Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Visible-Light-Induced Defluorinative Allylation of Difluoromethyl Ketones Using Alkylamines as Bifunctional Agents

Xiaorui Jiao, Zhonghou Huang, Weidong Meng, Shengqing Zhu,* and Lingling Chu*

Email: Lingling.chu1@dhu.edu.cn; zhusq@dhu.edu.cn

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1. General Information

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical, Adamas, Leyan.com and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. ^{1}H, ^{19}F NMR, and ^{13}C NMR spectra were recorded on Bruker 400 (400, 376, and 100 MHz), and are internally referenced to residual solvent signals (for $CDCl_3$, 7.26 and 77.16 ppm). Data for ^{1}H NMR and ^{19}F NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. Photochemical experiments have been performed using a 90W LEDs light (λ_{max} = 467 nm, commercialized from WATTCASTM). Parallel blue LEDs are placed perpendicular to the sidewall of reaction vials, so that the reactions vials can be equally exposed to the blue LEDs (at approximately 2 cm away from the light source, 393 mw/cm^2). Aryl difluoromethyl ketones[1] and allyl chlorides[2] were prepared according to known literature procedures.

2. Preparation of Substrates

2.1 Preparation of aryl difluoromethyl ketones

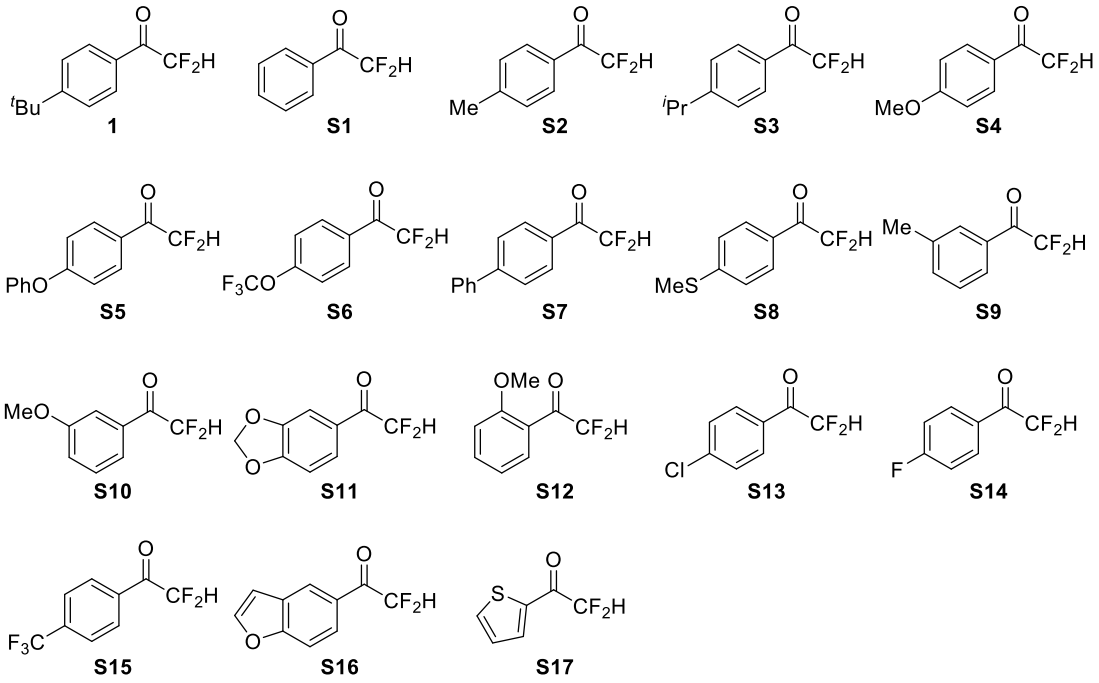
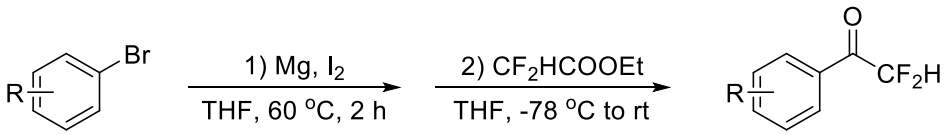


Figure S1. Aryl difluoromethyl ketones



The aryl difluoromethyl ketones was prepared according to a literature procedure[1] from the corresponding aryl bromide. Dried magnesium turnings (0.58g, 1.2 equiv.) were stirred 1 hour in a dry three necked round bottom flask at room temperature under argon. Catalytic amount of I_2 and dry THF (15 mL) were added and the reaction was heated to reflux. A solution of appropriate bromobenzene (20 mmol, 1.0 equiv.) in THF (20 mL) was slowly added to keep reflux and stirred 1 hour at 60 °C. To a dry round bottom flask, ethyl-2,2-difluoroacetate (2.5 g, 1.2 equiv.) was dissolved in dry THF (10 mL) and cooled to -78 °C. The Grignard intermediate was cannulated slowly into the 2,2-difluoroacetate solution and stirred continuously for 4 hours. The mixture was stirred for 1 hour at room temperature. Saturated aqueous NH_4Cl solution (10 mL) and 0.5 M HCl (5.0 mL) were added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, filtered

and concentrated under vacuum. The residue was purified by flash chromatography to afford the desired ketone.

2.2 Preparation of allyl chlorides

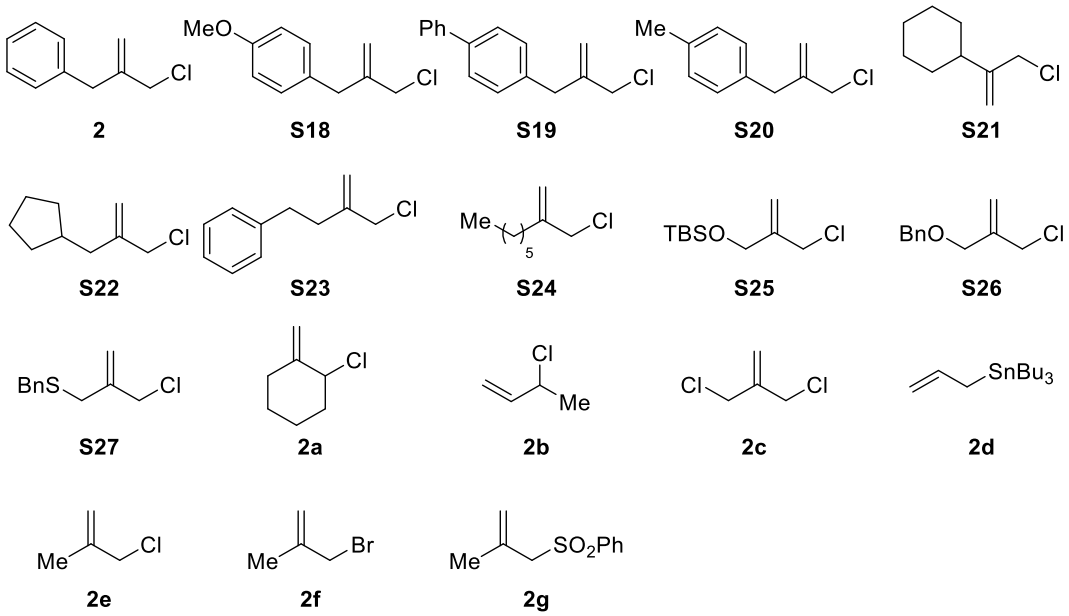
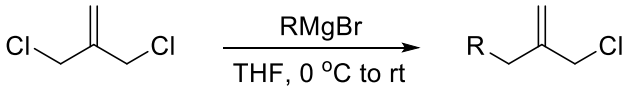
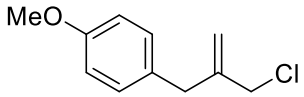


Figure S2. Allyl chlorides



S18, **S22**

Allyl chlorides **S18** and **S22** were prepared according to known literature procedure[2a]: To a flame dried round-bottom flask was added the 3-chloro-2-(chloromethyl)prop-1-ene (10 mmol, 1.0 equiv.) and THF (20 mL). The mixture was cooled to 0 °C and the aryl Grignard reagent (12 mmol, 1.2 equiv.) was added dropwise, and the mixture was warmed to room temperature and stirred overnight. TLC showed the disappearance of starting material. The reaction mixture was equenched with water and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo and purified by column chromatography on silica to afford allyl chloride **S18**, **S22**.



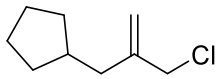
1-(2-(chloromethyl)allyl)-4-methoxybenzene (S18)

S18 was obtained as colorless liquid (1.5 g, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.18 (s, 1H), 4.97 (s, 1H), 3.96 (s, 2H), 3.80 (s, 3H), 3.46 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.40, 145.20, 130.48, 130.14, 115.95, 114.04, 55.39, 47.56, 39.04.

HRMS (ESI): calcd for $C_{11}H_{14}ClO^+$ ($M+H^+$): 197.0728, found: 197.0730.



(2-(chloromethyl)allyl)cyclopentane (S22)

S22 was obtained as colorless liquid (1.1 g, 71%).

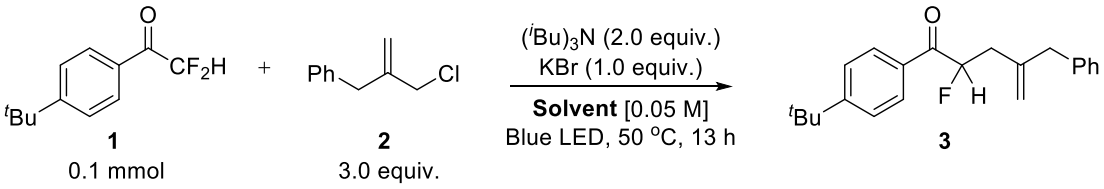
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (s, 1H), 4.95 (s, 1H), 4.04 (s, 2H), 2.19 – 2.17 (m, 2H), 2.04 – 1.99 (m, 1H), 1.77 – 1.71 (m, 2H), 1.62 – 1.59 (m, 2H), 1.55 – 1.52 (m, 2H), 1.15 – 1.10 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.06, 115.04, 48.54, 39.76, 37.65, 32.65, 25.25.

HRMS (ESI): calcd for $C_9H_{16}Cl^+$ ($M+H^+$): 159.0935, found: 159.0930.

3. Optimization of Reaction Conditions

Table S1. Solvent effect.

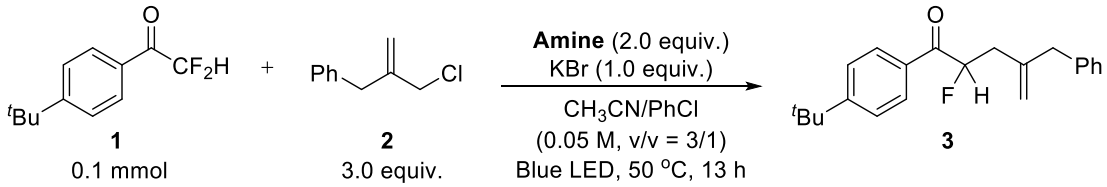


Entry	Solvent	Yield of 3 (%)
1	CH_3CN	65
2	DCE	64
3	PhCl	58
4	1,4-dioxane	53
5	DMF	50
6	DMAc	49
7	DMSO	14
8	CH_3CN/DCE (v/v = 3/1)	66
9	CH_3CN/DMF (v/v = 3/1)	61
10	**CH_3CN/PhCl (v/v = 3/1)**	**72**

Reactions conditions: **1** (0.1mmol, 1.0 equiv.), **2** (3.0 equiv.), (^{t}Bu)$_3$N (2.0 equiv.), KBr (1.0 equiv.), Solvent [0.05 M], 90 W blue LEDs (467 nm), 50 °C, 13 h. Yield was determined by GC using dodecane as an internal standard.

Comment: CH_3CN/PhCl (v/v = 3/1) performed better than other solvents.

Table S2. Amine effect.

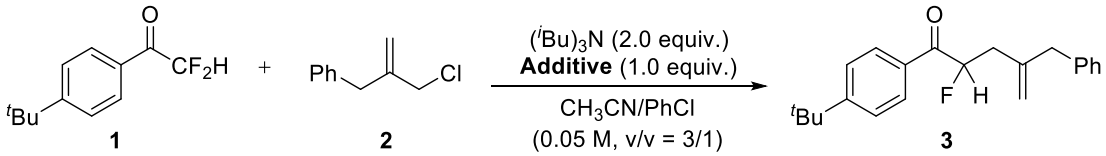


Entry	Amine	Yield of 3 (%)
1	**(^{i}Bu)$_3$N**	**72**
2	(Me)$_2$(^{t}Bu)N	66
3	(^{i}Pr)$_2$NH	55
4	DCHA	52
5	TMP	26
6	Ph$_3$N	19
7	Morpholine	9
8	DBU	8
9	Ph$_2$NH	4
10	PhNMe$_2$	3
11	HE	1
12	Et$_3$N	20
13	DIPEA	54

Reactions conditions: **1** (0.1mmol, 1.0 equiv.), **2** (3.0 equiv.), Amine (2.0 equiv.), KBr (1.0 equiv.), MeCN/PhCl (0.05 M, v/v = 3/1), 90 W blue LEDs (467 nm), 50 °C, 13 h. DCHA = dicyclohexylamine; TMP = 2,2,6,6-tetramethylpiperidine. Yield was determined by GC using dodecane as an internal standard.

Comment: (^{i}Bu)$_3$N performed better than other amines.

Table S3. Additive effect.



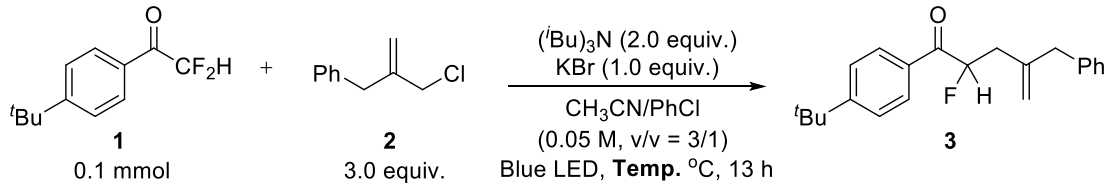
1 0.1 mmol + **2** 3.0 equiv. → **3**

Entry	Additive	Yield of 3 (%)
1	**KBr**	**72**
2	TBAB	69
3	TBACl	67
4	$Et_4N^+Br^-$	63
5	KCl	65
6	LiBr	50
7	Li_2CO_3	48
8	NaBr	43
9	KI	18
10	NaI	14

Reactions conditions: **1** (0.1mmol, 1.0 equiv.), **2** (3.0 equiv.), (^{t}Bu)$_3$N (2.0 equiv.), Additive (1.0 equiv.), MeCN/PhCl (0.05 M, v/v = 3/1), 90 W blue LEDs (467 nm), 50 ^{o}C, 13 h. TBAB = tetrabutylammonium bromide; TBACl = tetrabutylammonium chloride. Yield was determined by GC using dodecane as an internal standard.

Comment: KBr performed better than other additives.

Table S4. Temperature effect.



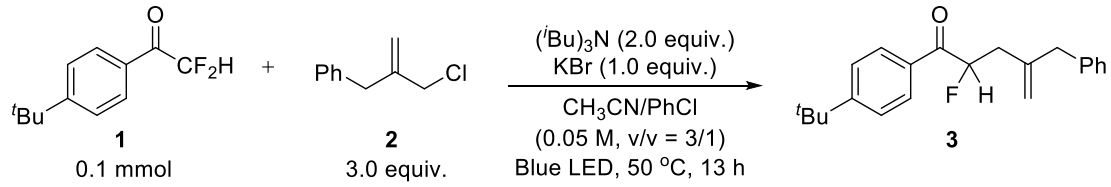
1 0.1 mmol | **2** 3.0 equiv. | **3**

Entry	Temp.	Yield of 3 (%)
1	30 °C	33
2	40 °C	68
3	**50 °C**	**72**
4	60 °C	64
5	70 °C	58

Reactions conditions: **1** (0.1mmol, 1.0 equiv.), **2** (3.0 equiv.), (^{i}Bu)$_3$N (2.0 equiv.), KBr (1.0 equiv.), MeCN/PhCl (0.05 M, v/v = 3/1), 90 W blue LEDs (467 nm), Temp. °C, 13 h. Yield was determined by GC using dodecane as an internal standard.

Comment: 50 °C is the best reaction temperature.

Table S5. Control experiment.



1 0.1 mmol | **2** 3.0 equiv. | **3**

Entry	Conditions	Yield of 3 (%)
1	Standard conditions	72
2	w/o ^{i}Bu$_3$N	0
3	w/o KBr	23
4	w/o light	0

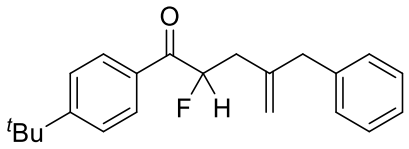
Reactions conditions: **1** (0.1mmol, 1.0 equiv.), **2** (3.0 equiv.), (^{i}Bu)$_3$N (2.0 equiv.), KBr (1.0 equiv.), MeCN/PhCl (0.05 M, v/v = 3/1), 90 W blue LEDs (467 nm), 50 °C, 13 h. Yield was determined by GC using dodecane as an internal standard.

Comment: Control experiments indicated that alkylamine and visible light were essential to this reaction.

4. General Procedure for Defluorinative Allylation

To a flame-dried 8 mL reaction vial equipped with a magnetic stir bar was charged with KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL). The reaction mixture was degassed by nitrogen sparging for 30 minutes, followed by the addition of aryl difluoromethyl ketone (0.1 mmol, 1.0 equiv.), allyl chloride (0.3 mmol, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.). The vial was sealed with parafilm. Then the reaction mixture was irradiated with a 90 W blue LEDs (at approximately 2 cm away from the light source, λ_{max} = 467 nm, 393 mw/cm^2) for 13 h at 50 °C. The reaction mixture was quenched with brine and extracted with EtOAc three times. The combined organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) to afford the products.

5. Characterization Data



4-benzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one (3)

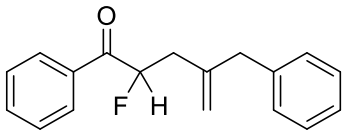
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (22.7 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.11 (m, 5H), 5.66 – 5.50 (m, 1H), 4.96 (s, 1H), 4.91 (s, 1H), 3.40 (s, 2H), 2.57 – 2.48 (m, 2H), 1.25 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.10 – -188.37 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.63 (d, *J* = 18.9 Hz), 157.80, 143.06, 138.88, 131.52, 129.22, 128.89 (d, *J* = 3.3 Hz), 128.63, 126.54, 125.81, 115.79, 92.22 (d, *J* = 185.1 Hz), 43.23, 38.39 (d, *J* = 21.6 Hz), 35.32, 31.13.

HRMS (ESI): calcd for $C_{22}H_{26}FO^+$ ($M+H^+$): 325.1962, found: 325.1959.



4-benzyl-2-fluoro-1-phenylpent-4-en-1-one (4)

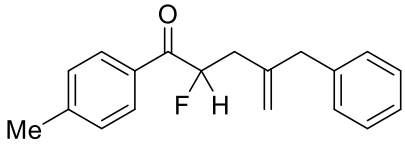
Prepared according to the *General Procedure*: 2,2-difluoro-1-phenylethan-1-one (13 μL, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (18.2 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.50 – 7.46 (m, 1H), 7.35 – 7.31 (m, 2H), 7.24 – 7.12 (m, 5H), 5.64 – 5.51 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.40 (s, 2H), 2.57 – 2.48 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.26 – -188.53 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.04 (d, J = 19.1 Hz), 142.89, 138.81, 134.14, 133.89, 129.19, 128.88 (d, J = 3.3 Hz), 128.83, 128.65, 126.57, 115.91, 92.16 (d, J = 185.3 Hz), 43.19, 38.25 (d, J = 21.6 Hz).

HRMS (ESI): calcd for $C_{18}H_{18}FO^+$ ($M+H^+$): 269.1336, found: 269.1334.



4-benzyl-2-fluoro-1-(*p*-tolyl)pent-4-en-1-one (5)

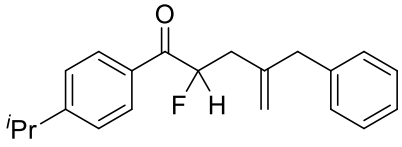
Prepared according to the *General Procedure*: 2,2-difluoro-1-(*p*-tolyl)ethan-1-one (17 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a white solid (17.2 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.25 – 7.13 (m, 7H), 5.65 – 5.49 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.40 (s, 2H), 2.56 – 2.48 (m, 2H), 2.32 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.20 – -188.48 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.61 (d, J = 18.9 Hz), 144.94, 143.01, 138.88, 131.62, 129.54, 129.22, 129.02 (d, J = 3.3 Hz), 128.66, 126.57, 115.85, 92.12 (d, J = 185.0 Hz), 43.21, 38.39 (d, J = 21.5 Hz), 21.86.

HRMS (ESI): calcd for $C_{19}H_{20}FO^+$ ($M+H^+$): 283.1493, found: 283.1490.



4-benzyl-2-fluoro-1-(4-isopropylphenyl)pent-4-en-1-one (6)

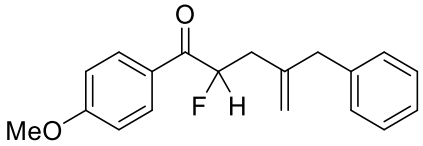
Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-isopropylphenyl)ethan-1-one (17 μL, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (19.2 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.12 (m, 7H), 5.66 – 5.50 (m, 1H), 4.96 (s, 1H), 4.92 (s, 1H), 3.41 (s, 2H), 2.90 – 2.86 (m, 1H), 2.58 – 2.49 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.10 – -188.38 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.64 (d, *J* = 18.8 Hz), 155.61, 143.06, 138.90, 131.97, 129.23, 129.20 (d, *J* = 3.4 Hz), 128.65, 126.97, 126.57, 115.83, 92.21 (d, *J* = 185.2 Hz), 43.24, 38.41 (d, *J* = 21.6 Hz), 34.46, 23.72.

HRMS (ESI): calcd for $C_{21}H_{24}FO^+$ ($M+H^+$): 311.1806, found: 311.1803.



4-benzyl-2-fluoro-1-(4-methoxyphenyl)pent-4-en-1-one (7)

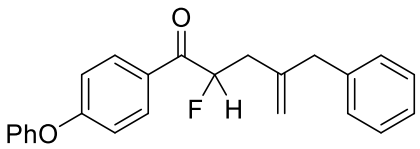
Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-methoxyphenyl) ethan-1-one (18.6 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a white solid (18.8 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.25 – 7.13 (m, 5H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.62 – 5.46 (m, 1H), 4.96 (s, 1H), 4.92 (s, 1H), 3.79 (s, 3H), 3.41 (s, 2H), 2.57 – 2.48 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.39 – -187.67 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.46 (d, *J* = 18.9 Hz), 164.11, 143.08, 138.91, 131.35 (d, *J* = 3.7 Hz), 129.23, 128.66, 127.07, 126.56, 115.79, 114.06, 92.20 (d, *J* = 184.9 Hz), 55.65, 43.23, 38.49 (d, *J* = 21.7 Hz).

HRMS (ESI): calcd for $C_{19}H_{20}FO_2^+$ ($M+H^+$): 299.1442, found: 299.1441.



4-benzyl-2-fluoro-1-(4-phenoxyphenyl)pent-4-en-1-one (8)

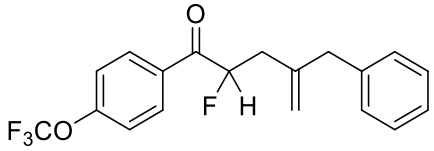
Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-phenoxyphenyl) ethan-1-one (25 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a white solid (28.0 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.24–7.12 (m, 6H), 7.00 – 6.86 (m, 4H), 5.60 – 5.45 (m, 1H), 4.96 (s, 1H), 4.92 (s, 1H), 3.40 (s, 2H), 2.57 – 2.49 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.26 – -187.53 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.57 (d, *J* = 19.1 Hz), 162.72, 155.22, 143.00, 138.86, 131.38 (d, *J* = 3.8 Hz), 130.25, 129.22, 128.67, 128.58, 126.59, 125.03, 120.49, 117.34, 115.87, 92.33 (d, *J* = 185.2 Hz), 43.25, 38.39 (d, *J* = 21.6 Hz).

HRMS (ESI): calcd for $C_{24}H_{22}FO_2^+$ ($M+H^+$): 361.1598, found: 361.1594.



4-benzyl-2-fluoro-1-(4-(trifluoromethoxy)phenyl)pent-4-en-1-one (9)

Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-(trifluoromethox

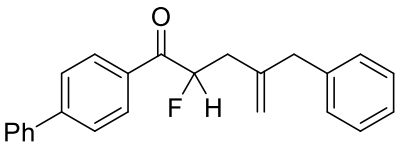
y)phenyl)ethan-1-one (24 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (26.4 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.12 (m, 7H), 5.58 – 5.43 (m, 1H), 4.96 – 4.65 (m, 2H), 3.41 (s, 2H), 2.58 – 2.50 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.58 (s, 3F), -187.15 – -187.42 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79 (d, *J* = 19.9 Hz), 153.13 (q, *J* = 1.8 Hz), 142.66 (q, *J* = 1.3 Hz), 138.76, 132.35 (q, *J* = 1.4 Hz), 131.19 (d, *J* = 4.2 Hz), 129.21, 128.72, 126.67, 120.39 (q, *J* = 257 Hz), 120.49, 116.11, 92.61 (d, *J* = 185.9 Hz), 43.27, 38.11 (d, *J* = 21.5 Hz).

HRMS (ESI): calcd for $C_{19}H_{17}F_4O_2^+$ ($M+H^+$): 353.1159, found: 353.1155.



1-([1,1'-biphenyl]-4-yl)-4-benzyl-2-fluoropent-4-en-1-one (10)

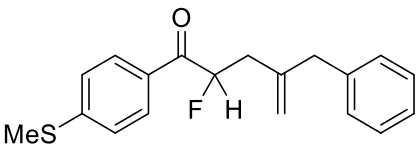
Prepared according to the *General Procedure*: 1-([1,1'-biphenyl]-4-yl)-2,2-difluoroethan-1-one (23.2 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (15.5 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.52 (m, 4H), 7.42 – 7.32 (m, 3H), 7.26 – 7.14 (m, 5H), 5.68 – 5.55 (m, 1H), 4.98 (s, 1H), 4.94 (s, 1H), 3.43 (s, 2H), 2.61 – 2.52 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.94 – -188.22 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.66 (d, *J* = 19.0 Hz), 146.61, 142.93, 139.75, 138.87, 132.81, 129.55 (d, *J* = 3.3 Hz), 129.24, 129.14, 128.70, 128.58, 127.46, 127.41, 126.61, 115.97, 92.33 (d, *J* = 185.3 Hz), 43.26, 38.35 (d, *J* = 21.6 Hz).

HRMS (ESI): calcd for $C_{24}H_{22}FO^+$ ($M+H^+$): 345.1649, found: 345.1647.



4-benzyl-2-fluoro-1-(4-(methylthio)phenyl)pent-4-en-1-one (11)

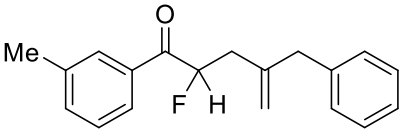
Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-(methylthio)phenyl)ethan-1-one (20 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a yellow oil (17.0 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.10 (m, 7H), 5.62 – 5.46 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.40 (s, 2H), 2.55 – 2.47 (m, 2H), 2.43 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.90 – -188.18 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.94 (d, *J* = 18.7 Hz), 147.25, 142.89, 138.80, 130.14, 129.24 (d, *J* = 3.3 Hz), 129.18, 128.64, 126.55, 124.94, 115.88, 92.16 (d, *J* = 185.0 Hz), 43.16, 38.34 (d, *J* = 22.9 Hz), 14.70.

HRMS (ESI): calcd for $C_{19}H_{20}FOS^+$ ($M+H^+$): 315.1213, found: 315.1216.



4-benzyl-2-fluoro-1-(*m*-tolyl)pent-4-en-1-one (12)

Prepared according to the *General Procedure*: 2,2-difluoro-1-(m-tolyl)ethan-1-one (17 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M,

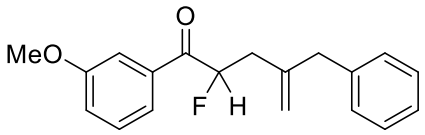
1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (17.2 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.32 – 7.12 (m, 7H), 5.67 – 5.52 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.41 (s, 2H), 2.57 – 2.48 (m, 2H), 2.30 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.28 – -188.56 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.22 (d, *J* = 18.9 Hz), 142.96, 138.87, 138.76, 134.73, 134.20, 129.32 (d, *J* = 2.9 Hz), 129.18, 128.70, 128.66, 126.59, 126.08 (d, *J* = 3.3 Hz), 115.89, 92.07 (d, *J* = 185.2 Hz), 43.21, 38.33 (d, *J* = 21.5 Hz), 21.47.

HRMS (ESI): calcd for $C_{19}H_{20}FO^+$ ($M+H^+$): 283.1493, found: 283.1498.



4-benzyl-2-fluoro-1-(3-methoxyphenyl)pent-4-en-1-one (13)

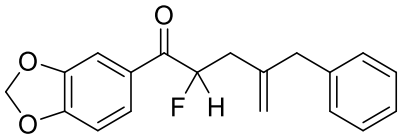
Prepared according to the *General Procedure*: 2,2-difluoro-1-(3-methoxyphenyl) ethan-1-one (18.6 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (15.8 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.35 (m, 1H), 7.25 – 7.03 (m, 8H), 5.64 – 5.52 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.76 (s, 3H), 3.40 (s, 2H), 2.58 – 2.49 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.97 – -188.24 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.84 (d, *J* = 18.9 Hz), 160.01, 142.97, 138.84, 135.44, 129.83, 129.20, 128.66, 126.59, 121.41 (d, *J* = 3.7 Hz), 120.59, 115.90, 113.05 (d, *J* = 3.0 Hz), 92.18 (d, *J* = 185.3 Hz), 55.60, 43.24, 38.38 (d, *J* = 21.5 Hz).

HRMS (ESI): calcd for $C_{19}H_{20}FO_2^+$ ($M+H^+$): 299.1442, found: 299.1445.



1-(benzo[*d*][1,3]dioxol-5-yl)-4-benzyl-2-fluoropent-4-en-1-one (14)

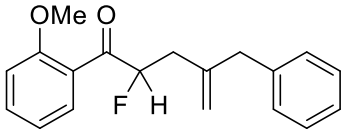
Prepared according to the *General Procedure*: 1-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoroethan-1-one (20 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (22.5 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.13 (m, 7H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.96 (s, 2H), 5.58 – 5.43 (m, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 3.40 (s, 2H), 2.54 – 2.46 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.13 – -187.40 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.94 (d, *J* = 18.9 Hz), 152.47, 148.37, 142.91, 138.82, 129.18, 128.65, 126.58, 125.48, 125.43, 115.87, 108.58 (d, *J* = 3.3 Hz), 108.13, 102.09, 92.00 (d, *J* = 184.9 Hz), 43.18, 38.46 (d, *J* = 21.7 Hz).

HRMS (ESI): calcd for $C_{19}H_{18}FO_3^+$ ($M+H^+$): 313.1234, found: 313.1232.



4-benzyl-2-fluoro-1-(2-methoxyphenyl)pent-4-en-1-one (15)

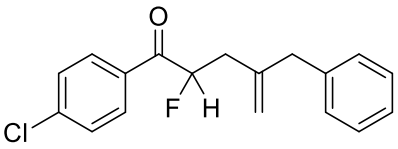
Prepared according to the *General Procedure*: 2,2-difluoro-1-(2-methoxyphenyl) ethan-1-one (18.6 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (20.0 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.39 (m, 2H), 7.20 – 6.83 (m, 7H), 5.89 – 5.73 (m, 1H), 4.91 (s, 1H), 4.84 (s, 1H), 3.71 (s, 3H), 3.35 (s, 2H), 2.57 – 2.27 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.82 – -189.10 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.59 (d, *J* = 18.1 Hz), 158.42, 143.86, 139.08, 134.72, 131.21 (d, *J* = 1.9 Hz), 129.11, 128.44, 126.30, 124.89, 121.22, 114.77, 111.54, 94.27 (d, *J* = 183.0 Hz), 55.61, 43.15, 37.46 (d, *J* = 21.4 Hz).

HRMS (ESI): calcd for $C_{19}H_{20}FO_2^+$ ($M+H^+$): 299.1442, found: 299.1445.



4-benzyl-1-(4-chlorophenyl)-2-fluoropent-4-en-1-one (16)

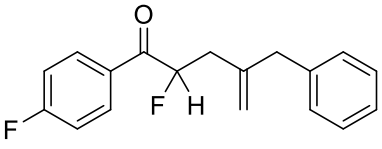
Prepared according to the *General Procedure*: 1-(4-chlorophenyl)-2,2-difluoro ethan-1-one (19 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (20.8 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.11 (m, 7H), 5.57 – 5.42 (m, 1H), 4.94 – 4.93 (m, 2H), 3.39 (s, 2H), 2.56 – 2.47 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.45 – -187.72 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.04 (d, *J* = 19.7 Hz), 142.66 (d, *J* = 1.3 Hz), 140.44, 138.75, 132.45 (d, *J* = 1.4 Hz), 130.41 (d, *J* = 4.0 Hz), 129.17, 129.18, 128.71, 126.65, 116.08, 92.42 (d, *J* = 185.7 Hz), 43.22, 38.13 (d, *J* = 21.5 Hz).

HRMS (ESI): calcd for $C_{18}H_{17}ClFO^+$ ($M+H^+$): 303.0946, found: 303.0944.



4-benzyl-2-fluoro-1-(4-fluorophenyl)pent-4-en-1-one (17)

Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-fluorophenyl)

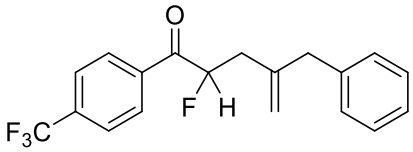
ethan-1-one (17.4 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (18.6 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.25 – 7.12 (m, 5H), 7.03 – 6.98 (m, 2H), 5.59 – 5.43 (m, 1H), 4.95 – 4.93 (m, 2H), 3.40 (s, 2H), 2.57 – 2.48 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.31 – -103.39 (m, 1F), -187.15 – -187.43 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.60 (d, J = 19.6 Hz), 166.13 (d, J = 256.4 Hz), 142.74 (d, J = 1.3 Hz), 138.79, 131.79 (dd, J = 9.5, 4.0 Hz), 130.57 (dd, J = 3.0, 1.3 Hz), 129.20, 128.70, 126.63, 116.15, 115.98 (d, J = 8.6 Hz), 92.43 (d, J = 185.6 Hz), 43.23, 38.19 (d, J = 21.5 Hz).

HRMS (ESI): calcd for $C_{18}H_{17}F_2O^+$ ($M+H^+$): 287.1242, found: 287.1239.



4-benzyl-2-fluoro-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (18)

Prepared according to the *General Procedure*: 2,2-difluoro-1-(4-(trifluoromethy l)phenyl)ethan-1-one (22.4 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (13.4 mg, 40%).

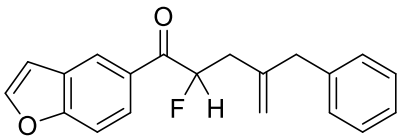
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.26 – 7.12 (m, 5H), 5.61 – 5.45 (m, 1H), 4.96 – 4.95 (m, 2H), 3.41 (s, 2H), 2.59 – 2.51 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.30 (s, 3F), -187.54 – -187.82 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.54 (d, J = 20.4 Hz), 142.53 (q, J = 1.3 Hz), 138.71, 136.96, 135.04 (q, J = 32.8 Hz), 129.40 (d, J = 4.0 Hz), 129.19, 128.74, 126.70, 125.84

(q, J = 3.8 Hz), 123.55 (q, J = 271 Hz) 116.21, 92.68 (d, J = 186.2 Hz), 43.28, 37.98 (d, J = 21.3 Hz).

HRMS (ESI): calcd for $C_{19}H_{17}F_4O^+$ ($M+H^+$): 337.1210, found: 337.1205.



1-(benzofuran-5-yl)-4-benzyl-2-fluoropent-4-en-1-one (19)

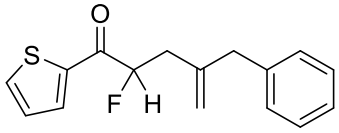
Prepared according to the *General Procedure*: 1-(benzofuran-5-yl)-2,2-difluoro ethan-1-one (19.6 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (17.6 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.74 – 7.71 (d, J = 8.8, 1H), 7.62 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1H), 7.26 – 7.14 (m, 5H), 6.75 (d, J = 2.2 Hz, 1H), 5.73 – 5.58 (m, 1H), 4.97 (s, 1H), 4.94 (s, 1H), 3.43 (s, 2H), 2.64 – 2.53 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.21 – -187.49 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.48 (d, J = 18.9 Hz), 157.84, 146.70, 142.94, 138.90, 129.56, 129.22, 128.69, 127.76, 126.60, 125.56 (d, J = 3.1 Hz), 123.37 (d, J = 4.2 Hz), 115.94, 111.93, 107.45, 92.24 (d, J = 185.2 Hz), 43.22, 38.49 (d, J = 21.7 Hz).

HRMS (ESI): calcd for $C_{20}H_{18}FO_2^+$ ($M+H^+$): 309.1285, found: 309.1282.



4-benzyl-2-fluoro-1-(thiophen-2-yl)pent-4-en-1-one (20)

Prepared according to the *General Procedure*: 2,2-difluoro-1-(thiophen-2-yl) ethan-1-one (16.2 mg, 0.1 mmol), (2-(chloromethyl)allyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M,

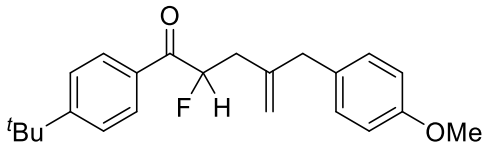
1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (10.0 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.25 – 7.05 (m, 6H), 5.41 – 5.26 (m, 1H), 4.97 (s, 1H), 4.91 (s, 1H), 3.39 (s, 2H), 2.61 – 2.53 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -185.54 – -185.82 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.77 (d, J = 21.9 Hz), 142.85, 140.36, 138.82, 135.36 (d, J = 2.4 Hz), 134.29 (d, J = 8.2 Hz), 129.21, 128.64, 128.55 (d, J = 1.8 Hz), 126.56, 115.91, 93.77 (d, J = 187.8 Hz), 43.24, 38.81 (d, J = 21.2 Hz).

HRMS (ESI): calcd for $C_{16}H_{16}FOS^+$ ($M+H^+$): 275.0900, found: 275.0897.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4-(4-methoxybenzyl)pent-4-en-1-one (21)

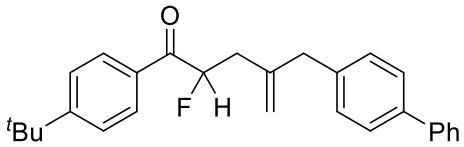
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluoroethan-1-one (20 μL, 0.1 mmol), 1-(2-(chloromethyl)allyl)-4-methoxybenzene (58 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (26.6 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.74 – 5.57 (m, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 3.80 (s, 3H), 3.43 (s, 2H), 2.65 – 2.56 (m, 2H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.34 – -188.62 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.66 (d, J = 18.9 Hz), 158.37, 157.81, 143.41, 131.50, 130.88, 130.18, 128.90 (d, J = 3.3 Hz), 125.79, 115.49, 114.05, 92.19 (d, J = 185.0 Hz), 55.37, 42.32, 38.35 (d, J = 21.5 Hz), 35.33, 31.13.

HRMS (ESI): calcd for $C_{23}H_{28}FO_2^+$ ($M+H^+$): 355.2068, found: 355.2065.



4-([1,1'-biphenyl]-4-ylmethyl)-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one (22)

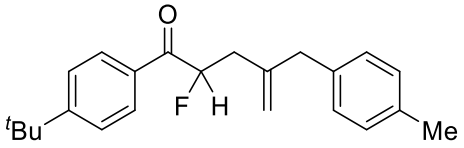
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 4-(2-(chloromethyl)allyl)-1,1'-biphenyl (72.6 mg, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (28.0 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.33 (m, 6H), 7.30 – 7.19 (m, 7H), 5.69 – 5.53 (m, 1H), 4.99 – 4.97 (m, 2H), 3.45 (s, 2H), 2.60 – 2.50 (m, 2H), 1.19 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.84 – -189.11 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.51 (d, J = 18.7 Hz), 157.81, 142.84, 140.86, 139.46, 137.95, 131.36, 129.67, 128.90, 128.81 (d, J = 3.2 Hz), 127.35, 127.32, 127.06, 125.79, 116.03, 91.98 (d, J = 184.9 Hz), 42.74, 38.36 (d, J = 21.6 Hz), 35.26, 31.05.

HRMS (ESI): calcd for $C_{28}H_{30}FO^+$ ($M+H^+$): 401.2275, found: 401.2280.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4-(4-methylbenzyl)pent-4-en-1-one (23)

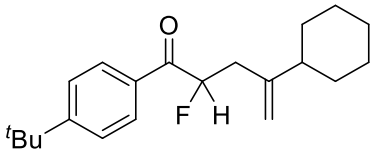
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 1-(2-(chloromethyl)allyl)-4-methylbenzene (54 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (21.3 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.12 – 7.11 (m, 4H), 5.74 – 5.59 (m, 1H), 5.04 (s, 1H), 5.01 (s, 1H), 3.46 (s, 2H), 2.66 – 2.56 (m, 2H), 2.35 (s, 3H), 1.35 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.42 – -188.70 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.54 (d, *J* = 18.8 Hz), 157.66, 143.10, 135.93, 135.68, 131.39, 129.24, 129.00, 128.79 (d, *J* = 3.2 Hz), 125.67, 115.54, 92.03 (d, *J* = 185.0 Hz), 42.67, 38.28 (d, *J* = 21.6 Hz), 35.22, 31.03, 21.08.

HRMS (ESI): calcd for $C_{23}H_{28}FO^+$ ($M+H^+$): 339.2119, found: 339.2117.



1-(4-(*tert*-butyl)phenyl)-4-cyclohexyl-2-fluoropent-4-en-1-one (24)

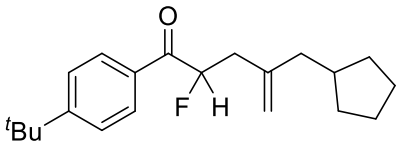
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), (3-chloroprop-1-en-2-yl)cyclohexane (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (20.5 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 5.75 – 5.59 (m, 1H), 4.93 – 4.92 (m, 2H), 2.76 – 2.62 (m, 2H), 1.92 – 1.83 (m, 1H), 1.79 – 1.77 (m, 4H), 1.76 – 1.75 (m, 1H), 1.35 (s, 9H), 1.30 – 1.11 (m, 5H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.68 – -186.95 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.14 (d, *J* = 19.5 Hz), 157.82, 149.42, 131.78, 129.07 (d, *J* = 3.7 Hz), 125.85, 110.90, 92.89 (d, *J* = 184.8 Hz), 44.20, 38.13, 37.92, 35.37, 32.46, 32.29, 31.16, 26.82 (d, *J* = 5.2 Hz), 26.44.

HRMS (ESI): calcd for $C_{21}H_{30}FO^+$ ($M+H^+$): 317.2275, found: 317.2271.



1-(4-(*tert*-butyl)phenyl)-4-(cyclopentylmethyl)-2-fluoropent-4-en-1-one (25)

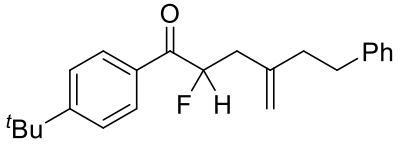
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), (2-(chloromethyl)allyl)cyclopentane (35 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (14.5 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 5.76 – 5.61 (m, 1H), 4.92 (s, 2H), 2.70 – 2.61 (m, 2H), 2.14 – 2.00 (m, 3H), 1.76 – 1.73 (m, 2H), 1.61 – 1.50 (m, 4H), 1.35 (s, 9H), 1.14 – 1.11 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.06 – -187.34 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.07 (d, *J* = 19.3 Hz), 157.83, 143.71, 131.68, 129.03 (d, *J* = 3.7 Hz), 125.86, 113.71, 92.62 (d, *J* = 185.2 Hz), 42.84, 39.17, 38.96, 37.72, 35.36, 32.68, 32.53, 31.15, 25.23 (d, *J* = 4.7 Hz).

HRMS (ESI): calcd for $C_{21}H_{30}FO^+$ ($M+H^+$): 317.2275, found: 317.2278.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4-methylene-6-phenylhexan-1-one (26)

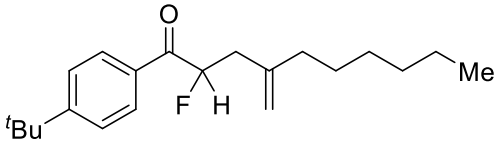
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), (3-(chloromethyl)but-3-en-1-yl)benzene (53 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (23.0 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.12 – 7.10 (m, 3H), 5.69 – 5.53 (m, 1H), 4.90 – 4.89 (m, 2H), 2.73 – 2.58 (m, 4H), 2.38 – 2.34 (m, 2H), 1.27 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.88 – -187.15 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.64 (d, *J* = 18.8 Hz), 157.77, 143.21, 136.03, 135.78, 131.49, 129.34, 129.11, 128.89 (d, *J* = 3.2 Hz), 125.77, 115.64, 92.13 (d, *J* = 185.0 Hz), 42.77, 38.38 (d, *J* = 21.6 Hz), 35.32, 31.13, 21.18.

HRMS (ESI): calcd for $C_{23}H_{28}FO^+$ ($M+H^+$): 339.2119, found: 339.2115.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4-methylenedecan-1-one (27)

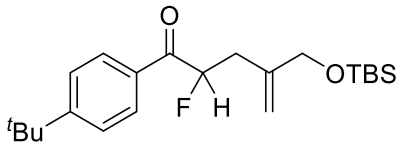
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 2-(chloromethyl)oct-1-ene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (21.6 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 5.76 – 5.60 (m, 1H), 4.92 – 4.91 (m, 2H), 2.71 – 2.61 (m, 2H), 2.12 (t, *J* = 7.7 Hz, 2H), 1.47 – 1.42 (m, 2H), 1.35 (s, 9H), 1.32 – 1.25 (m, 6H), 0.90 – 0.87 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.04 – -187.31 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.04 (d, *J* = 19.4 Hz), 157.85, 144.28 (d, *J* = 1.4 Hz), 131.73, 129.04 (d, *J* = 3.7 Hz), 125.87, 112.95, 92.63 (d, *J* = 185.1 Hz), 39.23 (d, *J* = 21.6 Hz), 36.24, 35.37, 31.86, 31.16, 29.10, 27.67, 22.76, 14.24.

HRMS (ESI): calcd for $C_{21}H_{32}FO^+$ ($M+H^+$): 319.2432, found: 319.2429.



1-(4-(*tert*-butyl)phenyl)-4-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-fluoropent-4-en-1-one (28)

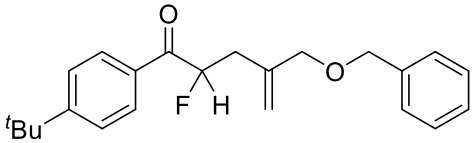
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluoroethan-1-one (20 μL, 0.1 mmol), *tert*-butyl((2-(chloromethyl)allyl)oxy)dimethylsilane (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (22.3 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.85 – 5.70 (m, 1H), 5.19 (s, 1H), 5.02 (s, 1H), 4.26 – 4.14 (m, 2H), 2.86 – 2.56 (m, 2H), 1.35 (s, 9H), 0.91 (s, 9H), 0.08 (d, *J* = 4.6 Hz, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.71 – -187.98 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.70 (d, *J* = 18.9 Hz), 157.85, 143.10, 131.63, 129.01 (d, *J* = 3.3 Hz), 125.86, 113.40, 92.26 (d, *J* = 184.5 Hz), 66.20, 36.32 (d, *J* = 21.8 Hz), 35.35, 31.15, 26.04, 18.50, -5.23 (d, *J* = 2.1 Hz).

HRMS (ESI): calcd for $C_{22}H_{36}FO_2Si^+$ ($M+H^+$): 379.2463, found: 379.2457.



4-((benzyloxy)methyl)-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one (29)

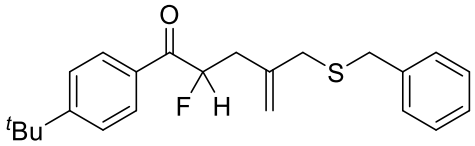
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluoroethan-1-one (20 μL, 0.1 mmol), (((2-(chloromethyl)allyl)oxy)methyl)benzene (48 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (22.0 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.31 (m, 7H), 5.92 – 5.76 (m, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 4.53 (s, 2H), 4.22 – 4.08 (m, 2H), 2.92 – 2.63 (m, 2H), 1.33 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -189.37 – -189.65 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.43 (d, *J* = 18.5 Hz), 157.72, 140.30, 138.04, 131.30, 128.84 (d, *J* = 2.9 Hz), 128.47, 127.87, 127.75, 125.73, 116.46, 91.49 (d, *J* = 184.0 Hz), 73.24, 72.26, 36.82 (d, *J* = 21.9 Hz), 35.22, 31.03.

HRMS (ESI): calcd for $C_{23}H_{28}FO_2^+$ ($M+H^+$): 355.2068, found: 355.2065.



4-((benzylthio)methyl)-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one (30)

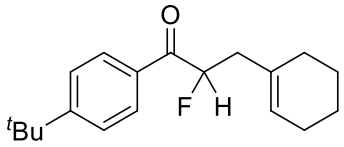
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), benzyl(2-(chloromethyl)allyl)sulfane (63.6 mg, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (24.4 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.22 (m, 5H), 5.86 – 5.70 (m, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.63 (s, 2H), 3.18 – 3.17 (m, 2H), 2.96 – 2.70 (m, 2H), 1.35 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.77 – -189.04 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.55 (d, *J* = 19.0 Hz), 157.97, 139.04, 138.10, 131.55, 129.19, 129.06 (d, *J* = 3.2 Hz), 128.63, 127.17, 125.92, 117.43, 92.10 (d, *J* = 184.9 Hz), 37.50, 37.22 (d, *J* = 21.7 Hz), 35.23, 31.18, 29.85.

HRMS (ESI): calcd for $C_{23}H_{28}FOS^+$ ($M+H^+$): 371.1839, found: 371.1835.



1-(4-(*tert*-butyl)phenyl)-3-(cyclohex-1-en-1-yl)-2-fluoropropan-1-one (31)

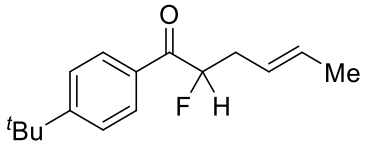
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 1-chloro-2-methylenecyclohexane (42 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (21.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 5.74 – 5.70 (m, 1H), 5.61 – 5.55 (m, 1H), 2.61 – 2.52 (m, 2H), 2.07 – 1.97 (m, 4H), 1.65 – 1.62 (m, 2H), 1.57 – 1.53 (m, 2H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.17 – -187.45 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.37 (d, *J* = 19.0 Hz), 157.67, 132.18 (d, *J* = 1.8 Hz), 131.80, 128.94 (d, *J* = 3.4 Hz), 125.78, 125.71, 92.62 (d, *J* = 185.0 Hz), 41.44 (d, *J* = 21.6 Hz), 35.31, 31.13, 28.65, 25.40, 22.88, 22.19.

HRMS (ESI): calcd for $C_{19}H_{26}FO^+$ ($M+H^+$): 289.1962, found: 289.1957.



1-(4-(*tert*-butyl)phenyl)-2-fluorohex-4-en-1-one (32)

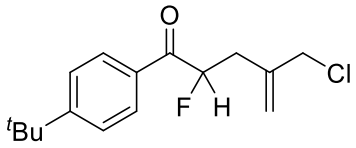
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 3-chlorobut-1-ene (30 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (16.0 mg, 65%, *Z/E* = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 5.64 – 5.47 (m, 3H), 2.72 – 2.60 (m, 2H), 1.68 – 1.64 (m, 2.27H), 1.61 – 1.59 (m, 0.75H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.06 – -188.32 (m, 0.25F), -188.38 – -188.64 (m, 0.75F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.03 (d, *J* = 19.3 Hz), 157.75, 131.89, 129.95, 129.01 (d, *J* = 3.7 Hz), 125.81, 124.15 (d, *J* = 3.7 Hz), 93.43 (d, *J* = 184.5 Hz), 36.14 (d, *J* = 21.5 Hz), 35.35, 31.16, 18.12.

HRMS (ESI): calcd for $C_{16}H_{22}FO^+$ ($M+H^+$): 249.1649, found: 249.1646.



1-(4-(*tert*-butyl)phenyl)-4-(chloromethyl)-2-fluoropent-4-en-1-one (33)

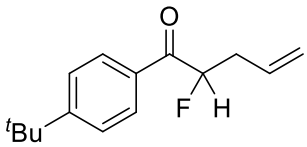
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 3-chloro-2-(chloromethyl)prop-1-ene (35 μL, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (14.0 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 5.88 – 5.72 (m, 1H), 5.32 (s, 1H), 5.15 (s, 1H), 4.23 – 4.13 (m, 2H), 2.99 – 2.72 (m, 2H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.52 – -188.79 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.14 (d, *J* = 18.8 Hz), 158.07, 139.61, 131.39, 128.97 (d, *J* = 3.3 Hz), 125.95, 118.82, 91.78 (d, *J* = 185.2 Hz), 48.28, 36.17 (d, *J* = 21.7 Hz), 35.36, 31.11.

HRMS (ESI): calcd for $C_{16}H_{21}ClFO^+$ ($M+H^+$): 283.1259, found: 283.1256.



1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one (34)

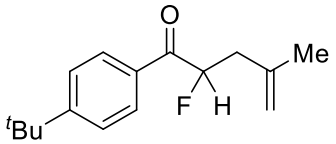
Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), allyltributylstannane (37 μL, 1.2 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil (14.0 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.51 – 7.49 (m, 2H), 5.94 – 5.84 (m, 1H), 5.67 – 5.52 (m, 1H), 5.22 – 5.16 (m, 2H), 2.80 – 2.68 (m, 2H), 1.35 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -188.25 – -188.53 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.78 (d, J = 19.3 Hz), 157.87, 131.78, 131.74, 129.05 (d, J = 3.9 Hz), 125.86, 119.17, 92.96 (d, J = 184.9 Hz), 37.13 (d, J = 21.5 Hz), 35.37, 31.15.

HRMS (ESI): calcd for $C_{15}H_{20}FO^+$ ($M+H^+$): 235.1493, found: 235.1490.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4-methylpent-4-en-1-one (35)

Prepared according to the *General Procedure*: 1-(4-(*tert*-butyl)phenyl)-2,2-difluo roethan-1-one (20 μL, 0.1 mmol), 3-chloro-2-methylprop-1-ene (30 μL, 3.0 equiv.) / 3-bromo-2-methylprop-1-ene (30 μL, 3.0 equiv.) / ((2-methylallyl)sulfonyl)benzene (58 mg, 3.0 equiv.), triisobutylamine (48 μL, 2.0 equiv.), KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL) were used. After 13 hours, the reaction mixture was processed as outlined in the general procedure and isolated by flash chromatography (silica gel, petroleum ether/ ethyl acetate = 300:1) as a colorless oil **35** (16.0 mg, 65%

with allyl chloride **2e**; 8.7 mg, 35% with allyl bromide **2f**; 11.0 mg, 45% with allyl sulfone **2g**).

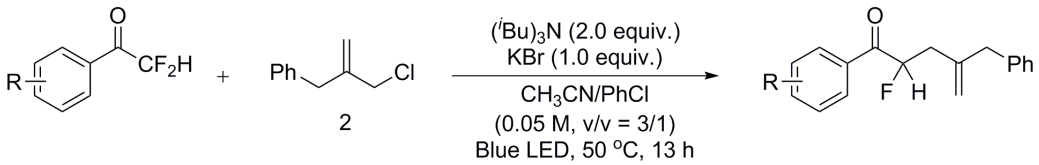
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 5.77 – 5.61 (m, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 2.71 – 2.62 (m, 2H), 1.86 (s, 3H), 1.35 (s, 9H).

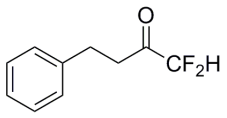
^{19}F NMR (376 MHz, $CDCl_3$) δ -187.22 – -187.49 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.96 (d, *J* = 19.3 Hz), 157.85, 140.12 (d, *J* = 1.5 Hz), 131.68, 129.02 (d, *J* = 3.7 Hz), 125.87, 114.34, 92.48 (d, *J* = 185.3 Hz), 40.89 (d, *J* = 21.6 Hz), 35.36, 31.15, 22.75.

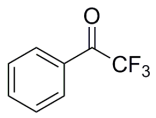
HRMS (ESI): calcd for $C_{16}H_{22}FO^+$ ($M+H^+$): 249.1649, found: 249.1645.

6. Unsuccessful Substrates

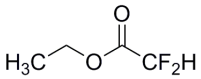




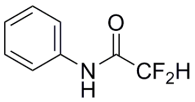
1a (S.M. remain)



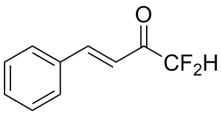
1b (S.M. remain)



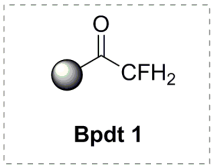
1c (S.M. remain)



1d (S.M. remain)



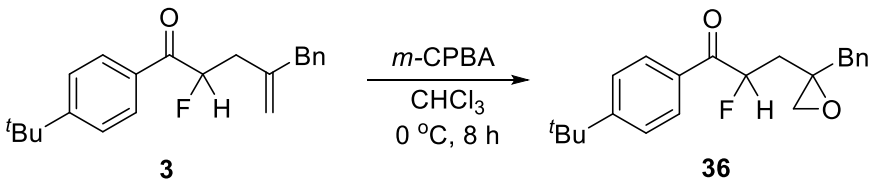
1e
ND (**Bpdt 1**, trace)



Bpdt 1

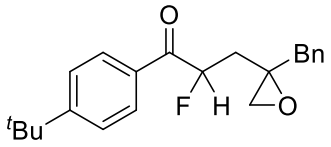
Figure S3. Unsuccessful substrates

7. Synthetic Applications



3 **36**

To a stirred solution of **3** (0.2 mmol, 1.0 equiv.) in $CHCl_3$ at 0 °C was added 3-chloroperbenzoic acid (*m*-CPBA, 0.4 mmol, 2.0 equiv.). The reaction mixture was warmed to room temperature and stirred for 8 hours. The reaction mixture was washed with saturated aqueous $NaHCO_3$, extracted with DCM. The combined organic layer was dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. This crude reaction mixture was purified by flash silica gel column chromatographyto give epoxide **36** (32.0 mg, 47%, d.r. = 1:1.9)[3].



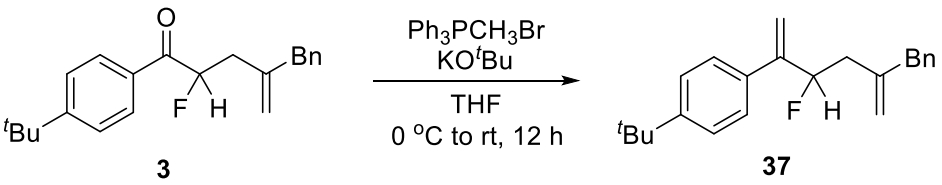
3-(2-benzyloxiran-2-yl)-1-(4-(*tert*-butyl)phenyl)-2-fluoropropan-1-one (36)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.35 (m, 4H), 7.26 – 7.14 (m, 5H), 5.61 – 5.58 (m, 0.35H), 5.49 – 5.46 (m, 0.65H), 3.09 – 2.95 (m, 0.73H), 2.90 – 2.86 (m, 2H), 2.67 – 2.63 (m, 1.30H), 2.27 – 2.00 (m, 2H), 1.26 (s, 5.81H), 1.25 (s, 3.20H).

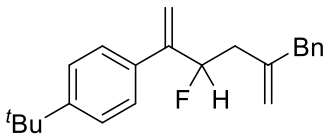
^{19}F NMR (376 MHz, $CDCl_3$) δ -187.16 – -187.44 (m, 0.66F), -189.15 – -189.43 (m, 0.34F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.08 (d, J = 18.8 Hz), 194.85(d, J = 18.8 Hz), 158.00, 157.98, 136.44, 136.18, 131.13, 131.04, 129.93, 129.80, 128.91 (d, J = 2.8 Hz), 128.84 (d, J = 2.9 Hz), 128.72, 128.63, 127.01, 125.91, 90.89 (d, J = 182.3 Hz), 89.56 (d, J = 182.3 Hz), 57.85, 57.25, 53.52, 51.35 (d, J = 3.4 Hz), 42.30, 40.91 (d, J = 1.7 Hz), 37.37 (d, J = 21.0 Hz), 35.81 (d, J = 21.8 Hz), 35.36, 31.13.

HRMS (ESI): calcd for $C_{22}H_{26}FO_2^+$ ($M+H^+$): 341.1911, found: 341.1906.



A solution of methyl triphenylphosphonium bromide (0.45 mmol, 1.5 equiv.) in anhydrous THF (1 mL) was cooled to 0 °C under argon, followed by addition of KO^{t}Bu (0.45 mmol, 1.5 equiv.). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of **3** (0.3 mmol, 1.5 equiv.) in anhydrous THF (1 mL) was added dropwise. The resulting mixture was warmed gradually to room temperature and kept stirring for 12 h. The resultant reaction solution was filtered over Celite, and the filtrate was concentrated under reduced pressure to yield a residue which was further purified over silica gel flash column chromatography to afford **37** (68.0 mg, 60%)[4].



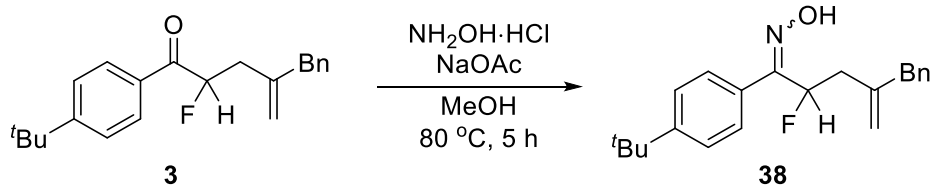
1-(5-benzyl-3-fluorohexa-1,5-dien-2-yl)-4-(*tert*-butyl)benzene (37)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.02 (m, 9H), 5.47 – 5.44 (m, 0.51H), 5.34 – 5.26 (m, 2.49H), 4.85 – 4.80 (m, 2H), 3.30 (s, 2H), 2.31 – 2.22 (m, 2H), 1.23 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -177.11 – -177.37 (m, 1F).

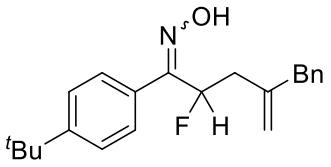
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.01, 147.01 (d, J = 16.4 Hz), 144.44 (d, J = 1.8 Hz), 139.23, 135.35 (d, J = 3.2 Hz), 129.22, 128.46, 126.46, 126.31, 125.48, 114.84, 113.54 (d, J = 10.9 Hz), 93.03 (d, J = 176.4 Hz), 43.23, 40.69 (d, J = 23.1 Hz), 34.65, 31.42.

HRMS (ESI): calcd for $C_{23}H_{28}F^+$ ($M+H^+$): 323.2170, found: 323.2172.



H_2NOH•HCl (1.2 mmol, 1.5 equiv.) and NaOAc (1.2 mmol, 1.5 equiv.) were added to a solution of **3** (0.8 mmol, 1.0 equiv.) in MeOH (4 mL) in a round-bottomed flask which was fitted with a reflux condenser. The mixture was heated at 80 ˚C until

consumption of starting material was observed by TLC. After cooling to room temperature, the mixture was diluted with EtOAc, washed with brine, dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatograph to afford **38** (210.0 mg, 78%, *Z/E* = 2:1)[5].



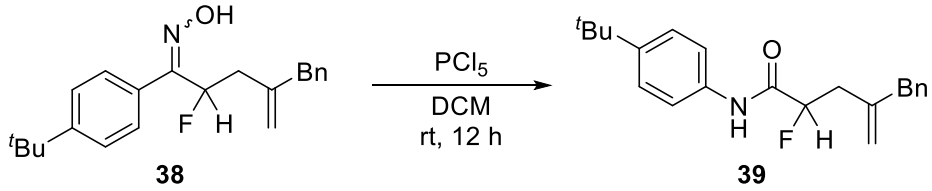
4-benzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one oxime (38)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.44 – 7.28 (m, 4H), 7.22 – 7.13 (m, 4H), 6.29 – 6.13 (m, 0.66H), 5.45 – 5.30 (m, 0.33H), 5.04 – 4.90 (m, 2H), 3.45 – 3.38 (m, 2H), 2.69 – 2.62 (m, 1H), 2.57 – 2.48 (m, 1H), 1.65 – 1.60 (m, 1H), 1.33 (s, 3H), 1.32 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -177.96 – -178.20 (m, 0.33F), -190.77 – -191.04 (m, 0.66F).

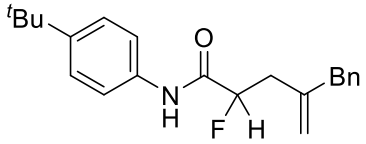
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.66 (d, *J* = 22.5 Hz), 152.81, 152.61, 143.87, 143.28, 139.17, 138.95, 129.30, 129.17, 128.53, 128.44, 128.28, 127.86 (d, *J* = 3.6 Hz), 126.42, 126.34, 125.42, 125.38, 115.31, 92.39 (d, *J* = 175.6 Hz), 86.60 (d, *J* = 176.3 Hz), 43.24, 42.97, 38.78 (d, *J* = 22.0 Hz), 34.91, 34.86, 31.33.

HRMS (ESI): calcd for $C_{22}H_{27}FNO^+$ ($M+H^+$): 340.2071, found: 340.2075.



38 **39**

In air, a 10 mL round-bottomed flask was charged with **38** (0.2 mmol, 1.0 equiv.) and DCM (2 mL). Then, PCl_5 (0.4 mmol, 2.0 equiv.) was added to the solution. The reaction was stirred at room temperature for overnight. Upon completion, saturated sodium bicarbonate solution (10 ml) was added, aqueous layer was extracted with DCM (10 mL) thrice. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue purified on silica gel to afford **39** (39.0 mg, 60%)[6].



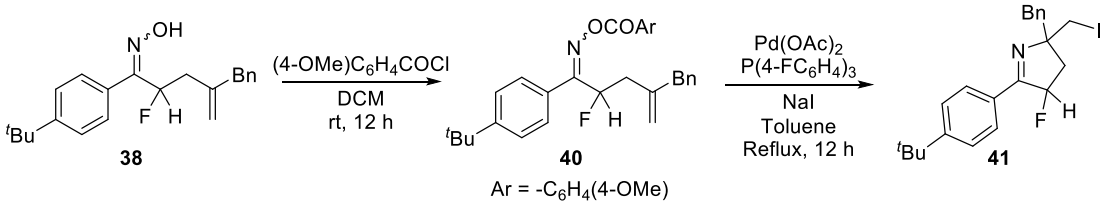
4-benzyl-*N*-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-enamide (39)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.16 – 7.12 (m, 3H), 5.11 – 5.08 (m, 0.5H), 4.98 – 4.96 (m, 1.5H), 4.89 (s, 1H), 3.36 (s, 2H), 2.76 – 2.42 (m, 2H), 1.23 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -185.87 – -186.17 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.50 (d, *J* = 18.1 Hz), 148.16, 143.07, 138.87, 134.09, 129.19, 128.57, 126.50, 119.95, 115.54, 91.02 (d, *J* = 189.9 Hz), 43.39, 38.11 (d, *J* = 20.0 Hz), 34.56, 31.46.

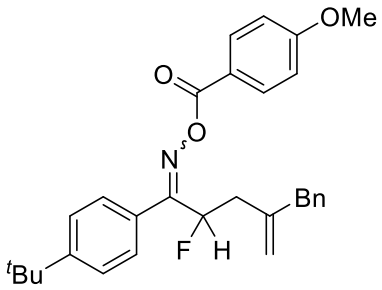
HRMS (ESI): calcd for $C_{22}H_{27}FNO^+$ ($M+H^+$): 340.2071, found: 340.2068.



To a solution of **38** (0.3 mmol, 1.0 equiv.) in anhydrous DCM (2 mL) at 0˚C was added Et_3N (0.6 mmol, 2 equiv.) followed by (4-OMe)C_6H_4COCl (0.45 mmol, 1.2 equiv.) dropwise via syringe. The mixture was then warmed to room temperature and stirred until the reaction was completed as observed by TLC. MeOH (3 mL) was then added and the mixture stirred for further 10 minutes. The mixture was diluted with DCM, washed with brine, dried with anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatograph to afford **40** (132.0 mg, 79%, *Z/E* = 2:1)[5].

In a 10 mL Schlenk tube, the mixture of **40** (0.28 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.014 mmol, 5 mmol%), P(4-$FC_6H_4)_3$ (22.1 mmol, 25 mmol%) and NaI (1.12 mmol, 4.0 equiv.) were dissolved in toluene (4 mL). Then, the reaction mixture was thoroughly degassed by vacuum purge-and-refill with argon. The reaction mixture was heated to reflux. The reaction mixture was monitored by TLC. When the reaction was finished,

the mixture was cooled to room temperature and directly subjected to silica gel column chromatography to give the product **41** (66.0 mg, 52%, d.r. = 1:1.4)[5].



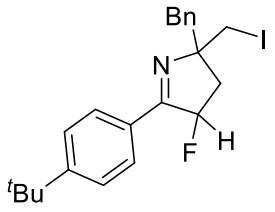
4-benzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-one *O*-(4-methoxybenzoyl) oxime (40)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.26 (m, 6H), 7.17 – 7.02 (m, 5H), 6.87 – 6.72 (m, 2H), 6.21 – 6.06 (m, 0.66H), 5.66 – 5.51 (m, 0.33H), 5.16 – 4.82 (m, 2H), 3.77 (s, 2H), 3.70 (s, 1H), 3.35 – 3.31 (m, 2H), 2.73 – 2.54 (m, 2H), 1.28 (s, 3H), 1.24 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -180.91 – -181.15 (m, 0.33F), -187.35 – -187.62 (m, 0.66F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.17 (d, J = 22.6 Hz), 163.95, 163.79, 162.85, 154.10, 153.26, 143.27 (d, J = 1.3 Hz), 142.82 (d, J = 4.1 Hz), 138.81, 138.65, 131.92, 131.84, 129.13, 129.05, 128.68 (d, J = 3.7 Hz), 128.49, 128.46, 128.06, 127.86, 126.45, 126.35, 125.45, 125.23, 120.70, 120.57, 115.73, 115.57, 114.07, 113.84, 92.02 (d, J = 177.3 Hz), 87.52 (d, J = 180.5 Hz), 55.59, 55.50, 43.18, 43.07, 39.13 (d, J = 22.0 Hz), 38.70 (d, J = 22.7 Hz), 34.95, 34.90, 31.28, 31.22.

HRMS (ESI): calcd for $C_{30}H_{33}FNO_3^+$ ($M+H^+$): 474.2439, found: 474.2435.



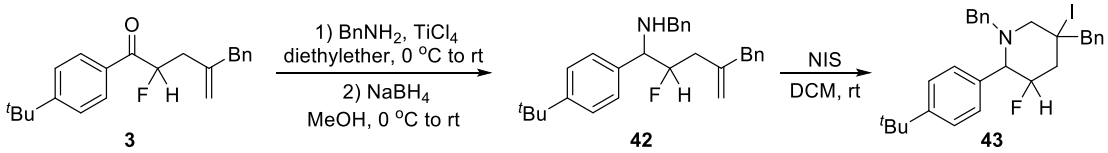
2-benzyl-5-(4-(*tert*-butyl)phenyl)-4-fluoro-2-(iodomethyl)-3,4-dihydro-2*H*-pyrrole (41)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.68 (m, 2H), 7.41 – 7.35 (m, 2H), 7.19 – 7.04 (m, 5H), 6.03 – 5.86 (m, 0.42H), 4.96 – 4.81 (m, 0.58H), 3.53 – 3.39 (m, 2H), 3.17 – 2.97 (m, 2H), 2.37 – 2.06 (m, 2H), 1.27 (s, 3.75H), 1.26 (s, 5.25H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -169.12 – -169.41 (m, 0.42F), -170.47 – -170.74 (m, 0.58F).

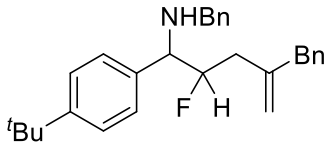
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.11 (d, J = 16.7 Hz), 168.97 (d, J = 16.0 Hz), 154.84, 154.73, 136.76, 136.62, 130.95, 130.73, 129.13 (d, J = 8.9 Hz), 128.35, 128.30, 128.20, 128.11, 126.98, 126.89, 125.80, 125.69, 96.05 (d, J = 183.1 Hz), 95.95 (d, J = 183.1 Hz), 77.59 (d, J = 1.6 Hz), 76.53 (d, J = 3.0 Hz), 46.40 (d, J = 1.7 Hz), 45.24 (d, J = 4.0 Hz), 40.38 (d, J = 21.0 Hz), 39.95 (d, J = 20.1 Hz), 35.09, 35.07, 31.29.

HRMS (ESI): calcd for $C_{22}H_{26}FIN^+$ ($M+H^+$): 450.1088, found: 450.1083.



A solution of **3** (0.5 mmol, 1.0 equiv.) and benzylamine (2.0 mmol, 4.0 equiv.) in 3 mL of dry diethylether was cooled to 0 °C, and $TiCl_4$ (0.3 mmol, 0.6 equiv.) was added dropwise. The mixture was stirred overnight allowing the temperature to rise to room temperature then it was quenched with aqueous 0.5 M NaOH solution and extracted with ether. The combined organic layer was dried and concentrated. The residue was dissolved in MeOH (3 mL), cooled to 0 °C and then $NaBH_4$ (0.6 mmol, 1.2 equiv.) was added portionwise. The mixture was stirred at room temperature for 1 hour then the solvent was removed under vacuum, water was added and the aqueous extacted with DCM. The organic layer was dried with anhydrous Na_2SO_4, concentrated and purified by chromatography to yield **42** (149.0 mg, 72%, d.r. = 2.8:1)[7].

To a solution of **42** (0.29 mmol, 1.0 equiv.) in DCM (3 mL) was added *N*-iodosuccinimide (0.29 mmol, 1.0 equiv.) and the mixture was stirred at room temperature for 10-15 minutes. The mixture was then purified on a short silicagel pad to yield iododerivatives **43** (123.0 mg, 78%, d.r. = 2:1)[7].



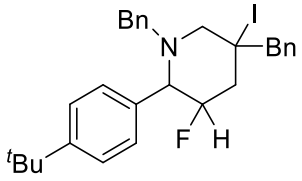
***N*,4-dibenzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-amine (42)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 6.92 (m, 14H), 4.85 – 4.70 (m, 3H), 3.76 – 3.37 (m, 3H), 3.26 – 3.17 (m, 2H), 2.19 – 2.04 (m, 2H), 1.89 – 1.86 (m, 1H), 1.26 (s, 6.65H), 1.25 (s, 2.35H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -185.97 – -186.28 (m, 0.26F), -187.29 – -187.61 (m, 0.74F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.92, 150.52, 144.85 (d, J = 2.0 Hz), 144.66 (d, J = 2.0 Hz), 140.51, 140.33, 139.26, 139.20, 135.45 (d, J = 4.0 Hz), 129.16, 129.10, 128.48, 128.41, 128.38, 128.32, 128.29, 128.07, 127.07, 126.99, 126.23, 126.20, 125.61, 125.46, 114.32, 114.19, 95.34 (d, J = 176.7 Hz), 96.03 (d, J = 176.7 Hz), 65.67 (d, J = 18.9 Hz), 64.61 (d, J = 20.1 Hz), 51.38, 51.12, 43.14, 42.97, 37.79 (d, J = 21.0 Hz), 36.71 (d, J = 21.5 Hz), 34.65, 31.54.

HRMS (ESI): calcd for $C_{29}H_{35}FN^+$ ($M+H^+$): 416.2748, found: 416.2744.



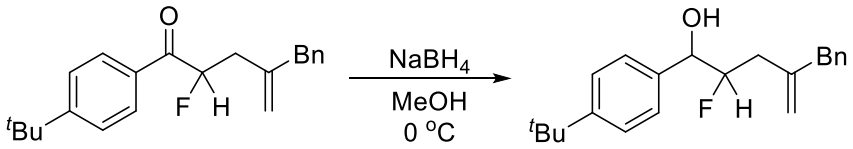
1,5-dibenzyl-2-(4-(*tert*-butyl)phenyl)-3-fluoro-5-iodopiperidine (43)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.02 (m, 14H), 4.81 – 4.69 (m, 0.66H), 4.52 – 4.39 (m, 0.33H), 3.81 – 3.72 (m, 1H), 3.50 – 2.51 (m, 8H), 1.26 (s, 6H), 1.25 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -180.81 – -180.99 (m, 0.66F), -182.30 – -182.87 (m, 0.33F).

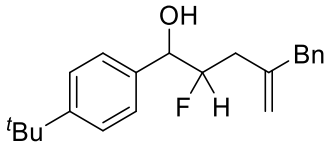
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.26, 151.01, 139.02, 138.12, 137.87, 136.64, 131.47 (d, J = 2.9 Hz), 130.91, 129.36, 129.31, 128.91, 128.51, 127.98, 127.62, 127.47, 127.10, 126.68, 125.90, 125.49, 90.79 (d, J = 177.3 Hz), 92.27 (d, J = 177.3 Hz)), 72.45 (d, J = 22.6 Hz), 70.60 (d, J = 17.1 Hz), 67.24, 65.79, 58.69, 57.62, 53.95, 49.18 (d, J = 12.7 Hz), 48.75 (d, J = 12.5 Hz), 46.84, 34.75, 34.71, 31.53, 29.86.

HRMS (ESI): calcd for $C_{29}H_{34}FIN^+$ ($M+H^+$): 542.1714, found: 542.1708.



3 **44**

Dissolve the **3** (0.8 mmol, 1.0 equiv.) in methanol (8 mL), stir at 0°C, and then slowly add sodium borohydride (0.96 mmol, 1.2 equiv.). The reaction was monitored by TLC. After the reaction, the mixture was quenched with saturated ammonium chloride and then partitioned between water and EtOAc. The combined organic extracts were dried with $MgSO_4$ and concentrated. The crude reaction product was purified by flash column chromatography to obtain **44** (248.0 mg, 95%, d.r. = 1:1)[8].



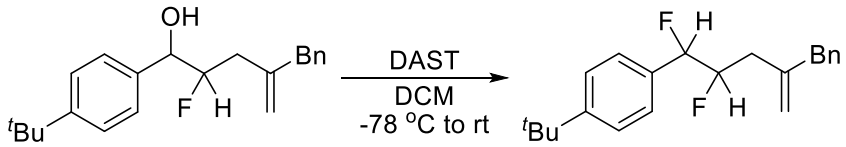
4-benzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropent-4-en-1-ol (44)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.18 – 7.01 (m, 5H), 6.99 – 6.97 (m, 2H), 4.85 – 4.80 (m, 2H), 4.78 – 4.69 (m, 1H), 4.57 – 4.49 (m, 1H), 3.26 – 3.24 (m, 2H), 2.29 – 2.19 (m, 1H), 2.17 – 1.95 (m, 1H), 1.24 (s, 4.5H), 1.23 (s, 4.5H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.10 – -187.41 (m, 0.5F), -189.19 – -189.50 (m, 0.5F).

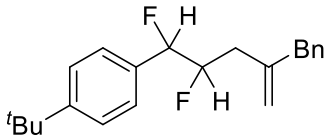
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.52, 151.12, 144.58 (d, J = 0.9 Hz), 144.15 (d, J = 1.8 Hz), 139.20, 139.08, 136.20 (d, J = 5.3 Hz), 129.16, 129.11, 128.45, 128.43, 126.85, 126.42, 126.29 (d, J = 4.4 Hz), 125.65, 125.50, 114.67, 114.36, 96.13 (d, J = 54.9 Hz), 94.38 (d, J = 54.6 Hz), 75.88 (d, J = 20.2 Hz), 75.03 (d, J = 22.9 Hz), 43.22 (d, J = 9.5 Hz), 36.97 (d, J = 21.1 Hz), 35.34 (d, J = 21.2 Hz), 34.70, 34.68, 31.46, 31.45.

HRMS (ESI): calcd for $C_{22}H_{28}FO^+$ ($M+H^+$): 327.2119, found: 327.2115.



44 **45**

In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **44** (0.27 mmol, 1.0 equiv.) and DCM (3 mL). The mixture was cooled to -78 °C, and the DAST (0.3 mmol, 1.1 equiv.) was added dropwise. Then the reaction mixture was stired at room temperature. Until the reaction was complete as indicated by TLC, the mixture was quenched with iced-water. The organic layer was washed with sat. $NaHCO_3$ solution, water and dried over $MgSO_4$. Then the solvent was evaporated under reduced pressure to leave a crude mixture, which was purified by flash column chromatography to afford **45** (60.0 mg, 68%, d.r. = 1.3:1)[8].



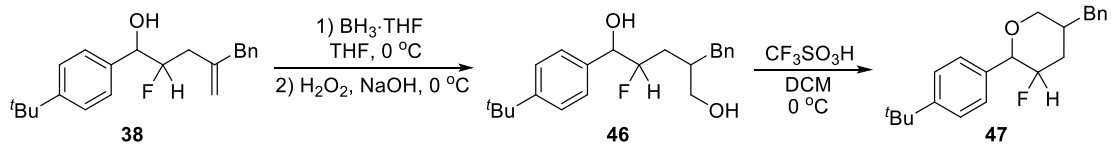
1-(4-benzyl-1,2-difluoropent-4-en-1-yl)-4-(*tert*-butyl)benzene (45)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.00 (m, 9H), 5.47 – 5.16 (m, 1H), 4.87 – 4.83 (m, 2H), 4.74 – 4.67 (m, 1H), 3.27 (s, 2H), 2.32 – 2.03 (m, 2H), 1.24 (s, 5.1H), 1.23 (s, 3.9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.06 – -186.27 (m, 0.43F), -188.98 – -189.25 (m, 0.57F), -189.45 – -189.66 (m, 0.57F), -191.58 – -191.92 (m, 0.43F).

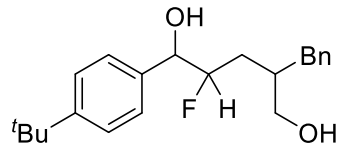
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.30 (d, J = 2.0 Hz), 151.97 (d, J = 1.7 Hz), 143.78 (d, J = 2.6 Hz), 143.55 (d, J = 2.6 Hz), 139.00, 138.97, 132.72 (d, J = 4.8 Hz), 132.51 (d, J = 5.1 Hz), 132.46 (d, J = 4.8 Hz), 132.26 (d, J = 4.6 Hz), 129.14, 129.12, 128.54, 128.50, 126.41 (d, J = 5.1 Hz), 126.17 (d, J = 7.0 Hz), 125.65, 125.54, 115.20, 114.87, 94.49 (d, J = 23.7 Hz), 92.73 (d, J = 23.6 Hz), 94.78 (d, J = 20.2 Hz), 93.01 (d, J = 20.2 Hz), 93.71 (d, J = 24.0 Hz), 91.96 (d, J = 23.9 Hz), 93.59 (d, J = 22.8 Hz), 91.78 (d, J = 22.8 Hz), 43.28, 43.22, 36.50 (dd, J = 21.4, 4.3 Hz), 35.16 (dd, J = 21.2, 4.8 Hz), 34.79, 34.77, 31.42, 31.40.

HRMS (ESI): calcd for $C_{22}H_{27}F_2^+$ ($M+H^+$): 329.2075, found: 329.2076.



A solution of **38** (0.3 mmol, 1.0 equiv.) in 2 mL of THF was treated with a solution of BH_3•THF complex (1.0 M solution in THF, 0.6 mmol, 2.0 equiv.) at ice-bath temperature. The reaction mixture was stirred for 4 h at room temperature, cooled in a water-ice bath, and carefully treated with 1.0 mL of a 10% solution of water in THF followed by addition of 1.0 mL of a 3.0 M aqueous solution of NaOH (3 mmol, 10.0 equiv.) and 0.78 mL of 30% H_2O_2 (7.8 mmol, 26.0 equiv.). The resulting mixture was stirred for 1.5 h at room temperature, poured into water, acidified with 10% HCl, and extracted with ether. The organic fraction was washed with water and dried over Na_2SO_4. Removal of solvents in vacuo and purified by flash column chromatography to afford **46** (91.0 mg, 85%, d.r. = 1:1)[9].

To a flame-dried flask charged with a stir bar was added **46** (0.1 mmol, 1.0 equiv.) and dry DCM (2 mL), this mixture was cooled to 0 °C under a nitrogen atmosphere. To this solution was added CF_3SO_3H (0.2 mmol, 2.0 equiv.) and the resulting reaction mixture was stirred at 0 °C for 1 h. After completion of the reaction, saturated aqueous $NaHCO_3$ (10 mL) was added. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by flash chromatography to give the desired product **47** (17.0 mg, 52%, d.r. = 1:3)[10].



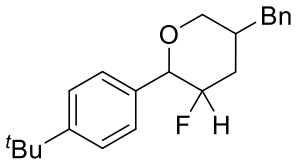
4-benzyl-1-(4-(*tert*-butyl)phenyl)-2-fluoropentane-1,5-diol (46)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.18 – 7.07 (m, 5H), 7.01 – 6.92 (m, 2H), 4.66 – 4.47 (m, 2H), 3.45 – 3.33 (m, 2H), 2.59 – 2.41 (m, 3H), 1.94 – 1.90 (m, 1H), 1.72 – 1.54 (m, 2H), 1.24 (s, 4.5H), 1.23 (s, 4.5H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.01 – -186.37 (m, 0.5F), -186.91 – -187.19 (m, 0.5F), -188.21 – -188.75 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.32 (d, *J* = 5.0 Hz), 150.94 (d, *J* = 7.9 Hz), 140.11 (d, *J* = 22.3 Hz), 139.94 (d, *J* = 28.6 Hz), 136.69, 136.27, 129.26 (d, *J* = 2.9 Hz), 129.16 (d, *J* = 5.2 Hz), 128.43, 128.39, 126.80 (d, *J* = 3.3 Hz), 126.54, 126.41, 126.06 (d, *J* = 4.4 Hz), 125.57, 125.41, 95.80 (d, *J* = 78.7 Hz), 94.08 (d, *J* = 78.5 Hz), 96.38 (d, *J* = 67.1 Hz), 94.66 (d, *J* = 67.1 Hz), 76.40 (d, *J* = 20.1 Hz), 75.93 (d, *J* = 19.9 Hz), 75.43 (d, *J* = 23.7 Hz), 75.11 (d, *J* = 23.2 Hz), 64.93 (d, *J* = 6.4 Hz), 64.01, 38.80 (d, *J* = 45.9 Hz), 37.90 (d, *J* = 10.4 Hz), 37.18 (d, *J* = 25.6 Hz), 34.64, 34.62, 31.43.

HRMS (ESI): calcd for $C_{22}H_{30}FO_2^+$ ($M+H^+$): 345.2224, found: 345.2227.



5-benzyl-2-(4-(*tert*-butyl)phenyl)-3-fluorotetrahydro-2*H*-pyran (47)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.08 (m, 9H), 4.70 – 4.58 (m, 1H), 4.40 – 4.22 (m, 1H), 4.06 – 3.96 (m, 1H), 3.69 – 3.68 (m, 0.23H), 3.26 (t, *J* = 10.8 Hz, 0.77H), 2.99 – 2.96 (m, 0.5H), 2.49 – 2.37 (m, 2H), 2.22 – 2.12 (m, 1H), 1.97 – 1.82 (m, 0.5H), 1.54 – 1.37 (m, 1H), 1.25 (s, 2.24H), 1.22 (s, 6.74H).

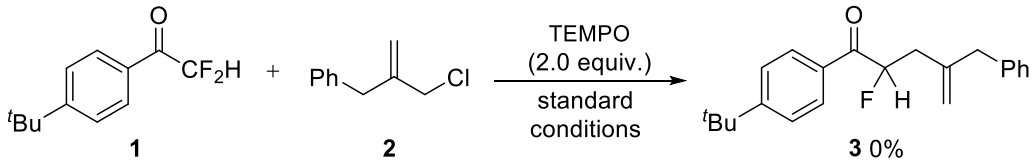
^{19}F NMR (376 MHz, $CDCl_3$) δ -190.27 – -190.64 (m, 0.25F), -198.60 – -198.95 (m, 0.75F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.69, 150.67, 141.39, 139.01, 135.59, 135.52, 129.64, 129.07, 128.56, 128.41, 126.45, 126.41, 126.38, 125.99, 125.29, 125.27, 88.54 (d, *J* = 180.0 Hz), 88.91 (d, *J* = 180.4 Hz), 80.76 (d, *J* = 18.5 Hz), 80.28 (d, *J* = 17.9 Hz), 73.33, 71.16, 38.73, 38.68, 35.40 (d, *J* = 22.0 Hz), 34.65, 34.63, 31.77, 31.48, 31.46.

HRMS (ESI): calcd for $C_{22}H_{28}FO^+$ ($M+H^+$): 327.2119, found: 327.2115.

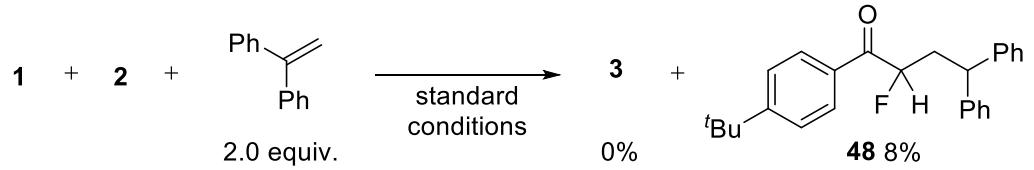
8. Mechanistic Studies

8.1 Radical inhibition experiment

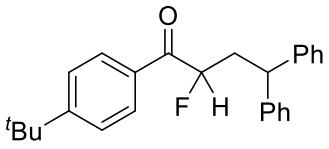


According to *General Procedure* with the addition of TEMPO (31.2 mg, 2.0 equiv), the reaction was completely shut down and resulted in no detection of the desired product **3**.

8.2 Radical trapping experiment



According to *General Procedure* with the addition of 1,1-diphenylethene (35 μL, 2.0 equiv.), The reaction was also completely shut down and resulted in no detection of the desired product **3**, forming defluoroalkylation product **48** in 8% yield.



1-(4-(*tert*-butyl)phenyl)-2-fluoro-4,4-diphenylbutan-1-one (48)

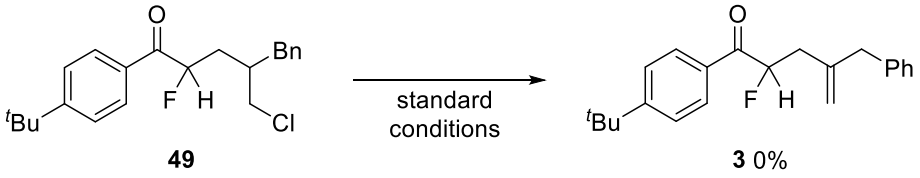
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.34 (m, 8H), 7.29 – 7.25 (m, 6H), 5.47 – 5.31 (m, 1H), 4.40 – 4.36 (m, 1H), 2.77 – 2.51 (m, 2H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -192.37 – -192.64 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.10 (d, J = 18.5 Hz), 157.87, 143.83, 142.73, 131.49, 129.04, 128.88 (d, J = 3.3 Hz), 128.69, 128.54, 127.71, 127.12, 126.64, 125.81, 91.49 (d, J = 182.6 Hz), 46.70 (d, J = 2.2 Hz), 38.75 (d, J = 21.5 Hz), 35.35, 31.15.

HRMS (ESI): calcd for $C_{26}H_{28}FO^+$ ($M+H^+$): 375.2119, found: 375.2120.

8.3 Control reaction with alkyl chloride 49



49 **3** 0%

According to *General Procedure*: To a flame-dried 8 mL reaction vial equipped with a magnetic stir bar was charged with KBr (12 mg, 1.0 equiv.), MeCN/PhCl (0.05 M, 1.5/0.5 mL). The reaction mixture was degassed by nitrogen sparging for 30 minutes, followed by the addition of triisobutylamine (48 μL, 2.0 equiv.), alkyl chloride **49** (36 mg, 0.1 mmol). The vial was sealed with parafilm. Then the reaction mixture was irradiated with a 90 W blue LEDs at 50 °C. The yield was determined by GC using dodecane as an internal standard. With the subjection of **49**, no dechlorination product **3** was observed in the reaction.

8.4 UV/vis absorption spectrometry

UV/Vis absorption spectra among DFMK **1** (0.1 M), triisobutylamine (TIBA) (0.1 M) and KBr (0.1 M) in 3.0 mL CH_3CN were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-2550 UV/Vis spectrometer (**Figure S4** and **Figure S5**).

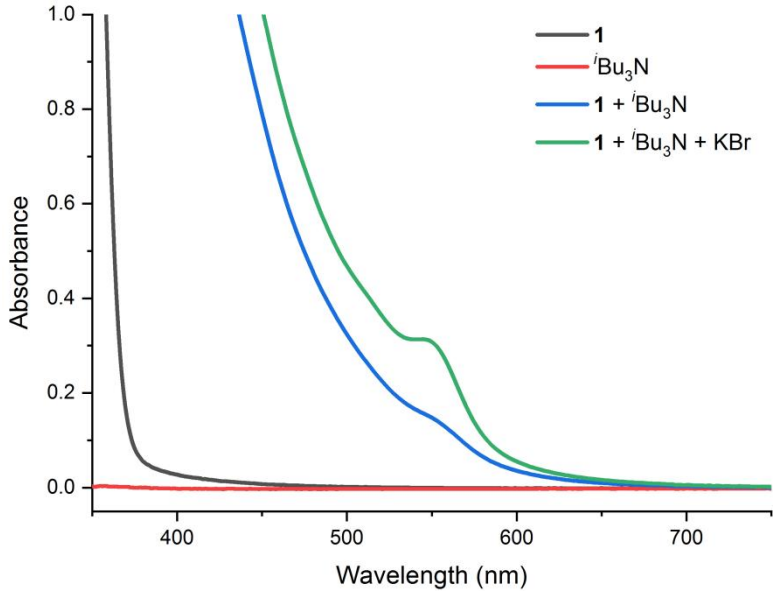


Figure S4. UV/Vis absorption spectrometry

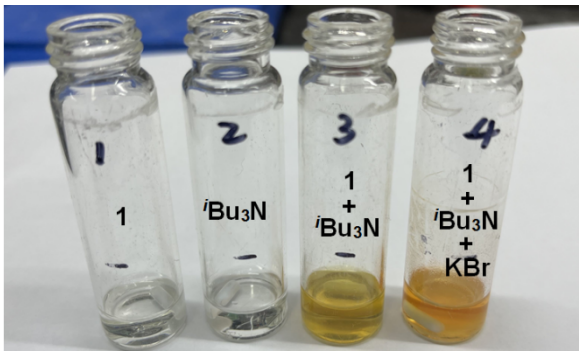
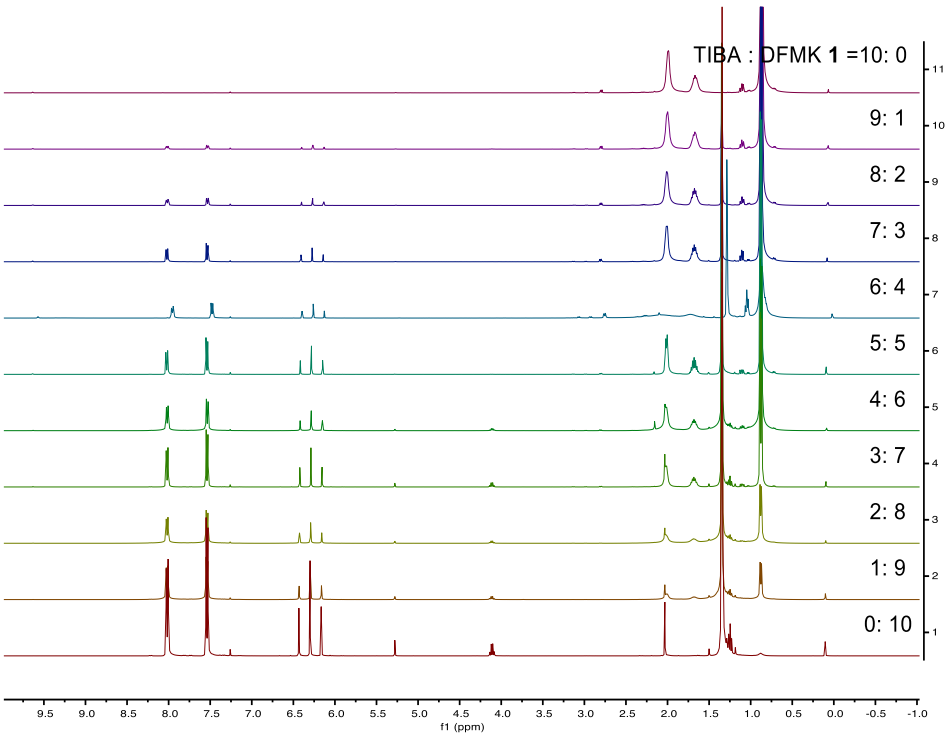


Figure S5. Visual appearance of the coloured EDA complex

8.5 ^{1}H NMR titration experiments

Solutions containing equal molar concentrations of the donor (TIBA, 0.1 M in $CDCl_3$) and the acceptor DFMK **1** , 0.1 M in $CDCl_3$) were prepared and mixed to cover acceptor/donor ratio from 0: 10, 1: 9, 2: 8 to 10: 0 (from 1 to 11) in **Figure S6**.



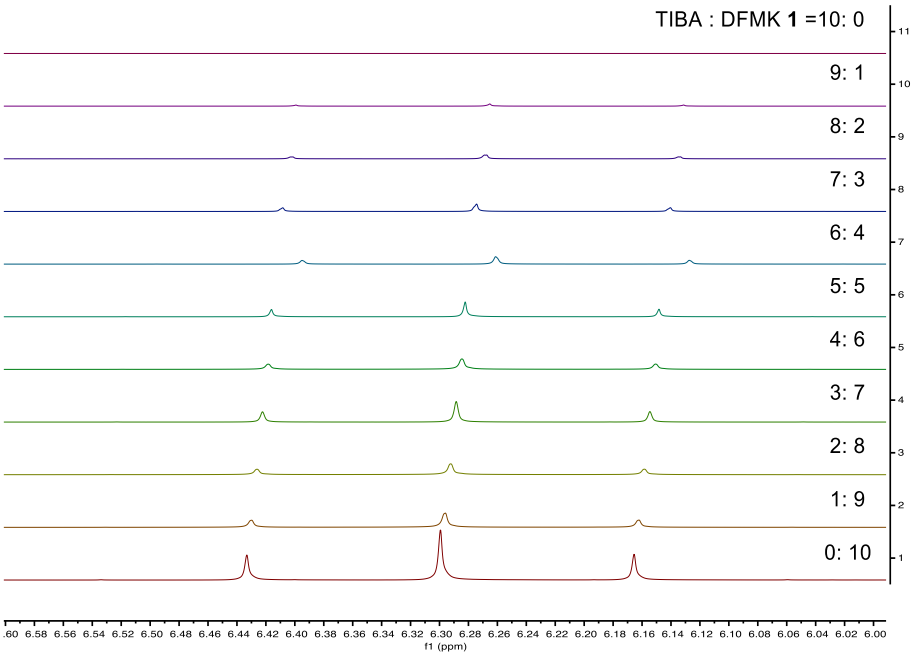


Figure S6. ^{1}H NMR titration experiments between TIBA and DFMK 1

8.6 Job's plot

The stoichiometry of the EDA complex was calculated using the Job's plot Method[15]. The Job's plot of the EDA complex between TIBA and DFMK **1** was calculated measuring the absorption of CH_3CN solutions at 380 nm with different donor/acceptor ratios with constant concentration (0.1 M) of the two components. The absorbance values were plotted against the molar fraction (%) of $^{i}Bu_3N$ (TIBA). The Job´s plot analysis of the EDA complex between TIBA and DFMK **1** showed a maximal absorbance at 50% molar fraction indicated the 1:1 stoichiometry of the EDA complex in solution in **Figure S7**.

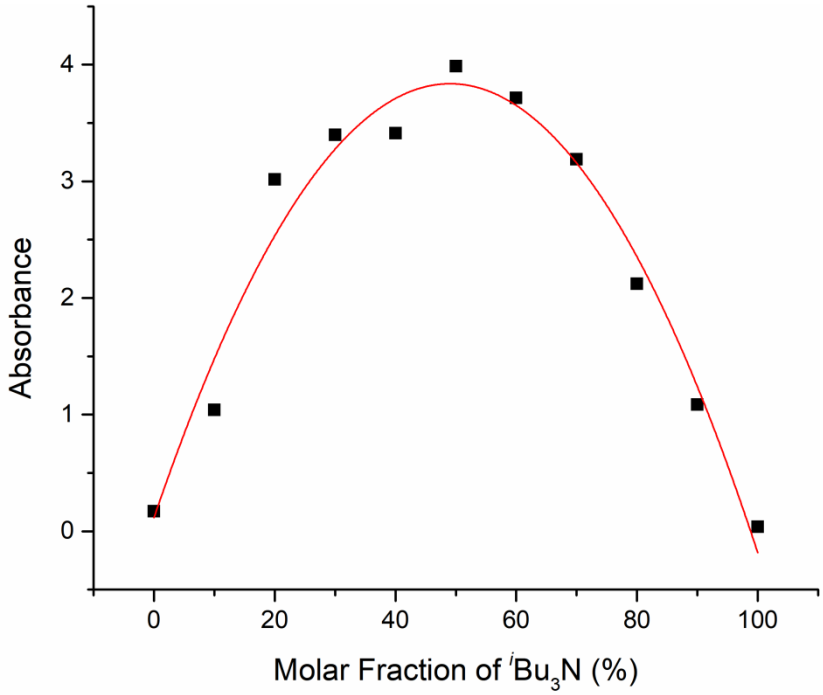


Figure S7. Job's plots of the EDA complex between TIBA and DFMK 1

8.7 Proposed mechanism for 2d and 2g

For different allyl electrophiles, the formation process of α-fluoro carbon radical intermediate **III** is same.

For the case of allyl tributylstannanes, α-fluoro alkyl radical III directly adds to allyl tributylstannane to produce alkyl radical **S-IV,** which then undergoes a SET event with amino radical cation **II** to afford alkyl cation species. Subsequently, F− assisted-elimination of the stannyl cation leads to Bu_3SnF and the final product.

For the case of allyl phenylsulfone, α-fluoro alkyl radical **III** adds to allyl phenyl sulfone, followed by a spontaneous sulfonyl group elimination, to afford the desired product. Concurrently, the sulfonyl radical undergoes single-electron reduction with amino alkyl radical **S-V'** to produce the side product **S-VI** (Figure S8b).

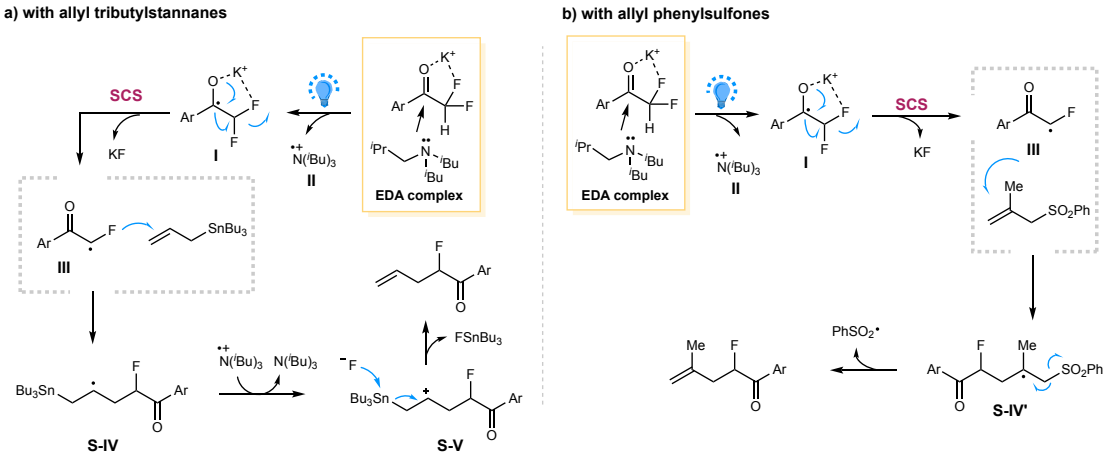


Figure S8. Proposed mechanism for allyl tributylstannanes and phenylsulfones

9. References

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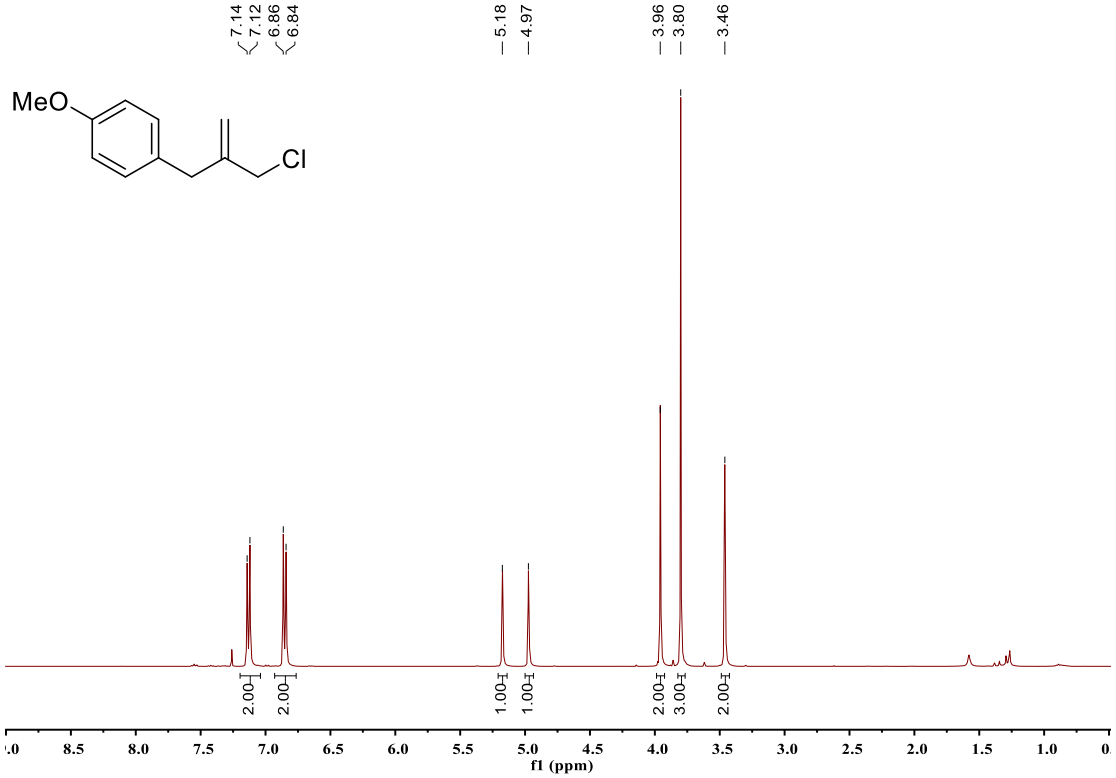
10. NMR Spectra

^{1}H-NMR of S18 (400 MHz, $CDCl_3$)



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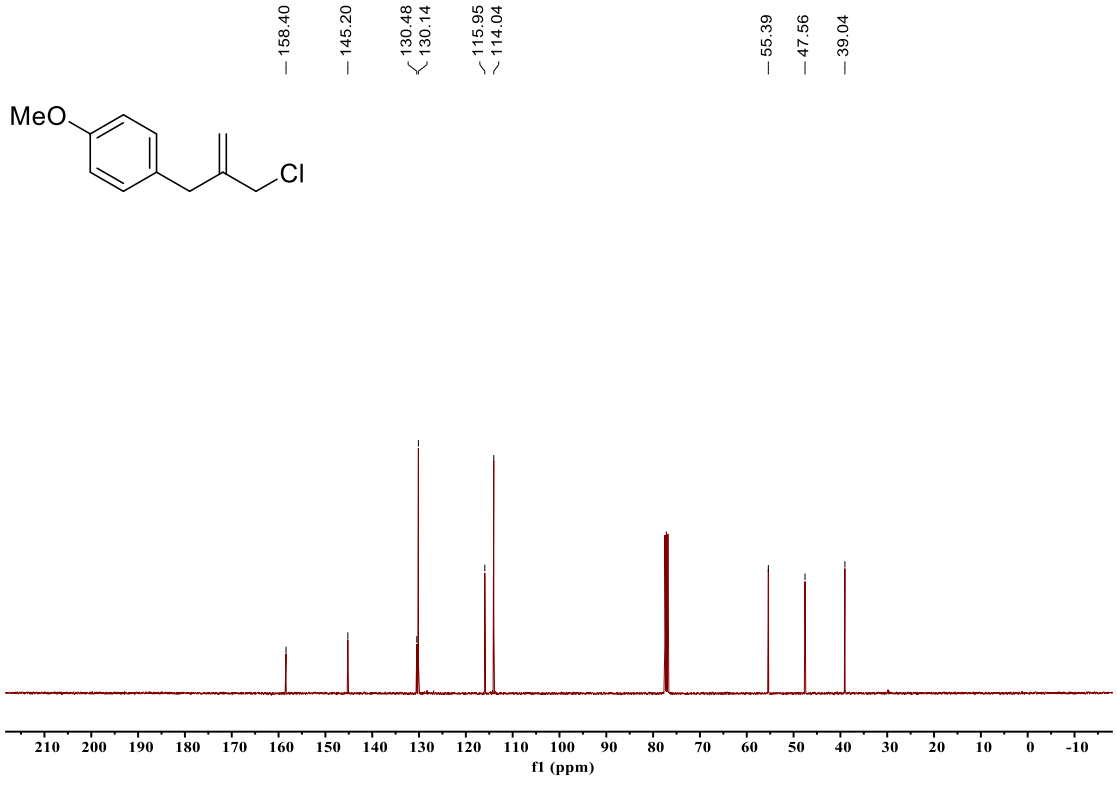

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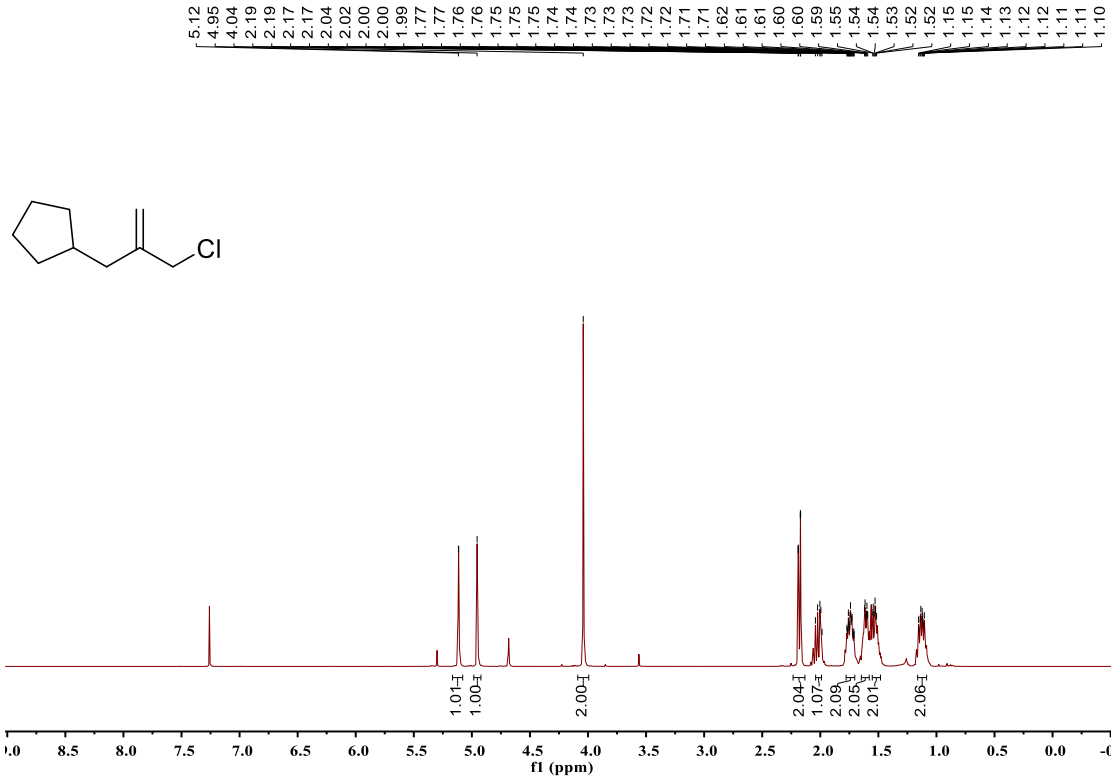

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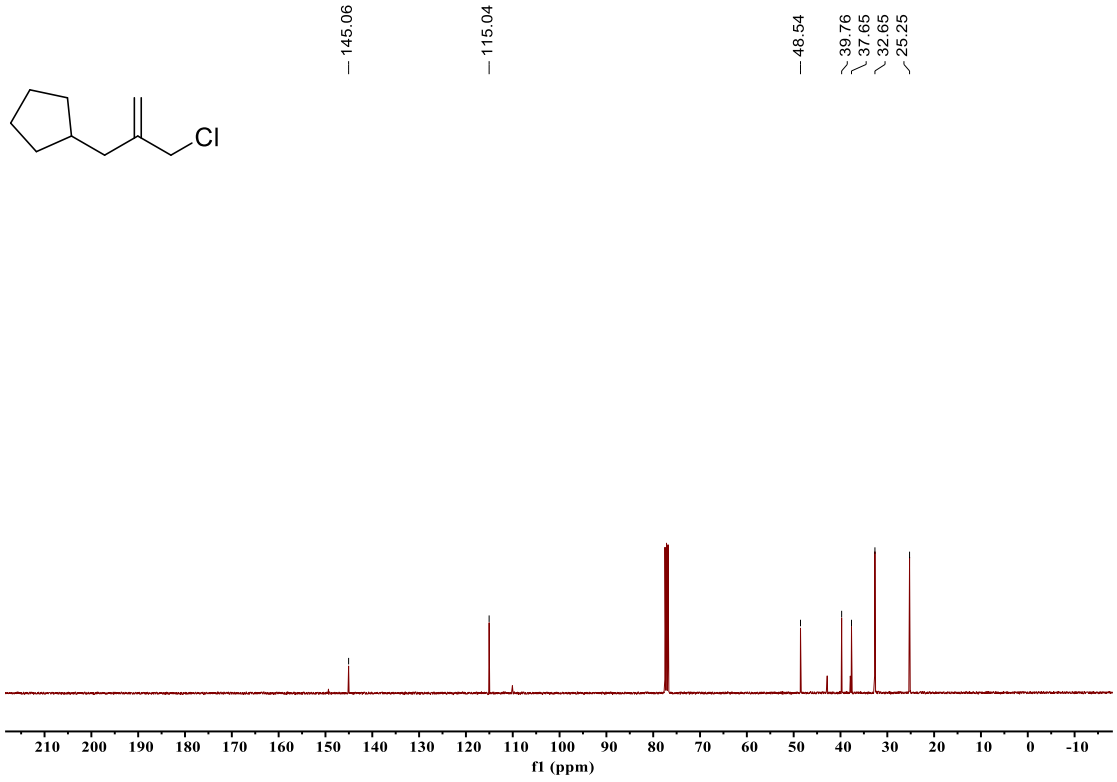

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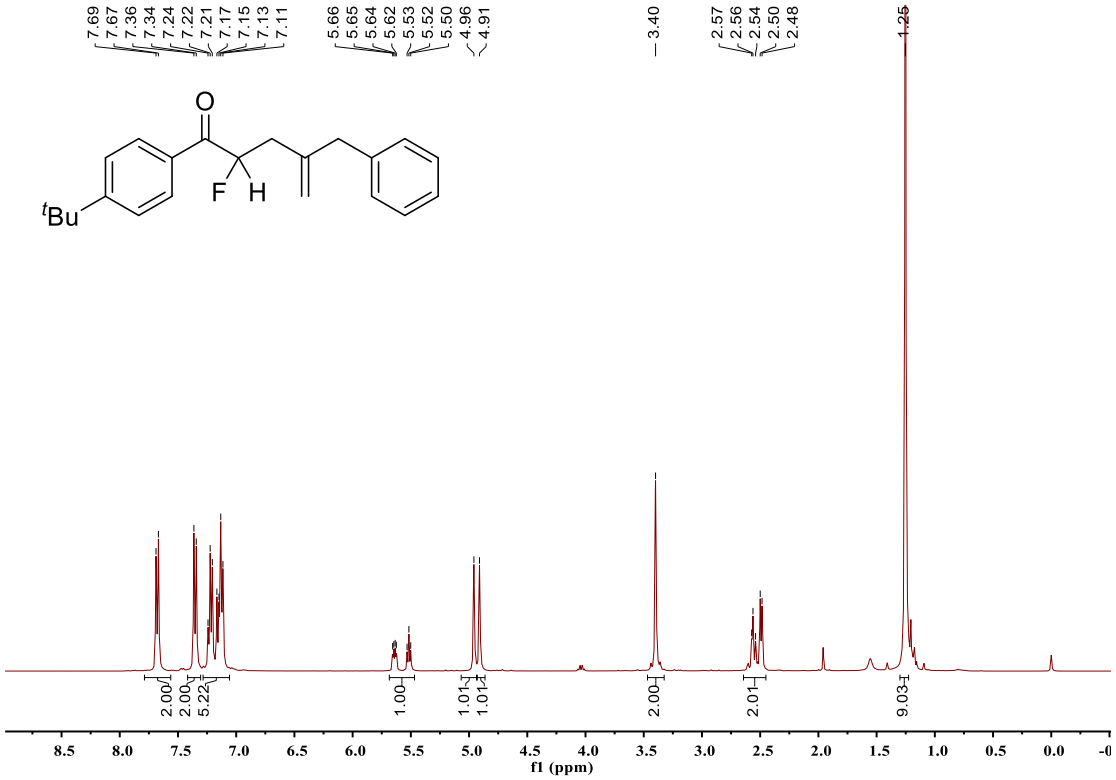
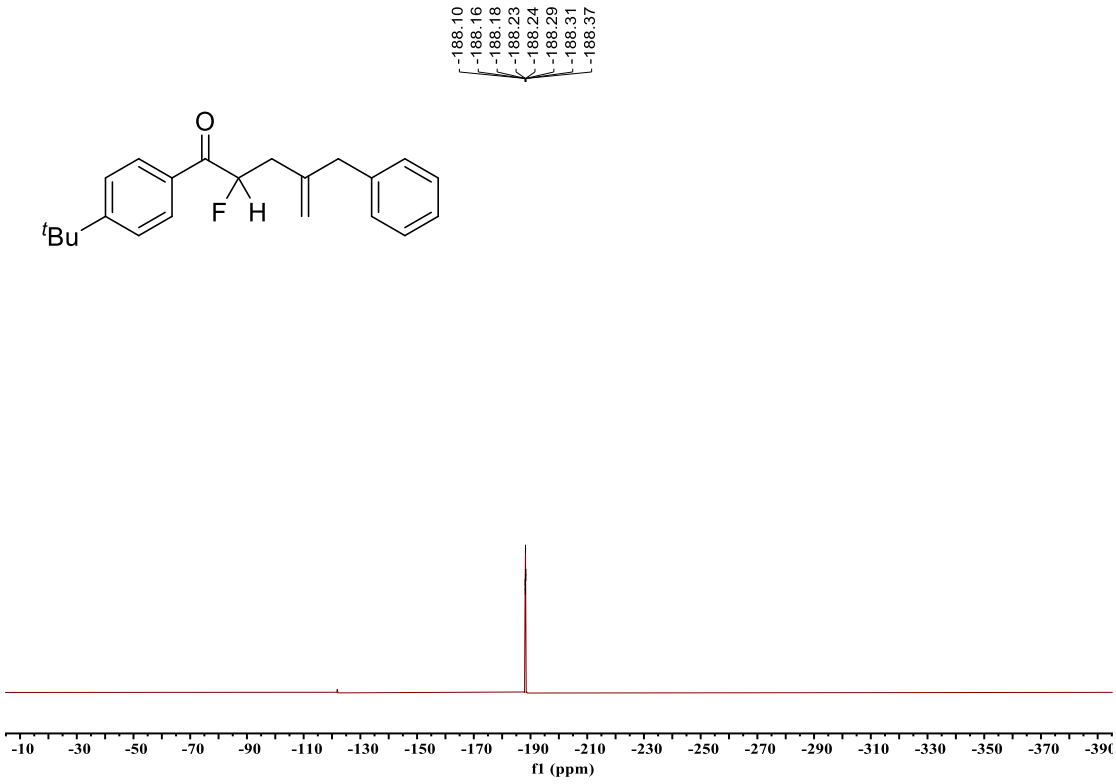


^{19}F NMR of 3 (376 MHz, $CDCl_3$)



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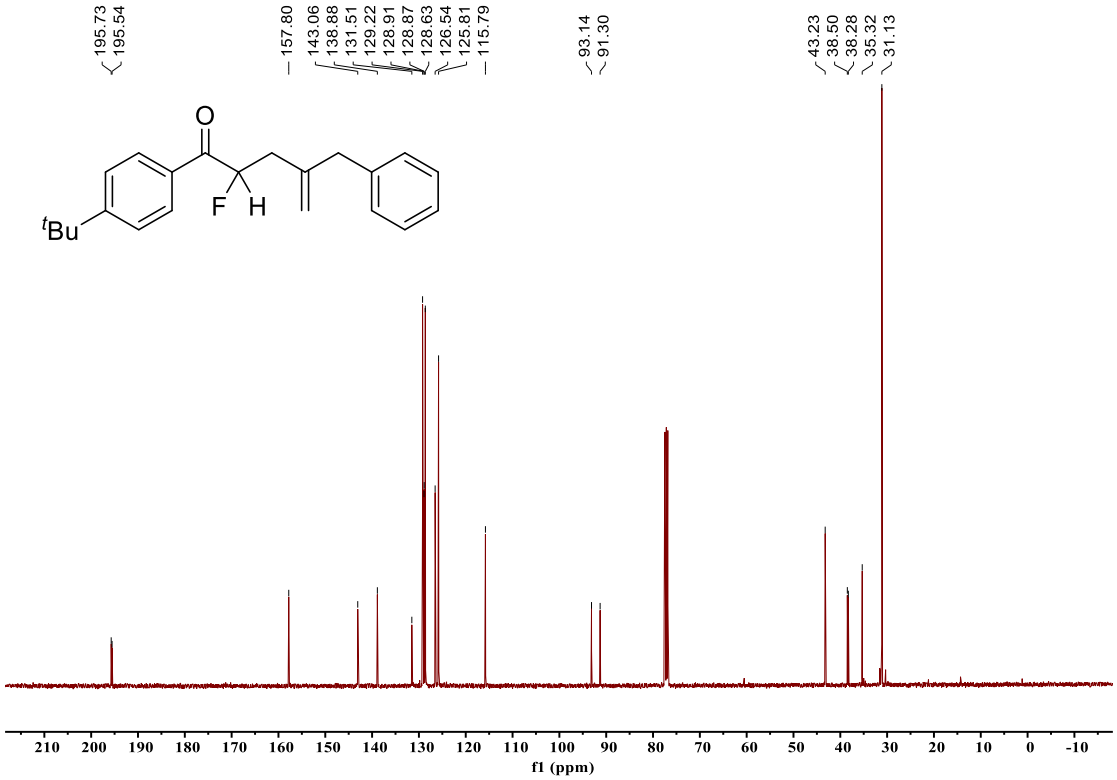
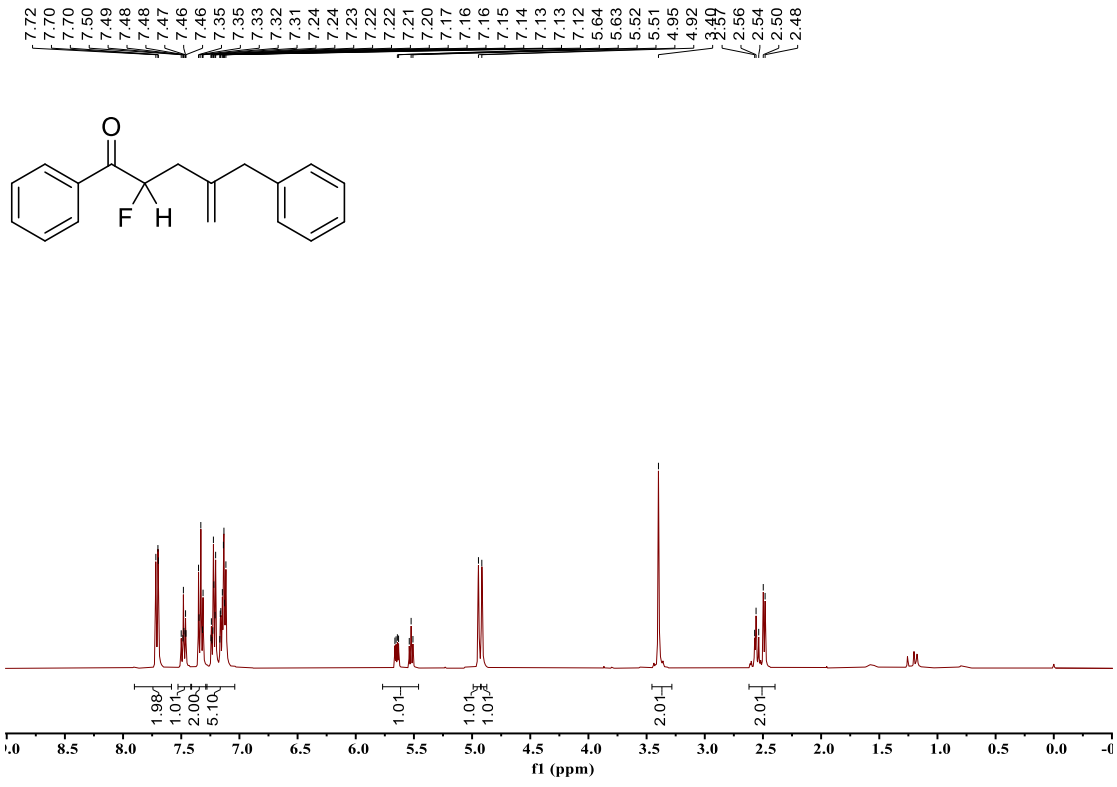
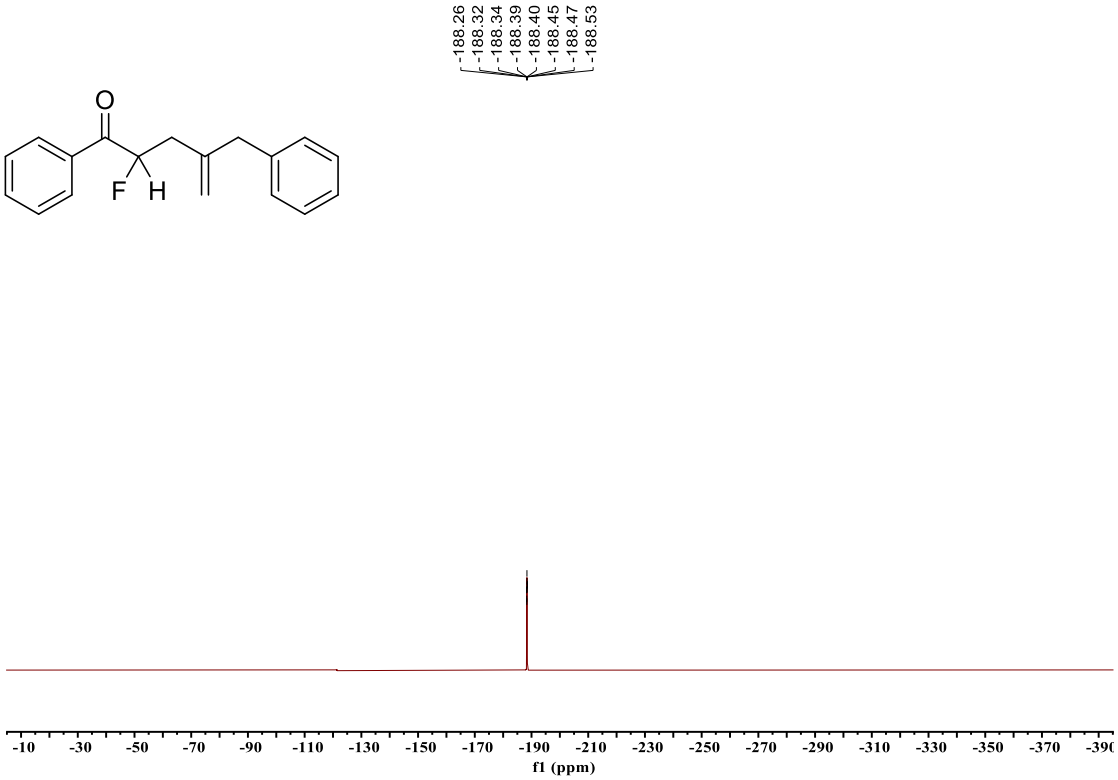


^{1}H-NMR of 4 (400 MHz, $CDCl_3$)



^{19}F NMR of 4 (376 MHz, $CDCl_3$)



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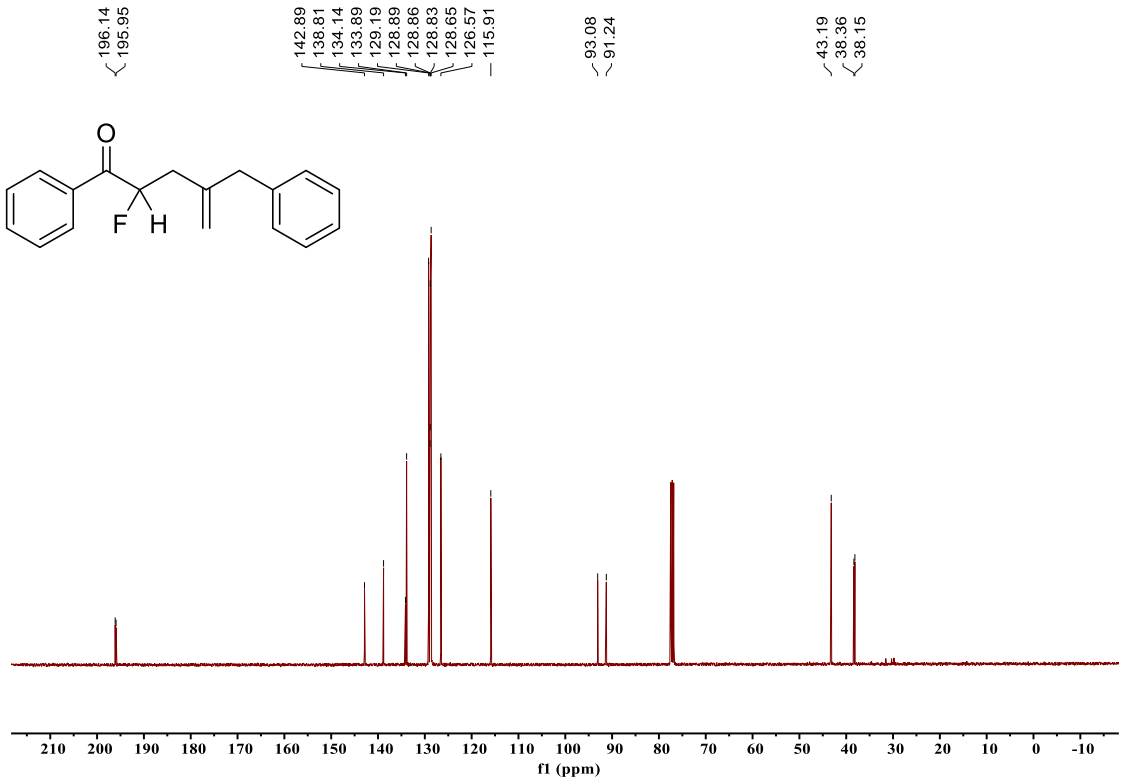
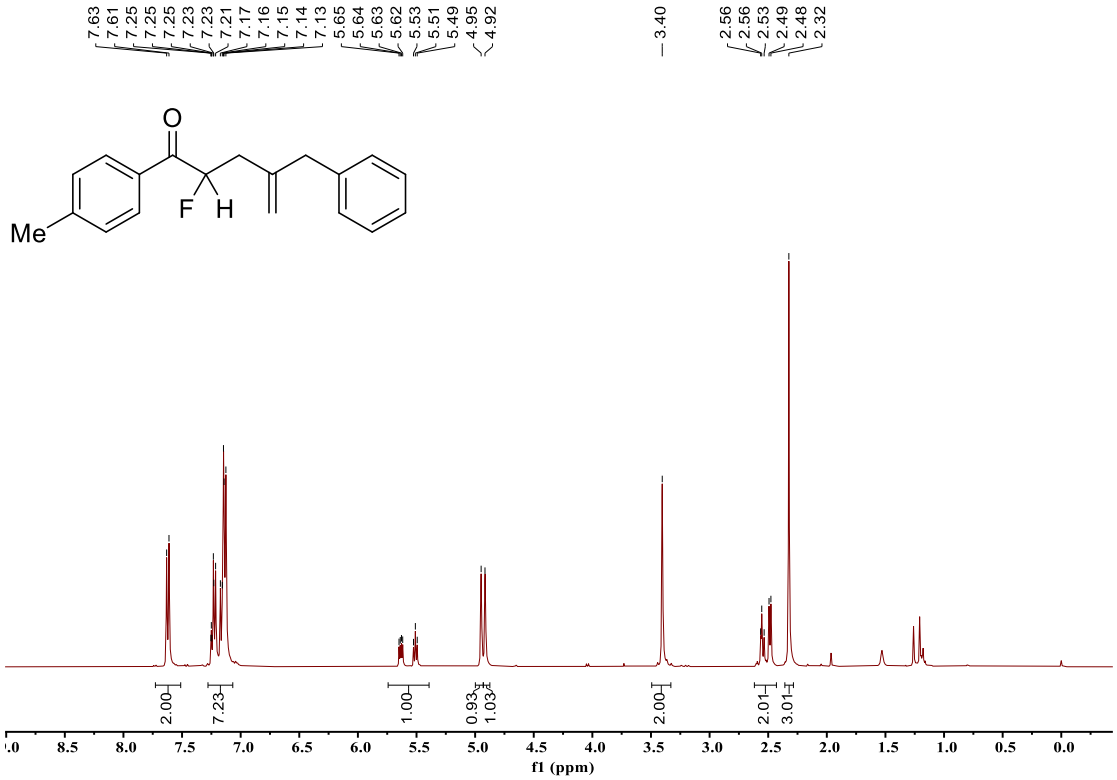


^{1}H-NMR of 5 (400 MHz, $CDCl_3$)



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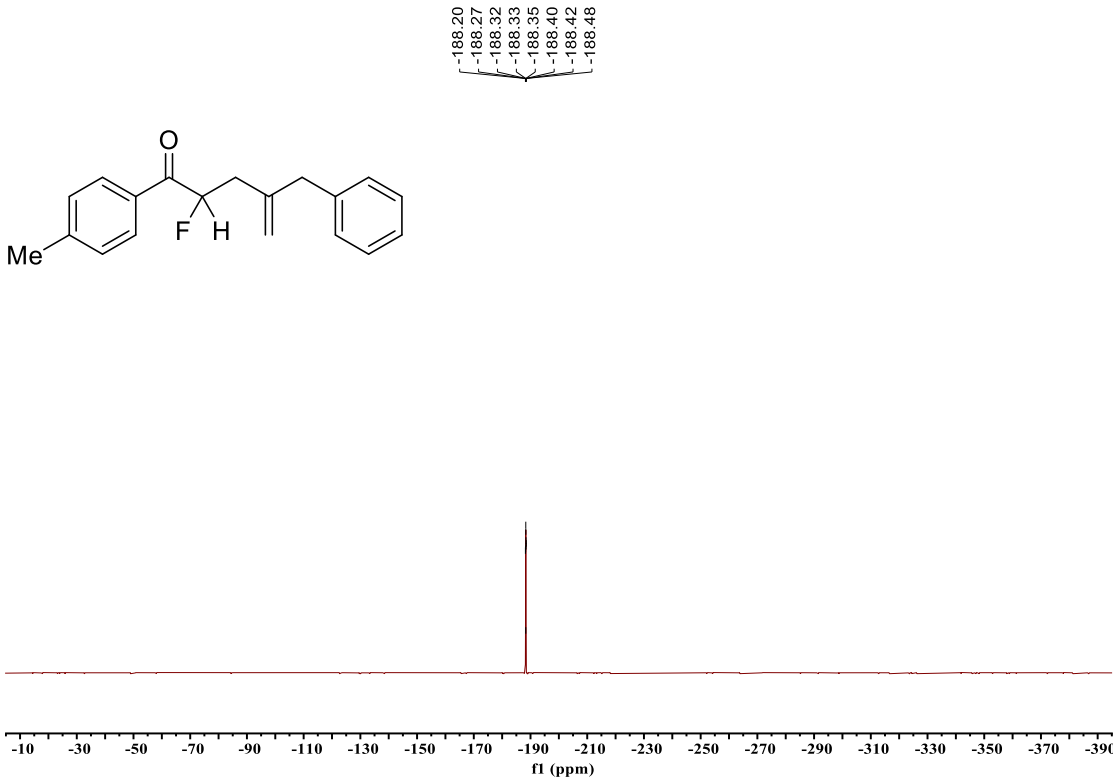

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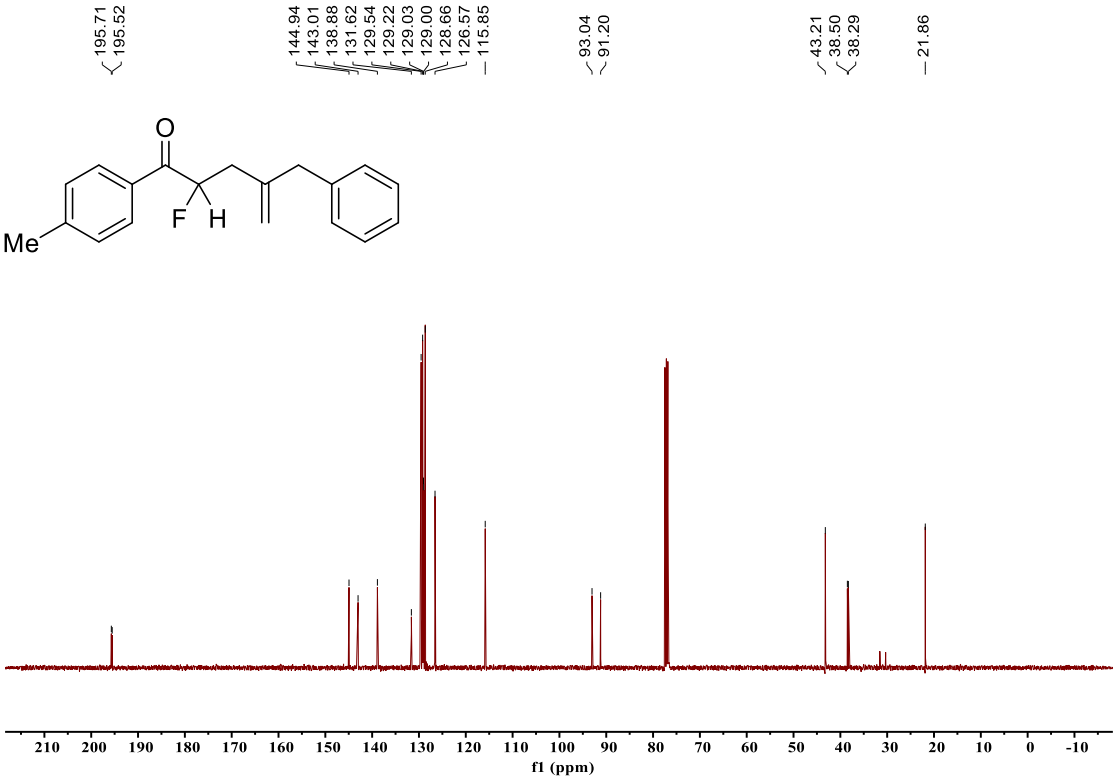

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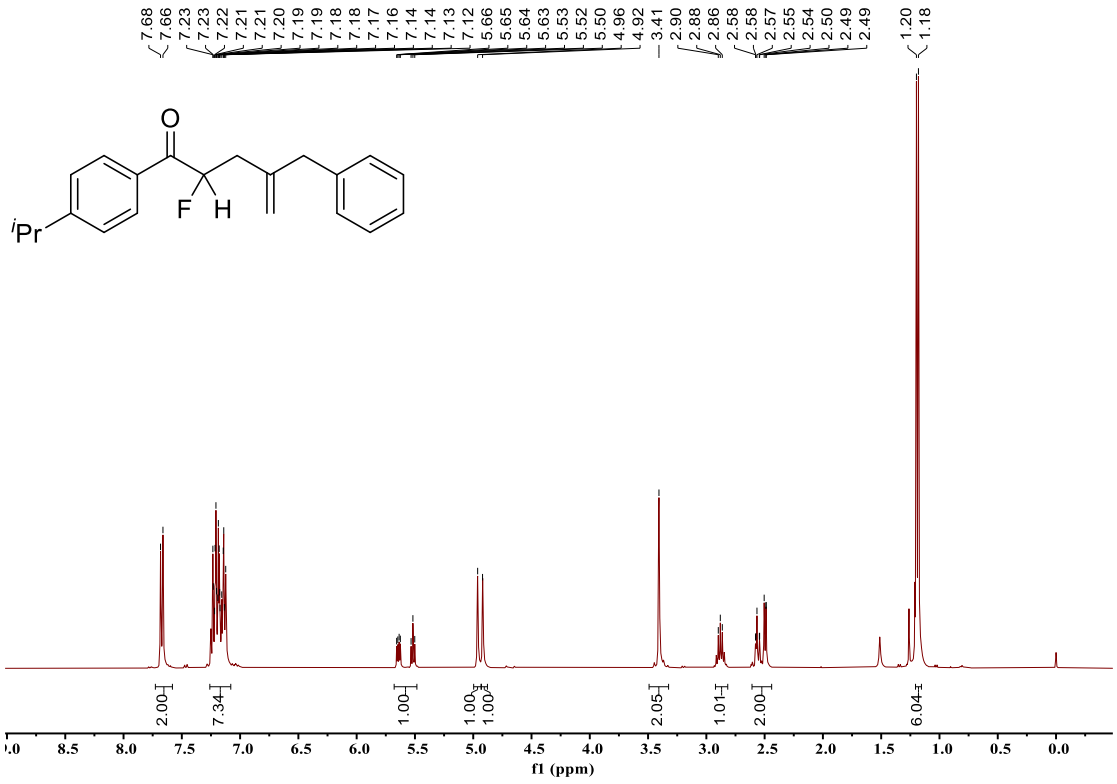

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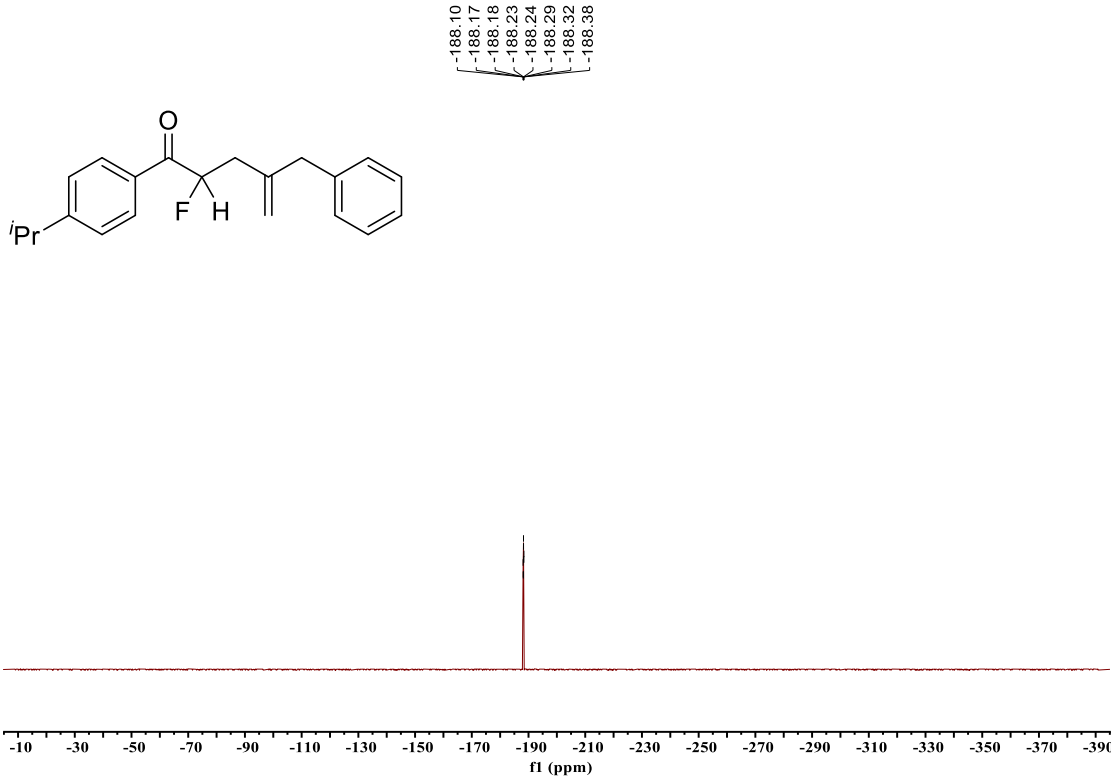

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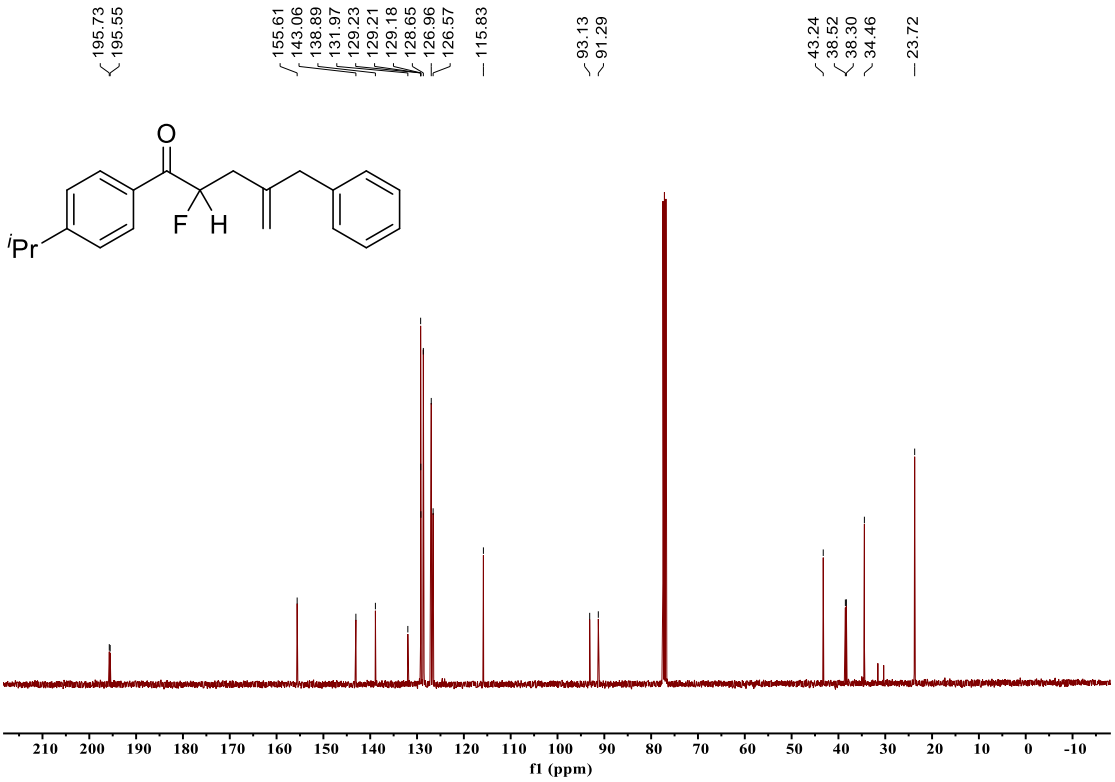

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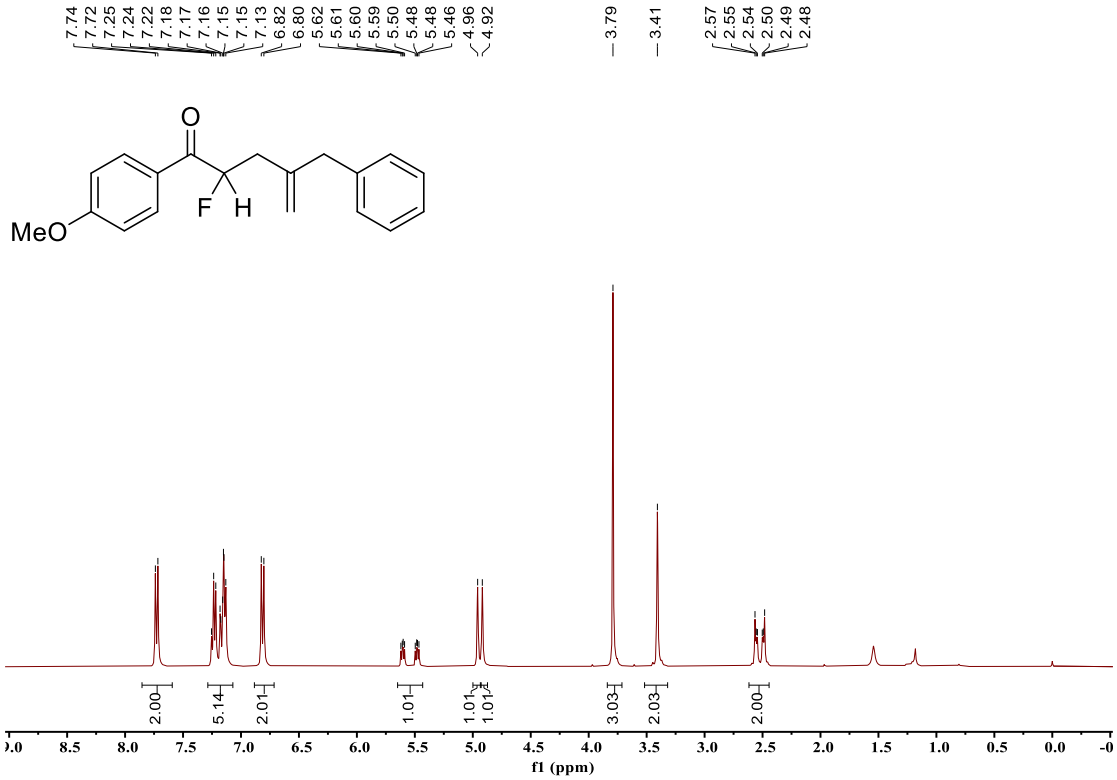

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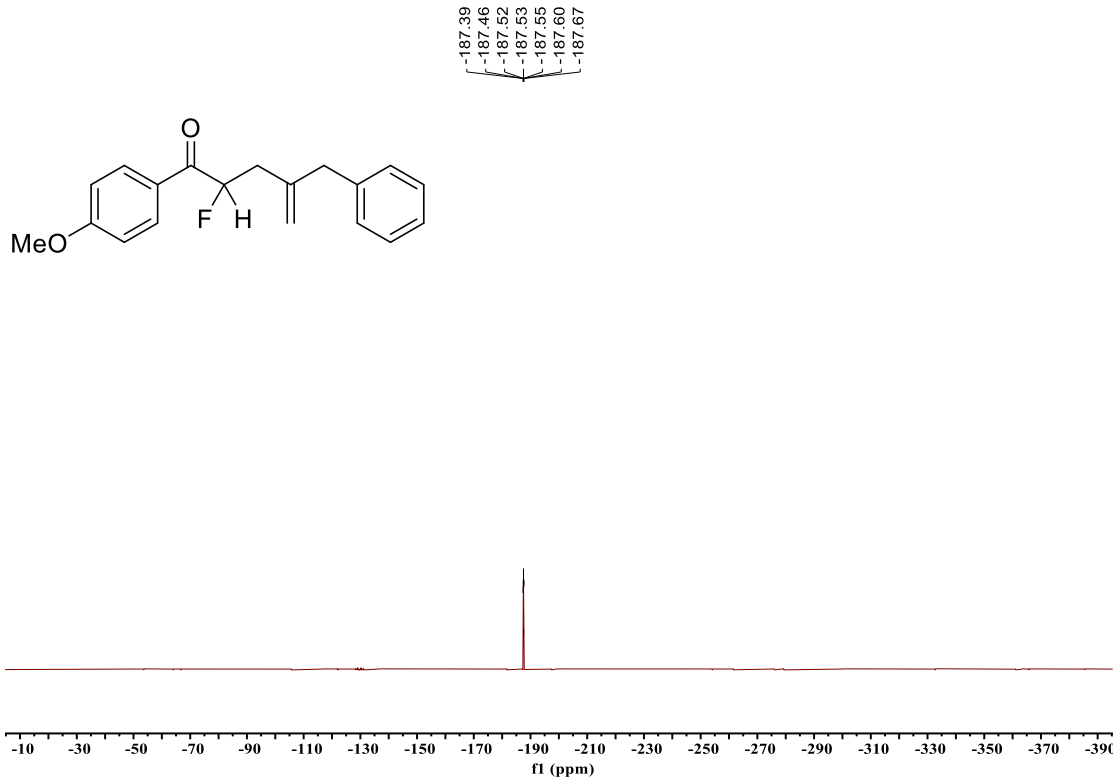

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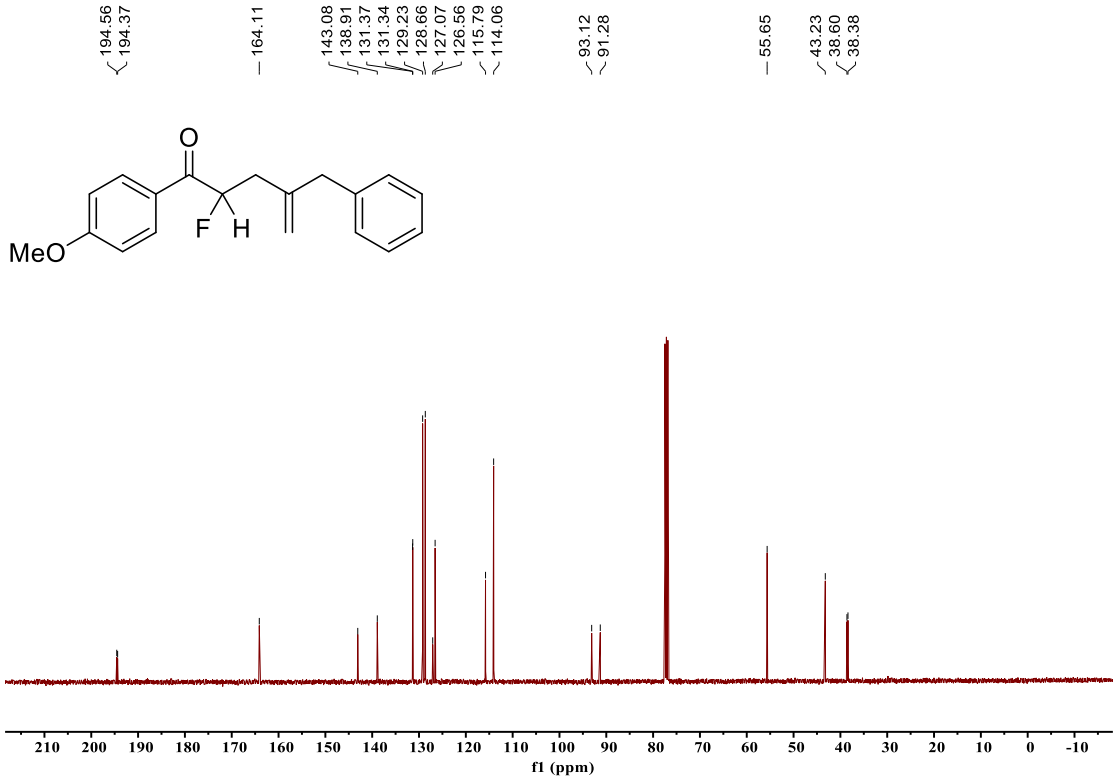

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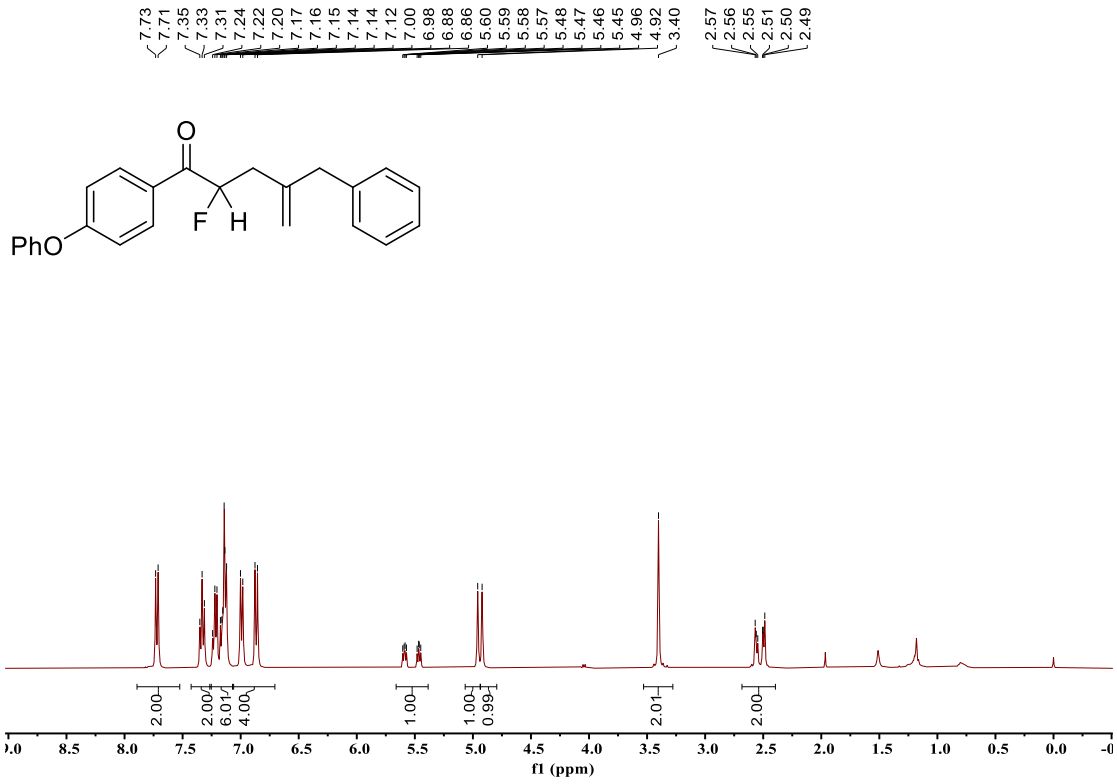

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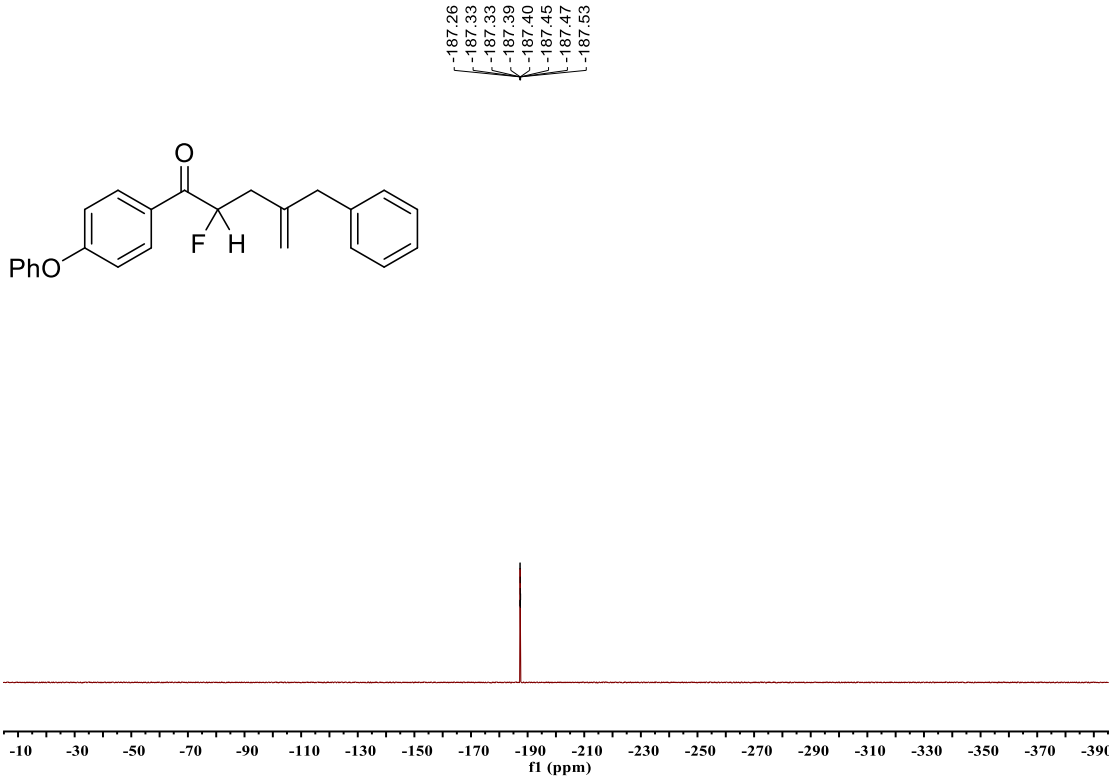

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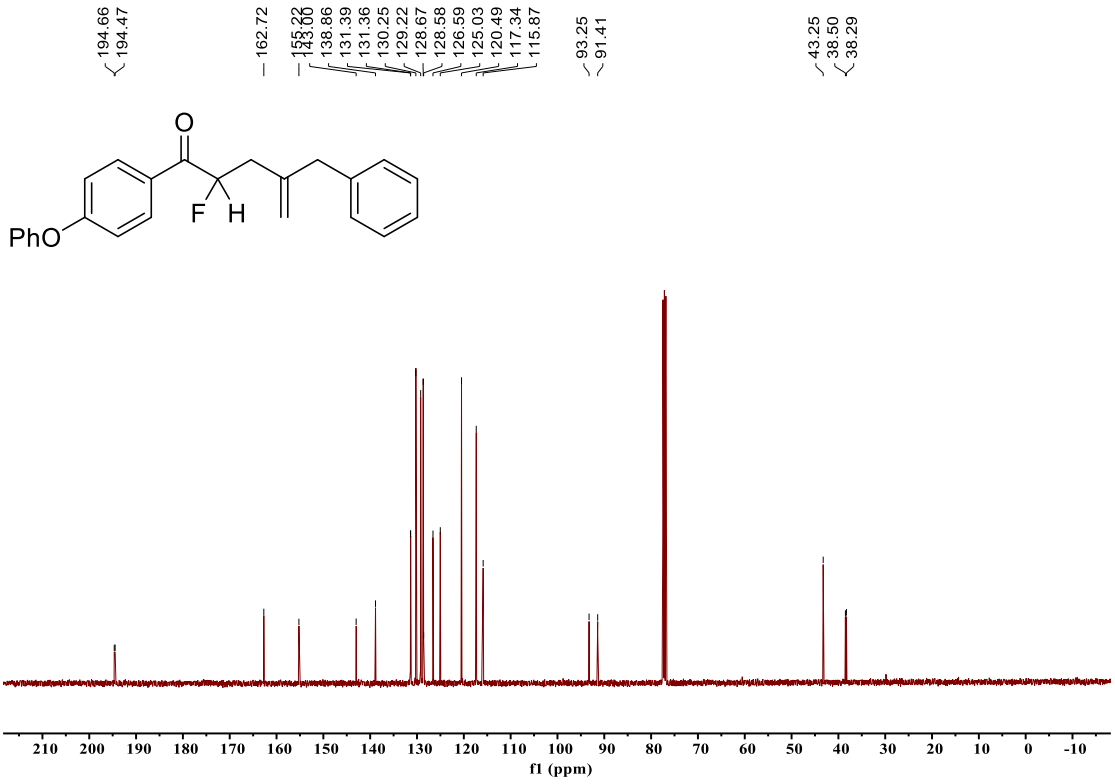

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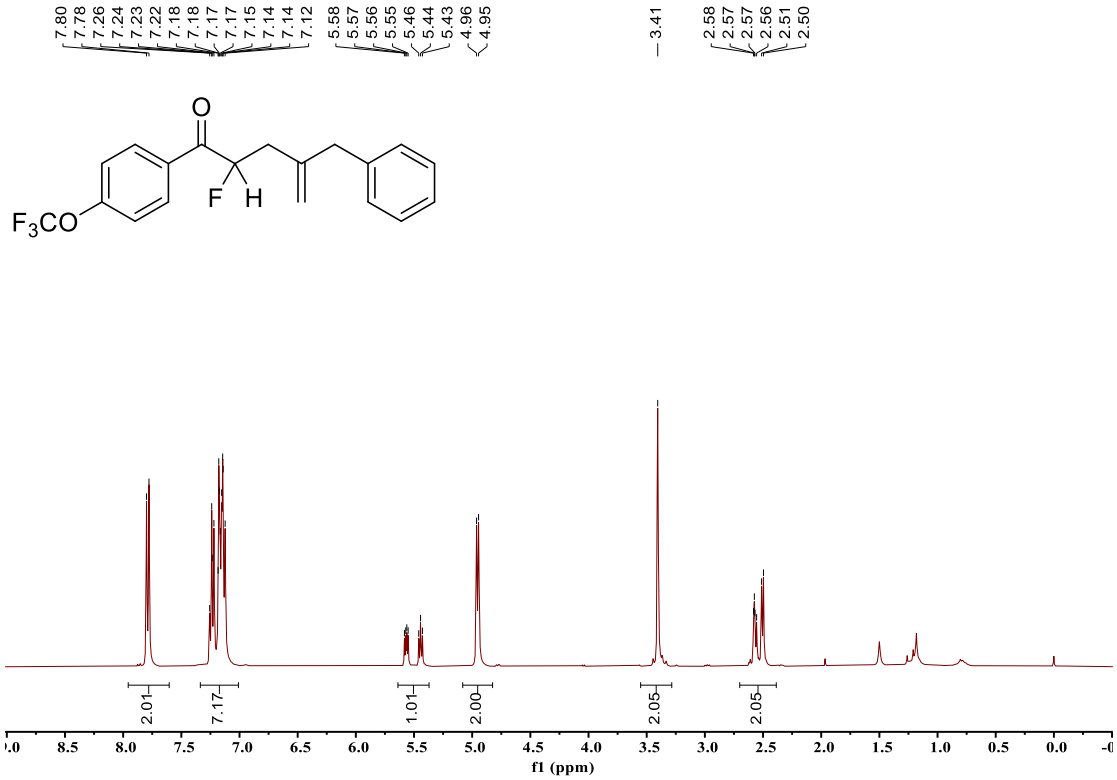

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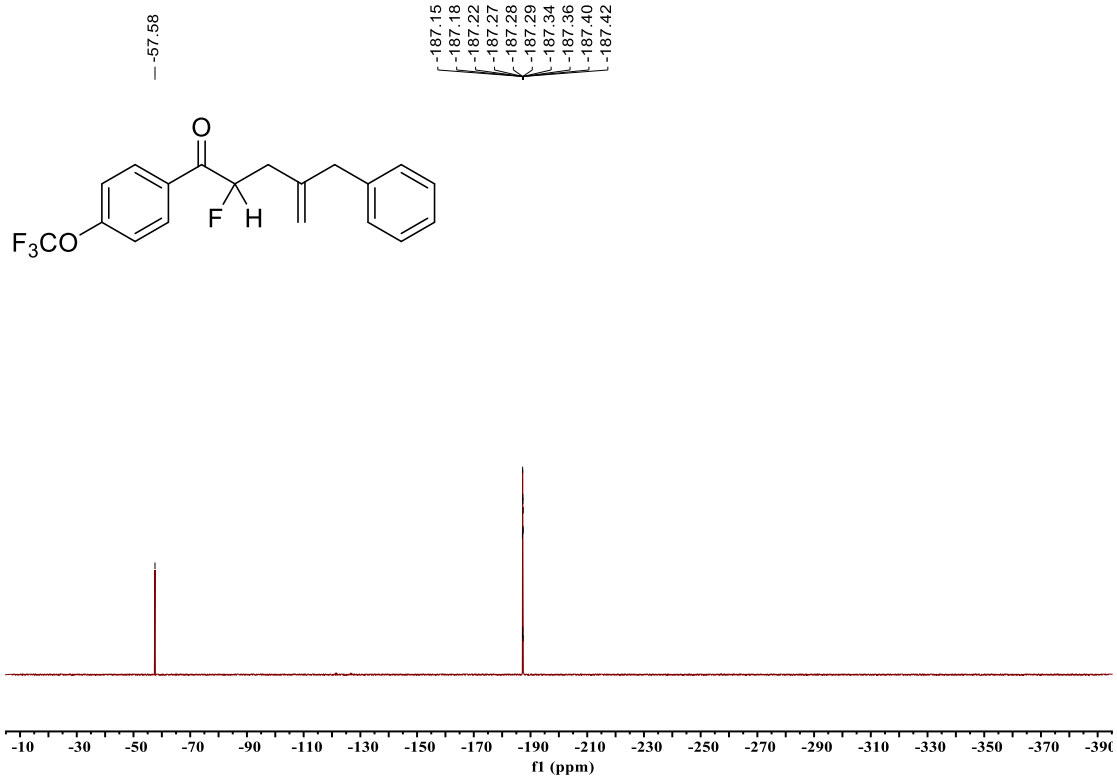

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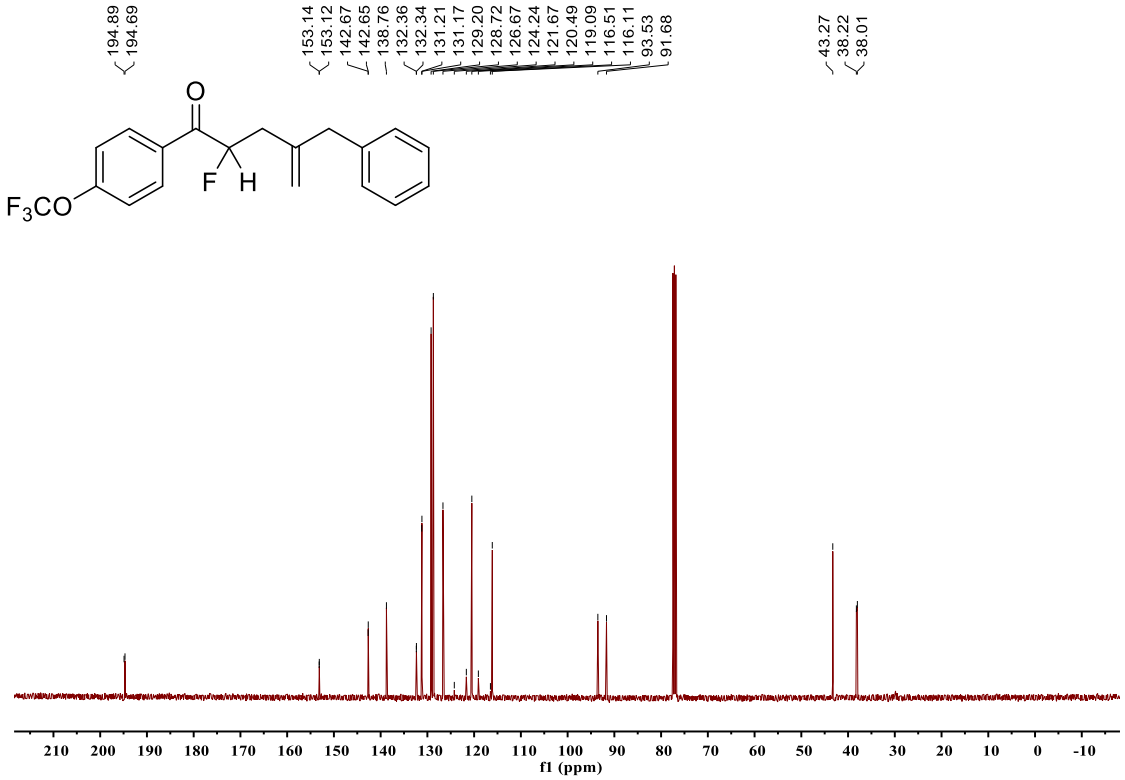

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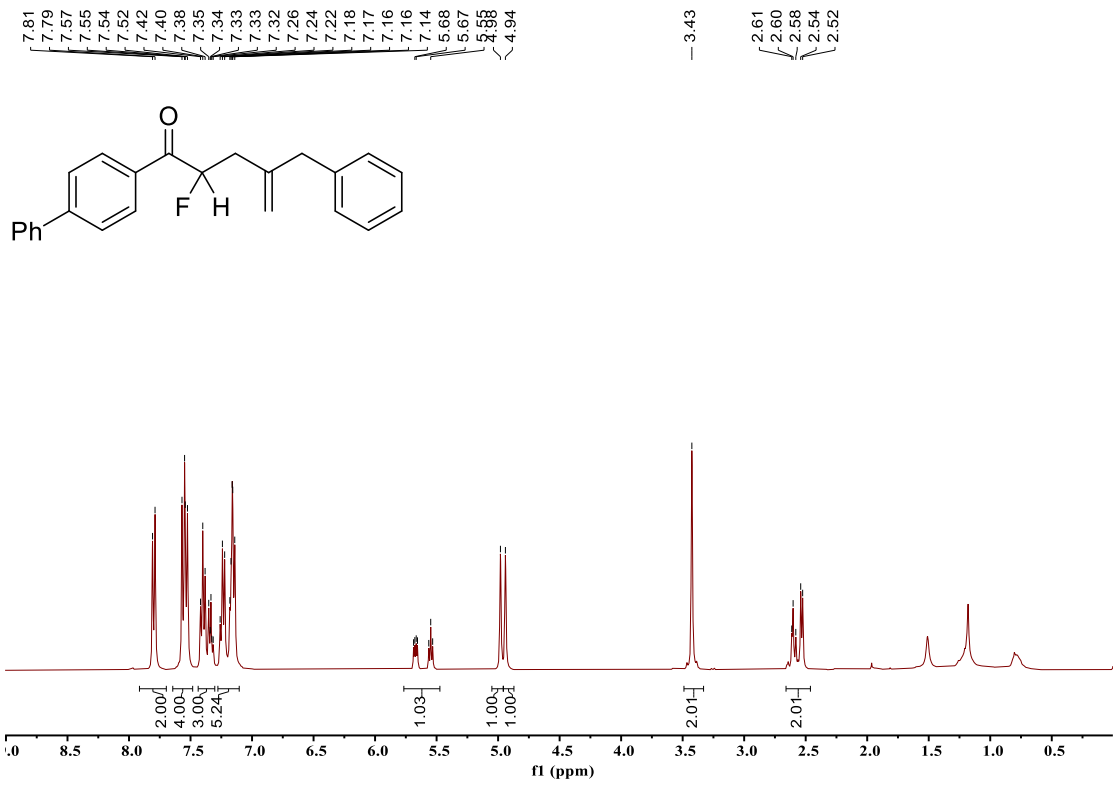

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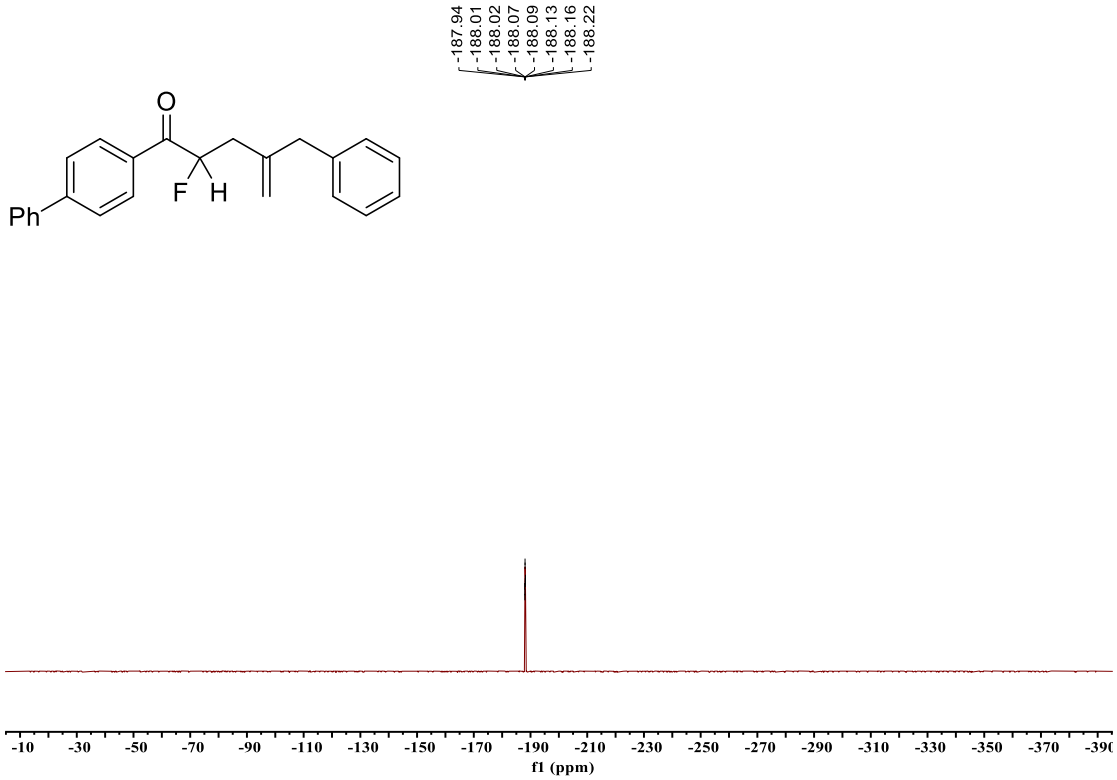

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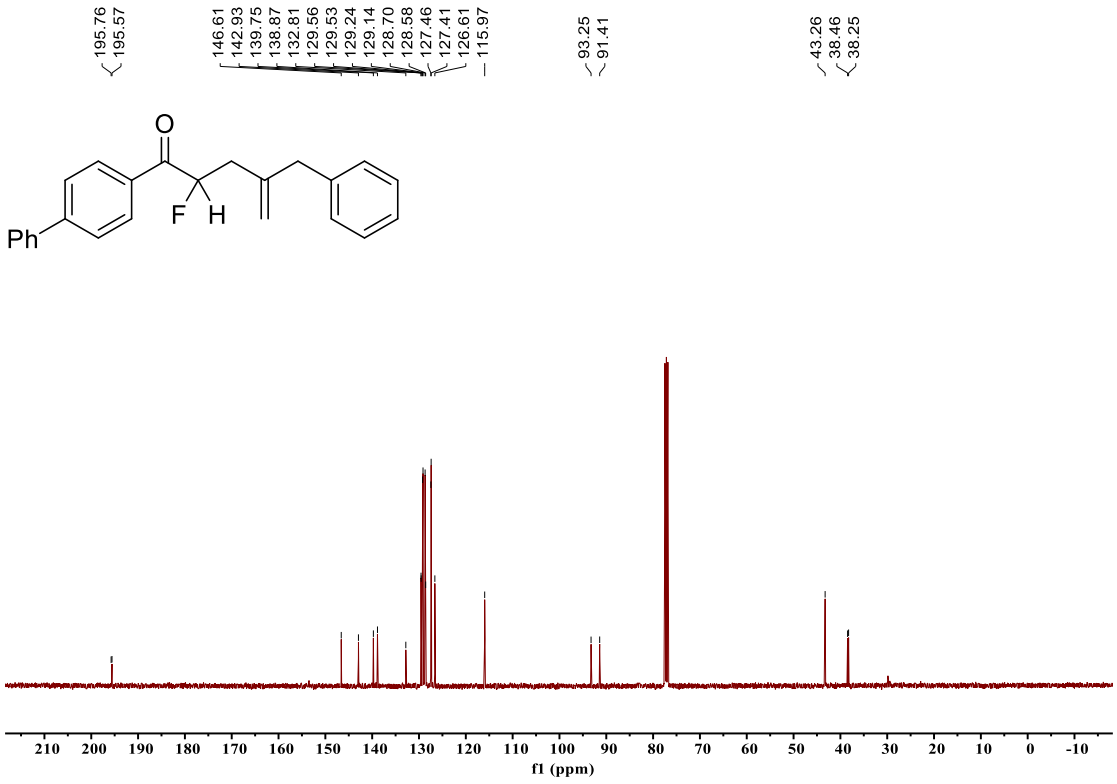

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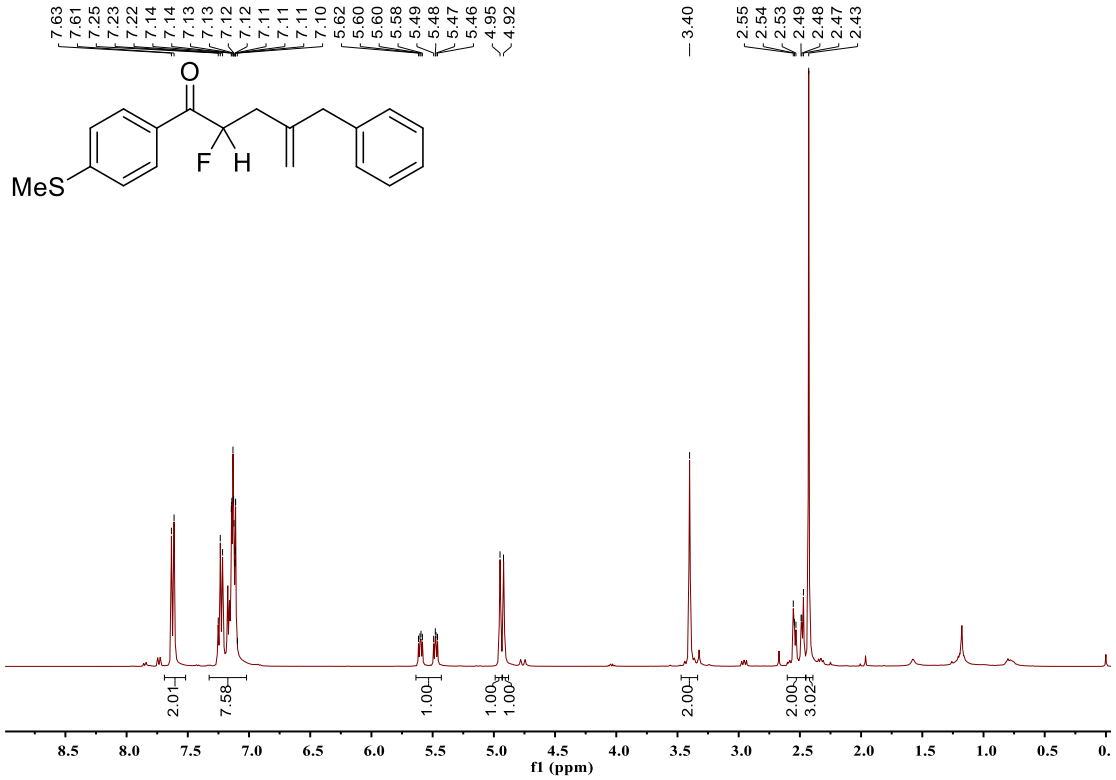
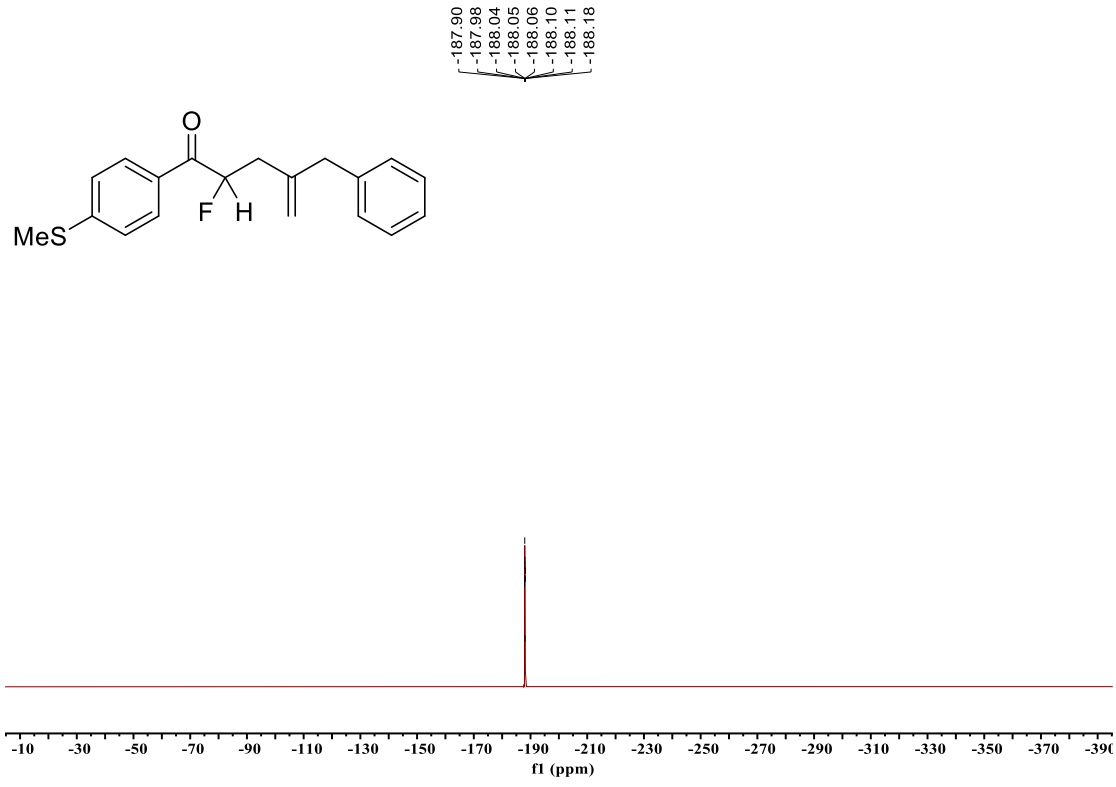


^{19}F NMR of 11 (376 MHz, $CDCl_3$)



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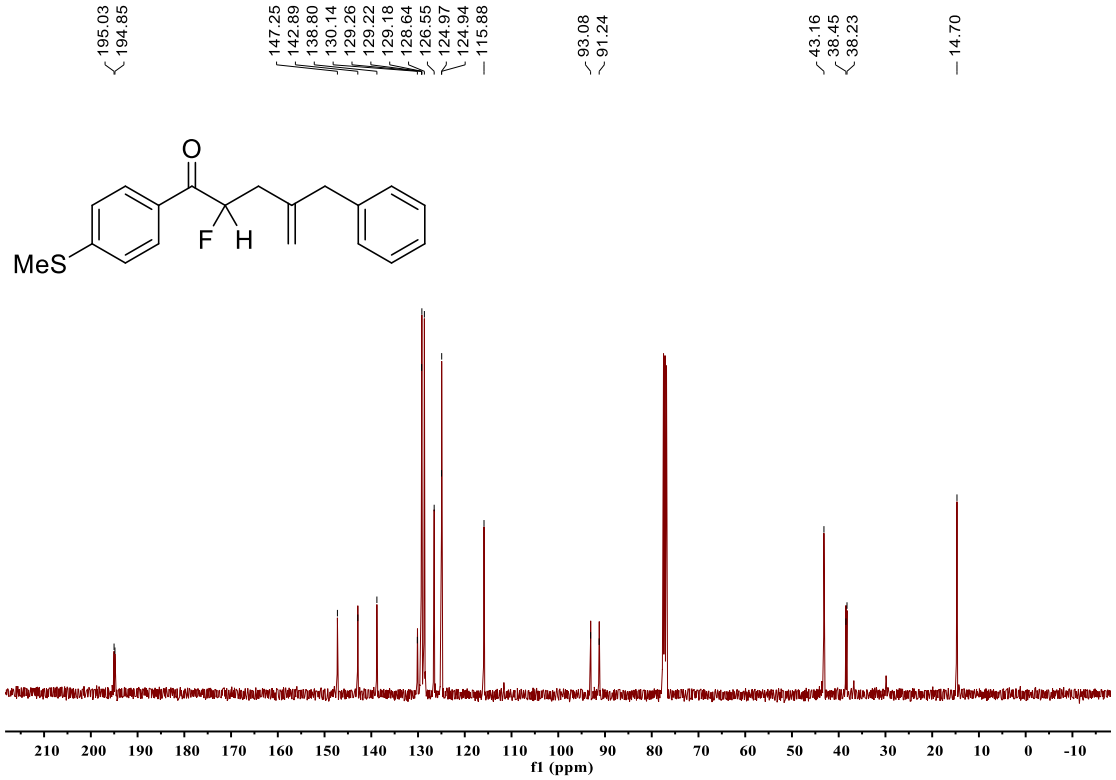

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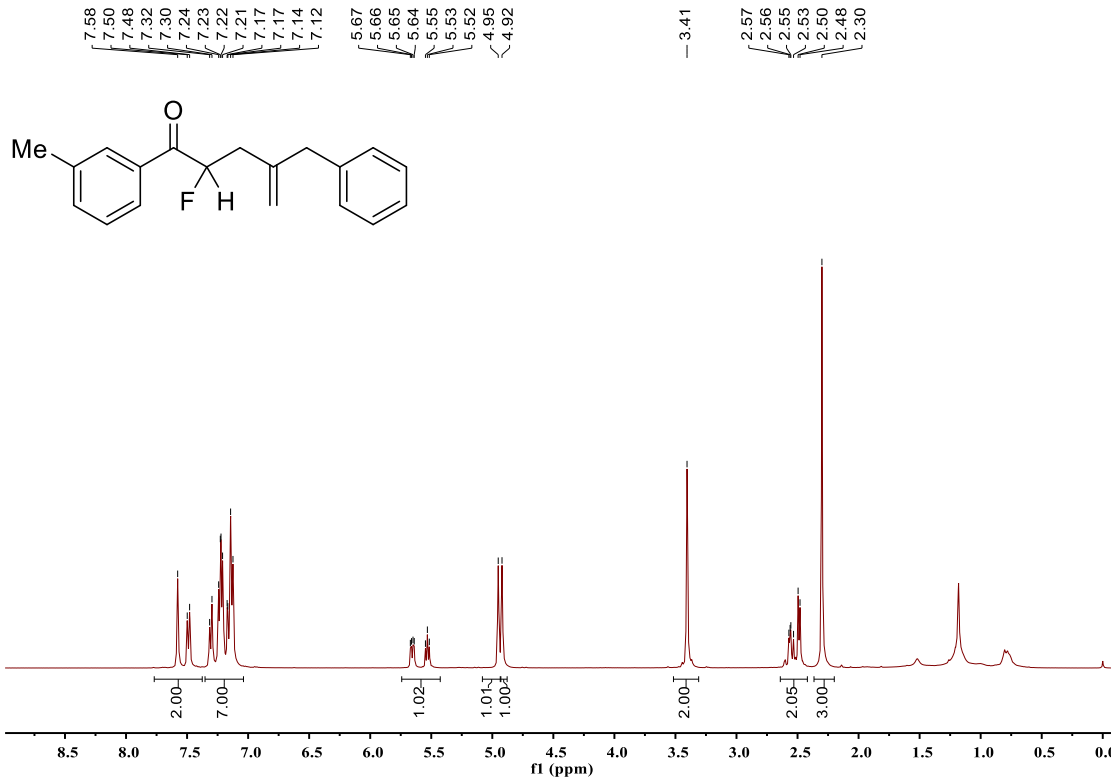

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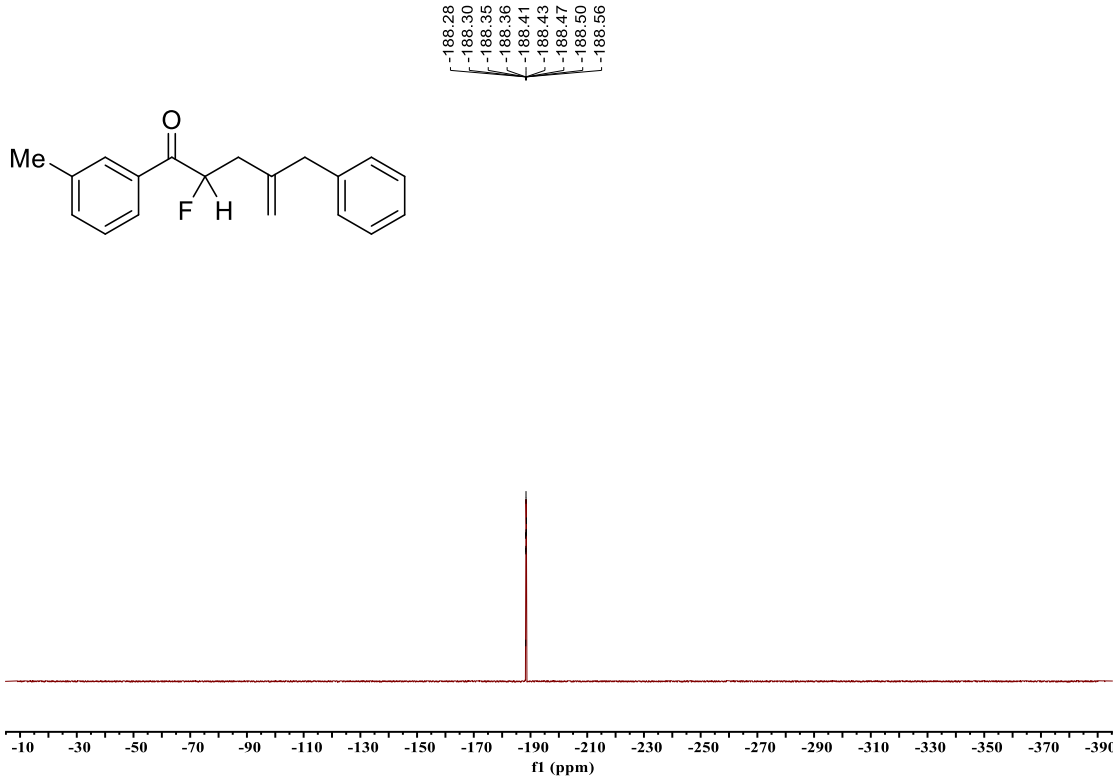

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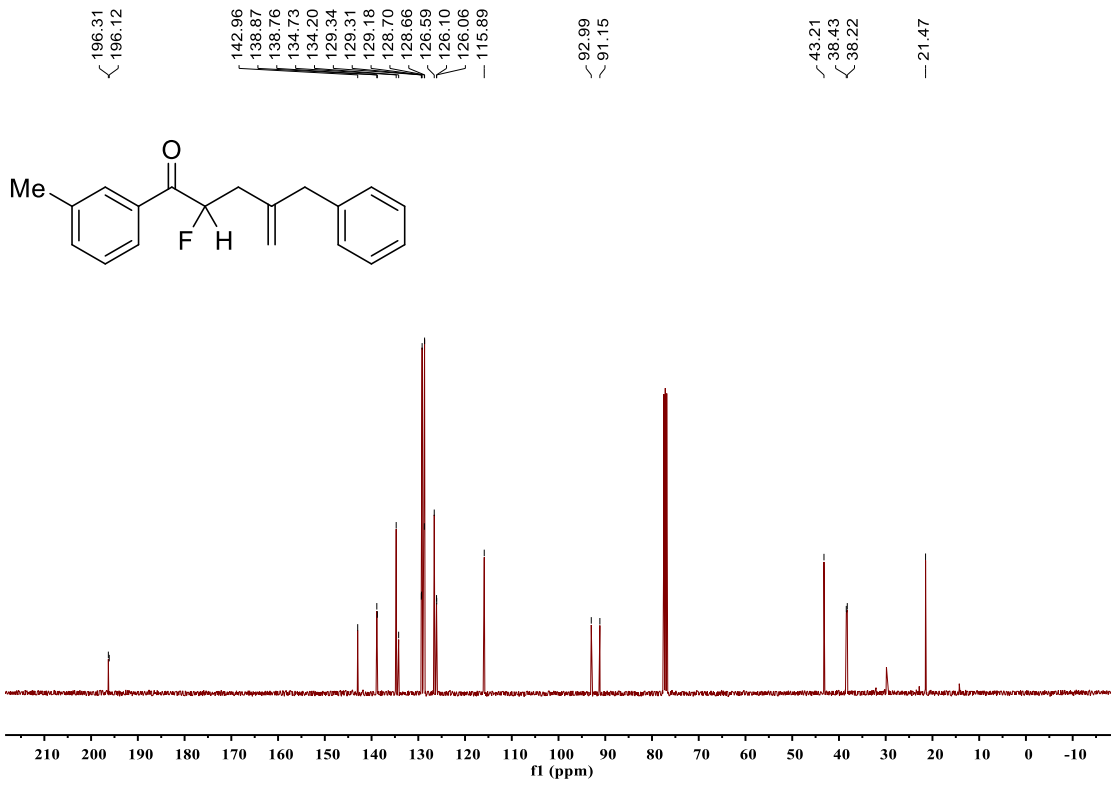

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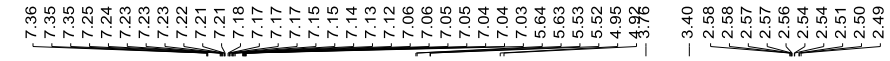
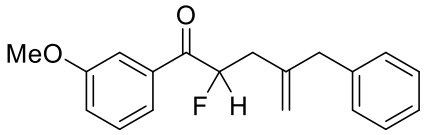
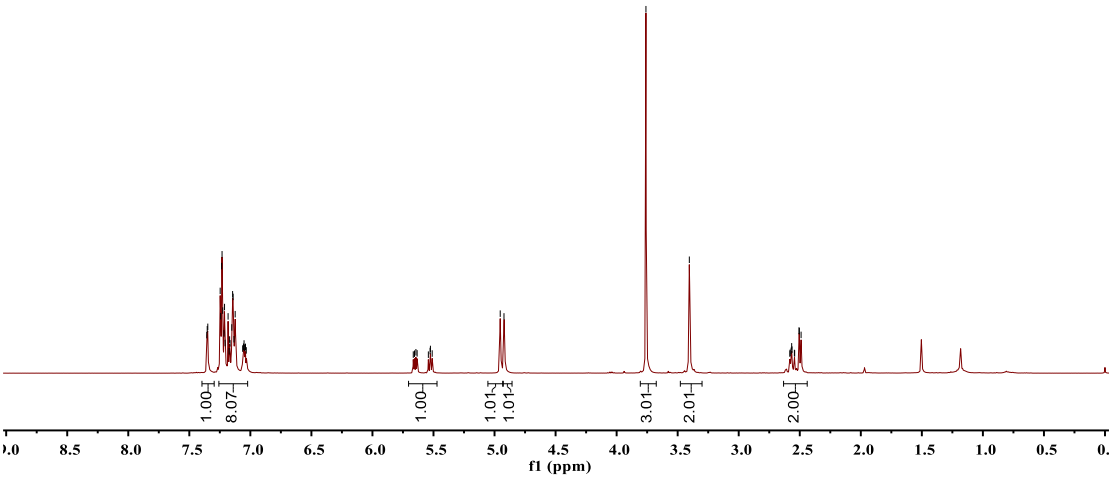
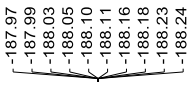
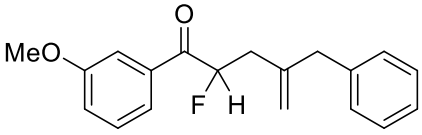


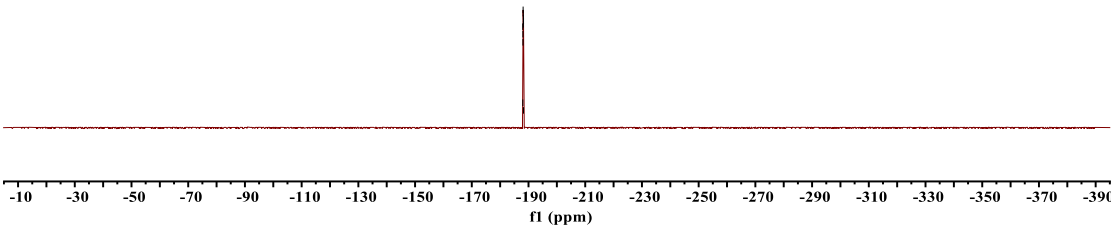




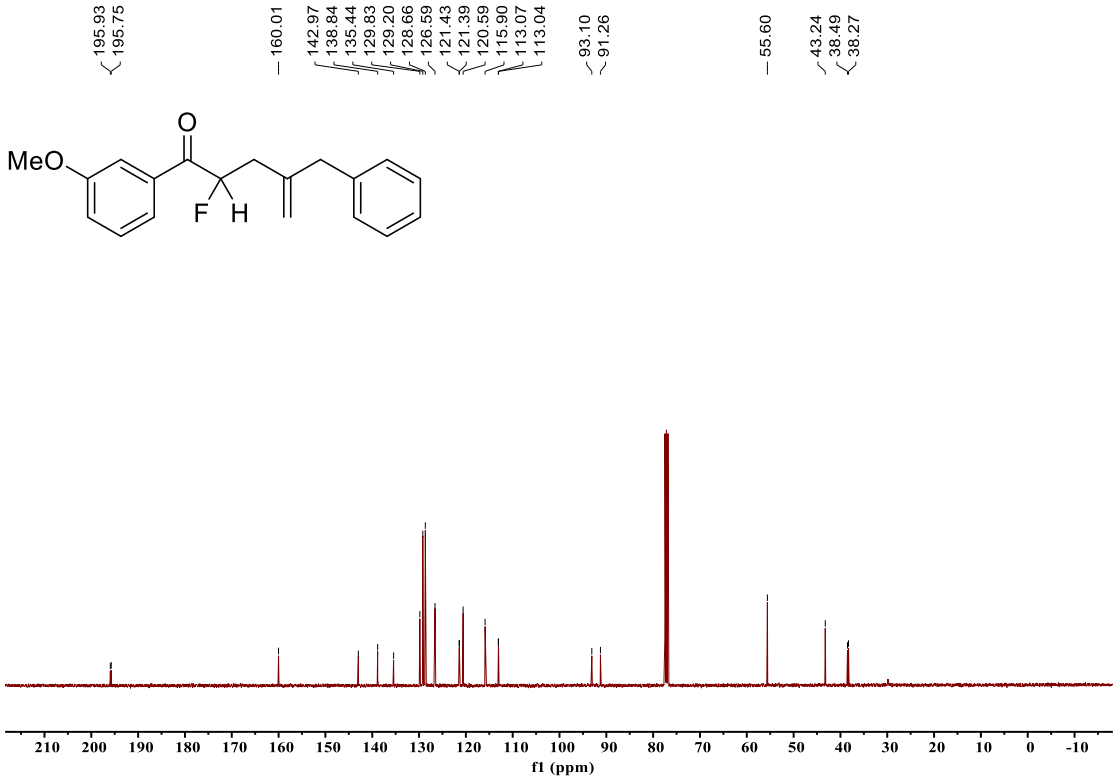
^{19}F NMR of 13 (376 MHz, $CDCl_3$)



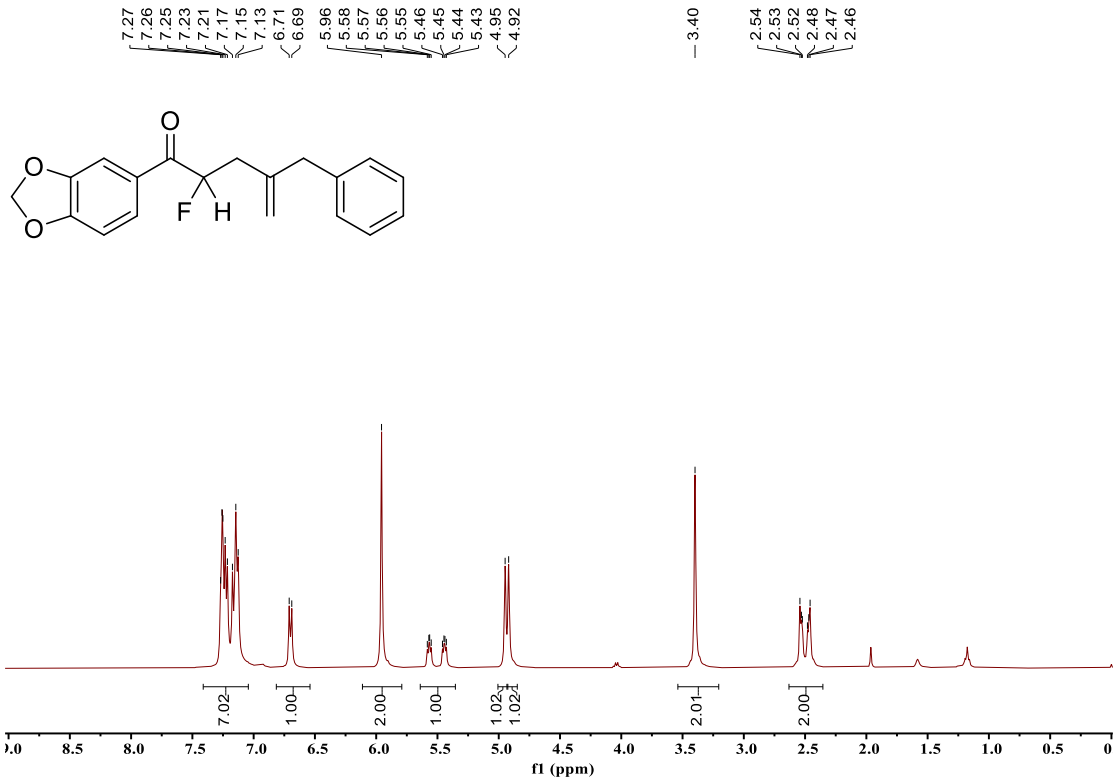




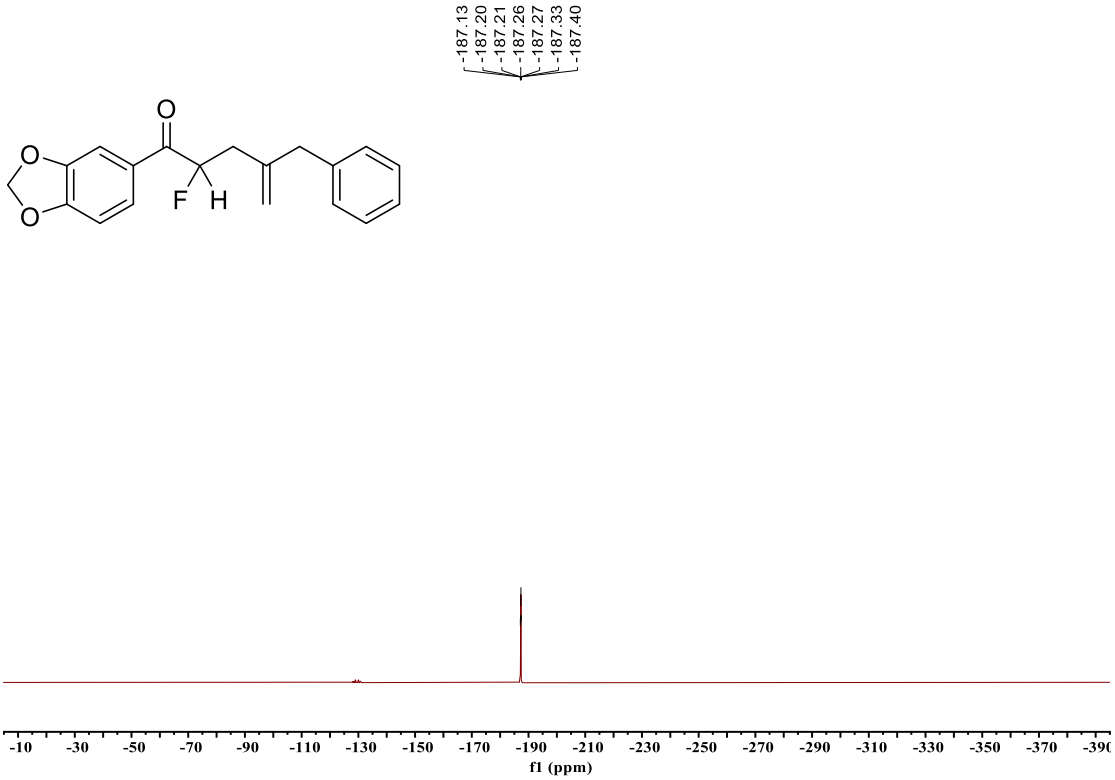
^{13}C-NMR of 13 (100 MHz, $CDCl_3$)



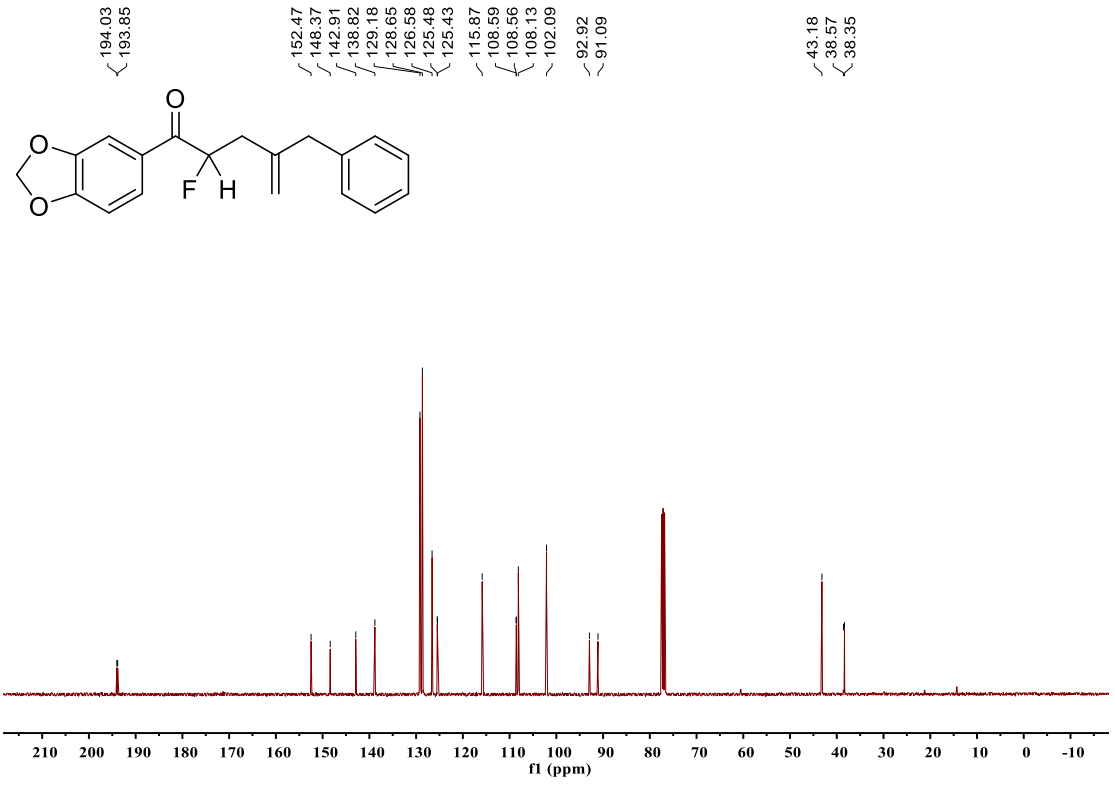
^{1}H-NMR of 14 (400 MHz, $CDCl_3$)



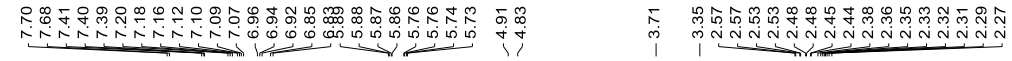
^{19}F NMR of 14 (376 MHz, $CDCl_3$)

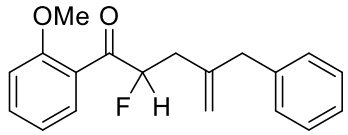


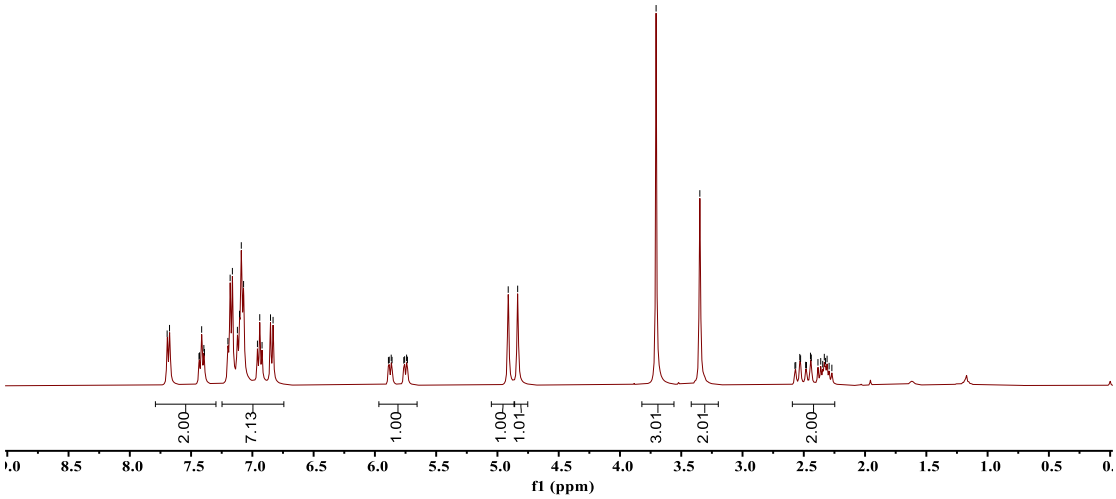
^{13}C-NMR of 14 (100 MHz, $CDCl_3$)



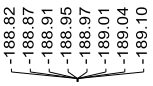
^{1}H-NMR of 15 (400 MHz, $CDCl_3$)

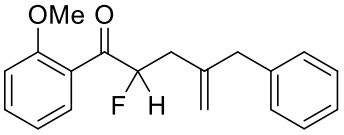


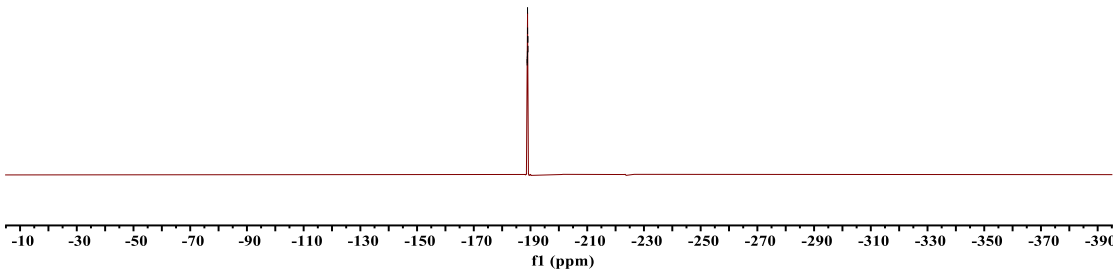




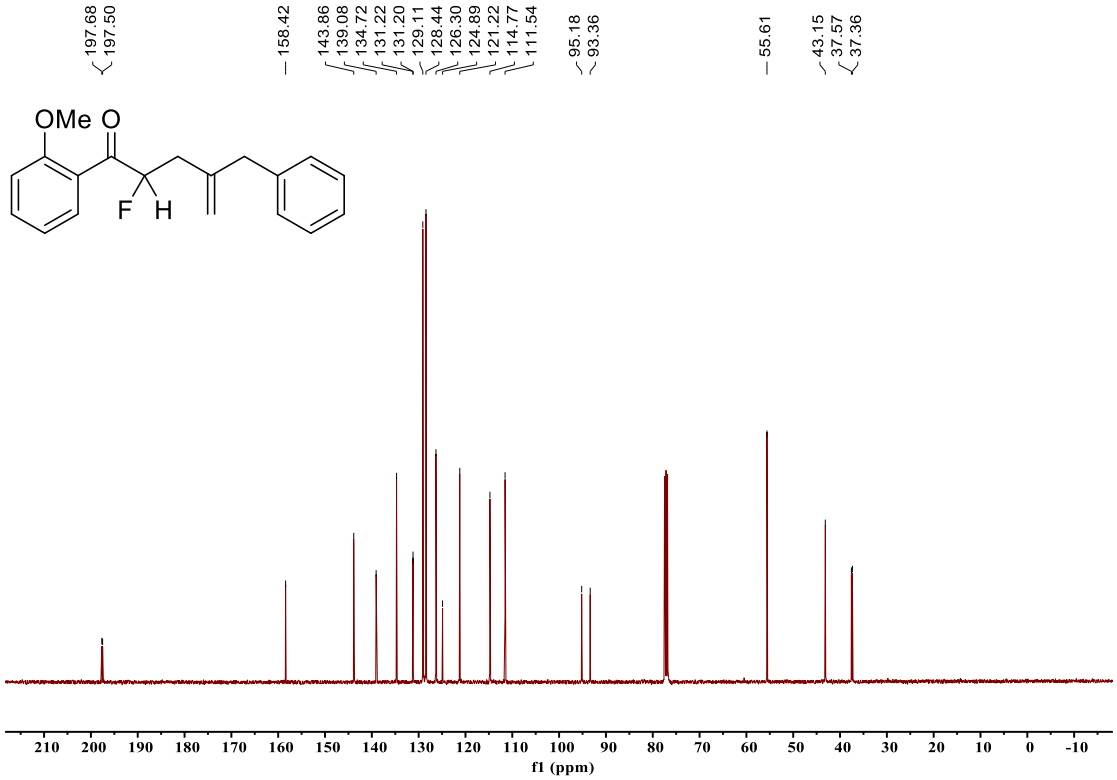
^{19}F NMR of 15 (376 MHz, $CDCl_3$)



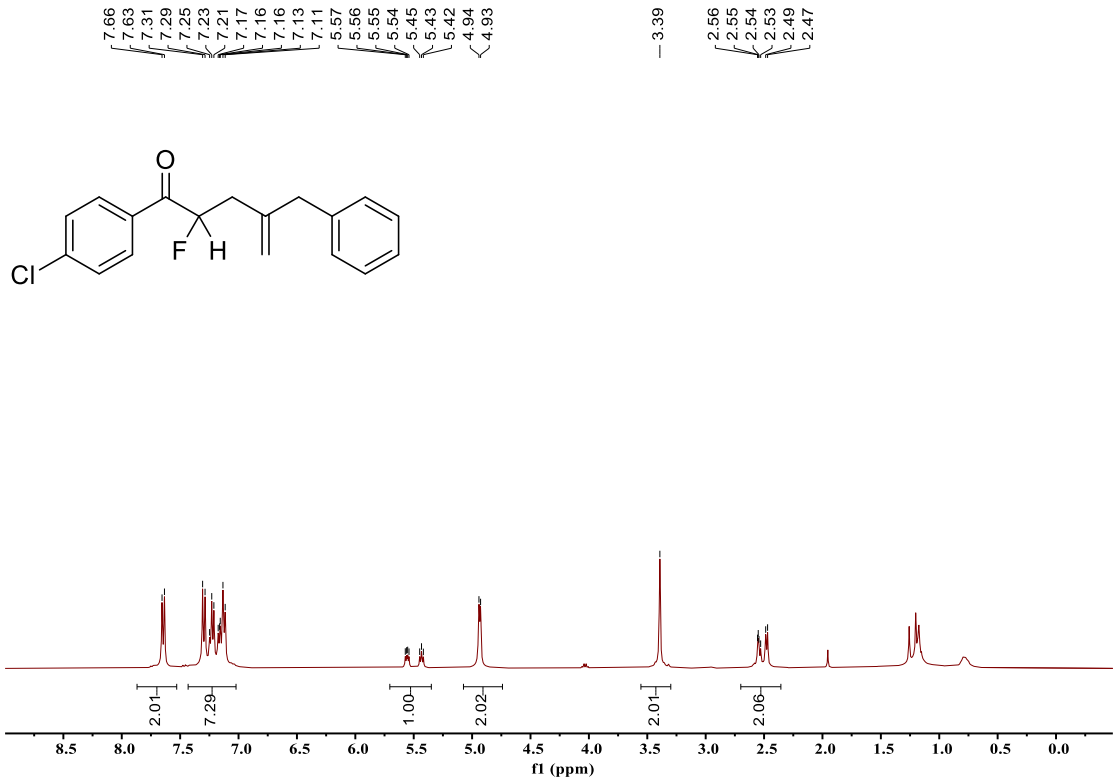




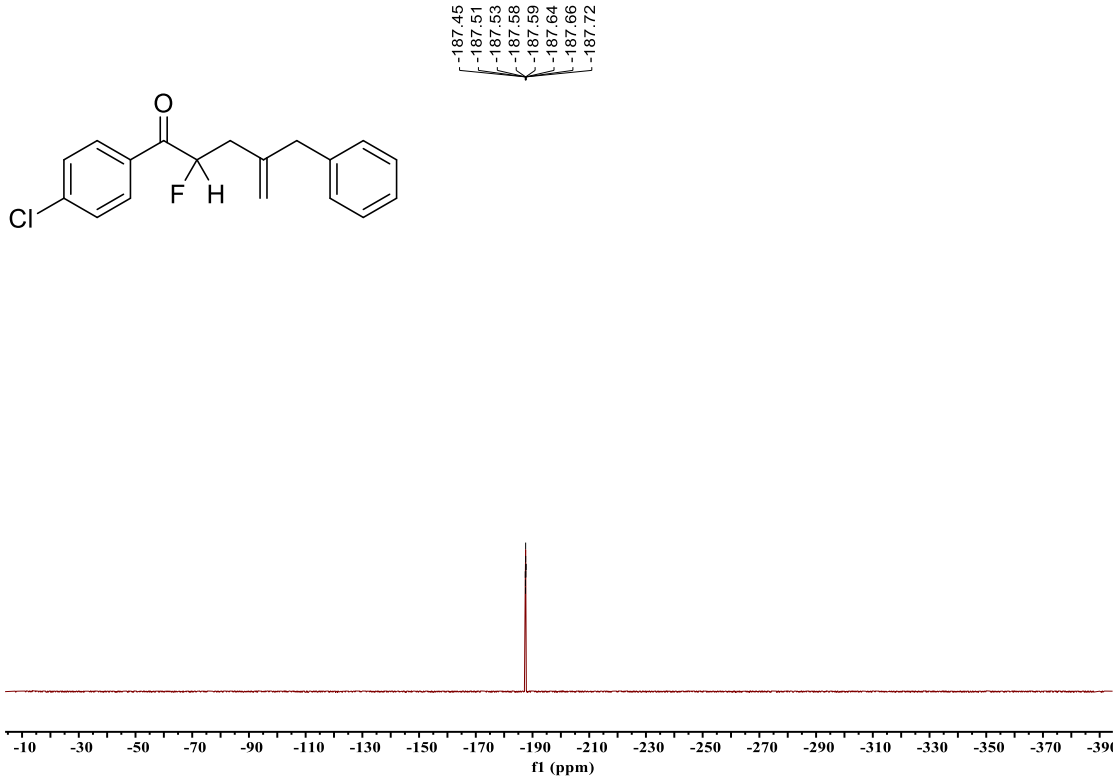
^{13}C-NMR of 15 (100 MHz, $CDCl_3$)



^{1}H-NMR of 16 (400 MHz, $CDCl_3$)



^{19}F NMR of 16 (376 MHz, $CDCl_3$)



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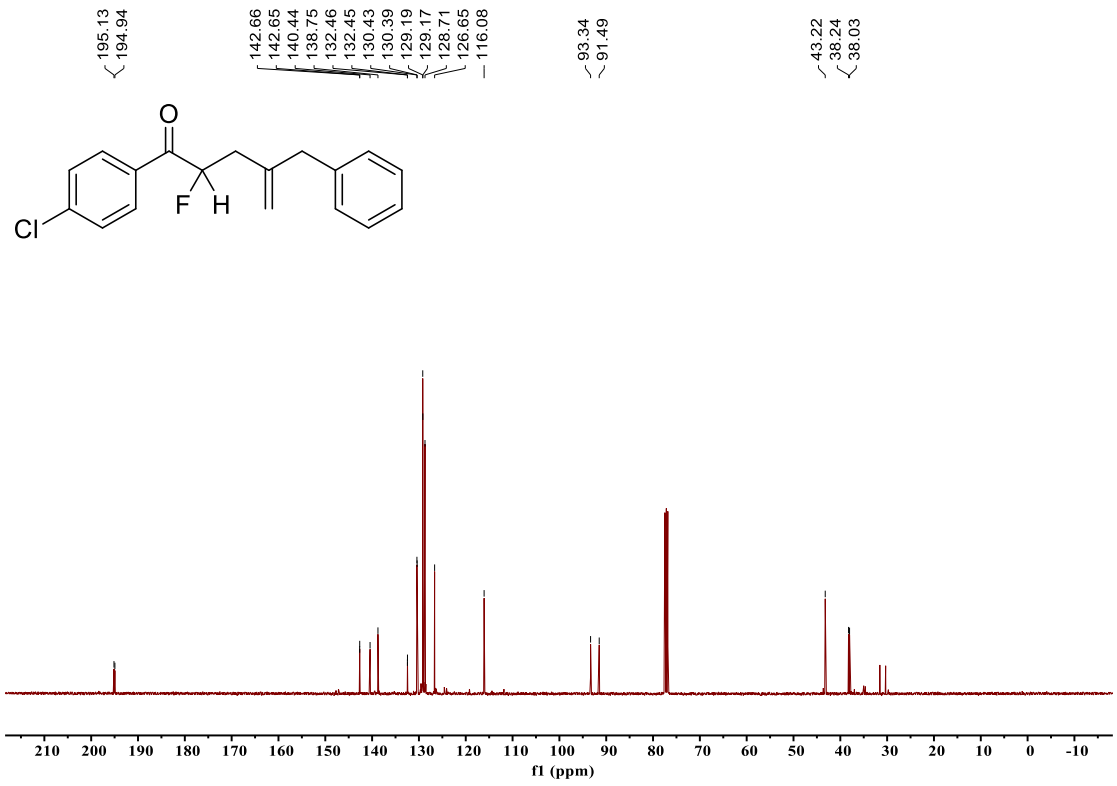
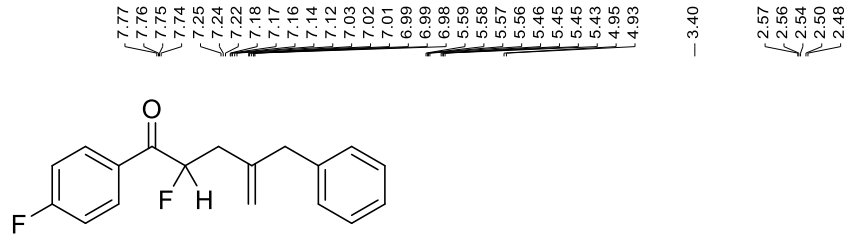
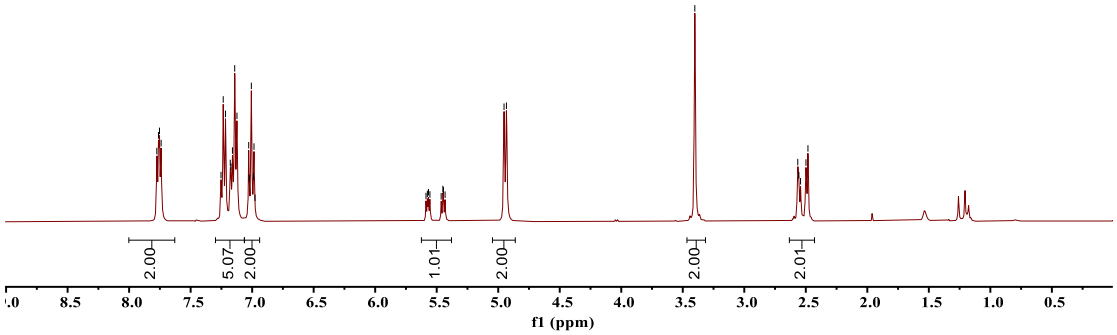
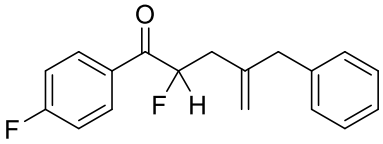


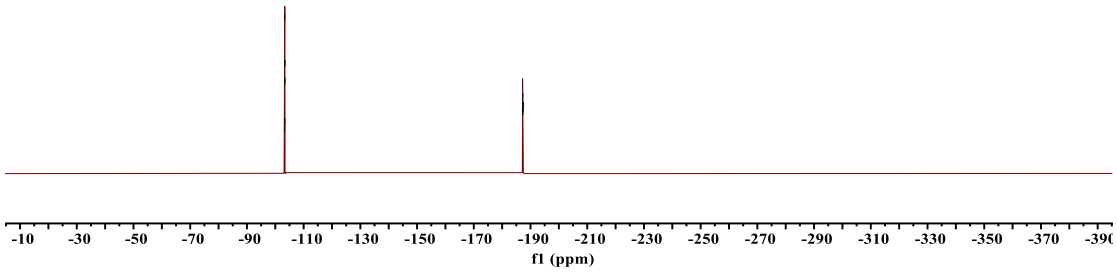
^{1}H-NMR of 17 (400 MHz, $CDCl_3$)



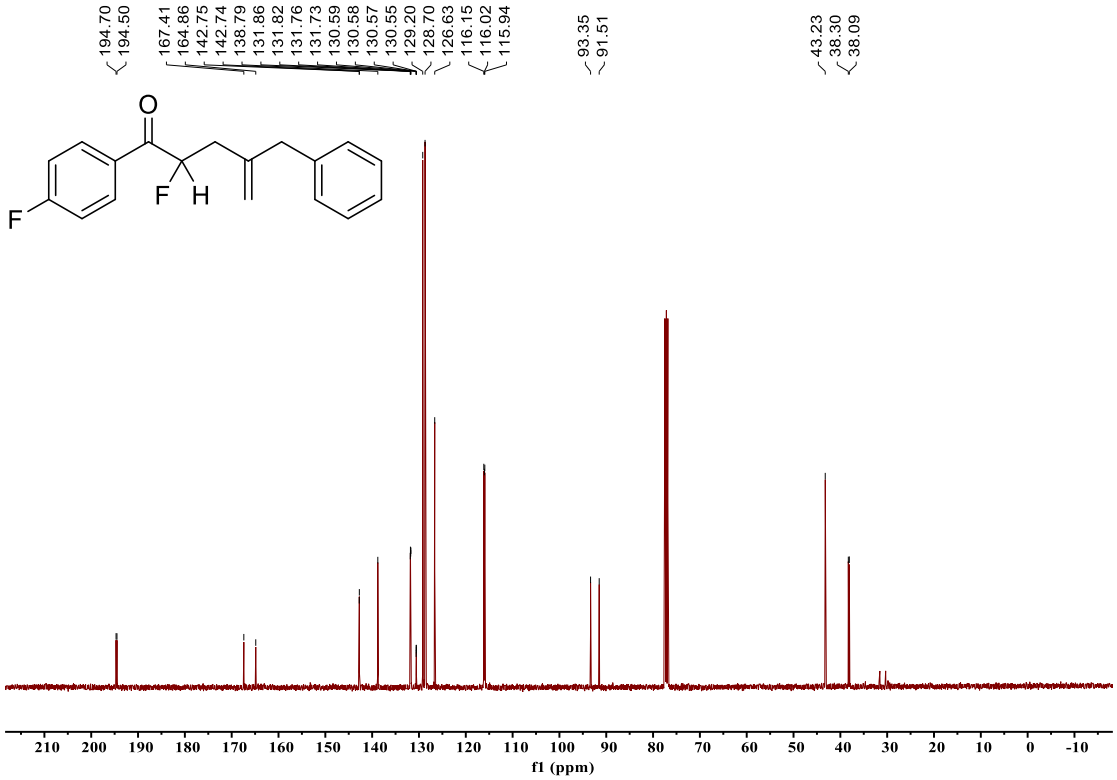


^{19}F NMR of 17 (376 MHz, $CDCl_3$)

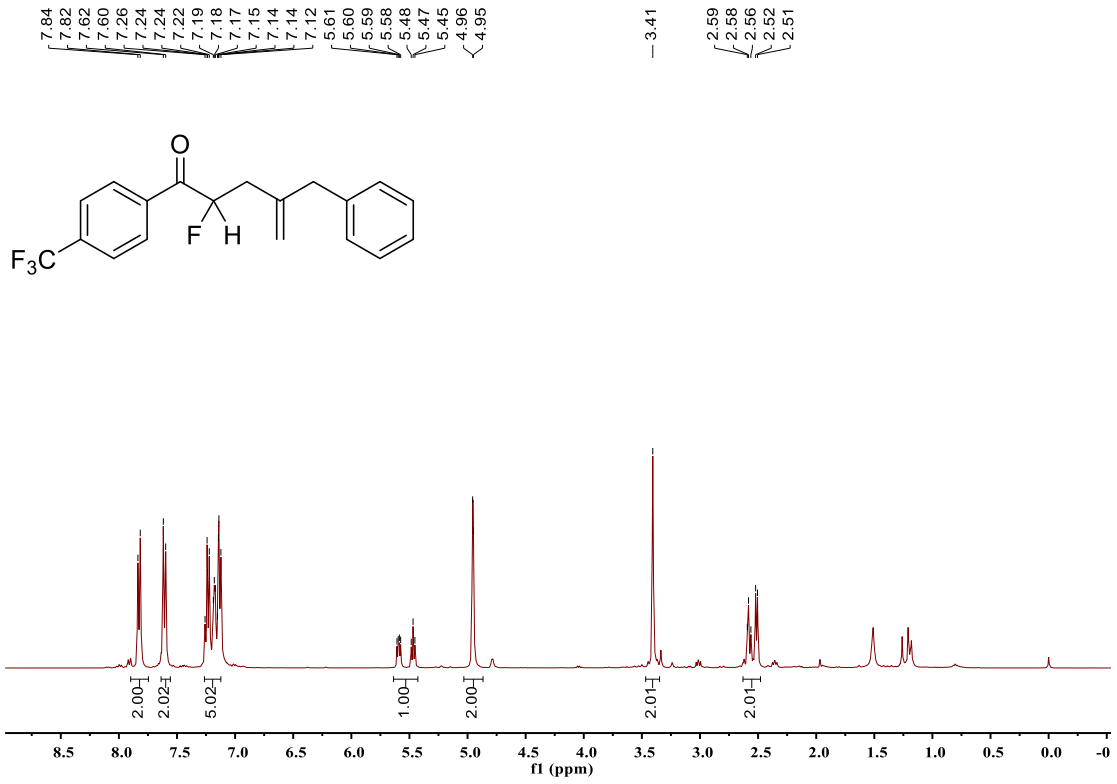




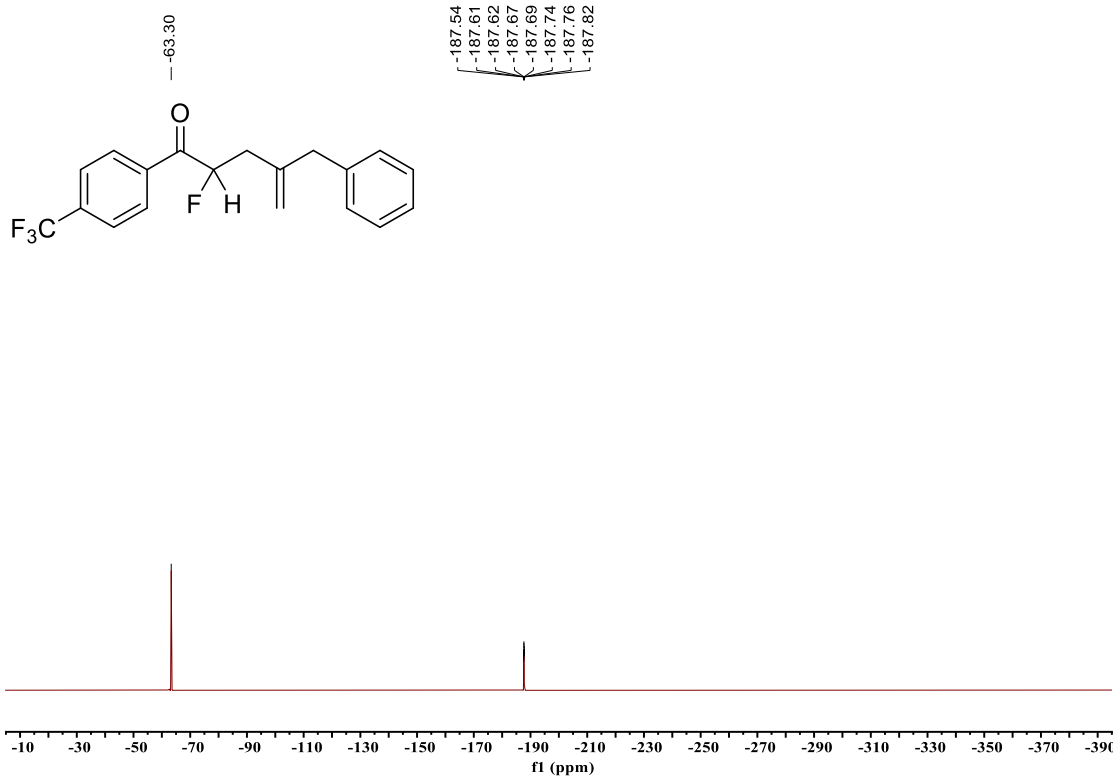
^{13}C-NMR of 17 (100 MHz, $CDCl_3$)



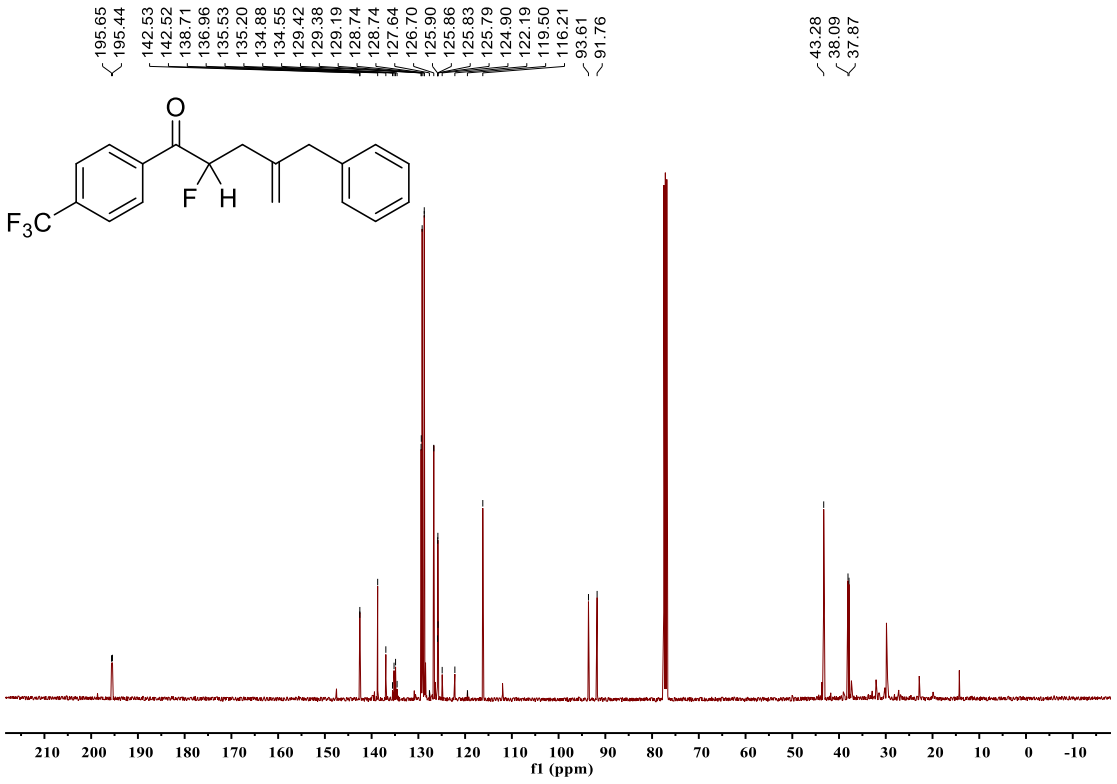
^{1}H-NMR of 18 (400 MHz, $CDCl_3$)



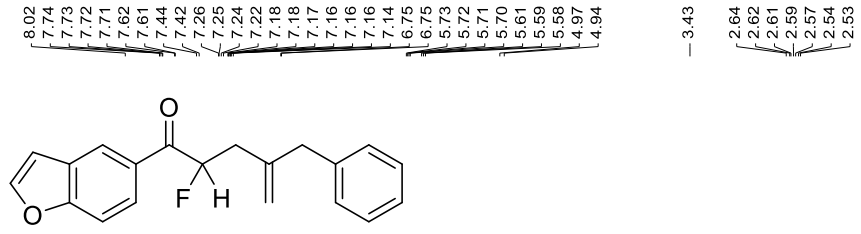
^{19}F NMR of 18 (376 MHz, $CDCl_3$)

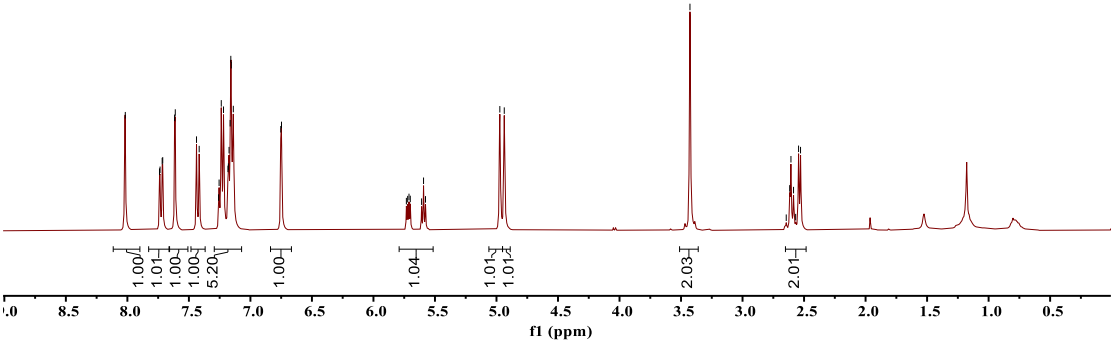


^{13}C-NMR of 18 (100 MHz, $CDCl_3$)

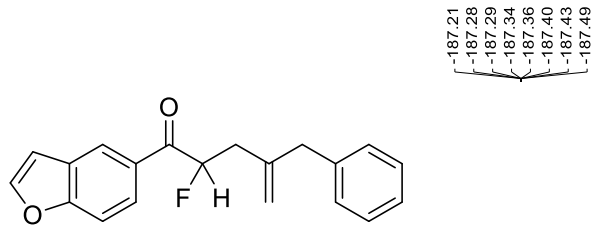


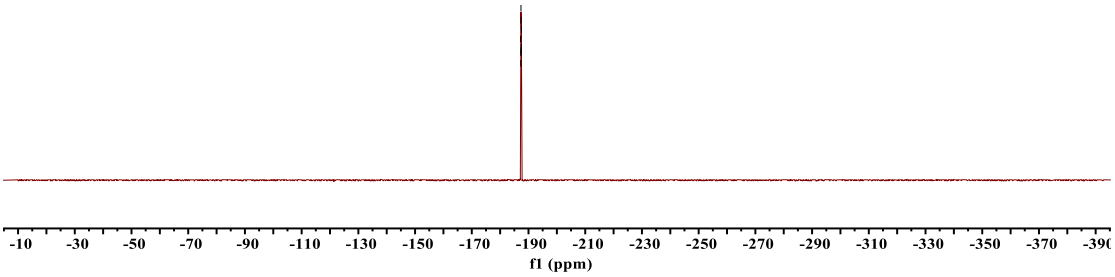
^{1}H-NMR of 19 (400 MHz, $CDCl_3$)





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





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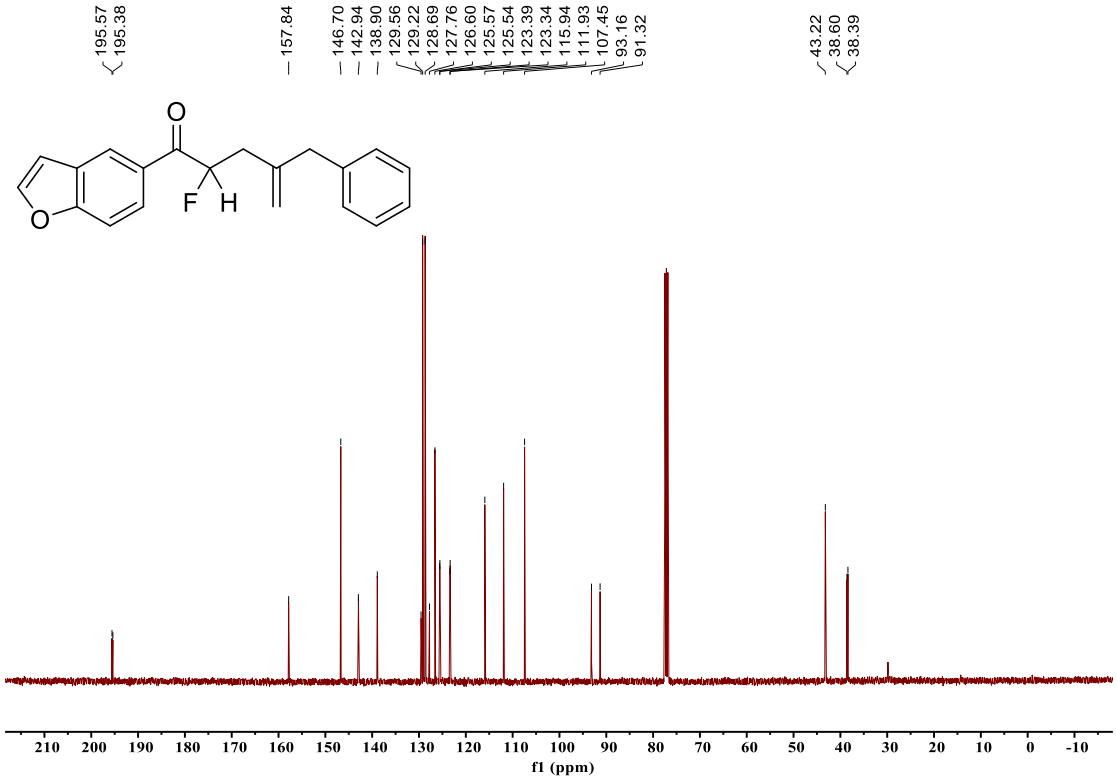

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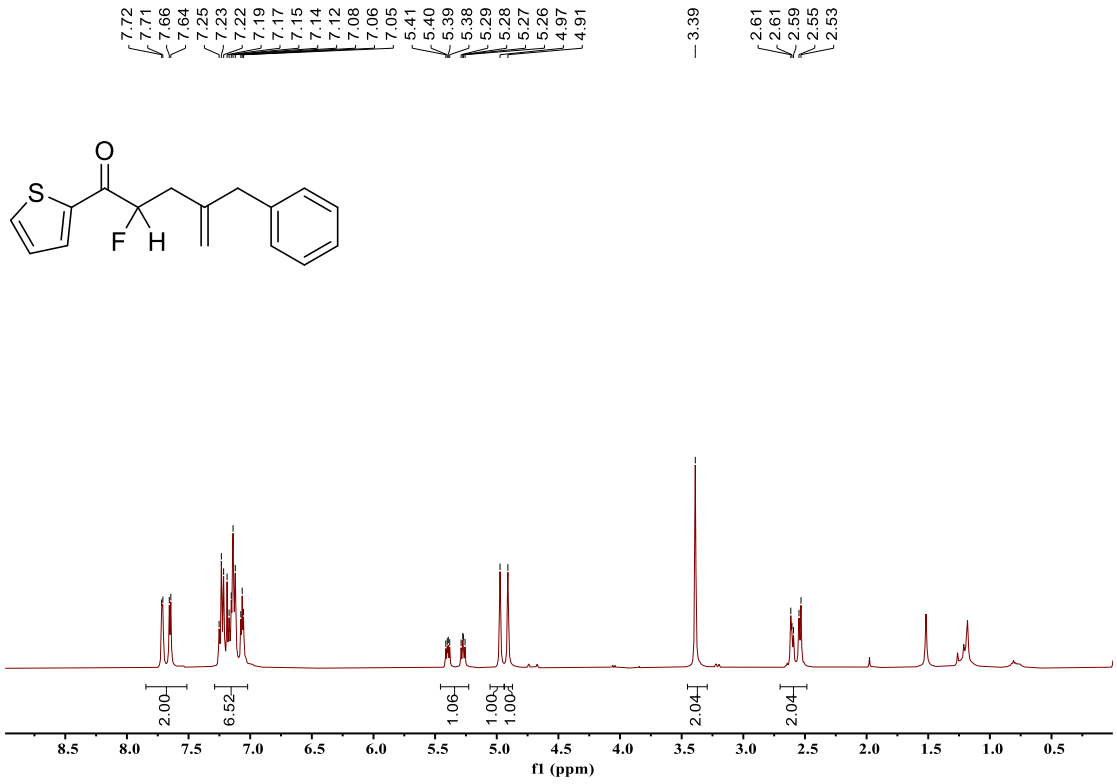
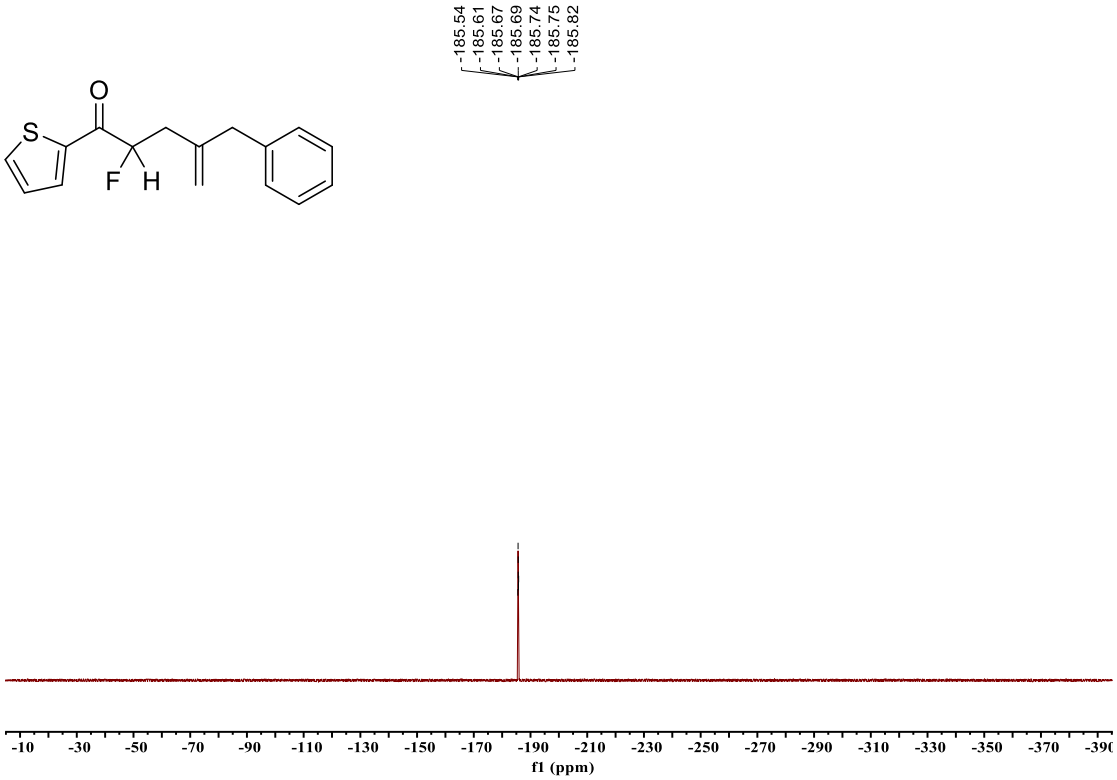


^{19}F NMR of 20 (376 MHz, $CDCl_3$)



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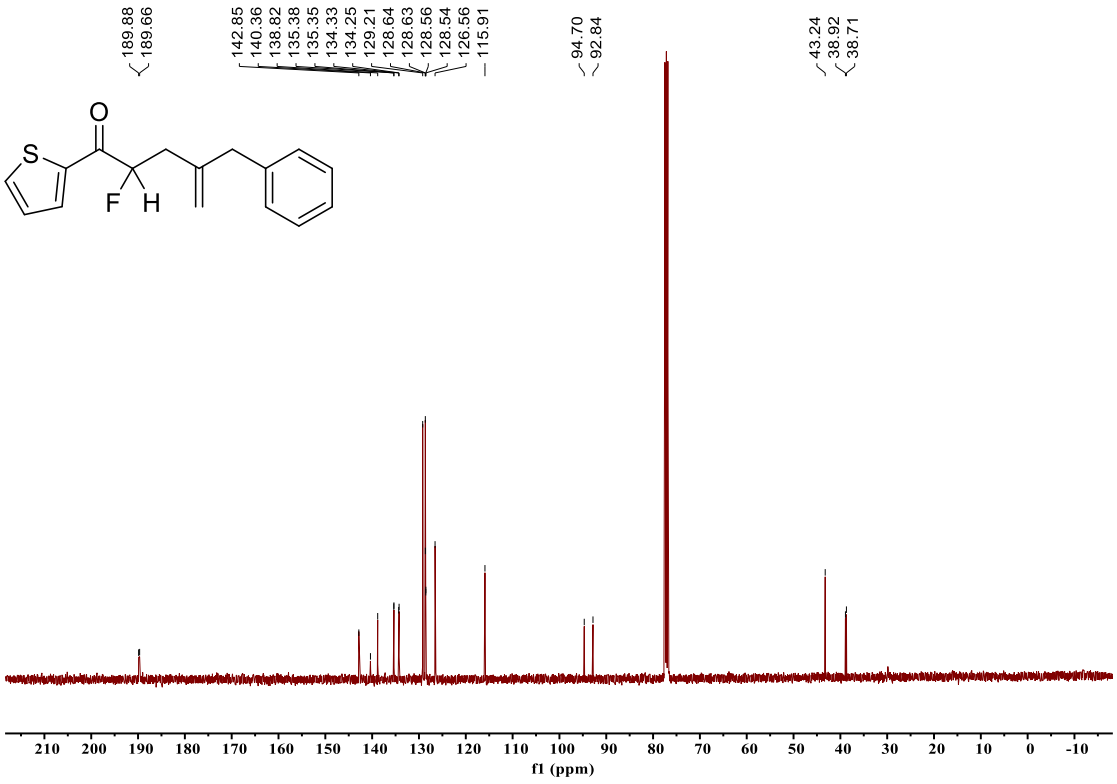
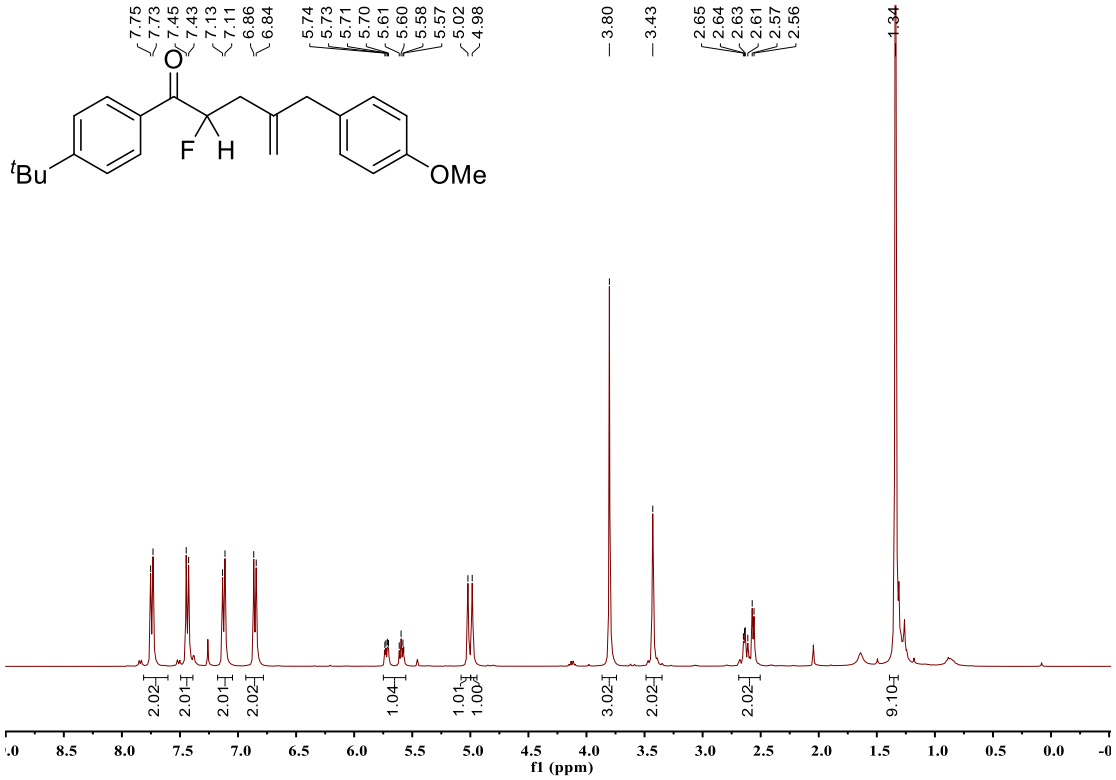
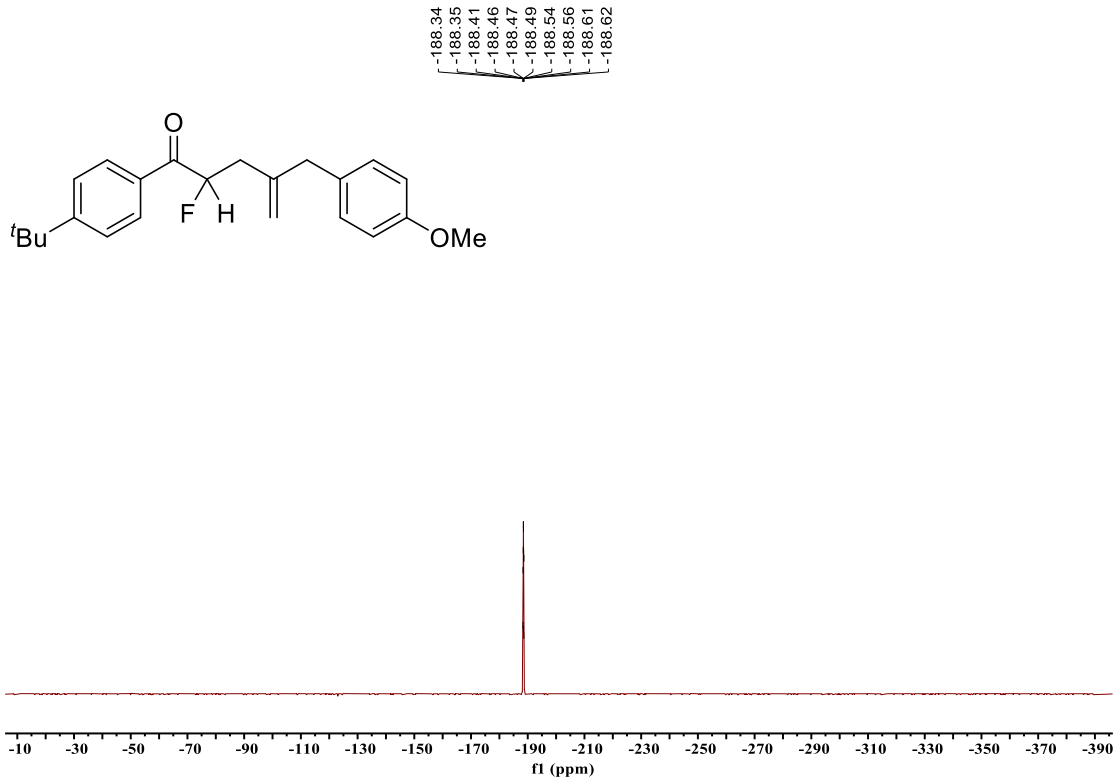


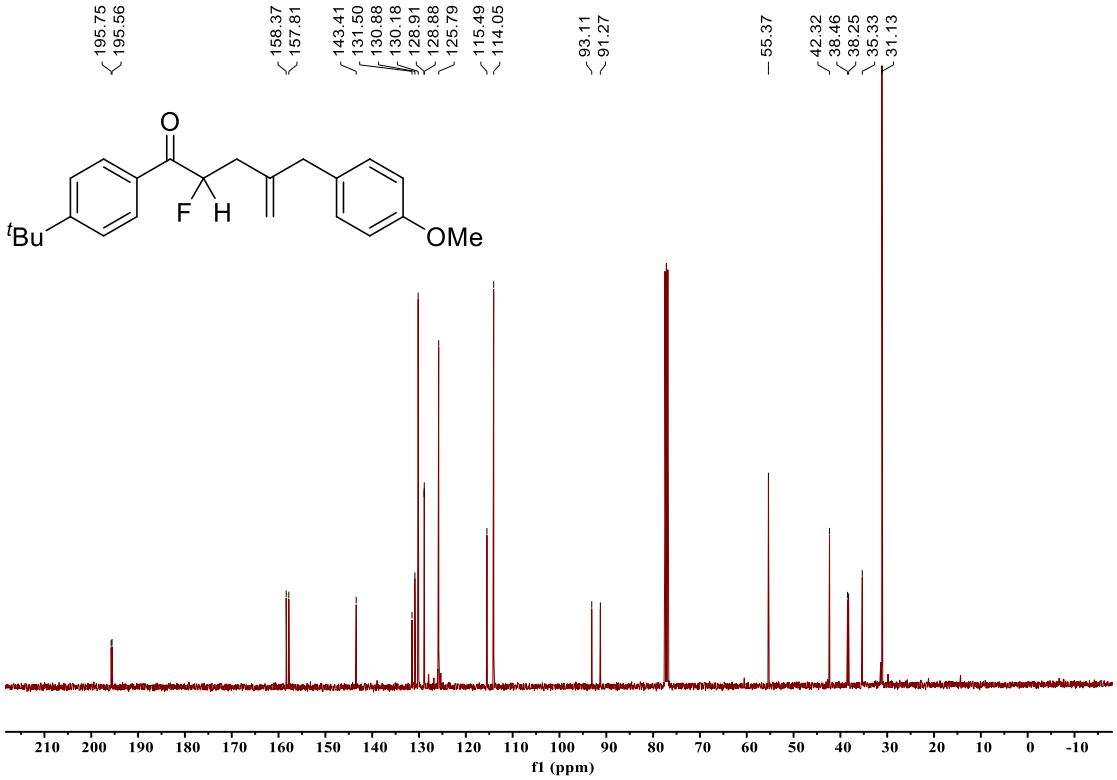
^{1}H-NMR of 21 (400 MHz, $CDCl_3$)



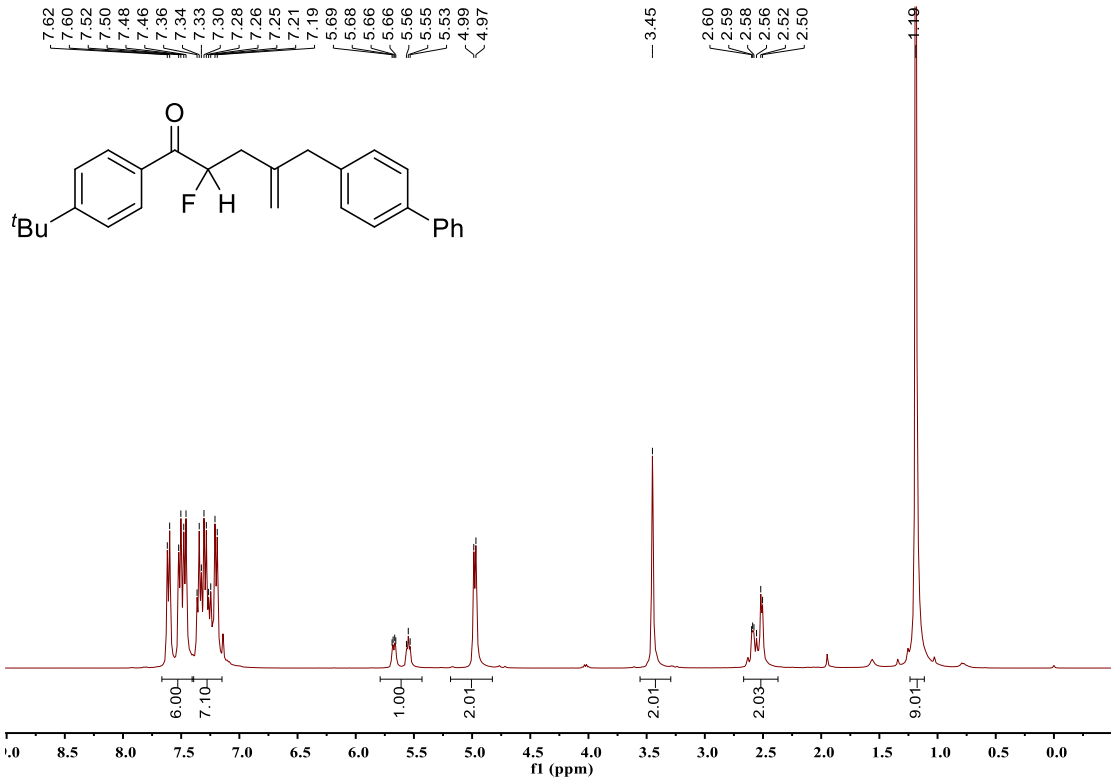
^{19}F NMR of 21 (376 MHz, $CDCl_3$)



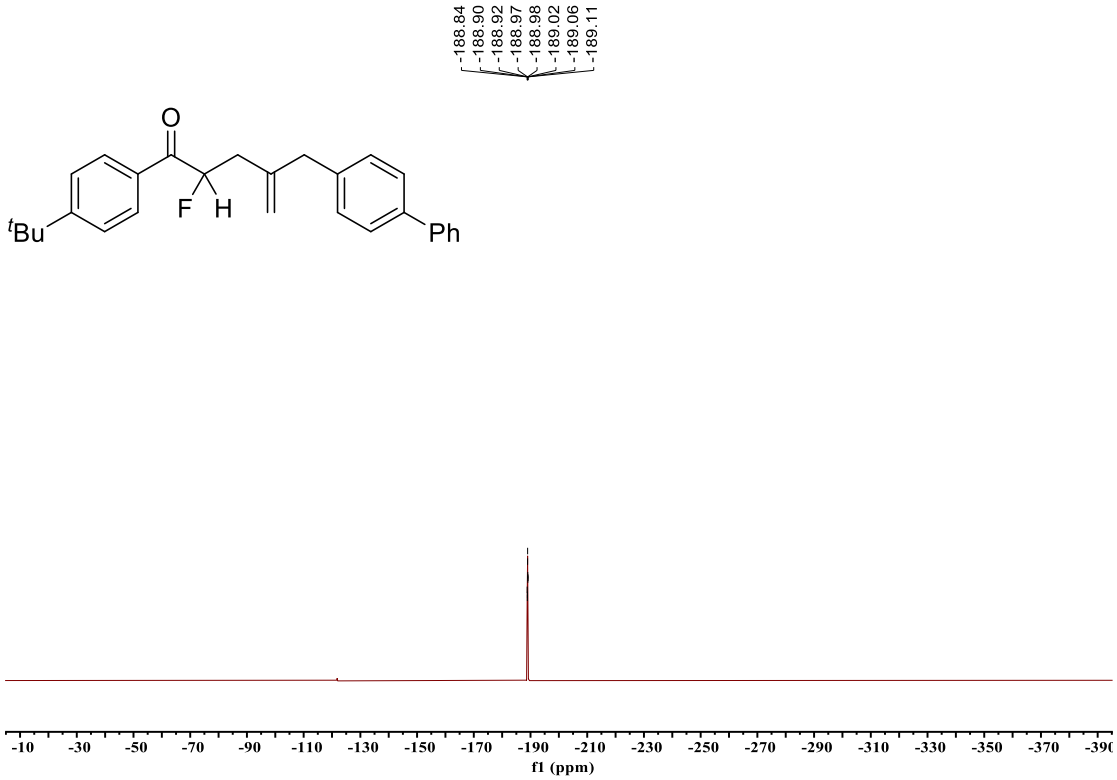
^{13}C-NMR of 21 (100 MHz, $CDCl_3$)



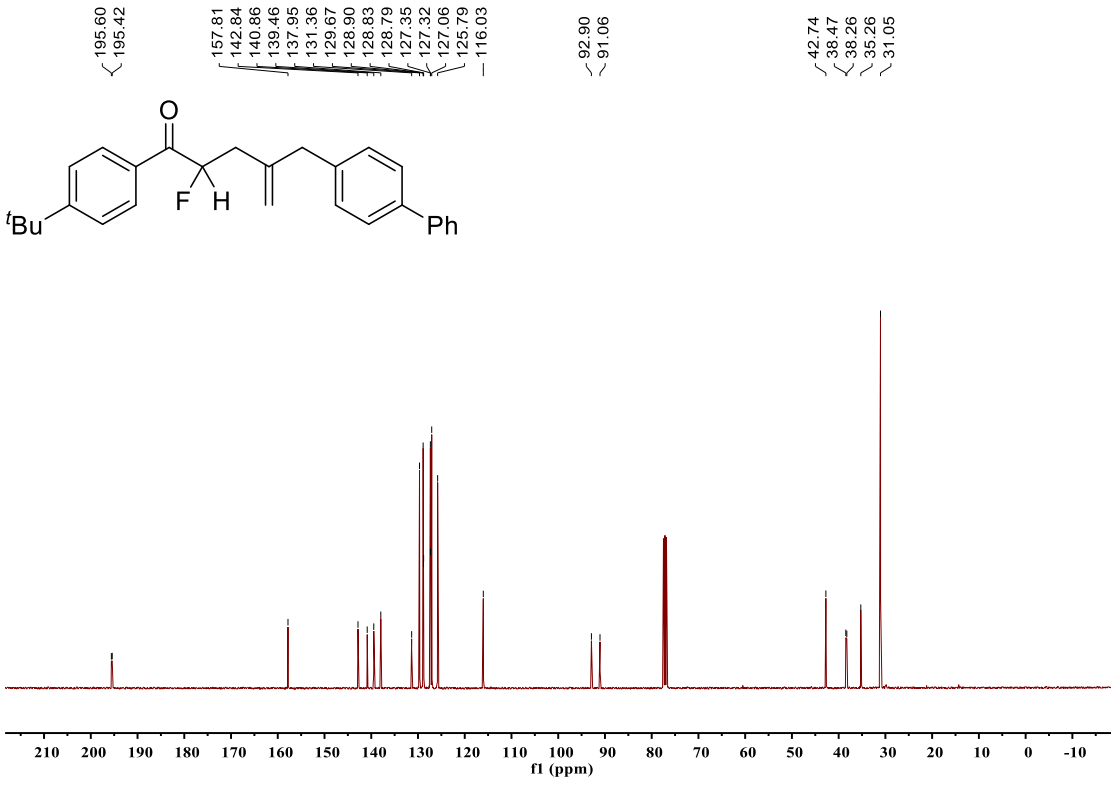
^{1}H-NMR of 22 (400 MHz, $CDCl_3$)



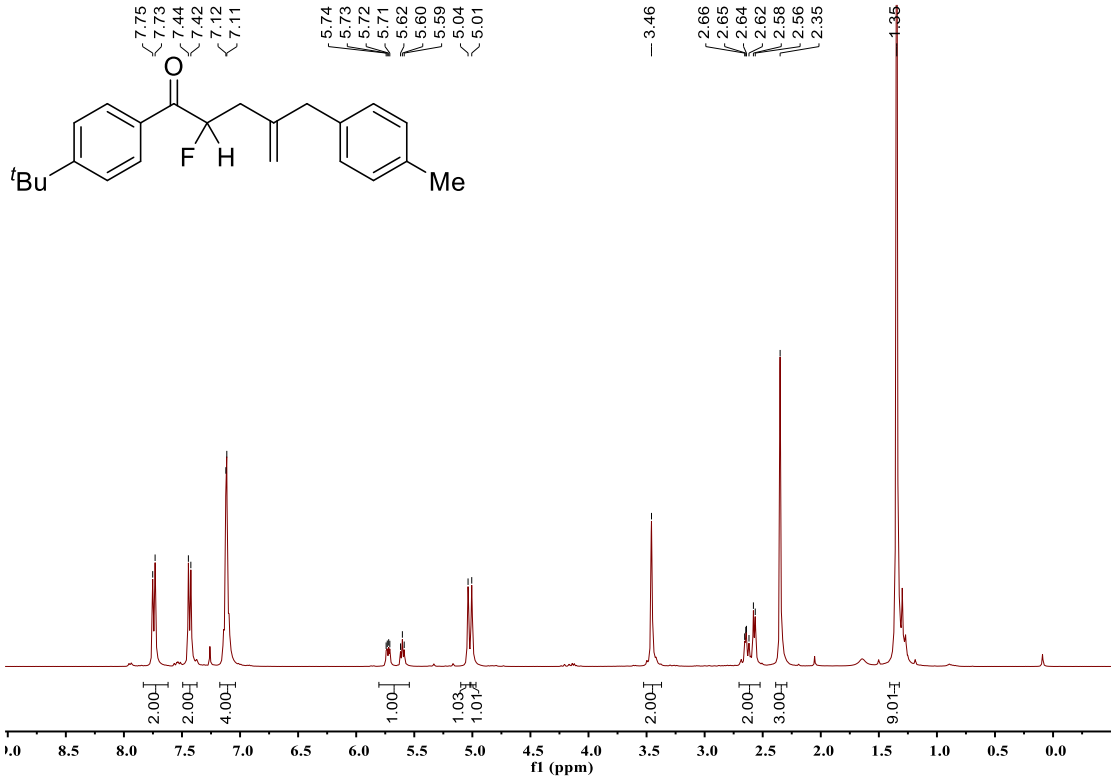
^{19}F NMR of 22 (376 MHz, $CDCl_3$)



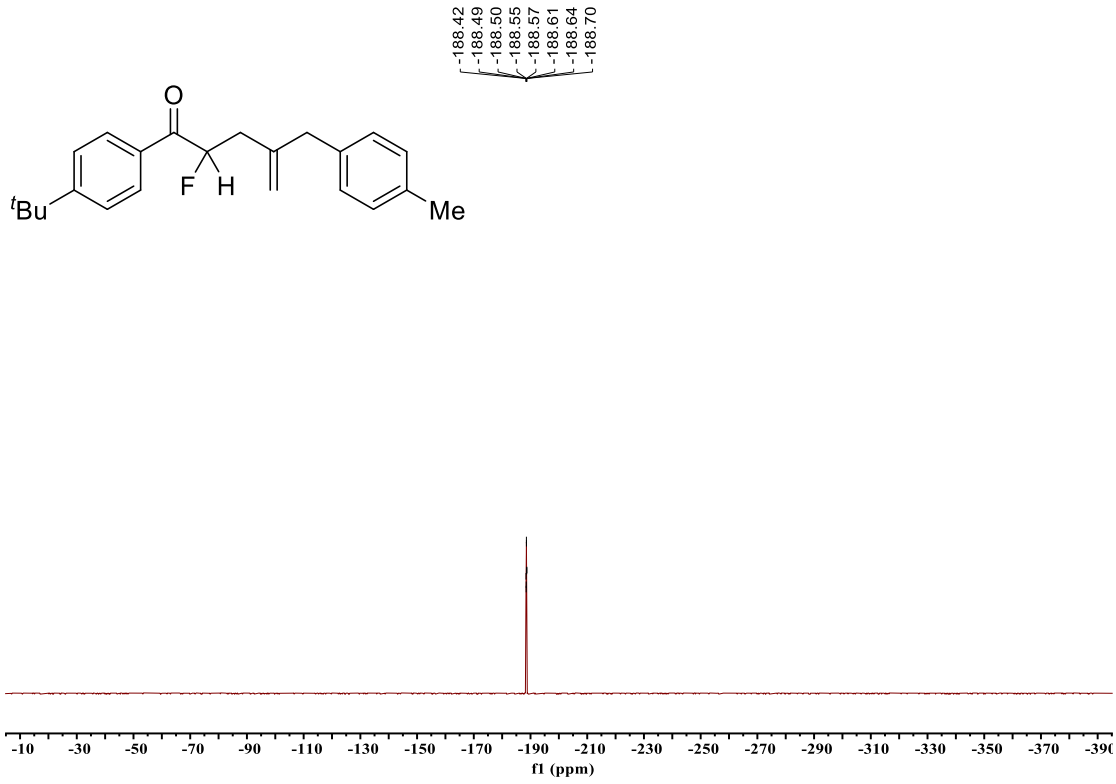
^{13}C-NMR of 22 (100 MHz, $CDCl_3$)



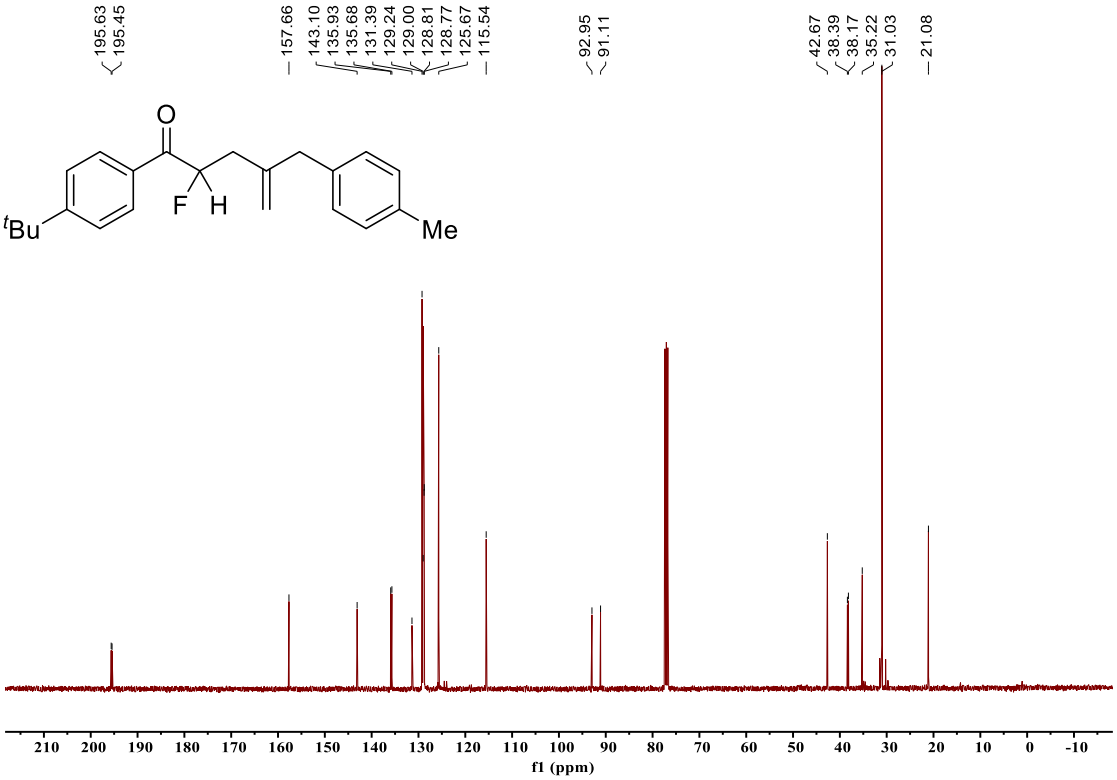
^{1}H-NMR of 23 (400 MHz, $CDCl_3$)



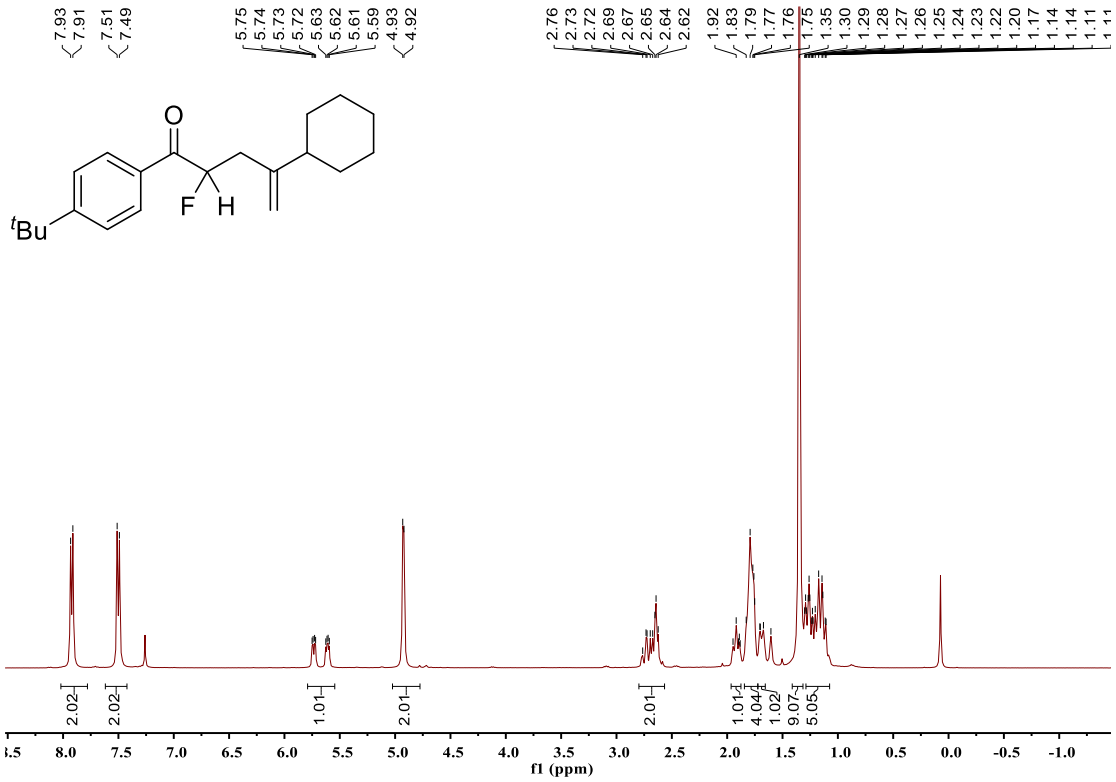
^{19}F NMR of 23 (376 MHz, $CDCl_3$)



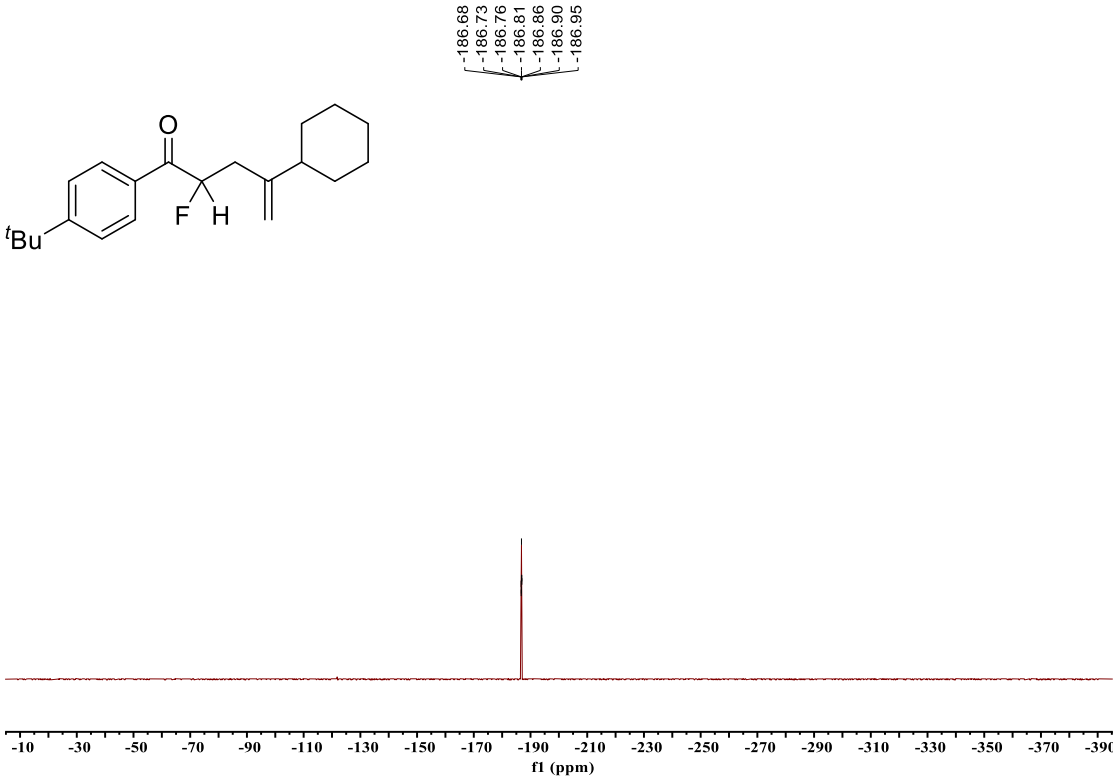
^{13}C-NMR of 23 (100 MHz, $CDCl_3$)



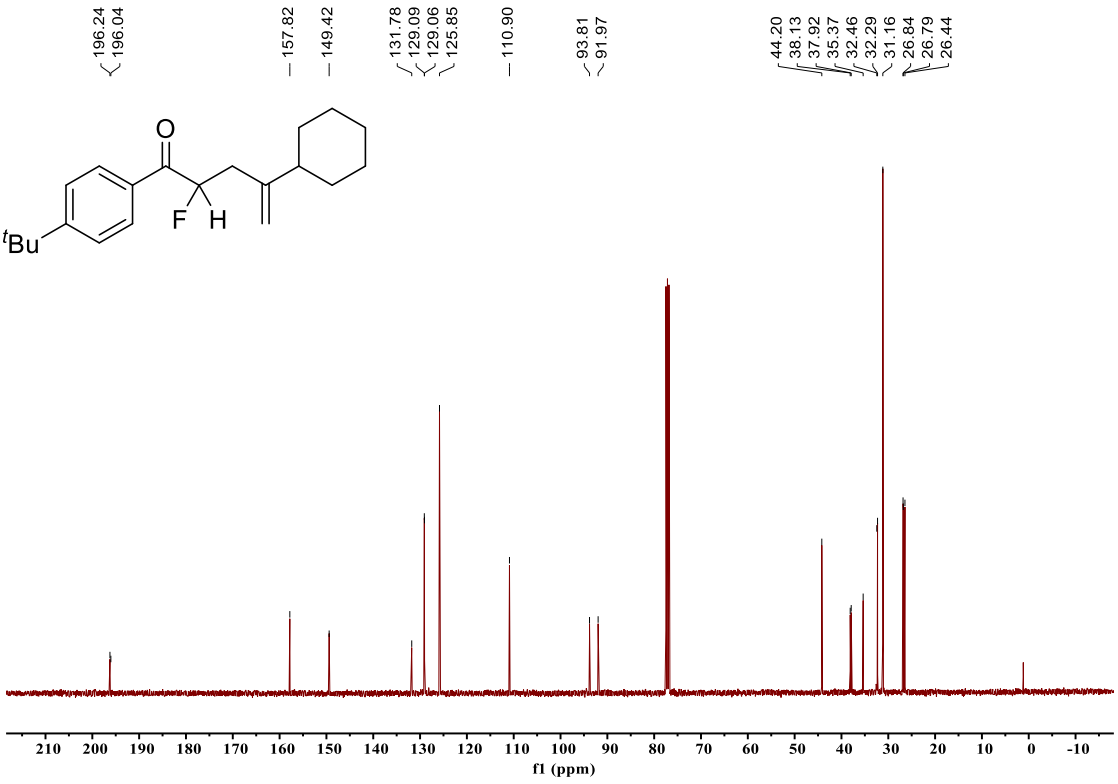
^{1}H-NMR of 24 (400 MHz, $CDCl_3$)



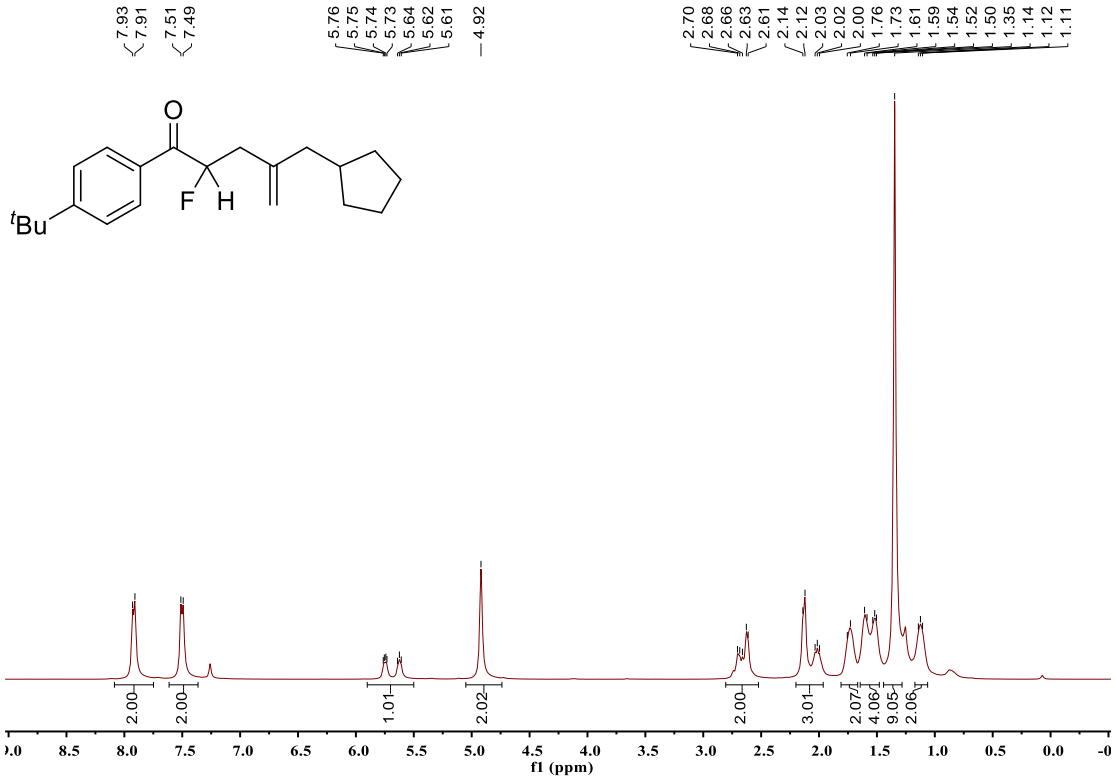
^{19}F NMR of 24 (376 MHz, $CDCl_3$)



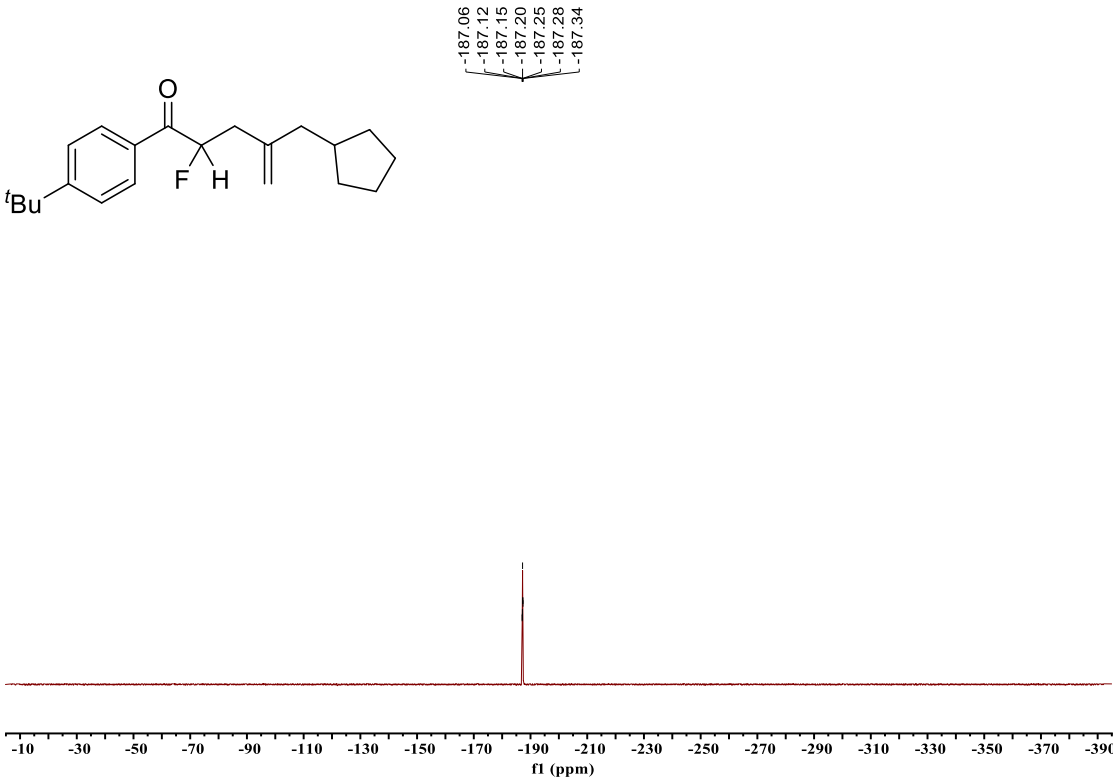
^{13}C-NMR of 24 (100 MHz, $CDCl_3$)



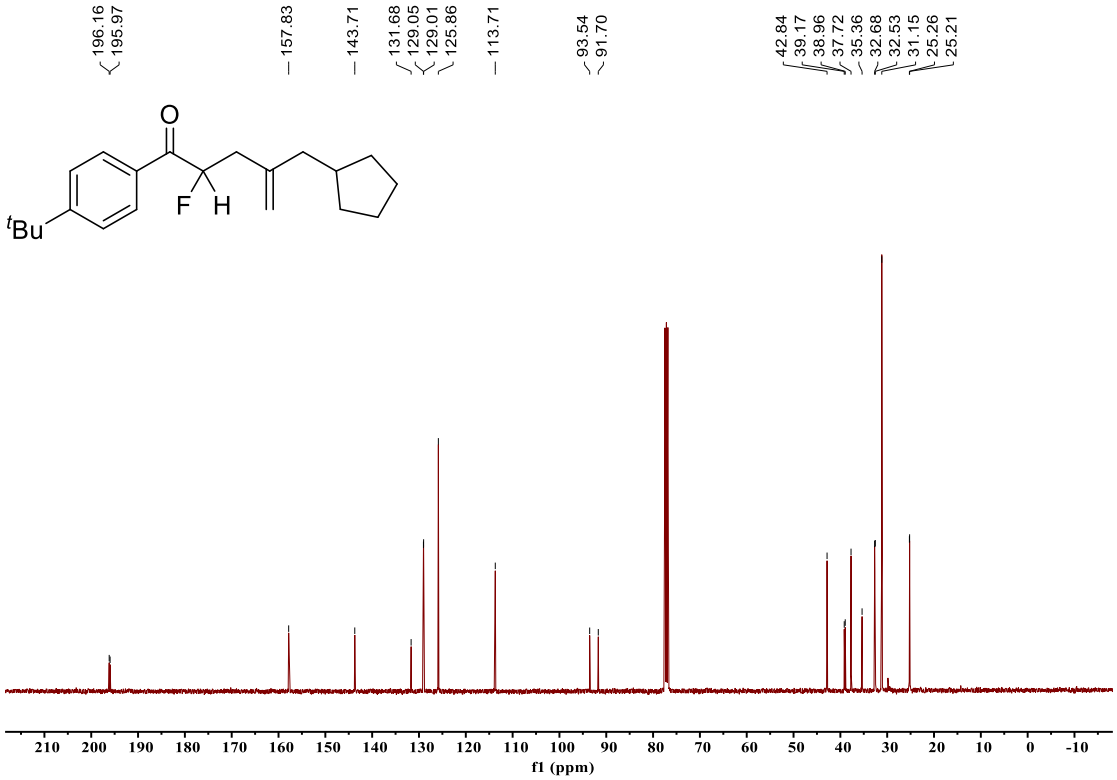
^{1}H-NMR of 25 (400 MHz, $CDCl_3$)



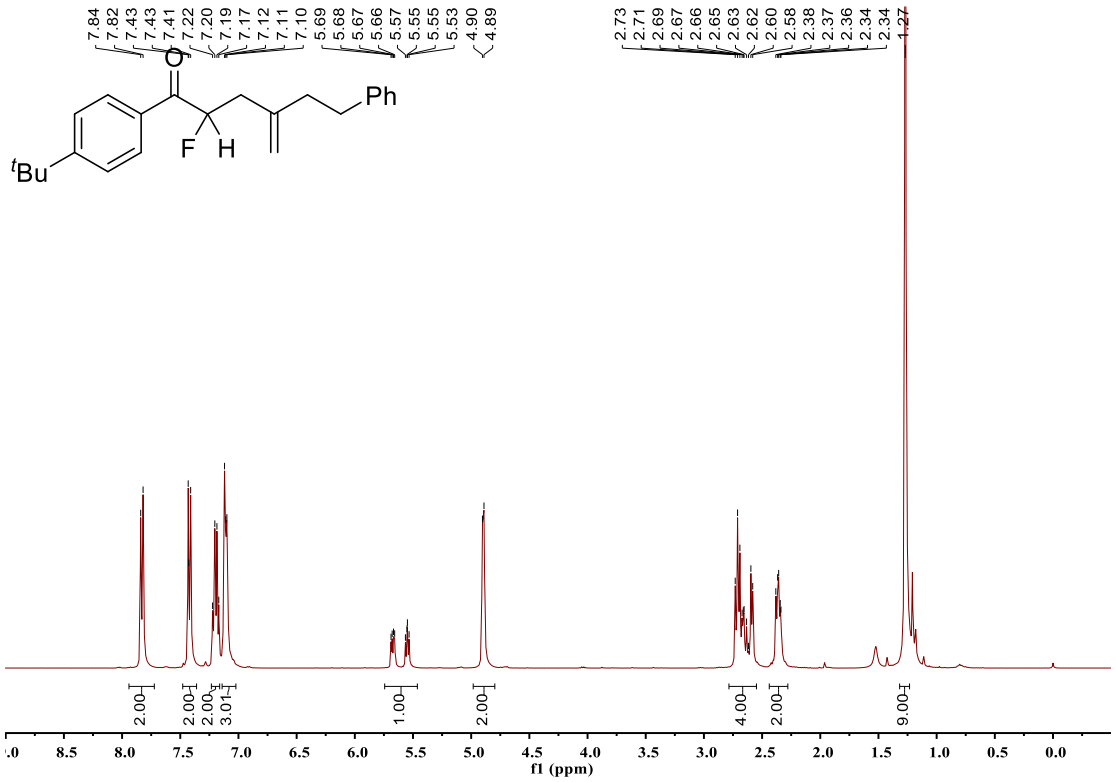
^{19}F NMR of 25 (376 MHz, $CDCl_3$)



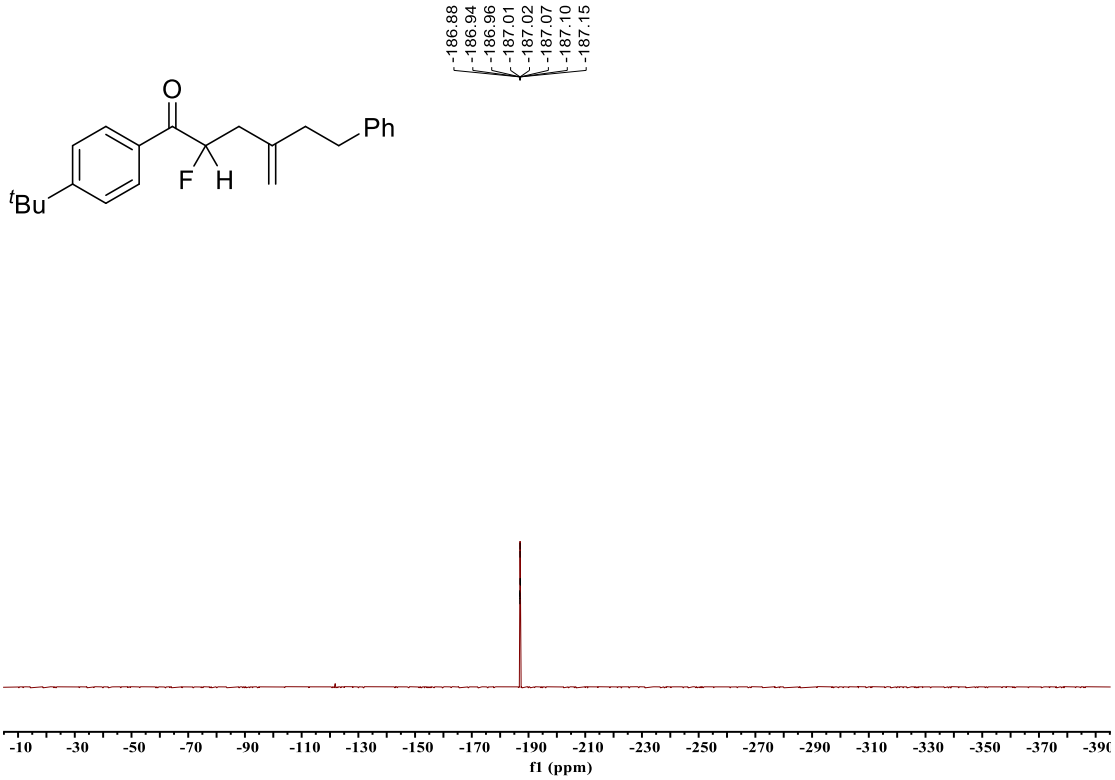
^{13}C-NMR of 25 (100 MHz, $CDCl_3$)



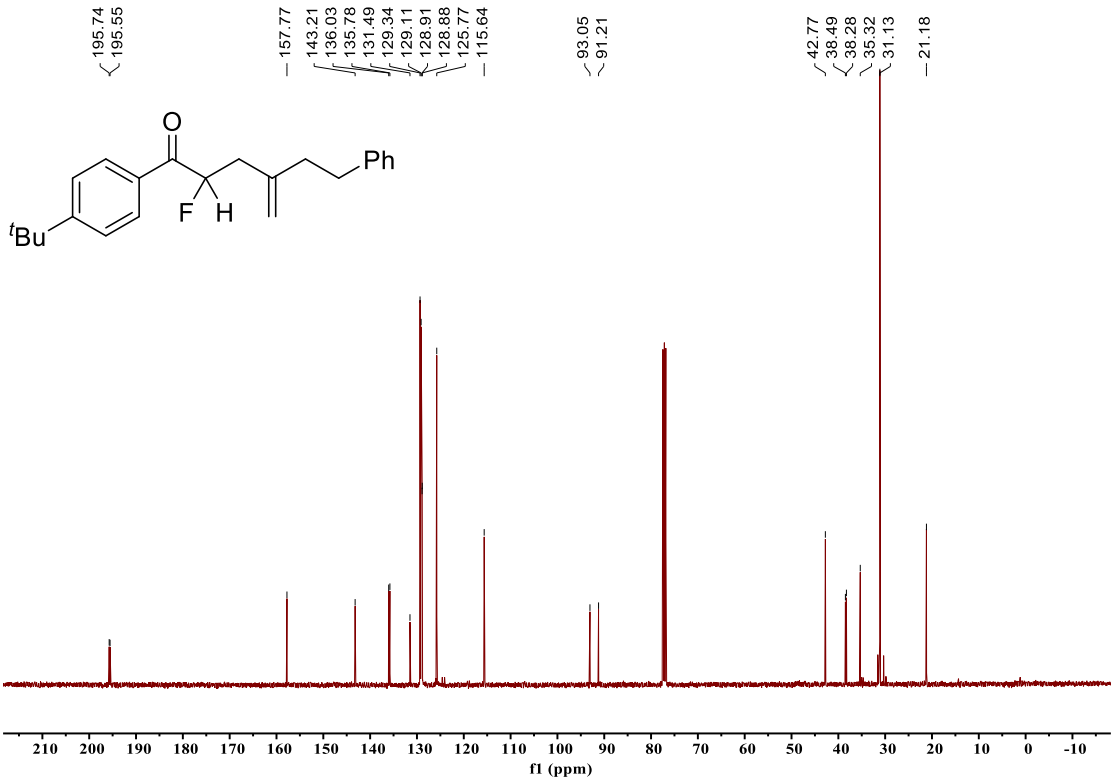
^{1}H-NMR of 26 (400 MHz, $CDCl_3$)



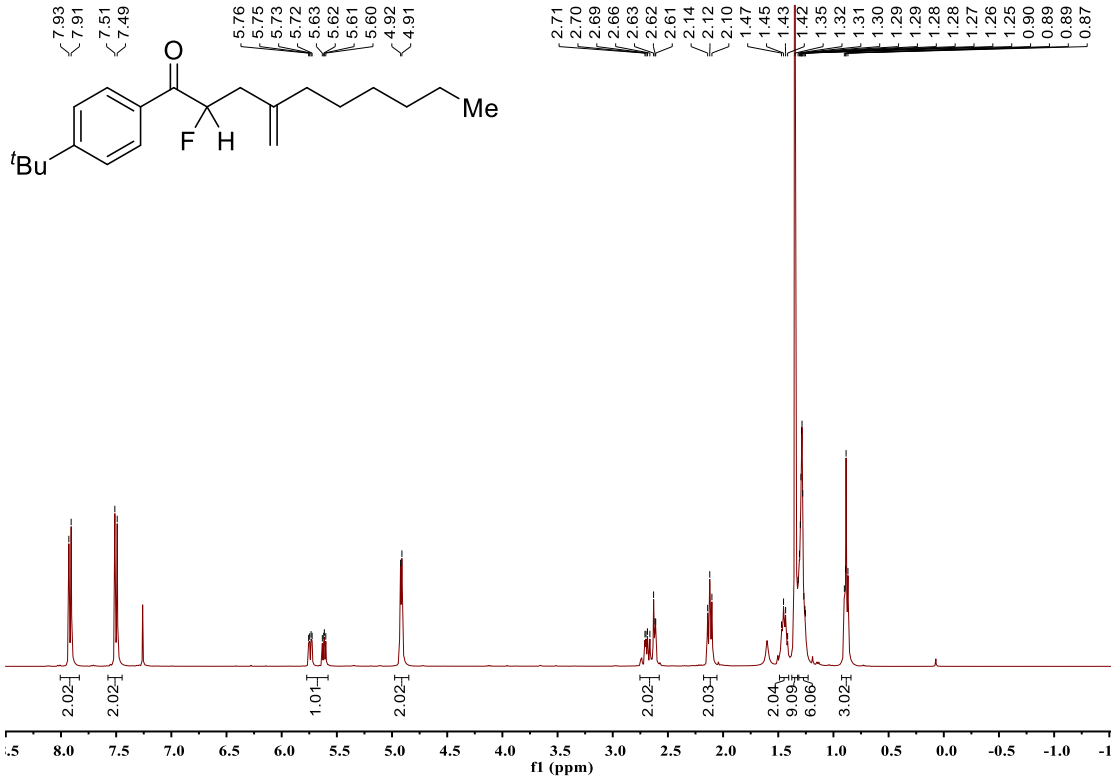
^{19}F NMR of 26 (376 MHz, $CDCl_3$)



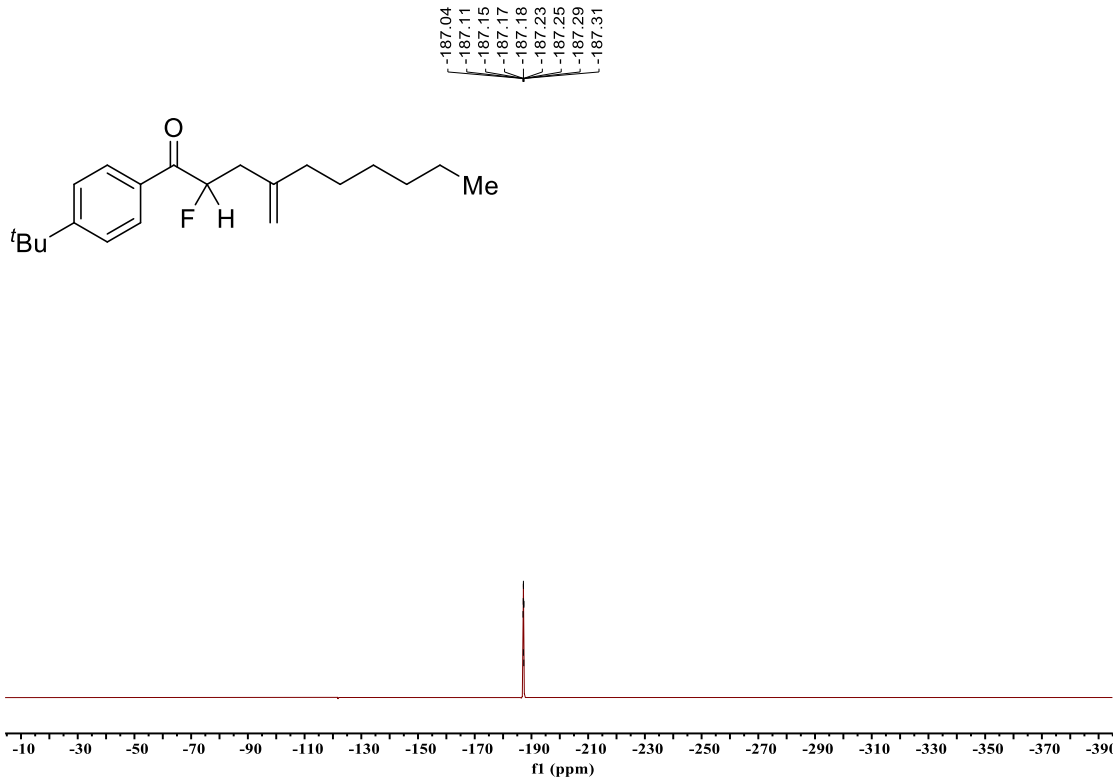
^{13}C-NMR of 26 (100 MHz, $CDCl_3$)



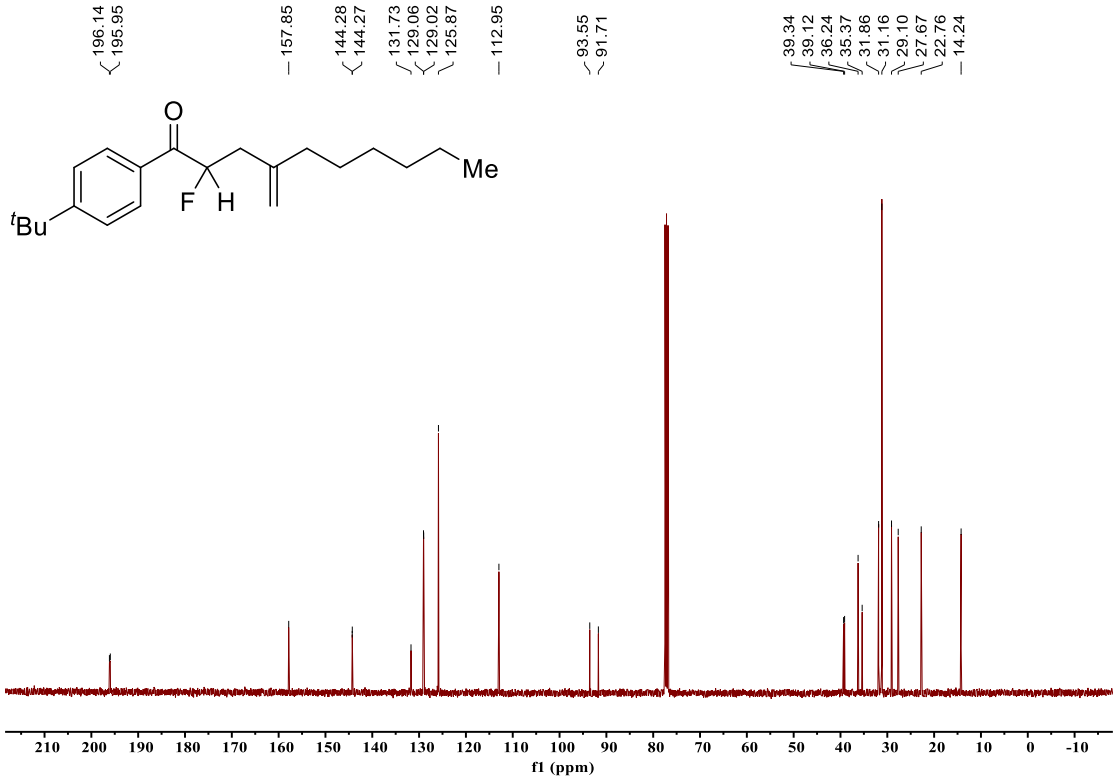
^{1}H-NMR of 27 (400 MHz, $CDCl_3$)



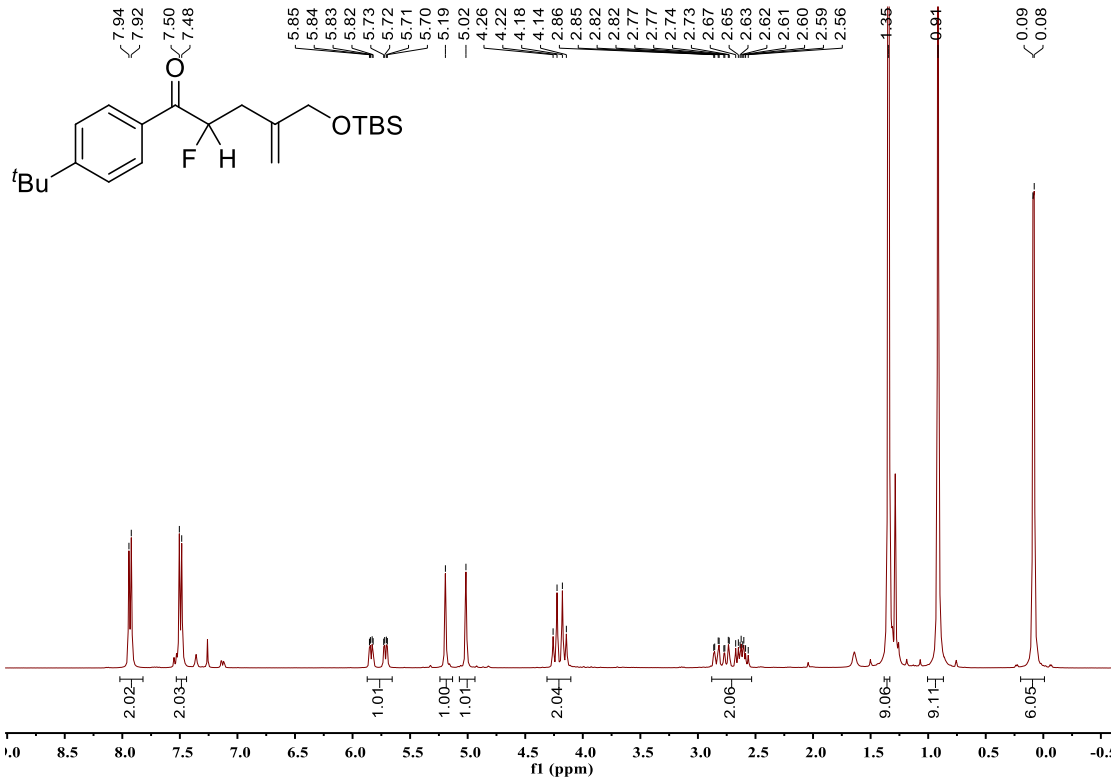
^{19}F NMR of 27 (376 MHz, $CDCl_3$)



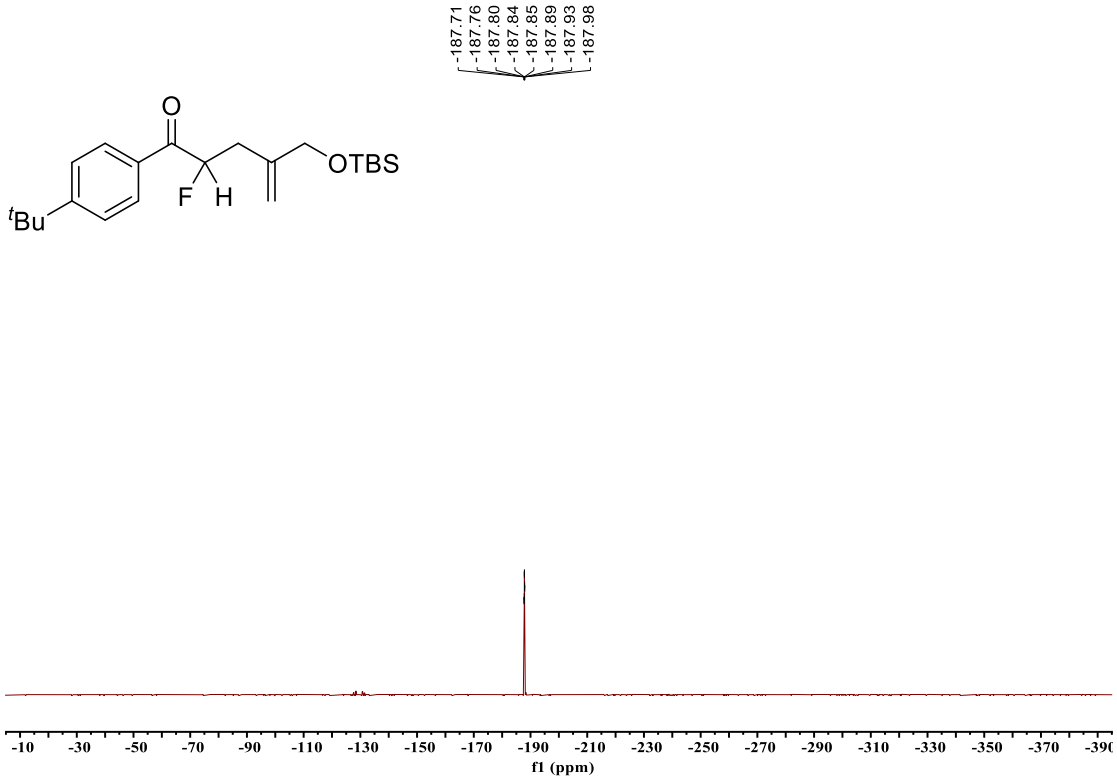
^{13}C-NMR of 27 (100 MHz, $CDCl_3$)



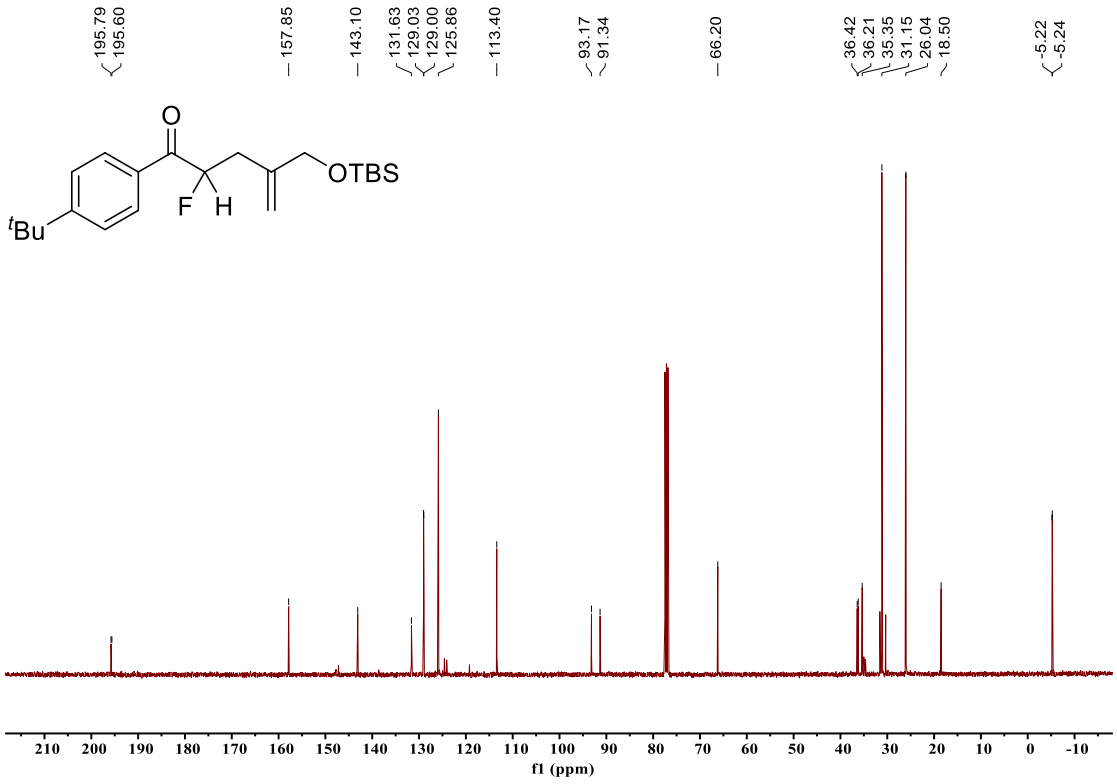
^{1}H-NMR of 28 (400 MHz, $CDCl_3$)



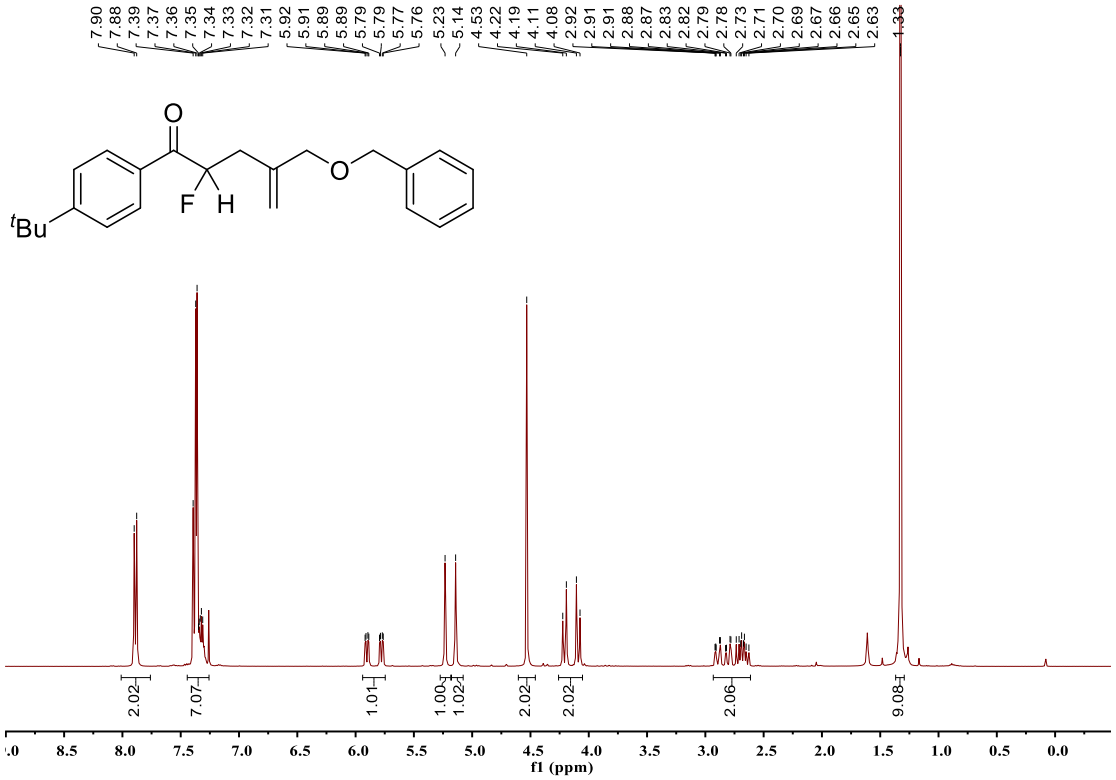
^{19}F NMR of 28 (376 MHz, $CDCl_3$)



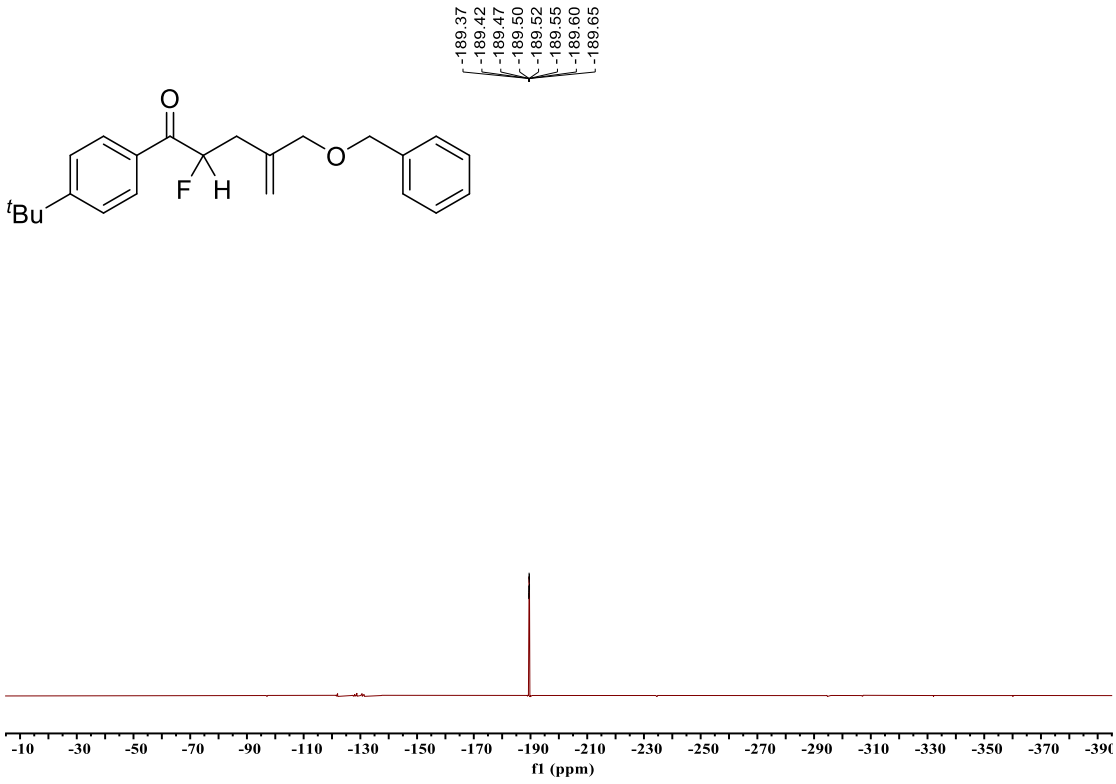
^{13}C-NMR of 28 (100 MHz, $CDCl_3$)



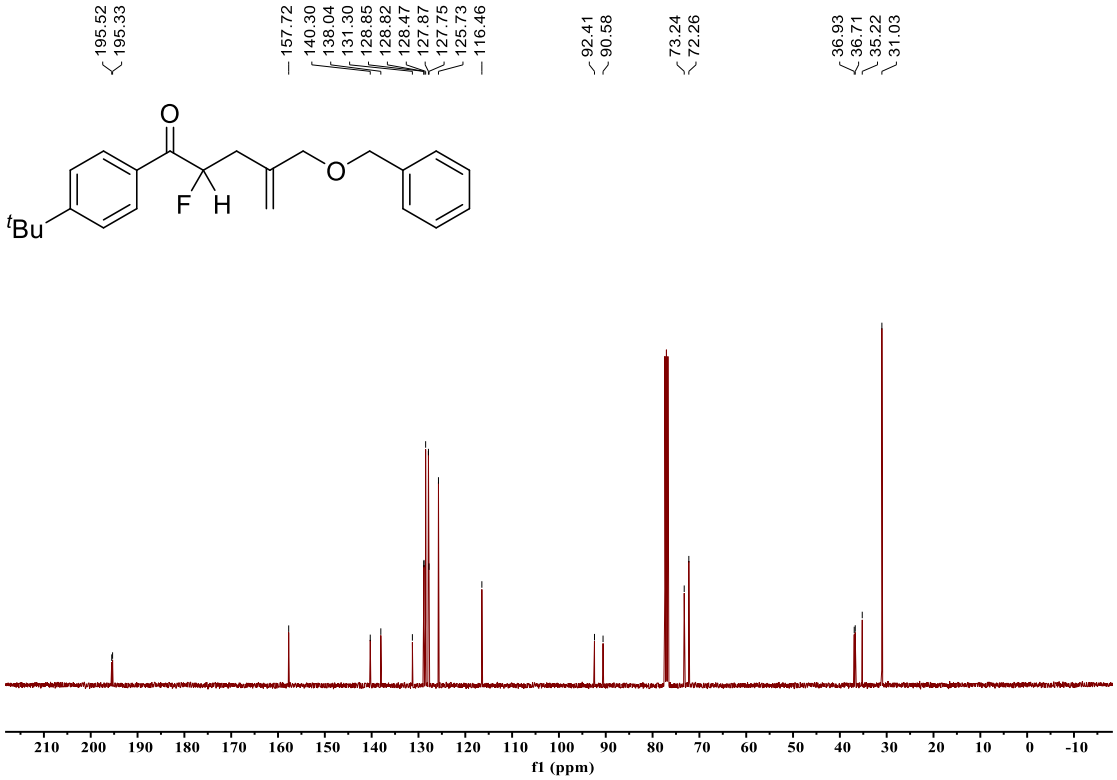
^{1}H-NMR of 29 (400 MHz, $CDCl_3$)



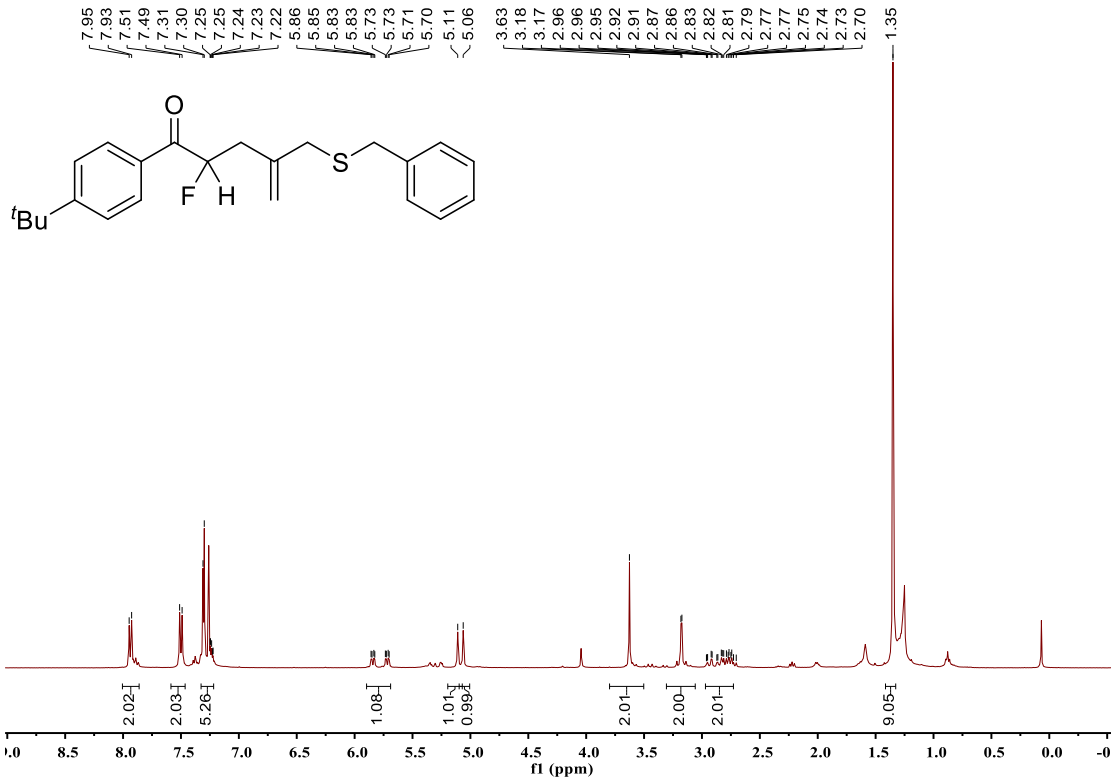
^{19}F NMR of 29 (376 MHz, $CDCl_3$)



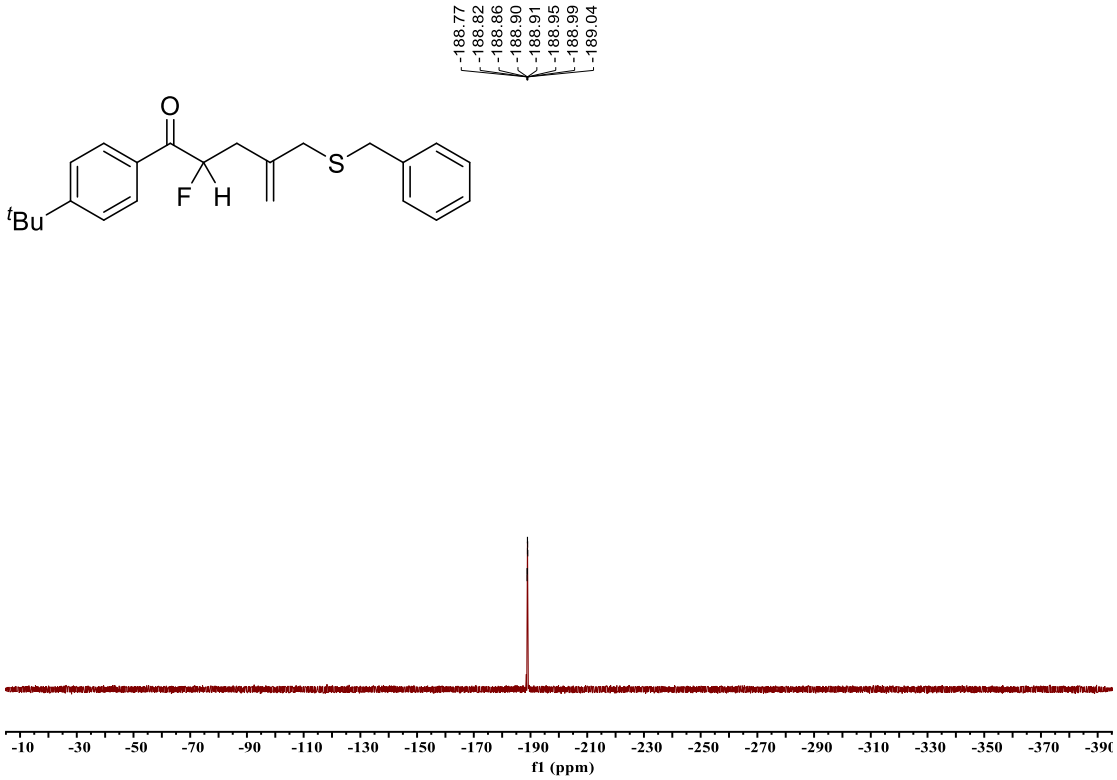
^{13}C-NMR of 29 (100 MHz, $CDCl_3$)



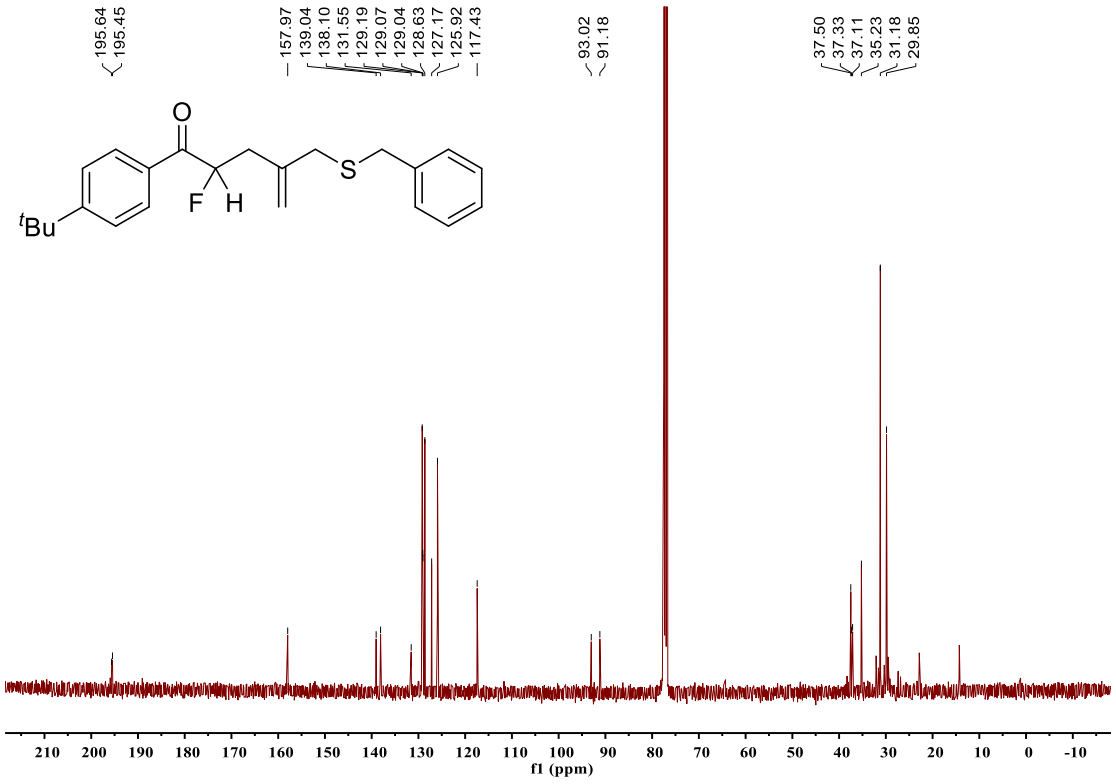
^{1}H-NMR of 30 (400 MHz, $CDCl_3$)



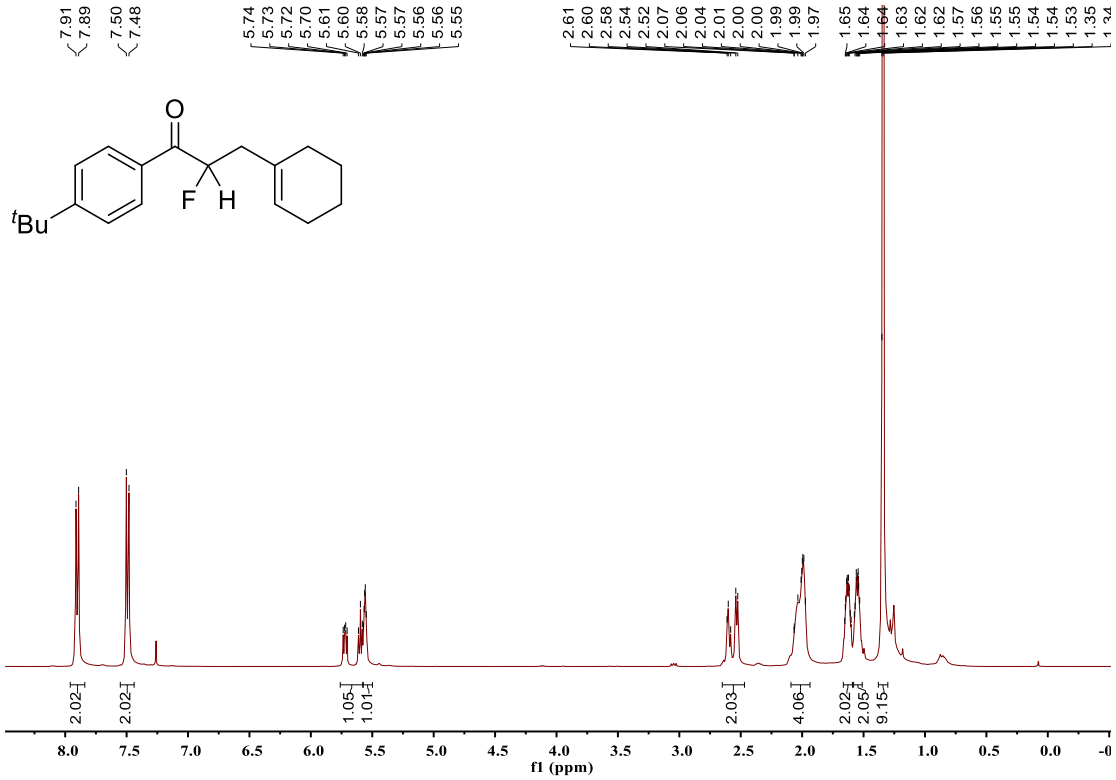
^{19}F NMR of 30 (376 MHz, $CDCl_3$)



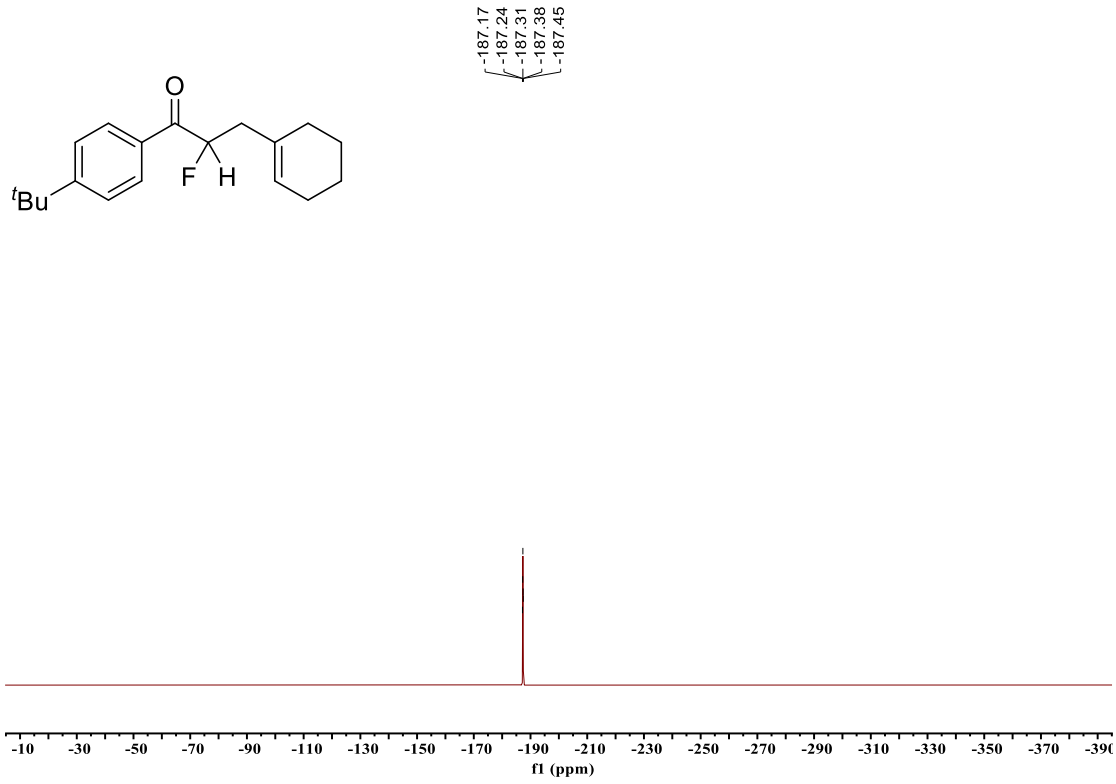
^{13}C-NMR of 30 (100 MHz, $CDCl_3$)



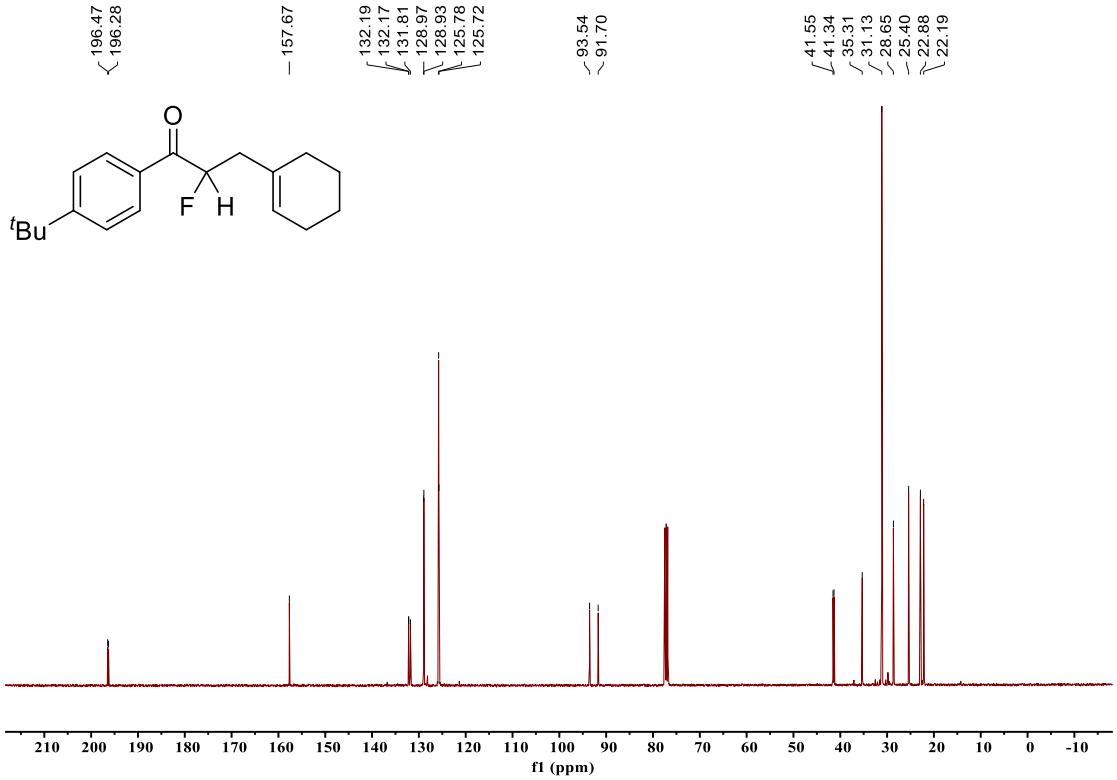
^{1}H-NMR of 31 (400 MHz, $CDCl_3$)



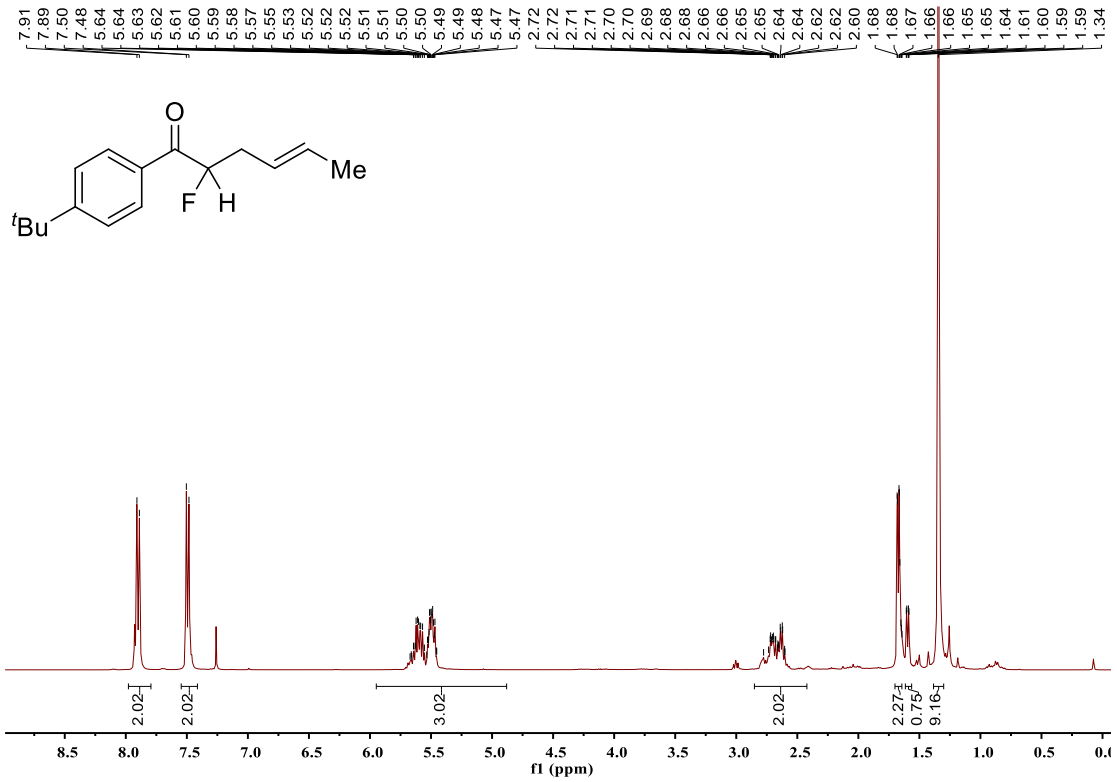
^{19}F NMR of 31 (376 MHz, $CDCl_3$)



^{13}C-NMR of 31 (100 MHz, $CDCl_3$)



^{1}H-NMR of 32 (400 MHz, $CDCl_3$)



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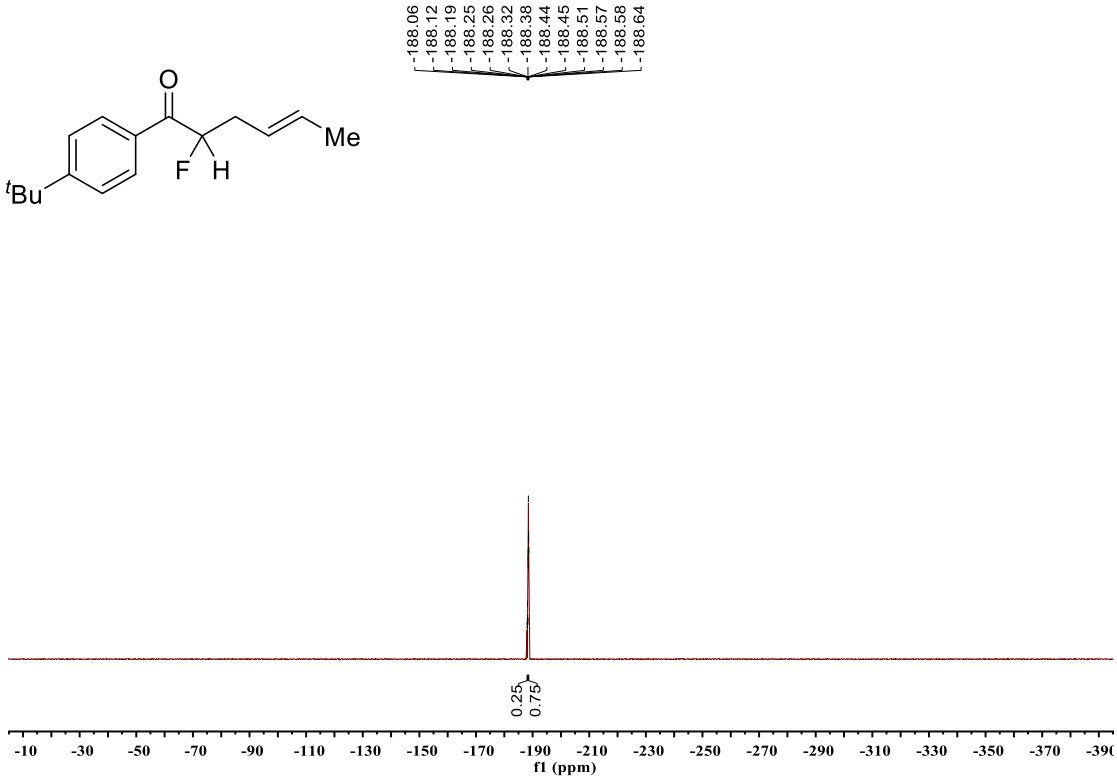
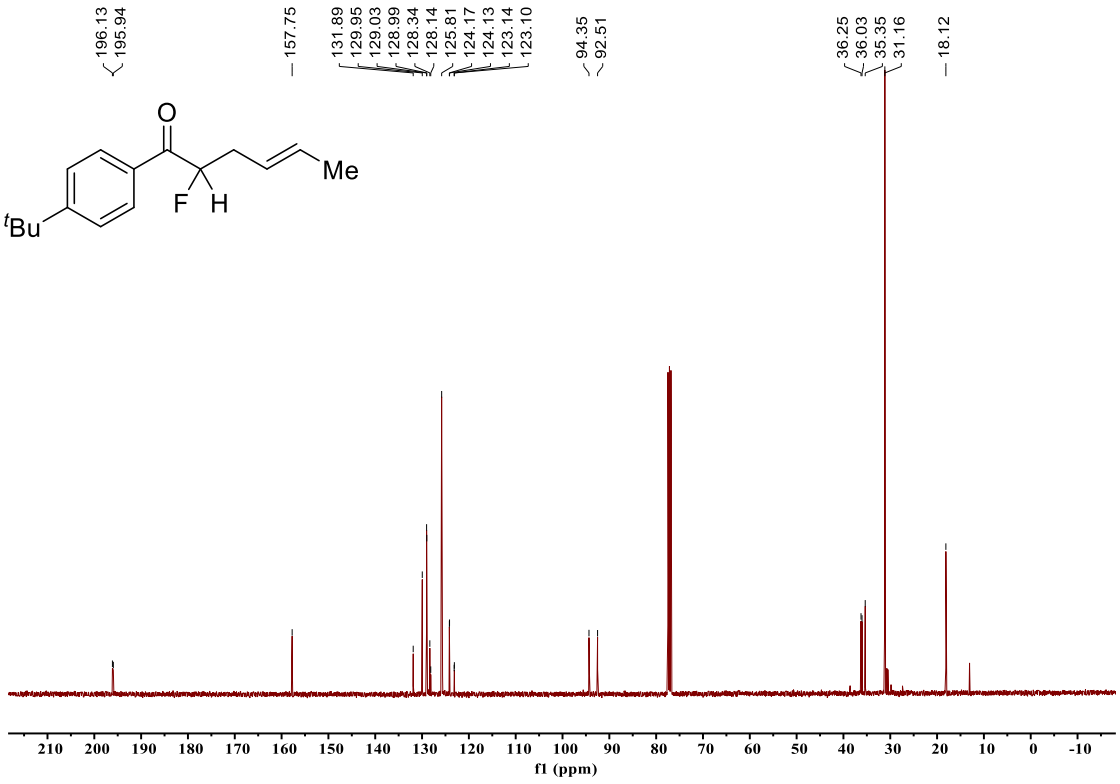
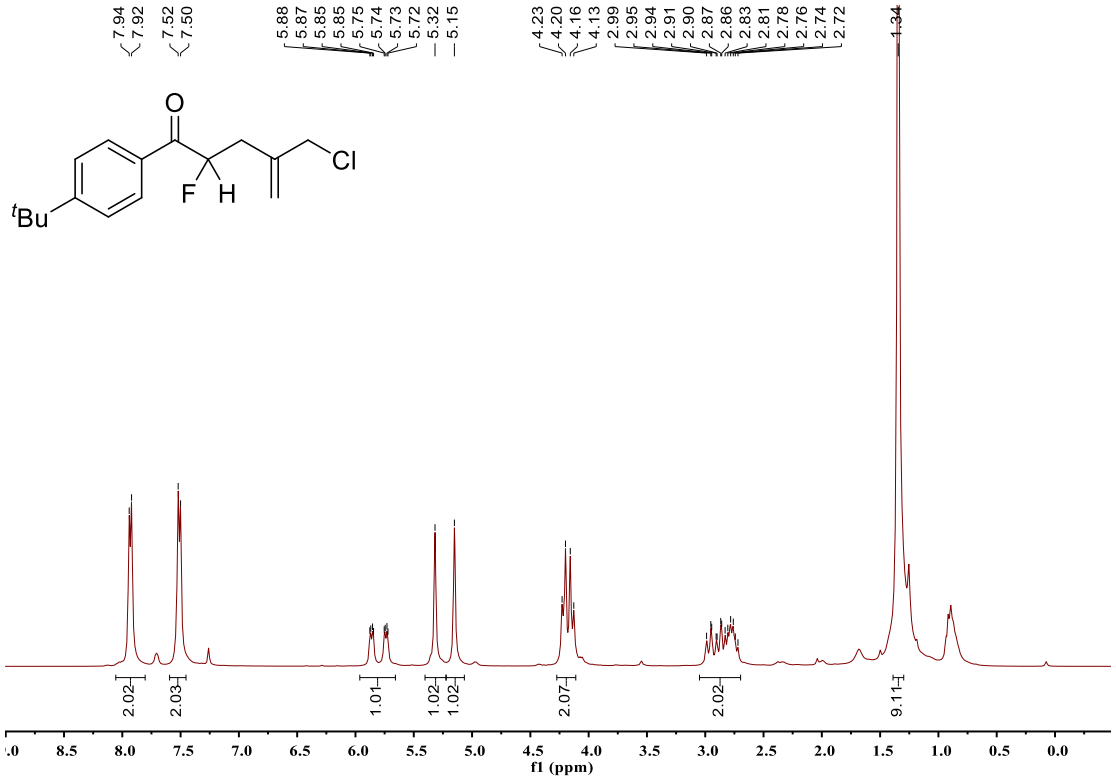


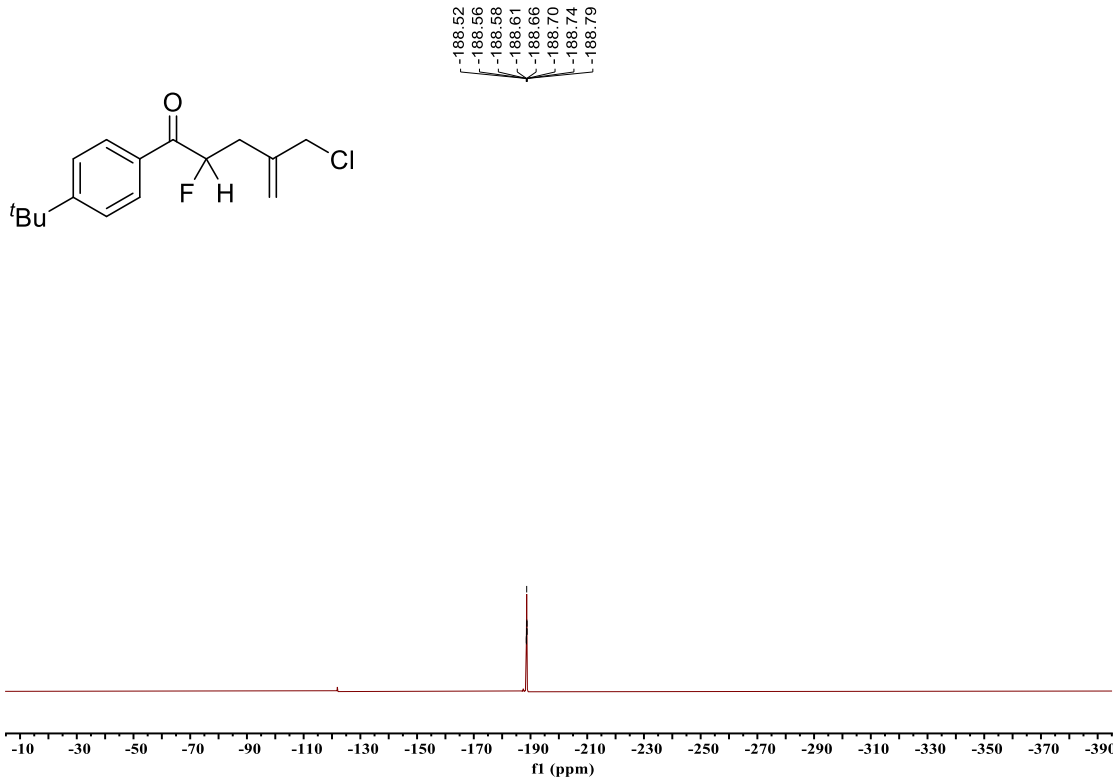
^{13}C-NMR of 32 (100 MHz, $CDCl_3$)



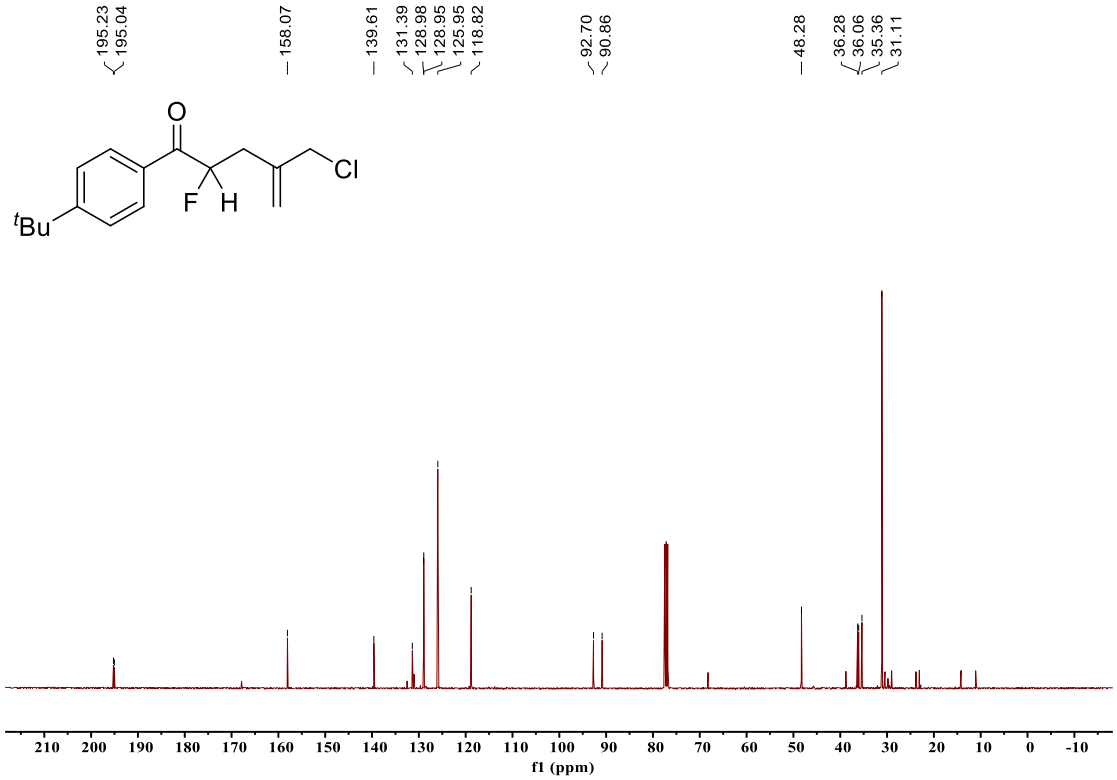
^{1}H-NMR of 33 (400 MHz, $CDCl_3$)



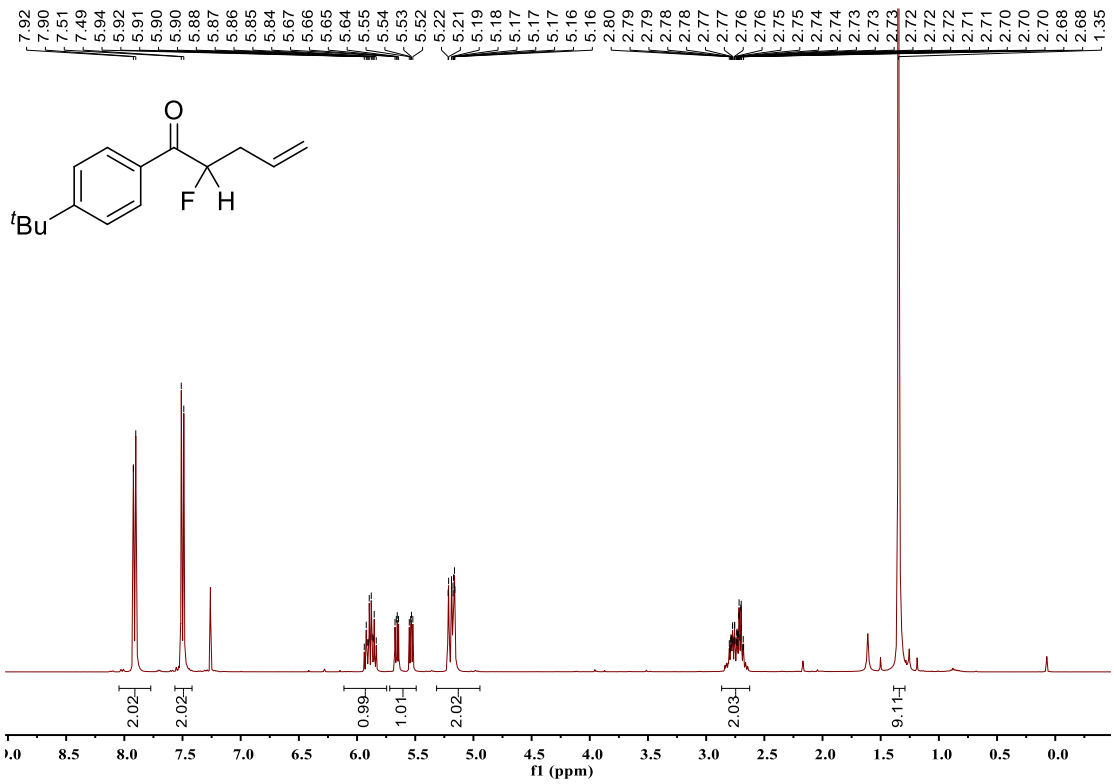
^{19}F NMR of 33 (376 MHz, $CDCl_3$)



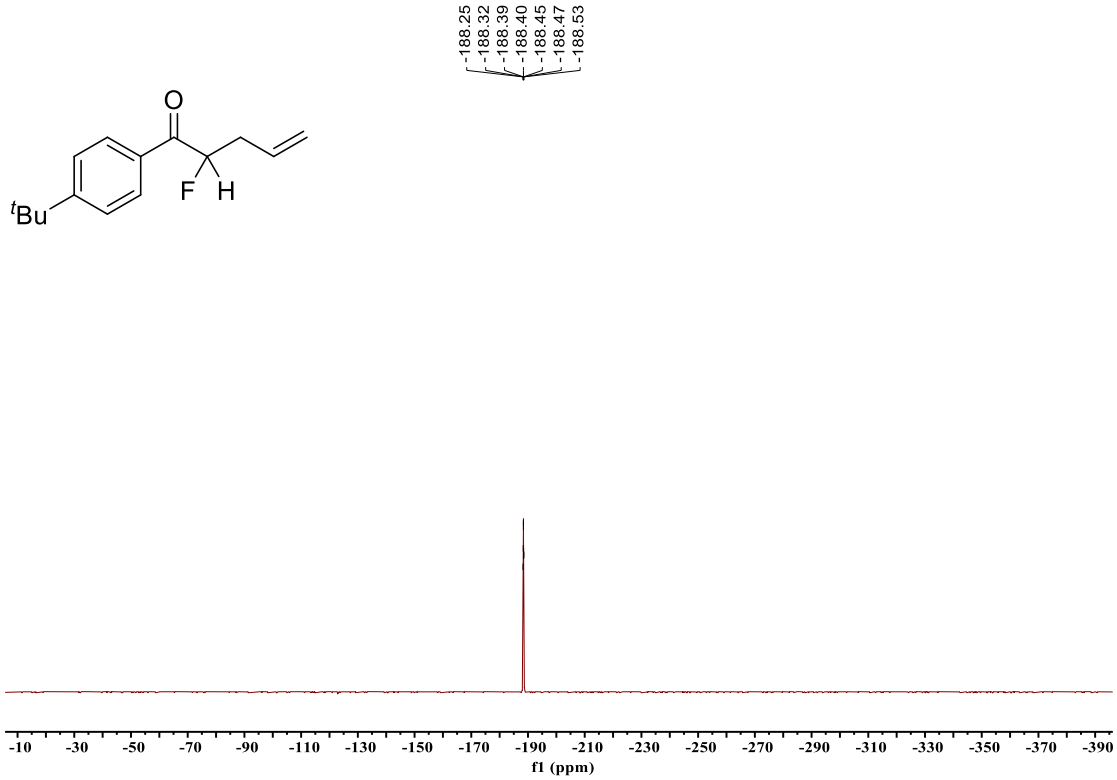
^{13}C-NMR of 33 (100 MHz, $CDCl_3$)



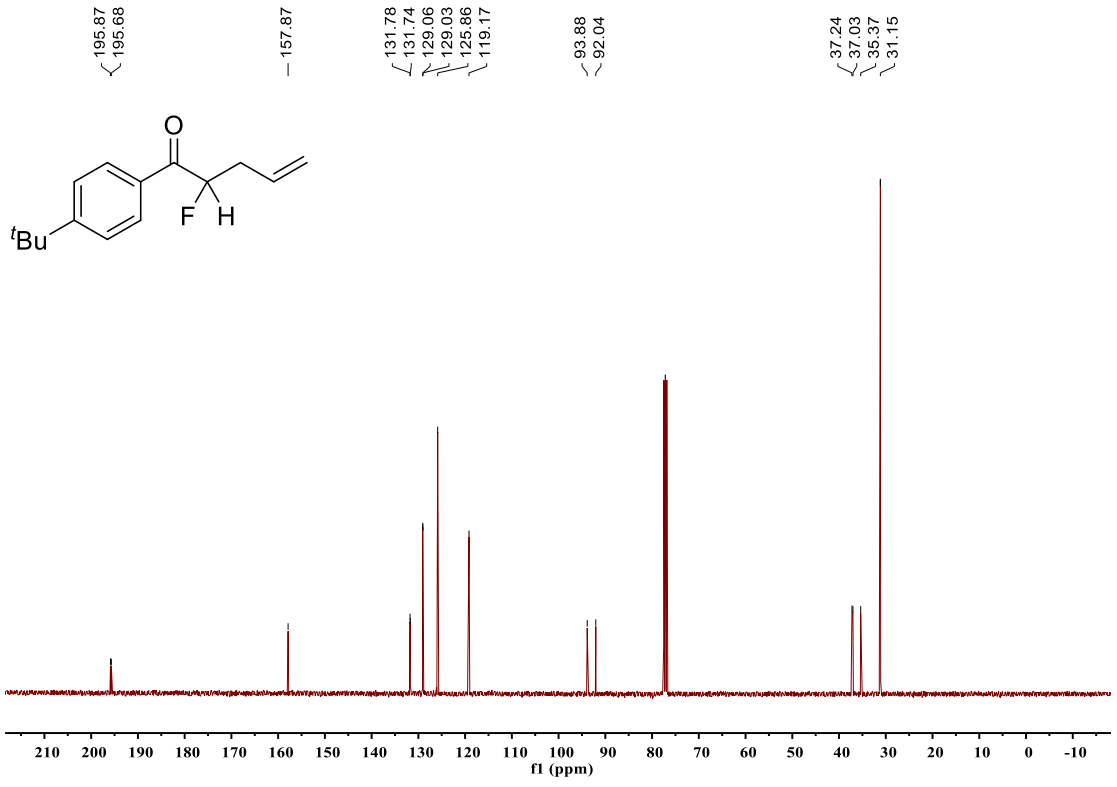
^{1}H-NMR of 34 (400 MHz, $CDCl_3$)



^{19}F NMR of 34 (376 MHz, $CDCl_3$)



^{13}C-NMR of 34 (100 MHz, $CDCl_3$)



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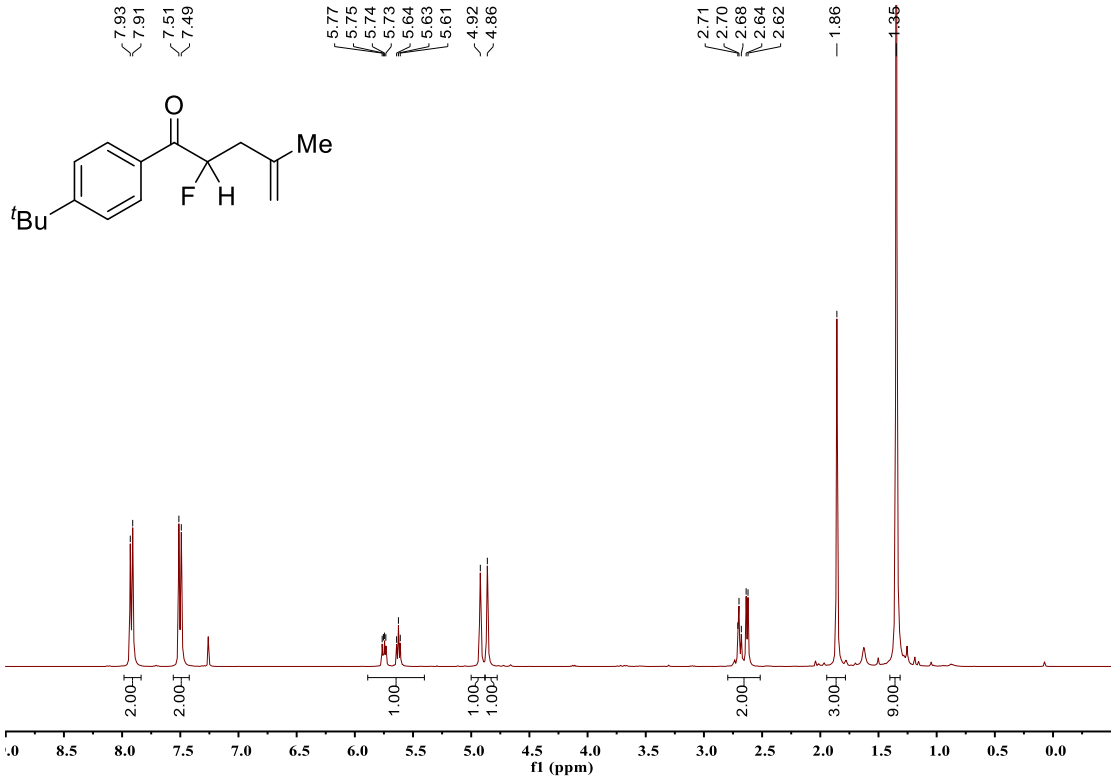

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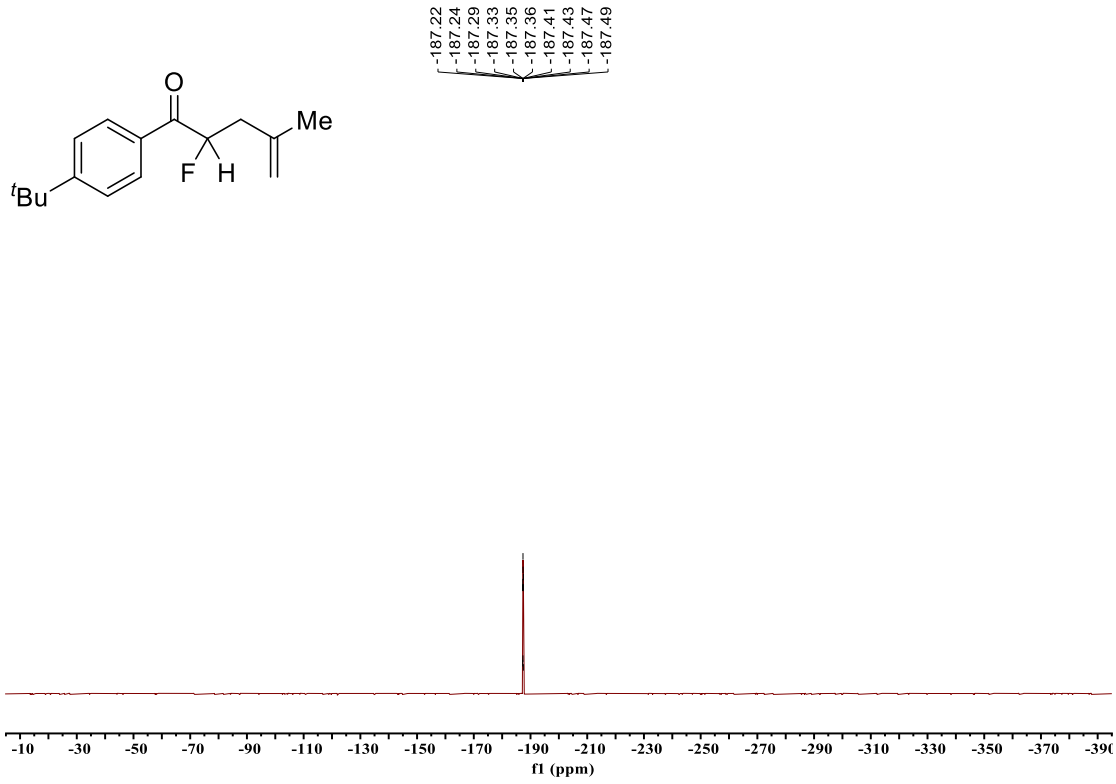
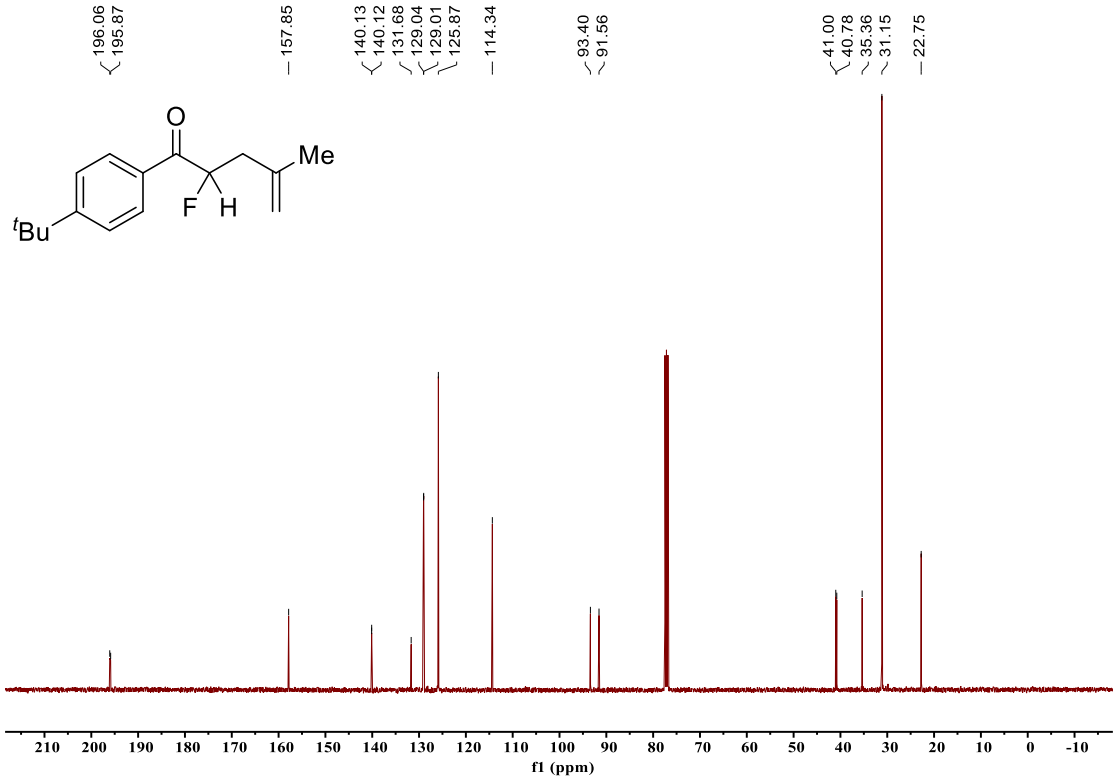
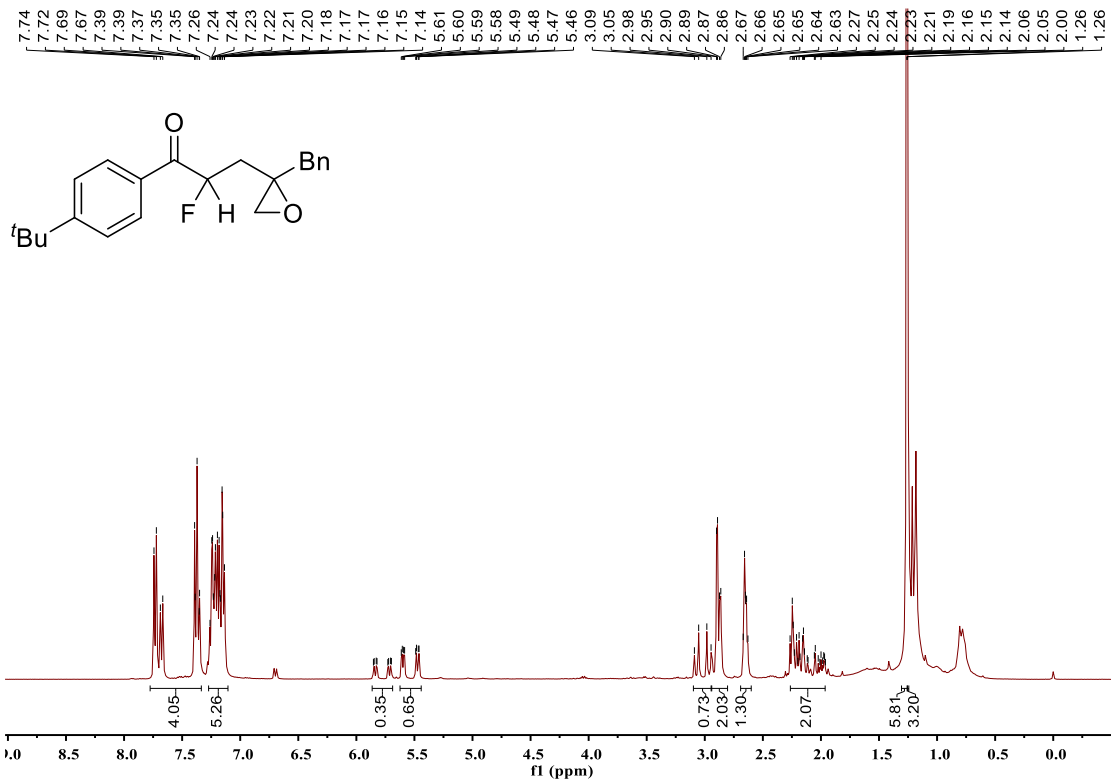


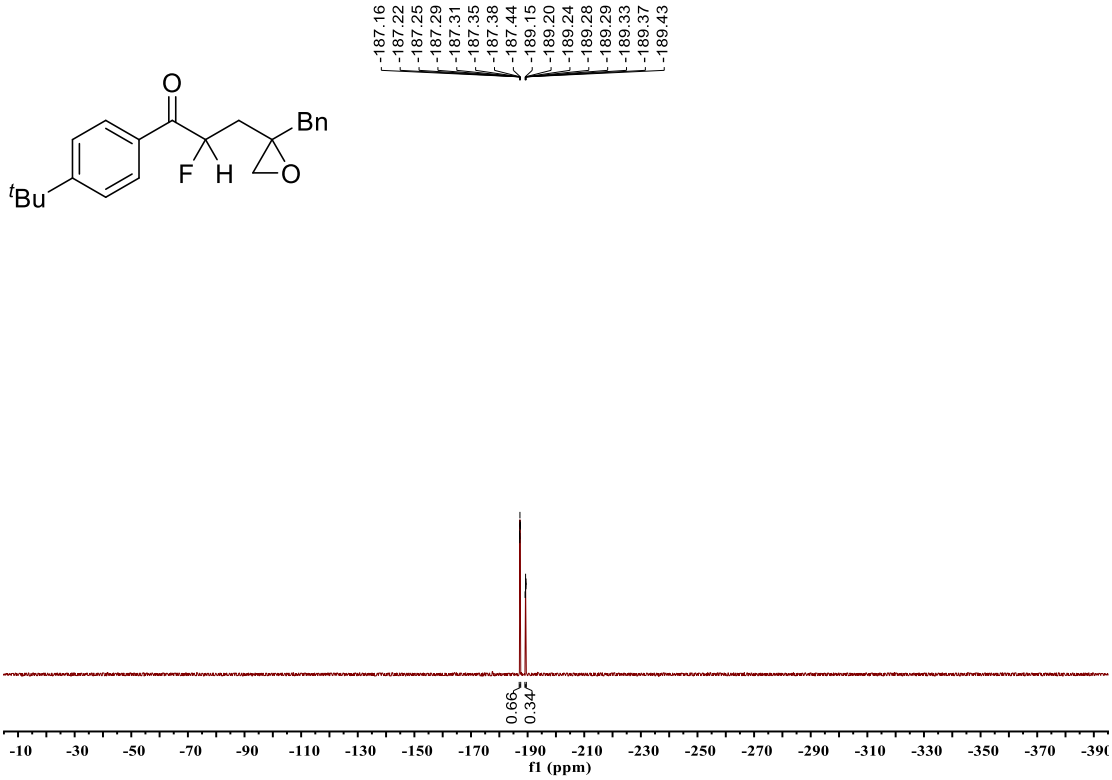
^{13}C-NMR of 35 (100 MHz, $CDCl_3$)



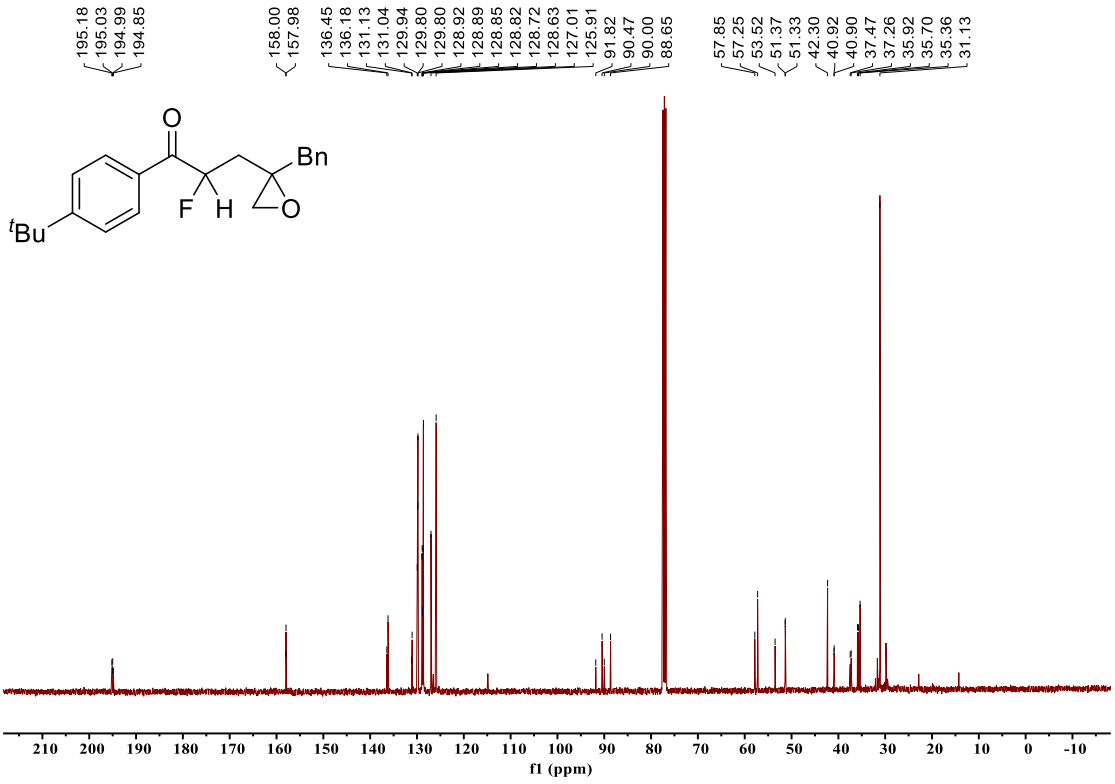
^{1}H-NMR of 36 (400 MHz, $CDCl_3$)



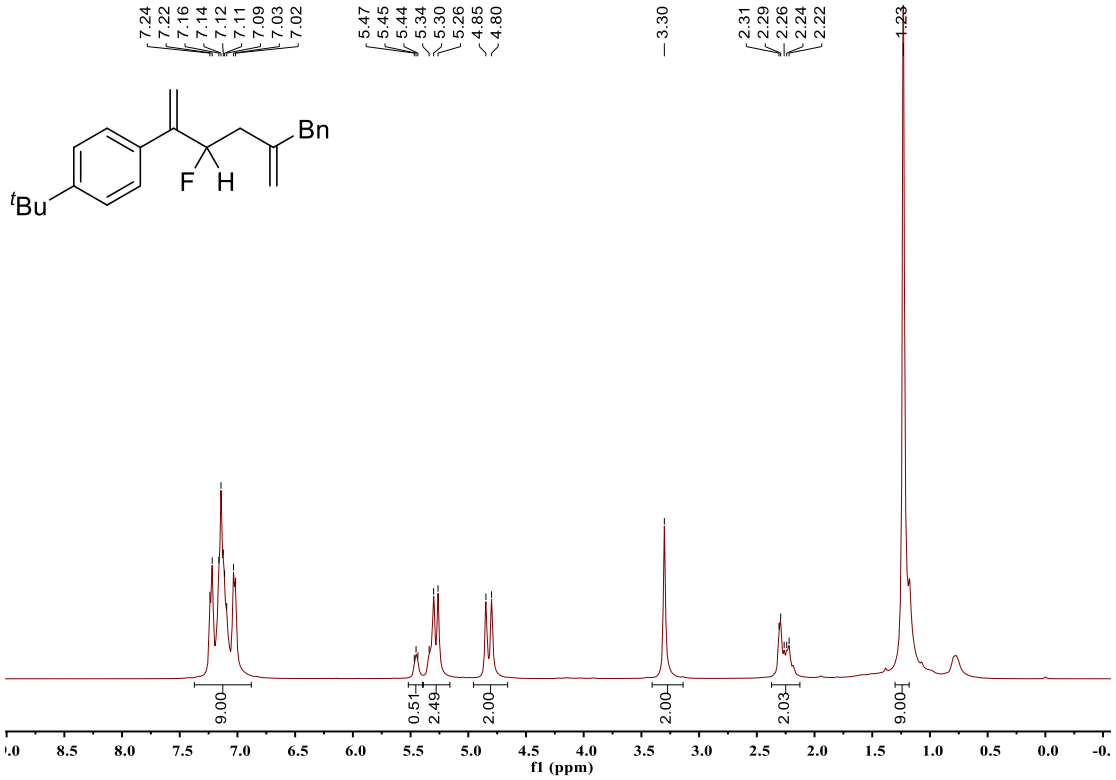
^{19}F NMR of 36 (376 MHz, $CDCl_3$)



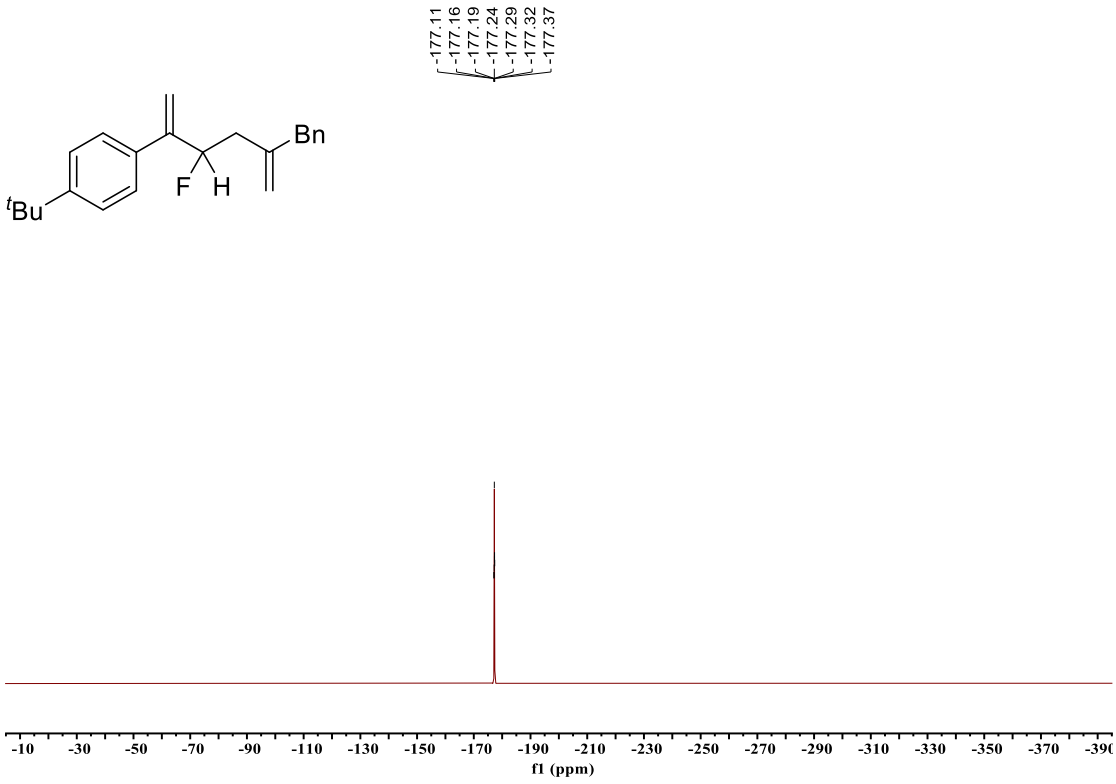
^{13}C-NMR of 36 (100 MHz, $CDCl_3$)



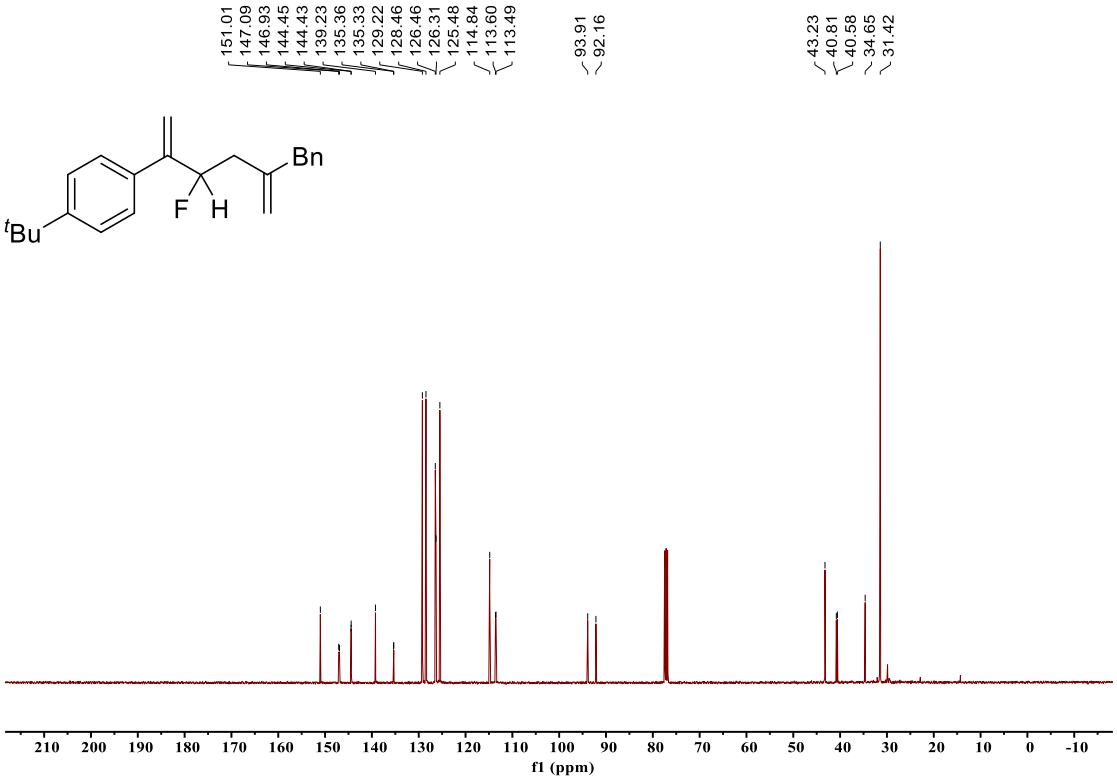
^{1}H-NMR of 37 (400 MHz, $CDCl_3$)



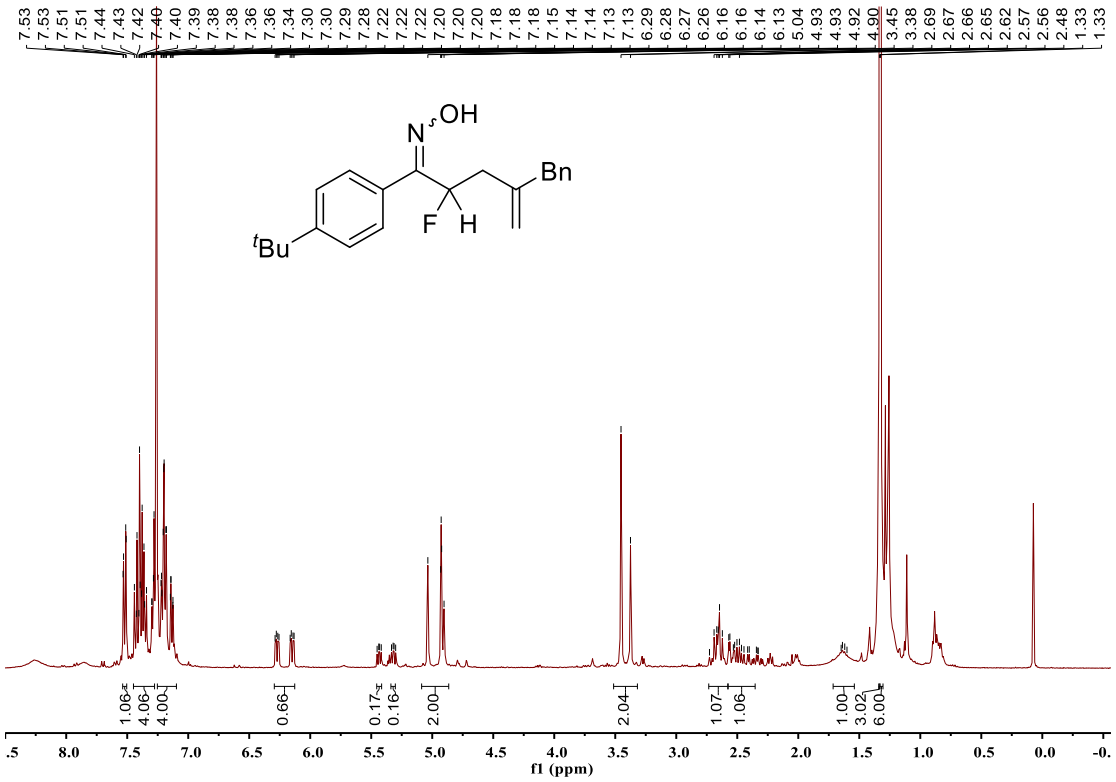
^{19}F NMR of 37 (376 MHz, $CDCl_3$)



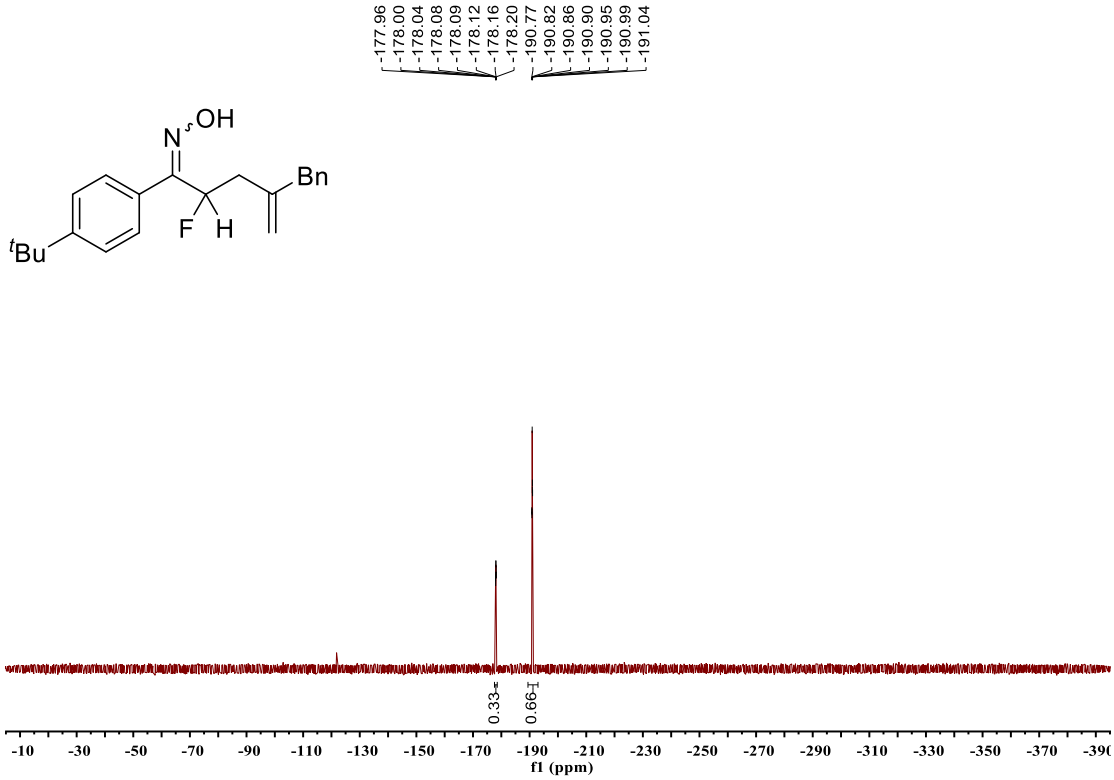
^{13}C-NMR of 37 (100 MHz, $CDCl_3$)



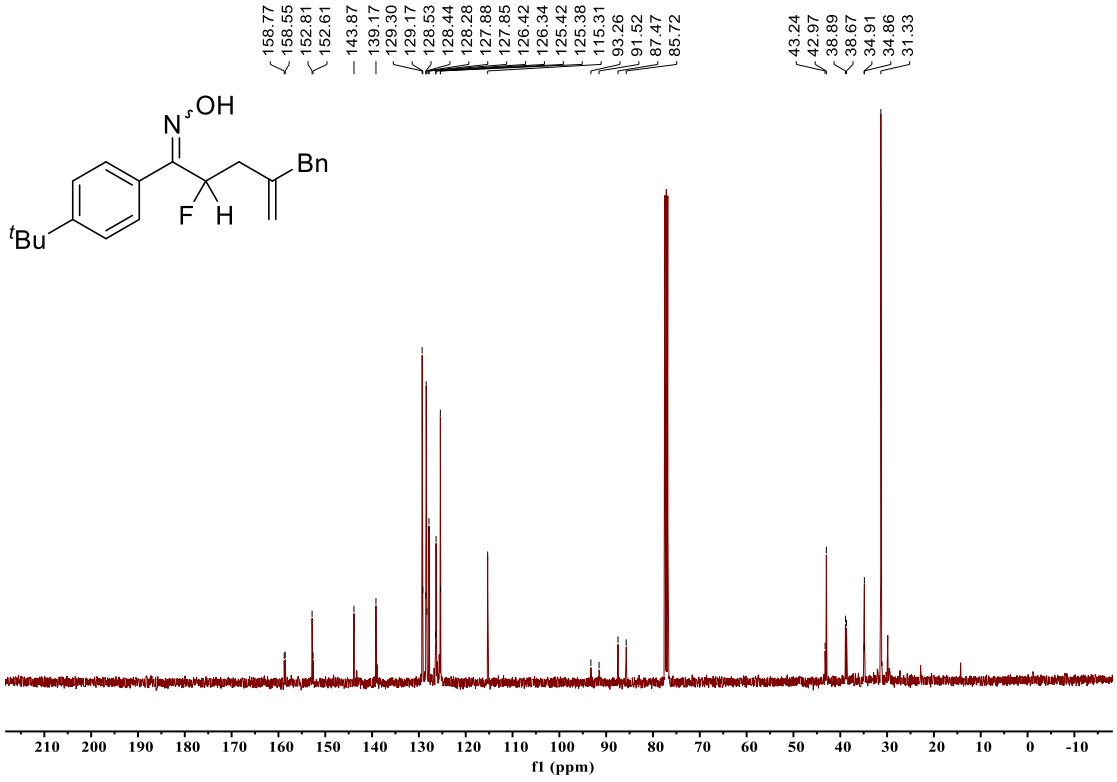
^{1}H-NMR of 38 (400 MHz, $CDCl_3$)



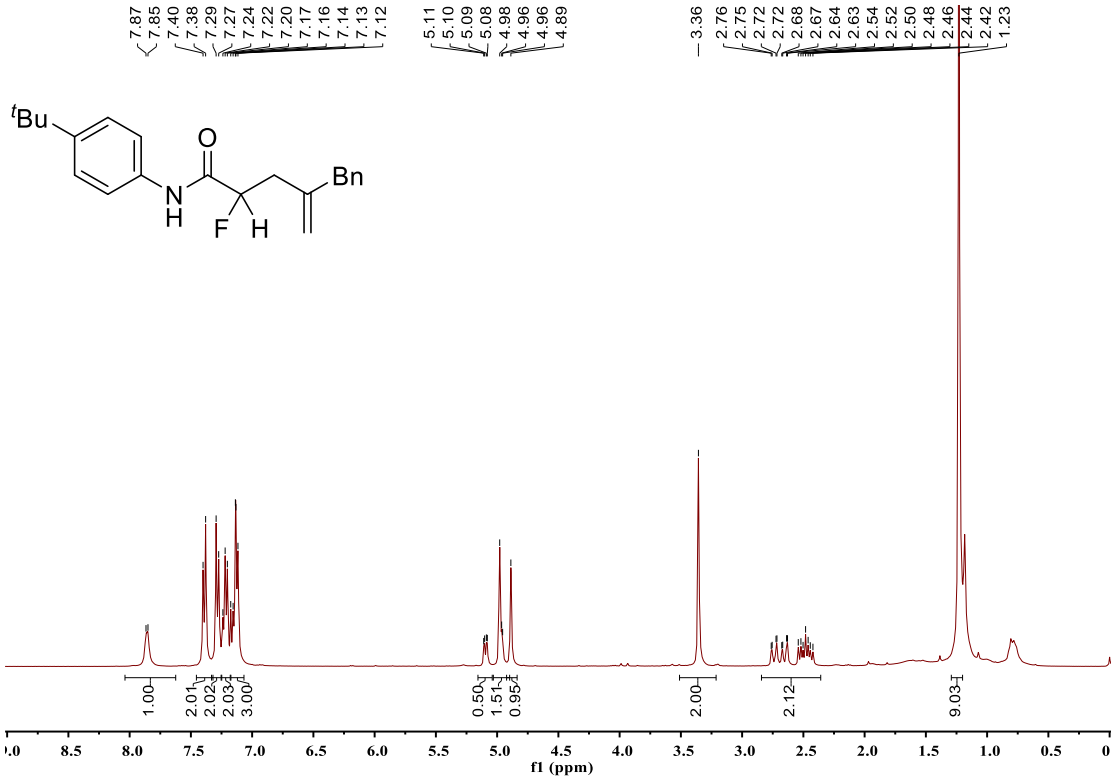
^{19}F NMR of 38 (376 MHz, $CDCl_3$)



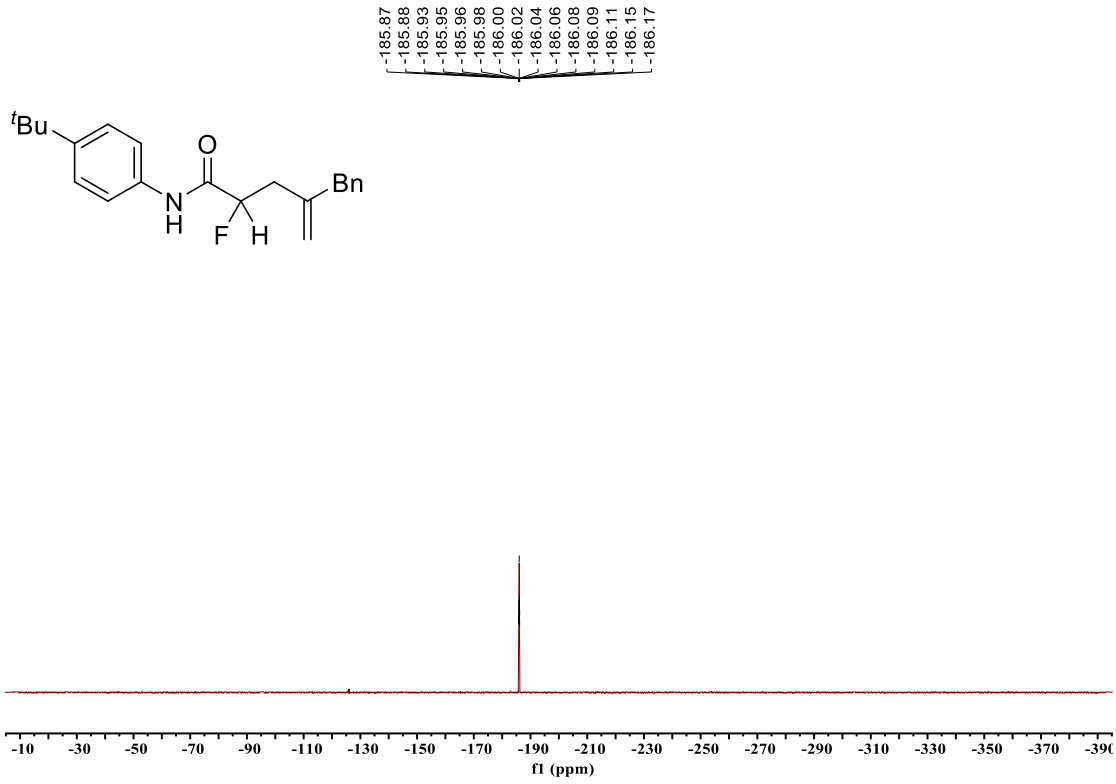
^{13}C-NMR of 38 (100 MHz, $CDCl_3$)



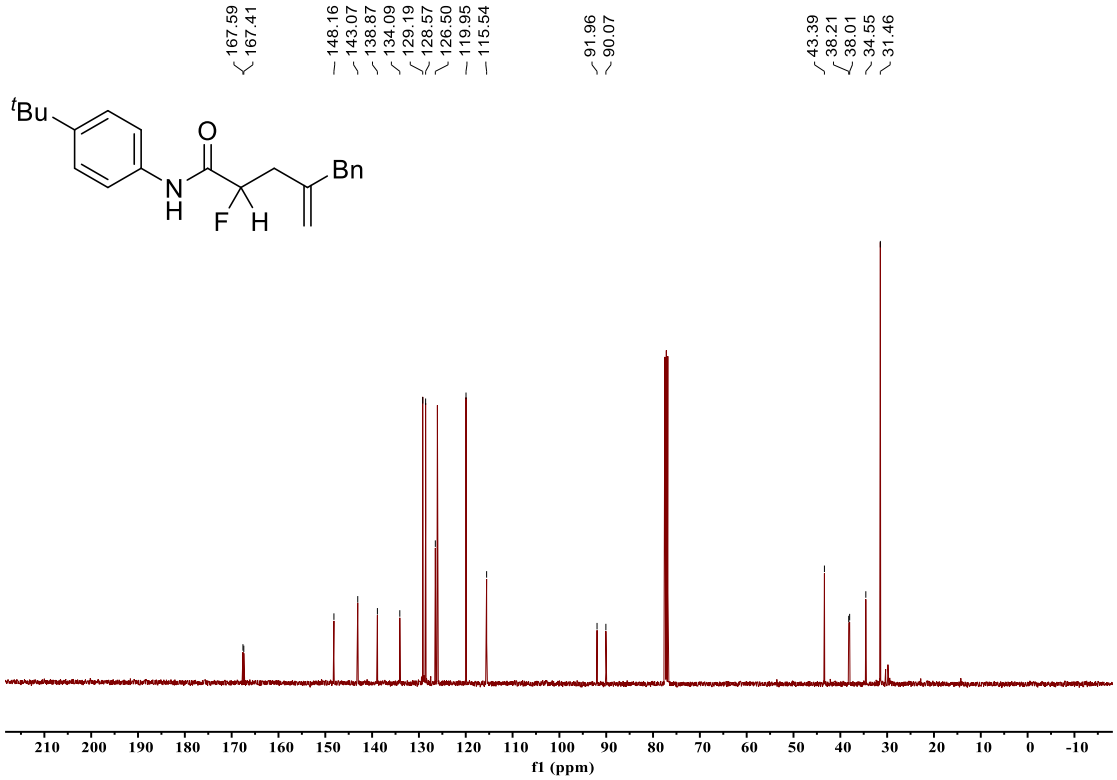
^{1}H-NMR of 39 (400 MHz, $CDCl_3$)



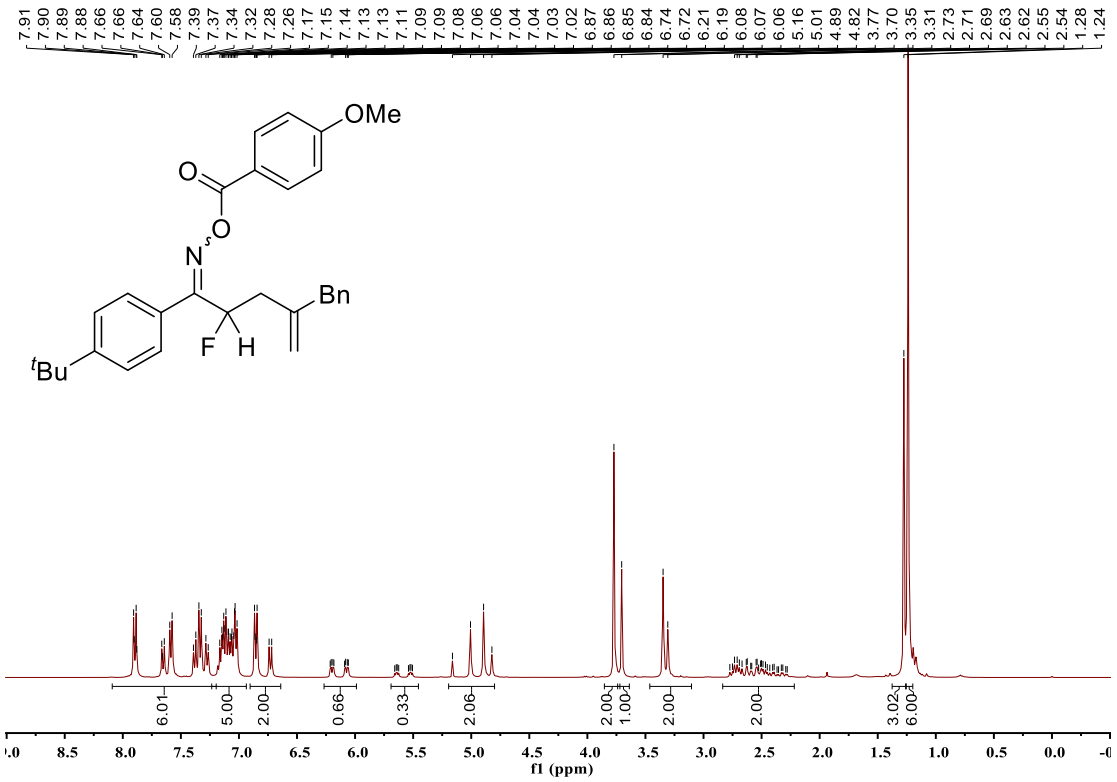
^{19}F NMR of 39 (376 MHz, $CDCl_3$)



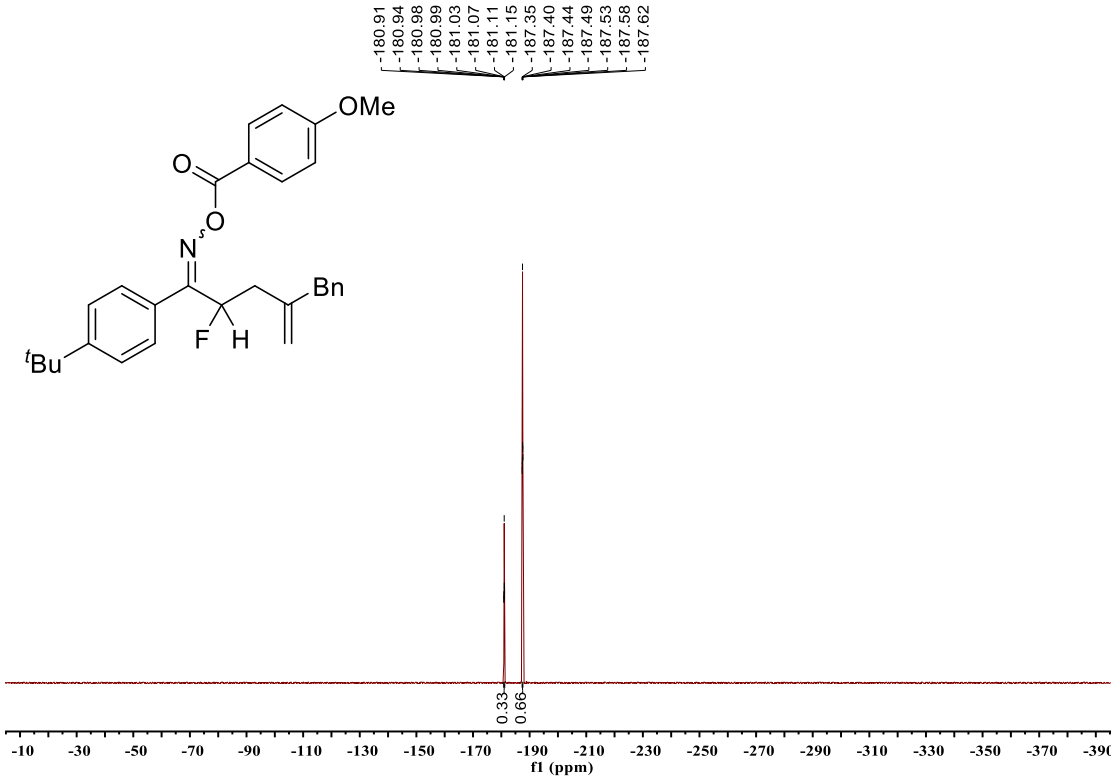
^{13}C-NMR of 39 (100 MHz, $CDCl_3$)



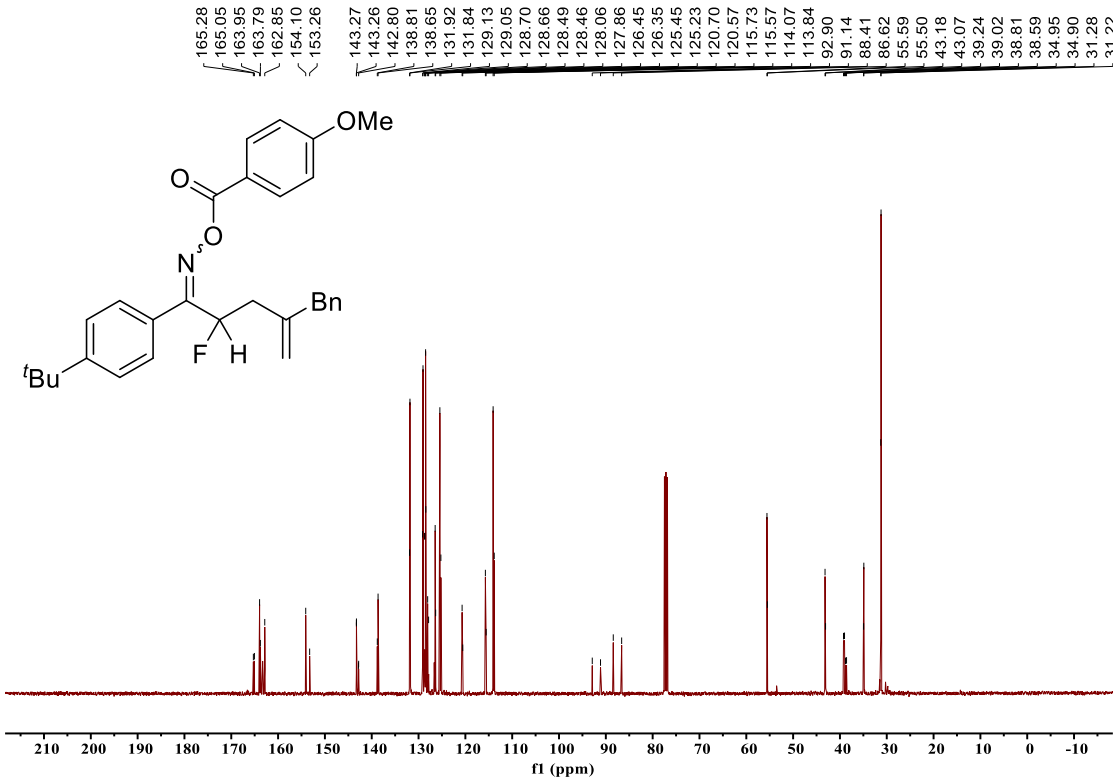
^{1}H-NMR of 40 (400 MHz, $CDCl_3$)



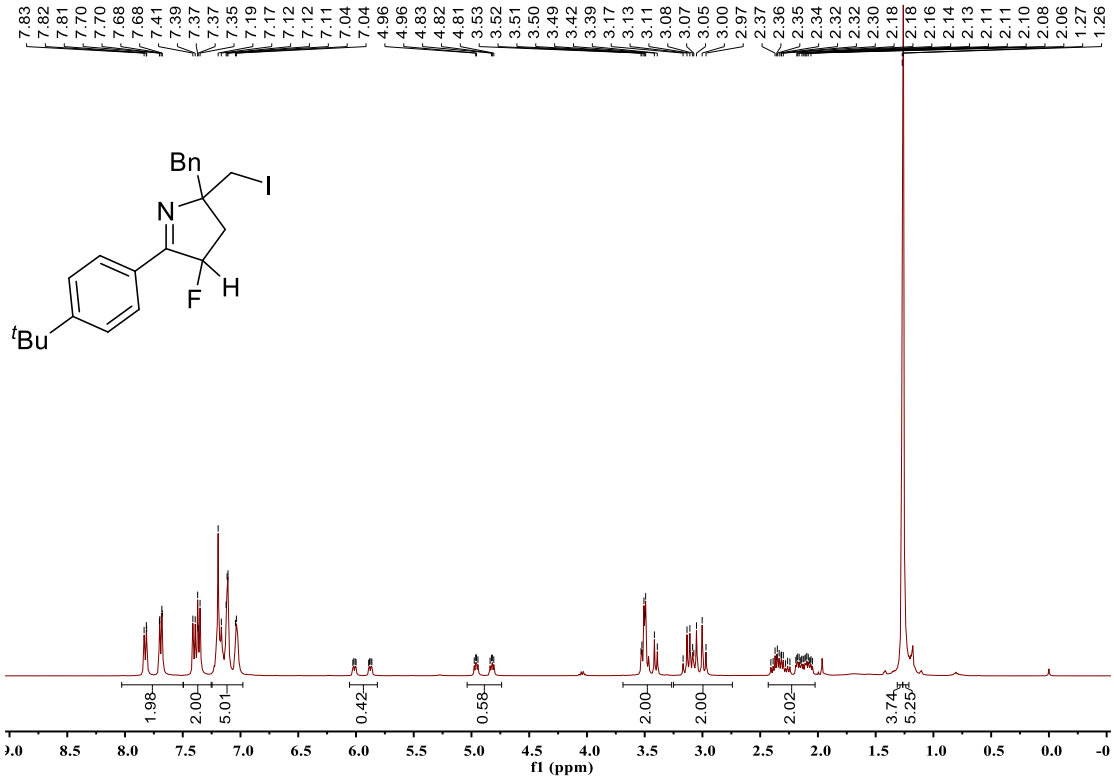
^{19}F NMR of 40 (376 MHz, $CDCl_3$)



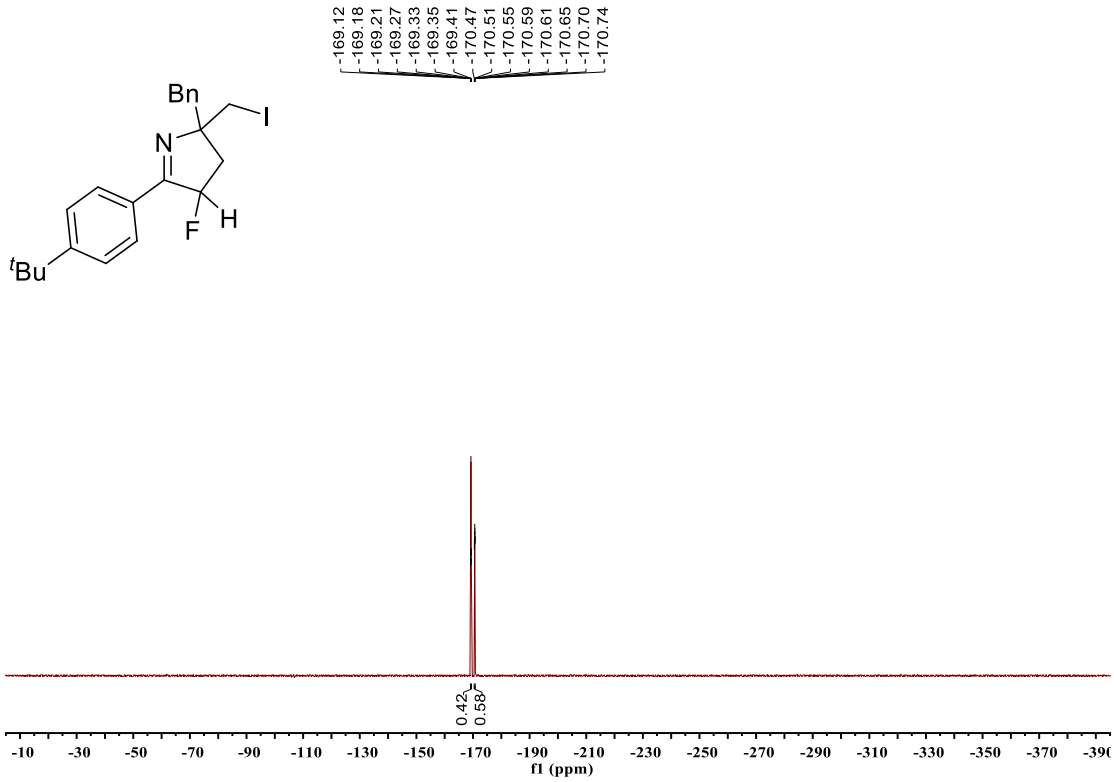
^{13}C-NMR of 40 (100 MHz, $CDCl_3$)



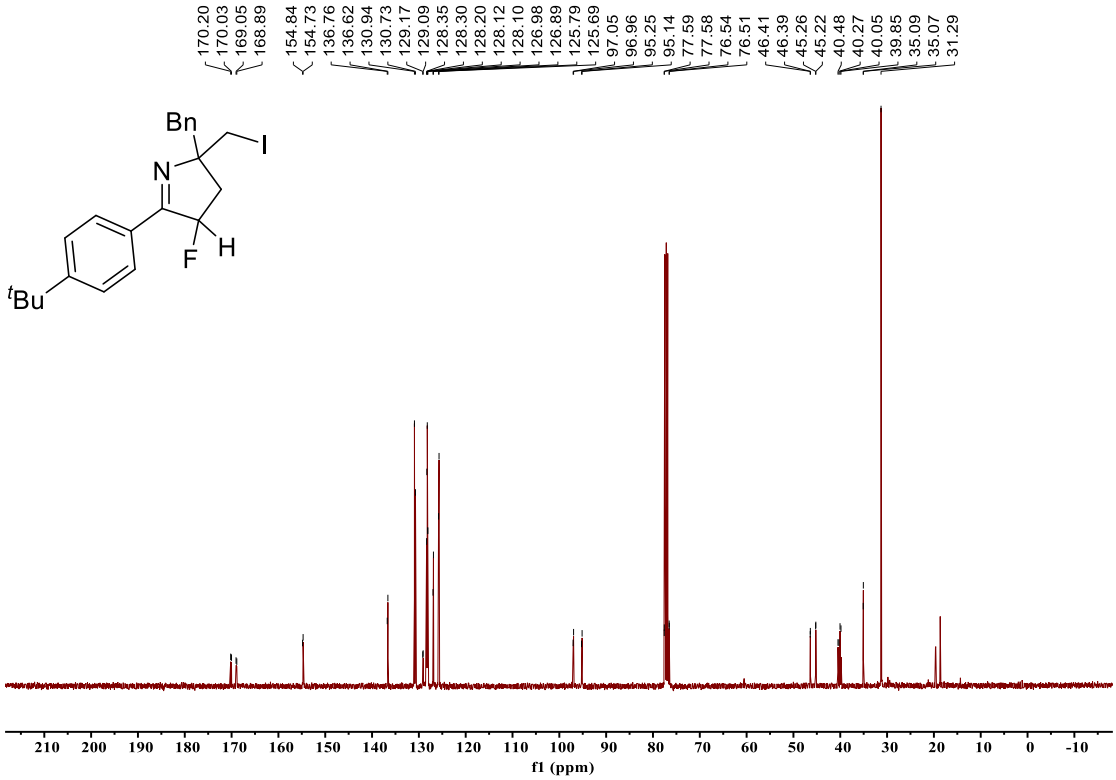
^{1}H-NMR of 41 (400 MHz, $CDCl_3$)



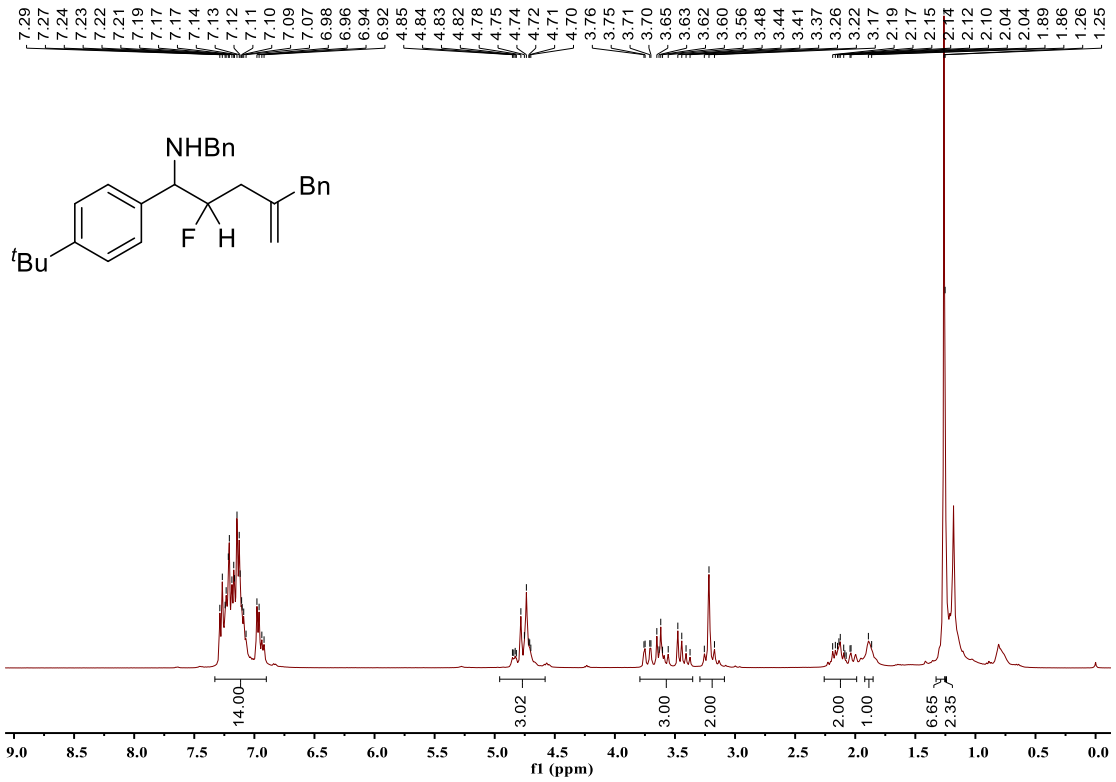
^{19}F NMR of 41 (376 MHz, $CDCl_3$)



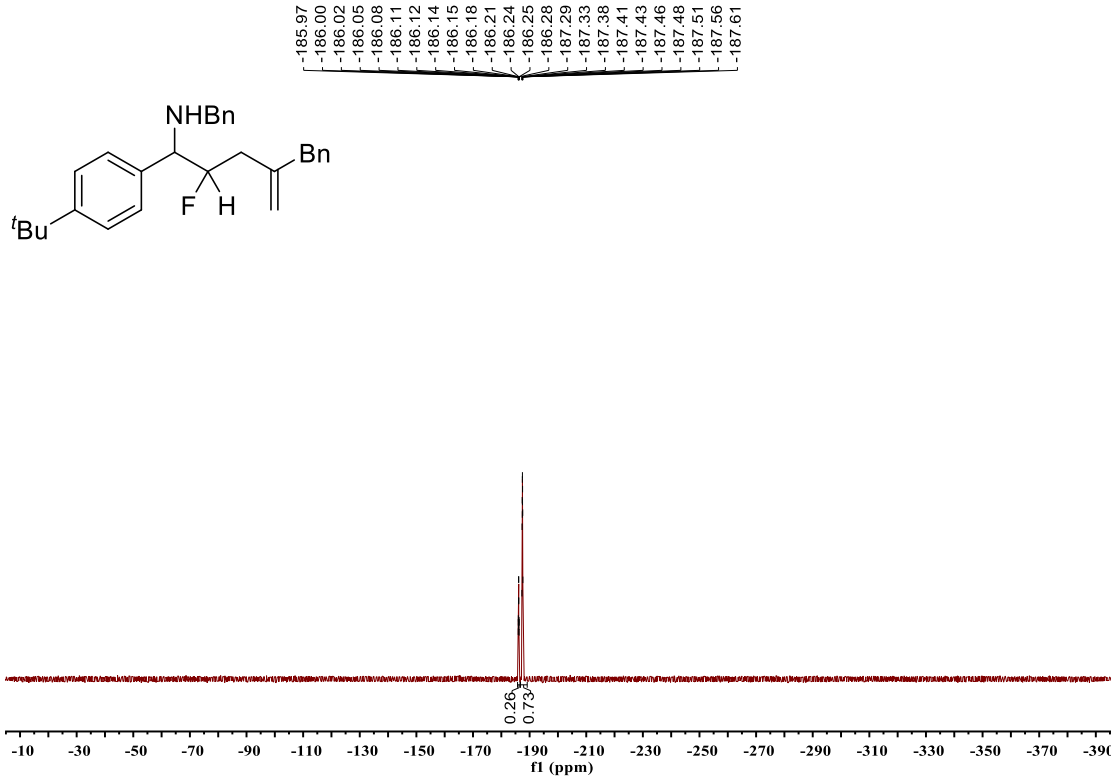
^{13}C-NMR of 41 (100 MHz, $CDCl_3$)



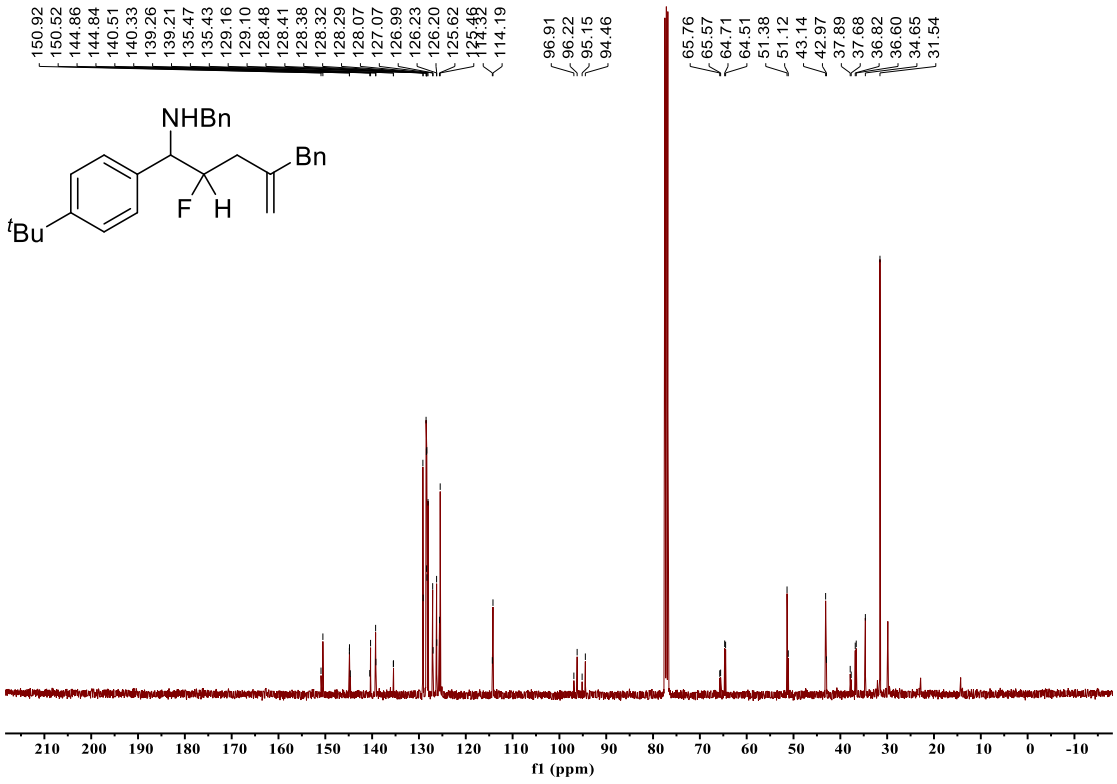
^{1}H-NMR of 42 (400 MHz, $CDCl_3$)



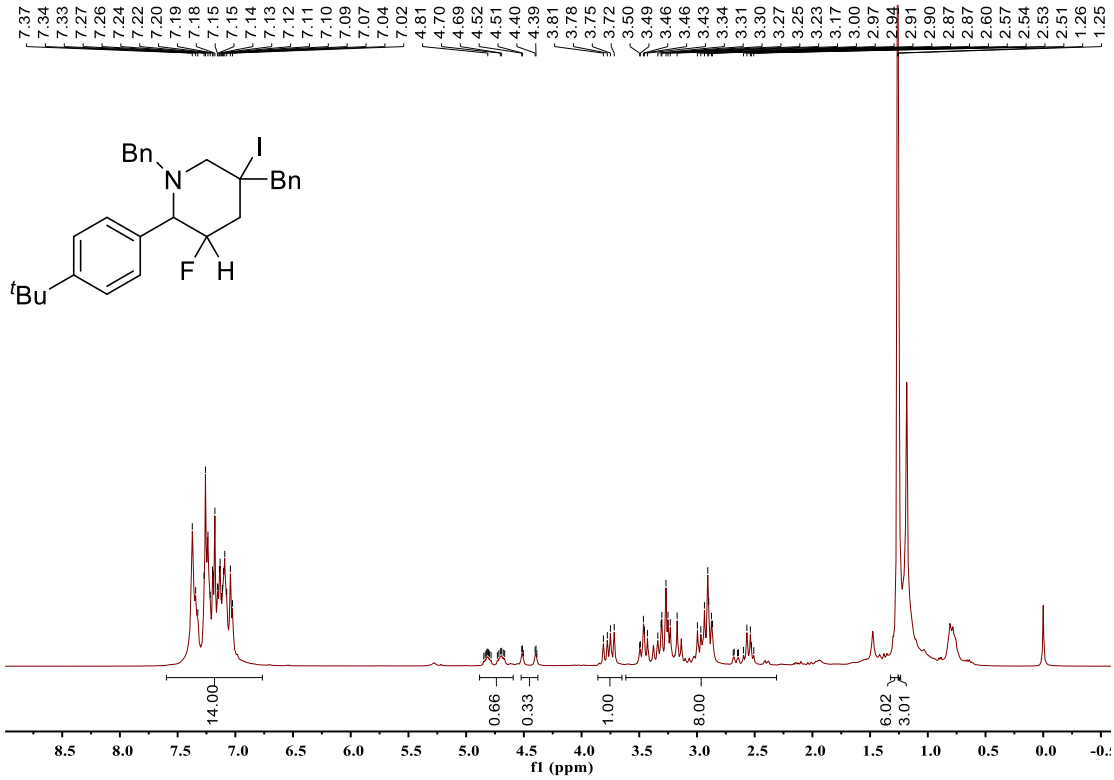
^{19}F NMR of 42 (376 MHz, $CDCl_3$)



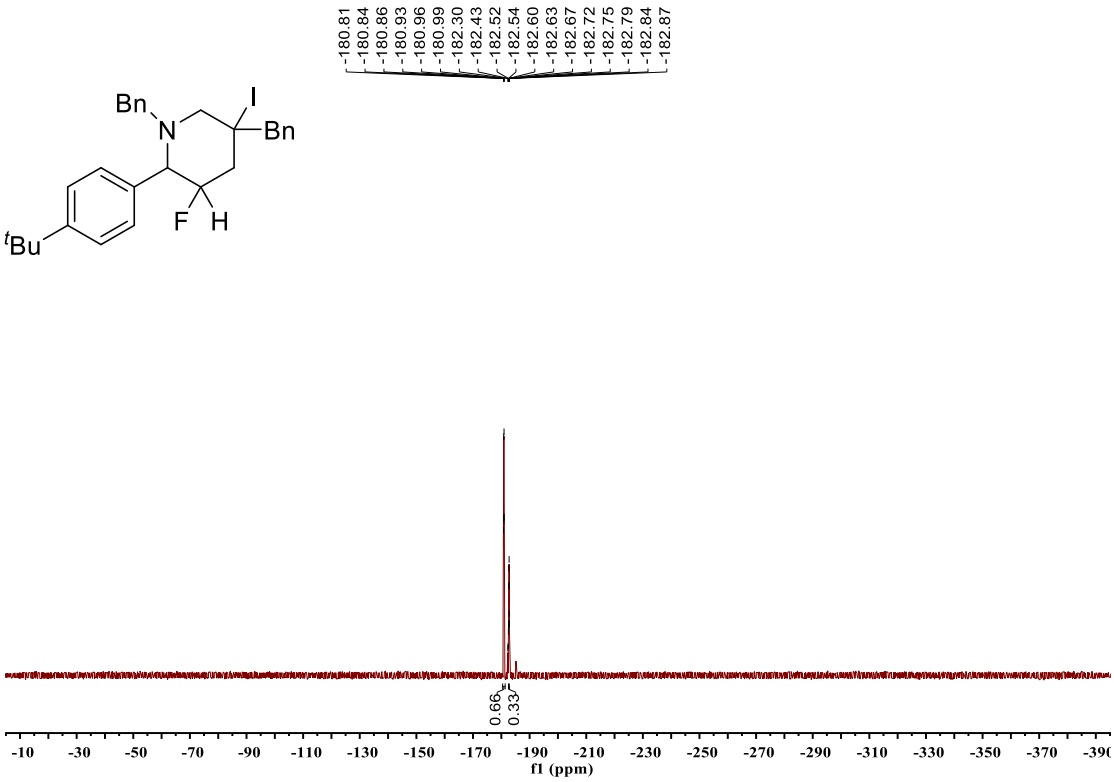
^{13}C-NMR of 42 (100 MHz, $CDCl_3$)



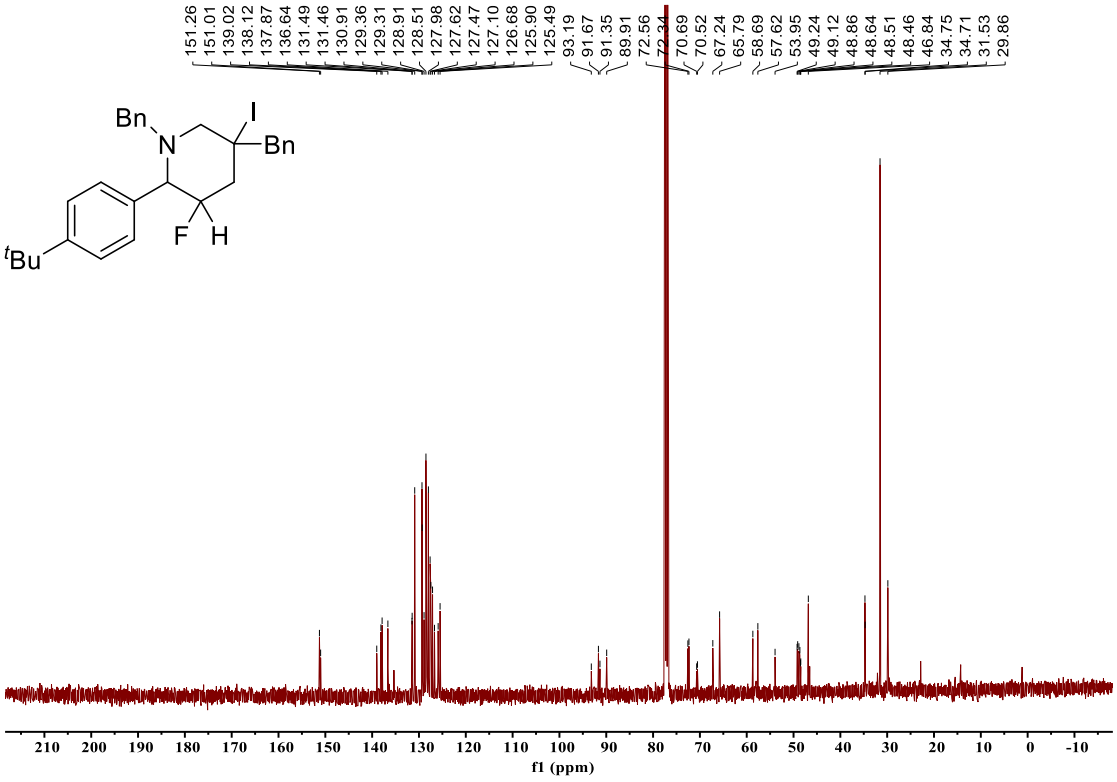
^{1}H-NMR of 43 (400 MHz, $CDCl_3$)



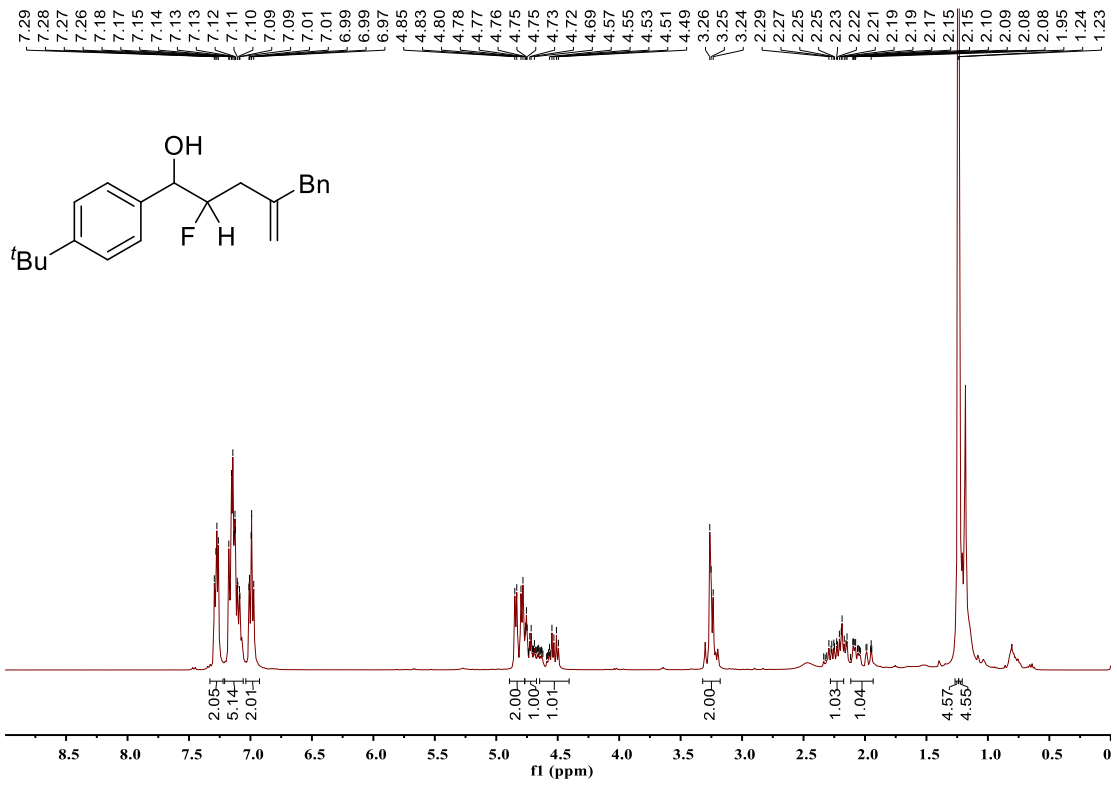
^{19}F NMR of 43 (376 MHz, $CDCl_3$)



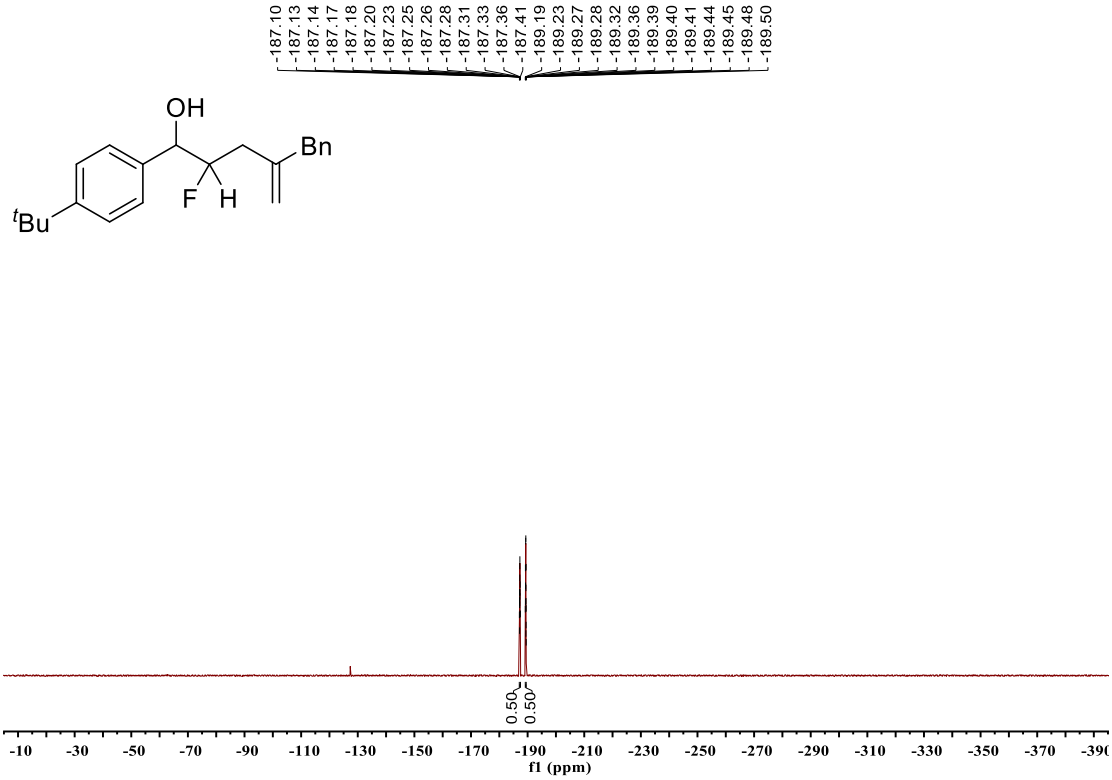
^{13}C-NMR of 43 (100 MHz, $CDCl_3$)



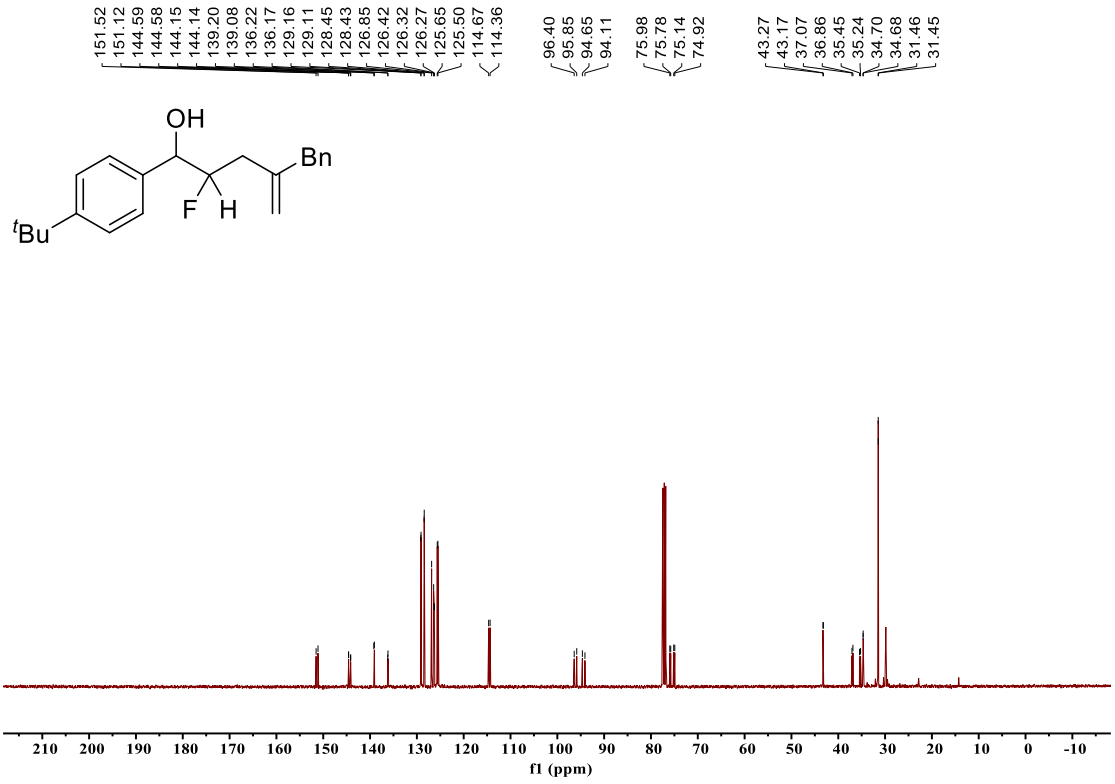
^{1}H-NMR of 44 (400 MHz, $CDCl_3$)



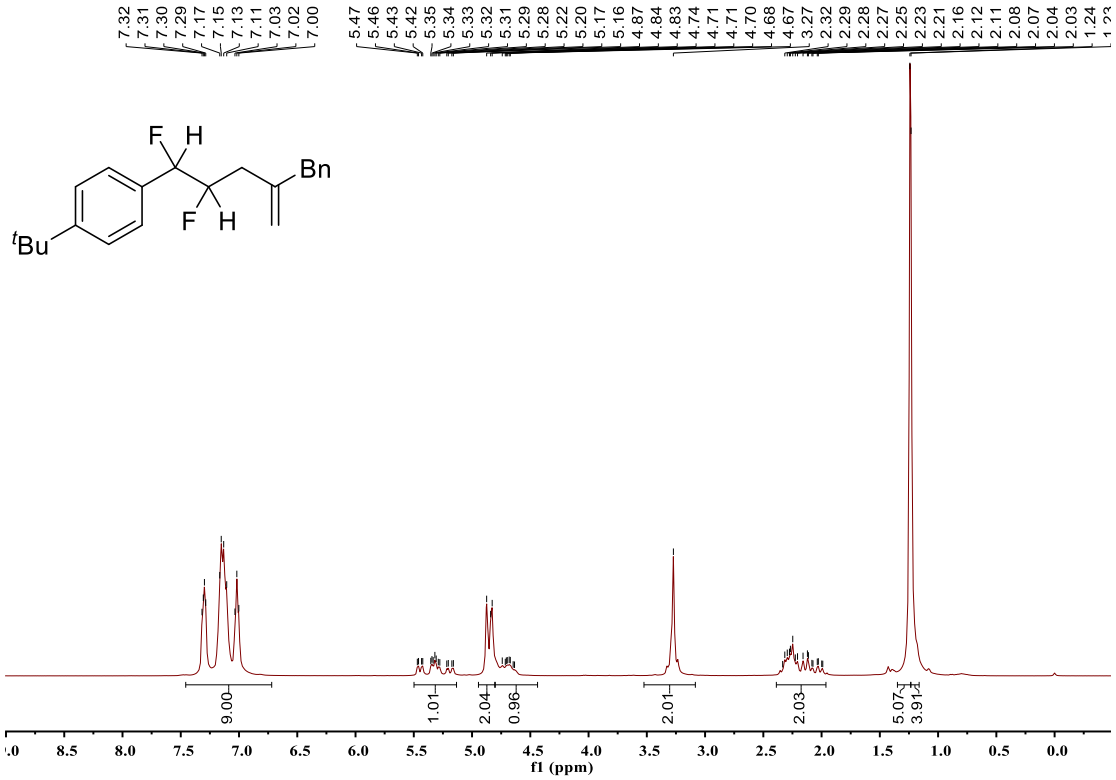
^{19}F NMR of 44 (376 MHz, $CDCl_3$)



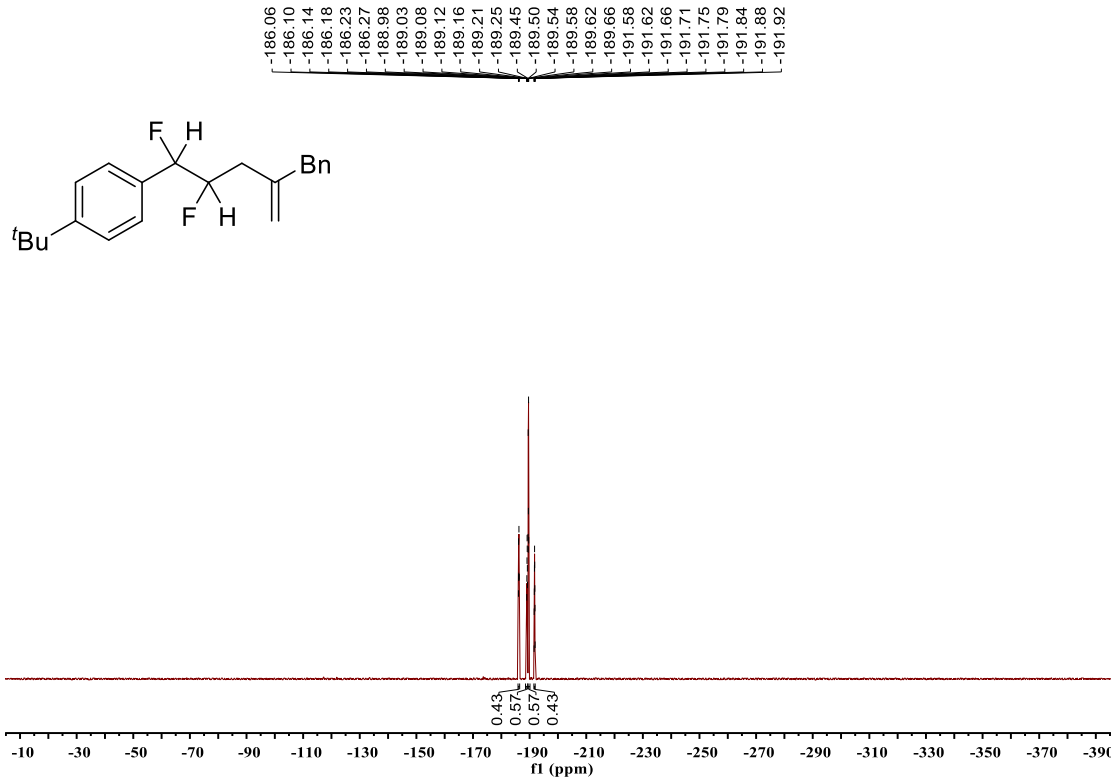
^{13}C-NMR of 44 (100 MHz, $CDCl_3$)



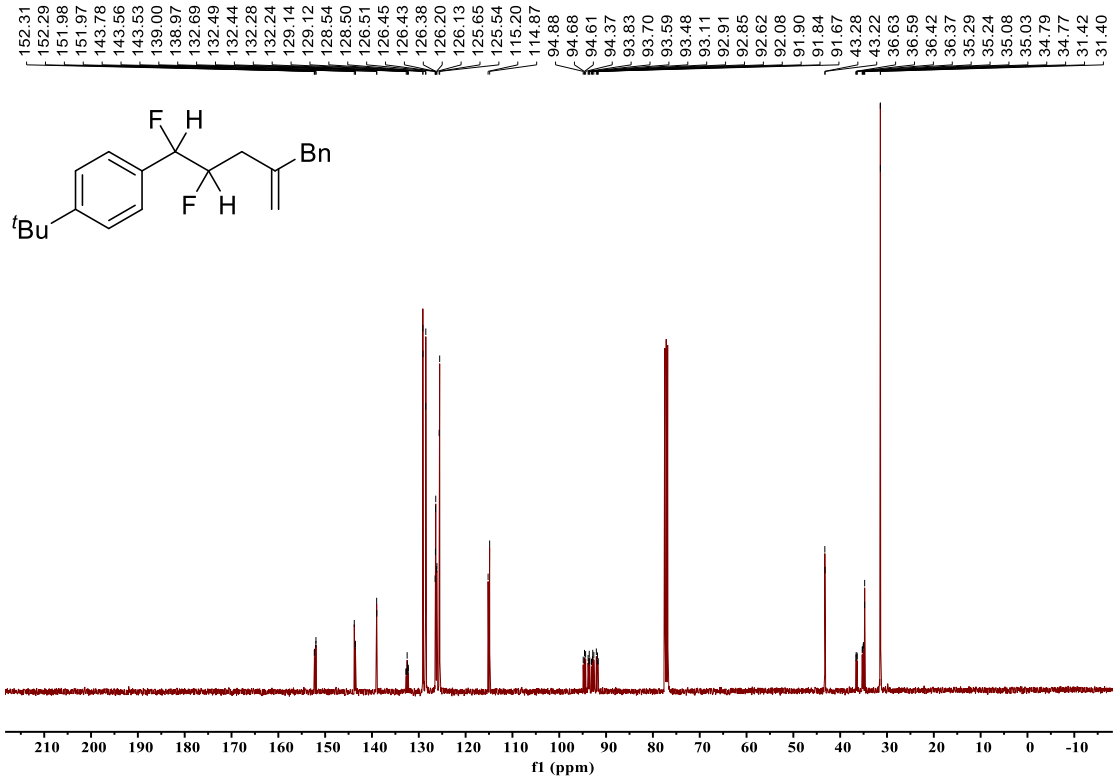
^{1}H-NMR of 45 (400 MHz, $CDCl_3$)



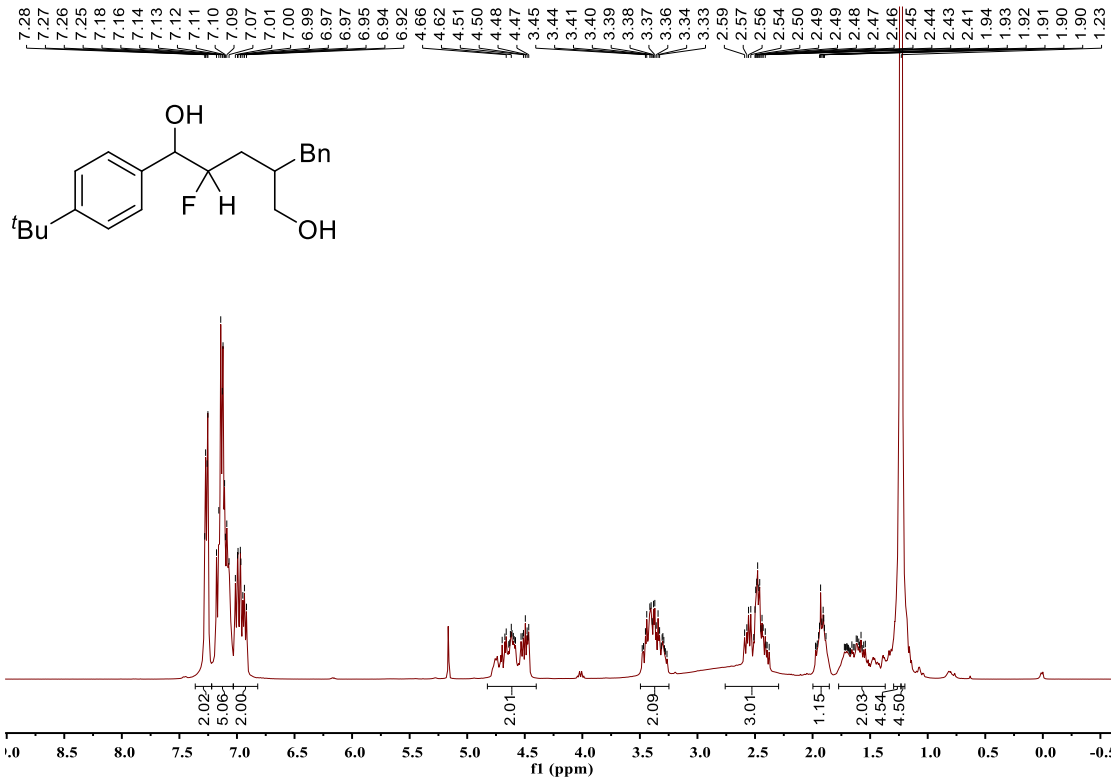
^{19}F NMR of 45 (376 MHz, $CDCl_3$)



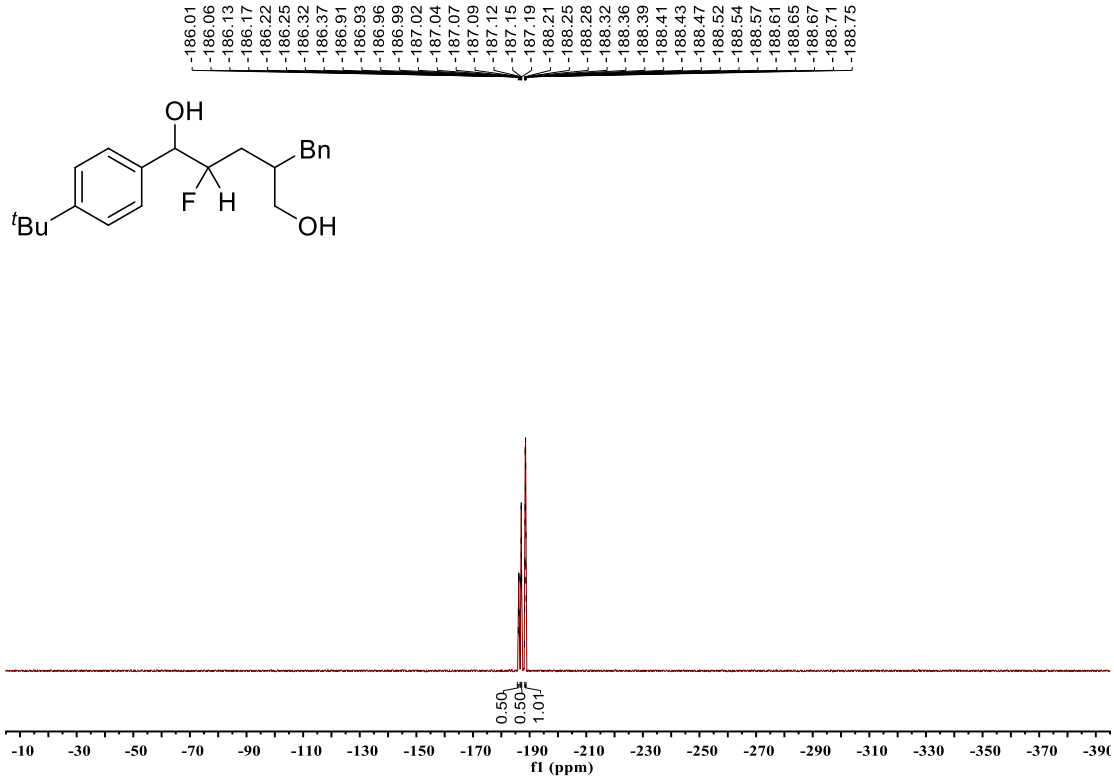
^{13}C-NMR of 45 (100 MHz, $CDCl_3$)



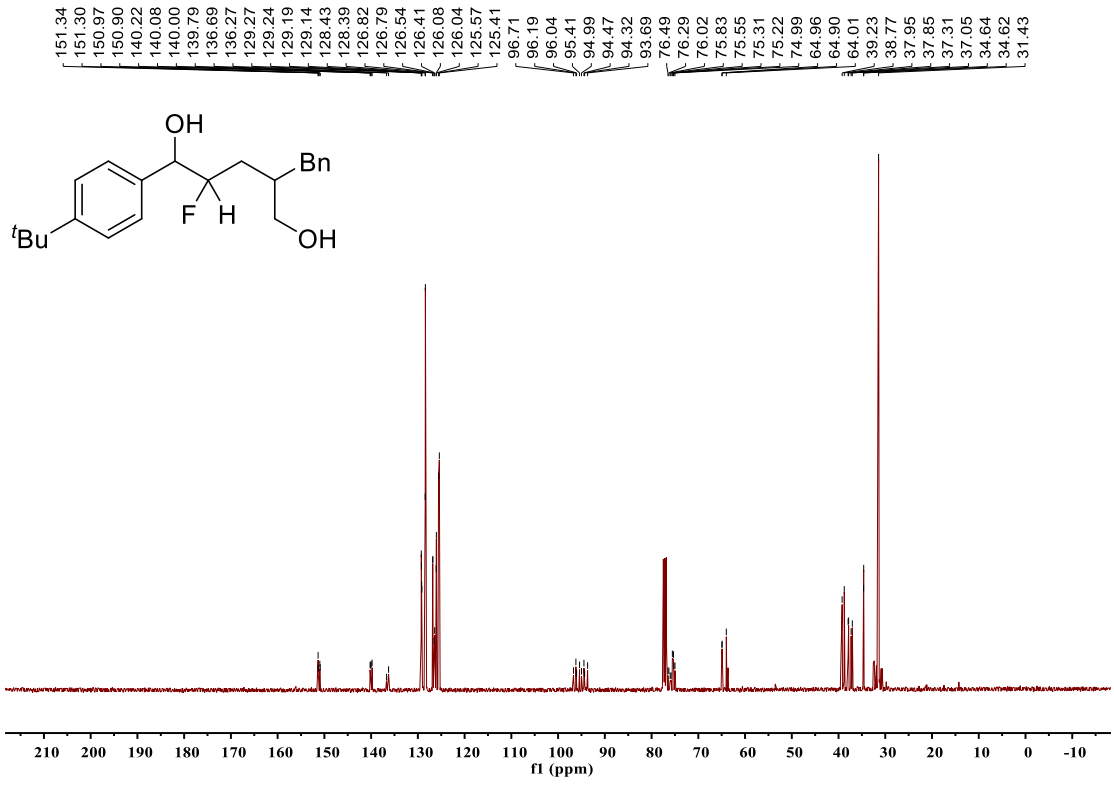
^{1}H-NMR of 46 (400 MHz, $CDCl_3$)



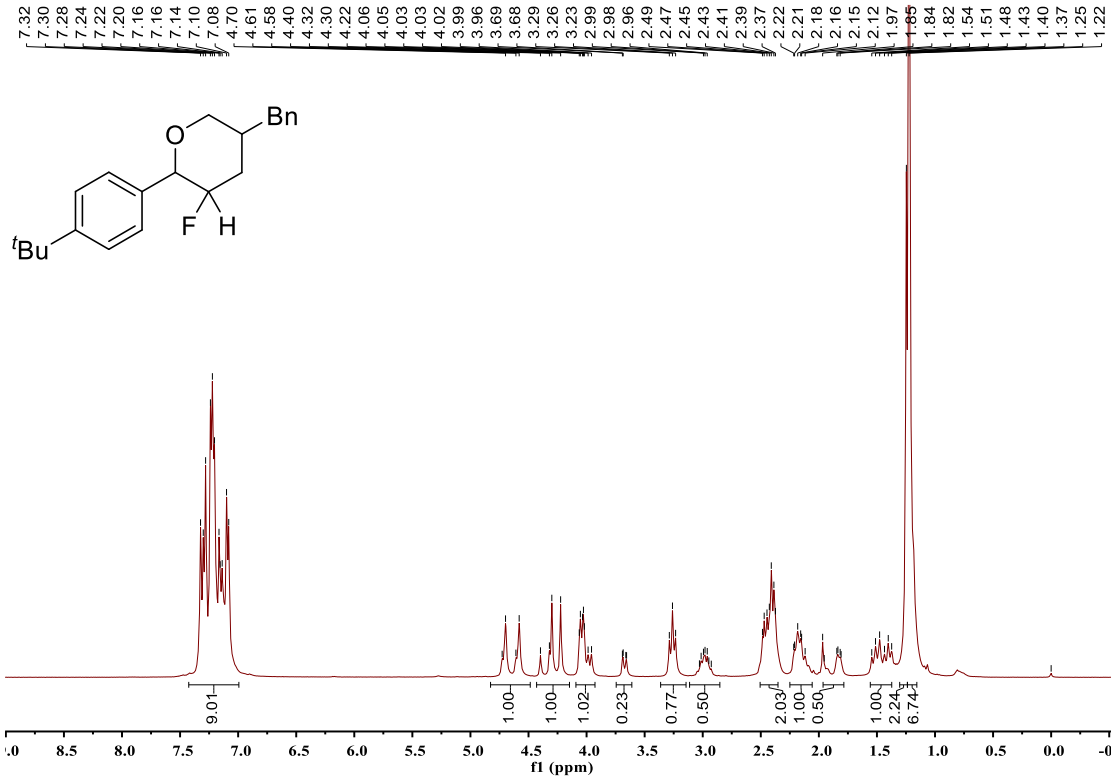
^{19}F NMR of 46 (376 MHz, $CDCl_3$)



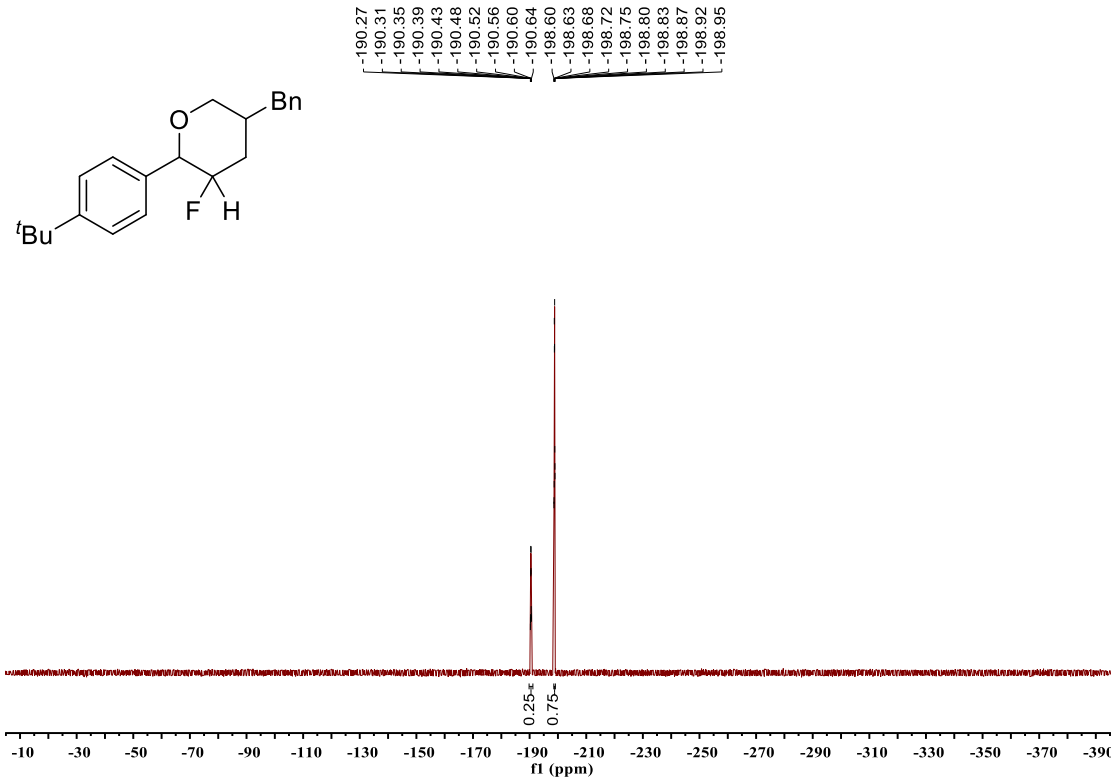
^{13}C-NMR of 46 (100 MHz, $CDCl_3$)



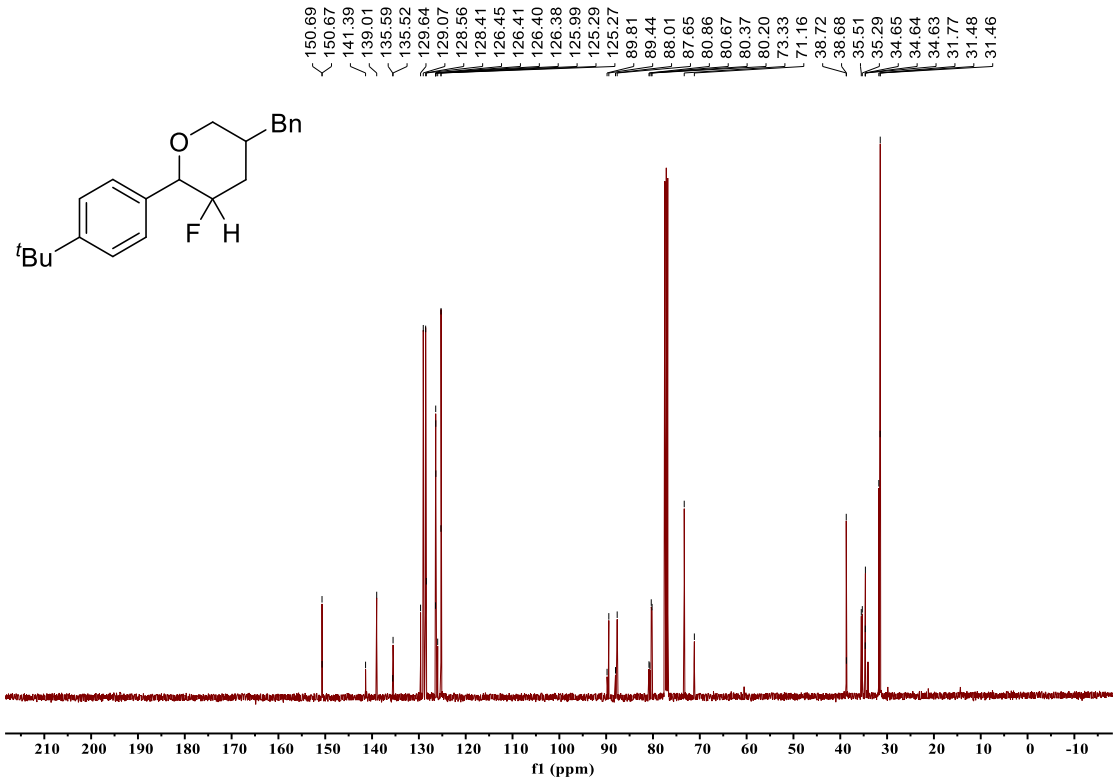
^{1}H-NMR of 47 (400 MHz, $CDCl_3$)



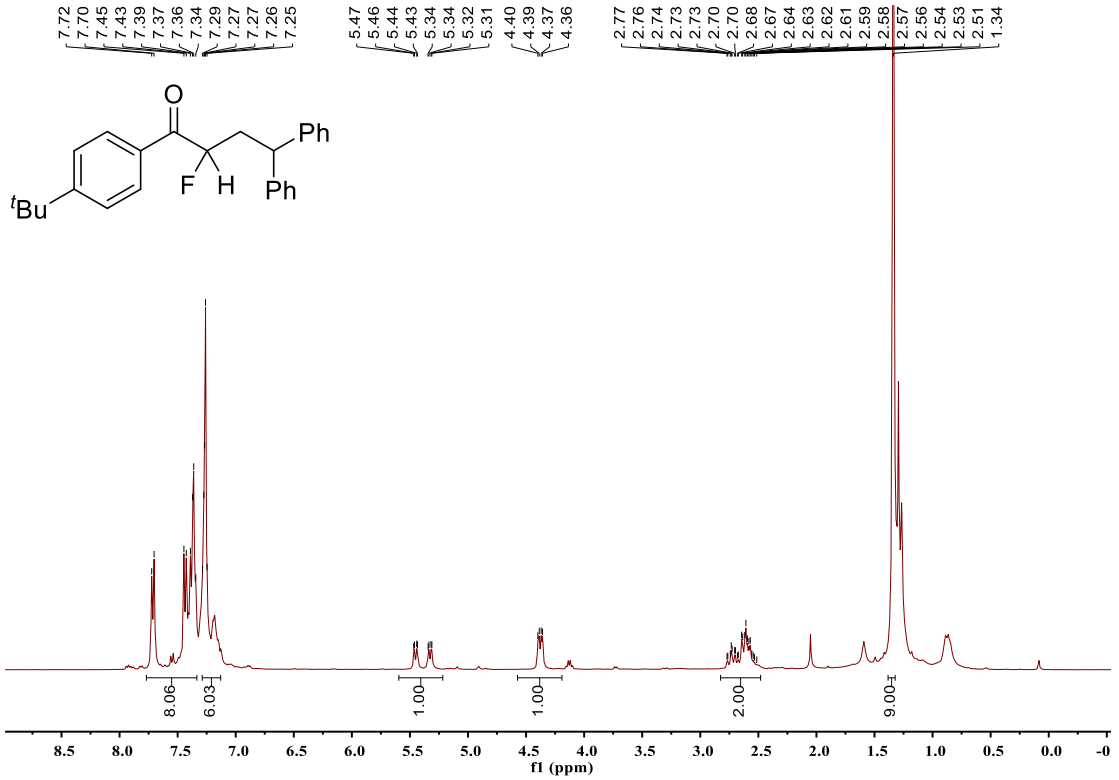
^{19}F NMR of 47 (376 MHz, $CDCl_3$)



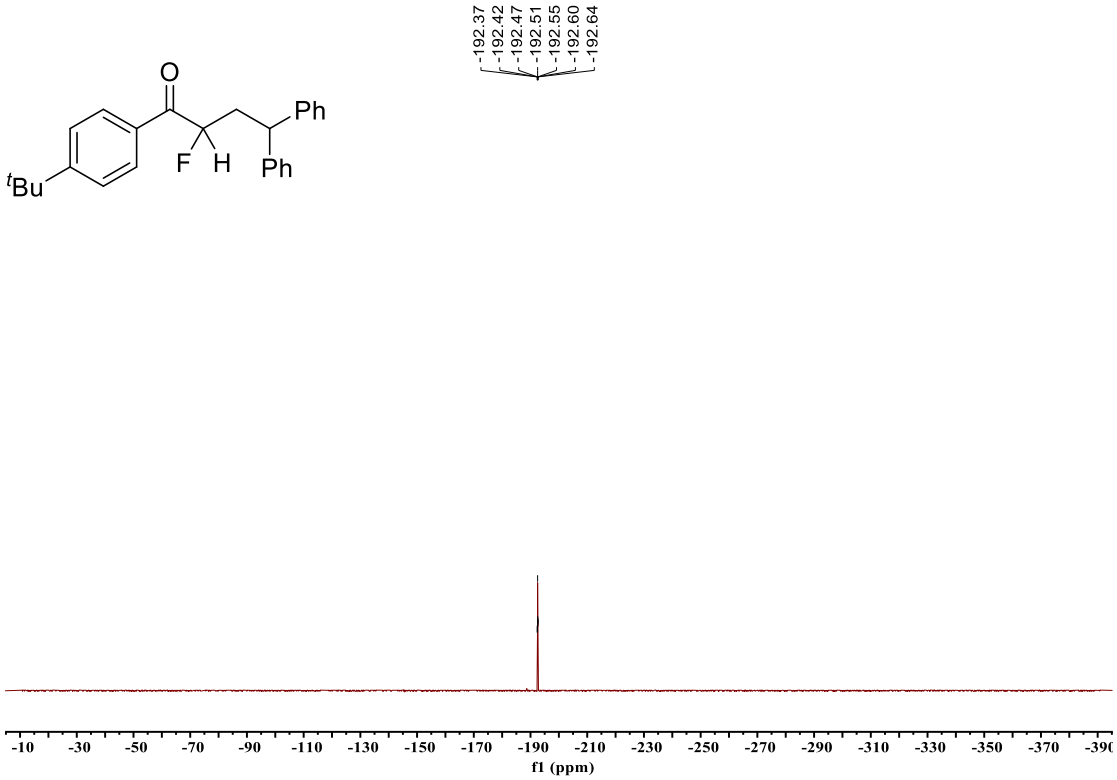
^{13}C-NMR of 47 (100 MHz, $CDCl_3$)



^{1}H-NMR of 48 (400 MHz, $CDCl_3$)



^{19}F NMR of 48 (376 MHz, $CDCl_3$)



^{13}C-NMR of 48 (100 MHz, $CDCl_3$)