Electronic Supplementary Material (ESI) for ChemComm.

Ligand Free Pd-Catalyzed Double Heck-Reaction of *N*-(*o*-Bromoaryl) Acrylamides with α-F/CF_3-Acrylates

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1. General Information:

Experimental: All the inert condition reactions are performed in nitrogen atmosphere using Glove box and Schlenk techniques. Catalytic reactions were performed in commercially available 7 mL screw cap vials fitted with PTFE/silicone septa purchased from Sigma-Aldrich and 1.5 mL screw cap vials (HPLC) purchased from Shimadzu.

Chromatography: Analytical thin layer chromatography (TLC) was performed on Merck and GLR precoated silica gel 60 F_{254} plates, using UV light as the visualization agent. Chromatographic purification of products was accomplished by Column chromatography on Finar silica gel (100-200 mesh). The solvents were removed under reduced pressure using rotary evaporator to obtain the desired compounds.

Characterization: The compounds were characterized using ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ESI-HRMS. NMR spectra were recorded at Bruker Ascend 500 MHz for ^{1}H, 126 MHz for ^{13}C and 471 MHz for ^{19}F NMR and MestReNova was used for data assessment. The chemical shift (δ) for ^{1}H and ^{13}C NMR are given in ppm relative to internal standard/residual signals of the solvents (for ^{1}H NMR ($CHCl_3$ @ 7.260 ppm) for ^{13}C NMR ($CHCl_3$ @ 77.00 ppm) and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are followed to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublets of doublets; dddd, doublet of doublets of doublets of doublets; td, triplet of doublet; and dt, doublet of triplet; qd, quartet of doublets; bs, broad singlet; bd, broad doublet; bt, broad triplet. High-resolution mass spectra (HRMS) were obtained using Waters Xevo-G2XQTOF instruments with the electrospray ionization (ESI) method. The Gas Chromatography-Mass spectrometry (GC-MS) analysis was performed using Agilent 5977B GC/MSD spectrometer. Single crystal X-ray diffractions were recorded using Bruker AXS Smart Apex CCD diffractometer. HR-TEM Images were recorded on a Technai G^2 20 (FEI) performing at 200 kV (accelerating voltage). X-ray photoelectron spectroscopy (XPS) measurement was done using AXIS SUPRA, XPS by Kratos Analytical Ltd., equipped with aluminium monochromator with aluminium source (Al Kα radiation hv =1486.7eV). Energy dispersive X-ray spectroscopy (EDX) was performed on JSM-IT300HR, JEOL instrument. Enantiomeric excesses were determined with a SHIMADZU P-series HPLC system using chiral columns (DAICEL) by comparing the samples with the corresponding racemic samples.

Materials: Chemicals like amines, carboxylic acids, methyl 2-fluoroacrylate, methyl 2-(trifluoromethyl)acrylate and DMAP were purchased from BLD Pharma, Spectrochem, GLR, TCI,

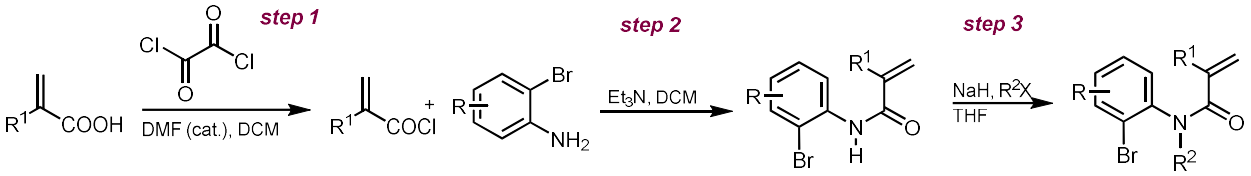
Sigma-Aldrich, SRL chemical and used without further purification. Pd-catalysts were purchased from Sigma-Aldrich and Spectrochem. Oxalyl chloride was purchased from Spectrochem and distilled under N_2. Dry DMF and DMA were purchased from Wako Pure Chemical Industries and used inside glove box without further drying. DCM, hexane, and ethyl acetate were purchased from Rankem and Finar (25 litre drums) and used after distillation for column chromatography. Dioxane was purchased from SRL. DCM and dioxane were dried by stirring over CaH_2 overnight and distilling under nitrogen atmosphere.

2. Synthesis of Starting Materials:

N-(2-bromoaryl)-*N*-substituted acrylamides (**1a-1y**) were prepared according to the previous reports.[1,2] All the characterization data of the starting materials are found consistent with the reported literature.

2.1. The synthesis of *N*-(2-bromoaryl)-*N*-substituted acrylamides (1a-1y):

General procedure-1 (GP-1):



Scheme S1. Synthesis of *N*-(2-bromoaryl)-*N*-substituted acrylamides.

Step 1: A two-necked round bottom flask equipped with a magnetic stir bar was charged with acrylic acid (1.2 equiv) and dry DCM (0.5 M) was added under nitrogen atmosphere. The flask was then cooled to 0 °C using an ice bath and 2-4 drops of dry DMF were added. Afterwards, freshly distilled oxalyl chloride (1.3 equiv) was added dropwise to the solution. Then, the solution was allowed to attain room temperature slowly and stirred for 5-6 h. The acyl chloride was used for the next step without further purification.

Step 2: In a separate two-necked round-bottom flask equipped with a magnetic stir bar, bromoaniline (1.0 equiv), triethylamine (1.5 equiv) and dry DCM (0.5 M) were added and stirred for 1 h. Then, freshly prepared acryloyl chloride (**Step 1**) was added dropwise for 10-15 min at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight until the aniline was consumed completely (monitored by TLC). The reaction mixture was washed with water and extracted with DCM (3 times). The organic layer was washed with 1N HCl solution, 1N

NaOH solution, and brine respectively. The final organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue acrylamide was used for the next step without further purification.

Step 3: A suspension of NaH (60% dispersion in mineral oil, 1.5 equiv) was added to the solution of acrylamide (**Step 2**) in dry THF (0.5 M) at 0 °C under nitrogen atmosphere. After being stirred at room temperature for 30 min, the reaction was cooled to 0 °C, and corresponding alkyl or aryl halide (1.2 equiv) was added dropwise under nitrogen atmosphere. The mixture was then stirred at room temperature overnight, then quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 times). The combined organic extracts were washed with water and brine respectively. The final organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue was purified by silica column chromatography (100-200 mesh) using a mixture of hexane and ethyl acetate as the eluent to afford the desired acrylamides (**1a-1y**).

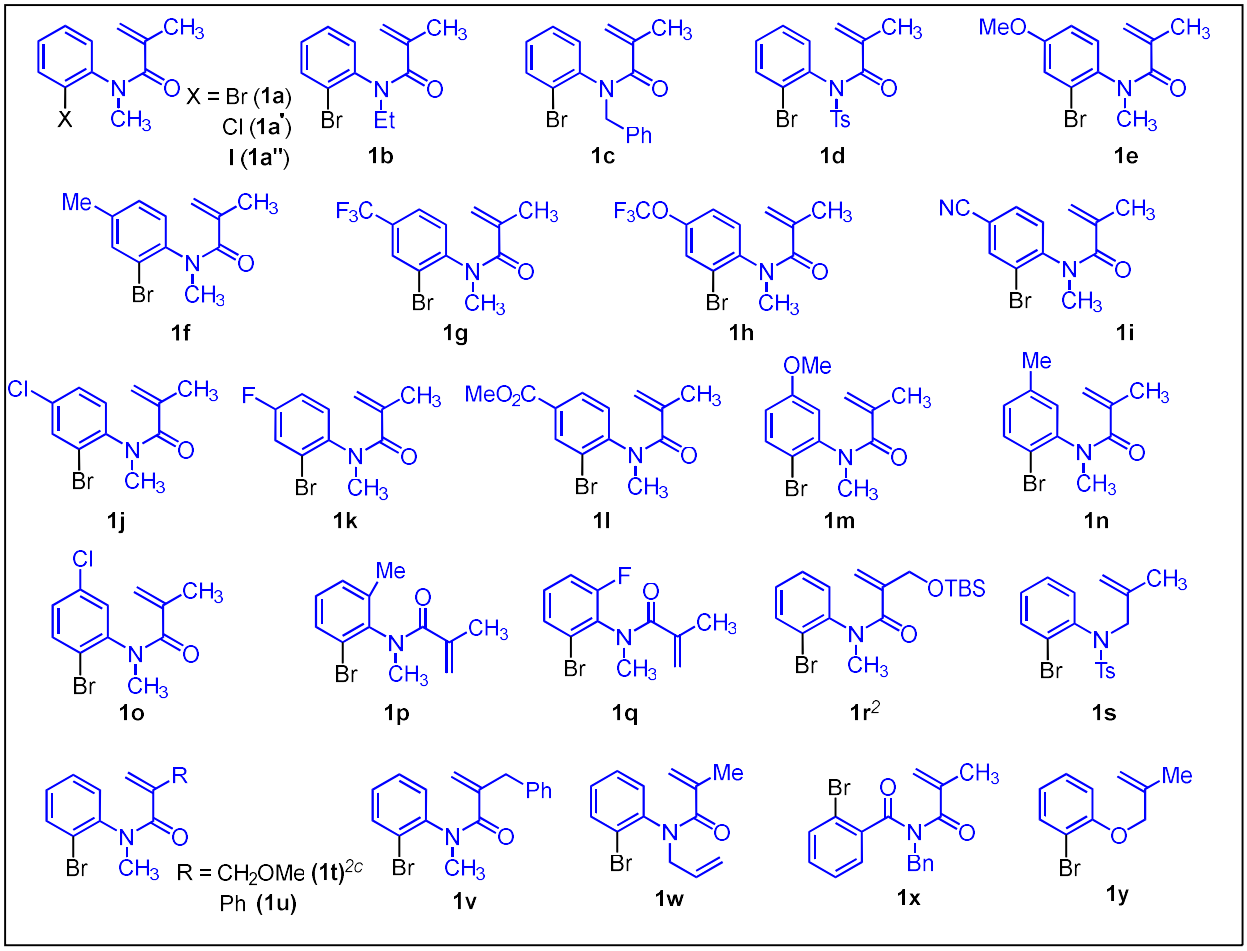
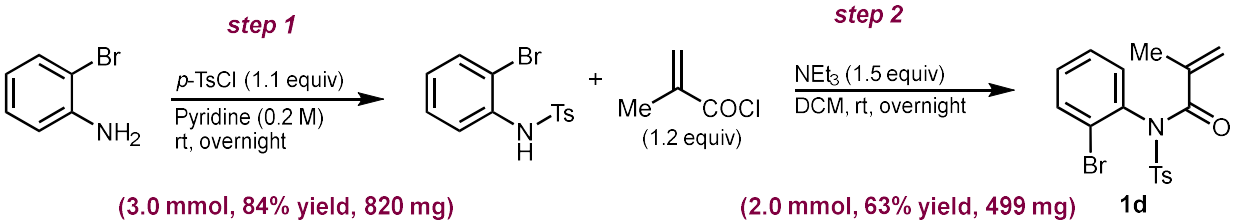


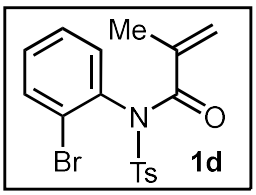
Figure S1. *N*-(2-bromoaryl)-*N*-substituted acrylamides.

N-(2-bromophenyl)-*N*-tosylmethacrylamide (1d)[1]



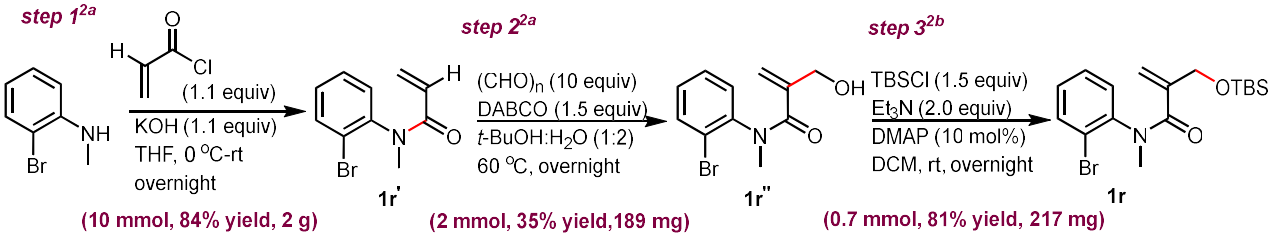
Scheme S2. Synthesis of **1d**.

The compound **1d** was prepared according to the literature precedent.[1] The crude mixture (**step 2**) was purified by column chromatography on silica gel (Hexane:Ethyl acetate = 9.0:1.0, R_f = 0.25) to afford the desired product **1d** as a white solid (M. pt. = 92–94 °C).



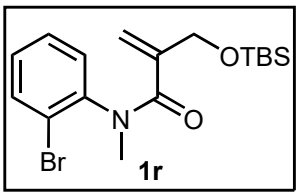
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (td, *J* = 7.7, 1.3 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 (td, *J* = 7.9, 1.6 Hz, 1H), 5.22 (bs, 1H), 5.18 (bd, *J* = 1.2, 1H), 2.43 (s, 3H), 1.77 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 169.8, 145.0, 138.8, 136.4, 135.7, 133.9, 133.2, 130.8, 129.8, 129.1, 128.0, 124.9, 122.7, 21.6, 19.5; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{16}BrNO_3SNa$: 415.9926, found 415.9932.

2.2 General Procedure for Synthesis of *N*-(2-bromophenyl)-2-(((tert-butyldimethylsilyl)oxy)methyl)-*N*-methylacrylamide (1r) (GP-2):



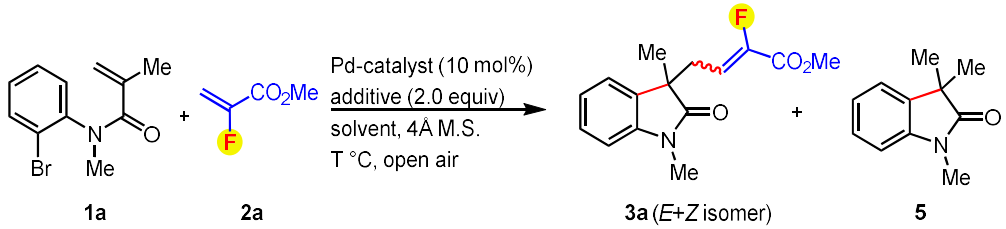
Scheme S3. Synthesis of **1r**.

The compound **1r** was prepared according to the literature precedent.[2] The final reaction mixture (**step 3**) was purified by column chromatography on silica gel (Hexane:Ethyl acetate = 9.0:1.0, R_f = 0.25) to afford the desired product **1r** as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.34–7.20 (m, 2H), 7.15 (t, J = 7.1 Hz, 1H), 5.24 (s, 1H), 5.02 (s, 1H), 4.40 (d, J = 14.2 Hz, 1H), 4.20 (d, J = 14.4 Hz, 1H), 3.23 (s, 3H), 0.86 (s, 9H), 0.01 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 169.7, 143.4, 143.2, 133.6, 130.3, 129.1, 128.4, 122.6, 116.5, 63.3, 36.4, 25.8, 18.2, -5.6; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{27}BrNO_2Si$: 384.0989, found 384.0978.

3. General Procedure for Optimization Reactions:



Scheme S4. Optimization reactions of double Heck reaction of **1a** with methyl 2-fluoroacrylate.

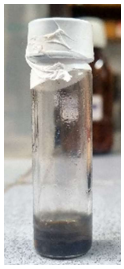
General procedure-3 (GP-3): In a 7.0 mL reaction vial equipped with a magnetic bead, *N*-(2-bromophenyl)-*N*-methyl acrylamide (**1a**) (0.1 mmol, 1.0 equiv), Pd-catalyst (x equiv.), additive (silver and non-silver salts) (2.0 equiv) were added, followed by addition of methyl 2-fluoroacrylate (**2a**) (2.0 equiv), solvent (0.2 M) and one 4Å molecular sieve under N_2 atmosphere. Then, the reaction was kept on stirring at desired temperature. It was observed that decreasing the vial size and concentrating the reaction mixture increased the conversion. The addition of molecular sieves diminished the side product **5** formation. After completion of the reaction (monitored by TLC), the crude reaction mixture was filtered through a celite pad, dried on sodium sulfate followed by high vacuum. Afterwards, fluorobenzene (9.4 μL, 0.1 mmol) was added to the dried reaction mixture as internal standard and crude ^{19}F NMR was recorded.

Table S1: Initial optimization of reaction.[a]

S. No.	Ligand	Additive	Solvent	Product 3a (%)	*Z:E*
1	XPhos	Ag_2CO_3	1,4-dioxane	58[b]	17:1
2	SPhos	Ag_2CO_3	1,4-dioxane	13[b]	20:1
3	Brettphos	Ag_2CO_3	1,4-dioxane	56[b]	20:1
4	PPh_3	Ag_2CO_3	1,4-dioxane	39[b]	20:1
5	-	Ag_2CO_3	1,4-dioxane	41[c]	15:1

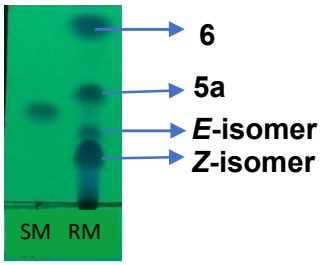
6	-	Ag_2CO_3	1,4-dioxane	64[c,d]	15:1
7	-	Ag_2CO_3	1,4-dioxane	78[c,d,e]	15:1

Conditions: [a]**1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), Ag_2CO_3 (2 equiv), dioxane (0.2 M), 75 °C, 30 h, under nitrogen. [b]crude ^{19}F NMR yield using fluorobenzene (9.4 μL, 0.1 mmol) as internal standard. [c]90 °C, 15 h, isolated yields. [d]all the starting materials were added in open air and run the reaction. [e]1.5 mL vial.



7 mL reaction vial

1.5 mL reaction vial



General TLC

Table S2: Optimization of reaction conditions.[a]

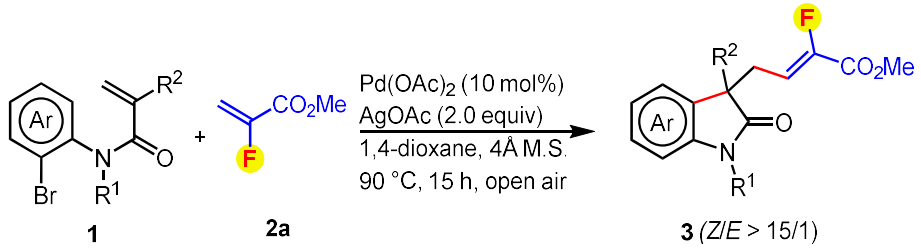
entry	additive	solvent	yield (%)
1	Ag_2CO_3	1,4-dioxane	41[c,d,e]
2	Ag_2CO_3	1,4-dioxane	64[c,d]
3	Ag_2CO_3	1,4-dioxane	78[c]
4	AgOAc	1,4-dioxane	87[c]
5	Ag_3PO_4	1,4-dioxane	80[c]
6	AgOTf	1,4-dioxane	30[f]
7	Na_2CO_3	1,4-dioxane	6
8	Cs_2CO_3	1,4-dioxane	<5
9	K_3PO_4	1,4-dioxane	20
10	AgOAc	DMF	17
11	AgOAc	DMA	16
12	AgOAc	MeCN	<5
13	AgOAc	toluene	<5
14	AgOAc	1,4-dioxane	56[g]
15	AgOAc	1,4-dioxane	37[h,f]
16	-	1,4-dioxane	NR
17	AgOAc	1,4-dioxane	NR[i]
18	AgOAc	1,4-dioxane	50[j,c]
19	AgOAc	1,4-dioxane	57[k], 68[l]

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), additive (2.0 equiv), solvent (0.5 mL), 4 Å MS, 90 °C, 15 h, vial size 1.5 mL. [b]Crude ^1H NMR yield using nitromethane as internal standard. [c]Isolated yield, *Z/E* (~15/1). [d]Vial size 7.0 mL. [e]Under N_2 gas. [f]Crude ^{19}F NMR

yield using fluorobenzene as internal standard, *Z/E* (>15/1). [g]$Pd(TFA)_2$ (10 mol%). [h]$Pd_2(dba)_3$ (5 mol%). [i]In absence of $Pd(OAc)_2$. [j]$Pd(OAc)_2$ (5 mol%). [k]70 °C, 24 h, *Z/E* (7/1). [l]80 °C, 24 h, *Z/E* (7/1).

4. General Procedure for Reaction Setup:

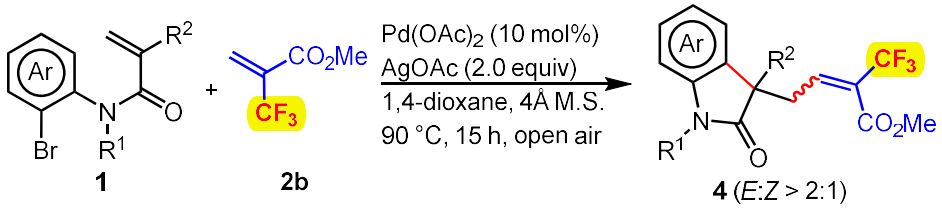
4.1. Double Heck-type Cyclization of Methyl 2-fluoroacrylate



Scheme S5. Scope study of double-Heck cyclization reaction of **1** with methyl 2-fluoroacrylate.

General procedure-4 (GP-4): In a 1.5 mL vial equipped with a magnetic bead, was added acrylamide substrate (**1**) (0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), AgOAc (33 mg, 0.2 mmol) and 4 Å molecular sieve (1 no.). Next, methyl-2-fluoroacrylate (**2a**) (19 μL, 0.2 mmol) and dry dioxane (0.2 M) were added to the reaction vial in open atmosphere. Then the reaction vial was sealed and stirred in a pre-heated oil bath at 90 °C for 15 h. The crude reaction mixture was then purified by silica gel column chromatography. *E/Z* ratio was assigned based on the ^{1}H NMR.

4.2. Double Heck-type Cyclization of Methyl 2-(trifluoromethyl)acrylate



Scheme S6. Double-Heck cyclization reaction of **1** with Methyl 2-(trifluoromethyl)acrylate.

General procedure-5 (GP-5): In a 1.5 mL reaction vial equipped with a magnetic bead, was added acrylamide substrate (**1**) (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), AgOAc (67 mg, 0.4 mmol) and 4 Å molecular sieve (1 no.). Next, methyl 2-(trifluoromethyl)acrylate (**2b**) (51 μL, 0.4 mmol) and dry dioxane (0.2 M) were added to the reaction vial in open atmosphere. Then the reaction vial was sealed and stirred in a pre-heated oil bath at 90 °C for 15 h. Them, the crude reaction mixture was purified by silica gel column chromatography. *E/Z* ratio was assigned based on the ^{1}H NMR.

5. Unsuccessful substrates[a]

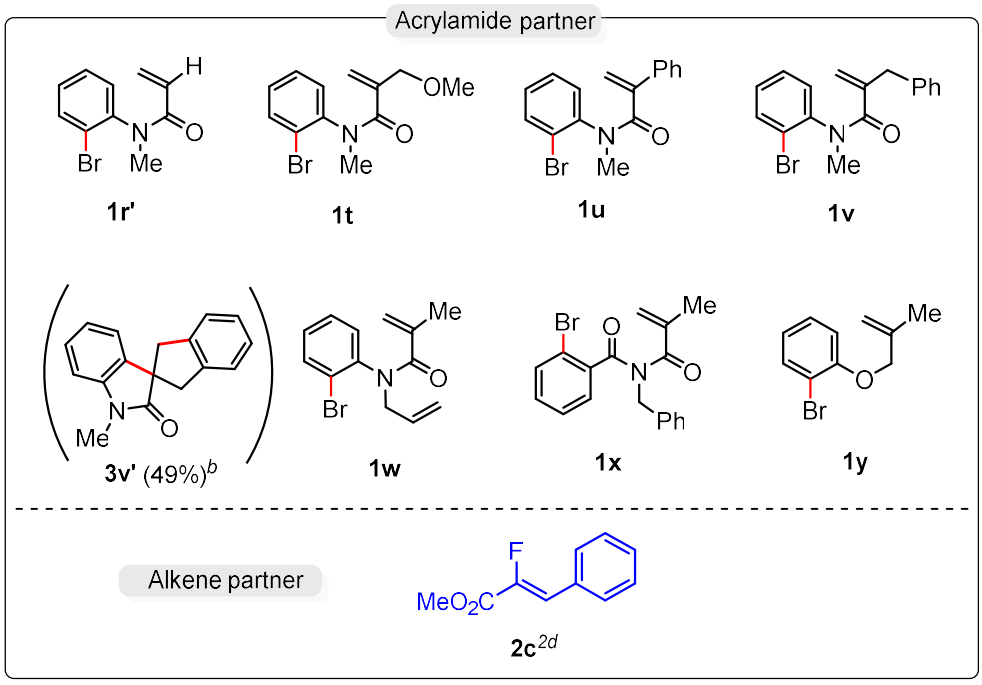
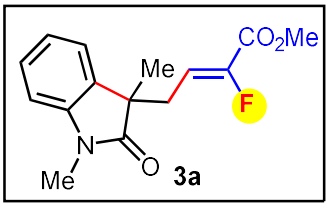


Figure S2. [a]**1** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), AgOAc (2.0 equiv), 1,4-dioxane (0.5 mL), 4 Å MS, 90 °C, open air, 15 h, vial size 1.5 mL. [b]obtained from reaction of **1v**.

6. Characterization of Products:



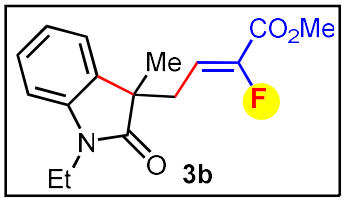
Methyl (*Z*)-4-(1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3a)

Following **GP-4**, the reaction of **1a** (25 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3a** (24 mg, 87%, *Z:E* = 15:1) as yellow oil; R_f = 0.27 (20% EtOAc in hexane). Reaction at 1.0 mmol scale in a 7 mL screw cap reaction vial afforded **3a** in 66% yield (182 mg). Reaction of **1a′** (*N*-(2-chlorophenyl)-*N*-methylmethacrylamide) (42 mg, 0.2 mmol) with **2a** (42 mg, 37 µl, 0.4 mmol) gave **3a** in 29% yield (16 mg) while **1a″** (*N*-(2-iodophenyl)-*N*-methylmethacrylamide) (30 mg, 0.1 mmol) with **2a** (21 mg, 19 µl, 0.2 mmol) gave **3a** in 68% yield (19 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.93 (dt, *J* = 31.9, 7.9 Hz, 1H), 3.76 (s, 3H), 3.23 (s, 3H), 2.75–2.68 (m, 2H), 1.42 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.4, 160.7 (d, *J* = 35.8 Hz), 149.0 (d, *J* = 259.4 Hz), 142.8, 132.8, 128.2, 122.8, 122.7, 115.0 (d, *J* = 10.8 Hz), 108.2, 52.4, 47.3 (d, *J* = 1.7

Hz), 32.5 (d, *J* = 2.1 Hz), 26.2, 22.8; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -119.1 (*E*-minor), -127.2 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{15}H_{17}FNO_3$: 278.1187, found 278.1190.

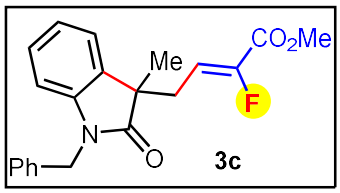
Methyl (*Z*)-4-(1-ethyl-3-methyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3b)



Following **GP-4**, the reaction of **1b** (27 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3b** (19 mg, 66%, *Z:E* = 17:1) as colorless oil; R_f = 0.25 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.88 (dt, *J* = 31.9, 7.8 Hz, 1H), 3.91–3.66 (m, 2H), 3.74 (s, 3H), 2.79–2.64 (m, 2H), 1.41 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 178.9, 160.7 (d, *J* = 39.1 Hz), 148.9 (d, *J* = 259.2 Hz), 141.9, 133.0, 128.2, 122.9, 122.5, 115.0 (d, *J* = 10.7 Hz), 108.3, 52.4, 47.3 (d, *J* = 1.6 Hz), 34.6, 32.7 (d, *J* = 1.7 Hz), 22.7, 12.6; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -119.2 (*E*-minor), -127.2 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{16}H_{19}FNO_3$: 292.1343, found 292.1350.

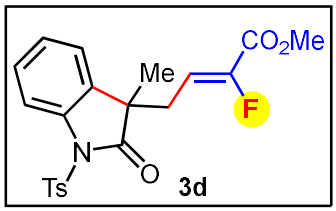
Methyl (*Z*)-4-(1-benzyl-3-methyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3c)



Following **GP-4**, the reaction of **1c** (33 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3c** (20 mg, 56%, *Z:E* = 13:1) as yellow oil; R_f = 0.35 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.34–7.19 (m, 6H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.91 (dt, *J* = 31.8, 8.0 Hz, 1H), 5.04 (d, *J* = 15.7 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 2.80 (ddd, *J* = 38.2, 14.5, 8.0 Hz, 2H), 1.48 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 179.4, 160.7 (d, *J* = 36.0 Hz), 149.0 (d, *J* = 259.3 Hz), 142.0, 135.8, 132.6, 128.8, 128.2, 127.6, 127.1, 122.8, 122.7, 114.9 (d, *J* = 10.7 Hz), 109.3, 52.4, 47.5 (d, *J* = 1.8 Hz), 43.5, 32.6 (d, *J* = 1.9 Hz), 23.3; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -118.8 (*E*-minor), -126.8 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{21}H_{21}FNO_3$: 354.1500, found 354.1501.

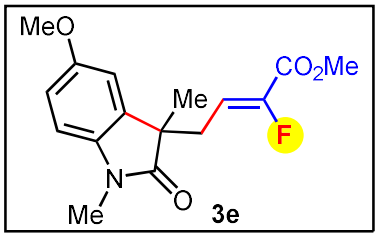
Methyl (*Z*)-2-fluoro-4-(3-methyl-2-oxo-1-tosylindolin-3-yl)but-2-enoate (3d)



Following **GP-4**, the reaction of **1d** (79 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3d** (35 mg, 42%, *Z:E* = 94:1) as yellow oil; R_f = 0.19 (15% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.90 (m, 3H), 7.38–7.32 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.23–7.14 (m, 2H), 5.63 (dt, *J* = 31.3, 8.0 Hz, 1H), 3.73 (s, 3H), 2.62 (dddd, *J* = 16.3, 14.6, 8.0, 1.5 Hz, 2H), 2.42 (s, 3H), 1.35 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 177.7, 160.3 (d, *J* = 35.9 Hz), 149.2 (d, *J* = 260.6 Hz), 145.7, 138.2, 135.1, 131.5, 129.7, 129.0, 127.8, 125.2, 123.0, 113.9, 113.4 (d, *J* = 10.7 Hz), 52.4, 47.9 (d, *J* = 2.0 Hz), 33.0 (d, *J* = 2.0 Hz), 23.5, 21.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -117.4 (*E*-minor), -125.9 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{21}H_{20}FNO_5SNa$: 440.0938, found 440.0943.

Methyl (*Z*)-2-fluoro-4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (3e)

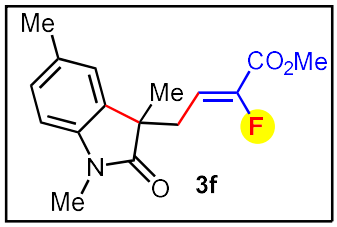


Following **GP-4**, the reaction of **1e** (28 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3e** (41 mg, 66%, *Z:E* = 11:1) as a yellow solid; melting point 63–65 °C; R_f = 0.20 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82–6.77 (m, 2H), 6.76–6.72 (m, 1H), 5.90 (dt, *J* = 31.9, 7.9 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.19 (s, 3H), 2.77–2.63 (m, 2H), 1.40 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.0, 160.8 (d, *J* = 35.7 Hz), 156.2, 149.0 (d, *J* = 259.0 Hz), 136.4, 134.2, 115.0 (d, *J* = 10.8 Hz), 112.4, 110.3, 108.5, 55.8, 52.4, 47.8 (d, *J* = 1.7 Hz), 32.5 (d, *J* = 2.1 Hz), 26.3, 23.0; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -119.1 (*E*-minor), -127.1 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{19}FNO_4$: 308.1293, found 308.1296.

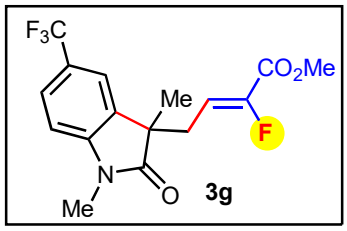
Methyl (*Z*)-2-fluoro-4-(1,3,5-trimethyl-2-oxoindolin-3-yl)but-2-enoate (3f)

Following **GP-4**, the reaction of **1f** (27 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3f** (35 mg, 60%, *Z:E* = 17:1) as yellow oil; R_f = 0.30 (20% EtOAc in hexane).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.92 (dt, *J* = 32.0, 7.9 Hz, 1H), 3.76 (s, 3H), 3.20 (s, 3H), 2.70 (dddd, *J* = 34.5, 14.8, 7.9, 2.1 Hz, 2H), 2.34 (s, 3H), 1.39 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.3, 160.8 (d, *J* = 35.8 Hz), 149.0 (d, *J* = 259.0 Hz), 140.5, 132.9, 132.3, 128.5, 123.5, 115.2 (d, *J* = 10.7 Hz), 107.9, 52.4, 47.4 (d, *J* = 1.8 Hz), 32.6 (d, *J* = 2.2 Hz), 26.3, 23.0, 21.1; **^{19}F{^{1}H} NMR (471 MHz, CDCl3)** δ -119.3 (*E*-minor), -127.3 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{19}FNO_3$: 292.1343, found 292.1346.

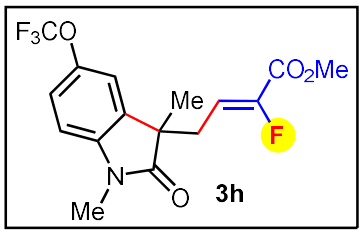
Methyl (*Z*)-4-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2-fluorobut-2-enoate (3g)



Following **GP-4**, the reaction of **1g** (32 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3g** (52 mg, 76%, *Z:E* = >20:1) as yellow oil; R_f = 0.13 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.56 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.88 (dt, *J* = 31.5, 8.0 Hz, 1H), 3.75 (s, 3H), 3.24 (s, 3H), 2.72 (dddd, *J* = 41.6, 14.7, 8.0, 2.0 Hz, 2H), 1.43 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 179.2, 160.6 (d, *J* = 35.5 Hz), 149.3 (d, *J* = 260.9 Hz), 145.9, 133.4, 126.2 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 32.6 Hz), 124.3 (q, *J* = 271.7 Hz), 119.7 (q, *J* = 3.4 Hz), 114.0 (d, *J* = 10.8 Hz), 108.0, 52.4, 47.3 (d, *J* = 1.8 Hz), 32.4 (d, *J* = 2.0 Hz), 26.4, 22.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** *δ* -61.5, -118.1 (*E*-minor), -126.4 (*Z*-major). **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{16}F_4NO_3$: 346.1061, found 346.1074.

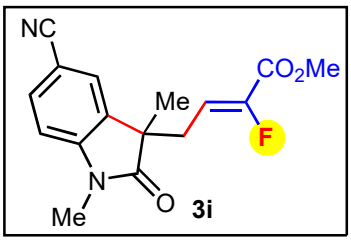
Methyl-(*Z*)-4-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)-2-fluorobut-2-enoate (3h)



Following **GP-4**, the reaction of **1h** (34 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3h** (27 mg, 74%, *Z:E* = 17:1) as yellow oil; R_f = 0.16 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.16 (d, *J* = 8.3 Hz, 1H), 7.08 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.91 (dt, *J* = 31.4, 8.0 Hz, 1H), 3.76 (s, 3H), 3.22 (s, 3H), 2.78–2.64 (m, 2H), 1.42 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 179.0, 160.6 (d, *J* = 35.5 Hz), 149.3 (d, *J* = 260.8 Hz), 144.8, 141.5, 134.3, 121.4, 120.5 (q, *J* = 256.6 Hz), 116.8, 114.1 (d, *J* = 10.8 Hz), 108.6, 52.4, 47.7 (d, *J* = 1.8 Hz), 32.4 (d, *J* = 2.1 Hz), 26.4, 22.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** *δ* -58.4, -118.3 (*E*-minor), -126.6 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_4NNaO_4$: 384.0829, found 384.0829.

Methyl (R,Z)-4-(5-cyano-1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3i)

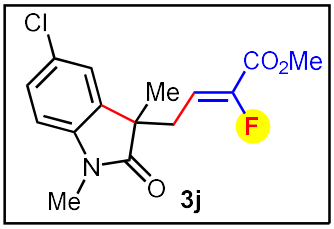


Following **GP-4**, the reaction of **1i** (28 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3i** (22 mg, 74%, *Z:E* = 19:1) as a yellow solid; melting point 90–92 °C; R_f = 0.36 (25% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.62 (d, *J* = 8.1 Hz, 1H), 7.45 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 5.86 (dt, *J* = 31.3, 8.0 Hz, 1H), 3.77 (s, 3H), 3.25 (s, 3H), 2.78–2.66 (m, 2H), 1.43 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 178.9, 160.5 (d, *J* = 35.3 Hz), 149.5 (d, *J* =

259.3 Hz), 146.8, 133.8, 133.7, 126.1, 119.0, 113.5 (d, *J* = 10.7 Hz), 108.7, 106.0, 52.5, 47.2 (d, *J* = 1.9 Hz), 32.2 (d, *J* = 2.1 Hz), 26.5, 22.7; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -117.7 (*E*-minor), -125.8 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{16}H_{16}FN_2O_3$: 303.1139, found 303.1145.

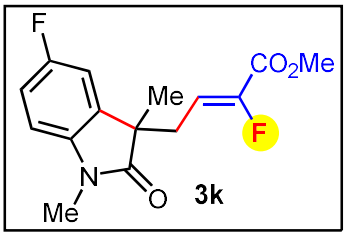
Methyl (*Z*)-4-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3j)



Following **GP-4**, the reaction of **1j** (29 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3j** (44 mg, 70%, *Z:E* = 13:1) as a white solid; melting point 66–68 °C; R_f = 0.19 (15% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.90 (dt, *J* = 31.6, 7.9 Hz, 1H), 3.77 (s, 3H), 3.22 (s, 3H), 2.72 (dddd, *J* = 40.0, 14.7, 7.9, 1.8 Hz, 2H), 1.42 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 178.8, 160.7 (d, *J* = 35.4 Hz), 149.2 (d, *J* = 260.4 Hz), 141.5, 134.5, 128.3, 128.2, 123.3, 114.3 (d, *J* = 10.8 Hz), 109.2, 52.4, 47.6 (d, *J* = 1.7 Hz), 32.4 (d, *J* = 2.2 Hz), 26.4, 22.9; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -118.4 (*E*-minor), -126.5 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{15}H_{16}ClFNO_3$: 312.0797, found 312.0808.

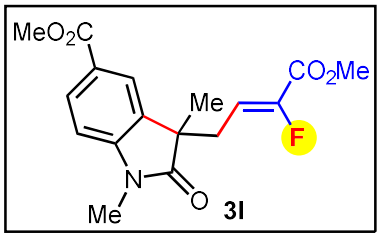
Methyl (*Z*)-2-fluoro-4-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (3k)



Following **GP-4**, the reaction of **1k** (27 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3k** (21 mg, 71%, *Z:E* = 14:1) as yellow oil; R_f = 0.13 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.07–6.91 (m, 2H), 6.84–6.72 (m, 1H), 5.89 (dt, *J* = 31.6, 8.0 Hz, 1H), 3.76 (s, 3H), 3.21 (s, 3H), 2.76–2.64 (m, 2H), 1.41 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 179.0, 160.7 (d, *J* = 35.7 Hz), 159.4 (d, *J* = 241.2 Hz), 149.2 (d, *J* = 260.0 Hz), 138.8, 134.4 (d, *J* = 7.8 Hz), 114.5 (d, *J* = 23.5 Hz), 114.406 (d, *J* = 10.7 Hz), 111.0 (d, *J* = 24.8 Hz), 108.7 (d, *J* = 8.0 Hz), 52.4, 47.8 (d, *J* = 1.7 Hz), 32.4 (d, *J* = 2.1 Hz), 26.4, 22.9; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -118.6 (*E*-minor), -120.1, -126.7 (*Z*-major); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{15}H_{16}F_2NO_3$: 296.1093, found 296.1101.

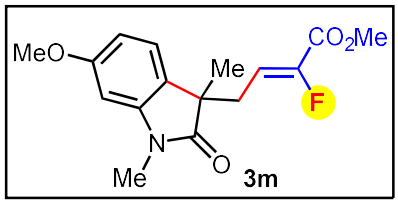
Methyl-(*Z*)-3-(3-fluoro-4-methoxy-4-oxobut-2-en-1-yl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3l)



Following **GP-4**, the reaction of **1l** (31 mg, 0.2 mmol) with **2a** (42 mg, 37 μL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3l** (41 mg, 61%, *Z:E* = 17:1) as a white solid; melting point 99–101 °C; R_f = 0.32 (25% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 7.2 Hz, 1H), 7.87 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.85 (dt, *J* = 31.6, 7.9 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.24 (s, 3H), 2.73 (ddd, *J* = 21.1, 13.9, 8.0 Hz, 2H), 1.42 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 179.6, 166.7, 160.6 (d, *J* = 35.6 Hz), 149.1 (d, *J* = 260.2 Hz), 147.0, 132.7, 131.0, 124.7, 123.9, 114.2 (d, *J* = 10.8 Hz), 107.8, 52.4, 52.0, 47.2 (d, *J* = 1.6 Hz), 32.4 (d, *J* = 1.9 Hz), 26.4, 22.8; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** *δ* -118.3 (*E*-minor), -126.4 (*Z*-major); **HRMS (ESI-TOF)** ***m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{18}FNO_5Na$: 358.1061, found 358.1058.

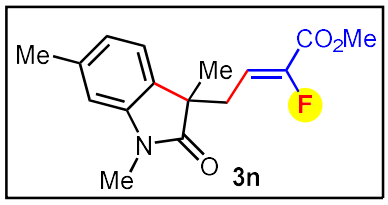
Methyl (*Z*)-2-fluoro-4-(6-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (3m)



Following **GP-4**, the reaction of **1m** (28 mg, 0.2 mmol) with **2a** (42 mg, 37 μL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3m** (48 mg, 77%, *Z:E* = 21:1) as a yellow solid; melting point 63–65 °C; R_f = 0.32 (25% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 6.82–6.77 (m, 2H), 6.76–672 (m, 1H), 5.90 (dt, *J* = 31.9, 7.9 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.19 (s, 3H), 2.69 (qdd, *J* = 14.7, 7.9, 1.8 Hz, 2H), 1.39 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 178.9, 160.7 (d, *J* = 35.8 Hz), 156.1, 148.9 (d, *J* = 259.1 Hz), 136.3, 134.1, 114.9 (d, *J* = 10.7 Hz), 112.3, 110.2, 108.5, 55.7, 52.3, 47.7 (d, *J* = 1.7 Hz), 32.5 (d, *J* = 2.1 Hz), 26.3, 22.9; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** *δ* -119.1 (*E*-minor), -127.1 (*Z*-major); **HRMS (ESI-TOF)** ***m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{18}FNO_4Na$: 330.1112, found 330.1115.

Methyl (*Z*)-2-fluoro-4-(1,3,6-trimethyl-2-oxoindolin-3-yl)but-2-enoate (3n)

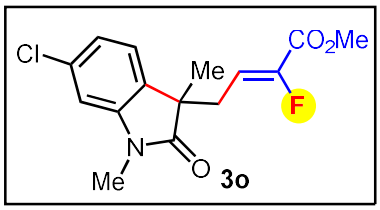


Following **GP-4**, the reaction of **1n** (27 mg, 0.1 mmol) with **2a** (21 mg, 19 μL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3n** (22 mg, 75%, *Z:E* = 12:1) as yellow oil; R_f = 0.21 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.07 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 5.92 (dt, *J* = 32.0, 7.9 Hz, 1H), 3.76 (s, 3H), 3.20 (s, 3H), 2.74–2.64 (m, 2H), 2.38 (s, 3H), 1.39 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** *δ* 179.7, 160.8 (d, *J* = 35.7 Hz), 149.0 (d, *J* = 259.2 Hz), 142.9, 138.4, 129.8, 123.2, 122.4, 115.2 (d, *J* = 10.9 Hz), 109.2, 52.4, 47.1 (d, *J* = 1.8 Hz), 32.6 (d, *J* = 2.0 Hz), 26.2, 23.0, 21.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)**

δ -119.3 (*E*-minor), -127.3 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{19}FNO_3$: 292.1343, found 292.1347.

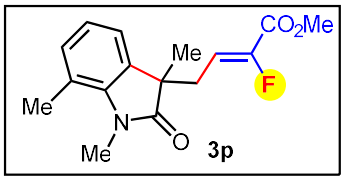
Methyl (*Z*)-4-(6-chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3o)



Following **GP-4**, the reaction of **1o** (29 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3o** (35 mg, 55%, *Z:E* = 15:1) as a yellow-white solid; melting point 66–68 °C; R_f = 0.24 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 5.86 (dt, *J* = 31.7, 7.9 Hz, 1H), 3.75 (s, 3H), 3.19 (s, 3H), 2.68 (d, *J* = 7.8 Hz, 2H), 1.38 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.2, 160.6 (d, *J* = 35.8 Hz), 149.1 (d, *J* = 260.0 Hz), 144.1, 134.0, 131.0, 123.6, 122.5, 114.4 (d, *J* = 10.9 Hz), 109.0, 52.4, 47.1 (d, *J* = 1.5 Hz), 32.3 (d, *J* = 1.8 Hz), 26.3, 22.9; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -118.5 (*E*-minor), -126.7 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{15}H_{16}ClFNO_3$: 312.0797, found 312.0806.

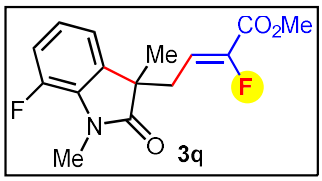
Methyl (*Z*)-2-fluoro-4-(1,3,7-trimethyl-2-oxoindolin-3-yl)but-2-enoate (3p)



Following **GP-4**, the reaction of **1p** (27 mg, 0.1 mmol) with **2a** (21 mg, 19 µL, 0.2 mmol) in 1,4-dioxane (0.2 M) afforded **3p** (20 mg, 69%, *Z:E* = 22:1) as a yellow oil; R_f = 0.33 (20% EtOAc in hexane).

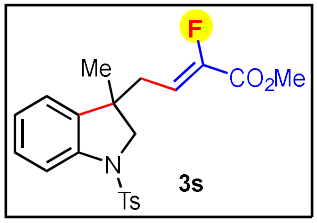
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07–6.95 (m, 2H), 6.95–6.91 (m, 1H), 5.92 (dt, *J* = 31.9, 7.8 Hz, 1H), 3.76 (s, 3H), 3.49 (s, 3H), 2.68 (ddd, *J* = 34.2, 14.8, 8.4 Hz, 2H), 2.58 (s, 3H), 1.38 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 180.1, 160.8 (d, *J* = 35.6 Hz), 148.9 (d, *J* = 258.9 Hz), 140.6, 133.5, 131.9, 122.6, 120.6, 119.8, 115.2 (d, *J* = 10.6 Hz), 52.4, 46.6 (d, *J* = 1.7 Hz), 32.7 (d, *J* = 2.1 Hz), 29.6, 23.3, 19.0; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -119.3 (*E*-minor), -127.3 (*Z*-major); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{19}FNO_3$: 292.1343, found 292.1346.

Methyl (*Z*)-2-fluoro-4-(7-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (3q)



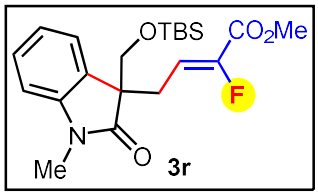
Following **GP-4**, the reaction of **1q** (54 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3q** (27 mg, 46%, *Z:E* = 16:1) as yellow oil; R_f = 0.22 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03–6.94 (m, 3H), 5.90 (dt, *J* = 31.7, 8.0 Hz, 1H), 3.76 (s, 3H), 3.43 (d, *J* = 2.6 Hz, 3H), 2.77–2.65 (m, 2H), 1.41 (s, 3H); **^{13}C{^{1}H} NMR (126**



MHz, $CDCl_3$) δ 178.9, 160.7 (d, *J* = 35.8 Hz), 149.1 (d, *J* = 259.8 Hz), 147.7 (d, *J* = 243.9 Hz), 135.7 (d, *J* = 2.8 Hz), 129.5 (d, *J* = 8.1 Hz), 123.4 (d, *J* = 6.4 Hz), 118.5 (d, *J* = 3.1 Hz), 116.2 (d, *J* = 19.2 Hz), 114.5 (d, *J* = 10.8 Hz), 52.4, 47.7 (d, *J* = 2.0 Hz), 32.6 (d, *J* = 2.2 Hz), 28.7 (d, *J* = 5.7 Hz), 23.1; **$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$)** δ -118.7 (*E*-minor), -126.8 (*Z*-major), -136.3 (major), -136.4 (minor); **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{15}H_{15}F_2NO_3Na$: 318.0912, found 318.0912.

Methyl (*Z*)-4-(3-(((tert-butyldimethylsilyl)oxy)methyl)-1-methyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (3r)



Following **GP-4**, the reaction of **1r** (54 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3r** (40 mg, 49%, *Z:E* = >20:1) as green oil; R_f = 0.30 (15% EtOAc in hexane).

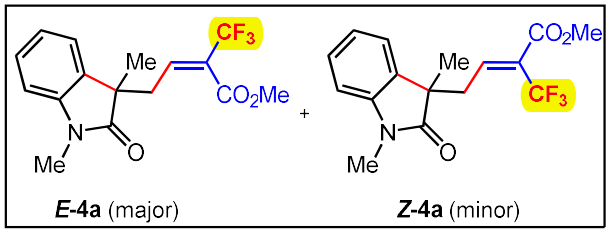
^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.1 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.89 (dt, *J* = 31.9, 7.8 Hz, 1H), 3.87 (d, *J* = 9.5 Hz, 1H), 3.78–3.70 (m, 4H), 3.20 (s, 3H), 2.87–2.74 (m, 2H), 0.75 (s, 9H), -0.07 (s, 3H), -0.11 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 177.1, 160.8 (d, *J* = 35.7 Hz), 148.9 (d, *J* = 258.8 Hz). 143.9, 130.2, 128.3, 123.9, 122.5, 115.0 (d, *J* = 10.8 Hz), 107.9, 67.3, 53.8 (d, *J* = 1.5 Hz), 52.3, 27.5 (d, *J* = 2.6 Hz), 26.2, 25.5, 18.0, -5.6, -5.8; **$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$)** δ -127.2 (*Z*); **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{21}H_{30}FNO_4SiNa$: 430.1820, found 430.1835.

Methyl (*Z*)-4-(1,3-dimethylindolin-3-yl)-2-fluorobut-2-enoate (3s)

Following **GP-4**, the reaction of **1s** (76 mg, 0.2 mmol) with **2a** (42 mg, 37 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **3s** (12 mg, 15%, *Z:E* = >20:1) as yellow oil; R_f = 0.20 (15% EtOAc in hexane). We couldn't get pure compound (**3s**) after several attempts.

^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.31–7.20 (m, 3H), 7.04–6.99 (m, 2H), 5.91 (dt, *J* = 32.0, 8.1 Hz, 1H), 3.81 (s, 3H), 3.75 (d, *J* = 10.5 Hz, 1H), 3.56 (d, *J* = 10.4 Hz, 1H), 2.45–2.27 (m, 2H), 2.37 (s, 3H), 1.17 (s, 3H); **$^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$)** δ 160.7 (d, *J* = 35.9 Hz), 149.3 (d, *J* = 258.9 Hz), 144.2, 141.0, 137.6, 133.8, 129.7, 128.5, 127.2, 123.8, 122.8, 115.5 (d, *J* = 10.9 Hz), 114.5, 61.2, 52.5, 43.4 (d, *J* = 1.9 Hz), 35.0, 25.8, 21.5; **$^{19}F\{1H\}$ NMR (470 MHz, $CDCl_3$)**: δ -127.4 (Z); **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{21}H_{22}FNO_4SNa$: 426.1146, found 426.1154.

Methyl (*E*)-2-fluoro-4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (*E*-4a) and methyl (*Z*)-2-fluoro-4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (*Z*-4a):

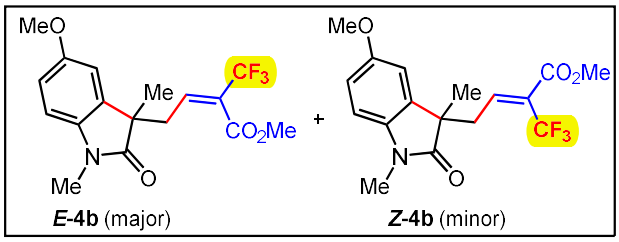


Following **GP-5**, the reaction of **1a** (51 mg, 0.2 mmol) with **2b** (56 mg, 38 µL, 0.3 mmol) in 1,4-dioxane (0.2 M) afforded **4a** (38 mg, 58%, *E:Z* = 2.6:1) as yellow oil; R_f = 0.56 (20% EtOAc in hexane).

Pure *E*-(4a); 13 mg (20%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (td, *J* = 7.7, 1.1 Hz, 1H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.57 (td, *J* = 7.3, 1.2 Hz, 1H), 3.79 (s, 3H), 3.22 (s, 3H), 3.20–3.06 (m, 2H), 1.44 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (*E*-4a)** δ 179.2, 162.4, 145.0 (q, *J* = 5.7 Hz), 142.9, 132.4, 128.5, 125.5 (q, *J* = 30.8 Hz), 122.8, 121.7 (q, *J* = 272.9 Hz), 108.3, 52.2, 47.4, 36.8, 26.2, 22.8 (one C peak merged with other peaks); **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) (*E*-4a)** δ -64.3; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{17}F_3NO_3$: 328.1155, found 328.1166.

Mixture of *E*+*Z*-(4a, 1.4:1 by ^{1}H NMR); 25.1 mg (38%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35–7.27 (m, 1.8H), 7.18 (d, *J* = 7.2 Hz, 1.7H), 7.08 (q, *J* = 7.2 Hz, 1.7H), 6.98 (t, *J* = 7.3 Hz, 0.7H, *Z*), 6.87 (t, *J* = 7.5 Hz, 1.7H), 6.57 (t, *J* = 7.3 Hz, 1H, *E*), 3.79 (s, 3H, *E*), 3.75 (s, 2.3H, *Z*), 3.24 (s, 2.2H, *Z*), 3.22 (s, 3H, *E*), 3.20–3.07 (m, 2H, *E*), 3.02–2.90 (m, 1.5H, *Z*), 1.44 (s, 5.1H); **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -58.5 (*Z*), -64.3 (*E*).

Methyl (*E*)-4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-2-(trifluoromethyl)but-2-enoate (*E*-4b) and methyl (*Z*)-4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-2-(trifluoromethyl)but-2-enoate (*Z*-4b):



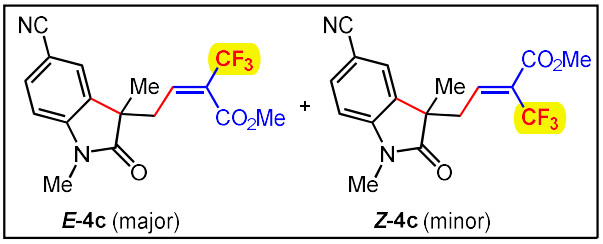
Following **GP-5**, the reaction of **1e** (57 mg, 0.2 mmol) with **2b** (62 mg, 51 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **4b** (33 mg, 46%, *E:Z* = 3:1) as yellow oil; R_f = 0.47 (20% EtOAc in hexane).

Pure *E*-(4b); 15 mg (21%); **^{1}H NMR (500 MHz, $CDCl_3$) (*E*-4b)** δ 6.85–6.72 (m, 3H), 6.55 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 6H), 3.19 (s, 3H), 3.16–3.06 (m, 2H), 1.42 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (*E*-4b)** δ 178.8, 162.4, 156.2, 145.0 (q, *J* = 5.4 Hz), 136.4, 133.7, 125.5 (q, *J* = 30.4 Hz), 121.6 (q, *J* = 272.9 Hz), 112.6, 110.5, 108.6, 55.8, 52.2, 47.9, 36.8, 26.3, 22.8; **^{19}F{^{1}H} NMR (471**

MHz, $CDCl_3$) (*E*-4b) δ -64.2 (*E*); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{19}F_3NO_4$: 358.1261, found 358.1265.

Mixture of *E*+*Z*-(4b, 1.3:1 by ^1H NMR**);** 18 mg (25%); **^1H NMR (500 MHz, $CDCl_3$)** δ 6.94 (t, *J* = 7.3 Hz, 0.72H, *Z*), 6.85–6.73 (m, 5.3H), 6.55 (t, *J* = 7.1 Hz, 1H, *E*), 3.79 (s, 8.2H), 3.74 (s, 2.2H), 3.22 (s, 2.1H, Z), 3.19 (s, 3H, *E*), 3.16–3.06 (m, 2H, *E*), 3.03–2.89 (m, 1.5H, *Z*), 1.42 (s, 5.2H); **$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) (*E*-4b+*Z*-4b)** δ -58.5 (*Z*), -64.2 (*E*).

Methyl (*E*)-4-(5-cyano-1,3-dimethyl-2-oxoindolin-3-yl)-2-(trifluoromethyl)but-2-enoate (*E*-4c) and methyl (*Z*)-4-(5-cyano-1,3-dimethyl-2-oxoindolin-3-yl)-2-(trifluoromethyl)but-2-enoate (*Z*-4c):

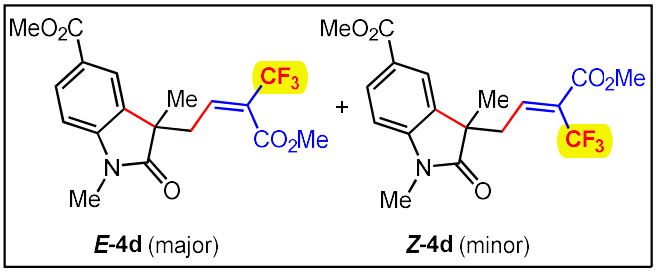


E-4c (major) *Z*-4c (minor)

Following **GP-5**, the reaction of **1i** (56 mg, 0.2 mmol) with **2b** (46 mg, 38 µL, 0.40 mmol) in 1,4-dioxane (0.2 M) afforded **4c** (33 mg, 47%, *E:Z* = 2:1) as yellow oil; R_f = 0.34 (20% EtOAc in hexane).

E*-(4c)–^1H NMR (500 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.44 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.53 (t, *J* = 7.3 Hz, 1H), 3.82 (s, 3H), 3.25 (s, 3H), 3.22–3.10 (m, 2H), 1.46 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 178.8, 162.2, 146.7, 143.6 (q, *J* = 5.7 Hz), 133.8, 133.5, 126.33, 126.27 (q, *J* = 31.3 Hz), 121.4 (q, *J* = 273.1 Hz), 118.9, 108.7, 106.0, 52.4, 47.4, 36.3, 26.5, 22.6; **$^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$)** δ -64.3 (*E*); **HRMS (ESI-TOF) *m/z: $[M+H]^+$ calcd. for $C_{17}H_{19}F_3NO_4$: 353.1108, found 353.1118.

Methyl (*E*)-1,3-dimethyl-2-oxo-3-(4,4,4-trifluoro-3-(methoxycarbonyl)but-2-en-1-yl)indoline-5-carboxylate (*E*-4d) and methyl (*Z*)-1,3-dimethyl-2-oxo-3-(4,4,4-trifluoro-3-(methoxycarbonyl)but-2-en-1-yl)indoline-5-carboxylate (*Z*-4d):



E-4d (major) *Z*-4d (minor)

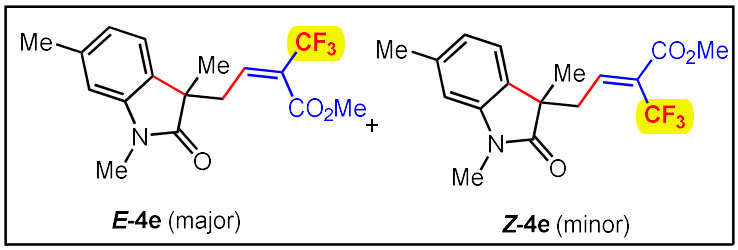
Following **GP-5**, the reaction of **1l** (62 mg, 0.2 mmol) with **2b** (62 mg, 51 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **4d** (40 mg, 52%, *E:Z* = 3.7:1) as a white solid; melting point 90–92 °C; R_f = 0.52 (20% EtOAc in hexane).

Pure *E*-(4d); 23 mg (30%); **^1H NMR (500 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.2 Hz, 1H), 7.85 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.53 (t, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 3.25 (s, 3H), 3.15 (ddd, *J* = 21.7, 14.8, 7.2 Hz, 2H), 1.46 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 179.4, 166.6, 162.2,

147.0, 144.0 (q, *J* = 5.7 Hz), 132.4, 131.2, 126.0 (q, *J* = 30.7 Hz), 124.9, 124.1, 121.5 (q, *J* = 273.1 Hz), 107.8, 52.1, 52.0, 47.4, 36.6, 26.4, 22.7; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -64.3; **HRMS (ESI-TOF) *m/z***: [M+Na]$^+$ calcd. for $C_{18}H_{18}F_3NO_5Na$: 408.1029, found 408.1038.

Mixture of *E*+*Z*-(4d, 1:1 by ^{1}H NMR**);** 17 mg (22%); **^{1}H NMR (500 MHz, CDCl$_3$)** *δ* 8.18–8.03 (m, 2H), 7.86 (s, 1.9H), 6.97–6.87 (m, 3H), 6.54 (t, *J* = 7.2 Hz, 1H, *E*), 3.91 (s, 6H), 3.79 (s, 3H, *E*), 3.75 (s, 3H, *Z*), 3.27 (s, 3H, *Z*), 3.25 (s, 3H, *E*), 3.23–3.09 (m, 2H, *E*), 3.00 (dddd, *J* = 54.6, 16.6, 7.5, 2.1 Hz, 2H, *Z*), 1.46 (s, 6H); **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$) (*E*-4d+*Z*-4d)** *δ* -58.6 (*Z*), -64.3 (*E*).

Methyl (*E*)-2-(trifluoromethyl)-4-(1,3,6-trimethyl-2-oxoindolin-3-yl)but-2-enoate (*E*-4e) and methyl (*Z*)-2-(trifluoromethyl)-4-(1,3,6-trimethyl-2-oxoindolin-3-yl)but-2-enoate (*Z*-4e):



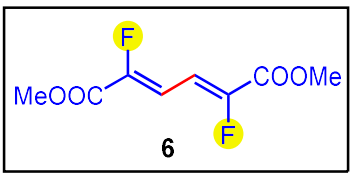
***E*-4e** (major) ***Z*-4e** (minor)

Following **GP-5**, the reaction of **1m** (54 mg, 0.2 mmol) with **2b** (62 mg, 51 µL, 0.4 mmol) in 1,4-dioxane (0.2 M) afforded **4e** (37 mg, 55%, *E:Z* = 5:1) as yellow oil; R_f = 0.65 (20% EtOAc in hexane).

Pure *E*-(4e); 19 mg (36%); **^{1}H NMR (500 MHz, CDCl$_3$)** *δ* 7.04 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.20 (s, 3H), 3.11 (ddd, *J* = 33.9, 15.9, 6.9 Hz, 2H), 2.39 (s, 3H), 1.41 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 179.5, 162.4, 145.2 (q, *J* = 5.3 Hz), 143.0, 138.7, 129.5, 125.4 (q, *J* = 31.1 Hz), 123.3, 122.6, 121.7 (q, *J* = 273.0 Hz), 109.2, 52.1, 47.2, 36.9, 26.2, 22.9, 21.8; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** *δ* -64.2 (*E*); **HRMS (ESI-TOF) *m/z***: [M+H]$^+$ calcd. for $C_{17}H_{19}F_3NO_3$: 342.1304, found 342.1308.

Mixture of *E*+*Z*-(4e, 2:1 by ^{1}H NMR**);** 18 mg (26%); **^{1}H NMR (500 MHz, CDCl$_3$)** *δ* 7.08–7.02 (m, 1.5H), 6.97 (t, *J* = 7.2 Hz, 0.5H, *Z*), 6.92–6.86 (m, 1.5H), 6.72–6. 76 (m, 1.5H), 6.56 (t, *J* = 6.6 Hz, 1H, *E*), 3.80 (s, 3H, *E*), 3.75 (s, 1.5H, *Z*), 3.22 (s, 1.4H, *Z*), 3.20 (s, 3H, *E*), 3.19–3.04 (m, 2H, *E*), 3.01–2.88 (m, 1.1H, *Z*), 2.39 (s, 4.6H), 1.41 (s, 4.2H); **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$) (*E*-4e+*Z*-4e)** *δ* -58.6 (*Z*), -64.2 (*E*).

Dimethyl (2*Z*,4*Z*)-2,5-difluorohexa-2,4-dienedioate (6): ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.02–6.94



6

(m, 1H), 6.94–6.87 (m, 1H), 3.88 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** *δ* 160.4 (d, *J* = 4.2 Hz), 160.1 (d, *J* = 4.3 Hz), 150.6 (d, *J* = 6.8 Hz), 148.4 (d, *J* = 6.8 Hz), 108.5 (d, *J* = 3.5 Hz), 108.4 (d, *J* = 3.6

Hz), 52.9; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -118.4; **HRMS (ESI-TOF)** ***m/z***: $[M\text{-}F]^+$ calcd. for $C_8H_8FO_4$: 187.0401, found 187.0407; **GCMS-EI (*m/z,* relative intensity)**: 206.1 (M^+, 30), 175.1 (15), 147.1 (100), 132.0 (7), 119.0 (9), 104.0 (9).

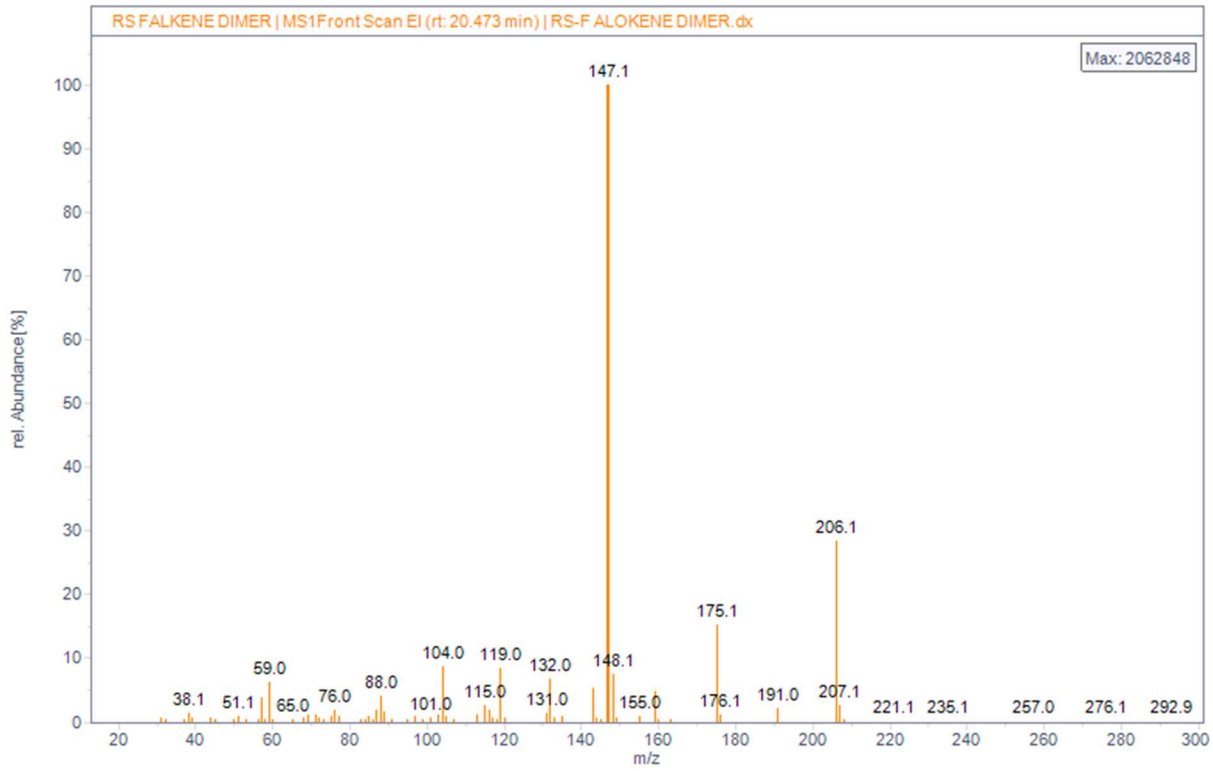
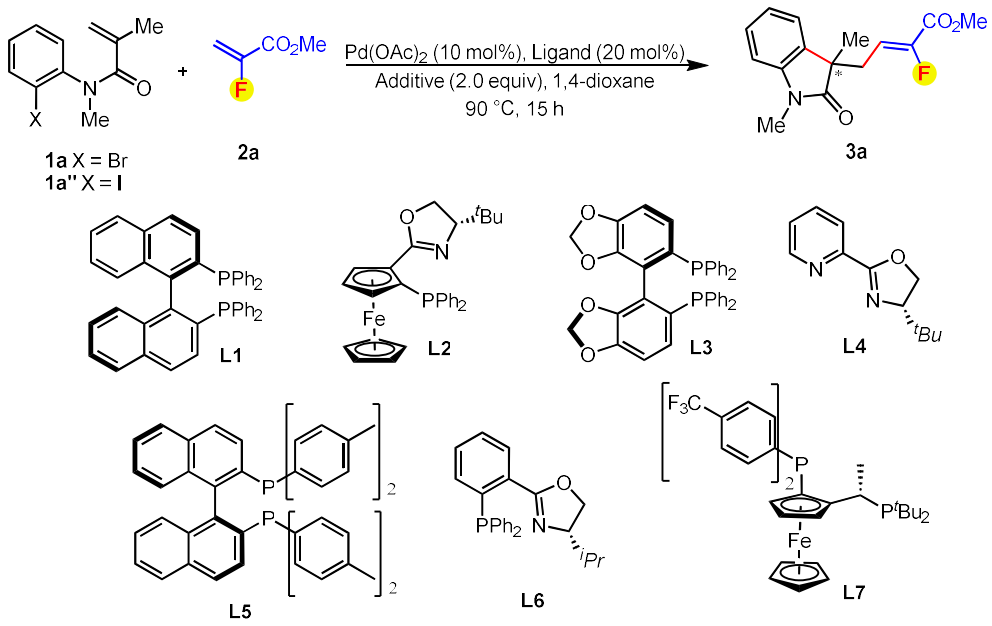


Figure S3 GC-MS spectra of compound **6**.

7. Optimization of chiral ligands for enantioselective reaction[a]

In a 1.5 mL reaction vial equipped with a magnetic bead, *N*-(2-halophenyl)-*N*-methyl acrylamide (**1a**) (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), additive (0.2 mmol) were added, followed by addition of methyl 2-fluoroacrylate (**2a**) (2.0 equiv), solvent (0.2 M) and one 4Å molecular sieve under N_2 atmosphere. Then, the reaction was kept on stirring at 90 °C temperature. After completion of the reaction (monitored by TLC), the crude reaction mixture was filtered through a celite pad using DCM, and then dried on sodium sulfate followed by high vacuum. Crude ^{1}H NMR yields were reported against nitromethane as internal standard.



Scheme S7: Enantioselective double Heck cyclization of **1a** with **2a**.

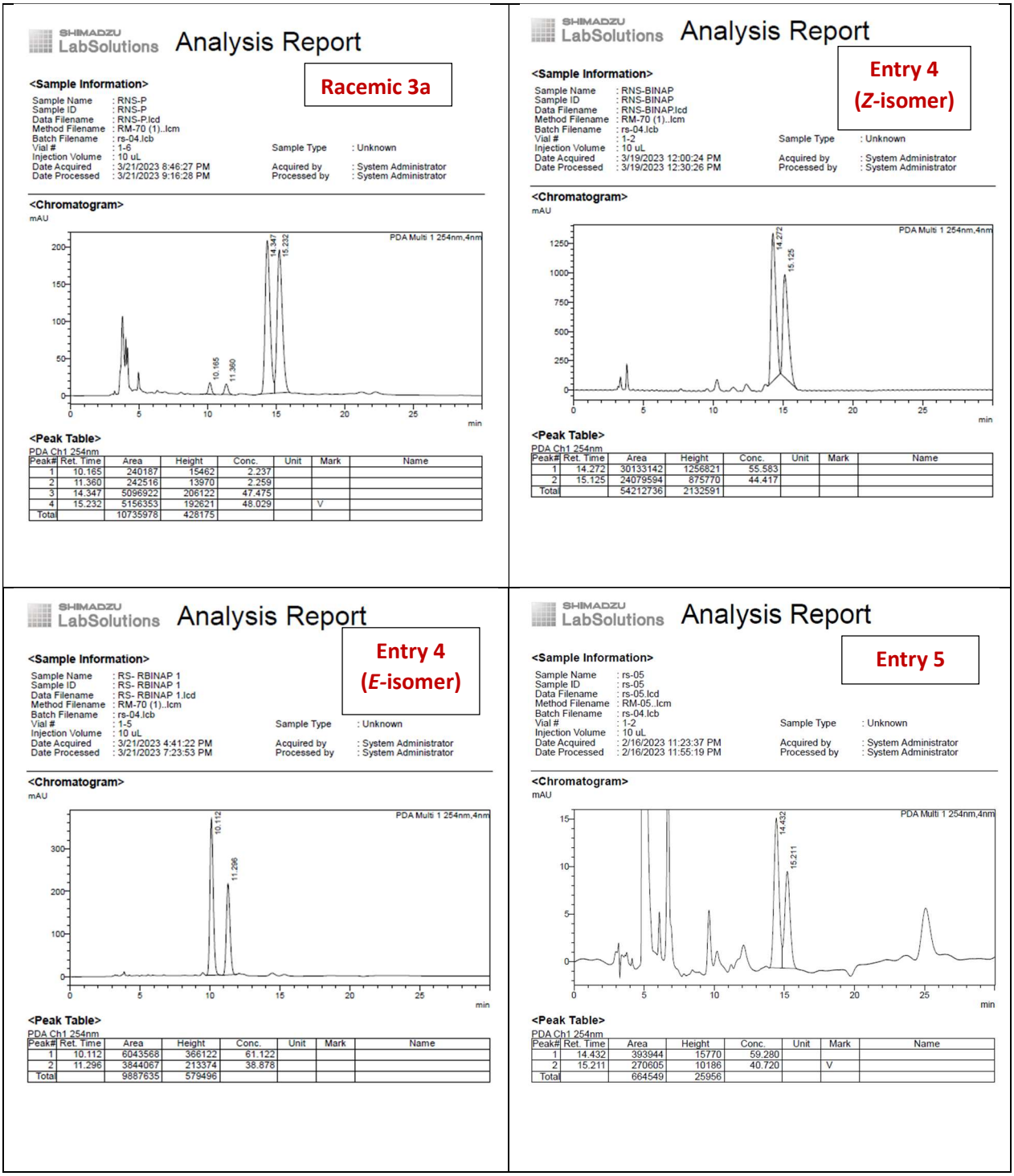
Table S3: Ligand screening.[a]

S. No.	1a (X)	Ligand	Additive	Yield (%)	ee (%)
1	Br	*R*-BINAP (**L1**)	AgOAc	~15	6
2	I	*R*-BINAP (**L1**)	AgOAc	~19	-
3	I	*R*-BINAP (**L1**)	Ag_3PO_4	11	-
4[b]	I	*R*-BINAP (**L1**)	Ag_2CO_3	36	11
5	I	^{t}Bu-PhosFerrox (**L2**)	Ag_2CO_3	36	19
6[c]	I	^{t}Bu-PhosFerrox (**L2**)	Ag_2CO_3	<5	10
7[d]	I	^{t}Bu-PhosFerrox (**L2**)	Ag_2CO_3	35	15
8	I	**L3**	Ag_2CO_3	<5	20
9	I	**L4**	Ag_2CO_3	<5	50
10	I	**L5**	Ag_2CO_3	48	14
11	I	**L6**	Ag_2CO_3	38	7
12	I	**L7**	Ag_2CO_3	-	-

[a]**1a** (0.025 mmol), **2a** (0.05 mmol), $Pd(OAc)_2$ (10 mol%), L (20 mol%), additive (2.0 equiv), solvent (0.5 mL) under nitrogen, 90 °C, 24 h, vial size 1.5 mL, crude ^{1}H-NMR yield against nitromethane. [b]**1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), L (20 mol%), additive (2.0 equiv), solvent (0.5 mL) under nitrogen, 90 °C, 24 h, vial size 1.5 mL, isolated yield. [c]**1a** (0.05 mmol), 70 °C, 24 h. [d]**1a** (0.05 mmol), 80 °C, 24 h.

Enantiomeric excess analysis by HPLC:

The enantiomeric purity was established by HPLC analysis using a Chiralcel® OD-H column (4.6 mmI.D. X 250 mmL), particle size 5 μm, 15 °C, *n*-Hexane/*i*-Propanol = 95/5 as eluent, 254 nm, 1 mL/min. For racemic product **3a**, the mixture of *E*-*Z* product (column purified) was kept for analysis, which gave *E*-isomer at tR = 10.165, 11.360 and *Z*-isomer at tR = 14.347, 15.1232.



SHIMADZU LabSolutions Analysis Report

Racemic 3a

<Sample Information>

Sample Name	: RNS-P		
Sample ID	: RNS-P		
Data Filename	: RNS-P.lcd		
Method Filename	: RM-70 (1)..lcm		
Batch Filename	: rs-04.lcb		
Vial #	: 1-6	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 3/21/2023 8:46:27 PM	Acquired by	: System Administrator
Date Processed	: 3/21/2023 9:16:28 PM	Processed by	: System Administrator

<Chromatogram>

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.165	240187	15462	2.237			
2	11.360	242516	13970	2.259			
3	14.347	5096922	206122	47.475			
4	15.232	5156353	192621	48.029		V	
Total		10735978	428175				

SHIMADZU LabSolutions Analysis Report

Entry 4 (*Z*-isomer)

<Sample Information>

Sample Name	: RNS-BINAP		
Sample ID	: RNS-BINAP		
Data Filename	: RNS-BINAP.lcd		
Method Filename	: RM-70 (1)..lcm		
Batch Filename	: rs-04.lcb		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 3/19/2023 12:00:24 PM	Acquired by	: System Administrator
Date Processed	: 3/19/2023 12:30:26 PM	Processed by	: System Administrator

<Chromatogram>

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.272	30133142	1256821	55.583			
2	15.125	24079594	875770	44.417			
Total		54212736	2132591				

SHIMADZU LabSolutions Analysis Report

Entry 4 (*E*-isomer)

<Sample Information>

Sample Name	: RS- RBINAP 1		
Sample ID	: RS- RBINAP 1		
Data Filename	: RS- RBINAP 1.lcd		
Method Filename	: RM-70 (1)..lcm		
Batch Filename	: rs-04.lcb		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 3/21/2023 4:41:22 PM	Acquired by	: System Administrator
Date Processed	: 3/21/2023 7:23:53 PM	Processed by	: System Administrator

<Chromatogram>

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.112	6043568	366122	61.122			
2	11.296	3844067	213374	38.878			
Total		9887635	579496				

SHIMADZU LabSolutions Analysis Report

Entry 5

<Sample Information>

Sample Name	: rs-05		
Sample ID	: rs-05		
Data Filename	: rs-05.lcd		
Method Filename	: RM-05..lcm		
Batch Filename	: rs-04.lcb		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 2/16/2023 11:23:37 PM	Acquired by	: System Administrator
Date Processed	: 2/16/2023 11:55:19 PM	Processed by	: System Administrator

<Chromatogram>

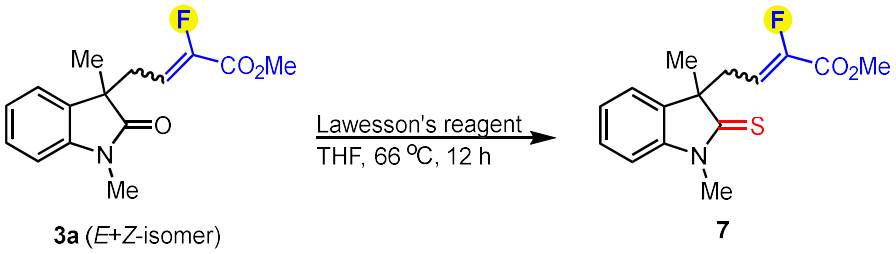
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.432	393944	15770	59.280			
2	15.211	270605	10186	40.720		V	
Total		664549	25956				

8. Applications:

8.1 Thiation reaction using Lawesson's reagent:[3]

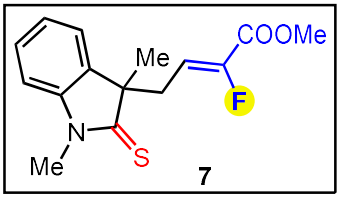


3a (*E*+*Z*-isomer) **7**

Scheme S8: Thiation of **3a** using Lawesson's reagent.

Compound **3a** (28 mg, 0.1 mmol) and Lawesson's reagent (202 mg, 0.5 mmol) were taken in a 7 ml reaction vial equipped with a magnetic stir bar. Then, dry THF (1.5 mL) was added, vial was sealed and kept for stirring at 66 °C for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated and purified by silica gel column chromatography (Hexane:EtOH = 9.0:1.0, R_f = 0.30) to afford **7** (28 mg, 94%) as green oil.

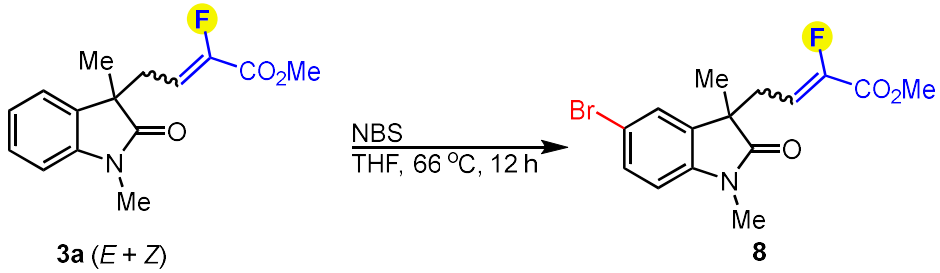
Methyl (*Z*)-4-(1,3-dimethyl-2-thioxoindolin-3-yl)-2-fluorobut-2-enoate (7):



7

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 5.67 (dt, *J* = 32.0 7.2 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 2.94 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.81 (ddd, *J* = 14.4, 7.0, 2.4 Hz, 1H), 1.48 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 208.9, 160.7 (d, *J* = 35.8 Hz), 148.8 (d, *J* = 259.6 Hz), 144.3, 137.1, 128.4, 124.4, 123.1, 115.1 (d, *J* = 10.8 Hz), 109.6, 58.0 (d, *J* = 1.8 Hz), 52.3, 35.7 (d, *J* = 1.4 Hz), 31.5, 27.2; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -119.3 (*E*), -126.7 (*Z*); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{15}H_{17}FNO_2S$: 294.0959, found 294.0970.

6.2 Bromination using NBS:[3]

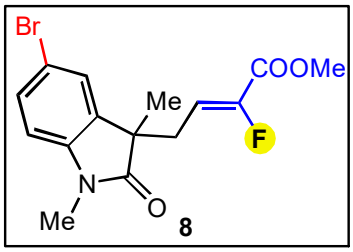


3a (*E* + *Z*) **8**

Scheme S9: Bromination of **3a** using NBS

Compound **3a** (28 mg, 0.1 mmol) and *N*-Bromosuccinimide (21 mg, 0.12 mmol) were taken in a 7 ml reaction vial equipped with a magnetic stir bar. Then, dry THF (1.5 mL) was added to the reaction mixture, vial was sealed and kept for stirring at 66 °C for 12 h. The TLC showed the spot on similar R_f as compound **3a**. Then, the solvent was dried and recorded crude ^{1}H and ^{19}F NMR, which indicated the product formation. After that, the reaction mixture was purified on silica gel column chromatography (Hexane:Ethyl acetate = 8.5:1.5, R_f = 0.25) to afford the desired brominated product **8** (27 mg, 77%,) as yellow solid; melting point 71–73 °C.

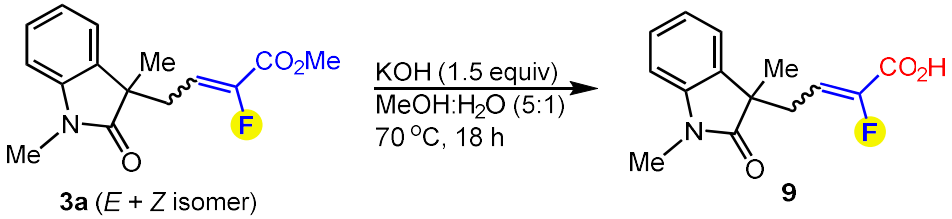
Methyl (*Z*)-4-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoate (8):



8

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.31 (d, *J* = 1.7 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.88 (dt, *J* = 31.6, 7.9 Hz, 1H), 3.77 (s, 3H), 3.20 (s, 3H), 2.70 (dddd, *J* = 46.2, 14.8, 7.9, 2.0 Hz, 2H), 1.40 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 178.7, 160.7 (d, *J* = 35.6 Hz), 149.2 (d, *J* = 260.4 Hz), 142.0, 134.9, 131.2, 126.0, 115.5, 114.3 (d, *J* = 10.7 Hz), 109.7, 52.5, 47.6, 32.4 (d, *J* = 2.2 Hz), 26.4, 22.9; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -126.5 (*Z*); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{15}H_{16}FNO_3Br$: 356.0292, found 356.0293.

8.3 Hydrolysis of Ester:[4]

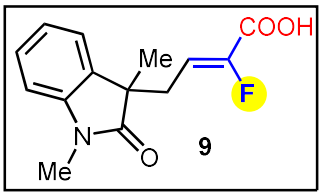


3a (*E* + *Z* isomer) **9**

Scheme S10: Hydrolysis of **3a** in alkaline medium.

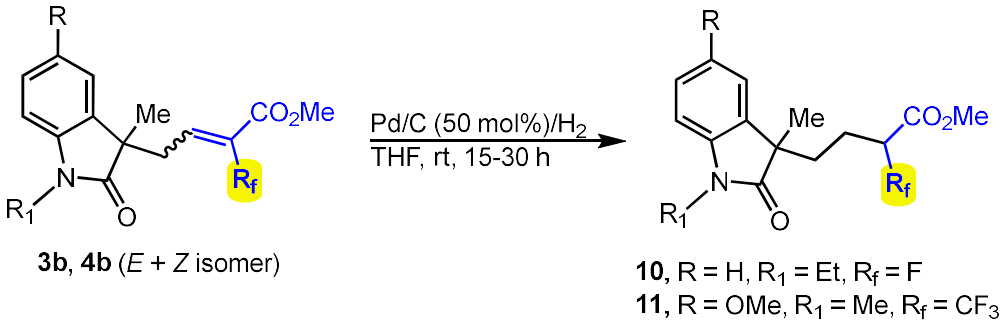
Compound **3a** (28 mg, 0.1 mmol) and KOH (~9 mg, 0.15 mmol) were taken in a 7 mL reaction vial equipped with a magnetic stir bar. Then, MeOH (1 mL) and H_2O (0.2 mL) were added sequentially, the vial was sealed and kept for stirring at 70 °C for 18 h. After cooling to room temperature, the reaction mixture was acidified with 1 mL of 3N HCl and concentrated, followed by water addition and extraction with EtOAc. The final organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator to afford the desired acid **9** (25 mg, 97%, *E/Z* = 1/11 by ^{1}H NMR) as grey sticky compound.

4-(1,3-dimethyl-2-oxoindolin-3-yl)-2-fluorobut-2-enoic acid (9):



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (bs, 1H, CO_2H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.1 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 6.01 (dt, J = 31.4, 7.9 Hz, 1H), 3.23 (s, 3H), 2.79–2.66 (m, 2H), 1.43 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.8, 163.6 (d, J = 36.5 Hz), 148.7 (d, J = 258.6 Hz), 142.6, 132.8, 128.4, 123.1, 122.7, 116.5 (d, J = 10.5 Hz), 108.4, 47.6 (d, J = 1.4 Hz), 32.6, 26.4, 22.6; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -117.7 (*E*), -127.3 (*Z*); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{14}H_{15}FNO_3$: 264.1030, found 264.1029.

8.4 Reduction of Alkene:



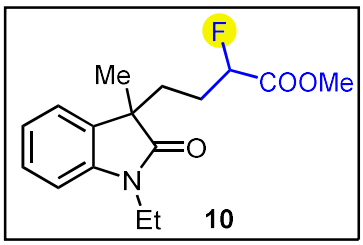
3b, **4b** (*E* + *Z* isomer)

10, R = H, R_1 = Et, R_f = F
11, R = OMe, R_1 = Me, R_f = CF_3

Scheme S11: Reduction of **3b** and **4b** using activated palladium on charcoal.

The substituted oxindole (**3b, 4b**) (0.1 mmol) was taken in a Schlenk flask, equipped with magnetic stir bar. Then, palladium on activated charcoal (0.05 mmol) was introduced in the flask, followed by addition of 3 mL dry THF. The reaction mixture was stirred overnight at room temperature (33 °C) under H_2 gas pressure using a rubber balloon. Then, the crude reaction mixture was washed with water and extracted with DCM, followed by purification on silica gel column chromatography**.** The diastereomeric ratio (dr) was analyzed by ^{19}F NMR.

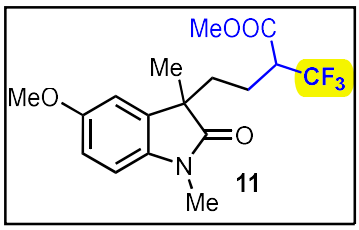
Methyl 4-(1-ethyl-3-methyl-2-oxoindolin-3-yl)-2-fluorobutanoate (10): The product **10** was obtained in 15 h with 86% yield (25 mg) as colorless liquid (Hexane:Ethyl acetate = 85:15, R_f = 0.18), dr = 1.0:1.0.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 4.78 (ddd, J = 49.0, 8.6, 3.7 Hz, 0.5H), 4.72 (ddd, J = 48.7, 6.8, 4.7 Hz, 0.5H), 3.85–368 (m, 2H), 3.75 (s, 1.5H), 3.71 (s, 1.5H), 2.12–1.98 (m, 1H), 1.98–1.85 (m, 1H), 1.70–1.44 (m, 2H), 1.37 (s, 1.5H), 1.36 (s, 1.5H), 1.25 (td, J = 7.2, 1.3 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.5, 179.4, 169.9 (d,

J = 3.1 Hz), 169.8 (d, *J* = 3.2 Hz), 142.22, 142.21, 133.34,133.28, 127.981, 127.977, 122.71, 122.69, 122.54, 122.50, 108.255, 108.246, 89.6 (d, *J* = 184.9 Hz), 88.3 (d, *J* = 185.0 Hz), 52.3, 52.2, 47.6, 47.4, 34.6 (2C), 33.1 (d, *J* = 3.0 Hz), 32.4 (d, *J* = 3.4 Hz), 27.6 (d, *J* = 10.9 Hz), 27.4 (d, *J* = 10.9 Hz), 23.9, 23.7, 12.7 (2C); **$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)** δ -192.2, -192.7**; HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{20}FNO_3Na$: 316.1319, found 316.1328.

Methyl 4-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-2-(trifluoromethyl)butanoate (11): Following the above procedure, **4b** (26 mg, 0.073 mmol) with Pd/C (6 mg, 0.056 mmol) in THF (3. mL) at 33 °C for 48 h afforded **11** (20 mg, 76%) as colorless liquid, (Hexane:Ethyl acetate = 85:15, R_f = 0.28), dr = 1.5:1.0.

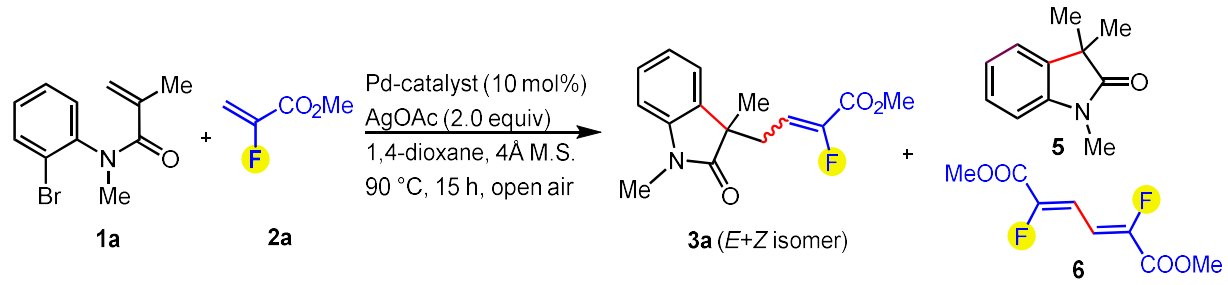


^{1}H NMR (500 MHz, $CDCl_3$) *δ* 6.85–6.72 (m, 3H), 3.80 (s, 3H), 3.76 (s, 1.5H), 3.74 (s, 1.5H), 3.196 (s, 1.5H), 3.192 (s, 1.5H), 3.07–2.88 (m, 1H), 1.98–1.88 (m, 1H), 1.82–1.70 (m, 1H), 1.63–1.54 (m, 1H), 1.50–1.41 (m, 1H), 1.343 (s, 1.5H), 1.338 (s, 1.5H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)** *δ* 179.4, 179.3, 167.51, 167.48, 156.29, 156.26, 136.73, 136.71, 134.4, 134.2, 124.4 (q, *J* = 280.3 Hz), 124.3 (q, *J* = 280.3 Hz), 112.1, 112.0, 110.31, 110.28, 108.5 (2C), 55.8 (2C), 52.69, 52.66, 50.1 (q, *J* = 27.7 Hz), 50.0 (q, *J* = 27.8 Hz), 48.3, 48.2, 35.0, 34.9, 26.3 (2C), 24.0, 23.8, 21.4 (d, *J* = 1.8 Hz), 21.2 (d, *J* = 1.9 Hz); **$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)** *δ* -67.8, -68.1; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{20}F_3NO_4Na$: 382.1237, found 382.1242.

9. Mechanistic Investigation:

To gain insight into the mechanism, a few control experiments were performed (Scheme 12). In a 1.5 mL vial equipped with a magnetic bead, was added acrylamide substrate (**1a**) (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), AgOAc (0.2 mmol) and 4 Å molecular sieve (1 no.). Next, fluoroacrylate (**2a**) (0.2 mmol) and dry dioxane (0.2 M) were added to the reaction vial in the open atmosphere. Then the reaction vial was sealed and stirred in a pre-heated oil bath at 90 °C for 15 h. After that, the reaction mixture was cooled to room temperature and dried on high vacuum. Then, in the dried reaction mixture, nitromethane (0.1 mmol) as an internal standard was added accordingly, followed by addition of $CDCl_3$ solvent. The mixture was analyzed by crude ^{1}H NMR in which the NMR yield was calculated by integrating the peak of product against the peak at 4.33 ppm corresponding to 3 protons of nitromethane.

9.1. Control Experiments:



Scheme S12: Control experiments.

Table S4: List of control experiments.[a]

S. No.	Variation from standard conditions	1a (%)	3a (%)	5a (%)	6 (%)
1[b]	-	-	87	8	10
2	No AgOAc	>95	-	-	-
3	No $Pd(OAc)_2$, No AgOAc	>95	-	-	-
4	No **2a**	20	-	40	-
5	No **2a**, No AgOAc	80	-	<5	-
6[b,c]	100 mol% $Pd(OAc)_2$, No AgOAc	40	19	<5	<5
7[b,d]	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2$, No AgOAc	49	14	10	<5
8[b,d]	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2$ with AgOAc	-	37	13	11
10[b,e,f]	NaOAc instead of AgOAc	-	48	35	-
11[g]	NaOAc instead of AgOAc	-	12	60	-

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), additive (2.0 equiv), solvent (0.5 mL) open air, 90 °C, 15 h, vial size 1.5 mL, 4 Å MS, *C*rude ^{1}H-NMR yield against nitromethane. [b]Isolated yield. [c]**1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (1.0 equiv), solvent (1.0 mL), 90 °C, 15 h, open air. [d]**1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(PPh_3)_4$ (10 mol%), additive (2.0 equiv), solvent (0.5 mL), 90 °C, 36 h, open air. [e]under nitrogen. [f]**1a** (0.10 mmol), **2a** (0.20 mmol), $Pd(OAc)_2$ (10 mol%), NaOAc (2.0 equiv), NMP solvent (0.5 mL), 100 °C, 15 h. [g]**1a** (0.05 mmol), **2a** (0.10 mmol), $Pd(OAc)_2$ (10 mol%), NaOAc (2.0 equiv), NMP solvent (0.5 mL), 100 °C, 15 h, open air, crude ^{1}H-NMR yield against nitromethane.

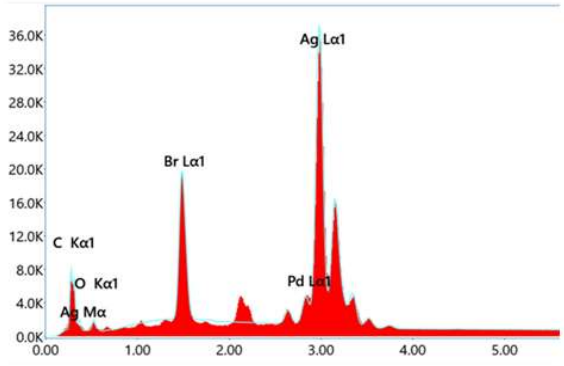
9.2. Quantification of elements: In a 1.5 mL reaction vial equipped with a magnetic bead, was added acrylamide substrate (**1a**) (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), AgOAc (0.2 mmol) and 4 Å molecular sieve (1 no.). Then, fluoroacrylate (**2a**) (0.2 mmol) and dry dioxane (0.2 M) were added

to the reaction vial. The vial was sealed with screw cap and stirred at 90 °C in an oil bath for 15 hours**.** After completion of the reaction (monitored by TLC), crude reaction mixture was filtered, and the solid components were washed with DCM and dried under vacuum.

9.2.1. Energy Dispersive X-ray Spectroscopy (EDS) Elemental Mapping:

The quantification of elements in the reaction mixture was determined by EDAX APEX. The atomic and mass concentrations of each element in the reaction mixture are shown in Figure S4.

a)



b)

Element	Weight%	Atomic %	Error %
C K	11.2	48.7	10.6
O K	2.2	7.1	12.9
Br L	14.5	9.5	6.6
Pd L	5.4	2.6	6.1
Ag L	66.6	32.2	3.3

Figure S4 a) Sum Spectra; **b)** eZAF Quant Result - Analysis Uncertainity: 9.34%.

Results of mapping studies portray the coexistence of Ag, Br, Pd, C, and O elements. The distribution of all the elements is homogeneous; however, the mapping distribution of shell elements, Ag and Br, displays a larger region compared to the core elements, Pd and O.

9.2.2. Electronic States and Chemical Composition Confirmation:

The surface electronic states and chemical compositions were obtained from XPS analysis, shown in Figure S5, where the presence of Pd(0) and Pd(II) is confirmed. The high-resolution XPS spectra shows the Pd 3d core level spectrum with two spin–orbit doublet peaks (*J*= 3/2 and 5/2) at 335.1 (Pd $3d_{5/2}$), 336.2 eV(Pd $3d_{5/2}$) and at 340.1 eV (Pd $3d_{3/2}$), 341.7 eV (Pd $3d_{3/2}$) with a peak separation of around 5.3 eV, which is in accordance with the literature, clarifying the existence of Pd in the 0 and +2 oxidation state as Pd metal and PdO_x.[5]

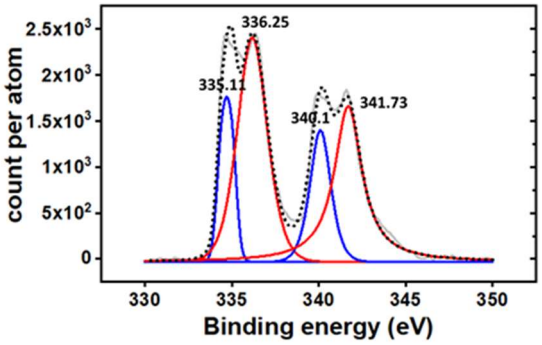


Figure S5. Deconvoluted data.

9.2.3. High-Resolution TEM (HRTEM):[6]

To achieve a detailed understanding of the morphology and confirm the existence of Pd nanoparticles, HRTEM studies were performed. Samples were prepared by ultrasonicating the resultant samples in ethanol and subsequently casting a drop of the sample onto an entirely carbon-coated 400-mesh copper grid. Images were recorded on a Technai G^2 20 (FEI) performing at 200 kV (accelerating voltage). As shown in Figure S6, palladium nanoparticles with average size of about 7.6 nm were observed.

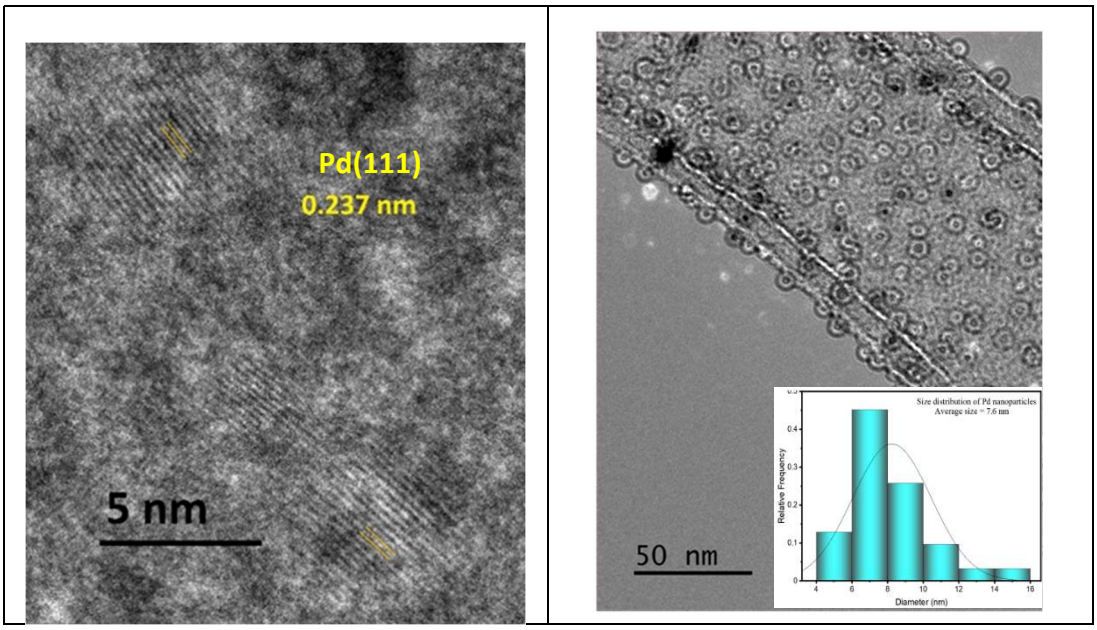


Figure S6 Characterization of Pd nanoparticles. a) HRTEM micrograph of Pd-nanoparticles; b) size distribution.

10. X-ray structural analysis:

To obtain crystals, a saturated solution of the compounds in ethyl acetate were kept at room temperature. Colorless crystals were observed after 3-4 days. A suitable crystal was selected and visualised on a Bruker APEX-II CCD diffractometer. The crystal was kept at 301.00 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation. The crystal structure was drawn on diamond-3 software.

Crystal Structure of compound 6:

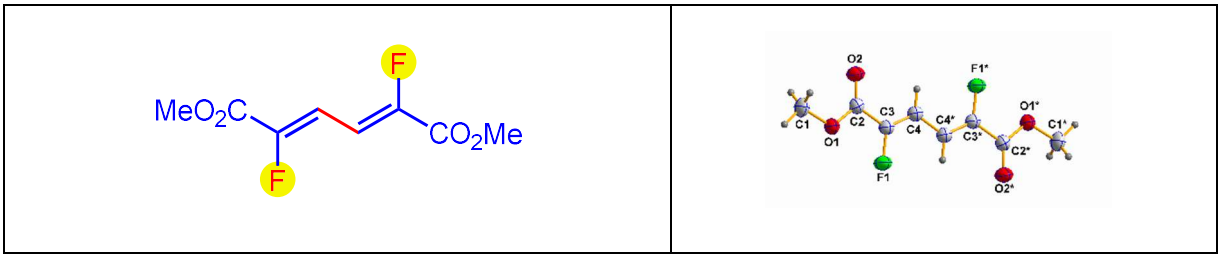


Figure S7: Crystal Structure of compound **6**.

Table S5: Crystal data and structure refinement for 6:

Empirical formula	**$C_8H_8F_2O_4$**
CCDC	**2233366**
Formula weight	206.14
Temperature/K	301.00
Crystal system	triclinic
Space group	P-1
a/Å	5.6570(4)
b/Å	6.5148(4)
c/Å	6.5836(5)
α/°	102.961(2)
β/°	109.449(2)
γ/°	96.622(2)
Volume/Å^3	218.14(3)
Z	1
ρ_{calc}(g/cm^3)	1.569
μ/mm^{-1}	0.151
F(000)	106.0
Crystal size/mm^3	0.22 × 0.15 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.56 to 52.88

Index ranges	-7 ≤ h ≤ 7, -8 ≤ k ≤ 8, -8 ≤ l ≤ 8
Reflections collected	5448
Independent reflections	898 [R_{int} = 0.0383, R_{sigma} = 0.0243]
Data/restraints/parameters	898/0/65
Goodness-of-fit on F^2	1.125
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0868
Final R indexes [all data]	R_1 = 0.0349, wR_2 = 0.0897
Largest diff. peak/hole/ e $Å^{-3}$	0.18/-0.14

Crystal Structure of compound 3k:

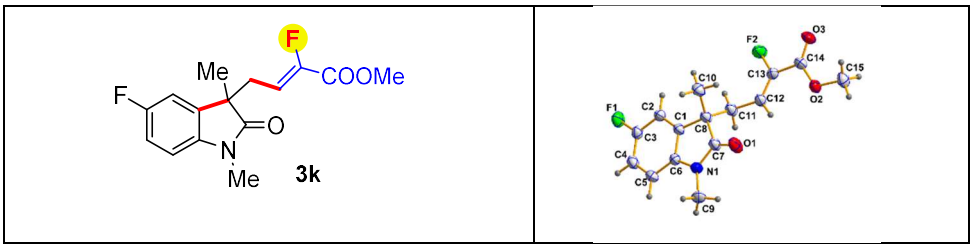


Figure S8: Crystal Structure of compound **3k**.

Table S6: Crystal data and structure refinement for 3k:

Empirical formula	**$C_{15}H_{15}F_2NO_3$**
CCDC	**2226735**
Formula weight	295.288
Temperature/K	301.00
Crystal system	triclinic
Space group	P-1
a/Å	8.5433(8)
b/Å	9.0498(8)
c/Å	10.3568(10)
α/°	69.658(3)
β/°	71.553(3)
γ/°	84.163(3)
Volume/$Å^3$	712.19(12)
Z	2
ρ_{calc}(g/cm^3)	1.377
μ/mm^{-1}	0.113
F(000)	308.3
Crystal size/mm^3	0.42 × 0.23 × 0.17
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.4 to 50.96
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -12 ≤ l ≤ 12
Reflections collected	20812
Independent reflections	2631 [R_{int} = 0.0482, R_{sigma} = 0.0264]
Data/restraints/parameters	2631/0/193
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0798, wR_2 = 0.2622
Final R indexes [all data]	R_1 = 0.0888, wR_2 = 0.2684
Largest diff. peak/hole/ e $Å^{-3}$	0.38/-0.33

Crystal Structure of compound 4d:

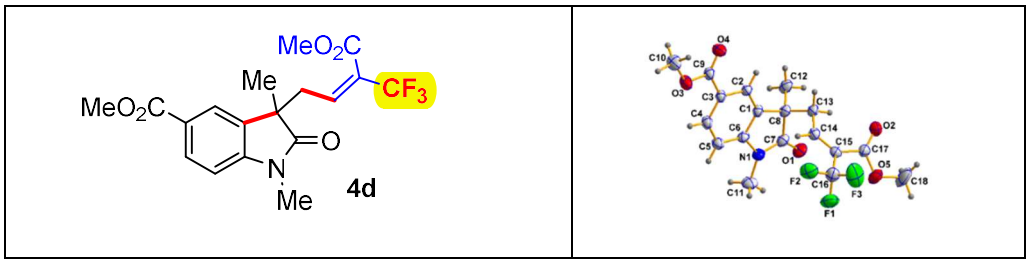


Figure S9: Crystal Structure of compound **4d.**

Table S7: Crystal data and structure refinement for 4d:

Empirical formula	**$C_{18}H_{18}F_3NO_5$**
CCDC	**2243622**
Formula weight	385.342
Temperature/K	299.00
Crystal system	triclinic
Space group	P-1
a/Å	8.6797(10)
b/Å	9.5445(13)
c/Å	12.4267(16)
α/°	72.122(4)
β/°	89.575(4)
γ/°	84.163(3)
Volume/$Å^3$	926.8(2)
Z	2
$ρ_{calc}$(g/cm^3)	1.381
μ/mm^{-1}	0.120
F(000)	400.4
Crystal size/mm^3	0.41 × 0.23 × 0.12
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.5 to 51.38
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 11, 0 ≤ l ≤ 15
Reflections collected	3501
Independent reflections	3497 [R_{int} = 0.0000, R_{sigma} = 0.0356]
Data/restraints/parameters	3497/0/248
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.1037, wR_2 = 0.2923
Final R indexes [all data]	R_1 = 0.1212, wR_2 = 0.3057
Largest diff. peak/hole/ e $Å^{-3}$	0.52/-0.35

Crystal Structure of compound 8:

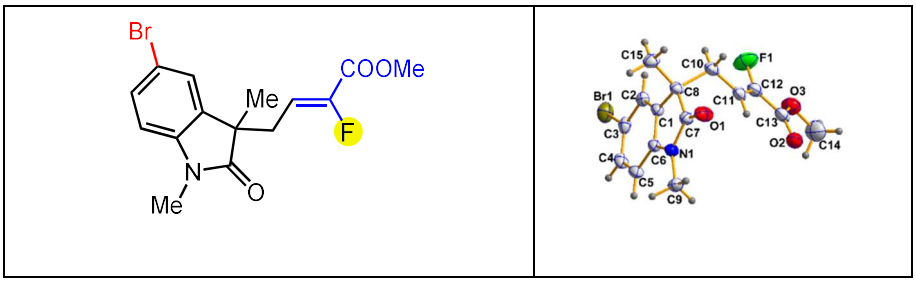


Figure S10: Crystal Structure of compound **8.**

Table S8: Crystal data and structure refinement for 8:

Empirical formula	**$C_{15}H_{15}BrFNO_3$**
CCDC	**2249830**
Formula weight	356.18
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.012(5)
b/Å	11.607(4)
c/Å	8.318(2)
α/°	90
β/°	93.053(10)
γ/°	90
Volume/$Å^3$	1543.7(8)
Z	4
ρ_{calc}(g/cm^3)	1.533
μ/mm^{-1}	2.682
F(000)	720.0
Crystal size/mm^3	0.54 × 0.36 × 0.22
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.34 to 50.86
Index ranges	-19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -10 ≤ l ≤ 19
Reflections collected	43441
Independent reflections	2848 [R_{int} = 0.0693, R_{sigma} = 0.0315]
Data/restraints/parameters	2848/0/193
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0369, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.1056
Largest diff. peak/hole/ e $Å^{-3}$	0.74/-0.85

11. References:

1. (a) K. Wang, Z. Ding, Z. Zhou and W. Kong, *J. Am. Chem. Soc.*, 2018, **140**, 12364–12368; (b) M. Zhang, F. Zhou, X. Xuchen, L. Zhou, G. Deng, Y. Liang and Y. Yang, *Org. Chem. Front.*, 2021**,** **8**, 5687–5692; (c) D. Shukla and S. A. Babu, *Adv. Synth. Catal.*, 2019**,** **361**, 2075–2093.

2. (a) Q. Dai, J. Yu, Y. Jiang, S. Guo, H. Yang and J. Cheng, *Chem. Commun.*, 2014, **50**, 3865–3867; (b) P. Patschinski, C. Zhang and H. Zipse, *J. Org. Chem*., 2014, **79**, 8348–8357; (c) Q. Dai, J. Yu, Y. Jiang, S. Guo, H. Yang and J. Cheng, *Chem. Comm*., 2014, **50**, 3865–3867; (d) K. Rousee, J. P. Bouillon, S. Couve-Bonnaire, and X. Pannecoucke, *Org. Lett.*, 2016, **18**, 540-543.

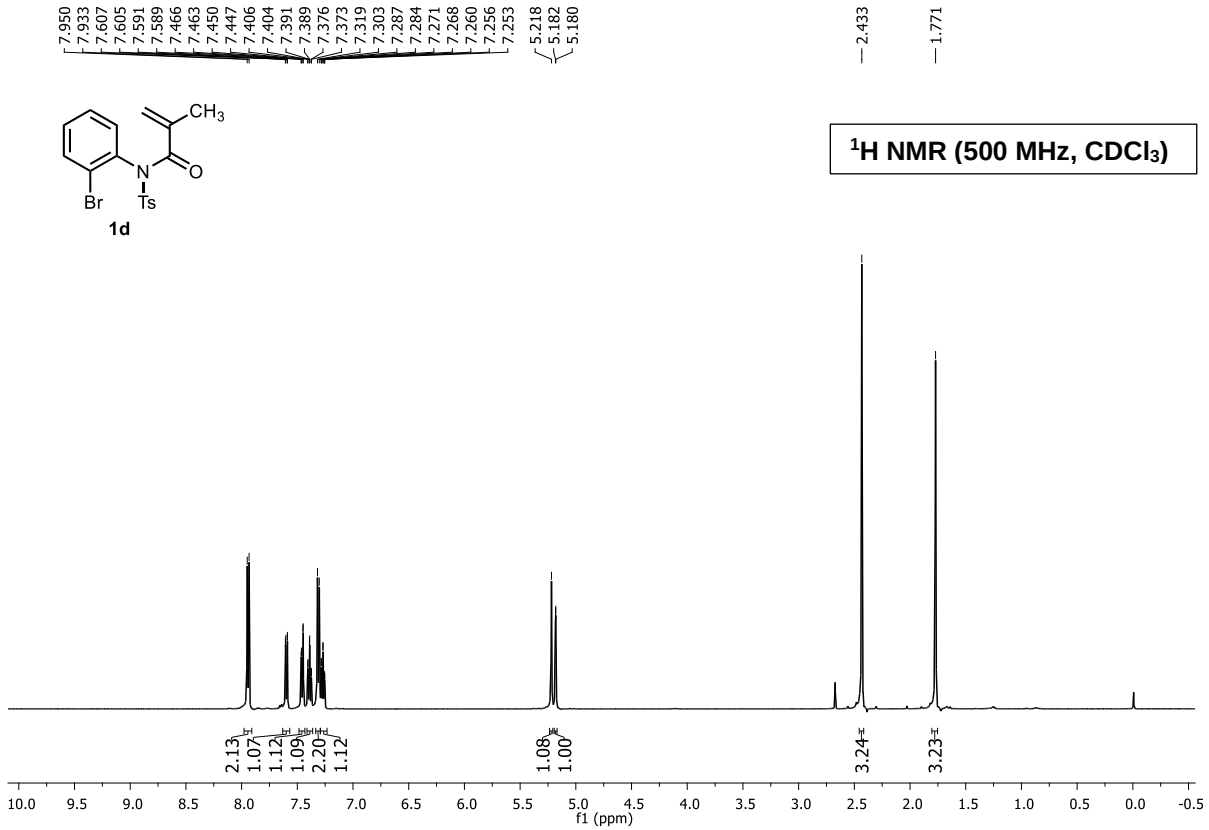
3. H. Lv, X. Xu, J. Li, X. Huang, G. Fang and L. Zheng, *Angew. Chem. Int. Ed*., 2022, **61**, e20220640.

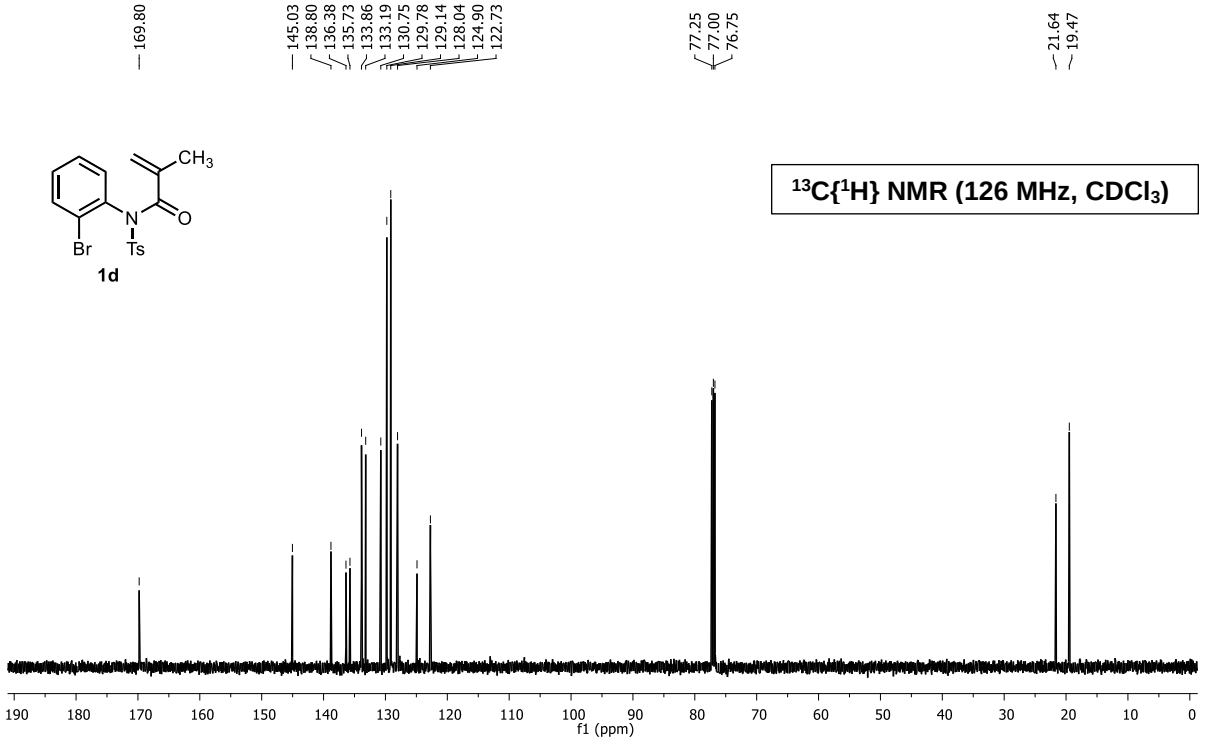
4. Q. Bouazzaoui, K. Rousée, J. K. Mulengi, X. Pannecoucke, J. P. Bouillon and S. C. Bonnaire, *Eur. J. Org. Chem*., 2018, 3705–3715.

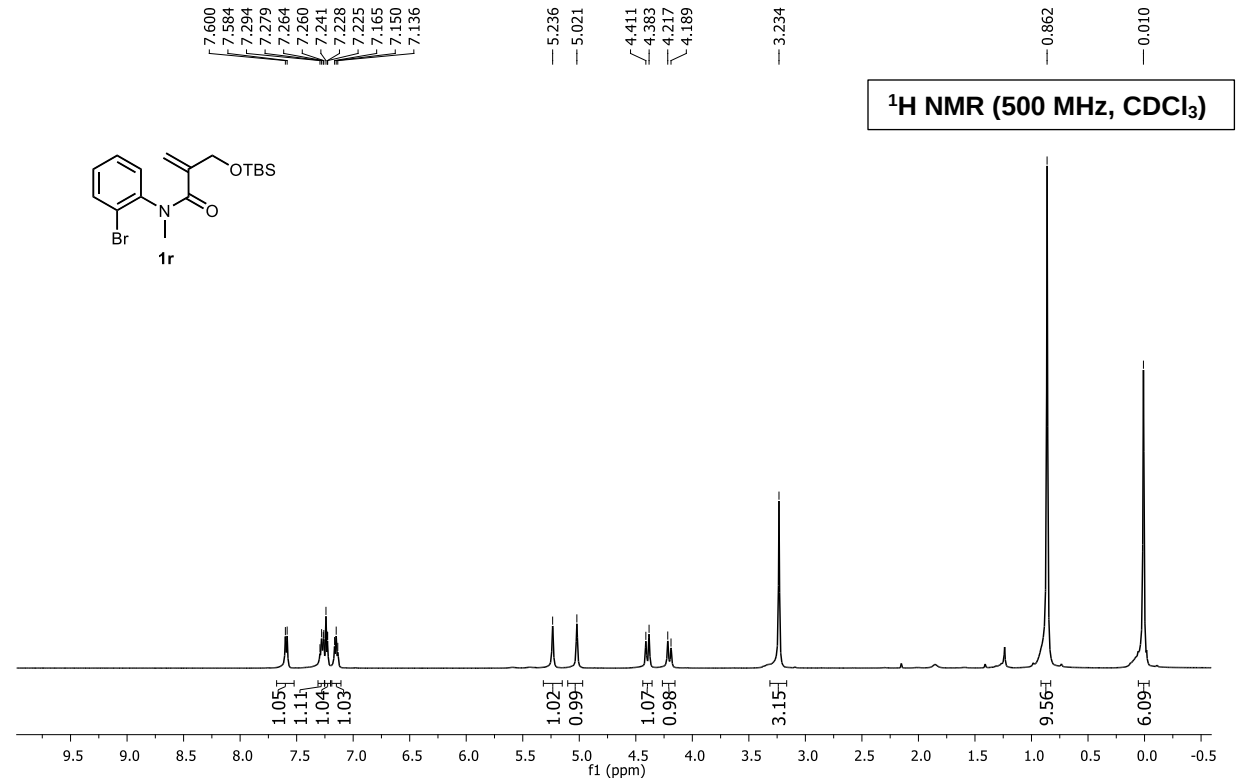
5. (a) S. Khanchandani, S. Kumar and A. K. Ganguli, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1487–1499; (b) NIST standard reference database 20, Version 4.1; NIST X-ray Photoelectron Spectroscopy Database.

6. J. Gomez-Bolivar, I. P. Mikheenko, L. E. Macaskie and M. L. Merroun, *Nanomaterials*, 2019, **9**, 857.

12. ^{1}H, ^{13}C, ^{19}F NMR spectra of starting materials and products:



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7.264
7.260
7.241
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7.150
7.136
5.236
5.021
4.411
4.383
4.217
4.189
3.234
0.862
0.010
1H NMR (500 MHz, CDCl3)
OTBS
N
O
Br
1r
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1.11
1.04
1.03
1.02
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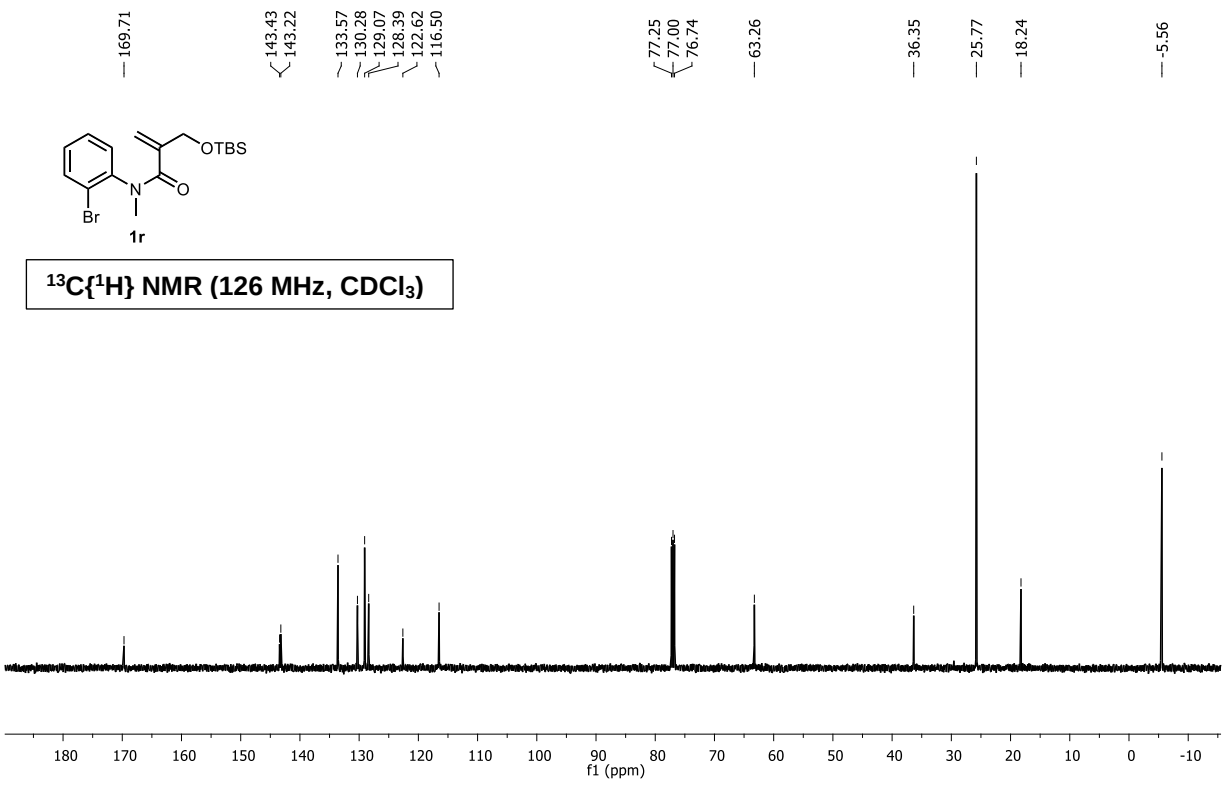
0.98
3.15
9.56
6.09
f1 (ppm)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63.26
36.35
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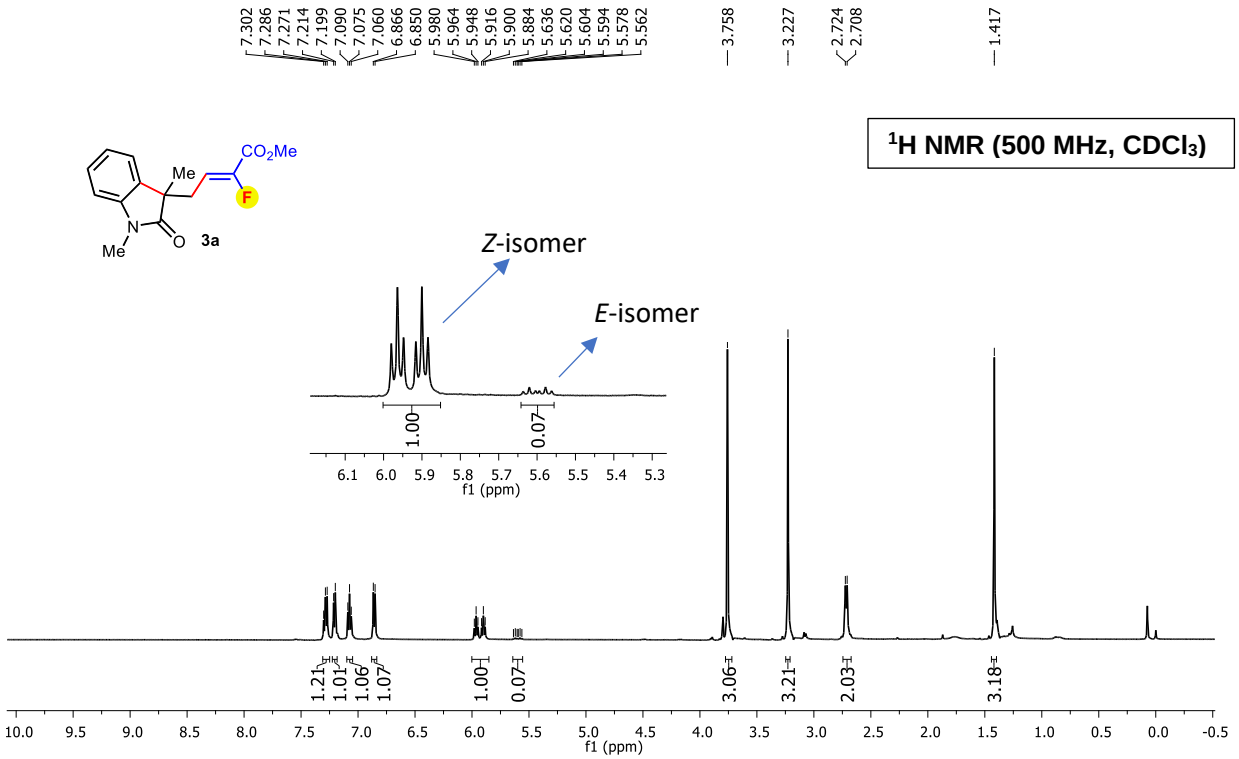
OTBS
N
O
Br
1r
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)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5.594
5.578
5.562
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3.227
2.724
2.708
1.417
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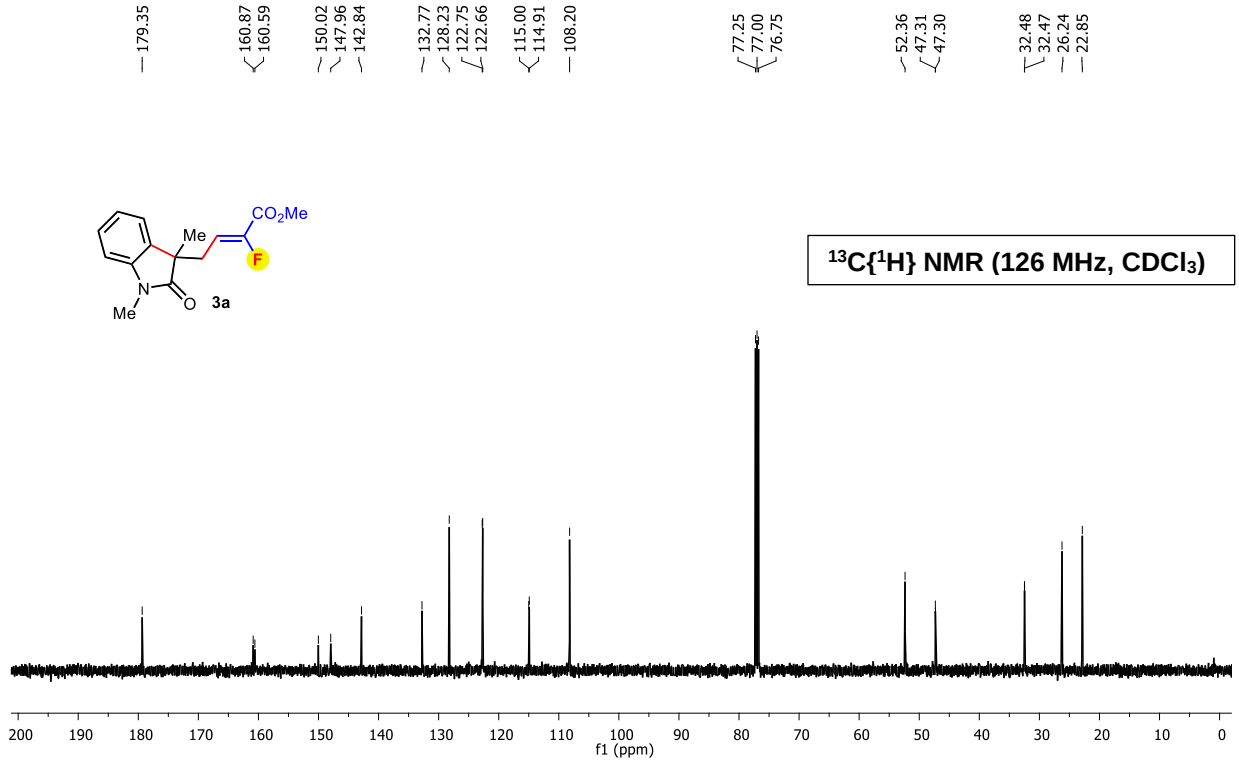
CO2Me
Me
F
N
Me
O
3a
Z-isomer
E-isomer
1.00
0.07
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3
f1 (ppm)
1.21
1.01
1.06
1.07
1.00
0.07
3.06
3.21
2.03
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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147.96
142.84
132.77
128.23
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122.66
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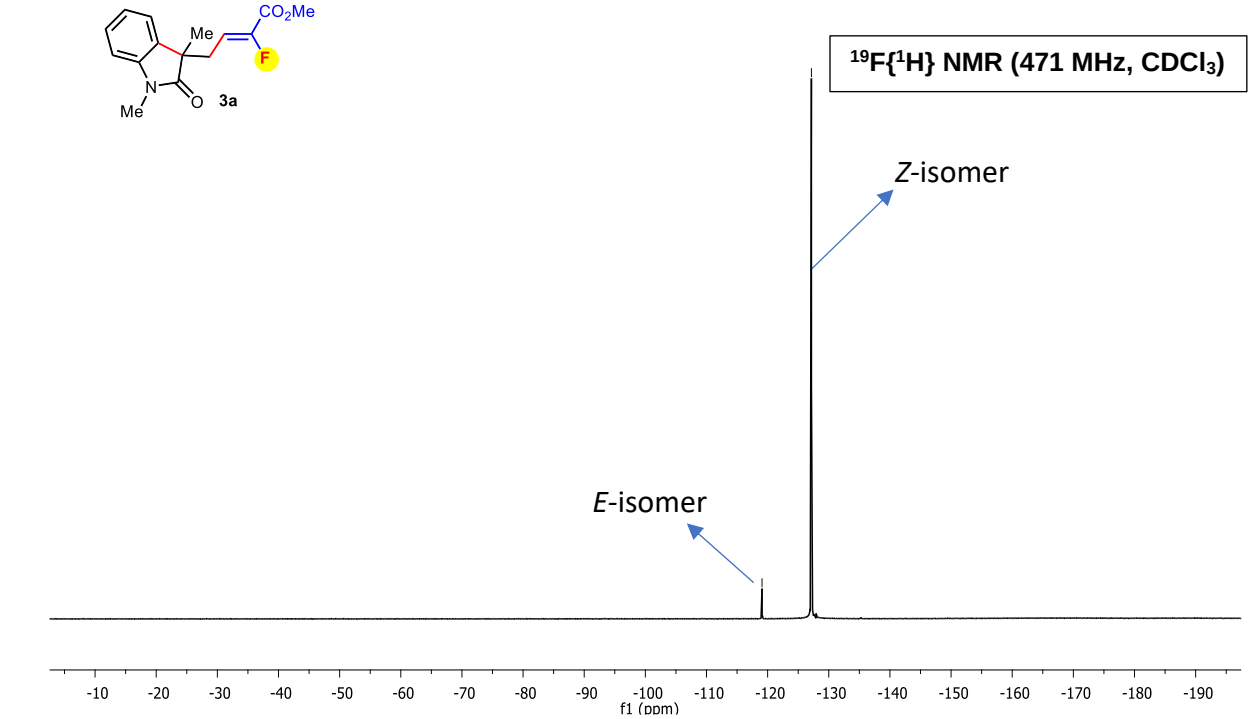
77.25
77.00
76.75
52.36
47.31
47.30
32.48
32.47
26.24
22.85
CO2Me
Me
F
N
Me
O
3a
13C{1H} NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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Z-isomer
E-isomer
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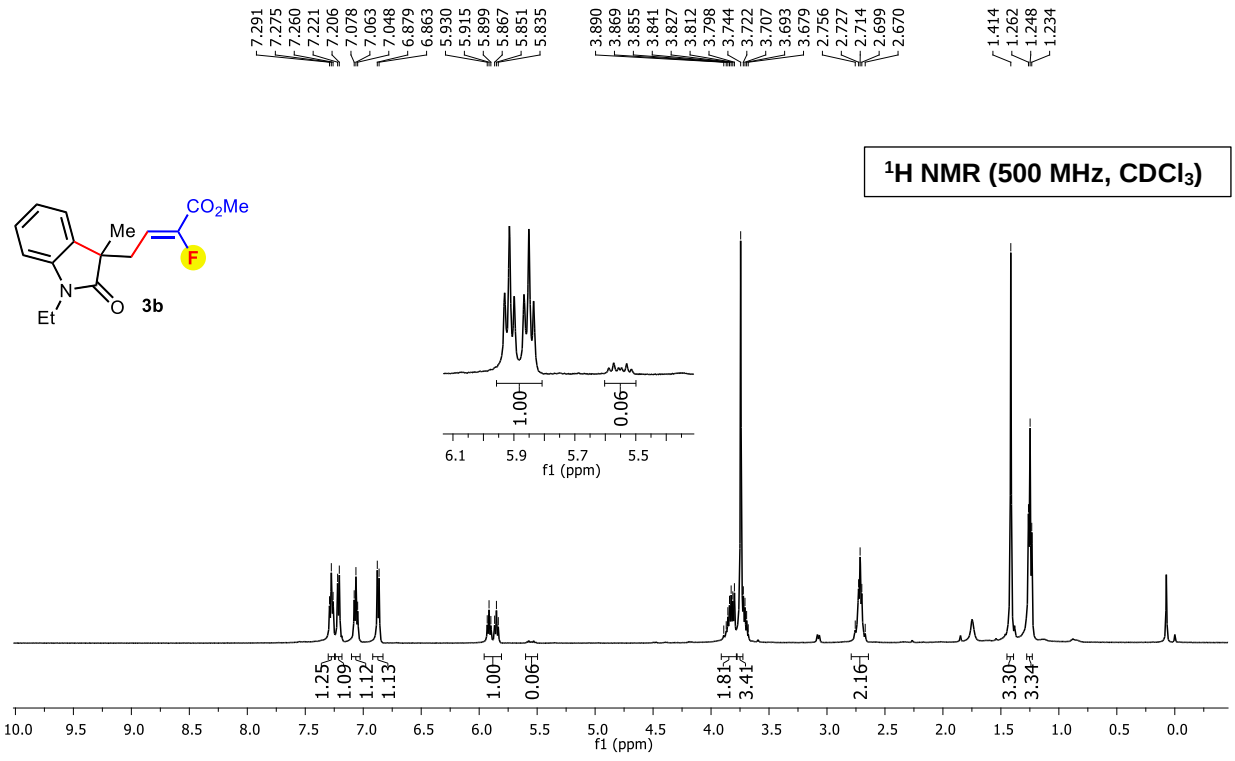
f1 (ppm)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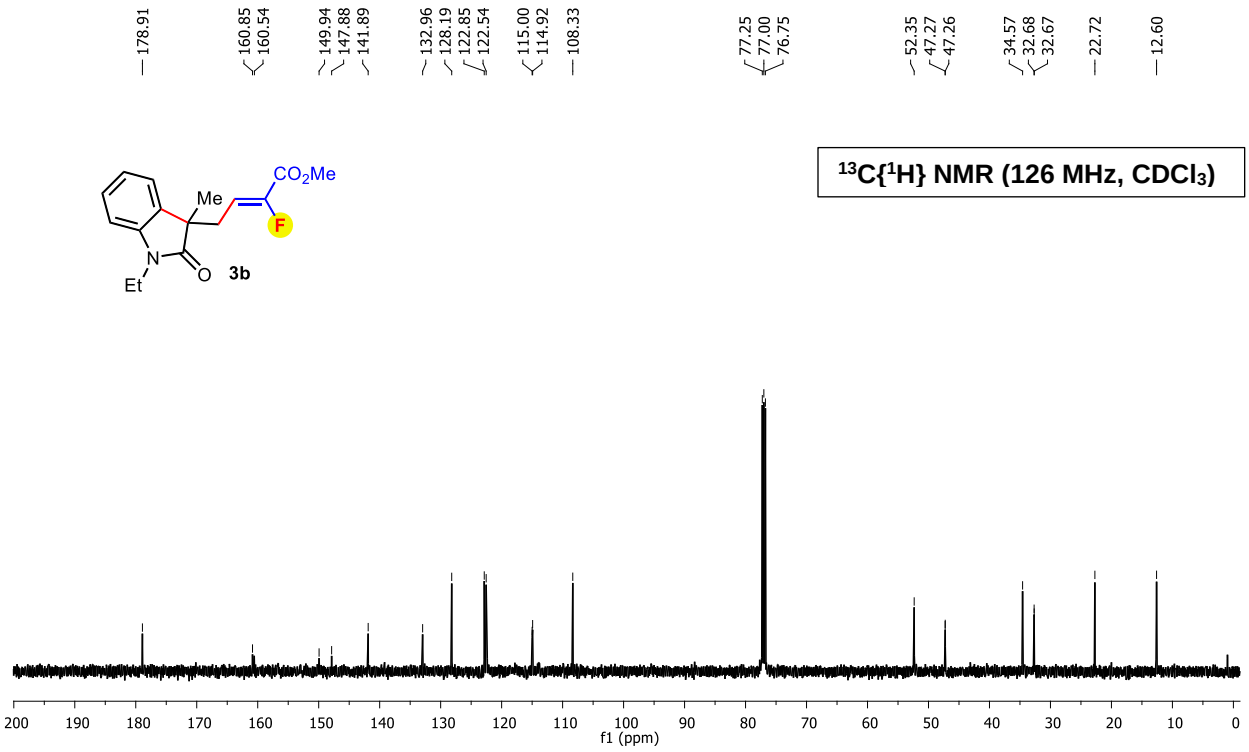
2.756 2.727 2.714 2.699 2.670
1.414 1.262 1.248 1.234
1H NMR (500 MHz, CDCl3)
CO2Me
Me
F
N
Et
O
3b
1.00
0.06
6.1 5.9 5.7 5.5
f1 (ppm)
1.25 1.09 1.12 1.13 1.00 0.06 1.81 3.41 2.16 3.30 3.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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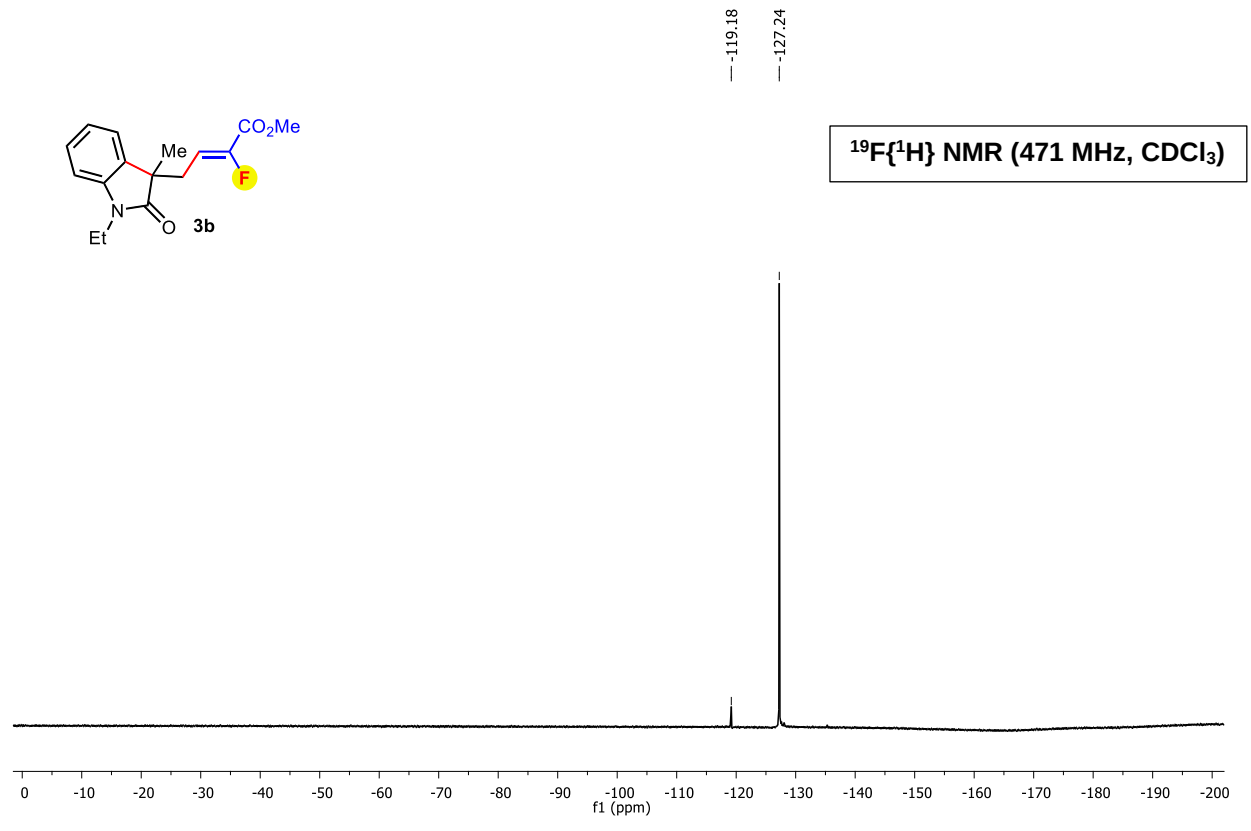
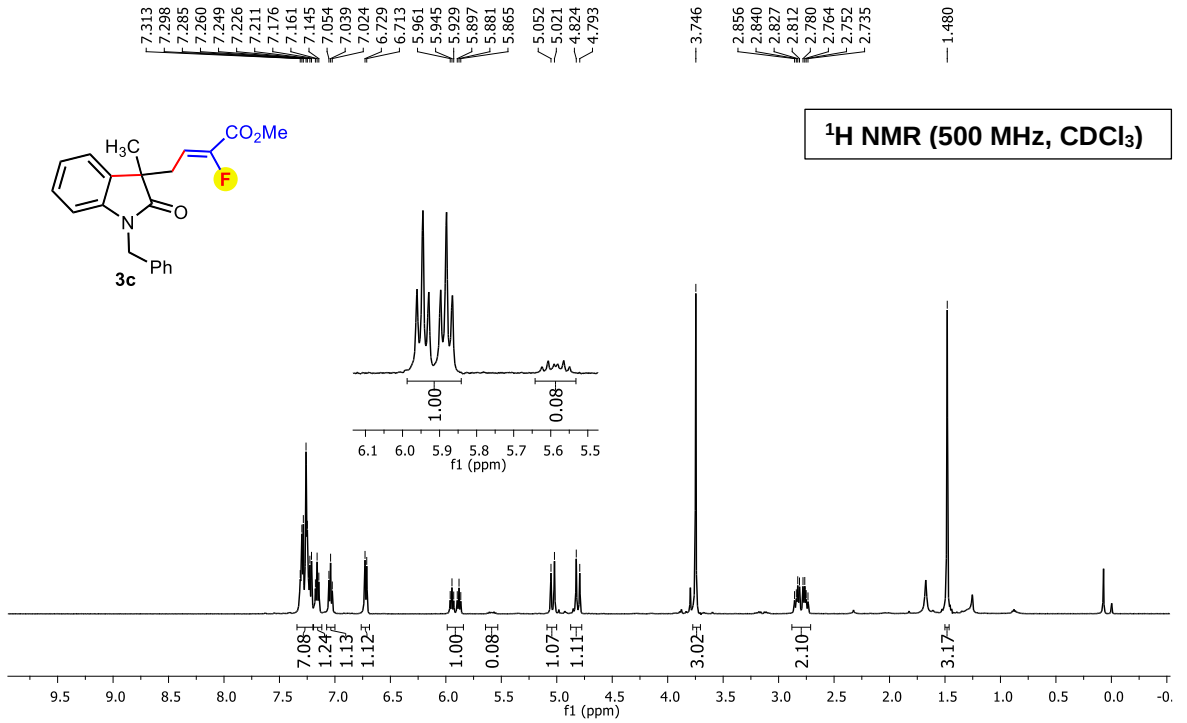


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)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H3C
F
O
N
Ph
3c
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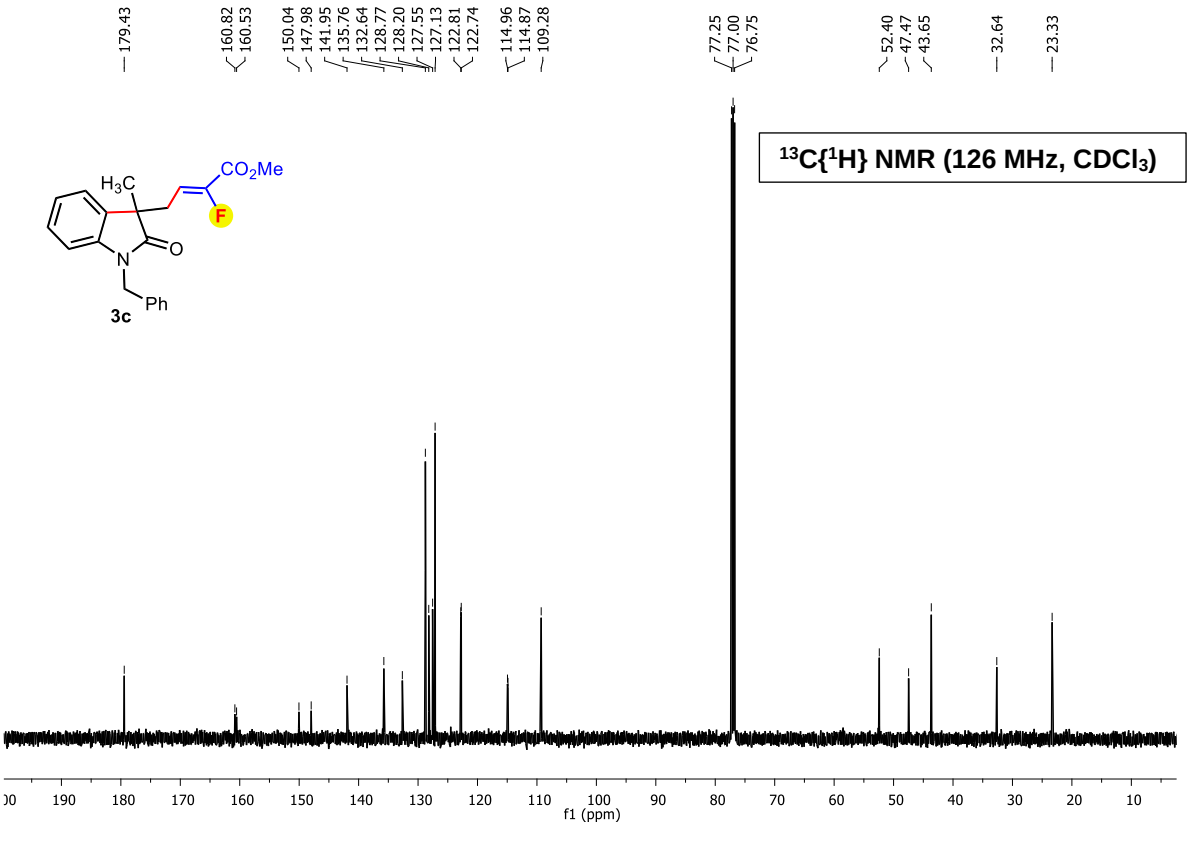
0.08
6.1 6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
7.08
1.24
1.13
1.12
1.00
0.08
1.07
1.11
3.02
2.10
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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23.33
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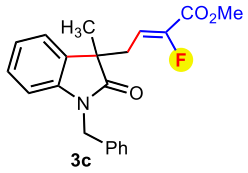
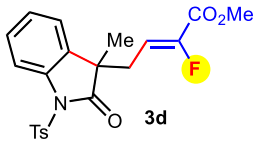
H3C
F
O
N
Ph
3c
13C{1H} NMR (126 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



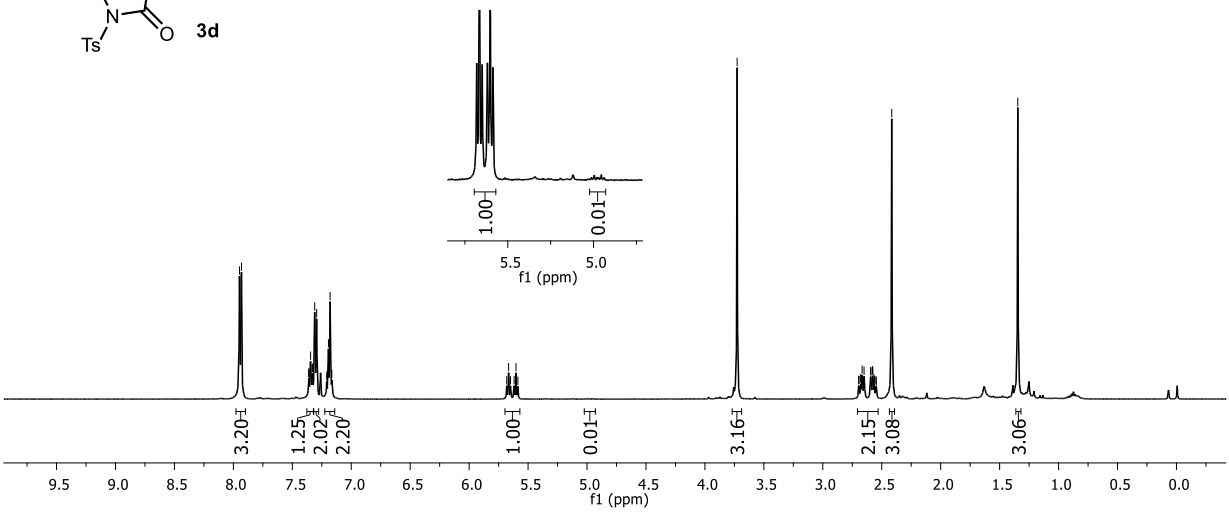
3c

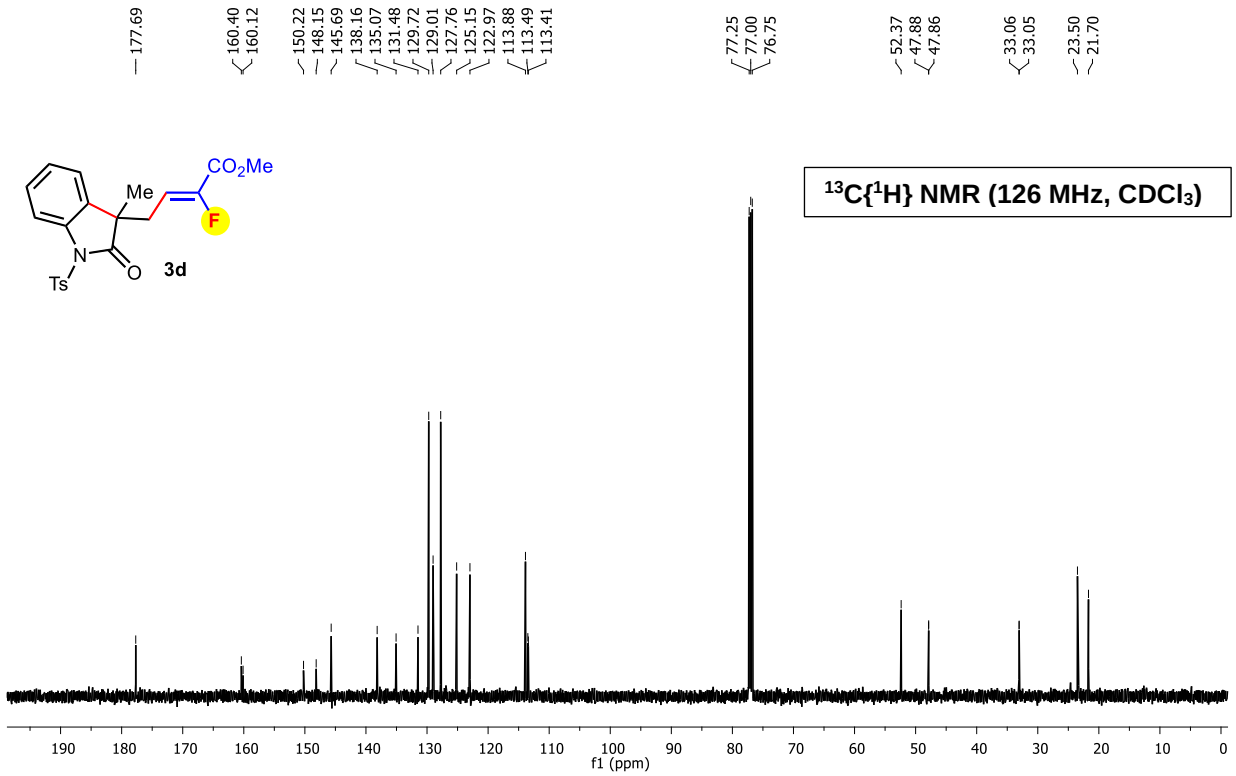
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

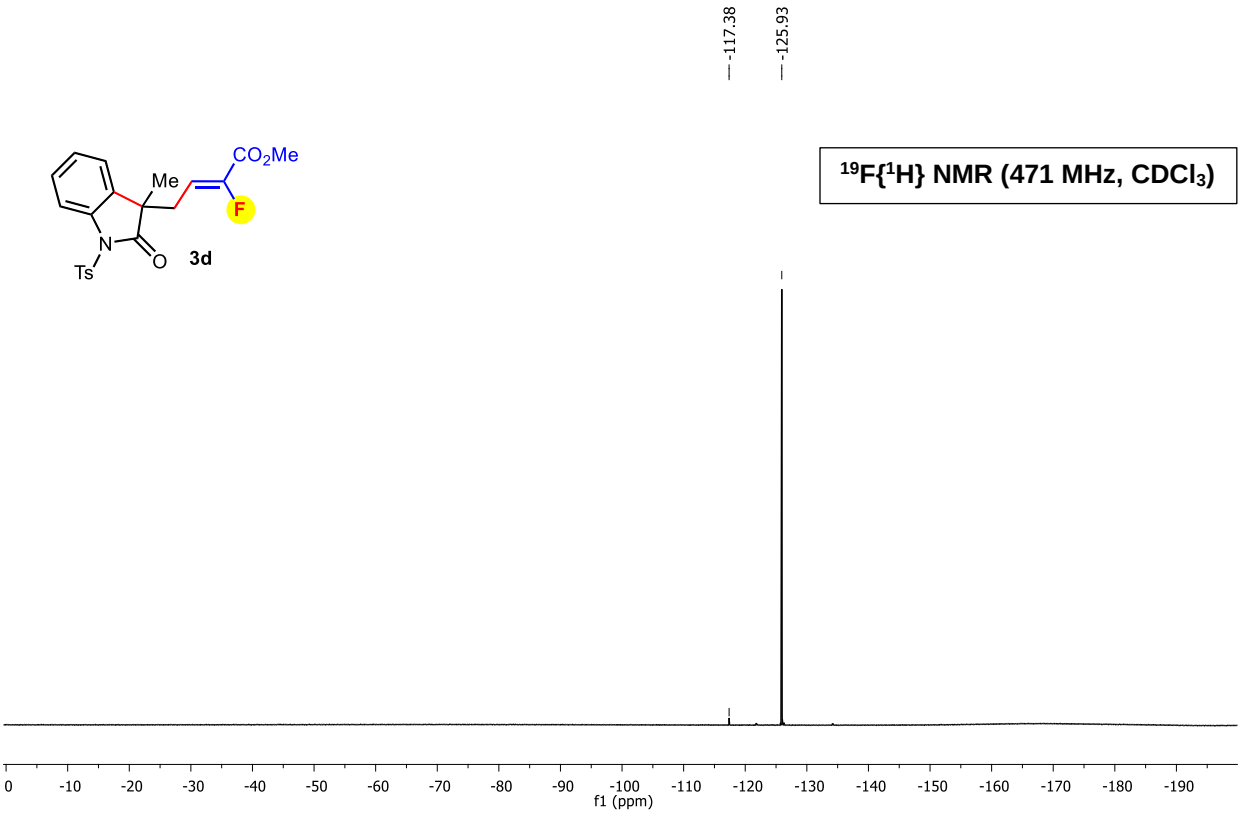


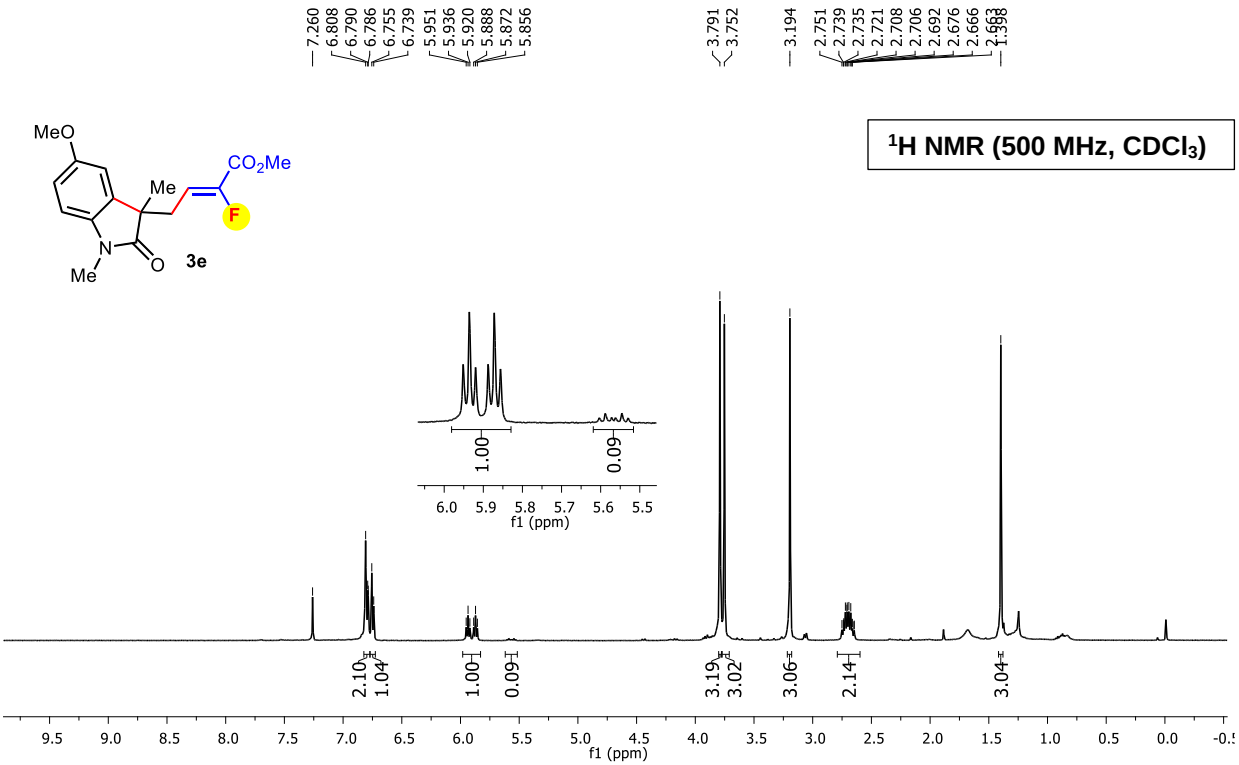
3d

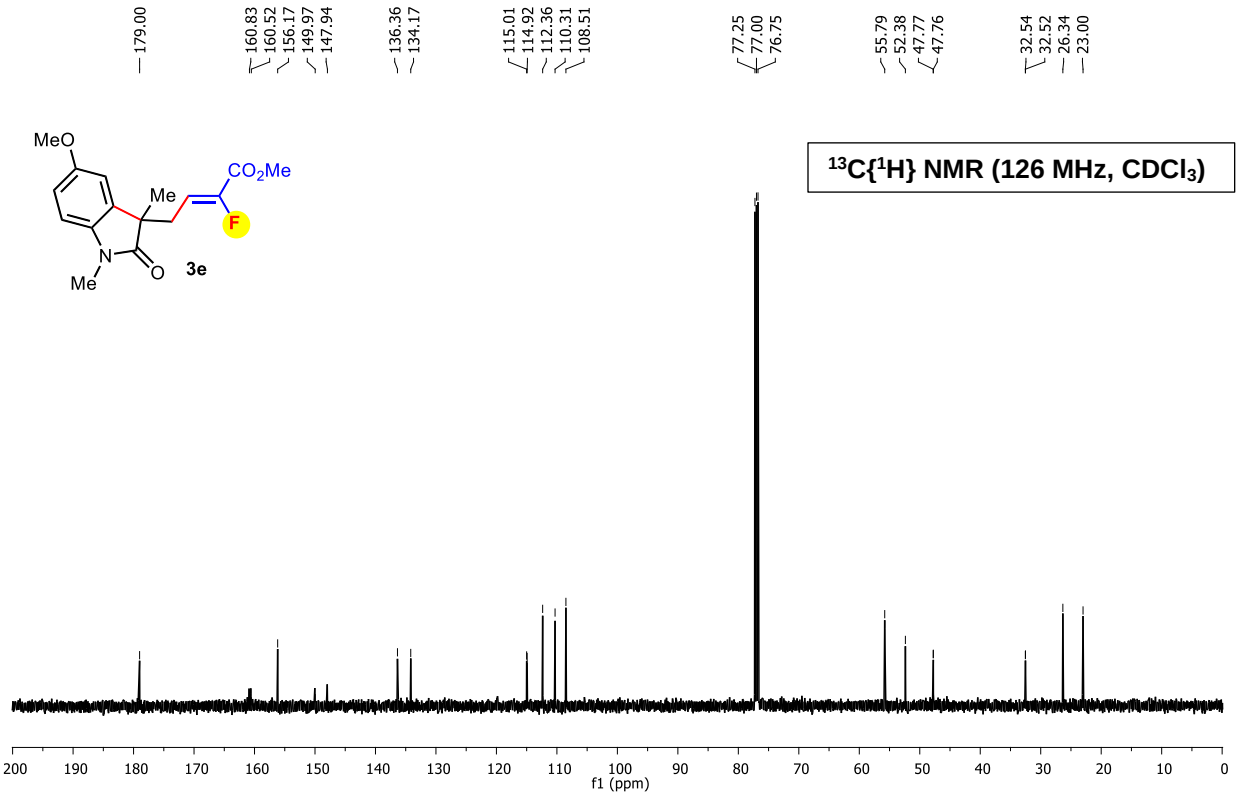
^{1}H NMR (500 MHz, $CDCl_3$)

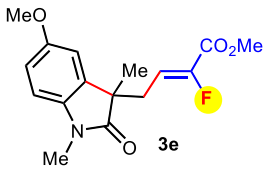



177.69
160.40
160.12
150.22
148.15
145.69
138.16
135.07
131.48
129.72
129.01
127.76
125.15
122.97
113.88
113.49
113.41
77.25
77.00
76.75
52.37
47.88
47.86
33.06
33.05
23.50
21.70
CO2Me
Me
F
N
Ts
O
3d
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)


-117.38
-125.93
CO2Me
Me
F
N
Ts
O
3d
19F{1H} NMR (471 MHz, CDCl3)
f1 (ppm)

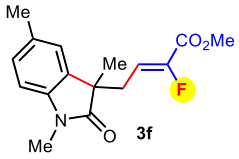

7.260
6.808
6.790
6.786
6.755
6.739
5.951
5.936
5.920
5.888
5.872
5.856
3.791
3.752
3.194
2.751
2.739
2.735
2.721
2.708
2.706
2.692
2.676
2.666
MeO
CO2Me
Me
F
N
O
Me
3e
1H NMR (500 MHz, CDCl3)
1.00
0.09
6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
2.10
1.04
1.00
0.09
3.19
3.02
3.06
2.14
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


179.00
160.83
160.52
156.17
149.97
147.94
136.36
134.17
115.01
114.92
112.36
110.31
108.51
77.25
77.00
76.75
55.79
52.38
47.77
47.76
32.54
32.52
26.34
23.00
MeO
CO2Me
Me
F
N
O
Me
3e
13C{1H} NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



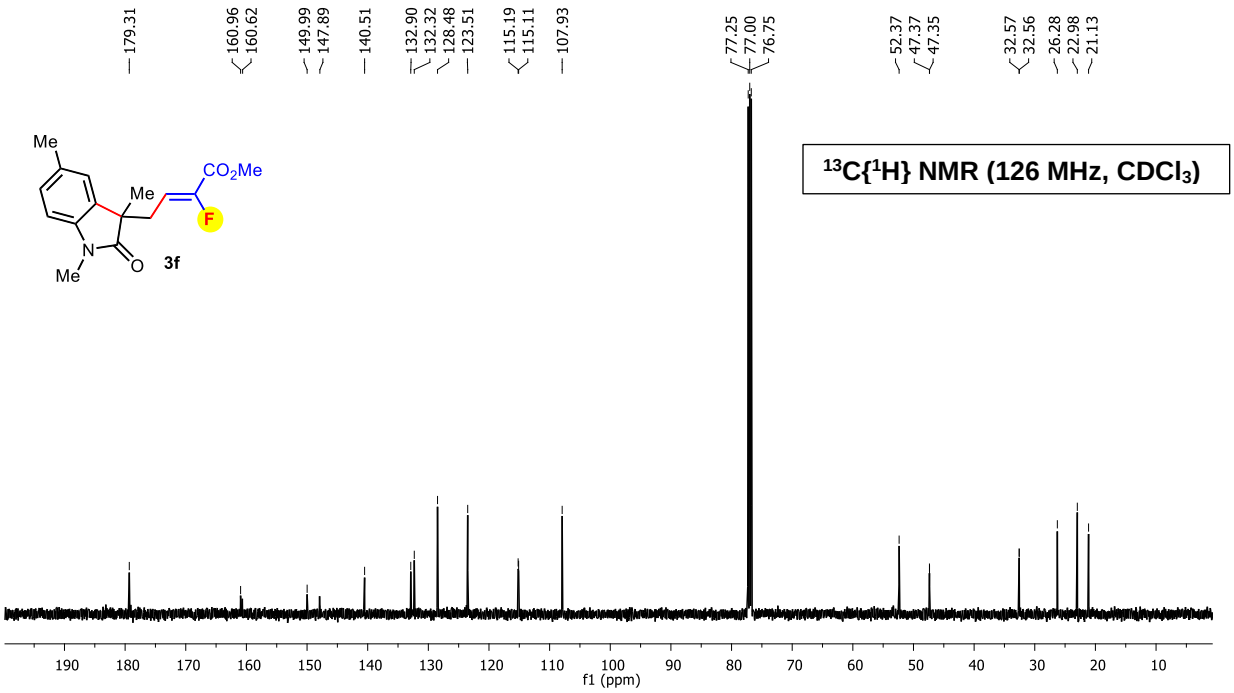
3e

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

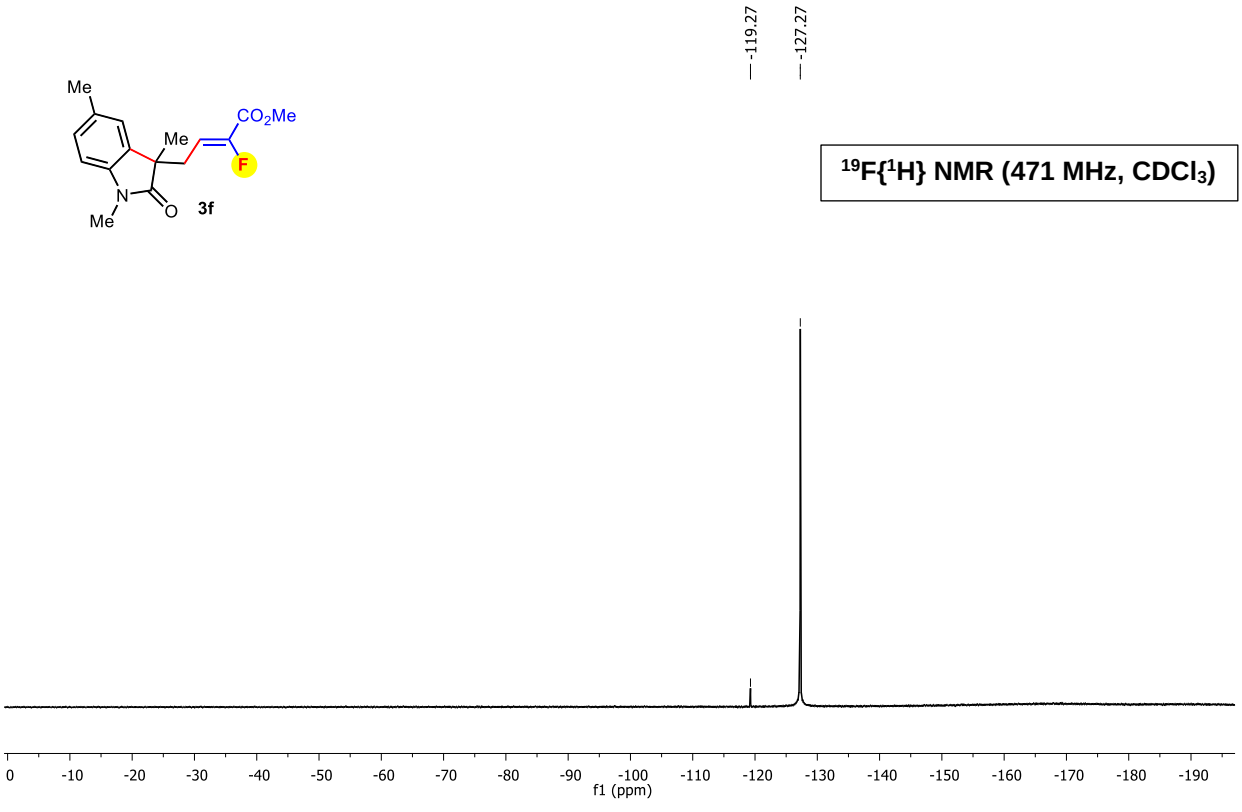


3f

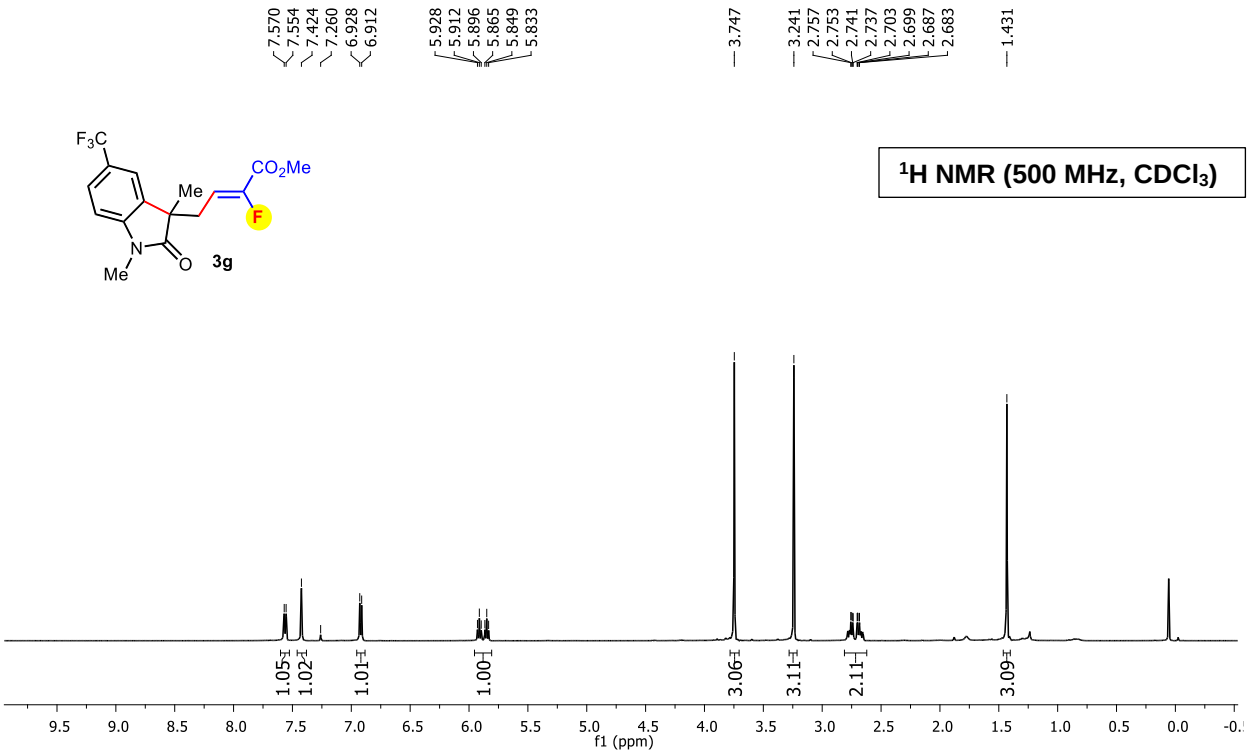
^{1}H NMR (500 MHz, $CDCl_3$)

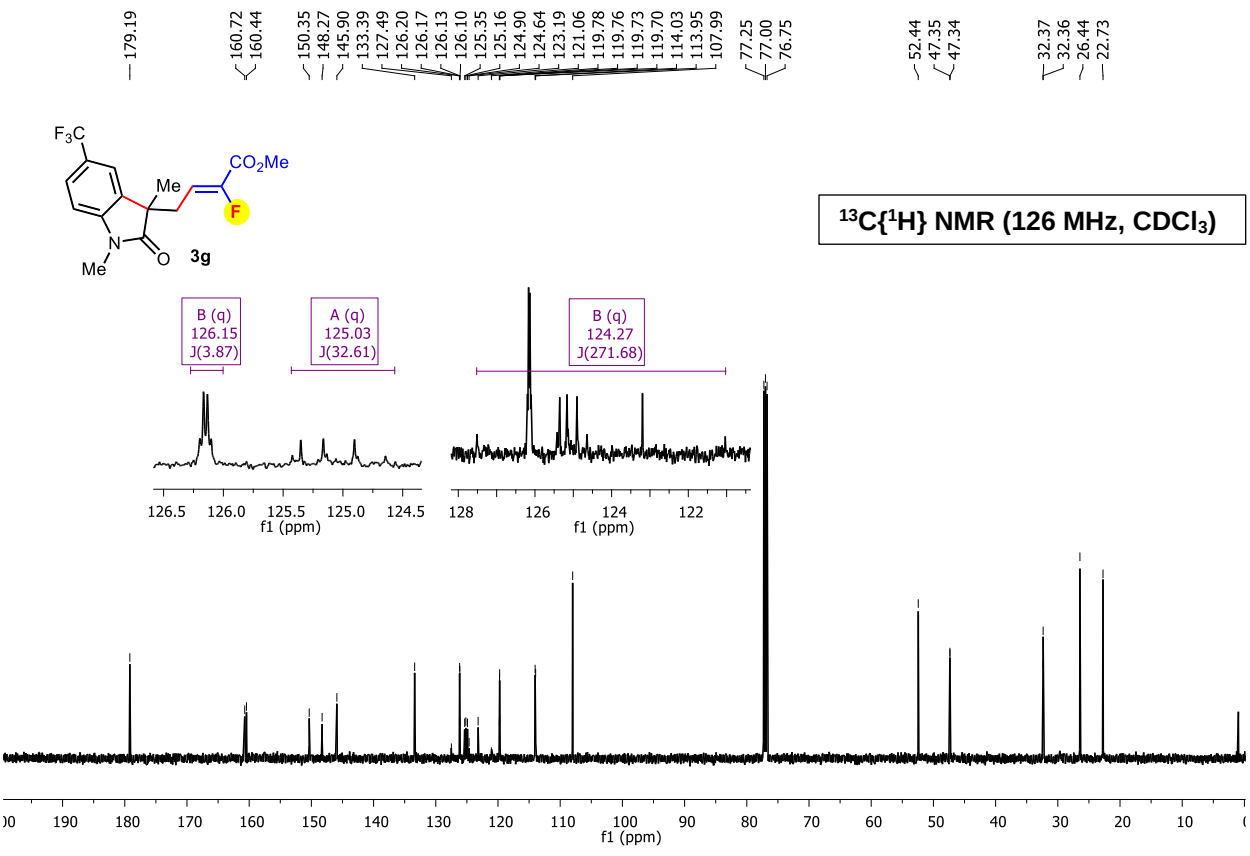


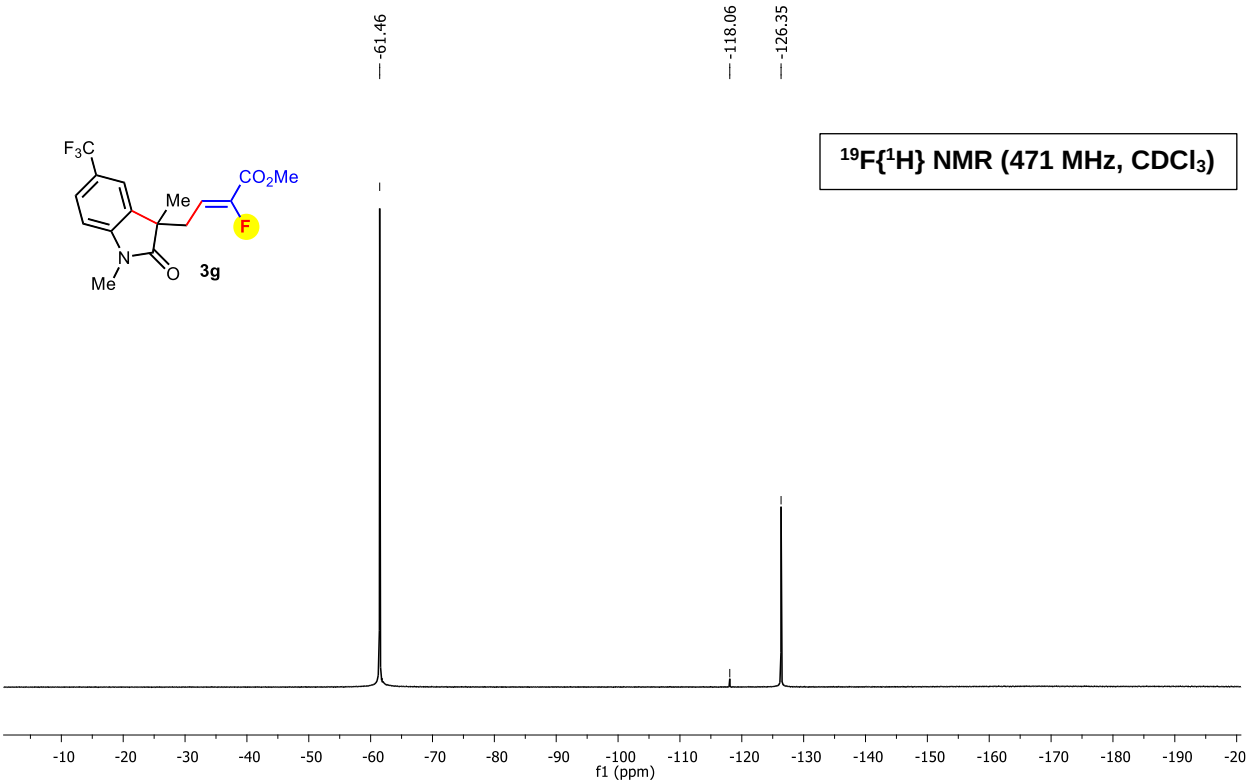
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

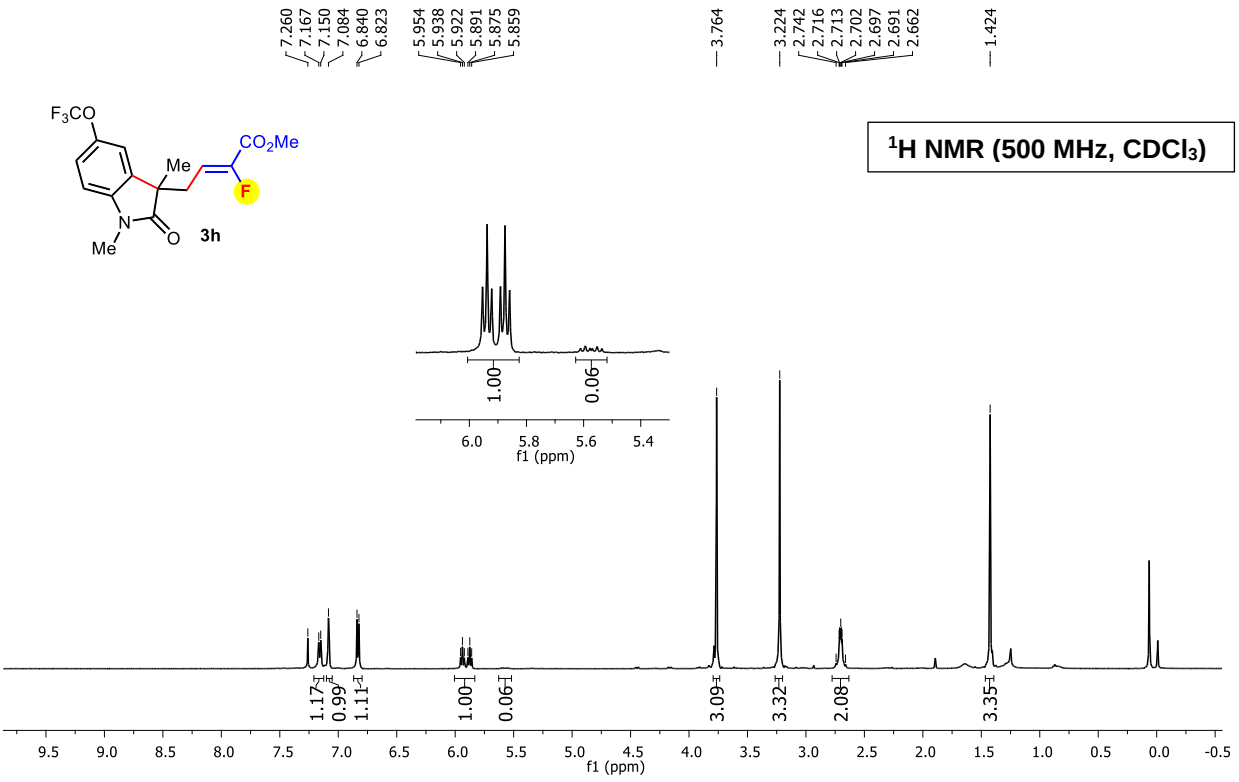


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

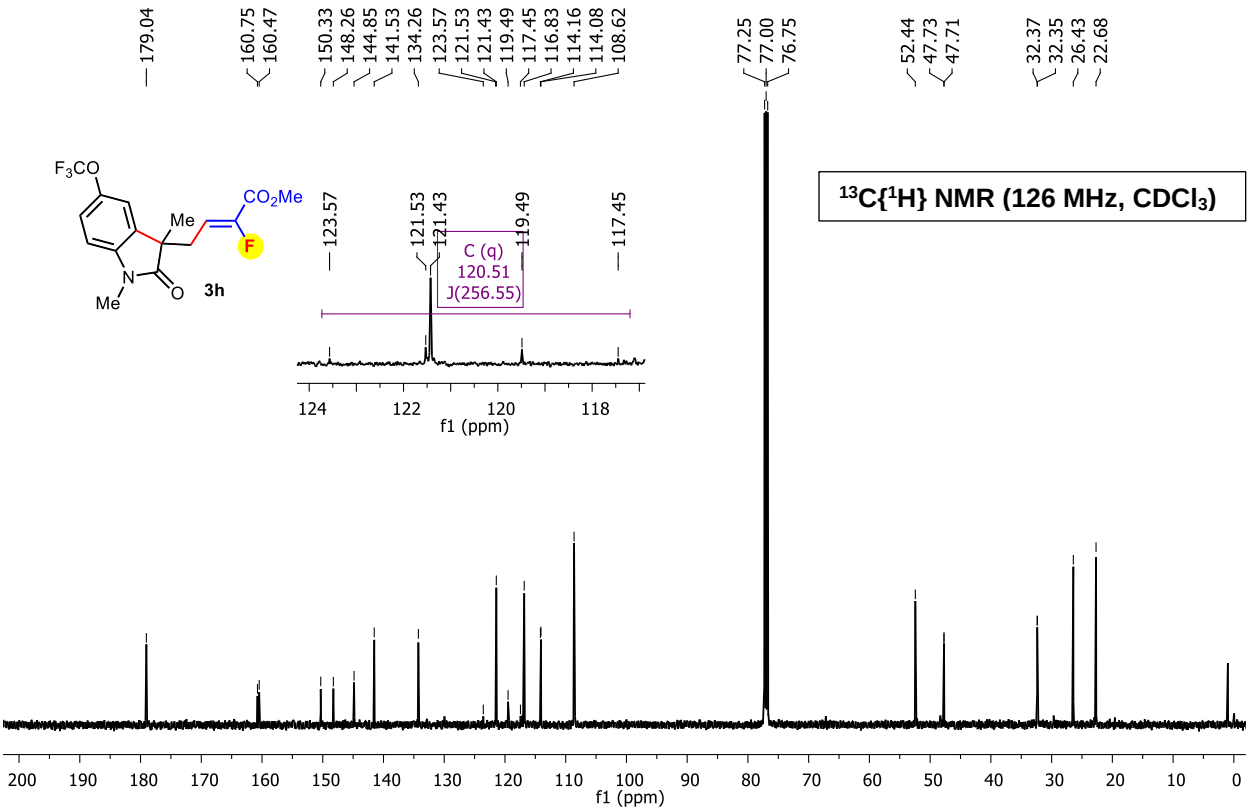

7.570
7.554
7.424
7.260
6.928
6.912
5.928
5.912
5.896
5.865
5.849
5.833
3.747
3.241
2.757
2.753
2.741
2.737
2.703
2.699
2.687
2.683
1.431
F3C
CO2Me
Me
F
N
O
Me
3g
1H NMR (500 MHz, CDCl3)
1.05
1.02
1.01
1.00
3.06
3.11
2.11
3.09
f1 (ppm)


179.19
160.72
160.44
150.35
148.27
145.90
133.39
127.49
126.20
126.17
126.13
126.10
125.35
125.16
124.90
124.64
123.19
121.06
119.78
119.76
119.73
119.70
114.03
113.95
107.99
77.25
77.00
76.75
52.44
47.35
47.34
32.37
32.36
26.44
22.73
F3C
CO2Me
Me
F
N
O
Me
3g
13C{1H} NMR (126 MHz, CDCl3)
B (q)
126.15
J(3.87)
A (q)
125.03
J(32.61)
B (q)
124.27
J(271.68)
f1 (ppm)
f1 (ppm)
f1 (ppm)

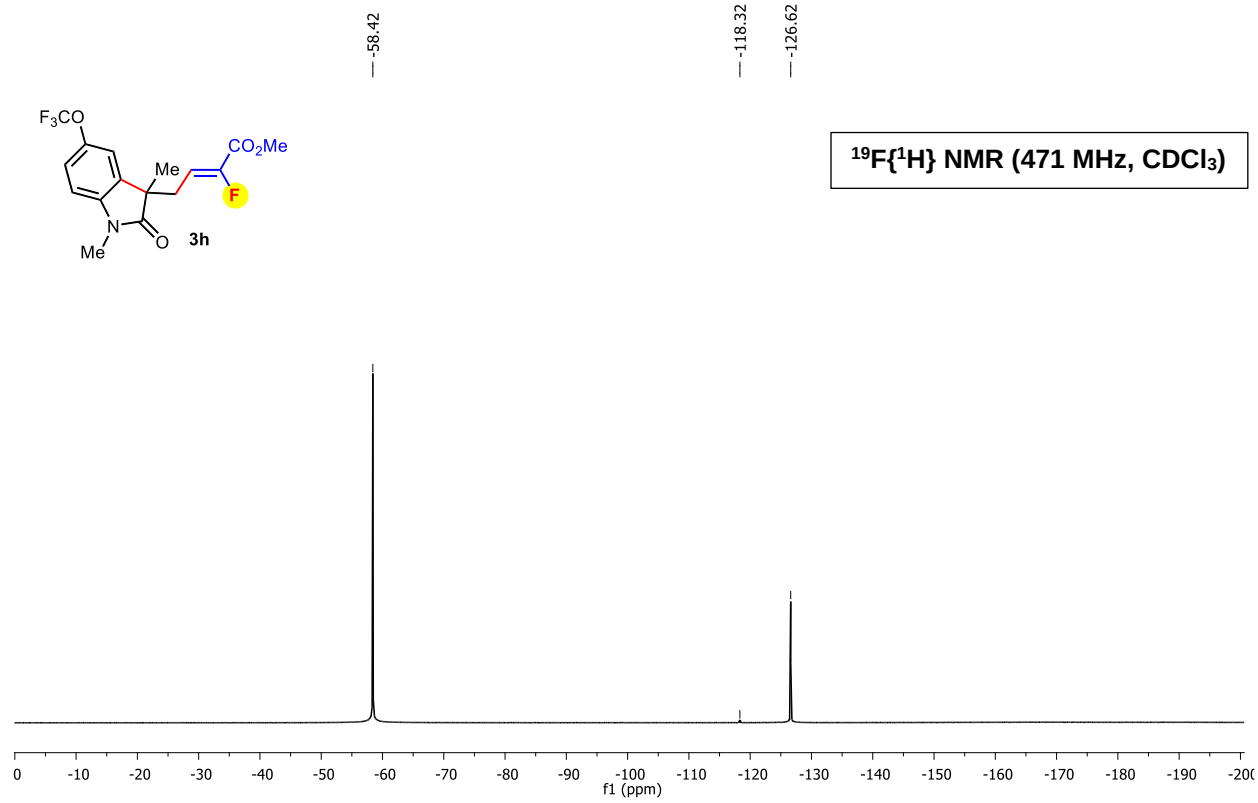




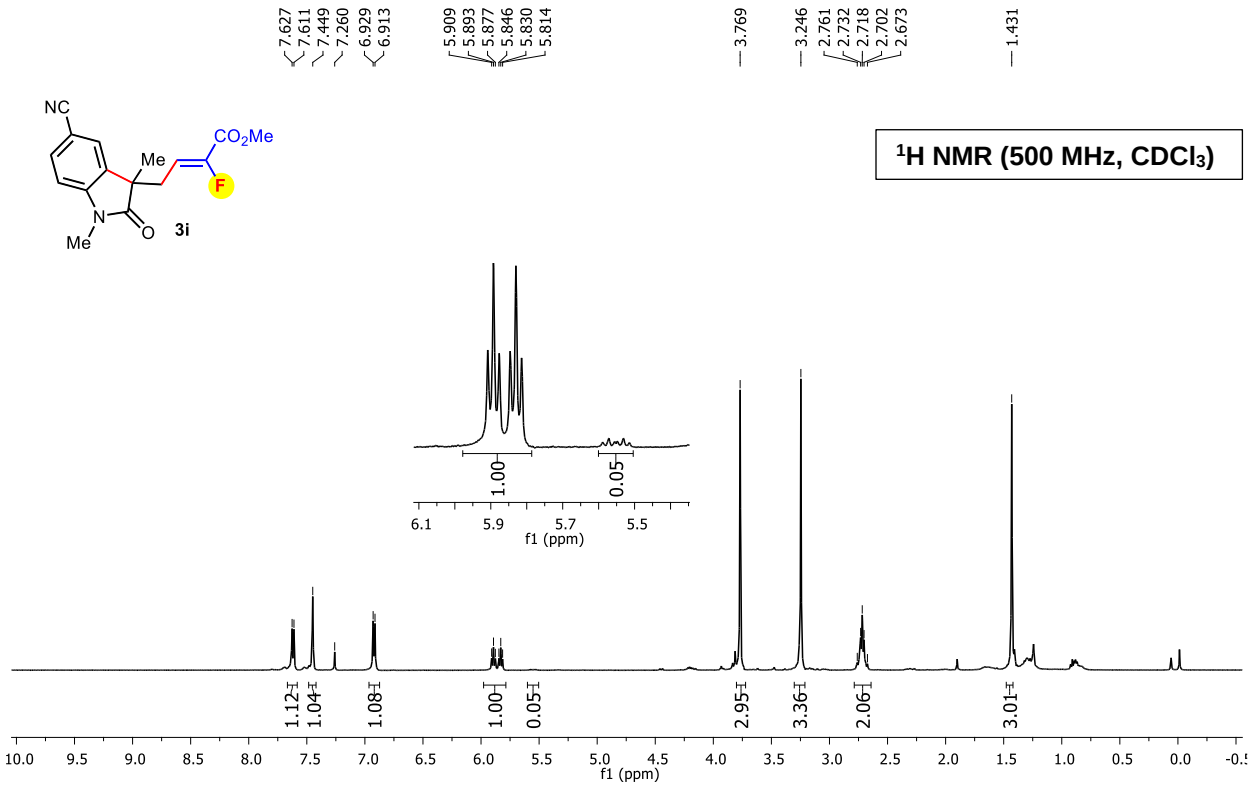
^{1}H NMR (500 MHz, $CDCl_3$)

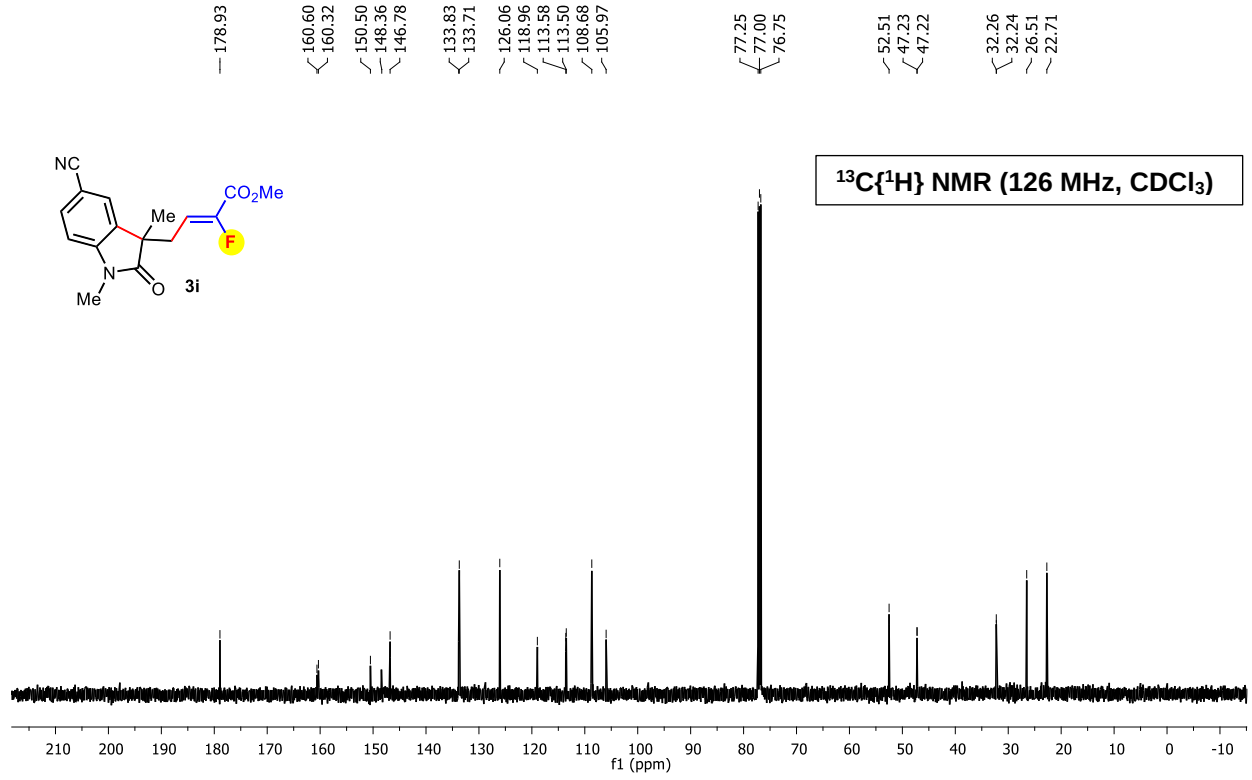


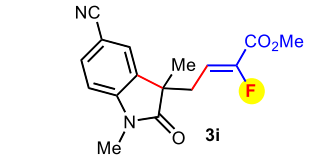
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

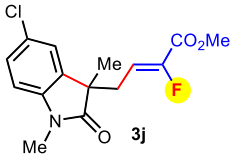

7.627
7.611
7.449
7.260
6.929
6.913
5.909
5.893
5.877
5.846
5.830
5.814
3.769
3.246
2.761
2.732
2.718
2.702
2.673
1.431
NC
CO2Me
Me
F
N
Me
O
3i
1H NMR (500 MHz, CDCl3)
1.00
0.05
6.1
5.9
5.7
5.5
f1 (ppm)
1.12
1.04
1.08
1.00
0.05
2.95
3.36
2.06
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.93
160.60
160.32
150.50
148.36
146.78
133.83
133.71
126.06
118.96
113.58
113.50
108.68
105.97
77.25
77.00
76.75
52.51
47.23
47.22
32.26
32.24
26.51
22.71
NC
CO2Me
Me
F
N
Me
O
3i
13C{1H} NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



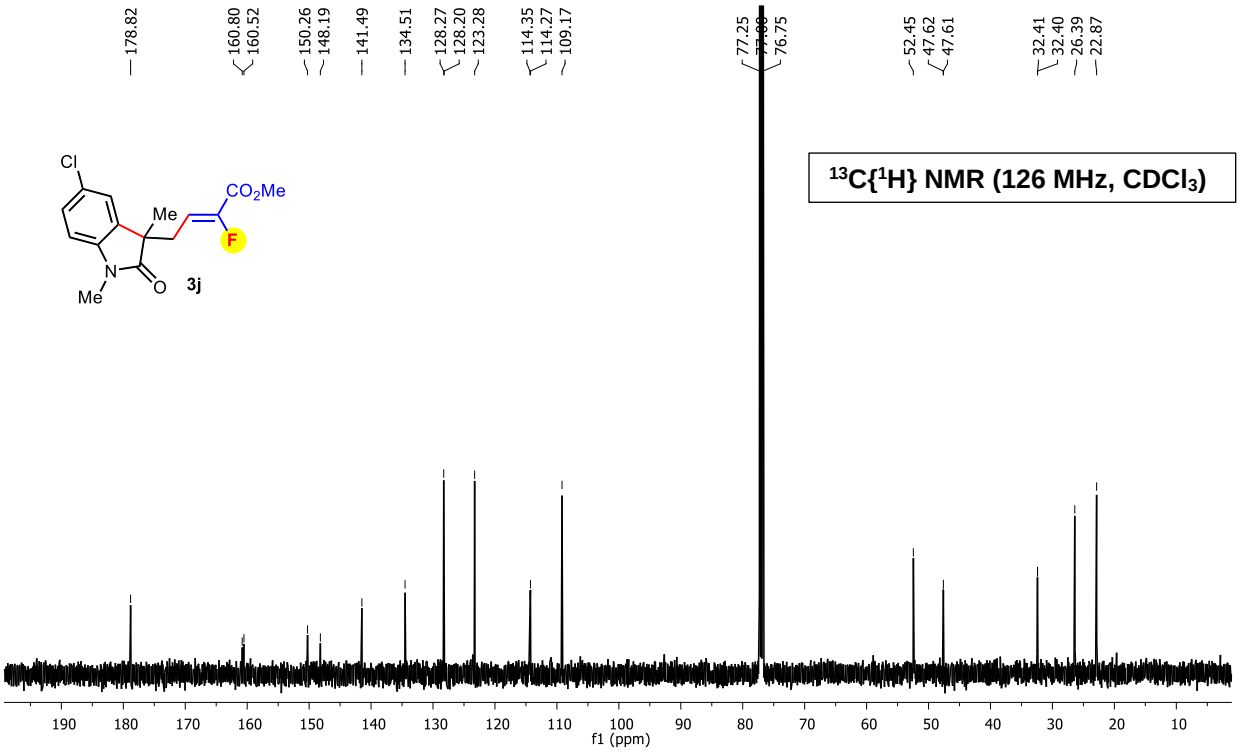
3i

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

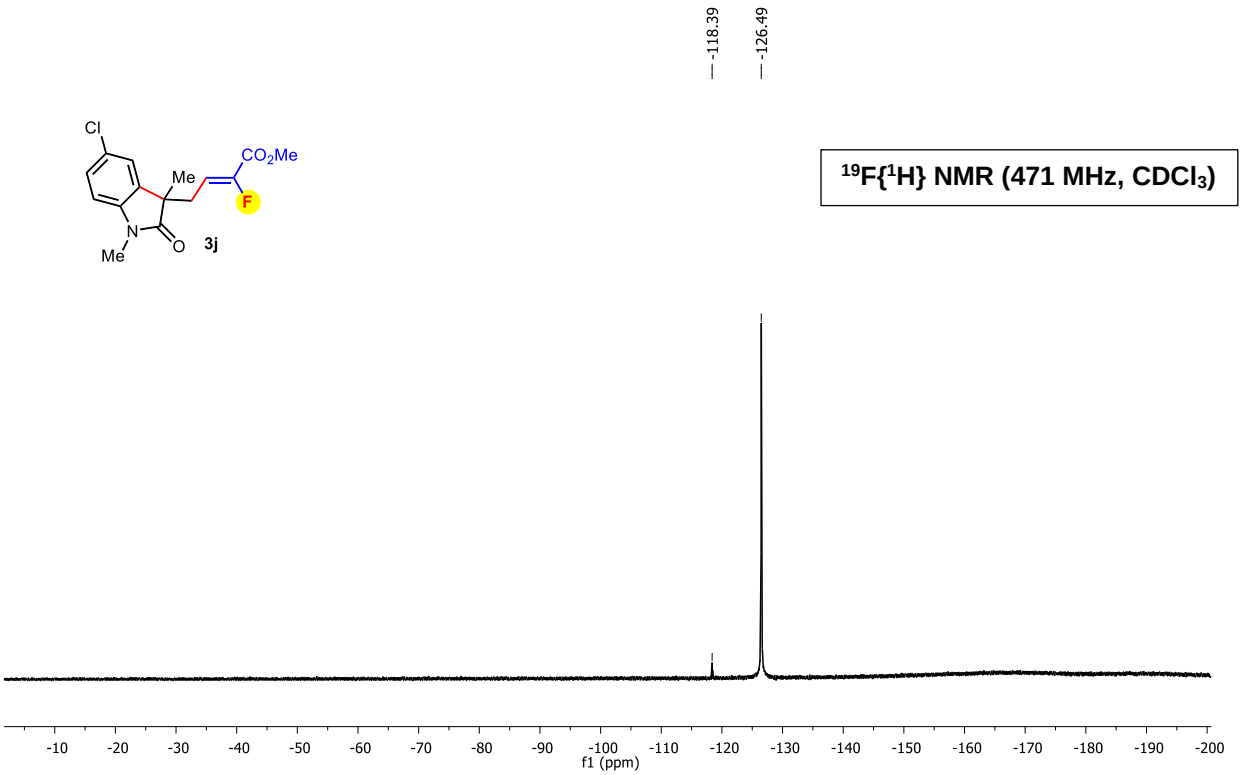


3j

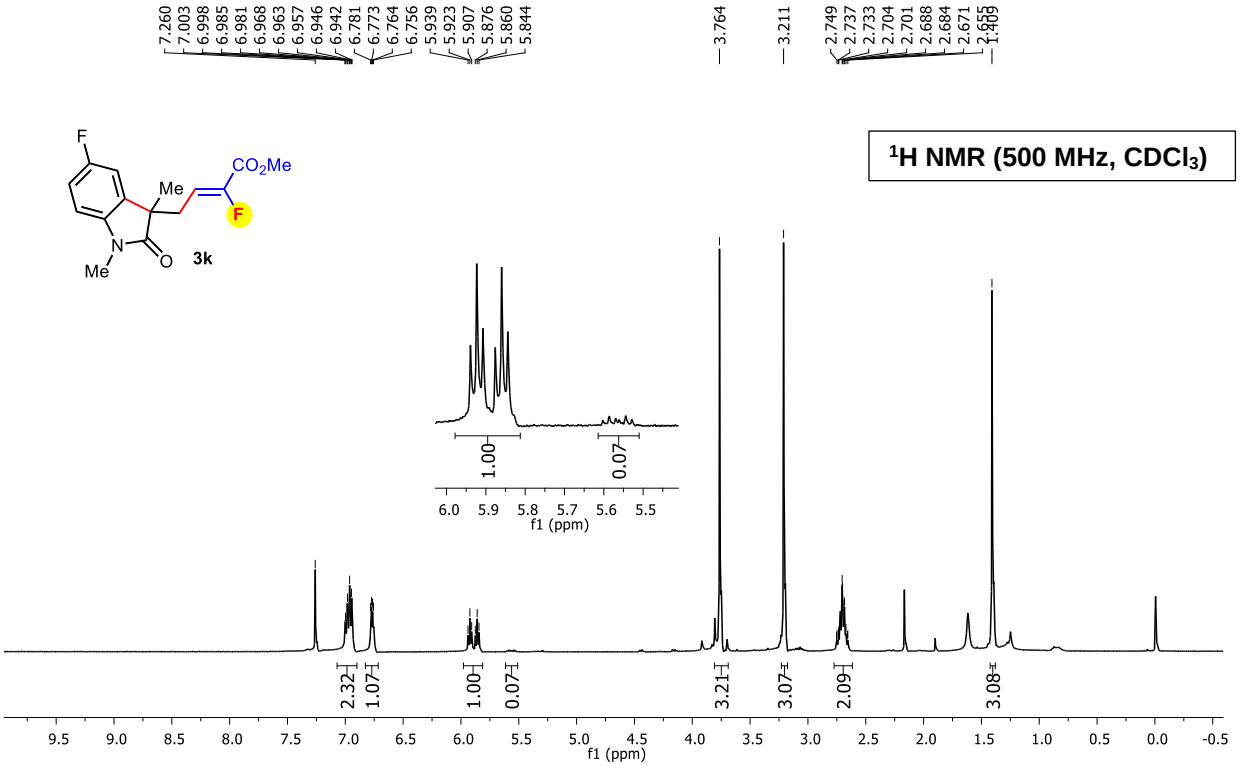
^{1}H NMR (500 MHz, $CDCl_3$)

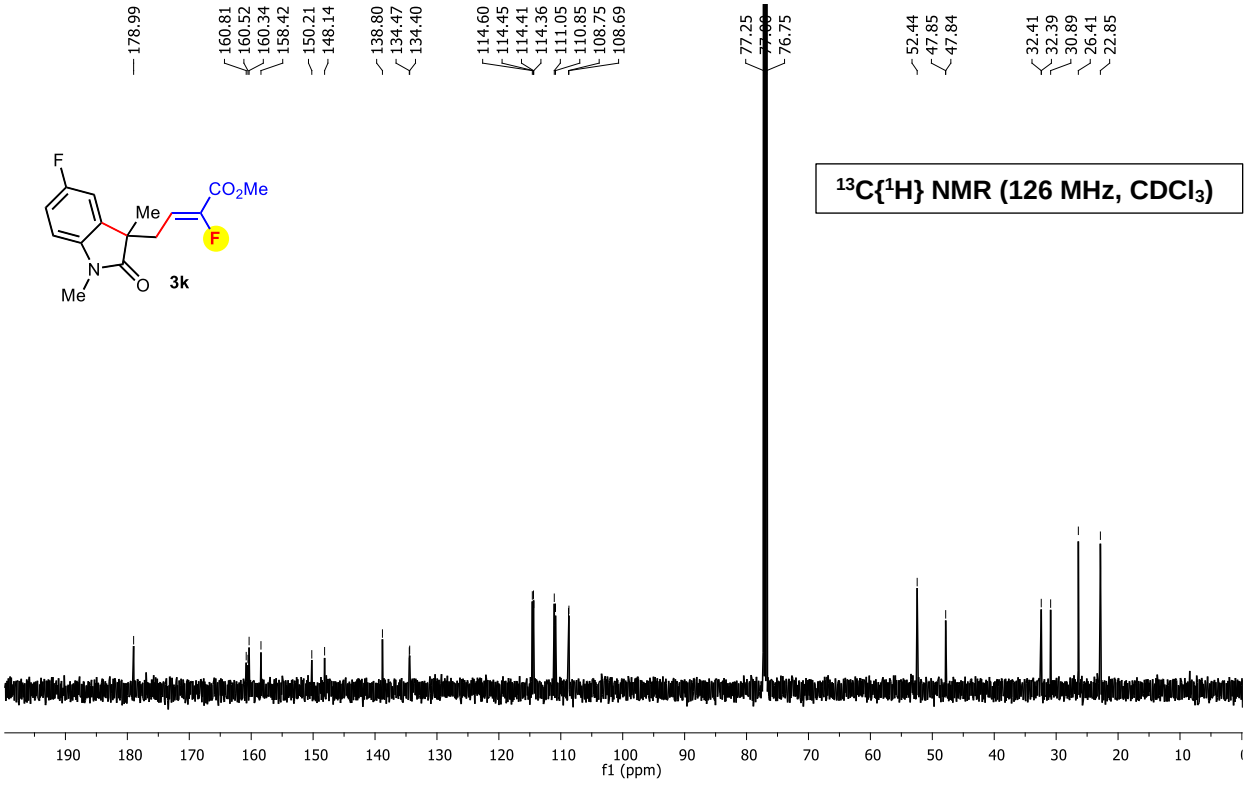


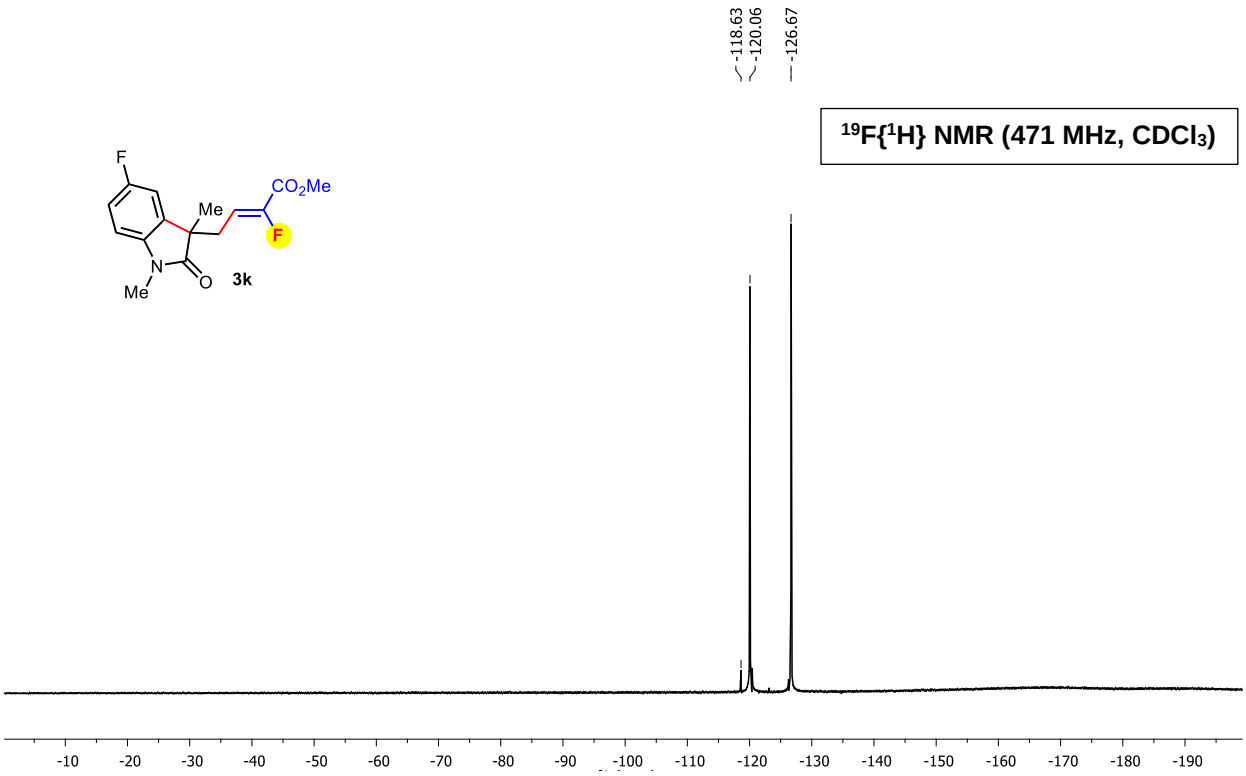
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



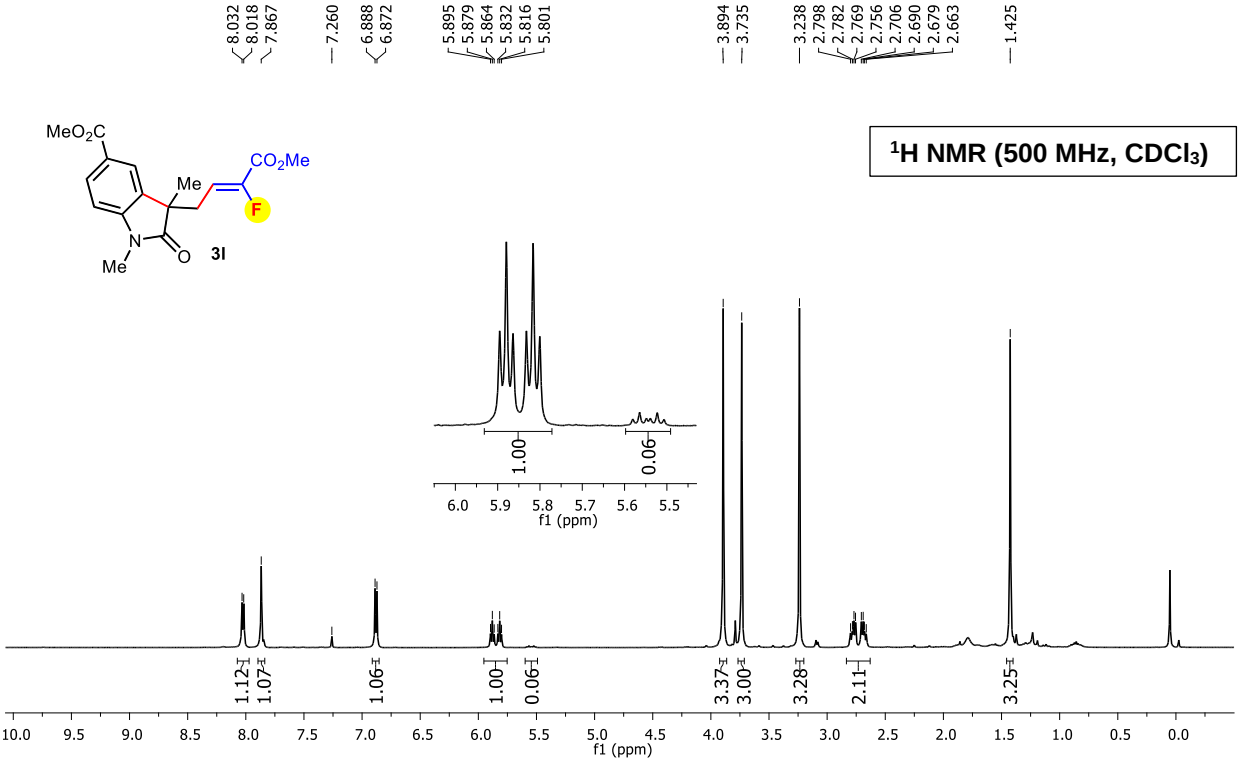
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


7.260
7.003
6.998
6.985
6.981
6.968
6.963
6.957
6.946
6.942
6.781
6.773
6.764
6.756
5.939
5.923
5.907
5.876
5.860
5.844
3.764
3.211
2.749
2.737
2.733
2.704
2.701
2.688
2.684
2.671
1.409
F
CO2Me
Me
F
N
O
Me
3k
1H NMR (500 MHz, CDCl3)
1.00
0.07
6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
2.32
1.07
1.00
0.07
3.21
3.07
2.09
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

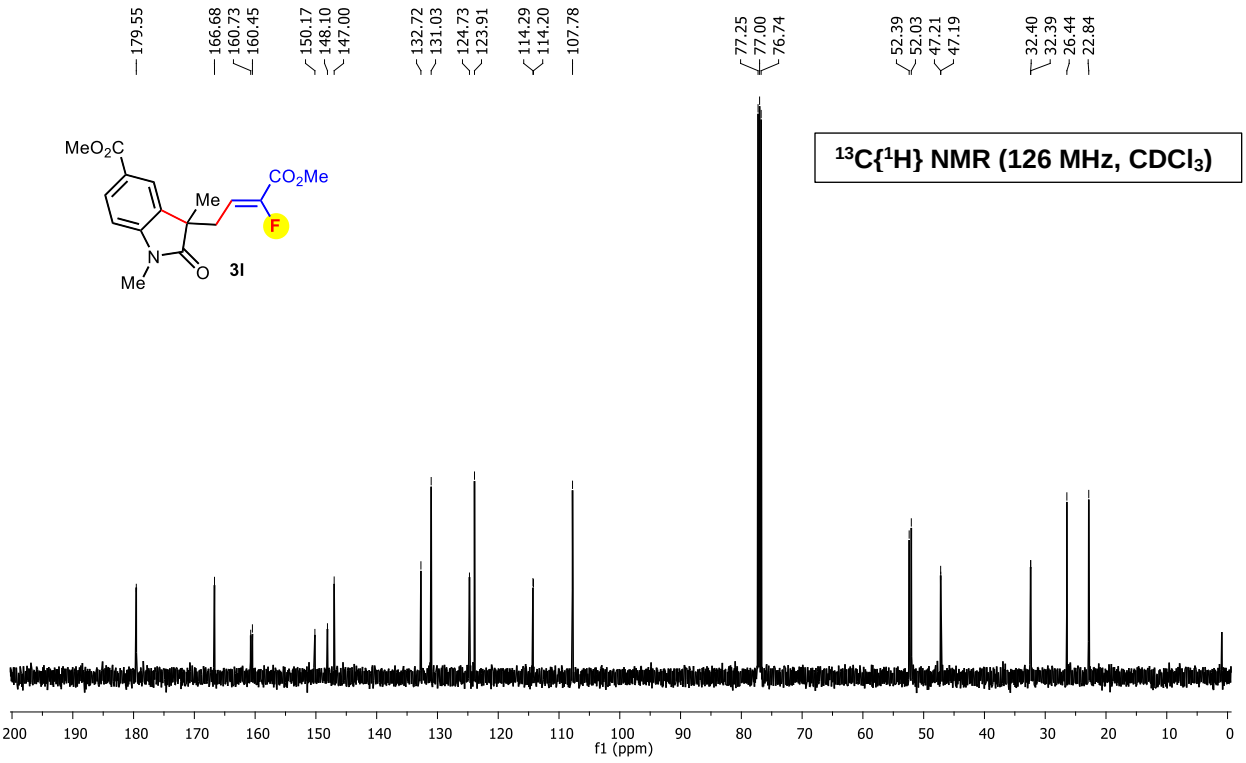

178.99
160.81
160.52
160.34
158.42
150.21
148.14
138.80
134.47
134.40
114.60
114.45
114.41
114.36
111.05
110.85
108.75
108.69
77.25
77.00
76.75
52.44
47.85
47.84
32.41
32.39
30.89
26.41
22.85
F
CO2Me
Me
F
N
O
Me
3k
13C{1H} NMR (126 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

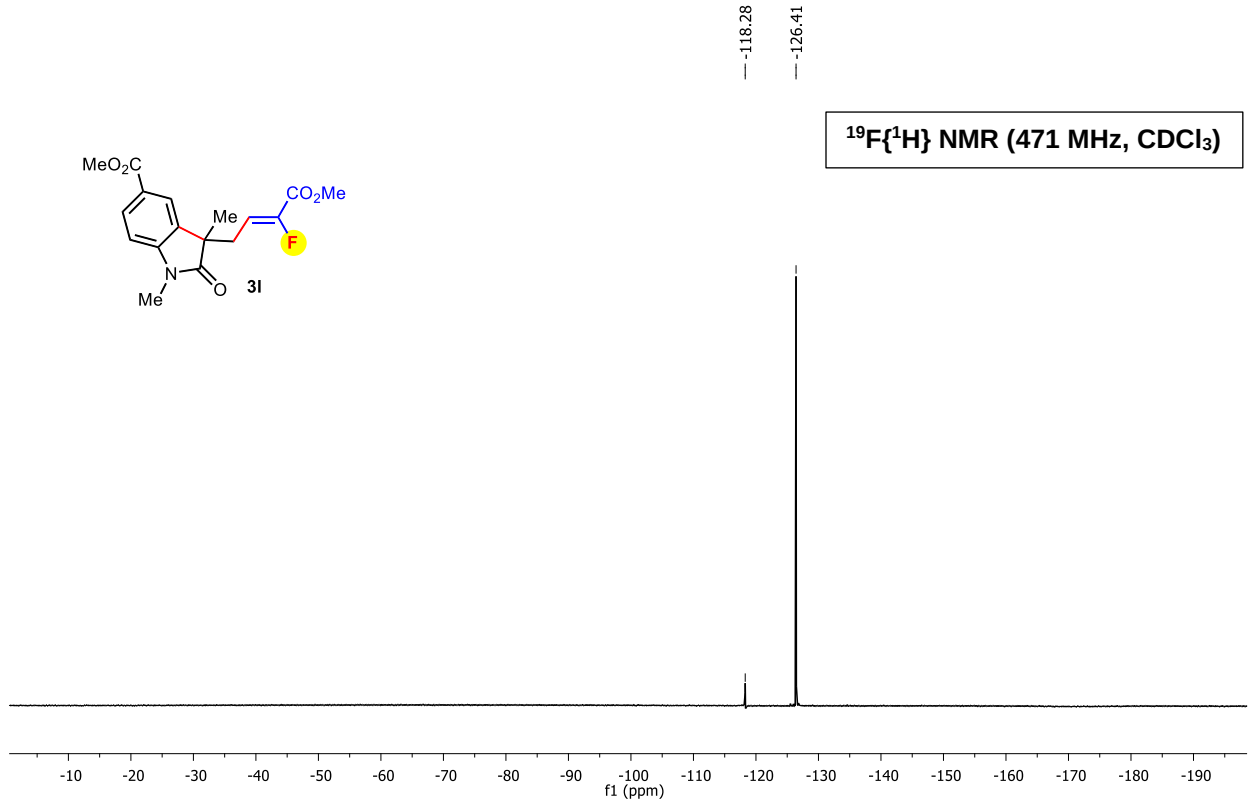


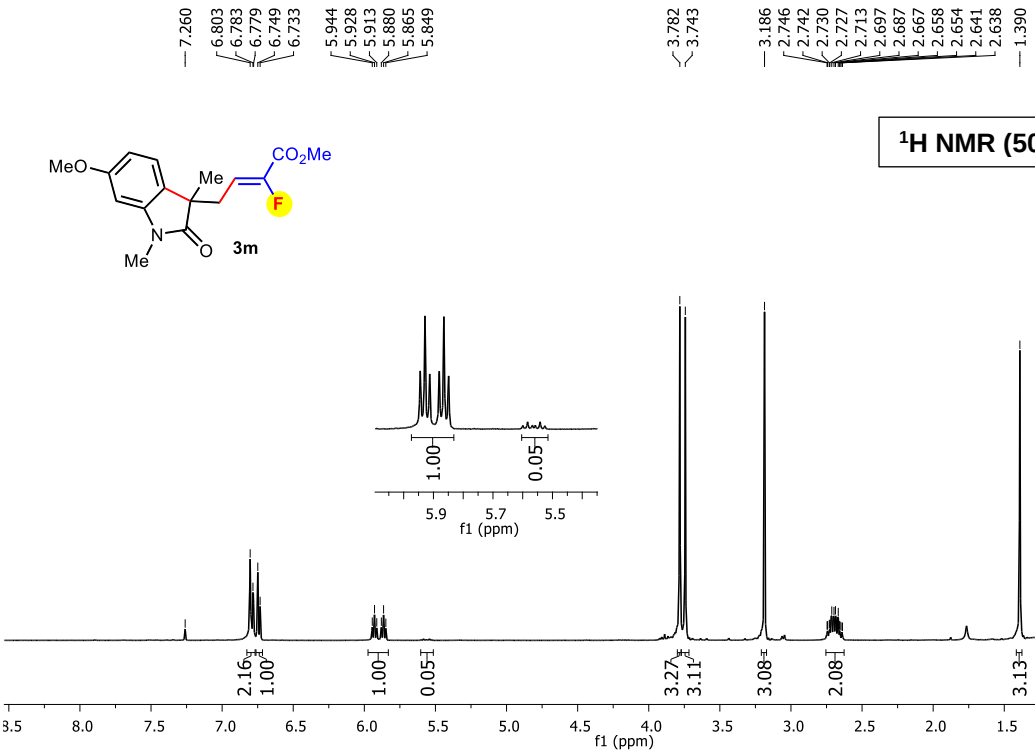
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



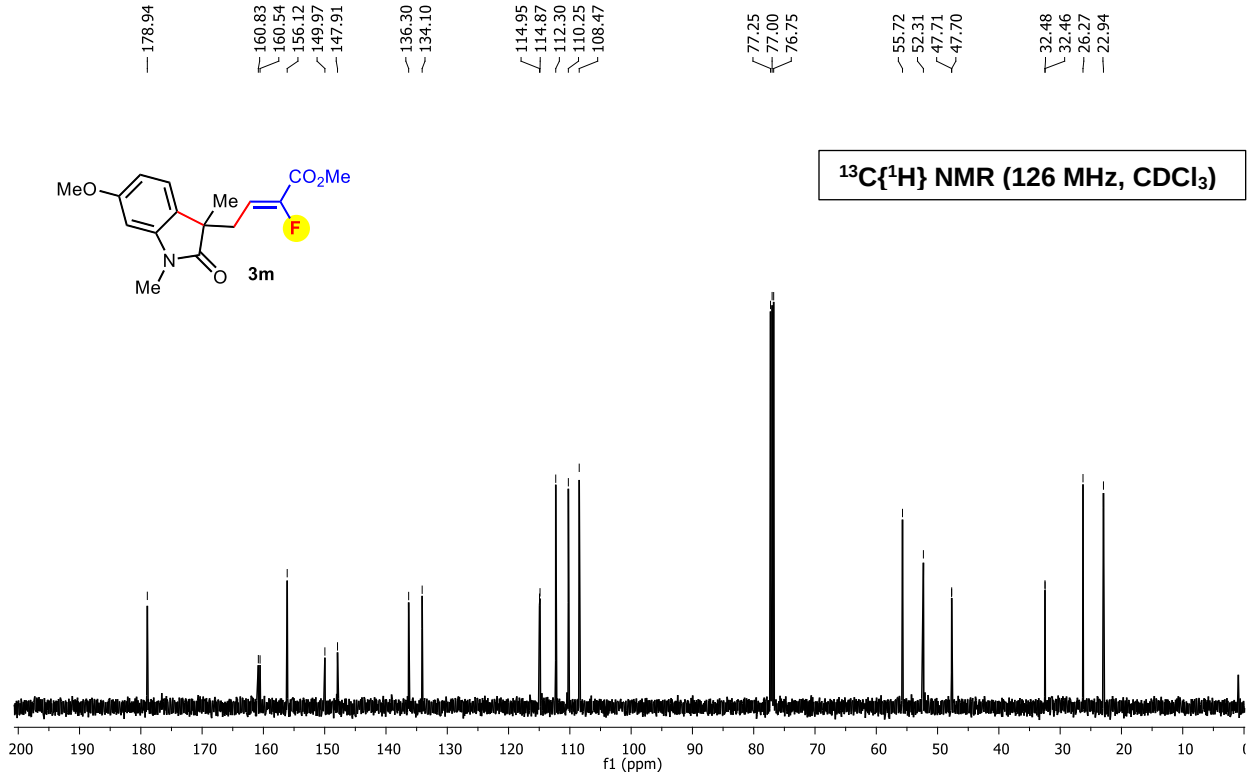
^{1}H NMR (500 MHz, $CDCl_3$)


179.55
166.68
160.73
160.45
150.17
148.10
147.00
132.72
131.03
124.73
123.91
114.29
114.20
107.78
77.25
77.00
76.74
52.39
52.03
47.21
47.19
32.40
32.39
26.44
22.84
MeO2C
CO2Me
Me
F
N
Me
O
3l
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)

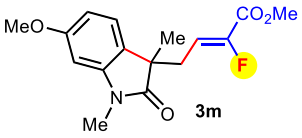

-118.28
-126.41
MeO2C
CO2Me
Me
F
N
Me
O
3l
19F{1H} NMR (471 MHz, CDCl3)
f1 (ppm)



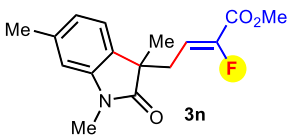
^{1}H NMR (500 MHz, $CDCl_3$)



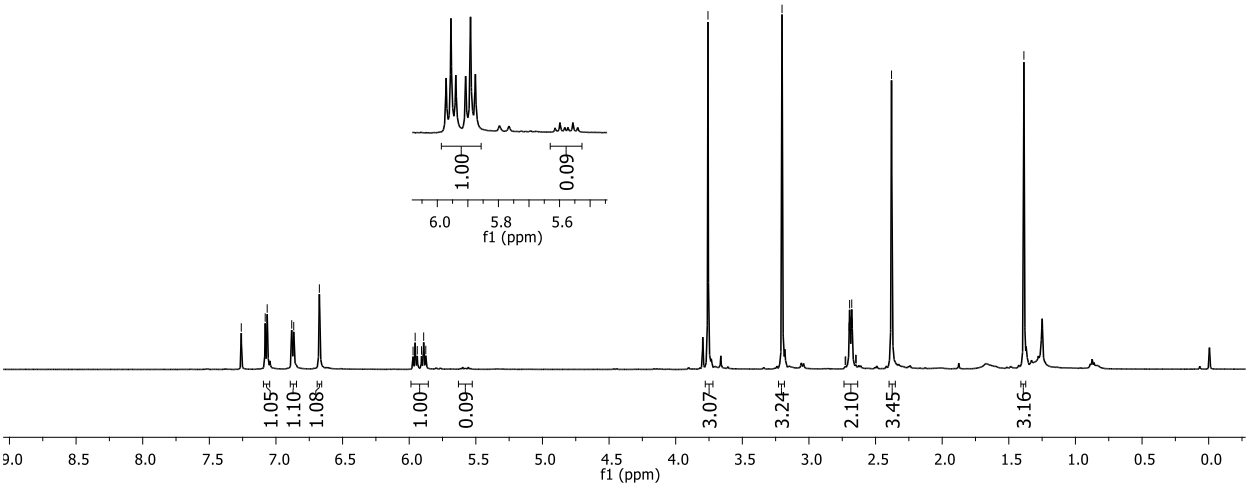
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

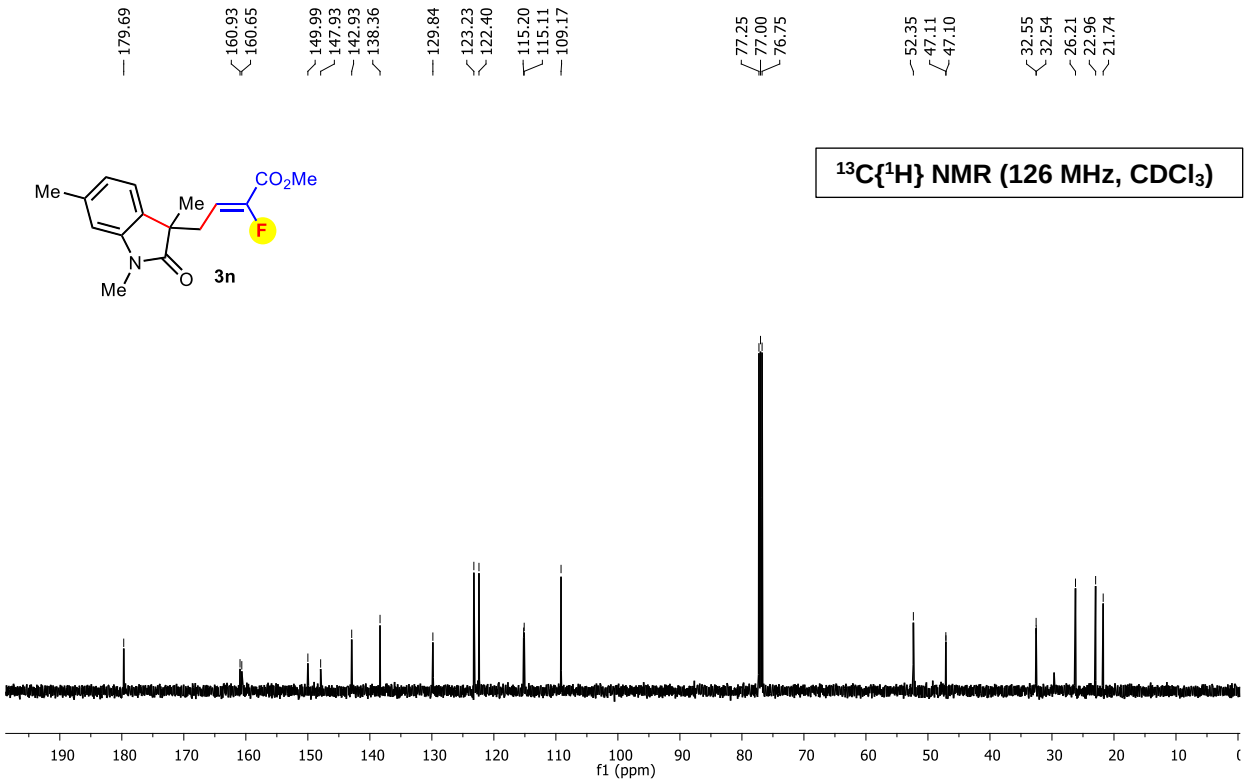


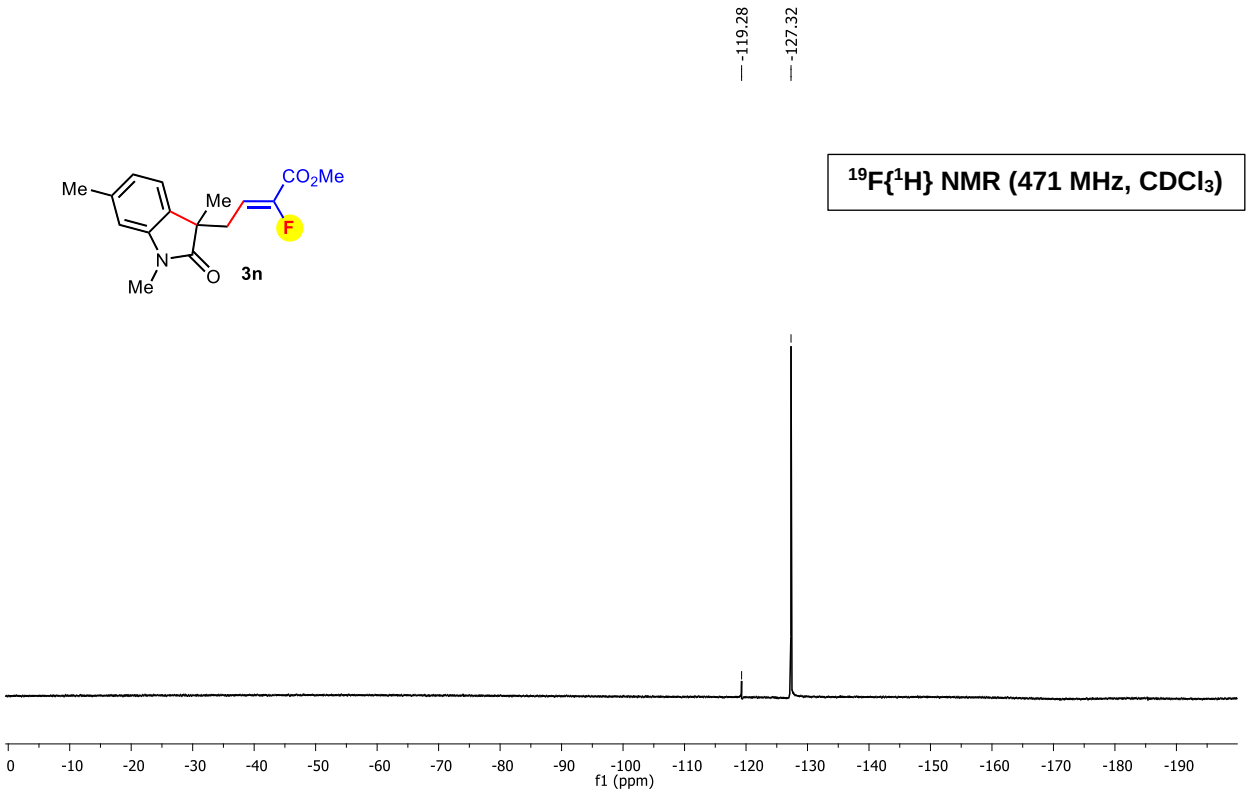
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

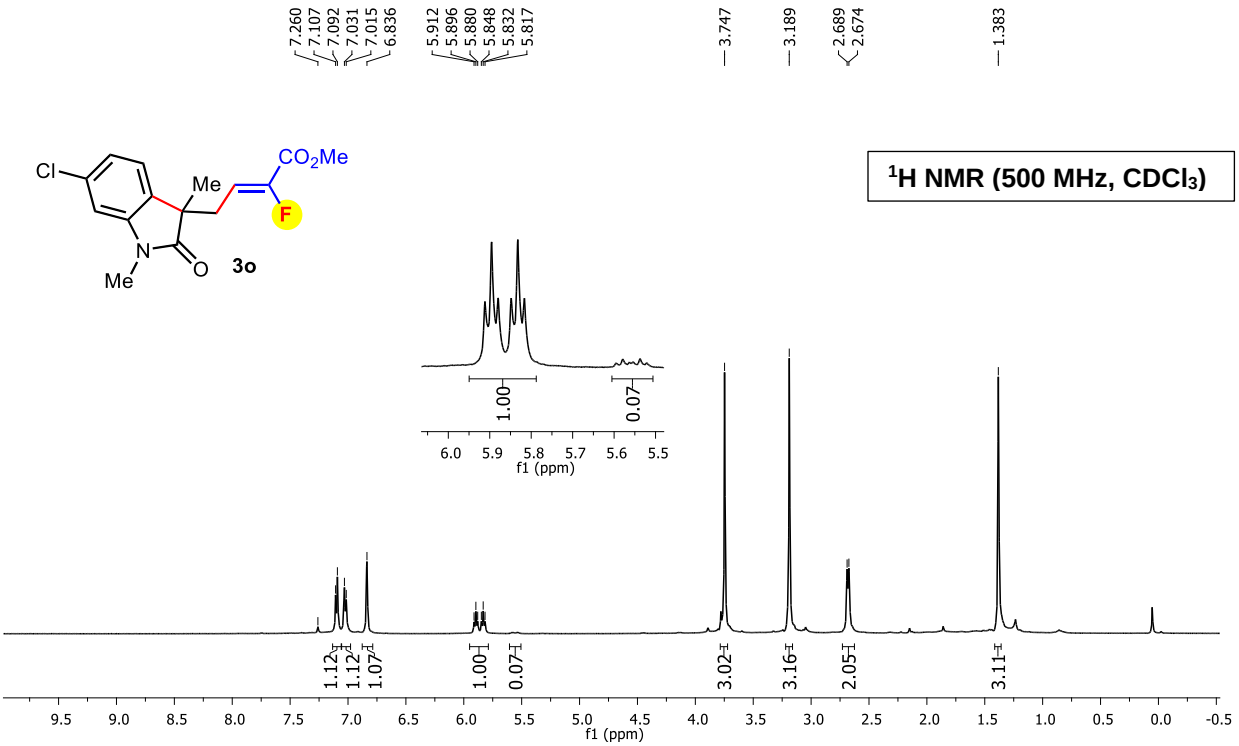


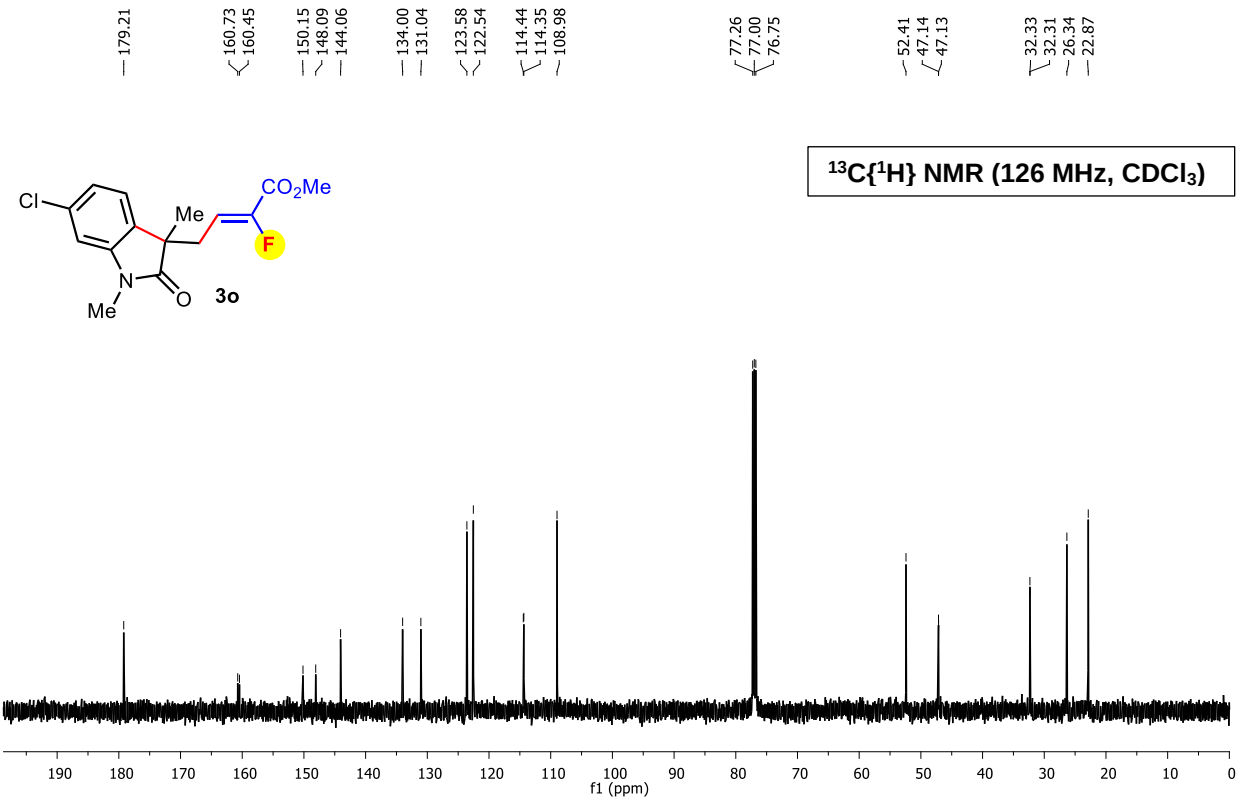
^{1}H NMR (500 MHz, $CDCl_3$)

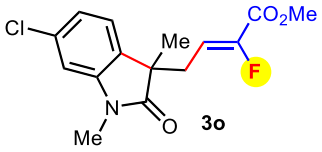



179.69
160.93
160.65
149.99
147.93
142.93
138.36
129.84
123.23
122.40
115.20
115.11
109.17
77.25
77.00
76.75
52.35
47.11
47.10
32.55
32.54
26.21
22.96
21.74
Me
Me
CO2Me
F
N
O
Me
3n
13C{1H} NMR (126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-119.28
-127.32
Me
Me
CO2Me
F
N
O
Me
3n
19F{1H} NMR (471 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

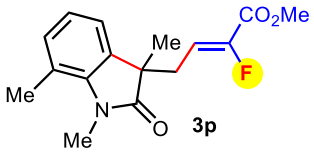

7.260
7.107
7.092
7.031
7.015
6.836
5.912
5.896
5.880
5.848
5.832
5.817
3.747
3.189
2.689
2.674
1.383
Cl
Me
CO2Me
F
N
O
Me
3o
1H NMR (500 MHz, CDCl3)
1.00
0.07
6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
1.12
1.12
1.07
1.00
0.07
3.02
3.16
2.05
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.21
160.73
160.45
150.15
148.09
144.06
134.00
131.04
123.58
122.54
114.44
114.35
108.98
77.26
77.00
76.75
52.41
47.14
47.13
32.33
32.31
26.34
22.87
Cl
Me
CO2Me
F
N
O
Me
3o
13C{1H} NMR (126 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



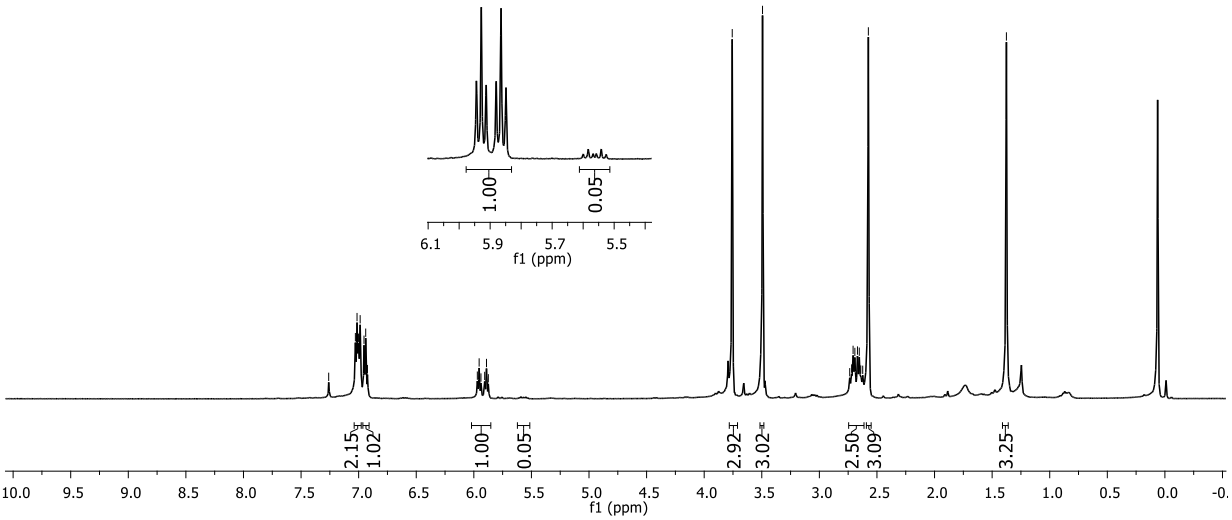
3o

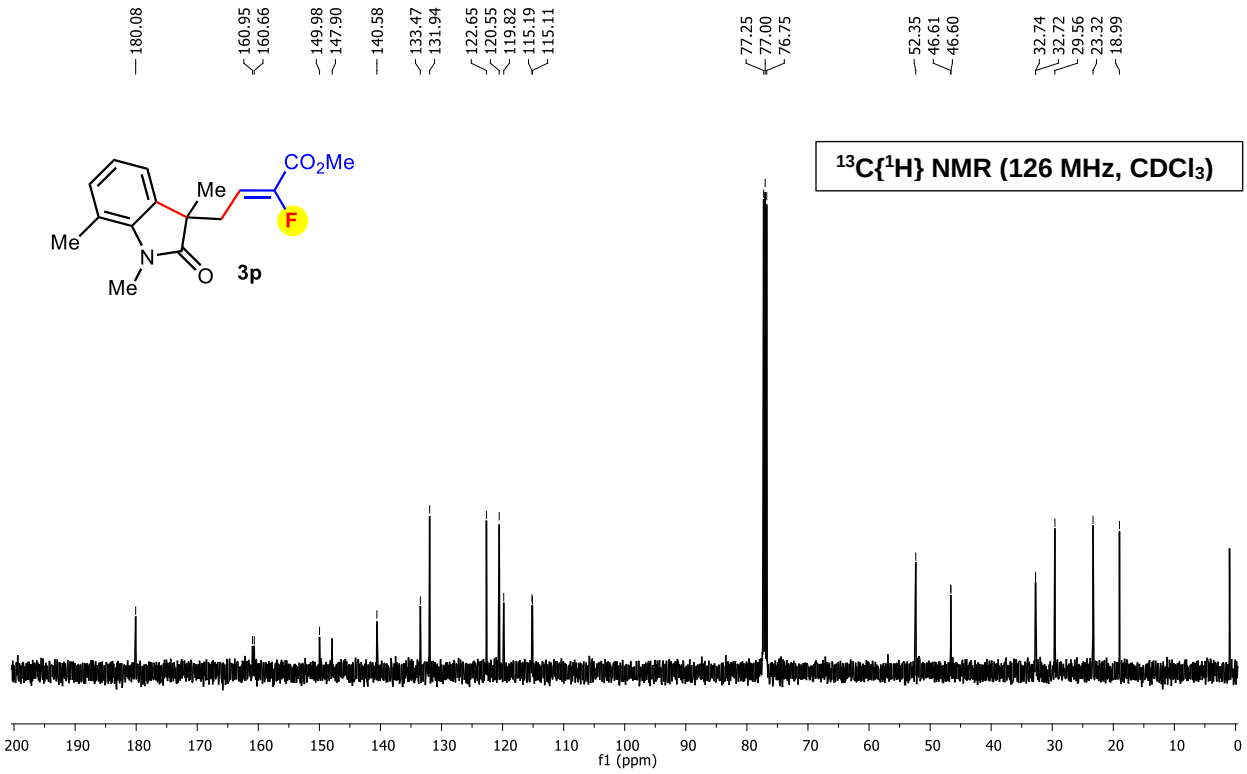
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

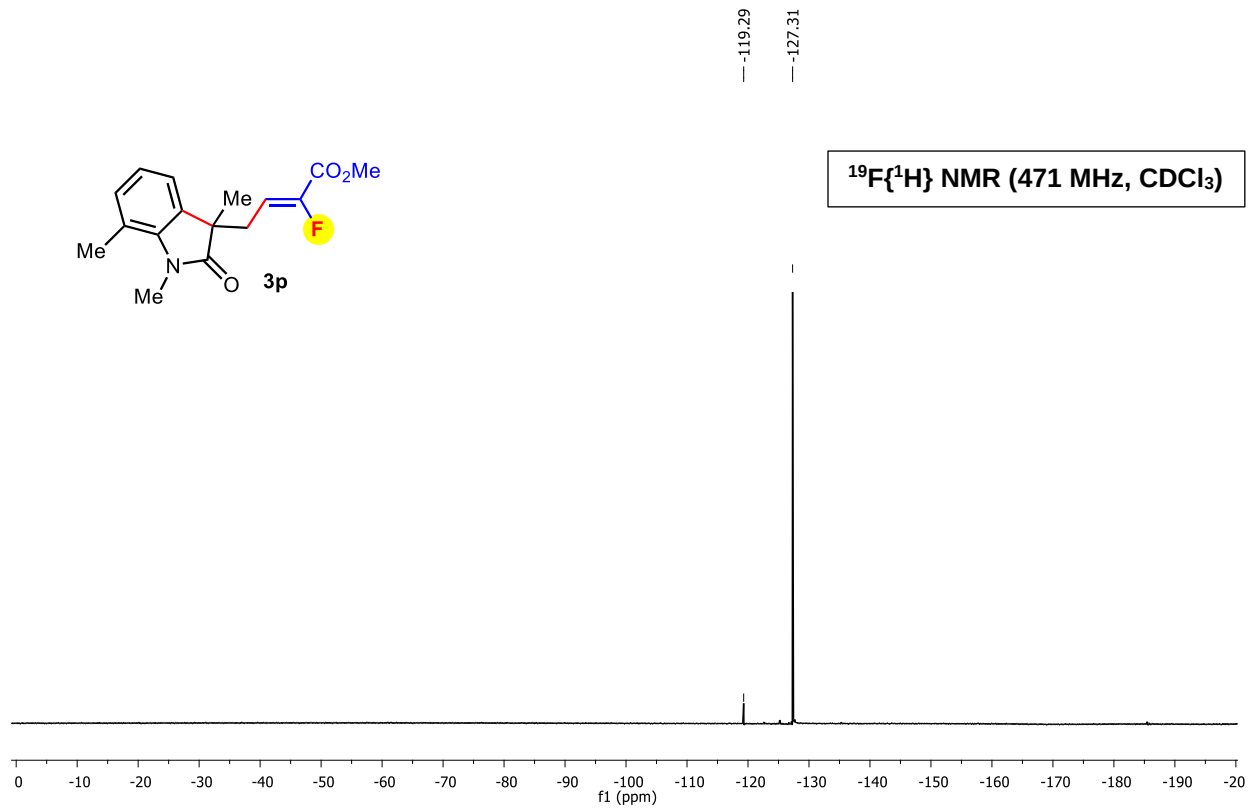


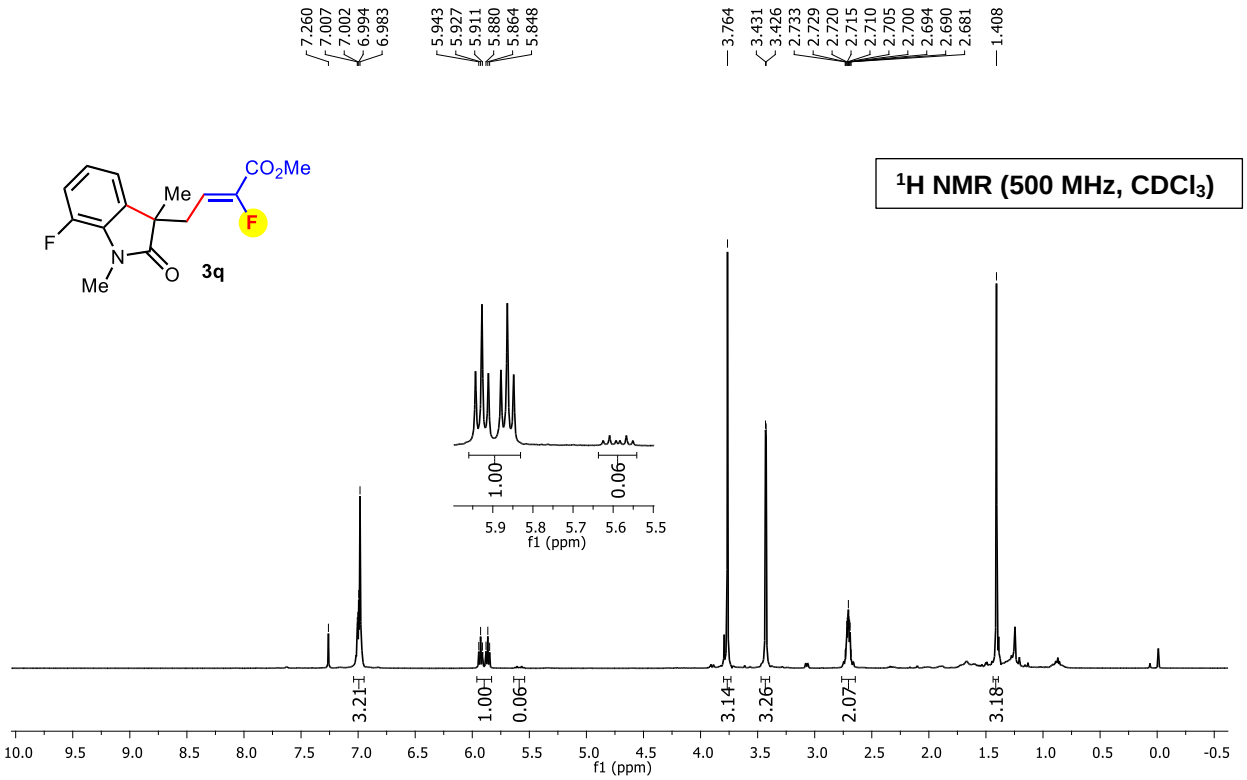
3p

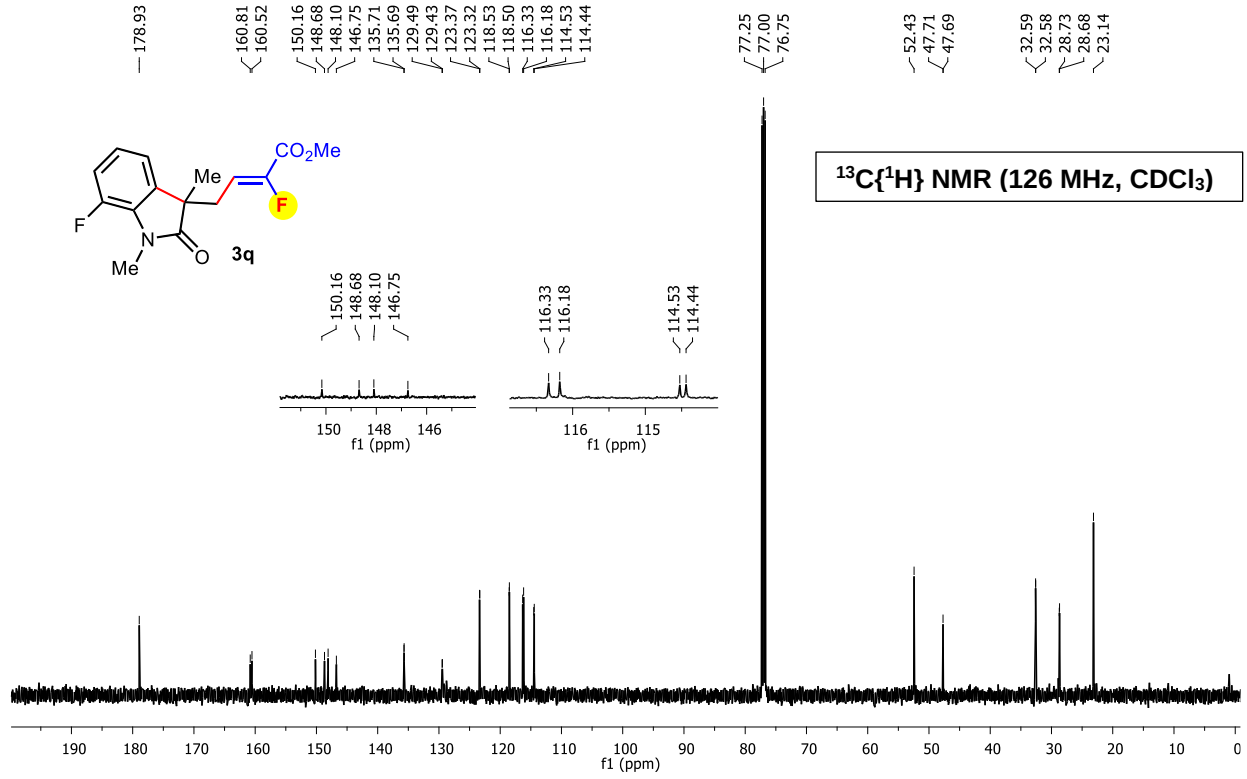
^{1}H NMR (500 MHz, $CDCl_3$)

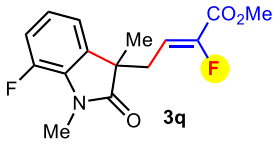



180.08
160.95
160.66
149.98
147.90
140.58
133.47
131.94
122.65
120.55
119.82
115.19
115.11
77.25
77.00
76.75
52.35
46.61
46.60
32.74
32.72
29.56
23.32
18.99
CO2Me
Me
F
Me
N
Me
O
3p
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)


-119.29
-127.31
CO2Me
Me
F
Me
N
Me
O
3p
19F{1H} NMR (471 MHz, CDCl3)
f1 (ppm)

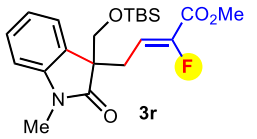

7.260
7.007
7.002
6.994
6.983
5.943
5.927
5.911
5.880
5.864
5.848
3.764
3.431
3.426
2.733
2.729
2.720
2.715
2.710
2.705
2.700
2.694
2.690
2.681
1.408
CO2Me
Me
F
N
O
Me
3q
1H NMR (500 MHz, CDCl3)
1.00
0.06
5.9 5.8 5.7 5.6 5.5
f1 (ppm)
3.21
1.00
0.06
3.14
3.26
2.07
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


178.93
160.81
160.52
150.16
148.68
148.10
146.75
135.71
135.69
129.49
129.43
123.37
123.32
118.53
118.50
116.33
116.18
114.53
114.44
77.25
77.00
76.75
52.43
47.71
47.69
32.59
32.58
28.73
28.68
23.14
CO2Me
Me
F
N
O
Me
3q
13C{1H} NMR (126 MHz, CDCl3)
150.16
148.68
148.10
146.75
116.33
116.18
114.53
114.44
150 148 146
f1 (ppm)
116 115
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



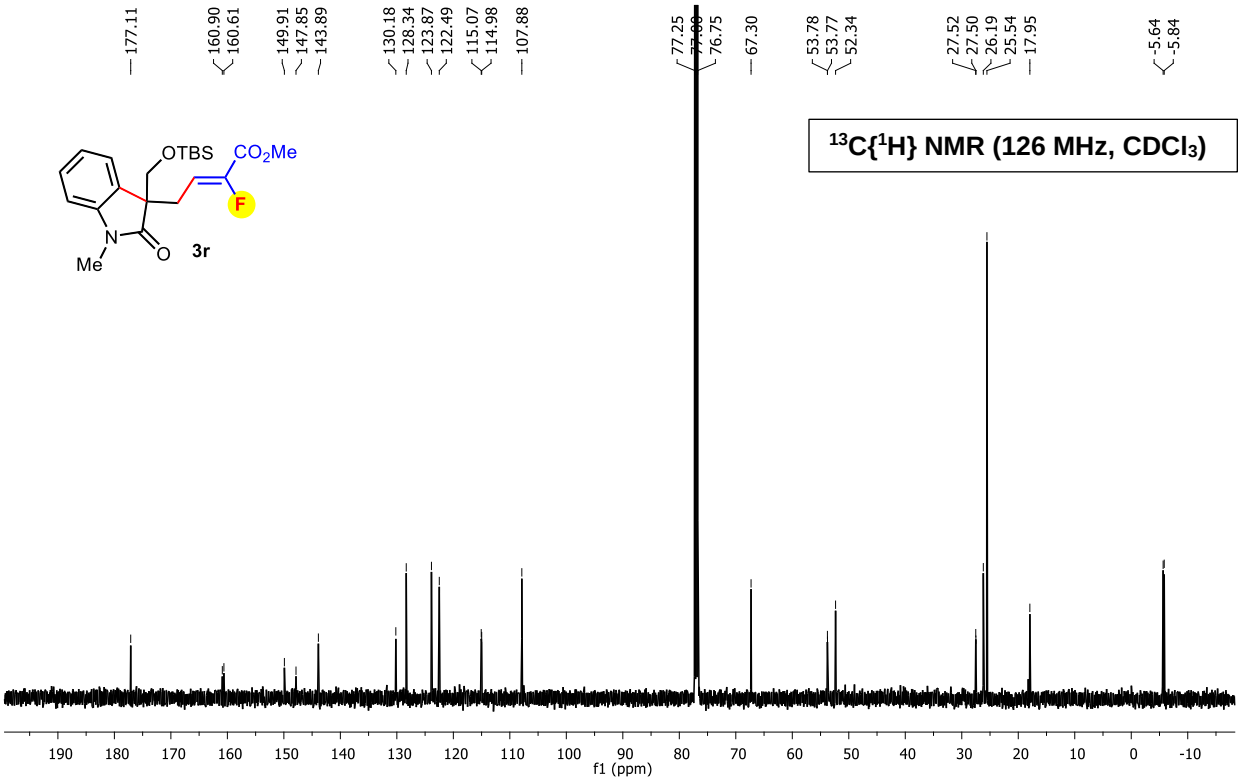
3q

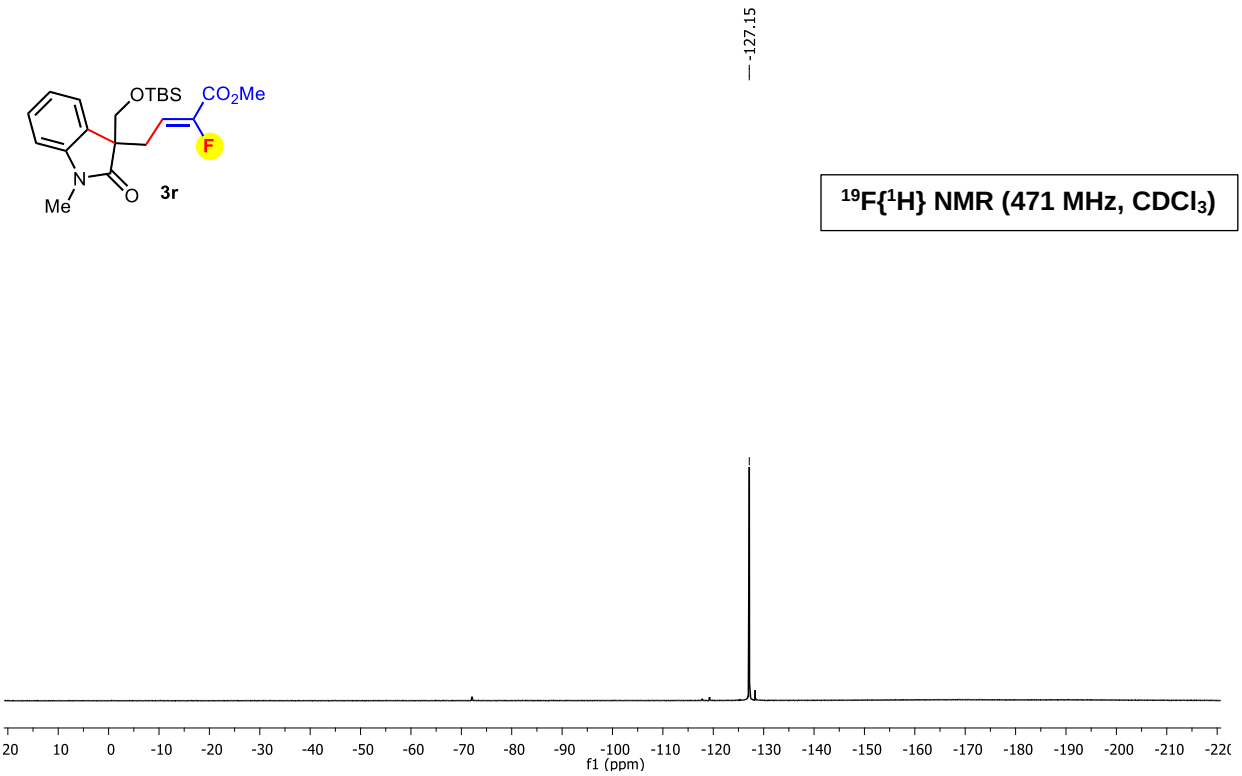
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

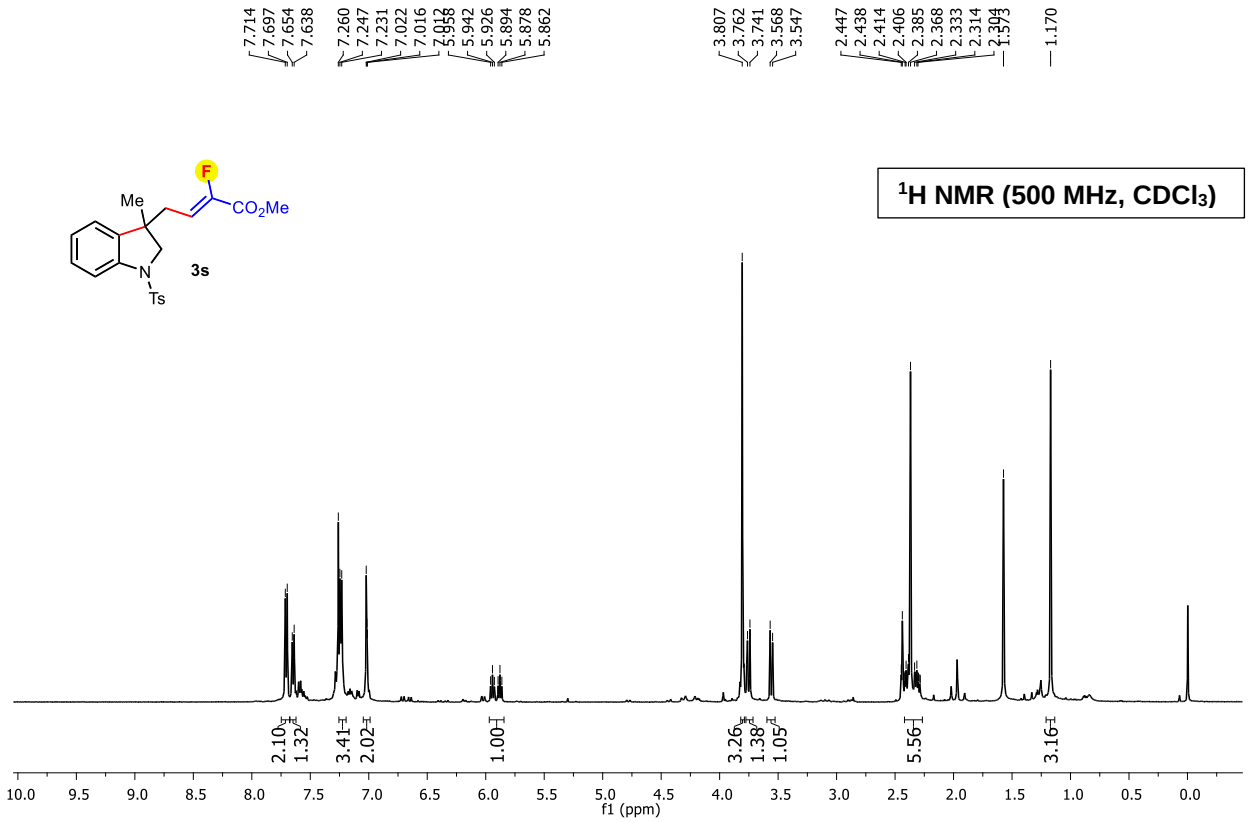


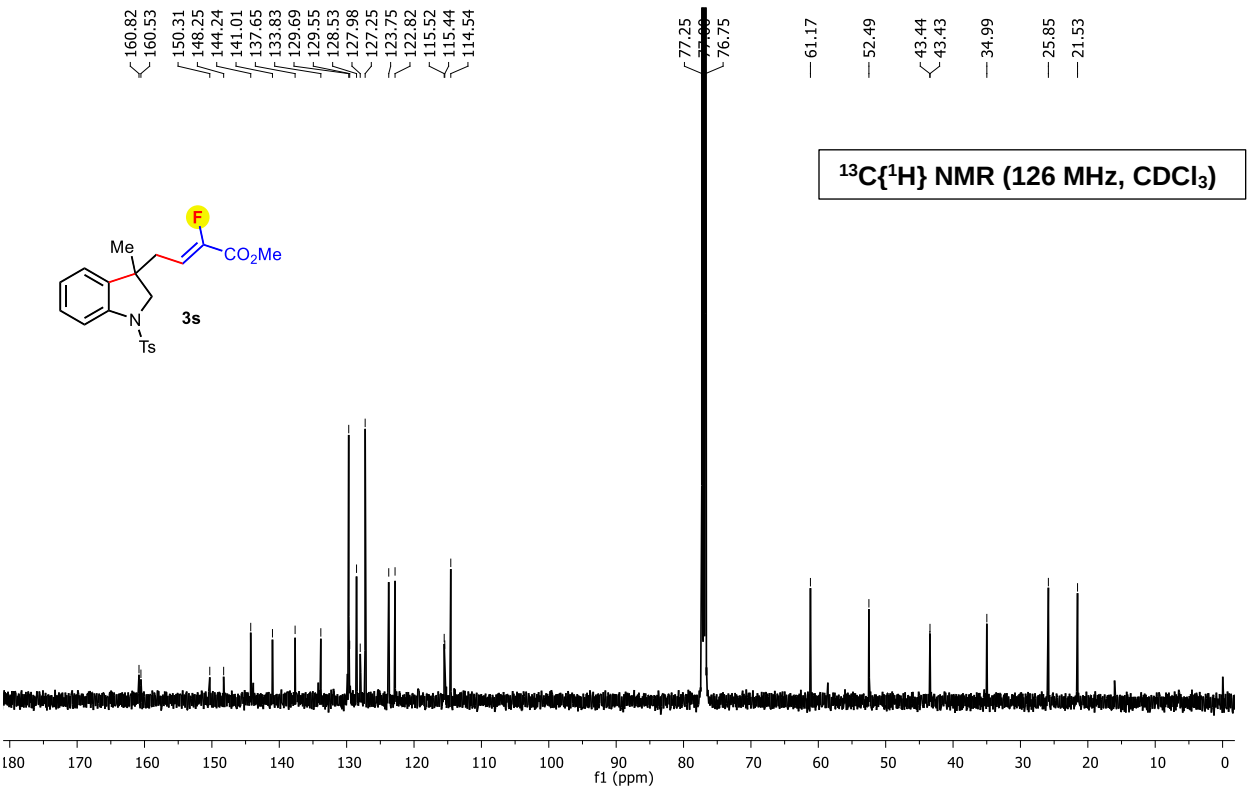
3r

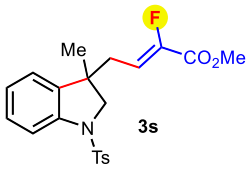
^{1}H NMR (500 MHz, $CDCl_3$)


177.11
160.90
160.61
149.91
147.85
143.89
130.18
128.34
123.87
122.49
115.07
114.98
107.88
77.25
77.00
76.75
67.30
53.78
53.77
52.34
27.52
27.50
26.19
25.54
17.95
-5.64
-5.84
OTBS
CO2Me
F
N
Me
O
3r
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)


-127.15
OTBS
CO2Me
F
N
Me
O
3r
19F{1H} NMR (471 MHz, CDCl3)
f1 (ppm)

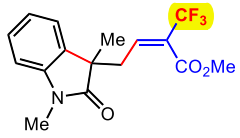

7.714
7.697
7.654
7.638
7.260
7.247
7.231
7.022
7.016
5.958
5.942
5.926
5.894
5.878
5.862
3.807
3.762
3.741
3.568
3.547
2.447
2.438
2.414
2.406
2.385
2.368
2.333
2.314
1.573
1.170
F
Me
CO2Me
N
Ts
3s
1H NMR (500 MHz, CDCl3)
2.10
1.32
3.41
2.02
1.00
3.26
1.38
1.05
5.56
3.16
f1 (ppm)


160.82
160.53
150.31
148.25
144.24
141.01
137.65
133.83
129.69
129.55
128.53
127.98
127.25
123.75
122.82
115.52
115.44
114.54
77.25
76.75
61.17
52.49
43.44
43.43
34.99
25.85
21.53
F
Me
CO2Me
N
Ts
3s
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)



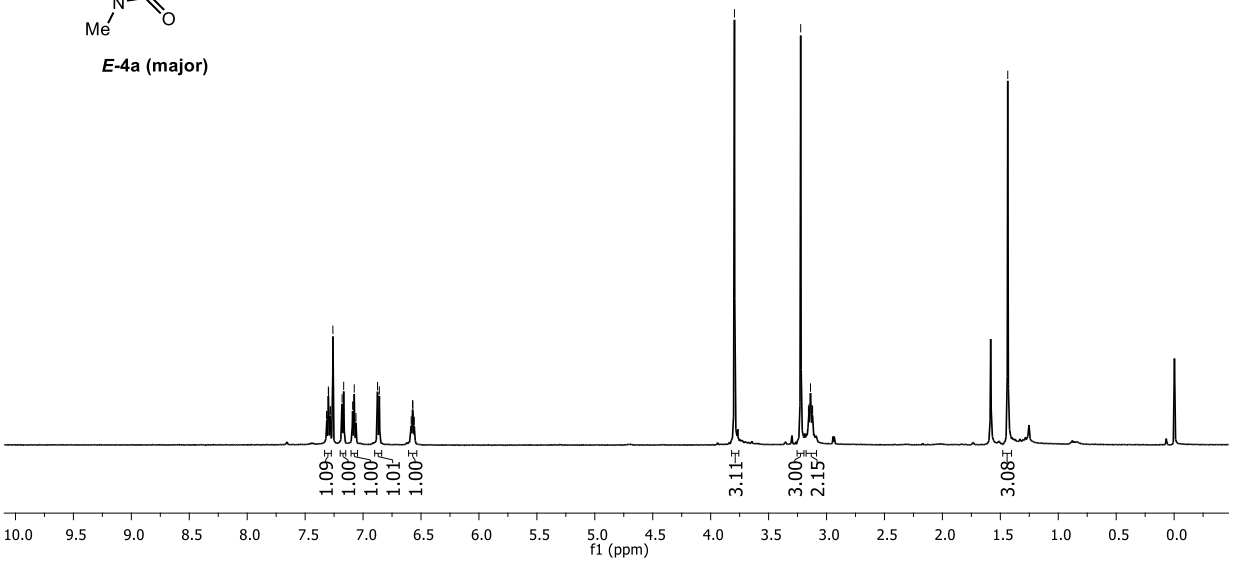
3s

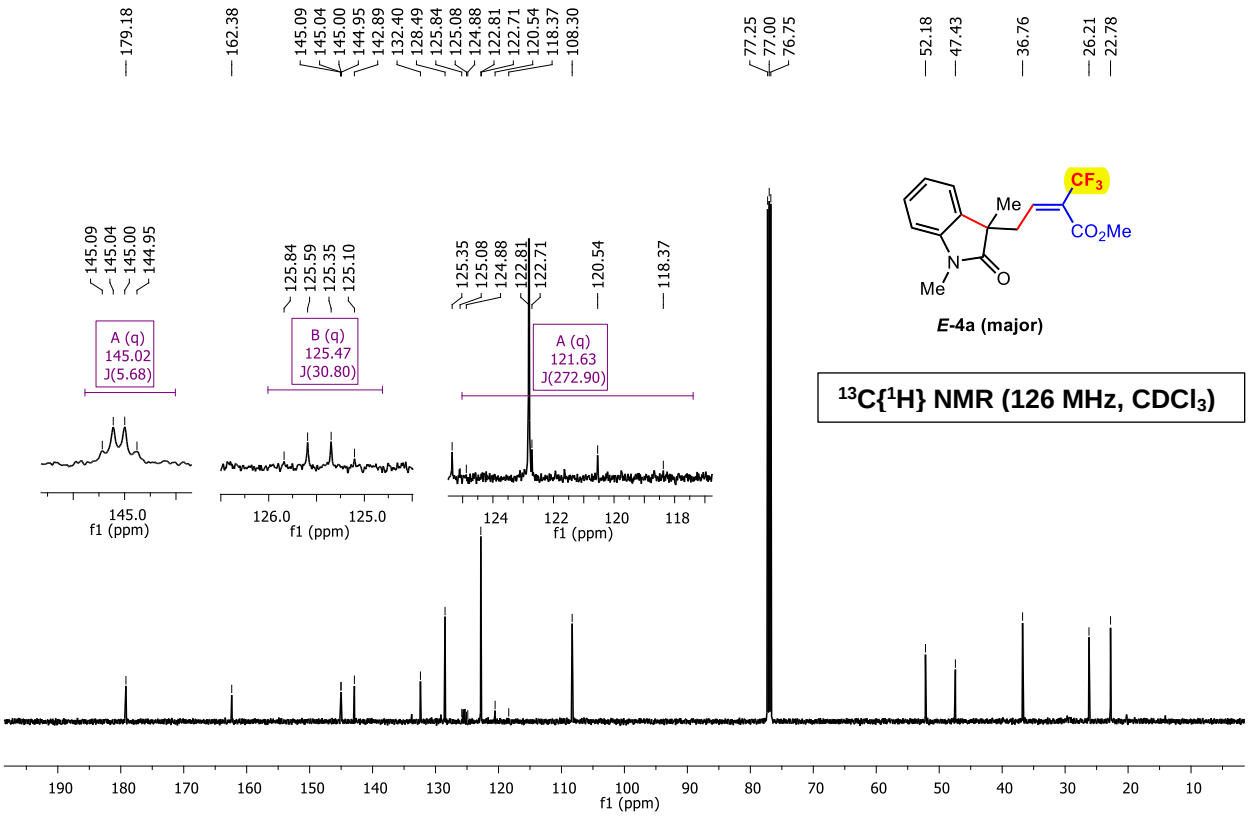
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

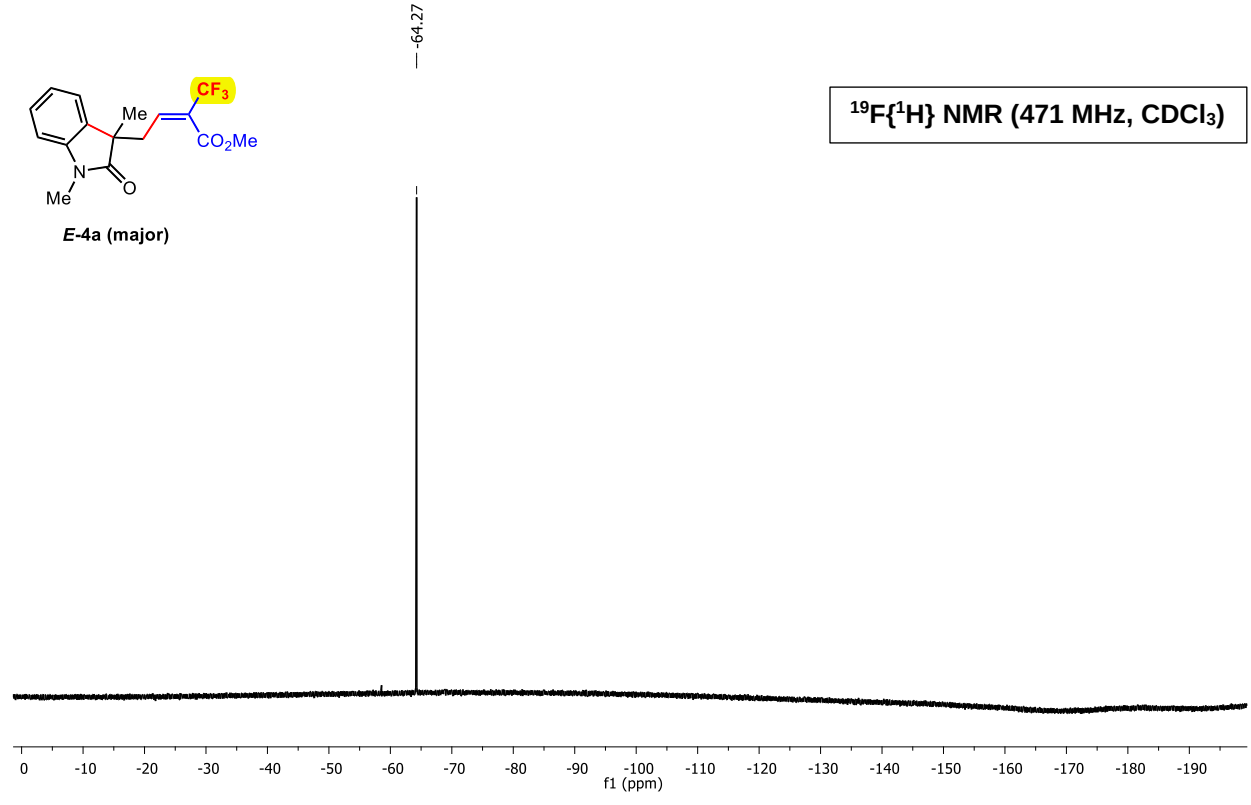


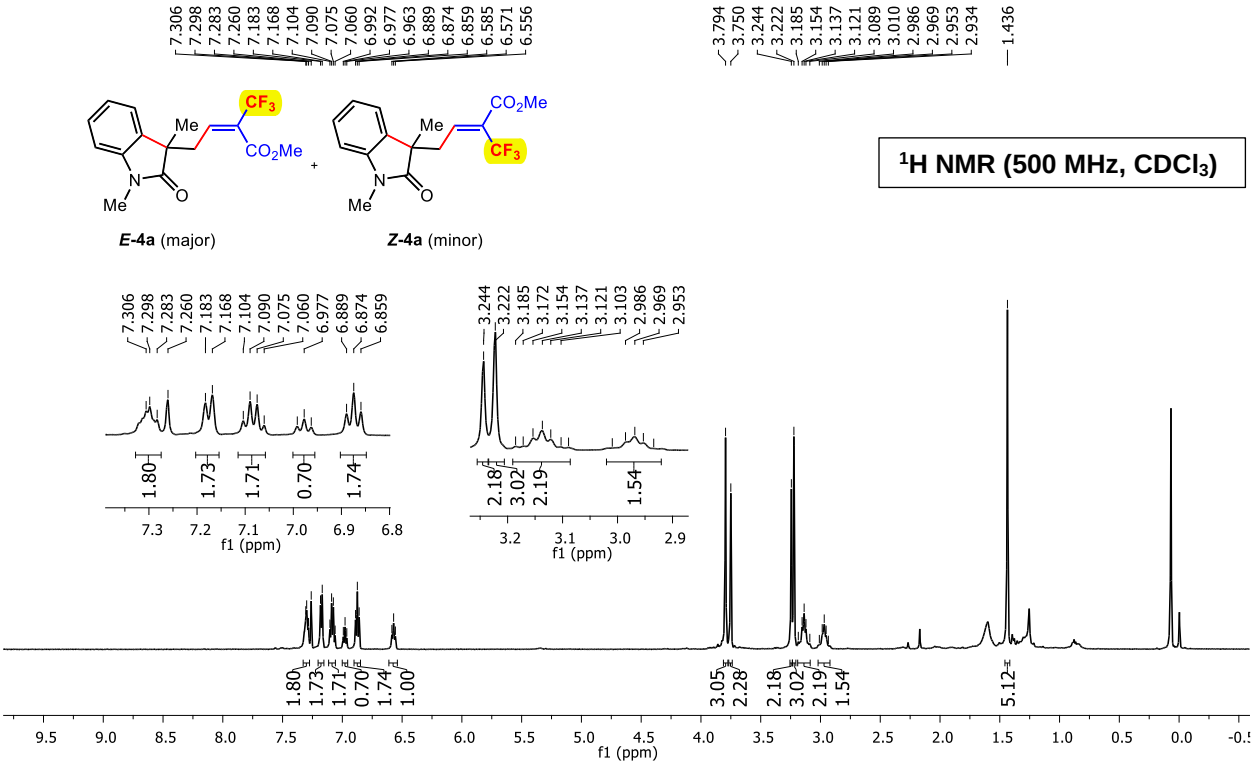
***E*-4a (major)**

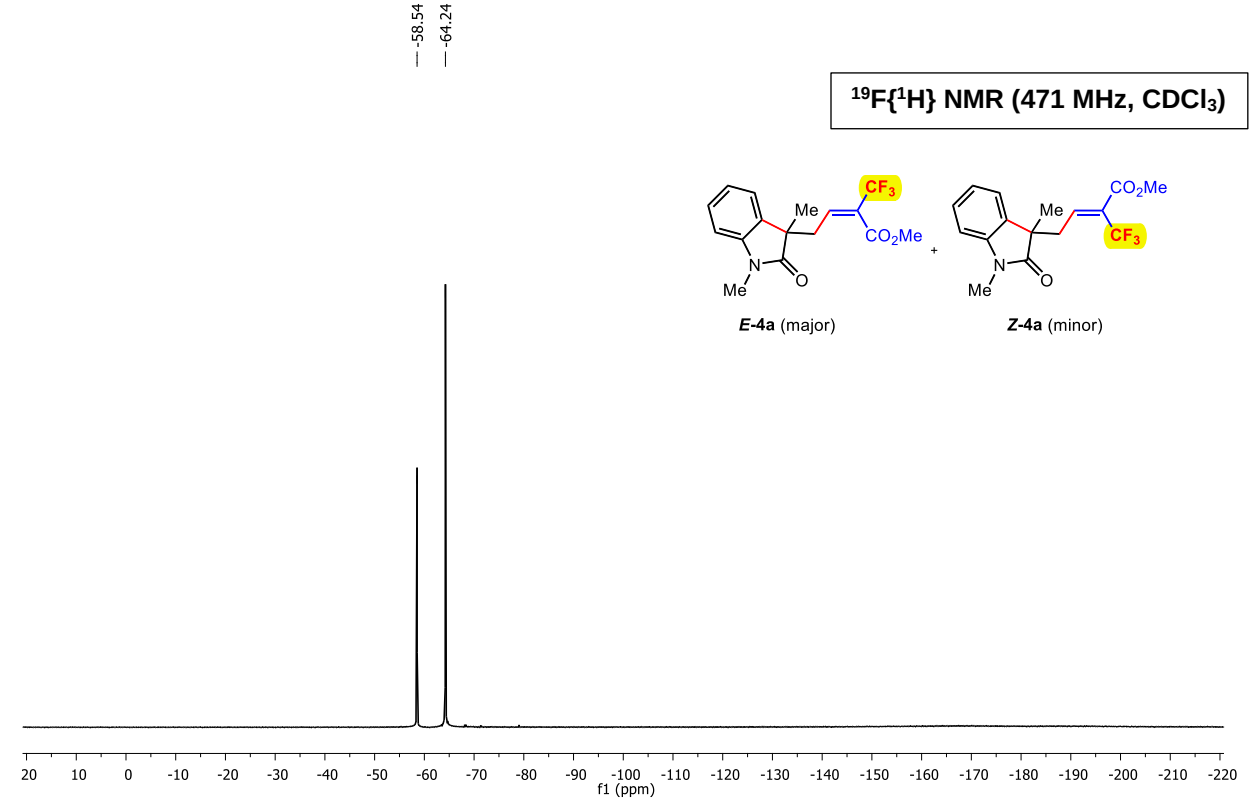
^{1}H NMR (500 MHz, $CDCl_3$)

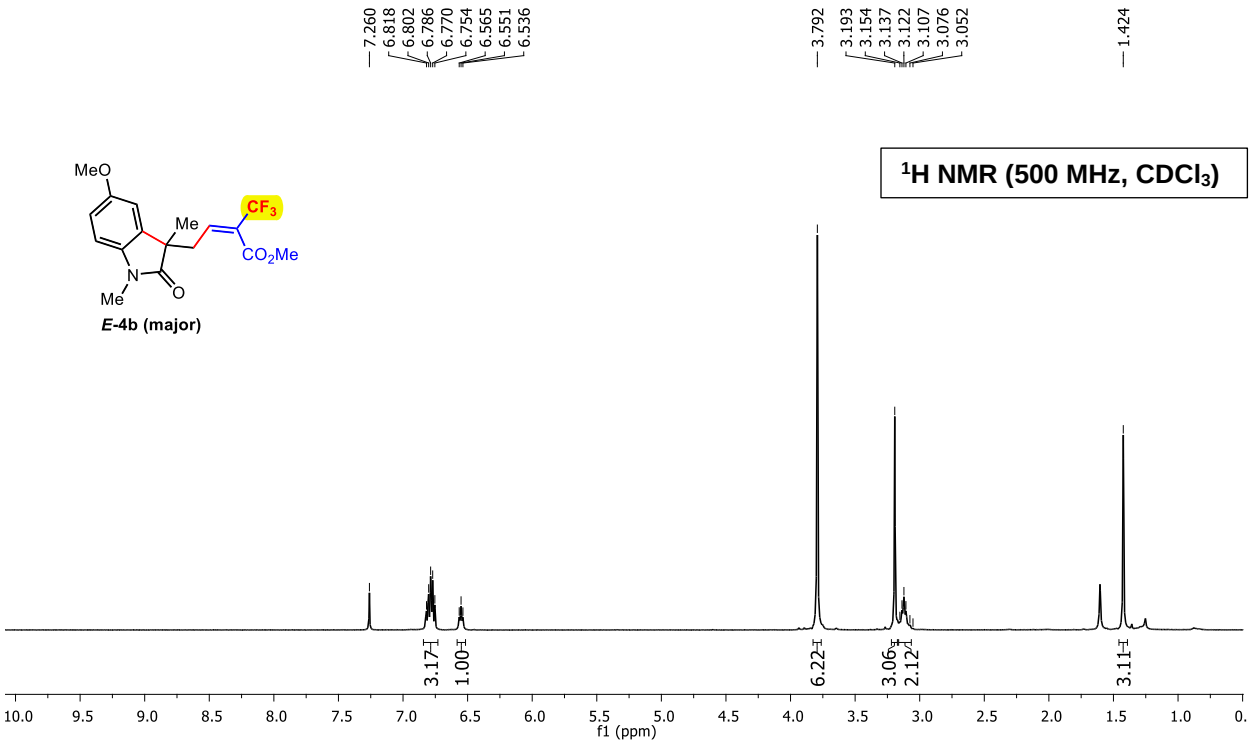


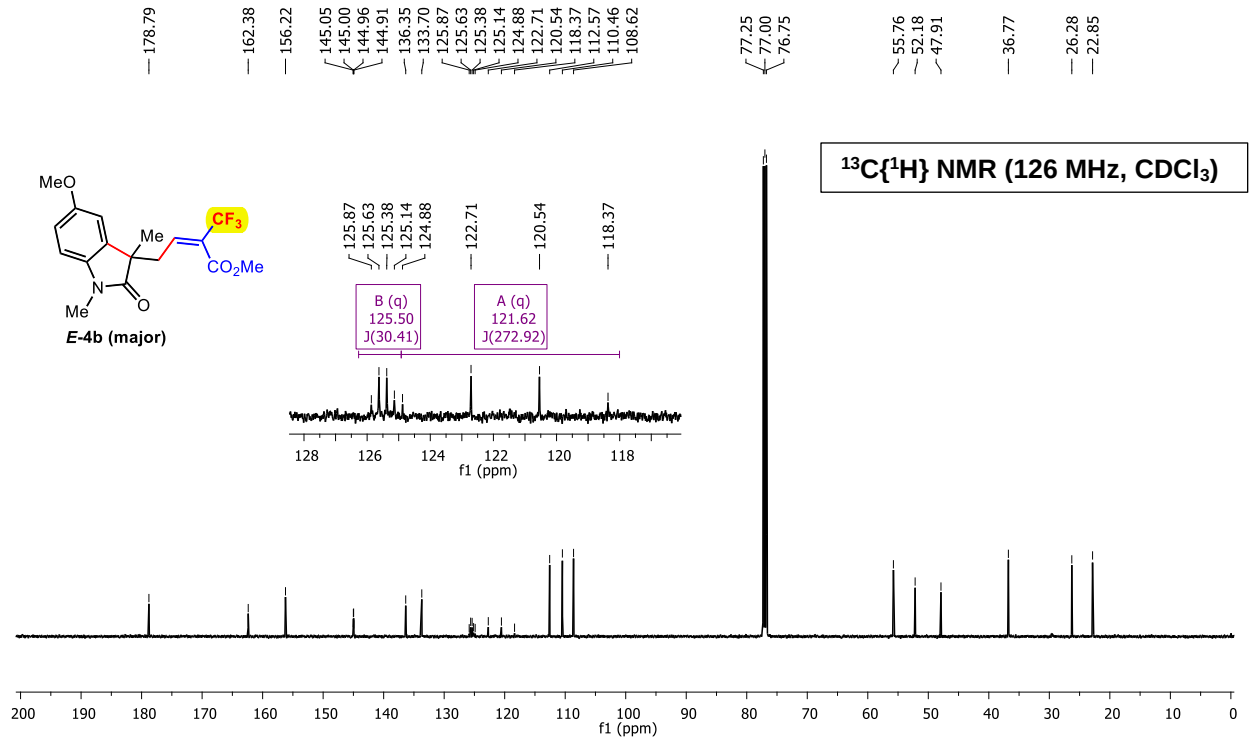

179.18
162.38
145.09
145.04
145.00
144.95
142.89
132.40
128.49
125.84
125.08
124.88
122.81
122.71
120.54
118.37
108.30
77.25
77.00
76.75
52.18
47.43
36.76
26.21
22.78
A (q)
145.02
J(5.68)
B (q)
125.47
J(30.80)
A (q)
121.63
J(272.90)
CF3
Me
CO2Me
N
O
Me
E-4a (major)
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)

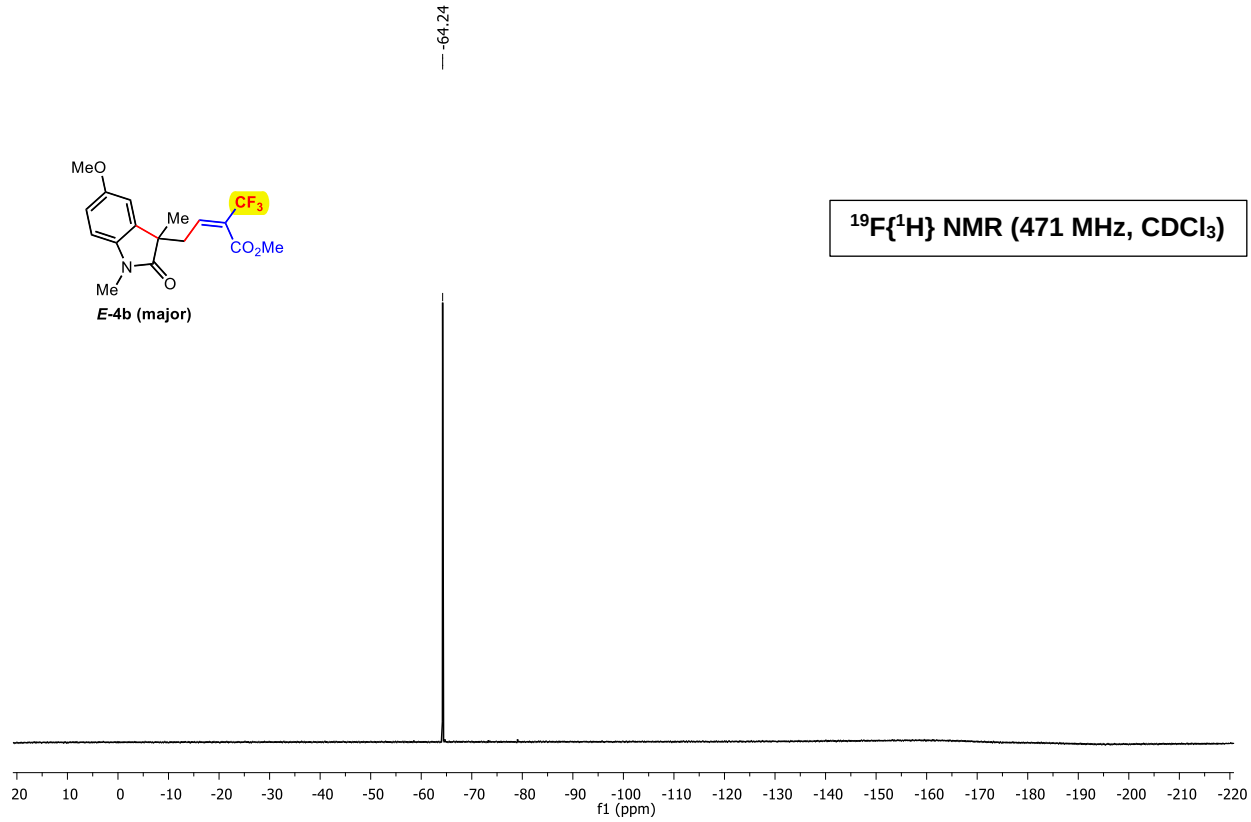

-64.27
CF3
Me
CO2Me
N
O
Me
E-4a (major)
19F{1H} NMR (471 MHz, CDCl3)
f1 (ppm)

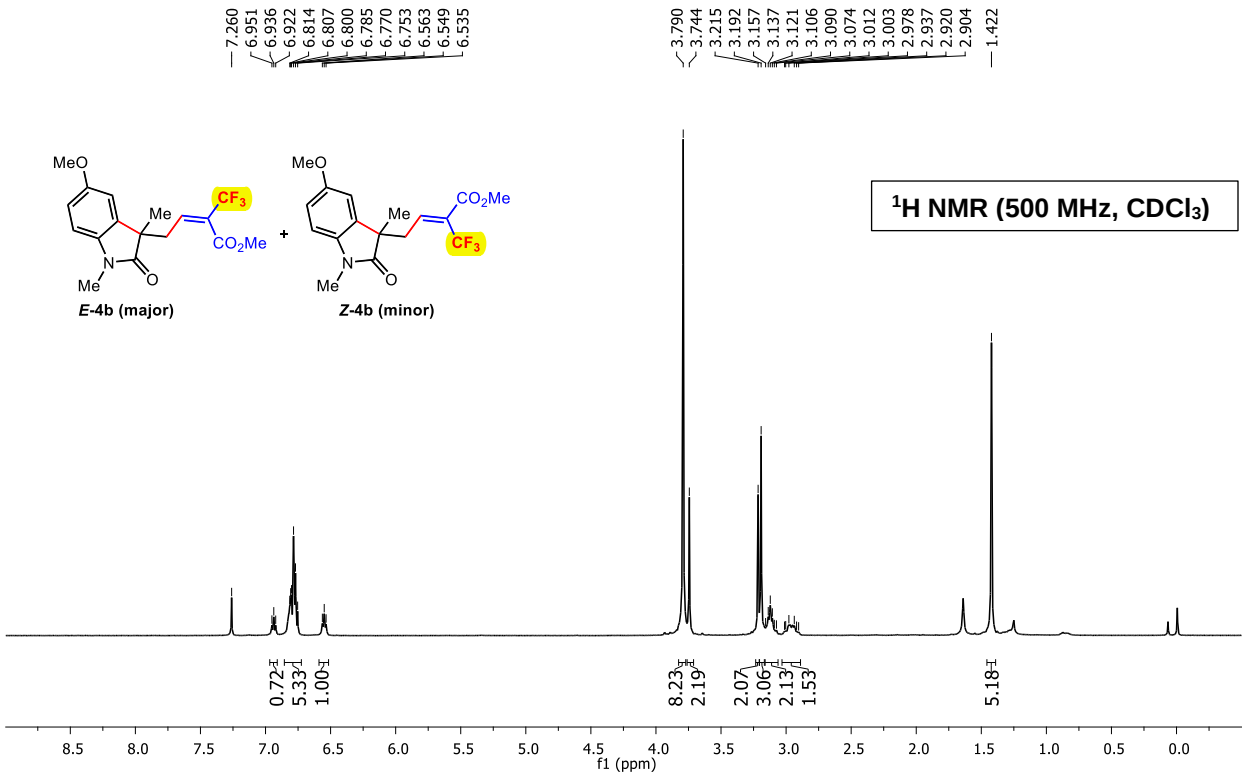

7.306
7.298
7.283
7.260
7.183
7.168
7.104
7.090
7.075
7.060
6.992
6.977
6.963
6.889
6.874
6.859
6.585
6.571
6.556
3.794
3.750
3.244
3.222
3.185
3.154
3.137
3.121
3.089
3.010
2.986
2.969
2.953
2.934
1.436
CF3
Me
CO2Me
N
O
Me
+
CO2Me
Me
CF3
N
O
Me
E-4a (major)
Z-4a (minor)
1H NMR (500 MHz, CDCl3)
1.80
1.73
1.71
0.70
1.74
2.18
3.02
2.19
1.54
f1 (ppm)
1.80
1.73
1.71
0.70
1.74
1.00
3.05
2.28
2.18
3.02
2.19
1.54
5.12
f1 (ppm)

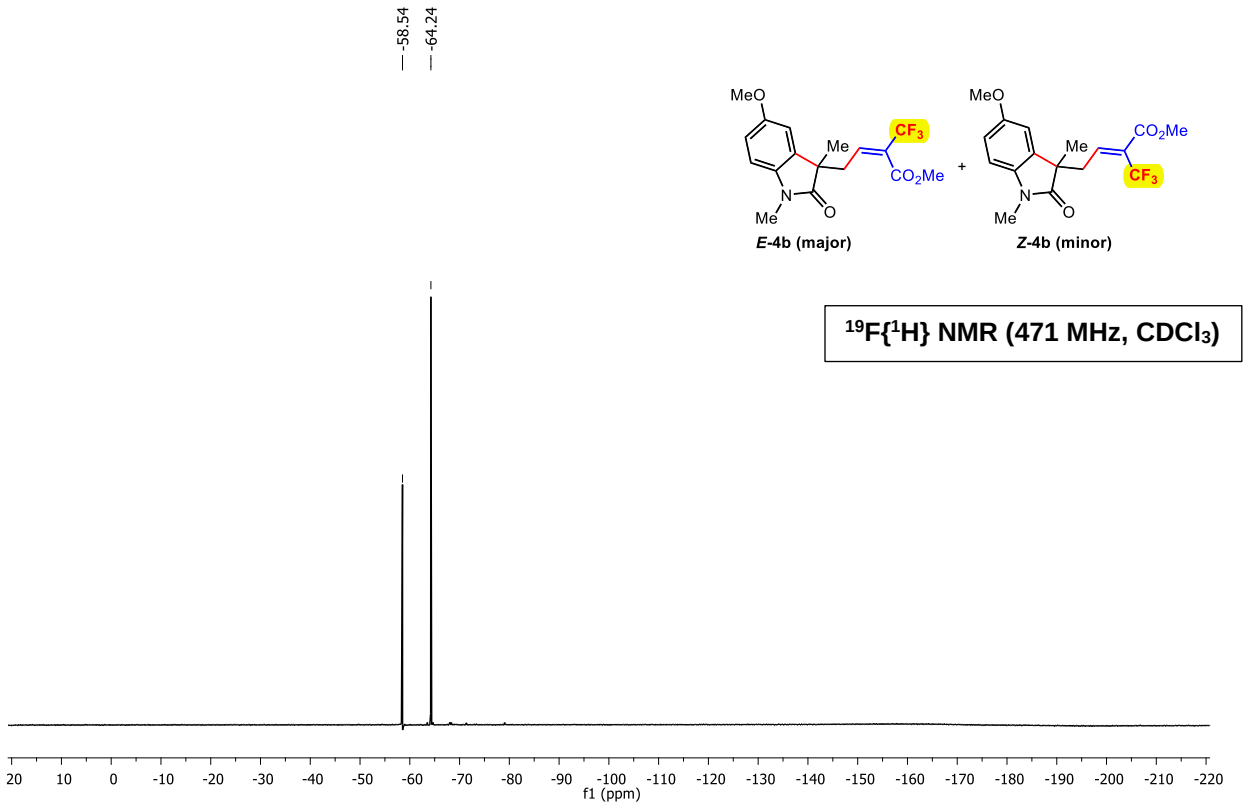

-58.54
-64.24
19F{1H} NMR (471 MHz, CDCl3)
CF3
Me
CO2Me
N
O
Me
+
CO2Me
Me
CF3
N
O
Me
E-4a (major)
Z-4a (minor)
f1 (ppm)

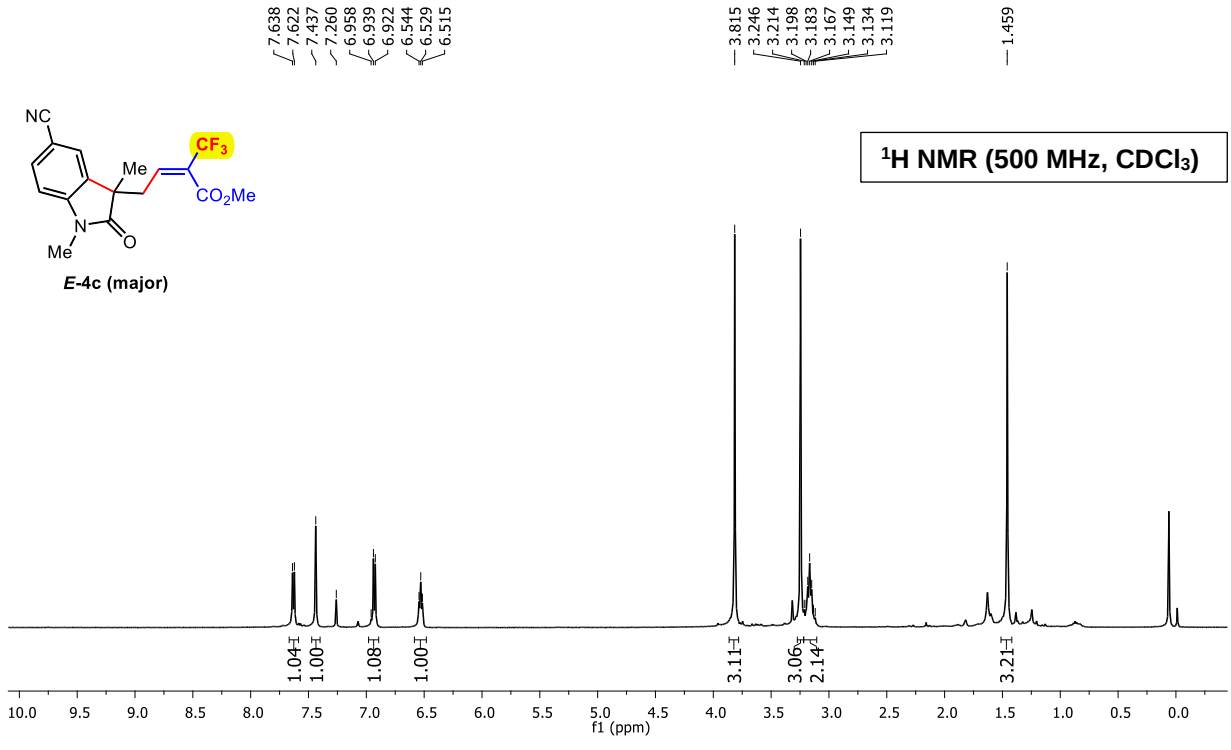

7.260
6.818
6.802
6.786
6.770
6.754
6.565
6.551
6.536
3.792
3.193
3.154
3.137
3.122
3.107
3.076
3.052
1.424
MeO
Me
CF3
CO2Me
N
O
Me
E-4b (major)
1H NMR (500 MHz, CDCl3)
3.17
1.00
6.22
3.06
2.12
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)

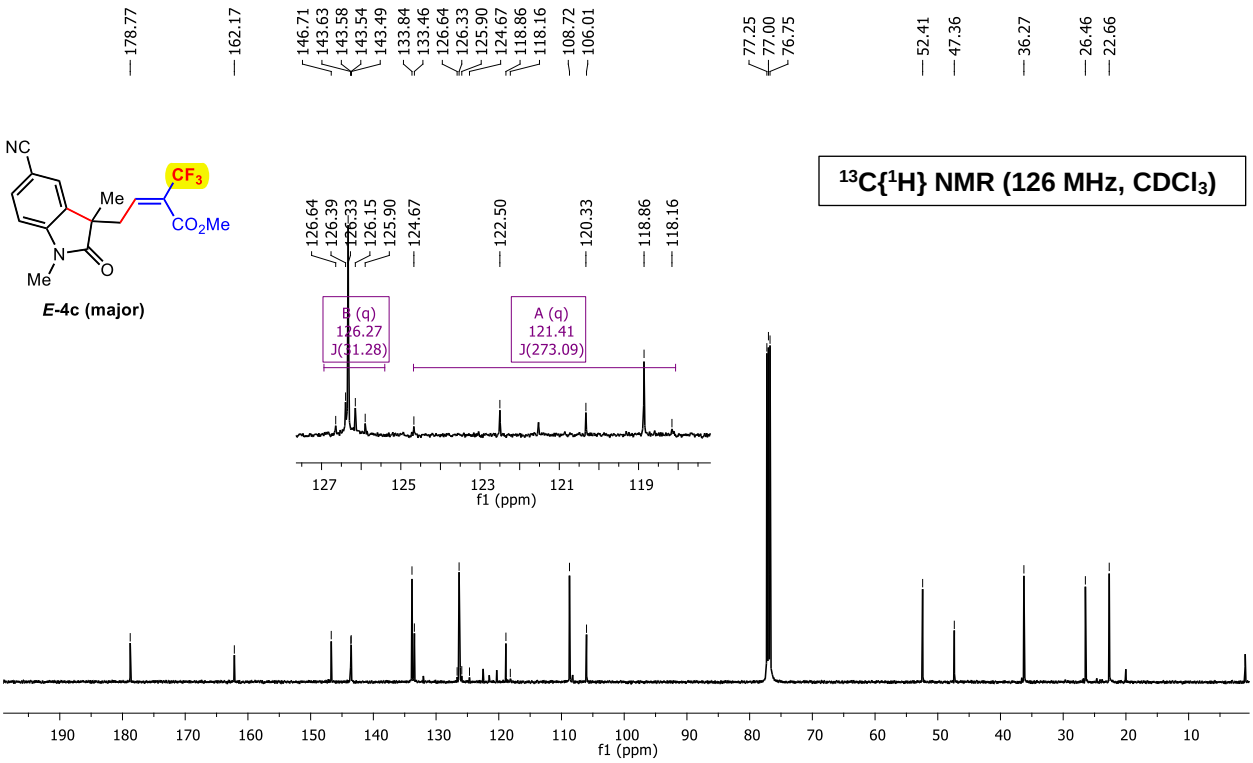

178.79
162.38
156.22
145.05
145.00
144.96
144.91
136.35
133.70
125.87
125.63
125.38
125.14
124.88
122.71
120.54
118.37
112.57
110.46
108.62
77.25
77.00
76.75
55.76
52.18
47.91
36.77
26.28
22.85
MeO
Me
CF3
CO2Me
N
O
Me
E-4b (major)
13C{1H} NMR (126 MHz, CDCl3)
125.87
125.63
125.38
125.14
124.88
122.71
120.54
118.37
B (q)
125.50
J(30.41)
A (q)
121.62
J(272.92)
128
126
124
122
120
118
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-64.24
MeO
Me
CF3
CO2Me
N
Me
O
E-4b (major)
19F{1H} NMR (471 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

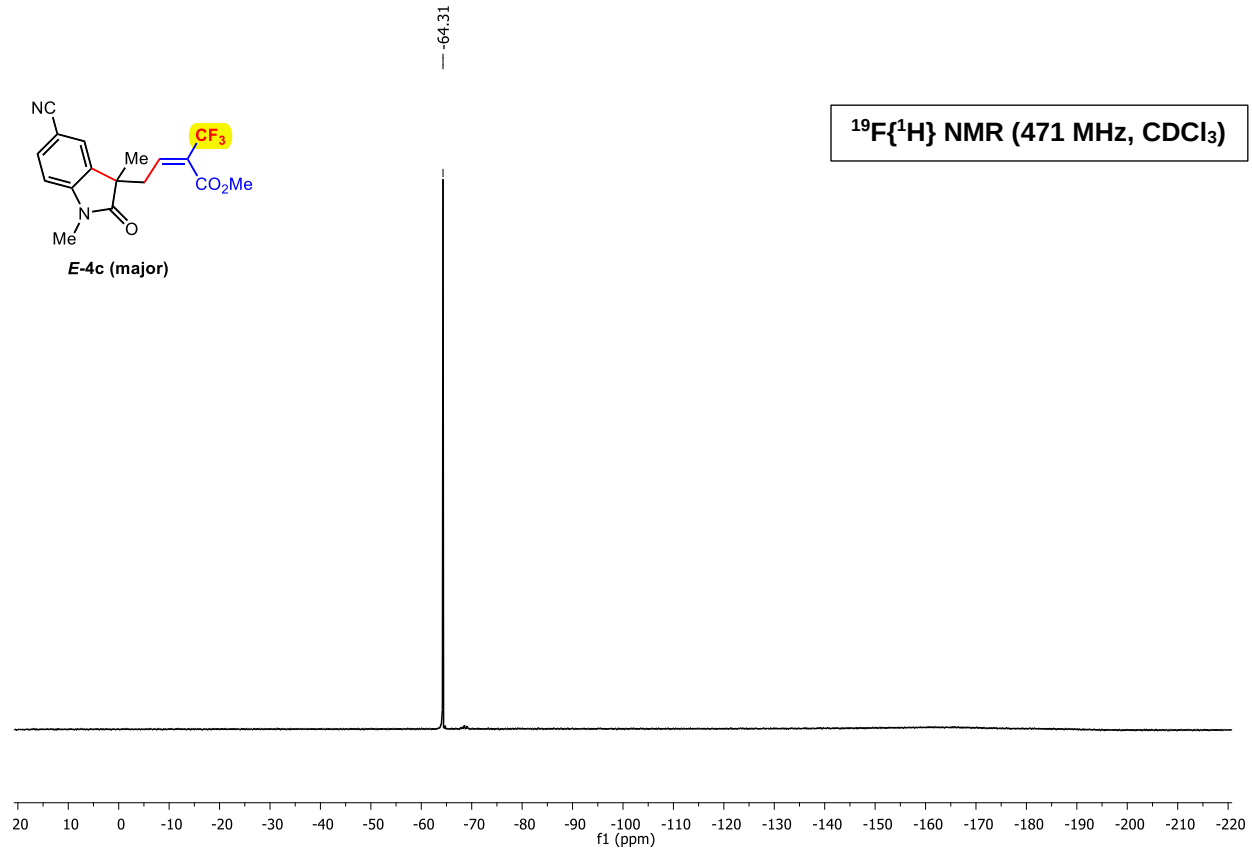

7.260
6.951
6.936
6.922
6.814
6.807
6.800
6.785
6.770
6.753
6.563
6.549
6.535
3.790
3.744
3.215
3.192
3.157
3.137
3.121
3.106
3.090
3.074
3.012
3.003
2.978
2.937
2.920
2.904
1.422
MeO
Me
CF3
CO2Me
N
Me
O
E-4b (major)
+
MeO
Me
CO2Me
CF3
N
Me
O
Z-4b (minor)
1H NMR (500 MHz, CDCl3)
0.72
5.33
1.00
8.23
2.19
2.07
3.06
2.13
1.53
5.18
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)


-58.54
-64.24
MeO
CF3
Me
CO2Me
N
O
Me
E-4b (major)
+
MeO
CO2Me
Me
CF3
N
O
Me
Z-4b (minor)
19F{1H} NMR (471 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

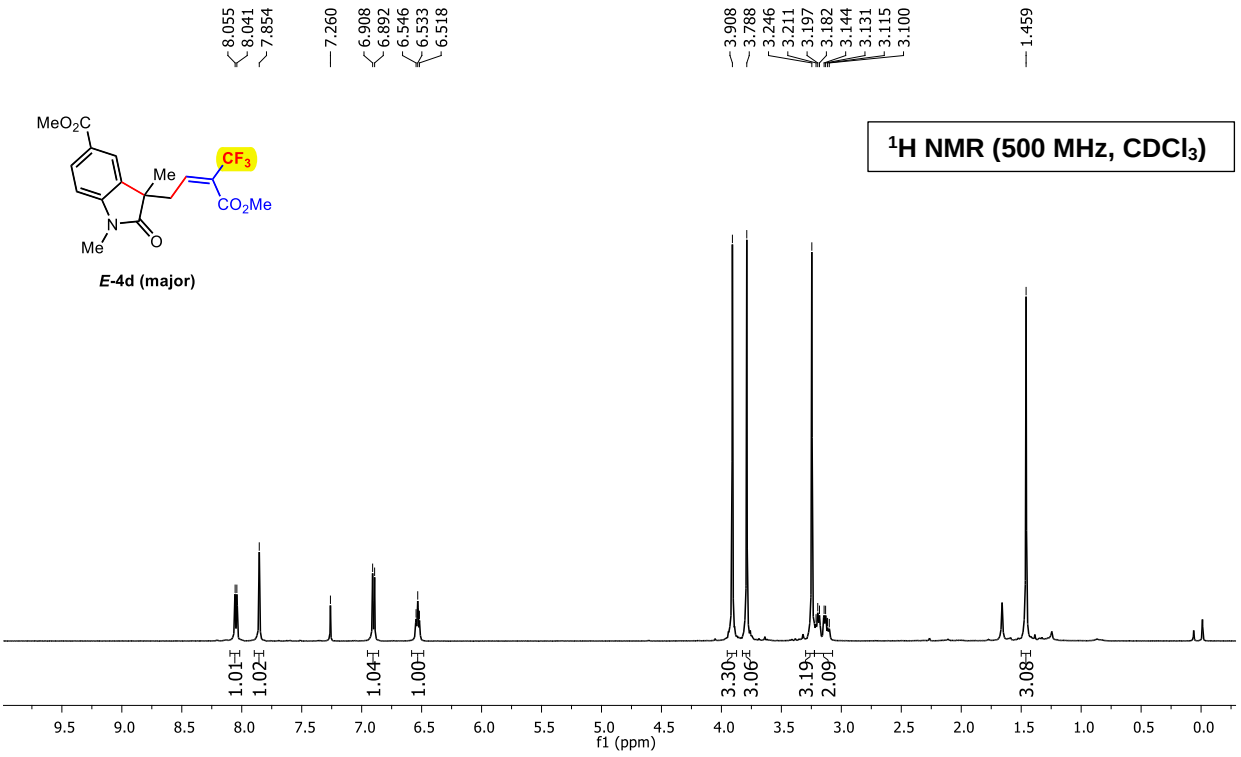

7.638
7.622
7.437
7.260
6.958
6.939
6.922
6.544
6.529
6.515
3.815
3.246
3.214
3.198
3.183
3.167
3.149
3.134
3.119
1.459
NC
CF3
Me
CO2Me
N
O
Me
E-4c (major)
1H NMR (500 MHz, CDCl3)
1.04
1.00
1.08
1.00
3.11
3.06
2.14
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

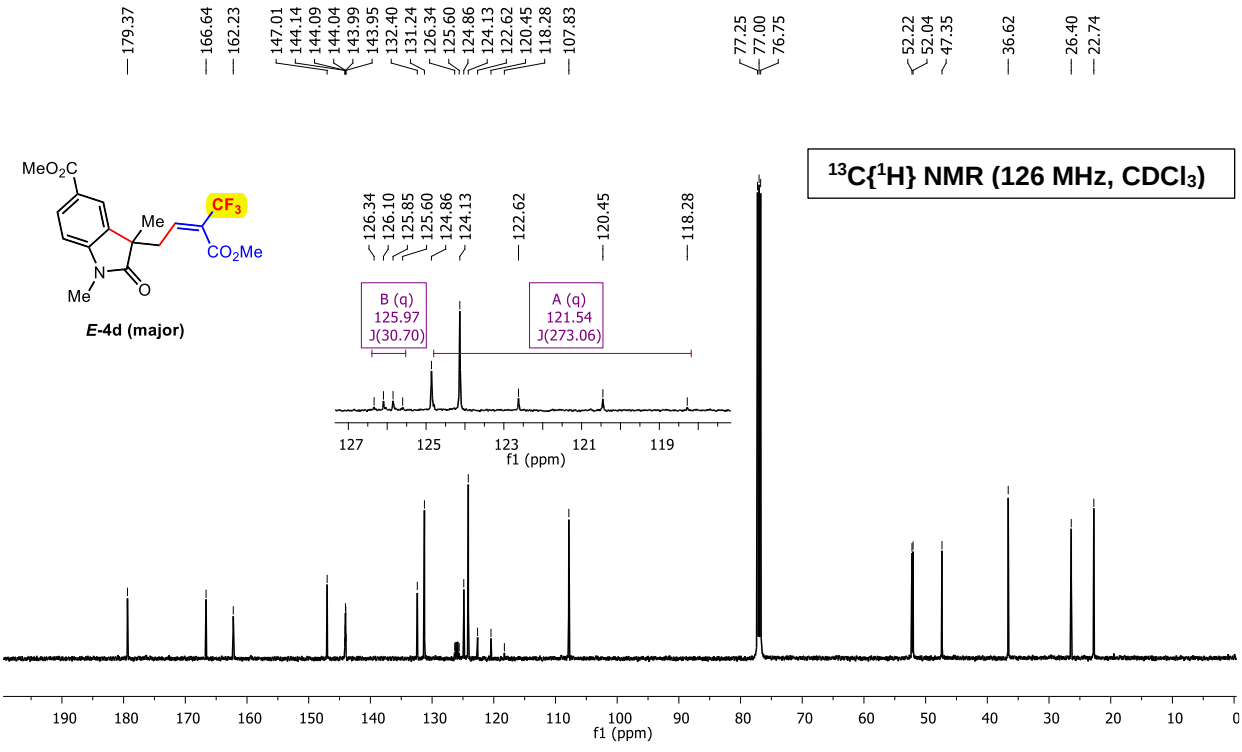


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

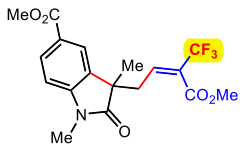


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


8.055
8.041
7.854
7.260
6.908
6.892
6.546
6.533
6.518
3.908
3.788
3.246
3.211
3.197
3.182
3.144
3.131
3.115
3.100
1.459
MeO2C
CF3
Me
CO2Me
N
O
Me
E-4d (major)
1H NMR (500 MHz, CDCl3)
1.01
1.02
1.04
1.00
3.30
3.06
3.19
2.09
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

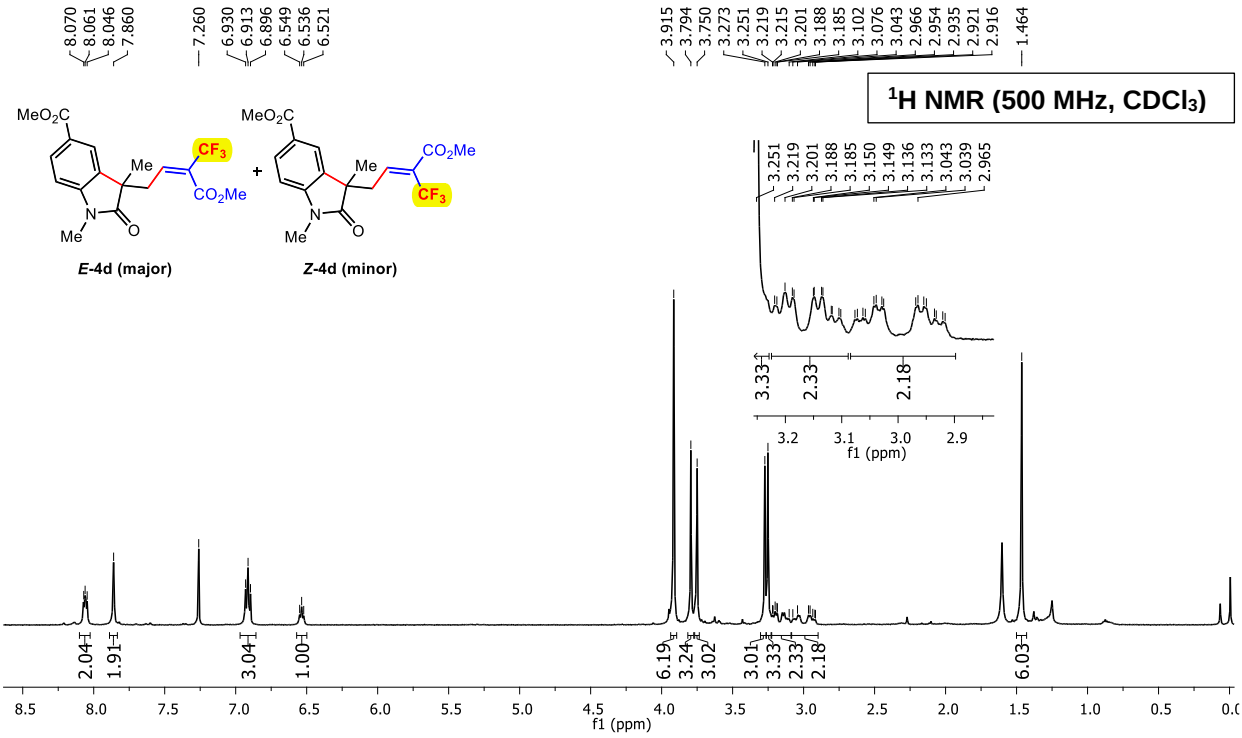

179.37
166.64
162.23
147.01
144.14
144.09
144.04
143.99
143.95
132.40
131.24
126.34
125.60
124.86
124.13
122.62
120.45
118.28
107.83
77.25
77.00
76.75
52.22
52.04
47.35
36.62
26.40
22.74
MeO2C
CF3
Me
CO2Me
N
O
Me
E-4d (major)
13C{1H} NMR (126 MHz, CDCl3)
126.34
126.10
125.85
125.60
124.86
124.13
122.62
120.45
118.28
B (q)
125.97
J(30.70)
A (q)
121.54
J(273.06)
127 125 123 121 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



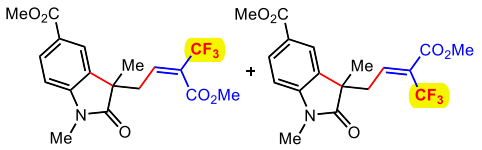
***E*-4d (major)**

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

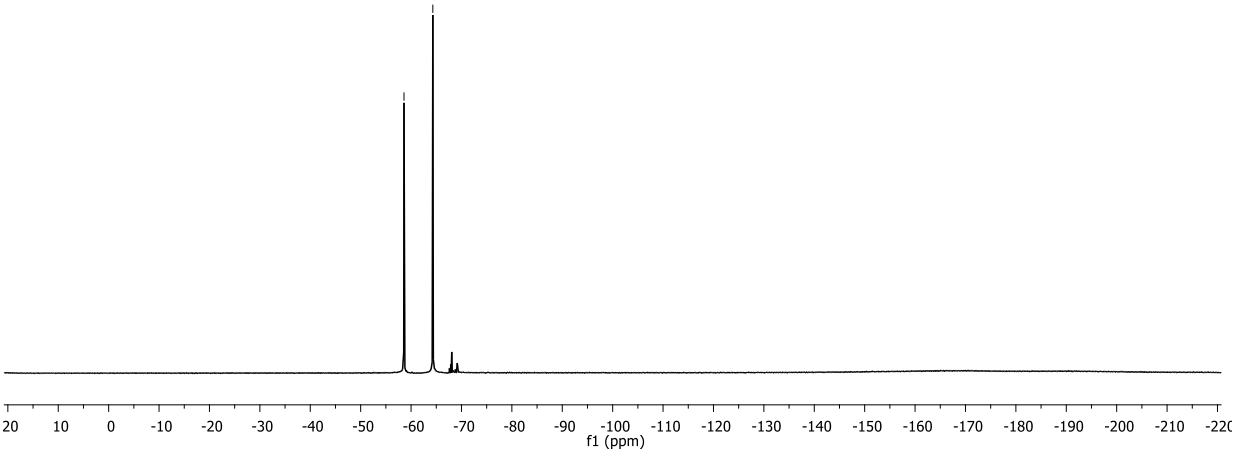


***E*-4d (major)** **+** ***Z*-4d (minor)**

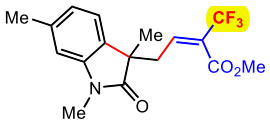
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



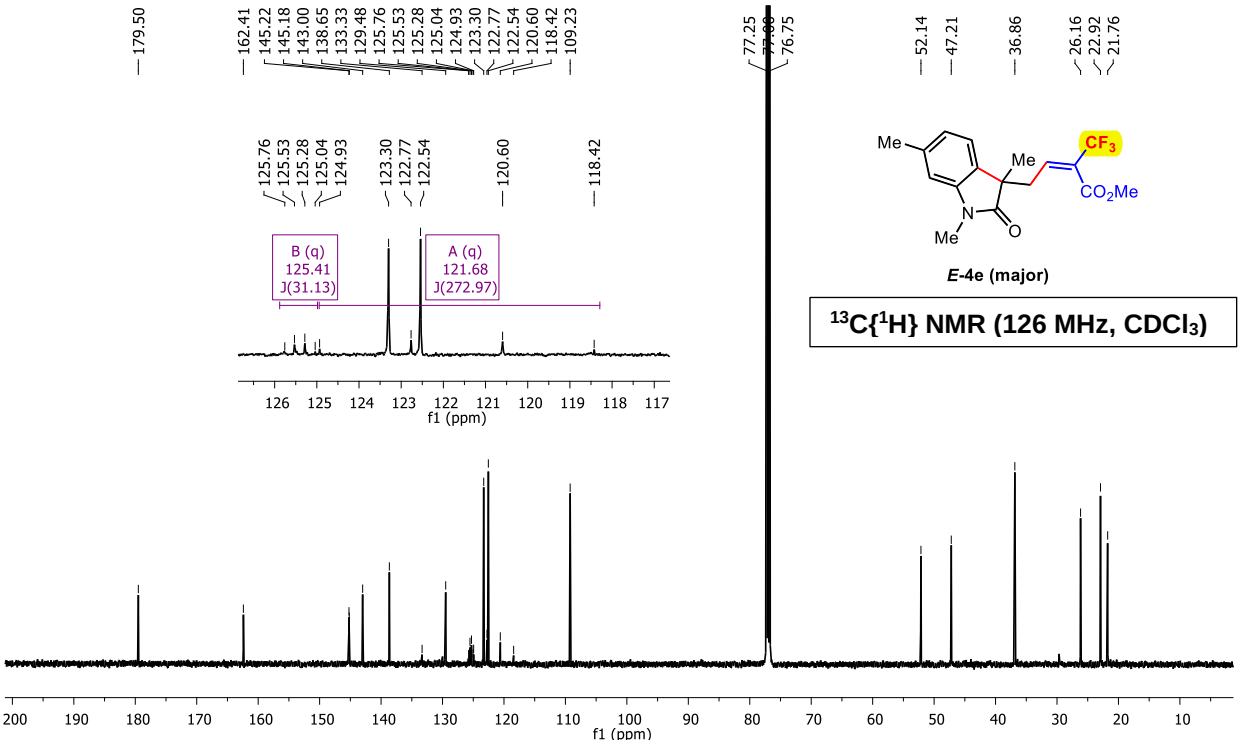
***E*-4d (major)** ***Z*-4d (minor)**



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

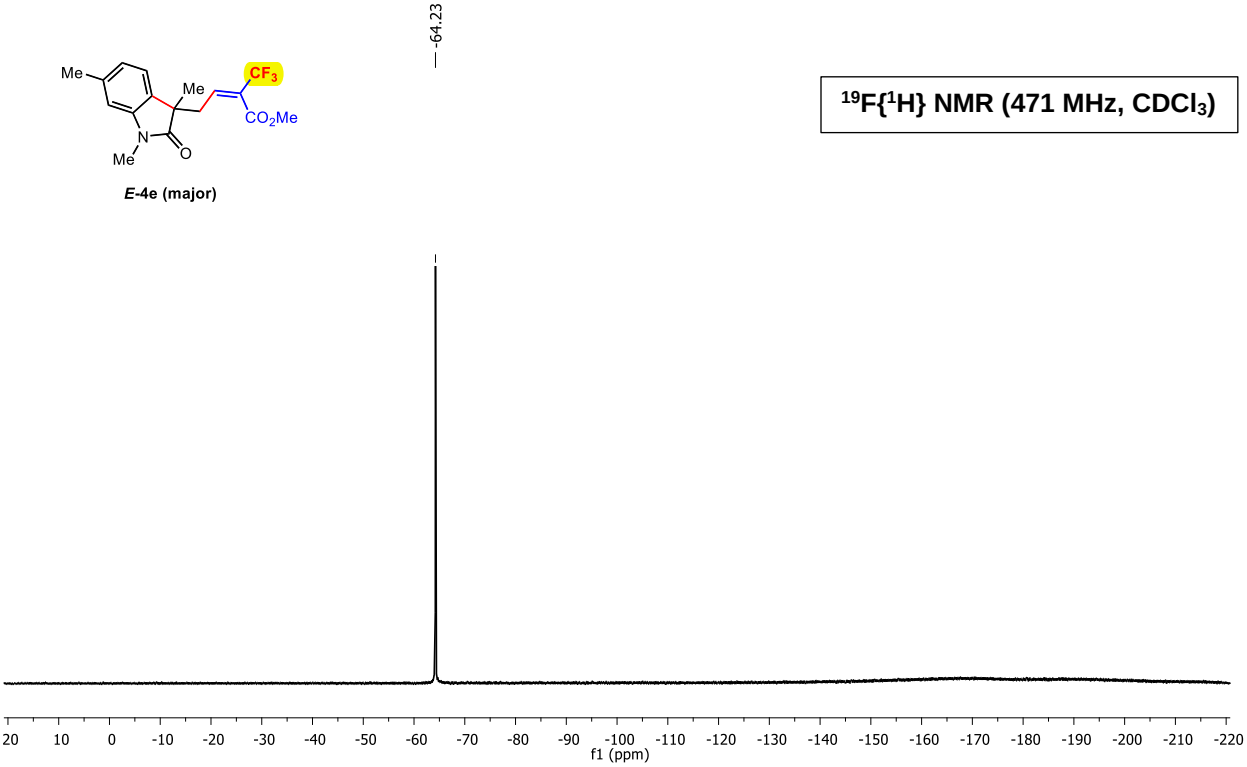


***E*-4e (major)**



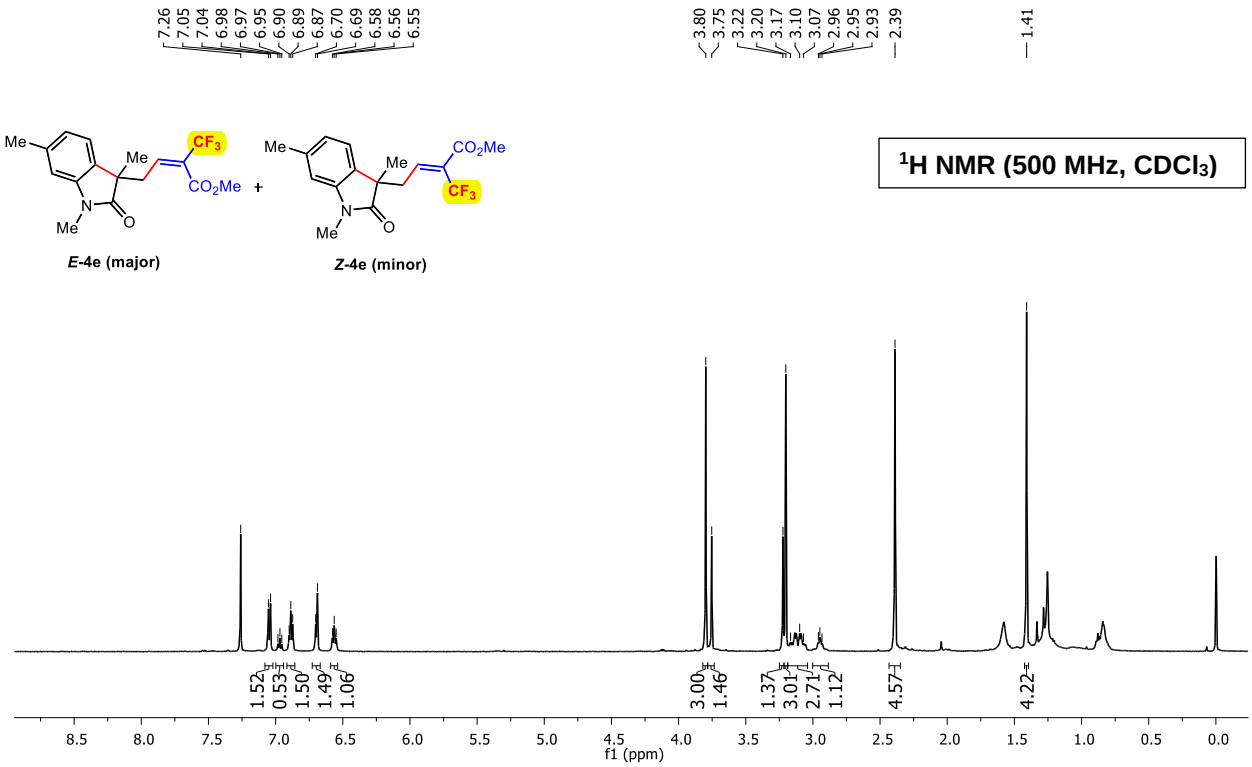
E-4e (major)

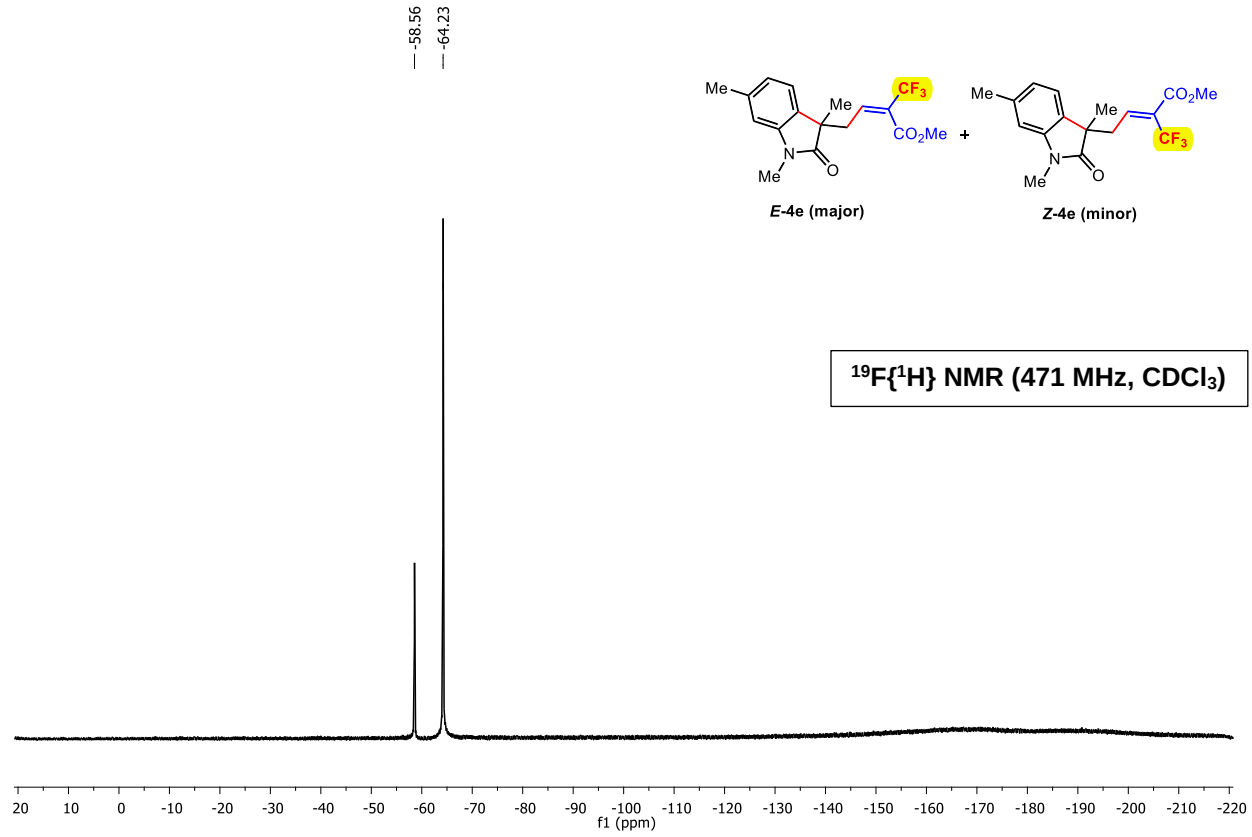
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

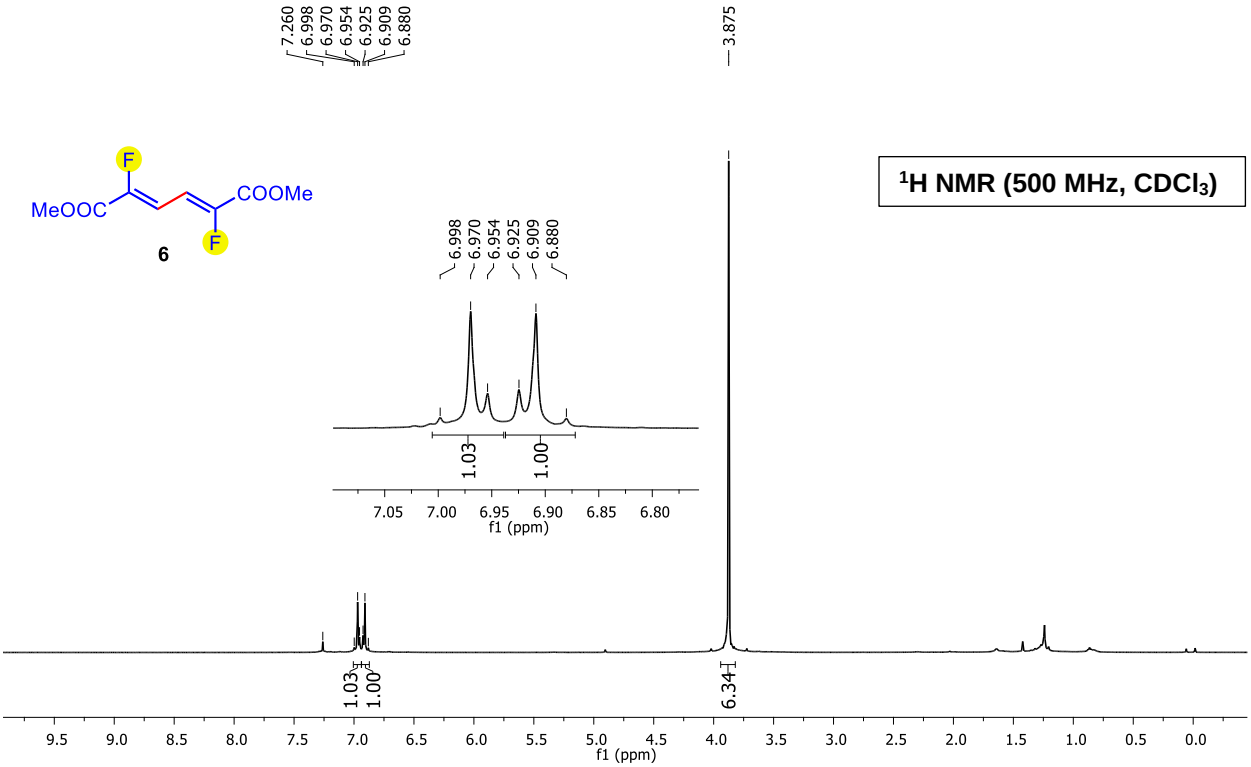


E-4e (major)

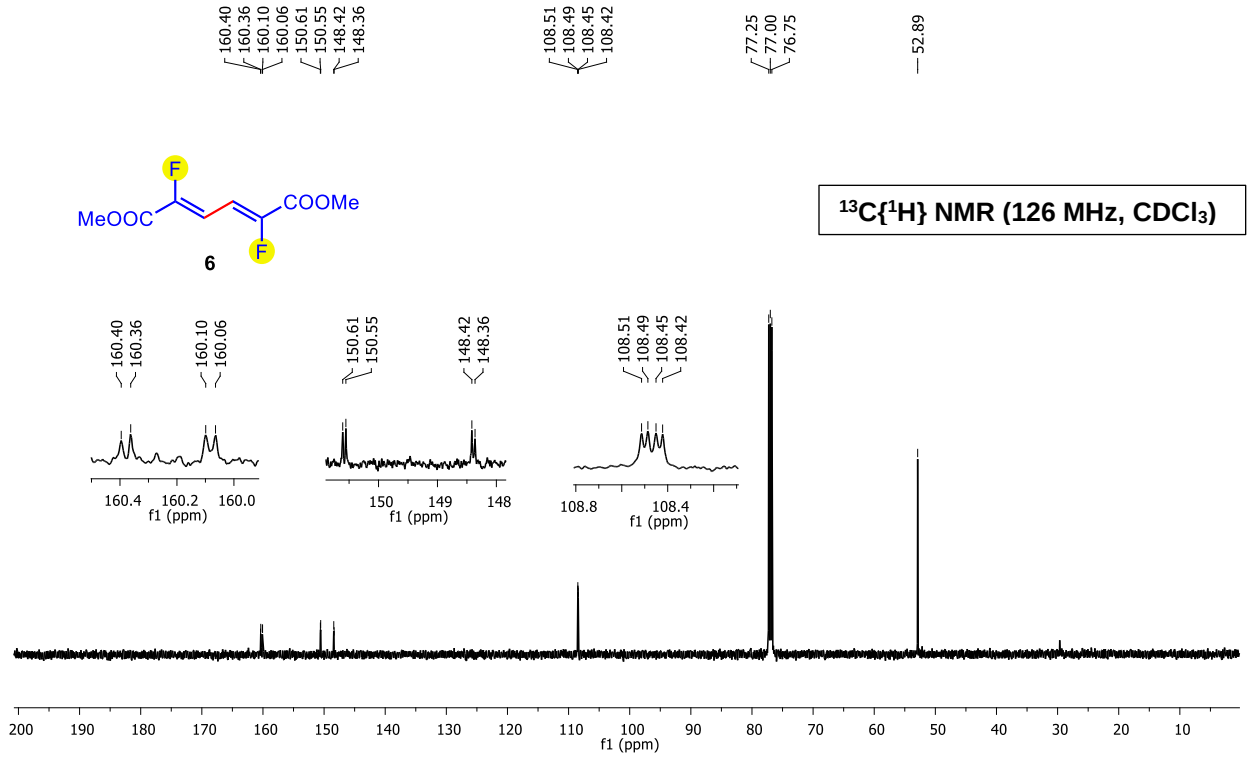
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


7.26
7.05
7.04
6.98
6.97
6.95
6.90
6.89
6.87
6.70
6.69
6.58
6.56
6.55
3.80
3.75
3.22
3.20
3.17
3.10
3.07
2.96
2.95
2.93
2.39
1.41
Me
Me
CF3
CO2Me
N
O
Me
+
Me
Me
CO2Me
CF3
N
O
Me
E-4e (major)
Z-4e (minor)
1H NMR (500 MHz, CDCl3)
1.52
0.53
1.50
1.49
1.06
3.00
1.46
1.37
3.01
2.71
1.12
4.57
4.22
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)

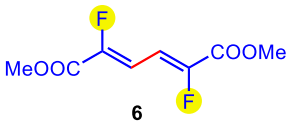

-58.56
-64.23
Me
Me
CF3
CO2Me
N
O
Me
+
Me
Me
CO2Me
CF3
N
O
Me
E-4e (major)
Z-4e (minor)
19F{1H} NMR (471 MHz, CDCl3)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)



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

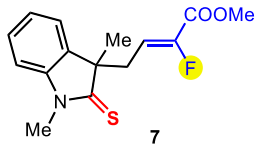


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



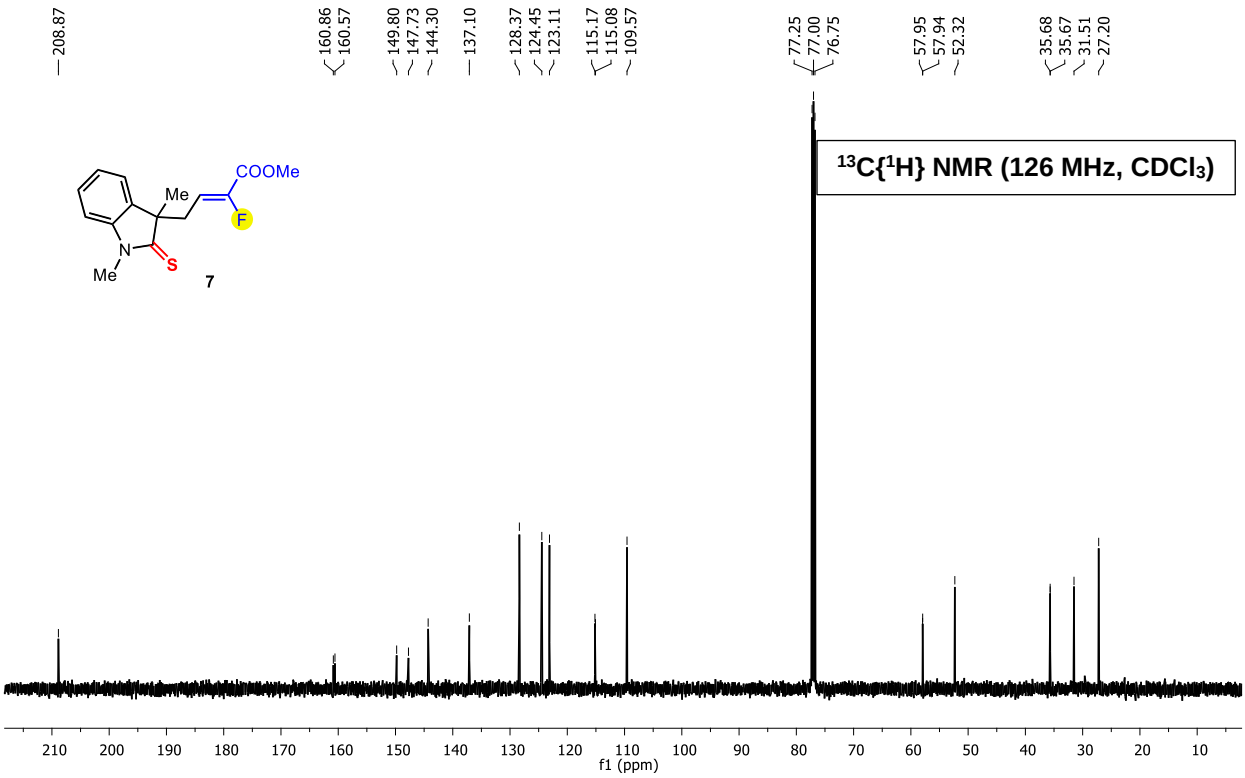
6

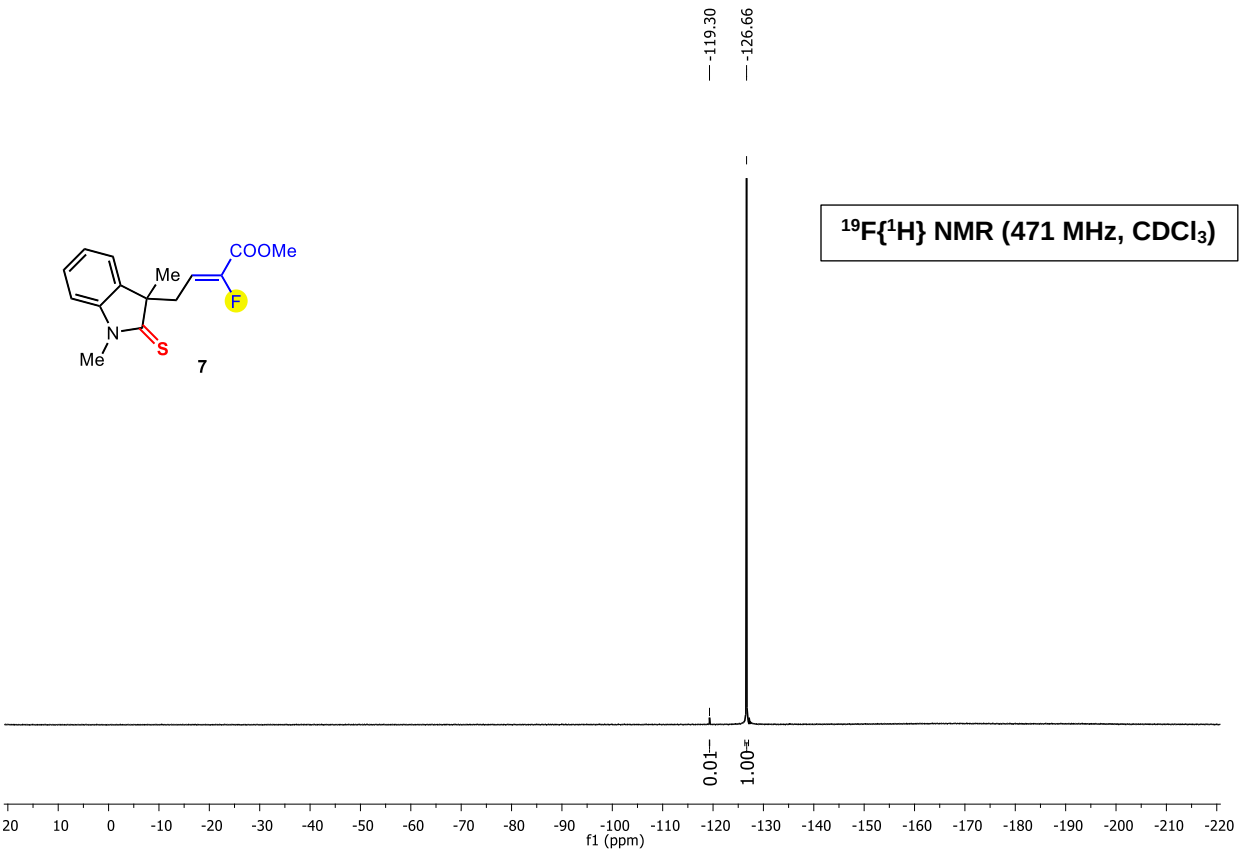
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

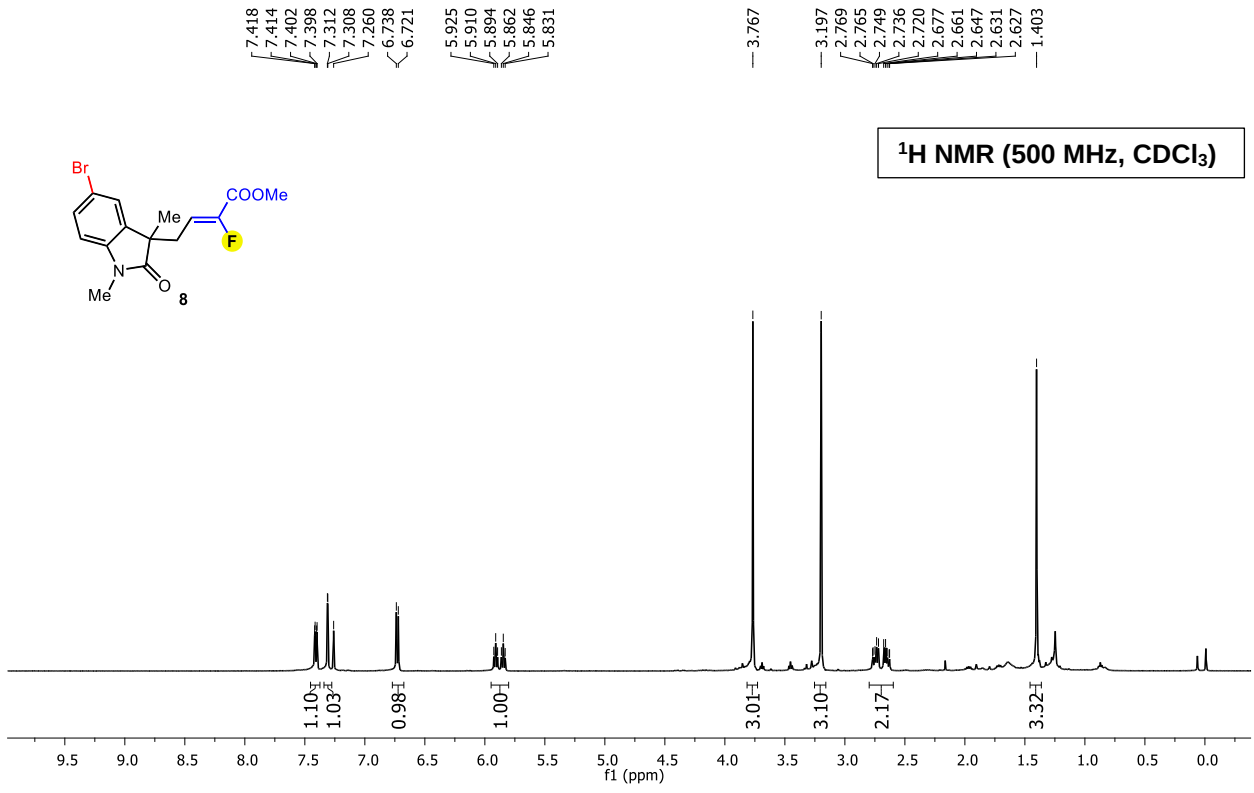


7

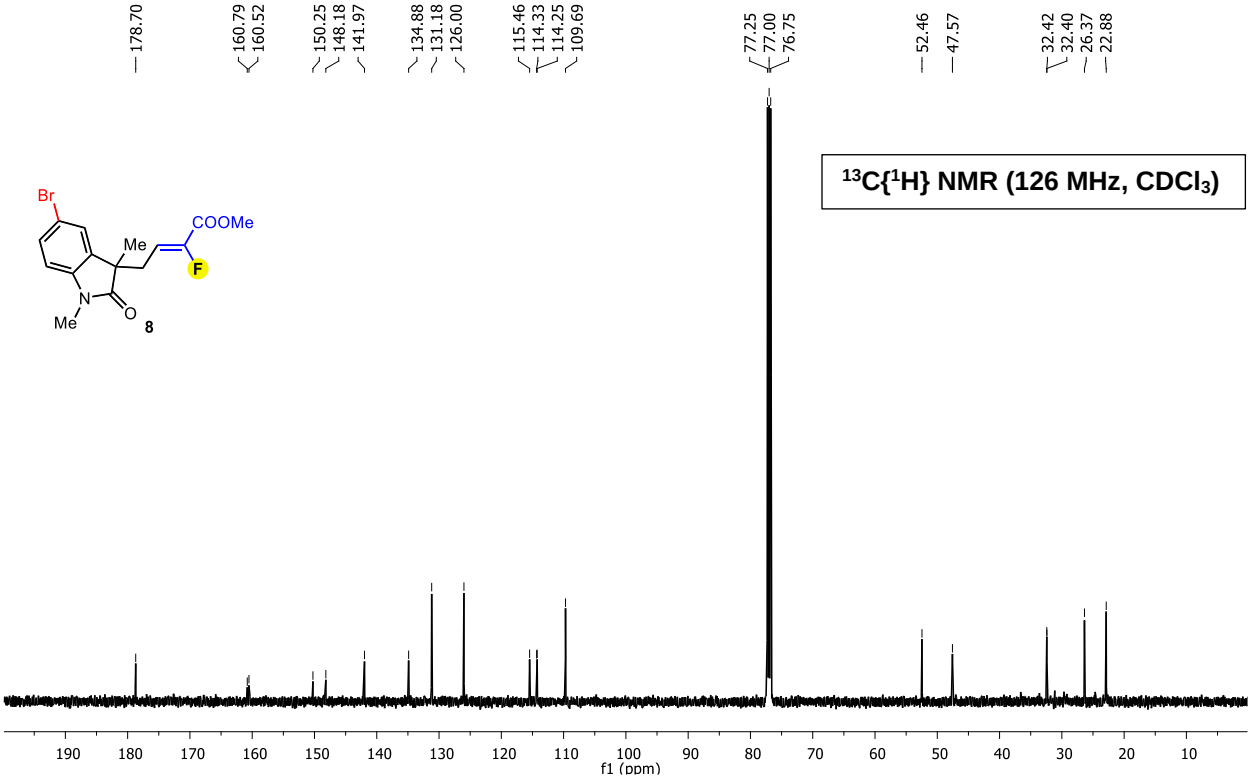
^{1}H NMR (500 MHz, $CDCl_3$)


208.87
160.86
160.57
149.80
147.73
144.30
137.10
128.37
124.45
123.11
115.17
115.08
109.57
77.25
77.00
76.75
57.95
57.94
52.32
35.68
35.67
31.51
27.20
COOMe
Me
F
N
Me
S
7
13C{1H} NMR (126 MHz, CDCl3)
f1 (ppm)

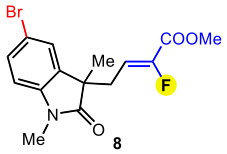

-119.30
-126.66
COOMe
Me
F
N
Me
S
7
19F{1H} NMR (471 MHz, CDCl3)
0.01
1.00
f1 (ppm)



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



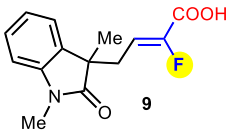
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



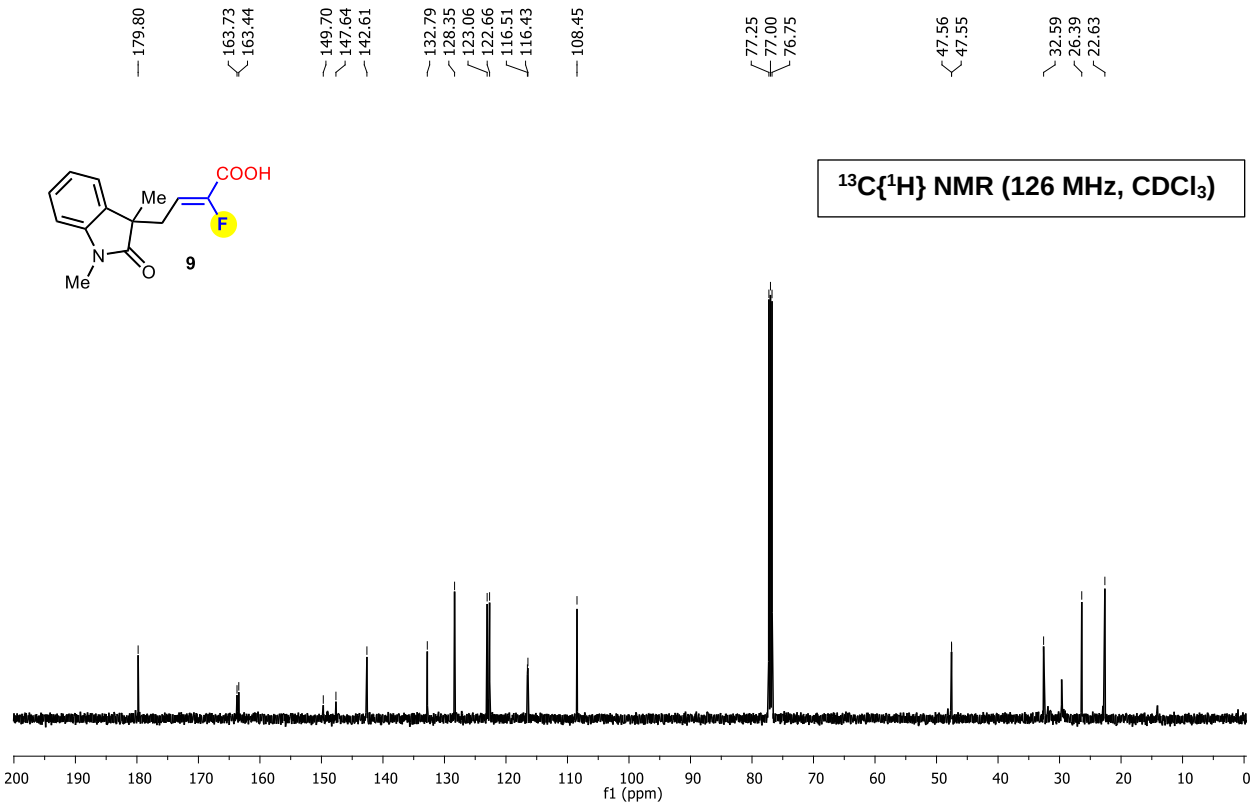
8

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

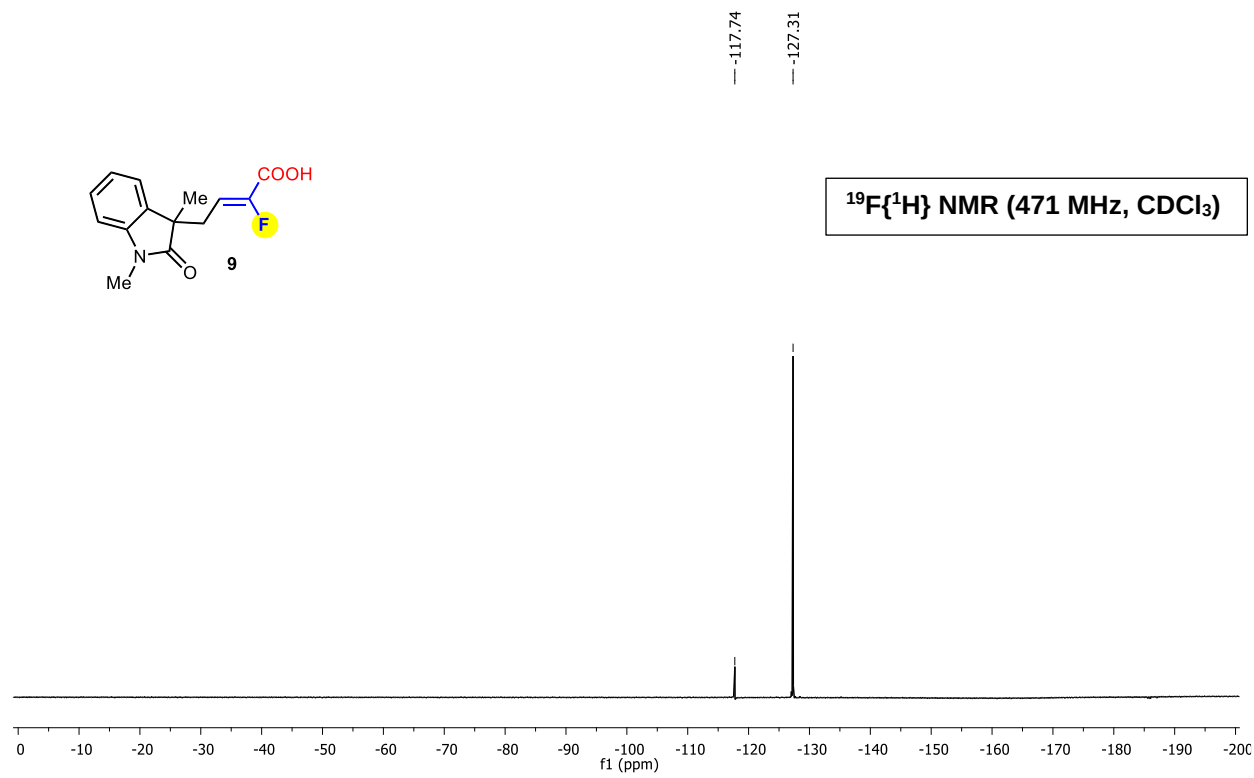
^{1}H NMR (500 MHz, $CDCl_3$)



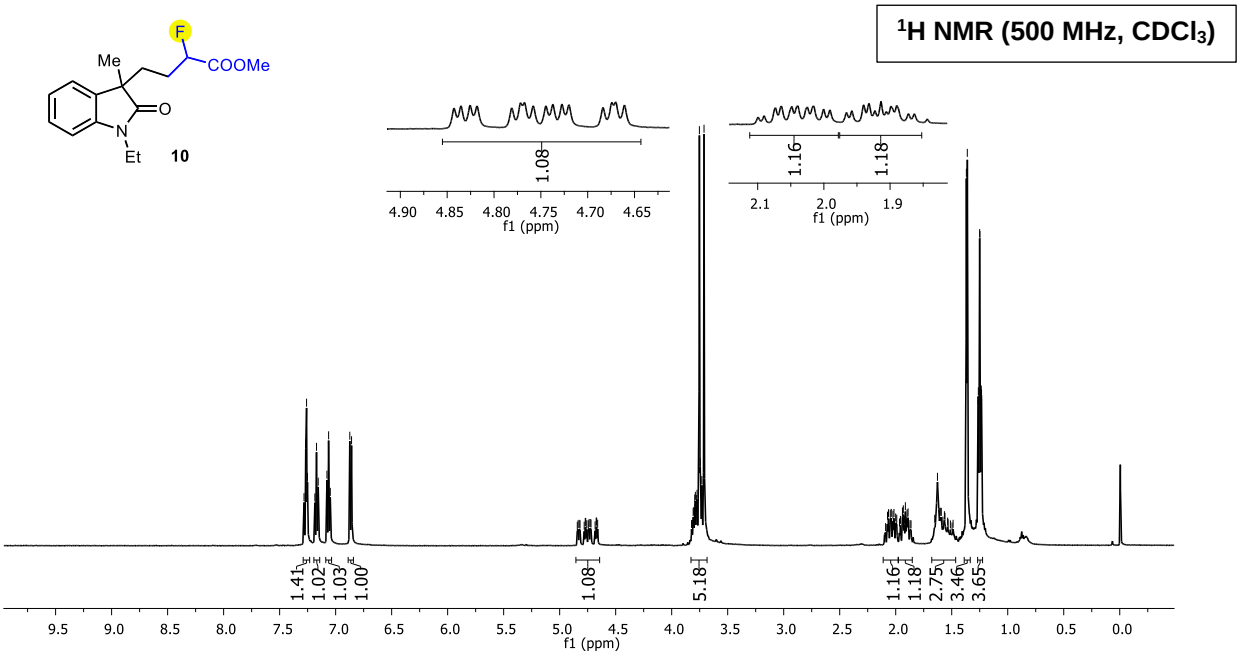
9

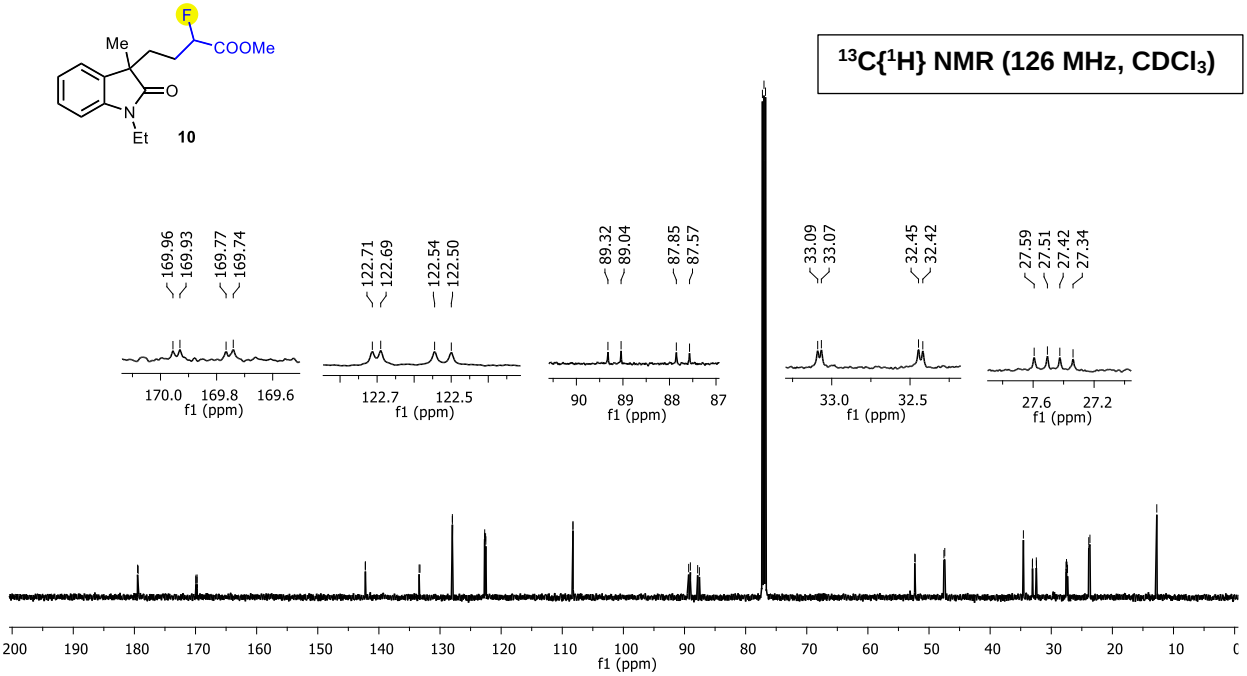


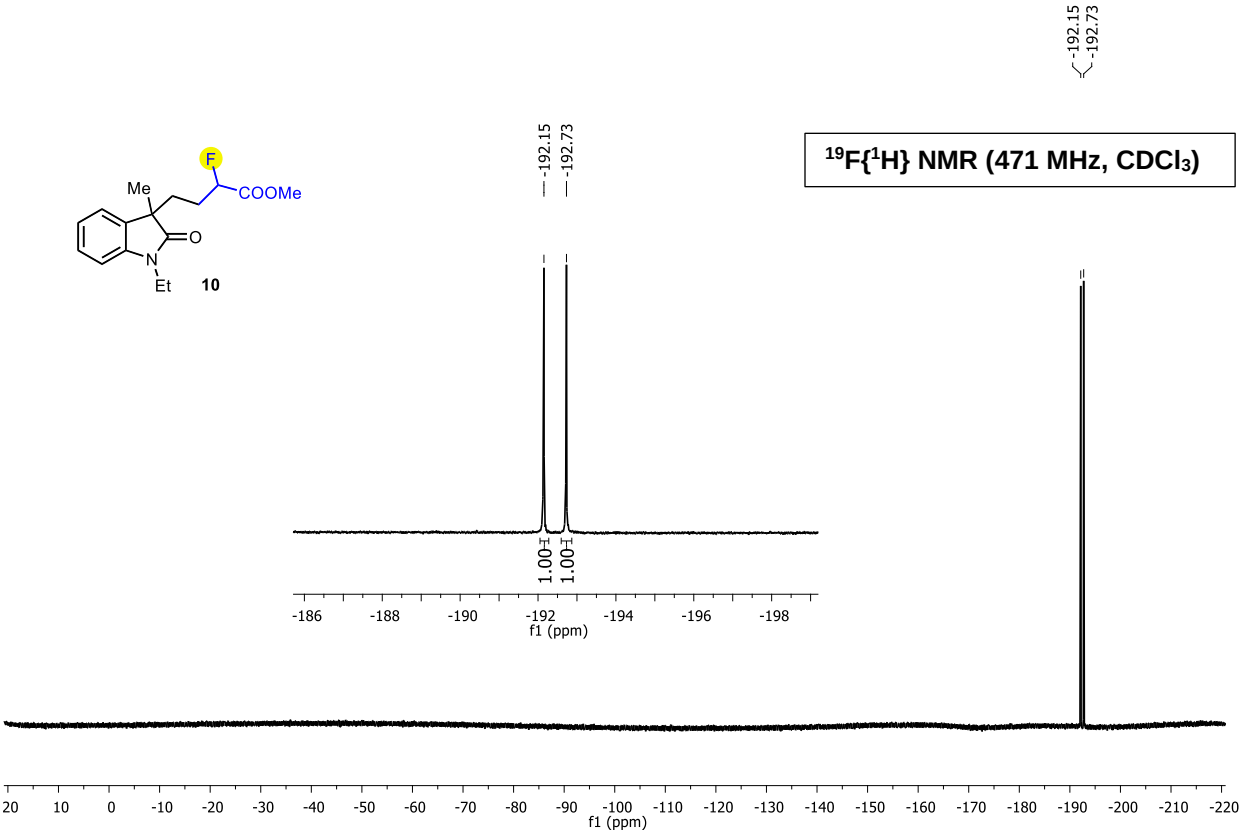
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

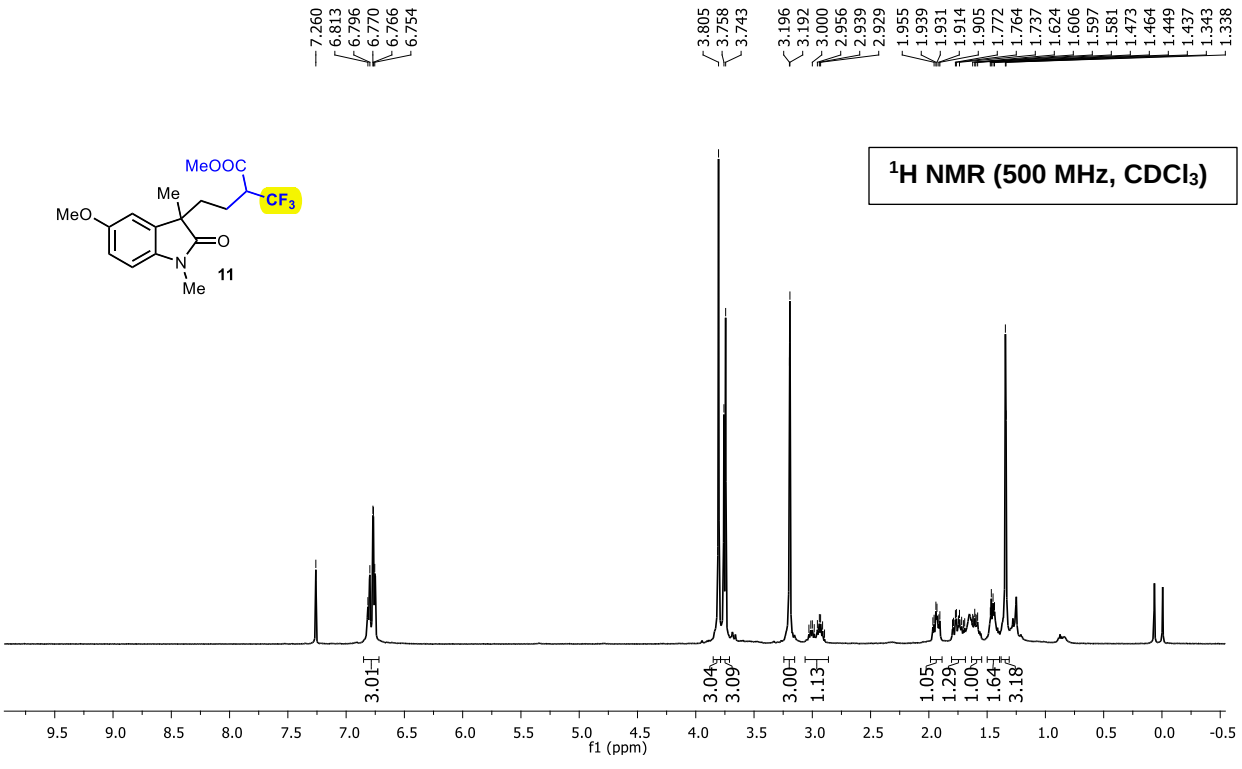


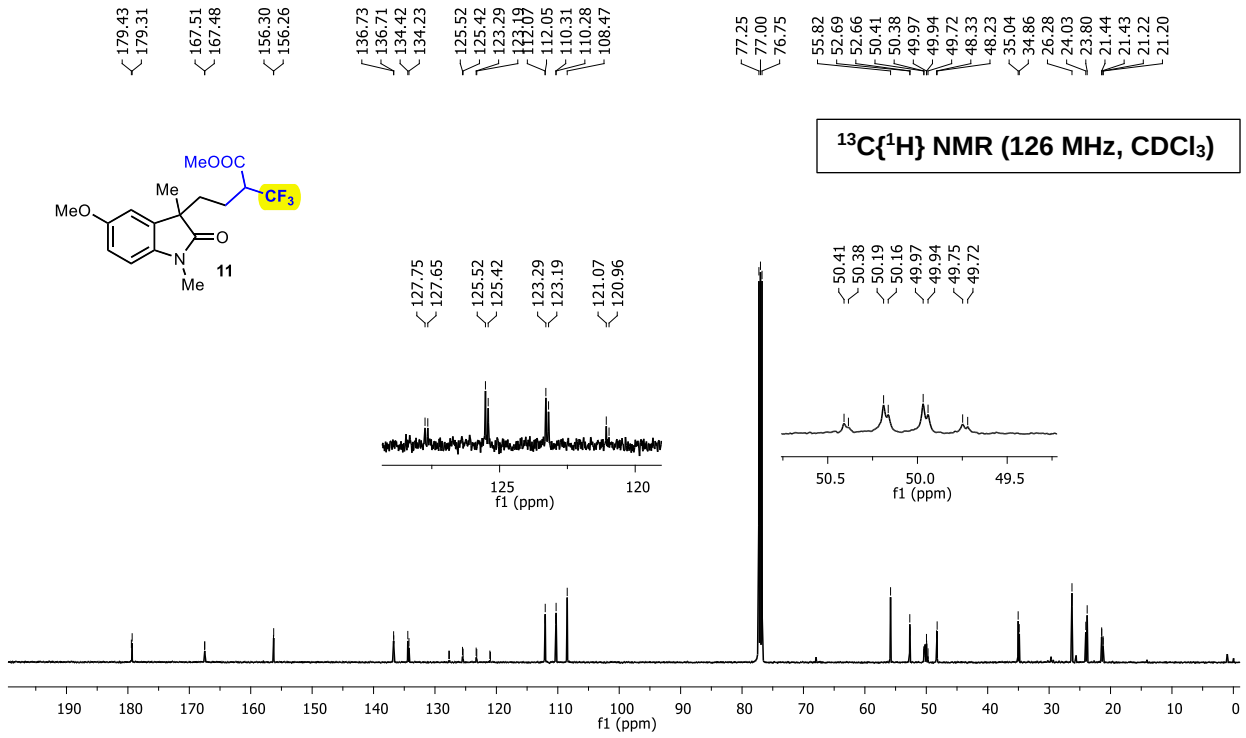
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


^{1}H NMR (500 MHz, CDCl$_3$)
F
COOMe
Me
O
N
Et
10
1.08
4.90 4.85 4.80 4.75 4.70 4.65
f1 (ppm)
1.16
1.18
2.1 2.0 1.9
f1 (ppm)
1.41
1.02
1.03
1.00
1.08
5.18
1.16
1.18
2.75
3.46
3.65
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

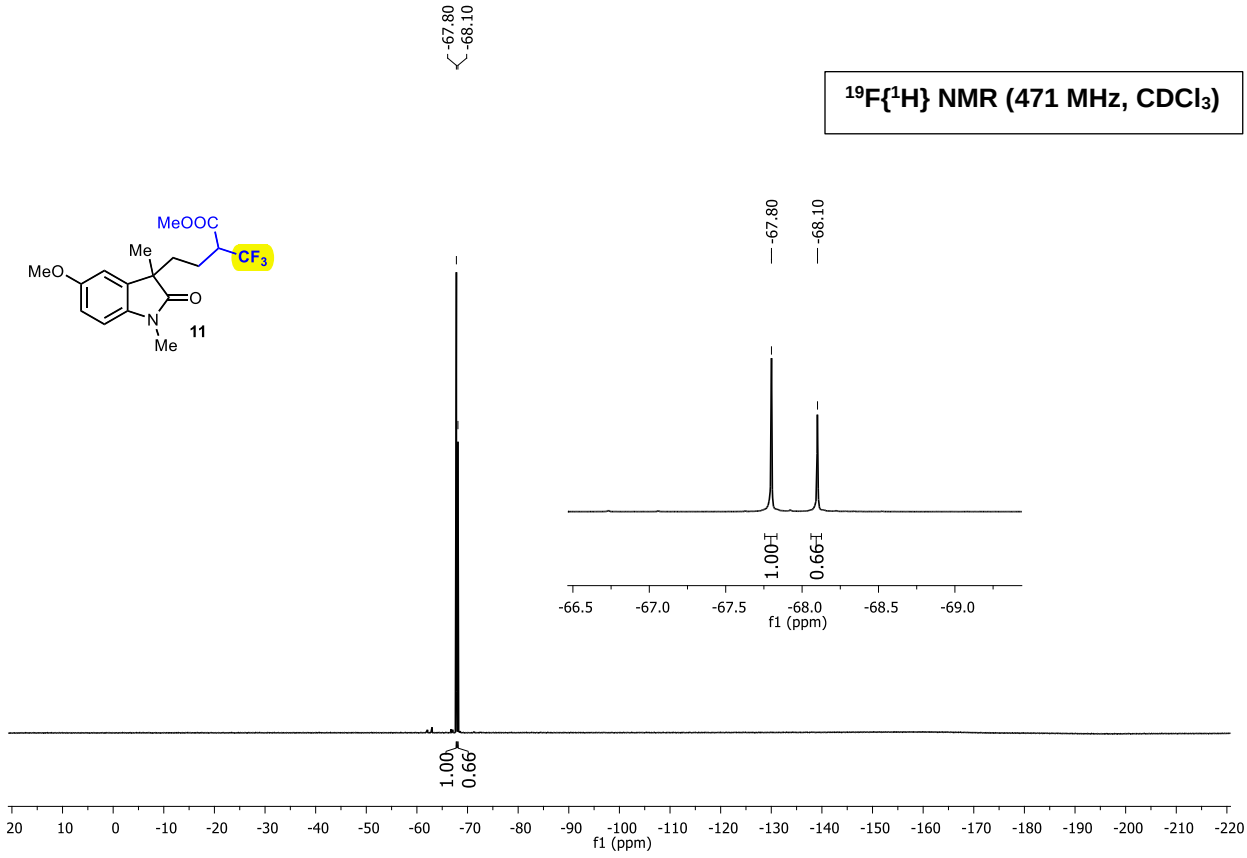

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)
F
COOMe
Me
O
N
Et
10
170.0 169.8 169.6
f1 (ppm)
122.7 122.5
f1 (ppm)
90 89 88 87
f1 (ppm)
33.0 32.5
f1 (ppm)
27.6 27.2
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-192.15
-192.73
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)
F
COOMe
Me
O
N
Et
10
-192.15
-192.73
1.00
1.00
-186
-188
-190
-192
-194
-196
-198
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


7.260
6.813
6.796
6.770
6.766
6.754
3.805
3.758
3.743
3.196
3.192
3.000
2.956
2.939
2.929
1.955
1.939
1.931
1.914
1.905
1.772
1.764
1.737
1.624
1.606
1.597
1.581
1.473
1.464
1.449
1.437
1.343
1.338
^{1}H NMR (500 MHz, $CDCl_3$)
MeOOC
Me
MeO
CF_3
O
N
Me
11
3.01
3.04
3.09
3.00
1.13
1.05
1.29
1.00
1.64
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)