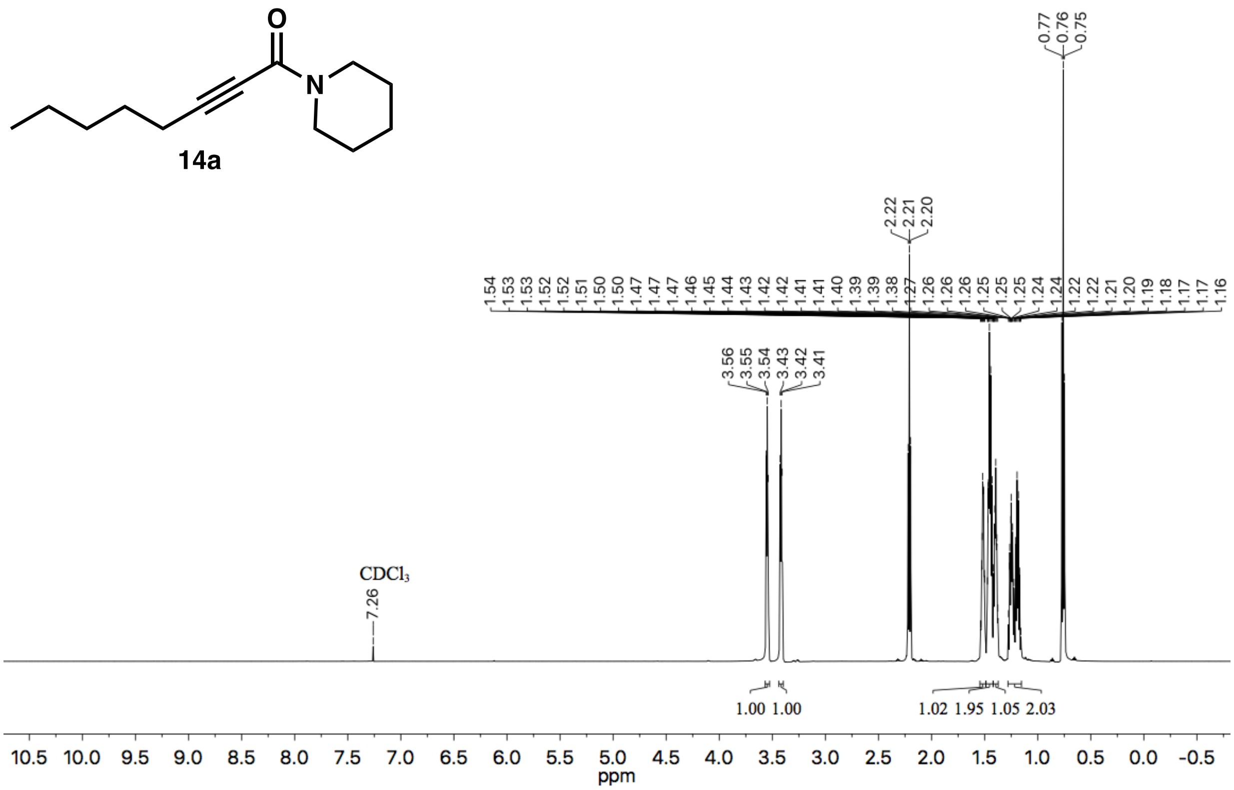
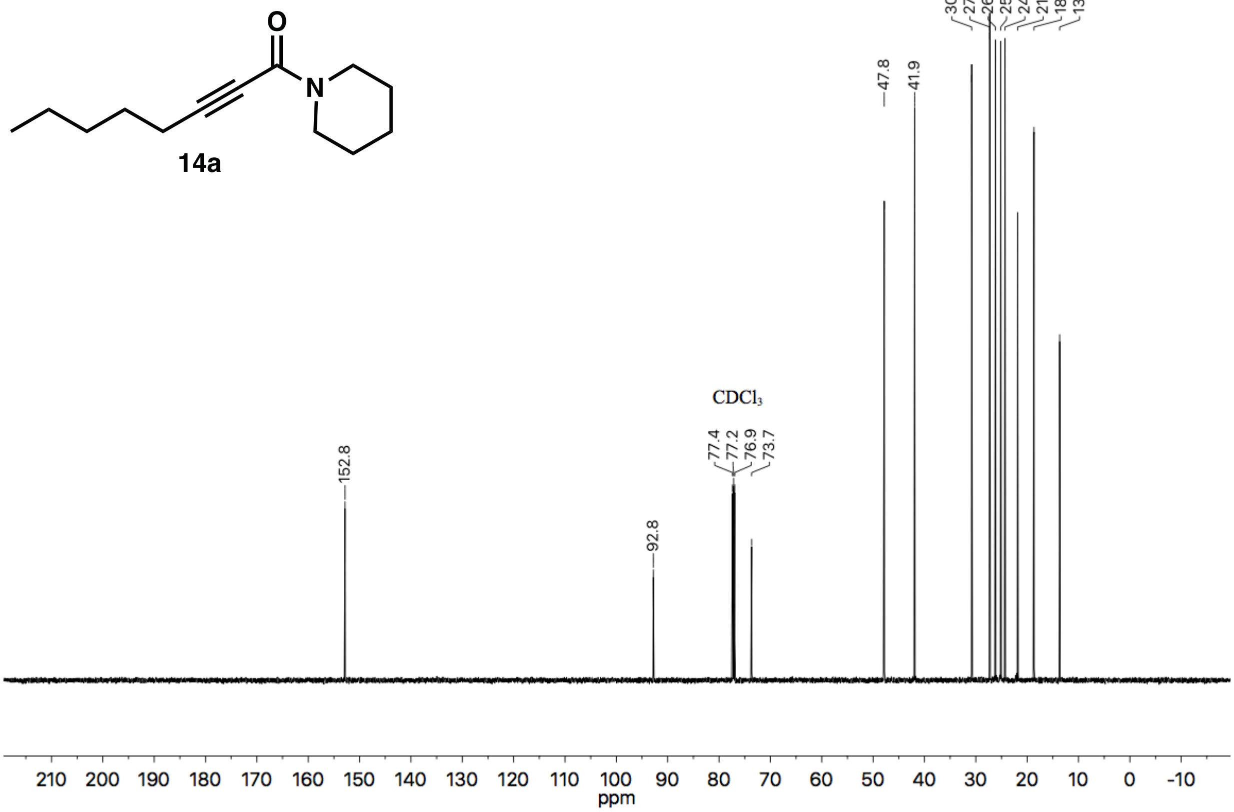


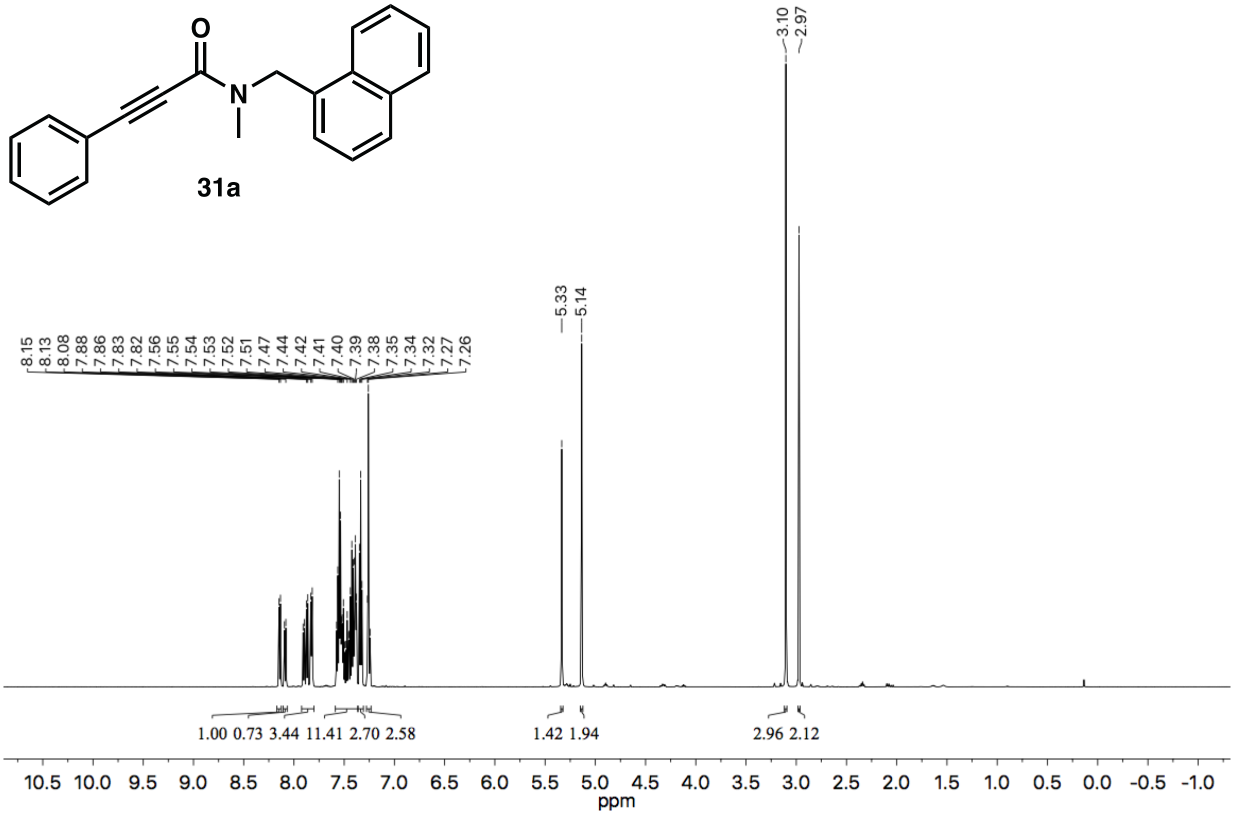
^{1}H NMR (600 MHz, CDCl$_3$)


14a

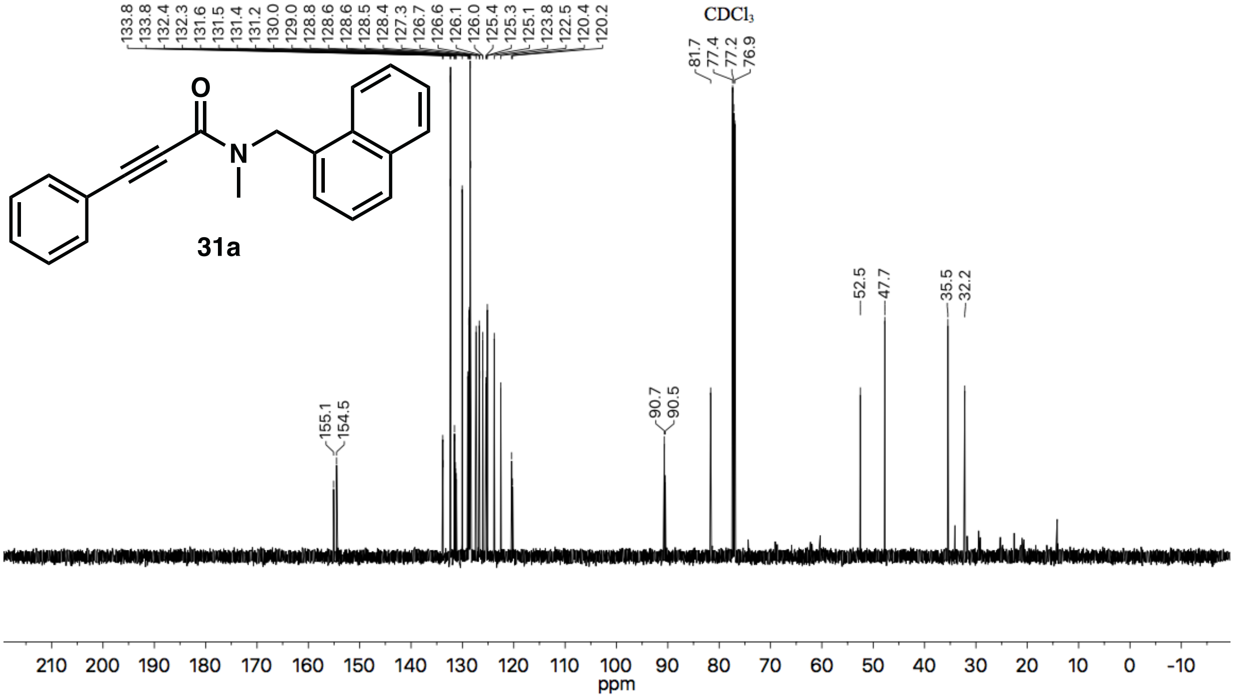
^{13}C NMR (151 MHz, CDCl$_3$)


14a

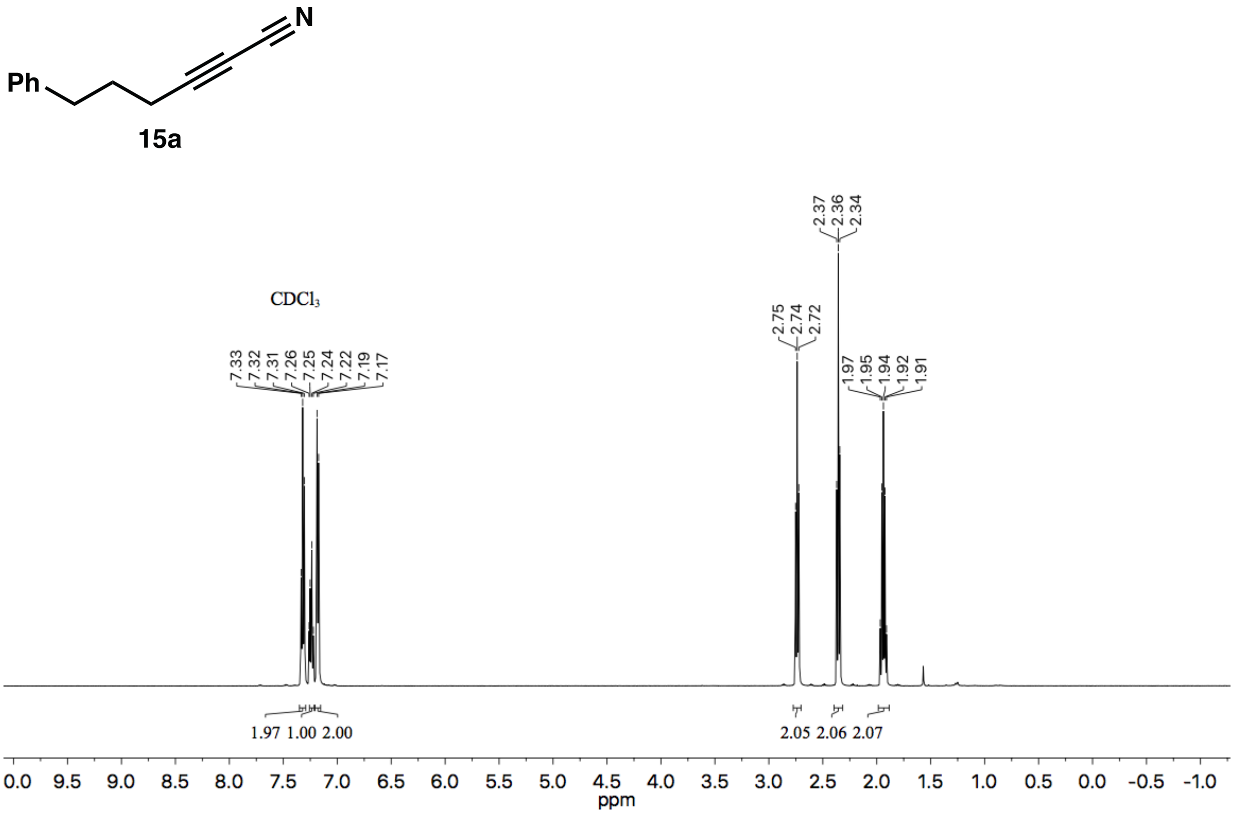
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

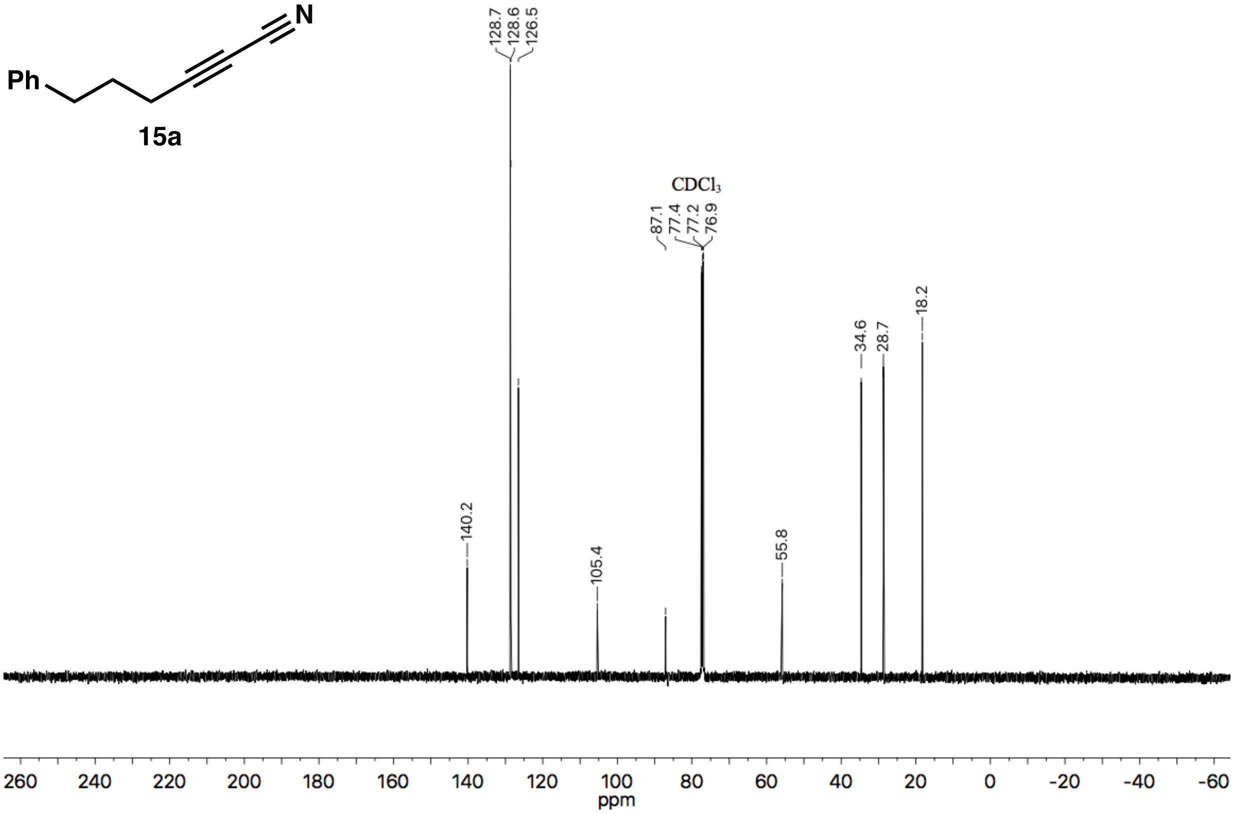


^{1}H NMR (500 MHz, CDCl$_3$)



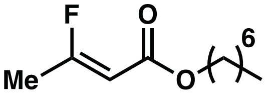
15a

^{13}C NMR (126 MHz, CDCl$_3$)

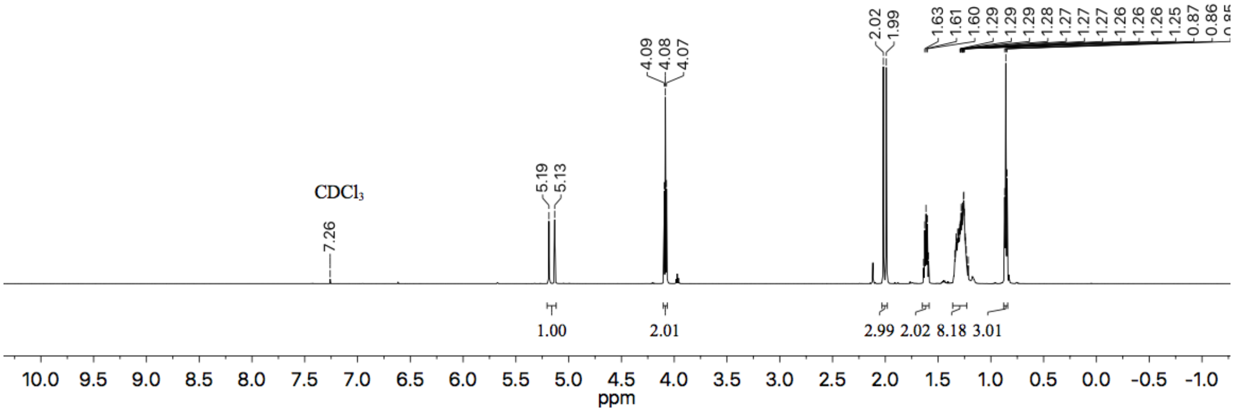


15a

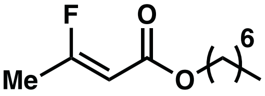
^{1}H NMR (600 MHz, CDCl$_3$)



2b



^{13}C NMR (151 MHz, CDCl$_3$)



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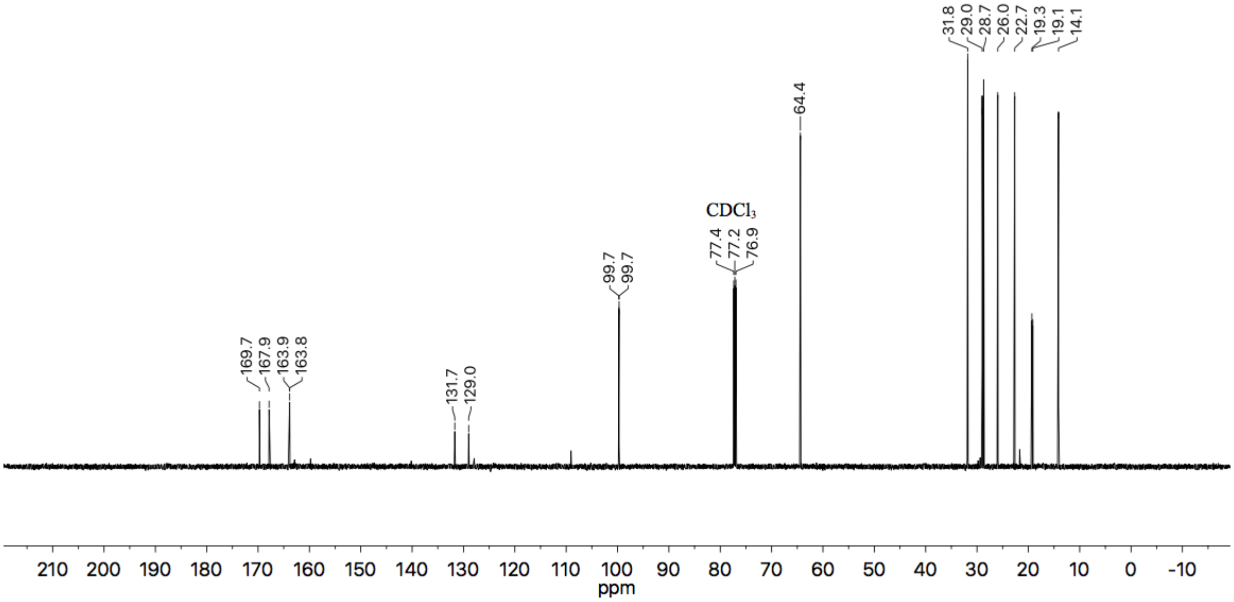
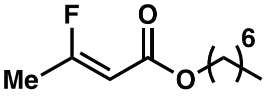


^{19}F NMR (565 MHz, CDCl$_3$)



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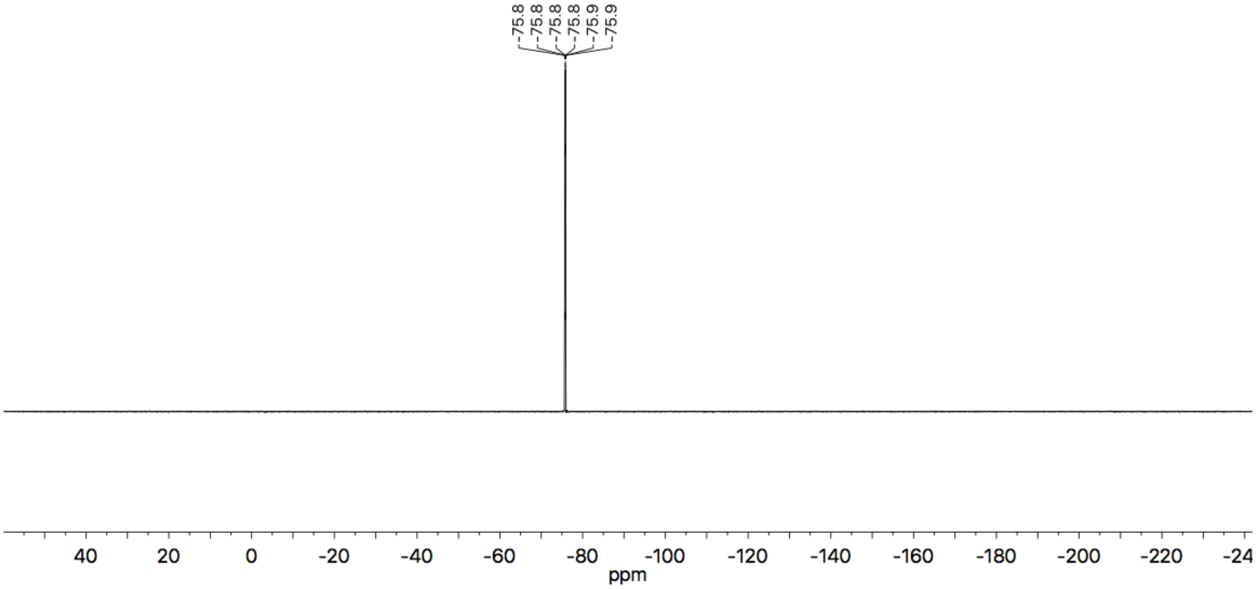
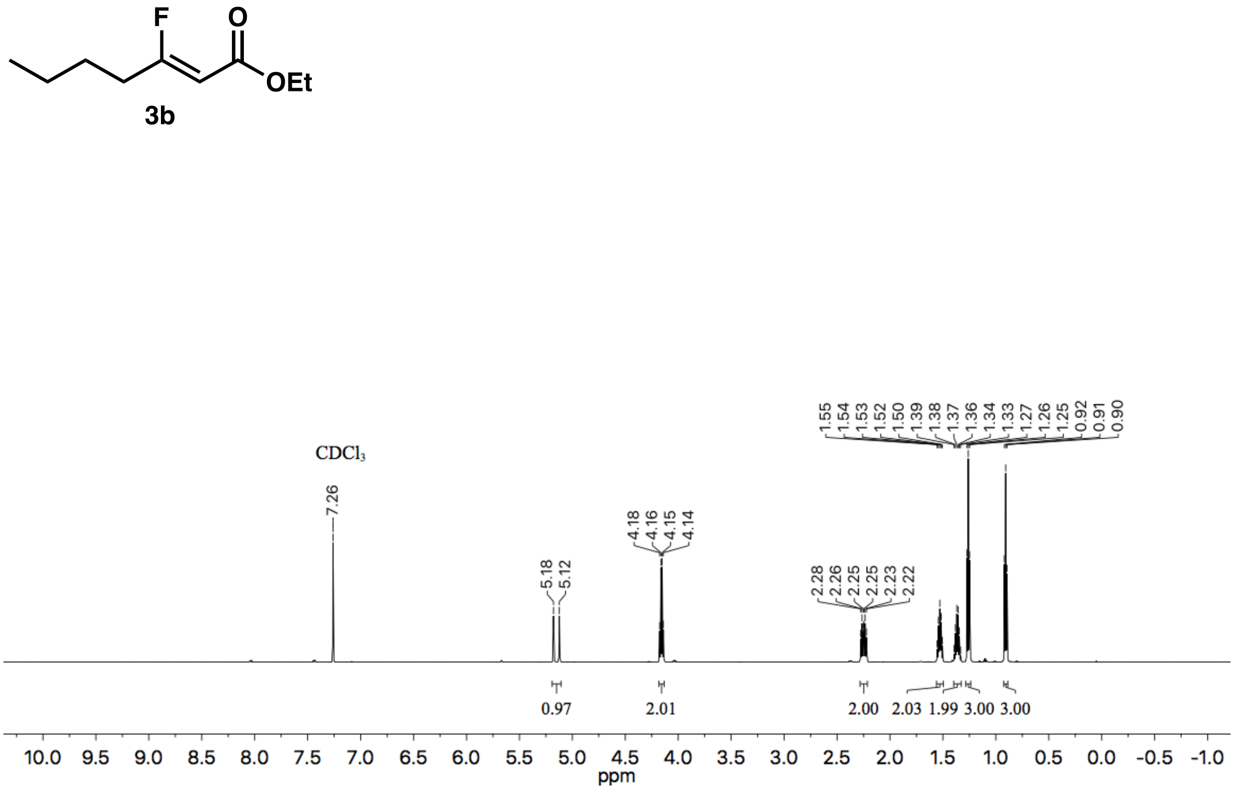
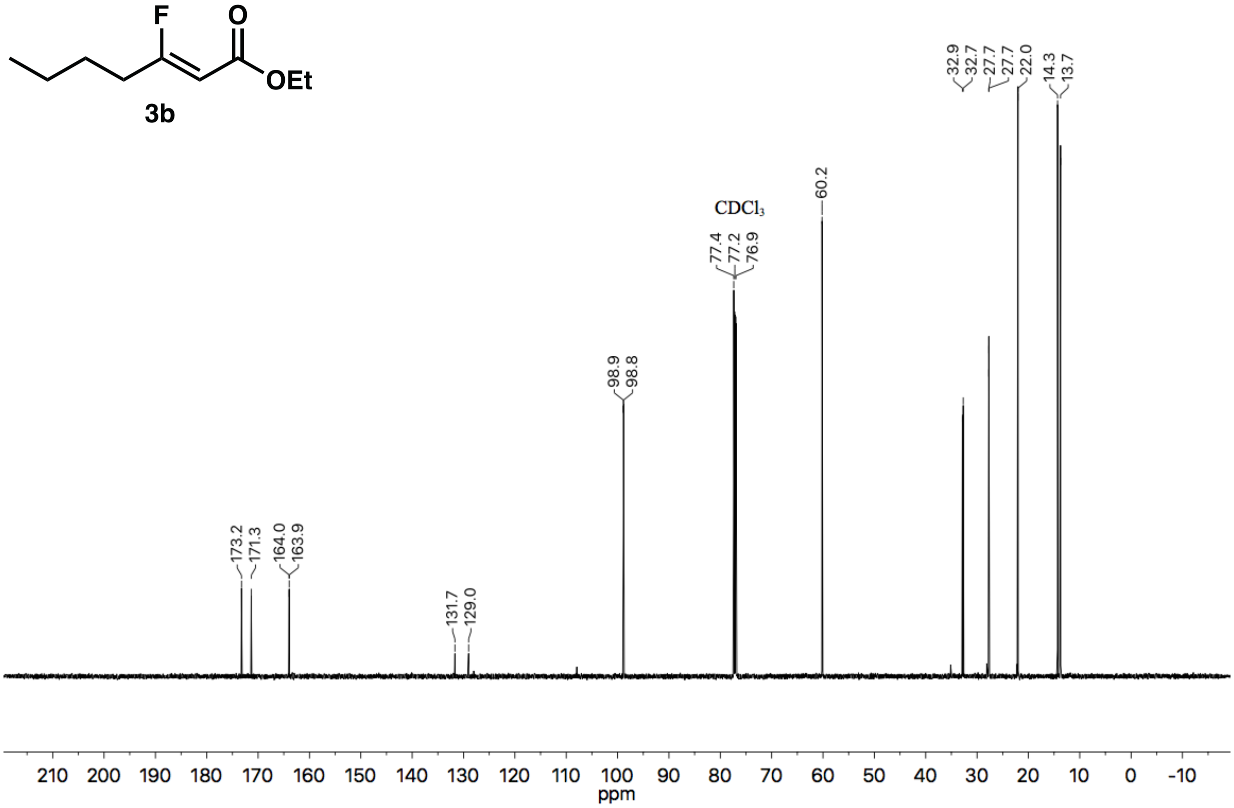


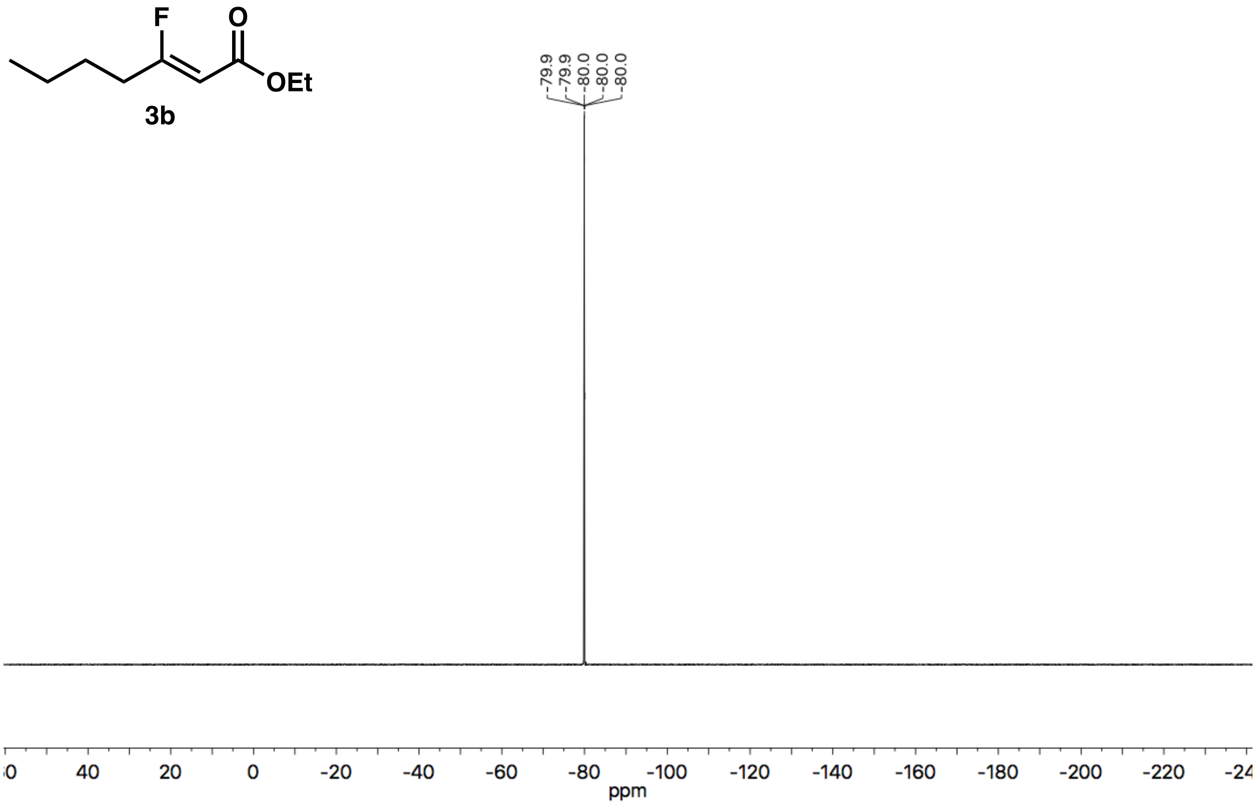
^{1}H NMR (600 MHz, CDCl$_3$)



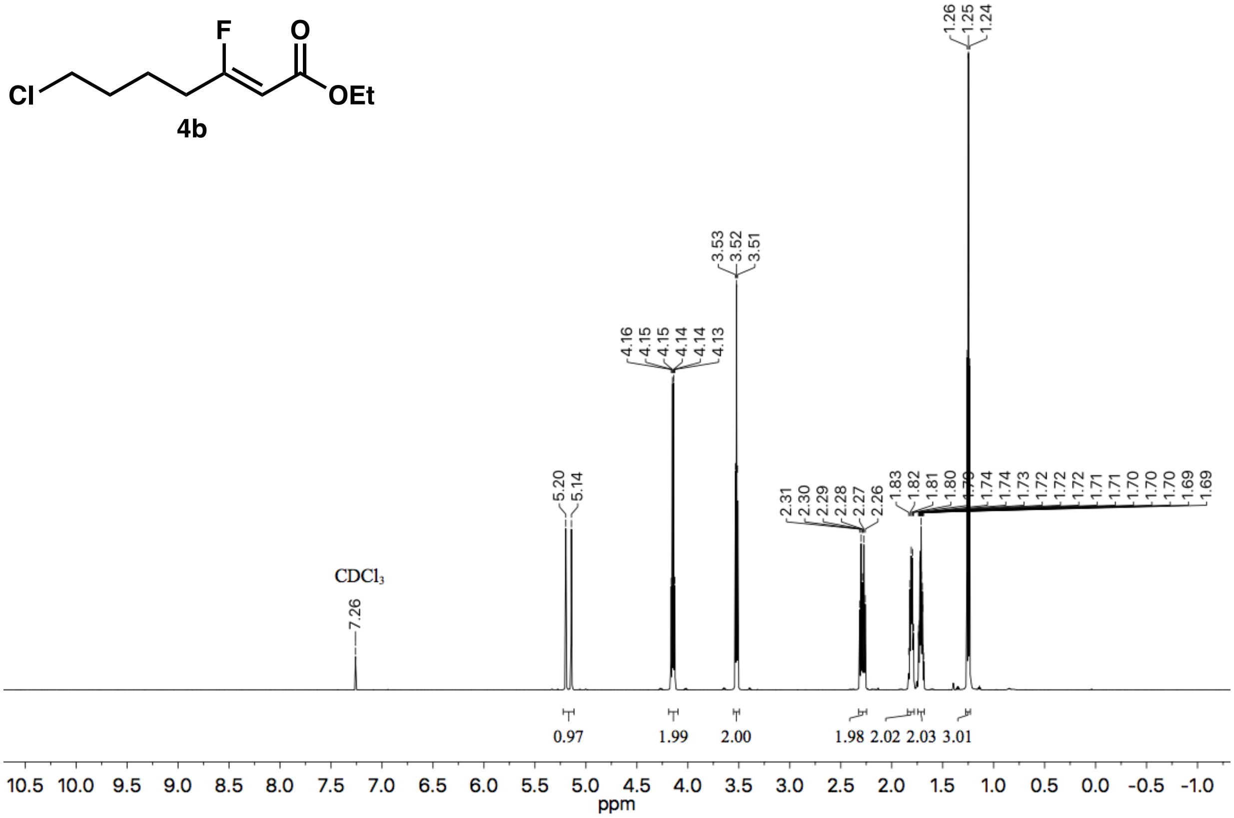
^{13}C NMR (151 MHz, CDCl$_3$)



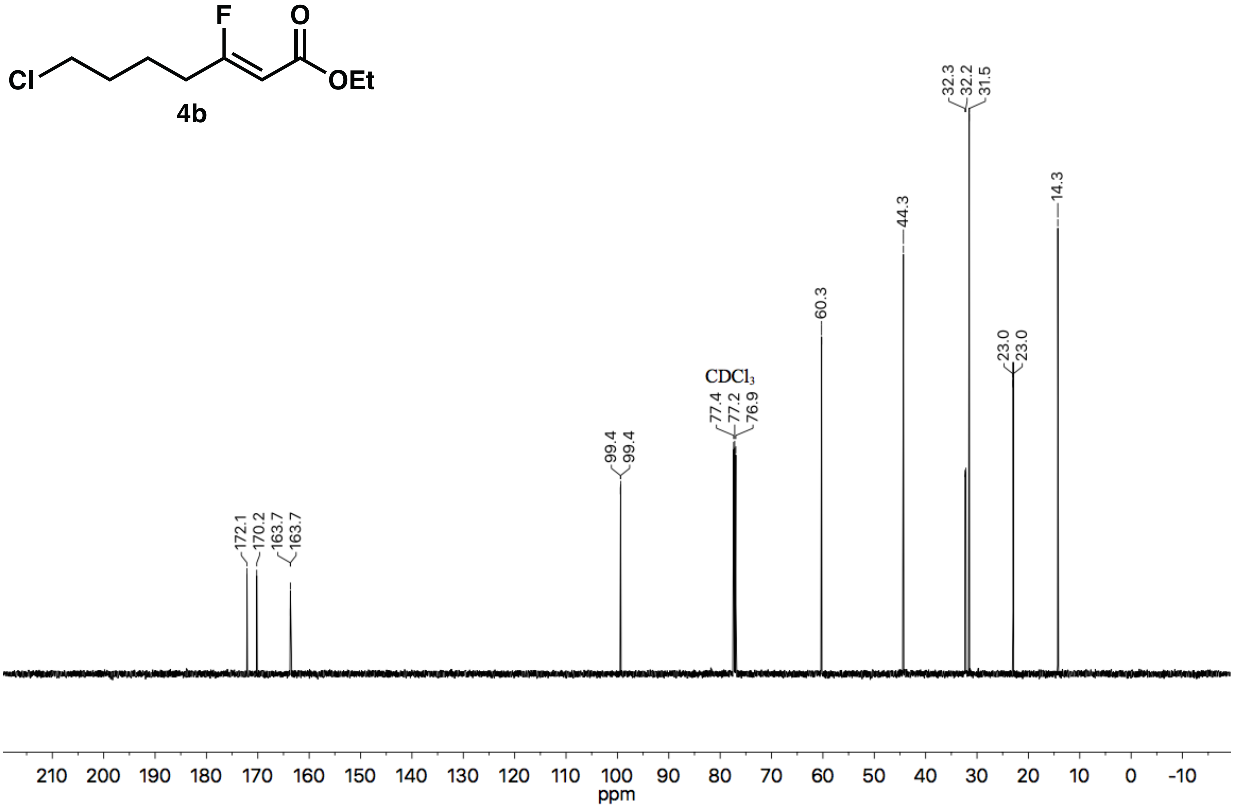
^{19}F NMR (565 MHz, CDCl$_3$)



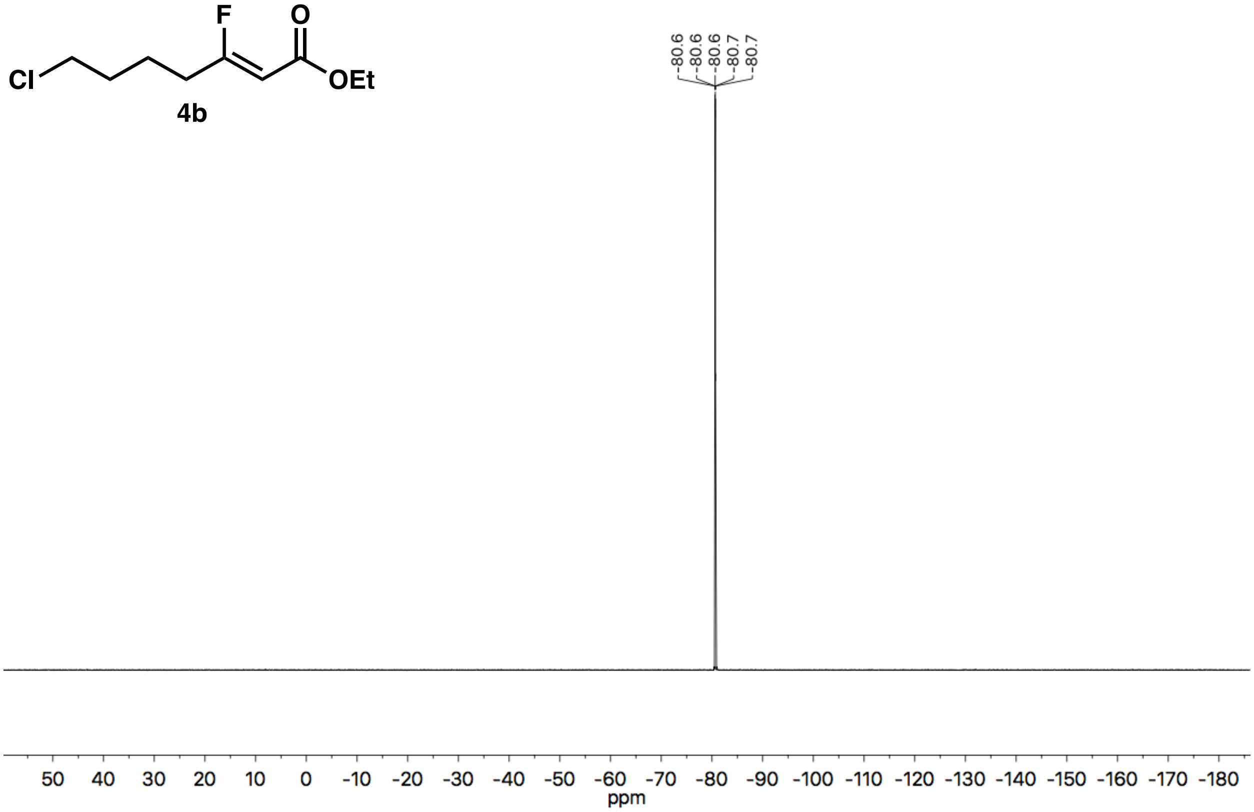
^{1}H NMR (600 MHz, CDCl$_3$)



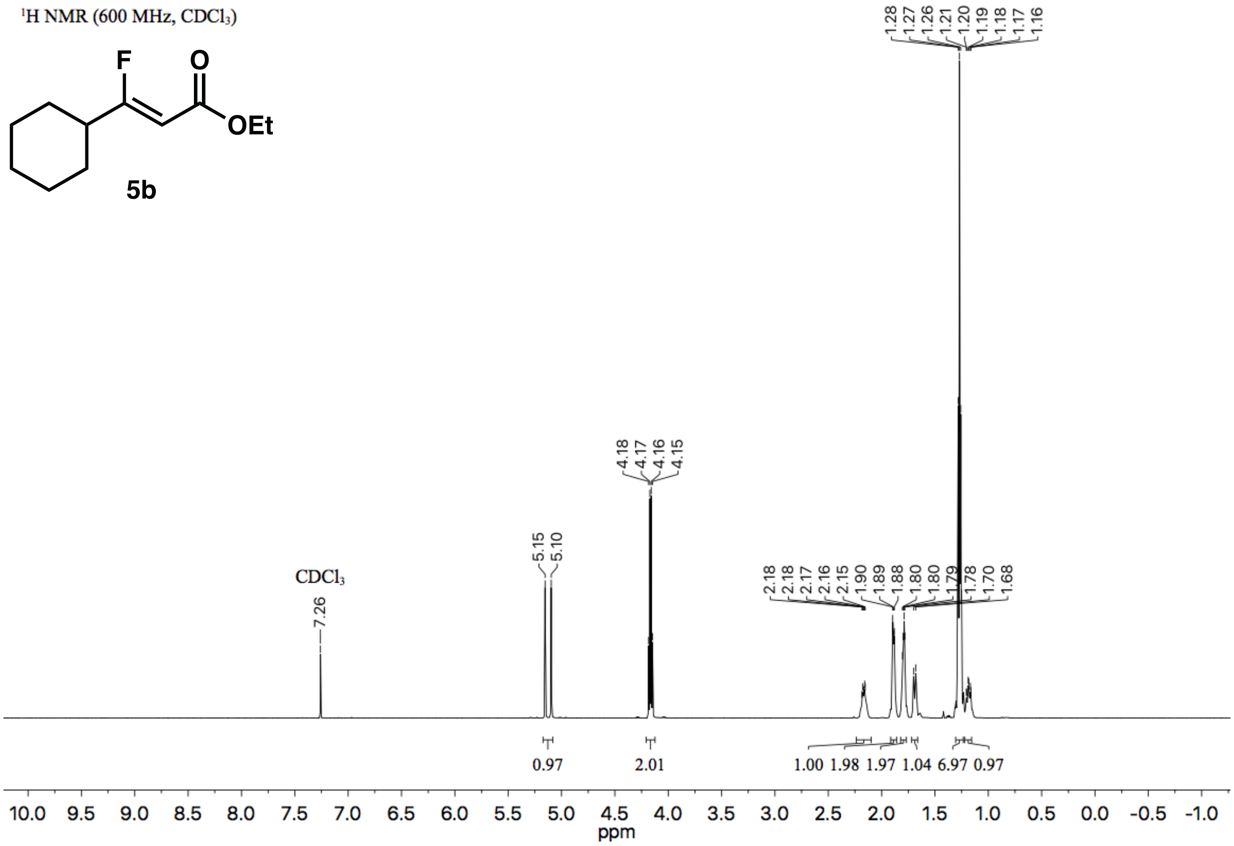
^{13}C NMR (151 MHz, CDCl$_3$)



^{19}F NMR (565 MHz, CDCl$_3$)

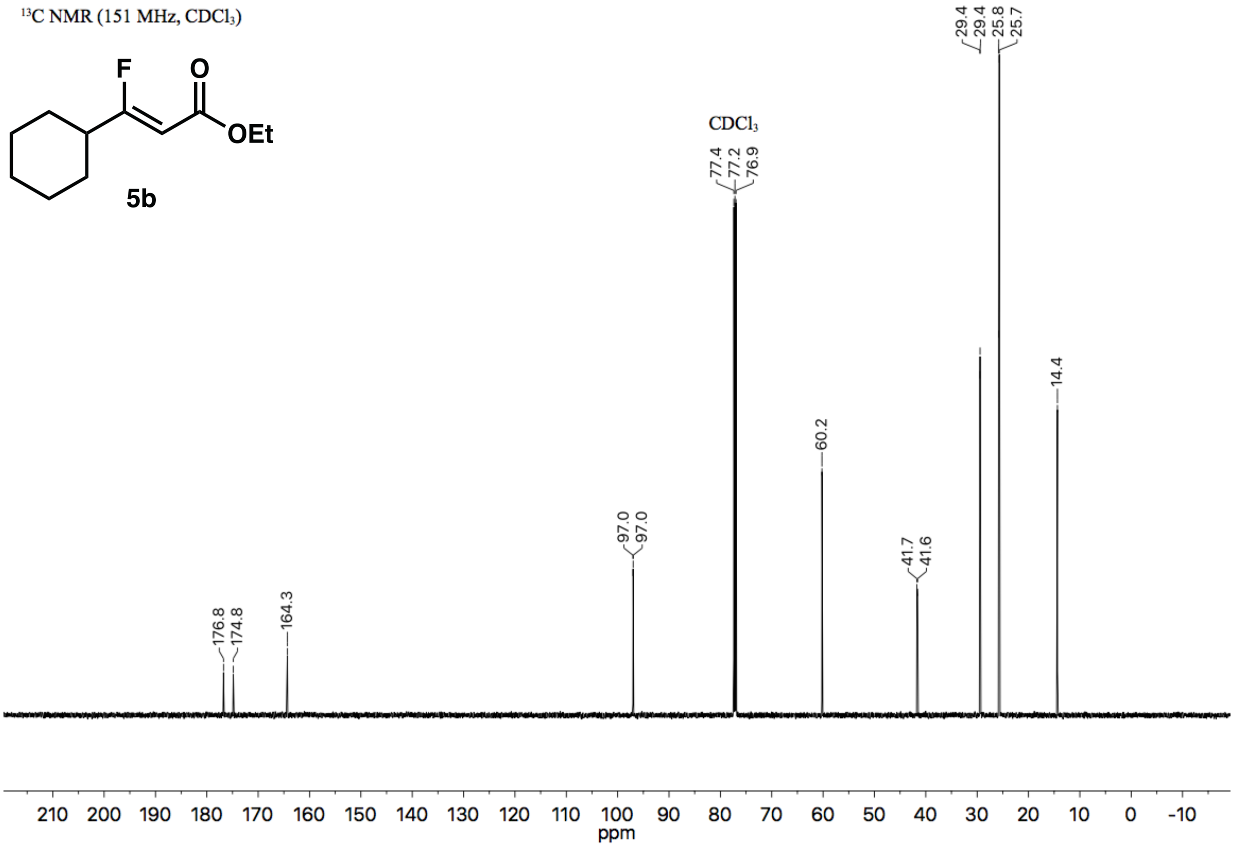


^{1}H NMR (600 MHz, CDCl$_3$)



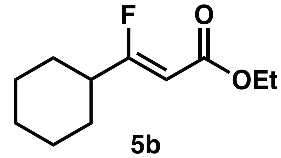
5b

^{13}C NMR (151 MHz, CDCl$_3$)

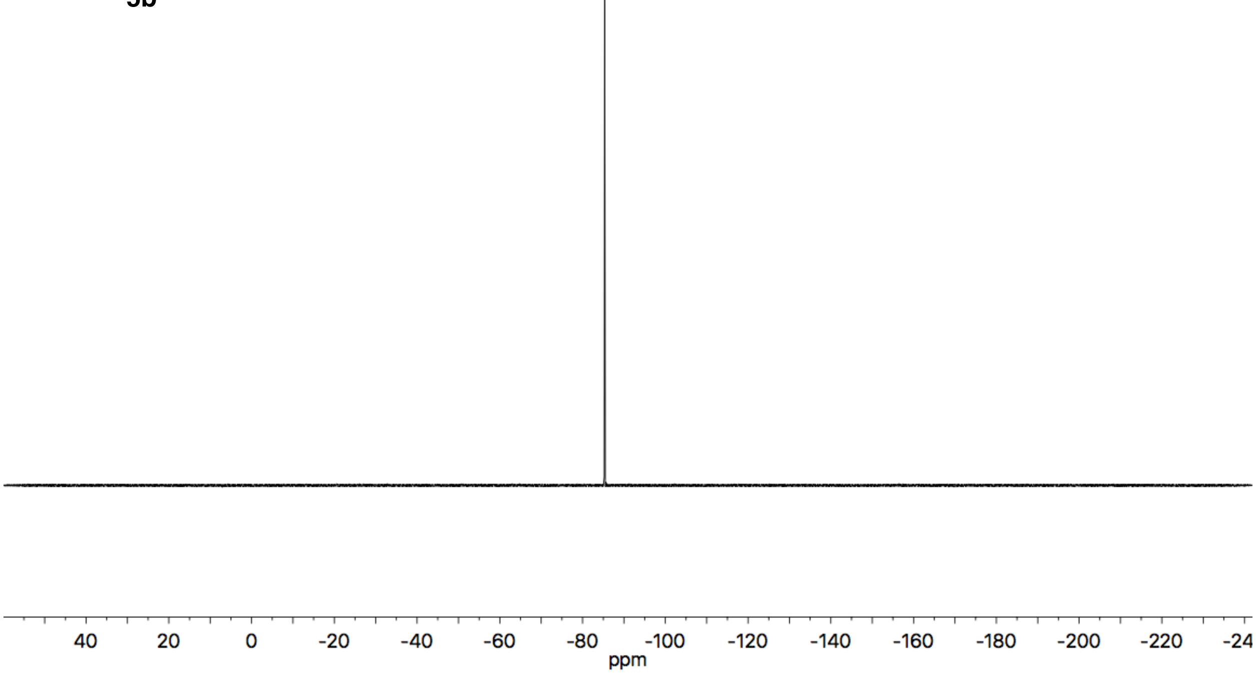


5b

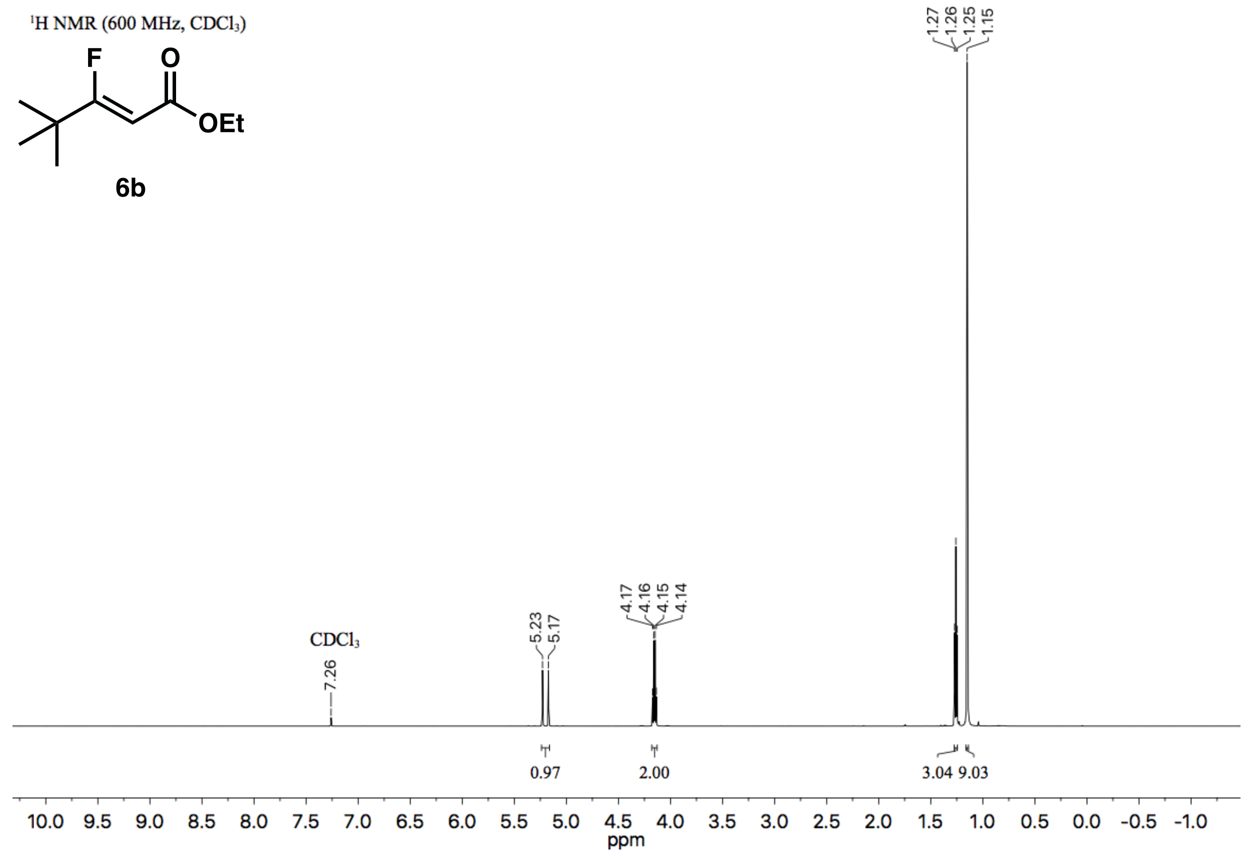
^{19}F NMR (565 MHz, $CDCl_3$)



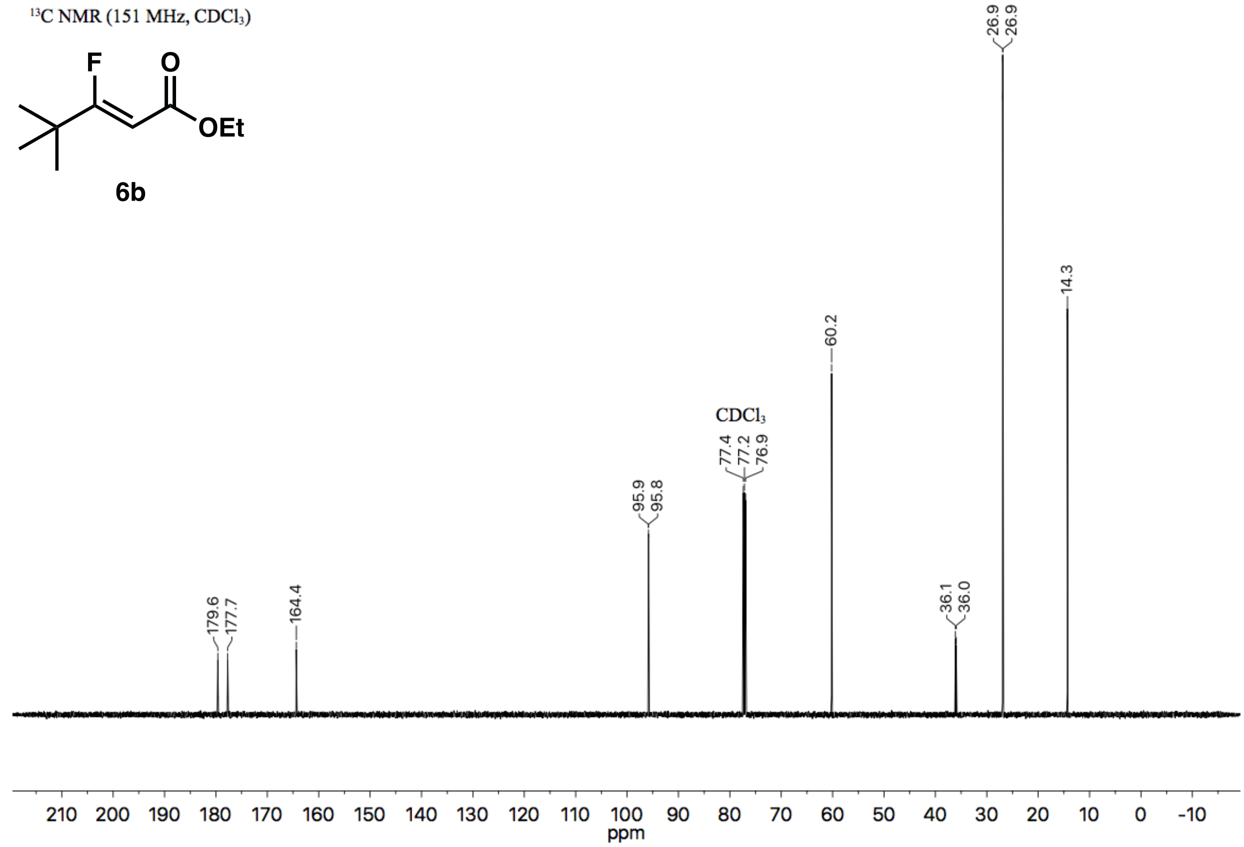
5b



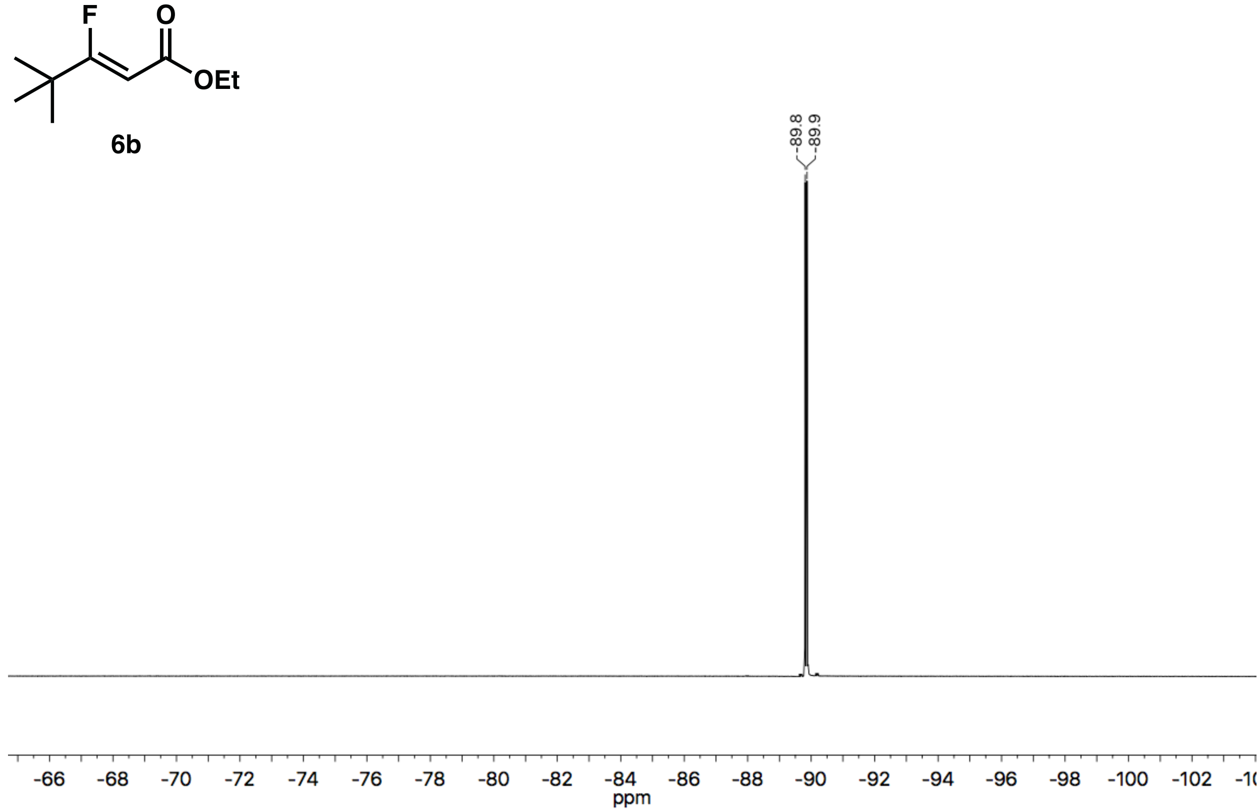
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

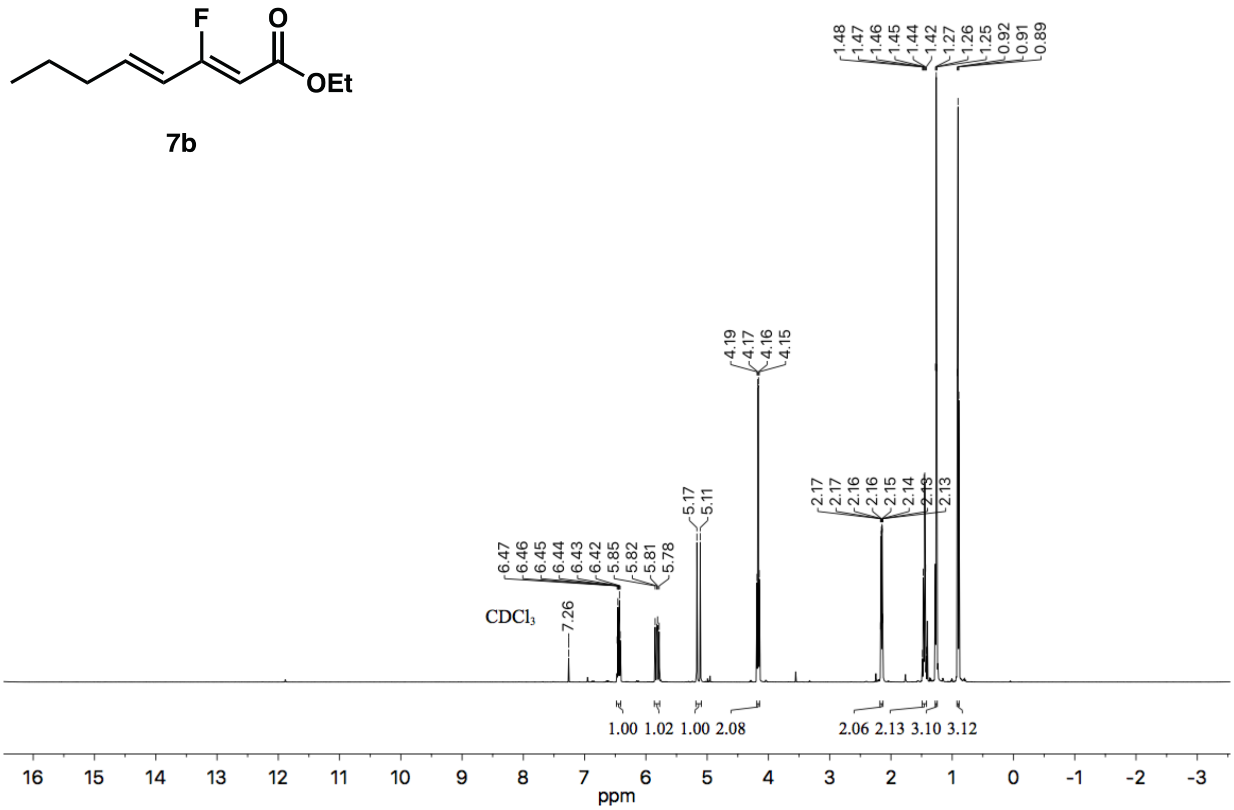


^{19}F NMR (565 MHz, CDCl$_3$)

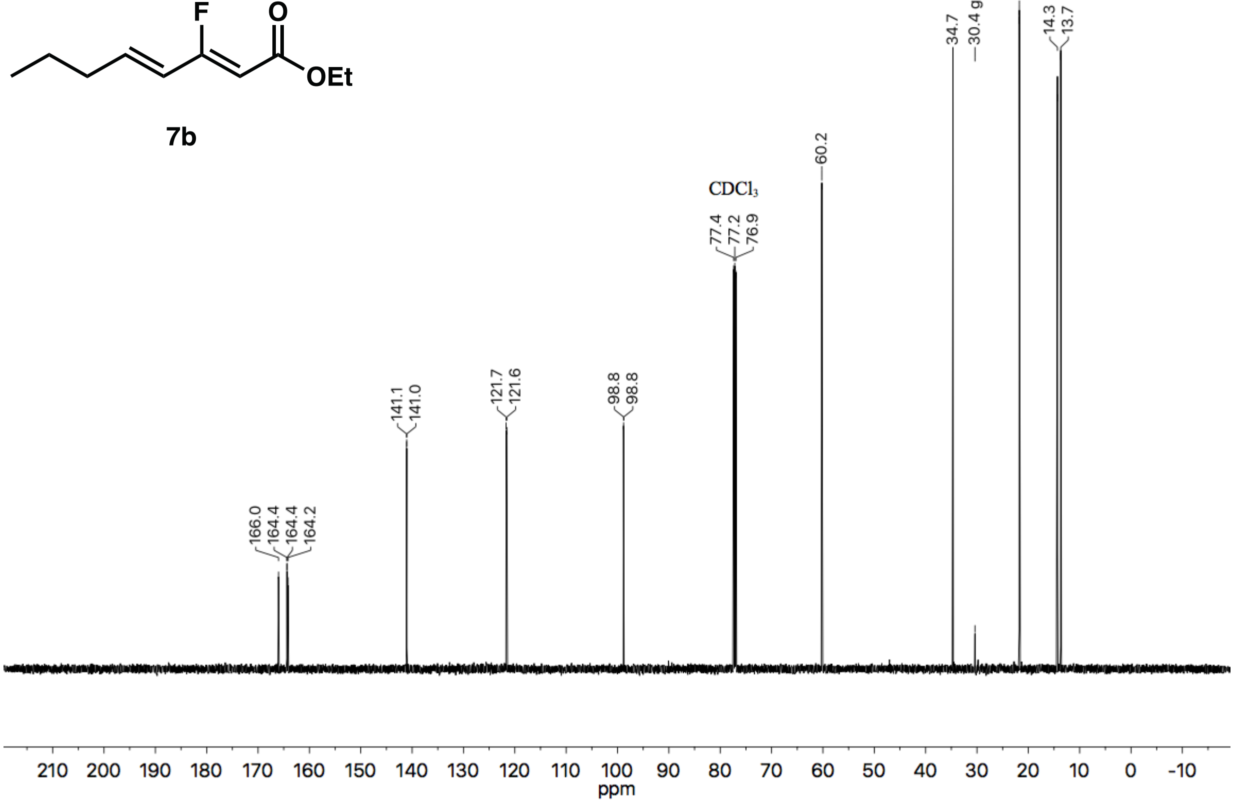


6b

^{1}H NMR (600 MHz, CDCl$_3$)

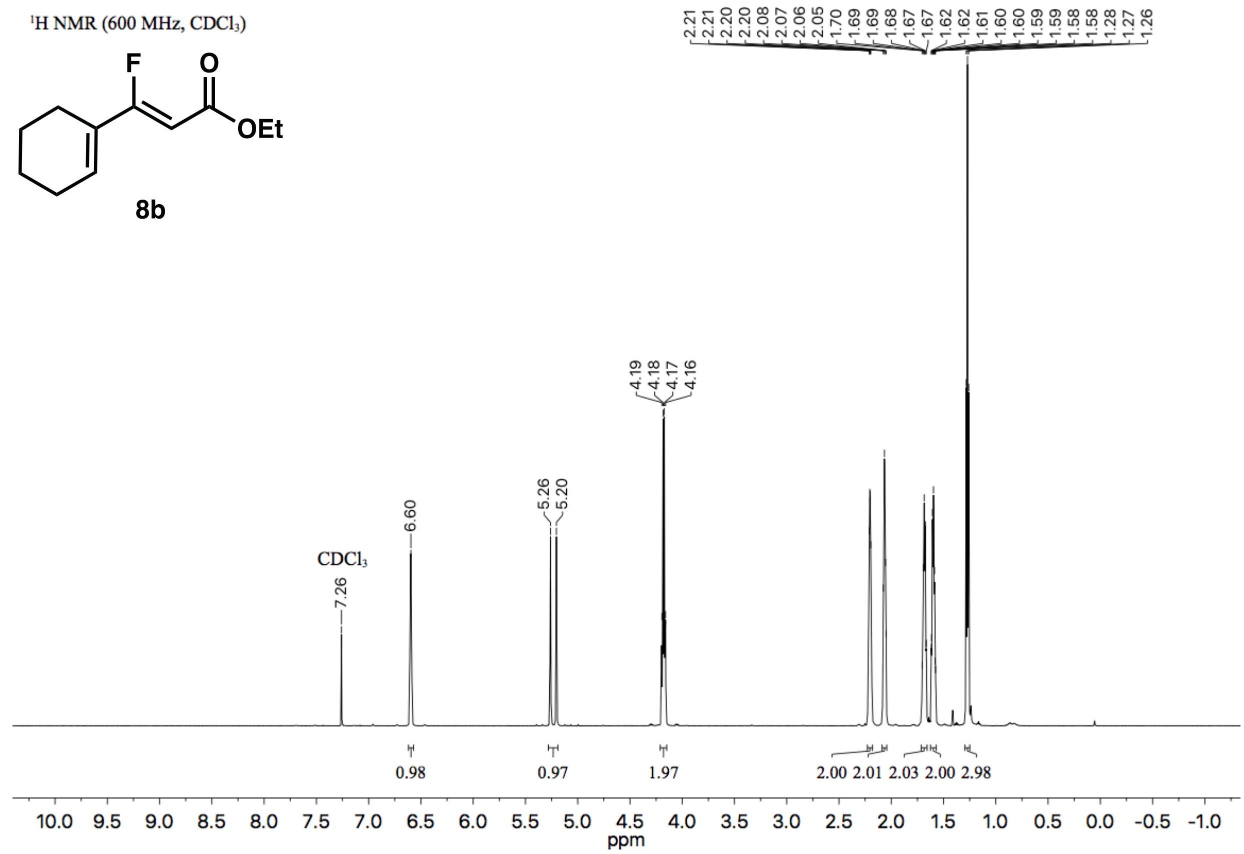


^{13}C NMR (151 MHz, CDCl$_3$)

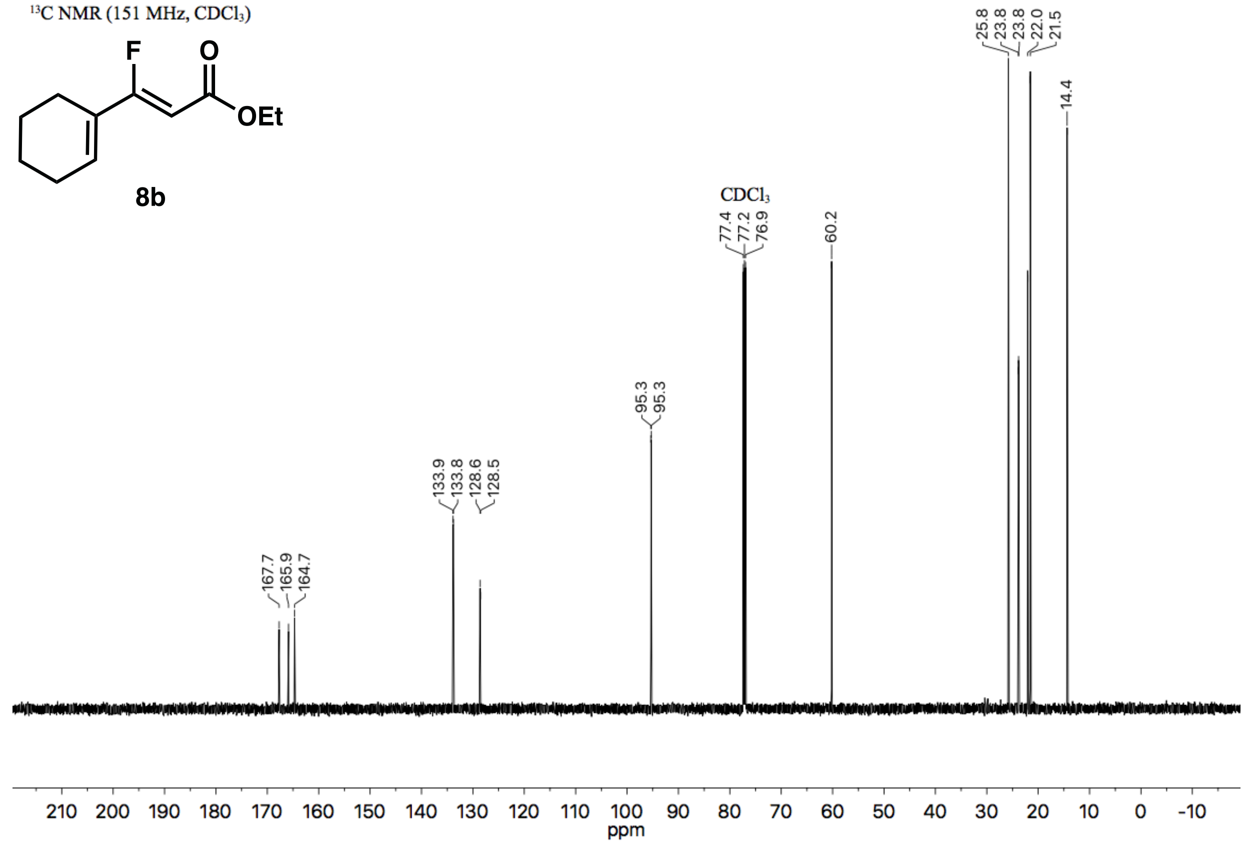


^{19}F NMR (565 MHz, $CDCl_3$)

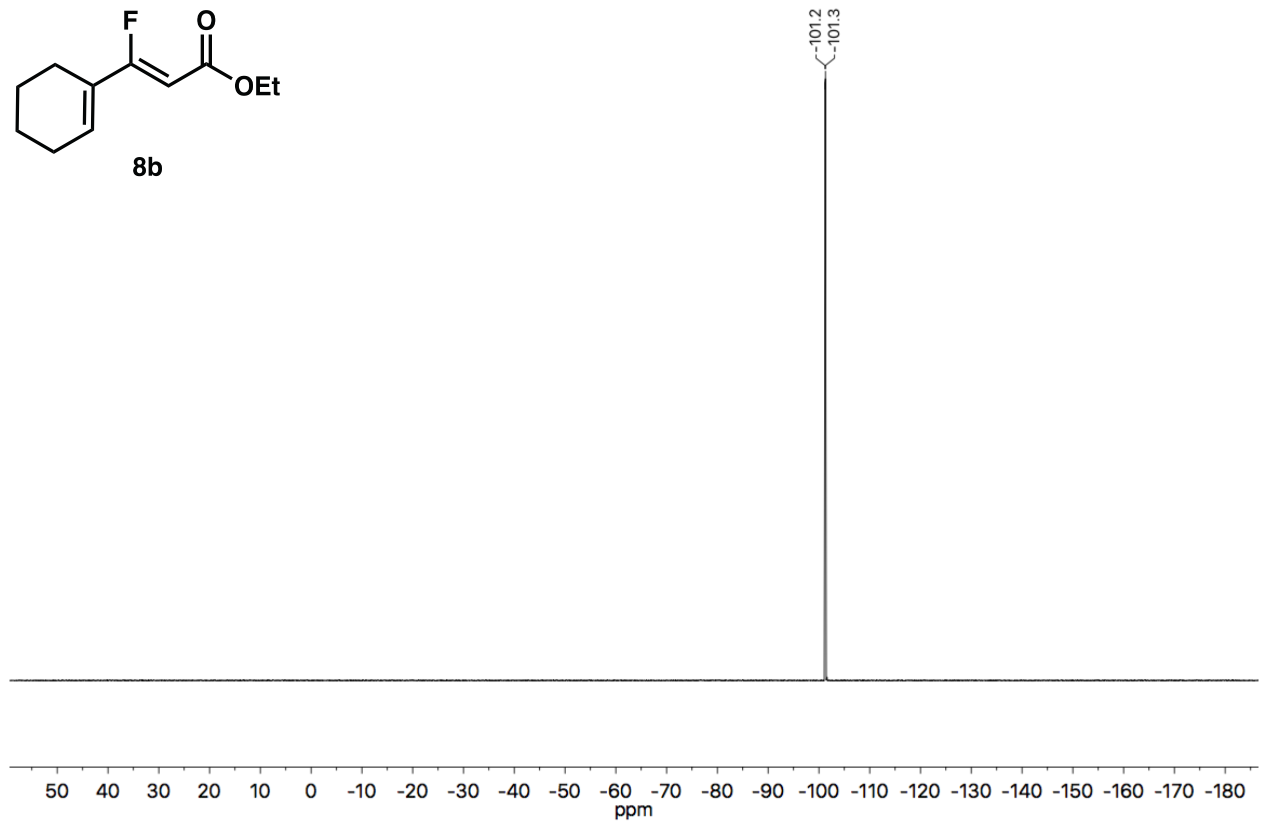
^{1}H NMR (600 MHz, CDCl$_3$)



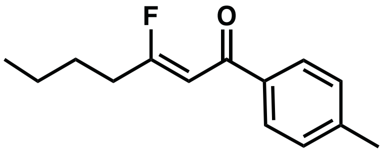
^{13}C NMR (151 MHz, CDCl$_3$)



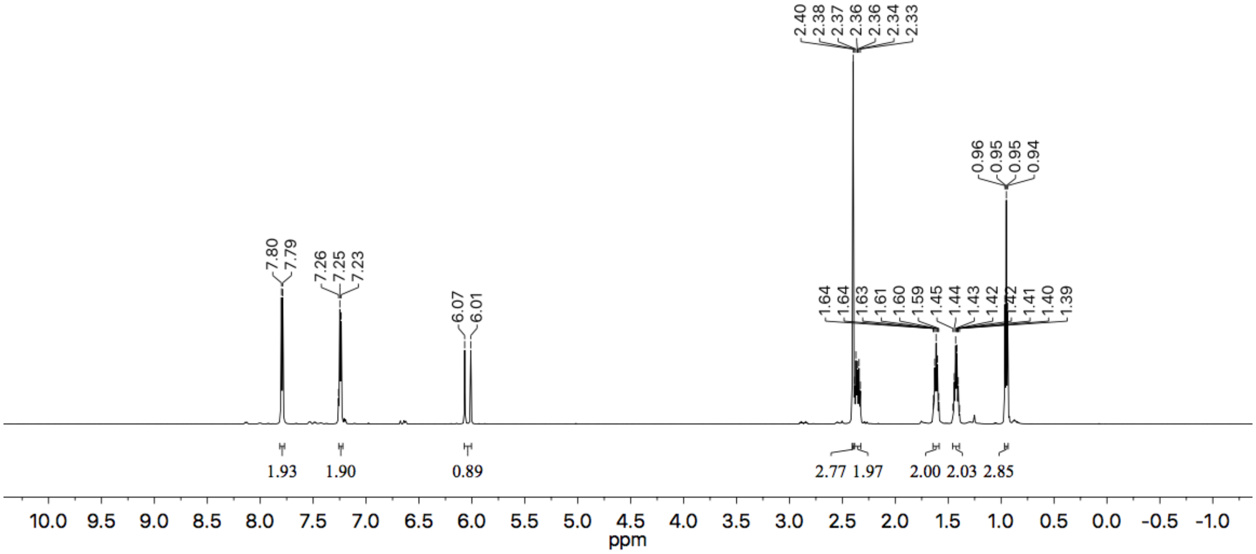
^{19}F NMR (565 MHz, CDCl$_3$)



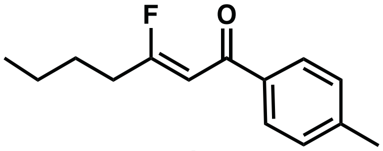
8b



9b



^{13}C NMR (151 MHz, CDCl$_3$)



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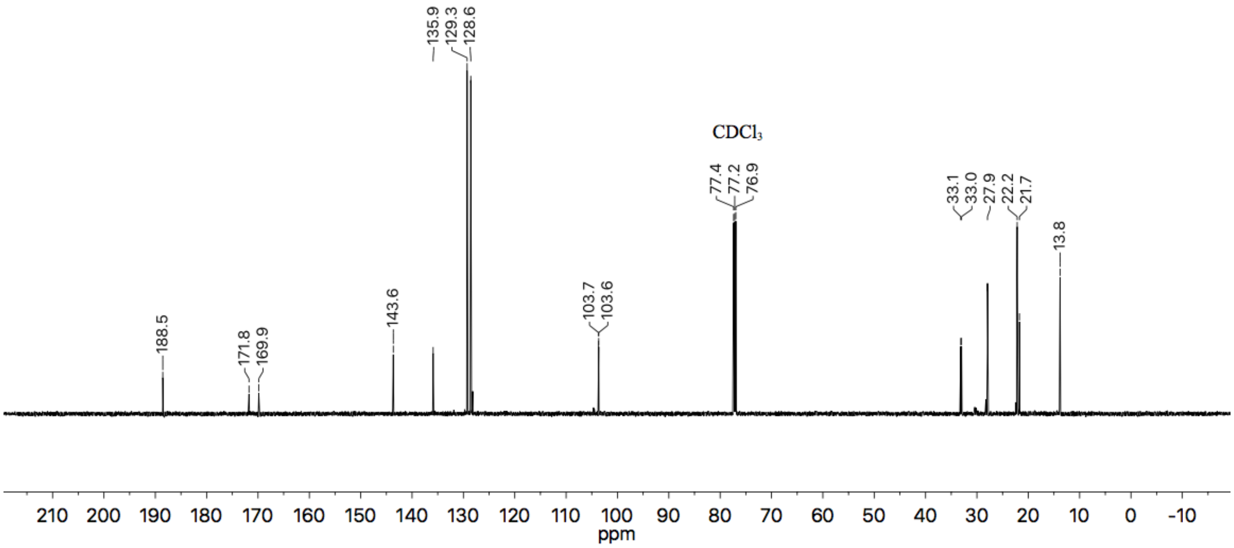
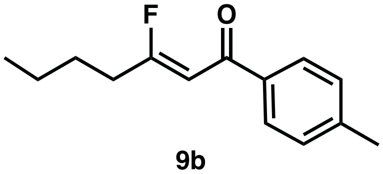


^{19}F NMR (565 MHz, CDCl$_3$)



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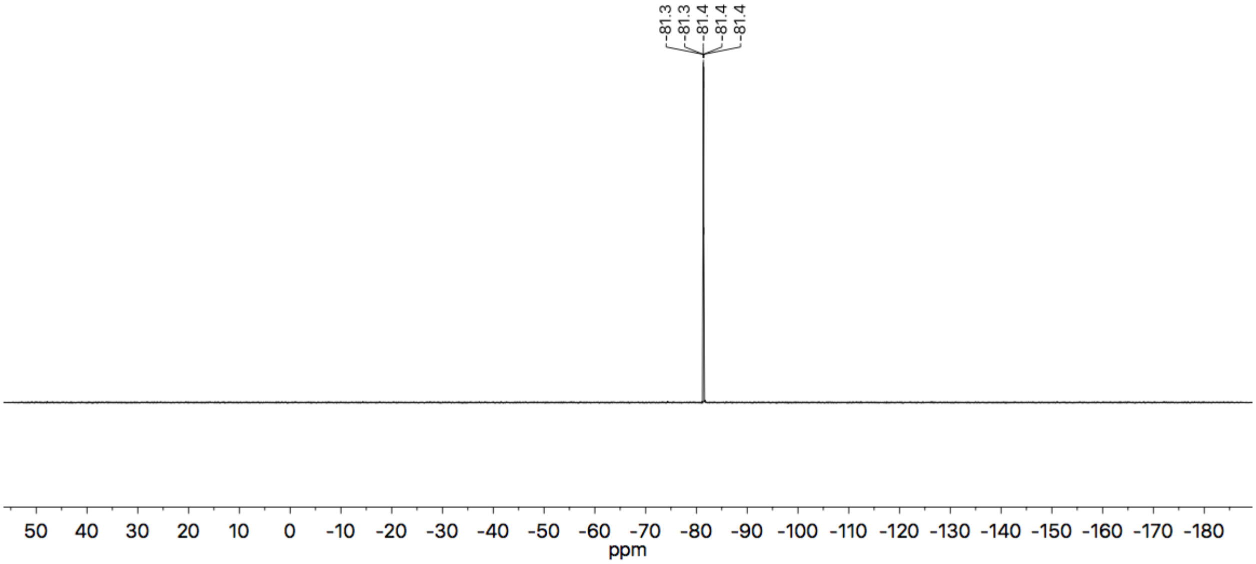
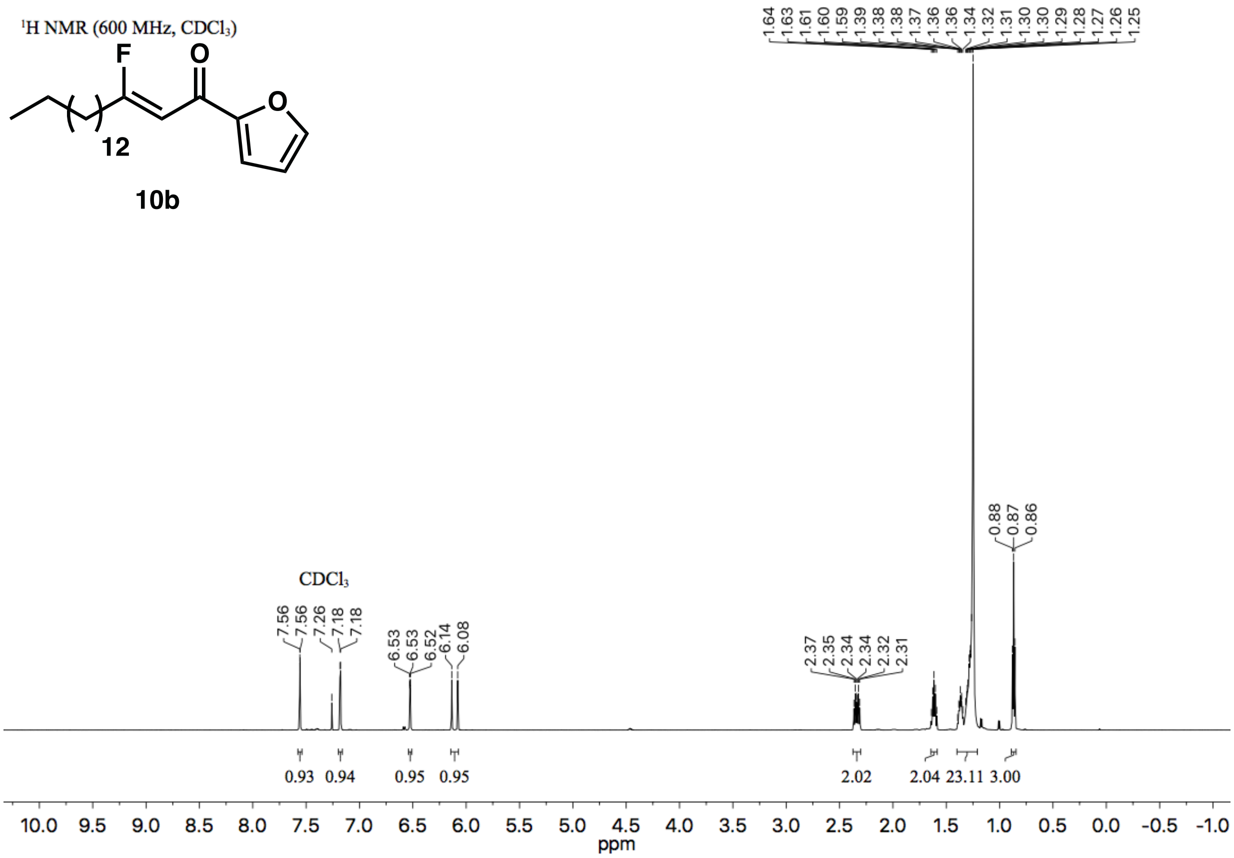
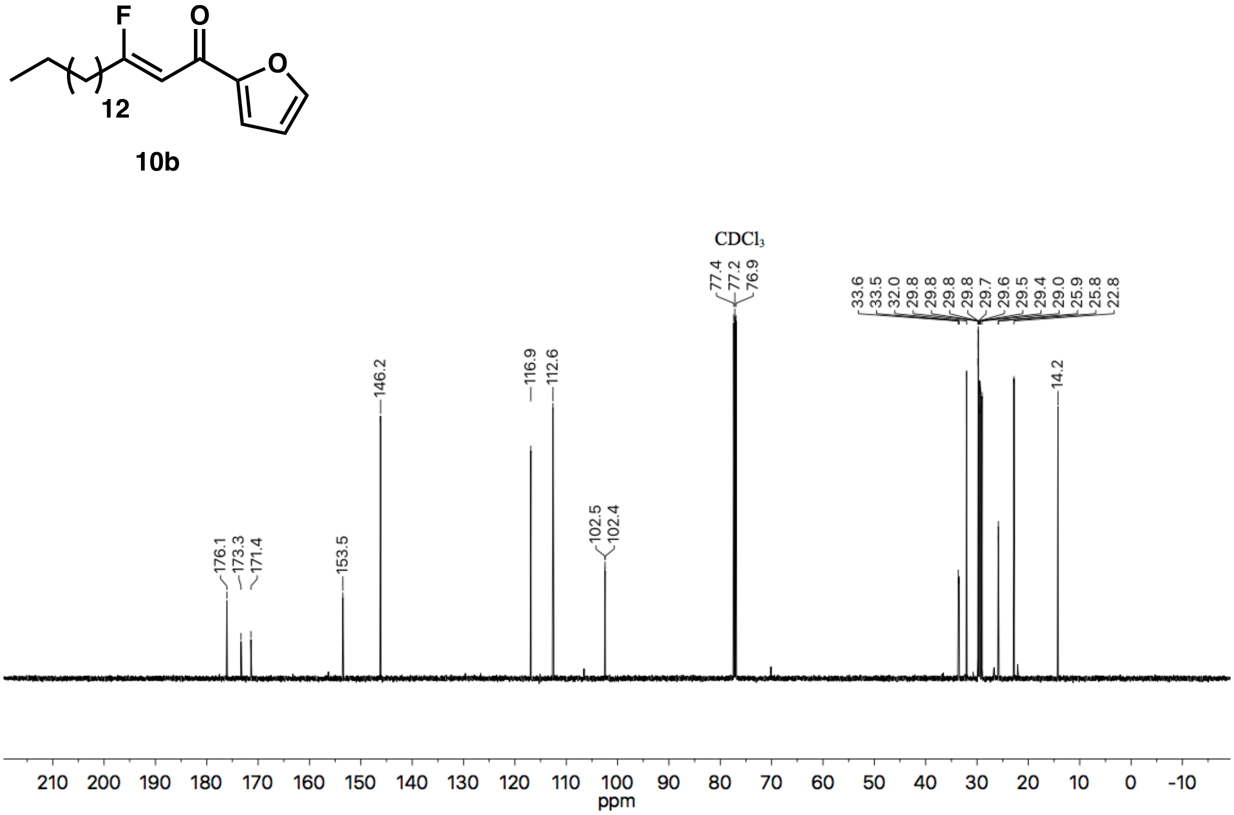


^{1}H NMR (600 MHz, $CDCl_3$)



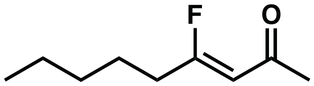
^{13}C NMR (151 MHz, $CDCl_3$)



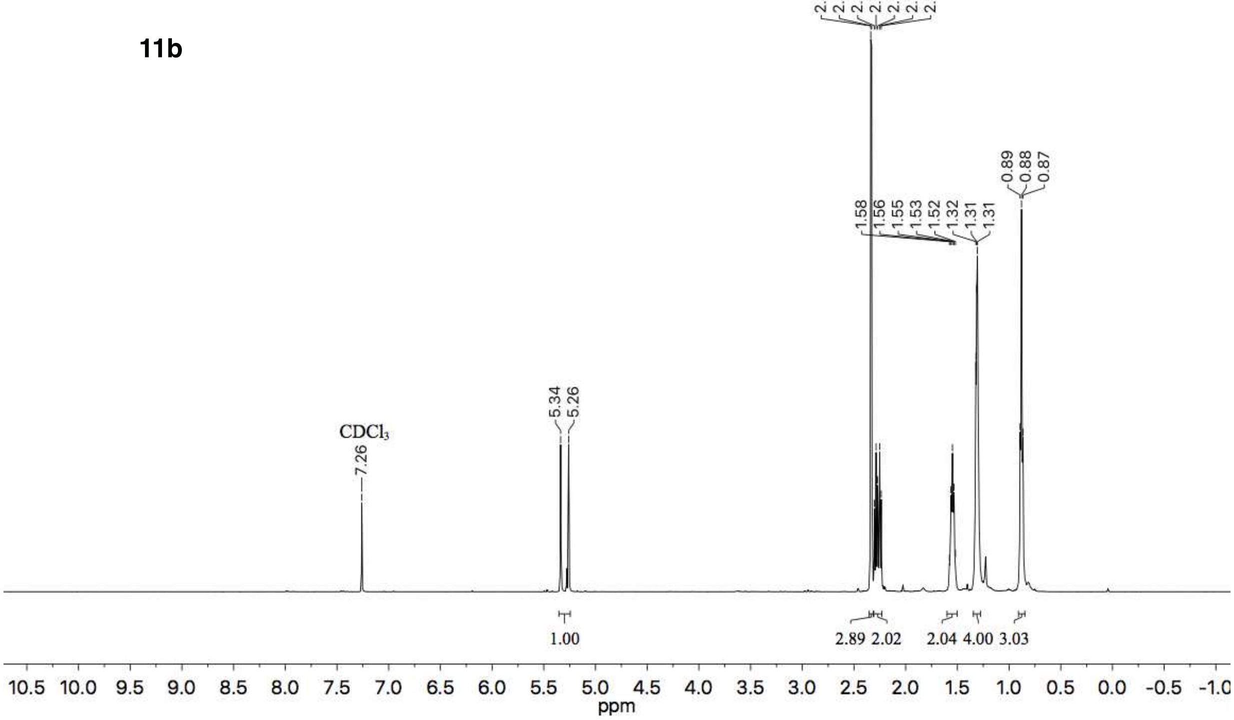
^{19}F NMR (565 MHz, CDCl$_3$)

10b

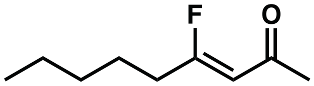
^{1}H NMR (500 MHz, CDCl$_3$)



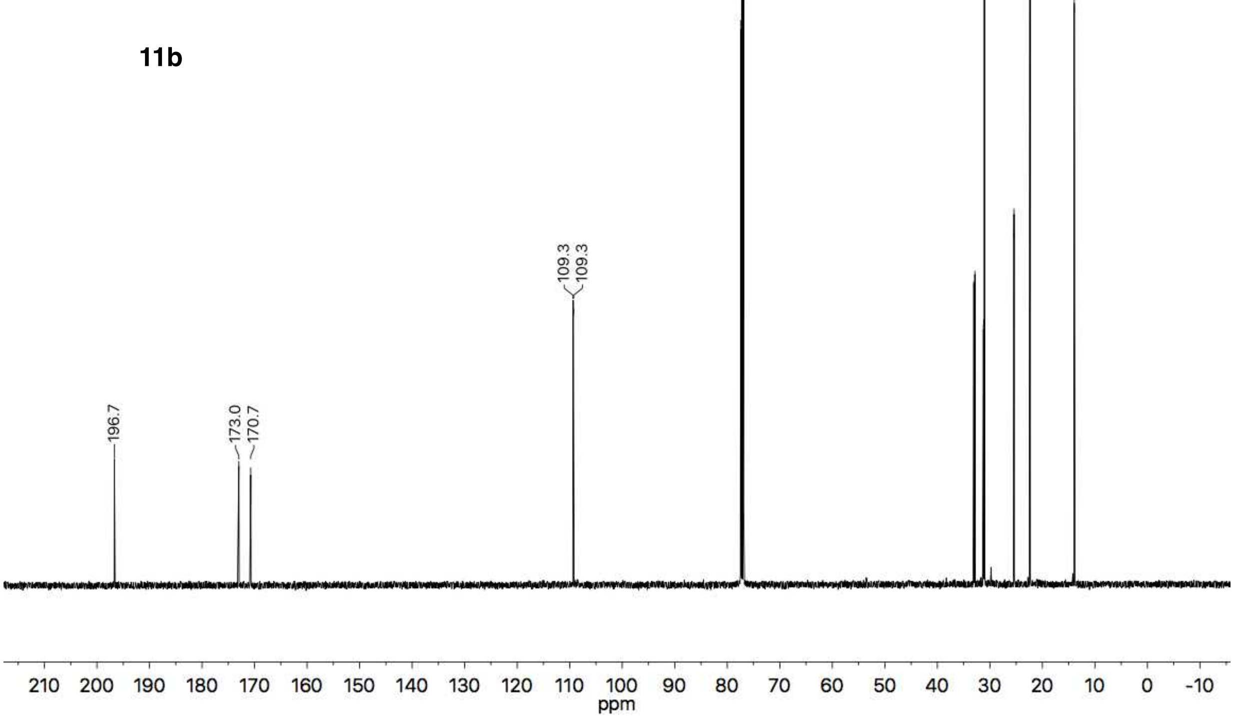
11b



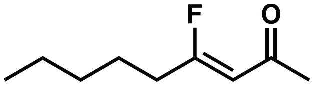
^{13}C NMR (126 MHz, CDCl$_3$)



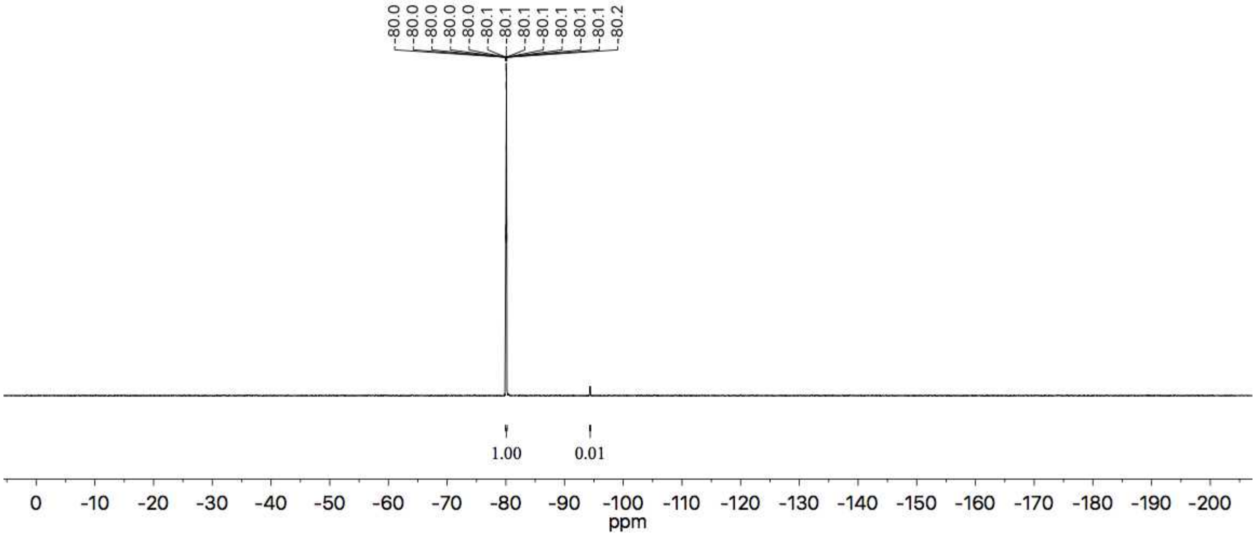
11b



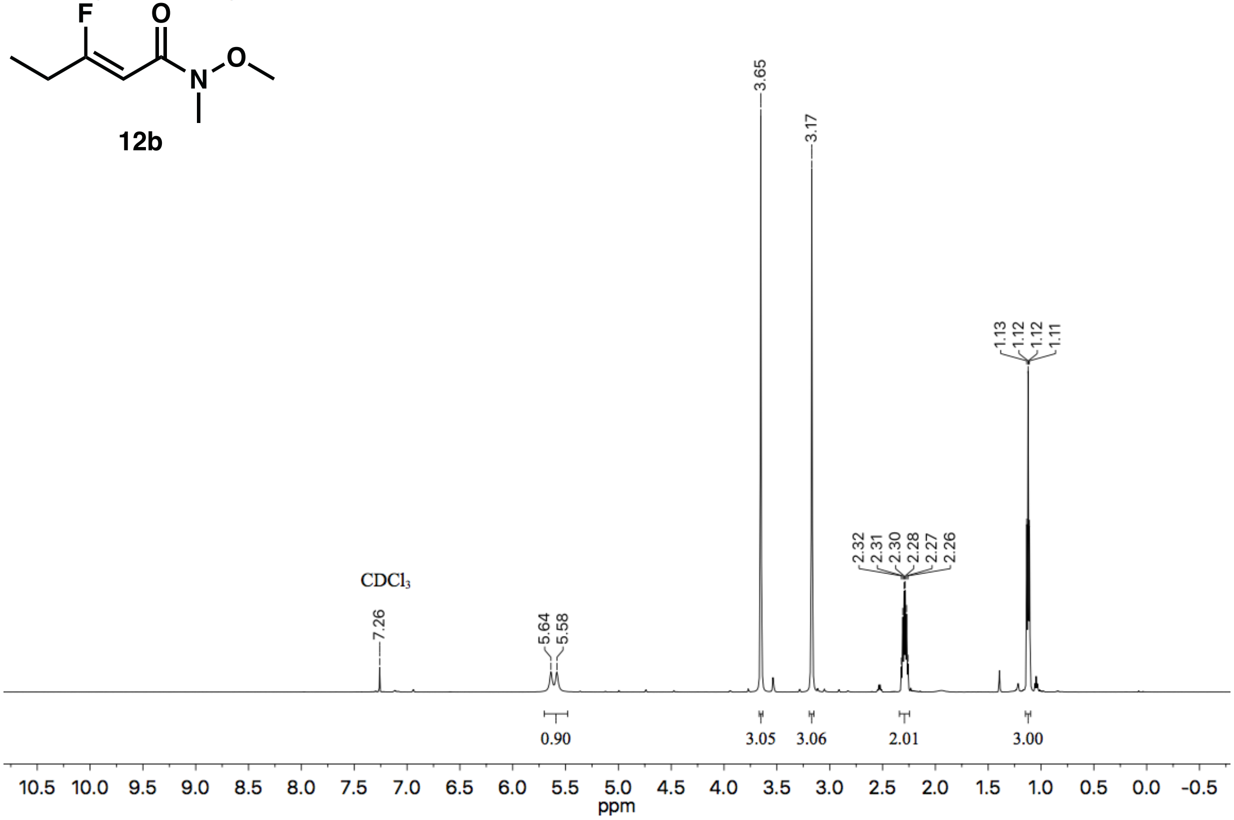
^{19}F NMR (470 MHz, CDCl$_3$)



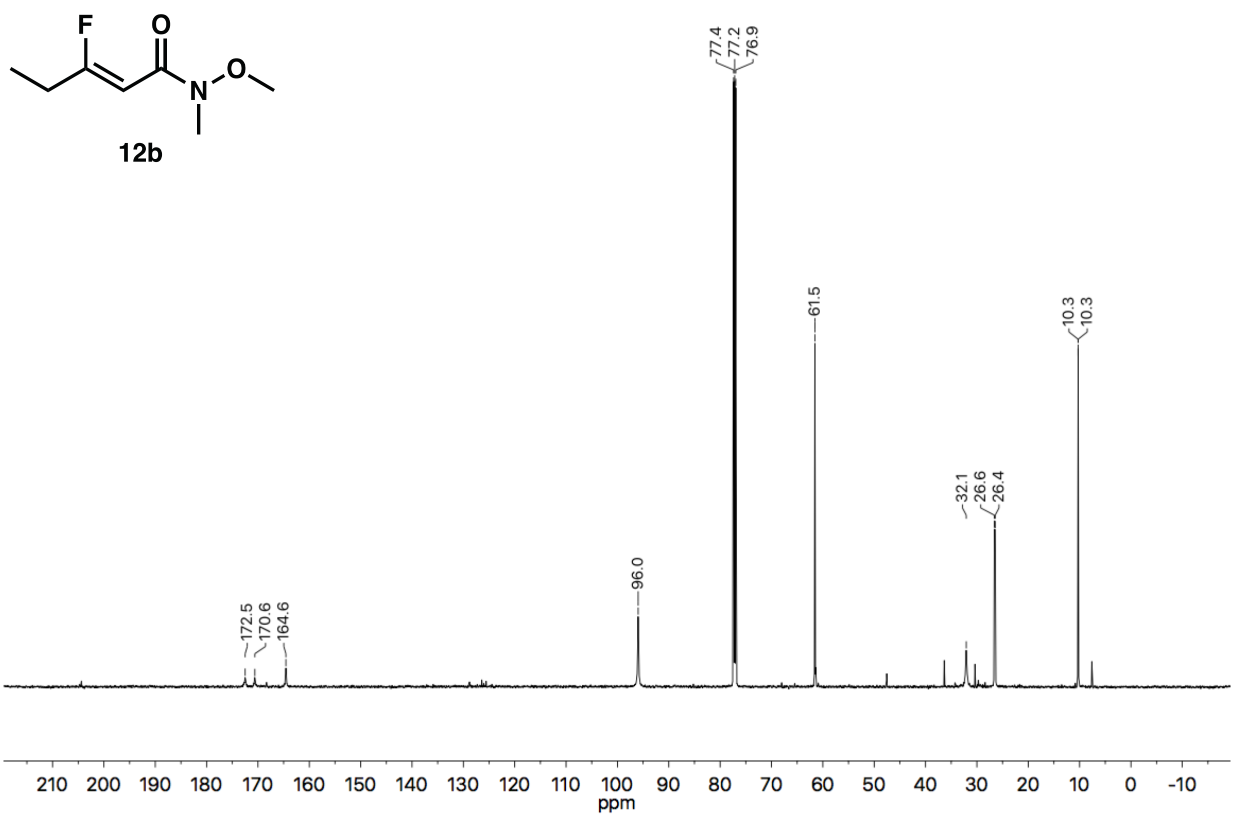
11b



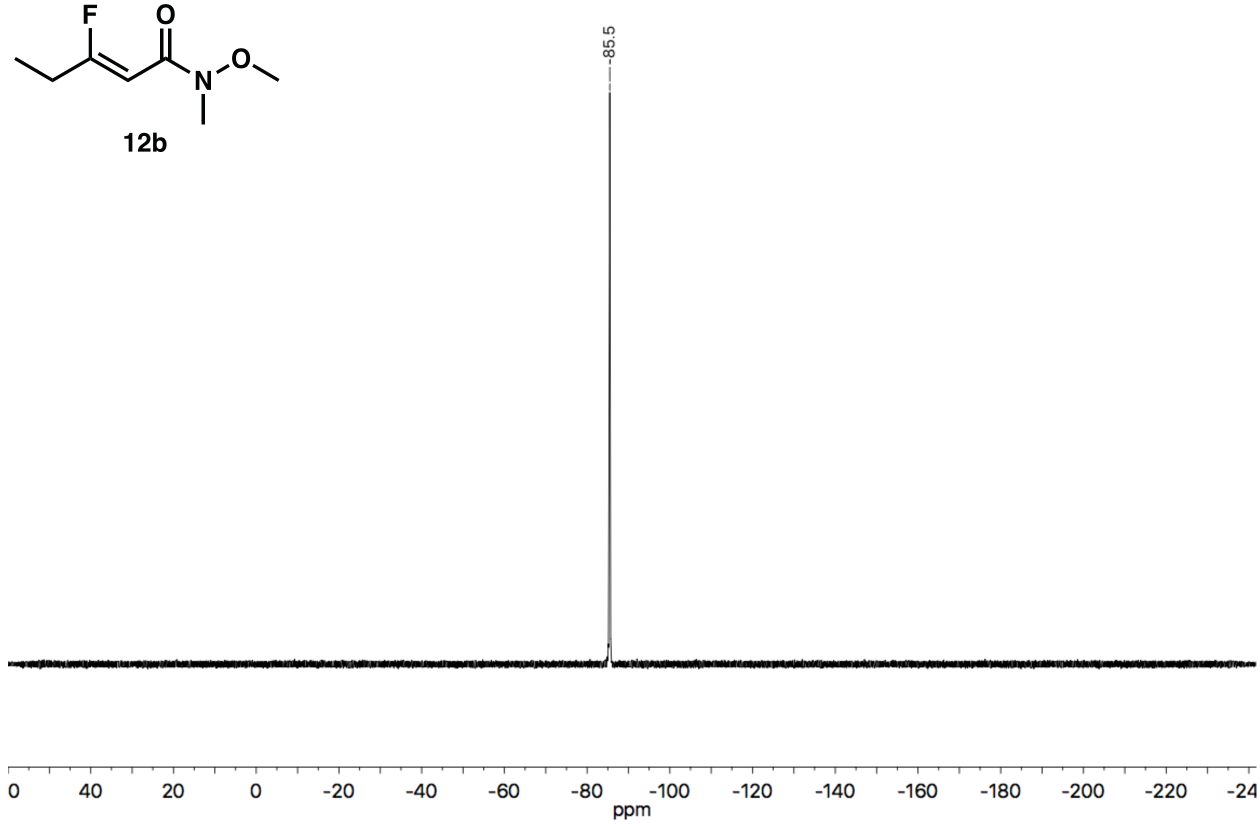
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

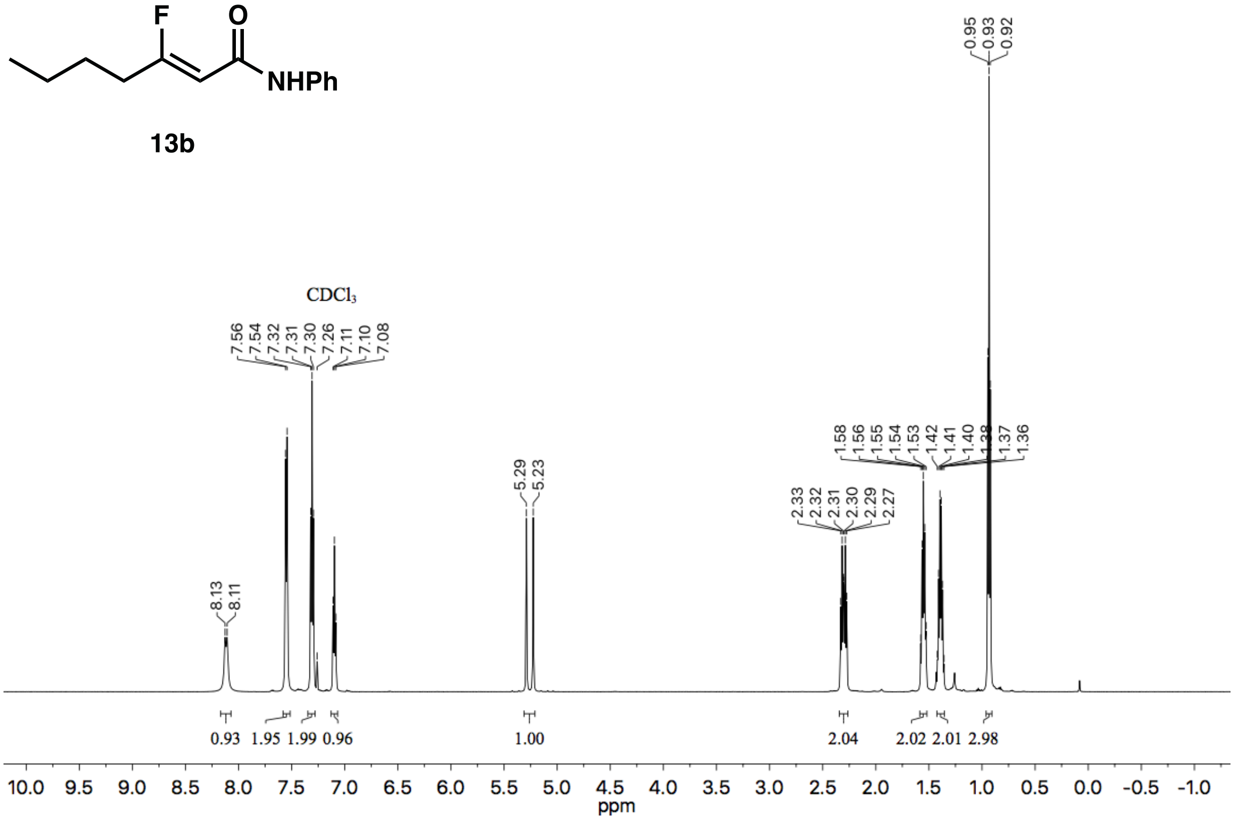


^{19}F NMR (565 MHz, CDCl$_3$)

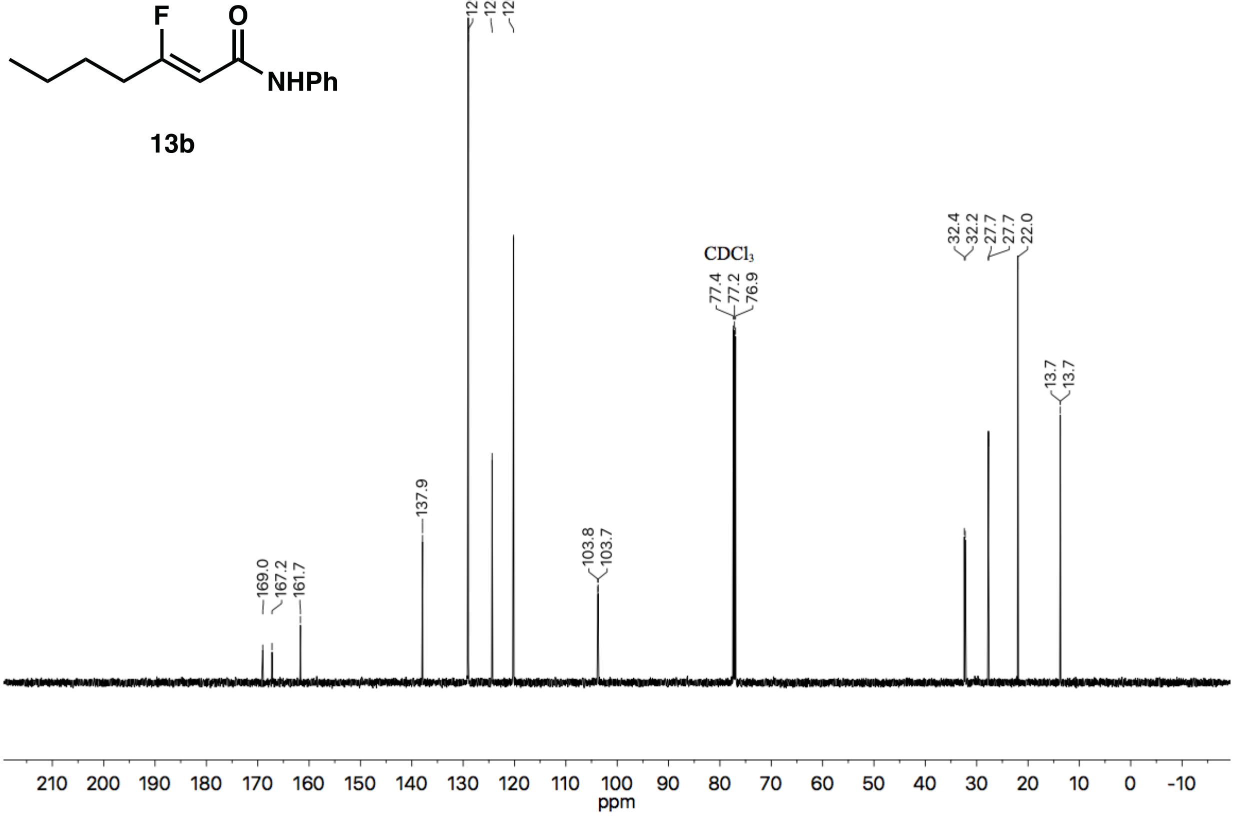


12b

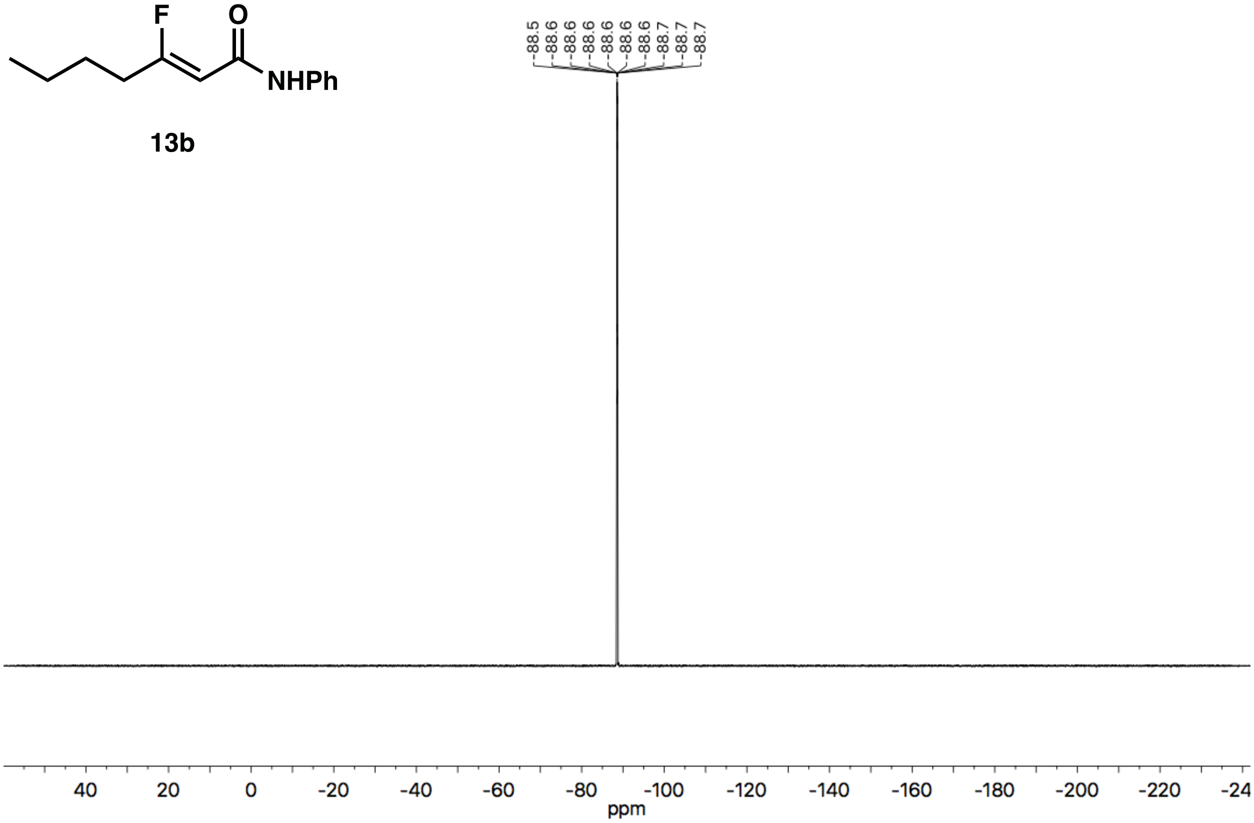
^{1}H NMR (600 MHz, CDCl$_3$)


13b

^{13}C NMR (151 MHz, CDCl$_3$)

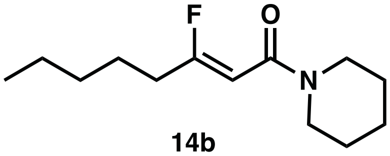

13b

^{19}F NMR (565 MHz, $CDCl_3$)

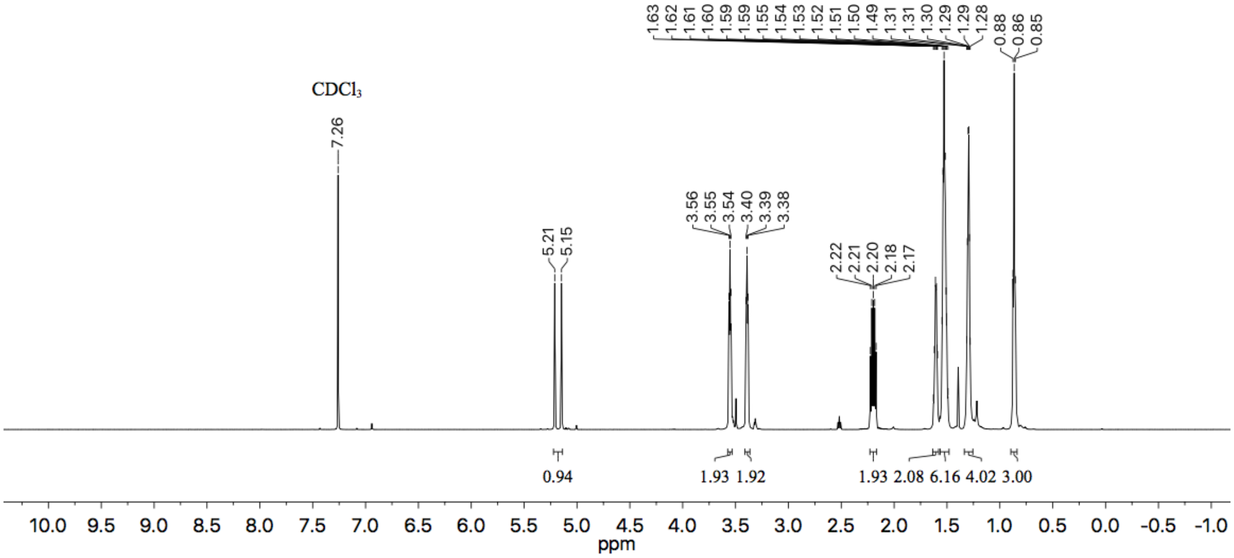


13b

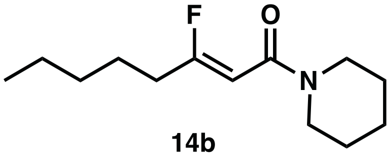
^{1}H NMR (600 MHz, CDCl$_3$)



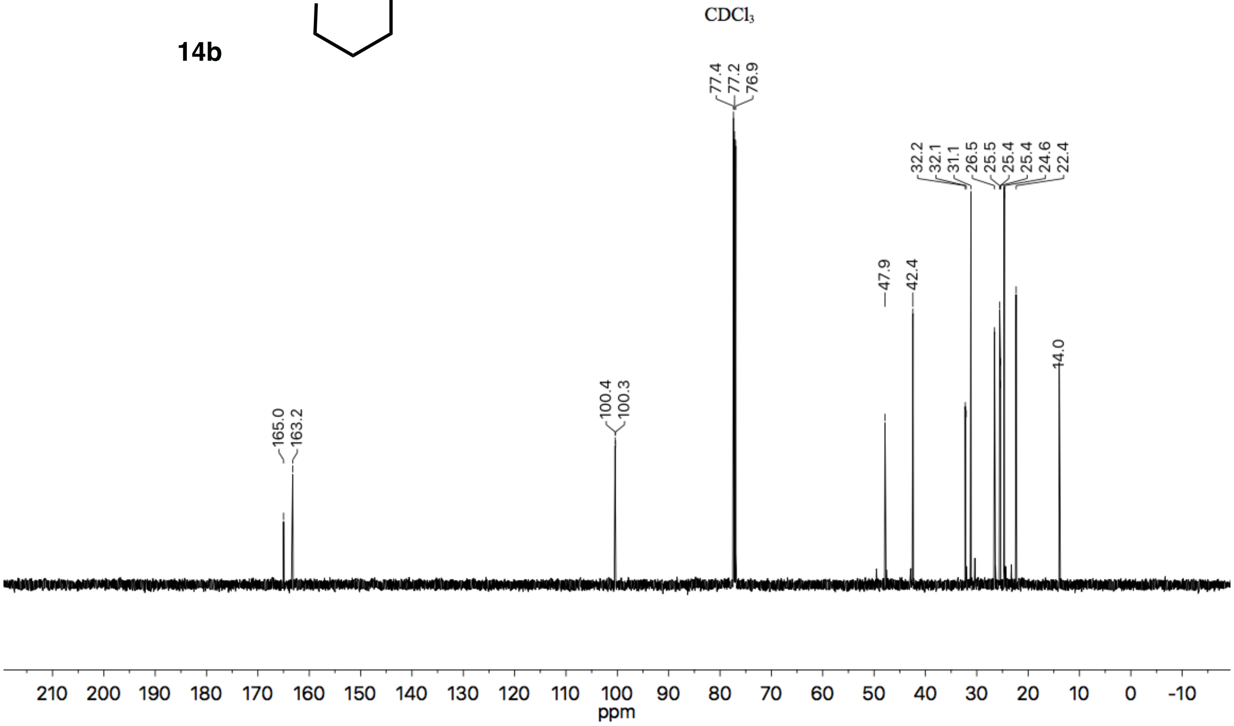
14b



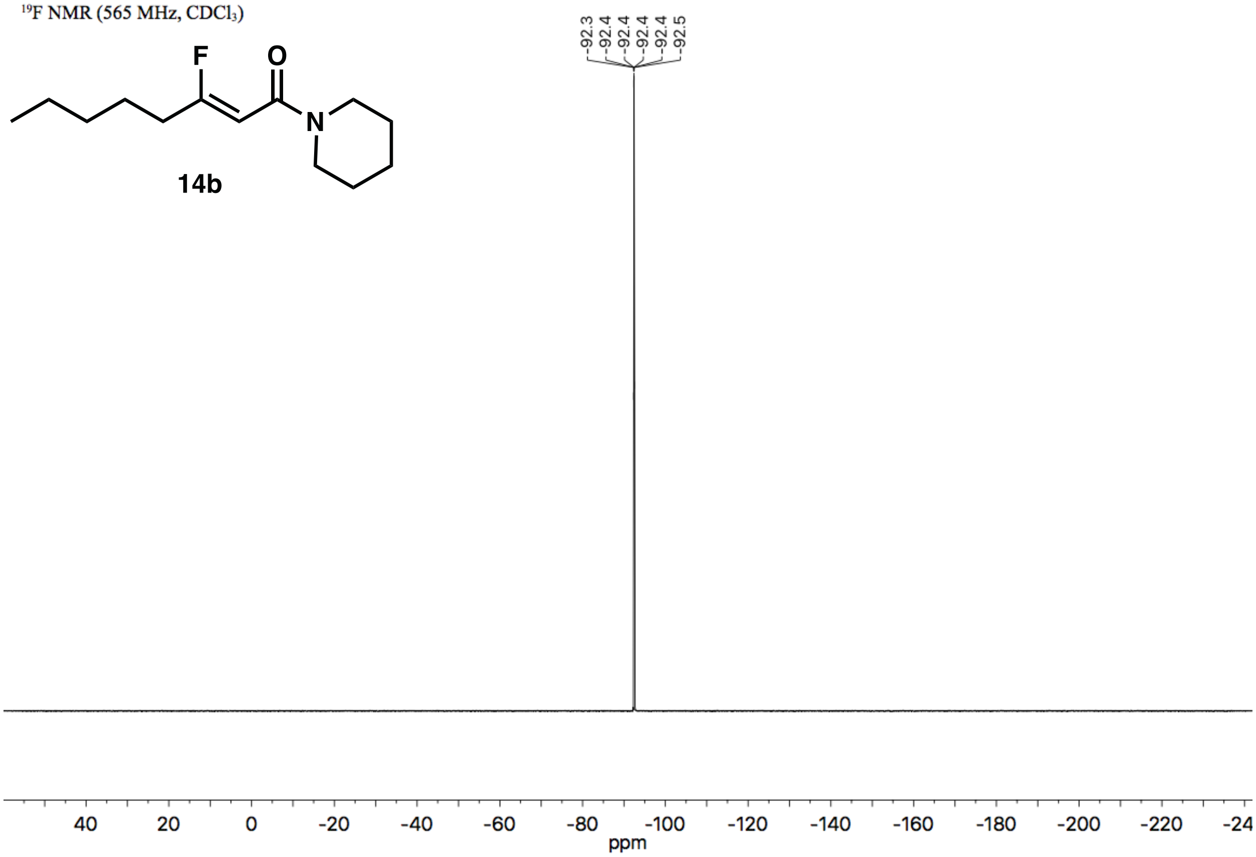
^{13}C NMR (151 MHz, CDCl$_3$)



14b

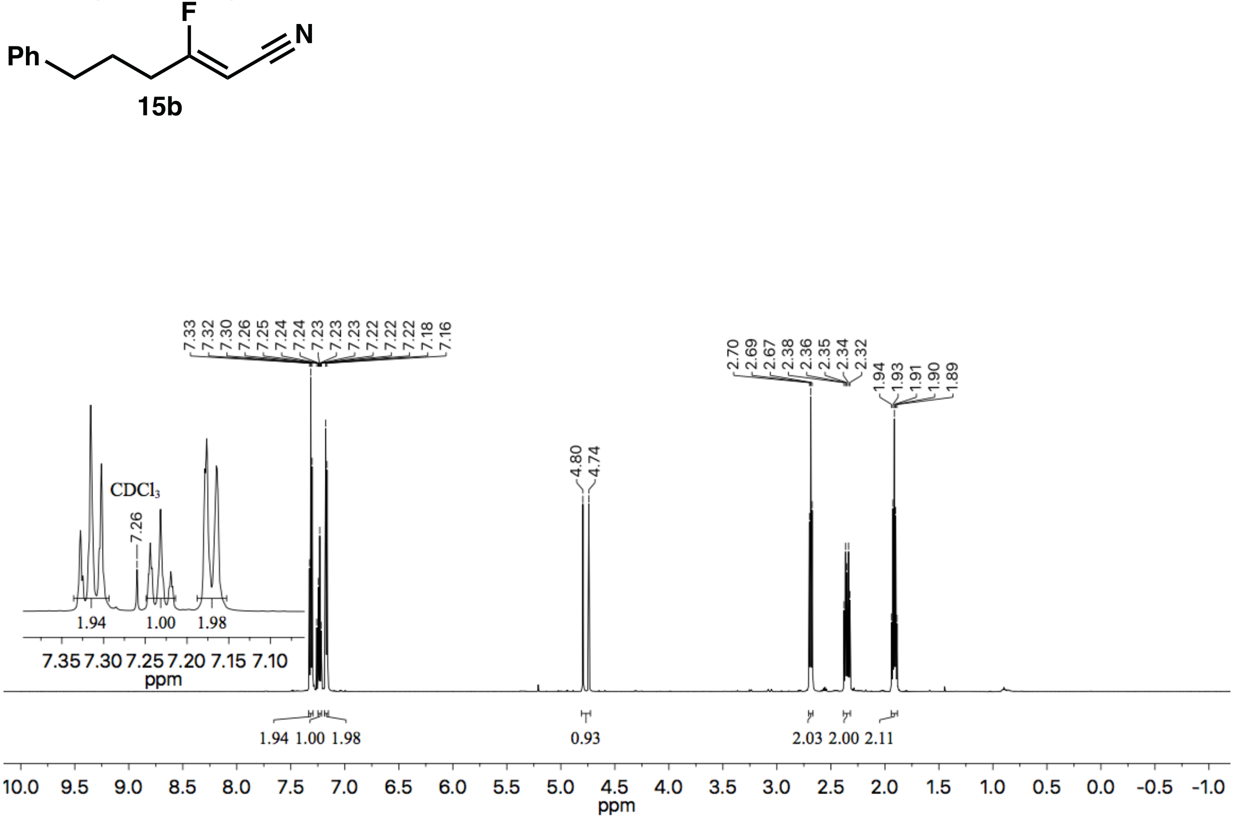


^{19}F NMR (565 MHz, $CDCl_3$)

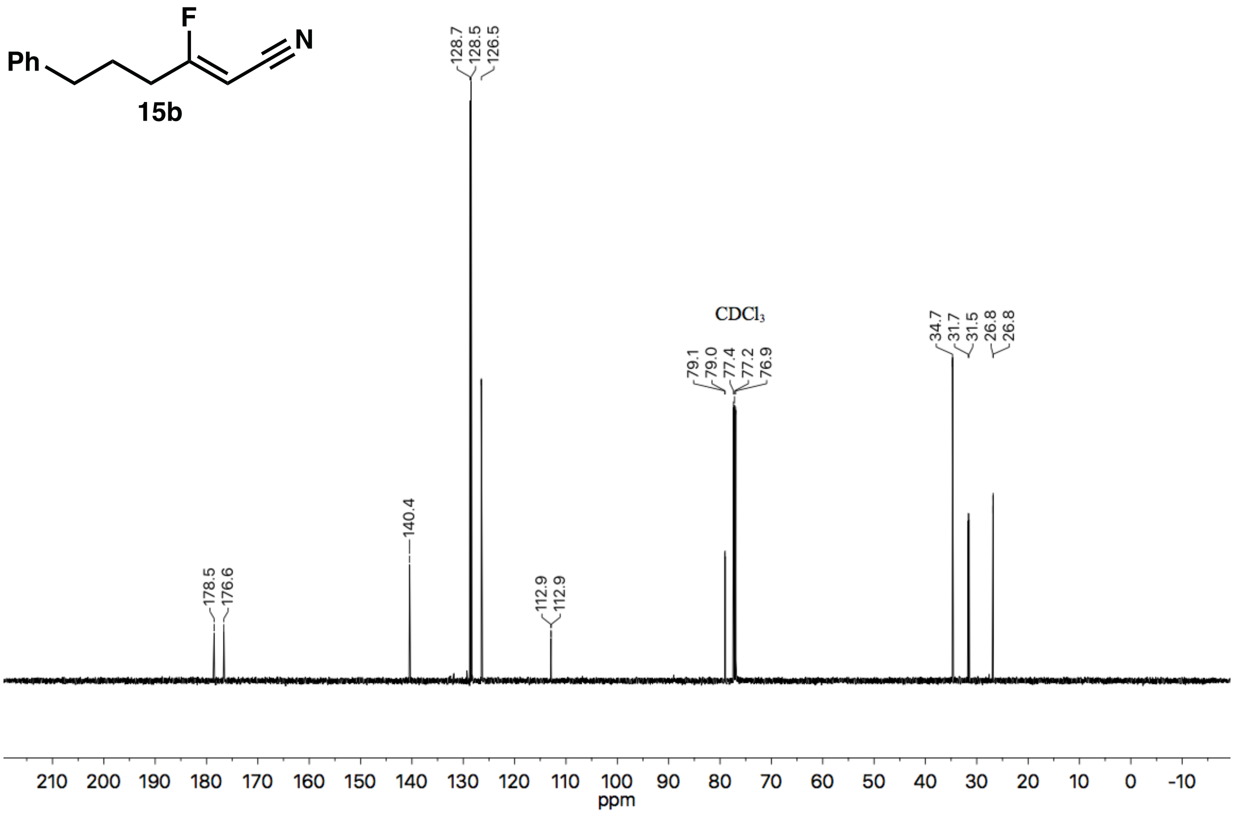


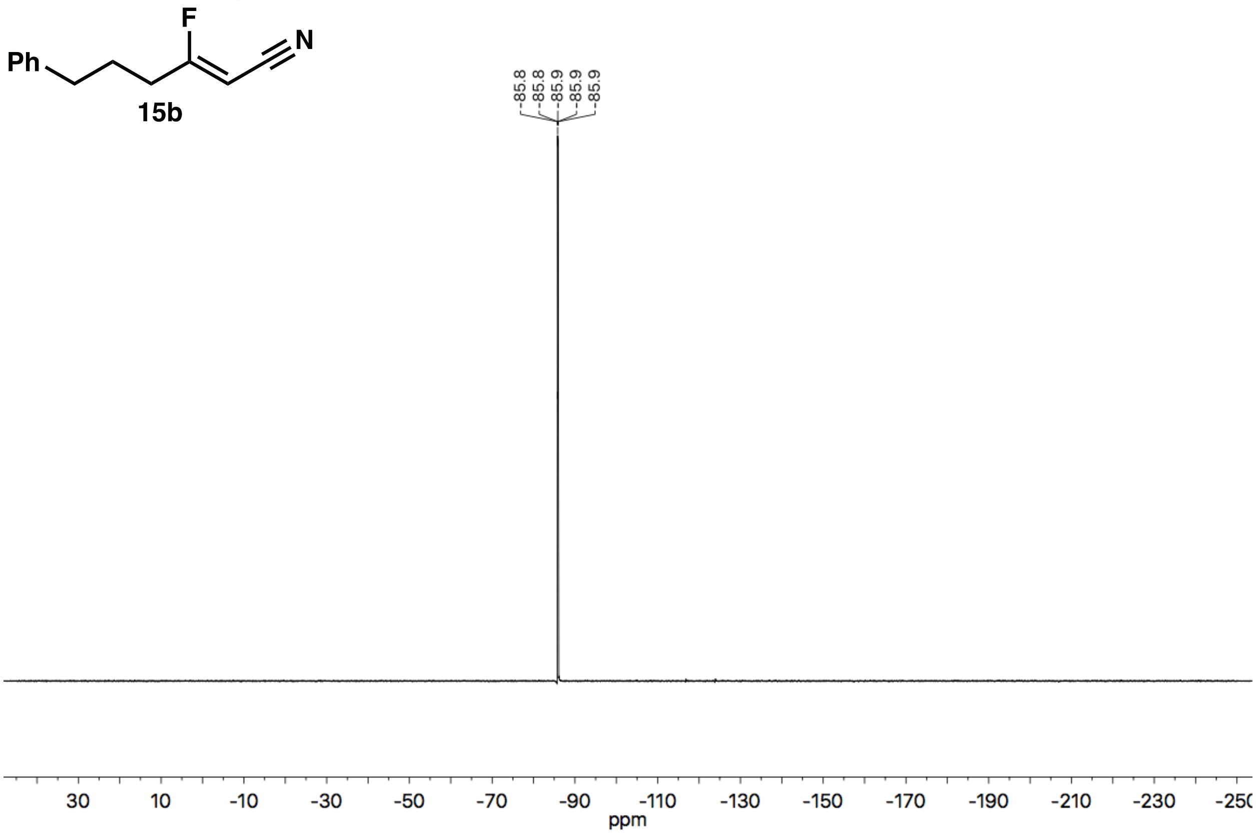
14b

^{1}H NMR (600 MHz, CDCl$_3$)



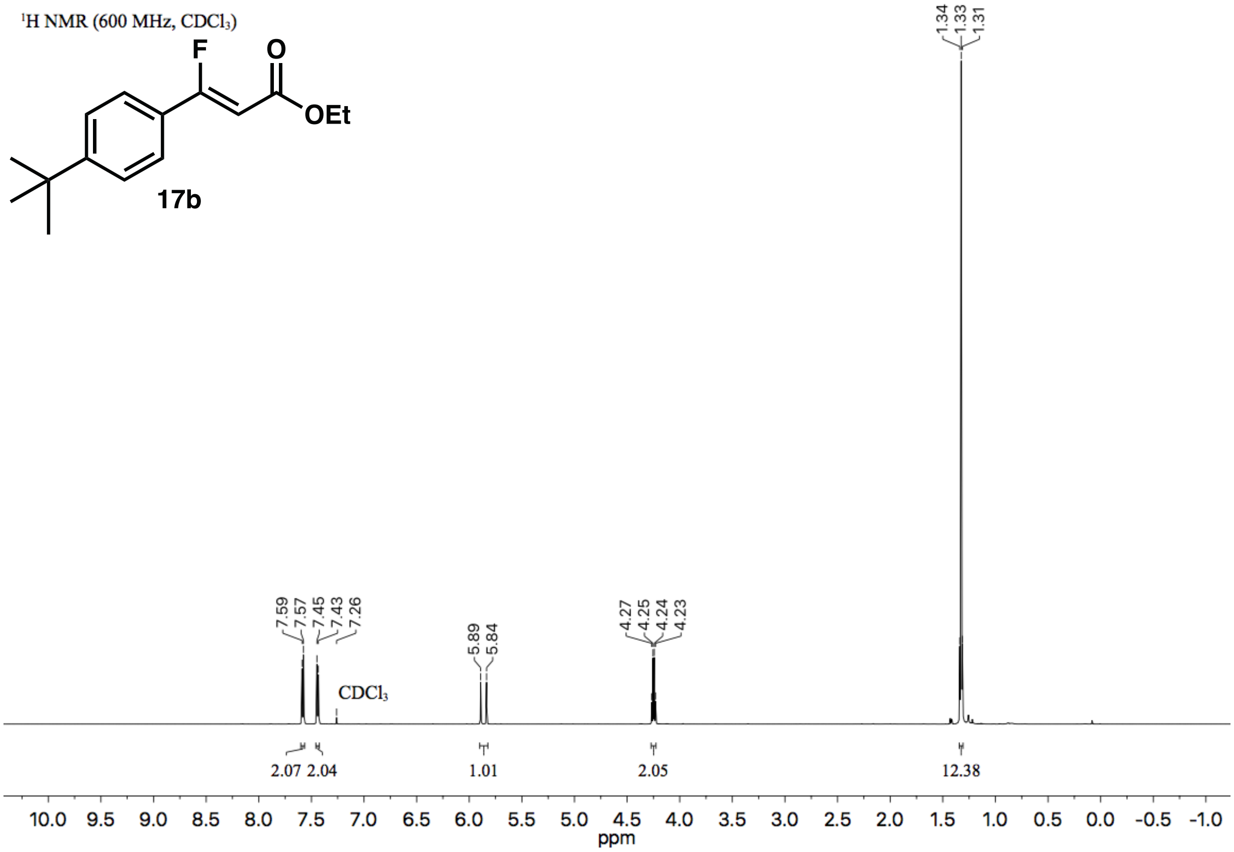
^{13}C NMR (151 MHz, CDCl$_3$)

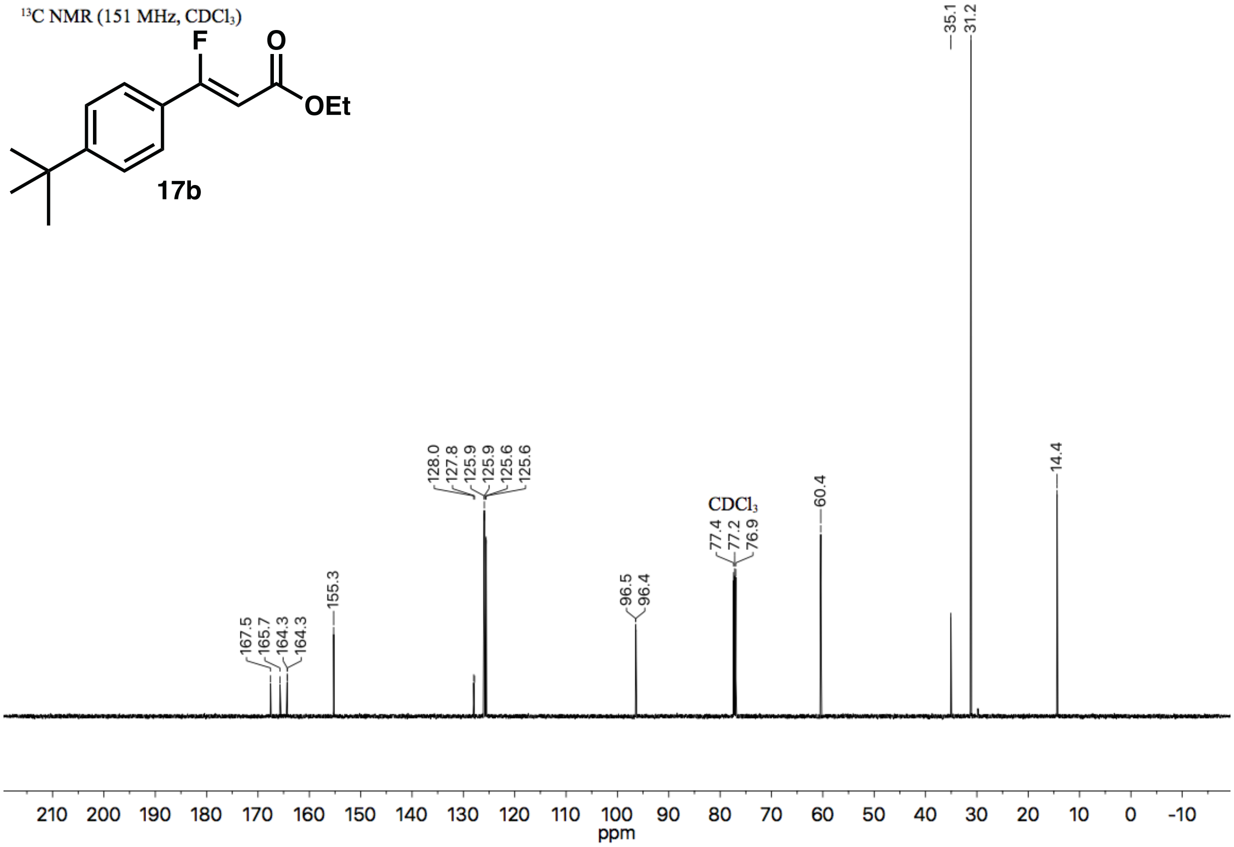




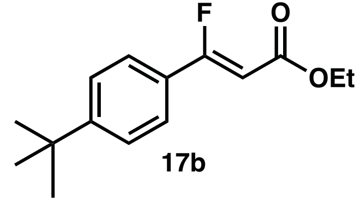
^{19}F NMR (565 MHz, $CDCl_3$)

15b

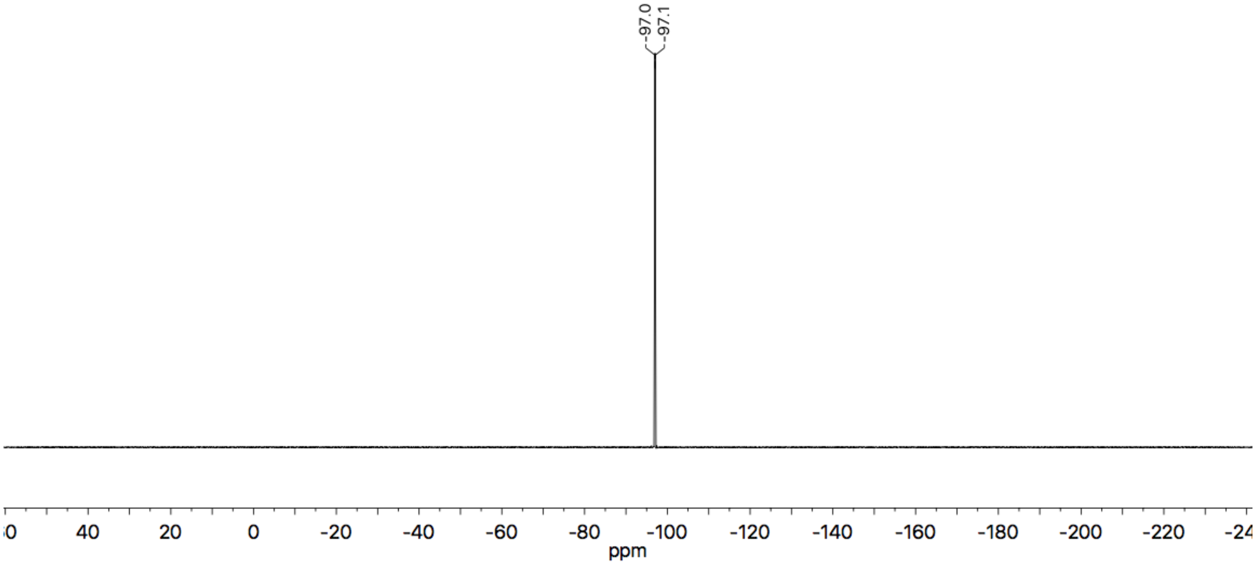

1H NMR (600 MHz, CDCl3)
F
O
OEt
17b
1.34
1.33
1.31
7.59
7.57
7.45
7.43
7.26
CDCl3
5.89
5.84
4.27
4.25
4.24
4.23
2.07
2.04
1.01
2.05
12.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


13C NMR (151 MHz, CDCl3)
F
O
OEt
17b
35.1
31.2
128.0
127.8
125.9
125.9
125.6
125.6
CDCl3
77.4
77.2
76.9
60.4
14.4
96.5
96.4
155.3
167.5
165.7
164.3
164.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

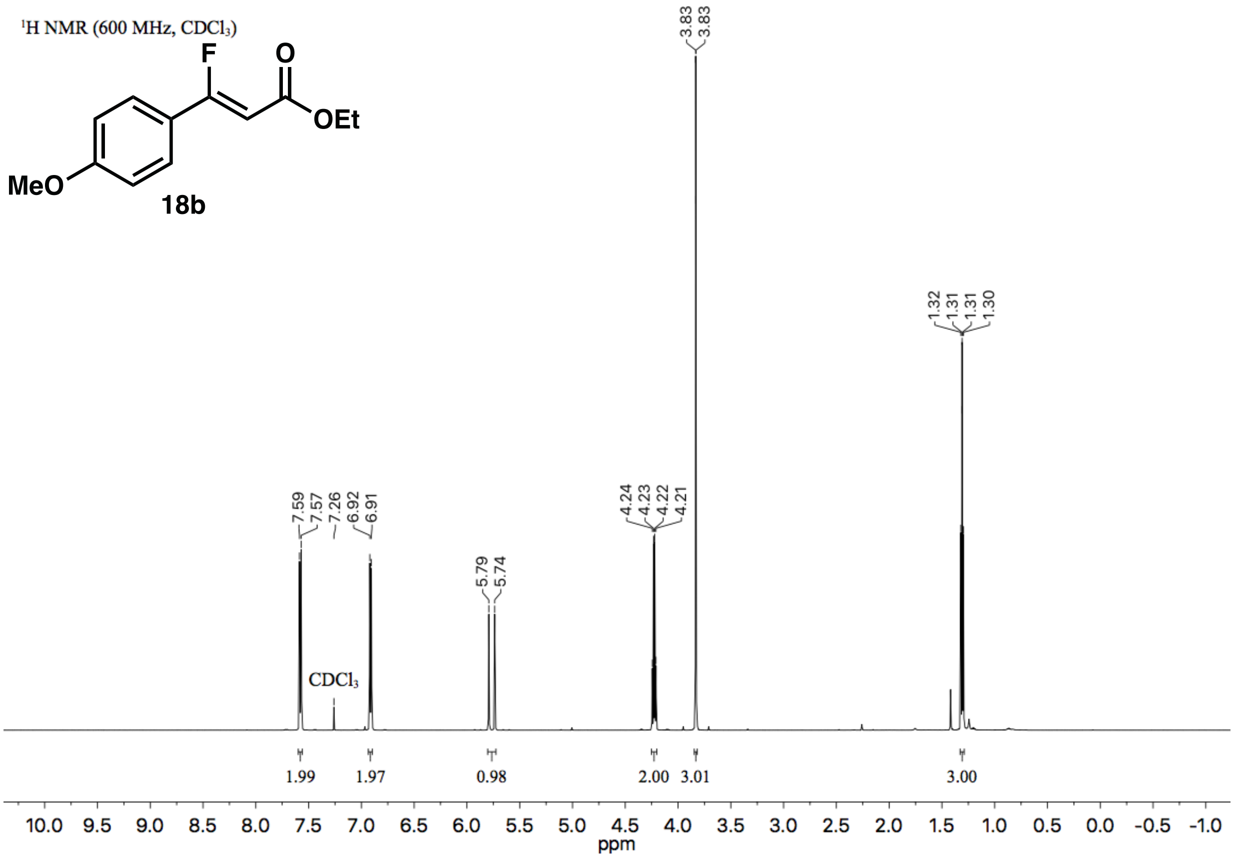
^{19}F NMR (565 MHz, CDCl$_3$)



17b

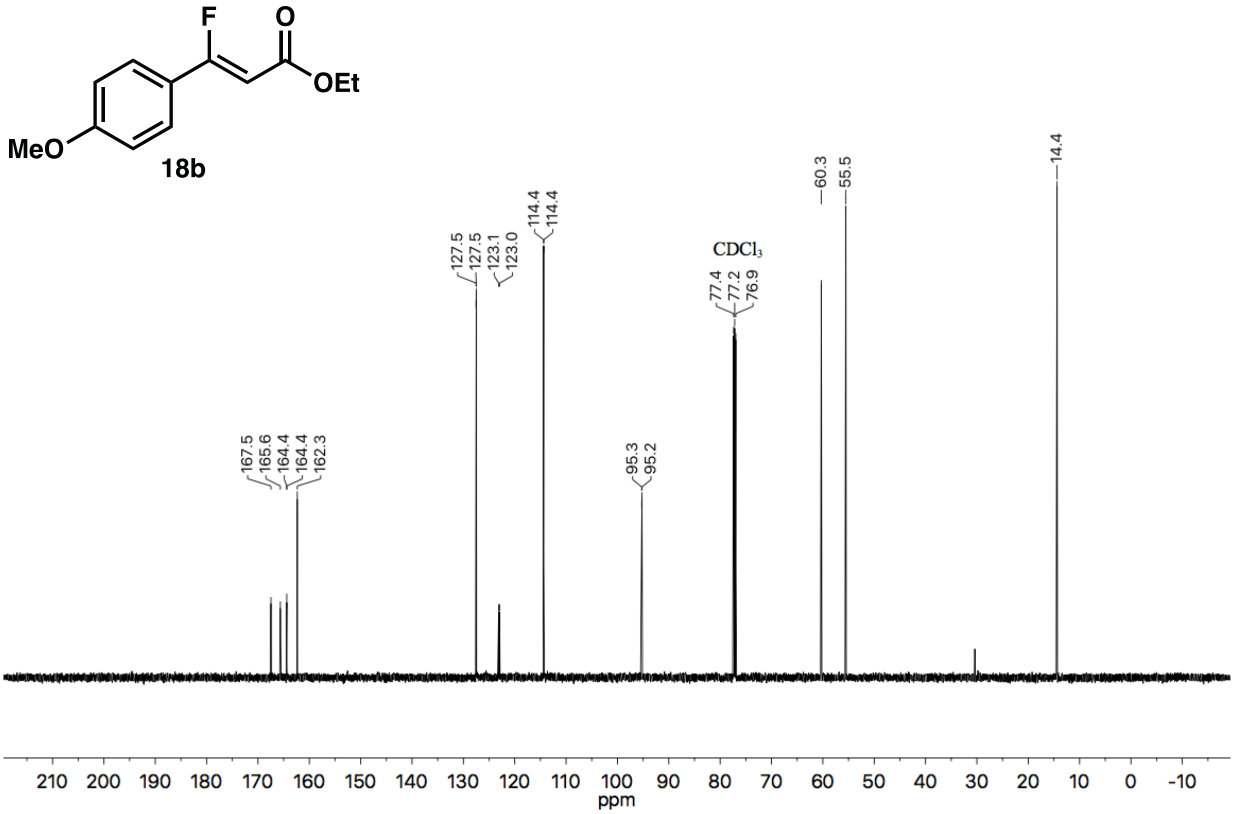


^{1}H NMR (600 MHz, CDCl$_3$)



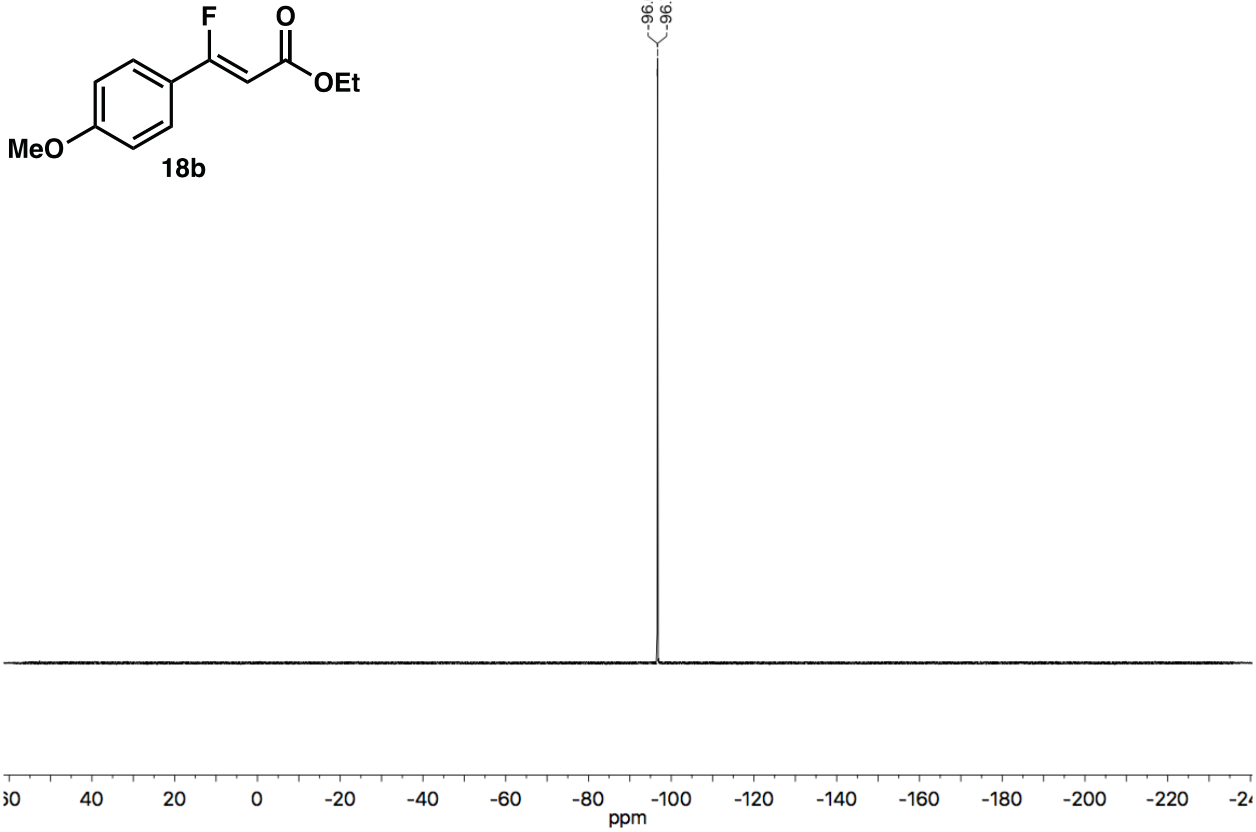
18b

^{13}C NMR (151 MHz, CDCl$_3$)



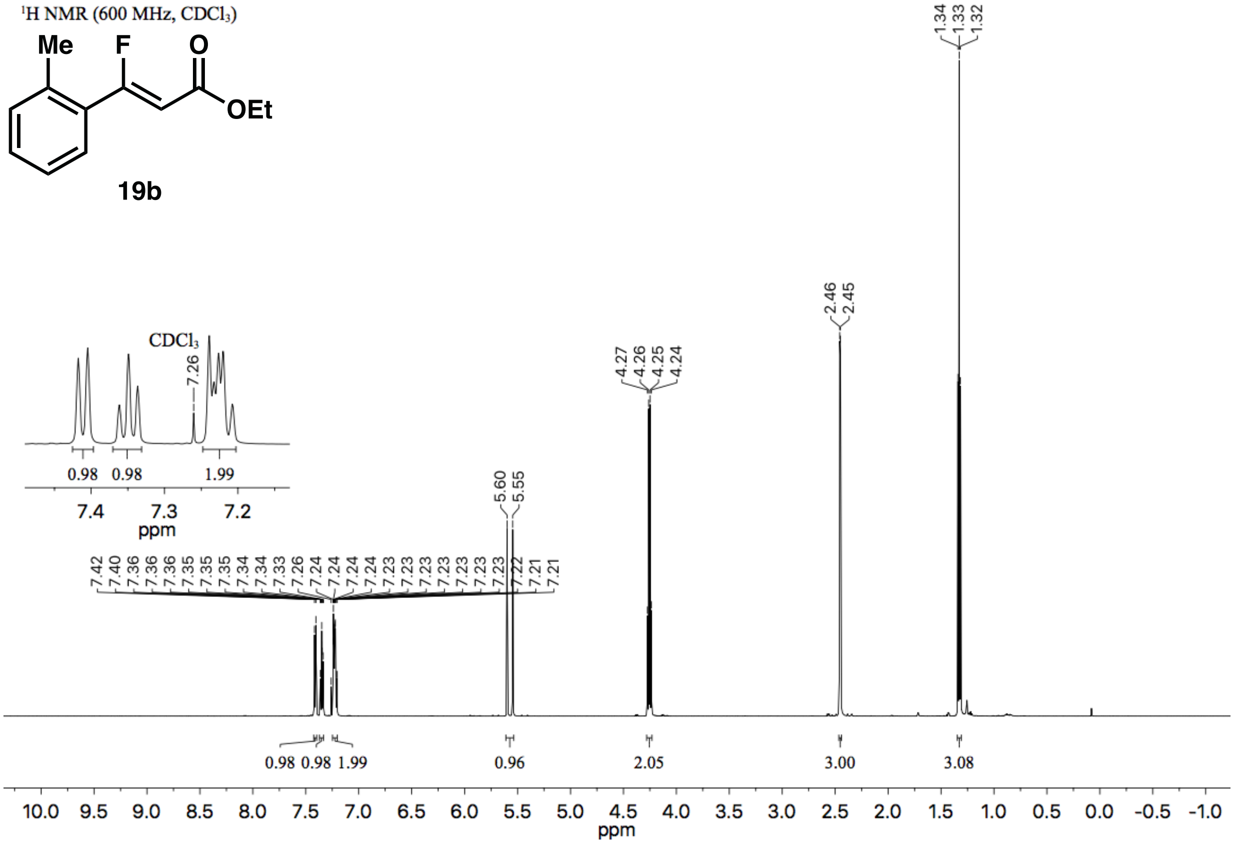
18b

^{19}F NMR (565 MHz, CDCl$_3$)



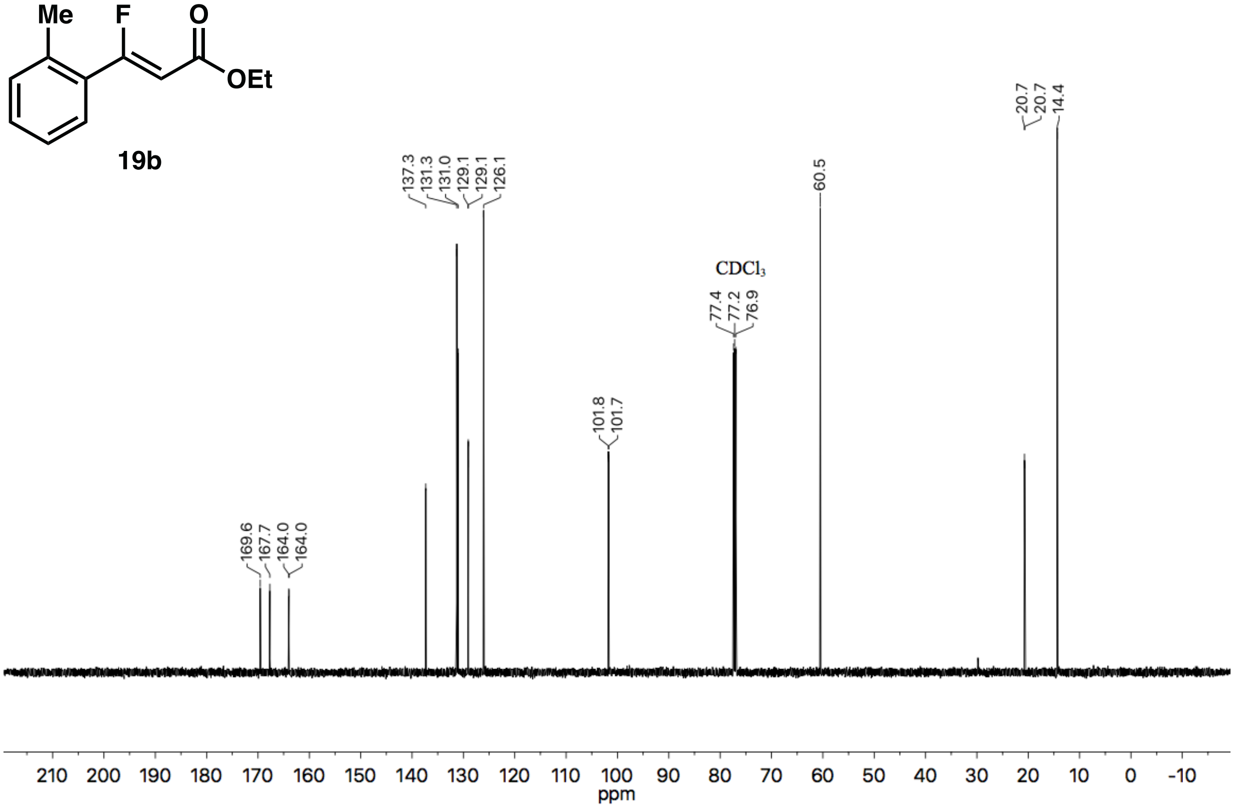
18b

^{1}H NMR (600 MHz, CDCl$_3$)



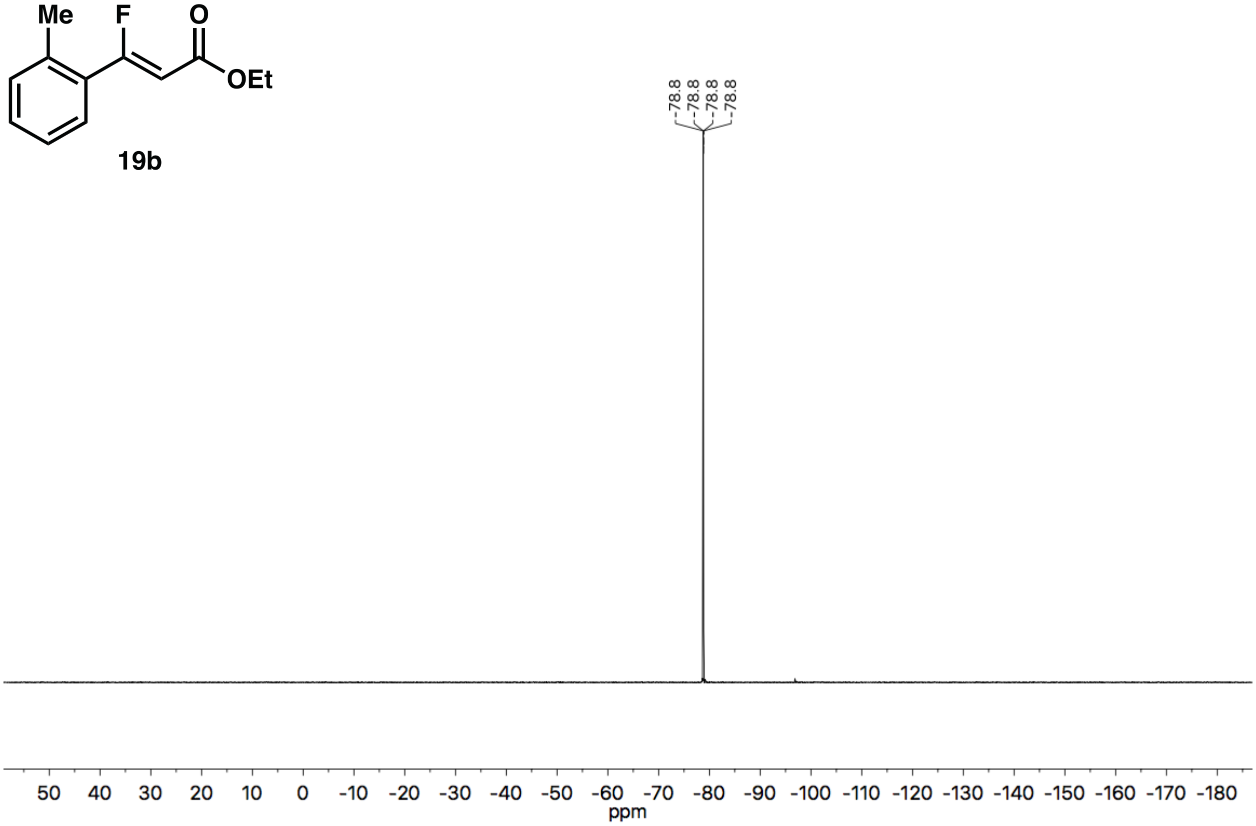
19b

^{13}C NMR (151 MHz, CDCl$_3$)



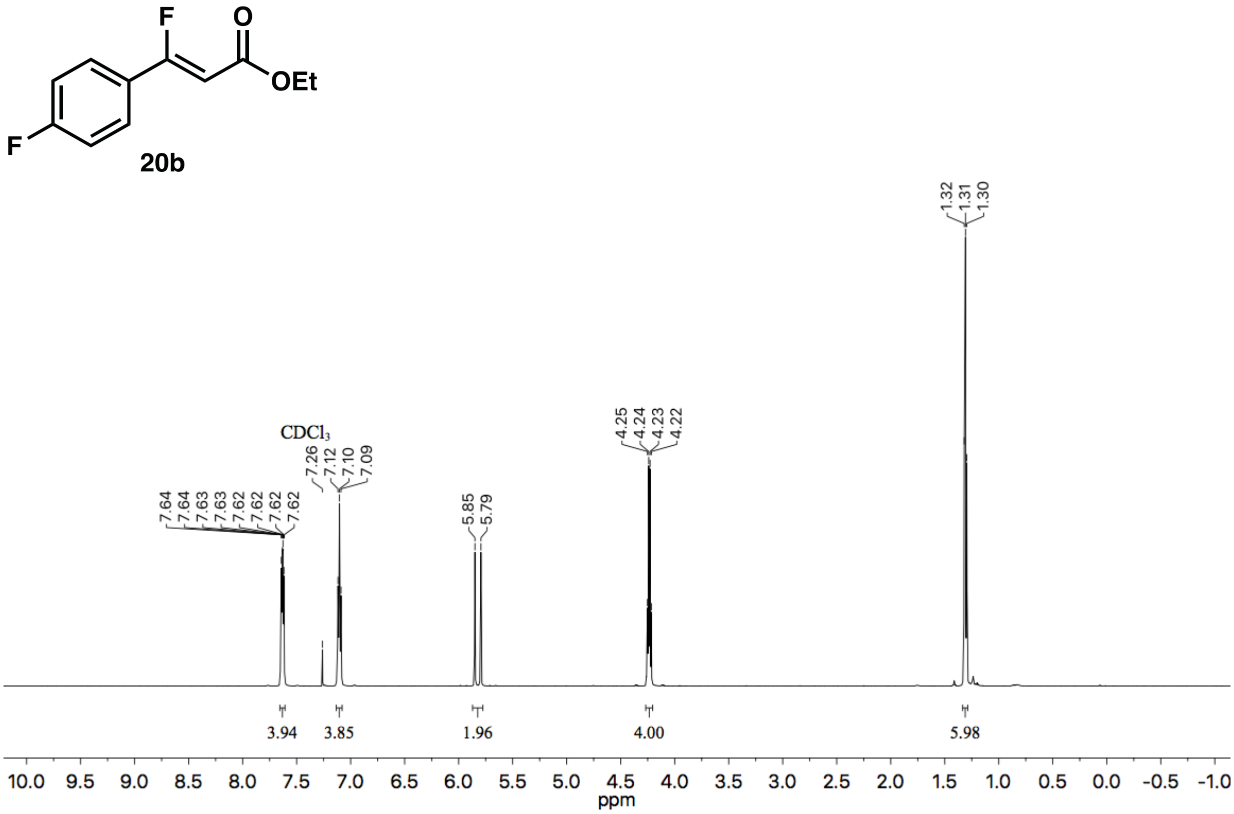
19b

^{19}F NMR (565 MHz, $CDCl_3$)



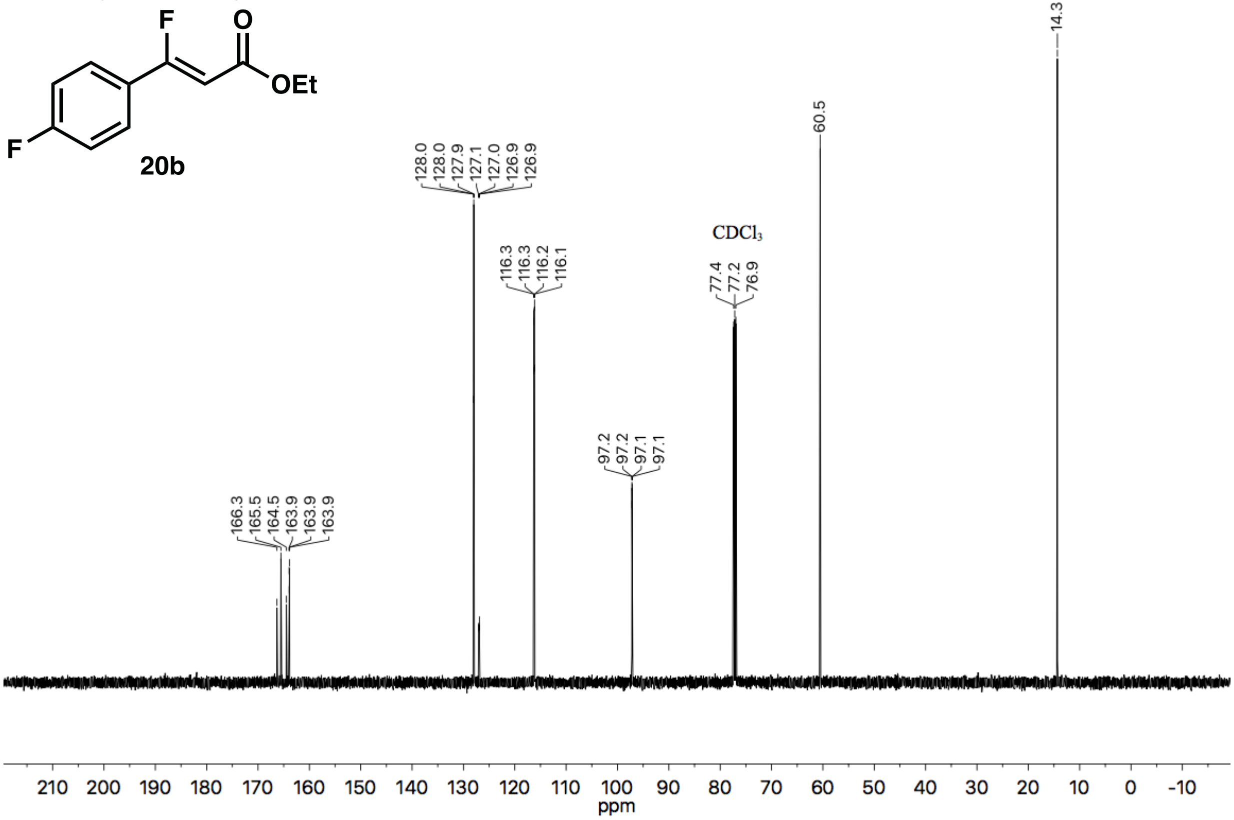
19b

^{1}H NMR (600 MHz, CDCl$_3$)



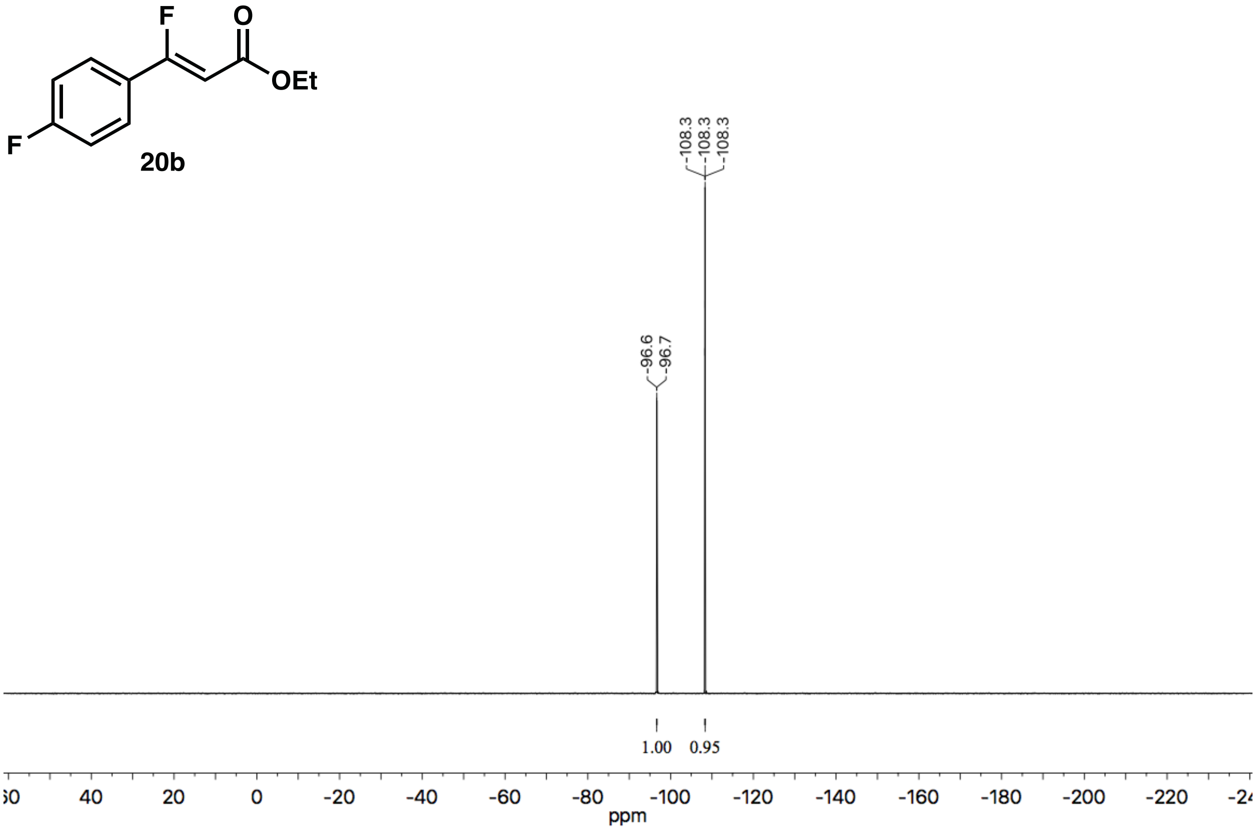
20b

^{13}C NMR (151 MHz, CDCl$_3$)

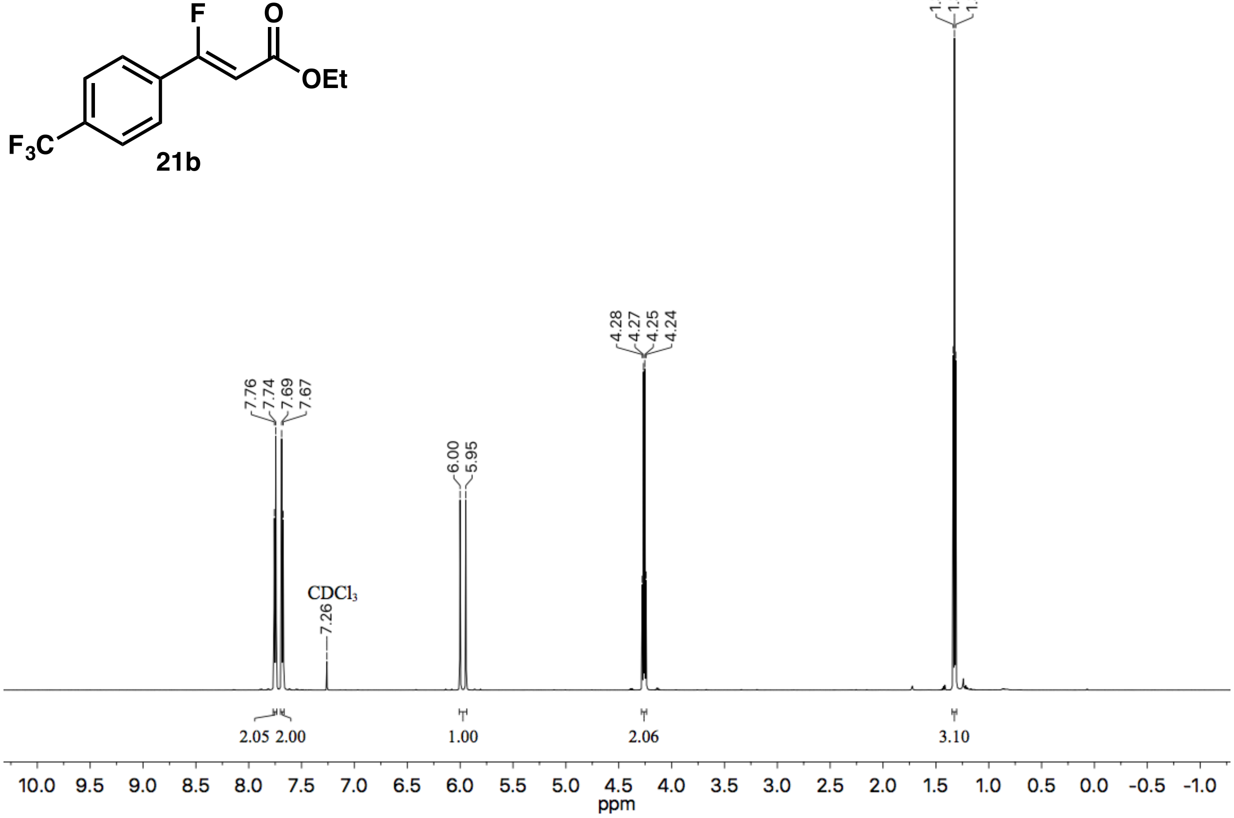


20b

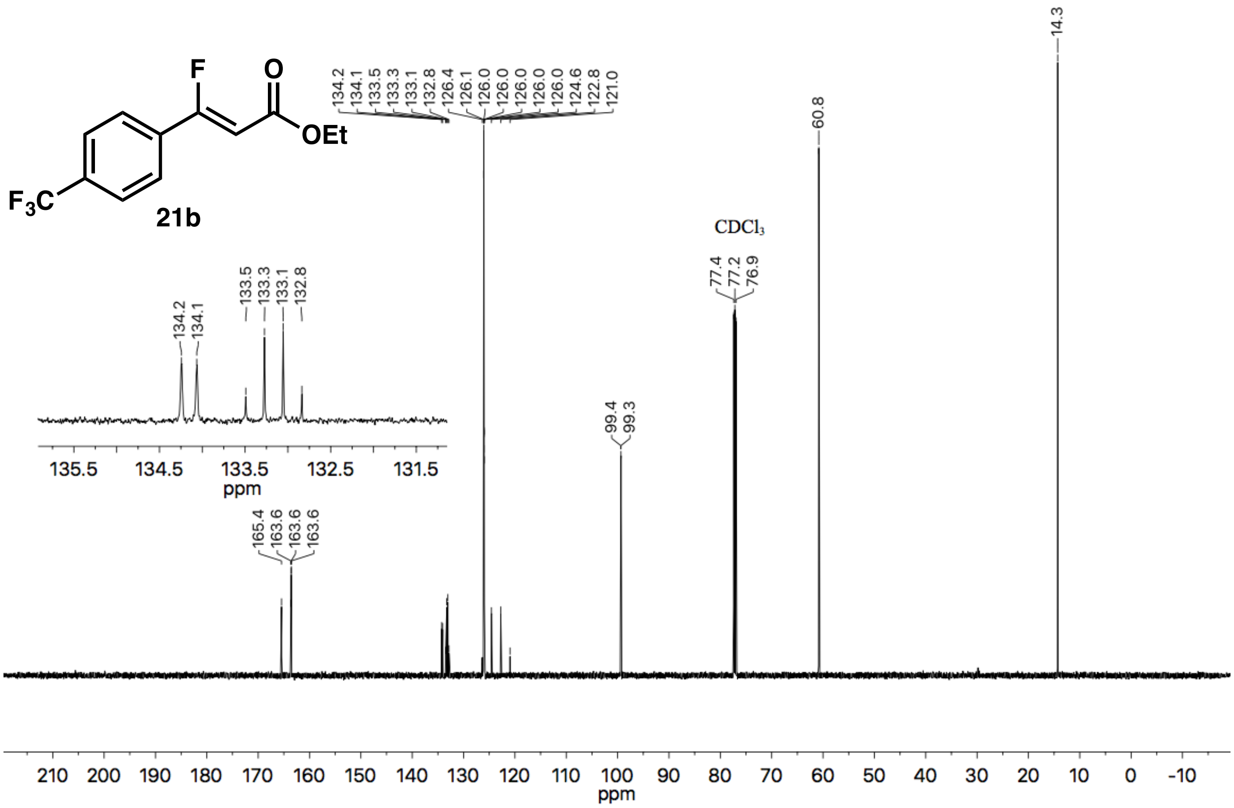
^{19}F NMR (565 MHz, CDCl$_3$)



^{1}H NMR (600 MHz, CDCl$_3$)

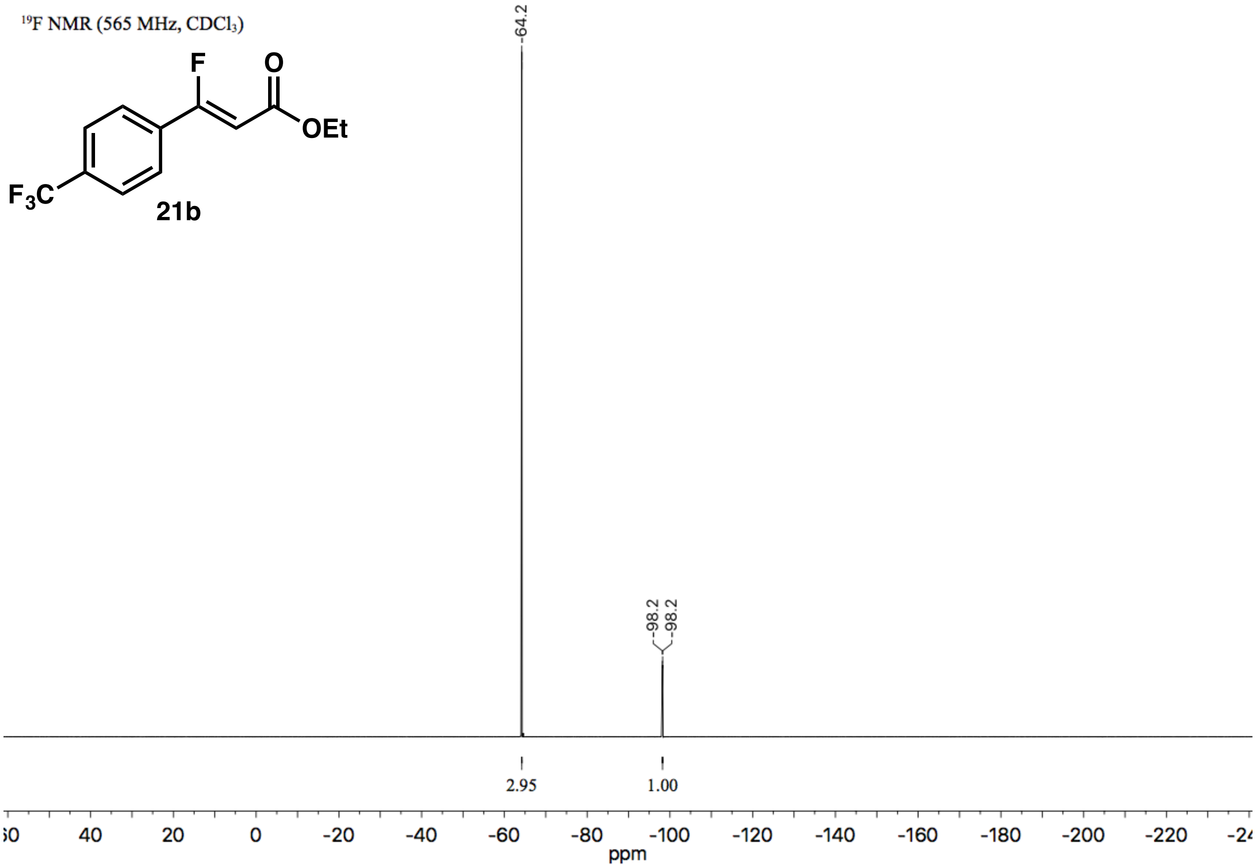


^{13}C NMR (151 MHz, CDCl$_3$)

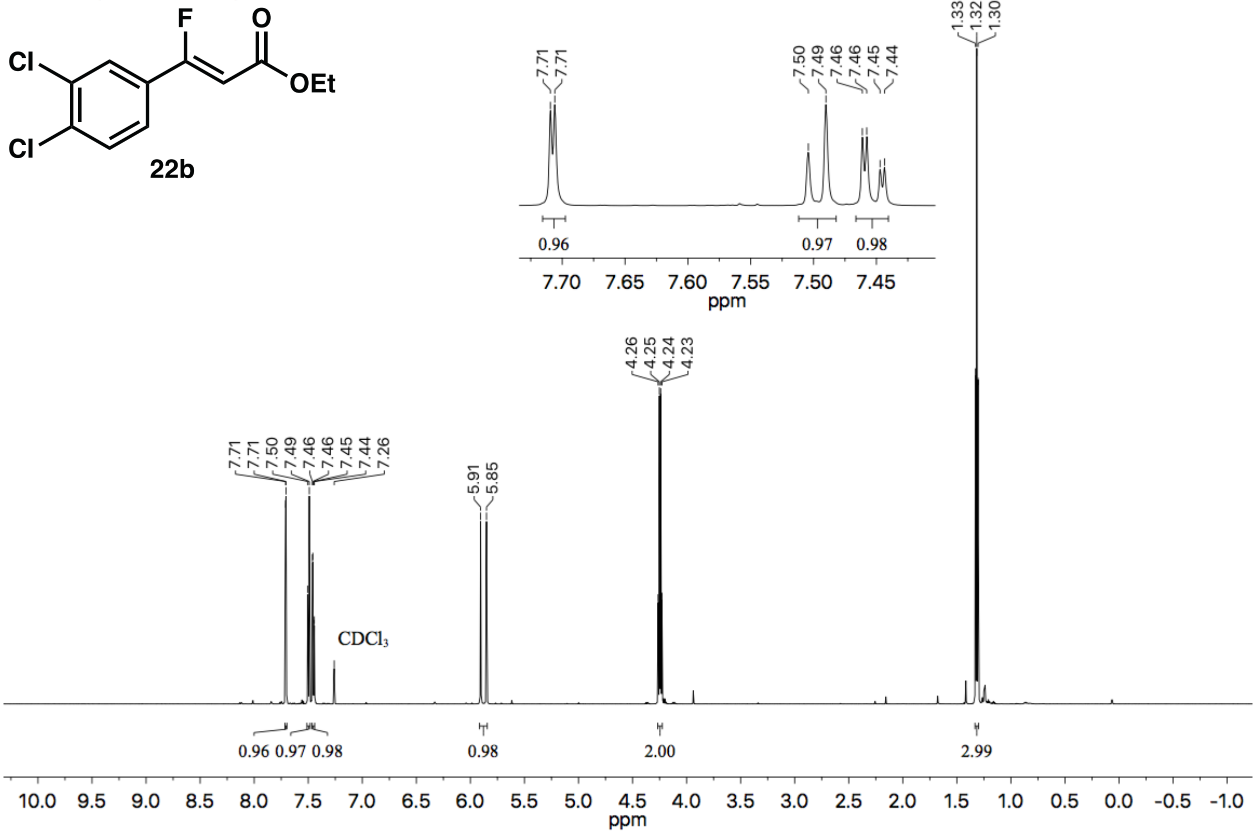


^{19}F NMR (565 MHz, CDCl$_3$)

21b

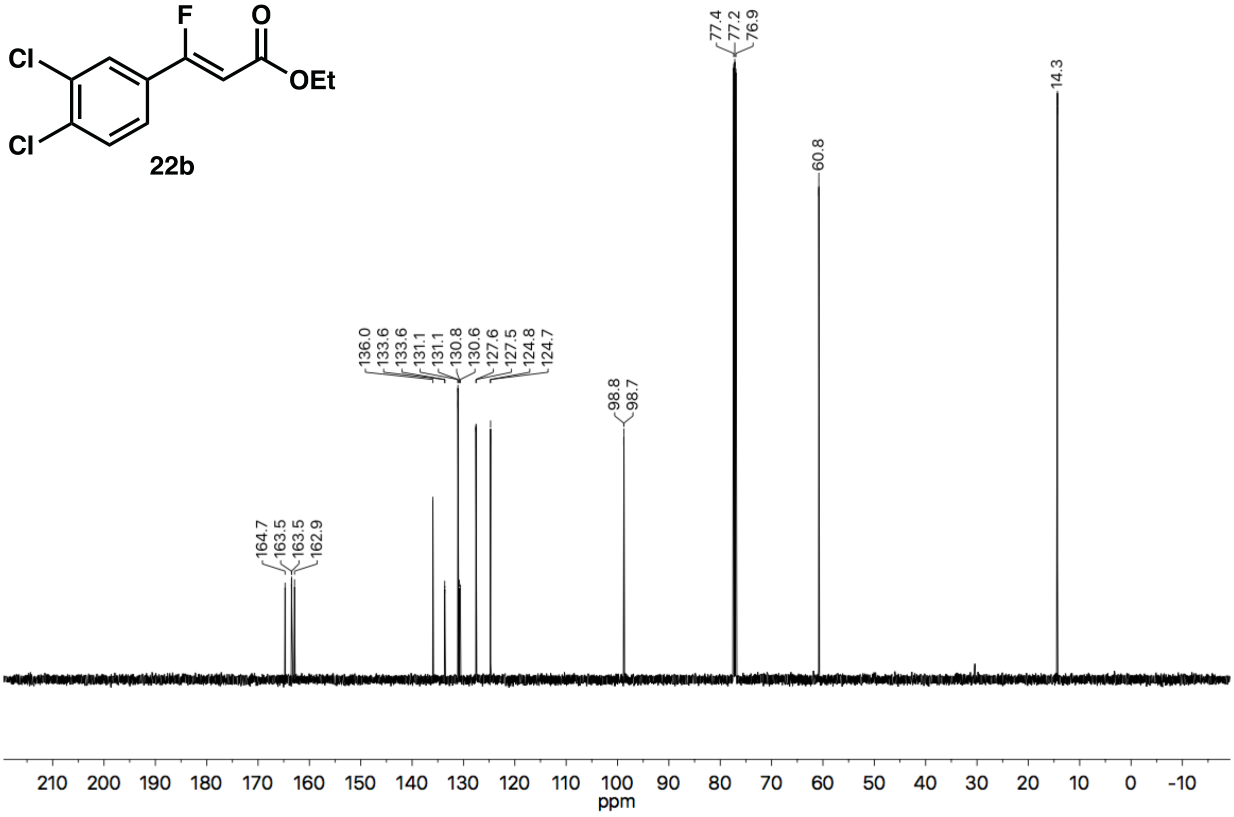


^{1}H NMR (600 MHz, CDCl$_3$)



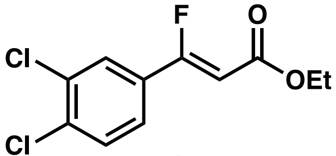
22b

^{13}C NMR (151 MHz, CDCl$_3$)

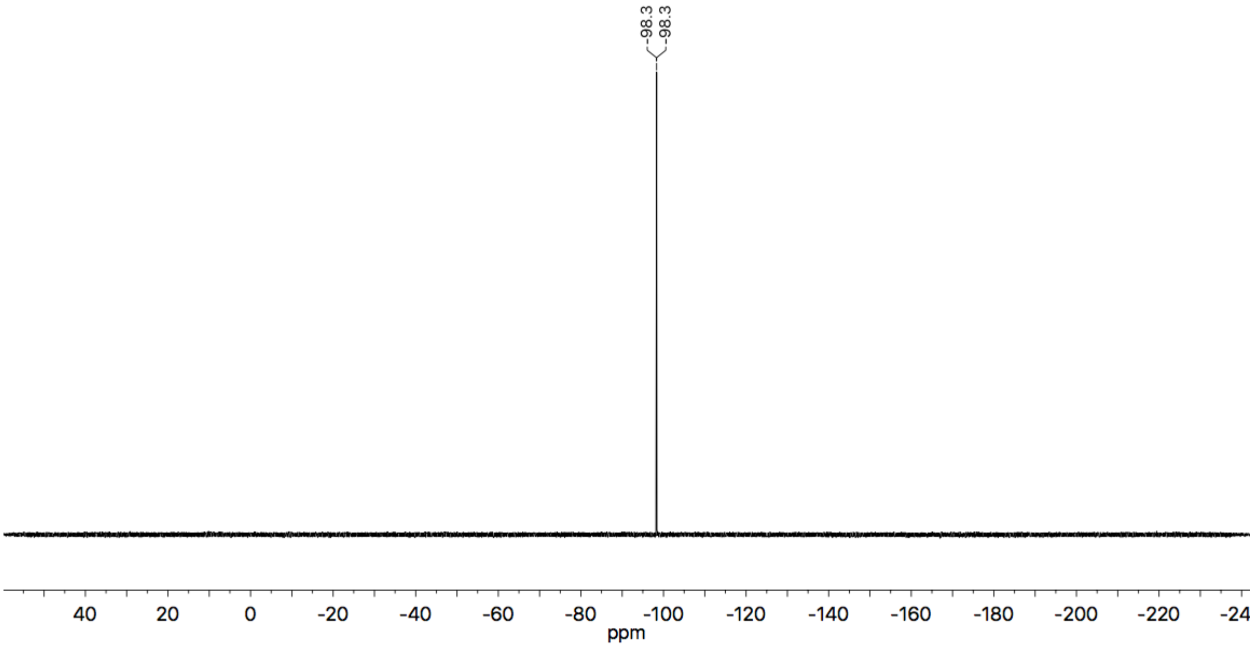


22b

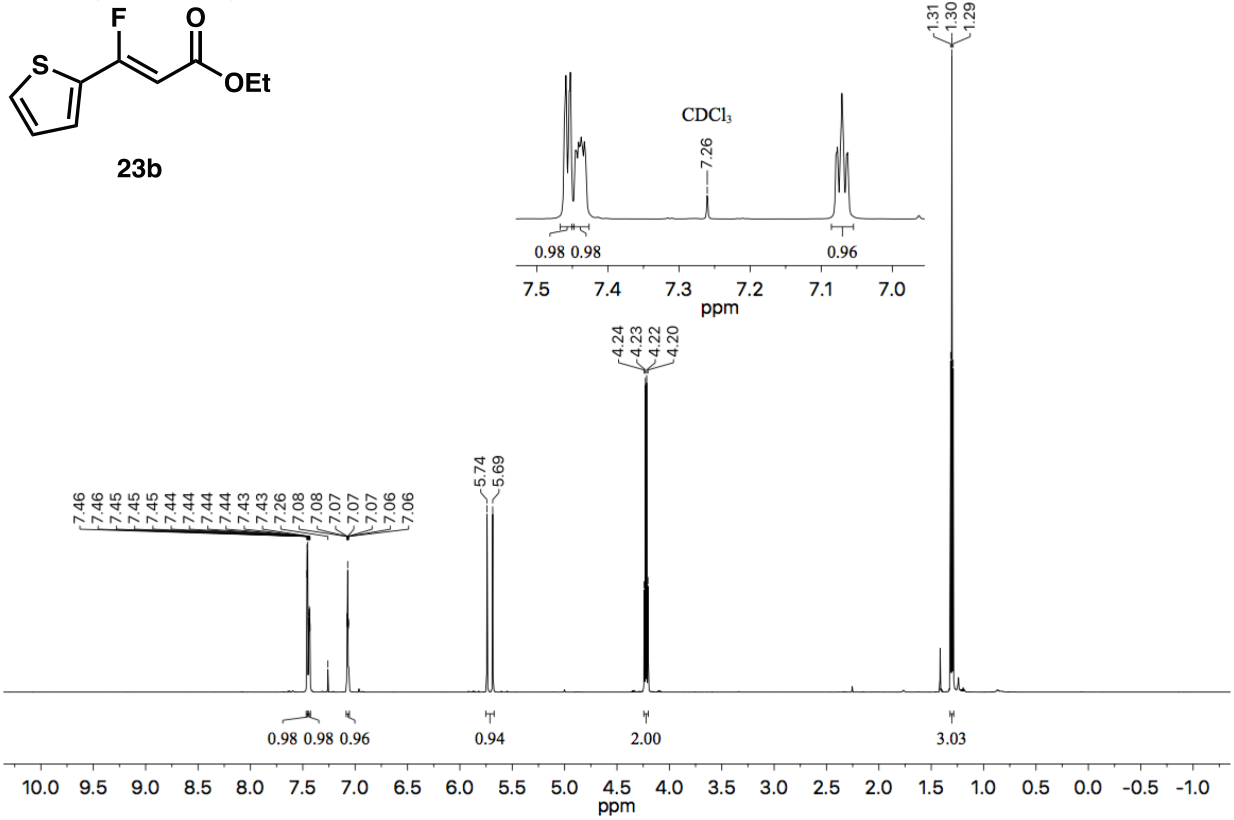
^{19}F NMR (565 MHz, $CDCl_3$)



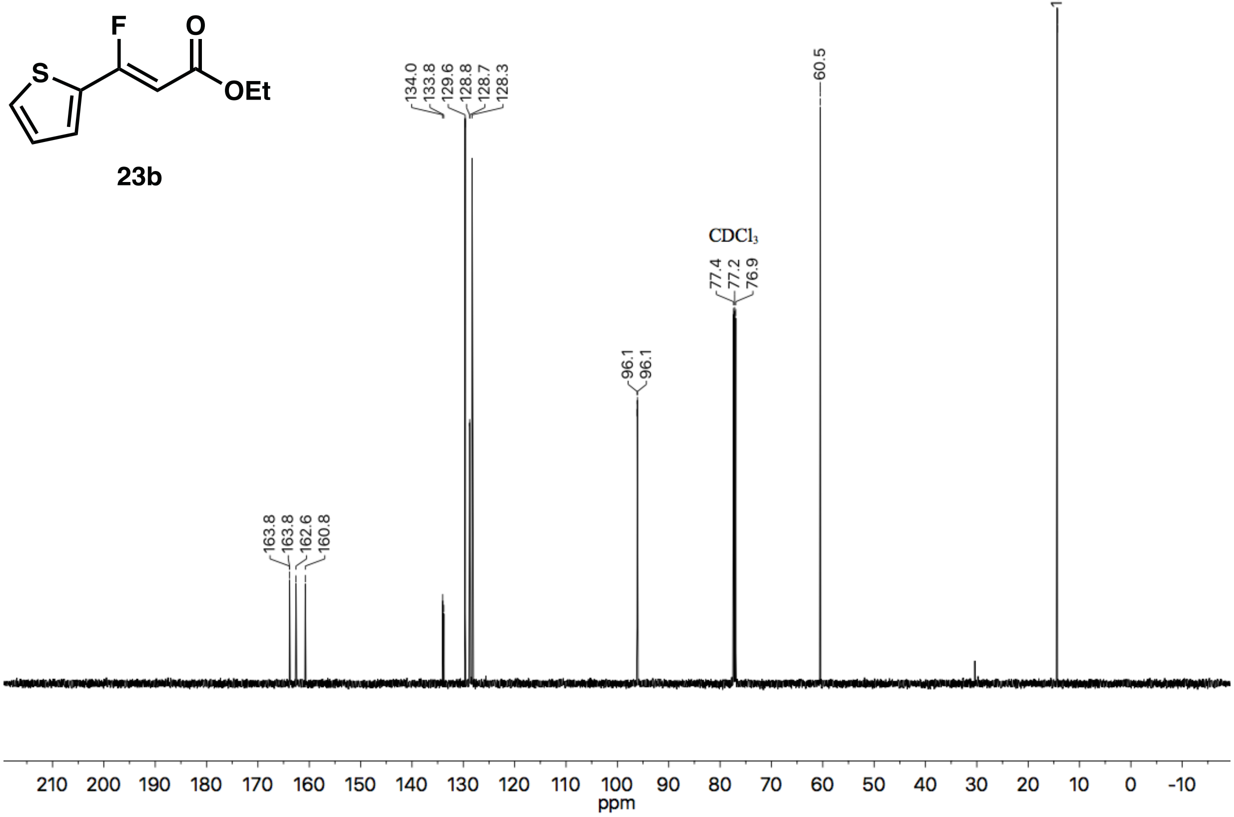
22b



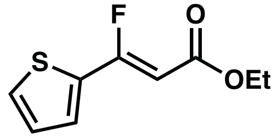
^{1}H NMR (600 MHz, CDCl$_3$)



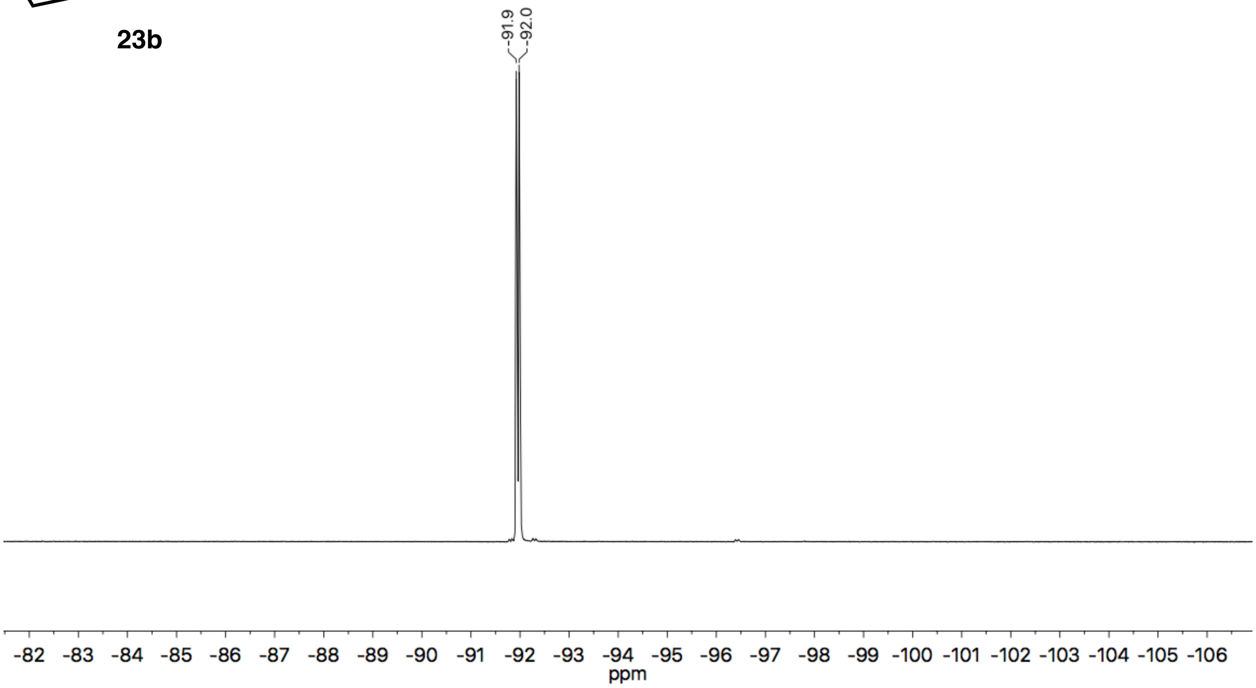
^{13}C NMR (151 MHz, CDCl$_3$)



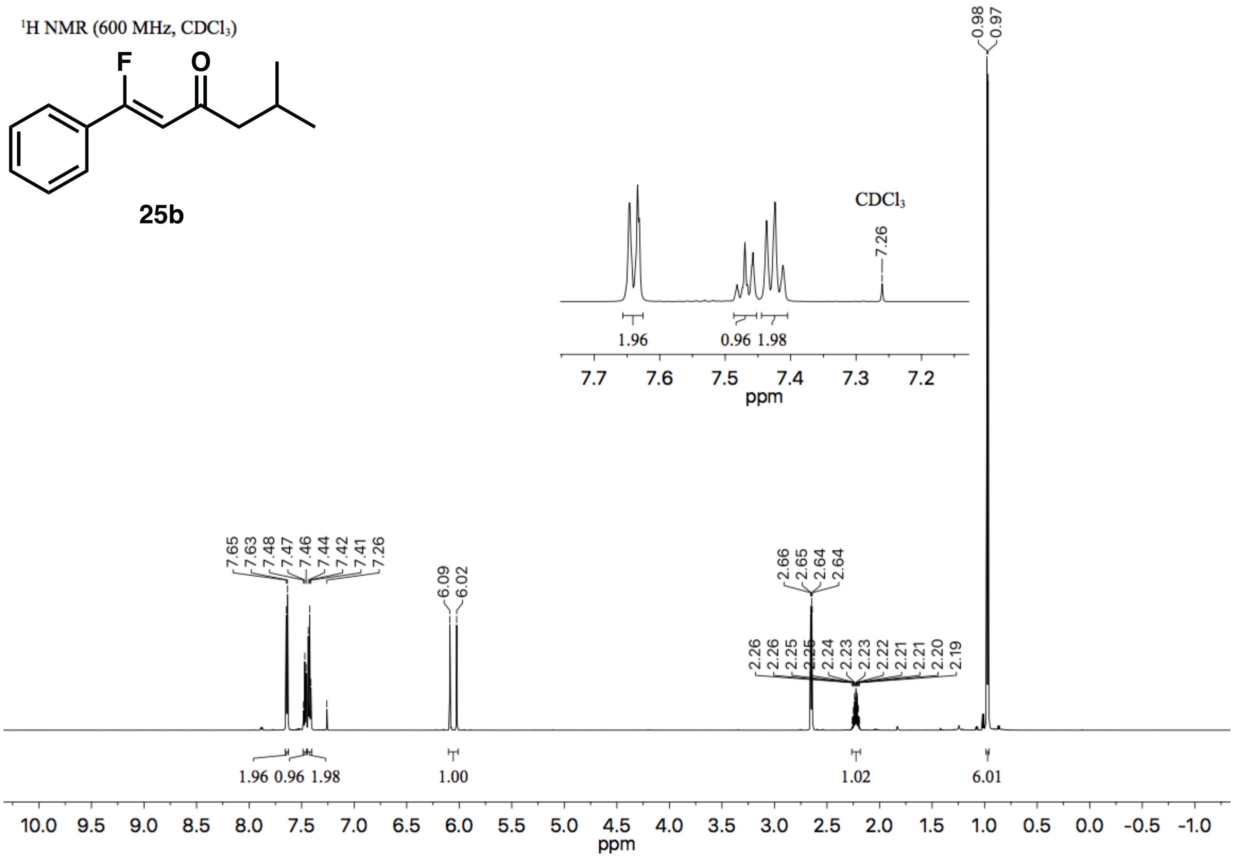
^{19}F NMR (565 MHz, CDCl$_3$)



23b

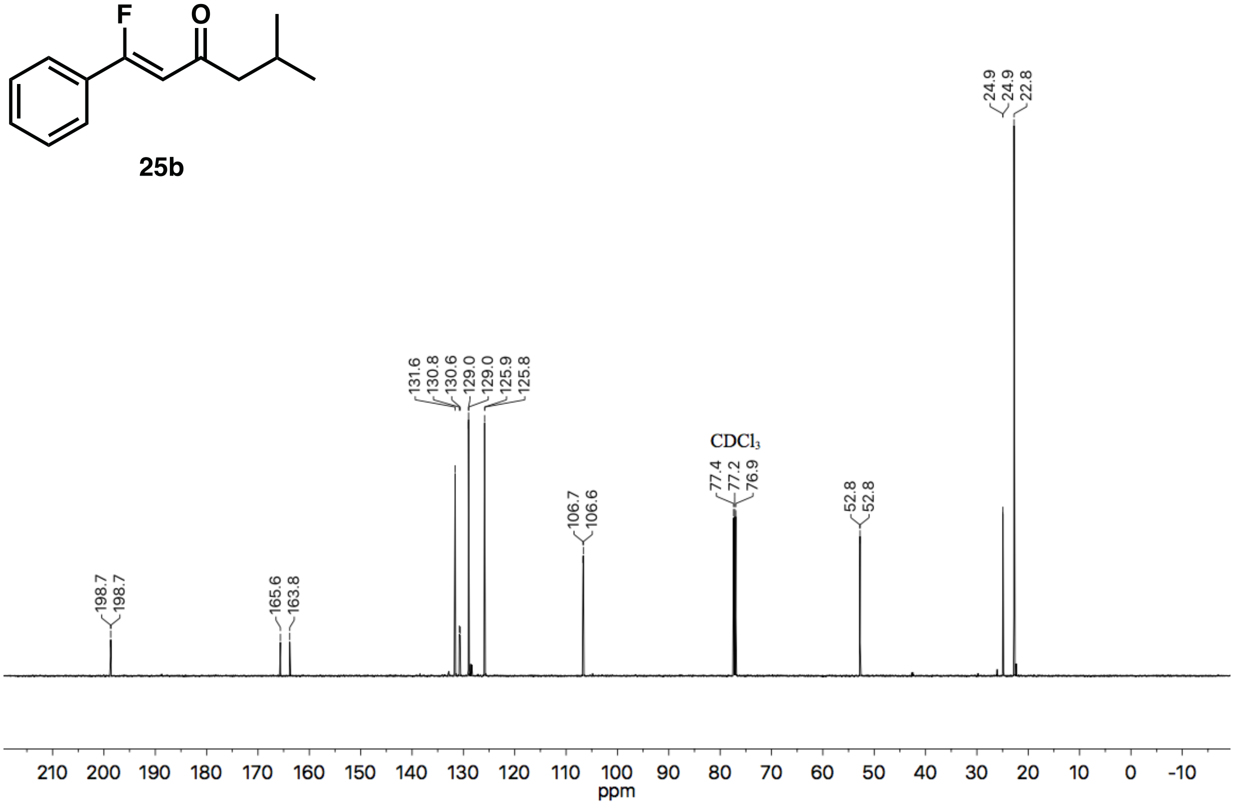


^{1}H NMR (600 MHz, CDCl$_3$)



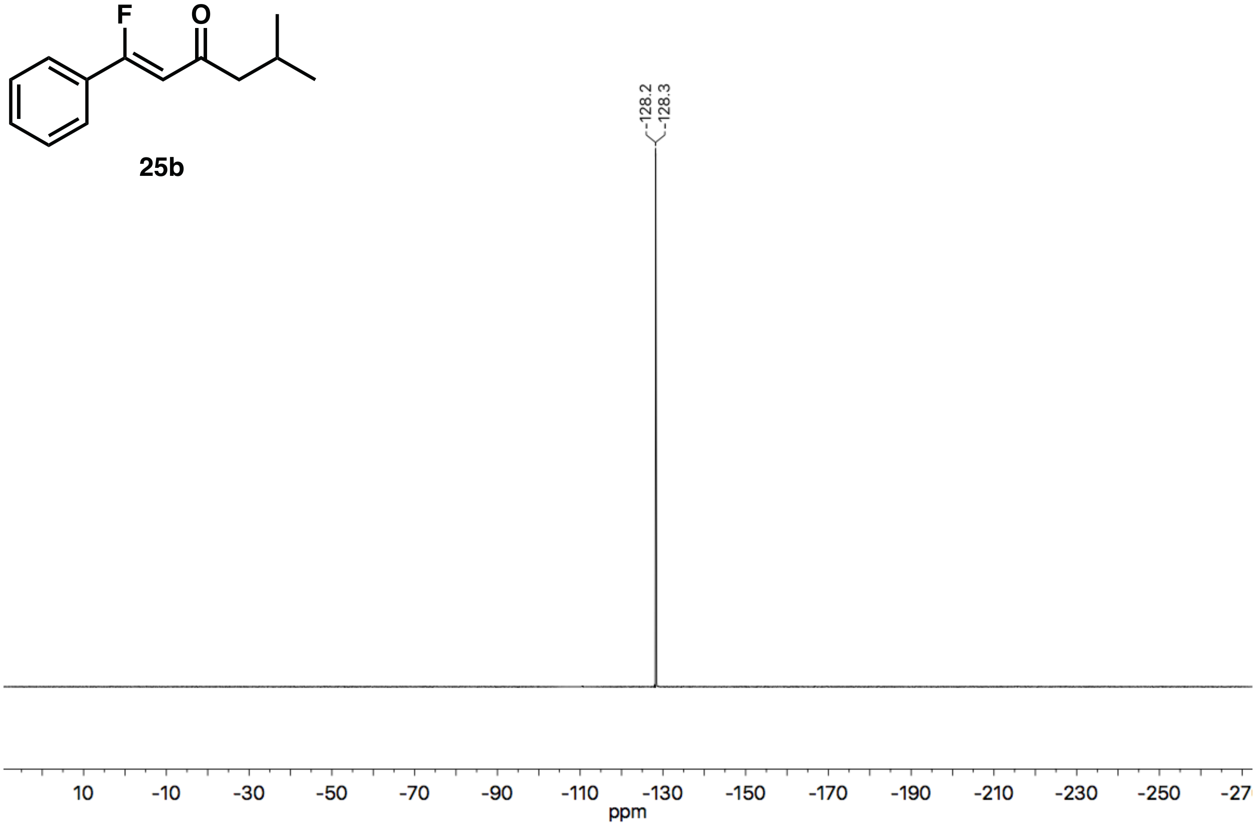
25b

^{13}C NMR (151 MHz, CDCl$_3$)



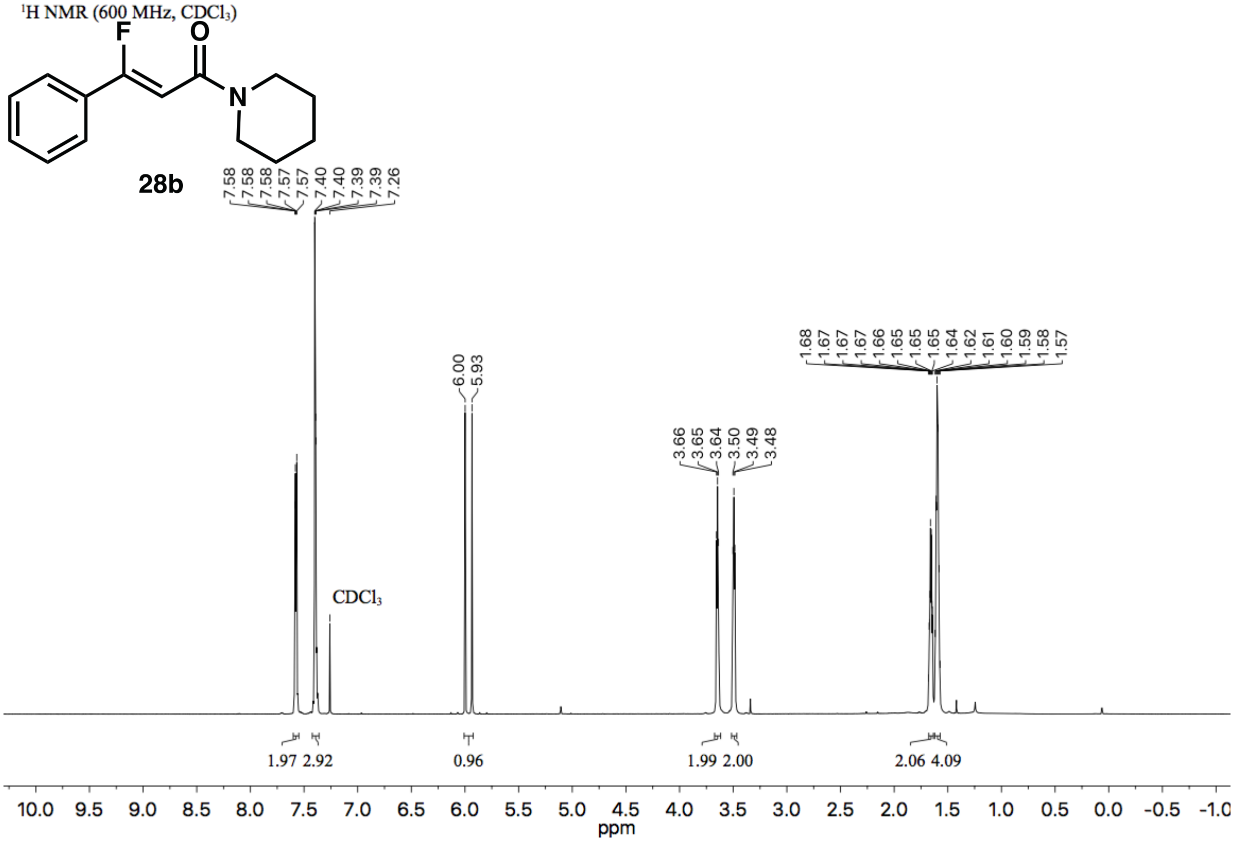
25b

^{19}F NMR (565 MHz, $CDCl_3$)

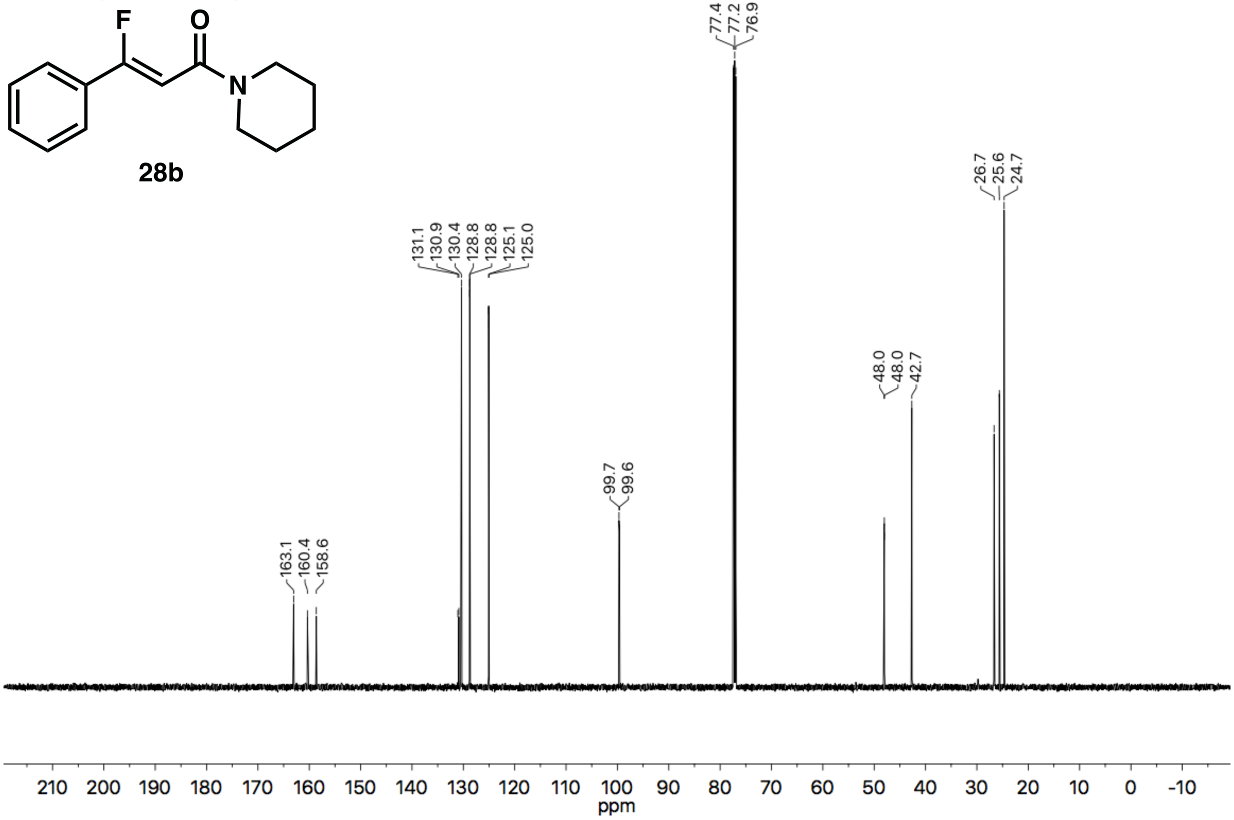


25b

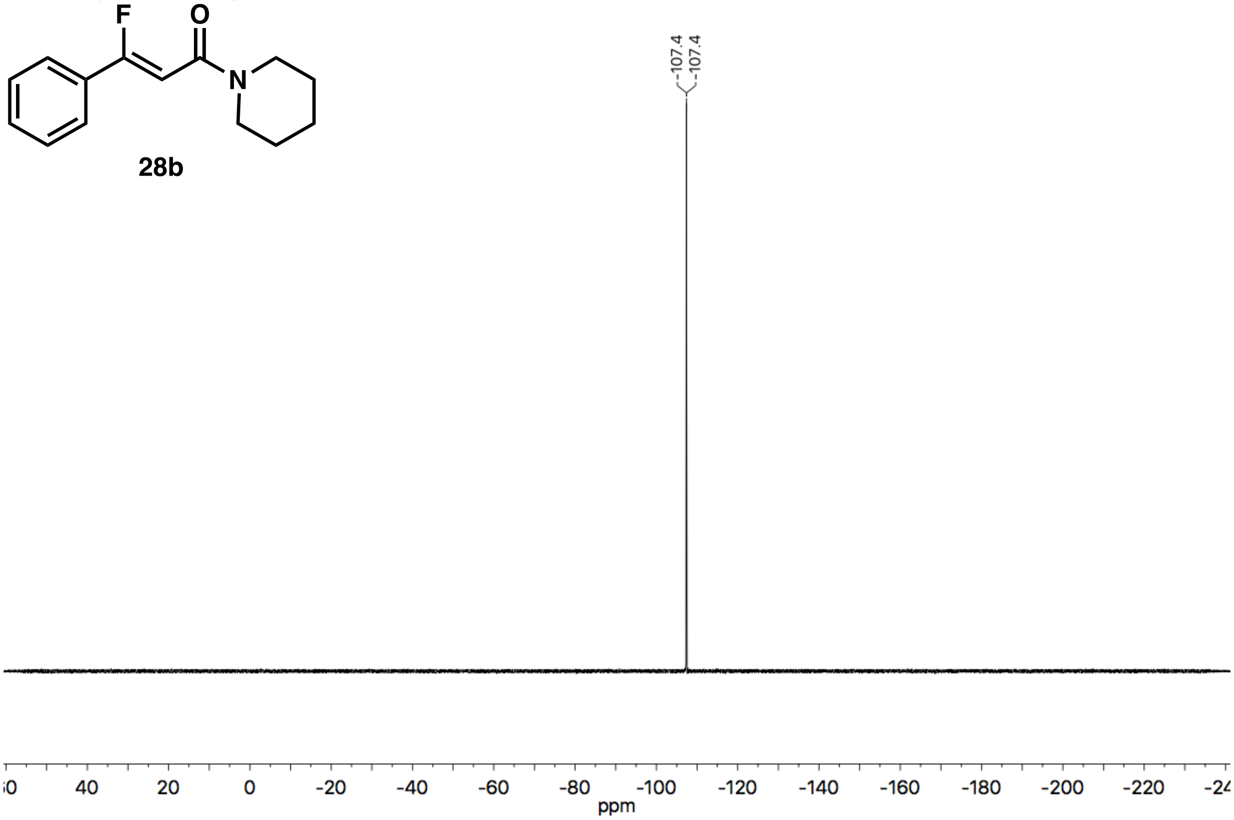
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

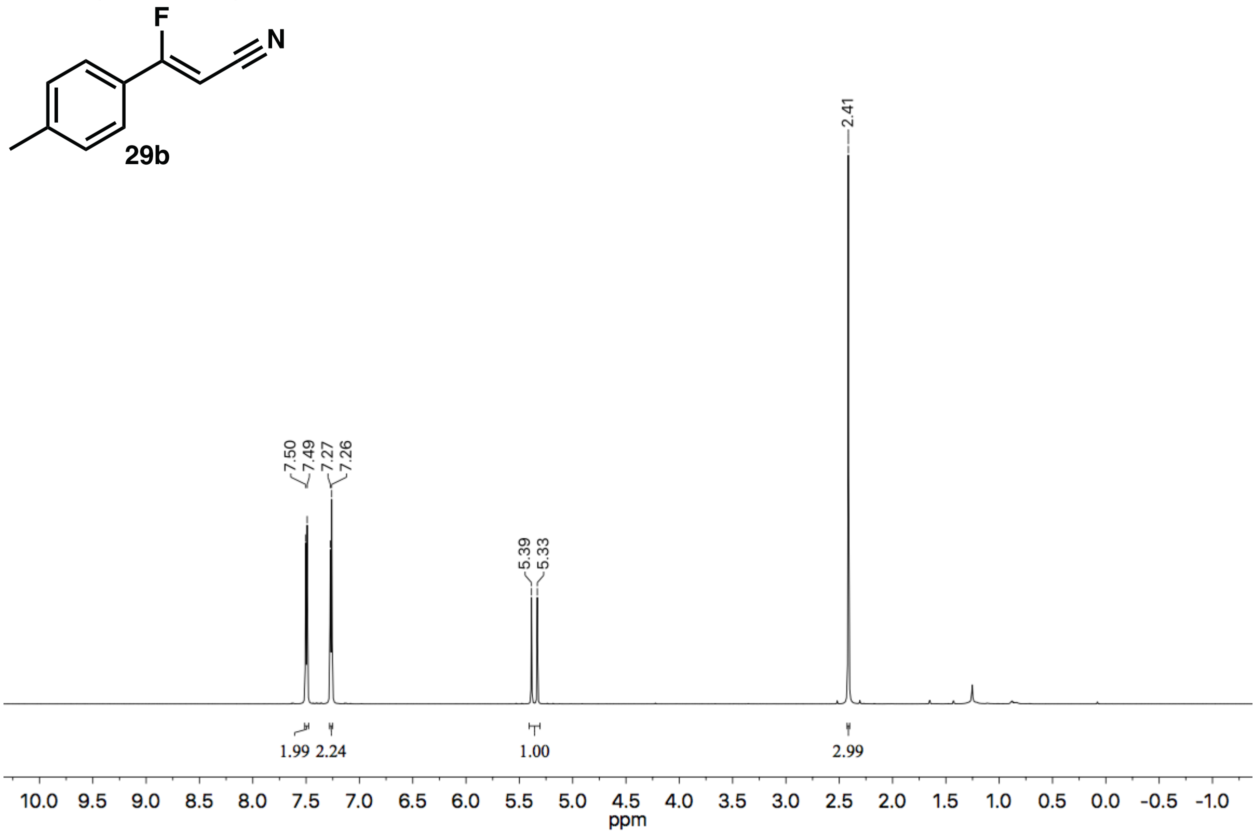


^{19}F NMR (565 MHz, CDCl$_3$)

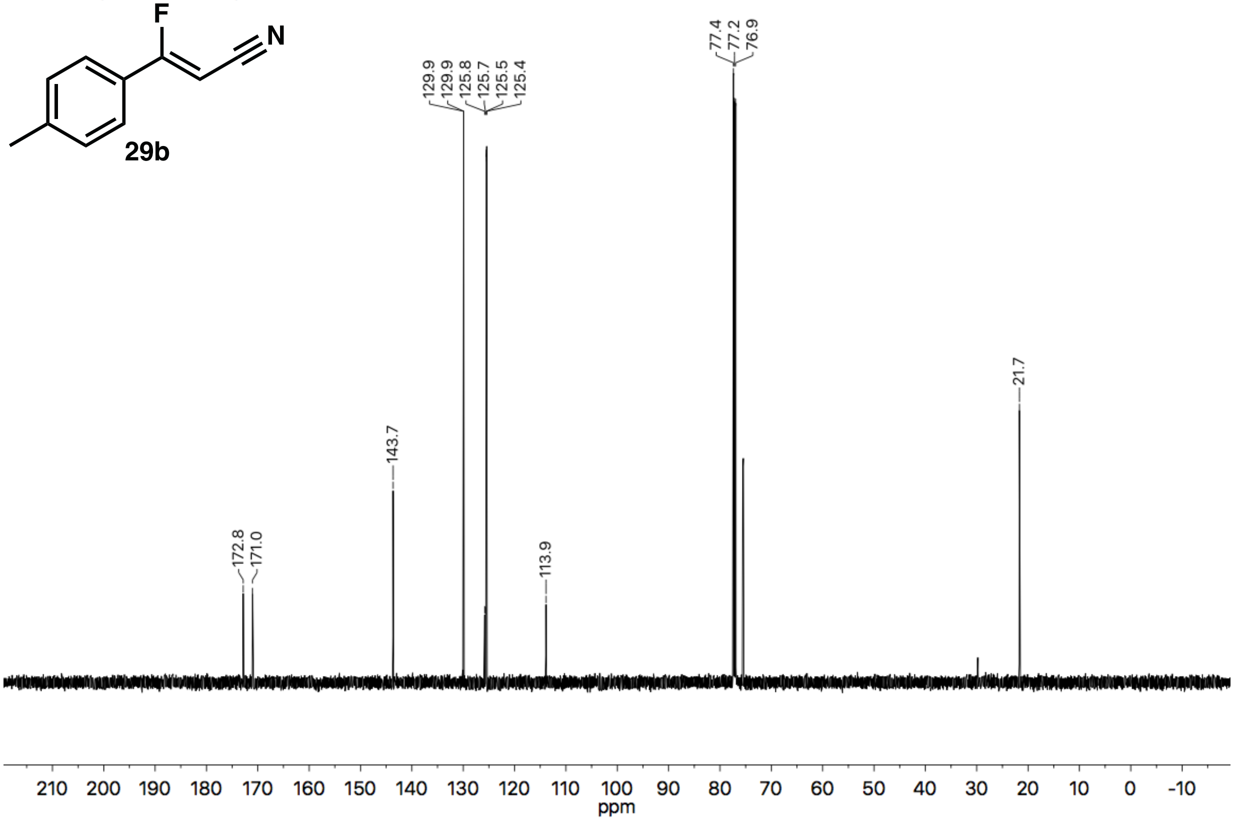


28b

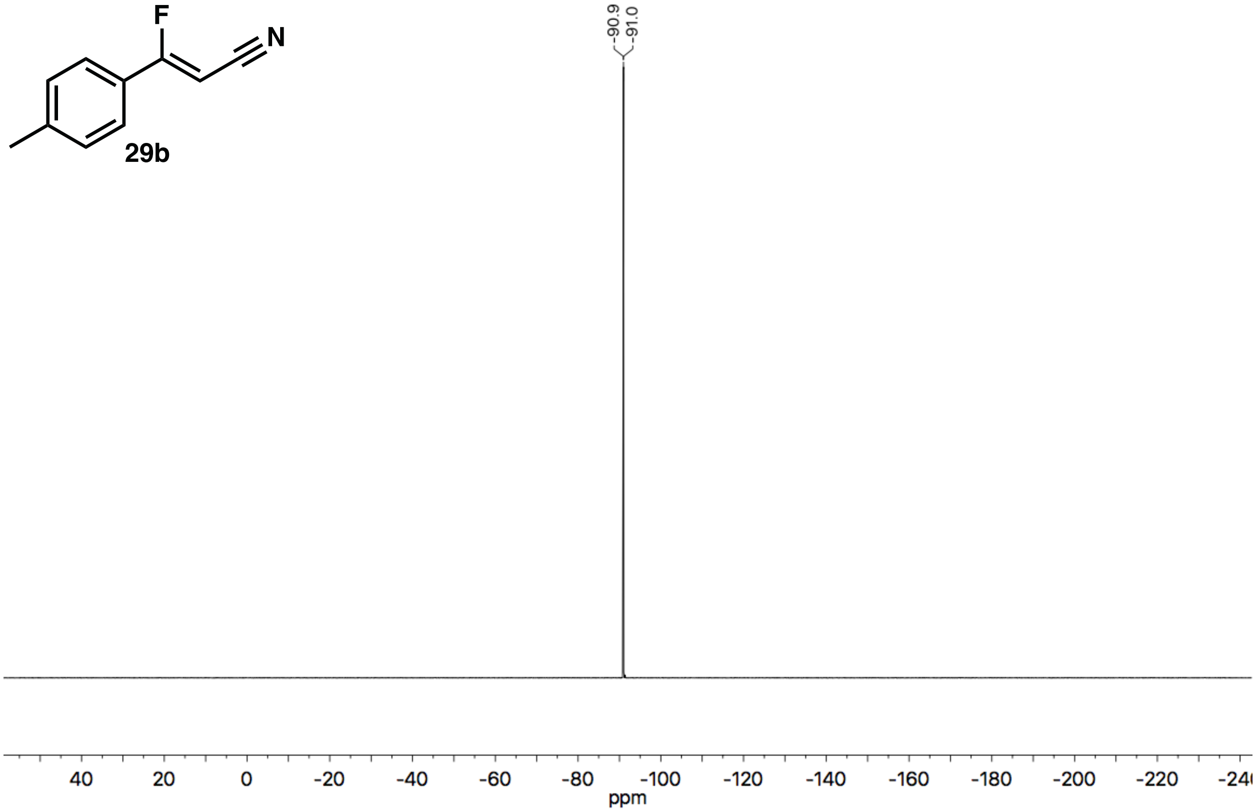
^{1}H NMR (600 MHz, CDCl$_3$)



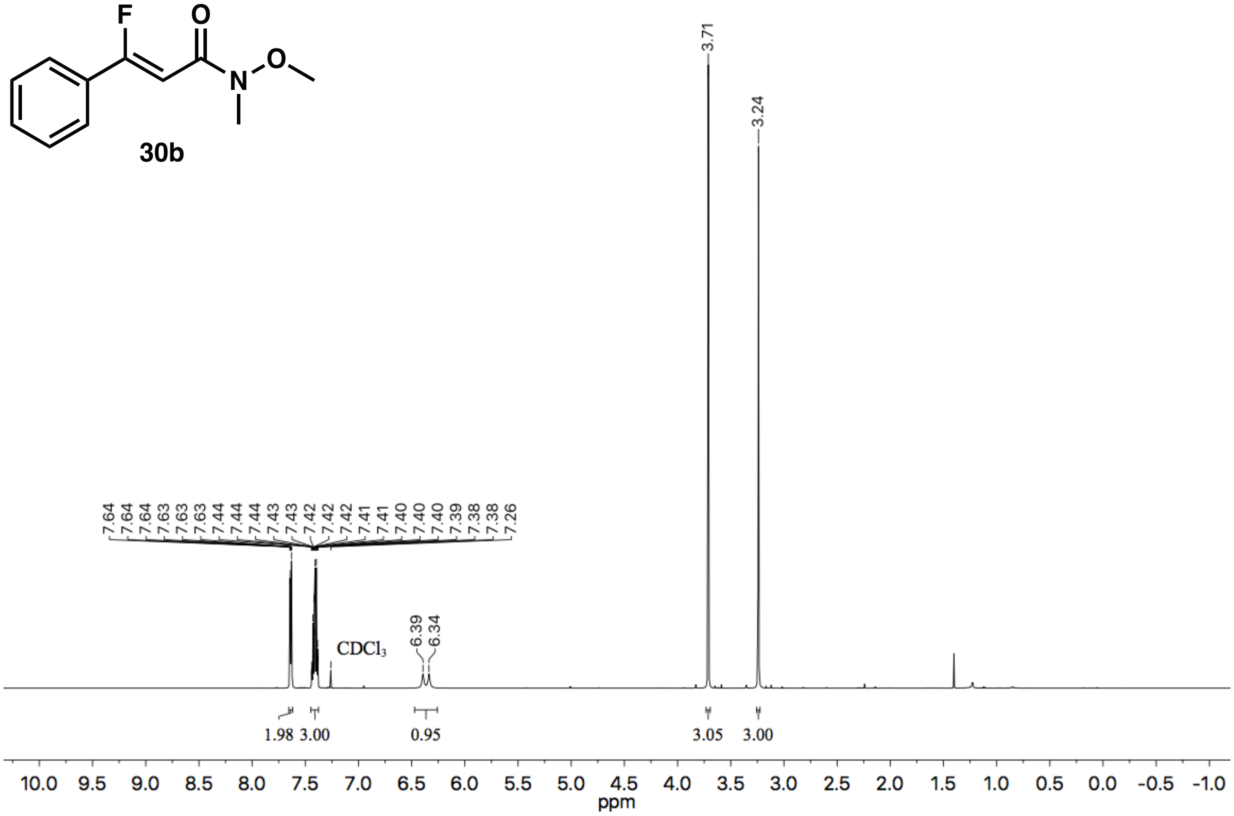
^{13}C NMR (151 MHz, CDCl$_3$)



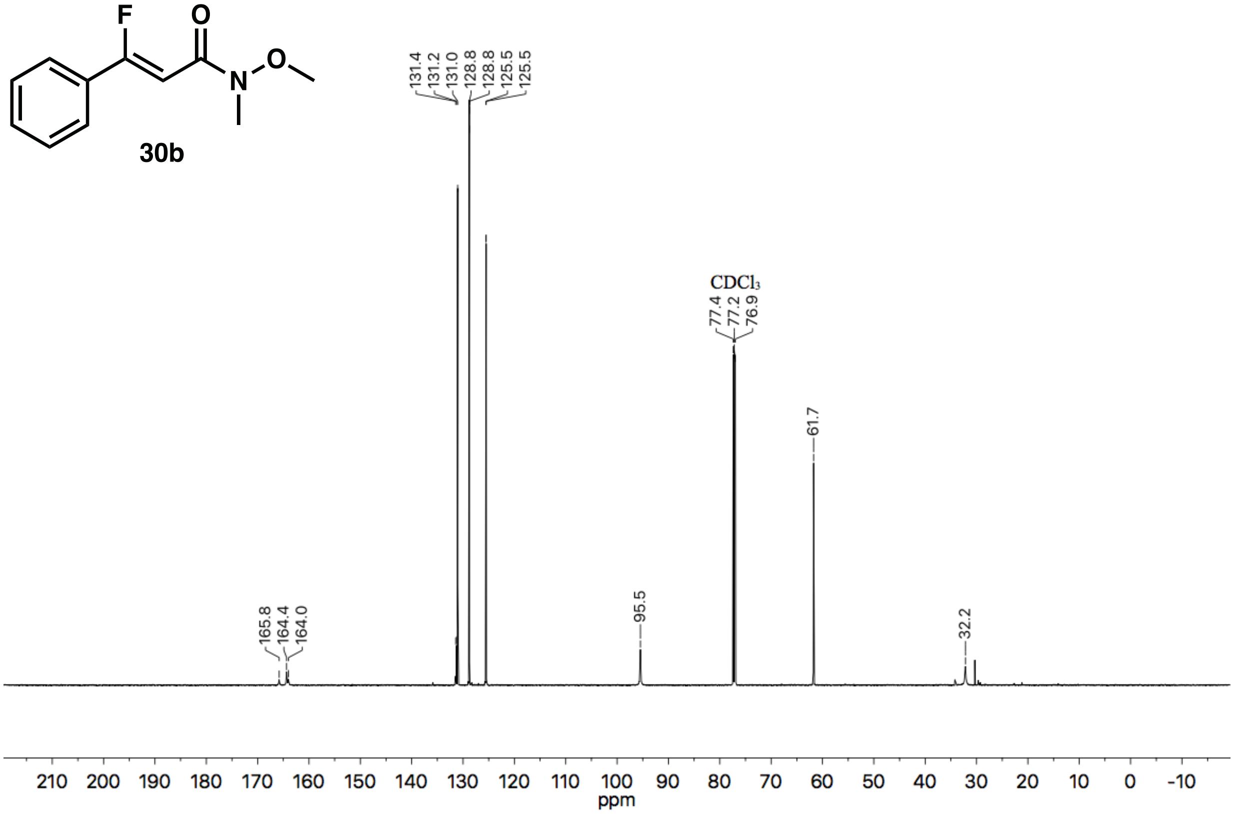
^{19}F NMR (565 MHz, CDCl$_3$)



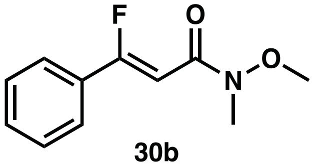
^{1}H NMR (600 MHz, CDCl$_3$)



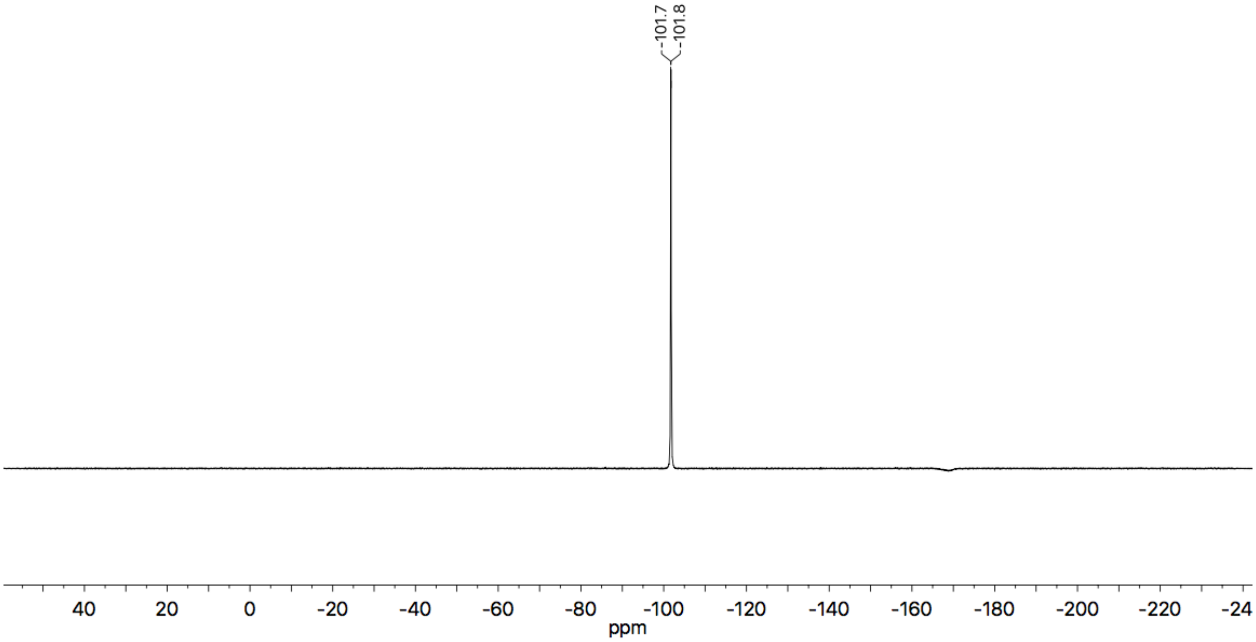
^{13}C NMR (151 MHz, CDCl$_3$)



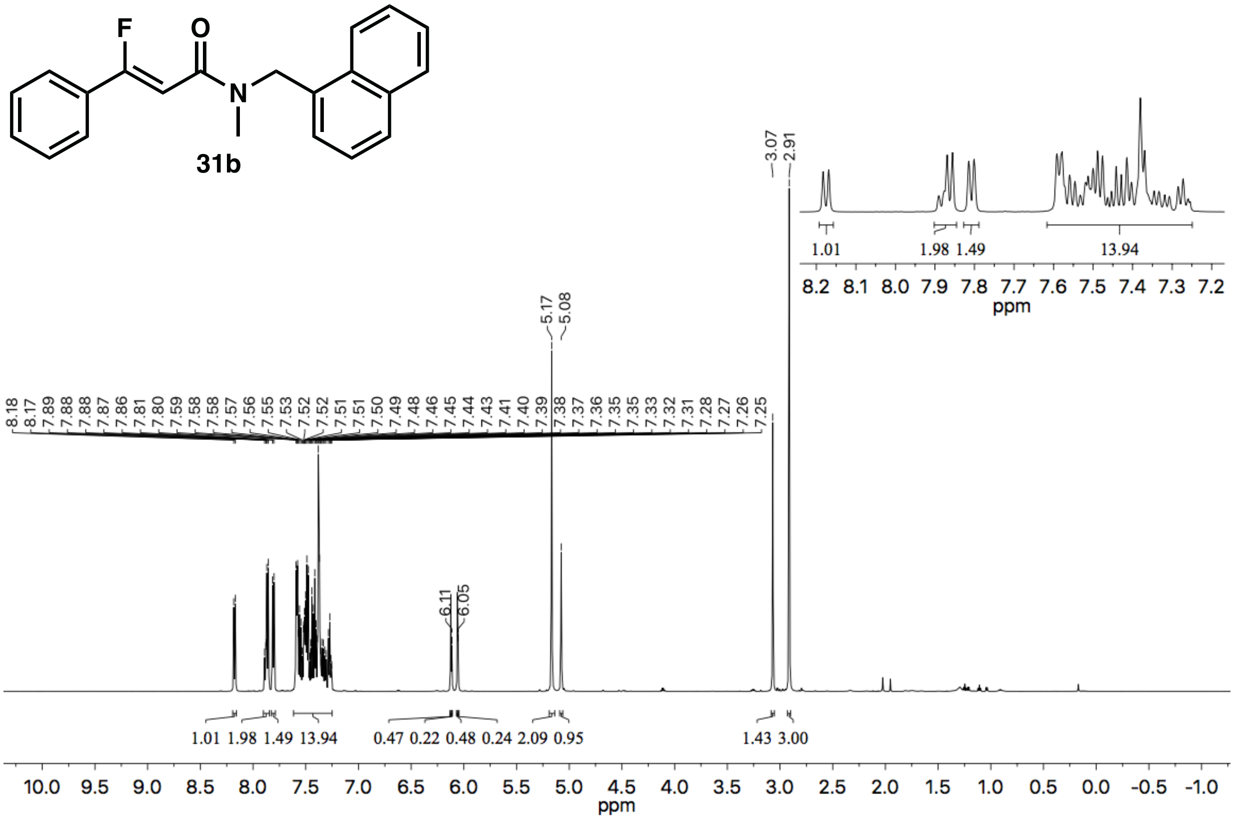
^{19}F NMR (565 MHz, CDCl$_3$)



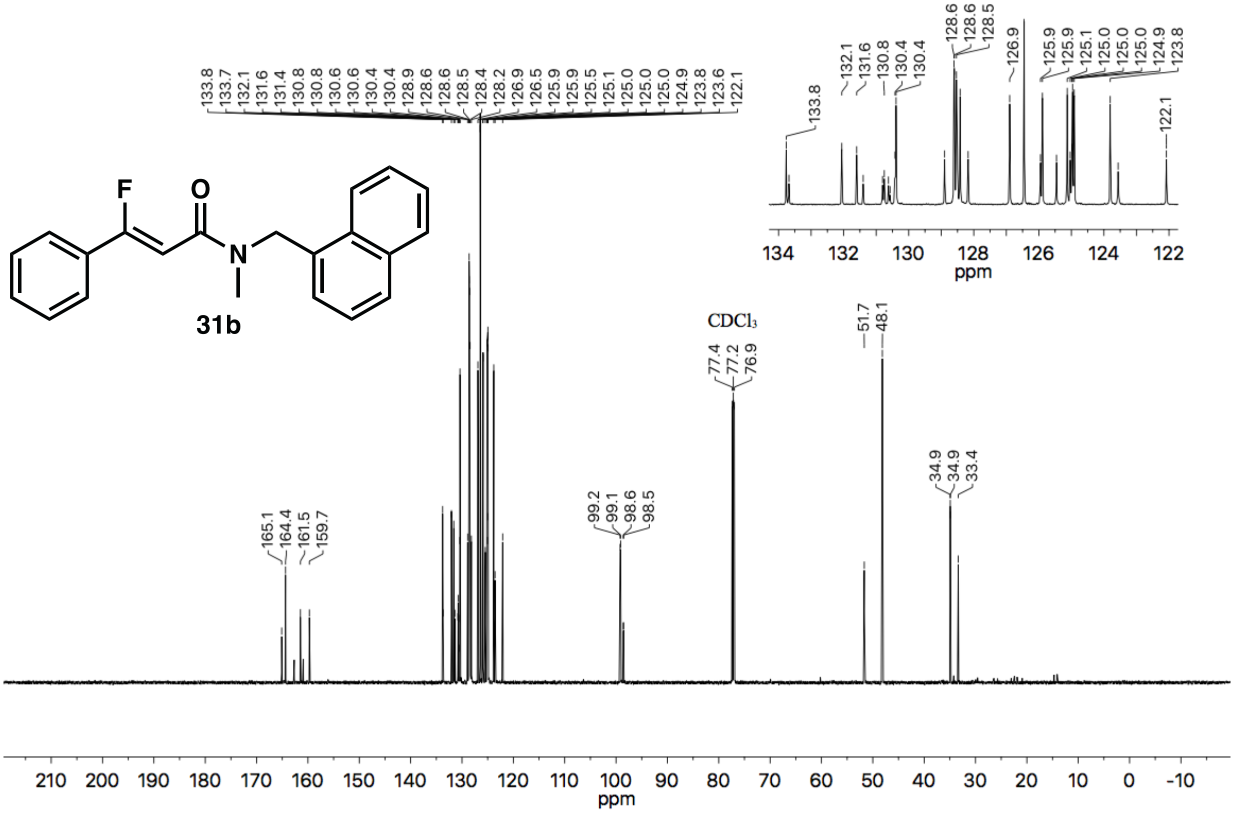
30b



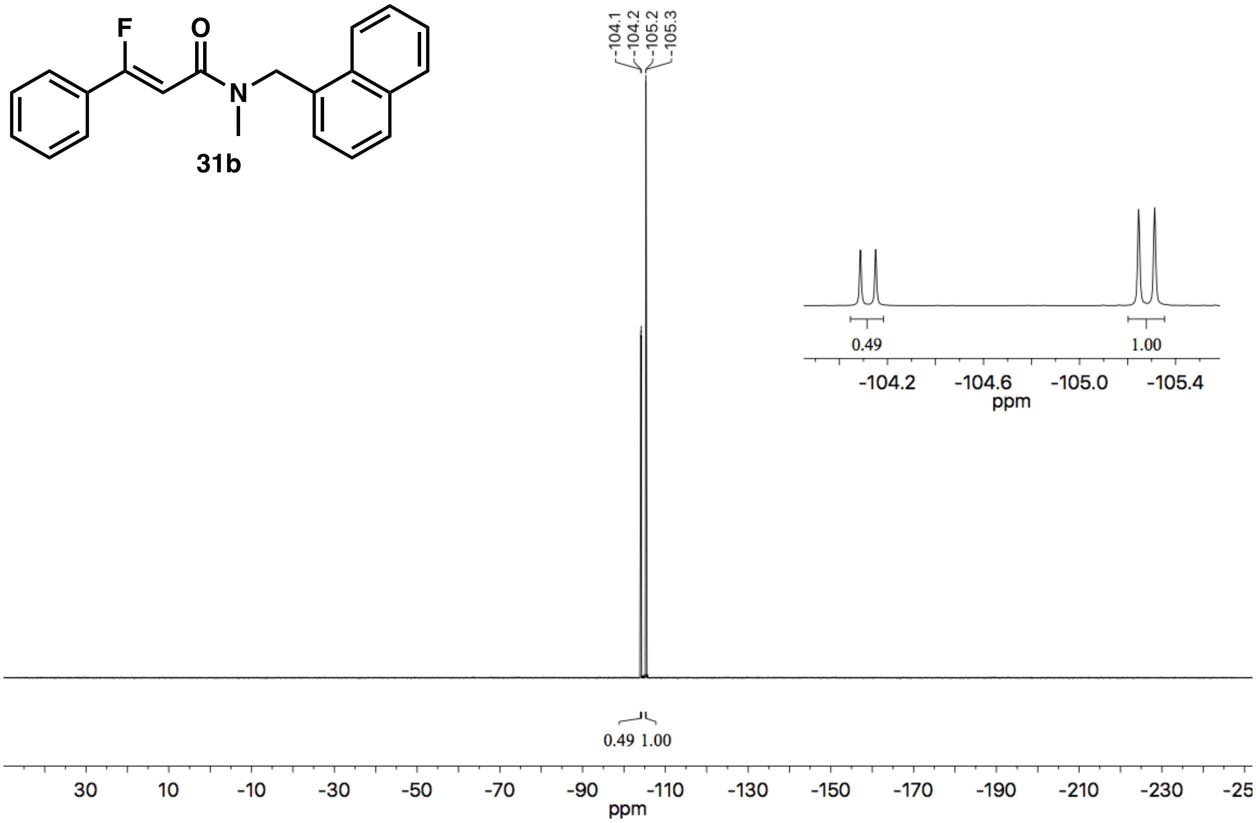
^{1}H NMR (600 MHz, CDCl$_3$)


31b

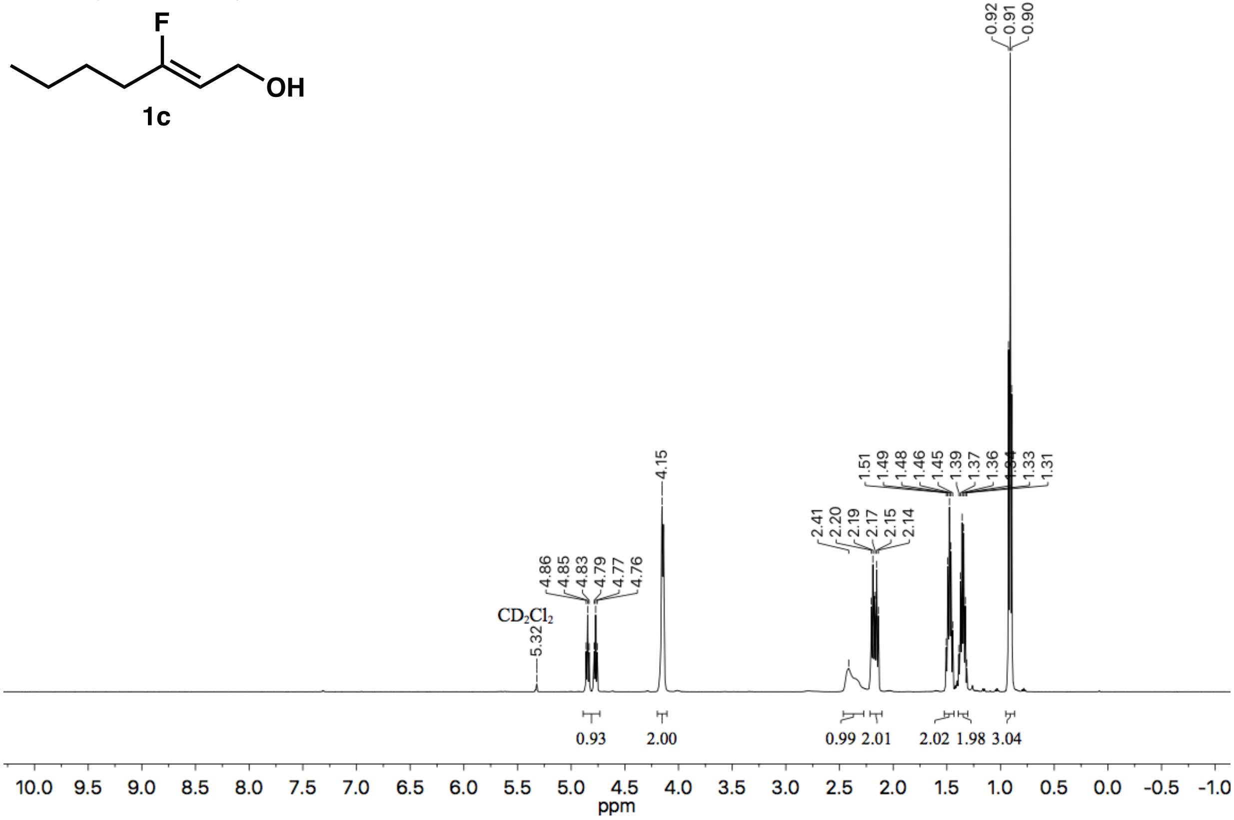
^{13}C NMR (151 MHz, CDCl$_3$)


31b

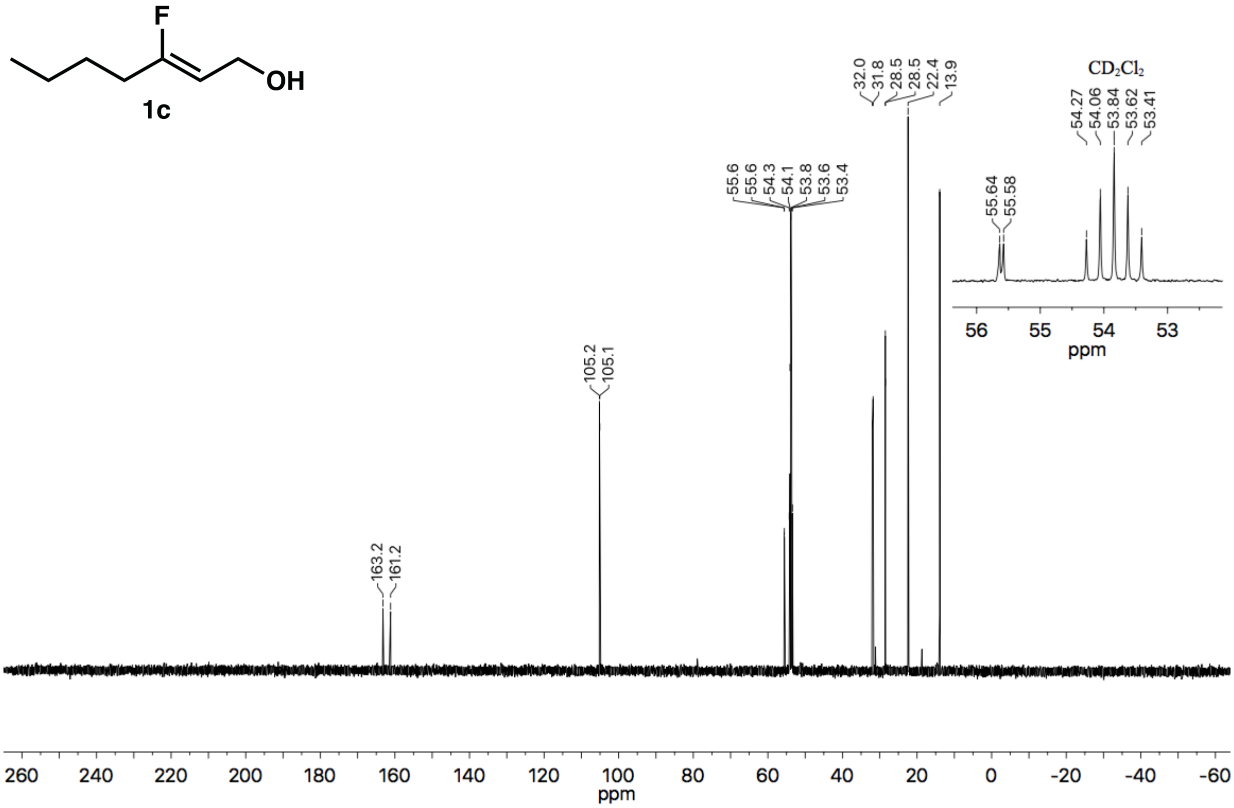
^{19}F NMR (565 MHz, CDCl$_3$)



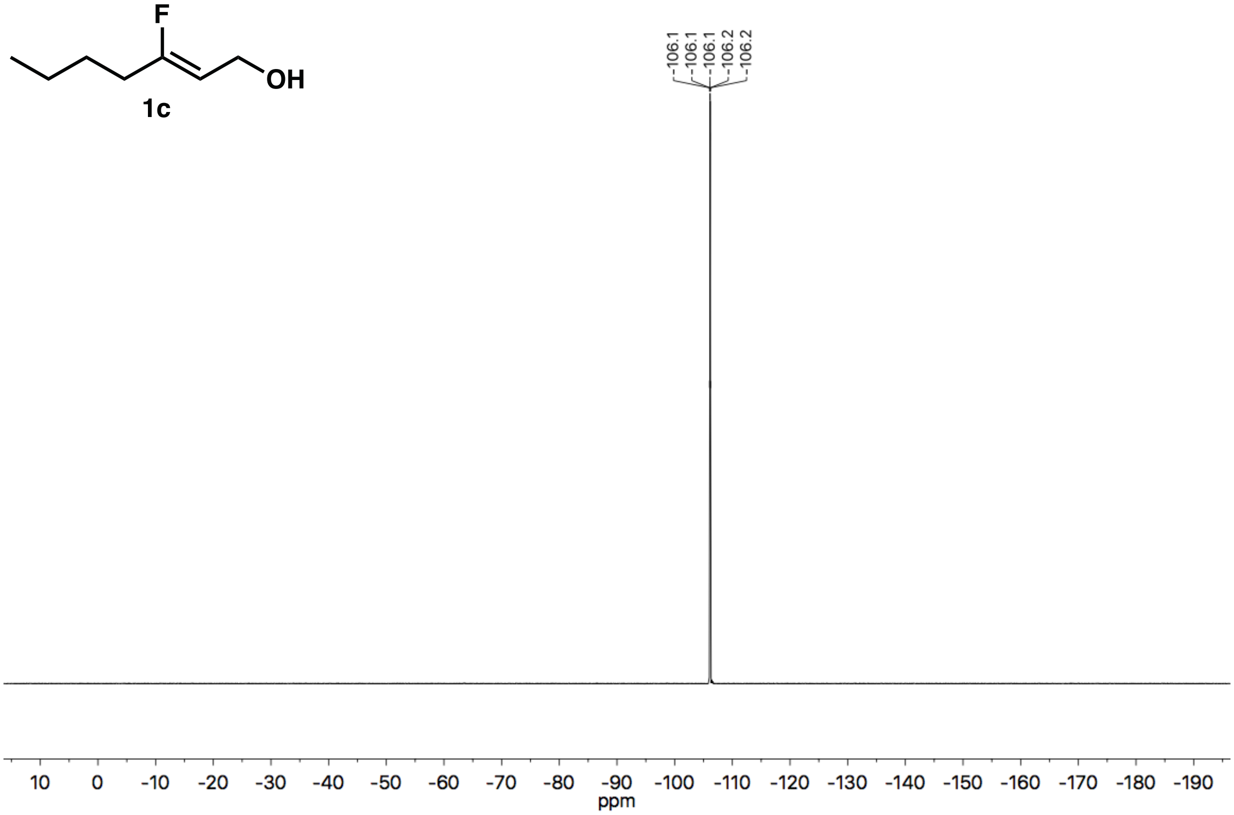
^{1}H NMR (500 MHz, CD_2Cl_2)



^{13}C NMR (126 MHz, CD_2Cl_2)

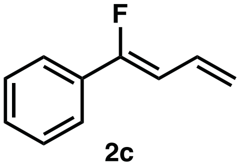


^{19}F NMR (470 MHz, CD$_2$Cl$_2$)

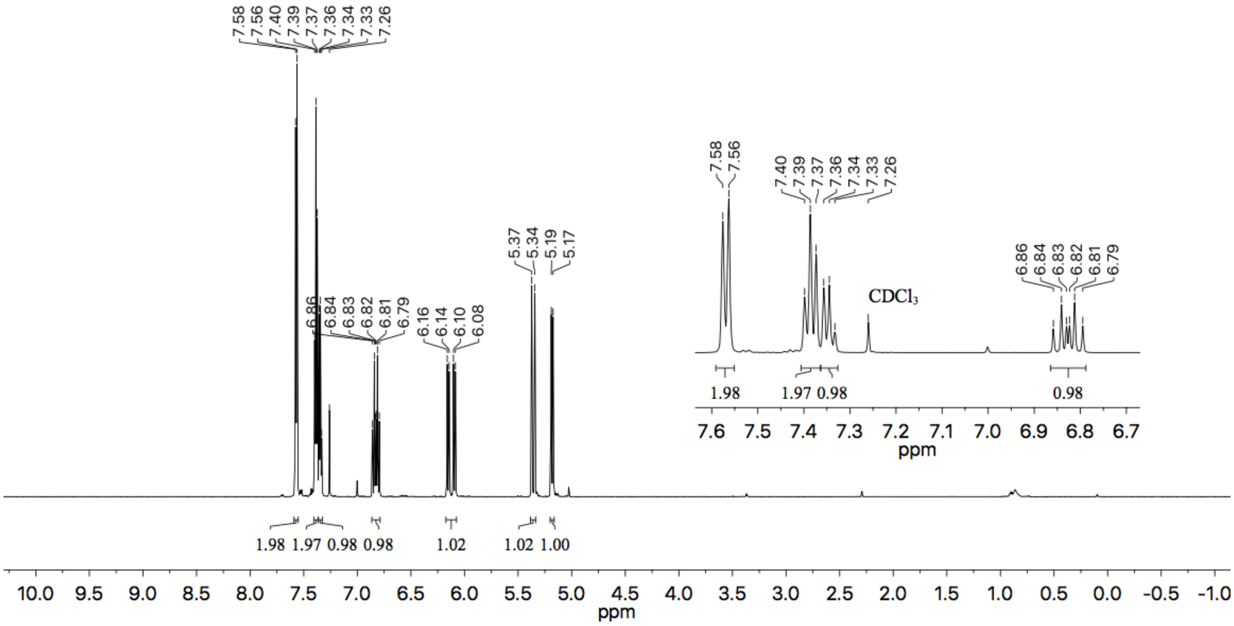


1c

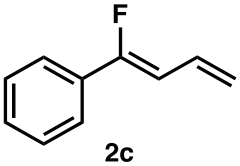
^{1}H NMR (600 MHz, CDCl$_3$)



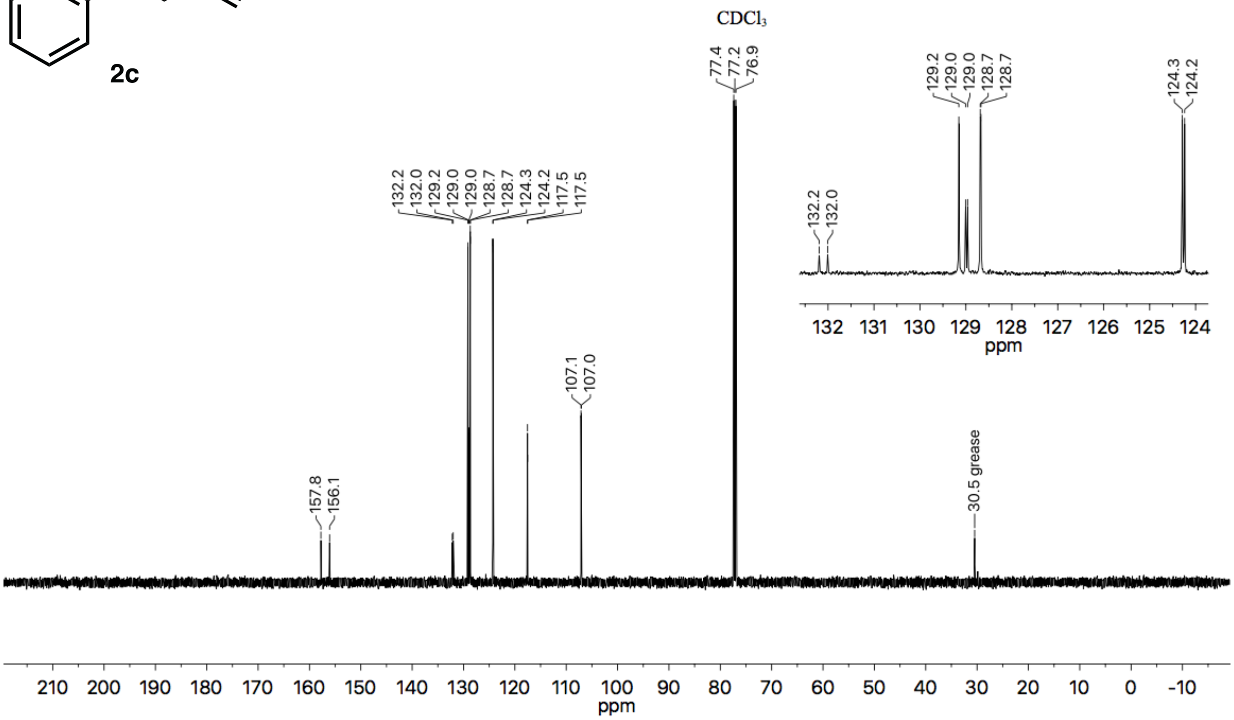
2c



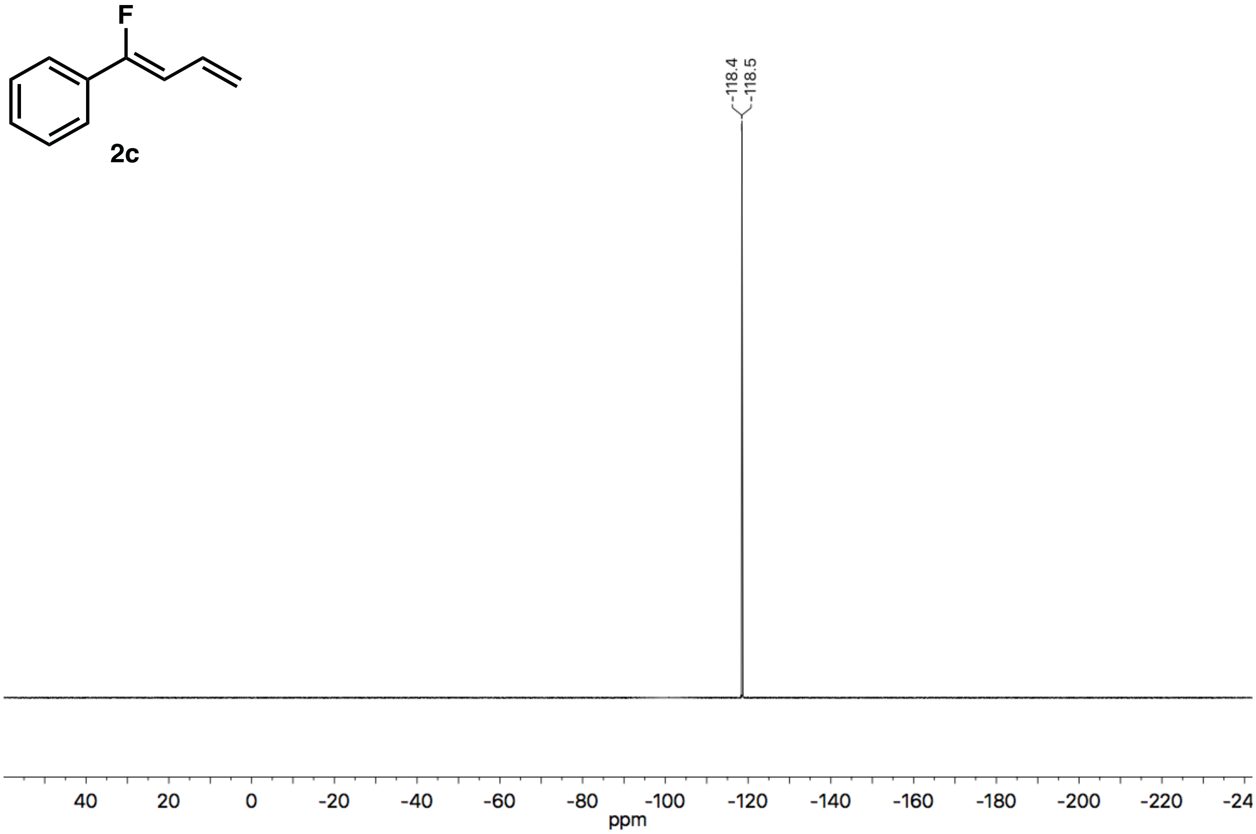
^{13}C NMR (151 MHz, CDCl$_3$)



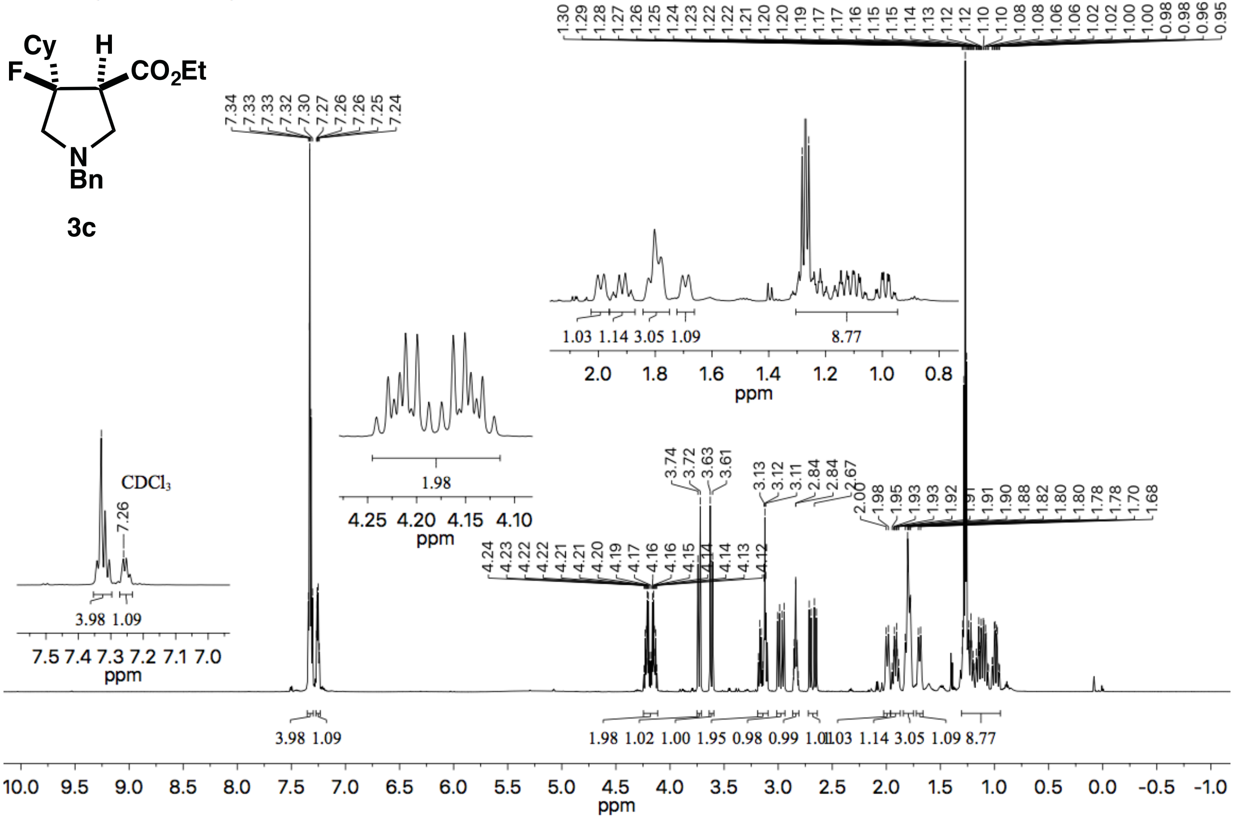
2c



^{19}F NMR (565 MHz, CDCl$_3$)

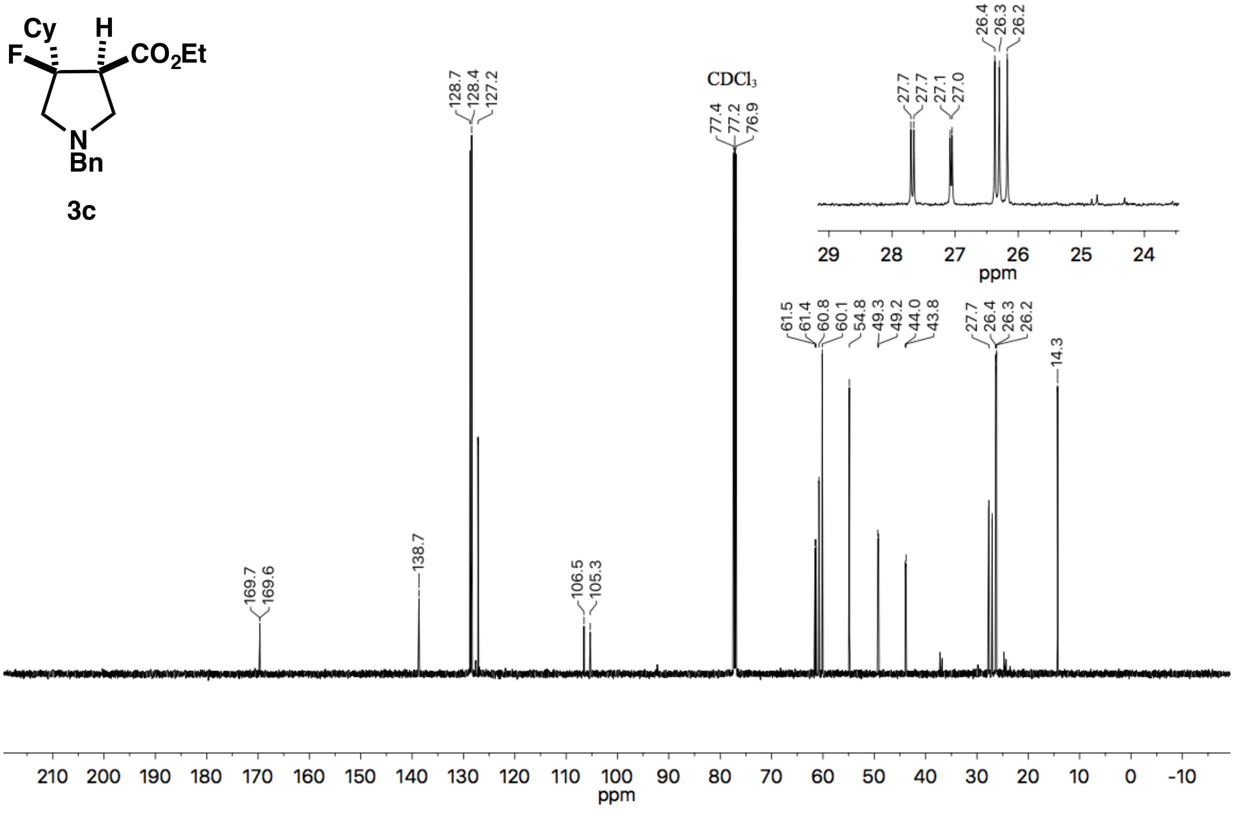

2c

^{1}H NMR (600 MHz, CDCl$_3$)



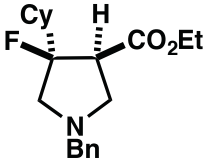
3c

^{13}C NMR (151 MHz, CDCl$_3$)



3c

^{19}F NMR (565 MHz, CDCl$_3$)



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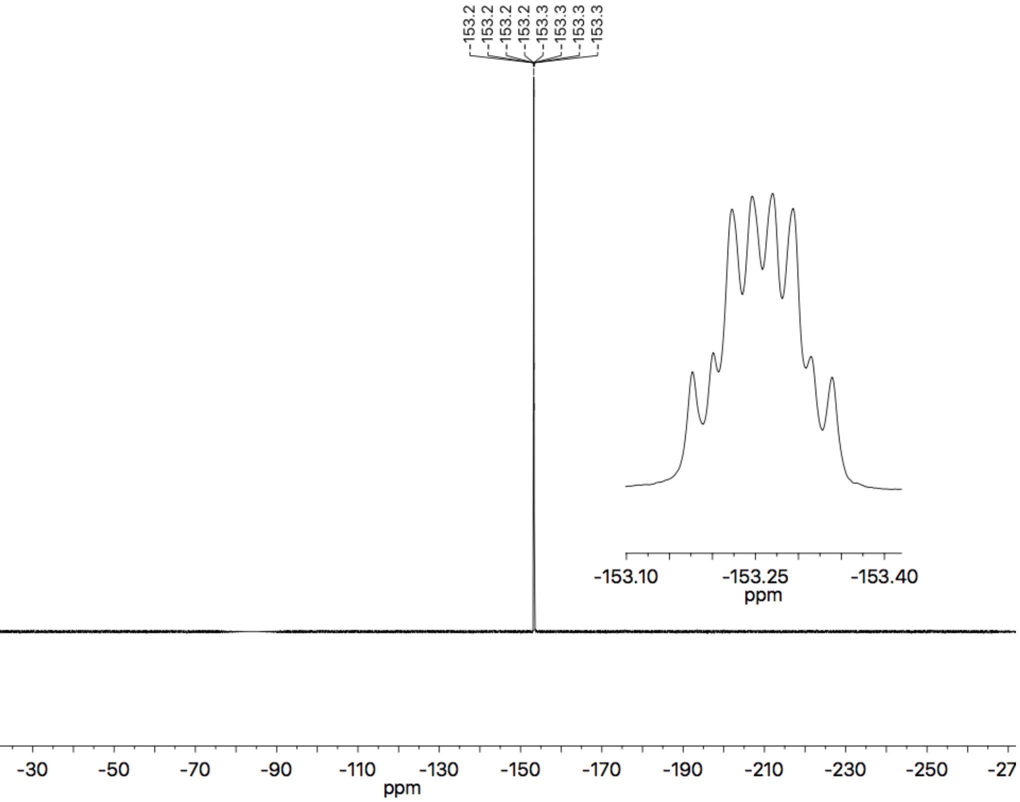
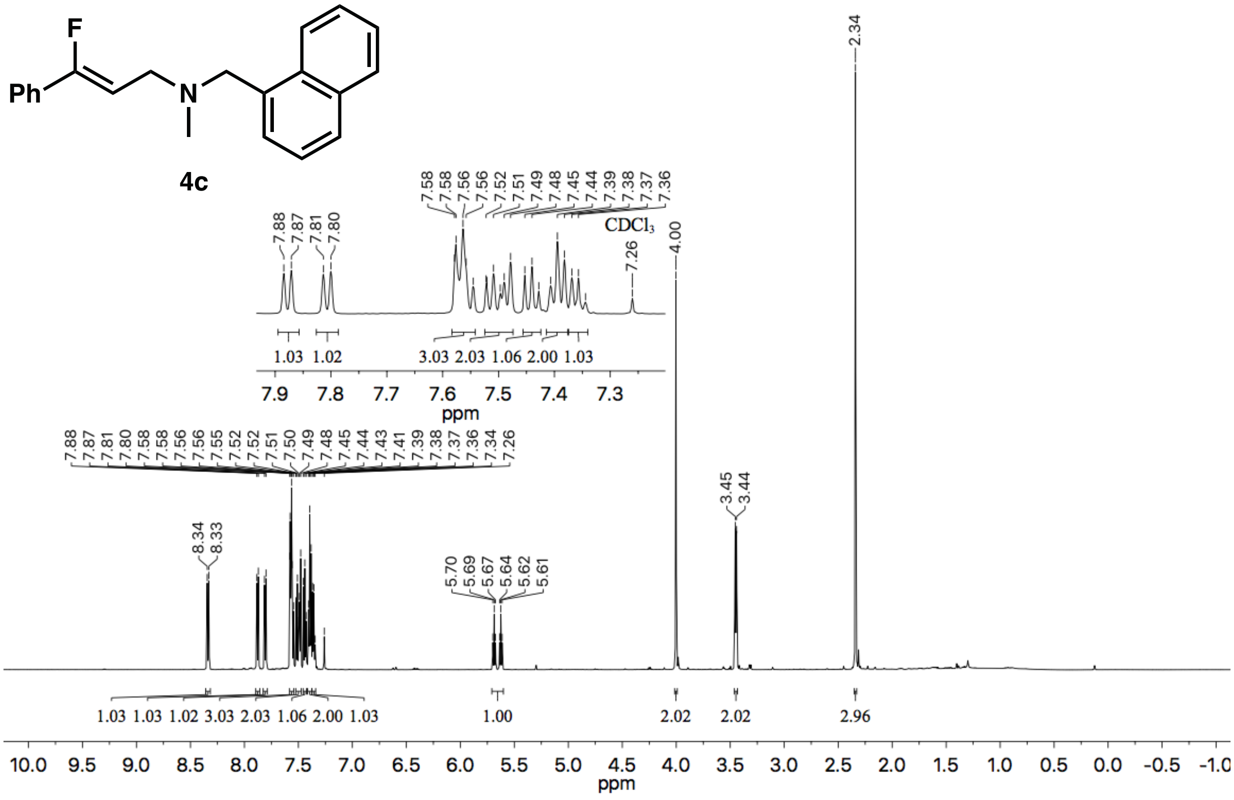
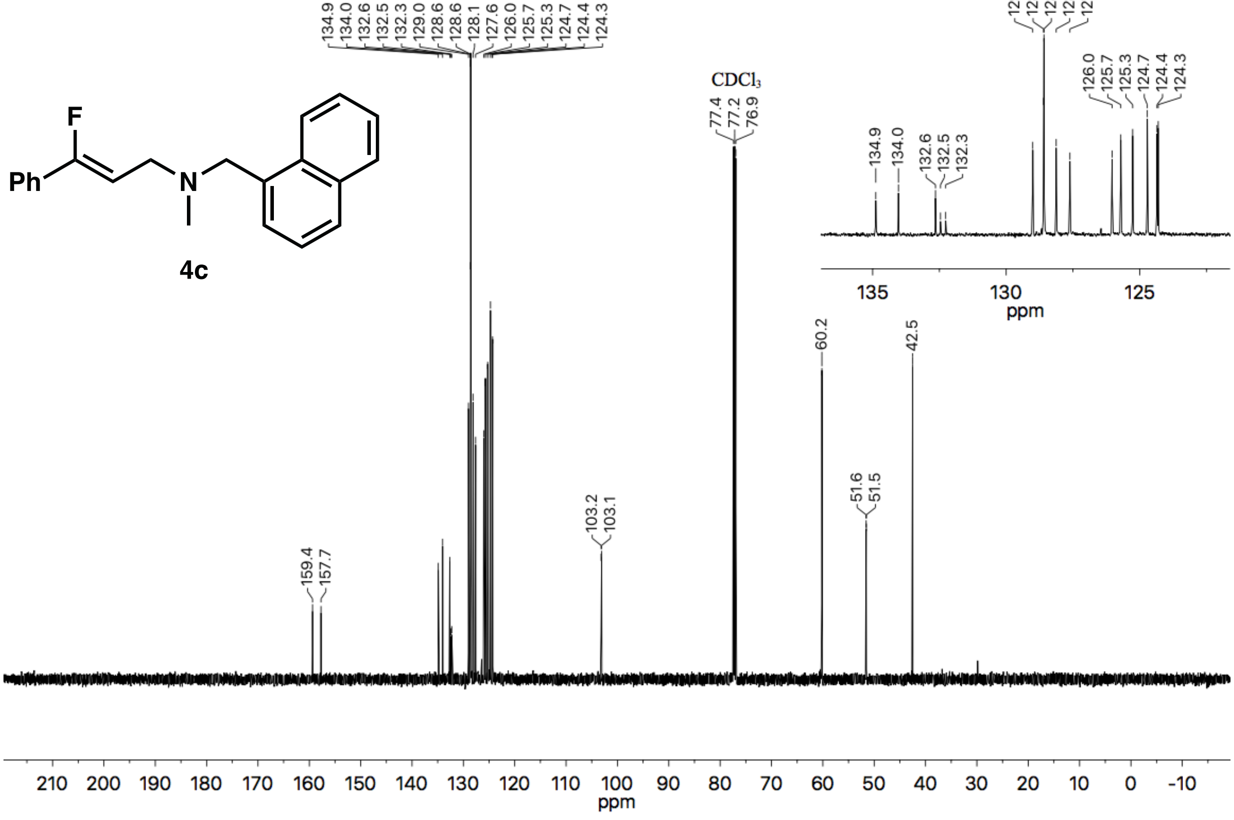


^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)



^{19}F NMR (565 MHz, CDCl$_3$)