

Acylmonofluoromethylation of Alkenes via Dual NHC/Photoredox Catalysis

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1. General information

General Experimental. Unless otherwise noted, all reactions were carried out under argon atmosphere in a glass tube with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was performed under a UV lamp (254 nm). Organic solutions were concentrated by rotary evaporation at 23-35 °C. Purification of products were generally carried out by flash column chromatography with 200-300 mesh silica gel.

Materials. Alkenes **1a-v**, aroyl fluorides **2w**, **2x**, **2ac**, **2ad**, and NHC catalysts **N10-36** were purchased from Leyan.com, Bide Pharmatech Ltd. and Energy Chemical and used as received. NHC catalysts **N1-9** were synthesized as previously methods reported.¹ Anhydrous solvents were purchased from J&K Scientific.

Instrumentation. Photocatalytic reactions were performed in a RLH-18 8-position photo reaction system, which was manufactured by Beijing Rogertech Co. Ltd (Figure S1). Proton nuclear magnetic resonance spectra (¹H NMR) spectra, carbon nuclear magnetic resonance spectra (¹³C NMR) and fluorine nuclear magnetic resonance spectra (¹⁹F NMR, decoupled) were recorded at 23 °C on a Bruker 400 spectrometer in CDCl₃, or CD₃OD (400 MHz for ¹H and 101 MHz for ¹³C and 376 MHz for ¹⁹F), Bruker

¹ Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. A Family of Thiazolium Salt Derived *N*-Heterocyclic Carbenes (NHCs) for Organocatalysis: Synthesis, Investigation and Application in Cross-Benzoin Condensation. *Eur. J. Org. Chem.* **2011**, *2011*, 5474-5484.

500 spectrometer in CDCl₃ (500 MHz for ¹H and 126 MHz for ¹³C) and Bruker 600 spectrometer in CDCl₃ or CD₃OD (600 MHz for ¹H and 151 MHz for ¹³C). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak (CHCl₃: 7.26 ppm and CD₃OD: 3.31 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ¹³C NMR spectra were reported in ppm from the central peak of CDCl₃ (77.16 ppm) and CD₃OD (49.00 ppm) on the δ scale. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization (ESI). GC-MS spectra were recorded on Agilent Intuvo 9000/5977B GC/MS using electron ionization (EI) source. EPR was performed on a Bruker A300.

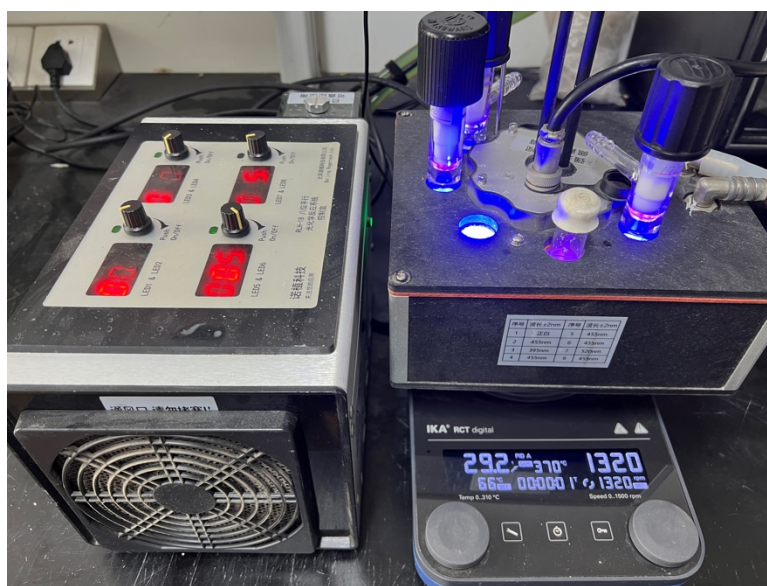
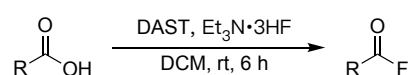


Figure S1. The photoreaction device

2. General procedure (A) for the synthesis of aroyl fluorides from carboxylic acid²



To a round-bottom flask was charged with diethylaminodifluorosulfonium tetrafluoroborate (DAST, 6.0 mmol, 1.5 equiv.) and carboxylic acid (4.0 mmol, 1.0 equiv.) in anhydrous DCM (5 mL/mmol substrate) at room temperature. Then Et₃N·3HF (4 mmol, 1.0 equiv.) was added and the reaction mixture was continued stirring at room temperature for 6 h. The reaction was quenched with a 5% NaHCO₃ solution and extracted with DCM. The combined organic layers were dried over Na₂SO₄, filtered and dried in vacuo. The crude residue was purified by column chromatography on silica gel to afford the aroyl fluorides.

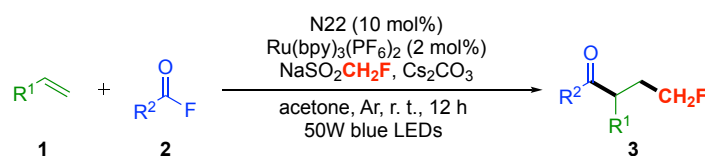
3. General procedure for acyl-monofluoromethylation

(1) General procedure (B) for optimizations to preparing product **3a**

² Han, J.; Zhou, W.; Zhang, P.-C.; Wang, H.; Zhang, R.; Wu, H.-H.; Zhang, J. Design and Synthesis of WJ-Phos, and Application in Cu-Catalyzed Enantioselective Boroacylation of 1,1-Disubstituted Allenes. *ACS Catal.* **2019**, *9*, 6890-6895.

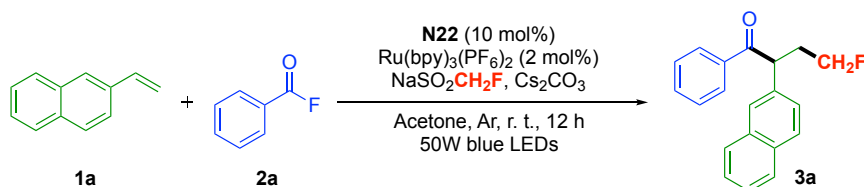
In a glove box, to a glass tube equipped with a magnetic stir bar was added 2-vinylnaphthalene **1a** (0.15 mmol, 1.0 equiv.), benzoyl fluoride **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), NHC catalyst (10 mol%), photocatalysts (2 mol%), base (0.3 mmol, 2.0 equiv.), and solvent (1.5 mL). The tube was tightly sealed and brought out. The reaction was allowed to stir at for 12 h under 50 W blue LED irradiation with argon atmosphere. After that, the mixture was diluted with diethyl ether, washed with water. The combined organic fractions were dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired product **3a**.

(2) General procedure (C) for the acylmonofluoromethylation to preparing products **3**



In a glove box, to a glass tube equipped with a stir bar was charged alkenes **1** (0.3 mmol, 1.0 equiv.), acyl fluorides **2** (0.6 mmol, 2.0 equiv.), NaSO₂CH₂F (0.6 mmol, 2.0 equiv.), NHC catalyst **N22** (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (0.6 mmol, 2.0 equiv.), and acetone (3 mL). The tube was capped and brought out. The reaction mixture was then stirred at room temperature for 12 h under 50 W blue LED irradiation with argon atmosphere. The mixture was diluted with diethyl ether, washed with water. The combined organic fractions were dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired product **3a-3ar**.

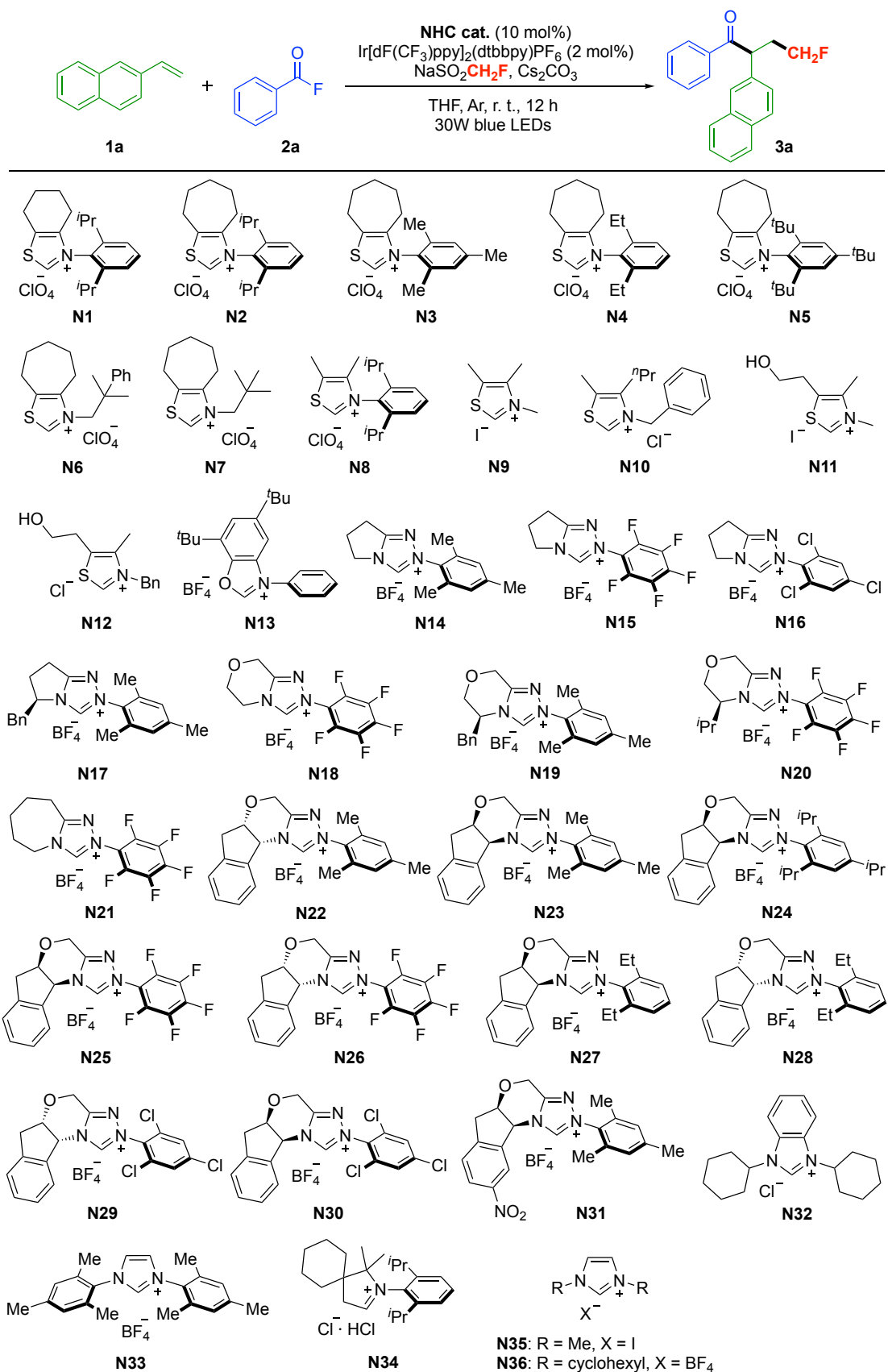
(3) Scale-up synthesis of the product **3a**



In a glovebox, to a flame-dried 100 mL round-bottom flask were added 2-vinylnaphthalene **1s** (1 mmol, 1.0 equiv.), benzoyl fluoride **2a** (2.0 mmol, 2.0 equiv.), NaSO₂CH₂F (2.0 mmol, 2.0 equiv.), NHC catalyst **N22** (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (2.0 mmol, 2.0 equiv.), and acetone (10 mL). And then resulting suspension stirred at room temperature for 12 h under 50 W blue LED irradiation with argon atmosphere, after which the reaction mixture was diluted with diethyl ether and washed with water. The separated organic layers were dried, concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel (hexane: ethyl acetate = 100: 1) to afford **3a** (195.4 mg) as yellow oil in 67% yield.

4. Optimization studies for the formation of 3a

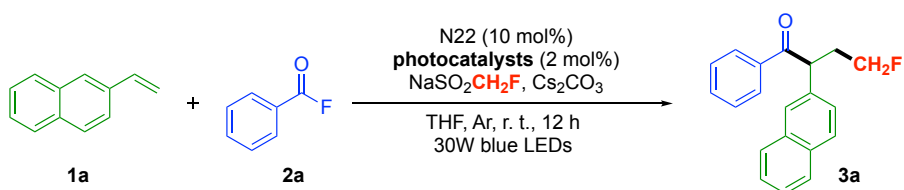
Table S1. Screening of NHC catalysts.^a



Entry	NHC catalysts	Isolated yield
1	N1	11%
2	N2	11%
3	N3	9%
4	N4	11%
5	N5	N. R. ^b
6	N6	10%
7	N7	16%
8	N8	27%
9	N9	14%
10	N10	27%
11	N11	27%
12	N12	27%
13	N13	23%
14	N14	40%
15	N15	34%
16	N16	42%
17	N17	34%
18	N18	29%
19	N19	39%
20	N20	23%
21	N21	31%
22	N22	53%
23	N23	42%
24	N24	45%
25	N25	44%
26	N26	43%
27	N27	43%
28	N28	45%
29	N29	35%
30	N30	37%
31	N31	41%
32	N32	26%
33	N33	34%
34	N34	28%
35	N35	19%
36	N36	20%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), NHC catalyst (10 mol%), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), THF (1.5 mL), r. t., Ar, 12 h, 30W blue LEDs; ^b N. R. = no reaction

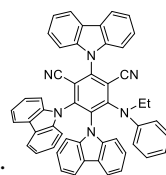
Table S2. Screening of photocatalysts^a



Entry	Photocatalysts	Isolated yield
1	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	53%
2	Ir(ppy) ₂ (dtbbpy)PF ₆	44%
3	Ir(ppy) ₃	33%
4	Ir[dF(Me)ppy] ₂ (phen)PF ₆	45%
5	Ru(dtbbpy) ₃ (PF ₆) ₂	42%
6	Ru(bpy)₃(PF₆)₂	63%
7	Ru(phen) ₃ (PF ₆) ₂	47%
8	Ru(phen) ₃ Cl ₂ •H ₂ O	47%
9	Mes-Acr ⁺ ClO ₄ ⁻	N.R. ^b
10	4-CzIPN	38%
11	3CzEPAIPN ^c	49%
12	TBADT	8%
13	Eosin Y	46%
14	Fluorescein	9%
15	Rhodamine B	3%
16	Rhodamine 6G	8%
17	Perylene	18%
18	2,4,6-triphenylpyrylium tetrafluoroborate	2%
19	10-phenyl-10 <i>H</i> -phenothiazine	4%
20	AQDS ^d	21%
21	[(^t Bu) ₂ Mes-PhAc]BF ₄	N.R. ^b
22	Rose bengal	46%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), photocatalyst (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), THF (1.5 mL),

r. t., Ar, 12 h, 30W blue LEDs; ^b N. R. = no reaction; ^c 3CzEPAIPN:



; ^d AQDS:

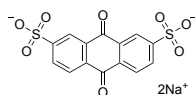
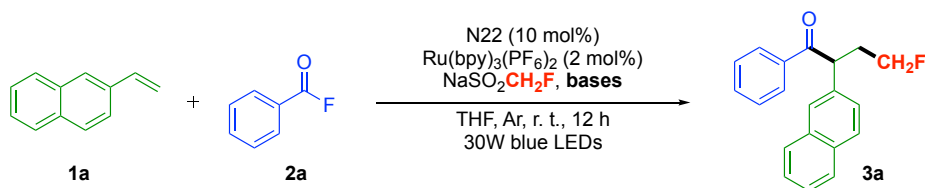


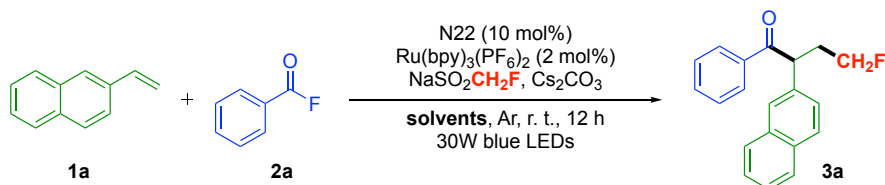
Table S3. Screening of bases^a



Entry	Bases	Isolated yield
1	Na ₂ CO ₃	42%
2	K ₂ CO ₃	45%
3	Rb ₂ CO ₃	52%
4	Cs₂CO₃	63%
5	CsOAc	32%
6	CsF	33%
7	KOAc	34%
8	DMAP	5%
9	Et ₃ N	19%
10	DBU	24%
11	Tetramethylguanidine	10%
12	Proton sponge	48%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), bases (0.3 mmol, 2.0 equiv.), THF (1.5 mL), r. t., Ar, 12 h, 30W blue LEDs.

Table S4. Optimization of solvents^a

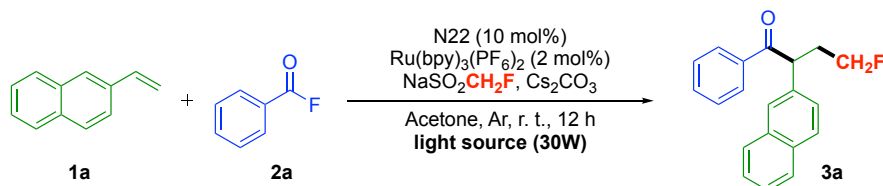


Entry	Solvents	Isolated yield
1	DCM	38%
2	DCE	51%
3	CH ₃ CN	47%
4	Toluene	31%
5	THF	63%
6	Dioxane	23%
7	DMF	30%
8	DMSO	41%
9	NMP	33%
10	PhCF ₃	34%
11	CH ₃ NO ₂	12%
12	Acetone	68%
13	THF: DMF = 3:1	49%

14	THF: Acetone = 1:1	56%
15	THF: Acetone = 3:1	53%
16	THF: Acetone = 1:3	62%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), solvent (1.5 mL), r. t., Ar, 12 h, 30W blue LEDs.

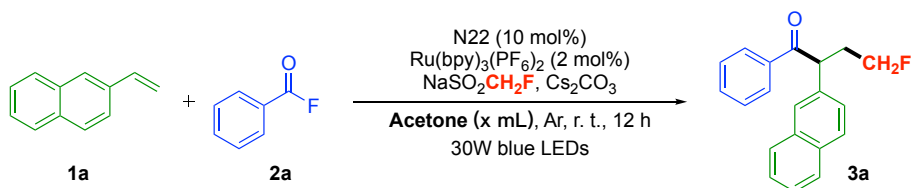
Table S5. Screening of light source^a



Entry	Light source	Isolated yield
1	Blue (455 nm)	68%
2	Purple (390 nm)	34%
3	Green (520 nm)	39%
4	CFL	49%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), acetone (1.5 mL), r. t., Ar, 12 h, light source (30W).

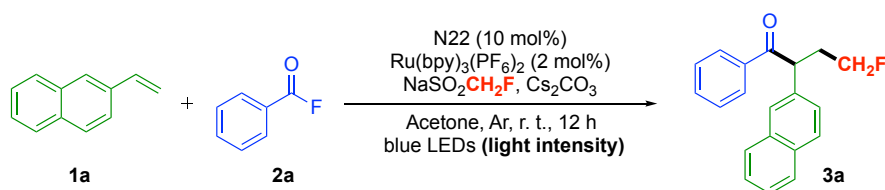
Table S6. Screening of reaction concentration^a



Entry	Acetone (x mL)	Isolated yield
1	1 mL	62%
2	1.5 mL	68%
3	2 mL	61%
4	3 mL	57%
5	4 mL	55%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), acetone (x mL), r. t., Ar, 12 h, 30W blue LEDs.

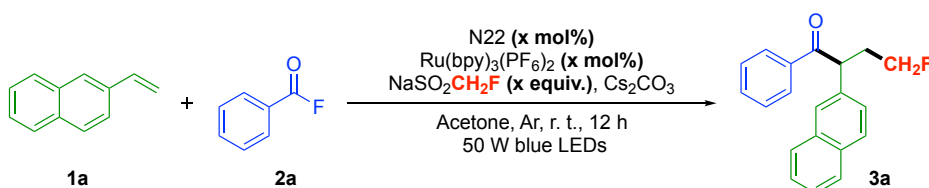
Table S7. Screening of light intensity^a



Entry	Light intensity	Isolated yield
1	5 W	52%
2	20 W	65%
3	30 W	68%
4	40 W	70%
5	50 W	73%
6	60 W	71%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), N22 (10 mol%), Ru(bpy)₃(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), acetone (1.5 mL), r. t., Ar, 12 h, blue LEDs.

Table S8. Screening of equivalents of N22, Ru(bpy)₃(PF₆)₂ and NaSO₂CH₂F^a



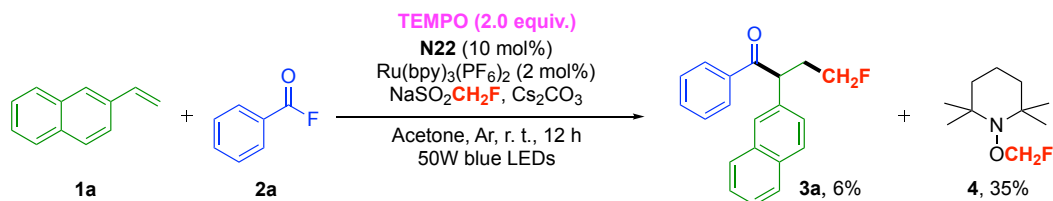
Entry	N22 (x mol%)	NaSO ₂ CH ₂ F (x equiv.)	Ru(bpy) ₃ (PF ₆) ₂ (x mol%)	Isolated yield
1	5	2.0	2	34%
2	20	2.0	2	66%
3	10	1.5	2	60%
4	10	2.5	2	65%
5	10	2.0	1	69%
6	10	2.0	3	68%
7	10	2.0	2	73%

^a Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (x equiv.), N22 (x mol%), Ru(bpy)₃(PF₆)₂ (x mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), acetone (1.5 mL), r. t., Ar, 12 h, blue LEDs.

5. Mechanistic studies

(1) Radical trapping experiment

a. Addition of TEMPO (2.0 equiv.) suppressed the transformation, and the desired product **3a** was obtained in 6% yield. TEMPO-CH₂F **4** adduct was detected in 35% yield by GCMS analysis (Figure S2).



According to the general procedure C, 2-vinylnaphthalene **1a** (0.15 mmol, 1.0 equiv.), benzoyl fluoride **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), NHC catalyst **N22** (10 mol%), Ru(bpy)₂(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), TEMPO (0.3 mmol, 2.0 equiv.) and acetone (1.5 mL) at room temperature for 12 h under 50 W blue LED irradiation with argon atmosphere. The reaction mixtures were analyzed by GCMS with *n*-dodecane as the internal standard.

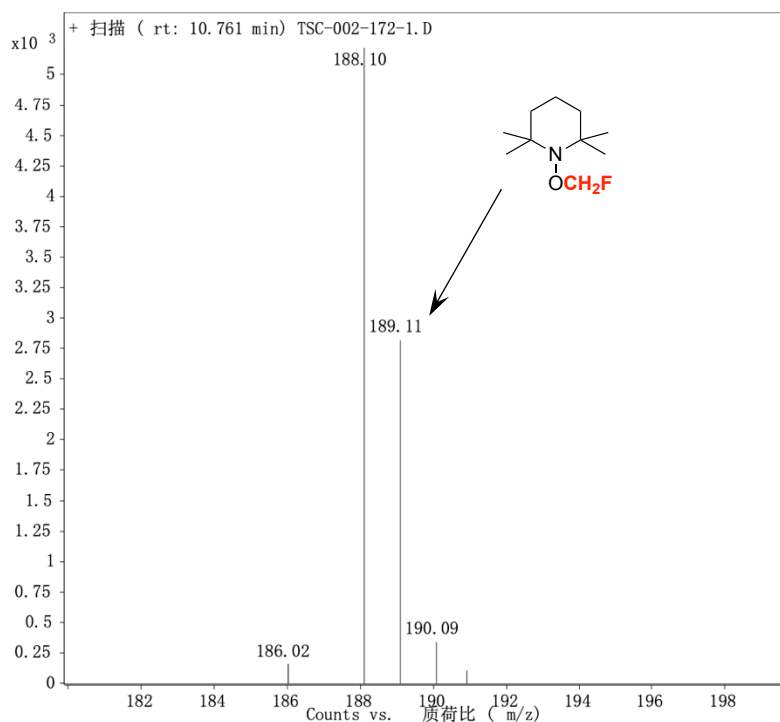
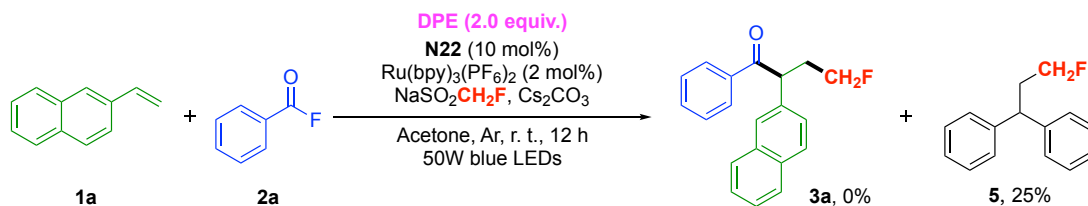


Figure S2. GC result of radical trapping experiment by TEMPO

b. Addition of diphenyl ethylene (DPE, 2.0 equiv.) completely shut down the desired transformation. The DPE trapping adduct **5** was obtained in 25% isolated yield.



According to the general procedure C, 2-vinylnaphthalene **1a** (0.15 mmol, 1.0 equiv.), benzoyl fluoride **2a** (0.3 mmol, 2.0 equiv.), NaSO₂CH₂F (0.3 mmol, 2.0 equiv.), NHC catalyst **N22** (10 mol%),

Ru(bpy)₂(PF₆)₂ (2 mol%), Cs₂CO₃ (0.3 mmol, 2.0 equiv.), DPE (0.3 mmol, 2.0 equiv.) and acetone (1.5 mL) at room temperature for 12 h under 50 W blue LED irradiation with argon atmosphere. The reaction mixtures were analyzed by GCMS with *n*-dodecane as the internal standard, and the product **5** was isolated by chromatography on silica gel (hexane: ethyl acetate = 250: 1) in 25% yield.

(2) EPR experiment

EPR spectra were recorded on a Bruker A300. Microcapillary with inner diameter 1 mm was used for analysis. The EPR instrumental settings was as follows: field sweep, 80G; microwave frequency, 9.85 GHz; microwave power, 2.22×10^{-1} mW; modulation amplitude, 0.8 G; conversion time 40 ms; time constant, 81.92 ms; sweep time 40.96 s; receiver gain, 1×10^4 ; resolution, 1024 points.

a. Procedure: In glovebox, to an oven-dried reaction tube equipped with NaSO₂CH₂F (0.1 mmol, 1.0 equiv.), Ru(bpy)₂(PF₆)₂ (2 mol%), PBN (*N*-benzylidene-*tert*-butylamineoxide) (0.2 mmol, 2.0 equiv.), acetone (1.0 mL) and a stir bar. The reaction mixture was brought out and stirred at room temperature for 30 min under 50 W blue LED irradiation with argon atmosphere and then rapid sampling analyzed by EPR (Figure S3).

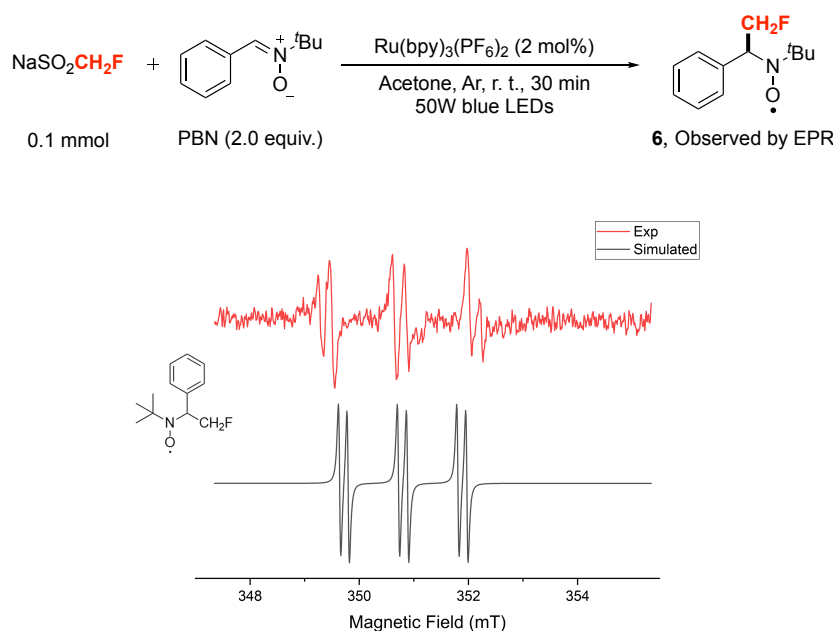


Figure S3. The X-band EPR spectrum (red line) of the radical **6** ($a_N = 13.7$ G, $a_H = 2.1$ G, g factor = 2.0064). The DFT simulated spectrum (black line) of the radical **6** based on hyperfine coupling constants of $a_N = 12.2$ G, $a_H = 1.8$ G and g factor = 2.0056.

b. Procedure: In glovebox, to an oven-dried reaction tube equipped with styrene (0.1 mmol, 1.0 equiv.), NaSO₂CH₂F (0.1 mmol, 1.0 equiv.), Ru(bpy)₂(PF₆)₂ (2 mol%), PBN (*N*-benzylidene-*tert*-butylamineoxide) (0.2 mmol, 2.0 equiv.), acetone (1.0 mL) and a stir bar. The reaction mixture was brought out and stirred at room temperature for 30 min under 50 W blue LED irradiation with argon atmosphere and then rapid sampling analyzed by EPR (Figure S4).

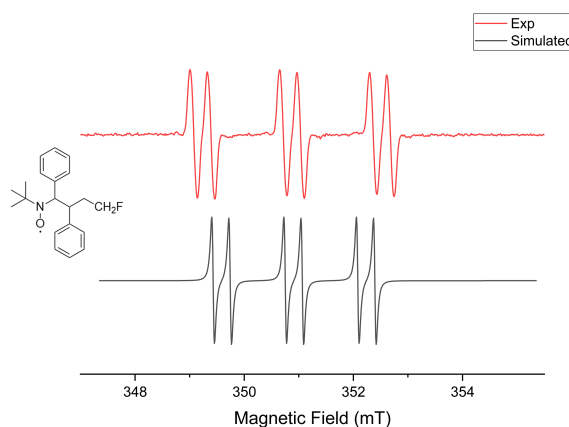
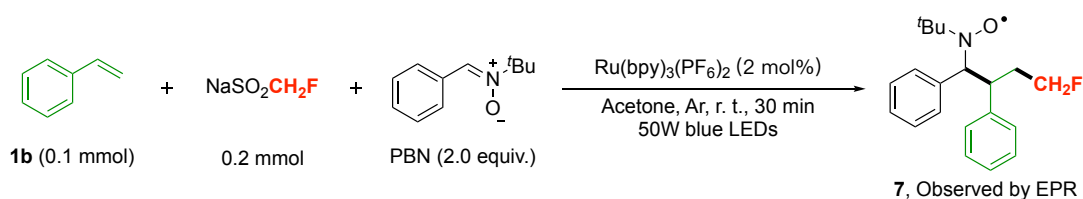
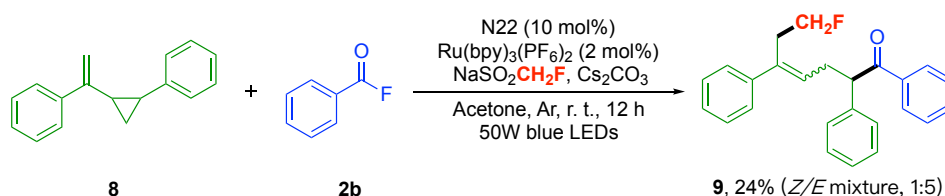


Figure S4. The X-band EPR spectrum (red line) of the radical **7** ($a_N = 14.3$ G, $a_H = 2.8$ G, g factor = 2.0062). The DFT simulated spectrum (black line) of radical **7** based on hyperfine coupling constants of $a_N = 13.3$ G, $a_H = 3.2$ G and g factor = 2.0058.

(3) Radical clock experiment

Radical clock probe **8** (0.3 mmol) underwent radical addition, ring-opening and radical cross-coupling, and the expected product **9** was isolated and purified by column chromatography on silica gel (hexane: EtOAc = 50: 1) in 24% yield as a mixture of *Z/E* stereoisomers with a ratio of 1:5. This strongly demonstrated that a radical pathway involved in the difunctionalization process.



(4) Light on/off experiments

Standard reactions were set up parallelly on a 0.3 mmol scale according to the general procedure for the preparation of **3a**. Yield was then determined by GCMS with *n*-dodecane as the internal standard. The reaction was irradiated with blue LEDs and kept in the dark in 2 h intervals at room temperature. The white area represents the light irradiation, while the grey area indicates time light-off. The reaction proceeded smoothly under the irradiation of blue LEDs, but no further transformation was observed without the light irradiation, showcasing that light is a necessary component for this catalytic reaction (Figure S5).

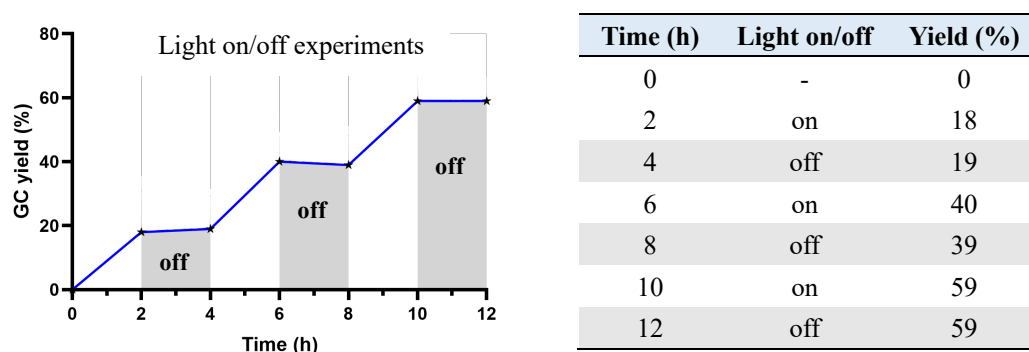
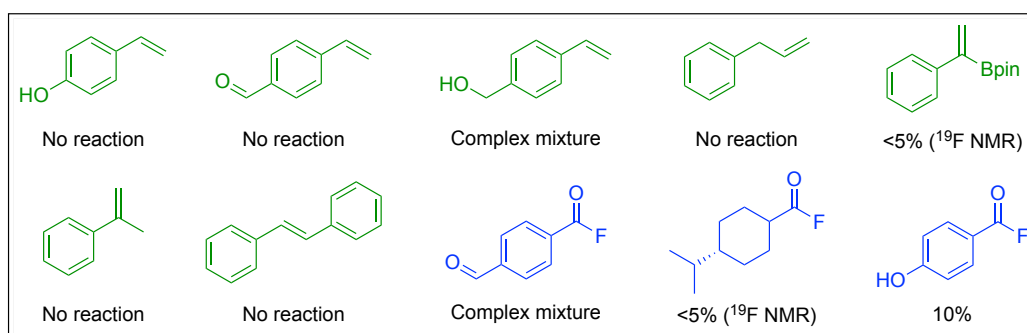


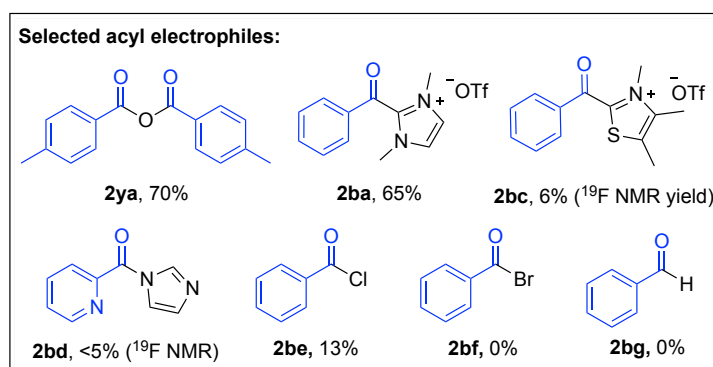
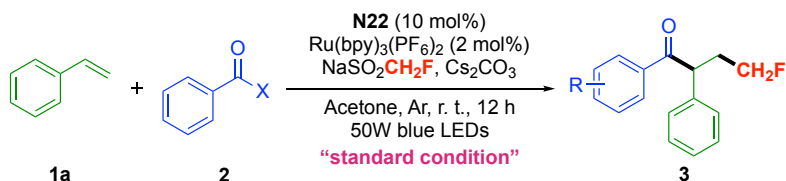
Figure S5. GC yield line chart of compound **3a** during light on-off experiments

6. Scope studies: less reactive substrates

The following compounds were employed using general procedure **C** and were analyzed by ^{19}F NMR using as an internal standard.



7. Acyl electrophile experiments

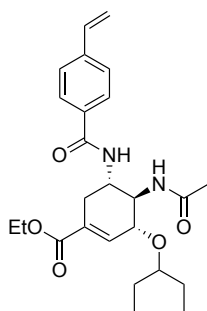


According to the general procedure **C**: In a glove box, to a glass tube equipped with a stir bar was charged styrene **1a** (0.3 mmol, 1.0 equiv.), acyl electrophiles **2** (0.6 mmol, 2.0 equiv.), $\text{NaSO}_2\text{CH}_2\text{F}$ (0.6 mmol, 2.0 equiv.), NHC catalyst **N22** (10 mol%), $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (2 mol%), Cs_2CO_3 (0.6 mmol, 2.0 equiv.), and acetone (3 mL). The tube was capped and brought out. The reaction mixture was then stirred at room temperature for 12 h under 50 W blue LED irradiation with argon atmosphere. The mixture was

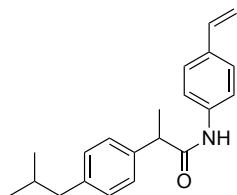
diluted with diethyl ether, washed with water. The combined organic fractions were dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired product.

Acetic anhydride **2ya**, acyl imidazolium salt **2ba** were successfully yield the difunctionalized product of styrene in 70% and 65% isolated yield respectively, which demonstrated that these two compounds were possible intermediate in the transformation process. Meanwhile, acyl thiazolium salt **2bc**, acyl imidazole **2bd** and acyl chloride **2be** showcased a relatively low reaction efficiency, and acyl bromide **2bf** and benzaldehyde **2bg** were not the appropriate substrate to achieve the catalytic reaction.

8. Synthesis of substrates and characterization data

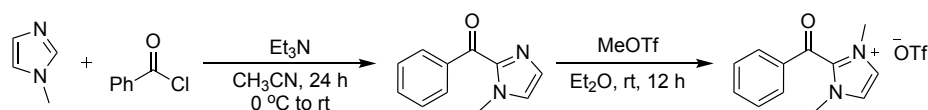


1al: Ethyl (3R,4R,5S)-4-acetamido-3-(pentan-3-yloxy)-5-(4-vinylbenzamido)cyclohex-1-ene-1-carboxylate. A solution of Oseltamivir phosphate (2 mmol, 1.0 equiv.), 4-vinylbenzoic acid (2.4 mmol, 1.2 equiv.), HATU (2.4 mmol, 1.2 equiv.) and Et₃N (8 mmol, 4.0 equiv.) in DCM (30 mL) was stirred at room temperature for 12 h. The reaction mixture was quenched with water and extracted with DCM. The separated organic layers were evaporated to dryness and the resulting residue was purified by column chromatography (hexane: ethyl acetate = 10: 1) to afford compound **1al** as white solid (772 mg, 87% yield). ¹H NMR (400 MHz, MeOD-*d*₄): δ 7.75 -7.73 (m, 2H), 7.52 – 7.50 (m, 2H), 6.83 – 6.75 (m, 2H), 5.89 (dd, *J* = 17.6, 0.6 Hz, 1H), 5.35 (dd, *J* = 11.0, 0.6 Hz, 1H), 4.34 – 4.19 (m, 4H), 4.09 – 4.04 (m, 1H), 6.45 (pent. 1H), 2.81 – 2.75 (m, 1H), 2.49 – 2.41 (m, 1H), 1.86 (s, 3H), 1.58 – 1.48 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm; ¹³C NMR (151 MHz, MeOD-*d*₄): δ 174.0, 169.8, 167.5, 142.3, 139.1, 137.2, 134.6, 130.4, 128.7, 127.3, 116.4, 83.9, 77.0, 62.1, 55.9, 50.0, 31.3, 27.4, 26.9, 22.8, 14.5, 9.89, 9.68 ppm.

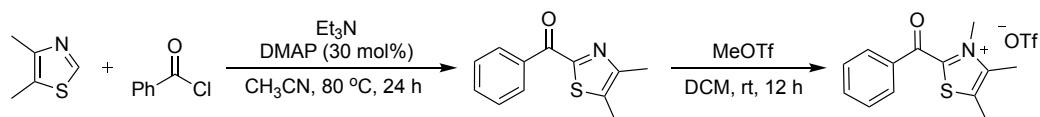


1ao: 2-(4-isobutylphenyl)-N-(4-vinylphenyl)propenamide. A solution of Ibuprofen (2 mmol, 1.0 equiv.), 4-vinylaniline (2.2 mmol, 1.1 equiv.), EDC (4 mmol, 2 equiv.), and DMAP (0.2 mmol, 0.1 equiv.) in DCM (20 mL) was stirred at room temperature for 12 h. The reaction mixture was quenched with water and extracted with DCM. The separated organic layers were evaporated to dryness and the resulting residue was purified by column chromatography (hexane: ethyl acetate = 15: 1) to afford compound **1ad** as white solid (562 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃): 7.4 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 5.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H),

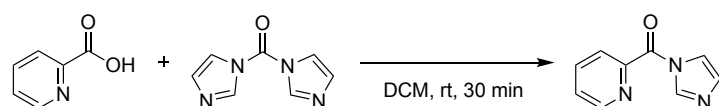
7.03 (brs, 1H), 6.67 – 6.60 (m, 1H), 5.65 (d, $J = 17.6$ Hz, 1H), 5.17 (d, $J = 10.9$ Hz, 1H), 3.69 (q, $J = 7.1$ Hz, 1H), 2.47 (d, $J = 7.2$ Hz, 2H), 1.92 – 1.81 (hept. 1H), 1.58 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H) ppm.



2ba: 2-Benzoyl-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate. Following a reported procedure,³ to a round-bottom flask was added with 1-methylimidazole (5 mmol) and acetonitrile (5 mL). The stirred reaction solution was then cooled to 0 °C and benzoyl chloride (5 mmol) was added by a dropping funnel, followed by the addition of Et₃N (5 mmol). The reaction mixture was continued stirring at room temperature for 24 h. The precipitated solid was filtered off and the solvents was evaporated to dryness. The crude product purified by column chromatography on silica gel (hexane: EtOAc = 15: 1) to give the target compound. To the above product was added diethyl ether and methyl triflate (1.1 equiv.) at room temperature and the reaction was stirred overnight. The resulting white precipitate was filtered off, washed with diethyl ether and dried to afford the corresponding product as a white solid (1.3g, 71% in two steps). ¹H NMR (400 MHz, CDCl₃): δ 8.01 – 8.00 (m, 2H), 7.83 – 7.78 (m, 3H), 7.68 – 7.64 (m, 2H), 3.88 (s, 6H) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.5 ppm.



2bc: 2-Benzoyl-3,4,5-trimethylthiazol-3-ium trifluoromethanesulfonate. Following a reported procedure,⁴ to a solution of 4,5-dimethylthiazole (5 mmol), DMAP (30 mol%) in CH₃CN (10 mL) was added Et₃N (3 equiv.) and benzoyl chloride (2 equiv.) under Ar atmosphere. The reaction mixture was heated at 80 °C for 24 h. Cooled the mixture to room temperature, diluted with EtOAc and sat. NaHCO₃ and extracted with EtOAc. The combined organic layers were concentrated to dryness. The crude product was purified by column chromatography on silica gel (hexane: EtOAc = 7: 1) to yield the target compound. To the above product was added anhydrous DCM and methyl triflate (1.1 equiv.) at room temperature and the reaction was stirred overnight. The solution was concentrated to half of its volume and then Et₂O was added to precipitate a white solid. The solid was filtered off, washed with Et₂O and dried in vacuo to give the title compound as a white solid (990.7 mg, 52%). ¹H NMR (400 MHz, CDCl₃): δ 7.97 -7.95 (m, 2H), 7.71 – 7.67 (m, 1H), 7.53 – 7.49 (m, 2H), 4.15 (s, 3H), 2.54 (s, 3H), 2.52 (s, 3H) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.5 ppm.

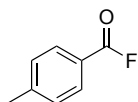


2bd: (1H-Imidazol-1-yl) (pyridin-2-yl)methanone. To a solution of picolinic acid (986 mg, 8.0 mmol, 1.0 equiv.) in dry DCM (10 mL) was added *N,N'*-carbonyldiimidazole (1.96 g, 9.6 mmol,

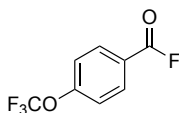
³ Meng, Q.-Y.; Döben, N.; Studer, A. Cooperative NHC and photoredox catalysis for the synthesis of β-trifluoromethylated alkyl aryl ketones. *Angew. Chem. Int. Ed.* **2020**, *59*, 19956-19960.

⁴ Lassalas, P.; Marsais, F.; Hoarau, C. DMAP-catalyzed Regel-type direct C-2 (hetero)arylation of oxazoles and thiazoles derivatives with acid chlorides. *Synlett*, **2013**, *24*, 2233-2240.

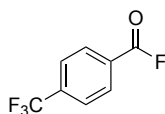
1.2 equiv.) in portions. After stirring for 30 mins at room temperature, water was added to the reaction mixture. The separated organic layer was evaporated to dryness and purified by column chromatography on silica gel (hexane: EtOAc = 40: 1) to provide **2bd** as yellow oil (720 mg, 52%). **¹H NMR (400 MHz, CDCl₃):** δ 8.82 (s, 1H), 8.64 – 8.63 (m, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.49 – 7.46 (m, 1H), 7.02 – 7.00 (m, 1H) ppm.



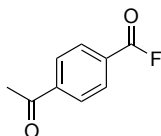
2y: 4-Methylbenzoyl fluoride. Prepared according to the general procedure **A** and purified by column chromatography (hexane). Clear oil (209.8 mg, 38% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ 17.4 ppm. Spectroscopic data are in accordance with those described in literature.²



2z: 4-(Trifluoromethoxy)benzoyl fluoride. Prepared according to the general procedure **A** and purified by column chromatography (hexane). Clear oil (316.2 mg, 38% yield). **¹H NMR (400 MHz, CDCl₃):** δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ 18.7, -57.6 ppm. Spectroscopic data are in accordance with those described in literature.⁵



2aa: 4-(Trifluoromethyl)benzoyl fluoride. Prepared according to the general procedure **A** and purified by column chromatography (hexane). Clear oil (276.5 mg, 36% yield). **¹H NMR (400 MHz, CDCl₃):** δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ 20.0, -63.5 ppm. Spectroscopic data are in accordance with those described in literature.⁶

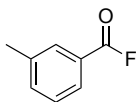


2ab: 4-Acetylbenzoyl fluoride. Prepared according to the general procedure **A** and purified by column chromatography (hexane). White solid (219.1 mg, 33% yield). **¹H NMR (400 MHz, CDCl₃):** δ 8.16 – 8.14 (m, 2H), 8.09 – 8.06 (m, 2H), 2.67 (s, 3H) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ 20.2 ppm. Spectroscopic data are in accordance with those described in literature.⁷

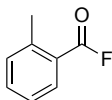
⁵ Liang, Y.; Zhao, Z.; Taya, A.; Shibata, N. Acyl Fluorides from Carboxylic Acids, Aldehydes, or Alcohols under Oxidative Fluorination. *Org. Lett.* **2021**, *23*, 847-852.

⁶ Wang, Z.; Wang, X.; Nishihara, Y. Nickel-Catalysed Decarbonylative Borylation of Aryl Fluorides. *Chem. Commun.* **2018**, *54*, 13969-13972.

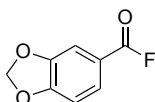
⁷ Munoz, S.; Dang, H.; Ispizua-Rodriguez, X.; Mathew, T. Prakash, G. K. S. Direct Access to Acyl Fluorides from Carboxylic Acids Using a Phosphine/Fluoride Deoxyfluorination Reagent System. *Org. Lett.* **2019**, *21*, 1659-1663.



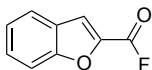
2ae: 3-Methylbenzoyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). Clear oil (193.2 mg, 35% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, $J = 7.4$ Hz, 2H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 2.43 (s, 3H) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 18.2 ppm. Spectroscopic data are in accordance with those described in literature.²



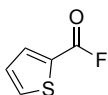
2af: 2-Methylbenzoyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). Clear oil (182.2 mg, 33% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01 – 7.99 (m, 1H), 7.57 – 7.53 (m, 1H), 7.35 – 7.31 (m, 2H), 2.66 (d, $J = 1.8$ Hz, 3H) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 29.2 ppm. Spectroscopic data are in accordance with those described in literature.⁸



2ag: Benzo[d][1,3]dioxole-5-carbonyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). White solid (275.5 mg, 41% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.67 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.42 (d, $J = 1.6$ Hz, 1H), 6.91 – 6.89 (m, 1H), 6.10 (s, 2H) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 16.4 ppm. Spectroscopic data are in accordance with those described in literature.²



2ah: Benzofuran-2-carbonyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). White solid (249.3 mg, 38% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.77 – 7.74 (m, 2H), 7.64 – 7.62 (m, 1H), 7.58 – 7.54 (m, 1H), 7.40 – 7.36 (m, 1H) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 17.4 ppm. Spectroscopic data are in accordance with those described in literature.⁹

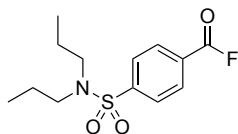


2ai: Thiophene-2-carbonyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). Clear oil (166.2 mg, 33% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3):

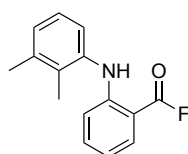
⁸ Mavroskoufis, A.; Rajes, K.; Golz, P.; Agrawal, A.; Ruß, V.; Götze, J. P.; Hopkinson, M. N. *N*-Heterocyclic Carbene Catalyzed Photoenolization/Diels–Alder Reaction of Acid Fluorides. *Angew. Chem. Int. Ed.* **2020**, *59*, 3190–3194.

⁹ Malapit, C. A.; Bour, J. R.; Beigham, C. E.; Sanford, M. S. Based-free Nickel-Catalysed Decarbonylative Suzuki–Miyaura Coupling of Acid Fluorides. *Nature*, **2018**, *563*, 100–104.

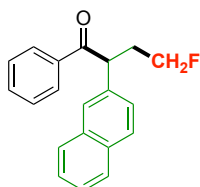
δ 7.95 (dd, $J = 3.9, 1.2$ Hz, 1H), 7.82 – 7.80 (m, 1H), 7.22 – 7.20 (m, 1H) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ 24.3 ppm. Spectroscopic data are in accordance with those described in literature.²



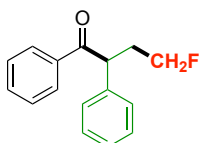
2aq: 4-(*N,N*-dipropylsulfamoyl)benzoyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). White solid (413.3 mg, 36% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, $J = 8.5$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 2H), 3.12 (t, $J = 7.7$ Hz, 4H), 1.56 (q, $J = 7.6$ Hz, 4H), 0.87 (t, $J = 7.4$ Hz, 6H) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ 20.2 ppm. Spectroscopic data are in accordance with those described in literature.⁵



2ar: 2-((2,3-Dimethylphenyl)amino)benzoyl fluoride. Prepared according to the general procedure A and purified by column chromatography (hexane). Yellow solid (349.9 mg, 36% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.64 (brs, 1H), 7.84 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.36 -7.32 (m, 1H), 7.17 – 7.09 (m, 3H), 6.72 – 6.65 (m, 2H), 2.34 (s, 3H), 2.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 159.3 (d, $J = 337.5$ Hz), 151.8 (d, $J = 10.5$ Hz), 138.7, 137.5, 136.9, 133.5, 132.6, 128.2, 126.4, 124.4, 116.6, 113.7 (d, $J = 3.9$ Hz), 104.9 (d, $J = 52.2$), 20.7, 14.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ 19.9 ppm.

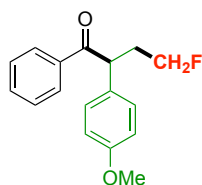


3a: 4-Fluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Colorless oil (63.8 mg, 73% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.03 – 8.00 (m, 2H), 7.82 – 7.77 (m, 4H), 7.48 – 7.42 (m, 4H), 7.39 – 7.35 (m, 2H), 5.02 (t, $J = 7.4$ Hz, 1H), 4.59 – 4.31 (m, 2H), 2.74 – 2.60 (m, 1H), 2.35 – 2.19 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.2, 136.5, 136.1, 133.8, 133.2, 132.7, 129.2, 129.0, 128.7, 127.9, 127.8, 127.5, 126.5, 126.22, 126.18, 81.9 (d, $J = 164.4$ Hz), 49.2 (d, $J = 3.0$ Hz), 34.5 (d, $J = 19.6$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{20}\text{H}_{17}\text{FONa}$ [$\text{M}+\text{Na}$] $^+$: 315.1156; found: 315.1149.

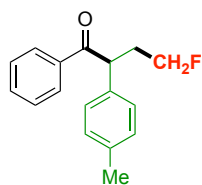


3b: 4-Fluoro-1,2-diphenylbutan-1-one. Prepared according to the general procedure C and

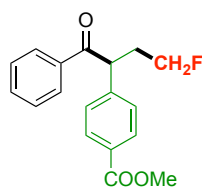
purified by column chromatography (hexane: ethyl acetate = 100: 1). Colorless oil (51.4 mg, 71% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.25 (m, 4H), 7.20 – 7.14 (m, 1H), 4.80 (t, *J* = 7.4 Hz, 1H), 4.50 – 4.22 (m, 2H), 2.60 – 2.46 (m, 1H), 2.20 – 2.04 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 199.2, 138.6, 136.5, 133.2, 129.3, 128.9, 128.7, 128.5, 127.5, 81.9 (d, *J* = 164.6 Hz), 49.1 (d, *J* = 3.2 Hz), 34.5 (d, *J* = 19.4 Hz) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₆H₁₅FO₂Na [M+Na]⁺: 265.0999; found: 265.0999.



3c: 4-Fluoro-2-(4-methoxyphenyl)-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Colorless oil (37.6 mg, 46% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.37 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 4.80 (t, *J* = 7.3 Hz, 1H), 4.56 – 4.28 (m, 2H), 3.75 (s, 3H), 2.62 – 2.48 (m, 1H), 2.22 – 2.07 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 199.4, 158.9, 136.5, 136.6, 133.1, 130.5, 129.5, 128.9, 128.7, 114.7, 81.9 (d, *J* = 164.3 Hz), 55.3, 48.2 (d, *J* = 3.0 Hz), 34.5 (d, *J* = 19.4 Hz) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₇H₁₇FO₂Na [M+Na]⁺: 295.1105; found: 295.1110.

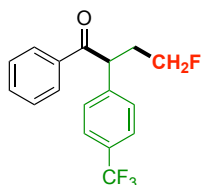


3d: 4-fluoro-1-phenyl-2-(p-tolyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (52.9 mg, 69% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.36 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.82 (t, *J* = 7.4 Hz, 1H), 4.56 – 4.29 (m, 2H), 2.64 – 2.49 (m, 1H), 2.29 (s, 3H), 2.24 – 2.08 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 199.4, 137.2, 136.6, 135.5, 133.1, 130.0, 128.9, 128.6, 128.3, 81.9 (d, *J* = 164.4 Hz), 48.7 (d, *J* = 3.3 Hz), 34.5 (d, *J* = 19.3 Hz), 21.1 ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₇H₁₈FO₂Na [M+Na]⁺: 279.1156; found: 279.1159.

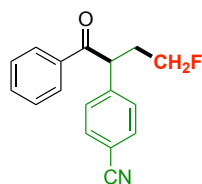


3e: Methyl-4-(4-fluoro-1-oxo-1-phenylbutan-2-yl)benzoate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (62.8 mg, 70% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.99 – 7.93 (m, 4H), 7.51 – 7.47 (m, 1H),

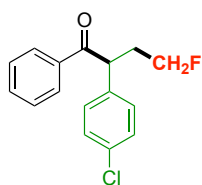
7.41 – 7.36 (m, 4H), 4.92 (t, $J = 7.3$ Hz, 1H), 4.56 – 4.26 (m, 2H), 3.87 (s, 3H), 2.68 – 2.54 (m, 1H), 2.25 – 2.09 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.6, 166.8, 143.8, 136.3, 133.4, 130.5, 129.4, 128.9, 128.8, 128.5, 81.6 (d, $J = 165.1$ Hz), 52.2, 49.1 (d, $J = 3.1$ Hz), 34.4 (d, $J = 19.4$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{17}\text{FO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 323.1054; found: 323.1048.



3f: 4-Fluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (64.1 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.97 – 7.95 (m, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.40 (m, 4H), 5.00 (t, $J = 7.4$ Hz, 1H), 4.57 – 4.27 (m, 2H), 2.69 – 2.55 (m, 1H), 2.26 – 2.10 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.6, 142.6, 136.2, 133.6, 130.1, 129.8 (q, $J = 32.8$ Hz), 129.2, 128.9, 126.2 (q, $J = 3.7$ Hz), 124.1 (q, $J = 273.2$ Hz), 81.6 (d, $J = 165.2$ Hz), 48.8 (d, $J = 2.9$ Hz), 34.5 (d, $J = 19.4$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -62.6, -221.5 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_4\text{ONa}$ $[\text{M}+\text{Na}]^+$: 333.0873; found: 333.0872.

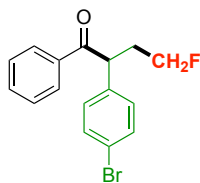


3g: 4-(4-Fluoro-1-oxo-1-phenylbutan-2-yl)benzotrile. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 30: 1). Yellow oil (52.1 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.94 – 7.92 (m, 2H), 7.62 – 7.60 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.40 (m, 4H), 4.94 (t, $J = 7.4$ Hz, 1H), 4.56 – 4.25 (m, 2H), 2.68 – 2.54 (m, 1H), 2.24 – 2.08 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.2, 144.0, 136.0, 133.7, 133.0, 129.3, 128.9, 128.8, 118.6, 111.6, 81.4 (d, $J = 165.5$ Hz), 48.9 (d, $J = 2.9$ Hz), 34.4 (d, $J = 19.6$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$: 268.1132; found: 268.1136.

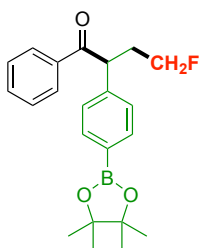


3h: 2-(4-Chlorophenyl)-4-fluoro-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (40.1 mg, 48% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, $J = 7.4$ Hz, 2H), 7.52 – 7.49 (m, 1H), 7.41 – 7.38 (m, 2H), 7.29 – 7.24 (m, 4H), 4.84 (t, $J = 7.4$ Hz, 1H), 4.56 – 4.26 (m, 2H), 2.64 –

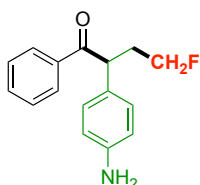
2.49 (m, 1H), 2.21 – 2.06 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.9, 137.0, 136.3, 133.5, 133.4, 129.8, 129.5, 128.9, 128.8, 81.7 (d, $J = 164.8$ Hz), 48.3 (d, $J = 3.2$ Hz), 34.4 (d, $J = 19.3$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{14}\text{FClONa}$ $[\text{M}+\text{Na}]^+$: 299.0609; found: 299.0605.



3i: 2-(4-Bromophenyl)-4-fluoro-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (63.2 mg, 66% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, $J = 7.6$ Hz, 2H), 7.53 – 7.49 (m, 1H), 7.44 – 7.38 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 2H), 4.83 (t, $J = 7.4$ Hz, 1H), 4.56 – 4.26 (m, 2H), 2.64 – 2.49 (m, 1H), 2.24 – 1.99 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.8, 137.6, 136.2, 133.4, 132.4, 130.2, 128.9, 128.8, 121.6, 81.6 (d, $J = 164.9$ Hz), 48.4 (d, $J = 3.2$ Hz), 34.4 (d, $J = 19.4$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{14}\text{FBrONa}$ $[\text{M}+\text{Na}]^+$: 343.0104; found: 343.0115.

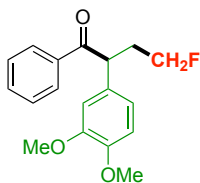


3j: 4-Fluoro-1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (60.5 mg, 55% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.95 – 7.93 (m, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.49 – 7.45 (m, 1H), 7.38 – 7.31 (m, 4H), 4.85 (t, $J = 7.3$ Hz, 1H), 4.55 – 4.27 (m, 2H), 2.66 – 2.51 (m, 1H), 2.24 – 2.08 (m, 1H), 1.31 (s, 12H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.0, 141.8, 136.5, 135.7, 133.2, 128.9, 128.7 (overlapped), 127.9, 84.0, 81.8 (d, $J = 164.4$ Hz), 49.4 (d, $J = 3.2$ Hz), 34.4 (d, $J = 19.6$ Hz), 24.98, 24.95 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{22}\text{H}_{26}\text{BFO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 391.1851; found: 391.1848.

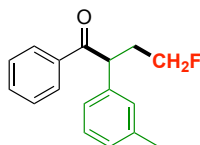


3k: 2-(4-Aminophenyl)-4-fluoro-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 10: 1). Yellow oil (40.7 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.97 – 7.94 (m, 2H), 7.49 – 7.45 (m, 1H), 7.39 – 7.35 (m, 2H), 7.09 – 7.07 (m, 2H), 6.63 – 6.60 (m, 2H), 4.73 (t, $J = 7.4$ Hz, 1H), 4.55 – 4.29

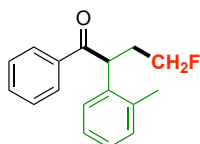
(m, 2H), 3.48 (brs, 2H), 2.59 – 2.44 (m, 1H), 2.21 – 2.04 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.6, 145.5, 136.7, 133.0, 129.4, 128.9, 128.6, 128.3, 115.9, 82.0 (d, $J = 163.9$ Hz), 48.3 (d, $J = 3.1$ Hz), 34.4 (d, $J = 19.4$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{17}\text{FNO}$ $[\text{M}+\text{H}]^+$: 258.1289; found: 258.1282.



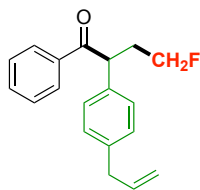
3l: 2-(3,4-Dimethoxyphenyl)-4-fluoro-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 20: 1). Yellow oil (50.5 mg, 56% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.97 – 7.795 (m, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.36 (m, 2H), 6.87 – 6.85 (m, 1H), 6.80 – 6.78 (m, 2H), 4.78 (t, $J = 7.4$ Hz, 1H), 4.55 – 4.30 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 2.61 – 2.47 (m, 1H), 2.23 – 2.07 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.4, 149.5, 148.4, 136.6, 133.1, 130.9, 128.8, 128.6, 121.0, 111.6, 111.0, 81.9 (d, $J = 164.3$ Hz), 56.0, 55.9, 48.6 (d, $J = 3.1$ Hz), 34.4 (d, $J = 19.3$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{20}\text{FO}_3$ $[\text{M}]^+$: 303.1391; found: 303.1399.



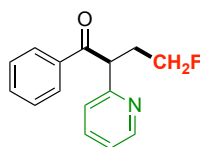
3m: 4-Fluoro-1-phenyl-2-(*m*-tolyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (45.1 mg, 59% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.00 – 7.97 (m, 2H), 7.51 – 7.46 (m, 1H), 7.41 – 7.37 (m, 2H), 7.22 – 7.18 (m, 1H), 7.13 – 7.11 (m, 2H), 7.04 – 7.02 (m, 1H), 4.82 (t, $J = 7.4$ Hz, 1H), 4.55 – 4.29 (m, 2H), 2.64 – 2.50 (m, 1H), 2.31 (s, 3H), 2.23 – 2.09 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.3, 139.0, 138.5, 136.6, 133.1, 129.1, 128.9, 128.7, 128.3, 125.6, 81.9 (d, $J = 164.4$ Hz), 49.0 (d, $J = 3.1$ Hz), 34.5 (d, $J = 19.4$ Hz), 21.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{17}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 279.1156; found: 279.1151.



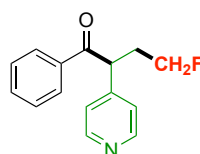
3n: 4-Fluoro-1-phenyl-2-(*o*-tolyl)butan-1-one. Prepared according to the general procedure and purified C by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (41.3 mg, 54% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 7.6$ Hz, 2H), 7.49 – 7.45 (m, 1H), 7.38 – 7.35 (m, 2H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.15 – 7.05 (m, 3H), 4.99 (t, $J = 7.1$ Hz, 1H); 4.57 – 4.33 (m, 2H), 2.67 – 2.57 (m, 1H), 2.55 (s, 3H), 2.14 – 1.99 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 200.0, 137.5, 136.9, 135.6, 133.0, 131.3, 128.7, 128.6, 127.4, 126.9, 82.2 (d, $J = 163.9$ Hz), 45.4 (d, $J = 2.8$ Hz), 34.2 (d, $J = 19.7$ Hz), 19.7 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -219.7 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{17}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 279.1156; found: 279.1154.



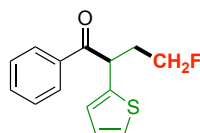
3o: 2-(4-Allylphenyl)-4-fluoro-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (47.6 mg, 56% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.98 – 7.96 (m, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.37 (m, 2H), 7.25 – 7.23 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 5.97 – 5.86 (m, 1H), 5.07 – 5.06 (m, 1H), 5.03 – 5.02 (m, 1H), 4.83 (t, J = 7.4 Hz, 1H), 4.55 – 4.28 (m, 2H), 3.33 (d, J = 6.8 Hz, 2H), 2.64 – 2.49 (m, 1H), 2.24 – 2.08 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.3, 139.3, 137.2, 136.6, 136.3, 133.1, 129.4, 128.9, 128.7, 128.5, 116.1, 81.9 (d, J = 164.3 Hz), 48.7 (d, J = 3.3 Hz), 39.9, 34.5 (d, J = 19.3 Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{19}\text{H}_{19}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 305.1312; found: 305.1304.



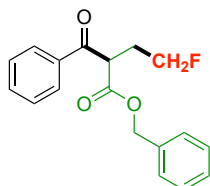
3p: 4-Fluoro-1-phenyl-2-(pyridin-2-yl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 10: 1). Yellow oil (47.3 mg, 65% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.55 (m, 1H), 8.04 – 8.02 (m, 2H), 7.64 – 7.60 (m, 1H), 7.51 – 7.47 (m, 1H), 7.41 – 7.37 (m, 2H), 7.30 (d, J = 7.8 Hz, 1H), 7.15 – 7.12 (m, 1H), 5.10 (t, J = 7.3 Hz, 1H), 4.59 – 4.34 (m, 2H), 2.74 – 2.59 (m, 1H), 2.39 – 2.20 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.3, 158.7, 150.1, 137.3, 136.5, 133.3, 129.1, 128.7, 122.9, 122.3, 82.0 (d, J = 165.4 Hz), 52.0 (d, J = 3.4 Hz), 33.4 (d, J = 19.6 Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -220.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{15}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$: 244.1132; found: 244.1123.



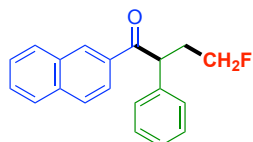
3q: 4-Fluoro-1-phenyl-2-(pyridin-4-yl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 10: 1). Yellow oil (49.7 mg, 68% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.55 (d, J = 5.5 Hz, 2H), 7.95 – 7.93 (m, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.40 (m, 2H), 7.29 (d, J = 5.9 Hz, 2H), 4.88 (t, J = 7.3 Hz, 1H), 4.57 – 4.27 (m, 2H), 2.68 – 2.54 (m, 1H), 2.24 – 2.09 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.0, 150.3, 148.1, 136.0, 133.8, 128.9, 128.8, 123.8, 81.4 (d, J = 165.6 Hz), 48.4 (d, J = 2.9 Hz), 34.2 (d, J = 19.4 Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{15}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$: 244.1132; found: 244.1126.



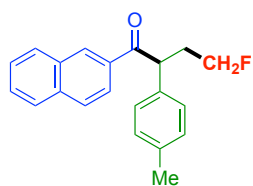
3r: 4-Fluoro-1-phenyl-2-(thiophen-2-yl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (43.1 mg, 58% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03 – 8.01 (m, 2H), 7.56 – 7.52 (m, 1H), 7.46 – 7.42 (m, 2H), 7.21 – 7.19 (m, 1H), 6.96 – 6.92 (m, 2H), 5.19 (t, $J = 7.4$ Hz, 1H), 4.58 – 4.36 (m, 2H), 2.66 – 2.51 (m, 1H), 2.33 – 2.18 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.1, 140.6, 136.1, 133.5, 128.9, 128.8, 127.2, 126.4, 125.5, 81.6 (d, $J = 164.9$ Hz), 43.6 (d, $J = 3.4$ Hz), 35.3 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.6 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{14}\text{H}_{13}\text{FOSNa}$ $[\text{M}+\text{Na}]^+$: 271.0563; found: 271.0566.



3s: Benzyl-2-benzoyl-4-fluorobutanoate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (31.3 mg, 35% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00 – 7.97 (m, 2H), 7.61 – 7.57 (m, 1H), 7.48 – 7.44 (m, 2H), 7.30 – 7.28 (m, 3H), 7.21 – 7.18 (m, 2H), 5.13 (s, 2H), 4.66 (t, $J = 7.0$ Hz, 1H), 4.62 – 4.44 (m, 2H), 2.48 – 2.43 (m, 1H), 2.41 – 2.37 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 194.6, 169.4, 136.0, 135.3, 133.9, 128.94, 128.90, 128.7, 128.5, 128.2, 81.7 (d, $J = 165.9$ Hz), 67.5, 49.9 (d, $J = 3.2$ Hz), 29.9 (d, $J = 19.5$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -220.7 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{17}\text{FO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 323.1054; found: 323.1051.

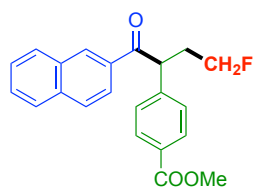


3t: 4-Fluoro-1-(naphthalen-2-yl)-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (44.4 mg, 51% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.51 (s, 1H), 8.03 – 8.01 (m, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.83 – 7.81 (m, 2H), 7.58 – 7.49 (m, 2H), 7.39 – 7.37 (m, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.19 (m, 1H), 5.02 (t, $J = 7.4$ Hz, 1H), 4.61 – 4.33 (m, 2H), 2.72 – 2.58 (m, 1H), 2.31 – 2.16 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.2, 138.7, 135.6, 133.9, 132.6, 130.8, 129.8, 129.3, 128.7, 128.53, 128.49, 127.8, 127.5, 126.8, 124.6, 82.0 (d, $J = 164.4$ Hz), 49.2 (d, $J = 3.2$ Hz), 34.6 (d, $J = 19.5$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{20}\text{H}_{17}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 315.1156; found: 315.1149.

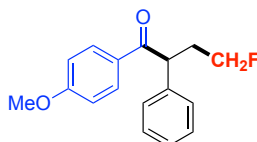


3u: 4-Fluoro-1-(naphthalen-2-yl)-2-(p-tolyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil

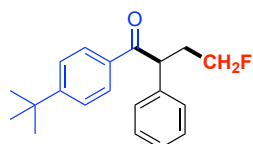
(40.5 mg, 44% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.50 (s, 1H), 8.02 – 8.00 (m, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.80 (m, 2H), 7.57 – 7.49 (m, 2H), 7.26 – 7.24 (m, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 4.97 (t, $J = 7.3$ Hz, 1H), 4.59 – 4.32 (m, 2H), 2.70 – 2.55 (m, 1H), 2.26 (s, 3H), 2.24 – 2.13 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.3, 137.2, 135.64, 135.59, 133.9, 132.6, 130.7, 130.0, 129.8, 128.6, 128.5, 128.3, 127.8, 126.8, 124.6, 82.0 (d, $J = 164.1$ Hz), 48.8 (d, $J = 3.0$ Hz), 34.5 (d, $J = 19.3$ Hz), 21.1 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{20}\text{H}_{19}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 329.1312; found: 329.1315.



3v: Methyl-4-(4-fluoro-1-(naphthalen-2-yl)-1-oxobutan-2-yl)benzoate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 30: 1). Yellow oil (47.4 mg, 45% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.48 (s, 1H), 8.01 – 7.97 (m, 3H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.81 (m, 2H), 7.59 – 7.50 (m, 2H), 7.47 – 7.45 (m, 2H), 5.09 (t, $J = 7.3$ Hz, 1H), 4.61 – 4.31 (m, 2H), 3.87 (s, 3H), 2.75 – 2.60 (m, 1H), 2.31 – 2.16 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.6, 166.8, 143.9, 135.7, 133.6, 132.5, 130.8, 130.6, 129.8, 129.5, 128.9, 128.7, 128.5, 127.8, 127.0, 124.4, 81.7 (d, $J = 165.0$ Hz), 52.3, 49.1 (d, $J = 3.1$ Hz), 34.5 (d, $J = 19.5$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{22}\text{H}_{19}\text{FO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 373.1210; found: 373.1206.

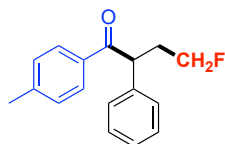


3w: 4-Fluoro-1-(4-methoxyphenyl)-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (50.5 mg, 62% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.98 – 7.94 (m, 2H), 7.32 – 7.28 (m, 4H), 7.23 – 7.19 (m, 1H), 6.88 – 6.84 (m, 2H), 4.80 (t, $J = 7.4$ Hz, 1H), 4.54 – 4.27 (m, 2H), 3.82 (s, 3H), 2.64 – 2.49 (m, 1H), 2.22 – 2.08 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.7, 165.5, 139.1, 131.3, 129.5, 129.2, 128.4, 127.4, 113.9, 82.0 (d, $J = 164.2$ Hz), 55.6, 48.7 (d, $J = 3.0$ Hz), 34.6 (d, $J = 19.6$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{17}\text{FO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 295.1105; found: 295.1105.

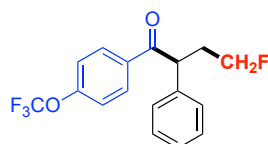


3x: 1-(4-(tert-Butyl)phenyl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (64.3 mg, 72% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.94 – 7.91 (m, 2H), 7.42 – 7.39 (m, 2H), 7.34 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 4.84 (t, $J = 7.4$ Hz, 1H), 4.54 – 4.27 (m, 2H), 2.64 – 2.50 (m, 1H),

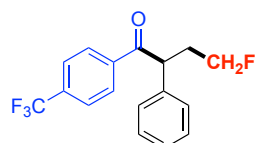
2.22 – 2.09 (m, 1H), 1.29 (s, 9H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.8, 156.9, 138.9, 133.9, 129.2, 128.9, 128.5, 127.4, 125.7, 82.0 (d, $J = 164.2$ Hz), 48.9 (d, $J = 3.4$ Hz), 35.2, 34.6 (d, $J = 19.4$ Hz), 31.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{20}\text{H}_{23}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 361.1625; found: 321.1620.



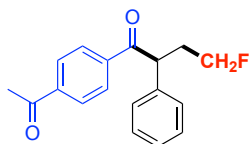
3y: 4-Fluoro-2-phenyl-1-(p-tolyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (52.0 mg, 68% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.32 – 7.27 (m, 4H), 7.23 – 7.16 (m, 3H), 4.83 (t, $J = 7.4$ Hz, 1H), 4.55 – 4.27 (m, 2H), 2.65 – 2.50 (m, 1H), 2.34 (s, 3H), 2.24 – 2.08 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.8, 144.0, 138.8, 134.0, 129.4, 129.2, 129.1, 128.4, 127.4, 81.9 (d, $J = 164.4$ Hz), 48.9 (d, $J = 3.2$ Hz), 34.5 (d, $J = 19.5$ Hz), 21.7 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{18}\text{FO}$ $[\text{M}+\text{H}]^+$: 257.1336; found: 257.1329.



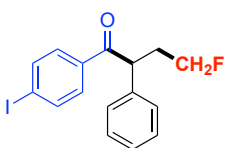
3z: 4-Fluoro-2-phenyl-1-(4-(trifluoromethoxy)phenyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (33.2 mg, 32% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 8.7$ Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.19 (m, 3H), 4.80 (t, $J = 7.3$ Hz, 1H), 4.82 – 4.27 (m, 2H), 2.65 – 2.51 (m, 1H), 2.24 – 2.08 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 197.6, 152.6, 138.2, 134.7, 131.0, 129.4, 128.4, 127.7, 120.40, 120.36 (d, $J = 259.9$ Hz), 81.7 (d, $J = 163.9$ Hz), 49.3 (d, $J = 3.3$ Hz), 34.5 (d, $J = 19.3$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -57.6 (s, 3F), -221.3 (s, 1F) ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_4\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 349.0822; found: 349.0816.



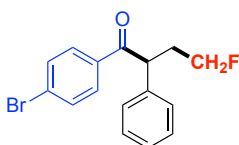
3aa: 4-Fluoro-2-phenyl-1-(4-(trifluoromethyl)phenyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (32.3 mg, 35% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.24 (m, 5H), 4.82 (t, $J = 7.3$ Hz, 1H), 4.57 – 4.28 (m, 2H), 2.67 – 2.53 (m, 1H), 2.25 – 2.09 (m, 1H) ppm; ^{13}C NMR (151 MHz, CDCl_3): δ 198.3, 139.2, 137.9, 134.3 (q, $J = 32.6$ Hz), 129.5, 129.2, 128.5, 127.8, 125.8 (q, $J = 3.6$ Hz), 123.6 (q, $J = 272.6$ Hz), 81.7 (d, $J = 1634.1$ Hz), 49.6 (d, $J = 2.8$ Hz), 34.3 (d, $J = 19.1$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -63.2 (s, 3F), -221.6 (s, 1F) ppm; HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_4\text{O}$ $[\text{M}+\text{H}]^+$: 311.1054; found: 311.1043.



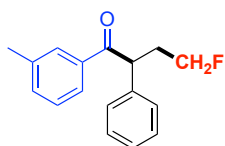
3ab: 1-(4-Acetylphenyl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 30: 1). Yellow oil (45.9 mg, 54% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03 – 8.01 (m, 2H), 7.95 – 7.93 (m, 2H), 7.33 – 7.22 (m, 5H), 4.84 (t, $J = 7.3$ Hz, 1H), 4.58 – 4.28 (m, 2H), 2.67 – 2.53 (m, 4H), 2.25 – 2.09 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.7, 197.5, 140.1, 139.8, 138.0, 129.4, 129.1, 128.54, 128.49, 127.7, 81.7 (d, $J = 164.7$ Hz), 49.7 (d, $J = 3.1$ Hz), 34.3 (d, $J = 19.4$ Hz), 27.0 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{18}\text{H}_{18}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 285.1285; found: 285.1290.



3ac: 4-Fluoro-1-(4-iodophenyl)-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (41.5 mg, 38% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.76 – 7.73 (m, 2H), 7.67 – 7.35 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.01 (m, 1H), 4.76 (t, $J = 7.3$ Hz, 1H), 4.55 – 4.26 (m, 2H), 2.64 – 2.49 (m, 1H), 2.22 – 2.07 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.5, 138.2, 138.0, 135.7, 130.3, 129.4, 128.4, 127.7, 101.2, 81.8 (d, $J = 164.4$ Hz), 49.2 (d, $J = 3.0$ Hz), 34.3 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.5 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{14}\text{FIO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 390.9966; found: 390.9955.

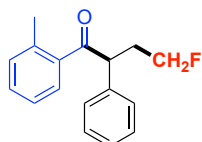


3ad: 1-(4-Bromophenyl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (38.6 mg, 40% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.83 – 7.80 (m, 2H), 7.53 – 7.50 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 4.77 (t, $J = 7.3$ Hz, 1H), 4.55 – 4.27 (m, 2H), 2.64 – 2.50 (m, 1H), 2.23 – 2.07 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 198.2, 138.2, 135.2, 132.0, 130.4, 129.4, 128.41, 128.38, 127.7, 81.8 (d, $J = 164.4$ Hz), 49.2 (d, $J = 3.1$ Hz), 34.4 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.5 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{14}\text{FBrO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 343.0104; found: 343.0099.

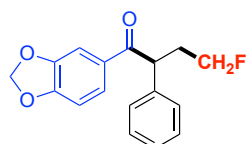


3ae: 4-Fluoro-2-phenyl-1-(*m*-tolyl)butan-1-one. Prepared according to the general procedure C

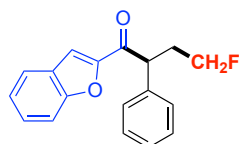
and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (46.7 mg, 61% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.78 – 7.75 (m, 2H), 7.32 – 7.19 (m, 7H), 4.84 (t, *J* = 7.4 Hz, 1H), 4.55 – 4.28 (m, 2H), 2.65 – 2.50 (m, 1H), 2.35 (s, 3H), 2.25 – 2.09 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 199.5, 138.7, 138.5, 136.6, 134.0, 139.4, 129.2, 128.52, 128.46, 127.4, 126.2, 81.9 (d, *J* = 164.4 Hz), 49.1 (d, *J* = 3.4 Hz), 34.5 (d, *J* = 19.5 Hz), 21.5 ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₇H₁₈FO [M+H]⁺: 257.1336; found: 257.1339.



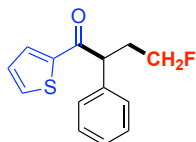
3af: 4-Fluoro-2-phenyl-1-(*o*-tolyl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (48.2 mg, 63% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.13 (m, 8H), 4.69 (t, *J* = 7.4 Hz, 1H), 4.58 – 4.30 (m, 2H), 2.70 – 2.55 (m, 1H), 2.31 (s, 3H), 2.25 – 2.09 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 203.3, 138.4, 138.2, 137.8, 131.8, 131.1, 129.1, 128.6, 128.2, 127.5, 125.6, 82.0 (d, *J* = 164.7 Hz), 52.1 (d, *J* = 3.1 Hz), 33.9 (d, *J* = 19.6 Hz), 20.9 ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₇H₁₈FO [M+H]⁺: 257.1336; found: 257.1346.



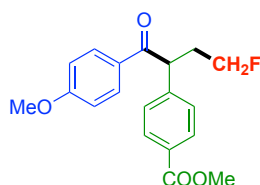
3ag: 1-(Benzo[*d*][1,3]dioxol-5-yl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (46.5 mg, 66% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.59 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.99 (s, 2H), 4.75 (t, *J* = 7.4 Hz, 1H), 4.54 – 4.26 (m, 2H), 2.63 – 2.48 (m, 1H), 2.24 – 2.05 (m, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃):** δ 197.3, 151.9, 148.3, 138.9, 131.3, 129.3, 128.4, 127.5, 125.3, 108.7, 108.0, 102.0, 81.9 (d, *J* = 164.2 Hz), 48.9 (d, *J* = 3.0 Hz), 34.6 (d, *J* = 19.4 Hz) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₇H₁₅FO₃Na [M+Na]⁺: 309.0897; found: 309.0900.



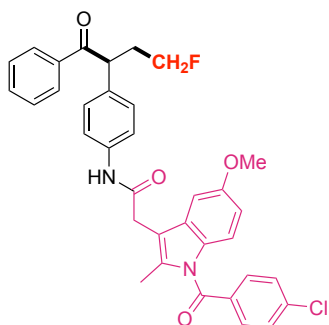
3ah: 1-(Benzofuran-2-yl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (25.0 mg, 30% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.45 – 7.38 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.9 Hz, 2H), 4.78 (t, *J* = 7.5 Hz, 1H), 4.58 – 4.29 (m, 2H), 2.70 – 2.56 (m, 1H), 2.30 – 2.14 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃):** δ 190.0, 155.8, 152.1, 137.9, 129.2, 128.6, 128.5, 127.7, 127.1, 124.0, 123.4, 114.3, 112.6, 81.7 (d, *J* = 164.4 Hz), 49.8 (d, *J* = 3.2 Hz), 33.6 (d, *J* = 19.6 Hz) ppm; **¹⁹F NMR (376 MHz, CDCl₃):** δ -221.3 ppm; **HRMS *m/z* (ESI):** calcd. for C₁₈H₁₆FO₂ [M+H]⁺: 283.1129; found: 283.1124.



3ai: 4-Fluoro-2-phenyl-1-(thiophen-2-yl)butan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (34.1 mg, 46% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.73 – 7.72 (m, 1H), 7.58 – 7.56 (m, 1H), 7.37 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 7.05 – 7.03 (m, 1H), 4.67 (t, $J = 7.4$ Hz, 1H), 4.56 – 4.27 (m, 2H), 2.66 – 2.51 (m, 1H), 2.25 – 2.10 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 192.1, 143.8, 138.6, 134.1, 132.9, 129.2, 128.4, 128.3, 127.6, 81.8 (d, $J = 164.7$ Hz), 50.6 (d, $J = 3.1$ Hz), 34.3 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.5 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{14}\text{H}_{13}\text{FOSNa}$ $[\text{M}+\text{Na}]^+$: 271.0563; found: 271.0560.

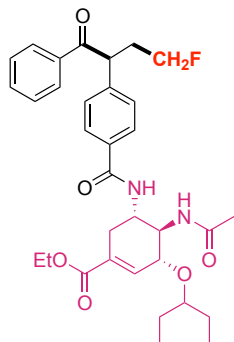


3aj: Methyl-4-(4-fluoro-1-(4-methoxyphenyl)-1-oxobutan-2-yl)benzoate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (36.8 mg, 37% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.98 – 7.92 (m, 4H), 7.40 – 7.38 (m, 2H), 6.88 – 6.85 (m, 2H), 4.87 (t, $J = 7.4$ Hz, 1H), 4.54 – 4.27 (m, 2H), 3.88 (m, 3H), 3.82 (m, 3H), 2.65 – 2.53 (m, 1H), 2.22 – 2.09 (m, 1H) ppm; $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 197.1, 166.9, 163.8, 144.3, 131.3, 130.5, 129.33, 129.27, 128.5, 114.0, 81.8 (d, $J = 164.7$ Hz), 55.6, 52.3, 48.7 (d, $J = 3.0$ Hz), 34.4 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.3 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{19}\text{H}_{19}\text{FO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 353.1160; found: 353.1161.

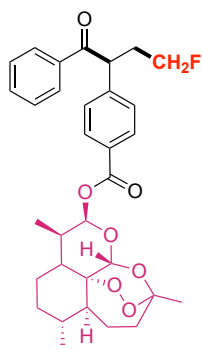


3ak: 2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(4-(4-fluoro-1-oxo-1-phenylbutan-2-yl)phenyl)acetamide. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). White solid (127.3 mg, 71% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.48 – 7.45 (m, 3H), 7.37 – 7.32 (m, 5H), 7.21 (d, $J = 8.3$ Hz, 2H), 6.91 – 6.84 (m, 2H), 6.71 – 6.68 (m, 1H), 4.79 (t, $J = 7.3$ Hz, 1H), 4.52 – 4.23 (m, 2H), 3.78 (s, 3H), 3.76 (s, 2H), 2.59 – 2.45 (m, 1H), 2.41 (s, 3H), 2.19 – 2.02 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.0, 168.4, 168.3, 156.5, 139.8, 136.8, 136.7, 134.7, 133.5, 133.2, 131.3, 131.0, 130.2, 129.4, 129.0, 128.8, 128.7, 120.9, 115.3, 112.5, 112.3, 100.8, 81.7 (d, $J = 164.5$ Hz), 55.9, 48.5 (d, $J = 3.0$ Hz), 34.3 (d, $J = 19.5$ Hz), 33.4, 13.4 ppm; ^{19}F

NMR (376 MHz, CDCl₃): δ -221.4 ppm; **HRMS m/z (ESI):** calcd. for C₃₅H₃₀ClFN₂O₄K [M+K]⁺: 635.1510; found: 635.1494.

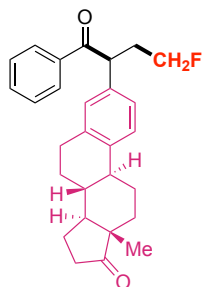


3al: Ethyl (3*R*,4*R*,5*S*)-4-acetamido-5-(4-((*S*)-4-fluoro-1-oxo-1-phenylbutan-2-yl)benzamido)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 5: 1). White solid (88.9 mg, 51% yield, 1:0.72 dr). **¹H NMR (400 MHz, MeOD-*d*₄, contained a isomer):** δ 8.32 – 7.98 (m, 2.5H), 7.77 – 7.70 (m, 2H), 7.54 – 7.37 (m, 4.4H), 6.83 – 6.80 (m, 1H), 5.02 (t, J = 7.3 Hz, 1H), 4.65 – 4.47 (m, 1H), 4.45 – 4.35 (m, 1H), 4.32 – 4.17 (m, 5H), 4.09 – 4.00 (m, 1H), 3.46 – 3.40 (m, 1H), 2.81 – 2.71 (m, 1H), 2.65 – 2.51 (m, 1H), 2.48 – 2.37 (m, 1H), 2.22 – 2.16 (m, 1H), 2.09 – 1.93 (m, 1H), 1.86 – 1.82 (m, 3H), 1.52 – 1.47 (m, 3H), 1.31 – 1.29 (m, 4H), 0.95 – 0.84 (m, 6H) ppm; Data of one isomer: **¹³C NMR (126 MHz, MeOD-*d*₄):** δ 200.41, 173.99, 169.77, 167.46, 144.1, 139.1, 137.6, 134.4, 130.8, 130.37, 129.7, 129.5, 129.1, 128.7, 83.87, 82.6 (d, J = 164.1 Hz), 76.94, 62.1, 55.9, 50.1 (d, J = 4.0 Hz), 49.97, 35.3 (d, J = 19.5 Hz), 31.17, 27.3, 26.8, 22.79, 14.4, 9.8, 9.6 ppm; Data of the other isomer: **¹³C NMR (126 MHz, MeOD-*d*₄):** δ 200.39, 174.03, 169.91, 167.49, 144.1, 139.1, 137.6, 134.7, 130.8, 130.42, 129.8, 129.5, 129.1, 128.7, 83.89, 82.5 (d, J = 165.1 Hz), 76.99, 62.1, 55.9, 50.1 (d, J = 4.0 Hz), 50.0, 35.3 (d, J = 19.5 Hz), 31.24, 28.1, 26.9, 22.81, 14.4, 9.8, 9.6 ppm; **¹⁹F NMR (376 MHz, MeOD-*d*₄):** δ -221.57, -221.6, -222.0 ppm; **HRMS m/z (ESI):** calcd. for C₃₄H₄₁FN₂O₆Na [M+Na]⁺: 603.2841; found: 603.2844.

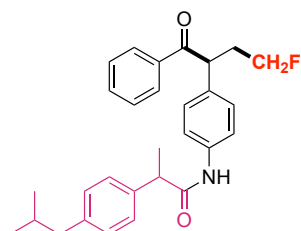


3am: (5*aS*,6*R*,9*R*,10*R*,12*R*,12*aR*)-3,6,9-trimethyldecahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*ij*]isochromen-10-yl 4-(4-fluoro-1-oxo-1-phenylbutan-2-yl)benzoate. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 7: 1). White solid (54.6 mg, 33% yield, dr = 1:1). **¹H NMR (400 MHz, CDCl₃):** δ 8.06 (d, J = 7.9 Hz, 2H), 7.94 (d, J = 7.8 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.41 – 7.38 (m, 4H), 5.96 (d, J = 9.8 Hz, 1H), 5.49 (s, 1H), 4.92 (t, J = 7.3 Hz, 1H), 4.57 – 4.26 (m, 2H), 2.74 – 2.57 (m, 2H), 2.42 – 2.34 (m, 1H), 2.24 – 2.11 (m, 1H),

2.05 – 2.01 (m, 1H), 1.92 – 1.88 (m, 1H), 1.82 – 1.63 (m, 3H), 1.51 – 1.43 (m, 2H), 1.40 (s, 3H), 1.33 – 1.28 (m, 2H), 1.07 – 1.01 (m, 1H), 0.97 (d, $J = 5.9$ Hz, 3H), 0.88 (d, $J = 6.7$ Hz, 3H) ppm; Data of one isomer: ^{13}C NMR (151 MHz, CDCl_3): δ 198.63, 165.0, 144.2, 136.29, 133.47, 131.14, 128.94, 128.89, 128.8, 128.5, 104.6, 92.7, 91.7, 81.7 (d, $J = 164.7$ Hz), 80.30, 51.7, 49.2 (d, $J = 3.3$ Hz), 45.4, 37.4, 36.4, 34.4 (d, $J = 19.3$ Hz), 34.2, 32.1, 36.1, 24.7, 22.2, 20.4, 12.4 ppm; Data of the other isomer: ^{13}C NMR (151 MHz, CDCl_3): 198.58, 165.0, 144.2, 136.26, 133.46, 131.11, 128.94, 128.91, 128.8, 128.5, 104.6, 92.7, 91.7, 81.7 (d, $J = 164.7$ Hz), 80.28, 51.7, 49.1 (d, $J = 3.3$ Hz), 45.4, 37.4, 36.4, 34.4 (d, $J = 19.3$ Hz), 34.2, 31.7, 26.1, 24.7, 22.2, 20.4, 14.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.39, -221.43 ppm. HRMS m/z (ESI): calcd. for $\text{C}_{32}\text{H}_{37}\text{FO}_7\text{Na}$ $[\text{M}+\text{Na}]^+$: 575.2416; found: 575.2409.

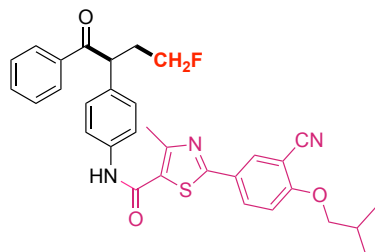


3an: (8*R*,9*S*,13*S*,14*S*)-3-((*S*)-4-fluoro-1-oxo-1-phenylbutan-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 7: 1). White solid (60.1 mg, 48% yield, dr = 1:1). ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 7.6$ Hz, 2H), 7.51 – 7.48 (m, 1H), 7.42 – 7.38 (m, 2H), 7.23 – 7.20 (m, 1H), 7.11 – 7.08 (m, 1H), 7.01 (d, $J = 6.0$ Hz, 1H), 4.80 (t, $J = 7.3$ Hz, 1H), 4.54 – 4.30 (m, 2H), 2.87 – 2.84 (m, 2H), 2.63 – 2.46 (m, 2H), 2.40 – 2.32 (m, 1H), 2.26 – 1.92 (m, 7H), 1.66 – 1.52 (m, 3H), 1.46 – 1.38 (m, 2H), 0.89 (s, 1.5H), 0.88 (s, 1.5H) ppm; Data of one isomer: ^{13}C NMR (101 MHz, CDCl_3): 221.0, 199.32, 139.0, 137.45, 136.6, 135.9, 133.1, 130.01, 129.0, 128.67, 126.2, 126.0, 82.0 (d, $J = 164.3$ Hz), 50.6, 48.5 (d, $J = 2.2$ Hz), 48.1, 44.4, 38.1, 35.96, 34.57 (d, $J = 19.7$ Hz), 31.7, 29.44, 26.54, 25.7, 21.7, 13.9 ppm; Data of the other isomer: ^{13}C NMR (101 MHz, CDCl_3): 221.0, 199.30, 139.0, 137.42, 136.6, 135.9, 133.1, 130.05, 129.0, 128.71, 126.2, 125.97, 82.0 (d, $J = 164.3$ Hz), 50.6, 48.5 (d, $J = 2.2$ Hz), 48.1, 44.4, 38.1, 36.0, 34.59 (d, $J = 19.3$ Hz), 32.0, 29.49, 26.53, 25.7, 22.8, 14.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.2 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{28}\text{H}_{32}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 419.2381; found: 419.2384.

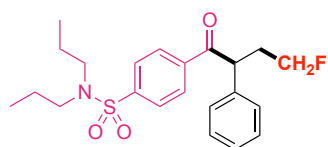


3ao: *N*-(4-(4-fluoro-1-oxo-1-phenylbutan-2-yl)phenyl)-2-(4-isobutylphenyl)propanamide. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 6). Yellow oil (70.6 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 7.7$ Hz, 2H), 7.48 – 7.44 (m, 1H), 7.37 – 7.34 (m, 4H), 7.23 – 7.19 (m, 4H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.11 (s, 1H), 4.79 (t, $J = 7.3$ Hz, 1H), 4.53 – 4.24 (m, 2H), 3.66 (q, $J = 7.1$ Hz, 1H), 2.60 – 2.48 (m, 1H), 2.45 (d, $J = 7.2$ Hz, 2H), 2.24 – 2.06 (m, 1H), 1.89 – 1.79 (m, 1H), 1.55 (d, $J = 7.1$ Hz, 3H), 0.90 (s, 3H),

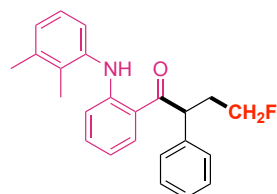
0.89 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.1, 172.8, 141.3, 138.0, 137.2, 136.4, 134.2, 133.2, 130.0, 129.0, 128.9, 128.7, 127.5, 120.4, 81.8 (d, $J = 164.4$ Hz), 48.5 (d, $J = 3.1$ Hz), 47.8, 45.1, 34.3 (d, $J = 19.4$ Hz), 30.3, 22.5, 18.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.4 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{29}\text{H}_{32}\text{FNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 468.2309; found: 468.2301.



3ap: 2-(3-Cyano-4-isobutoxyphenyl)-*N*-(4-(4-fluoro-1-oxo-1-phenylbutan-2-yl)phenyl)-4-methylthiazole-5-carboxamide. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). White solid (121.8 mg, 73% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.04 – 8.03 (m, 1H), 8.01 – 7.94 (m, 3H), 7.79 (brs, 1H), 7.56 – 7.54 (m, 2H), 7.50 – 7.47 (m, 1H), 7.40 – 7.36 (m, 2H), 7.31 – 7.29 (m, 2H), 6.98 – 6.96 (d, $J = 8.9$ Hz, 1H), 4.85 (t, $J = 7.3$ Hz, 1H), 4.55 – 4.28 (m, 2H), 3.87 (d, $J = 6.5$ Hz, 2H), 2.71 (s, 3H), 2.64 – 2.49 (m, 1H), 2.23 – 2.09 (m, 2H), 1.07 (s, 3H), 1.05 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 199.1, 165.0, 162.5, 159.9, 157.2, 136.8, 136.4, 135.0, 133.3, 132.6, 131.9, 129.2, 128.9, 128.7, 125.8, 125.7, 121.2, 115.6, 112.7, 102.8, 81.8 (d, $J = 164.7$ Hz), 75.8, 48.5 (d, $J = 3.0$ Hz), 34.4 (d, $J = 19.6$ Hz), 28.2, 19.1, 17.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.2 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{32}\text{H}_{30}\text{FN}_3\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 578.1884; found: 578.1882.

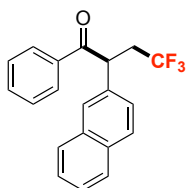


3aq: 4-(4-Fluoro-2-phenylbutanoyl)-*N,N*-dipropylbenzenesulfonamide. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 30: 1). Yellow oil (51.1 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.35 – 7.25 (m, 5H), 4.81 (t, $J = 7.3$ Hz, 1H), 4.59 – 4.28 (m, 2H), 3.05 (t, $J = 7.7$ Hz, 4H), 2.66 – 2.52 (m, 1H), 2.25 – 2.09 (m, 1H), 1.57 – 1.47 (m, 4H), 0.84 (t, $J = 7.4$ Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 198.2, 144.1, 139.3, 137.8, 129.5, 129.4, 128.5, 127.8, 127.3, 81.6 (d, $J = 164.1$ Hz), 50.1, 49.7 (d, $J = 3.0$ Hz), 34.3 (d, $J = 19.5$ Hz), 22.1, 11.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -221.6 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{22}\text{H}_{28}\text{FNO}_3\text{SK}$ $[\text{M}+\text{K}]^+$: 444.1406; found: 444.1393.

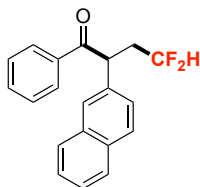


3ar: 1-(2-((2,3-Dimethylphenyl)amino)phenyl)-4-fluoro-2-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100:

1). Yellow oil (44.8 mg, 41% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.4 (brs, 1H), 7.91 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.24 – 7.21 (m, 1H), 7.18 – 7.07 (m, 3H), 7.03 – 7.01 (m, 1H), 6.75 – 6.73 (m, 1H), 6.60 – 6.56 (m, 1H), 4.94 (t, $J = 7.4$ Hz, 1H), 4.57 – 4.29 (m, 2H), 2.66 – 2.52 (m, 1H), 2.32 (s, 3H), 2.27 – 2.20 (m, 1H), 2.16 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 201.7, 150.2, 139.6, 138.5, 138.4, 134.6, 132.6, 132.0, 129.2, 128.3, 127.3, 127.1, 126.0, 123.4, 117.7, 115.8, 114.5, 82.1 (d, $J = 164.0$ Hz), 49.1 (d, $J = 2.9$ Hz), 34.9 (d, $J = 19.4$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -221.0 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{24}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$: 362.1915; found: 362.1887.

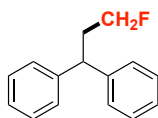


3as: 4,4,4-Trifluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Colorless oil (24.1 mg, 37% yield, 0.2 mmol scale). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03 – 8.01 (m, 2H), 7.84 – 7.77 (m, 4H), 7.49 – 7.38 (m, 6H), 5.10 (dd, $J = 5.7$, 5.1 Hz, 1H), 3.49 – 3.35 (m, 1H), 2.72 – 2.59 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 196.8, 135.8, 134.9, 133.7, 133.5, 132.8, 129.5, 129.0, 128.8, 128.0, 127.8, 127.4, 126.7, 126.54 (d, $J = 274.7$ Hz), 126.50, 125.7, 47.4 (q, $J = 2.4$ Hz), 37.5 (q, $J = 28.2$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -64.5 ppm. Spectroscopic data are in accordance with those described in literature.¹⁰

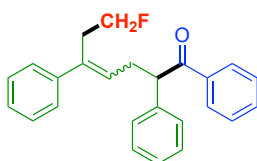


3at: 4,4-Difluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Colorless oil (31.6 mg, 51% yield, 0.2 mmol scale). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02 – 8.00 (m, 2H), 7.84 – 7.77 (m, 4H), 7.49 – 7.43 (m, 4H), 7.40 – 7.36 (m, 2H), 5.10 (tt, $J = 56.7$, 4.8 Hz, 1H), 4.99 (t, $J = 7.4$ Hz, 1H), 2.95 – 2.80 (m, 1H), 2.54 – 2.39 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.8, 135.9, 135.3, 133.7, 133.4, 132.7, 129.5, 129.0, 128.8, 127.9, 127.8, 127.3, 126.7, 126.4, 125.8, 116.3 (t, $J = 238.8$ Hz), 47.9 (t, $J = 5.5$ Hz), 38.1 (t, $J = 21.7$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -115.8 (d, $^2J_{\text{F-F}} = 284.8$ Hz, 1F), -117.7 (d, $^2J_{\text{F-F}} = 284.8$ Hz, 1F) ppm.

¹⁰ Li, J.-L.; Liu, Y.-Q.; Zou, W.-L.; Zeng, R.; Zhang, X.; Liu, Y.; Han, B.; He, Y.; Leng, H.-J.; Li, Q.-Z. Radical Acylfluoroalkylation of Olefins through N-Heterocyclic Carbene Organocatalysis. *Angew. Chem. Int. Ed.* **2020**, *59*, 1863-1870.

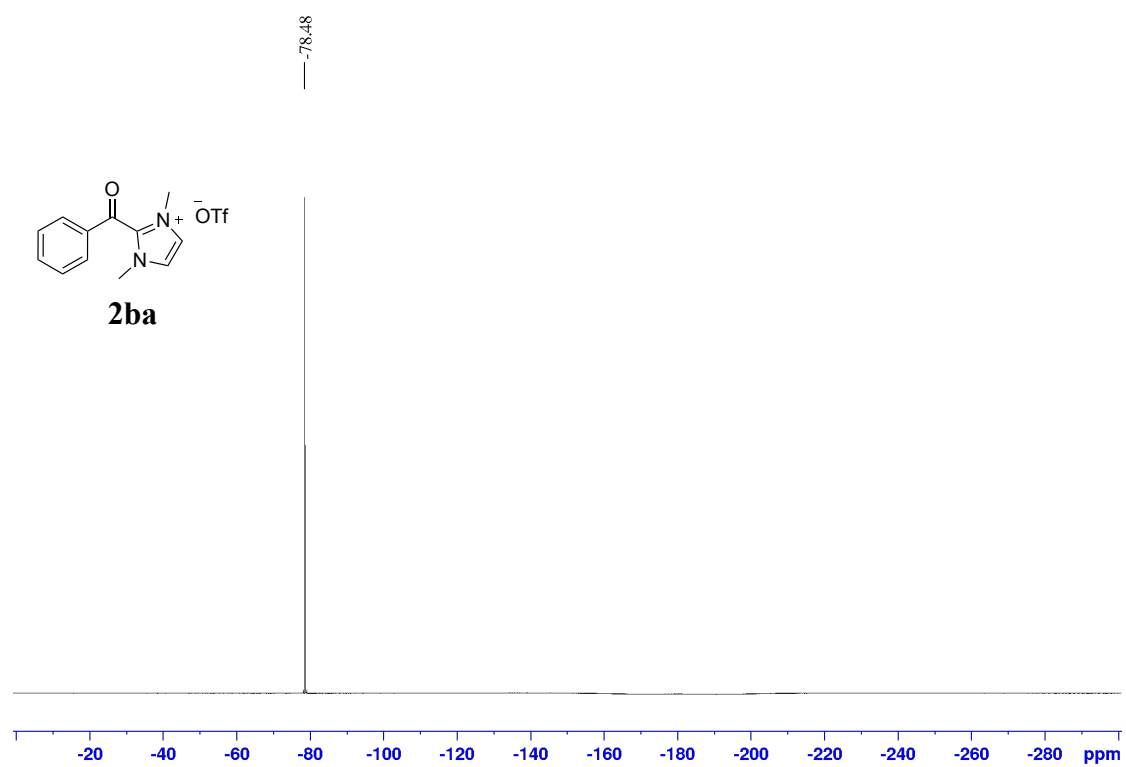
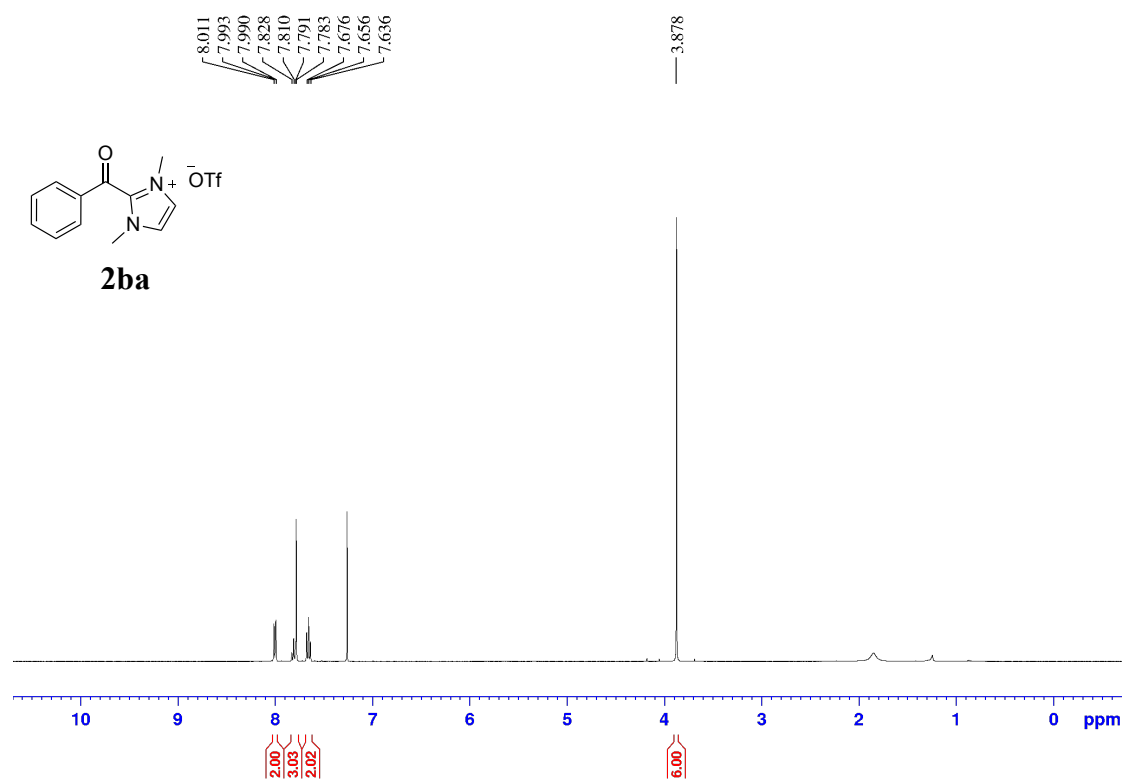


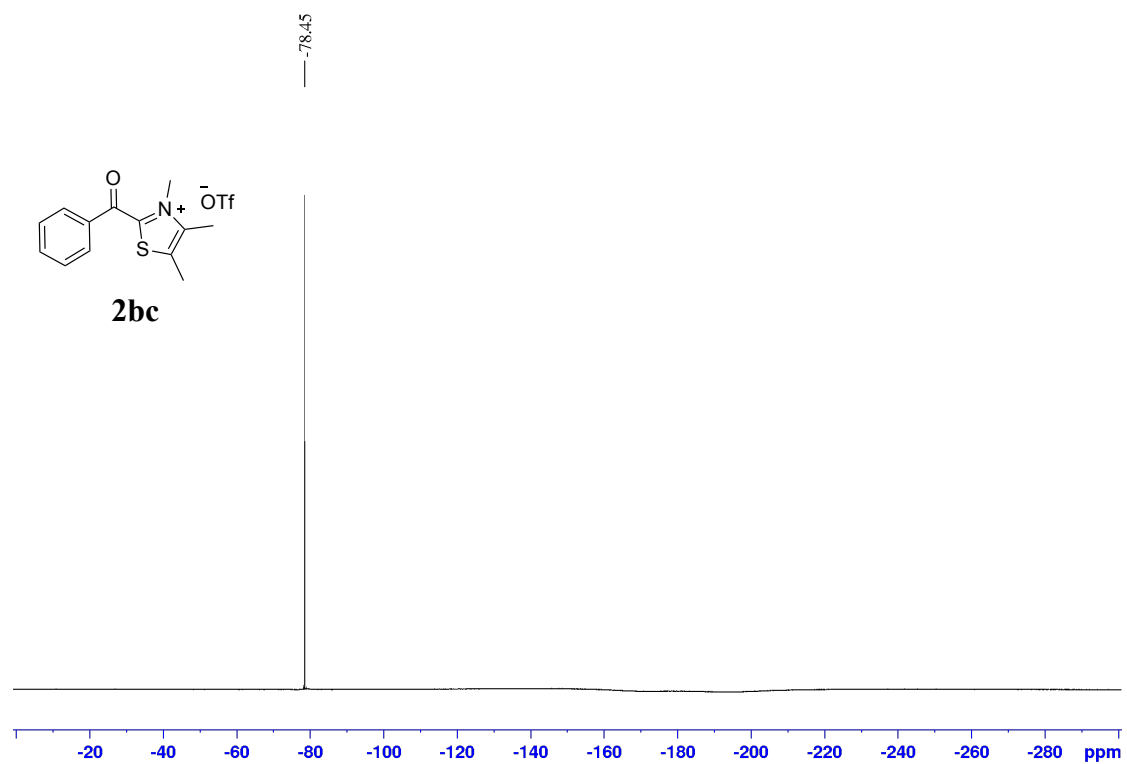
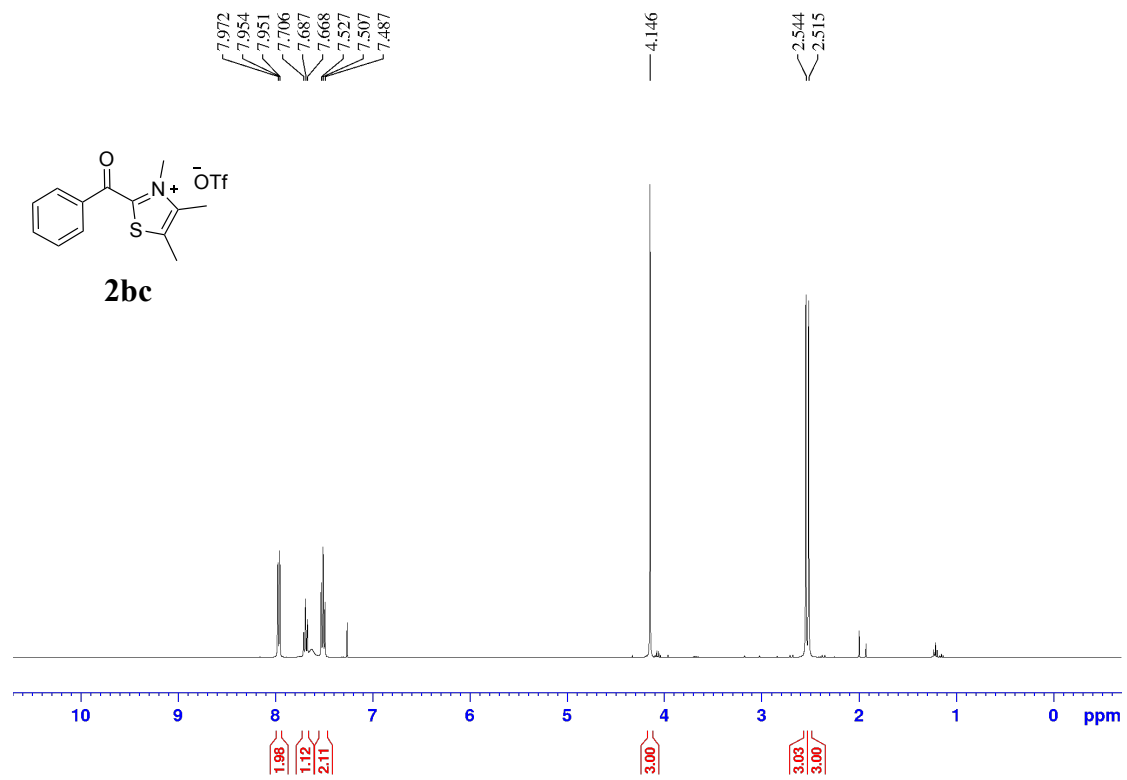
5: (3-Fluoropropane-1,1-diyl)dibenzene. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (16.2 mg, 25% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.24 – 7.16 (m, 8H), 7.14 – 7.10 (m, 2H), 4.37 (t, $J = 6.0$ Hz, 1H), 4.25 (t, $J = 6.0$ Hz, 1H), 4.10 (t, $J = 8.0$ Hz, 1H), 2.42 – 2.31 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.0, 128.7, 128.0, 126.6, 82.2 (d, $J = 165.3$ Hz), 46.5 (d, $J = 5.2$ Hz), 36.2 (d, $J = 19.9$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -220.8 ppm; HRMS m/z (ESI): calcd. for $\text{C}_{15}\text{H}_{14}\text{F}$ $[\text{M}+\text{H}]^+$: 215.1231; found: 215.1232.

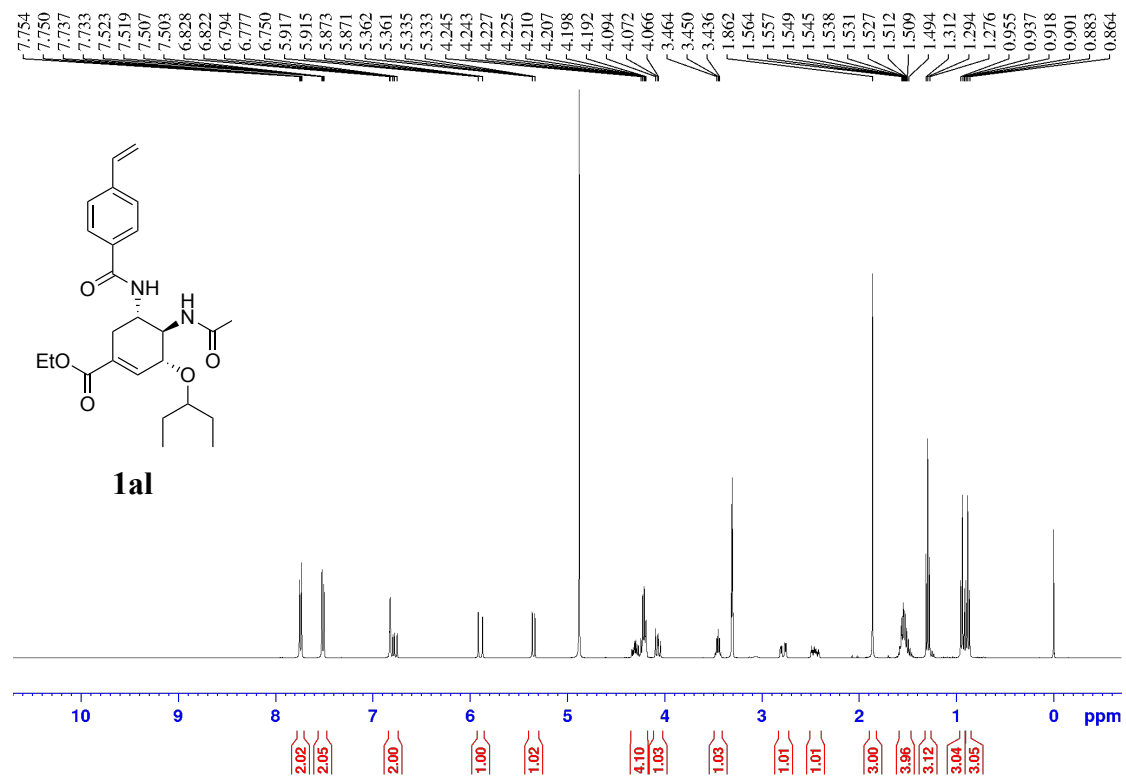
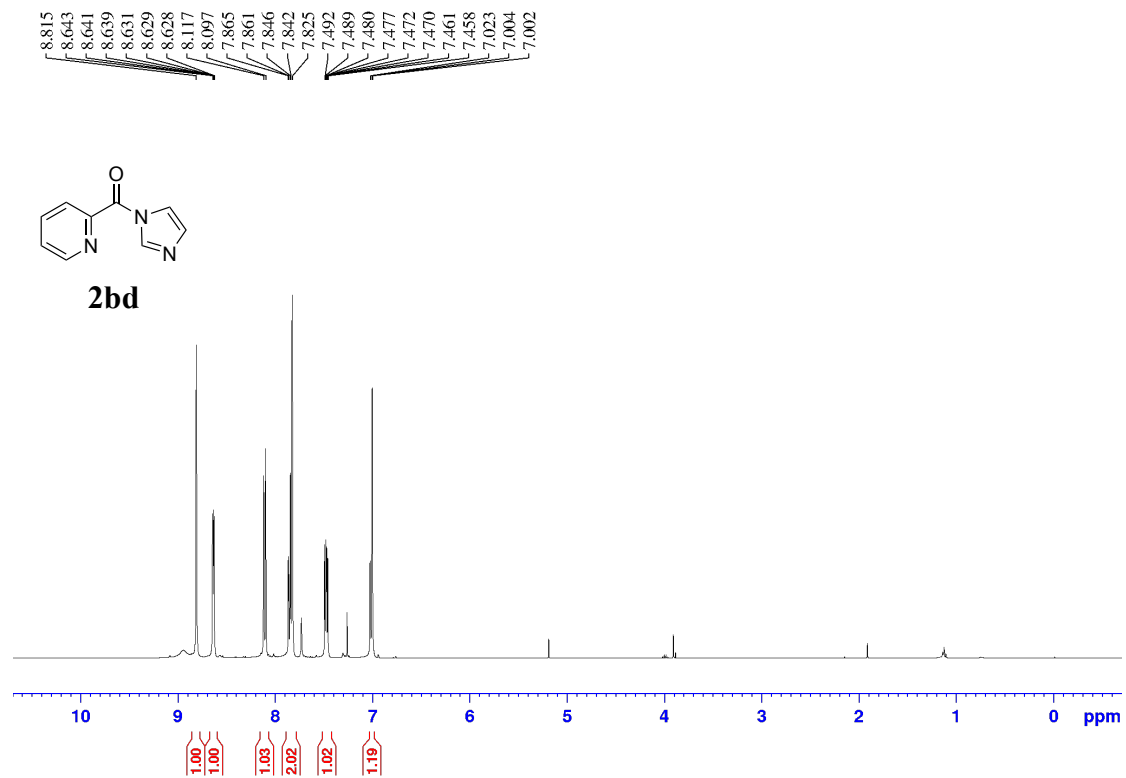


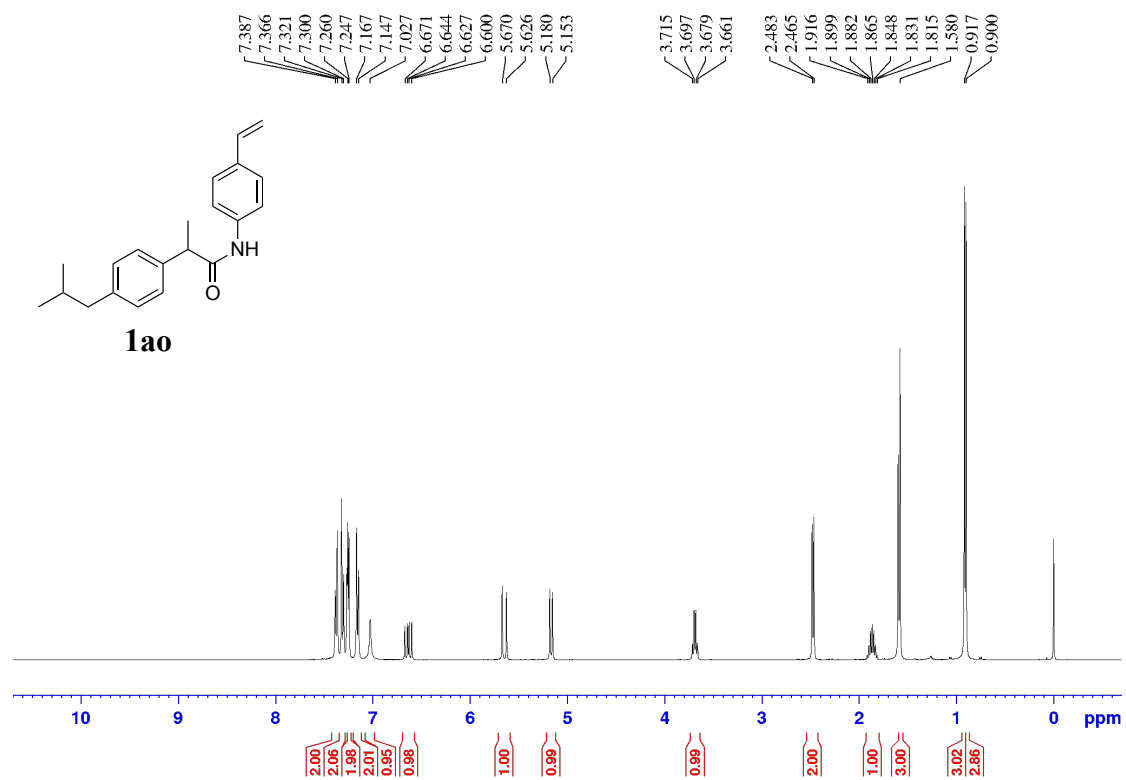
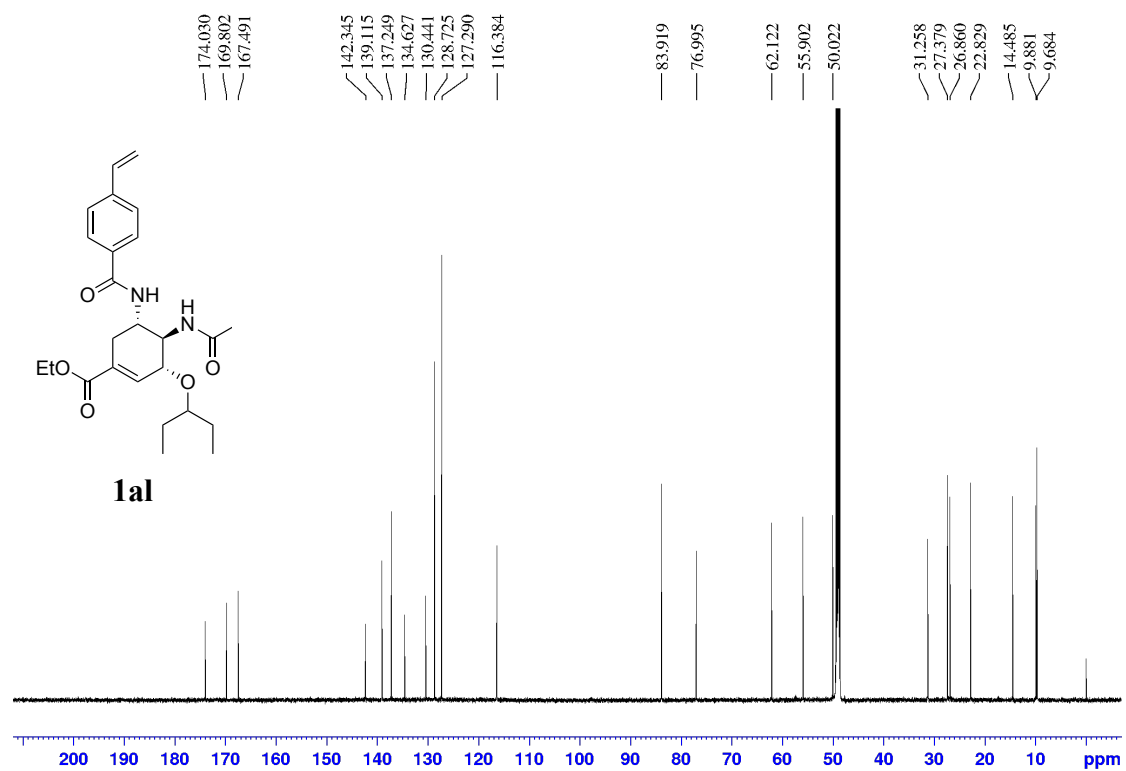
9: 7-Fluoro-1,2,5-triphenylhept-4-en-1-one. Prepared according to the general procedure C and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (25.8 mg, 24% yield, $Z/E = 1:5$). The Z/E ratio is based on $^1\text{H-NMR}$ and NOE analysis. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97 – 7.95 (m, 2H), 7.90 – 7.88 (m, 0.4H), 7.49 – 7.46 (m, 1H + 0.2H), 7.40 – 7.21 (m, 12H + 2H), 6.99 – 6.97 (m, 0.4H), 5.73 (t, $J = 7.5$ Hz, 1H), 5.51 (t, $J = 7.3$ Hz, 0.2 H), 4.68 (t, $J = 7.3$ Hz, 1H), 4.50 (t, $J = 7.3$ Hz, 0.2H), 4.42 – 4.16 (m, 2H + 0.4H), 3.11 – 3.04 (m, 1H), 2.93 – 2.73 (m, 3H + 0.2H), 2.68 – 2.59 (m, 0.4H), 2.55 – 2.47 (m, 0.2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.4, 142.3, 139.2, 136.74, 136.69, 133.1, 129.2, 129.1, 128.9, 128.7, 128.5, 128.4, 127.4, 127.2, 126.5, 82.2 (d, $J = 168.5$ Hz), 54.1, 33.3, 31.3 (d, $J = 21.0$ Hz) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -215.3, -217.7 (minor) ppm; HRMS m/z (ESI): calcd. for $\text{C}_{25}\text{H}_{23}\text{FONa}$ $[\text{M}+\text{Na}]^+$: 381.1625; found: 381.1632.

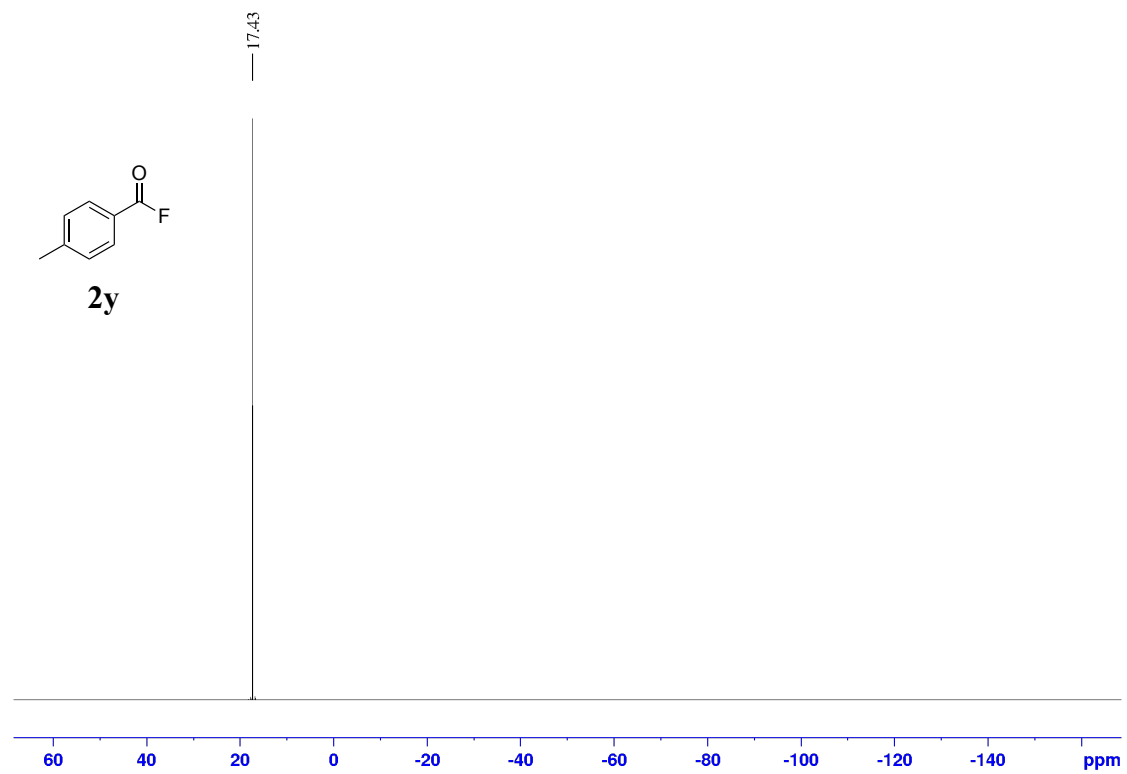
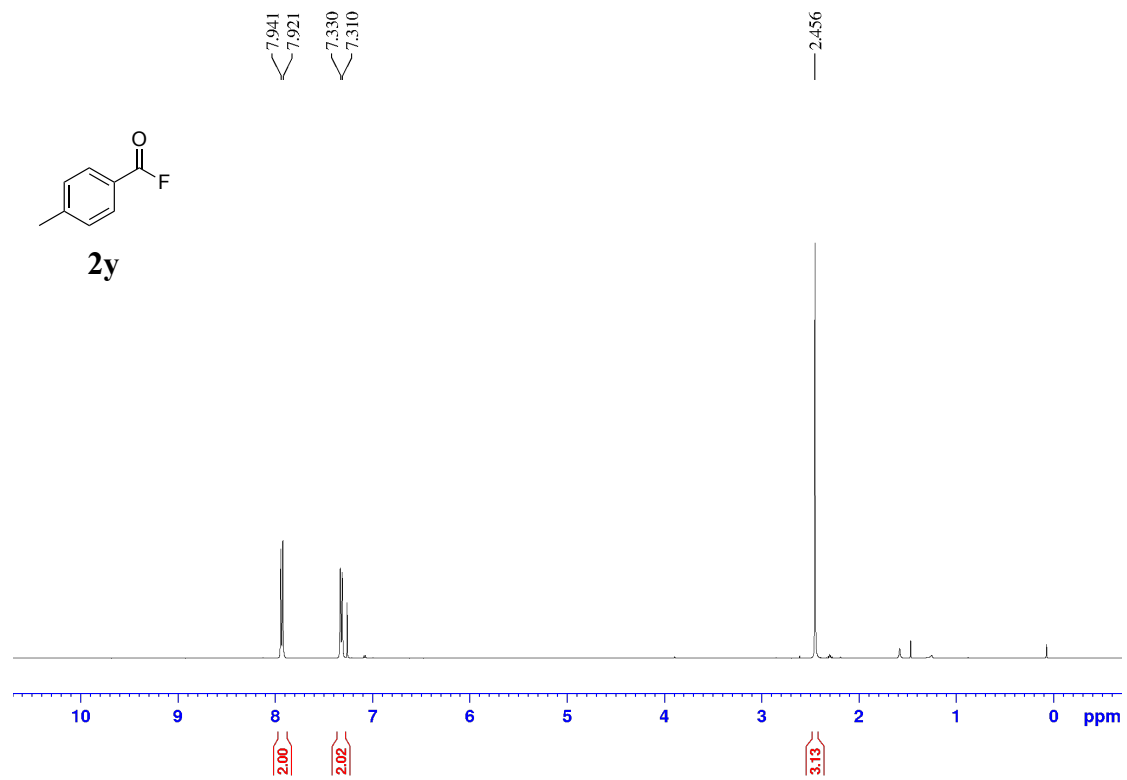
9. Spectra

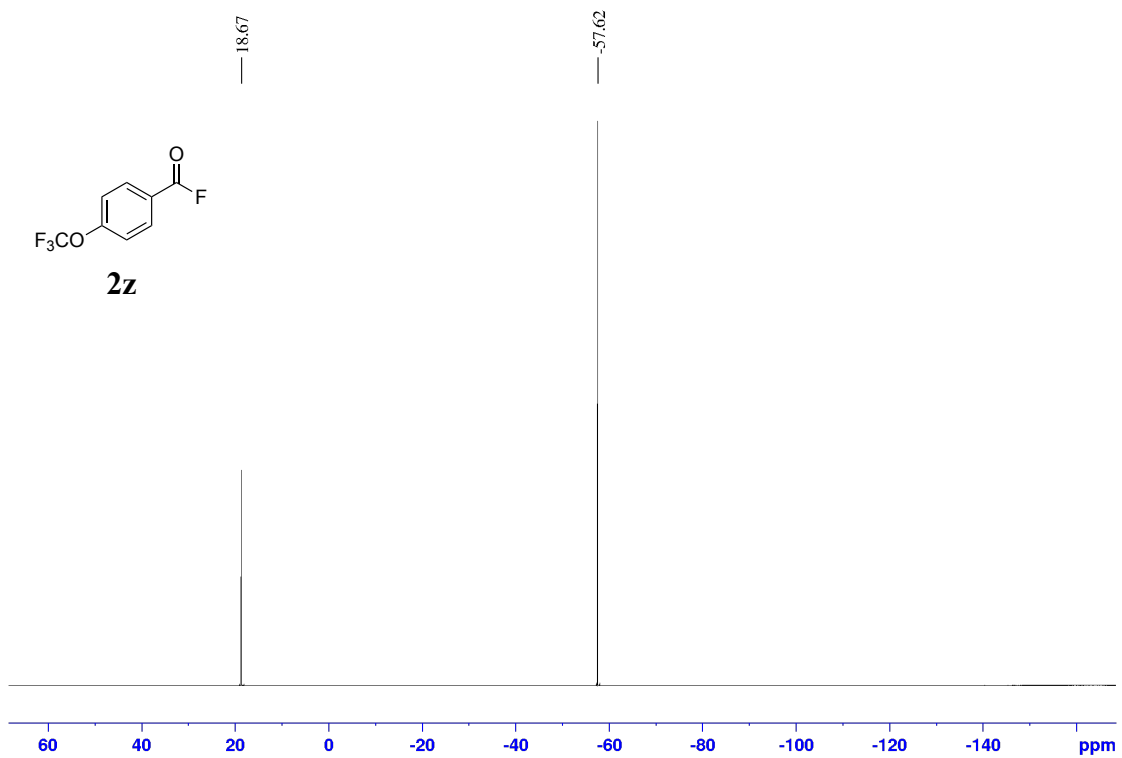
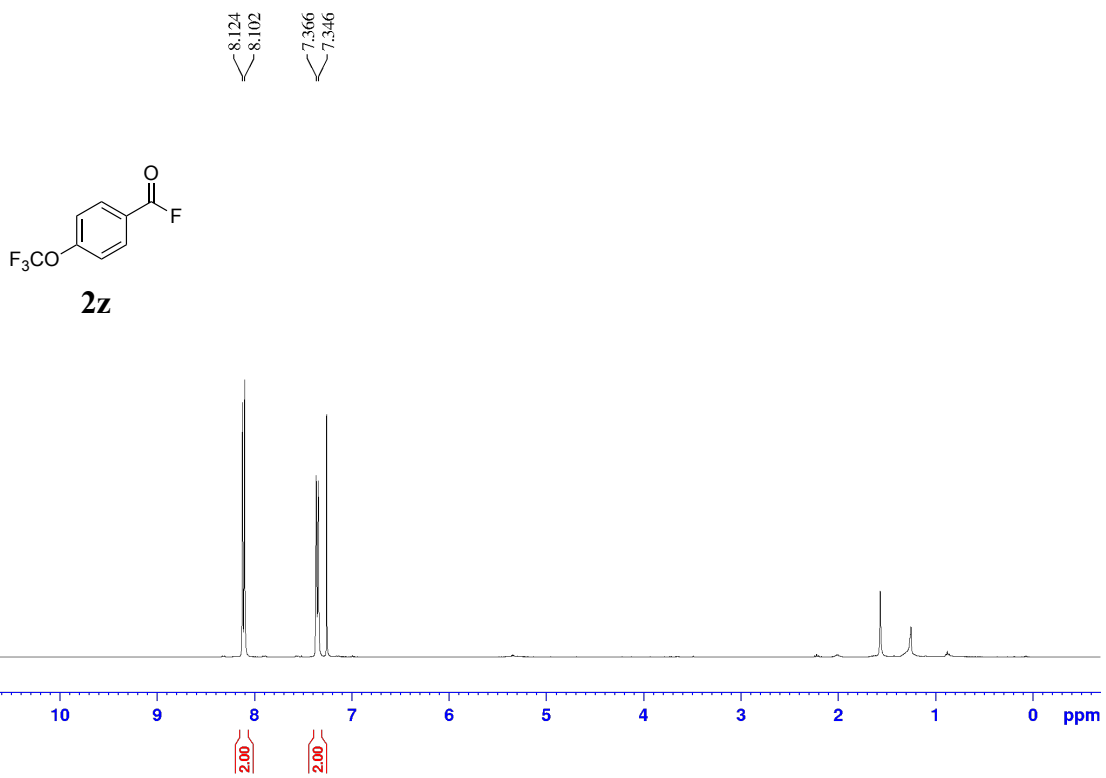


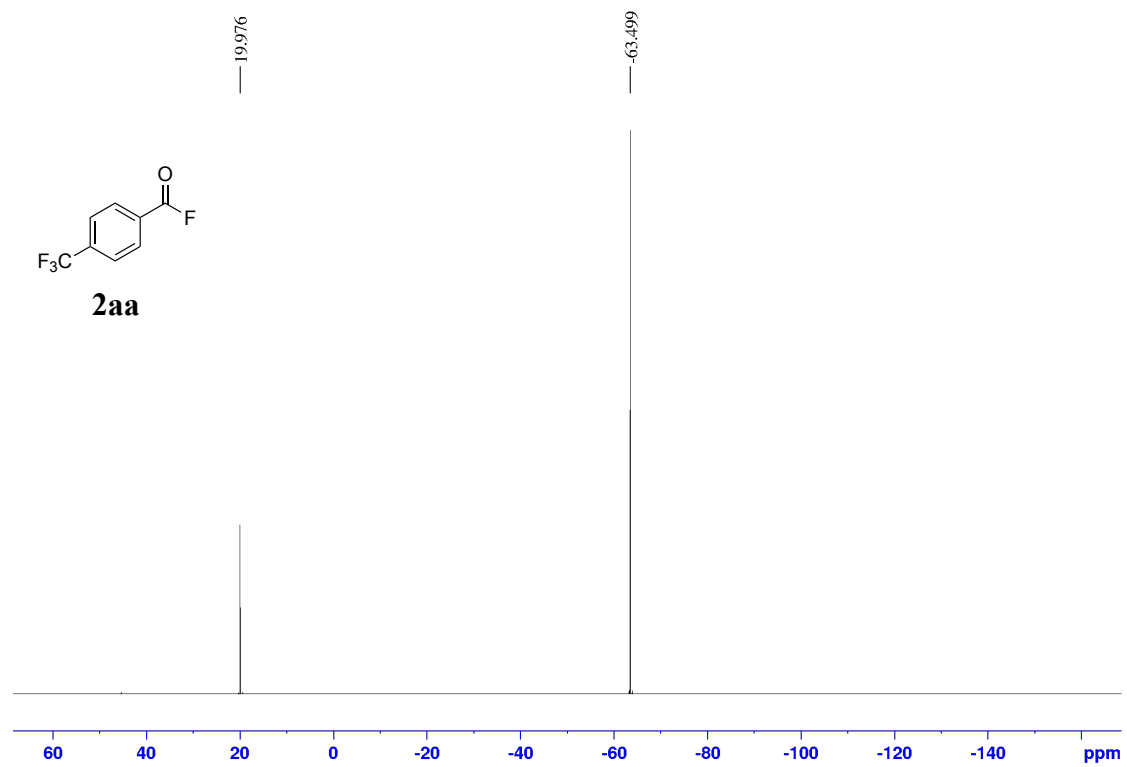
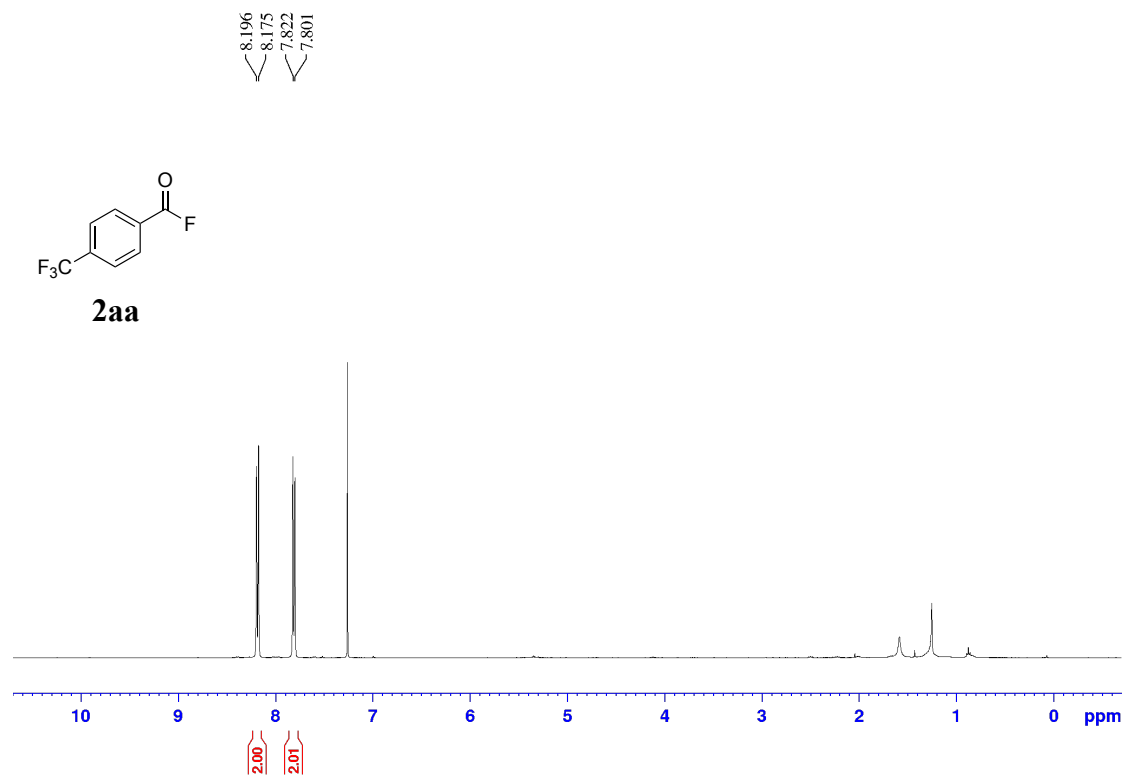


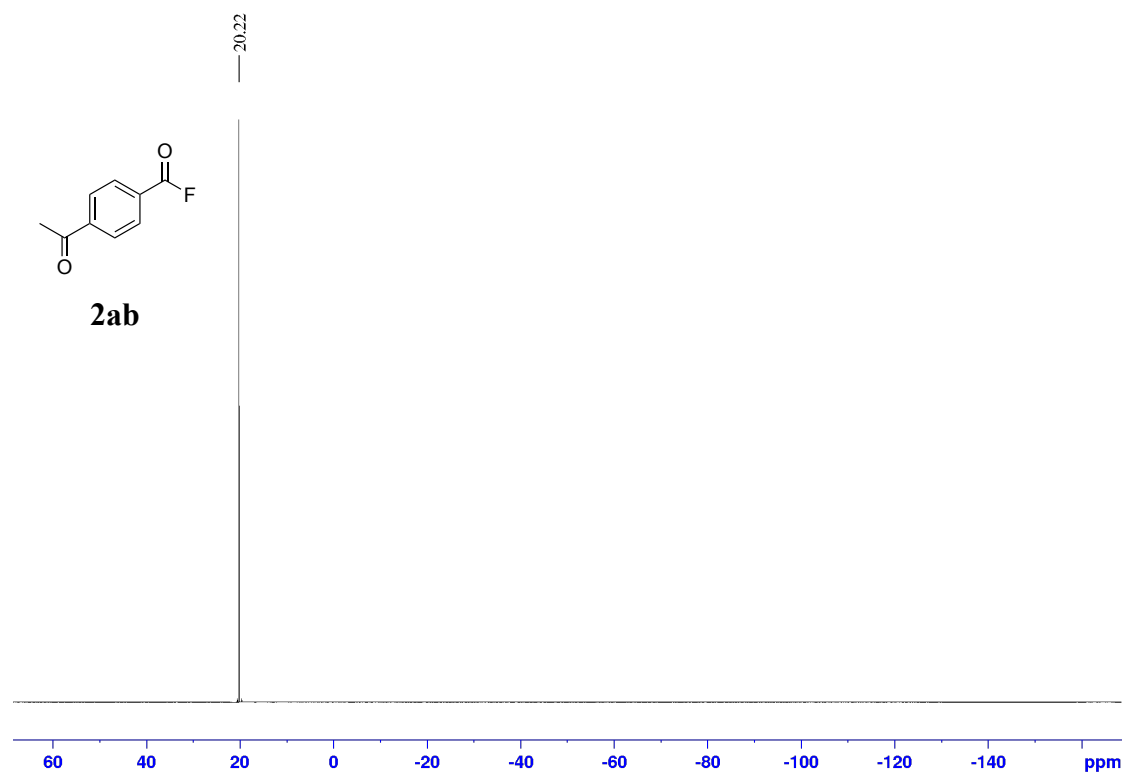
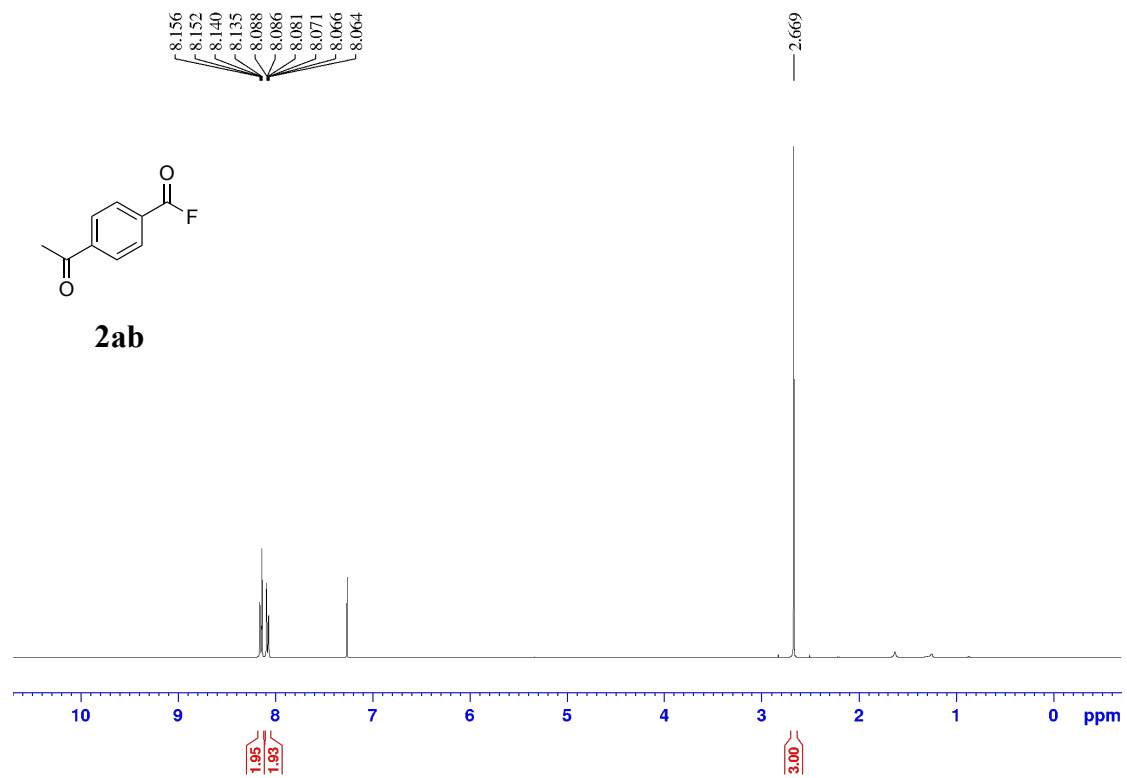


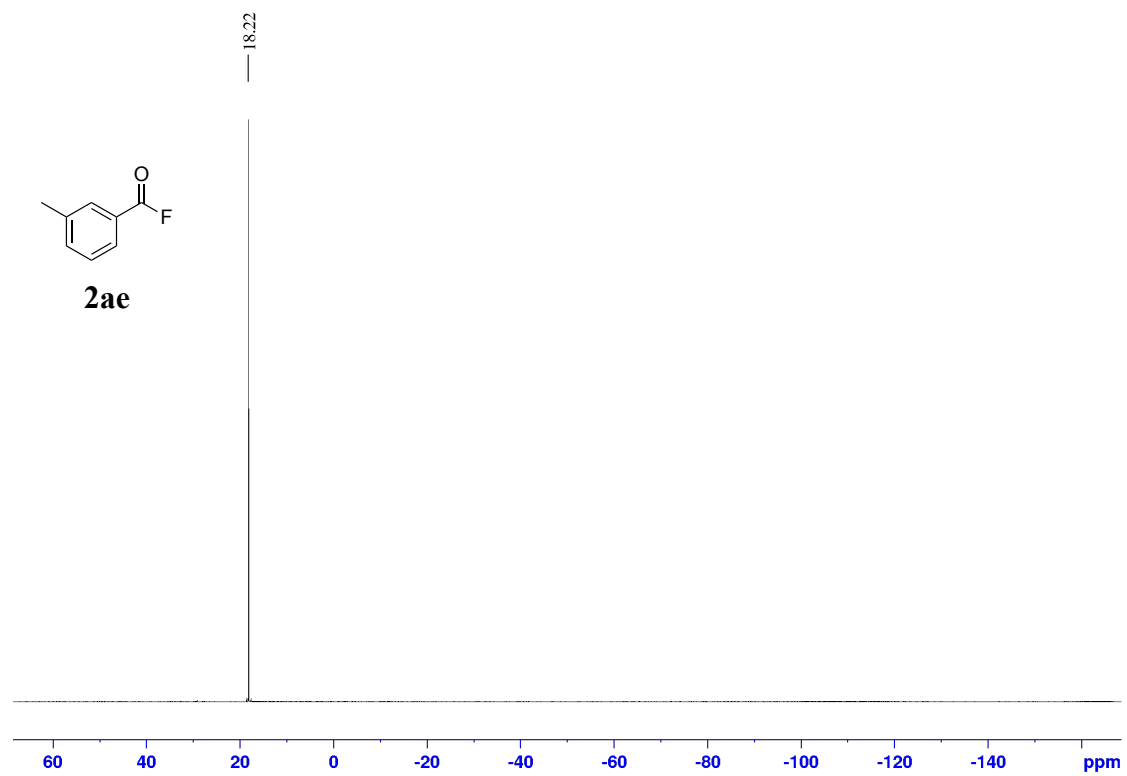
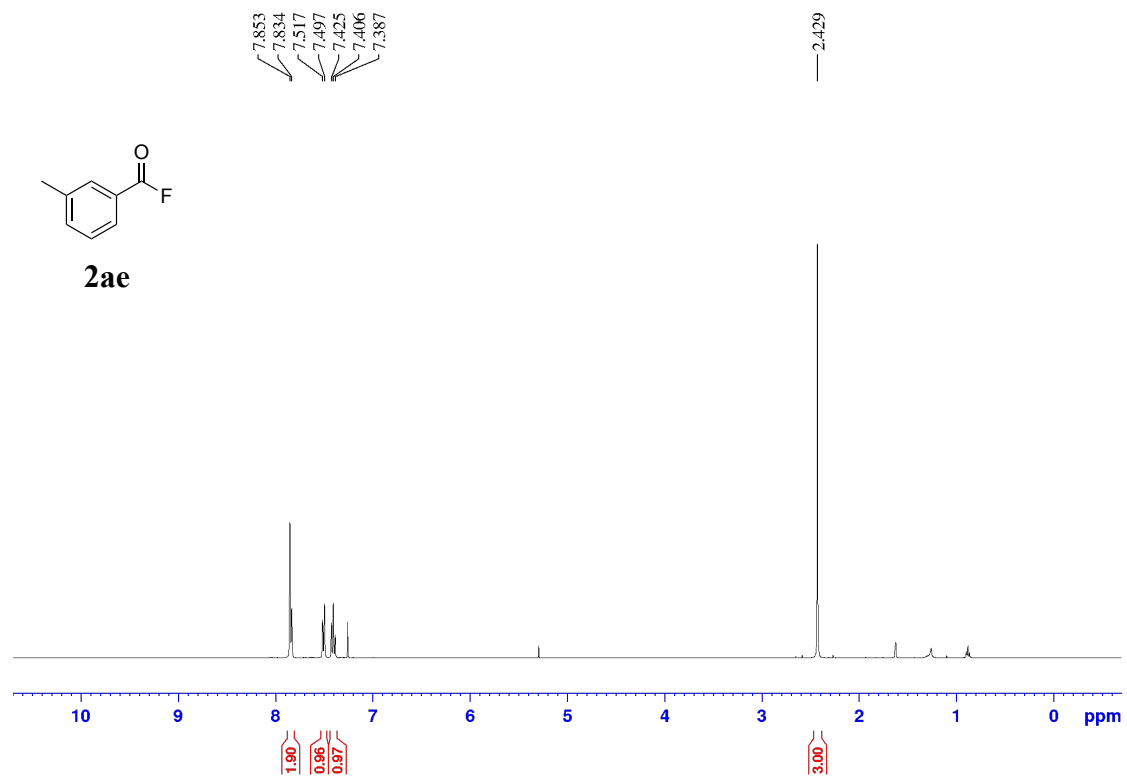


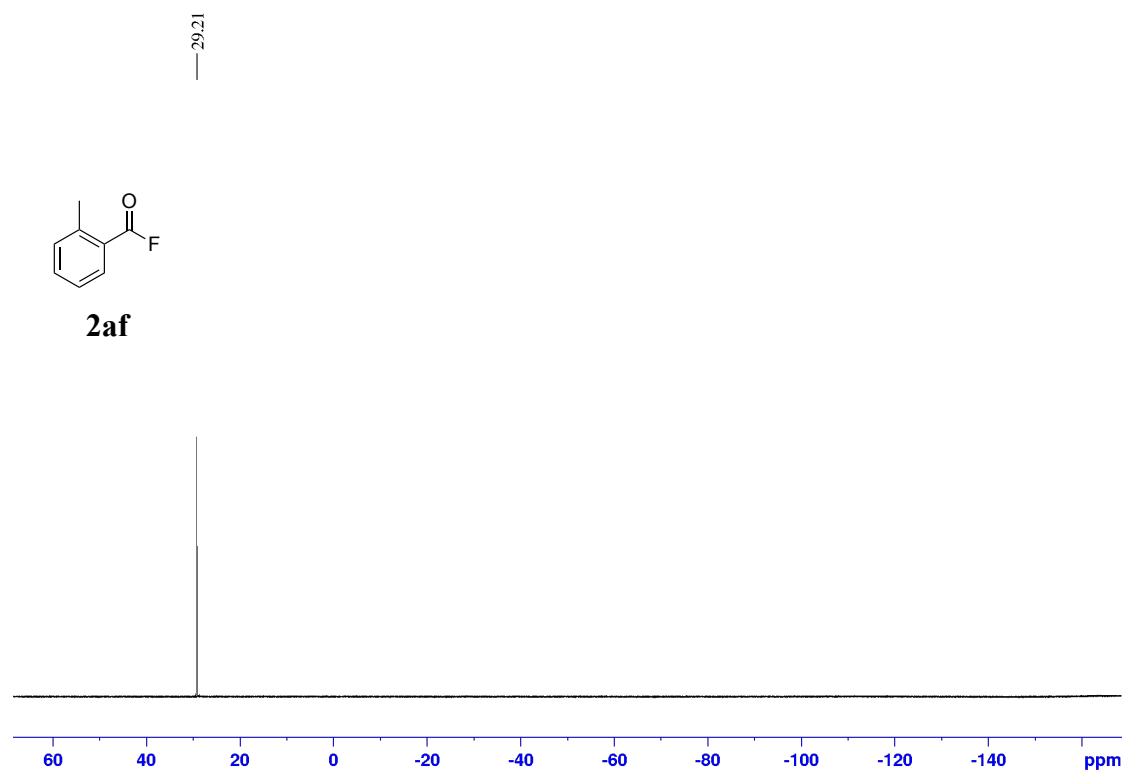
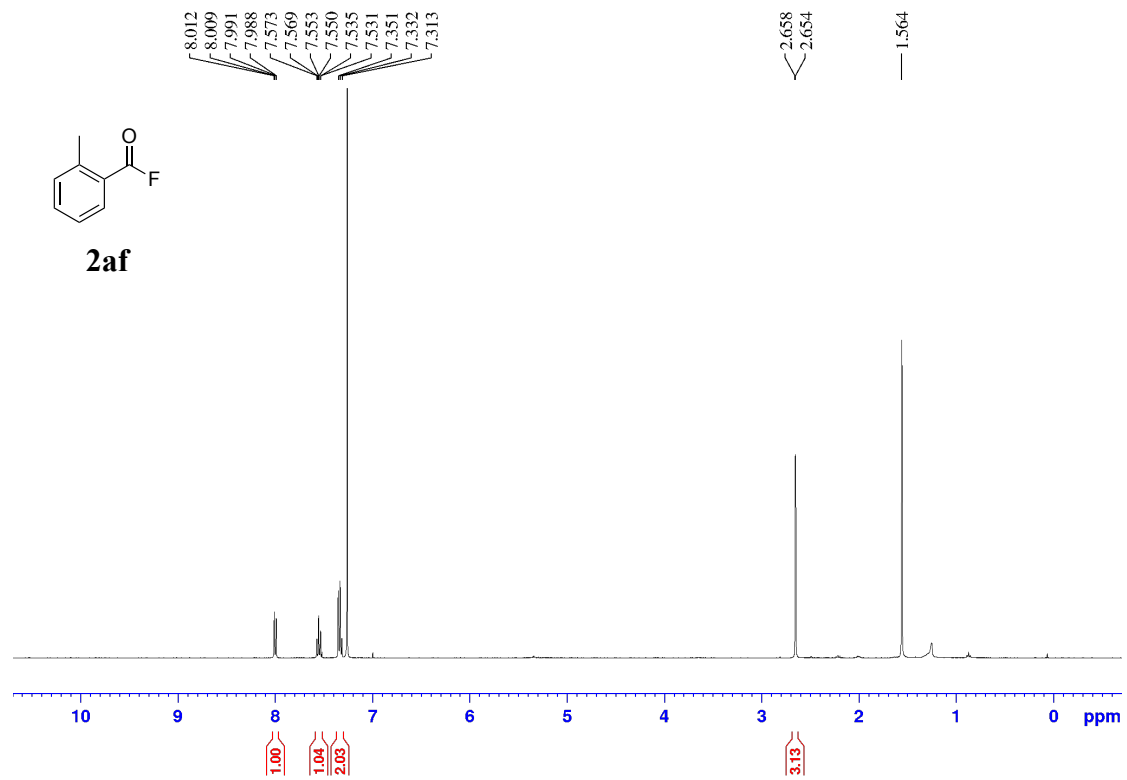


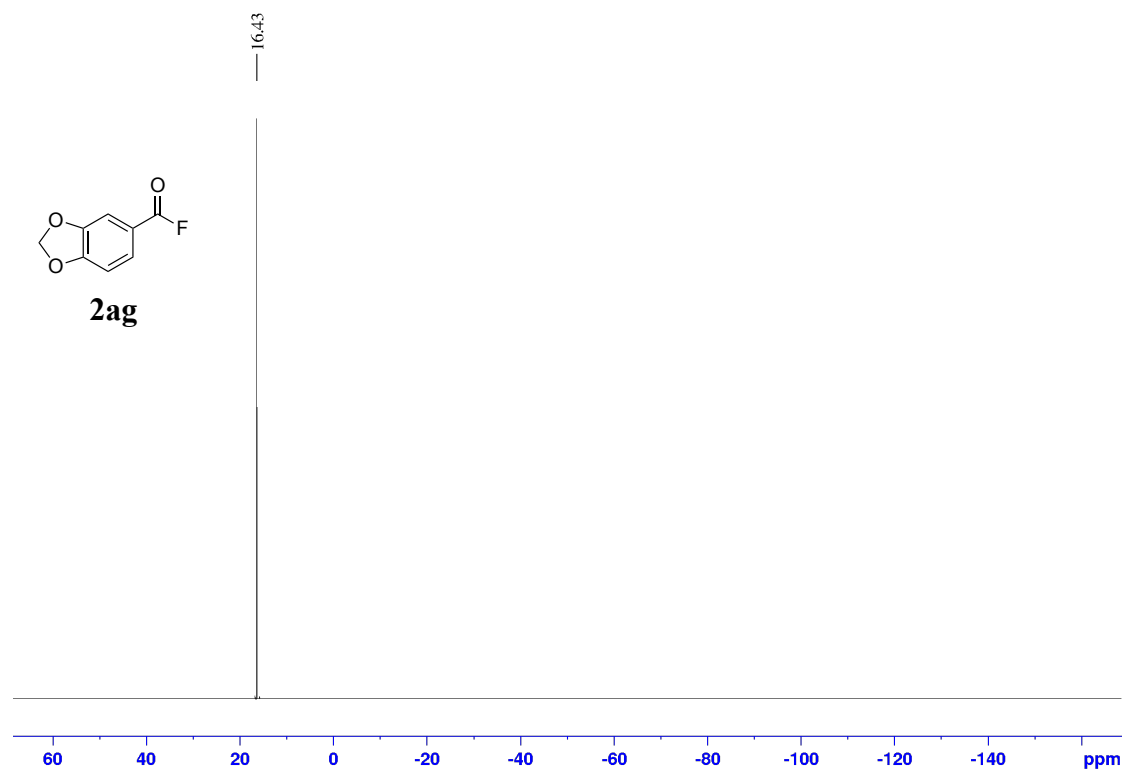
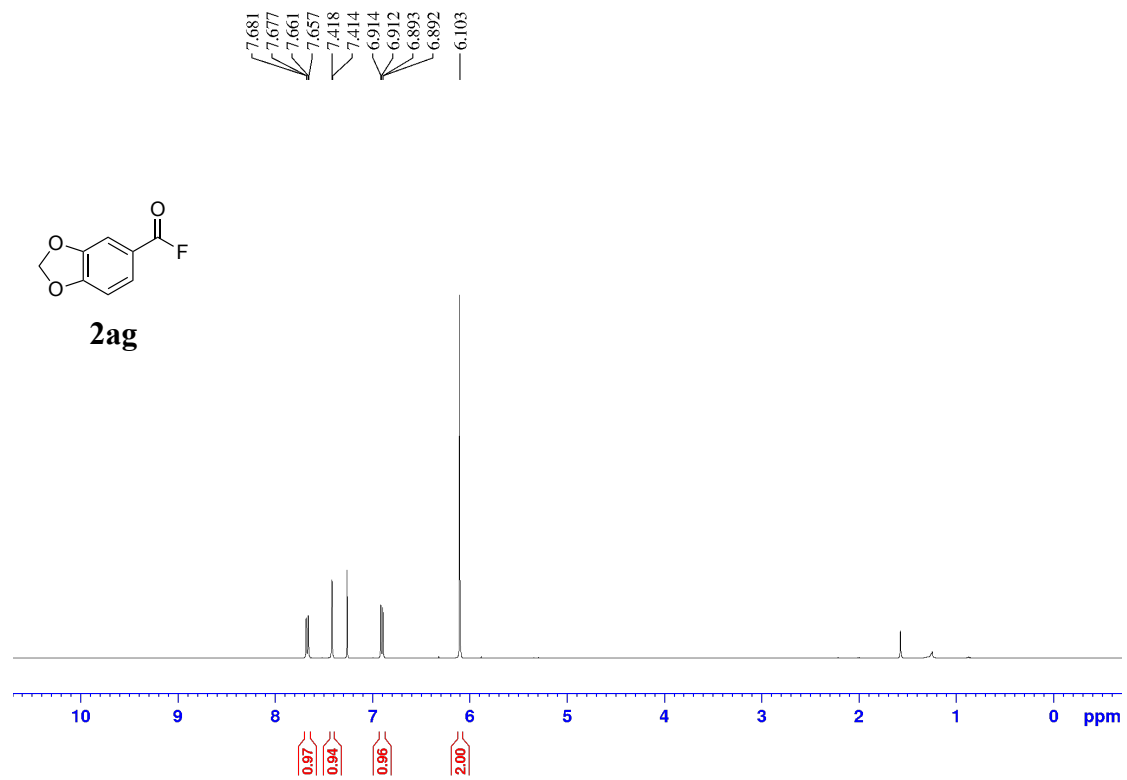


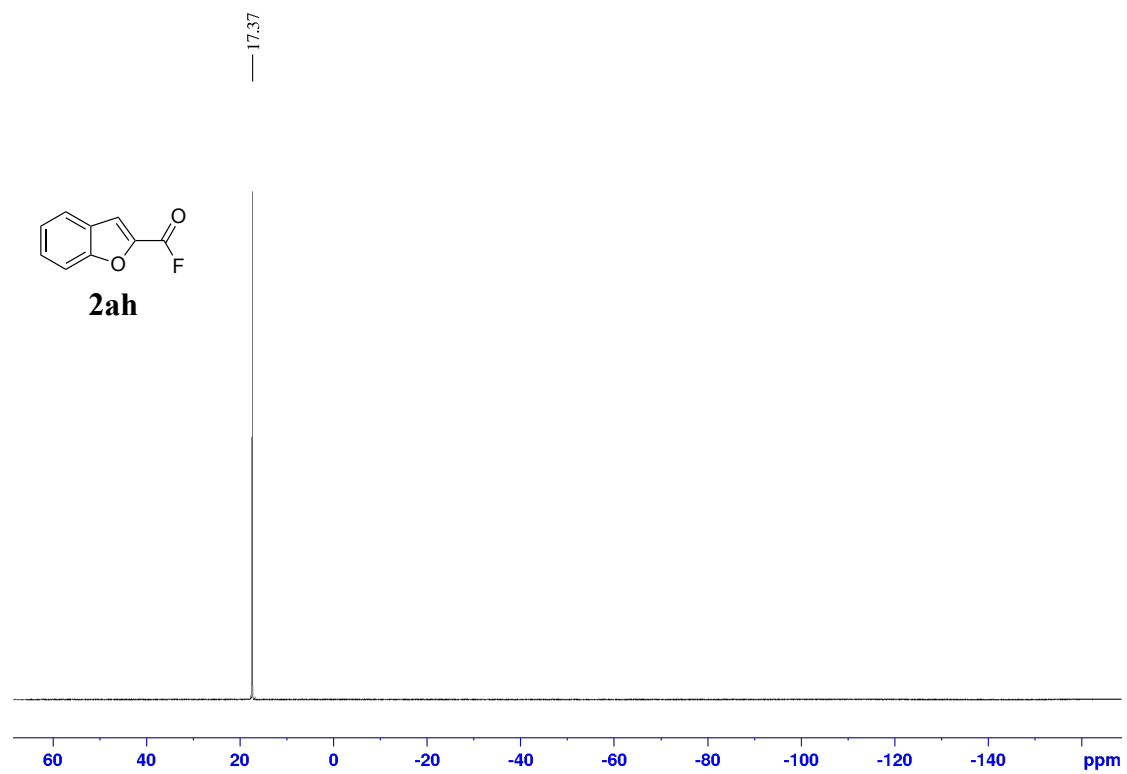
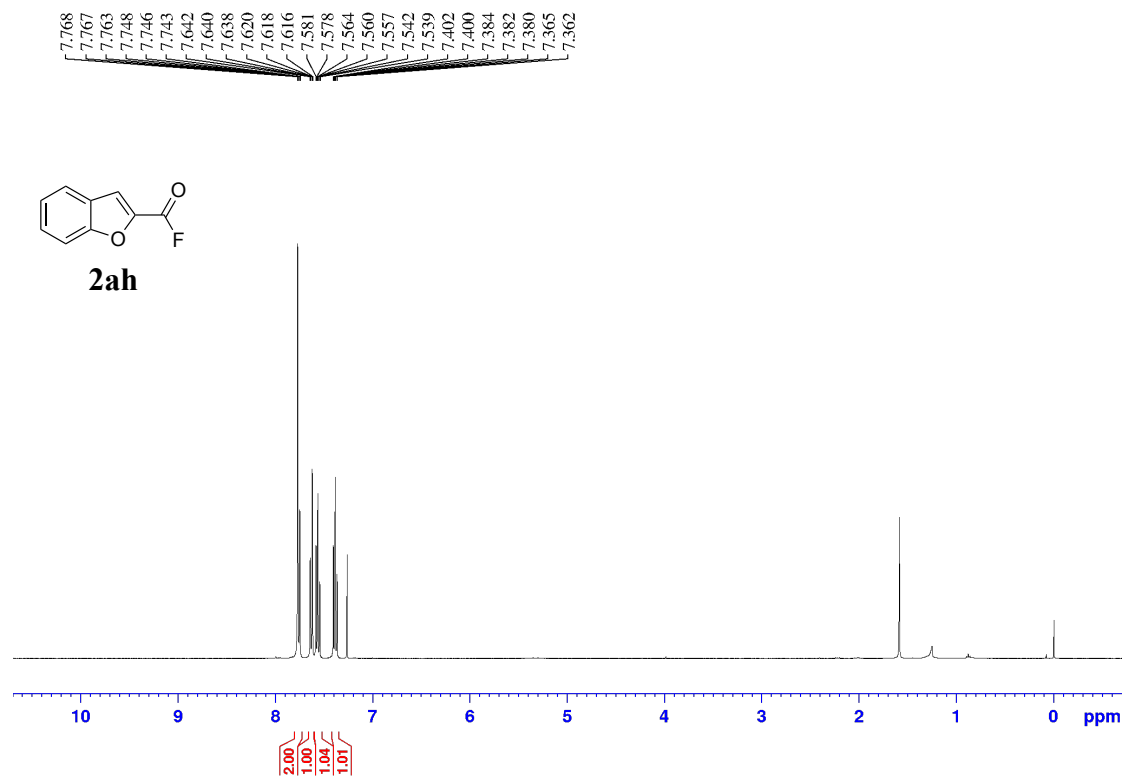


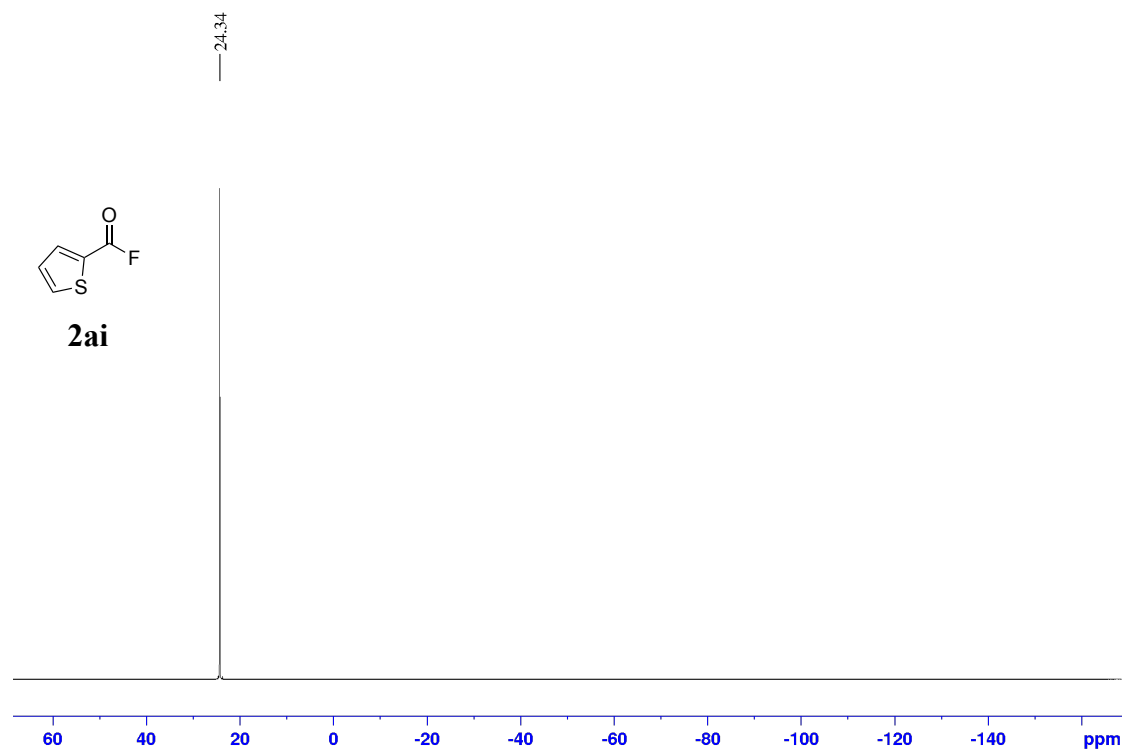
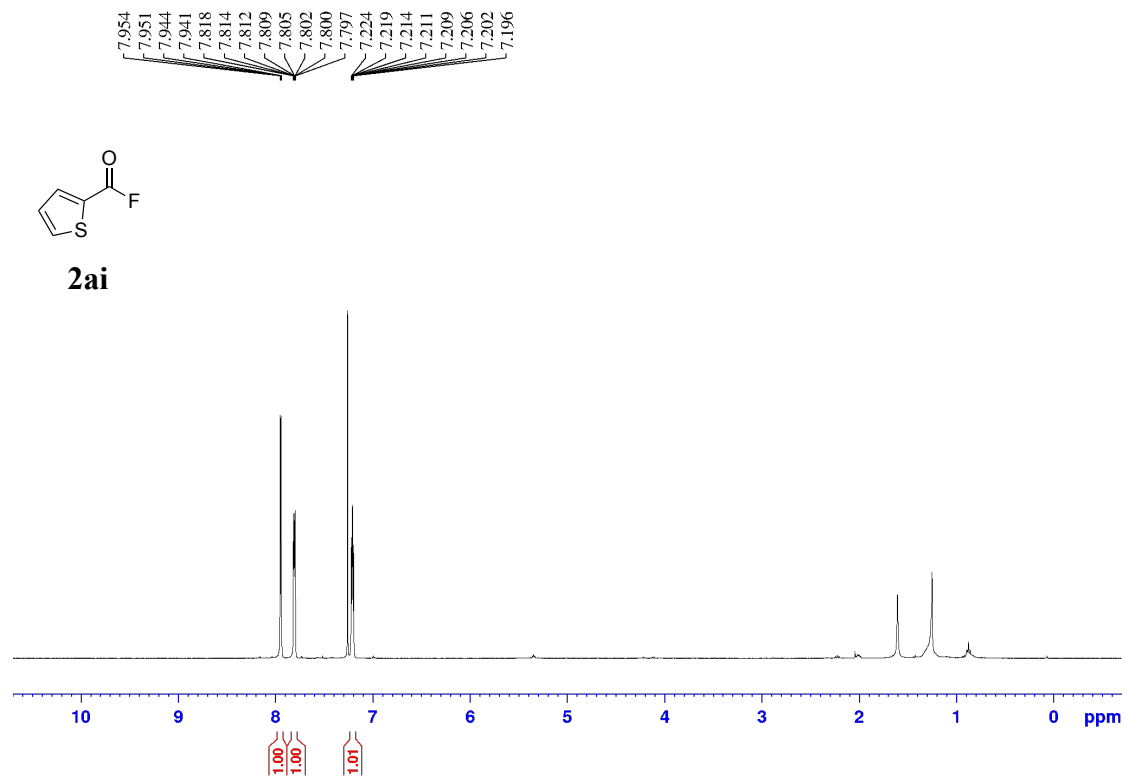


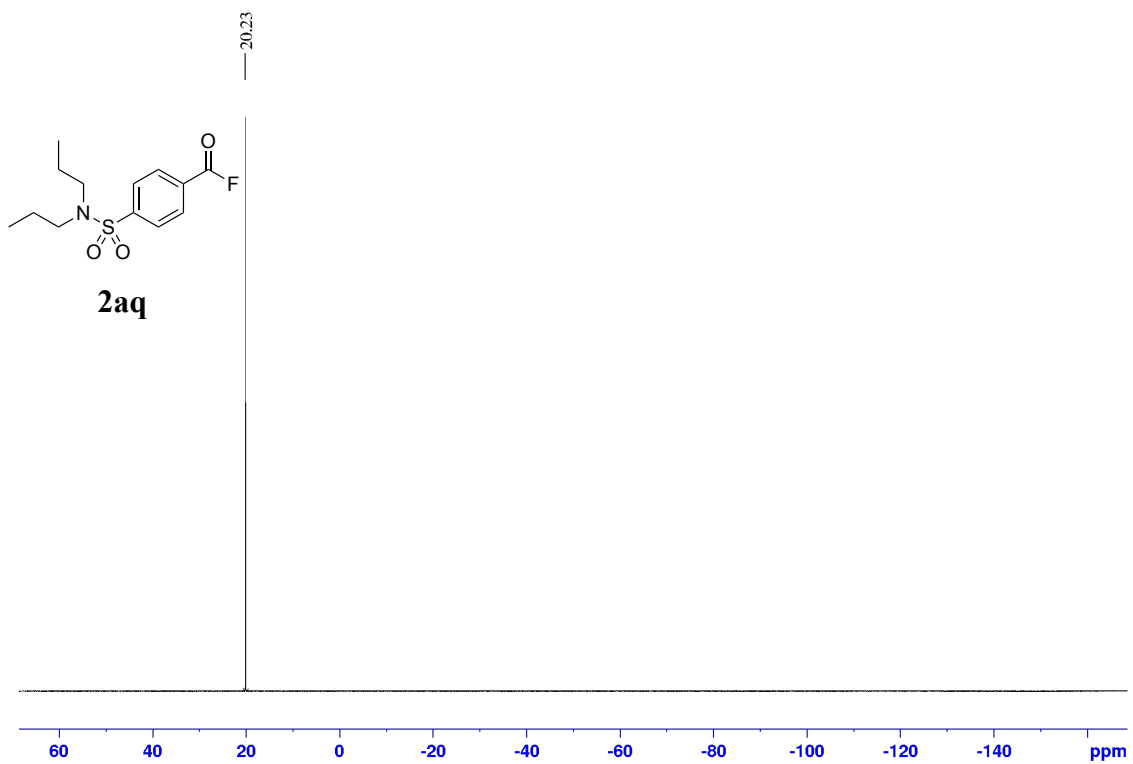
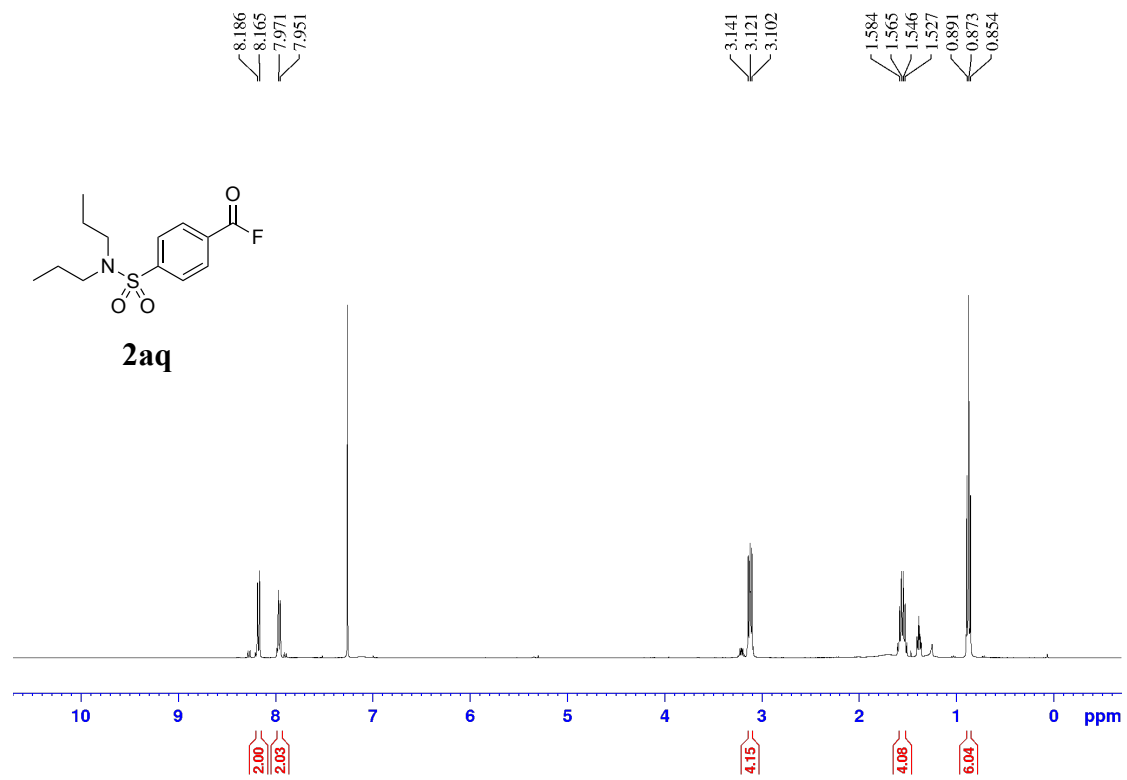


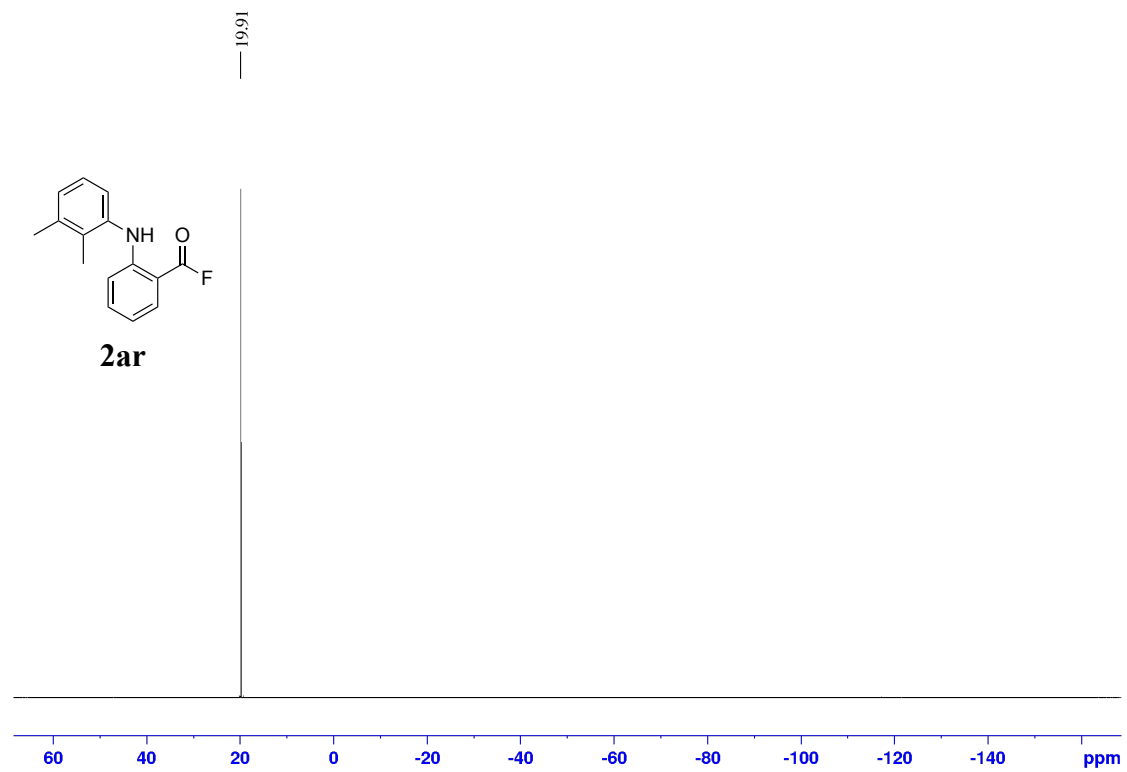
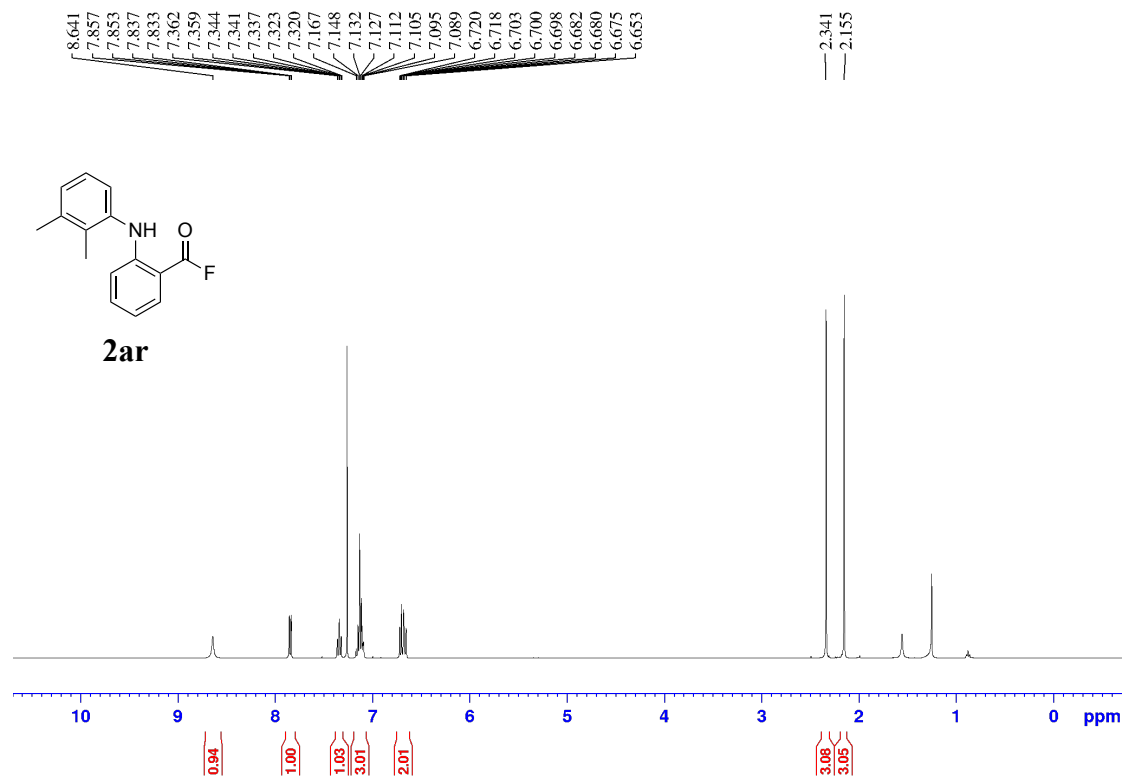


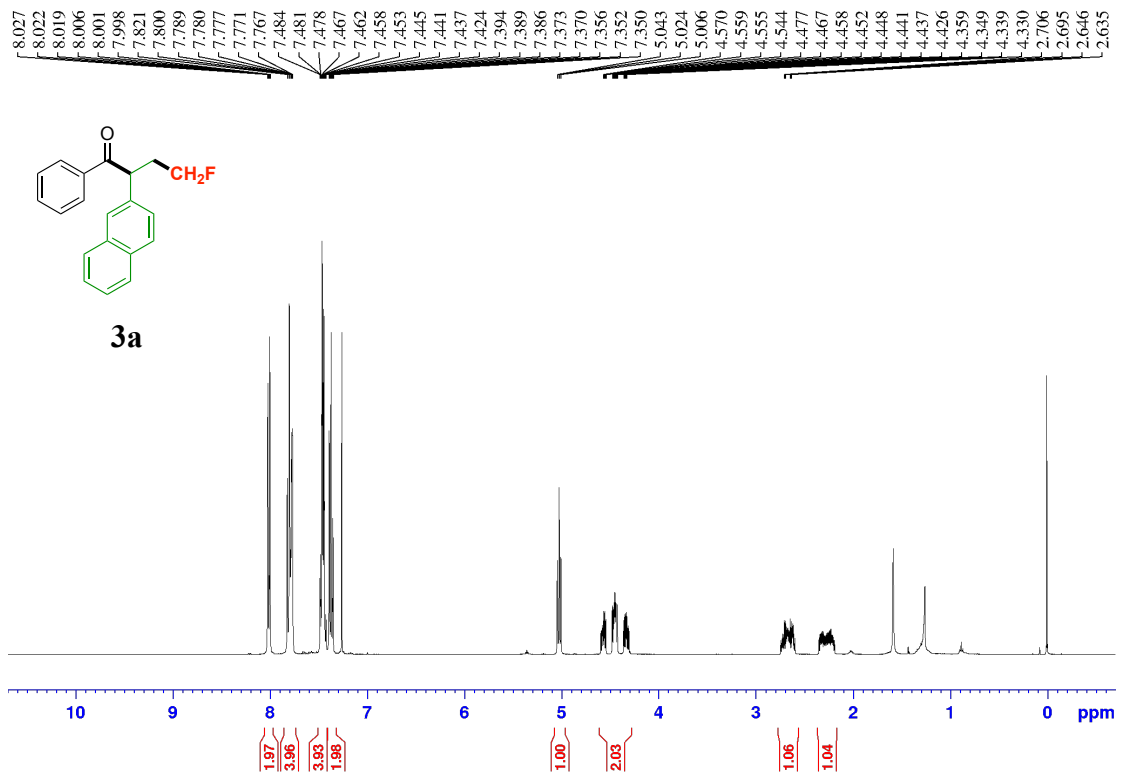
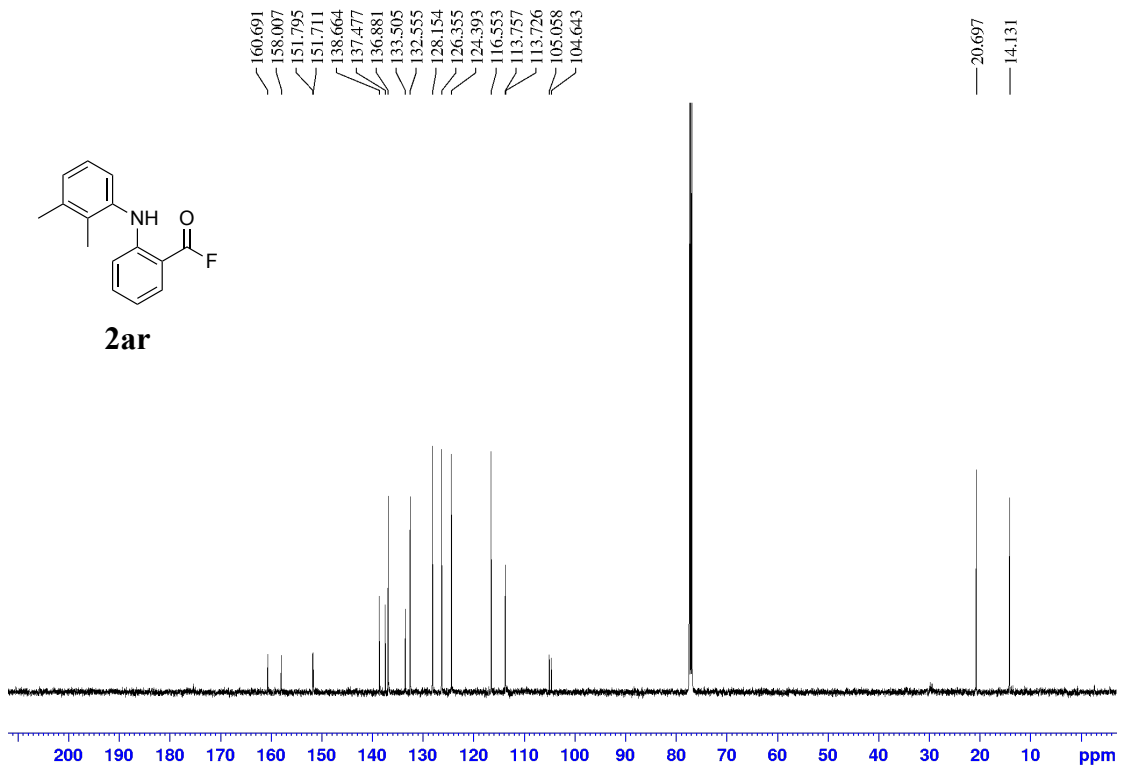


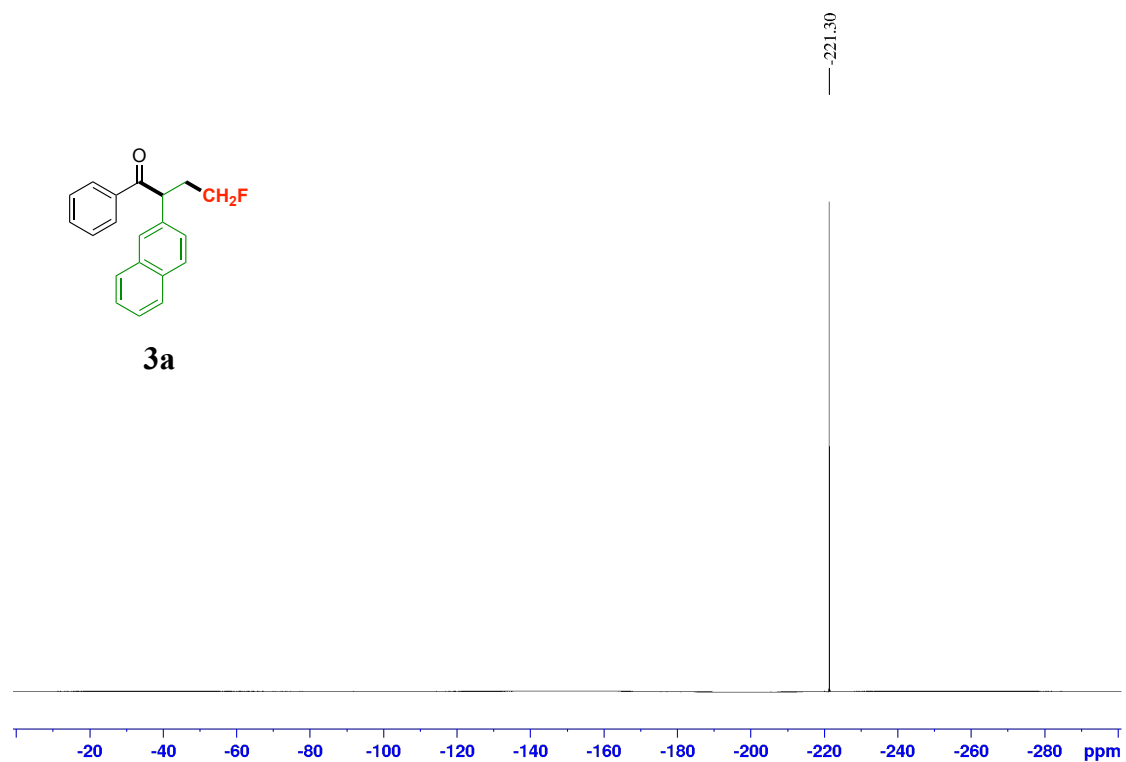
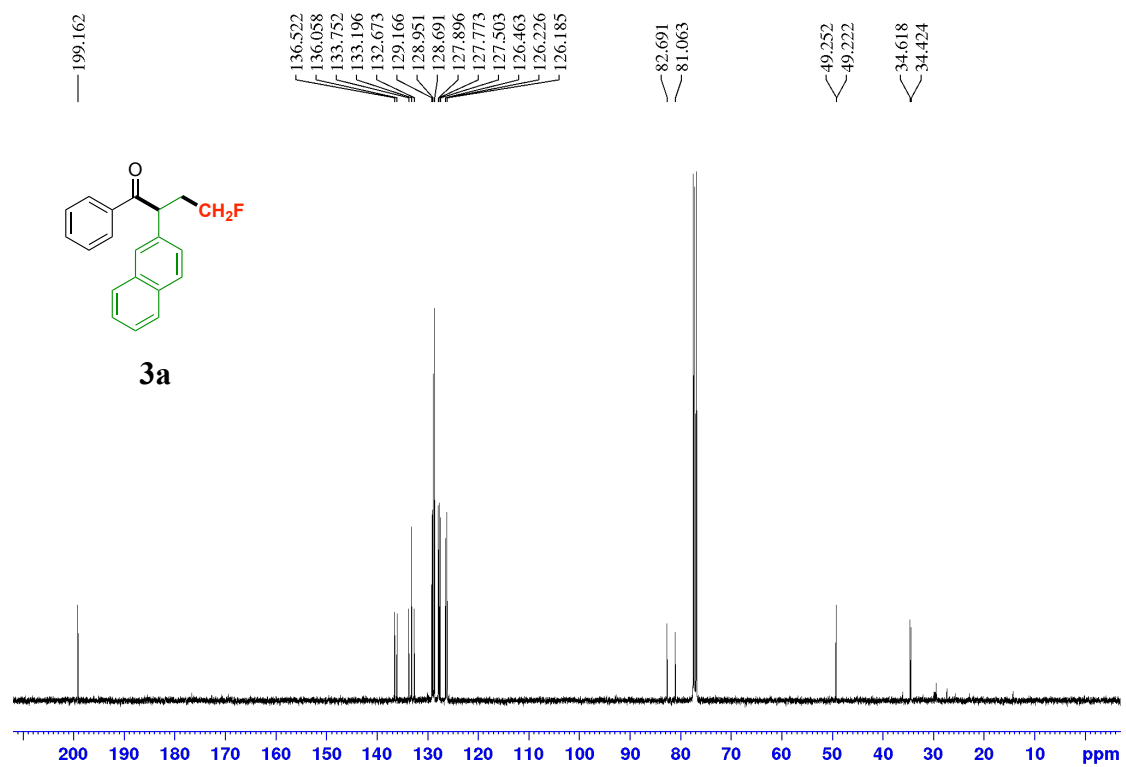


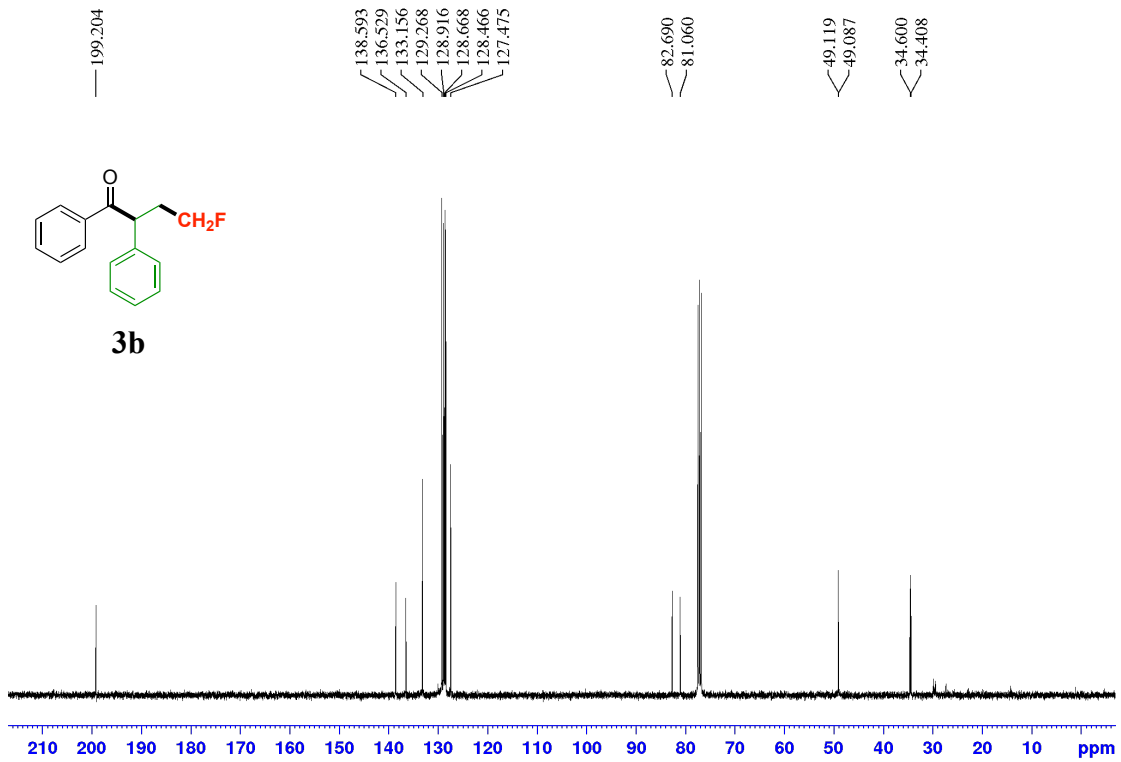
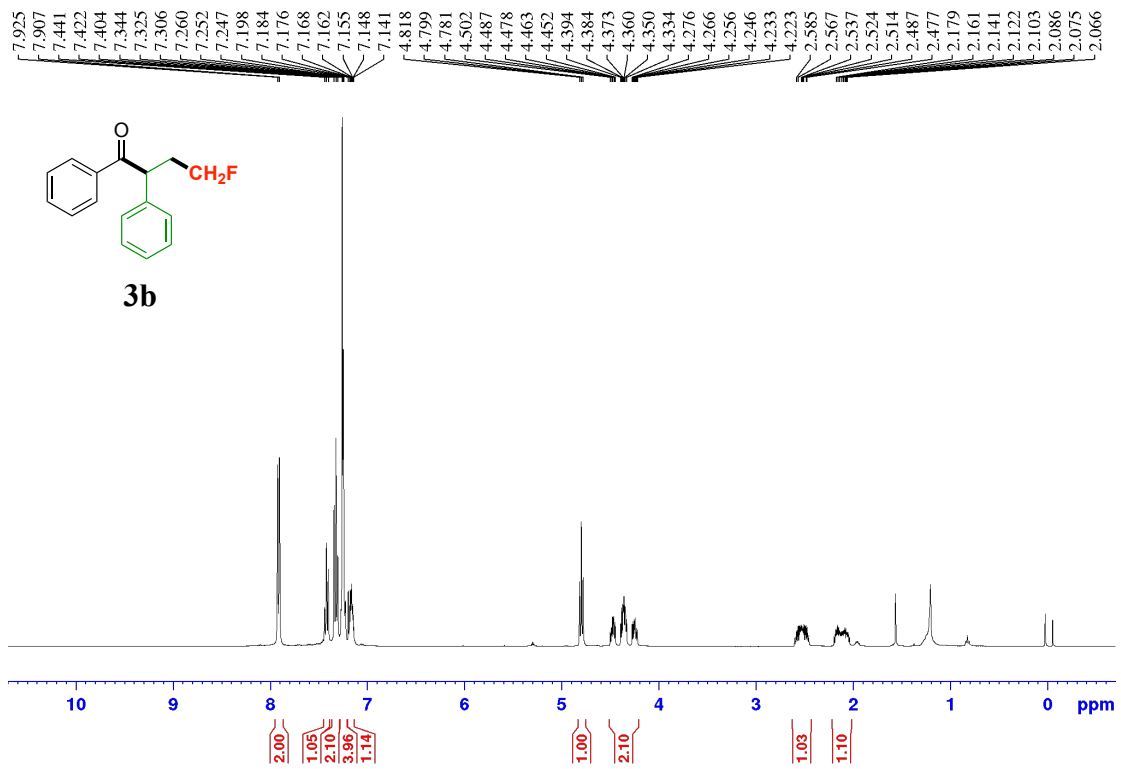


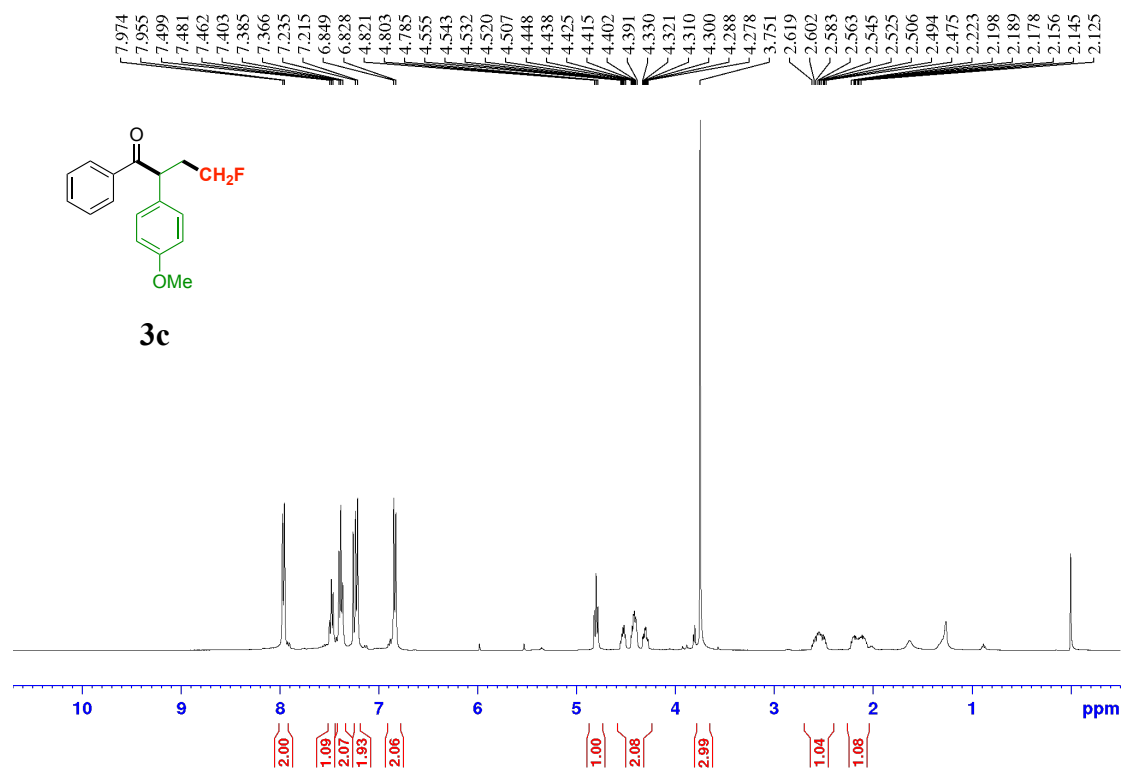
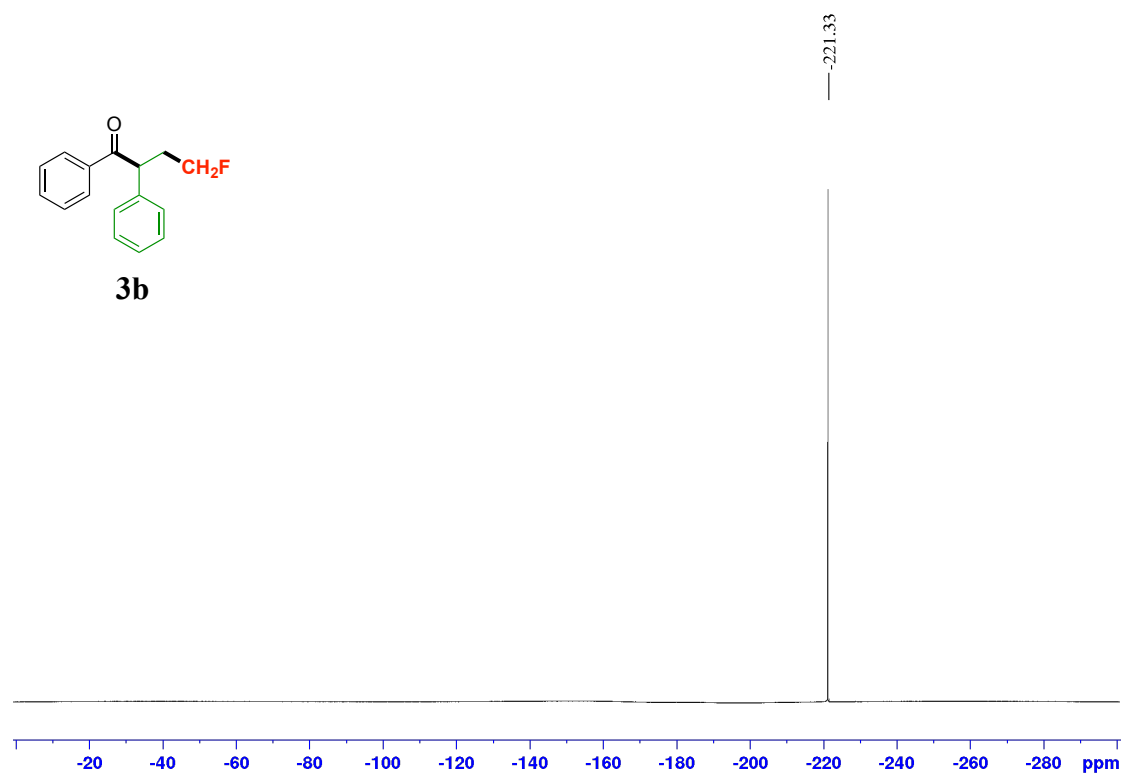


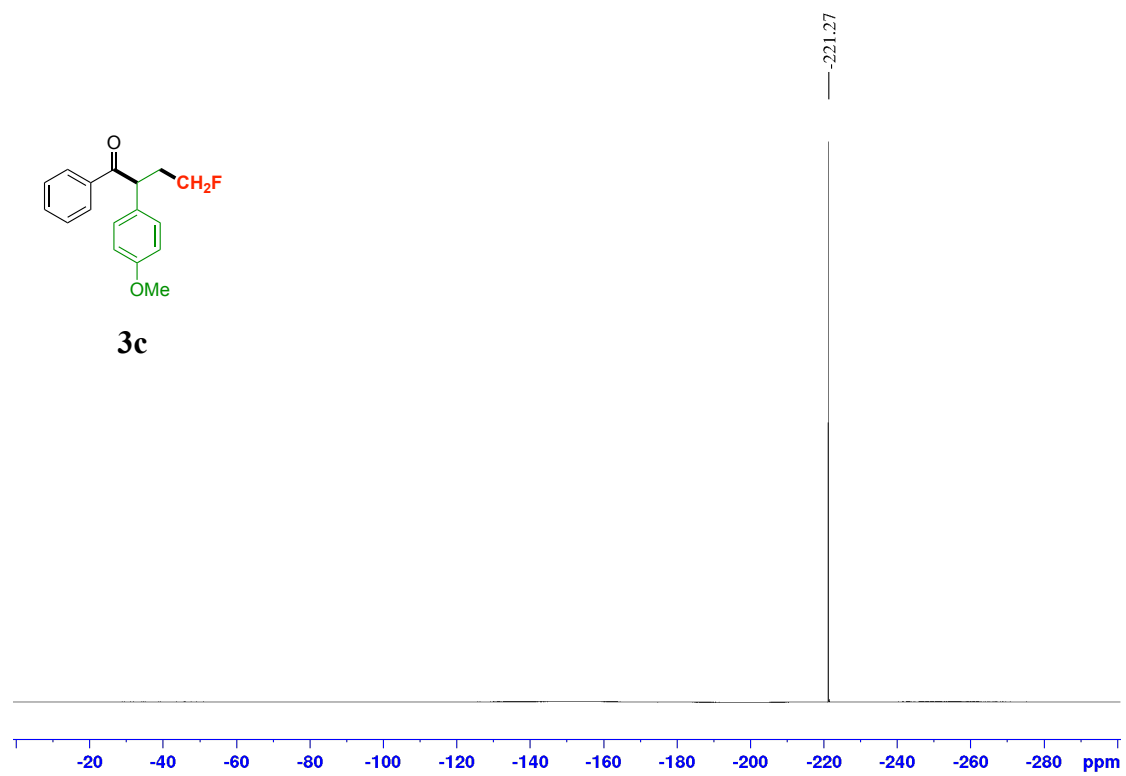
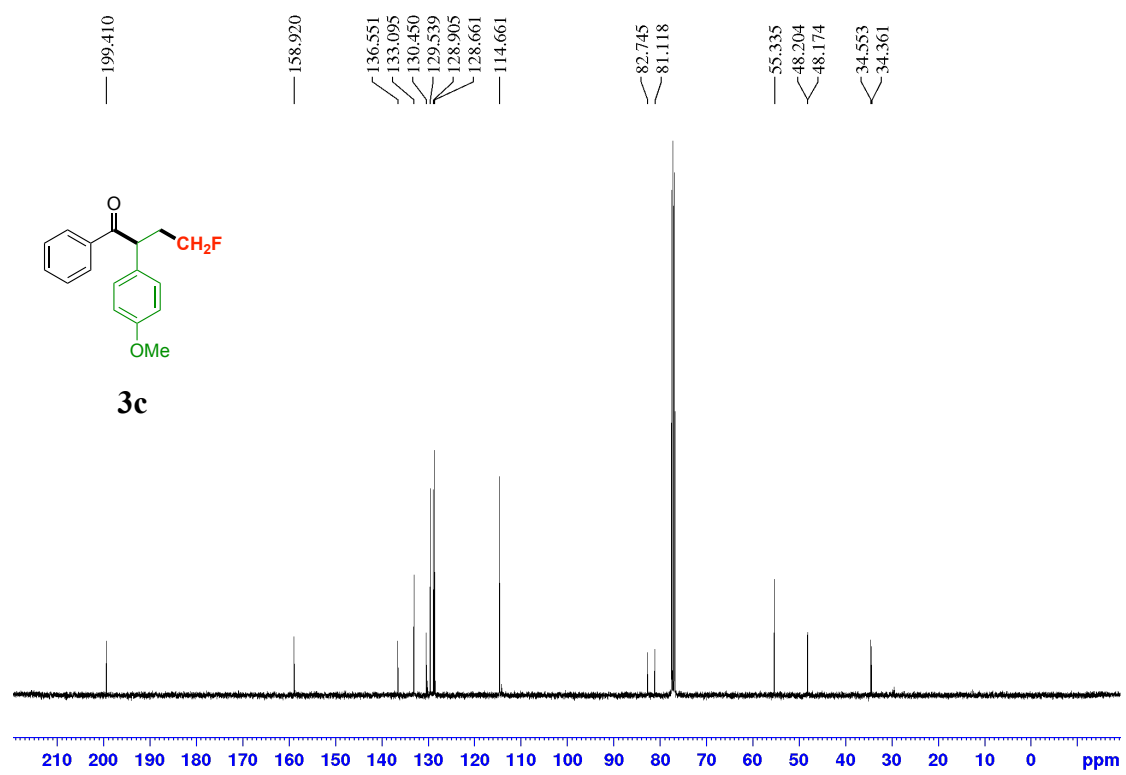


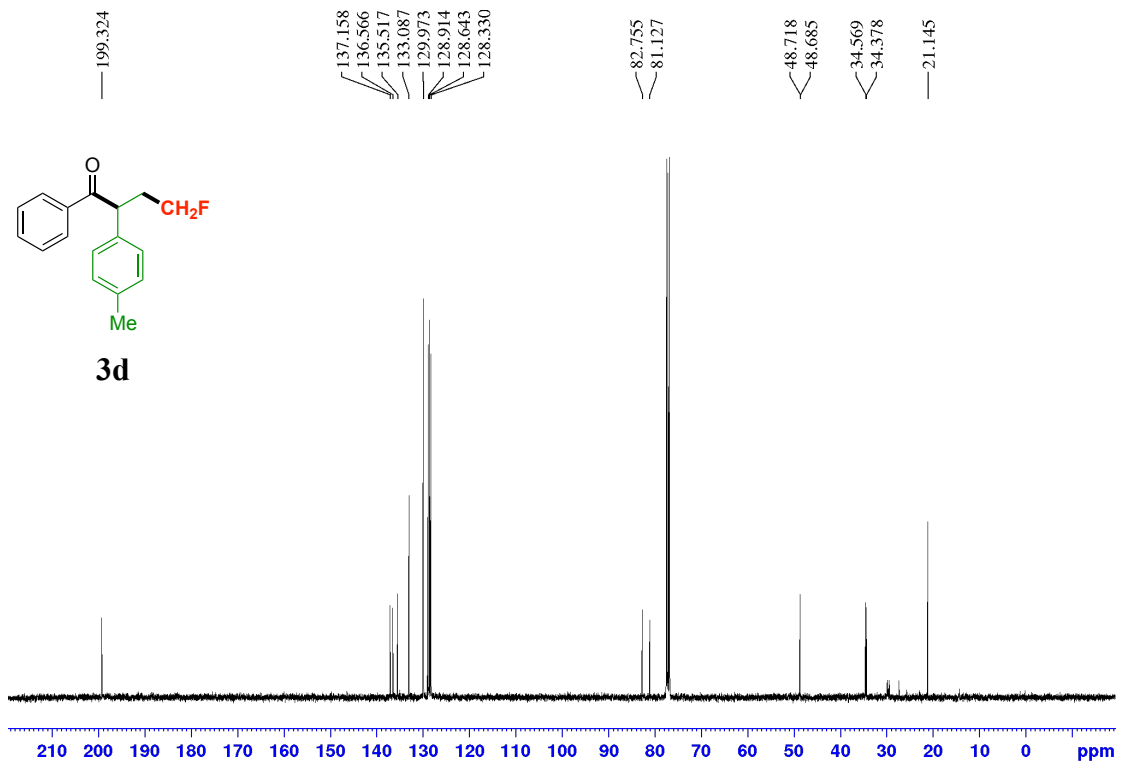
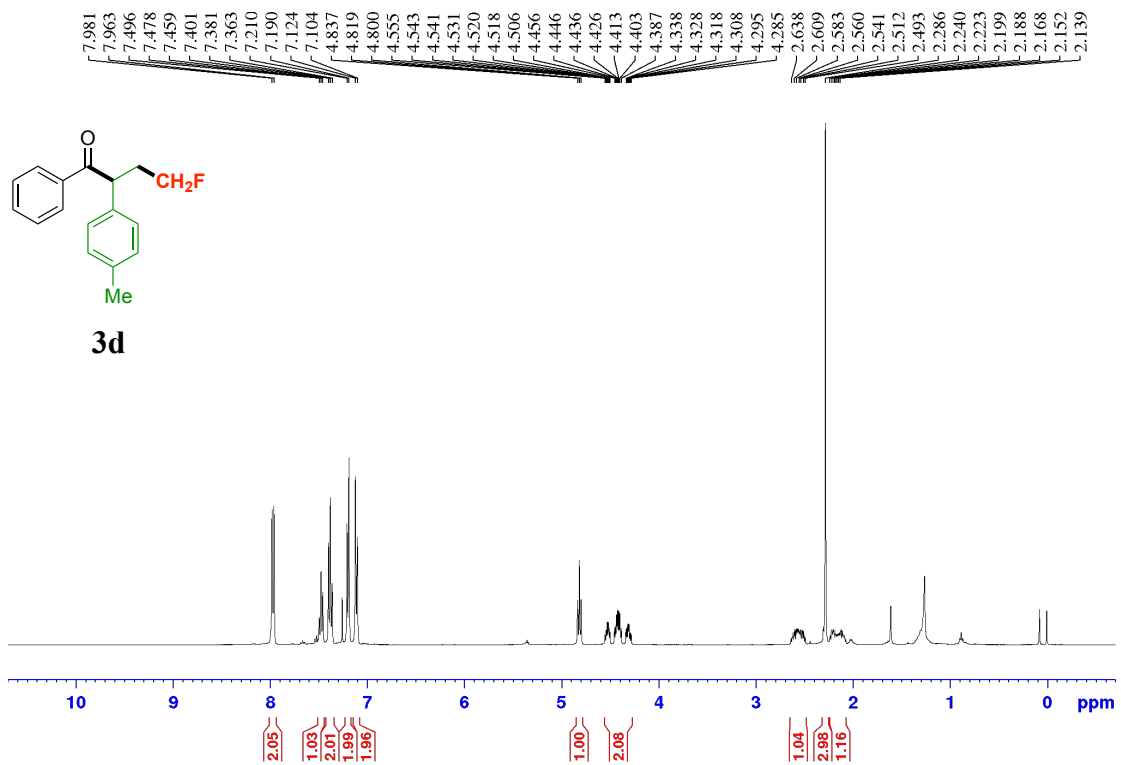


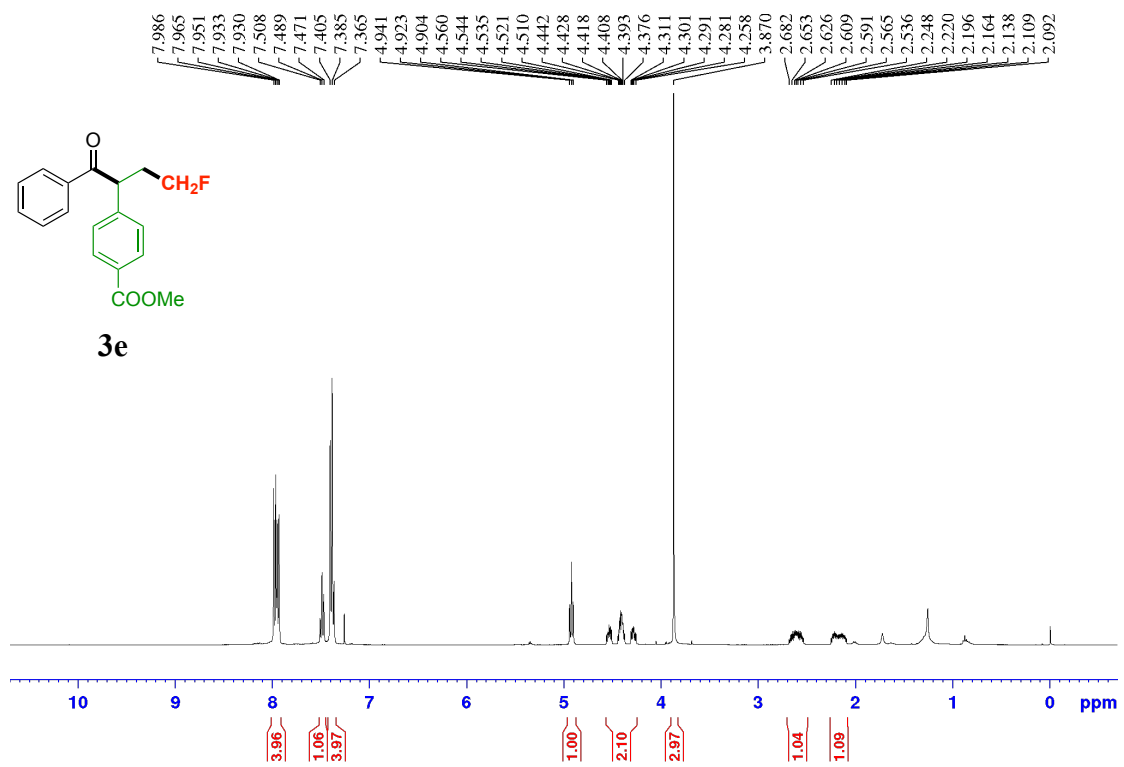
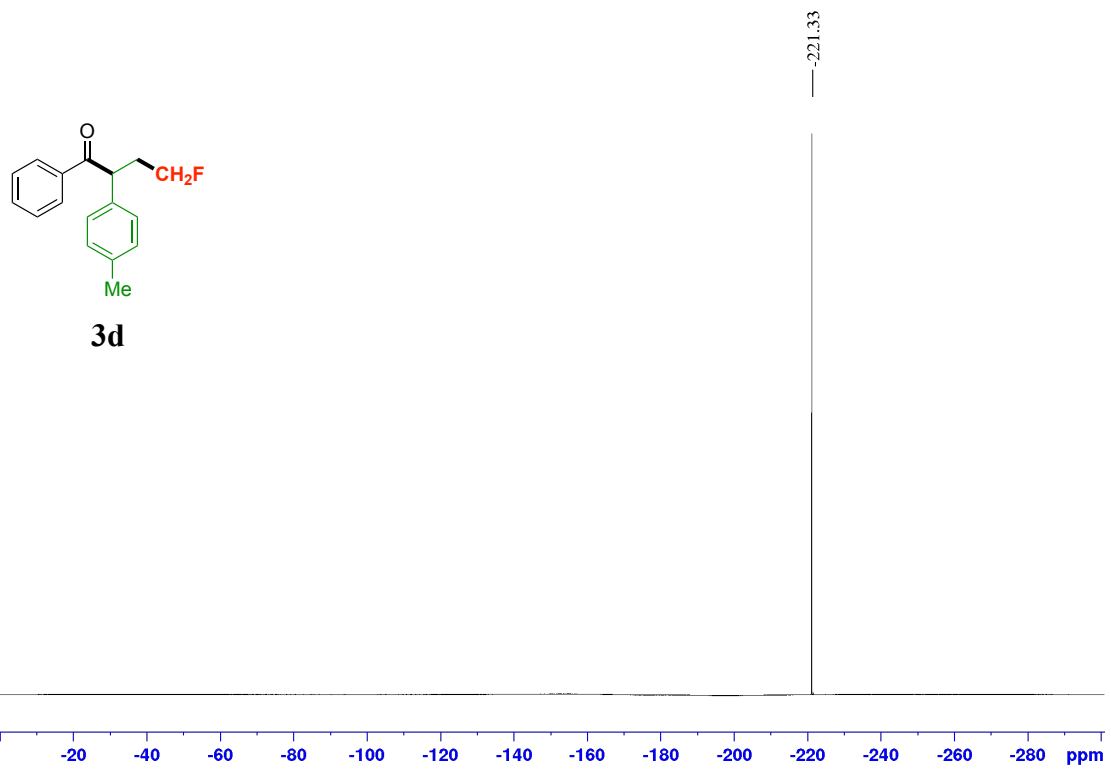


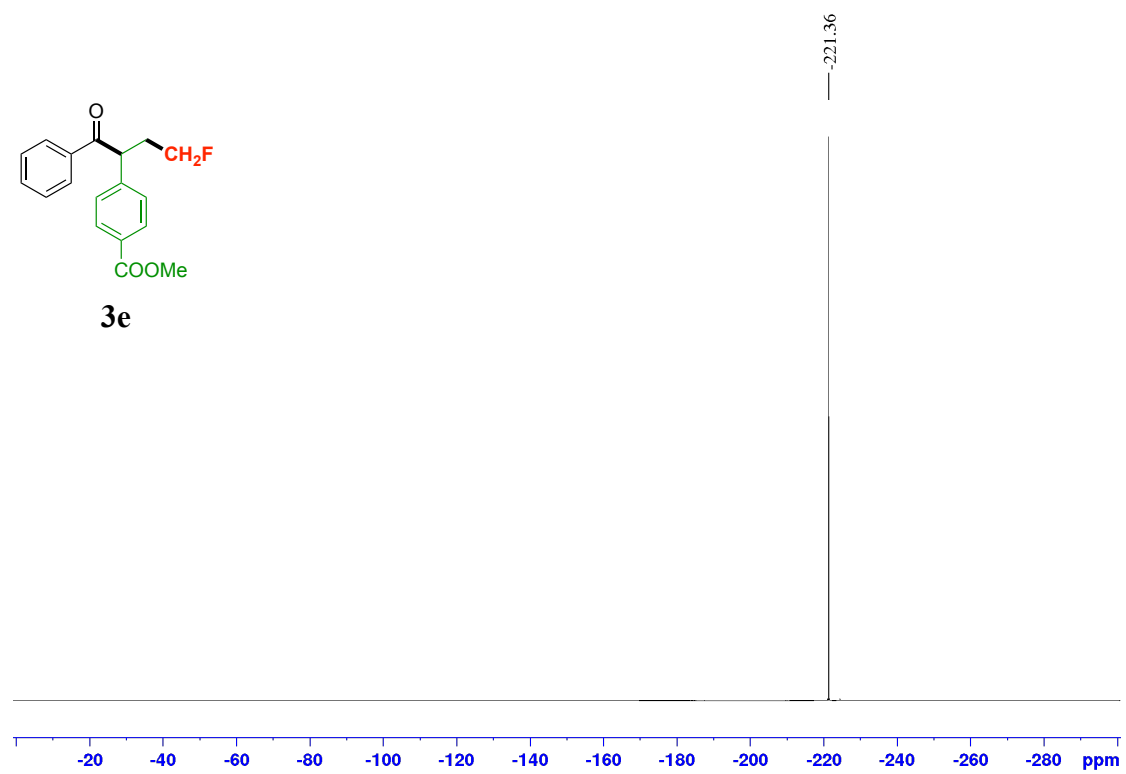
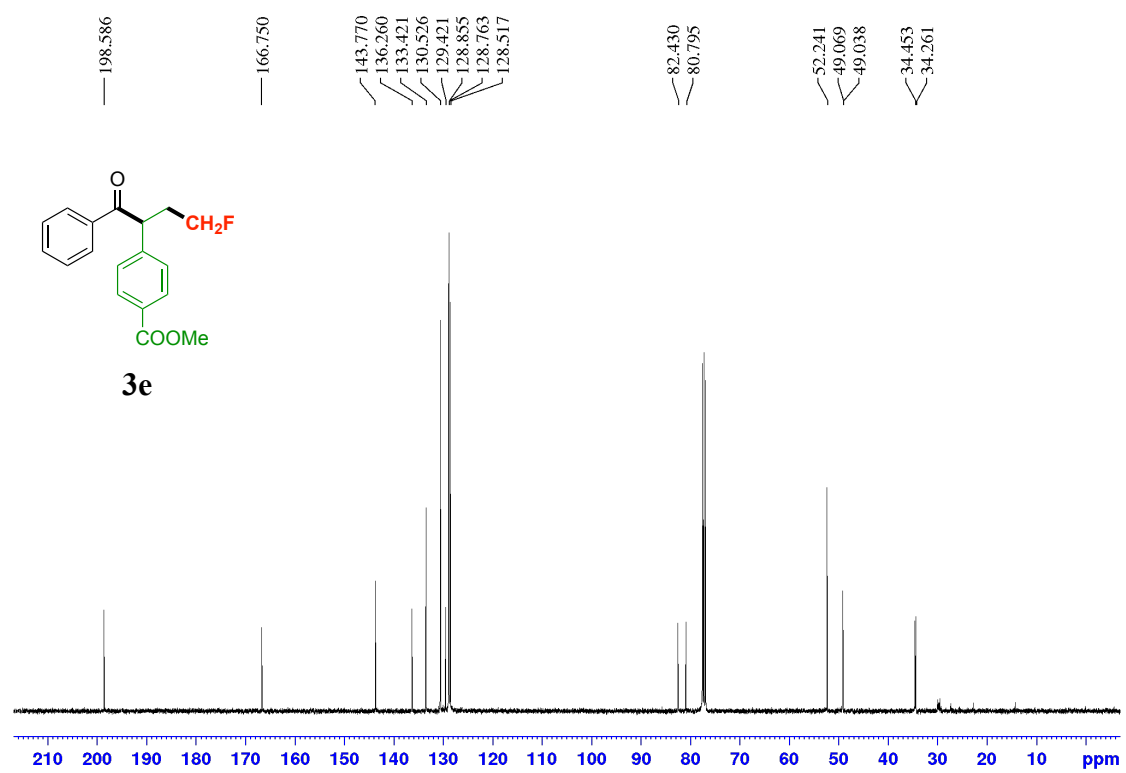


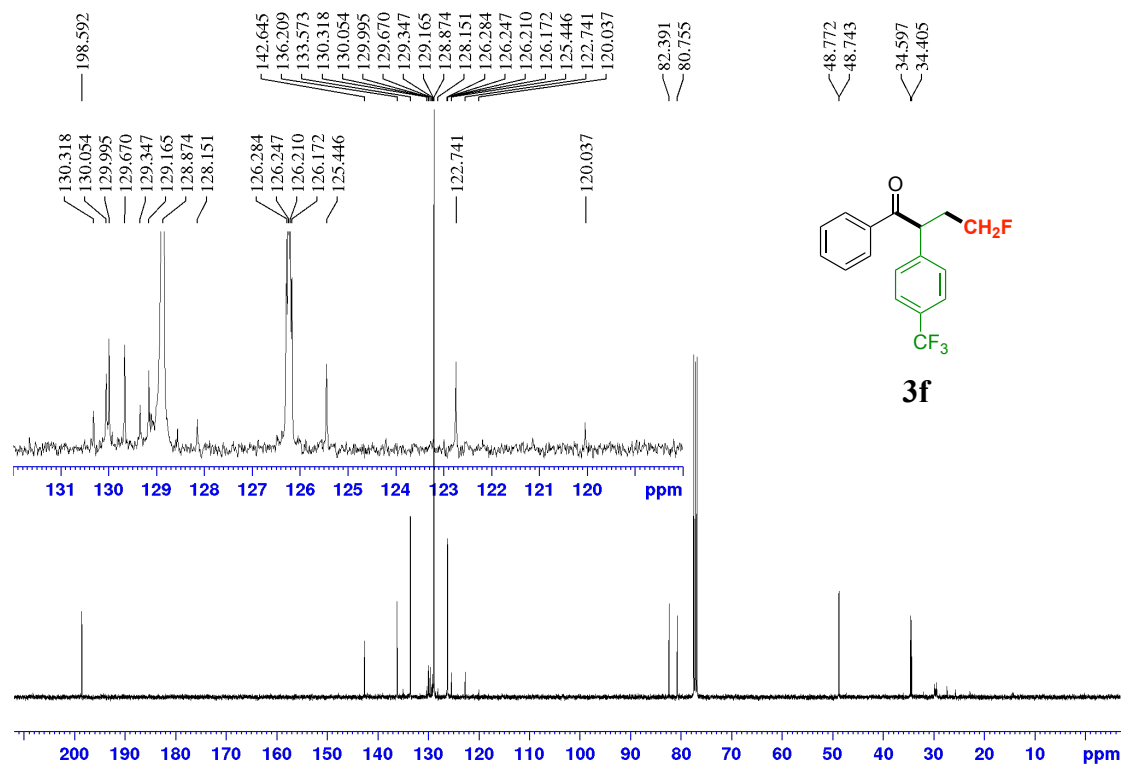
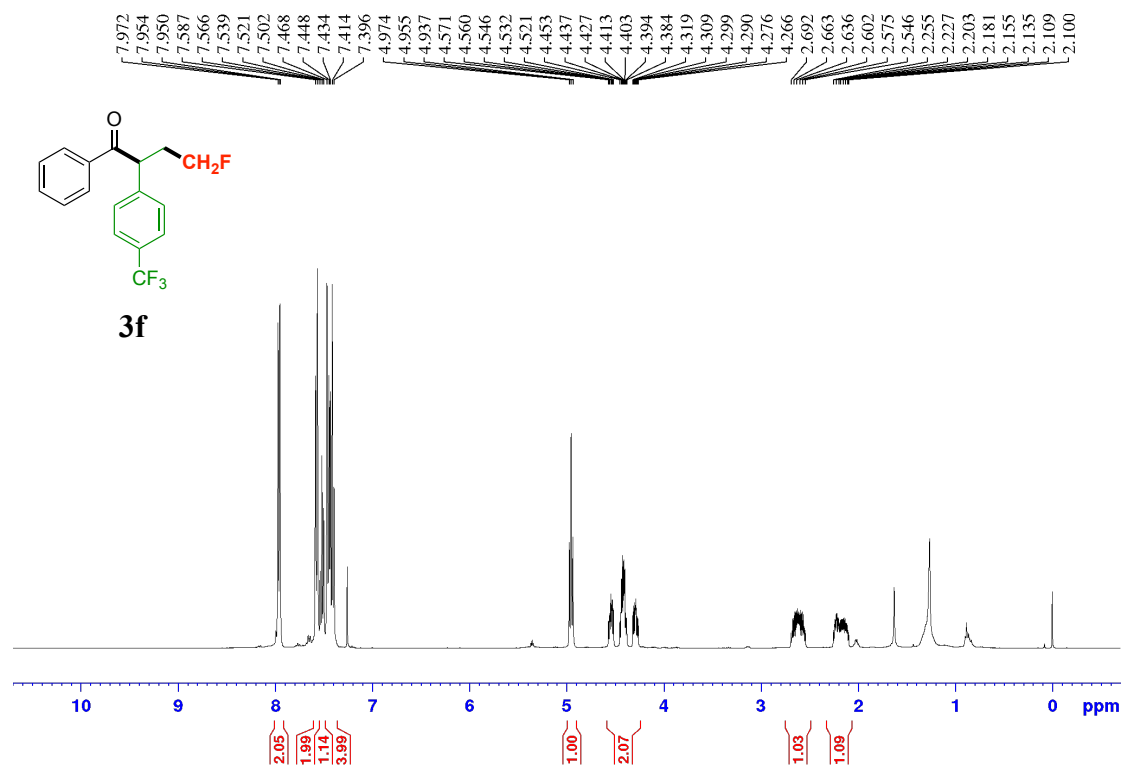


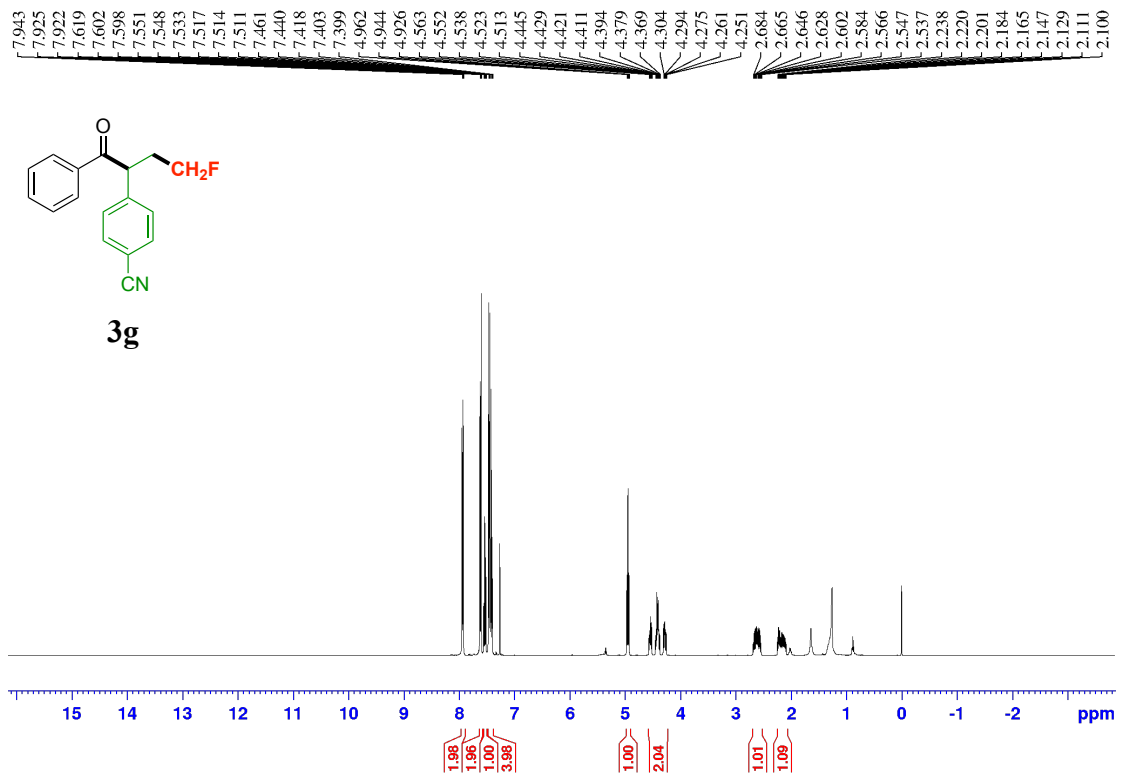
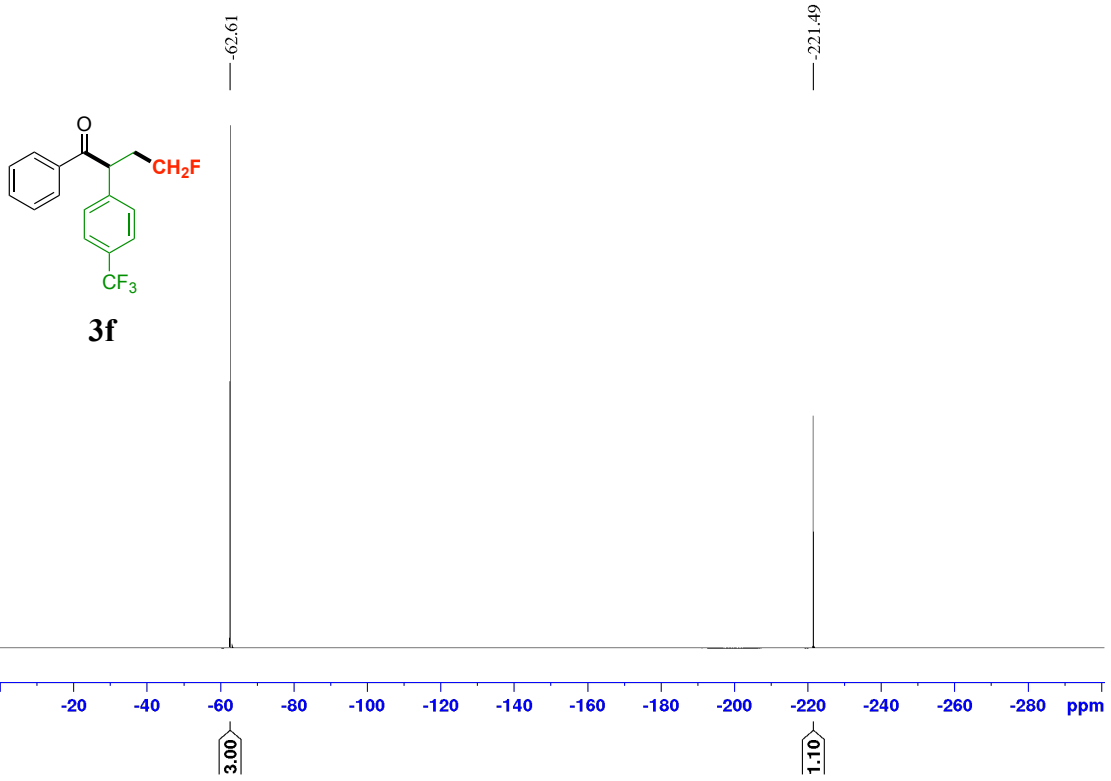


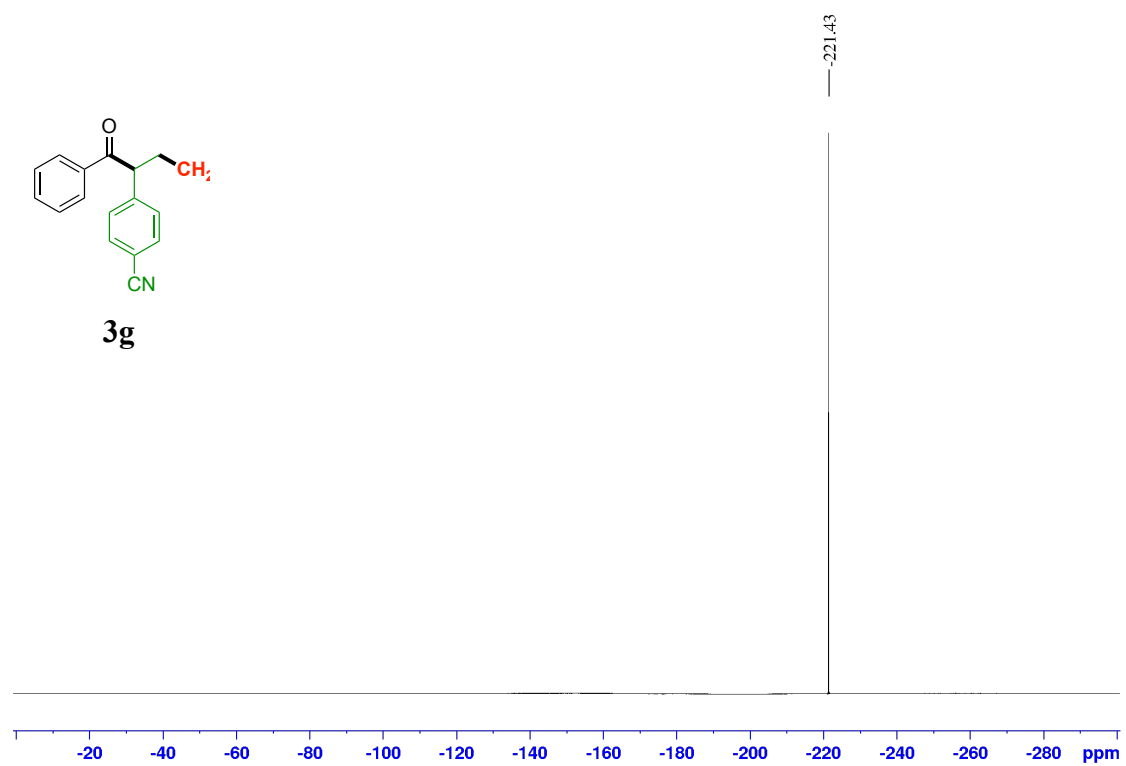
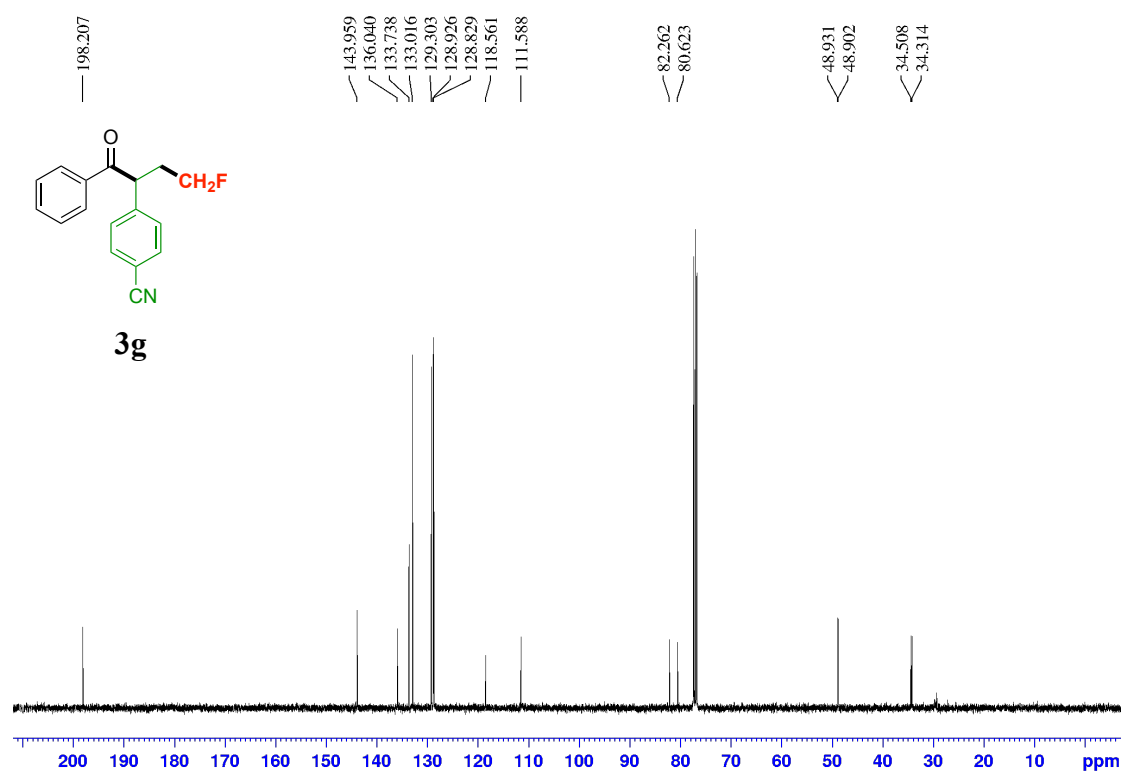


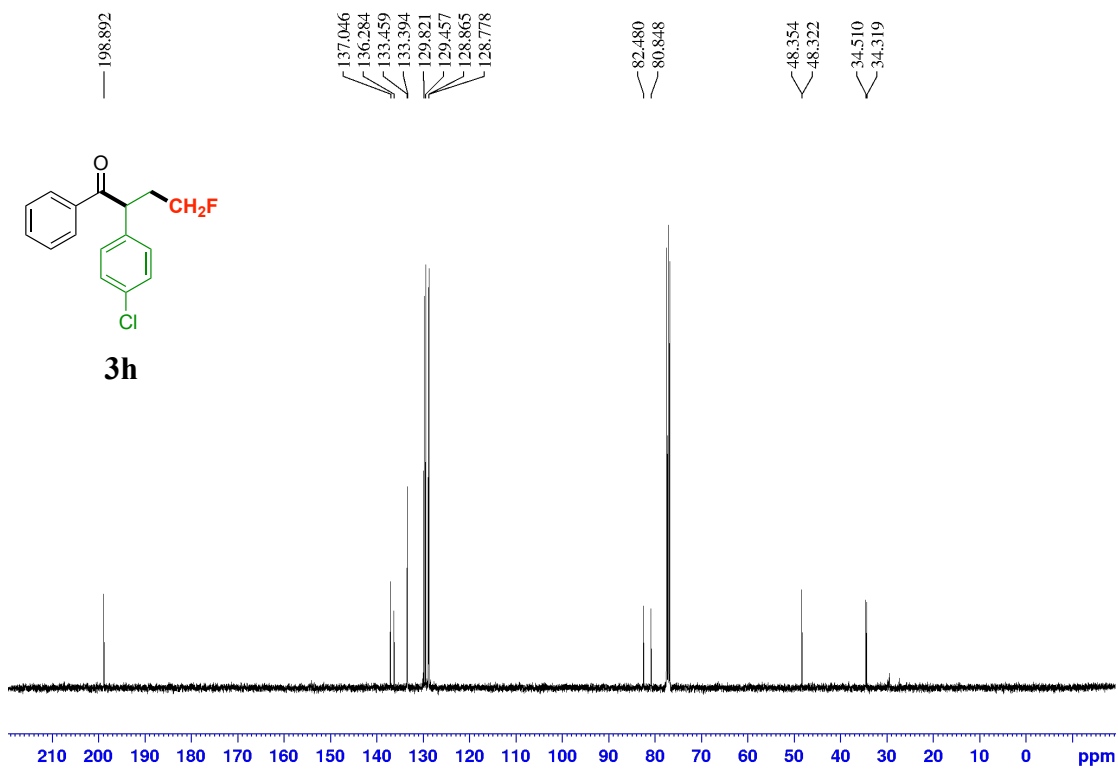
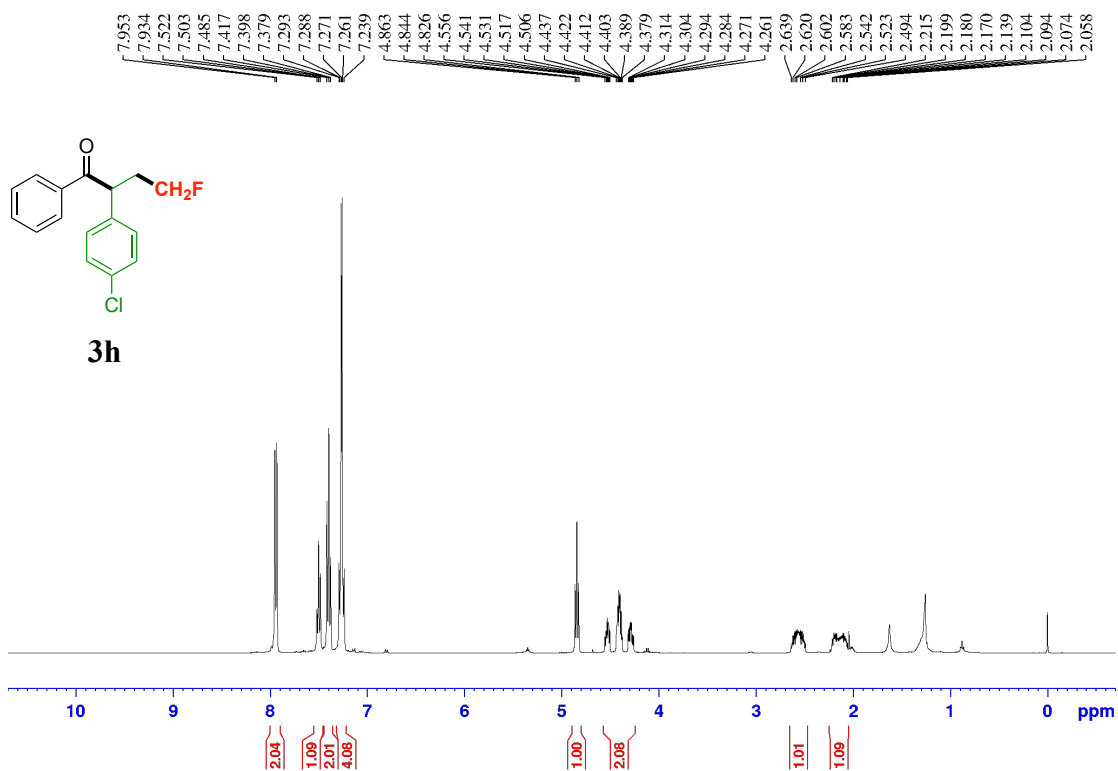


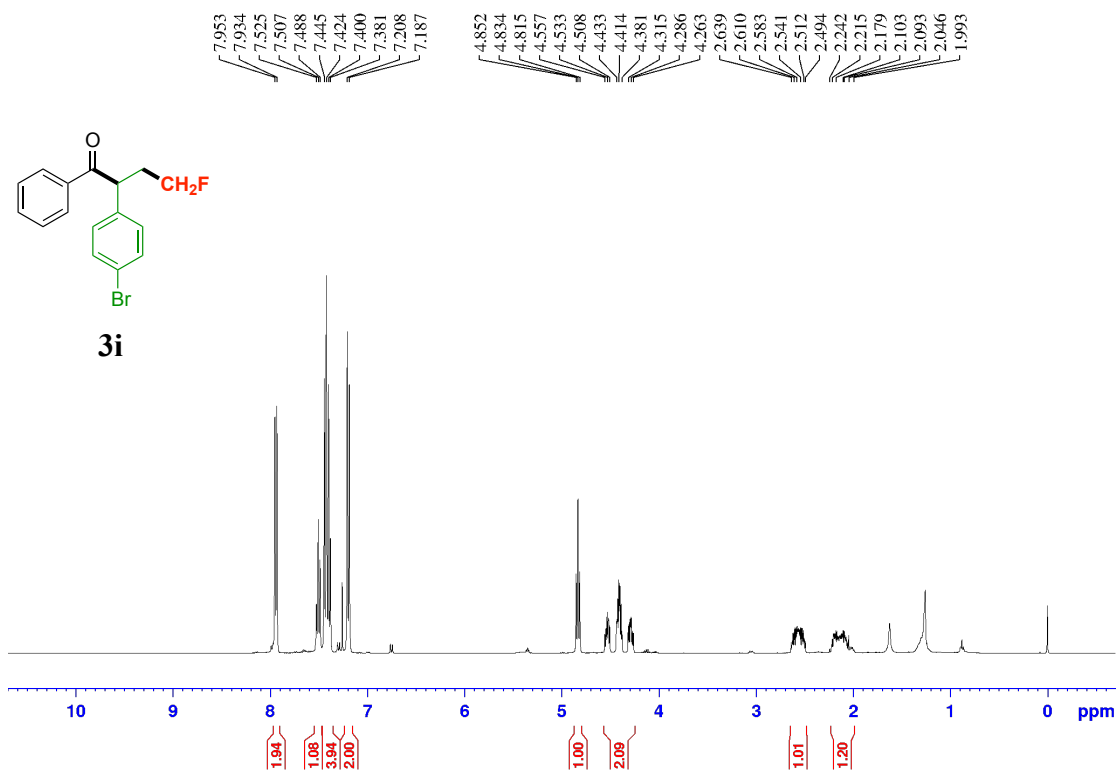
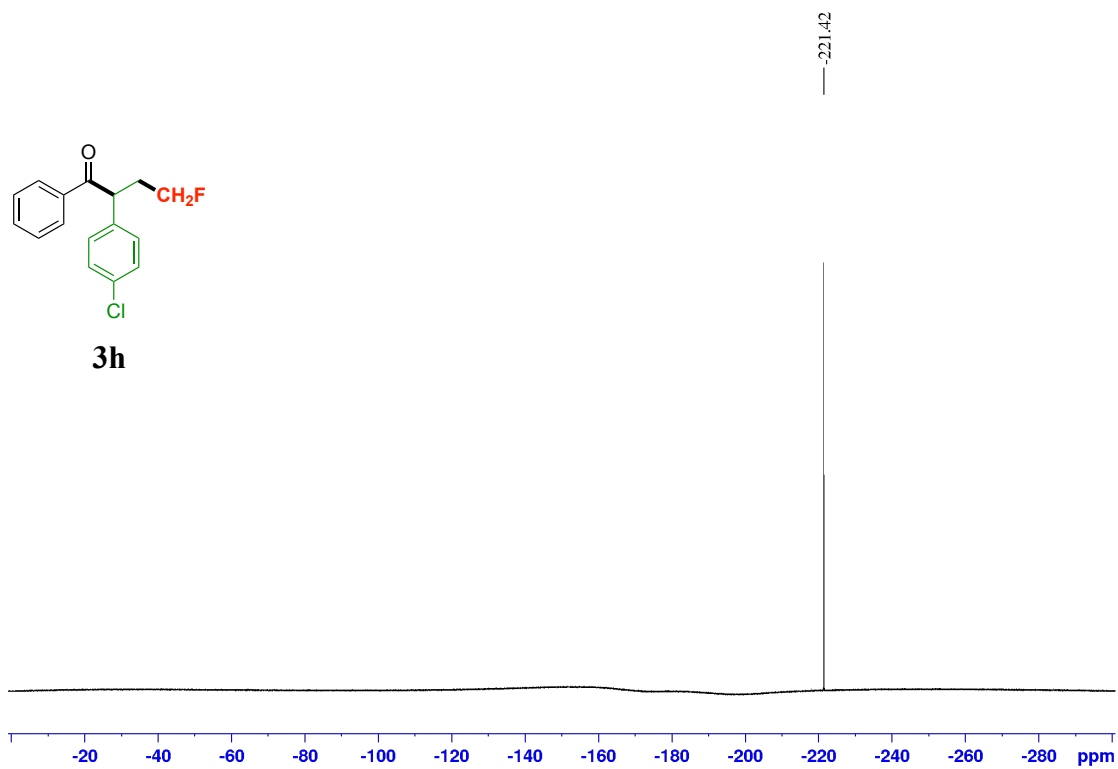


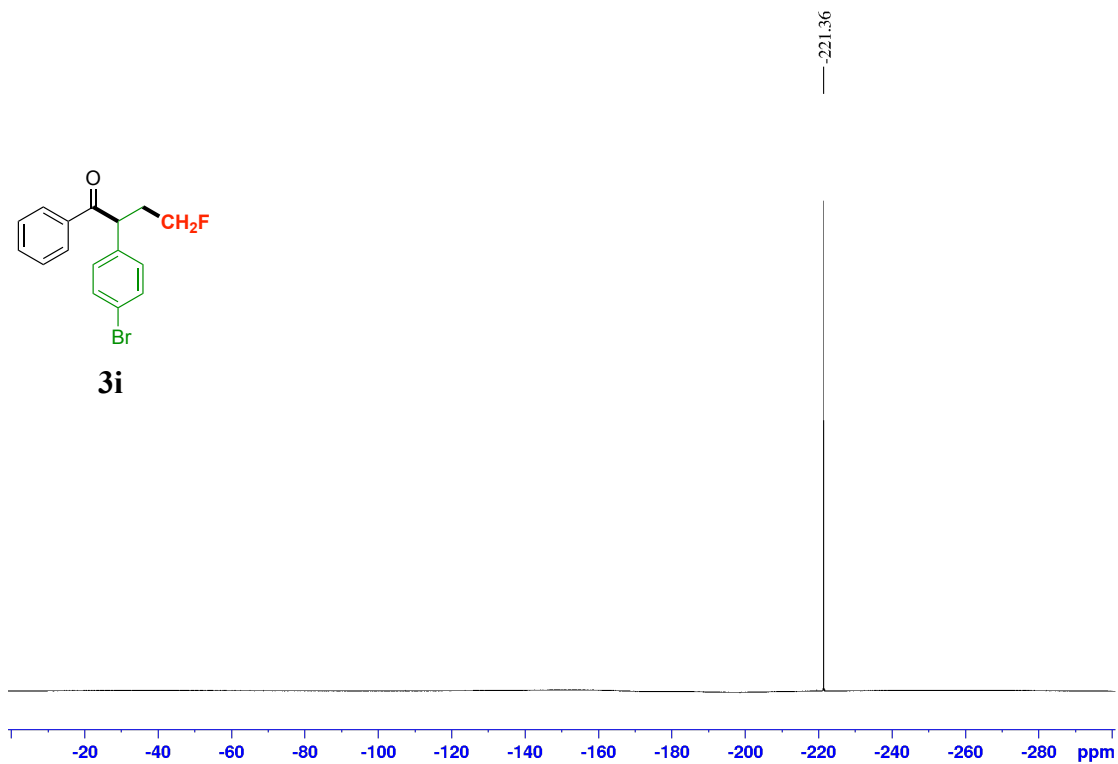
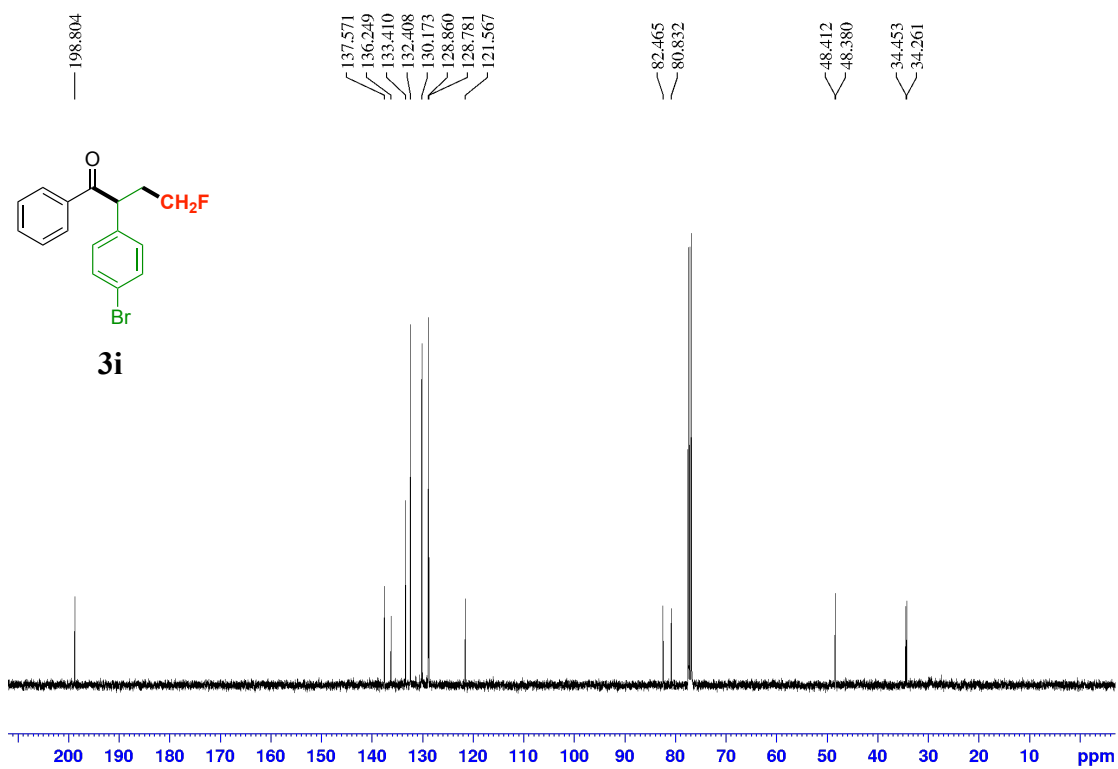


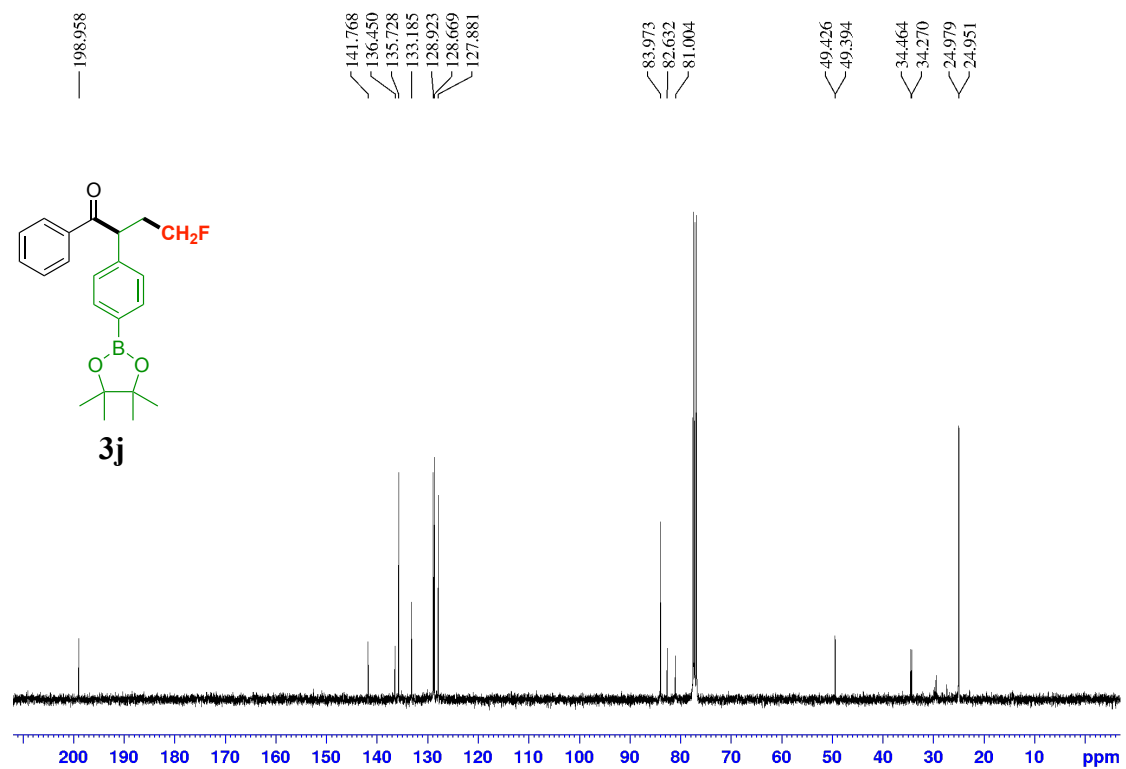
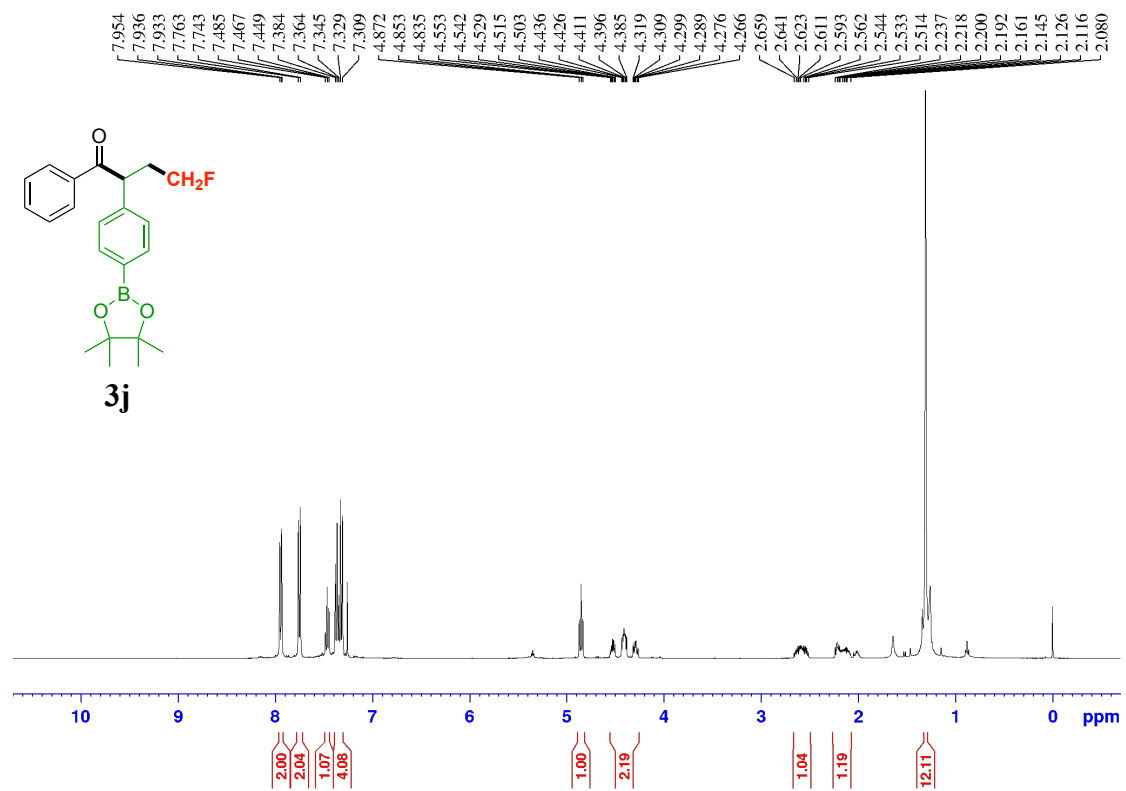


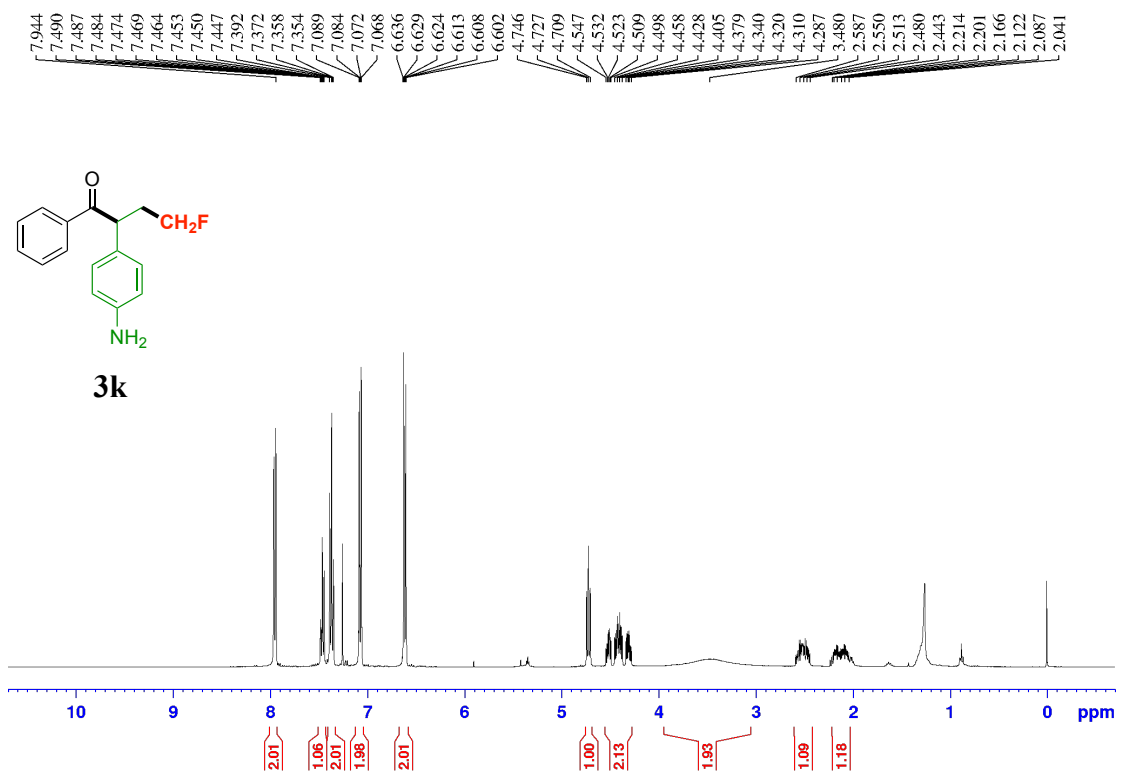
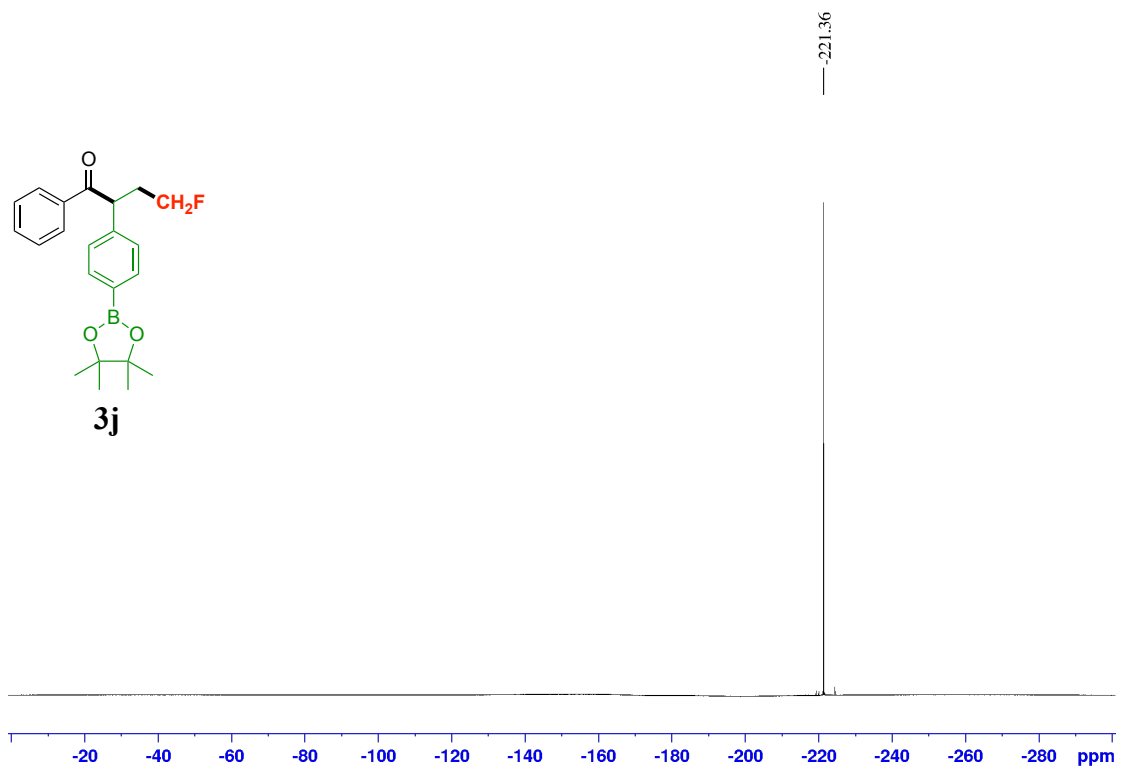


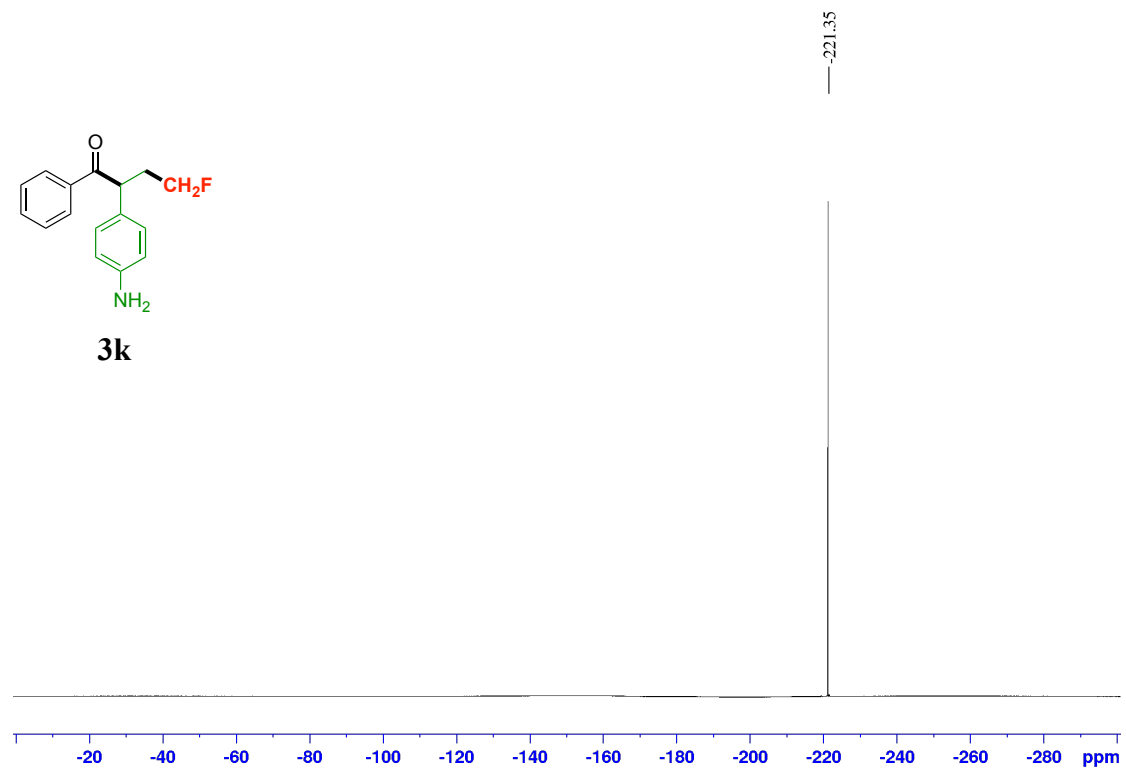
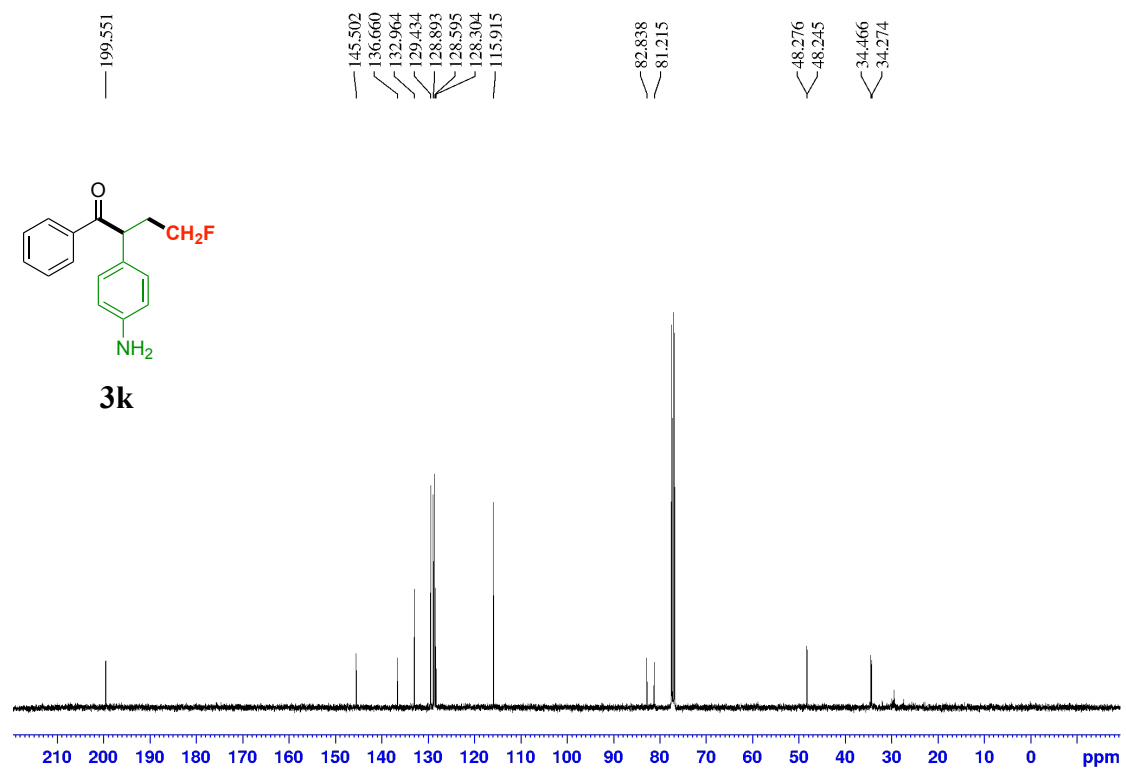


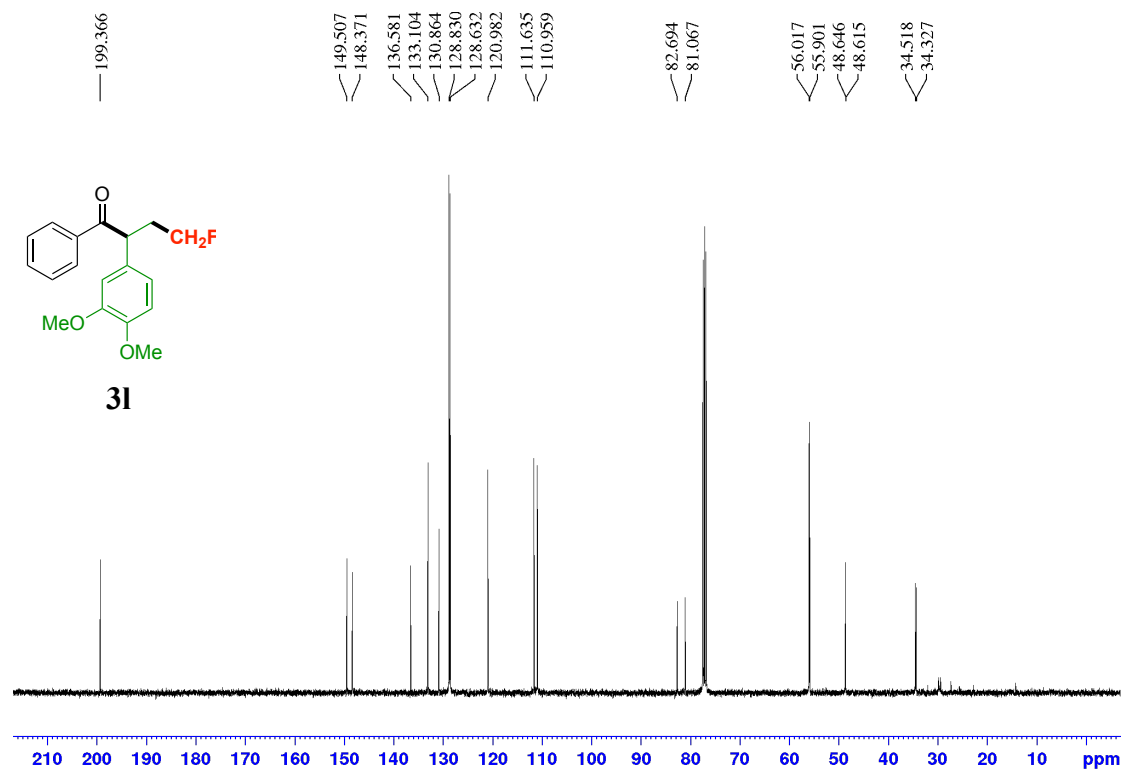
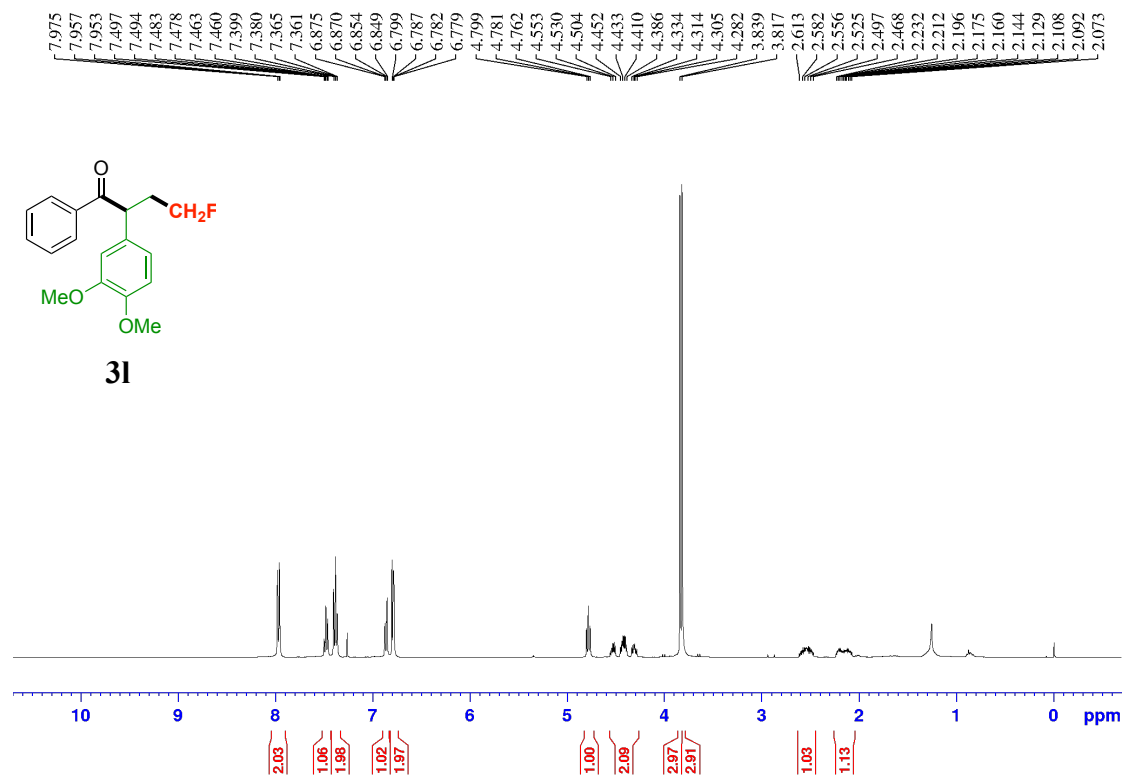


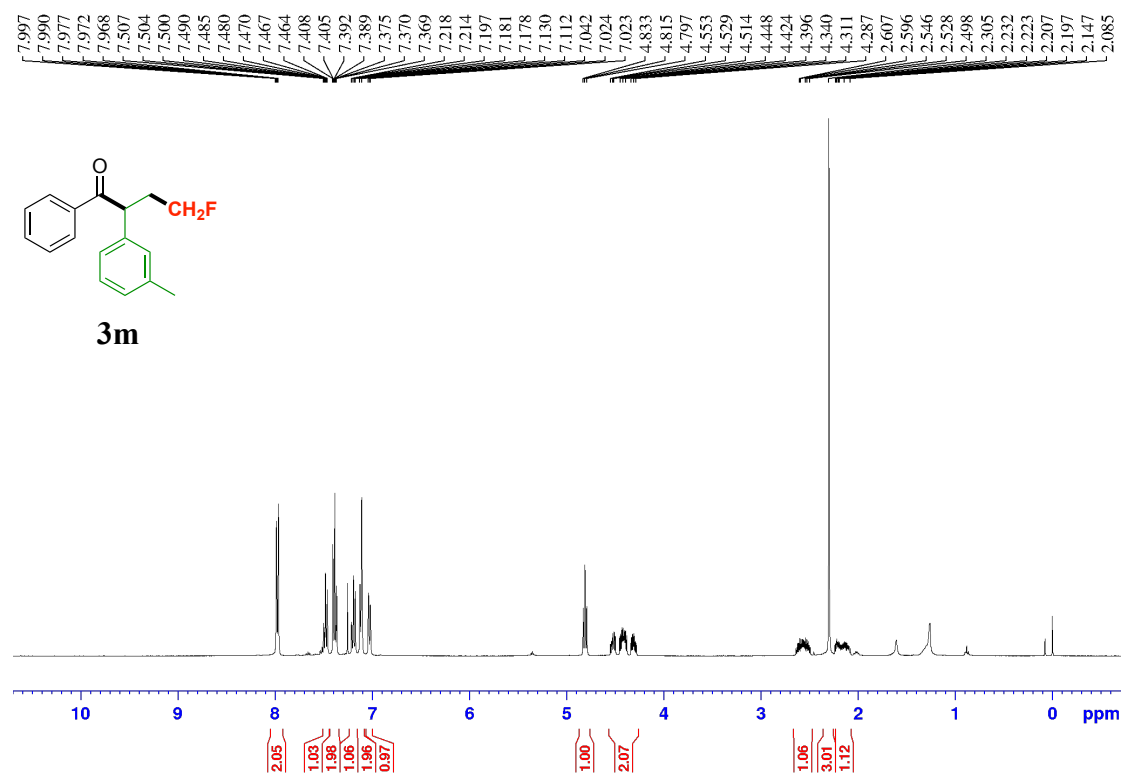
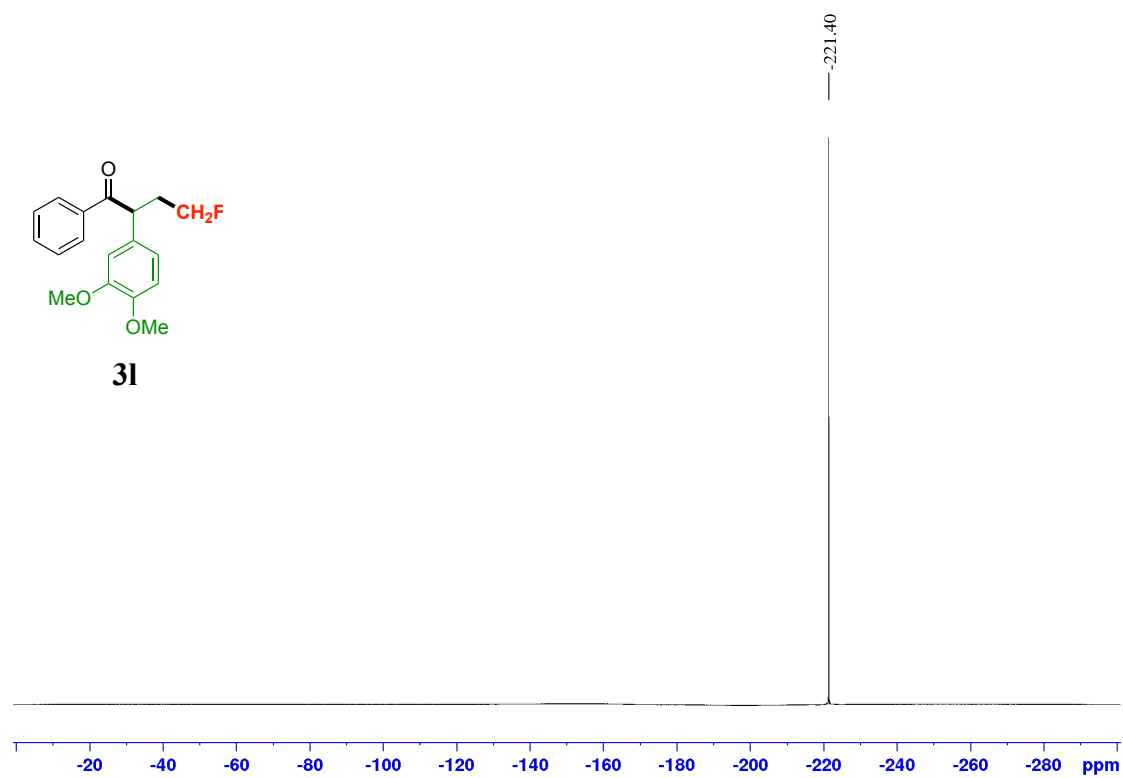


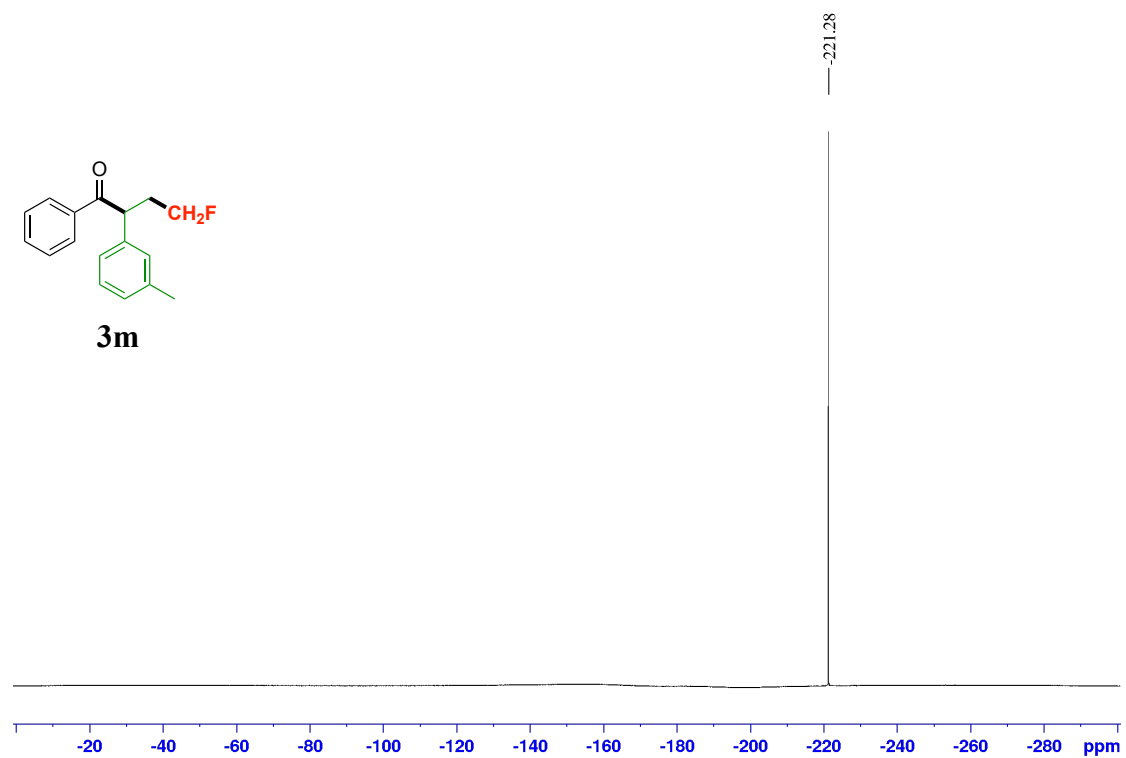
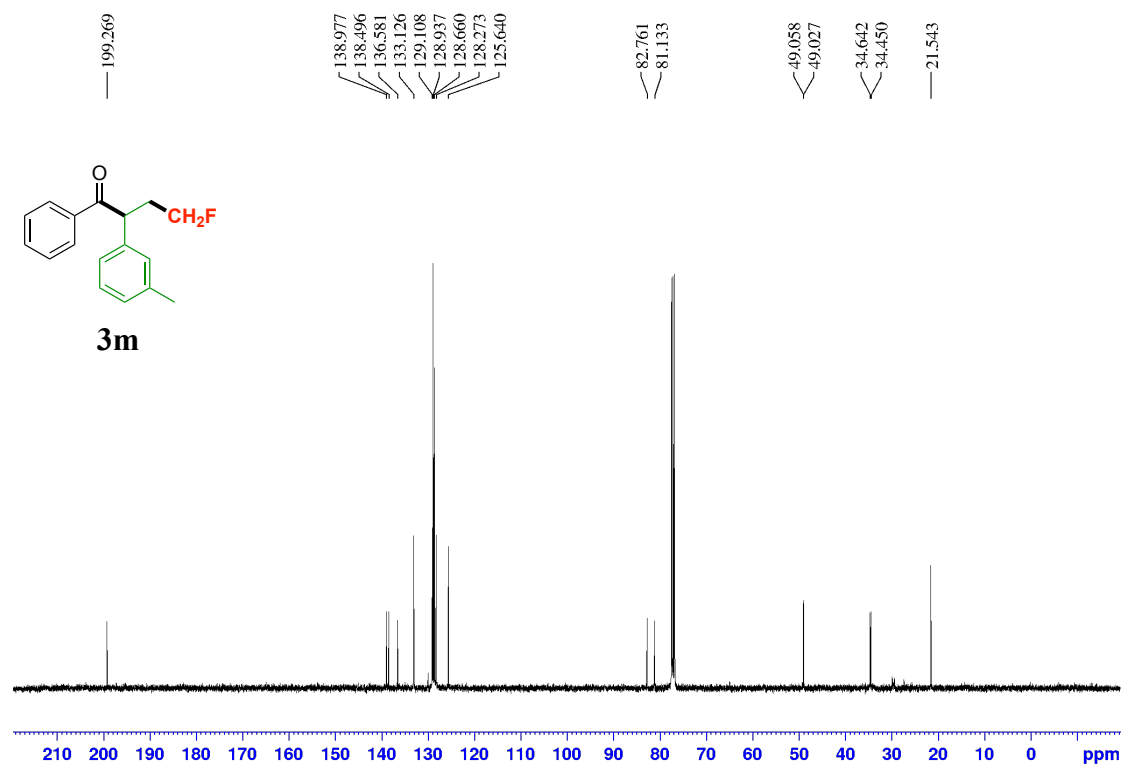


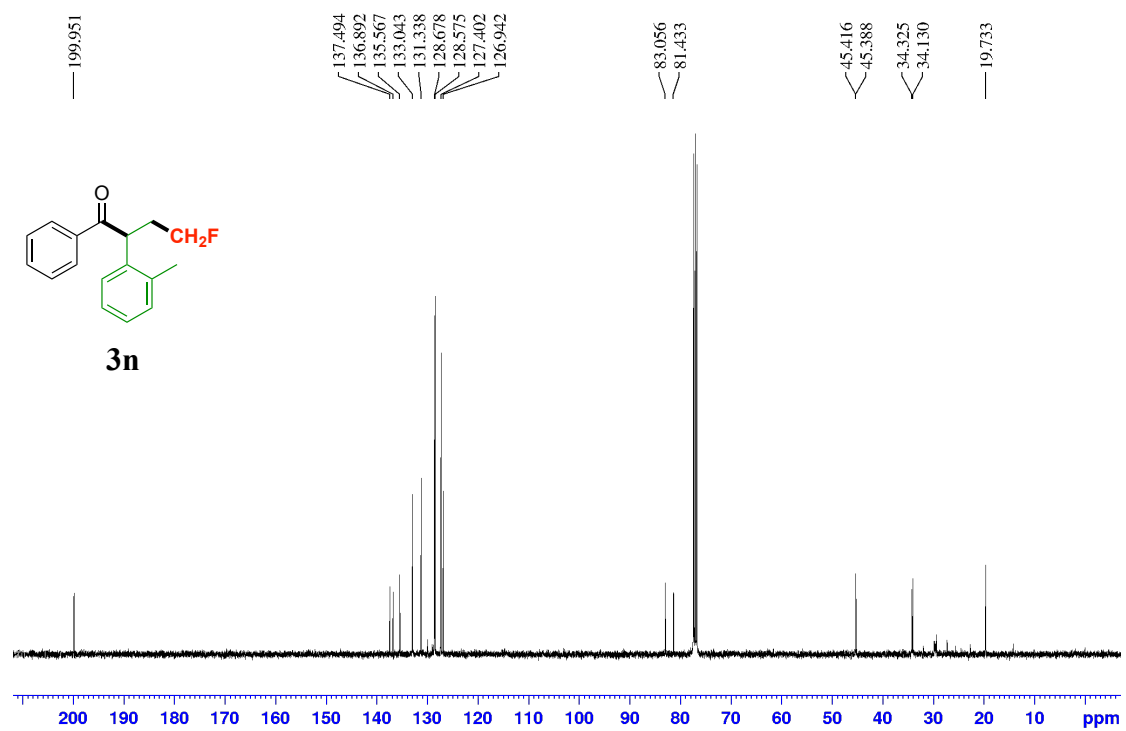
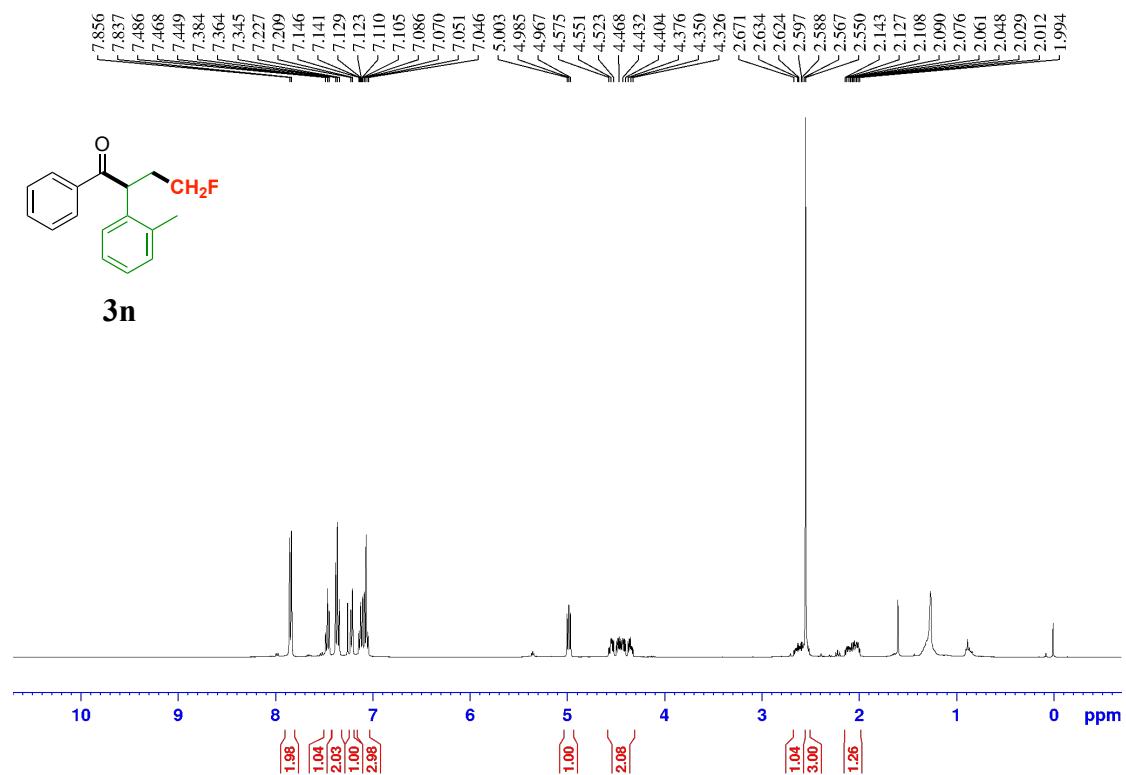


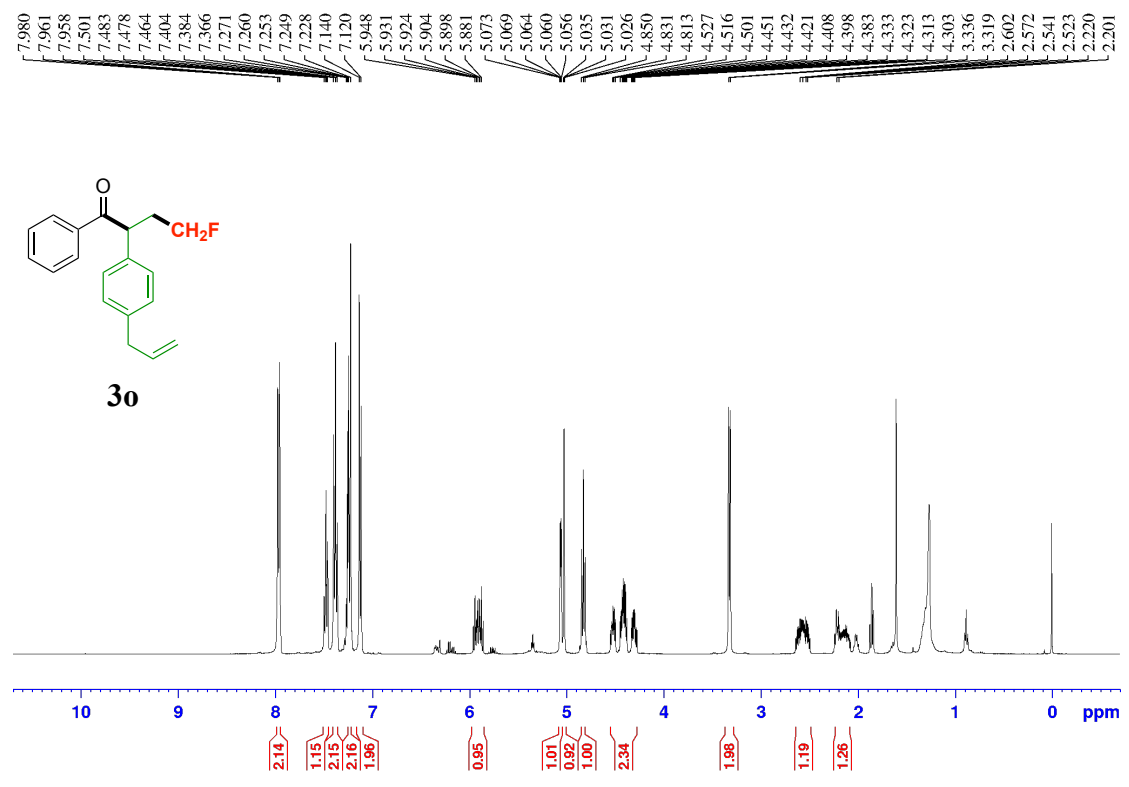
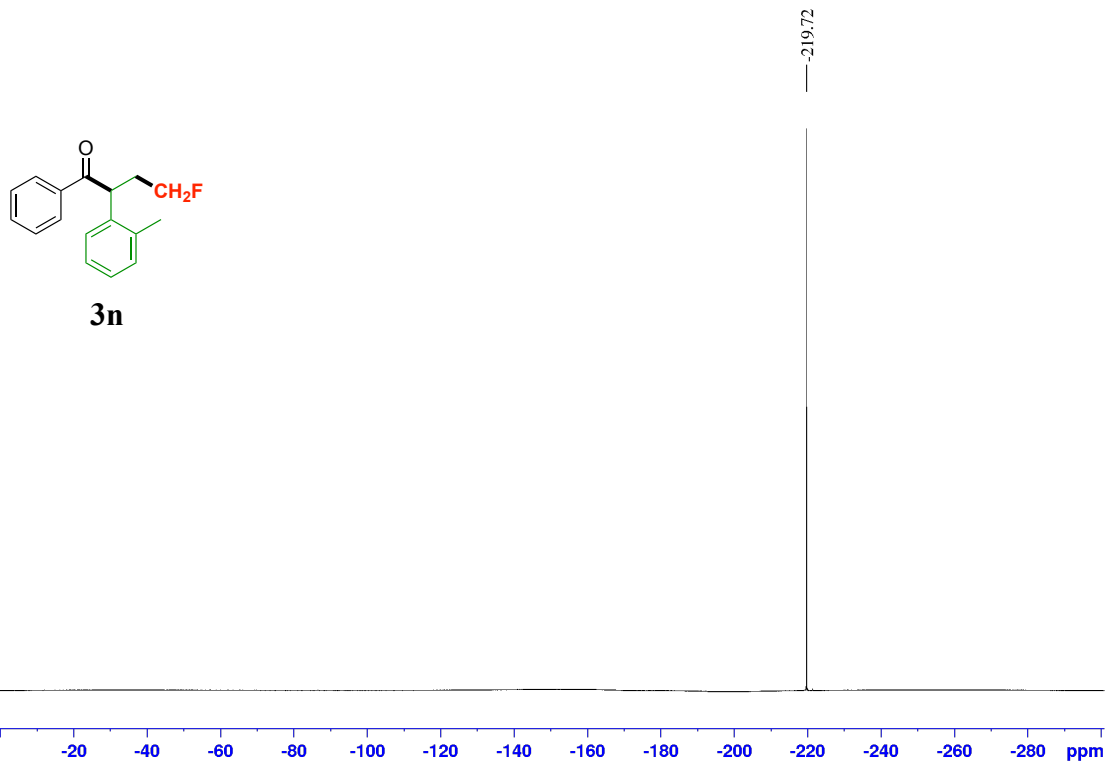


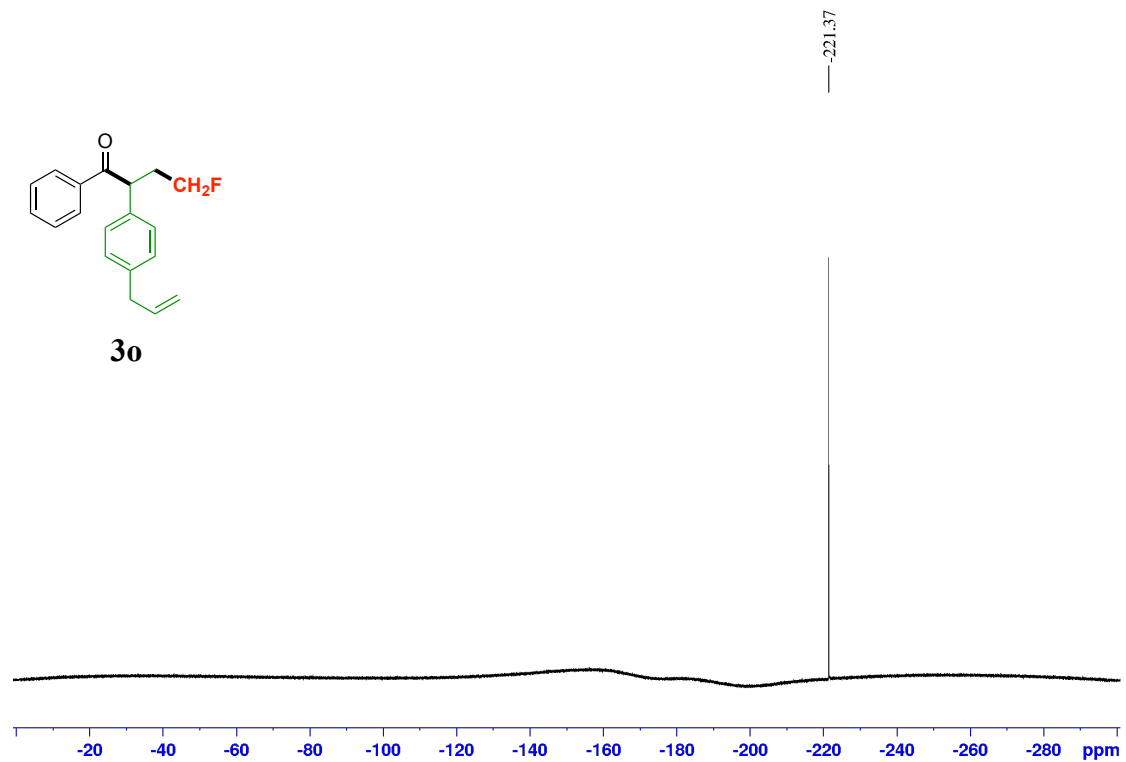
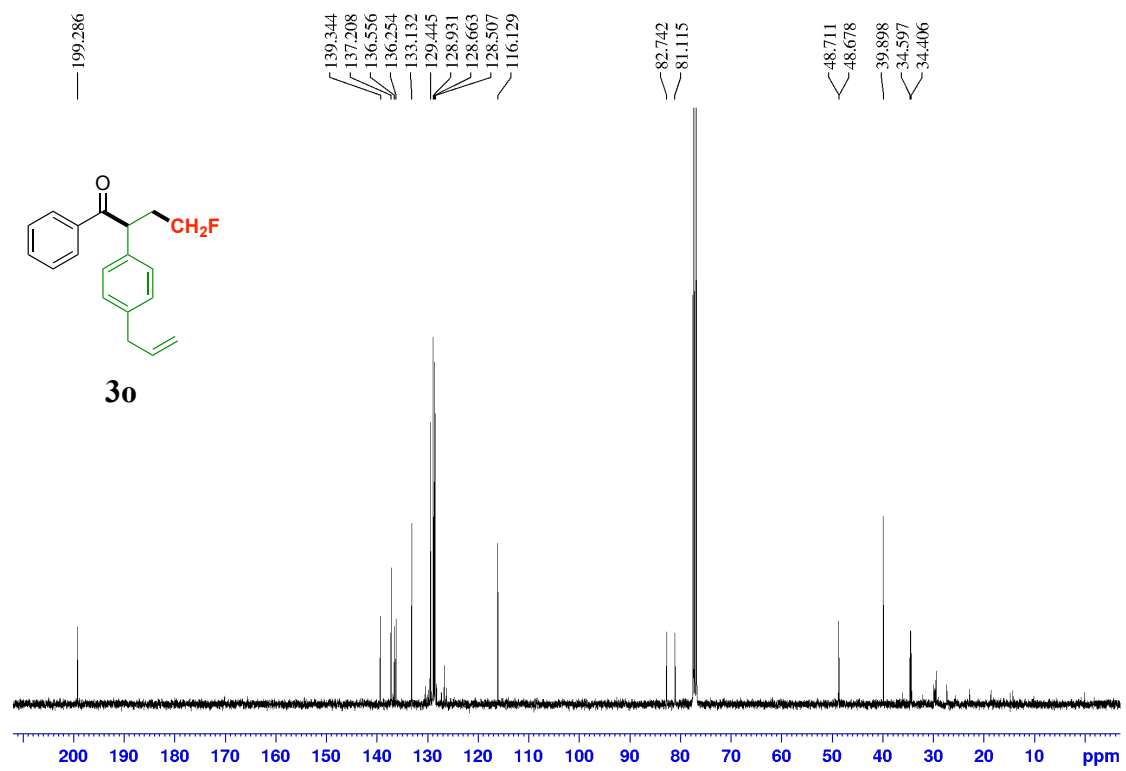


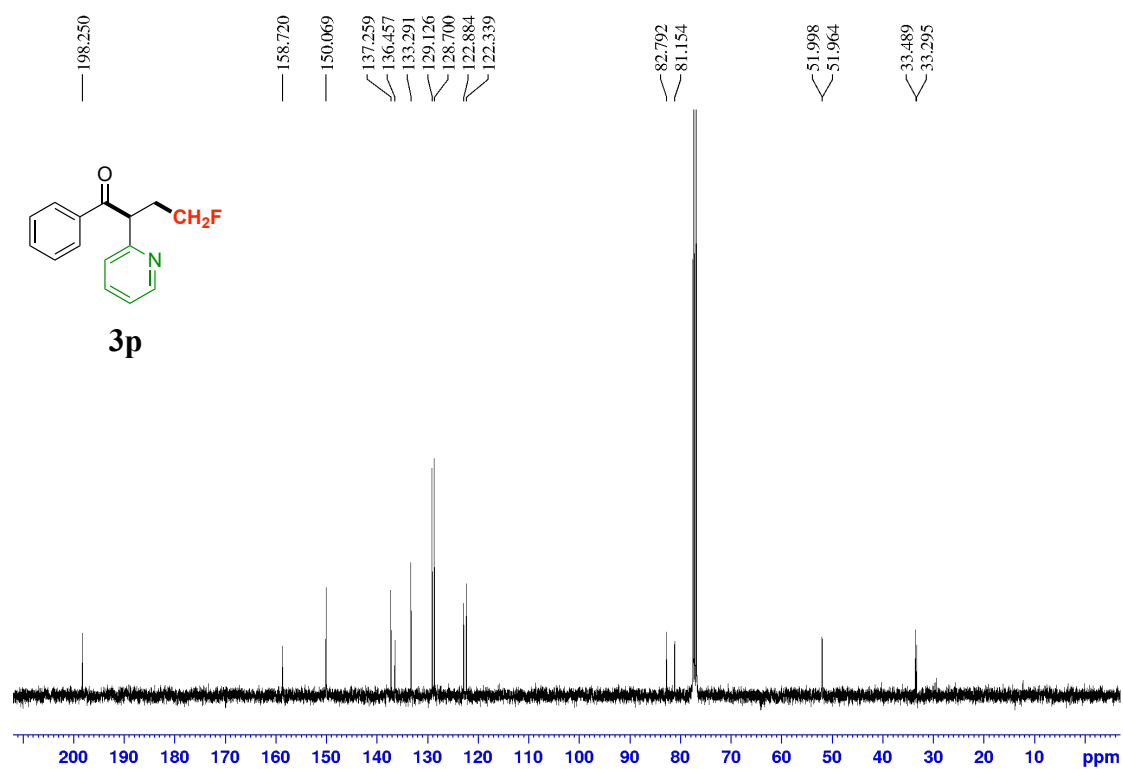
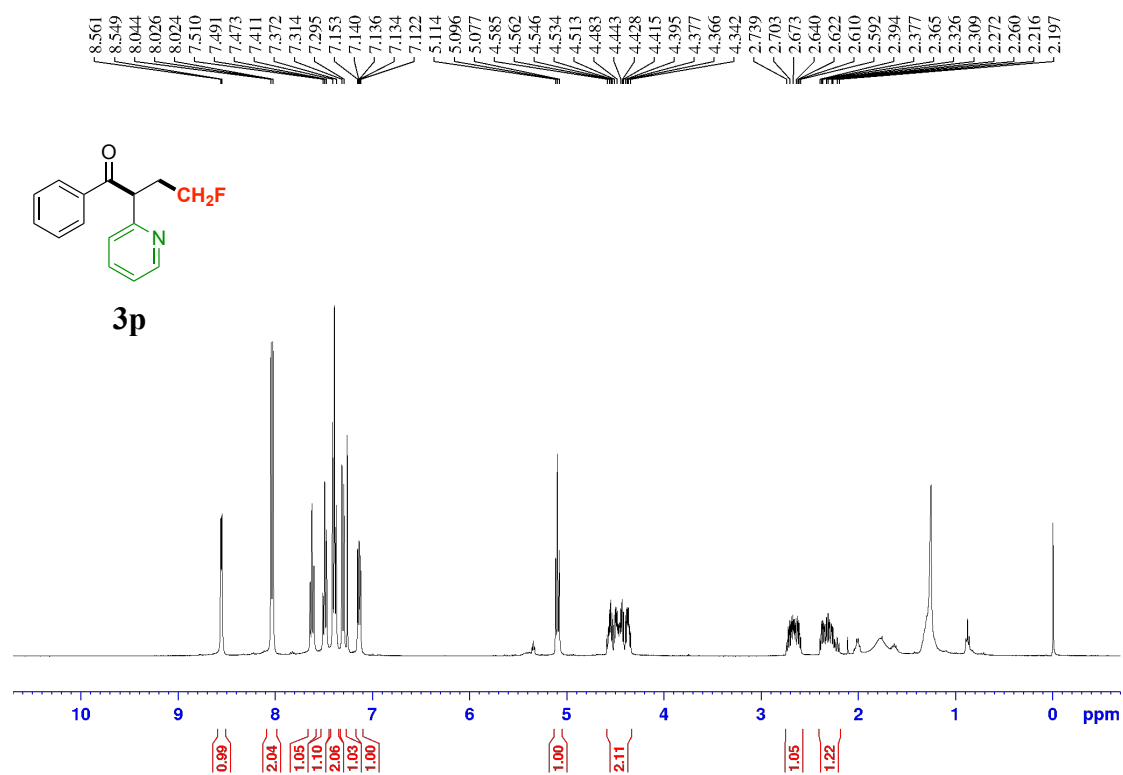


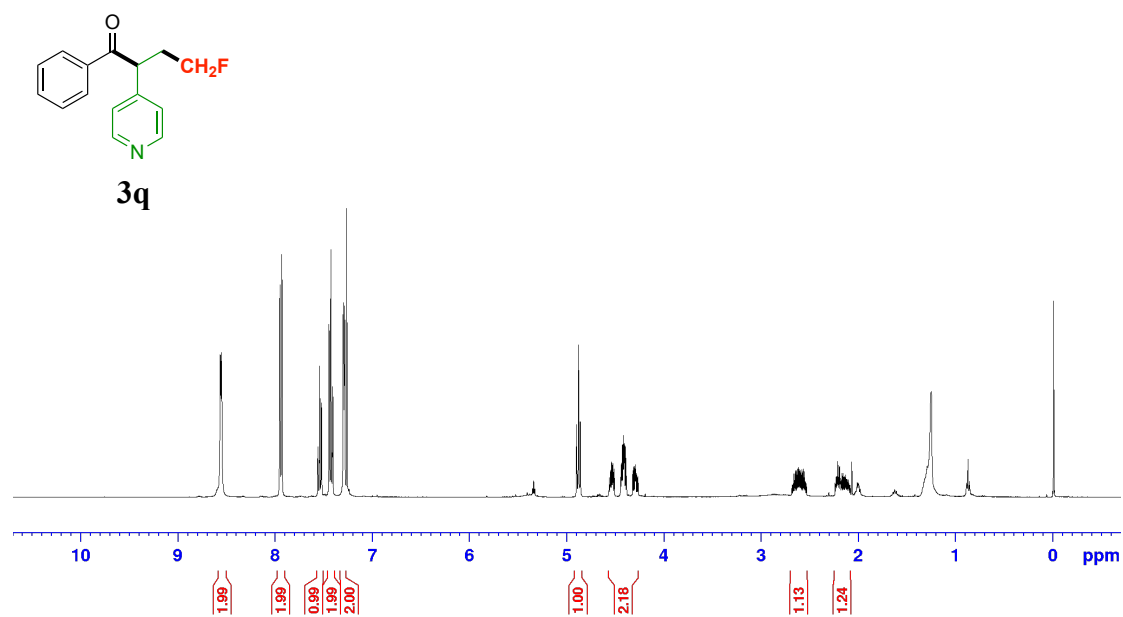
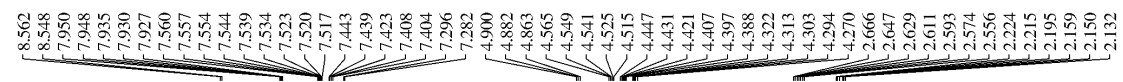
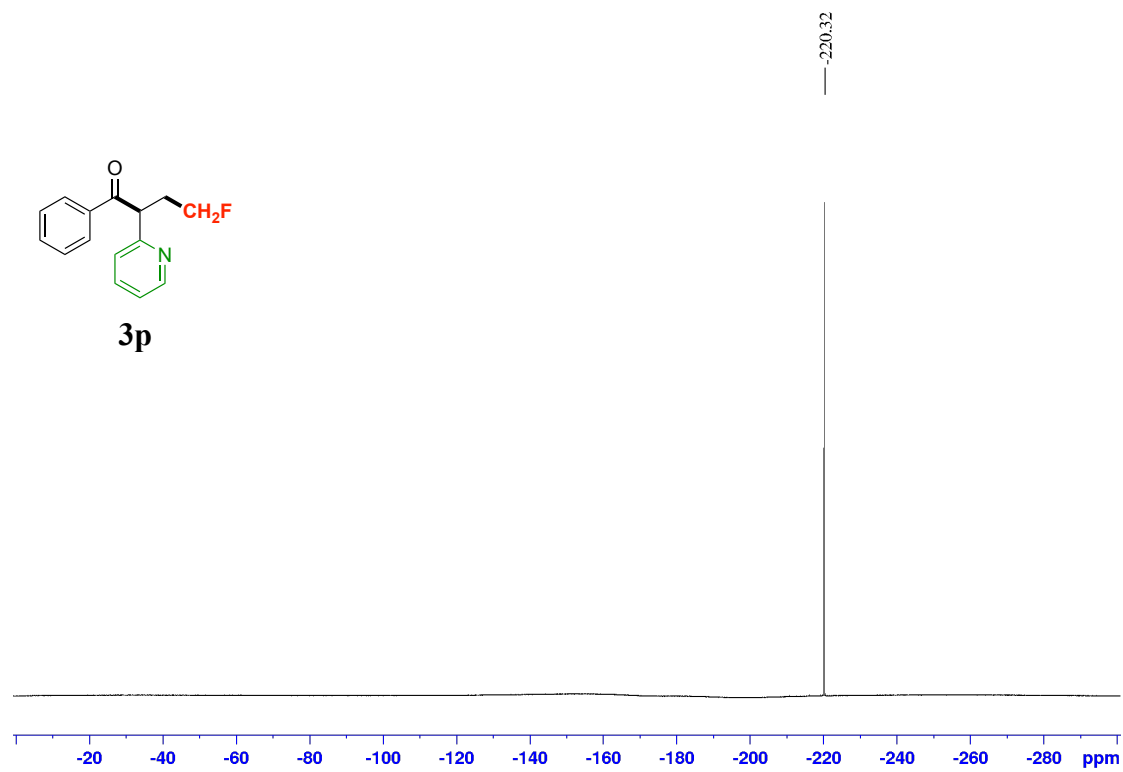


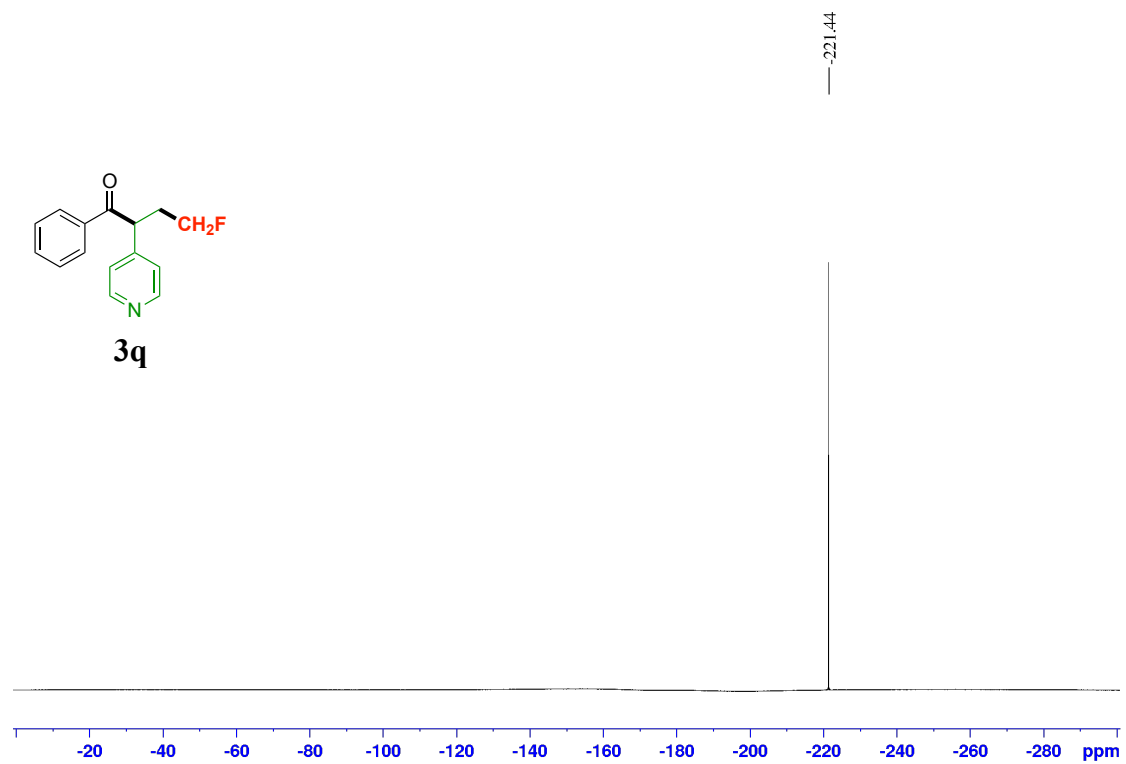
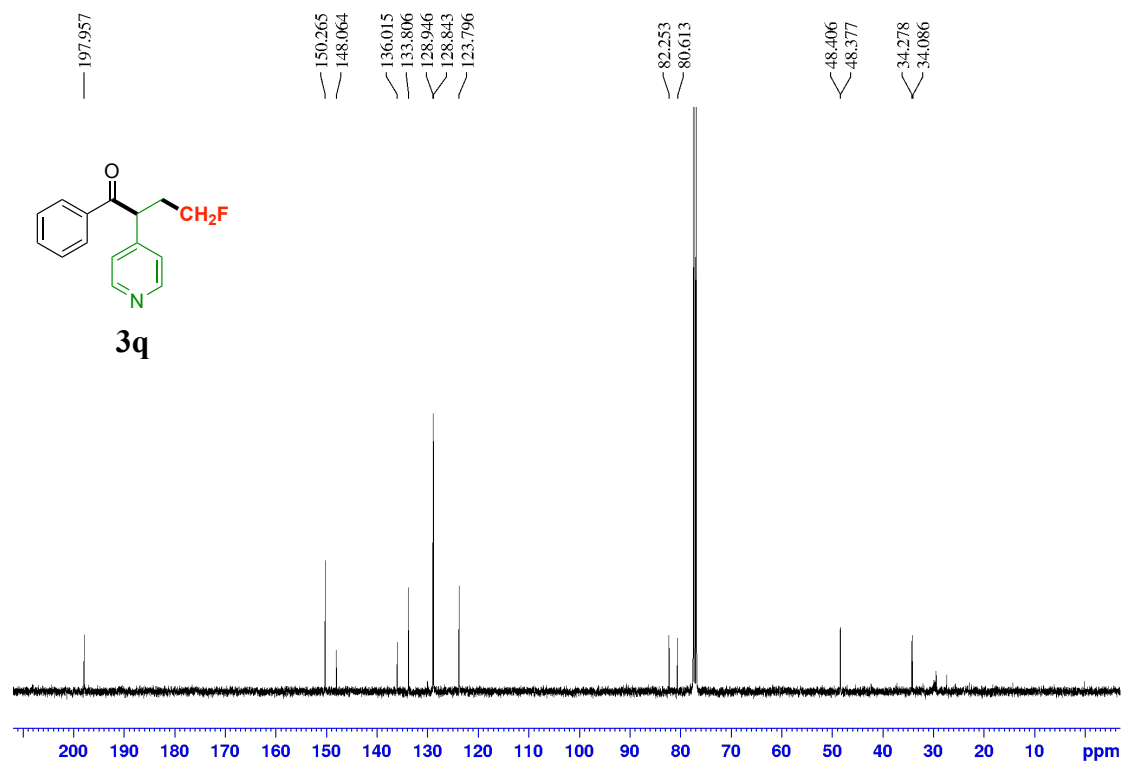


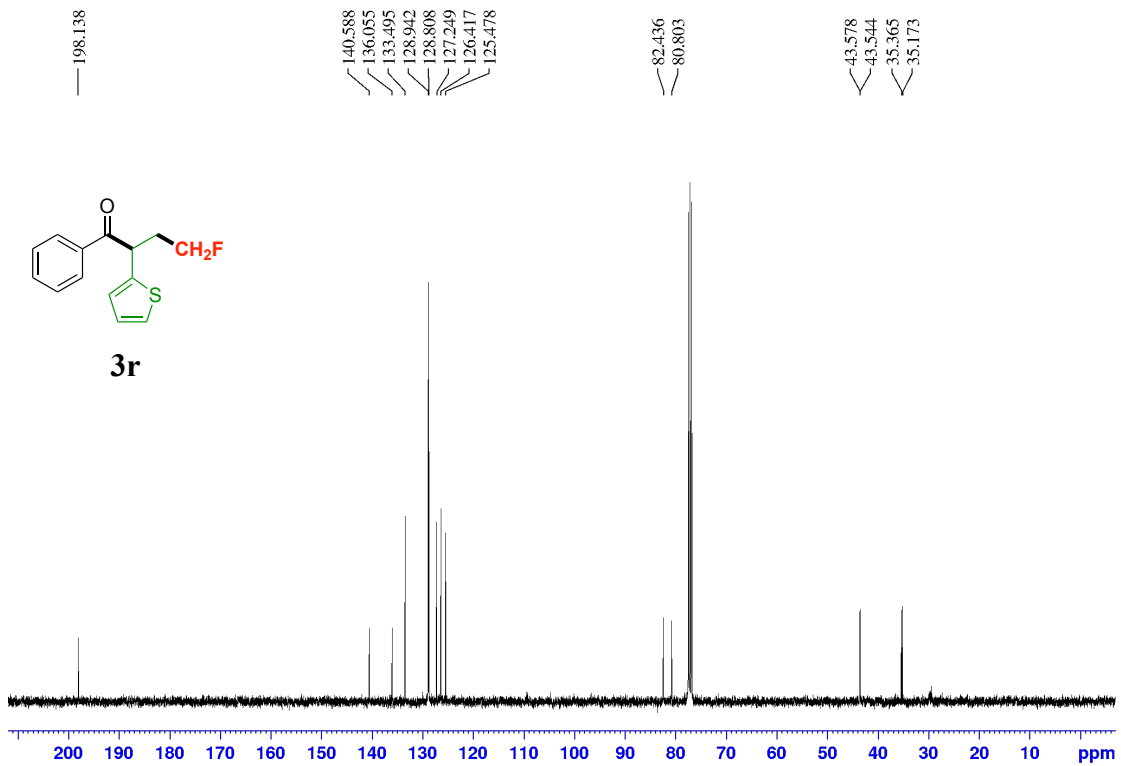
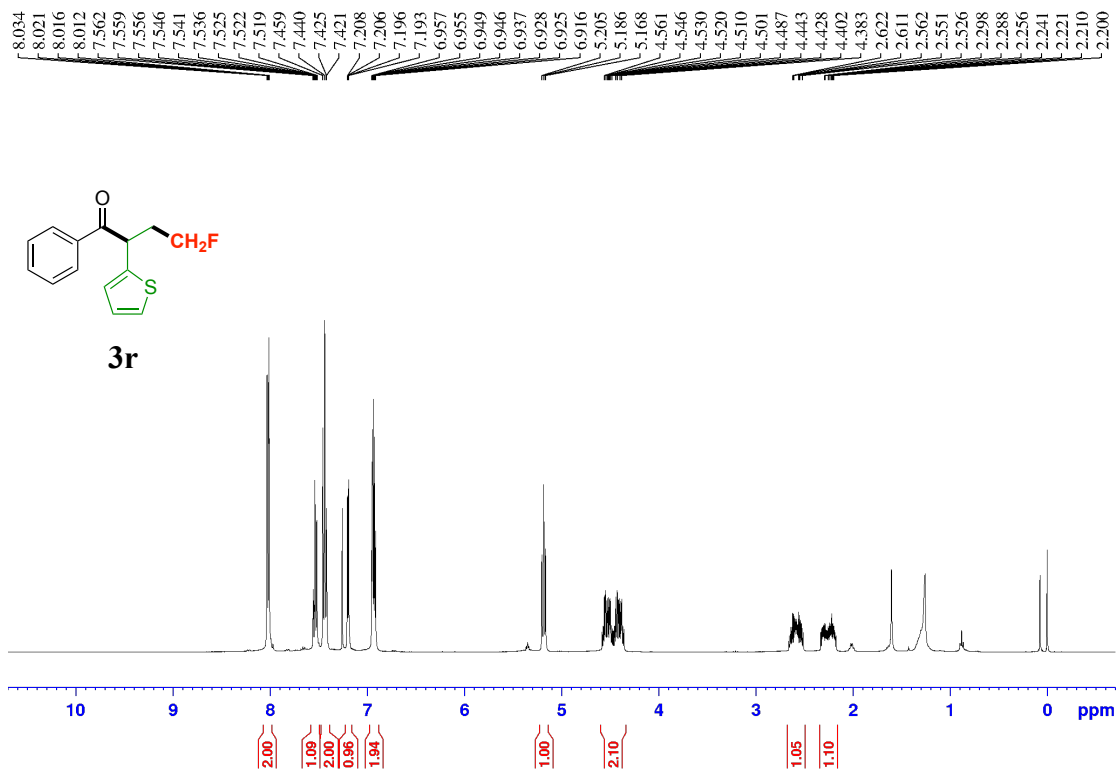


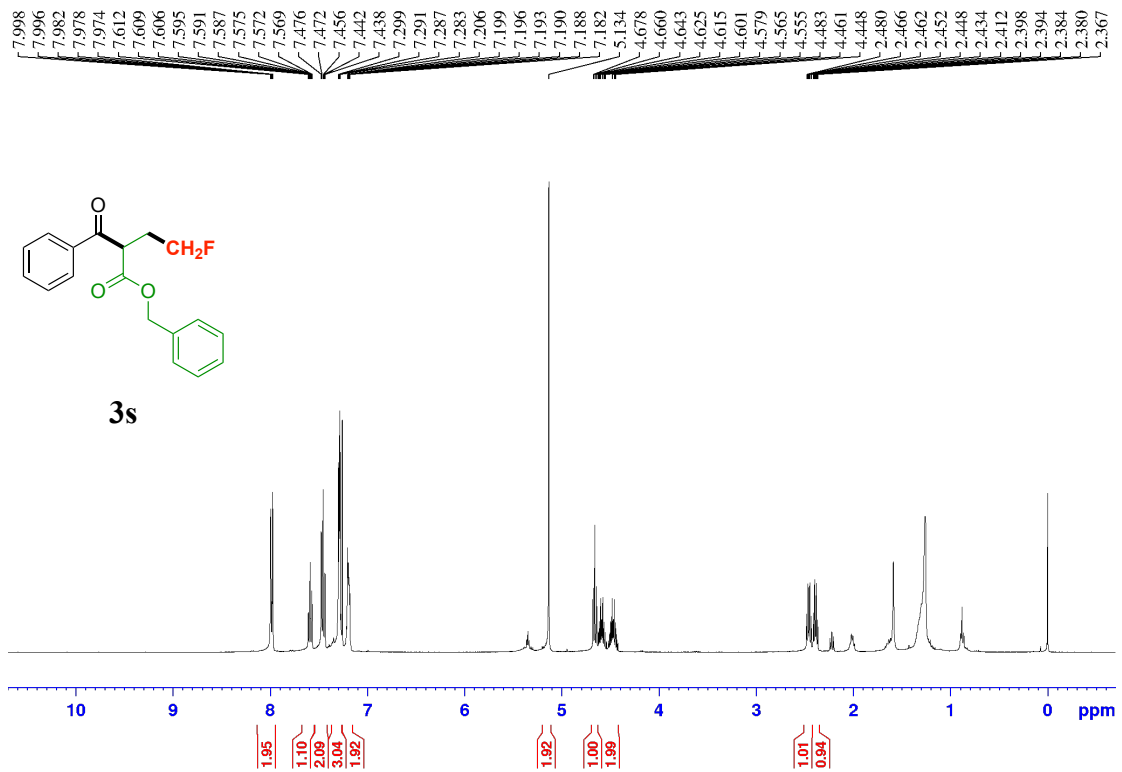
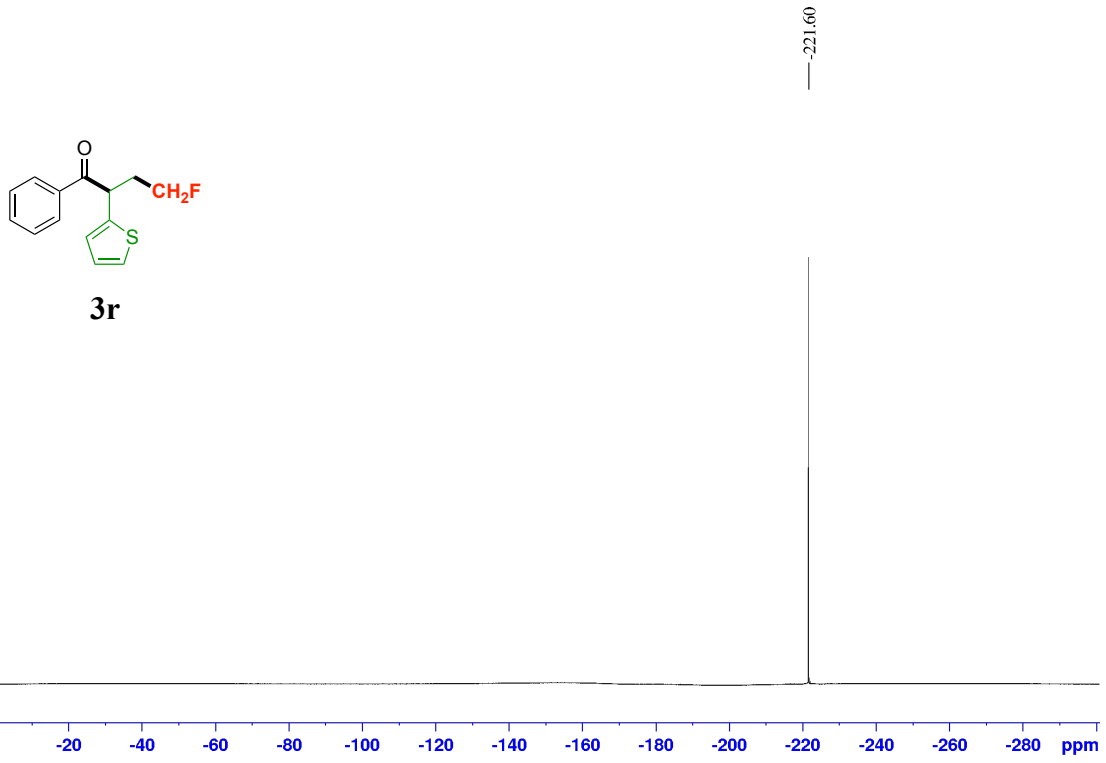


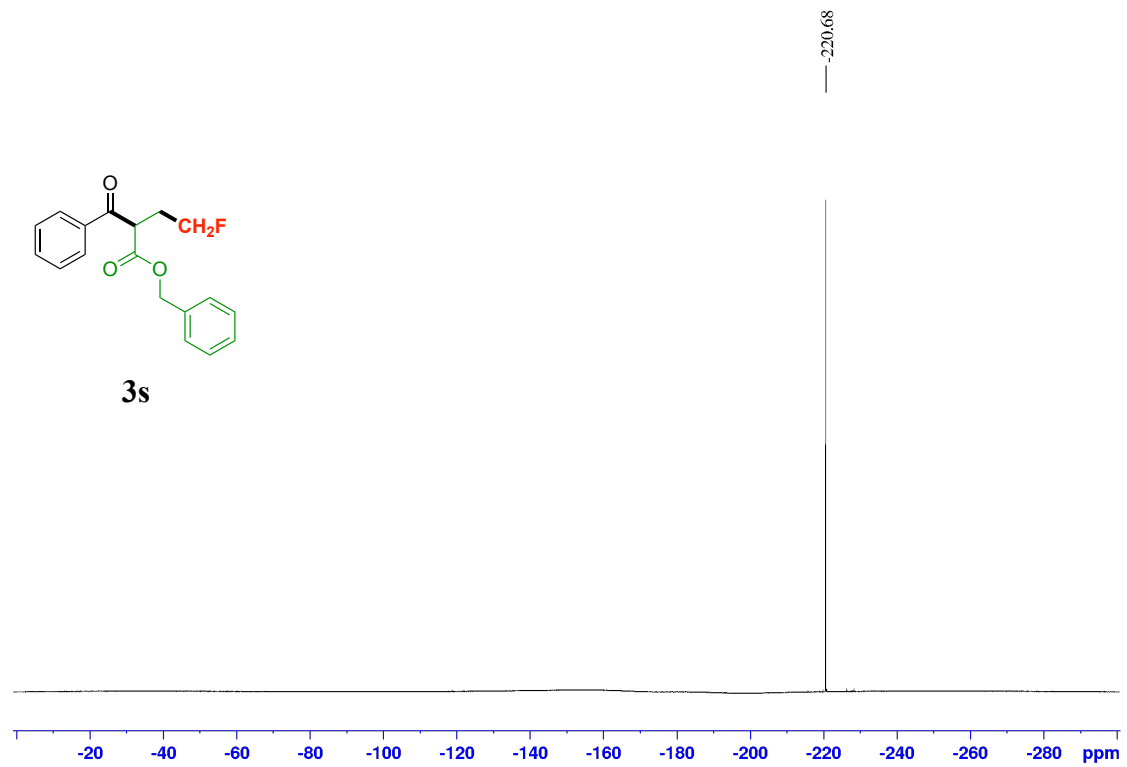
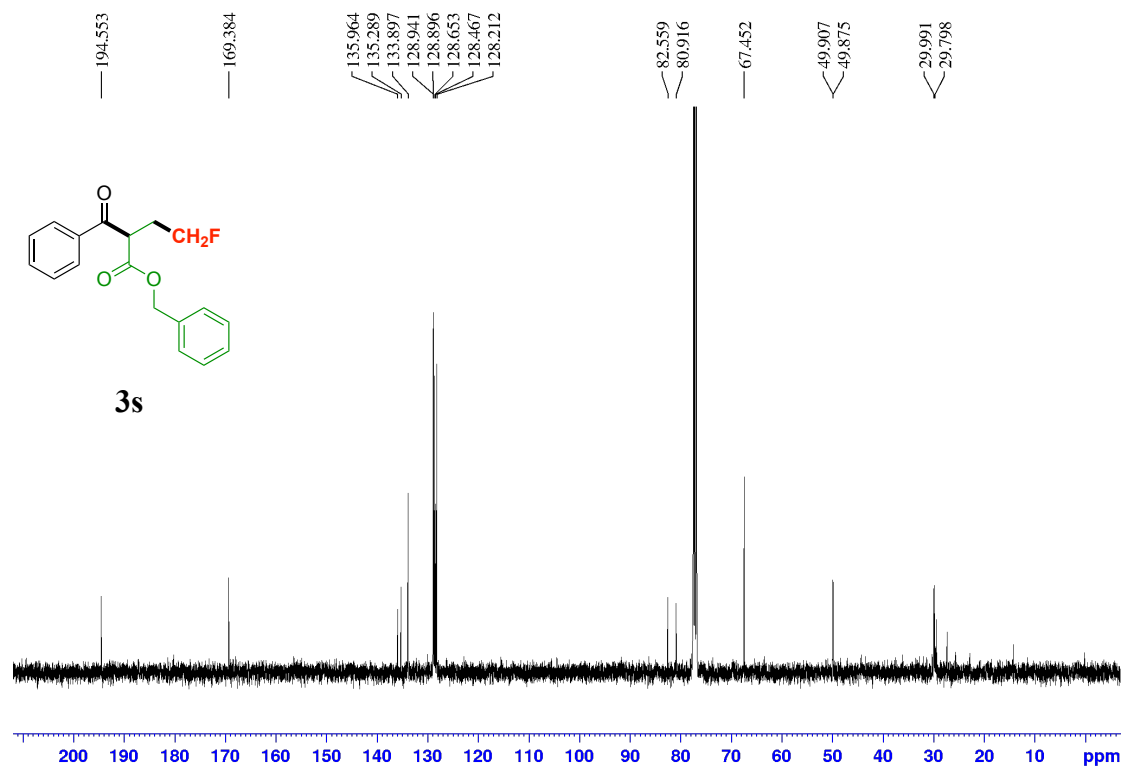


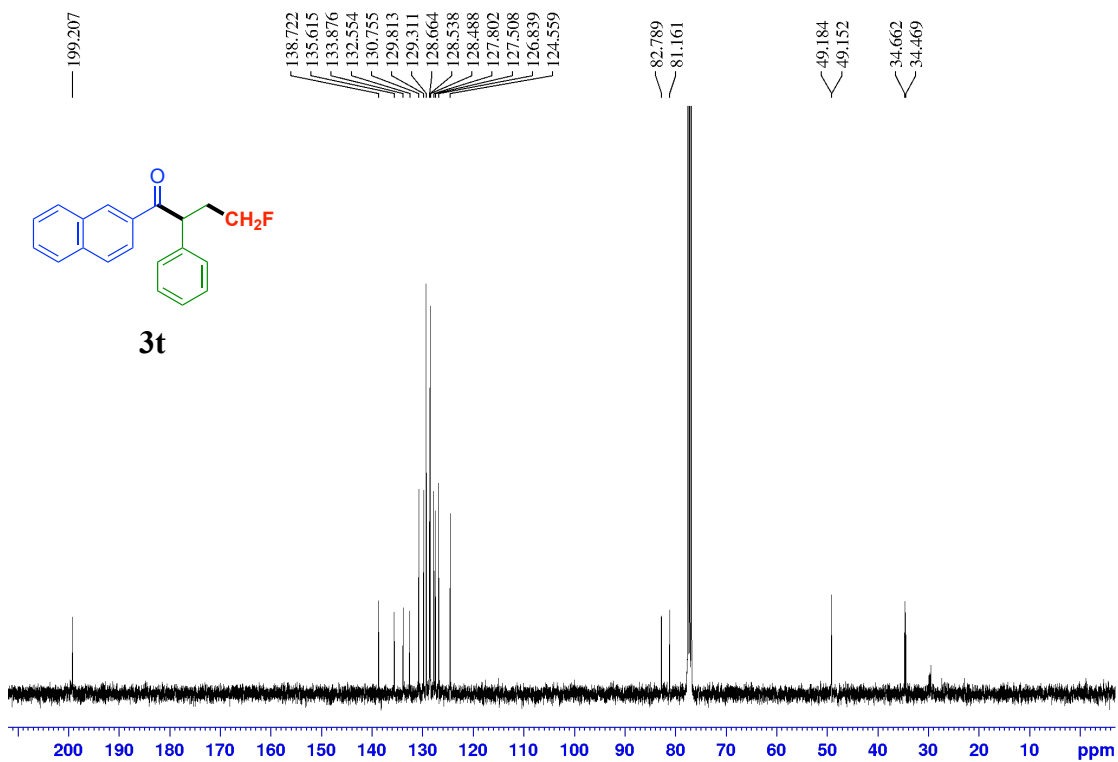
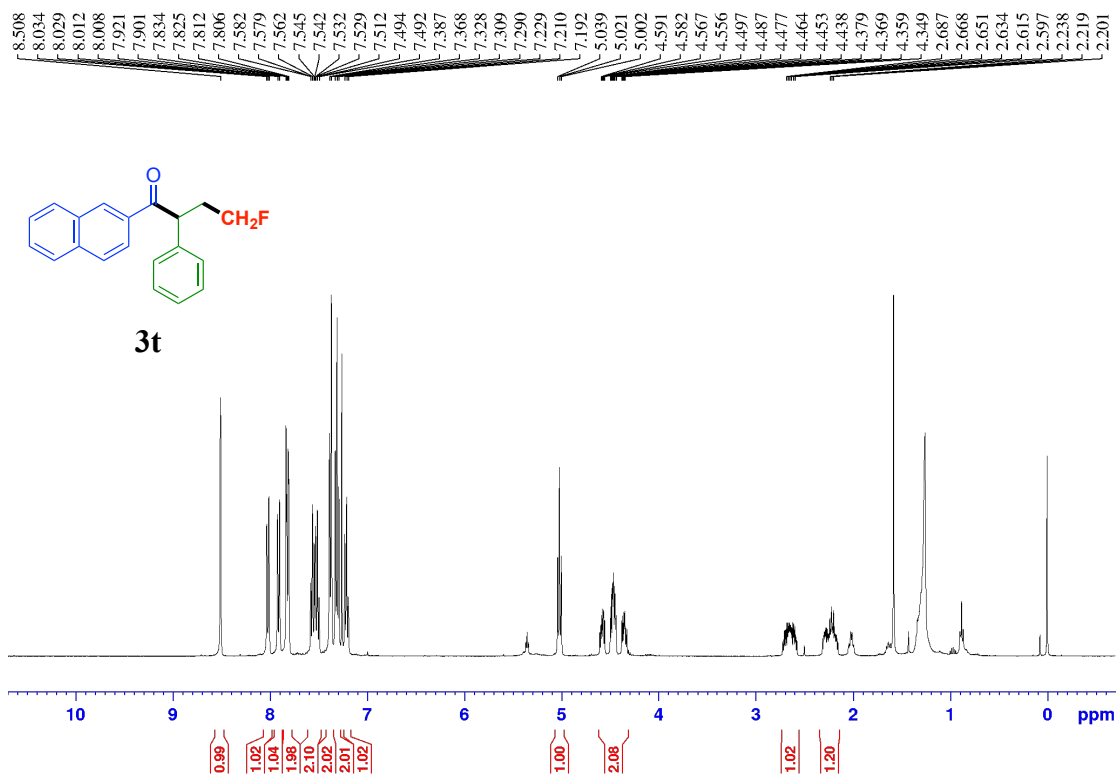


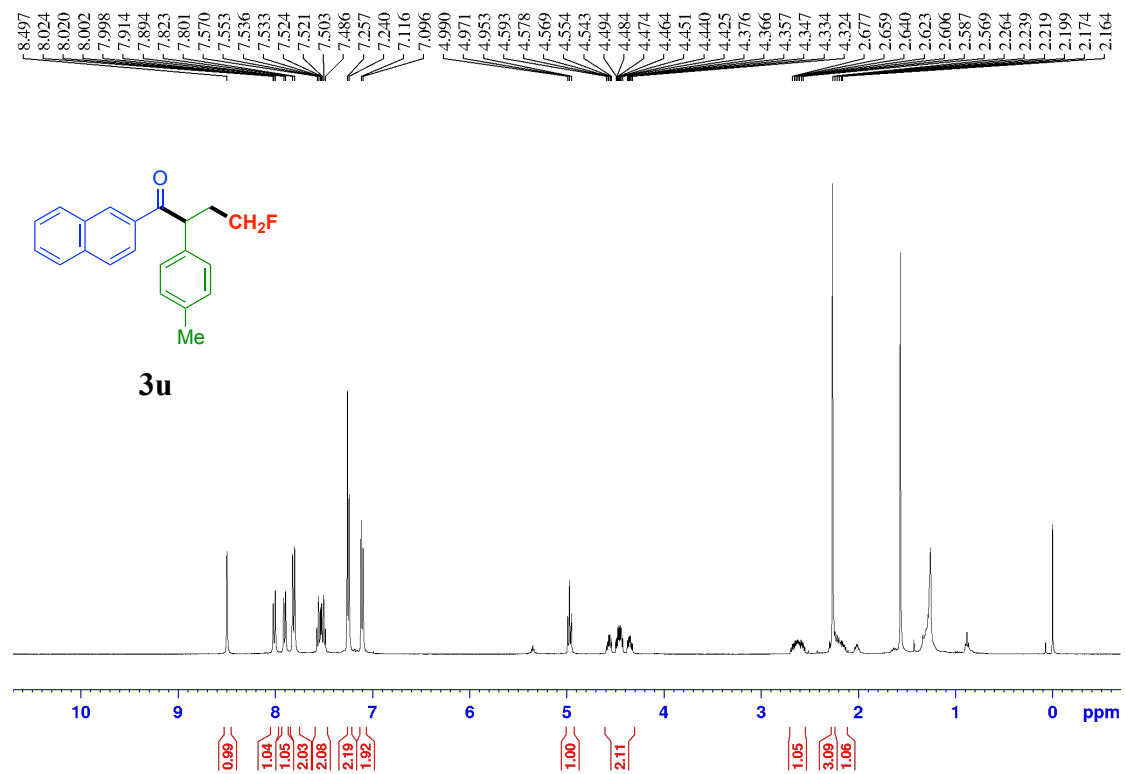
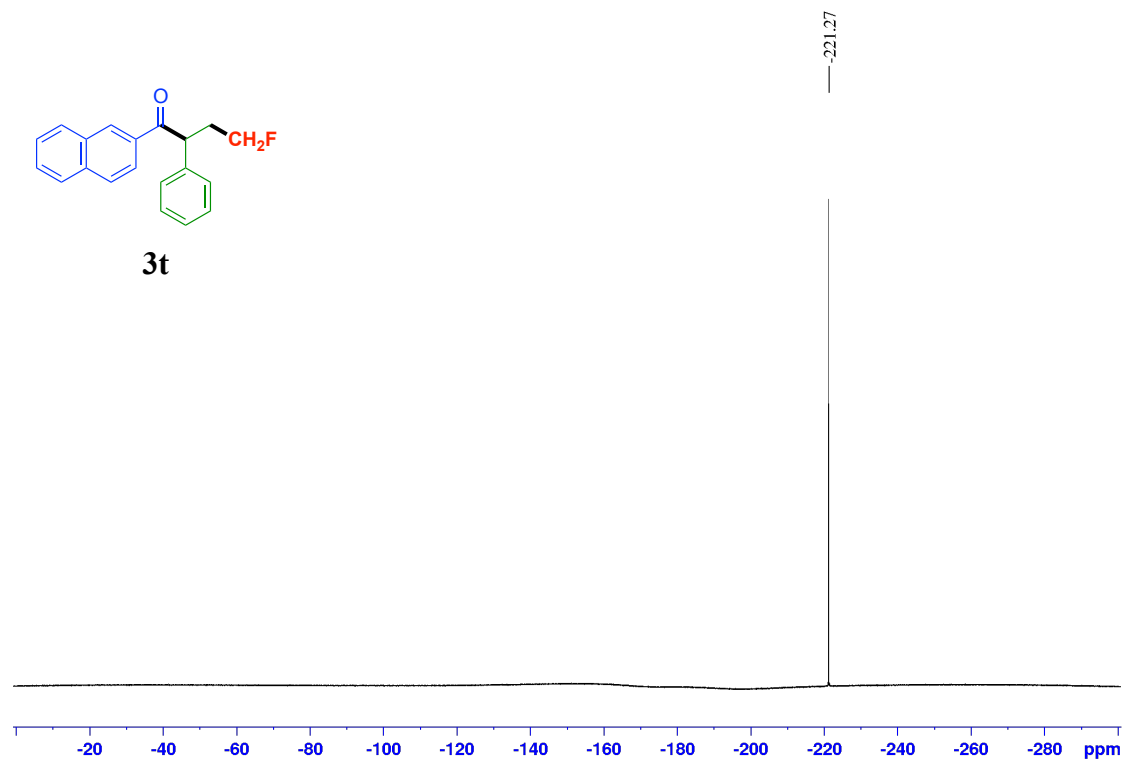


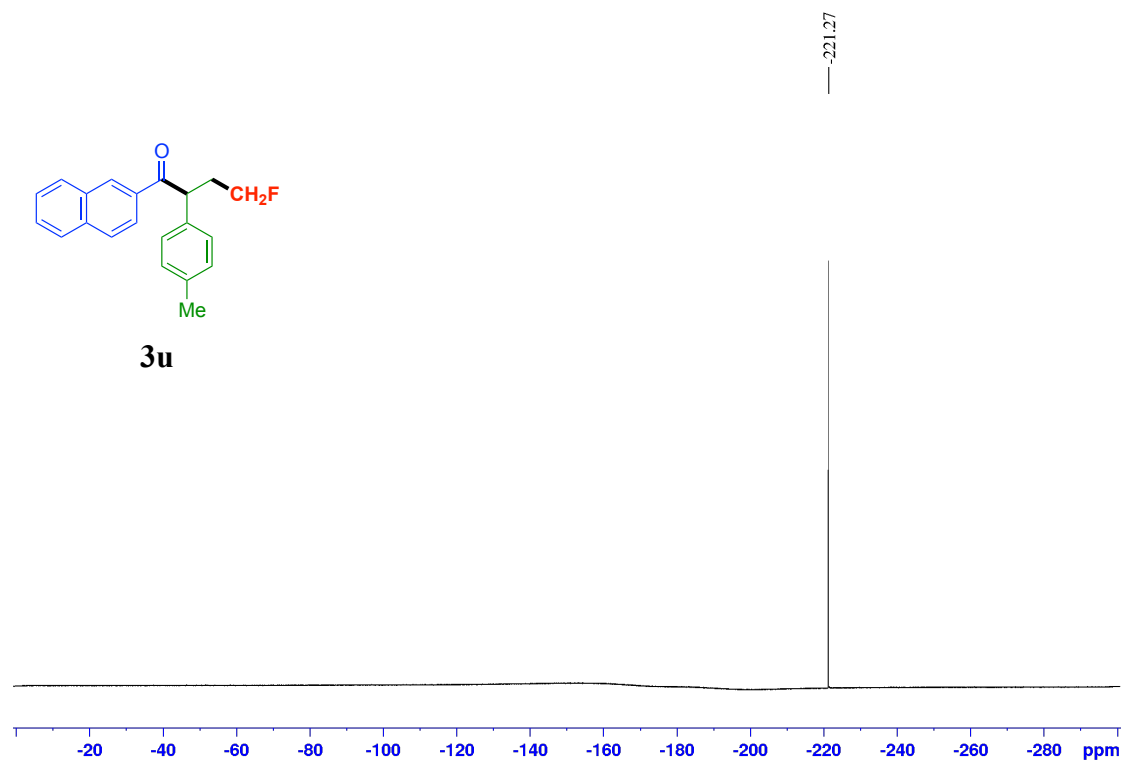
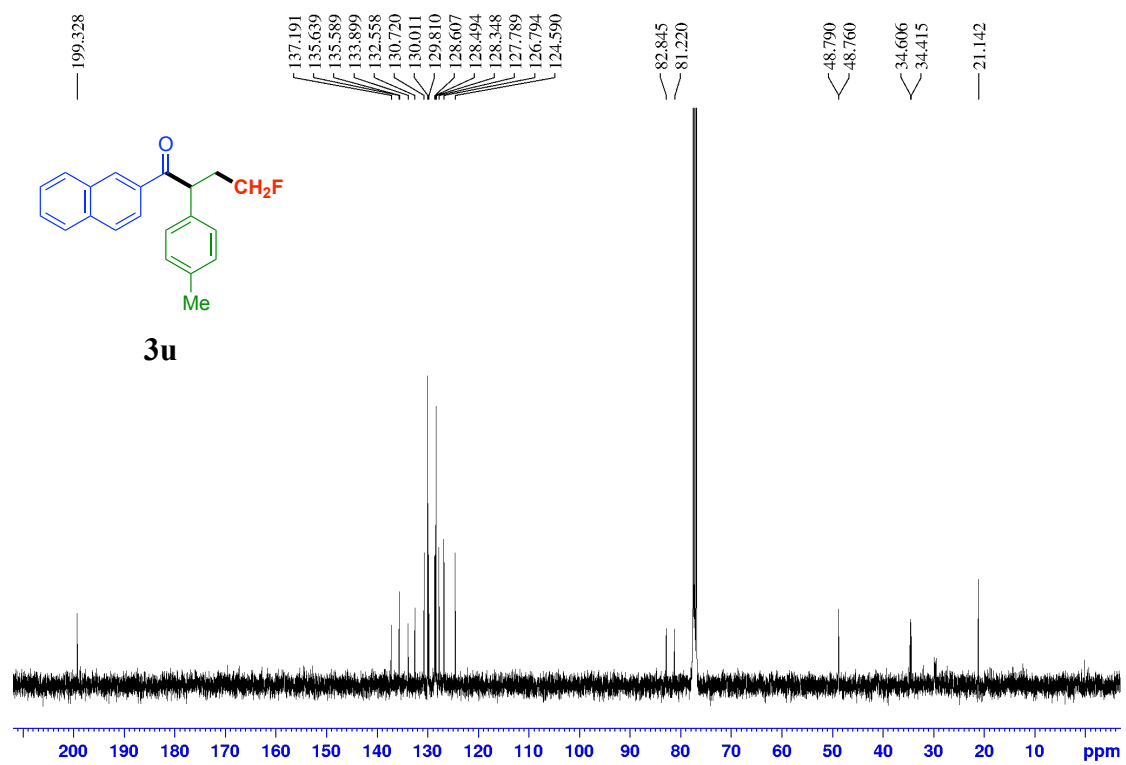


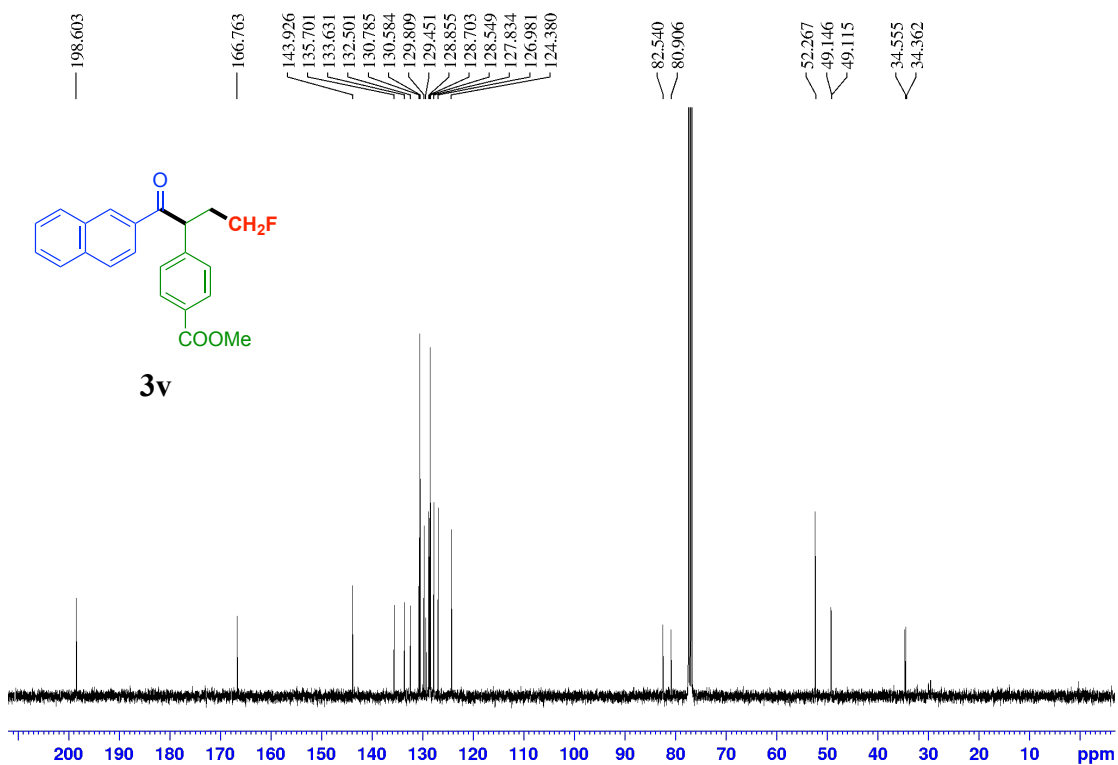
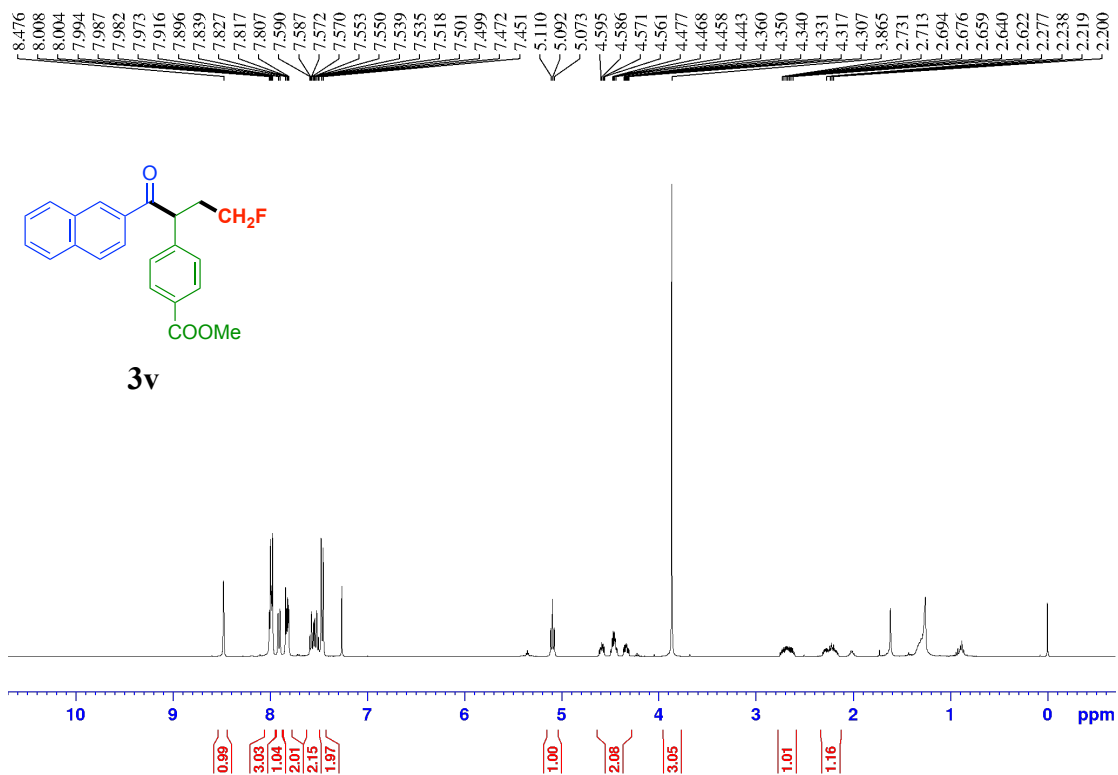


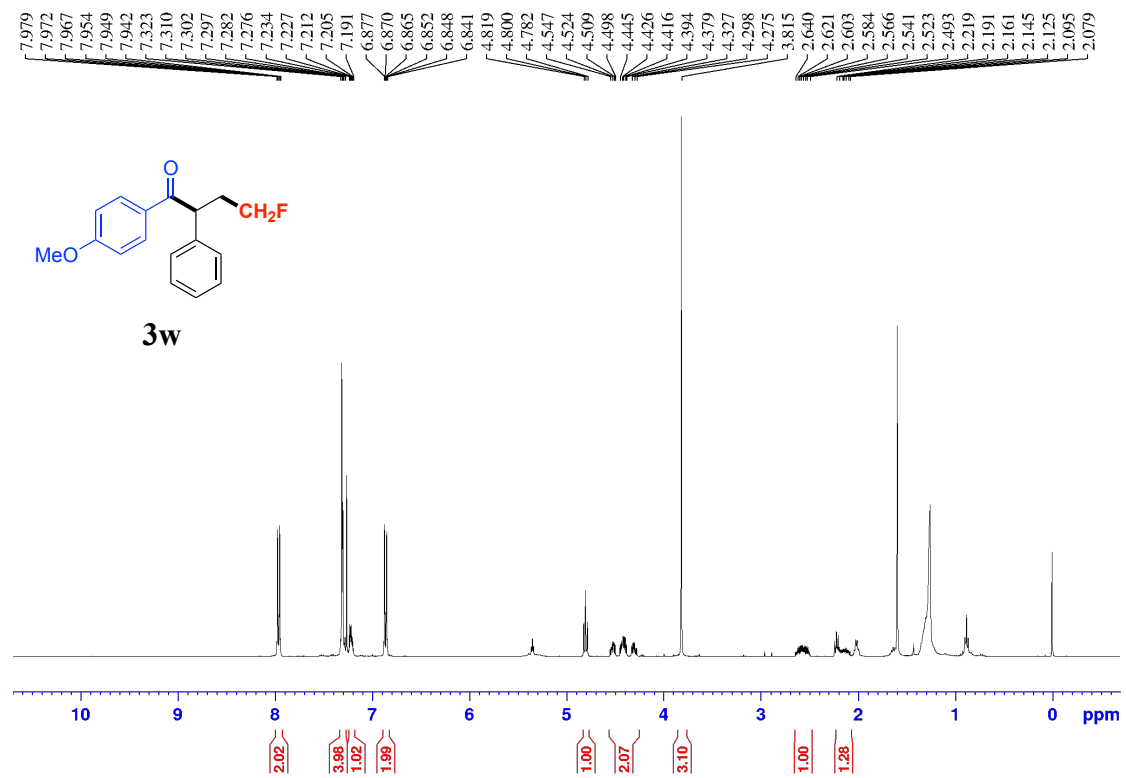
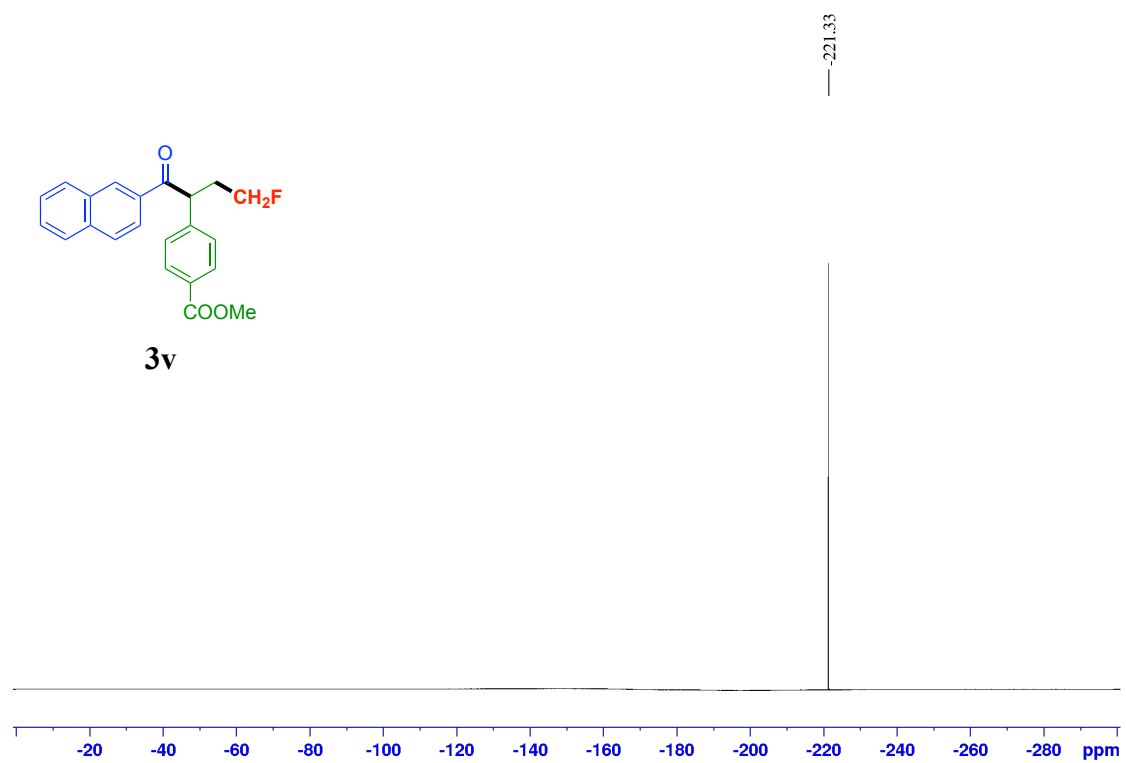


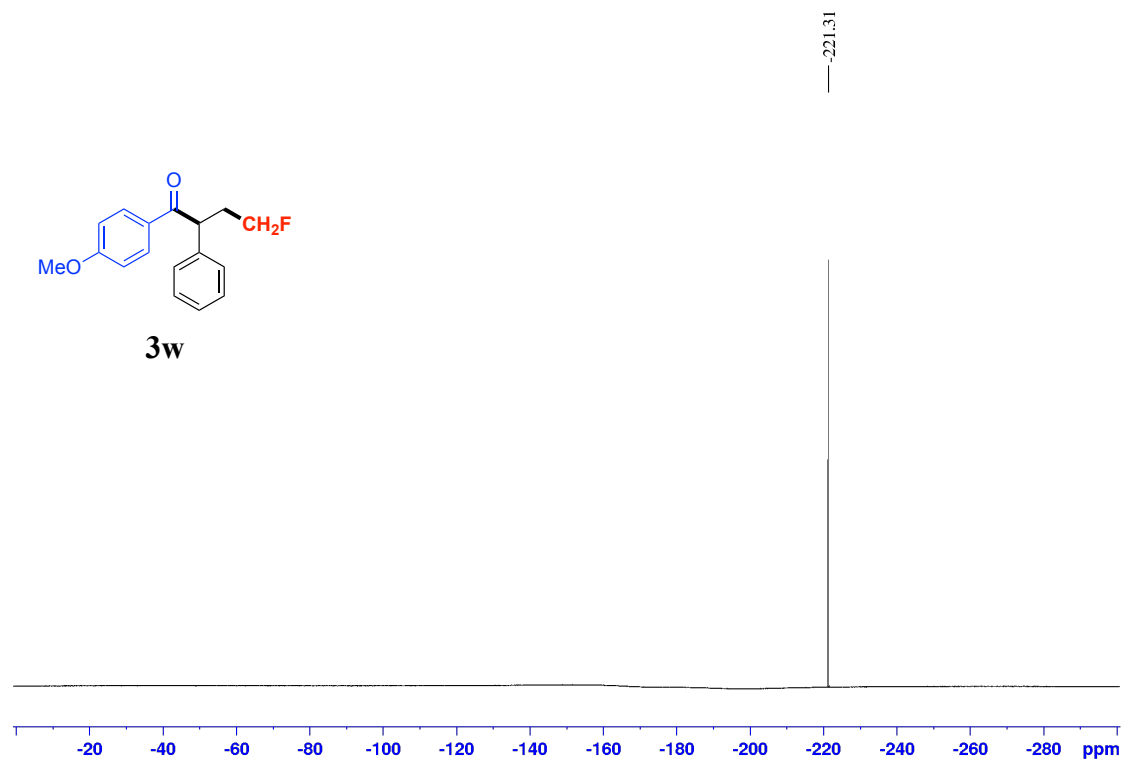
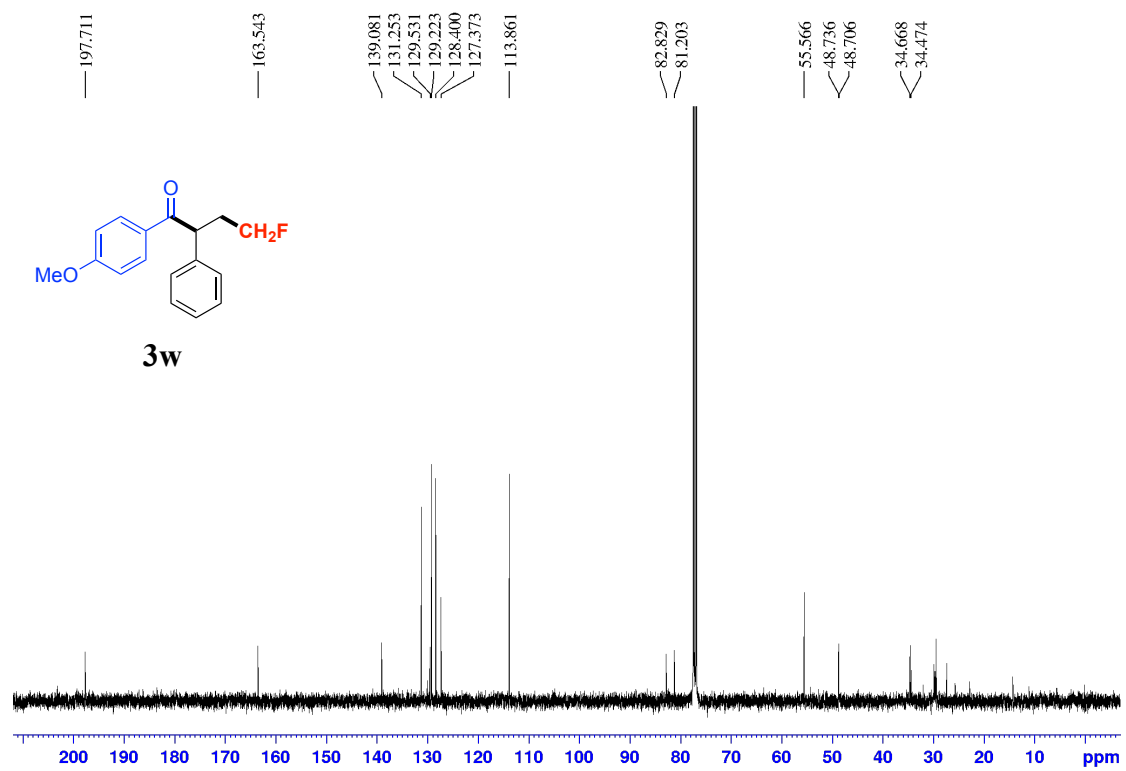


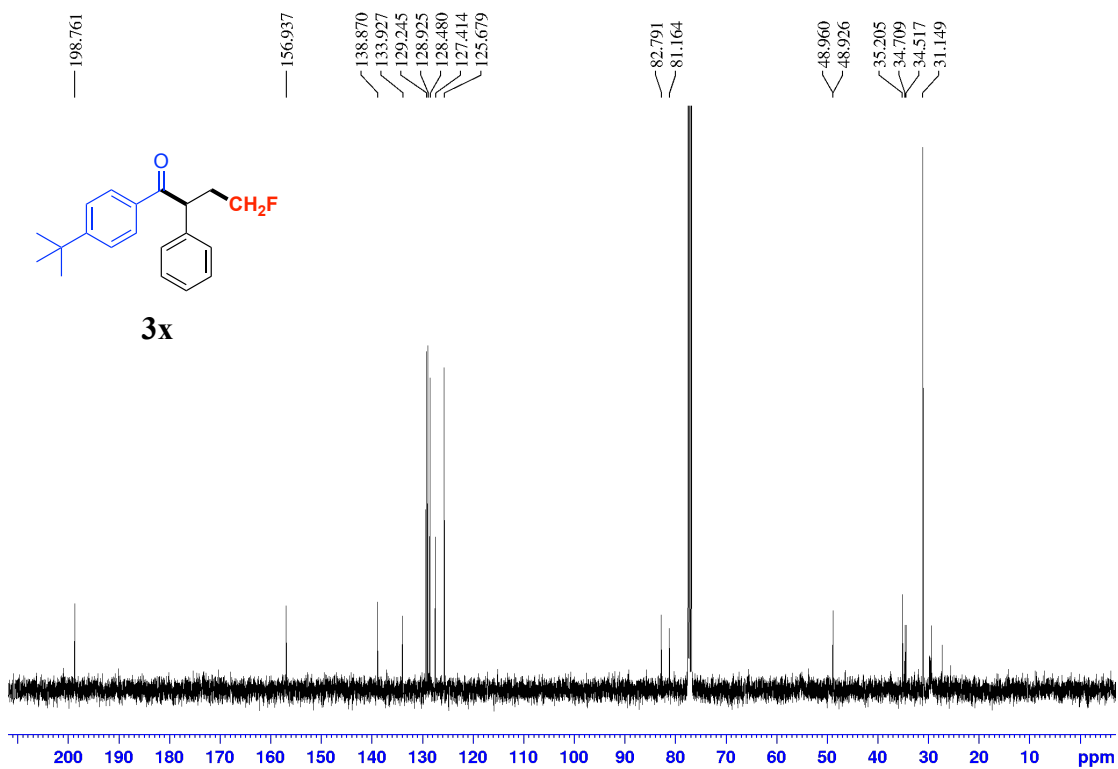
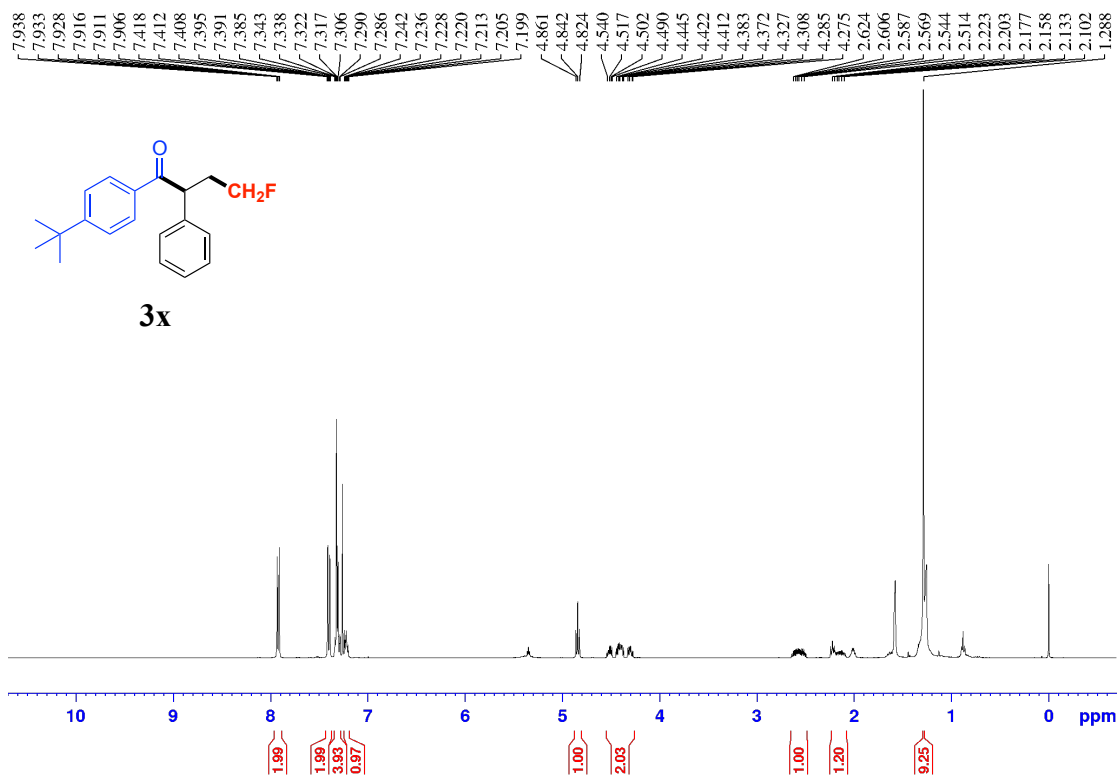


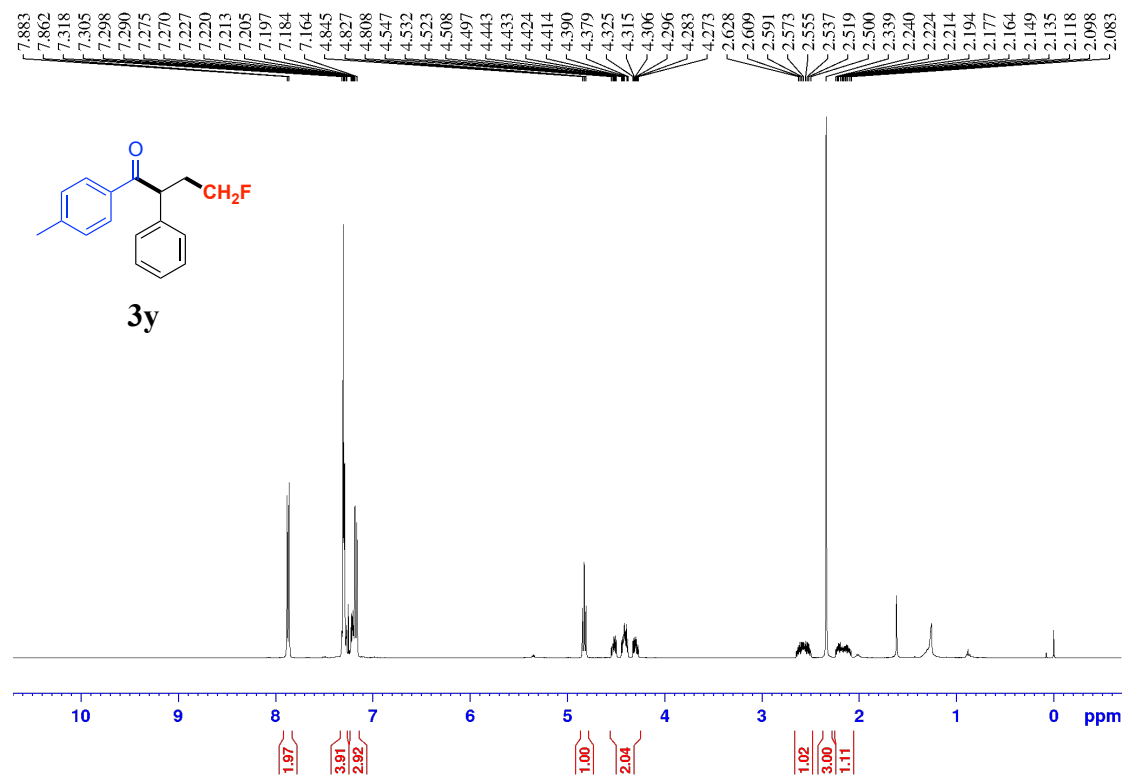
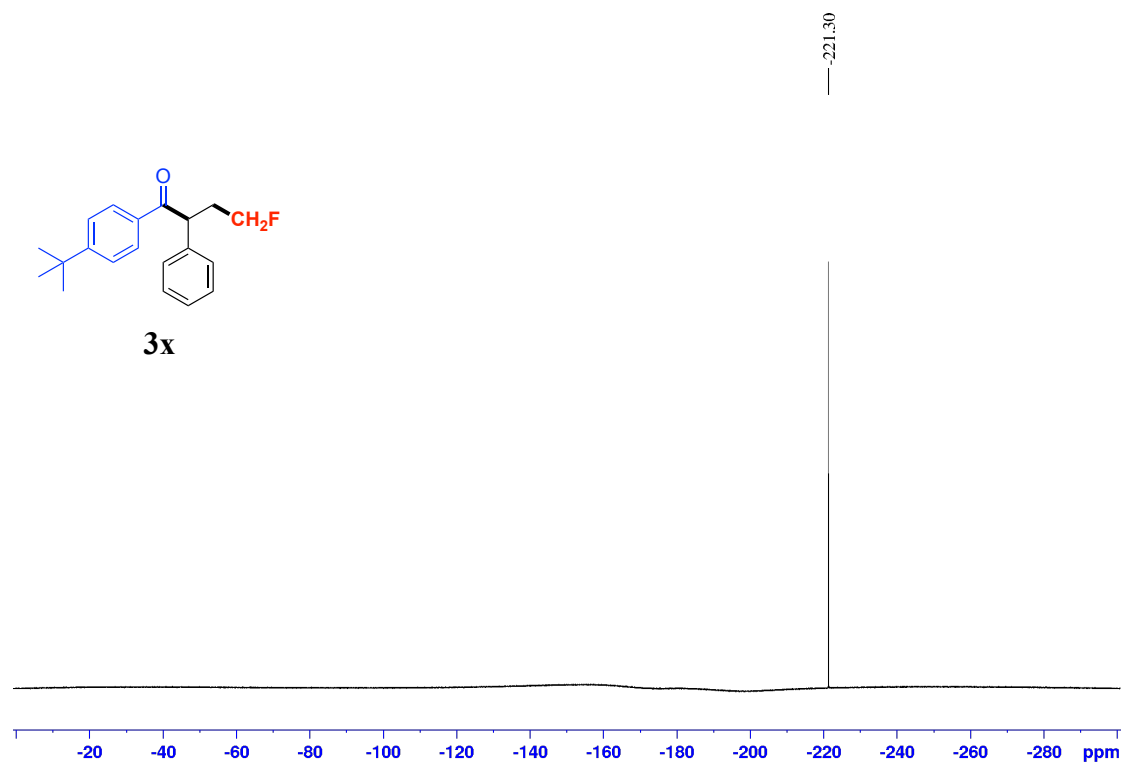


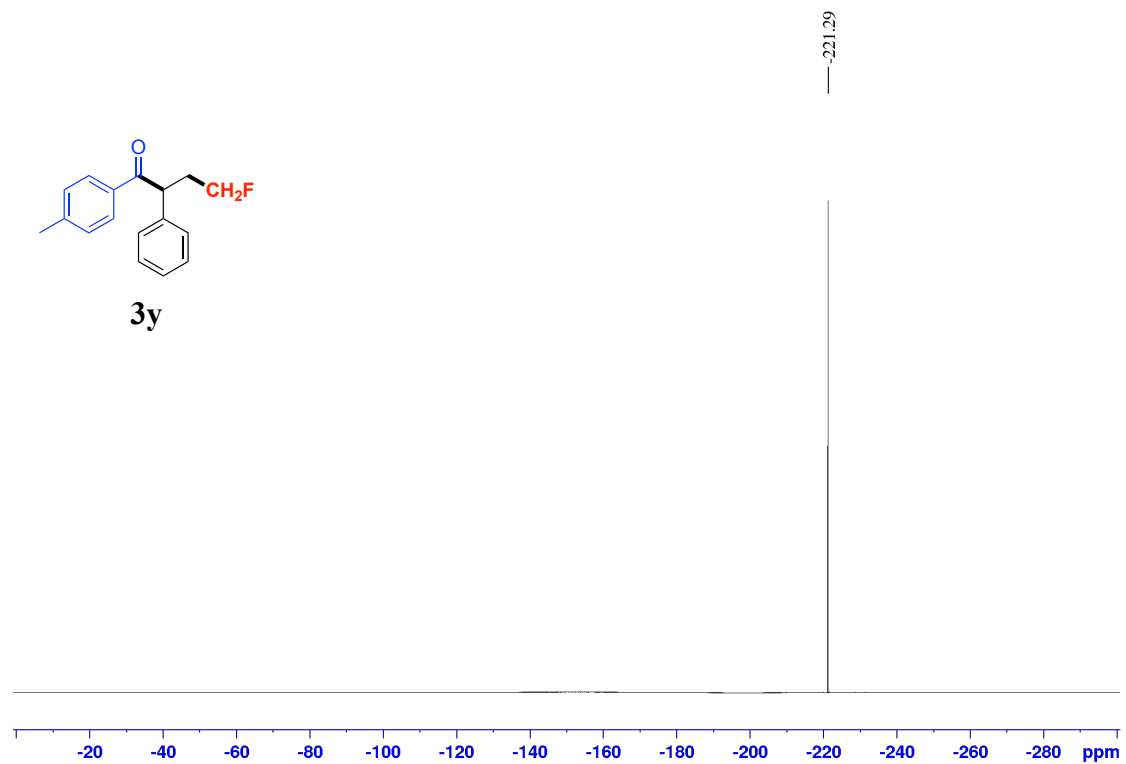
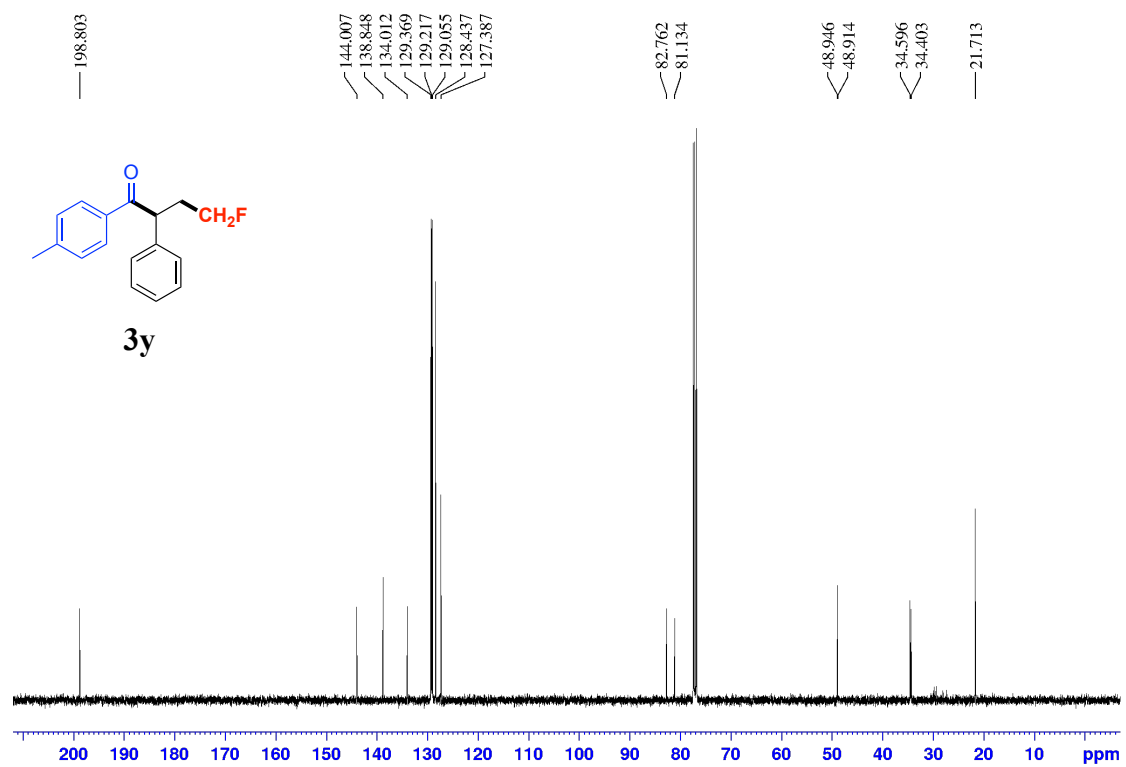


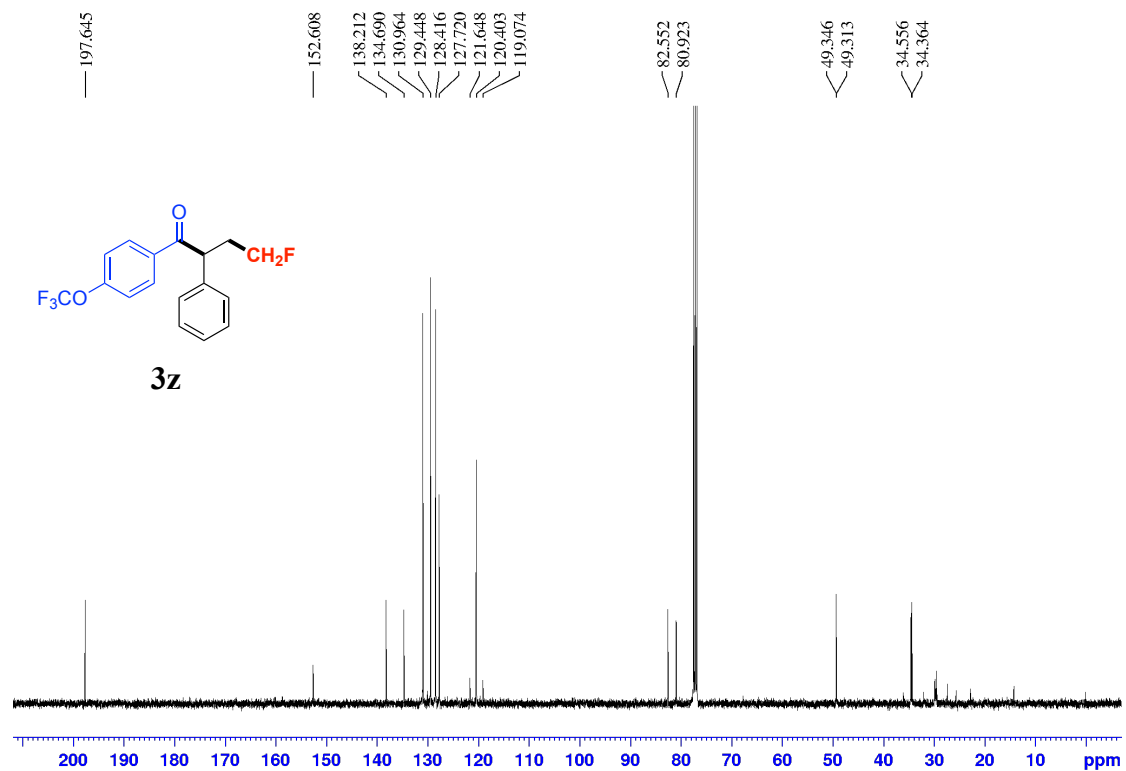
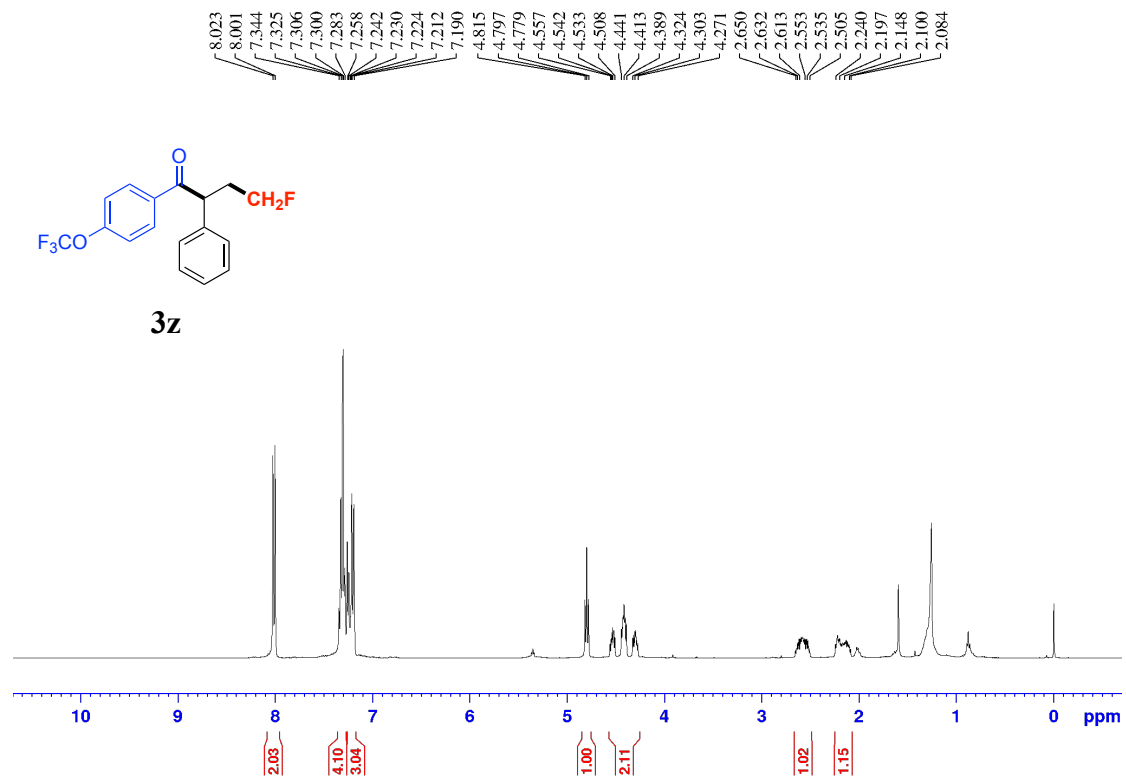


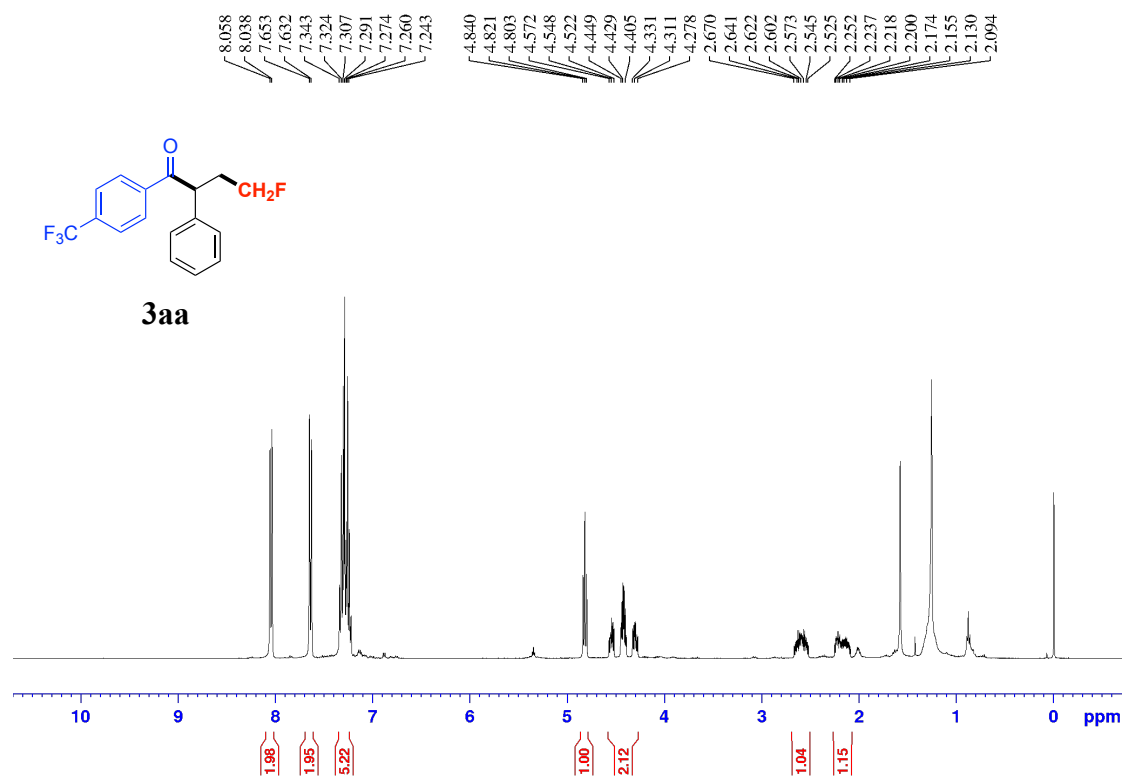
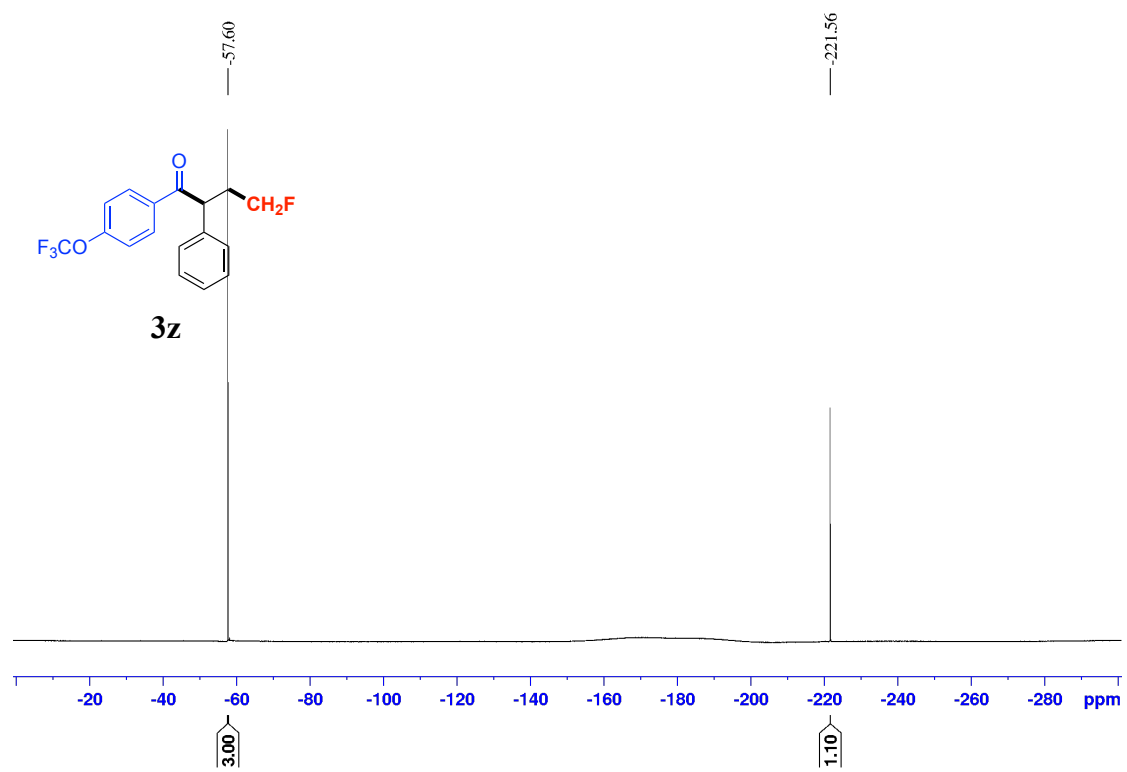


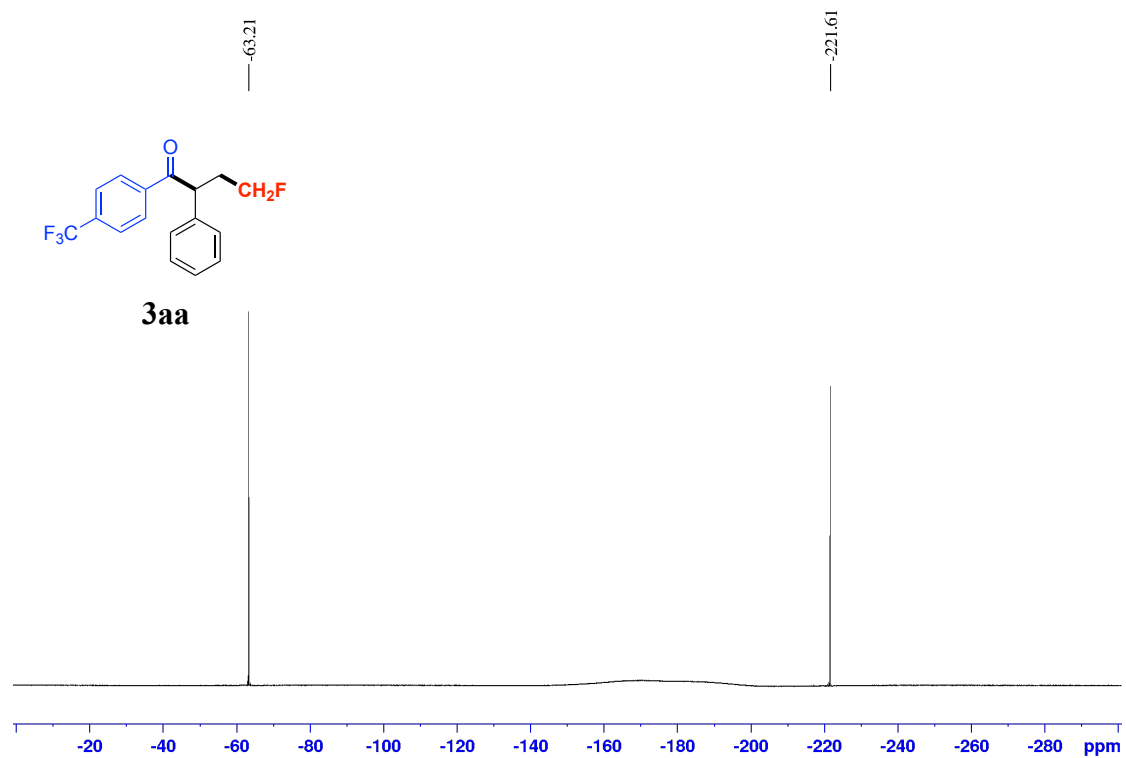
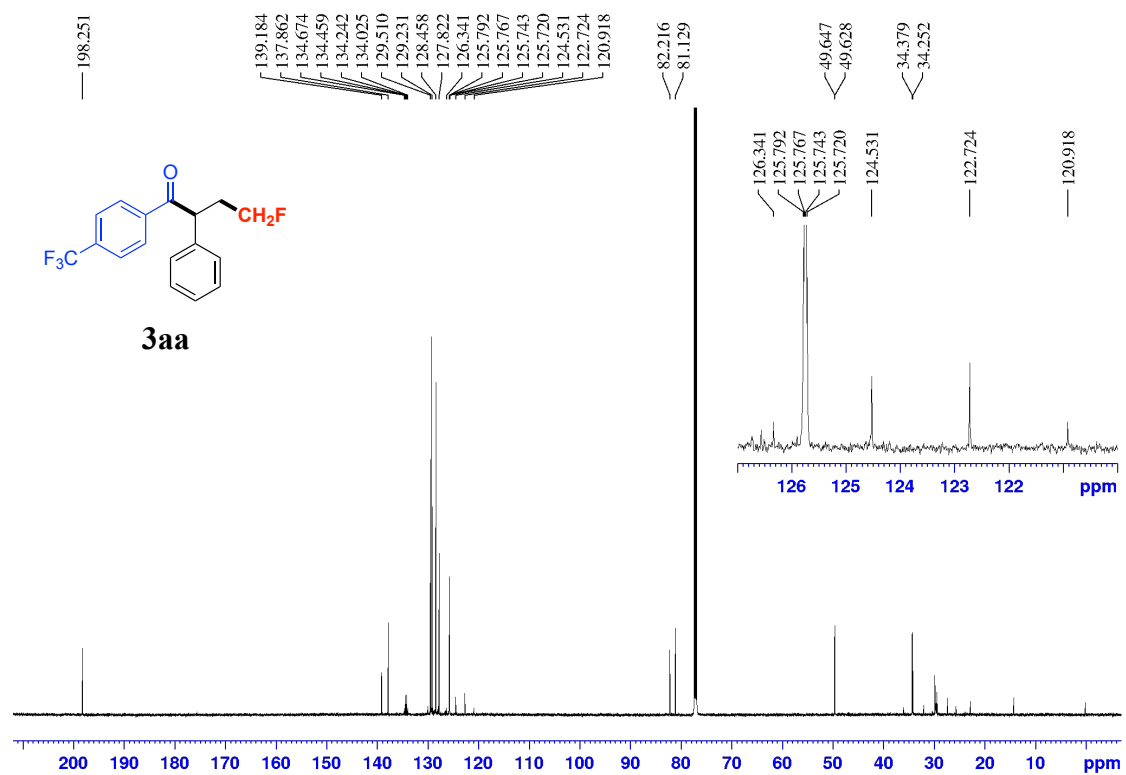


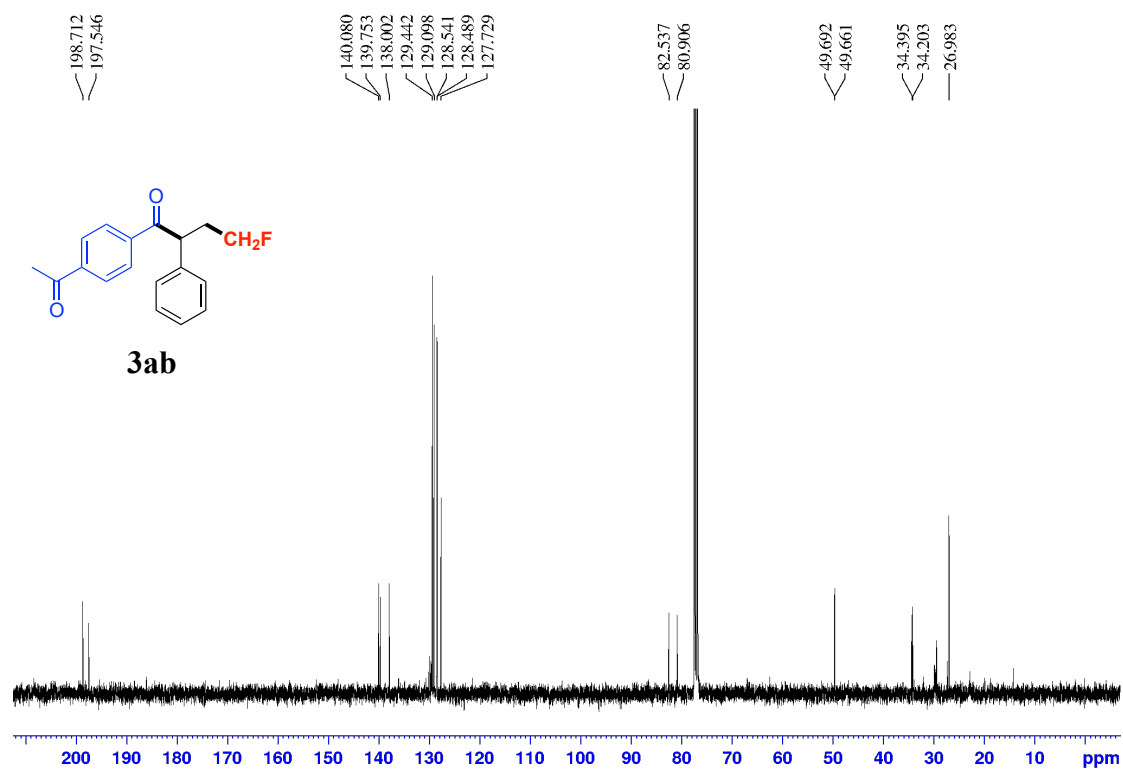
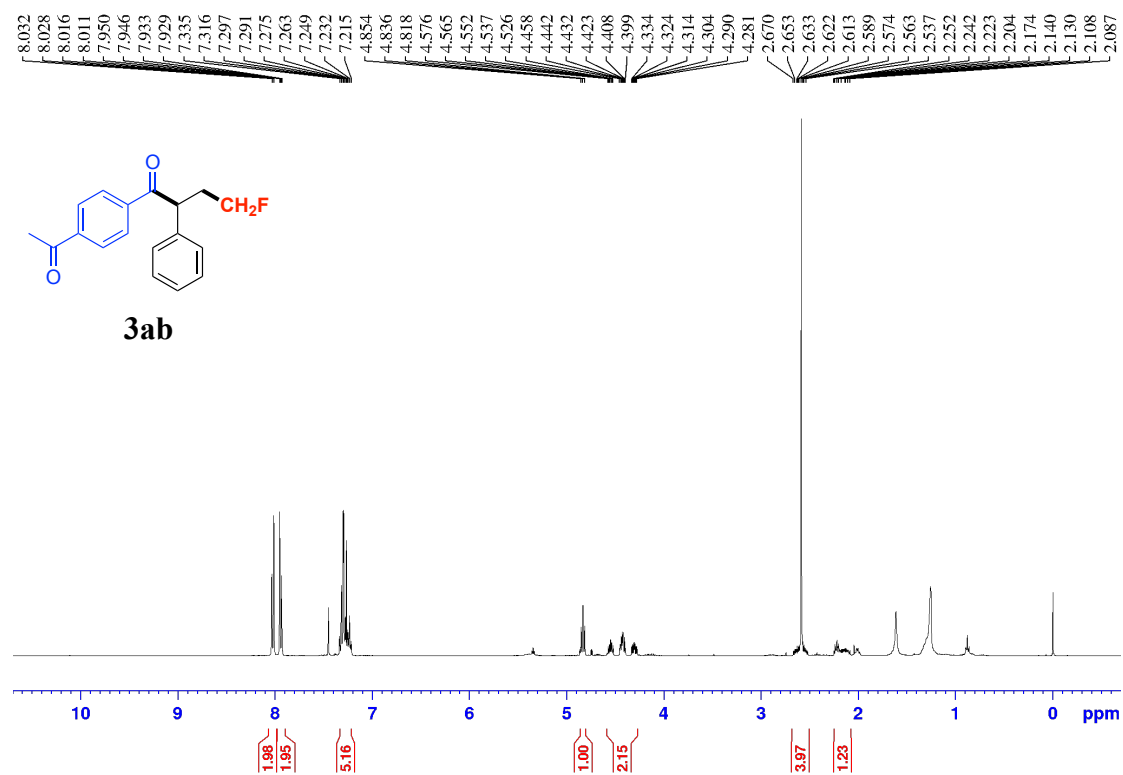


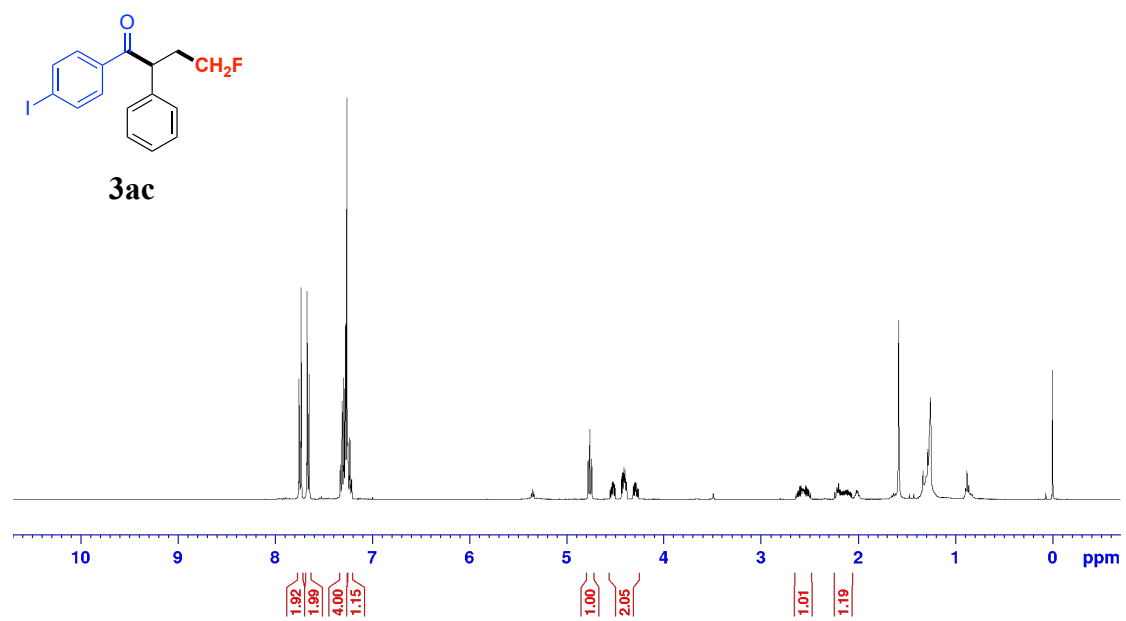
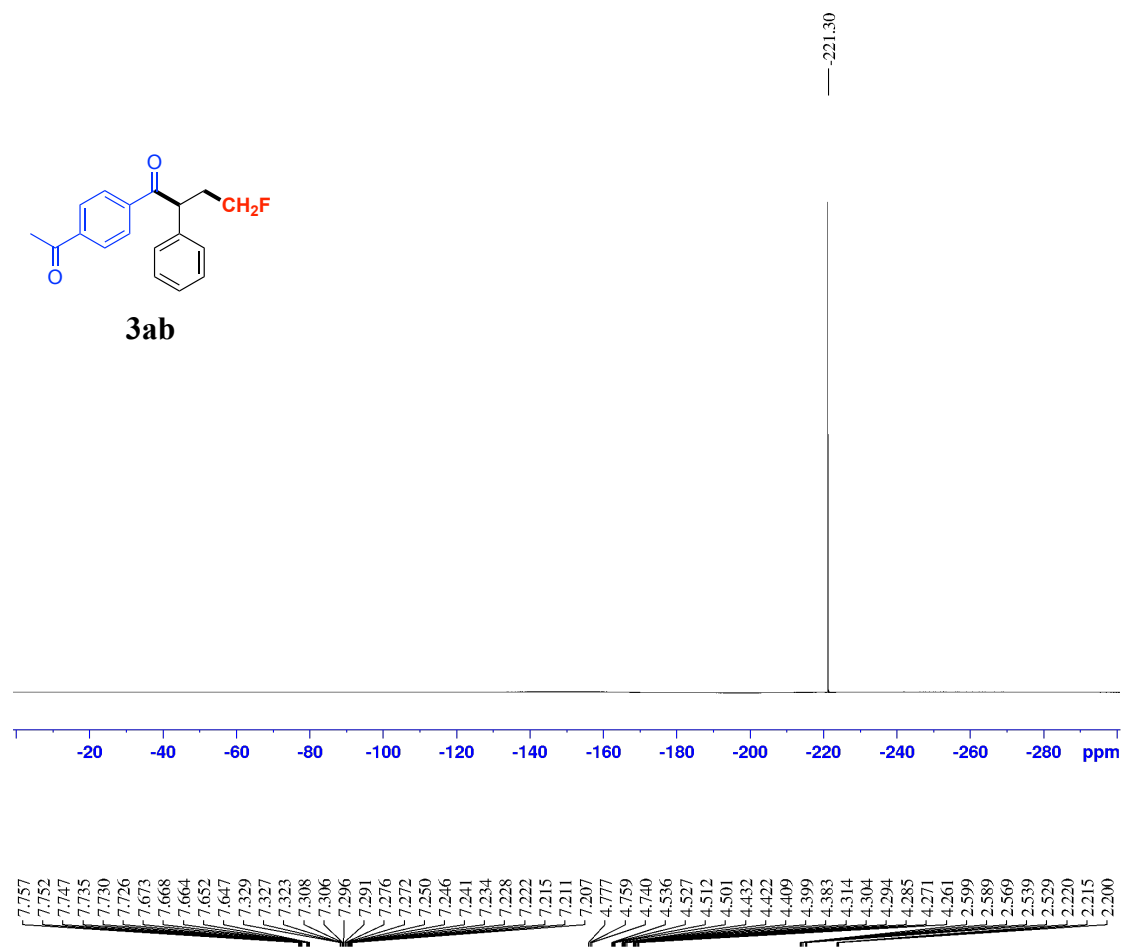


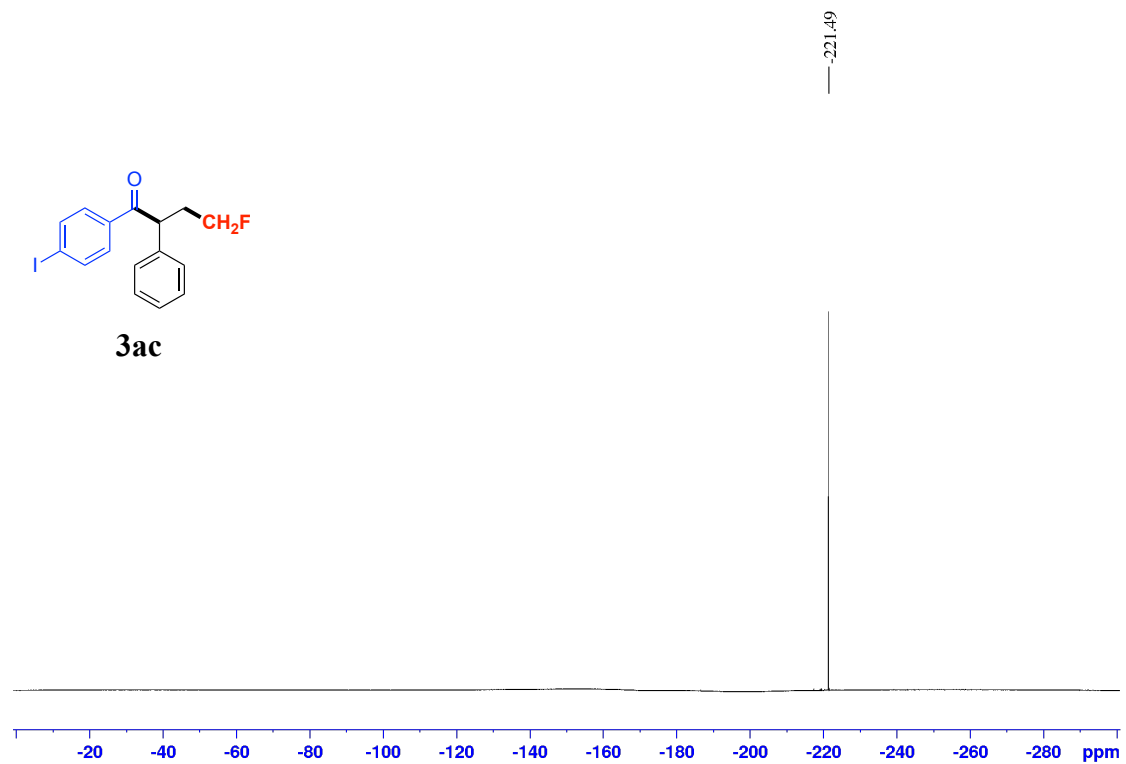
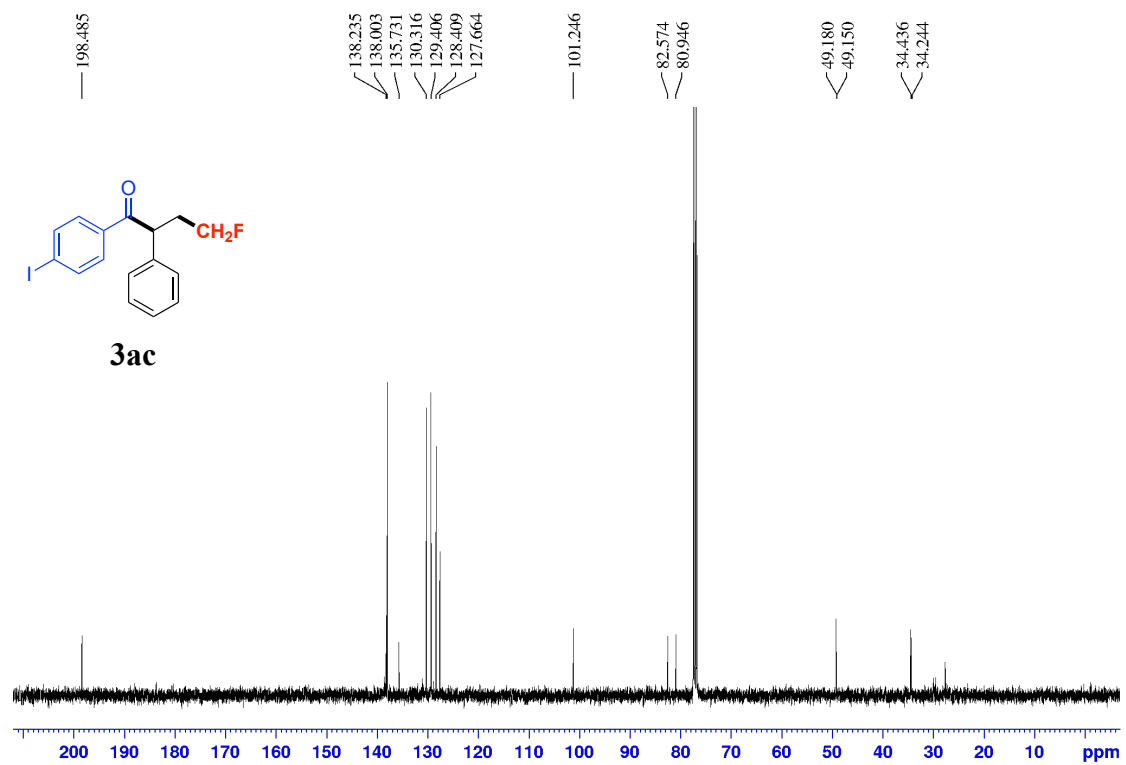


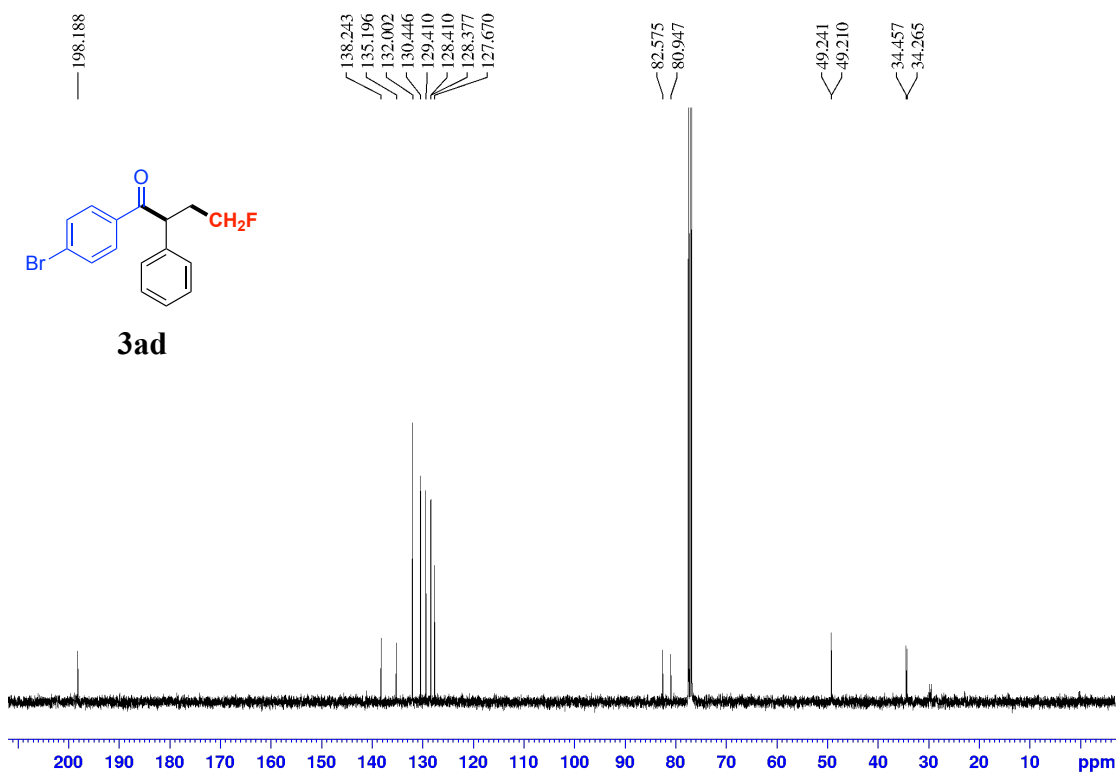
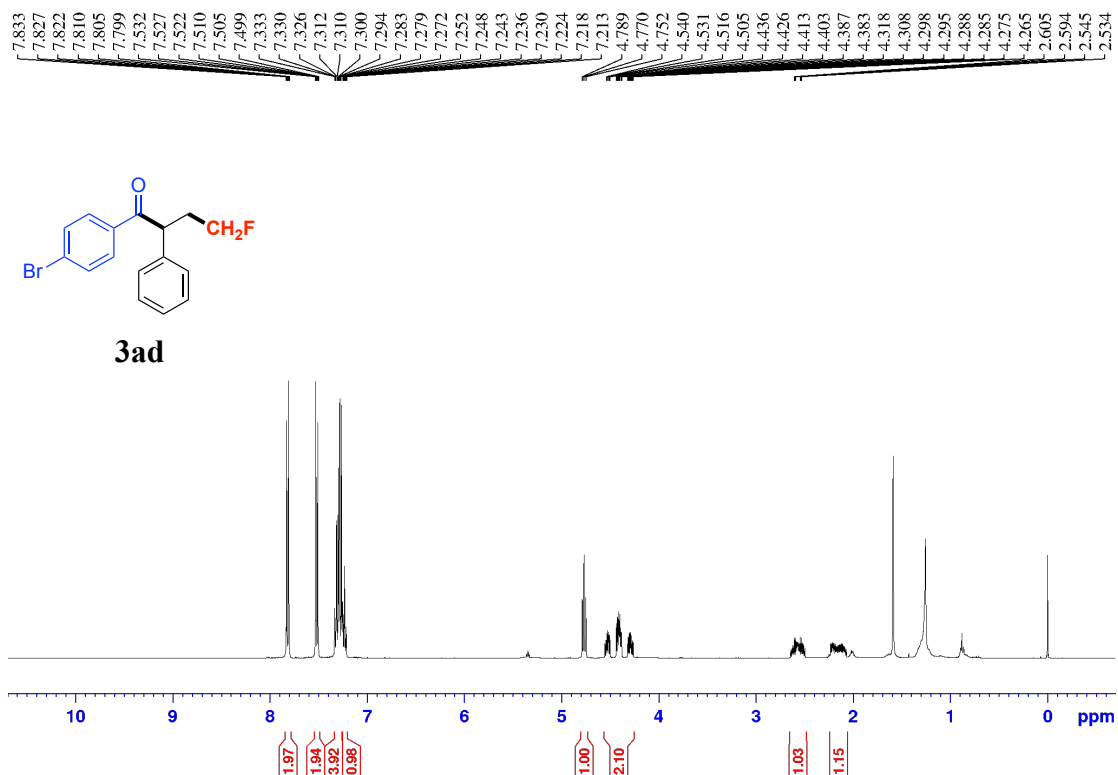


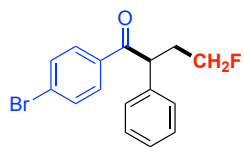




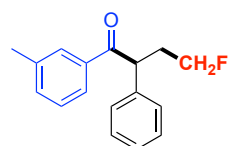
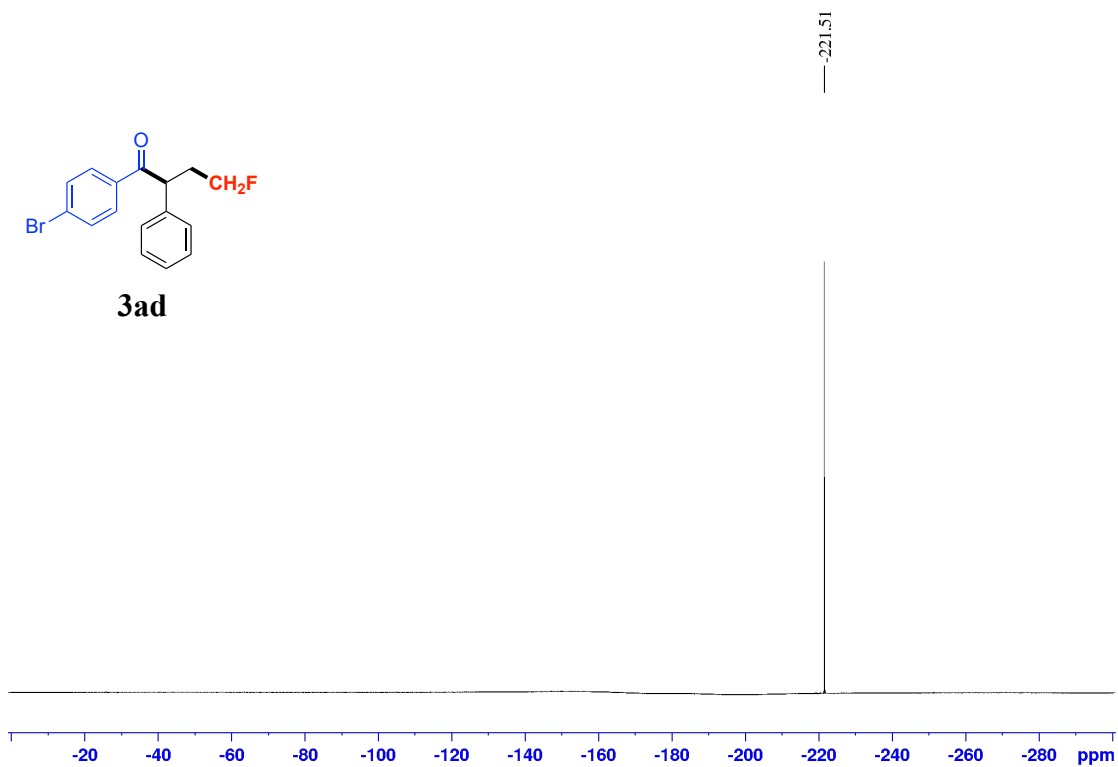








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