Electronic Supporting Information for

Iridium(III)-Catalyzed *β*-Trifluoromethyl Enone Carbonyl Directed Regio-Selective *Ortho*-C(sp^2)-H Olefination

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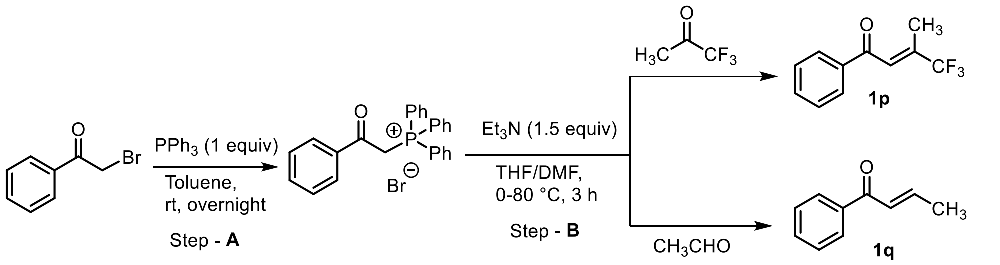
1. General Information

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer in $CDCl_3$, DMSO-d_6, with TMS (tetramethyl silane) as an internal standard. ^{19}F NMR was also recorded on the same instrument. Data are reported as follows: Chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, p = pentet, dq = doublet of quartet, hept = heptet, m = multiplet), Coupling constants (*J*), are reported in hertz (Hz). High-resolution Mass Spectrometry (HRMS) was done on Agilent Q-TOF LC/MS. Melting point was recorded on Buchi M-560. Materials were purchased from Sigma Aldrich, TCI, and used without any further purification. The starting materials **1a-1o**,[1] **1p**-**1q**[2] were prepared as reported in previous literature. Column chromatography was performed on silica gel (230-400 mesh) using ethyl acetate and hexane as mobile phase.

2. Experimental Details

2.1. Synthesis of β-Substituted Enone (1p and 1q)[2]

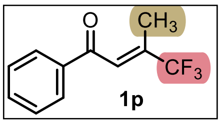


Scheme 2. Synthesis of β-Substituted Enone

Step - A: To a solution of aryl-2-bromoethanone (1.0 equiv, 10 mmol) in toluene (15 mL) was added a solution of triphenylphosphine (PPh_3) (1.0 equiv, 10 mmol) in toluene (15 mL) dropwise for 10 min. Then, the reaction mixture was stirred at room temperature overnight, and the resulting mixture was concentrated under reduced pressure. The resulting precipitate was washed with Et_2O. Then phosphonium bromide was obtained in quantitative yield and was used without purification.

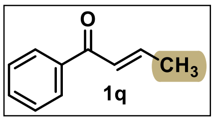
Step - B: To an oven dried round bottomed flask was added triphenylphosphonium bromide salt (7.5 mmol) and triethylamine (759 mg, 7.5 mmol) in THF (20 mL), followed by the addition of a solution of a trifluoromethyl ketone/acetaldehyde (5.0 mmol) in DMF (1.6 mL) at 0 °C in an ice bath. The mixture was then stirred for 15 min at this temperature. Warming to room temperature, the solution was heated further stirred at 80 °C for 3 h. Then, the solution was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. Further the residue was purified by silica gel (230-400 mesh size) column chromatography (Hexane/ethyl acetate: 100:1) to give the pure β-Substituted Enone **1p** in 40% and **1q** in 35% yield.

(*E*)-4,4,4-Trifluoro-3-methyl-1-phenylbut-2-en-1-one (1p):



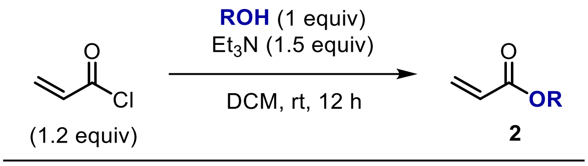
Yellow liquid; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.94 – 7.92 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 (tt, *J* = 7.5, 1.7 Hz, 2H), 7.23 (hept, *J* = 1.5 Hz, 1H), 2.16 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 191.2, 139.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz), 137.3, 133.9, 129.0, 128.7, 125.9 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 124.6 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 12.9; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -70.8.

(*E*)-1-Phenylbut-2-en-1-one (1q):



Yellow liquid; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.93 – 7.91 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.45 (m, 2H), 7.08 (dq, *J* = 15.4, 6.9 Hz, 1H), 6.91 (dq, *J* = 15.3, 1.6 Hz, 1H), 2.01 (dd, *J* = 6.9, 1.5 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 190.8, 145.0, 137.9, 132.5, 128.5, 127.5, 18.6.

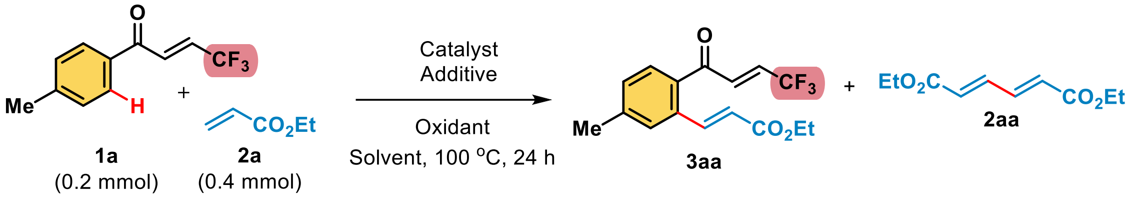
2.2. Synthesis of Acrylates (2):



Scheme 3. Synthesis of Acrylates

Alcohol (3 mmol, 1 equiv) was mixed with Et_3N (1.5 equiv) in dry CH_2Cl_2 (10 mL) and cooled to 0 °C in an ice-water bath. Then acryloyl chloride (1.2 equiv) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to get the desired acrylates 80-95% yield.

3. Complete Optimization for Ortho-olefinated product (3aa):



Scheme 4. Complete optimization for ortho-olefinated product **3aa**

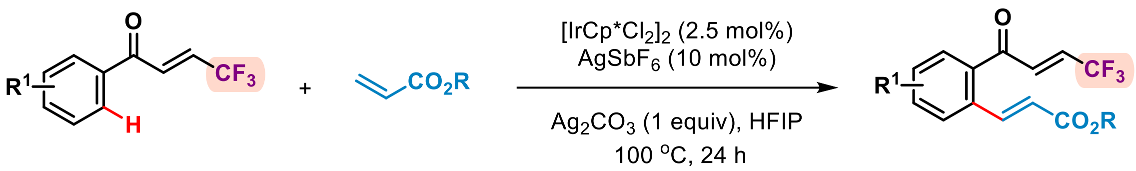
Entry	Catalyst (mol%)	Additive (mol%)	Oxidant (x equiv)	Solvent	Yield (%)	
					3aa	2aa
1	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DCE	45	10
2[a]	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DCE	53	17
3[a]	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (2)	DCE	58	20
4	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	-	DCE	trace	-
5[b]	$[RhCp^*Cl_2]_2$ (2.5)	-	$Cu(OAc)_2.H_2O$ (1)	DCE	-	-
6	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	AgOAc (1)	DCE	52	7
7	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	DCE	55	5
8	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	CuCl (1)	DCE	-	-
9	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	CuBr (1)	DCE	-	-
10	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	KOAc (1)	DCE	-	-
11	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	NaOAc (1)	DCE	-	-
12	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$K_2S_2O_8$ (1)	DCE	-	-
13	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DCM	60	10
14	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	THF	25	-
15	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	EtOAc	27	-
16	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	1,4-dioxane	44	10
17	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	TFE	21	traces
18	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	Xylene	-	-
19	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	Toluene	-	-
20	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DMSO	-	-
21	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	CAN	-	-
22	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DMF	-	-
23	$[Ru(p\text{-cymene})Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DCE	40	10
24	$[Ru(p\text{-cymene})Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	DCE	46	8
25	$[Ru(p\text{-cymene})Cl_2]_2$ (5)	$AgSbF_6$ (20)	Ag_2CO_3 (1)	DCE	52	15
26	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (1)	DCE	60	5
27	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	DCE	52	-
28	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	EtOAc	21	-
29	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	1,4-dioxane	50	-
30	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	Toluene	-	-
31	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	MeCN	-	-
32	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	TFE	30	-
33	**$[IrCp^*Cl_2]_2$ (2.5)**	$AgSbF_6$ (10)	**Ag_2CO_3 (1)**	**HFIP**	**82**	**-**
34[c]	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	HFIP	-	15
35	$[IrCp^*Cl_2]_2$ (1)	$AgSbF_6$ (4)	Ag_2CO_3 (1)	HFIP	40	-

36	$[IrCp^*Cl_2]_2$ (5)	$AgSbF_6$ (20)	Ag_2CO_3 (1)	HFIP	86	-
37	$[IrCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10)	Ag_2CO_3 (1)	HFIP	70	-
38	$[IrCp^*Cl_2]_2$ (2.5)	$AgPF6_6$ (10)	Ag_2CO_3 (1)	HFIP	64	-
39	$[IrCp^*Cl_2]_2$ (2.5)	KPF_6 (10)	Ag_2CO_3 (1)	HFIP	20	-
40	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1) + AgOPiv (1)	HFIP	80	-
41	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1) + PivOH (1)	HFIP	75	5
42	$[Ru(p\text{-cymene})Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	HFIP	20	-
43	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (1)	HFIP	10	-
44	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (2)	HFIP	84	-

[a]PivOH (1 equiv) was added; [b] reaction was performed without $AgsbF_6$. [c] reaction was performed without **1a.**

It is to be noted that compound **3aa** and **2aa** were found to have same Rf on TLC in hexane-ethyl acetate mobile phase. The yields were calculated based on NMR after isolating the mixture of **3aa** and **2aa** from column chromatography.

4. General procedure for C-H olefination and characterization data of compounds (3aa-3ra, 3ab-3ao):

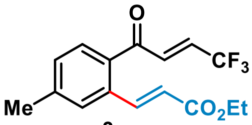


1 (0.2 mmol) 2 (0.4 mmol) 3

Scheme 5. General procedure for the *Ortho*-C-H Olefination

To an oven-dried sealed tube with (*E*)-4,4,4-Trifluoro-1-(*aryl*)but-2-en-1-one (**1**) (0.2 mmol, 100 mol %), acrylate (**2**) (0.4 mmol, 200 mol %), $[IrCp^*Cl_2]_2$ (4.0 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %) and Ag_2CO_3 (55.1 mg, 0.2 mmol, 100 mol %) was added in HFIP (1 mL). The reaction mixture was allowed to stir at 100 ºC for 24 h. After cooling at room temperature, the reaction mixture was evaporated and the residue was purified by column chromatography on silica gel (230-400 mesh) (eluent; hexane/EtOAc = 20:1) to provide desired olefinated product **3**.

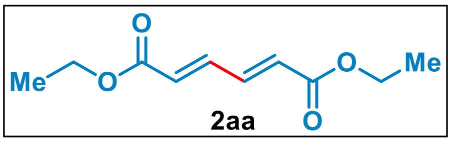
Ethyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3aa):



3aa

50 mg (82%); white solid; mp = 45-48 °C; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 8.02 (d, *J* = 15.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 0.9 Hz, 1H), 7.31 (dd, *J* = 7.9, 2.5 Hz, 1H), 7.26 (dq, *J* = 15.7, 2 Hz, 1H), 6.70 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.32 (d, *J* = 15.7, 1H), 4.27 (q, *J* = 7 Hz, 2H), 2.45 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 190.3, 166.3, 143.7, 142.7, 135.7, 134.1, 133.6 (q, $^{3}J_{C\text{-}F}$ = 5.5 Hz), 130.6 (q, $^{2}J_{C\text{-}F}$ = 34.7 Hz), 130.1, 129.7, 129.2, 122.4 (q, $^{1}J_{C\text{-}F}$ = 269.8 Hz), 121.8, 60.7, 21.6, 14.2; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ* cm^{-1}** 2986, 2903, 1714, 1642, 1603, 1490, 1368, 1304, 1278, 1225, 1179, 1041, 971, 867, 654, 600, 532, 438, 419; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{16}F_3O_3^+$ $[M+H]^+$ 313.1046, found 313.1047.

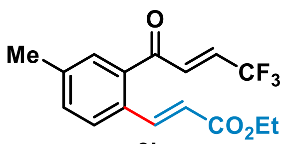
Diethyl (2*E*,4*E*)-hexa-2,4-dienedioate (2aa):



2aa

White liquid; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.31 (dd, *J* = 11.4, 3.1 Hz, 2H), 6.20 (dd, *J* = 11.4, 3.0 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 4H), 1.32 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 165.9, 140.8, 128.4, 60.8, 14.2; **IR** (**KBr**) ***υ* cm^{-1}** 3066, 2960, 2925, 2853, 1698, 1613, 1464, 1367, 1313, 1258, 1158, 1025, 862, 803, 694; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{18}H_{15}F_3NO$ $[M+H]^+$ 199.0965, found 199.0969.

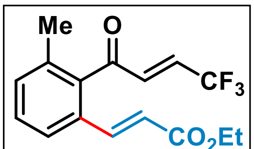
Ethyl (*E*)-3-(4-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ba):



3ba

44 mg (70%); white solid; mp = 60–62 °C; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.95 (d, *J* = 15.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.24 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 2.1 Hz, 1H), 6.70 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H) 4.27 (q, *J* = 7 Hz, 2H), 2.45 (s, 3H), 1.33 (t, *J* = 7.1, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 191.3, 166.3, 141.9, 140.7, 140.1, 137.0, 133.8 (q, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 133.4, 132.3, 130.8 (q, $^{2}J_{C\text{-}F}$ = 35.1 Hz), 129.7, 128.4, 128.2, 122.3 (q, $^{1}J_{C\text{-}F}$ = 268.6 Hz), 121.1, 60.6, 21.2, 14.2; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm^{-1}** 3476, 3415, 3071, 2983, 2928, 1703, 1638, 1318, 1299, 1188, 1175, 1034, 972, 634, 535; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{16}F_3O_3^+$ $[M+H]^+$ 313.1046, found 313.1055

Ethyl (*E*)-3-(3-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ca):

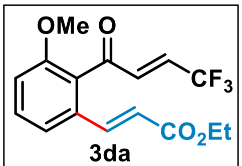


3ca

37 mg (60%); White solid; mp = 63–65 °C; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.53 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 15.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.92 (dq, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 1.8 Hz, 1H), 6.37 (d, *J* = 15.7, 1H), 6.35 (dq, $J_{H\text{-}H}$ = 16.2, $J_{H\text{-}F}$ = 6.25 Hz, 1H), 4.26 (q,

J = 7.1 Hz, 2H), 2.26 (s, 3H) 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 196.9, 166.0, 140.5, 138.2, 136.0 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 135.2, 132.3 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 132.1, 130.2, 124.6, 122.1 (q, $^1J_{C\text{-}F}$ = 269.1 Hz), 122.0, 60.7, 19.4, 14.2; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -65.2; **IR** (**KBr**) ***υ* cm^{-1}** 3407, 3069, 1709, 1664, 1464, 1367, 1317, 1262, 1231, 1190, 989, 664, 606; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{16}F_3O_3^+$ [M+H]$^+$ 313.1046, found 313.1052.

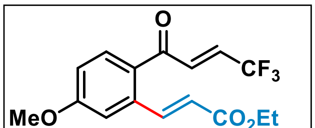
Ethyl (*E*)-3-(3-methoxy-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3da):



3da

40 mg (61%); Yellow semi-solid; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.56 (d, J = 15.9 Hz, 1H), 7.45 (t, J = 8.1 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.03 (dq, $J_{H\text{-}H}$ = 15.8, $J_{H\text{-}F}$ = 2.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.50 (dq, $J_{H\text{-}H}$ = 15.9, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.37 (d, J = 15.9 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 192.9, 166.1, 157.7, 140.6, 136.0 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 134.7, 132.0, 129.3 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 128.0, 123.6 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 122.1, 119.5, 112.3, 60.7, 55.9, 14.2; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -64.9; **IR** (**KBr**) ***υ* cm^{-1}** 3390, 2900, 1712, 1670, 1600, 1495, 1300, 1185, 1020, 965, 820, 605; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{16}F_3O_4$ [M+H]$^+$ 329.0995, found 329.0985.

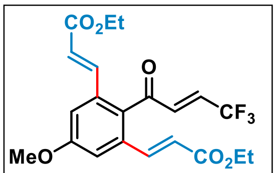
Ethyl (*E*)-3-(5-methoxy-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ea):



3ea

45 mg (69%); Off white solid; mp = 102–104 °C; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 8.13 (d, J = 15.9 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.35 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 2.1 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H), 7.00 (dd, J = 8.7, 2.6 Hz, 1H), 6.73 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.32 (d, J = 15.7 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 188.6, 166.2, 163.0, 143.3, 138.8, 133.3 (q, $^3J_{C\text{-}F}$ = 5.4 Hz); 132.3, 130.1 (q, $^2J_{C\text{-}F}$ = 34.7 Hz), 129.1, 122.5 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 121.9, 114.4, 114.1, 60.7, 55.7, 14.2; **^{19}F NMR** (**470 MHz, $CDCl_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ* cm^{-1}** 3410, 2924, 1710, 1679, 1633, 1594, 1305, 1199, 1028, 973, 821, 662; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{15}F_3NaO_4^+$ [M+Na]$^+$ 351.0815, found 351.0829.

Diethyl3,3'-(5-methoxy-2-((*E*)-4,4,4-trifluorobut-2-enoyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (3ea'):

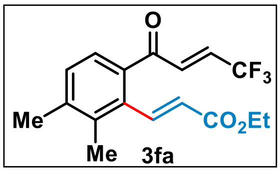


3ea'

20 mg (23%); Yellow solid; mp = 94–97 °C; **^{1}H NMR** (**500 MHz, $CDCl_3$**) ***δ*** 7.54 (d, J = 15.7 Hz, 2H), 7.14 (s, 2H), 6.91 (dq, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.40 (dq, $J_{H\text{-}H}$ = 15.9, $J_{H\text{-}F}$ = 6.4 Hz, 1H), 6.34 (d, J = 15.7 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 3.90 (s, 3H), 1.31 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (**125 MHz, $CDCl_3$**) ***δ*** 194.0, 165.6, 161.0, 140.3, 136.2 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 135.5, 131.5 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 131.2, 123.1, 122.1 (q, $^1J_{C\text{-}F}$ = 269.5 Hz), 113.7, 60.9, 55.6, 14.1;

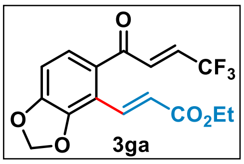
^{19}F NMR (**470 MHz, CDCl$_3$**) ***δ*** -65.2; **IR** (**KBr**) ***υ* cm^{-1}** 3478, 2989, 1705, 1635, 1368, 1301, 1250, 1136, 1043, 970, 864, 654, 624; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{21}H_{22}F_3O_6^+$ [M+H]$^+$ 427.1363, found 427.1355

Ethyl (*E*)-3-(2,3-dimethyl-6-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3fa):



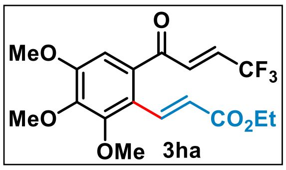
36 mg (55%); Light yellow semisolid; **^{1}H NMR** (**500 MHz, DMSO**) ***δ*** 7.98 (d, *J* = 15.9 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.65 (dq, J_{H-H} = 15.7, J_{H-F} = 2.2 Hz, 1H), 6.95 (dq, J_{H-H} = 15.7, J_{H-F} = 7.0 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, DMSO**) ***δ*** 190.8, 166.5, 143.3, 142.9, 139.4, 135.5 (q, $^3J_{C-F}$ = 5.4 Hz), 134.4, 132.5, 131.7, 129.7, 129.2 (q, $^2J_{C-F}$ = 33.5 Hz), 124.5 (q, $^1J_{C-F}$ = 268.6 Hz),120.1, 60.5, 19.9, 19.5, 14.6; **^{19}F NMR** (**470 MHz, DMSO**) ***δ*** -63.3; **IR** (**KBr**) ***υ* cm^{-1}** 2981, 2923, 2853, 1706, 1636, 1548, 1511, 1450, 1369, 1305, 1269, 1169, 1132, 1043, 972, 861, 773, 651, 614, 441; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{17}H_{18}F_3O_3$ [M+H]$^+$ 327.1203, found 327.1198.

Ethyl (*E*)-3-(5-((*E*)-4,4,4-trifluorobut-2-enoyl)benzo[d][1,3]dioxol-4-yl)acrylate (3ga):



42 mg (61%); Light yellow solid; mp = 98–101 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.91 (d, *J* = 16.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.23 (dq, J_{H-H} = 16.1, J_{H-F} =1.8Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H); 6.76-6.67 (m, 2H), 6.17 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 188.9, 166.7, 151.4, 147.9, 136.3, 133.9 (q, $^3J_{C-F}$ = 5.9 Hz), 131.3, 130.5 (q, $^2J_{C-F}$ = 35.1 Hz), 126.0, 124.7, 123.5 (q, $^1J_{C-F}$ = 268.6 Hz), 117.5, 108.0, 102.4, 60.6, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ* cm^{-1}** 3412, 2908, 1711, 1676, 1632, 1587, 1448, 1298, 1186, 1127, 1059,970, 626; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{14}F_3O_5$ [M+H]$^+$ 343.0788, found 343.0781.

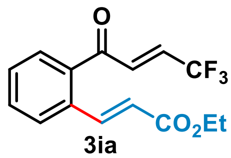
Ethyl (*E*)-3-(2,3,4-trimethoxy-6-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ha):



43 mg (55%); Yellow semi-solid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.82 (d, *J* = 16.0 Hz, 1H), 6.94 (dq, J_{H-H} = 15.7, J_{H-F} = 2.0 Hz, 1H), 6.88 (s, 1H), 6.65 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 191.6, 166.1, 154.2, 152.9, 145.3, 137.5, 134.7 (q, $^3J_{C-F}$ = 5.9 Hz), 134.4, 129.5 (q, $^2J_{C-F}$ = 35.1 Hz), 125.2, 123.4 (q, $^1J_{C-F}$ = 268.6 Hz), 122.0, 108.2, 61.1, 61.0, 60.6, 56.2, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**)

***υ* cm**$^{-1}$ 2924, 2853, 1717, 1630, 1582, 1464, 1340, 1304, 1177, 1133, 970, 849, 835, 702, 633; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{18}H_{20}F_3O_6^+$ [M+H]$^+$ 389.1206, found 389.1178.

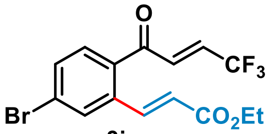
Ethyl (*E*)-3-(2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ia):



3ia

37 mg (62%); yellow semi-solid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.00 (d, *J* = 15.9 Hz, 1H), 7.70-7.67 (m, 2H), 7.61 (td, *J* = 7.6, 1.8 Hz, 1H), 7.53 (td, *J* = 7.6, 1.4 Hz, 1H), 7.27 (dq, J_{H-H} = 15.7, J_{H-F} = 2 Hz, 1H), 6.71 (dq, J_{H-H} = 15.9, J_{H-F} = 6.6 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 191.0, 166.1, 142.1, 140.7, 136.8, 135.2, 133.7 (q, $^3J_{C-F}$ = 5.5 Hz), 132.7, 131.5 (q, $^2J_{C-F}$ = 35.1 Hz), 129.5, 129.3, 128.3, 123.4 (q, $^1J_{C-F}$ = 268.6 Hz), 122.1, 60.7, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm**$^{-1}$ 3478, 2985, 2928, 1713, 1635, 1617, 1468, 1368, 1301, 1268, 1138, 1037, 760, 613; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{14}F_3O_3^+$ [M+H]$^+$ 299.0890, found 299.0894.

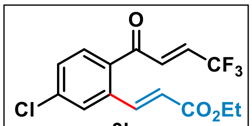
Ethyl (*E*)-3-(4-bromo-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ja):



3ja

30 mg (40%); white solid; mp = 64–66 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.93 (d, *J* = 15.8 Hz, 1H), 7.83 (d, *J* = 1.95 Hz, 1H), 7.67 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.24 (dq, J_{H-H} = 15.7, J_{H-F} = 2 Hz, 1H), 6.73 (dq, J_{H-H} = 15.7, J_{H-F} =6.5 Hz, 1H), 6.36 (d, *J* = 15.8, 1H), 4.3 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.9, 165.7, 140.7, 137.3, 135.3, 133.2 (q, $^3J_{C-F}$ = 5.9 Hz), 132.4, 131.5 (q, $^2J_{C-F}$ = 35.1 Hz), 131.4, 130.6, 127.7, 123.3, 123.2 (q, $^1J_{C-F}$ = 269.1 Hz), 60.9, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm**$^{-1}$ 3407, 2952, 1713, 1685, 1637, 1300, 1268, 1187, 1152, 971, 860, 639; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{13}F_3BrO_3$ [M+H]$^+$ 376.9995, found 376.9978.

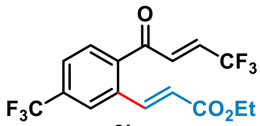
Ethyl (*E*)-3-(5-chloro-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ka):



3ka

23 mg (35%); white solid; mp = 67–69 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.93 (d, *J* = 15.9 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.48 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.22 (dq, J_{H-H} = 15.7, J_{H-F} = 2.0 Hz, 1H), 6.71 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.7, 165.8, 140.9, 139.2, 137.3, 134.9, 133.2 (q, $^3J_{C-F}$ = 5.4 Hz), 131.5 (q, $^3J_{C-F}$ = 35.1 Hz), 130.7, 129.5, 128.5, 123.3 (q, $^3J_{C-F}$ = 269.1 Hz), 123.2,60.9, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm**$^{-1}$ 3475, 2979, 1712, 1685, 1638, 1552, 1480, 1130, 1010, 969, 918, 831, 766, 644; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{13}F_3ClO_3$ [M+H]$^+$ 333.0500, found 333.0485.

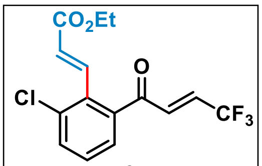
Ethyl (*E*)-3-(2-((*E*)-4,4,4-trifluorobut-2-enoyl)-5-(trifluoromethyl)phenyl)acrylate (3la):



3la

11 mg (15%); light yellow liquid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.95 (d, *J* = 15.4 Hz, 1H), 7.94-7.93 (m, 1H), 7.79-7.75 (m, 2H), 7.22 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 1.9 Hz, 1H), 6.72 (dq, $J_{H\text{-}H}$ = 15.9, $J_{H\text{-}F}$ = 6.4 Hz, 1H), 6.45 (d, *J* = 15.9, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.5, 165.6, 140.2, 139.6, 135.8, 134.2 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 133.2 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 132.1 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 129.5, 126.1 (q, $^4J_{C\text{-}F}$ = 3.6 Hz), 125.1 (q, $^4J_{C\text{-}F}$ = 3.6 Hz), 123.9, 124.1 ($q_{(Ar)}$, $^1J_{C\text{-}F}$ = 271.3 Hz), 123.1 ($q_{(\beta)}$, $^1J_{C\text{-}F}$ = 269.5 Hz), 61.0, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -63.3, -65.2; **IR** (**KBr**) ***υ* cm^{-1}** 3470, 2960, 1700, 1680, 1638, 1550, 14700, 1202, 1015, 960, 910, 825, 755, 645; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{13}F_6O_3$ $[M+H]^+$ 367.0763, found 367.0761.

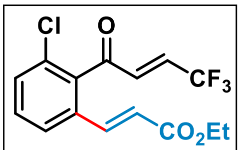
Ethyl (*E*)-3-(2-chloro-6-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ma):



3ma

18 mg (27%); Yellow liquid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.92 (d, *J* = 16.0 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 6.88 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 1.9 Hz, 1H), 6.60 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 5.96 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 191.5, 165.0, 139.8, 139.1, 135.0, 134.3 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 133.1, 130.1 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 130.0, 128.4, 127.5, 123.3 (q, $^1J_{C\text{-}F}$ = 269.0 Hz), 61.0, 14.1; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm^{-1}** 3472, 2970, 1710, 1682, 1638, 1550, 1481, 1132, 1100, 9500, 920, 825, 544, 430; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{13}F_3ClO_3$ $[M+H]^+$ 333.0500, found 333.0448.

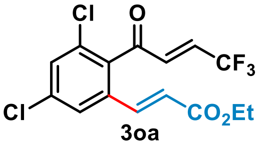
Ethyl (*E*)-3-(3-chloro-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3na):



3na

30 mg (45%); Yellow semi-solid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.62 (dd, *J* = 6.5, 2.4 Hz, 1H), 7.49-7.44 (m, 3H), 7.00 (dq, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 1.8 Hz, 1H), 6.46 (dq, $J_{H\text{-}H}$ = 16.7, $J_{H\text{-}F}$ = 6.4 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 192.6, 165.7, 139.0, 137.2, 135.1 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 135.1 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 134.5, 131.3, 130.9, 125.5, 123.3, 123.2 (q, $^1J_{C\text{-}F}$ = 269.0 Hz), 60.9, 14.2; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.2; **IR** (**KBr**) ***υ* cm^{-1}** 3060, 2978, 2930, 1706, 1679, 1641, 1453, 1369, 1316, 1268, 1243, 1194, 1144, 1043, 1000, 974, 869, 791, 759, 650, 597, 428; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{13}F_3ClO_3$ $[M+H]^+$ 333.0500, found 333.0498.

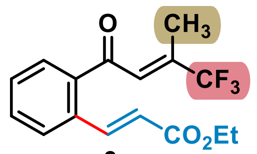
Ethyl (*E*)-3-(3,5-dichloro-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3oa):



3oa

19 mg (26%); White liquid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.58 (d, J = 1.8 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.37 (d, J = 15.9 Hz, 1H), 6.96 (dq, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 1.8 Hz, 1H), 6.45 (dq, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 6.4 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 191.6, 165.3, 137.8, 137.1, 135.9, 135.5, 134.8 (q, $^{3}J_{C\text{-}F}$ = 5.5 Hz), 132.2, 131.9 (q, $^{2}J_{C\text{-}F}$ = 35.6 Hz), 130.6, 125.7, 124.4, 123.1 (q, $^{1}J_{C\text{-}F}$ = 269.5 Hz), 61.1, 14.1; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.2; **IR** (**KBr**) ***u* cm^{-1}** 3072, 2984, 2932, 1719, 1686, 1643, 1579, 1547, 1368, 1313, 1267, 1178, 1140, 1037, 972, 861, 831, 650, 599, 505; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{12}F_3Cl_2O_3$ [M+H]$^+$ 367.0110, found 367.0102.

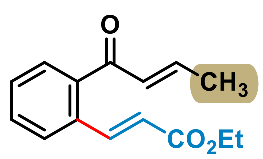
Ethyl (*E*)-3-(2-((*E*)-4,4,4-trifluoro-3-methylbut-2-enoyl)phenyl)acrylate (3pa):



3pa

38 mg (60%); Yellow liquid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.10 (d, J = 15.9 Hz, 1H), 7.70 (dd, J = 7.7, 1.4 Hz, 1H), 7.66 (dd, J = 7.9, 1.5 Hz, 1H), 7.59 (td, J = 7.6, 1.7 Hz, 1H), 7.52 (td, J = 7.6, 1.4 Hz, 1H), 7.06 (hept, J = 1.5 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 2.23 (d, J = 1.7 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 193.0, 166.2, 142.7, 140.8 (q, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 138.0, 135.2, 132.6, 129.5, 129.4, 128.4, 127.2 (q, $^{3}J_{C\text{-}F}$ = 5.5 Hz), 124.4 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 121.8, 60.7, 14.2, 12.8; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -70.9; **IR** (**KBr**) ***u* cm^{-1}** 3488, 3475, 3415, 2984, 2930, 1715, 1679, 1637, 1618, 1480, 1367, 1297, 1228, 1179, 1130, 1097, 1035, 971, 885, 765, 612, 484, 417; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{16}F_3O_3^+$ [M+H]$^+$ 313.1046, found 313.1028.

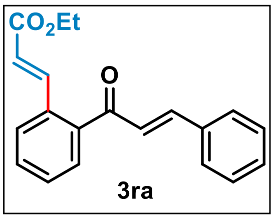
Ethyl (*E*)-3-(2-((*E*)-but-2-enoyl)phenyl)acrylate (3qa):



3qa

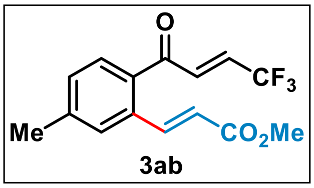
17 mg (35%); Yellow liquid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.85 (d, J = 16.0 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.48 – 7.40 (m, 3H), 6.75 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 6.9 Hz, 1H), 6.54 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 1.6 Hz, 1H), 6.37 (d, J = 15.9 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 1.96 (dd, J = 6.9, 1.5 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 195.5, 166.5, 148.2, 142.2, 139.8, 133.6, 132.2, 130.6, 129.3, 128.5, 127.3, 120.7, 60.6, 18.6, 14.3; **IR** (**KBr**) ***u* cm^{-1}** 3469, 3410, 3070, 2980, 2900, 1700, 1628, 1300, 1250, 1175, 1150, 1020, 970, 610; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{17}O_3^+$ [M+H]$^+$ 245.1172, found 245.1166.

Ethyl (*E*)-3-(2-cinnamoylphenyl)acrylate (3ra):



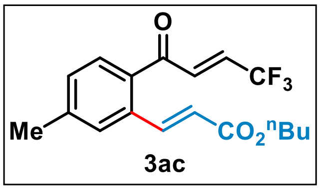
25 mg (40%); Yellow semi-solid; ^{1}**H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.94 (d, *J* = 15.9 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.52 – 7.45 (m, 3H), 7.43 – 7.38 (m, 3H), 7.16 (d, *J* = 16.2 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}**C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 195.0, 166.4, 146.8, 142.2, 139.8, 134.4, 133.9, 130.98, 130.92, 129.4, 129.0, 128.6, 128.5, 127.5, 126.3, 121.0, 60.5, 14.2; **IR** (**KBr**) ***υ*** **cm^{-1}** 3474, 3415, 2982, 1711, 1637, 1600, 1574, 1448, 1366, 1314, 1274, 1179, 1031, 978, 865, 764, 681, 569, 484. **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{20}H_{19}O_3^+$ [M+H]$^+$ 307.1329, found 307.1322.

Methyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ab):



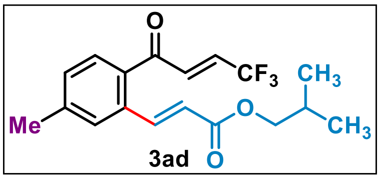
48 mg (80%); Off white solid; mp = 44–46 °C; ^{1}**H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.06 (d, *J* = 15.9 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.71 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.47 (s, 3H); ^{13}**C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.2, 166.7, 143.8, 143.0, 135.7, 134.0, 133.6 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 130.8 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 130.2, 129.7, 129.2, 123.5 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 121.2, 51.8, 21.6; ^{19}**F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ*** **cm^{-1}** 3475, 3414, 2958, 2925, 2853, 1718, 1641, 1490, 1434, 1171, 1305, 1279, 1171, 1125, 979, 890, 683, 652, 602, 579; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{15}H_{14}F_3O_3^+$ [M+H]$^+$ 299.0890, found 299.0896.

Butyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ac):



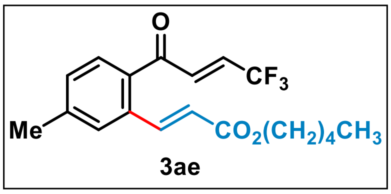
34 mg (50%); Light yellow semi-solid; ^{1}**H NMR** (**500 MHz, DMSO**) ***δ*** 8.05 (d, *J* = 15.9 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.33 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.31 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.72 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.47 (s, 3H), 1.73-1.68 (m, 2H), 1.49-1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}**C NMR** (**125 MHz, DMSO**) ***δ*** 190.3, 166.4, 143.7, 142.7, 135.7, 134.1, 133.6 (q, $^3J_{C\text{-}F}$ = 5.9 Hz), 130.8 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 130.2, 129.7, 129.2, 123.5 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 121.7, 64.6, 30.7, 21.6, 19.1, 13.7; ^{19}**F NMR** (**470 MHz, DMSO**) ***δ*** -65.0; **IR** (**KBr**) ***υ*** **cm^{-1}** 2959, 2926, 2854, 1716, 1686, 1641, 1603, 1490, 1463, 1303, 1278, 1224, 1175, 1138, 972, 891, 847, 833, 655, 601, 438; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{18}H_{20}F_3O_3^+$ [M+H]$^+$ 341.1359, found 341.1351.

Isobutyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ad):



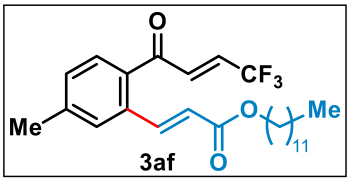
54 mg (79%); White solid; mp = 59–61 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.06 (d, *J* = 15.9 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.29 (dq, J_{H-H} = 15.7, J_{H-F} = 2.0 Hz, 1H), 6.71 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.02 (d, *J* = 6.7 Hz, 2H), 2.47 (s, 3H), 2.09-1.98 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.3, 166.3, 143.7, 142.7, 135.7, 134.1, 133.6 (q, $^{3}J_{C-F}$ = 5.4 Hz), 130.7 (q, $^{2}J_{C-F}$ = 34.7 Hz), 130.2, 129.7, 129.1, 123.5 (q, $^{1}J_{C-F}$ = 269.1 Hz), 121.7, 70.8, 27.8, 21.6, 19.1; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm^{-1}** 3412, 3085, 2965, 1707, 1685, 1639, 1305, 1269, 1227, 1132, 1031, 984, 816, 655; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{18}H_{20}F_3O_3^+$ [M+H]$^+$ 341.1359, found 341.1351.

Pentyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ae):



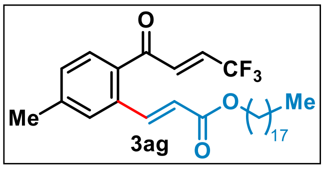
37 mg (52%); Yellow semi-solid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.03 (d, *J* = 15.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.27 (dq, J_{H-H} = 15.7, J_{H-F} = 2.0 Hz, 1H), 6.69 (dq, J_{H-H} = 15.7, J_{H-F} = 6.5 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 3H), 2.45 (s, 3H), 1.73 – 1.68 (m, 1H), 1.39 – 1.36 (m, 4H), 0.93 – 0.91 (m, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.3, 166.3, 143.6, 142.6, 135.7, 134.1, 133.7 (q, $^{3}J_{C-F}$ = 5.4 Hz), 130.6 (q, $^{2}J_{C-F}$ = 35.1 Hz), 130.1, 129.6, 129.1, 123.5 (q, $^{1}J_{C-F}$ = 268.6 Hz), 121.8, 64.8, 28.3, 28.0, 22.3, 21.5, 13.9; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ* cm^{-1}** 2957, 2933, 2873, 1715, 1686, 1641, 1603, 1490, 1303, 1278, 1224, 1175, 1137, 1048, 971, 864, 825, 654, 600, 439; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{19}H_{22}F_3O_3^+$ [M+H]$^+$ 354.1443, found 354.1435.

Dodecyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3af):



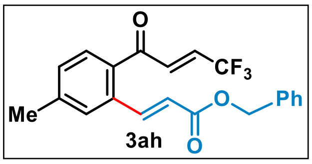
54 mg (60%); White solid; mp = 47–49 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.03 (d, *J* = 15.9 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.31 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.30 (dq, J_{H-H} = 15.7, J_{H-F} = 2.0 Hz, 1H), 6.71 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 1.72 – 1.66 (m, 2H), 1.41-1.35 (m, 2H), 1.31-1.25 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.2, 166.4, 143.7, 142.7, 135.7, 134.1, 133.6 (q, $^{3}J_{C-F}$ = 5.4 Hz), 130.8 (q, $^{2}J_{C-F}$ = 35.1 Hz), 130.1, 129.7, 129.2, 123.5 (q, $^{1}J_{C-F}$ = 269.0 Hz), 121.7, 64.9, 31.9, 29.67, 29.65, 29.60, 29.5, 29.37, 29.30, 28.6, 25.9, 22.7, 21.6, 14.1; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ* cm^{-1}** 3474, 2916, 2849, 1716, 1684, 1650, 1631, 1313, 1281, 1119, 972, 817, 780, 720, 579; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{26}H_{36}F_3O_3^+$ [M+H]$^+$ 453.2611, found 453.2602.

Octadecyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ag):



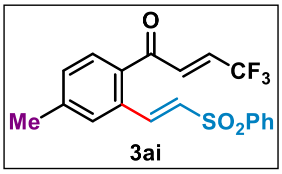
48 mg (45%); White solid; mp = 65–67 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.02 (d, *J* = 15.9 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.31 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.27 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 1.9 Hz, 1H), 6.67 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H); 4.20 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 1.70 (p, *J* = 6.8 Hz, 2H), 1.40 – 1.24 (m, 30H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.3, 166.4, 143.7, 142.7, 135.7, 134.1, 133.6 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 130.5 (q, $^2J_{C\text{-}F}$ = 34.7 Hz), 130.1, 129.7, 129.1, 123.5 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 121.8, 64.9, 31.9, 29.71, 29.67, 29.60, 29.55, 29.37, 29.30, 28.68, 25.9, 22.7, 21.6, 14.1; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ*** **cm^{-1}** 3414, 2917, 1716, 1684, 1632, 1632, 1617, 1312, 1281, 972, 868, 817, 720, 655; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{32}H_{48}F_3O_3^+$ [M+H]$^+$ 537.3550, found 537.3542.

Benzyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ah):



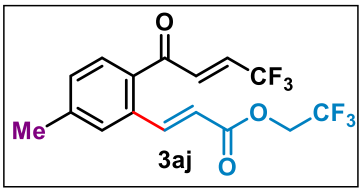
57 mg (76%); Light yellow solid; mp = 59–62 °C; **^{1}H NMR** (**500 MHz, DMSO**) ***δ*** 8.05 (d, *J* = 15.9 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.61 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 2.1 Hz, 1H), 7.43-7.34 (m, 6H), 6.92 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 7.0 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 5.23 (s, 2H), 2.4 (s, 3H); **^{13}C NMR** (**125 MHz, DMSO**) ***δ*** 190.8, 166.2, 144.12, 144.10, 136.6, 135.6 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 135.0, 134.1, 131.1, 130.9, 129.5, 129.0 (q, $^2J_{C\text{-}F}$ = 33.8 Hz), 128.9, 128.6, 128.5, 124.4 (q, $^1J_{C\text{-}F}$ = 268.6 Hz), 120.6, 66.1, 21.4; **^{19}F NMR** (**470 MHz, DMSO**) ***δ*** -63.3; **IR** (**KBr**) ***υ*** **cm^{-1}** 3477, 3068, 2925, 1707, 1784, 1379, 1301, 1271, 1224, 1138, 1002, 878, 654, 614; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{21}H_{18}F_3O_3^+$ [M+H]$^+$ 375.1203, found 375.1213.

(*E*)-4,4,4-Trifluoro-1-(4-methyl-2-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)but-2-en-1-one (3ai):



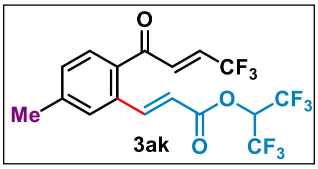
38 mg (50%); Light yellow solid; mp = 112–114 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.10 (d, *J* = 15.4 Hz, 1H), 8.04 – 8.03 (m, 1H), 8.03 – 8.02 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.59 – 7.56 (m, 2H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.34-7.30 (m, 1H), 6.78-6.71 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.4, 144.3, 142.1, 132.8 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 131.1 (q, $^2J_{C\text{-}F}$ = 35.1 Hz), 130.9, 130.1, 129.9, 129.7, 129.3, 127.8, 123.4 (q, $^1J_{C\text{-}F}$ = 269.0 Hz), 21.5; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ*** **cm^{-1}** 3476, 3053, 2924, 1682, 1639, 1615, 1086, 983, 967, 909, 715, 622, 591, 544; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{19}H_{16}F_3O_3S^+$ [M+H]$^+$ 381.0767, found 381.0760.

2,2,2-Trifluoroethyl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3aj):



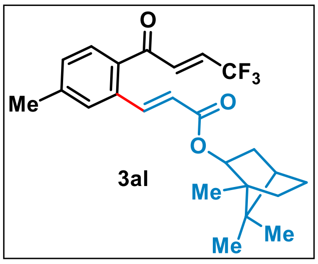
44 mg (60%); White solid; mp = 62-63 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.17 (d, *J* = 15.9 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.30 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 1.9 Hz, 1H), 6.71 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 4.60 (q, *J* = 8.5 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.9, 164.5, 145.6, 144.0, 135.3, 134.1, 133.2 (q, $^{3}J_{C\text{-}F}$ = 5.9 Hz), 131.0 (q, $^{2}J_{C\text{-}F}$ = 35.1 Hz), 130.7, 129.8, 129.3, 124.1 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 268.6 Hz), 119.1, 60.6 (q, $^{2}J_{C\text{-}F}$ = 36.1 Hz), 21.6; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1, -73.7; **IR** (**KBr**) ***υ* cm^{-1}** 3412, 2963, 1722, 1686, 1642, 1307, 1263, 1225, 1179, 1158, 801, 673, 650; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{13}F_6O_3^+$ [M+H]$^+$ 367.0763, found 367.0760.

1,1,1,3,3,3-hexafluoropropan-2-yl(*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3ak):



66 mg (76%); Off white solid; mp = 111–113 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.32 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.41 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.34 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.75 (dq, $J_{H\text{-}H}$ = 15.6, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 5.93 (hept, *J* = 6.1 Hz, 1H), 2.50 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.7, 162.8, 148.0, 144.1, 134.8, 134.2, 133.1 (q, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 131.2 (q, $^{2}J_{C\text{-}F}$ = 35.1 Hz), 131.1, 129.9, 129.4, 123.9 (q, $^{1}J_{C\text{-}F}$ = 282.7 Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 268.6 Hz), 117.3, 66.6 (q, $^{2}J_{C\text{-}F}$ = 34.7 Hz), 21.6; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.2, -73.2; **IR** (**KBr**) ***υ* cm^{-1}** 3551, 2982, 1745, 1685, 1632, 1364, 1278, 1231, 1201, 1110, 1084, 909, 689, 598; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{17}H_{12}F_9O_3$ [M+H]$^+$ 435.0637, found 435.0630.

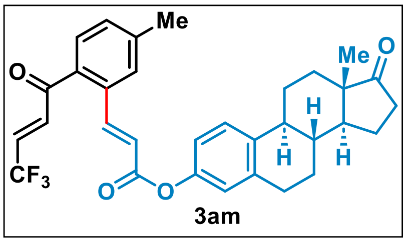
(1S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3al):



34 mg (40%); White solid; mp = 148–151 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.01 (d, *J* = 15.9 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.32 (dd, *J* = 7.9, 2.4 Hz, 1H), 6.69 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.69 (dq, $J_{H\text{-}H}$ = 15.7, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 4.82 (dd, *J* = 7.4, 4.2 Hz, 1H), 2.47 (s, 3H), 1.89-1.86 (m, 1H), 1.80-1.78 (m, 1H), 1.75-1.71 (m, 1H), 1.63-1.57 (m, 2H), 1.25-1.19 (m, 1H), 1.16-1.11 (m, 1H), 1.07 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.4, 165.8, 143.6, 142.3, 135.6, 134.1, 133.7 (q, $^{3}J_{C\text{-}F}$ = 5.4 Hz),

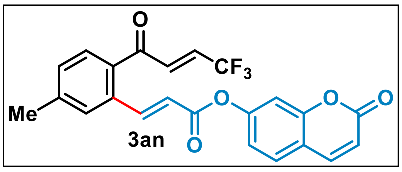
130.7 (q, $^{2}J_{C-F}$ = 35.1 Hz), 130.1, 129.6, 129.0, 123.5 (q, $^{1}J_{C-F}$ = 268.6 Hz), 121.3, 81.3, 48.9, 47.0, 45.0, 38.8, 33.7, 27.0, 21.6, 20.1, 19.9, 11.5; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.1; **IR** (**KBr**) ***υ*** **cm^{-1}** 3478, 2955, 2874, 1703, 1608, 1475, 1455, 1371, 1318, 1244, 1155, 1051, 1022, 962, 625; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{24}H_{28}F_3O_3$ [M+H]$^+$ 421.1985, found 421.1980.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-*6H* cyclopenta[*a*]phenanthren-3-yl(*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)phenyl)acrylate (3am):



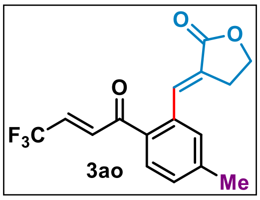
37 mg (35%); White solid; mp = 118–122 °C; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 8.22 (d, *J* = 15.9 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.35 (dd, *J* = 7.7, 2.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.71 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 2.93-2.91 (m, 2H), 2.54-2.50 (m, 1H), 2.47 (s, 3H), 2.43-2.40 (m, 1H), 2.35-2.27 (m, 1H), 2.18-2.11 (m, 1H), 2.09-2.01 (m, 2H), 1.98-1.96 (m, 1H), 1.67-1.58 (m, 3H), 1.54-1.42 (m, 4H), 0.9 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 190.1, 165.0, 148.6, 144.6, 143.9, 138.0, 137.4, 135.5, 134.1, 133.5 (q, $^{3}J_{C-F}$ = 5.9 Hz), 130.9 (q, $^{2}J_{C-F}$ = 35.1 Hz), 130.5, 129.8, 129.4, 126.4, 123.5 (q, $^{1}J_{C-F}$ = 269.1 Hz), 121.6, 120.8, 118.8, 50.4, 47.9, 44.1, 38.0, 35.8, 31.5, 29.4, 26.3, 25.7, 21.69, 21.61, 13.8; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ*** **cm^{-1}** 3413, 2926, 1738, 1686, 1637, 1493, 1308, 1278, 1223, 1138, 970, 656; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{32}H_{32}F_3O_3^+$ [M+H]$^+$ 537.2247, found 537.2240.

2-Oxo-2H-chromen-7-yl(*E*)-3-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2 enoyl)phenyl)acrylate (3an):



38 mg (44%); Light yellow solid; mp = 159–161 °C; **^{1}H NMR** (**500 MHz, DMSO**) ***δ*** 8.23 (d, *J* = 15.9 Hz, 1H), 8.08 (d, *J* = 9.6 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.63 (dq, J_{H-H} = 15.7, J_{H-F} = 2.1 Hz, 1H), 7.46 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.93 (dq, J_{H-H} = 15.7, J_{H-F} = 6.8 Hz, 1H), 6.81 (d, *J* = 15.8 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (**125 MHz, DMSO**) ***δ*** 195.4, 169.4, 164.9, 159.3, 157.9, 151.1, 149.04, 149.02, 140.2 (q, $^{3}J_{C-F}$ = 5.9 Hz), 139.5, 139.0, 136.1, 135.9, 134.6, 134.4, 134.1 (q, $^{2}J_{C-F}$ = 33.8 Hz), 129.2 (q, $^{1}J_{C-F}$ = 269.1 Hz), 124.1, 123.8, 121.9, 120.8, 115.3, 26.2; **^{19}F NMR** (**470 MHz, DMSO**) ***δ*** -65.0; **IR** (**KBr**) ***υ*** **cm^{-1}** 3467, 3066, 2924, 1731, 1614, 1561, 1491, 1400, 1327, 1306, 1283, 1232, 1133, 991, 877, 843, 704, 654, 601, 459, 444; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{24}H_{19}F_3O_5^+$ [M+H]$^+$ 429.0944, found 429.0942.

3-((*E*)-5-Methyl-2-((*E*)-4,4,4-trifluorobut-2-enoyl)benzylidene)dihydrofuran-2(*3H*)-one (3ao):



32 mg (52%); Yellow semi-solid; **^{1}H NMR** (**500 MHz, CDCl$_3$**) ***δ*** 7.81 (t, *J* = 3.0 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 9.7, 2.1 Hz, 2H), 7.30 (dq, J_{H-H} = 15.6, J_{H-F} = 2 Hz, 1H), 6.70 (dq, J_{H-H} = 15.7, J_{H-F} = 6.6 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 3.12 (td, *J* = 7.2, 3.1 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR** (**125 MHz, CDCl$_3$**) ***δ*** 189.9, 171.5, 143.5, 135.5, 135.2, 134.5, 133.2 (q, $^3J_{C-F}$ = 5.4 Hz), 131.0 (q, $^2J_{C-F}$ = 35.1 Hz), 130.1, 129.9, 129.7, 126.2, 123.4 (q, $^1J_{C-F}$ = 268.6 Hz), 65.6, 27.1, 21.7; **^{19}F NMR** (**470 MHz, CDCl$_3$**) ***δ*** -65.0; **IR** (**KBr**) ***υ* cm^{-1}** 3443, 2988, 1743, 1682, 1648, 1308, 1195, 1126, 1050, 962, 893, 731, 662, 590; **HRMS** (**Q-TOF**, **ESI**) calcd for $C_{16}H_{14}F_3O_3^+$ [M+H]$^+$ 311.0890, found 311.0874.

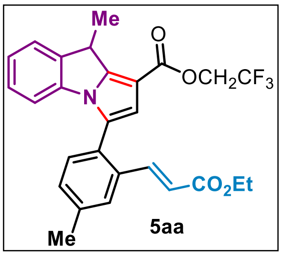
5. Procedure for Scale-Up (3aa):

To an oven dried reaction tube equipped with magnetic stirring bar, added $[IrCp^*Cl_2]_2$ (46.8 mg, 2.5 mol%), **1a** (500 mg, 2.33 mmol, 1 equiv), **2a** (467 mg, 4.66 mmol, 2 equiv), Ag_2CO_3 (642 mg, 2.33 mmol, 1 equiv), $AgSbF_6$ (80 mg, 10 mol%), HFIP (10 mL) and the mixture was stirred at 100 °C for 24 h. After reaction completion (monitored by Thin Layer Chromatography), the reaction mixture was passed through the celite pad and then purified by silica gel column chromatography (230-400 mesh) in Hexane/EtOAc (19:1) to get the desired olefinated product in 65% (477 mg) yield (**3aa**).

6. Procedure for synthetic diversification:

6.1. Synthetic procedure for 2,2,2-trifluoroethyl (*E*)-3-(2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-9-methyl-*9H*-pyrrolo[1,2-*a*]indole-1-carboxylate (5aa):

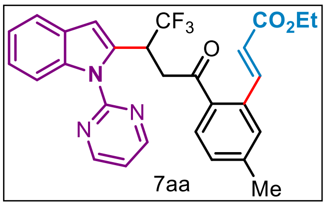
To the oven dried reaction tube with magnetic stir bar, 3-methylindole (**4**), (26 mg, 0.2 mmol), olefinated β-CF_3-enone (**3aa**), (62.5 mg, 0.2 mmol), PTSA (3.5 mg, 10 mol%), followed by addition of 0.5 mL Trifluoroethanol (TFE). The reaction mixture was allowed to stir at 100 °C for 2 h. The completion of the reaction was monitored by TLC. The reaction mixture was diluted with EtOAc (3 mL) and concentrated under vacuum. The residue was purified using silica gel column chromatography (5% EtOAc/Hexane) to afford compound **5aa** in 40%. The compound is a mixture of diastereomers (atropisomers) having dr 1:1.



38 mg (40%); Light yellow semi-solid; **^{1}H NMR (500 MHz, $CDCl_3$) *δ*** 7.63 (d, *J* = 16 Hz, 1H), 7.59 (d, *J* = 16 Hz, 1H, *diastereomeric*),7.61-7.60 (m, 1H), 7.40-7.33 (m, 2H), 7.28-7.26 (m, 1H), 7.10 (t, *J* = 7.8, Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.65 (s, 1H, *diastereomeric*), 6.51 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H, *diastereomeric*), 6.33 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H, diastereomeric), 4.77-4.64 (m, 2H), 4.35-4.28 (m, 1H), 4.18-4.09 (m, 2H), 2.50 (s, 3H), 1.71 (d, *J* = 7.3 Hz, 3H), 1.25-1.19 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) *δ*** 166.6, 162.6, 142.2, 142.1, 140.9, 139.4, 139.2, 134.5, 131.7, 130.7, 129.2, 129.1, 127.5, 127.2, 125.3, 124.9, 124.8, 124.5, 119.8, 119.7, 116.2, 115.8, 111.94, 111.91, 107.5, 60.4, 60.3 (diastereomeric), 60.1 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 37.35, 37.31 (diastereomeric), 21.4, 17.5, 17.2, 14.1; **^{19}F NMR (470 MHz, $CDCl_3$) *δ*** -73.42, -73.46 (diastereomeric); **IR (KBr) *υ* cm^{-1}** 3475, 3415, 2933, 1721, 1637, 1617, 1571, 1469, 1313, 1278, 1167, 979, 839, 771, 750, 623, 481; **HRMS (Q-TOF, ESI)** calcd for $C_{27}H_{25}F_3NO_4$ $[M+H]^+$ 484.1731, found 484.1722

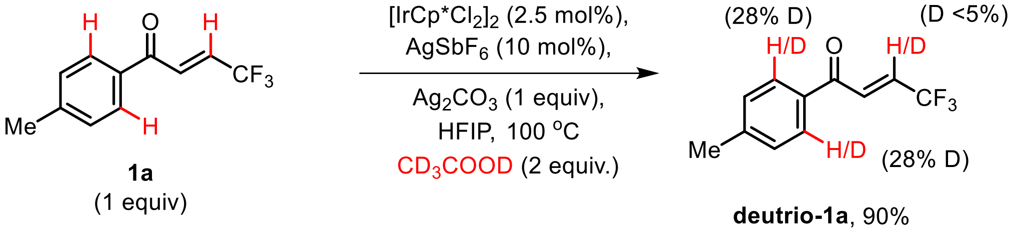
6.2. Synthetic procedure for Ethyl(*E*)-3-(5-methyl-2-(4,4,4-trifluoro-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)butanoyl)phenyl)acrylate (7aa):

To an oven-dried sealed tube with 1-(Pyrimidin-2-yl)-1*H*-indole (**6**) (39 mg, 0.2 mmol, 100 mol %), olefinated β-CF_3-enone (**3aa**) (62.5 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (1.2 mg, 0.002 mmol, 1 mol %) and $AgSbF_6$ (2.7 mg, 0.008 mmol, 4 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 70 °C for 24 h. After cooling at room temperature, the reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO_2: *n*-hexanes/EtOAc = 10:1) to provide **7aa** in 30% yield.



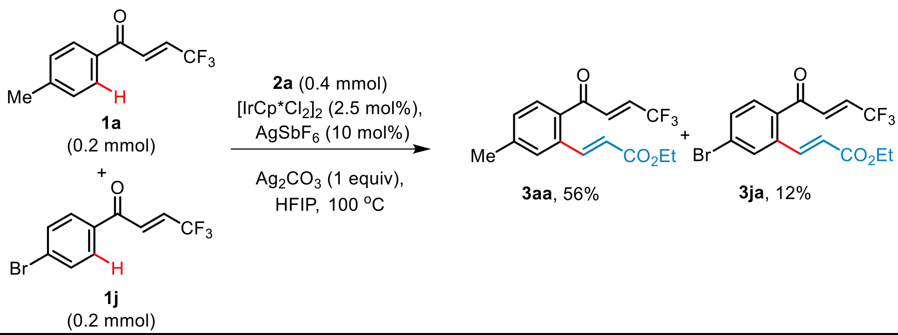
30 mg (30%); Light yellow semi-solid; **^{1}H NMR (500 MHz, DMSO-d6) *δ*** 8.98 (d, *J* = 4.9 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.59 (dd, *J* = 7.8, 2.1 Hz, 2H), 7.51 (t, *J* = 4.8 Hz, 1H), 7.38 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.26-7.23 (m, 1H), 7.19-7.16 (m, 1H), 7.04 (s, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.89 (td, *J* = 8.9, 5.0 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 4.02 (dd, *J* = 17.9, 9.2 Hz, 1H), 3.81 (dd, *J* = 17.9, 5.2 Hz, 1H), 2.37 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, DMSO-d6) *δ*** 198.9, 166.3, 159.4, 157.6, 143.8, 143.2, 136.9, 134.9. 134.3, 134.0, 130.8, 130.1, 129.3, 128.2, 124.0, 122.4, 120.9, 120.4, 119.0, 114.6, 107.9, 60.4, 21.3, 14.5; **^{19}F NMR (470 MHz, DMSO-d6) *δ*** -68.1; **IR (KBr) *υ* cm^{-1}** 3550, 3475, 3415, 1713, 1636, 1617, 1565, 1454, 1425, 1314, 1278, 1228, 1158, 967, 748, 673, 623, 484; **HRMS (Q-TOF, ESI)** calcd for $C_{28}H_{25}F_3N_3O_3^+$ $[M+H]^+$ 508.1843, found 508.1840.

7. Mechanistic studies: H/D exchange Experiment



To an oven-dried sealed tube with (*E*)-4,4,4-Trifluoro-1-(4-methylphenyl)but-2-en-1-one (**1a**) (43 mg, 0.2 mmol, 100 mol %), [IrCp*Cl$_2$]$_2$ (4.0 mg, 0.005 mmol, 2.5 mol %), AgSbF$_6$ (6.9 mg, 0.02 mmol, 10 mol %), Ag$_2$CO$_3$ (55.1 mg, 0.2 mmol, 100 mol %) and acetic acid-d4 (25 mg, 0.4mmol) was added in HFIP (1 mL). The reaction mixture was allowed to stir at 100 ºC for 24 h. After cooling at room temperature, the reaction mixture was evaporated and the residue was purified by column chromatography on silica gel (230-400 mesh) (eluent; hexane/EtOAc = 20:1) to provide desired *deuterio*-**1a** in 90 % yield with 28% incorporation of D at both ortho-position of aryl ring. .

7.1 Mechanistic studies: Intermolecular Competitive Experiment



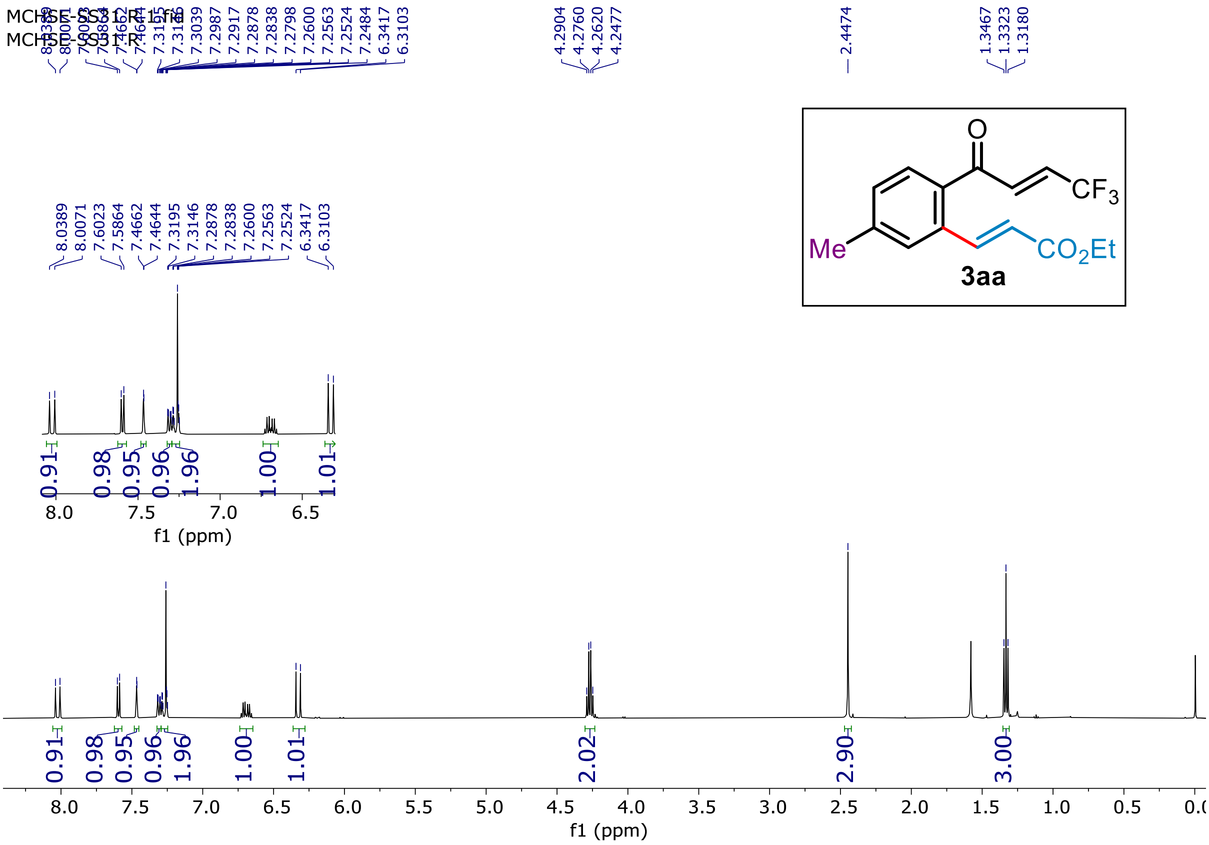
To an oven dried reaction tube equipped with magnetic stirring bar, was added [IrCp*Cl$_2$]$_2$ (4.0 mg, 2.5 mol%),(*E*)-4,4,4-Trifluoro-1-(4-methylphenyl)but-2-en-1-one **(1a)** (43 mg, 0.2 mmol, 1 equiv), (*E*)-4,4,4-Trifluoro-1-(4-bromophenyl)but-2-en-1-one (56 mg, 0.2 mmol, 1 equiv), AgSbF$_6$ (6.9 mg, 0.02 mmol, 10 mol %), Ag$_2$CO$_3$ (55.1 mg, 0.2 mmol, 100 mol %) and ethylacrylate (**2a**) (40 mg, 0.4 mmol, 200 mol%) in HFIP (1 mL). The reaction mixture was stirred at 100 °C for 24 h. After reaction completion (monitored by Thin Layer Chromatography), the reaction mixture was passed through the celite pad and then purified by silica gel column chromatography (230-400 mesh) in Hexane/EtOAc (20:1) to get the olefinated products **3aa** and **3ja** in 56% and 12% yield, respectively.

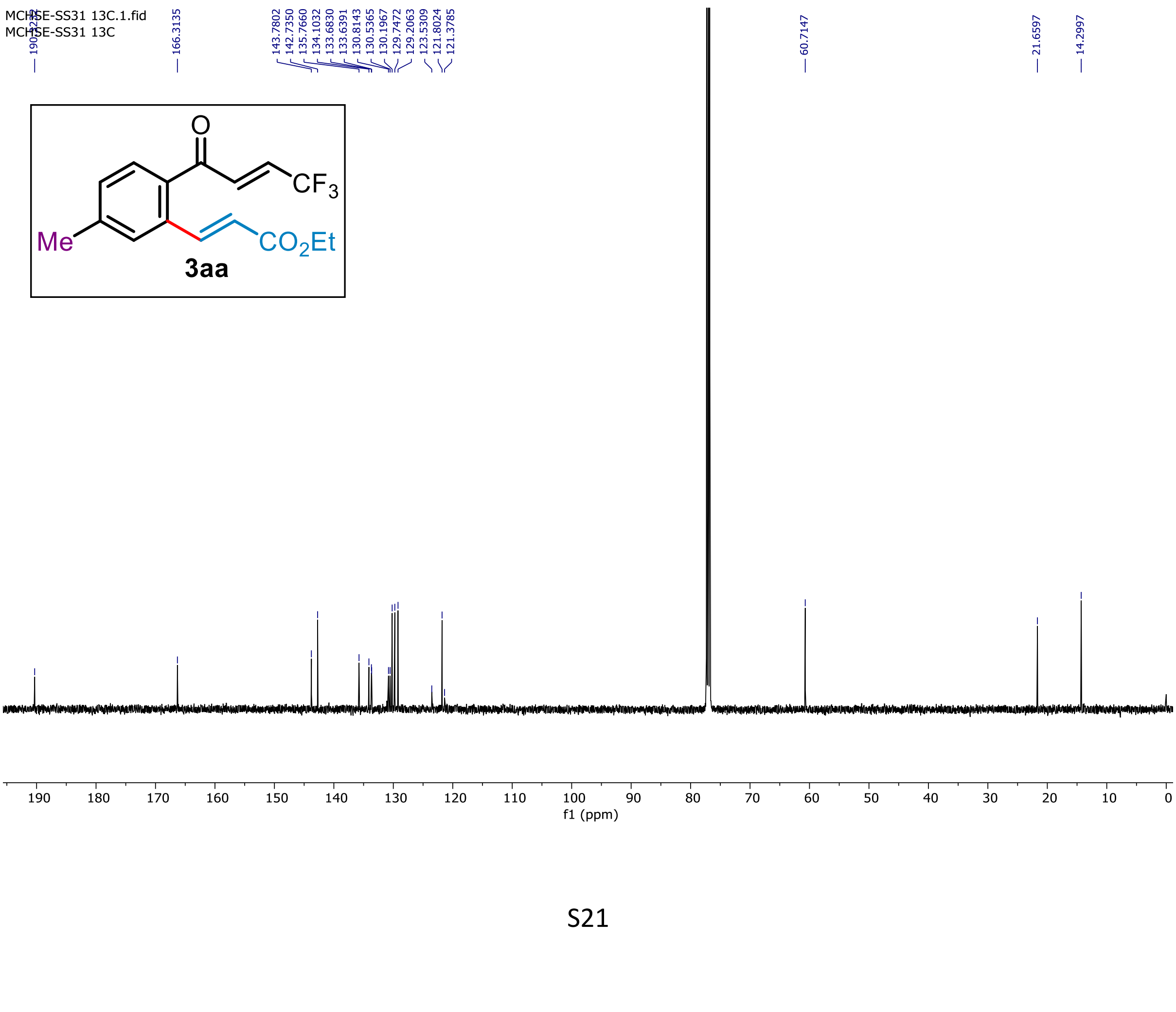
8. References

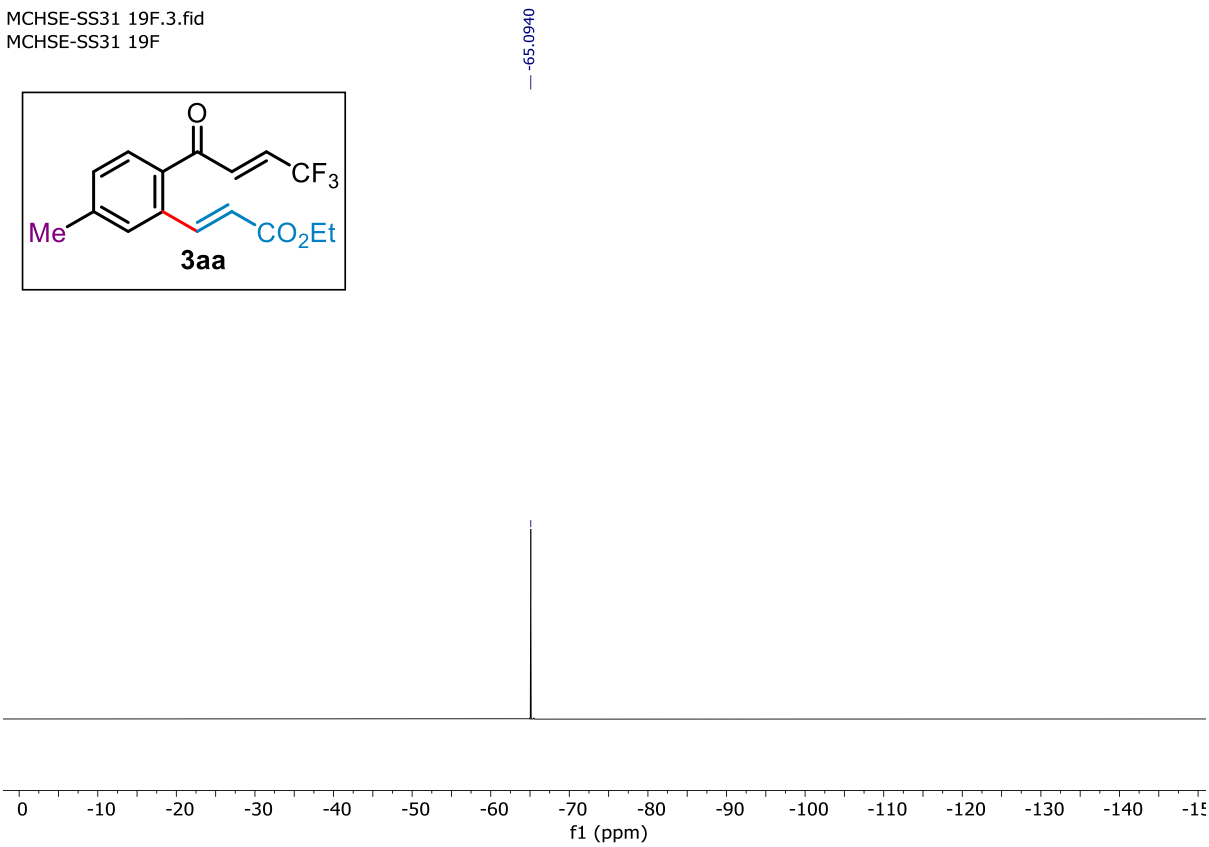
1**.** (a) Q. Jiang, T. Guo, K. Wu and Z. Yu, *Chem. Commun*., 2016, **52**, 2913-2915; (b) B. Chaudhary, P. Auti, S.D. Shinde, P.A. Yakkala, D. Giri and S. Sharma, *Org. Lett*., 2019, **21**, 2763-2767.

2. (a) X.Q. Chu, L.W. Sun, Y.L. Chen, J.W. Chen, X. Ying, M. Ma and Z.L. Shen, *Green Chem.*, 2022, **24**, 2777-2782; (b) Q. Sha, H. Liu, and Y. Wei, *Eur. J. Org. Chem.* 2014*,* **34**, 7707-7715.

9. NMR Spectra of all products:



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MCHSE-SS31 19F
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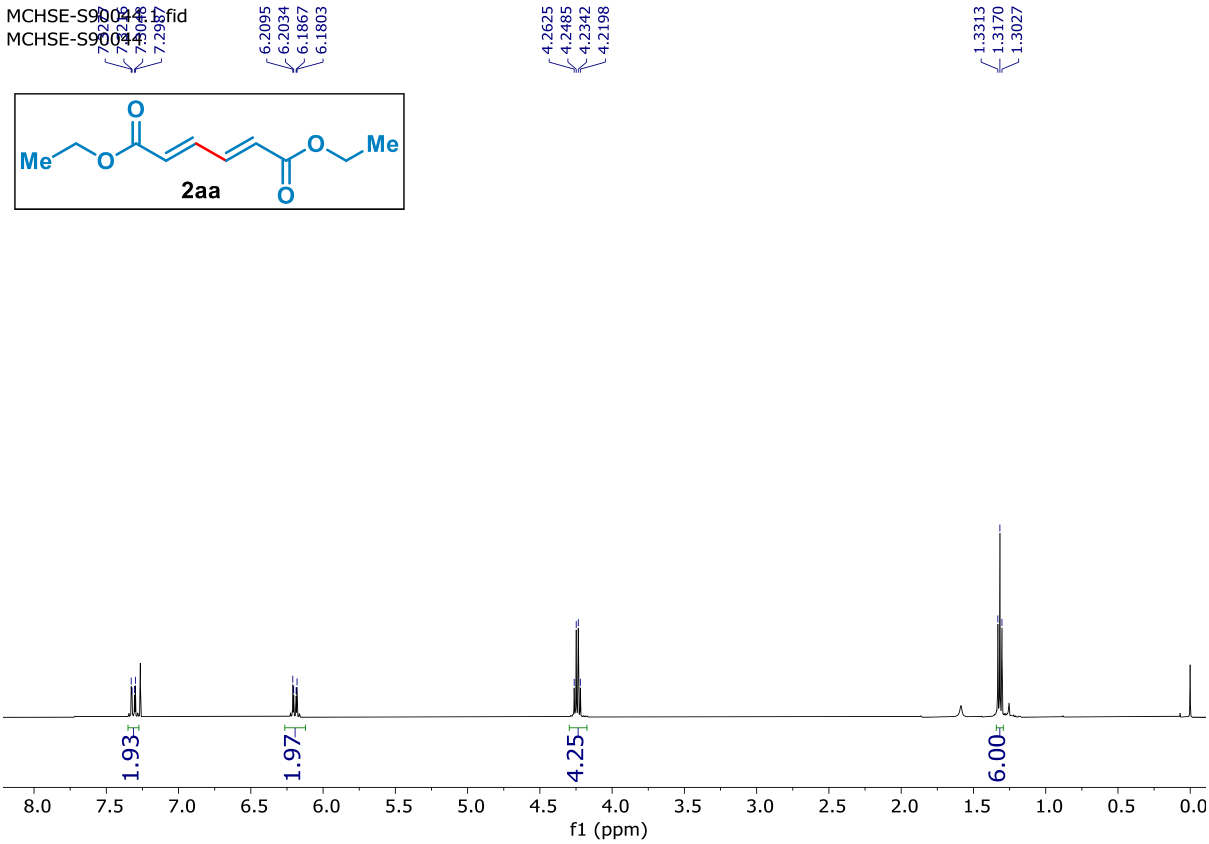
CF3
Me
CO2Et
3aa
f1 (ppm)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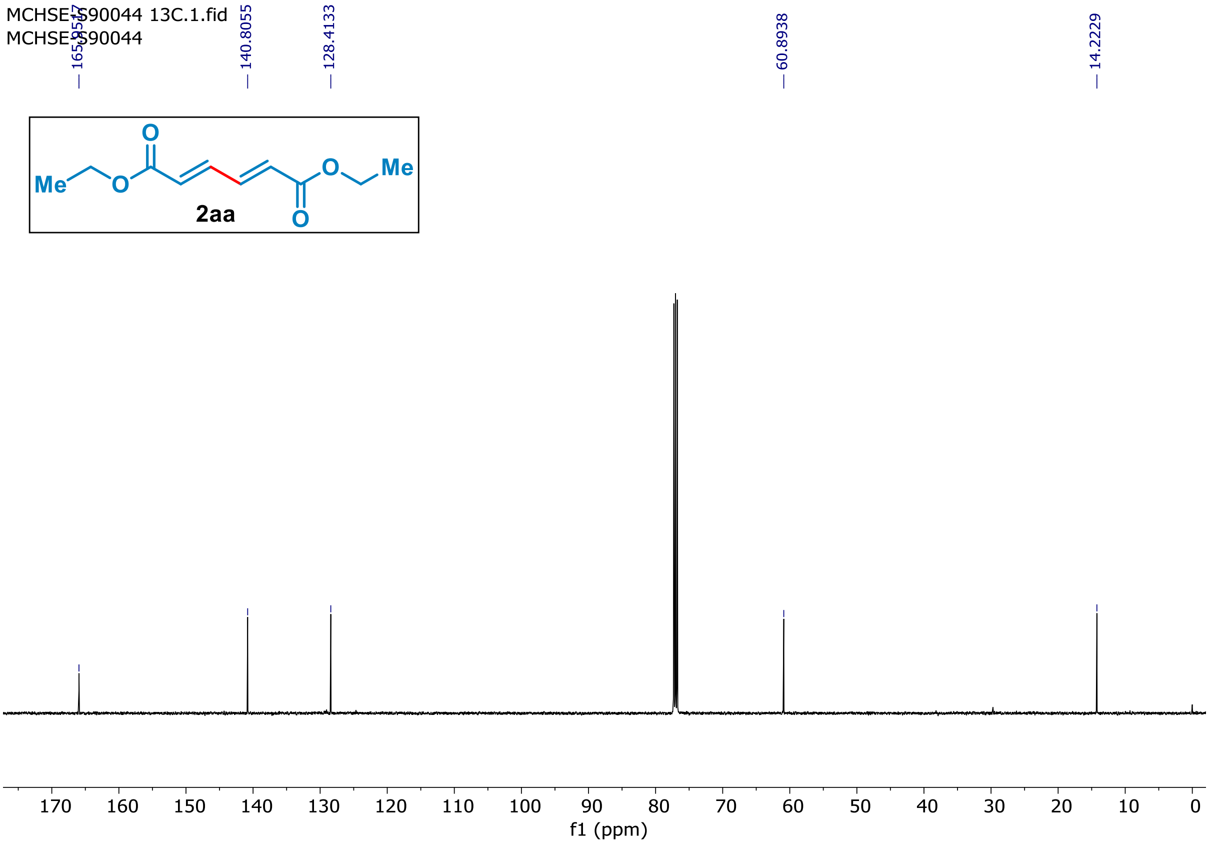
Me
O
Me
2aa
1.93
1.97
4.25
6.00
f1 (ppm)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O
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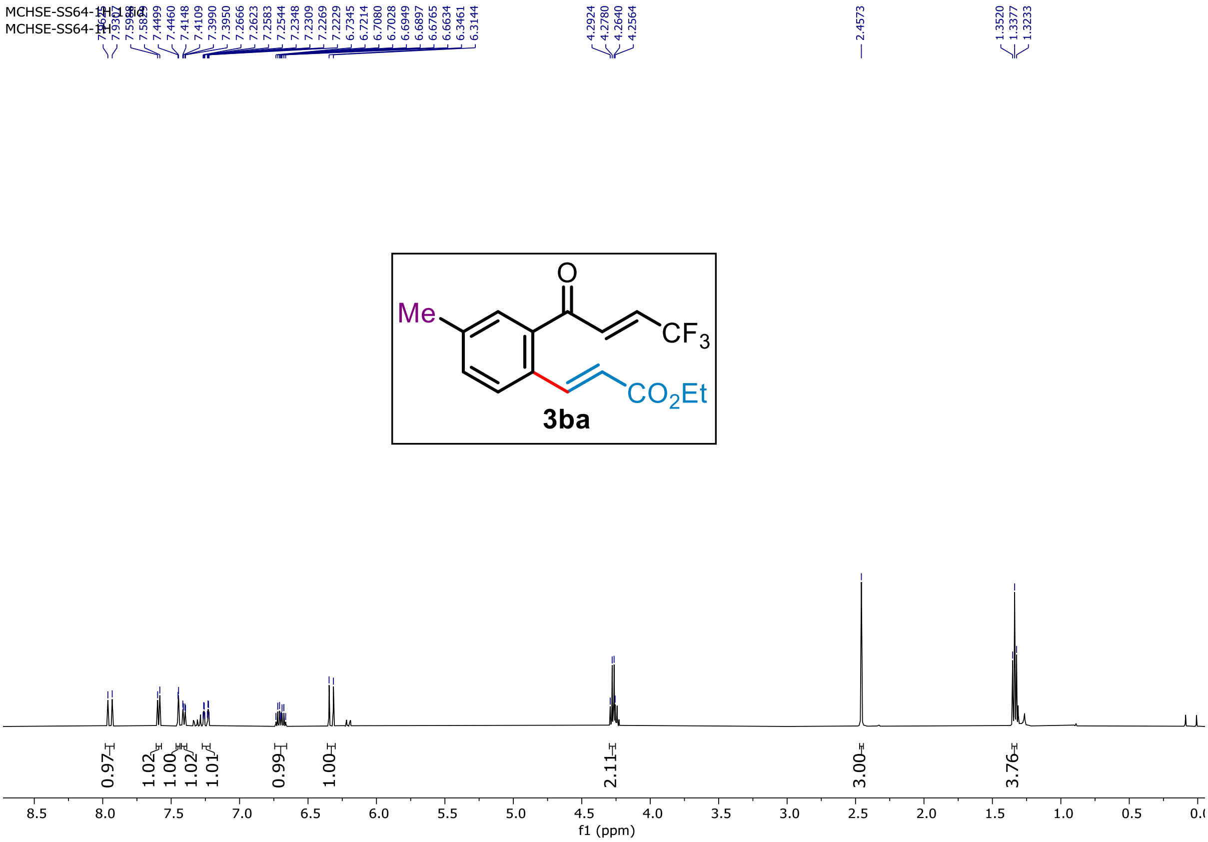
2aa
f1 (ppm)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1.00
1.02
1.01
0.99
1.00
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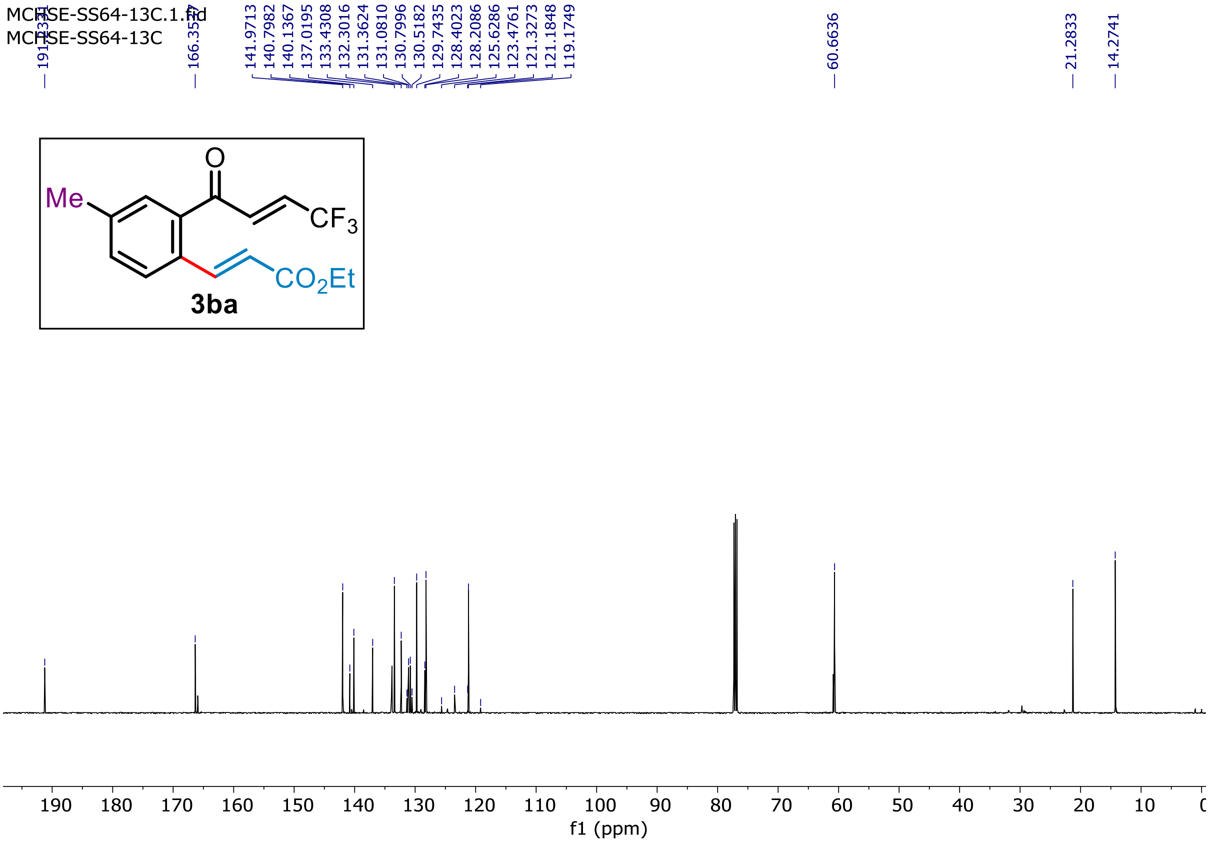
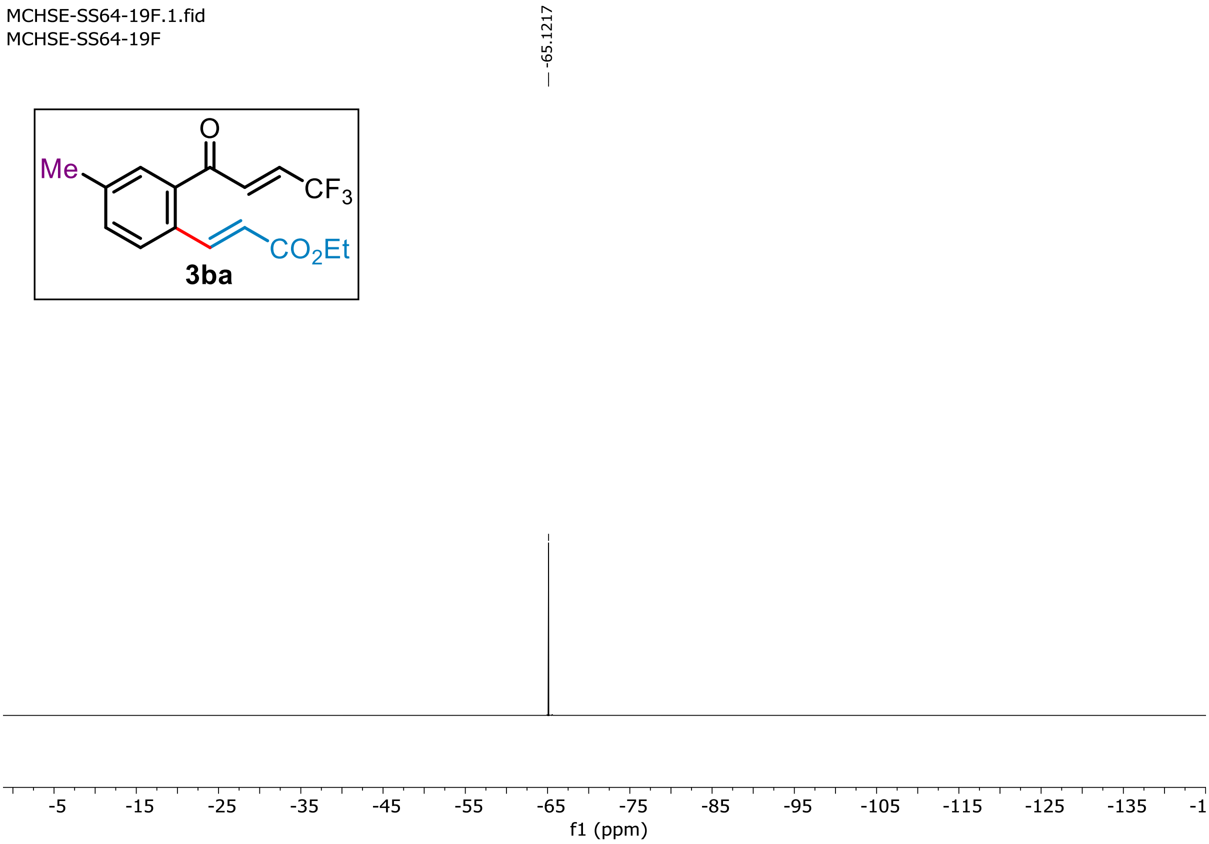
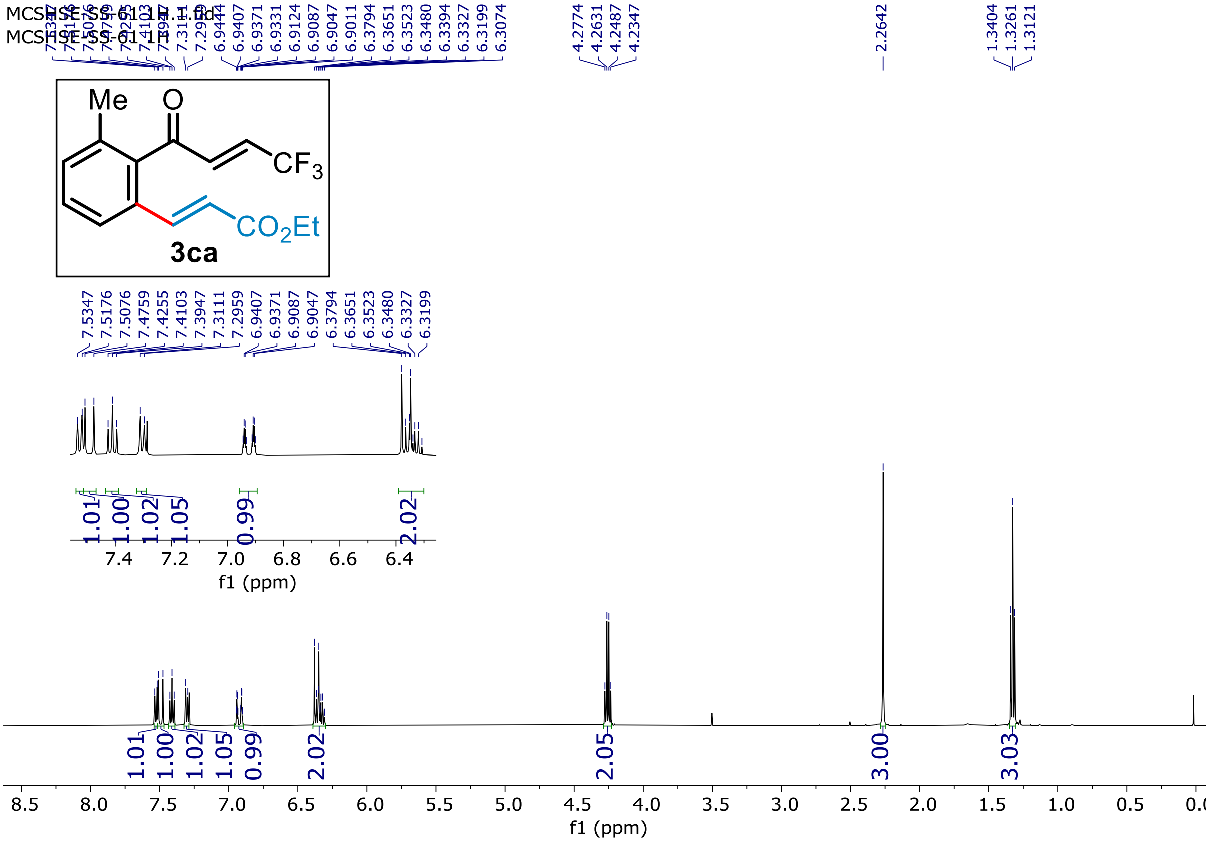
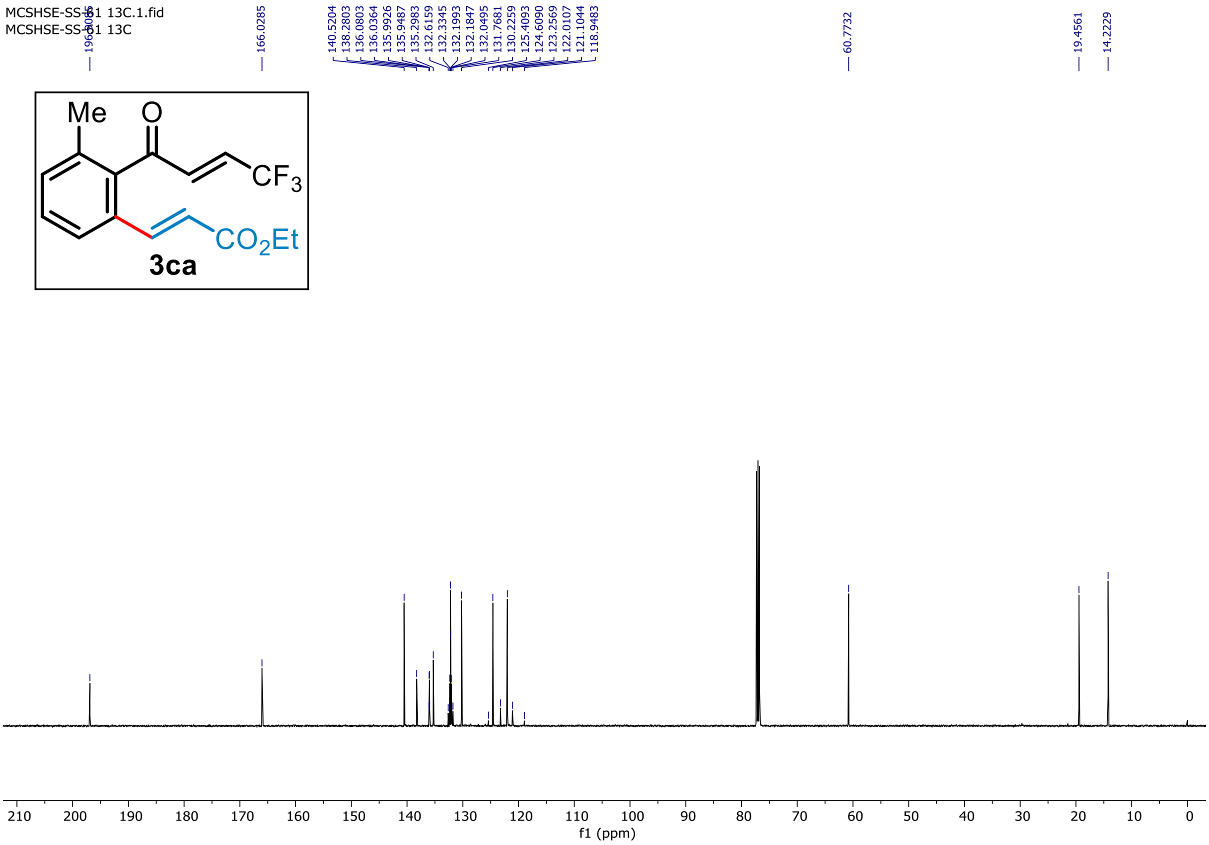
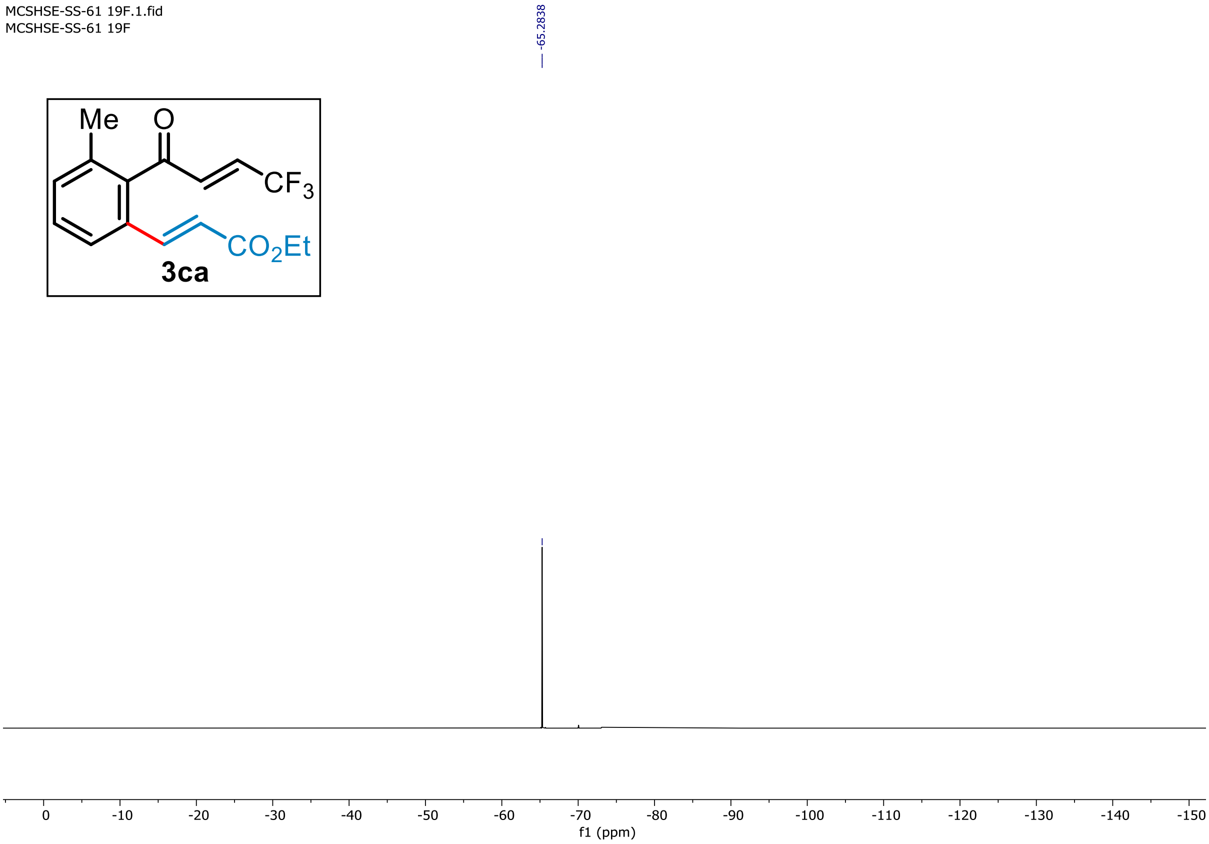
3.00
3.76
f1 (ppm)

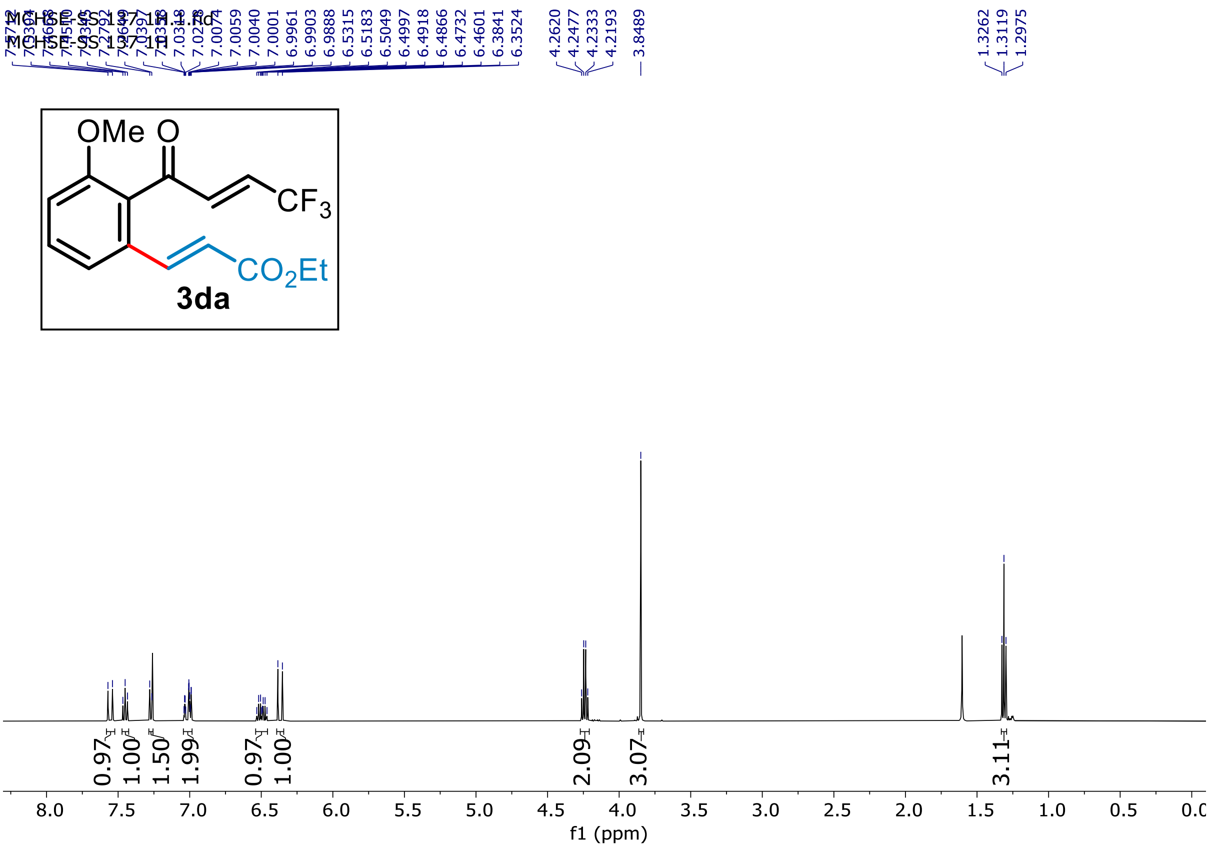

MCHSE-SS64-13C.1.fid
MCHSE-SS64-13C
166.3527
141.9713
140.7982
140.1367
137.0195
133.4308
132.3016
131.3624
131.0810
130.7996
130.5182
129.7435
128.4023
128.2086
125.6286
123.4761
121.3273
121.1848
119.1749
60.6636
21.2833
14.2741
Me
O
CF3
CO2Et
3ba
f1 (ppm)

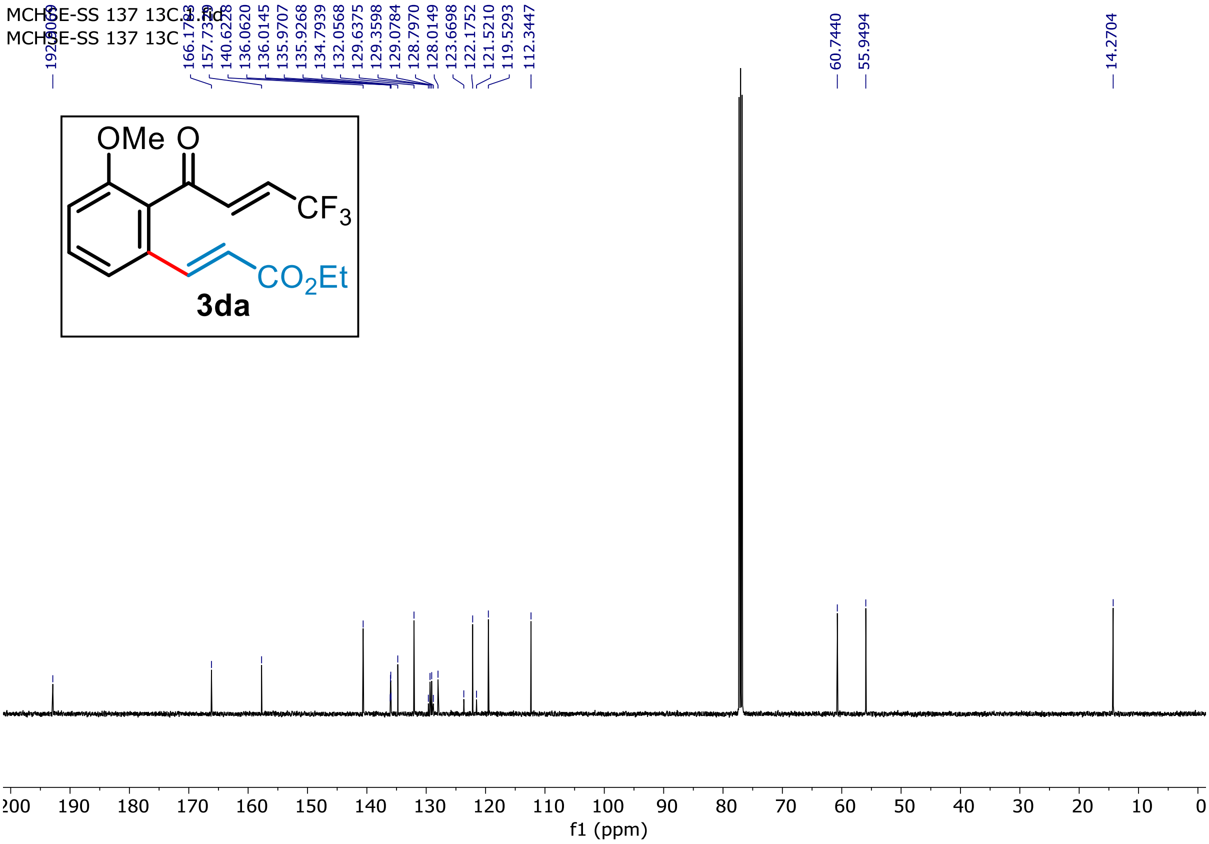

MCHSE-SS64-19F.1.fid
MCHSE-SS64-19F
-65.1217
Me
O
CF3
CO2Et
3ba
f1 (ppm)


MCSHSE-SS-61 1H.1.fid
MCSHSE-SS-61 1H
Me
O
CF3
CO2Et
3ca
f1 (ppm)

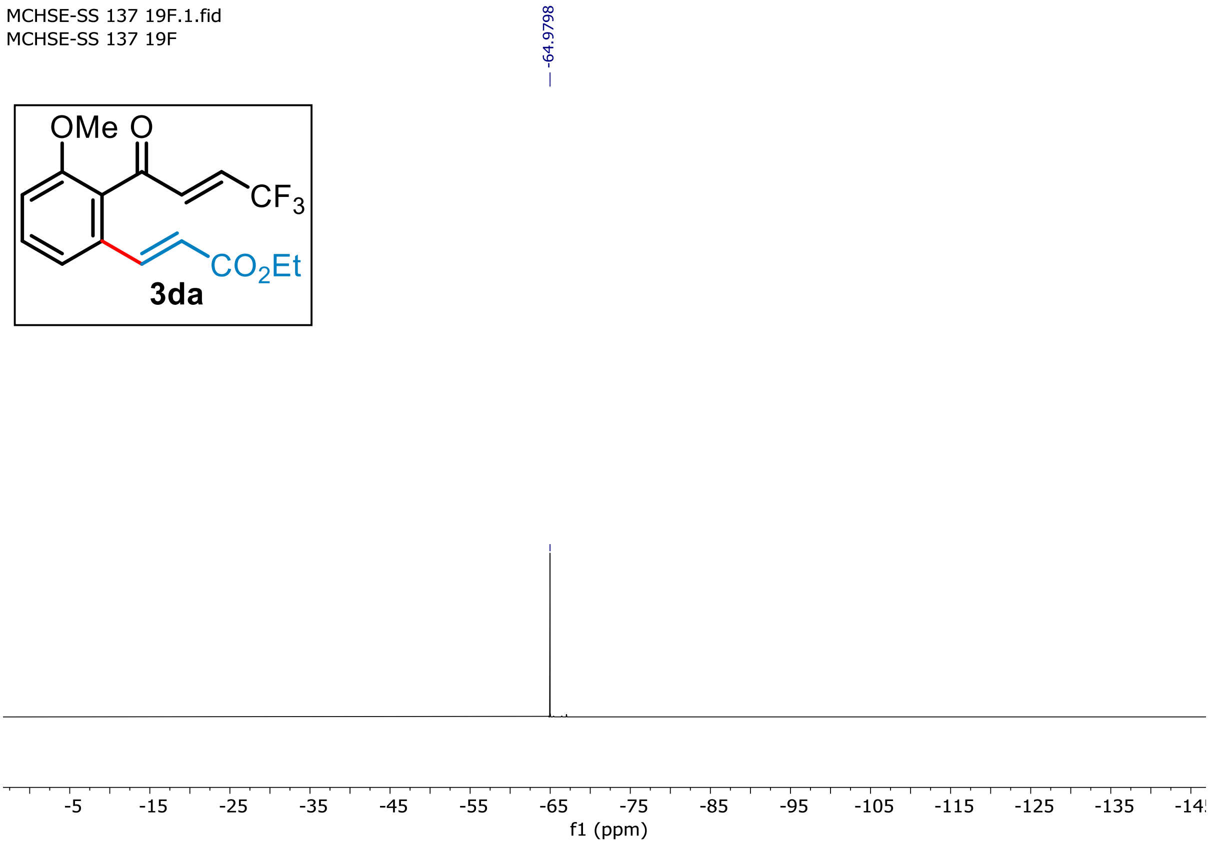

MCSHSE-SS-61 13C.1.fid
MCSHSE-SS-61 13C
Me
O
CF3
CO2Et
3ca
f1 (ppm)


MCSHSE-SS-61 19F.1.fid
MCSHSE-SS-61 19F
-65.2838
Me
O
CF3
CO2Et
3ca
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

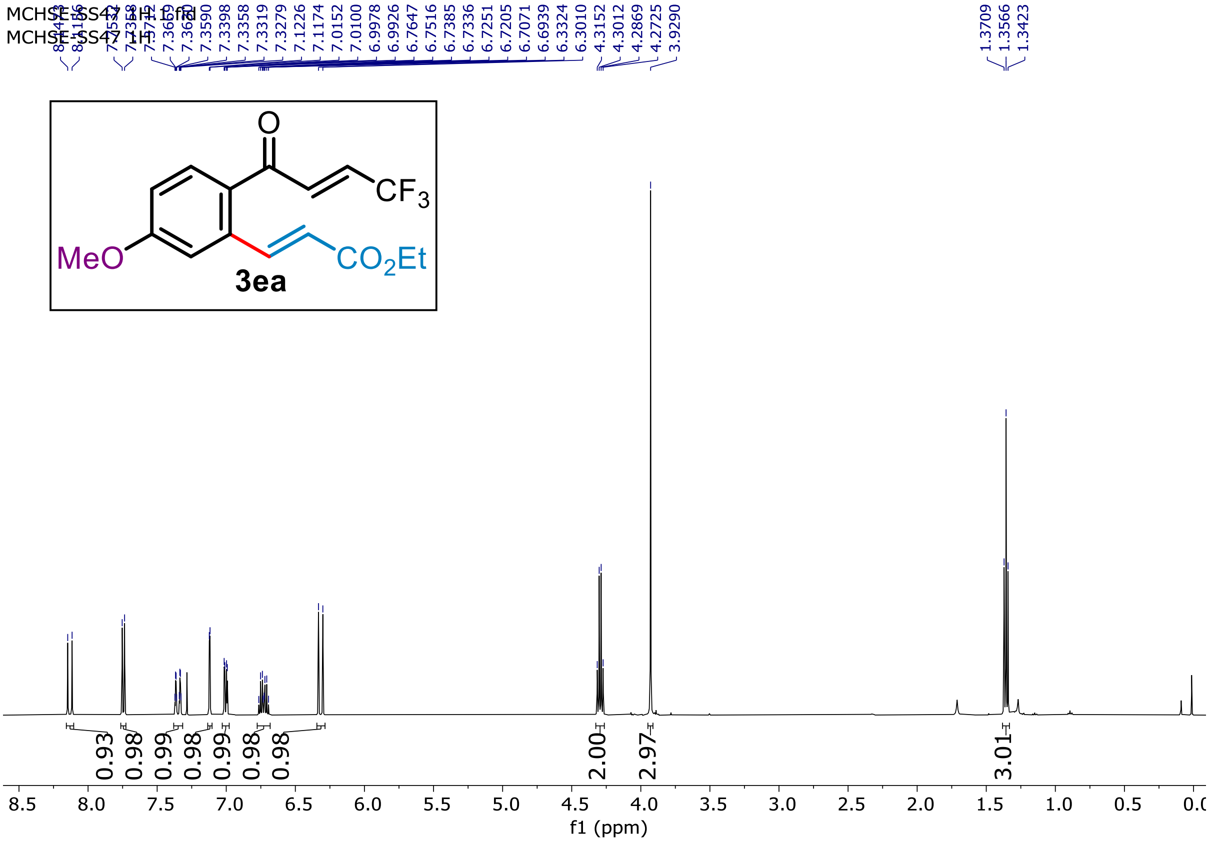

7.0338
7.0278
7.0074
7.0059
7.0040
7.0001
6.9961
6.9903
6.9888
6.5315
6.5183
6.5049
6.4997
6.4918
6.4866
6.4732
6.4601
6.3841
6.3524
4.2620
4.2477
4.2333
4.2193
3.8489
1.3262
1.3119
1.2975
OMe
O
CF3
CO2Et
3da
0.97
1.00
1.50
1.99
0.97
1.00
2.09
3.07
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

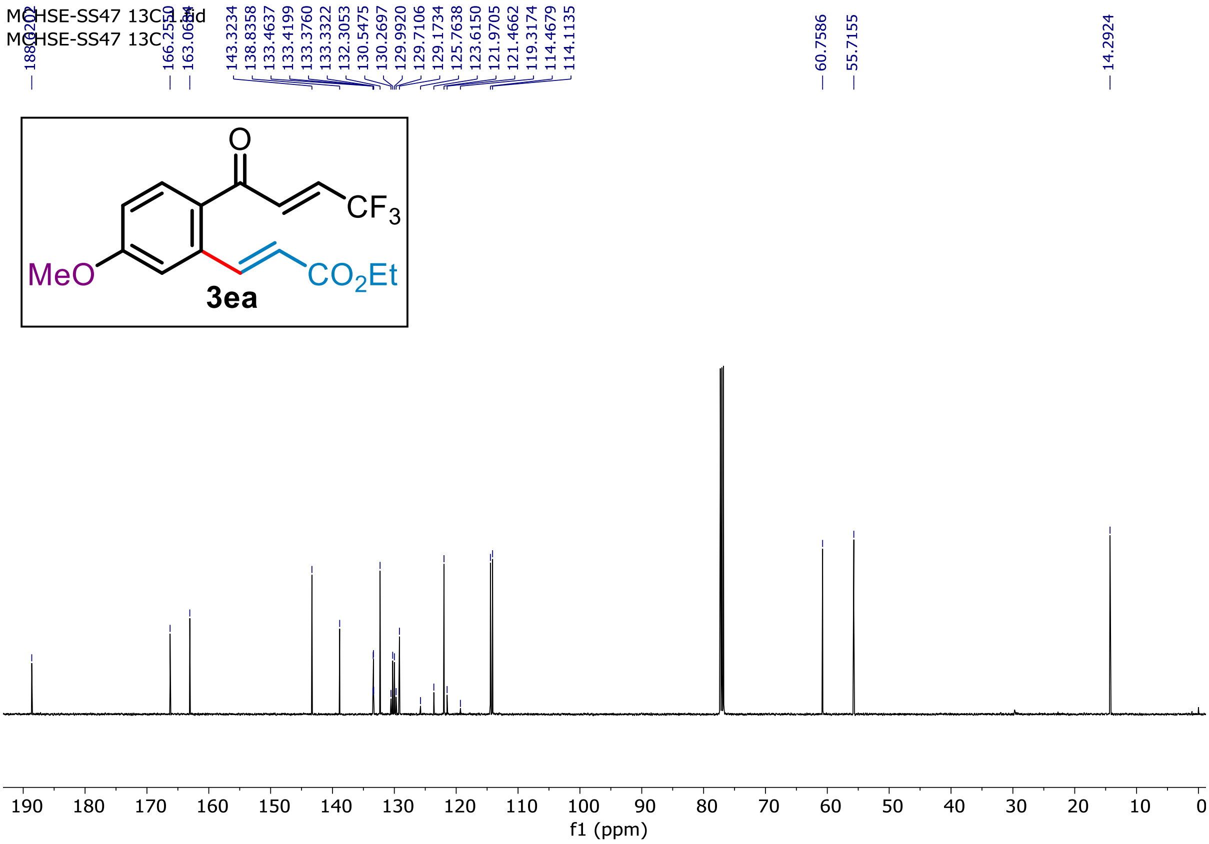


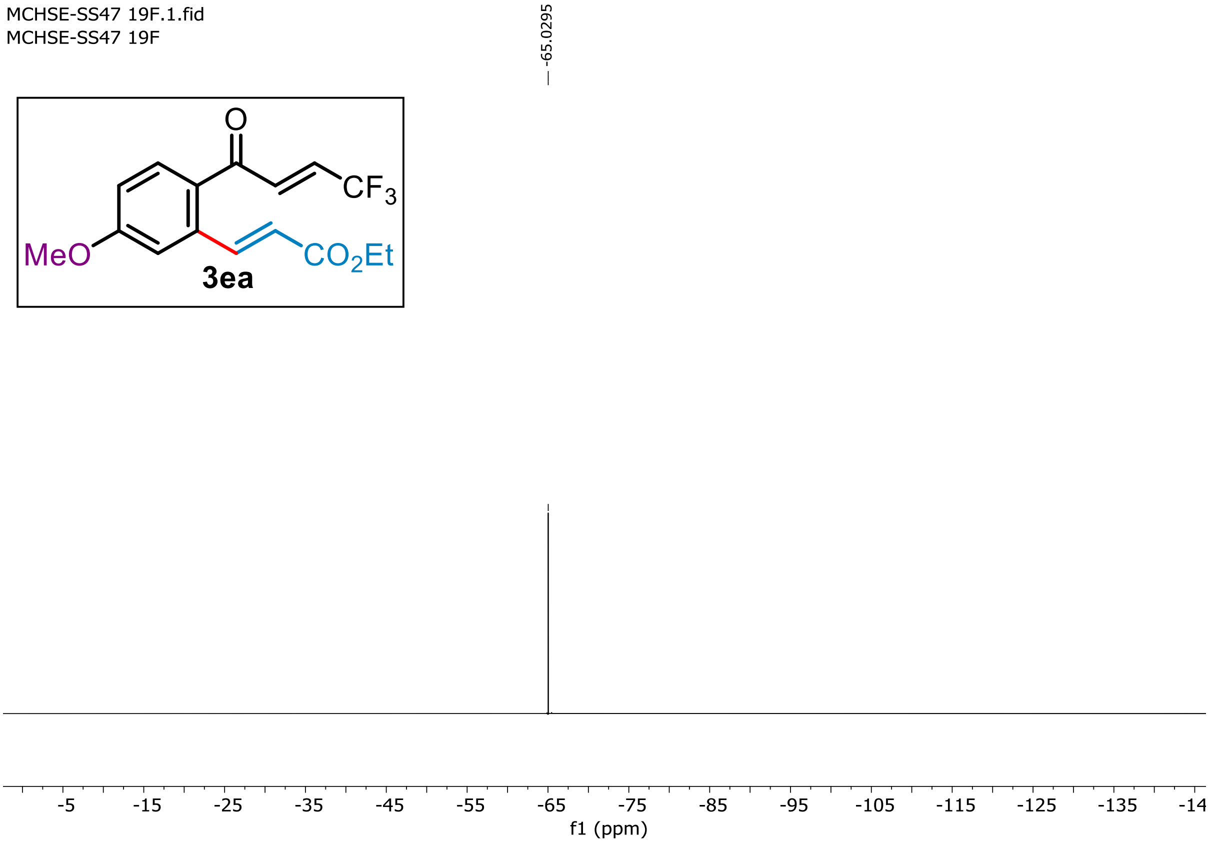
MCHSE-SS 137 13C.1.fid
MCHSE-SS 137 13C
166.1783
157.7329
140.6228
136.0620
136.0145
135.9707
135.9268
134.7939
132.0568
129.6375
129.3598
129.0784
128.7970
128.0149
123.6698
122.1752
121.5210
119.5293
112.3447
60.7440
55.9494
14.2704
OMe O
CF3
CO2Et
3da
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

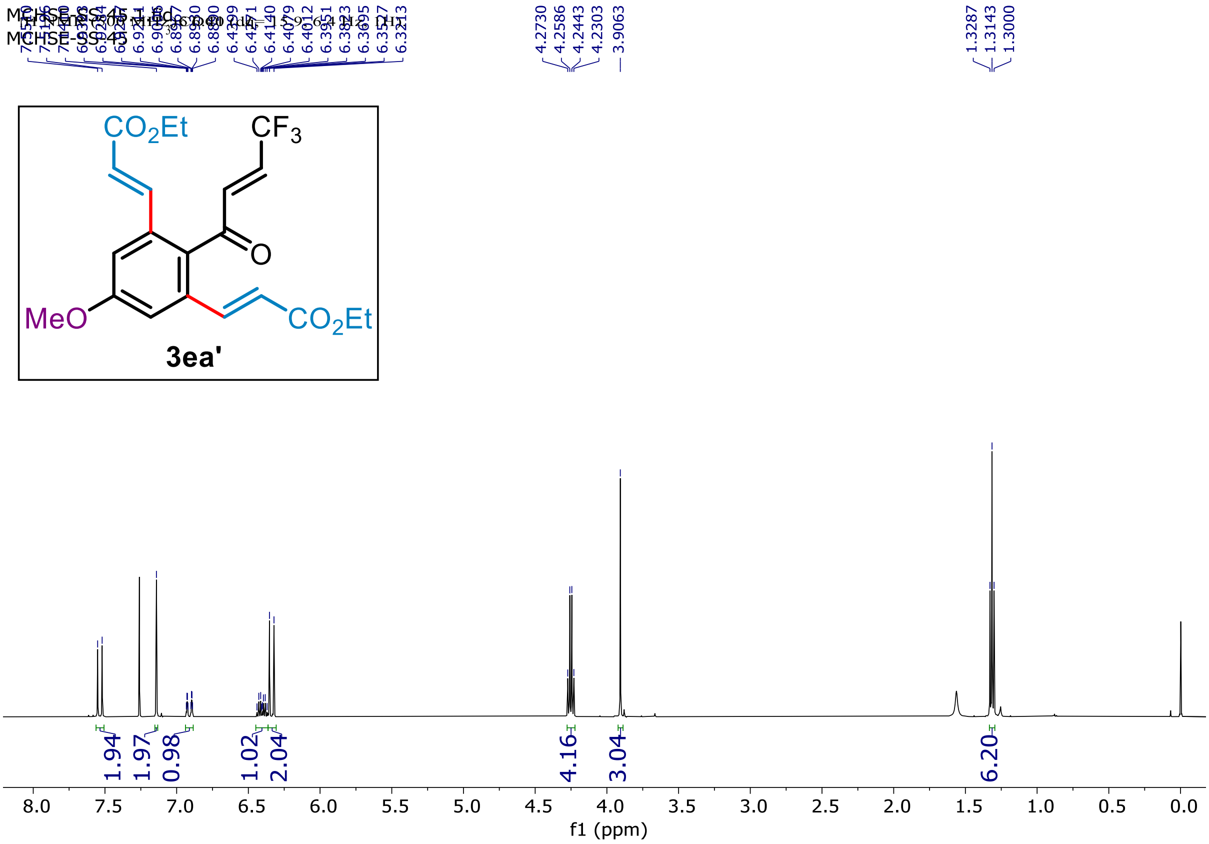


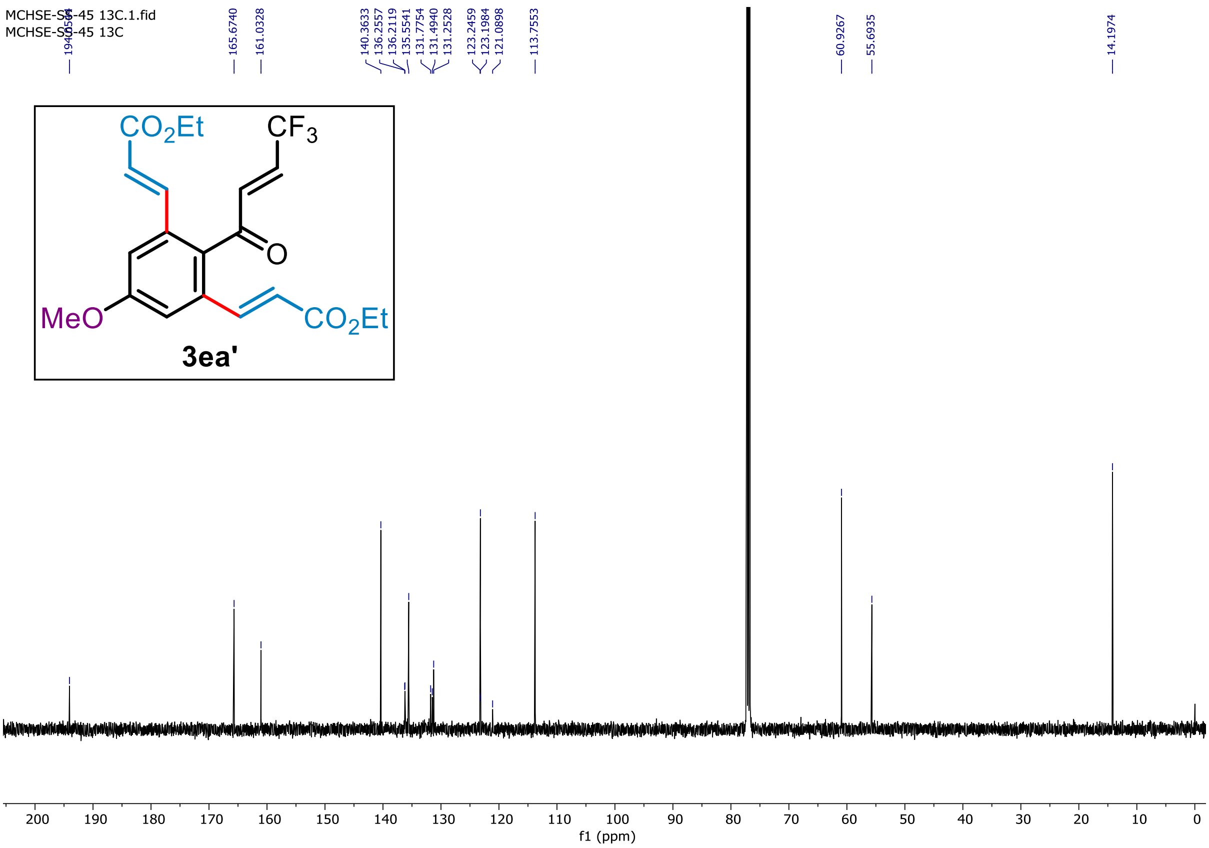
MCHSE-SS 137 19F.1.fid
MCHSE-SS 137 19F
-64.9798
OMe O
CF3
CO2Et
3da
-5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135
f1 (ppm)

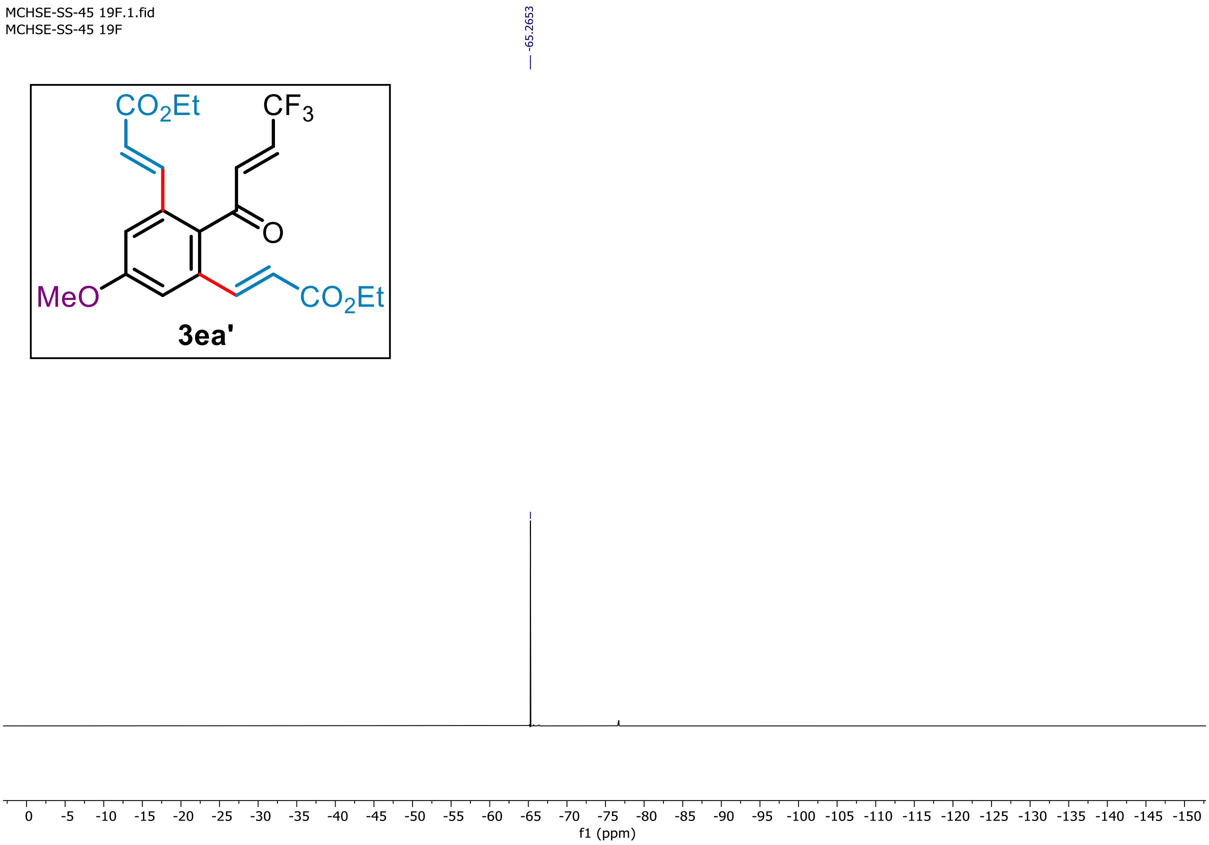

MCHSE-SS47 1H
7.3665
7.3620
7.3590
7.3398
7.3358
7.3319
7.3279
7.1226
7.1174
7.0152
7.0100
6.9978
6.9926
6.7647
6.7516
6.7385
6.7336
6.7251
6.7205
6.7071
6.6939
6.3324
6.3010
4.3152
4.3012
4.2869
4.2725
3.9290
1.3709
1.3566
1.3423
O
CF3
MeO
CO2Et
3ea
0.93
0.98
0.99
0.98
0.99
0.98
0.98
2.00
2.97
3.01
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)

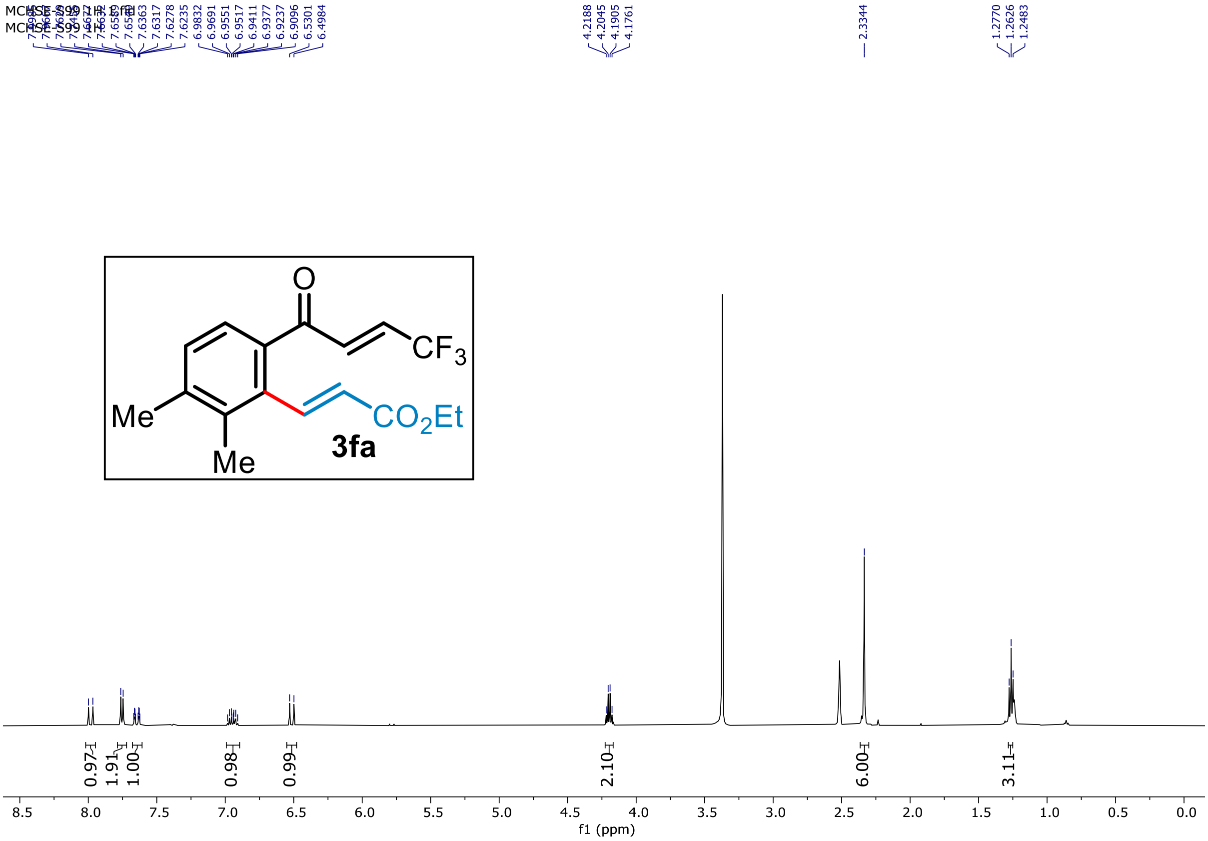

MCHSE-SS47 13C
166.2510
163.0684
143.3234
138.8358
133.4637
133.4199
133.3760
133.3322
132.3053
130.5475
130.2697
129.9920
129.7106
129.1734
125.7638
123.6150
121.9705
121.4662
119.3174
114.4679
114.1135
60.7586
55.7155
14.2924
O
CF3
MeO
CO2Et
3ea
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

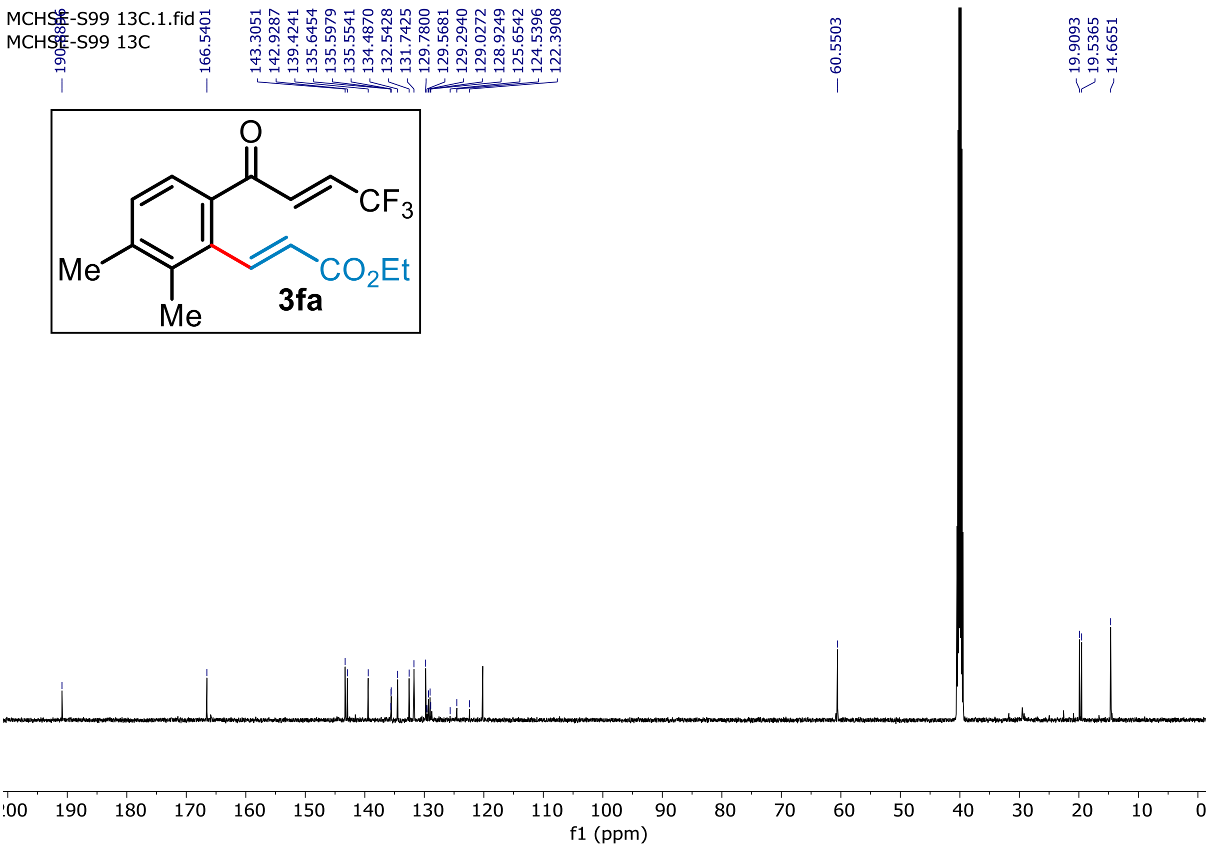

MCHSE-SS47 19F.1.fid
MCHSE-SS47 19F
-65.0295
O
CF3
MeO
CO2Et
3ea
-5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 -14
f1 (ppm)


4.2730
4.2586
4.2443
4.2303
3.9063
1.3287
1.3143
1.3000
CO2Et
CF3
O
MeO
CO2Et
3ea'
1.94
1.97
0.98
1.02
2.04
4.16
3.04
6.20
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)

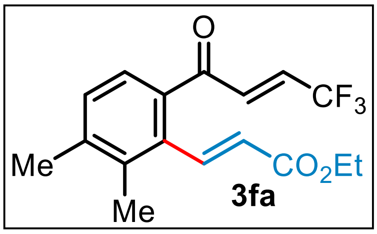

MCHSE-SS-45 13C.1.fid
MCHSE-SS-45 13C
165.6740
161.0328
140.3633
136.2557
136.2119
135.5541
131.7754
131.4940
131.2528
123.2459
123.1984
121.0898
113.7553
60.9267
55.6935
14.1974
CO2Et
CF3
O
MeO
CO2Et
3ea'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

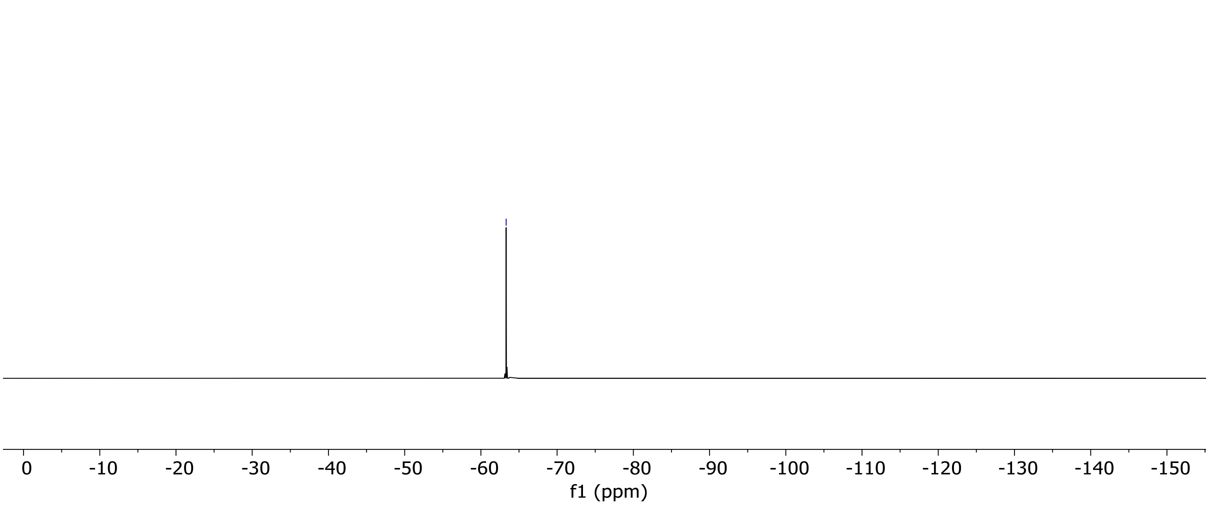

MCHSE-SS-45 19F.1.fid
MCHSE-SS-45 19F
-65.2653
CO2Et
CF3
O
MeO
CO2Et
3ea'
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)


4.2188
4.2045
4.1905
4.1761
2.3344
1.2770
1.2626
1.2483
O
CF3
Me
CO2Et
Me
3fa
0.97
1.91
1.00
0.98
0.99
2.10
6.00
3.11
f1 (ppm)

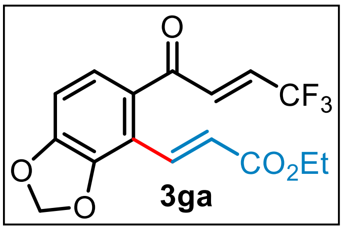

MCHSF-S99 13C.1.fid
MCHSF-S99 13C
166.5401
143.3051
142.9287
139.4241
135.6454
135.5979
135.5541
134.4870
132.5428
131.7425
129.7800
129.5681
129.2940
129.0272
128.9249
125.6542
124.5396
122.3908
60.5503
19.9093
19.5365
14.6651
O
CF3
Me
CO2Et
Me
3fa
f1 (ppm)

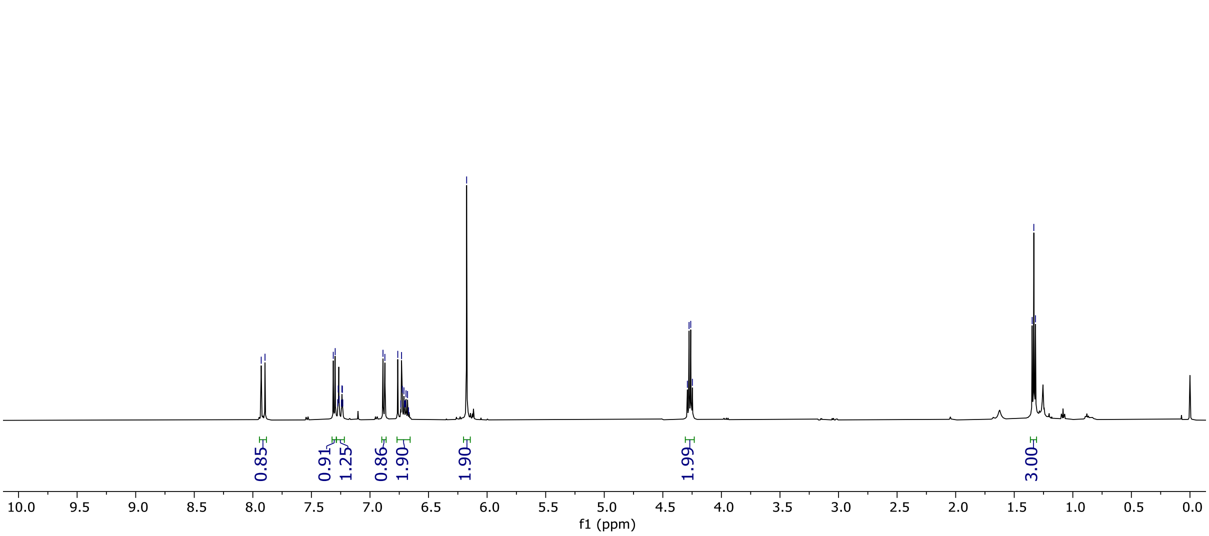
MCHSE-S99 19F.1.fid
MCHSE-S99 19F

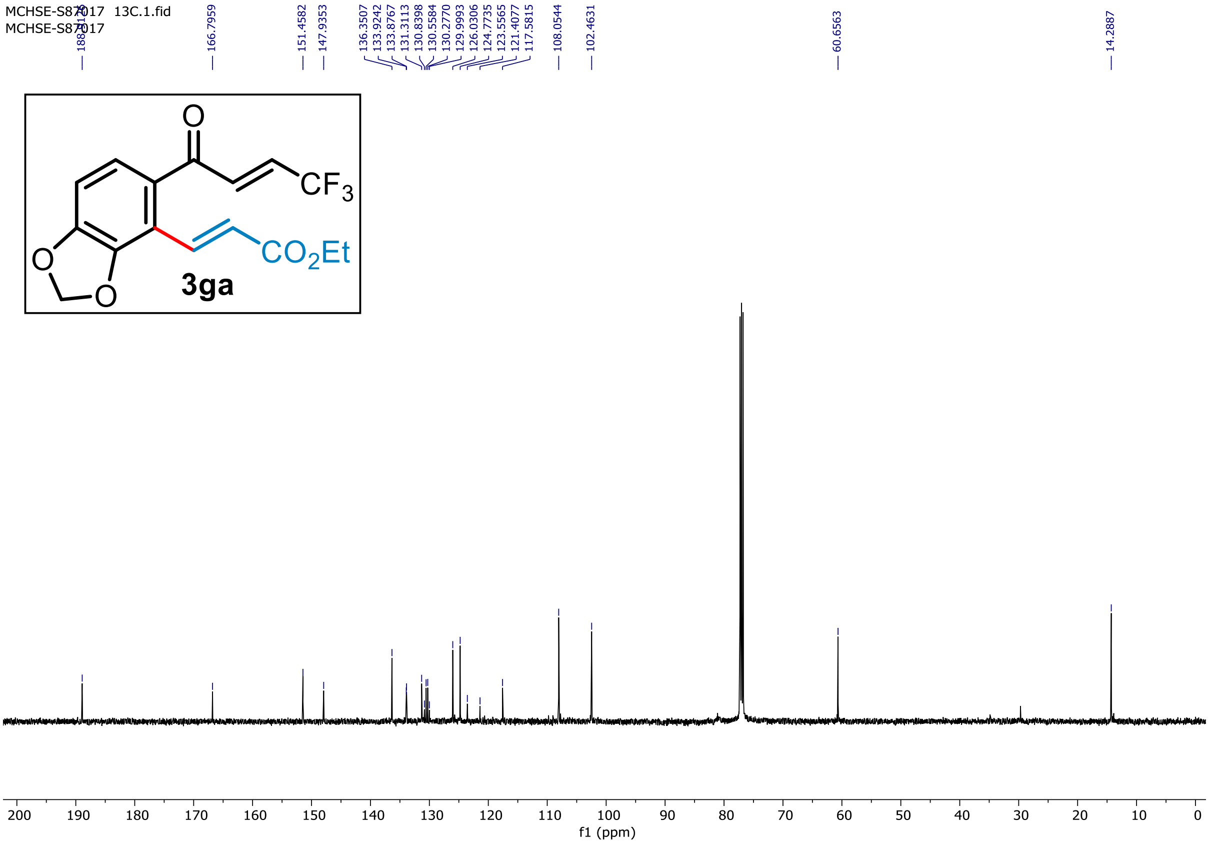




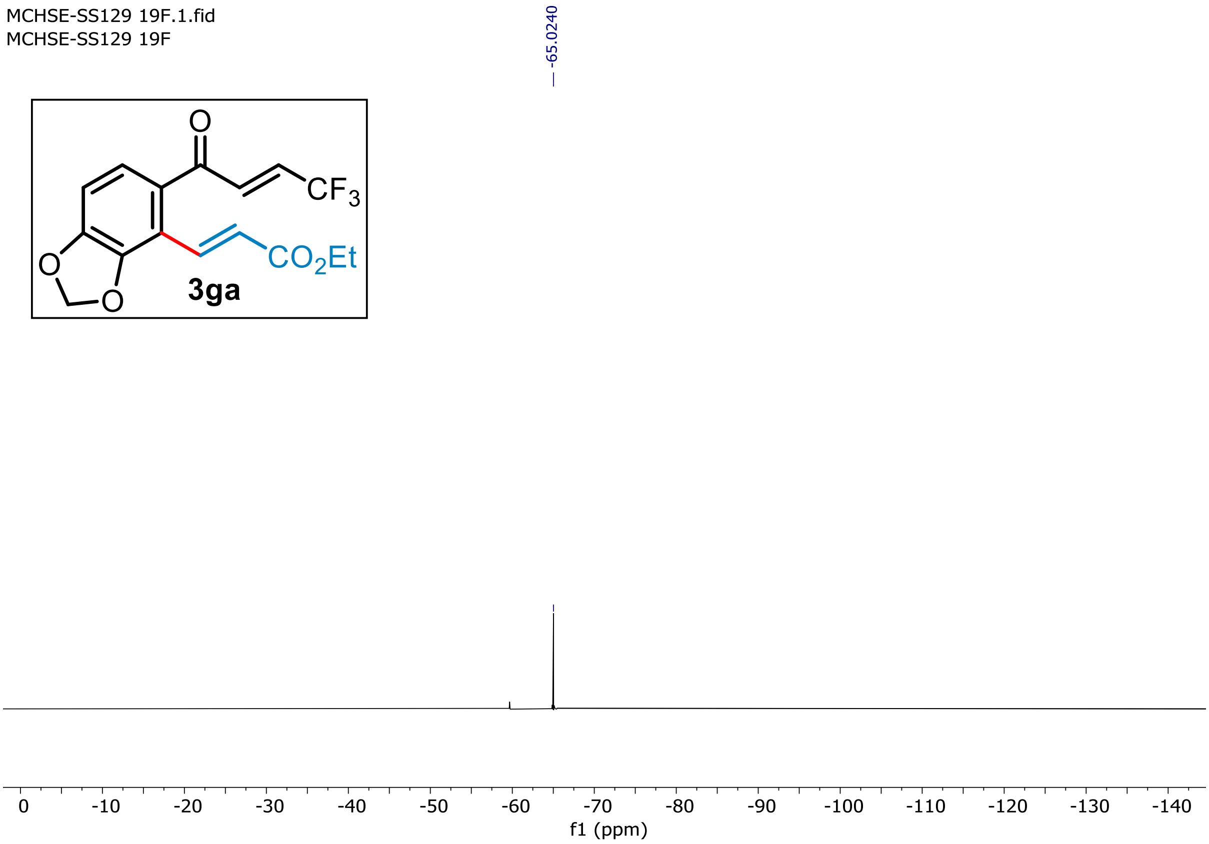
MCHSE-S87017.1.fid
MCHSE-S87017



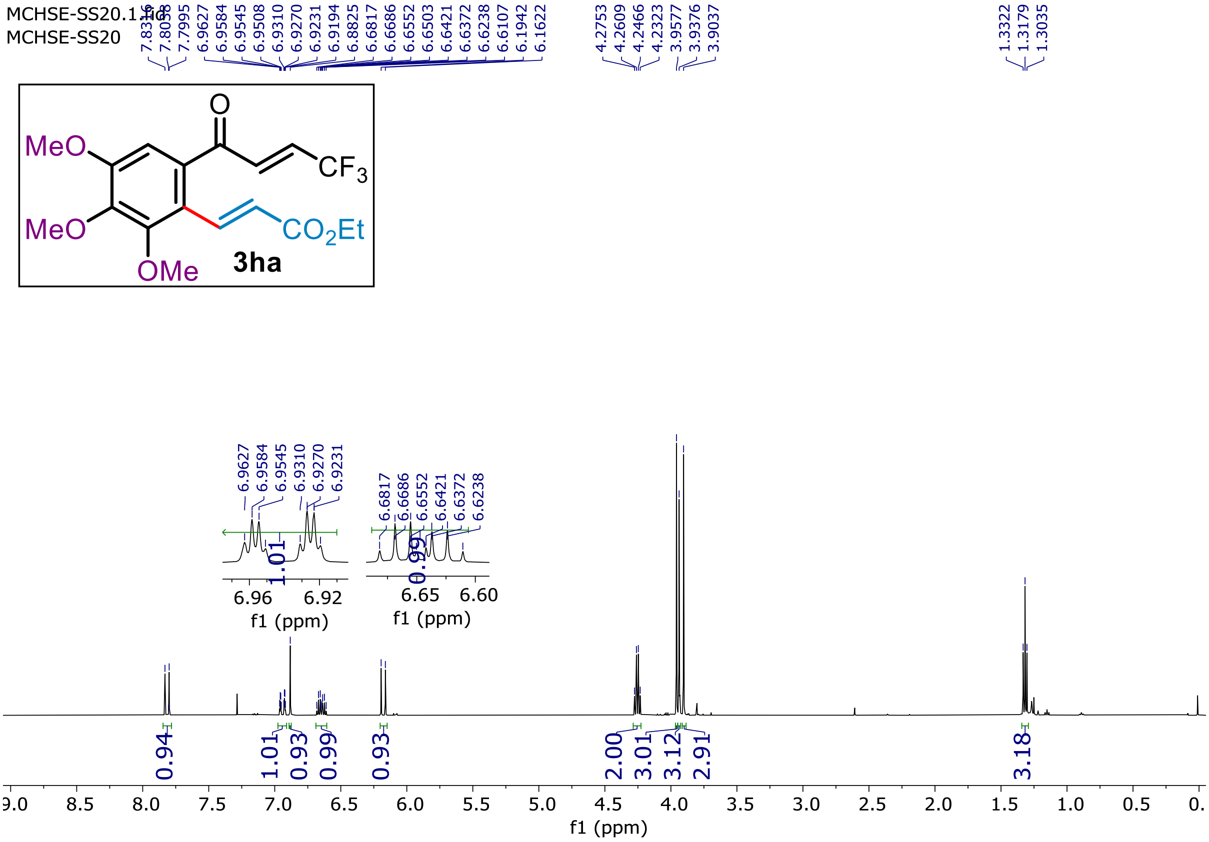


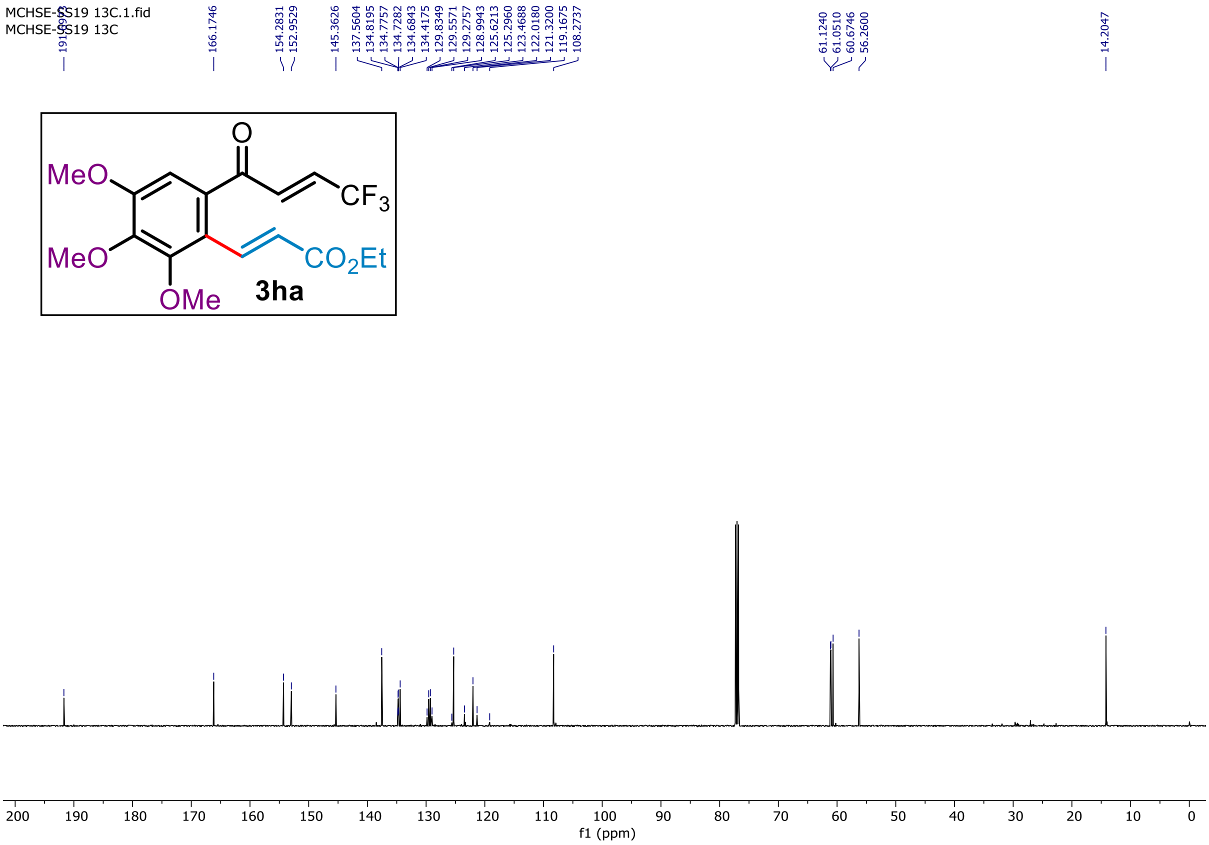


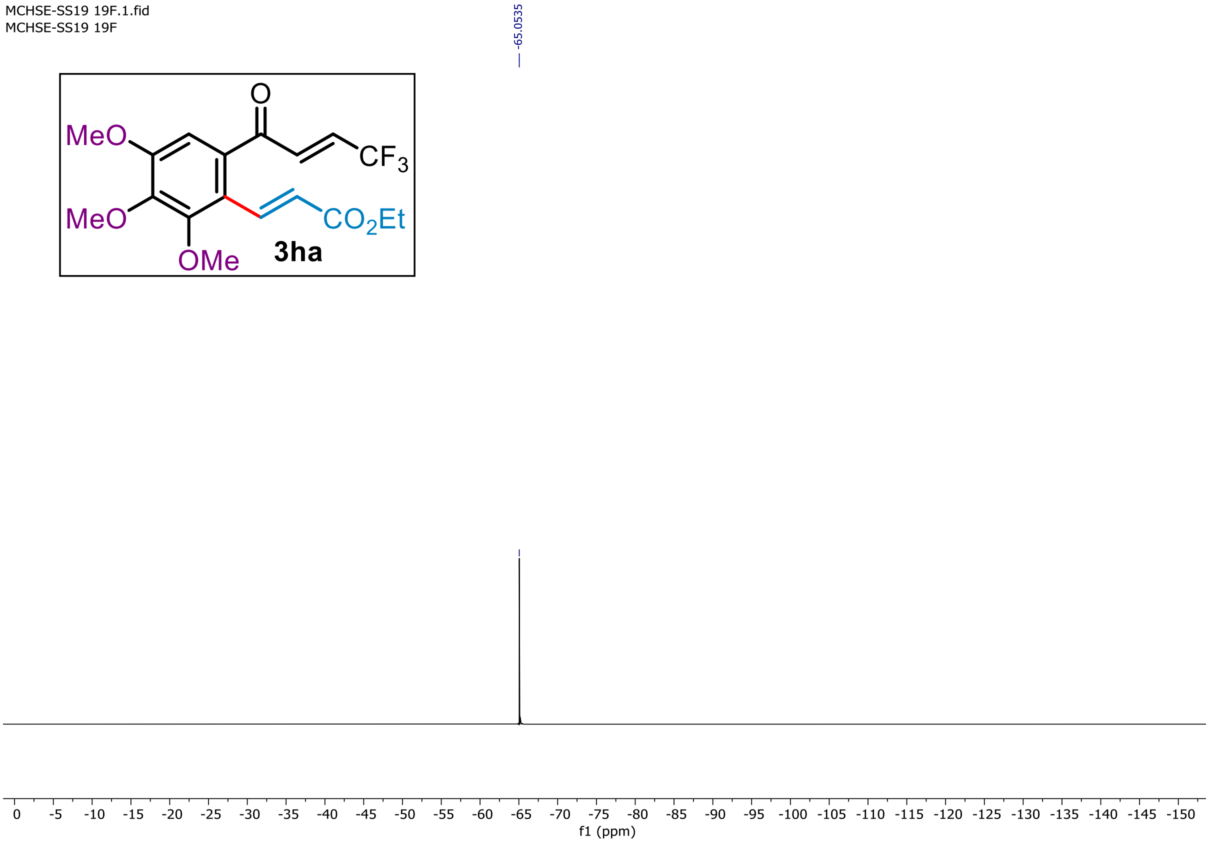
MCHSE-S87017 13C.1.fid
MCHSE-S87017
166.7959
151.4582
147.9353
136.3507
133.9242
133.8767
131.3113
130.8398
130.5584
130.2770
129.9993
126.0306
124.7735
123.5565
121.4077
117.5815
108.0544
102.4631
60.6563
14.2887
O
CF_3
CO_2Et
O
O
3ga
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

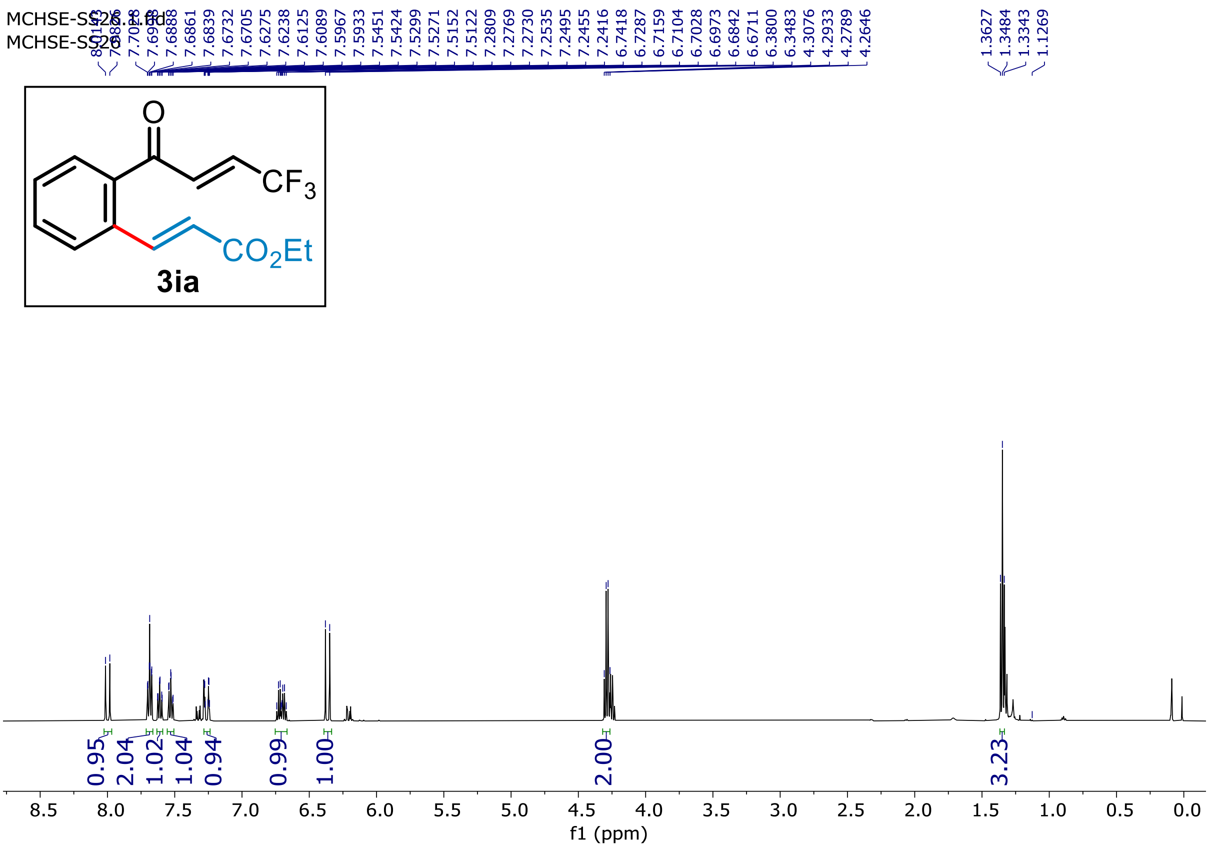


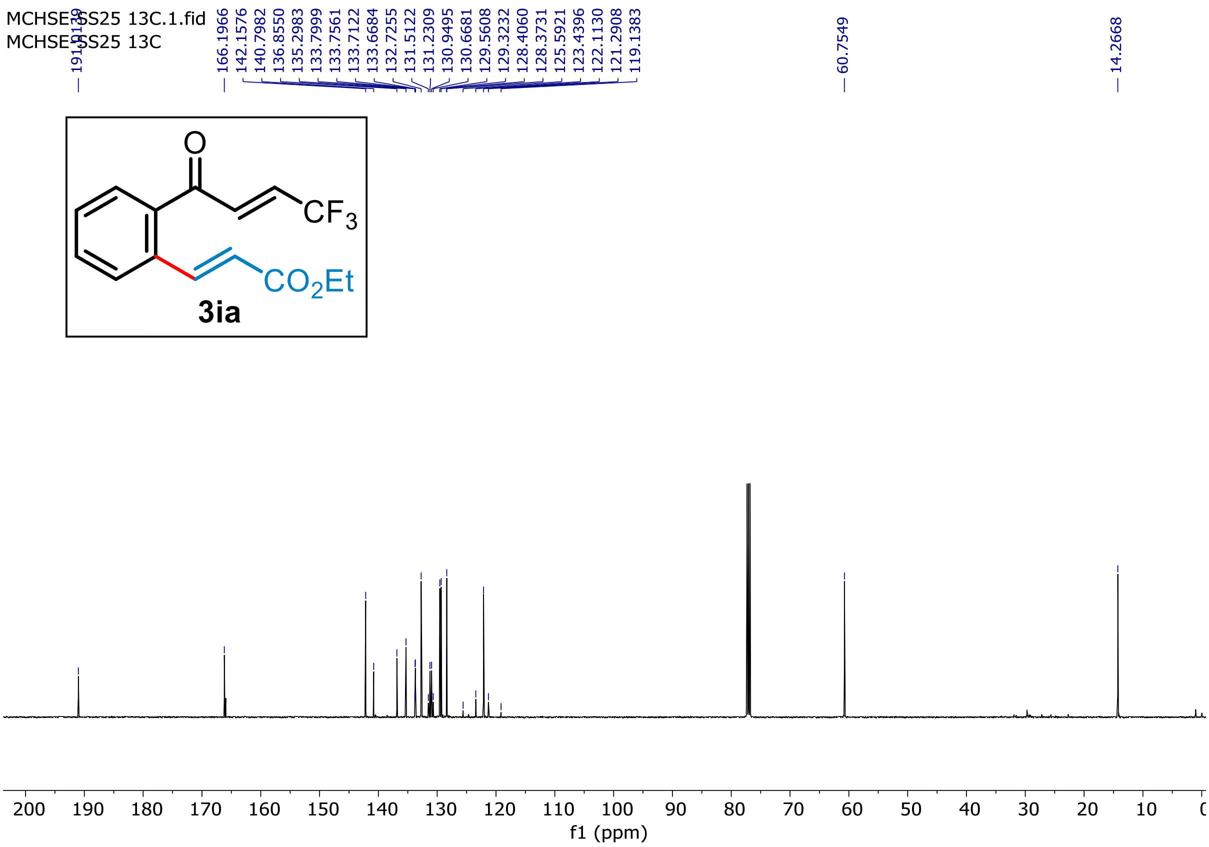
MCHSE-SS129 19F.1.fid
MCHSE-SS129 19F
-65.0240
O
CF_3
CO_2Et
O
O
3ga
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

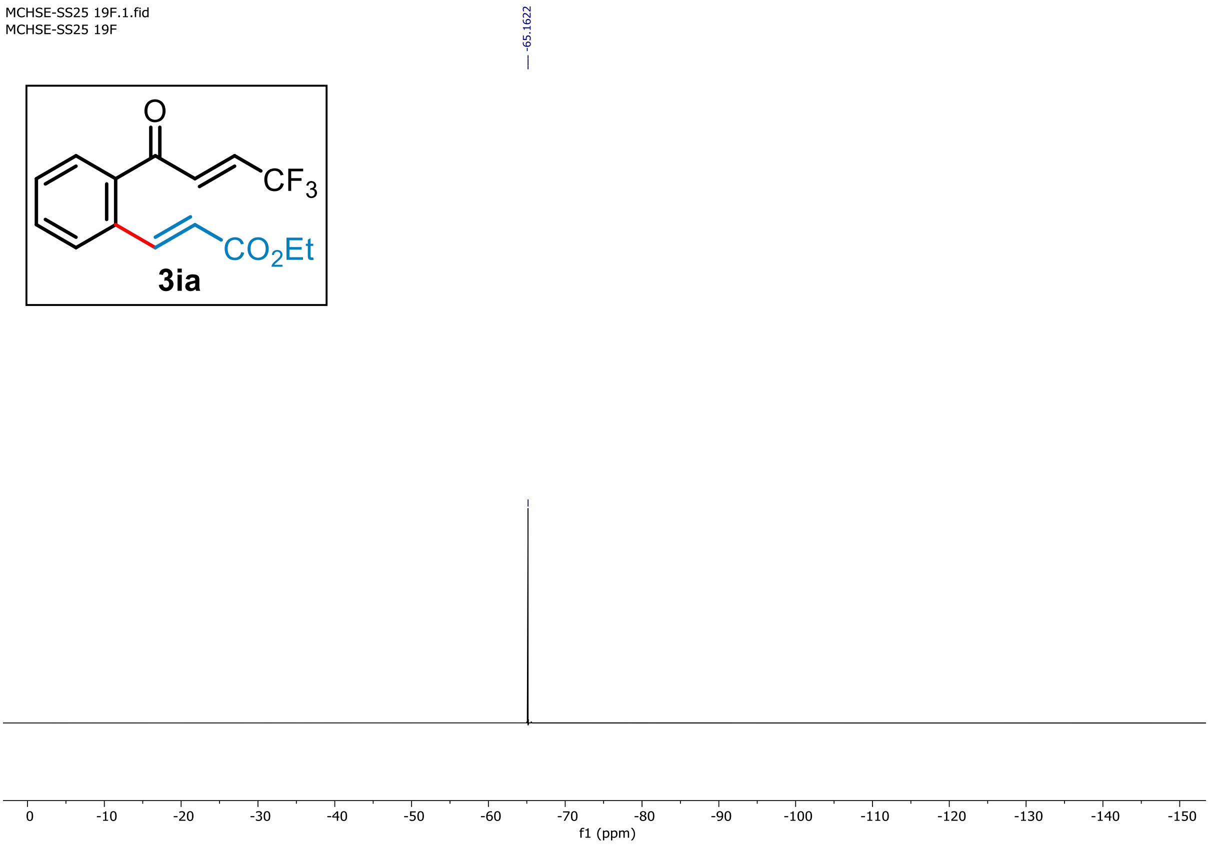

MCHSE-SS20.1.fid
MCHSE-SS20
MeO
MeO
OMe
O
CF3
CO2Et
3ha
f1 (ppm)

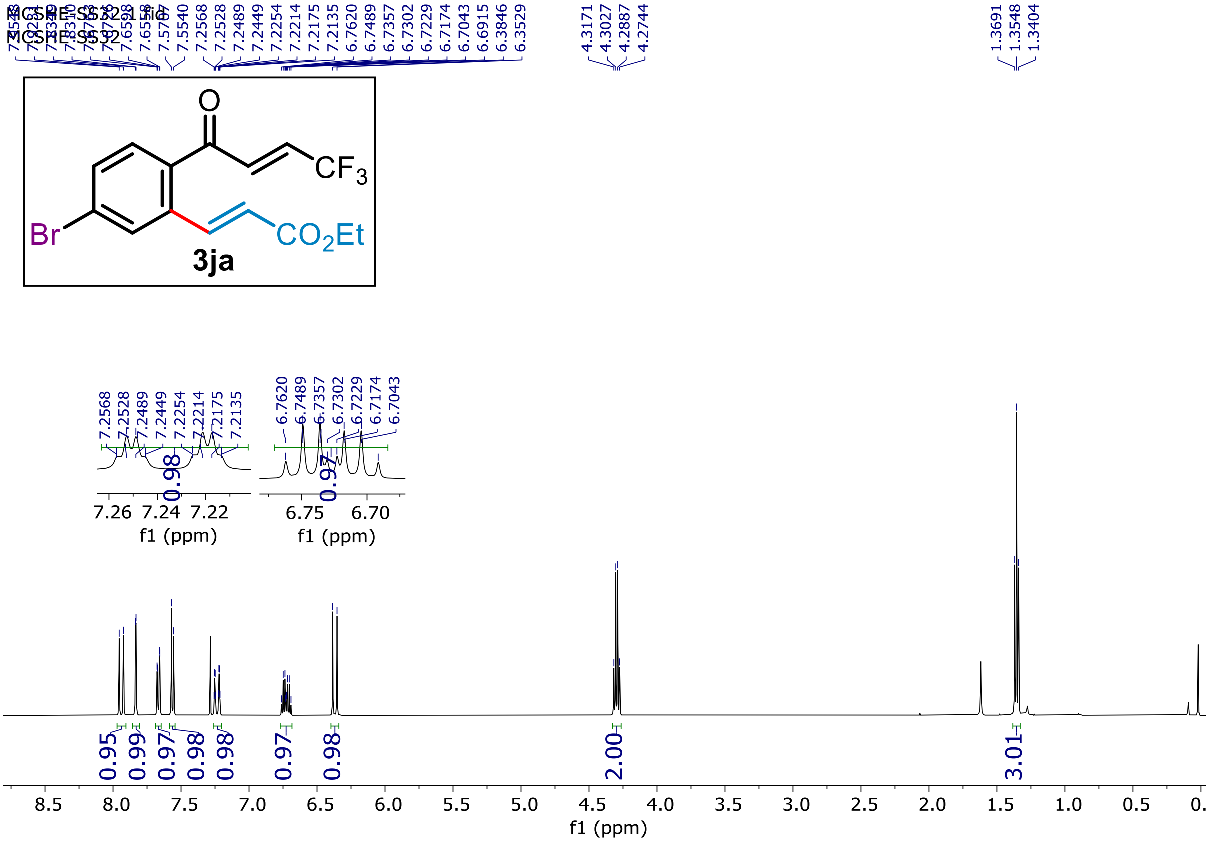

MCHSE-SS19 13C.1.fid
MCHSE-SS19 13C
MeO
MeO
OMe
O
CF3
CO2Et
3ha
f1 (ppm)

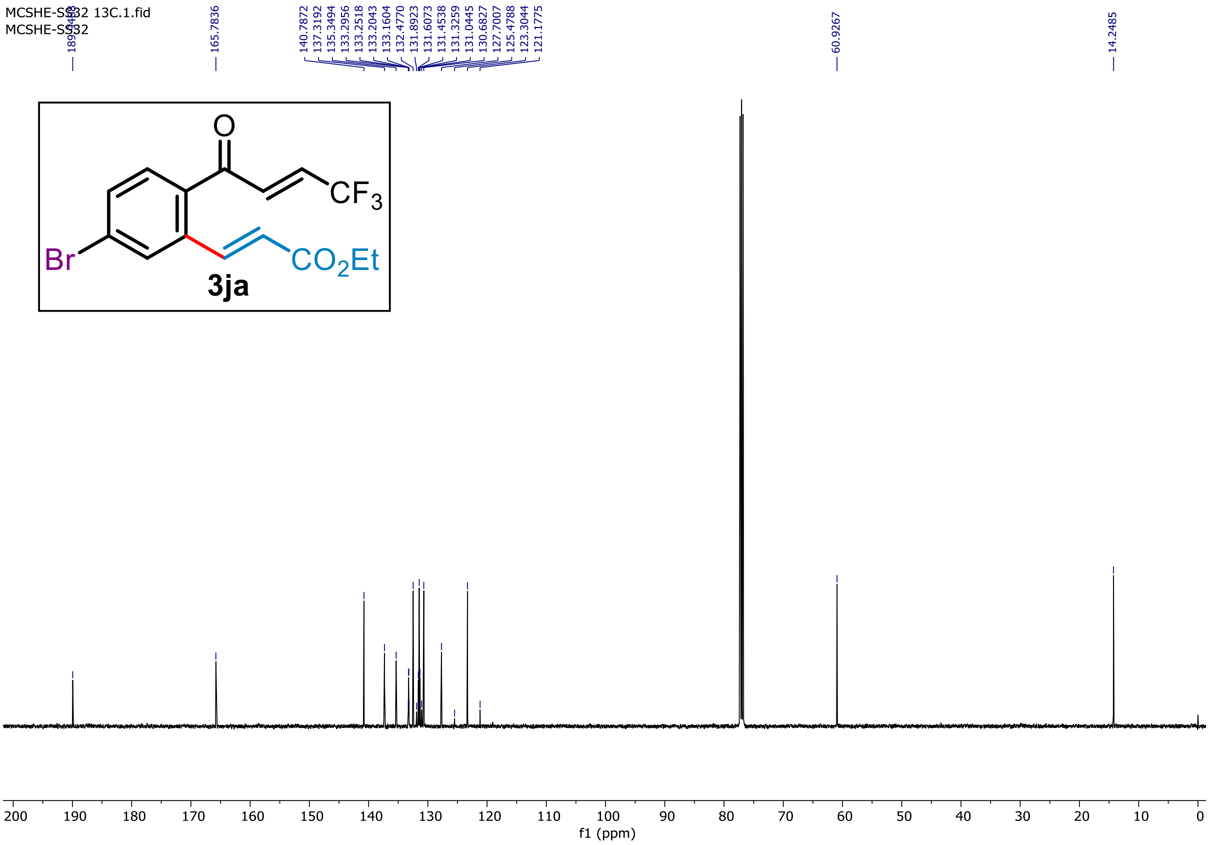

MCHSE-SS19 19F.1.fid
MCHSE-SS19 19F
-65.0535
MeO
MeO
OMe
O
CF_3
CO_2Et
3ha
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

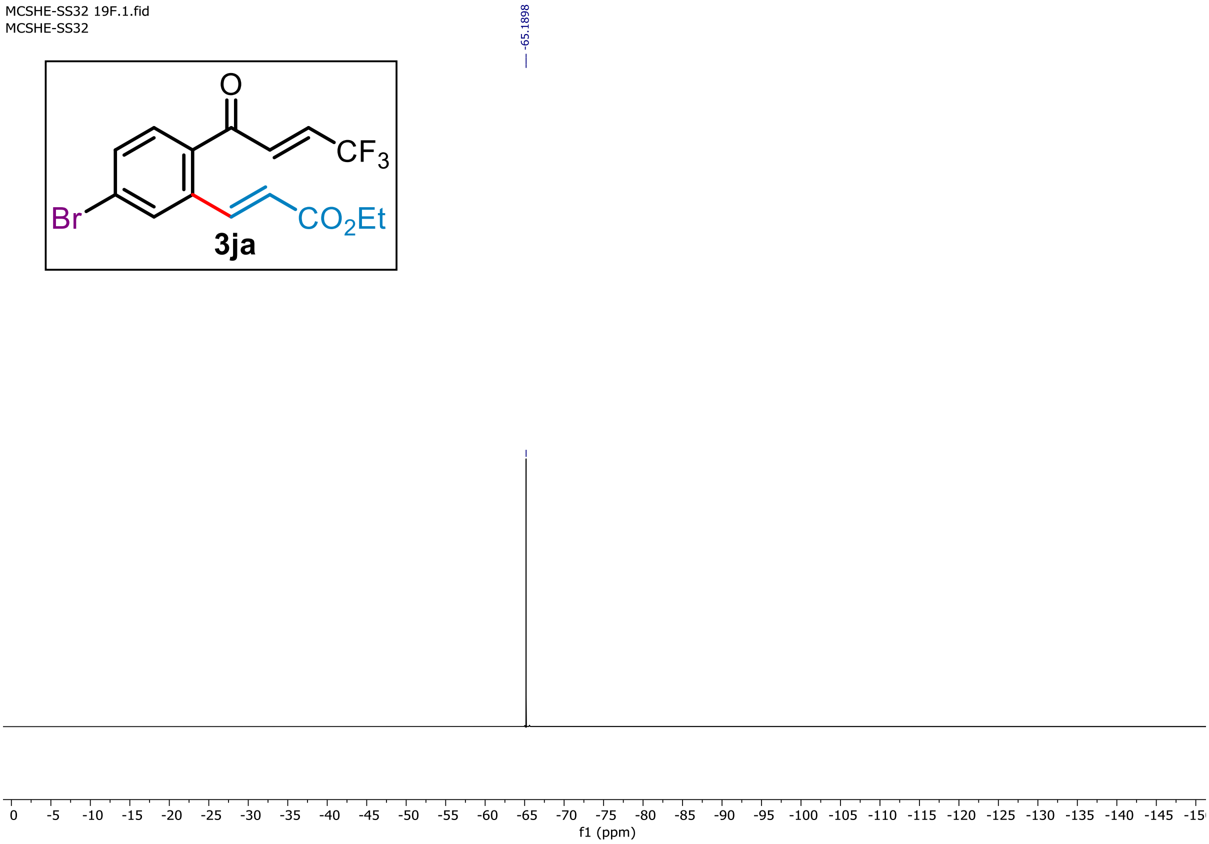

7.6888
7.6861
7.6839
7.6732
7.6705
7.6275
7.6238
7.6125
7.6089
7.5967
7.5933
7.5451
7.5424
7.5299
7.5271
7.5152
7.5122
7.2809
7.2769
7.2730
7.2535
7.2495
7.2455
7.2416
6.7418
6.7287
6.7159
6.7104
6.7028
6.6973
6.6842
6.6711
6.3800
6.3483
4.3076
4.2933
4.2789
4.2646
1.3627
1.3484
1.3343
1.1269
O
CF_3
CO_2Et
3ia
0.95
2.04
1.02
1.04
0.94
0.99
1.00
2.00
3.23
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)

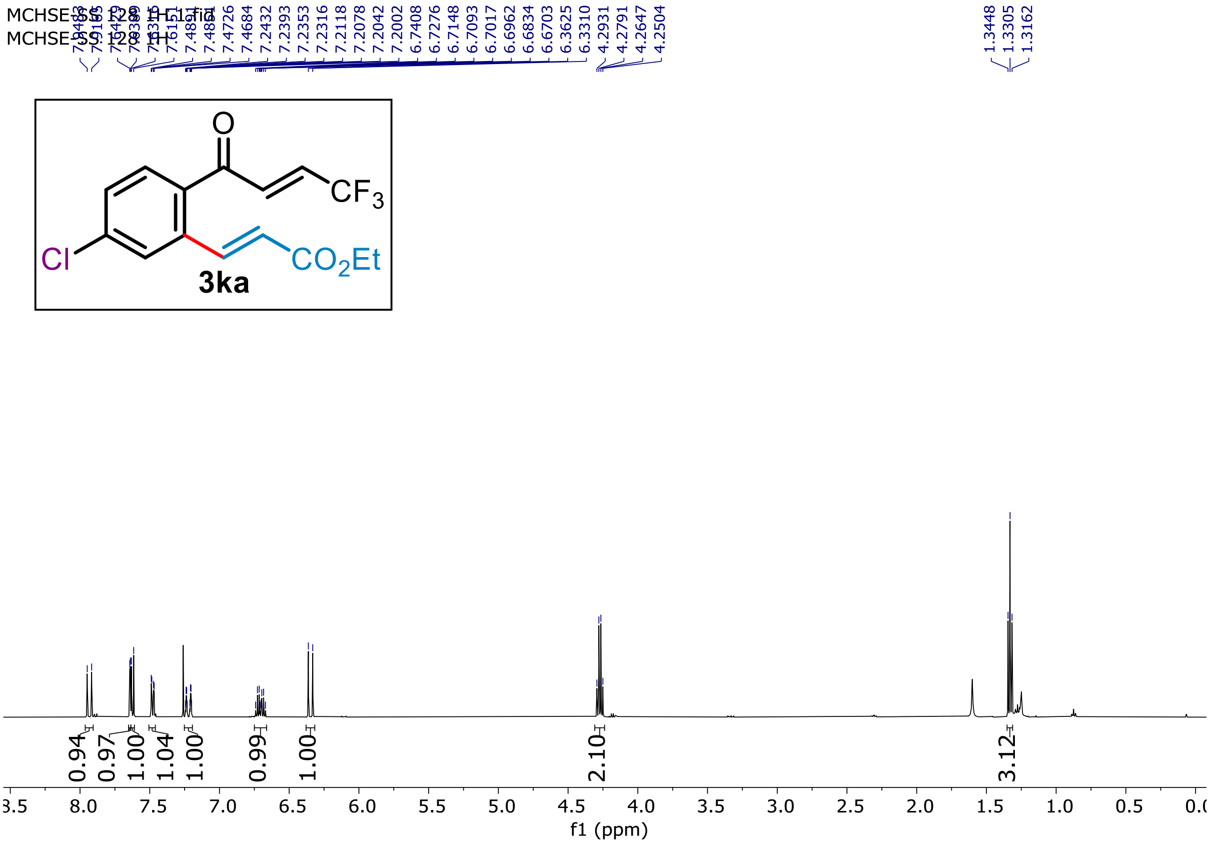

MCHSE-SS25 13C.1.fid
MCHSE-SS25 13C
191.9139
166.1966
142.1576
140.7982
136.8550
135.2983
133.7999
133.7561
133.7122
133.6684
132.7255
131.5122
131.2309
130.9495
130.6681
129.5608
129.3232
128.4060
128.3731
125.5921
123.4396
122.1130
121.2908
119.1383
60.7549
14.2668
O
CF3
CO2Et
3ia
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

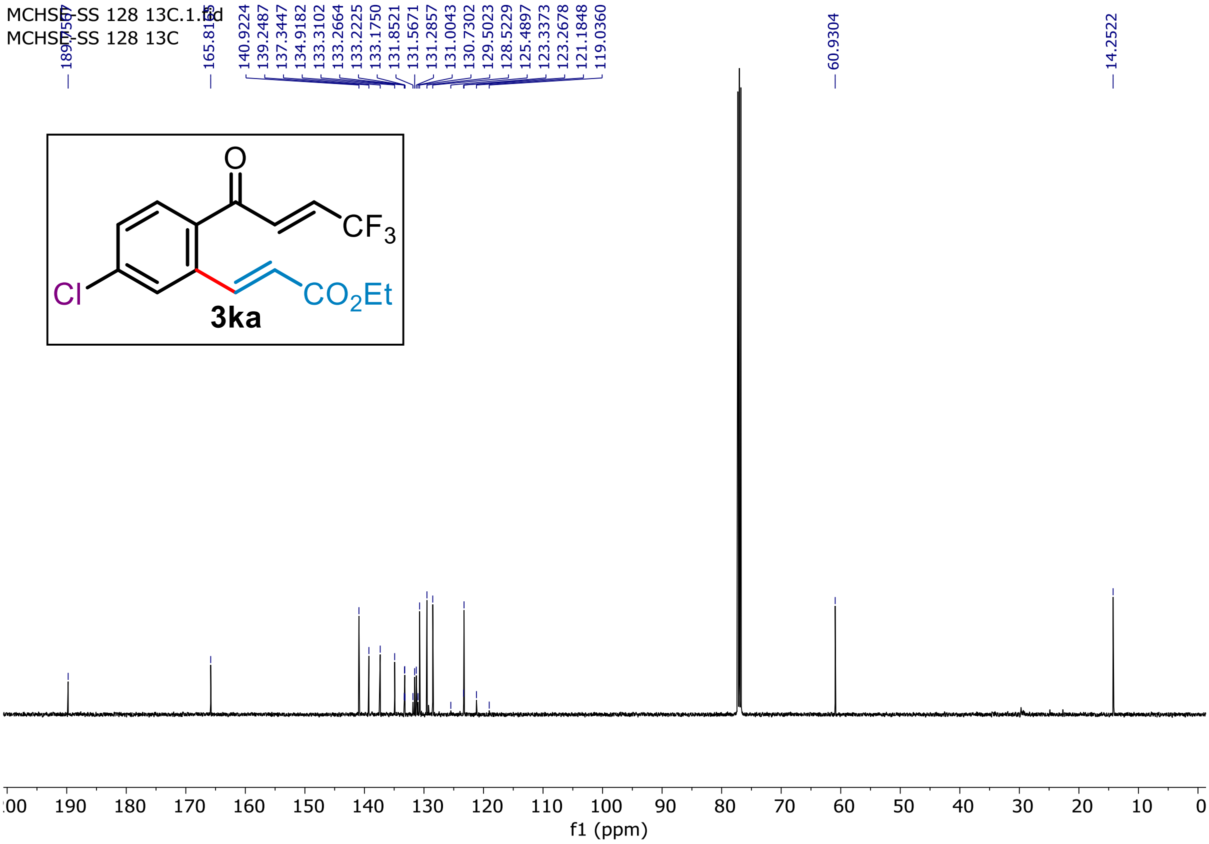

MCHSE-SS25 19F.1.fid
MCHSE-SS25 19F
-65.1622
O
CF3
CO2Et
3ia
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

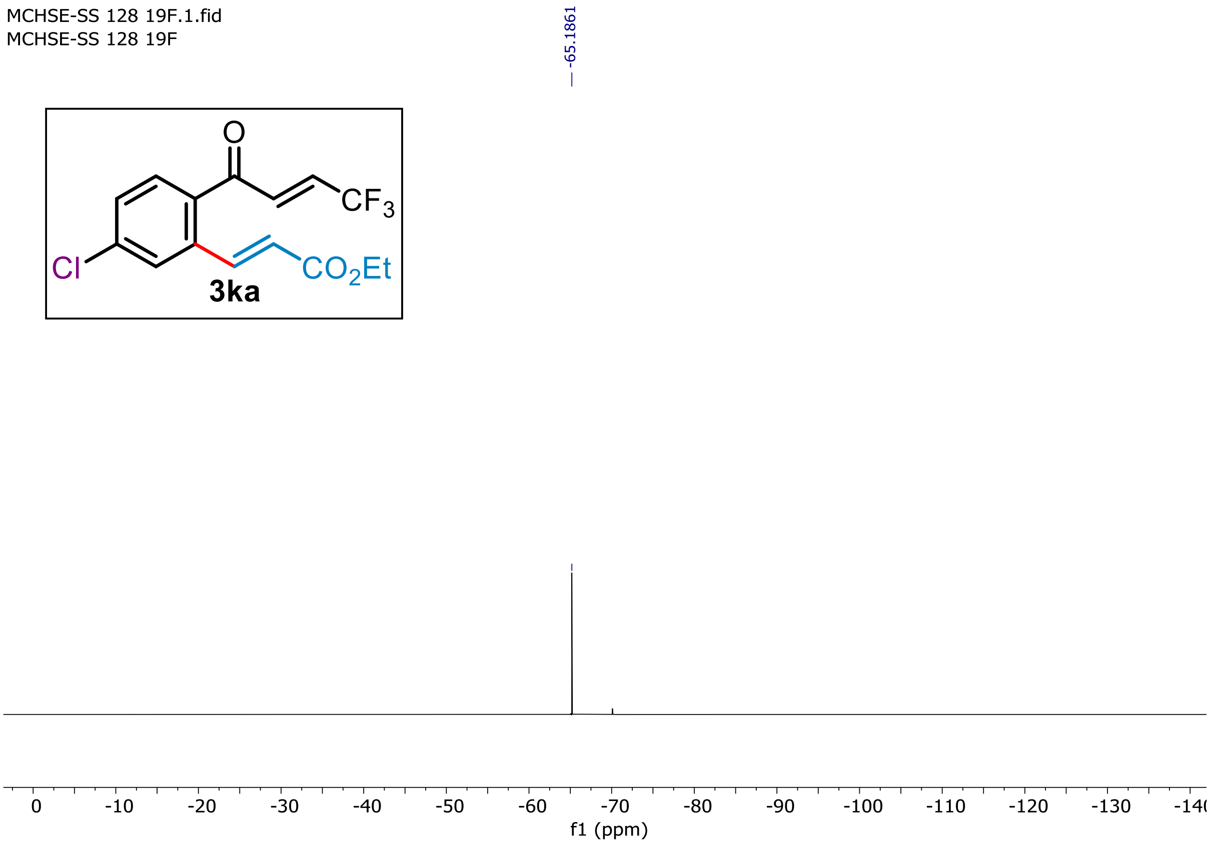

MCSHE-SS32 1H.1.fid
MCSHE-SS32
7.5540
7.2568
7.2528
7.2489
7.2449
7.2254
7.2214
7.2175
7.2135
6.7620
6.7489
6.7357
6.7302
6.7229
6.7174
6.7043
6.6915
6.3846
6.3529
4.3171
4.3027
4.2887
4.2744
1.3691
1.3548
1.3404
O
CF3
Br
CO2Et
3ja
0.95
0.99
0.97
0.98
0.98
0.97
0.98
2.00
3.01
f1 (ppm)

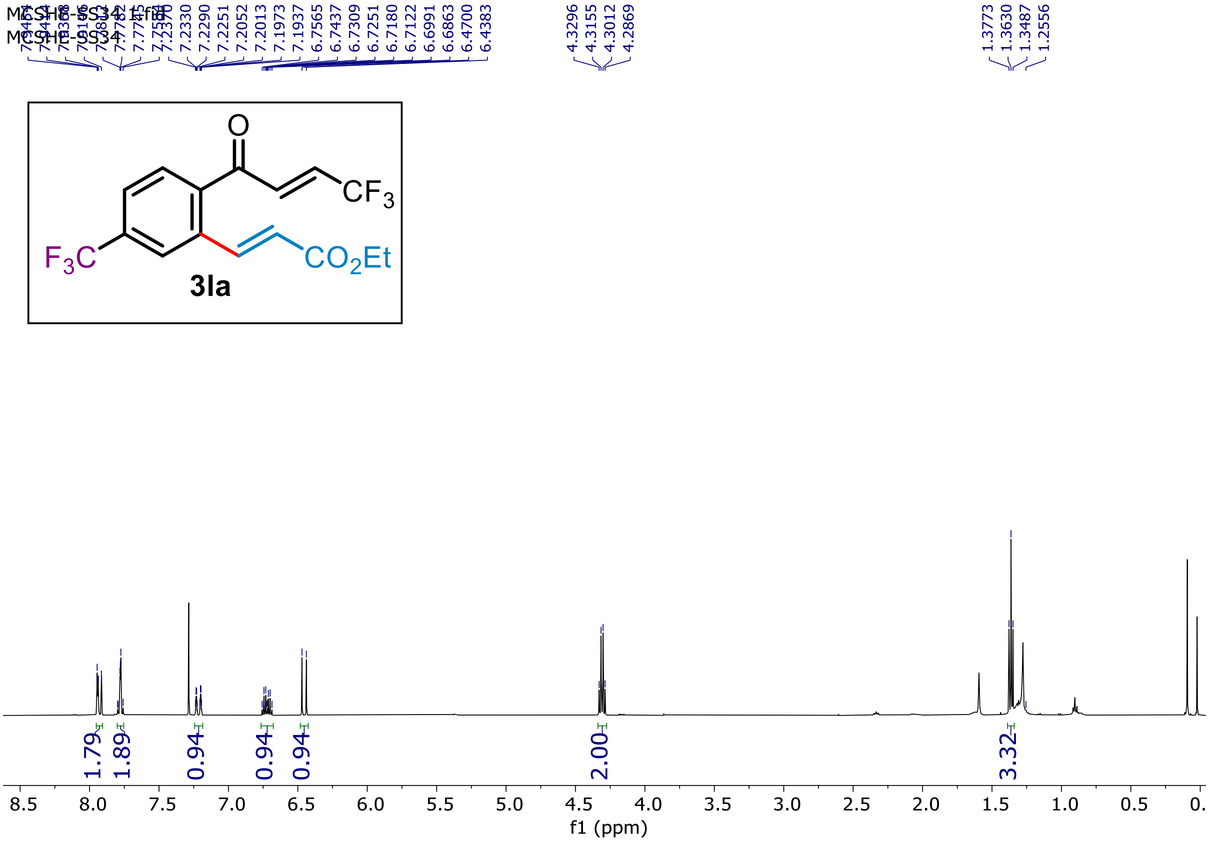

MCSHE-SS32 13C.1.fid
MCSHE-SS32
165.7836
140.7872
137.3192
135.3494
133.2956
133.2518
133.2043
133.1604
132.4770
131.8923
131.6073
131.4538
131.3259
131.0445
130.6827
127.7007
125.4788
123.3044
121.1775
60.9267
14.2485
O
CF3
Br
CO2Et
3ja
f1 (ppm)


MCSHE-SS32 19F.1.fid
MCSHE-SS32
-65.1898
CF3
Br
CO2Et
3ja
f1 (ppm)

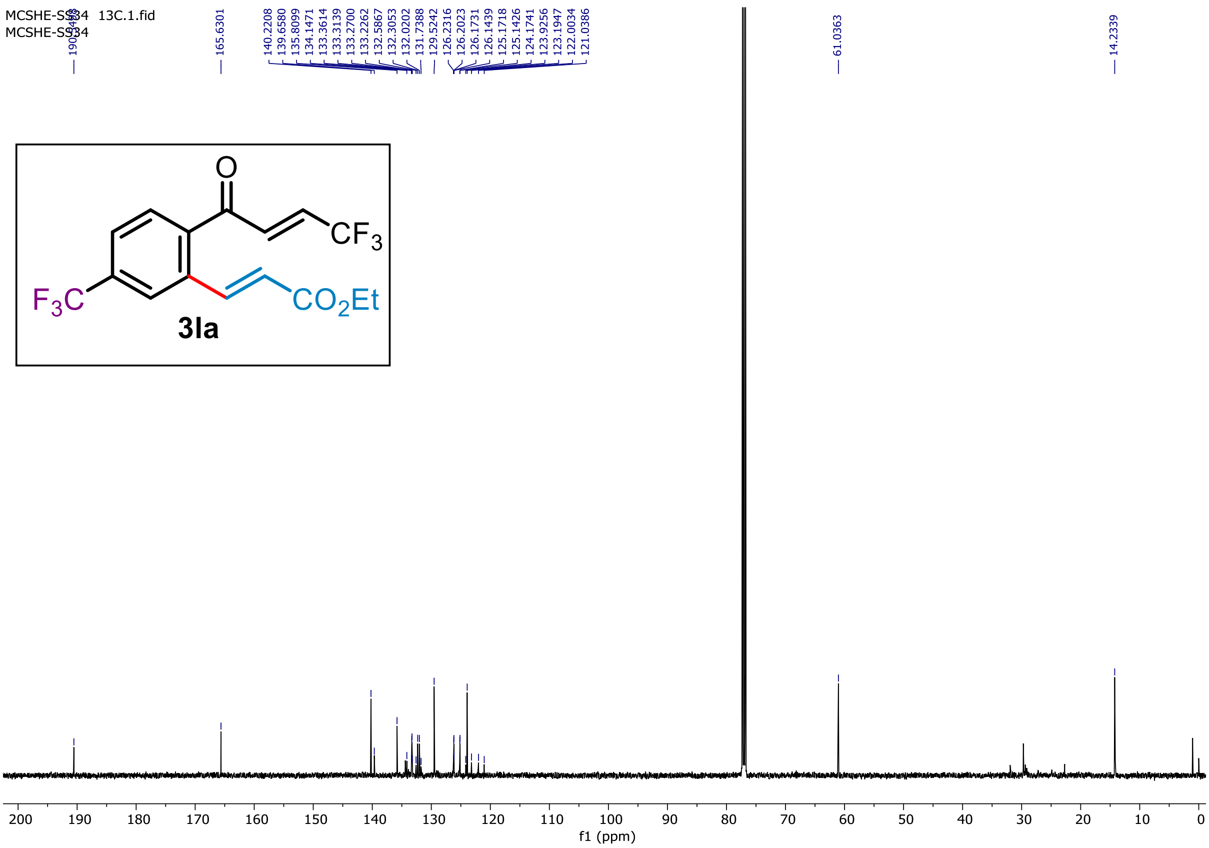

CF3
Cl
CO2Et
3ka
7.2432
7.2393
7.2353
7.2316
7.2118
7.2078
7.2042
7.2002
6.7408
6.7276
6.7148
6.7093
6.7017
6.6962
6.6834
6.6703
6.3625
6.3310
4.2931
4.2791
4.2647
4.2504
1.3448
1.3305
1.3162
0.94
0.97
1.00
1.04
1.00
0.99
1.00
2.10
3.12
f1 (ppm)



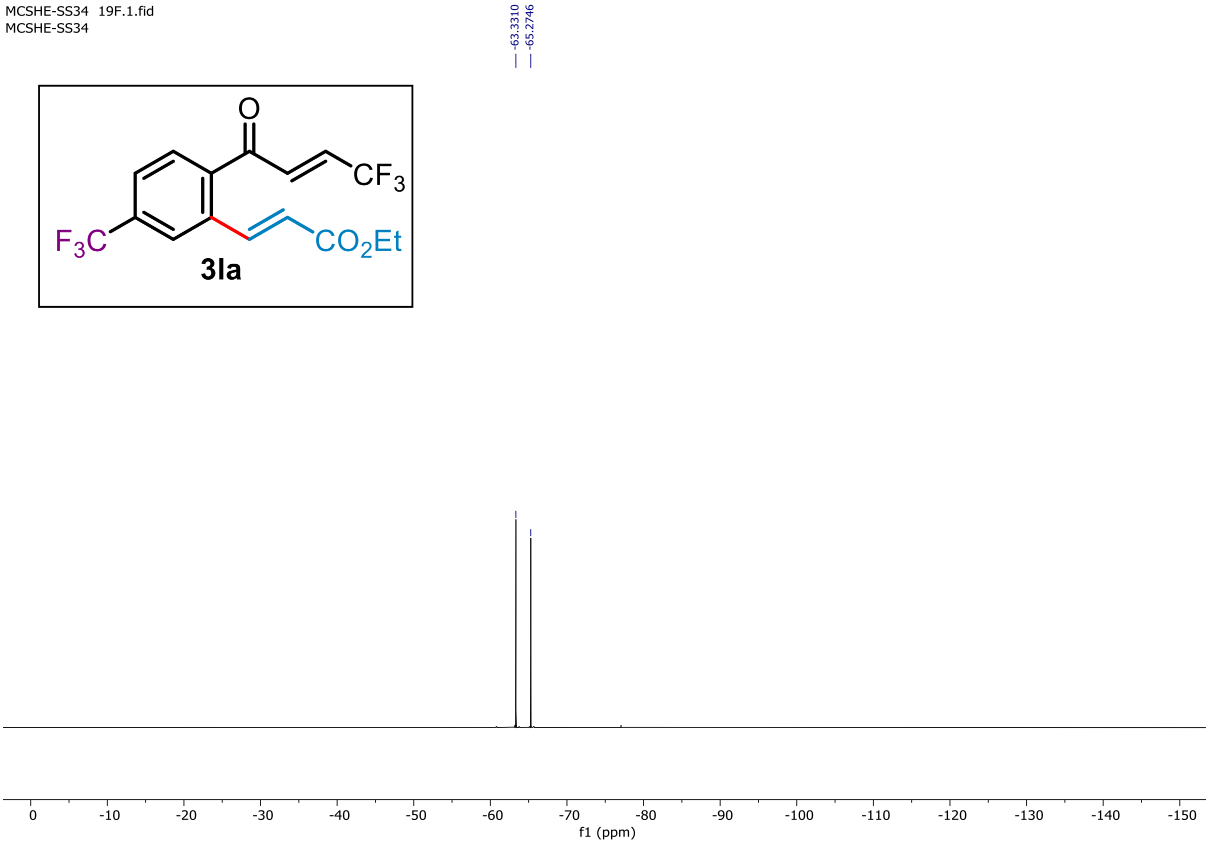


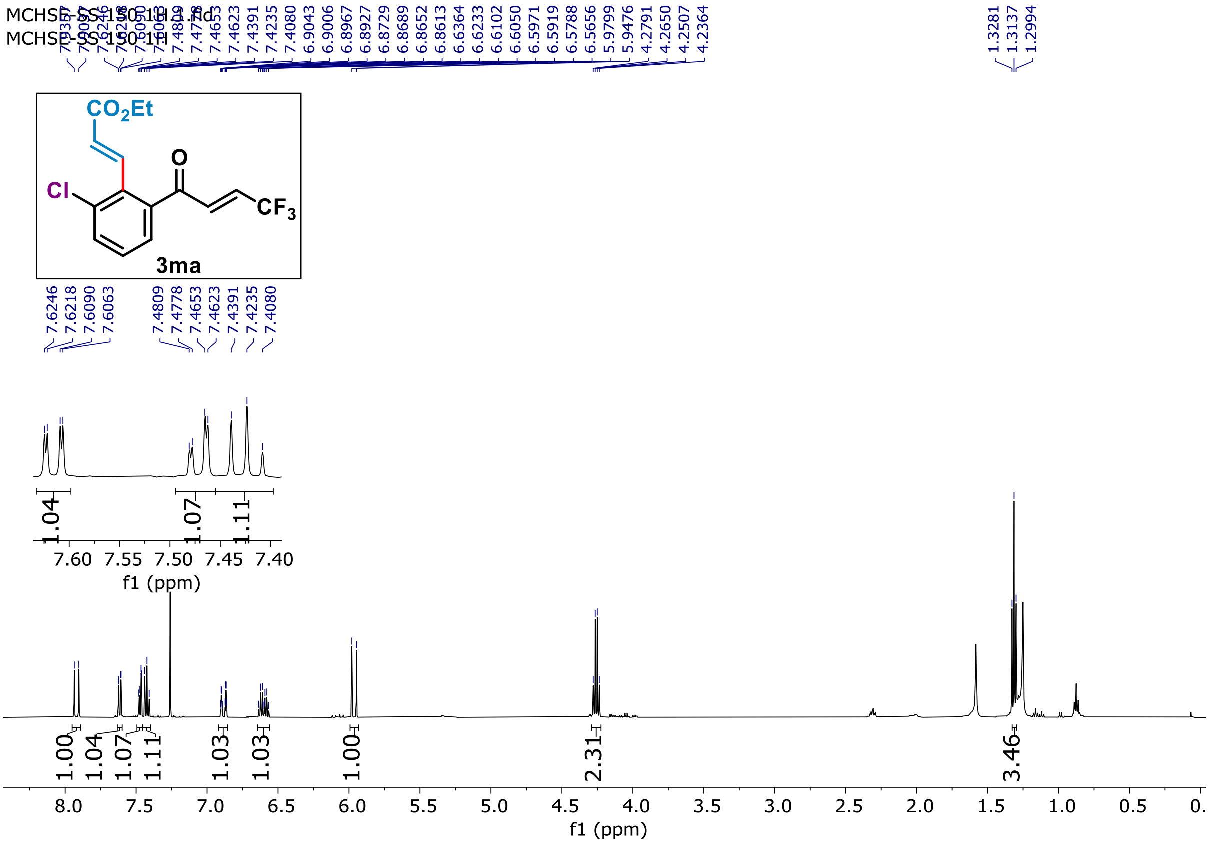


MCSHE-SS34
7.2330
7.2290
7.2251
7.2052
7.2013
7.1973
7.1937
6.7565
6.7437
6.7309
6.7251
6.7180
6.7122
6.6991
6.6863
6.4700
6.4383
4.3296
4.3155
4.3012
4.2869
1.3773
1.3630
1.3487
1.2556
O
CF3
F3C
CO2Et
3la
1.79
1.89
0.94
0.94
0.94
2.00
3.32
f1 (ppm)

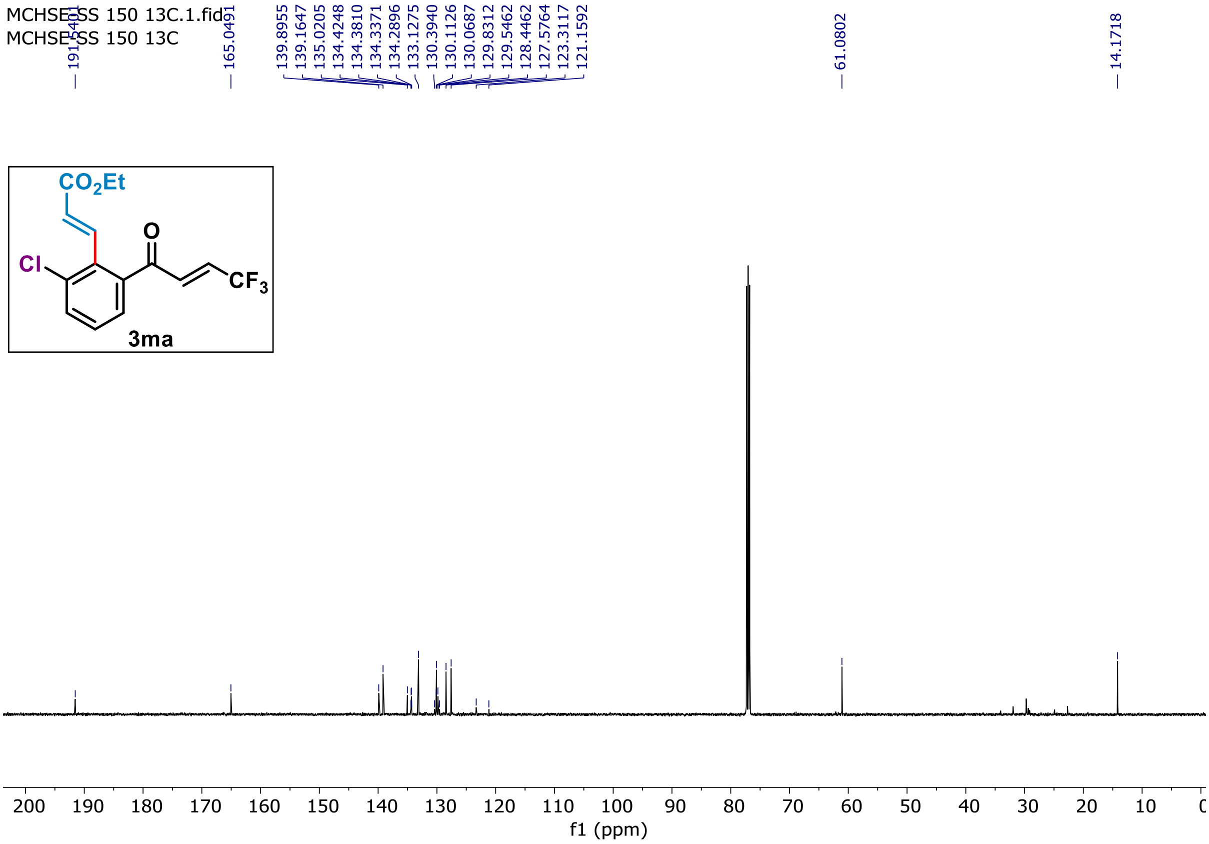


MCSHE-SS34 13C.1.fid
MCSHE-SS34
165.6301
140.2208
139.6580
135.8099
134.1471
133.3614
133.3139
133.2700
133.2262
132.5867
132.3053
132.0202
131.7388
129.5242
126.2316
126.2023
126.1731
126.1439
125.1718
125.1426
124.1741
123.9256
123.1947
122.0034
121.0386
61.0363
14.2339
O
CF3
F3C
CO2Et
3la
f1 (ppm)

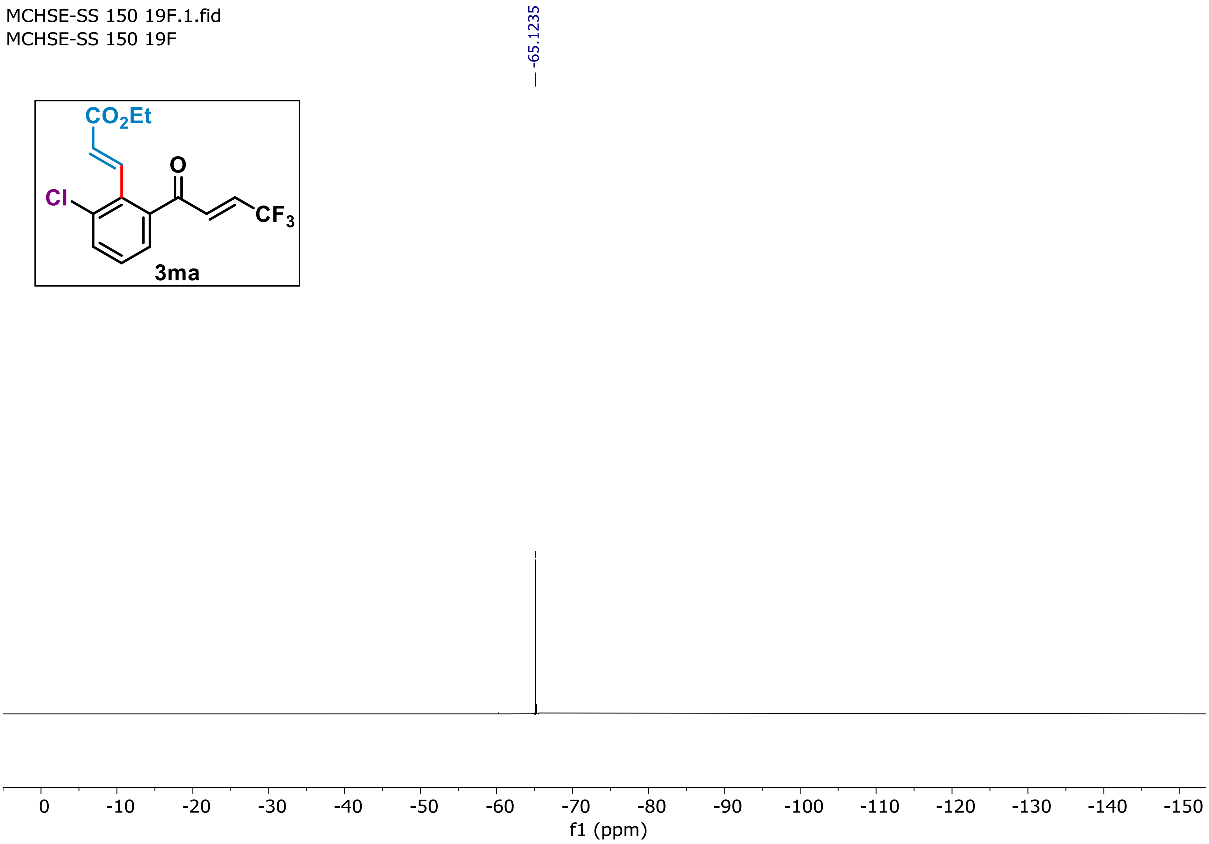

MCSHE-SS34 19F.1.fid
MCSHE-SS34
-63.3310
-65.2746
O
CF3
F3C
CO2Et
3la
f1 (ppm)

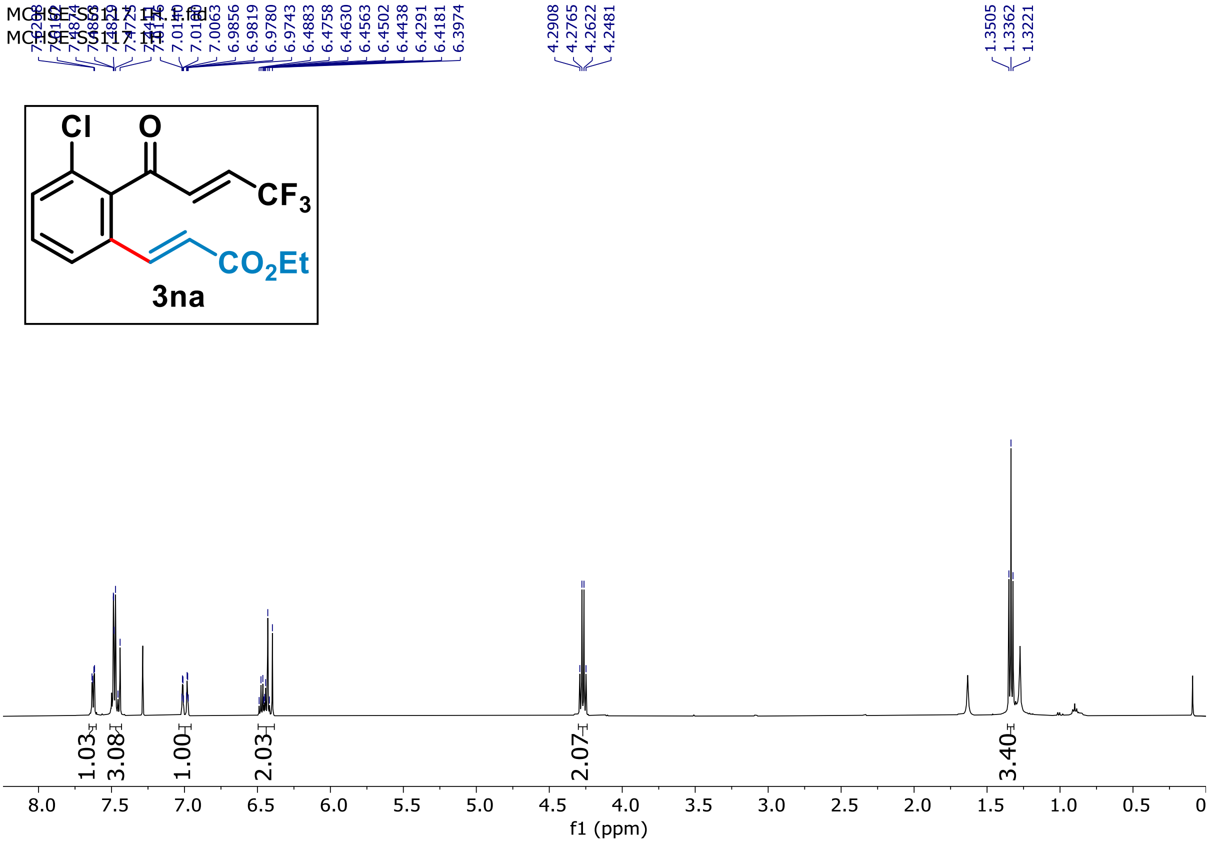

7.6246
7.6218
7.6090
7.6063
7.4809
7.4778
7.4653
7.4623
7.4391
7.4235
7.4080
6.9043
6.9006
6.8967
6.8927
6.8729
6.8689
6.8652
6.8613
6.6364
6.6233
6.6102
6.6050
6.5971
6.5919
6.5788
6.5656
5.9799
5.9476
4.2791
4.2650
4.2507
4.2364
1.3281
1.3137
1.2994
CO2Et
Cl
O
CF3
3ma
1.04
1.07
1.11
f1 (ppm)
1.00
1.04
1.07
1.11
1.03
1.03
1.00
2.31
3.46
f1 (ppm)

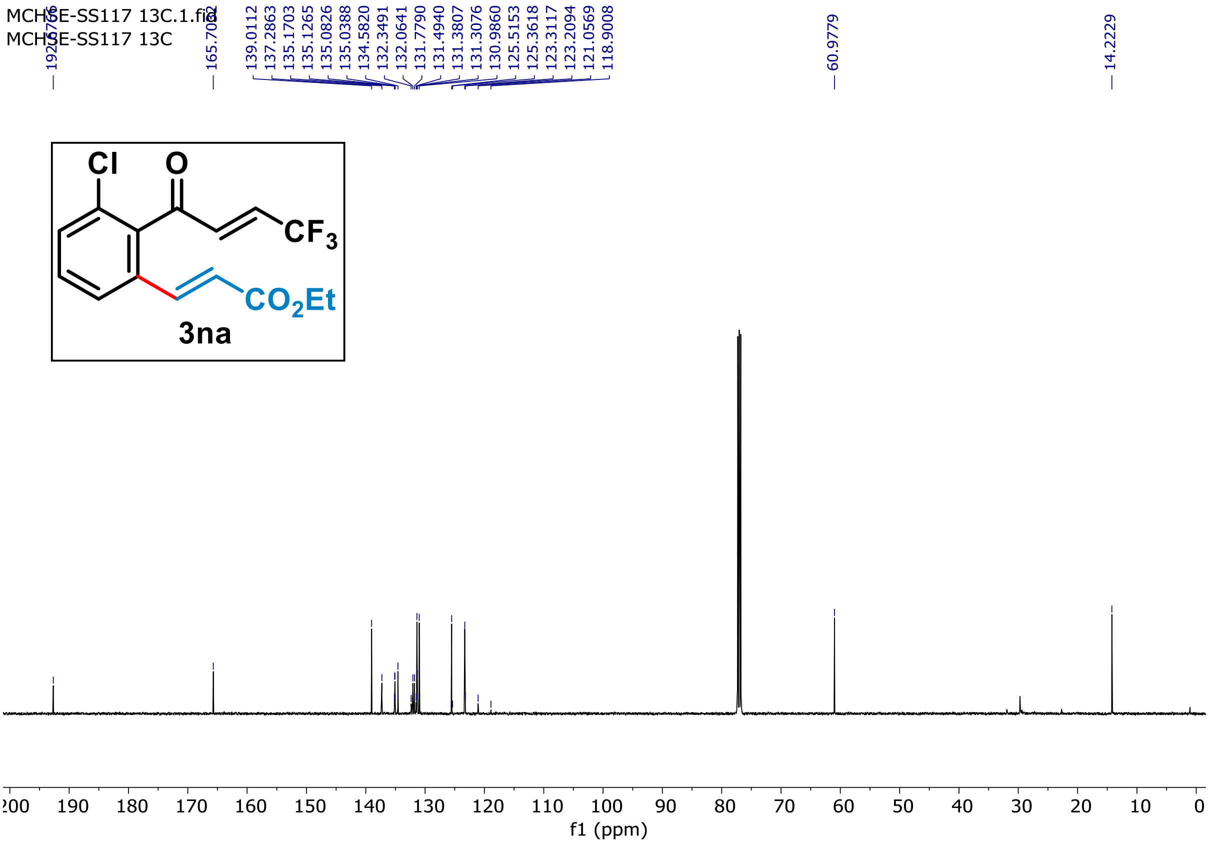
MCHSE-SS 150 13C.1.fid
MCHSE-SS 150 13C

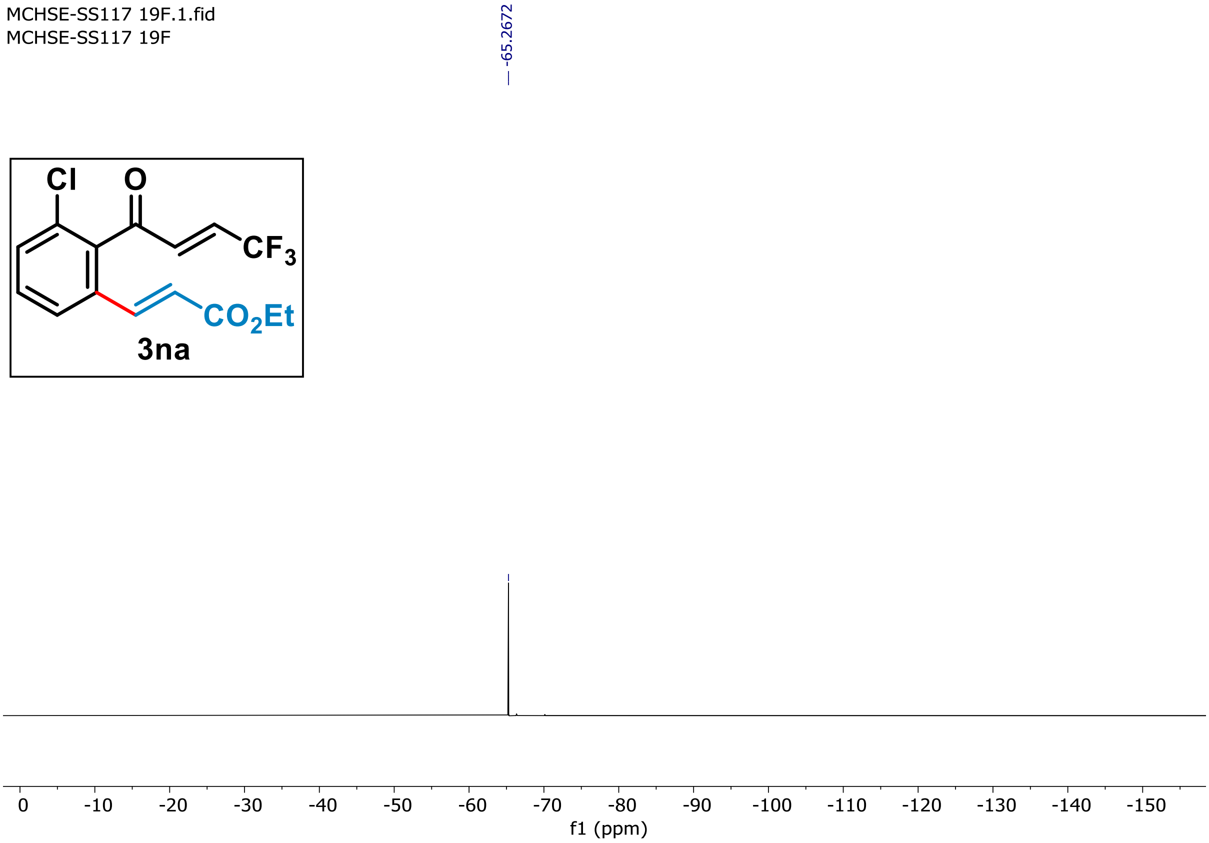


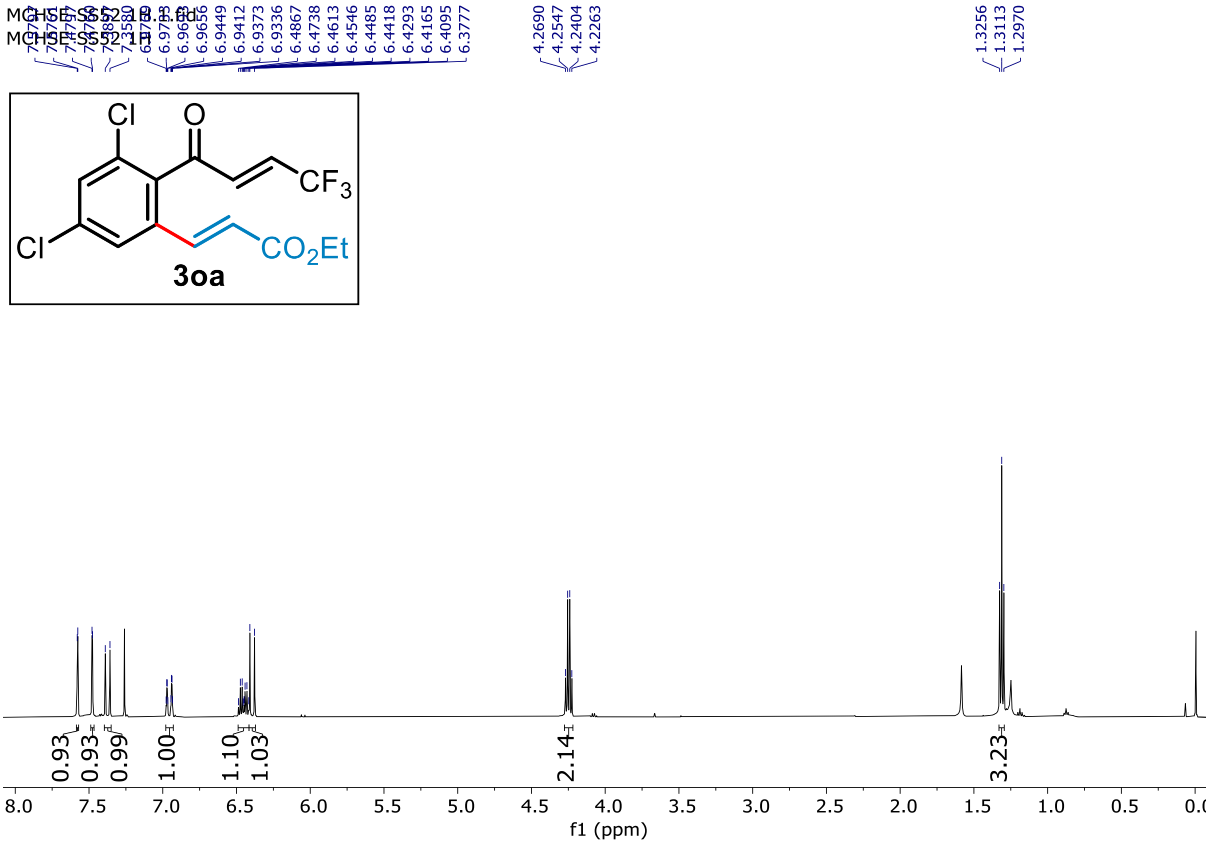
MCHSE-SS 150 19F.1.fid
MCHSE-SS 150 19F

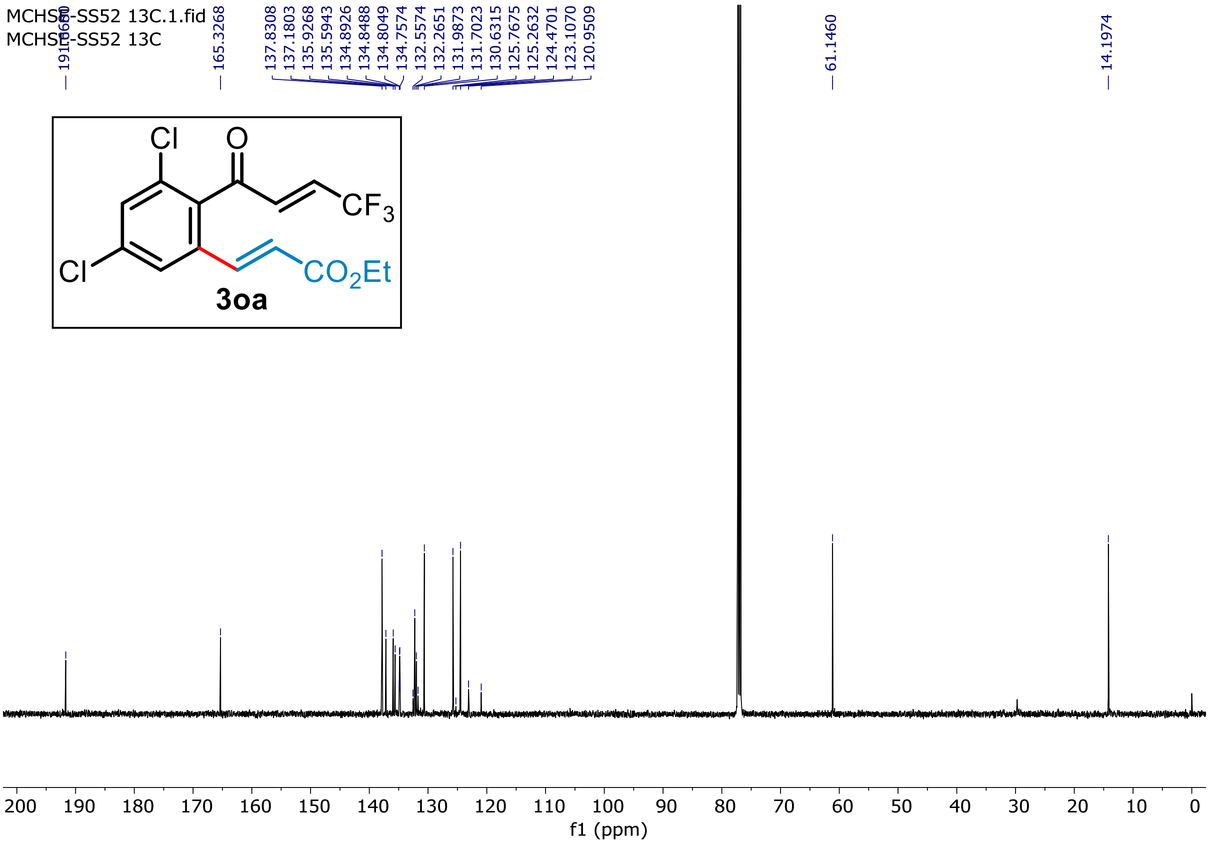


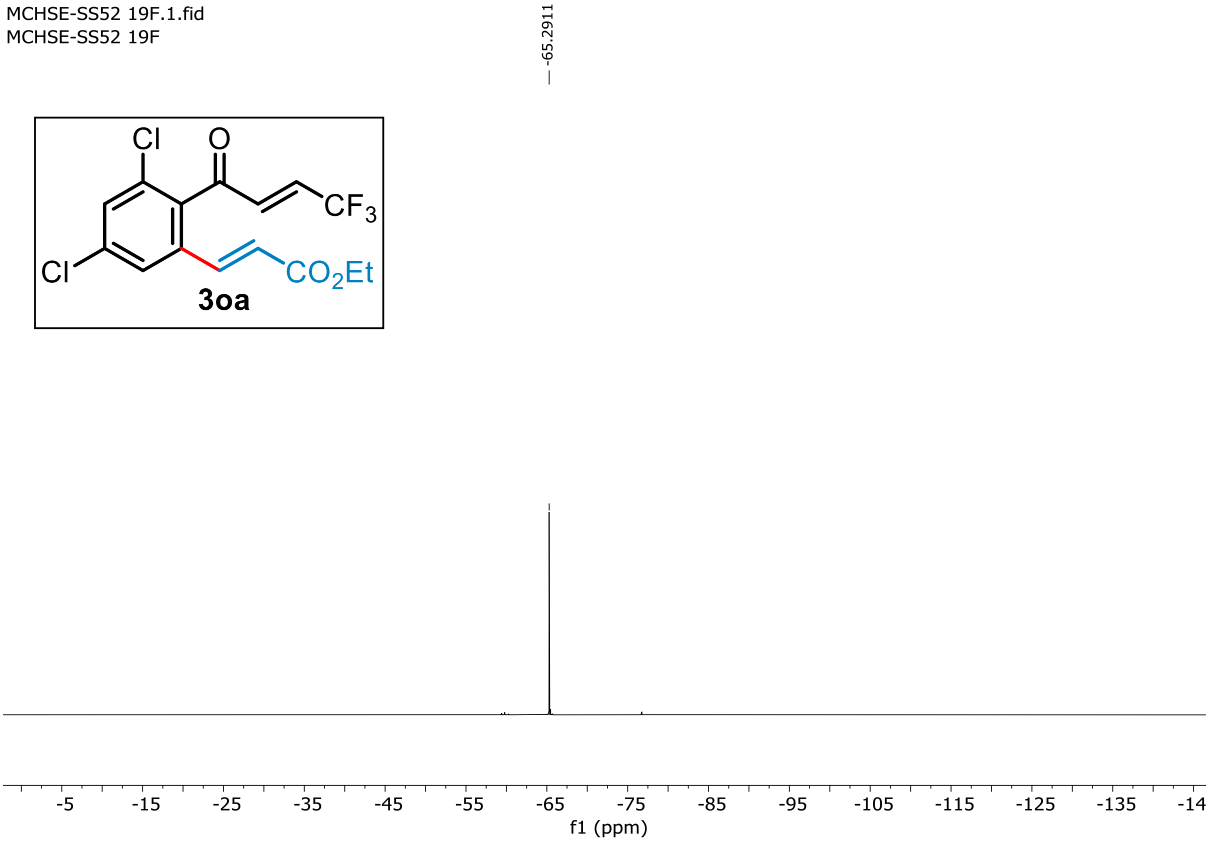


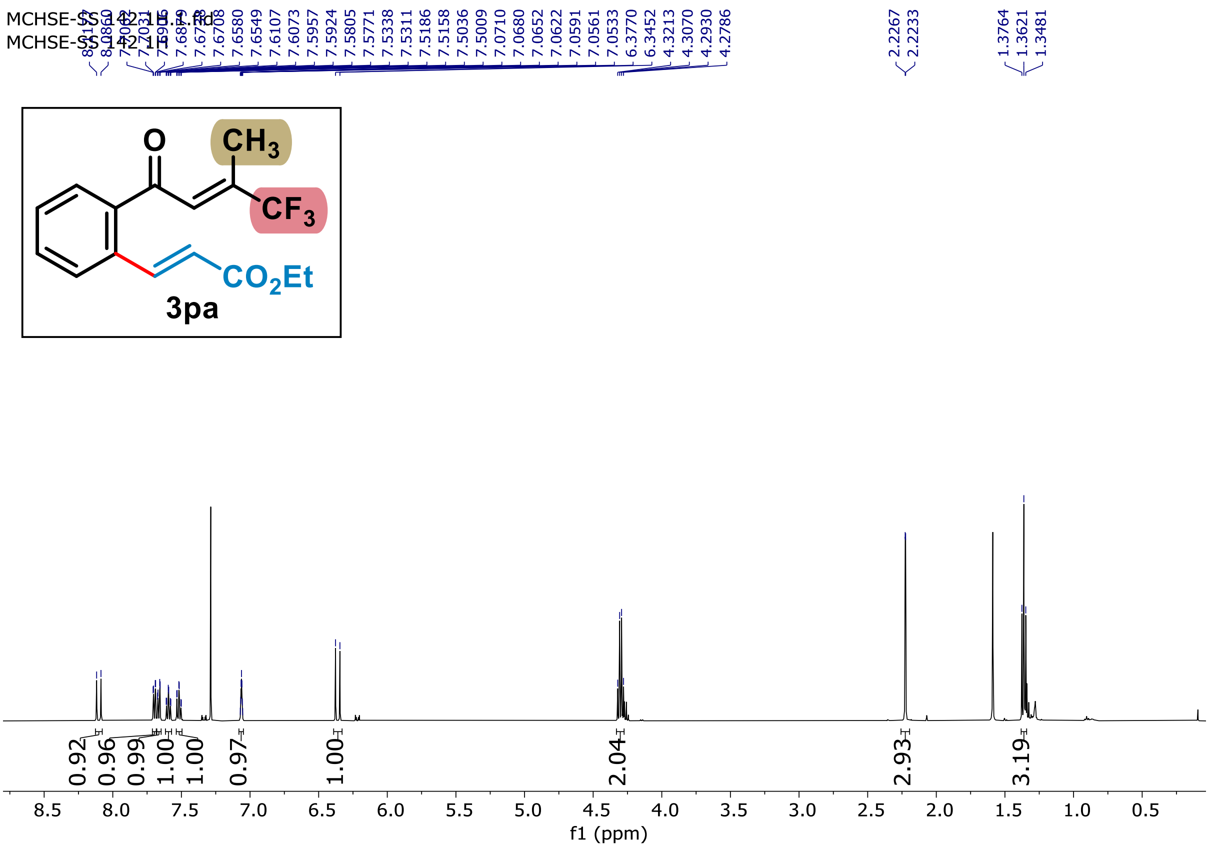


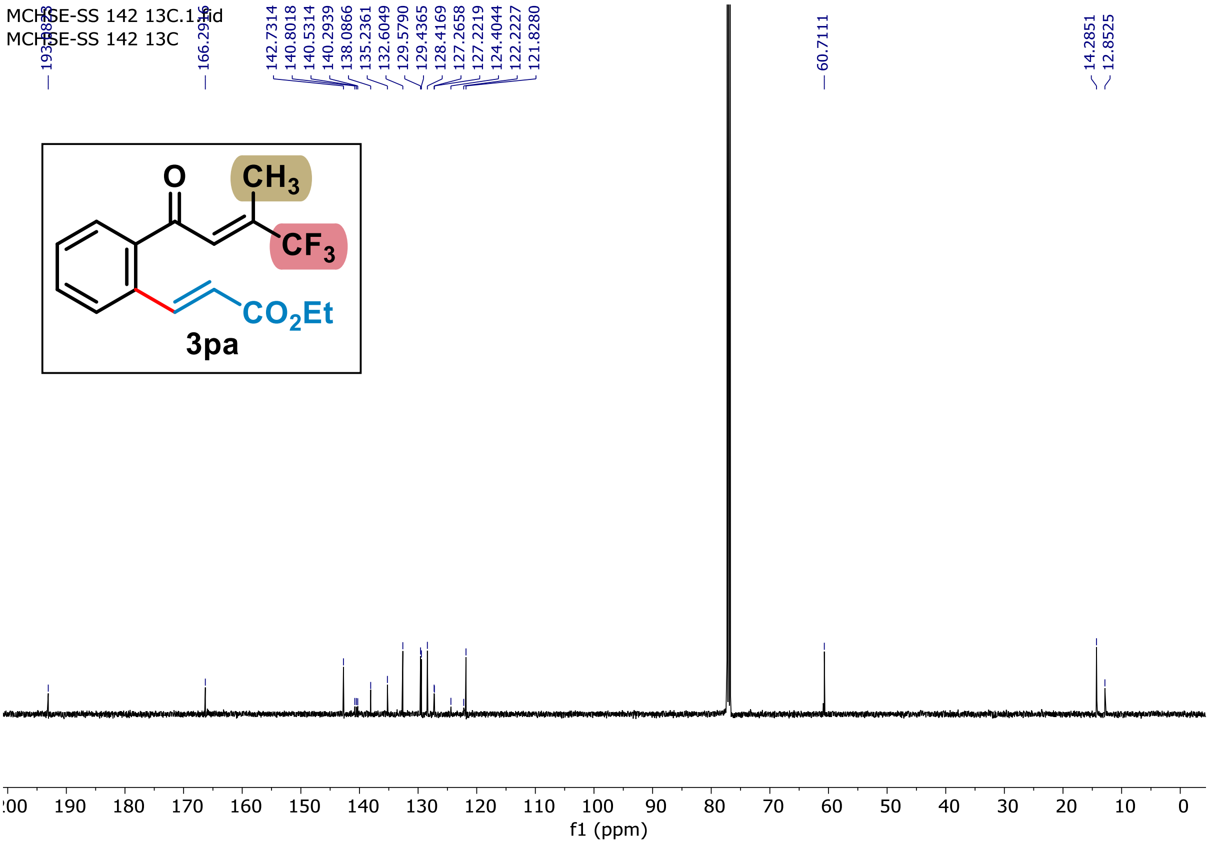

MCHSE-SS117 19F.1.fid
MCHSE-SS117 19F
-65.2672
3na
f1 (ppm)

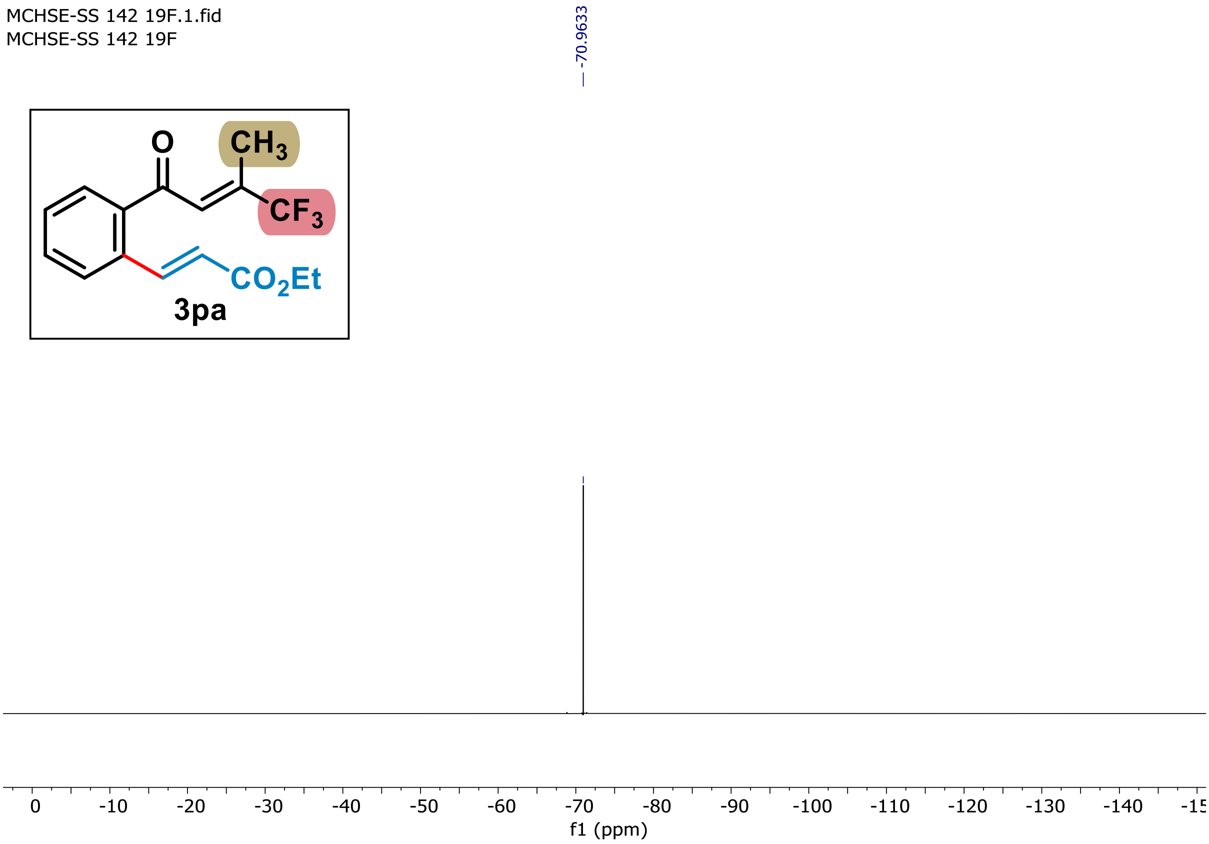

4.2690
4.2547
4.2404
4.2263
1.3256
1.3113
1.2970
3oa
0.93
0.93
0.99
1.00
1.10
1.03
2.14
3.23
f1 (ppm)

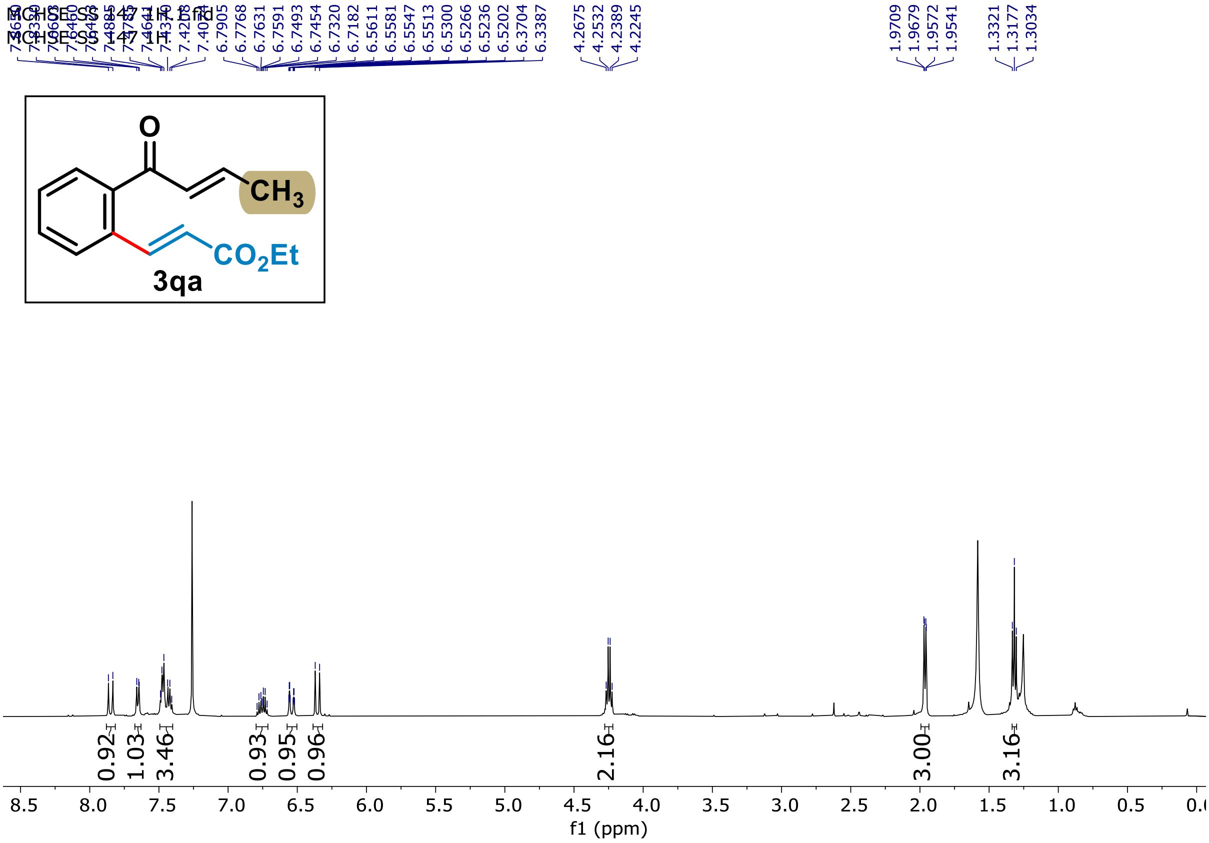

MCHSE-SS52 13C.1.fid
MCHSE-SS52 13C
165.3268
137.8308
137.1803
135.9268
135.5943
134.8926
134.8488
134.8049
134.7574
132.5574
132.2651
131.9873
131.7023
130.6315
125.7675
125.2632
124.4701
123.1070
120.9509
61.1460
14.1974
Cl
O
CF3
Cl
CO2Et
3oa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

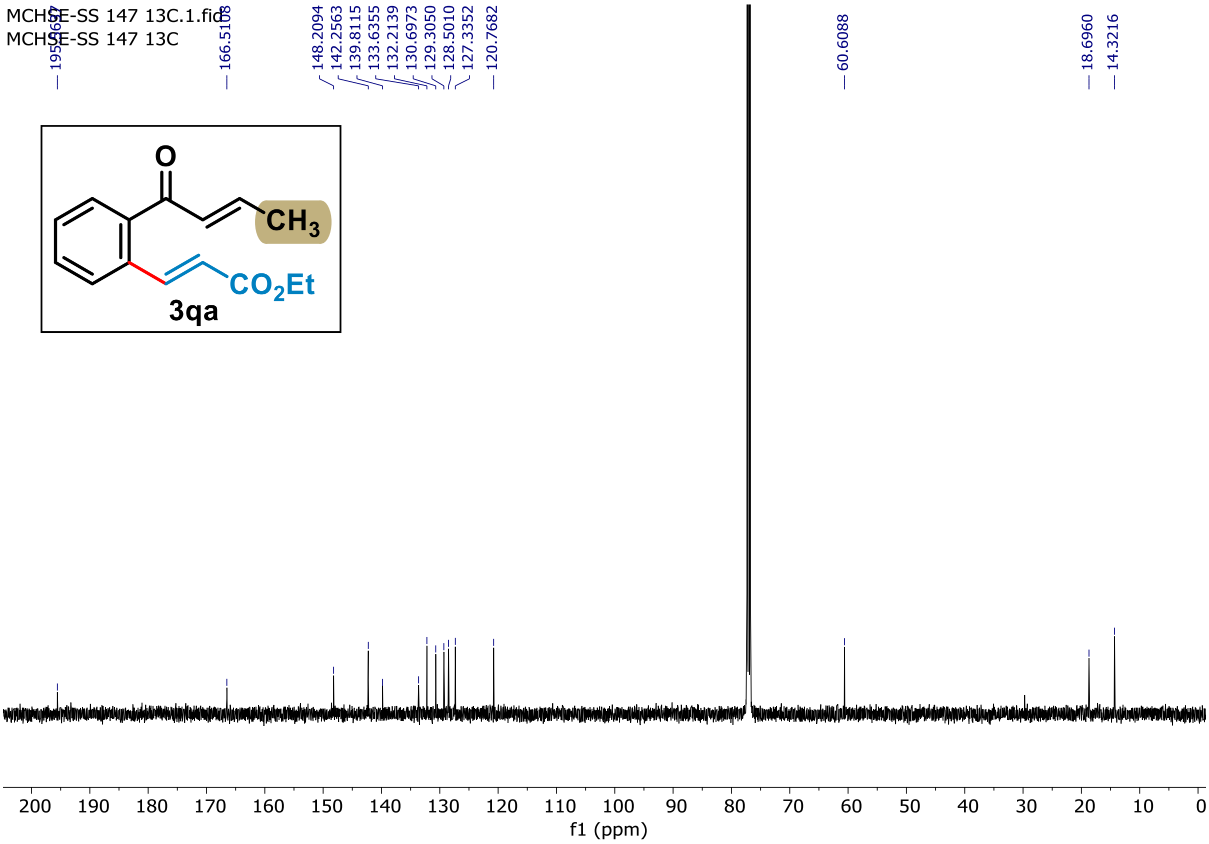

MCHSE-SS52 19F.1.fid
MCHSE-SS52 19F
-65.2911
Cl
O
CF3
Cl
CO2Et
3oa
-5
-15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
-14
f1 (ppm)

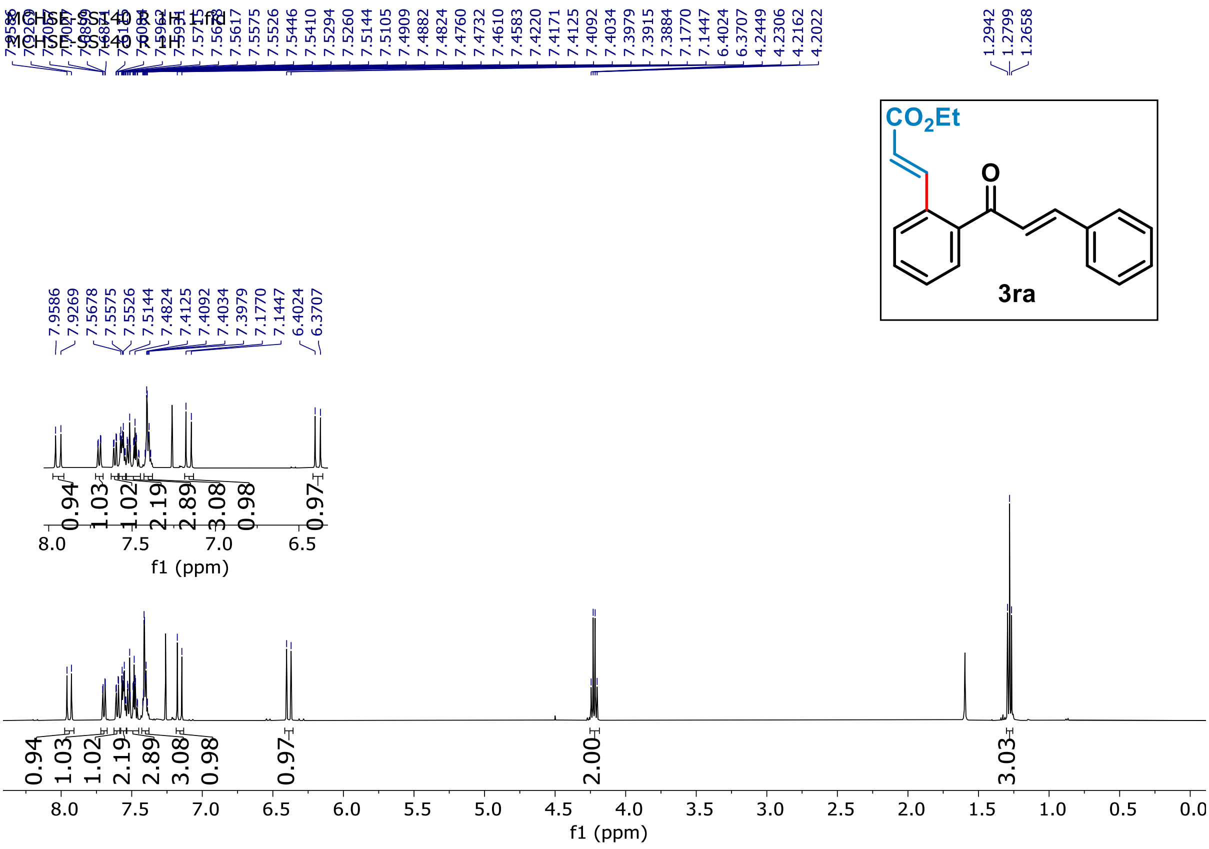

7.6580
7.6549
7.6107
7.6073
7.5957
7.5924
7.5805
7.5771
7.5338
7.5311
7.5186
7.5158
7.5036
7.5009
7.0710
7.0680
7.0652
7.0622
7.0591
7.0561
7.0533
6.3770
6.3452
4.3213
4.3070
4.2930
4.2786
2.2267
2.2233
1.3764
1.3621
1.3481
O
CH3
CF3
CO2Et
3pa
0.92
0.96
0.99
1.00
1.00
0.97
1.00
2.04
2.93
3.19
f1 (ppm)

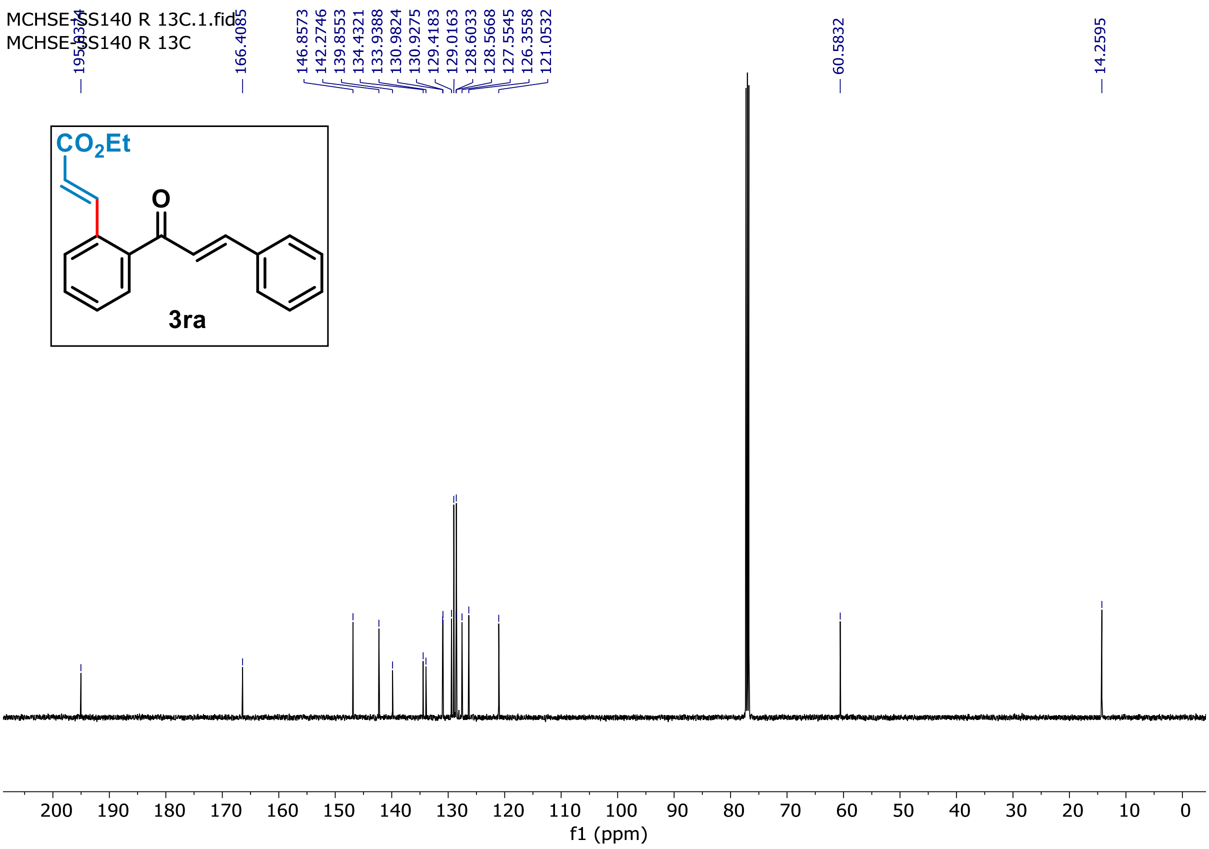

MCHSE-SS 142 13C.1.fid
MCHSE-SS 142 13C
166.2916
142.7314
140.8018
140.5314
140.2939
138.0866
135.2361
132.6049
129.5790
129.4365
128.4169
127.2658
127.2219
124.4044
122.2227
121.8280
60.7111
14.2851
12.8525
O
CH3
CF3
CO2Et
3pa
f1 (ppm)

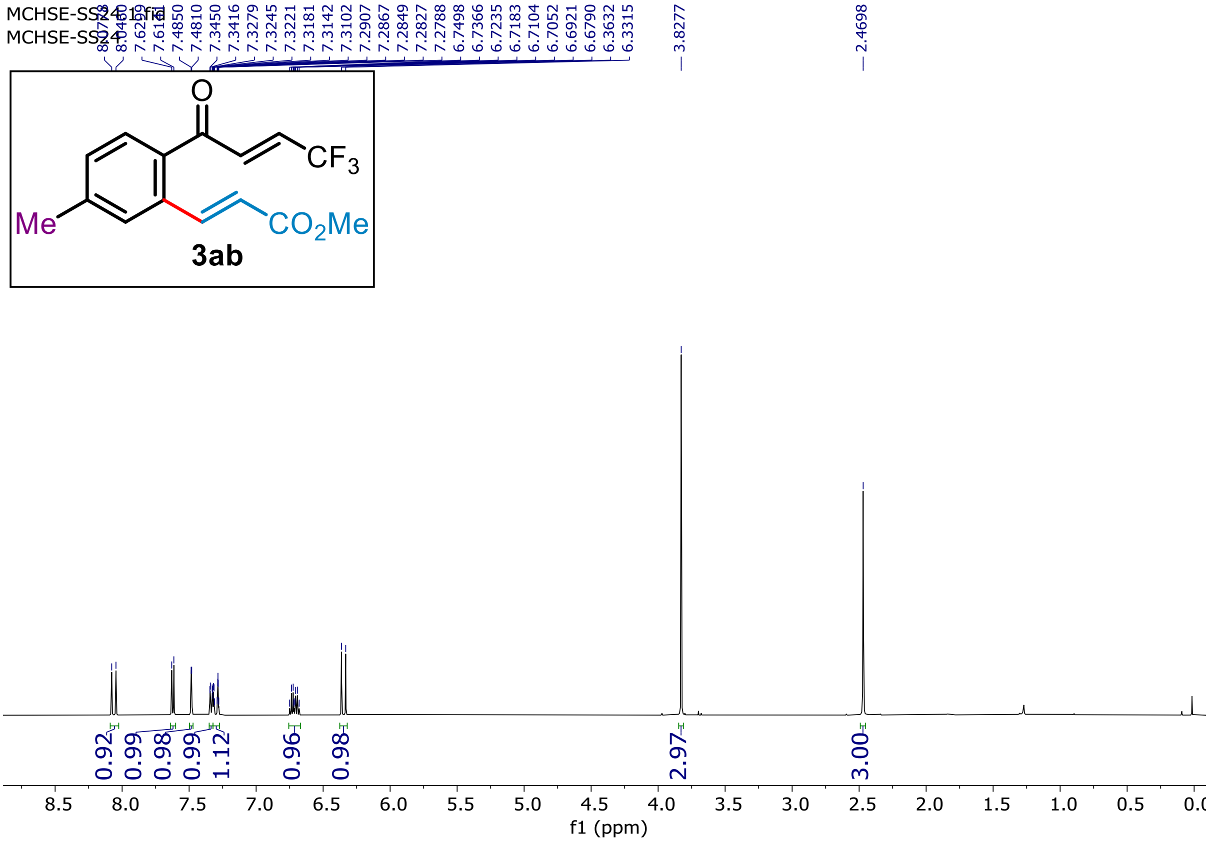

MCHSE-SS 142 19F.1.fid
MCHSE-SS 142 19F
-70.9633
O
CH3
CF3
CO2Et
3pa
f1 (ppm)

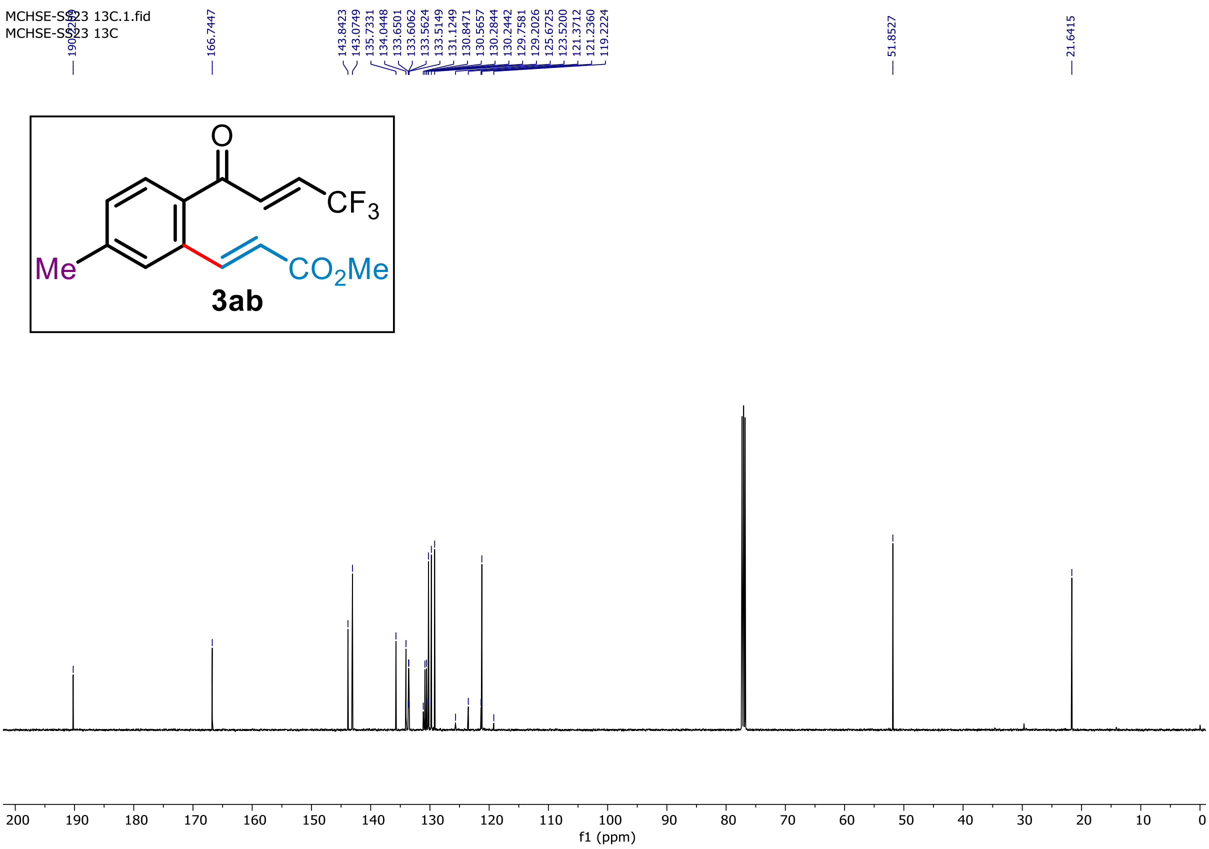

MCHSE-SS 147 1H.1.fid
MCHSE-SS 147 1H
CH3
CO2Et
3qa
0.92
1.03
3.46
0.93
0.95
0.96
2.16
3.00
3.16
f1 (ppm)


MCHSE-SS 147 13C.1.fid
MCHSE-SS 147 13C
166.5108
148.2094
142.2563
139.8115
133.6355
132.2139
130.6973
129.3050
128.5010
127.3352
120.7682
60.6088
18.6960
14.3216
CH3
CO2Et
3qa
f1 (ppm)

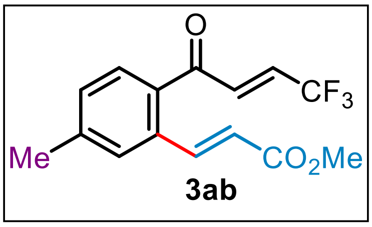

MCHSE-SS140 R 1H.1.fid
MCHSE-SS140 R 1H
CO2Et
O
3ra
f1 (ppm)

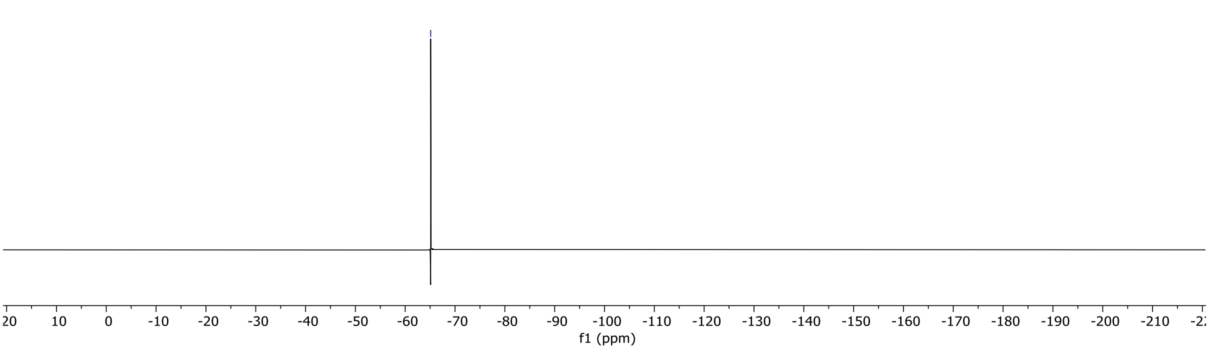

MCHSE-SS140 R 13C.1.fid
MCHSE-SS140 R 13C
166.4085
60.5832
14.2595
CO2Et
O
3ra
f1 (ppm)


MCHSE-SS24
7.4850
7.4810
7.3450
7.3416
7.3279
7.3245
7.3221
7.3181
7.3142
7.3102
7.2907
7.2867
7.2849
7.2827
7.2788
6.7498
6.7366
6.7235
6.7183
6.7104
6.7052
6.6921
6.6790
6.3632
6.3315
3.8277
2.4698
CF3
Me
CO2Me
3ab
0.92
0.99
0.98
0.99
1.12
0.96
0.98
2.97
3.00
f1 (ppm)

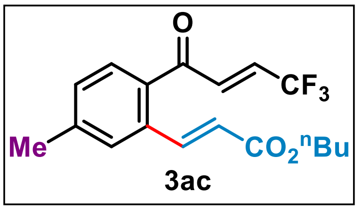

MCHSE-SS23 13C.1.fid
MCHSE-SS23 13C
166.7447
143.8423
143.0749
135.7331
134.0448
133.6501
133.6062
133.5624
133.5149
131.1249
130.8471
130.5657
130.2844
130.2442
129.7581
129.2026
125.6725
123.5200
121.3712
121.2360
119.2224
51.8527
21.6415
CF3
Me
CO2Me
3ab
f1 (ppm)

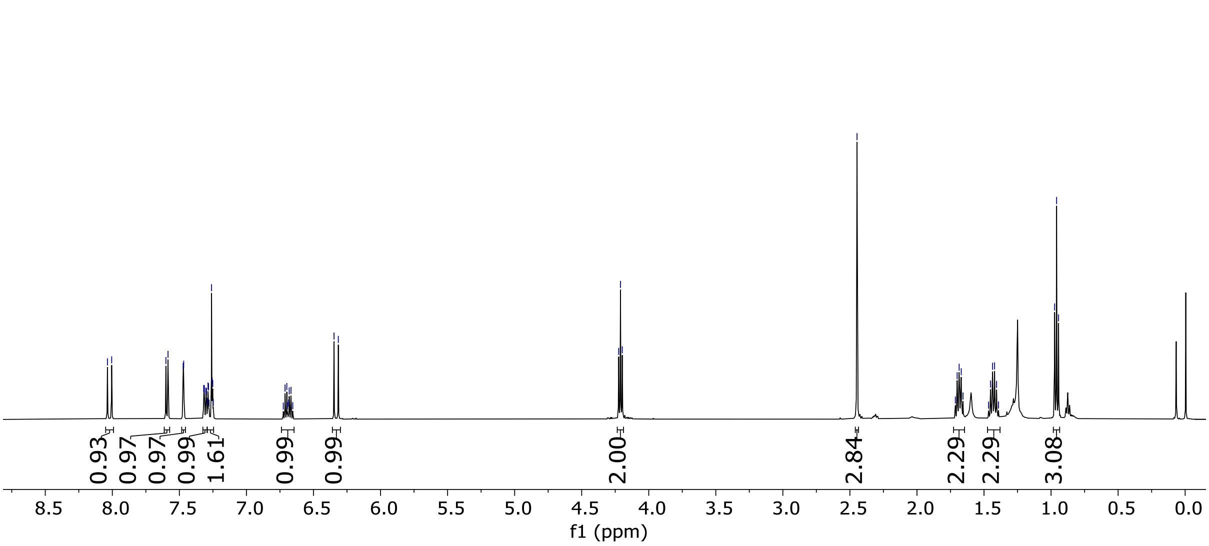
MCHSE-SS23 19F.1.fid
MCHSE-SS23 19F



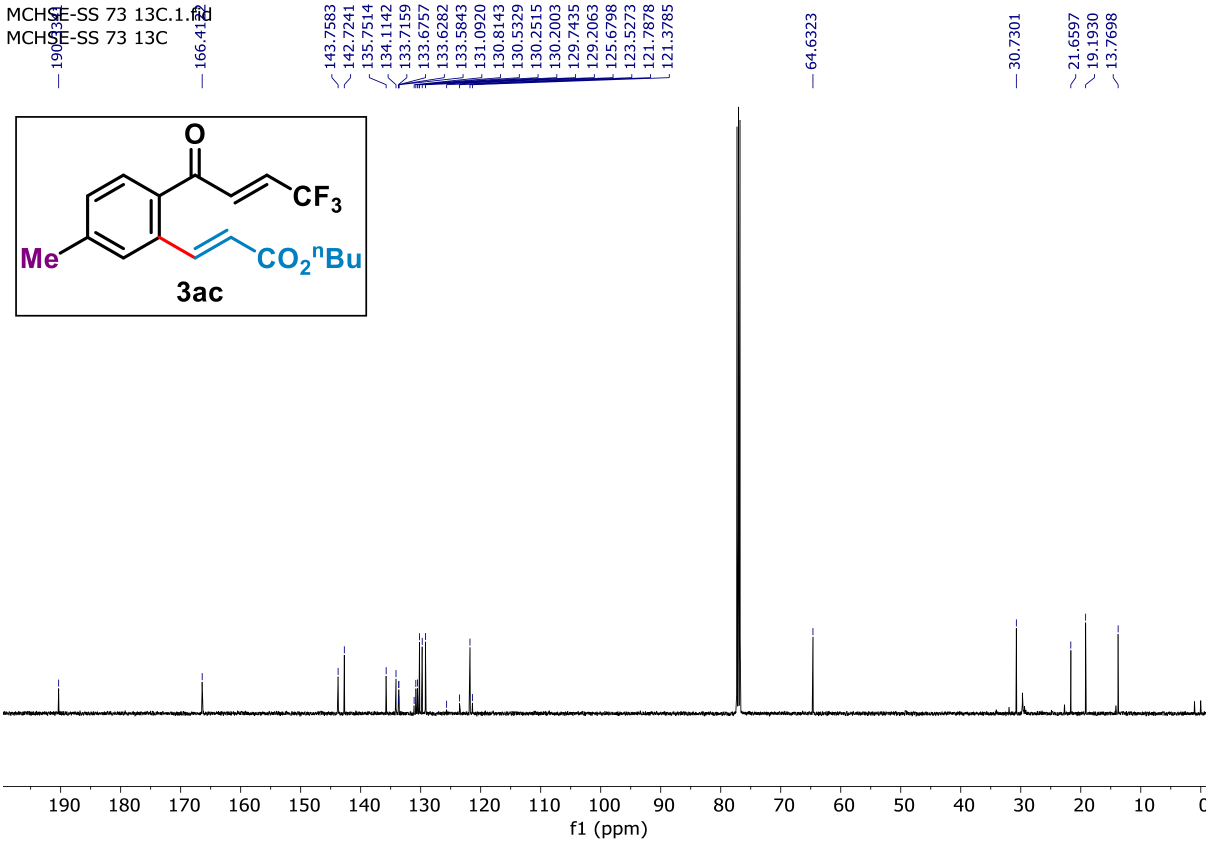


MCHSE-SS73 1H.1.fid
MCHSE-SS73 1H

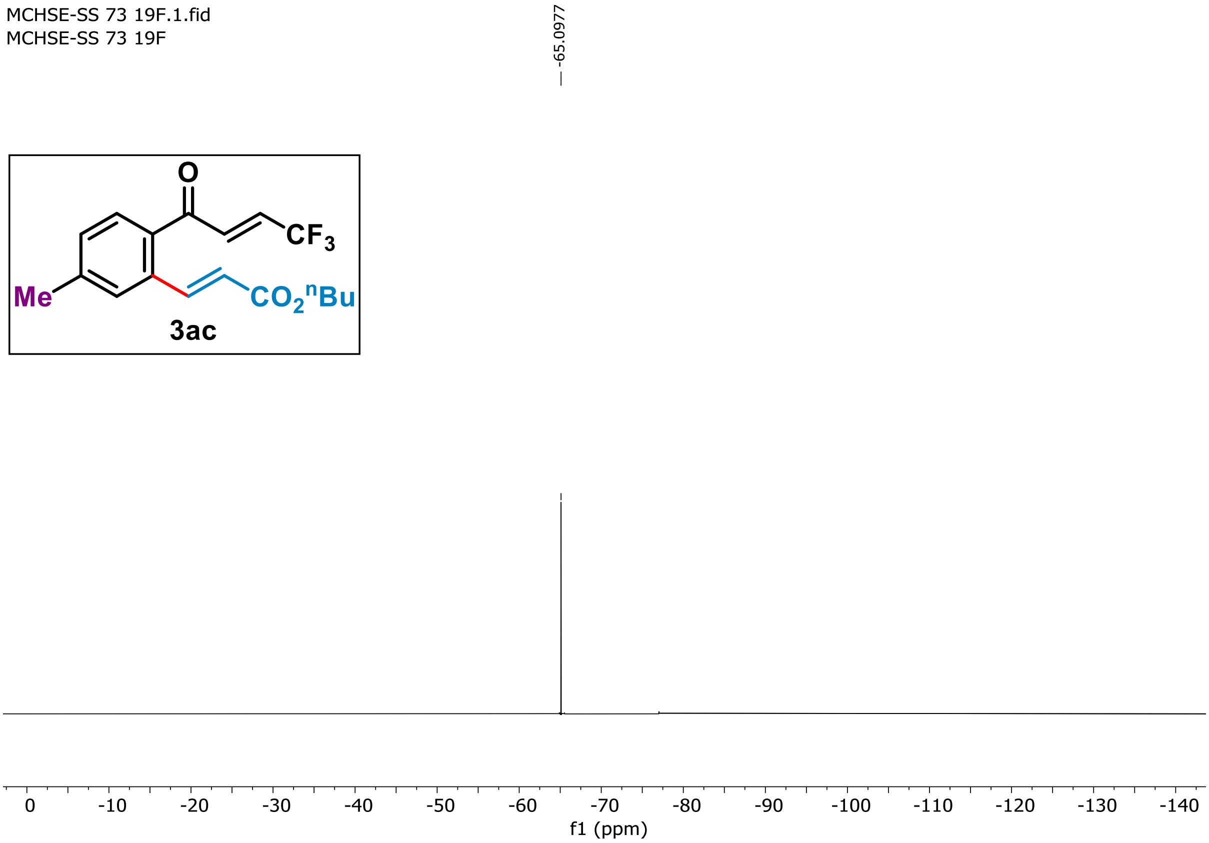


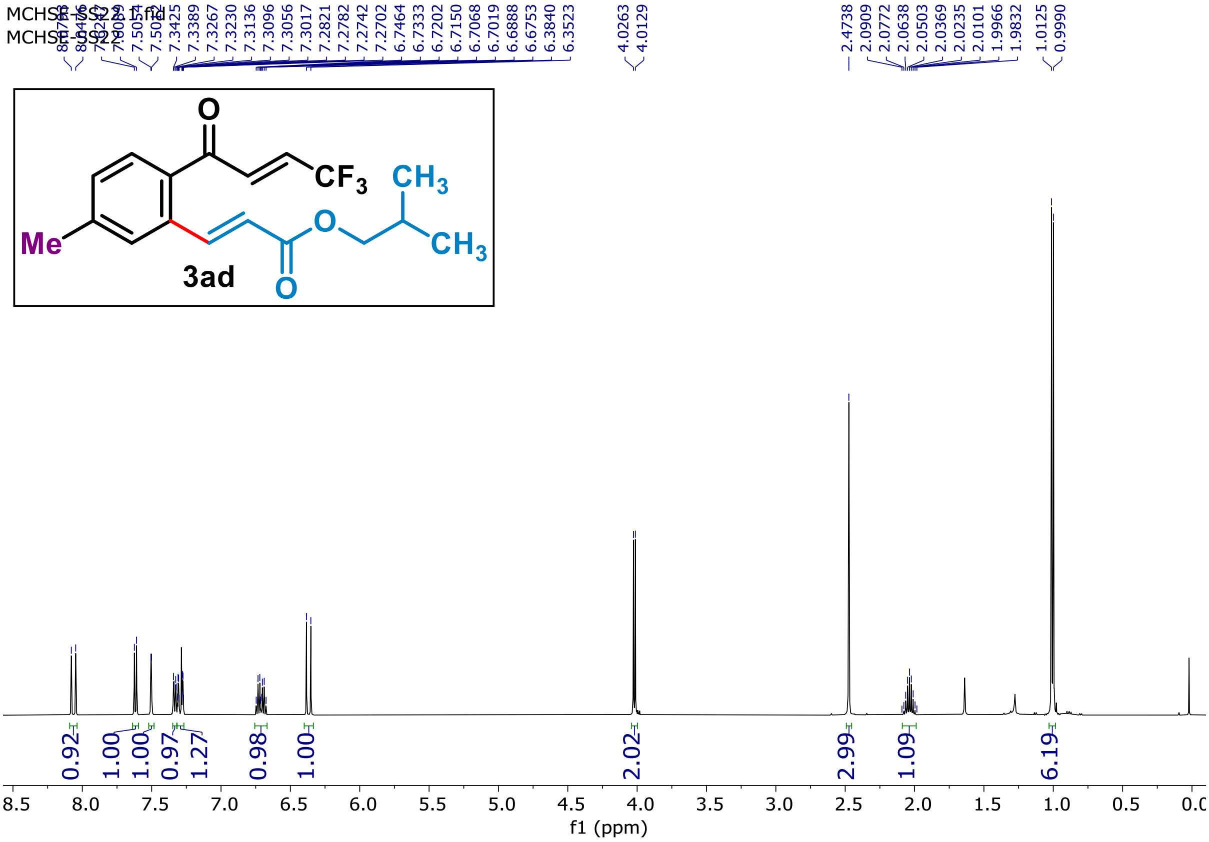


MCHSE-SS 73 13C.1.fid
MCHSE-SS 73 13C

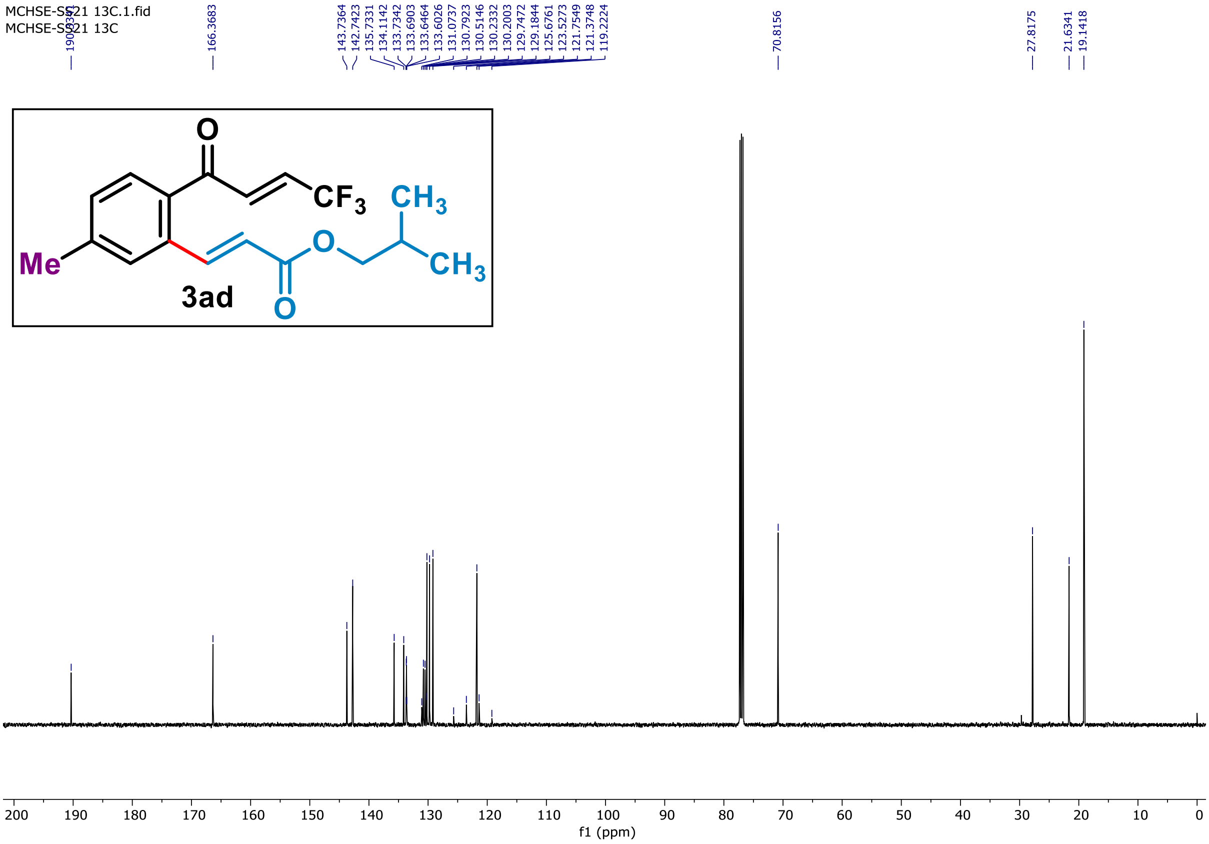


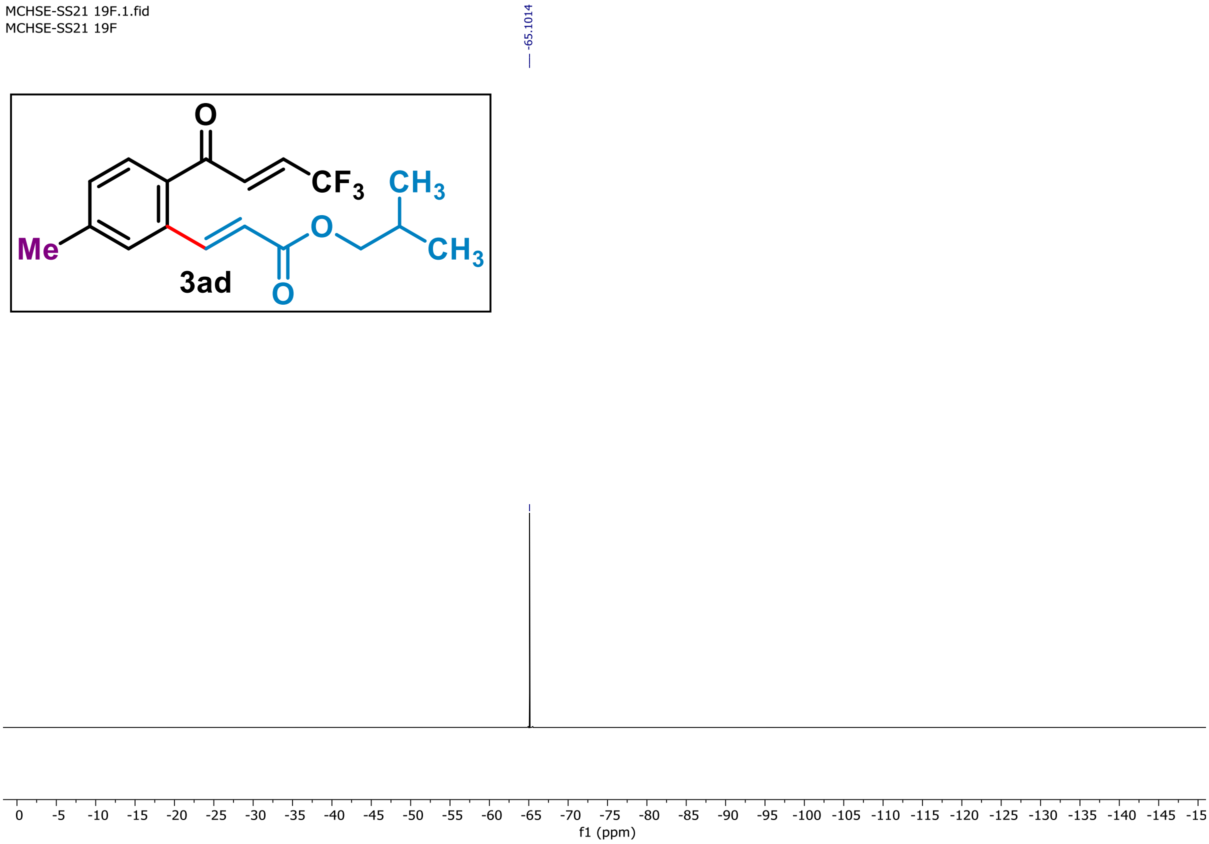
MCHSE-SS 73 19F.1.fid
MCHSE-SS 73 19F

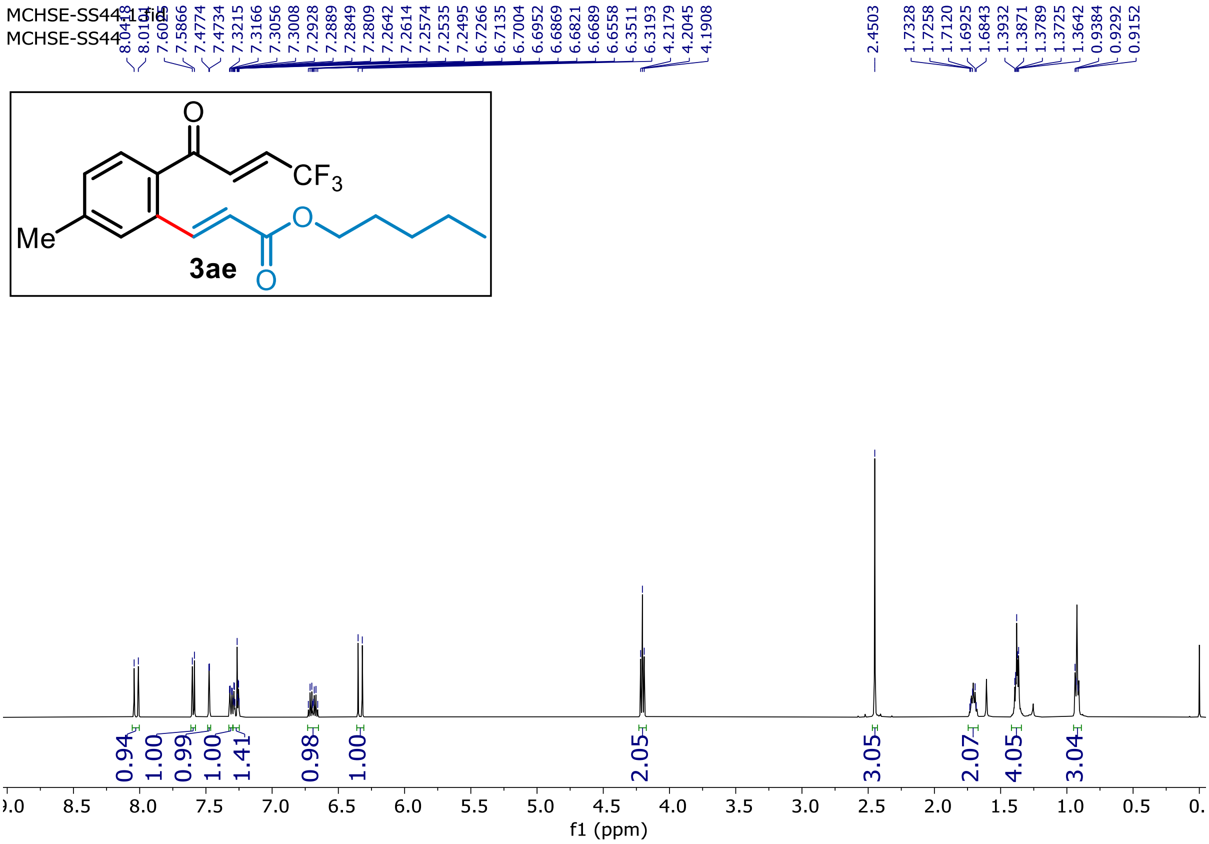


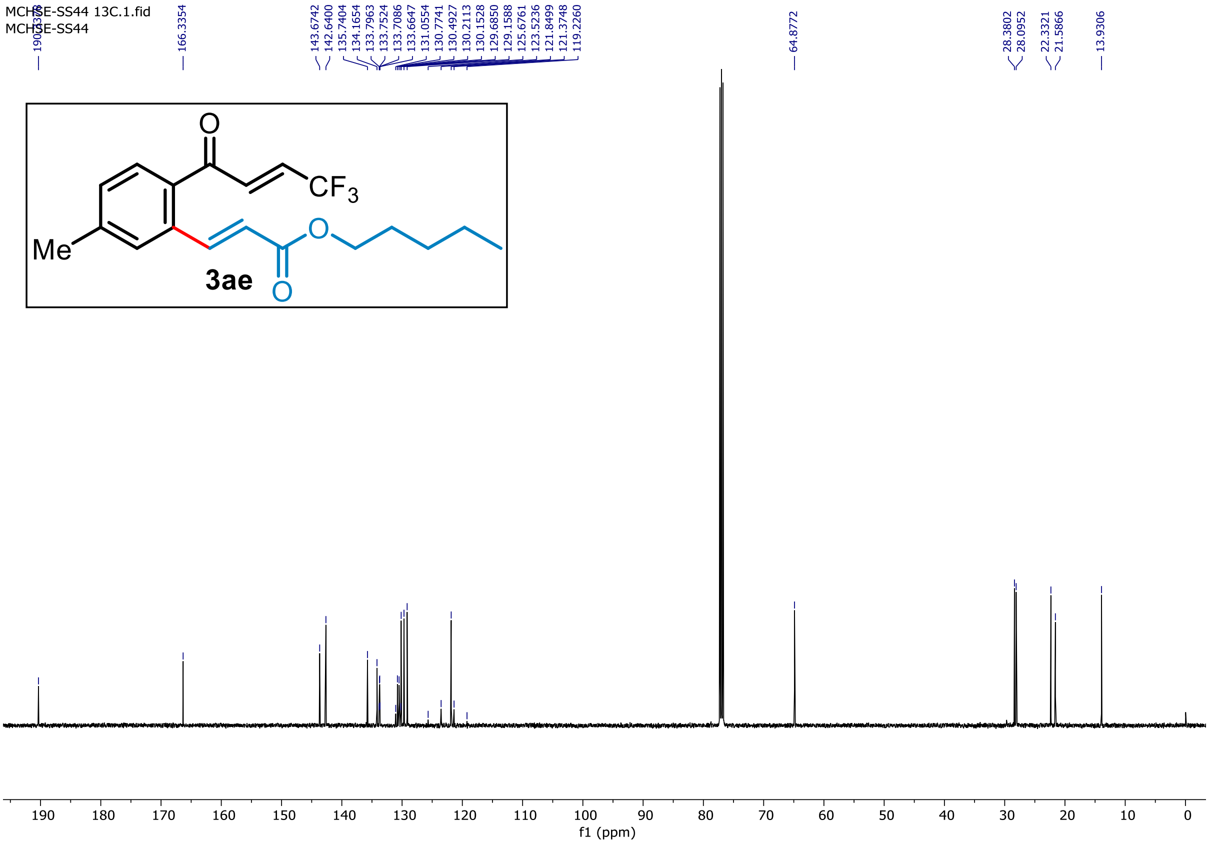

MCHSE-SS22
7.3425
7.3389
7.3267
7.3230
7.3136
7.3096
7.3056
7.3017
7.2821
7.2782
7.2742
7.2702
6.7464
6.7333
6.7202
6.7150
6.7068
6.7019
6.6888
6.6753
6.3840
6.3523
4.0263
4.0129
2.4738
2.0909
2.0772
2.0638
2.0503
2.0369
2.0235
2.0101
1.9966
1.9832
1.0125
0.9990
O
CF3
CH3
Me
CH3
O
3ad
O
0.92
1.00
1.00
0.97
1.27
0.98
1.00
2.02
2.99
1.09
6.19
f1 (ppm)

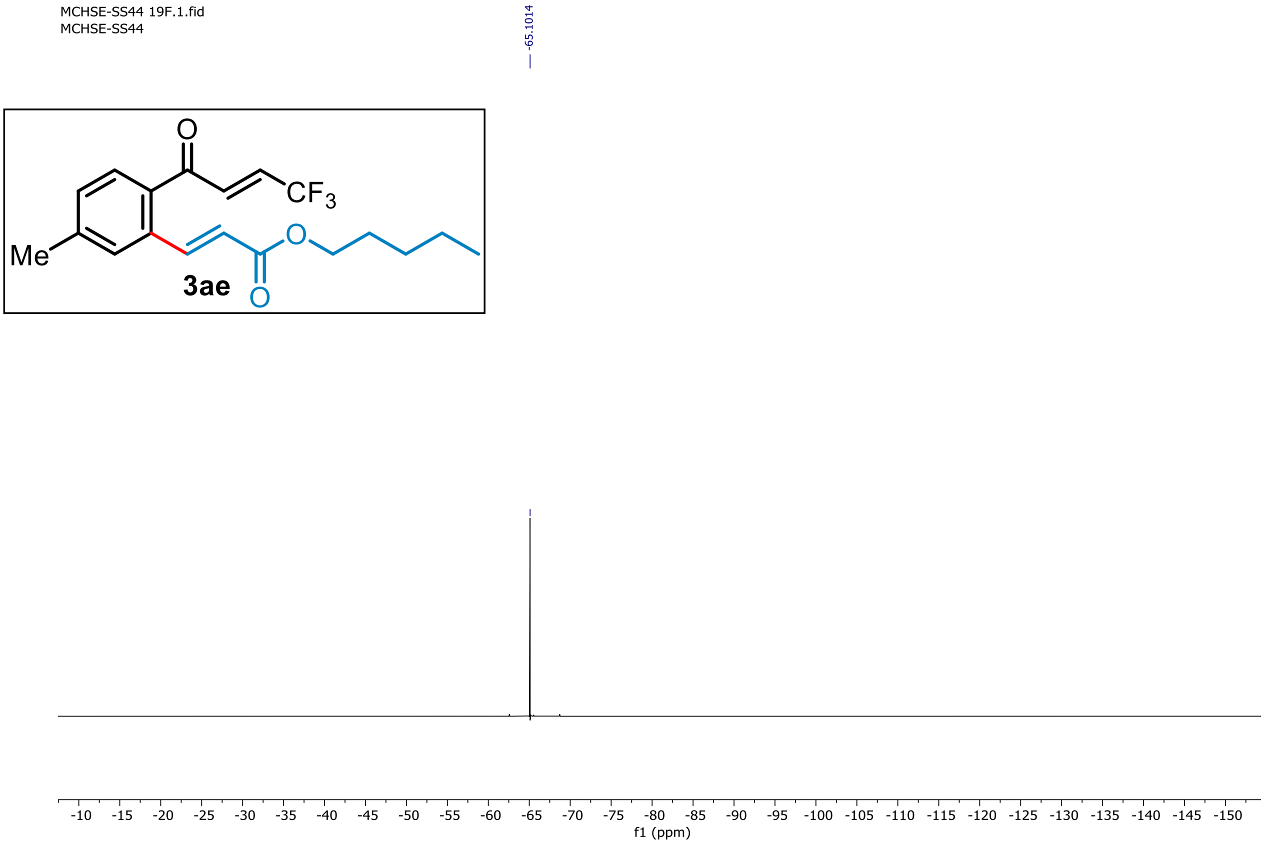
S

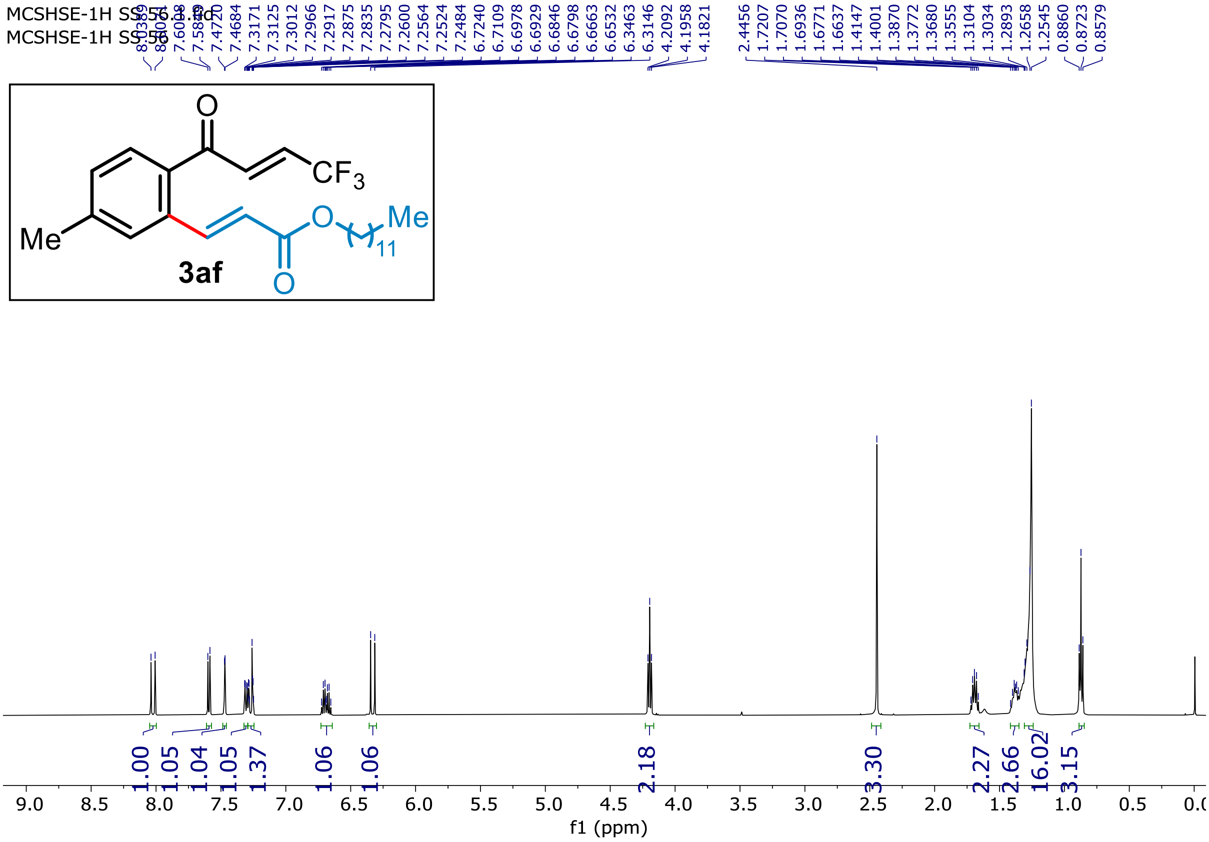

MCHSE-SS21 13C.1.fid
MCHSE-SS21 13C
166.3683
143.7364
142.7423
135.7331
134.1142
133.7342
133.6903
133.6464
133.6026
131.0737
130.7923
130.5146
130.2332
130.2003
129.7472
129.1844
125.6761
123.5273
121.7549
121.3748
119.2224
70.8156
27.8175
21.6341
19.1418
O
CF3
CH3
Me
CH3
O
3ad
O
f1 (ppm)

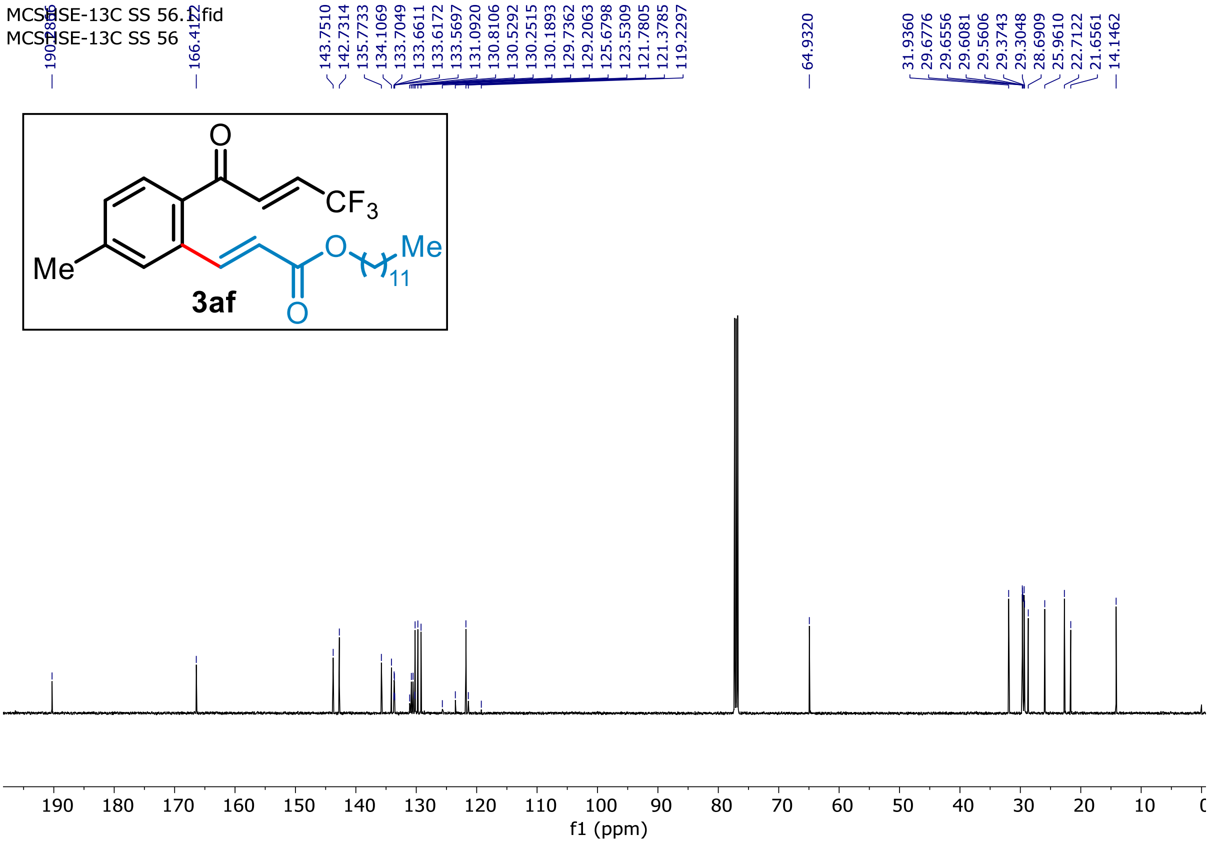

MCHSE-SS21 19F.1.fid
MCHSE-SS21 19F
-65.1014
3ad
Me
CF3
CH3
CH3
f1 (ppm)


MCHSE-SS44.1.fid
MCHSE-SS44
8.0418
8.0101
7.6030
7.5866
7.4774
7.4734
7.3215
7.3166
7.3056
7.3008
7.2928
7.2889
7.2849
7.2809
7.2642
7.2614
7.2574
7.2535
7.2495
6.7266
6.7135
6.7004
6.6952
6.6869
6.6821
6.6689
6.6558
6.3511
6.3193
4.2179
4.2045
4.1908
2.4503
1.7328
1.7258
1.7120
1.6925
1.6843
1.3932
1.3871
1.3789
1.3725
1.3642
0.9384
0.9292
0.9152
3ae
Me
CF3
0.94
1.00
0.99
1.00
1.41
0.98
1.00
2.05
3.05
2.07
4.05
3.04
f1 (ppm)

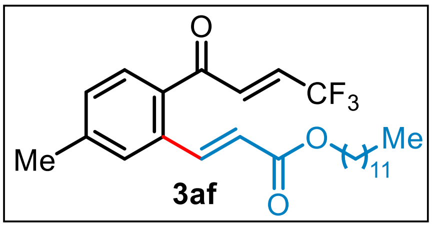

MCHSE-SS44 13C.1.fid
MCHSE-SS44
190.3378
166.3354
143.6742
142.6400
135.7404
134.1654
133.7963
133.7524
133.7086
133.6647
131.0554
130.7741
130.4927
130.2113
130.1528
129.6850
129.1588
125.6761
123.5236
121.8499
121.3748
119.2260
64.8772
28.3802
28.0952
22.3321
21.5866
13.9306
O
CF3
Me
3ae
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

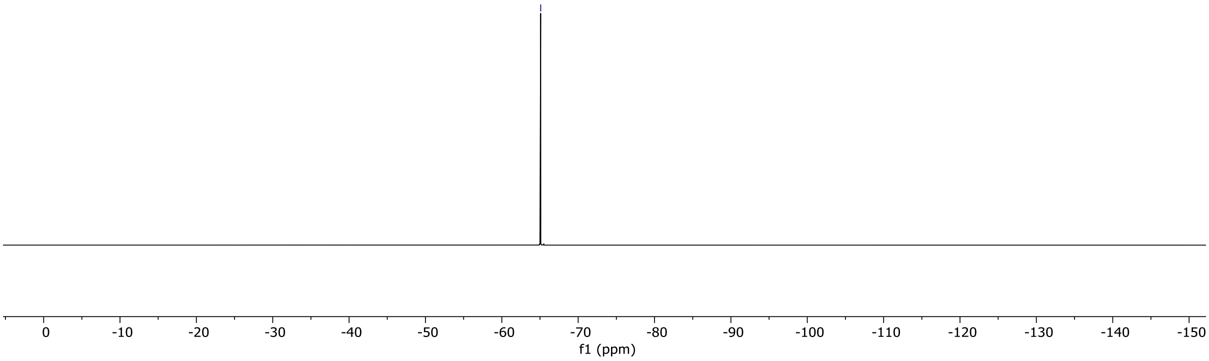

MCHSE-SS44 19F.1.fid
MCHSE-SS44
-65.1014
O
CF3
Me
3ae
O
O
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)


MCSHSE-1H SS56
7.6038
7.4720
7.4684
7.3171
7.3125
7.3012
7.2966
7.2917
7.2875
7.2835
7.2795
7.2600
7.2564
7.2524
7.2484
6.7240
6.7109
6.6978
6.6929
6.6846
6.6798
6.6663
6.6532
6.3463
6.3146
4.2092
4.1958
4.1821
2.4456
1.7207
1.7070
1.6936
1.6771
1.6637
1.4147
1.4001
1.3870
1.3772
1.3680
1.3555
1.3104
1.3034
1.2893
1.2658
1.2545
0.8860
0.8723
0.8579
O
CF3
Me
Me
11
3af
O
1.00
1.05
1.04
1.05
1.37
1.06
1.06
2.18
3.30
2.27
2.66
16.02
3.15
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)

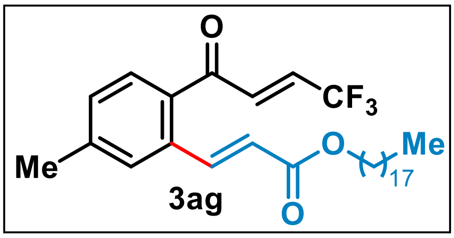

MCSHSE-13C SS 56
166.4122
143.7510
142.7314
135.7733
134.1069
133.7049
133.6611
133.6172
133.5697
131.0920
130.8106
130.5292
130.2515
130.1893
129.7362
129.2063
125.6798
123.5309
121.7805
121.3785
119.2297
64.9320
31.9360
29.6776
29.6556
29.6081
29.5606
29.3743
29.3048
28.6909
25.9610
22.7122
21.6561
14.1462
O
CF3
Me
Me
11
3af
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

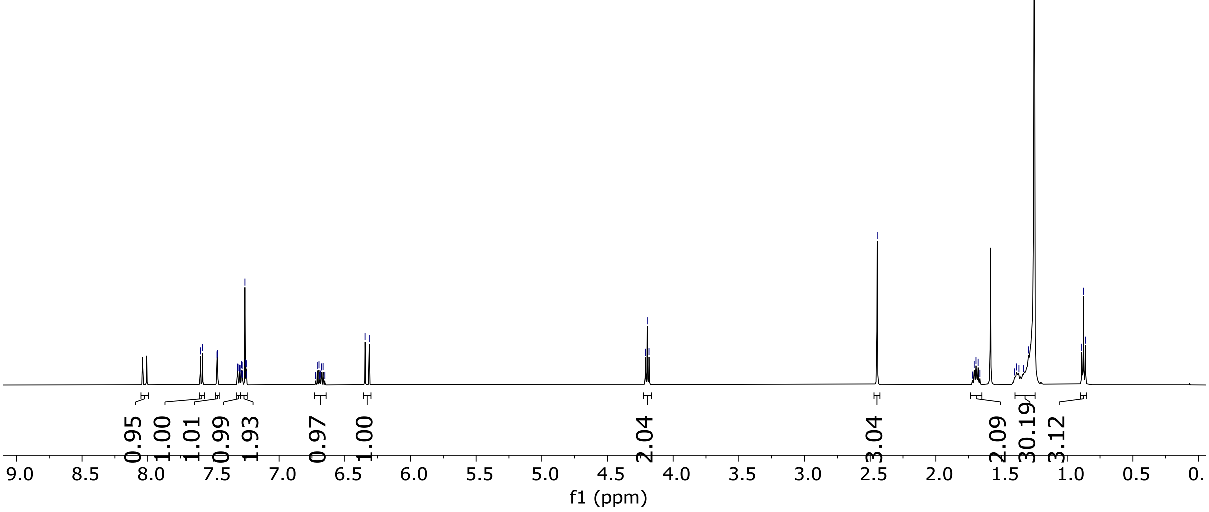
MCSHSE-19F SS 56.1.fid
MCSHSE-1H9FSS 56

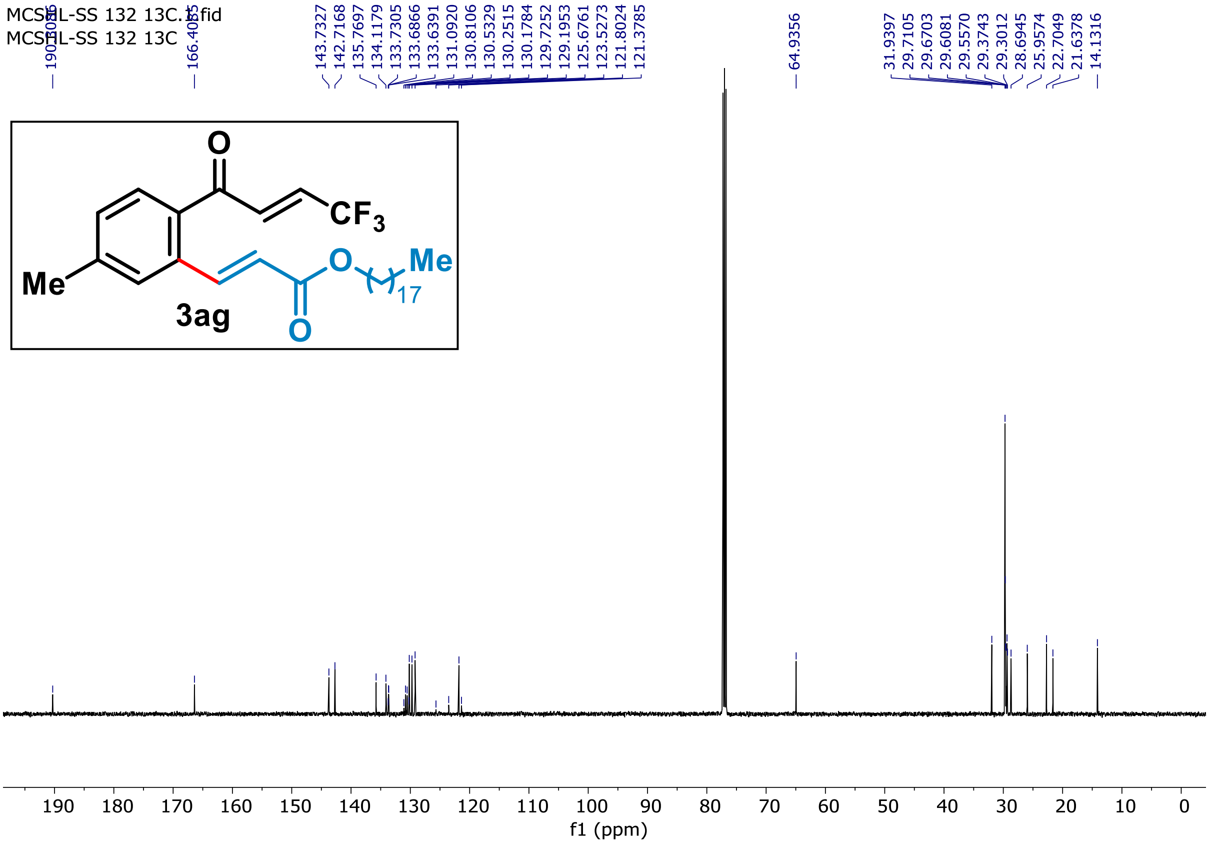


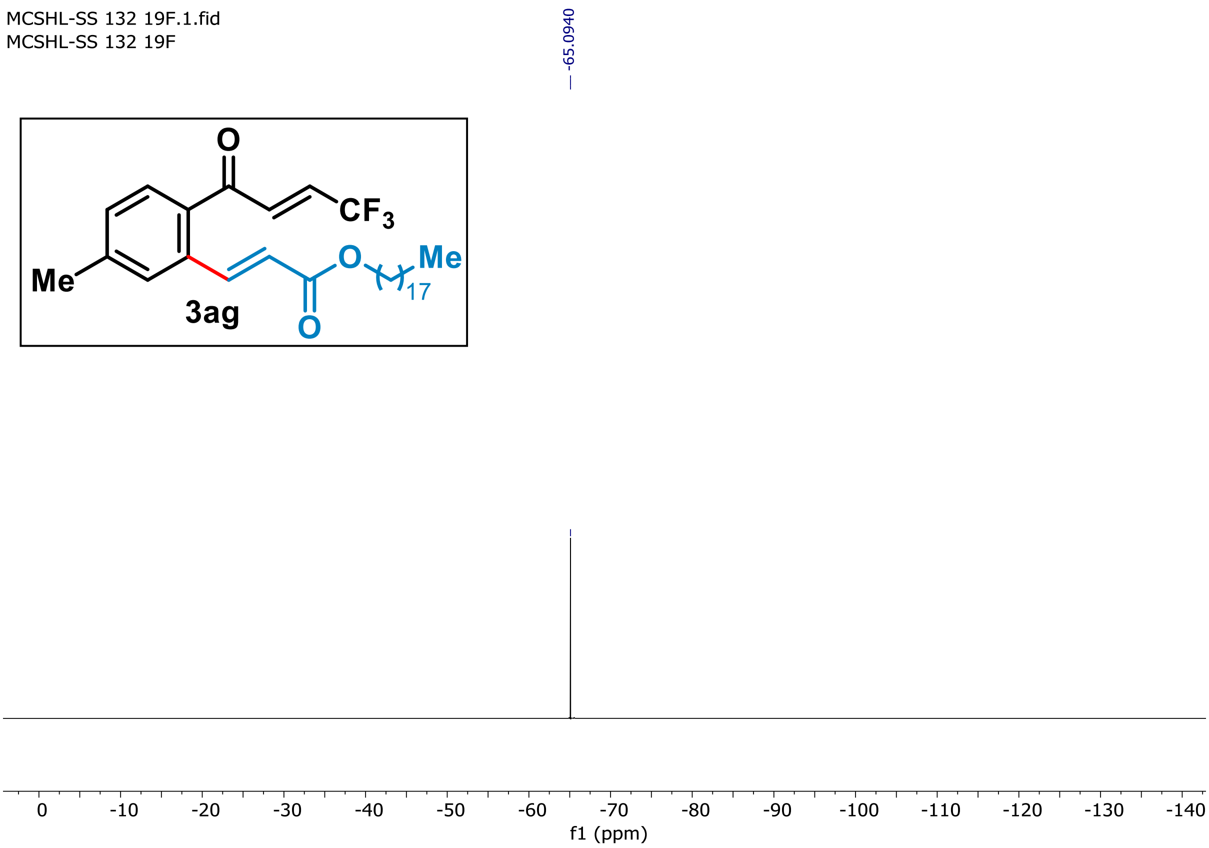


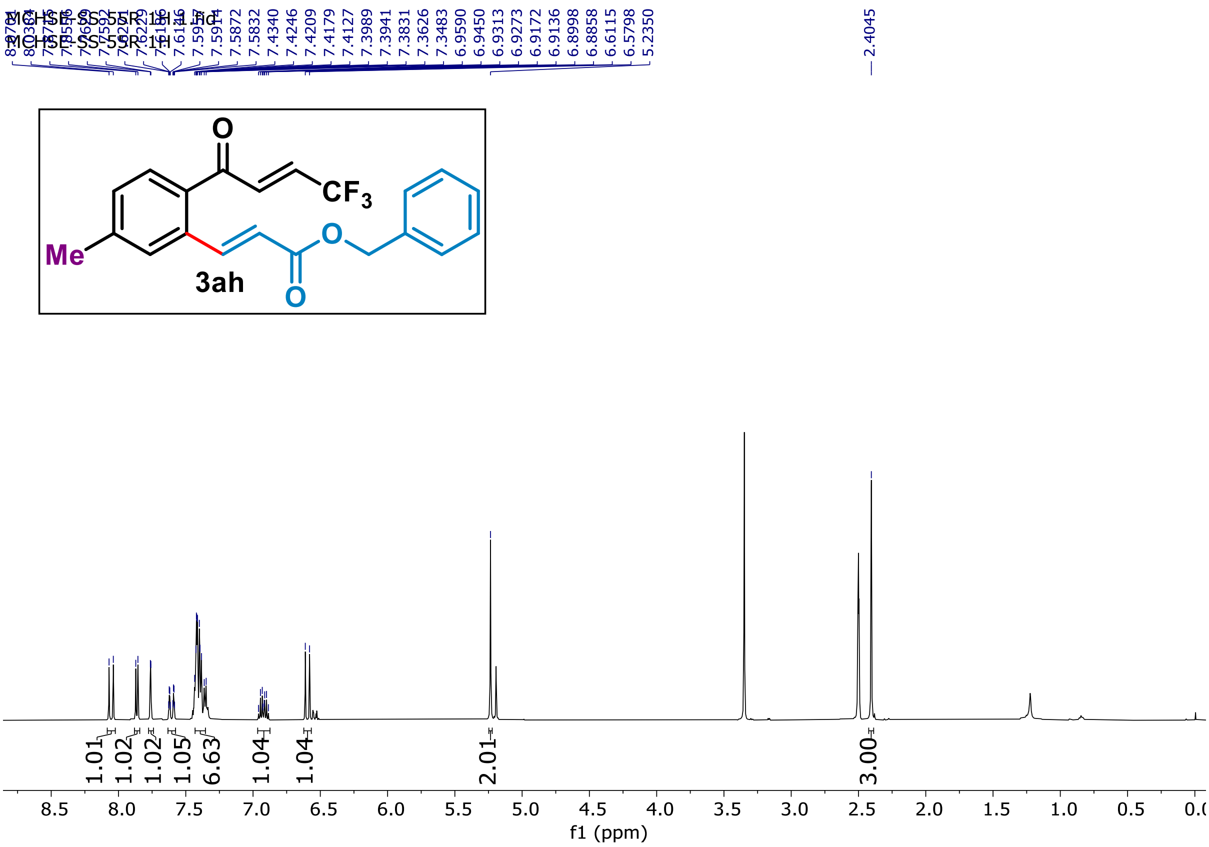
MCHSE-SS 132 1H.1.fid
MCHSE-SS 132 1H

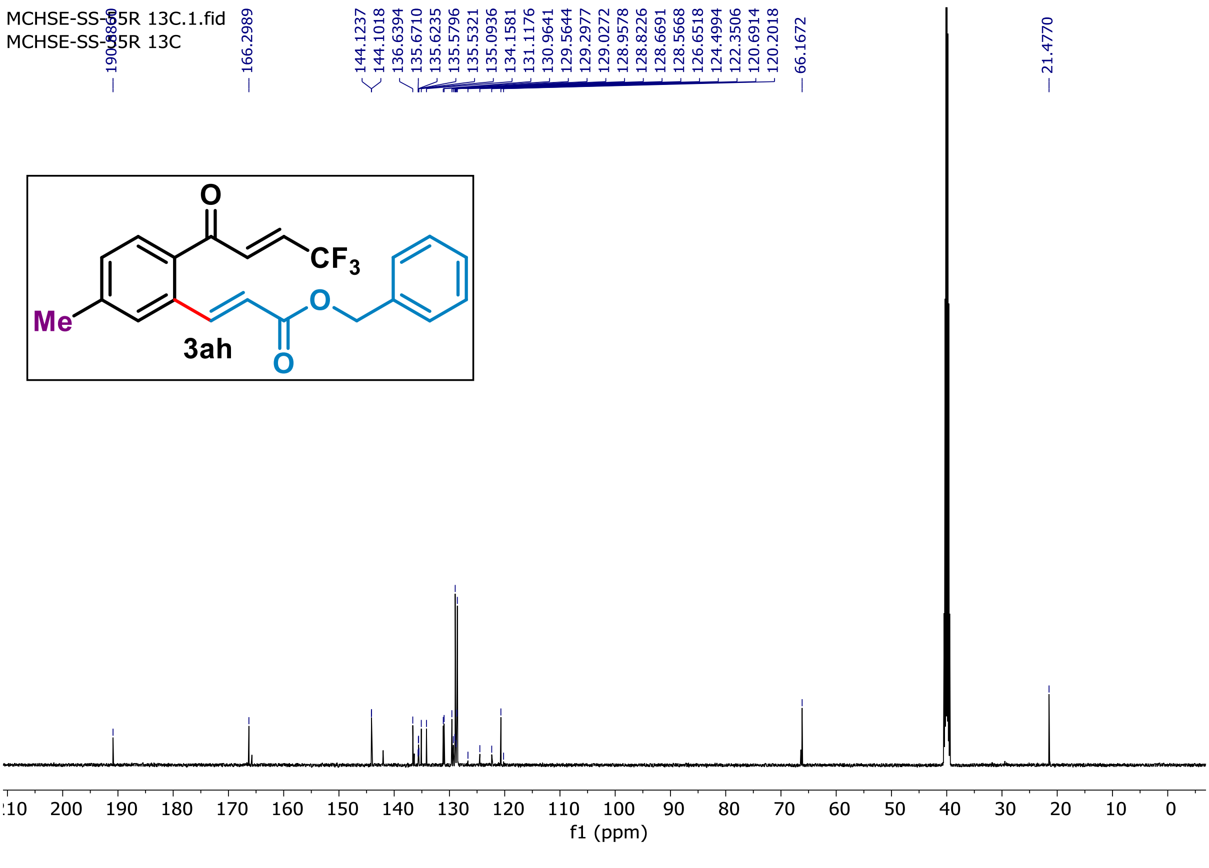


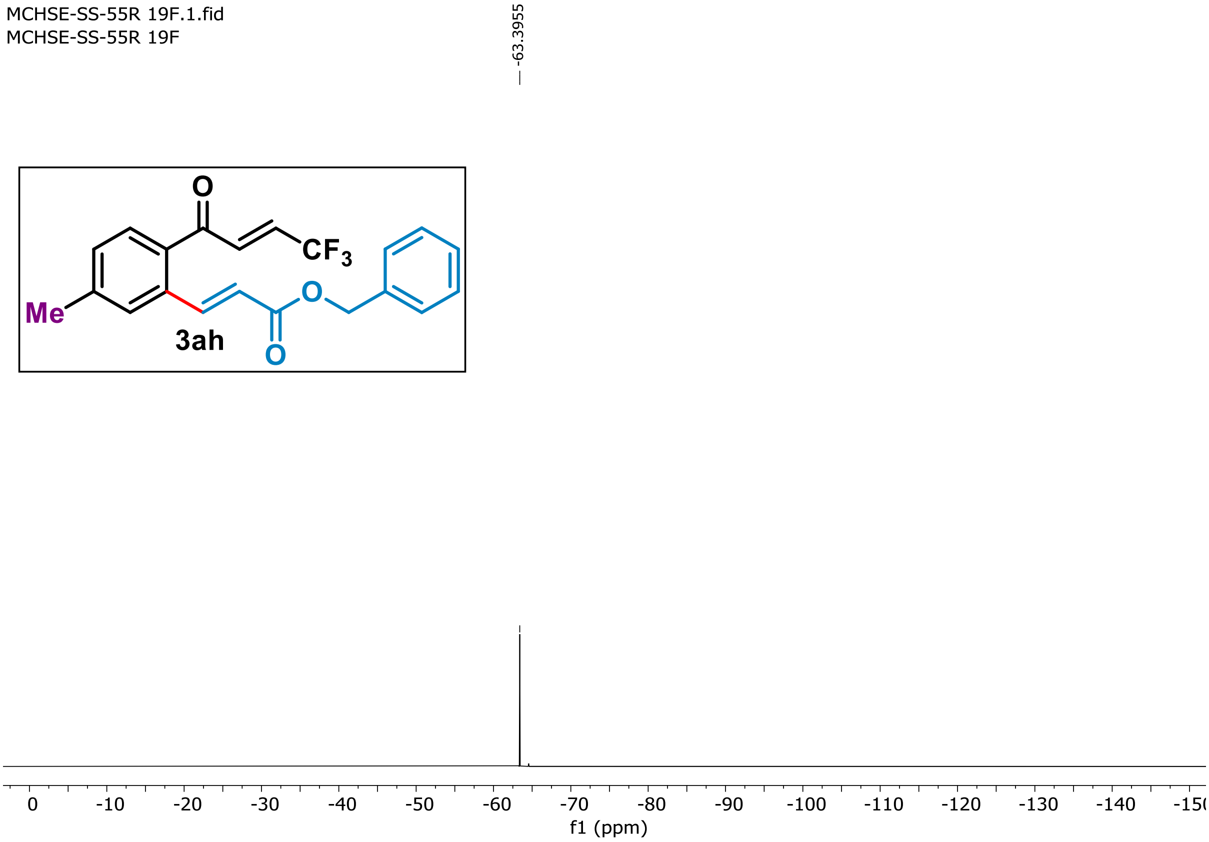


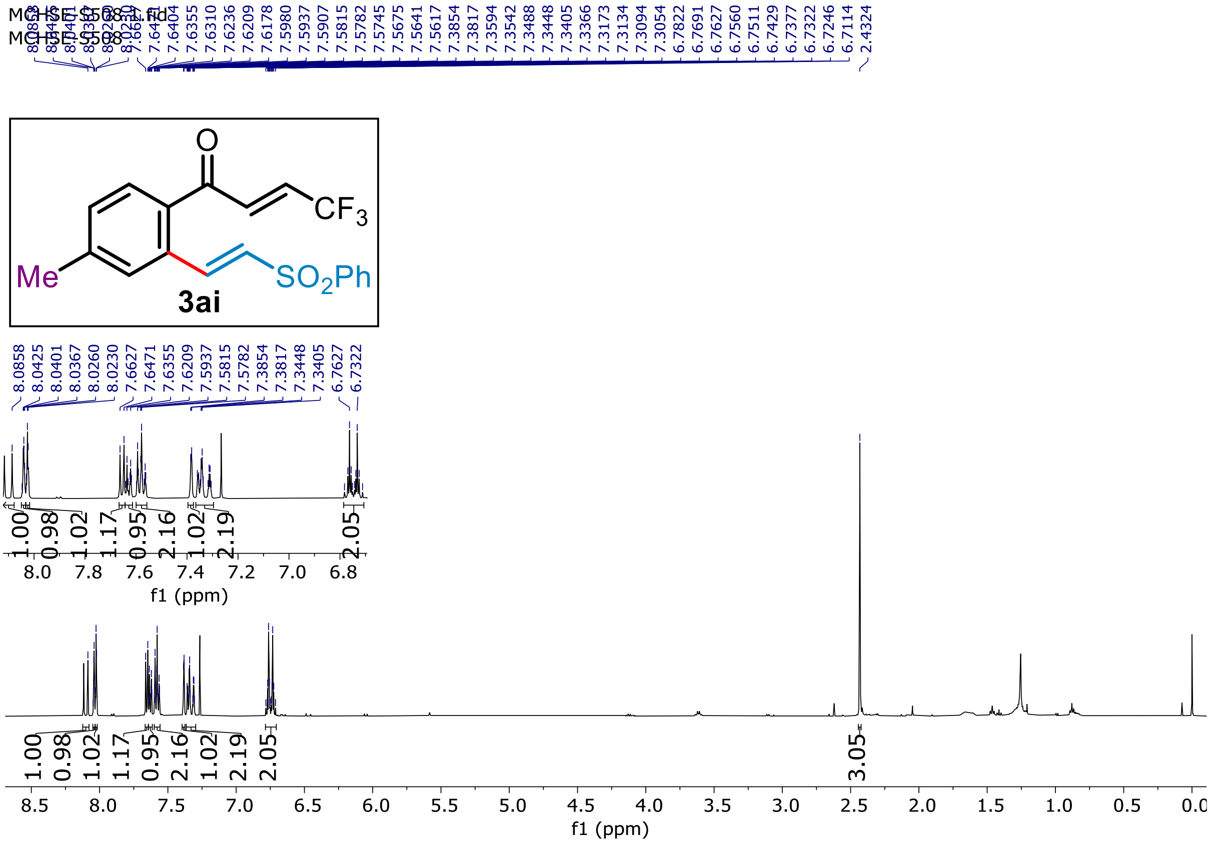

MCSHL-SS 132 13C.1.fid
MCSHL-SS 132 13C
143.7327
142.7168
135.7697
134.1179
133.7305
133.6866
133.6391
131.0920
130.8106
130.5329
130.2515
130.1784
129.7252
129.1953
125.6761
123.5273
121.8024
121.3785
64.9356
31.9397
29.7105
29.6703
29.6081
29.5570
29.3743
29.3012
28.6945
25.9574
22.7049
21.6378
14.1316
O
CF3
Me
O
Me
17
3ag
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MCSHL-SS 132 19F.1.fid
MCSHL-SS 132 19F
-65.0940
O
CF3
Me
O
Me
17
3ag
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

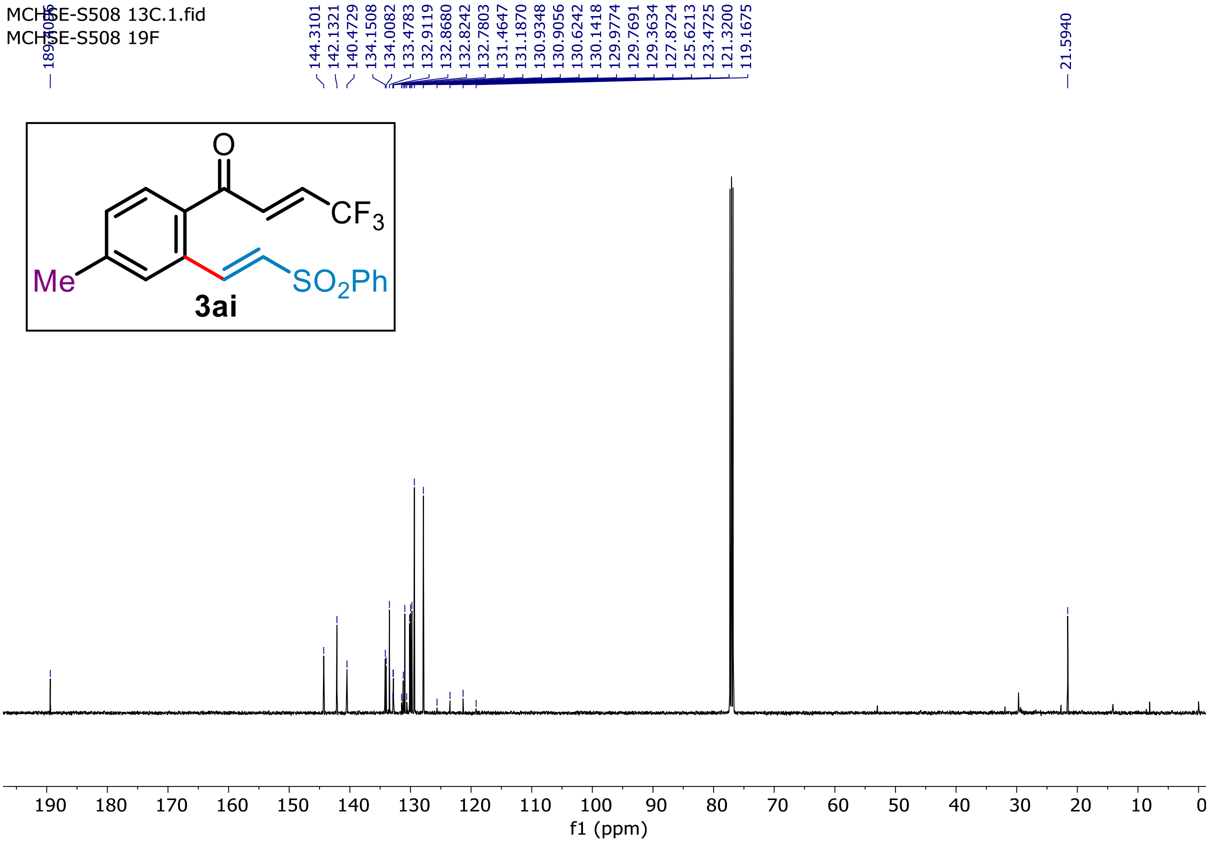




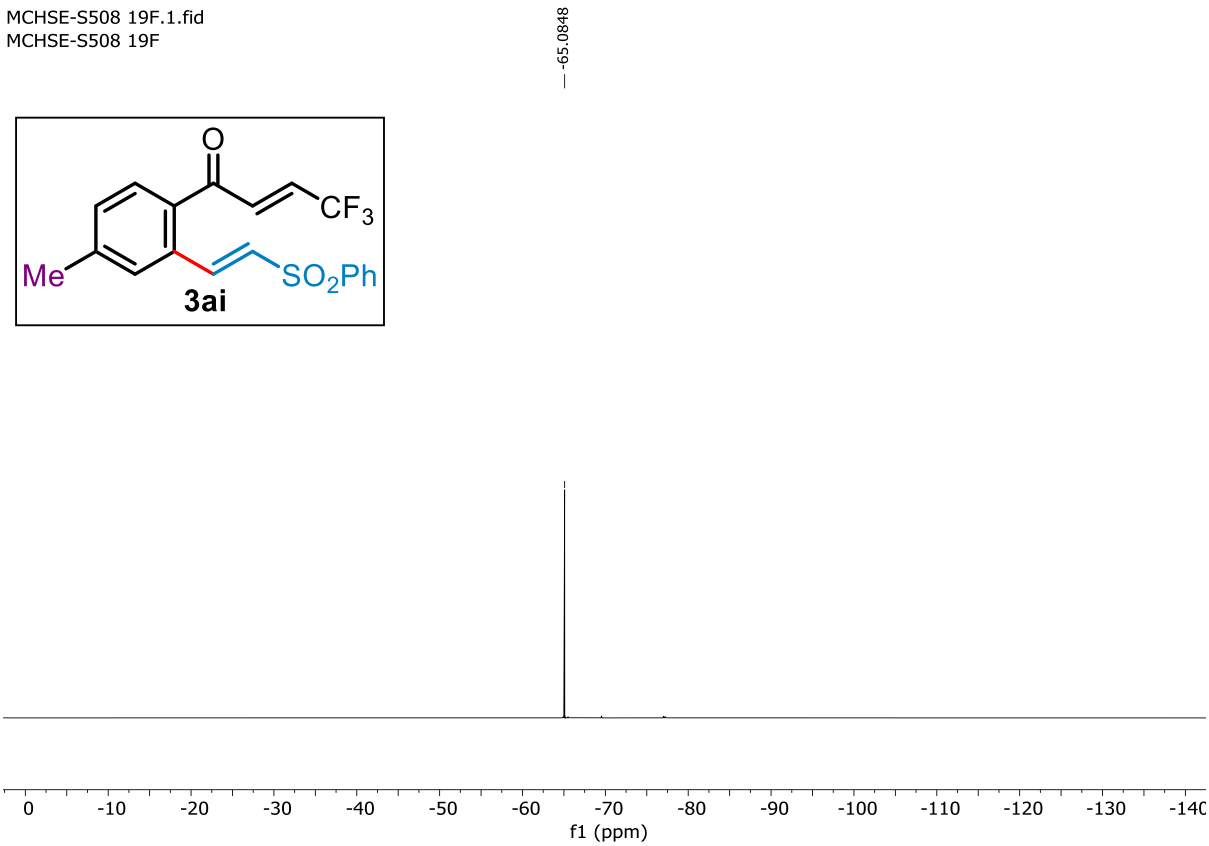

MCHSE-SS-55R 19F.1.fid
MCHSE-SS-55R 19F
-63.3955
O
CF3
Me
3ah
O
O
f1 (ppm)

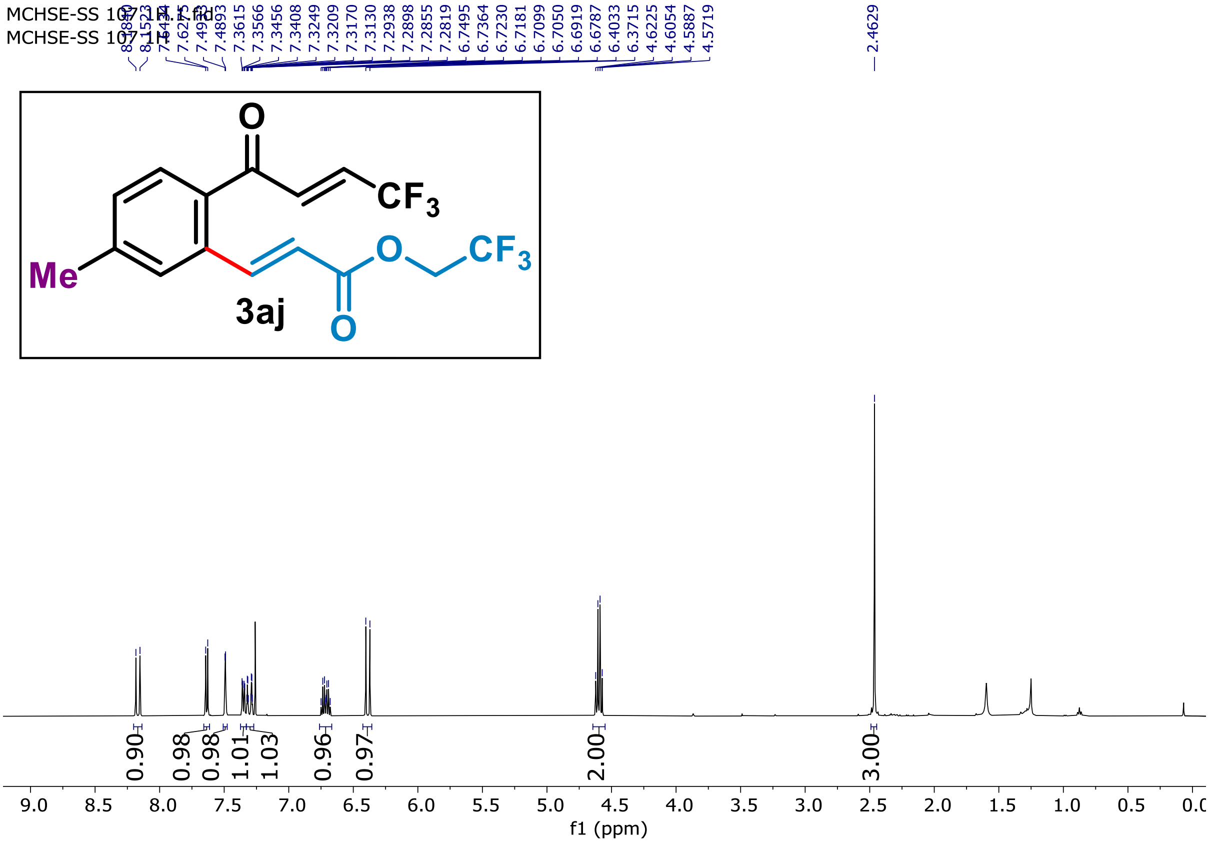

O
CF3
Me
SO2Ph
3ai
8.0858
8.0425
8.0401
8.0367
8.0260
8.0230
7.6627
7.6471
7.6355
7.6209
7.5937
7.5815
7.5782
7.3854
7.3817
7.3448
7.3405
6.7627
6.7322
2.4324
1.00
0.98
1.02
1.17
0.95
2.16
1.02
2.19
2.05
3.05
f1 (ppm)

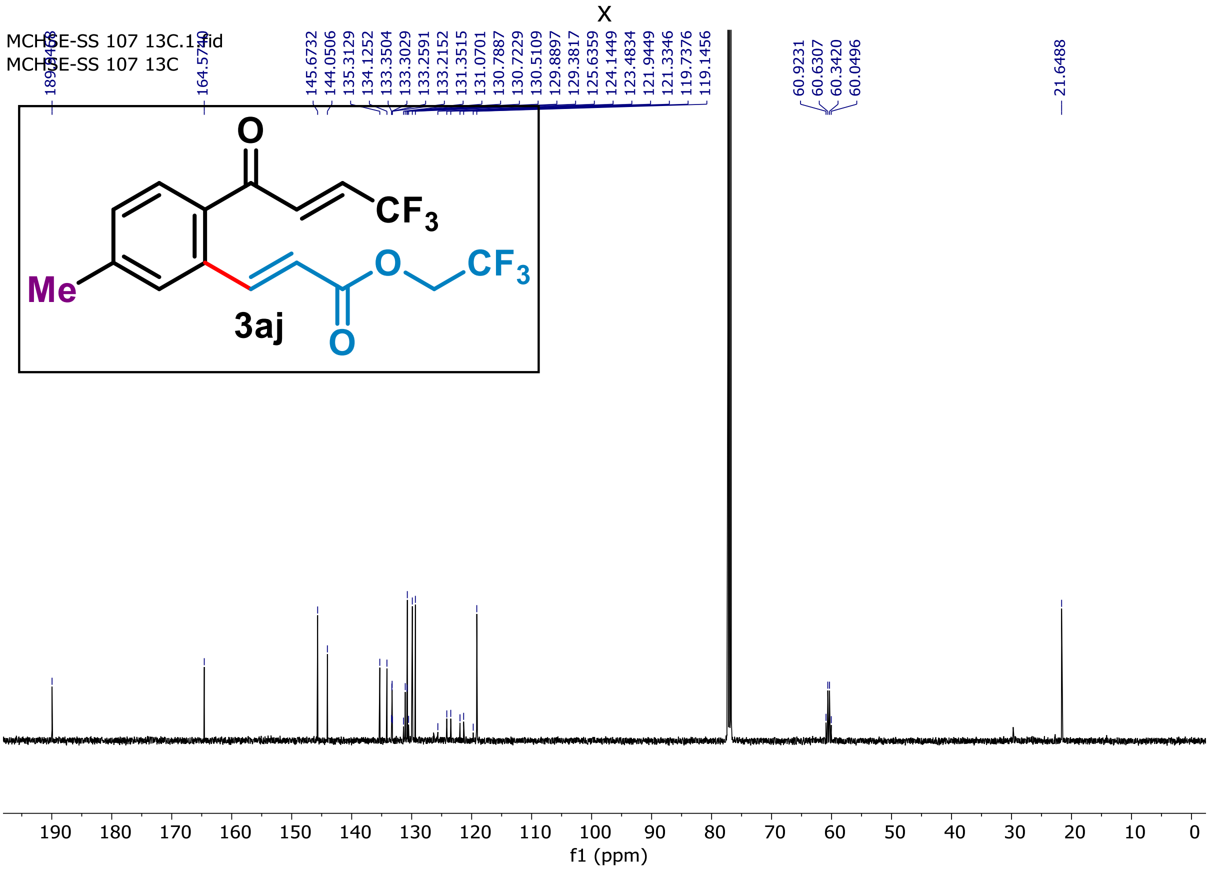
MCHSE-S508 13C.1.fid
MCHSE-S508 19F

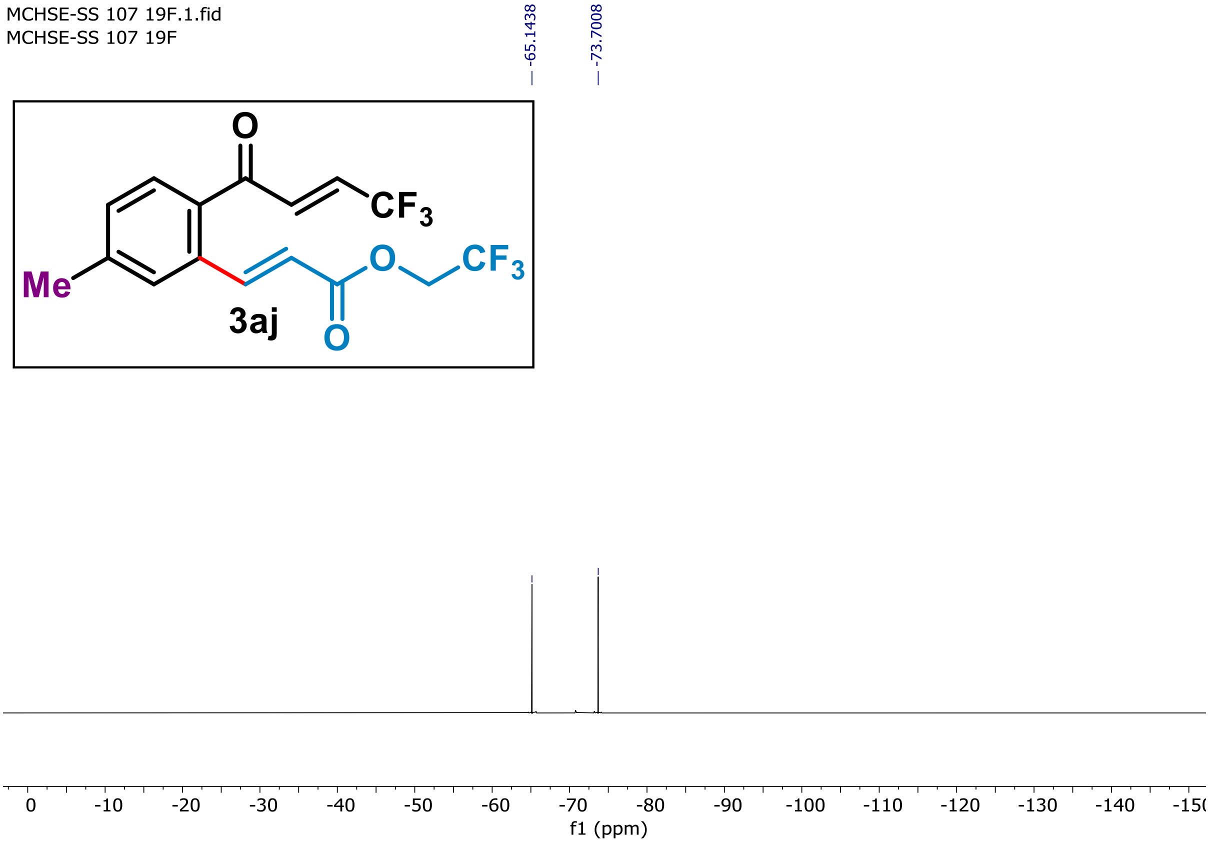


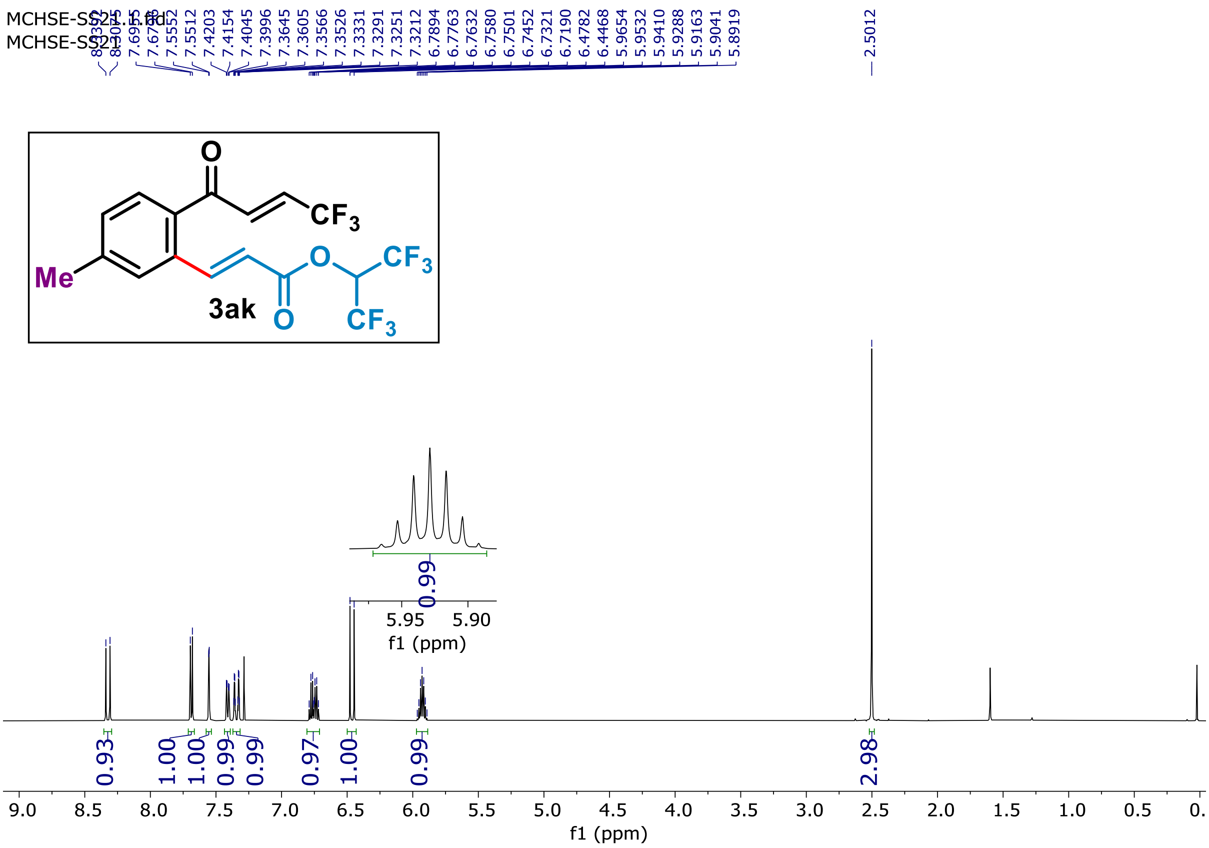
MCHSE-S508 19F.1.fid
MCHSE-S508 19F

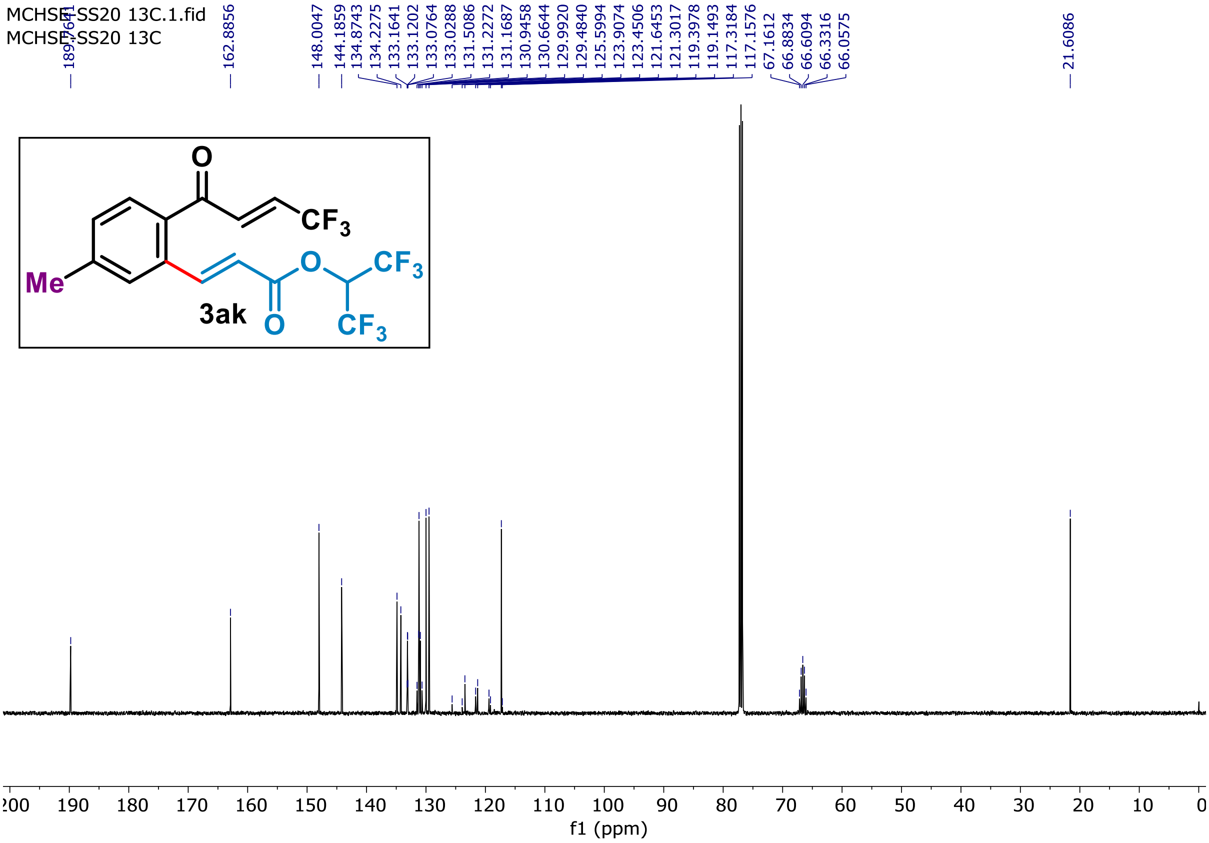


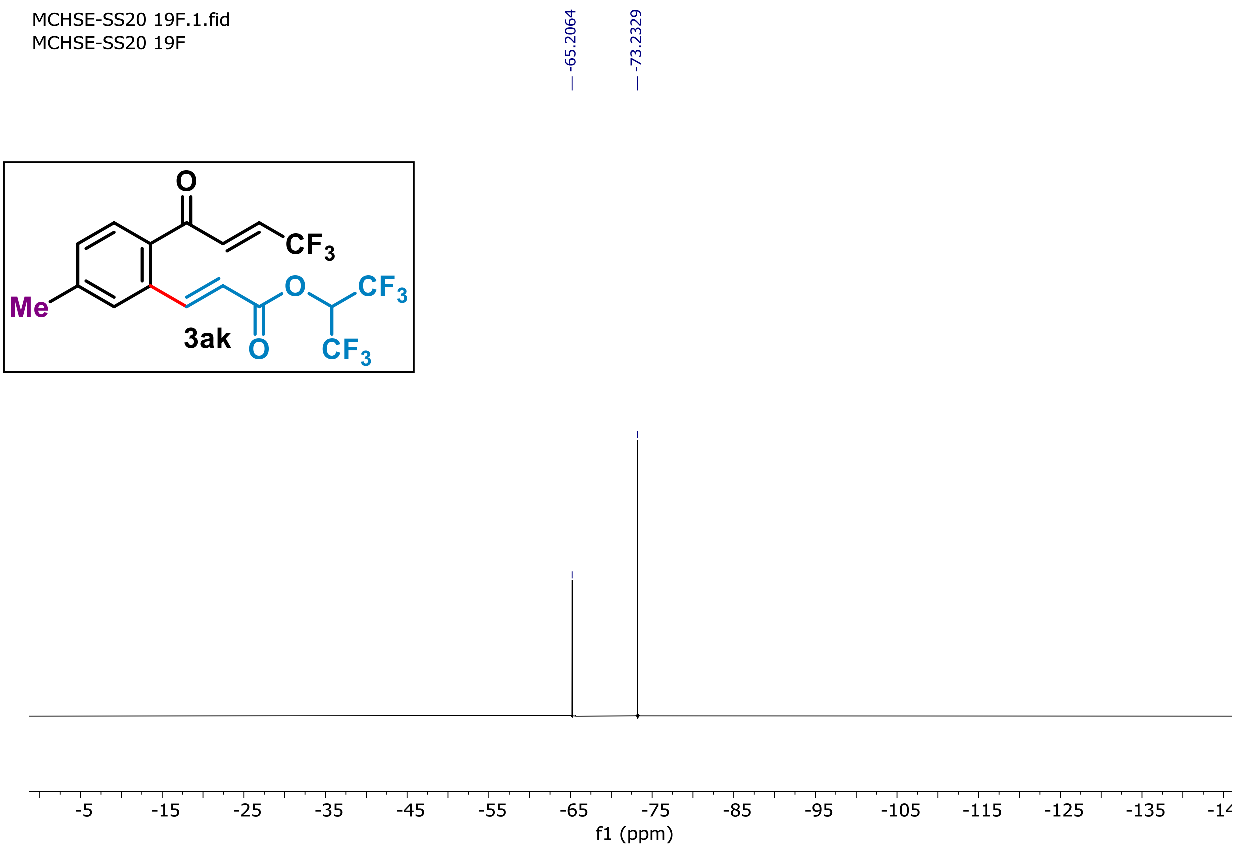

MCHSE-SS 107 1H
7.3615
7.3566
7.3456
7.3408
7.3249
7.3209
7.3170
7.3130
7.2938
7.2898
7.2855
7.2819
6.7495
6.7364
6.7230
6.7181
6.7099
6.7050
6.6919
6.6787
6.4033
6.3715
4.6225
4.6054
4.5887
4.5719
2.4629
CF3
O
O
Me
3aj
CF3
O
0.90
0.98
0.98
1.01
1.03
0.96
0.97
2.00
3.00
f1 (ppm)

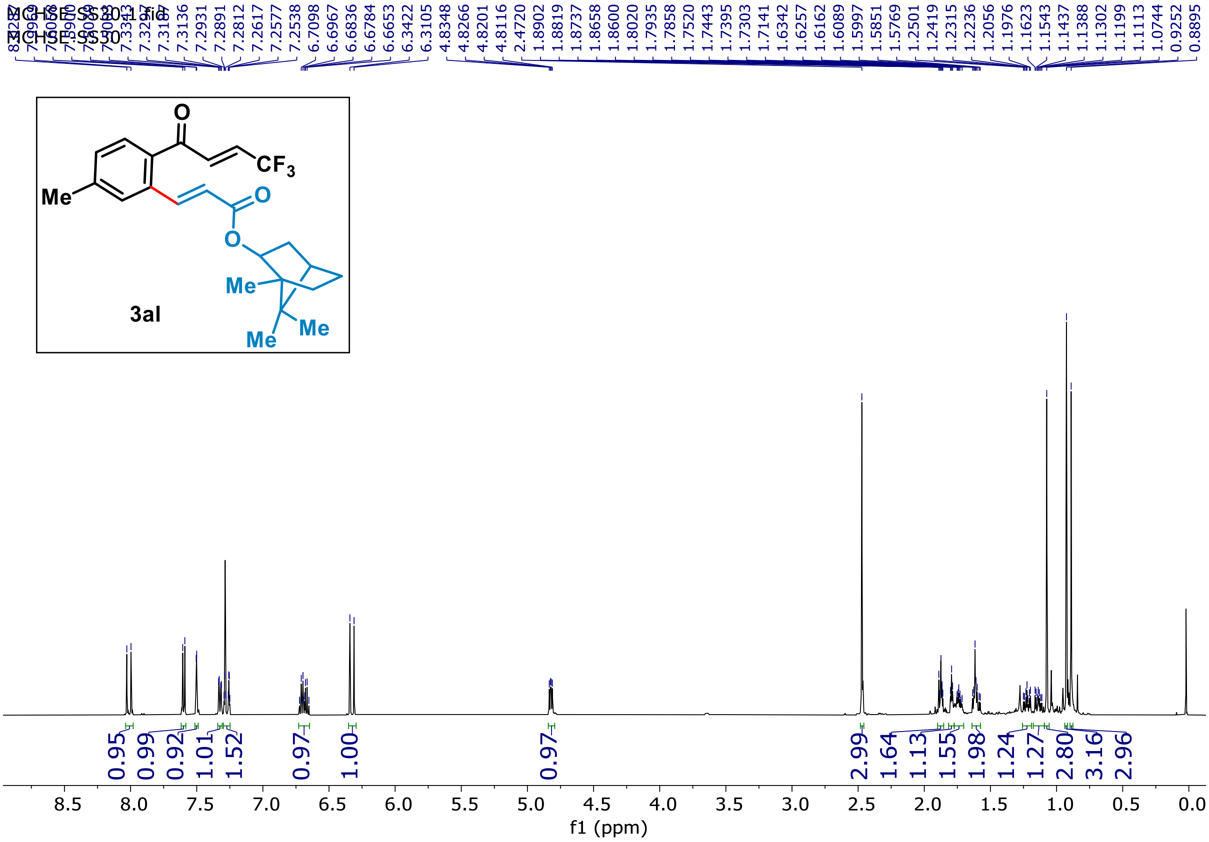

MCHSE-SS 107 13C
164.5740
145.6732
144.0506
135.3129
134.1252
133.3504
133.3029
133.2591
133.2152
131.3515
131.0701
130.7887
130.7229
130.5109
129.8897
129.3817
125.6359
124.1449
123.4834
121.9449
121.3346
119.7376
119.1456
60.9231
60.6307
60.3420
60.0496
21.6488
X
CF3
O
O
Me
3aj
CF3
O
f1 (ppm)


MCHSE-SS 107 19F.1.fid
MCHSE-SS 107 19F
-65.1438
-73.7008
O
CF3
Me
3aj
O
CF3
O
f1 (ppm)

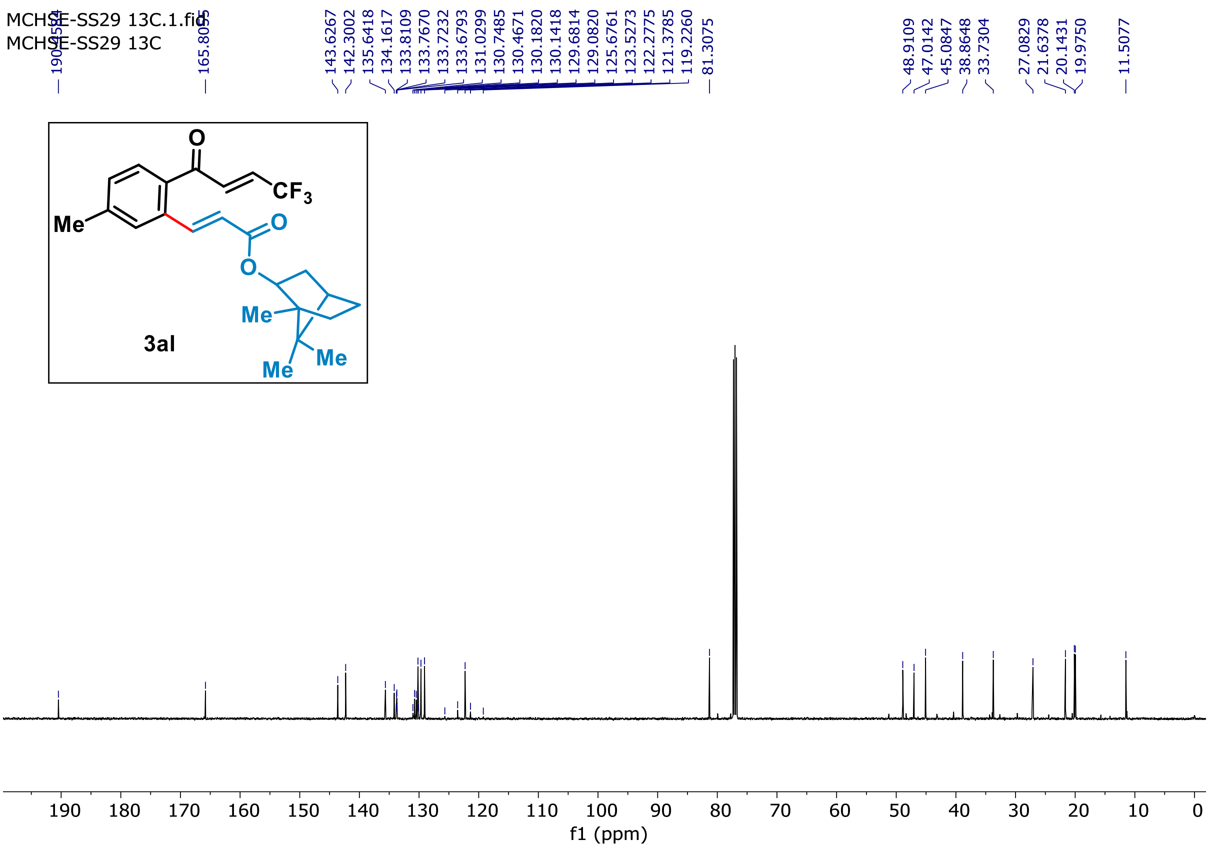

7.6955
7.6786
7.5552
7.5512
7.4203
7.4154
7.4045
7.3996
7.3645
7.3605
7.3566
7.3526
7.3331
7.3291
7.3251
7.3212
6.7894
6.7763
6.7632
6.7580
6.7501
6.7452
6.7321
6.7190
6.4782
6.4468
5.9654
5.9532
5.9410
5.9288
5.9163
5.9041
5.8919
2.5012
O
CF3
Me
O
CF3
3ak
O
CF3
0.99
5.95
5.90
f1 (ppm)
0.93
1.00
1.00
0.99
0.99
0.97
1.00
0.99
2.98
f1 (ppm)


MCHSE-SS20 13C.1.fid
MCHSE-SS20 13C
189.7641
162.8856
148.0047
144.1859
134.8743
134.2275
133.1641
133.1202
133.0764
133.0288
131.5086
131.2272
131.1687
130.9458
130.6644
129.9920
129.4840
125.5994
123.9074
123.4506
121.6453
121.3017
119.3978
119.1493
117.3184
117.1576
67.1612
66.8834
66.6094
66.3316
66.0575
21.6086
Me
CF3
3ak
f1 (ppm)

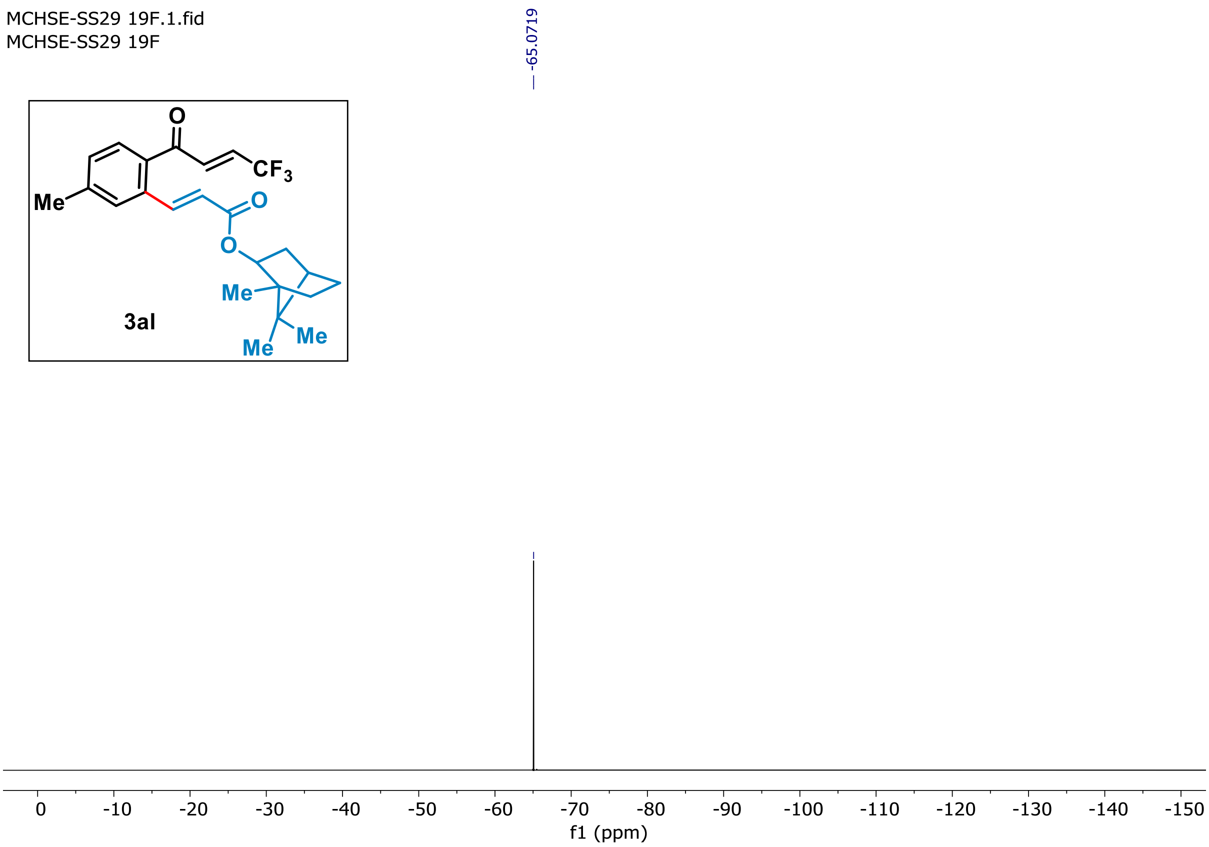

MCHSE-SS20 19F.1.fid
MCHSE-SS20 19F
-65.2064
-73.2329
Me
CF3
3ak
f1 (ppm)

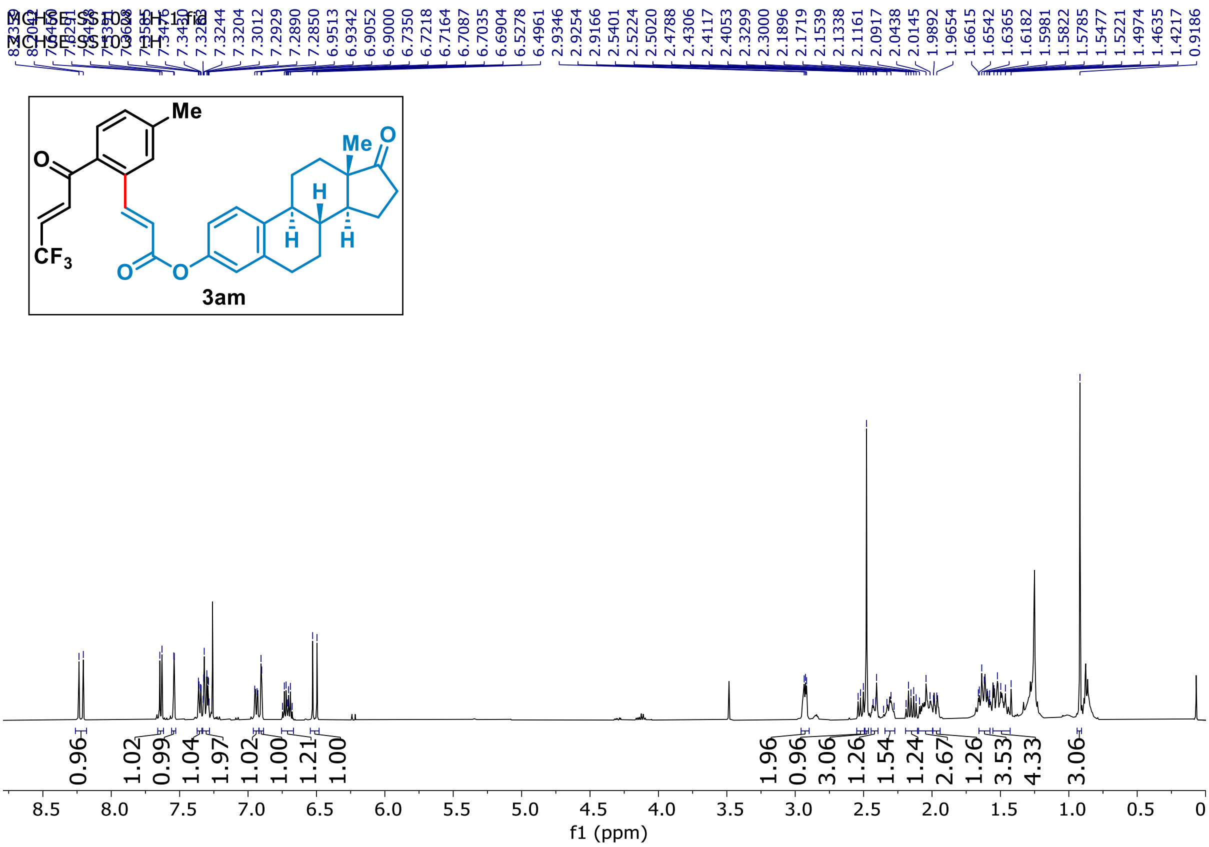


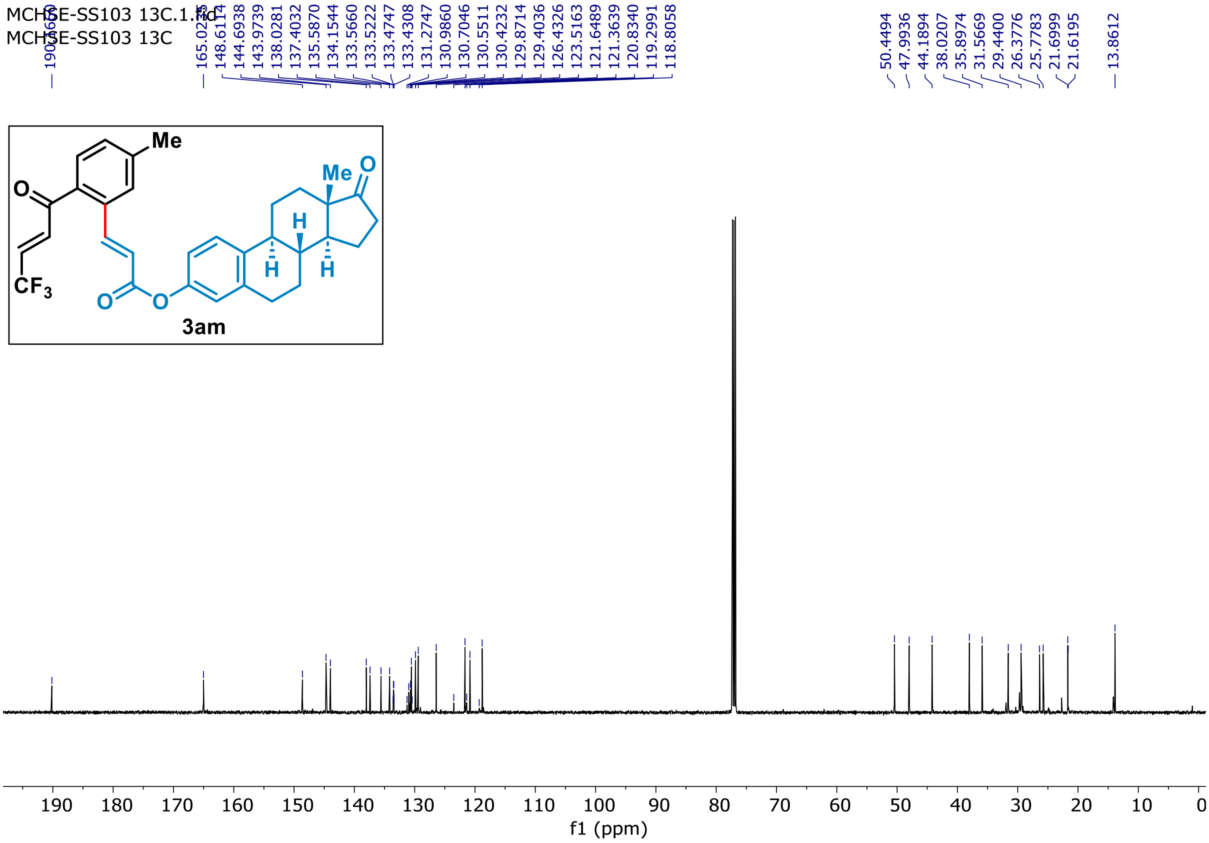
MCHSE-SS30.1.fid
MCHSE-SS30
7.3136
7.2931
7.2891
7.2812
7.2617
7.2577
7.2538
6.7098
6.6967
6.6836
6.6784
6.6653
6.3422
6.3105
4.8348
4.8266
4.8201
4.8116
2.4720
1.8902
1.8819
1.8737
1.8658
1.8600
1.8020
1.7935
1.7858
1.7520
1.7443
1.7395
1.7303
1.7141
1.6342
1.6257
1.6162
1.6089
1.5997
1.5851
1.5769
1.2501
1.2419
1.2315
1.2236
1.2056
1.1976
1.1623
1.1543
1.1437
1.1388
1.1302
1.1199
1.1113
1.0744
0.9252
0.8895
O
CF3
Me
O
O
Me
Me
Me
3al
0.95
0.99
0.92
1.01
1.52
0.97
1.00
0.97
2.99
1.64
1.13
1.55
1.98
1.24
1.27
2.80
3.16
2.96
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)

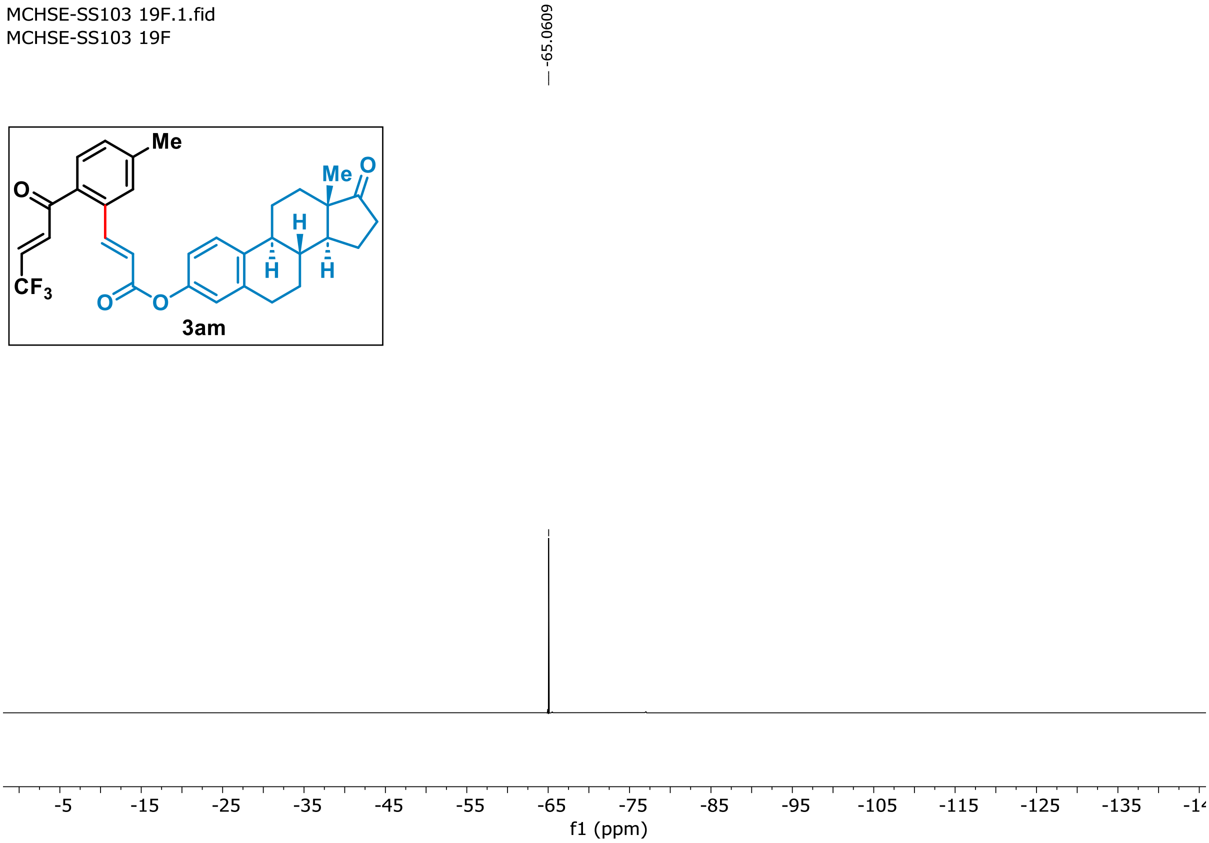


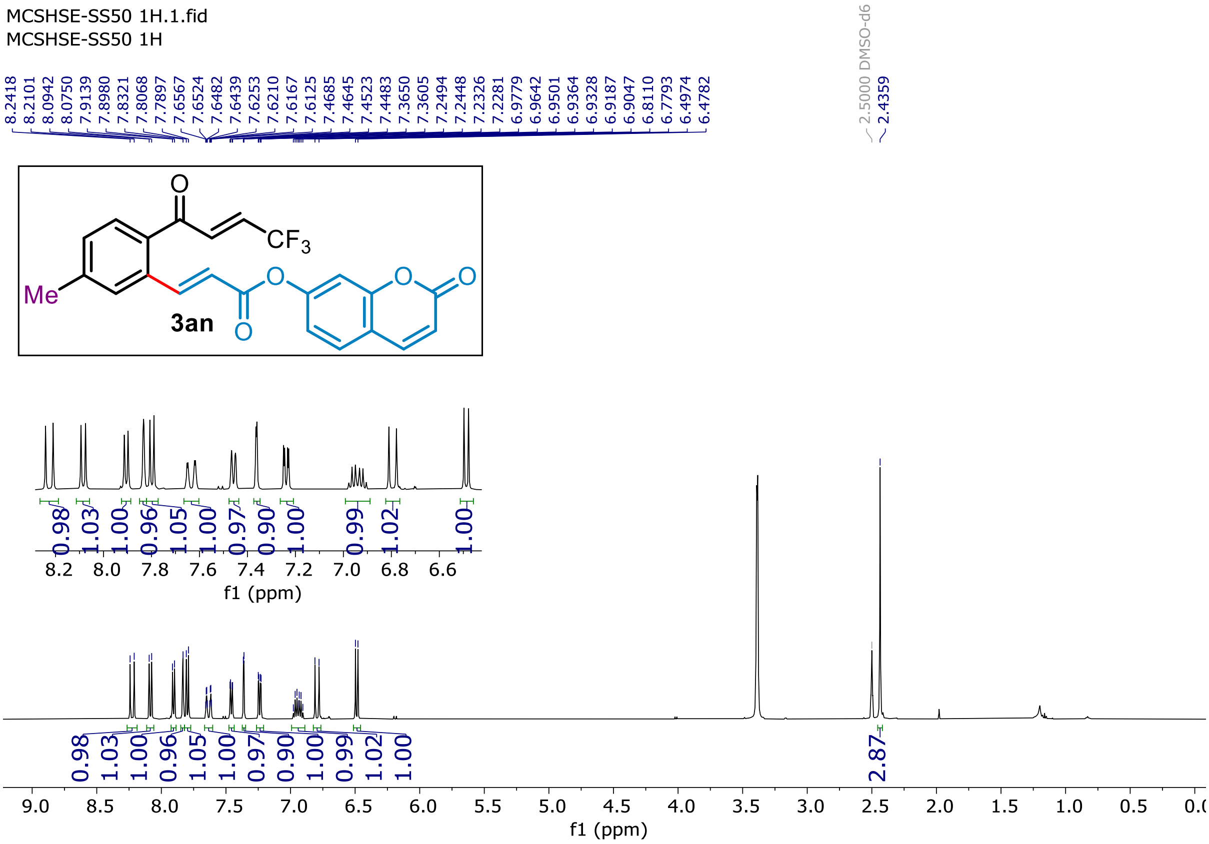
MCHSE-SS29 13C.1.fid
MCHSE-SS29 13C
165.8055
143.6267
142.3002
135.6418
134.1617
133.8109
133.7670
133.7232
133.6793
131.0299
130.7485
130.4671
130.1820
130.1418
129.6814
129.0820
125.6761
123.5273
122.2775
121.3785
119.2260
81.3075
48.9109
47.0142
45.0847
38.8648
33.7304
27.0829
21.6378
20.1431
19.9750
11.5077
O
CF3
Me
O
O
Me
Me
Me
3al
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

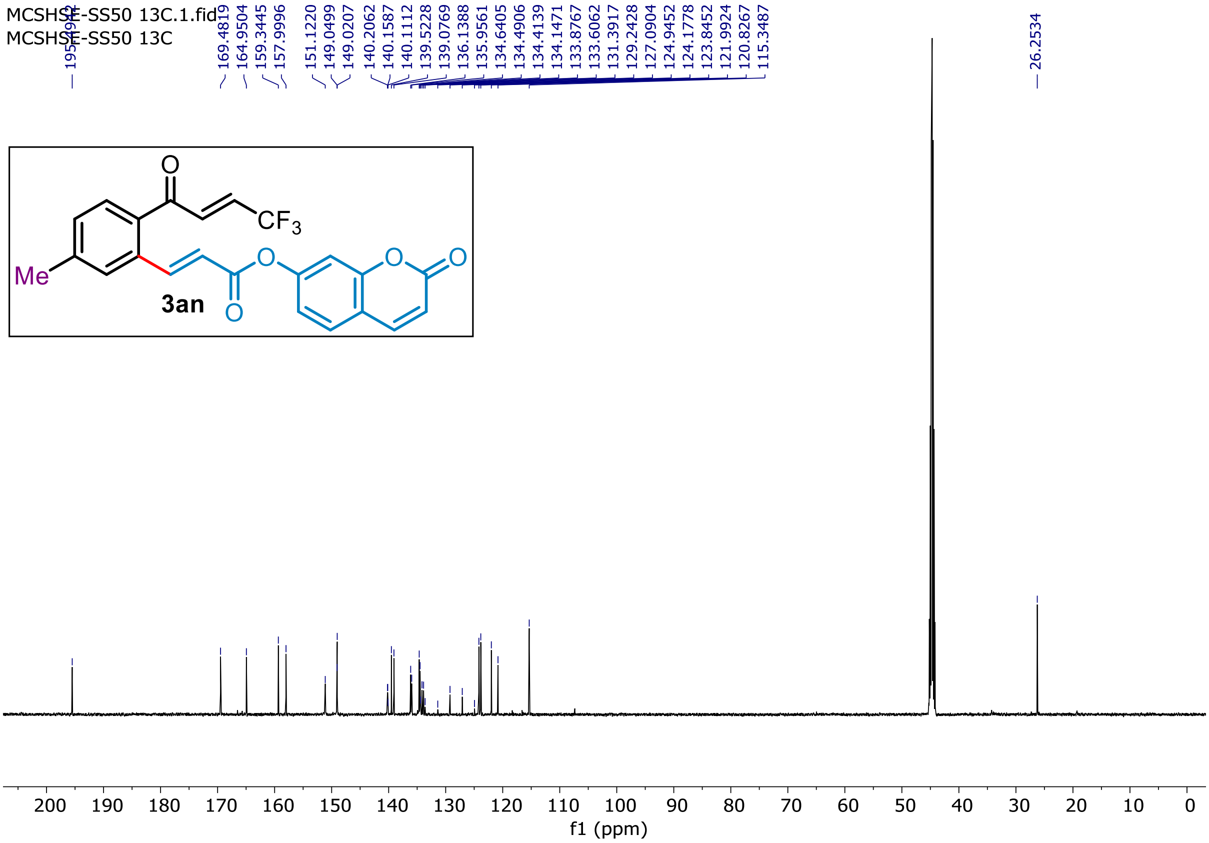

MCHSE-SS29 19F.1.fid
MCHSE-SS29 19F
-65.0719
O
CF3
Me
O
O
Me
3al
Me
Me
f1 (ppm)

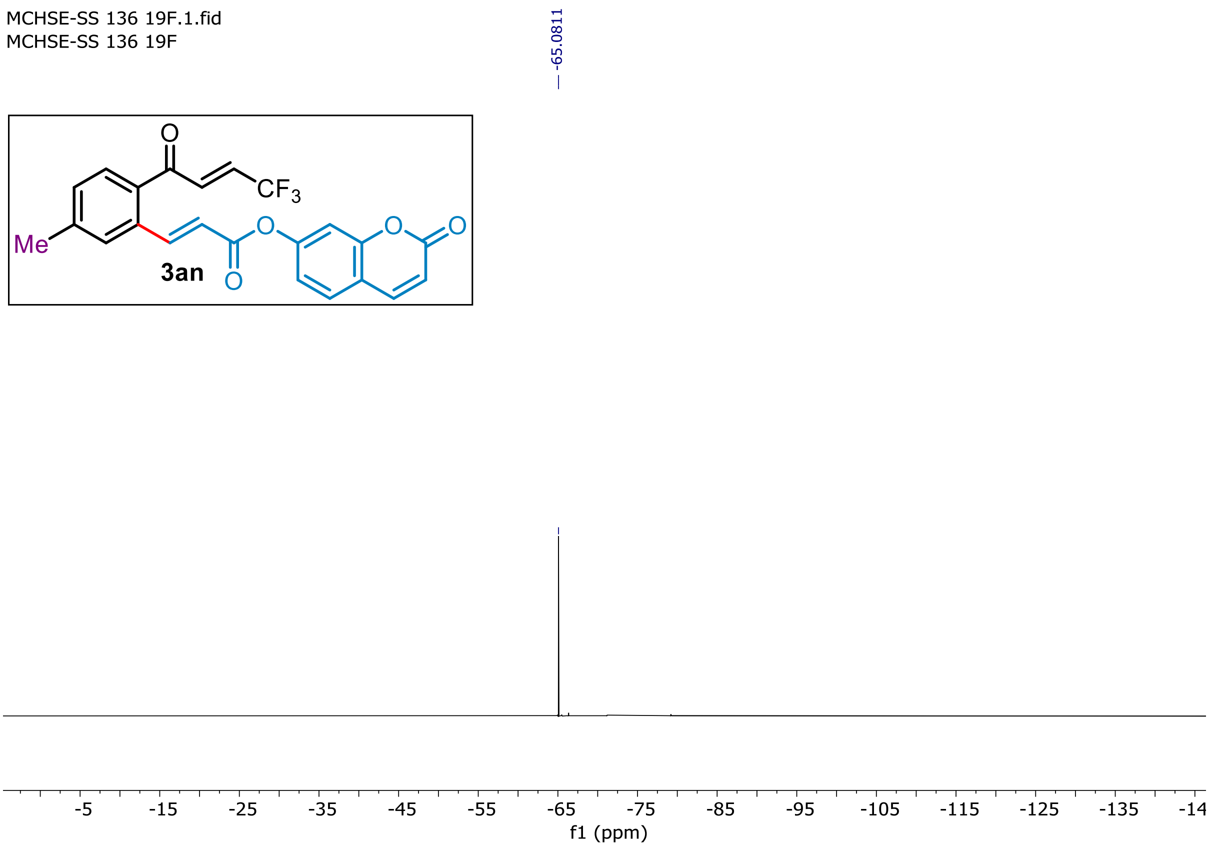

Me
O
Me
O
H
H
H
CF3
O
O
3am
0.96
1.02
0.99
1.04
1.97
1.02
1.00
1.21
1.00
1.96
0.96
3.06
1.26
1.54
1.24
2.67
1.26
3.53
4.33
3.06
f1 (ppm)

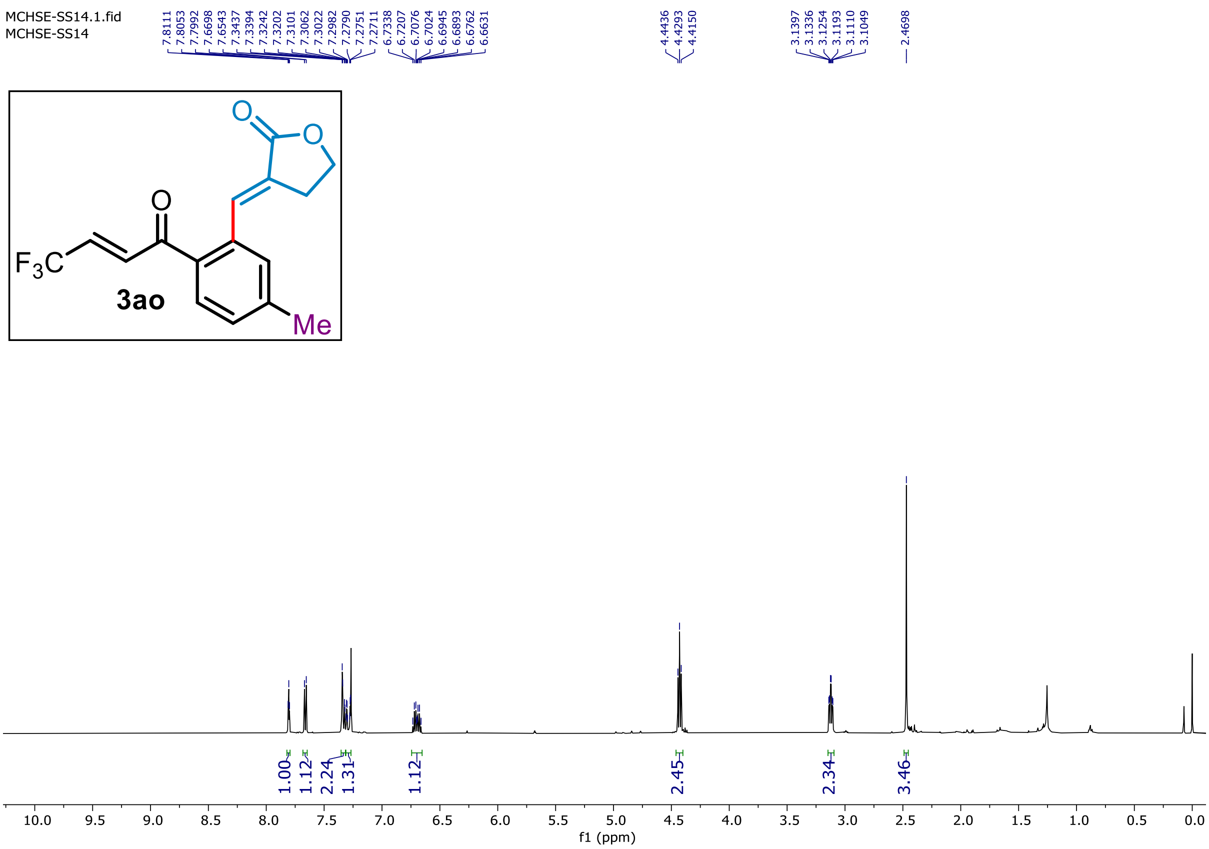

MCHSE-SS103 13C.1.fid
MCHSE-SS103 13C
190.0660
165.0235
148.6114
144.6938
143.9739
138.0281
137.4032
135.5870
134.1544
133.5660
133.5222
133.4747
133.4308
131.2747
130.9860
130.7046
130.5511
130.4232
129.8714
129.4036
126.4326
123.5163
121.6489
121.3639
120.8340
119.2991
118.8058
50.4494
47.9936
44.1894
38.0207
35.8974
31.5669
29.4400
26.3776
25.7783
21.6999
21.6195
13.8612
Me
O
Me
O
H
H
H
CF3
O
O
3am
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

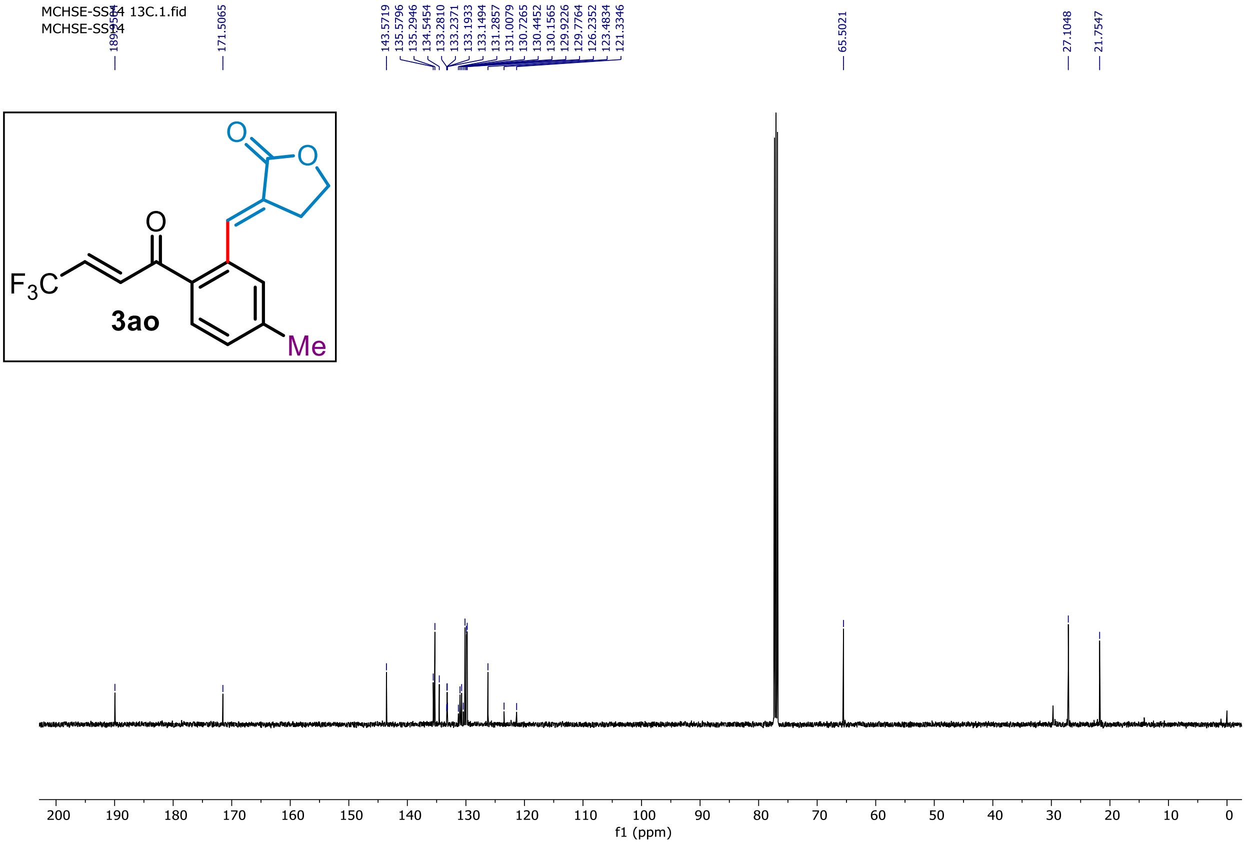

MCHSE-SS103 19F.1.fid
MCHSE-SS103 19F
-65.0609
Me
O
Me
O
H
H
H
CF3
O
O
3am
-5
-15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
f1 (ppm)

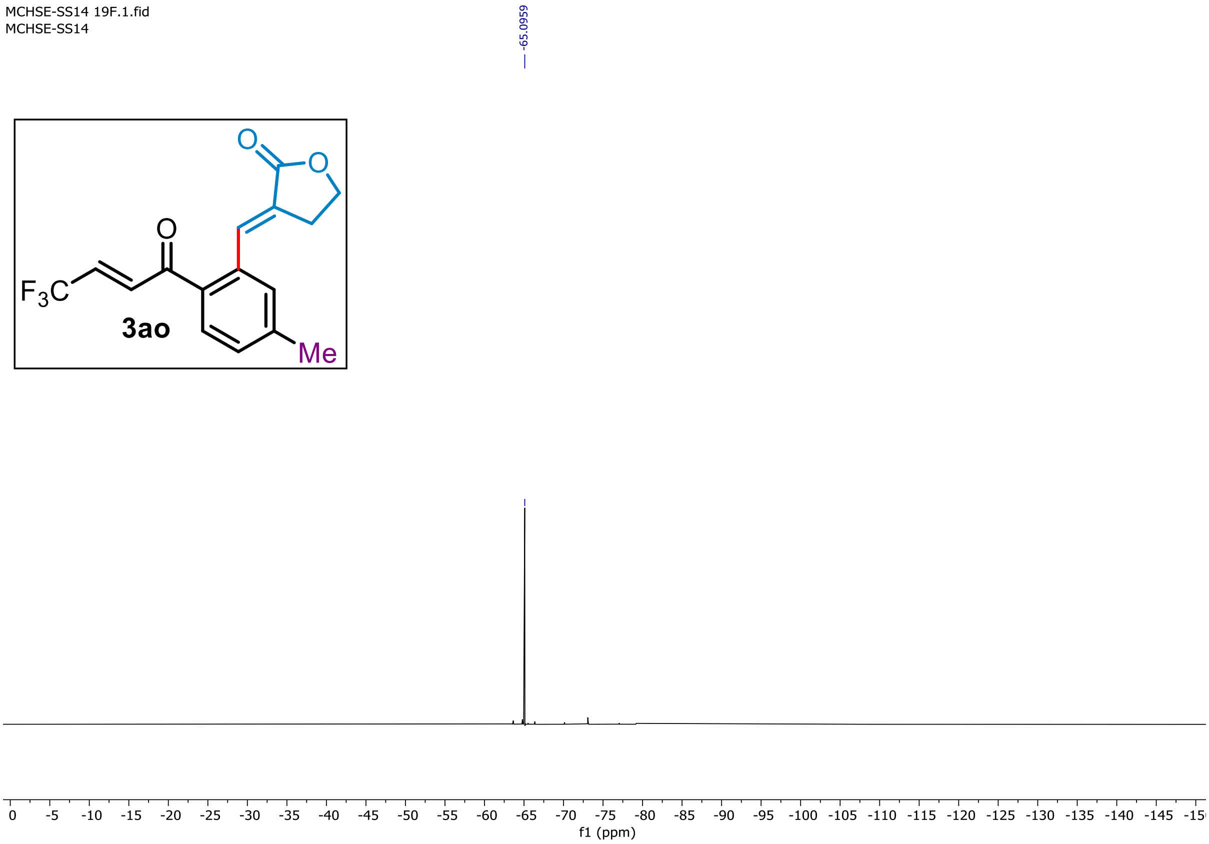

MCSHSE-SS50 1H.1.fid
MCSHSE-SS50 1H
8.2418 8.2101 8.0942 8.0750 7.9139 7.8980 7.8321 7.8068 7.7897 7.6567 7.6524 7.6482 7.6439 7.6253 7.6210 7.6167 7.6125 7.4685 7.4645 7.4523 7.4483 7.3650 7.3605 7.2494 7.2448 7.2326 7.2281 6.9779 6.9642 6.9501 6.9364 6.9328 6.9187 6.9047 6.8110 6.7793 6.4974 6.4782
2.5000 DMSO-d6
2.4359
O
CF3
O
O
O
Me
3an
O
0.98 1.03 1.00 0.96 1.05 1.00 0.97 0.90 1.00 0.99 1.02 1.00
2.87
f1 (ppm)

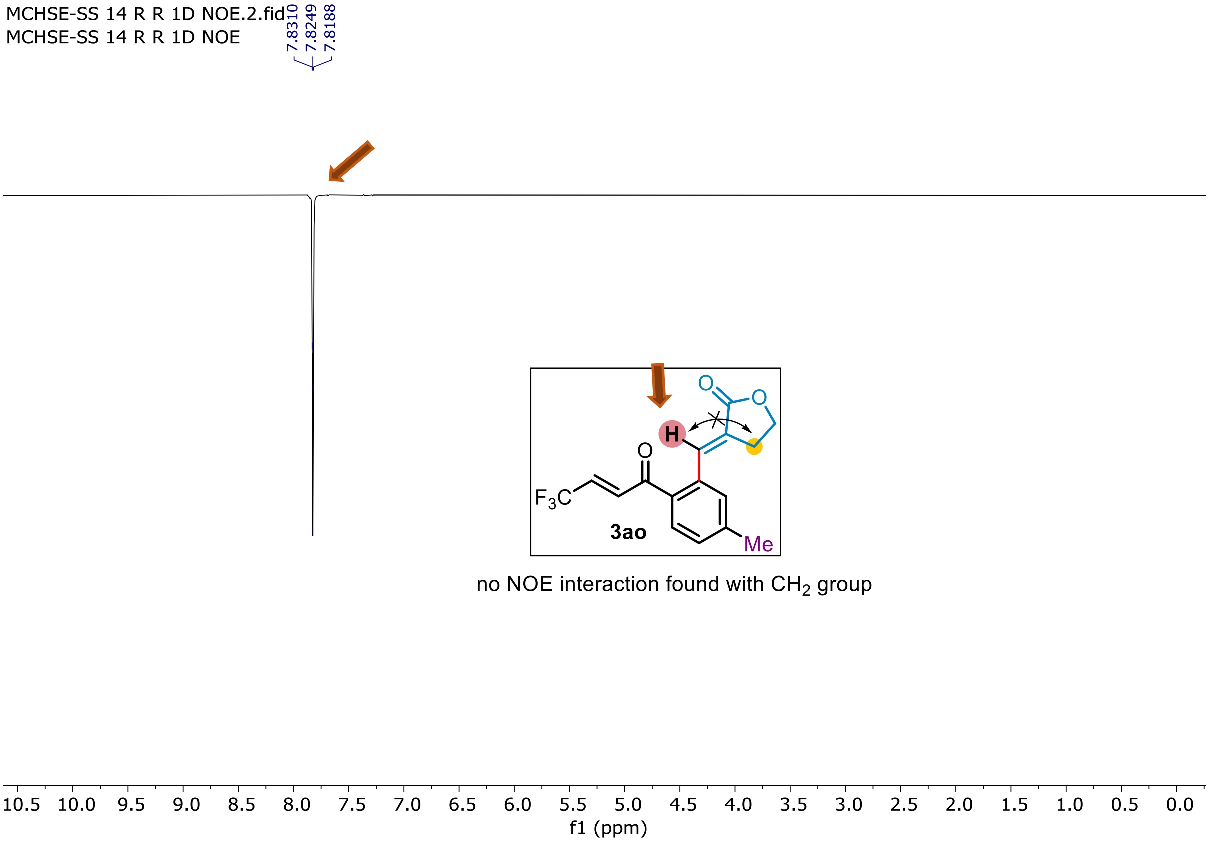

MCSHSE-SS50 13C.1.fid
MCSHSE-SS50 13C
169.4819 164.9504 159.3445 157.9996 151.1220 149.0499 149.0207 140.2062 140.1587 140.1112 139.5228 139.0769 136.1388 135.9561 134.6405 134.4906 134.4139 134.1471 133.8767 133.6062 131.3917 129.2428 127.0904 124.9452 124.1778 123.8452 121.9924 120.8267 115.3487
26.2534
O
CF3
O
O
O
Me
3an
O
f1 (ppm)


MCHSE-SS 136 19F.1.fid
MCHSE-SS 136 19F
-65.0811
3an
f1 (ppm)

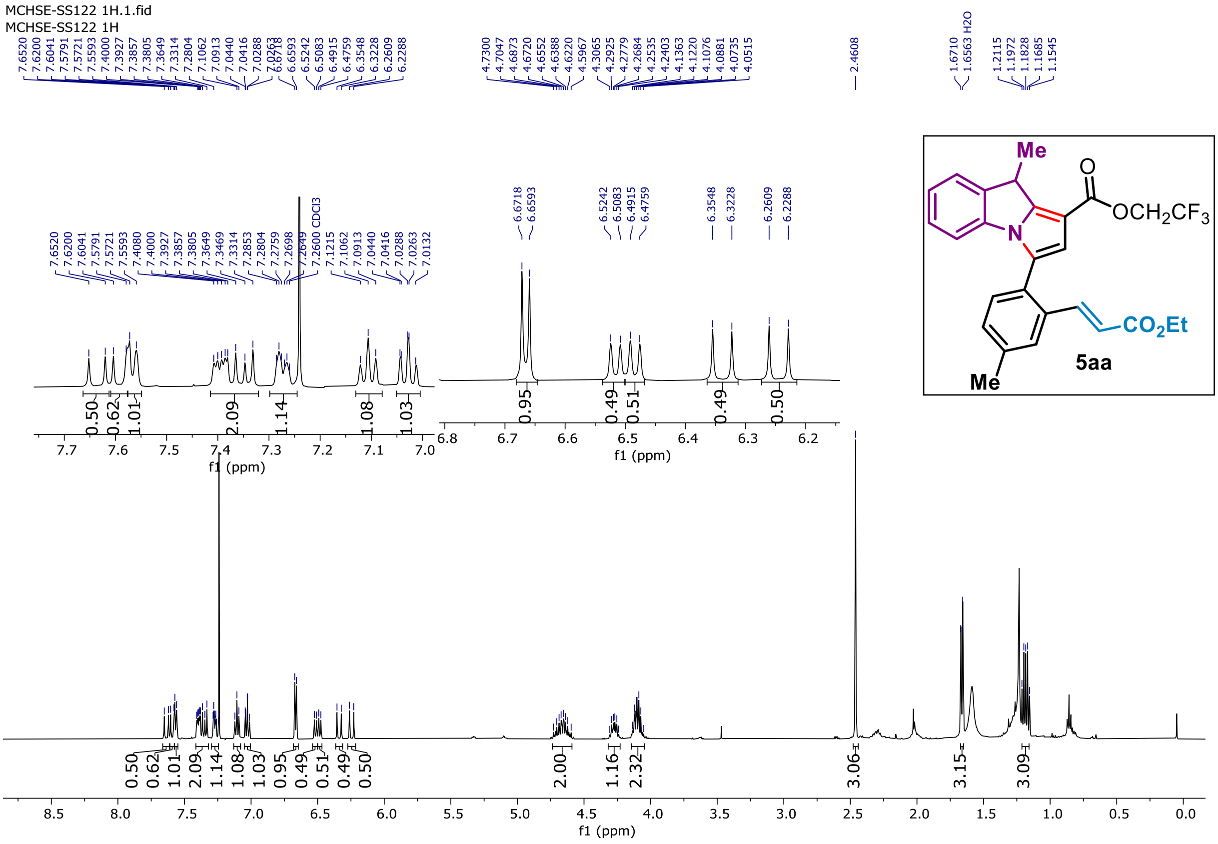

MCHSE-SS14.1.fid
MCHSE-SS14
7.8111 7.8053 7.7992 7.6698 7.6543 7.3437 7.3394 7.3242 7.3202 7.3101 7.3062 7.3022 7.2982 7.2790 7.2751 7.2711 6.7338 6.7207 6.7076 6.7024 6.6945 6.6893 6.6762 6.6631
4.4436 4.4293 4.4150
3.1397 3.1336 3.1254 3.1193 3.1110 3.1049
2.4698
1.00 1.12 2.24 1.31 1.12 2.45 2.34 3.46
3ao
f1 (ppm)

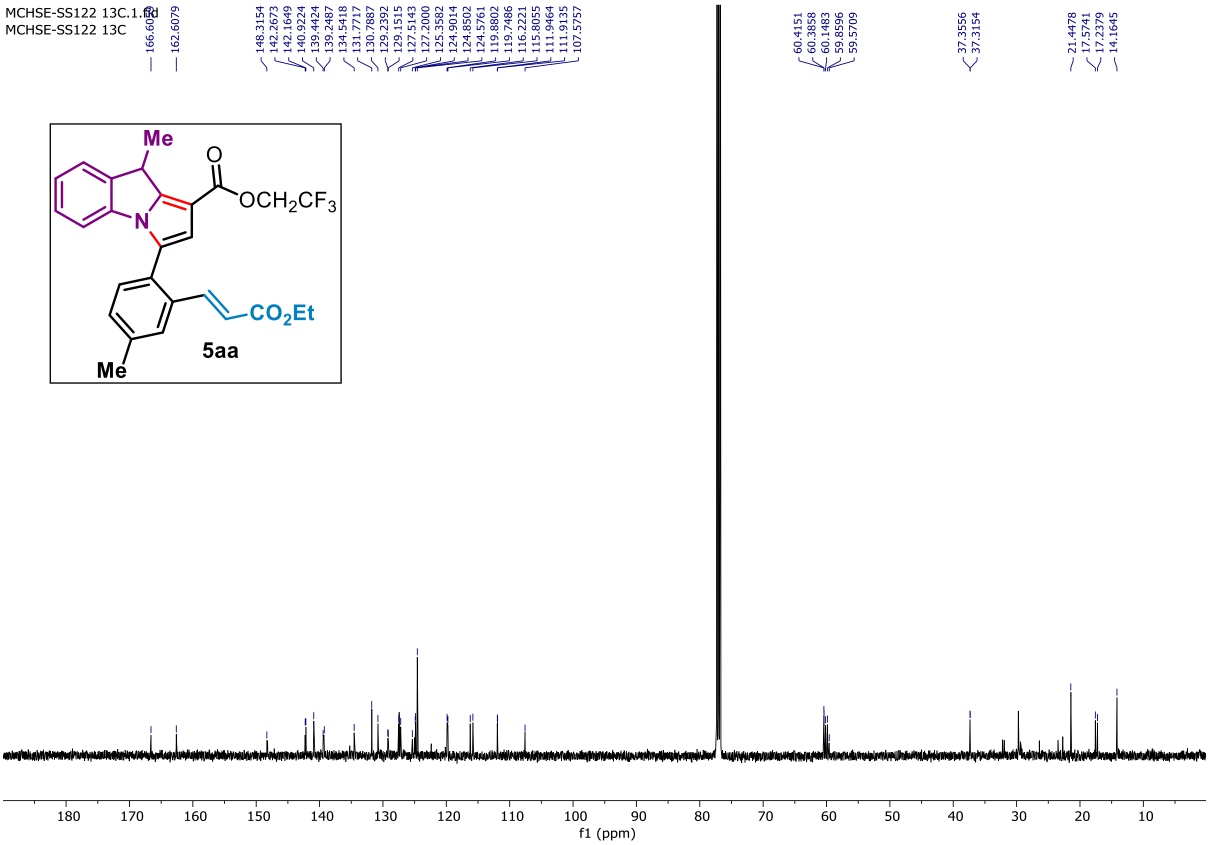

MCHSE-SS14 13C.1.fid
MCHSE-SS14
171.5065
143.5719
135.5796
135.2946
134.5454
133.2810
133.2371
133.1933
133.1494
131.2857
131.0079
130.7265
130.4452
130.1565
129.9226
129.7764
126.2352
123.4834
121.3346
65.5021
27.1048
21.7547
F3C
3ao
Me
f1 (ppm)

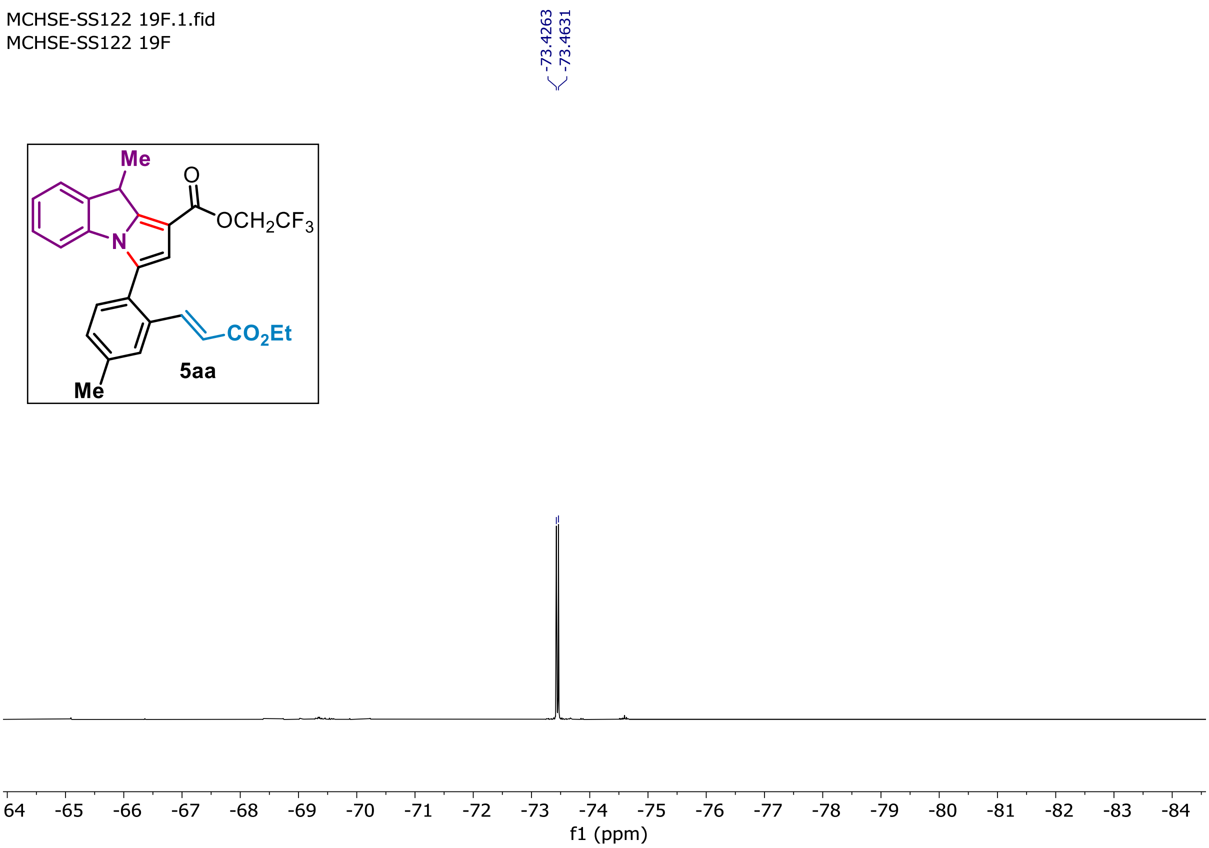

MCHSE-SS14 19F.1.fid
MCHSE-SS14
-65.0959
F3C
3ao
Me
f1 (ppm)

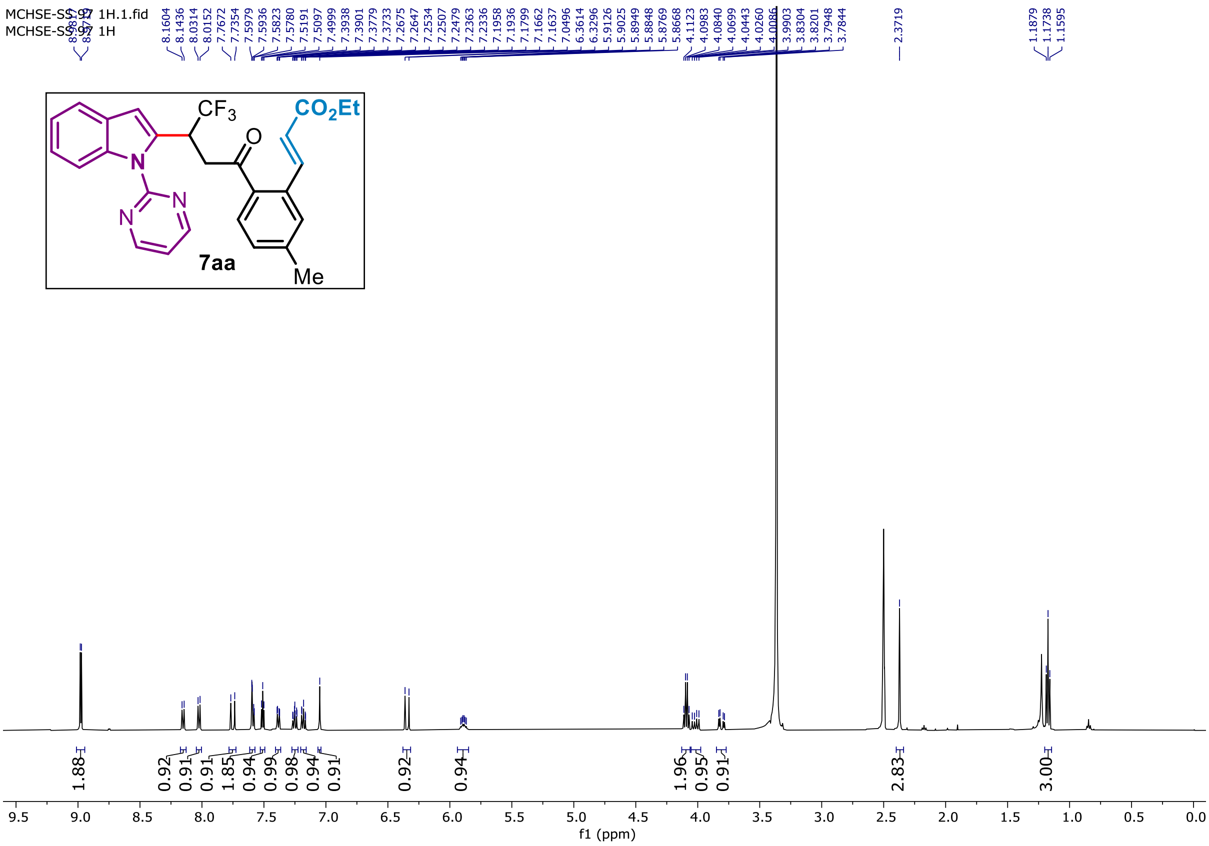


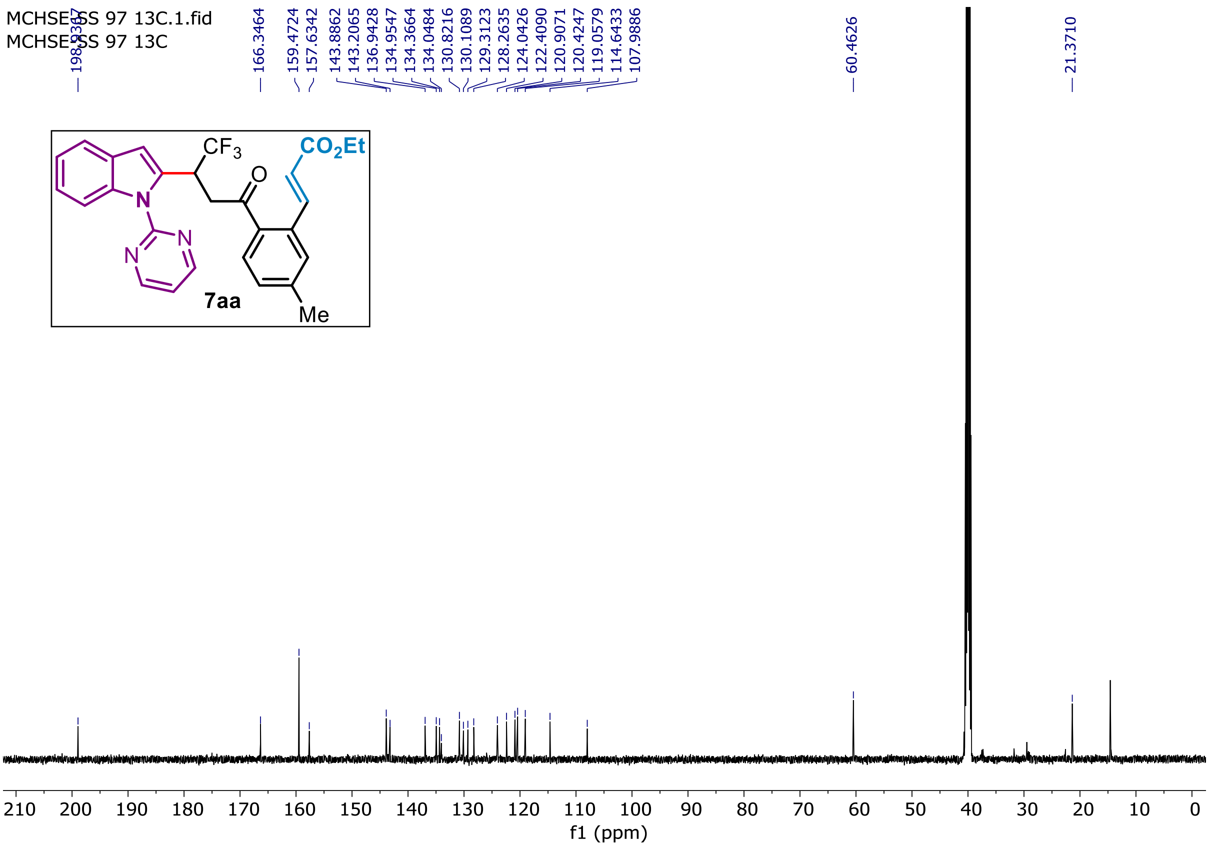
no NOE interaction found with CH_2 group

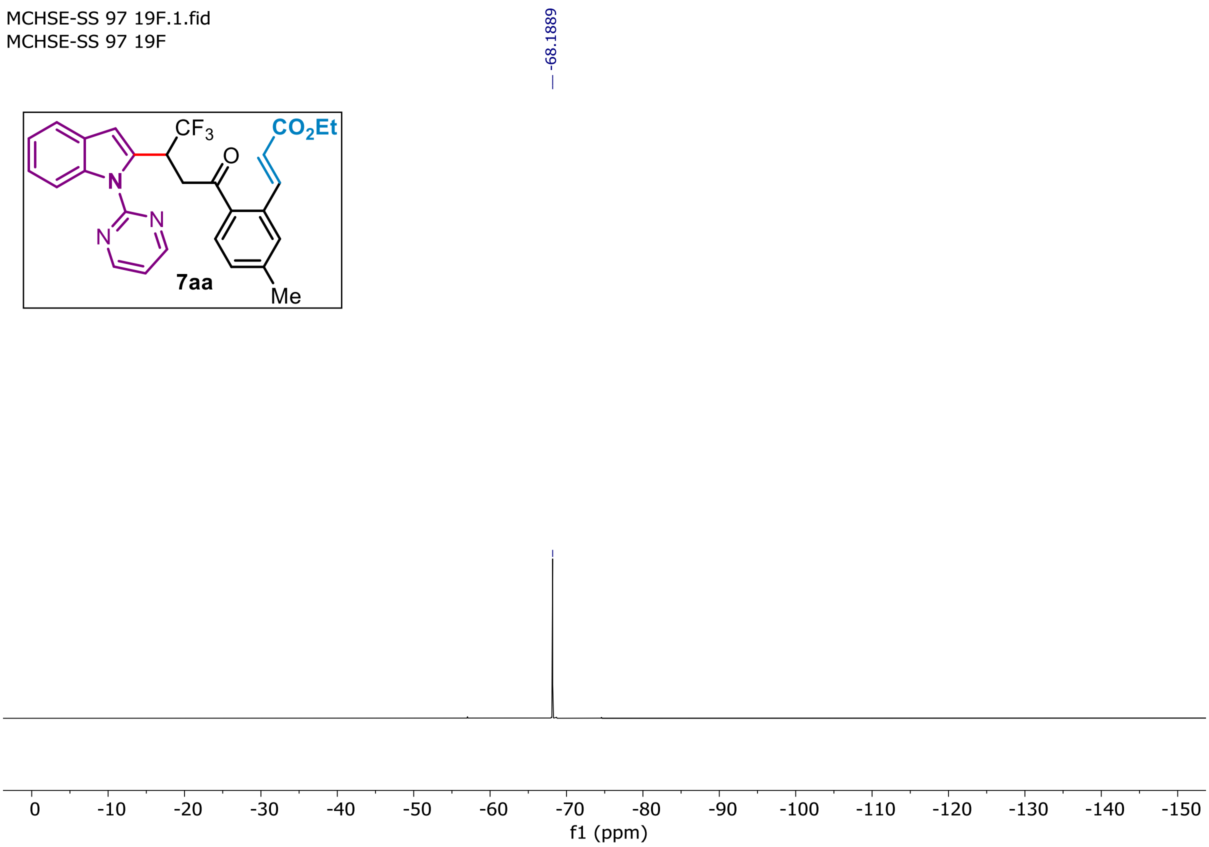


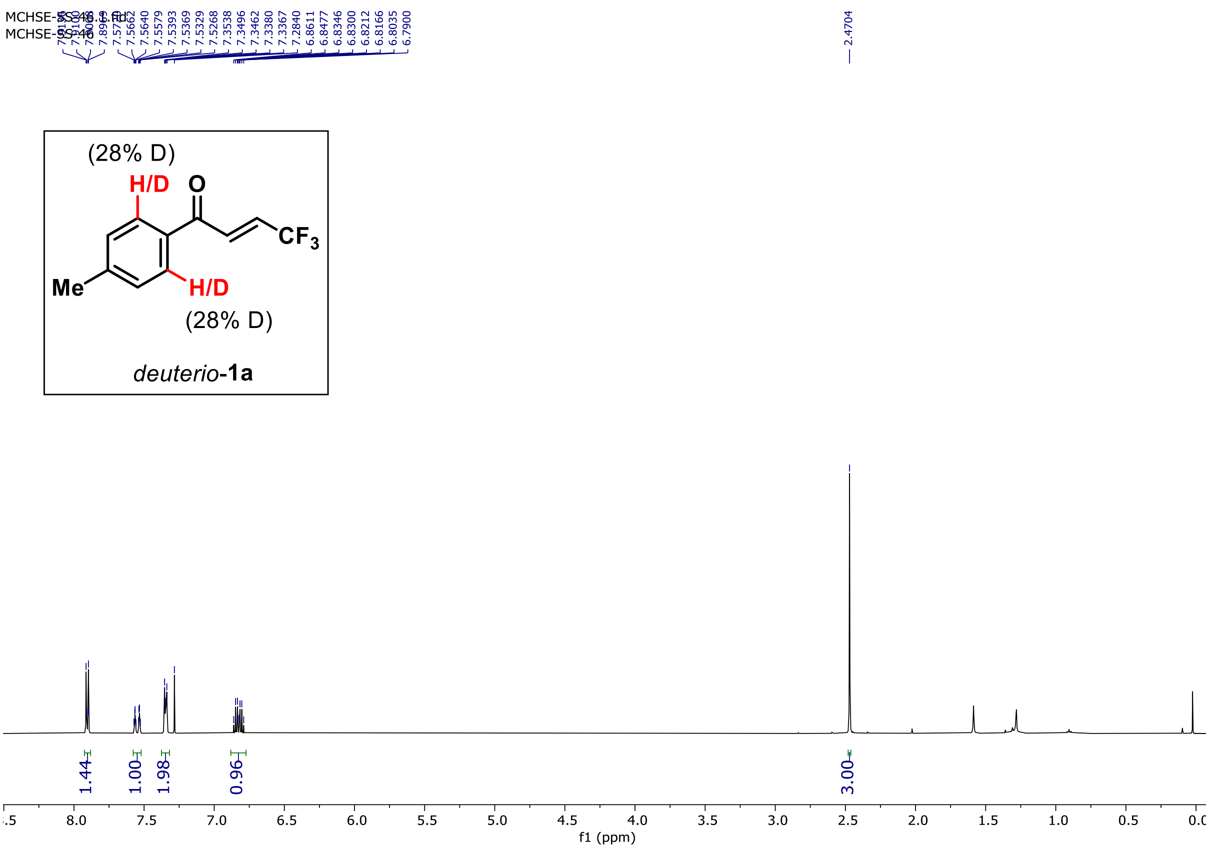

MCHSE-SS122 13C.1.fid
MCHSE-SS122 13C
166.6022
162.6079
148.3154
142.2673
142.1649
140.9224
139.4424
139.2487
134.5418
131.7717
130.7887
129.2392
129.1515
127.5143
127.2000
125.3582
124.9014
124.8502
124.5761
119.8802
119.7486
116.2221
115.8055
111.9464
111.9135
107.5757
60.4151
60.3858
60.1483
59.8596
59.5709
37.3556
37.3154
21.4478
17.5741
17.2379
14.1645
Me
O
OCH2CF3
N
CO2Et
5aa
Me
f1 (ppm)

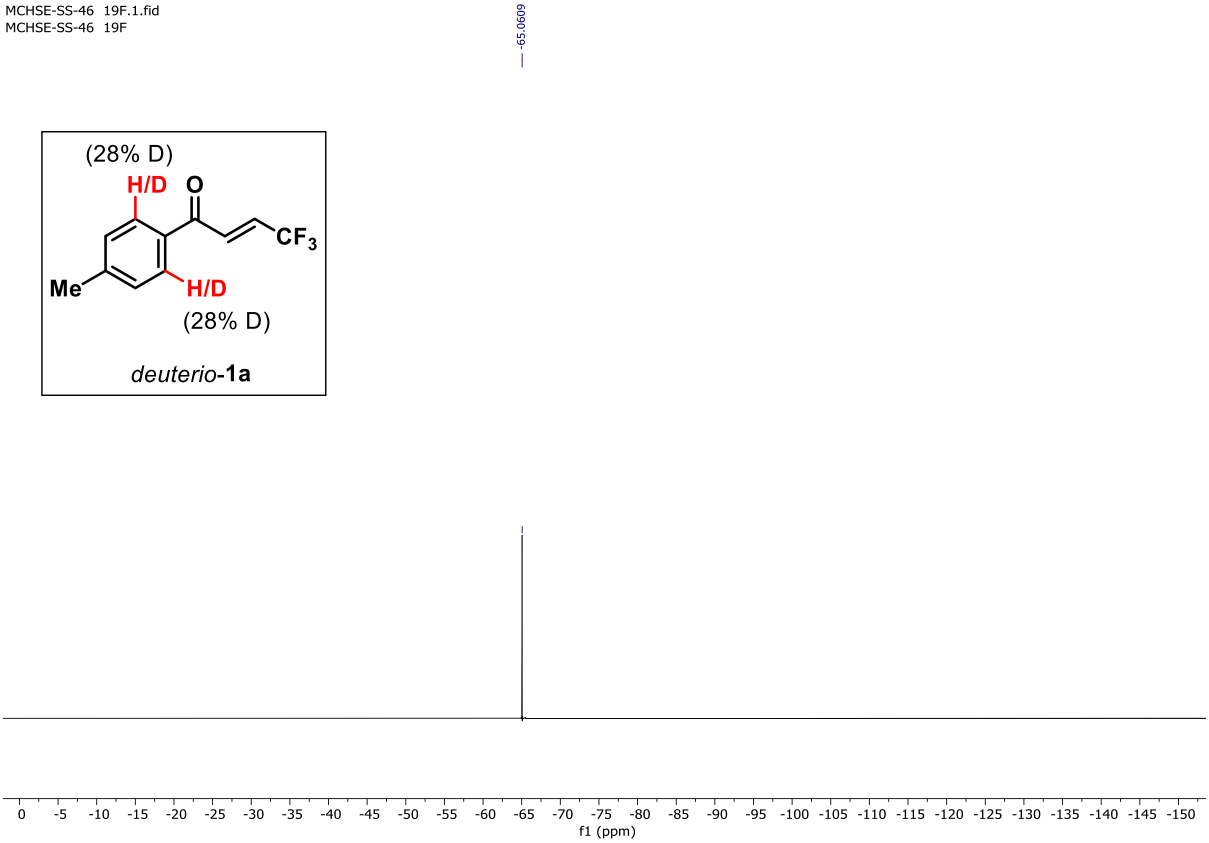

MCHSE-SS122 19F.1.fid
MCHSE-SS122 19F
-73.4263
-73.4631
Me
O
OCH2CF3
N
CO2Et
5aa
Me
f1 (ppm)

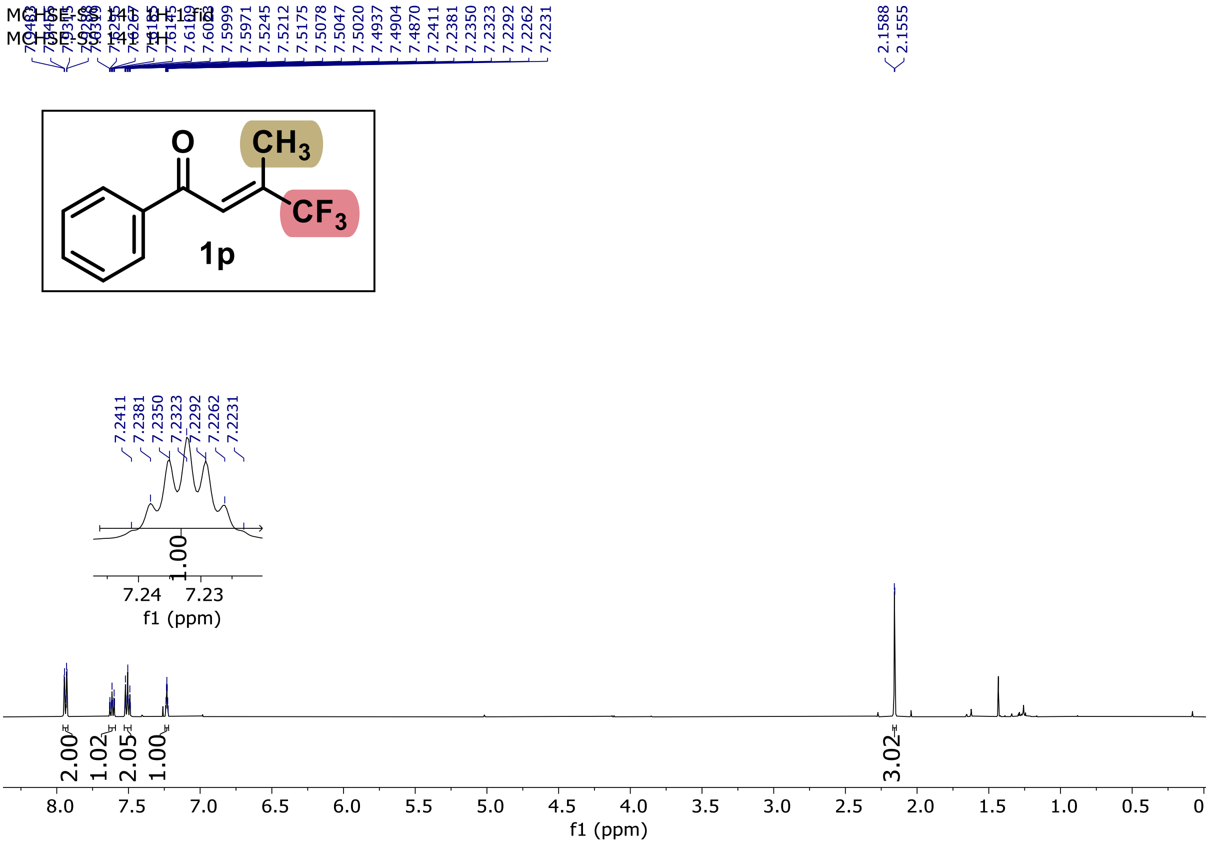

MCHSE-SS 97 1H.1.fid
MCHSE-SS 97 1H
8.1604
8.1436
8.0314
8.0152
7.7672
7.7354
7.5979
7.5936
7.5823
7.5780
7.5191
7.5097
7.4999
7.3938
7.3901
7.3779
7.3733
7.2675
7.2647
7.2534
7.2507
7.2479
7.2363
7.2336
7.1958
7.1936
7.1799
7.1662
7.1637
7.0496
6.3614
6.3296
5.9126
5.9025
5.8949
5.8848
5.8769
5.8668
4.1123
4.0983
4.0840
4.0699
4.0443
4.0260
4.0086
3.9903
3.8304
3.8201
3.7948
3.7844
2.3719
1.1879
1.1738
1.1595
CF3
CO2Et
O
N
N
N
7aa
Me
1.88
0.92
0.91
0.91
1.85
0.94
0.99
0.98
0.94
0.91
0.92
0.94
1.96
0.95
0.91
2.83
3.00
f1 (ppm)

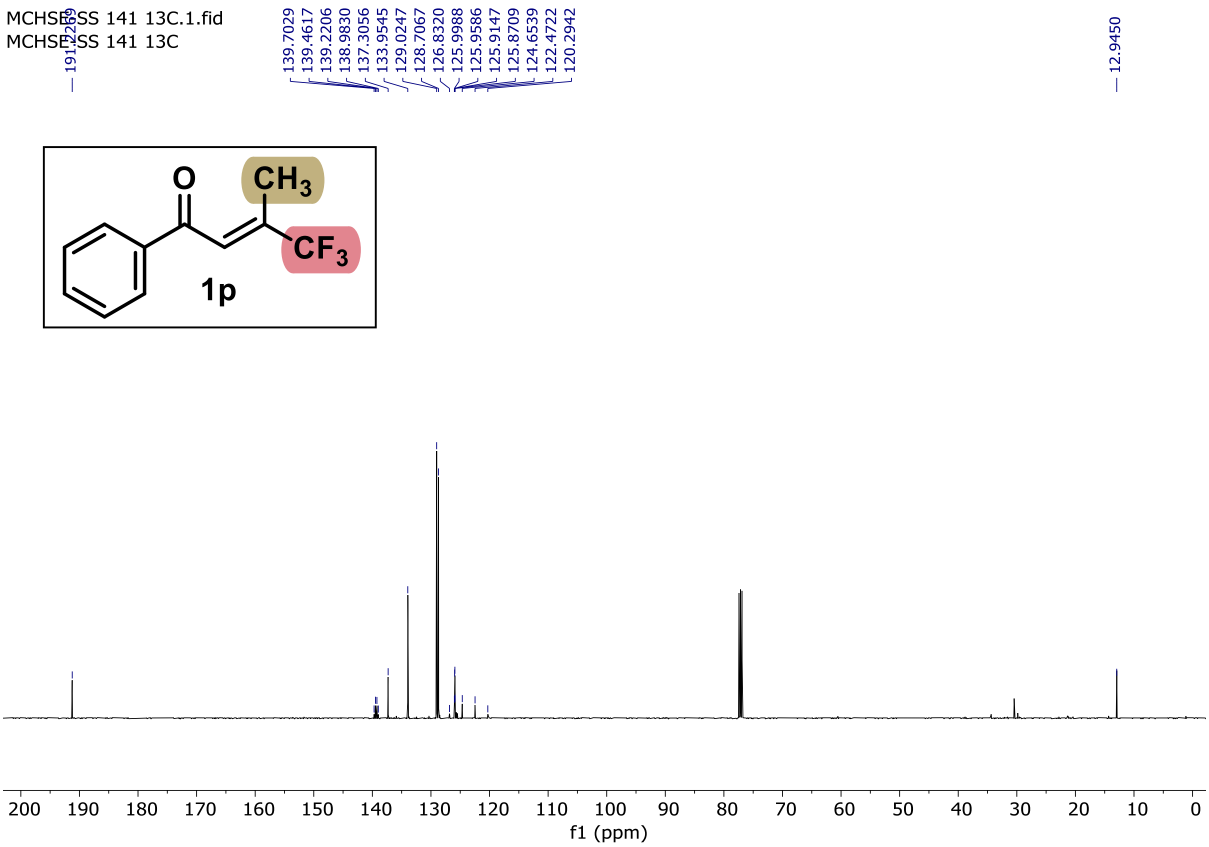

MCHSE-SS 97 13C.1.fid
MCHSE-SS 97 13C
198.9367
166.3464
159.4724
157.6342
143.8862
143.2065
136.9428
134.9547
134.3664
134.0484
130.8216
130.1089
129.3123
128.2635
124.0426
122.4090
120.9071
120.4247
119.0579
114.6433
107.9886
60.4626
21.3710
CF3
CO2Et
O
N
N
N
7aa
Me
f1 (ppm)

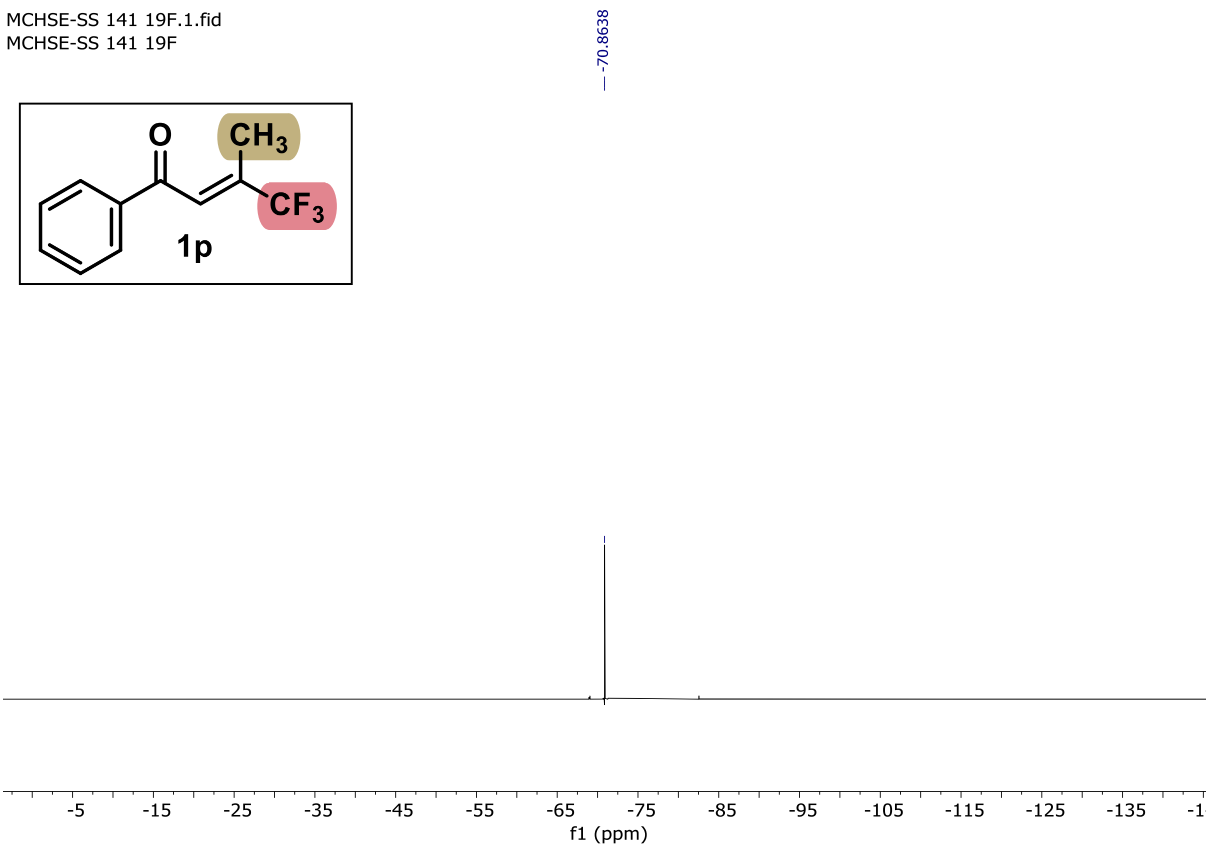

MCHSE-SS 97 19F.1.fid
MCHSE-SS 97 19F
-68.1889
CF3
CO2Et
O
N
N
N
7aa
Me
f1 (ppm)

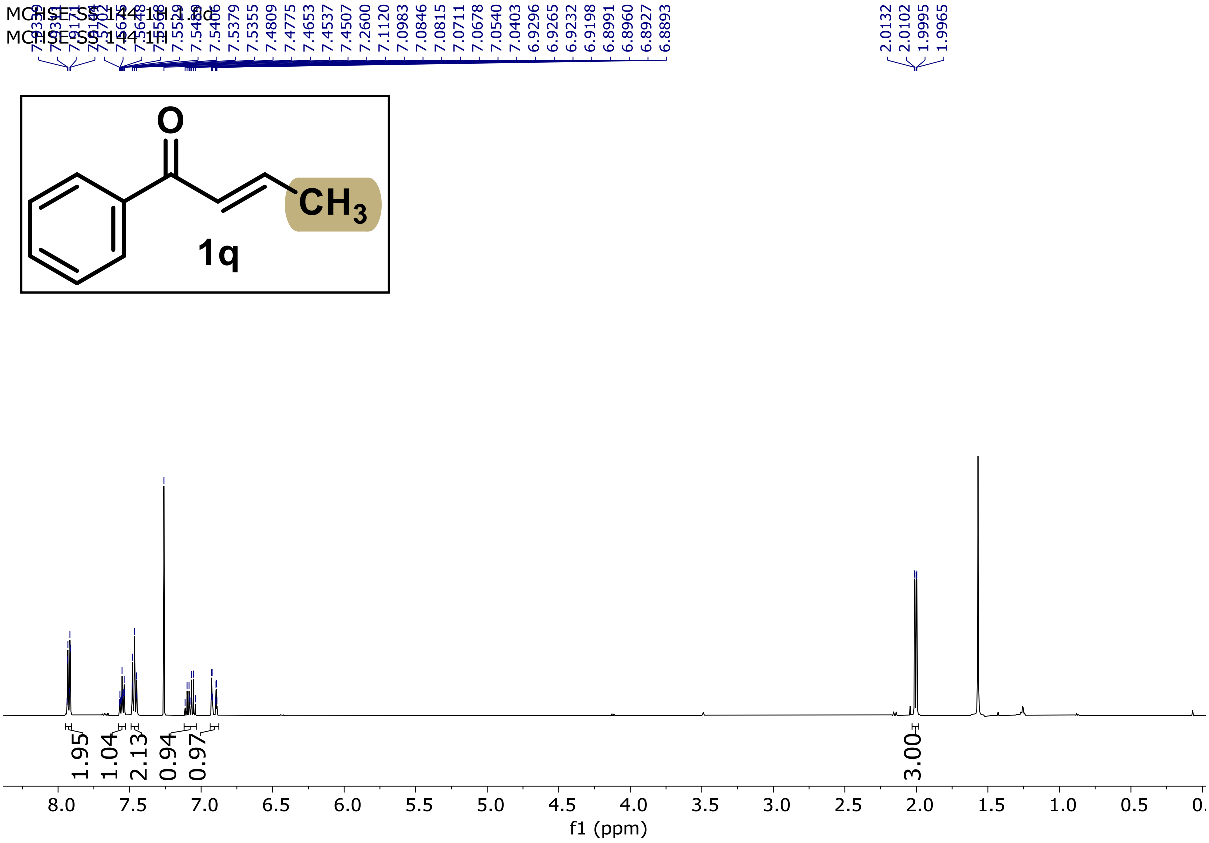

7.8969
7.5662
7.5640
7.5579
7.5393
7.5369
7.5329
7.5268
7.3538
7.3496
7.3462
7.3380
7.3367
7.2840
6.8611
6.8477
6.8346
6.8300
6.8212
6.8166
6.8035
6.7900
2.4704
(28% D)
H/D
O
CF3
Me
H/D
(28% D)
deuterio-1a
1.44
1.00
1.98
0.96
3.00
f1 (ppm)

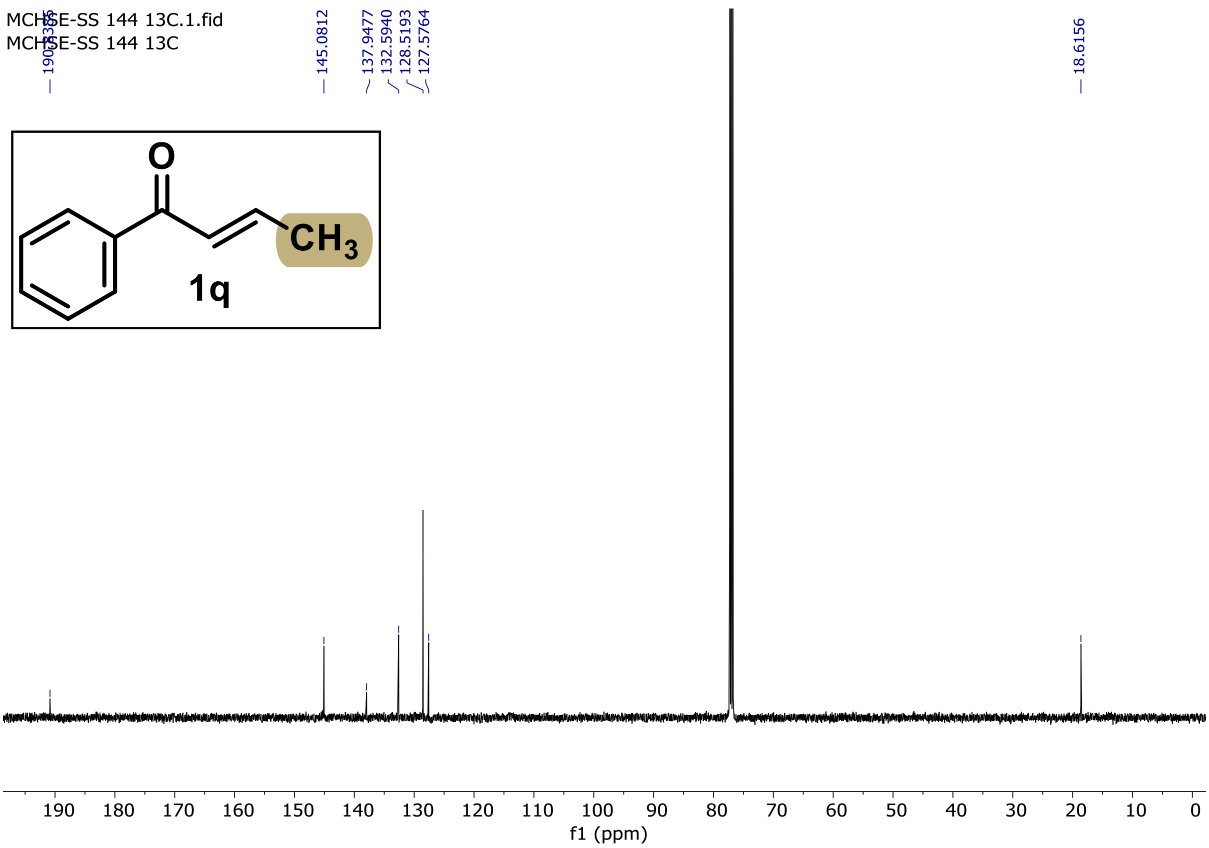

MCHSE-SS-46 19F.1.fid
MCHSE-SS-46 19F
-65.0609
(28% D)
H/D
O
CF3
Me
H/D
(28% D)
deuterio-1a
f1 (ppm)


7.6145
7.6119
7.6093
7.5999
7.5971
7.5245
7.5212
7.5175
7.5078
7.5047
7.5020
7.4937
7.4904
7.4870
7.2411
7.2381
7.2350
7.2323
7.2292
7.2262
7.2231
2.1588
2.1555
O
CH3
CF3
1p
1.00
7.24
7.23
f1 (ppm)
2.00
1.02
2.05
1.00
3.02
f1 (ppm)


MCHSE-SS 141 13C.1.fid
MCHSE-SS 141 13C
139.7029
139.4617
139.2206
138.9830
137.3056
133.9545
129.0247
128.7067
126.8320
125.9988
125.9586
125.9147
125.8709
124.6539
122.4722
120.2942
12.9450
O
CH3
CF3
1p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MCHSE-SS 141 19F.1.fid
MCHSE-SS 141 19F
-70.8638
O
CH3
CF3
1p
-5
-15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
f1 (ppm)


7.5403
7.5379
7.5355
7.4809
7.4775
7.4653
7.4537
7.4507
7.2600
7.1120
7.0983
7.0846
7.0815
7.0711
7.0678
7.0540
7.0403
6.9296
6.9265
6.9232
6.9198
6.8991
6.8960
6.8927
6.8893
2.0132
2.0102
1.9995
1.9965
O
CH3
1q
1.95
1.04
2.13
0.94
0.97
3.00
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)


MCHSE-SS 144 13C.1.fid
MCHSE-SS 144 13C
145.0812
137.9477
132.5940
128.5193
127.5764
18.6156
O
CH3
1q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)