Electronic Supplementary Material (ESI) for ChemComm.

Photo-induced energy transfer relay of N-heterocyclic carbene catalysis: An asymmetric α-fluorination/isomerization cascade

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Support Information

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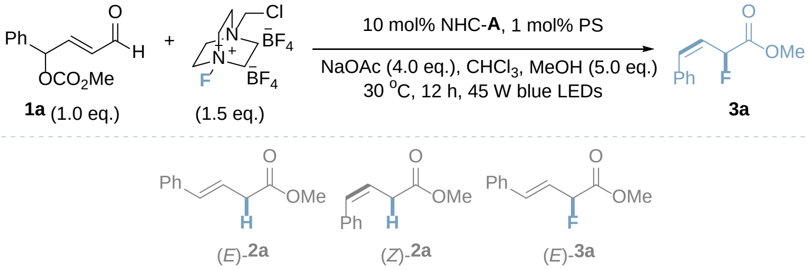
General methods and materials.

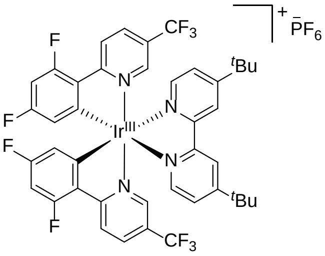
All solvents were distilled according to general practice prior to use. All reagents were purchased and used without further purification unless specified otherwise. Solvents for flash column chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and appropriate stains. Flash column chromatography was performed using Qingdao Haiyang Chemical HG/T2354-92 silica gel (200-300 mesh) with the indicated solvent system according to standard techniques. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker 400 MHz (100 MHz for ^{13}C, 376MHz for ^{19}F) and 500 MHz (126 MHz for ^{13}C) nuclear resonance spectrometers unless otherwise specified, respectively. Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform (^{1}H 7.26 ppm and ^{13}C 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (J) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling. Chiral HPLC was recorded on a Shimadzu LC-20A spectrometer using Daicel Chiralcel^{TM} columns. Chiral GC was recorded on a Shimadzu GC-2014 Gas Chromatography using Astec CHIRALDEXTM β-DM column. HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at Peking University; Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

Condition screening

A series of photosensitizers (PSs) were tested in this reaction, and we found using PS-**C** (E_T = 54.2 kcal mol^{-1}) as the photosensitizer can obtain relative high (*Z*/*E*)-selectivity with the overall good yield and enantioselectivity (**Table S1**, entry 3)[1, 2].

Table S1. Screening of photosensitizers (PSs) for the synergistic energy transfer relay[a]



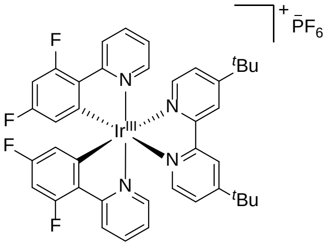


PS-A

[Ir(dF-CF$_3$-ppy)$_2$(dtbbpy)]PF$_6$

E_T = 60.1 kcal mol^{-1} (Weaver[1])

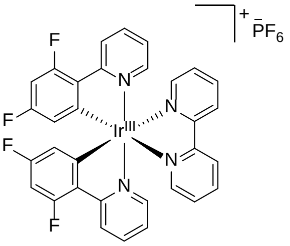
E_T = 59.4 kcal mol^{-1} (Rueping[2])



PS-B

[Ir(dF-ppy)$_2$(dtbbpy)]PF$_6$

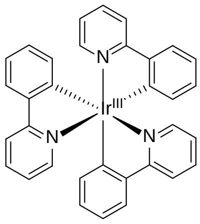
E_T = 55.4 kcal mol^{-1} (Weaver[1])



PS-C

[Ir(dF-ppy)$_2$(bpy)]PF$_6$

E_T = 54.2 kcal mol^{-1} (Weaver[1])

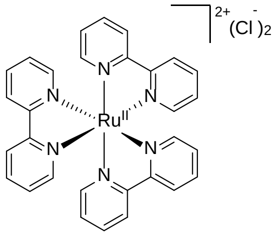


PS-D

Ir(ppy)$_3$

E_T = 55.2 kcal mol^{-1} (Weaver[1])

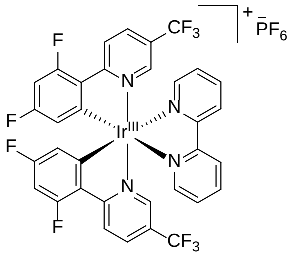
E_T = 53.6 kcal mol^{-1} (Rueping[2])



PS-E

Ru(bpy)$_3$Cl$_2$

E_T = 46.8 kcal mol^{-1} (PF$_6$, Rueping[2])

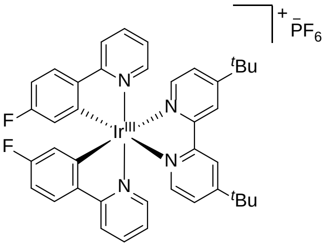


PS-F

[Ir(dF-CF$_3$-ppy)$_2$(bpy)]PF$_6$

E_T = 60.4 kcal mol^{-1} (Weaver[1])

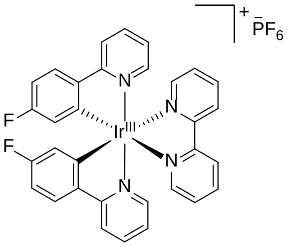
E_T = 60.4 kcal mol^{-1} (Rueping[2])



PS-G

[Ir(4-F-ppy)$_2$(dtbbpy)]PF$_6$

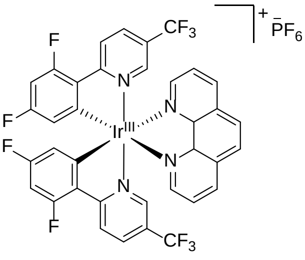
E_T = 53.0 kcal mol^{-1} (Weaver[1])



PS-H

[Ir(4-F-ppy)$_2$(bpy)]PF$_6$

E_T = 51.4 kcal mol^{-1} (Weaver[1])



PS-I

[Ir(dF-CF$_3$-ppy)$_2$(1, 10-Phen)]PF$_6$

E_T = 60.2 kcal mol^{-1} (Weaver[1])

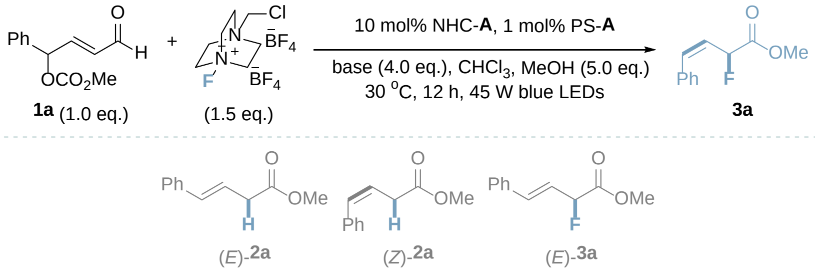
entry	PS	**1a** / %[b]	(*E*)-**2a** / %[b]	(*Z*)-**2a** / %[b]	(*E*)-**3a** / %[b]	**3a** / %[b]	ee of **3a** / %[c]	**3a**/(*E*)-**3a**
1	PS-**A**	7	15	8	5	33	83	6.8:1
2	PS-**B**	12	7	5	3	27	83	9.3:1
3	PS-**C**	13	10	7	4	32	83	9.2:1
4	PS-**D**	-	-	-	-	-	-	-

5	PS-**E**	15	1	3	17	1	n.d.	0.1:1
6	PS-**F**	20	7	4	3	17	84	7.7:1
7	PS-**G**	17	9	6	4	25	83	9.2:1
8	PS-**H**	27	17	14	1	8	85	10.4:1
9	PS-**I**	21	11	5	4	21	83	6.4:1

[a] Reaction conditions: **1a** (0.1 mmol), selectfluor (0.15 mmol), NHC-**A** (10 mol%), PS (1 mol%), NaOAc (0.4 mmol), $CHCl_3$ (1.5 mL), MeOH (0.5 mmol), irradiation with 45 W blue LEDs, 30 °C (with fan cooling), 12 h. [b] Determined by GC. [c] Determined by chiral GC.

Several bases were tested in this reaction, and we found using PivONa as the base can obtain highest yield with relatively high enantioselectivity and (*Z*/*E*)-selectivity (**Table S2**, entry 7).

Table S2. Screening of bases for the synergistic energy transfer realy[a]

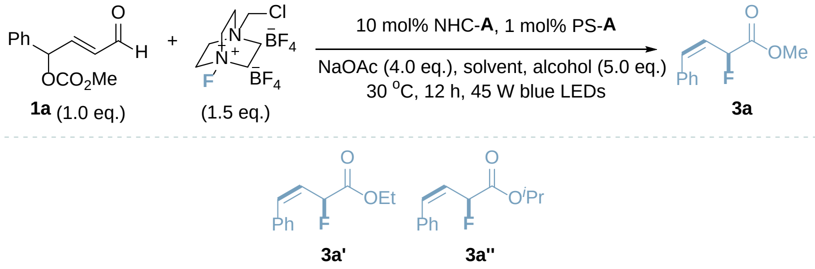


entry	base	**1a** / %[b]	(*E*)-**2a** / %[b]	(*Z*)-**2a** / %[b]	(*E*)-**3a** / %[b]	**3a** / %[b]	ee of **3a** / %[c]	**3a**/(*E*)-**3a**
1	NaOAc	7	15	8	5	33	83	6.8:1
2[d]	K_2CO_3	67	-	1	1	1	n.d.	0.7:1
3[d]	Cs_2CO_3	2	1	4	20	11	39	0.5:1
4[d]	KOAc	-	9	13	5	31	59	6.8:1
5[d]	CsOAc	-	14	16	4	25	54	6.4:1
6	lithium isobutyrate	9	4	5	4	24	84	6.5:1
7	PivONa	2	7	8	6	39	83	6.8:1

[a] Reaction conditions: **1a** (0.1 mmol), selectfluor (0.15 mmol), NHC-**A** (10 mol%), PS-**A** (0.001 mmol), base (0.4 mmol), $CHCl_3$ (1.5 mL), MeOH (0.5 mmol), irradiation with 45 W blue LEDs, 30 °C (with fan cooling), 12 h. [b] Determined by GC. [c] Determined by chiral GC. [d] Base (0.2 mmol). N.d. = not determined.

A series of solvents were tested in this reaction, and we found using $CHCl_3$/MeOH (15:1) as the mixed solvent can obtain relative high (*Z*/*E*)-selectivity with the highest yield and enantioselectivity (**Table S3**, entry 9).

Table S3. Screening of solvents for the synergistic energy transfer relay[a]



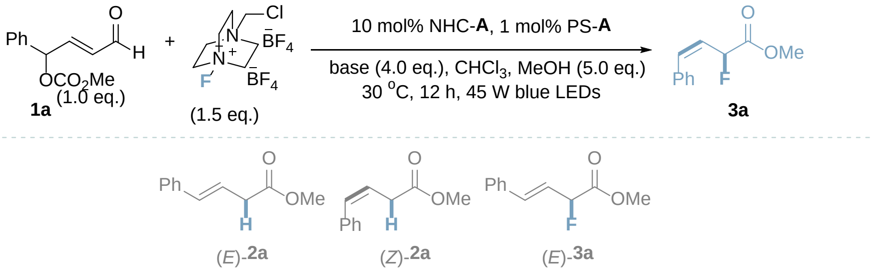
entry	solvent	co-solvent	**1a** / %[b]	**3a'**/**3a''** / %[b]	ee / %[c]	*Z*/*E*	**3a** / %[b]	ee of **3a**	**3a**/(*E*)-**3a**

								/ %^{c}	
1	$CHCl_3$	5.0 eq. MeOH	6	-	-	-	33	83	6.8:1
2	$CHCl_3$	5.0 eq. EtOH	10	14	82	-	8	83	-
3	$CHCl_3$	5.0 eq. ^{i}PrOH	34	1	n.d.	-	17	84	-
4	DCE	5.0 eq. MeOH	9	-	-	-	28	81	2.9:1
5	DCE	0.05 mL MeOH	8	-	-	-	33	79	4.3:1
6	DCE	0.1 mL MeOH	10	-	-	-	33	78	5.5:1
7	MeCN	5.0 eq. MeOH	96	-	-	-	trace	-	-
8	$CHCl_3$	0.05 mL MeOH	11	-	-	-	38	83	6.6:1
9	$CHCl_3$	0.1 mL MeOH	2	-	-	-	45	84	6.5:1
10	-	1.5 mL MeOH	11	-	-	-	18	60	2.7:1
11	$CHCl_3$	0.1 mL EtOH	3	32	84	5.9:1	6	83	-
12	$CHCl_3$	0.1 mL ^{i}PrOH	12	4	n.d.	-	18	84	6.7:1

[a]Reaction conditions: **1a** (0.1 mmol), selectfluor (0.15 mmol), NHC-**A** (10 mol%), PS-**A** (0.001 mmol), NaOAc (0.4 mmol), $CHCl_3$ (1.5 mL), alcohol (0.5 mmol), irradiation with 45 W blue LEDs, 30 °C (with fan cooling), 12 h. [b]Determined by GC. [c]Determined by chiral GC. DCE = 1,2-dichloroethane. ^{i}PrOH = isopropyl alcohol.

Different loading ratios of **1a** and selectfluor were tested in this reaction, and we found using **1a**/selectfluor (1.5:1) as the starting materials can obtain relative high yield with the enantioselectivity and (*Z*/*E*)-selectivity staying untouched (**Table S4**, entry 3).

Table S4. Screening of the loading ratio of **1a** and selectfluor for the synergistic energy transfer realy[a]



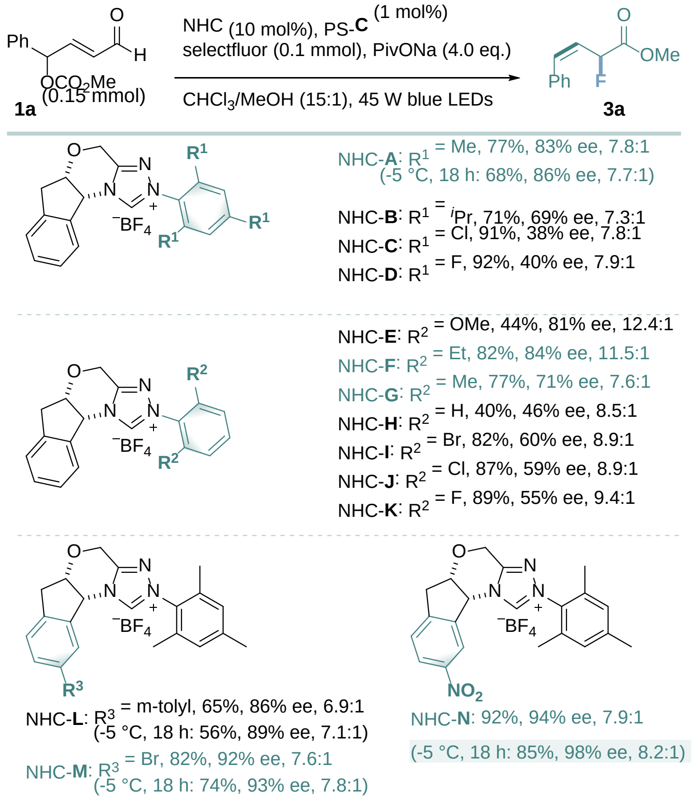
entry	**1a**	select-fluor	**1a** / %^{b}	(*E*)-**2a** / %^{b}	(*Z*)-**2a** / %^{b}	(*E*)-**3a** / %^{b}	**3a** / %^{b}	ee of **3a** / %^{c}	**3a**/(*E*)-**3a**
1	0.1 mmol	0.15 mmol	6	15	8	5	33	83	6.8:1
2	0.125 mmol	0.1 mmol	8	4	6	7	48	83	6.7:1

3	0.15 mmol	0.1 mmol	10	4	7	9	58	83	6.8:1
4	0.175 mmol	0.1 mmol	-	19	15	9	59	83	6.7:1

[a]Reaction conditions: **1a** (0.1 mmol), selectfluor (0.15 mmol), NHC-**A** (10 mol%), PS-**A** (0.001 mmol), NaOAc (0.4 mmol), $CHCl_3$ (1.5 mL), MeOH (0.5 mmol), irradiation with 45 W blue LEDs, 30 ℃ (with fan cooling), 12 h. [b]Determined by GC. [c]Determined by chiral GC.

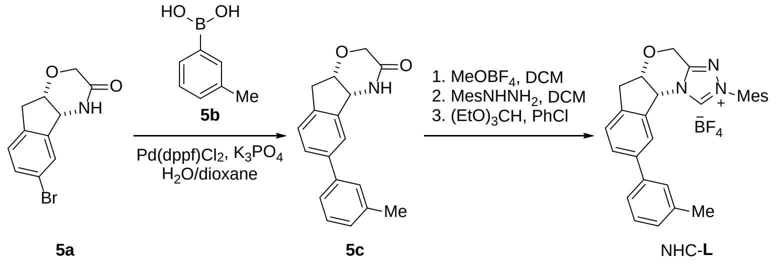
A series of NHCs were tested in this reaction, and we found using NHC-**N** as the pre-catalyst can obtain highest yield and enantioselectivity with satisfactory (*Z*/*E*)-selectivity (**Table S5**).

Table S5. The influence of NHC skeleton[a]



[a]Reaction conditions: enal **1a** (0.15 mmol), selectfluor (0.1 mmol), NHC (10 mol%), PS-**C** (1 mmol%), PivONa (0.4 mmol), $CHCl_3$/MeOH (1.5 mL/0.1 mL), irradiation with 45 W blue LEDs, 30 ℃ (with fan cooling), 12 h. The yield and (*Z*/*E*) ratio were determined by GC. The ee value was determined by chiral GC.

Synthesis of NHC-L[3]

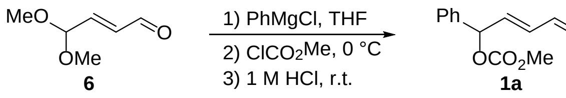


Following the reported procedure by Wang et al., we synthesized NHC-**L** as below[3]:

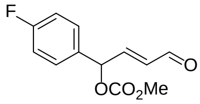
To a suspension of **5a** (2.66 g, 10.0 mmol), arylboronic acid **5b** (13.0 mmol), Pd(dppf)Cl_2 (0.365 g, 0.5 mmol) in dioxane (30.0 mL) was added 2 M aq. K_3PO_4 (4.24 g, 10.0 mmol). After being degassed under Ar for 15 min, the reaction mixture was heated at 80 °C until all the starting materials consumed. The dioxane was evaporated under vacuum and the aqueous layer was extracted with ethyl acetate (EtOAc, 3×50.0 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The remained mixture was purified by flash column chromatography (1:2 hexane/EtOAc) to afford **5c**.

To a solution of **5c** (5.0 mmol) in CH_2Cl_2 (30.0 mL) was added Me_3OBF_4 (0.78 g, 5.5 mmol), and then stirred overnight at room temperature. Freshly prepared $MesNHNH_2$ (1.50 g, 10.0 mmol) in CH_2Cl_2 (5.0 mL) was added, and the mixture was stirred for 10 h. Then, CH_2Cl_2 was evaporated in vacuo, and the residue was dissolved in PhCl (30.0 mL) followed by the addition of $(EtO)_3CH$ (8.0 mL, 50 mmol). The mixture was heated at 110 ℃ for 48 h. The solvent was evaporated, and the residue was purified by flash column chromatography (1:1 to 1:2 hexane/EtOAc) to afford NHC-**L**. Yield = 28%, white solid; ^1H NMR (400 MHz, DMSO) δ 11.21 (s, 1H), 7.83 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.26-7.08 (m, 3H), 6.13 (d, J = 4.0 Hz, 1H), 5.26 (d, J = 16.0 Hz, 1H), 5.09 (d, J = 16.0 Hz, 1H), 5.02 (t, J = 4.4 Hz, 1H), 3.51 (dd, J = 17.2, 4.8 Hz, 1H), 3.19 (d, J = 17.2 Hz, 1H), 2.36 (s, 6H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.27, 146.68, 144.99, 144.82, 143.15, 142.02, 139.98, 136.42, 134.64, 133.95, 133.37, 133.11, 132.63, 131.08, 129.05, 127.26, 82.18, 66.24, 64.90, 41.86, 26.30, 25.82, 22.06. HRMS (ESI-TOF) $[M-BF_4]^+$ calculated for $[C_{28}H_{28}ON_3]^+$ 422.2232, observed 422.2233. $[\alpha]^{25}_D$ = 7.8 (c = 1.0, $CHCl_3$).

Synthesis of enal substrates[4]



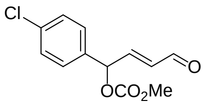
(*E*)-Methyl (4-oxo-1-phenylbut-2-en-1-yl) (1a)[4]. To a solution of enal **6** (1.3 g, 10.0 mmol) in anhydrous THF (25.0 ml) at 0 °C was added PhMgCl (12.0 mL, 1.0 M in THF, 12.0 mmol) over 5 min. The reaction mixture was stirred for 30 min at the same temperature and methyl chloroformate (0.93 mL, 12.0 mmol) was added via syringe. After 2 h, the reaction mixture was quenched by 1 M HCl (5.0 mL) and stirred for 2 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $NaSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 to 10:1 hexane/EtOAc) to afford enal **1a** (1.65 g, 75% overall yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, J = 7.8 Hz, 1H), 7.47-7.23 (m, 5H), 6.87 (dd, J = 15.7, 4.8 Hz, 1H), 6.49-6.13 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.70 (s), 154.60 (s), 151.80 (s), 135.98 (s), 131.41 (s), 129.23 (s), 128.98 (s), 127.29 (s), 77.77 (s), 55.12 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{12}O_4Na]^+$ 243.0628, observed 243.0629.



1b

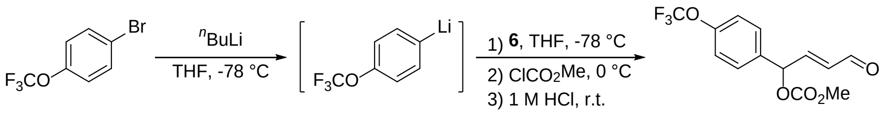
(*E*)-1-(4-fluorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from enal **6,** 4-

fluorophenylmagnesium bromide, methyl chloroformate following the same procedure that was used for preparation of enal **1a** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.7 Hz, 1H), 7.50-7.28 (m, 2H), 7.17-6.96 (m, 2H), 6.84 (dd, J = 15.8, 4.6 Hz, 1H), 6.32 (ddd, J = 8.1, 7.0, 3.2 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.54 (s), 163.05 (d, J = 248.9 Hz), 154.52 (s), 151.33 (s), 131.55 (s), 129.37 (d, J = 8.5 Hz), 116.01 (d, J = 21.8 Hz), 77.02 (s), 55.17 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{12}H_{11}O_4FNa]^+$ 261.0534, observed 261.0531.



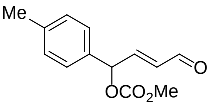
1c

(*E*)-1-(4-chlorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from enal **6,** 4-chlorophenylmagnesium bromide, methyl chloroformate following the same procedure that was used for preparation of enal **1a** (purified by flash column chromatography: 5-10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.6 Hz, 1H), 7.59-7.15 (m, 4H), 6.82 (dd, J = 15.7, 4.8 Hz, 1H), 6.30 (ddd, J = 10.3, 6.0, 4.6 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.46 (s), 154.49 (s), 151.00 (s), 135.28 (s), 134.50 (s), 131.69 (s), 129.23 (s), 128.70 (s), 76.98 (s), 55.22 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{12}H_{11}O_4ClNa]^+$ 277.0238, observed 277.0239.



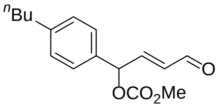
1d

(*E*)-methyl (4-oxo-1-(4-(trifluoromethoxy)phenyl)but-2-en-1-yl) carbonate (1d)[4]. To a solution of bromo-4-(trifluoromethoxy)benzene (6.0 mmol) in anhydrous THF (10.0 mL) at -78 °C was added ^{n}BuLi (6.0 mmol) over 5 min. The reaction was stirred for 30 min at the same temperature and a solution of enal **6** (5.0 mmol) in THF (5 mL) was added via syringe. The mixture was slowly warmed to 0 ^{o}C and methyl chloroformate (6.0 mmol) was added at the same temperature. The reaction was monitored by TLC and quenched with 1 M HCl (5.0 mL). The resulting mixture was stirred at room temperature for 2 h. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×20.0 mL). The combined organic layer was washed with brine, dried over $NaSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 to 10:1 hexane/EtOAc) to afford enal **1d** (40% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, J = 7.7 Hz, 1H), 7.50-7.33 (m, 2H), 7.25 (d, J = 8.8 Hz, 2H), 6.84 (dd, J = 15.9, 4.6 Hz, 1H), 6.33 (m, J = 8.1, 4.8, 1.6 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.45 (s), 176.61 (s), 154.57 (s), 150.90 (s), 149.77 (s), 134.75 (s), 131.86 (s), 129.01 (s), 121.48 (s), 120.37 (d, *J* = 257.8 Hz), 55.32 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{13}H_{11}O_5F_3Na]^+$ 327.0451, observed 327.0449.



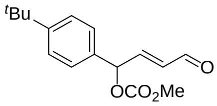
1e

(*E*)-methyl (4-oxo-1-(p-tolyl)but-2-en-1-yl) carbonate was prepared from 4-bromotoluene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, J = 7.7 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.86 (dd, J = 15.7, 4.8 Hz, 1H), 6.33 (ddd, J = 15.7, 7.7, 1.7 Hz, 1H), 6.28 (dd, J = 4.7, 1.6 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.83 (s), 154.72 (s), 152.11 (s), 139.39 (s), 133.07 (s), 131.37 (s), 129.73 (s), 127.40 (s), 77.81 (s), 55.15 (s), 21.23 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{13}H_{14}O_4Na]^+$ 257.0784, observed 257.0781.



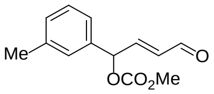
1f

(*E*)-1-(4-butylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-4-butylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 5.9 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.87 (dd, J = 15.7, 4.8 Hz, 1H), 6.38 – 6.30 (m, 1H), 6.31 – 6.28 (m, 1H), 3.79 (s, 3H), 2.60 (d, J = 7.8 Hz, 2H), 1.65 – 1.49 (m, 2H), 1.34 (dq, J = 14.7, 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.82 (s), 154.73 (s), 152.14 (s), 144.37 (s), 133.19 (s), 131.35 (s), 129.09 (s), 127.41 (s), 77.83 (s), 55.14 (s), 35.38 (s), 33.48 (s), 22.32 (s), 13.91 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{16}H_{20}O_4Na]^+$ 299.1254, observed 299.1255.



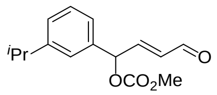
1g

(*E*)-1-(4-(tert-butyl)phenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-4-tert-butylbenzene, *n*-butyllithium, enal **6**, and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ9.58 (d, J = 7.7 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 6.87 (dd, J = 15.6, 4.8 Hz, 1H), 6.40 – 6.27 (m, 2H), 3.79 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.84 (s), 154.75 (s), 152.54 (s), 152.12 (s), 132.95 (s), 131.38 (s), 127.19 (s), 126.01 (s), 77.75 (s), 55.15 (s), 34.71 (s), 31.23 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{16}H_{20}O_4Na]^+$ 299.1254, observed 299.1256.



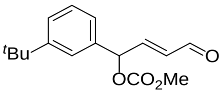
1h

(*E*)-methyl (4-oxo-1-(m-tolyl)but-2-en-1-yl) carbonate was prepared from 1-bromo-3-isopropylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ9.58 (d, J = 7.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.20 – 7.11 (m, 2H), 6.86 (dd, J = 15.7, 4.8 Hz, 1H), 6.33 (ddd, J = 15.7, 7.7, 1.6 Hz, 1H), 6.28 (dd, J = 4.8, 1.6 Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.76 (s), 154.62 (s), 151.97 (s), 138.86 (s), 135.85 (s), 131.30 (s), 130.01 (s), 128.87 (s), 127.86 (s), 124.34 (s), 77.85 (s), 55.12 (s), 21.30 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{13}H_{14}O_4Na$]$^+$ 257.0784, observed 257.0785.



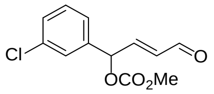
1i

(*E*)-1-(3-isopropylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-3-methylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ9.59 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25 (m, 1H), 7.22 – 7.16 (m, 2H), 6.88 (dd, J = 15.6, 4.9 Hz, 1H), 6.44 – 6.24 (m, 2H), 3.80 (s, 3H), 2.91 (dd, J = 13.8, 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.85 (s), 154.73 (s), 152.14 (s), 149.92 (s), 135.92 (s), 131.36 (s), 129.05 (s), 127.39 (s), 125.54 (s), 124.82 (s), 78.08 (s), 55.18 (s), 34.09 (s), 23.91 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{15}H_{18}O_4Na$]$^+$ 285.1097, observed 285.1100.



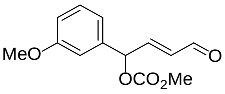
1j

(*E*)-1-(3-(tert-butyl)phenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-3-(tert-butyl)benzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ9.59 (d, J = 7.8 Hz, 1H), 7.41 (m,, 1H), 7.35 (m, 2H), 7.21 – 7.16 (m, 1H), 6.95 – 6.78 (m, 1H), 6.34 (m, 2H), 3.81 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.83 (s), 176.61 (s), 154.75 (s), 152.21 (s), 135.64 (s), 131.35 (s), 128.80 (s), 126.44 (s), 124.48 (s), 124.30 (s), 78.27 (s), 55.17 (s), 34.82 (s), 31.28 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{16}H_{20}O_4Na$]$^+$ 299.1254, observed 299.1255.



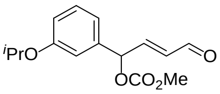
1k

(*E*)-1-(3-chlorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from enal **6**, 3-chlorophenylmagnesium bromide and methyl chloroformate following the same procedure that was used for preparation of enal **1a** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ9.58 (d, J = 7.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.28 – 7.21 (m, 1H), 6.82 (dd, J = 15.7, 4.8 Hz, 1H), 6.33 (ddd, J = 15.7, 7.6, 1.6 Hz, 1H), 6.28 (dd, J = 4.8, 1.5 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.47 (s), 154.45 (s), 150.77 (s), 137.96 (s), 134.93 (s), 131.80 (s), 130.29 (s), 129.41 (s), 127.33 (s), 125.37 (s), 76.91 (s), 55.27 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{12}H_{11}O_4ClNa$]$^+$ 277.0238, observed 277.0231.



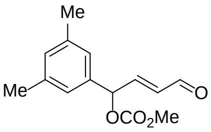
1l

(*E*)-1-(3-methoxyphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from enal **6**, 3-methoxyphenylmagnesium bromide and methyl chloroformate following the same procedure that was used for preparation of enal **1a** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ9.57 (d, J = 7.7 Hz, 1H), 7.38 – 7.20 (m, 1H), 7.00 – 6.73 (m, 4H), 6.48 – 6.21 (m, 2H), 3.80 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.72 (s), 159.96 (s), 154.58 (s), 151.71 (s), 137.43 (s), 131.39 (s), 130.08 (s), 119.40 (s), 114.65 (s), 112.71 (s), 77.64 (s), 55.20 (d, J = 9.8 Hz). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{14}O_5Na]^+$ 273.0733, observed 273.0734.



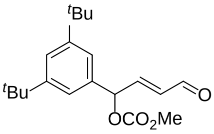
1m

(*E*)-1-(3-isopropoxyphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-3-isopropoxybenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ9.58 (d, J = 7.7 Hz, 1H), 7.33 – 7.24 (m, 1H), 6.94 – 6.78 (m, 4H), 6.33 (ddd, J = 15.7, 7.7, 1.6 Hz, 1H), 6.27 (dd, J = 4.8, 1.6 Hz, 1H), 4.55 (dt, J = 12.1, 6.1 Hz, 1H), 3.80 (s, 3H), 1.33 (d, J = 6.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.78 (s), 158.38 (s), 154.69 (s), 151.84 (s), 137.50 (s), 131.46 (s), 130.13 (s), 119.22 (s), 116.21 (s), 114.85 (s), 77.74 (s), 69.97 (s), 55.20 (s), 21.97 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{18}O_5Na]^+$ 301.1046, observed 301.1048



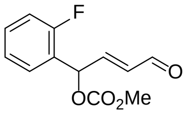
1n

(*E*)-1-(3,5-dimethylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-3,5-dimethylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 7.7 Hz, 1H), 6.99 (d, J = 13.7 Hz, 3H), 6.85 (dd, J = 15.7, 4.8 Hz, 1H), 6.33 (ddd, J = 15.7, 7.7, 1.6 Hz, 1H), 6.24 (dd, J = 4.8, 1.6 Hz, 1H), 3.80 (s, 3H), 2.32 (d, J = 0.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.89 (s), 154.72 (s), 152.20 (s), 138.79 (s), 135.89 (s), 131.27 (s), 130.96 (s), 125.03 (s), 78.00 (s), 55.16 (s), 21.24 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{18}O_5Na]^+$ 271.0941, observed 271.0942.



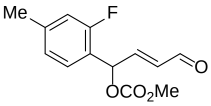
1o

(*E*)-1-(3,5-di-tert-butylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-3,5-di-tert-butylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.59 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 1.6 Hz, 1H), 7.19 (d, J = 1.6 Hz, 2H), 6.90 (dd, J = 15.9, 4.6 Hz, 1H), 6.46 – 6.27 (m, 2H), 3.81 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.95 (s), 154.80 (s), 152.59 (s), 151.74 (s), 135.11 (s), 131.15 (s), 123.54 (s), 121.56 (s), 78.64 (s), 55.15 (s), 34.98 (s), 31.40 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{15}H_{18}O_5Na$]$^+$ 355.1880, observed 355.1879.



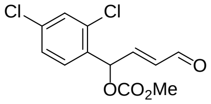
1p

(*E*)-1-(2-fluorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 2-bromofluorobenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.59 (d, J = 7.7 Hz, 1H), 7.37 (m,, 2H), 7.19 (m, 1H), 7.13 – 7.07 (m, 1H), 6.92 – 6.84 (m, 1H), 6.63 (dd, J = 4.8, 1.6 Hz, 1H), 6.32 (ddd, J = 15.8, 7.7, 1.6 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.63 (s), 159.82 (d, J = 249.2 Hz), 154.51 (s), 150.54 (s), 131.85 (s), 130.99 (d, J = 8.2 Hz), 128.30 (d, J = 3.0 Hz), 124.81 (d, J = 3.6 Hz), 123.65 (d, J = 13.4 Hz), 116.00 (d, J = 21.1 Hz), 71.97 (d, J = 3.1 Hz), 55.34 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{12}H_{11}O_4FNa$]$^+$ 261.0534, observed 261.0532



1q

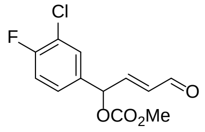
(*E*)-1-(2-fluoro-4-methylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-2-fluoro-4-methylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.57 (d, J = 7.7 Hz, 1H), 7.24 (m, 1H), 6.98 (d, J = 7.9 Hz, 1H), 6.94 – 6.83 (m, 2H), 6.57 (dd, J = 4.8, 1.6 Hz, 1H), 6.30 (ddd, J = 15.8, 7.7, 1.6 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.73 (s), 159.75 (d, J = 248.9 Hz), 152.72 (d, J = 459.1 Hz), 141.92 (d, J = 8.2 Hz), 131.71 (s), 126.82 (dd, J = 330.6, 3.3 Hz), 120.45 (d, J = 13.9 Hz), 116.48 (d, J = 21.0 Hz), 72.02 (d, J = 2.9 Hz), 55.27 (s), 21.17 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [$C_{13}H_{13}O_4FNa$]$^+$ 275.0690, observed 275.0689.



1r

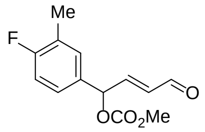
(*E*)-1-(2,4-dichlorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 1-bromo-2,4-dichlorobenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.57 (d, J = 7.6 Hz, 1H), 7.40 (m, 2H), 7.30 (dd, J = 8.4, 1.9 Hz, 1H), 6.82 (dd, J = 15.8, 4.7 Hz, 1H), 6.72 – 6.61 (m, 1H), 6.31 (ddd, J =

15.8, 7.6, 1.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.46 (s), 154.34 (s), 149.52 (s), 135.64 (s), 133.25 (s), 132.91 (s), 132.00 (s), 129.80 (s), 128.93 (s), 128.08 (s), 73.81 (s), 55.47 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{12}H_{10}O_4 Cl_2Na]^+$ 310.9848, observed 310.9849.



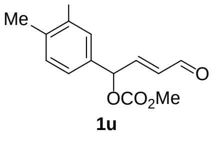
1s

(*E*)-1-(3-chloro-4-fluorophenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 4-bromo-2-chloro-1-fluorobenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 7.6 Hz, 1H), 7.42 (dd, J = 7.8, 7.3 Hz, 1H), 7.32 – 7.19 (m, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.86 (dd, J = 15.8, 4.8 Hz, 1H), 6.60 (d, J = 4.8 Hz, 1H), 6.34 – 6.28 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.46 (s), 156.36 (s), 154.38 (s), 149.67 (s), 132.11 (s), 131.51 (s), 126.48 (s), 125.45 (d, J = 13.3 Hz), 125.24 (d, J = 4.6 Hz), 121.85 (d, J = 17.8 Hz), 71.79 (d, J = 2.8 Hz), 55.46 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{12}H_{10}O_4FClNa]^+$ 295.0144, observed 295.0142.



1t

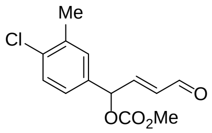
(*E*)-1-(4-fluoro-3-methylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 4-bromo-1-fluoro-2-methylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 7.7 Hz, 1H), 7.17 (m, 2H), 7.01 (t, J = 8.8 Hz, 1H), 6.83 (dd, J = 15.7, 4.7 Hz, 1H), 6.31 (ddd, J = 15.7, 7.7, 1.6 Hz, 1H), 6.26 (dd, J = 4.7, 1.6 Hz, 1H), 3.79 (s, 3H), 2.27 (d, J = 1.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.65 (s), 162.67 (s), 160.70 (s), 154.63 (s), 151.61 (s), 131.55 (d, J = 8.3 Hz), 130.69 (d, J = 5.6 Hz), 126.63 (d, J = 8.5 Hz), 125.87 (d, J = 17.9 Hz), 115.62 (d, J = 22.9 Hz), 77.26(s), 5.21 (s), 14.54 (d, J = 3.1 Hz). HRMS (ESI-TOF) [M+Na]$^+$ calculated for $[C_{13}H_{13}O_4Na]^+$ 275.0690, observed 275.0691.



1u

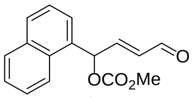
(*E*)-1-(3-fluoro-4-methylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 4-bromo-2-fluoro-1-methylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 7.7 Hz, 1H), 7.20 (m, 1H), 7.07 – 7.00 (m, 1H), 6.83 (dd, J = 15.7, 4.8 Hz, 1H), 6.32 (ddd, J = 15.7, 7.7, 1.6 Hz, 1H), 6.26 (dd, J = 4.8, 1.5 Hz, 1H), 3.80 (s, 1H), 2.26 (d, J = 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.60 (s), 161.37 (d, J = 246.6 Hz), 154.60 (s), 151.21 (s), 135.56 (s), 132.06 (d, J = 5.4 Hz), 131.73

(s), 126.24 (d, J = 17.2 Hz), 122.71 (d, J = 3.2 Hz), 113.97 (d, J = 23.6 Hz), 77.29 (s), 55.25 (s), 14.38 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{13}H_{13}O_4Na]^+$ 275.0690, observed 275.0689.



1v

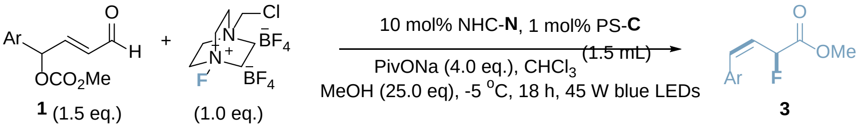
(*E*)-1-(4-chloro-3-methylphenyl)-4-oxobut-2-en-1-yl methyl carbonate was prepared from 4-bromo-1-chloro-2-methylbenzene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (dd, J = 7.7, 2.2 Hz, 1H), 7.36 (dd, J = 8.2, 1.7 Hz, 1H), 7.28-7.21 (m, 1H), 7.13 (dd, J = 8.2, 1.6 Hz, 1H), 6.82 (dd, J = 15.7, 4.7 Hz, 1H), 6.32 (ddd, J = 15.8, 7.7, 1.3 Hz, 1H), 6.25 (dd, J = 4.7, 1.3 Hz, 3H), 3.80 (d, J = 1.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.59 (s), 154.60 (s), 151.28 (s), 137.07 (s), 135.47 (s), 134.58 (s), 131.66 (s), 129.82 (s), 129.72 (s), 126.05 (s), 77.20 (s), 55.27 (s), 20.10 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{13}H_{13}O_4ClNa]^+$ 291.0395, observed 275.0696.



1w

(*E*)-methyl (1-(naphthalen-1-yl)-4-oxobut-2-en-1-yl) carbonate was prepared from 1-bromonaphthalene, *n*-butyllithium, enal **6** and methyl chloroformate following the same procedure that was used for preparation of enal **1d** (purified by flash column chromatography with 20:1 to 10:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ9.60 (s, 1H), 8.04-7.84 (m, 4H), 7.71-7.51 (m, 2H), 7.45 (dd, J = 8.4, 1.8 Hz, 1H), 6.94 (dd, J = 15.8, 4.7 Hz, 1H), 6.49 (dd, J = 4.7, 1.6 Hz, 1H), 6.40 (ddd, J = 15.8, 7.7, 1.6 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.67 (s), 154.65 (s), 151.67 (s), 133.46 (s), 133.21 (s), 133.05 (s), 131.59 (s), 129.05 (s), 128.10 (s), 127.72 (s), 126.97 (s), 126.86 (s), 126.67 (s), 124.27 (s), 77.95 (s), 55.18 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{16}H_{14}O_4Na]^+$ 293.0784, observed 293.0784.

Synthesis of the chiral (*Z*)-allylic fluorides

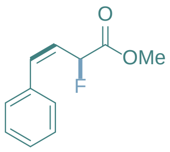


General procedure: NHC-**N** (10 mol%), PS-**C** ($[Ir(dF\text{-}ppy)_2(bpy)]PF_6$, 1 mol%), Selectfluor (0.1 mmol) and PivONa (0.4 mmol) were weighted into a 10 mL vial successively. Mixed solvent ($CHCl_3$/MeOH (1.5 mL/0.1 mL)) was added, followed by the addition of enal **1** (0.15 mmol). The reaction flask was sealed with a rubber septum, degassed and back-filled with argon (3x). The resulting mixture was stirred and irradiated with 45 W blue LEDs at -5 °C for 18h. Upon complete consumption of the enal, the reaction was filtered through a plug of silica gel and concentrated under reduced pressure. The residue was purified by flash column chromatography (50:1 hexane/EtOAc) to afford the desired product **3**. The ee value was determined by chiral GC. The (*Z*/*E*) ratio was determined by GC.

The racemic products was obtained using racemic NHC-A with the same procedure as asymmetric one.

Characterization of the chiral (*Z*)-allylic fluorides

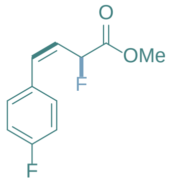
methyl (S,Z)-2-fluoro-4-phenylbut-3-enoate



3a

Colorless oil, 15.7 mg, yield : 81%. ee: 98%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.57-7.27 (m, 5H), 6.98 (dd, J = 11.3, 3.6 Hz, 1H), 5.82 (dt, J = 11.3, 9.9 Hz, 1H), 5.75 – 5.54 (m, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.46 (d, *J* = 26.5 Hz), 138.41 (d, *J* = 10.6 Hz), 135.05 (s), 128.99 (d, *J* = 2.7 Hz), 128.67 (s), 128.55 (s), 122.98 (d, *J* = 20.2 Hz), 84.50 (d, *J* = 177.5 Hz), 52.84 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.72 (s); HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{11}H_{11}O_2FNa]^+$ 217.0635, observed 217.0635. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 110 °C isotherm, hold time: 50 min): t_{major} = 34.689 min; t_{minor} = 31.936 min. $[\alpha]^{25}_D$ = 159.4 (c = 1.0, $CHCl_3$).

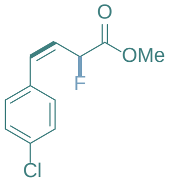
methyl (S,Z)-2-fluoro-4-(4-fluorophenyl)but-3-enoate



3b

Colorless oil, 14.8 mg, yield : 70%. ee: 97%, determined by chiral GC. *Z*/*E* = 10:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.29 (m, 2H), 7.06 (t, J = 8.6 Hz, 2H), 6.92 (dd, J = 11.3, 3.4 Hz, 1H), 5.80 (dd, J = 20.9, 10.1 Hz, 1H), 5.59 (dd, J = 47.8, 9.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.34 (d, *J* = 26.7 Hz), 162.88 (d, *J* = 248.7 Hz), 137.21 (d, *J* = 10.4 Hz), 130.84 (dd, *J* = 8.2, 2.7 Hz), 122.99 (d, *J* = 20.4 Hz), 115.71 (d, *J* = 21.6 Hz), 84.37 (d, *J* = 178.1 Hz), 52.89 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.76 (s), -174.86 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{11}H_{10}O_2F_2Na]^+$ 235.0541, observed 235.0539. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 110 °C isotherm, hold time: 50 min): t_{major} = 36.840 min; t_{minor} = 34.874 min. $[\alpha]^{25}_D$ = 108.7 (c = 1.0, $CHCl_3$).

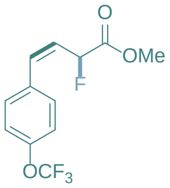
methyl (S,Z)-4-(4-chlorophenyl)-2-fluorobut-3-enoate



3c

Colorless oil, 16.2 mg, yield : 71%. ee: 92%, determined by chiral GC. *Z*/*E* = 6:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.25 (m, 4H), 6.92 (dd, J = 11.4, 3.5 Hz, 1H), 5.84 (dt, J = 11.4, 9.9 Hz, 1H), 5.59 (ddd, J = 47.8, 9.6, 0.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.01 (d, J = 26.3 Hz), 136.83 (d, J = 10.4 Hz), 134.44 (s), 133.21 (d, J = 3.1 Hz), 130.11 (d, J = 2.8 Hz), 128.70 (s), 123.43 (d, J = 20.4 Hz), 84.11 (d, J = 178.4 Hz), 52.71 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -175.14 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{11}H_{10}O_2FClNa]^+$ 251.0246, observed 251.0245. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 130 °C isotherm, hold time: 50 min): t_{major} = 38.335 min; t_{minor} = 37.237 min. $[\alpha]^{25}_D$ = 105.5 (c = 1.0, $CHCl_3$).

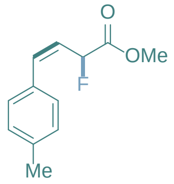
methyl (S,Z)-2-fluoro-4-(4-(trifluoromethoxy)phenyl)but-3-enoate



3d

Colorless oil, 17.0 mg, yield : 61%. ee: 94%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 7.29 – 7.13 (m, 2H), 6.94 (dd, J = 11.4, 3.5 Hz, 1H), 5.99 – 5.76 (m, 1H), 5.58 (dd, J = 47.8, 9.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.19 (d, *J* = 26.3 Hz), 149.33 (s), 136.78 (d, *J* = 10.4 Hz), 133.64 (s), 130.52 (d, *J* = 2.7 Hz), 123.90 (d, *J* = 20.5 Hz), 121.07 (s), 120.55 (d, *J* = 257.6 Hz), 84.29 (d, *J* = 178.6 Hz), 52.94 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.82 (s), -175.33 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{10}O_3F_4Na]^+$ 301.0458, observed 301.0458. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 105 °C isotherm, hold time: 60 min): t_{major} = 48.790 min; t_{minor} = 46.418 min. $[\alpha]^{25}_D$ = 112.8 (c = 1.0, $CHCl_3$).

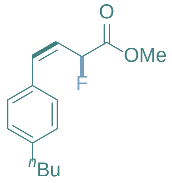
methyl (S,Z)-2-fluoro-4-(p-tolyl)but-3-enoate



3e

Colorless oil, 12.1 mg, yield : 58%. ee: 98%, determined by chiral GC. *Z*/*E* = 6:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.94 (dd, J = 11.0, 3.6 Hz, 1H), 5.84 – 5.39 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57 (d, J = 26.6 Hz), 138.58 (s), 138.40 (d, J = 10.5 Hz), 132.22 (s), 129.39 (s), 128.99 (d, J = 2.7 Hz), 122.26 (d, J = 20.1 Hz), 84.58 (d, J = 177.4 Hz), 52.81 (s), 21.37 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.25 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{13}O_2FNa]^+$ 231.0792, observed 231.0799. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 120 °C isotherm, hold time: 50 min): t_{major} = 37.374 min; t_{minor} = 34.940 min. $[\alpha]^{25}_D$ = 66.6 (c = 1.0, $CHCl_3$).

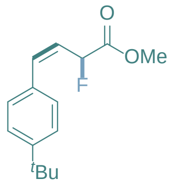
methyl (S,Z)-4-(4-butylphenyl)-2-fluorobut-3-enoate



3f

Colorless oil, 12.5 mg, yield : 50%. ee: 94%, determined by chiral GC. *Z*/*E* = 5:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.96 (dd, J = 10.7, 3.7 Hz, 1H), 5.95-5.51 (m, 2H), 3.84 (s, 3H), 2.83-2.53 (m, 2H), 1.82-1.51 (m, 3H), 1.43-1.25 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.37 (d, J = 26.7 Hz), 143.40 (s), 138.23 (d, J = 10.5 Hz), 132.17 (s), 128.78 (d, J = 2.7 Hz), 128.53 (s), 121.99 (d, J = 20.0 Hz), 84.39 (d, J = 177.3 Hz), 52.60 (s), 35.31 (s), 33.40 (s), 22.25 (s), 13.84 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.19 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{19}O_2FNa]^+$ 273.1261, observed 273.1261. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 150 °C isotherm, hold time: 50 min): t_{major} = 37.956 min; t_{minor} = 36.651 min. $[\alpha]^{25}_D$ = 199.8 (c = 1.0, $CHCl_3$).

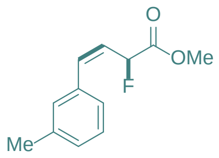
methyl (S,Z)-4-(4-(tert-butyl)phenyl)-2-fluorobut-3-enoate



3g

Colorless oil, 18.8 mg, yield : 75%. ee: 95%, determined by chiral GC. *Z*/*E* = 6:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.34 (d, J = 8.3 Hz, 2H), 6.96 (dd, J = 10.5, 3.7 Hz, 1H), 5.89-5.44 (m, 2H), 3.84 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35 (d, J = 26.7 Hz), 151.56 (s), 138.07 (d, J = 10.4 Hz), 132.02 (s), 128.64 (d, J = 2.7 Hz), 125.41 (s), 122.14 (d, J = 20.3 Hz), 84.40 (d, J = 177.3 Hz), 52.58 (s), 34.59 (s), 31.15 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.21 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{19}O_2FNa]^+$ 273.1261, observed 273.1261. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 145 °C isotherm, hold time: 50 min): t_{major} = 35.246 min; t_{minor} = 33.961 min. $[\alpha]^{25}_D$ = 147.2 (c = 1.0, $CHCl_3$).

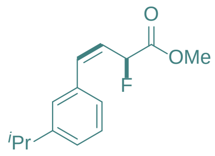
methyl (S,Z)-2-fluoro-4-(m-tolyl)but-3-enoate



3h

Colorless oil, 17.5 mg, yield : 84%. ee: 95%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 1H), 7.20-7.12 (m, 3H), 6.95 (dd, J = 11.2, 3.6 Hz, 1H), 5.98-5.42 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.52 (d, J = 26.6 Hz), 138.61 (d, J = 10.5 Hz), 138.34 (s), 135.00 (s), 129.68 (d, J = 2.6 Hz), 129.32 (s), 128.57 (s), 126.06 (d, J = 2.7 Hz), 122.76 (d, J = 20.1 Hz), 84.56 (d, J = 177.3 Hz), 52.81 (s), 21.53 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.62 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{13}O_2FNa]^+$ 231.0792, observed 231.0789. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 120 °C isotherm, hold time: 50 min): t_{major} = 32.632 min; t_{minor} = 30.694 min. $[\alpha]^{25}_D$ = 169.7 (c = 1.0, $CHCl_3$).

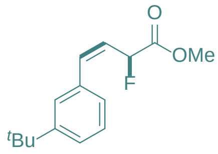
methyl (S,Z)-2-fluoro-4-(3-isopropylphenyl)but-3-enoate



3i

Colorless oil, 19.8 mg, yield : 84%. ee: 95%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 1H), 7.24 (s, 1H), 7.24-7.14 (m, 2H), 6.98 (dd, *J* = 11.2, 3.6 Hz, 1H), 5.80 (dd, *J* = 21.1, 10.1 Hz, 1H), 5.66 (dd, *J* = 47.3, 9.8 Hz, 1H), 3.84 (s, 3H), 2.92 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.54 (d, *J* = 26.4 Hz), 149.34 (s), 138.76 (d, *J* = 10.6 Hz), 135.03 (s), 128.62 (s), 127.15 (d, *J* = 2.7 Hz), 126.85 (s), 126.44 (d, *J* = 2.7 Hz), 122.69 (d, *J* = 20.3 Hz), 84.65 (d, *J* = 177.2 Hz), 52.83 (s), 34.16 (s), 24.04 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.25 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{14}H_{17}O_2FNa]^+$ 259.1105, observed 259.1108. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 130 °C isotherm, hold time: 50 min): t_{major} = 39.116 min; t_{minor} = 37.509 min. $[\alpha]^{25}_D$ = 145.3 (c = 1.0, $CHCl_3$).

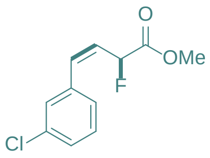
methyl (S,Z)-4-(3-(tert-butyl)phenyl)-2-fluorobut-3-enoate



3j

Colorless oil, 12.3 mg, yield : 52%. ee: 97%, determined by chiral GC. *Z*/*E* = 8:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.41-7.29 (m, 2H), 7.20 (d, J = 7.4 Hz, 1H), 7.01 (dd, J = 11.2, 3.6 Hz, 1H), 5.89-5.40 (m, 2H), 3.86 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.33 (d, J = 26.7 Hz), 151.43 (s), 138.69 (d, J = 10.5 Hz), 134.49 (s), 128.18 (s), 126.02 (d, J = 2.7 Hz), 125.88 (d, J = 2.7 Hz), 125.39 (s), 122.43 (d, J = 20.5 Hz), 84.47 (d, J = 177.2 Hz), 52.62 (s), 34.63 (s), 31.18 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.14 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{19}O_2FNa]^+$ 273.1261, observed 259.1108. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 135 °C isotherm, hold time: 50 min): t_{major} = 39.322min; t_{minor} = 37.596 min. $[\alpha]^{25}_D$ = 164.4 (c = 1.0, $CHCl_3$). $[\alpha]^{25}_D$ = 149.5 (c = 1.0, $CHCl_3$).

methyl (S,Z)-4-(3-chlorophenyl)-2-fluorobut-3-enoate

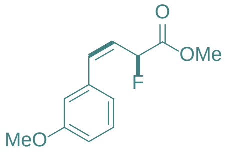


3k

Colorless oil, 14.3 mg, yield : 63%. ee: 94%, determined by chiral GC. *Z*/*E* = 7:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.39 (s, 1H), 7.37-7.27 (m, 3H), 6.91 (dd, J = 11.4, 3.4 Hz, 1H), 5.87 (dt, J = 11.3, 9.9 Hz, 1H), 5.60 (ddd, J = 47.8, 9.6, 0.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.94 (d, J = 26.3 Hz), 136.62 (s), 136.52 (s), 134.44 (s), 129.74 (s), 128.76 (d, J = 2.8 Hz), 128.44 (s), 126.90 (d, J = 2.7 Hz), 124.08 (d, J =

20.5 Hz), 84.05 (d, J = 178.4 Hz), 52.73 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.61 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{11}H_{10}O_2FClNa]^+$ 251.0246, observed 251.0247. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 130 °C isotherm, hold time: 50 min): t_{major} = 33.258min; t_{minor} = 31.450 min. $[\alpha]^{25}_{D}$ = 133.9 (c = 1.0, $CHCl_3$).

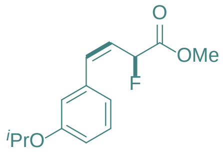
methyl (S,Z)-2-fluoro-4-(3-methoxyphenyl)but-3-enoate



3l

Colorless oil, 16.3 mg, yield : 75%. ee: 93%, determined by chiral GC. *Z*/*E* = 8:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.01-6.91 (m, 3H), 6.88 (dd, *J* = 7.5, 2.0 Hz, 1H), 5.80 (dd, *J* = 21.1, 10.3 Hz, 1H), 5.68 (dd, *J* = 47.4, 9.7 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45 (d, J = 26.4 Hz), 159.77 (s), 138.24 (d, J = 10.6 Hz), 136.33 (s), 129.70 (s), 123.20 (d, J = 20.4 Hz), 121.41 (d, J = 2.7 Hz), 114.42 (s), 114.31 (d, J = 2.8 Hz), 84.58 (d, J = 177.6 Hz), 55.39 (s), 52.85 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.87 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{13}O_3FNa]^+$ 247.0741, observed 247.0742. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 135 °C isotherm, hold time: 50 min): t_{major} = 34.960min; t_{minor} = 32.344 min. $[\alpha]^{25}_{D}$ = 101.5 (c = 1.0, $CHCl_3$).

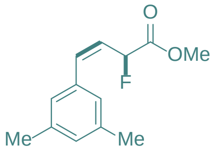
methyl (S,Z)-2-fluoro-4-(3-isopropoxyphenyl)but-3-enoate



3m

Colorless oil, 16.3 mg, yield : 73%. ee: 95%, determined by chiral GC. *Z*/*E* = 7:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 1H), 6.95-6.92 (m, 3H), 6.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.94-5.53 (m, 2H), 4.55 (dt, *J* = 12.1, 6.0 Hz, 1H), 3.83 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.48 (d, J = 26.5 Hz), 158.11 (s), 138.41 (d, J = 10.5 Hz), 136.34 (s), 129.72 (s), 122.98 (d, J = 20.3 Hz), 121.21 (d, J = 2.7 Hz), 116.33 (s), 116.10 (s), 84.57 (d, J = 177.6 Hz), 70.10 (s), 52.84 (s), 22.16 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.72 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{14}H_{17}O_3FNa]^+$ 247.0741, observed 247.0747. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 140 °C isotherm, hold time: 50 min): t_{major} = 37.935 min; t_{minor} = 35.719 min. $[\alpha]^{25}_{D}$ = 147.4 (c = 1.0, $CHCl_3$).

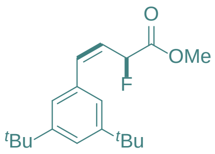
methyl (S,Z)-4-(3,5-dimethylphenyl)-2-fluorobut-3-enoate



3n

Colorless oil, 17.5 mg, yield : 79%. ee: 94%, determined by chiral GC. *Z*/*E* = 7:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-7.00 (m, 3H), 6.94 (dd, *J* = 11.1, 3.7 Hz, 1H), 5.89-5.52 (m, 2H), 3.85 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.55 (d, J = 26.4 Hz), 138.78 (d, J = 10.4 Hz), 138.22 (s), 134.95 (s), 130.21 (s), 126.78 (d, J = 2.7 Hz), 122.58 (d, J = 19.8 Hz), 84.62 (d, J = 177.2 Hz), 52.75 (s), 21.40 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.34 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{13}H_{15}O_2FNa]^+$ 245.0948, observed 245.0945. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 130 °C isotherm, hold time: 50 min): t_{major} = 29.467 min; t_{minor} = 27.635 min. $[\alpha]^{25}_{D}$ = 70.0 (c = 1.0, $CHCl_3$).

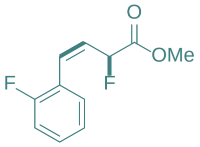
methyl (S,Z)-4-(3,5-di-tert-butylphenyl)-2-fluorobut-3-enoate



3o

Colorless oil, 24.2 mg, yield : 79%. ee: 96%, determined by chiral GC. *Z*/*E* = 7:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 1.6 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 2H), 7.03 (dd, *J* = 10.9, 3.6 Hz, 1H), 6.00-5.48 (m, 2H), 3.88 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57 (d, J = 26.8 Hz), 151.16 (s), 139.34 (d, J = 10.6 Hz), 134.32 (d, J = 3.0 Hz), 123.40 (d, J = 2.6 Hz), 122.66 (s), 122.34 (d, J = 20.8 Hz), 84.87 (d, J = 176.9 Hz), 52.76 (s), 34.99 (s), 31.52 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.64 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{19}H_{27}O_2FNa]^+$ 329.1887, observed 329.1888. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 155 °C isotherm, hold time: 50 min): t_{major} = 34.624 min; t_{minor} = 32.882 min. $[\alpha]^{25}_{D}$ = 121.7 (c = 1.0, $CHCl_3$).

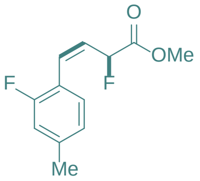
methyl (S,Z)-2-fluoro-4-(2-fluorophenyl)but-3-enoate



3p

Colorless oil, 11.0 mg, yield : 52%. ee: 95%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (tdd, *J* = 7.3, 5.4, 1.7 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 12.1 Hz, 1H), 5.94 (dt, *J* = 11.4, 9.7 Hz, 1H), 5.59 (dd, *J* = 47.8, 9.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.15 (d, *J* = 26.1 Hz), 131.20 (dd, *J* = 10.4, 4.1 Hz), 130.84 (s), 130.81 (s), 130.78 (s), 130.57 (d, *J* = 8.5 Hz), 124.83 (d, *J* = 20.2 Hz), 124.23 (d, *J* = 3.8 Hz), 115.71 (d, *J* = 21.4 Hz), 84.64 (d, *J* = 178.2 Hz), 52.88 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.28 (s), -176.35 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{11}H_{10}O_2F_2Na]^+$ 235.0541, observed 235.0540. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 110 °C isotherm, hold time: 50 min): t_{major} = 31.556 min; t_{minor} = 28.600 min. $[\alpha]^{25}_{D}$ = 59.3 (c = 1.0, $CHCl_3$).

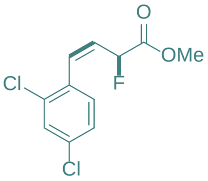
methyl (S,Z)-2-fluoro-4-(2-fluoro-4-methylphenyl)but-3-enoate



3q

Colorless oil, 15.4 mg, yield : 68%. ee: 94%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42 – 7.29 (m, 1H), 7.13 – 6.96 (m, 2H), 6.91 (d, J = 11.0 Hz, 1H), 5.88 (dt, J = 11.3, 9.7 Hz, 1H), 5.59 (dd, J = 47.8, 9.6 Hz, 1H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.06 (d, *J* = 26.3 Hz), 160.08 (d, *J* = 251.5 Hz), 141.23 (d, *J* = 7.9 Hz), 131.05 (dd, *J* = 10.5, 4.0 Hz), 130.21 (d, *J* = 3.0 Hz), 124.73 (d, *J* = 3.2 Hz), 123.87 (d, *J* = 20.2 Hz), 119.67 (dd, *J* = 14.3, 3.2 Hz), 116.05 (d, *J* = 21.3 Hz), 84.49 (d, *J* = 177.9 Hz), 52.65 (s), 21.12 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38 (s), -175.87 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{12}O_2F_2Na]^+$ 249.0698, observed 249.0698. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 120 °C isotherm, hold time: 50 min): t_{major} = 34.498 min; t_{minor} = 31.909 min. $[\alpha]^{25}_{D}$ = 151.2 (c = 1.0, $CHCl_3$).

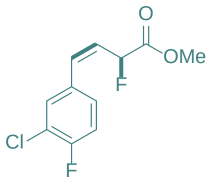
methyl (S,Z)-4-(2,4-dichlorophenyl)-2-fluorobut-3-enoate



3r

Colorless oil, 18.0 mg, yield : 69%. ee: 88%, determined by chiral GC. *Z*/*E* = 9:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47-7.39 (m, 2H), 7.34-7.14 (m, 1H), 6.97 (dd, J = 11.4, 3.3 Hz, 1H), 5.94 (dt, J = 11.4, 9.6 Hz, 1H), 5.43 (ddd, J = 47.8, 9.6, 0.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.94 (d, J = 26.1 Hz), 135.25 (s), 134.72 (d, J = 2.9 Hz), 134.36 (d, J = 10.3 Hz), 131.92 (d, J = 2.9 Hz), 131.58 (d, J = 2.7 Hz), 129.66 (s), 127.25 (s), 125.02 (d, J = 20.4 Hz), 84.40 (d, J = 179.3 Hz), 52.97 (s). ^{19}F NMR (376 MHz, CDCl$_3$) δ -176.83 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [C$_{11}$H$_9$O$_2$FCl$_2$Na]$^+$ 284.9856, observed 284.9857. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 140 °C isotherm, hold time: 50 min): t$_{major}$ = 39.296 min; t$_{minor}$ = 37.594 min. [α]$^{25}_{D}$ = 115.2 (c = 1.0, CHCl$_3$).

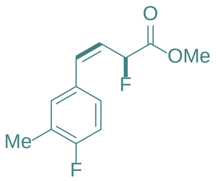
methyl (S,Z)-4-(3-chloro-4-fluorophenyl)-2-fluorobut-3-enoate



3s

Colorless oil, 14.8 mg, yield : 60%. ee: 88%, determined by chiral GC. *Z*/*E* = 3:1, determined by GC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46-7.32 (m, 2H), 7.11 (td, *J* = 7.9, 0.9 Hz, 1H), 6.98 (d, *J* = 11.6 Hz, 1H), 5.98 (dt, *J* = 11.4, 9.8 Hz, 1H), 5.53 (ddd, *J* = 47.8, 9.5, 0.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.69 (d, J = 26.0 Hz), 155.59 (d, J = 251.4 Hz), 130.85 (s), 130.01 (dd, J = 10.3, 3.8 Hz), 128.84 (t, J = 2.5 Hz), 125.73 (d, J = 20.6 Hz), 124.42 (d, J = 4.9 Hz), 124.24 (dd, J = 14.4, 2.9 Hz), 121.46 (d, J = 17.8 Hz), 84.25 (d, J = 179.1 Hz), 52.76 (s). ^{19}F NMR (376 MHz, CDCl$_3$) δ -116.42 (s), -177.10 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [C$_{11}$H$_9$O$_2$F$_2$ClNa]$^+$ 269.0151, observed 269.0150. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 130 °C isotherm, hold time: 50 min): t$_{major}$ = 32.409 min; t$_{minor}$ = 30.030 min. [α]$^{25}_{D}$ = 121.8 (c = 1.0, CHCl$_3$).

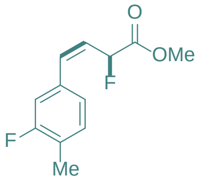
methyl (S,Z)-2-fluoro-4-(4-fluoro-3-methylphenyl)but-3-enoate



3t

Colorless oil, 16.5 mg, yield : 73%. ee: 96%, determined by chiral GC. *Z*/*E* = 8:1, determined by GC. ^{1}H NMR (400 MHz, CDCl$_3$) δ7.21-7.12 (m, 2H), 7.06-6.95 (m, 1H), 6.89 (dd, J = 11.3, 3.6 Hz, 1H), 5.77 (dd, J = 21.0, 9.9 Hz, 1H), 5.61 (dd, J = 47.8, 9.7 Hz, 1H), 3.83 (s, 3H), 2.28 (d, J = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.42 (d, J = 26.6 Hz), 161.49 (d, J = 247.5 Hz), 137.54 (d, J = 10.5 Hz), 132.26 (dd, J = 5.4, 2.8 Hz), 130.81 (s), 128.11 (dd, J = 8.1, 2.9 Hz), 125.26 (d, J = 17.8 Hz), 122.66 (d, J = 20.3 Hz), 115.28 (d, J = 22.6 Hz), 84.45 (d, J = 178.0 Hz), 52.87 (s), 14.69 (d, J = 3.5 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -117.09 (s), -174.61 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [C$_{12}$H$_{12}$O$_2$F$_2$Na]$^+$ 249.0698, observed 249.0702. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 120 °C isotherm, hold time: 50 min): t$_{major}$ = 33.745 min; t$_{minor}$ = 31.740 min. [α]$^{25}_{D}$ = 135.8 (c = 1.0, CHCl$_3$).

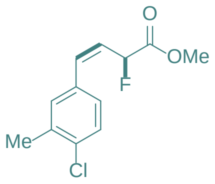
methyl (S,Z)-2-fluoro-4-(3-fluoro-4-methylphenyl)but-3-enoate



3u

Colorless oil, 16.3 mg, yield: 72%. ee: 96%, determined by chiral GC. *Z*/*E* = 6:1, determined by GC. ^{1}H NMR (400 MHz, CDCl$_3$) δ7.21-7.13 (m, 1H), 7.05 (d, J = 9.1 Hz, 1H), 6.88 (dd, J = 11.3, 3.5 Hz, 1H), 5.80 (dd, J = 21.1, 10.1 Hz, 1H), 5.72-5.50 (m, 1H), 3.83 (s, 1H), 2.28 (d, J = 1.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.30 (d, J = 26.4 Hz), 161.25 (d, J = 245.7 Hz), 137.10 (dd, J = 10.5, 2.0 Hz), 134.40 (dd, J = 7.9, 3.2 Hz), 131.67 (d, J = 5.6 Hz), 125.42 (d, J = 17.1 Hz), 124.55 (t, J = 3.0 Hz), 123.34 (d, J = 20.4 Hz), 115.48 (d, J = 20.4 Hz), 84.37 (d, J = 178.0 Hz), 52.89 (s), 14.54 (s). ^{19}F NMR (376 MHz, CDCl$_3$) δ -116.91 (s), -175.15 (s). HRMS (ESI-TOF) [M+Na]$^+$ calculated for [C$_{12}$H$_{12}$O$_2$F$_2$Na]$^+$ 249.0698, observed 249.0700. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 120 °C isotherm, hold time: 50 min): t$_{major}$ = 36.900 min; t$_{minor}$ = 34.063 min. [α]$^{25}_{D}$ = 164.4 (c = 195.7, CHCl$_3$).

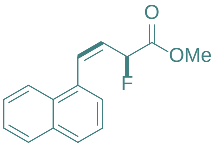
methyl (S,Z)-4-(4-chloro-3-methylphenyl)-2-fluorobut-3-enoate



3v

Colorless oil, 17.6 mg, yield: 73%. ee: 96%, determined by chiral GC. *Z*/*E* = 5:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 1H), 7.24 (s, 1H), 7.16 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.89 (dd, *J* = 11.3, 3.5 Hz, 1H), 5.81 (dt, *J* = 11.3, 9.8 Hz, 1H), 5.60 (ddd, *J* = 47.8, 9.6, 0.6 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31 (d, *J* = 26.2 Hz), 137.33 (d, *J* = 10.5 Hz), 136.43 (s), 134.82 (s), 133.52 (s), 131.48 (d, *J* = 2.8 Hz), 129.33 (s), 127.66 (d, *J* = 2.8 Hz), 123.36 (d, *J* = 20.3 Hz), 84.41 (d, *J* = 178.2 Hz), 52.89 (s), 20.22 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.93 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{12}H_{12}O_2FClNa]^+$ 265.0402, observed 265.0399. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 140 °C isotherm, hold time: 50 min): t_{major} = 35.405 min; t_{minor} = 33.976 min. $[\alpha]^{25}_D$ = 164.4 (c = 1.0, $CHCl_3$).

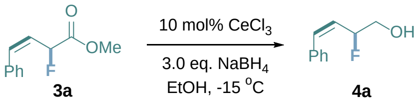
methyl (S,Z)-2-fluoro-4-(naphthalen-1-yl)but-3-enoate



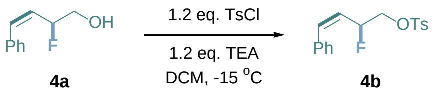
3w

Colorless oil, 6.1 mg, yield : 25%. ee: 97%, determined by chiral GC. *Z*/*E* = 0.5:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.90-7.81 (m, 3H), 7.56-7.49 (m, 2H), 7.47 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.15 (dd, *J* = 11.3, 3.6 Hz, 1H), 5.92 (dd, *J* = 21.1, 9.8 Hz, 1H), 5.76 (dd, *J* = 47.5, 9.7 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.28 (d, *J* = 26.5 Hz), 138.29 (d, *J* = 10.5 Hz), 132.97 (d, *J* = 13.9 Hz), 132.30 (d, *J* = 3.3 Hz), 128.24 (s), 128.20 (s), 128.14 (s), 127.58 (s), 126.50 (d, *J* = 11.5 Hz), 126.36 (d, *J* = 2.5 Hz), 123.07 (d, *J* = 20.2 Hz), 84.44 (d, *J* = 177.8 Hz), 52.68 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.52 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{15}H_{13}O_2FNa]^+$ 267.0792, observed 267.0790. GC (Astec CHIRALDEX^{TM} β-DM column(cat# 77023 AST; serial# 58478-03B), 165 °C isotherm, hold time: 50 min): t_{major} = 37.483 min; t_{minor} = 36.302 min. $[\alpha]^{25}_D$ = 202.1 (c = 1.0, $CHCl_3$).

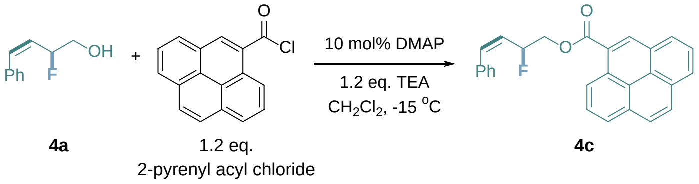
Derivatization of the chiral (*Z*)-allylic fluoride (3a)^{5,6}



To a solution of **3a** (0.1 mmol) in EtOH (1.0 mL) was added $NaBH_4$ (6.0 mg, 0.3 mmol) and $CeCl_3{\cdot}7H_2O$ (4.0 mg, 0.01 mmol). The resulting suspension was stirred at -15 °C for 24 h. The solvent was evaporated, and the residue was treated with 1N HCl (2.0 mL) at 0 °C. The aqueous solution was extracted with ethyl acetate (3×5.0 mL). The organic layer was combined and subsequently washed with saturated $NaHCO_3$ and brine. After drying over anhydrous Na_2SO_4, the solvent was evaporated, and the residue was purified by flash column chromatography (10:1 hexane/EtOAc) to afford homoallylic alcohol **4a**^{5}. Colorless oil, 20.7 mg, yield = 78%. ee = 91% ee, determined by chiral HPLC. *Z*/*E* = 8:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.61-7.16 (m, 5H), 6.84 (dd, J = 11.7, 3.3 Hz, 1H), 5.78 (dt, J = 11.7, 9.3 Hz, 1H), 5.60-5.14 (m, 1H), 3.91-3.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.44 (d, J = 10.8 Hz), 135.53 (d, J = 3.1 Hz), 128.66 (d, J = 2.7 Hz), 128.44 (s), 127.96 (s), 124.82 (d, J = 19.1 Hz), 89.63 (d, J = 162.1 Hz), 64.96 (d, J = 24.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -177.06 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{10}H_{12}OF]^+$ 167.0867, observed 167.0864. HPLC (Chiralpak-IA column, 98: 2 hexane/ethanol, flow rate: 1.0 mL/min): t_{major} = 19.410 min; t_{minor} = 14.982 min. $[\alpha]^{25}_D$ = 5.3 (c = 1.0, $CHCl_3$).



A flame-dried round bottom flask charged with 4-methylbenzenesulfonyl chloride (20.6 mg, 0.12 mmol), CH_2Cl_2 (1.0 mL), TEA (0.12 mmol), and **4a** (0.1 mmol) was stirred at -15 °C for 12 h. The reaction mixture was quenched with H_2O (1.0 mL), and extracted with CH_2Cl_2 (3×5.0 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 hexane/EtOAc) to afford **4b**[6]. Colorless oil, 18.9 mg, yield = 59%. ee = 90%, determined by chiral HPLC. *Z*/*E* > 10:1, determined by GC.. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.80 (d, J = 8.3 Hz, 2H), 7.41-7.28 (m, 5H), 7.24-7.18 (m, 2H), 6.84 (dd, J = 11.6, 3.2 Hz, 1H), 5.67 (dt, J = 11.6, 9.2 Hz, 1H), 5.53-5.18 (m, 1H), 4.28-4.23 (m, 1H), 4.19 (d, J = 4.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04 (s), 137.54 (d, J = 10.4 Hz), 134.97 (d, J = 3.0 Hz), 132.57 (s), 129.84 (s), 128.57 (s), 128.53 (s), 128.23 (s), 127.92 (s), 123.07 (d, J = 19.2 Hz), 85.65 (d, J = 169.6 Hz), 70.25 (d, J = 25.8 Hz), 21.61 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.20 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{17}H_{17}O_3FNaS]^+$ 343.0775, observed 343.0773. HPLC (Chiralpak-IA column, 98: 2 hexane/ethanol, flow rate: 1.0 mL/min): t_{major} = 19.879 min; t_{minor} = 18.145min. $[\alpha]^{25}_D$ = 10.4 (c = 1.0, $CHCl_3$).



To a solution of **4a** (0.1 mmol) in CH_2Cl_2 (1.0 mL) was added 2-pyrenyl acyl chloride (0.12 mmol), TEA (0.12 mmol) and DMAP (0.01 mmol). The reaction mixture was stirred at -15 °C for 12 h. Then, the reaction mixture was quenched with H_2O (1.0 mL), and extracted with CH_2Cl_2 (3×30.0 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 hexane/EtOAc) to afford **4c**[6]. Yellow solid, 20.5 mg, yield : 52%. ee: 90%, determined by chiral HPLC. *Z*/*E* >10:1, determined by GC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 9.4 Hz, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.35-8.22 (m, 3H), 8.17 (t, *J* = 8.3 Hz, 2H), 8.07 (dd, *J* = 12.2, 4.5 Hz, 2H), 7.51-7.23 (m, 5H), 6.95 (dd, *J* = 11.6, 3.2 Hz, 1H), 5.97 (dt, *J* = 11.6, 9.3 Hz, 1H), 5.88-5.53 (m, 1H), 4.94-4.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.45 (s), 136.93 (d, *J* = 10.5 Hz), 135.39 (d, *J* = 2.9 Hz), 134.51 (s), 131.29 (s), 130.91 (s), 130.27 (s), 129.65 (d, *J* = 14.8 Hz), 128.77 (d, *J* = 2.7 Hz), 128.56 (s), 128.55 (s), 128.11 (s), 127.08 (s), 126.30 (d, *J* = 5.3 Hz), 126.22 (s), 124.74 (s), 124.71 (s), 124.60 (s), 124.41 (s), 124.06 (s), 122.68 (s), 86.57 (d, *J* = 166.7 Hz), 66.10 (d, *J* = 24.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.83 (s). HRMS (ESI-TOF) $[M+Na]^+$ calculated for $[C_{27}H_{19}O_2FNa]^+$ 417.1261, observed 417.1260. HPLC (Chiralpak-IA column, 99.5: 0.5 hexane/ethanol, flow rate: 1.0 mL/min): t_{major} = 21.961 min; t_{minor} = 20.758 min. $[\alpha]^{25}_D$ = 32.9 (c = 1.0, $CHCl_3$).

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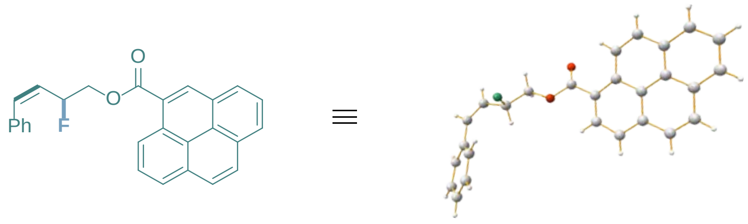
X-ray crystal structure



4c CCDC: 2005670

Figure S1. ORTEP drawing of the compound **4c** (CCDC: 2005670)

Table S6. Crystal data and structure refinement for **4c**.

Identification code	**4c**
Empirical formula	$C_{27}H_{19}FO_2$
Formula weight	394.42
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.5867(11)
b/Å	4.3673(4)
c/Å	16.8442(12)
α/°	90
β/°	104.545(8)
γ/°	90
Volume/Å^3	967.45(14)
Z	2
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.733
F(000)	412.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.42 to 149.418
Index ranges	$-16 \leq h \leq 16$, $-5 \leq k \leq 5$, $-9 \leq l \leq 20$
Reflections collected	3636
Independent reflections	3636 [R_{int} = 0.0505, R_{sigma} = 0.0473]
Data/restraints/parameters	3636/1/272
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0973, wR_2 = 0.2945
Final R indexes [all data]	R_1 = 0.0997, wR_2 = 0.2962
Largest diff. peak/hole / e Å^{-3}	0.53/-0.44

Flack/Hooft parameter	0.01(15)/0.00(10)

Table S7. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4c**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	2531(2)	1315(6)	4802.3(15)	38.0(7)
O1	386(2)	5278(10)	6175.1(17)	41.5(9)
O2	1880(2)	5385(9)	5834.4(17)	36.1(8)
C1	1945(3)	6085(10)	7221(2)	29.4(10)
C2	2805(3)	7881(12)	7309(3)	36.8(11)
C3	3394(3)	8633(11)	8068(3)	34.9(11)
C4	3178(3)	7459(11)	8774(3)	34.2(11)
C5	2319(3)	5517(12)	8710(2)	31.2(10)
C6	1675(3)	4855(10)	7913(2)	29.1(10)
C7	3792(4)	8126(12)	9581(3)	38.3(12)
C8	3593(3)	6937(14)	10256(3)	42.1(13)
C9	2752(3)	4898(11)	10211(2)	33.2(11)
C10	2105(3)	4252(11)	9417(3)	31.2(10)
C11	1267(3)	2300(11)	9360(3)	32.3(11)
C12	1074(4)	1024(13)	10066(3)	39.0(12)
C13	1709(4)	1727(12)	10838(3)	41.2(13)
C14	2528(4)	3618(11)	10902(3)	37.6(12)
C15	627(3)	1668(12)	8562(3)	36.3(12)
C16	818(3)	2899(12)	7879(3)	33.7(11)
C17	1292(3)	5492(12)	6372(2)	35.0(11)
C18	1345(3)	5075(13)	4981(2)	33.9(11)
C19	2161(3)	4268(11)	4550(2)	33.1(11)
C20	1784(3)	4350(11)	3630(3)	33.0(11)

Table S8. Anisotropic Displacement Parameters (Å^2×10^3) for **4c**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	42.9(12)	30.5(14)	41.8(11)	0.0(11)	13.1(10)	3.8(11)
O1	30.5(13)	64(2)	33.5(13)	2.0(16)	13.6(10)	2.3(16)
O2	32.8(13)	49.8(19)	28.6(11)	-3.2(13)	13.1(10)	0.5(15)
C1	36.5(19)	20(2)	34.5(17)	-1.0(16)	14.1(14)	3.5(17)
C2	42(2)	39(3)	34.2(18)	-0.8(19)	17.3(15)	6(2)
C3	36.1(19)	31(2)	39.2(19)	-6.6(18)	12.3(16)	2.7(19)
C4	33.7(19)	34(2)	36.4(19)	-4.3(18)	11.0(15)	6.5(18)

Table S8. Anisotropic Displacement Parameters (Å^2×10^3) for **4c**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5	27.2(16)	37(2)	31.4(16)	-2.0(17)	11.3(13)	11.8(18)
C6	27.4(17)	29(2)	33.5(17)	-5.9(16)	12.5(13)	7.3(16)
C7	33(2)	37(3)	44(2)	-11(2)	7.8(17)	-1(2)
C8	32(2)	61(3)	32.1(18)	-18(2)	4.8(16)	5(2)
C9	33.4(19)	35(2)	31.8(17)	-7.1(17)	8.4(15)	10.6(19)
C10	30.7(18)	31(2)	34.1(18)	-2.1(17)	13.0(14)	10.0(17)
C11	32.3(19)	31(2)	35.6(18)	1.1(17)	11.4(15)	8.4(18)
C12	40(2)	42(3)	37.0(19)	5(2)	12.1(16)	3(2)
C13	58(3)	39(3)	29.4(17)	5.2(18)	15.8(16)	13(2)
C14	47(2)	35(3)	32.5(19)	0.1(18)	13.2(16)	9(2)
C15	34.0(19)	40(3)	35.5(19)	-1.8(19)	10.5(15)	-4(2)
C16	32.0(19)	38(2)	31.3(17)	-0.6(19)	8.3(15)	5.0(19)
C17	40.8(19)	39(2)	31.3(16)	3.2(18)	19.9(13)	7.4(19)
C18	32.0(18)	42(3)	29.3(16)	4.8(18)	9.9(14)	2(2)
C19	39(2)	32(2)	29.9(18)	-2.0(17)	11.4(16)	2.3(19)
C20	34(2)	29(2)	34.4(19)	-3.9(17)	5.2(16)	0.4(18)
C21	41(2)	37(2)	25.0(16)	-4.4(18)	5.2(15)	8(2)
C22	42(2)	26(2)	30.8(16)	-6.2(16)	16.2(14)	3.8(18)
C23	50(2)	45(3)	31.2(18)	-1(2)	15.9(16)	1(2)
C24	39(2)	33(2)	48(2)	-2.0(19)	20.6(16)	1(2)
C25	32.7(19)	34(2)	55(2)	-16(2)	17.7(16)	-12.5(19)
C26	38(2)	40(3)	36.0(18)	-11.2(19)	10.7(16)	2(2)
C27	35.5(19)	35(2)	31.5(17)	-3.9(17)	12.7(14)	6.7(19)

Table S9. Bond Lengths for **4c**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C19	1.410(5)	C9	C14	1.391(7)
O1	C17	1.195(5)	C10	C11	1.406(6)
O2	C17	1.351(5)	C11	C12	1.397(7)
O2	C18	1.445(5)	C11	C15	1.433(6)
C1	C2	1.384(7)	C12	C13	1.402(6)
C1	C6	1.412(6)	C13	C14	1.369(7)
C1	C17	1.504(5)	C15	C16	1.353(7)
C2	C3	1.368(6)	C18	C19	1.511(7)
C3	C4	1.391(7)	C19	C20	1.505(6)
C4	C5	1.425(7)	C20	C21	1.299(7)
C4	C7	1.435(6)	C21	C22	1.495(6)

Table S9. Bond Lengths for **4c**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C6	1.436(5)	C22	C23	1.394(7)
C5	C10	1.407(6)	C22	C27	1.394(6)
C6	C16	1.435(6)	C23	C24	1.373(7)
C7	C8	1.338(7)	C24	C25	1.371(6)
C8	C9	1.436(7)	C25	C26	1.382(7)
C9	C10	1.433(5)	C26	C27	1.399(7)

Table S10. Bond Angles for **4c**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	O2	C18	115.8(3)	C12	C11	C10	120.4(4)
C2	C1	C6	121.0(4)	C12	C11	C15	121.5(4)
C2	C1	C17	118.7(4)	C11	C12	C13	120.0(5)
C6	C1	C17	120.4(4)	C14	C13	C12	120.2(5)
C3	C2	C1	121.1(4)	C13	C14	C9	121.4(4)
C2	C3	C4	120.7(5)	C16	C15	C11	121.4(4)
C3	C4	C5	120.0(4)	C15	C16	C6	122.0(4)
C3	C4	C7	122.5(4)	O1	C17	O2	123.6(4)
C5	C4	C7	117.5(4)	O1	C17	C1	126.7(4)
C4	C5	C6	119.0(4)	O2	C17	C1	109.6(4)
C10	C5	C4	120.6(4)	O2	C18	C19	104.7(3)
C10	C5	C6	120.3(4)	F1	C19	C18	108.5(4)
C1	C6	C5	118.1(4)	F1	C19	C20	109.6(4)
C1	C6	C16	124.7(4)	C20	C19	C18	112.8(4)
C16	C6	C5	117.1(4)	C21	C20	C19	127.6(4)
C8	C7	C4	122.3(5)	C20	C21	C22	128.0(4)
C7	C8	C9	121.6(4)	C23	C22	C21	119.2(4)
C10	C9	C8	117.7(4)	C27	C22	C21	122.6(4)
C14	C9	C8	122.9(4)	C27	C22	C23	118.1(4)
C14	C9	C10	119.4(4)	C24	C23	C22	120.8(4)
C5	C10	C9	120.3(4)	C25	C24	C23	121.2(5)
C11	C10	C5	121.1(4)	C24	C25	C26	119.4(4)
C11	C10	C9	118.6(4)	C25	C26	C27	120.0(4)
C10	C11	C15	118.1(4)	C22	C27	C26	120.4(4)

Table 11. Torsion Angles for **4c**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C19	C20	C21	-93.6(6)	C8	C9	C14	C13	178.8(5)
O2	C18	C19	F1	67.8(5)	C9	C10	C11	C12	0.0(7)

Table 11. Torsion Angles for **4c**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C18	C19	C20	-170.6(4)	C9	C10	C11	C15	-179.9(4)
C1	C2	C3	C4	3.9(8)	C10	C5	C6	C1	-177.6(4)
C1	C6	C16	C15	176.6(5)	C10	C5	C6	C16	0.4(6)
C2	C1	C6	C5	-0.1(6)	C10	C9	C14	C13	0.7(7)
C2	C1	C6	C16	-178.0(5)	C10	C11	C12	C13	1.0(7)
C2	C1	C17	O1	-144.1(6)	C10	C11	C15	C16	0.1(7)
C2	C1	C17	O2	32.6(6)	C11	C12	C13	C14	-1.2(8)
C2	C3	C4	C5	-1.7(7)	C11	C15	C16	C6	1.0(8)
C2	C3	C4	C7	178.4(5)	C12	C11	C15	C16	-179.8(5)
C3	C4	C5	C6	-1.3(7)	C12	C13	C14	C9	0.3(8)
C3	C4	C5	C10	178.5(4)	C14	C9	C10	C5	-179.8(4)
C3	C4	C7	C8	-178.5(5)	C14	C9	C10	C11	-0.8(7)
C4	C5	C6	C1	2.2(6)	C15	C11	C12	C13	-179.1(5)
C4	C5	C6	C16	-179.8(4)	C17	O2	C18	C19	-167.0(4)
C4	C5	C10	C9	-0.2(7)	C17	C1	C2	C3	176.3(5)
C4	C5	C10	C11	-179.1(4)	C17	C1	C6	C5	-179.4(4)
C4	C7	C8	C9	0.3(8)	C17	C1	C6	C16	2.7(7)
C5	C4	C7	C8	1.6(7)	C18	O2	C17	O1	1.7(8)
C5	C6	C16	C15	-1.3(7)	C18	O2	C17	C1	-175.2(4)
C5	C10	C11	C12	179.0(5)	C18	C19	C20	C21	145.3(5)
C5	C10	C11	C15	-0.9(7)	C19	C20	C21	C22	3.7(9)
C6	C1	C2	C3	-2.9(7)	C20	C21	C22	C23	-151.8(5)
C6	C1	C17	O1	35.2(8)	C20	C21	C22	C27	32.1(8)
C6	C1	C17	O2	-148.1(4)	C21	C22	C23	C24	-178.7(5)
C6	C5	C10	C9	179.6(4)	C21	C22	C27	C26	178.8(4)
C6	C5	C10	C11	0.6(7)	C22	C23	C24	C25	0.0(8)
C7	C4	C5	C6	178.6(4)	C23	C22	C27	C26	2.6(7)
C7	C4	C5	C10	-1.6(7)	C23	C24	C25	C26	2.2(8)
C7	C8	C9	C10	-2.1(7)	C24	C25	C26	C27	-2.0(7)
C7	C8	C9	C14	179.8(5)	C25	C26	C27	C22	-0.4(7)
C8	C9	C10	C5	2.0(7)	C27	C22	C23	C24	-2.4(7)
C8	C9	C10	C11	-179.0(4)					

Table 12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4c**.

Atom	*x*	*y*	*z*	U(eq)
H2	2984.65	8587.98	6844.01	44
H3	3944.99	9942.96	8113.54	42

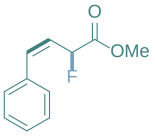
Table 12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4c**.

Atom	*x*	*y*	*z*	U(eq)
H7	4346.39	9429.07	9637	46
H8	4010.54	7442.17	10766.9	50
H12	525.36	-290.88	10024.2	47
H13	1572.51	905.21	11308.75	49
H14	2944.65	4056.86	11418.16	45
H15	68.99	384.56	8512.51	44
H16	379.14	2463.38	7371.59	40
H18A	1012.35	6978.58	4770.4	41
H18B	838.13	3467.12	4909.51	41
H19	2720.58	5735.07	4717.06	40
H20	1114.69	3737.17	3414.55	40
H21	1917.72	5199.29	2555.57	42
H23	3189.25	8903.84	2283.22	49
H24	4856.06	10316.29	2483.05	46
H25	6079.55	8489.89	3581.24	47
H26	5640.29	4931.33	4452.88	45
H27	3952.88	3442.5	4257.56	40

Crystal structure determination of 4c

Crystal Data for $C_{27}H_{19}FO_2$ (*M* =394.42 g/mol): monoclinic, space group P2_1 (no. 4), *a* = 13.5867(11) Å, *b* = 4.3673(4) Å, *c* = 16.8442(12) Å, *β* = 104.545(8)°, *V* = 967.45(14) Å^3, *Z* = 2, *T* = 100.0(2) K, μ(Cu Kα) = 0.733 mm^{-1}, *Dcalc* = 1.354 g/cm^3, 3636 reflections measured (5.42° ≤ 2Θ ≤ 149.418°), 3636 unique (R_{int} = 0.0505, R_{sigma} = 0.0473) which were used in all calculations. The final R_1 was 0.0973 (I > 2σ(I)) and wR_2 was 0.2962 (all data).

Chiral GC spectra



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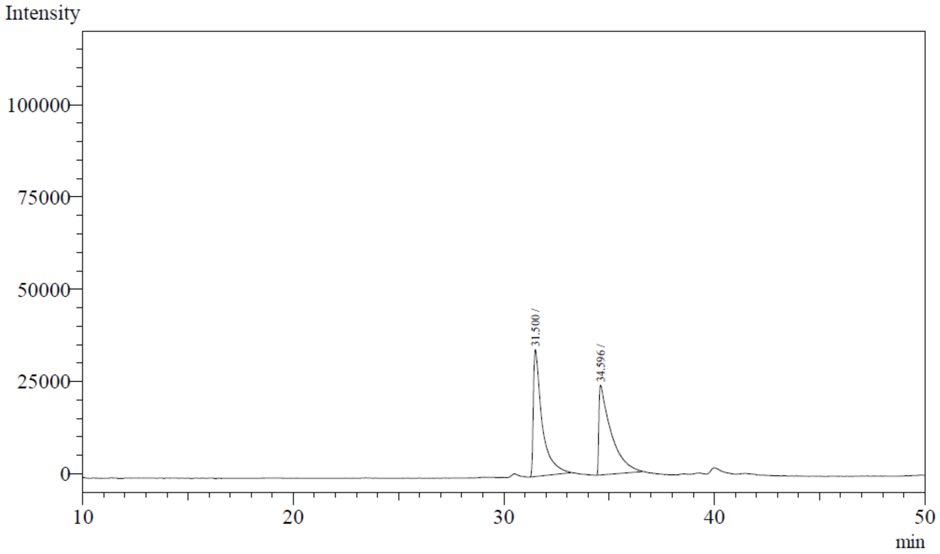

Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.500	995984	34414	50.41	58.56
2	34.596	979930	24351	49.59	41.44
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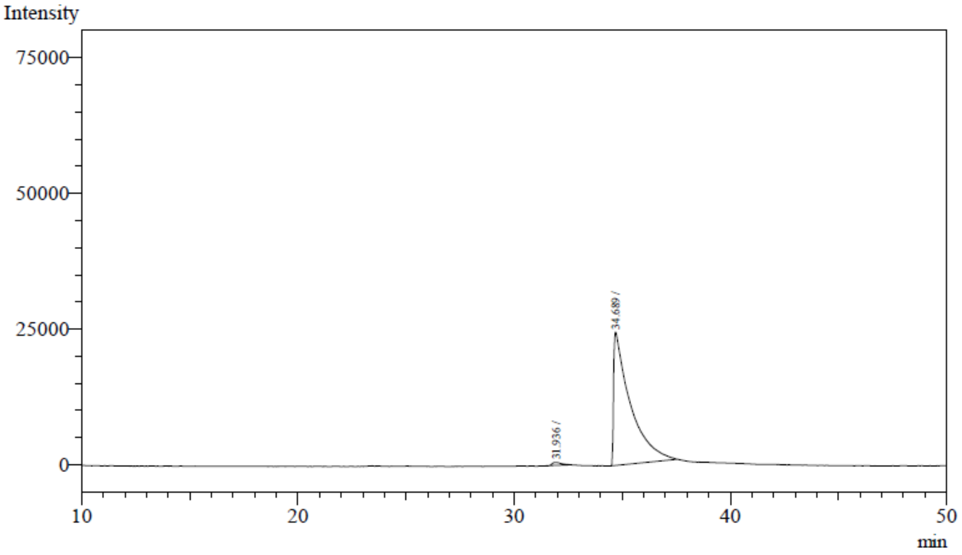
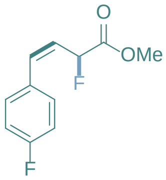


Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.936	15757	549	1.19	2.19
2	34.689	1311864	24575	98.81	97.81
Total		1327621	25124	100.00	100.00



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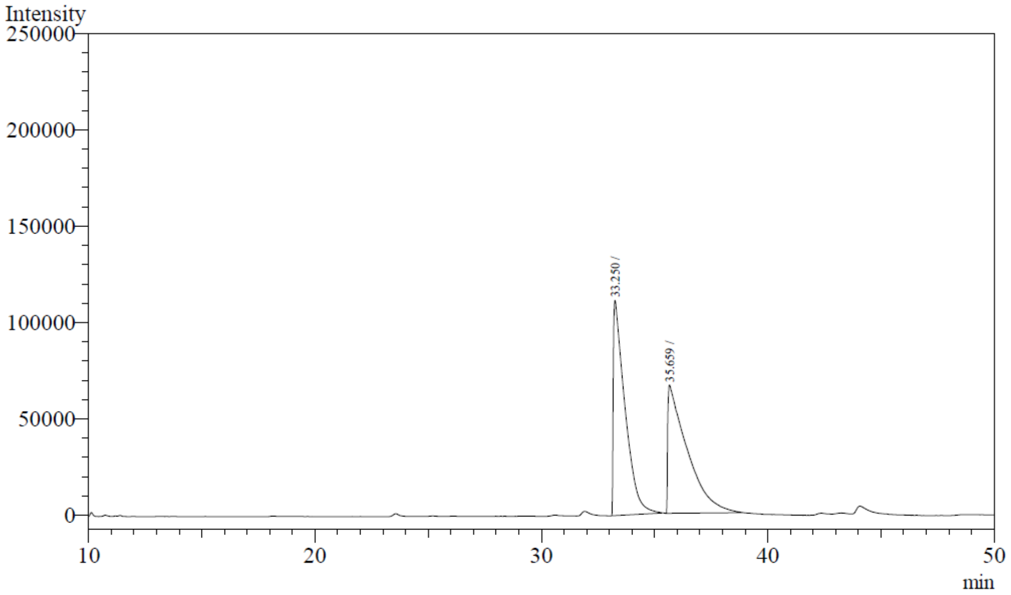
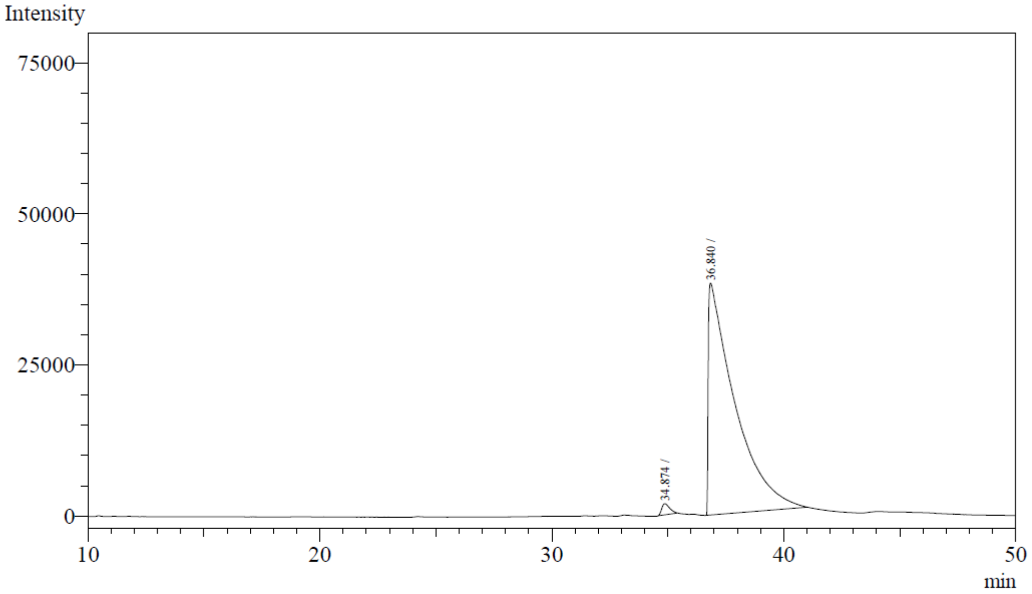
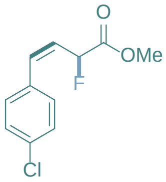


Peak#	Ret.Time	Area	Height	Area%	Height%
1	33.250	4007329	111586	50.24	62.66
2	35.659	3968459	66497	49.76	37.34
Total		7975788	178083	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	34.874	43543	1846	1.41	4.59
2	36.840	3034198	38386	98.59	95.41
Total		3077741	40232	100.00	100.00



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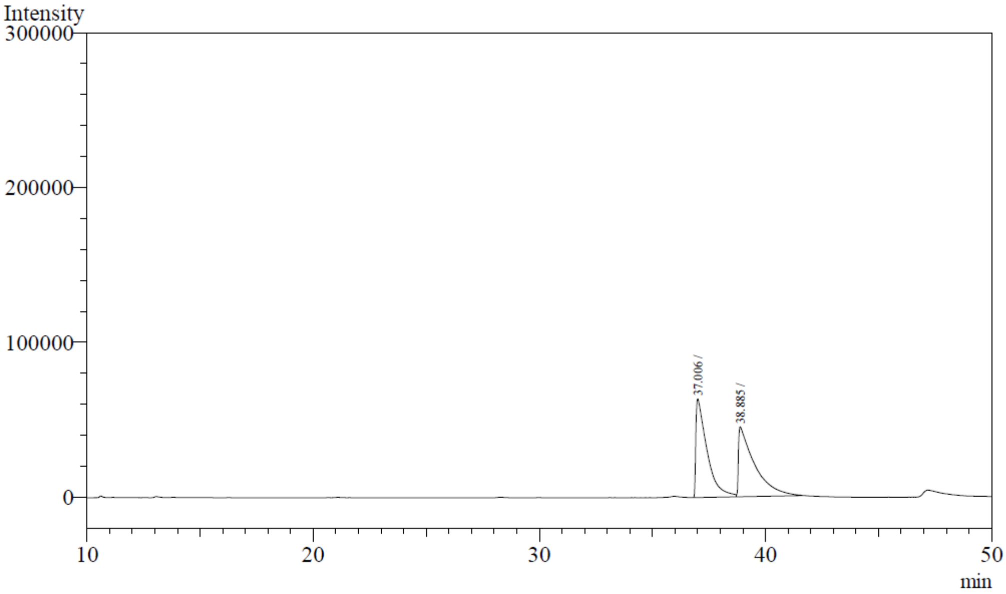
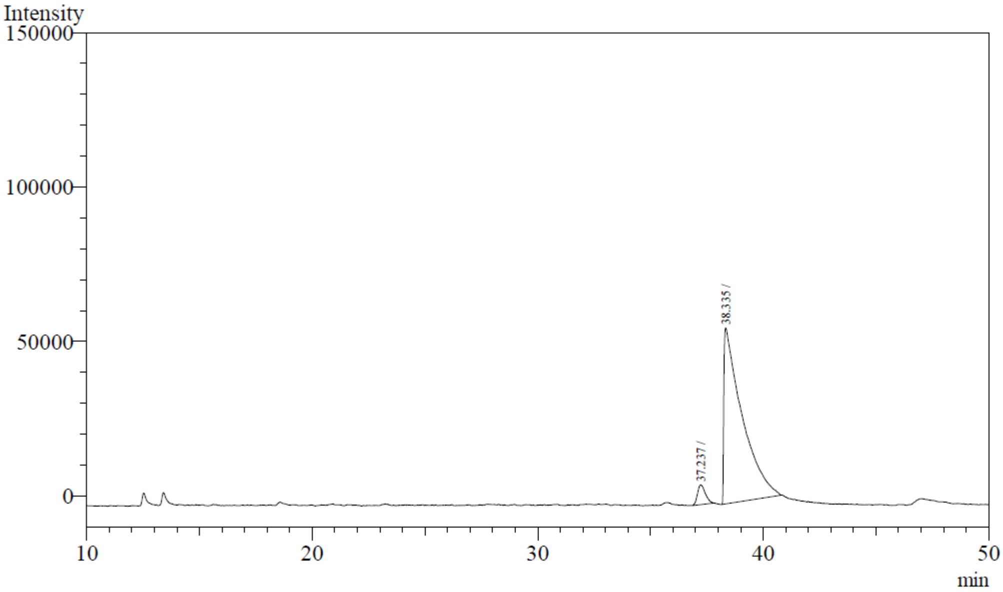
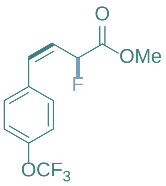


Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.006	2183497	63797	49.50	58.54
2	38.885	2227202	45190	50.50	41.46
Total		4410699	108987	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.237	153825	6365	4.61	10.04
2	38.335	3186548	57023	95.39	89.96
Total		3340373	63388	100.00	100.00



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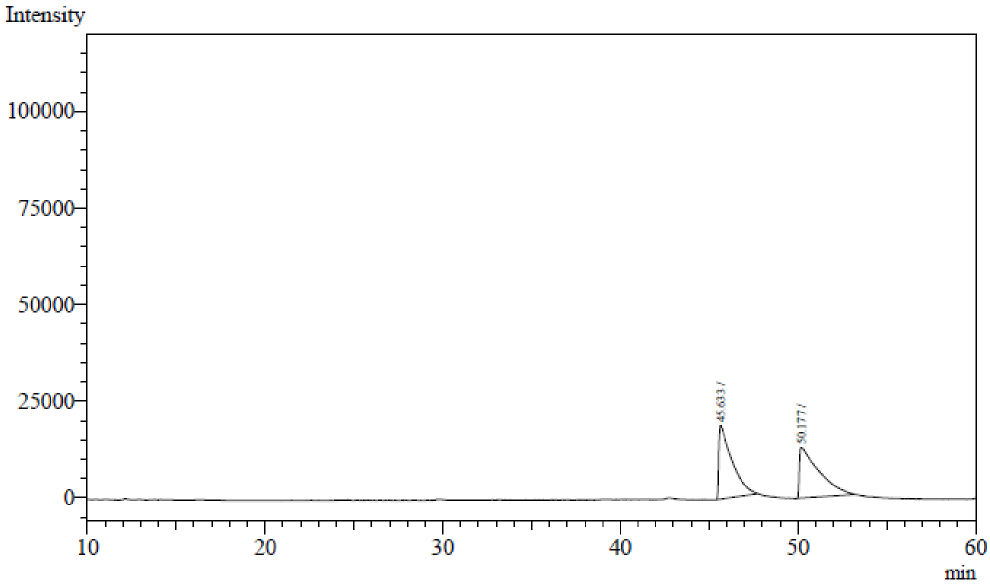
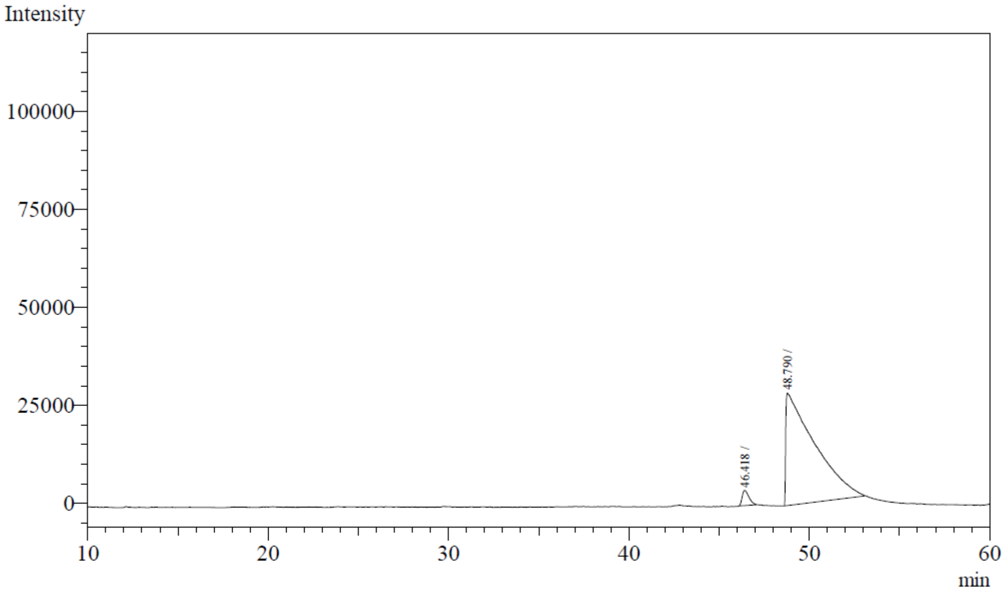
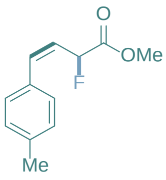


Peak#	Ret.Time	Area	Height	Area%	Height%
1	45.633	984294	19080	49.78	59.31
2	50.177	992824	13092	50.22	40.69
Total		1977118	32172	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	46.418	101516	3872	3.09	11.88
2	48.790	3178685	28722	96.91	88.12
Total		3280201	32594	100.00	100.00



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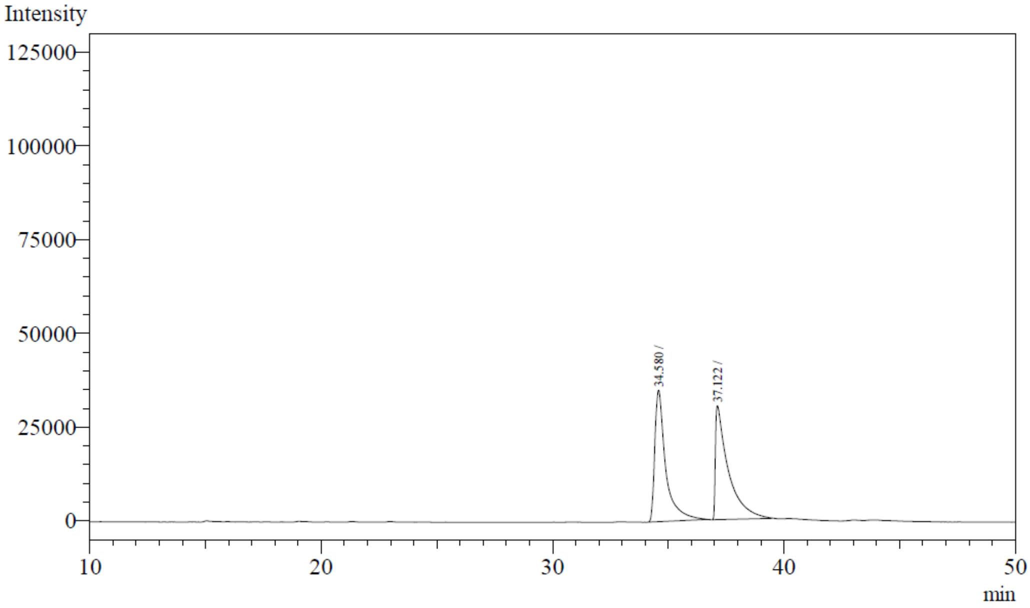
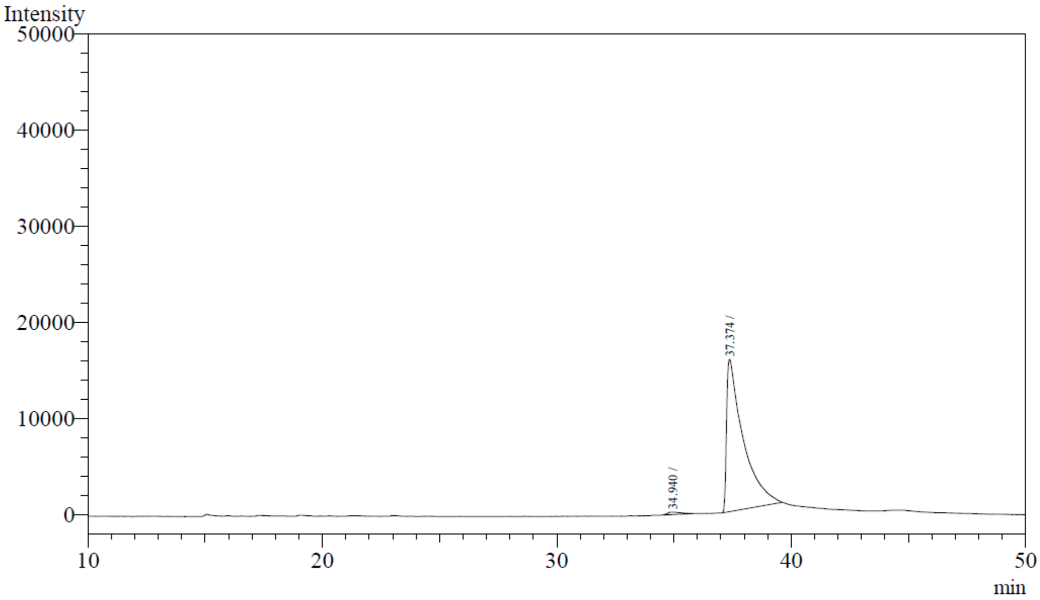
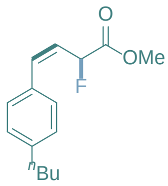


Peak#	Ret.Time	Area	Height	Area%	Height%
1	34.580	1153166	35037	49.55	53.57
2	37.122	1174238	30373	50.45	46.43
Total		2327404	65410	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	34.940	9839	258	1.25	1.61
2	37.374	777990	15829	98.75	98.39
Total		787829	16087	100.00	100.00



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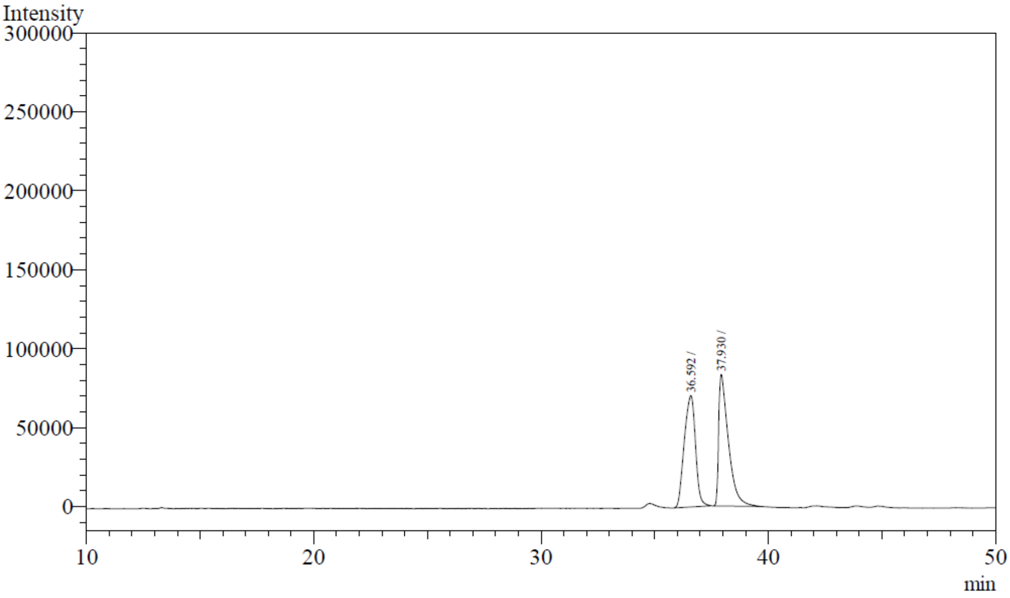
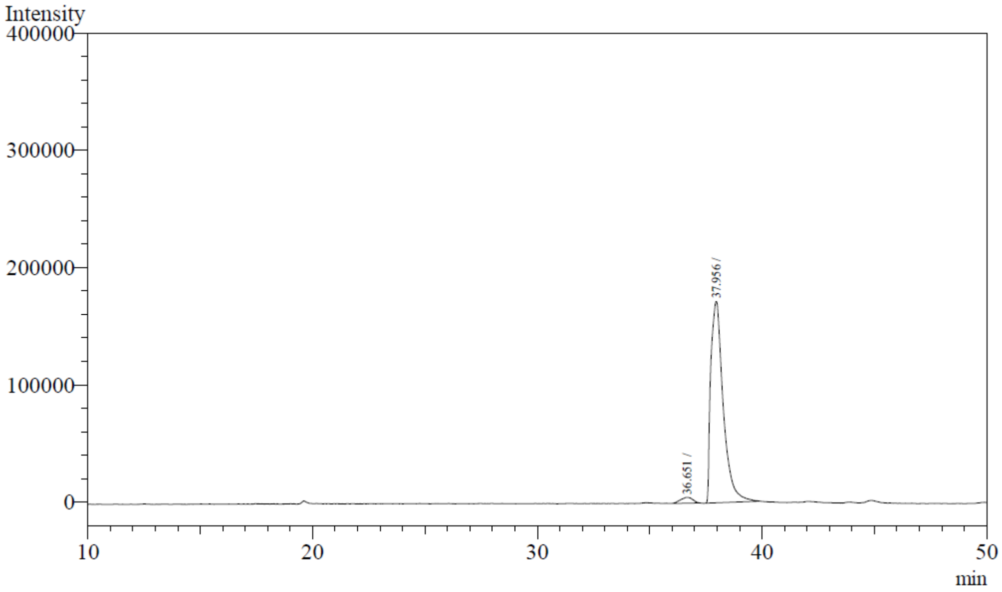
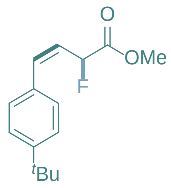


Peak#	Ret.Time	Area	Height	Area%	Height%
1	36.592	2417212	70624	49.34	45.88
2	37.930	2482037	83324	50.66	54.12
Total		4899249	153948	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	36.651	188549	5065	2.78	2.87
2	37.956	6591773	171661	97.22	97.13
Total		6780322	176726	100.00	100.00



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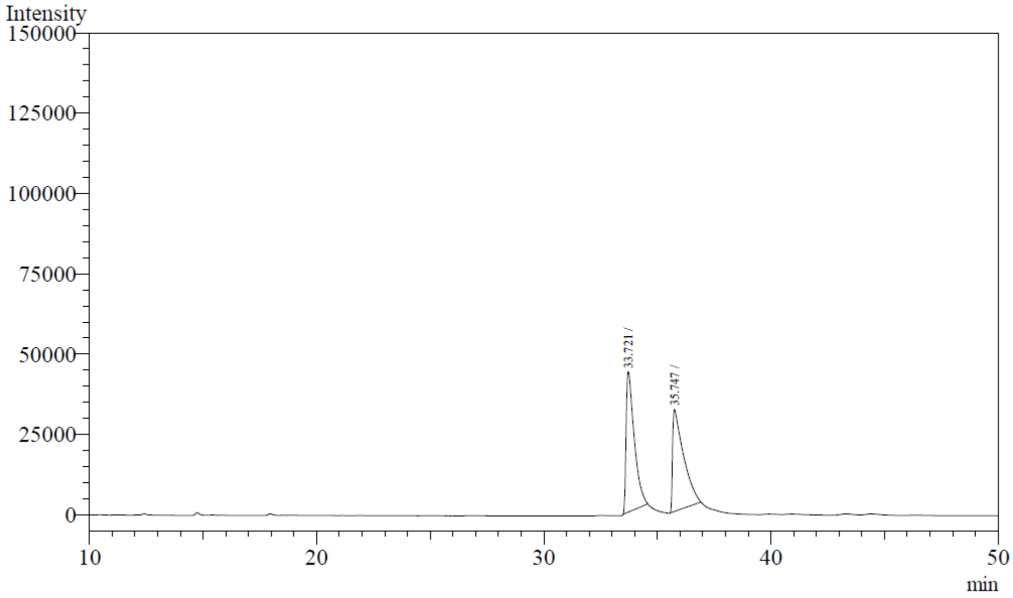
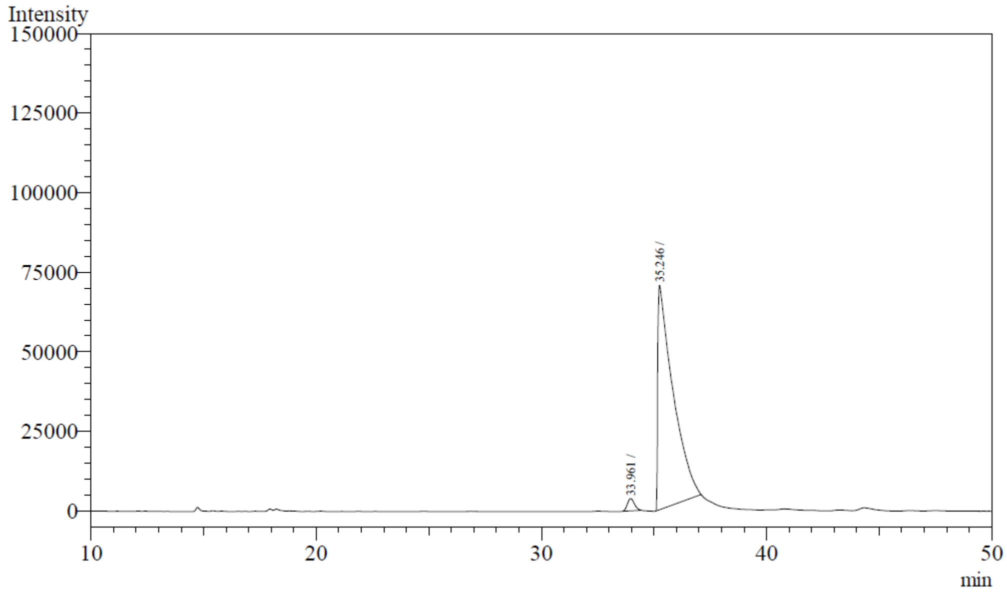
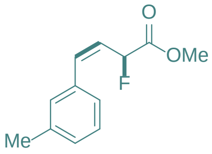


Peak#	Ret.Time	Area	Height	Area%	Height%
1	2.370	153378253	25370875	98.61	99.70
2	33.721	1090065	43769	0.70	0.17
3	35.747	1068340	31789	0.69	0.12
Total		155536658	25446433	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	33.961	84107	3881	2.48	5.22
2	35.246	3310672	70504	97.52	94.78
Total		3394779	74385	100.00	100.00



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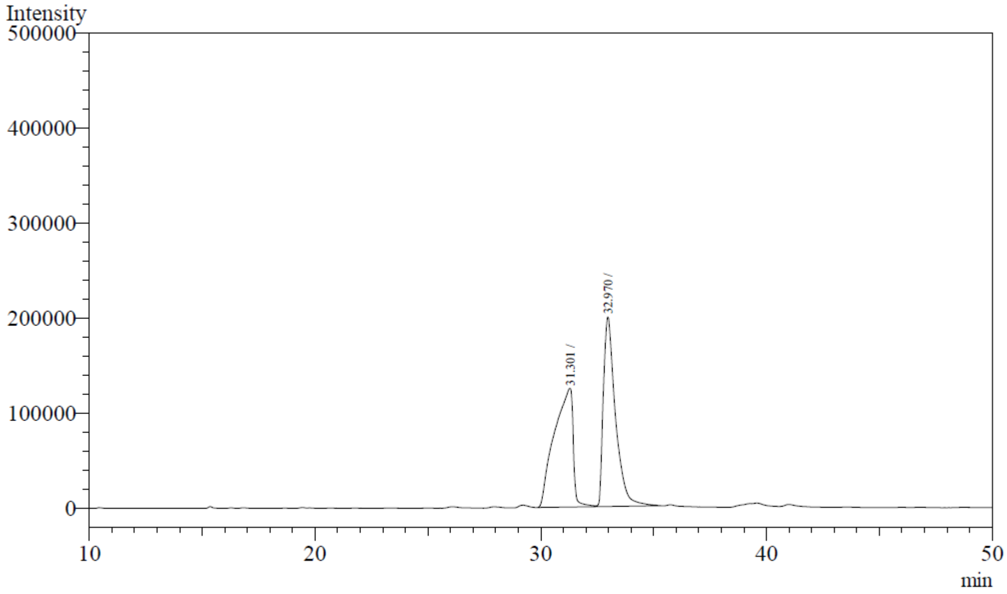
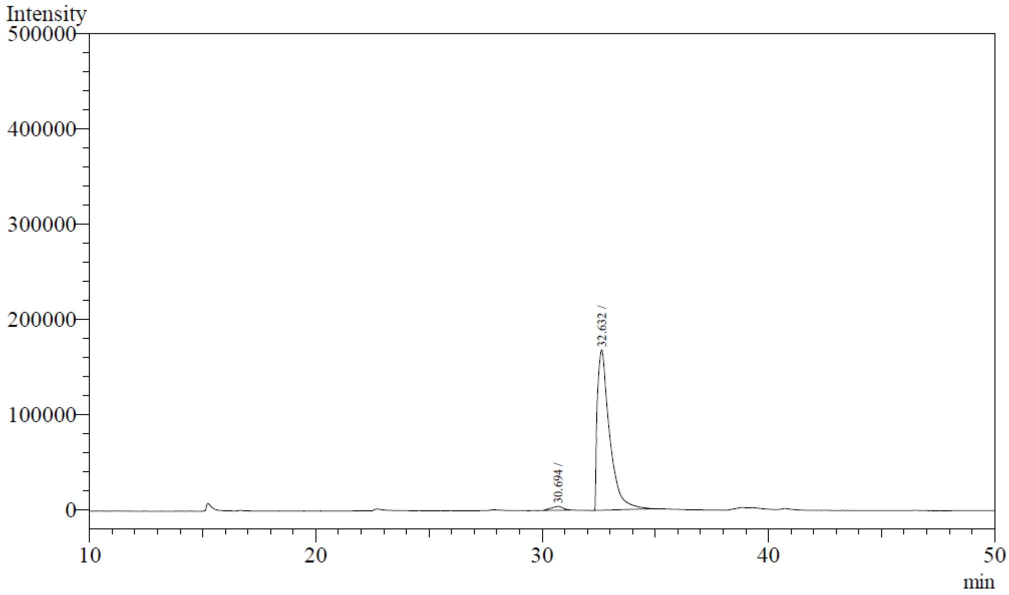
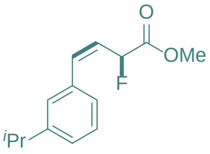


Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.301	7285359	124729	49.43	38.50
2	32.970	7453113	199277	50.57	61.50
Total		14738472	324006	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	30.694	153830	4073	2.37	2.36
2	32.632	6333438	168442	97.63	97.64
Total		6487268	172515	100.00	100.00



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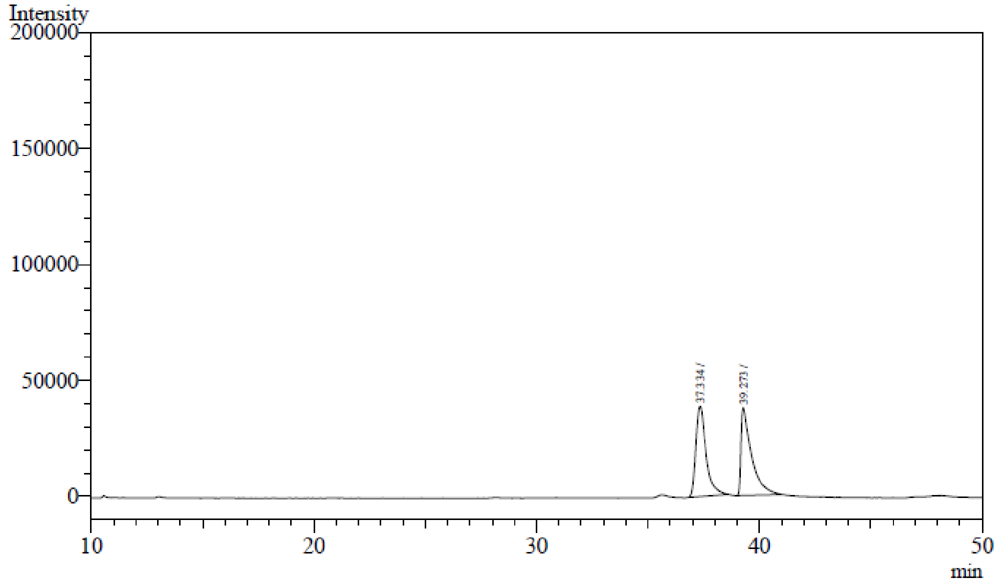
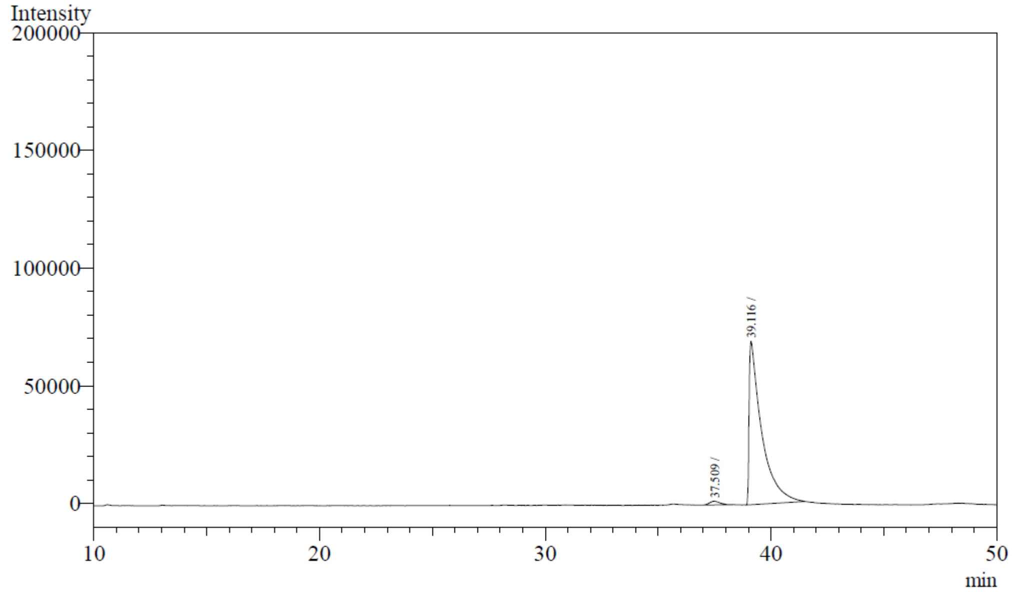
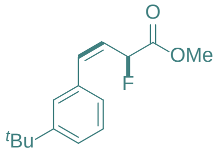


Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.334	1239252	38960	49.65	50.68
2	39.273	1256875	37912	50.35	49.32
Total		2496127	76872	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.509	50580	1585	1.86	2.23
2	39.116	2671682	69373	98.14	97.77
Total		2722262	70958	100.00	100.00



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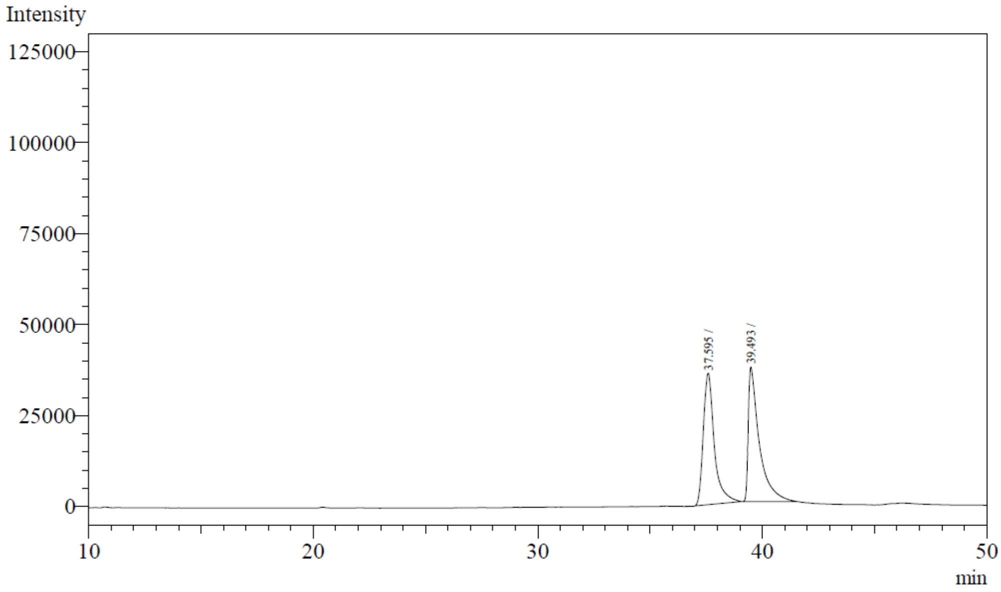
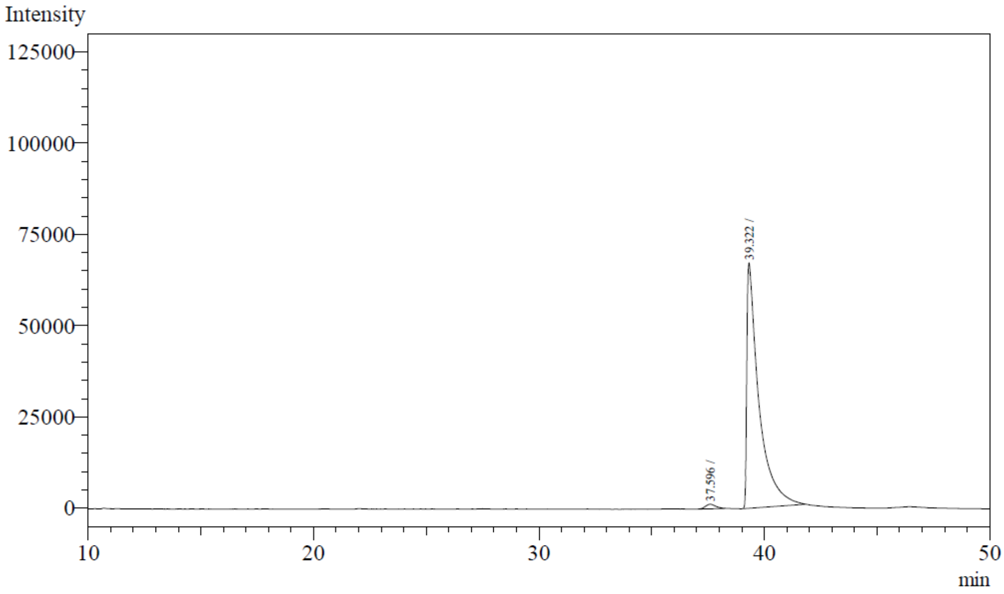
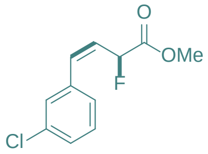


Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.595	1231049	36118	49.45	49.40
2	39.493	1258391	36992	50.55	50.60
Total		2489440	73110	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.596	39669	1246	1.57	1.82
2	39.322	2488585	67232	98.43	98.18
Total		2528254	68478	100.00	100.00



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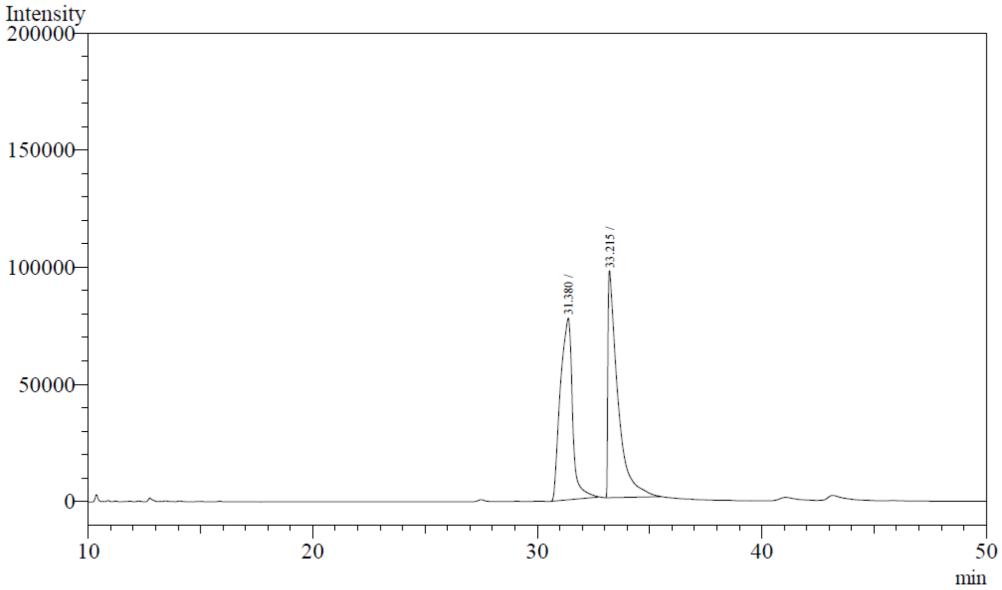
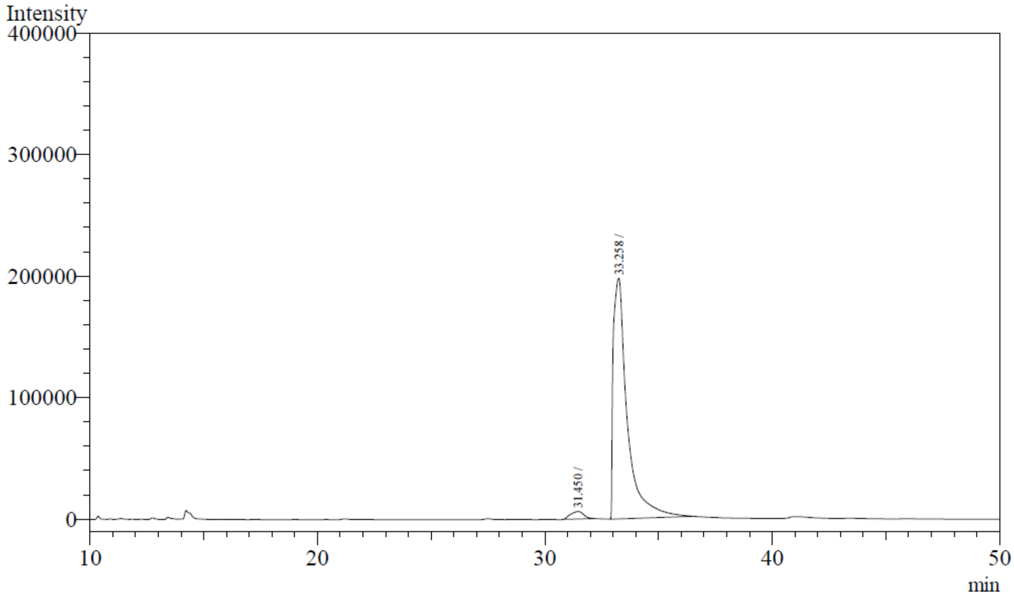
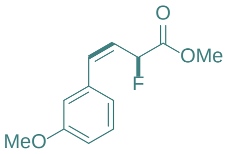


Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.380	2927113	77547	49.73	44.44
2	33.215	2959363	96939	50.27	55.56
Total		5886476	174486	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.450	251250	6189	2.89	3.03
2	33.258	8446231	197958	97.11	96.97
Total		8697481	204147	100.00	100.00



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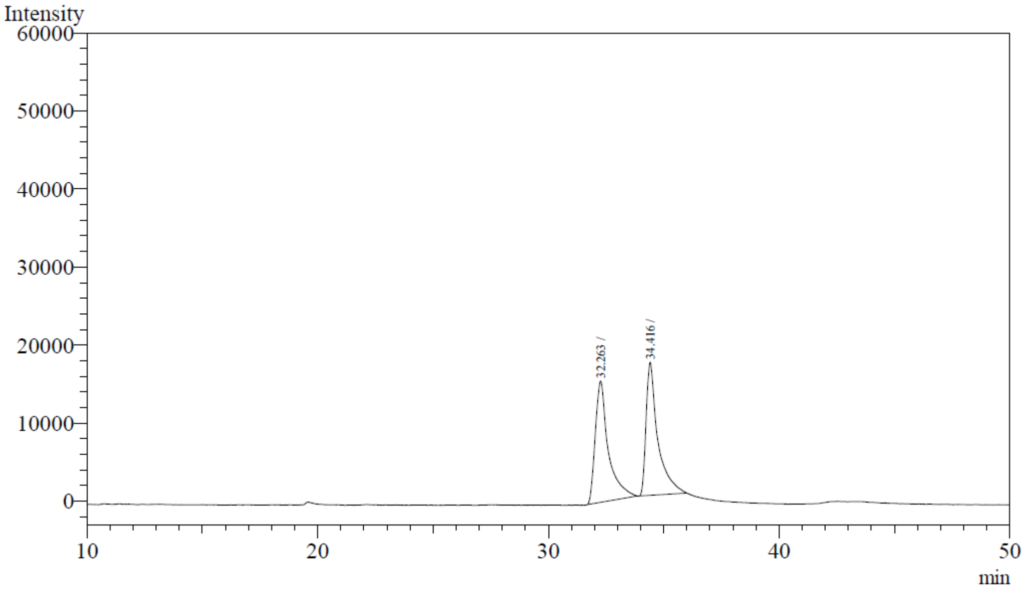
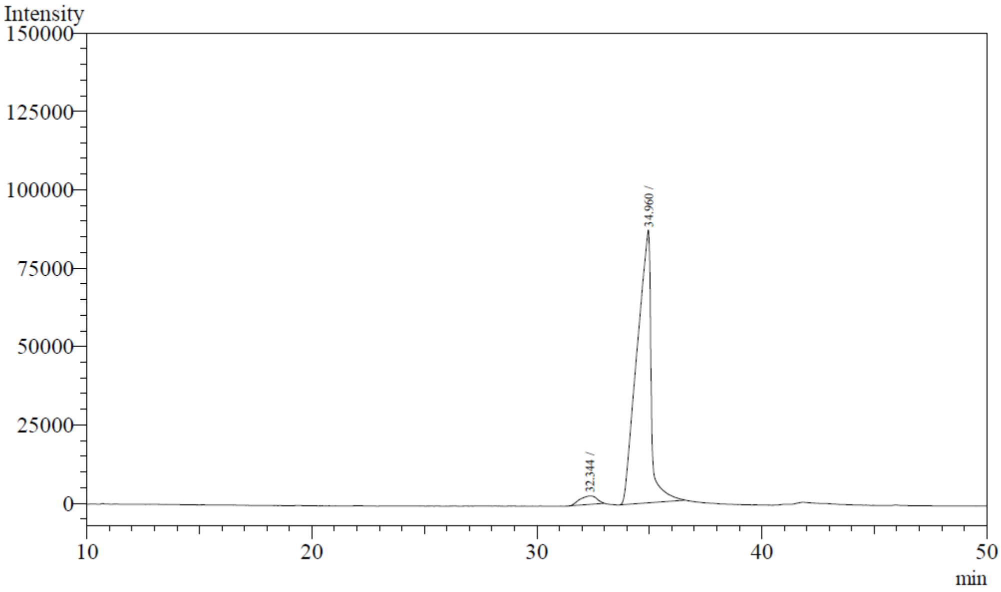
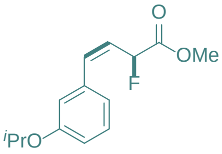


Peak#	Ret.Time	Area	Height	Area%	Height%
1	32.263	610154	15534	50.28	47.68
2	34.416	603425	17048	49.72	52.32
Total		1213579	32582	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	32.344	141119	2700	3.56	3.01
2	34.960	3823411	87013	96.44	96.99
Total		3964530	89713	100.00	100.00



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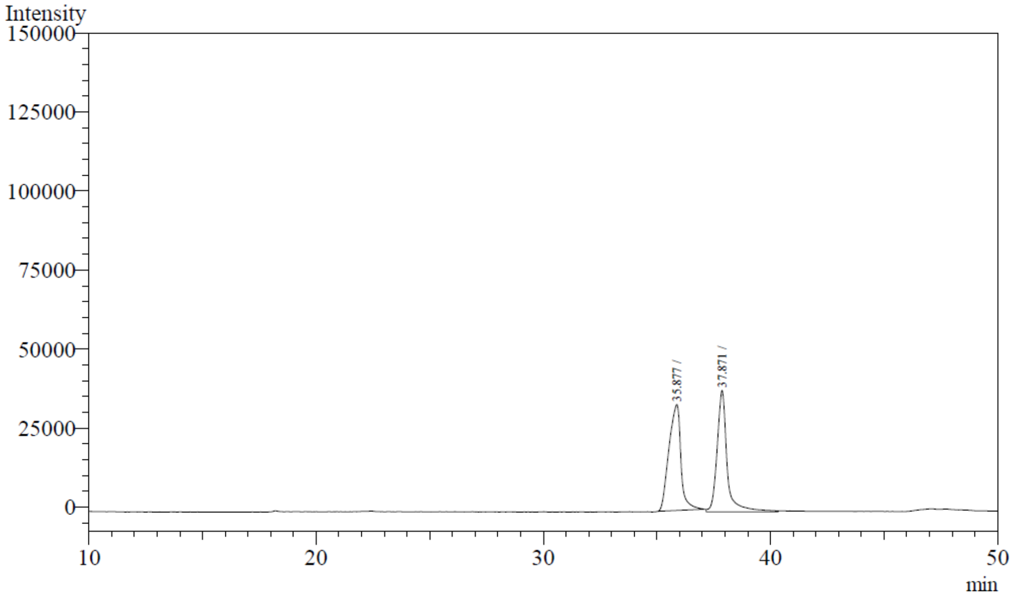
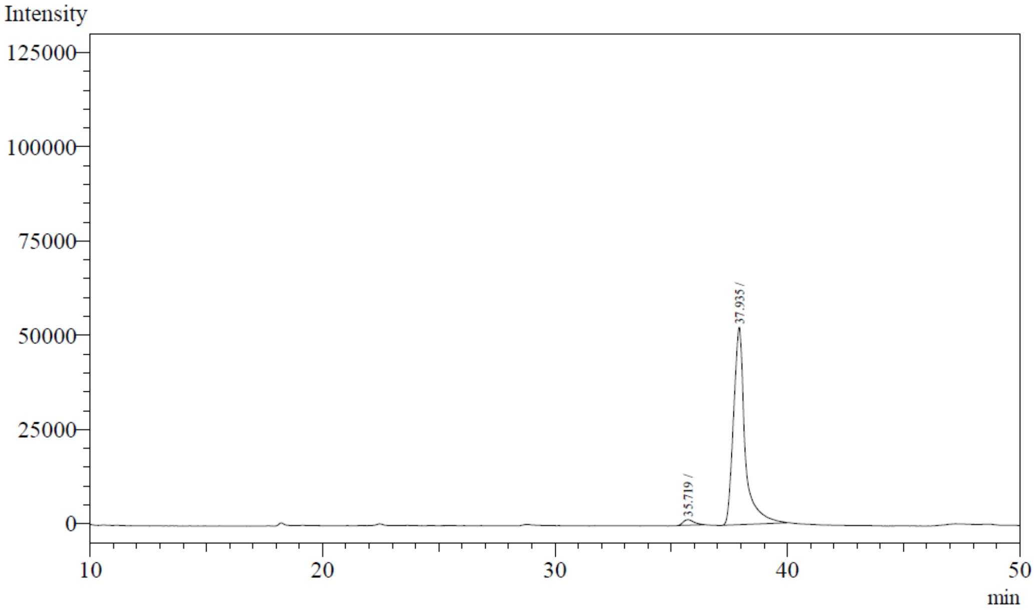
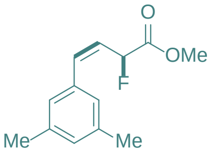


Peak#	Ret.Time	Area	Height	Area%	Height%
1	35.877	1230533	33503	50.93	46.59
2	37.871	1185827	38407	49.07	53.41
Total		2416360	71910	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	35.719	46712	1470	2.52	2.73
2	37.935	1808561	52374	97.48	97.27
Total		1855273	53844	100.00	100.00



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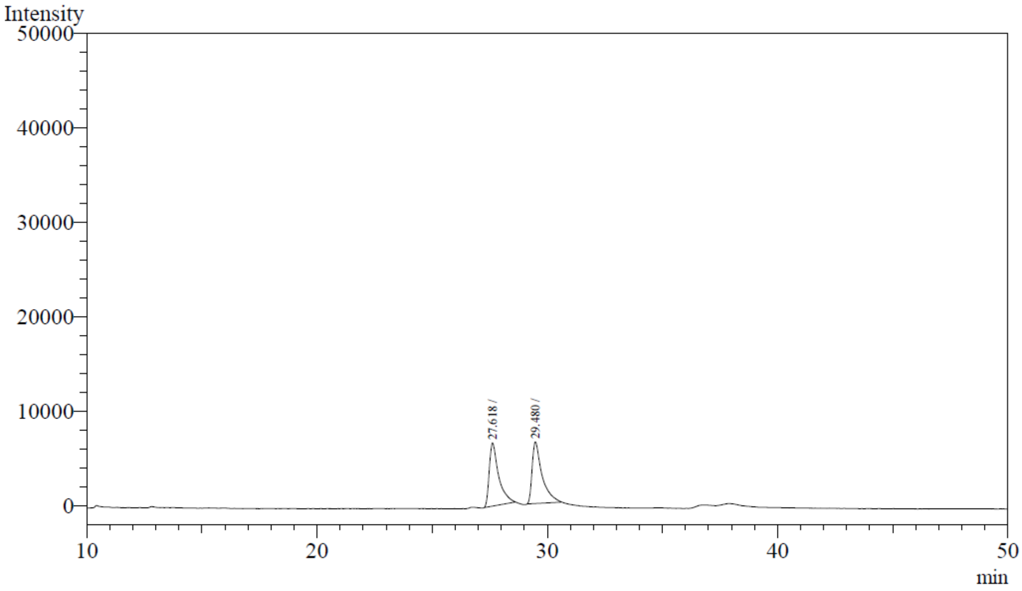
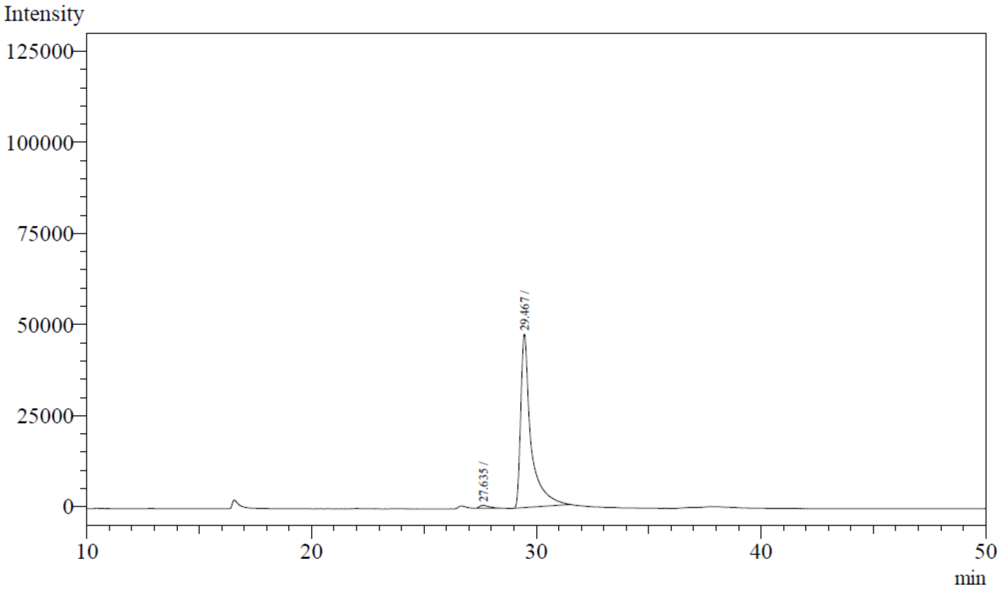
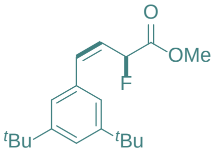


Peak#	Ret.Time	Area	Height	Area%	Height%
1	27.618	189911	6690	49.30	50.64
2	29.480	195334	6522	50.70	49.36
Total		385245	13212	100.00	100.00



Peak#	Ret.Time	Area	Height	Area%	Height%
1	27.635	24653	813	1.61	1.68
2	29.467	1509342	47616	98.39	98.32
Total		1533995	48429	100.00	100.00



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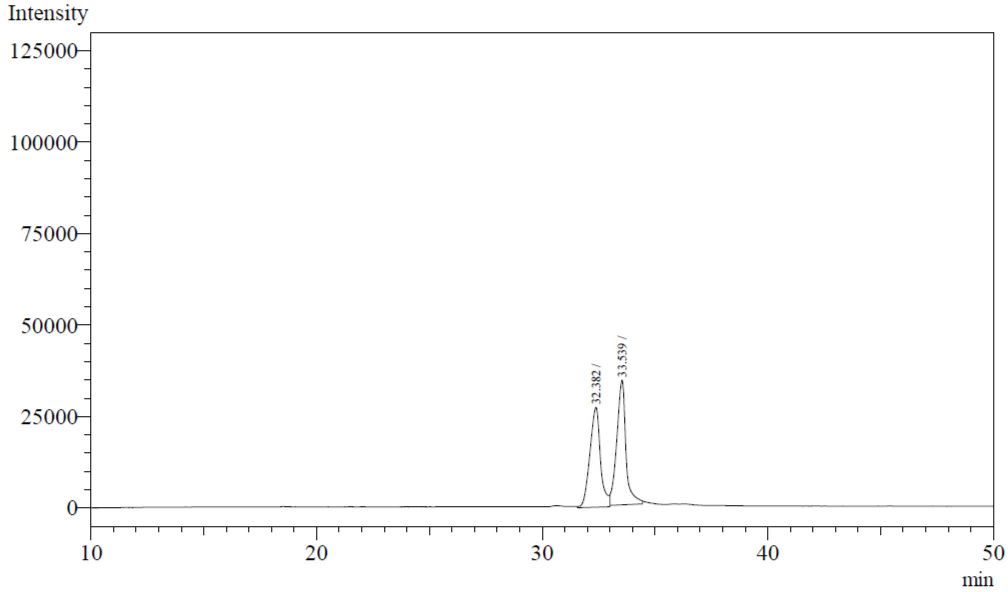
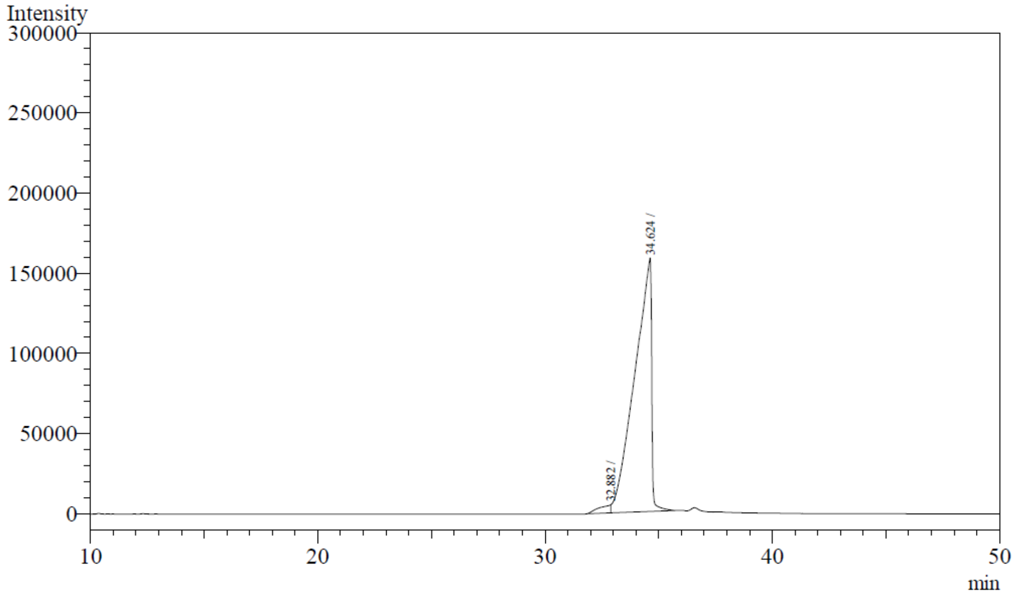
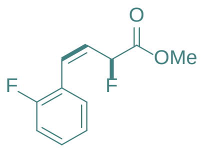


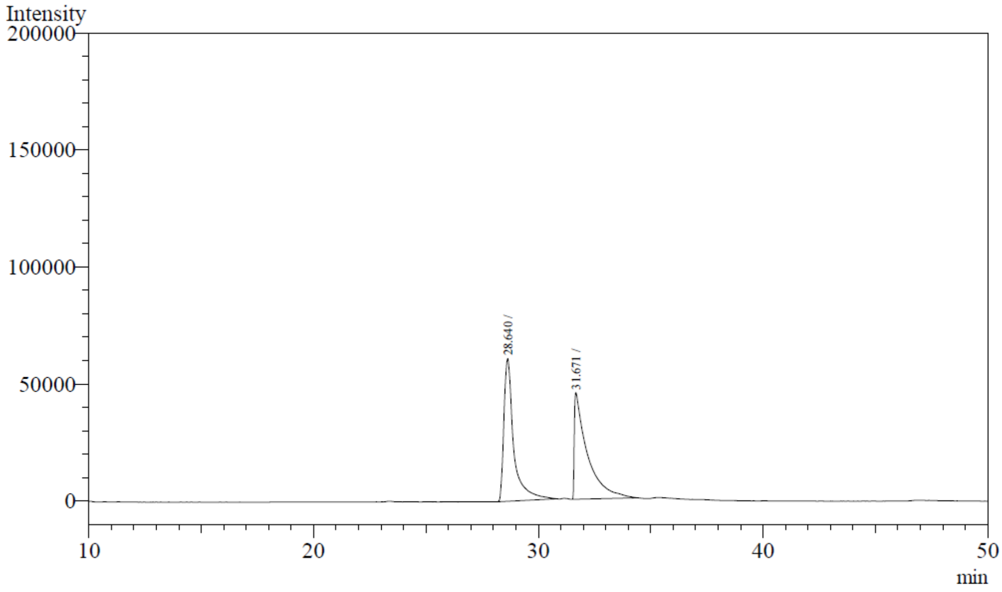
Peak#	Ret.Time	Area	Height	Area%	Height%
1	32.382	893846	27293	48.20	44.46
2	33.539	960747	34089	51.80	55.54
Total		1854593	61382	100.00	100.00



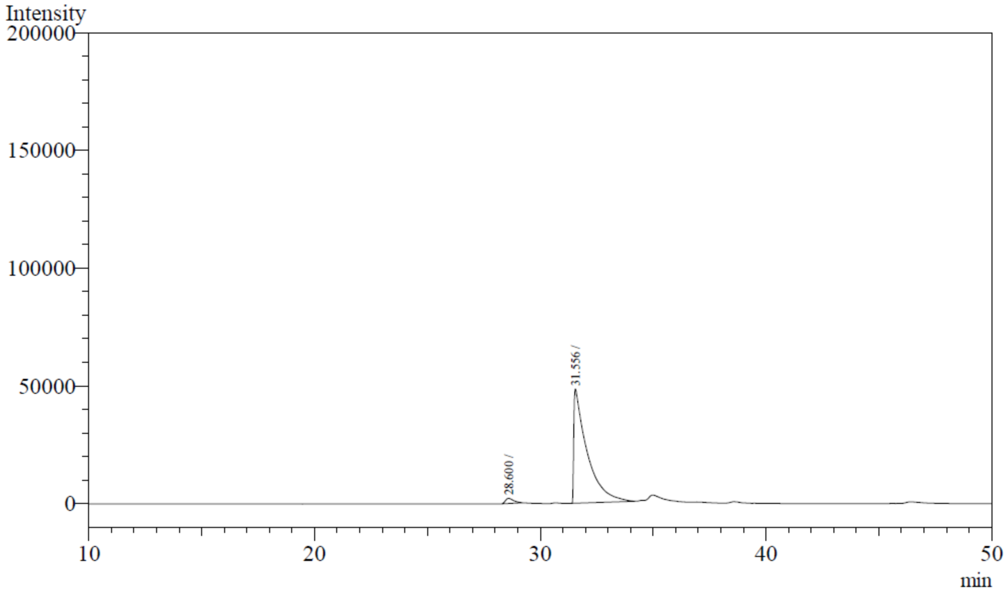
Peak#	Ret.Time	Area	Height	Area%	Height%
1	32.882	181406	5029	2.17	3.08
2	34.624	8183150	158214	97.83	96.92
Total		8364556	163243	100.00	100.00



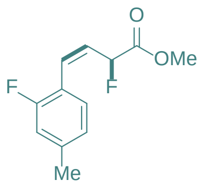
3p



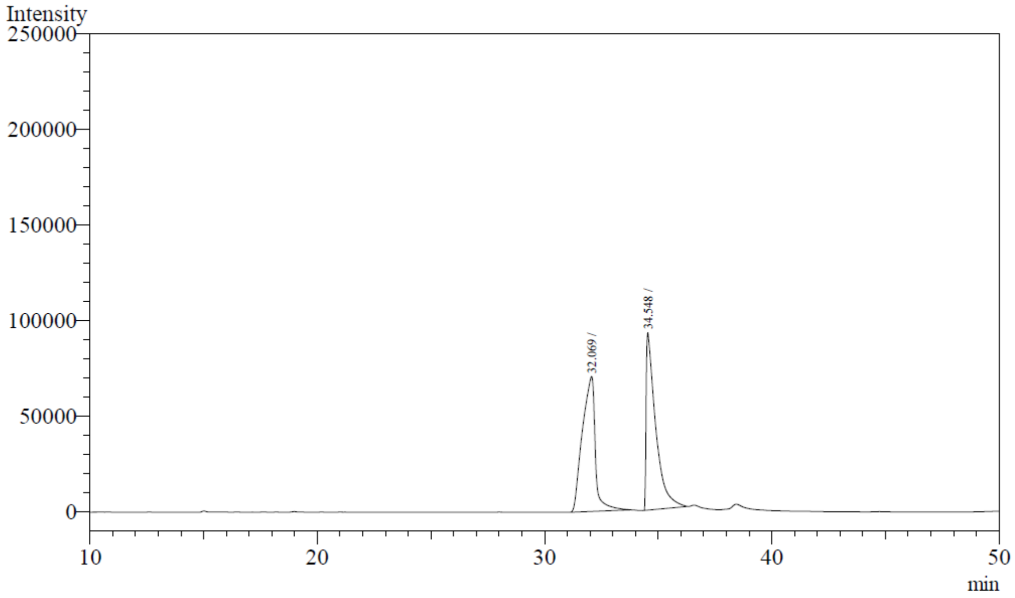
Peak#	Ret.Time	Area	Height	Area%	Height%
1	28.640	1853828	60950	50.41	57.23
2	31.671	1823642	45557	49.59	42.77
Total		3677470	106507	100.00	100.00



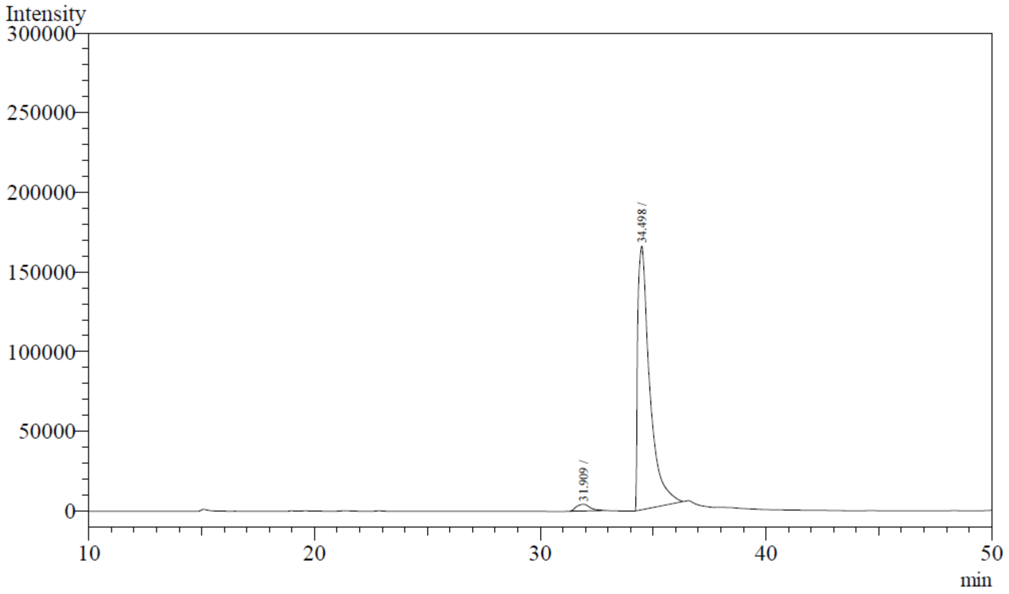
Peak#	Ret.Time	Area	Height	Area%	Height%
1	28.600	55175	2186	2.72	4.31
2	31.556	1975451	48546	97.28	95.69
Total		2030626	50732	100.00	100.00



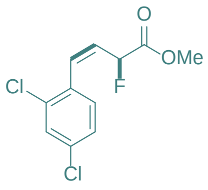
3q



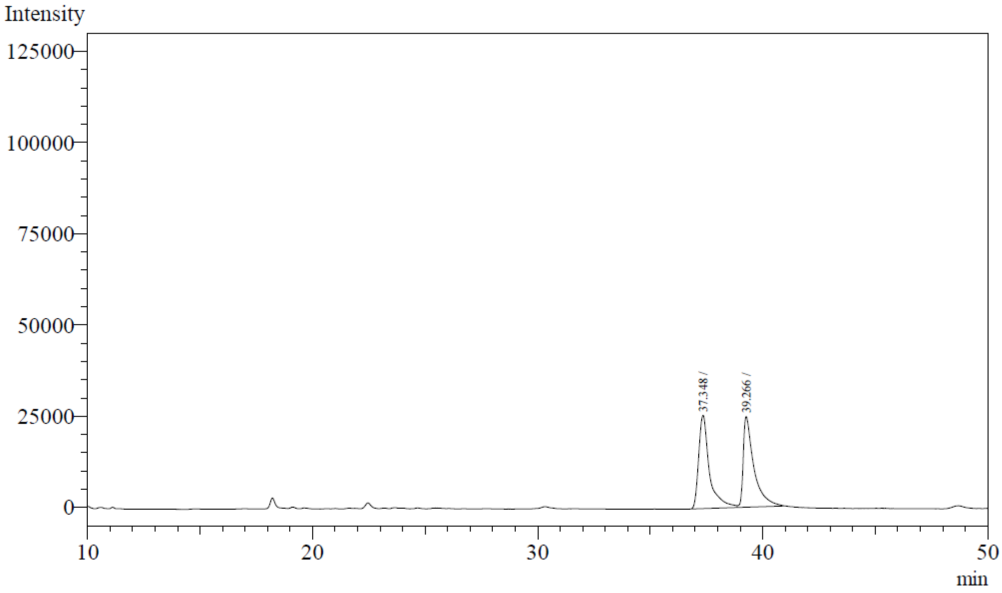
Peak#	Ret.Time	Area	Height	Area%	Height%
1	32.069	2803058	70559	50.92	43.20
2	34.548	2701487	92764	49.08	56.80
Total		5504545	163323	100.00	100.00



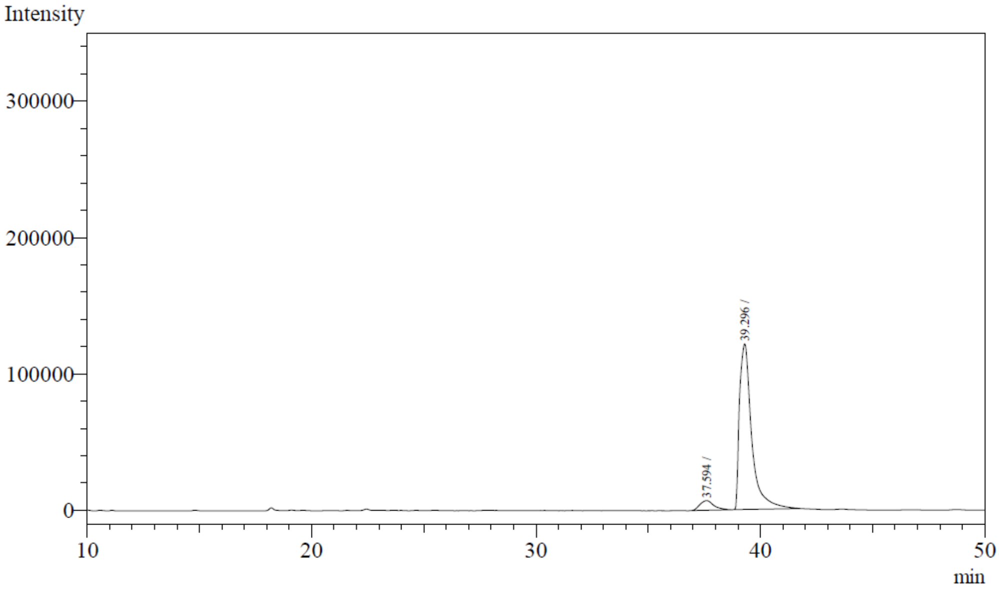
Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.909	180743	4218	2.88	2.49
2	34.498	6101948	165475	97.12	97.51
Total		6282691	169693	100.00	100.00



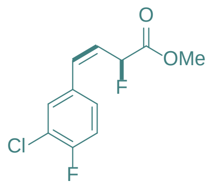
3r



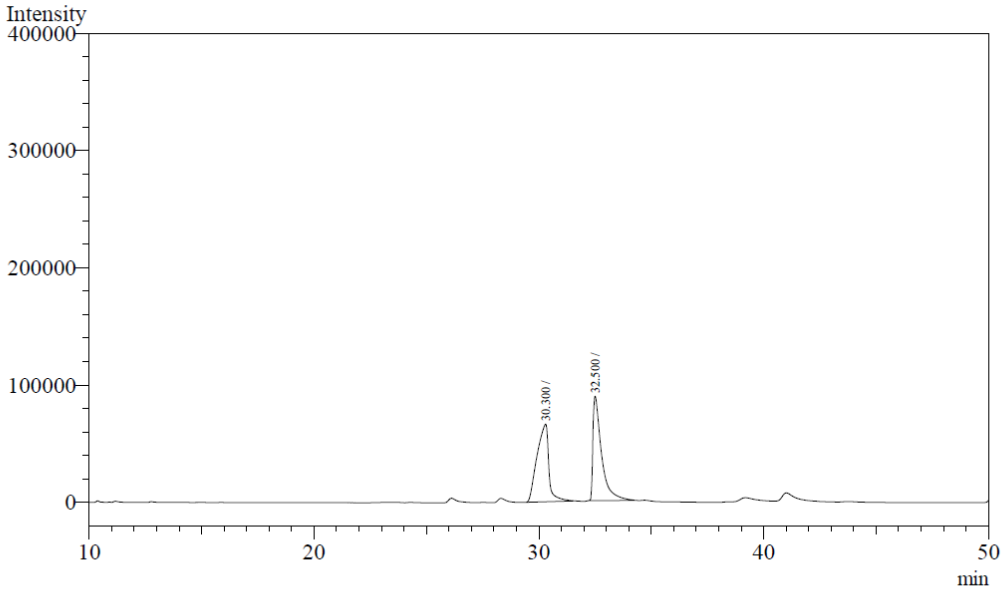
Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.348	846356	25534	50.98	50.70
2	39.266	813975	24832	49.02	49.30
Total		1660331	50366	100.00	100.00



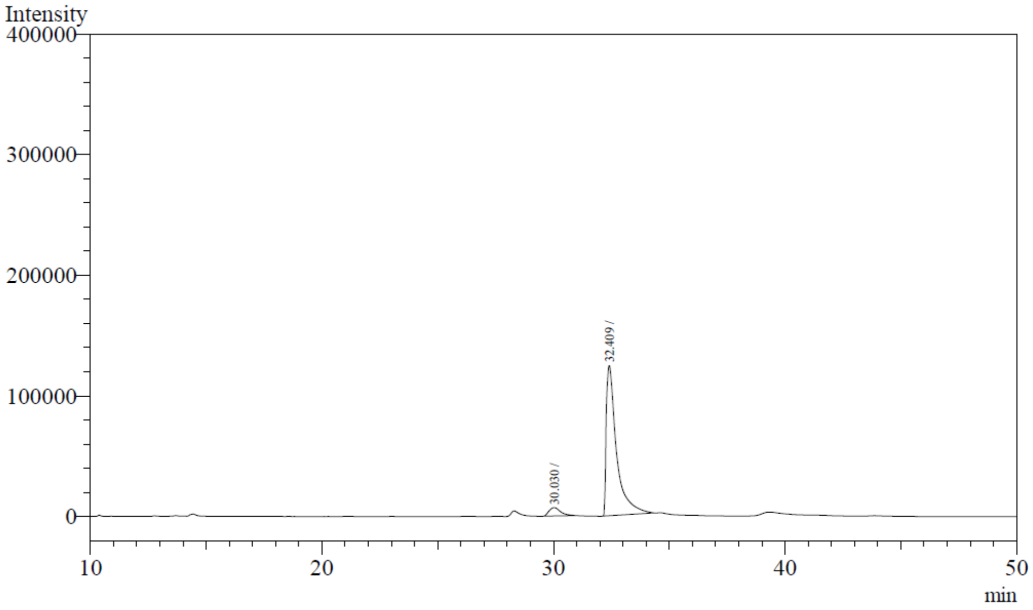
Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.594	305803	7129	6.24	5.54
2	39.296	4598129	121486	93.76	94.46
Total		4903932	128615	100.00	100.00



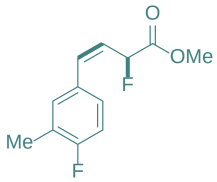
3s



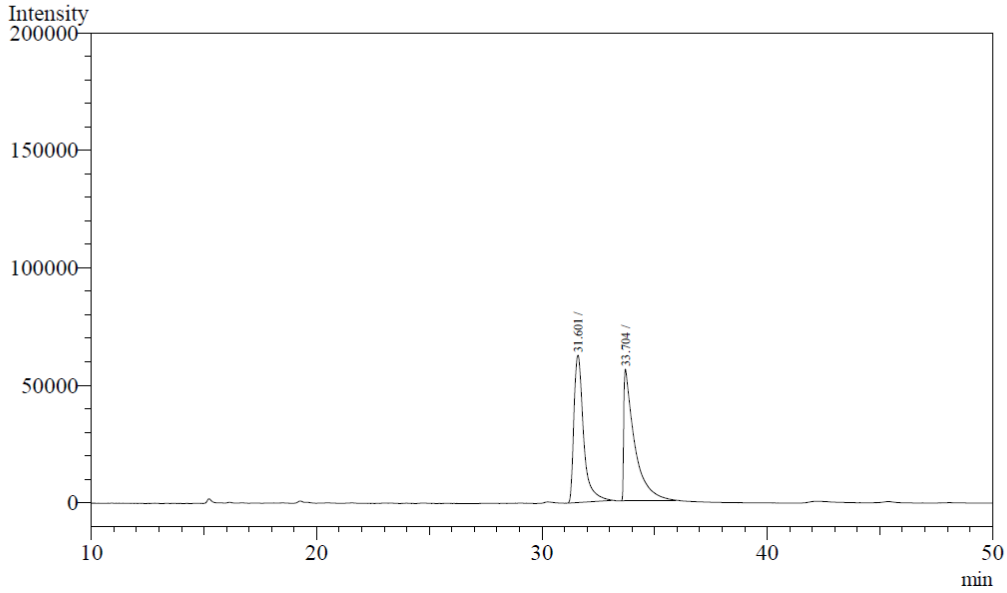
Peak#	Ret.Time	Area	Height	Area%	Height%
1	30.300	2415094	66249	50.38	42.68
2	32.500	2378479	88963	49.62	57.32
Total		4793573	155212	100.00	100.00



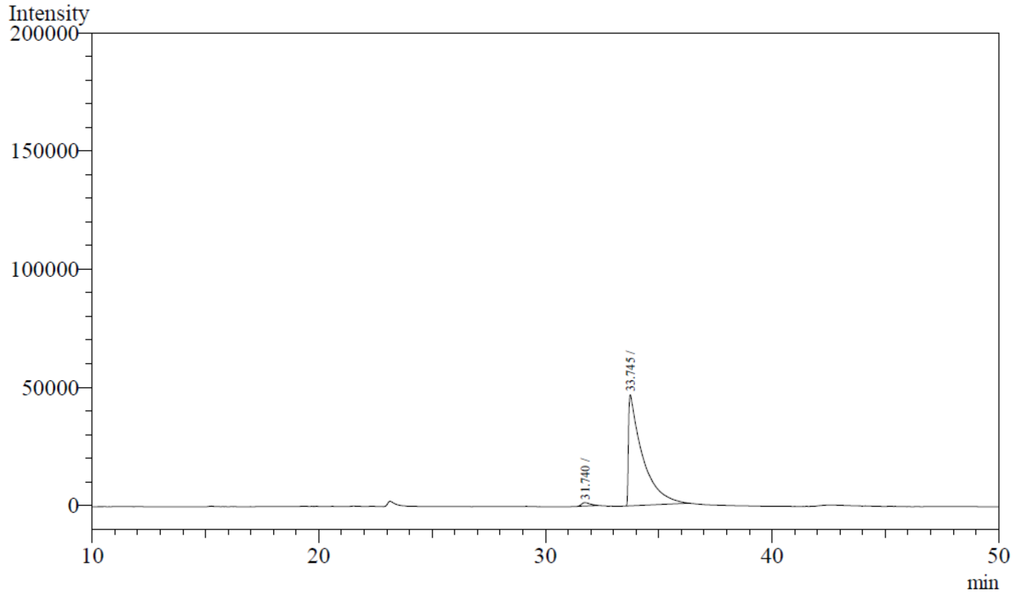
Peak#	Ret.Time	Area	Height	Area%	Height%
1	30.030	235802	6871	5.79	5.23
2	32.409	3836632	124537	94.21	94.77
Total		4072434	131408	100.00	100.00



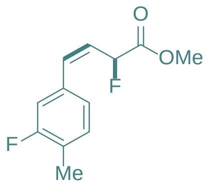
3t



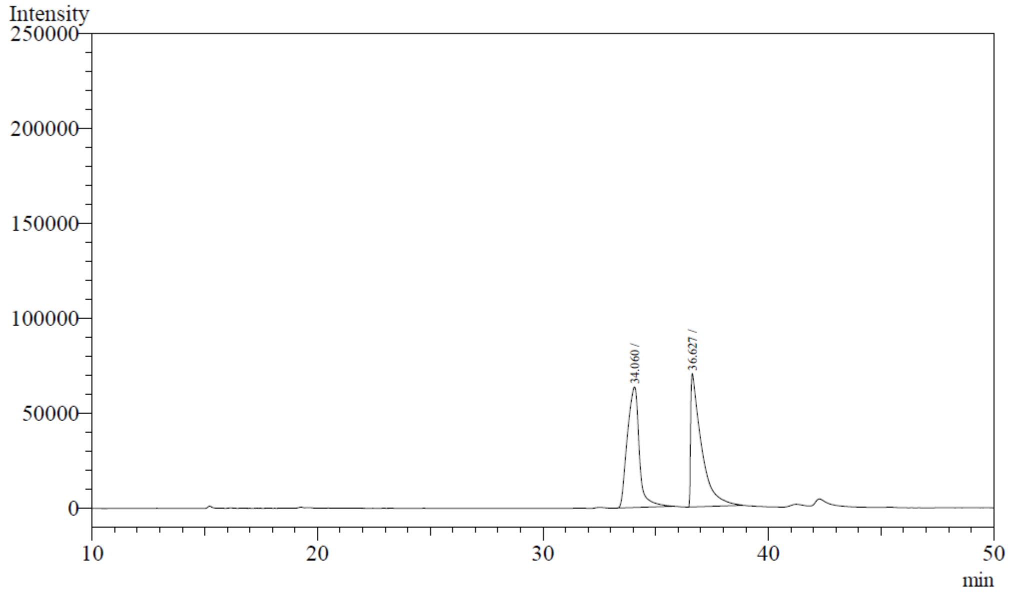
Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.601	1870805	62661	50.18	52.83
2	33.704	1857484	55938	49.82	47.17
Total		3728289	118599	100.00	100.00



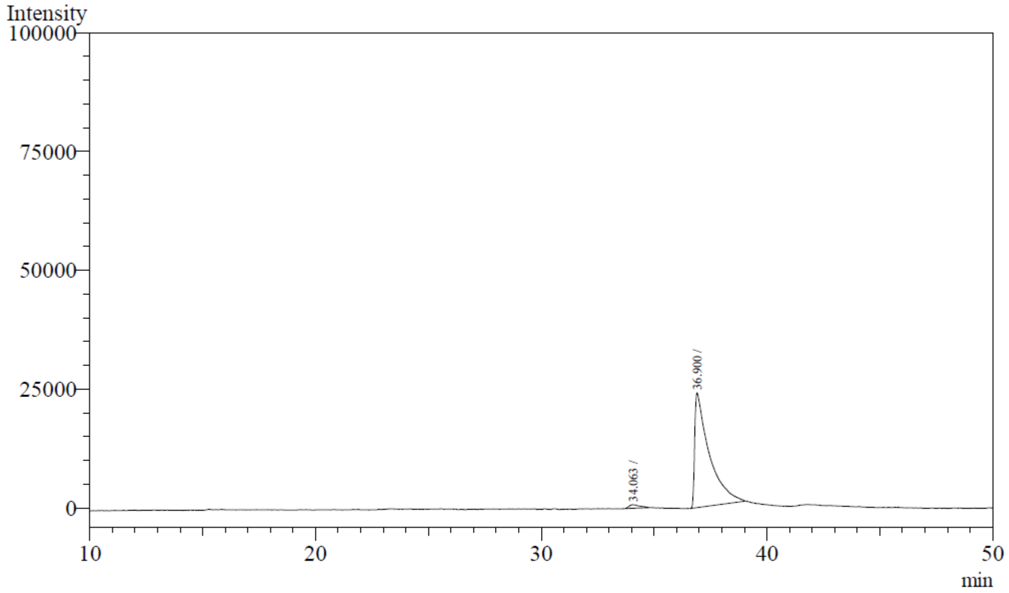
Peak#	Ret.Time	Area	Height	Area%	Height%
1	31.740	37837	1437	1.84	2.97
2	33.745	2016217	46961	98.16	97.03
Total		2054054	48398	100.00	100.00



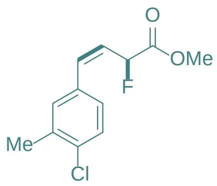
3u



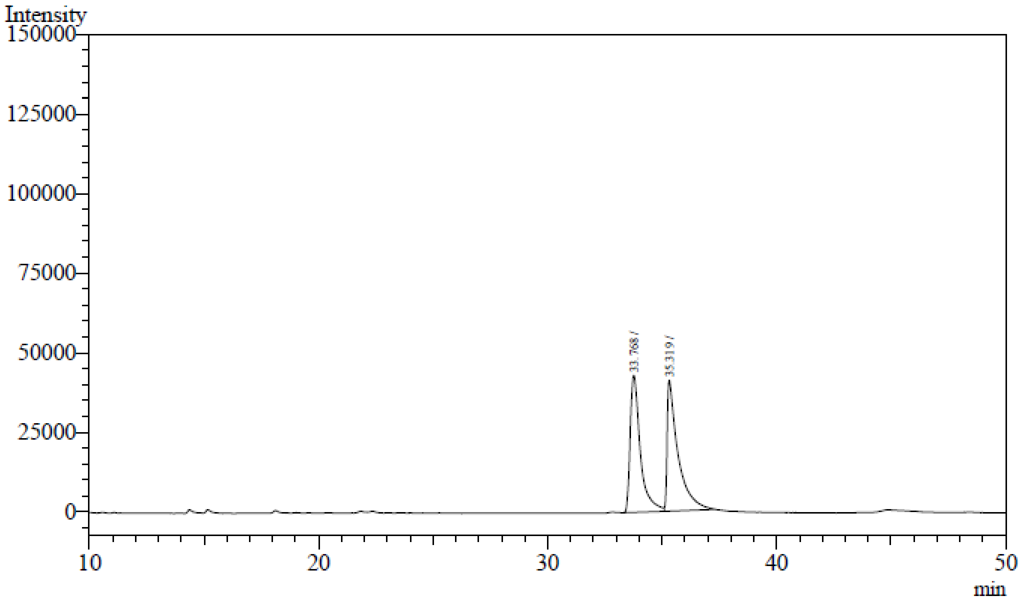
Peak#	Ret.Time	Area	Height	Area%	Height%
1	34.060	2339469	63447	50.09	47.44
2	36.627	2330899	70298	49.91	52.56
Total		4670368	133745	100.00	100.00



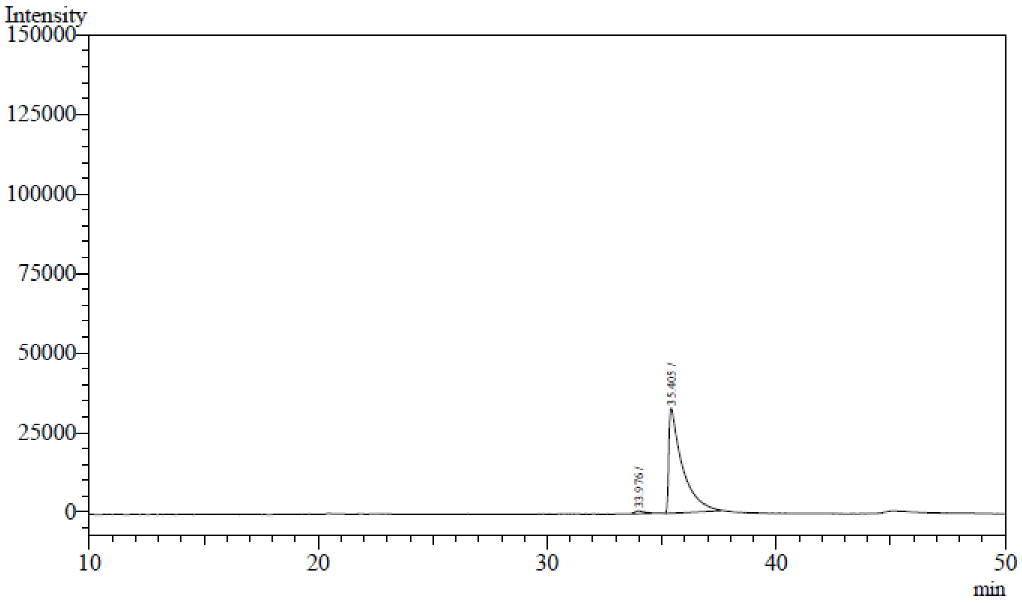
Peak#	Ret.Time	Area	Height	Area%	Height%
1	34.063	24238	756	2.20	3.04
2	36.900	1078144	24143	97.80	96.96
Total		1102382	24899	100.00	100.00



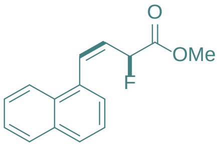
3v



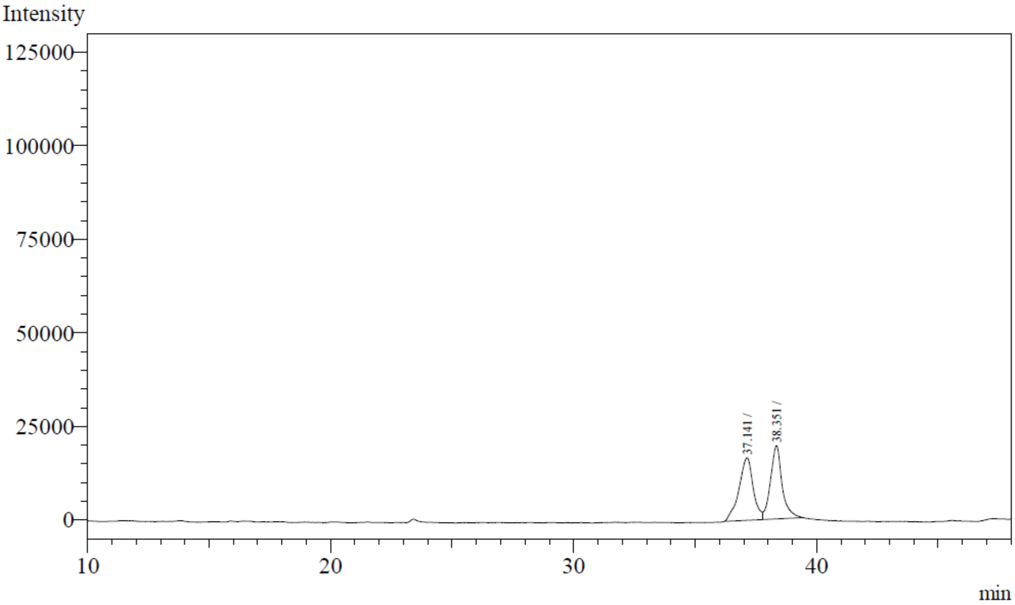
Peak#	Ret.Time	Area	Height	Area%	Height%
1	33.768	1326262	42994	49.47	51.17
2	35.319	1354559	41026	50.53	48.83
Total		2680821	84020	100.00	100.00



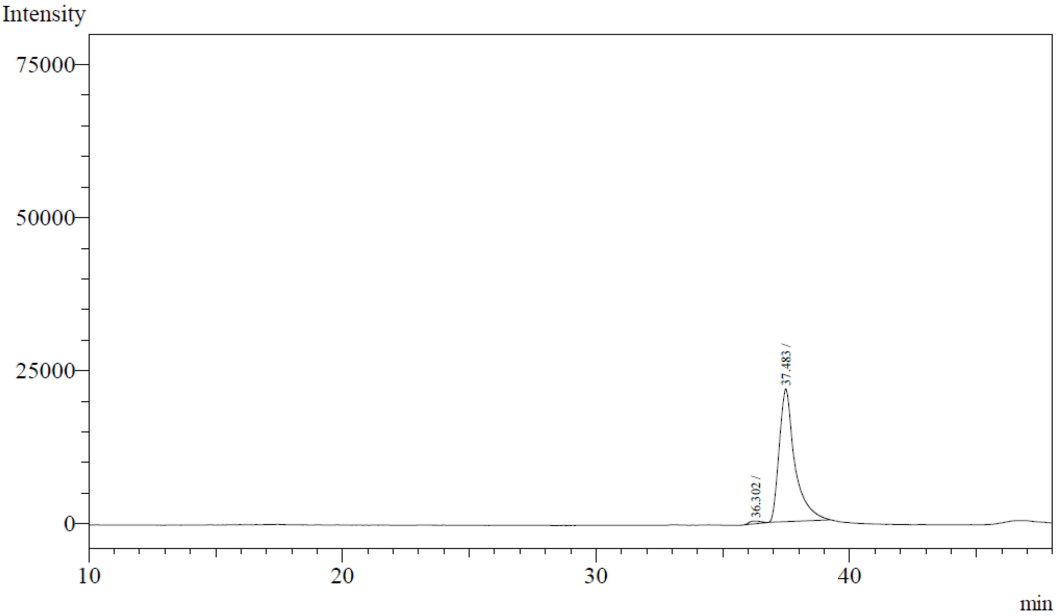
Peak#	Ret.Time	Area	Height	Area%	Height%
1	33.976	26561	891	1.92	2.63
2	35.405	1359293	33036	98.08	97.37
Total		1385854	33927	100.00	100.00



3w

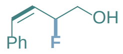


Peak#	Ret.Time	Area	Height	Area%	Height%
1	37.141	679531	16692	50.99	46.03
2	38.351	653273	19574	49.01	53.97
Total		1332804	36266	100.00	100.00



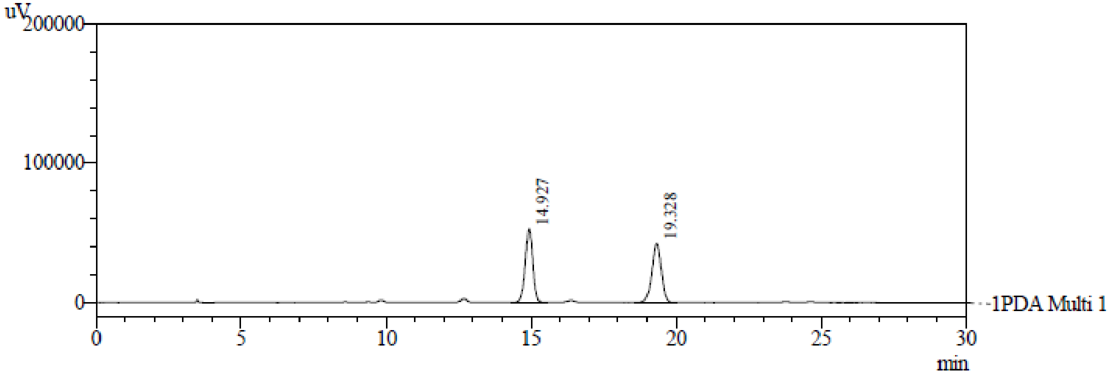
Peak#	Ret.Time	Area	Height	Area%	Height%
1	36.302	13568	424	1.44	1.92
2	37.483	928689	21693	98.56	98.08
Total		942257	22117	100.00	100.00

HPLC spectra



4a

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\reduction\rac\YH00220-038-2,IA-2%.lcd



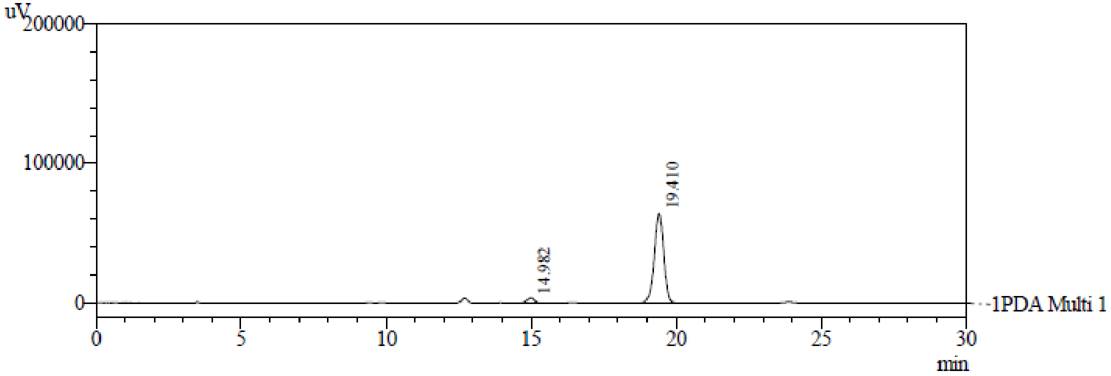
1 PDA Multi 1 / 254nm 4nm

PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.927	951537	52841	49.897	55.578
2	19.328	955465	42234	50.103	44.422
Total		1907002	95075	100.000	100.000

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\reduction\ee\YH00220-038-1,IA-2%.lcd

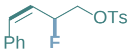


1 PDA Multi 1 / 254nm 4nm

PeakTable

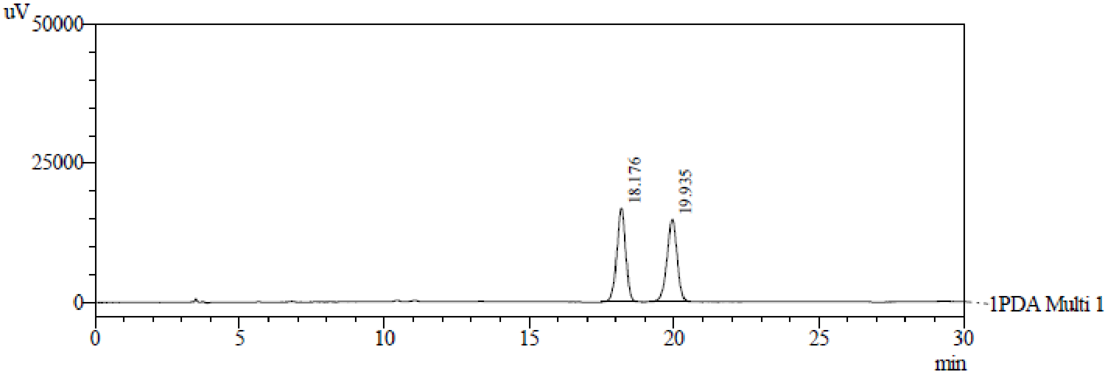
Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.982	64423	3701	4.272	5.440
2	19.410	1443504	64337	95.728	94.560
Total		1507927	68038	100.000	100.000



4b

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\tosylation\rac\YH00220-054",IA-2%.lcd



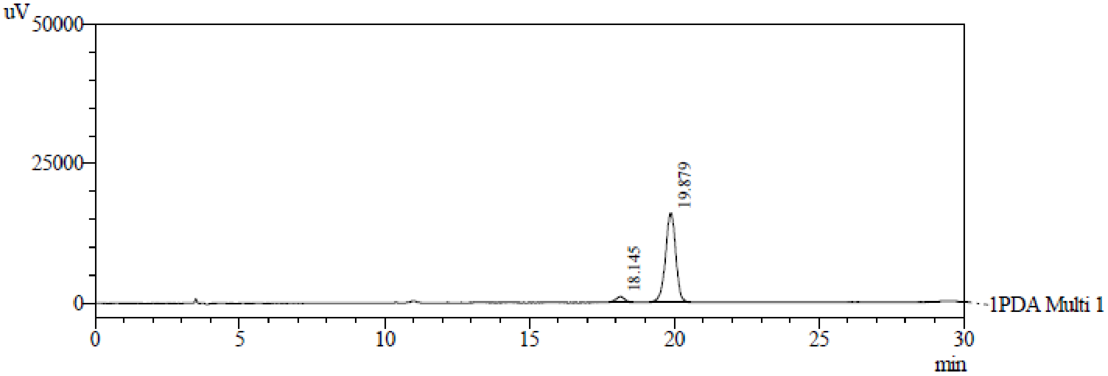
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.176	359610	16827	49.873	53.221
2	19.935	361444	14790	50.127	46.779
Total		721054	31618	100.000	100.000

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\tosylation\ee\YH00220-052",IA-2%.lcd

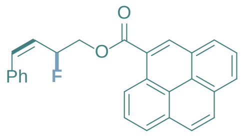


1 PDA Multi 1 / 254nm 4nm

PeakTable

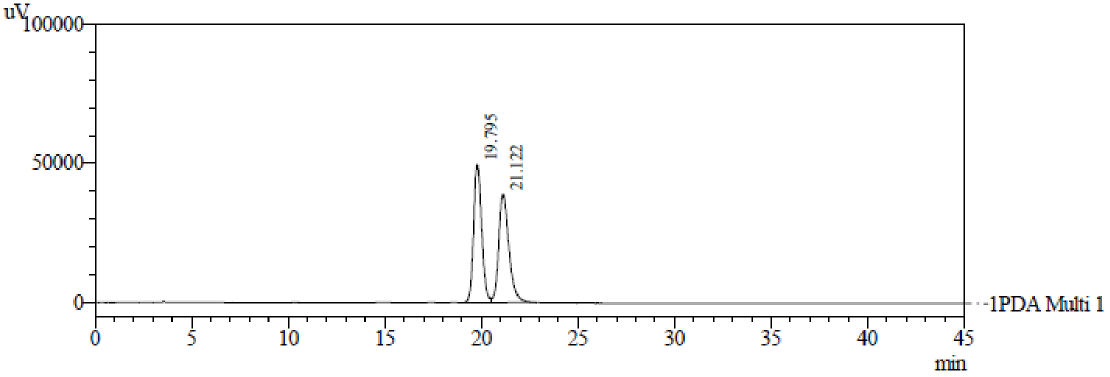
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.145	19588	995	4.764	5.836
2	19.879	391567	16046	95.236	94.164
Total		411155	17041	100.000	100.000



4c

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\esterification\rac\YH00220-050,IA-0.5%.lcd



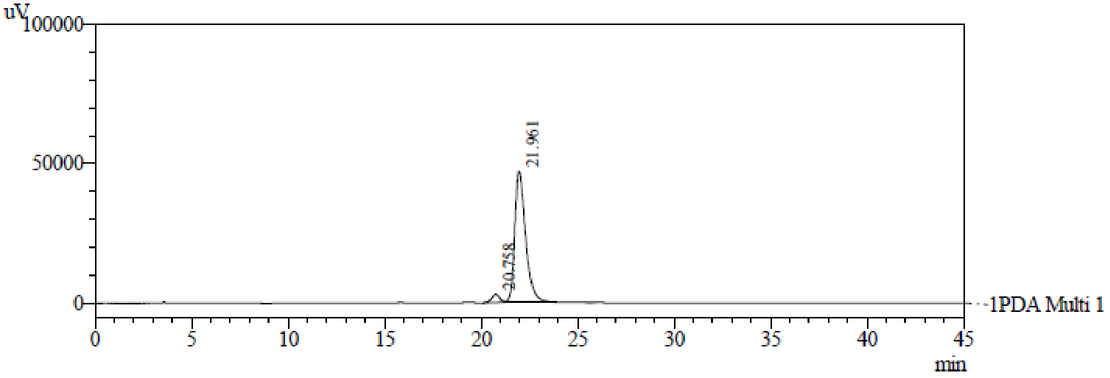
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.795	1417953	49590	49.912	56.118
2	21.122	1422931	38778	50.088	43.882
Total		2840884	88367	100.000	100.000

Chromatogram
D:\HPLC data\Huang Group\JXH\project\gama-F likely\application\esterification\ee\YH00220-046,IA-0.5%.lcd



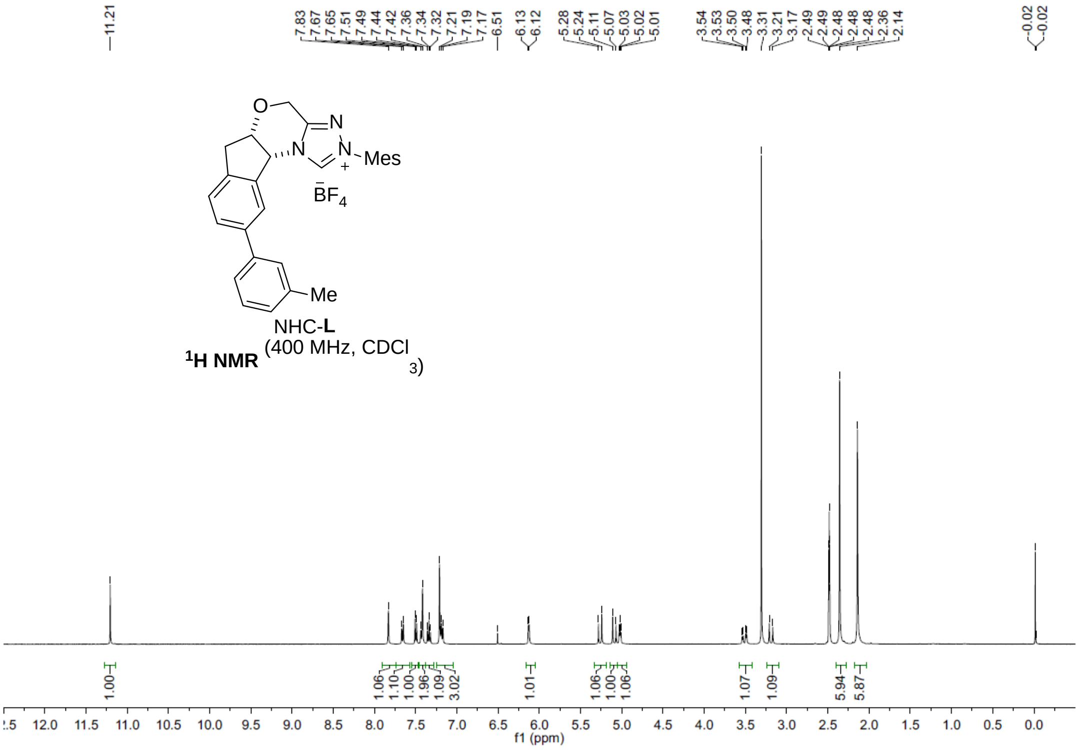
1 PDA Multi 1 / 254nm 4nm

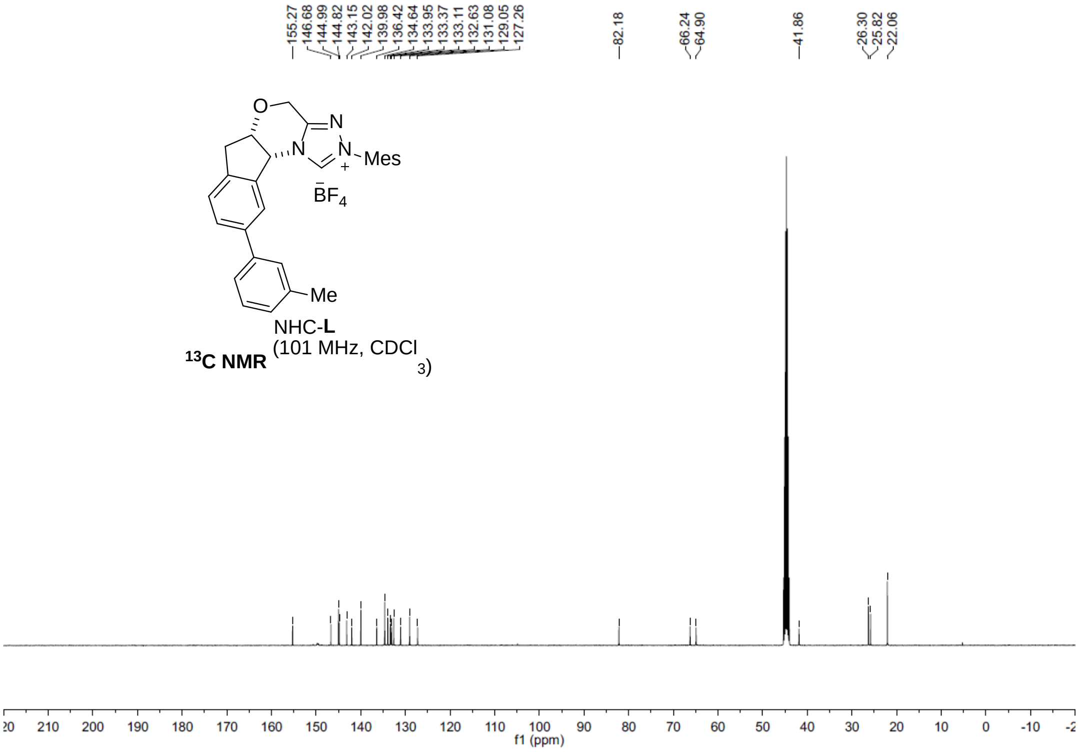
PeakTable

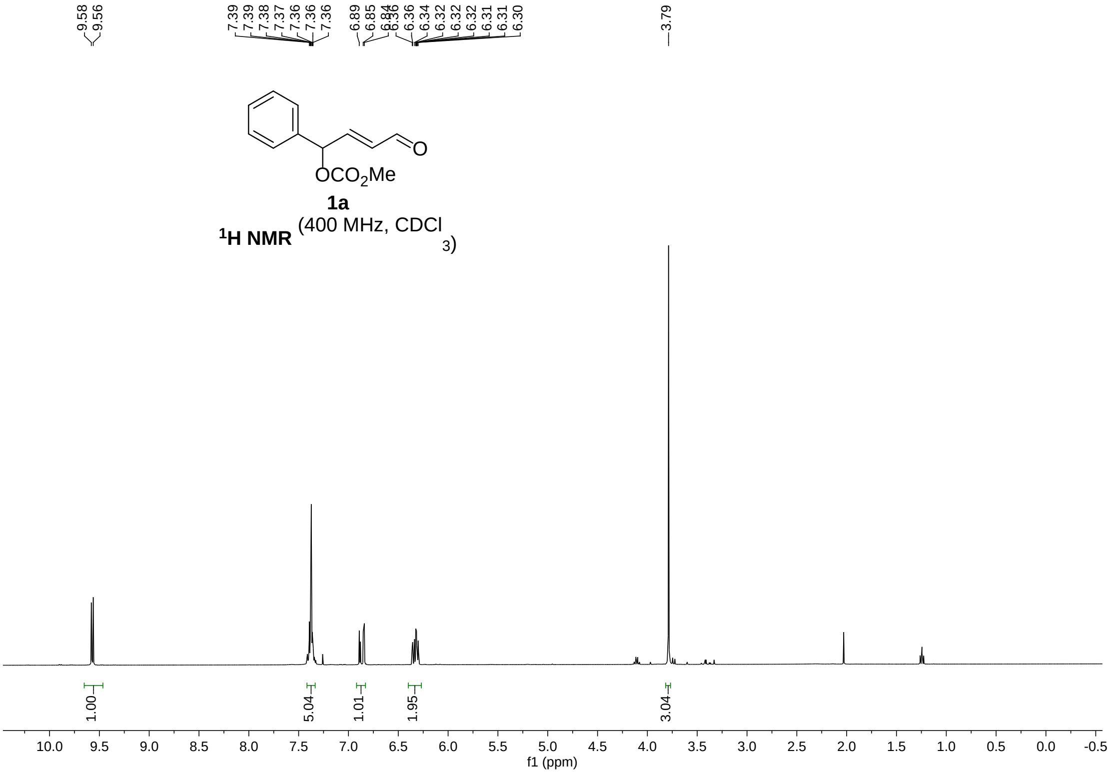
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.758	83414	2932	4.373	5.864
2	21.961	1824043	47067	95.627	94.136
Total		1907457	49999	100.000	100.000

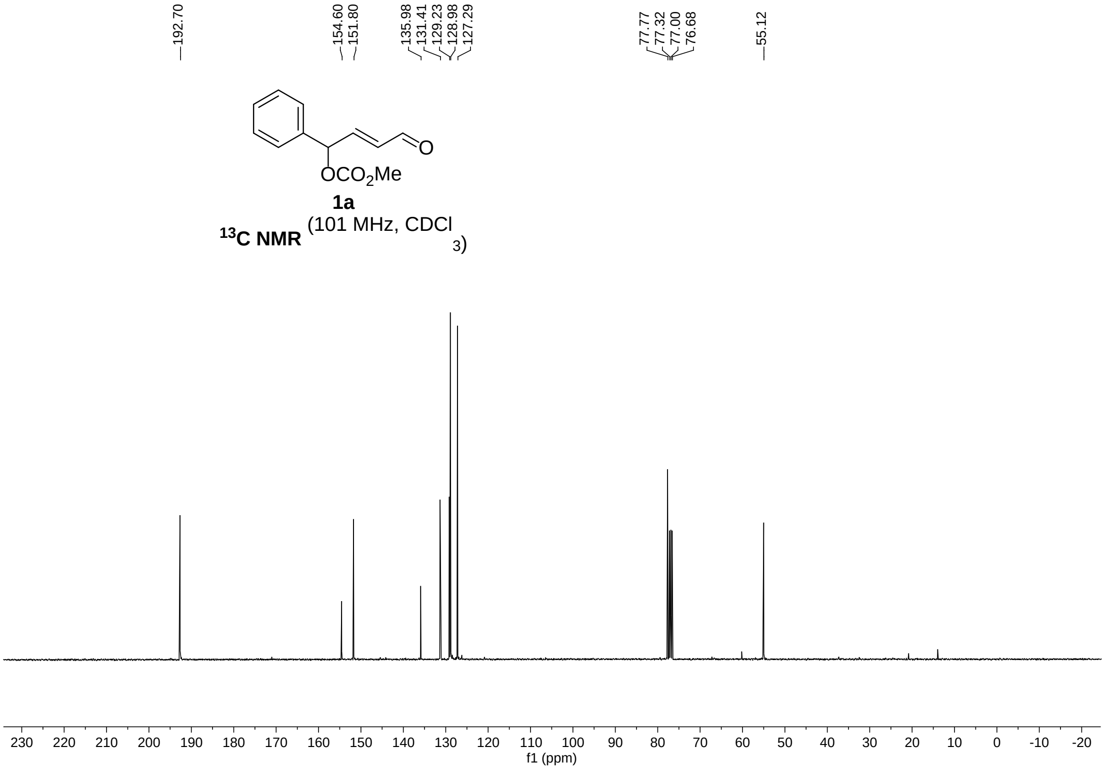
NMR spectra


11.21
7.83
7.67
7.65
7.51
7.49
7.44
7.42
7.36
7.34
7.32
7.21
7.19
7.17
6.51
6.13
6.12
5.28
5.24
5.11
5.07
5.03
5.02
5.01
3.54
3.53
3.50
3.48
3.31
3.21
3.17
2.49
2.49
2.48
2.48
2.48
2.36
2.14
0.02
-0.02
O
N
N
N
+
Mes
BF4
Me
NHC-L
1H NMR (400 MHz, CDCl3)
1.00
1.06
1.10
1.00
1.96
1.09
3.02
1.01
1.06
1.00
1.06
1.07
1.09
5.94
5.87
12.0
11.5
11.0
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
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

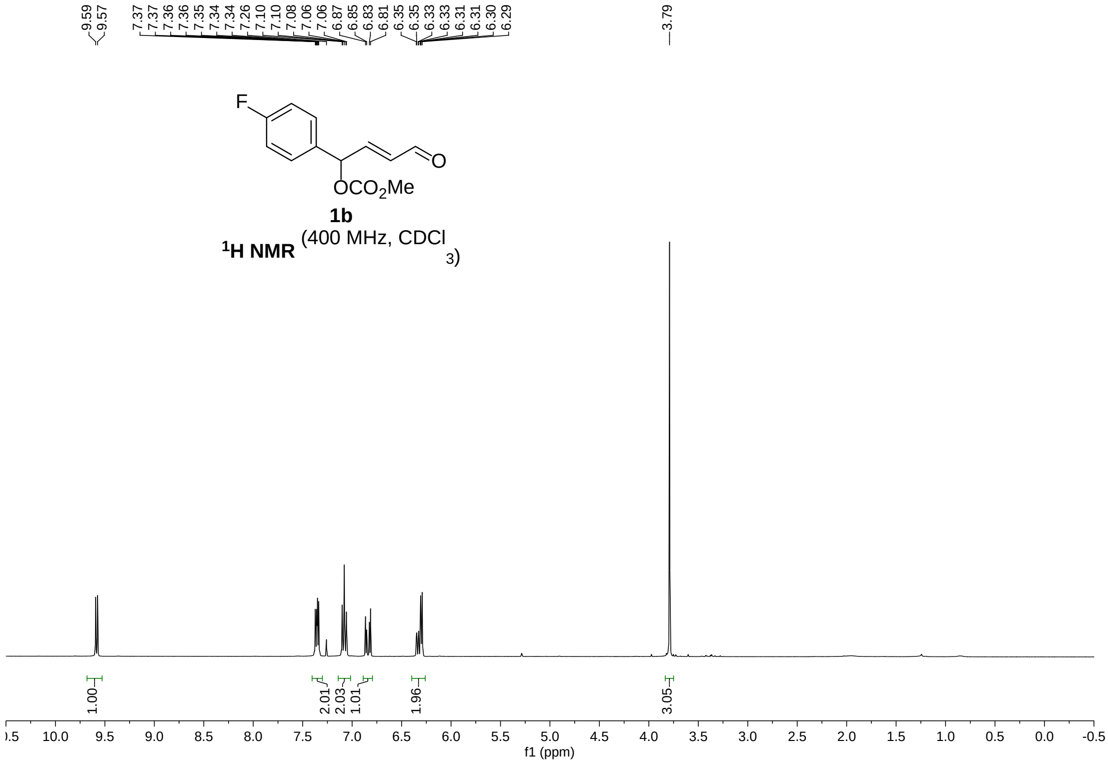

155.27
146.68
144.99
144.82
143.15
142.02
139.98
136.42
134.64
133.95
133.37
133.11
132.63
131.08
129.05
127.26
82.18
66.24
64.90
41.86
26.30
25.82
22.06
O
N
N
N
+
Mes
BF4
Me
NHC-L
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



9.58
9.56
7.39
7.39
7.38
7.37
7.36
7.36
7.36
6.89
6.85
6.84
6.36
6.36
6.34
6.32
6.32
6.32
6.31
6.31
6.30
3.79
OCO2Me
O
1a
1H NMR (400 MHz, CDCl3)
1.00
5.04
1.01
1.95
3.04
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
f1 (ppm)

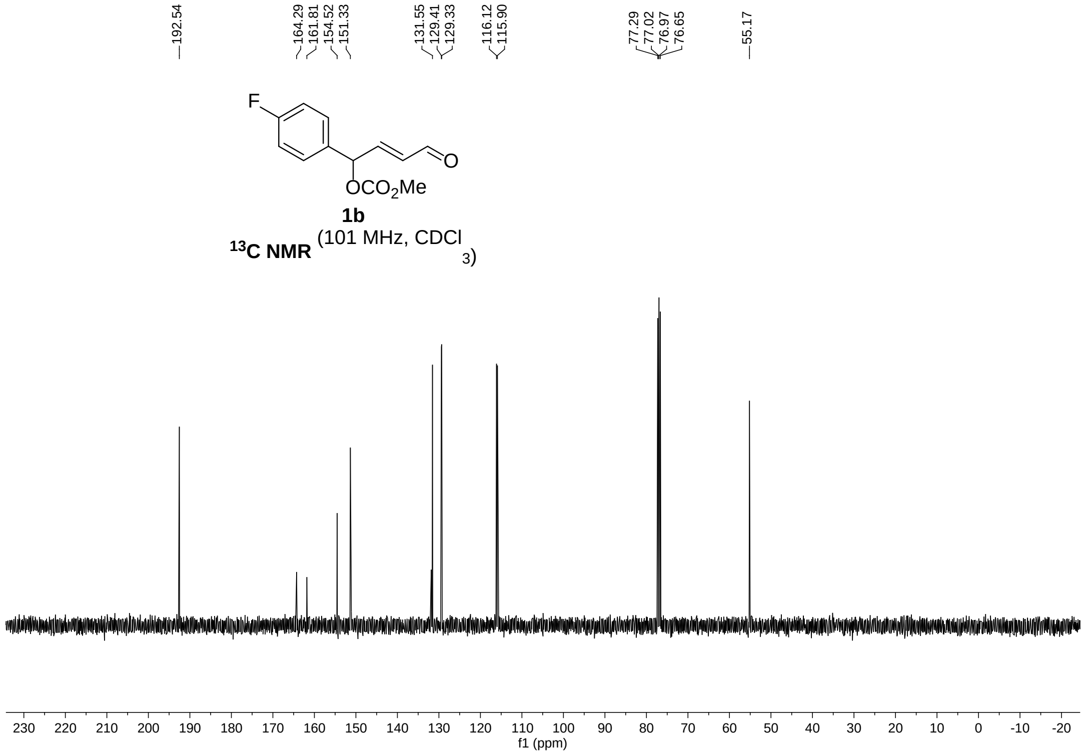


192.70
154.60
151.80
135.98
131.41
129.23
128.98
127.29
77.77
77.32
77.00
76.68
55.12
OCO2Me
O
1a
13C NMR (101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



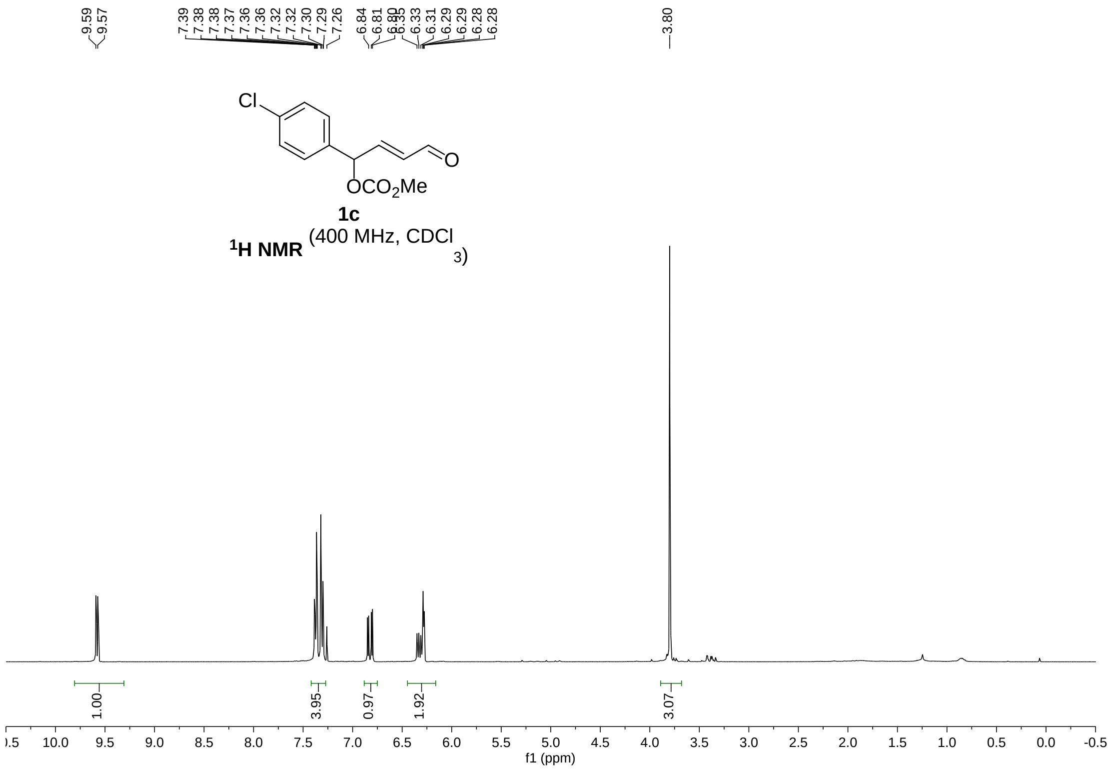
1b

^{1}H NMR (400 MHz, CDCl$_3$)



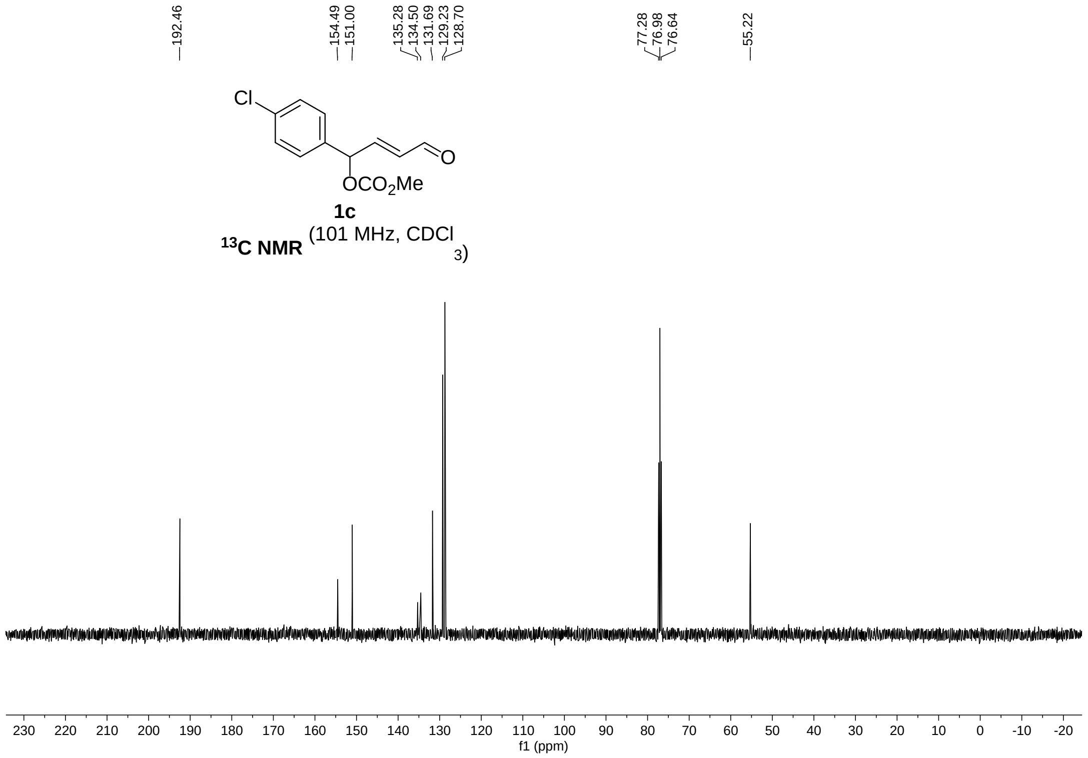
1b

^{13}C NMR (101 MHz, CDCl$_3$)



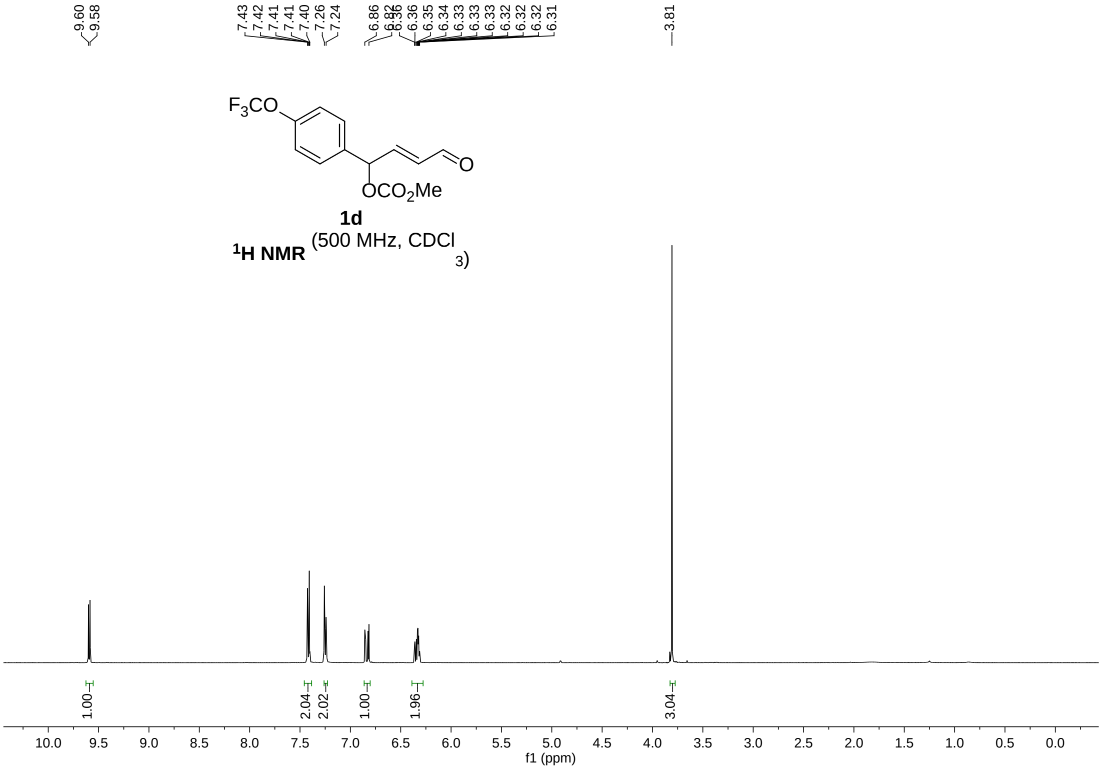
1c

^{1}H NMR (400 MHz, $CDCl_3$)



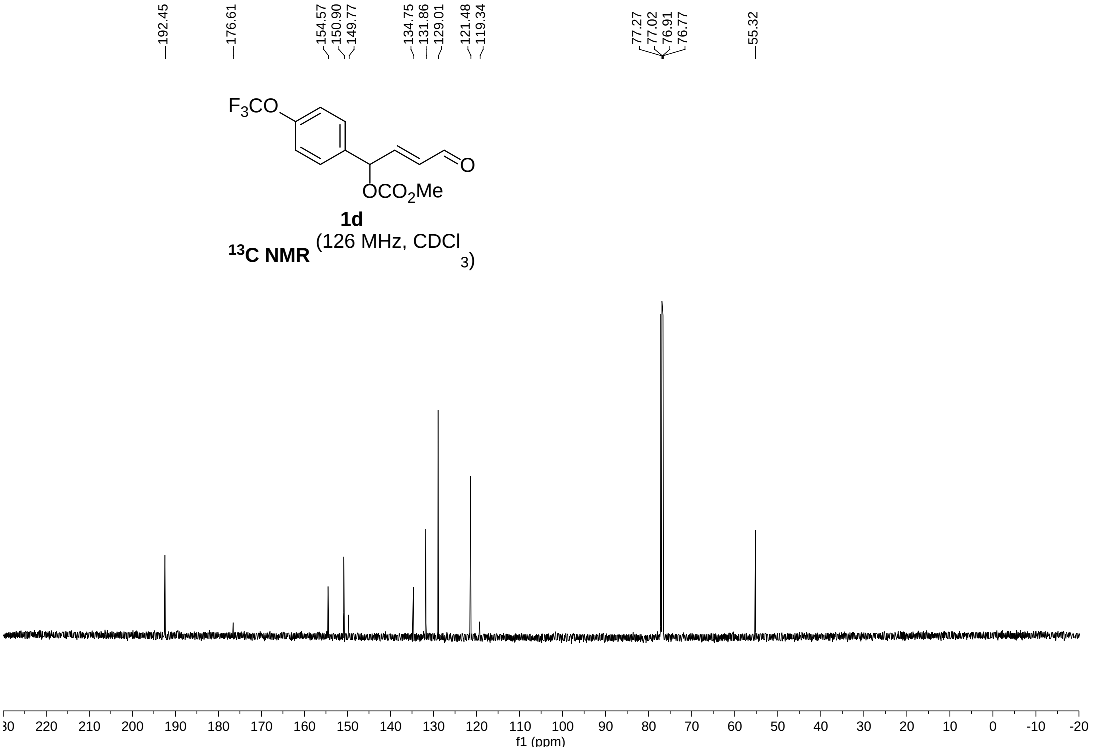
1c

^{13}C NMR (101 MHz, $CDCl_3$)



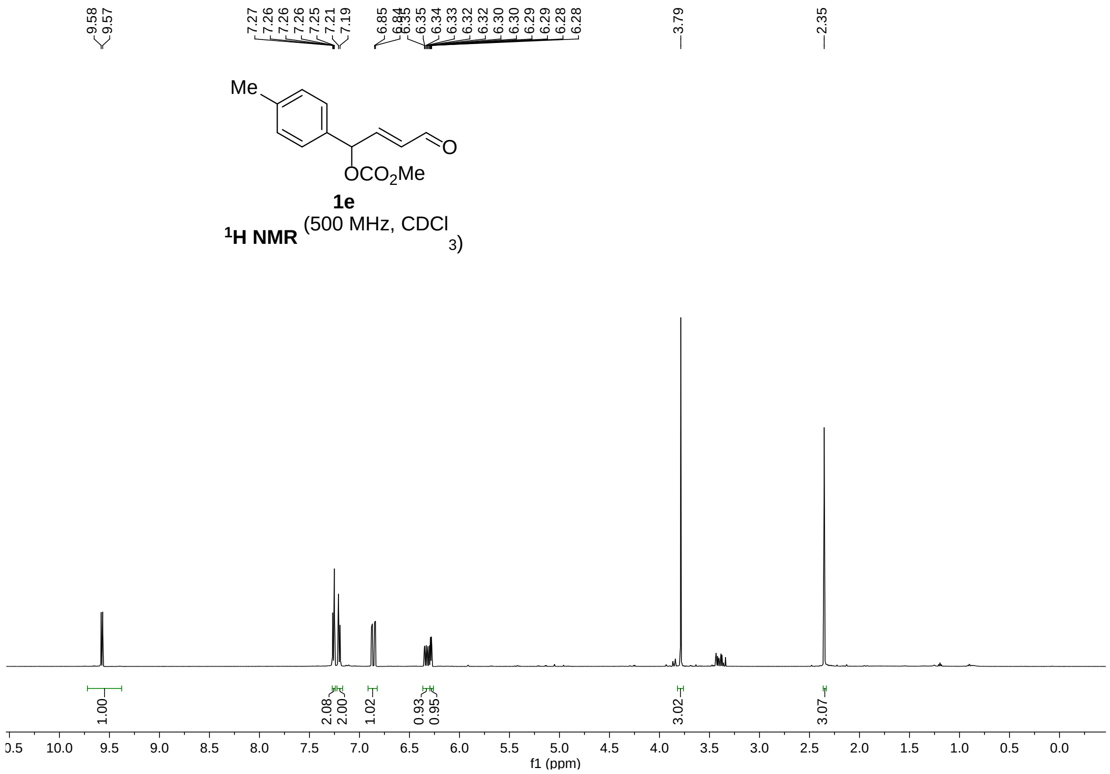
1d

^{1}H NMR (500 MHz, $CDCl_3$)



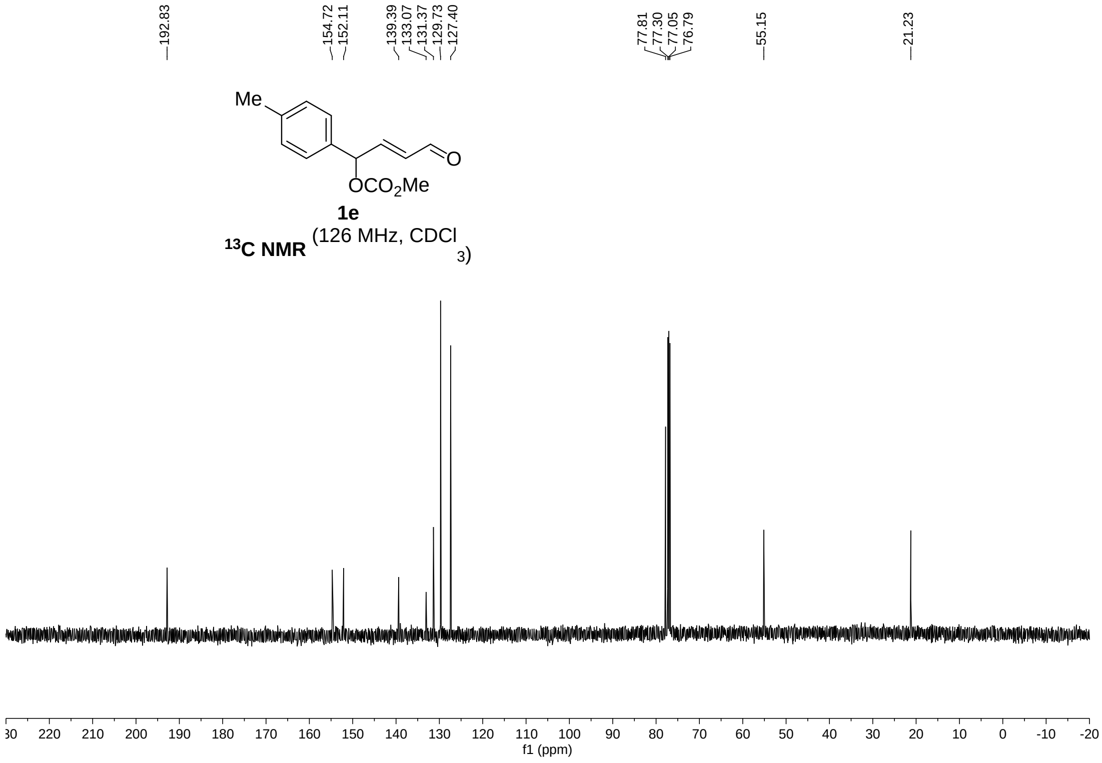
1d

^{13}C NMR (126 MHz, $CDCl_3$)



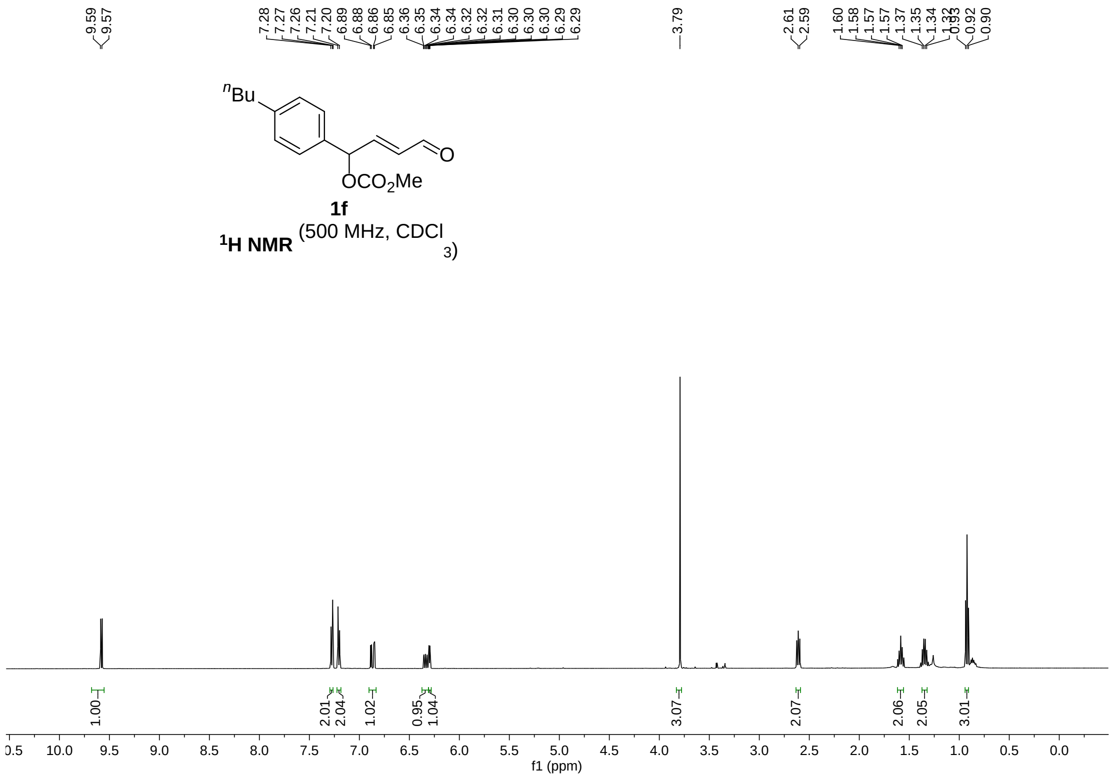
1e

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



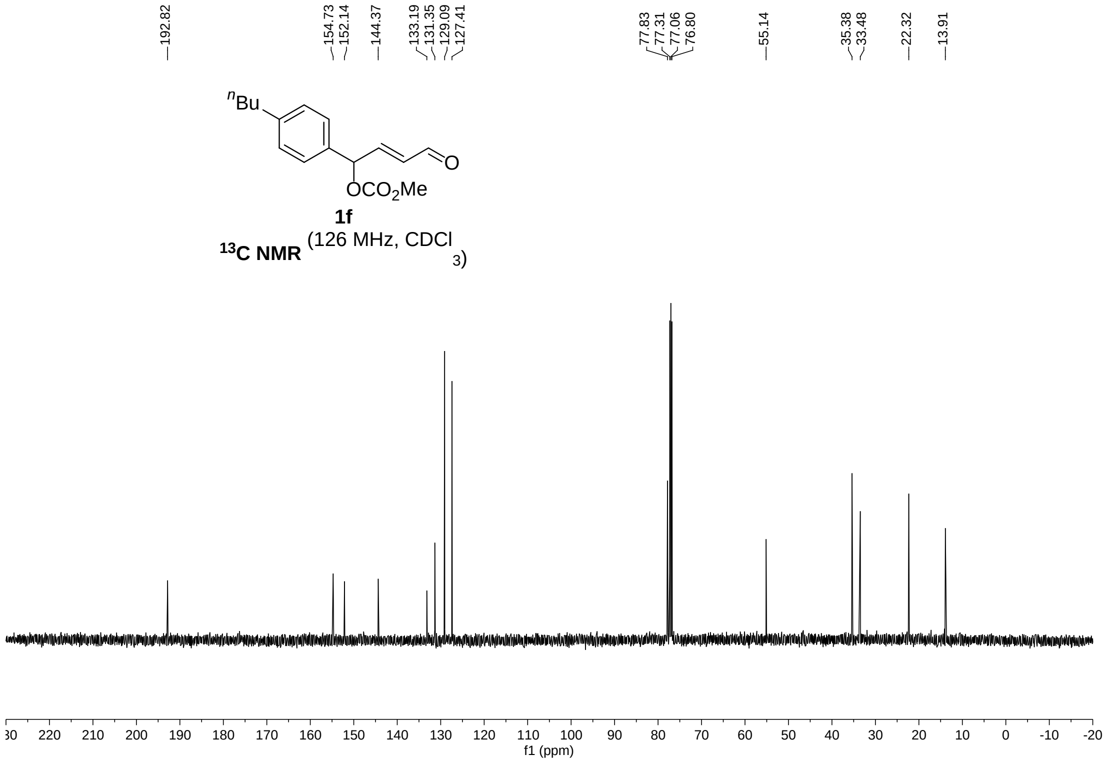
1e

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



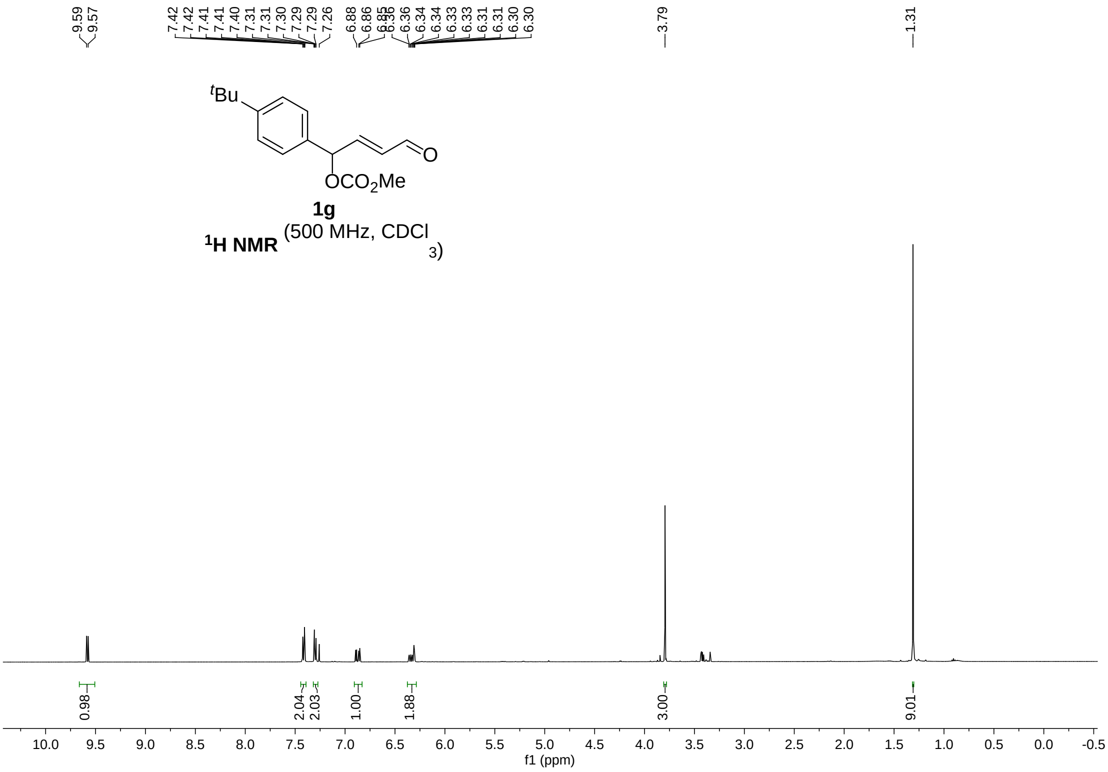
1f

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



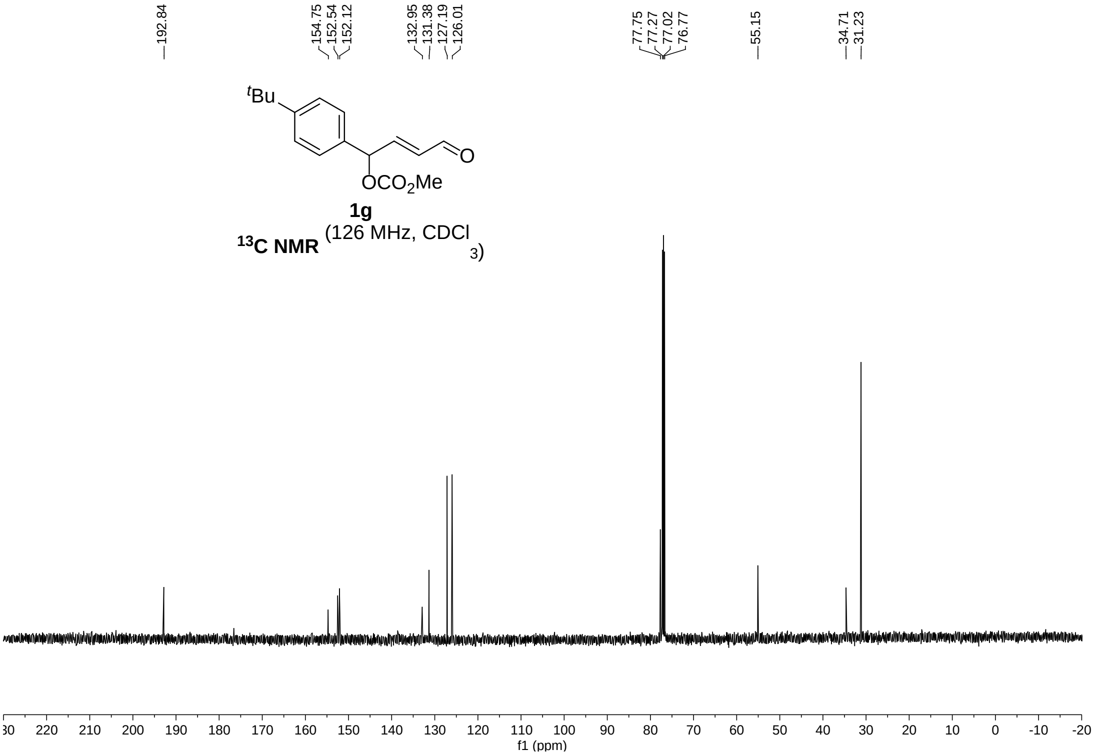
1f

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



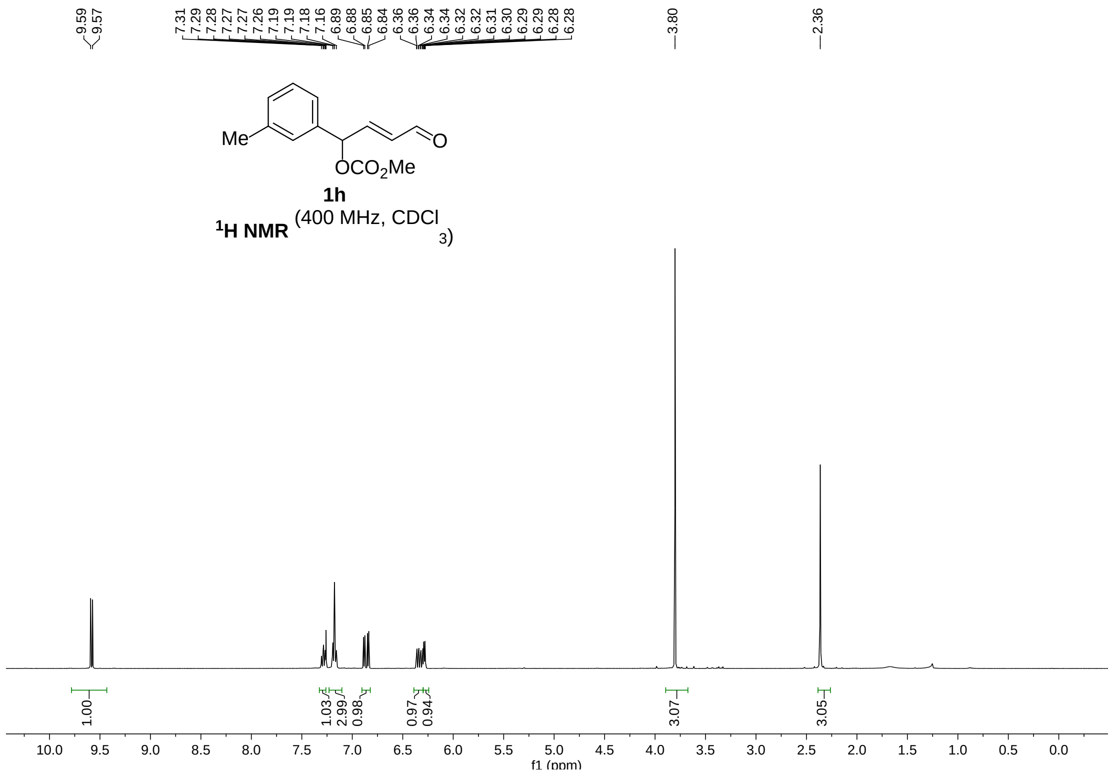
1g

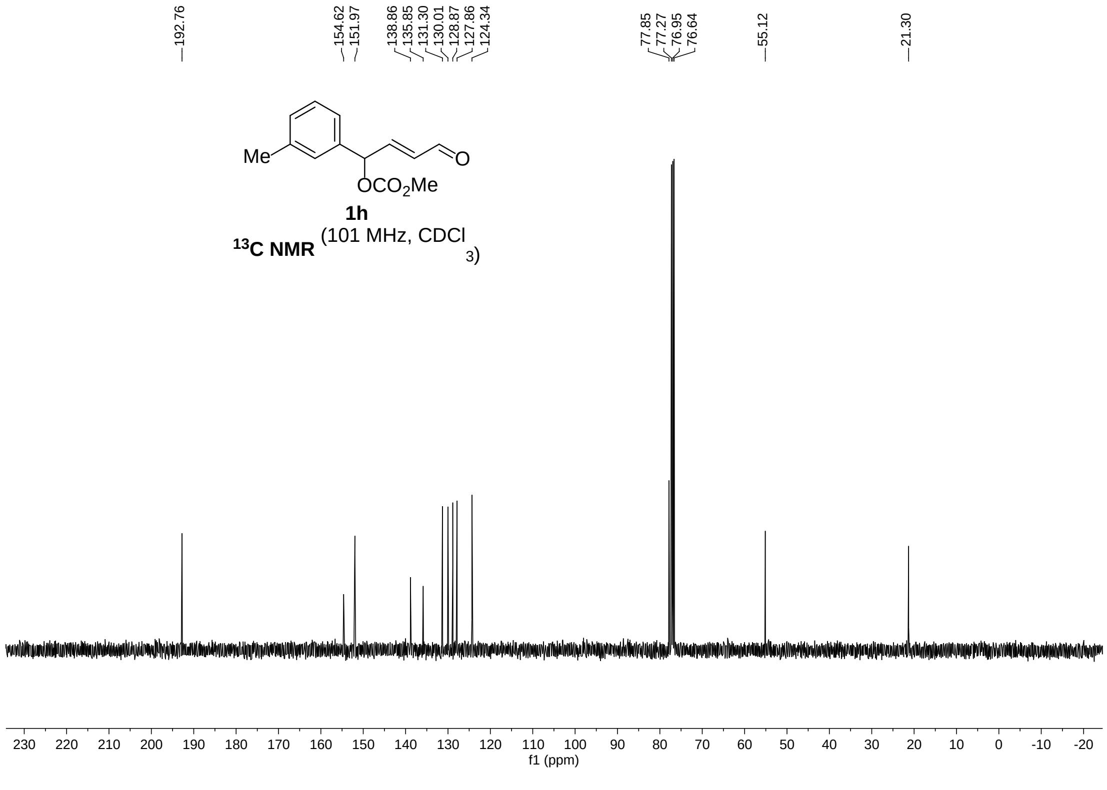
^{1}H NMR (500 MHz, $CDCl_3$)

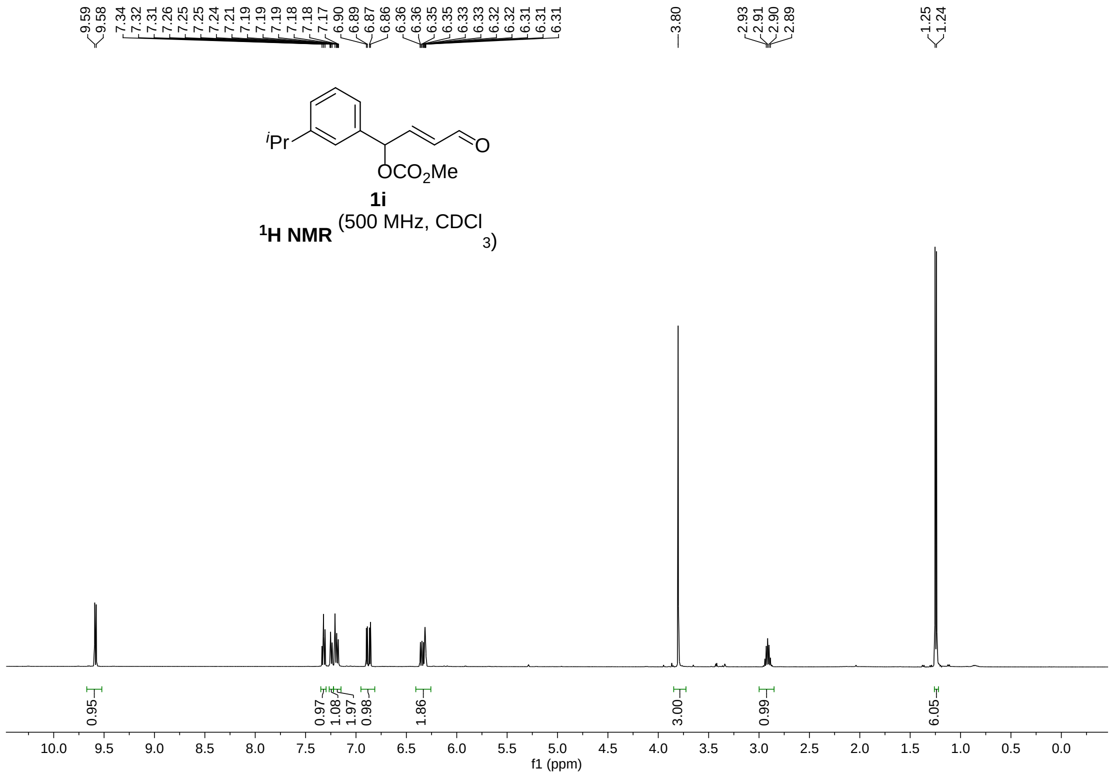


1g

^{13}C NMR (126 MHz, $CDCl_3$)

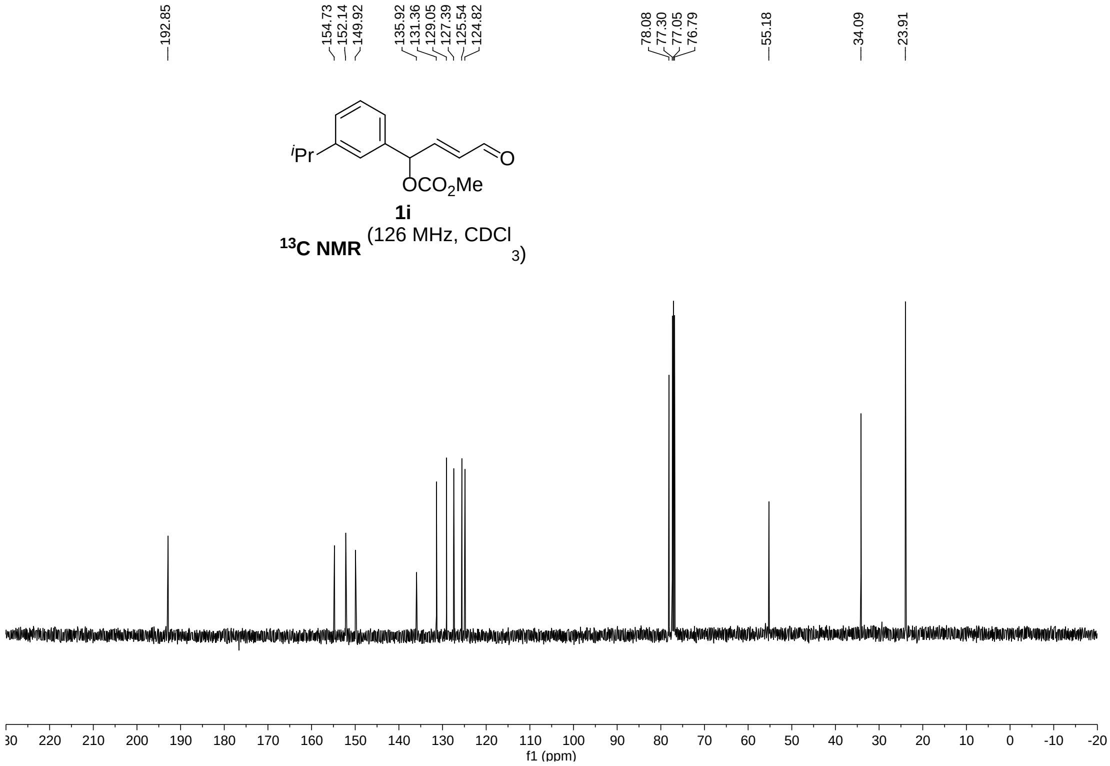

9.59
9.57
7.31
7.29
7.28
7.27
7.27
7.26
7.19
7.19
7.18
7.16
6.89
6.88
6.85
6.84
6.36
6.36
6.34
6.34
6.32
6.32
6.31
6.30
6.29
6.29
6.28
6.28
3.80
2.36
Me
O
OCO$_2$Me
1h
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.03
2.99
0.98
0.97
0.94
3.07
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.76
154.62
151.97
138.86
135.85
131.30
130.01
128.87
127.86
124.34
77.85
77.27
76.95
76.64
55.12
21.30
Me
O
OCO$_2$Me
1h
^{13}C NMR (101 MHz, CDCl$_3$)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



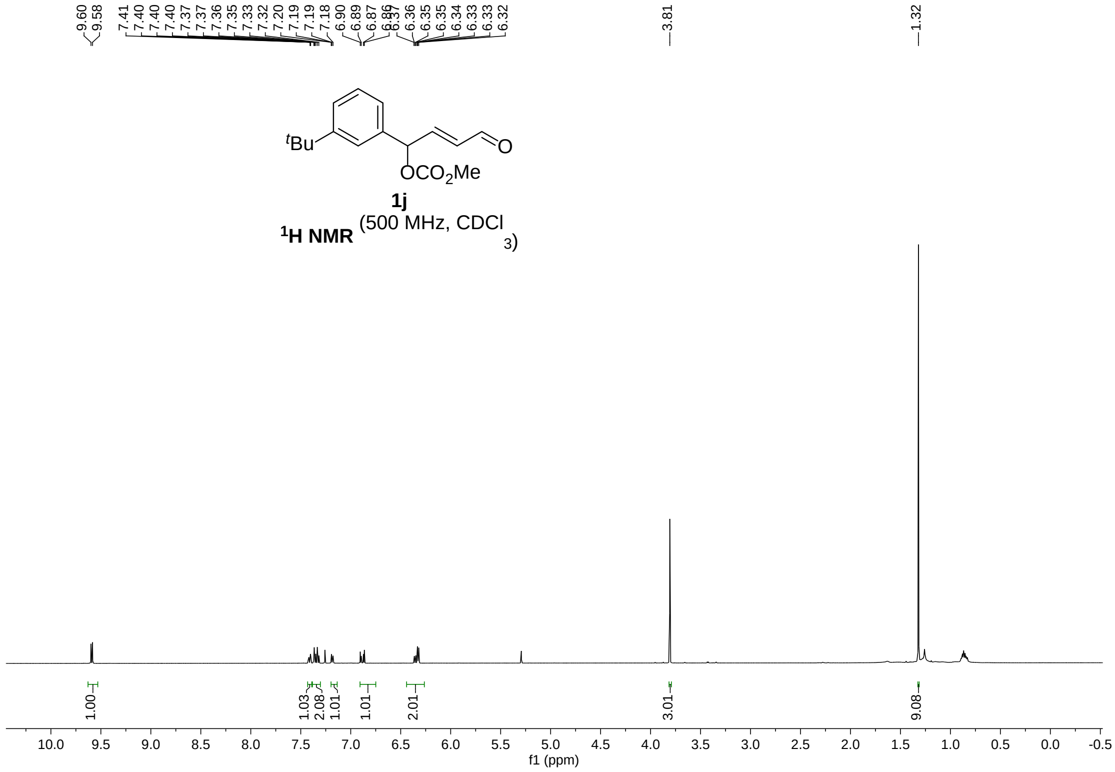
1i

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



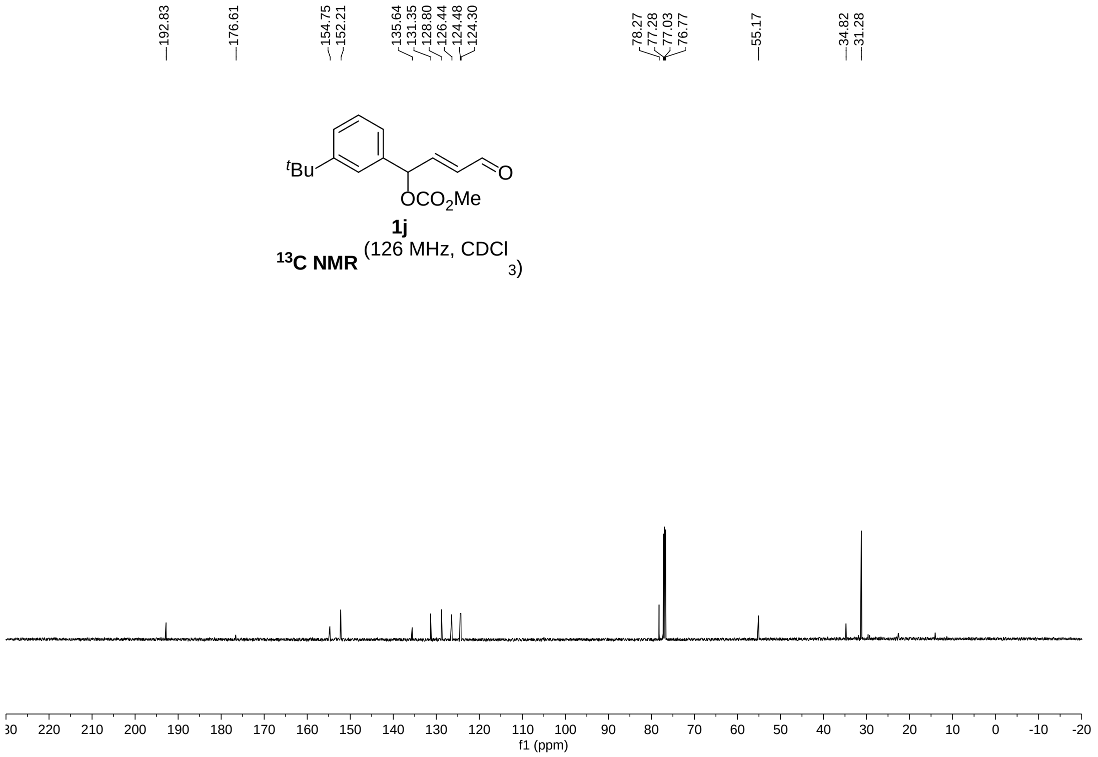
1i

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



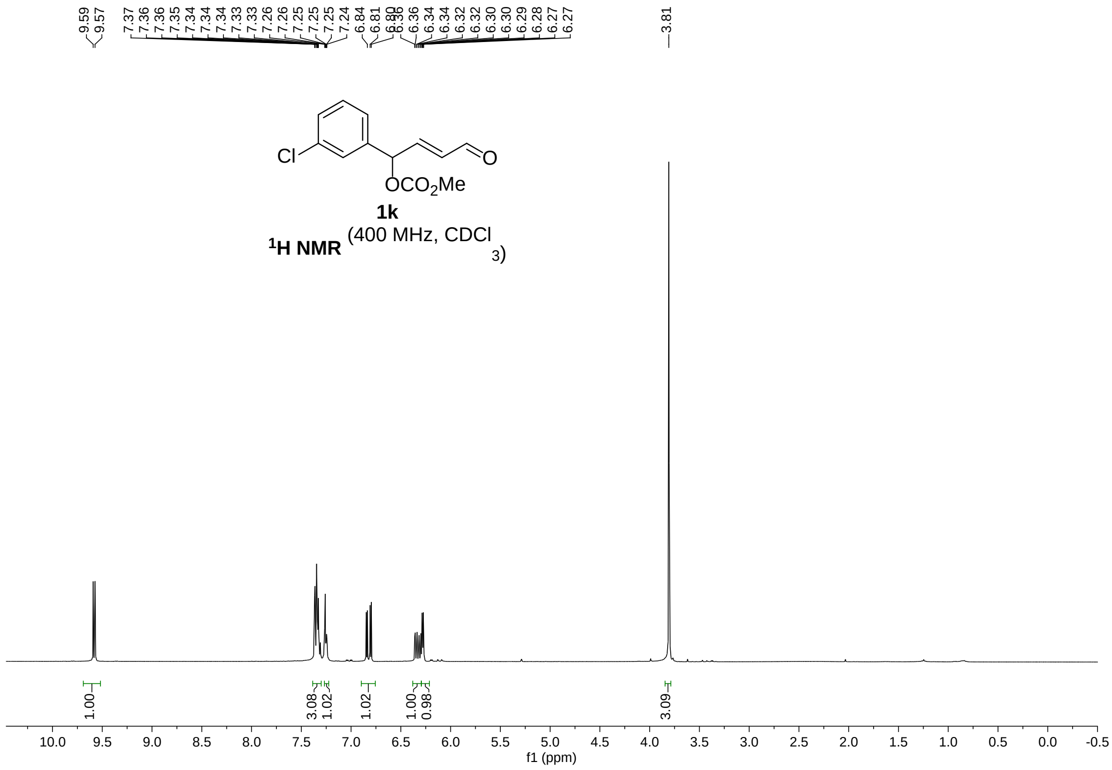
1j

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



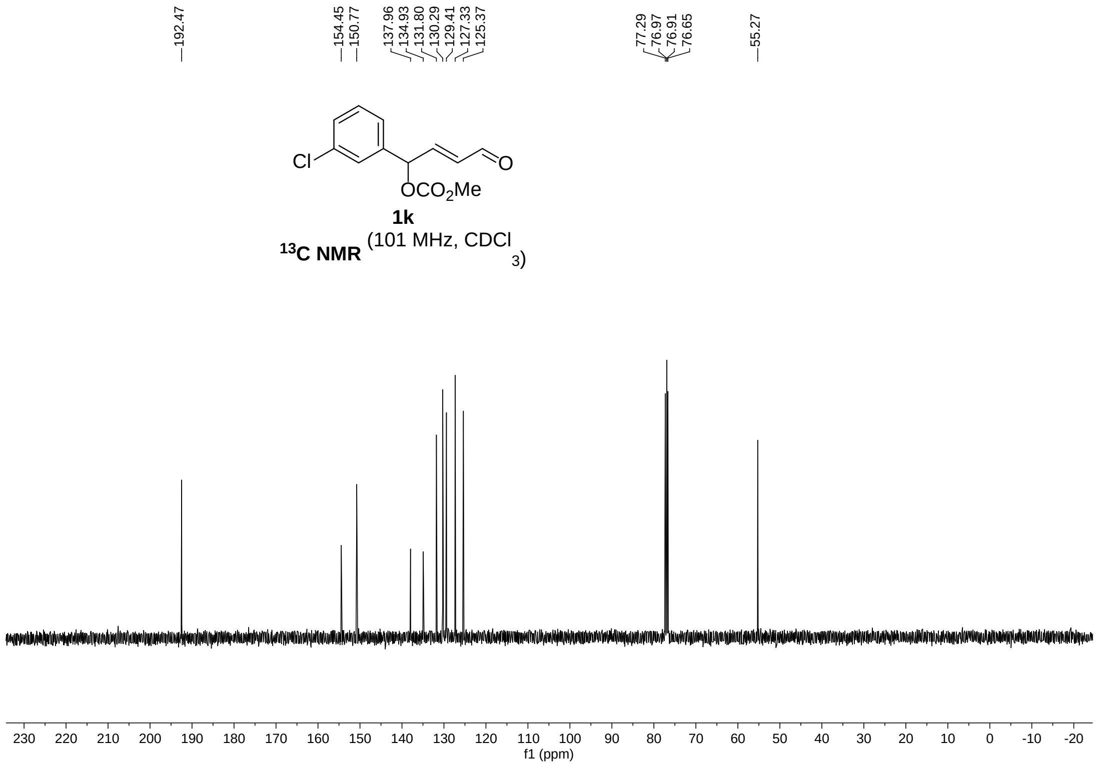
1j

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



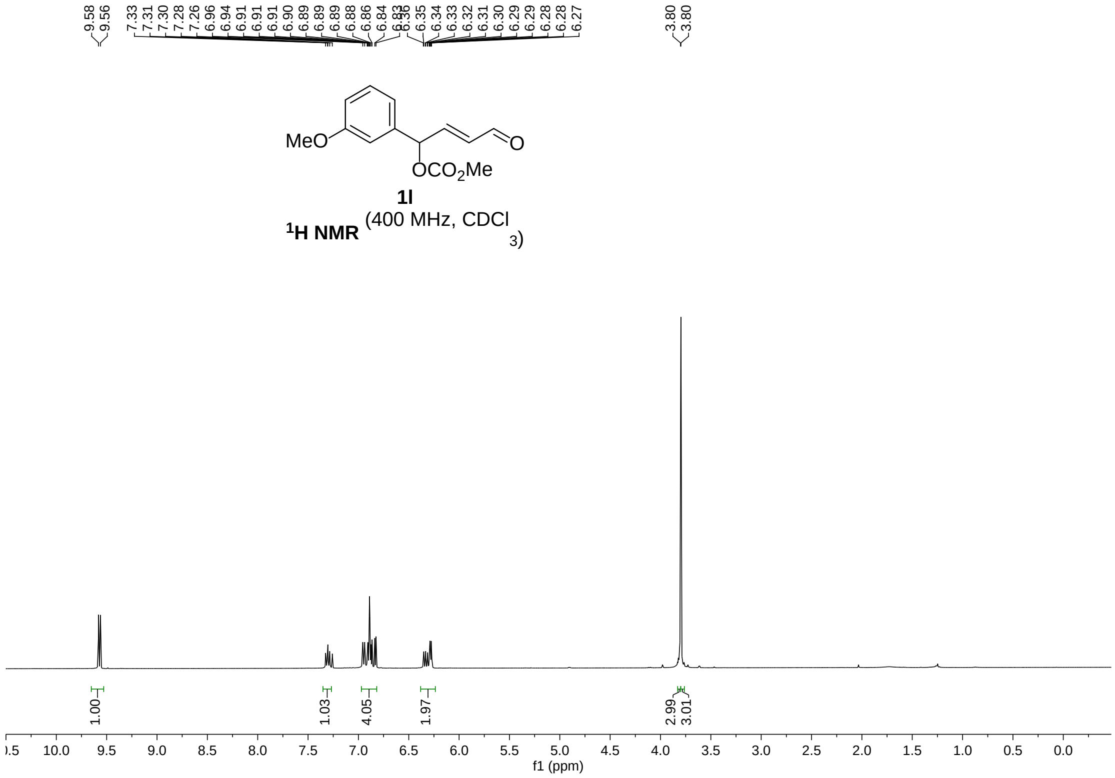
1k

^{1}H NMR (400 MHz, CDCl$_3$)



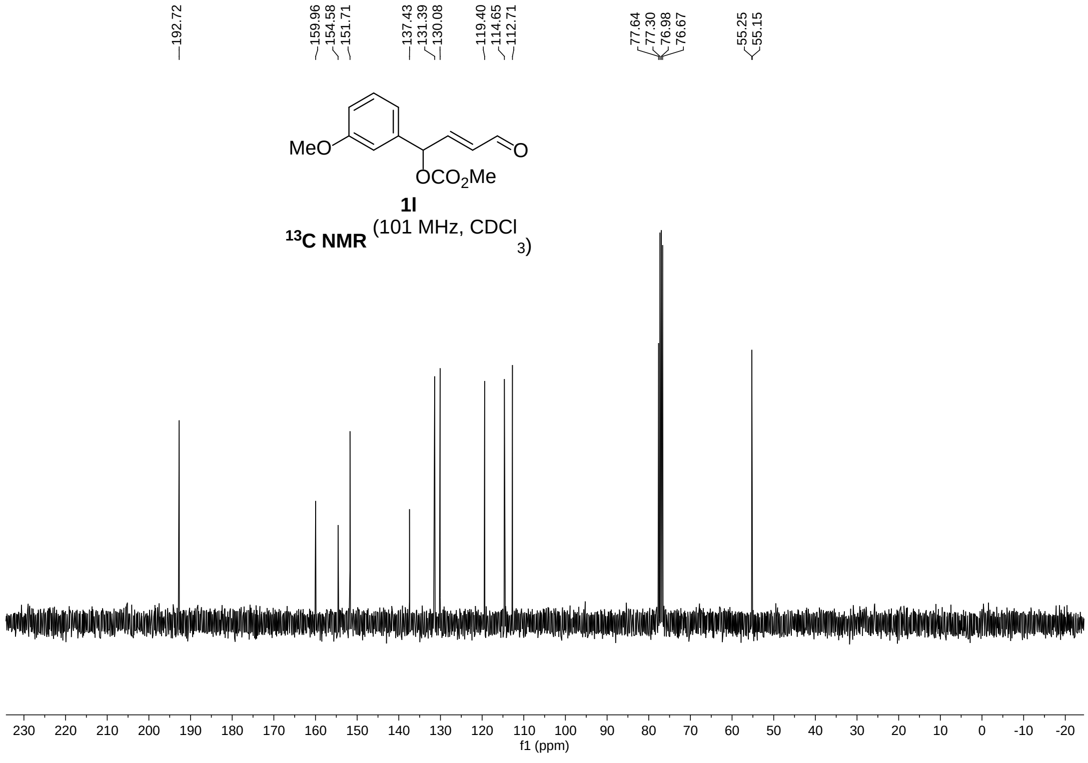
1k

^{13}C NMR (101 MHz, CDCl$_3$)



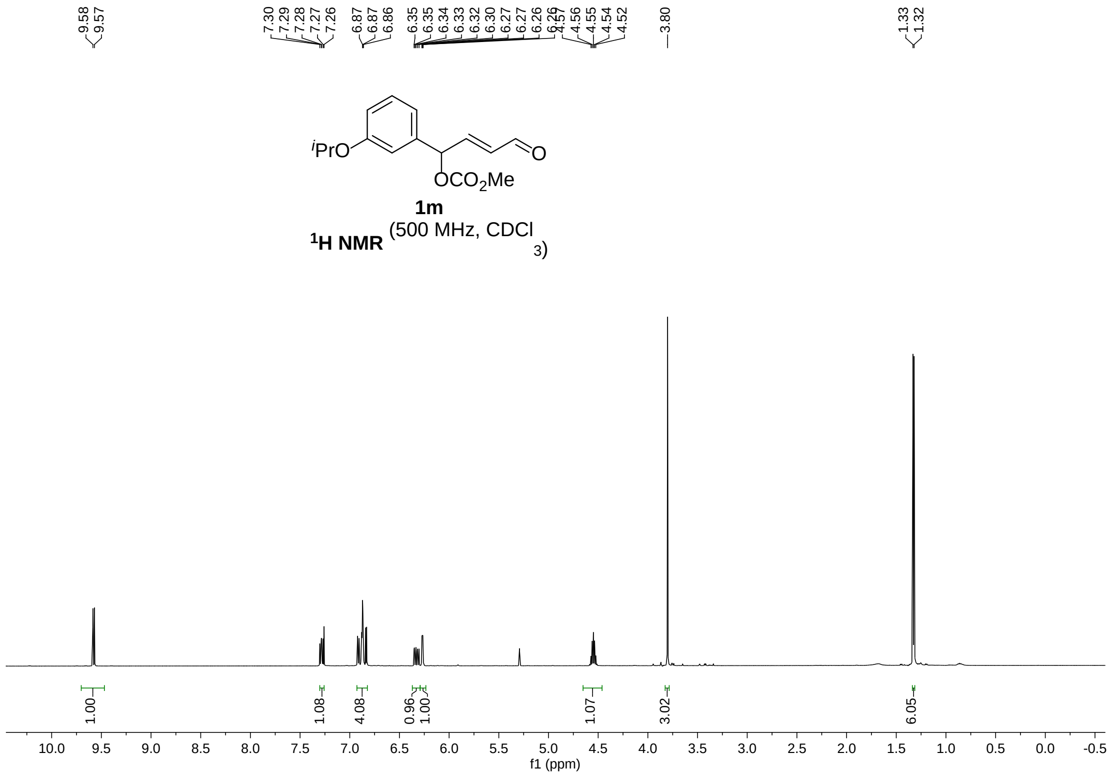
1l

^{1}H NMR (400 MHz, CDCl$_3$)



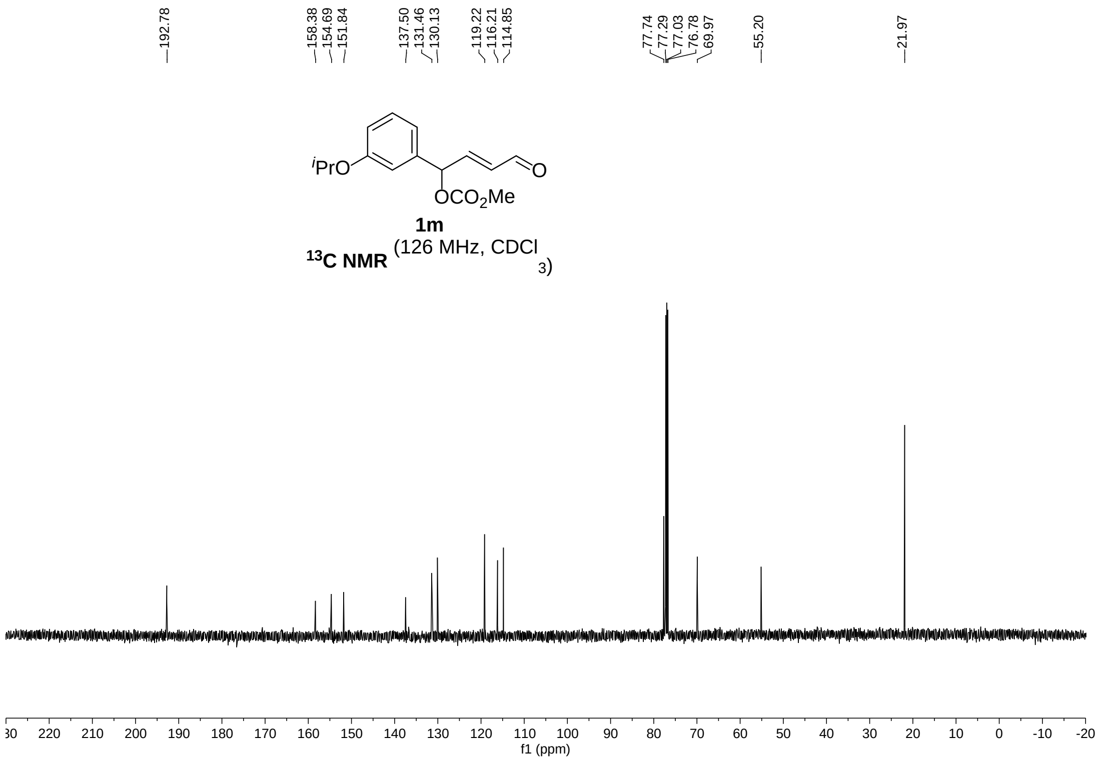
1l

^{13}C NMR (101 MHz, CDCl$_3$)



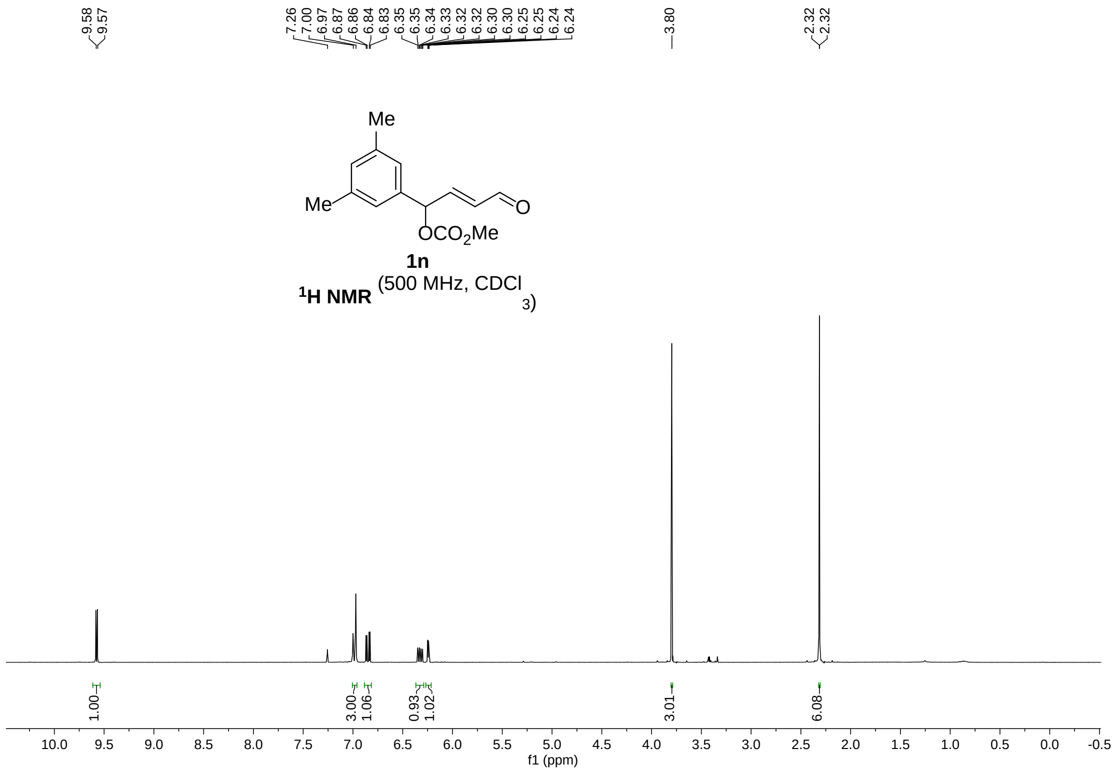
1m

^{1}H NMR (500 MHz, $CDCl_3$)



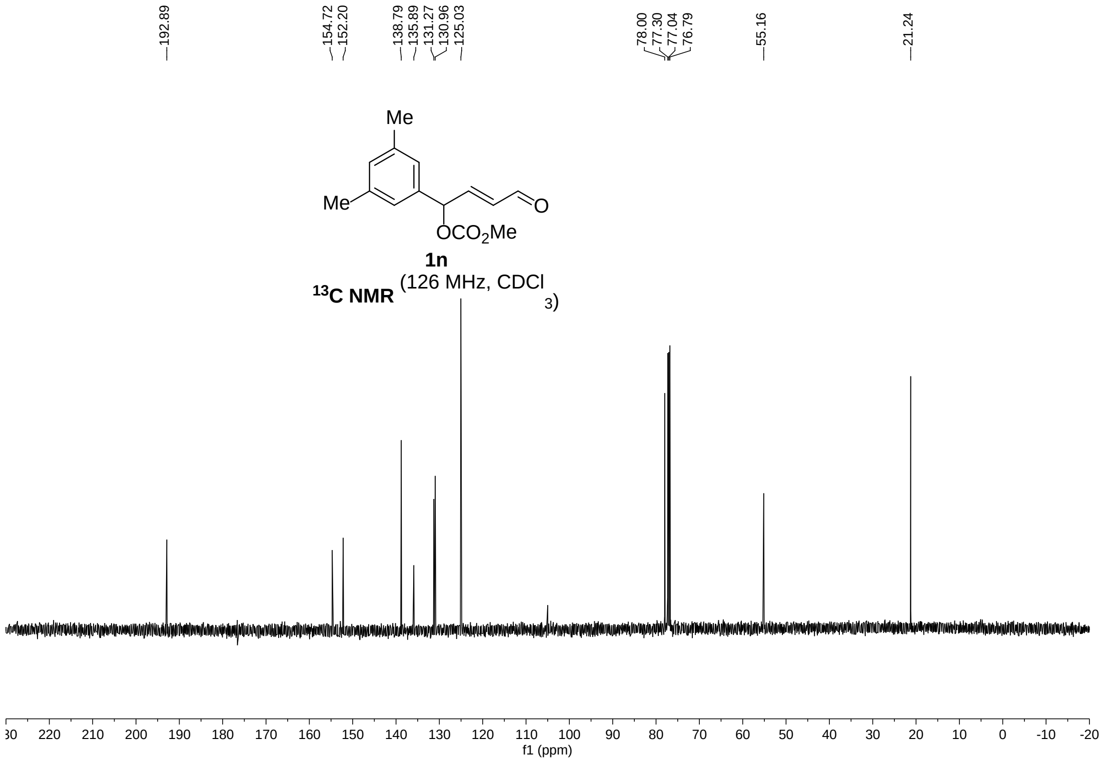
1m

^{13}C NMR (126 MHz, $CDCl_3$)



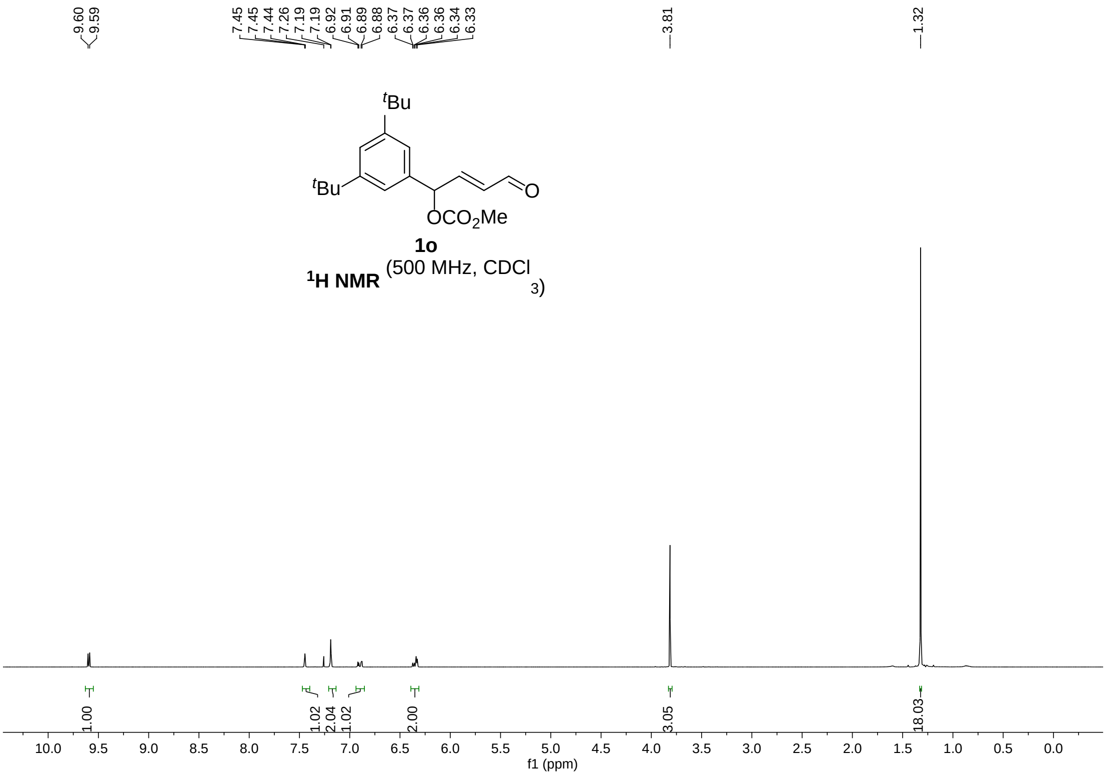
1n

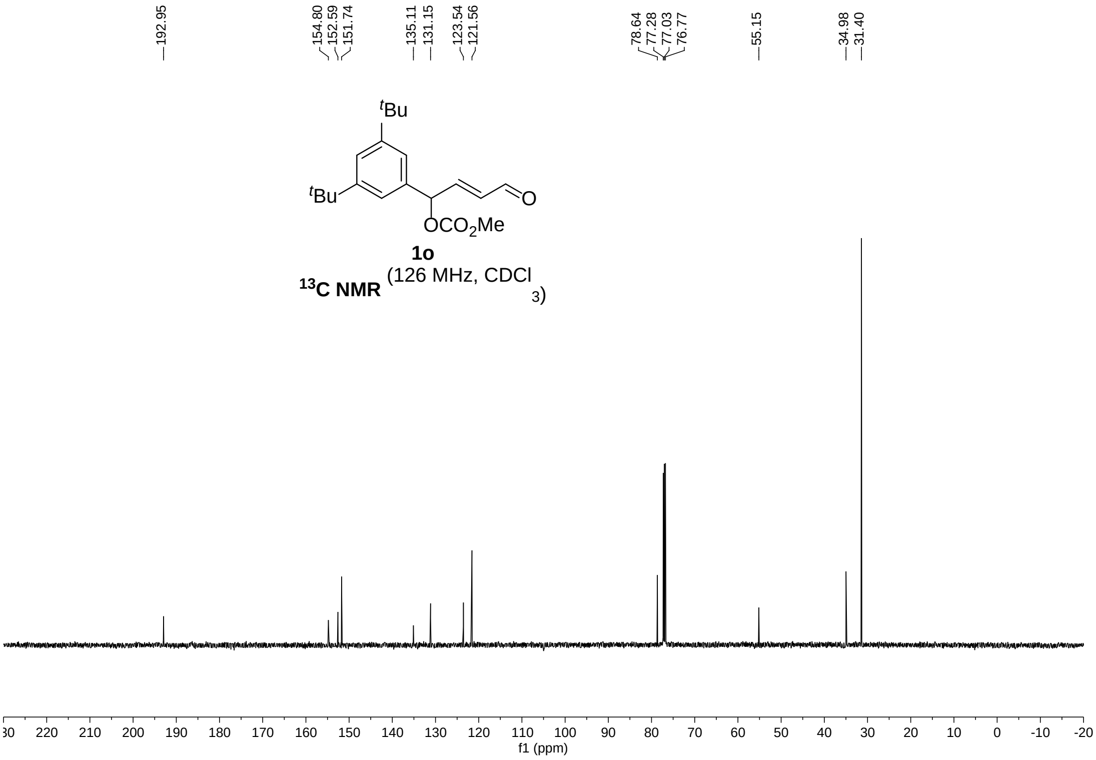
^{1}H NMR (500 MHz, CDCl$_3$)

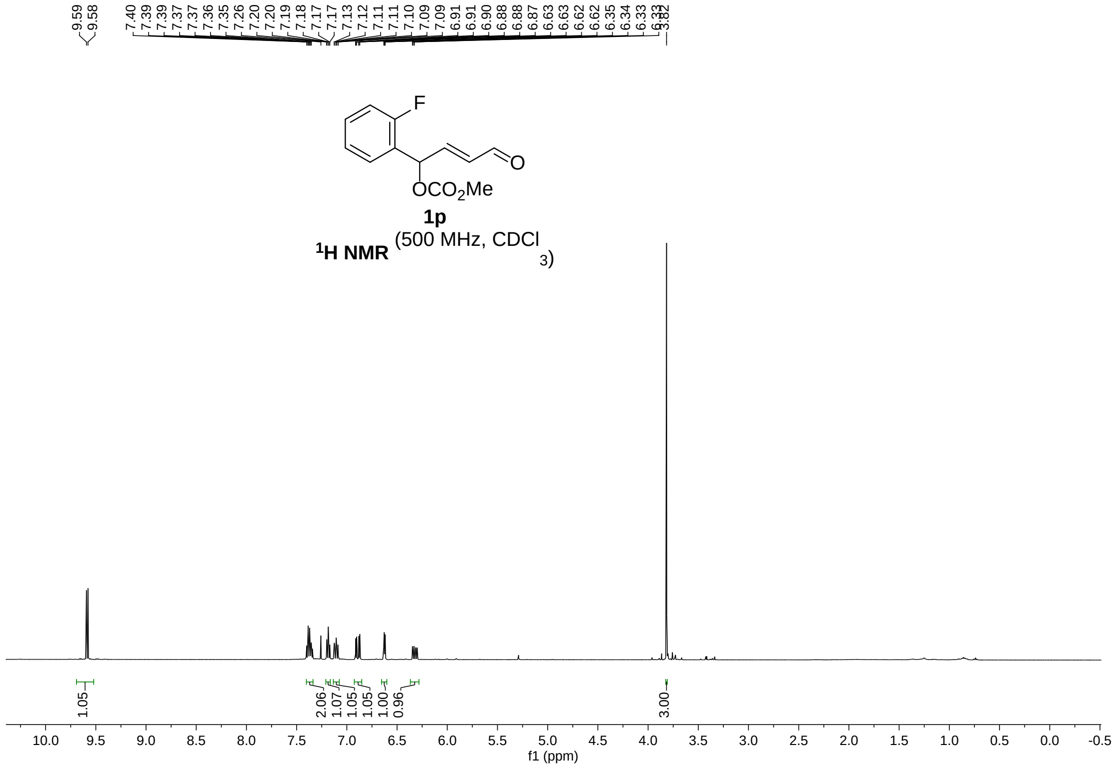


1n

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

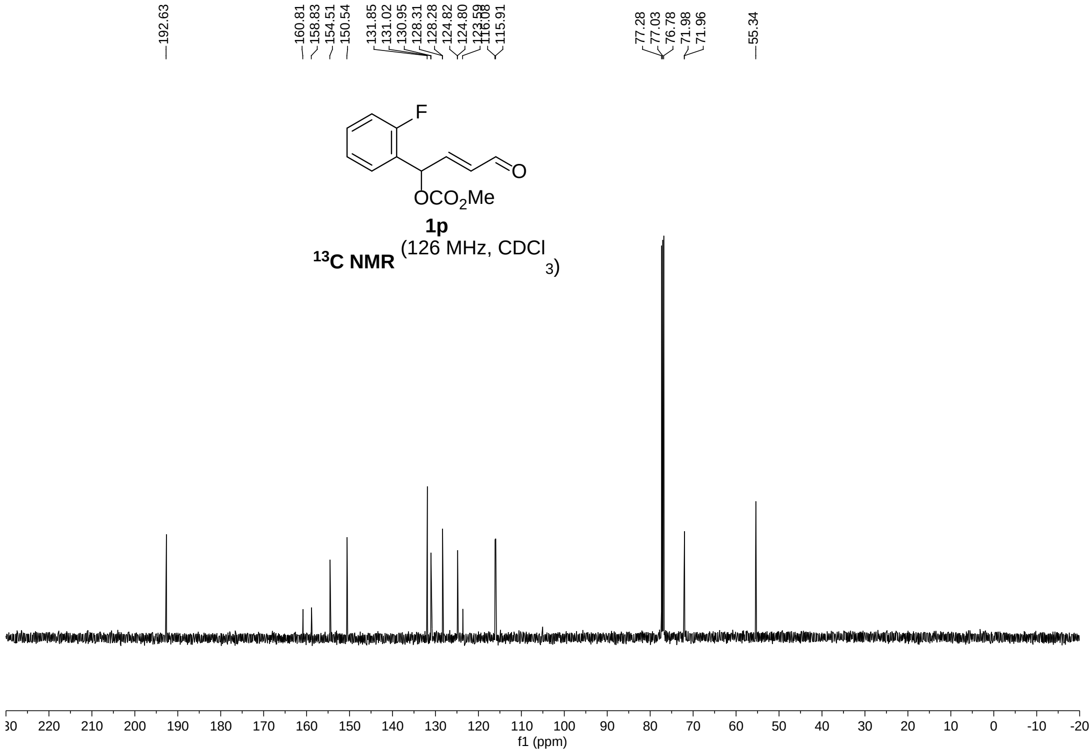

9.60
9.59
7.45
7.45
7.44
7.26
7.19
7.19
6.92
6.91
6.89
6.88
6.37
6.37
6.36
6.36
6.34
6.33
3.81
1.32
tBu
tBu
OCO2Me
O
1o
1H NMR (500 MHz, CDCl3)
1.00
1.02
2.04
1.02
2.00
3.05
18.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.95
154.80
152.59
151.74
135.11
131.15
123.54
121.56
78.64
77.28
77.03
76.77
55.15
34.98
31.40
tBu
tBu
OCO2Me
O
1o
13C NMR (126 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



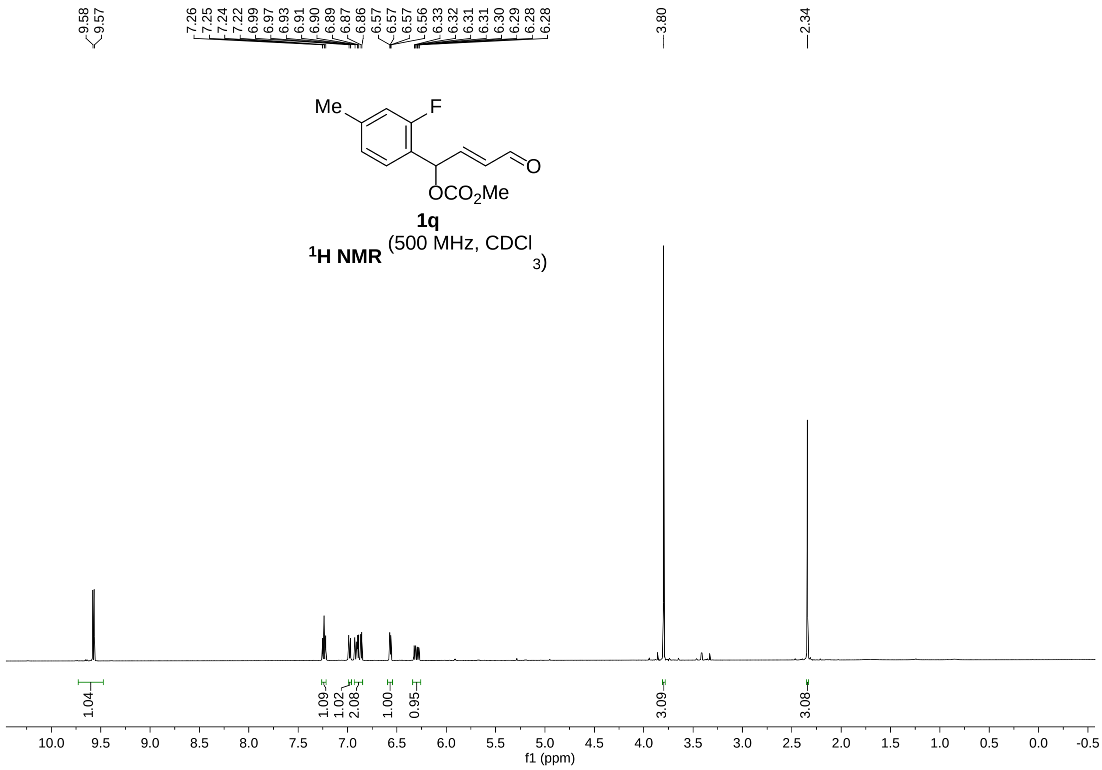
1p

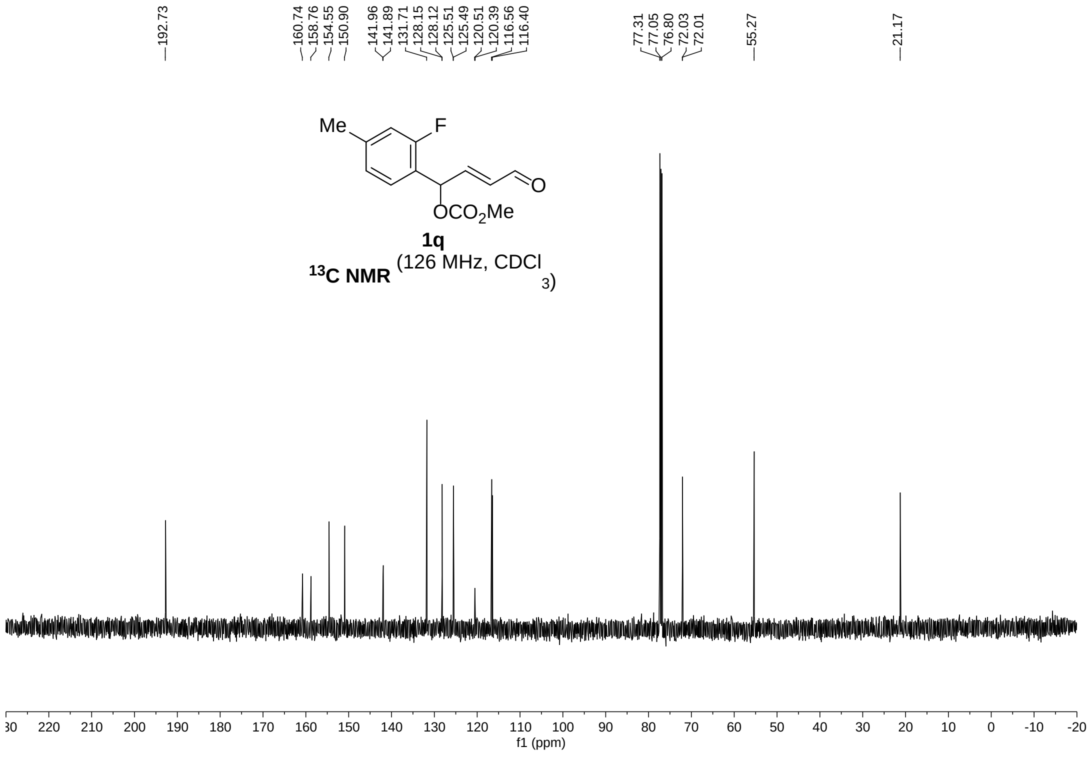
^{1}H NMR (500 MHz, CDCl$_3$)

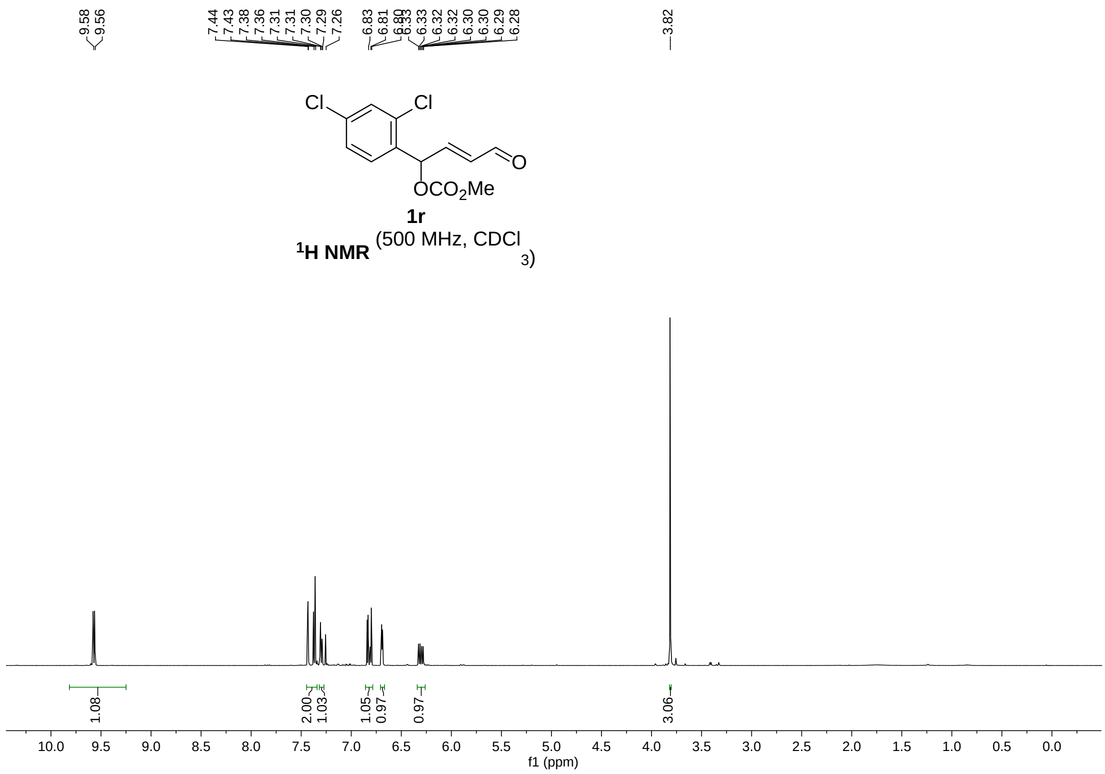


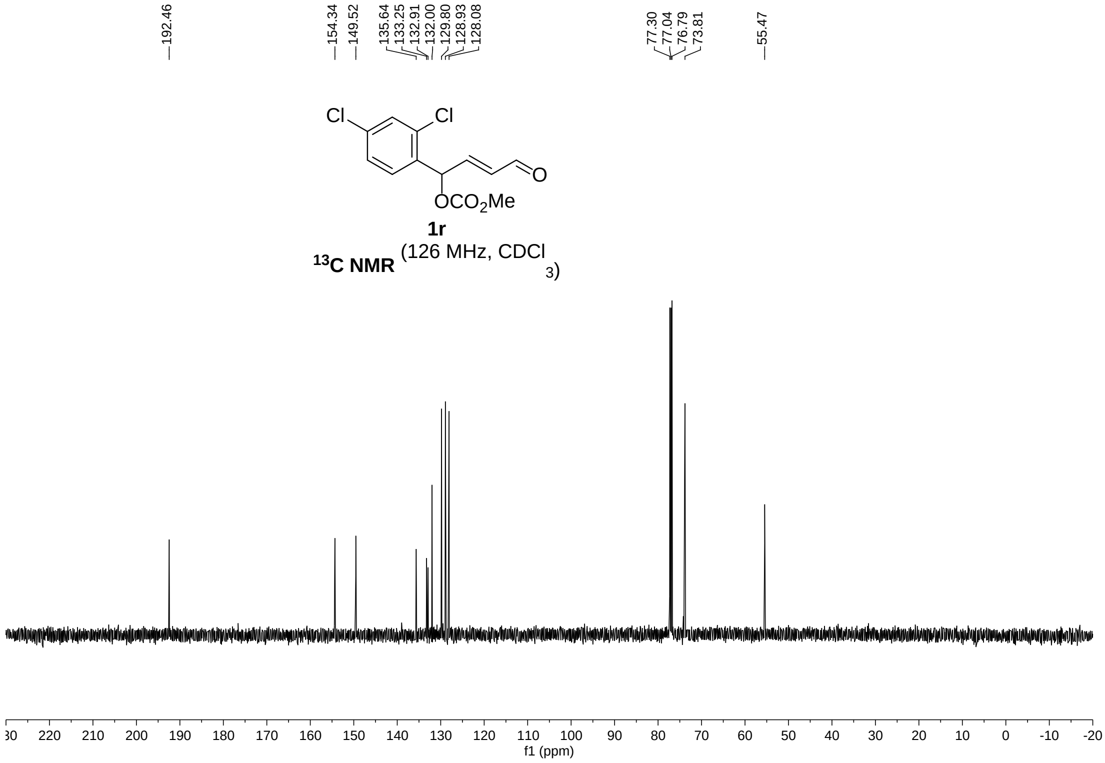
1p

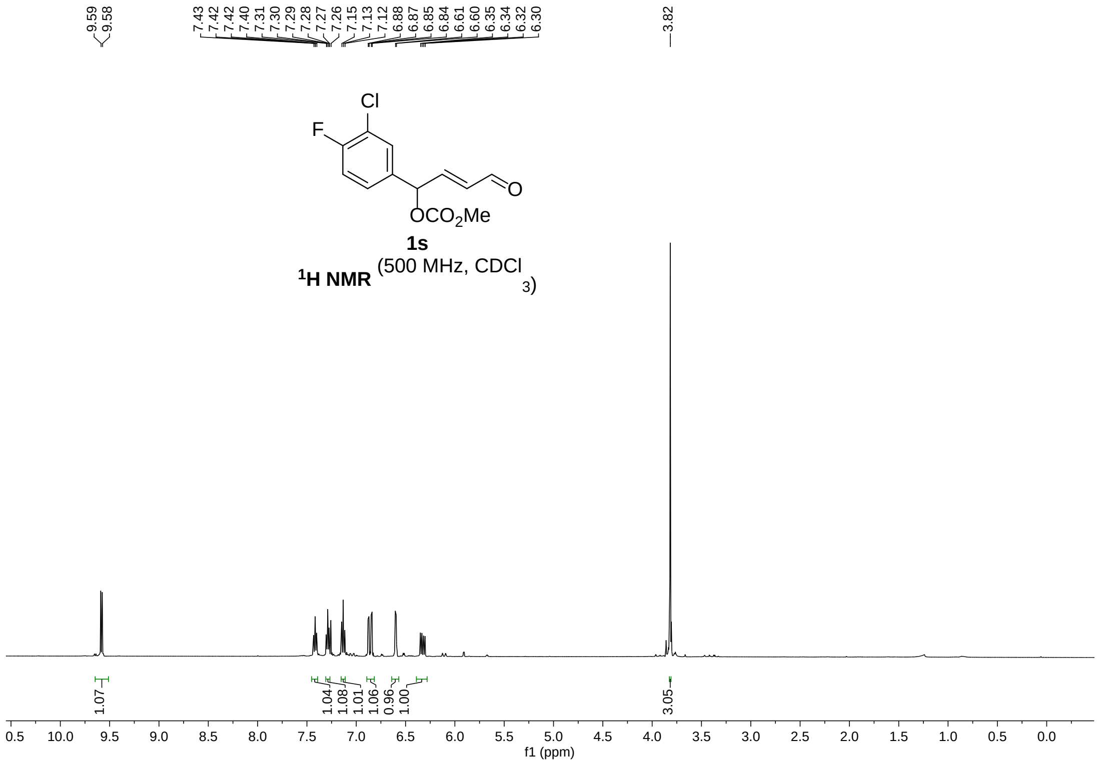
^{13}C NMR (126 MHz, CDCl$_3$)


9.58
9.57
7.26
7.25
7.24
7.22
6.99
6.97
6.93
6.91
6.90
6.89
6.87
6.86
6.57
6.57
6.57
6.56
6.33
6.32
6.31
6.31
6.30
6.29
6.28
6.28
3.80
2.34
Me
F
O
OCO2Me
1q
1H NMR (500 MHz, CDCl3)
1.04
1.09
1.02
2.08
1.00
0.95
3.09
3.08
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
f1 (ppm)

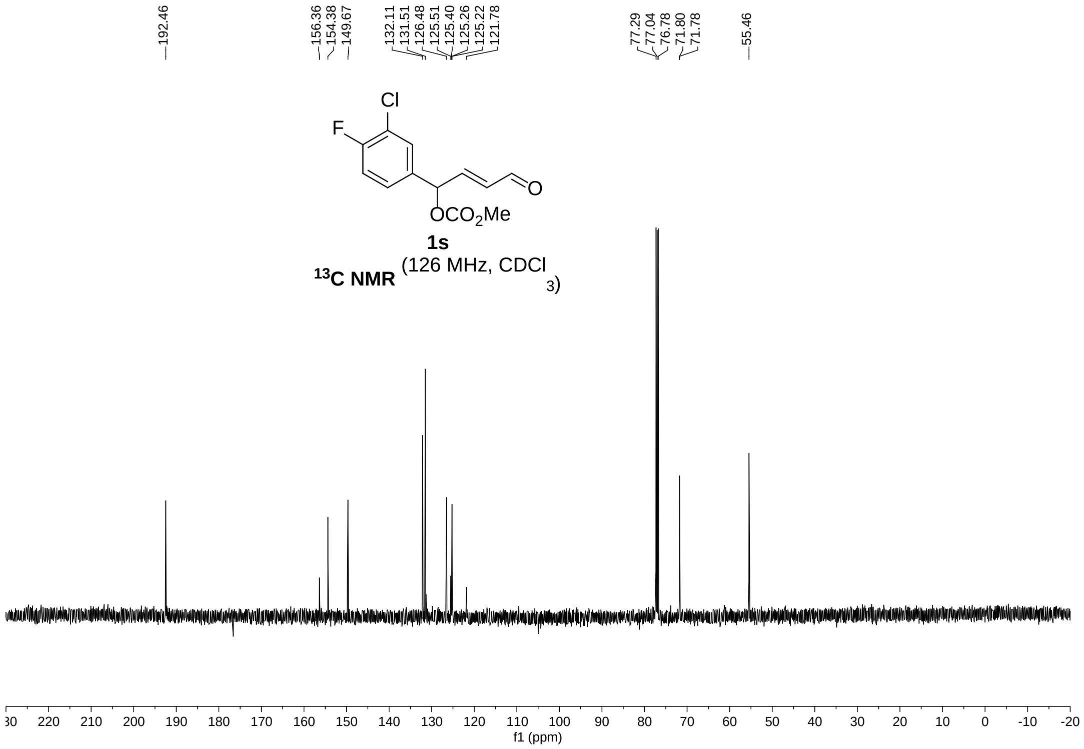

192.73
160.74
158.76
154.55
150.90
141.96
141.89
131.71
128.15
128.12
125.51
125.49
120.51
120.39
116.56
116.40
77.31
77.05
76.80
72.03
72.01
55.27
21.17
Me
F
O
OCO2Me
1q
13C NMR (126 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


9.58
9.56
7.44
7.43
7.38
7.36
7.31
7.31
7.30
7.29
7.26
6.83
6.81
6.80
6.33
6.33
6.32
6.32
6.30
6.30
6.29
6.28
3.82
Cl
Cl
O
OCO2Me
1r
1H NMR (500 MHz, CDCl3)
1.08
2.00
1.03
1.05
0.97
0.97
3.06
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
f1 (ppm)

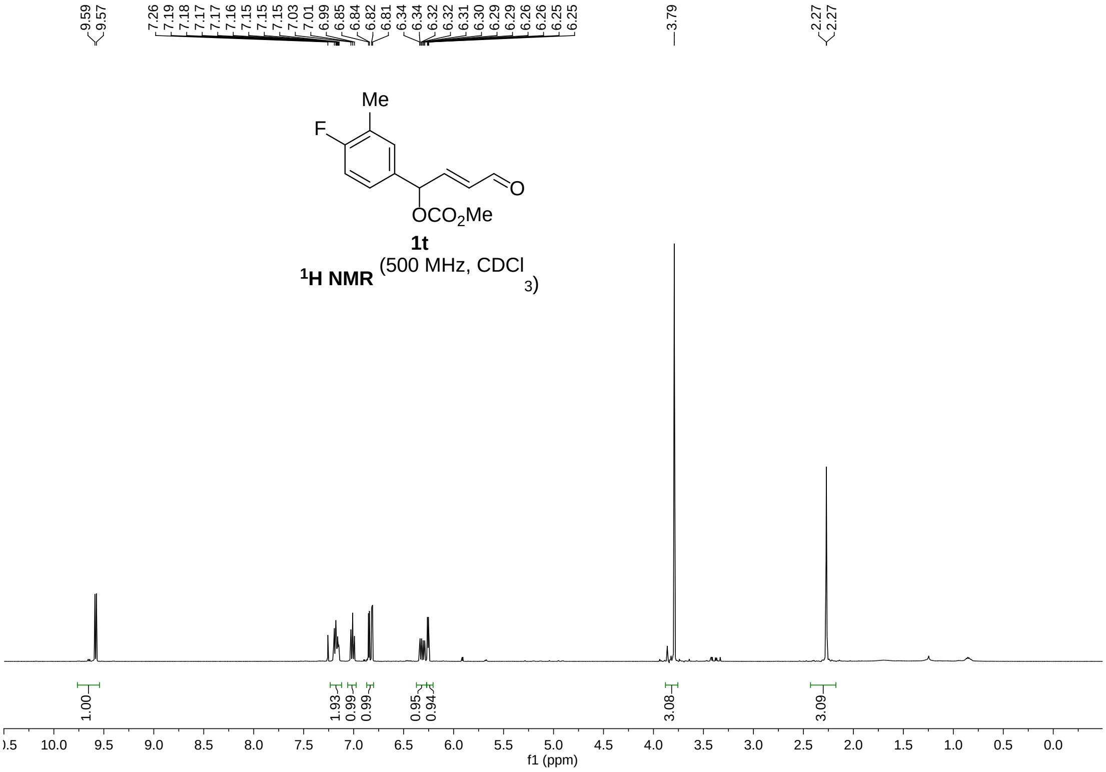

192.46
154.34
149.52
135.64
133.25
132.91
132.00
129.80
128.93
128.08
77.30
77.04
76.79
73.81
55.47
Cl
Cl
O
OCO2Me
1r
13C NMR (126 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

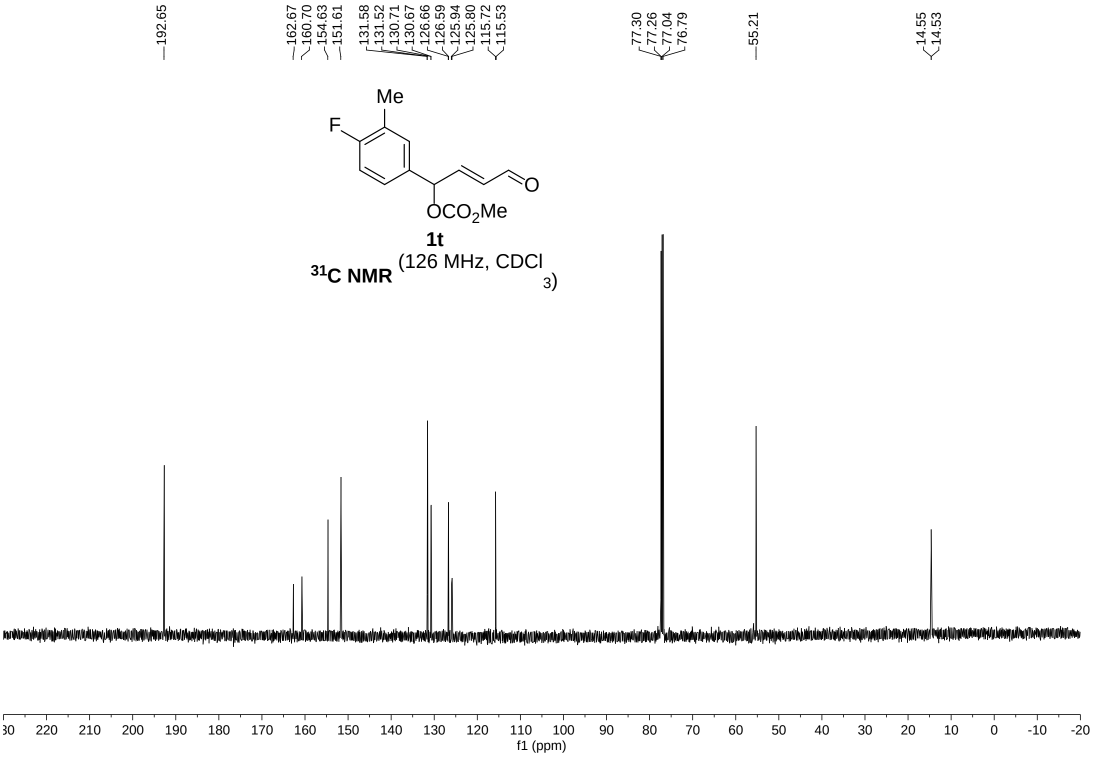

1s

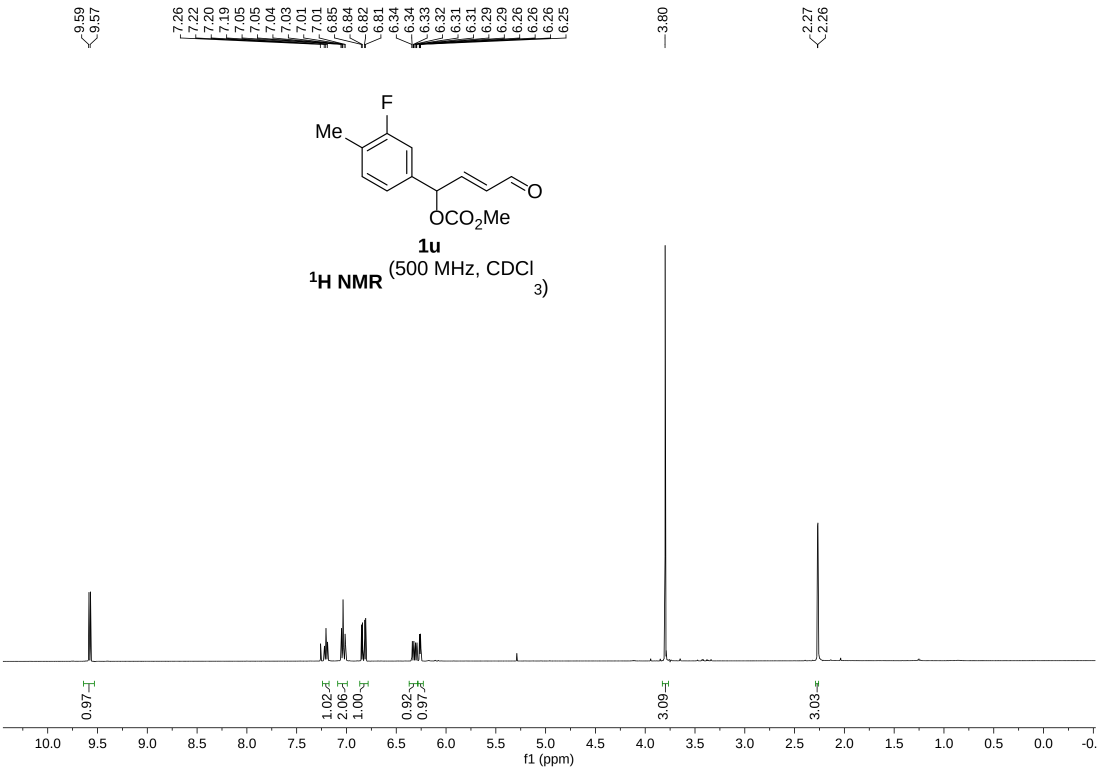
^{1}H NMR (500 MHz, CDCl$_3$)


1s

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

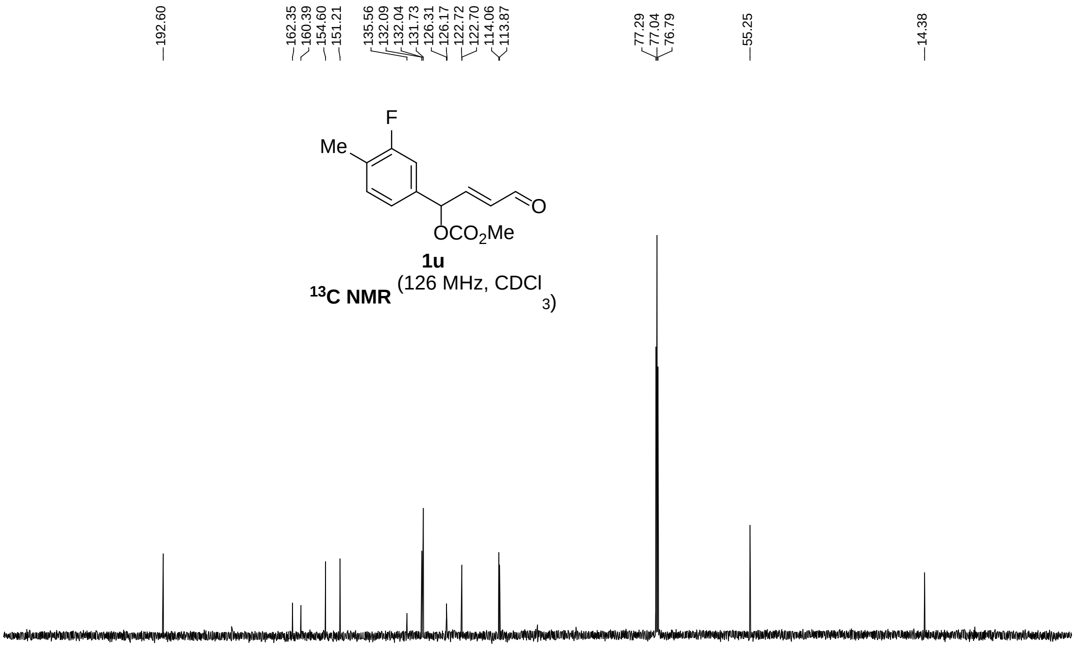

9.59
9.57
7.26
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.15
7.03
7.01
6.99
6.85
6.84
6.82
6.81
6.34
6.34
6.32
6.32
6.31
6.30
6.29
6.29
6.26
6.26
6.25
6.25
3.79
2.27
2.27
Me
F
O
OCO2Me
1t
1H NMR (500 MHz, CDCl3)
1.00
1.93
0.99
0.99
0.95
0.94
3.08
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.65
162.67
160.70
154.63
151.61
131.58
131.52
130.71
130.67
126.66
126.59
125.94
125.80
115.72
115.53
77.30
77.26
77.04
76.79
55.21
14.55
14.53
Me
F
O
OCO2Me
1t
31C NMR (126 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



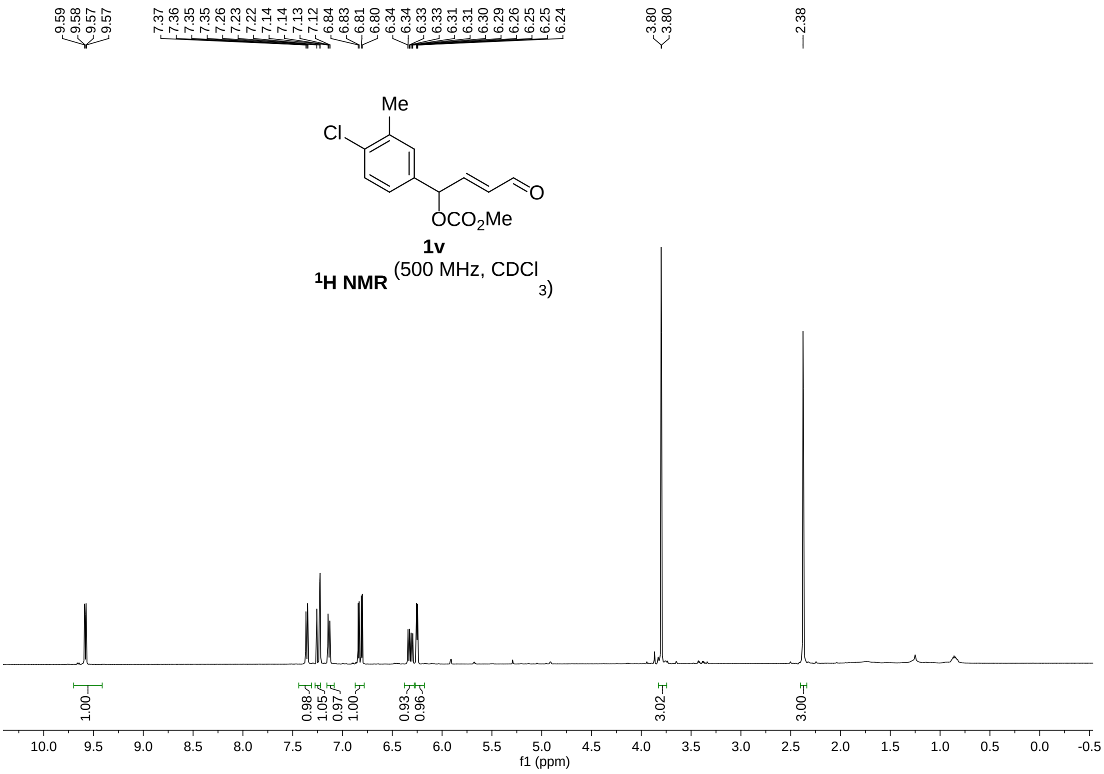
1u

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

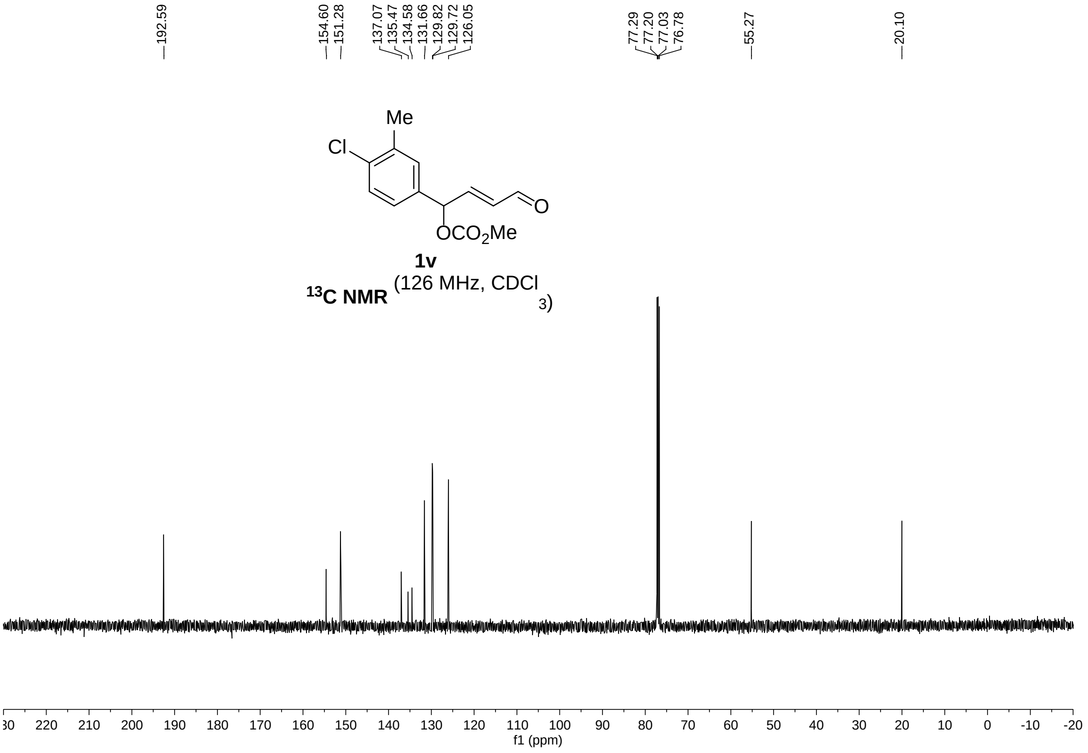


1u

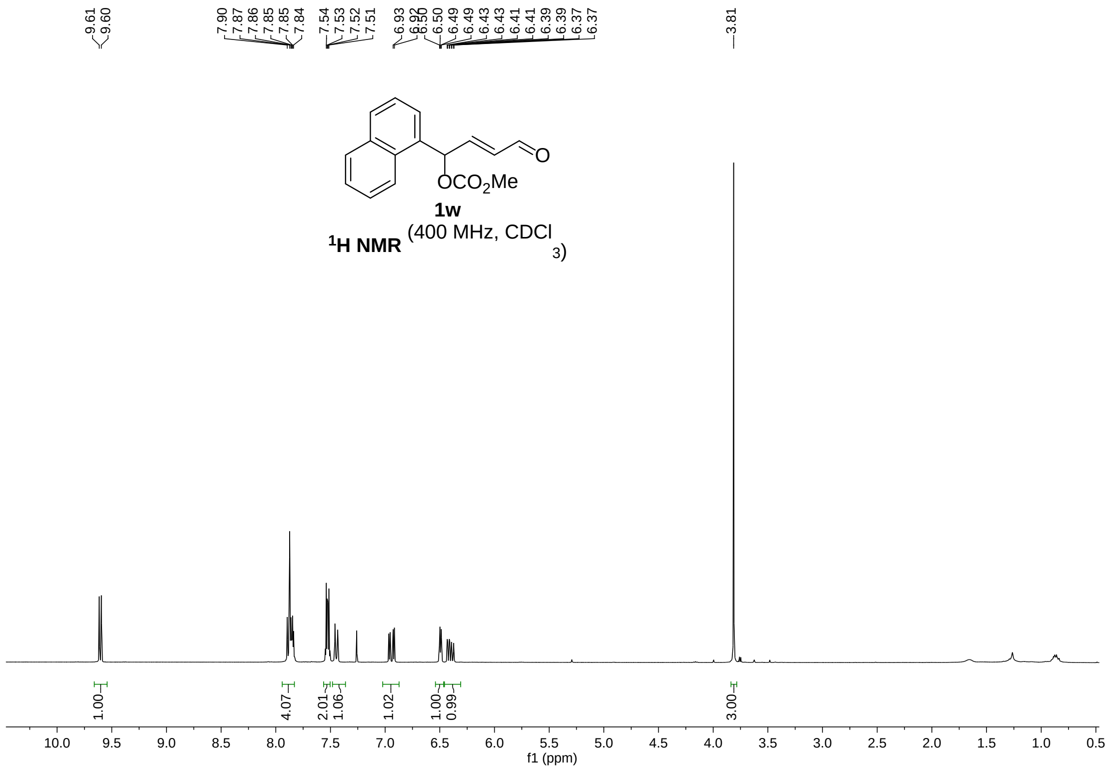
^{13}C NMR (126 MHz, CDCl$_3$)

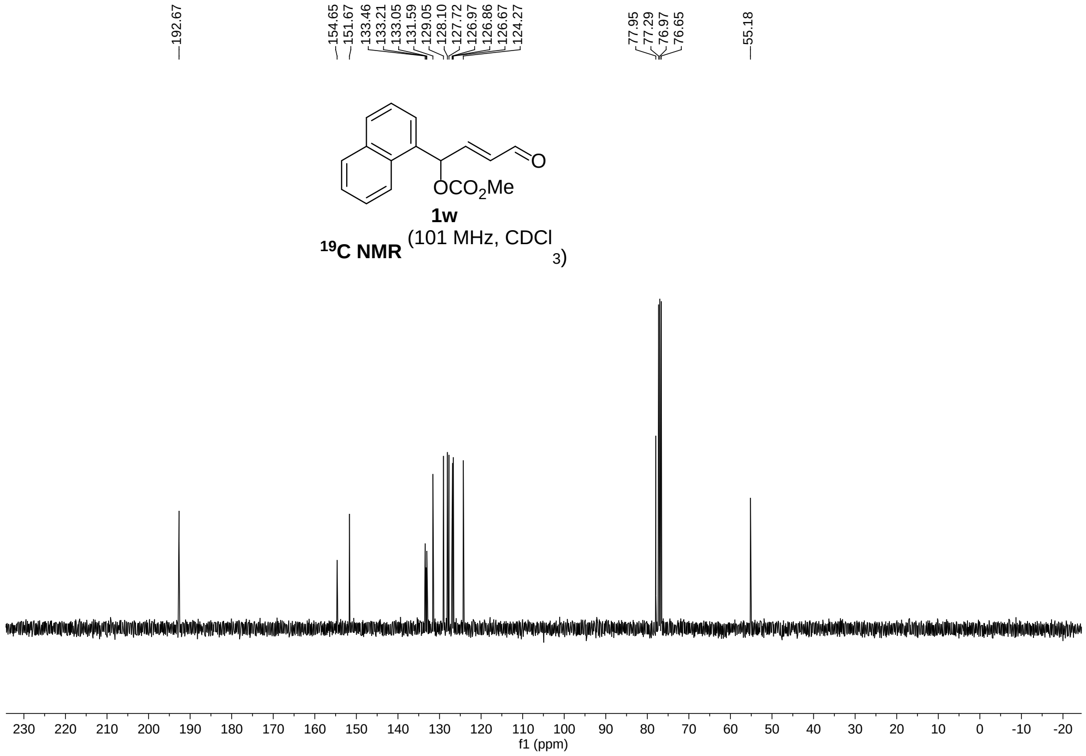

1v

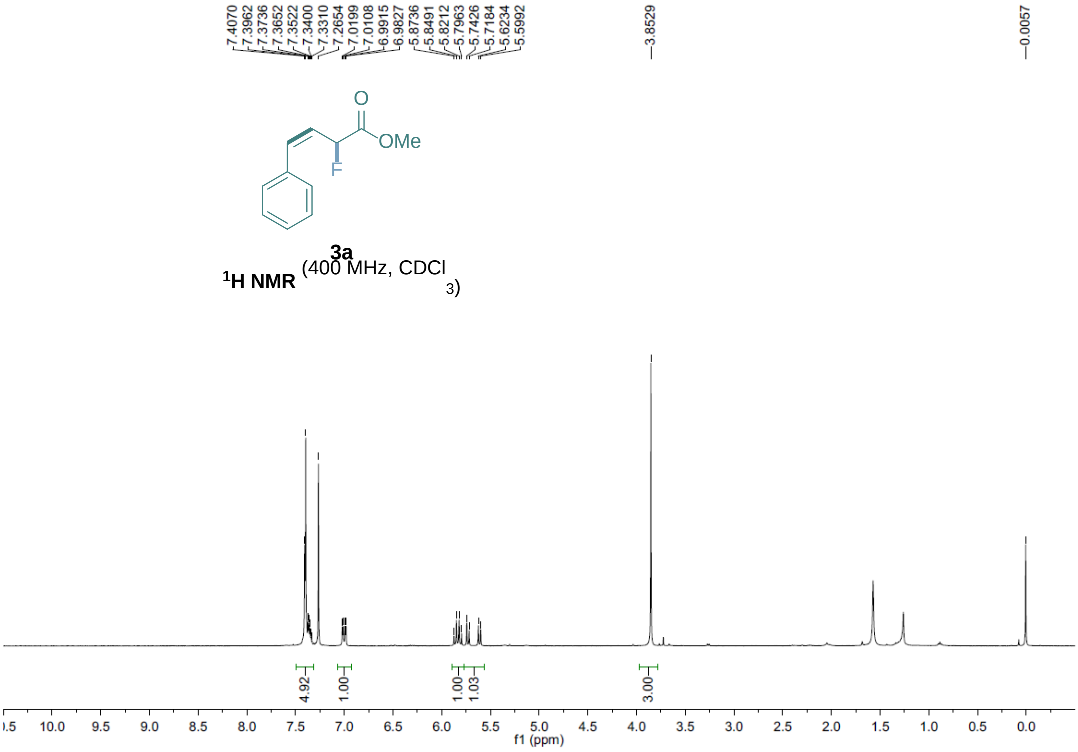
^{1}H NMR (500 MHz, CDCl$_3$)


1v

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

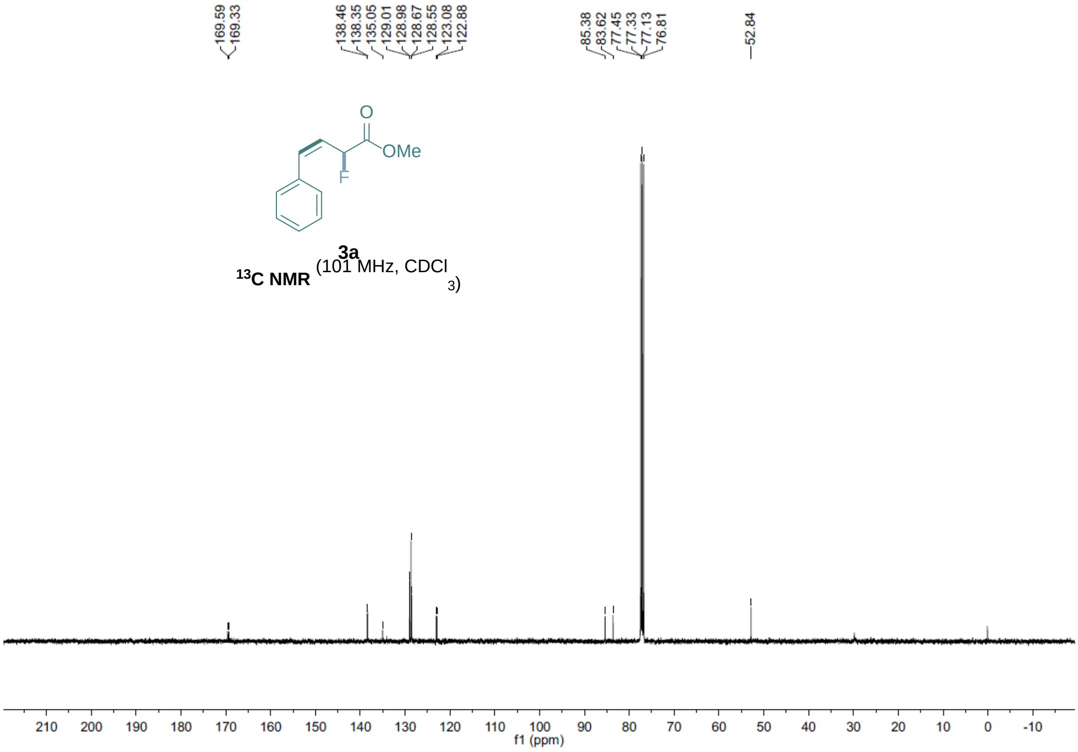

9.61
9.60
7.90
7.87
7.86
7.85
7.85
7.84
7.54
7.53
7.52
7.51
6.93
6.92
6.50
6.50
6.49
6.49
6.43
6.43
6.41
6.41
6.39
6.39
6.37
6.37
3.81
OCO$_2$Me
O
1w
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
4.07
2.01
1.06
1.02
1.00
0.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


192.67
154.65
151.67
133.46
133.21
133.05
131.59
129.05
128.10
127.72
126.97
126.86
126.67
124.27
77.95
77.29
76.97
76.65
55.18
OCO$_2$Me
O
1w
^{19}C NMR (101 MHz, CDCl$_3$)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



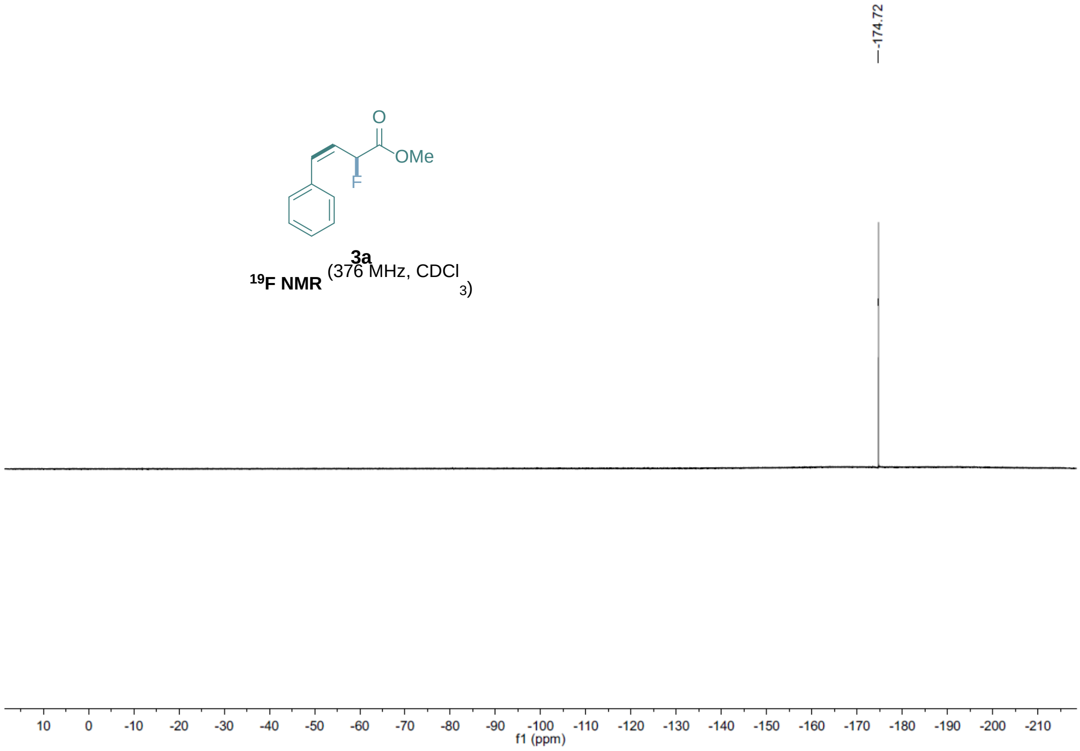
3a

^{1}H NMR (400 MHz, CDCl$_3$)



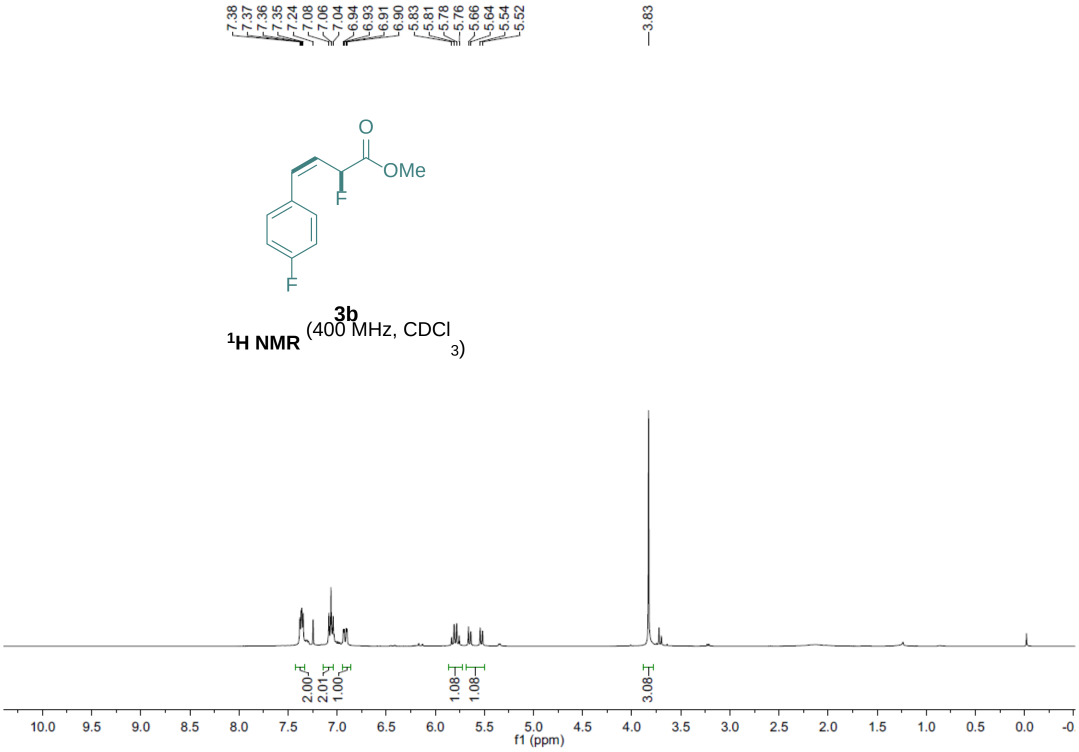
3a

^{13}C NMR (101 MHz, CDCl$_3$)



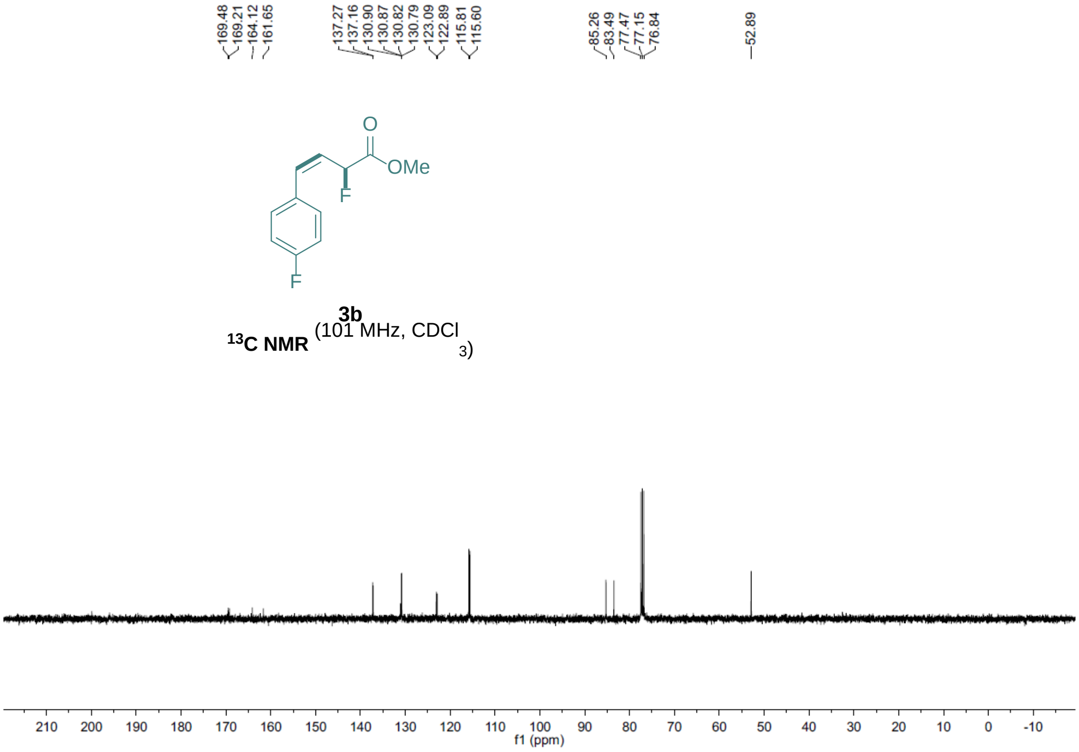
3a

^{19}F NMR (376 MHz, $CDCl_3$)



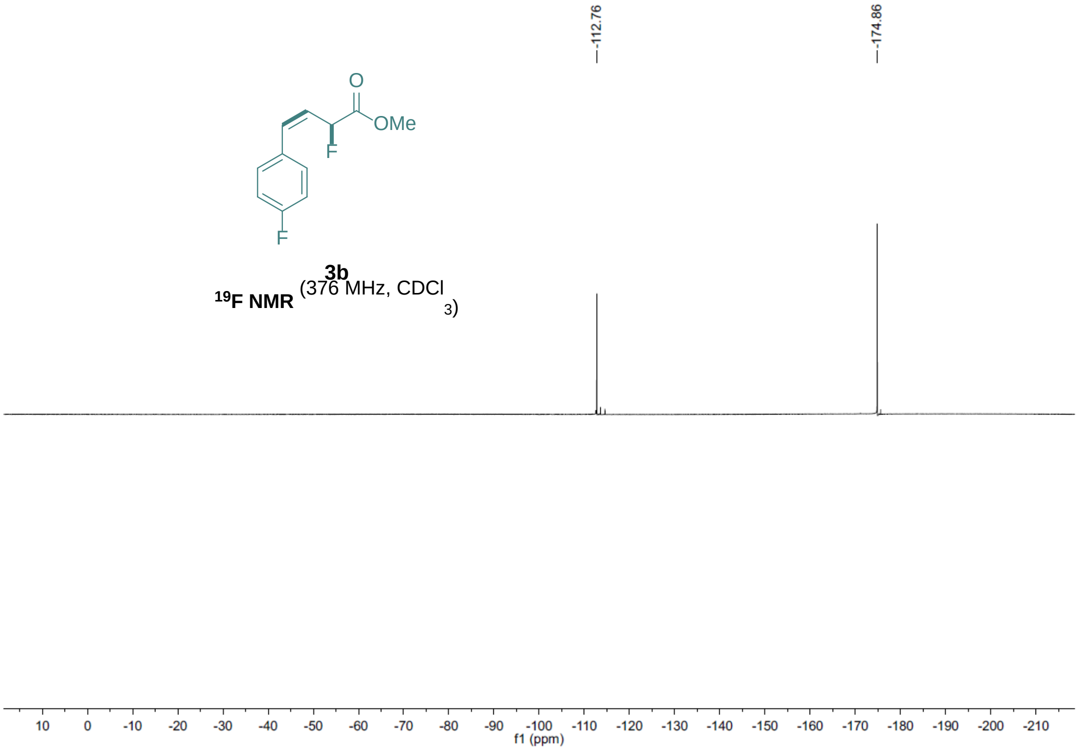
3b

^{1}H NMR (400 MHz, $CDCl_3$)



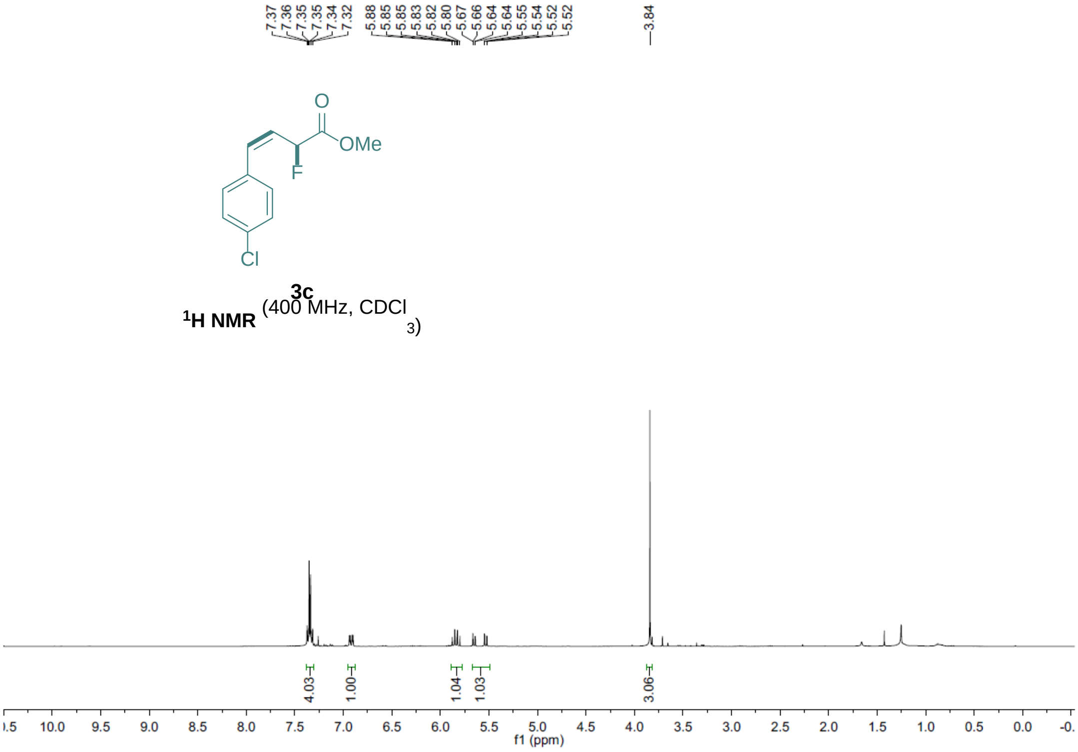
3b

^{13}C NMR (101 MHz, $CDCl_3$)



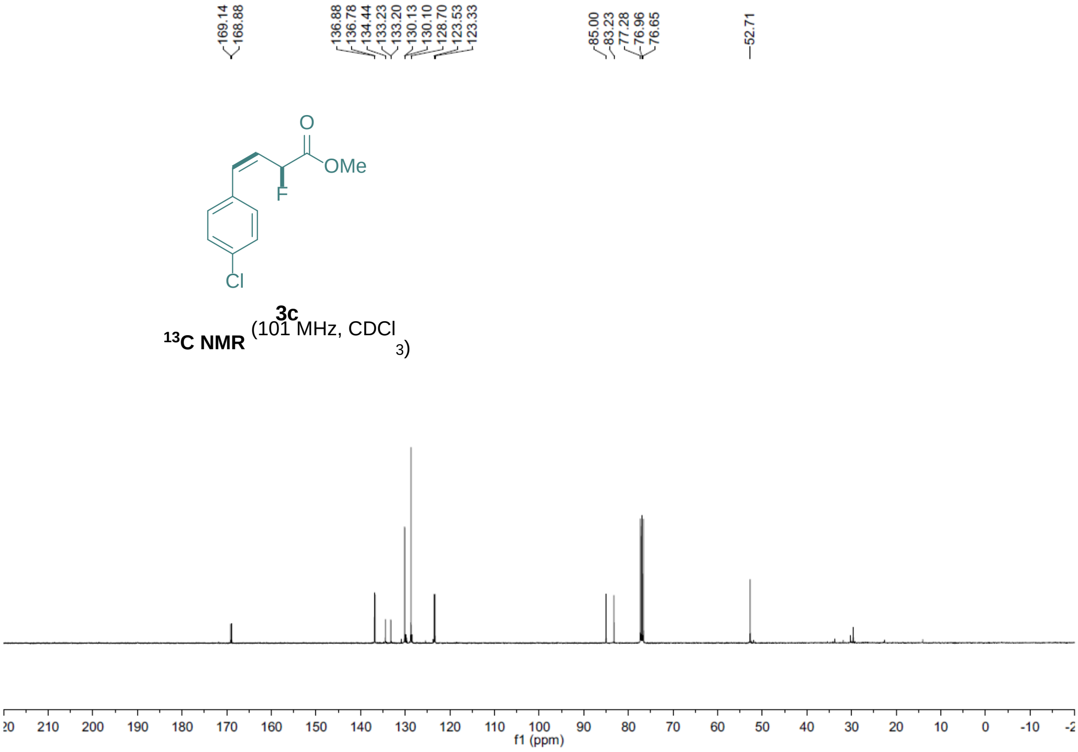
3b

^{19}F NMR (376 MHz, $CDCl_3$)



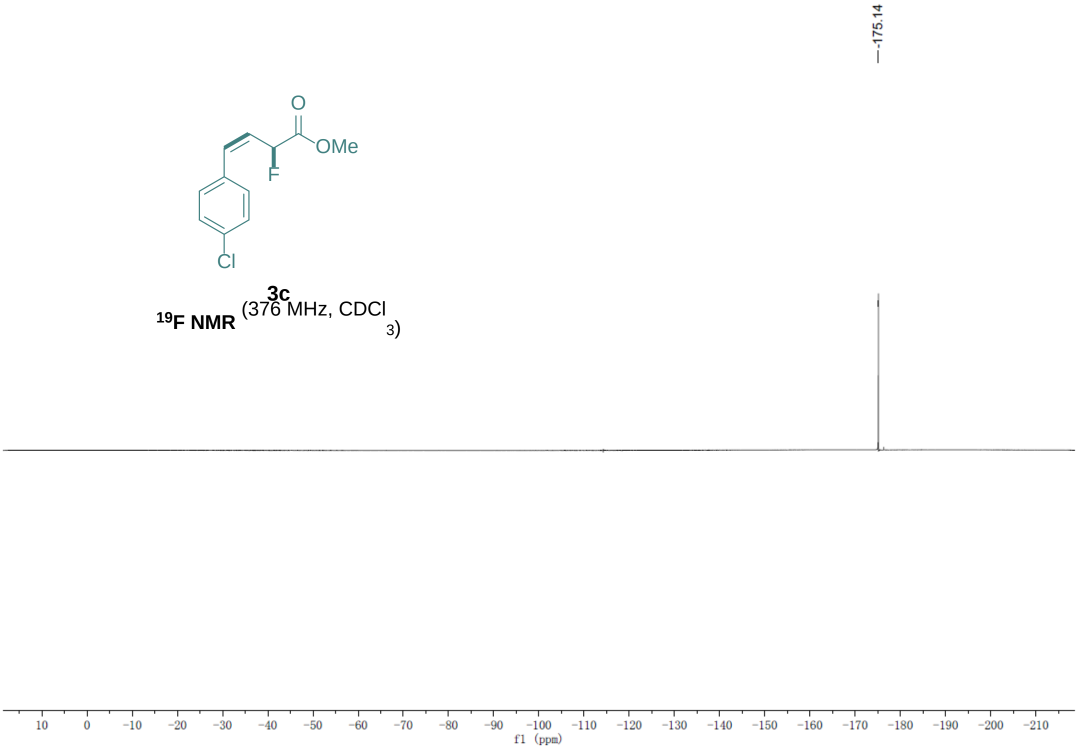
3c

^{1}H NMR (400 MHz, $CDCl_3$)



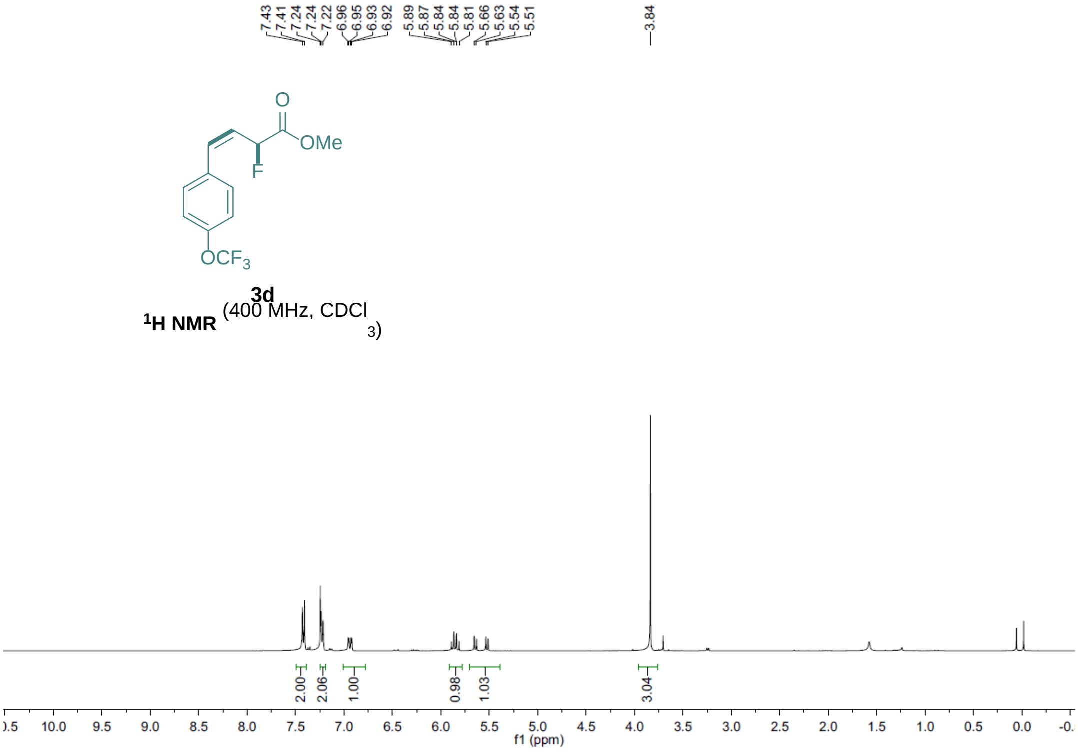
3c

^{13}C NMR (101 MHz, $CDCl_3$)



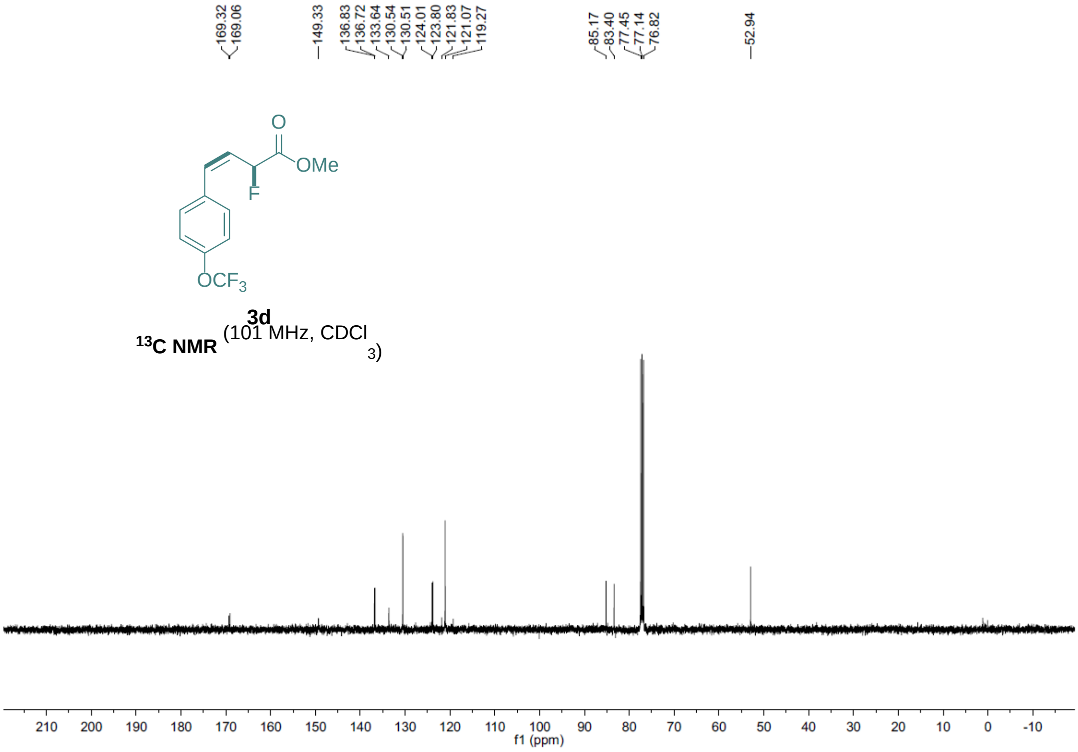
3c

^{19}F NMR (376 MHz, $CDCl_3$)



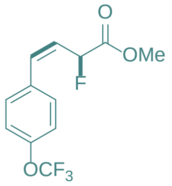
3d

^{1}H NMR (400 MHz, $CDCl_3$)



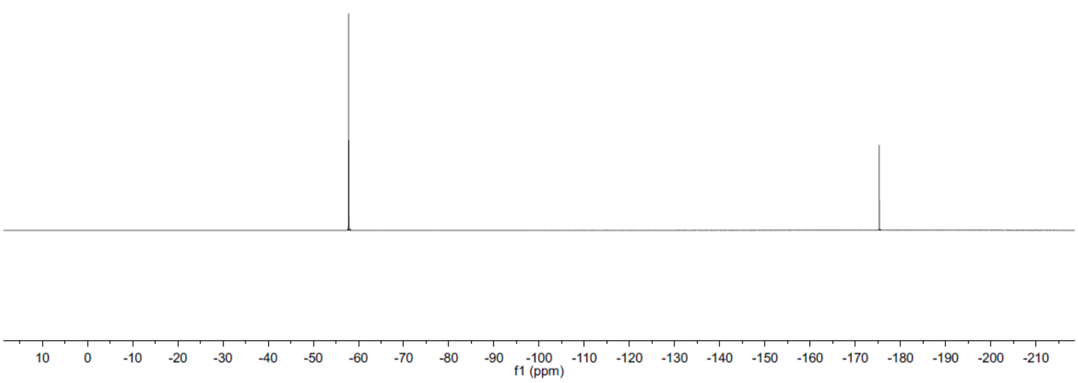
3d

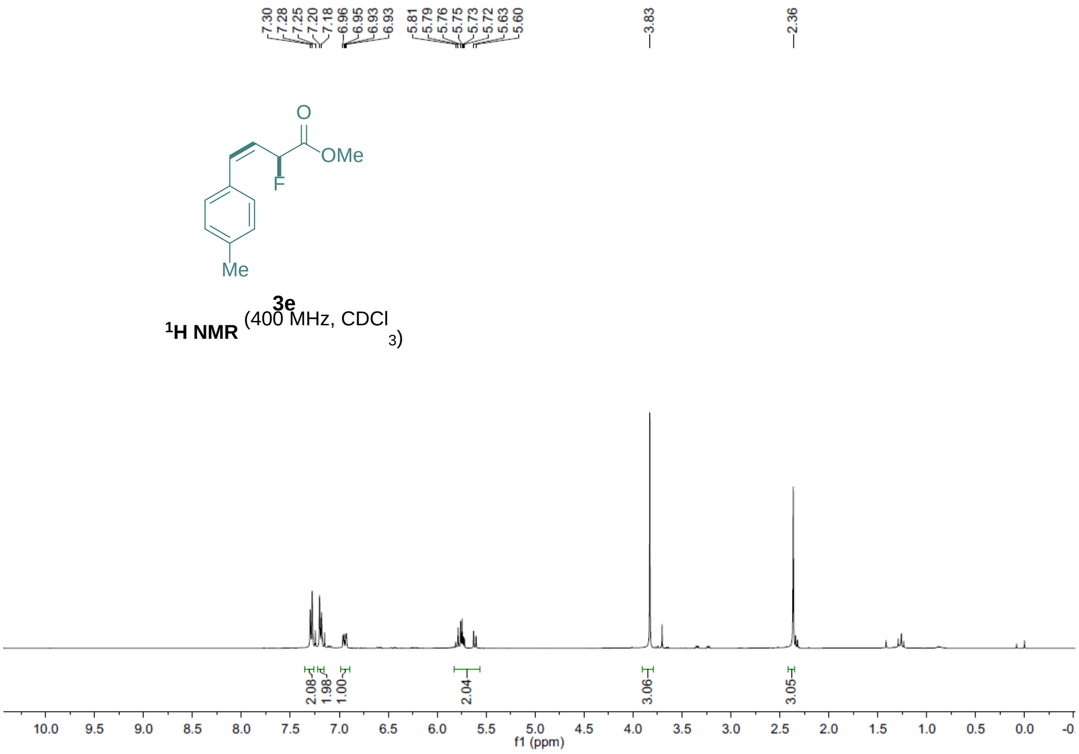
^{13}C NMR (101 MHz, $CDCl_3$)



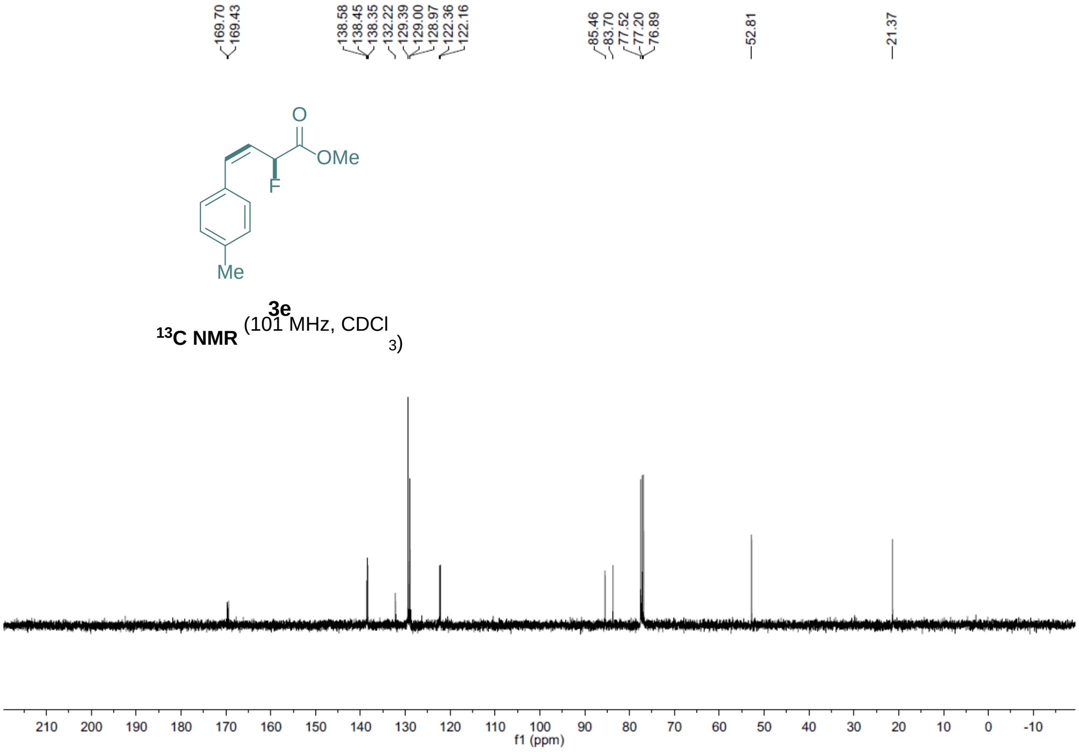
3d

^{19}**F NMR** (376 MHz, $CDCl_3$)

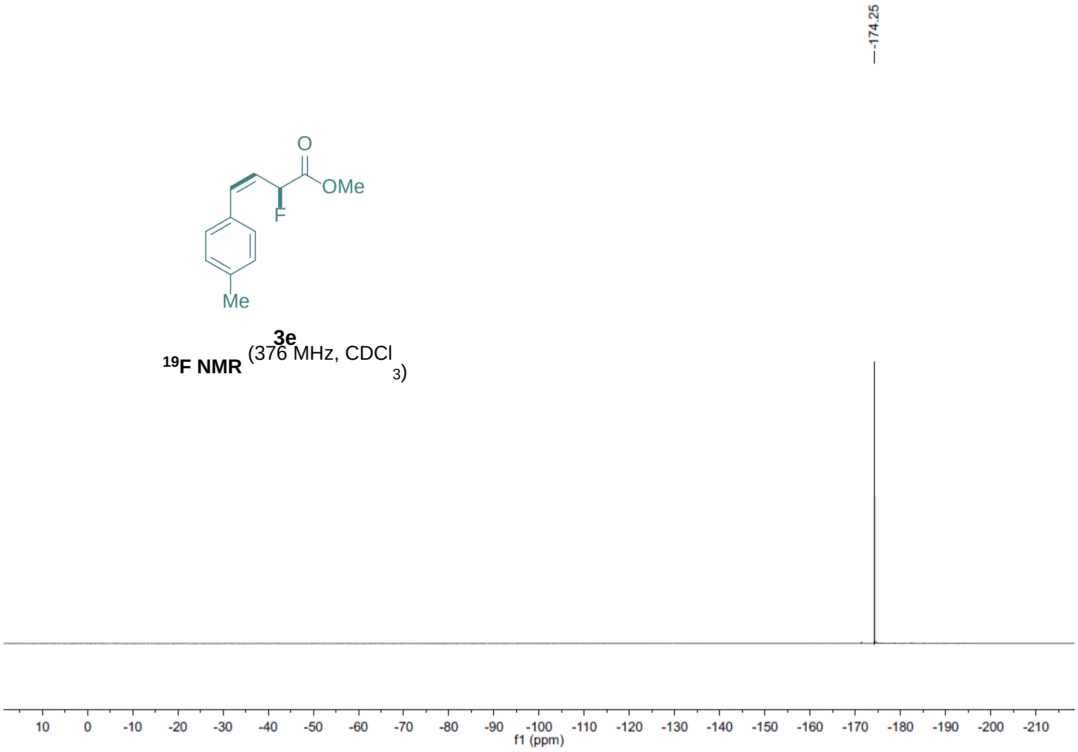



3e

^{1}H NMR (400 MHz, $CDCl_3$)

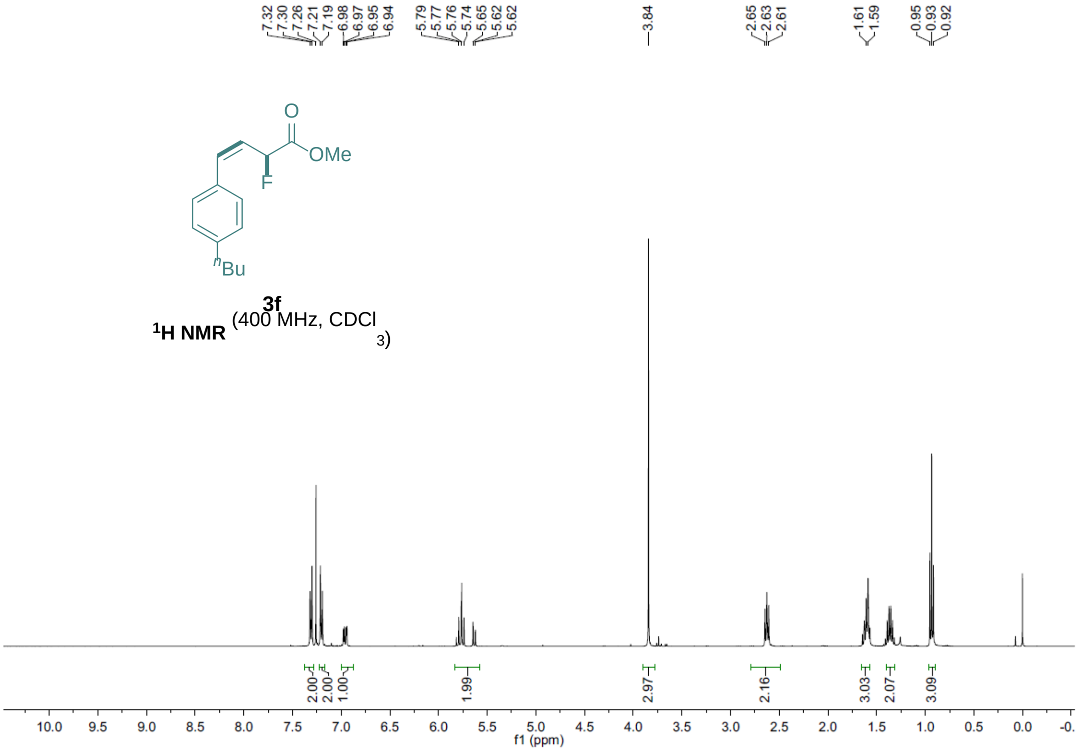

3e

^{13}C NMR (101 MHz, $CDCl_3$)



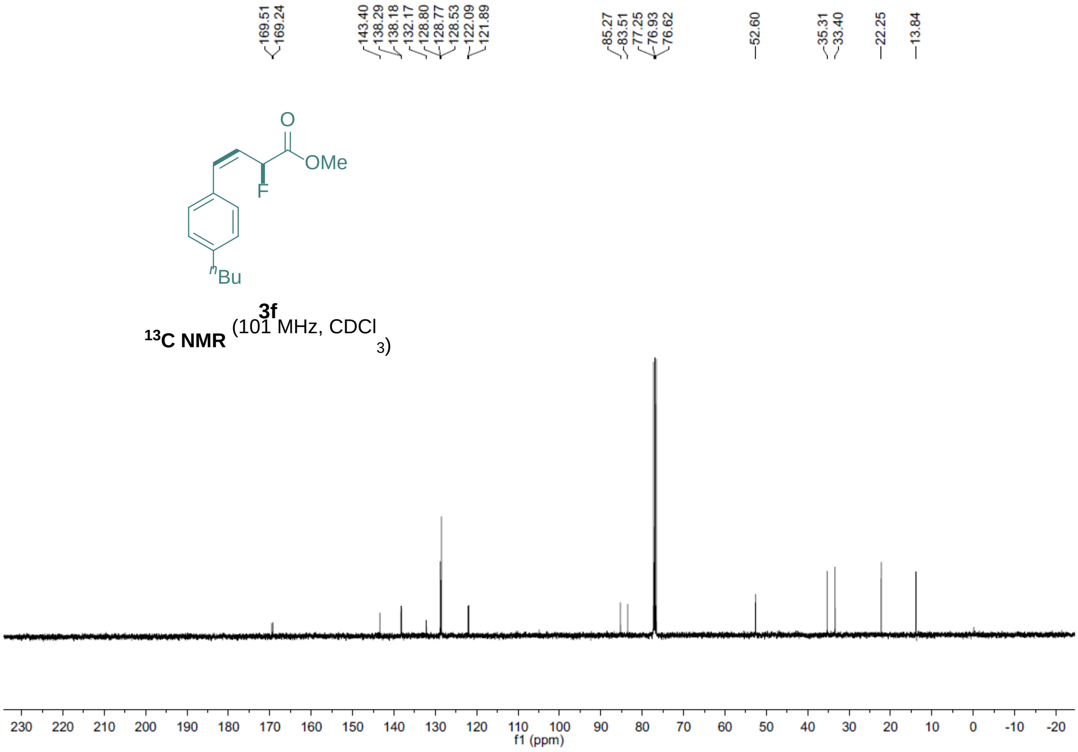
3e

^{19}F NMR (376 MHz, $CDCl_3$)



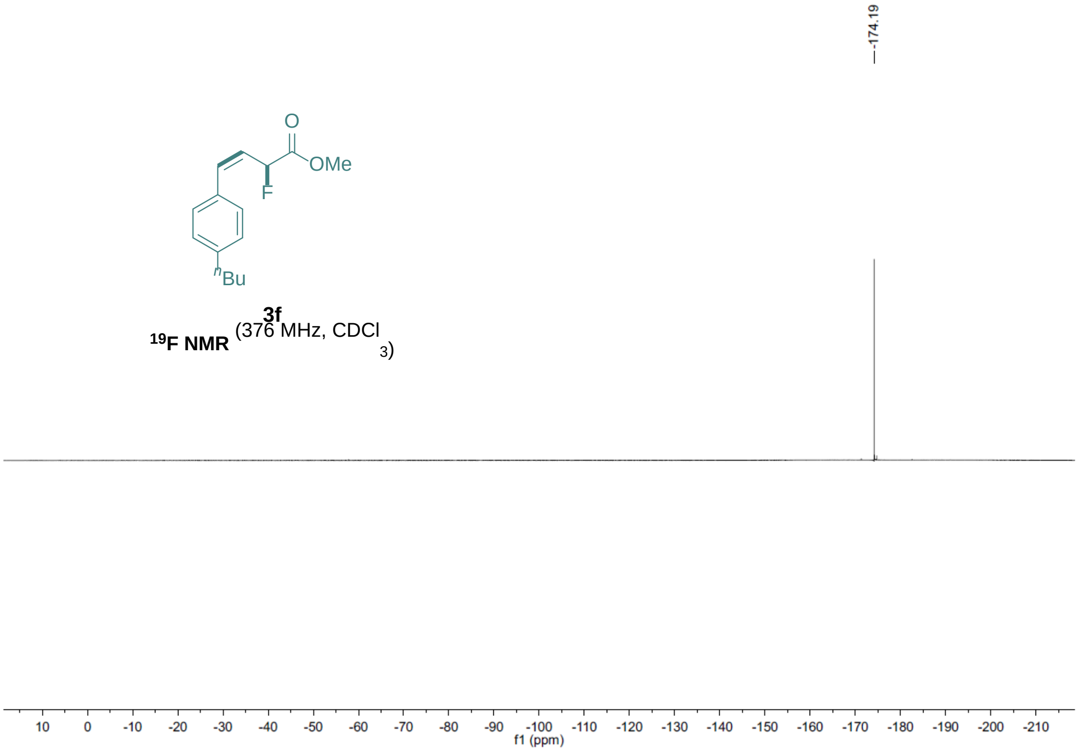
3f

^{1}H NMR (400 MHz, CDCl$_3$)



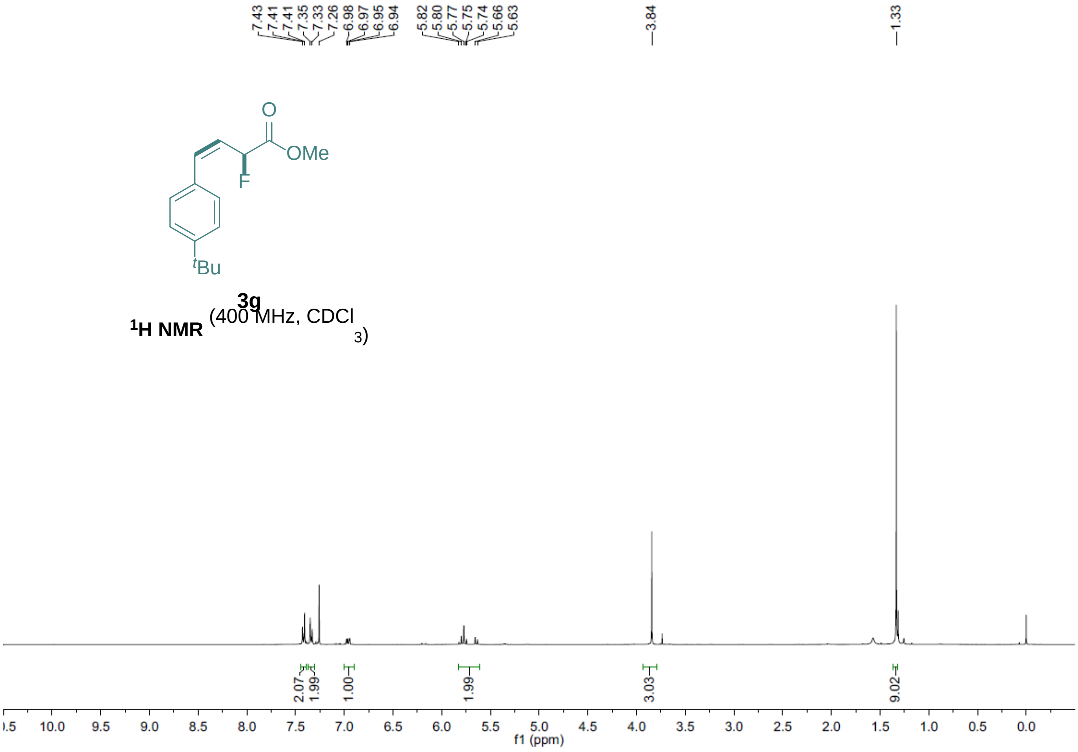
3f

^{13}C NMR (101 MHz, CDCl$_3$)



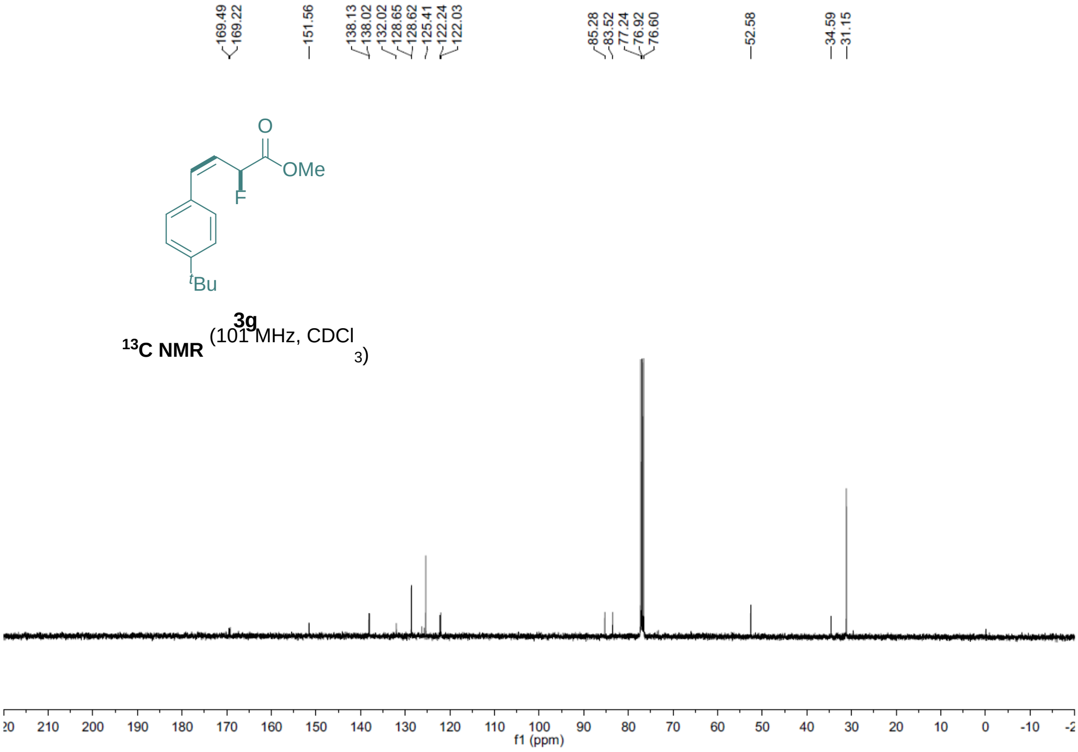
3f

^{19}F NMR (376 MHz, $CDCl_3$)



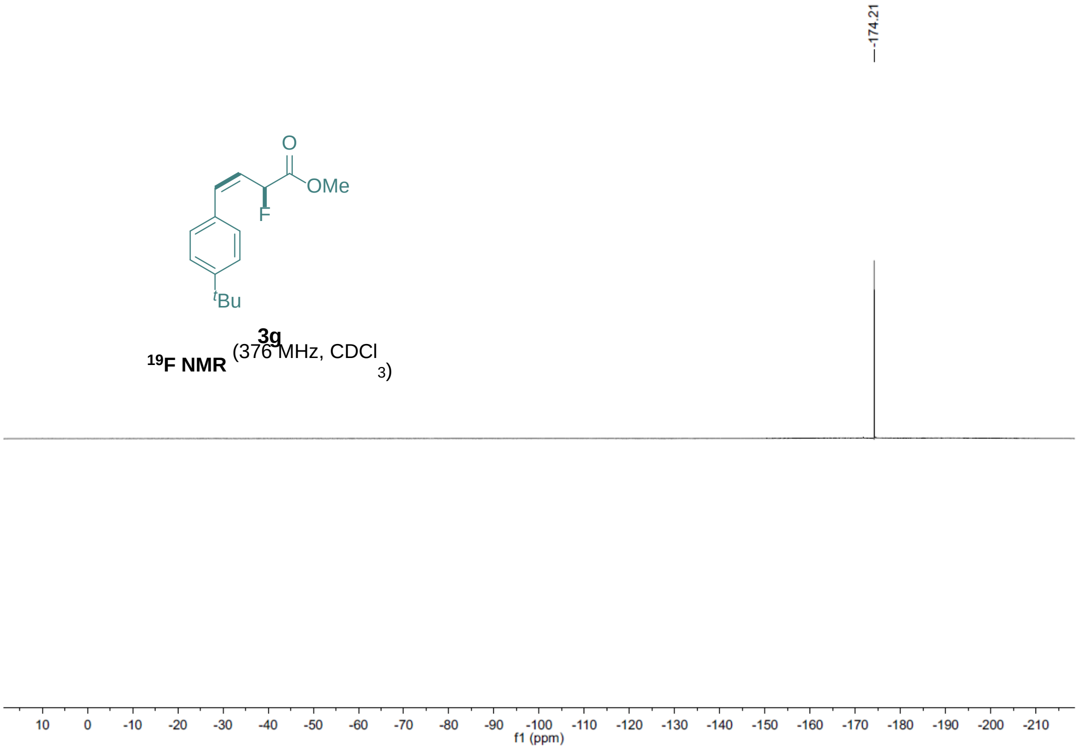
3g

^{1}H NMR (400 MHz, $CDCl_3$)



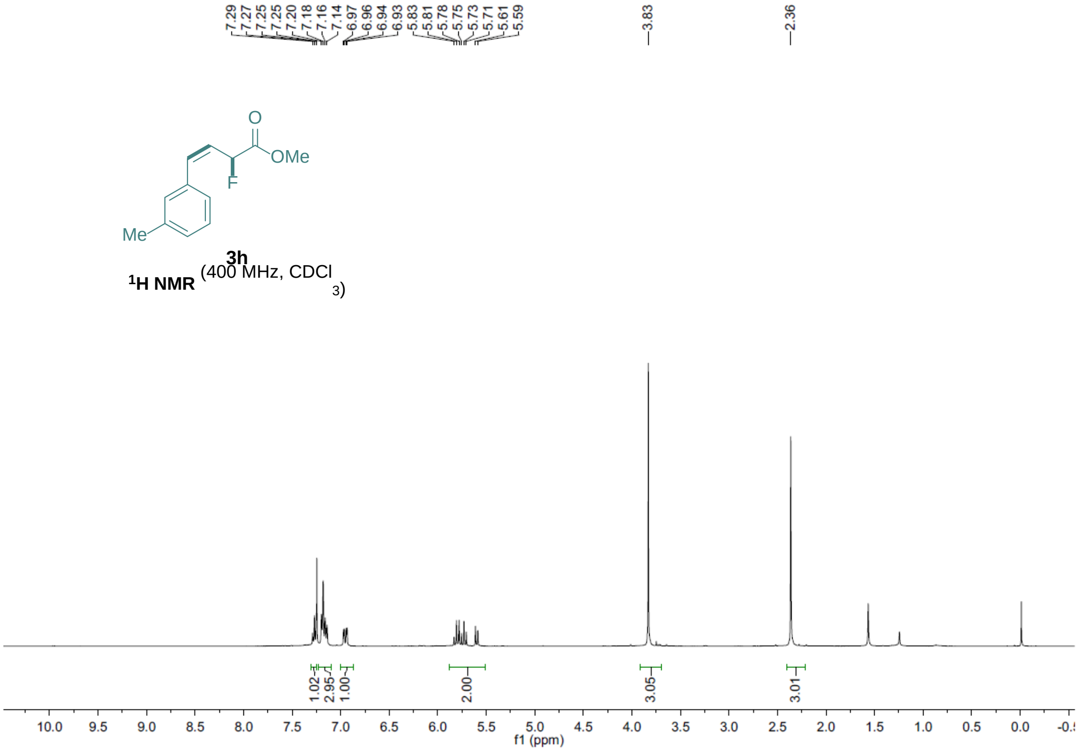
3g

^{13}C NMR (101 MHz, $CDCl_3$)



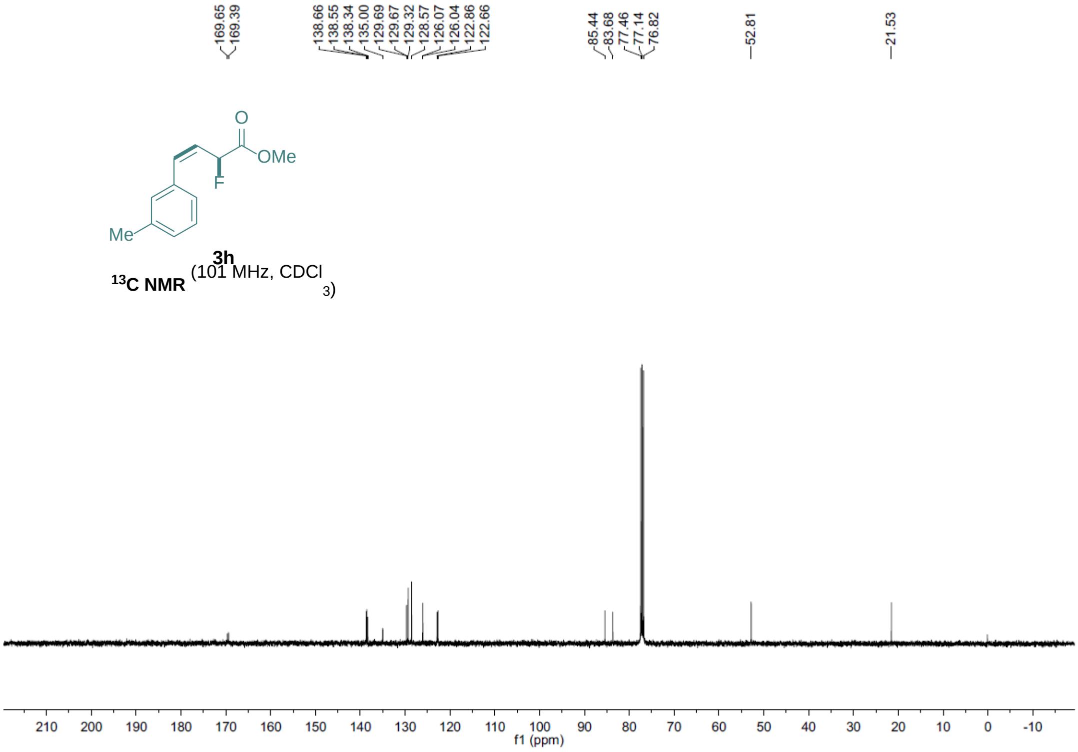
3g

^{19}F NMR (376 MHz, $CDCl_3$)



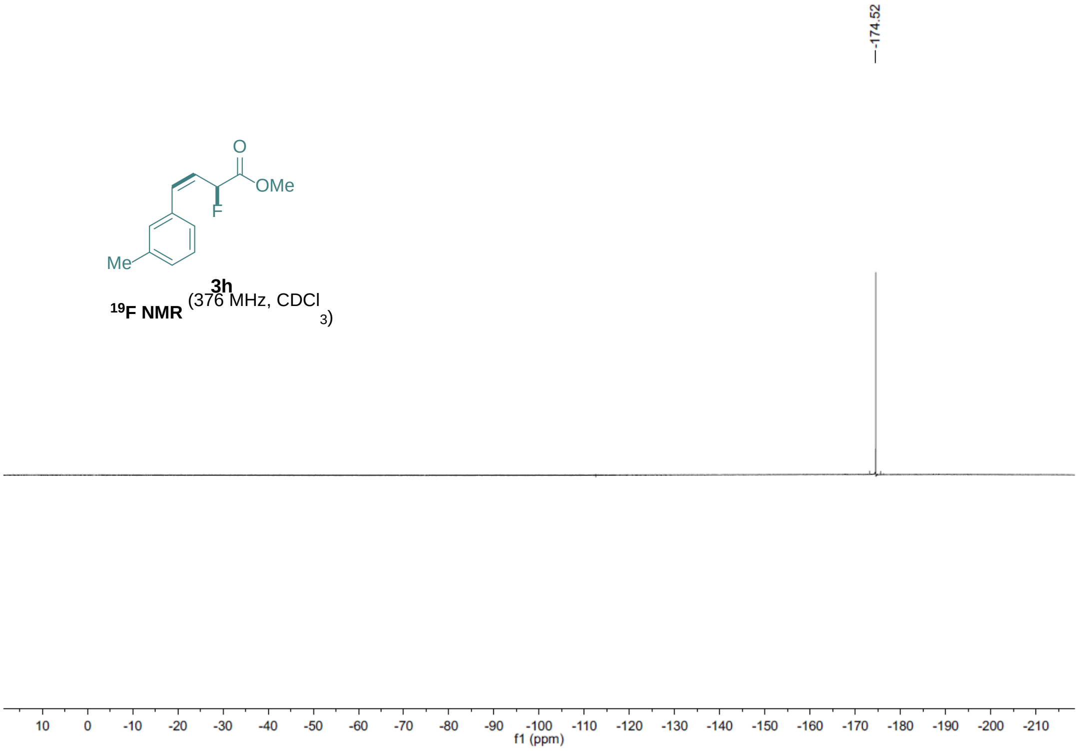
3h

^{1}H NMR (400 MHz, $CDCl_3$)

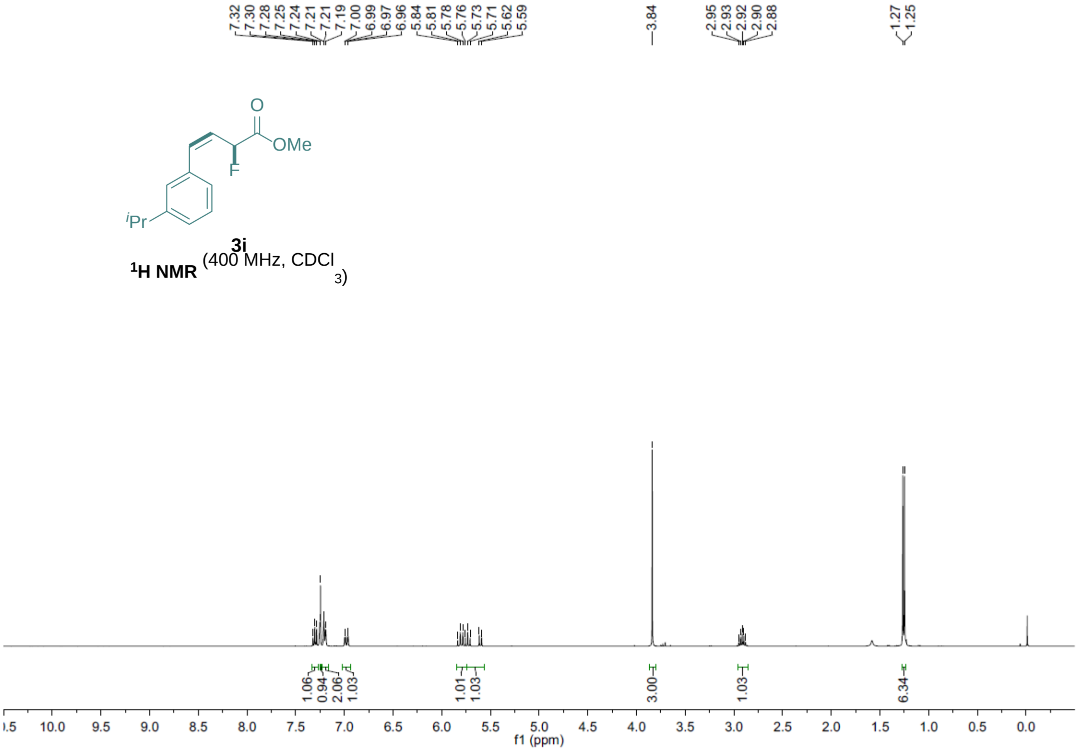


3h

^{13}C NMR (101 MHz, $CDCl_3$)

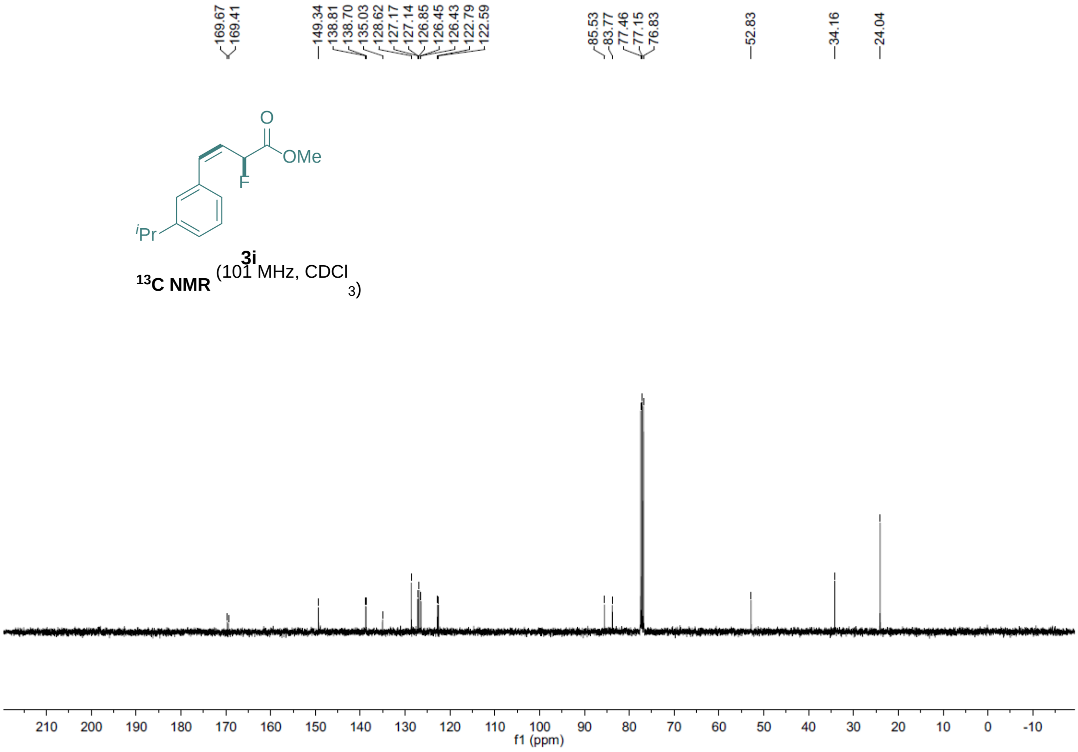

3h

^{19}F NMR (376 MHz, $CDCl_3$)



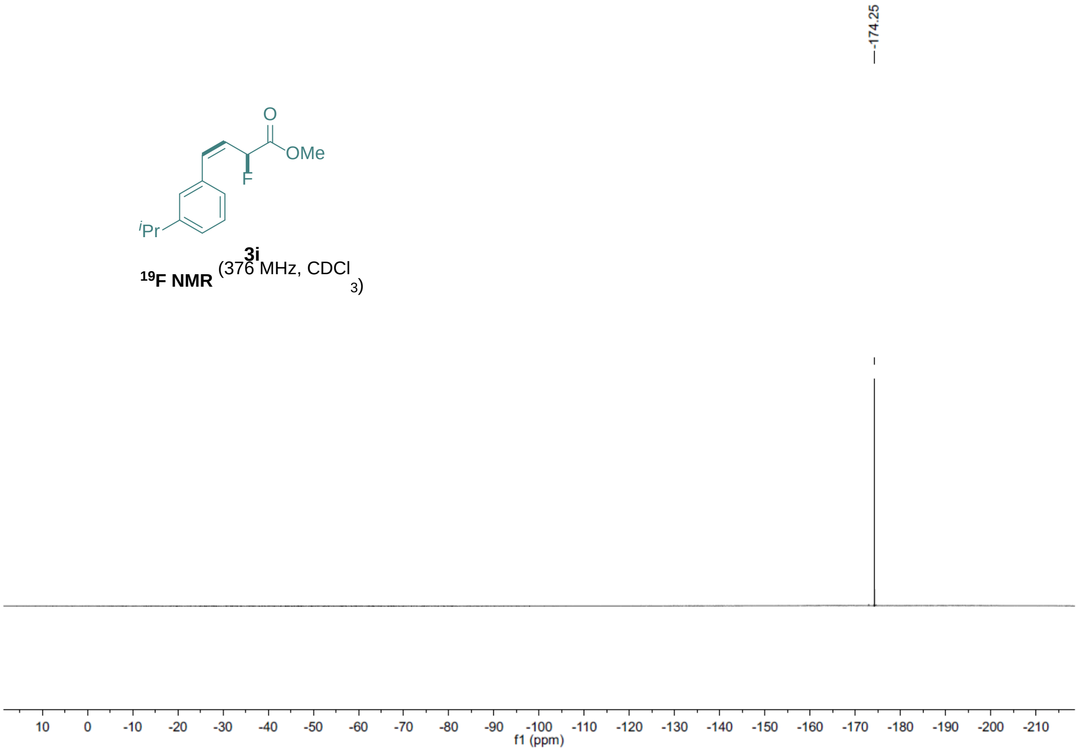
3i

^{1}H NMR (400 MHz, CDCl$_3$)



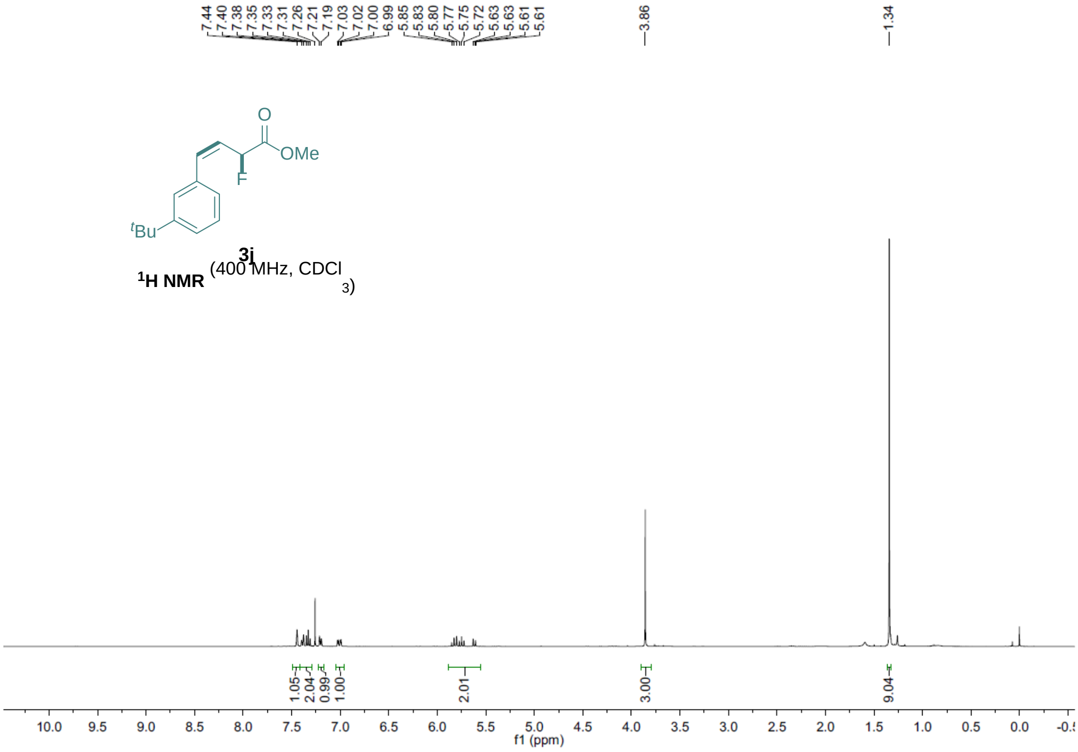
3i

^{13}C NMR (101 MHz, CDCl$_3$)



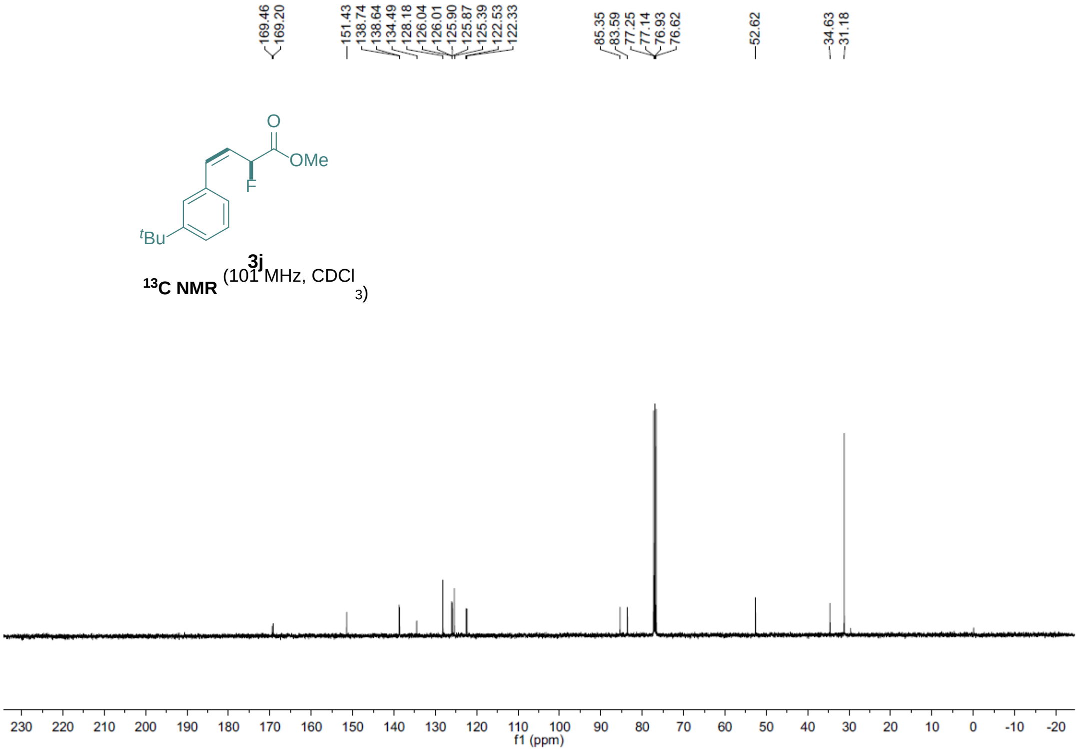
3i

^{19}F NMR (376 MHz, $CDCl_3$)



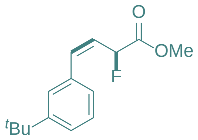
3j

^{1}H NMR (400 MHz, $CDCl_3$)



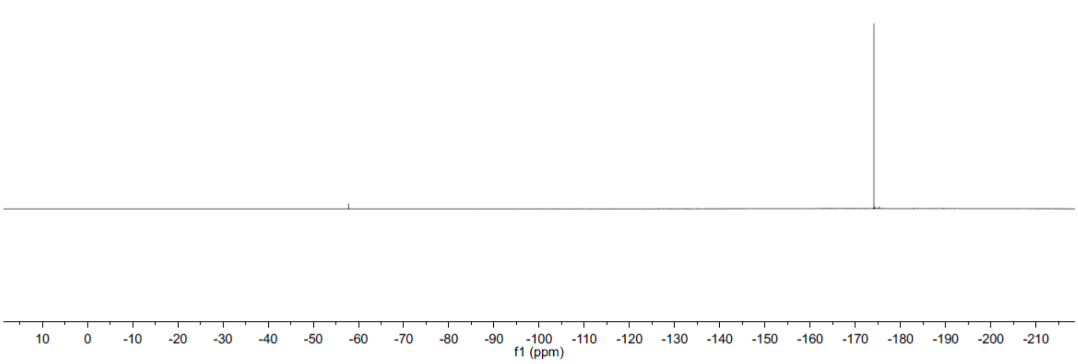
3j

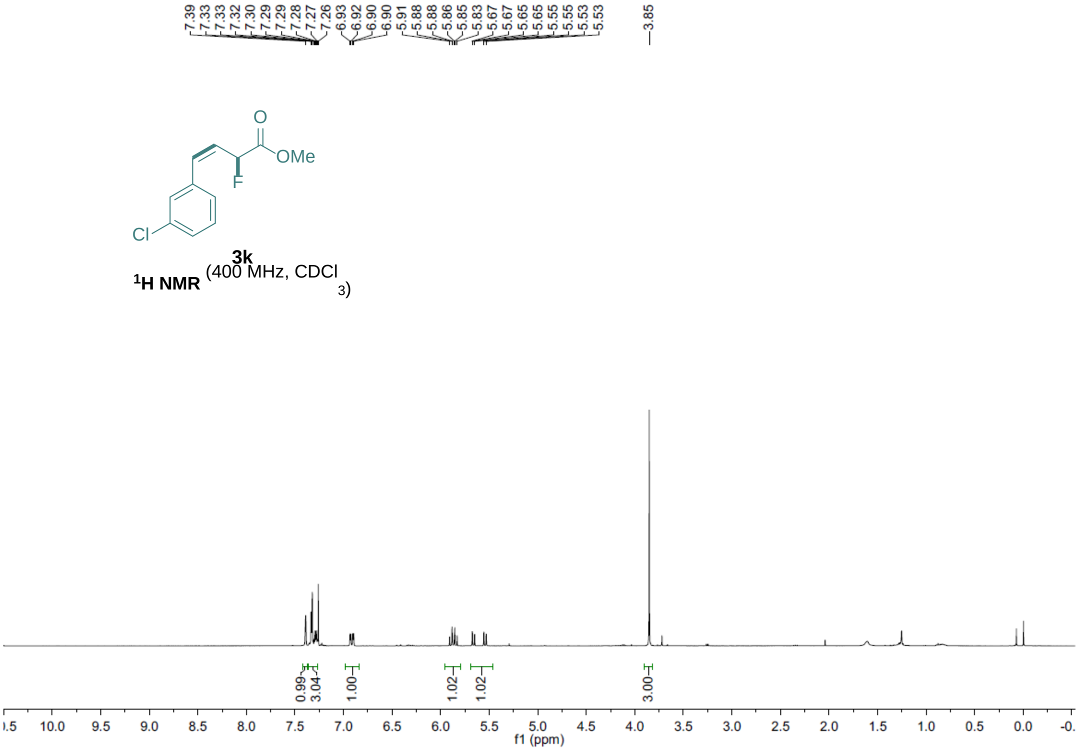
^{13}C NMR (101 MHz, $CDCl_3$)



3j

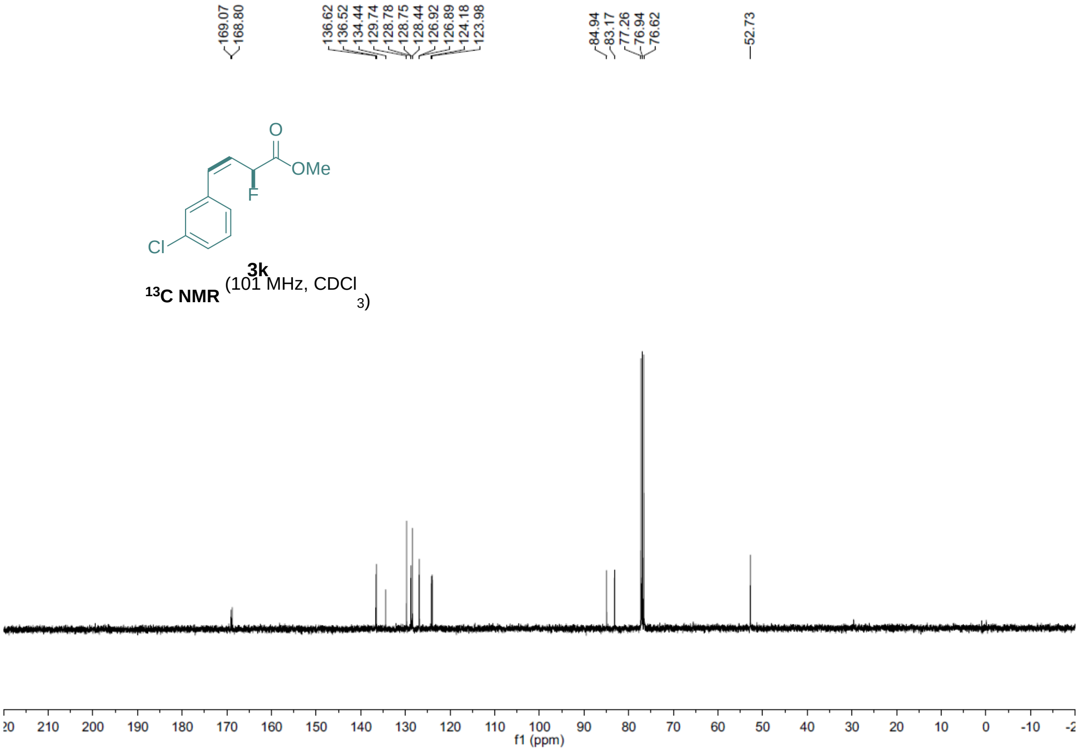
^{19}F NMR (376 MHz, $CDCl_3$)





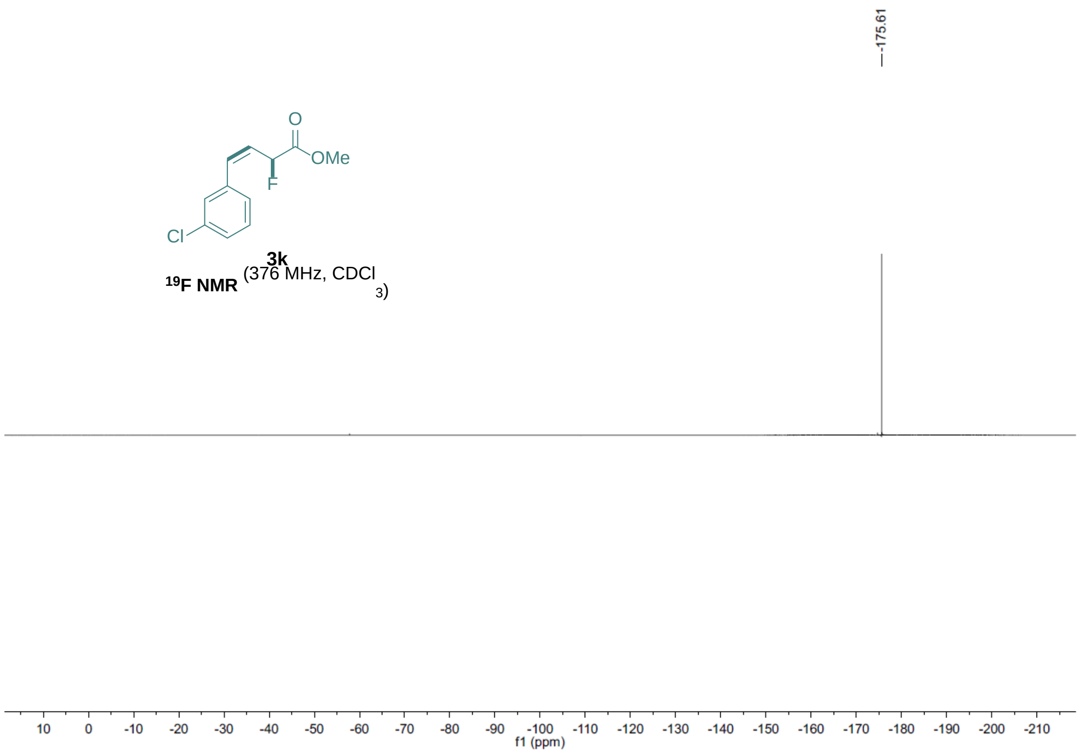
3k

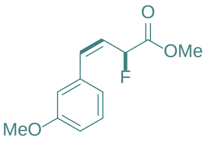
^{1}H NMR (400 MHz, $CDCl_3$)



3k

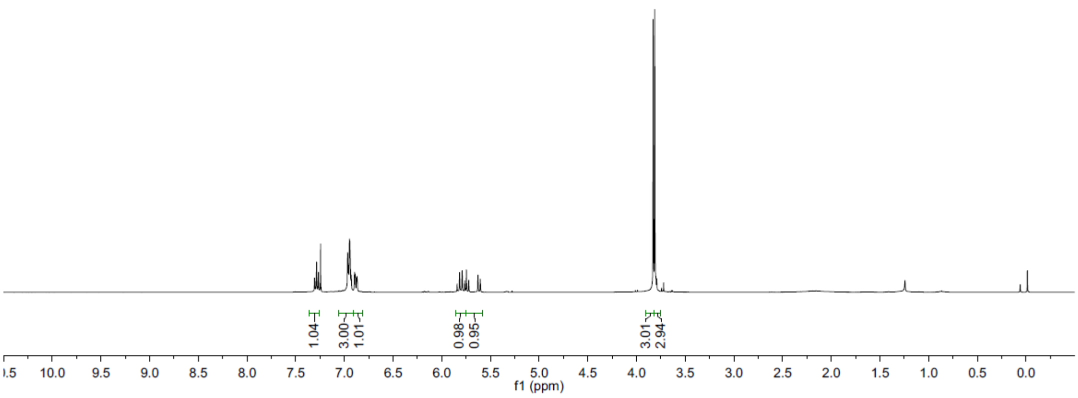
^{13}C NMR (101 MHz, $CDCl_3$)

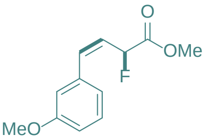

-175.61
O
OMe
F
Cl
3k
^{19}F NMR (376 MHz, CDCl$_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



3l

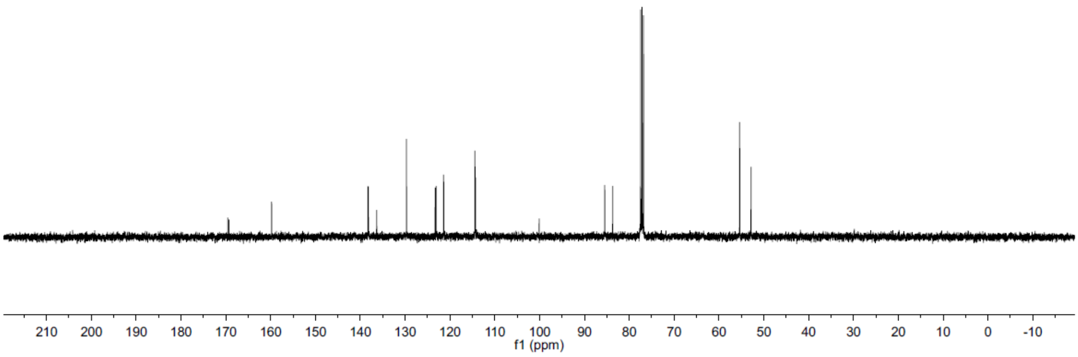
^{1}H NMR (400 MHz, CDCl$_3$)

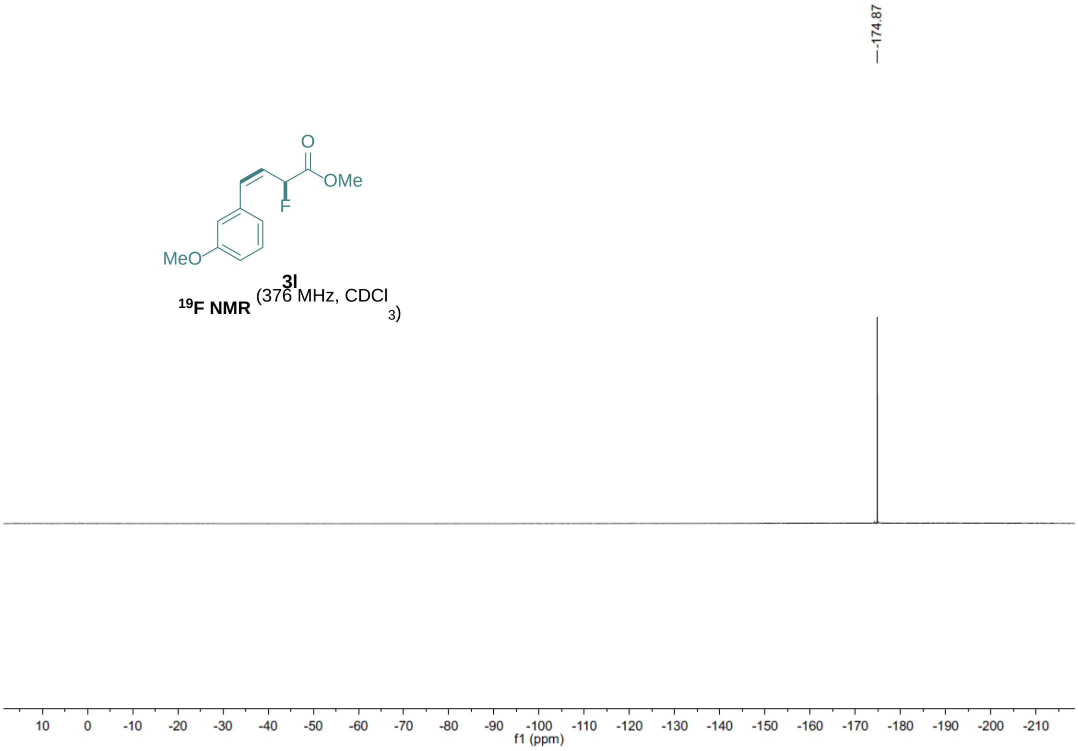




3l

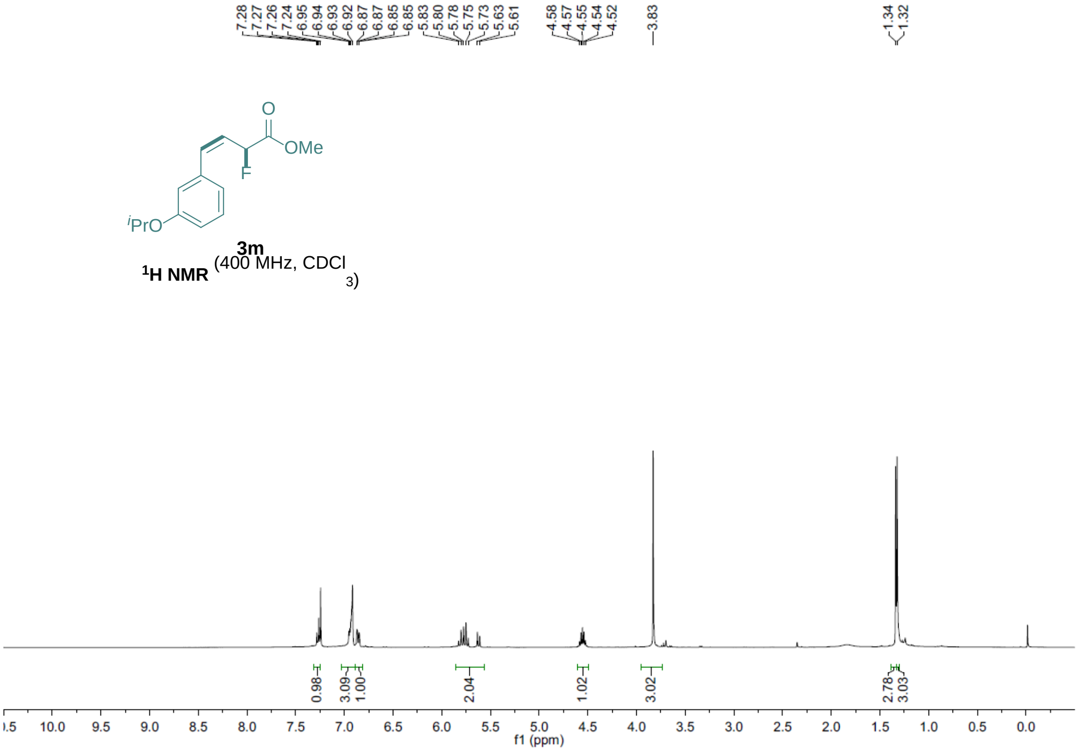
^{13}C NMR (101 MHz, CDCl$_3$)





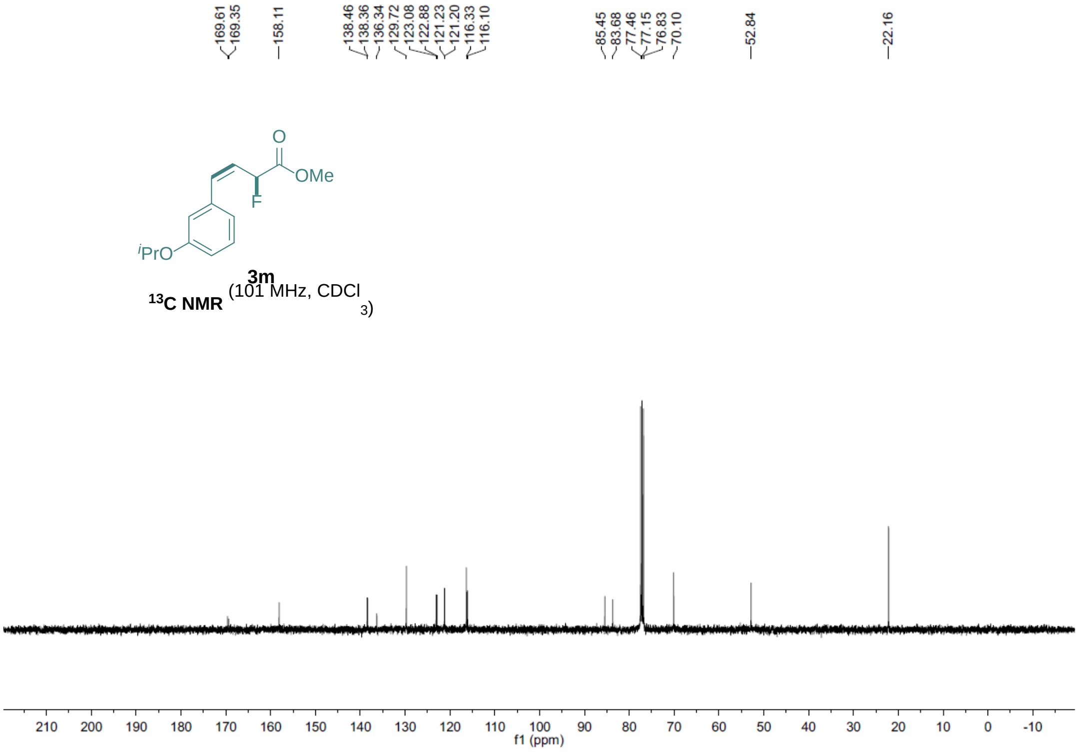
3l

^{19}F NMR (376 MHz, $CDCl_3$)



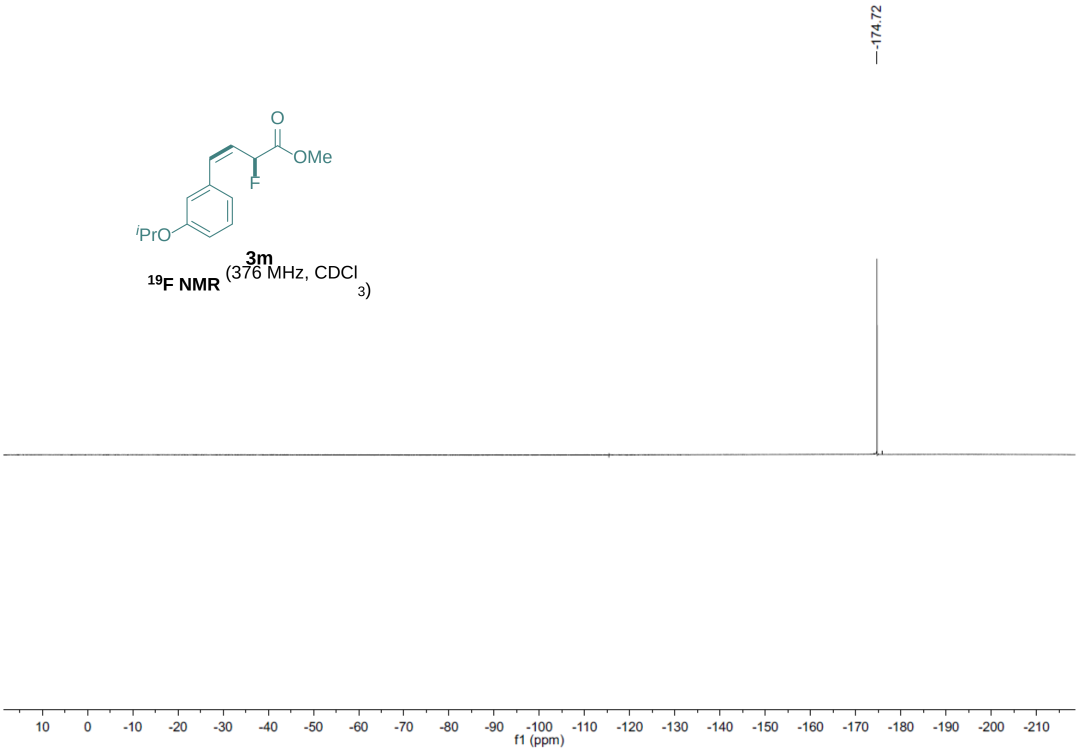
3m

^{1}H NMR (400 MHz, CDCl$_3$)



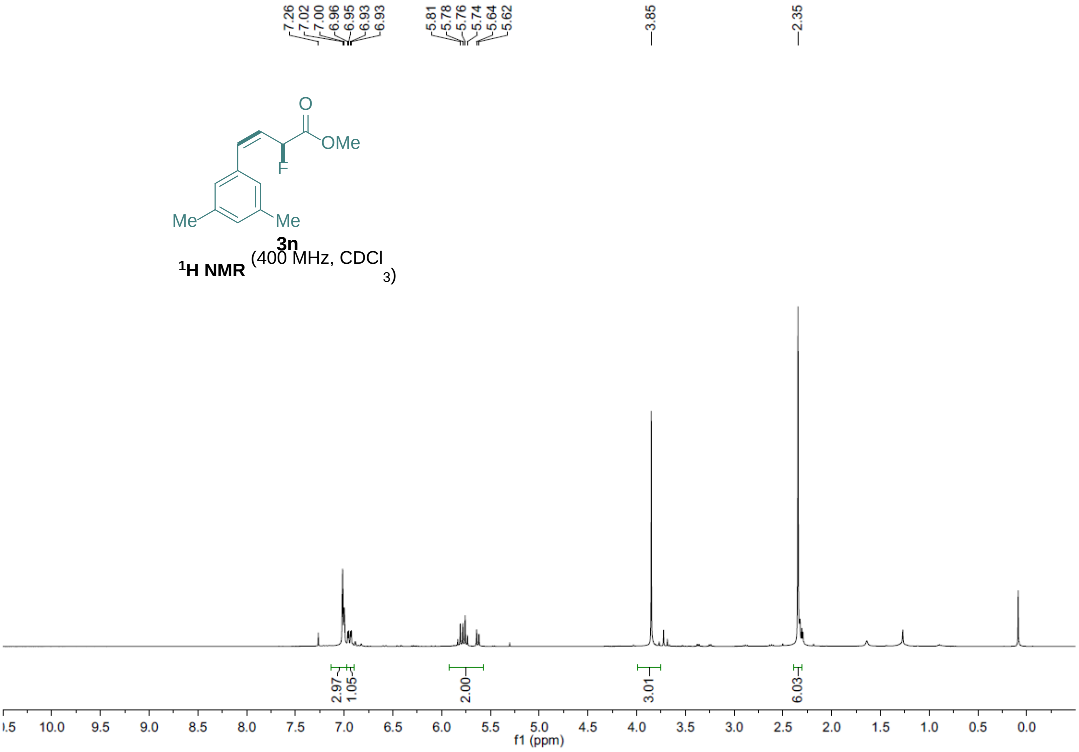
3m

^{13}C NMR (101 MHz, CDCl$_3$)



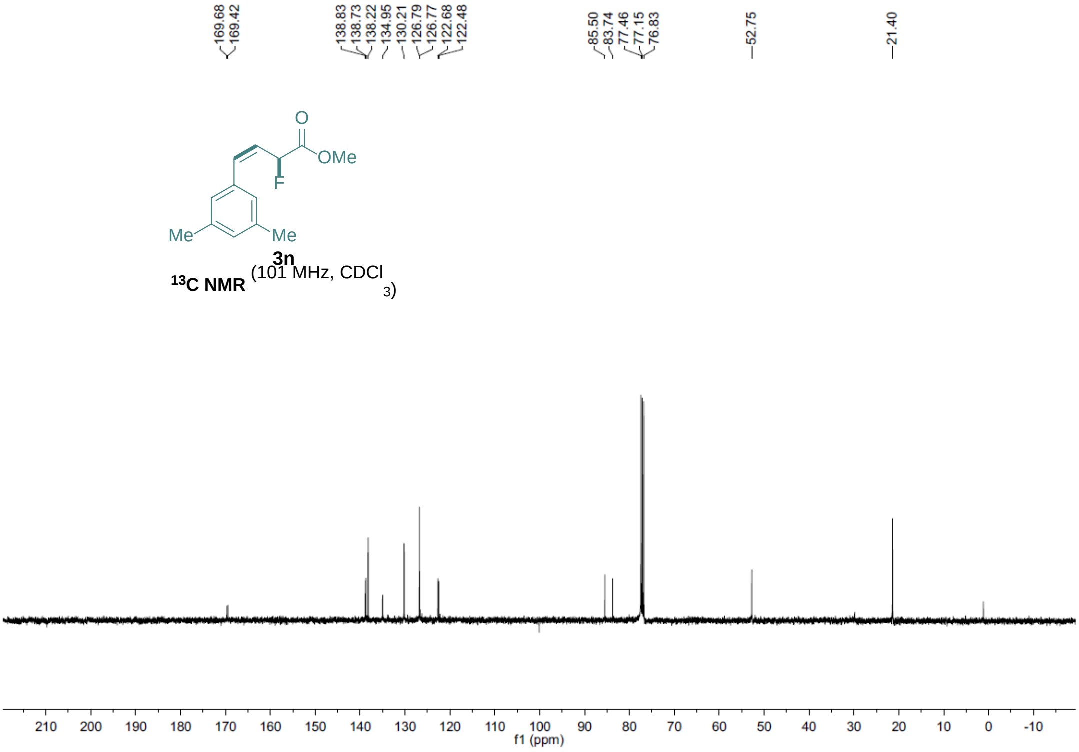
3m

^{19}F NMR (376 MHz, $CDCl_3$)



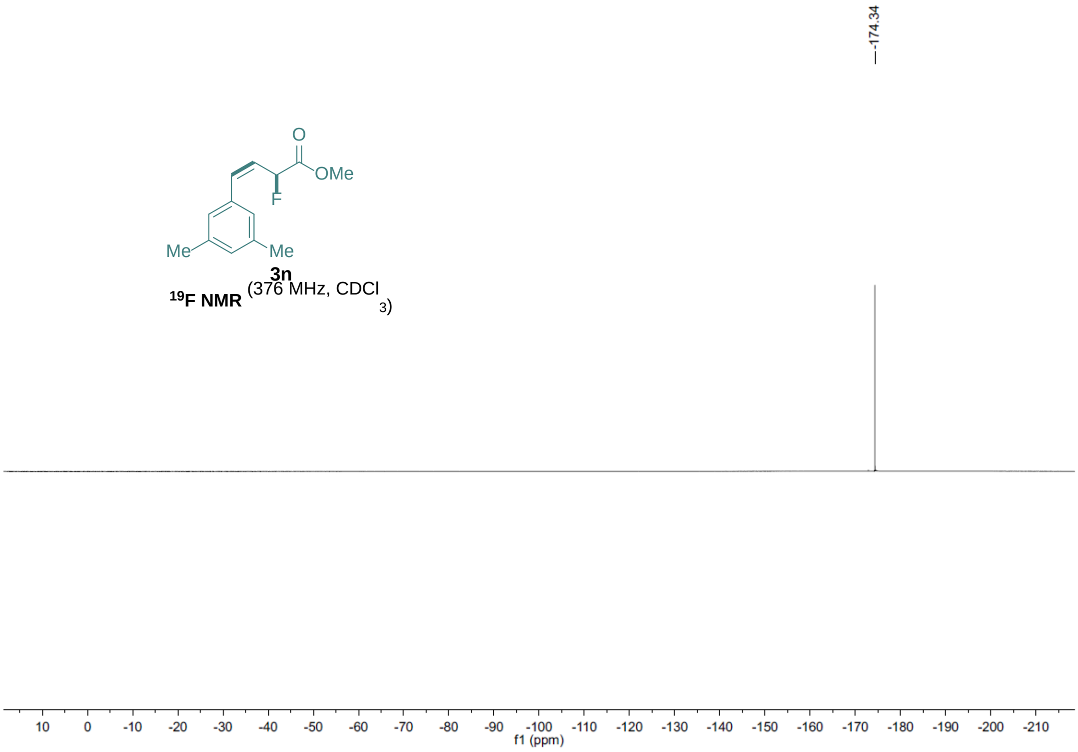
3n

^{1}H NMR (400 MHz, $CDCl_3$)



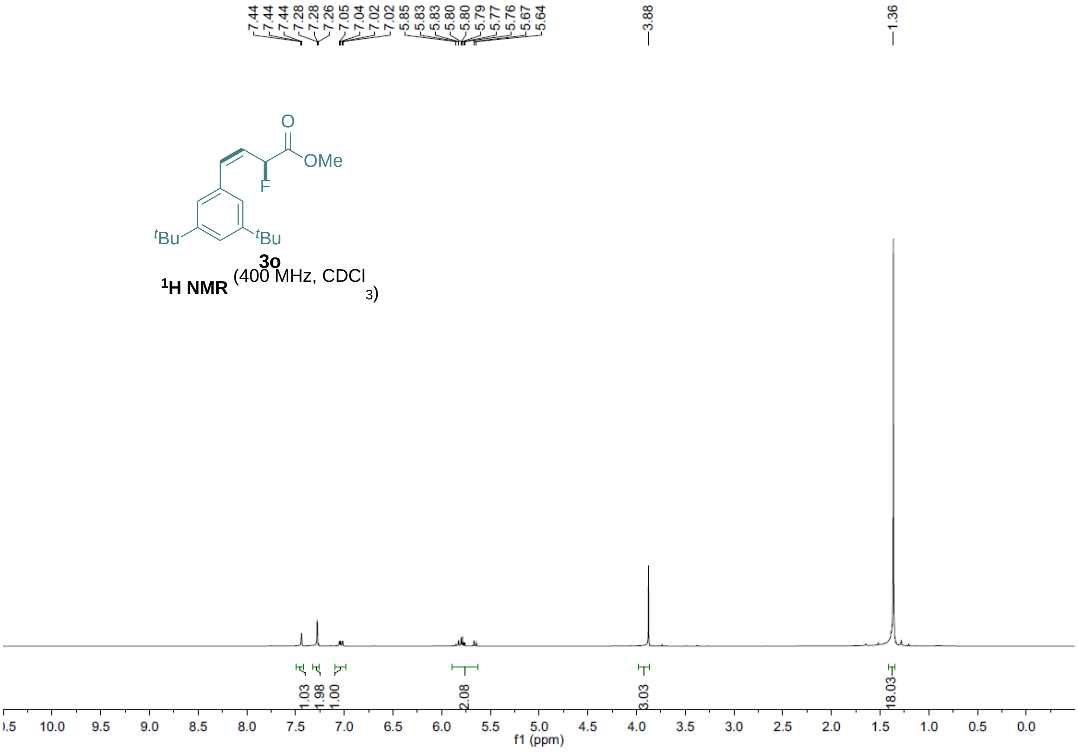
3n

^{13}C NMR (101 MHz, $CDCl_3$)



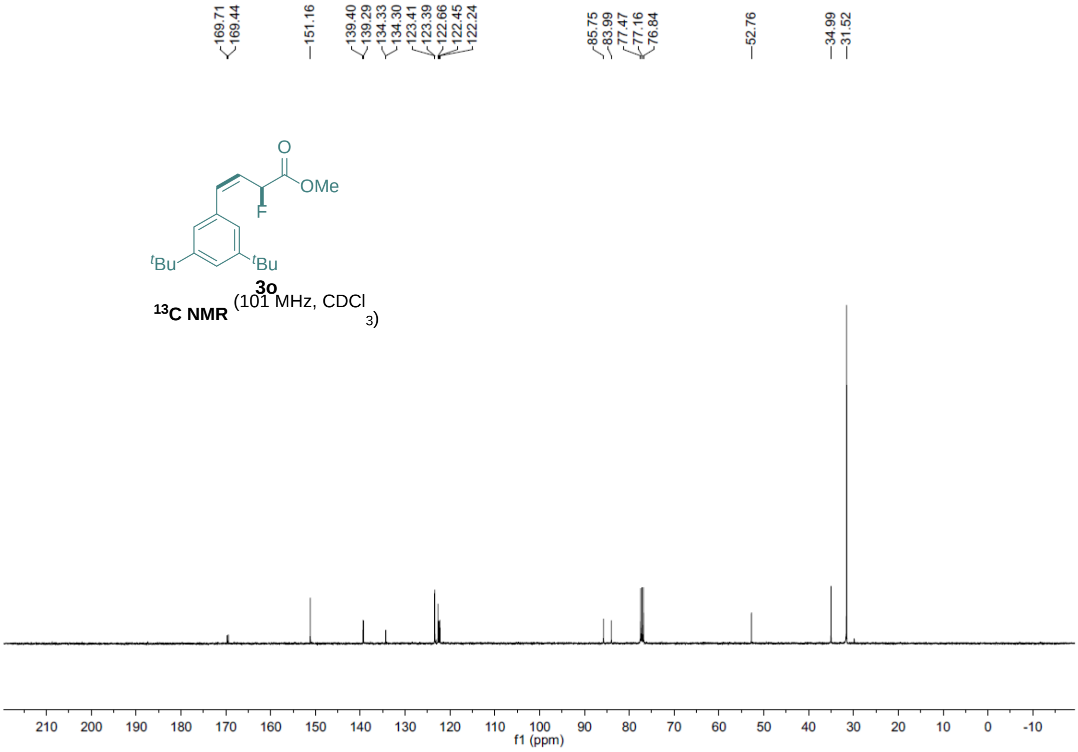
3n

^{19}F NMR (376 MHz, $CDCl_3$)



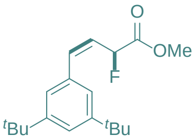
3o

^{1}H NMR (400 MHz, $CDCl_3$)



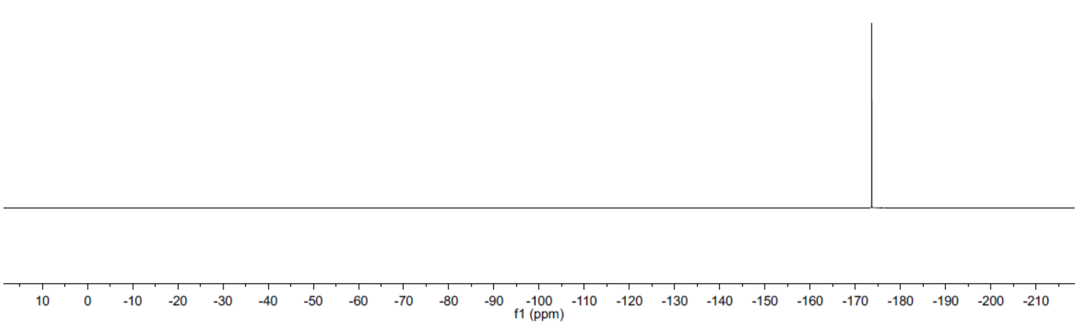
3o

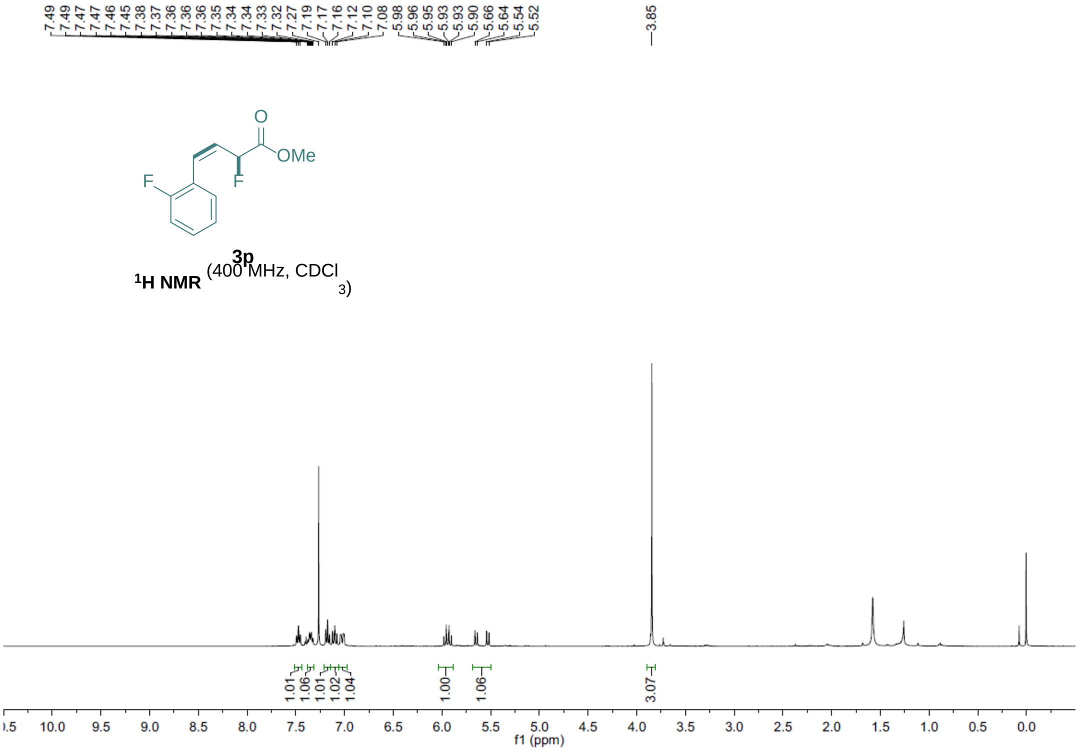
^{13}C NMR (101 MHz, $CDCl_3$)



3o

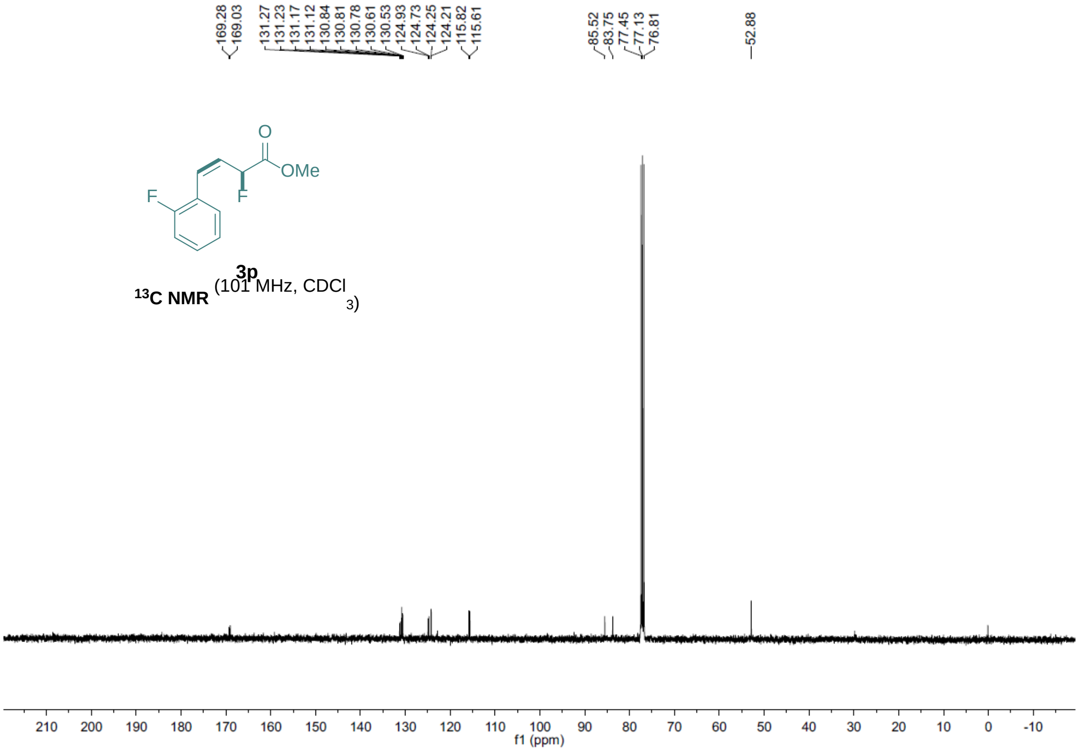
^{19}F NMR (400 MHz, $CDCl_3$)





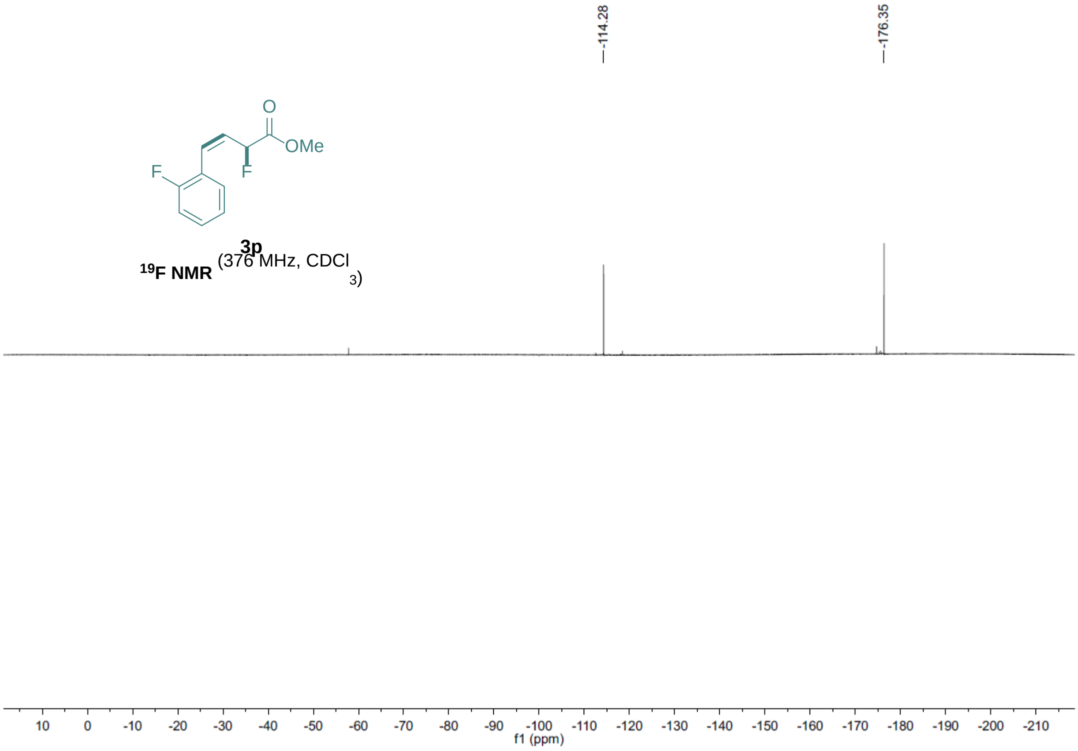
3p

¹H NMR (400 MHz, CDCl$_3$)



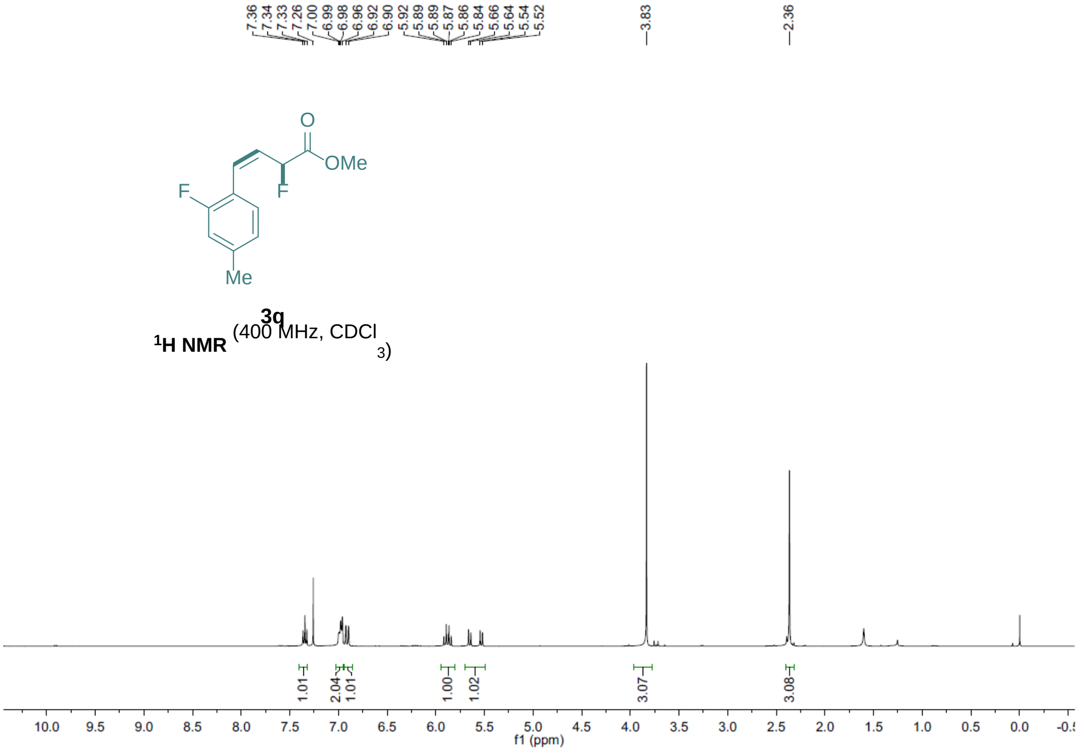
3p

¹³C NMR (101 MHz, CDCl$_3$)



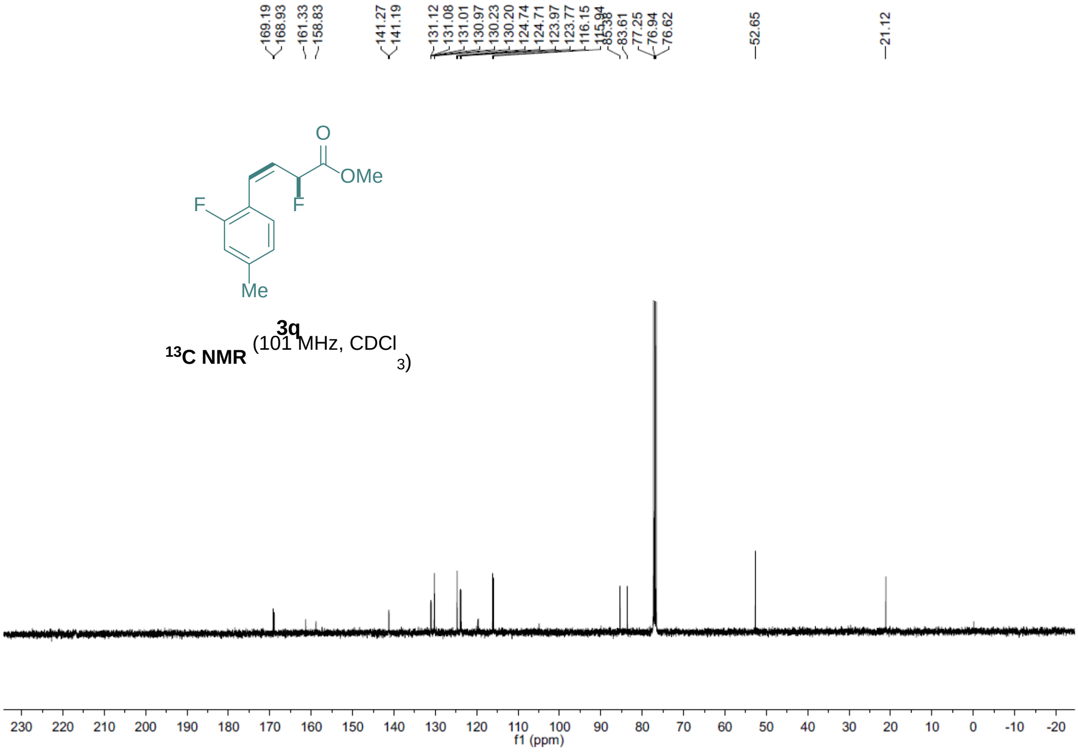
3p

^{19}F NMR (376 MHz, CDCl$_3$)



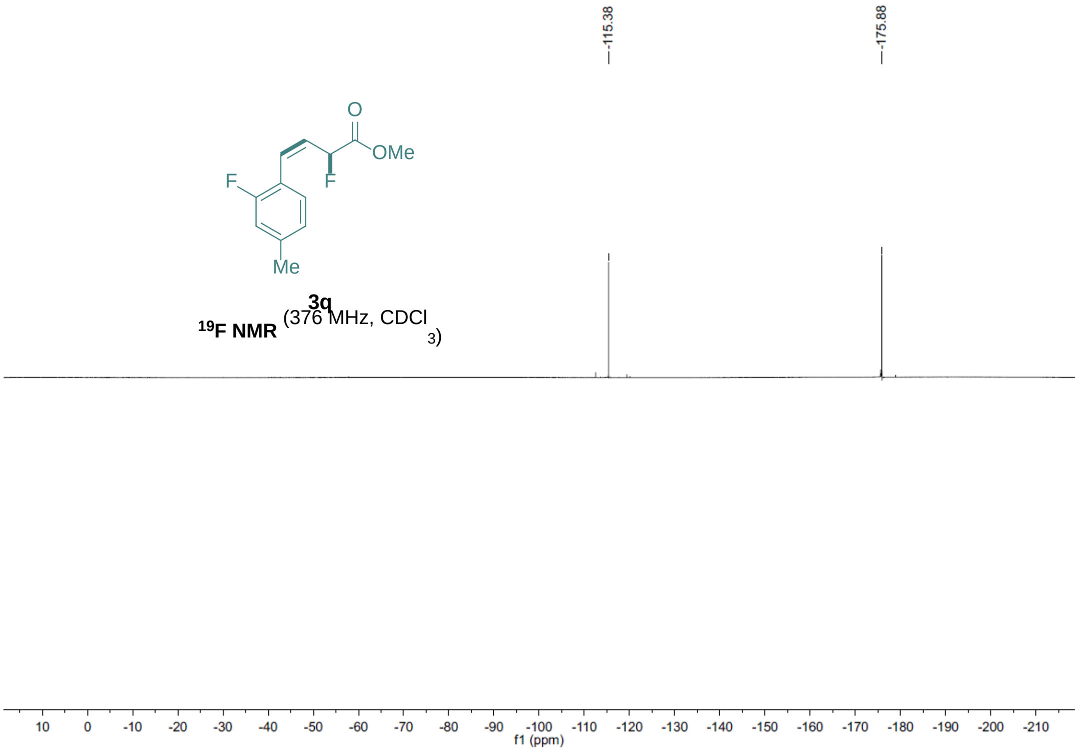
3q

¹H NMR (400 MHz, CDCl$_3$)



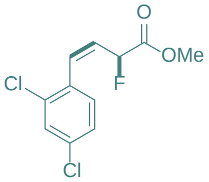
3q

¹³C NMR (101 MHz, CDCl$_3$)



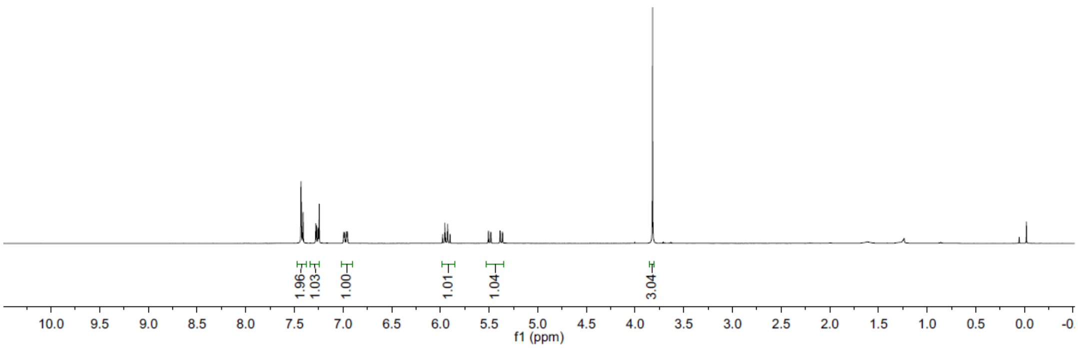
3q

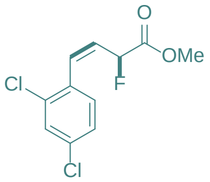
^{19}F NMR (376 MHz, $CDCl_3$)



3r

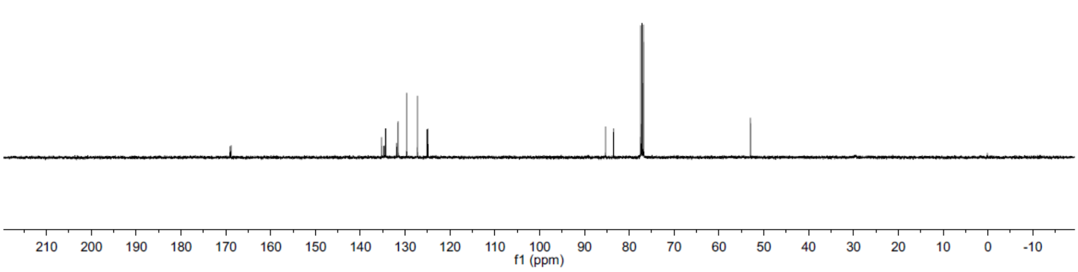
^{1}H NMR (400 MHz, CDCl$_3$)

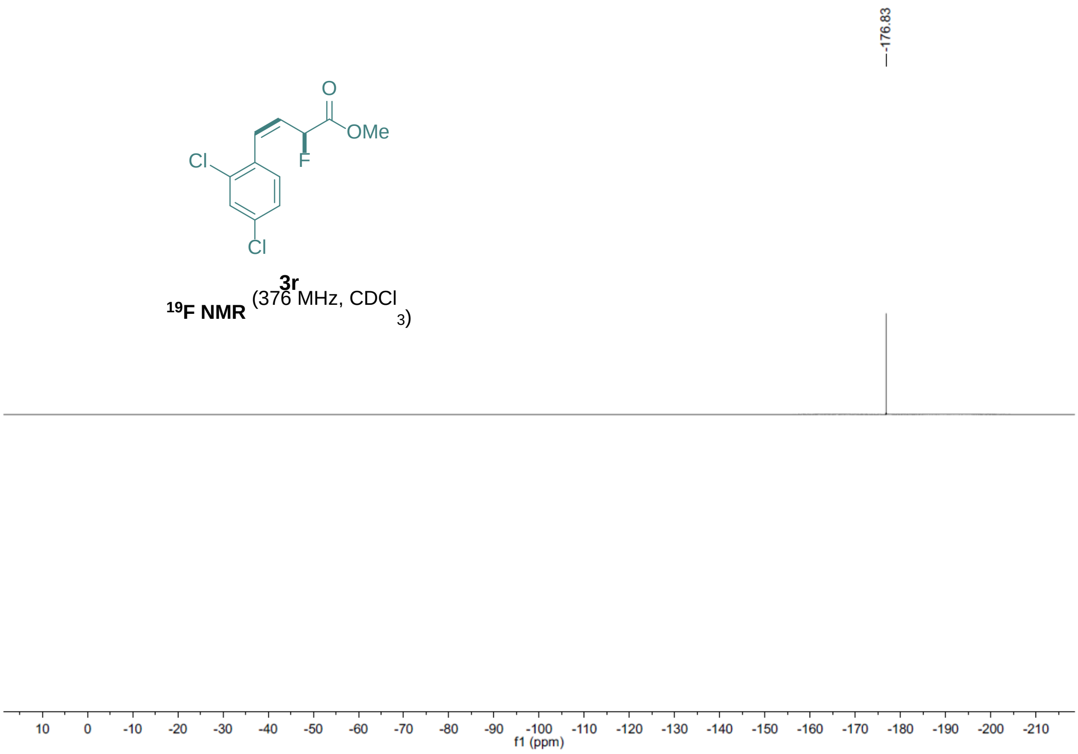




3r

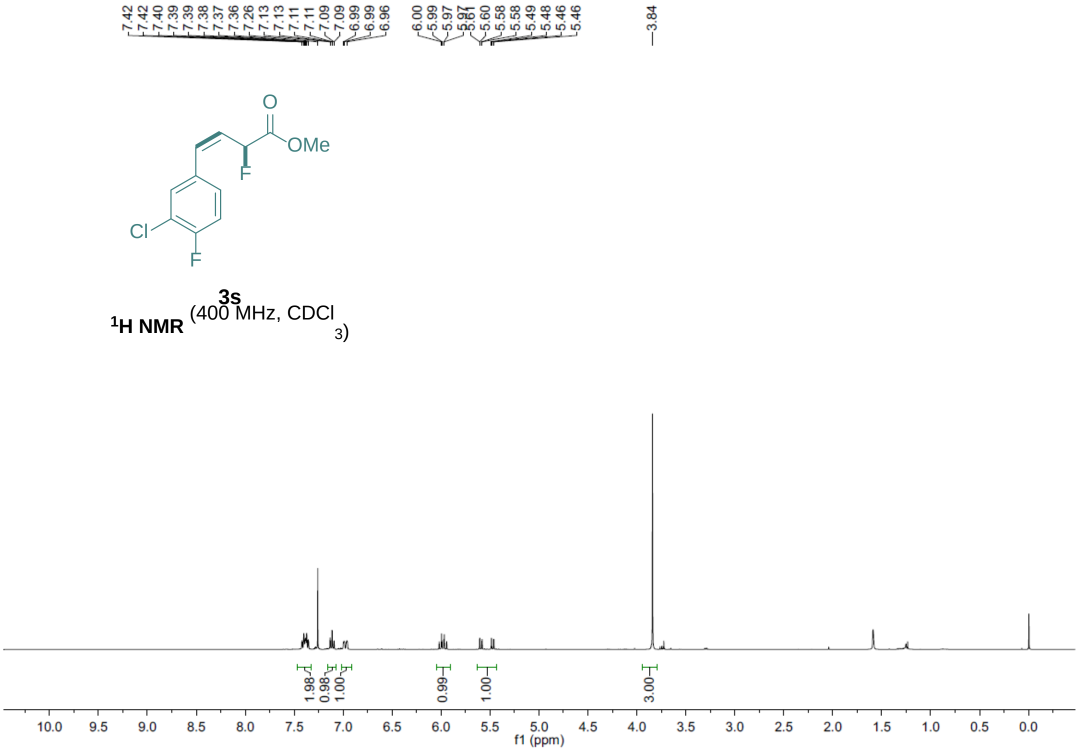
^{13}C NMR (101 MHz, CDCl$_3$)





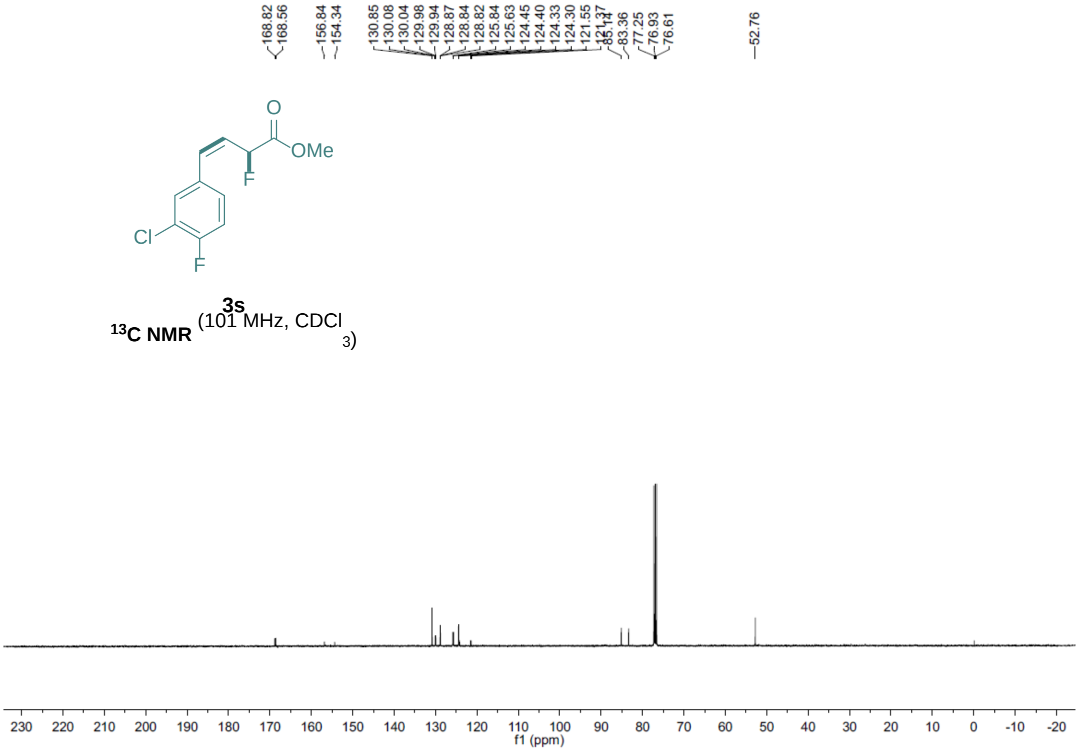
3r

^{19}F NMR (376 MHz, $CDCl_3$)



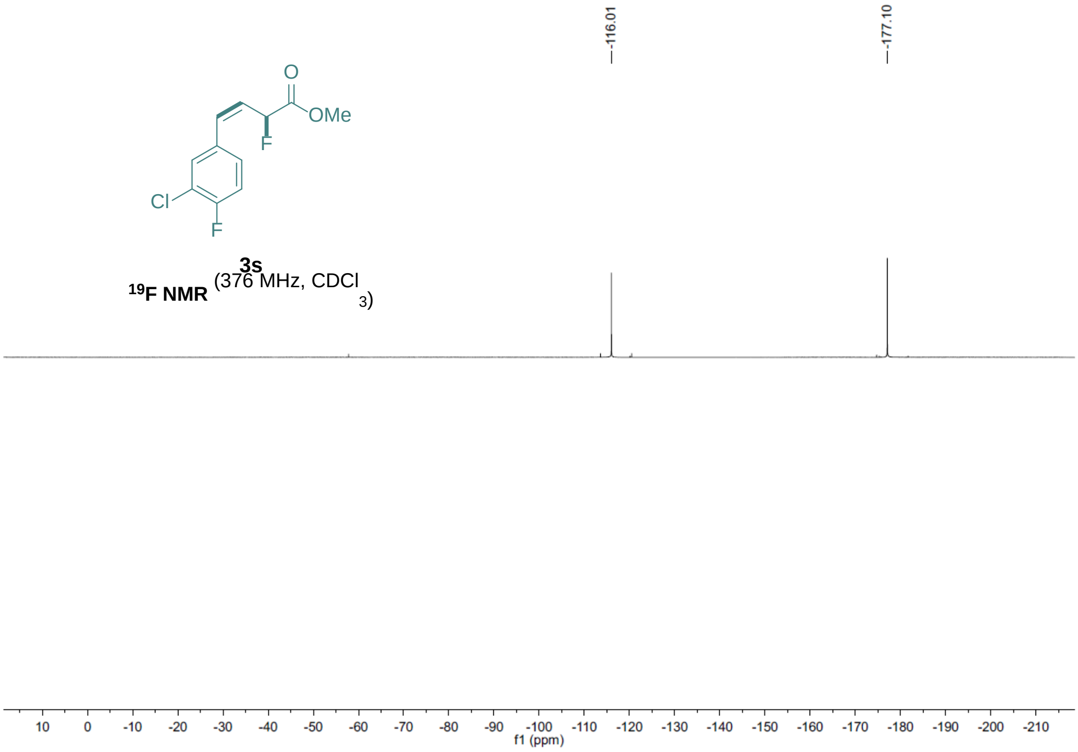
3s

^{1}H NMR (400 MHz, $CDCl_3$)



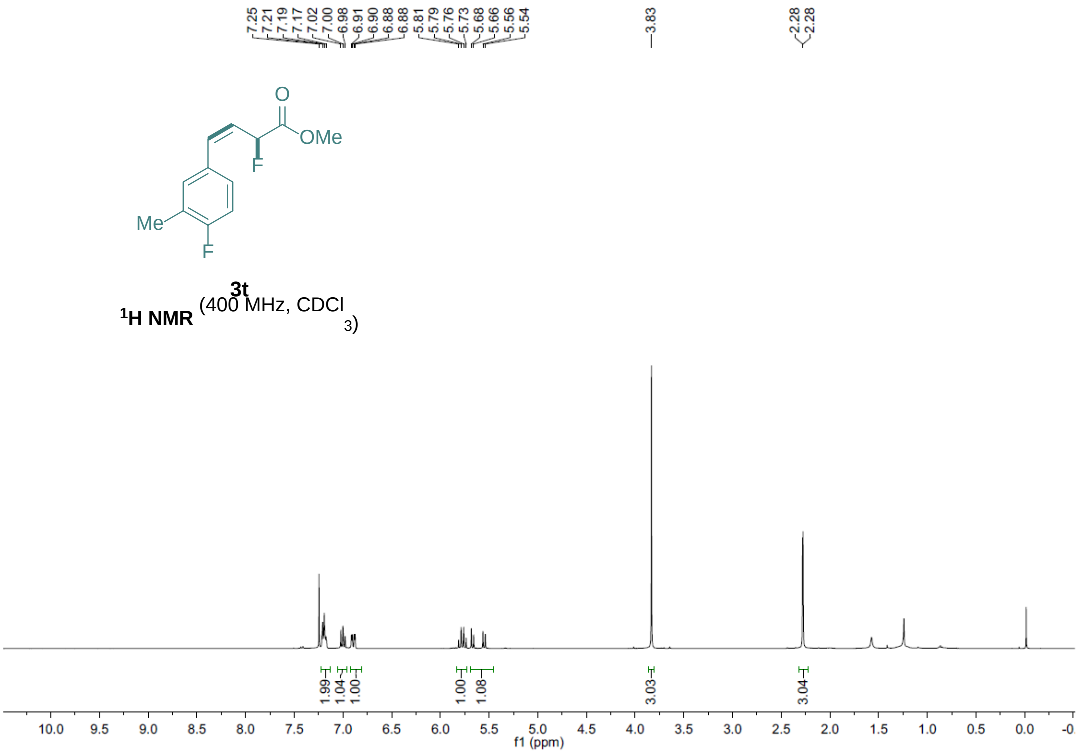
3s

^{13}C NMR (101 MHz, $CDCl_3$)



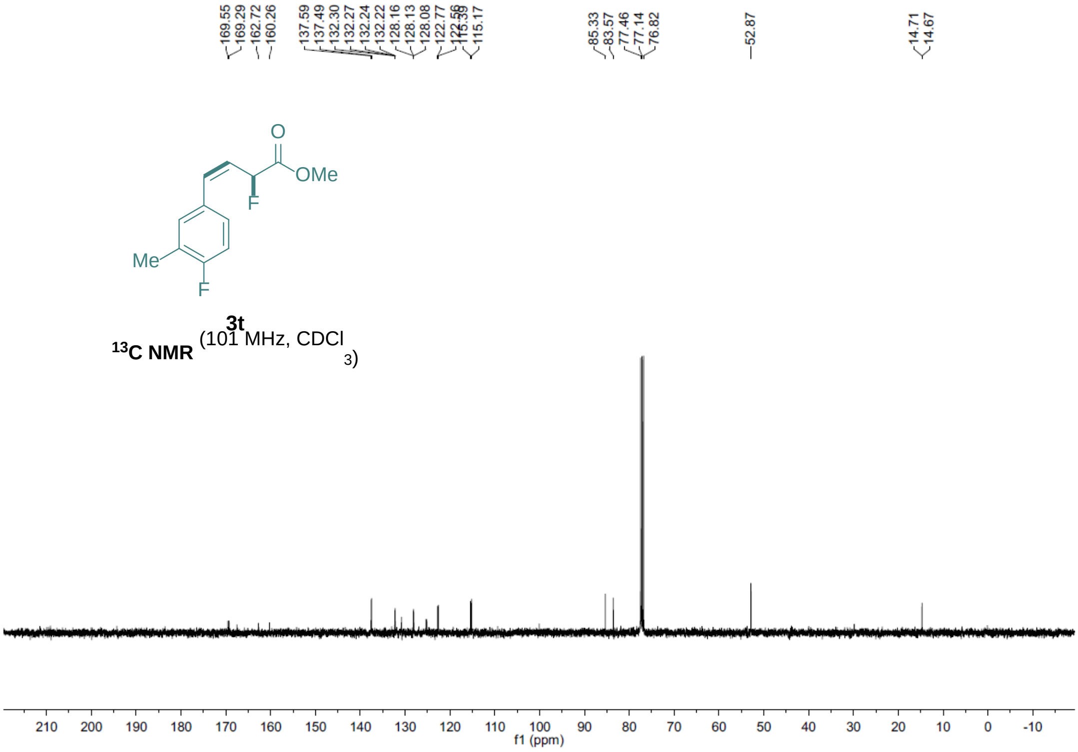
3s

^{19}F NMR (376 MHz, CDCl$_3$)



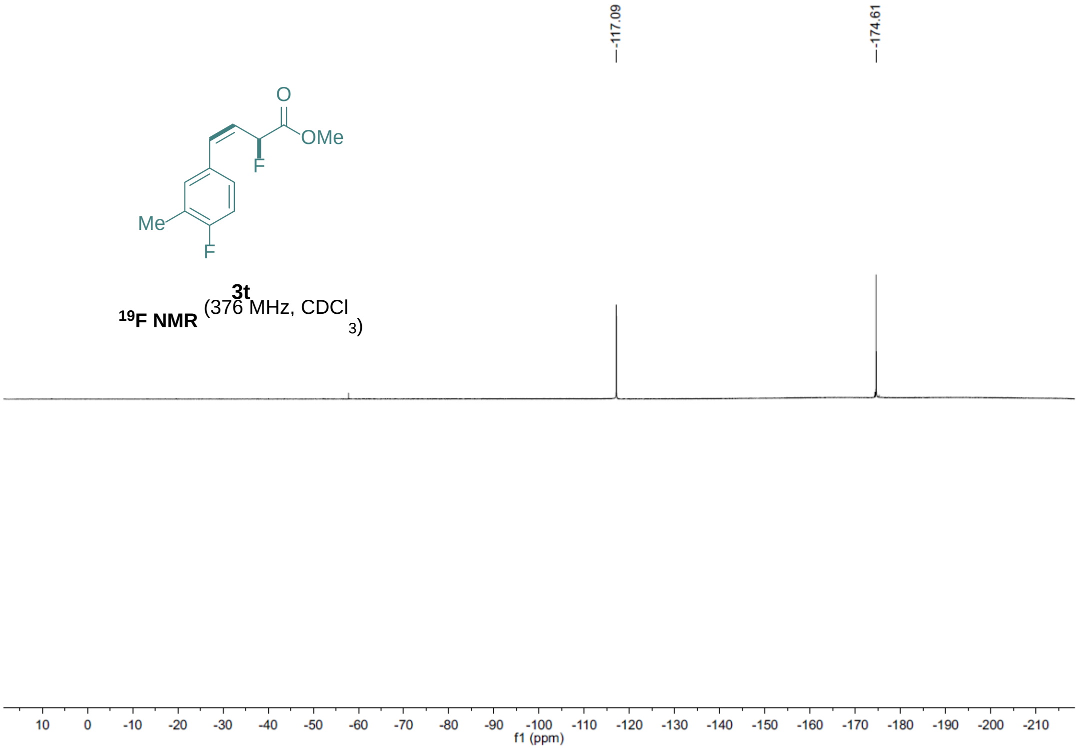
3t

^{1}H NMR (400 MHz, $CDCl_3$)



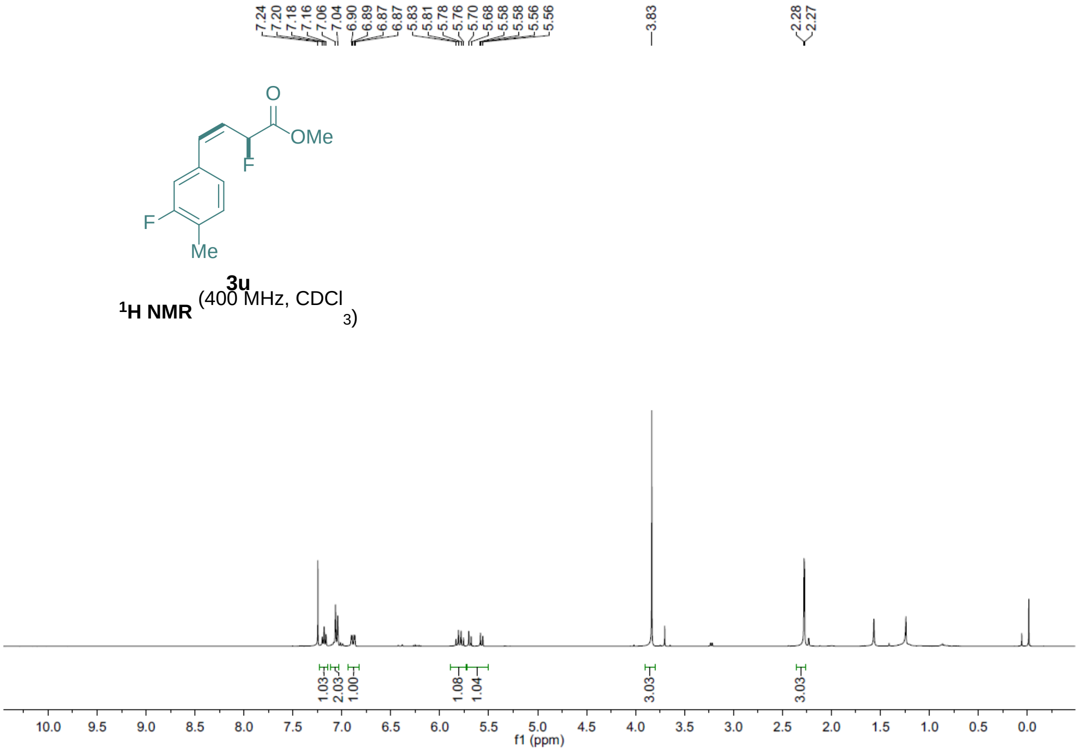
3t

^{13}C NMR (101 MHz, $CDCl_3$)



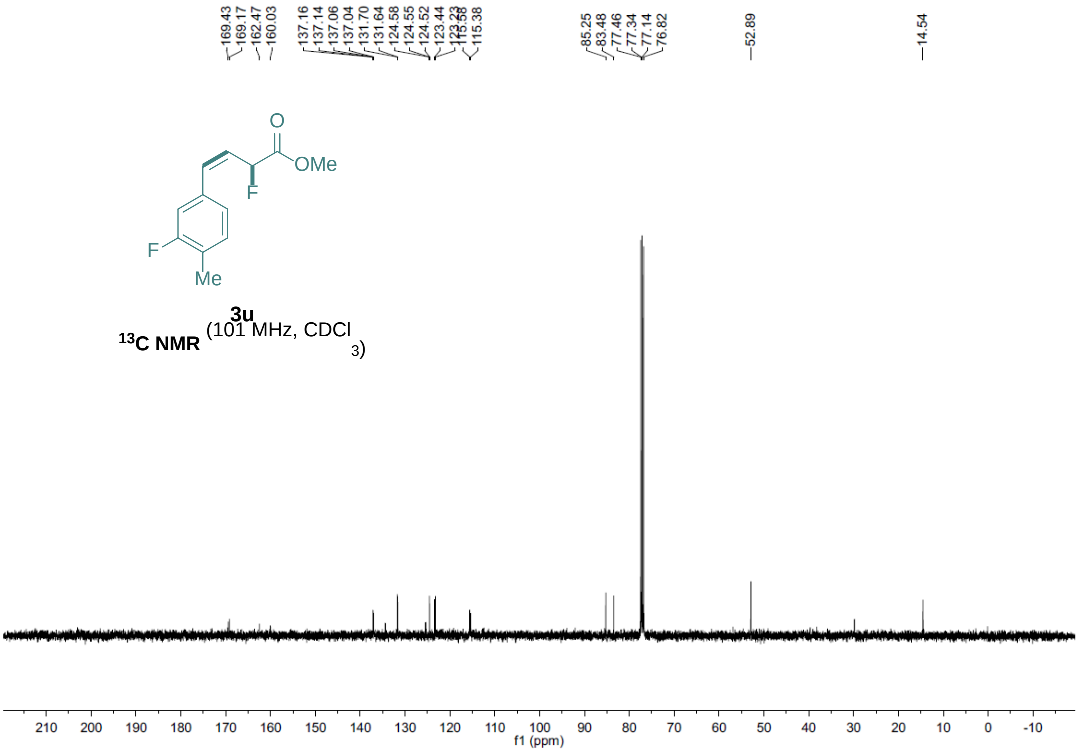
3t

^{19}F NMR (376 MHz, $CDCl_3$)



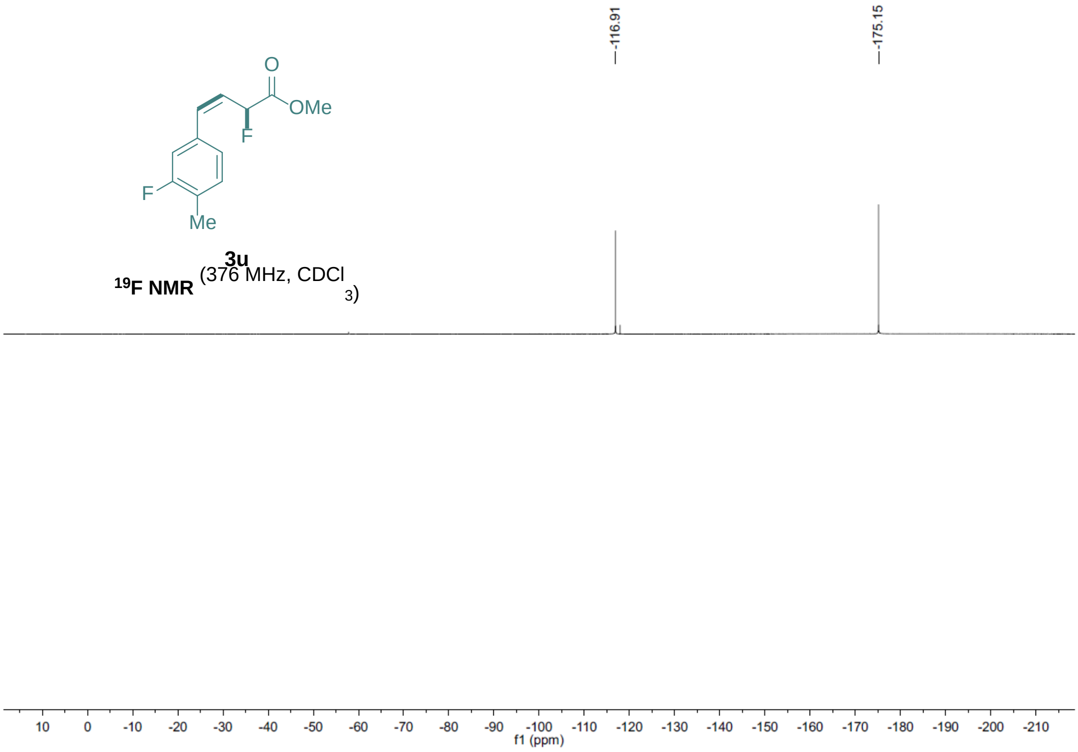
3u

^{1}H NMR (400 MHz, $CDCl_3$)



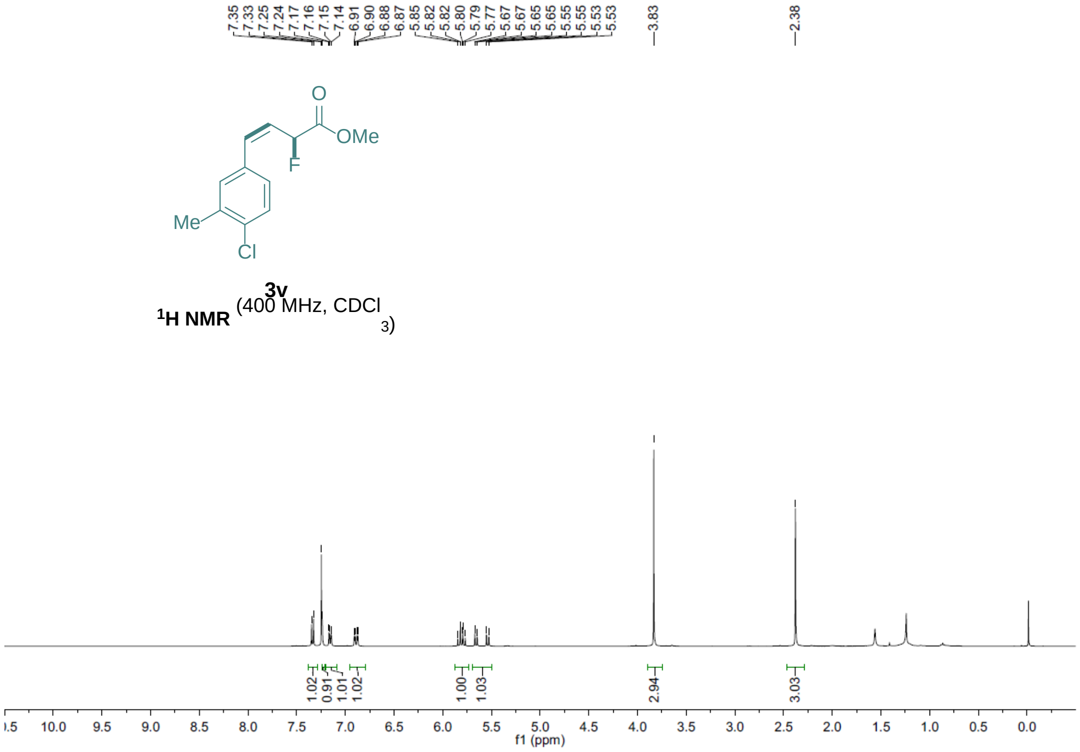
3u

^{13}C NMR (101 MHz, $CDCl_3$)



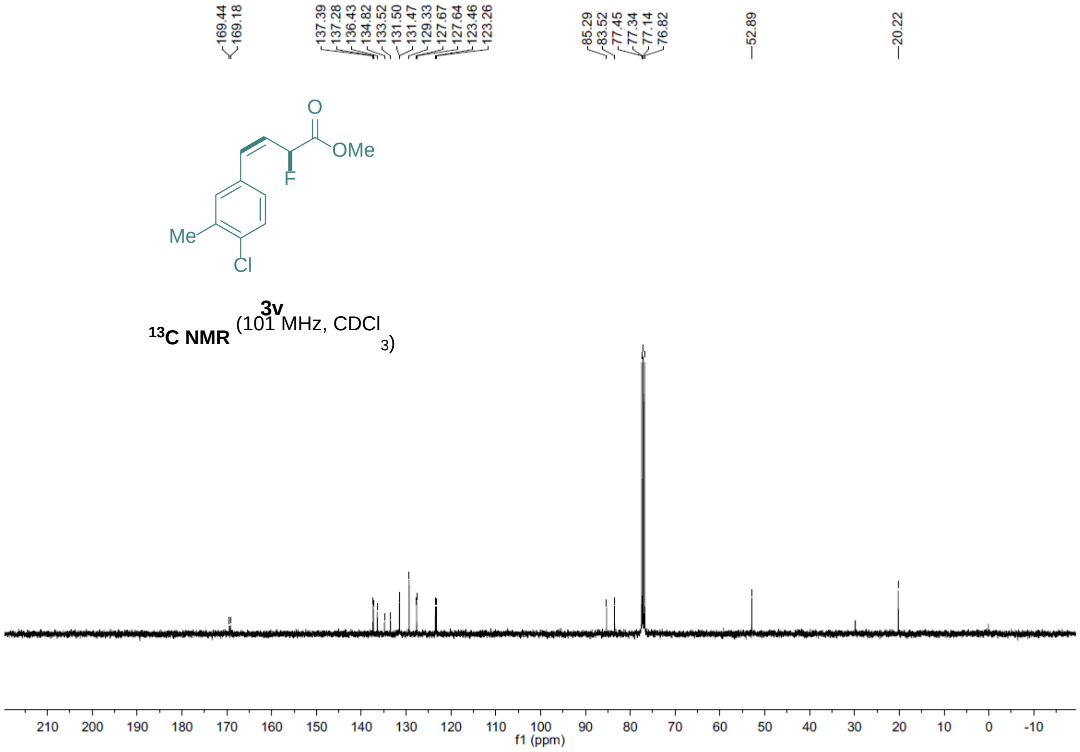
3u

^{19}F NMR (376 MHz, $CDCl_3$)



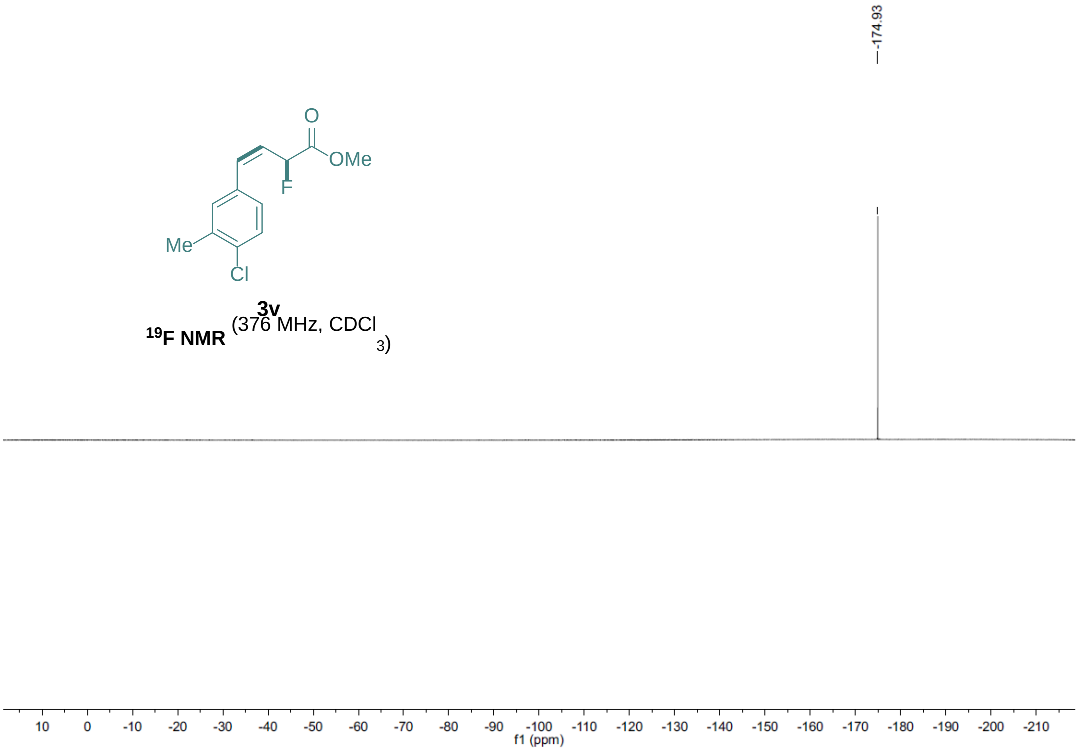
3v

^{1}H NMR (400 MHz, CDCl$_3$)



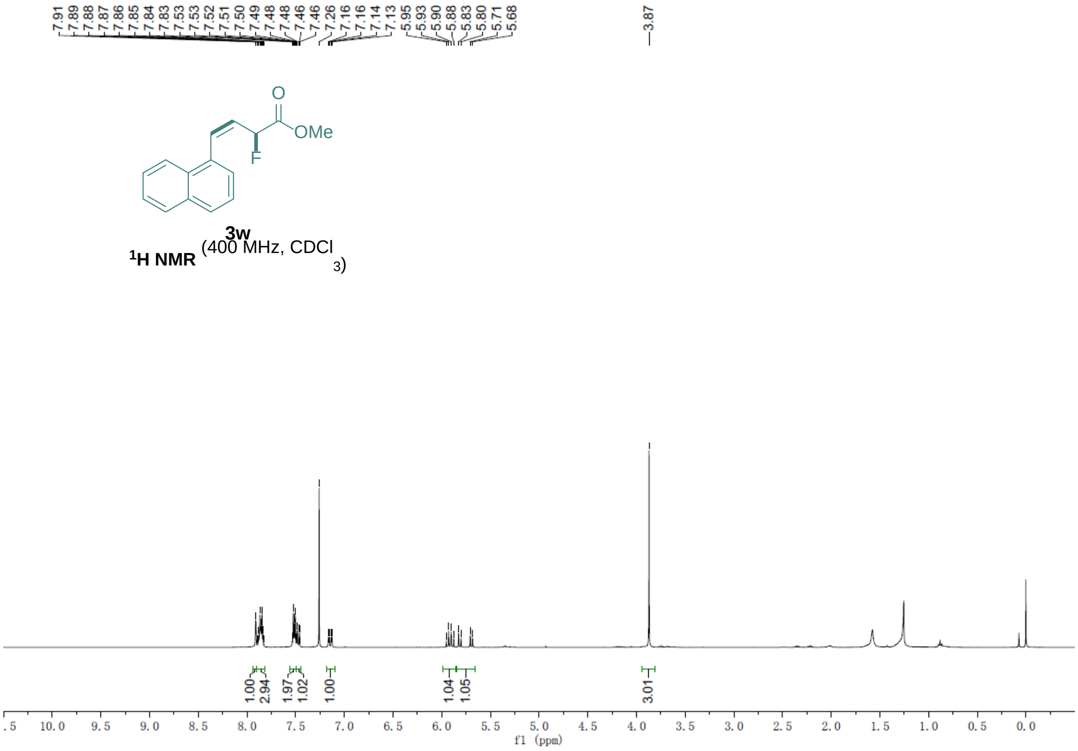
3v

^{13}C NMR (101 MHz, CDCl$_3$)



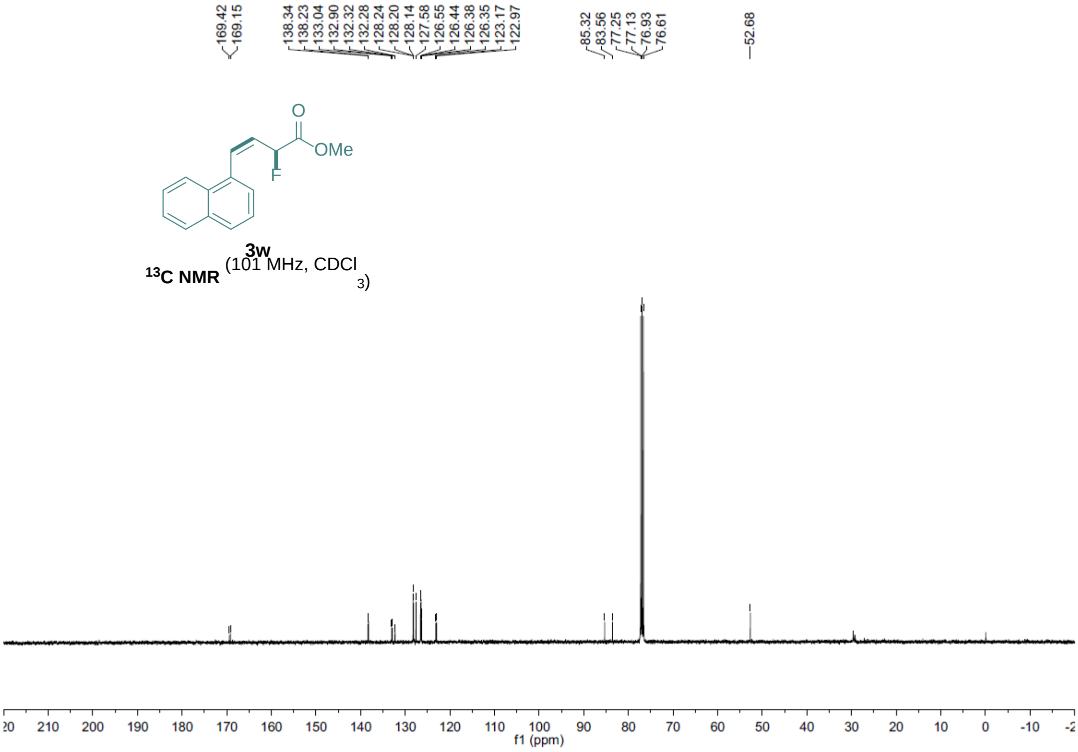
3v

^{19}F NMR (376 MHz, $CDCl_3$)



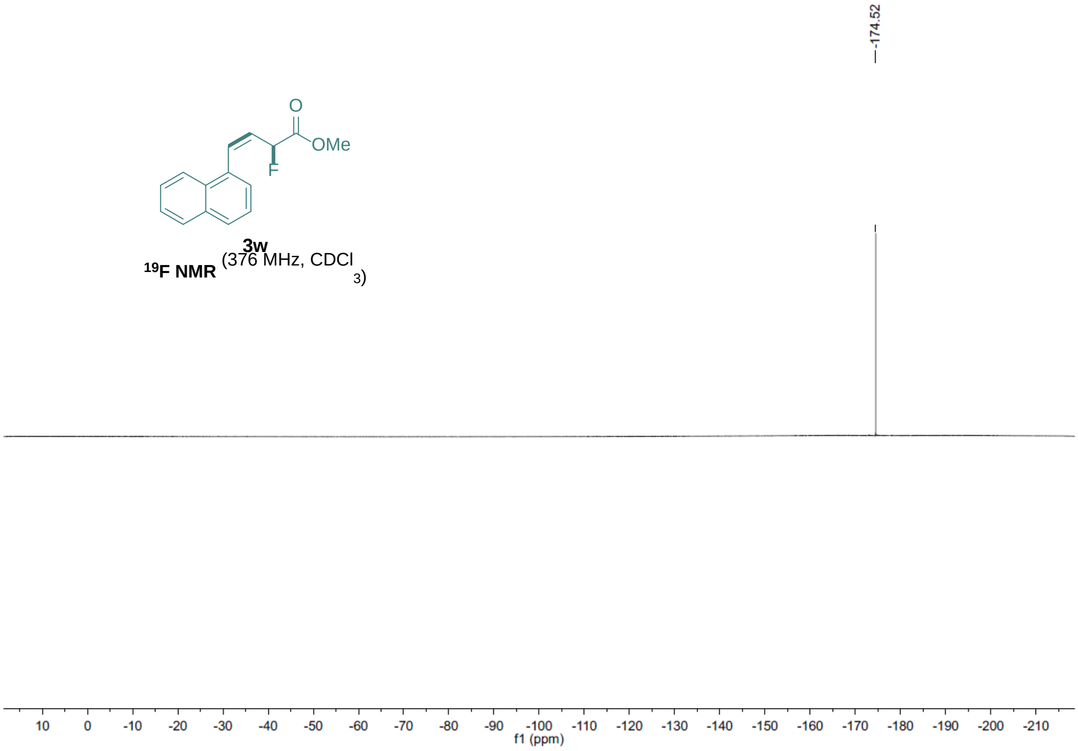
3w

^{1}H NMR (400 MHz, $CDCl_3$)



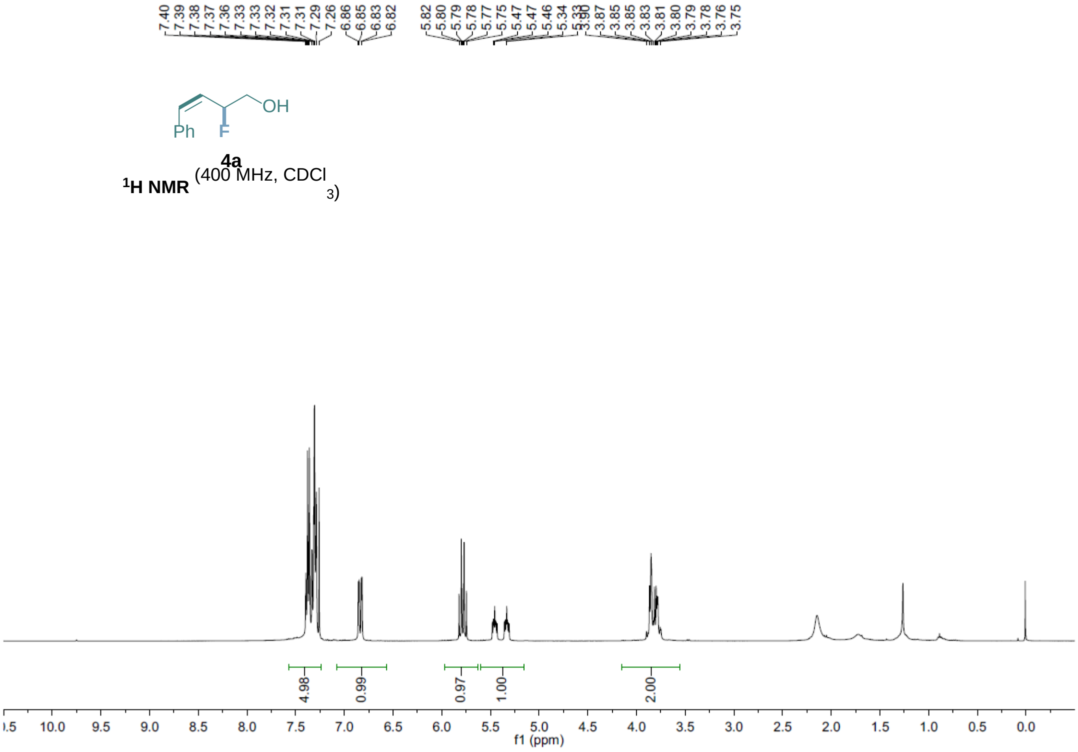
3w

^{13}C NMR (101 MHz, $CDCl_3$)



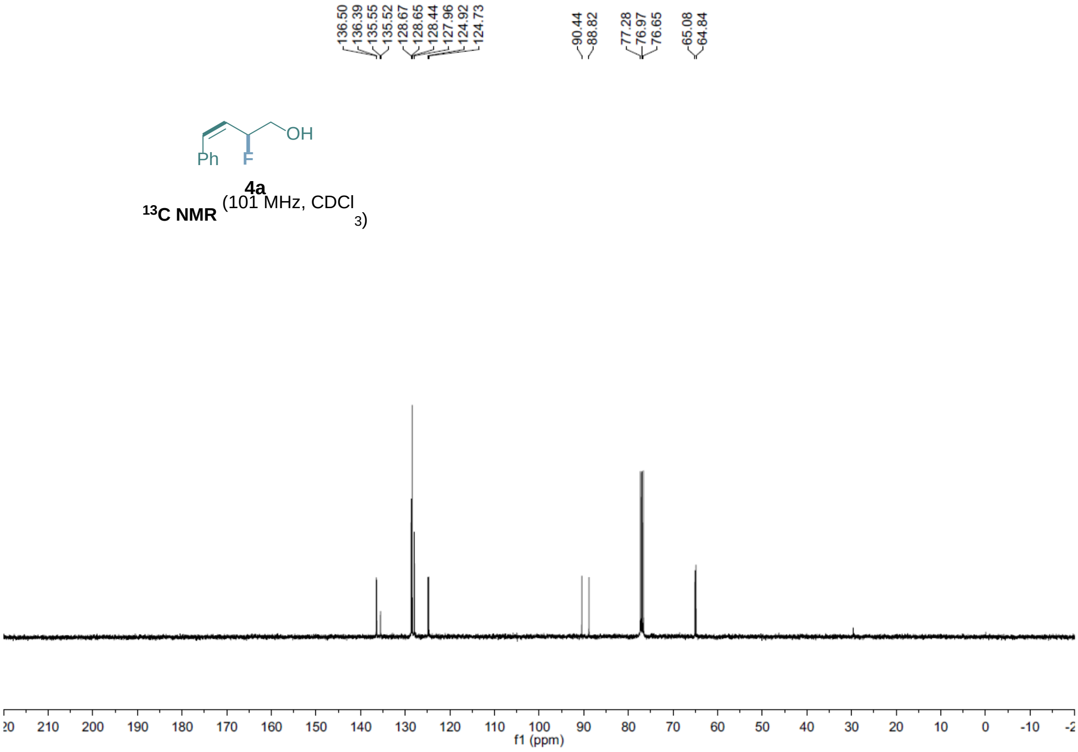
3w

^{19}F NMR (376 MHz, $CDCl_3$)



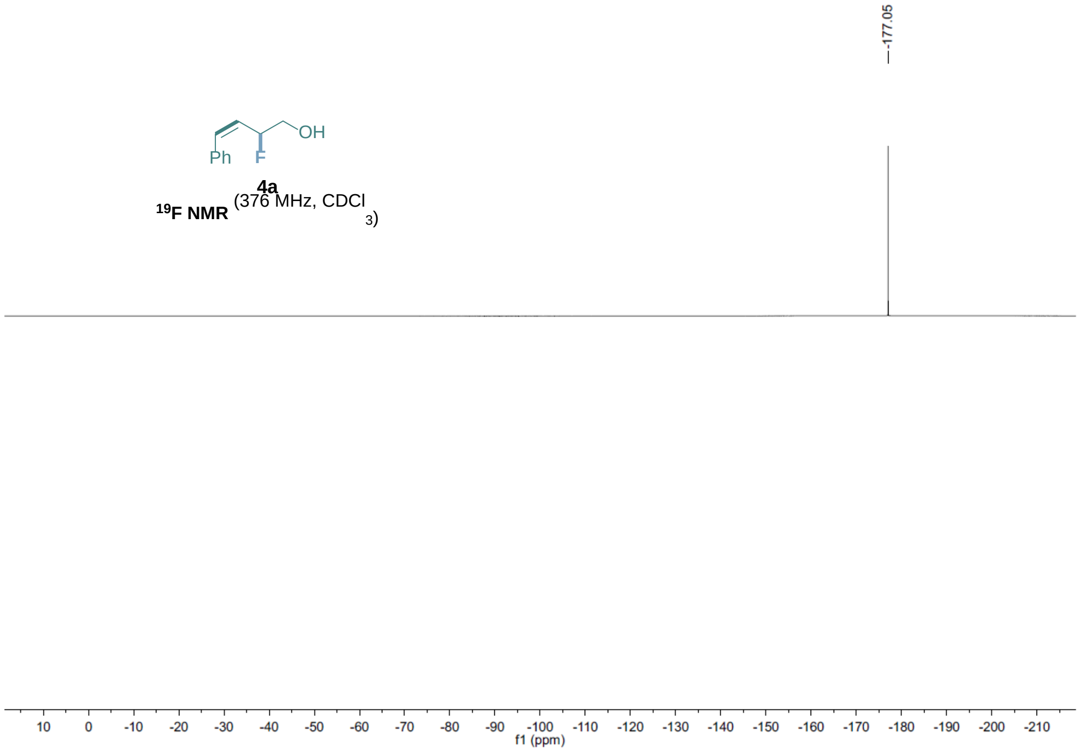
4a

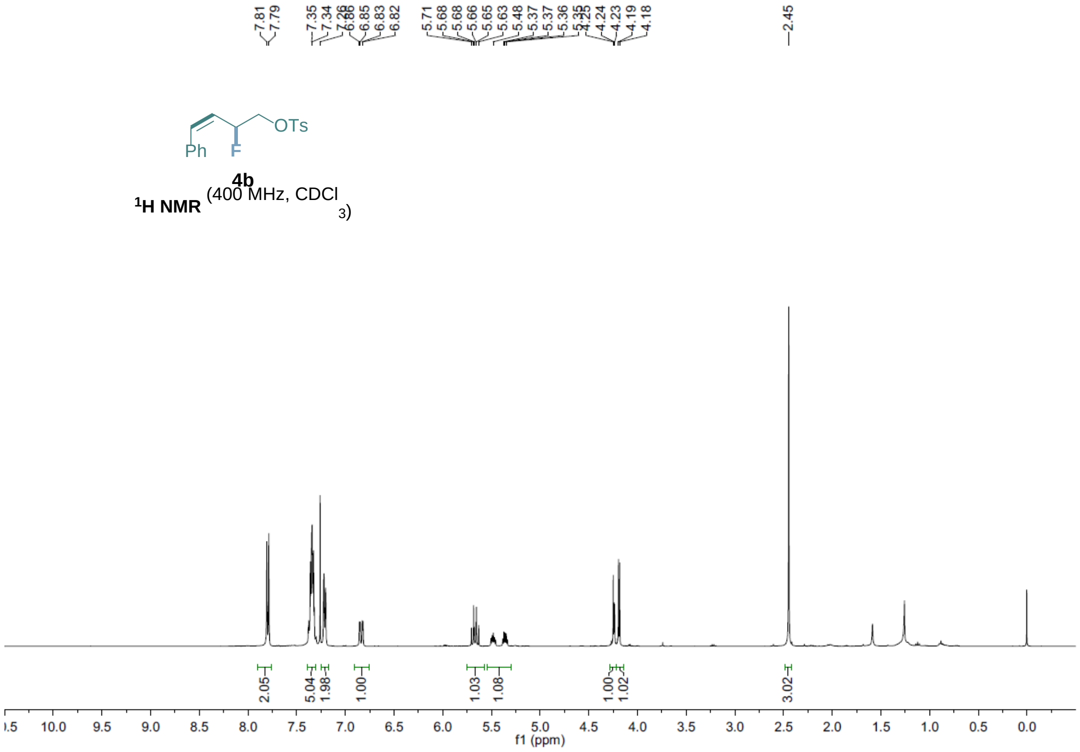
^{1}H NMR (400 MHz, CDCl$_3$)



4a

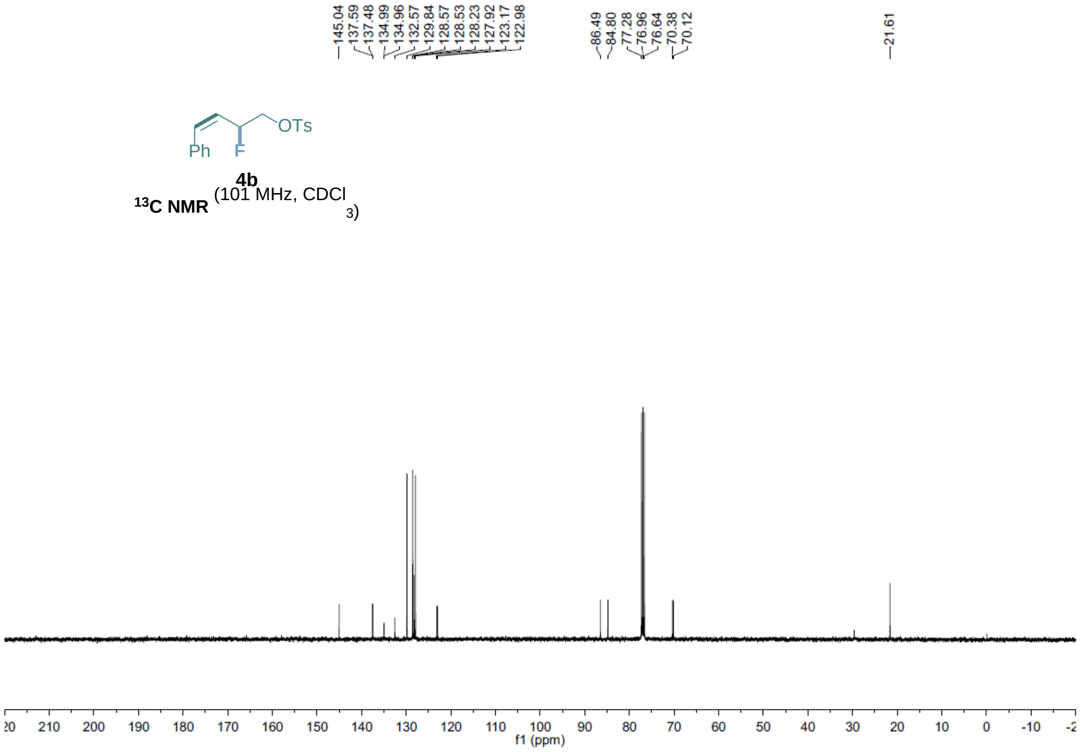
^{13}C NMR (101 MHz, CDCl$_3$)


-177.05
Ph
F
OH
4a
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



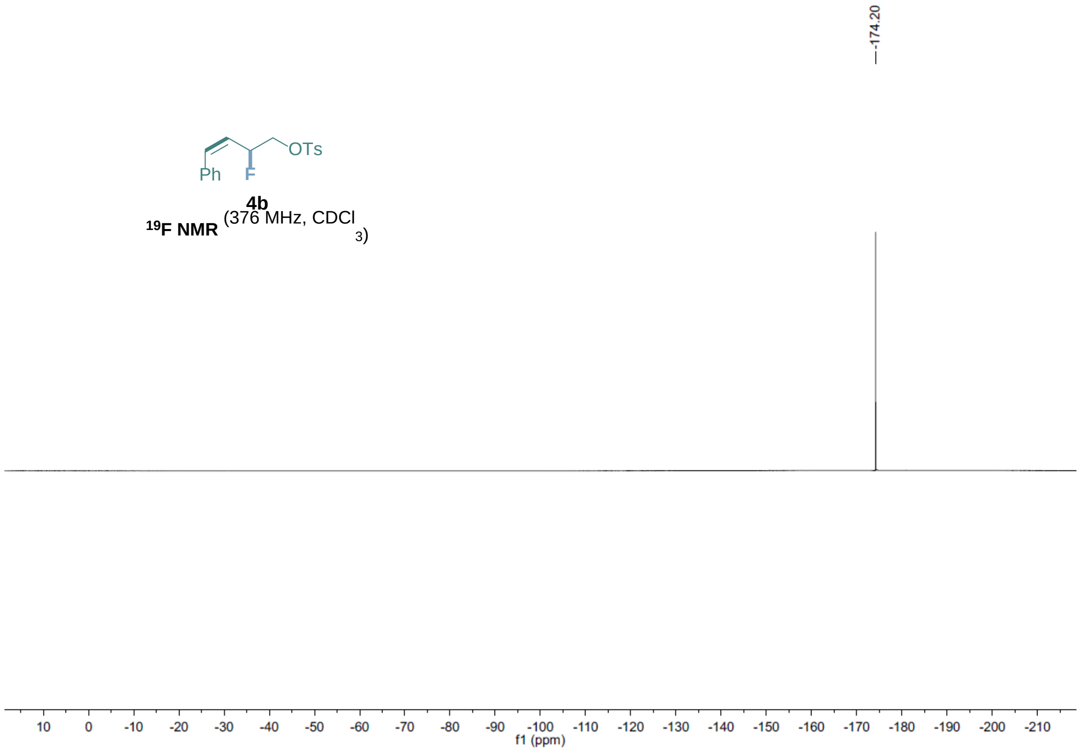
4b

^{1}H NMR (400 MHz, $CDCl_3$)



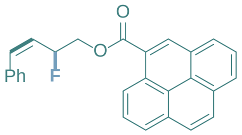
4b

^{13}C NMR (101 MHz, $CDCl_3$)



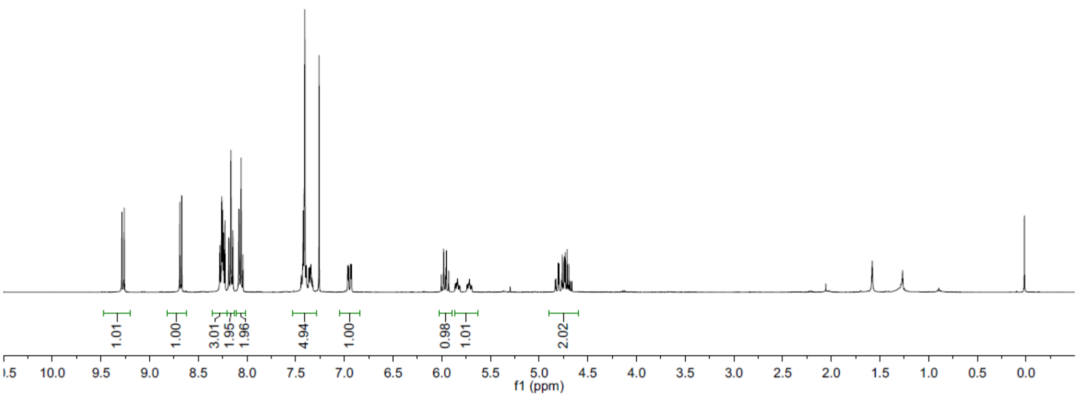
4b

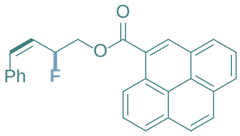
^{19}F NMR (376 MHz, $CDCl_3$)



4c

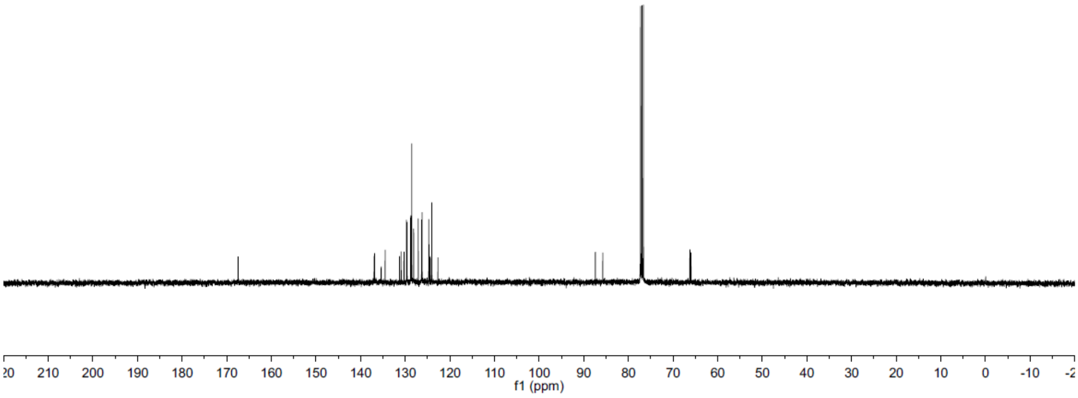
^{1}H NMR (400 MHz, CDCl$_3$)

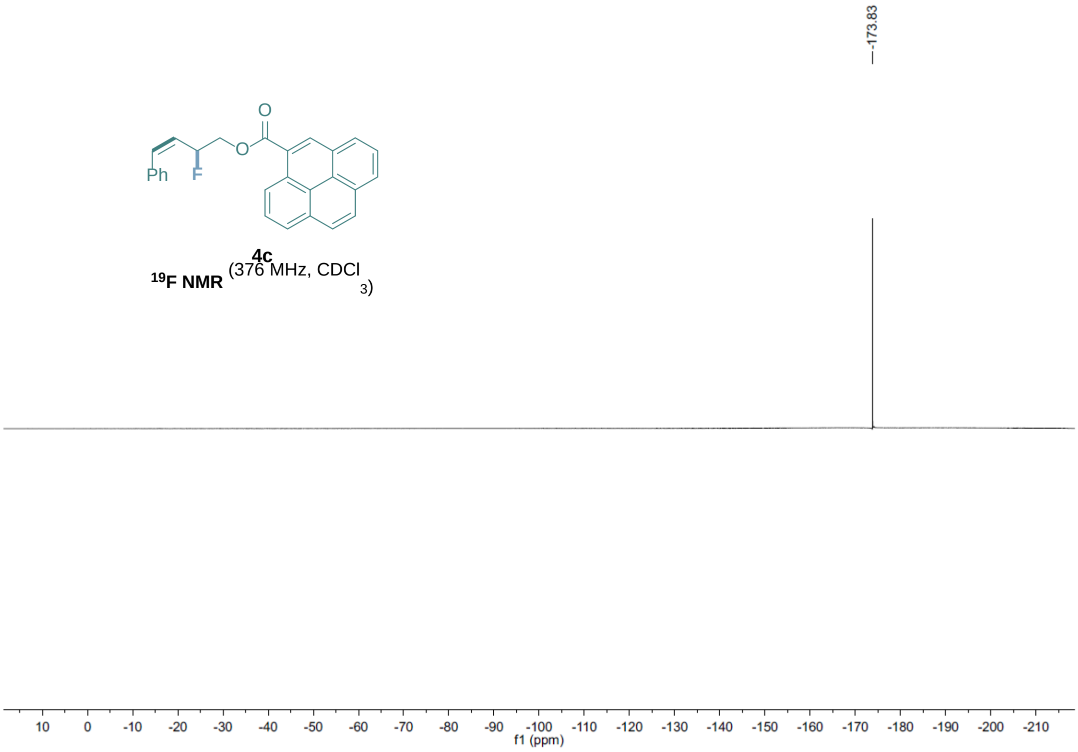




4c

^{13}C NMR (101 MHz, CDCl$_3$)




-173.83
O
O
Ph
F
4c
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)