Unlocking geminal fluorohaloalkanes in nucleophilic fluoroalkylation chemistry: generation and trapping of lithiumfluorocarbenoids enabled by flow microreactors

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1. Instrumentation and General methods

Infrared spectra were recorded in reciprocal centimeters (cm^{-1}) by using a PerkinElmer 283 spectrometer. Melting points (uncorrected) were measured with Büchi melting point B-545. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Varian Mercury 300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) and an Agilent 500 spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C, 470 MHz for ^{19}F). The residual solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.00 ppm (^{13}C in $CDCl_3$). Spin-spin coupling constants (*J*) are given in Hz. When possible, unambiguous assignment of all resonances was performed by combined application of 2D NMR techniques, *i.e.* HSQC and COSY experiments. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet and bs = broad singnal), coupling constant (in Hz), integration and assignment]. NOESY experiments were performed for structure elucidation. High resolution mass spectrometry (HRMS) spectra were performed on Agilent 6530 accurate mass Q-TOF instrument and Excalibur data system. Diastereomeric ratios were assessed by ^{1}H NMR analysis on the reaction crude. Silica (70−230 mesh and 230−400 mesh) was used for flash chromatography on glass columns. TLC analysis were performed on a 0.25 mm precoated silica gel thick plates (Merck) with a fluorescence indicator F-254; the spots were visualized under UV light (λ = 254 nm) and/or $KMnO_4$ (aq.) was used as revealing system.

Chemicals were purchased from Sigma-Aldrich, Fluorochem, TCI Europe and Alfa Aesar unless otherwise specified and used without further purification. THF was distilled prior to use. Organolithium reagents were titrated prior to use (using N-benzylbenzamide as titrating agent).[1]

Flow equipment: Stainless steel (SUS304) T-shaped micromixers with inner diameters of 250 µm were manufactured by Sanko Seiki Co., Inc. Stainless steel (SUS316) microtube reactors with inner diameter of 1000 µm purchased from GL Sciences were used unless otherwise stated. The micromixers and microtube reactors were connected with stainless steel fittings (GL Sciences, 1/16 OUW). A cryogenic bath was used to control the temperature. Solutions of reagents were fluxed using syringe pumps Harvard PHD 2000, equipped with gastight syringes purchased from SGE.

1.1 Picture of the continuous flow microreactor system

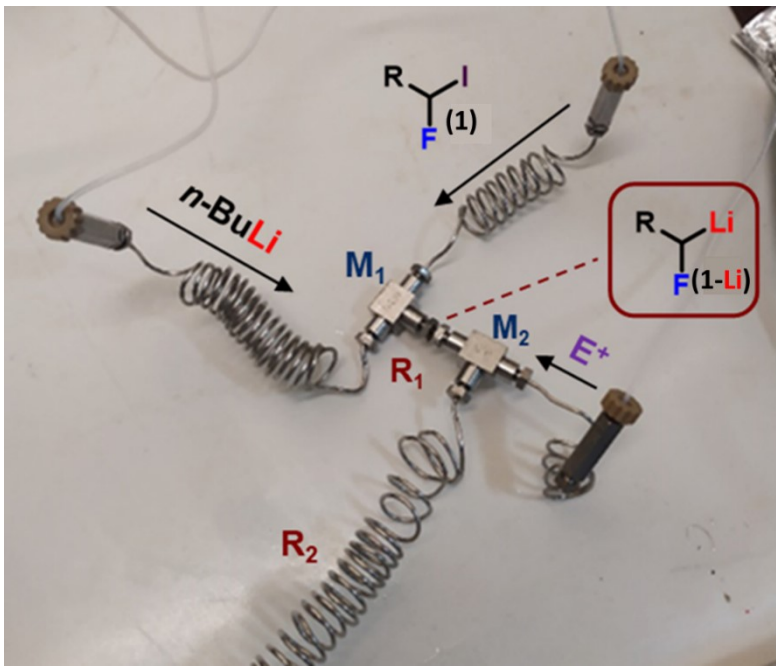


Figure S1. Continuous flow system.

Fluoroiodoalkanes were reacted with *n*-BuLi using T-shaped micromixer M_1 and microtube reactor R_1. The resulting solutions were reacted with electrophile in T-shaped micromixer M_2 and microtube reactor R_2. The flow microreactor system was dipped in a cooling bath to control the reaction temperature. Precooling units were used.

2. Batch procedures

2.1 Preparation of substrates

Substrates **1a-c** were prepared adopting reported procedures.[2,3] Spectroscopic data are consistent with those reported in the literature. [2,4,5]

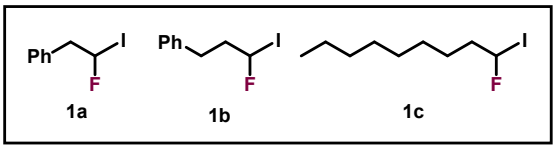


Figure S2. Substrates **1a-c**.

2.1 Electrophiles collection

The following compounds are available from Sigma-Aldrich, TCI Europe, Fluorochem and Alfa Aesar except for electrophile **2v**, which was prepared adopting a reported procedure.[6] Spectroscopic data are consistent with those reported in the literature.

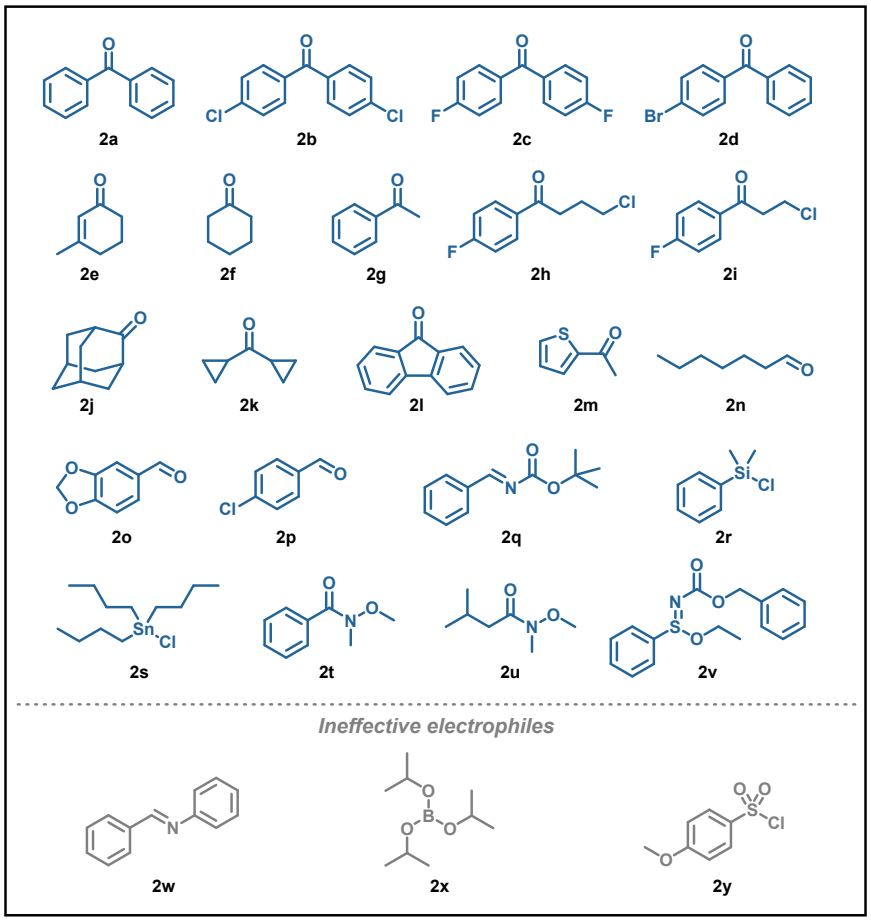
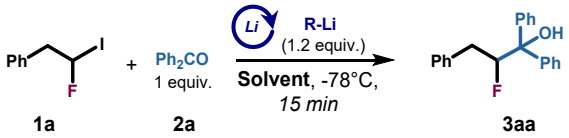


Figure S3. Collection of electrophiles used in this work.

2.2 Table S1. Screening of solvents and organolithiums under internal quenching regime



To a stirred solution of **(2-fluoro-2-iodoethyl)benzene** (**1a)** (50 mg, 0.2 mmol) and **benzophenone** (**2a**) (36 mg, 0.2 mmol, 1 equiv.) at -78°C, in **solvent** (2 mL), the organolithium solution (**R-Li)** was added dropwise. The resulting mixture was stirred for 15 min at -78°C and then quenched with 150 µL of methanol. The crude was washed with distilled water (2 x 2 mL) and the aqueous layers were extracted with ethyl acetate (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Yields of **3aa** were evaluated using CH_2Br_2 as an NMR-internal standard.

Entry	Solvent	R-Li	Yield(%) of 3aa
1	THF-Et_2O 1:1 (v/v)	MeLi	75%
2	Toluene	MeLi	0%
3	CPME	MeLi	0%
4	Et_2O	MeLi	4%
5	2-MeTHF	MeLi	81%
6	THF	MeLi	90%
7	THF	n-BuLi	54%
8	THF	n-HexLi	50%

Table S1

2.3 Reactivity of 1a-Li, (1-fluoro-2-phenylethyl)lithium

To a stirred solution of **(2-fluoro-2-iodoethyl)benzene** (**1a)** (50 mg, 0.2 mmol) at -78°C, in THF (2 mL), ***n*-BuLi** (1.2 eq.) was added dropwise. The resulting mixture was stirred for 10 min at -78°C and then 5 min at room temperature. The volatiles were evaporated, and the crude was analyzed by ^{1}H, ^{19}F-NMR and GC-MS.

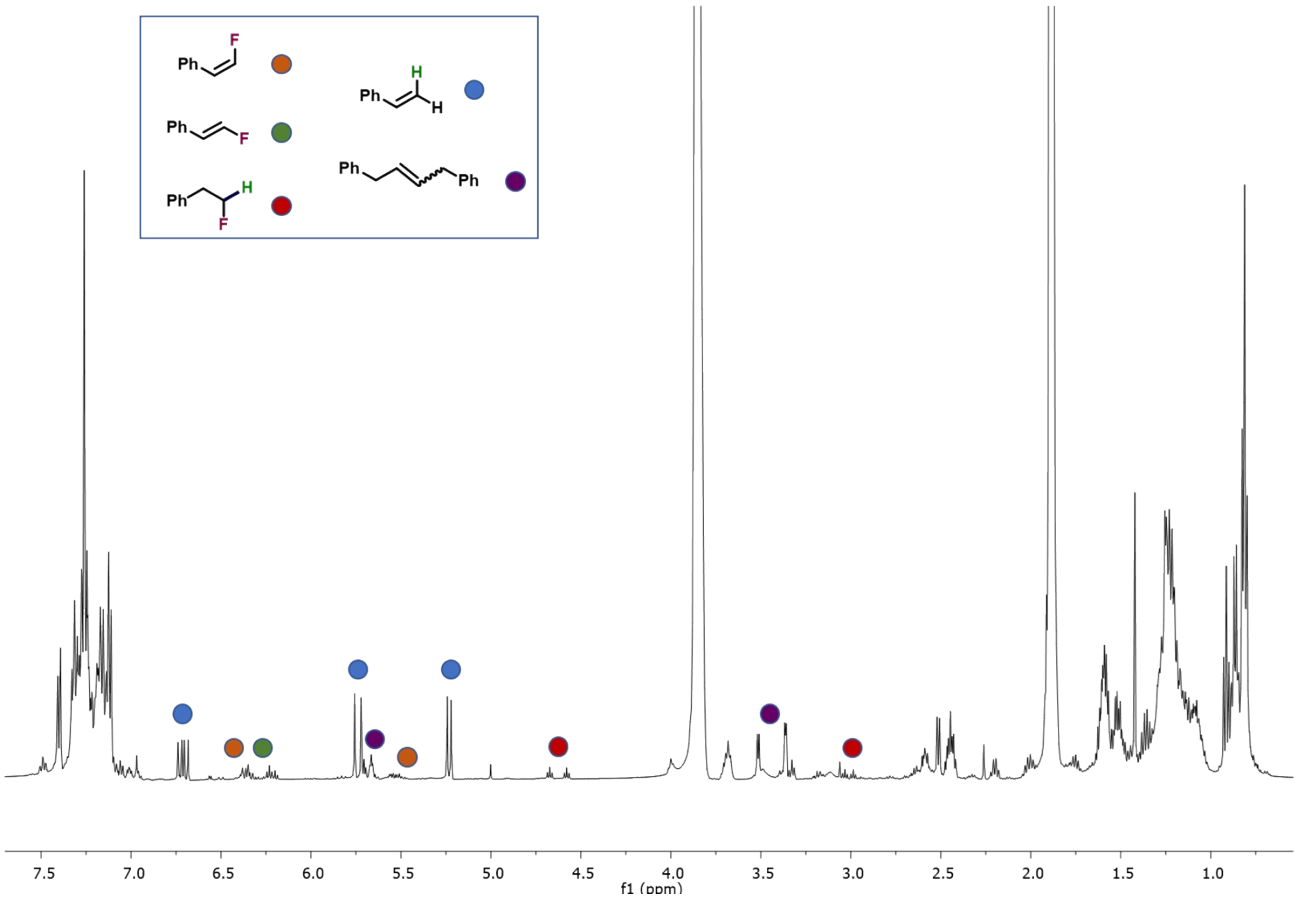
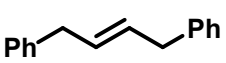


Figure S4. ^{1}H-NMR spectrum of the crude



(*E*)-1,4-diphenylbut-2-ene

(*Z*)-1,4-diphenylbut-2-ene

Reported data for (*E*)-1,4-diphenylbut-2-ene. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 9.0 Hz, 4H), 7.24 (m, 6H), 5.75-6.68 (m, 2H), 3.42 (d, *J* = 5.0 Hz, 4H).[7]

Reported data for (*Z*)-1,4-diphenylbut-2-ene. ^{1}H NMR (500 MHz, $CDCl_3$) r (400 MHz, CDCl3) δ (ppm) 7.39-7.20 (m, 10H), 5.87-5.63 (m, 2H), 3.56 (d, J = 5.1 Hz, 4H).[8]

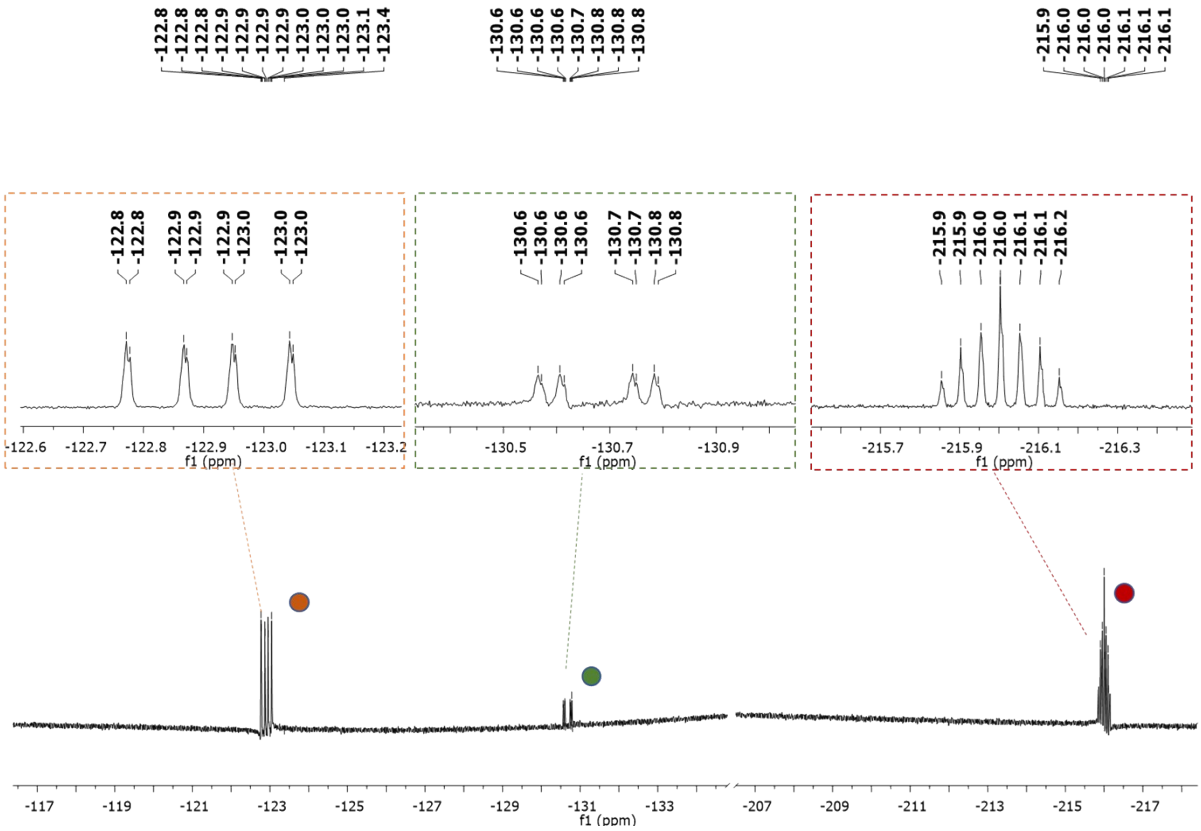
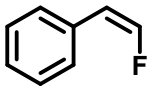
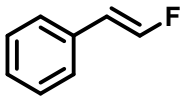


Figure S5. ^{19}F-NMR spectrum of the crude



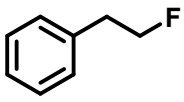
4a; (*Z*)-(2-fluorovinyl)benzene

^{19}F NMR (470 MHz, $CDCl_3$) δ -122.9 (ddd, $^{2}J_{(H-F)}$ = 83.2 Hz, $^{3}J_{(H-F)}$ = 45.1, 2.7 Hz, 1F, CHF). Spectroscopic data consistent with literature.[9]



4b; (*E*)-(2-fluorovinyl)benzene

^{19}F NMR (470 MHz, $CDCl_3$) δ -130.7 (ddd, $^{2}J_{(H-F)}$ = 83.1 Hz, $^{3}J_{(H-F)}$ = 19.4, 3.3 Hz, 1F, CHF). Spectroscopic data consistent with literature.[10]



5; 2-fluoroethylbenzene

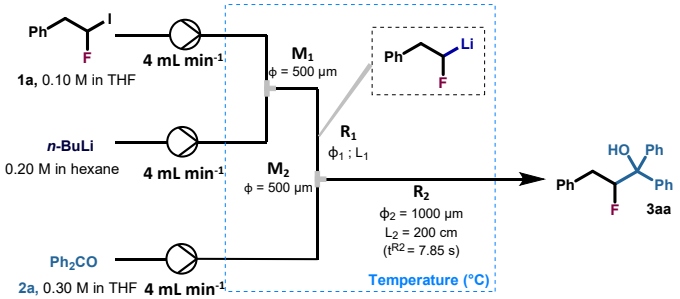
^{19}F NMR (470 MHz, $CDCl_3$) δ -216.1 – -215.8 (m, 1F, CH_2F). Spectroscopic data consistent with literature.[11]

2.4 General procedure for the "batch" monofluoroalkylation

To a stirred solution of **fluoroiodoalkane** (**1**) (0.3 mmol) and **electrophile** (**2**) (0.3 mmol, 1 equiv.) at -78°C, in **solvent** (3 mL), the *n*-butyllithium solution (***n*-BuLi**) (0.36 mmol, 1.2 equiv) was added dropwise. The resulting mixture was stirred for 15 min at -78°C and then quenched with 150 µL of methanol. The crude was washed with distilled water (2 x 2 mL) and the aqueous layers were extracted with ethyl acetate (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Yields of products **3** were evaluated using CH_2Br_2 as an NMR-internal standard.

3. General procedures for the continuous-flow nucleophilic fluoroalkylation

3.1 General procedure for lithiation of (2-fluoro-2-iodoethyl)benzene (1a) and trapping with benzophenone using a flow microreactor system.



A microfluidic system consisting of two T-shaped micromixers (**M_1** and **M_2**), two microtube reactors (**R_1** and **R_2**), and three tube precooling units was used. The microfluidic system was cooled with a cooling bath (T °C). A solution of **(2-fluoro-2-iodoethyl)benzene** (**1a**) (0.10 M in THF) (flow rate: 4.0 mL/min) and a solution of *n*-BuLi (0.20 M in hexane, 2 equiv.) (flow rate: 4.0 mL/min) were introduced to **M_1** (φ = 500 µm) by syringe pumps. The resulting solution was passed through **R_1** and was mixed with a solution of **benzophenone** (**2a**) (0.30 M in THF, 3 equiv.) (flow rate: 4.0 mL/min) in **M_2** (φ = 500 µm). The resulting solution was passed through **R_2** (φ = 1000 µm, L = 200 cm ; t^{R2} = 7.85 s). After reaching the steady state, the outcoming solution was collected for 1 minute in a vessel containing 2 mL of distilled water. The yield of **3aa** was determined by GC analysis using decane as the internal standard. The results obtained by screening the residence time and the temperature are summarized in the following table and 3D-maps.

Table S2. Evaluation of residence time and temperature effects on yield**.**

Entry	T (°C)	φ_1	L_1	t^{R1}(ms)	Yield (%)
1	0°C	250µm	3.5cm	13ms	0%
2	-30°C	250µm	3.5cm	13ms	36%
3	-30°C	500µm	3.5cm	52ms	30%
4	-30°C	750µm	3.5cm	116ms	26%
5	-30°C	1000µm	3.5cm	206ms	17%
6	-30°C	1000µm	6cm	353ms	13%
7	-50°C	250µm	3.5cm	13ms	79%
8	-50°C	500µm	3.5cm	52ms	63%
9	-50°C	750µm	3.5cm	116ms	58%

10	-50°C	1000µm	3.5cm	206ms	57%
11	-50°C	1000µm	6cm	353ms	48%
12	-78°C	250µm	3.5cm	13ms	68%
13	-78°C	500µm	3.5cm	52ms	63%
14	-78°C	750µm	3.5cm	116ms	53%
15	-78°C	1000µm	3.5cm	206ms	80%
16	-78°C	1000µm	6cm	353ms	38%
17	-78°C	1000µm	12.5cm	736ms	24%

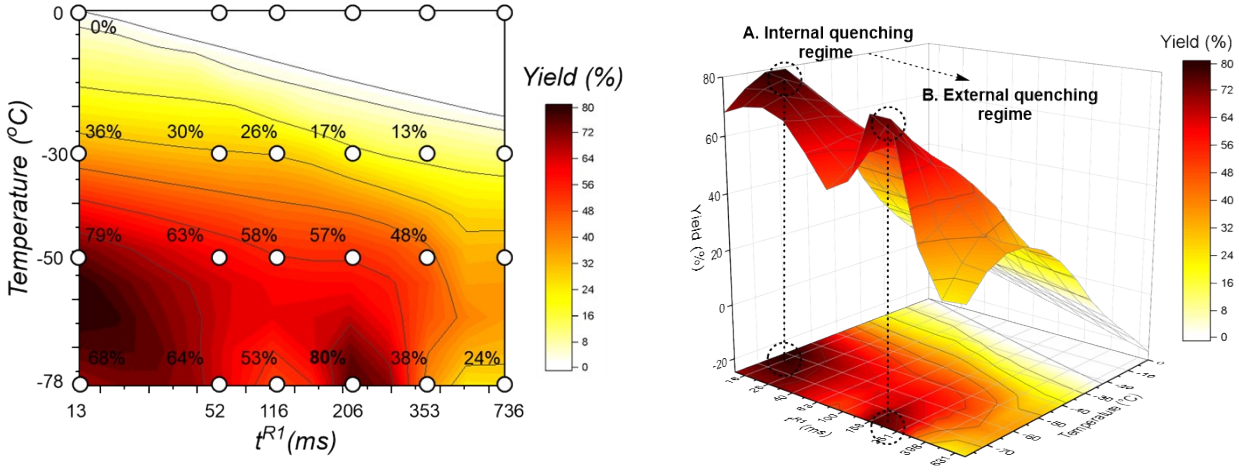
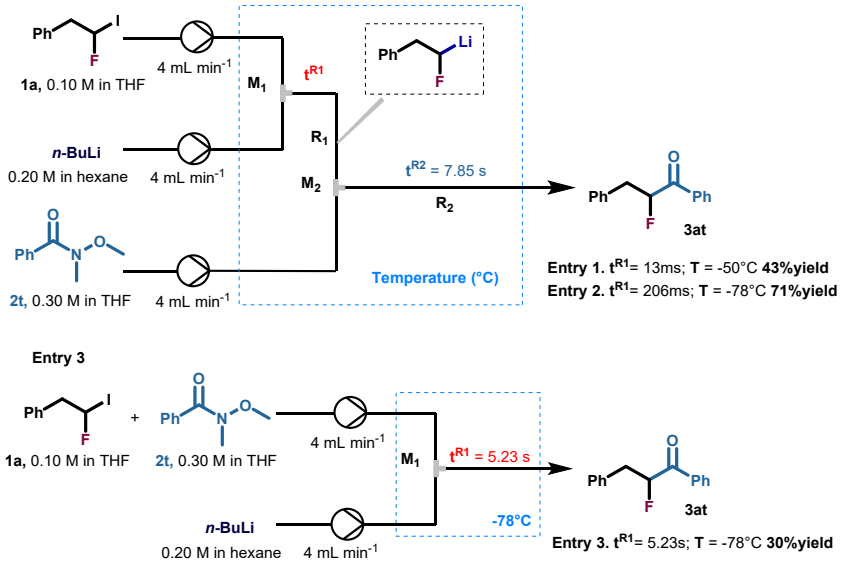


Figure S6. 3-D map.

3.2 Evaluation of the transition between internal and external regime



Entry 1 and 2: A microfluidic system consisting of two T-shaped micromixers ($\mathbf{M_1}$ and $\mathbf{M_2}$), two microtube reactors ($\mathbf{R_1}$ and $\mathbf{R_2}$), and three tube precooling units was used. The microfluidic system was The flow system was cooled with a cooling bath (Entry 1: T = -50°C ; Entry 2: T = -78°C). A solution of **(2-fluoro-2-iodoethyl)benzene** (**1a**) (0.10 M in THF) (flow rate: 4.0 mL/min) and a solution of ***n*-BuLi** (0.20 M in hexane, 2 equiv.) (flow rate: 4.0 mL/min) were introduced to $\mathbf{M_1}$ (φ = 500 µm) by syringe pumps. The resulting solution was passed through $\mathbf{R_1}$ (Entry 1: φ = 250 µm, L = 3.5 cm , t^{R1} = 13 ms ; Entry 2: φ = 1000 µm, L = 3.5 cm , t^{R1} = 206 ms) and was mixed

with a solution of ***N*-methyl-*N*-methoxybenzamide** (**2t**) (0.30 M in THF, 3 equiv.) (flow rate: 4.0 mL/min) in $\mathbf{M_2}$ (φ = 500 µm). The resulting solution was passed through $\mathbf{R_2}$ (φ = 1000 µm, L = 200 cm ; t^{R2} = 7.85 s) at -78°C. After a steady state was reached, the outcoming solution was collected for 1 minute in a vessel containing 2 mL of distilled water. The yield of **3ab** was determined using CH_2Br_2 as an NMR-internal standard.

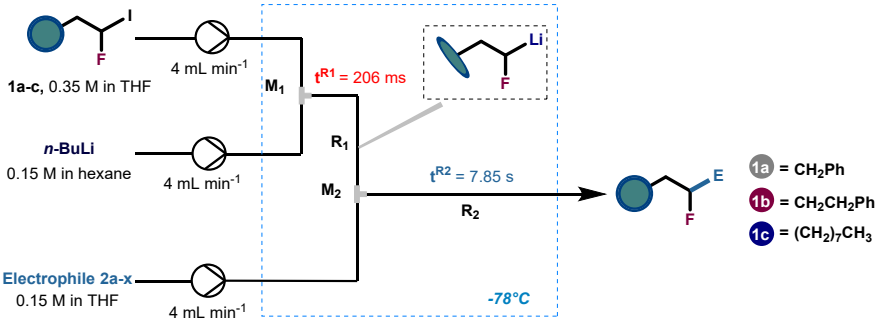
Entry 3: A microfluidic system consisting of one T-shaped micromixer ($\mathbf{M_1}$), one microtube reactor ($\mathbf{R_1}$), and two tube precooling units was used. The microfluidic system was cooled to -78°C with a cooling bath (T °C) . A solution of **(2-fluoro-2-iodoethyl)benzene** (**1a**) (0.10 M in THF) and ***N*-methyl-*N*-methoxybenzamide** (**2t**) (0.30 M in THF, 3 equiv.) (flow rate: 4.0 mL/min) and a solution of ***n*-BuLi** (0.20 M in hexane, 2 equiv.) (flow rate: 4.0 mL/min) were introduced to $\mathbf{M_1}$ (φ = 500 µm) by syringe pumps. The resulting solution was passed through $\mathbf{R_1}$ (φ = 1000 µm, L = 200 cm , t^{R1} = 5.23 s) (flow rate: 4.0 mL/min). After a steady state was reached, the outcoming solution was collected for 1 minute in a vessel containing 2 mL of distilled water. The yield of **3ab** was determined using CH_2Br_2 as an NMR-internal standard.

Table S3. Evaluation of the transition between internal and external regime.

Entry	T (°C)	φ_1	L_1	t^{R1}(ms)	Yield (%)
1	-50°C	250µm	3.5cm	13ms	43%
2	-78°C	1000µm	3.5cm	206ms	71%
3	-78°C	1000µm	200cm	5.23s	30%

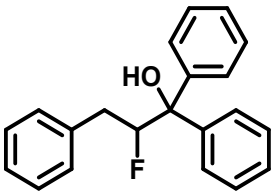
These results suggest that the trapping of the reactive intermediate after 206ms at -78°C occurs under an external quenching regime.

3.3 General procedure (GP) for the continuous flow nucleophilic-monofluoroalkylation



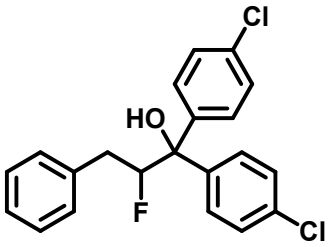
A microfluidic system consisting of two T-shaped micromixers ($\mathbf{M_1}$ and $\mathbf{M_2}$), two microtube reactors ($\mathbf{R_1}$ and $\mathbf{R_2}$), and three tube precooling units was used. The microfluidic system was cooled to -78°C with a cooling bath. A solution of **1-fluoro-1-iodoalkane** (**1a-c**) (0.35 M in THF, 2.3 equiv.) (flow rate: 4.0 mL/min) and a solution of ***n*-BuLi** (0.15 M in hexane, 1 equiv.) (flow rate: 4.0 mL/min) were introduced to $\mathbf{M_1}$ (φ = 500 µm) by syringe pumps. The resulting solution was passed through $\mathbf{R_1}$ (φ = 1000 µm, L = 3.5 cm , t^{R1} = 206 ms) and was mixed with a solution of **electrophile** (**2a-x**) (0.15 M in THF, 1 equiv.) (flow rate: 4.0 mL/min) in $\mathbf{M_2}$ (φ = 500 µm). The resulting solution was passed through $\mathbf{R_2}$ (φ = 1000 µm, L = 200 cm ; t^{R2} = 7.85 s). After reaching the steady state, the outcoming solution was collected for 1 minute in a vessel containing 2 mL of distilled water. The aqueous and the organic phase were separated, and the aqueous layer was extracted with Et_2O (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and the crude was purified through flash column chromatography, affording the desired product. Purification allowed the recovery of the residual 1-fluoro-1-iodoalkane (up to 70%), which was re-used. Stereochemistry of the products was not assigned.

4. Characterization of compounds 3aa-3ck



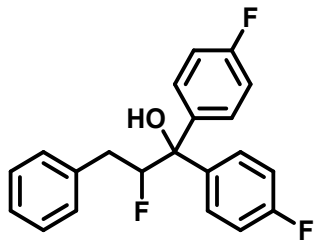
3aa; 2-fluoro-1,1,3-triphenylpropan-1-ol

Prepared according to general procedure GP to afford **3aa** as a white waxy solid (174 mg, 95%) after column chromatography (R_f = 0.3, hexane/Et_2O 9:1) ; IR (film)/cm^{-1} 3436, 3089, 2935, 1954, 1638, 1495, 1449, 1274; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H, 2 × Ar–H), 7.46 (d, *J* = 7.4 Hz, 2H, 2 × Ar–H), 7.34 (t, *J* = 7.6 Hz, 4H, 4 × Ar–H), 7.30–7.21 (m, 5H, 5 × Ar–H, overlapping with $CDCl_3$), 7.15 (d, *J* = 7.4 Hz, 2H, 2 × Ar–H), 5.57 (ddd, $^2J_{(H–F)}$ = 47.1 Hz, $^3J_{(H–H)}$ = 10.0 , 1.6 Hz, 1H, C*H*FCH_2), 3.08–2.99 (m, 1H, PhC*H*HCHF), 2.72 (d, $^4J_{(H–F)}$ = 1.7, 1H, O–H), 2.68 (ddd, $^3J_{(H–F)}$ = 42.0 Hz, $^2J_{(H–H)}$ = 14.9, $^3J_{(H–H)}$ = 1.6 Hz, 1H, PhC*H*HCHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5 (Ar–C_q), 143.1 (d, $^3J_{(C–F)}$ = 4.1 Hz, Ar–C_q), 138.3 (Ar–C_q), 129.3 (2 × Ar–C), 129.4 (2 × Ar–C), 128.6 (2 × Ar–C), 128.5 (2 × Ar–C), 128.4 (2 × Ar–C), 127.6 (Ar–C), 127.5 (Ar–C), 126.9 (d, $^4J_{(C–F)}$ = 1.7 Hz, 2 × Ar–C), 126.6 (Ar–C), 97.0 (d, $^1J_{(C-F)}$ = 181.5 Hz, CHF), 79.4 (d, $^2J_{(C-F)}$ = 20.7 Hz, C_qOHCHF), 35.8 (d, $^2J_{(C-F)}$ = 21.4 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ --187.4 (ddd, $^2J_{(H-F)}$ = 47.1 Hz, $^3J_{(H-F)}$ = 42.0, 16.6 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{21}H_{18}FO$ $[M-H]^-$ 305.1347; Found: 305.1338.



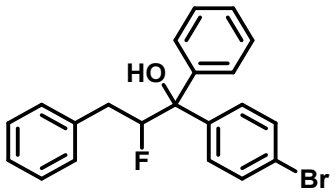
3ab; 1,1-bis(4-chlorophenyl)-2-fluoro-3-phenylpropan-1-ol

Prepared according to general procedure GP to afford **3ab** as a white waxy solid (202 mg, 90%) after column chromatography (R_f = 0.3, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3583, 3063, 2932, 1904, 1593, 1492, 1321, 823; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H, 2 × Ar–H), 7.37–7.36 (m, 2H, 2 × Ar–H), 7.33–7.28 (m, 6H, 6 × Ar–H), 7.26–7.23 (m, 1H, Ar–H), 7.14 (d, *J* = 7.6 Hz, 2H, 2 × Ar–H), 5.47 (ddd, $^2J_{(H–F)}$ = 47.0 Hz, $^3J_{(H–H)}$ = 9.9 , 1.7 Hz, 1H, C*H*FCH_2), 3.04–2.95 (m, 1H, PhC*H*HCHF), 2.73-2.60 (m, 2H, PhC*H*HCHF overlapping with O–H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5 (Ar–C_q), 141.2 (d, $^3J_{(C–F)}$ = 3.9 Hz, Ar–C_q), 137.6 (Ar–C_q), 133.8 (d, $^3J_{(C–F)}$ = 4.0 Hz, Ar–C_q), 129.3 (2 × Ar–C), 128.9 (2 × Ar–C), 128.7 (2 × Ar–C), 128.6 (2 × Ar–C), 128.4 (2 × Ar–C), 127.5 (2 × Ar–C), 126.8 (Ar–C), 96.6 (d, $^1J_{(C-F)}$ = 182.2 Hz, CHF), 78.8 (d, $^2J_{(C-F)}$ = 21.1 Hz, C_qOHCHF), 35.7 (d, $^2J_{(C-F)}$ = 21.3 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -186.8 (ddd, $^2J_{(H-F)}$ = 47.0 Hz, $^3J_{(H-F)}$ = 41.9, 16.6 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{21}H_{16}Cl_2FO$ $[M-H]^-$ 373.0568; Found: 373.0546.



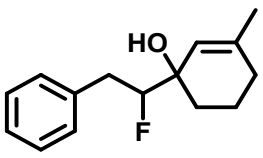
3ac; 2-fluoro-1,1-bis(4-fluorophenyl)-3-phenylpropan-1-ol

Prepared according to general procedure GP to afford **3ac** as a white waxy solid (195 mg, 95%) after column chromatography (R_f = 0.4, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3585, 3065, 2936, 1897, 1604, 1505, 1233, 835; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H, 2 × Ar–H), 7.41–7.38 (m, 2H, 2 × Ar–H), 7.30–7.22 (m, 3H, 3 × Ar–H), 7.13 (d, J = 7.3 Hz, 2H, 2 × Ar–H), 7.05–7.00 (m, 4H, 4 × Ar–H), 5.47 (ddd, $^2J_{(H–F)}$ = 47.1 Hz, $^3J_{(H–H)}$ = 9.9 , 1.8 Hz, 1H, C*H*FCH_2), 3.02–2.94 (m, 1H, PhC*H*HCHF), 2.72-2.60 (m, 2H, PhC*H*HCHF overlapping with O–H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, $^1J_{(C-F)}$ = 246.9 Hz, Ar–C_q), 162.1 (d, $^1J_{(C-F)}$ = 247.0 Hz, Ar–C_q), 140.0 (d, $^3J_{(C–F)}$ = 3.3 Hz, Ar–C_q), 138.9 (t, $^3J_{(C–F)}$ and $^4J_{(C–F)}$ = 3.5 Hz, Ar–C_q), 137.8 (Ar–C_q), 129.3 (2 × Ar–C), 128.2 (d, $^3J_{(C–F)}$ = 8.1 Hz, $^4J_{(C–F)}$ = 2.0 Hz, 2 × Ar–C), 128.6 (2 × Ar–C), 127.9 (d, $^3J_{(C–F)}$ = 8.1 Hz, 2 × Ar–C), 126.8 (Ar–C), 115.6 (d, $^2J_{(C-F)}$ = 21.4 Hz, 2 × Ar–C), 115.3 (d, $^2J_{(C-F)}$ = 21.3 Hz, 2 × Ar–C), 96.9 (d, $^1J_{(C-F)}$ = 182.1 Hz, CHF), 78.7 (d, $^2J_{(C-F)}$ = 21.1 Hz, C_qOHCHF), 35.7 (d, $^2J_{(C-F)}$ = 21.4 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.7–114.8 (m, 1F, Ar–F), 114.8–114.9 (m, 1F, Ar–F), -186.3 (ddd, $^2J_{(H-F)}$ = 47.1 Hz, $^3J_{(H-F)}$ = 41.9, 16.6 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{21}H_{16}F_3O$ $[M-H]^-$ 341.1159; Found: 341.1177.



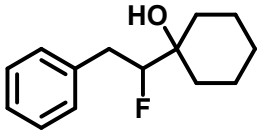
3ad; 1-(4-bromophenyl)-2-fluoro-1,3-diphenylpropan-1-ol

Prepared according to general procedure GP to afford **3ad** as a white waxy solid (dr = *50:50*, 212 mg, 92%) after column chromatography (R_f= 0.3, hexane/Et_2O 9:1); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3564, 3062, 2966, 1953, 1603, 1487, 1397, 1071; ^1H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.53–7.51 (m, 2H, 2 × Ar–H), 7.47–7.45 (m, 4H, 4 × Ar–H), 7.43–7.41 (m, 4H, 4 × Ar–H), 7.36–7.32 (m, 6H, 6 × Ar–H), 7.30–7.27 (m, 6H, 6 × Ar–H), 7.25–7.21 (m, 2H, 2 × Ar–H), 7.14 (d, J = 7.3 Hz, 4H, 4 × Ar–H), 5.58–5.45 (m , 2H, 2 × C*H*FCH_2), 3.08–2.94 (m, 2H, 2 × PhC*H*HCHF), 2.74–2.59 (m, 4H, 2 × PhC*H*HCHF overlapping with 2 × O–H); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 144.0 (Ar–C_q), 143.5 (Ar–C_q), 142.6 (d, $^3J_{(C–F)}$ = 3.9 Hz, Ar–C_q), 142.2 (d, $^3J_{(C–F)}$ = 4.2 Hz, Ar–C_q), 138.0 (Ar–C_q), 137.9 (Ar–C_q), 131.7 (2 × Ar–C), 131.5 (2 × Ar–C), 129.4 (4 × Ar–C), 128.9 (Ar–C), 128.8 (3 × Ar–C), 128.6 (4 × Ar–C), 127.8 (6 × Ar–C), 126.8 (2 × Ar–C), 126.7 (2 × Ar–C), 125.9 (2 × Ar–C), 121.7 (2 × Ar–C_q), 96.8 (d, $^1J_{(C-F)}$ = 181.7 Hz, CHF), 96.6 (d, $^1J_{(C-F)}$ = 182.0 Hz, CHF), 79.2 (d, $^2J_{(C-F)}$ = 21.1 Hz, C_qOHCHF), 79.1 (d, $^2J_{(C-F)}$ = 20.9 Hz, C_qOHCHF), 35.8 (d, $^2J_{(C-F)}$ = 21.2 Hz, Ph*C*H_2CHF), 35.7 (d, $^2J_{(C-F)}$ = 21.5 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -187.0 – -187.3 (m, 2F, 2 × CHF); HRMS (ESI) m/z Calcd for $C_{21}H_{17}BrFO$ $[M-H]^-$ 383.0452; Found: 383.0448.



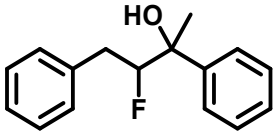
3ae; 1-(1-fluoro-2-phenylethyl)-3-methylcyclohex-2-en-1-ol

Prepared according to general procedure GP to afford **3ae** (dr = *80:20*) obtained as a white waxy solid (dr = *71:29*, 91 mg, 65%) after column chromatography (R_f = 0.5, hexane/Et_2O 7:3); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3583, 3418, 3029, 2931, 1947, 1670, 1454, 1063; ^1H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.32–7.30 (m, 2H *major* + 0.8H *minor*, Ar–H), 7.27–7.22 (m, 3H *major* + 1.2H *minor*, Ar–H), 5.50 (s, 0.4H, CH), 5.42 (s, 1H, CH), 5.47–5.43 (m , 1H *major* + 0.4H *minor*, C*H*FCH_2), 3.05–2.86 (m, 2H *major* + 0.8H *minor*, 2 × PhC*H*HCHF), 2.03–1.93 (m, 3H *major* + 1.2H *minor*, CH_2 overlapping with O–H), 1.82–1.71 (m, 7H *major* + 2.8H *minor*, 2 × CH_2 overlapping with CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 141.7 (d, $^4J_{(C–F)}$ = 1.2 Hz *Csp*^{2}CH3), 141.3 (d, $^4J_{(C–F)}$ = 1.6 Hz *Csp*^{2}CH_3), 138.4 (Ar–C_q), 138.3 (Ar–C_q), 129.4 (2 × Ar–C), 129.3 (2 × Ar–C), 128.6 (2 × Ar–C), 128.5 (2 × Ar–C), 126.6 (Ar–C), 126.5 (Ar–C), 122.5 (d, $^3J_{(C–F)}$ = 4.2 Hz *Csp*^{2}COH), 122.1 (d, $^3J_{(C–F)}$ = 6.4 Hz *Csp*^{2}COH), 99.9 (d, $^1J_{(C-F)}$ = 177.6 Hz, CHF), 98.5 (d, $^1J_{(C-F)}$ = 178.5 Hz, CHF), 71.9 (d, $^2J_{(C-F)}$ = 20.5 Hz, C_qOHCHF), 71.5 (d, $^2J_{(C-F)}$ = 19.5 Hz, C_qOHCHF), 36.2 (d, $^2J_{(C-F)}$ = 21.8 Hz, Ph*C*H_2CHF), 35.8 (d, $^2J_{(C-F)}$ = 21.7 Hz, Ph*C*H_2CHF), 31.3 (d, ^3J = 3.2 Hz, CH_2), 30.8 (d, ^3J = 3.2 Hz, CH_2), 30.5 (CH_2), 30.3 (CH_2), 24.1 (2 × CH_3), 18.9 (CH_2), 18.6 (CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ -190.4 – -190.6 (m, 1F *major*, CHF), -193.6 (ddd, $^2J_{(H-F)}$ = 47.9 Hz, $^3J_{(H-F)}$ = 40.5, 18.2 Hz, 0.4F *minor*, CHF); HRMS (ESI) m/z Calcd for $C_{15}H_{19}FNaO$ $[M+Na]^+$ 257.1312; Found: 257.1319.



3af; 1-(1-fluoro-2-phenylethyl)cyclohexan-1-ol

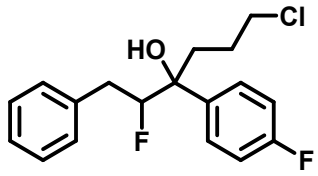
Prepared according to general procedure GP to afford **3af** as a colorless waxy solid (93 mg, 70%) after column chromatography (R_f = 0.3, hexane/EtOAc 9:1); IR (film)/cm^{-1} 3565, 3428, 3029, 2933, 1945, 1454, 1269, 975; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H, 2 × Ar–H), 7.26–7.22 (m, 3H, 3 × Ar–H), 4.42 (ddd, $^2J_{(H–F)}$ = 47.7 Hz, $^3J_{(H–H)}$ = 8.3 , 4.2 Hz, 1H, C*H*FCH_2), 3.00–2.89 (m, 2H, 2 × PhC*H*HCHF), 1.78–1.46 (m, 9H, 4 × CH_2 overlapping with O–H), 1.34–1.25 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (d, $^3J_{(C-F)}$ = 1.1 Hz, Ar–C_q), 129.4 (2 × Ar–C), 128.6 (2 × Ar–C), 126.6 (Ar–C), 99.8 (d, $^1J_{(C-F)}$ = 175.5 Hz, CHF), 72.6 (d, $^2J_{(C-F)}$ = 19.5 Hz, C_qOHCHF), 37.6 (CH_2), 35.5 (d, $^2J_{(C-F)}$ = 21.9 Hz, Ph*C*H_2CHF), 33.4 (d, $^3J_{(C-F)}$ = 4.1 Hz, CH_2), 32.7 (d, $^3J_{(C-F)}$ = 3.5 Hz, CH_2), 25.8 (2 × CH_2), 21.4 (2 × CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ -193.6– -193.8 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{14}H_{18}FO$ $[M-H]^-$ 221.1347; Found: 221.1351.



3ag; 3-fluoro-2,4-diphenylbutan-2-ol

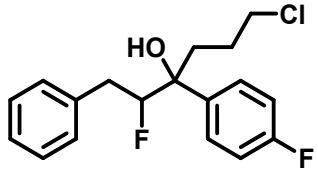
Prepared according to general procedure GP to afford **3ag** as a colorless waxy solid (dr = *50:50*, 110 mg, 75%) after column chromatography (R_f = 0.4, hexane/EtOAc 9:1); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3565, 3433, 3029, 2978, 1953, 1447, 1069, 699; ^1H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.54 (d, *J* = 7.4 Hz, 2H, 2 × Ar–H), 7.50–7.48 (m, 2H, 2 × Ar–H), 7.40 (t, *J* = 7.8 Hz, 4H, 4 × Ar–H), 7.34–7.31 (m, 2H, 2 × Ar–H), 7.27–7.17 (m, 6H, 6 × Ar–H overlapping with $CDCl_3$), 7.14 (d, *J* = 7.4 Hz, 2H, 2 × Ar–H), 7.09 (d, *J* = 7.3 Hz, 2H, 2 × Ar–H), 4.82–4.70 (m , 2H, 2 × C*H*FCH_2), 2.87–2.67 (m, 3H, 3 × PhC*H*HCHF), 2.55 (ddd, $^3J_{(H–F)}$ = 42.3 Hz, $^2J_{(H–H)}$ = 15.2 Hz $^3J_{(H–H)}$ = 1.5 Hz, 1H, PhC*H*HCHF), 2.33 (s, 1H,O–H), 2.20 (s, 1H, O–H), 1.69 (s, 6H, 2 × CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 143.6 (d, $^3J_{(C–F)}$ = 4.5 Hz, Ar–C_q), 143.4 (d, $^3J_{(C–F)}$ = 2.0 Hz, Ar–C_q), 138.3 (Ar–C_q), 137.9 (Ar–C_q), 129.2 (4 × Ar–C), 128.6 (4 × Ar–C), 128.5 (4 × Ar–C), 127.7 (Ar–C), 127.5 (Ar–C), 126.6 (Ar–C), 126.5 (Ar–C), 125.9 (2 × Ar–C), 125.1 (2 × Ar–C), 99.8 (d, $^1J_{(C-F)}$ = 180.2 Hz, CHF), 99.7 (d, $^1J_{(C-F)}$ = 180.4 Hz, CHF), 75.8 (d, $^2J_{(C-F)}$ = 20.6 Hz, 2 × C_qOHCHF), 36.4 (d, $^2J_{(C-F)}$ = 21.4 Hz, Ph*C*H_2CHF), 35.7 (d, $^2J_{(C-F)}$ = 21.6 Hz, Ph*C*H_2CHF), 27.4 (d, $^3J_{(C–F)}$ = 4.0 Hz, CH_3), 24.9 (d, $^3J_{(C–F)}$ = 3.4

Hz, CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -187.8 (ddd, $^2J_{(H-F)}$ = 48.0 Hz, $^3J_{(H-F)}$ = 41.7, 17.5 Hz, 1F, CHF), -191.7 (ddd, $^2J_{(H-F)}$ = 46.2 Hz, $^3J_{(H-F)}$ = 42.3, 17.0 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{16}H_{16}FO$ $[M-H]^-$ 243.1191; Found: 243.1186.



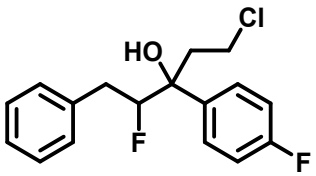
3ah-*major*; 6-chloro-2-fluoro-3-(4-fluorophenyl)-1-phenylhexan-3-ol

Prepared according to general procedure GP to afford **3ah-*major*** as a white waxy solid (105 mg, 90%) after column chromatography (R_f = 0.4, hexane/Et_2O 8:2); IR (film)/cm^{-1} 3430, 2919, 2850, 1645, 1510, 1225, 1094, 830; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H, 2 × Ar–H), 7.26 (t, *J* = 7.2 Hz, 2H, 2 × Ar–H, overlapping with $CDCl_3$), 7.22–7.19 (m, 1H, Ar–H), 7.12–7.08 (m, 2H, 2 × Ar–H), 7.06 (d, *J* = 7.2 Hz, 2H, 2 × Ar–H), 4.79 (ddd, $^2J_{(H–F)}$ = 47.6 Hz, $^3J_{(H–H)}$ = 10.0 , 2.0 Hz, 1H, C*H*FCH_2), 3.48 (t, $^3J_{(H–H)}$ = 6.5 Hz, 2H, CH_2Cl), 2.91 (ddd, $^3J_{(H–F)}$ = 17.3 Hz, $^2J_{(H–H)}$ = 15.2 Hz $^3J_{(H–H)}$ = 10.0 Hz, 1H, PhC*H*HCHF), 2.45 (ddd, $^3J_{(H–F)}$ = 41.3 Hz, $^2J_{(H–H)}$ = 15.2 Hz $^3J_{(H–H)}$ = 2.0 Hz, 1H, PhC*H*HCHF), 2.28–2.20 (m, 2H, C*H*HCOH overlapping with O–H), 2.11–2.05 (m, 1H, C*H*HCOH), 1.87–1.79 (m, 1H, C*H*HCH_2Cl), 1.49–1.41 (m, 1H, C*H*HCH_2Cl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, $^1J_{(C-F)}$ = 246.5 Hz, Ar–C_q), 137.8 (Ar–C_q), 136.4 (dd, $^3J_{(C–F)}$ = 4.8 Hz, $^4J_{(C–F)}$ = 3.3 Hz, Ar–C_q), 129.2 (2 × Ar–C), 128.5 (2 × Ar–C), 127.3 (d, $^3J_{(C–F)}$ = 8.0 Hz, 2 × Ar–C), 126.6 (Ar–C), 115.7 (d, $^2J_{(C–F)}$ = 21.3 Hz, 2 × Ar–C), 99.8 (d, $^1J_{(C-F)}$ = 180.3 Hz, CHF), 77.8 (d, $^2J_{(C-F)}$ = 19.7 Hz, C_qOHCHF), 45.4 (CH_2Cl), 36.7 (d, $^3J_{(C-F)}$ = 3.4 Hz, *C*H_2COH), 35.5 (d, $^2J_{(C-F)}$ = 21.7 Hz, Ph*C*H_2CHF), 26.6 (*C*H_2CH_2Cl); ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.2 – -115.1 (m, 1F, Ar–F), -191.5 (ddd, $^2J_{(H-F)}$ = 47.6 Hz, $^3J_{(H-F)}$ = 41.3, 17.3 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{18}H_{19}Cl_2F_2$ $[M+Cl]^-$ 359.0787; Found: 359.0784.



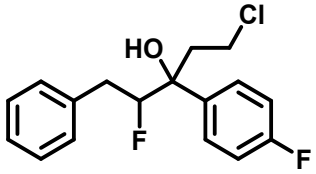
3ah-*minor*; 6-chloro-2-fluoro-3-(4-fluorophenyl)-1-phenylhexan-3-ol

Prepared according to general procedure GP to afford **3ah-*minor*** as a white waxy solid (70 mg, 90%) after column chromatography (R_f = 0.3, hexane/Et_2O 8:2); IR (film)/cm^{-1} 3434, 2918, 2850, 1645, 1506, 1455, 1226, 1063; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H, 2 × Ar–H), 7.29 (t, *J* = 7.3 Hz, 2H, 2 × Ar–H), 7.23 (t, *J* = 7.3 Hz, 1H, Ar–H), 7.15 (d, *J* = 7.4 Hz, 2H, 2 × Ar–H), 7.11–7.08 (m, 2H, 2 × Ar–H), 4.70 (ddd, $^2J_{(H–F)}$ = 47.7 Hz, $^3J_{(H–H)}$ = 10.0 , 2.2 Hz, 1H, C*H*FCH_2), 3.55–3.52 (m, 2H, CH_2Cl), 2.90 (ddd, $^3J_{(H–F)}$ = 41.4 Hz, $^2J_{(H–H)}$ = 14.8 Hz $^3J_{(H–H)}$ = 2.2 Hz, 1H, PhC*H*HCHF), 2.67 (ddd, $^3J_{(H–F)}$ = 16.8 Hz, $^2J_{(H–H)}$ = 14.8 Hz $^3J_{(H–H)}$ = 10.0 Hz, 1H, PhC*H*HCHF), 2.30–2.24 (m, 1H, C*H*HCOH) 2.22 (d, $^4J_{(H–F)}$ = 1.1 Hz, 1H, O–H), 2.08–2.02 (m, 1H, C*H*HCOH), 1.92–1.84 (m, 1H, C*H*HCH_2Cl), 1.63–1.54 (m, 1H, C*H*HCH_2Cl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{(C-F)}$ = 246.4 Hz, Ar–C_q), 137.6 (d, $^4J_{(C-F)}$ = 0.6 Hz, Ar–C_q), 136.9 (d, $^3J_{(C–F)}$ = 3.2 Hz, Ar–C_q), 129.3 (2 × Ar–C), 128.6 (2 × Ar–C), 128.1 (dd, $^3J_{(C–F)}$ = 8.0 Hz, $^4J_{(C–F)}$ = 1.8 Hz, 2 × Ar–C), 126.8 (Ar–C), 115.4 (d, $^2J_{(C–F)}$ = 21.3 Hz, 2 × Ar–C), 99.3 (d, $^1J_{(C-F)}$ = 181.0 Hz, CHF), 77.5 (d, $^2J_{(C-F)}$ = 20.4 Hz, C_qOHCHF overlapping with $CDCl_3$), 45.4 (CH_2Cl), 36.1 (d, $^2J_{(C-F)}$ = 21.4 Hz, Ph*C*H_2CHF), 34.8 (d, $^3J_{(C-F)}$ = 2.8 Hz, *C*H_2COH), 26.5 (*C*H_2CH_2Cl); ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.3 (tt, $^3J_{(H–F)}$ = 8.7 Hz, $^4J_{(H–F)}$ = 5.4, 1F, Ar–F), -186.8(ddd, $^2J_{(H-F)}$ = 47.7 Hz, $^3J_{(H-F)}$ = 41.4, 16.8 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{18}H_{19}Cl_2F_2$ $[M+Cl]^-$ 359.0787; Found: 359.0787.



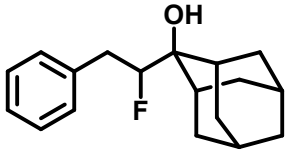
3ai-*major*; 5-chloro-2-fluoro-3-(4-fluorophenyl)-1-phenylpentan-3-ol

Prepared according to general procedure GP to afford **3ai-*major*** as a yellow waxy solid (100 mg, 90%) after column chromatography (R_f = 0.5, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3564, 3065, 2964, 1899, 1513, 1228, 1010, 835; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H, 2 × Ar–H), 7.26–7.23 (m, 2H, 2 × Ar–H), 7.21–7.18 (m, 1H, Ar–H), 7.13–7.08 (m, 2H, 2 × Ar–H), 7.04 (d, J = 7.3 Hz, 2H, 2×Ar–H), 4.76 (ddd, $^2J_{(H–F)}$ = 47.5 Hz, $^3J_{(H–H)}$ = 9.9 , 2.1 Hz, 1H, C*H*FCH_2), 3.52 (dt, ^2J = 10.5 Hz, ^3J = 5.9 Hz, 1H, C*H*HCl), 3.19 (dt, ^2J = 10.5 Hz, ^3J = 5.2 Hz, 1H, C*H*HCl), 2.89 (ddd, $^3J_{(H–F)}$ = 17.4 Hz, $^2J_{(H–H)}$ = 15.2 Hz $^3J_{(H–H)}$ = 9.9 Hz, 1H, PhC*H*HCHF), 2.66–2.59 (m, 1H, C*H*HCH_2Cl), 2.49–2.37 (m, 3H, PhC*H*HCHF overlapping with O–H and C*H*HCH_2Cl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{(C-F)}$ = 247.1 Hz, Ar–C_q), 137.5 (d, $^3J_{(C–F)}$ = 0.5 Hz, Ar–C_q), 135.6 (dd, $^3J_{(C–F)}$ = 4.8 Hz, $^4J_{(C–F)}$ = 3.3 Hz, Ar–C_q), 129.2 (2 × Ar–C), 128.6 (2 × Ar–C), 127.2 (d, $^3J_{(C–F)}$ = 8.0 Hz, 2 × Ar–C), 126.7 (Ar–C), 115.9 (d, $^2J_{(C–F)}$ = 21.4 Hz, 2 × Ar–C), 99.4 (d, $^1J_{(C-F)}$ = 181.2 Hz, CHF), 77.6 (d, $^2J_{(C-F)}$ = 19.8 Hz, C_qOHCHF), 42.4 (d, $^3J_{(C-F)}$ = 3.7 Hz, *C*H_2CH_2Cl), 39.7 (CH_2Cl), 35.2 (d, $^2J_{(C-F)}$ = 21.7 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.5 (tt, $^3J_{(H–F)}$ = 8.6 Hz, $^4J_{(H–F)}$ = 5.4, 1F, Ar–F), -191.3 (ddd, $^2J_{(H-F)}$ = 47.4 Hz, $^3J_{(H-F)}$ = 41.2, 17.4 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{17}H_{16}ClF_2O$ $[M-H]^-$ 309.0863; Found: 309.0861.



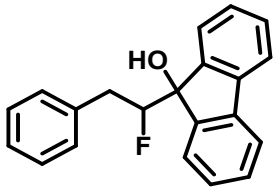
3ai-*minor*; 5-chloro-2-fluoro-3-(4-fluorophenyl)-1-phenylpentan-3-ol

Prepared according to general procedure GP to afford **3ai-*minor*** as a yellow waxy solid (67 mg, 90%) after column chromatography (R_f = 0.4, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3564, 3087, 2966, 1898, 1604, 1228, 1067, 837; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H, 2 × Ar–H), 7.30–7.27 (m, 2H, 2 × Ar–H), 7.25–7.21 (m, 1H, Ar–H), 7.15–7.09 (m, 4H, 4 × Ar–H), 4.69 (ddd, $^2J_{(H–F)}$ = 47.8 Hz, $^3J_{(H–H)}$ = 10.0 , 2.1 Hz, 1H, C*H*FCH_2), 3.57 (ddd, ^2J = 11.0 Hz, ^3J = 8.5 , 6.9 Hz, 1H, C*H*HCl), 3.42 (ddd, ^2J = 11.0 Hz, ^3J = 8.7, 5.4 Hz, 1H, C*H*HCl), 2.89 (ddd, $^3J_{(H–F)}$ = 41.9 Hz, $^2J_{(H–H)}$ = 14.9 Hz $^3J_{(H–H)}$ = 2.1 Hz, 1H, PhC*H*HCHF), 2.71 (s, 1H, O–H), 2.66–2.60 (m, 1H, C*H*HCH_2Cl), 2.58–2.51 (m, 1H, PhC*H*HCHF), 2.46–2.40 (m, 1H, C*H*HCH_2Cl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, $^1J_{(C-F)}$ = 246.9 Hz, Ar–C_q), 137.4 (d, $^3J_{(C–F)}$ = 0.7 Hz, Ar–C_q), 135.9 (d, $^3J_{(C–F)}$ = 3.1 Hz, Ar–C_q), 129.3 (2 × Ar–C), 128.7 (2 × Ar–C), 128.1 (2 × d, $^3J_{(C–F)}$ = 8.0 Hz, 2× Ar–C), 126.8 (Ar–C), 115.5 (d, $^2J_{(C–F)}$ = 21.3 Hz, 2 × Ar–C), 98.9 (d, $^1J_{(C-F)}$ = 181.8 Hz, CHF), 77.5 (d, $^2J_{(C-F)}$ = 21.3 Hz, C_qOHCHF), 40.3 (d, $^3J_{(C-F)}$ = 3.2 Hz, *C*H_2CH_2Cl), 40.2 (CH_2Cl), 35.9 (d, $^2J_{(C-F)}$ = 21.1 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.8 – -114.7 (m, 1F, Ar–F), -186.7 (ddd, $^2J_{(H-F)}$ = 47.8 Hz, $^3J_{(H-F)}$ = 41.9, 17.0 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{17}H_{16}ClF_2O$ $[M-H]^-$ 309.0863; Found: 309.0898.



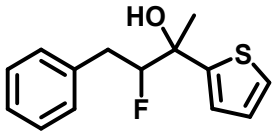
3aj; 2-(1-fluoro-2-phenylethyl)adamantan-2-ol

Prepared according to general procedure GP to afford **3aj** as a white waxy solid (98 mg, 60%) after column chromatography (R_f = 0.6, hexane/EtOAc 9:1); IR (film)/cm^{-1} 3435, 3065, 2916, 2860, 1638, 1455, 1331, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H, 2 × Ar–H), 7.27–7.23 (m, 3H, 2 × Ar–H overlapping with $CDCl_3$), 5.19 (ddd, $^2J_{(H–F)}$ = 47.6 Hz, $^3J_{(H–H)}$ = 10.3 , 2.1 Hz, 1H, C*H*FCH$_2$), 3.07 (td, $^2J_{(H–H)}$ = 15.0 Hz $^3J_{(H–H)}$ = 10.3 Hz, 1H, PhC*H*HCHF), 2.86 (ddd, $^3J_{(H–F)}$ = 42.9 Hz, $^2J_{(H–H)}$ = 14.9, 2.1 Hz, 1H, PhC*H*HCHF), 2.30 (d, *J* = 12.4 Hz, 1H, CH), 2.24 (d, *J* = 12.4 Hz, 1H, CH), 2.06 (s, 1H, CH), 1.94 (s, 2H, CH overlapping with O–H) 1.88–1.85 (m, 2H, 2 × CH), 1.79–1.70 (m, 6H, 3 × CH$_2$), 1.63–1.56 (m, 2H, CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (d, $^3J_{(C–F)}$ = 0.9 Hz, Ar–C$_q$), 129.5 (2 × Ar–C), 128.6 (2 × Ar–C), 126.6 (Ar–C), 95.5 (d, $^1J_{(C-F)}$ = 171.5 Hz, CHF), 75.8 (d, $^2J_{(C-F)}$ = 18.6 Hz, *C*OHCHF), 38.2 (CH$_2$), 34.6 (d, $^2J_{(C-F)}$ = 21.7 Hz, PhCH$_2$CHF), 34.2 (CH$_2$), 33.7 (CH$_2$), 33.6 (d, $^3J_{(C-F)}$ = 4.8 Hz, *C*HCOH), 32.9 (d, $^3J_{(C-F)}$ = 1.5 Hz, *C*HCOH), 32.7 (CH$_2$), 27.2 (CH), 27.1 (CH); ^{19}F NMR (470 MHz, $CDCl_3$) δ -201.2 – -201.0 (m, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{18}H_{23}FNaO$ [M+Na]$^+$ 297.1625; Found: 297.1634.



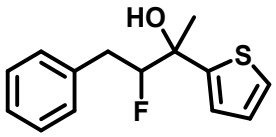
3al; 9-(1-fluoro-2-phenylethyl)-9*H*-fluoren-9-ol

Prepared according to general procedure GP to afford **3al** as a white waxy solid (116 mg, 64%) after column chromatography (R_f = 0.3, hexane/Et$_2$O 8:2); IR (film)/cm^{-1} 3524, 3392, 3063, 2924, 2852, 1607, 1451, 1064; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.67 (m, 2H, 2 × Ar–H), 7.52 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.46–7.41 (m, 2H, 2 × Ar–H), 7.40–7.31 (m, 3H, 3 × Ar–H), 7.22–7.19 (m, 2H, 2 × Ar–H), 7.17–7.14 (m, 1H, 1 × Ar–H), 6.99 (d, *J* = 7.2 Hz, 2H, 2 × Ar–H), 5.20 (ddd, $^2J_{(H–F)}$ = 48.9 Hz, $^3J_{(H–H)}$ = 9.8, 2.2 Hz, 1H, C*H*FCH$_2$), 2.88 (s, 1H, O–H), 2.44 (ddd, $^3J_{(H–F)}$ = 17.6 Hz, $^2J_{(H–H)}$ = 15.0 Hz, $^3J_{(H–H)}$ = 9.8 Hz, 1H, PhC*H*HCHF), 2.31 (ddd, $^3J_{(H–F)}$ = 40.1 Hz, $^2J_{(H–H)}$ = 15.0, $^3J_{(H–H)}$ = 2.2 Hz, 1H, PhC*H*HCHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9 (Ar–C$_q$), 144.8 (d, $^3J_{(C–F)}$ = 5.5 Hz, Ar–C$_q$), 140.6 (d, $^3J_{(C–F)}$ = 2.8 Hz, 2 × Ar–C$_q$), 137.5 (Ar–C$_q$), 130.1 (Ar–C), 129.7 (Ar–C), 129.1 (2 × Ar–C), 128.5 (2 × Ar–C), 128.4 (2 × Ar–C), 126.6 (Ar–C), 125.5 (d, $^4J_{(C–F)}$ = 3.2 Hz, Ar–C), 124.2 (Ar–C), 120.5 (Ar–C), 120.4 (Ar–C), 98.9 (d, $^1J_{(C-F)}$ = 182.5 Hz, CHF), 83.5 (d, $^2J_{(C-F)}$ = 19.3 Hz, C_qOHCHF), 36.3 (d, $^2J_{(C-F)}$ = 21.1 Hz, PhCH$_2$CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -191.1 (ddd, $^2J_{(H-F)}$ = 48.9 Hz, $^3J_{(H-F)}$ = 40.1, 17.6 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{21}H_{17}FNaO$ [M+Na]$^+$ 327.1161; Found: 327.1159.



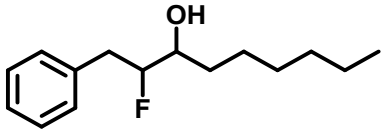
3am-A; 3-fluoro-4-phenyl-2-(thiophen-2-yl)butan-2-ol

Prepared according to general procedure GP to afford **3am-A** as a yellow waxy solid (66 mg, 89%) after column chromatography (R_f = 0.45, hexane/Et$_2$O 8:2); IR (film)/cm^{-1} 3583, 3026, 2924, 1496, 1454, 1237, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.26 (m, 3H, 3 × Ar–H overlapping with $CDCl_3$), 7.23–7.20 (m, 1H, Ar–H), 7.17 (d, *J* = 6.8 Hz, 2H, 2 × Ar–H), 7.04–7.01 (m, 2H, 2 × Ar–H), 4.71 (ddd, $^2J_{(H–F)}$ = 47.7 Hz, $^3J_{(H–H)}$ = 10.1 , 2.0 Hz, 1H, C*H*FCH$_2$), 2.99–2.91 (m, 1H, C*H*HCHF), 2.85–2.74 (m, 1H, C*H*HCHF), 2.42 (d, $^4J_{(H–F)}$ = 1.5 Hz, 1H, O–H), 1.75–1.74 (m, 3H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9 (d, $^3J_{(C-F)}$ = 4.2 Hz, Ar–C$_q$), 137.8 (Ar–C$_q$), 129.1 (2 × Ar–C), 128.4 (2 × Ar–C), 127.1 (Ar–C), 126.5 (Ar–C), 124.7 (Ar–C), 123.4 (Ar–C), 99.3 (d, $^1J_{(C-F)}$ = 182.2 Hz, CHF), 75.2 (d, $^2J_{(C-F)}$ = 21.7 Hz, C_qOHCHF), 35.8 (d, $^2J_{(C-F)}$ = 21.5 Hz, PhCH$_2$CHF), 27.3 (d, $^3J_{(C-F)}$ = 3.4 Hz, CH$_3$); ^{19}F NMR (470 MHz, $CDCl_3$) -188.3 (ddd, $^2J_{(H-F)}$ = 47.7 Hz, $^3J_{(H-F)}$ = 42.3, 17.4 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{14}H_{14}FOS$ [M-H]$^-$ 249.0755; Found: 249.0750.



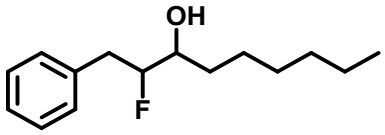
3am-B; 3-fluoro-4-phenyl-2-(thiophen-2-yl)butan-2-ol

Prepared according to general procedure GP to afford **3am-B** as a yellow waxy solid (66 mg, 89%) after column chromatography (R_f = 0.4, hexane/Et_2O 8:2); IR (film)/cm^{-1} 3419, 3030, 2917, 2849, 1604, 1455, 1265, 851; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 3H, 3 × Ar–H), 7.24–7.21 (m, 1H, Ar–H), 7.17 (d, J = 7.3 Hz, 2H, 2 × Ar–H), 7.07 (dd, ^3J = 3.5 Hz ^4J = 0.9 Hz, 1H, Ar–H), 7.03 (dd, ^3J = 5.0 , 3.5 Hz, 1H, Ar–H), 4.74 (ddd, $^2J_{(H–F)}$ = 48.3 Hz, $^3J_{(H–H)}$ = 10.0 , 2.0 Hz, 1H, C*H*FCH$_2$), 2.94–2.72 (m, 2H, 2 × C*H*HCHF), 2.58 (d, $^4J_{(H–F)}$ = 1.5 Hz, 1H, O–H), 1.75 (d, $^4J_{(H–F)}$ = 1.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (d, $^3J_{(C-F)}$ = 2.4 Hz, Ar–C_q), 137.7 (Ar–C_q), 129.3 (2 × Ar–C), 128.6 (2 × Ar–C), 127.1 (Ar–C), 126.7 (Ar–C), 125.3 (Ar–C), 124.4 (d, $^4J_{(C-F)}$ = 1.4 Hz, Ar–C), 99.7 (d, $^1J_{(C-F)}$ = 181.4 Hz, CHF), 75.1 (d, $^2J_{(C-F)}$ = 22.1 Hz, C_qOHCHF), 36.5 (d, $^2J_{(C-F)}$ = 21.2 Hz, Ph*C*H$_2$CHF), 25.2 (d, $^3J_{(C-F)}$ = 3.0 Hz, CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) -187.2 (ddd, $^2J_{(H-F)}$ = 48.3 Hz, $^3J_{(H-F)}$ = 41.3, 17.8 Hz, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{14}H_{15}FNaOS$ $[M+Na]^+$ 273.0725; Found: 273.0723.



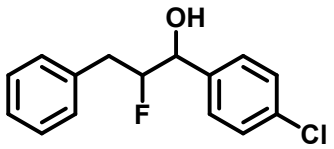
3an-A; 2-fluoro-1-phenylnonan-3-ol

Prepared according to general procedure GP to afford **3an-A** as (47 mg, 66%) after column chromatography (R_f= 0.3, hexane/EtOAc 95:5); IR (film)/cm^{-1} 3400, 3064, 2928, 2857, 1605, 1455, 1060, 699; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H, 2 × Ar–H), 7.26–7.23 (m, 3H, 2 × Ar–H overlapping with $CDCl_3$), 4.55 (dddd, $^2J_{(H–F)}$ = 47.8 Hz, $^3J_{(H–H)}$ = 7.9 , 5.3 , 3.8 Hz, 1H, C*H*FCH$_2$), 3.61–3.52 (m, 1H, CHOH), 3.09–2.95 (m, 2H, 2 × PhC*H*HCHF), 1.77 (d, $^3J_{(H–H)}$ = 6.5 Hz, 1H, O–H) 1.58–1.46 (m, 4H, 2 × CH_2), 1.37–1.26 (m, 6H, 3 × CH_2) 0.88 (t, $^3J_{(H–H)}$ = 6.9 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1 (d, $^3J_{(C–F)}$ = 5.2 Hz, Ar–C_q), 129.5 (2 × Ar–C), 128.7 (2 × Ar–C), 126.8 (Ar–C), 96.4 (d, $^1J_{(C-F)}$ = 173.9 Hz, CHF), 72.2 (d, $^2J_{(C-F)}$ = 19.5 Hz, *C*OHCHF), 37.8 (d, $^2J_{(C-F)}$ = 21.9 Hz, Ph*C*H$_2$CHF), 33.3 (d, $^3J_{(C-F)}$ = 4.0 Hz, *C*H$_2$CHOH), 31.9 (CH_2), 29.4 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -195.0 – -194.7 (m, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{15}H_{23}FNaO$ $[M+Na]^+$ 261.1631; Found: 261.1623.



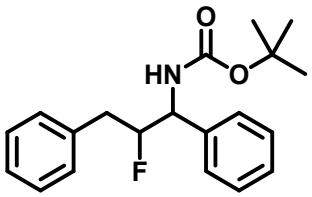
3an-B; 2-fluoro-1-phenylnonan-3-ol

Prepared according to general procedure GP to afford **3an-B** as (47 mg, 66%) after column chromatography (R_f= 0.2, hexane/Et_2O 95:5); IR (film)/cm^{-1} 3584, 3402, 3065, 2926, 2857, 1497, 1455, 1061, 699; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H, 2 × Ar–H), 7.26–7.23 (m, 3H, 2 × Ar–H overlapping with $CDCl_3$), 4.66–4.53 (m, 1H, C*H*FCH$_2$), 3.80–3.76 (m, 1H, CHOH), 3.07–2.88 (m, 2H, 2 × PhC*H*HCHF), 1.78 (d, $^3J_{(H–H)}$ = 5.1 Hz, 1H, O–H) 1.62–1.47 (m, 4H, 2 × CH_2), 1.34–1.30 (m, 6H, 3 × CH_2) 0.88 (t, $^3J_{(H–H)}$ = 6.9 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5 (d, $^3J_{(C–F)}$ = 2.2 Hz, Ar–C_q), 129.4 (2 × Ar–C), 128.6 (2 × Ar–C), 126.7 (Ar–C), 96.8 (d, $^1J_{(C-F)}$ = 173.1 Hz, CHF), 72.8 (d, $^2J_{(C-F)}$ = 22.1 Hz, *C*OHCHF), 36.4 (d, $^2J_{(C-F)}$ = 21.3 Hz, Ph*C*H$_2$CHF), 32.1 (d, $^3J_{(C-F)}$ = 5.2 Hz, *C*H$_2$CHOH), 31.9 (CH_2), 29.4 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -188.5 – -188.2 (m, 1F, CHF) ; HRMS (ESI) m/z Calcd for $C_{15}H_{23}FNaO$ $[M+Na]^+$ 261.1631; Found: 261.1613.



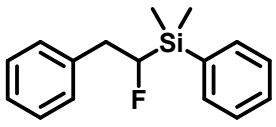
3ap; 1-(4-chlorophenyl)-2-fluoro-3-phenylpropan-1-ol

Prepared according to general procedure GP to afford **3ap** (dr = *50:50*, 119 mg, 75%) obtained as a white waxy solid after column chromatography (R_f = 0.3, hexane/Et_2O 9:1); *Inseparable mixture of diastereoisomers* dr = *77:23;* IR (film)/cm^{-1} 3396, 3031, 2922, 2850, 1600, 1493, 1455, 1090, 699; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.37–7.22 (m overlapping $CDCl_3$, 7H major + 2.1H *minor*, Ar–H), 7.18–7.16 (m, 2H *major* + 0.6H *minor*, Ar–H), 4.89–4.64 (m , 2H *major* + 0.6H *minor*, C*H*FCH_2 overlapping with C*H*OH), 2.99 (ddd, $^3J_{(H–F)}$ = 19.2 Hz, $^2J_{(H–H)}$ = 14.7 Hz $^3J_{(H–H)}$ = 8.7 Hz, 0.3H *minor*, PhC*H*HCHF), 2.90–2.77 (m, 2H *major* + 0.3H *minor*, PhC*H*HCHF), 2.53 (s, 1H *major*,O–H), 2.29 (s, 0.3H *minor*, O–H); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 137.9 (d, $^3J_{(C–F)}$ = 4.9 Hz, 2 × Ar–C_q), 136.6 (d, $^3J_{(C–F)}$ = 3.3 Hz, 2 × Ar–C_q), 134.5 (Ar–C_q), 134.2 (Ar–C_q), 129.5 (2 × Ar–C), 129.4 (2 × Ar–C), 129.0 (2 × Ar–C), 128.9 (2 × Ar–C), 128.7 (2 × Ar–C), 128.6 (4 × Ar–C), 128.2 (2 × Ar–C), 127.0 (Ar–C), 126.8 (Ar–C), 97.0 (d, $^1J_{(C-F)}$ = 177.8 Hz, CHF), 96.5 (d, $^1J_{(C-F)}$ = 177.0 Hz, CHF), 74.8 (d, $^2J_{(C-F)}$ = 20.8 Hz, *C*OHCHF), 74.3 (d, $^2J_{(C-F)}$ = 23.5 Hz, *C*OHCHF), 37.4 (d, $^2J_{(C-F)}$ = 21.1 Hz, Ph*C*H_2CHF), 36.1 (d, $^2J_{(C-F)}$ = 21.1 Hz, Ph*C*H_2CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -188.0 – -187.8 (m, 0.3F *minor*, CHF), -189.7 – -189.5 (m, 1F *major*, CHF); HRMS (ESI) m/z Calcd for $C_{15}H_{12}ClO$ [(M-HF)-H]$^-$ 243.0582; Found: 243.0369.



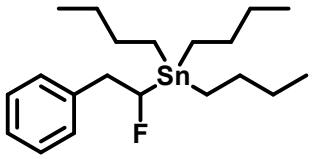
3aq; *tert*-butyl (2-fluoro-1,3-diphenylpropyl)carbamate

Prepared according to general procedure GP to afford **3aq (**dr = *60:40*) otained as a yellow oil (dr = *75:25* 128 mg, 65%) after column chromatography (R_f = 0.2, hexane/EtOAc/Net_3 9:1:0.1); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3433, 3031, 2918, 2850, 1704, 1495, 1366, 1166, 876; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.40–7.22 (m overlapping with $CDCl_3$, 8H *major* + 3H *minor*, Ar–H), 7.14 (d, *J* = 7.3 Hz, 2H, 2 × Ar–H), 5.34 (broad s, 1H *major* + 0.3H *minor*, 2 × N–H), 5.09–4.59 (m , 2H *major* + 0.6H *minor*, 2 × C*H*FCH_2 overlapping with 2 × C*H*NH), 3.13–2.94 (m, 0.6H *minor*, 2 × PhC*H*HCHF), 2.76–2.67 (m, 2H *major*, 2 × PhC*H*HCHF), 1.46 (s, 1.8H *minor*, 3 × CH_3), 1.41 (s, 9H *major*, 3 × CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 155.6 (CO_2N), 155.1 (CO_2N), 136.7 (d, $^3J_{(C–F)}$ = 2.4 Hz, 2 × Ar–C_q), 136.7 (d, $^3J_{(C–F)}$ = 3.6 Hz, 2 × Ar–C_q), 129.5 (2 × Ar–C), 129.3 (2 × Ar–C), 128.8 (2 × Ar–C), 128.7 (2 × Ar–C), 128.5 (2 × Ar–C), 128.6 (4 × Ar–C), 128.2 (Ar–C), 127.8 (Ar–C), 127.0 (2 × Ar–C), 126.9 (2 × Ar–C), 96.7 (d, $^1J_{(C-F)}$ = 173.2 Hz, CHF), 96.0 (d, $^1J_{(C-F)}$ = 181.5 Hz, CHF), 80.1 (2 × O*C*(CH_3)$_3$), 57.7 (d, $^2J_{(C-F)}$ = 19.1 Hz, 2 × *C*NHCHF), 38.9 (d, $^2J_{(C-F)}$ = 22.1 Hz, Ph*C*H_2CHF), 38.7 (d, $^2J_{(C-F)}$ = 20.5 Hz, Ph*C*H_2CHF), 29.8 (3 × CH_3), 28.5 (3 × CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -192.2 – -192.0 (m, 0.3F *minor*, CHF), -193.6 – -193.3 (m, 1F *major*, CHF); HRMS (ESI) m/z Calcd for $C_{20}H_{24}FNNaO_2$ $[M+Na]^+$ 352.1683; Found: 352.1689.



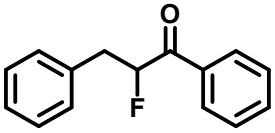
3ar; (1-fluoro-2-phenylethyl)dimethyl(phenyl)silane

Prepared according to general procedure GP, with slight modifications. The solution resulting from the microfluidic system was quenched with 150 µL of MeOH, filtered on Na_2SO_4 and concentrated under reduced pressure to afford **3ar** as a colorless oil (47 mg, 30%) after column chromatography (R_f= 0.1, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3068, 3028, 2958, 2925, 1953, 1604, 1251, 834; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.5 , 1.6 Hz, 2H, 2 × Ar–H), 7.42–7.39 (m, 3H, 3 × Ar–H), 7.28–7.25 (m, 2H, 2 × Ar–H overlapping with $CDCl_3$), 7.21–7.17 (m, 3H, 3 × Ar–H), 4.85 (ddd, $^2J_{(H–F)}$ = 46.1 Hz, $^3J_{(H–H)}$ = 10.8 , 3.6 Hz, 1H, C*H*FCH_2), 3.03 (ddd, $^3J_{(H–F)}$ = 17.9 Hz, $^2J_{(H–H)}$ = 15.0 Hz $^3J_{(H–H)}$ = 10.8 Hz, 1H, PhC*H*HCHF), 2.85 (ddd, $^3J_{(H–F)}$ = 41.8 Hz, $^2J_{(H–H)}$ = 15.0 Hz $^3J_{(H–H)}$ = 3.6 Hz, 1H, PhC*H*HCHF), 0.38 (s, 3H, $SiCH_3$), 0.36 (s, 3H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2 (d, $^3J_{(C-F)}$ = 3.8 Hz, Ar–C_q), 135.5 (d, $^3J_{(C-F)}$ = 3.0 Hz, Ar–C_q), 134.3 (2 × Ar–C), 129.8 (Ar–C), 129.1 (2 × Ar–C), 128.5 (2 × Ar–C), 128.1 (2 × Ar–C), 126.5 (Ar–C), 92.7 (d, $^1J_{(C-F)}$ = 167.2 Hz, CHF), 38.4 (d, $^2J_{(C-F)}$ = 19.7 Hz, Ph*C*H_2CHF), -5.3 (CH_3), -5.5 (CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -186.7 (ddd, $^2J_{(H-F)}$ = 46.1 Hz, $^3J_{(H-F)}$ = 41.8, 17.9 Hz, 1F, CHF); The product **3ar** decomposed during high-resolution mass (HRMS) analysis.



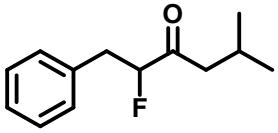
3as; tributyl(1-fluoro-2-phenylethyl)stannane

Prepared according to general procedure GP to afford **3as** as a colorless oil (156 mg, 63%) after column chromatography (R_f= 0.3, hexane); IR (film)/cm^{-1} 3584, 3064, 2956, 2924, 2852, 1495, 1455, 1075, 960; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H, 2 × Ar–H), 7.24–7.21 (m, 3H, 3 × Ar–H), 4.91 (ddd, $^2J_{(H–F)}$ = 46.1 Hz, $^3J_{(H–H)}$ = 8.9 , 5.8 Hz, 1H, C*H*FCH_2), 3.36–3.27 (m, 1H, PhC*H*HCHF), 3.13 (ddd, $^3J_{(H–F)}$ = 32.8 Hz, $^2J_{(H–H)}$ = 14.3 Hz $^3J_{(H–H)}$ = 5.8 Hz, 1H, PhC*H*HCHF), 1.48–1.41 (m, 6H, 3 × CH_2), 1.32–1.24 (m, 6H, 3 × CH_2), 0.90–0.83 (m, 15H, 3 × CH_3 overlapping with 3 × CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3 (d, $^3J_{(C–F)}$ = 6.7 Hz, Ar–C_q), 129.2 (2 × Ar–C), 128.6 (2 × Ar–C), 126.6 (Ar–C), 95.7 (d, $^1J_{(C-F)}$ = 189.4 Hz, CHF), 42.4 (d, $^2J_{(C-F)}$ = 18.5 Hz, Ph*C*H_2CHF), 29.1 (3 × CH_2), 27.5 (3 × CH_2), 29.1 (3 × CH_2), 13.8 (3 × CH_3), 9.1 (d, $^3J_{(C–F)}$ = 3.1 Hz, 3 × CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ -208.9(ddd, $^2J_{(H-F)}$ = 46.1 Hz, $^3J_{(H-F)}$ = 32.8, 21.6 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{20}H_{34}FSn$ $[M-H]^-$ 413.1672; Found: 413.1667.



3at; 2-fluoro-1,3-diphenylpropan-1-one

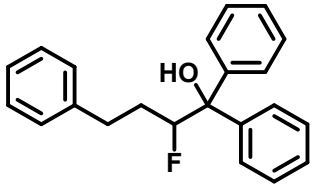
Prepared according to general procedure GP to afford **3at** as a white solid (97 mg, 71%) after column chromatography (R_f= 0.4, hexane/Et_2O 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H, 2 × Ar–H), 7.62–7.59 (m, 1H, Ar–H), 7.50–7.46 (m, 2H, 2 × Ar–H), 7.34–7.25 (m, 5H, 5 × Ar–H), 5.74 (ddd, $^2J_{(H–F)}$ = 49.0 Hz, $^3J_{(H–H)}$ = 8.3 , 4.0 Hz, 1H, C*H*FCH_2), 3.38-3.20 (m, 2H, 2 × PhC*H*HCHF); in according to spectral data reported in the literature. [9]



3au; 2-fluoro-5-methyl-1-phenylhexan-3-one

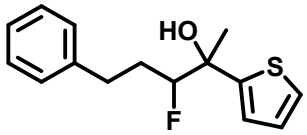
Prepared according to general procedure GP to afford **3au** as a white waxy solid (61 mg, 49%) after column chromatography (R_f= 0.3, hexane/EtOAc 8:2); IR (film)/cm^{-1} 3032, 2958, 2929, 2872, 1722, 1497, 1455, 1368,

1047; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.2 Hz, 2H, 2 × Ar–H), 7.27–7.26 (m, 1H, Ar–H overlapping with $CDCl_3$), 7.23 (d, J = 7.2 Hz, 2H, 2 × Ar–H), 4.91 (ddd, $^2J_{(H–F)}$ = 49.8 Hz, $^3J_{(H–H)}$ = 7.7 , 3.7 Hz, 1H, C*H*FCH$_2$), 3.18 (ddd, $^3J_{(H–F)}$ = 29.3 Hz, $^2J_{(H–H)}$ = 14.8 Hz $^3J_{(H–H)}$ = 3.7 Hz, 1H, PhC*H*HCHF), 3.03 (ddd, $^3J_{(H–F)}$ = 25.9 Hz, $^2J_{(H–H)}$ = 14.8 Hz $^3J_{(H–H)}$ = 7.7 Hz, 1H, PhC*H*HCHF), 2.46 (ddd, $^2J_{(H–H)}$ = 17.5 Hz, $^4J_{(H–F)}$ = 6.5 Hz $^3J_{(H–H)}$ = 3.7 Hz, 1H, C*H*HCO), 2.24 (ddd, $^2J_{(H–H)}$ = 17.5 Hz, $^4J_{(H–F)}$ = 7.0 Hz $^3J_{(H–H)}$ = 2.9 Hz, 1H, C*H*HCO), 2.16–2.08 (m, 1H, CH_2CH(CH$_3$)$_2$), 0.90 (d, ^3J = 6.7 Hz, 3H, CH$_3$), 0.85 (d, ^3J = 6.6 Hz, 3H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5 (d, $^2J_{(C–F)}$ = 24.4 Hz, CO), 135.6 (Ar–C$_q$), 129.7 (2 × Ar–C), 128.7 (2 × Ar–C), 127.2 (Ar–C), 96.1 (d, $^1J_{(C-F)}$ = 187.6 Hz, CHF), 47.5 (s, *C*H$_2$CO), 38.3 (d, $^2J_{(C-F)}$ = 20.5 Hz, Ph*C*H$_2$CHF), 23.5 (d, $^4J_{(C-F)}$ = 1.9 Hz, CH$_2$*C*H(CH$_3$)$_2$), 22.7 (CH$_3$), 22.6 (CH$_3$); ^{19}F NMR (470 MHz, $CDCl_3$) δ -190.3 – -190.1 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{13}H_{17}FNaO$ $[M+Na]^+$ 231.1156; Found: 231.1161.



3ba; 2-fluoro-1,1,4-triphenylbutan-1-ol

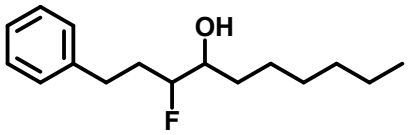
Prepared according to general procedure GP to afford **3ba** as a white waxy solid (182 mg, 95%) after column chromatography (R_f = 0.3, hexane/Et$_2$O 9:1); IR (film)/cm^{-1} 3400, 2917, 1599, 1493, 1447, 1168, 976, 748; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2H, 2 × Ar–H), 7.32 (t, J = 8.0 Hz, 4H, 4 × Ar–H), 7.28–7.23 (m, 5H, 5 × Ar–H, overlapping with $CDCl_3$), 7.22–7.17 (m, 2H, 2 × Ar–H), 7.10 (d, J = 7.2 Hz, 2H, 2 × Ar–H), 5.36 (ddd, $^2J_{(H–F)}$ = 47.2 Hz, $^3J_{(H–H)}$ = 10.1 , 2.0 Hz, 1H, C*H*FCH$_2$), 2.88–2.82 (m, 1H, PhC*H*HCH$_2$), 2.65–2.59 (m, 2H, PhC*H*HCH$_2$ overlapping with O–H), 2.17–2.05 (m, 1H, C*H*HCHF), 1.73–1.57 (m, 1H, C*H*HCHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8 (Ar–C$_q$), 143.1 (d, $^3J_{(C–F)}$ = 4.2 Hz, Ar–C$_q$), 141.3 (Ar–C$_q$), 128.6 (2 × Ar–C), 128.5 (4 × Ar–C), 128.4 (2 × Ar–C), 127.5 (Ar–C), 127.4 (Ar–C), 126.9 (d, $^4J_{(C–F)}$ = 1.7 Hz, 2 × Ar–C), 126.1 (Ar–C), 126.0 (2 × Ar–C), 95.3 (d, $^1J_{(C-F)}$ = 178.6 Hz, CHF), 79.2 (d, $^2J_{(C-F)}$ = 20.7 Hz, C_qOHCHF), 31.8 (d, $^3J_{(C-F)}$ = 3.5 Hz, Ph*C*H$_2$CH$_2$), 30.6 (d, $^2J_{(C-F)}$ = 21.3 Hz, CH$_2$*C*H$_2$CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -190.3 (ddd, $^2J_{(H-F)}$ = 47.4 Hz, $^3J_{(H-F)}$ = 40.1, 13.4 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{22}H_{21}FNaO$ $[M-H]^-$ 343.1469; Found: 343.1449.



3bm; 3-fluoro-5-phenyl-2-(thiophen-2-yl)pentan-2-ol

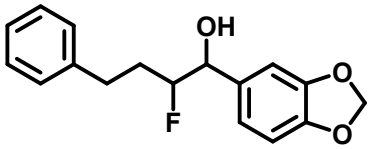
Prepared according to general procedure GP to afford **3bm** (dr = *60:40*) obtained as a waky solid (dr = *70:30*, 123 mg, 78%) after column chromatography (R_f = 0.3, hexane/Et$_2$O 85:15); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3435, 3027, 2918, 2849, 1496, 1455, 1237, 698; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.37–7.12 (m overlapping with $CDCl_3$, 6H *major* + 2.4H *minor*, Ar–H), 6.98–6.88 (m, 2H *major* + 0.8H *minor*, Ar–H), 4.61-4.43 (m, 1H *major* + 0.4H *minor*, C*H*FCH$_2$), 2.89–2.81 (m, 1H *major* + 0.4H *minor*, PhC*H*HCH$_2$), 2.66–2.58 (m, 1H *major* + 0.4H *minor*, PhC*H*HCH$_2$), 2.54 (d, $^4J_{(H–F)}$ = 1.9 Hz, 1H *major*, O–H), 2.36 (d, $^4J_{(H–F)}$ = 1.2 Hz, 0.4H *minor*, O–H), 2.01-1.97 (m, 1H *major* + 0.4H *minor*), 1.67 (d, $^4J_{(H–F)}$ = 2.0 Hz, 1.2H *minor*, CH$_3$), 1.66 (d, $^4J_{(H–F)}$ = 1.4 Hz, 3H *major*, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 148.0 (d, $^3J_{(C–F)}$ = 3.8 Hz, Ar–C$_q$), 147.9 (d, $^3J_{(C–F)}$ = 2.9 Hz, Ar–C$_q$), 141.3 (Ar–C$_q$), 141.2 (Ar–C$_q$), 128.6 (8 × Ar–C), 127.1 (Ar–C), 127.0 (Ar–C), 126.2 (Ar–C), 126.1 (Ar–C), 125.2 (Ar–C), 124.7 (Ar–C), 124.2 (d, $^4J_{(C–F)}$ = 1.2 Hz, Ar–C), 123.5 (d, $^4J_{(C–F)}$ = 0.7 Hz, Ar–C), 98.4 (d, $^1J_{(C-F)}$ = 178.5 Hz, CHF), 98.1 (d, $^1J_{(C-F)}$ = 179.2 Hz, CHF), 75.2 (d, $^2J_{(C-F)}$ = 21.4 Hz, C_qOHCHF), 75.1 (d, $^2J_{(C-F)}$ = 21.8 Hz, C_qOHCHF), 31.9 (d, $^3J_{(C-F)}$ = 2.8 Hz, Ph*C*H$_2$CH$_2$), 31.8 (d, $^3J_{(C-F)}$ = 3.2 Hz, Ph*C*H$_2$CH$_2$), 31.9 (d, $^2J_{(C-F)}$ = 21.1 Hz, CH$_2$*C*H$_2$CHF), 31.1 (d, $^2J_{(C-F)}$ = 21.3 Hz, CH$_2$*C*H$_2$CHF), 27.3 (d, $^3J_{(C–F)}$ = 3.6 Hz, CH$_3$), 24.9 (d, $^3J_{(C–F)}$ = 3.0 Hz, CH$_3$); ^{19}F NMR (470 MHz,

$CDCl_3$) δ -190.0 (ddd, $^2J_{(H-F)}$ = 48.5 Hz, $^3J_{(H-F)}$ = 39.0, 16.0 Hz, 1F *major*, CHF), -191.0 (ddd, $^2J_{(H-F)}$ = 47.9 Hz, $^3J_{(H-F)}$ = 40.9, 13.8 Hz, 0.4F *minor*, CHF); HRMS (ESI) m/z Calcd for $C_{15}H_{16}FOS$ $[M-H]^-$ 263.0911; Found: 263.0917; Calcd for $C_{15}H_{15}OS$ $[(M-HF)-H]^-$ 243.0849; Found: 243.0842 .



3bn; 3-fluoro-1-phenyldecan-4-ol

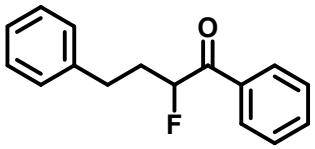
Prepared according to general procedure GP to afford **3bn** as a white waxy solid (dr = *60:40*, 75 mg, 50%) after column chromatography (R_f = 0.5, hexane/EtOAc 9:1); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3400, 3028, 2925, 2856, 1496, 1455, 1029, 699; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.30 (t, *J* = 7.4 Hz, 2H *major* + 1.2H *minor*, Ar–H), 7.22–7.19 (m, 3H *major* + 1.8H *minor*, Ar–H), 4.39 (dddd, $^2J_{(H-F)}$ = 48.0 Hz, $^3J_{(H-H)}$ = 10.1 , 3.8 , 2.6 Hz, 1H *major*, $CH_2CHFCHOH$, overlapping with *minor*'s $CH_2CHFCHOH$), 4.33 (dddd, $^2J_{(H-F)}$ = 48.6 Hz, $^3J_{(H-H)}$ = 9.3 , 4.6 , 3.4 Hz, 0,6H *minor*, $CH_2CHFCHOH$, overlapping with *major*'s $CH_2CHFCHOH$), 3.77–3.73 (m, 1H *major*, $CHOH$), 3.60–3.56 (m, 0.6H *minor*, $CHOH$), 2.93–2.82 (m, 1H *major* + 0.6H *minor*, $PhCHHCH_2$), 2.75–2.66 (m, 1H *major* + 0.6H *minor*, $PhCHHCH_2$), 2.11–2.02 (m, 1H *major* + 0.6H *minor,* $CH_2CHHCHF$), 1.92–1.79 (m, 1H *major* + 0.6H *minor*, $CH_2CHHCHF$), 1.72 (broad s, 1H *major*, O–H), 1.56 (broad s, 0.6H *minor*, O–H), 1.48–1.26 (m, 10H *major* + 6H *minor*, CH_2), 0.88 (t, *J* = 6.9 Hz, 3H *major* + 1.8H *minor*, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 141.5 (Ar–C_q), 141.4 (Ar–C_q), 128.6 (8 × Ar–C), 126.2 (2 × Ar–C), 95.8 (d, $^1J_{(C-F)}$ = 170.2 Hz, CHF), 95.7(d, $^1J_{(C-F)}$ = 170.1 Hz, CHF), 73.2 (d, $^2J_{(C-F)}$ = 19.5 Hz, *C*OHCHF), 73.1 (d, $^2J_{(C-F)}$ = 21.6 Hz, *C*OHCHF), 33.1 (d, $^2J_{(C-F)}$ = 21.2 Hz, CH_2CH_2CHF), 33.0 (d, $^3J_{(C-F)}$ = 9.5 Hz, CH_2CHOH), 31.9 (d $^3J_{(C-F)}$ = 6.3 Hz, CH_2CHOH, overlapping with CH_2), 31.5 (d, $^3J_{(C-F)}$ = 3.4 Hz, $PhCH_2CH_2$), 31.4 (d, $^3J_{(C-F)}$ = 4.4 Hz, $PhCH_2CH_2$), 31.3 (d, $^2J_{(C-F)}$ = 21.1 Hz, CH_2CH_2CHF), 29.9 (CH_2), 29.4 (2 × CH_2), 25.8 (CH_2), 25.5 (CH_2), 22.7 (2 × CH_2), 14.2 (2 × CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -192.1 (ddt, $^2J_{(H-F)}$ = 48.0 Hz, $^3J_{(H-F)}$ = 39.3, 14.8 Hz, 1F *major*, CHF), -196.7 – -196.5 (m, 0.6F *minor*, CHF); HRMS (ESI) m/z Calcd for $C_{16}H_{24}FO$ $[M-H]^-$ 251.1817; Found: 251.1815.



3bo; 1-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-4-phenylbutan-1-ol

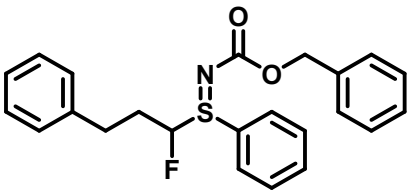
Prepared according to general procedure GP to afford **3bo** as a white waxy solid (dr = *50:50*, 103 mg, 60%) after column chromatography (R_f = 0.2, hexane/Et_2O 8:2); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3408, 3027, 2917, 1504, 1488, 1247, 1038, 930; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 7.28–7.24 (m, 4H, 4 × Ar–H), 7.19–7.10 (m, 6H, 6 × Ar–H), 6.88–6,82 (m, 2H, 2 × Ar–H), 6.78–6.77 (m, 4H, 4 × Ar–H), 5.96 (s, 2H, CH_2O_2), 5.95 (s, 2H, CH_2O_2), 4.79–4.43 (m, 4H, 2 × $CH_2CHFCHOH$ overlapping with 2 × $CHFCHOH$), 2.87–2.80 (m, 2H, 2 × $PhCHHCH_2$), 2.66–2.59 (m, 2H, 2 × $PhCHHCH_2$), 2.54 (t, *J* = 2.7 Hz, 1H, O–H), 2.17 (d, $^4J_{(H-F)}$ = 3.6 Hz, 1H, O–H), 2.04–1.60 (m, 4H, 4 × $CH_2CHHCHF$); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 148.1 (Ar–C_q), 148.0 (Ar–C_q), 147.9 (Ar–C_q), 147.5 (Ar–C_q), 133.2 (d, $^3J_{(C-F)}$ = 4.9 Hz, Ar–C_q), 132.9 (d, $^3J_{(C-F)}$ = 6.5 Hz, Ar–C_q), 128.6 (3 × Ar–C), 128.5 (Ar–C), 126.2 (2 × Ar–C), 120.9 (Ar–C), 120.3 (Ar–C), 119.5 (Ar–C), 108.5 (Ar–C), 108.3 (Ar–C), 108.2 (Ar–C), 107.5 (Ar–C), 107.3 (2 × Ar–C), 106.5 (Ar–C), 101.3 (2 × CH_2O_2) 96.6 (d, $^1J_{(C-F)}$ = 174.1 Hz, CHF), 95.6 (d, $^1J_{(C-F)}$ = 174.3 Hz, CHF), 76.4 (d, $^2J_{(C-F)}$ = 20.9 Hz, *C*OHCHF), 75.2 (d, $^2J_{(C-F)}$ = 22.6 Hz, *C*OHCHF), 32.9 (d, $^2J_{(C-F)}$ = 20.6 Hz, CH_2CH_2CHF), 31.5 (d, $^3J_{(C-F)}$ = 9.5 Hz, $PhCH_2CH_2$), 31.4 (d $^2J_{(C-F)}$ = 20.4 Hz, CH_2CH_2CHF), 31.3 (d, $^3J_{(C-F)}$ = 3.7 Hz, $PhCH_2CH_2$), 31.4 (d, $^3J_{(C-F)}$ = 4.4 Hz, $PhCH_2CH_2$), 31.3 (d, $^2J_{(C-F)}$ = 21.1 Hz, CH_2CH_2CHF), 29.9 (CH_2), 29.4 (2 × CH_2), 25.8 (CH_2), 25.5 (CH_2),

22.7 (2 × CH_2), 14.2 (2 × CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -191.2 (ddt, $^2J_{(H-F)}$ = 47.9 Hz, $^3J_{(H-F)}$ = 37.8, 14.4 Hz, 1F, CHF), -190.0 – -189.8 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{17}H_{17}FNaO_3$ $[M+Na]^+$ 311.1054; Found: 311.1057.



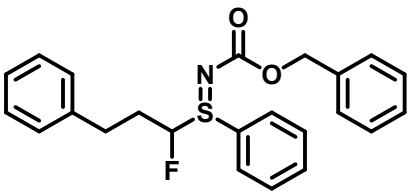
3bt; 2-fluoro-1,4-diphenylbutan-1-one

Prepared according to general procedure GP to afford **3bt** as a white waxy solid (87 mg, 60%) after column chromatography (R_f = 0.4, hexane/Et_2O 98:2); IR (film)/cm^{-1} 3029, 2959, 2930, 2863, 1640, 1580, 1496, 1449, 1249; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H, 2 × Ar–H), 7.60–7.57 (m, 1H, Ar–H), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × Ar–H), 7.32 (t, *J* = 7.5 Hz, 2H, 2 × Ar–H), 7.25–7.22 (m, 3H, 3 × Ar–H), 5.61–5.49 (m, 1H, CHF), 2.94–2.82 (m, 2H, PhC$H_2$$CH_2$), 2.32–2.22 (m, 2H, C$H_2$CHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7 (d, $^2J_{(C–F)}$ = 19.2 Hz, CO), 140.4 (Ar–C_q), 133.9 (Ar–C), 129.0 (d, $^3J_{(C–F)}$ = 3.6 Hz, Ar–C_q), 128.9 (2 × Ar–C), 128.8 (6 × Ar–C), 126.5 (Ar–C), 92.7 (d, $^1J_{(C-F)}$ = 183.4 Hz, CHF), 34.5 (d, $^2J_{(C-F)}$ = 21.4 Hz, CH_2*C*H_2CHF), 31.0 (d, $^3J_{(C-F)}$ = 3.2 Hz, Ph*C*$H_2$$CH_2$); ^{19}F NMR (470 MHz, $CDCl_3$) δ -191.5 – -191.3 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.0999; Found: 265.0995.



3bv-A; benzyl (1-fluoro-3-phenylpropyl)(phenyl)-l^4-sulfanylidene carbamate

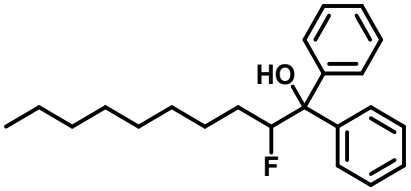
Prepared according to general procedure GP to afford **3bv-A** as yellow oil (35 mg, 30%) after column chromatography (R_f = 0.3, hexane/Et_2O 6:4); IR (film)/cm^{-1} 3063, 3030, 2918, 2850, 1738, 1644, 1454, 1254; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H, 2 × Ar–H), 7.63–7.60 (m, 1 H, Ar–H), 7.55 (t, *J* = 7.5 Hz, 2H, 2 × Ar–H), 7.38 (d, *J* = 7.1 Hz, 2H, 2 × Ar–H), 7.33–7.27 (m, 5H, 5 × Ar–H), 7.22 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.15 (d, *J* = 7.1 Hz, 2H, 2 × Ar–H), 5.28 (ddd, $^2J_{(H–F)}$ = 49.2 Hz, $^3J_{(H–H)}$ = 8.7 , 2.7 Hz, 1H, SC*H*FCH$_2$), 5.14 (d, $^2J_{(H–H)}$ = 12.4 Hz, 1H, PhC*H*HO), 5.11 (d, $^2J_{(H–H)}$ = 12.4 Hz, 1H, PhC*H*HO), 2.98–2.92 (m, 1H, PhC*H*HCH$_2$), 2.82–2.78 (m, 1H, PhC*H*HCH$_2$), 2.56–2.30 (m, 2H, 2 × C*H*HCHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (d, $^4J_{(C–F)}$ = 1.7 Hz, CO_2N), 139.2 (2 × Ar–C_q), 137.3 (Ar–C_q), 133.5 (Ar–C), 129.9 (2 × Ar–C), 128.8 (2 × Ar–C), 128.6 (2 × Ar–C), 128.4 (2 × Ar–C), 128.3 (2 × Ar–C), 128.0 (2 × Ar–C), 127.9 (Ar–C), 126.7 (Ar–C), 105.3 (d, $^1J_{(C-F)}$ = 226.2 Hz, SCHF), 68.1 (OCH_2Ph), 32.3 (d, $^2J_{(C-F)}$ = 18.7 Hz, CH_2*C*H_2CHF), 30.5 (d, $^3J_{(C-F)}$ = 2.5 Hz, Ph*C*$H_2$$CH_2$); ^{19}F NMR (470 MHz, $CDCl_3$) δ -177.0 – -176.8 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{23}H_{22}FNaO_2S$ $[M+Na]^+$ 418.1247; Found: 418.1262.



3bv-B; benzyl (1-fluoro-3-phenylpropyl)(phenyl)-l^4-sulfanylidene carbamate

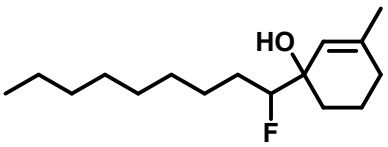
Prepared according to general procedure GP to afford **3bv-B** as a yellow oil (35 mg, 30%) after column chromatography (R_f = 0.2, hexane/Et_2O 6:4); IR (film)/cm^{-1} 3063, 2921, 2851, 1634, 1446, 1376, 1244, 1086; ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H, 2 × Ar–H), 7.61–7.58 (m, 1 H, Ar–H), 7.54 (t, *J* = 7.5 Hz, 2H, 2 × Ar–H), 7.40 (d, *J* = 7.2 Hz, 2H, 2 × Ar–H), 7.34–7.26 (m, 5H, 5 × Ar–H overlapping with $CDCl_3$), 7.21 (t, *J* = 7.2 Hz, 1H, Ar–H), 7.10 (d, *J* = 7.2 Hz, 2H, 2 × Ar–H), 5.38 (ddd, $^2J_{(H–F)}$ = 46.8 Hz, $^3J_{(H–H)}$ = 9.6 , 3.0 Hz, 1H, SC*H*FCH$_2$), 5.16 (d, $^2J_{(H–H)}$ = 12.5 Hz, 1H, PhC*H*HO), 5.13 (d, $^2J_{(H–H)}$ = 12.5 Hz, 1H, PhC*H*HO), 2.86–2.81 (m, 1H, PhC*H*HCH$_2$), 2.77–2.71 (m, 1H, PhC*H*HCH$_2$), 2.39–2.25 (m, 1H, C*H*HCHF), 1.99–1.89 (m, 1H, C*H*HCHF); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1 (CO_2N), 139.1 (2 × Ar–C_q), 137.4 (Ar–C_q), 133.0 (Ar–C), 129.9 (2 × Ar–C), 128.9 (2 × Ar–C), 128.6 (2 × Ar–C), 128.4 (4 × Ar–C), 128.0 (2 × Ar–C), 127.9 (Ar–C), 126.8 (Ar–C), 105.2 (d, $^1J_{(C-F)}$ = 230.6 Hz, SCHF), 68.2 (OCH$_2$Ph), 30.6 (d, $^3J_{(C-F)}$ = 3.0 Hz, Ph*C*H$_2$CH$_2$), 30.5 (d, $^2J_{(C-F)}$ = 19.2 Hz, CH$_2$*C*H$_2$CHF); ^{19}F NMR (470 MHz, $CDCl_3$) δ -179.0 – -178.8 (m, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{23}H_{22}FNaO_2S$ $[M+Na]^+$ 418.1247; Found: 418.1249.



3ca; 2-fluoro-1,1-diphenyldecan-1-ol

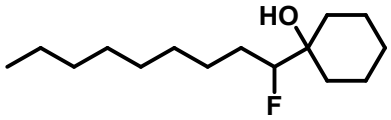
Prepared according to general procedure GP to afford **3ca** as a white waxy solid (191 mg, 97%) after column chromatography (R_f = 0.6, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3559, 3010, 2919, 2851, 1660, 1493, 1448, 1171; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H, 2 × Ar–H), 7.39–7.28 (m, 6H, 6 × Ar–H), 7.24–7.20 (m, 2H, 2 × Ar–H), 5.36 (ddd, $^2J_{(H–F)}$ = 47.0 Hz, $^3J_{(H–H)}$ = 10.0 , 1.7 Hz, 1H, C*H*FCH$_2$), 2.60 (d, $^4J_{(H–F)}$ = 2.1, 1H, O–H), 1.82–1.78 (m, 1H, C*H*HCHF), 1.52–1.46 (m, 1H, C*H*HCH$_2$CHF), 1.37–1.21 (m, 12H, 5 × CH$_2$ overlapping with C*H*HCHF and C*H*HCH$_2$CHF), 0.86 (t, *J* = 7.0 Hz, 3H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8 (Ar–C_q), 143.1 (d, $^3J_{(C–F)}$ = 4.1 Hz, Ar–C_q), 128.2 (4 × Ar–C), 127.2 (Ar–C), 127.1 (Ar–C), 126.7 (d, $^4J_{(C–F)}$ = 1.6 Hz, 2 × Ar–C), 125.8 (2 × Ar–C), 96.3 (d, $^1J_{(C-F)}$ = 177.9 Hz, CHF), 79.1 (d, $^2J_{(C-F)}$ = 21.0 Hz, *C*$_q$OHCHF), 31.8 (CH$_2$), 29.4 (CH$_2$), 29.3 (CH$_2$), 29.2 (CH$_2$), 28.8 (d, $^2J_{(C–F)}$ = 21.3 Hz, *C*H$_2$CHF), 25.7 (d, $^3J_{(C–F)}$ = 2.9 Hz, *C*H$_2$CH$_2$CHF), 22.6 (CH$_2$), 14.1 (CH$_3$); ^{19}F NMR (470 MHz, $CDCl_3$) δ -189.4 (ddd, $^2J_{(H-F)}$ = 47.0 Hz, $^3J_{(H-F)}$ = 42.7, 14.2 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{22}H_{28}FO$ $[M-H]^-$ 327.2130; Found: 327.2127.



3ce; 1-(1-fluorononyl)-3-methylcyclohex-2-en-1-ol

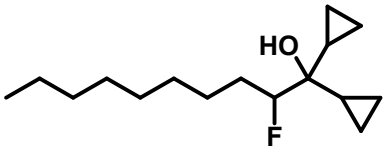
Prepared according to general procedure GP to afford **3ce** as a white waxy solid (dr = *70:30,* 104mg, 68%) after column chromatography (R_f = 0.3, hexane/Et_2O 8:2); *Inseparable mixture of diastereoisomers;* IR (film)/cm^{-1} 3400, 2924, 2855, 1671, 1454, 1377, 1169, 1070, 967; ^{1}H NMR (500 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 5.41 (s, 0.4H *minor*, Csp^2*H*COH), 5.34 (s, 1H *major*, Csp^2*H*COH), 4.35–4.21 (m, 1H *major* + 0.4H *minor*, C*H*FCH$_2$), 1.99–1.80 (m, 3H *major* + 1.2H *minor*, CH$_2$ overlapping OH), 1.80–1.28 (m, 19H *major* + 7.6H *minor*), 0.88 (t, *J* = 6.9 Hz, 3H *majo*r + 1.2H *minor*, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 141.1 (d, $^4J_{(C–F)}$ = 1.0 Hz, *Csp*^{2}CH$_3$), 140.8 (d, $^4J_{(C–F)}$ = 1.6 Hz, *Csp*^{2}CH$_3$), 122.6 (d, $^3J_{(C–F)}$ = 4.5 Hz, *Csp*^{2}COH), 122.4 (d, $^3J_{(C–F)}$ = 6.7 Hz, *Csp*^{2}COH), 99.9 (d, $^1J_{(C-F)}$ = 174.0 Hz, CHF), 98.6 (d, $^1J_{(C-F)}$ = 174.8 Hz, CHF), 71.9 (d, $^2J_{(C-F)}$ = 20.2 Hz, *C*$_q$OHCHF), 71.6 (d, $^2J_{(C-F)}$ = 19.6 Hz, *C*$_q$OHCHF), 32.0 (2 × CH$_2$), 31.4 (d, $^3J_{(C–F)}$ = 3.3 Hz, *C*H$_2$COH), 30.5 (d, $^3J_{(C–F)}$ = 3.3 Hz, *C*H$_2$COH), 30.5 (2 × CH$_2$), 30.3 (2 × CH$_2$), 29.7 (2 × CH$_2$), 29.6 (2 × CH$_2$), 29.3 (d, $^2J_{(C–F)}$ = 21.6 Hz, 2 × *C*H$_2$CHF), 26.1 (d, $^3J_{(C–F)}$ = 2.4 Hz, *C*H$_2$CH$_2$CHF), 26.0 (d, $^3J_{(C–F)}$ = 2.8 Hz, *C*H$_2$CH$_2$CHF), 24.1 (2 × *C*H$_3$Csp^2) 22.8 (2 × CH$_2$), 18.9 (2 × CH$_2$), 18.6 (2 × CH$_2$), 14.3 (2 × CH$_3$); ^{19}F NMR (470 MHz, $CDCl_3$, *mixture*

of diastereoisomers) δ -194.4 – -193.1 (m, 1F *major*, CHF), -196.2 (ddd, $^{2}J_{(H-F)}$ = 47.9 Hz, $^{3}J_{(H-F)}$ = 42.4, 15.2 Hz, 0.4F *minor*, CHF); HRMS (ESI) m/z Calcd for $C_{16}H_{29}FNaO$ $[M+Na]^{+}$ 279.2095; Found: 279.2106.



3cf; 1-(1-fluorononyl)cyclohexan-1-ol

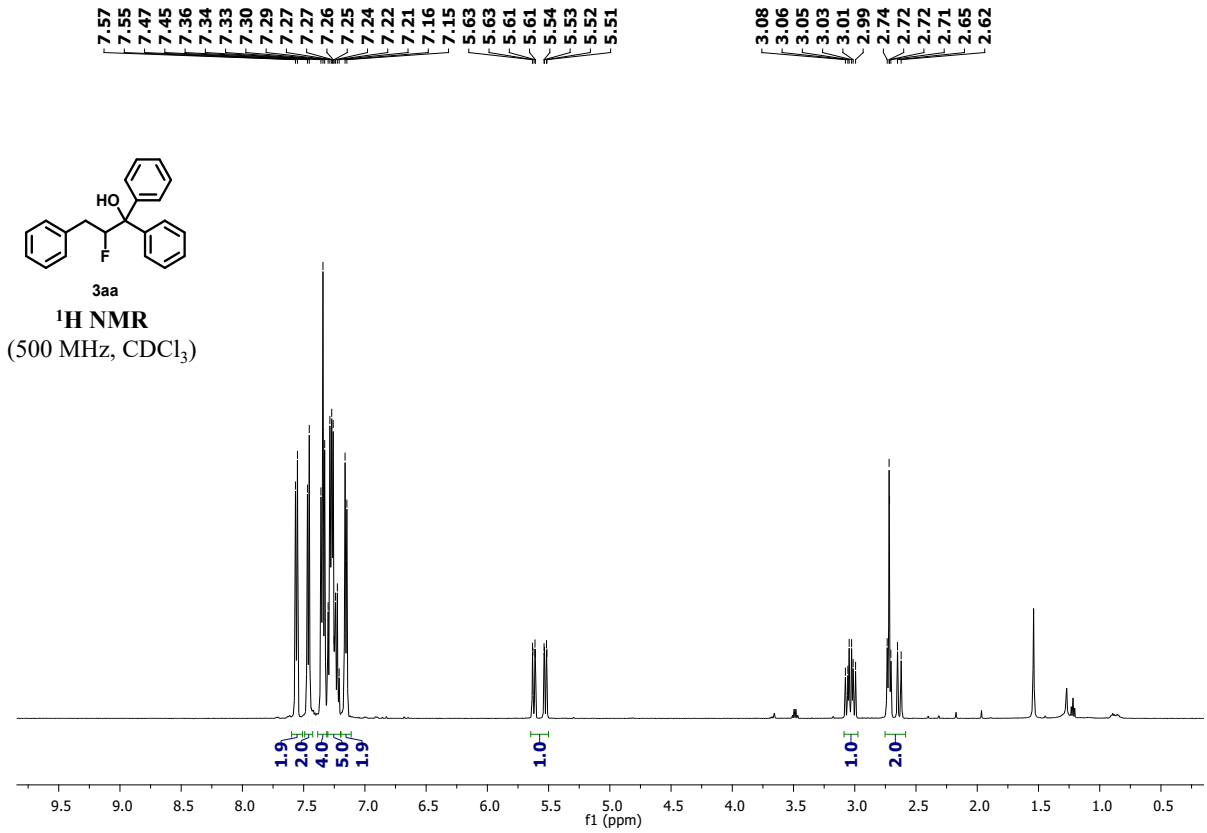
Prepared according to general procedure GP to afford **3cf** as a white waxy solid (107 mg, 73%) after column chromatography (R_f = 0.4, hexane/EtOAc 95:5); IR (film)/cm^{-1} 3436, 2987, 2956, 1450, 1378, 1258, 974, 905; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26–4.14 (m, 1H, C*H*FCH_2), 1.71–1.62 (m, 5H, C*H*HCHF overlapping with C*H*HCH_2CHF, C*H*HCOH and CH_2), 1.58–1.48 (m, 1H, C*H*HCHF overlapping with O–H, C*H*HCOH, C*H*HCH_2CHF and 2 × CH_2), 1.41–1.19 (m, 12H, 2 × C*H*HCOH overlapping with 5 × CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 99.8 (d, $^{1}J_{(C-F)}$ = 171.7 Hz, CHF), 72.6 (d, $^{2}J_{(C-F)}$ = 19.5 Hz, C_qOHCHF), 33.5 (d, $^{3}J_{(C–F)}$ = 4.2 Hz, *C*H_2COH), 32.3 (d, $^{3}J_{(C–F)}$ = 3.7 Hz, *C*H_2COH), 32.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 28.8 (d, $^{2}J_{(C–F)}$ = 21.7 Hz, *C*H_2CHF), 26.0 (d, $^{3}J_{(C–F)}$ = 2.9 Hz, *C*H_2CH_2CHF), 25.9 (CH_2), 22.8 (CH_2), 21.4 (2 × CH_2), 14.3 (CH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ -189.4 (ddd, $^{2}J_{(H-F)}$ = 47.0 Hz, $^{3}J_{(H-F)}$ = 42.7, 14.2 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{15}H_{29}FNaO$ $[M+Na]^{+}$ 267.2095; Found: 267.2079.



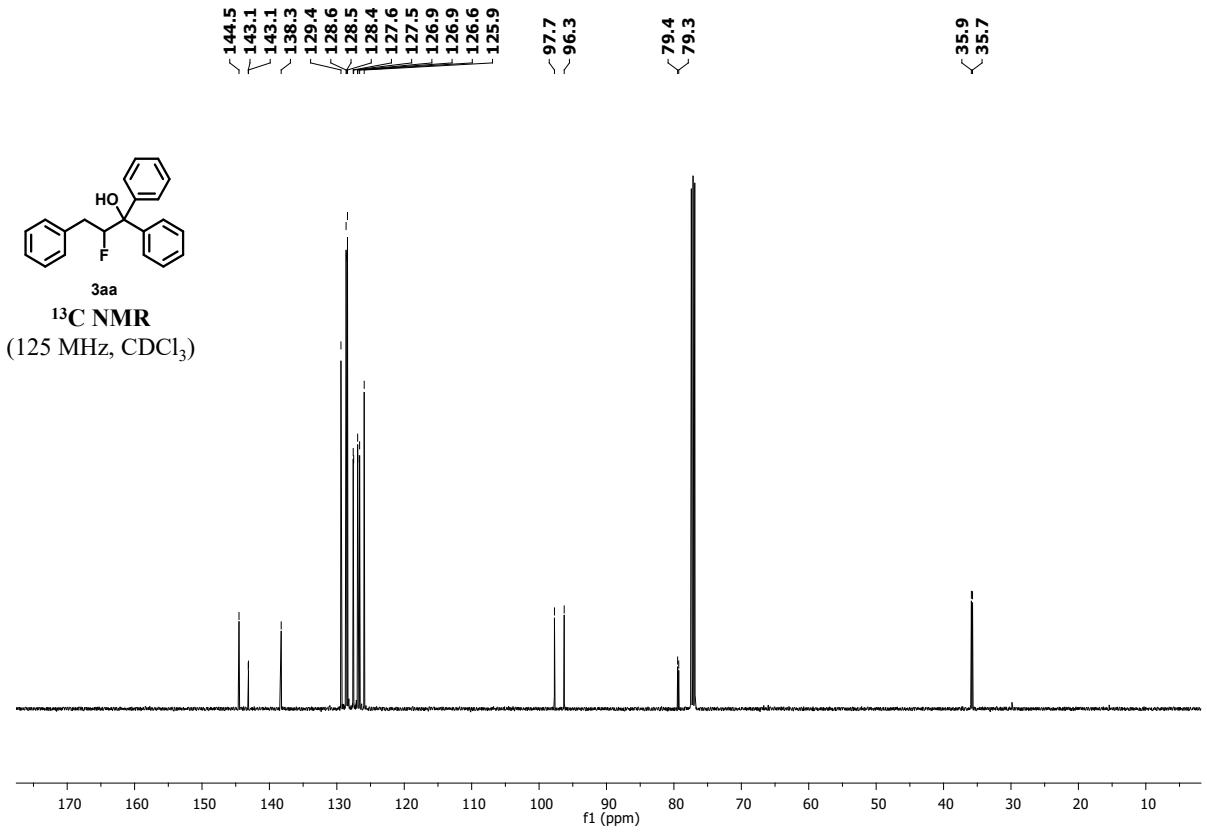
3ck; 1,1-dicyclopropyl-2-fluorodecan-1-ol

Prepared according to general procedure GP to afford **3ck** as (100 mg, 65%) after column chromatography (R_f = 0.5, hexane/Et_2O 9:1); IR (film)/cm^{-1} 3494, 2925, 2855, 1465, 1378, 1023, 914, 827; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (ddd, $^{2}J_{(H–F)}$ = 49.0 Hz, $^{3}J_{(H–H)}$ = 10.4 , 2.2 Hz, 1H, C*H*FCH_2), 1.83–1.75 (m, 2H, CH_2), 1.71–1.56 (m, 2H, C*H*HCHF overlapping with, C*H*HCH_2CHF), 1.55 (s, 1H, O–H), 1.43–1.25 (m, 10H, C*H*HCHF overlapping with C*H*HCH_2CHF and 4 × CH_2), 0.92–0.86 (m, 4H, CH_3 overlapping with C*H*COH), 0.79–0.73 (m, 1H, C*H*COH), 0.49–0.29 (m, 8H, 4 × CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 100.7 (d, $^{1}J_{(C-F)}$ = 174.6 Hz, CHF), 71.9 (d, $^{2}J_{(C-F)}$ = 18.6 Hz, C_qOHCHF), 32.0 (CH_2), 30.0 (d, $^{2}J_{(C–F)}$ = 21.4 Hz, *C*H_2CHF), 29.7 (2 × CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 26.2 (d, $^{3}J_{(C–F)}$ = 2.6 Hz, *C*H_2CH_2CHF), 22.8 (CH_2), 15.1 (d, $^{3}J_{(C–H)}$ = 4.7 Hz, CHCOH), 14.6 (d, $^{3}J_{(C–H)}$ = 3.6 Hz, CHCOH), 14.3 (CH_3), 0.8 (CH_2), 0.4 (d, $^{4}J_{(C–F)}$ = 0.8 Hz, CH_2), -0.7 (CH_2), -0.9 (CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ -193.0 (ddd, $^{2}J_{(H-F)}$ = 49.0 Hz, $^{3}J_{(H-F)}$ = 42.5, 15.7 Hz, 1F, CHF); HRMS (ESI) m/z Calcd for $C_{16}H_{29}FNaO$ $[M+Na]^{+}$ 279.2095; Found: 279.2118.

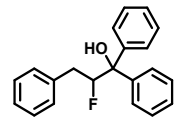
5. Copy of ^{1}H, ^{13}C and ^{19}F NMR spectra for compounds 3aa-3ck



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



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



3aa

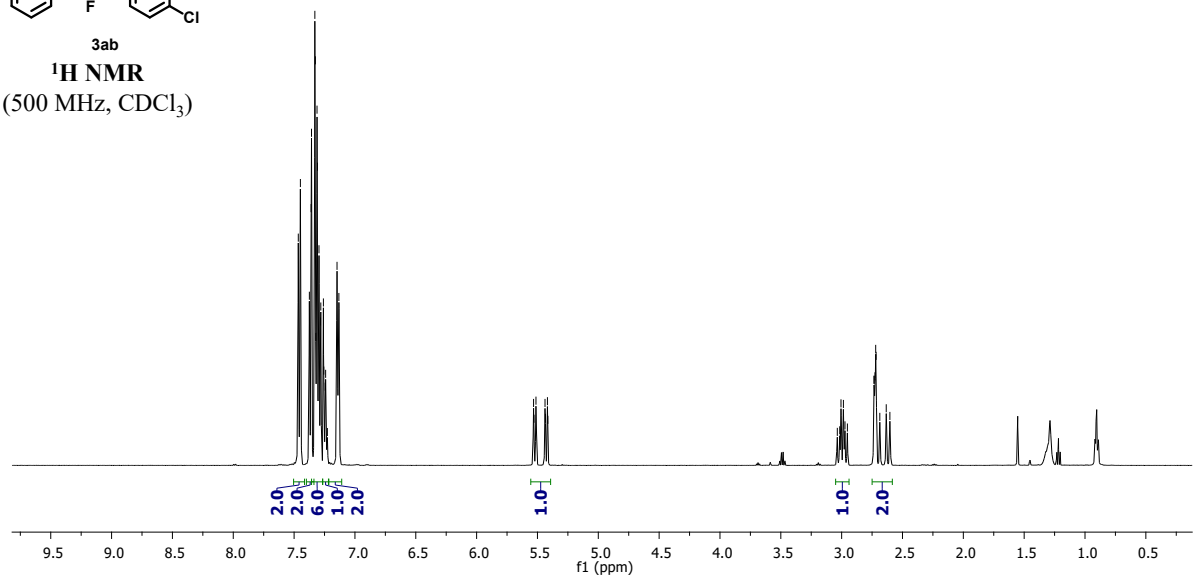
^{19}F NMR

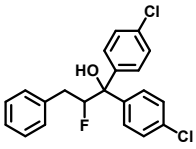
(470 MHz, $CDCl_3$)

3ab

^{1}H NMR

(500 MHz, $CDCl_3$)

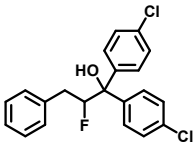




3ab

^{13}C NMR

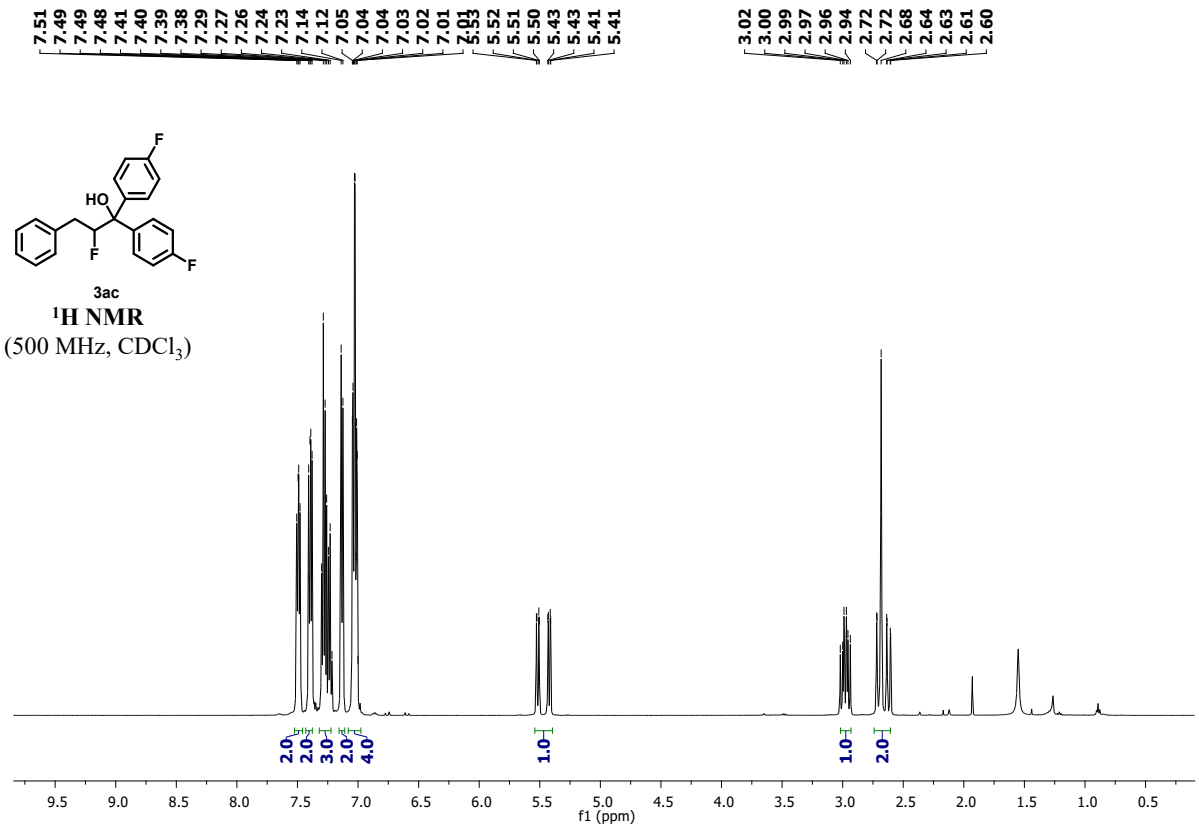
(125 MHz, $CDCl_3$)



3ab

^{19}F NMR

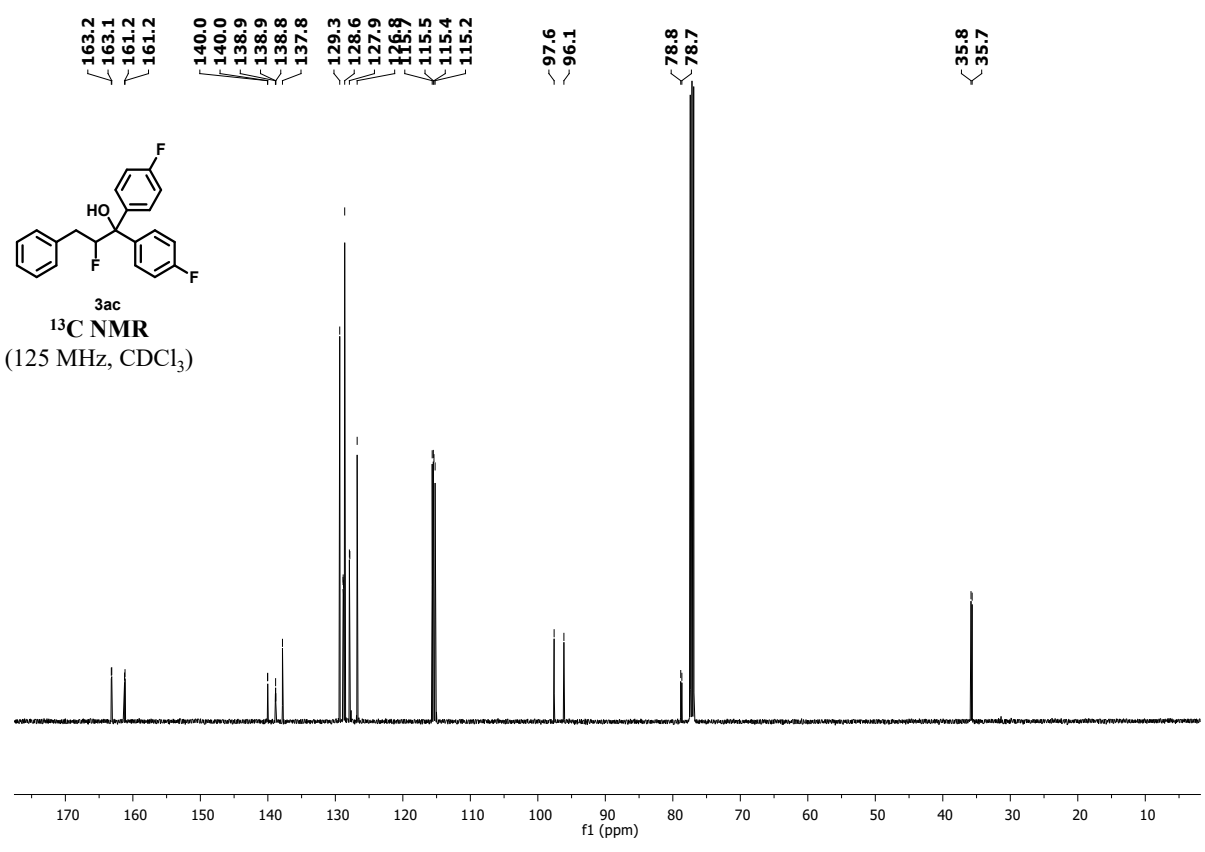
(470 MHz, $CDCl_3$)



3ac

^{1}H NMR

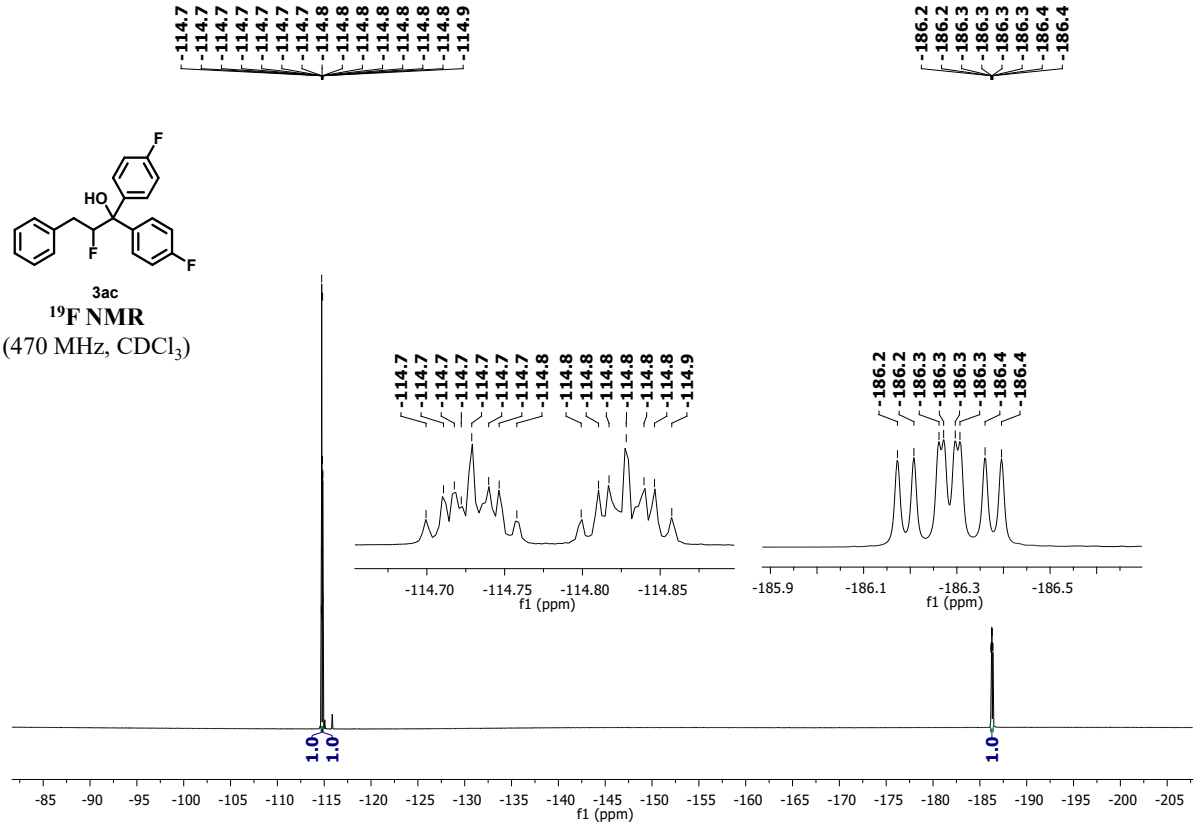
(500 MHz, $CDCl_3$)



3ac

^{13}C NMR

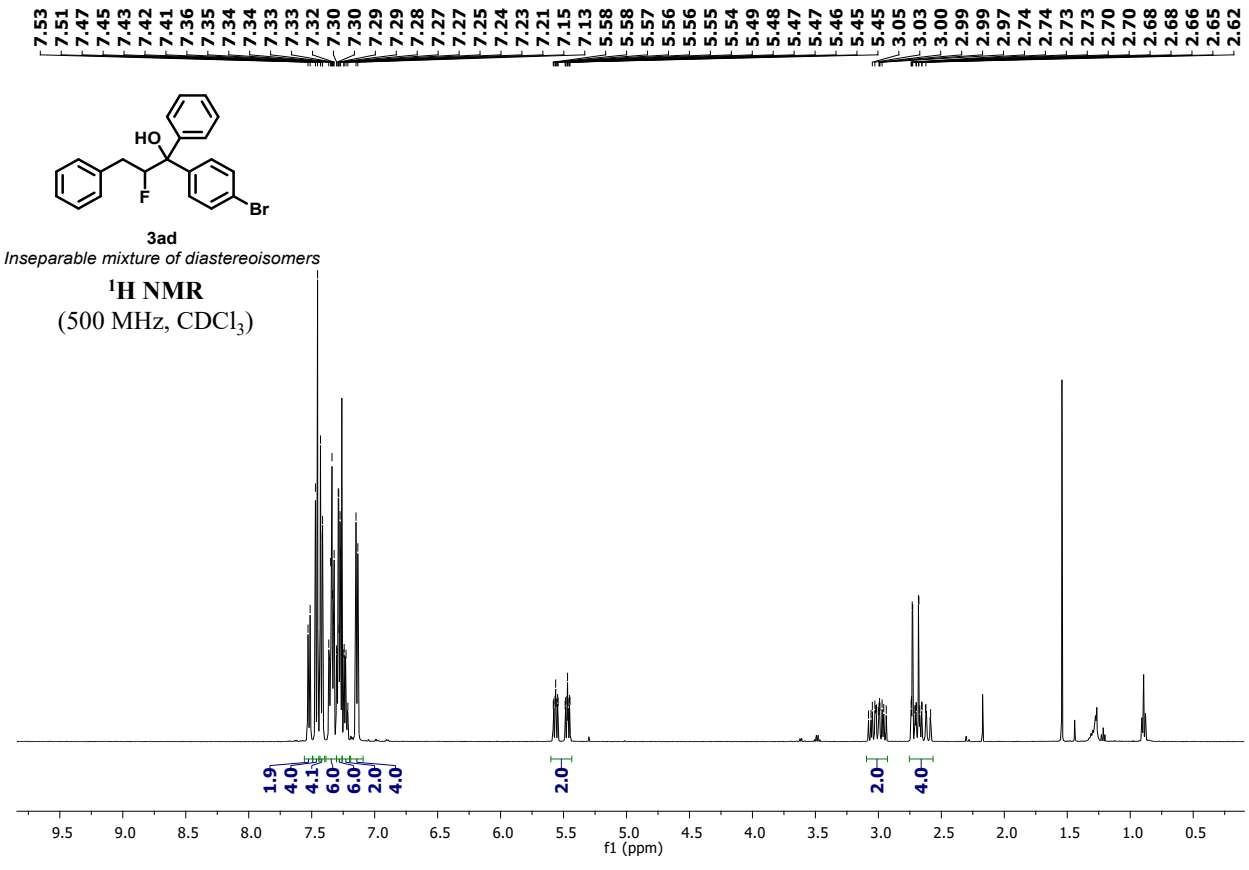
(125 MHz, $CDCl_3$)



3ac

^{19}F NMR

(470 MHz, $CDCl_3$)

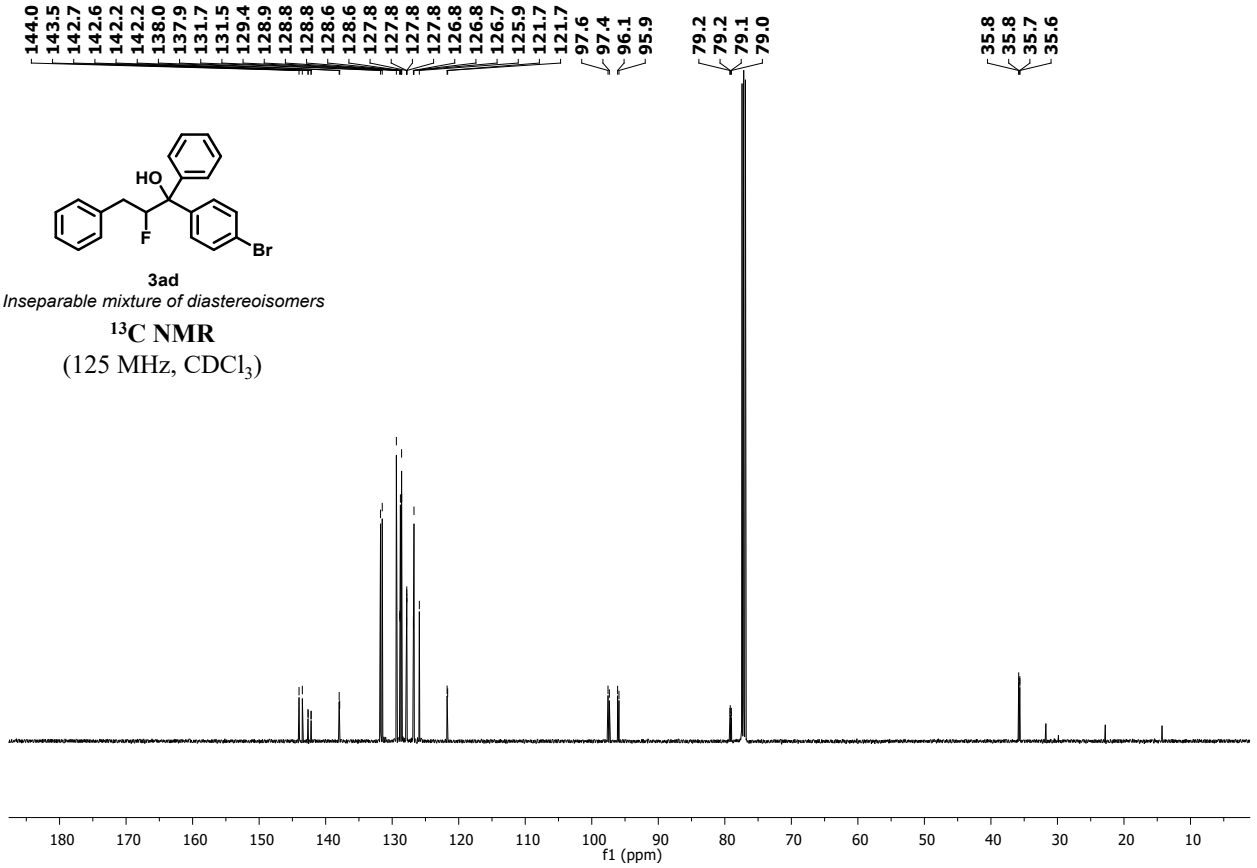


3ad

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

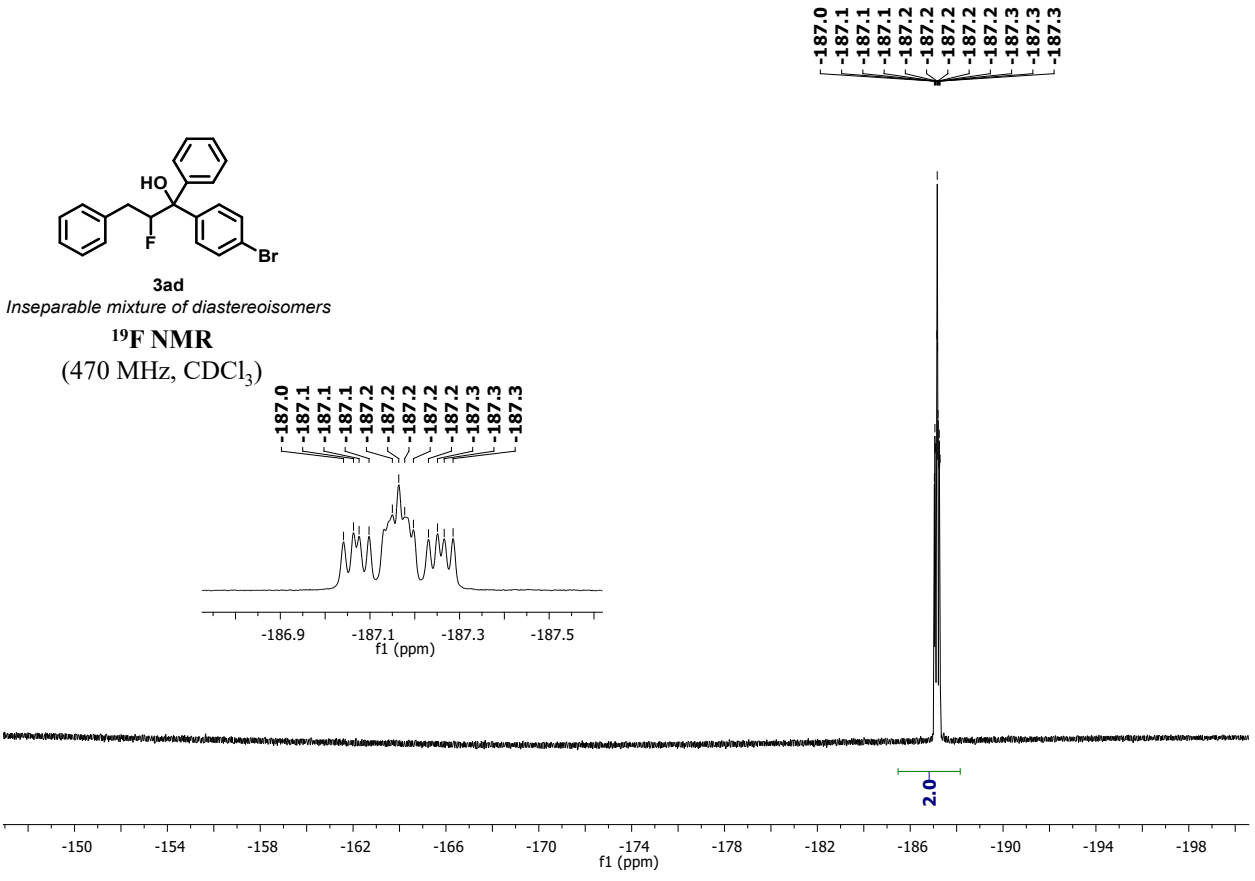


3ad

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

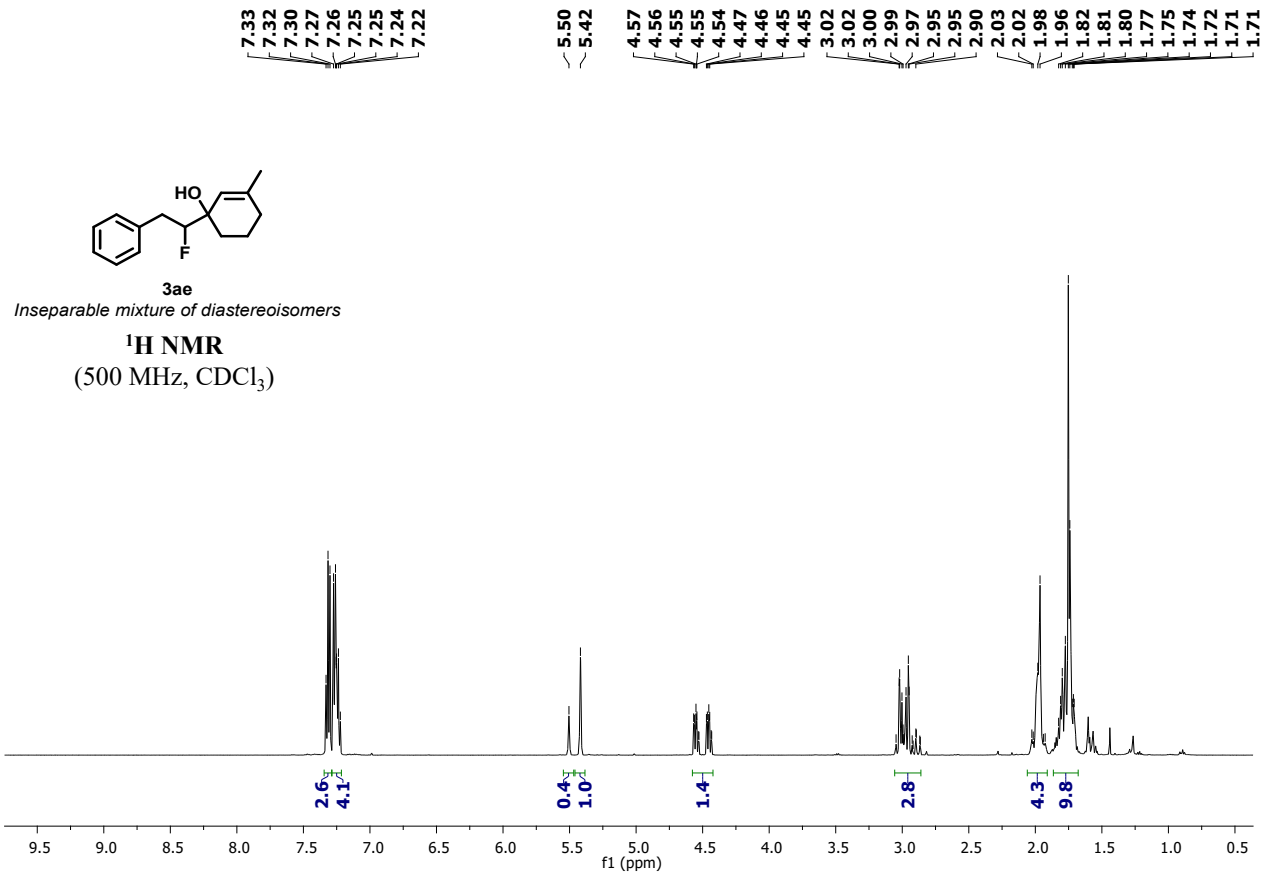


3ad

Inseparable mixture of diastereoisomers

^{19}F NMR

(470 MHz, $CDCl_3$)

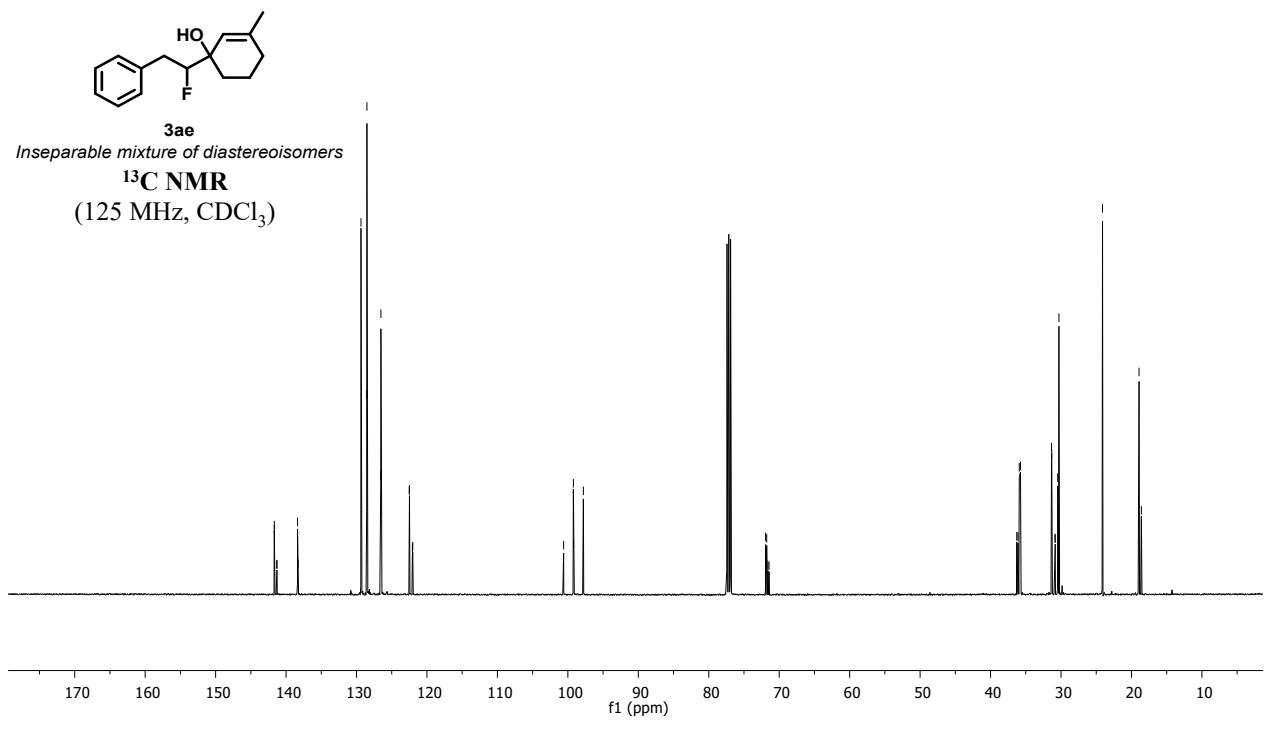


3ae

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

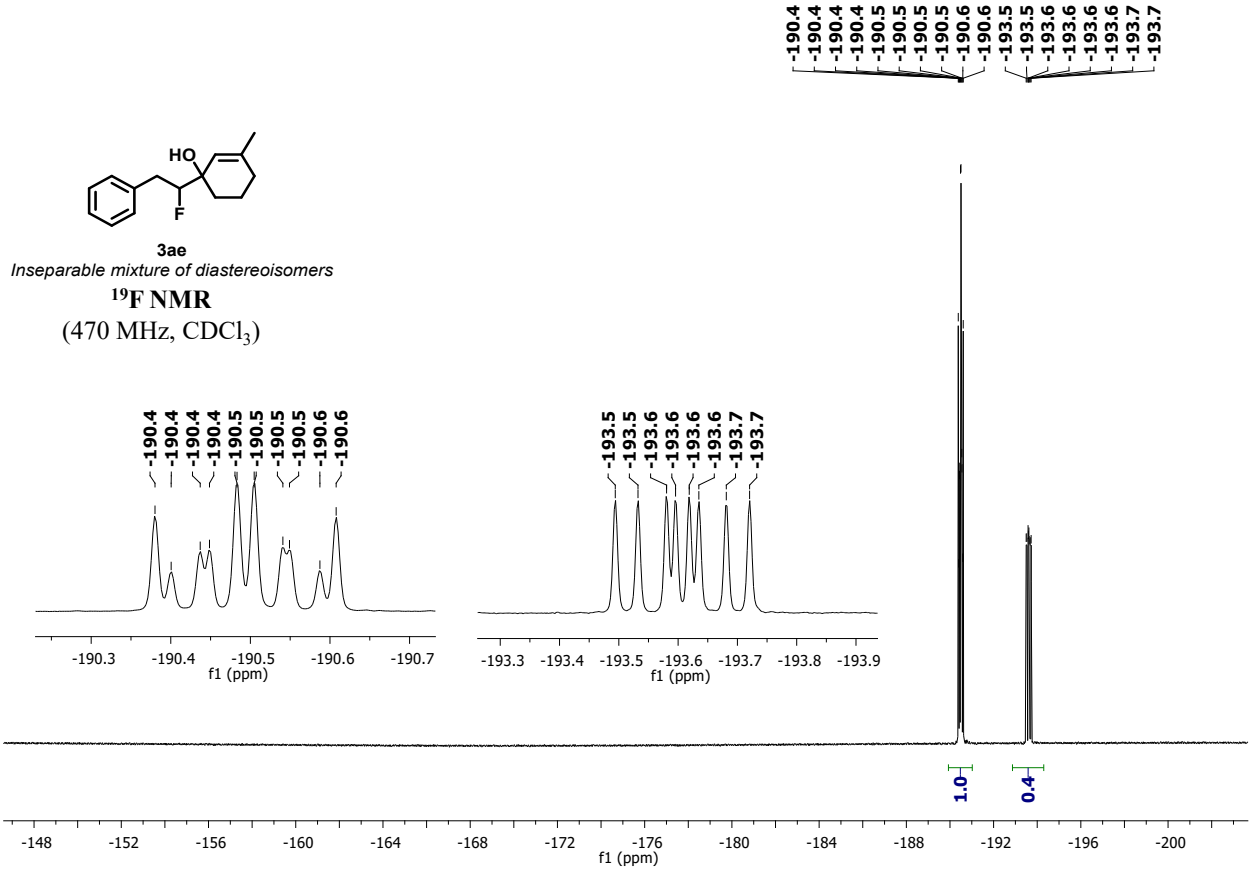


3ae

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

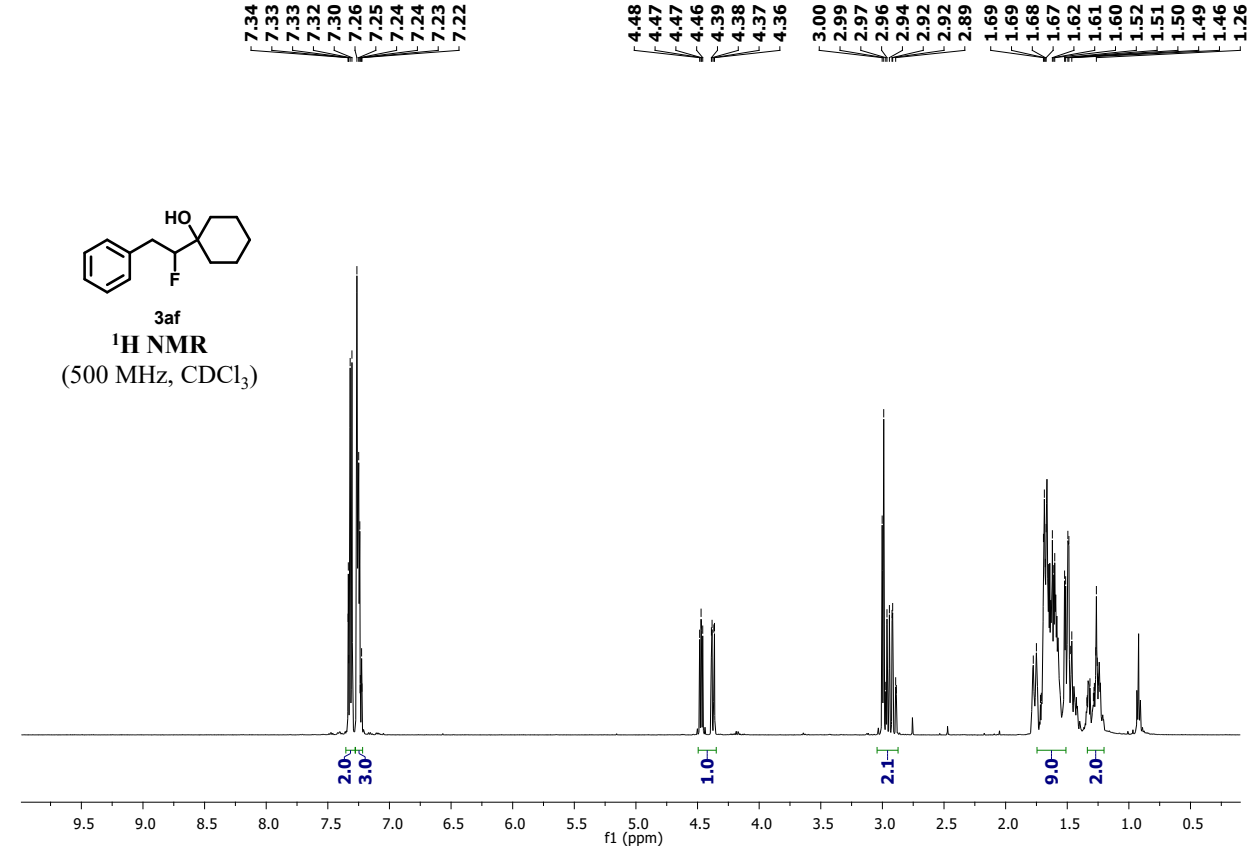


3ae

Inseparable mixture of diastereoisomers

^{19}F NMR

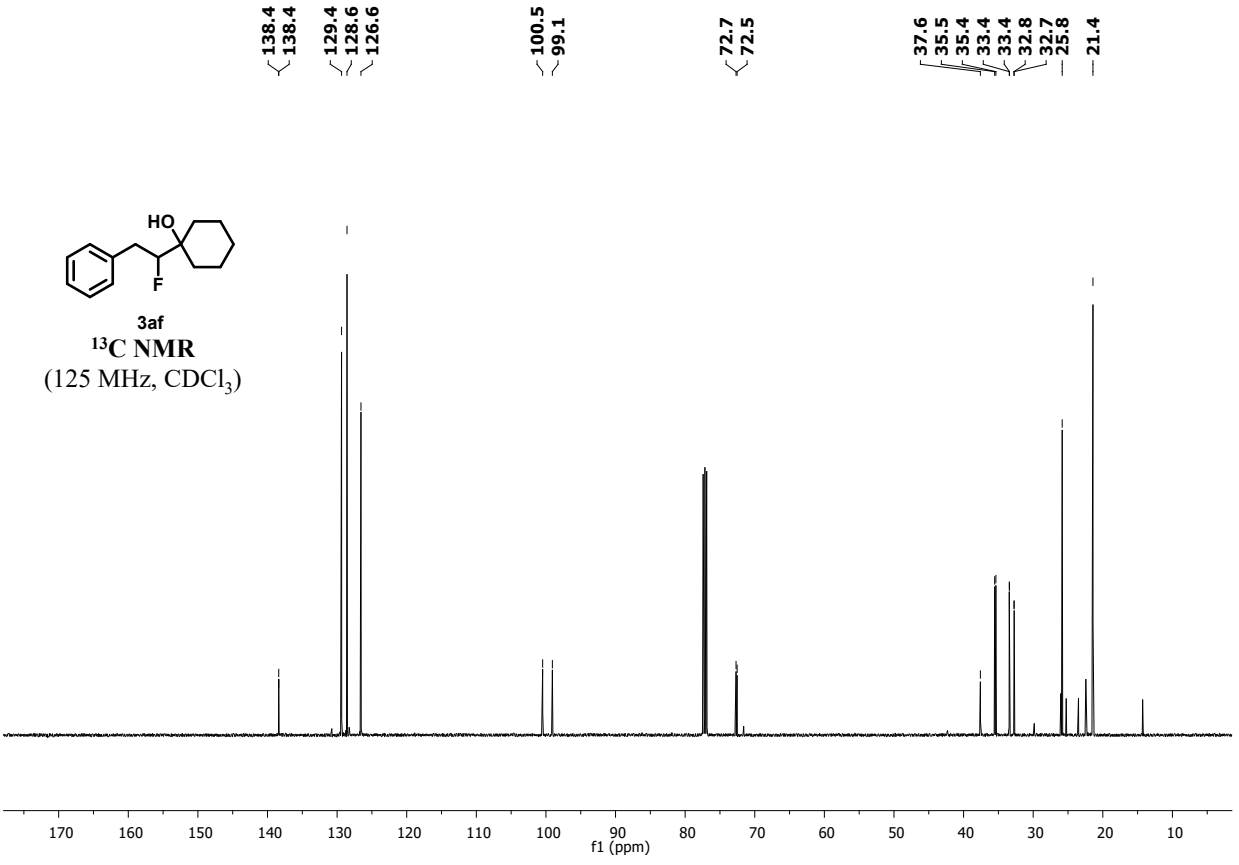
(470 MHz, $CDCl_3$)



3af

^{1}H NMR

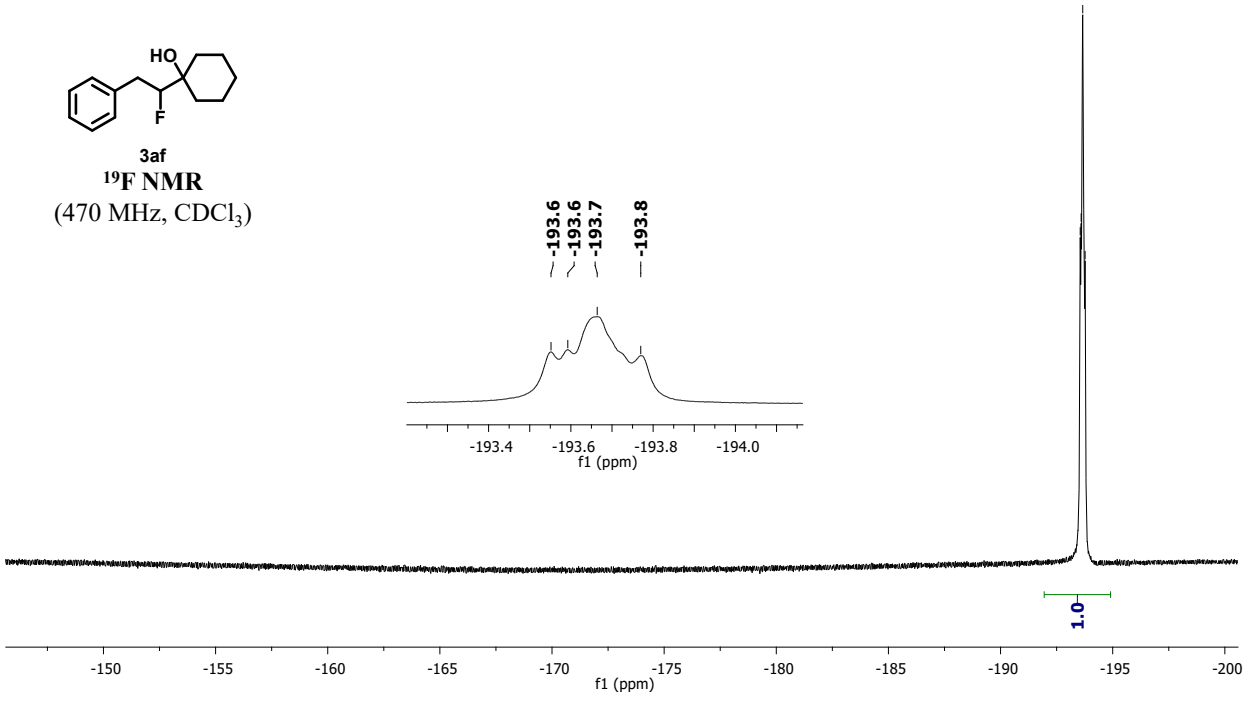
(500 MHz, $CDCl_3$)



3af

^{13}C NMR

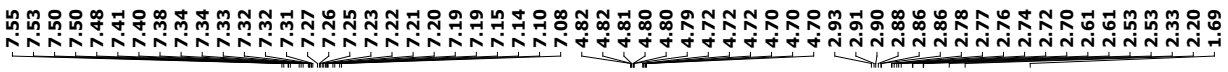
(125 MHz, $CDCl_3$)

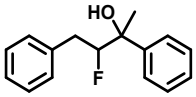


3af

^{19}F NMR

(470 MHz, $CDCl_3$)



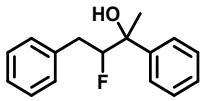


3ag

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

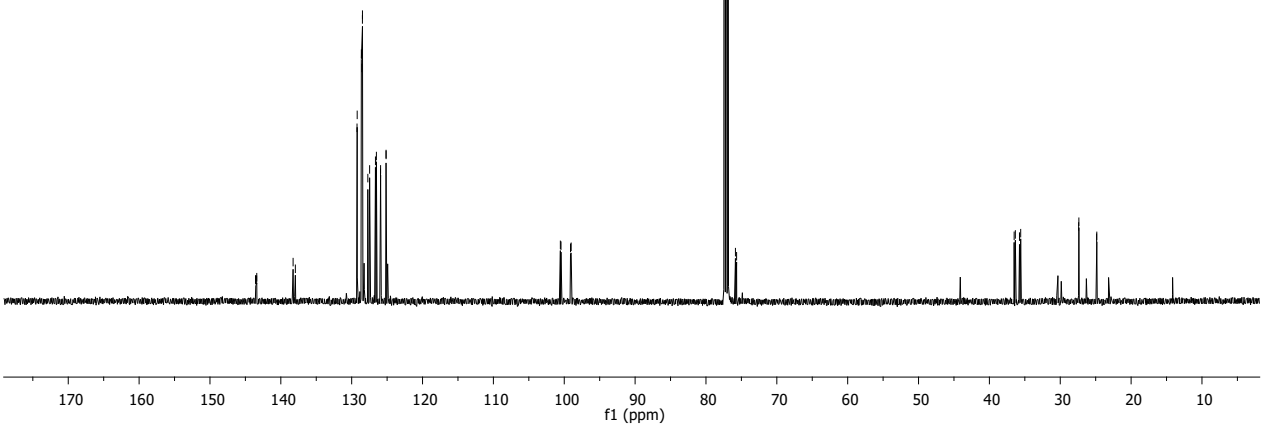


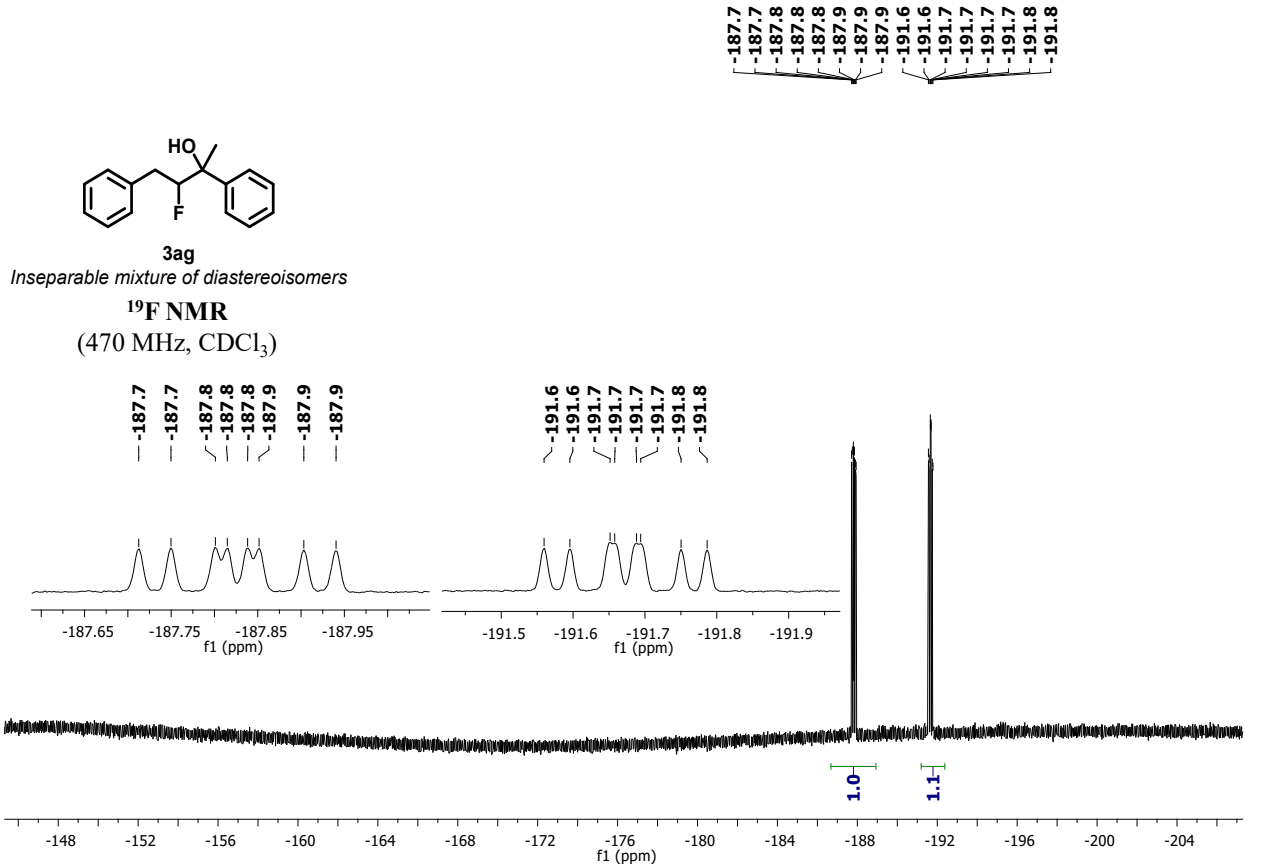
3ag

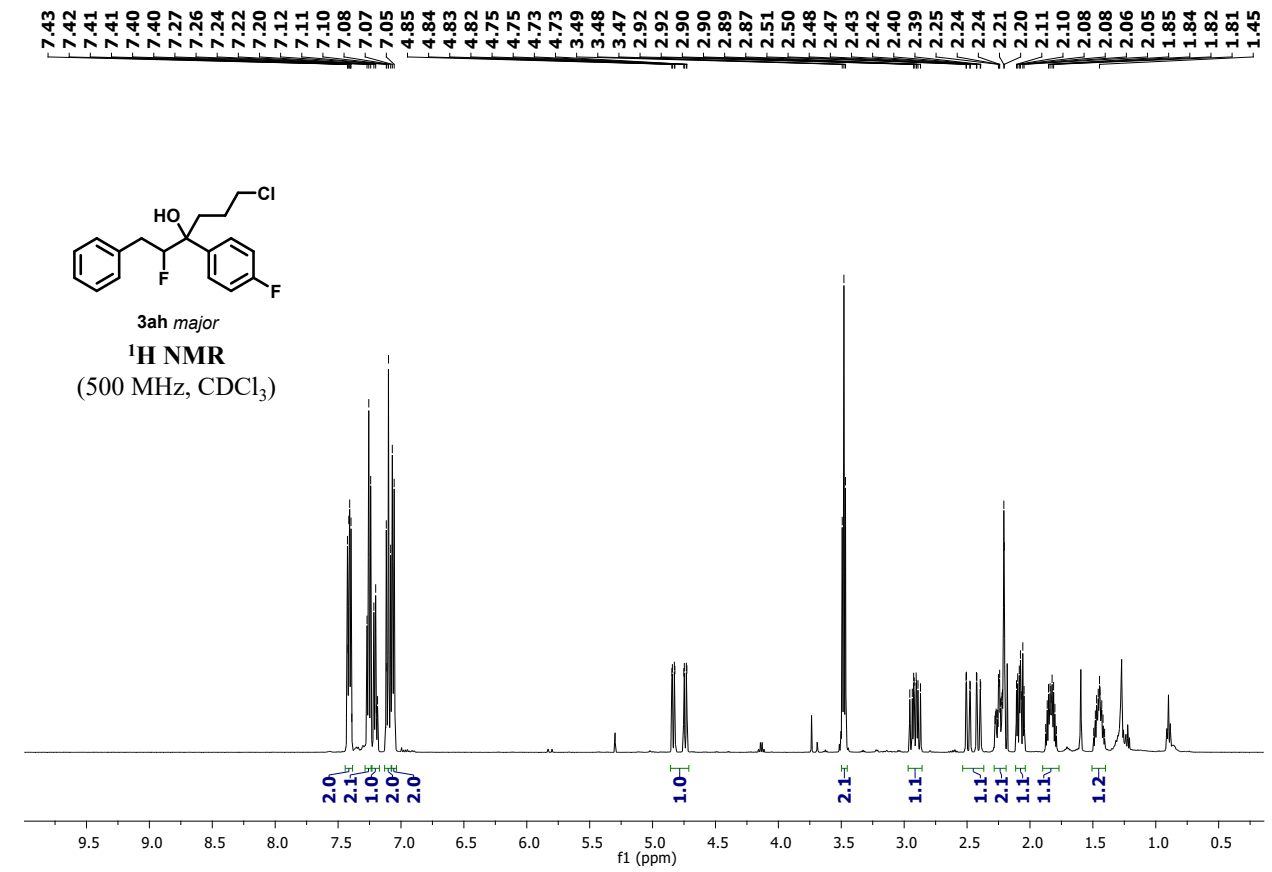
Inseparable mixture of diastereoisomers

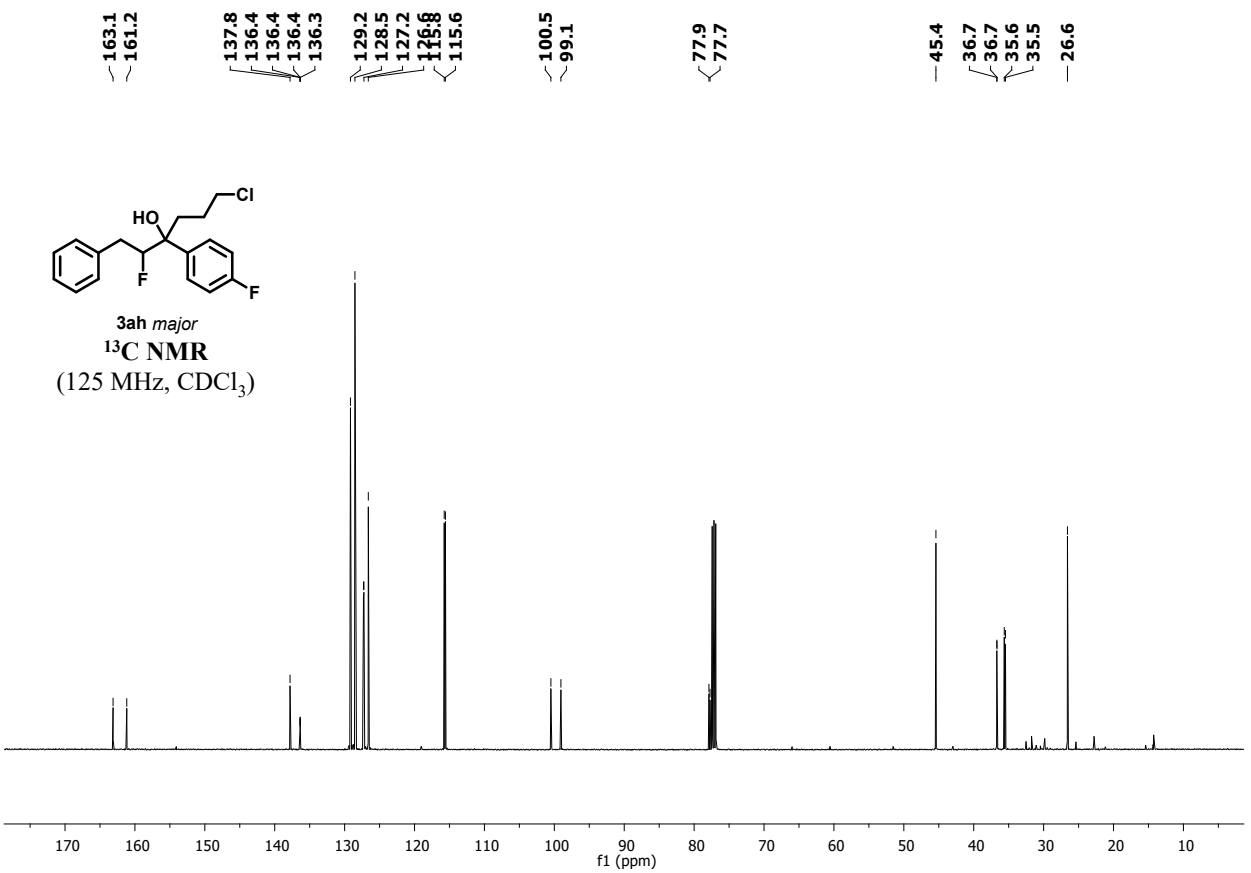
^{13}C NMR

(125 MHz, $CDCl_3$)




-187.7
-187.7
-187.8
-187.8
-187.8
-187.9
-187.9
-187.9
-191.6
-191.7
-191.7
-191.7
-191.7
-191.8
-191.8
HO
F
3ag
Inseparable mixture of diastereoisomers
19F NMR
(470 MHz, CDCl3)
-187.65
-187.75
-187.85
-187.95
f1 (ppm)
-191.5
-191.6
-191.7
-191.8
-191.9
f1 (ppm)
1.0
1.1
-148
-152
-156
-160
-164
-168
-172
-176
-180
-184
-188
-192
-196
-200
-204
f1 (ppm)

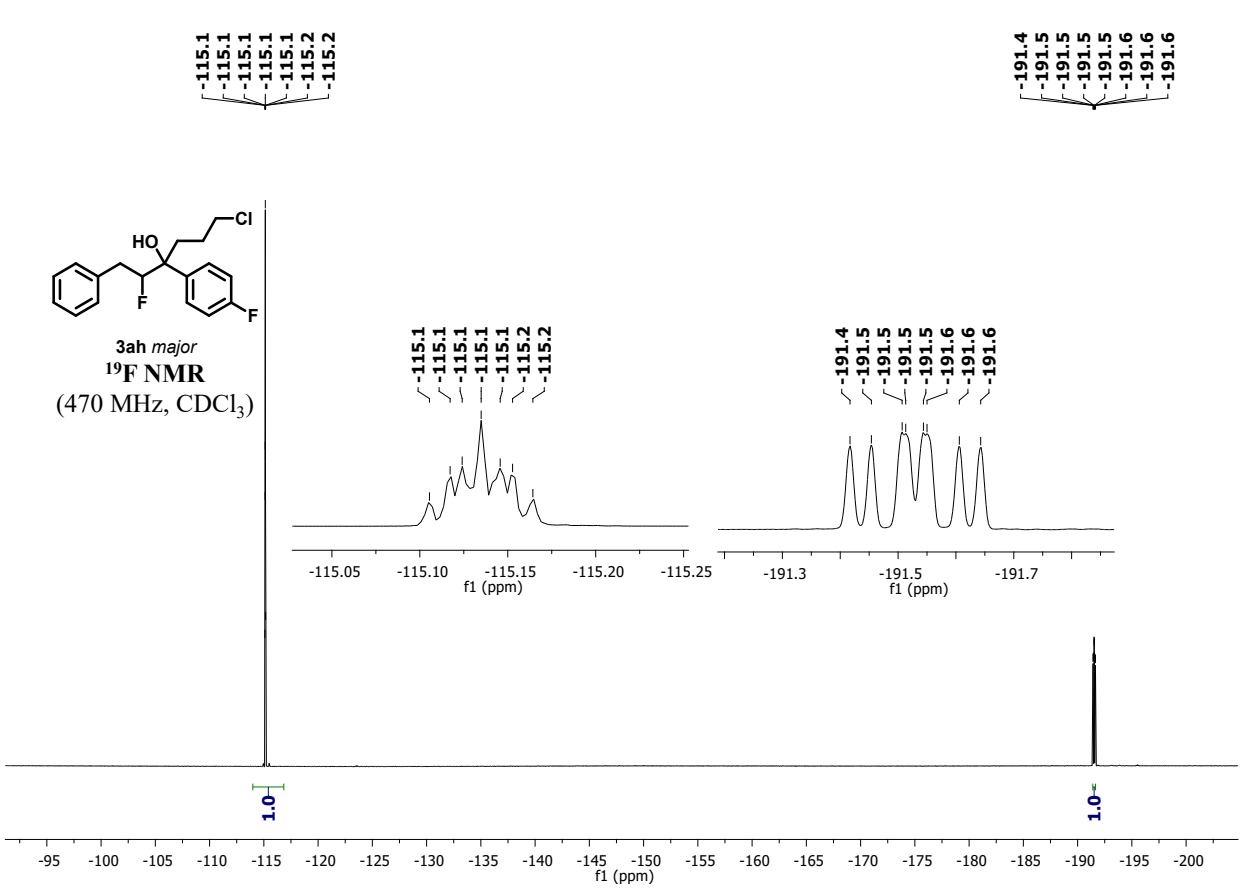

7.43
7.42
7.41
7.41
7.40
7.40
7.27
7.26
7.24
7.22
7.20
7.12
7.11
7.10
7.08
7.07
7.05
4.85
4.84
4.83
4.82
4.75
4.75
4.73
4.73
3.49
3.48
3.47
2.92
2.92
2.90
2.90
2.89
2.87
2.51
2.50
2.48
2.47
2.43
2.42
2.40
2.39
2.25
2.24
2.24
2.21
2.20
2.11
2.10
2.08
2.08
2.06
2.05
1.85
1.84
1.82
1.81
1.45
Cl
HO
F
F
3ah major
1H NMR
(500 MHz, CDCl3)
2.0
2.1
1.0
2.0
2.0
1.0
2.1
1.1
1.1
2.1
1.1
1.1
1.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



3ah *major*

^{13}C NMR

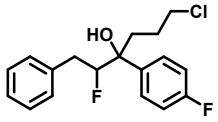
(125 MHz, $CDCl_3$)



3ah *major*

^{19}F NMR

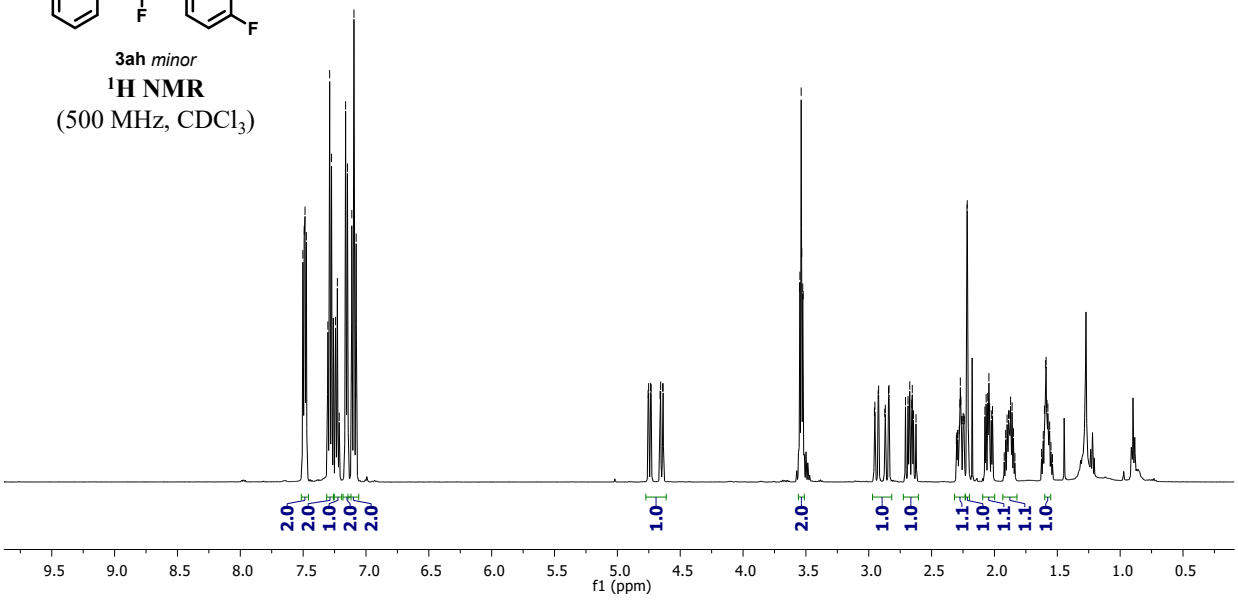
(470 MHz, $CDCl_3$)

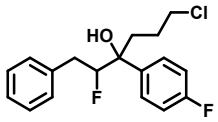


3ah *minor*

^{1}H NMR

(500 MHz, $CDCl_3$)

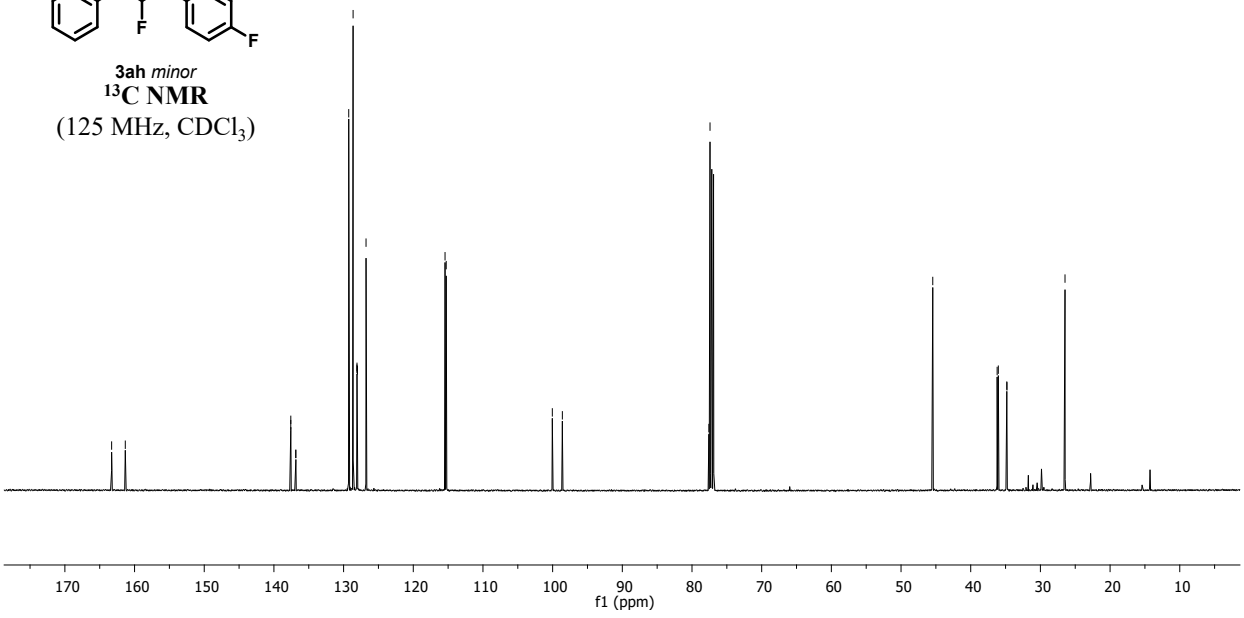


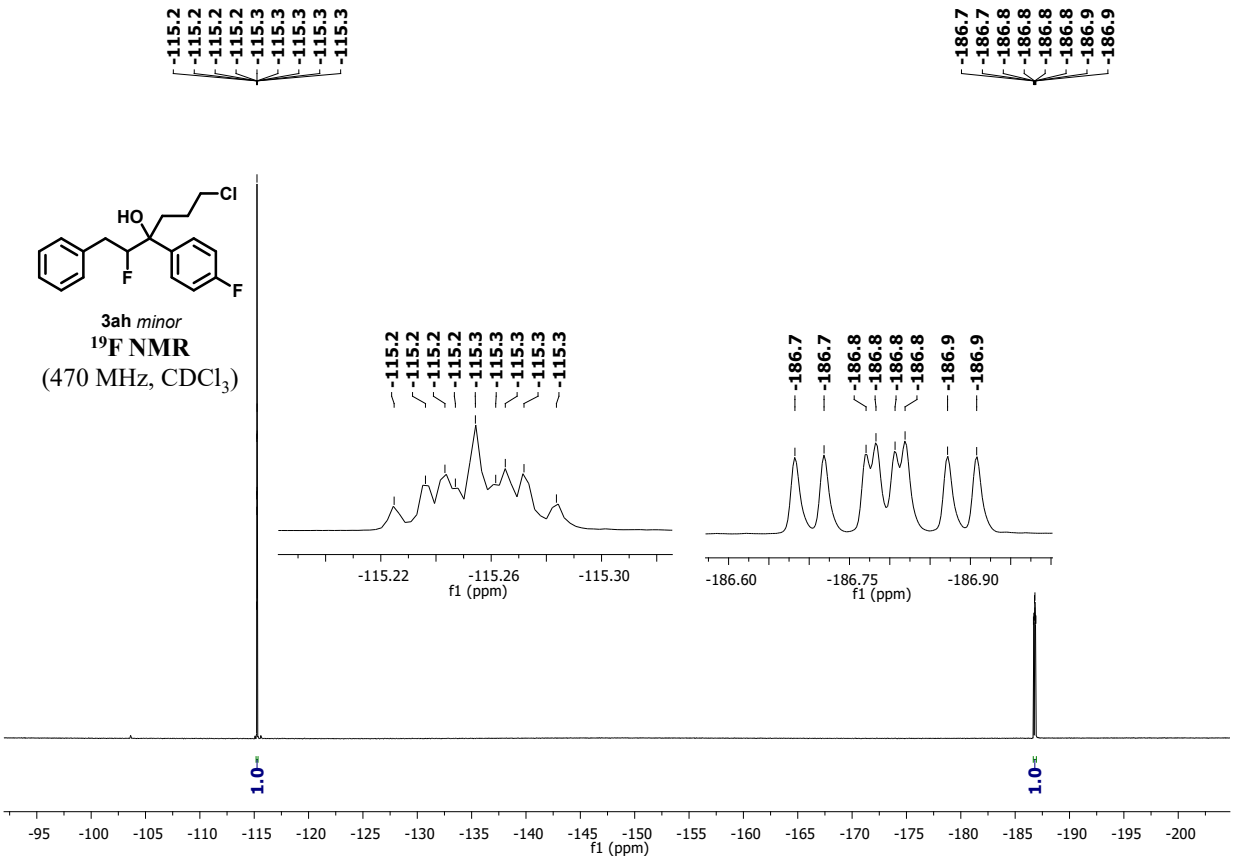


3ah *minor*

^{13}C NMR

(125 MHz, $CDCl_3$)

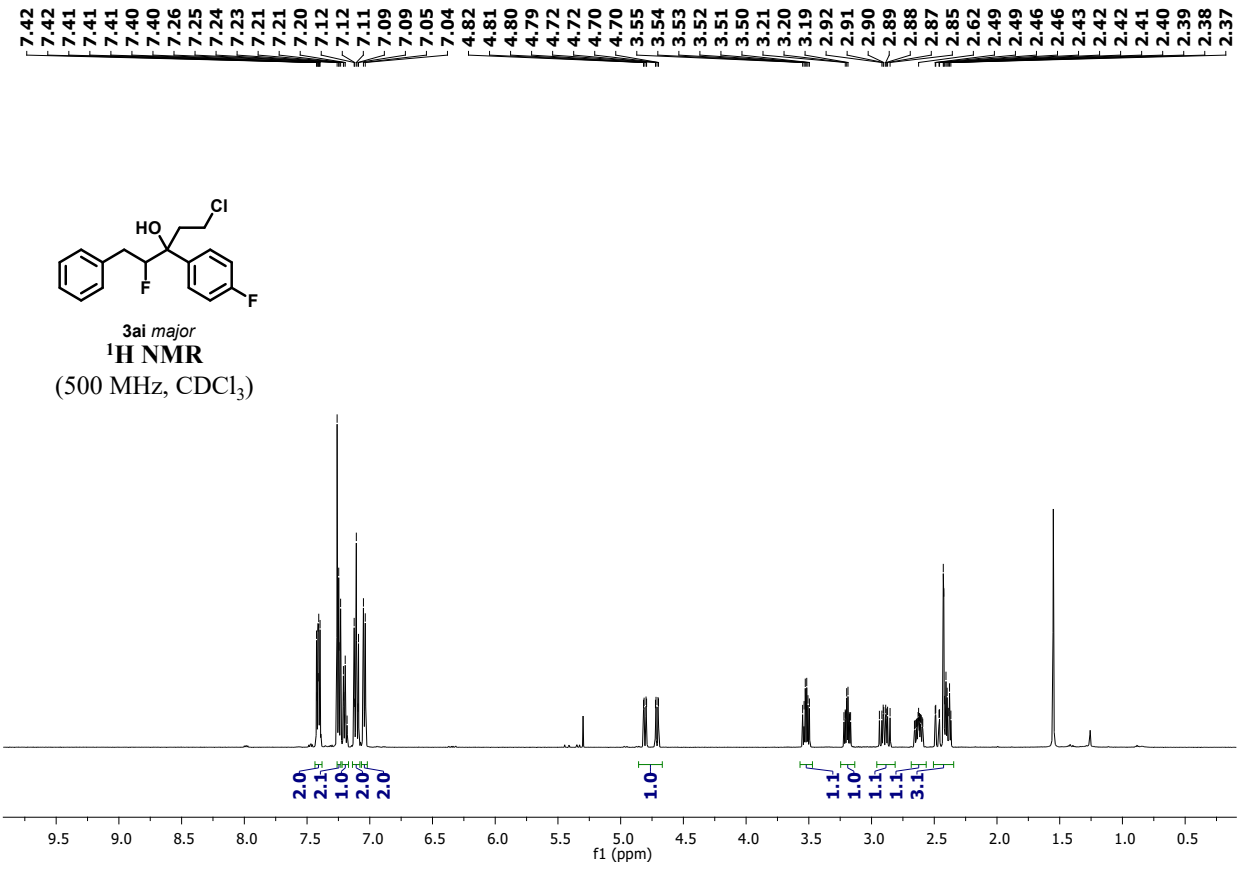




3ah *minor*

^{19}F NMR

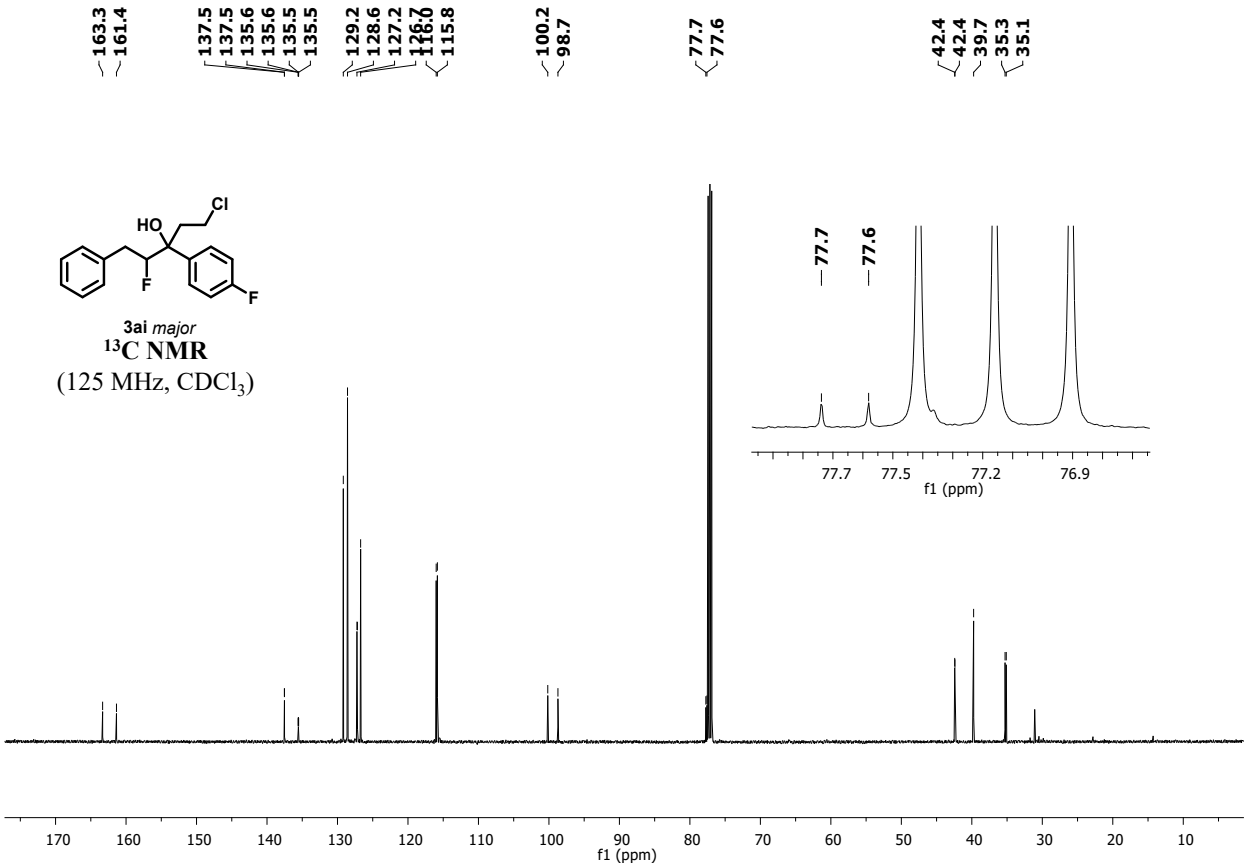
(470 MHz, $CDCl_3$)

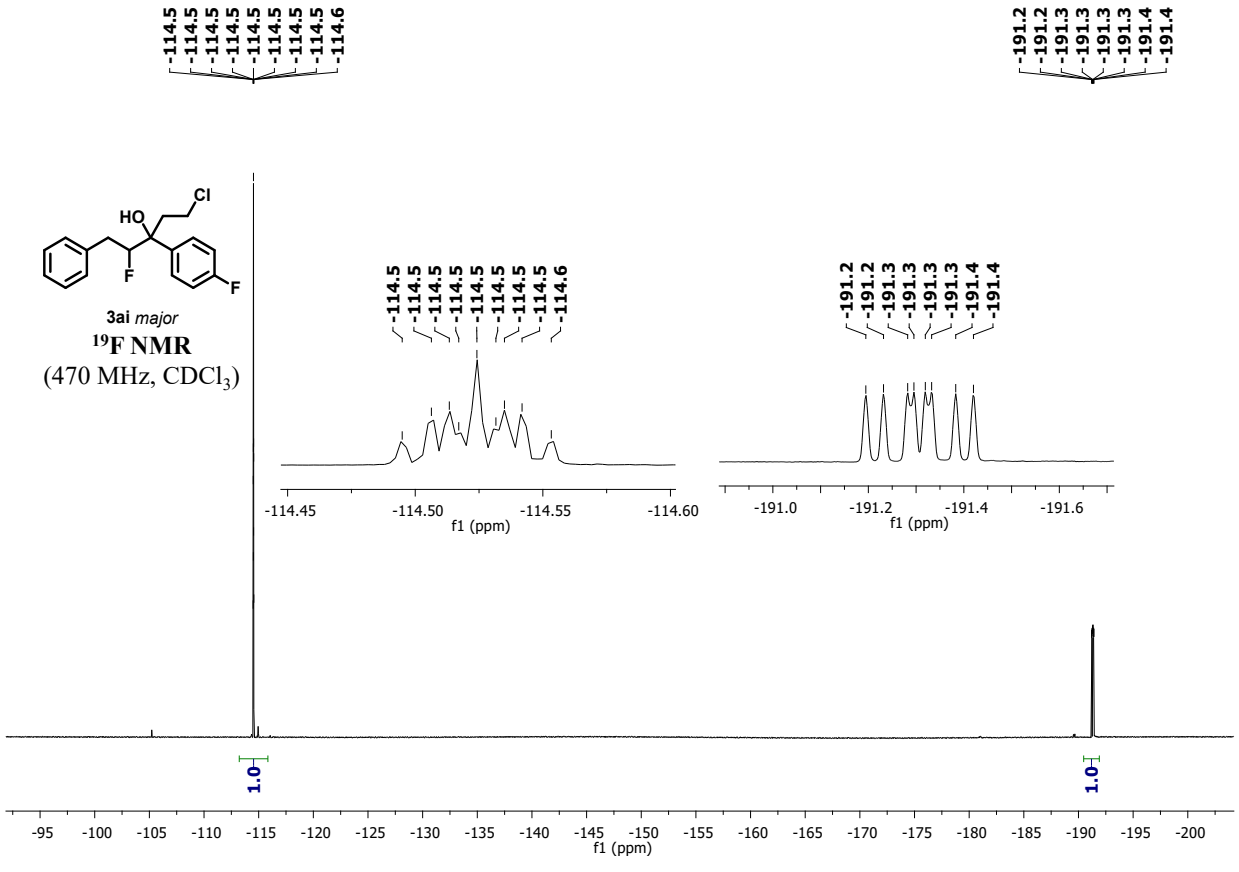


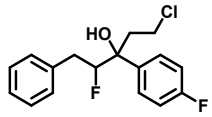
3ai *major*

^{1}H NMR

(500 MHz, $CDCl_3$)


163.3
161.4
137.5
137.5
135.6
135.6
135.5
135.5
129.2
128.6
127.2
116.0
115.8
100.2
98.7
77.7
77.6
42.4
42.4
39.7
35.3
35.1
Cl
HO
F
F
3ai major
13C NMR
(125 MHz, CDCl3)
77.7
77.6
77.7
77.5
77.2
76.9
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

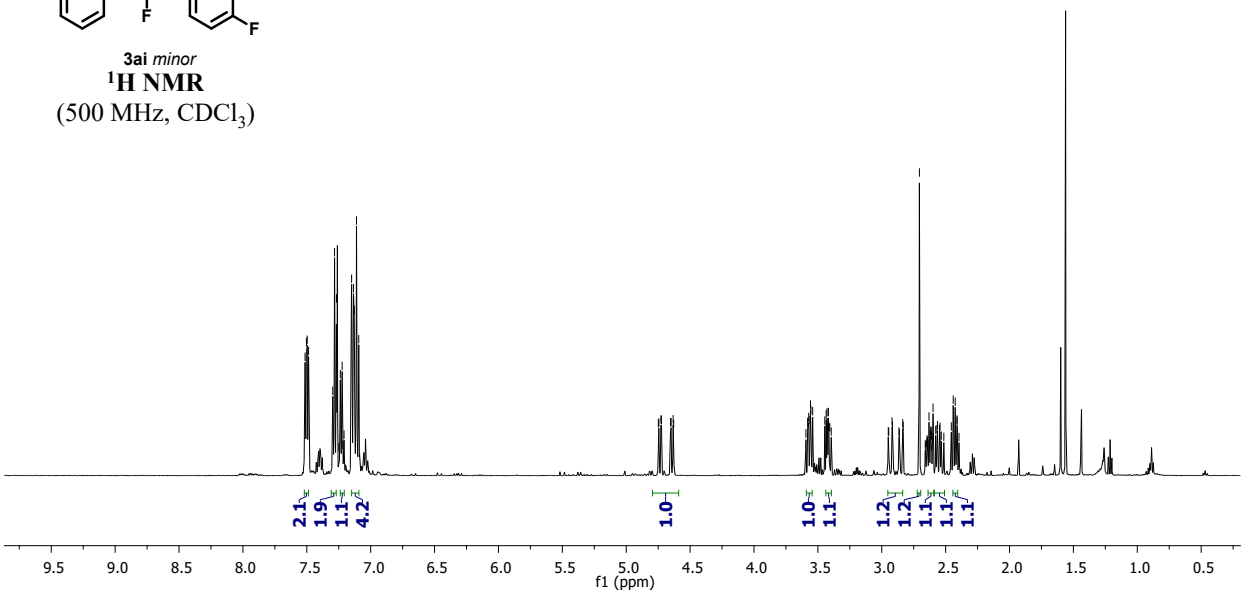

-114.5
-114.5
-114.5
-114.5
-114.5
-114.5
-114.5
-114.6
-191.2
-191.2
-191.3
-191.3
-191.3
-191.4
-191.4
Cl
HO
F
F
3ai major
19F NMR
(470 MHz, CDCl3)
-114.45
-114.50
-114.55
-114.60
f1 (ppm)
-191.0
-191.2
-191.4
-191.6
f1 (ppm)
1.0
1.0
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
f1 (ppm)

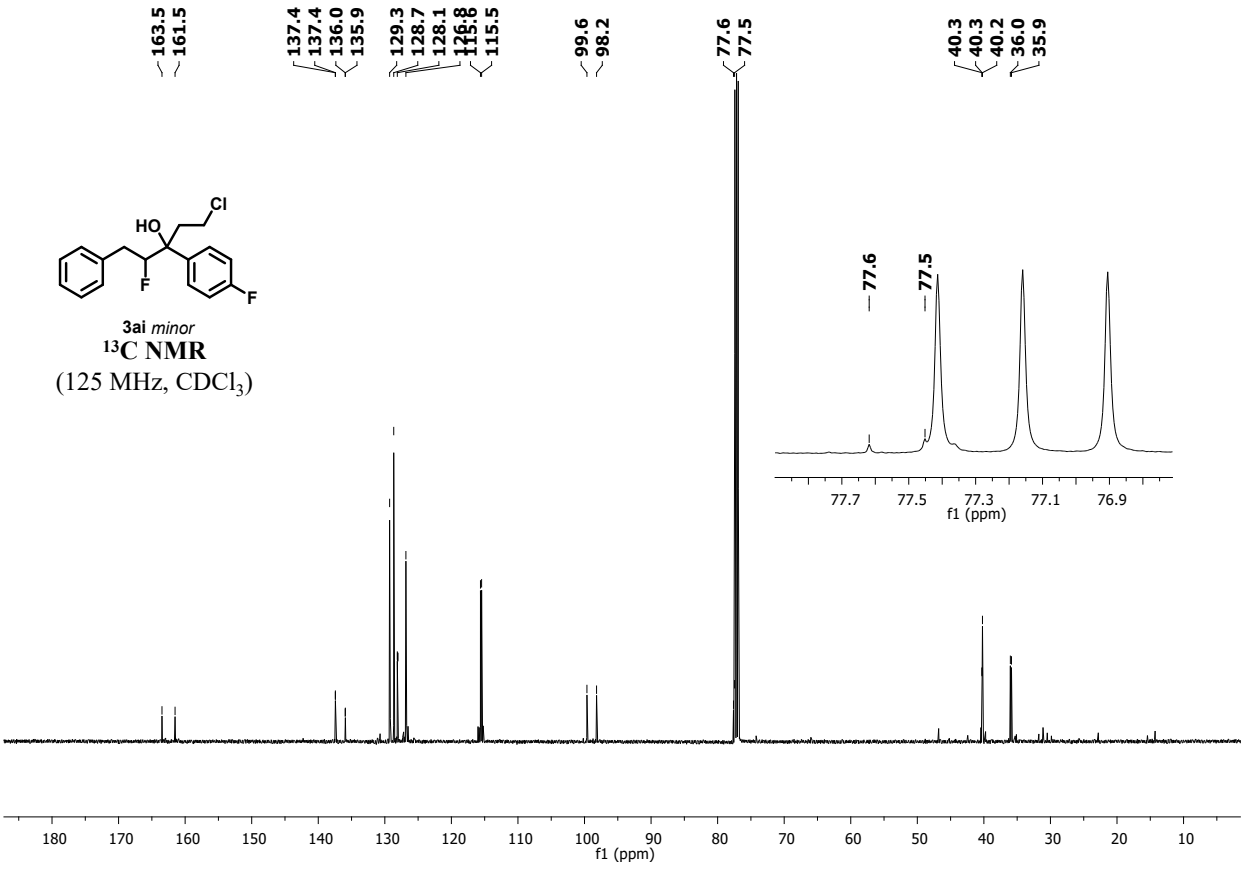


3ai *minor*

^{1}H NMR

(500 MHz, $CDCl_3$)

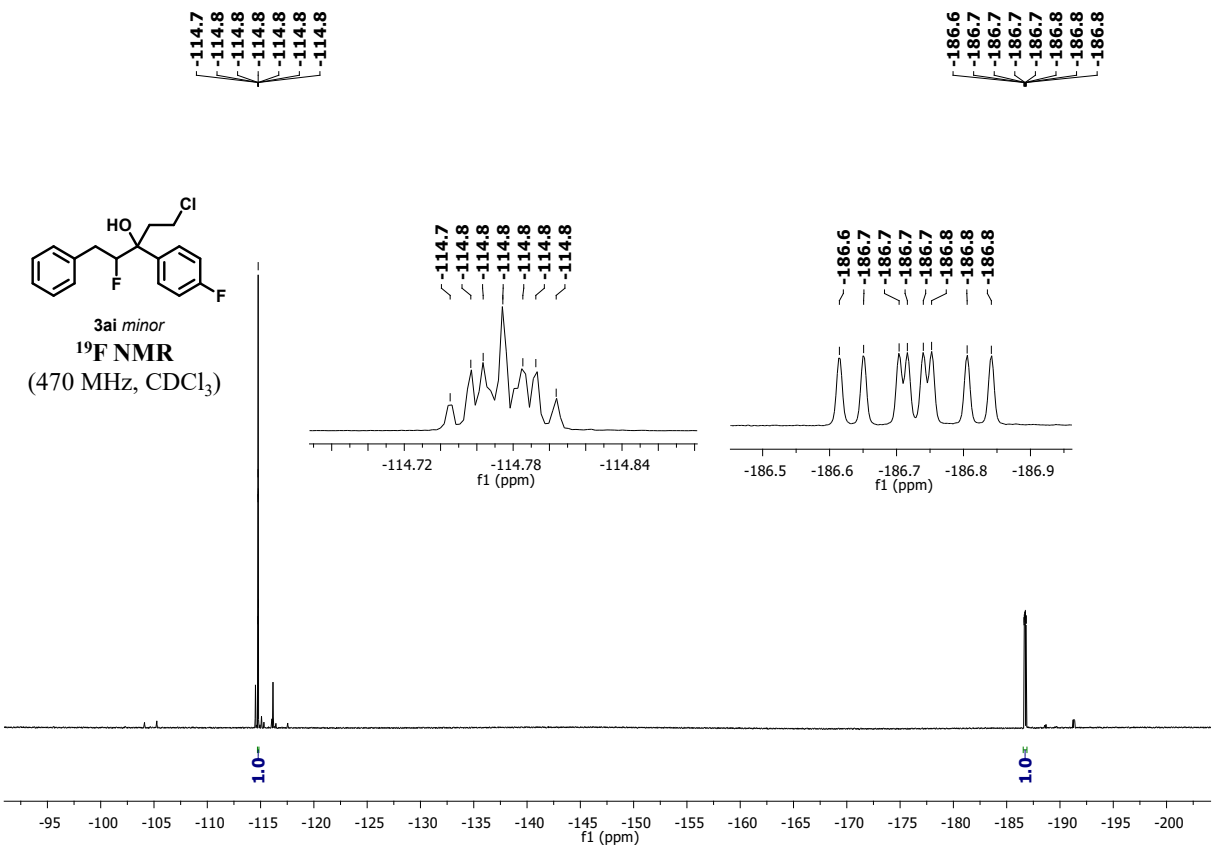


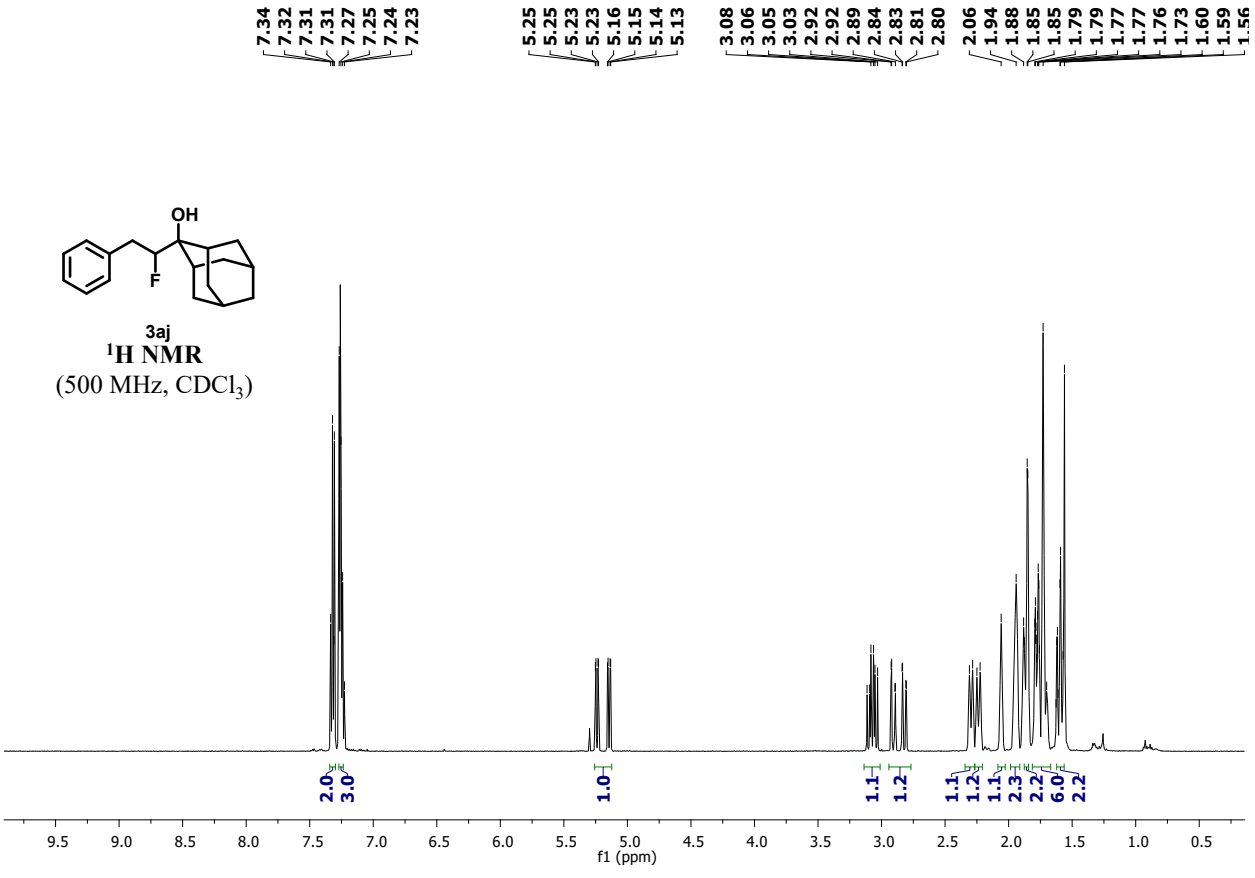


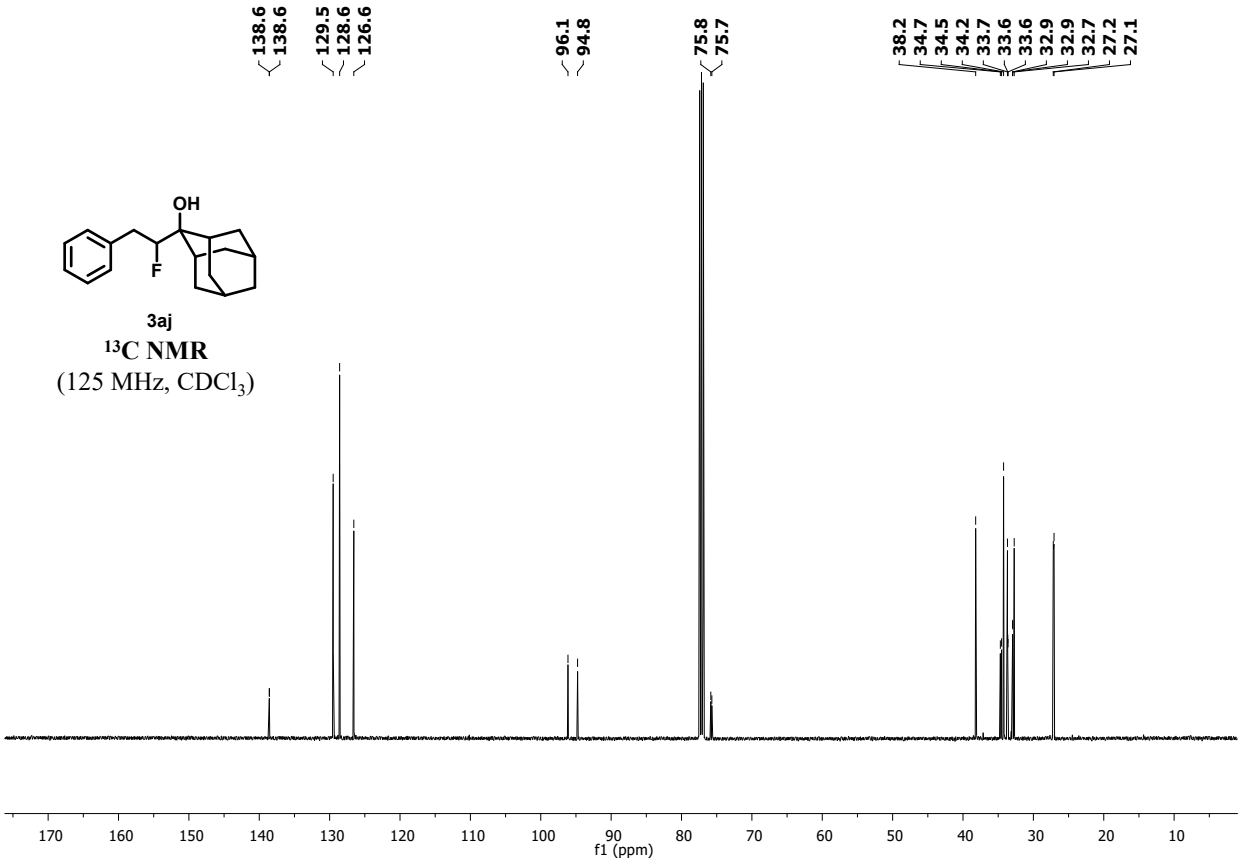
3ai *minor*

^{13}C NMR

(125 MHz, $CDCl_3$)


-114.7
-114.8
-114.8
-114.8
-114.8
-114.8
-114.8
-186.6
-186.7
-186.7
-186.7
-186.7
-186.8
-186.8
-186.8
Cl
HO
F
F
3ai minor
19F NMR
(470 MHz, CDCl3)
-114.72
-114.78
-114.84
f1 (ppm)
-186.5
-186.6
-186.7
-186.8
-186.9
f1 (ppm)
1.0
1.0
-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
f1 (ppm)

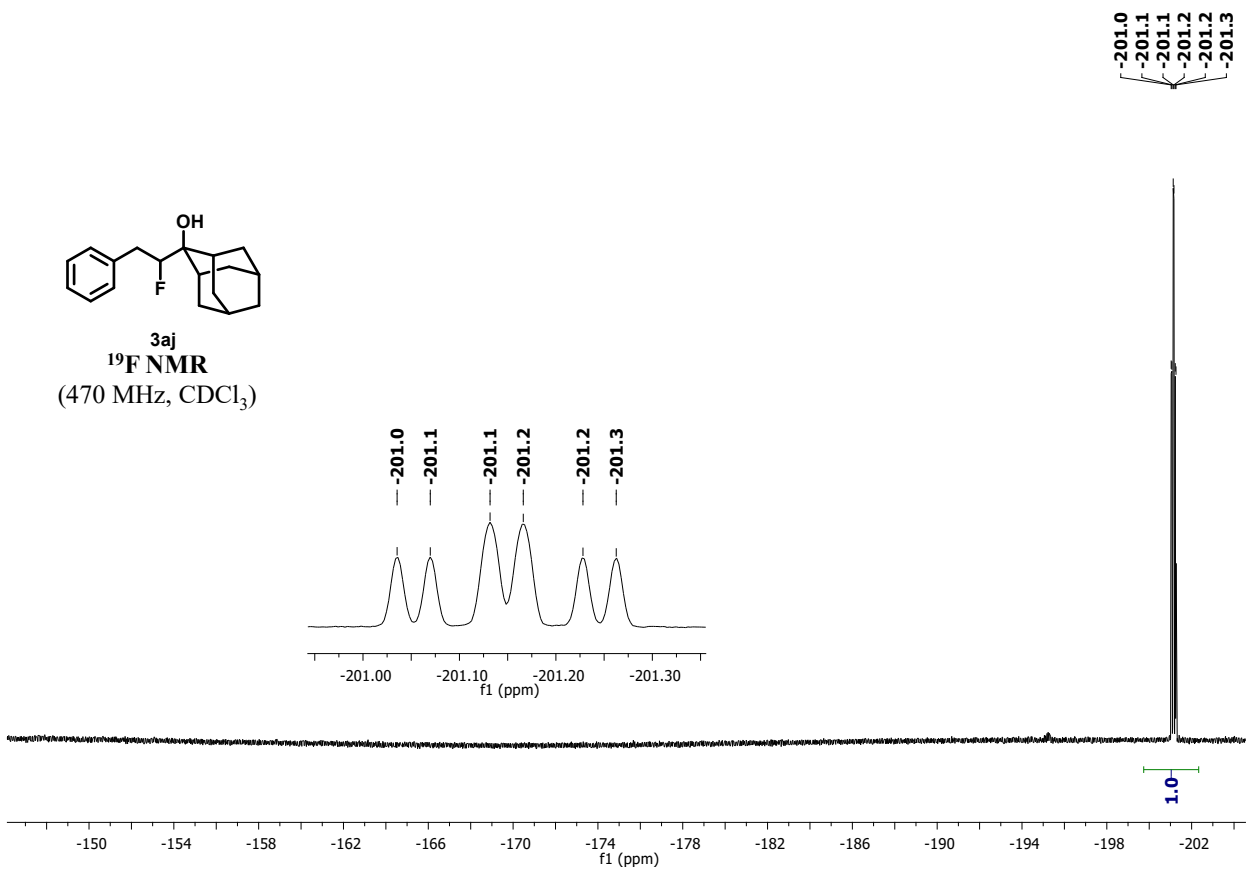

7.34
7.32
7.31
7.31
7.27
7.25
7.24
7.23
5.25
5.25
5.23
5.23
5.16
5.15
5.14
5.13
3.08
3.06
3.05
3.03
2.92
2.92
2.89
2.84
2.83
2.81
2.80
2.06
1.94
1.88
1.85
1.85
1.79
1.79
1.77
1.77
1.76
1.73
1.60
1.59
OH
F
3aj
1H NMR
(500 MHz, CDCl3)
2.0
3.0
1.0
1.1
1.2
1.1
1.2
1.1
2.3
2.2
6.0
2.2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



3aj

^{13}C NMR

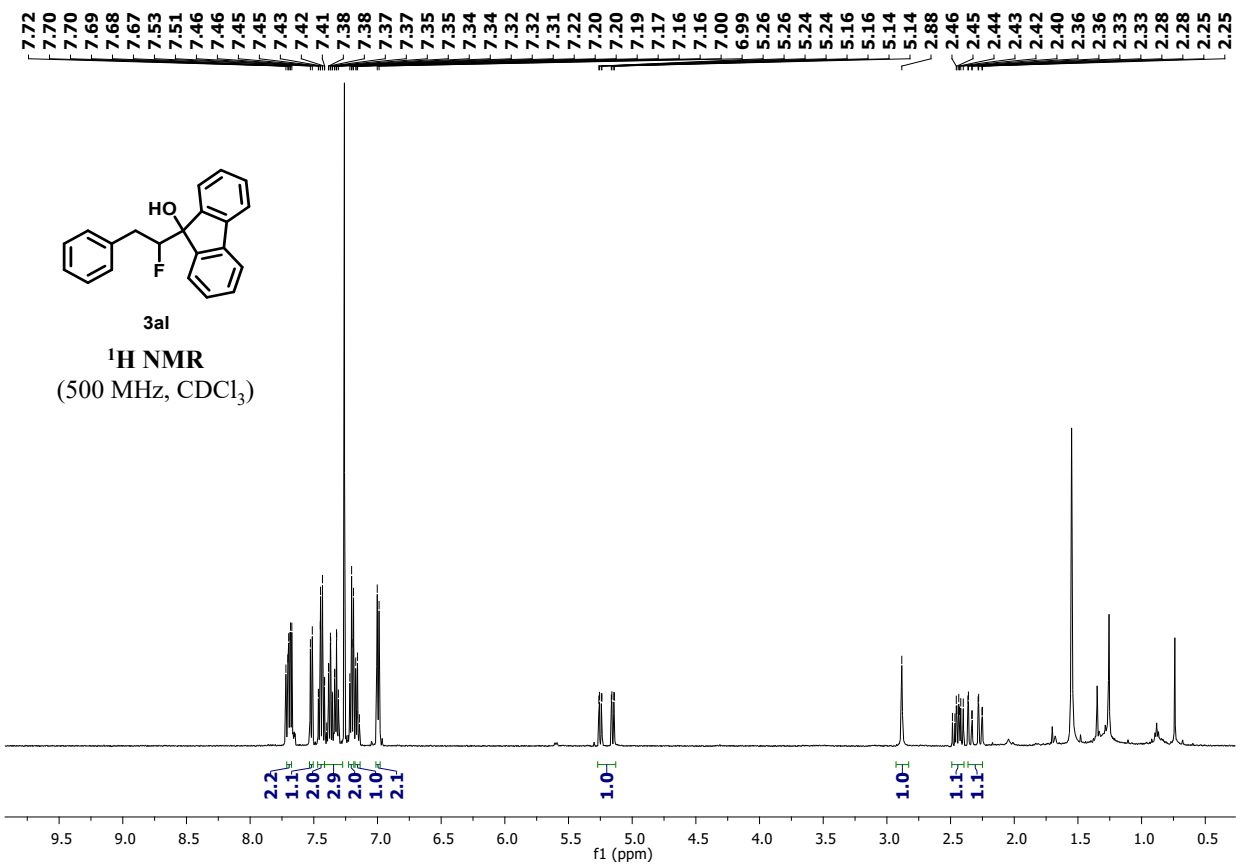
(125 MHz, $CDCl_3$)



3aj

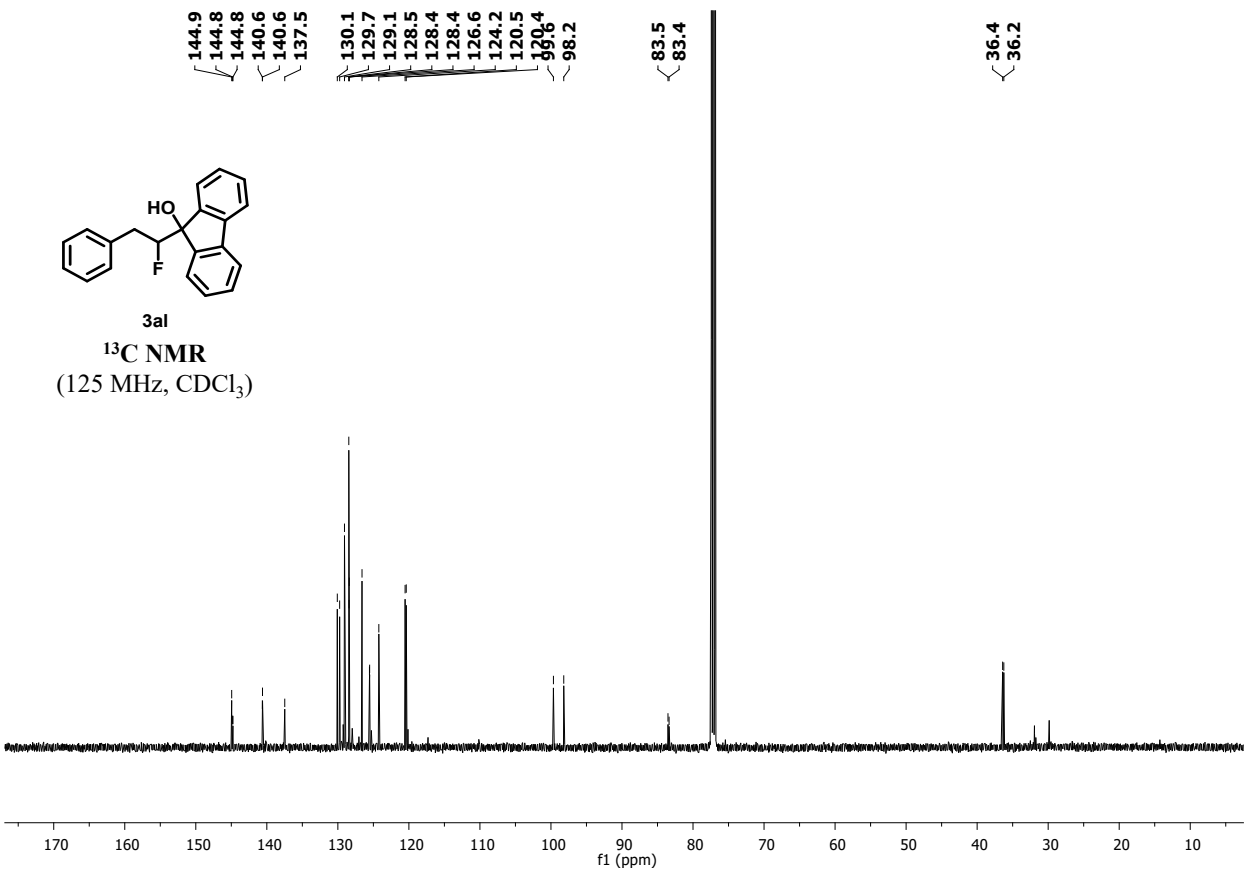
^{19}F NMR

(470 MHz, $CDCl_3$)



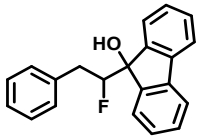
3al

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



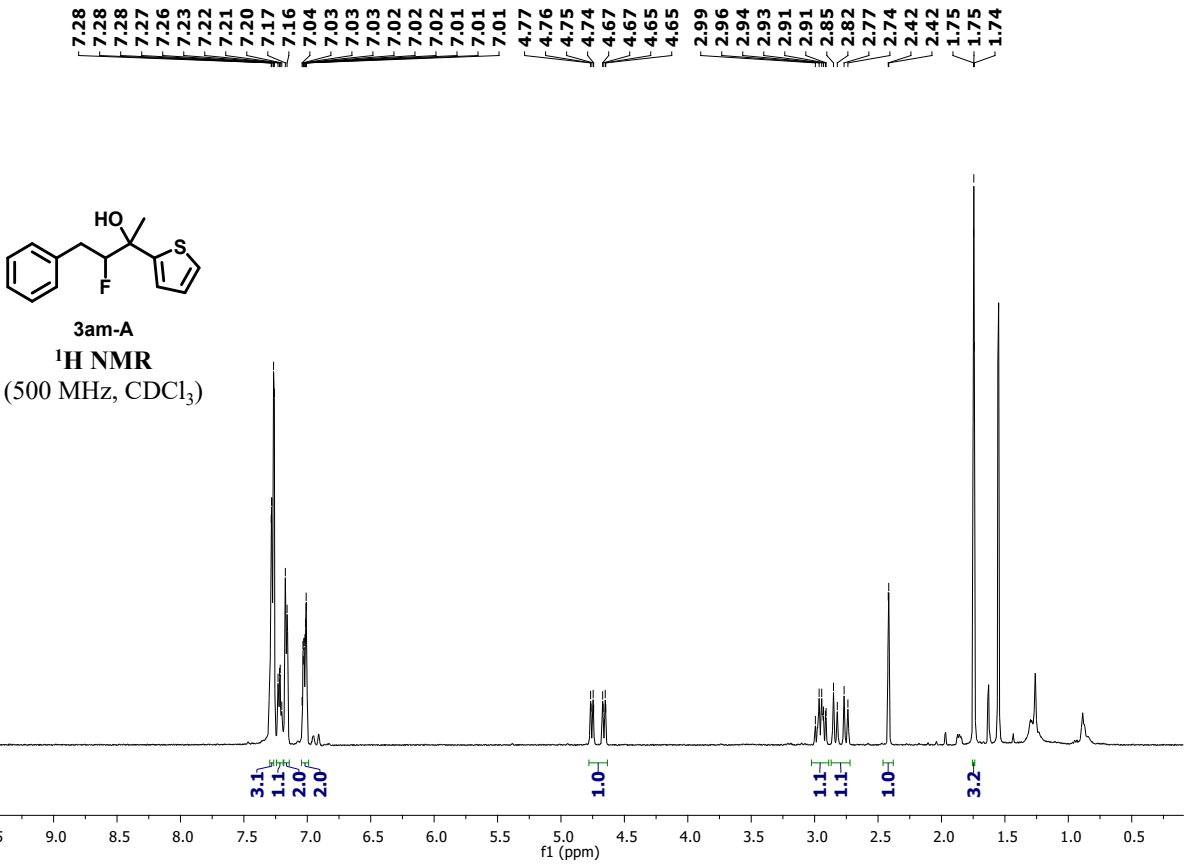
3al

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



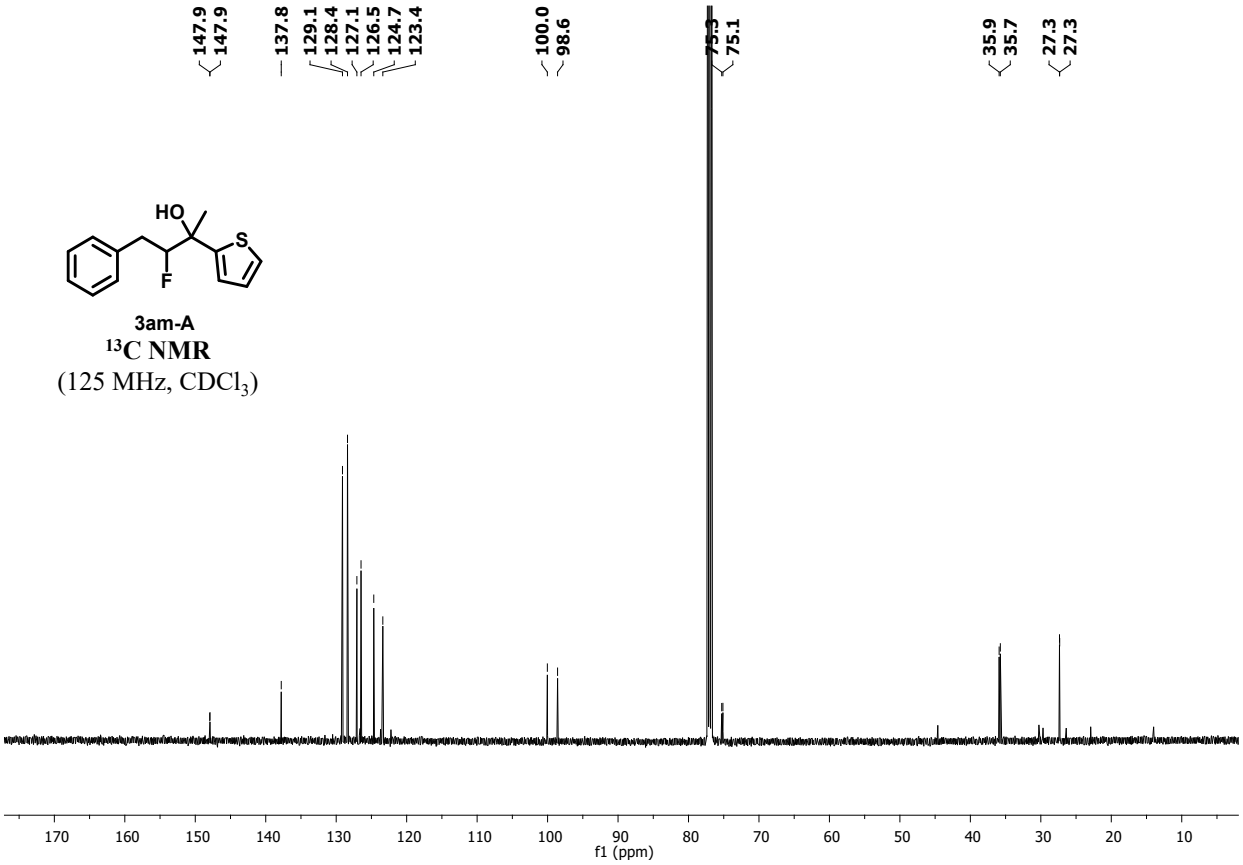
3al

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



3am-A

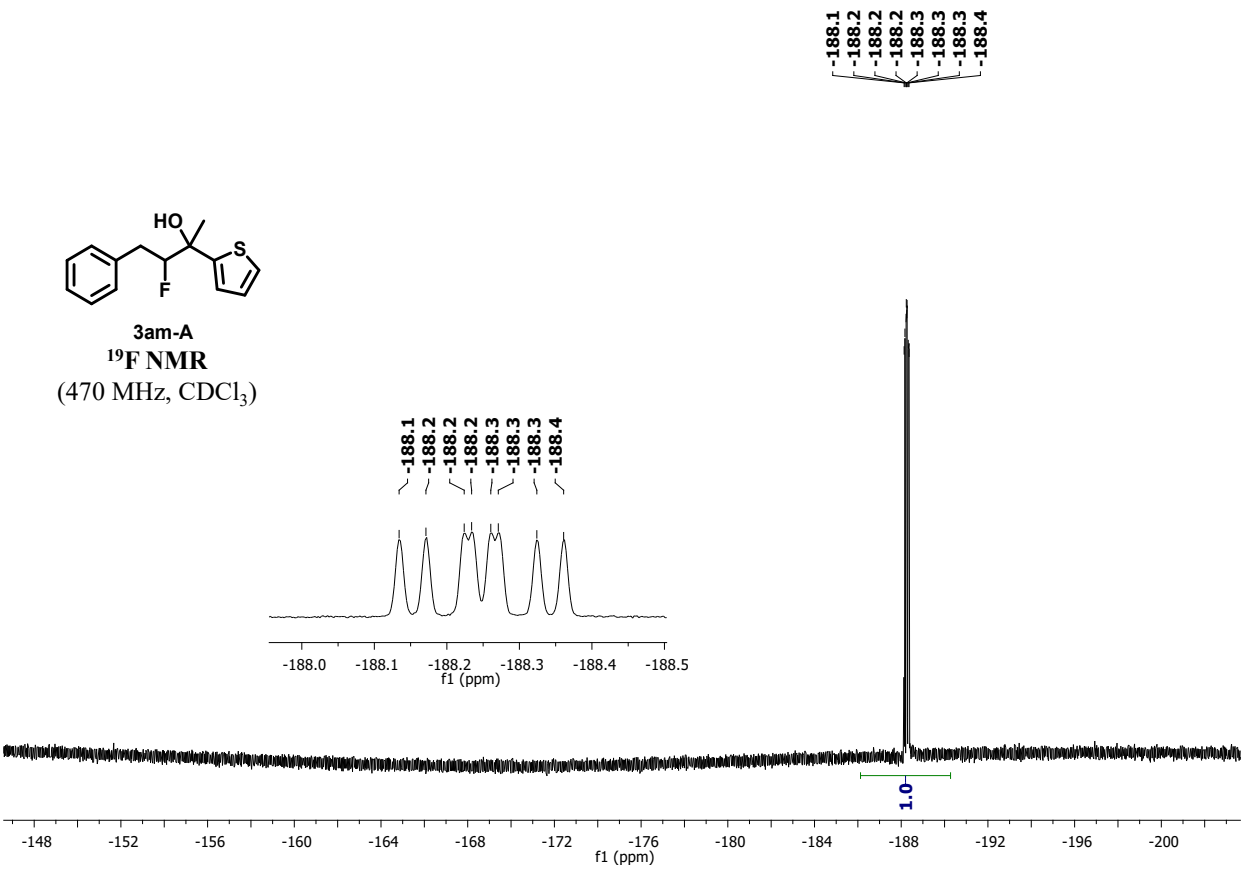
^{1}H NMR
(500 MHz, $CDCl_3$)



3am-A

^{13}C NMR

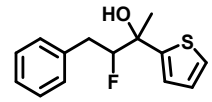
(125 MHz, $CDCl_3$)



3am-A

^{19}F NMR

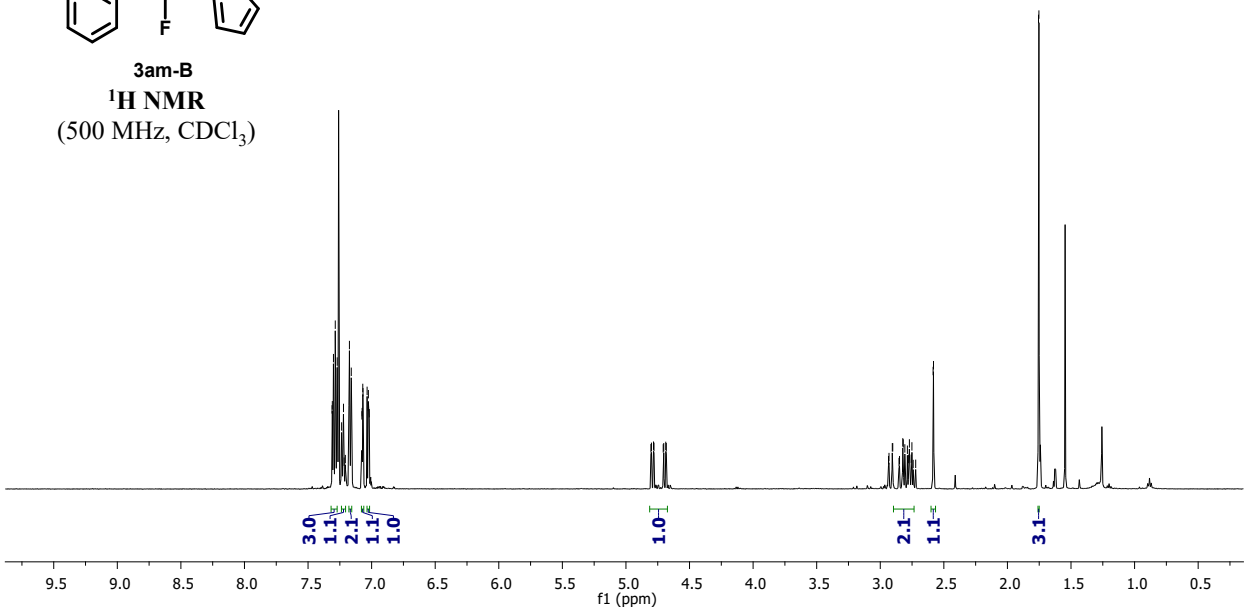
(470 MHz, $CDCl_3$)

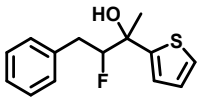


3am-B

^{1}H NMR

(500 MHz, $CDCl_3$)

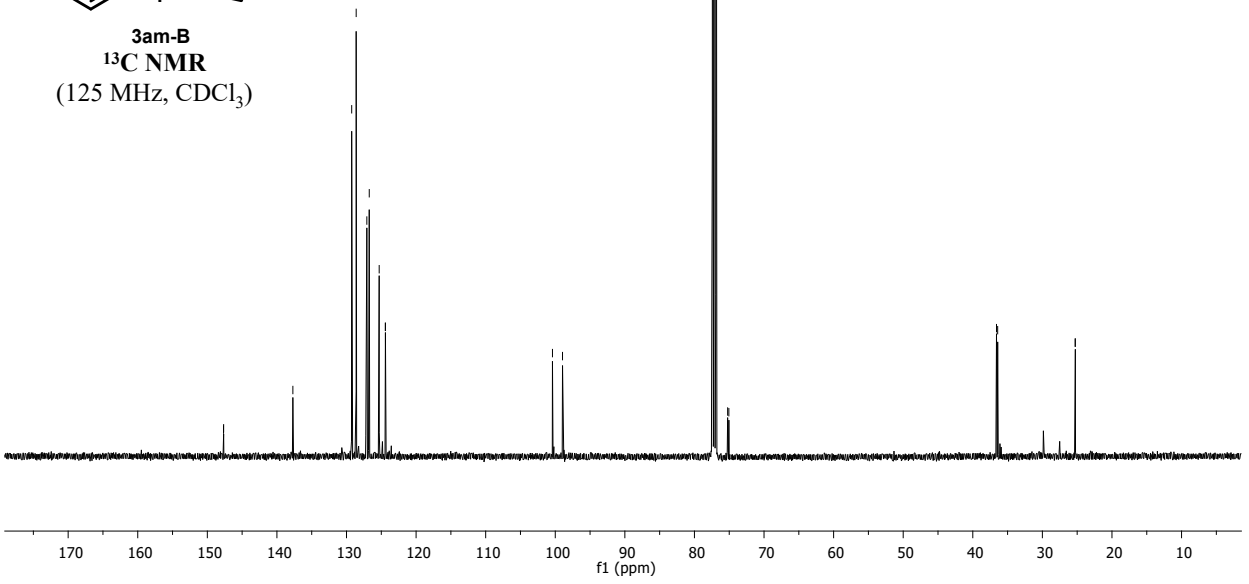


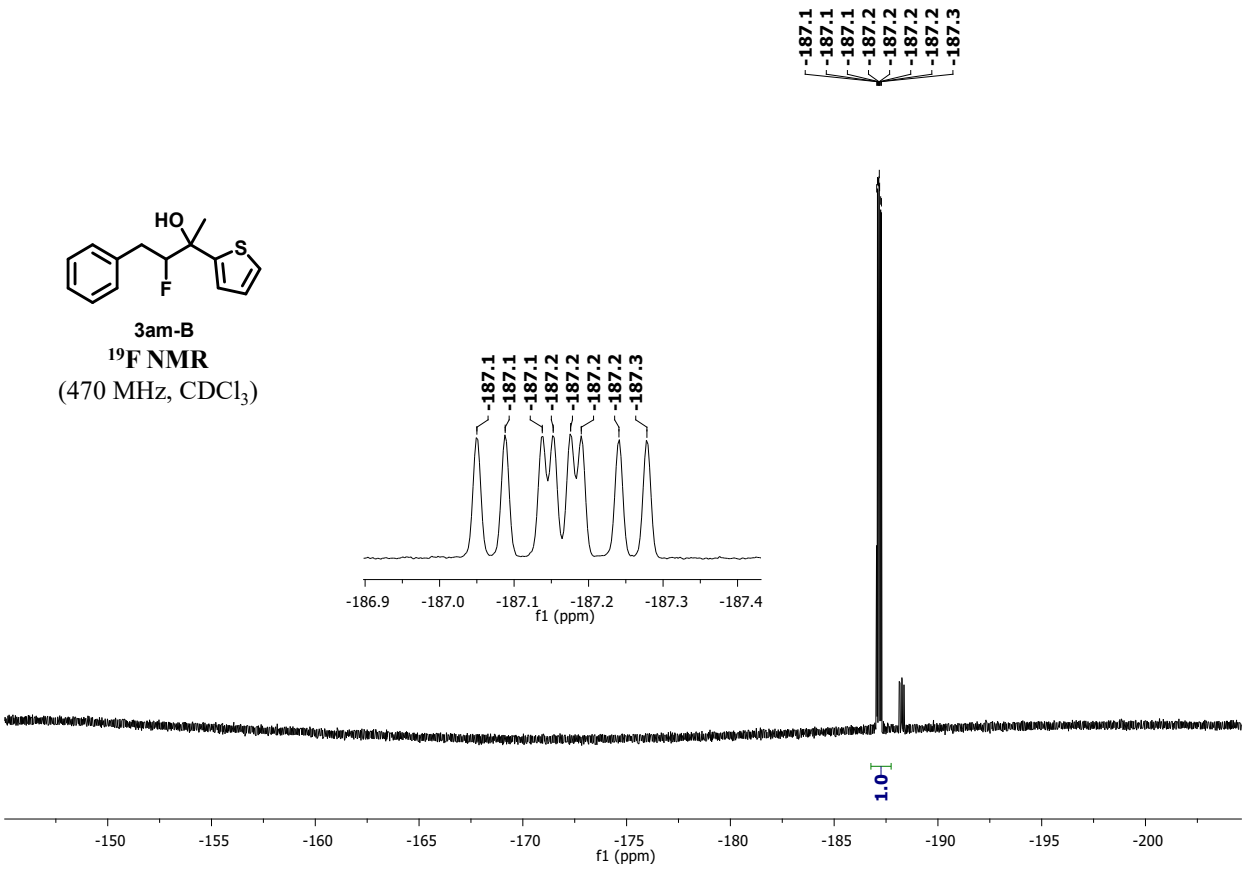


3am-B

^{13}C NMR

(125 MHz, $CDCl_3$)

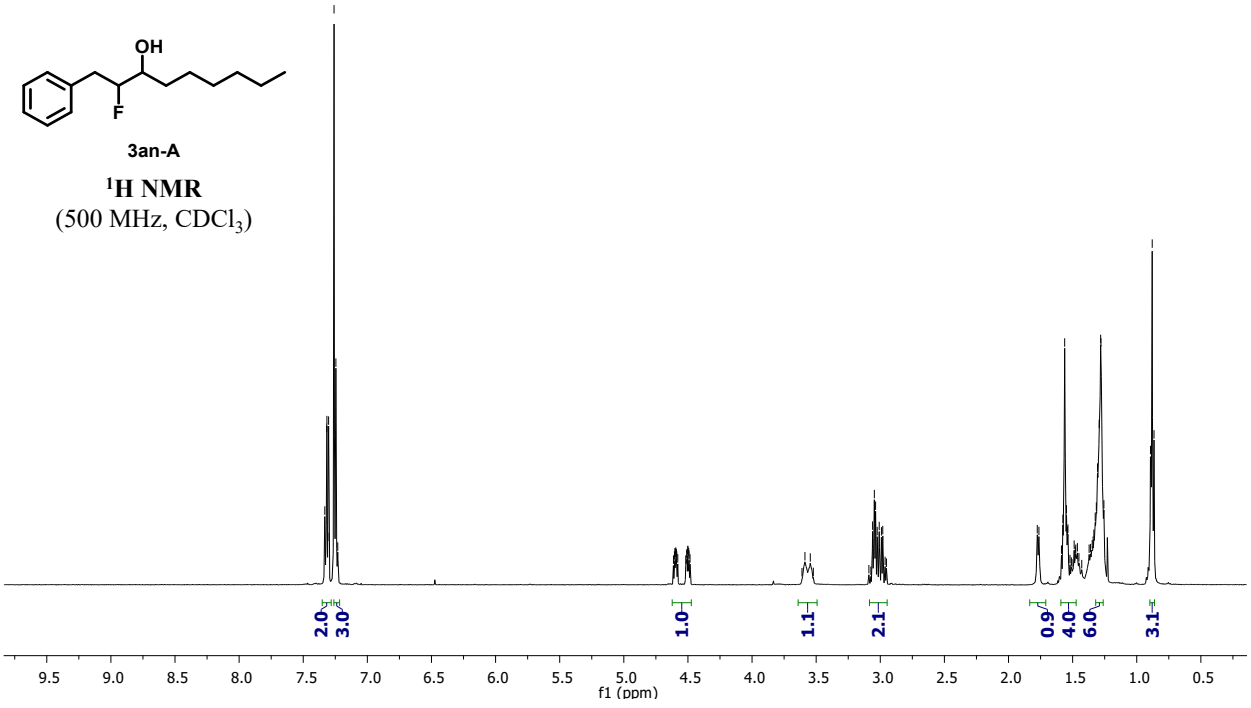




3am-B

^{19}F NMR

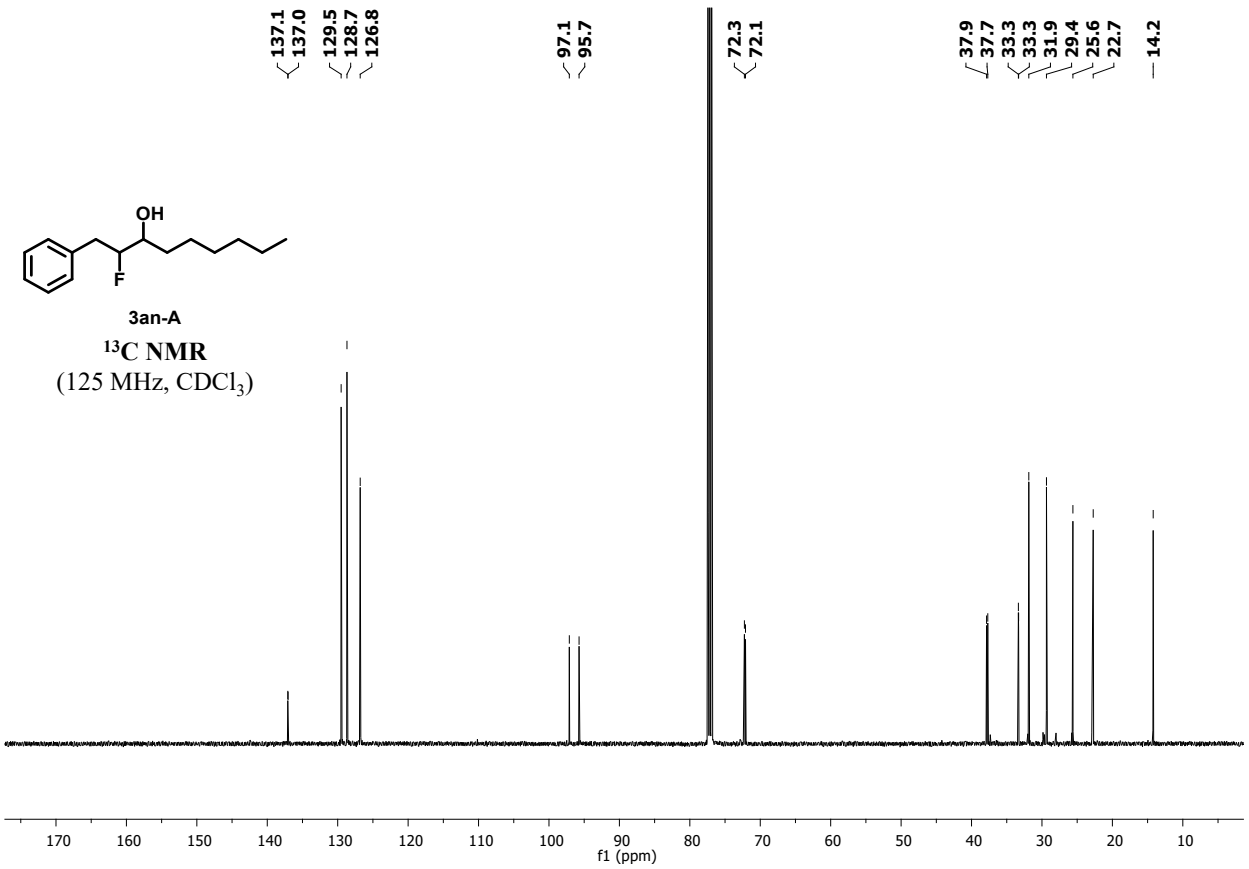
(470 MHz, $CDCl_3$)



3an-A

^{1}H NMR

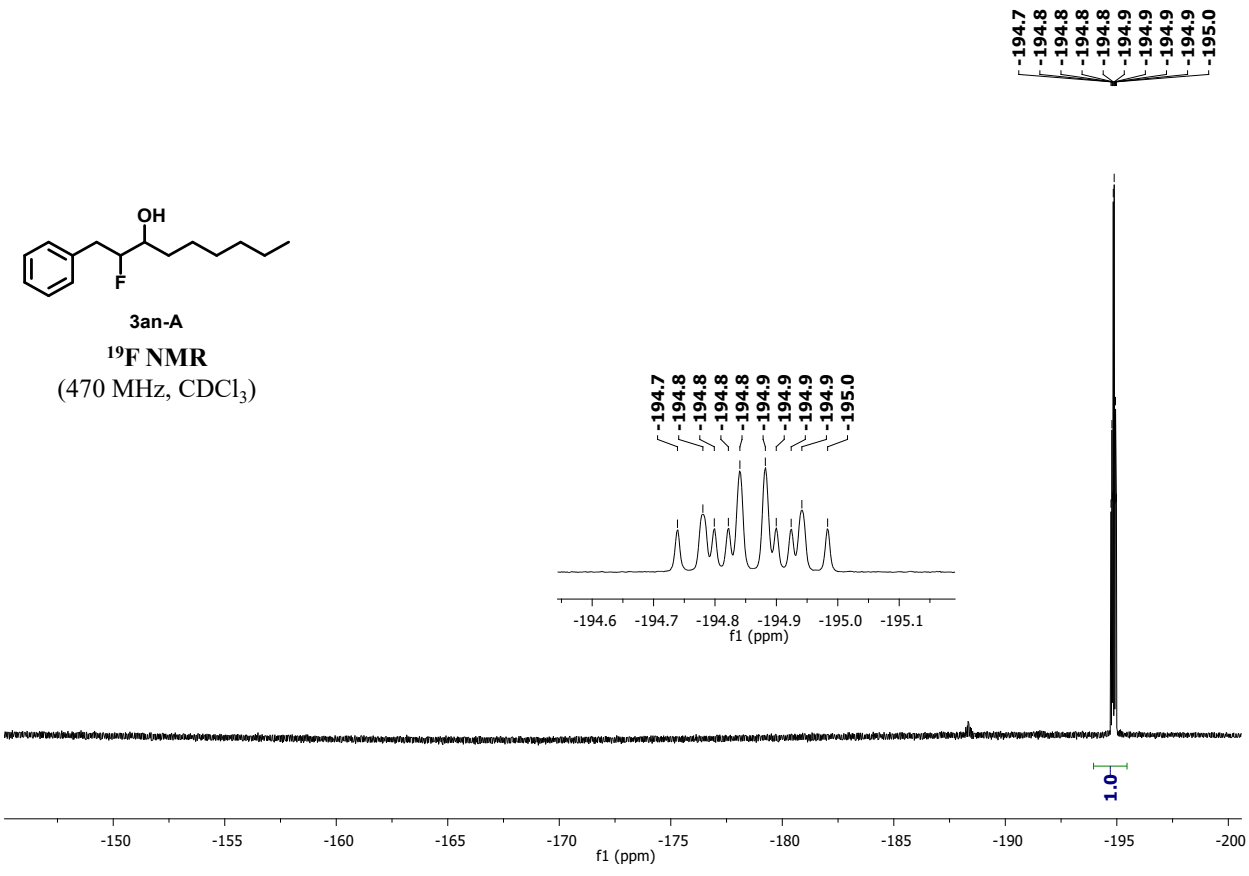
(500 MHz, $CDCl_3$)



3an-A

^{13}C NMR

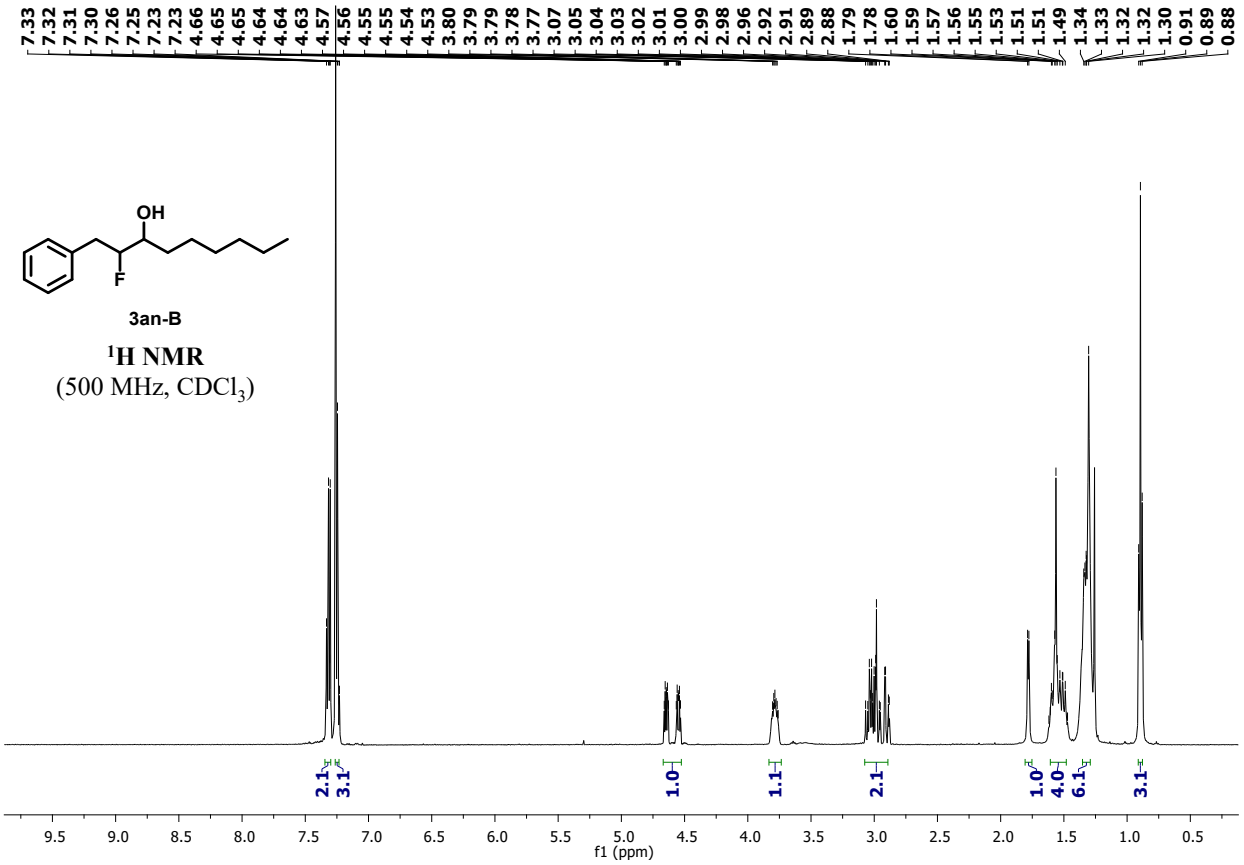
(125 MHz, $CDCl_3$)



3an-A

^{19}F NMR

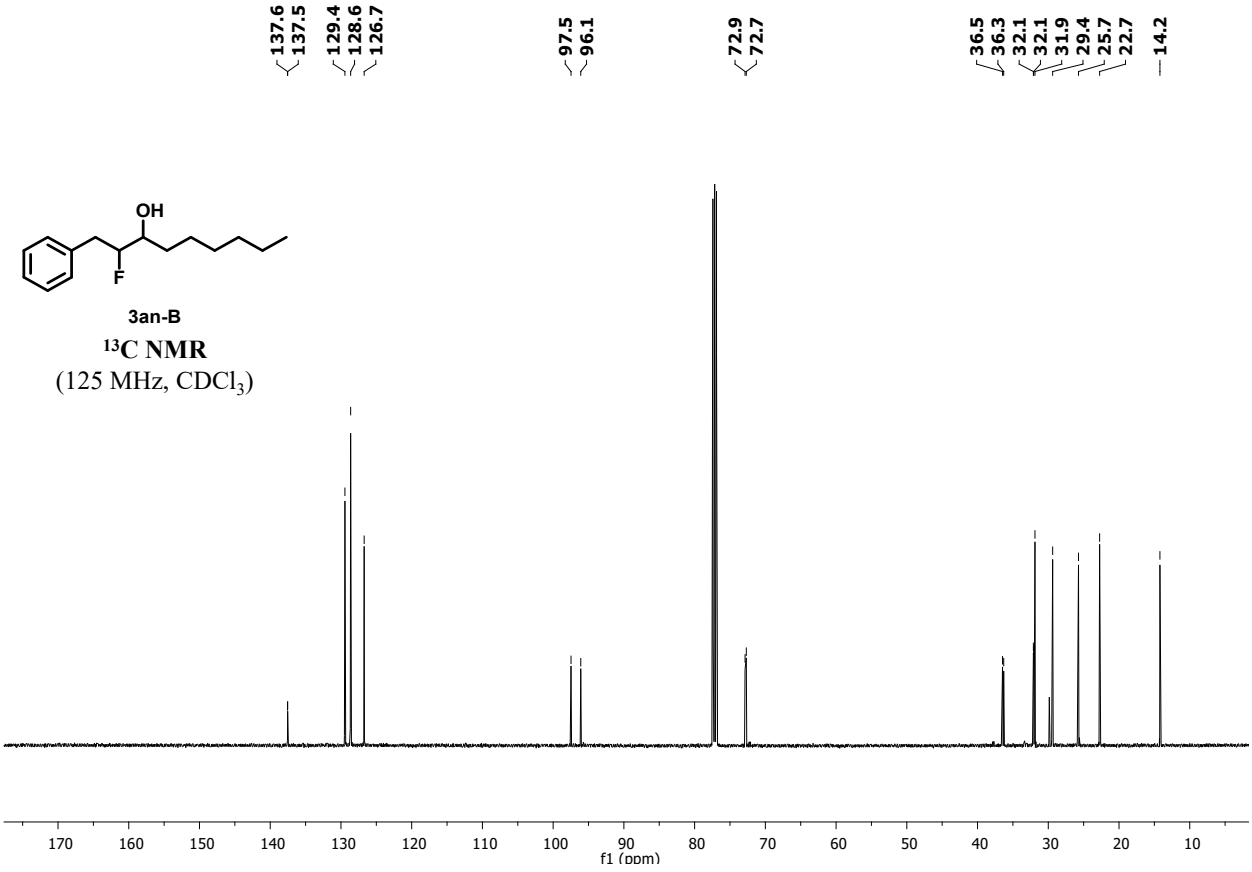
(470 MHz, $CDCl_3$)



3an-B

^{1}H NMR

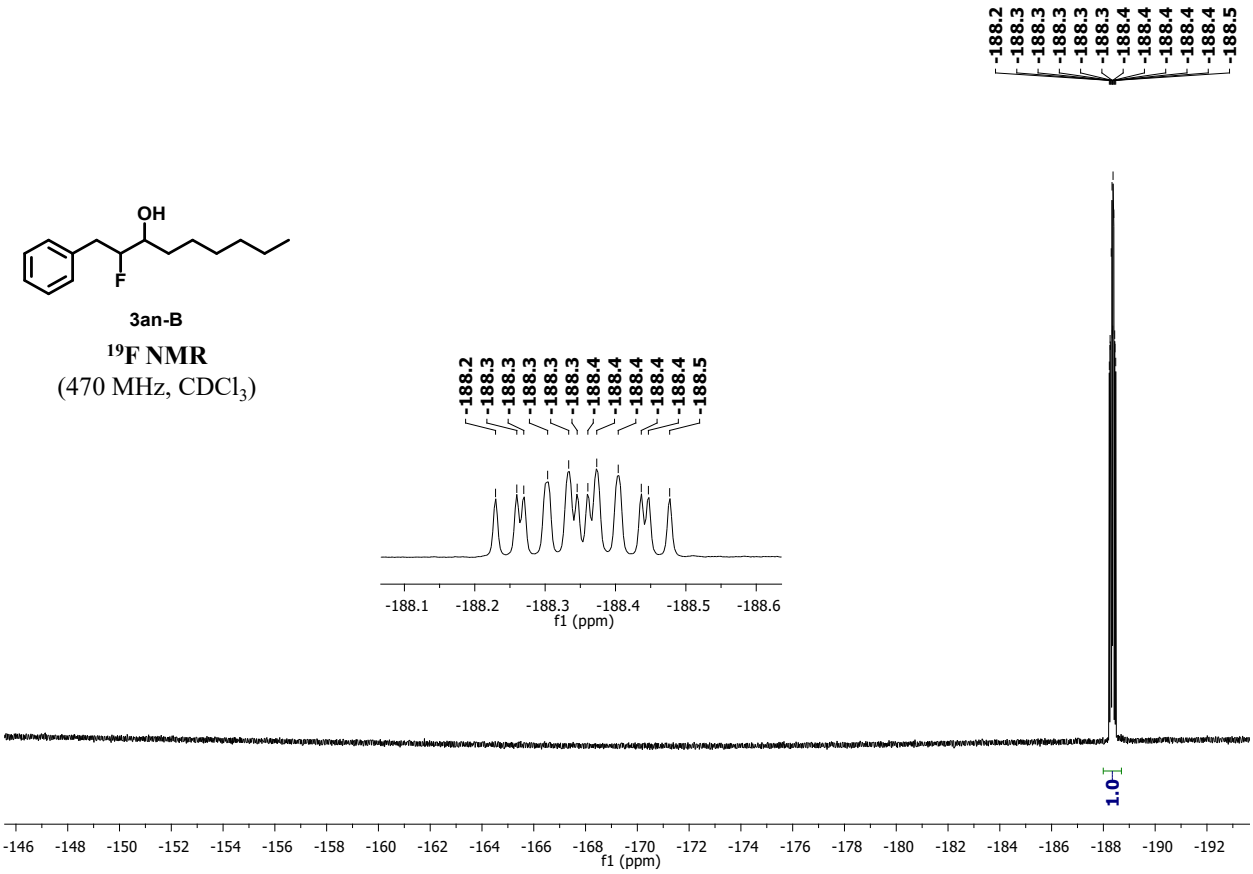
(500 MHz, $CDCl_3$)



3an-B

^{13}C NMR

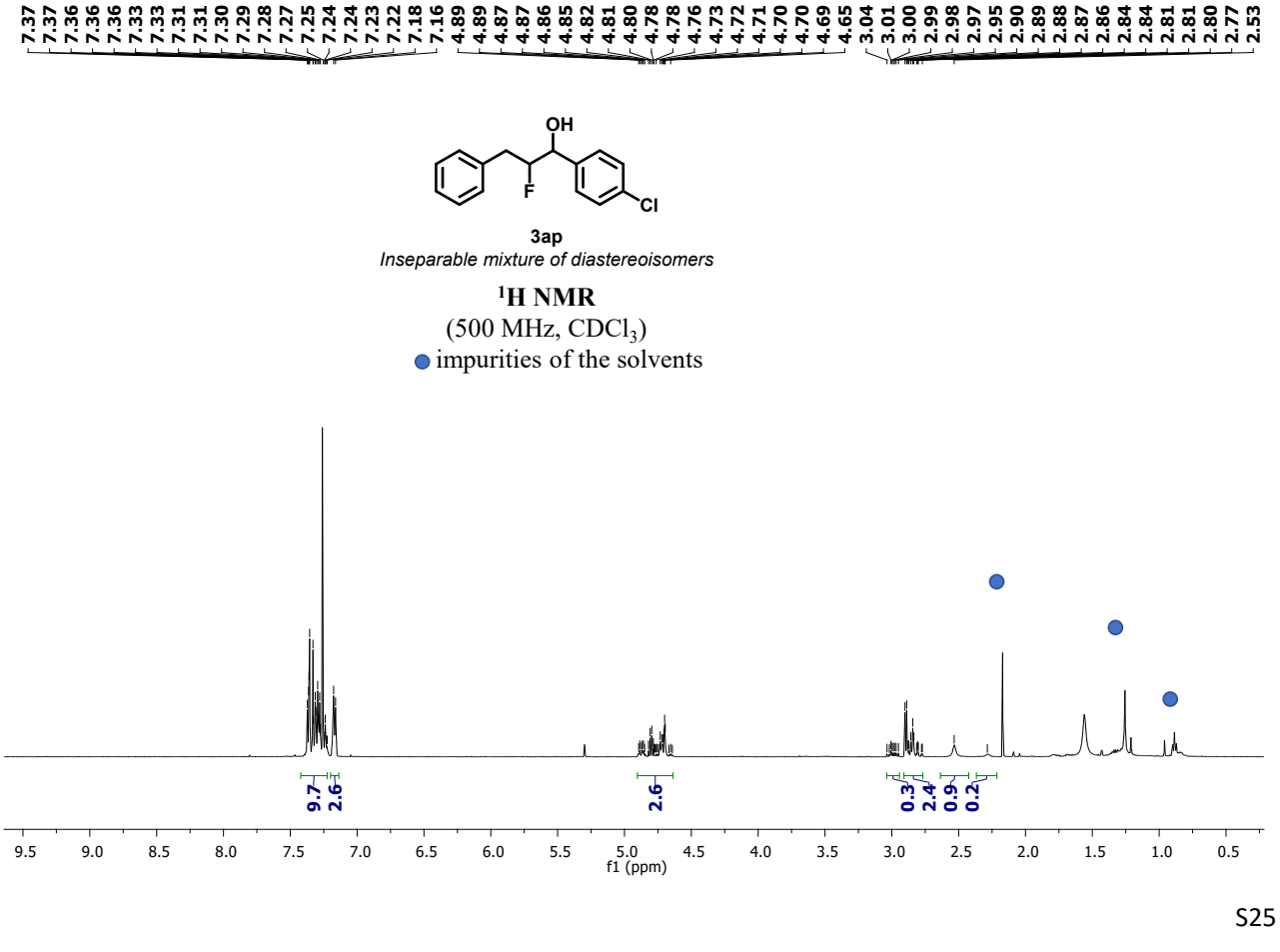
(125 MHz, $CDCl_3$)



3an-B

^{19}F NMR

(470 MHz, $CDCl_3$)



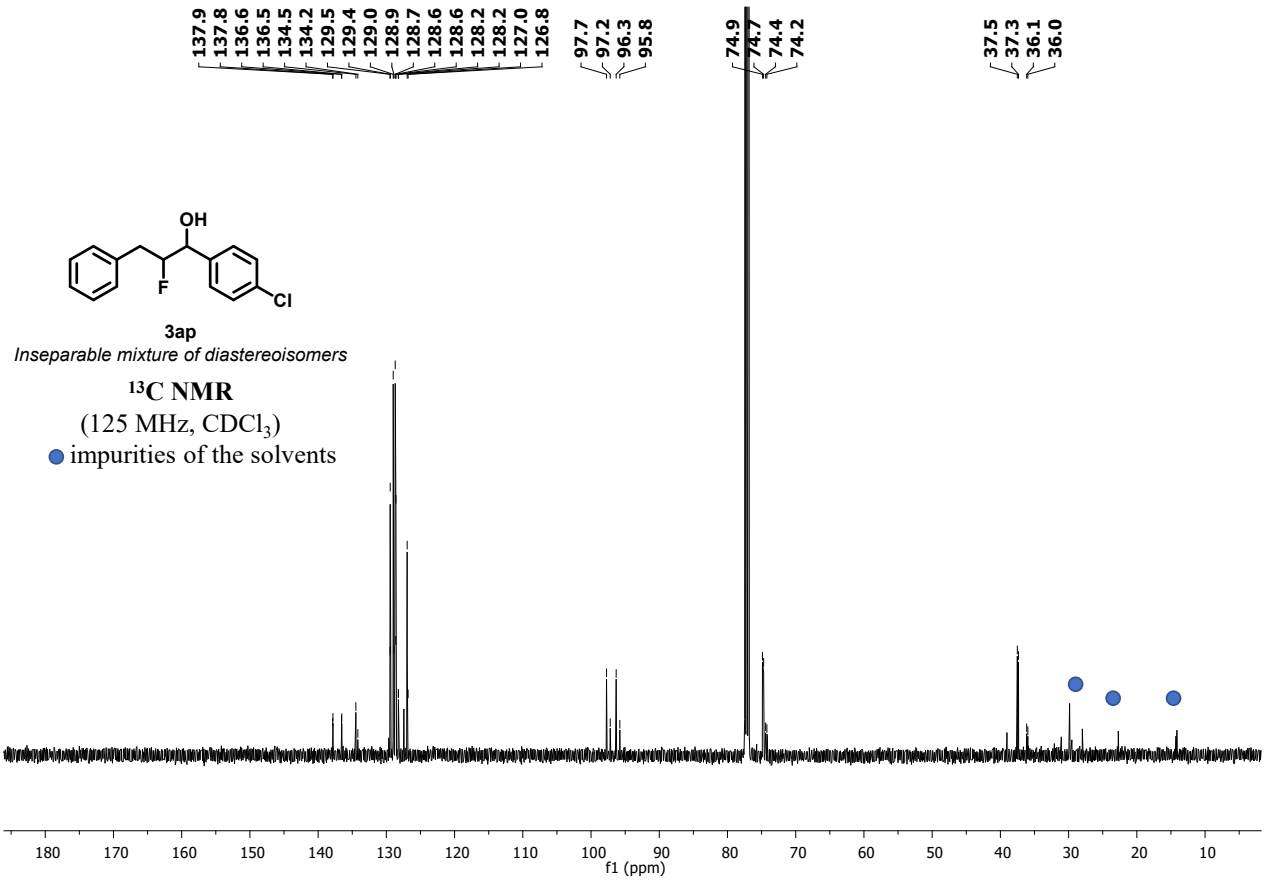
3ap

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

● impurities of the solvents



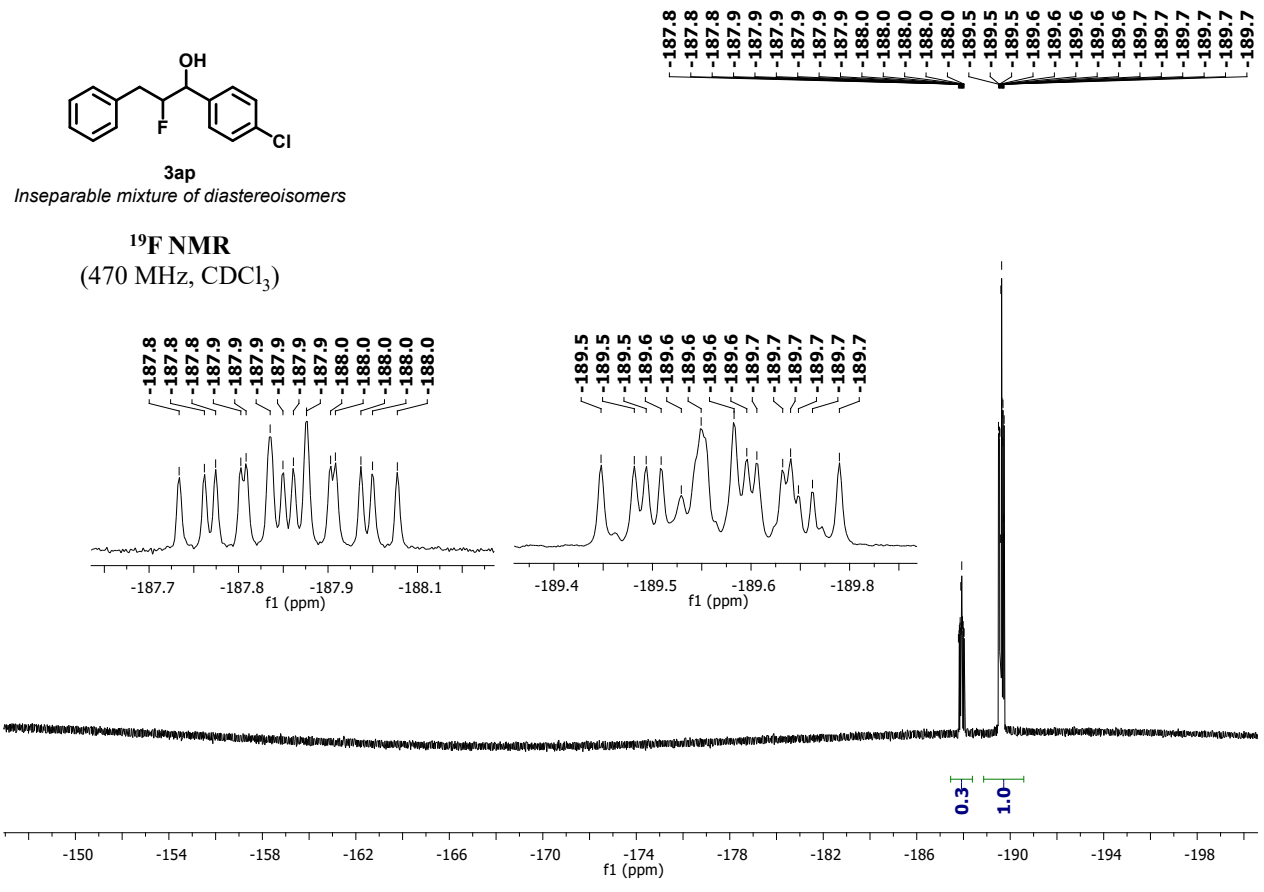
3ap

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

● impurities of the solvents

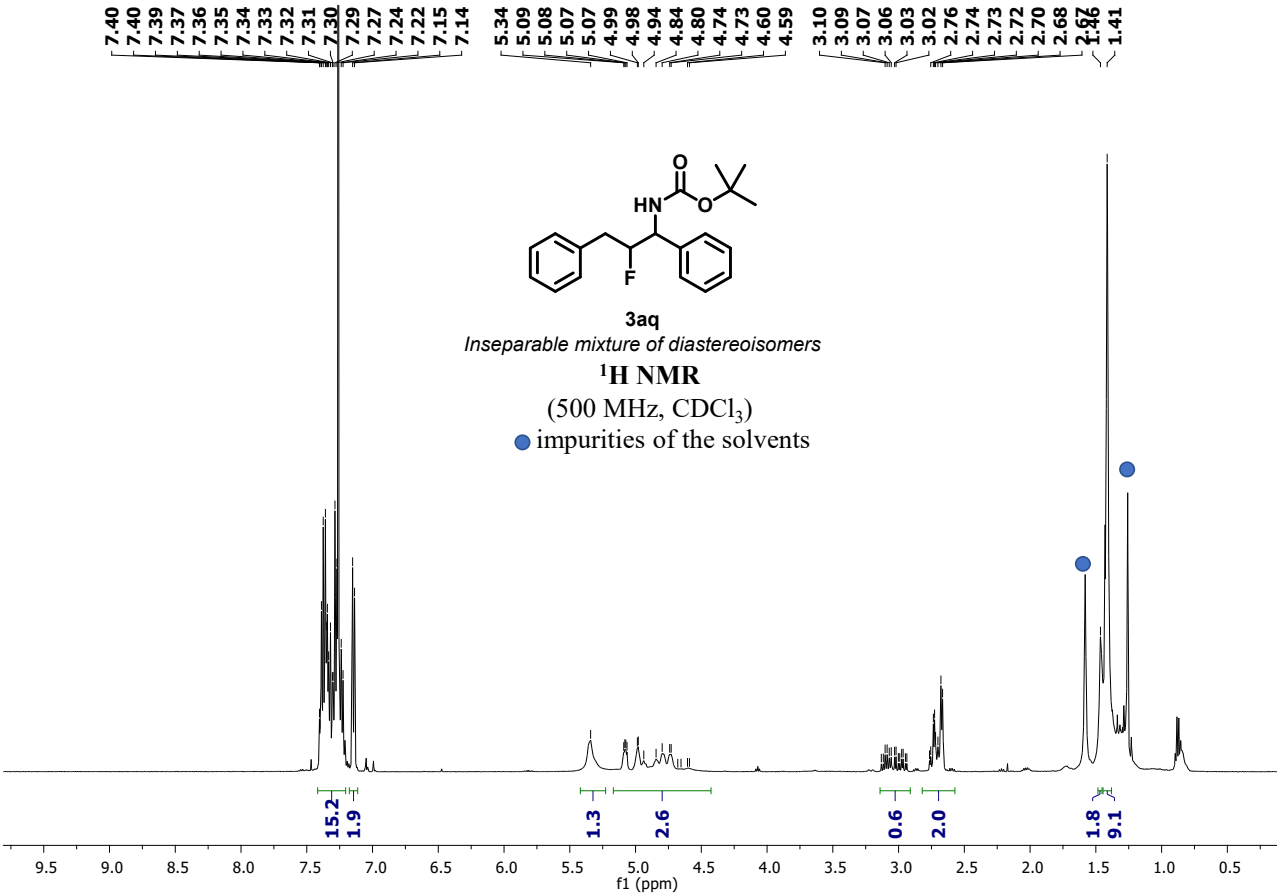


3ap

Inseparable mixture of diastereoisomers

^{19}F NMR

(470 MHz, $CDCl_3$)



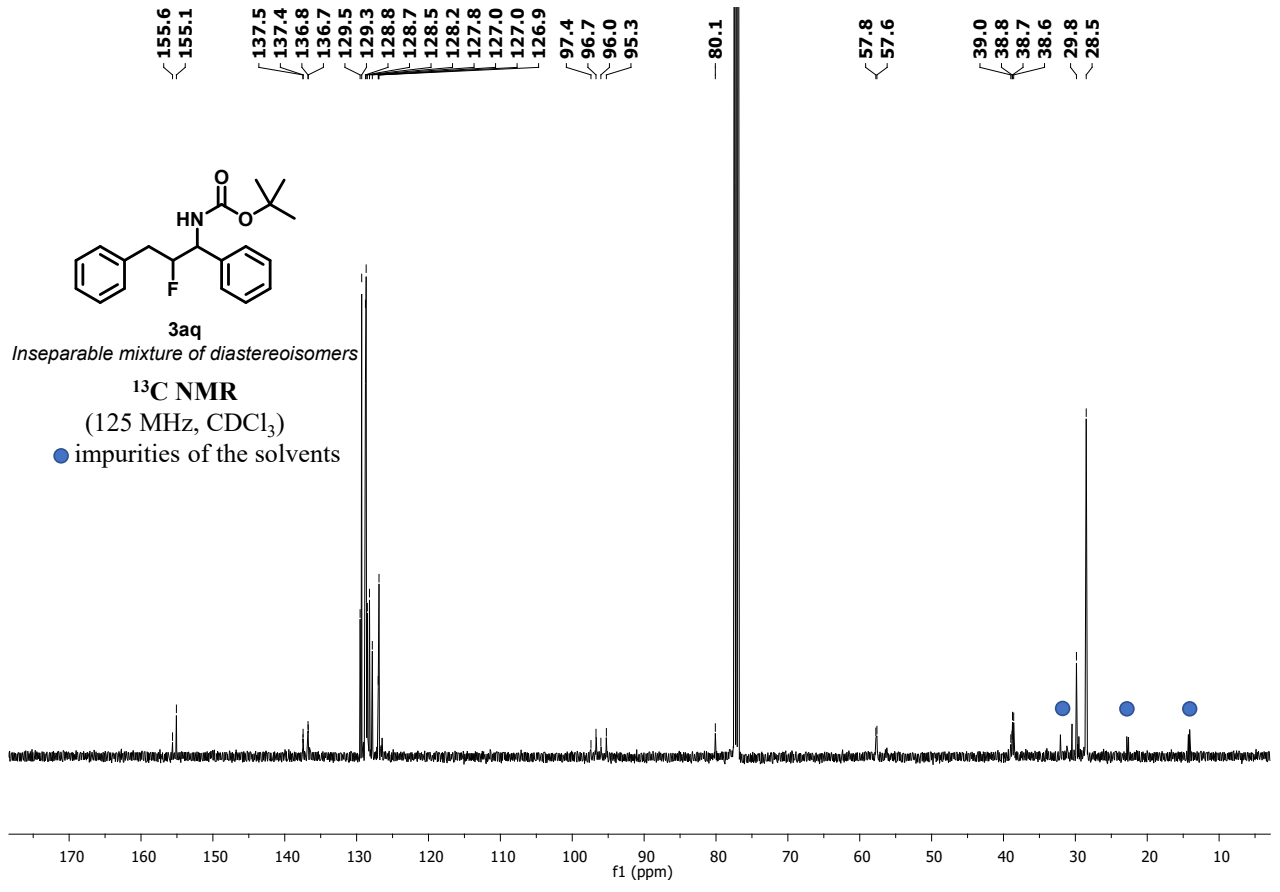
3aq

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

● impurities of the solvents



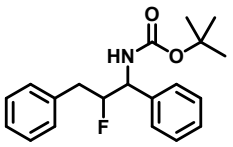
3aq

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

● impurities of the solvents

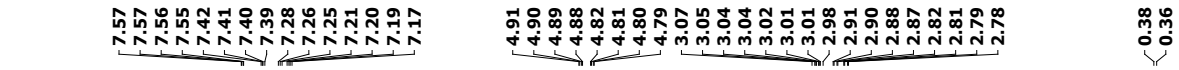


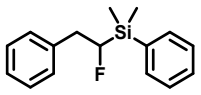
3aq

Inseparable mixture of diastereoisomers

^{19}F NMR

(470 MHz, $CDCl_3$)

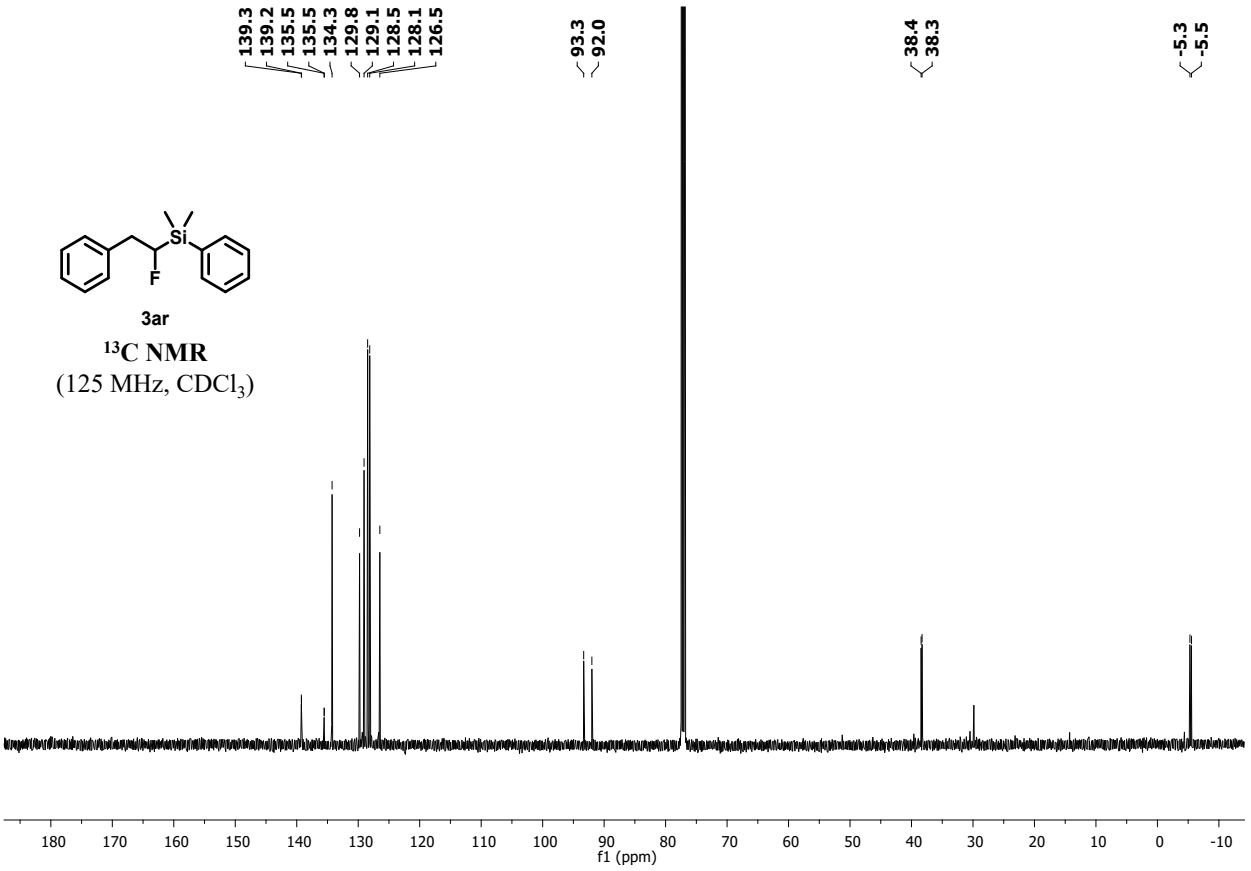




3ar

^{1}H NMR

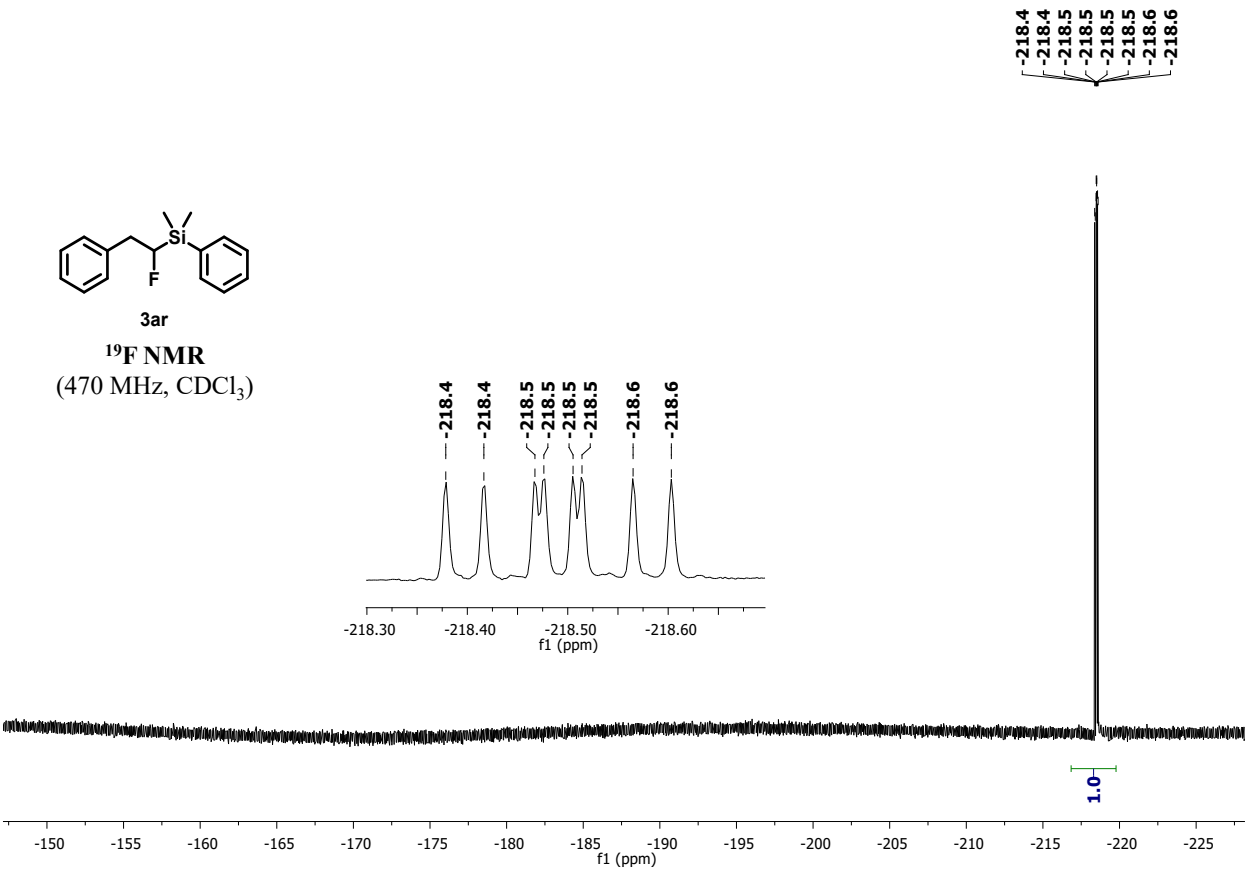
(500 MHz, $CDCl_3$)



3ar

^{13}C NMR

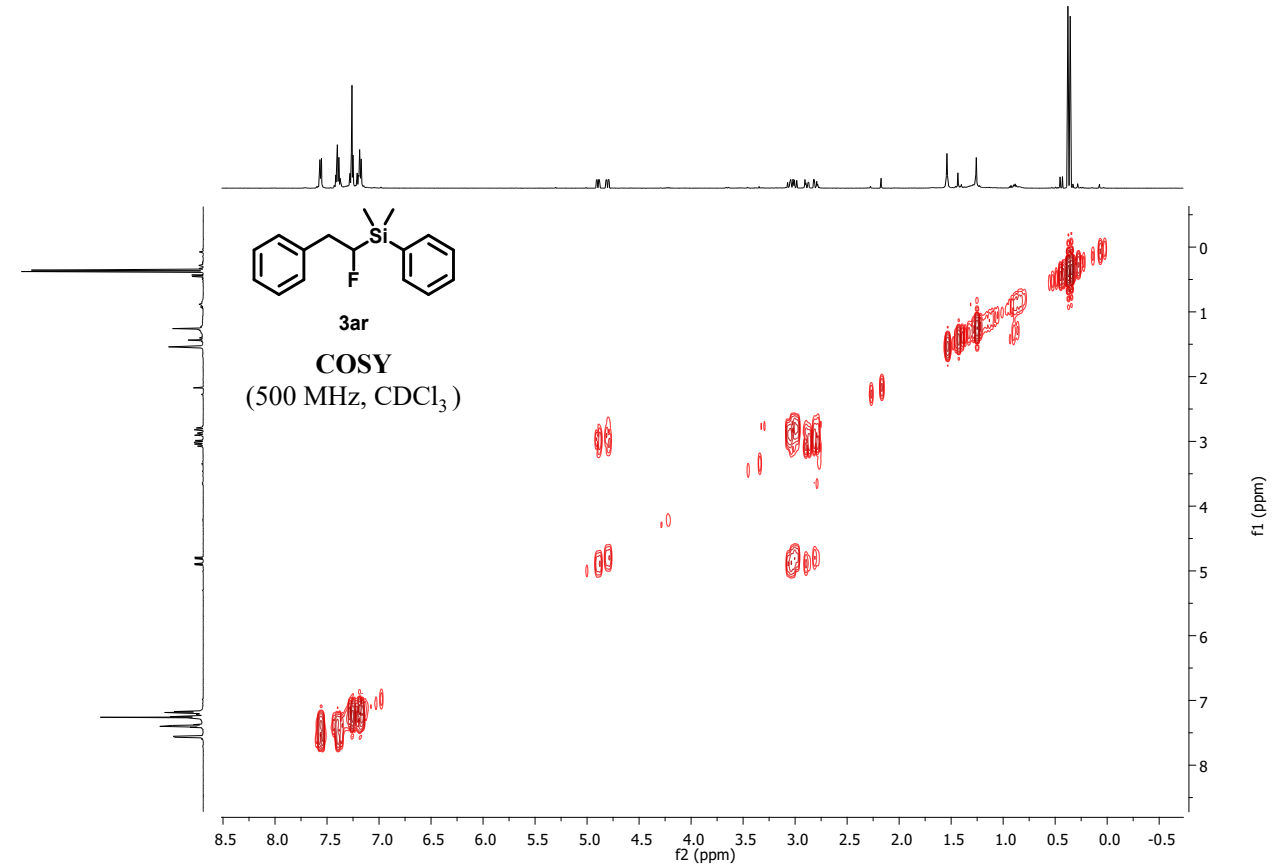
(125 MHz, $CDCl_3$)

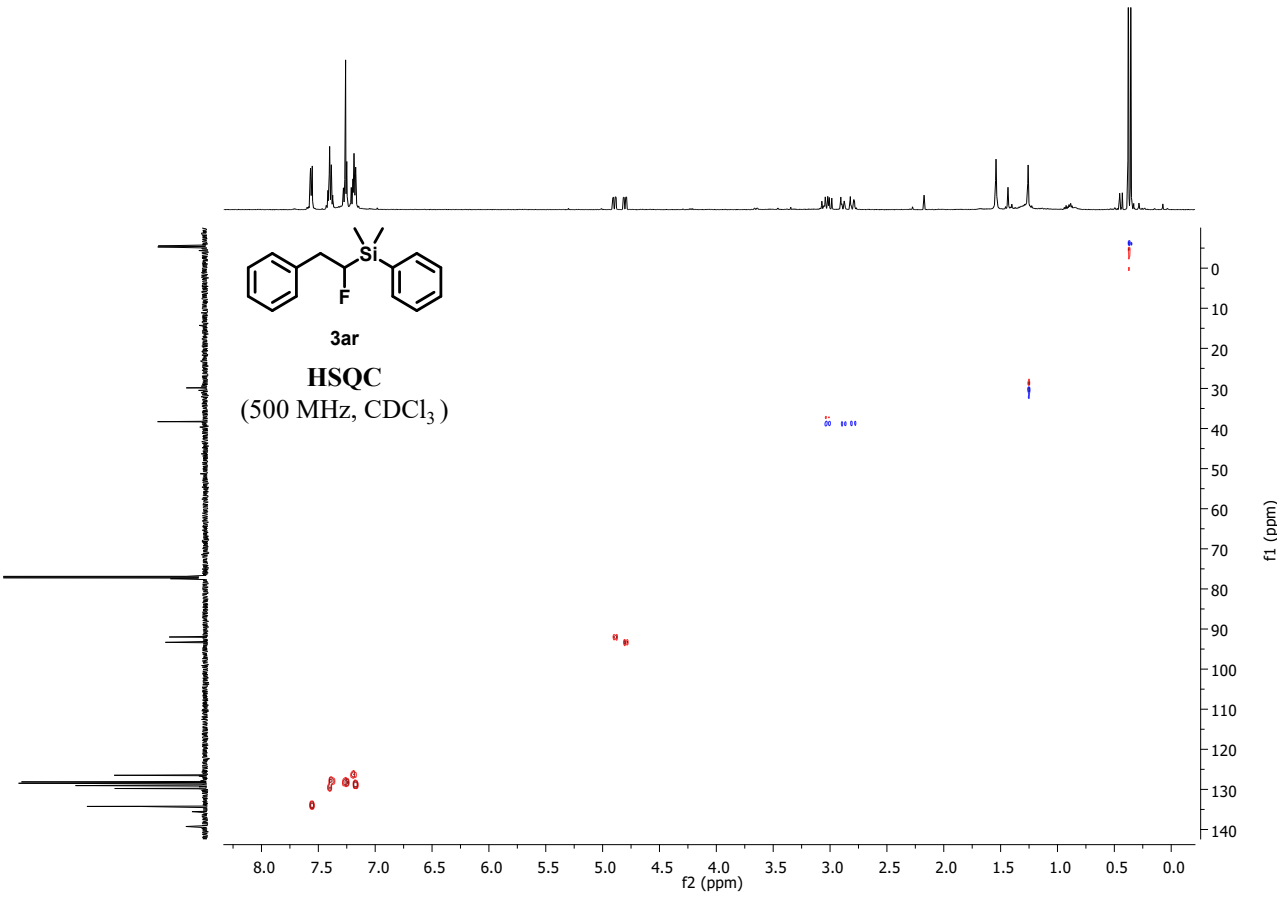


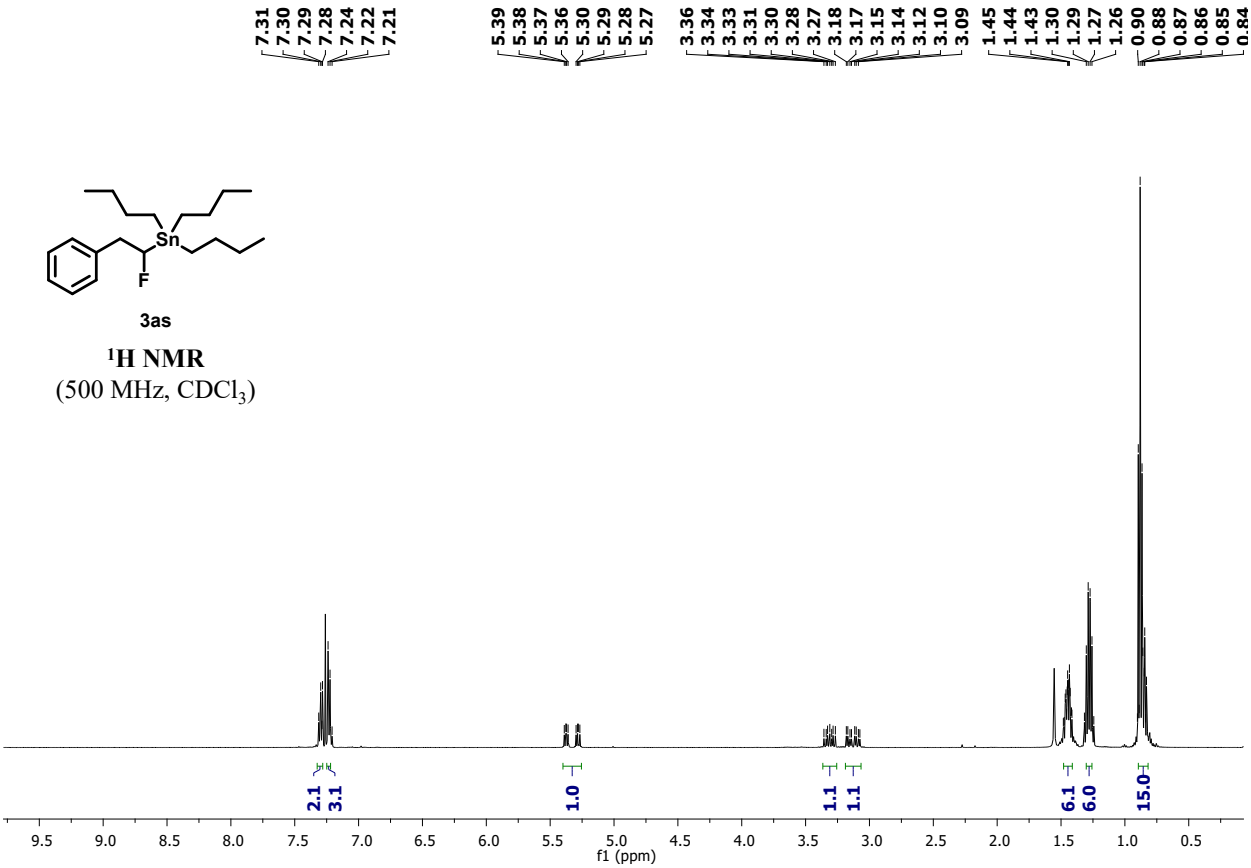
3ar

^{19}F NMR

(470 MHz, $CDCl_3$)

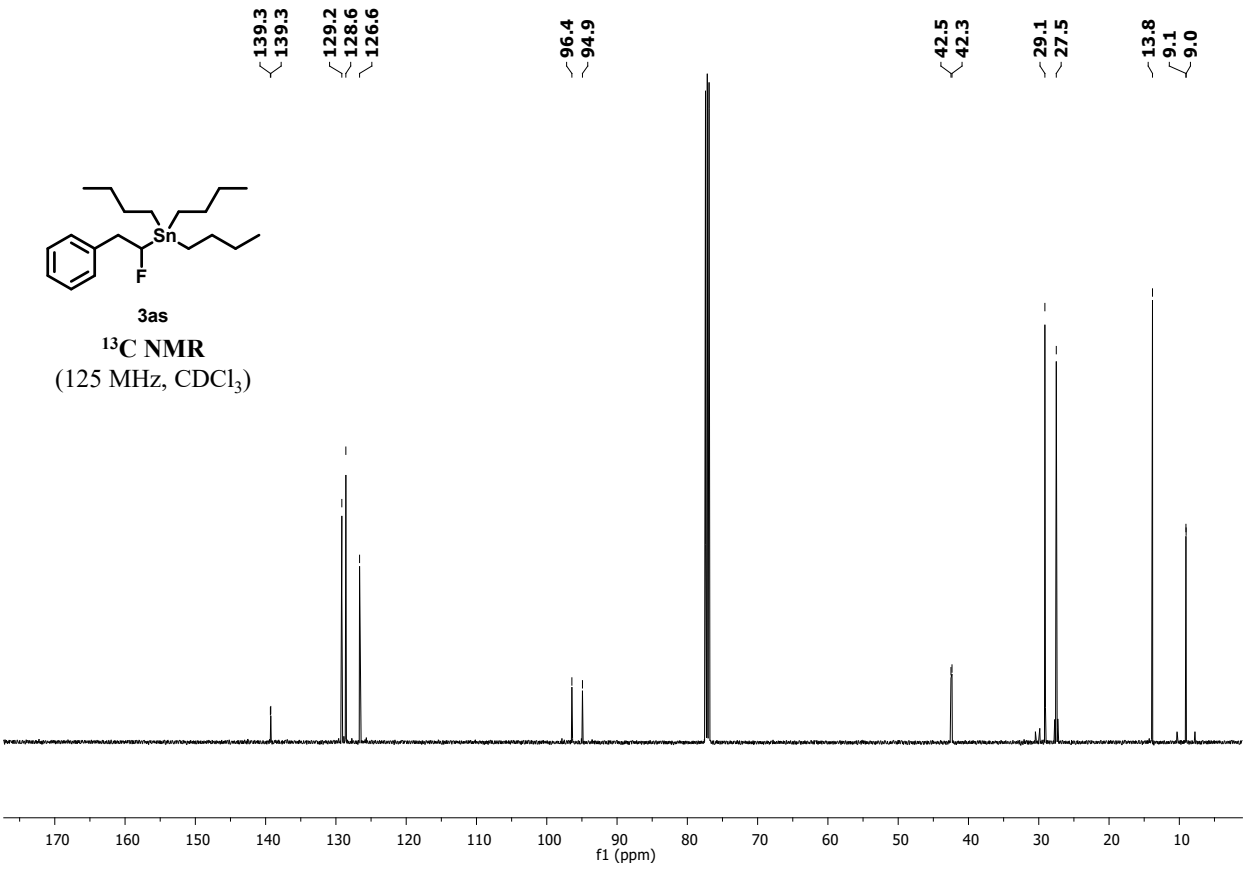

Si
F
3ar
COSY
(500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


Si
F
3ar
HSQC
(500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)



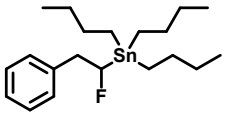
3as

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



3as

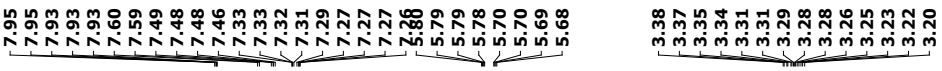
^{13}C NMR
(125 MHz, $CDCl_3$)

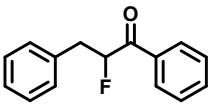


3as

^{19}F NMR

(470 MHz, $CDCl_3$)

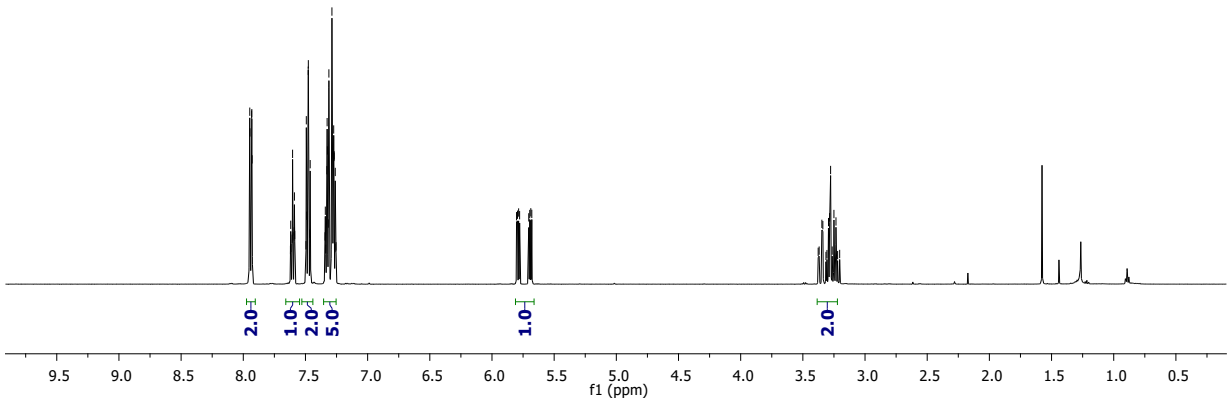


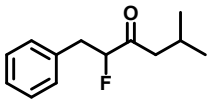


3at

^{1}H NMR

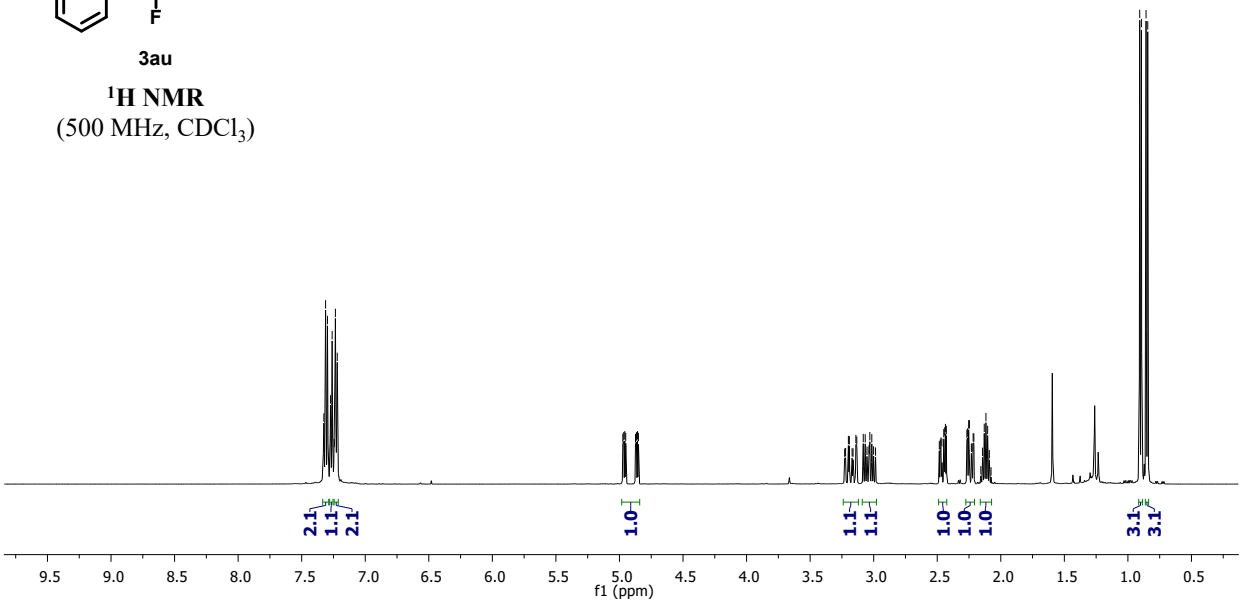
(500 MHz, $CDCl_3$)

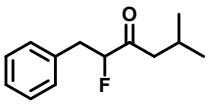




3au

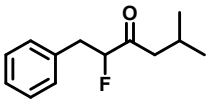
^{1}H NMR
(500 MHz, $CDCl_3$)





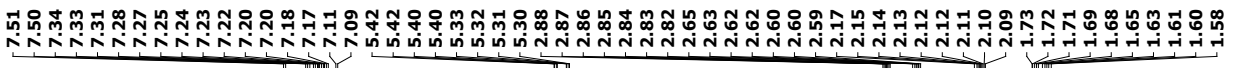
3au

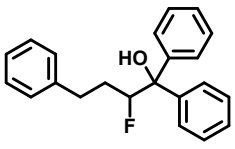
^{13}C NMR
(125 MHz, $CDCl_3$)



3au

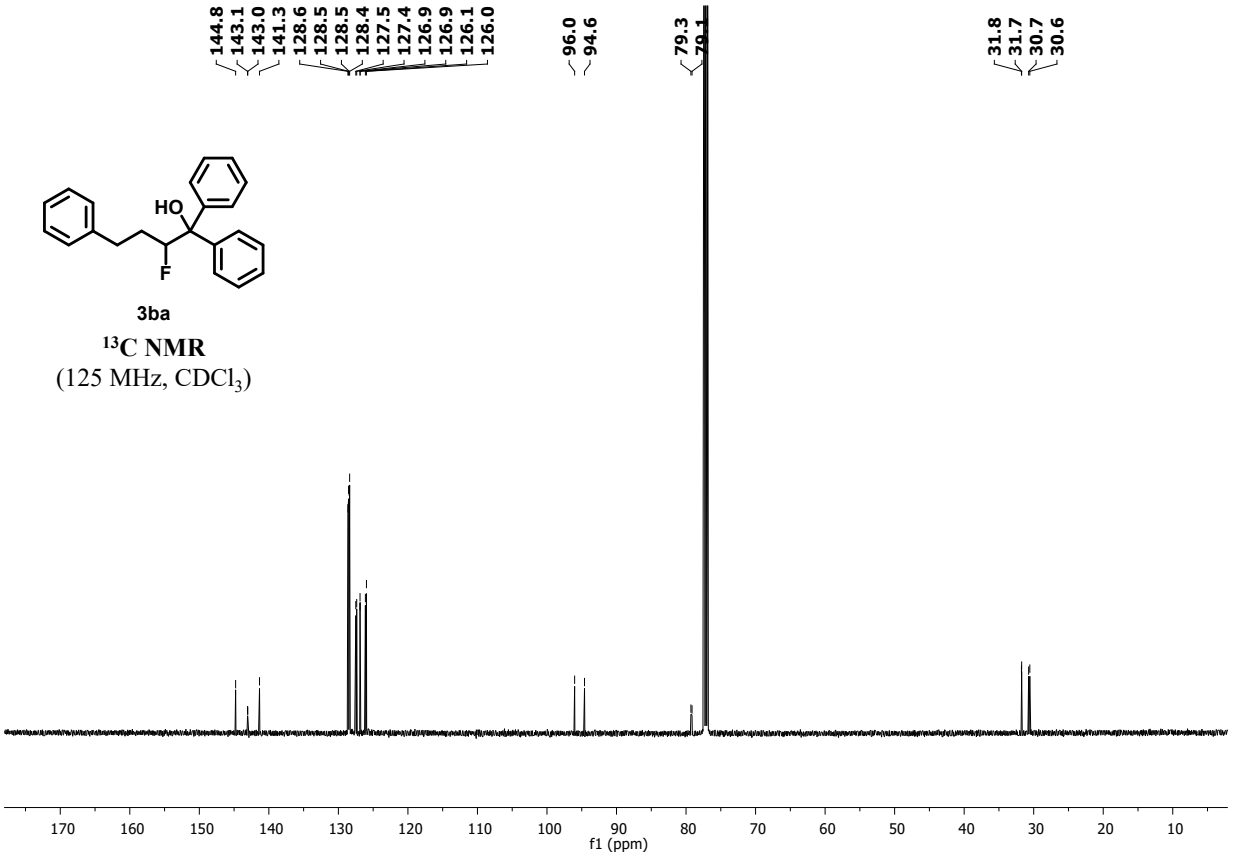
^{19}F NMR
(470 MHz, $CDCl_3$)





3ba

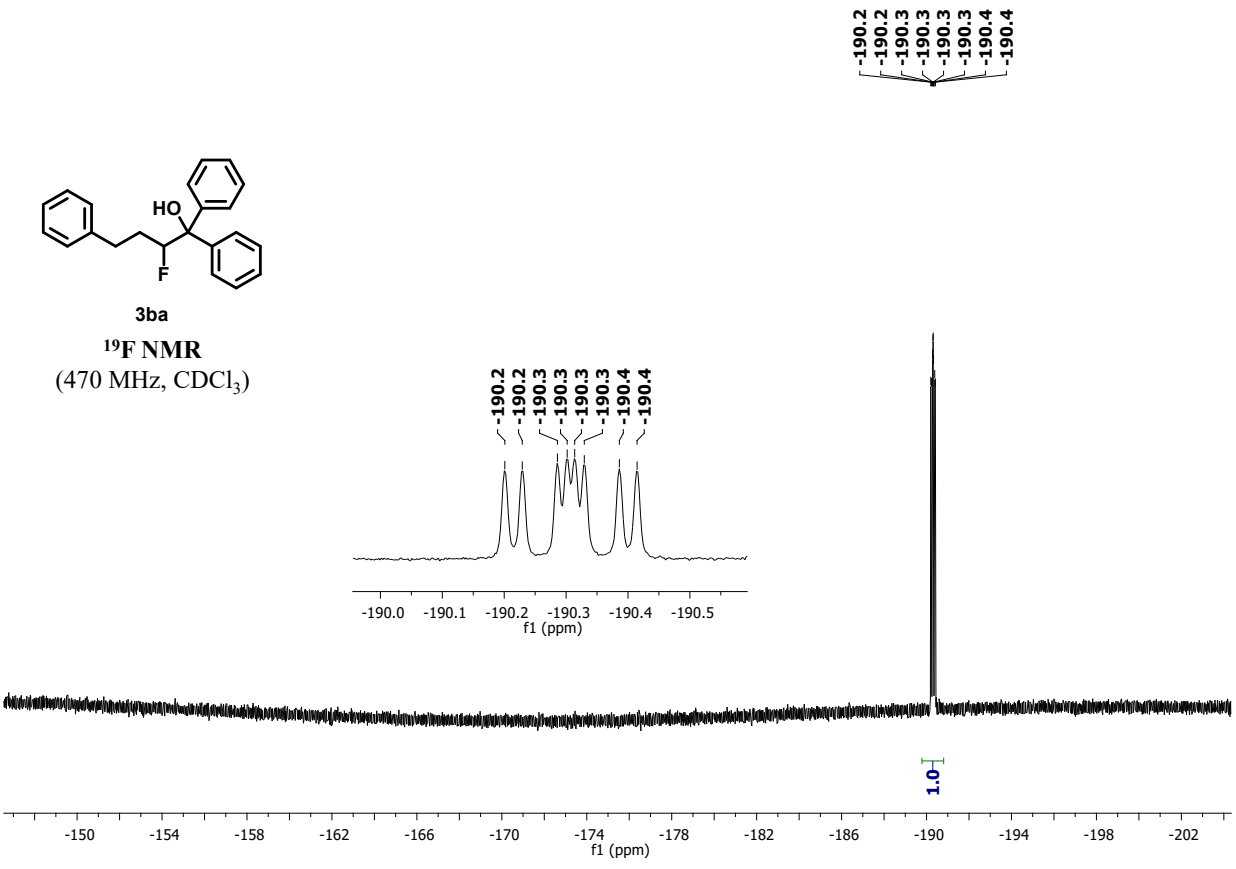
^{1}H NMR
(500 MHz, $CDCl_3$)



3ba

^{13}C NMR

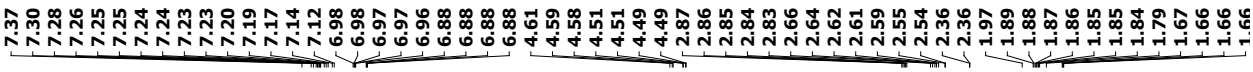
(125 MHz, $CDCl_3$)

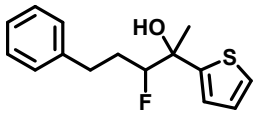


3ba

^{19}F NMR

(470 MHz, $CDCl_3$)



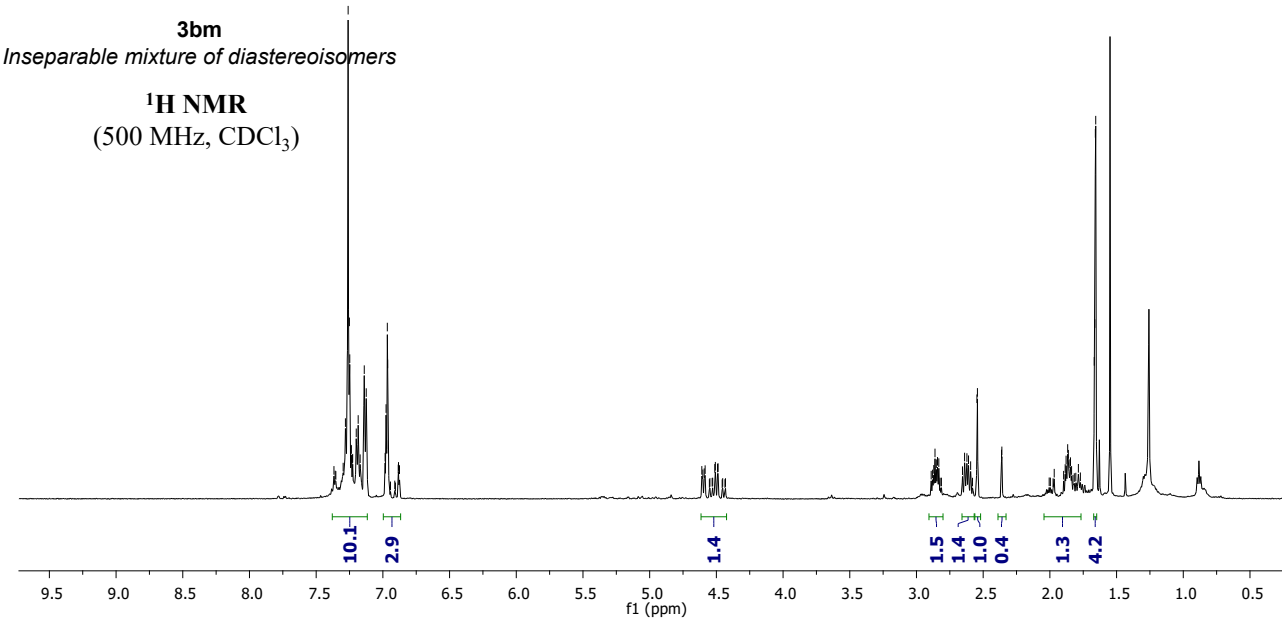


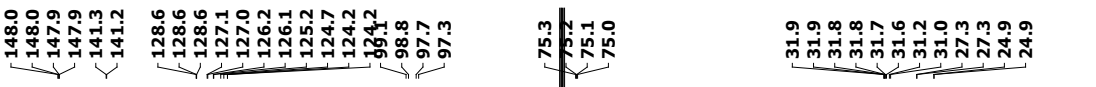
3bm

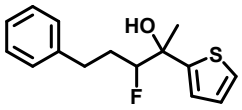
Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)





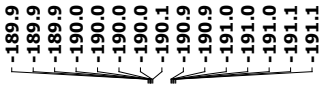


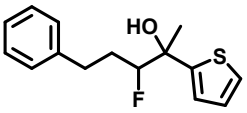
3bm

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)



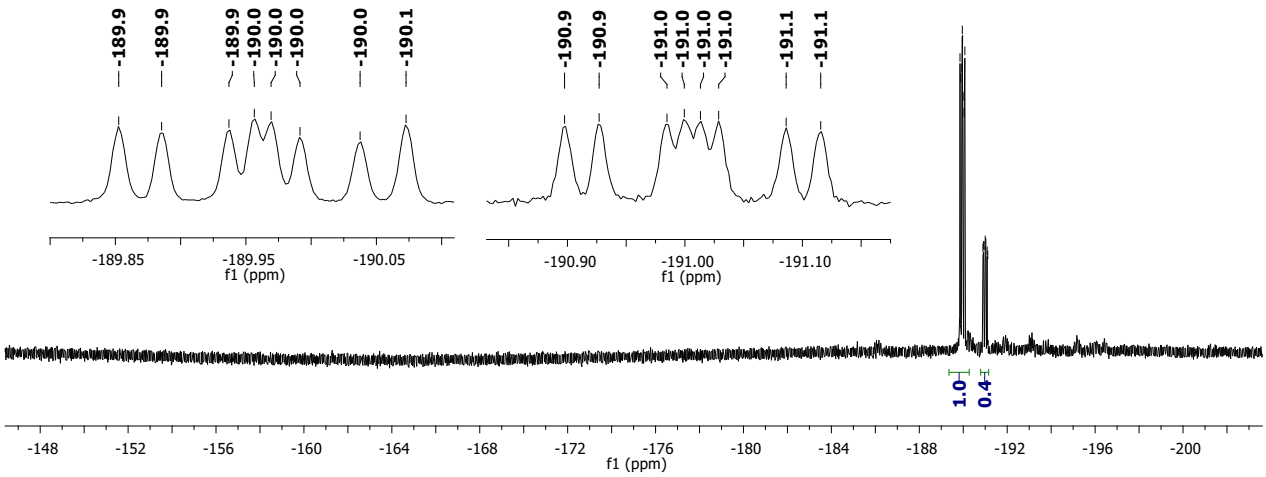


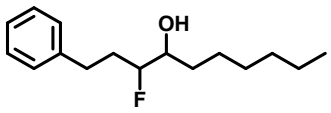
3bm

Inseparable mixture of diastereoisomers

^{19}F NMR

(470 MHz, $CDCl_3$)



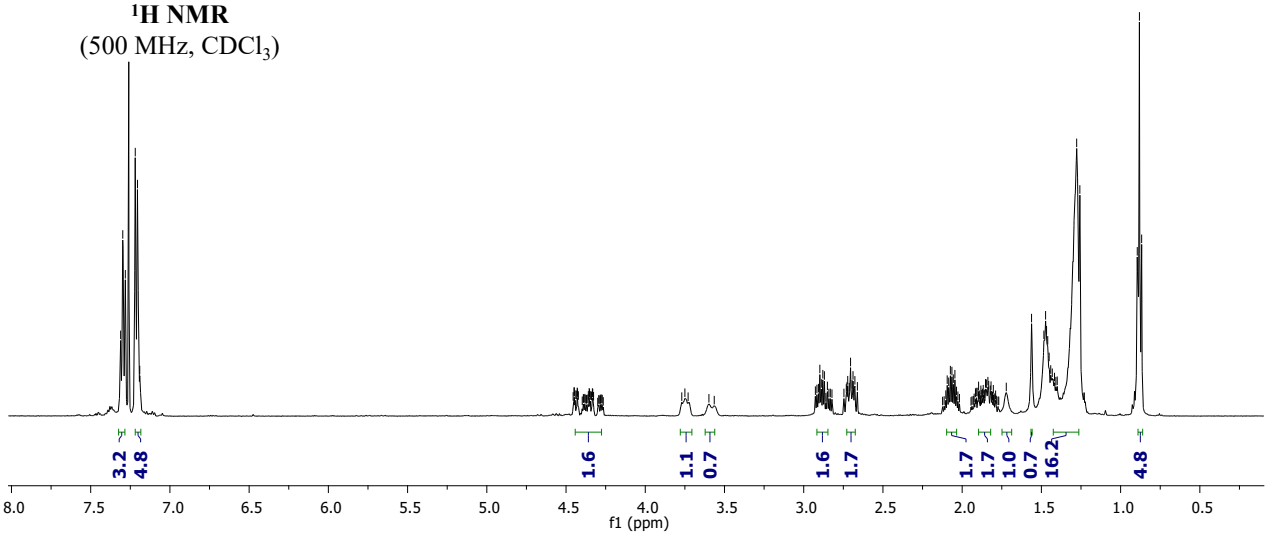


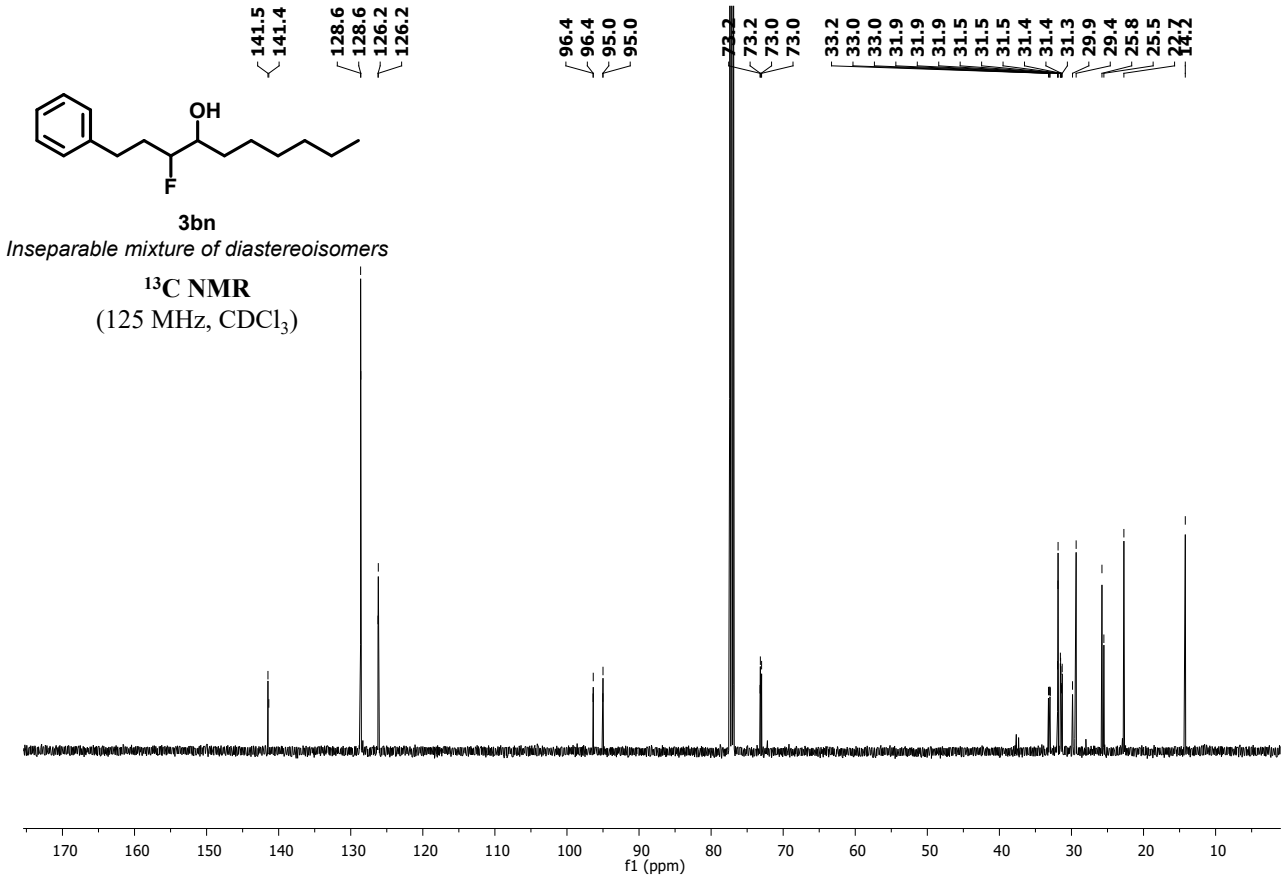
3bn

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)



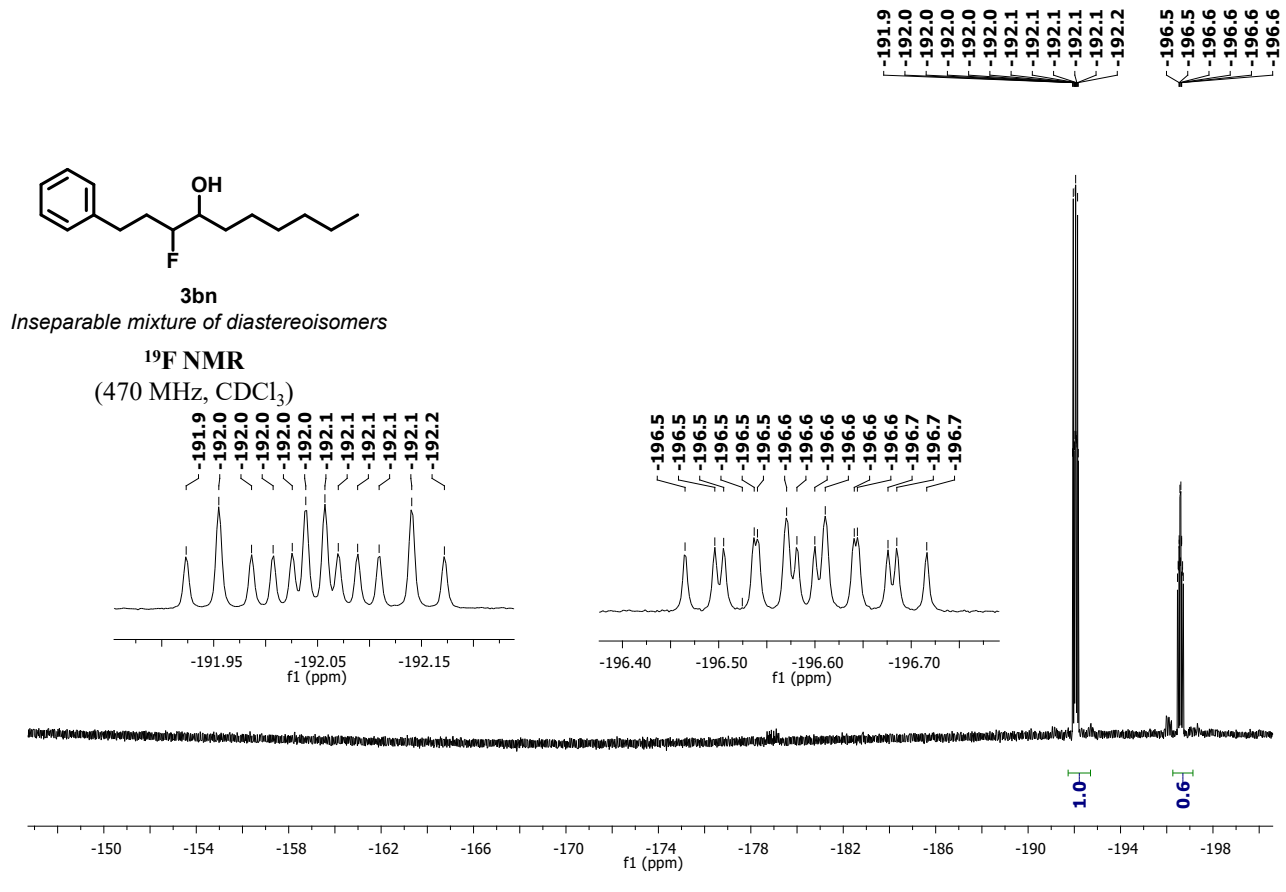


3bn

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

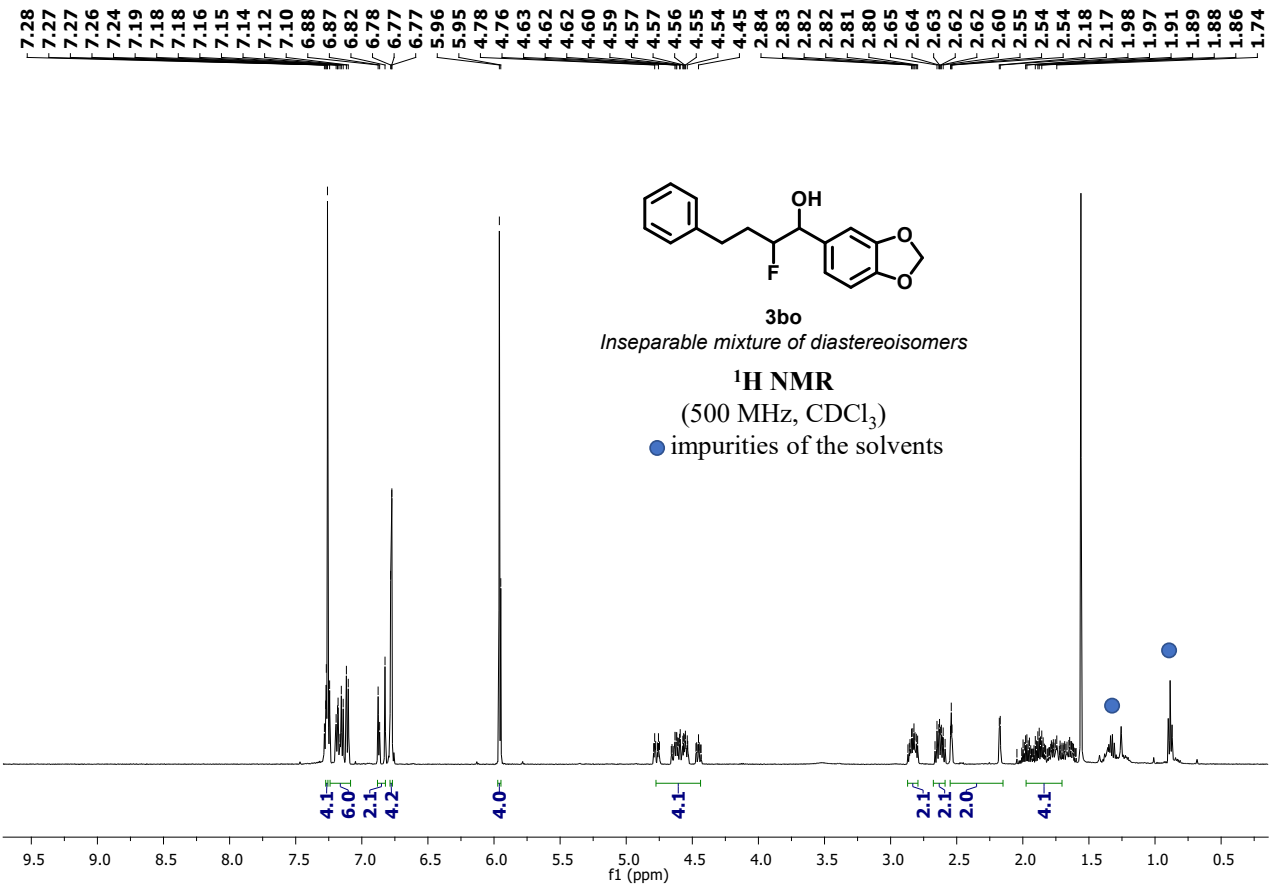


3bn

Inseparable mixture of diastereoisomers

^{19}F NMR

(470 MHz, $CDCl_3$)



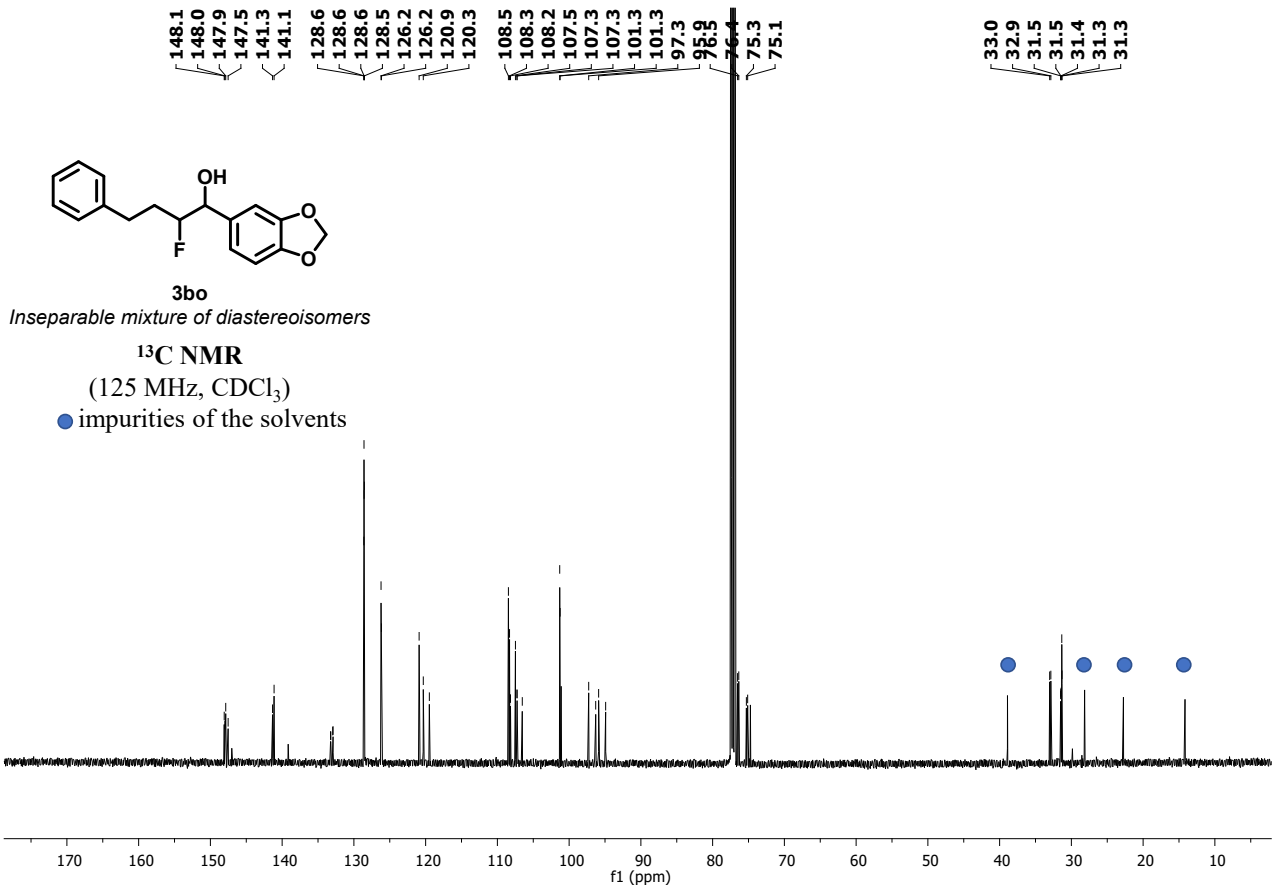
3bo

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)

● impurities of the solvents



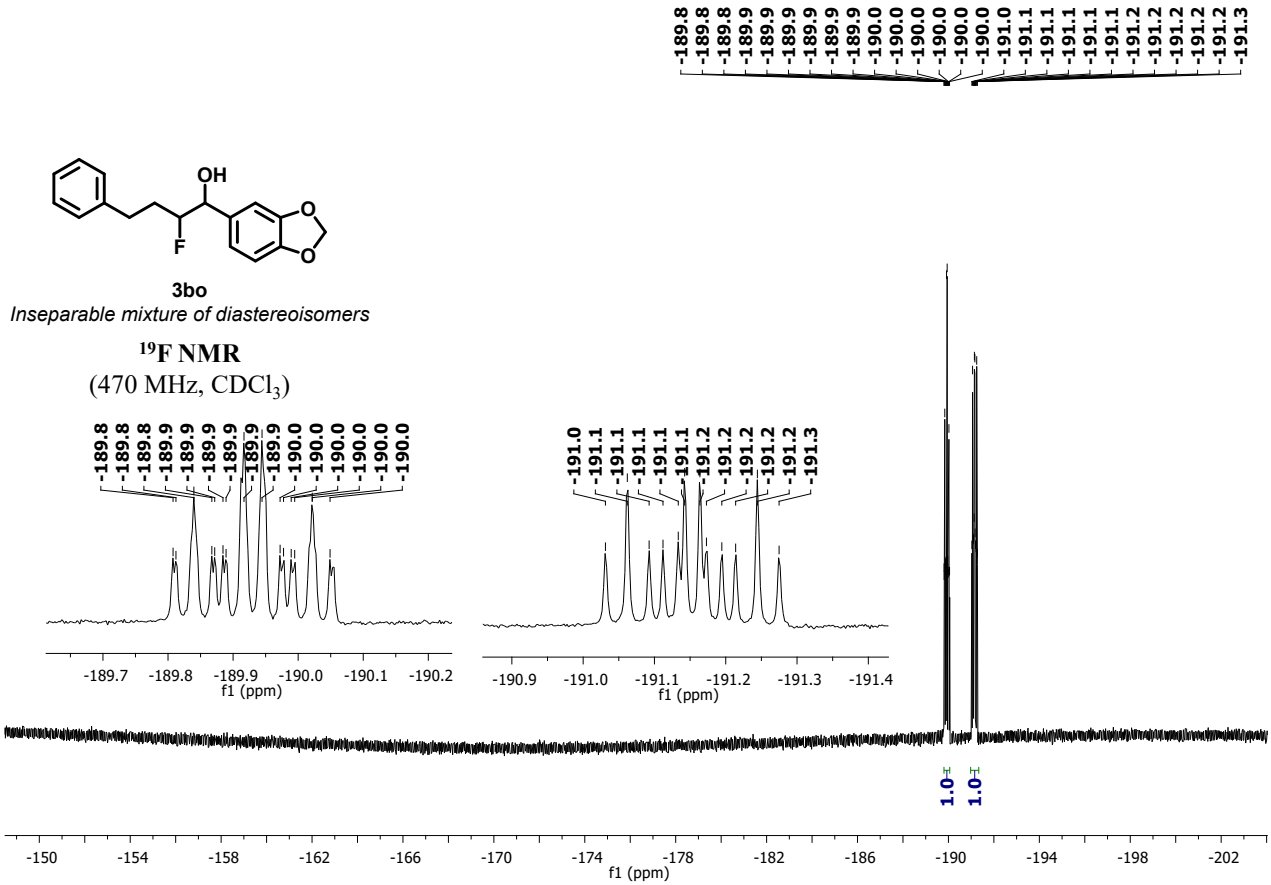
3bo

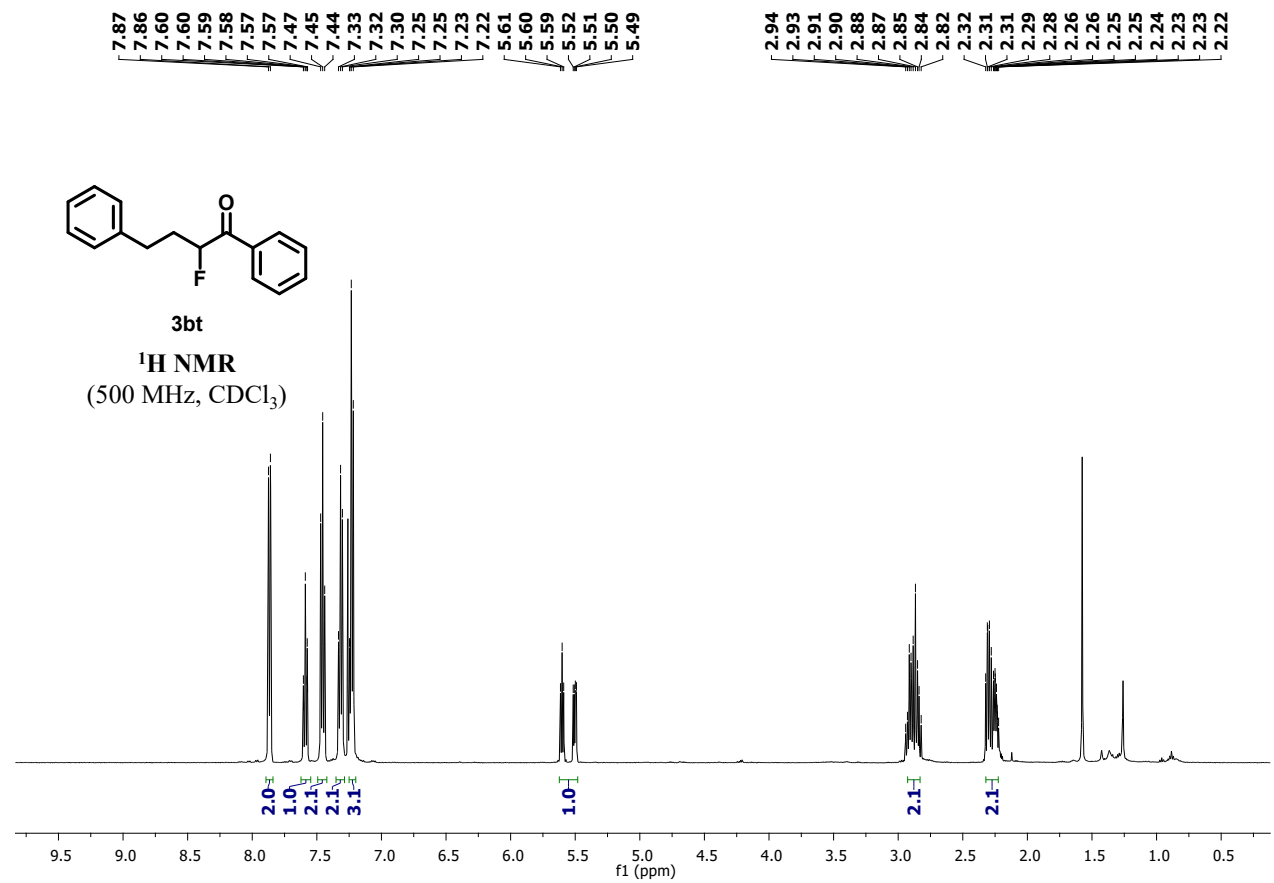
Inseparable mixture of diastereoisomers

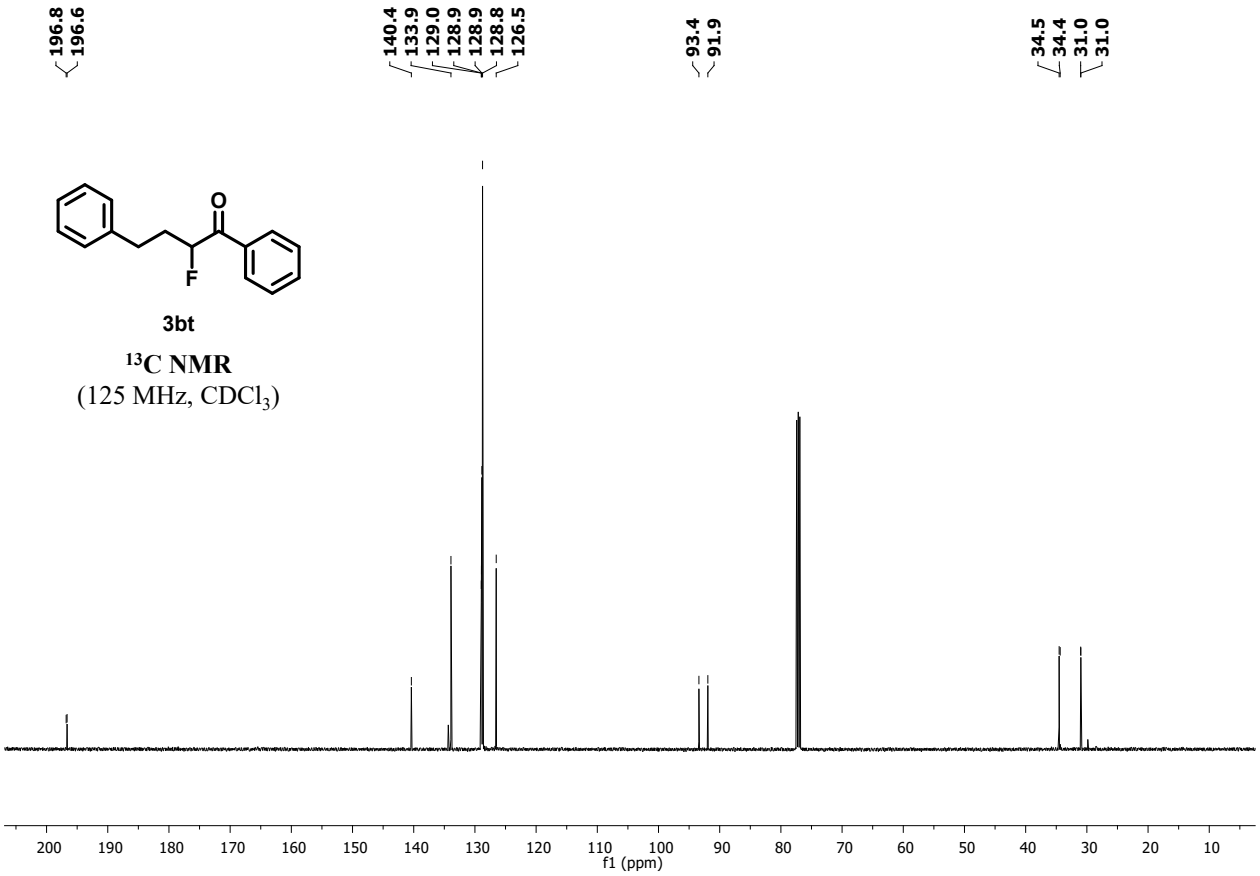
^{13}C NMR

(125 MHz, $CDCl_3$)

● impurities of the solvents

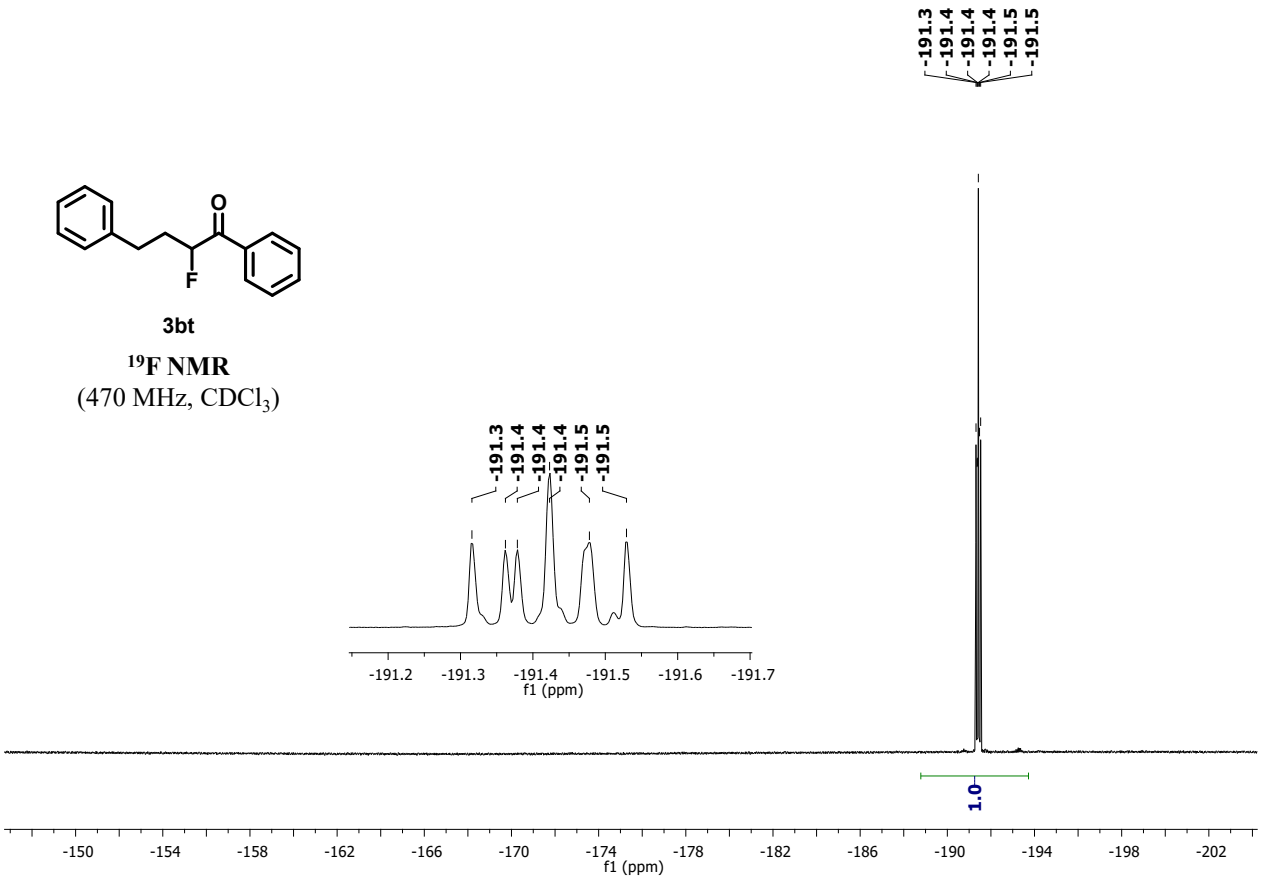

OH
F
O
O
3bo
Inseparable mixture of diastereoisomers
19F NMR
(470 MHz, CDCl3)
f1 (ppm)
1.0
1.0


O
F
3bt
1H NMR
(500 MHz, CDCl3)
f1 (ppm)
2.0
1.0
2.1
2.1
3.1
1.0
2.1
2.1



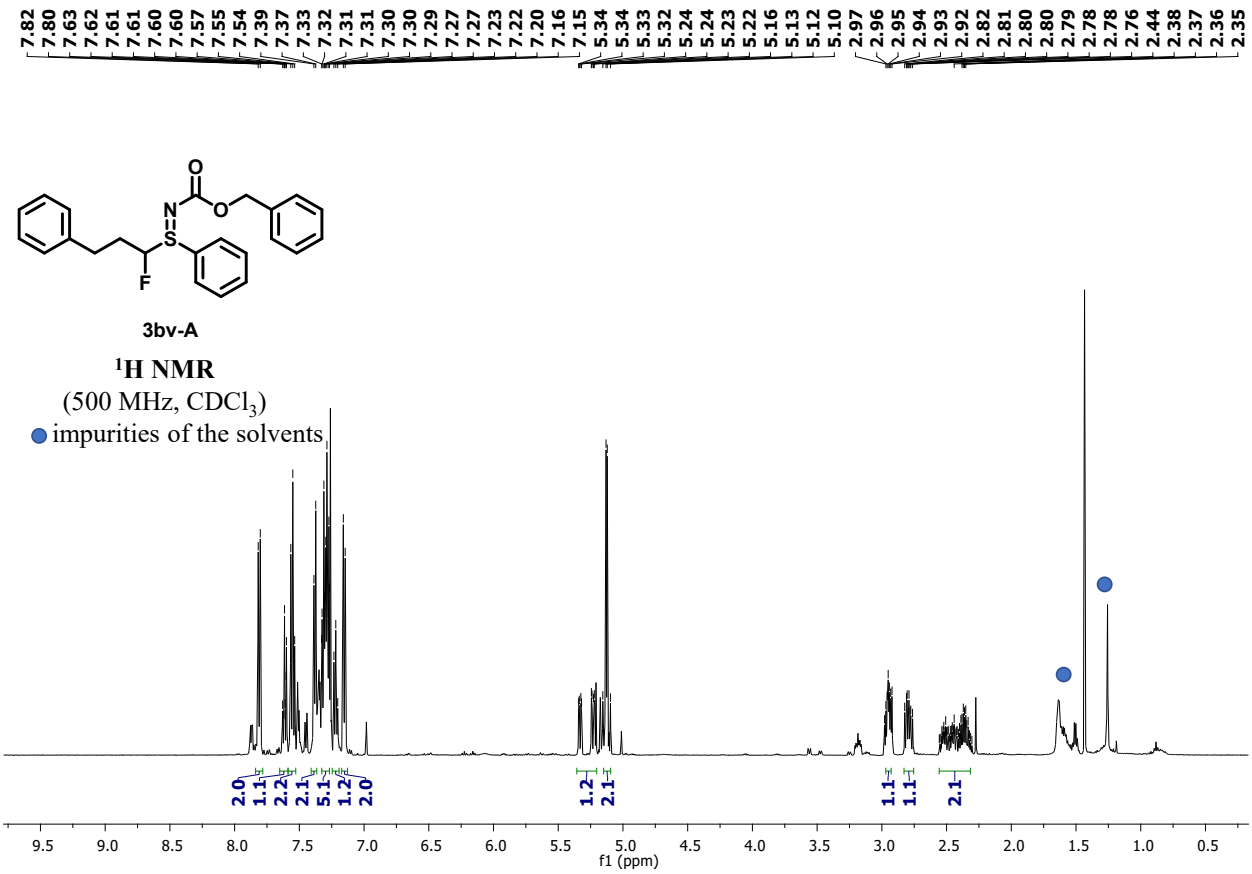
3bt

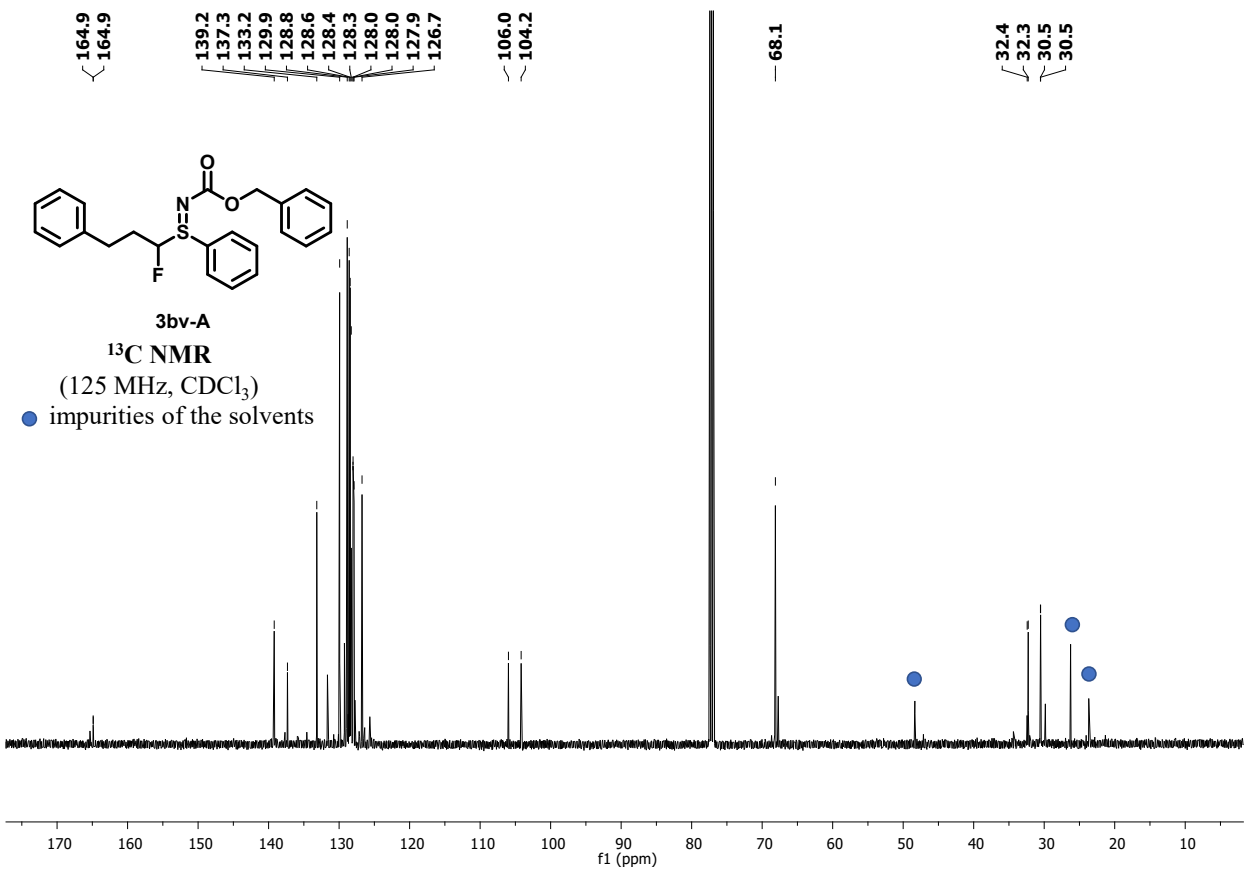
^{13}C NMR
(125 MHz, $CDCl_3$)

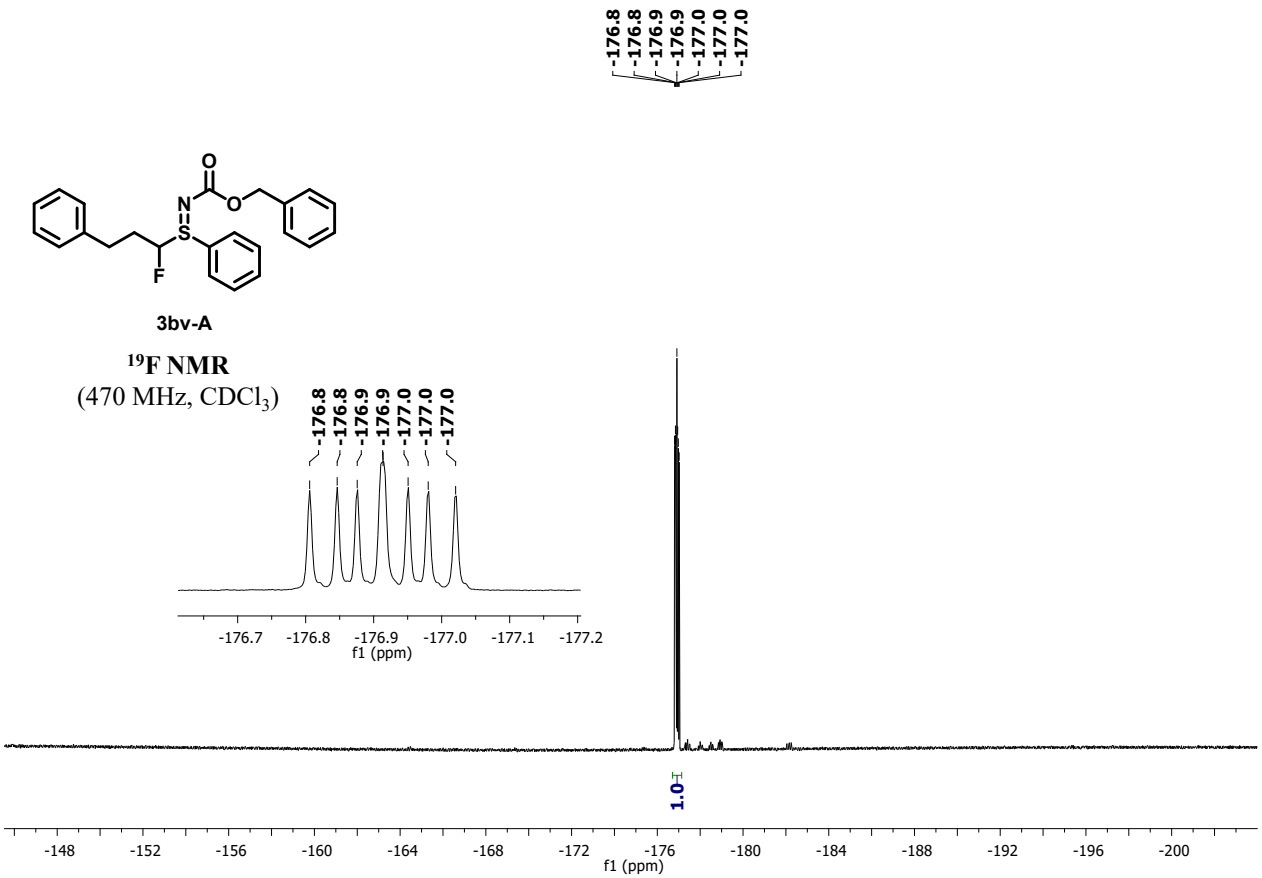


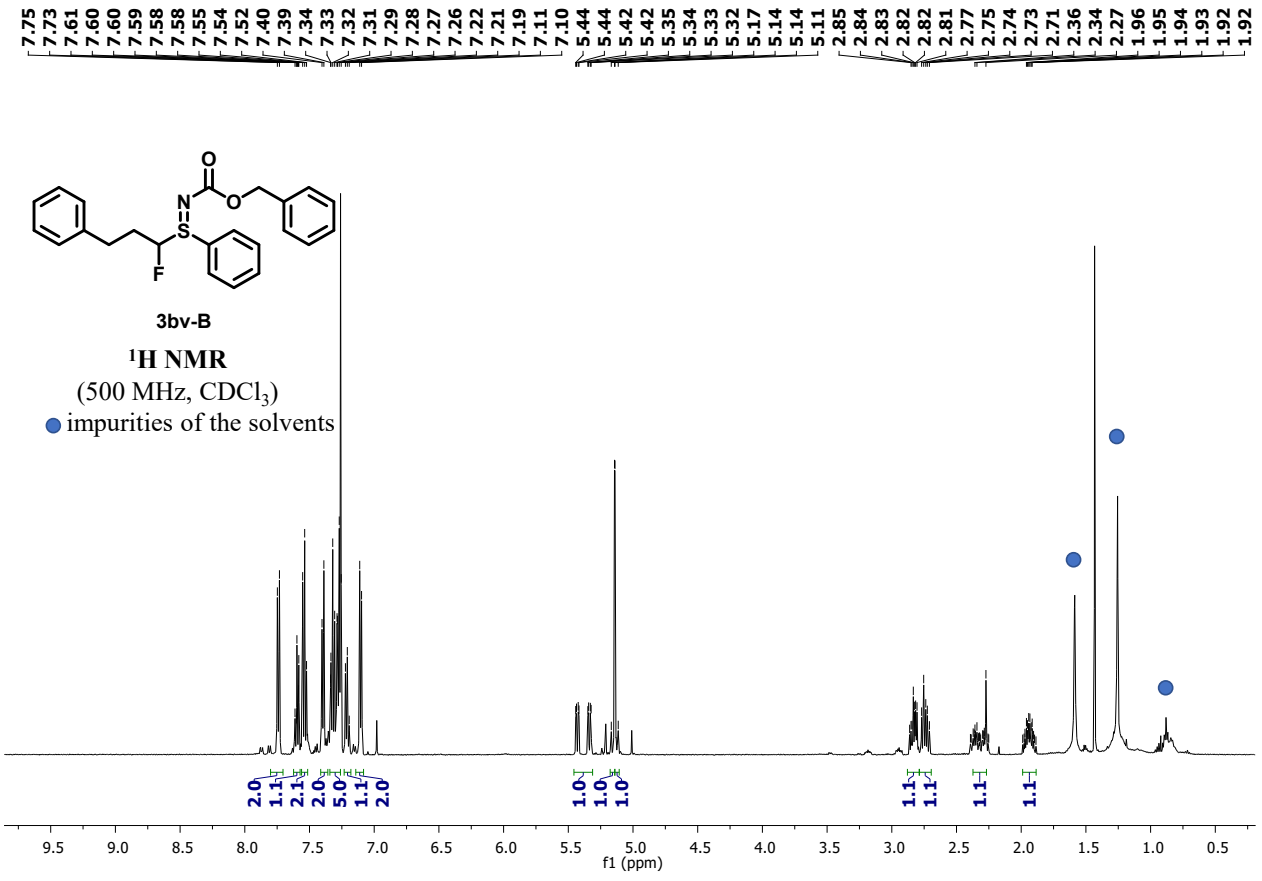
3bt

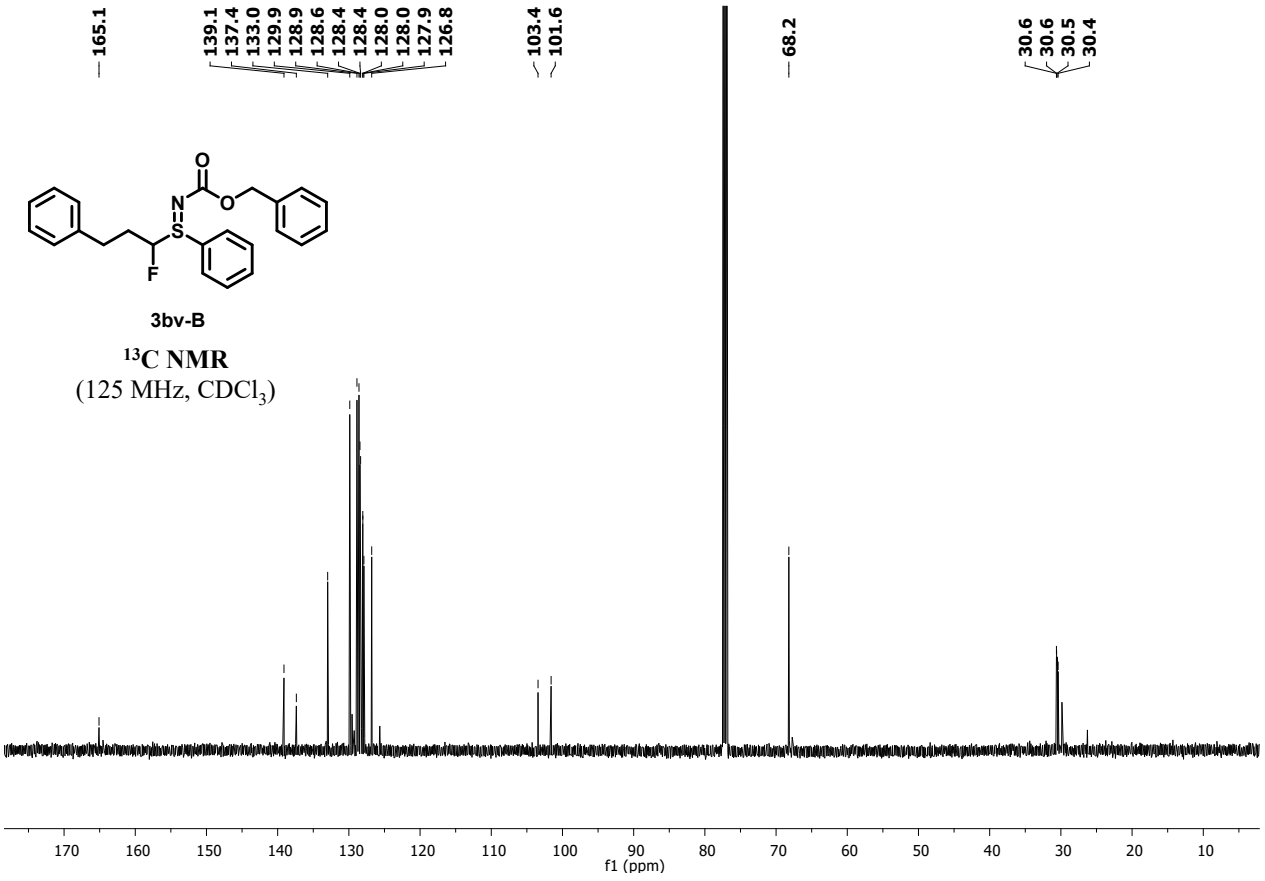
^{19}F NMR
(470 MHz, $CDCl_3$)


7.82 7.80 7.63 7.62 7.61 7.61 7.60 7.60 7.57 7.55 7.54 7.39 7.37 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.27 7.27 7.23 7.22 7.20 7.16 7.15 5.34 5.34 5.33 5.32 5.24 5.24 5.23 5.22 5.16 5.13 5.12 5.10 2.97 2.96 2.95 2.94 2.93 2.92 2.82 2.81 2.80 2.80 2.79 2.78 2.78 2.76 2.44 2.38 2.37 2.36 2.35
3bv-A
1H NMR
(500 MHz, CDCl3)
impurities of the solvents
2.0 1.1 2.2 2.1 5.1 1.2 2.0 1.2 2.1 1.1 1.1 2.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


164.9 164.9 139.2 137.3 133.2 129.9 128.8 128.6 128.4 128.3 128.0 128.0 127.9 126.7 106.0 104.2 68.1 32.4 32.3 30.5 30.5
3bv-A
13C NMR
(125 MHz, CDCl3)
impurities of the solvents
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

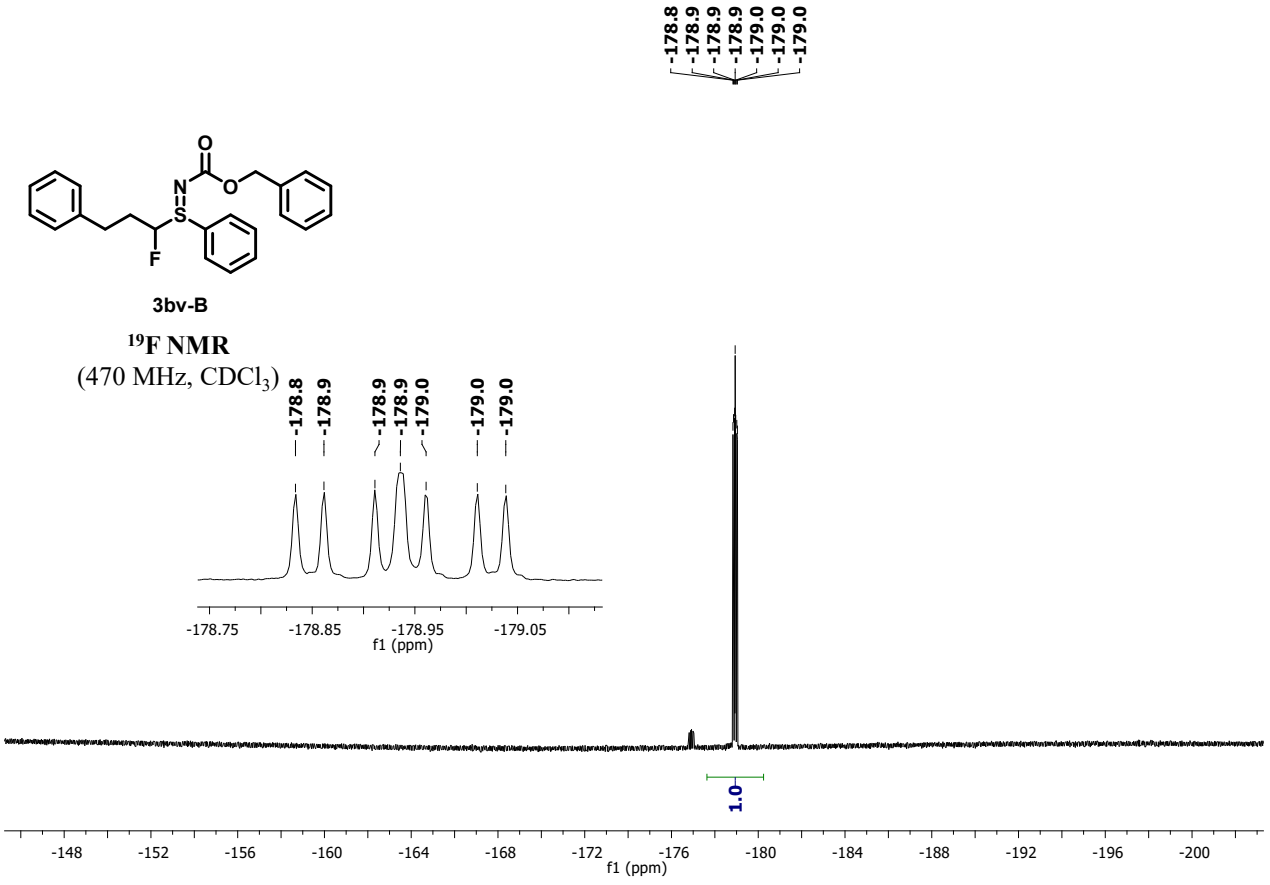

-176.8
-176.8
-176.9
-176.9
-177.0
-177.0
-177.0
3bv-A
19F NMR
(470 MHz, CDCl3)
-176.7
-176.8
-176.9
-177.0
-177.1
-177.2
f1 (ppm)
1.0
-148
-152
-156
-160
-164
-168
-172
-176
-180
-184
-188
-192
-196
-200
f1 (ppm)


7.75
7.73
7.61
7.60
7.60
7.59
7.58
7.58
7.55
7.54
7.52
7.40
7.39
7.34
7.33
7.32
7.31
7.29
7.28
7.27
7.26
7.22
7.21
7.19
7.11
7.10
5.44
5.44
5.42
5.42
5.35
5.34
5.33
5.32
5.17
5.14
5.14
5.11
2.85
2.84
2.83
2.82
2.82
2.81
2.77
2.75
2.74
2.73
2.71
2.36
2.34
2.27
1.96
1.95
1.94
1.93
1.92
1.92
3bv-B
1H NMR
(500 MHz, CDCl3)
impurities of the solvents
2.0
1.1
2.1
2.0
5.0
1.1
2.0
1.0
1.0
1.0
1.1
1.1
1.1
1.1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



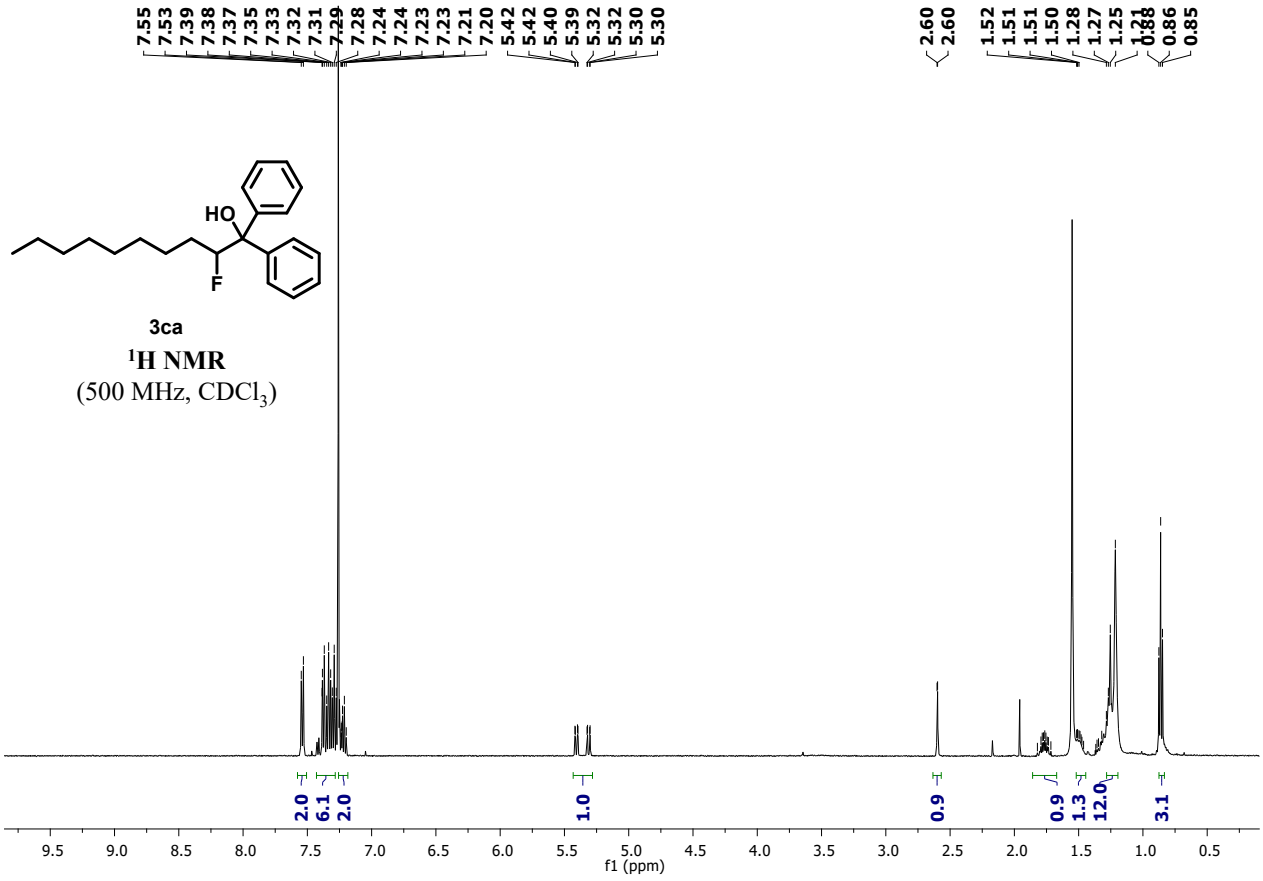
3bv-B

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



3bv-B

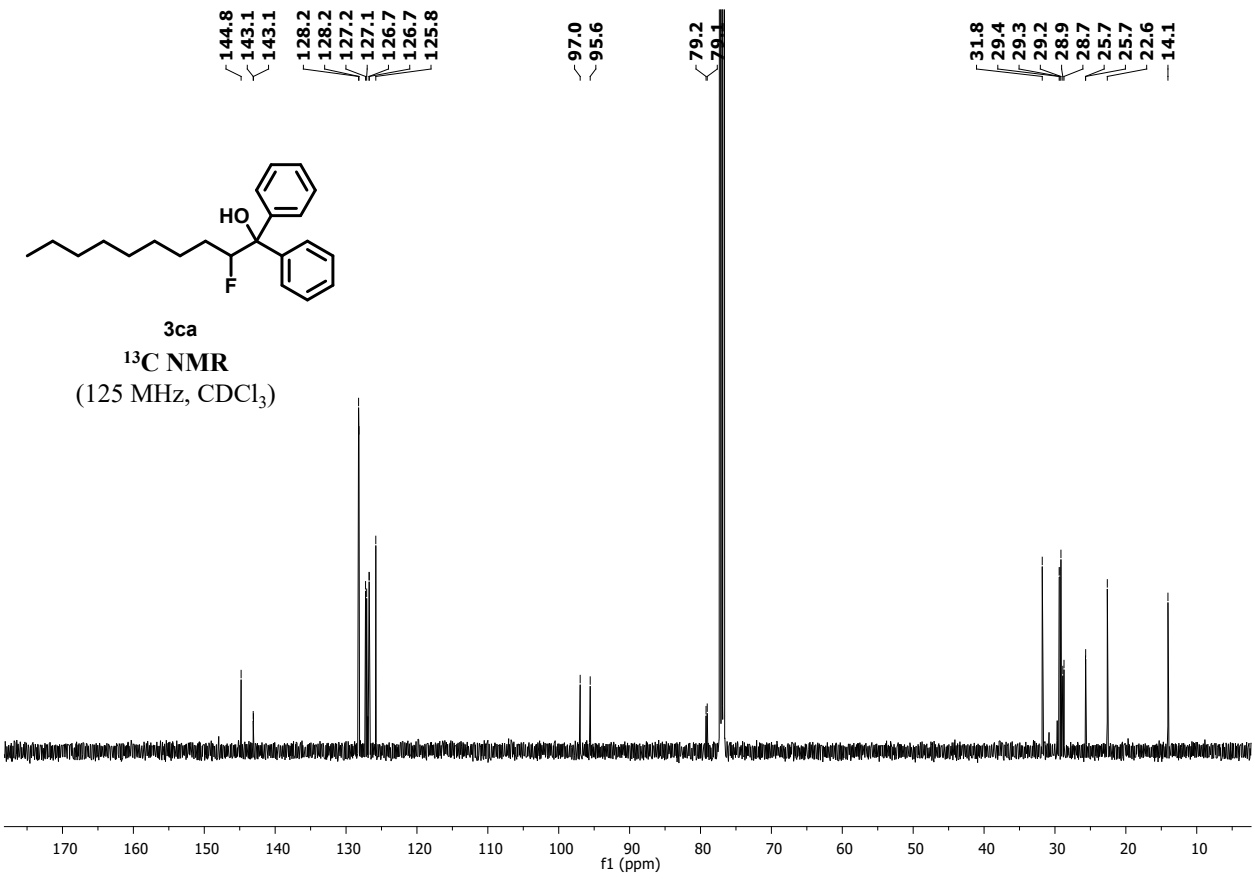
^{19}F NMR
(470 MHz, $CDCl_3$)



3ca

^{1}H NMR

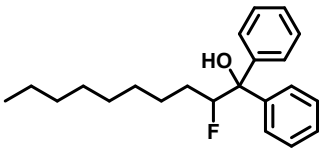
(500 MHz, $CDCl_3$)



3ca

^{13}C NMR

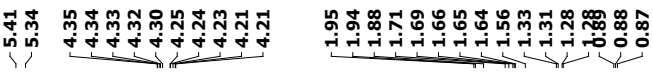
(125 MHz, $CDCl_3$)

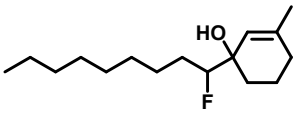


3ca

^{19}F NMR

(470 MHz, $CDCl_3$)



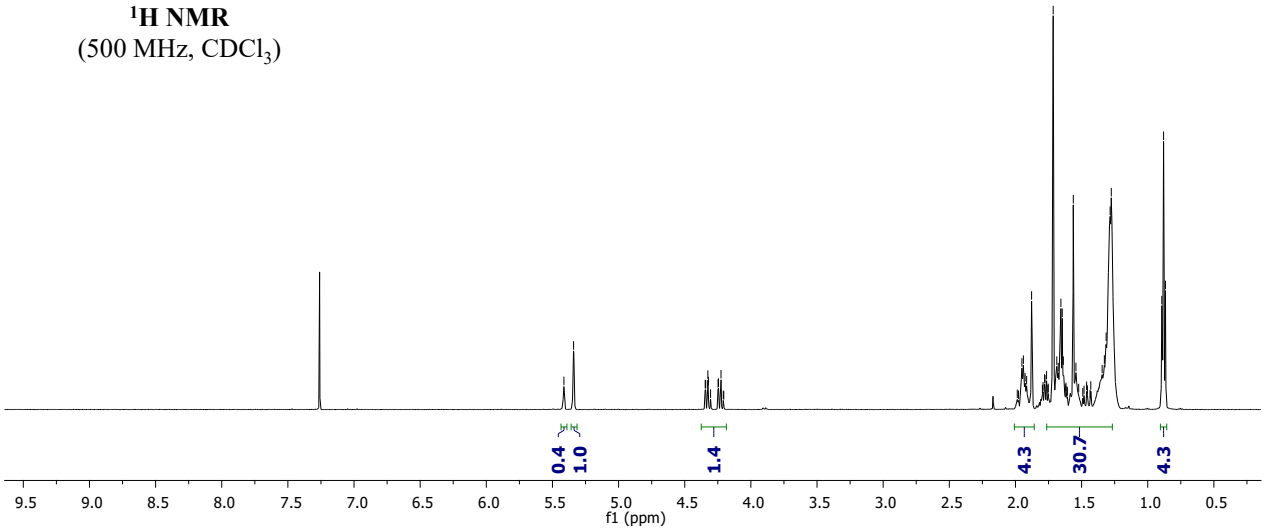


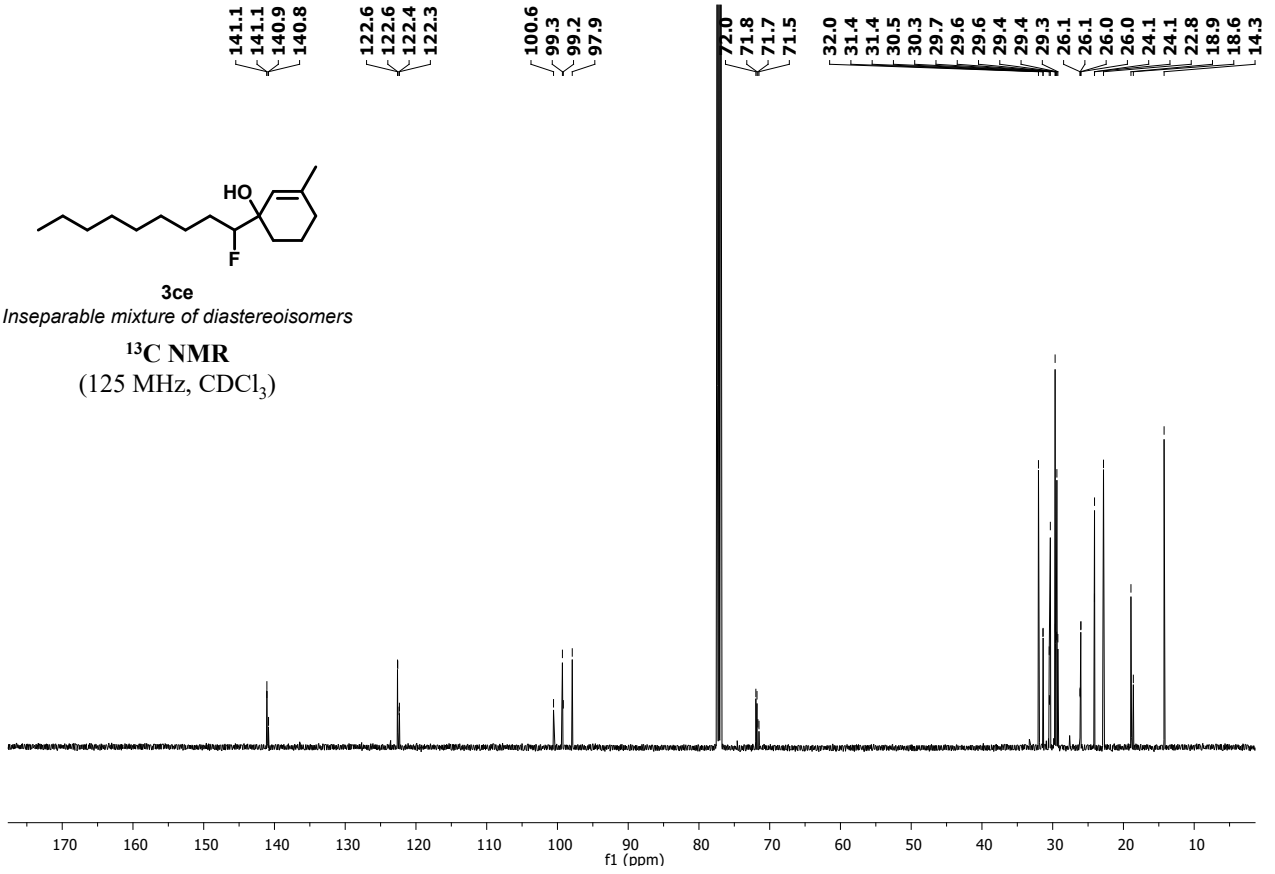
3ce

Inseparable mixture of diastereoisomers

^{1}H NMR

(500 MHz, $CDCl_3$)



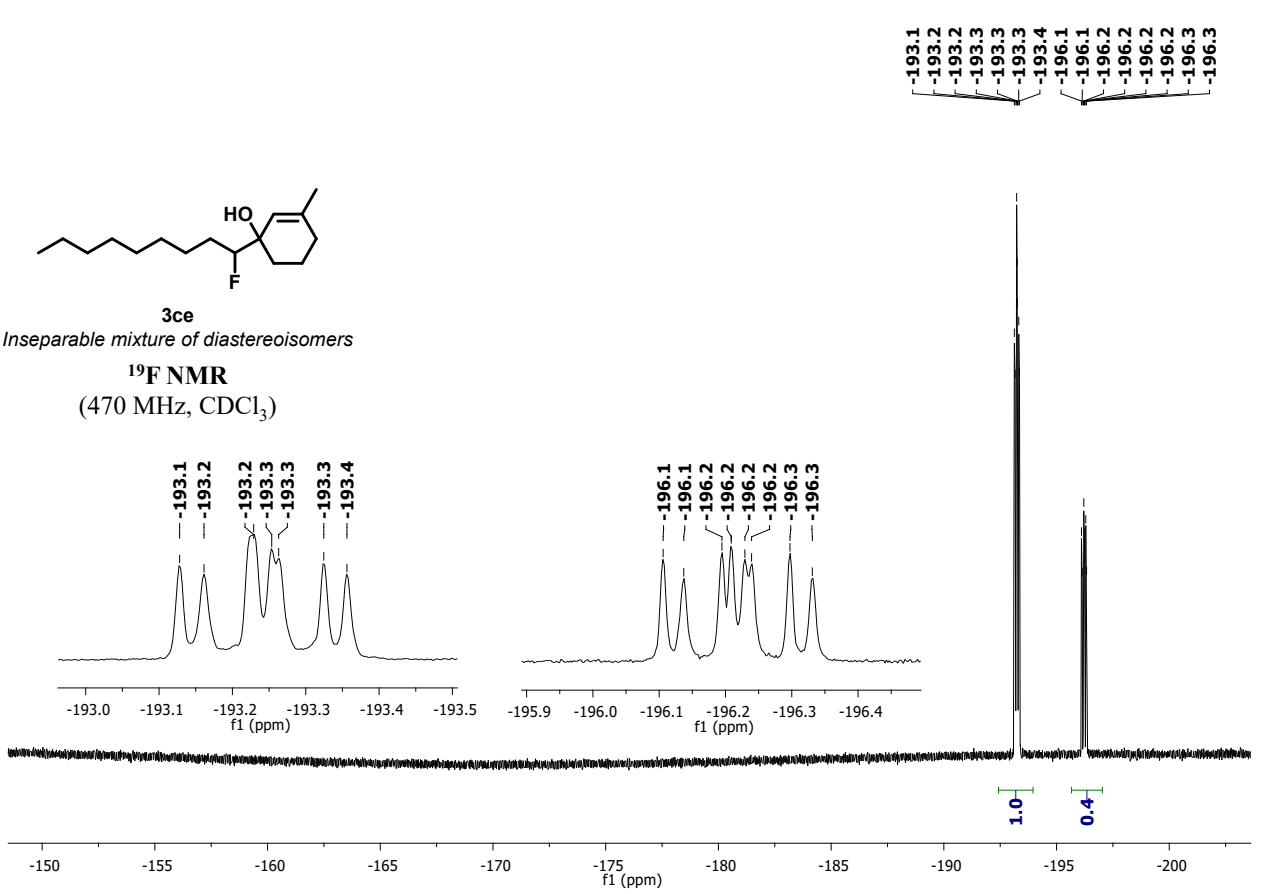


3ce

Inseparable mixture of diastereoisomers

^{13}C NMR

(125 MHz, $CDCl_3$)

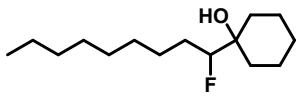


3ce

Inseparable mixture of diastereoisomers

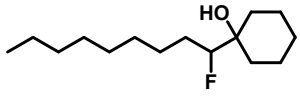
^{19}F NMR

(470 MHz, $CDCl_3$)



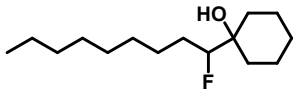
3cf

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



3cf

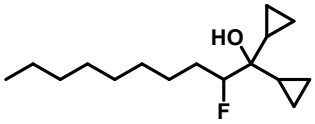
^{13}C NMR
(125 MHz, $CDCl_3$)



3cf

^{19}F NMR

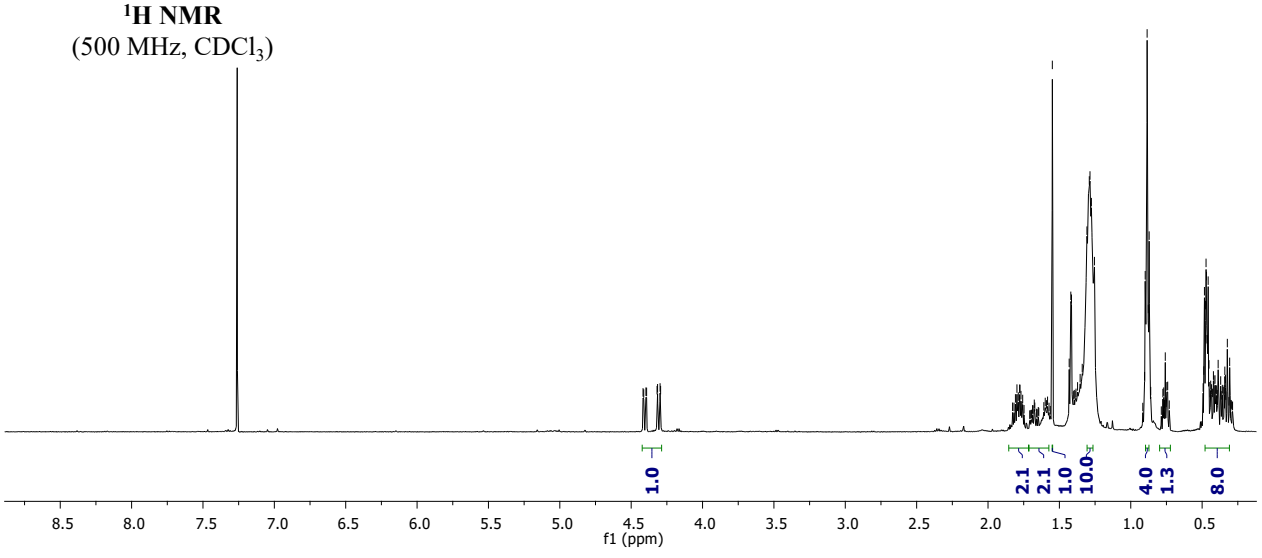
(470 MHz, $CDCl_3$)

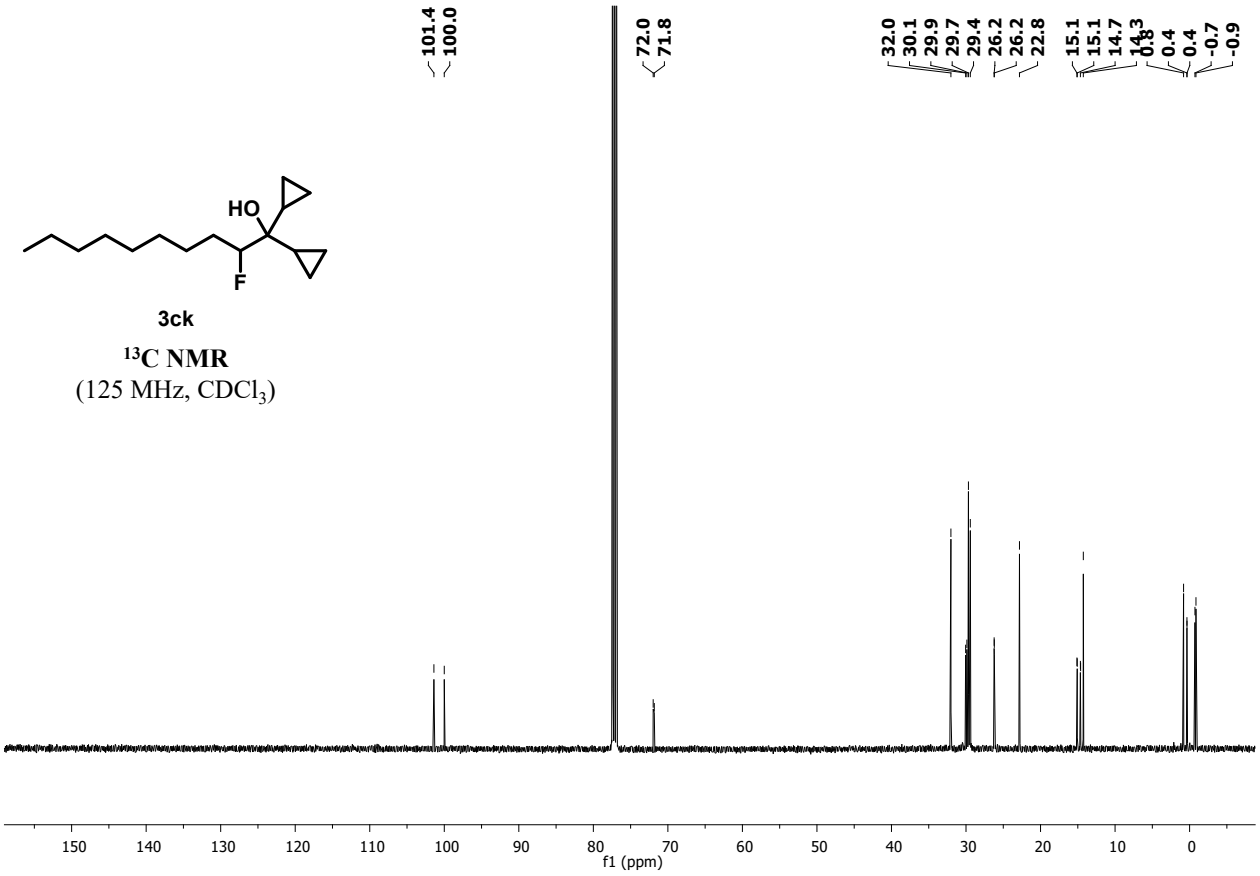


3ck

^{1}H NMR

(500 MHz, $CDCl_3$)

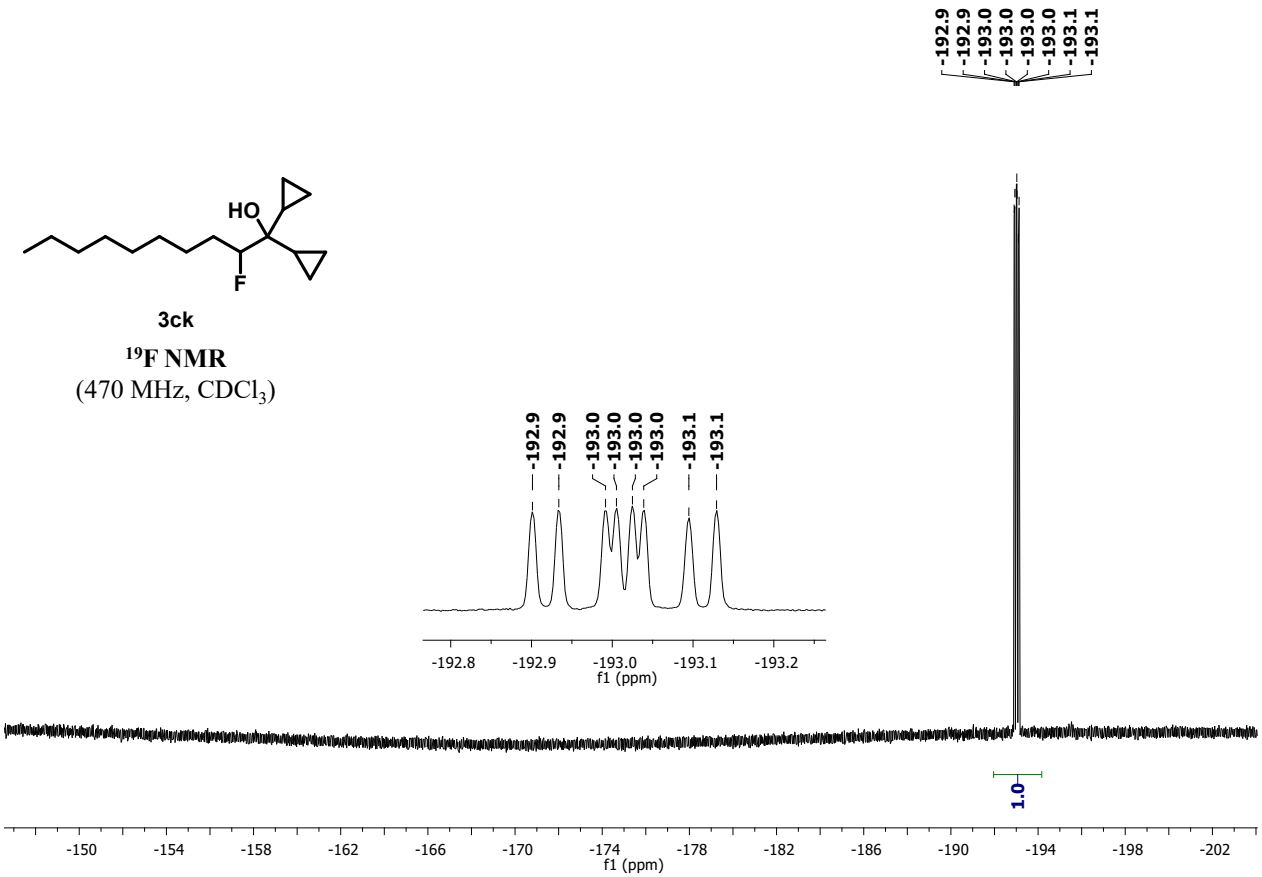




3ck

^{13}C NMR

(125 MHz, $CDCl_3$)



3ck

^{19}F NMR

(470 MHz, $CDCl_3$)

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