Supporting Information

for

$AgBF_4$-Catalyzed Insertion of Unactivated Alkynes into C–F Bonds of Acyl Fluorides

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CONTENTS

I. General Information

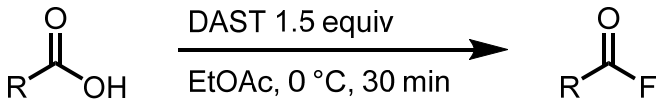
^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethyl silane (δ 0.00) or $CHCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.00). The chemical shifts in ^{19}F NMR spectra were recorded relative to benzotrifluoride ($PhCF_3$, δ –65.64). The data is reported as follows: chemical shift (δ) in ppm, coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh)).

II. Materials

$AgBF_4$ was purchased from Aldrich and used as received in the glovebox. 1,1,2,2-Tetrachloroethane (TCE) was purchased from TCI and used as received in the glovebox. Unless otherwise stated, all commercially available reagents and solvents were supplied from TCI, Wako Chemical, Aldrich and BLD and used as received. Acyl fluorides **1a** [CAS:701-53-1],[1] **1c** [CAS: 350-42-5],[1] **1d** [CAS: 72398-40-4],[1] **1e** [CAS: 2254447-02-2],[2] **1f** [CAS: 370-12-7],[3] **1g** [CAS: 37827-83-1],[1] **1h** [CAS: 3020788-99-9],[4] **1i** [CAS: 364-20-5],[1] **1j** [CAS: 138421-49-5],[5] **1o** [CAS: 334-47-4],[6] **1p** [CAS: 1977-87-3],[1] **1q** [CAS: 10405-61-5],[1] **1r** [CAS: 38986-89-9],[1] **1t** [2921955-03-3],[7] **1u** [CAS: 359699-03-9],[1] were prepared according to the literature procedures.

III. Synthesis of Acyl Fluorides

A general procedure for the synthesis of starting acyl fluorides.

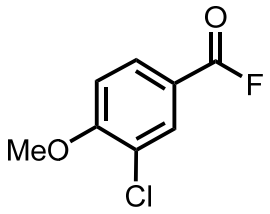


A carboxylic acid (5.0 mmol) and dehydrated EtOAc (15 mL) were added to a round-bottom flask under N_2 atmosphere. After the mixture was cooled to 0 ºC, DAST (1.0 mL, 7.5 mmol, 1.5 equiv) was added dropwise, and the resulting mixture was stirred at 0 ºC for 30 min. An aqueous saturated solution of $NaHCO_3$ (30 mL) was then added, and the organic layer was separated and dried using Na_2SO_4.

After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography to give the desired acyl fluoride.

Spectroscopic data of 1.

3-Chloro-4-methoxybenzoyl fluoride (1k).



The synthesis was performed on a 3.0 mmol scale according to General Procedures using the commercially available 3-chloro-4-methoxybenzoic acid.

Brown solid (322.8 mg, 60%). R_f 0.43 (SiO_2, Hexane/EtOAc = 9/1). M.p. 59–61 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02-7.93 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 4.00 (s, 3H).

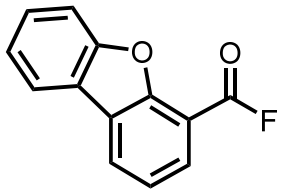
^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 160.5, 156.2, 133.2, 132.1, 123.4, 117.5, 111.7, 56.6.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 13.8.

IR (ATR): 2961 w, 1793 s, 1595 s, 1500 s, 1441 m, 1410 m, 1319 m, 1273 s, 1219 s, 1155 w, 1064 s, 1011 s, 900 m, 849 m, 822 m, 740 s, 693 m, 615 s.

HRMS (DART+, $[M+H]^+$) Calcd for $C_8H_7{}^{35}ClFO_2$: 189.0113. Found: 189.0117.

Dibenzo[*b*,*d*]furan-4-carbonyl fluoride (1l).



The synthesis was performed on a 3.0 mmol scale according to General Procedures using the commercially available dibenzo[b,d]furan-4-carboxylic acid.

White solid (322 mg, 50%). R_f 0.50 (SiO_2, Hexane/EtOAc = 9/1). M.p. 106–108 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.25 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.08 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.98-7.96 (m, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.40 (m, 2H).

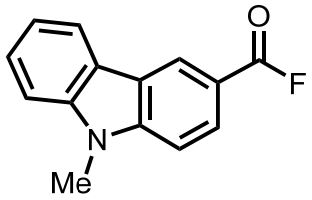
^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 156.5, 155.8, 154.8, 130.4, 128.4, 127.8, 126.5, 123.7, 122.8, 122.5, 120.7, 112.3, 109.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 26.3.

IR (ATR): 1800 s, 1597 w, 1450 m, 1421 s, 1278 m, 1250 m, 1188 s, 1130 m, 1096 m, 1015 m, 867 m, 819 w, 772 s, 741 s, 715 s, 628 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{13}H_8FO_2$: 215.0503. Found: 215.0512.

9-Methyl-9*H*-carbazole-3-carbonyl fluoride (1m).



The synthesis was performed on a 1.0 mmol scale according to General Procedures using the corresponding carboxylic acid.[8]

White solid (78 mg, 31%). R_f 0.25 (SiO_2, Hexane/EtOAc = 9/1). M.p. 125–126 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.75 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.59-7.54 (m, 1H), 7.46-7.33 (m, 3H), 3.87 (s, 3H).

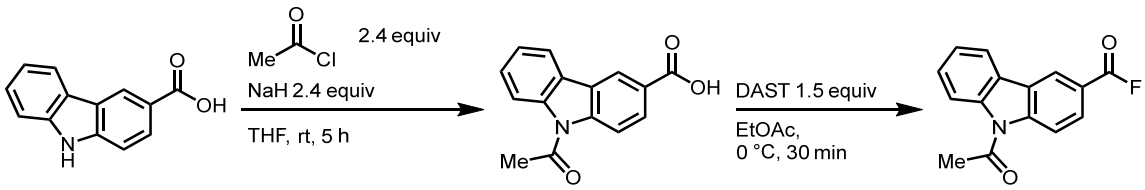
^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 158.5, 144.6, 141.7, 128.8, 127.0, 125.0, 123.0, 122.5, 120.7, 120.6, 114.6, 109.1, 108.6, 29.3.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 12.5.

IR (ATR): 2945 w, 1787 s, 1595 s, 1472 w, 1442 w, 1365 m, 1327 m, 1252 s, 1202 m, 1144 w, 1000 m, 902 w, 826 m, 769 s, 749 m, 715 s, 617 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{14}H_{11}FNO$: 228.0819. Found: 228.0818.

Synthesis of 9-Acetyl-9*H*-carbazole-3-carbonyl fluoride (1n).



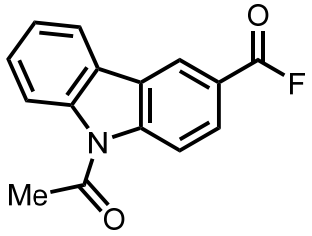
S1 **S2** **1n**

Synthesis of S2. In a round-bottom flask, **S1**[9] (0.75 g, 3.5 mmol) was added at 0 °C to a suspension of NaH (0.33 g, 8.4 mmol, 60% dispersion in mineral oil) in THF (10 mL). After the mixture was stirred for 30 min at 0 °C, acetyl chloride (0.60 mL, 8.4 mmol) in THF (10 mL) was added dropwise and the resulting mixture was stirred at rt for 5 h. After HCl (1.0 M, 10 mL) was added, the reaction mixture was extracted with EtOAc (10 mL × 2). The combined organic extracts were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuo to give crude **S2**, which was used for next step without further purification.

Synthesis of 1n. Crude carboxylic acid **S2** (0.63g, ca. 2.5 mmol) and dehydrated EtOAc (10 mL) were added to a round-bottom flask under N_2 atmosphere. After the mixture was cooled to 0 ºC, DAST (0.50

mL, 3.8 mmol, 1.5 equiv) was added dropwise, and the resulting mixture was stirred at 0 ºC for 30 min. An aqueous saturated solution of $NaHCO_3$ (15 mL) was then added, and the organic layer was separated and dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired acyl fluoride **1n** (383 mg, 43%).

9-Acetyl-9*H*-carbazole-3-carbonyl fluoride (1n).



White solid (383 mg, 43% for two steps). R_f 0.43 (SiO_2, Hexane/EtOAc = 9/1). M.p. 130–133 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.69 (d, *J* = 1.4 Hz, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 8.18-8.08 (m, 3H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 1H), 2.94 (s, 3H).

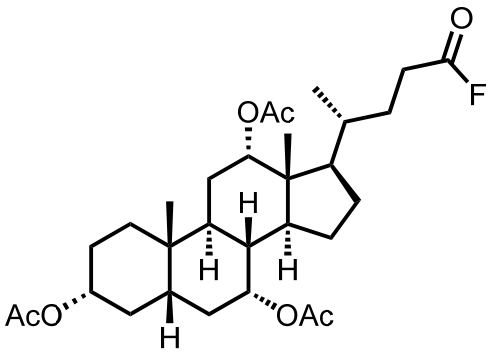
^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 170.1, 157.5, 142.8, 139.0, 130.4, 128.5, 126.7, 125.3, 124.4, 123.6, 120.5, 119.9, 116.8, 115.9, 27.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 14.8.

IR (ATR): 1797 s, 1697 m, 1600 w, 1425 w, 1367 m, 1301 m, 1246 m, 1221 s, 1136 w, 1014 m, 912 w, 836 w, 773 s, 753 s. 718 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{11}FNO_2$: 256.0768. Found: 256.0769.

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-Fluoro-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,7,12-triyltriacetate (1s).



The synthesis was performed on a 4.3 mmol scale according to General Procedures using the corresponding carboxylic acid.[10]

White solid (1.3g, 56%). R_f 0.72 (SiO_2, Hexane/EtOAc = 9/1). M.p. 95–98 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.07 (s, 1H), 4.89 (s, 1H), 4.55 (t, *J* = 10.9 Hz, 1H), 2.57-2.23 (m, 2H), 2.12 (d, *J* = 1.4 Hz, 3H), 2.07 (d, *J* = 1.1 Hz, 3H), 2.03 (t, *J* = 1.0 Hz, 3H), 1.98-1.19 (m, 20H), 1.14-

1.02 (m, 2H), 0.90 (s, 3H), 0.81 (t, J = 5.6 Hz, 3H), 0.71 (d, J = 1.6 Hz, 3H).

^{13}C NMR{^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 170.5, 170.4, 170.3, 169.8, 75.3, 74.1, 70.7, 47.3, 45.1, 43.4, 40.9, 37.8, 34.7, 34.6, 34.5, 34.4, 34.3, 31.2, 29.8, 28.9, 27.2, 26.9, 25.6, 22.8, 22.5, 21.6, 21.5, 21.4, 17.4, 12.2.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 43.0

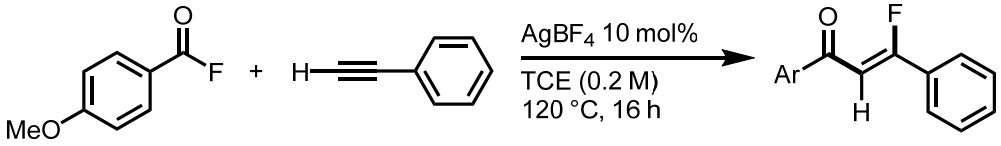
IR (ATR): 2941 w, 2871 w, 1841 w, 1730 s, 1376 m, 1232 s, 1023 m, 965 w, 938 w, 889 w, 771 m, 666 w, 636 w, 608 w, 584 w.

HRMS (ESI+, $[M+Na]^+$) Calcd for $C_{30}H_{45}FO_7Na$: 559.3042. Found: 559.3051.

IV. Optimization Studies

IV-I. Optimization for the reaction conditions

In a glove box filled with nitrogen, $AgBF_4$ (0.020–0.030 mmol, 10–15 mol%) was added to a screw-capped vial and dissolved in TCE (0.5–1.0 mL). Acyl fluoride **1a** (0.20 mmol), alkyne **2a** and TCE (0.5–1.0 mL) were then added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 120–140 ºC for 16–24 h. After the mixture was cooled to rt, $PhCF_3$ was added to the reaction mixture as an internal standard and the reaction was analyzed using ^{19}F NMR.



1a **2a** (2 equiv) **3aa**

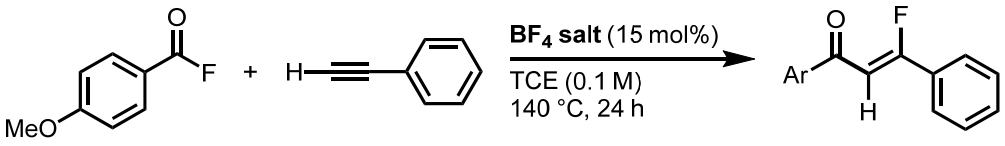
TCE = 1,1,2,2-tetrachloroethane

deviation from standard conditions	^{19}F NMR yields (%)		
	3aa	*Z:E*	recovered **1a**
	25	13:1	68
0.1 M	52	12:1	40
$AgBF_4$ 15 mol%, 0.1 M	62	>20:1	20
$AgBF_4$ 15 mol%, 0.1 M, 140 °C, 24 h	**72**	**>20:1**	**3**

IV-II. BF_4 salt screening in the reaction of 1a

In a glove box filled with nitrogen, BF_4 salt (0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). Acyl fluoride **1a** (0.20 mmol), alkyne **2a** and TCE (1.0 mL) were then added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After the mixture was cooled to rt, $PhCF_3$ was added to the

reaction mixture as an internal standard and the reaction was analyzed using ^{19}F NMR. Based on the results of BF_4 salt screening, $AgBF_4$ was identified as the most effective BF_4 salt.



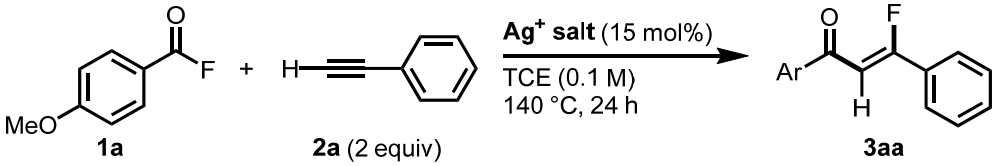
1a **2a** (2 equiv) **3aa**

TCE = 1,1,2,2-tetrachloroethane

BF_4 salt	^{19}F NMR yields (%)		
	3aa	*Z:E*	recovered **1a**
$AgBF_4$	**72**	**>20:1**	3
$ZnBF_4 \cdot nH_2O$	6	*Z* only	3
$LiBF_4$	31	*Z* only	50
$NaBF_4$	4	*Z* only	17
$Ph_3C^+BF_4^-$	61	19:1	1
HBF_4	20	*Z* only	18

IV-III. Ag^+ salt screening in the reaction of 1a

In a glove box filled with nitrogen, Ag^+ salt (0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). Acyl fluoride **1a** (0.20 mmol), alkyne **2a** and TCE (1.0 mL) were then added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After the mixture was cooled to rt, $PhCF_3$ was added into the reaction mixture as an internal standard and the reaction was analyzed using ^{19}F NMR. Based on the results of Ag^+ salt screening, $AgBF_4$ was identified as the most effective Ag^+ salt.



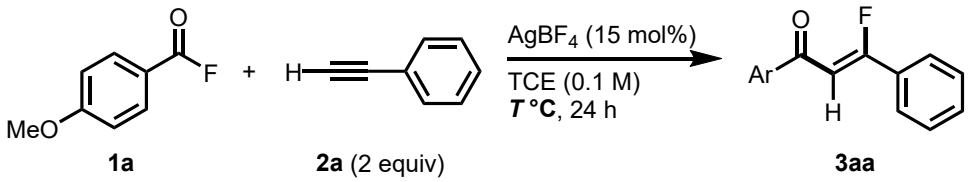
1a **2a** (2 equiv) **3aa**

TCE = 1,1,2,2-tetrachloroethane

Ag^+ salt	^{19}F NMR yields (%)		
	3aa	*Z:E*	recovered **1a**
$AgBF_4$	**72**	**>20:1**	3
$AgSbF_6$	0		18
$AgPF_6$	9	Z only	85
AgOTf	0		>99
AgF	0		>99

IV-IV. Effect of reaction temperature

In a glove box filled with nitrogen, $AgBF_4$ (0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). Acyl fluoride **1a** (0.20 mmol), alkyne **2a** and TCE (1.0 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated for 24 h. After the mixture was cooled to rt, $PhCF_3$ was added into the reaction mixture as an internal standard and the reaction was analyzed using ^{19}F NMR. As a result, 140 ºC was identified as the most effective temperature.



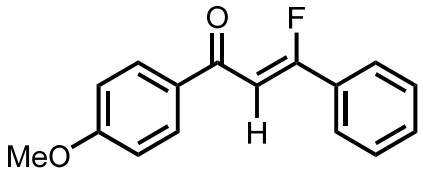
1a **2a** (2 equiv) **3aa**

TCE = 1,1,2,2-tetrachloroethane

***T* (°C)**	^{19}F NMR yields (%)		
	3aa	*Z:E*	recovered **1a**
40	12	*Z* only	88
60	19	16:1	67
80	32	16:1	47
100	43	14:1	28
120	59	12:1	12
140	**72**	**>20:1**	3

V. Spectroscopic Data of Products

(*Z*)-3-Fluoro-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (3aa) [CAS: 2169701-03-3].[11]



This compound was synthesized by following the typical procedure except that $AgBF_4$ (15 mol%) was used. This product **3aa** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5aa** was also formed as a side product in 12% yield.

Pale yellow solid (35.3 mg, 69%). R_f 0.23 (SiO_2, Hexane/EtOAc = 9/1).

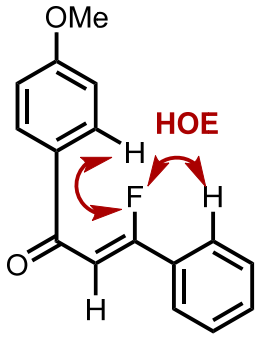
^1H NMR ($CDCl_3$, 400 MHz) δ: 7.98 (d, *J* = 8.9 Hz, 2H), 7.75-7.73 (m, 2H), 7.51-7.44 (m, 3H), 6.98-6.96 (m, 2H), 6.75 (d, *J* = 34.4 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR {^1H} ($CDCl_3$, 101 MHz) δ: 187.2, 164.4 (d, $J_{C\text{-}F}$ = 276.5 Hz), 163.4, 131.27, 131.25, 130.9 (d, $J_{C\text{-}F}$ = 26.5 Hz), 130.6, 128.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 113.6, 101.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 55.3.

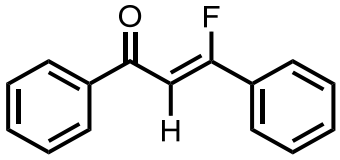
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -101.1 (d, *J* = 34.7 Hz), *E isomer* δ:

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{14}FO_2$: 257.0972. Found: 257.0967.

The stereochemistry of **3aa** was determined by HOESY spectroscopy.



(*Z*)-3-Fluoro-1,3-diphenylprop-2-en-1-one (3ba) [CAS: 82754-29-8].[12]



This compound was synthesized by following the typical procedure, except that **1b** was used instead of **1a**. This product **3ba** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ba** was also formed as a side product in 23% yield.

Pale yellow oil (21.2 mg, 47%). R_f 0.33 (SiO_2, Hexane/EtOAc = 9/1).

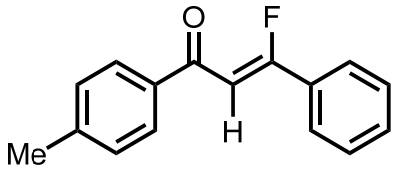
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.99-7.97 (m, 2H), 7.77-7.74 (m, 2H), 7.61-7.56 (m, 1H), 7.54-7.45 (m, 5H), 6.81 (d, *J* = 34.1 Hz, 1H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 188.9, 165.3, 138.6, 132.9, 131.6, 130.8, 128.9, 128.6, 128.3, 125.8, 101.7.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.5 (d, *J* = 34.7 Hz), *E isomer* δ: -81.7 (d, *J* = 22.4 Hz).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{12}FO$: 227.0867. Found: 227.0863.

(*Z*)-3-Fluoro-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (3ca) [CAS: 1420041-40-2].[12]



This compound was synthesized by following the typical procedure, except that **1c** was used instead of **1a**. This product **3ca** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ca** was also formed as a side product in 15% yield.

Pale yellow oil (26.7 mg, 56%). R_f 0.59 (SiO_2, Hexane/EtOAc = 9/1).

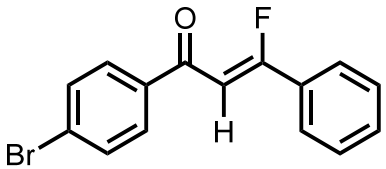
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.88 (d, *J* = 8.2 Hz, 2H), 7.76-7.74 (m, 2H), 7.53-7.44 (m, 3H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 34.4 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 188.5, 164.9, 143.8, 136.0, 131.5, 130.9, 129.2, 128.9, 128.5, 125.8, 101.8, 21.7.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -100.3 (d, *J* = 34.7 Hz), *E isomer* δ: -82.9 (d, *J* = 21.7 Hz)

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{14}FO$: 241.1023. Found: 241.1022.

(*Z*)-1-(4-Bromophenyl)-3-fluoro-3-phenylprop-2-en-1-one (3da) [CAS: 1420041-44-6].[12]



This compound was synthesized by following the typical procedure, except that **1d** was used instead of **1a**. This product **3da** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR, together with an unidentified byproduct (<5%) that could not be separated. Corresponding alkynyl ketone **5da** was also formed as a side product in 20% yield.

Pale yellow solid (24.4 mg, 40%). R_f 0.43 (SiO_2, Hexane/EtOAc = 9/1).

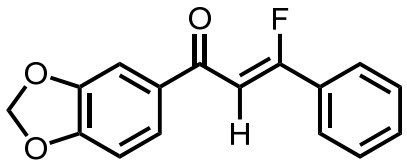
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.83 (m, 2H), 7.76-7.73 (m, 2H), 7.63 (m, 2H), 7.55-7.45 (m, 3H), 6.73 (d, *J* = 33.9 Hz, 1H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 187.8, 165.6 (d, $J_{C\text{-}F}$ = 275.5 Hz), 137.3, 131.8, 131.8, 130.6 (d, $J_{C\text{-}F}$ = 26.0 Hz), 129.9, 129.0 (d, $J_{C\text{-}F}$ = 1.4 Hz), 128.0, 125.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 101.3 (d, $J_{C\text{-}F}$ = 6.7 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: -98.3 (d, J = 34.0 Hz).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{11}{}^{79}BrFO$: 304.9972. Found: 304.9971.

(*Z*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-fluoro-3-phenylprop-2-en-1-one (3ea).



This compound was synthesized by following the typical procedure, except that **1e** was used instead of **1a**. This product **3ea** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ea** was also formed as a side product in 14% yield.

Pale yellow solid (23.7 mg, 43%). R_f 0.33 (SiO_2, Hexane/EtOAc = 9/1). M.p. 102–104 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.52-7.45 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 34.1 Hz, 1H), 6.07 (s, 2H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 186.9, 151.8, 148.2, 131.5, 128.9, 128.9, 125.8, 125.7, 124.7, 108.2, 107.9, 101.9, 101.7, 101.6.

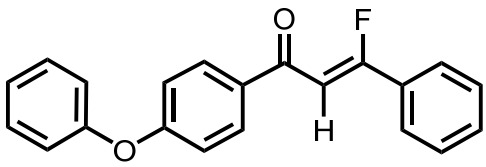
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -100.7 (d, J = 34.0 Hz), *E isomer* δ: -83.9 (d, J = 21.7 Hz).

IR (ATR): 2984 w, 2360 w, 2344 w, 1734 s, 1446 w, 1373 m, 1237 s, 1097 w, 1044 s, 915 m, 848 w, 772 w, 730 s, 648 w, 634 w, 607 w.

MS, *m/z* (relative intensity, %): 270 (M^+, 59), 269 (84), 149 (100), 122 (13), 121 (39), 101 (44), 91 (14), 75 (11), 65 (24), 63 (20),

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{12}FO_3$: 271.0765. Found: 271.0765.

(Z)-3-Fluoro-1-(4-phenoxyphenyl)-3-phenylprop-2-en-1-one (3fa).



This compound was synthesized by following the typical procedure, except that **1f** was used instead of **1a**. This product **3fa** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5fa** was also formed as a side product in 18% yield.

Pale yellow oil (40.1 mg, 62%). R_f 0.33 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (m, 2H), 7.75-7.73 (m, 2H), 7.53-7.38 (m, 5H), 7.23-7.19 (m,

1H), 7.10-7.01 (m, 4H), 6.76 (d, J = 34.1 Hz, 1H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 187.4, 164.8 (d, $J_{C\text{-}F}$ = 277.4 Hz), 161.9, 155.4, 133.0, 131.5, 130.8 (d, $J_{C\text{-}F}$ = 26.5 Hz), 130.7, 130.0, 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.7 (d, $J_{C\text{-}F}$ = 8.2 Hz), 124.6, 120.1, 117.3, 101.6 (d, $J_{C\text{-}F}$ = 7.2 Hz).

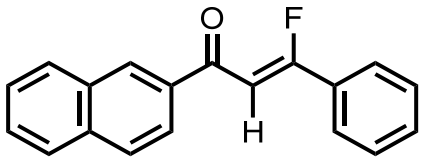
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -100.3 (d, J = 34.0 Hz) *E isomer* δ: -82.9 (d, J = 21.7 Hz).

IR (ATR): 3065 w, 1670 m, 1613 m, 1584 m, 1488 s, 1350 w, 1285 m, 1243 s, 1213 s, 1165 s, 996 m, 870 m, 819 m, 746 m, 689 m, 582 m.

MS, *m/z* (relative intensity, %): 319 (11), 318 (M^+, 58), 317 (100), 290 (13), 197 (37), 149 (37), 141 (23), 121 (12), 115 (31), 101 (35), 77 (26), 51 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{21}H_{16}FO_2$: 319.1129. Found: 319.1129.

(*Z*)-3-Fluoro-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-one (3ga) [CAS: 1420041-50-4].[12]



This compound was synthesized by following the typical procedure, except that **1g** was used instead of **1a**. This product **3ga** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ga** was also formed as a side product in 22% yield.

Pale yellow solid (21.3 mg, 43%). R_f 0.32 (SiO_2, Hexane/EtOAc = 9/1).

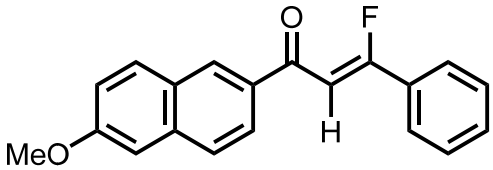
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.47 (s, 1H), 8.08-7.89 (m, 4H), 7.80 (d, J = 7.8 Hz, 2H), 7.63-7.48 (m, 5H), 6.94 (d, J = 34.1 Hz, 1H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 188.7, 165.2, 135.9, 135.5, 132.5, 131.6, 130.9, 129.9, 129.5, 128.9, 128.5, 128.4, 127.8, 126.8, 125.9, 124.2, 101.8.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.6 (d, J = 34.0 Hz), *E isomer* δ: -82.2 (d, J = 21.7 Hz).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{19}H_{14}FO$: 277.1023. Found: 277.1020.

(Z)-3-Fluoro-1-(6-methoxynaphthalen-2-yl)-3-phenylprop-2-en-1-one (3ha).



This compound was synthesized by following the typical procedure, except that **1h** was used instead of **1a**. This product **3ha** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ha** was also formed as a side product in 20% yield.

Pale yellow solid (28.2 mg, 46%). R_f 0.20 (SiO_2, Hexane/EtOAc = 9/1). M.p. 130–132 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.41 (d, J = 0.7 Hz, 1H), 8.05 (dd, J = 8.7, 1.8 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.82-7.78 (m, 3H), 7.55-7.47 (m, 3H), 7.23-7.17 (m, 2H), 6.93 (d, J = 34.4 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 188.4, 164.9, 159.7, 137.2, 133.9, 131.5, 131.1, 131.0, 129.9, 128.9, 127.8, 127.2, 125.8, 124.9, 119.7, 105.7, 101.8, 55.4.

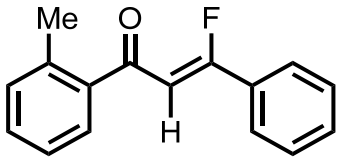
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -100.5 (d, J = 34.7 Hz).

IR (ATR): 2984 w, 1734 s, 1373 m, 1237 s, 1044 s, 915 m, 848 w, 730 s, 648 w, 607 w.

MS, *m/z* (relative intensity, %): 307 (24), 306 (M^+, 100), 305 (79), 278 (18), 263 (12), 185 (36), 158 (13), 157 (28), 149 (35), 142 (18), 121 (10), 114 (25), 101 (30).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{20}H_{16}FO_2$: 307.1129. Found: 307.1127.

(*Z*)-3-Fluoro-3-phenyl-1-(o-tolyl)prop-2-en-1-one (3ia) [Cas: 2222483-29-4].[1]



This compound was synthesized by following the typical procedure, except that **1i** was used instead of **1a**. This product **3ca** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ia** was also formed as a side product in 13% yield.

Pale yellow oil (30.8 mg, 64%). R_f 0.49 (SiO_2, Hexane/EtOAc = 9/1).

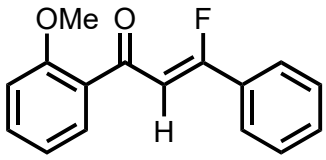
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72-7.70 (m, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.54-7.45 (m, 3H), 7.39 (td, J = 7.3, 1.4 Hz, 1H), 7.30-7.26 (m, 2H), 6.55 (d, J = 34.8 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 193.2, 165.1 (d, $J_{C\text{-}F}$ = 278.0 Hz), 140.0, 136.9, 131.5 (d, $J_{C\text{-}F}$ = 31.6 Hz), 130.7, 130.5, 128.9, 128.9, 128.0, 125.8 (d, $J_{C\text{-}F}$ = 8.6 Hz), 125.6, 105.3 (d, $J_{C\text{-}F}$ = 6.7 Hz), 20.3.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.4 (d, J = 34.7 Hz), *E isomer* δ: -82.2 (d, J = 23.1 Hz).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{14}FO$: 241.1023. Found: 241.1012.

(*Z*)-3-Fluoro-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one (3ja) [CAS: 1420041-42-4].[12]



This compound was synthesized by following the typical procedure, except that **1j** was used instead of **1a**. This product **3ja** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 17/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ja** was also formed as a side product in 12% yield.

Pale yellow oil (20.5 mg, 40%). R_f 0.29 (SiO_2, Hexane/EtOAc = 9/1).

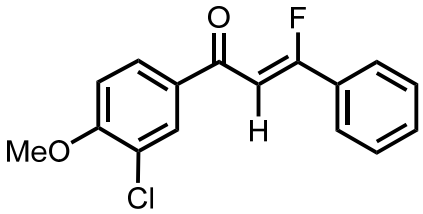
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72-7.63 (m, 3H), 7.51-7.38 (m, 4H), 7.06-6.97 (m, 2H), 6.85 (d, J = 34.8 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 189.8, 164.3 (d, $J_{C\text{-}F}$ = 276.0 Hz), 157.9, 133.0, 133.0, 131.3, 131.2 (d, $J_{C\text{-}F}$ = 26.0 Hz), 130.3, 128.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 120.8, 111.4, 105.9 (d, $J_{C\text{-}F}$ = 4.3 Hz), 55.8.

^{19}F NMR ($CDCl_3$, 376 MHz) *E isomer* δ: -101.6 (d, J = 34.7 Hz), *E isomer* δ: -82.6 (d, J = 21.7 Hz).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{14}FO_2$: 257.0972. Found: 257.0971.

(*Z*)-1-(3-Chloro-4-methoxyphenyl)-3-fluoro-3-phenylprop-2-en-1-one (3ka).



This compound was synthesized by following the typical procedure, except that **1k** was used instead of **1a**. This product **3la** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ka** was also formed as a side product in 17% yield.

Yellow solid (31.3 mg, 54%). R_f 0.2 (SiO_2, Hexane/EtOAc = 9/1). M.p. 138–140 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (d, J = 2.1 Hz, 1H), 7.89 (dd, J = 8.6, 1.9 Hz, 1H), 7.74 (d, J = 7.1 Hz, 2H), 7.51-7.45 (m, 3H), 6.99 (d, J = 8.7 Hz, 1H), 6.72 (d, J = 34.1 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 186.3, 165.2 (d, $J_{C\text{-}F}$ = 274.5 Hz), 158.6, 131.9, 131.6, 130.7 (d, $J_{C\text{-}F}$ = 25.5 Hz), 130.6, 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.9, 125.8 (d, $J_{C\text{-}F}$ = 8.2 H), 122.8, 111.3, 101.2 (d, $J_{C\text{-}F}$ = 7.2 Hz), 56.4.

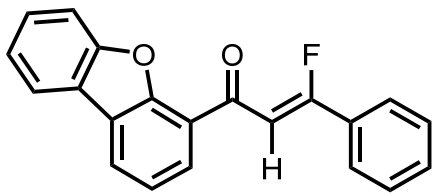
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.6 (d, J = 34.0 Hz), *E isomer* δ: -82.1 (d, J = 21.7 Hz).

IR (ATR): 1667 m, 1609 s, 1593 s, 1496 m, 1449 w, 1409 w, 1344 w, 1276 s, 1202 m, 1058 m, 1012 m, 808 m, 767 m, 701 m, 596 w, 490 w.

MS, *m/z* (relative intensity, %): 292 (M^++2, 16), 291 (41), 290 (M^+, 50), 289 (100), 247 (11), 183 (10), 171 (10), 169 (31), 149 (69), 126 (16), 121 (15), 111 (810), 101 (49), 77 (19), 75 (19), 63 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{13}{}^{35}ClFO$: 291.0583. Found: 291.0583.

(*Z*)-1-(Dibenzo[b,d]furan-4-yl)-3-fluoro-3-phenylprop-2-en-1-one (3la).



This compound was synthesized by following the typical procedure, except that **1l** was used instead

of **1a**. This product **3la** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR, together with an unidentified byproduct (<5%) that could not be separated. Corresponding alkynyl ketone **5la** was also formed as a side product in 16% yield.

Pale yellow solid (33.7 mg, 53%). R_f 0.41 (SiO_2, Hexane/EtOAc = 9/1). M.p. 145–146 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.14 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.10 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.00-7.98 (m, 1H), 7.86-7.84 (m, 2H), 7.65 (m, 1H), 7.57-7.38 (m, 7H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 185.4, 165.7 (d, $J_{C\text{-}F}$ = 278.4 Hz), 156.0, 154.0, 131.7, 131.2 (d, $J_{C\text{-}F}$ = 25.5 Hz), 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.2, 127.8, 126.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 125.6, 125.1, 124.1, 123.4, 123.3, 123.0, 120.7, 111.8, 104.4 (d, $J_{C\text{-}F}$ = 3.9 Hz).

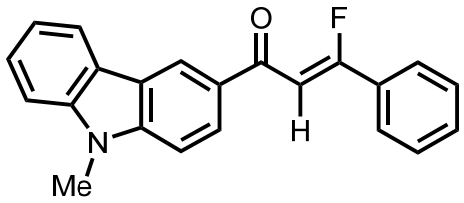
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -98.9 (d, *J* = 34.0 Hz), *E isomer* δ: -78.6 (d, *J* = 21.7 Hz).

IR (ATR): 1667 s, 1608 s, 1494 m, 1450 m, 1412 m, 1287 s, 1224 m, 1181 s, 1115 m, 1057 w, 1031 w, 996 m, 910 w, 843 m, 754 s, 687 m, 637 w, 557 m, 496 w.

MS, *m/z* (relative intensity, %): 317 (10), 316 (M^+, 58), 315 (100), 306 (16), 288 (15), 287 (16), 259 (10), 195 (19), 162 (10), 158 (26), 149 (57), 148 (10), 143 (10), 139 (60), 138 (11), 121 (19), 120 (10), 101 (59), 75 (12), 63 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{21}H_{14}FO_2$: 317.0972. Found: 317.0969.

(*Z*)-3-Fluoro-1-(9-methyl-9H-carbazol-3-yl)-3-phenylprop-2-en-1-one (3ma).



This compound was synthesized by following the typical procedure, except that **1m** was used instead of **1a** and $AgBF_4$ 15 mol% was used. This product **3la** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ma** was also formed as a side product in 16% yield.

Pale yellow solid (24.2 mg, 43%). R_f 0.15 (SiO_2, Hexane/EtOAc = 9/1). M.p. 58–60 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.74 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.81-7.79 (m, 2H), 7.54-7.47 (m, 4H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 34.6 Hz, 1H), 3.87 (s, 3H).

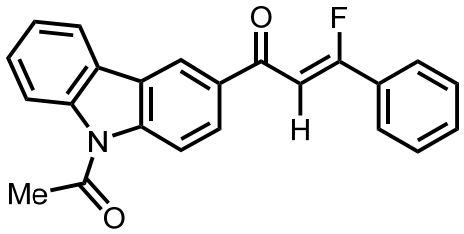
^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 188.3, 164.1 (d, $J_{C\text{-}F}$ = 275.5 Hz), 143.7, 141.7, 131.3 (d, $J_{C\text{-}F}$ = 26.5 Hz), 131.2, 129.9, 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 126.7, 126.5, 125.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 123.0, 122.6, 121.9, 120.6, 120.0, 109.0, 108.2, 102.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 29.3.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -101.9 (d, *J* = 34.7 Hz), *E isomer* δ: -86.0 (d, *J* = 21.7 Hz).

IR (ATR): 3058 w, 1770 w, 1664 s, 1592 s. 1495 m, 1366 m,, 1324 m, 1247 s, 1187 m, 1122 m, 995 m, 914 w, 807 w, 770 s, 749 m, 687 m, 602 w, 542 w.

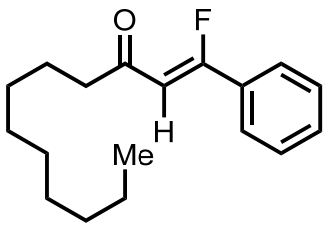
MS, *m/z* (relative intensity, %): 330 (26), 329 (M^+, 100), 328 (38), 302 (10), 301 (47), 300 (13), 285 (10), 208 (45), 181 (17), 180 (29), 164 (20), 152 (31), 151 (11), 149 (13), 142 (10), 101 (18).
HRMS (DART+, $[M+H]^+$) Calcd for $C_{22}H_{17}FNO$: 330.1289. Found: 330.1287.

(*Z*)-1-(9-Acetyl-9*H*-carbazol-3-yl)-3-fluoro-3-phenylprop-2-en-1-one (3na).



This compound was synthesized by following the typical procedure, except that **1n** was used instead of **1a** and $AgBF_4$ 15 mol% was used. This product **3la** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5na** was also formed as a side product in 14% yield.
Yellow solid (29.4 mg, 41%). R_f 0.12 (SiO_2, Hexane/EtOAc = 9/1). M.p. 63–64 °C.
^1H NMR ($CDCl_3$, 400 MHz) δ: 8.63 (d, *J* = 1.4 Hz, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.13-8.09 (m, 2H), 7.81-7.79 (m, 2H), 7.56-7.42 (m, 5H), 6.91 (d, *J* = 34.1 Hz, 1H), 2.93 (s, 3H).
^{13}C NMR {^1H} ($CDCl_3$, 101 MHz) δ: 188.1, 170.1, 165.2 (d, J_{C-F} = 277.9 Hz), 141.5, 139.1, 134.2, 131.6, 130.9 (d, J_{C-F} = 26.5 Hz), 129.0 (d, J_{C-F} = 1.9 Hz), 128.0 (d, J_{C-F} = 10.1 Hz) 128.0, 127.9, 126.6, 126.0, 125.9, 125.8, 124.1, 120.4, 116.1 (d, J_{C-F} = 5.3 Hz), 101.9 (d, J_{C-F} = 7.2 Hz), 27.8.
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.5 (d, J = 34.0 Hz), *E isomer* δ: -82.3 (d, *J* = 21.7 Hz).
IR (ATR): 1734 w, 1698 s, 1668 s, 1606 s, 1484 m, 1451 m, 1425 m, 1368 s, 1291 s, 1242 s, 1197 s, 1009 s, 913 w, 812 w, 751 m, 687 m, 619 w, 542 w.
MS, m/z (relative intensity, %): 358 (33), 357 (M^+, 92), 337 (10), 316 (23), 315 (100), 314 (83), 298 (16), 295 (18), 288 (17), 287 (78), 286 (36), 285 (18), 284 (13), 267 (21), 266 (13), 264 (11), 195 (14), 194 (44), 193 (24), 167 (39), 166 (44), 165 (20), 164 (17), 157 (12), 149 (47), 140 (23), 139 (45), 138 (15), 137 (12), 129 (10), 121 (17), 120 (11), 102 (12), 101 (51), 51 (10).
HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{17}FNO_2$: 358.1238. Found: 358.1233.

(*Z*)-1-Fluoro-1-phenyldodec-1-en-3-one (3oa).



This compound was synthesized by following the typical procedure, except that **1o** was used instead

of **1a**. This product **3ga** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5oa** was also formed as a side product in 20% yield.

Pale yellow oil (31.1 mg, 58%). R_f 0.63 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68-7.65 (m, 2H), 7.51-7.42 (m, 3H), 6.07 (d, *J* = 39.2 Hz, 1H), 2.78 (td, *J* = 7.4, 2.4 Hz, 2H), 1.70-1.63 (m, 2H), 1.30-1.27 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 199.2, 164.8, 131.5, 130.6, 128.9, 125.7, 106.4, 43.8, 31.9, 29.5, 29.3, 29.3, 29.3, 24.1, 22.7, 14.1.

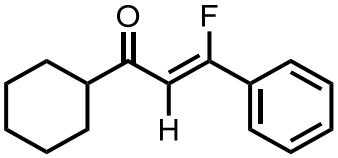
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -99.5 (d, *J* = 39.0 Hz).

IR (ATR): 2984 w, 1769 w, 1737 s, 1447 w, 1372 m, 1301 w, 1234 s, 1097 w, 1043 s, 938 w, 848 w, 773 m, 634 w, 607 w, 468 w.

MS, *m/z* (relative intensity, %): 177 (14), 165 (18), 164 (99), 163 (83), 150 (34), 149 (100), 122 (13), 121 (25), 101 (53), 55 (13), 41 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{18}H_{26}FO$: 277.1962. Found: 277.1960.

(*Z*)-1-Cyclohexyl-3-fluoro-3-phenylprop-2-en-1-one (3pa) [CAS: 2222483-39-6].[1]



This compound was synthesized by following the typical procedure, except that **1p** was used instead of **1a**. This product **3pa** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5pa** was also formed as a side product in 22% yield.

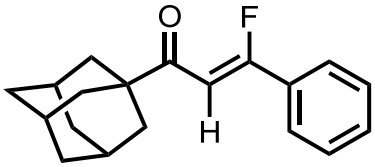
Pale yellow oil (25.5 mg, 48%). R_f 0.50 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.67-7.65 (m, 2H), 7.50-7.42 (m, 3H), 6.11 (d, *J* = 38.5 Hz, 1H), 2.82-2.76(m, 1H), 1.95-1.92 (m, 2H), 1.84-1.81 (m, 2H), 1.73-1.69 (m, 1H), 1.46-1.19 (m, 5H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 201.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 164.3 (d, $J_{C\text{-}F}$ = 275.1 Hz), 131.5, 130.9 (d, $J_{C\text{-}F}$ = 27.8 Hz), 128.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 105.0 (d, $J_{C\text{-}F}$ = 8.6 Hz), 51.0 (d, $J_{C\text{-}F}$ = 3.8 Hz), 28.8, 26.0, 25.9.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{18}FO$: 233.1336. Found: 233.1336.

(*Z*)-1-(Adamantan-1-yl)-3-fluoro-3-phenylprop-2-en-1-one (3qa).



This compound was synthesized by following the typical procedure, except that **1q** was used instead

of **1a**. This product **3qa** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5qa** was also formed as a side product in 19% yield.

Pale yellow solid (32.4 mg, 57%). R_f 0.64 (SiO_2, Hexane/EtOAc = 9/1). M.p. 91–93 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.70-7.67 (m, 2H), 7.50-7.41 (m, 3H), 6.49 (d, *J* = 33.9 Hz, 1H), 2.08 (s, 3H), 1.87 (d, *J* = 2.7 Hz, 6H), 1.78-1.68 (m, 6H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 202.1, 165.2 (d, $J_{C\text{-}F}$ = 276.5 Hz), 131.3, 131.2 (d, $J_{C\text{-}F}$ = 26.5 Hz), 128.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.7 (d, $J_{C\text{-}F}$ = 8.2 Hz), 99.3 (d, $J_{C\text{-}F}$ = 5.3 Hz), 46.4, 38.1, 36.5, 27.9.

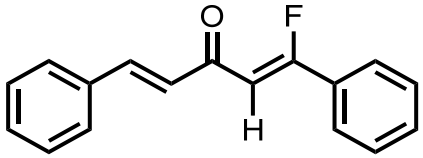
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -101.7 (d, *J* = 34.0 Hz), *E isomer* δ: -80.5 (d, *J* = 24.1 Hz).

IR (ATR): 2901 s, 2849 m, 1684 s, 1612 s, 1577 m, 1496 w, 1449 m, 1347 w, 1277 m, 1197 w, 1159 m, 1059 w, 1032 m, 1012 s, 999 w, 973 w, 853 w, 766 m, 741 w, 687 m, 677 w, 591 m.

MS, *m/z* (relative intensity, %): 257 (13), 256 (68), 149 (38), 136 (70), 135 (100), 121 (11), 107 (51), 101 (37), 93 (86), 91 (23), 81 (23), 79 (87), 77 (27), 67 (32), 55 (18), 41 (22).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{19}H_{22}FO$: 285.1649. Found: 285.1651.

(1*Z*,4*E*)-1-Fluoro-1,5-diphenylpenta-1,4-dien-3-one (3ra).



This compound was synthesized by following the typical procedure, except that **1r** was used instead of **1a**. This product **3ra** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 5/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ra** was also formed as a side product in 10% yield.

Pale yellow oil (16.7 mg, 33%). R_f 0.29 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73-7.69 (m, 3H), 7.64-7.60 (m, 2H), 7.53-7.39 (m, 6H), 7.28 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.33 (d, *J* = 37.3 Hz, 1H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 187.5, 164.9 (d, $J_{C\text{-}F}$ = 270.7 Hz), 143.2, 134.8, 131.6, 130.8, 130.4, 128.9, 128.4, 126.1 (d, $J_{C\text{-}F}$ = 5.8 Hz), 125.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 106.1, 106.1.

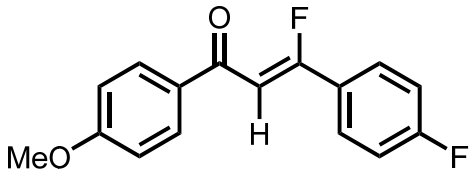
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.5 (d, *J* = 37.6 Hz), *E isomer* δ: -82.1 (d, *J* = 21.7 Hz).

IR (ATR): 3060 w, 3027 w, 1648 s, 1625 s, 1593 s, 1576 m, 1496 m, 1448 m, 1337 s, 1284 m, 1194 m,1098 m, 1053 m, 1031 w, 979 m, 923 w, 874 w, 839 w, 767 m, 758 m, 726 w, 687 m, 634 w, 557 m, 490 w.

MS, *m/z* (relative intensity, %): 253 (M^+, 11), 252 (74), 251 (100), 203 (13), 202 (10), 149 (41), 147 (10), 146 (18), 131 (23), 121 (16), 109 (17), 103 (44), 102 (29), 101 (58), 91 (22), 77 (47), 76 (11), 75 (18), 51 (24).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{17}H_{14}FO$: 253.1023. Found: 253.1016.

(*Z*)-3-Fluoro-3-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (3ab).



This compound was synthesized by following the typical procedure, except that **2b** was used instead of **2a**. This product **3ab** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 10/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ab** was also formed as a side product in 18% yield.

Pale yellow solid (30.2 mg, 55%). R_f 0.17 (SiO_2, Hexane/EtOAc = 9/1). M.p. 166–169 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.96 (d, *J* = 4.4 Hz, 2H), 7.75-7.71 (m, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 6.96 (dt, *J* = 9.5, 2.4 Hz, 2H), 6.68 (d, *J* = 34.3 Hz, 1H), 3.89 (d, *J* = 5.5 Hz, 3H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 187.2, 164.5 (d, $J_{C\text{-}F}$ = 253.0 Hz), 163.6 (d, $J_{C\text{-}F}$ = 276.0 Hz), 163.5, 131.3, 130.7, 127.9 (d, $J_{C\text{-}F}$ = 17.3 Hz), 127.9, 127.2 (dd, $J_{C\text{-}F}$ = 26.8, 2.9 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.1 Hz), 113.8, 101.6 (d, $J_{C\text{-}F}$ = 6.8 Hz).

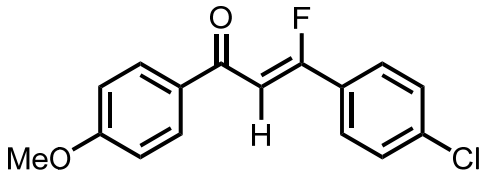
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -100.6 (d, *J* = 34.7 Hz), -110.5.

IR (ATR): 2923 w, 1737 w, 1663 m, 1600 s, 1573 m, 1508 s, 1423 m, 1290 m, 1227 s, 1189 m, 1165 m, 1109 w, 1029 m, 889 w, 843 m, 813 s, 557 w, 508 w

MS, *m/z* (relative intensity, %): 274 (54), 273 (77), 246 (19), 231 (19), 167 (32), 139 (15), 135 (100), 119 (21), 108 (21), 107 (22), 92 (18), 77 (29).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{13}F_2O_2$: 275.0878. Found: 275.0879.

(*Z*)-3-(4-Chlorophenyl)-3-fluoro-1-(4-methoxyphenyl)prop-2-en-1-one (3ac).



This compound was synthesized by following the typical procedure, except that **2c** was used instead of **2a**. This product **3ac** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 10/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ac** was also formed as a side product in 18% yield.

Pale yellow solid (35.0 mg, 60%). R_f 0.15 (SiO_2, Hexane/EtOAc = 9/1). M.p. 140–144 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.95 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.44 (s, 1H), 7.42 (s, 1H), 6.96 (d, *J* = 9.2 Hz, 2H), 6.71 (d, *J* = 34.3 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 187.2, 163.6, 163.3 (d, $J_{C\text{-}F}$ = 275.1 Hz), 137.5, 131.2, 130.7, 129.5 (d, $J_{C\text{-}F}$ = 26.8 Hz), 129.2, 126.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 113.8, 102.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 55.5.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -101.8 (d, *J* = 34.7 Hz), *E isomer* δ: -84.6 (d, *J* = 23.1 Hz).

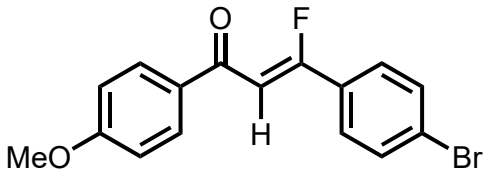
IR (ATR): 1660 m, 1607 s, 1572 m, 1491 m, 1422 m, 1345 m, 1287 m, 1259 s, 1221 m, 1185 m, 1091

m, 1029 m, 1011 m, 889 m, 814 s, 768 w, 606 w, 502 w.

MS, *m/z* (relative intensity, %): 292 (M^+, 13), 291 (27), 290 (37), 289 (69), 262 (16), 247 (12), 183 (27), 135 (100), 120 (30), 108 (22), 107 (21), 92 (19), 77 (29).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{13}{}^{35}ClFO_2$: 291.0583. Found: 291.0583.

(*Z*)-3-(4-Bromophenyl)-3-fluoro-1-(4-methoxyphenyl)prop-2-en-1-one (3ad).



This compound was synthesized by following the typical procedure, except that **2d** was used instead of **2a** and alkyne (3equiv) was used. This product **3ad** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 8/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ad** was also formed as a side product in 17% yield. When 2 equiv of alkyne was used, the yield was slightly decreased.

Pale yellow solid (39.5 mg, 58%). R_f 0.09 (SiO_2, Hexane/EtOAc = 9/1). M.p. 146–148 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.95 (d, *J* = 7.0 Hz, 2H), 7.59 (s, 4H), 6.96 (d, *J* = 6.9 Hz, 2H), 6.72 (d, *J* = 34.4 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR {^1H} ($CDCl_3$, 101 MHz) δ: 187.2, 163.6, 163.3, 132.2, 131.2, 130.8, 130.0, 127.1, 125.9, 113.8, 102.3, 55.5.

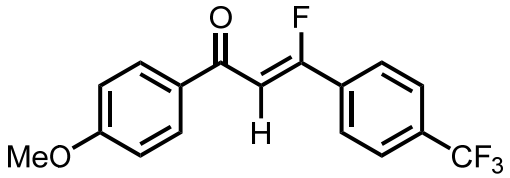
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -102.0 (d, *J* = 34.7 Hz), *E isomer*: -85.0 (d, *J* = 22.4 Hz).

IR (ATR): 2987 w, 1660 m, 1607 s, 1488 m, 1421 m, 1344 w, 1287 m, 1258 m, 1221 m, 1187 m, 1006 m, 889 w, 813 s, 773 m, 689 w, 601 w, 502 w.

MS, *m/z* (relative intensity, %): 336 (M^+, 100), 335 (53), 334 (27), 333 (52), 306 (11), 226 (11), 184 (11), 183 (11), 148 (18), 135 (100), 120 (31), 108 (25), 107 (21), 92 (21), 77 (31).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{13}{}^{79}BrFO_2$: 335.0078. Found: 335.0077.

(*Z*)-3-Fluoro-1-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3ae).



This compound was synthesized by following the typical procedure, except that **2e** was used instead of **2a** and $AgBF_4$ 30 mol% was used for 48 h. This product **3ae** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 10/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ae** was also formed as a side product in 25% yield.

Pae yellow solid (29.8 mg, 46%). R_f 0.19 (SiO_2, Hexane/EtOAc = 9/1). M.p. 144–148 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.99-7.96 (m, 2H), 7.85 (s, 1H), 7.83 (s, 1H), 7.74 (s, 1H), 7.71 (s, 1H), 6.99-6.96 (m, 2H), 6.79 (d, J = 34.3 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 187.1, 163.8, 161.0, 134.4 (d, J_{C-F} = 27.8 Hz), 132.8 (q, J_{C-F} = 32.6 Hz,), 130.9, 129.0 (d, J_{C-F} = 6.7 Hz,), 125.9, 125.1 (q, J_{C-F} = 3.7 Hz), 123.6 (q, J_{C-F} = 272.5 Hz), 113.9, 103.7 (d, J_{C-F} = 7.7 Hz), 56.5.

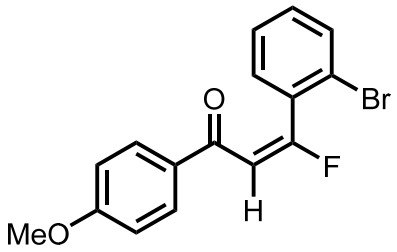
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -65.9, -102.7 (d, J = 34.7 Hz), *E isomer* δ: -66.0, -85.4 (d, J = 23.1 Hz).

IR (ATR): 1738 s, 1668 m, 1612 s, 1509 w, 1373 m, 1326 s, 1290 w, 1242 s, 1175 s, 1120 s, 1046 m, 1015 m, 849 m, 773 m, 506 w.

MS, *m/z* (relative intensity, %): 325 (M^+, 10), 324 (59), 323 (68), 296 (25), 281 (13), 217 (18), 169 (11), 135 (100), 120 (11) 108 (17), 107 (17), 92 (16), 77 (24).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{17}H_{13}F_4O_2$: 325.0846. Found: 325.0843.

(*E*)-3-(2-Bromophenyl)-3-fluoro-1-(4-methoxyphenyl)prop-2-en-1-one (3af).



This compound was synthesized by following the typical procedure, except that **2f** was used instead of **2a** and alkyne 3 equiv was used. This product **3ga** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 1/2.5), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5af** was also formed as a side product in 14% yield. When 2 equiv of alkyne was used, the yield was slightly decreased.

Pale yellow oil (45.6 mg, 68%). R_f 0.12 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 6.98-6.96 (m, 2H), 6.63 (dd, J = 34.0, 1.3 Hz, 1H), 3.88 (d, J = 1.1 Hz, 3H)

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 187.3, 163.7, 162.5, 134.0, 132.8, 131.8, 131.0, 130.9, 130.7, 127.6, 121.6, 113.8, 108.2, 55.5.

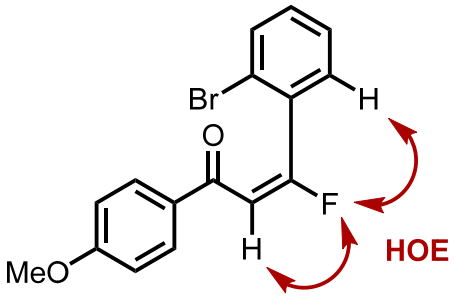
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -89.3 (d, J = 34.0 Hz).

IR (ATR): 1675 m, 1599 s, 1510 m, 1469 w, 1308 w, 1252 s, 1171 s, 1027 m, 996 m, 828 m, 785 s, 760 s, 580 w.

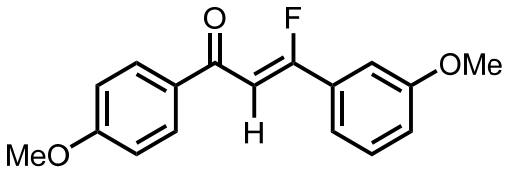
MS, *m/z* (relative intensity, %): 256 (18), 255 (100), 212 (21), 135 (41), 120 (27), 107 (14), 92 (25), 77 (34), 64 (16), 63 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{13}{}^{79}BrFO_2$: 335.0078. Found: 335.0075.

The stereochemistry of **3af** was determined by HOESY spectroscopy.



(*Z*)-3-Fluoro-3-(3-methoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (3ag).



This compound was synthesized by following the typical procedure, except that **2g** was used instead of **2a** at 120 °C. This product **3ga** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = 18/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ag** was also formed as a side product in 20% yield.

Pale yellow solid (28.1 mg, 49%). R_f 0.10 (SiO_2, Hexane/EtOAc = 9/1). M.p. 55–58 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.96 (d, *J* = 8.7 Hz, 2H), 7.39-7.31 (m, 2H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.03 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.99-6.95 (m, 2H), 6.72 (d, *J* = 34.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 187.4, 164.2, 163.5, 159.8, 132.3, 131.4, 130.7, 129.9, 118.1, 117.0, 113.7, 111.1, 102.1, 55.5, 55.4.

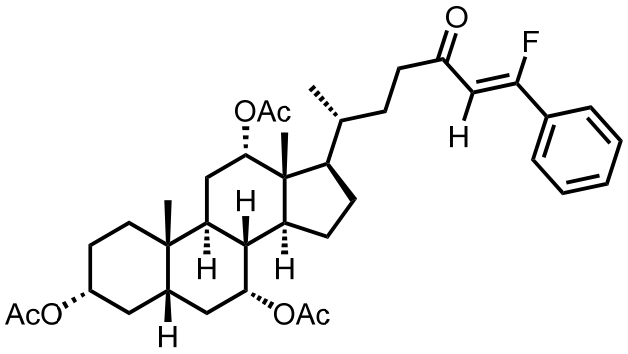
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -100.6 (d, *J* = 34.7 Hz), *E isomer* δ: -85.4 (d, *J* = 22.4 Hz).

IR (ATR): 2839 w, 1667 m, 1599 s, 1509 m, 1489 m, 1456 w, 1258 m, 1233 s, 1170 s, 1046 m, 895 w, 822 m, 787 m, 691 w, 587 w, 509 w.

MS, *m/z* (relative intensity, %): 286 (50), 285 (72), 255 (19), 179 (20), 136 (29), 135 (100), 108 (29), 107 (36), 92 (31), 77 (52), 64 (17), 63 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{17}H_{16}FO_3$: 287.1078. Found: 287.1078.

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*,*Z*)-7-Fluoro-5-oxo-7-phenylhept-6-en-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate (3sa).



This compound was synthesized by following the typical procedure, except that **1s** was used instead of **1a** and $AgBF_4$ 10 mol% at 120 °C. This product **3sa** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5sa** was also formed as a side product in 18% yield.

Pale yellow solid (46.0 mg, 36%). R_f 0.15 (SiO_2, Hexane/EtOAc = 9/1). M.p. 80–83 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.65-7.63 (m, 2H), 7.50-7.42 (m, 3H), 6.05 (d, *J* = 39.2 Hz, 1H), 5.09 (s, 1H), 4.89 (d, *J* = 2.5 Hz, 1H), 4.59-4.53 (m, 1H), 2.79-2.69 (m, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.96-1.19 (m, 20H), 1.08-0.95 (m, 2H), 0.90 (s, 3H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.73 (s, 3H).

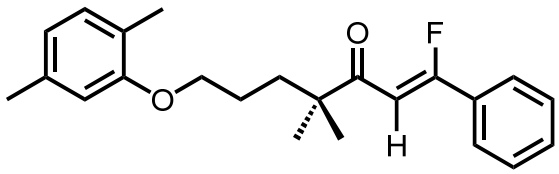
^{13}C NMR {^1H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 198.9, 170.3, 170.3, 170.1, 164.6, 131.4, 130.3, 128.7, 125.5, 106.2, 75.2, 73.8, 70.5, 47.2, 44.9, 43.2, 40.7, 40.4, 37.5, 34.5, 34.5, 34.4, 34.1, 31.0, 29.6, 28.7, 27.0, 26.7, 25.4, 22.6, 22.3, 21.4, 21.3, 21.2, 17.5, 12.0.

^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -99.4 (d, *J* = 39.0 Hz), *E isomer* δ: -81.3 (d, *J* = 22.4 Hz).

IR (ATR): 2940 w, 2870 w, 2158 w, 1982 w, 1733 s, 1572 w, 1448 w, 1377 w, 1249 s, 1200 w, 1024 w, 773 w, 703 w, 455 m. 433 m, 418 m, 410 m.

HRMS ESI+, $[M+Na]^+$) Calcd for $C_{38}H_{51}FO_7Na$: 661.3511. Found: 661.3512.

(Z)-7-(2,5-Dimethylphenoxy)-1-fluoro-4,4-dimethyl-1-phenylhept-1-en-3-one (3ta).



This compound was synthesized by following the typical procedure, except that **1t** was used instead of **1a** at 80 °C. This product **3ta** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ta** was also formed as a side product in 24% yield.

Pale yellow oil (15.7 mg, 31%). R_f 0.37 (SiO_2, Hexane/EtOAc = 9/1).

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.68-7.66 (m, 2H), 7.49-7.42 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 6.50 (d, *J* = 33.2 Hz, 1H), 3.93 (t, *J* = 5.6 Hz, 2H), 2.29 (s, 3H), 2.13

(s, 3H), 1.84-1.74 (m, 4H), 1.25 (s, 6H).

^{13}C NMR {^{1}H} ($CDCl_3$, 101 MHz) δ: 201.9, 165.4 (d, $J_{C\text{-}F}$ = 277.0 Hz), 156.8, 136.5, 131.4, 131.0 (d, $J_{C\text{-}F}$ = 26.0 Hz), 130.2, 128.8 (d, $J_{C\text{-}F}$ = 1.4 Hz), 125.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 123.4, 120.6, 111.8, 99.7 (d, $J_{C\text{-}F}$ = 4.8 Hz), 67.7, 47.3, 36.6, 24.9, 24.4, 21.4, 15.7.

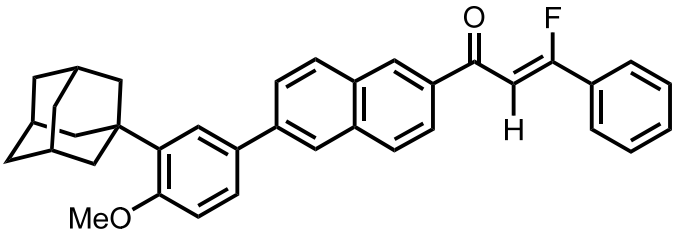
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -101.0 (d, *J* = 48.4 Hz), *E isomer* δ: -78.5 (d, *J* = 23.1 Hz).

IR (ATR): 2957 w, 1691 m, 1614 s, 1578 m, 1508 m, 1449 m, 1389 w, 1345 w, 1309 w, 1265 m, 1157 m, 1130 m, 1038 s, 804 m, 767 m, 688 m, 640 w, 587 w.

MS, *m/z* (relative intensity, %): 257 (13), 256 (68), 149 (38), 136 (70), 135 (100), 121 (11), 107 (51), 101 (37), 93 (86), 91 (23), 81 (23), 79 (87), 77 (27), 67 (32), 55 (18), 41 (22).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{28}FO_2$: 355.2068. Found: 355.2074.

(*Z*)-1-(6-(3-((3r,5r,7r)-Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-3-fluoro-3-phenylprop-2-en-1-one (3ua).



This compound was synthesized by following the typical procedure, except that **1u** was used instead of **1a**. This product **3ua** was obtained as a mixture of *E*/*Z* isomers (*Z*/*E* = >20/1), which was determined by ^{19}F NMR. Corresponding alkynyl ketone **5ua** was also formed as a side product in 18% yield.

Pale yellow solid (67.4 mg, 64%). R_f 0.26 (SiO_2, Hexane/EtOAc = 9/1). M.p. 172–175 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.48 (s, 1H), 8.09-7.95 (m, 4H), 7.82-7.74 (m, 3H), 7.62 (s, 1H), 7.56-7.50 (m, 4H), 7.01-6.91 (m, 2H), 3.91 (s, 3H), 2.20 (s, 6H), 2.12 (s, 3H), 1.82 (s, 6H).

^{13}C NMR {^{1}H, ^{19}F} ($CDCl_3$, 101 MHz) δ: 188.5, 165.1, 158.9, 141.6, 139.0, 136.0, 135.5, 132.4, 131.5, 131.2, 131.0, 129.9, 129.7, 128.9, 128.5, 126.5, 125.9, 125.8, 125.7, 124.7, 124.5, 112.1, 101.9, 55.1, 40.6, 37.2, 37.1, 29.1.

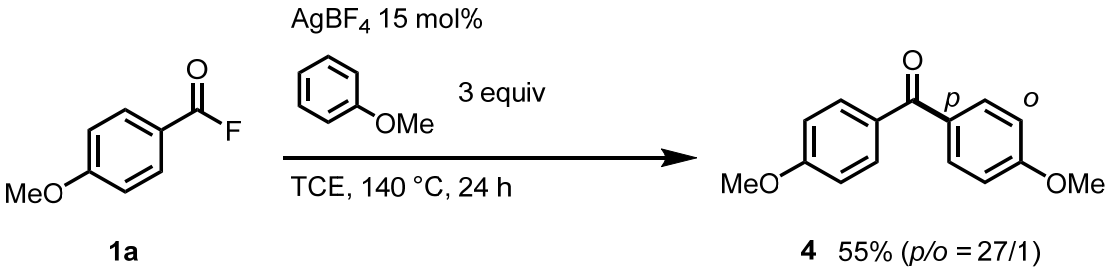
^{19}F NMR ($CDCl_3$, 376 MHz) *Z isomer* δ: -100.0 (d, *J* = 34.7 Hz), *E isomer* δ: -82.6 (d, *J* = 21.7 Hz).

IR (ATR): 2901 s, 1667 s, 1604 s, 1472 m, 1342 w, 1285 s, 1237s, 1173 m, 1139 m, 1030 m, 907 s, 768 m, 730 s, 687 m, 648 w, 601 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{36}H_{34}FO_2$: 517.2537. Found: 517.2537.

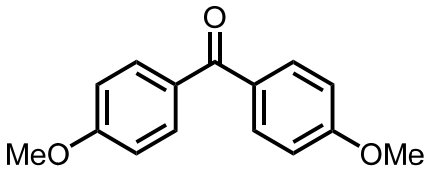
VI. Mechanistic Studies

VI-I. Silver-catalyzed Friedel-Crafts acylation of anisole using 1a



In a glove box filled with nitrogen, $AgBF_4$ (5.7 mg, 0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). Acyl fluoride **1a** (30.8 mg, 0.20 mmol), anisole (64.9 mg, 0.60 mmol, 3 equiv) and TCE (1.0 mL) were then added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After the mixture was cooled to rt, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give **4**.

Bis(4-methoxyphenyl)methanone (4) [CAS: 90-96-0].[13]



This product **4** was obtained as a mixture of regioisomers (*p*/*o* = 27/1), which was determined by ^{1}H NMR.

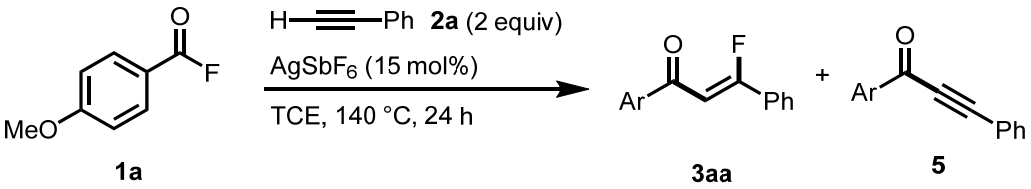
White solid (26.7 mg, 55%). R_f 0,50 (SiO_2, Hexane/EtOAc = 9/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78-7.77 (m, 4H), 6.98-6.94 (m, 4H), 3.88 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 194.4, 162.8, 132.2, 130.7, 113.4, 55.4.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{15}O_3$: 243.1016. Found: 243.1017.

VI-II. Intermolecular insertion of 1a using $AgSbF_6$ in the presence of ^{n}Bu$_4$NBF$_4$

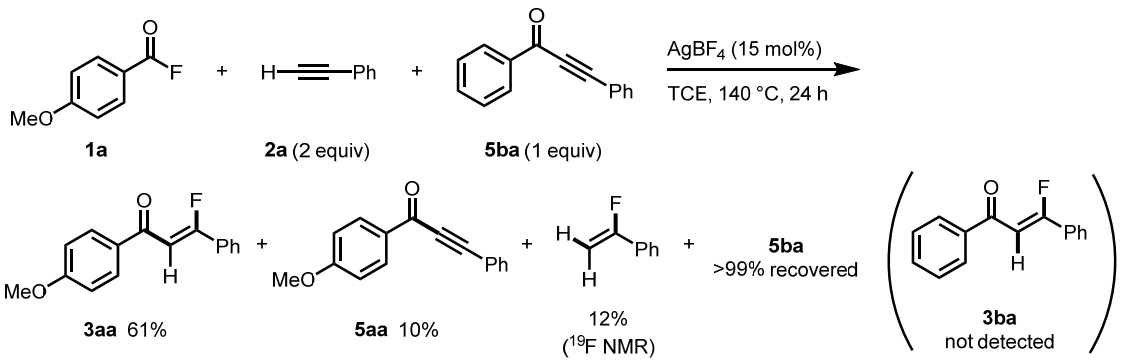


deviation of reaction conditions	**3aa** (%)	**5** (%)	**1a** (%)
none	0	15	18
^{n}Bu$_4$NBF$_4$ 1 equiv	55	10	2

In a glove box filled with nitrogen, $AgSbF_6$ (5.7 mg, 0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). **1a** (30.8 mg, 0.20 mmol), **2a** (40.8 mg, 0.40 mmol, 2 equiv), and TCE (1.0 mL) were then added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After the mixture was cooled to rt, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give **5** (7.0 mg, 15%) with **1a** (5.6 mg, 18%) being recovered. The desired **3aa** was not observed.

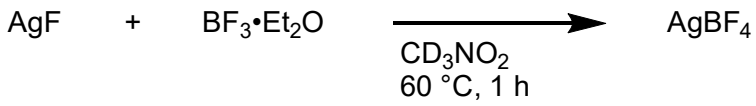
When the same reaction was conducted with $^{n}Bu_4NBF_4$ (65.9 mg, 0.20 mmol, 1.0 equiv), **3aa** was obtained in 55% isolated yield (28 mg), along with **5** (4.7 mg, 10%) and recovered **1a** (0.6 mg, 2%).

VI-III. Disproof of the intermediacy of alkynyl ketones using 1a in the presence of 5ba.

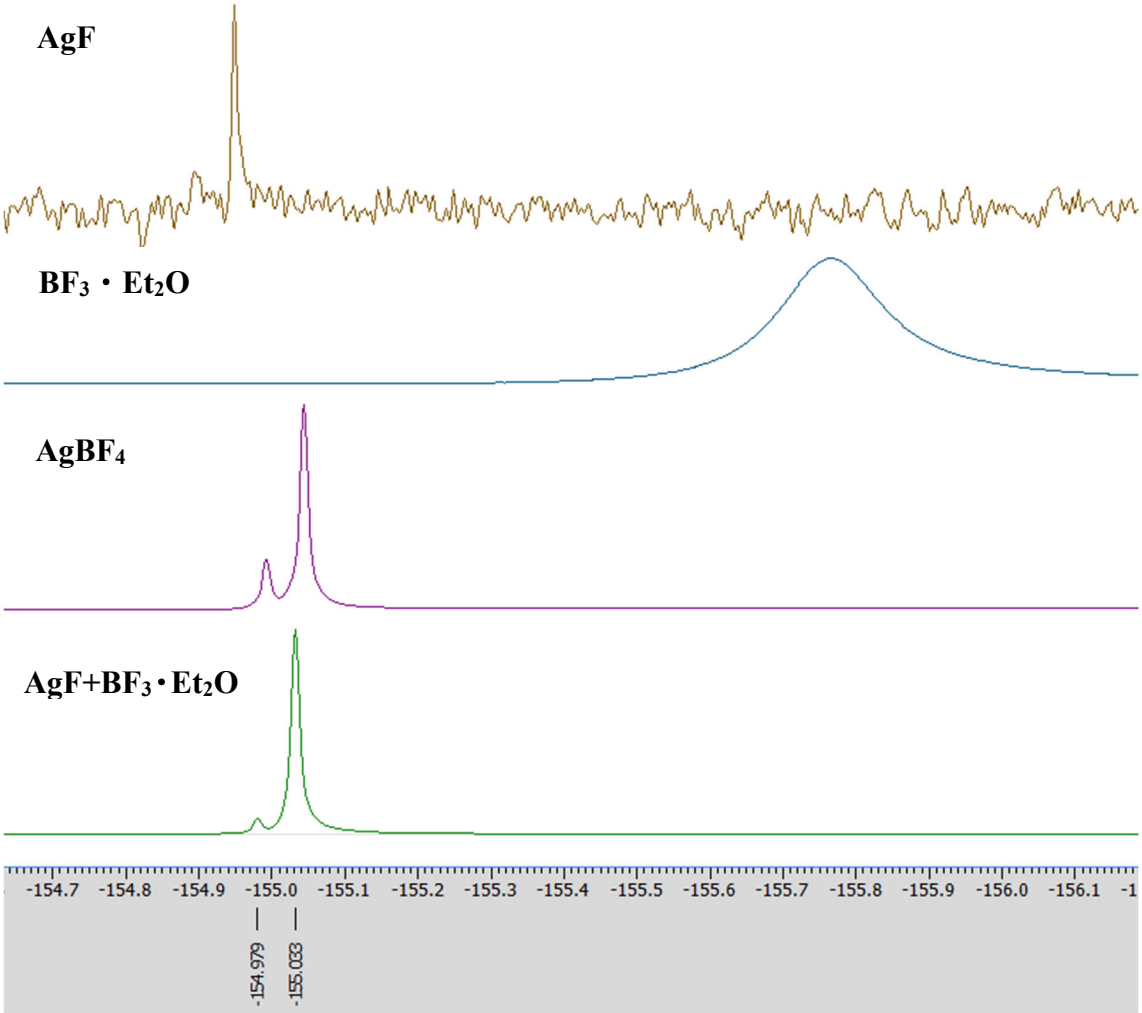


In a glove box filled with nitrogen, $AgBF_4$ (5.7 mg, 0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). **1a** (30.8 mg, 0.20 mmol), **2a** (40.8 mg, 0.40 mmol, 2 equiv), **5ba** (41.2 mg, 0.20 mmol, 1 equiv) and TCE (1.0 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After the mixture was cooled to rt, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give **3aa** (31.2 mg, 61%), **5aa** (4.7 mg, 10%) and α-fluorostyrene (12% in ^{19}F NMR). HF adduct of **5ba** (i.e., **3ba**) was not observed, and **5ba** was quantitatively recovered. As outlined in Scheme 4, the formation of byproduct **5** is accompanied by the generation of a proton. We propose that this proton can protonate phenylacetylene (**2a**) to form a vinyl cation intermediate, which is subsequently trapped by BF_4^- to afford the observed α-fluorostyrene. Notably, the yield of α-fluorostyrene (12%) closely matches that of byproduct 5aa (10%), providing supporting evidence for a common origin involving proton generation. This correlation is consistent with the proposed mechanism.

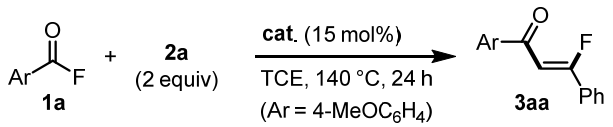
VI-IV. Generation of $AgBF_4$ by reacting AgF and BF_3[14]



The formation of $AgBF_4$ from AgF and BF_3 was confirmed by NMR spectroscopy. In a glove box filled with nitrogen, AgF (3.7 mg, 0.030 mmol), $BF_3{\cdot}Et_2O$ (4.2 mg, 0.020 mmol) and $PhCF_3$ as an internal standard were added to a J-Young NMR tube and dissolved in CD_3NO_2 (0.50 mL). The tube was sealed and removed from the glove box. The reaction mixture was heated at 60 °C for 1 h. The ^{19}F NMR spectrum of the reaction mixture was consistent with that of an authentic sample of $AgBF_4$. Minor ^{19}F NMR signals observed downfield of the BF_4^- species are attributed to F species bound to ^{10}B.[15]

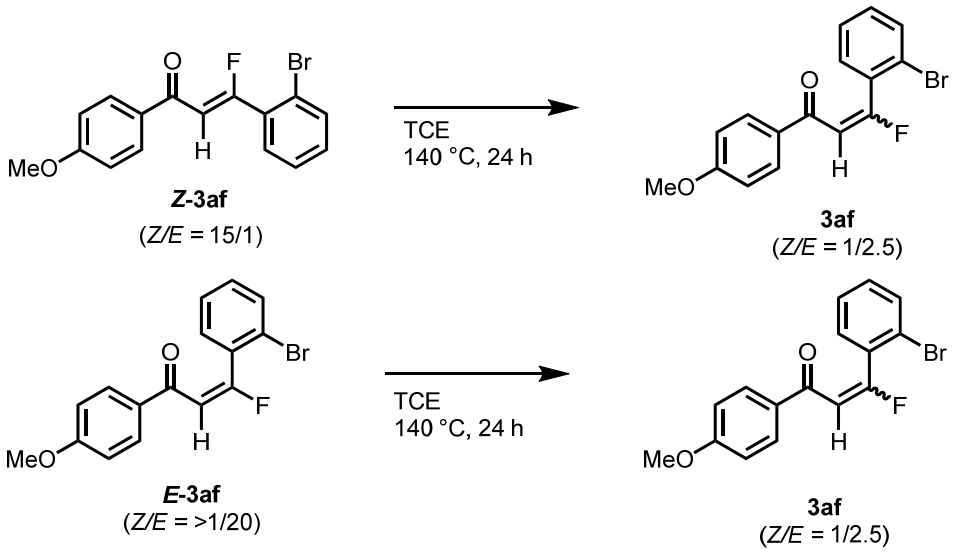


The in situ formation of $AgBF_4$ from AgF and BF_3 under the reaction conditions was further supported by the following experiments. In a glove box filled with nitrogen, the catalyst (0.030 mmol, 15 mol%) was added to a screw-capped vial and dissolved in TCE (1.0 mL). **1a** (30.8 mg, 0.20 mmol), **2a** (40.8 mg, 0.40 mmol, 2 equiv) and TCE (1.0 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 140 ºC for 24 h. After cooling to room temperature, the reaction mixtures were analyzed by ^{19}F NMR spectroscopy. AgF alone did not afford **3aa**; however, combining AgF with $BF_3{\cdot}OEt_2$ resulted in a higher yield of **3aa** than that obtained using $BF_3{\cdot}OEt_2$ alone. These results indicate that a more active catalyst, $AgBF_4$, is generated in situ from AgF and $BF_3{\cdot}OEt_2$ under these conditions.



cat.	yield of **3aa** [%]	recovered **1a** [%]
AgF	0	>99
$BF_3{\cdot}Et_2O$	52	2
AgF + $BF_3{\cdot}Et_2O$	60	5
$AgBF_4$	**72**	**3**

VI-V. *E*/*Z* isomerization of the product



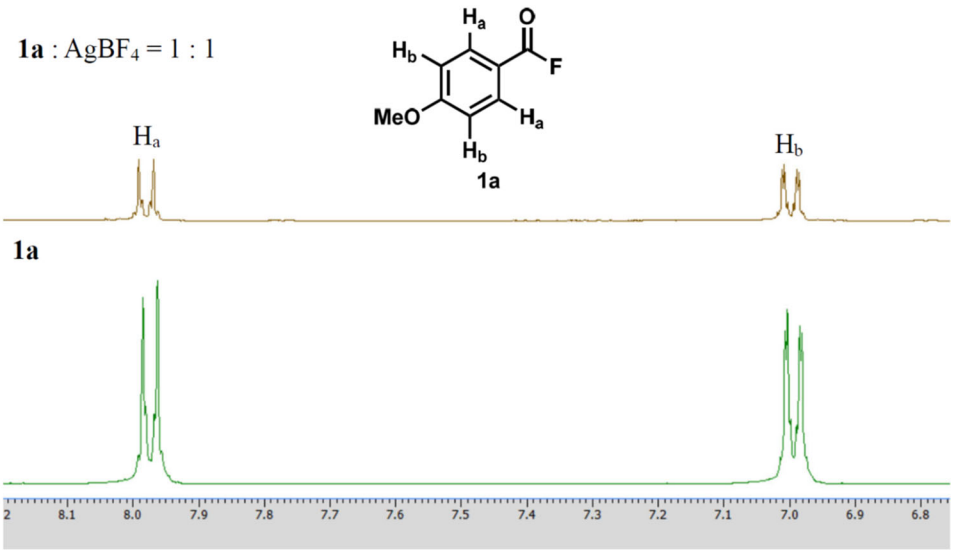
Independently prepared *E*- and *Z*-isomers of **3af** (35.0 mg, 0.10 mmol) were each dissolved in TCE (1.0 mL) in screw-capped vials and heated at 140 °C for 24 h. After cooling to room temperature, the reaction mixtures were analyzed by ^{19}F NMR spectroscopy. In both cases, the same isomeric ratio (*Z*/*E* = 1/2.5) was obtained in the absence of $AgBF_4$. These results indicate that thermal *E*/*Z* isomerization

occurs without a catalyst, and that the observed isomer ratio reflects the thermodynamic equilibrium between the two isomers.

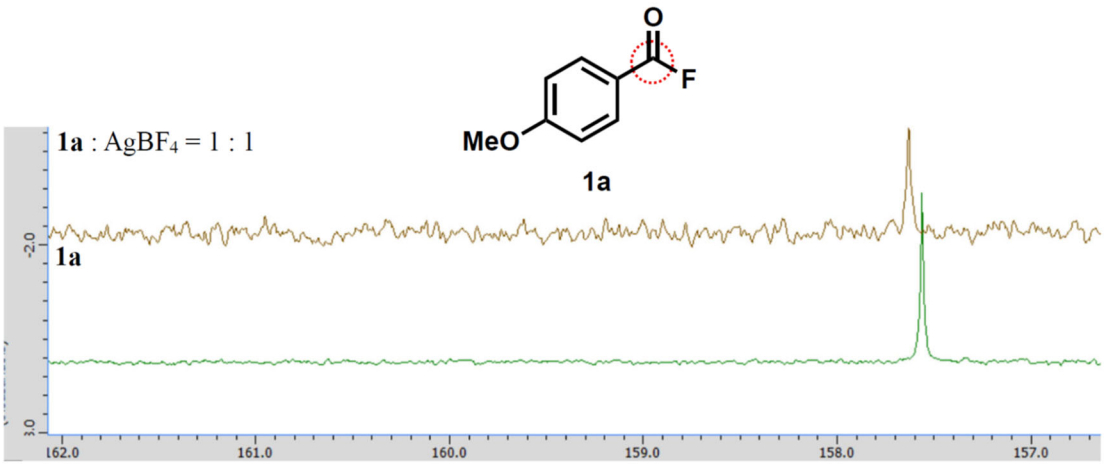
VI-VI. NMR analysis of a mixture of acyl fluoride and $AgBF_4$

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded for CD_2Cl_2 solutions of **1a** and a 1:1 mixture of **1a** and $AgBF_4$ (ca. 0.10 M). Comparison of these spectra revealed several downfield shifts upon addition of $AgBF_4$, consistent with the formation of a coordination complex between **1a** and Ag^{+}.

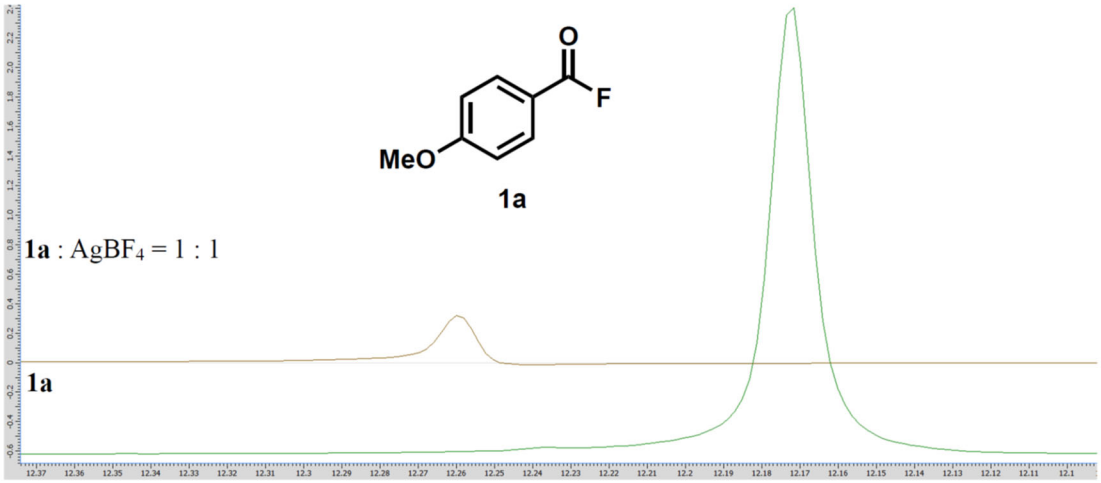
^{1}HNMR



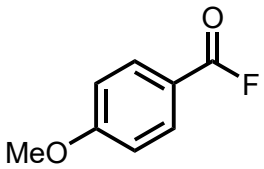
^{13}CNMR



^{19}F NMR



4-Methoxybenzoyl fluoride.

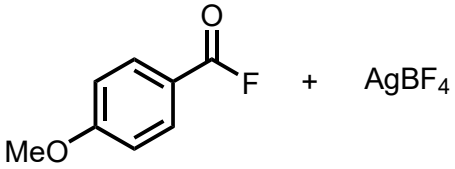


^{1}H NMR (CD_2Cl_2, 400 MHz):δ 7.98 (d, J = 8.7 Hz, 2H), δ7.00 (dd, J = 8.9, 1.2 Hz, 2H), 3.89 (s, 3H).

^{13}C{^{19}F} NMR (CD_2Cl_2, 101 MHz): δ 165.707, 157.562, 134.003, 117.003, 114.775, 56.071.

^{19}F NMR (CD_2Cl_2, 376 MHz): δ 12.2.

4-Methoxybenzoyl fluoride with $AgBF_4$.



^{1}H NMR (CD_2Cl_2, 400 MHz):δ 7.99 (d, J = 8.7 Hz, 2H), 7.01 (dd, J = 8.5, 1.4, 1.2 Hz, 2H), 3.89 (s, 3H).

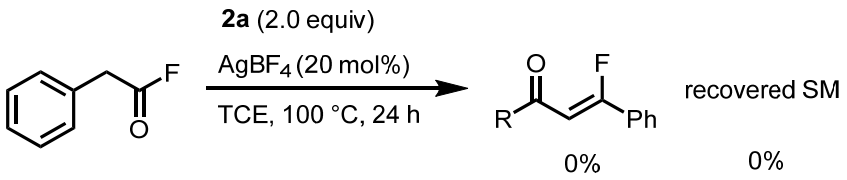
^{13}C{^{19}F} NMR (CD_2Cl_2, 101 MHz): δ 165.722, 157.634, 134.0222 116.969, 114.770, 56.090.

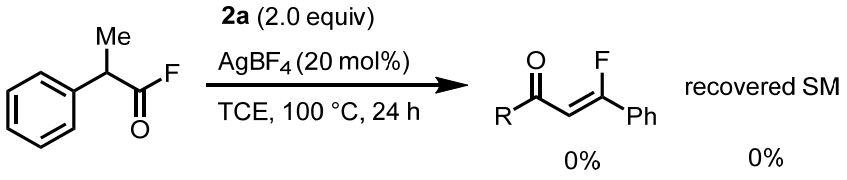
^{19}F NMR (CD_2Cl_2, 376 MHz): δ 12.3.

VII. List of Unsuccessful Substrates

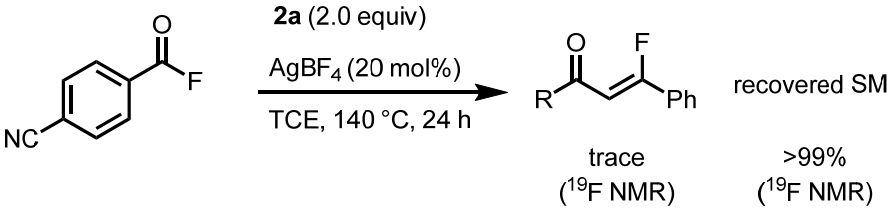
VII-I. Limitation of acyl fluorides

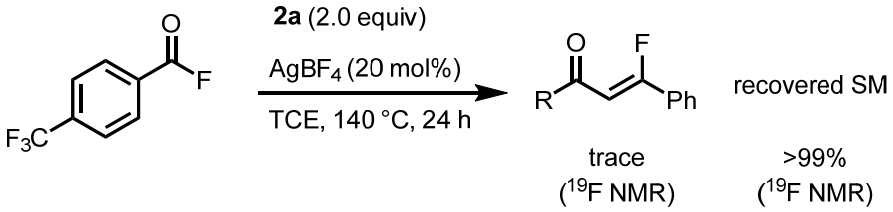
• Benzyl acyl fluorides





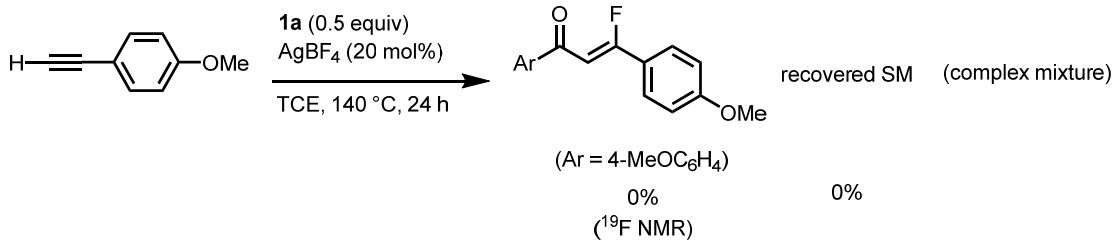
• Electron-deficient acyl fluorides



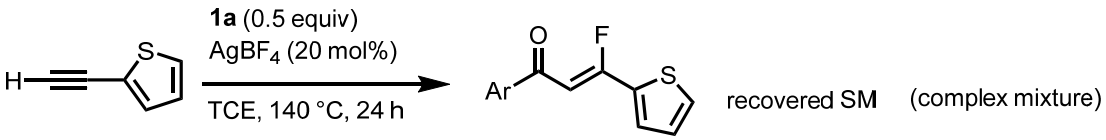


VII-II. Limitation of alkynes

• Electron-rich terminal alkyne



• Hetero-substituted terminal alkyne

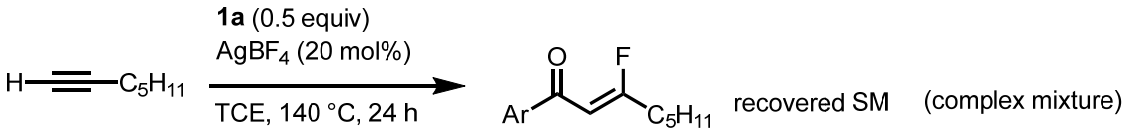


(Ar = 4-MeOC$_6$H$_4$)

10% (^{19}F NMR)

13%

• Aliphatic terminal alkyne

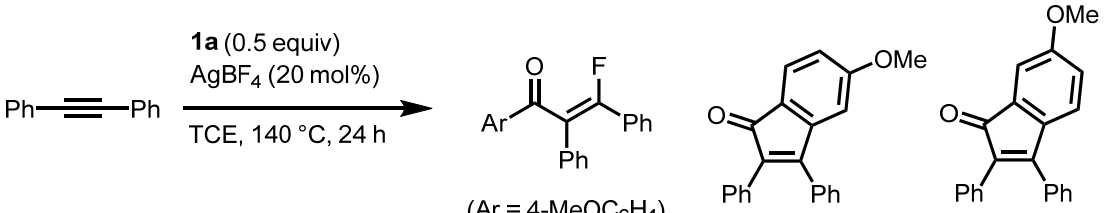


(Ar = 4-MeOC$_6$H$_4$)

10% (^{19}F NMR)

13%

• Aromatic internal alkynes



(Ar = 4-MeOC$_6$H$_4$)

trace

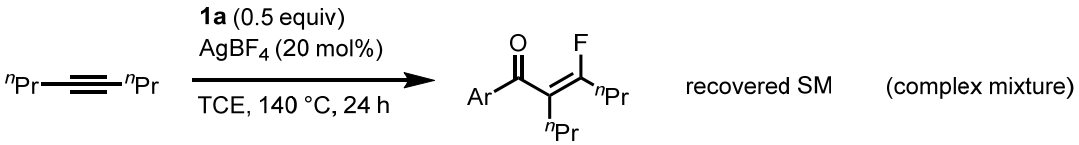
ca. 20%

ca. 20%

recovered **1a**

<10%

• Aliphatic internal alkyne

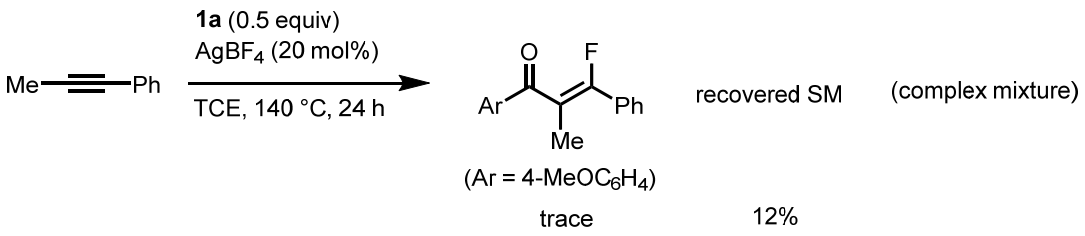


(Ar = 4-MeOC$_6$H$_4$)

trace

5%

• **Aryl–alkyl-substituted alkyne**

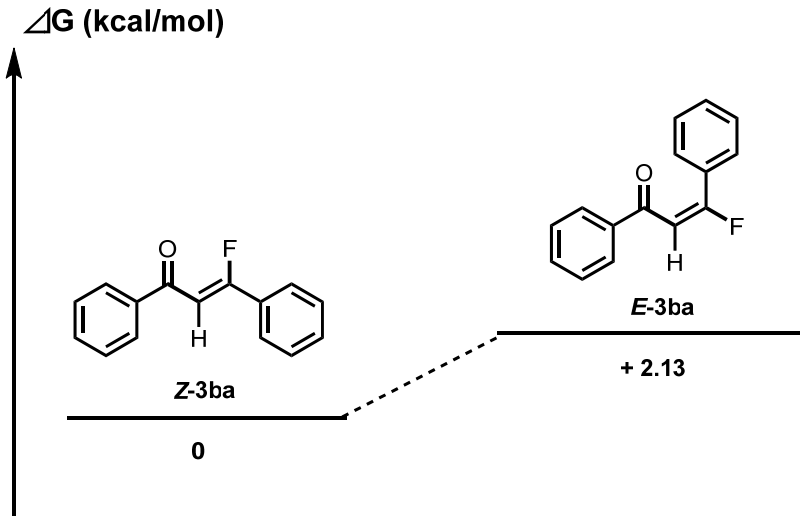


VIII. DFT Calculations

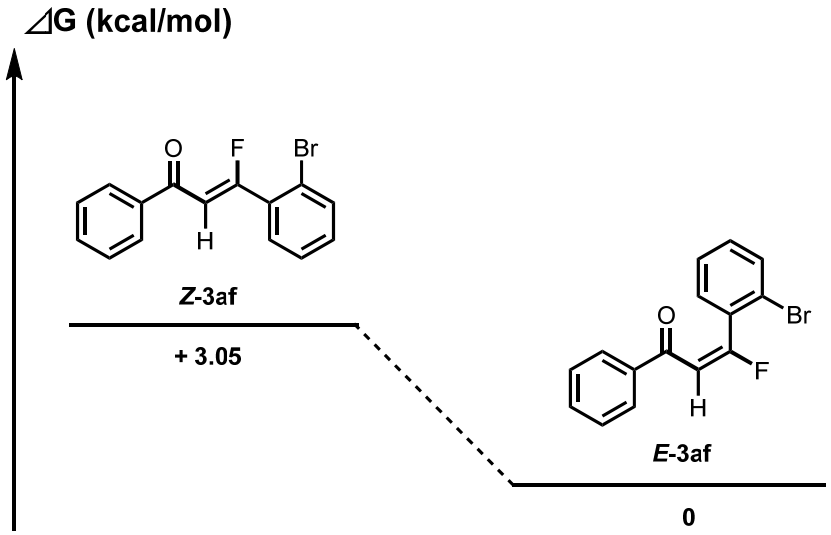
VIII-I. Computational Details

Calculations were performed with the Gaussian 09 (G09) program. Geometry optimizations for all the reported structures were performed using M06-2X with the 6-31+G* basis set and the frequency calculations were performed using M06-2X with the 6-31+G* basis set.[16] PCM solvent effects were incorporated for all calculations with dichloroethane as the solvent. Single-point calculations on optimized geometries were separately calculated using M06-2X with the 6-31+G* basis set. Energy changes were shown by the use of Gibbs free energies (T = 298.15 K and P = 1 atm).

VIII-II. Relative Gibbs Free Energies of 3ba



VIII-III. Relative Gibbs Free Energies of 3af



According to DFT calculations, the E isomer is more stable than the Z isomer, consistent with the experimental results. Although the E isomer is normally less stable due to steric repulsion between the carbonyl and phenyl groups, the isomer is stabilized by donation of the lone pair on the bromine atom into the π* orbital of the carbonyl group.

VIII-IV. Cartesian coordinates of the optimized geometries and energies

・**3ba-*Z*** (G = -752.827987 Hartree, no imaginary frequency)

C	-0.01390100	-0.19660300	0.22472500
C	1.18830800	-0.74623500	-0.00369300
H	-0.04134600	0.86387500	0.44232200
C	-1.29172500	-0.94388200	0.19578600
F	1.26787900	-2.04406100	-0.34123300
C	2.50456300	-0.08867400	0.02841100
O	-1.34617200	-2.18349600	0.30928500
C	-2.55567200	-0.14328300	0.04748600
C	-2.56519600	1.16068100	-0.46214800
C	-3.77078100	1.84655900	-0.60887000
C	-4.96989400	1.24033000	-0.23635100
C	-4.96584600	-0.06008900	0.27412900
C	-3.76529100	-0.75016700	0.40828000
C	3.62128900	-0.75550400	-0.49367200
C	4.87223900	-0.14193100	-0.48049100
C	5.02109700	1.13593800	0.05567900
C	3.91204500	1.80079400	0.58432200

C	2.66093500	1.19467600	0.57373800
H	-1.64136000	1.64227800	-0.76957000
H	-3.77175700	2.85369800	-1.01554100
H	-5.90740800	1.77849500	-0.34523500
H	-5.89882100	-0.53409900	0.56532100
H	-3.74968700	-1.76364500	0.79826400
H	3.51203700	-1.74985200	-0.91363000
H	5.73058700	-0.66566500	-0.89076000
H	5.99715100	1.61236500	0.06678300
H	4.02360400	2.79278600	1.01193200
H	1.81244800	1.71861800	1.00293800

• **3ba-*E*** (G = -752.824583 Hartree, no imaginary frequency)

C	-4.40023900	-1.20710500	-0.45429800
C	-4.96808800	-0.31343500	0.45770900
C	-4.18853300	0.69219400	1.02846800
C	-2.84335500	0.81348900	0.68233400
C	-2.26975800	-0.08046800	-0.22939400
C	-3.05562100	-1.09476200	-0.79158400
C	-0.82153300	-0.01053000	-0.60494400
C	-0.10501700	1.25722100	-0.32408000
O	-0.27878200	-0.95618800	-1.15831000
C	1.21517300	1.36264500	-0.12775700
F	1.71031200	2.62336300	-0.05028600
C	2.26735700	0.35247600	0.06412900
C	2.01948400	-0.81439500	0.79686900
C	3.03600200	-1.74493200	0.98480900
C	4.30416800	-1.51748300	0.44524300
C	4.55717700	-0.34998800	-0.27449600
C	3.54489300	0.58930700	-0.45870600
H	-5.00746900	-1.98963500	-0.89999300
H	-6.01786400	-0.40268900	0.72308100
H	-4.62616100	1.38291000	1.74324700
H	-2.24337000	1.59498700	1.13974200
H	-2.60041000	-1.78550500	-1.49527800
H	-0.67796800	2.17977400	-0.32907100

H	1.03744400	-0.98561900	1.22792800
H	2.84099300	-2.64585500	1.55903100
H	5.09533900	-2.24716600	0.59254000
H	5.54339300	-0.16764600	-0.69112400
H	3.74086200	1.50027600	-1.01686000

· **3af-*Z*** (G = -3438.496739 Hartree, no imaginary frequency)

C	-4.14640300	1.41544700	-0.26725500
C	-5.19253100	0.48070800	-0.26111000
C	-4.92002700	-0.87280100	-0.01970000
C	-3.60779400	-1.27003100	0.21193300
C	-2.55291500	-0.35163500	0.19717700
C	-2.84323600	1.00124900	-0.04647300
C	-1.17473500	-0.85319700	0.46437600
C	-0.04119500	0.04889400	0.14219600
O	-0.99307800	-1.97709600	0.91482700
C	1.20249900	-0.09845500	0.61164500
O	-6.42720100	0.97444500	-0.49555300
C	-7.52264800	0.06645700	-0.49687200
C	2.33576800	0.80912900	0.33182600
F	1.51861100	-1.09648100	1.45084700
C	3.55460700	0.34410600	-0.17527000
C	4.61088900	1.21460000	-0.41785300
C	4.45322400	2.57532400	-0.15888600
C	3.24280500	3.06107500	0.33129300
C	2.19315900	2.18014900	0.57527600
H	-4.38015700	2.46055900	-0.44660000
H	-5.71296000	-1.61183900	-0.01176300
H	-3.38952600	-2.31669500	0.40293600
H	-2.05502300	1.74813900	-0.04447500
H	-0.20342900	0.88440500	-0.52897900
H	-8.40663700	0.66900300	-0.70510300
H	-7.40153200	-0.69097200	-1.27876500
H	-7.62989100	-0.41851900	0.47927500
H	5.54786500	0.83700000	-0.81467300
H	5.28120300	3.25200600	-0.34765200

H	3.11718400	4.12025000	0.53281800
H	1.25149600	2.54487900	0.97591300
Br	3.77506700	-1.48842300	-0.59310200

• **3af-*E*** (G = -752.827987 Hartree, no imaginary frequency)

C	-1.87483300	-1.24481600	1.57258700
C	-2.20846000	0.02030300	1.30948800
H	-2.56745700	-1.84131100	2.16116200
C	-0.69669700	-1.97373100	1.02880200
C	-1.54408300	1.05536500	0.49295300
F	-3.33509700	0.49885300	1.89574500
O	-0.82625500	-3.15706100	0.74470200
C	0.61017800	-1.28458800	0.85207300
C	1.02722700	-0.23483600	1.68466800
C	-1.26694700	2.27992300	1.11771500
C	-0.57113100	3.28323500	0.45484500
C	-0.14222200	3.07410600	-0.85560000
C	-0.43383000	1.87706000	-1.50439300
C	-1.12512300	0.87451500	-0.83005500
H	-0.35766300	4.21952400	0.96089400
H	0.40550800	3.84752100	-1.38565600
H	-0.12907600	1.72413500	-2.53457700
C	2.26292300	0.36188700	1.49888400
C	3.10446600	-0.07504900	0.46398400
C	2.70338100	-1.12600300	-0.37167700
C	1.46452400	-1.72413100	-0.16177200
H	0.38600600	0.10901500	2.49223100
H	2.59987200	1.16899400	2.14262300
O	4.28322400	0.57561100	0.34887000
H	3.33799500	-1.47614900	-1.17765600
H	1.14536100	-2.53879900	-0.80605900
C	5.17928400	0.16092000	-0.67487700
H	6.05224500	0.80722900	-0.58490300
H	5.47870100	-0.88309800	-0.53278800
H	4.72847400	0.28861600	-1.66499900
Br	-1.60179900	-0.67526500	-1.81405300

H	-1.58880800	2.42557900	2.14552600

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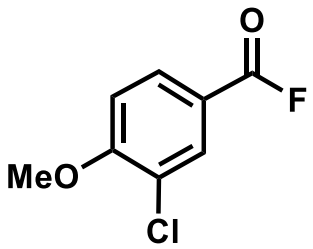
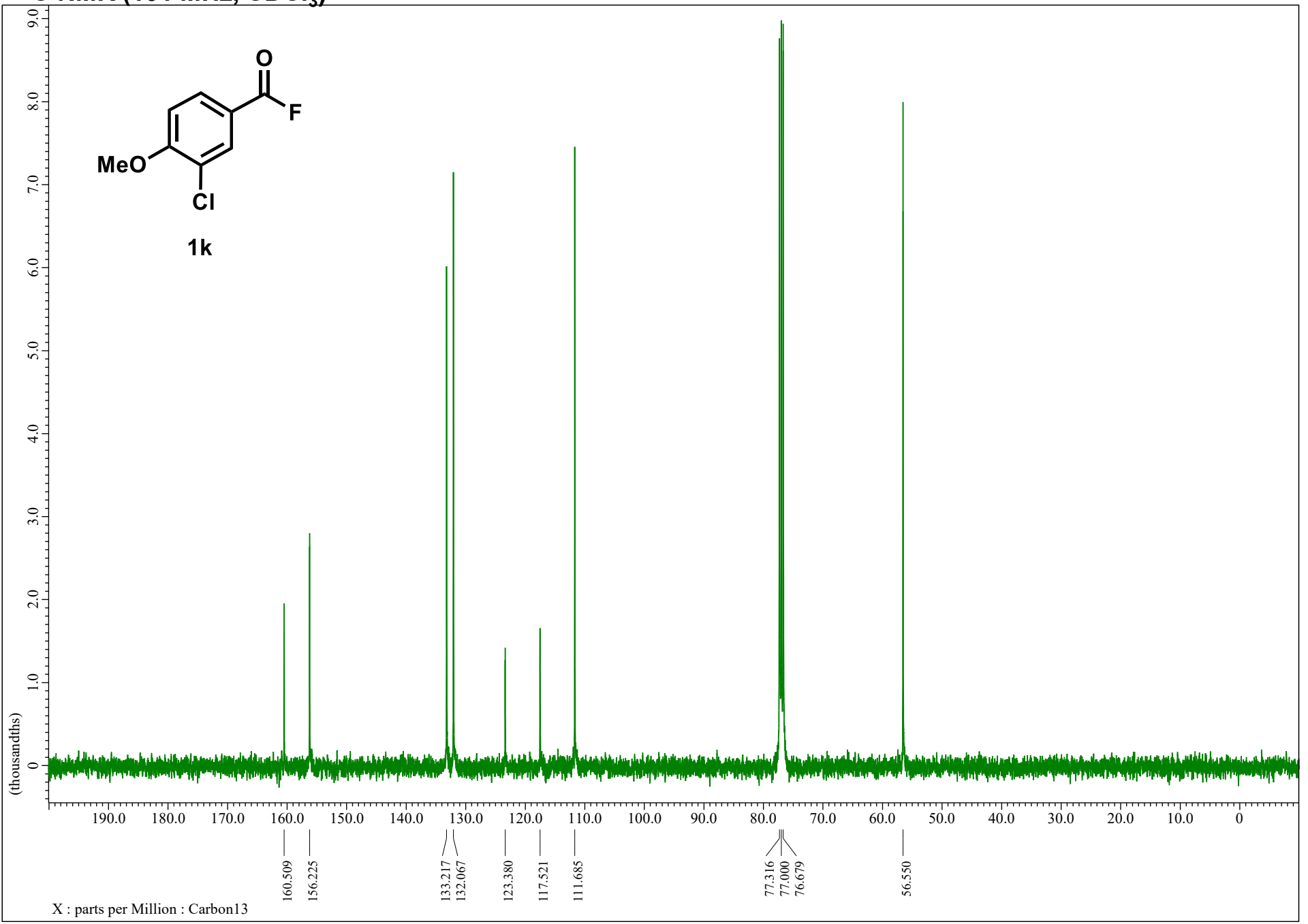
X. Copies of NMR Spectra

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

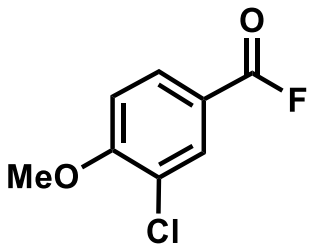


1k

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



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



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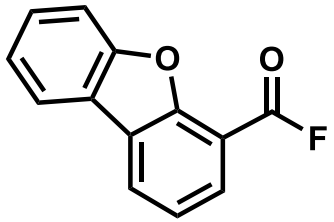
^{1}H NMR (400 MHz, $CDCl_3$)



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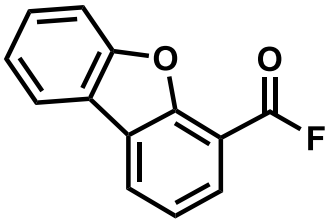

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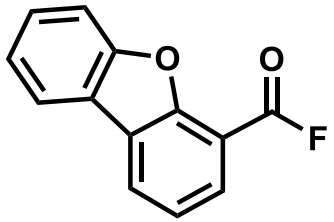

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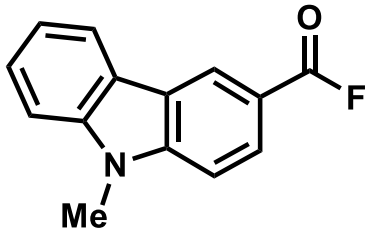

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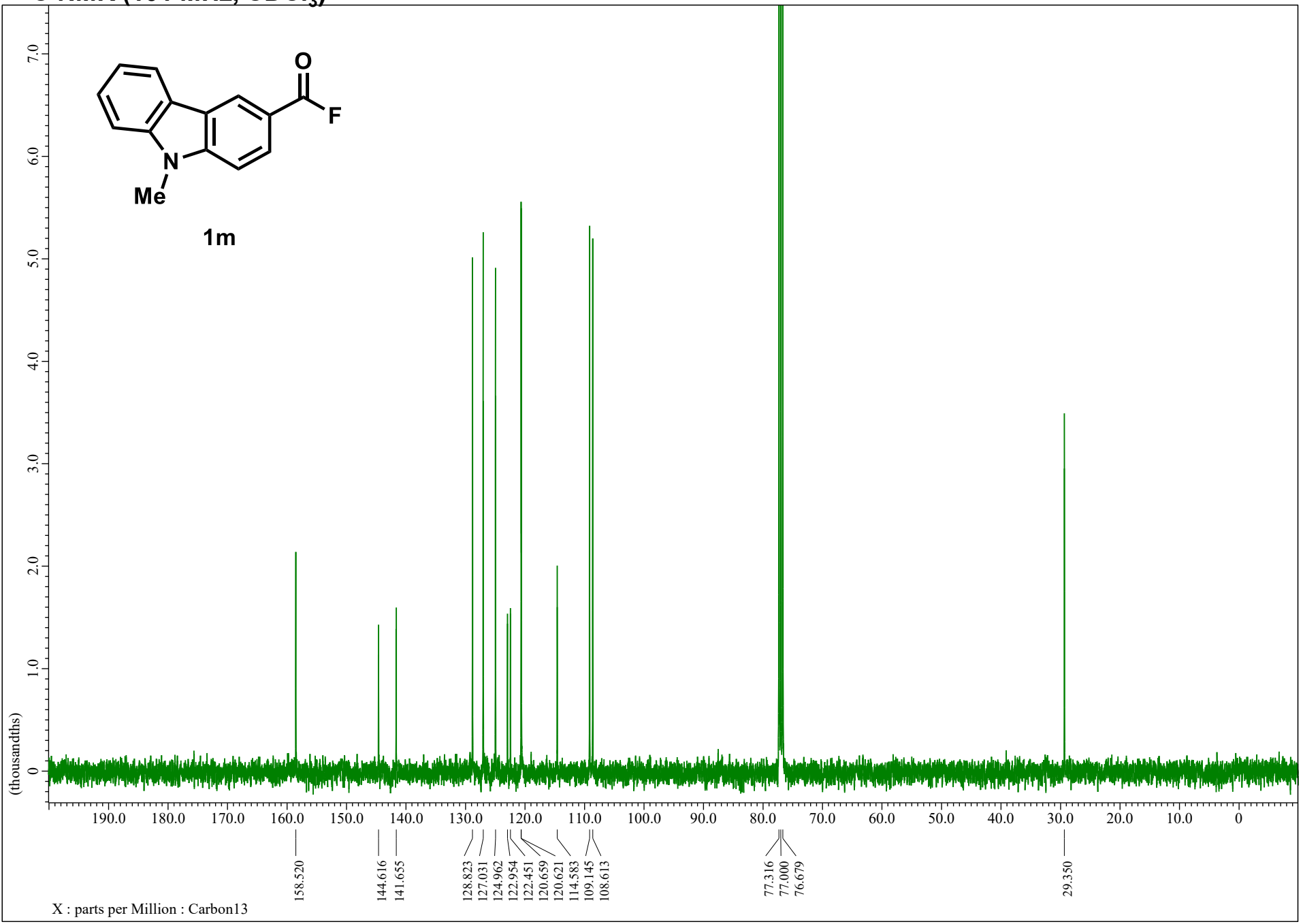

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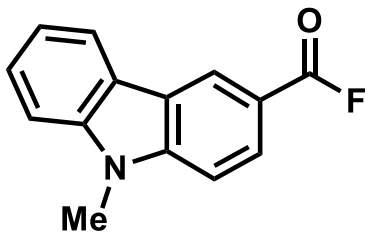

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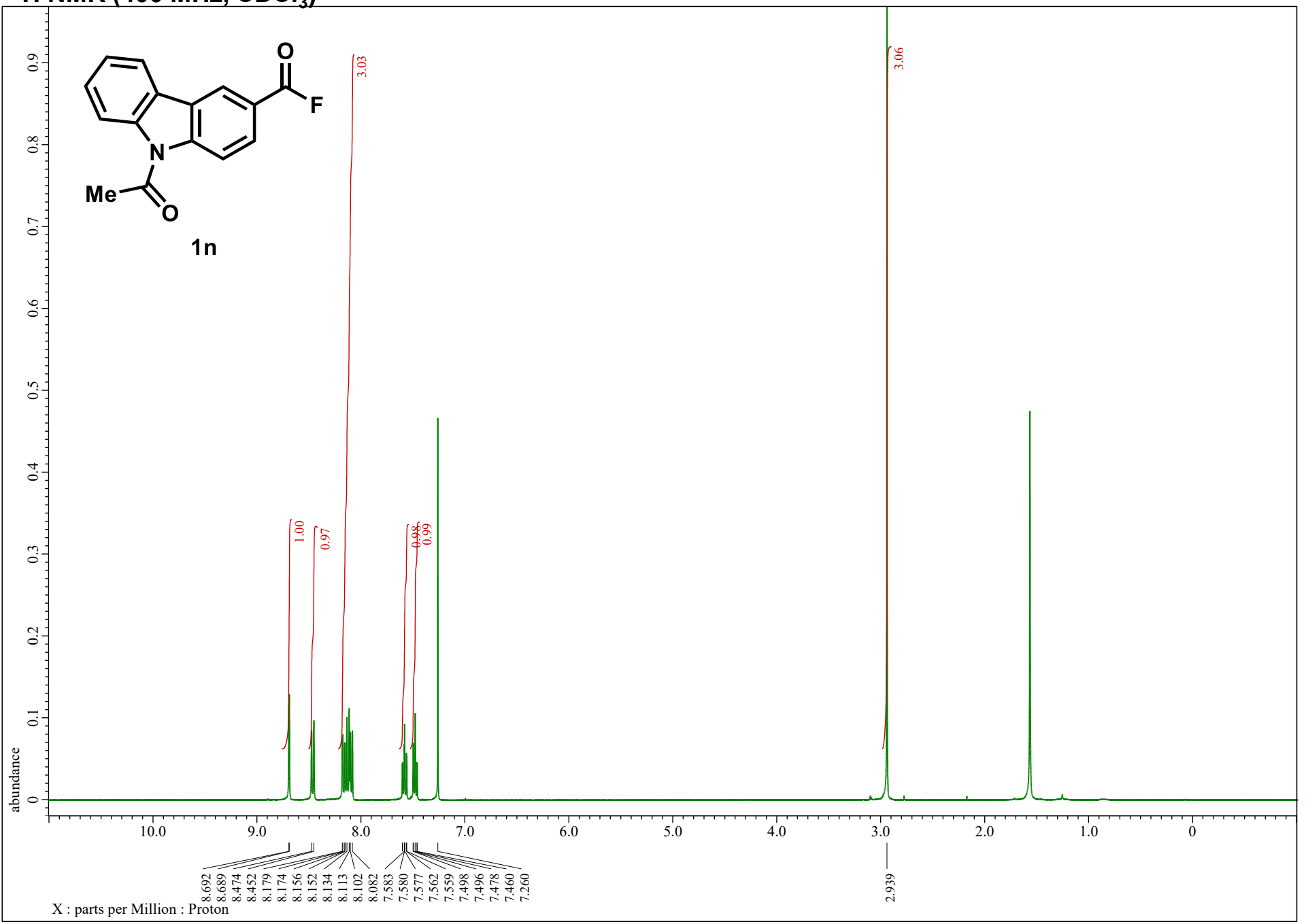

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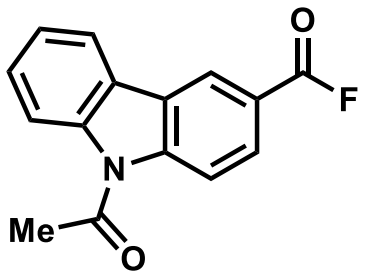

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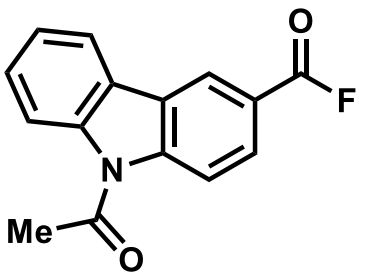

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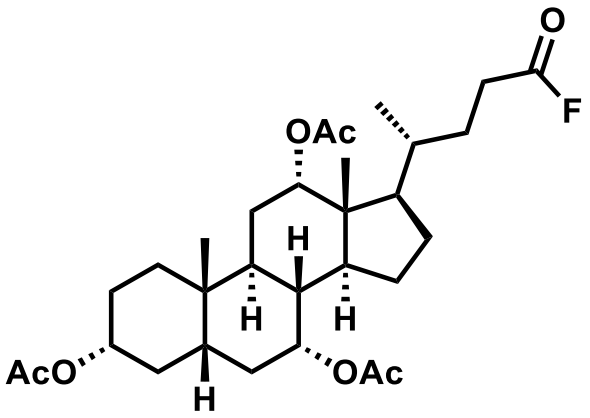

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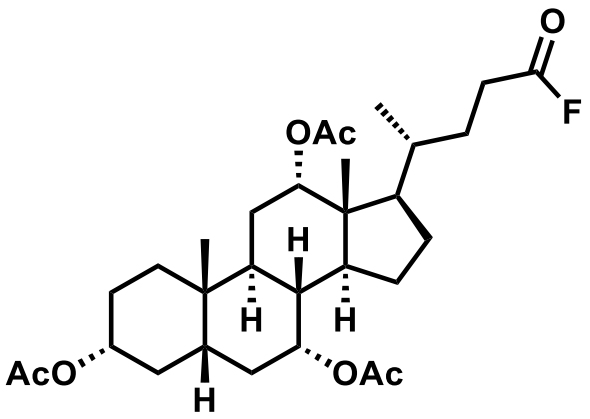

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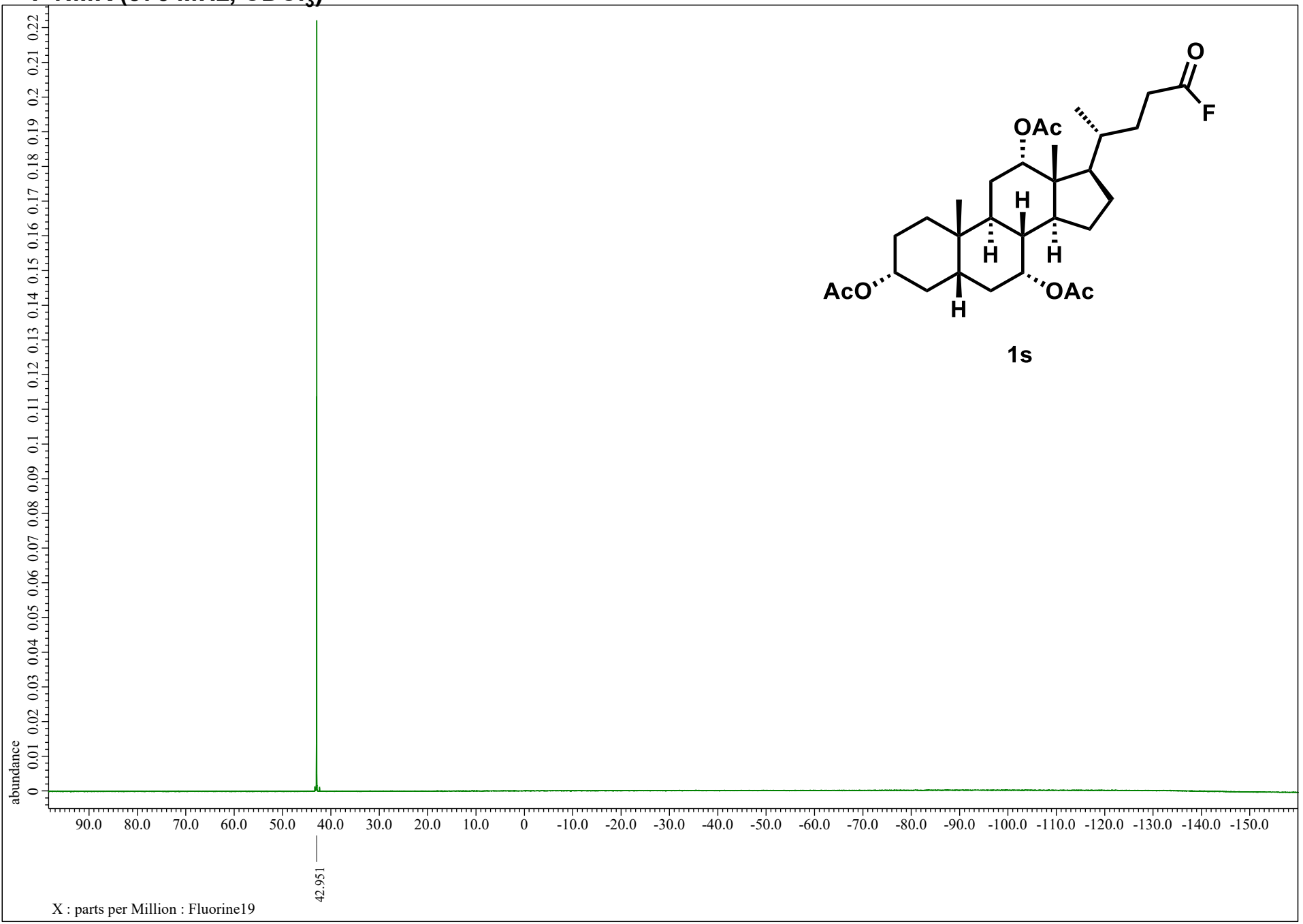
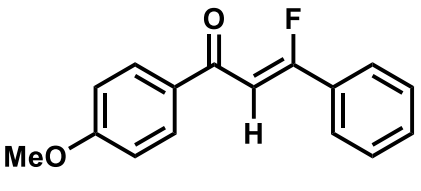


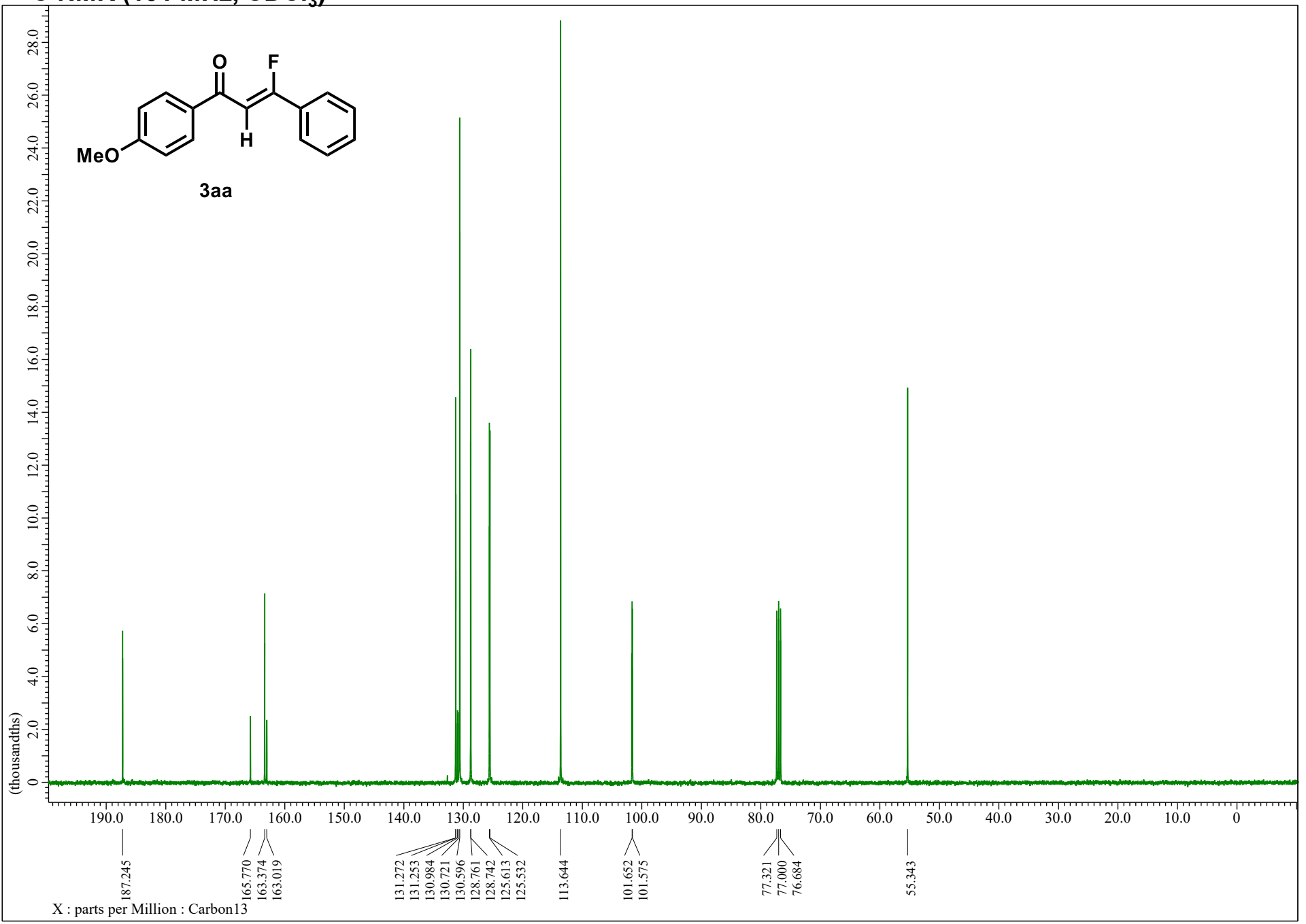
1s

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

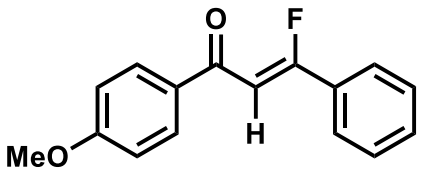


3aa

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

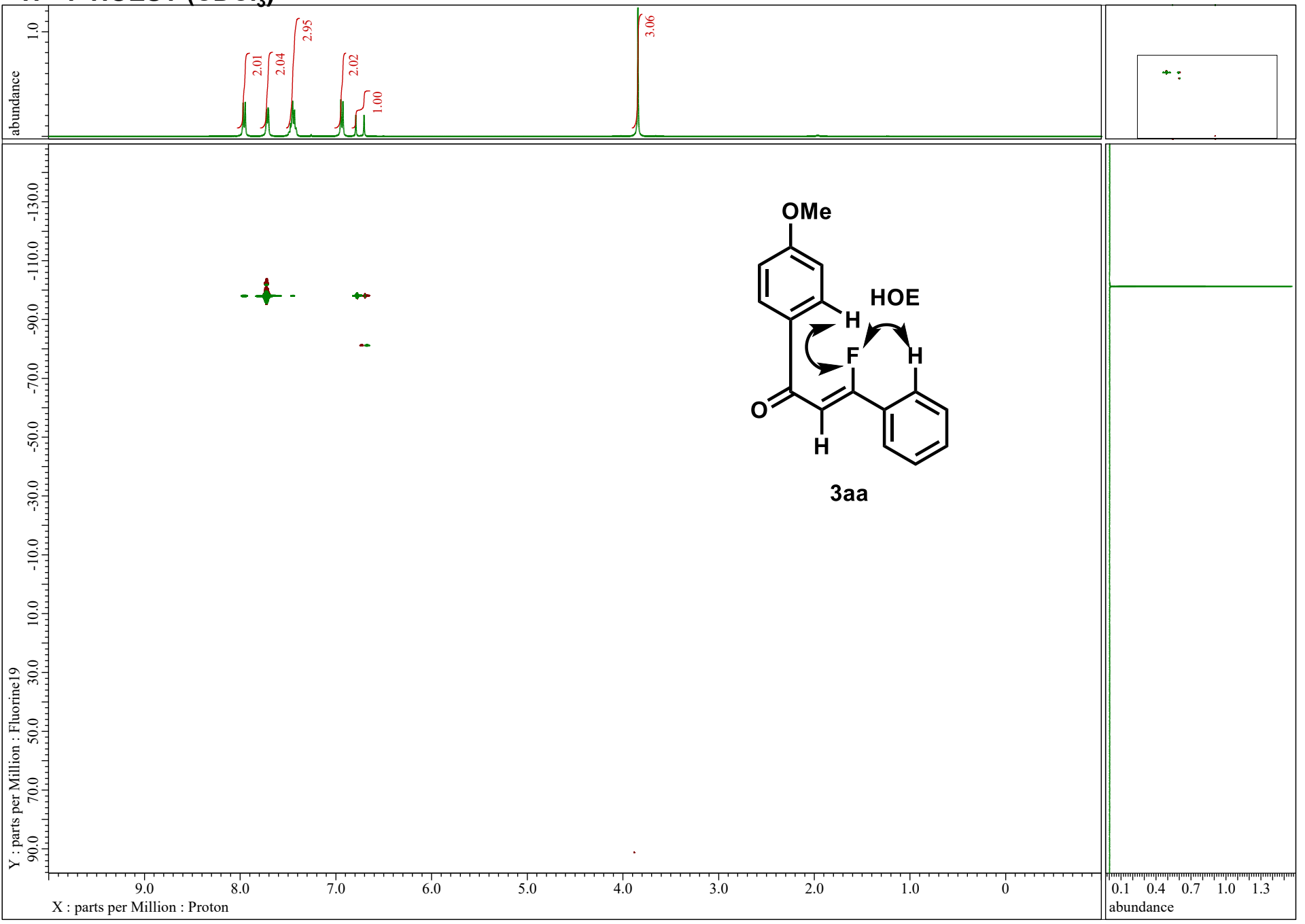


^{19}F NMR (376 MHz, $CDCl_3$)

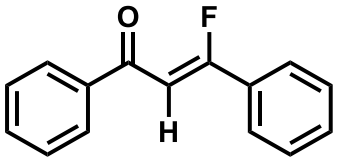


3aa

^{1}H-^{19}F HOESY ($CDCl_3$)

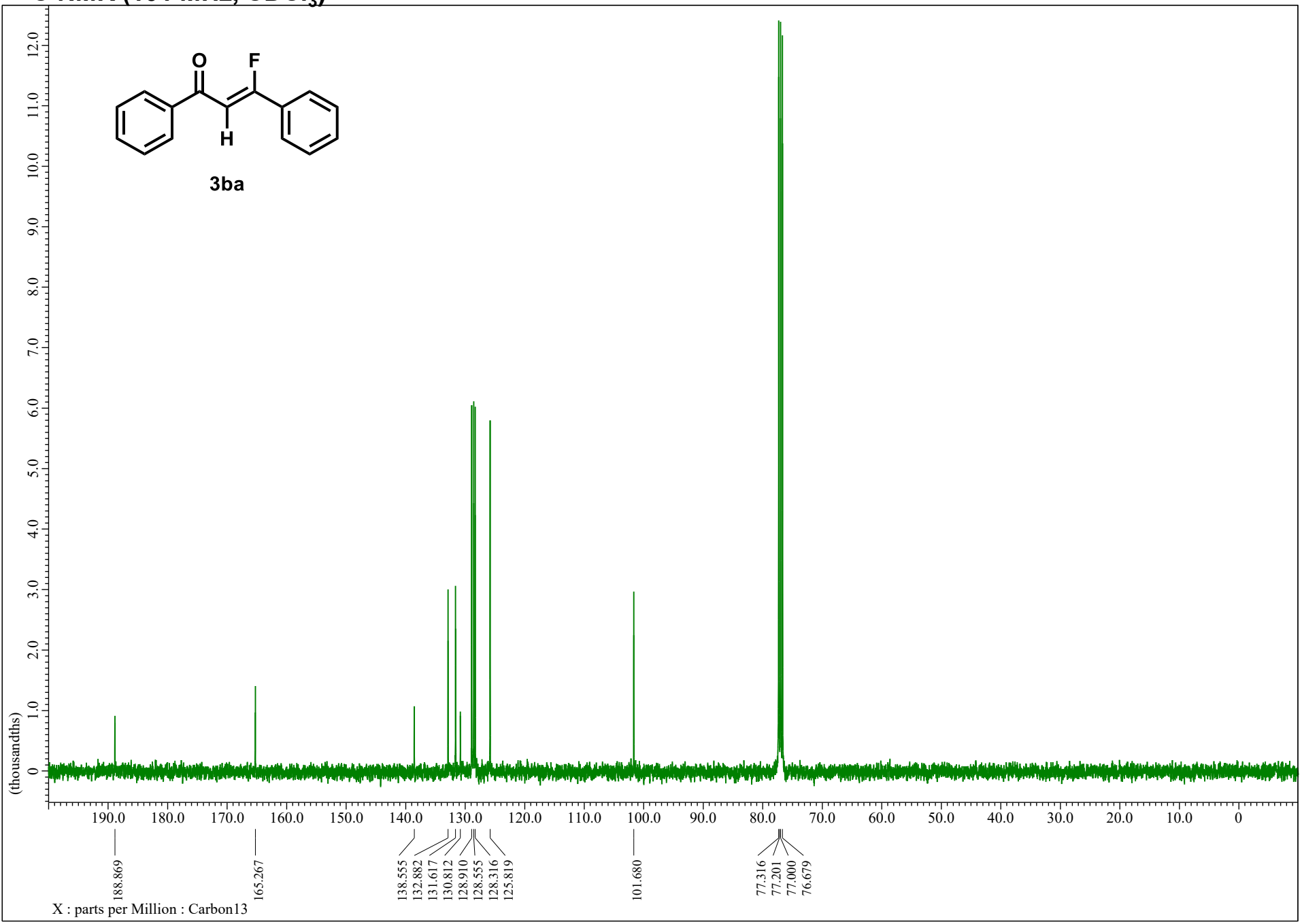


^{1}H NMR (400 MHz, $CDCl_3$)

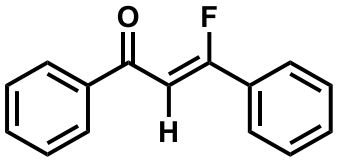


3ba

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



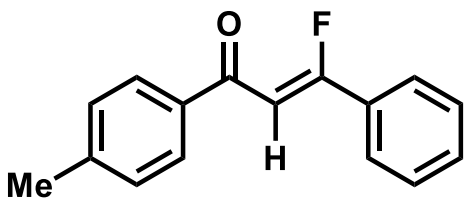
^{19}F NMR (376 MHz, $CDCl_3$)



3ba

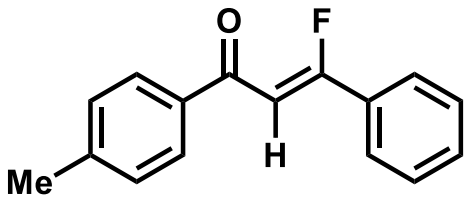
+ *E* isomer

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



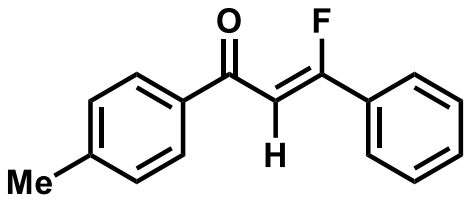
3ca

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



3ca

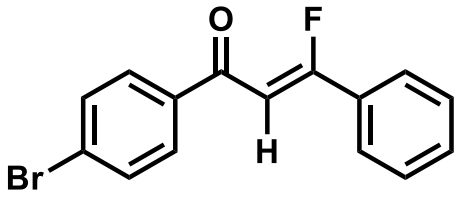
^{19}F NMR (376 MHz, $CDCl_3$)



3ca

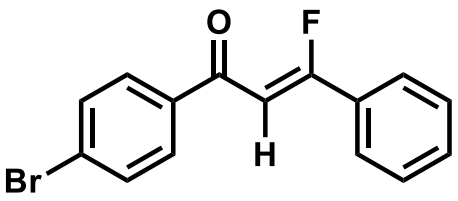
+ *E* isomer

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



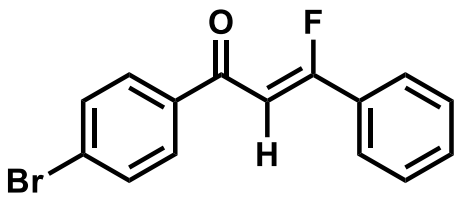
3da

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



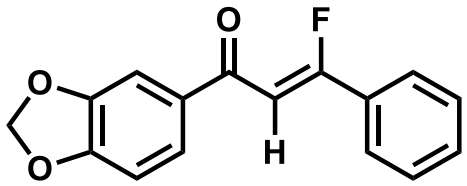
3da

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



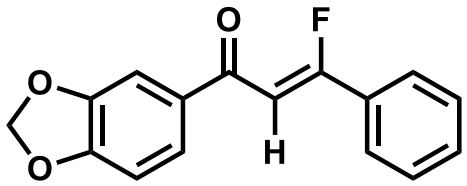
3da

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



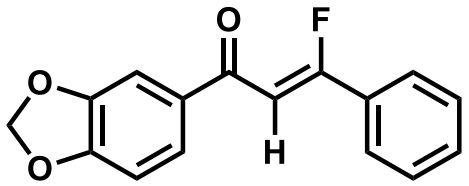
3ea

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



3ea

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



3ea

+ *E* isomer

abundance

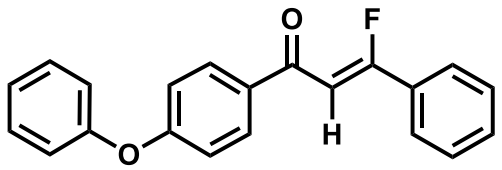
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15

90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0

-83.845
-83.903
-100.705
-100.795

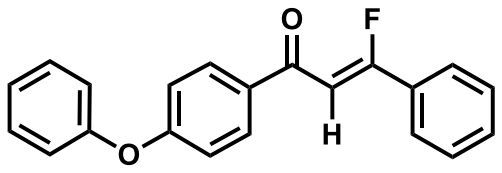
X : parts per Million : Fluorine19

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



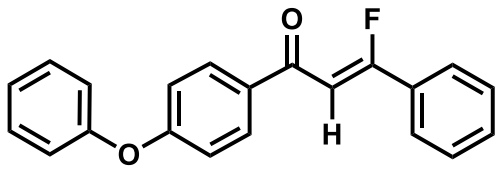
3fa

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



3fa

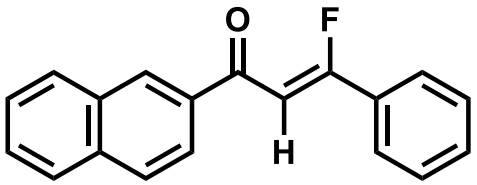
^{19}F NMR (376 MHz, $CDCl_3$)



3fa

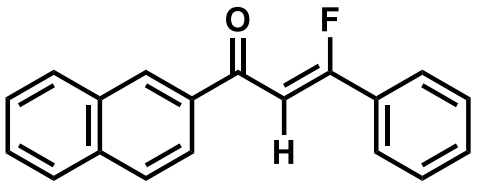
+ *E* isomer

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



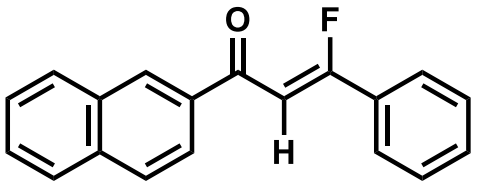
3ga

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



3ga

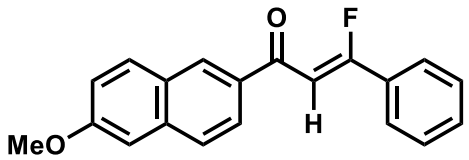
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

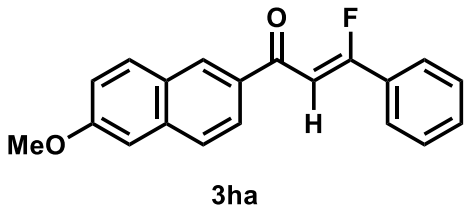
3ga

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



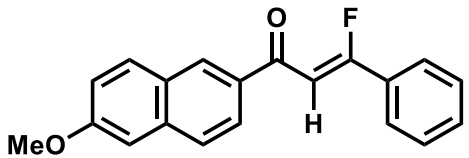
3ha

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



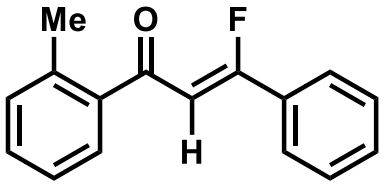
3ha

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



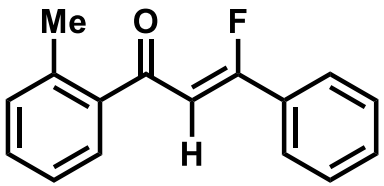
3ha

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



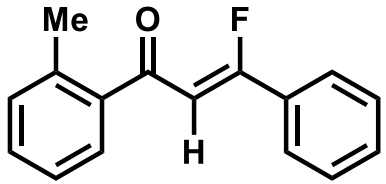
3ia

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



3ia

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



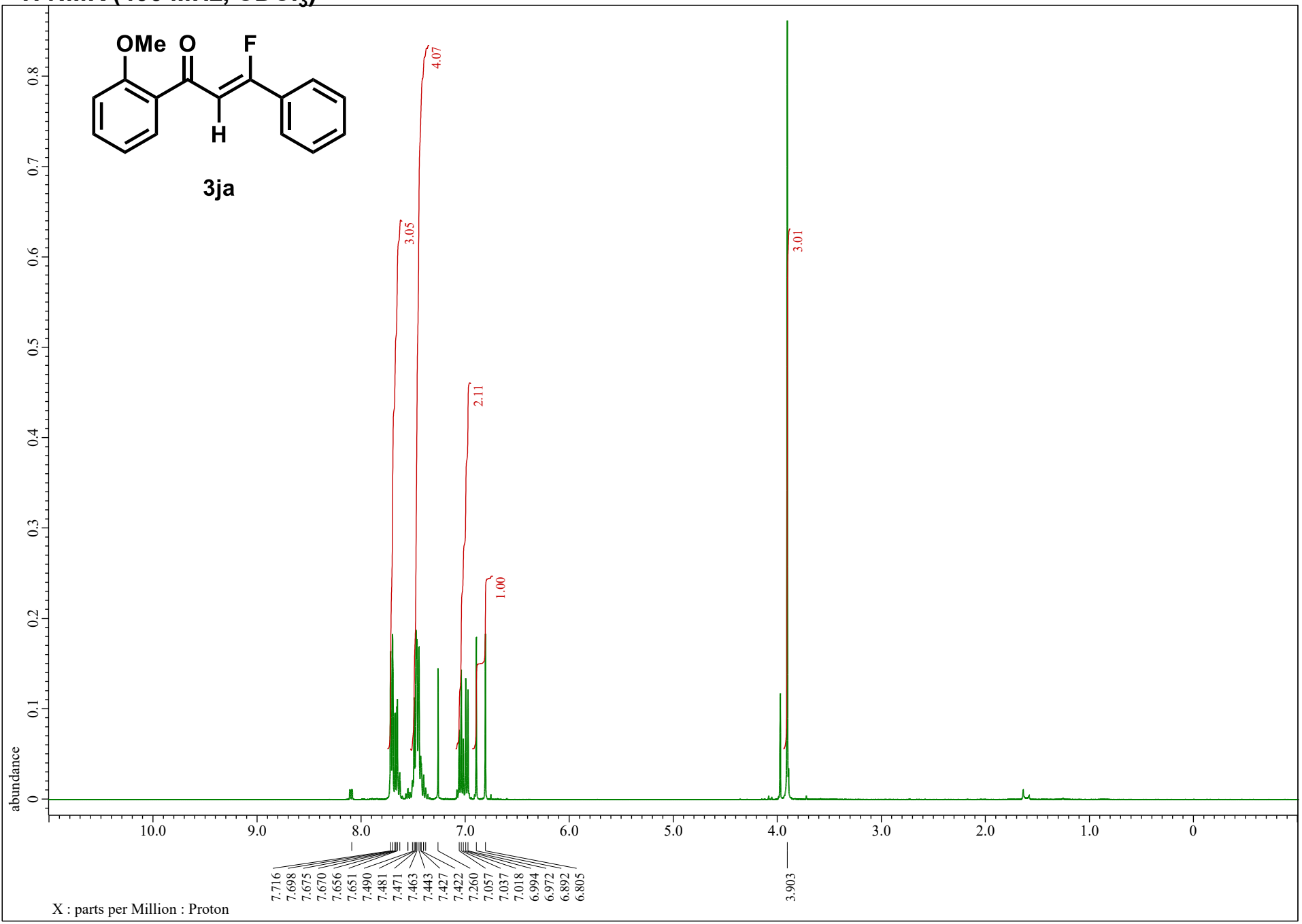
3ia

+ *E* isomer

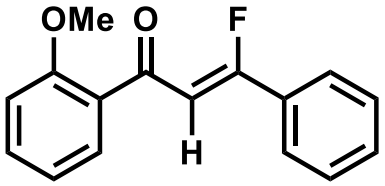
abundance

X : parts per Million : Fluorine19

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

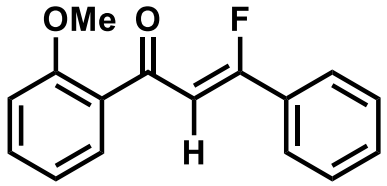


^{13}C NMR (101 MHz, $CDCl_3$)



3ja

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



3ja

+ *E* isomer

abundance

0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2 0.21 0.22 0.23

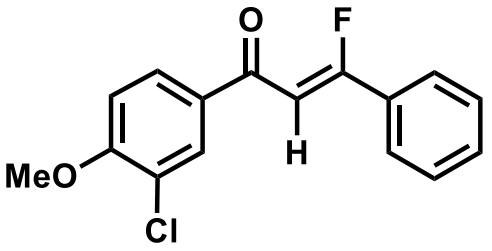
90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0

-82.609
-82.668

-101.515
-101.607

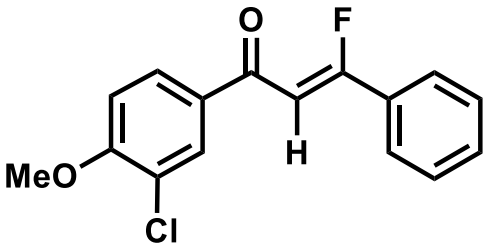
X : parts per Million : Fluorine19

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



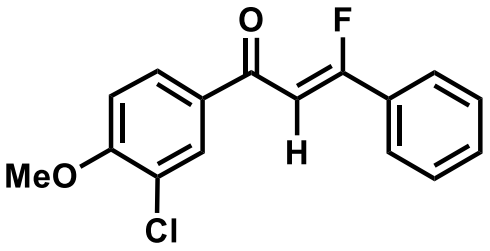
3ka

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



3ka

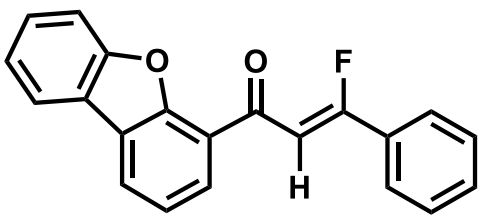
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

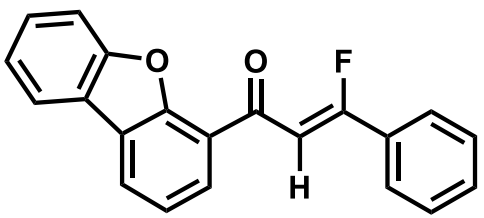
3ka

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



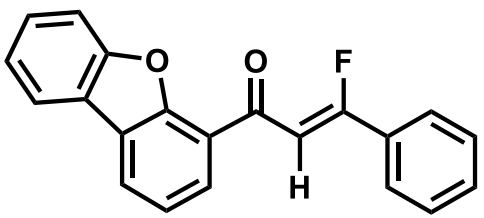
3la

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



3la

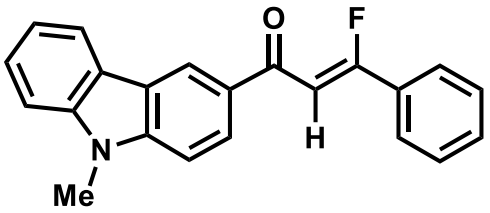
^{19}F NMR (376 MHz, $CDCl_3$)



3la

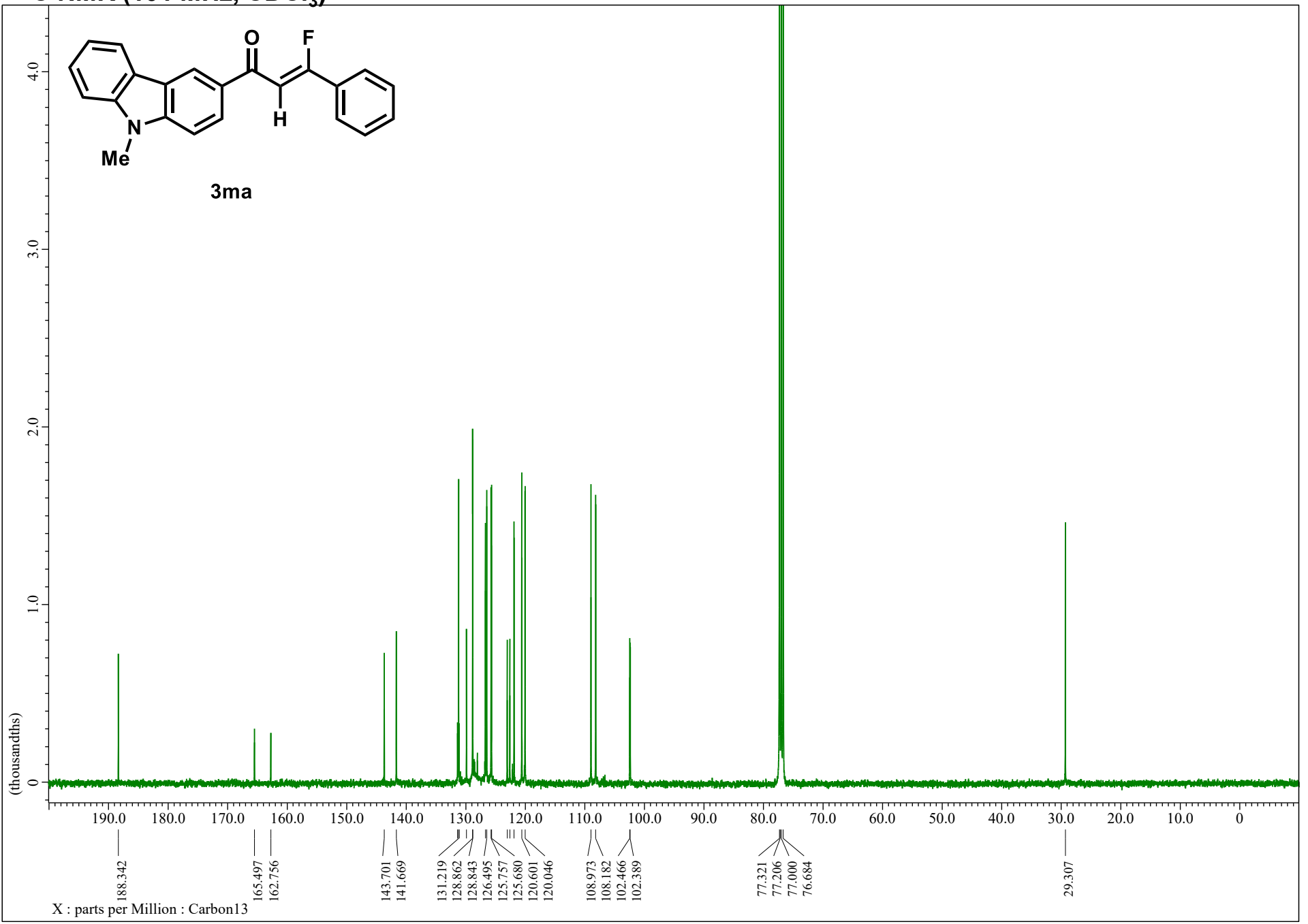
+ *E* isomer

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

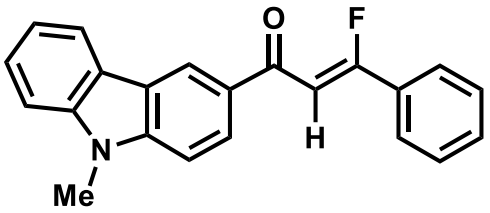


3ma

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



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



3ma

+ *E* isomer

abundance

0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19

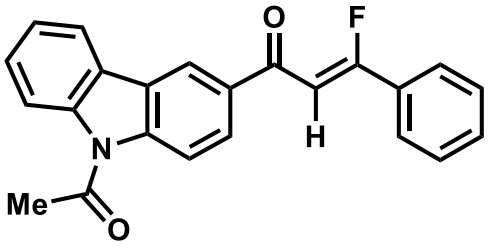
90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0

-85.924
-85.983

-101.884
-101.976

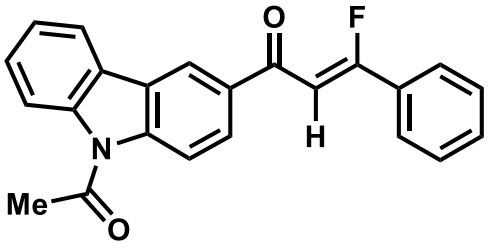
X : parts per Million : Fluorine19

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



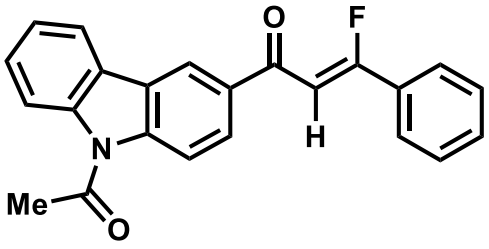
3na

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



3na

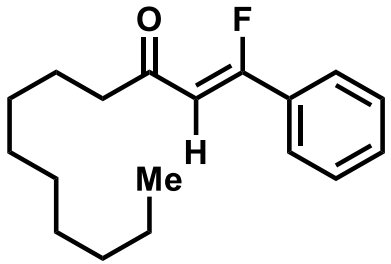
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

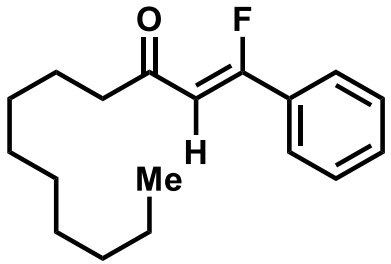
3na

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



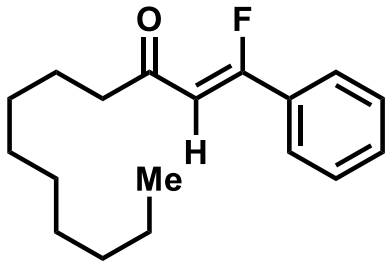
3oa

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



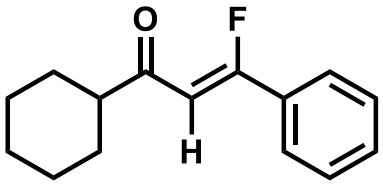
3oa

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



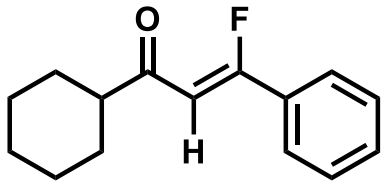
3oa

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



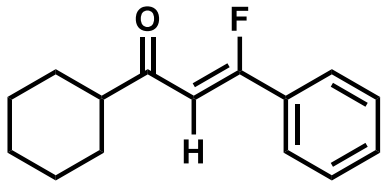
3pa

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



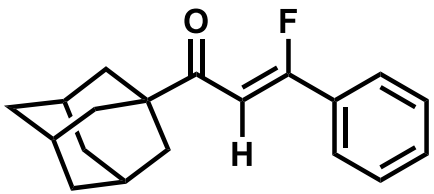
3pa

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



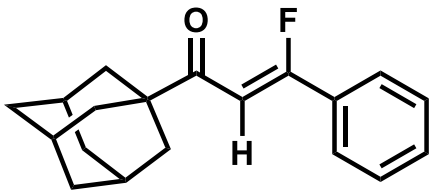
3pa

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



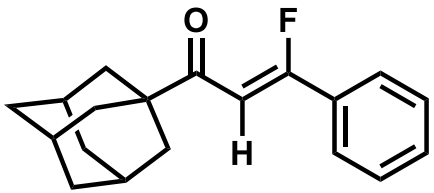
3qa

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



3qa

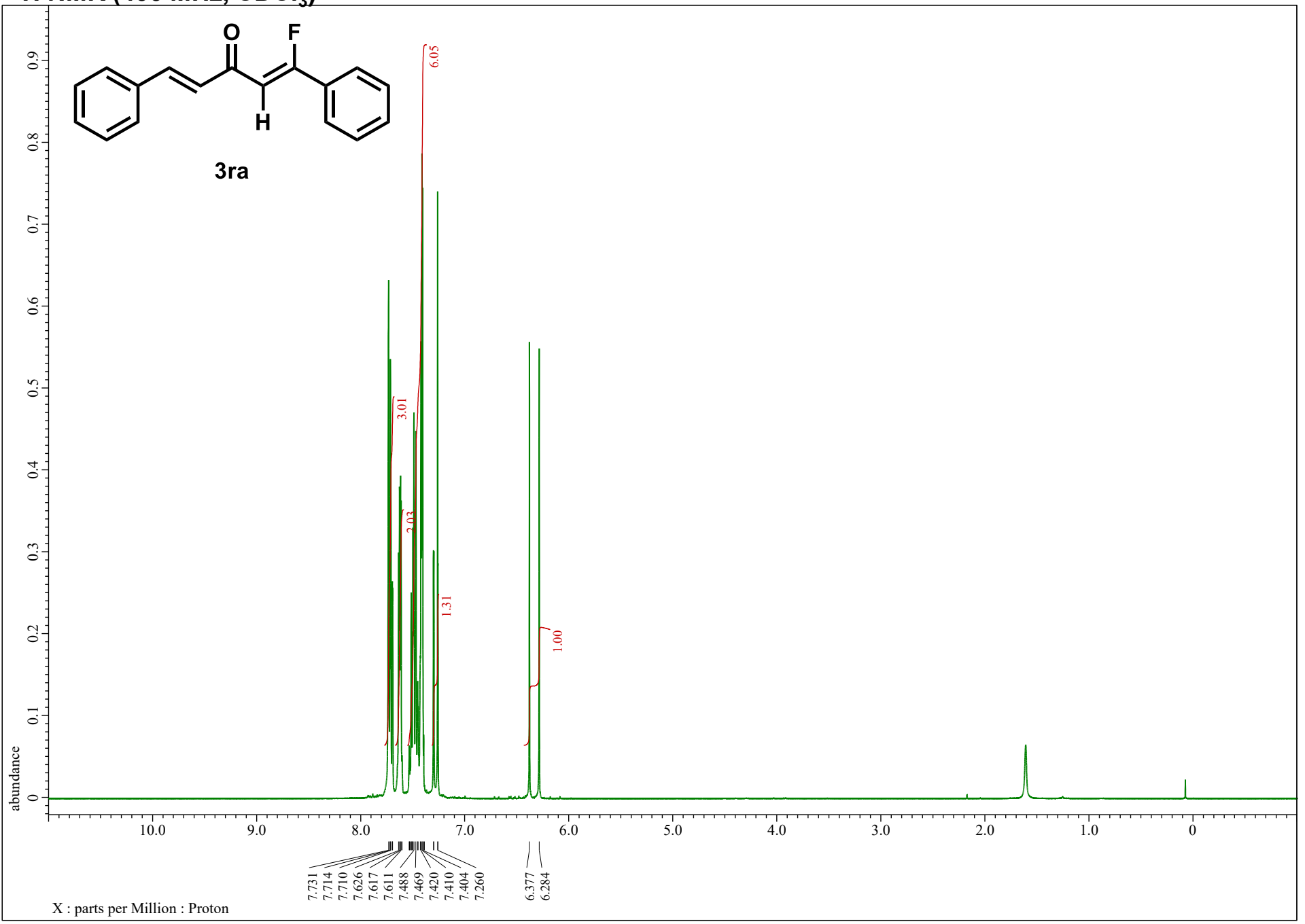
^{19}F NMR (376 MHz, $CDCl_3$)



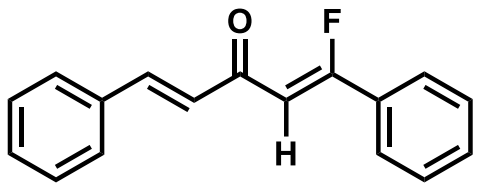
3qa

+ *E* isomer

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

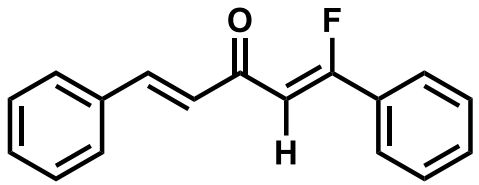


^{13}C NMR (101 MHz, $CDCl_3$)



3ra

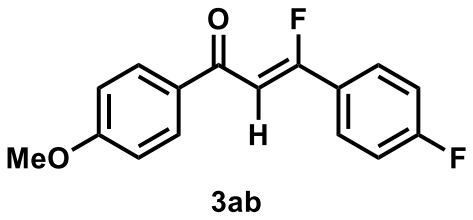
^{19}F NMR (376 MHz, $CDCl_3$)



3ra

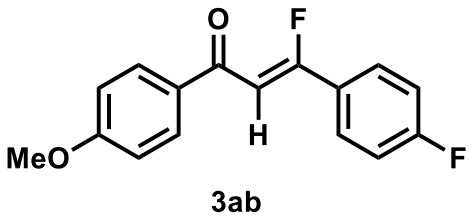
+ *E* isomer

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



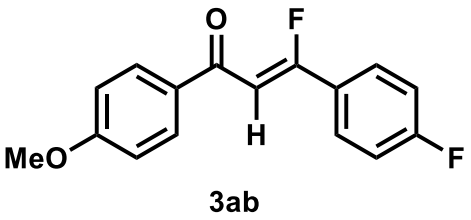
3ab

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



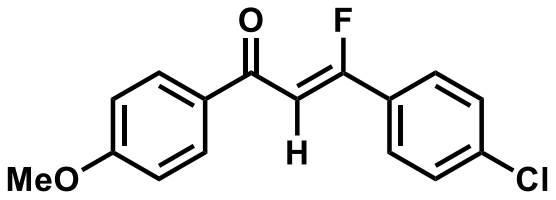
3ab

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



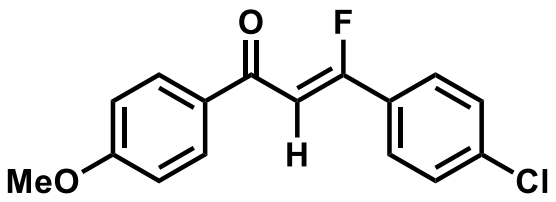
3ab

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



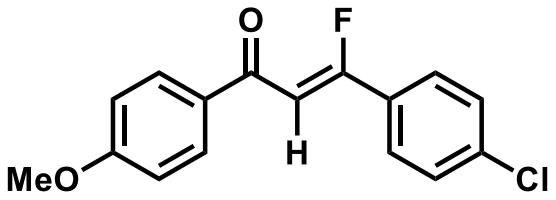
3ac

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



3ac

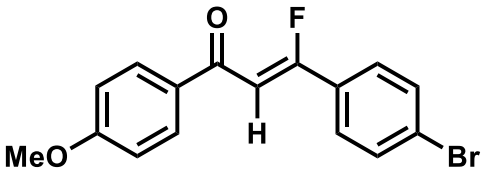
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

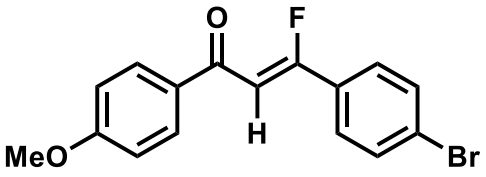
3ac

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



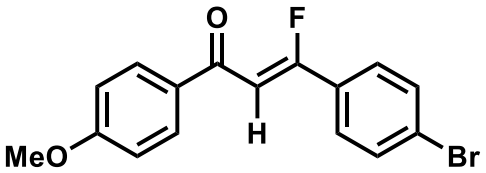
3ad

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



3ad

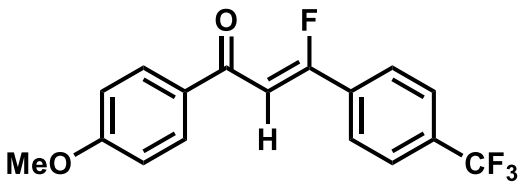
^{19}F NMR (376 MHz, $CDCl_3$)



3ad

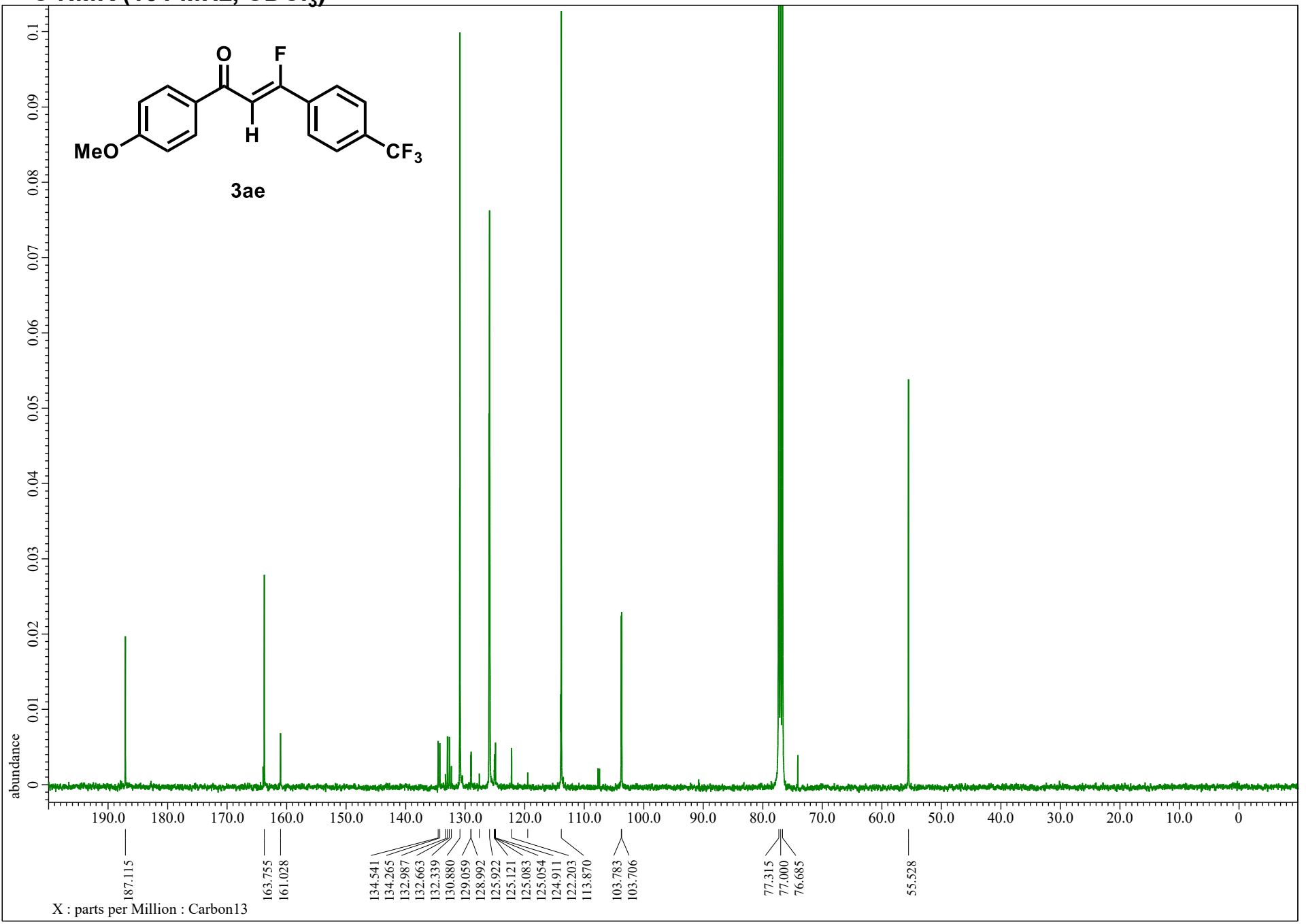
+ *E* isomer

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

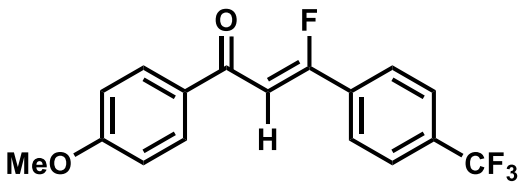


3ae

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



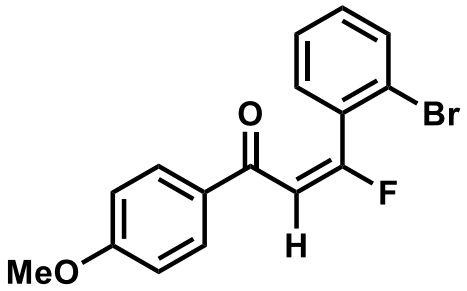
^{19}F NMR (376 MHz, $CDCl_3$)



3ae

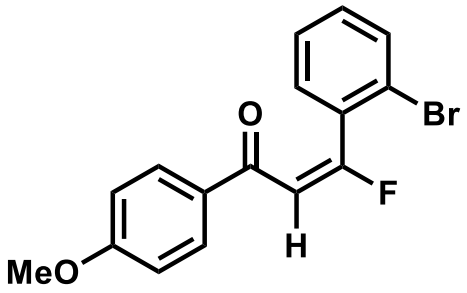
+ *E* isomer

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



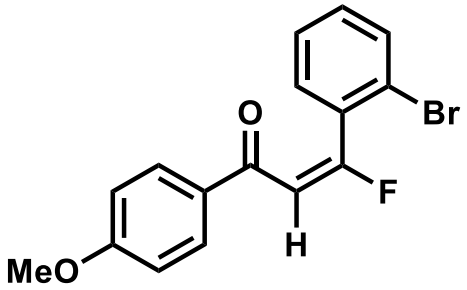
3af

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



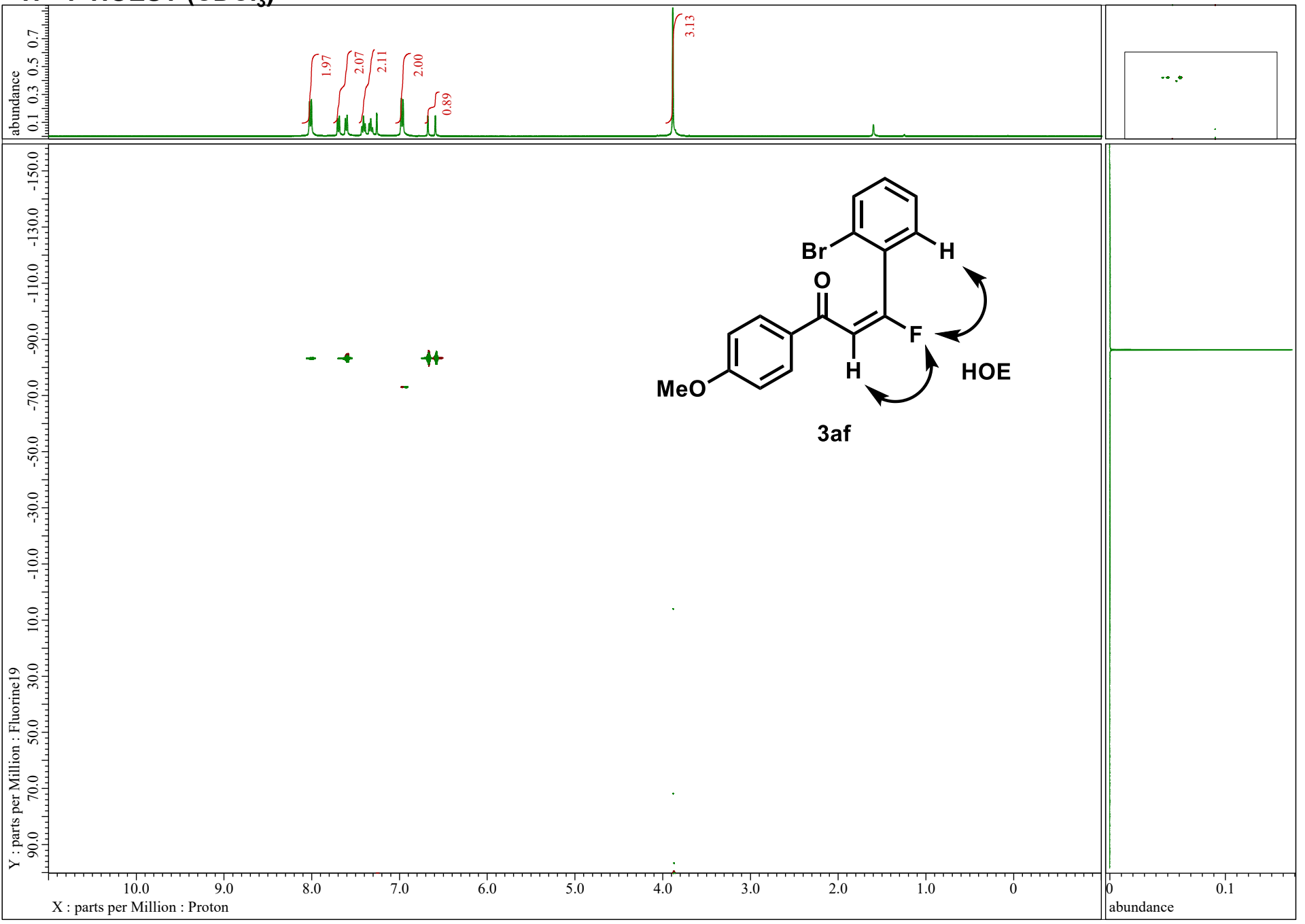
3af

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

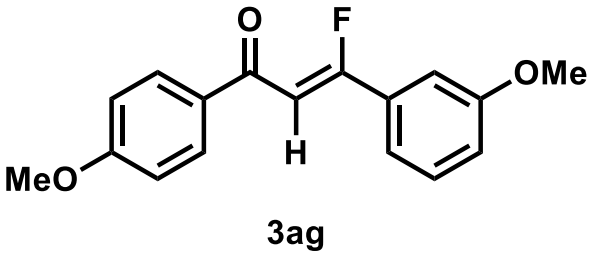


3af

^{1}H-^{19}F HOESY ($CDCl_3$)

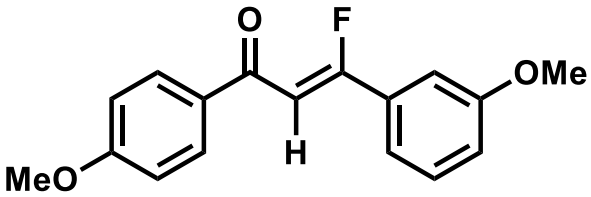


^{1}H NMR (400 MHz, $CDCl_3$)



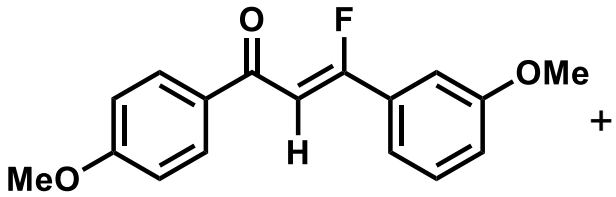
3ag

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



3ag

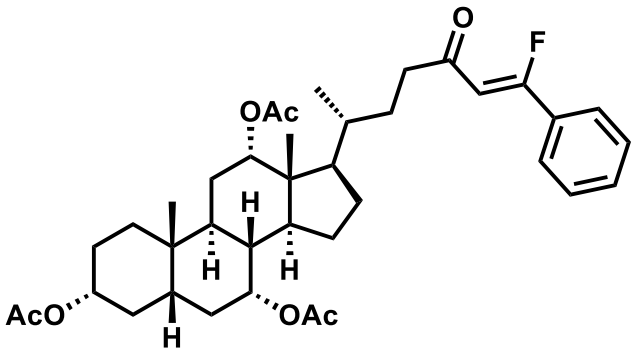
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

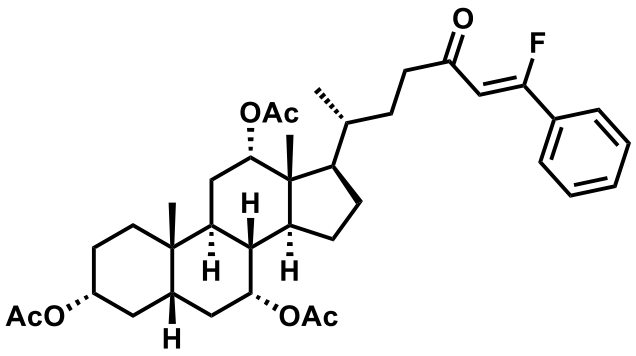
3ag

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



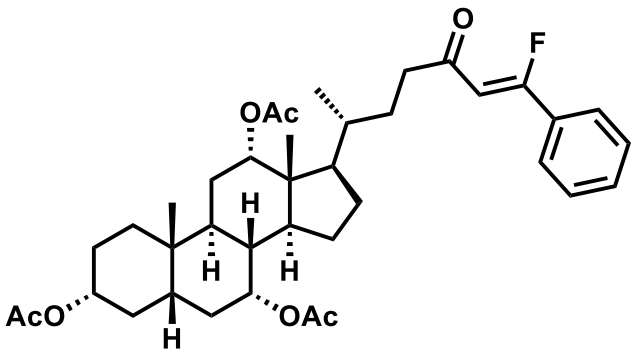
3sa

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



3sa

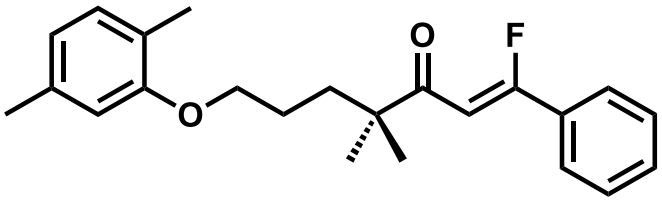
^{19}F NMR (376 MHz, $CDCl_3$)



+ *E* isomer

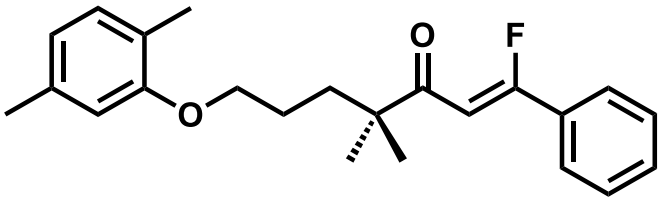
3sa

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



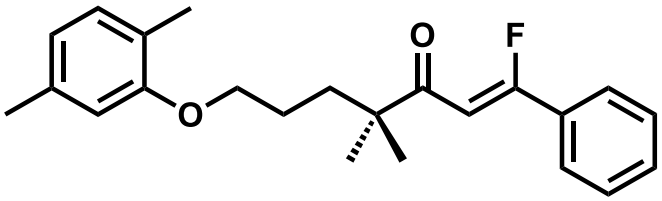
3ta

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



3ta

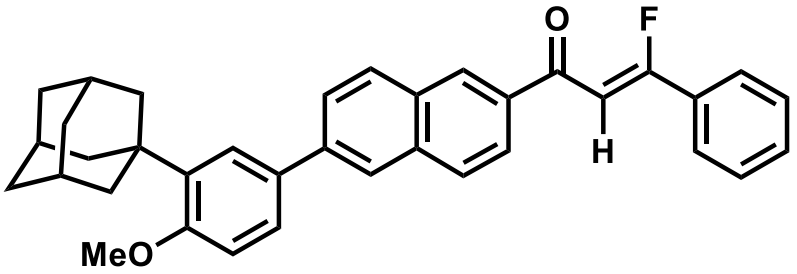
^{19}F NMR (376 MHz, $CDCl_3$)



3ta

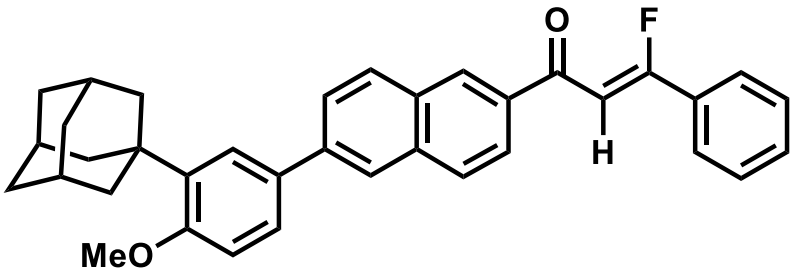
+ *E* isomer

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



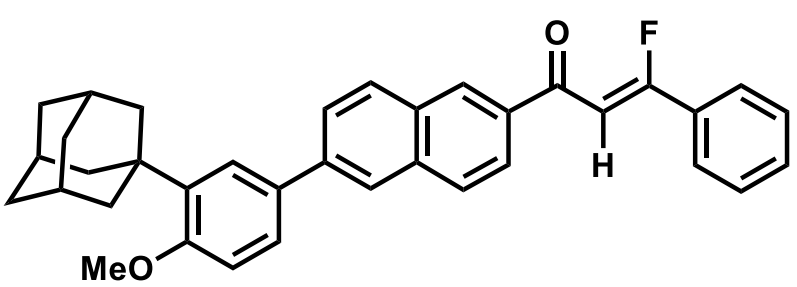
3ua

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



3ua

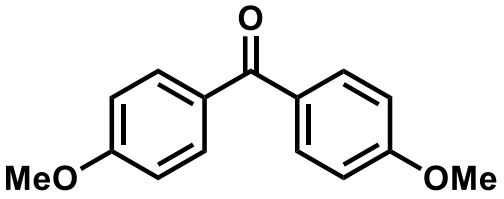
^{19}F NMR (376 MHz, $CDCl_3$)



3ua

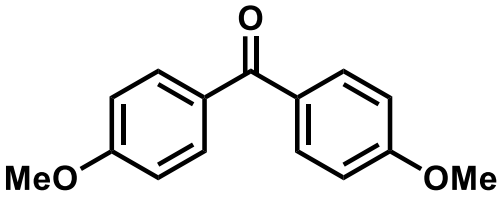
+ *E* isomer

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



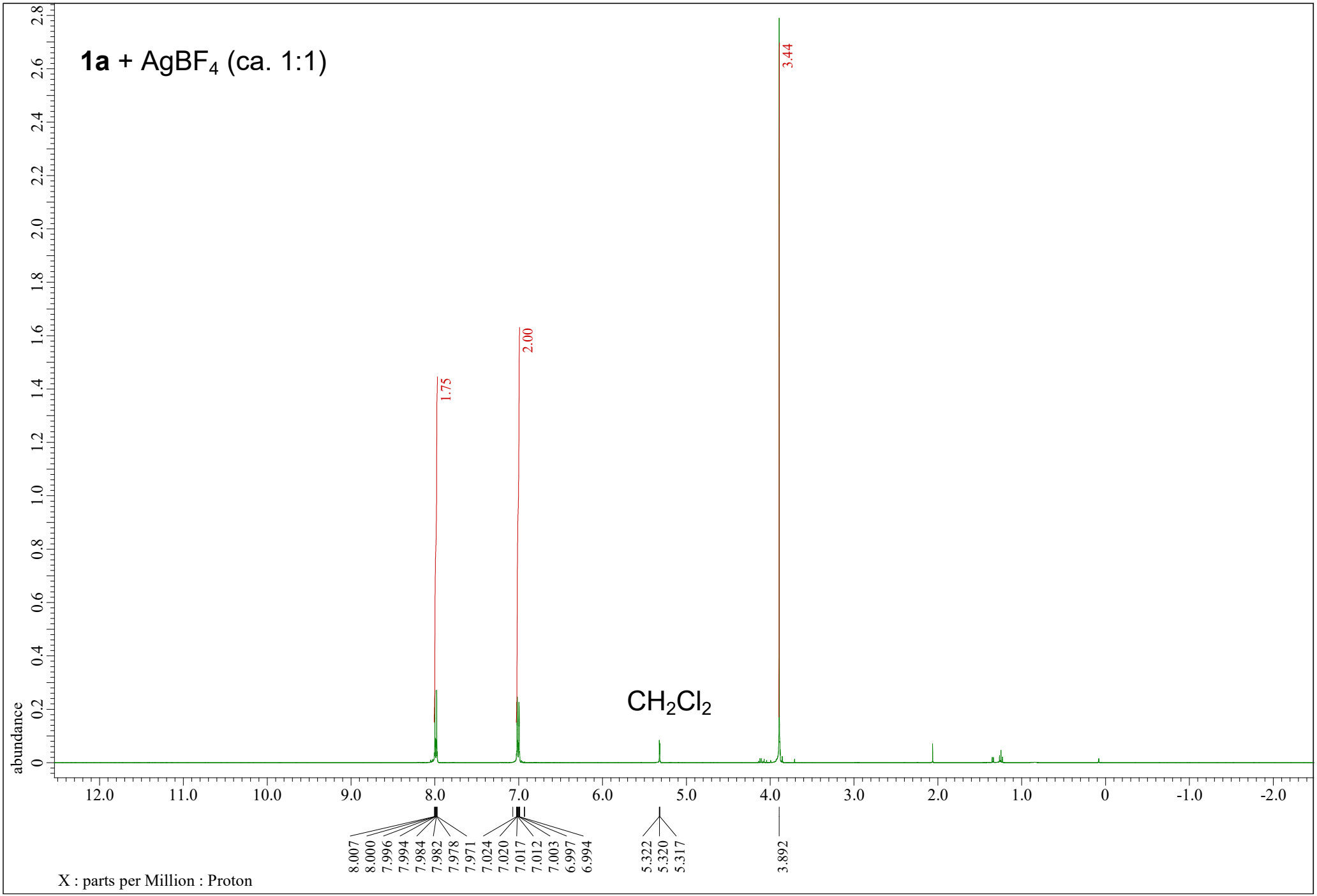
4

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

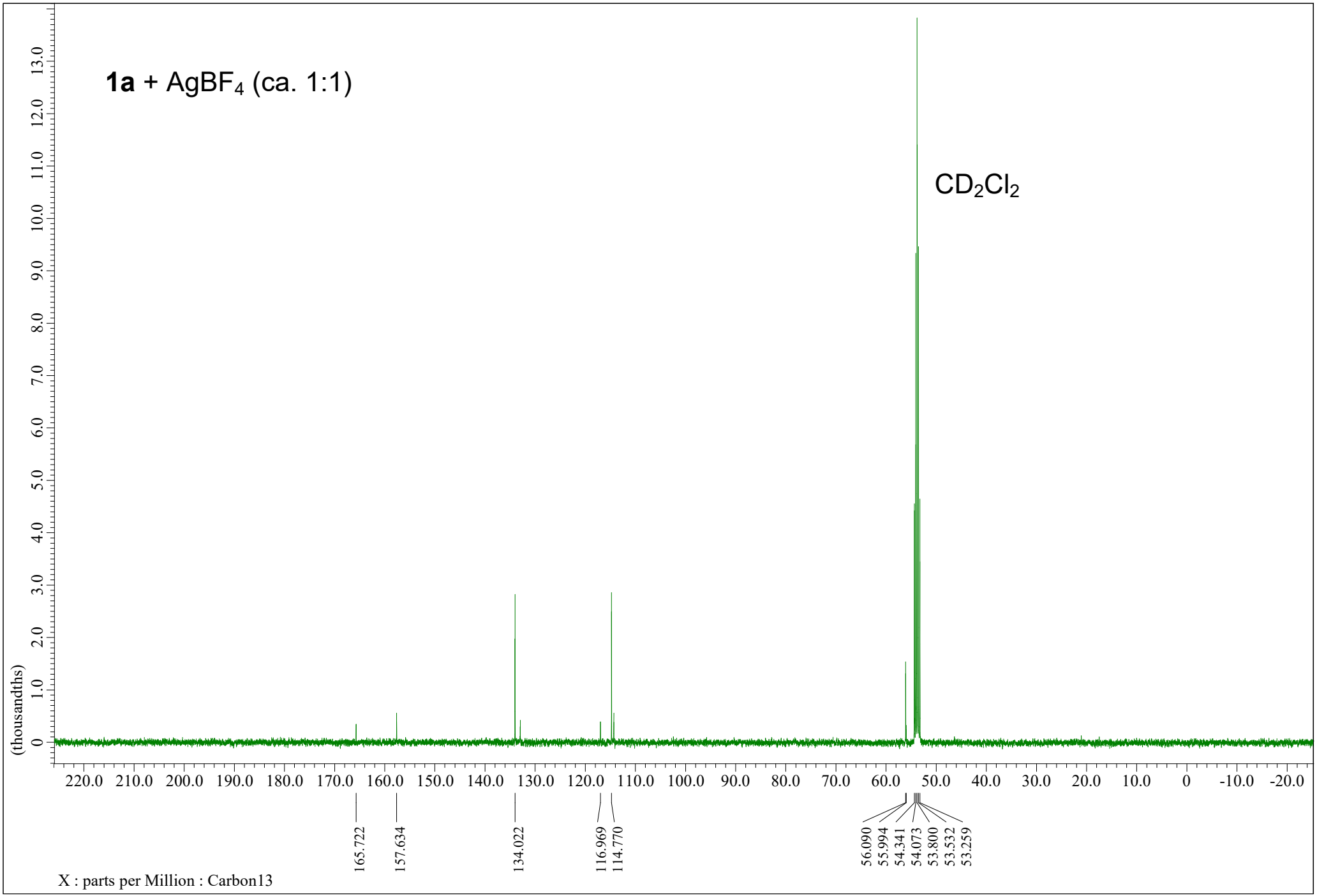


4

^{1}H NMR (400 MHz, CD_2Cl_2)



$^{13}C\{^{19}F\}$ NMR (101 MHz, CD_2Cl_2)



^{19}F NMR (376 MHz, CD_2Cl_2)