Supporting Information for

Catalytic, Enantioselective 1,2-Difluorination of Cinnamamides

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General Experimental Procedures

All reactions for the preparation of substrates and catalysts were performed in standard, dry glassware fitted with rubber septa under an inert atmosphere of nitrogen unless otherwise described. All difluorination reactions were performed in polyethylene tubes sealed with a high density polyethylene cap under an atmosphere of air. Stainless steel gas-tight syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Reported concentrations refer to solution volumes at room temperature. Concentration of organic solutions under reduced pressure was performed using house vacuum (ca. 40 mm Hg) at 30 ºC. Column chromatography was performed with SiliaFlash® P60 (40-63μm, 60 Å) silica gel from Silicycle. Thin layer chromatography (TLC) was used for reaction monitoring, and product detection was performed using pre-coated glass plates covered with 0.20 mm silica gel with fluorescent indicator; plates were visualized by exposure to UV light (λ = 254 nm) or by staining with potassium permanganate or ninhydrin.

Note of Caution

Pyridine•9HF is a corrosive and toxic substance that will corrode glassware. Safe handling can be conducted with plastic syringes and metal needles, with $NaHCO_3$ (aq.) or NaOH (aq.) employed to quench excess HF. Though reactions should not be conducted in glassware when employing pyridine•9HF, glassware may be used to quench reactions provided sufficient quantities of base are present. Always handle pyridine•9HF while wearing gloves and in a fume hood. As a precautionary measure, have calcium gluconate gel nearby and apply immediately and liberally on skin exposed to pyridine•9HF.

Materials

Reagents were purchased in reagent grade from commercial suppliers and used as received, unless otherwise described. Anhydrous solvents (benzene, dichloromethane, diethyl ether, *N, N*-dimethylformamide, tetrahydrofuran, and toluene) were prepared by passing the solvent through an activated alumina column. Triethylamine and diisopropylethylamine were distilled over calcium hydride at atmospheric pressure.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an Inova-500 spectrometer, are reported in parts per million downfield from tetramethylsilane, and are referenced to the residual protium resonances of the NMR solvent ($CDCl_3$: 7.26 [$CHCl_3$], acetone-d6: 2.05 [acetone-d5], DMSO-d6: 2.50 [DMSO-d5]). Proton-decoupled carbon-13 nuclear magnetic resonance (13C {1 H} NMR) spectra were recorded on an Inova-500 spectrometer, are reported in parts per million downfield from tetramethylsilane, and are referenced to the carbon resonances of the NMR solvent (CDCl3: 77.23, acetone-d6: 29.92, DMSO-d6: 39.61). Chemical shifts for fluorine-19 nuclear magnetic resonance (19F NMR) were recorded on an Inova-500 spectrometer, are reported in parts per million downfield from chlorotrifluoromethane, and are referenced to the fluorine resonance of chlorotrifluoromethane (δ = 0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet), coupling constants in Hertz (Hz), integration.

Infrared spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer.

High-resolution mass spectrometric data were obtained on an Agilent 6210 time-of-flight HPLC/MS spectrometer (ESI-TOF).

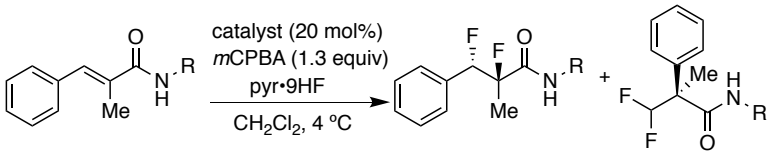
Chiral GC analysis was performed using an Agilent 7890A GC system using commercially available columns. Chiral HPLC analysis was performed using an Agilent 1200 series quaternary HPLC system using commercially available CHIRALCEL analytical columns (4.6 x 250 mm).

Optical rotations were measured using a 1 mL cell with a 5 cm path length on a Jasco P-2000 digital polarimeter.

Optimization Studies

General procedure for optimization of *N*-alkyl group and HF loading

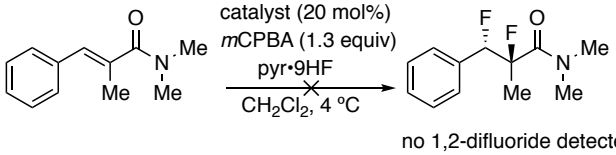
Catalyst **1b** (15.4 mg, 20.0 μmol, 20.0 mol %), cinnamamide (100 μmol, 1.00 equiv), and dichloromethane (200 μL) were combined in a polyethylene tube at room temperature. Pyridinium poly(hydrogen fluoride) (pyr•9HF, 70% hydrogen fluoride by weight, 260 μL, 100 equiv hydrogen fluoride) was added via syringe at -78 ˚C, followed by *m*-chloroperbenzoic acid (*m*CPBA, 77% by weight, 29.1 mg, 1.30 equiv). The reaction was warmed to 4 ˚C and stirred for 24 h at that temperature. The reaction was diluted with dichloromethane and poured slowly into a slurry of basic alumina in dichloromethane at -78 ˚C. The reaction was warmed to room temperature with stirring, filtered, and concentrated under reduced pressure. The crude product mixture was analyzed by ^{1}H NMR using nitrobenzene as an internal standard to determine the yield of product, by ^{19}F NMR to determine the product ratio, and by chiral GC to determine the enantiomeric excess.



2a–f **3a–f** **4a–f**

entry	substrate	R	pyr•9HF (equiv)	**3 : 4**	yield of **3** (%)	e.e. of **3** (%)
1	**2a**	H	11	1.1 : 1.0	17	91
2	**2b**	Me	11	1.1 : 1.0	38	95
3	**2c**	Et	11	1.3 : 1.0	44	95
4	**2d**	*i*-Pr	11	1.6 : 1.0	46	96
5	**2e**	*n*-Bu	11	1.7 : 1.0	48	94
6	**2f**	*t*-Bu	11	5.9 : 1.0	65	96
7[a]	**2f**	*t*-Bu	5.6	39 : 1.0	81	96
8	**2f**	*t*-Bu	2.8	56 : 1.0	64	96
9	**2a**	H	5.6	1.2 : 1.0	19	91

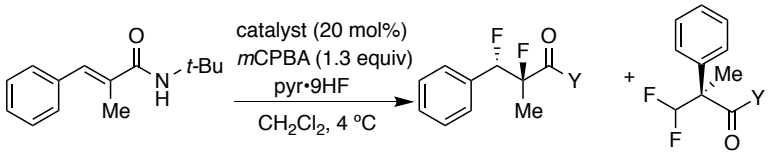
Table S1. Optimization of *N*-alkyl group and HF loading. Unless otherwise noted, reactions were performed on 0.10 mmol scale, with yields of 1,2-difluoride determined by ^{1}H NMR using nitrobenzene as an internal standard. Reported ratios of 1,2-difluoride to 1,1-difluoride were determined by ^{19}F NMR analysis of crude product mixtures. [a]Reaction was conducted on 1.00 mmol scale, and the isolated yield of **3** is listed.



no 1,2-difluoride detected

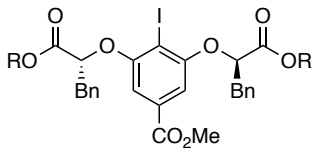
General procedure for catalyst optimization

Catalyst (20.0 μmol, 20.0 mol %), cinnamamide **2f** (21.7 mg, 100 μmol, 1.00 equiv), and dichloromethane (200 μL) were combined in a polyethylene tube at room temperature. Pyridinium poly(hydrogen fluoride) (pyr•9HF, 70% hydrogen fluoride by weight, 30 or 50 equiv hydrogen fluoride) was added via syringe at -78 ˚C, followed by *m*-chloroperbenzoic acid (*m*CPBA, 77% by weight, 29.1 mg, 1.30 equiv). The reaction was warmed to 4 ˚C or room temperature and stirred for 24 h at that temperature. The reaction was diluted with dichloromethane and poured slowly into a slurry of basic alumina in dichloromethane at -78 ˚C. The reaction was warmed to room temperature with stirring, filtered, and concentrated under reduced pressure. The crude product mixture was analyzed by ^{1}H NMR using nitrobenzene as an internal standard to determine the yield of product, by ^{19}F NMR to determine the product ratio, and by chiral GC to determine the enantiomeric excess.

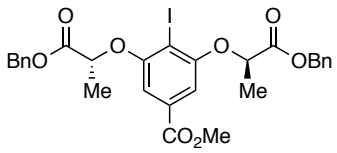


2f **3f** **4f**

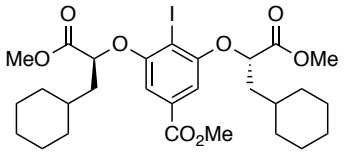
entry	catalyst	pyr•9HF (equiv)	T (˚C)	yield of **3** (%)	e.e. of **3** (%)
1[b]	**1a**	5.6	4	78	96
2[a,b]	**1b**	5.6	4	81	96
3	**S-1**	5.6	4	67	68
4	**1b**	3.4	rt	69	91
5	**S-2**	3.4	rt	42	−48
6	**S-3**	3.4	rt	38	11
7	**S-4**	3.4	rt	33	41
8	**S-5**	3.4	rt	41	−9



1a: R = Me
1b: R = Bn



S-1



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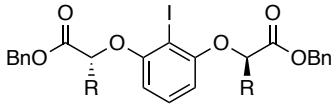
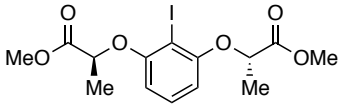


S-3: R = Me
S-4: R = Bn

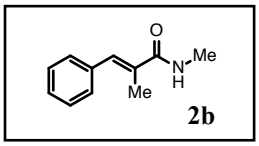


S-5

Table S2. Catalyst optimization. Unless otherwise noted, reactions were performed on 0.10 mmol scale, with yields of 1,2-difluoride determined by ^{1}H NMR using nitrobenzene as an internal standard. [a]Reaction was conducted on 1.00 mmol scale, and the isolated yield of **3** is listed. [b]A higher product ratio (**3f:4f** = 39:1.0 vs. 17:1.0) was achieved with catalyst **1b** than with catalyst **1a**.

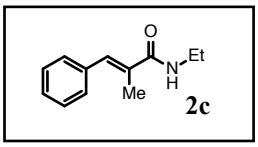
Preparation and Characterization of Catalysts and Substrates

General Procedure A: To a stirred solution of carboxylic acid (1 equiv) in dichloromethane (0.1 M) was added 1-hydroxybenzotriazole hydrate (1.5 equiv) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (1.7 equiv). *N,N*-Diisopropylethylamine (4.0 equiv) and amine coupling partner (3.0 equiv) were added sequentially by syringe. After stirring for 12–18 h, the solution was diluted with dichloromethane (10 mL per 1.00 mmol of substrate) and washed with 1.0 M aqueous HCl (10 mL per 1.00 mmol of substrate), then with brine (10 mL per 1.00 mmol of substrate). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.



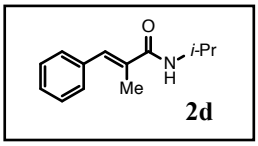
2b

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and methylamine (2.0 M in THF, 9.25 mL, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (50% ethyl acetate in hexanes) to give **2b** (959 mg, 89%) as a white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.32 (m, 3H), 7.31 – 7.27 (m, 1H), 5.88 (br s, 1H), 2.95 (d, *J* = 4.9 Hz, 3H), 2.10 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.4, 136.3, 133.8, 132.1, 129.4, 128.5, 127.9, 26.9, 14.4; FTIR (thin film) ν 3311, 2937, 1649, 1611, 1531, 702 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{11}H_{14}NO$ $[M+H]^+$: 176.1070; found 176.1068.



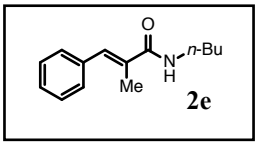
2c

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and ethylamine (2.0 M in THF, 9.25 mL, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (20 to 50% ethyl acetate in hexanes) to give **2c** (1.006 g, 86%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.27 (m, 4H), 5.84 (br s, 1H), 3.43 (qd, *J* = 7.3, 5.6 Hz, 2H), 2.10 (d, *J* = 1.4 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.6, 136.4, 133.7, 132.3, 129.4, 128.5, 127.9, 35.0, 15.1, 14.4; FTIR (thin film) ν 3291, 2968, 2943, 2876, 1641, 1617, 1532, 705 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226; found 190.1225.



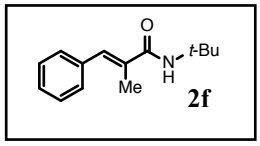
2d

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and isopropylamine (1.51 mL, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (30% ethyl acetate in hexanes) to give **2d** (1.054 g, 84%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.27 (m, 4H), 5.67 (br s, 1H), 4.20 (m, 1H), 2.09 (d, *J* = 1.4 Hz, 3H), 1.24 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.0, 136.3, 133.7, 132.5, 129.4, 128.5, 127.9, 41.9, 23.0, 14.4; FTIR (thin film) ν 3295, 2975, 1638, 1614, 1530, 1358, 706 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1383; found 204.1382.



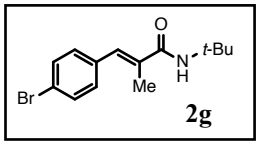
2e

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and *n*-butylamine (1.83 mL, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (30% ethyl acetate in hexanes) to give **2e** (1.269 g, 95%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ δ 7.40 – 7.35 (m, 2H), 7.33 (dd, *J* = 6.7, 1.5 Hz, 3H), 7.31 – 7.27 (m, 1H), 5.85 (br s, 1H), 3.39 (td, *J* = 7.2, 5.7 Hz, 2H), 2.10 (d, *J* = 1.4 Hz, 3H), 1.63 – 1.51 (m, 4H), 1.41 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.7, 136.4, 133.7, 132.4, 129.4, 128.5, 127.9, 39.9, 31.9, 20.3, 14.5, 13.9; FTIR (thin film) ν 3296, 2959, 2934, 2872, 1638, 1613, 1527, 706 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found 218.1539.



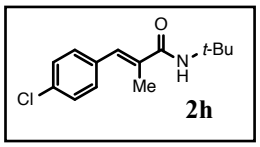
2f

Prepared according to General Procedure A using α-methylcinnamic acid (3.00 g, 18.5 mmol) and *tert*-butylamine (5.83 mL, 55.5 mmol). After workup, the crude residue was purified by silica gel chromatography (20% ethyl acetate in hexanes) to give **2f** (3.538 g, 88%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 7.25 (s, 1H), 5.70 (br s, 1H), 2.06 (d, J = 1.4 Hz, 3H), 1.44 (s, 9H);^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.2, 136.5, 133.6, 133.0, 129.4, 128.4, 127.8, 51.5, 29.0, 14.5; FTIR (thin film) ν 3315, 2967, 1647, 1619, 1527, 1450, 702 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found 218.1539.



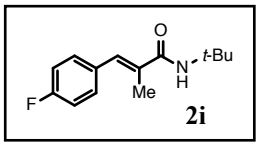
2g

To a stirred solution of ethyl (*E*)-3-(4-bromophenyl)-2-methylacrylate[1] (1.275 g, 4.74 mmol) in THF (13.5 mL) and ethanol (13.5 mL) was added 1.0 M aqueous NaOH (13.5 mL). After 21 h, 1.0 M aqueous HCl (20 mL) and ethyl acetate (40 mL) were sequentially added. The organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford (*E*)-3-(4-bromophenyl)-2-methylacrylic acid, which was used without further purification. The title compound was prepared according to General Procedure A using (*E*)-3-(4-bromophenyl)-2-methylacrylic acid (1.062 g, 4.41 mmol) and *tert*-butylamine (1.39 mL, 13.2 mmol). After workup, the crude residue was purified by silica gel chromatography (30% ethyl acetate in hexanes) to give **2g** (1.087 g, 83%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.20 – 7.16 (m, 3H), 5.68 (s, 1H), 2.03 (d, J = 1.4 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.9, 135.4, 134.2, 131.9, 131.6, 130.9, 121.8, 51.6, 28.9, 14.5; FTIR (thin film) ν 3323, 2968, 1649, 1622, 1527, 1487, 1221 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}BrNO$ $[M+H]^+$: 296.0645; found 296.0643.



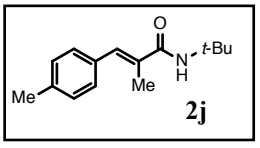
2h

Prepared according to General Procedure A using (*E*)-3-(4-chlorophenyl)-2-methylacrylic acid[2] (785 mg, 3.99 mmol) and *tert*-butylamine (1.26 mL, 12.0 mmol). After workup, the crude residue was purified by silica gel chromatography (10 to 30% diethyl ether in hexanes) to give **2h** (739 mg, 74%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.20 (s, 1H), 5.68 (br s, 1H), 2.04 (d, J = 1.4 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.9, 134.9, 134.1, 133.6, 131.8, 130.6, 128.7, 51.6, 28.9, 14.5; FTIR (thin film) ν 3314, 2968, 2922, 1648, 1621, 1528, 1452, 1091 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}ClNO$ $[M+H]^+$: 252.1150; found 252.1146.



2i

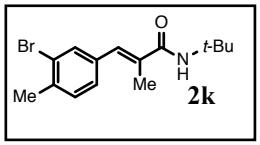
Prepared according to General Procedure A using (*E*)-3-(4-fluorophenyl)-2-methylacrylic acid (300 mg, 1.67 mmol) and *tert*-butylamine (0.53 mL, 5.01 mmol). After workup, the crude residue was purified by silica gel chromatography (35% diethyl ether in hexanes) to give **2i** (350 mg, 89%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 (s, 1H), 7.09 – 7.03 (m, 2H), 5.68 (s, 1H), 2.04 (d, J = 1.5 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.0, 162.2 (d, J = 247.9 Hz), 133.4, 132.5 (d, J = 3.6 Hz), 132.0, 131.1 (d, J = 8.1 Hz), 115.5 (d, J = 21.5 Hz), 51.5, 29.0, 14.5; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -113.69 (tt, J = 8.6, 5.4 Hz); FTIR (thin film) ν 3317, 2968, 2926, 1651, 1622, 1508, 1226 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}FNO$ $[M+H]^+$: 236.1445; found 236.1443.



2j

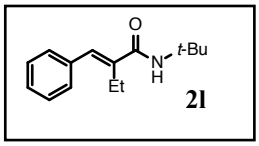
Prepared according to General Procedure A using (*E*)-2-methyl-3-(*p*-tolyl)acrylic acid[2] (500 mg, 2.84 mmol) and *tert*-butylamine (0.90 mL, 8.52 mmol). After workup, the crude residue was purified by silica gel chromatography (0 to 20% diethyl ether in hexanes) to give **2j** (532 mg, 81%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, J = 8.1 Hz, 3H), 7.20 – 7.15 (m, 2H), 5.68 (s, 1H), 2.36 (s, 3H), 2.06 (d, J = 1.4 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.4, 137.7, 133.6, 133.0, 132.8, 129.4, 129.2, 51.5, 29.0, 21.4, 14.5; FTIR (thin film) ν 3298, 2972, 2951, 2918, 1646, 1619,

1527, 1512, 1451, 1224, 812 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1696; found 232.1694.



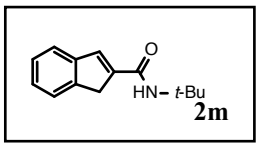
2k

Triethyl 2-phosphonopropionate (1.63 mL, 7.54 mmol, 1.5 equiv) was slowly added to a dispersion of sodium hydride (349 mg, 8.53 mmol, 1.7 equiv) in THF (7.50 mL) at 0 ˚C. The resulting mixture was stirred for 1 h. The mixture was then cooled to -78 ˚C, and 3-bromo-4-methylbenzaldehyde (1.00 g, 5.02 mmol, 1.0 equiv) was slowly added. After stirring at room temperature for 15 h, the mixture was poured over saturated aqueous ammonium chloride, and the phases were separated. The aqueous phase was extracted with diethyl ether, and the combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (0 to 10% ethyl acetate in hexanes). The resulting colorless oil (1.275 g, 4.74 mmol) was dissolved in THF (13.5 mL) and ethanol (13.5 mL) To the stirred solution was added 1.0 M aqueous NaOH (13.5 mL). After 21 h, 1.0 M aqueous HCl (20 mL) and ethyl acetate (40 mL) were sequentially added. The organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford (*E*)-3-(3-bromo-4-methylphenyl)-2-methylacrylic acid, which was used without further purification. The spectral data for this compound were in accordance with the literature.[3] The title compound was prepared according to General Procedure A using (*E*)-3-(3-bromo-4-methylphenyl)-2-methylacrylic acid (896 mg, 3.51 mmol) and *tert*-butylamine (1.10 mL, 10.5 mmol). After workup, the crude residue was purified by silica gel chromatography (25% ethyl acetate in hexanes) to give **2k** (979.4 mg, 90%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.6 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 2.40 (s, 3H), 2.05 (d, *J* = 1.4 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.9, 137.5, 135.9, 134.2, 133.0, 131.4, 130.7, 128.3, 124.9, 51.6, 29.0, 22.9, 14.5; FTIR (thin film) ν 3308, 2967, 2922, 1649, 1619, 1527, 1221 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{21}BrNO$ $[M+H]^+$: 310.0801; found 310.0800.



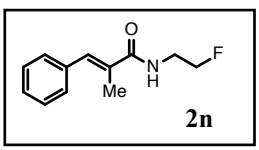
2l

Prepared according to General Procedure A using (*E*)-2-benzylidenebutanoic acid[4] (723 mg, 4.10 mmol) and *tert*-butylamine (1.29 mL, 12.3 mmol). After workup, the crude residue was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give **2l** (816.6 mg, 86%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 7.01 (s, 1H), 5.70 (br s, 1H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.44 (s, 9H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.5, 141.6, 136.4, 131.0, 128.9, 128.5, 127.7, 51.5, 29.0, 21.4, 13.6; FTIR (thin film) ν 3310, 2965, 1642, 1619, 1536, 700 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1696; found 232.1695.



2m

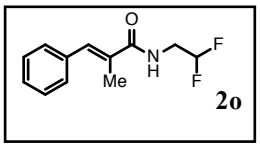
Prepared according to General Procedure A using 1*H*-indene-2-carboxylic acid (200 mg, 1.25 mmol) and *tert*-butylamine (0.39 mL, 3.75 mmol). After workup, the crude residue was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give **2m** (212 mg, 79%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.36 (td, *J* = 1.8, 0.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 5.73 (br s, 1H), 3.65 – 3.63 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 164.5, 143.9, 143.3, 142.6, 134.9, 127.0, 126.9, 124.6, 122.8, 51.6, 38.4, 29.1; FTIR (thin film) ν 3246, 3069, 3055, 2980, 2960, 2929, 1628, 1588, 1563, 1532, 1270, 1218, 758, 713 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1383; found 216.1380.



2n

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and 2-fluoroethylamine hydrochloride (1.84 g, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (50% diethyl ether in hexanes) to give **2n** (1.037 g, 81%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.36 – 7.28 (m, 3H), 6.24 (br s,

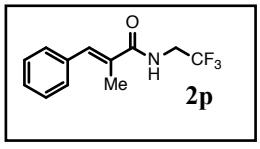
1H), 4.59 (dt, J = 47.5, 4.7 Hz, 2H), 3.72 (ddt, J = 28.5, 5.7, 4.6 Hz, 2H), 2.12 (d, J = 1.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.8, 136.1, 134.6, 131.7, 129.5, 128.5, 128.1, 83.0 (d, J = 166.2 Hz), 40.5 (d, J = 19.5 Hz), 14.4; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -224.2 (tt, J = 47.3, 28.4 Hz, 1F); FTIR (thin film) ν 3279, 3052, 2960, 1643, 1619, 1531, 705 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{12}H_{15}FNO$ $[M+H]^+$: 208.1132; found 208.1129.



2o

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and with the following modification: 2.0 equiv of 2,2-difluoroethan-1-amine (0.87 mL, 12.3 mmol) were used. After workup, the crude residue was purified by silica gel chromatography (10 to 50% diethyl ether in hexanes) to give **2o** (1.094 g, 79%) as a white solid.

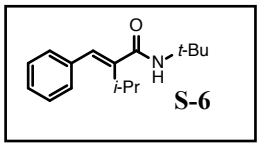
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.36 – 7.30 (m, 3H), 6.10 (br s, 1H), 5.94 (tt, J = 56.3, 4.2 Hz, 1H), 3.77 (tdd, J = 14.8, 6.2, 4.2 Hz, 2H), 2.13 (d, J = 1.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.0, 135.9, 135.2, 131.2, 129.5, 128.6, 128.3, 113.8 (t, J = 241.3 Hz), 42.4 (t, J = 26.5 Hz), 14.4; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -122.9 (dt, J = 56.4, 14.8 Hz, 2F); FTIR (thin film) ν 3290, 1646, 1616, 1524, 1113, 1057, 695 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{12}H_{14}F_2NO$ $[M+H]^+$: 226.1038; found 226.1035.



2p

Prepared according to General Procedure A using α-methylcinnamic acid (1.00 g, 6.17 mmol) and 2,2,2-trifluoroethan-1-amine (1.45 mL, 18.5 mmol). After workup, the crude residue was purified by silica gel chromatography (20 to 50% ethyl acetate in hexanes) to give **2p** (1.365 g, 91%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.37 – 7.30 (m, 3H), 6.10 (br s, 1H), 4.07 (qd, J = 9.1, 6.4 Hz, 2H), 2.14 (d, J = 1.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.6, 135.7, 135.5, 131.1, 129.5, 128.6, 128.4, 124.4 (q, J = 278.4 Hz), 41.2 (q, J = 34.6 Hz), 14.4; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -72.4 (t, J = 9.2 Hz, 3F); FTIR (thin film) ν 3277, 1649, 1625, 1532, 1258, 1153 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{12}H_{13}F_3NO$ $[M+H]^+$: 244.0944; found 244.0942.



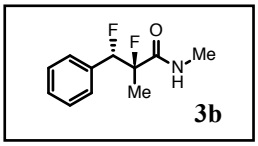
S-6

Prepared according to General Procedure A using (*E*)-2-benzylidene-3-methylbutanoic acid[5] (187 mg, 0.98 mmol) and *tert*-butylamine (0.31 mL, 2.94 mmol). After workup, the crude residue was purified by silica gel chromatography (20% ethyl acetate in hexanes) to give **S-6** (153 mg, 63%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.29 – 7.25 (m, 3H), 6.65 (s, 1H), 5.57 (s, 1H), 3.08 – 2.97 (m, 1H), 1.43 (s, 9H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.7, 147.0, 136.2, 128.8, 128.5, 128.3, 127.5, 51.6, 36.5, 29.0, 28.4, 21.7; FTIR (thin film) ν 3312, 2973, 2922, 1640, 1617, 1532, 702 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1852; found 246.1850.

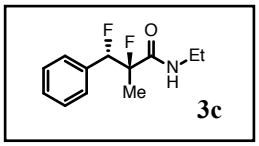
Synthesis and Characterization of 1,2-Difluorides

General Procedure B: A polyethylene conical tube equipped with a stir bar was charged with the alkene substrate (1 equiv), catalyst **1b** (20.0 mol%), and dichloromethane (2.00 mL per 1.00 mmol of substrate) at room temperature. The resulting mixture was cooled to -78 ˚C, and pyridinium poly(hydrogen fluoride) (pyr•9HF, 70% hydrogen fluoride by weight, 50 equiv hydrogen fluoride) was added via syringe, followed by *m*-chloroperbenzoic acid (*m*CPBA, 77% by weight, 1.30 equiv). The tube was sealed, and the mixture was warmed to 4 ˚C and stirred for 24 h. The mixture was then cooled to -78 ˚C, diluted with dichloromethane (10.0 mL per 1.00 mmol of substrate), and pipetted slowly into a suspension of basic alumina (10 g per 1.00 mmol of substrate) in dichloromethane (50 mL per 1.00 mmol of substrate) at -78 ˚C. The resulting suspension was warmed to room temperature with stirring. The suspension was then filtered, and the filter cake was washed with dichloromethane (200 mL per 1.00 mmol of substrate). The combined filtrates were concentrated under reduced pressure. The crude product mixture was analyzed by ^{19}F NMR to determine the ratio of 1,2-difluoride to 1,1-difluoride. The 1,1-difluoride products were assigned by analogy to previously reported 1,1-difluorides.[3] The crude product mixture was then purified by flash column chromatography on silica gel, and pure 1,2-difluoride was isolated and characterized.



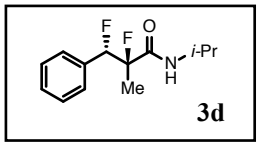
3b

Prepared according to General Procedure B using **2b** (175 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 3.3:1.0. After workup, the crude residue was purified by silica gel chromatography (10 to 30% diethyl ether in hexanes) to give **3b** (108 mg, 51%) as a white solid. **3b** was determined to be of 94% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1 ˚/min, 7 psi, t_R(major) = 94.910 min, t_R(minor) = 96.848 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.31 (m, 5H), 5.99 (br s, 1H), 5.72 (dd, *J* = 44.1, 25.7 Hz, 1H), 2.63 (dd, *J* = 5.1, 0.6 Hz, 3H), 1.79 (dd, *J* = 22.5, 1.8 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.0 (dd, *J* = 19.4, 7.3 Hz), 135.8 (dd, *J* = 23.0, 1.3 Hz), 129.0, 128.1, 127.1 (d, *J* = 7.2 Hz), 98.5 (dd, *J* = 196.1, 23.0 Hz), 94.4 (dd, *J* = 184.2, 19.4 Hz), 25.8, 20.2 (dd, *J* = 24.4, 5.3 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -171.42 – -171.71 (m, 1F), -196.87 (dd, *J* = 44.2, 9.7 Hz, 1F); FTIR (thin film) ν 3342, 1658, 1552, 729 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{11}H_{14}F_2NO$ $[M+H]^+$: 214.1038; found 214.1036; $[\alpha]_D^{22}$ = –37.7 (c = 0.030, $CHCl_3$).



3c

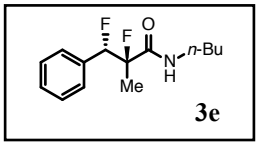
Prepared according to General Procedure B using **2c** (189 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 4.3:1.0. After workup, the crude residue was purified by silica gel chromatography (5 to 20% diethyl ether in hexanes) to give **3c** (138 mg, 61%) as a white solid. **3c** was determined to be of 95% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(major) = 60.848 min, t_R(minor) = 61.554 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.33 (m, 5H), 5.96 (br s, 1H), 5.71 (dd, *J* = 44.2, 25.7 Hz, 1H), 3.22 – 3.11 (m, 1H), 3.11 – 3.00 (m, 1H), 1.79 (dd, *J* = 22.5, 1.6 Hz, 3H), 0.87 (dd, *J* = 7.7, 7.0 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.2 (dd, *J* = 19.2, 7.3 Hz), 134.2 (d, *J* = 21.8 Hz), 129.0, 128.1, 127.2 (d, *J* = 7.1 Hz), 98.2 (dd, *J* = 196.3, 22.7 Hz), 94.4 (dd, *J* = 184.6, 19.2 Hz), 33.9, 20.1 (dd, *J* = 24.4, 5.0 Hz), 14.5; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -171.60 (dtdd, *J* = 48.8, 22.4, 9.7, 5.4 Hz, 1F), -196.61 (ddd, *J* = 44.1, 10.0, 1.8 Hz, 1F); FTIR (thin film) ν 3336, 1651, 1550, 1109, 693 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{12}H_{16}F_2NO$ $[M+H]^+$: 228.1194; found 228.1192; ; $[\alpha]_D^{21}$ = –12.7 (c = 0.069, $CHCl_3$).



3d

Prepared according to General Procedure B using **2d** (203 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 4.8:1.0. After workup, the crude residue was purified by silica gel chromatography (0 to 12% diethyl ether in hexanes) to give **3d** (135 mg, 56%) as a white solid. **3d** was determined to be of 95% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 59.224 min, t_R(major) = 59.726 min).

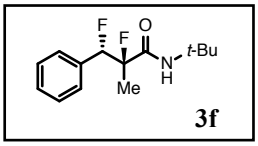
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.33 (m, 5H), 5.69 (m, 2H), 4.03 – 3.67 (m, 1H), 1.79 (dd, *J* = 22.5, 1.7 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.3 (dd, *J* = 19.1, 7.1 Hz), 134.19 (d, *J* = 21.8 Hz), 129.0, 128.1, 127.3 (d, *J* = 7.3 Hz), 98.1 (dd, *J* = 196.4, 22.7 Hz), 94.5 (dd, *J* = 184.4, 18.9 Hz), 41.1, 22.4, 22.2, 20.1 (dd, *J* = 24.5, 4.9 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -171.43 – -171.76 (m, 1F), -196.40 (dd, *J* = 44.1, 9.8 Hz, 1F); FTIR (thin film) ν 3333, 1646, 1544, 720 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{13}H_{18}F_2NO$ $[M+H]^+$: 242.1351; found 242.1348; ; $[\alpha]_D^{22}$ = –3.9 (c = 0.058, $CHCl_3$).



3e

Prepared according to General Procedure B using **2e** (217 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 6.9:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 16% diethyl ether in hexanes) to give **3e** (161 mg, 63%) as a white solid. **3e** was determined to be of 94% e.e. by chiral GC analysis (CP-Chirasil-Dex CB, 120 ˚C, 14 psi, t_R(major) = 34.262 min, t_R(minor) = 35.790 min).

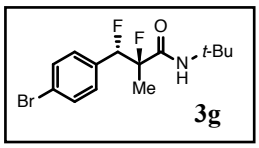
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.33 (m, 5H), 5.97 (br s, 1H), 5.70 (dd, *J* = 44.1, 25.7 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.99 (m, 1H), 1.79 (dd, *J* = 22.5, 1.7 Hz, 1H), 1.28 – 1.10 (m, 2H), 1.10 – 0.94 (m, 2H), 0.82 – 0.77 (m, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.2 (dd, *J* = 19.0, 7.2 Hz), 134.2 (d, *J* = 21.6 Hz), 129.0 (d, *J* = 1.7 Hz), 128.1, 127.3 (d, *J* = 7.0 Hz), 98.3 (dd, *J* = 196.3, 22.9 Hz), 94.5 (dd, *J* = 184.0, 19.0 Hz), 38.7, 31.2, 20.2 (dd, *J* = 24.4, 5.0 Hz), 19.7, 13.7; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -171.50 – -171.73 (m, 1F), -196.19 (ddd, *J* = 44.1, 9.6, 1.8 Hz, 1F); FTIR (thin film) ν 3341, 2955, 1652, 1545 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{20}F_2NO$ $[M+H]^+$: 256.1507; found 256.1506; $[\alpha]_D^{21}$ = –13.5 (c = 0.11, $CHCl_3$).



3f

Prepared according to General Procedure B using **2f** (217 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 39:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 10% diethyl ether in hexanes) to give **3f** (207 mg, 81%) as a white solid. **3f** was determined to be of 96% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 57.689 min, t_R(major) = 58.359 min).

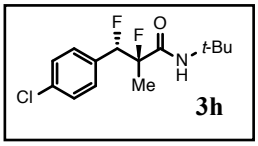
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 5H), 5.77 (br s, 1H), 5.68 (dd, *J* = 55, 25 Hz, 1H), 1.77 (dd, *J* = 22.5, 1.7 Hz, 3H), 1.14 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.4 (dd, *J* = 17.6, 7.2 Hz), 134.2 (d, *J* = 21.9 Hz), 129.0, 128.1, 127.5 (d, *J* = 6.8 Hz), 97.9 (dd, *J* = 197.3, 22.5 Hz), 94.6 (dd, *J* = 184.0, 19.0 Hz), 51.2, 28.4, 20.2 (dd, *J* = 24.6, 5.0 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -169.28 – -169.57 (m, 1F), -196.25 (dd, *J* = 44.1, 9.7 Hz, 1F); FTIR (thin film) ν 3443, 3387, 2970, 1682, 1528, 1022, 714 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{20}F_2NO$ $[M+H]^+$: 256.1507; found 256.1505; $[\alpha]_D^{21}$ = –11.0 (c = 0.048, $CHCl_3$).



3g

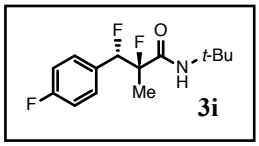
Prepared according to General Procedure B using **2g** (296 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of >100:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 10% diethyl ether in hexanes) to give **3g** (289 mg, 83%) as a white solid. **3g** was determined to be of 98% e.e by chiral HPLC analysis (AD-H, 1 mL/min, 2% IPA/hexanes, 220 nm, t_R(major) = 6.280 min, t_R(minor) = 8.468 min).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.25 – 7.21 (m, 2H), 5.81 (br s, 1H), 5.67 (dd, *J* = 44.1, 25.5 Hz, 1H), 1.75 (dd, *J* = 22.5, 1.7 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.3 (dd, *J* = 17.7, 7.2 Hz), 133.3 (d, *J* = 22.1 Hz), 131.3, 129.1 (d, *J* = 6.6 Hz), 123.2 (d, *J* = 1.9 Hz), 97.7 (dd, *J* = 197.5, 22.4 Hz), 93.9 (dd, *J* = 184.5, 19.2 Hz), 51.4, 28.5, 20.2 (dd, *J* = 24.5, 5.0 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -169.33 – -169.89 (m, 1F), -197.08 (dd, *J* = 44.1, 10.1 Hz, 1F); FTIR (thin film) ν 3440, 2972, 1682, 1528, 1012, 777 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}BrF_2NO$ $[M+H]^+$: 334.0613; found 334.0610; $[\alpha]_D^{22}$ = –0.7 (c = 0.19, $CHCl_3$).



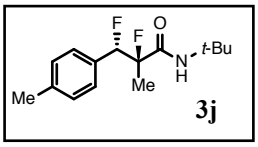
Prepared according to General Procedure B using **2h** (252 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 86:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 6% diethyl ether in hexanes) to give **3h** (243 mg, 84%) as a white solid. **3h** was determined to be of 97% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 0.2 ˚/min, 14 psi, t_R(minor) = 402.049 min, t_R(major) = 403.697 min).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 5.81 (br s, 1H), 5.69 (dd, *J* = 44.1, 25.5 Hz, 1H), 1.76 (dd, *J* = 22.5, 1.7 Hz, 3H), 1.17 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.3 (dd, *J* = 17.7, 7.2 Hz), 135.0 (d, *J* = 1.8 Hz), 132.8 (d, *J* = 22.4 Hz), 128.9 (d, *J* = 6.8 Hz), 128.3, 97.8 (dd, *J* = 197.5, 22.6 Hz), 93.9 (dd, *J* = 184.3, 19.2 Hz), 51.4, 28.4, 20.2 (dd, *J* = 24.5, 5.1 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -169.44 – -169.74 (m, 1F), -196.72 (dd, *J* = 44.2, 9.9 Hz, 1F); FTIR (thin film) ν 3441, 2969, 1681, 1530, 779 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}ClF_2NO$ $[M+H]^+$: 290.1118; found 290.1115; $[\alpha]_D^{21}$ = –2.2 (c = 0.14, $CHCl_3$).



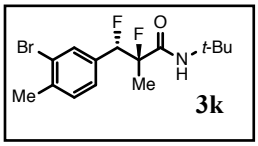
Prepared according to General Procedure B using **2i** (235 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 16:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 8% diethyl ether in hexanes) to give **3i** (197 mg, 72%) as a white solid. **3i** was determined to be of 98% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 57.213 min, t_R(major) = 57.730 min).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.08 – 6.99 (m, 2H), 5.79 (br s, 1H), 5.68 (dd, *J* = 43.9, 25.6 Hz, 1H), 1.76 (dd, *J* = 22.5, 1.7 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.4 (dd, *J* = 17.7, 7.2 Hz), 163.2 (d, *J* = 247.8 Hz), 130.1 (d, *J* = 22.8 Hz), 129.8 – 129.3 (m), 115.1 (d, *J* = 21.7 Hz), 97.9 (dd, *J* = 197.5, 22.6 Hz), 94.0 (dd, *J* = 184.0, 18.9 Hz), 51.3, 28.4, 20.2 (dd, *J* = 24.7, 4.8 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -112.66 (ttd, *J* = 8.1, 5.3, 2.5 Hz, 1F), -169.70 – -170.01 (m, 1F), -195.10 (dd, *J* = 44.0, 10.0 Hz, 1F); FTIR (thin film) ν 3388, 2984, 1663, 1532, 1228, 788 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{19}F_3NO$ $[M+H]^+$: 274.1413; found 274.1413; $[\alpha]_D^{22}$ = –8.1 (c = 0.11, $CHCl_3$).



Prepared according to General Procedure B using **2j** (231 mg, 1.00 mmol) and with the following modification: 25 equiv hydrogen fluoride were used. Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 2.2:1.0. After workup, the crude residue was purified by silica gel chromatography (1 to 7% diethyl ether in hexanes) to give **3j** (107 mg, 40%) as a white solid. **3j** was determined to be of 98% e.e by chiral HPLC analysis (AD-H, 1 mL/min, 2% IPA/hexanes, 220 nm, t_R(major) = 6.029 min, t_R(minor) = 7.590 min).

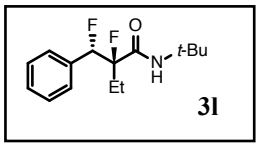
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.80 (br s, 1H), 5.65 (dd, *J* = 44.0, 25.8 Hz, 2H), 2.35 (d, *J* = 0.9 Hz, 3H), 1.75 (dd, *J* = 22.4, 1.7 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 168.57 (dd, *J* = 17.6, 7.1 Hz), 138.83 (d, *J* = 1.7 Hz), 131.30 (d, *J* = 22.1 Hz), 128.75, 127.38 (dd, *J* = 7.7, 1.3 Hz), 98.04 (dd, *J* = 197.0, 22.7 Hz), 94.57 (dd, *J* = 183.4, 19.2 Hz), 51.24, 28.43, 21.34, 20.21 (dd, *J* = 24.5, 5.1 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -169.08 – -169.31 (m, 1F), -195.50 (dd, *J* = 44.2, 9.7 Hz, 1F); FTIR (thin film) ν 3441, 2965, 1684, 1526, 1034, 777 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{22}F_2NO$ $[M+H]^+$: 270.1664; found 270.1661; $[\alpha]_D^{22}$ = –5.8 (c = 0.053, $CHCl_3$).



Prepared according to General Procedure B using **2k** (310 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 79:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 10% diethyl ether in hexanes) to give **3k** (289 mg, 83%) as a white solid. **3k** was determined to be of 98% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 82.246 min, t_R(major) = 82.683 min).

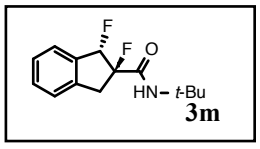
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.20 (dd, *J* = 1.3, 0.7 Hz, 2H), 5.83 (s, 1H), 5.66 (dd, *J* = 44.1, 25.6 Hz, 1H), 2.39 (d, *J* = 1.0 Hz, 3H), 1.75 (dd, *J* = 22.5, 1.8 Hz, 3H), 1.19 (s, 9H); ^{13}C NMR (125.7 MHz,

$CDCl_3$) δ 168.4 (dd, *J* = 17.7, 7.3 Hz), 138.7, 133.7 (d, *J* = 22.3 Hz), 131.0 (d, *J* = 7.2 Hz), 130.4, 126.2 (d, *J* = 7.0 Hz), 124.6, 97.9 (dd, *J* = 197.5, 22.5 Hz), 93.6 (dd, *J* = 184.7, 19.3 Hz), 51.5, 28.5, 22.9, 20.2 (dd, *J* = 24.6, 5.3 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -169.23 – -169.52 (m, 1F), -197.31 (dd, *J* = 43.8, 9.9 Hz, 1F); FTIR (thin film) ν 3401, 2976, 1665, 1531, 1048, 781 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{21}BrF_2NO$ $[M+H]^+$: 348.0769; found 348.0767; $[\alpha]_D^{22}$ = +5.0 (c = 0.23, $CHCl_3$).



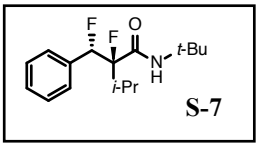
3l

Prepared according to General Procedure B using **2l** (231 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of >100:1.0. After workup, the crude residue was purified by silica gel chromatography (2 to 6% diethyl ether in hexanes) to give **3l** (156 mg, 58%) as a colorless oil. **3l** was determined to be of 95% e.e. by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 64.469 min, t_R(major) = 65.011 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 5.78 (br s, 1H), 5.69 (dd, *J* = 44.3, 25.8 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.18 – 2.09 (m, 1H), 1.14 (s, 9H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.4 (dd, *J* = 17.8, 7.1 Hz), 134.4 (d, *J* = 22.0 Hz), 129.0 (d, *J* = 1.8 Hz), 128.0, 127.5 (d, *J* = 6.4 Hz), 100.8 (dd, *J* = 200.2, 21.8 Hz), 94.6 (dd, *J* = 183.8, 18.9 Hz), 51.4, 28.4, 26.4 (dd, *J* = 23.2, 4.4 Hz), 7.4 (d, *J* = 3.8 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -181.01 – -181.20 (m, 1F), -196.00 (dd, *J* = 44.3, 10.0 Hz, 1F); FTIR (thin film) ν 3444, 2973, 1681, 1526, 1457, 717 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{15}H_{22}F_2NO$ $[M+H]^+$: 270.1664; found 270.1663; $[\alpha]_D^{22}$ = –2.5 (c = 0.076, $CHCl_3$).



3m

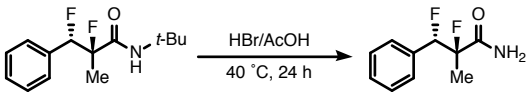
Prepared according to General Procedure B using **2m** (215 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of >100:1.0. After workup, the crude residue was purified by silica gel chromatography (5–20% diethyl ether in hexanes) to give **3m** (108 mg, 43%) as a pale yellow solid. **3m** was determined to be of 77% e.e by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 76.993 min, t_R(major) = 77.287 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 1H), 7.40–7.35 (m, 1H), 7.33–7.27 (m, 1H), 6.26 (s, 1H), 5.99 (dd, *J* = 54.9, 19.2 Hz, 1H), 3.93 (dd, *J* = 18.2, 17.1 Hz, 1H), 3.20 (ddd, *J* = 23.5, 17.1, 1.9 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 20.6, 3.0 Hz), 141.0 (dd, *J* = 5.1, 2.1 Hz), 136.2 (dd, *J* = 19.5, 4.4 Hz), 130.7 (d, *J* = 3.6 Hz), 127.8 (d, *J* = 2.9 Hz), 125.6, 124.9 (d, *J* = 1.8 Hz), 103.8 (dd, *J* = 196.5, 22.3 Hz), 99.9 (dd, *J* = 190.1, 35.7 Hz), 51.9, 40.1 (d, *J* = 24.5 Hz), 28.8; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -156.56 – -156.72 (m, 1F), -179.96 (dd, *J* = 54.5, 4.9 Hz, 1F); FTIR (thin film) ν 3439, 3351, 2969, 2932, 1686, 1526, 1227, 1018, 753 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{14}H_{18}F_2NO$ $[M+H]^+$: 254.1351; found 254.1349; ; $[\alpha]_D^{22}$ = 51.9 (c = 0.079, $CHCl_3$).



S-7

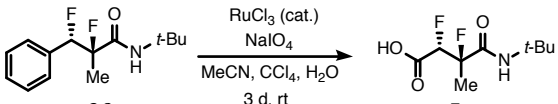
Prepared according to General Procedure B using **S-6** (49.1 mg, 0.20 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of >100:1.0. After workup, the crude residue was purified by silica gel chromatography (10% diethyl ether in hexanes) to give **S-7** (24.7 mg, 44%) as a colorless oil. **S-7** was determined to be of 97% e.e by chiral GC analysis (CP-Chirasil-Dex CB, 40 → 160 ˚C, 1.5 ˚/min, 14 psi, t_R(minor) = 69.959 min, t_R(major) = 70.983 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 5.95 (dd, *J* = 44.1, 26.9 Hz, 1H), 5.75 (s, 1H), 2.51 (dpd, *J* = 17.5, 6.9, 1.4 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.13 (s, 9H), 1.05 (dd, *J* = 6.9, 1.1 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.0 (dd, *J* = 18.0, 7.9 Hz), 134.6 (d, *J* = 21.8 Hz), 128.9 (d, *J* = 1.6 Hz), 128.0, 127.7 (d, *J* = 7.6 Hz), 101.7 (dd, *J* = 199.6, 21.9 Hz), 93.2 (dd, *J* = 183.6, 18.8 Hz), 51.4, 32.7 (dd, *J* = 23.4, 3.3 Hz), 28.5, 17.9 (d, *J* = 8.6 Hz), 17.0; ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -174.72 – -174.94 (m), -197.81 (dd, *J* = 44.1, 10.0 Hz); FTIR (thin film) ν 3445, 2971, 1681, 1524, 1456, 1021, 716 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{24}F_2NO$ $[M+H]^+$: 284.1820; found 284.1819.

Derivatization of 1,2-Difluoride Products



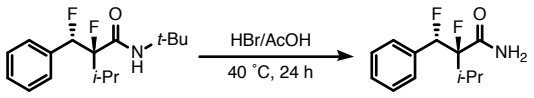
3f **3a**

3a: To a screw-cap vial charged with **3f** (51.1 mg, 0.20 mmol) and a stir bar, hydrogen bromide solution (1.00 mL, 33 wt. % in acetic acid) was added. The vial was capped tightly with a Teflon-lined cap and warmed to 40 ˚C for 24 h. The reaction mixture was then cooled to room temperature and diluted with ethyl acetate (10 mL). Saturated aqueous $NaHCO_3$ was added slowly until the aqueous layer reached pH = 8. The layers were separated, and the organic layer was washed with water (3 × 5 mL), washed with brine (5 mL), dried over anhydrous $MgSO_4$, and concentrated. The resulting residue was purified by flash column chromatography on silica gel (50% ethyl acetate in hexanes) to give **3a** as a white solid (35.4 mg, 89%). **3a** was determined to be of 96% e.e by chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1.5 ˚/min, 14 psi, t_R(major) = 67.968 min, t_R(minor) = 68.946 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 5H), 5.96 (br s, 1H), 5.71 (dd, *J* = 44.1, 25.2 Hz, 1H), 5.19 (br s, 1H), 1.81 (dd, *J* = 22.3, 1.7 Hz, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 171.0 (dd, *J* = 21.2, 6.8 Hz), 134.4 (d, *J* = 21.5 Hz), 128.9, 128.0, 127.3 (d, *J* = 7.2 Hz), 96.9 (dd, *J* = 196.1, 22.6 Hz), 94.2 (dd, *J* = 179.5, 19.6 Hz), 20.4 (dd, *J* = 25.2, 3.9 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$) δ -168.84 – -169.24 (m, 1F), -195.80 (dd, *J* = 44.1, 9.7 Hz, 1F); FTIR (thin film) ν 3394, 3189, 1661, 1639, 1112, 1038, 674 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{10}H_{12}F_2NO$ $[M+H]^+$: 200.0881; found 200.0880; $[\alpha]_D^{22}$ = –103 (c = 0.0062, $CHCl_3$).



3f **5**

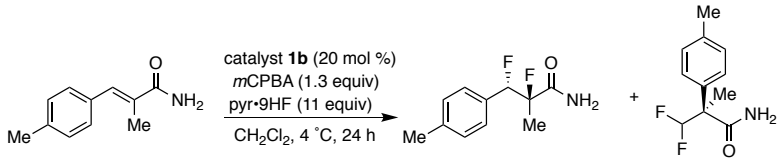
5: A catalytic amount of ruthenium trichloride hydrate and sodium periodate (770 mg, 3.6 mmol, 18 equiv) were added to a vigorously stirred solution of **3f** (51.1 mg, 0.20 mmol, 1.0 equiv) in carbon tetrachloride (0.75 mL), acetonitrile (0.75 mL), and water (2.0 mL). The reaction vessel was equipped with a vent needle, and the biphasic mixture was stirred for 72 h at room temperature. After 72 h, the reaction mixture was cooled to 0 ˚C and diethyl ether (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford **5** (33.1 mg, 74%) as a tan solid. **5** was determined to be of 96% e.e. by chiral GC analysis of its corresponding methyl ester **S-8**. To prepare methyl ester **S-8**, a solution of (diazomethyl)trimethylsilane (2.0 M in diethyl ether, 16.0 µL, 0.032 mmol, 1.5 equiv) was added dropwise via syringe to a stirred solution of **5** (5.0 mg, 0.022 mmol, 1 equiv) in benzene (150 µL) and methanol (43 µL) at room temperature. After 30 minutes, acetic acid (5 µL) was added dropwise via syringe to quench the unreacted (diazomethyl)trimethylsilane, and an aliquot of the reaction mixture was subjected to chiral GC analysis (β-Cyclosil, 40 → 200 ˚C, 1 ˚/min, 20 psi, t_R(major) = 53.977 min, t_R(minor) = 54.311 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (br s, 1H), 5.30 (dd, *J* = 47.7, 24.5 Hz, 1H), 1.72 (dd, *J* = 23.0, 1.9 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (125.7 MHz, acetone-d_6) δ 168.5 (dd, *J* = 18.7, 6.4 Hz), 166.8 (dd, *J* = 25.7, 5.7 Hz), 97.8 (dd, *J* = 195.4, 20.7 Hz), 91.0 (dd, *J* = 192.2, 22.4 Hz), 51.9, 28.7, 20.8 (dd, *J* = 23.9, 7.6 Hz); ^{19}F NMR (470.4 MHz, DMSO-d_6) δ -161.51 (pd, *J* = 23.5, 11.0 Hz, 1F), -202.93 (dd, *J* = 46.4, 11.6 Hz, 1F); FTIR (thin film) ν 3434, 2972, 1758, 1654, 1540, 1230, 1221, 1191, 1083 cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_9H_{16}F_2NO_3$ $[M+H]^+$: 224.1093; found 224.1092; $[\alpha]_D^{22}$ = 3.7 (c = 0.029, $CHCl_3$).



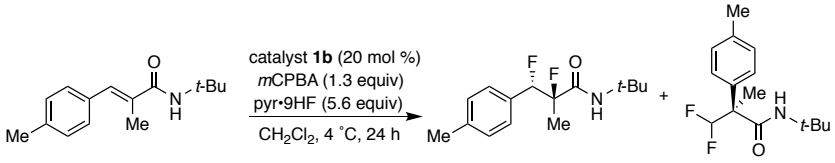
S-7 **3q**

3q: To a screw-cap vial charged with **S-7** (10.0 mg, 0.035 mmol) and a stir bar, hydrogen bromide solution (0.50 mL, 33 wt. % in acetic acid) was added. The vial was capped tightly and warmed to 40 ˚C for 24 h. The reaction mixture was then cooled to room temperature and diluted with ethyl acetate. Saturated aqueous $NaHCO_3$ was added slowly until the aqueous layer reached pH = 8. The layers were separated, and the organic layer was washed with water (3 × 5 mL), washed with brine (5 mL), dried over anhydrous $MgSO_4$, and concentrated. The resulting residue was purified by flash column chromatography on silica gel (0 to 10% diethyl ether in dichloromethane) to give **3q** as a white solid. The spectral data for **3q** were in accordance with the literature.[6] $[\alpha]_D^{21}$ = +14.3 (c = 0.00275, $CHCl_3$). The absolute stereochemistry of **3q** was assigned by comparison of the sign of the optical rotation with the literature value. The assignment of absolute stereochemistry was confirmed by verifying that the major and minor enantiomer of product eluted in the same order as previously reported (β-Cyclosil, 120 → 200 ˚C, 1 ˚/min, 7 psi, t_R(major) = 46.538 min, t_R(minor) = 47.017 min).[6]

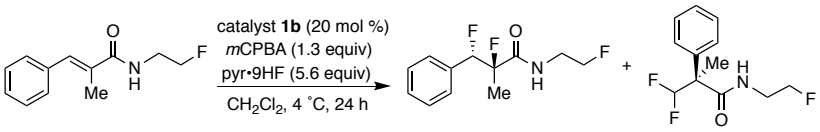
Measurement of Product Ratios for Selected Cinnamamides



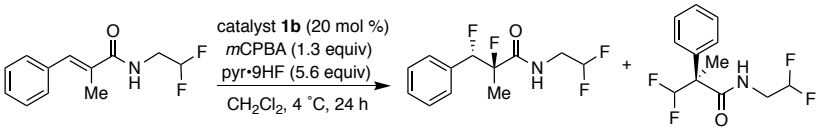
The reaction was conducted according to General Procedure B using (*E*)-2-methyl-3-(*p*-tolyl)acrylamide[7] (175.2, 1.00 mmol) and with the following modifications: 100 equiv of hydrogen fluoride were used, and the reaction was quenched after 72 h. Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 1.0:36.



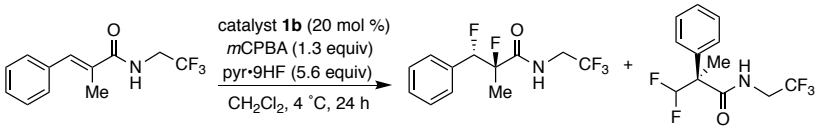
The reaction was conducted according to General Procedure B using **2j** (12.9 mg, 0.056 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 1.4:1.0.



The reaction was conducted according to General Procedure B using **2n** (207.3 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 3.4:1.0.



The reaction was conducted according to General Procedure B using **2o** (225.2 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 2.1:1.0.



The reaction was conducted according to General Procedure B using **2p** (243.2 mg, 1.00 mmol). Analysis of the crude product mixture by ^{19}F NMR indicated a 1,2:1,1 ratio of 1.1:1.0.

Correlations Between Product Ratios and Steric and Electronic Parameters for Amide *N*-Substituents

Steric and electronic parameters for the amide *N*-substituents of **2a–f** were plotted versus the product ratio (ln(1,2 : 1,1)) obtained for each substrate.

Chart 1. Correlation with Taft Steric Parameter[8, 9]

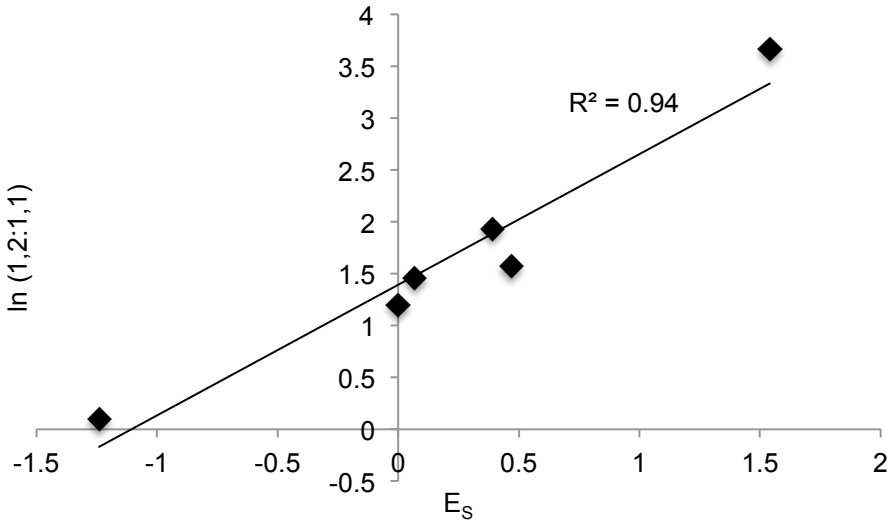


Chart 2. Correlation with A-Value[10]

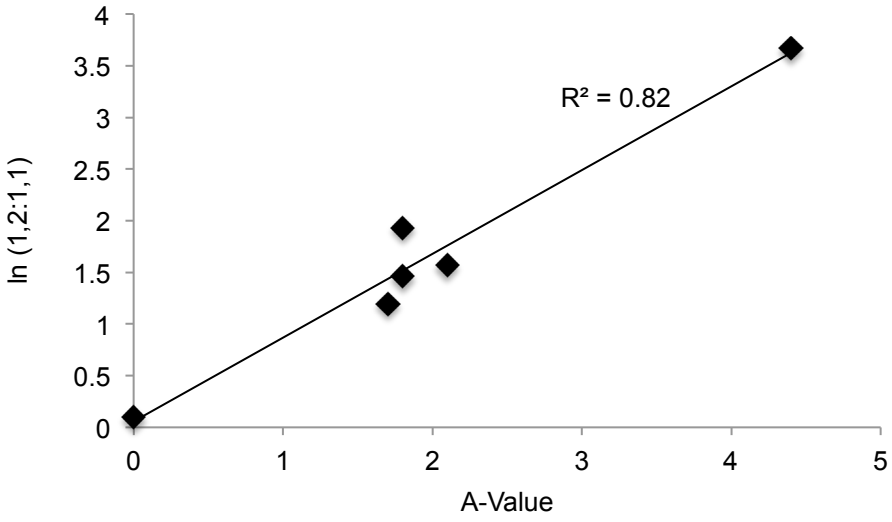


Chart 3. Correlation with Sterimol L[11]

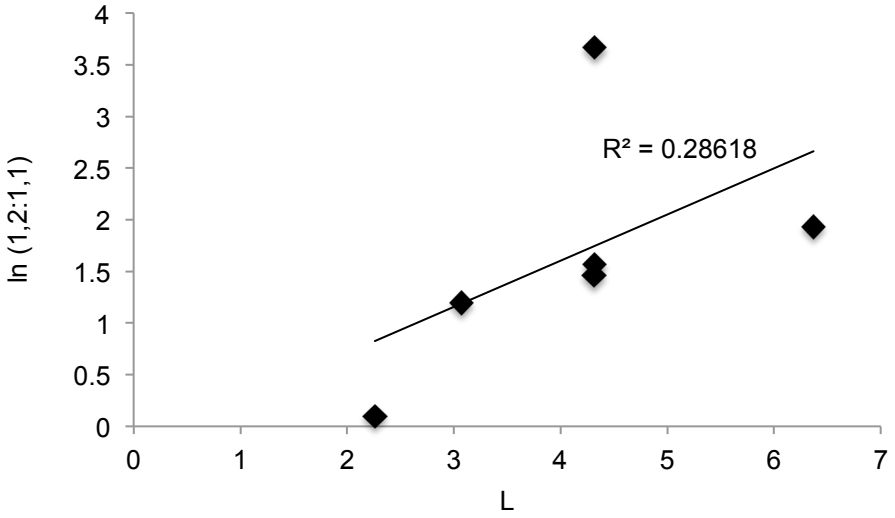


Chart 4. Correlation with Sterimol B_1 [11]

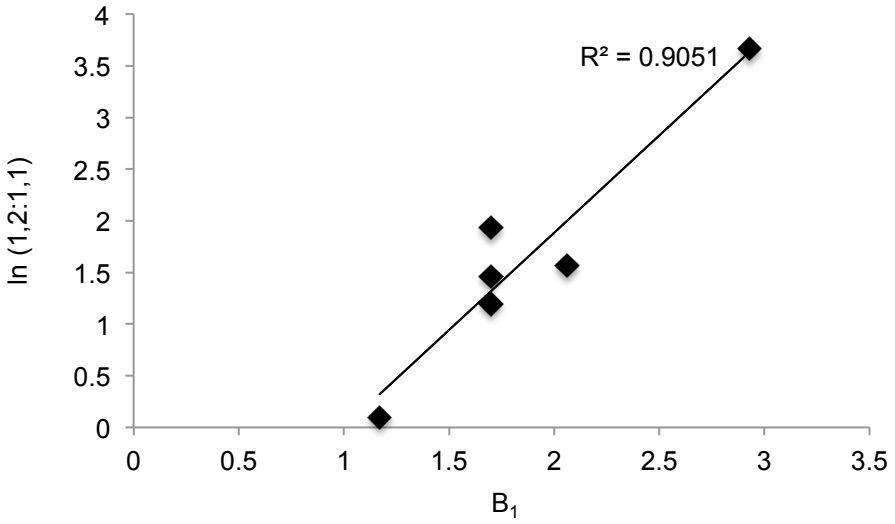


Chart 5. Correlation with Sterimol B_5 [11]

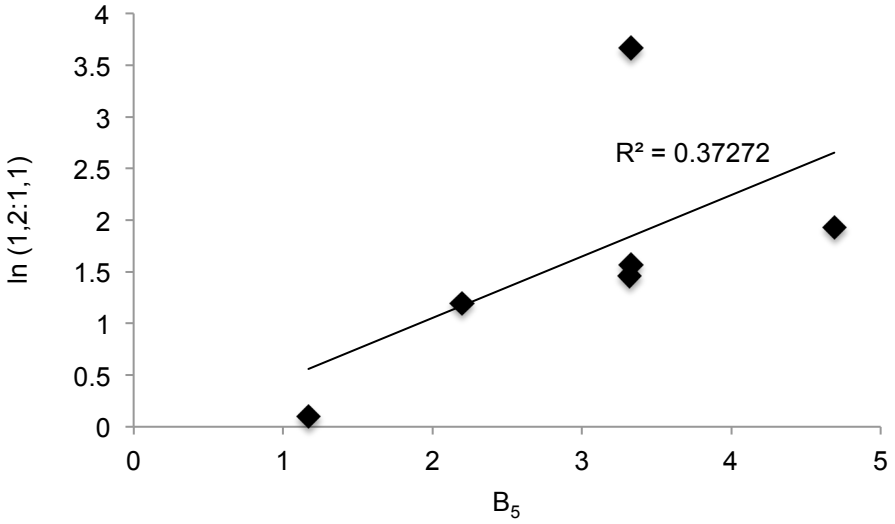
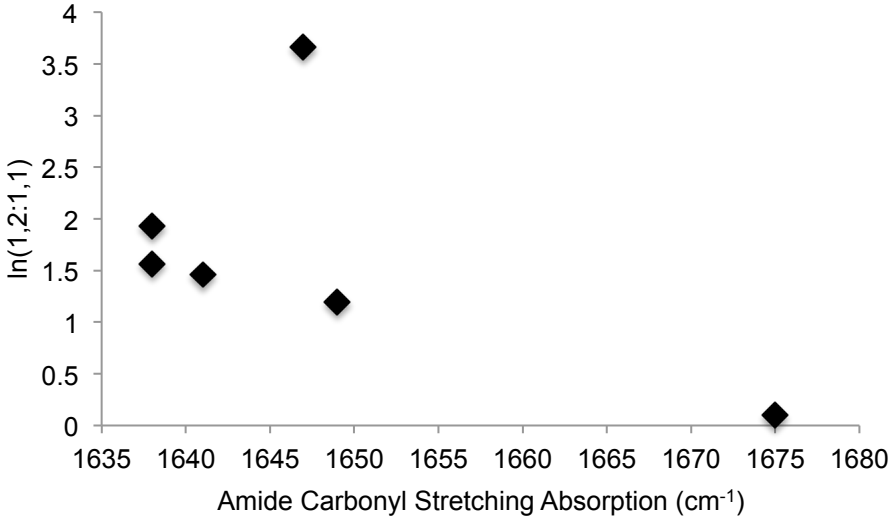
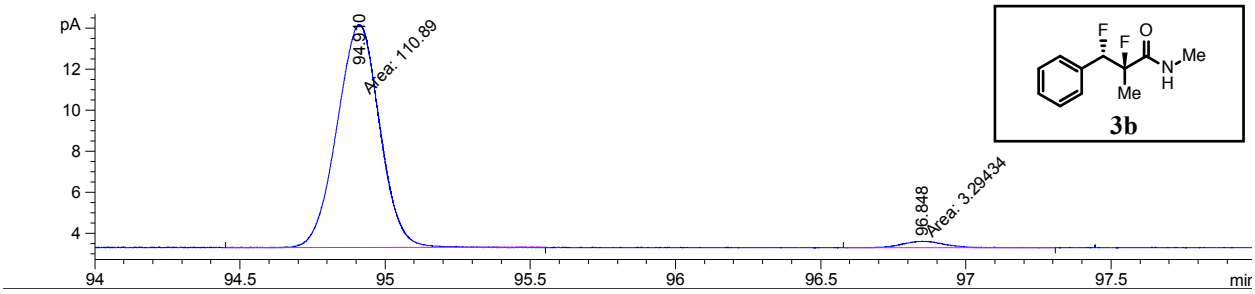


Chart 6. Correlation with Amide Carbonyl Stretching Absorption[12]

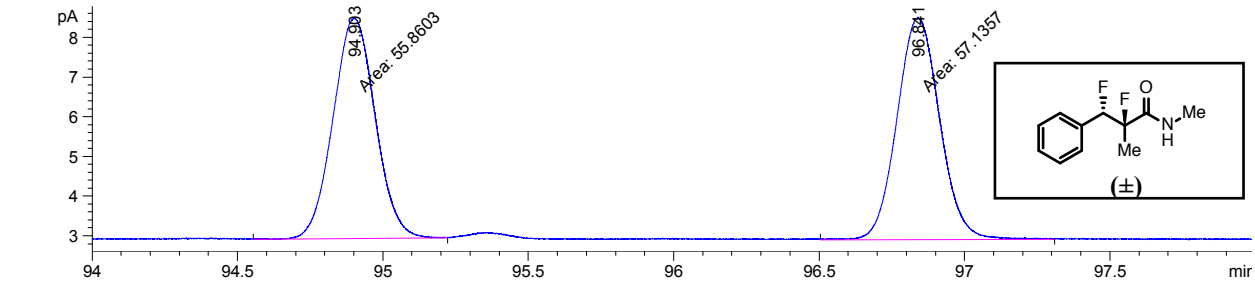


Chiral GC and HPLC Traces of 1,2-Difluoride Products and Derivatives

β-Cyclosil, 40→200 ˚C, 1 ˚/min, 7 psi

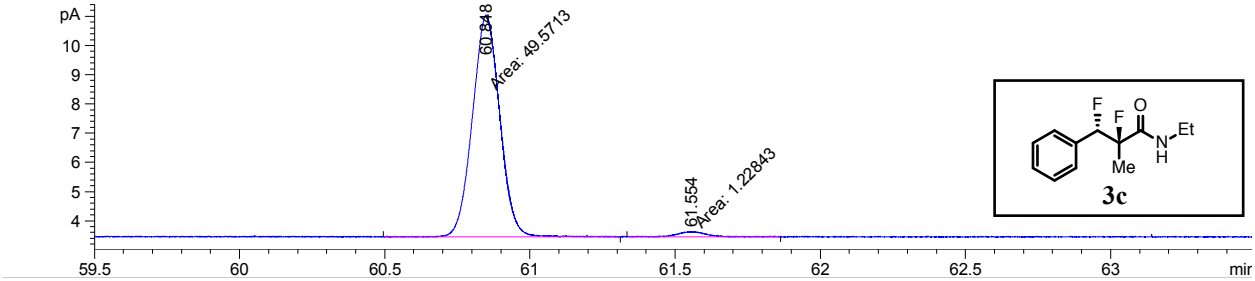


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	94.910	MM	0.1698	110.89005	10.88456	97.11489
2	96.848	MM	0.1658	3.29434	3.31124e-1	2.88511

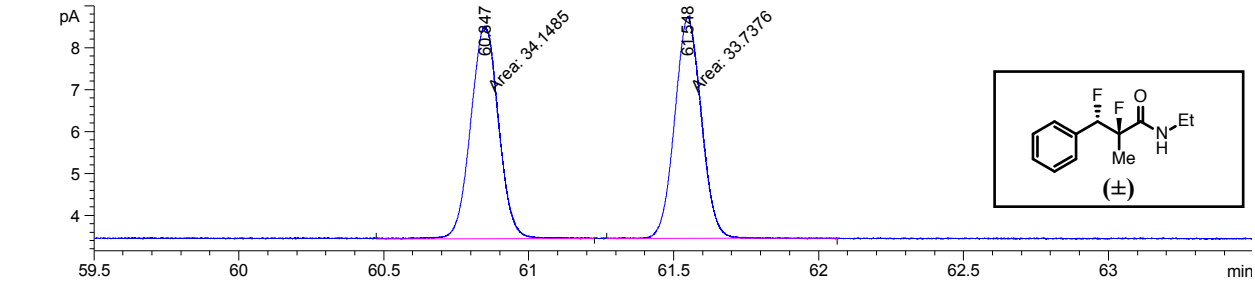


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	94.903	MM	0.1675	55.86035	5.55951	49.43568
2	96.841	MM	0.1704	57.13567	5.58984	50.56432

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

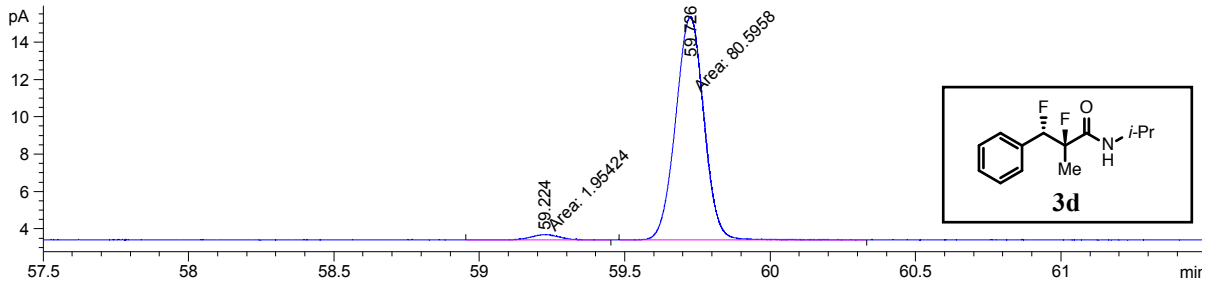


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	60.848	MF	0.1089	49.57135	7.58576	97.58182
2	61.554	FM	0.1179	1.22843	1.73609e-1	2.41818

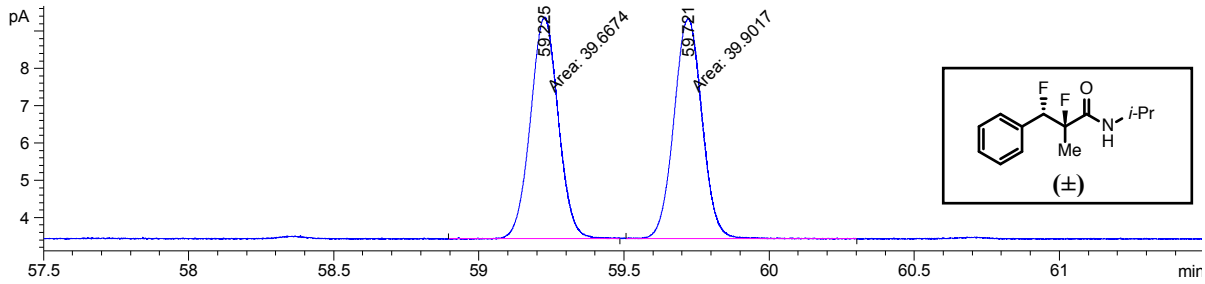


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	60.847	MF	0.1125	34.14846	5.06002	50.30260
2	61.548	FM	0.1064	33.73762	5.28506	49.69740

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

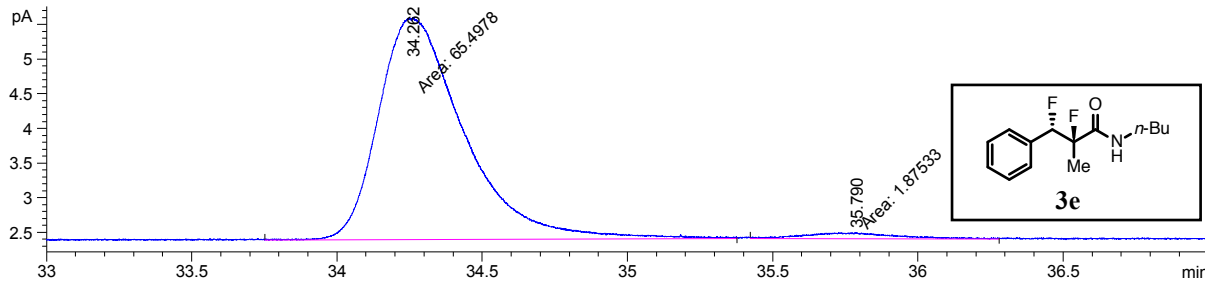


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	59.224	MF	0.1123	1.95424	2.89971e-1	2.36734
2	59.726	FM	0.1124	80.59579	11.94595	97.63266

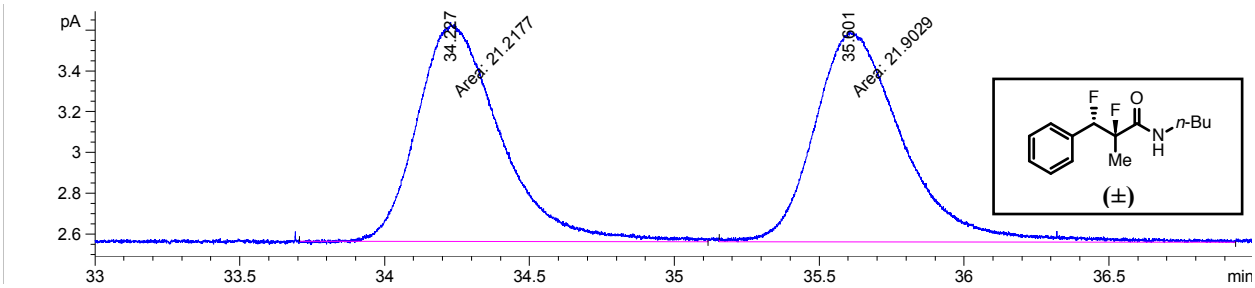


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	59.225	MF	0.1112	39.66742	5.94299	49.85278
2	59.721	FM	0.1124	39.90170	5.91511	50.14722

CP-Chirasil-Dex CB, 120 ˚C, 14 psi

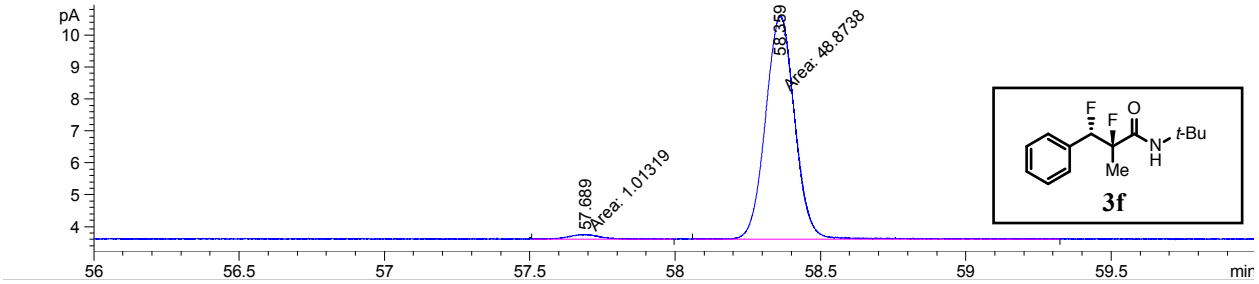


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	34.262	MM	0.3416	65.49781	3.19604	97.21650
2	35.790	MM	0.3603	1.87533	8.67437e-2	2.78350

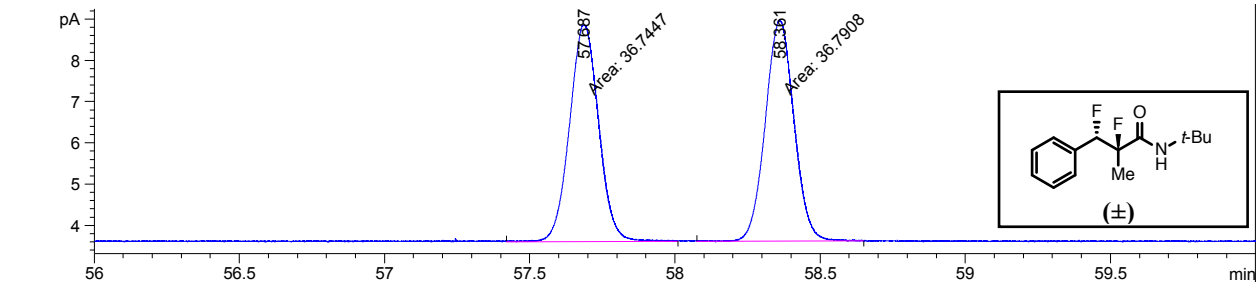


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	34.227	MF	0.3321	21.21774	1.06498	49.20558
2	35.601	FM	0.3547	21.90285	1.02917	50.79442

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

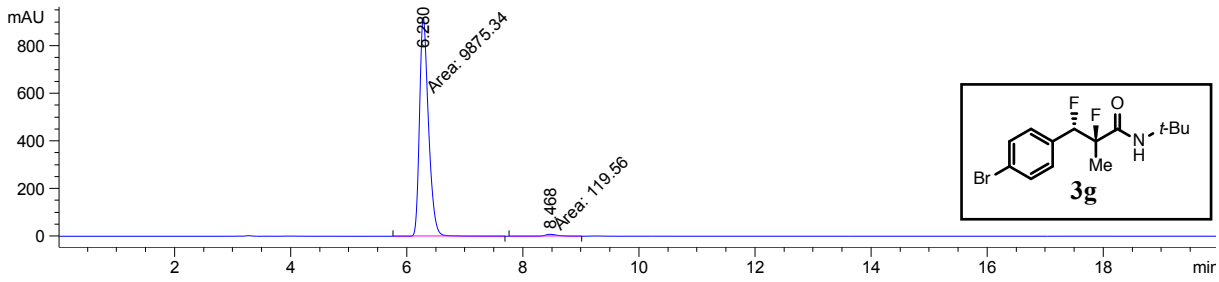


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	57.689	MF	0.1168	1.01319	1.44567e-1	2.03097
2	58.359	FM	0.1166	48.87377	6.98369	97.96903

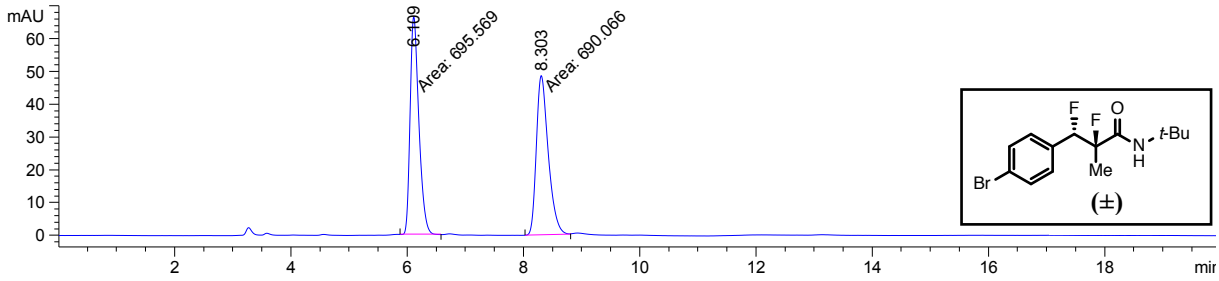


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	57.687	MF	0.1166	36.74467	5.25123	49.96862
2	58.361	FM	0.1145	36.79082	5.35560	50.03138

AD-H, 1 mL/min, 2% IPA/hexanes, 220 nm

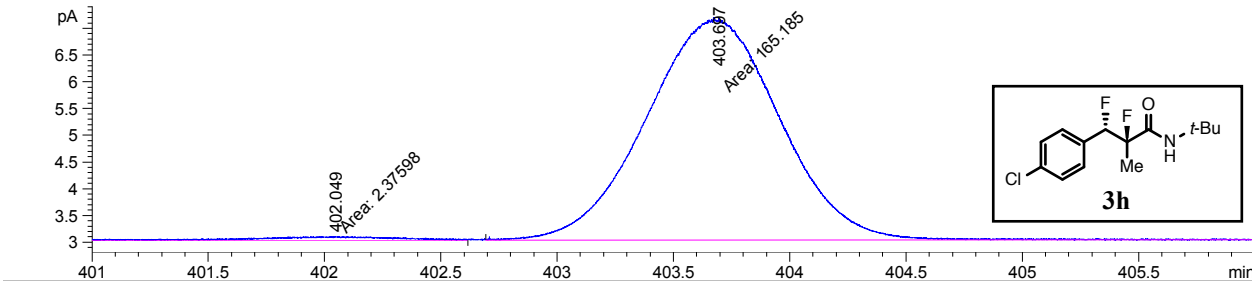


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.280	MF	0.1789	9875.33594	919.87378	98.8038
2	8.468	FM	0.2477	119.56028	8.04568	1.1962

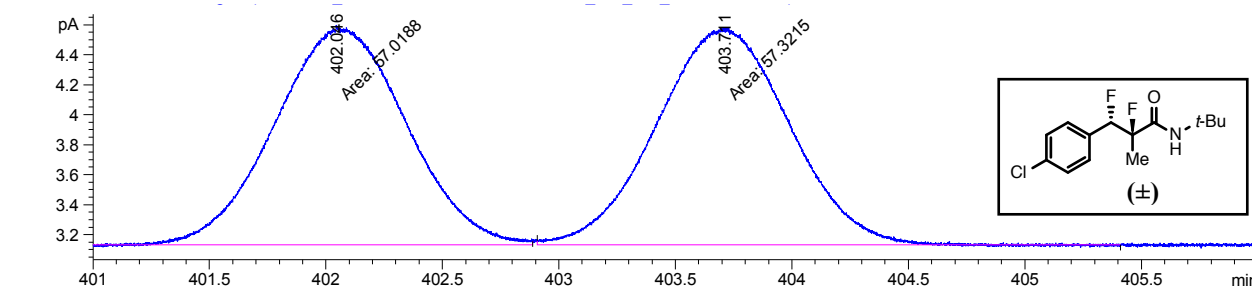


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.109	MM	0.1742	695.56879	66.54630	50.1986
2	8.303	MM	0.2366	690.06641	48.61501	49.8014

β-Cyclosil, 40→200 ˚C, 0.2˚/min, 14 psi

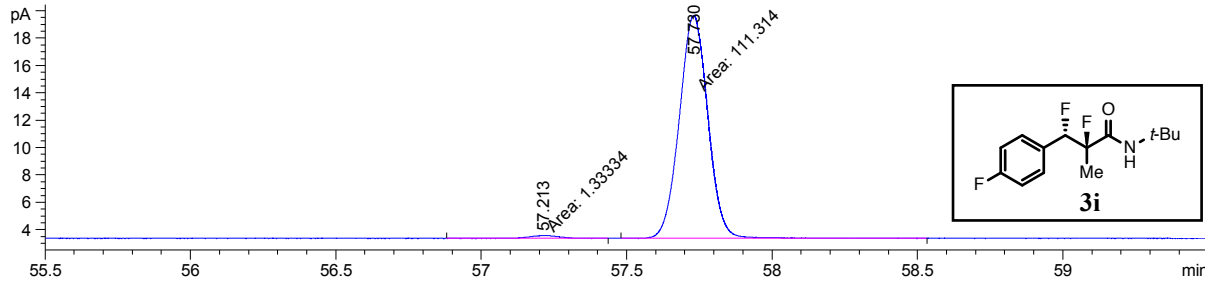


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	402.049	MF	0.6276	2.37598	6.30999e-2	1.41798
2	403.697	FM	0.6645	165.18474	4.14332	98.58202

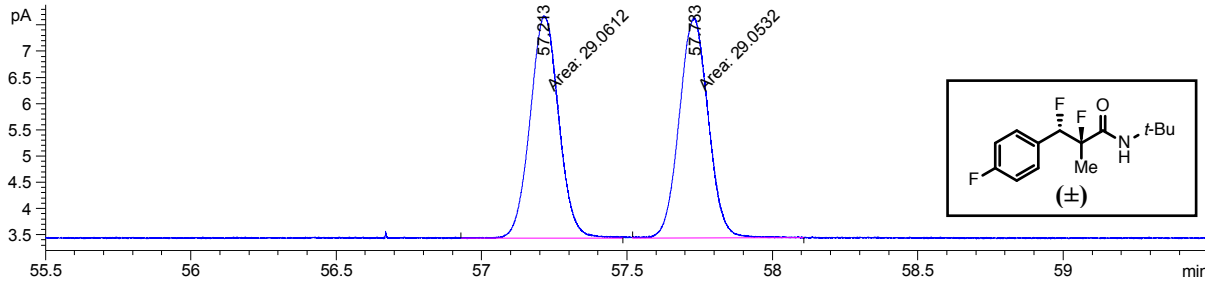


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	402.046	MF	0.6522	57.01876	1.45698	49.86762
2	403.711	FM	0.6590	57.32150	1.44978	50.13238

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

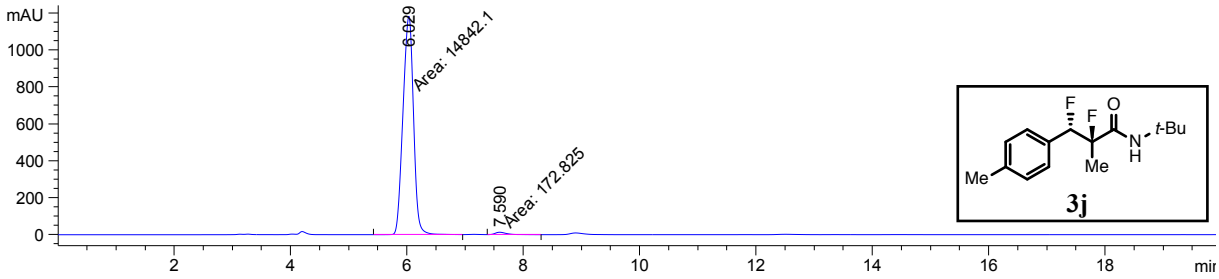


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	57.213	MF	0.1074	1.33334	2.06846e-1	1.18364
2	57.730	FM	0.1139	111.31385	16.28446	98.81636

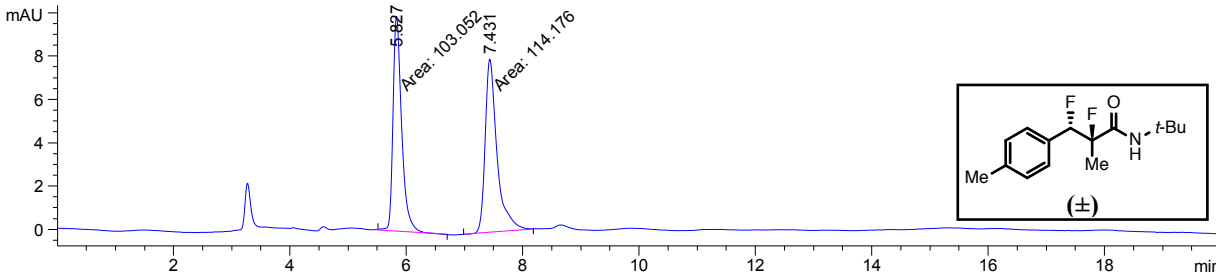


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	57.213	MF	0.1144	29.06118	4.23258	50.00688
2	57.733	FM	0.1158	29.05319	4.18074	49.99312

AD-H, 1 mL/min, 2% IPA/hexanes, 220 nm

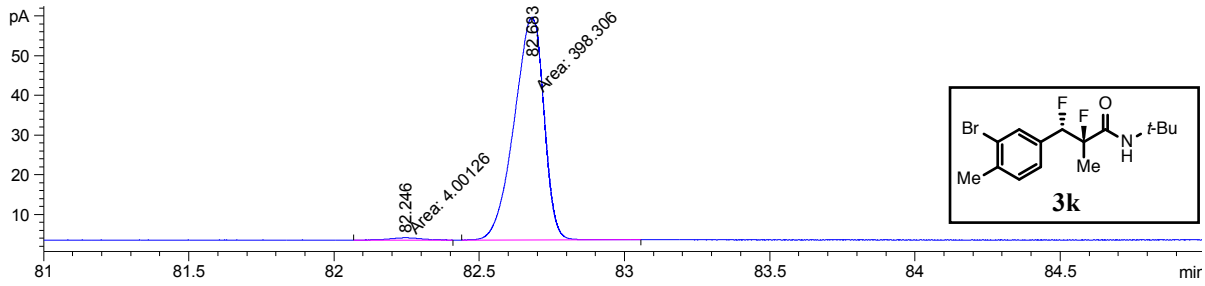


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.029	MM	0.2090	1.48421e4	1183.62939	98.8490
2	7.590	MM	0.2217	172.82478	12.99449	1.1510

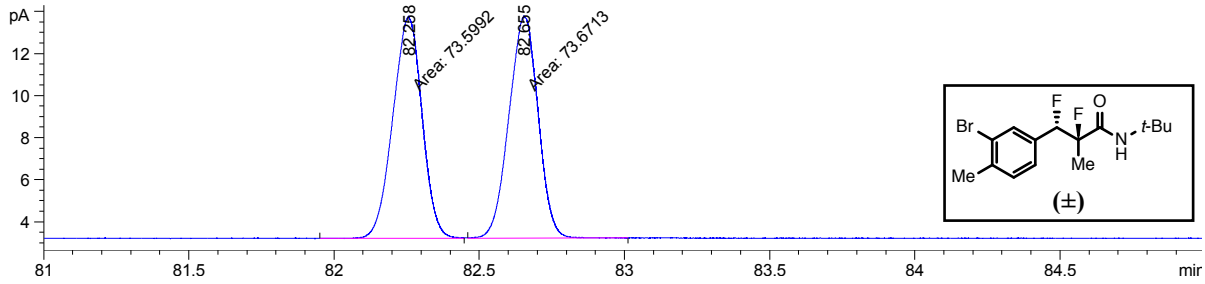


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.827	MM	0.1728	103.05161	9.94025	47.4396
2	7.431	MM	0.2378	114.17554	8.00156	52.5604

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

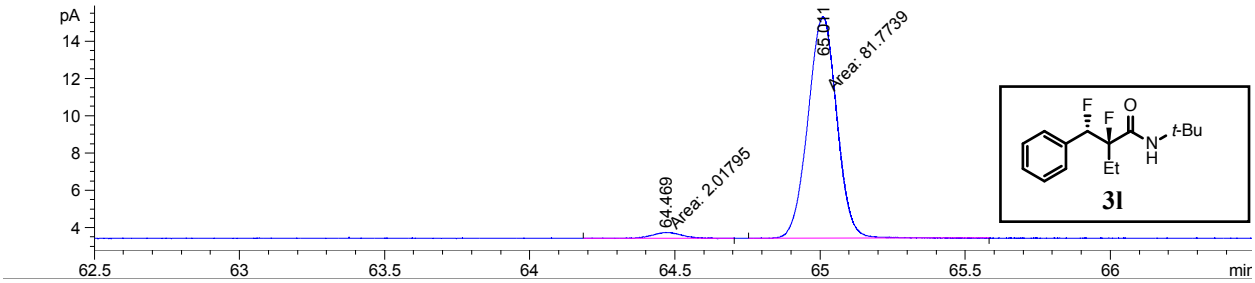


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	82.246	MF	0.1192	4.00126	5.59478e-1	0.99458
2	82.683	FM	0.1181	398.30585	56.20433	99.00542

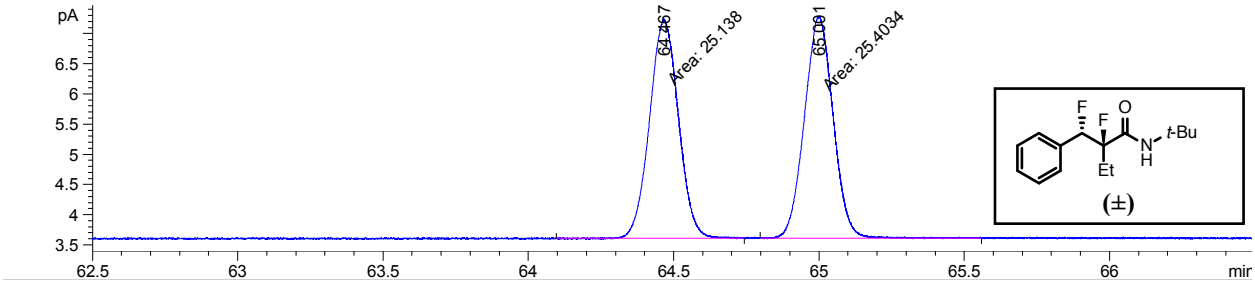


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	82.258	MF	0.1161	73.59922	10.56298	49.97551
2	82.655	FM	0.1164	73.67134	10.55102	50.02449

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

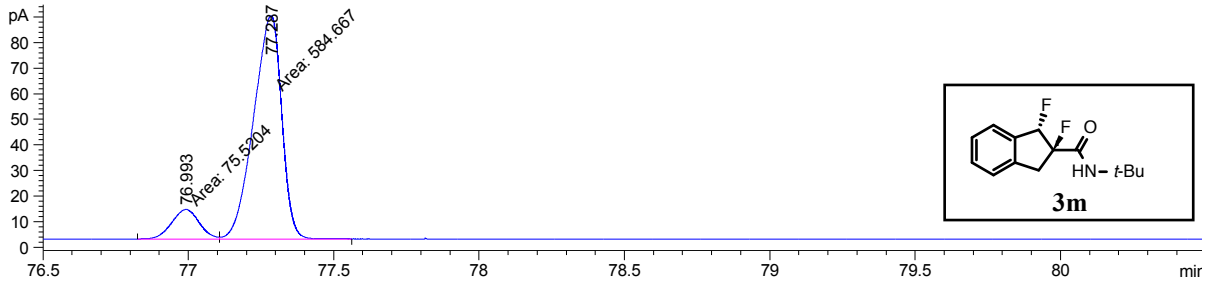


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	64.469	MF	0.1077	2.01795	3.12359e-1	2.40828
2	65.011	FM	0.1147	81.77390	11.88415	97.59172

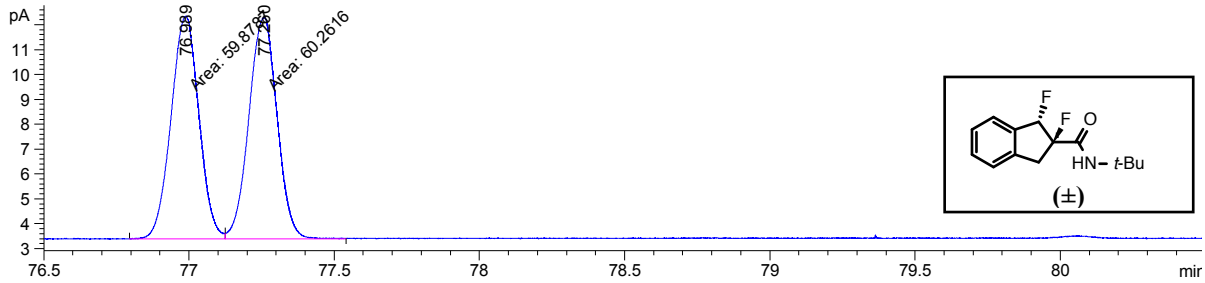


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	64.467	MF	0.1156	25.13804	3.62285	49.73749
2	65.001	FM	0.1150	25.40339	3.68101	50.26251

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

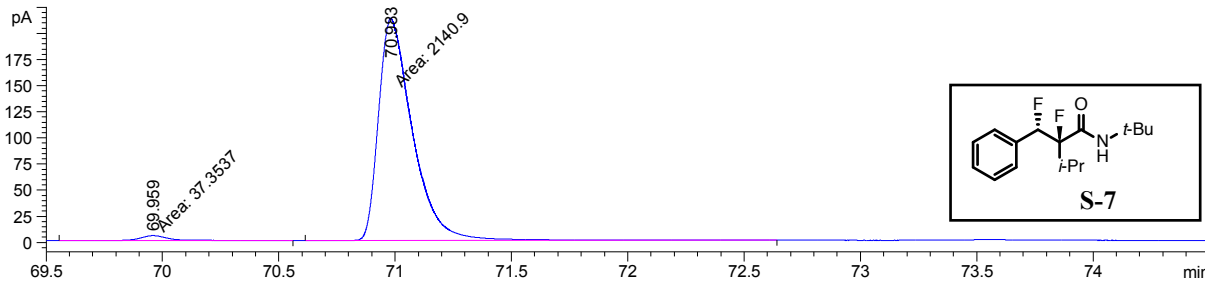


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	76.993	MF	0.1088	75.52040	11.56651	11.43923
2	77.287	FM	0.1118	584.66730	87.17343	88.56077

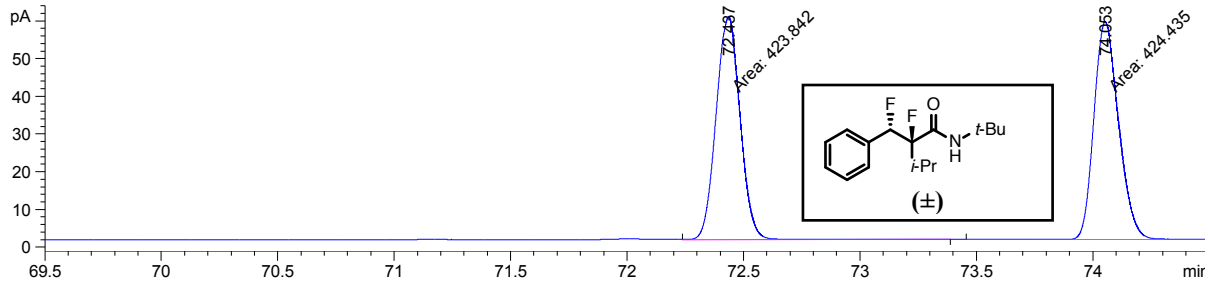


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	76.989	MF	0.1114	59.87873	8.95794	49.84067
2	77.260	FM	0.1130	60.26156	8.88825	50.15933

CP-Chirasil-Dex CB, 40→160 ˚C, 1.5˚/min, 14 psi

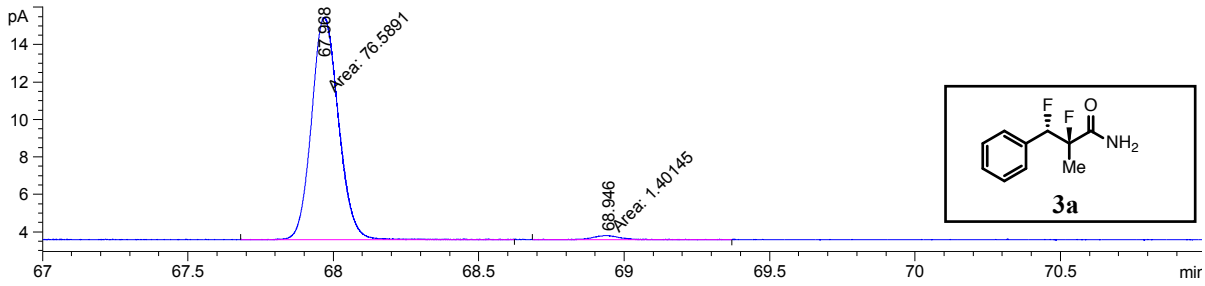


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	69.959	MF	0.1346	37.35367	4.62651	1.71485
2	70.983	FM	0.1674	2140.89941	213.09407	98.28515

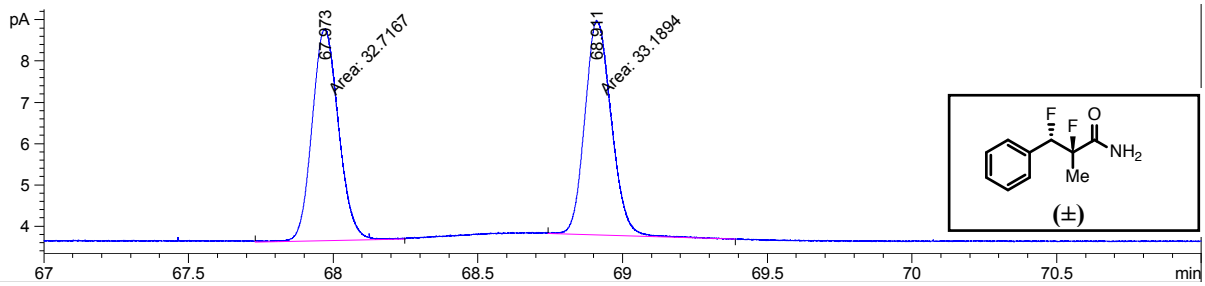


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	72.437	MF	0.1195	423.84232	59.11995	49.96504
2	74.053	FM	0.1221	424.43536	57.91782	50.03496

β-Cyclosil, 40→200 ˚C, 1.5˚/min, 14 psi

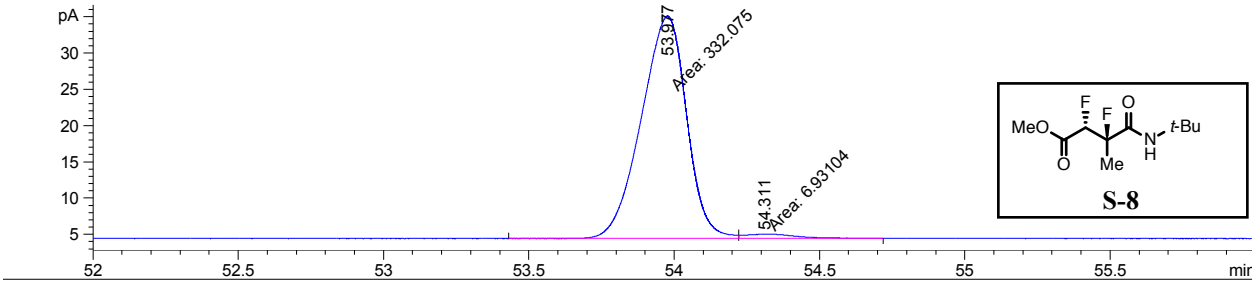


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.968	MF	0.1075	76.58907	11.87658	98.20305
2	68.946	FM	0.1081	1.40145	2.16027e-1	1.79695

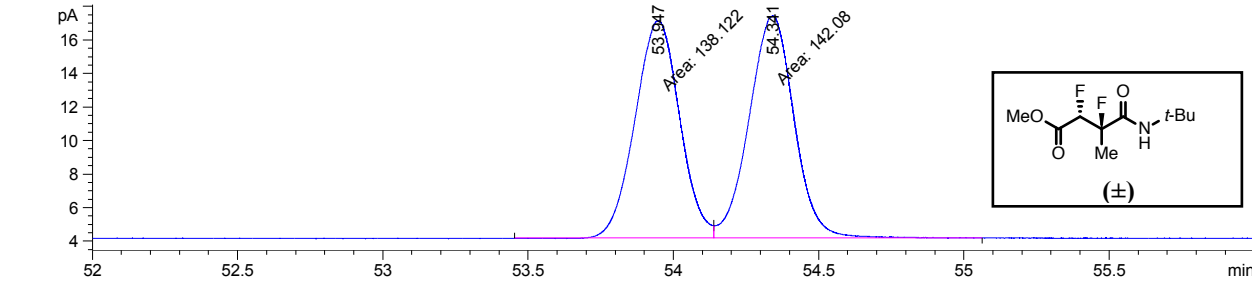


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.973	MM	0.1065	32.71674	5.12111	49.64138
2	68.911	MM	0.1064	33.18945	5.19898	50.35862

β-Cyclosil, 40→200 ˚C, 1˚/min, 20 psi

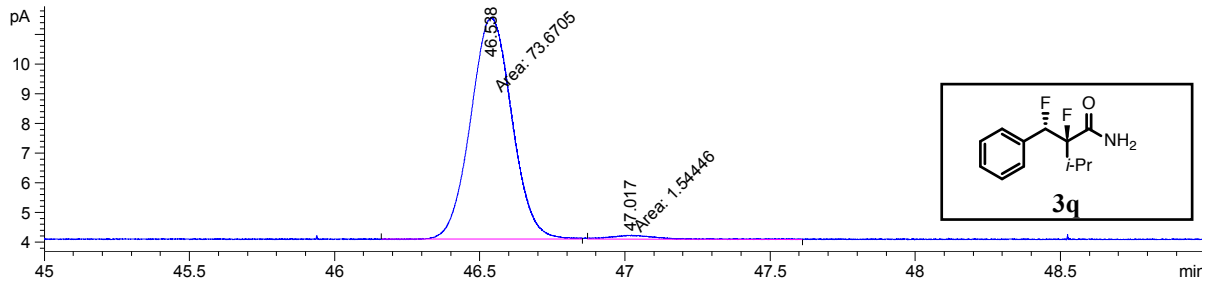


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	53.977	MF	0.1803	332.07541	30.69834	97.95548
2	54.311	FM	0.1952	6.93104	5.91823e-1	2.04452



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	53.947	MF	0.1781	138.12201	12.92898	49.29365
2	54.341	FM	0.1786	142.08043	13.25977	50.70635

β-Cyclosil, 120 → 200 ˚C, 1 ˚/min, 7 psi



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.538	MF	0.1643	73.67052	7.47315	97.94660
2	47.017	FM	0.1993	1.54446	1.29133e-1	2.05340

The absolute stereochemistry of this product and the trace for a racemic sample have been previously reported.[6]

References and Notes

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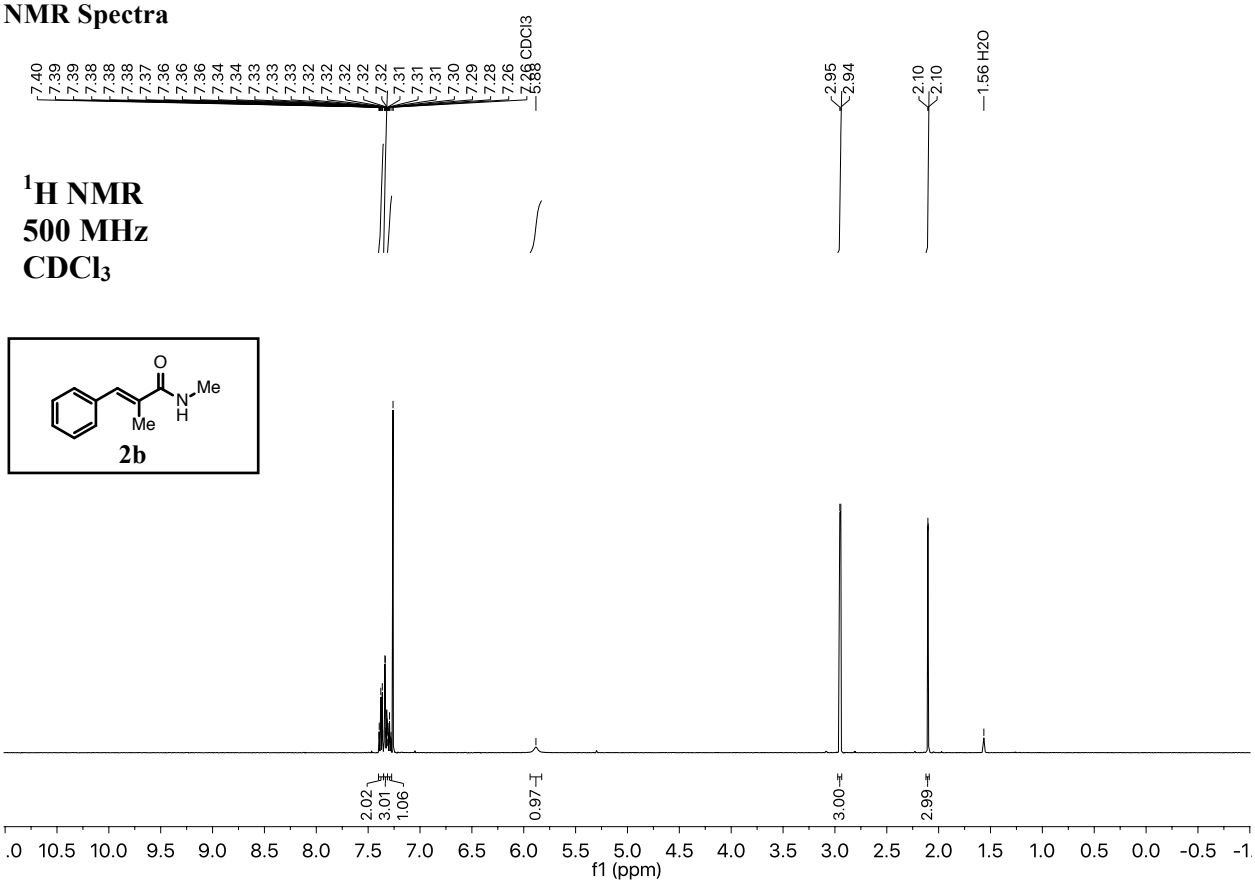
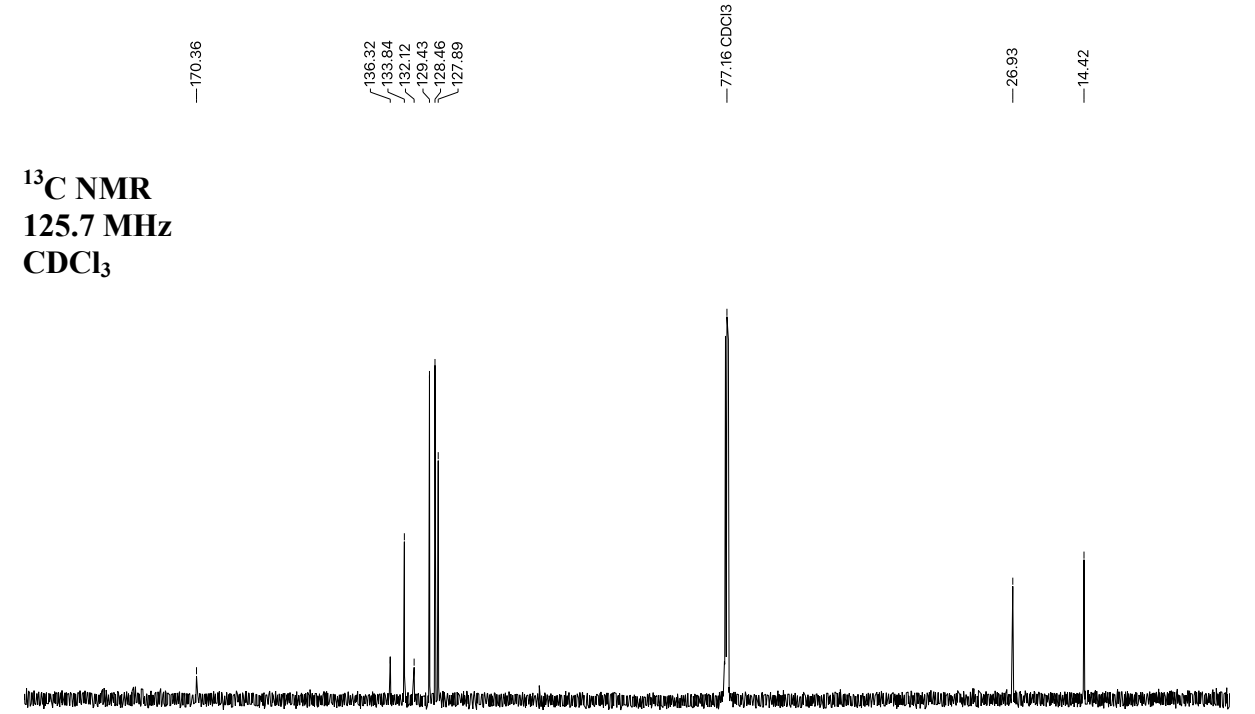
(11) Sterimol parameters were obtained using Molecular Modeling Pro Version 6.3.6.

(12) The amide carbonyl IR stretching absorption for **2a** was obtained from: Lewis, F. D.; Elbert, J. E.; Upthagrove, A. L.; Hale, P. D. Structure and Photoisomerization of (*E*)- and (*Z*)-Cinnamamides and Their Lewis Acid Complexes. *J. Org. Chem.* **1991**, *56,* 553.

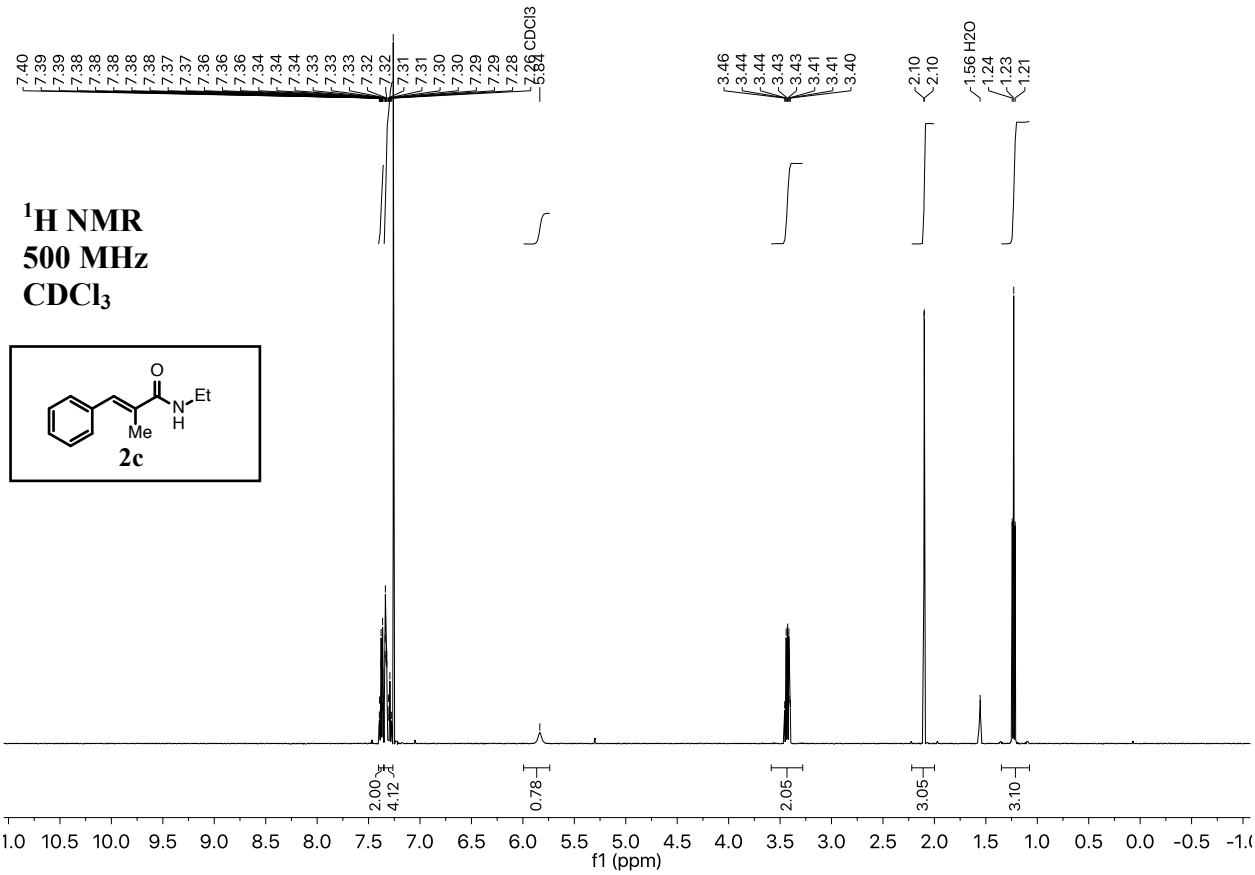
NMR Spectra



^{1}H NMR
500 MHz
$CDCl_3$



^{13}C NMR
125.7 MHz
$CDCl_3$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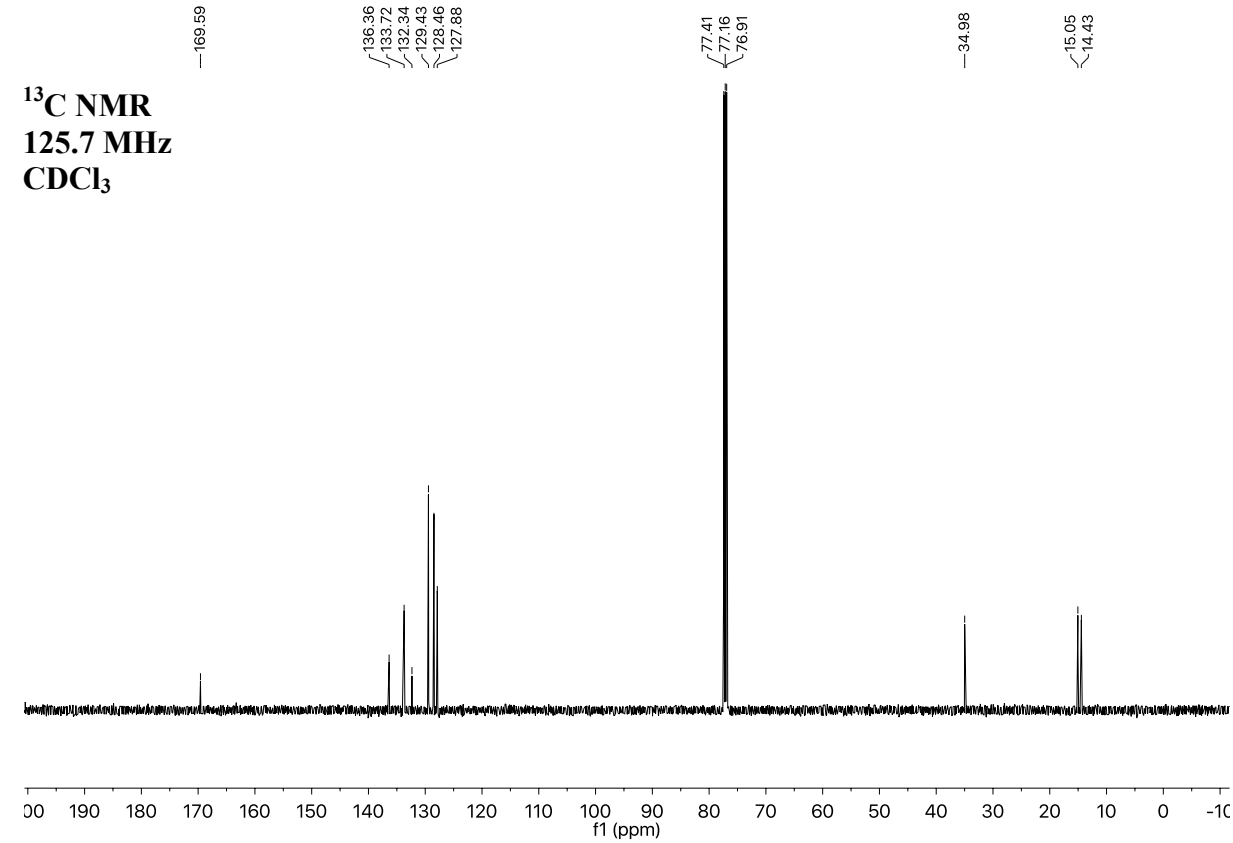
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26 CDCl3
5.84
3.46
3.44
3.44
3.43
3.43
3.41
3.41
3.40
2.10
2.10
1.56 H2O
1.24
1.23
1.21
1H NMR
500 MHz
CDCl3
O
N
Et
H
Me
2c
2.00
4.12
0.78
2.05
3.05
3.10
f1 (ppm)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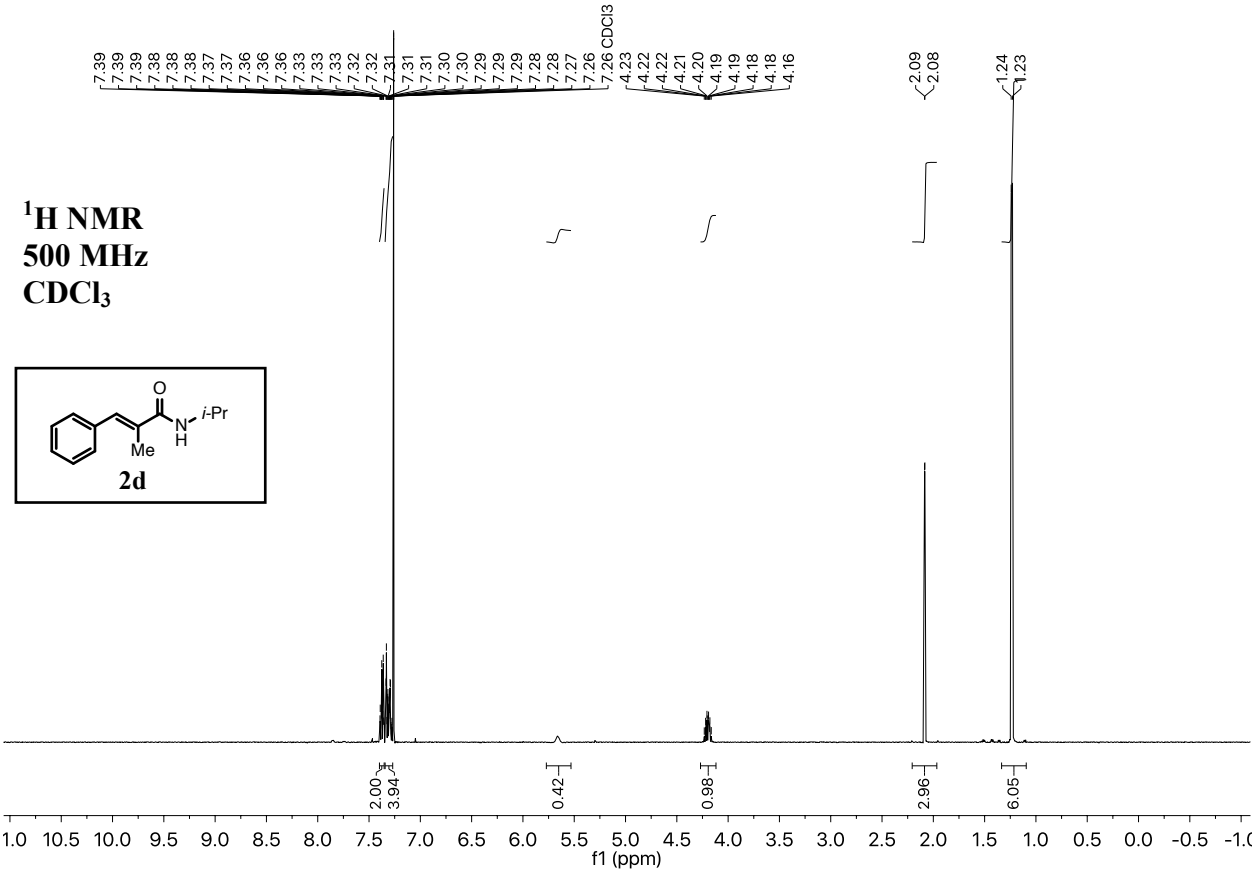
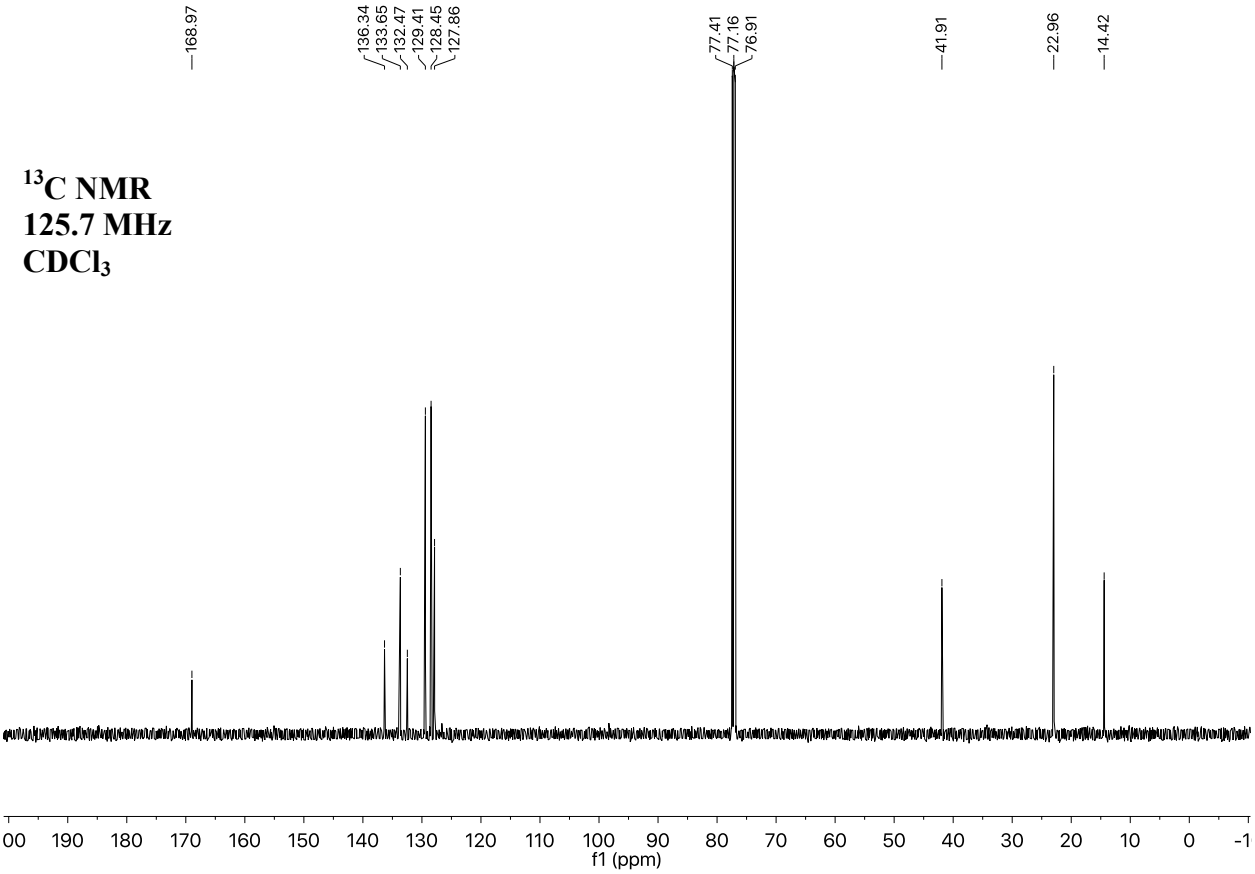
14.43
13C NMR
125.7 MHz
CDCl3
f1 (ppm)

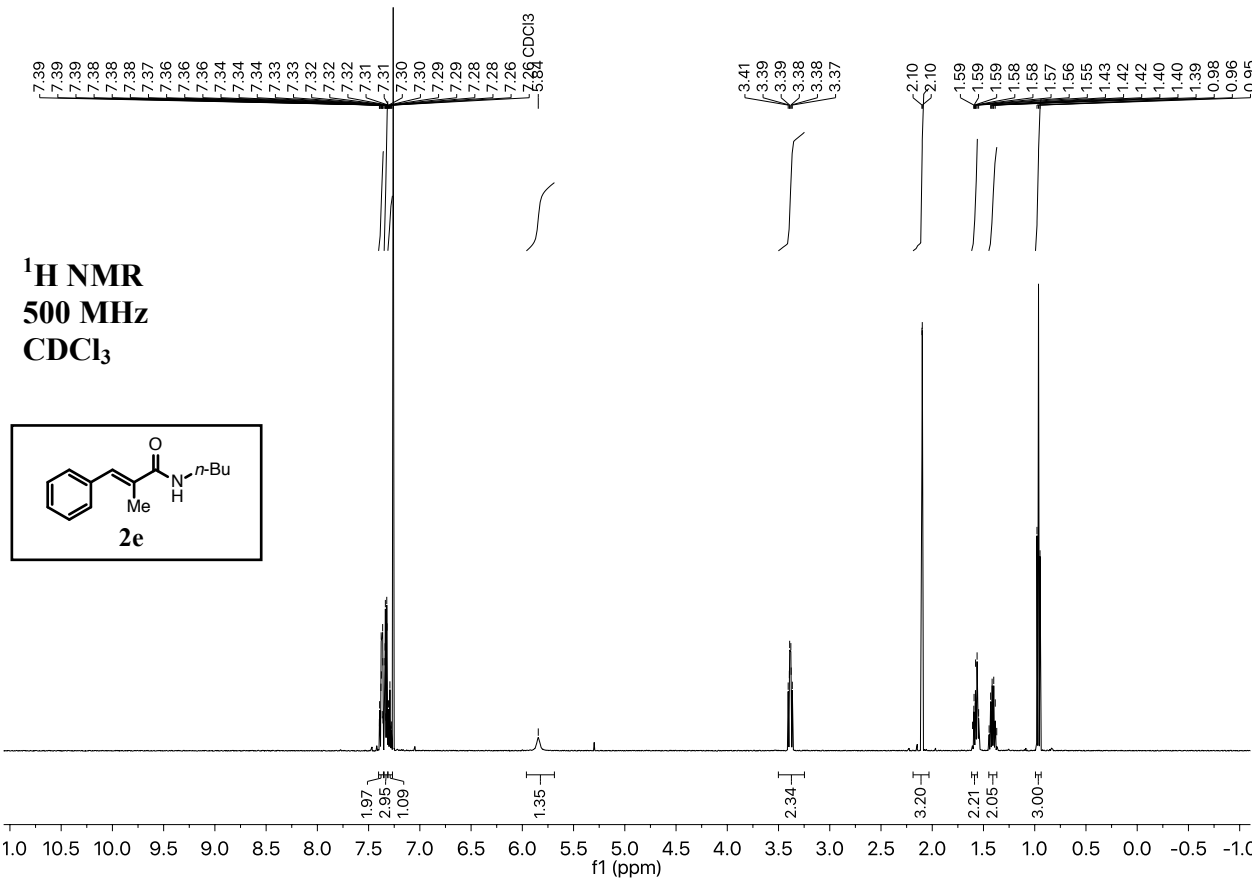


^{1}H NMR
500 MHz
$CDCl_3$

2d



^{13}C NMR
125.7 MHz
$CDCl_3$



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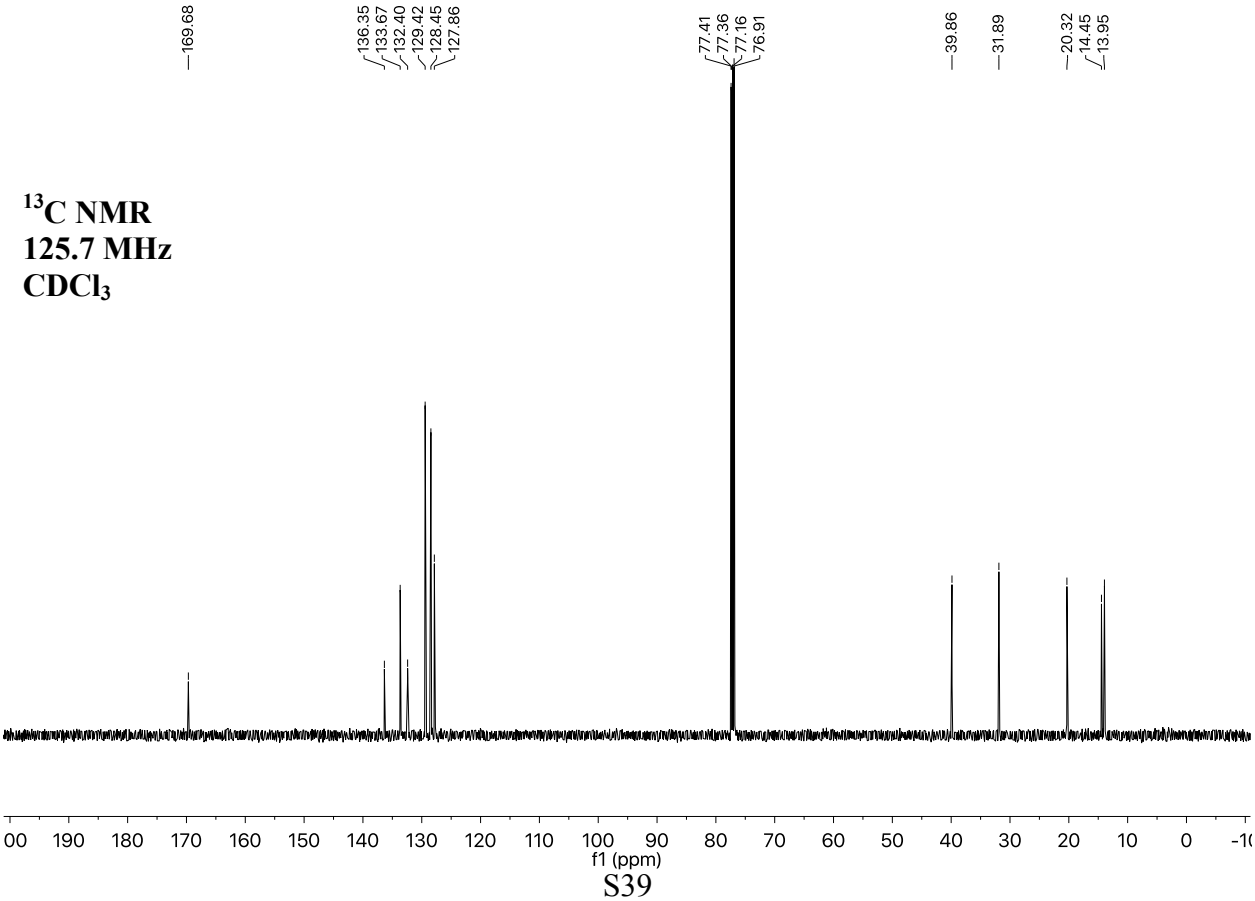
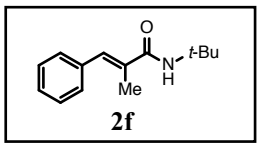
500 MHz
$CDCl_3$

2e



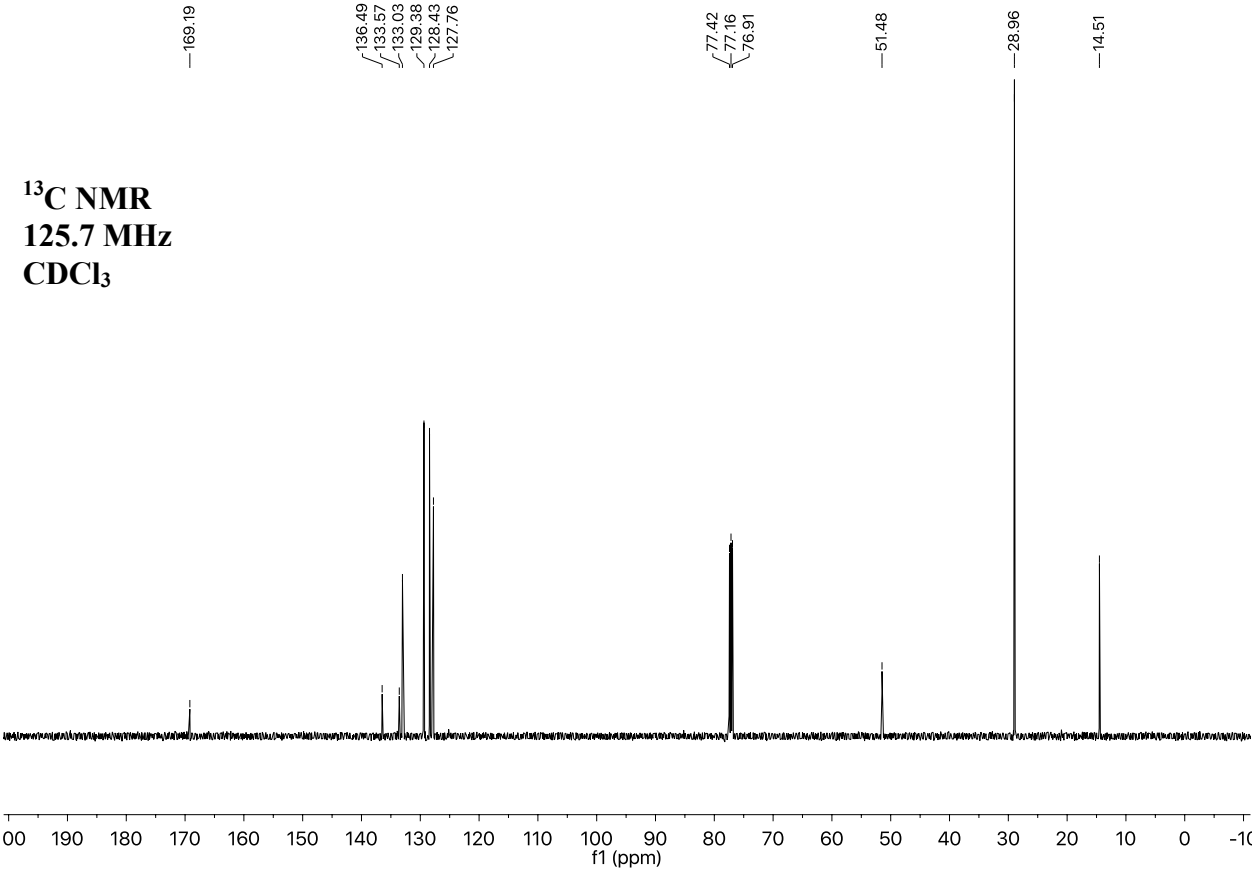
^{13}C NMR
125.7 MHz
$CDCl_3$

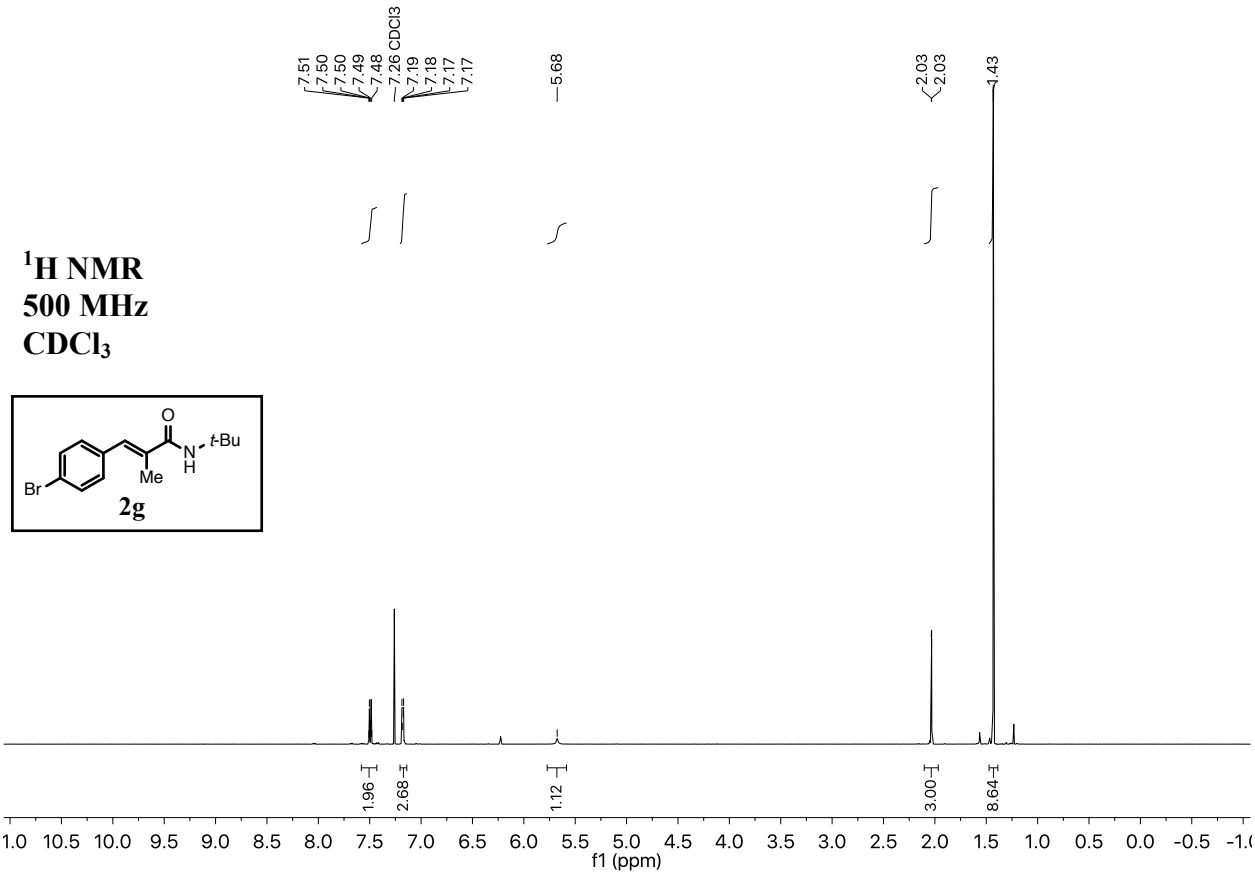
^{1}H NMR
500 MHz
$CDCl_3$



2f

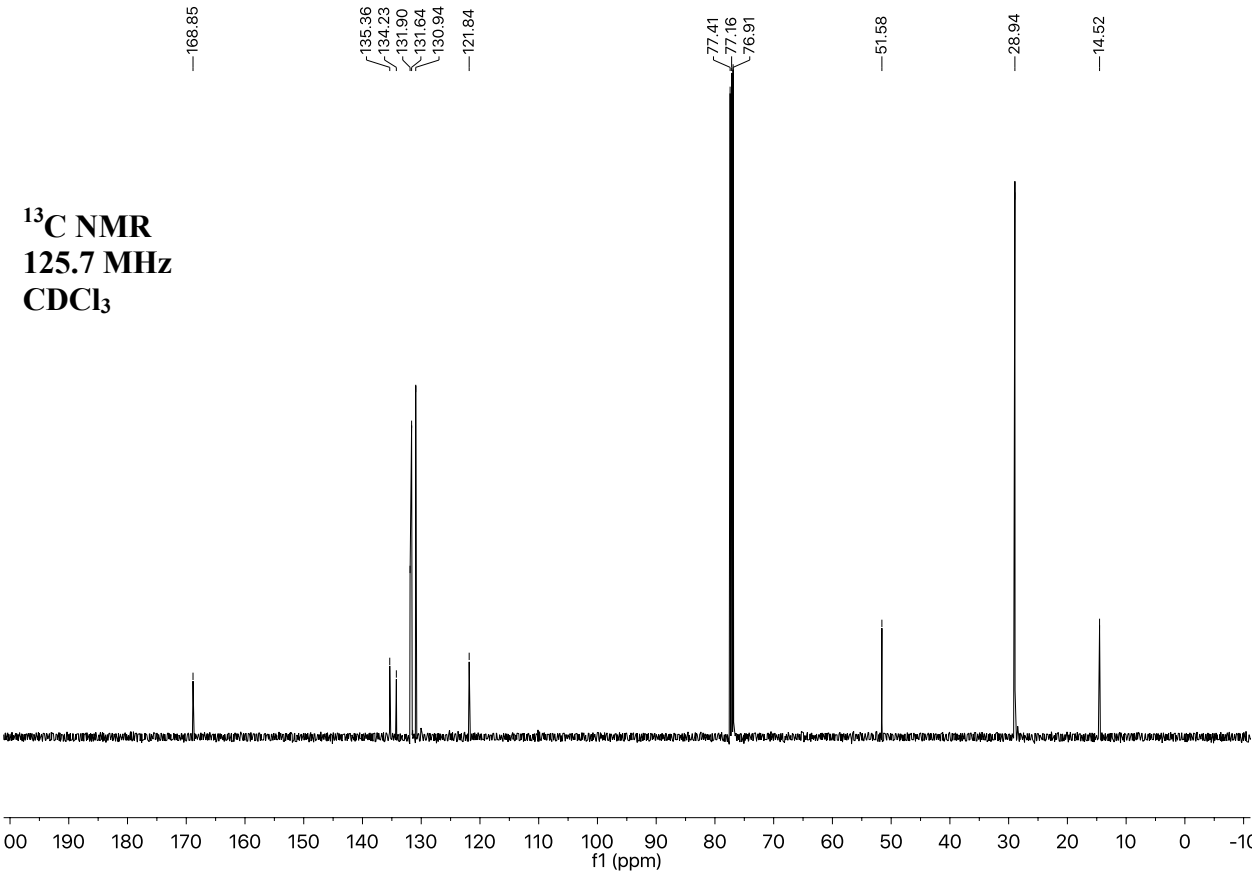
^{13}C NMR
125.7 MHz
$CDCl_3$





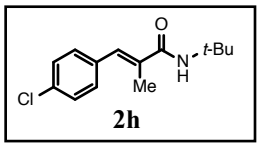
^{1}H NMR
500 MHz
$CDCl_3$

2g



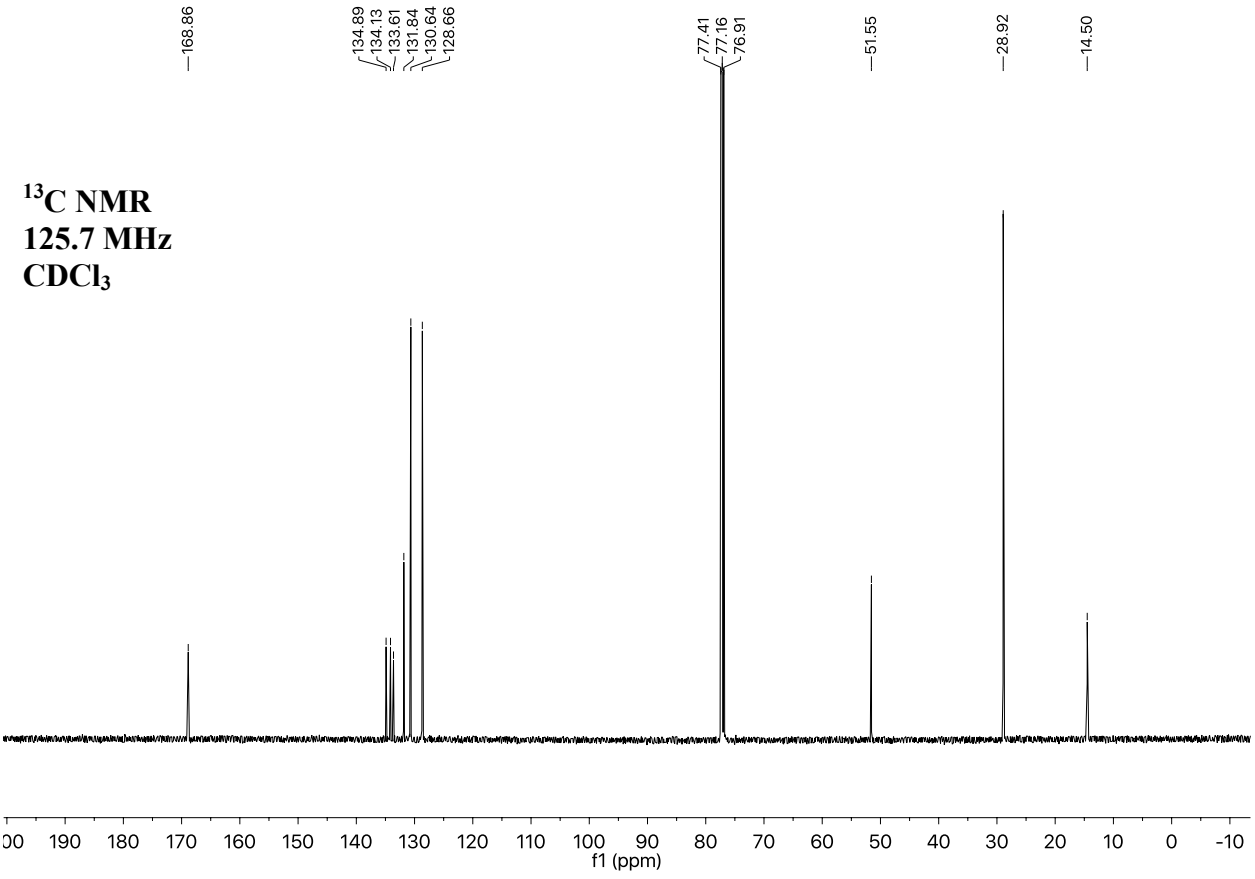
^{13}C NMR
125.7 MHz
$CDCl_3$

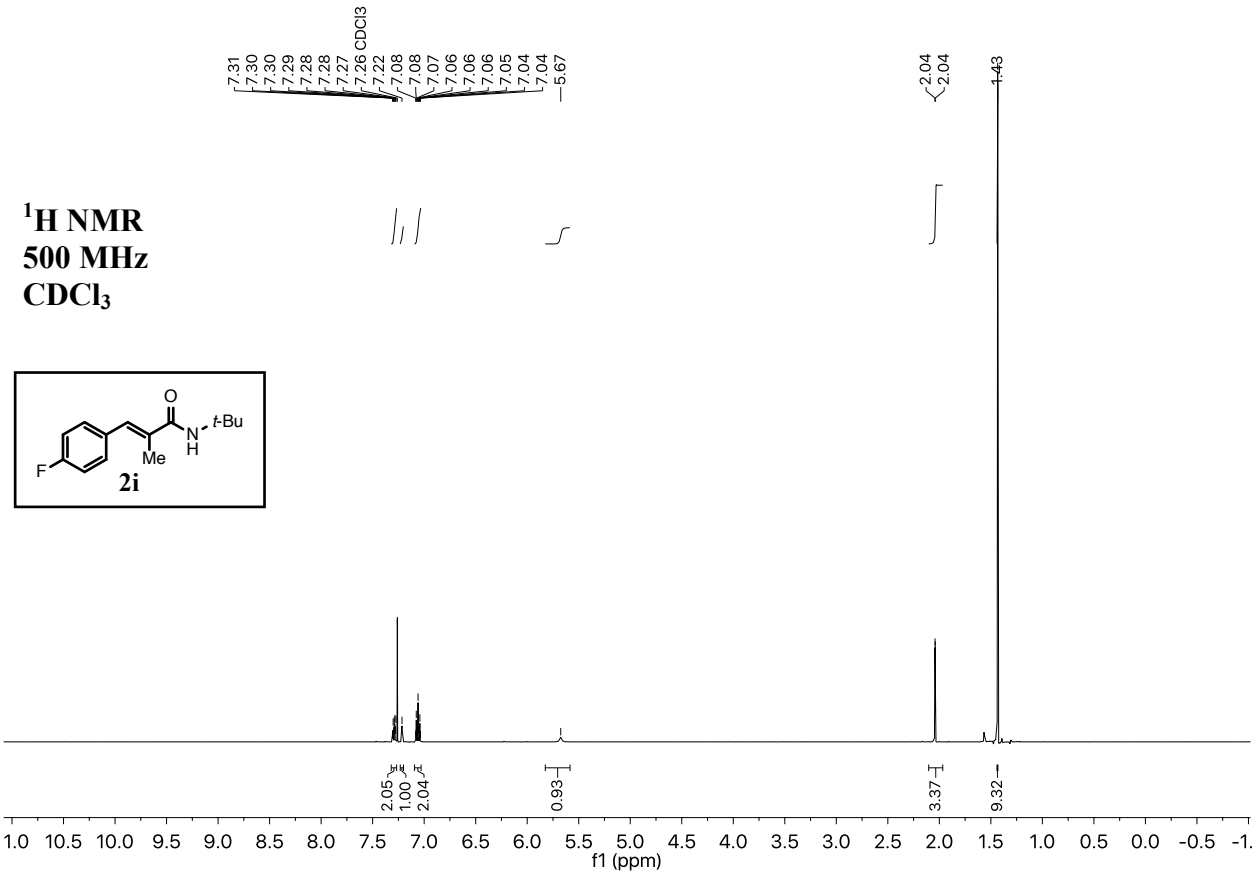
^{1}H NMR
500 MHz
$CDCl_3$



2h

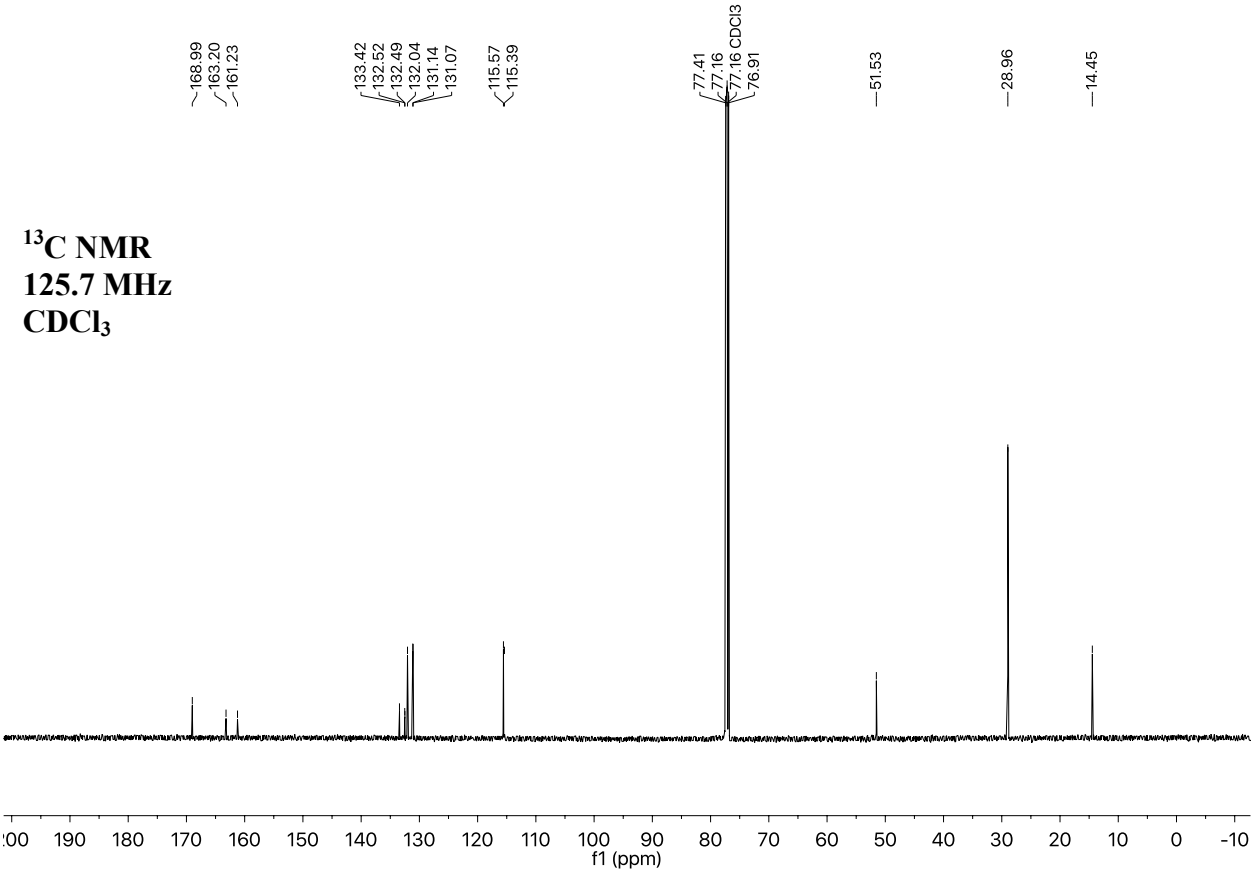
^{13}C NMR
125.7 MHz
$CDCl_3$



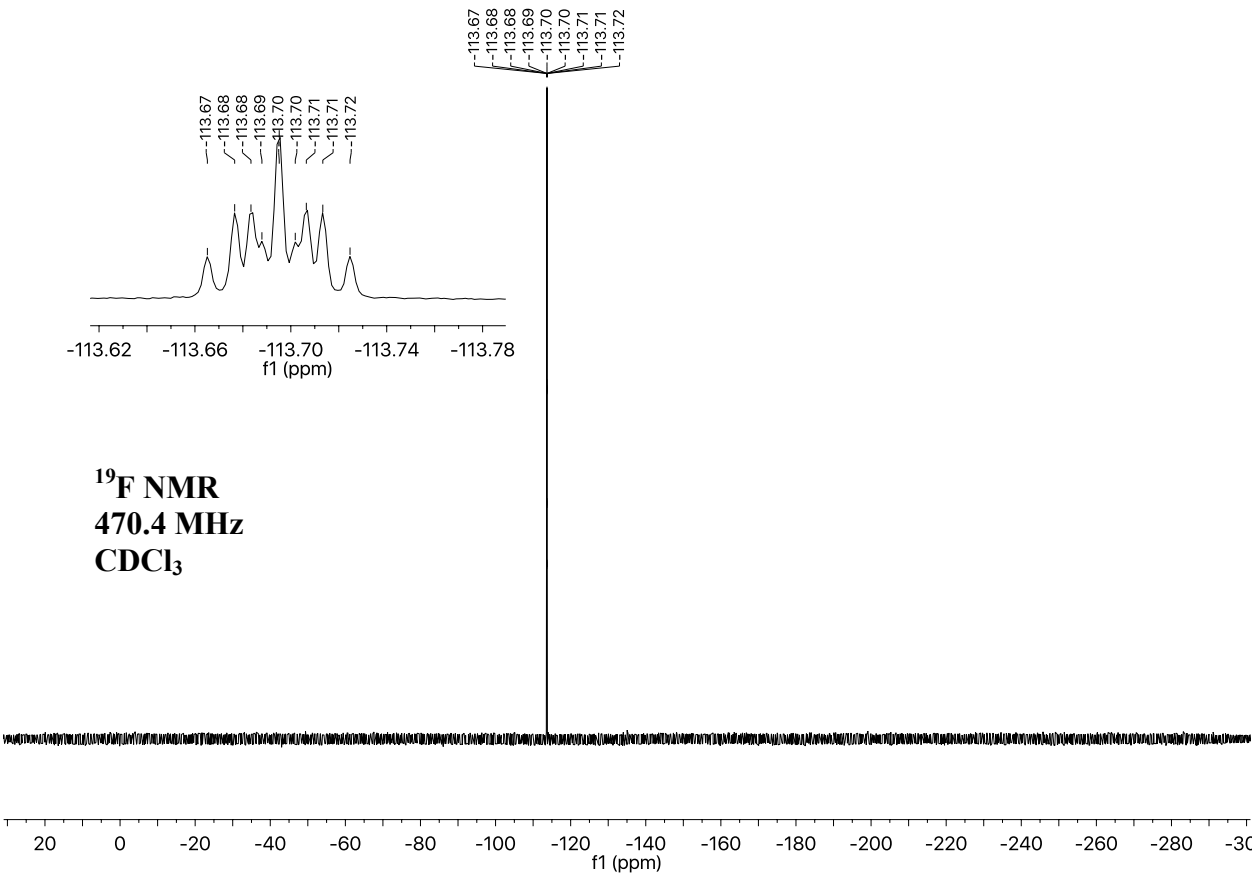


^{1}H NMR
500 MHz
$CDCl_3$

2i



^{13}C NMR
125.7 MHz
$CDCl_3$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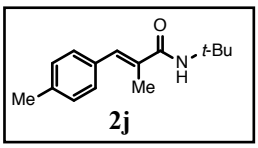
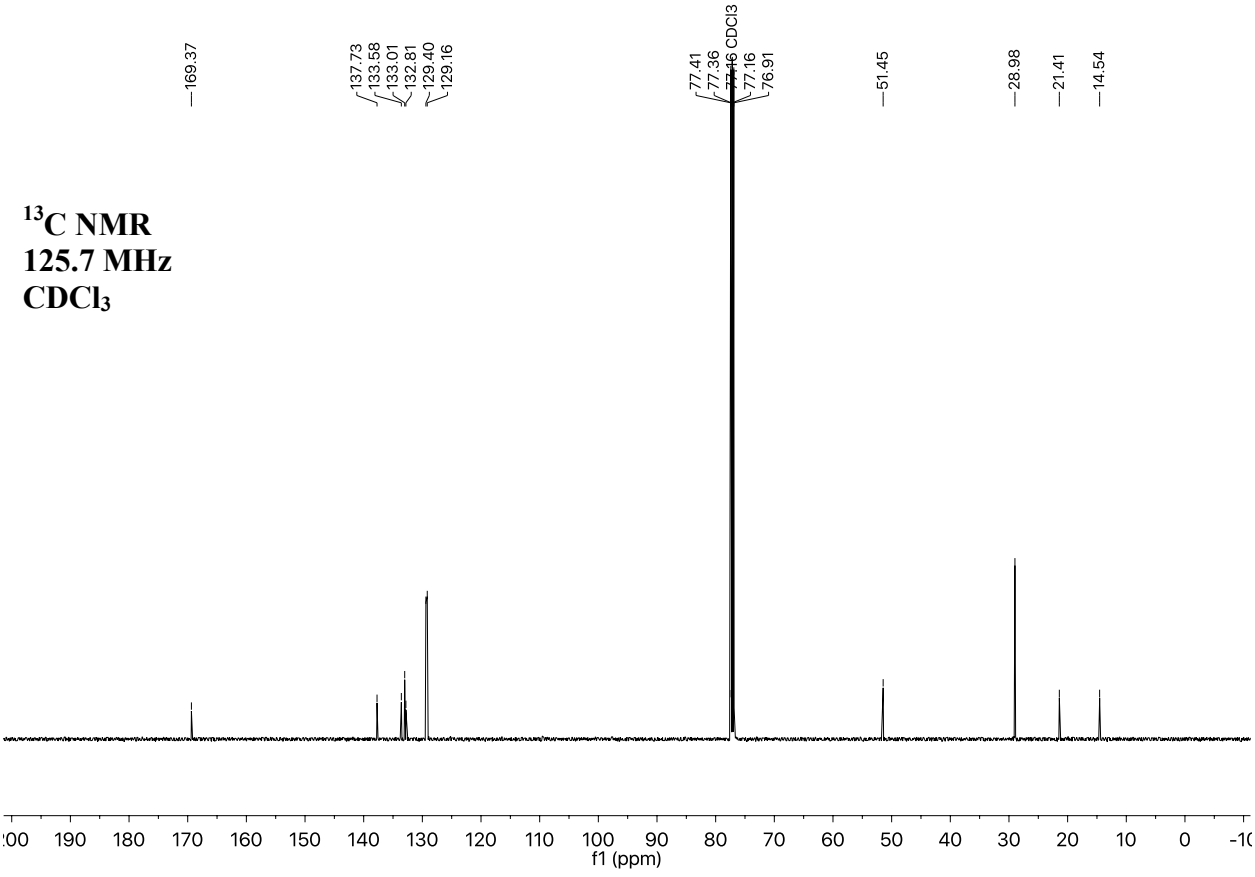
-113.70
-113.74
-113.78
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

^{1}H NMR
500 MHz
$CDCl_3$



2j

^{13}C NMR
125.7 MHz
$CDCl_3$



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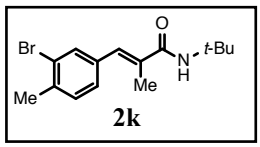
500 MHz
$CDCl_3$



2k

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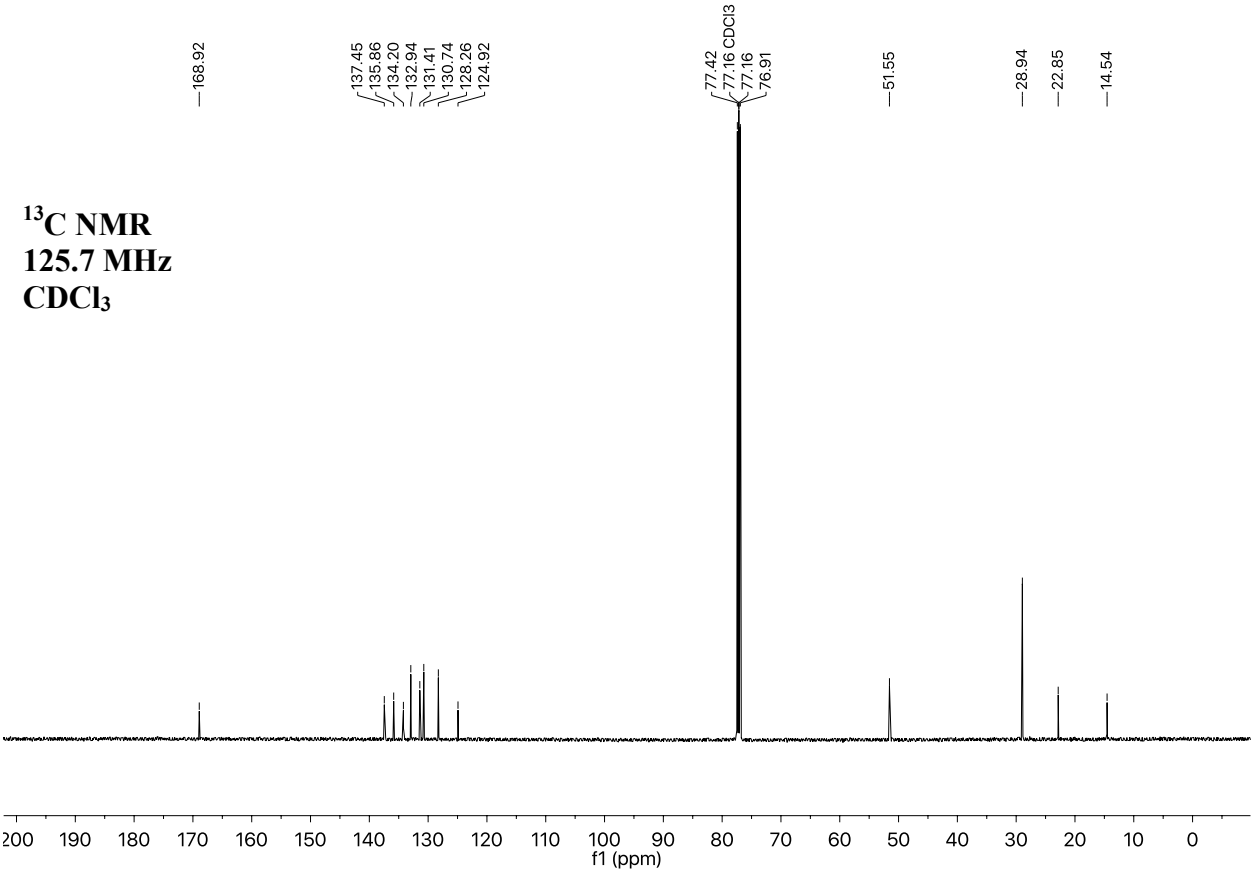
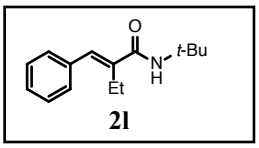
$CDCl_3$

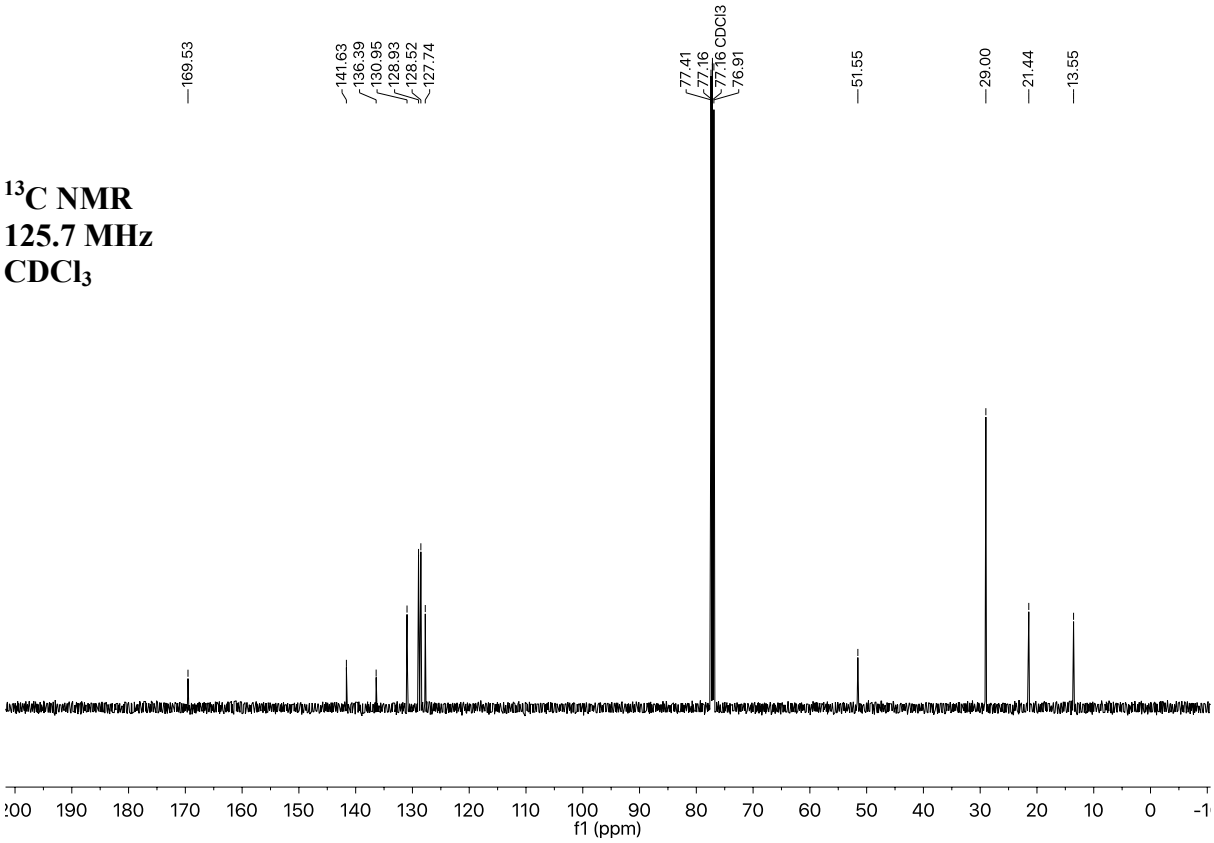


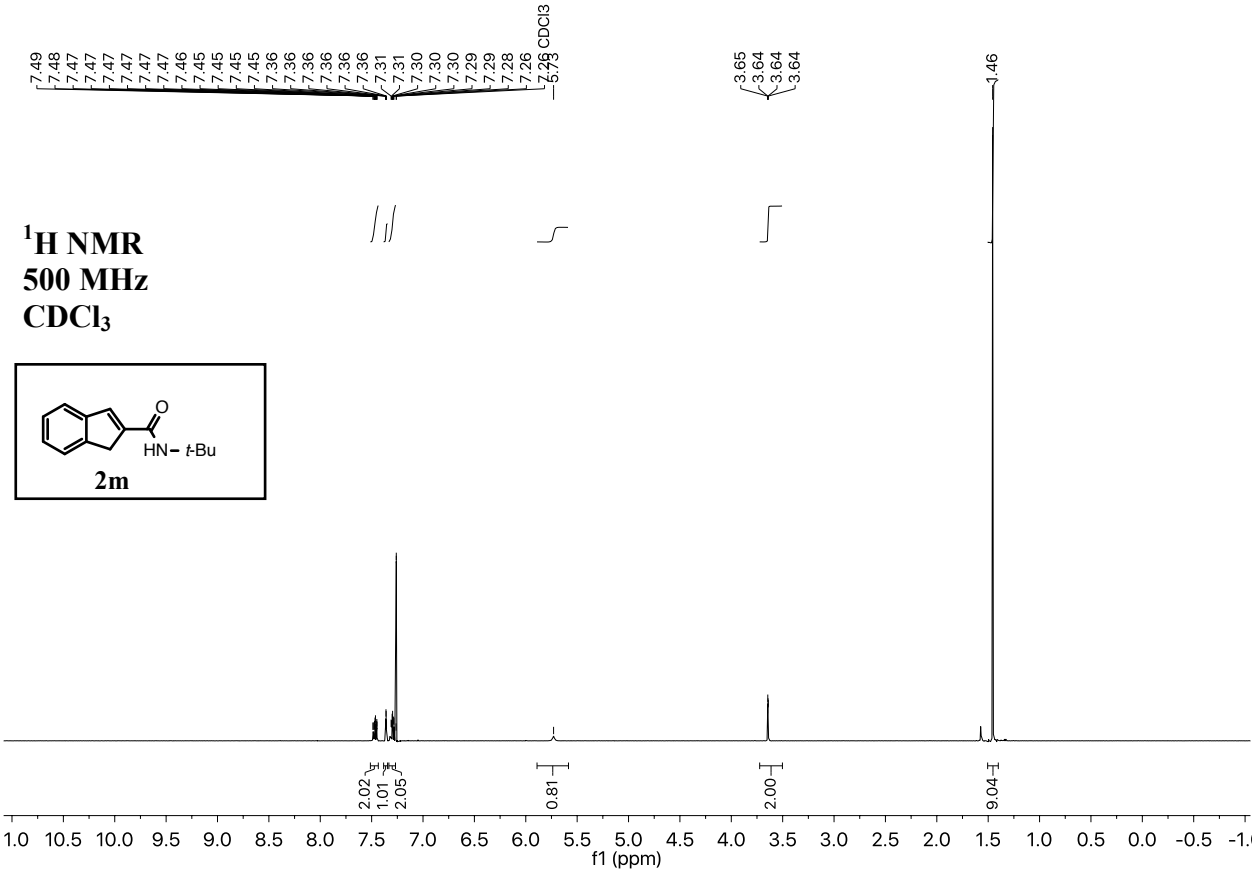
^{1}H NMR
500 MHz
$CDCl_3$



2l

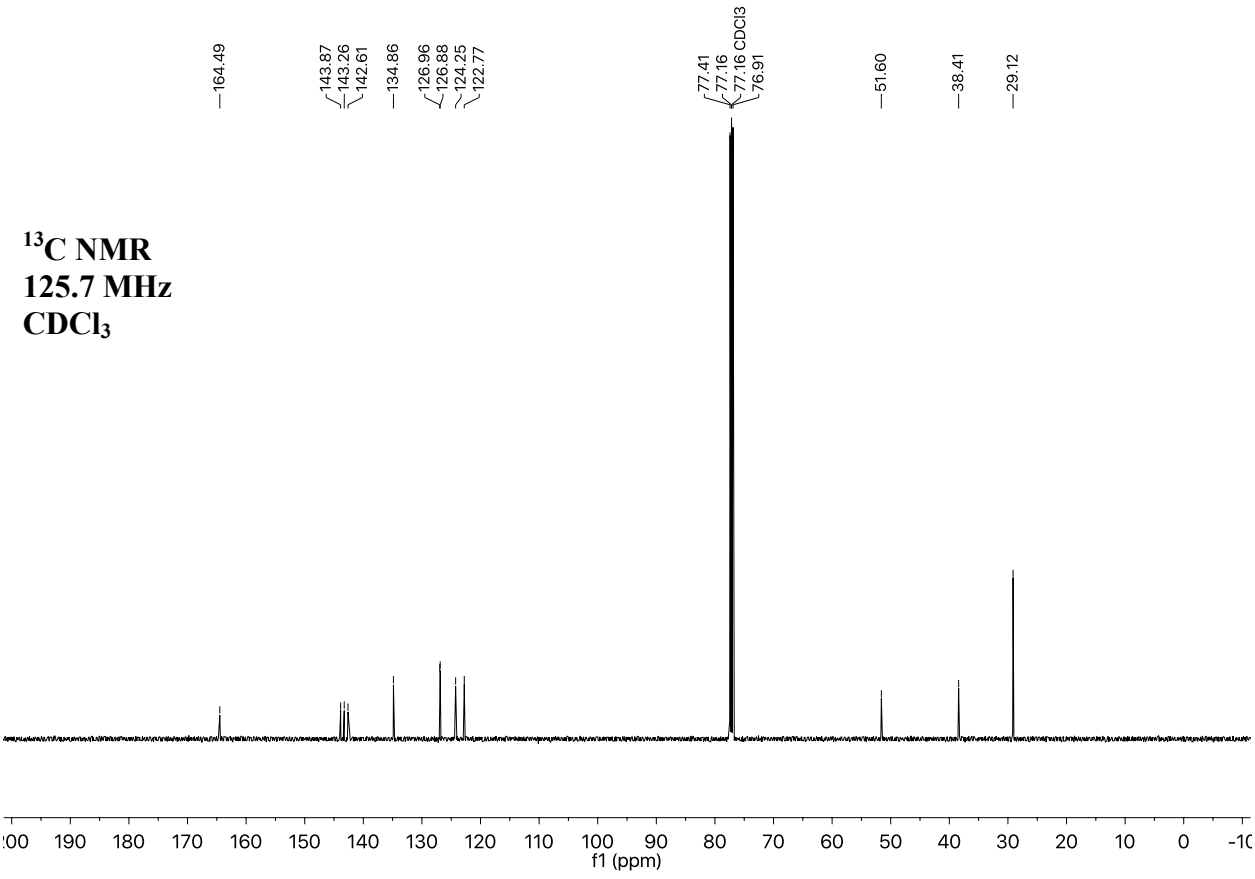
^{13}C NMR
125.7 MHz
$CDCl_3$





^{1}H NMR
500 MHz
$CDCl_3$

2m



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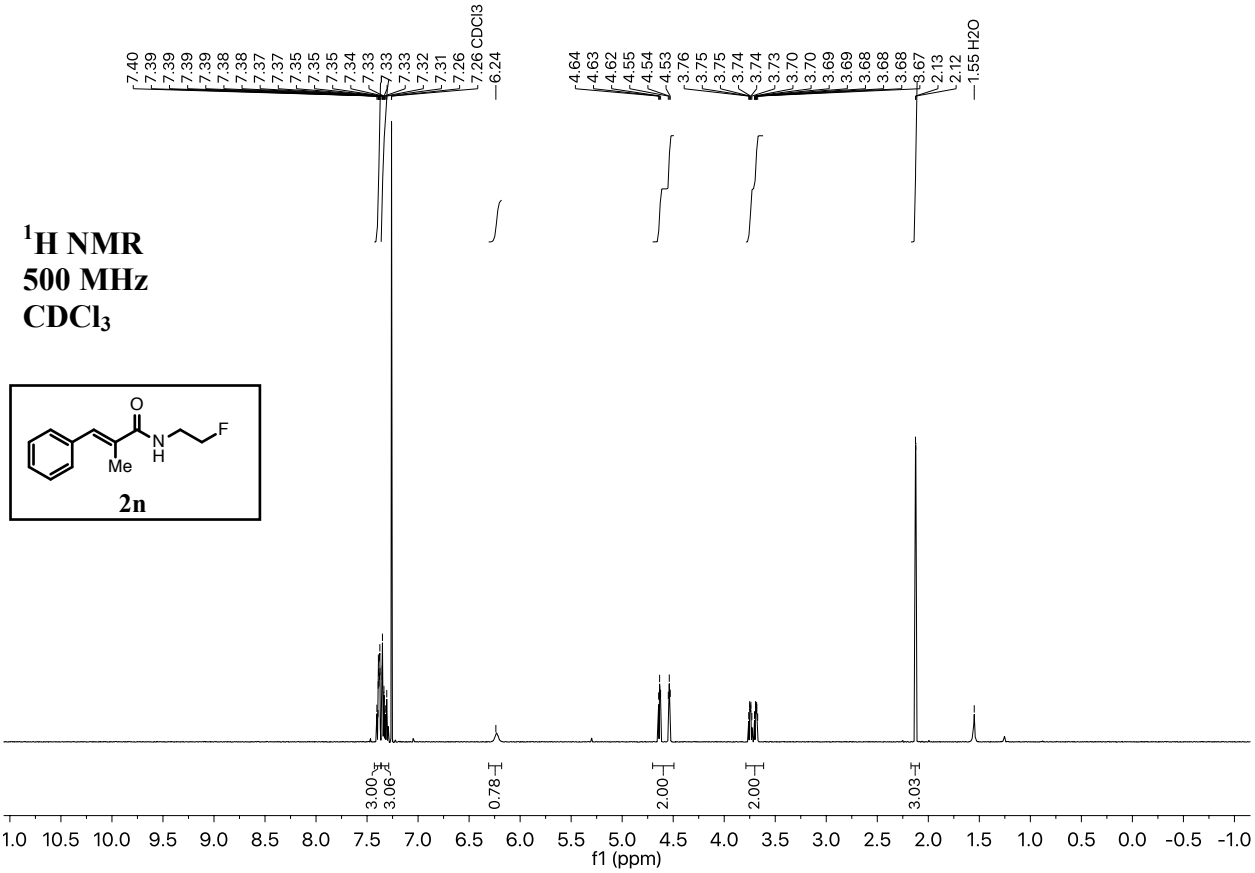
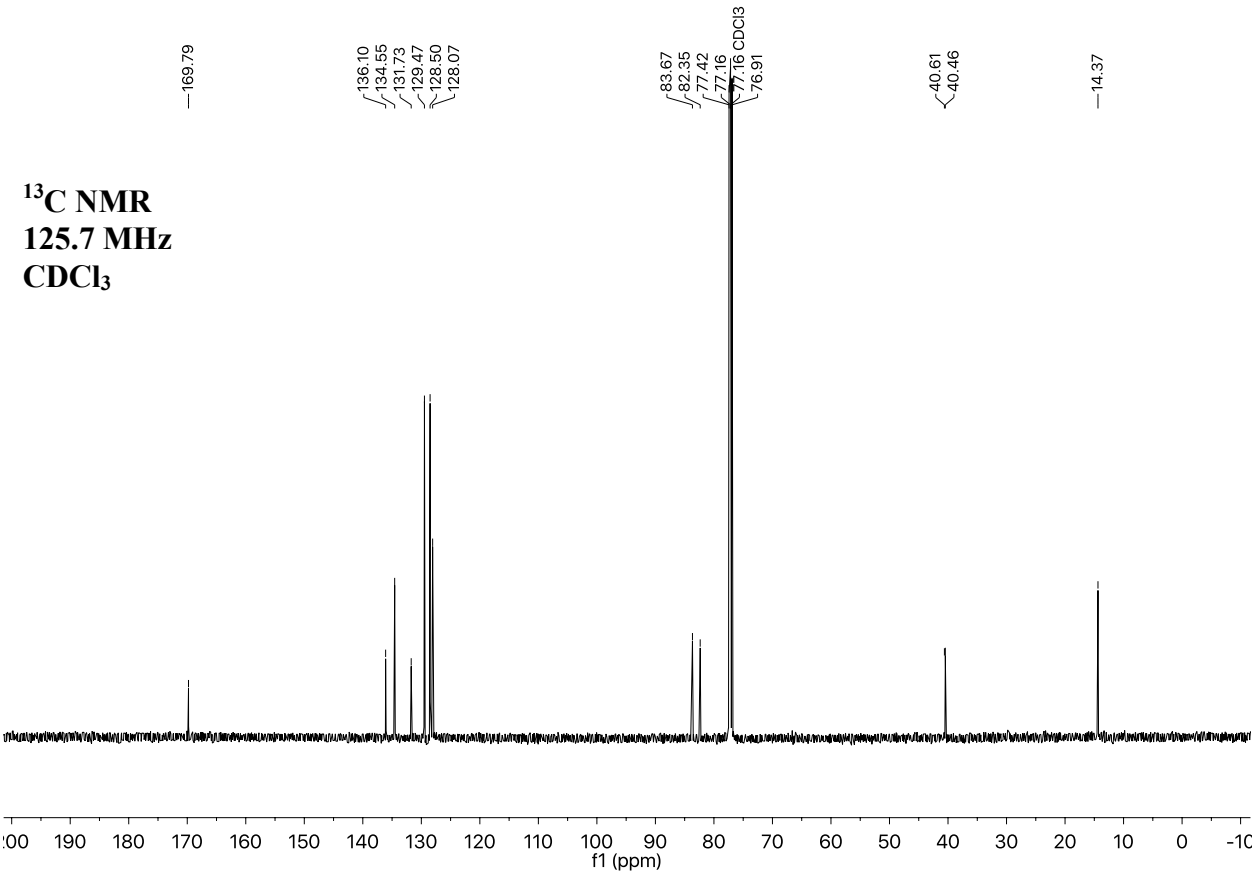


^{1}H NMR
500 MHz
$CDCl_3$

2n



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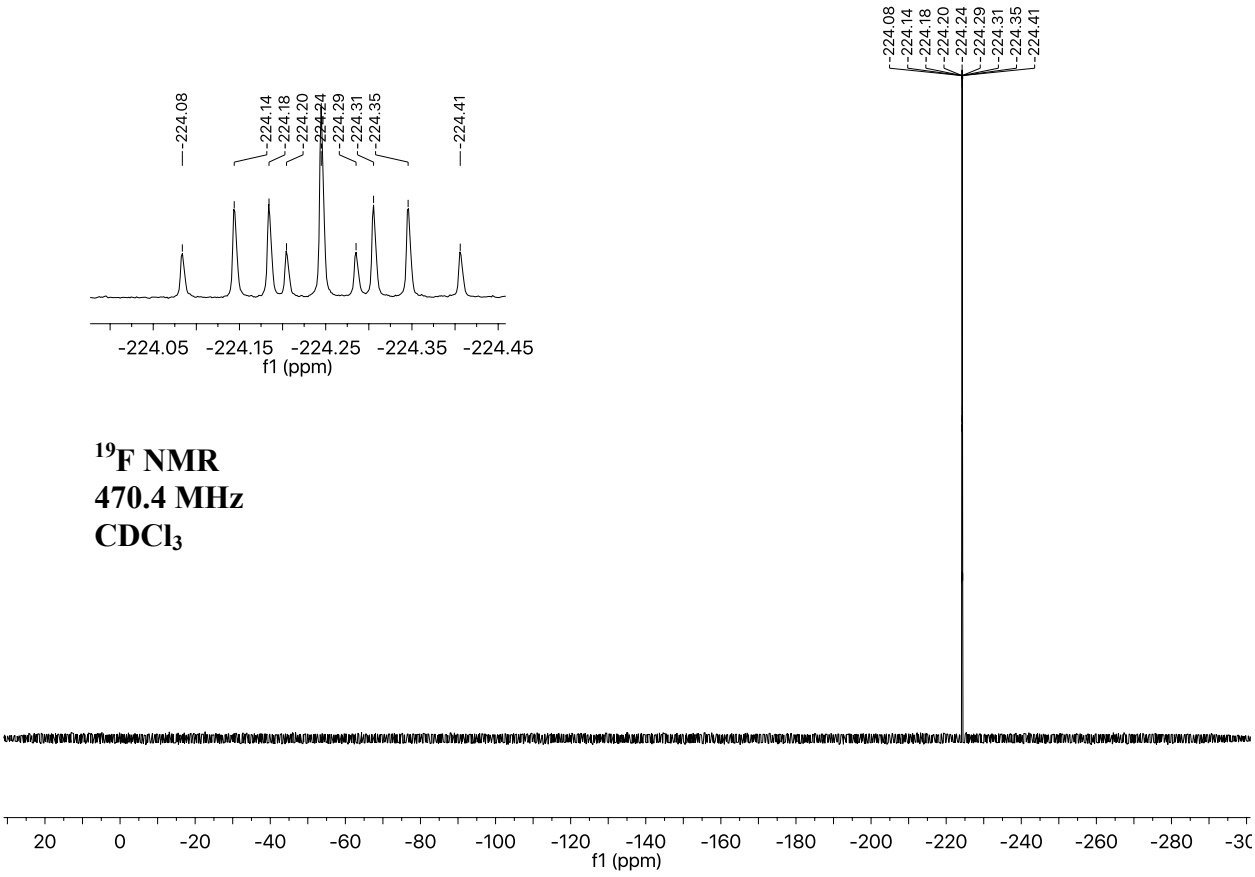

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470.4 MHz
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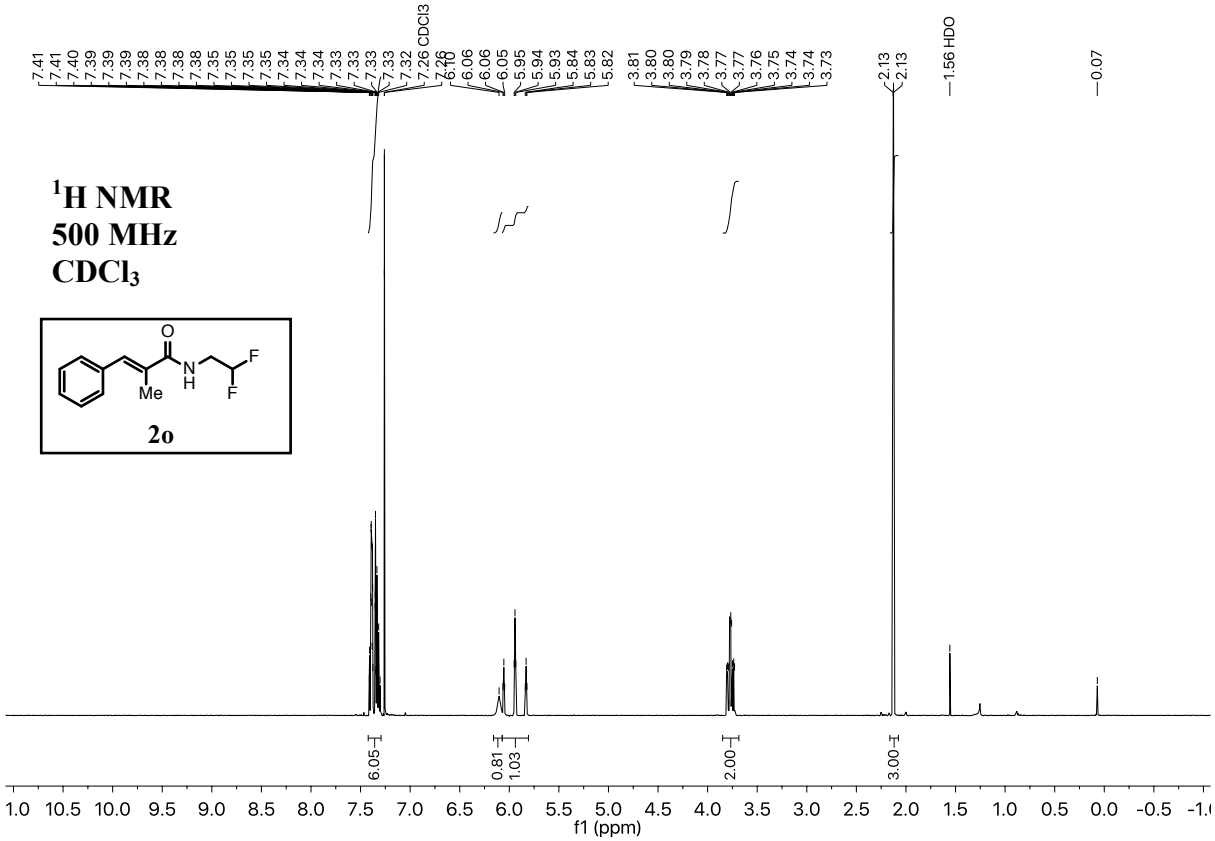
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3.75
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3.74
3.73
2.13
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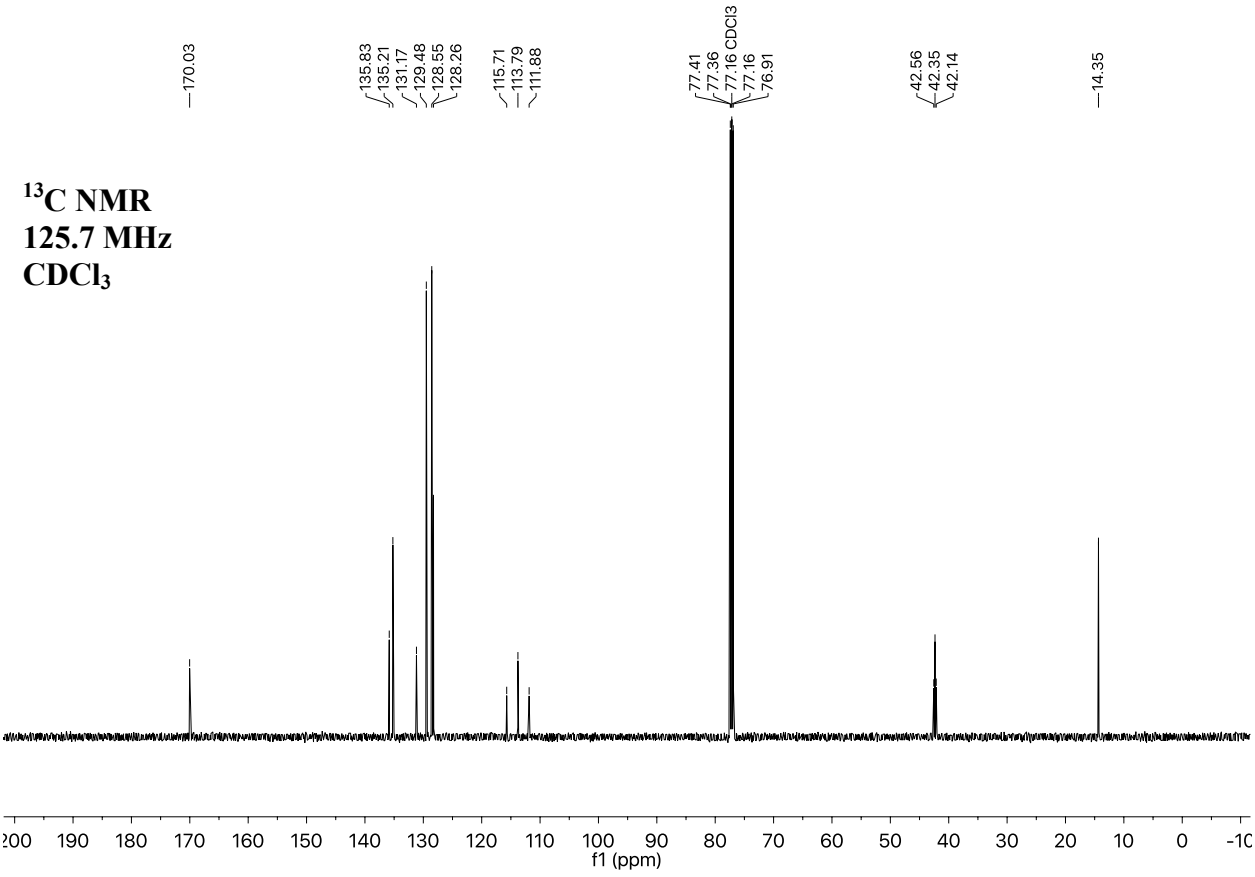
1.56 HDO
0.07
1H NMR
500 MHz
CDCl3
O
N
H
F
F
Me
2o
6.05
0.81
1.03
2.00
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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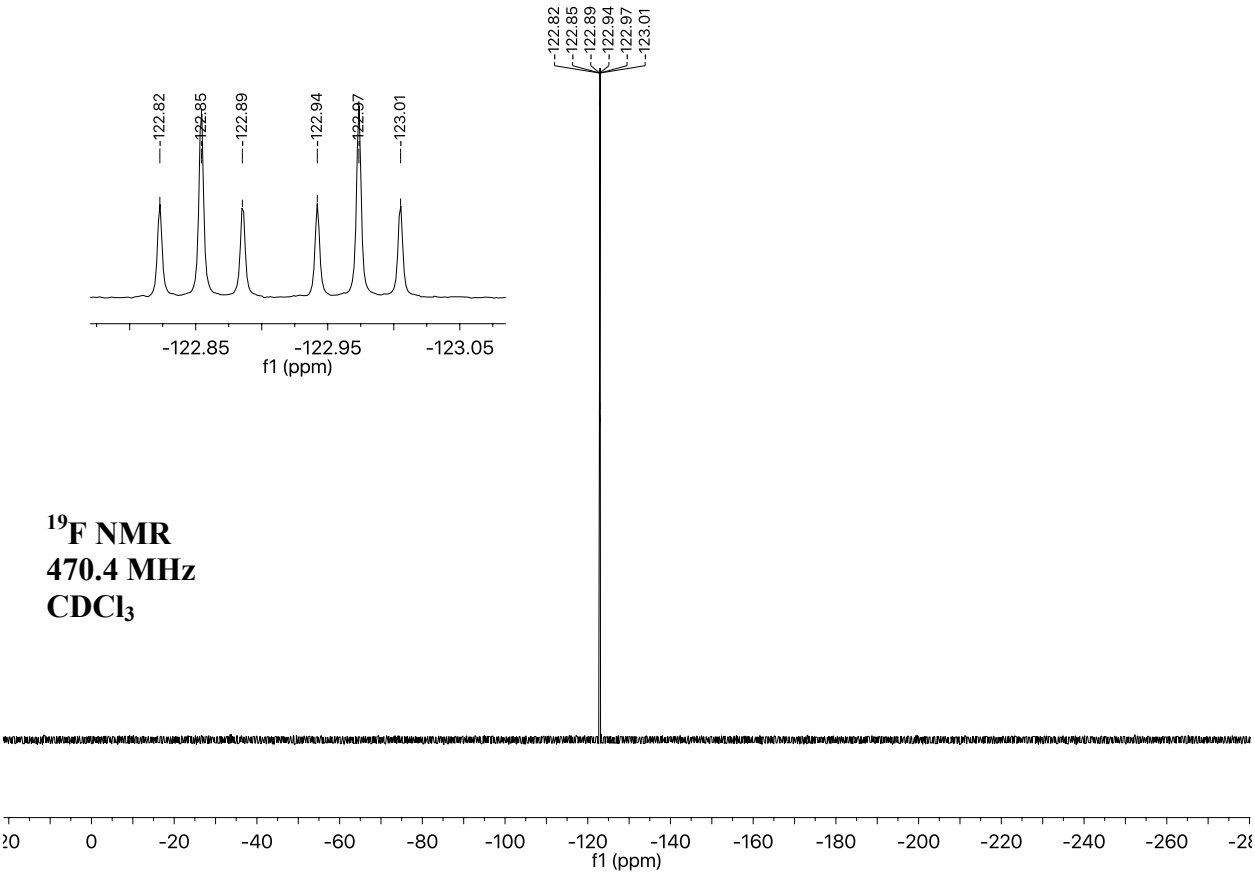
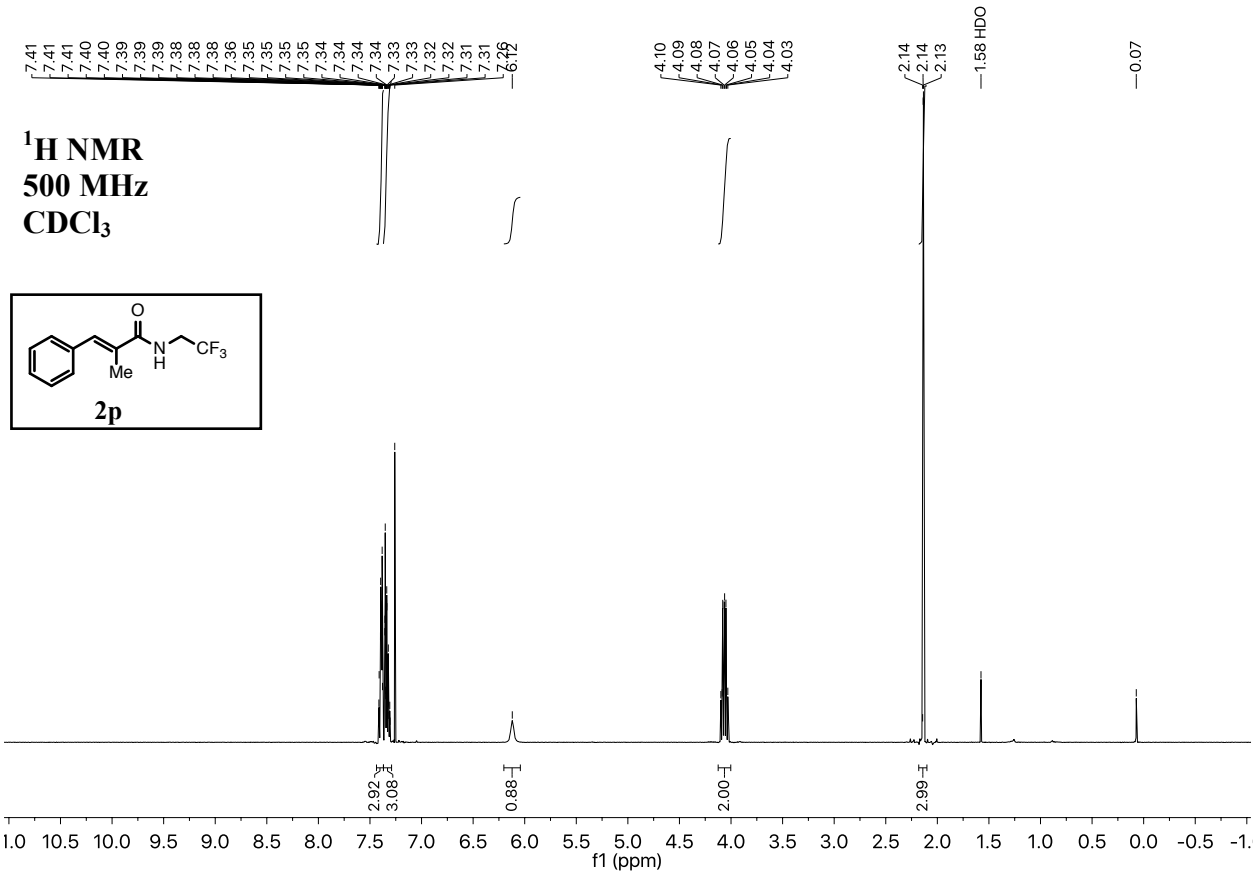
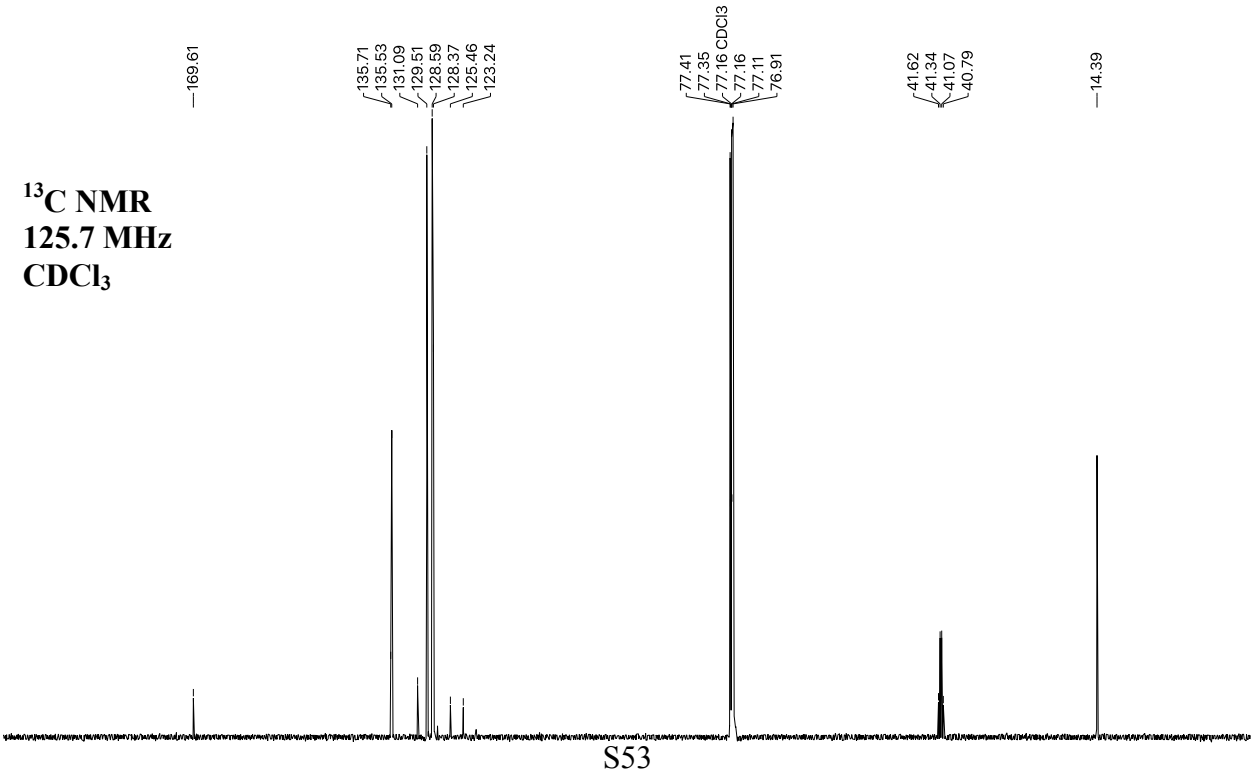
111.88
77.41
77.36
77.16 CDCl3
77.16
76.91
42.56
42.35
42.14
14.35
13C NMR
125.7 MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-122.82
-122.85
-122.89
-122.94
-122.97
-123.01
-122.85
-122.95
-123.05
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)



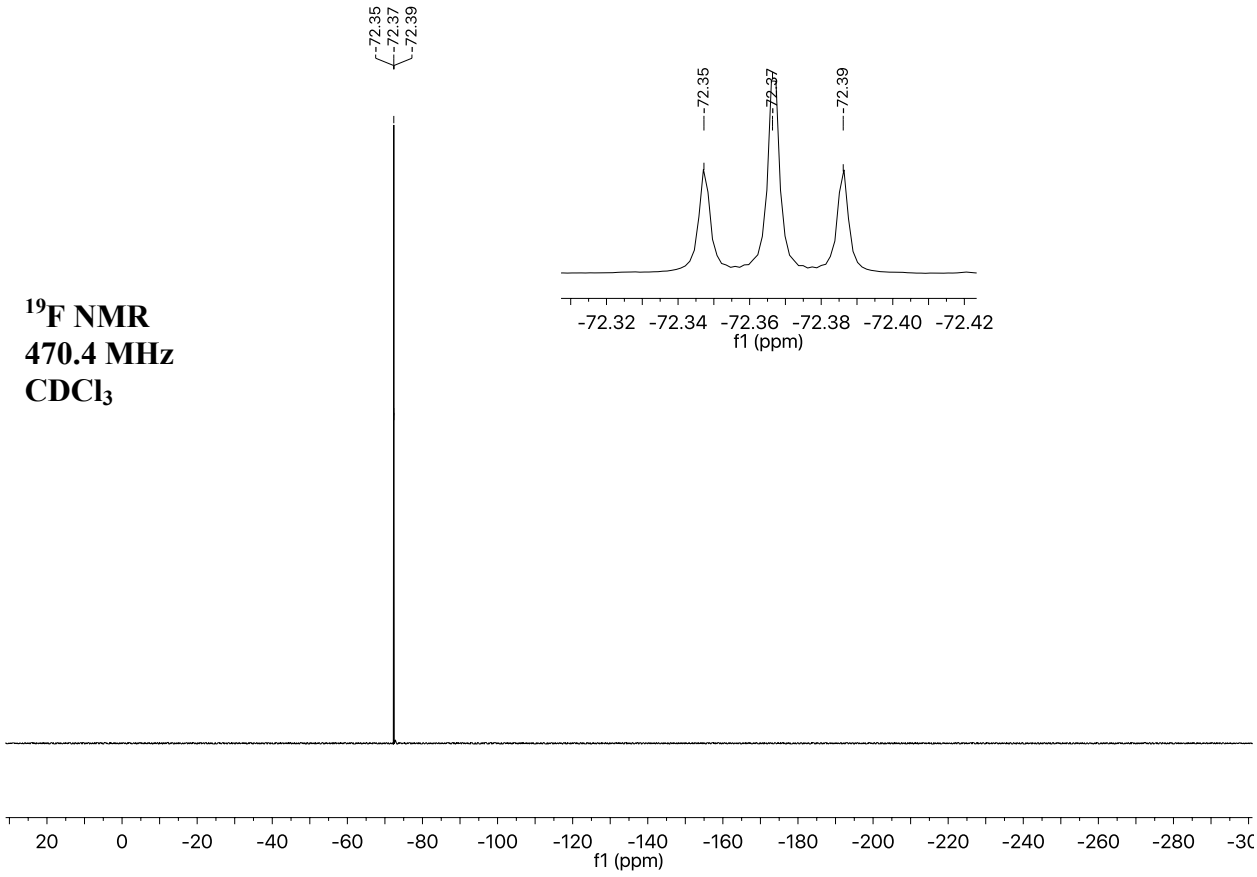
^{1}H NMR
500 MHz
$CDCl_3$

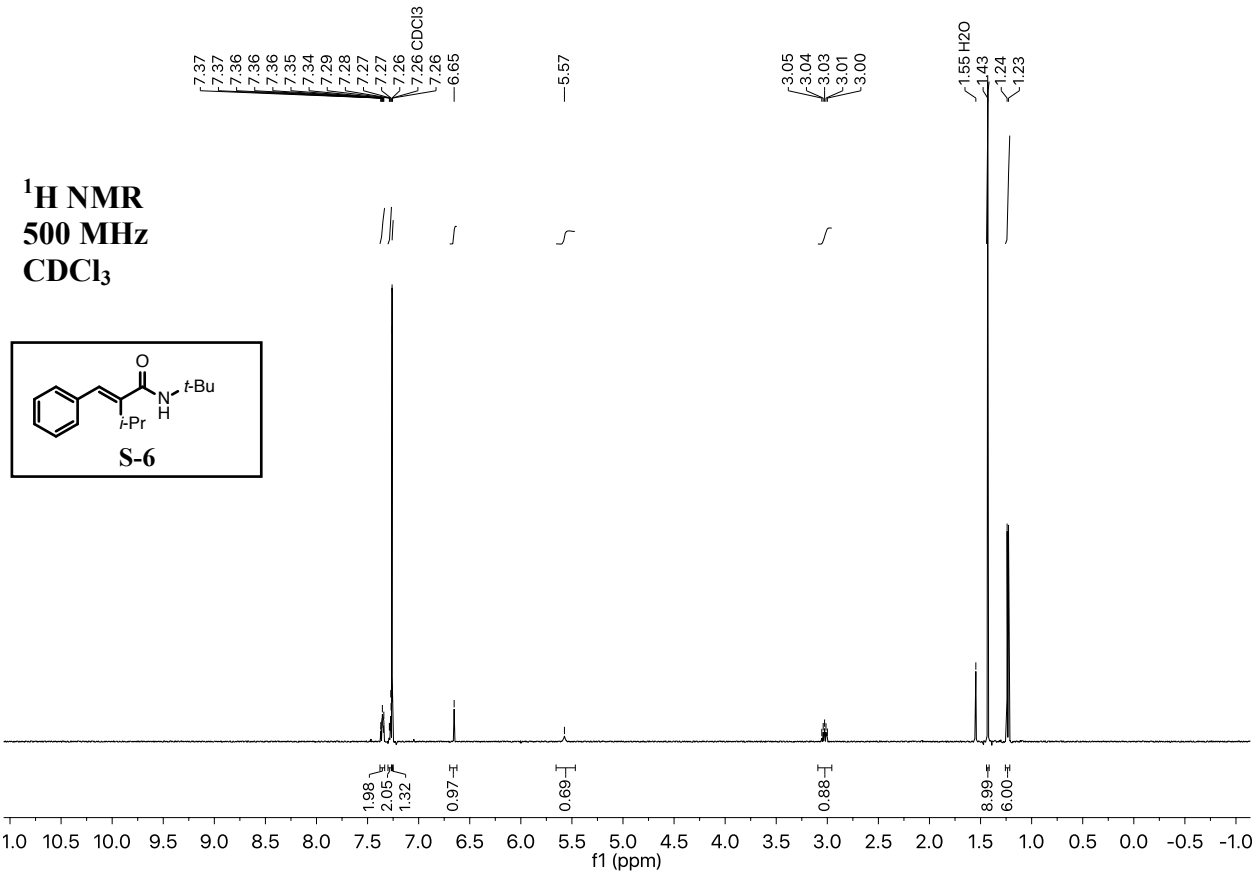
2p



^{13}C NMR
125.7 MHz
$CDCl_3$

^{19}F NMR
470.4 MHz
$CDCl_3$




7.37
7.37
7.36
7.36
7.36
7.35
7.34
7.29
7.28
7.27
7.27
7.26
7.26 CDCl3
7.26
6.65
5.57
3.05
3.04
3.03
3.01
3.00
1.55 H2O
1.43
1.24
1.23
1H NMR
500 MHz
CDCl3
O
N
H
t-Bu
i-Pr
S-6
1.98
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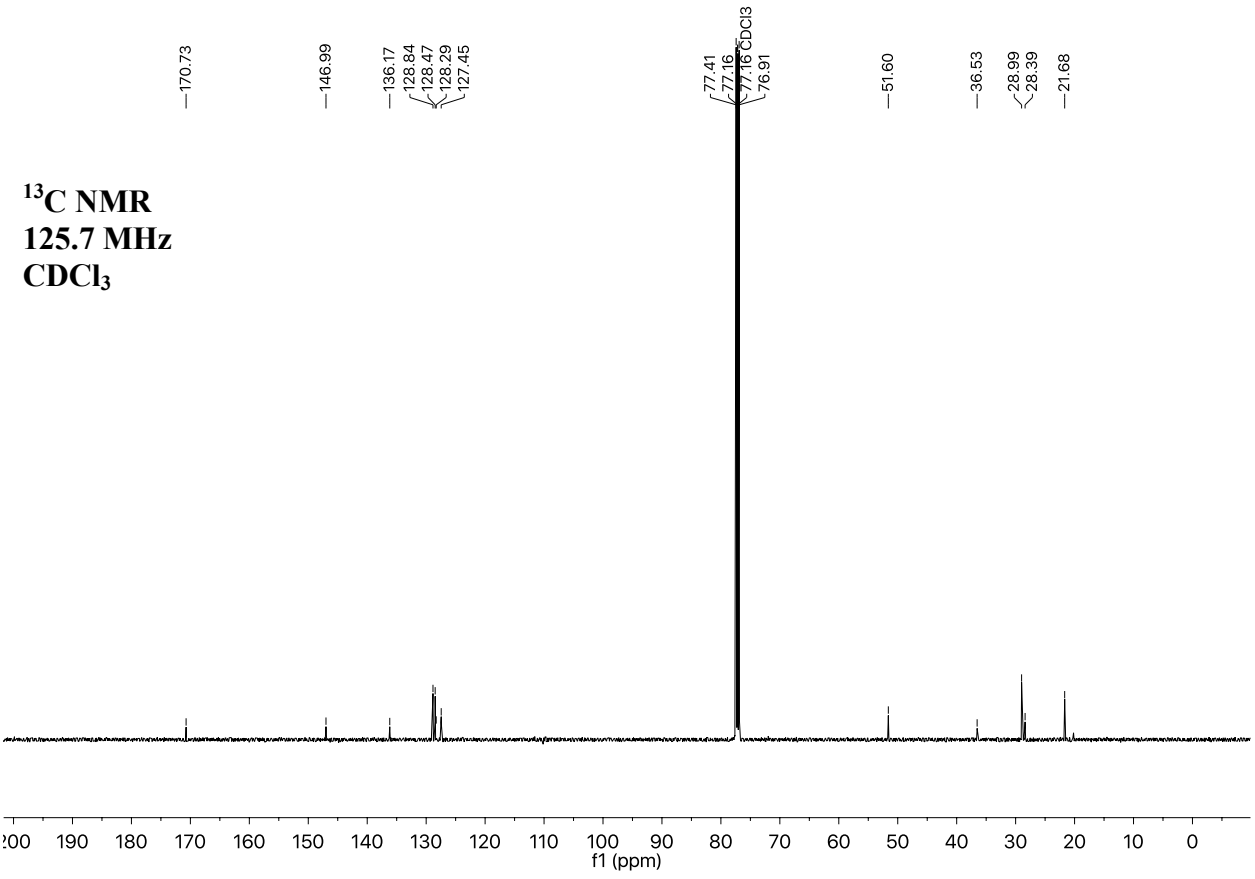
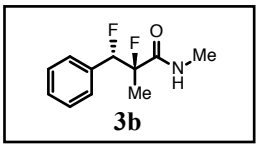
1.32
0.97
0.69
0.88
8.99
6.00
f1 (ppm)

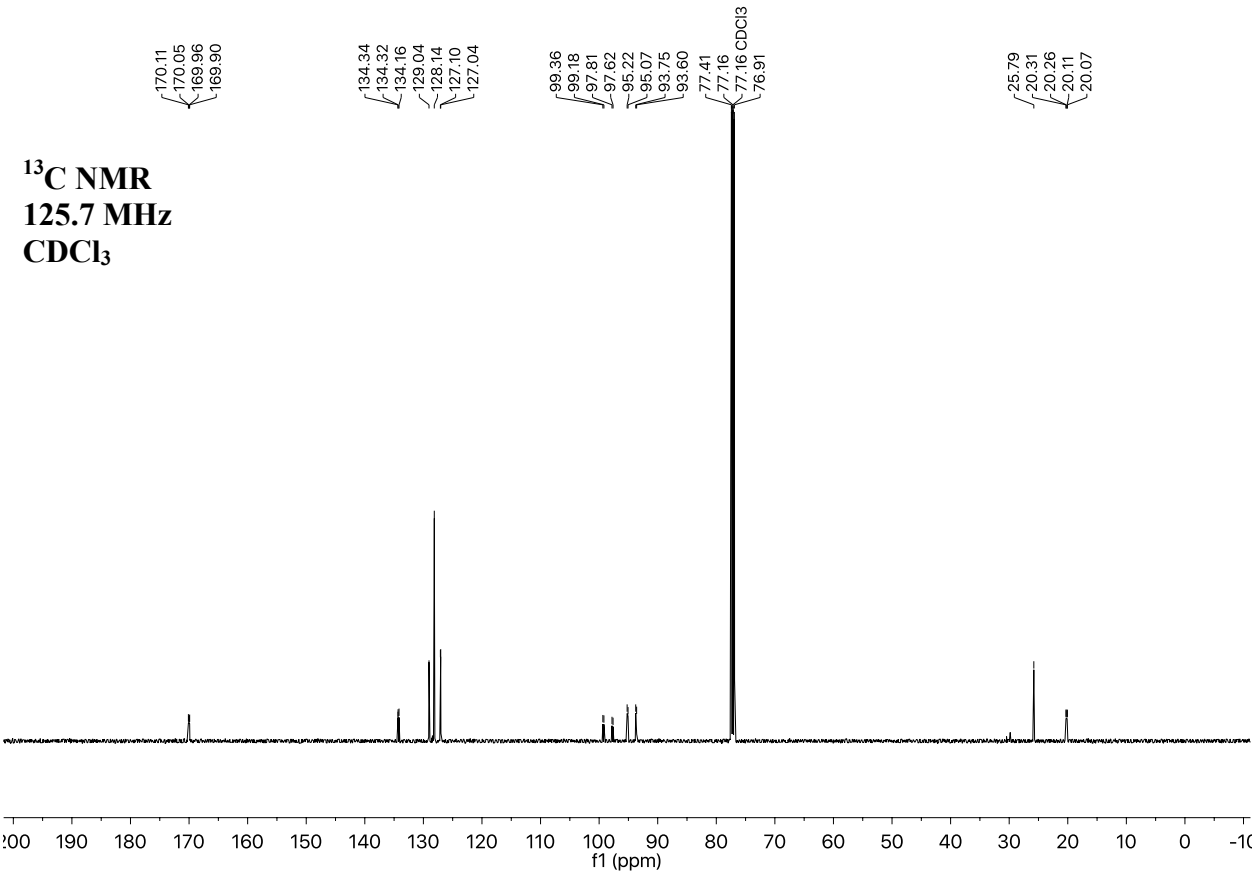

170.73
146.99
136.17
128.84
128.47
128.29
127.45
77.41
77.16
77.16 CDCl3
76.91
51.60
36.53
28.99
28.39
21.68
13C NMR
125.7 MHz
CDCl3
f1 (ppm)

^{1}H NMR
500 MHz
$CDCl_3$

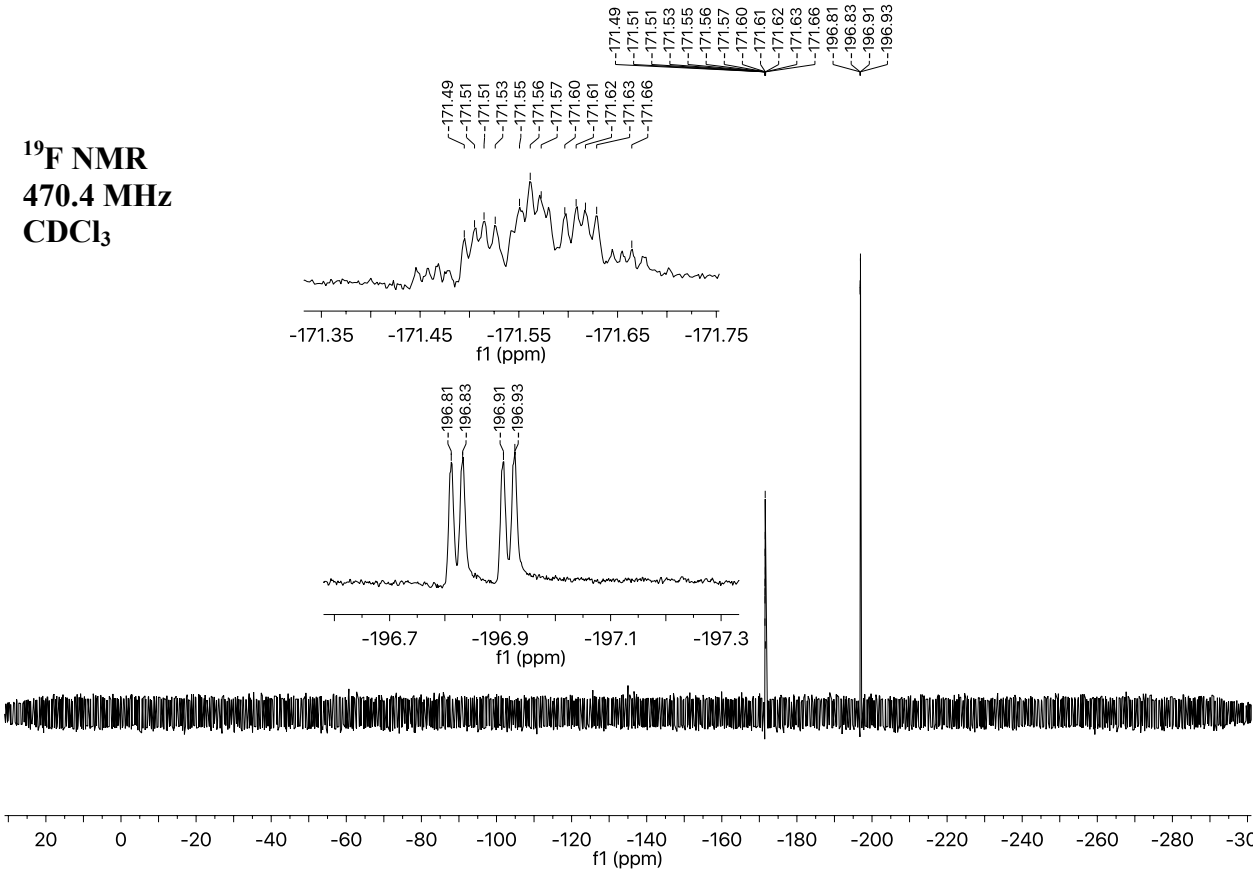


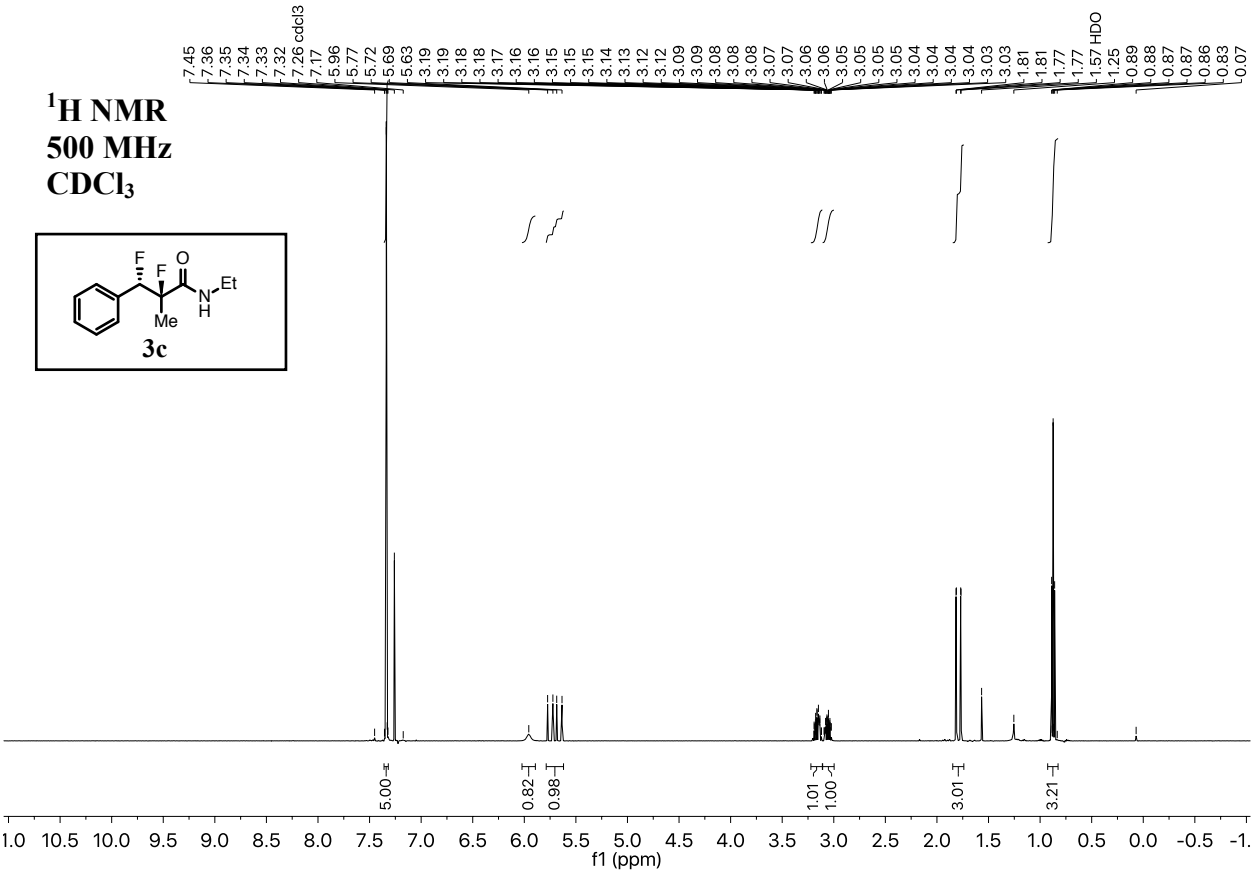
3b

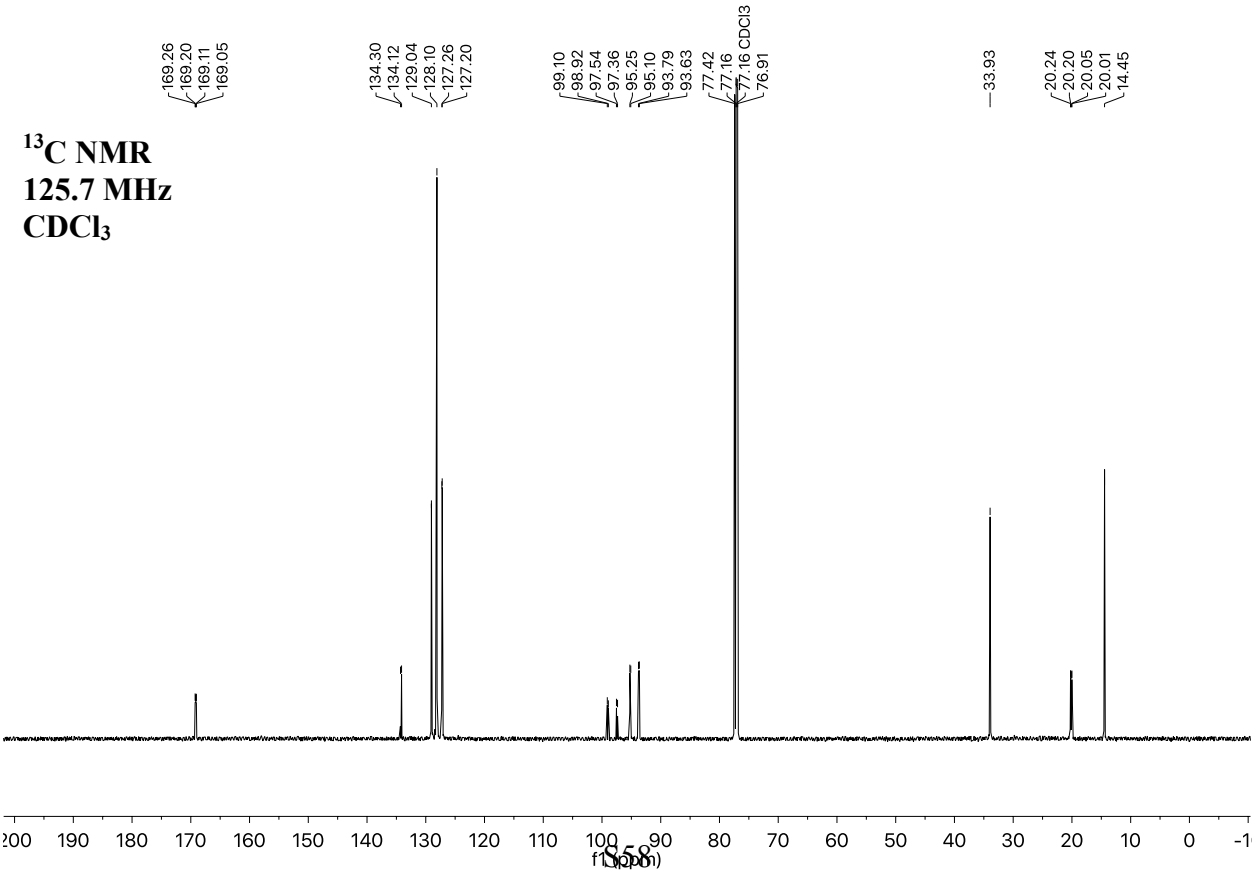
^{13}C NMR
125.7 MHz
$CDCl_3$

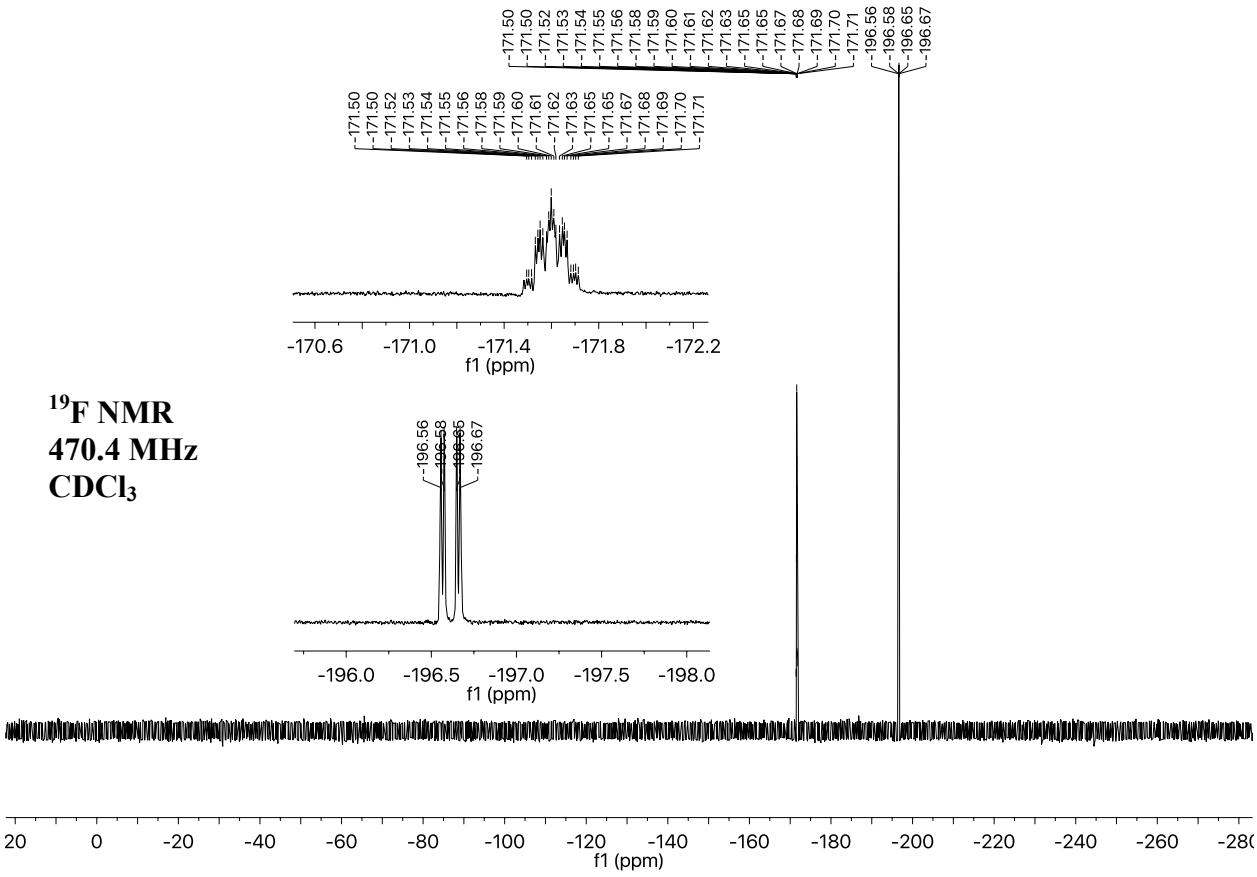


^{19}F NMR
470.4 MHz
$CDCl_3$

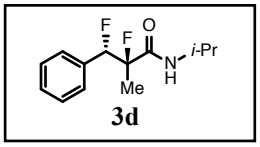



7.45 7.36 7.35 7.34 7.33 7.32 7.26 cdcl3 7.17 5.96 5.77 5.72 5.69 5.63 3.19 3.19 3.18 3.18 3.17 3.16 3.16 3.15 3.15 3.15 3.14 3.13 3.12 3.12 3.09 3.09 3.08 3.08 3.08 3.07 3.07 3.06 3.06 3.05 3.05 3.05 3.05 3.04 3.04 3.04 3.04 3.03 3.03 1.81 1.81 1.77 1.77 1.57 HDO 1.25 0.89 0.88 0.87 0.87 0.86 0.83 0.07
1H NMR
500 MHz
CDCl3
F F O
N Et
H
Me
3c
5.00 0.82 0.98 1.01 1.00 3.01 3.21
f1 (ppm)


169.26 169.20 169.11 169.05 134.30 134.12 129.04 128.10 127.26 127.20 99.10 98.92 97.54 97.36 95.25 95.10 93.79 93.63 77.42 77.16 77.16 CDCl3 76.91 33.93 20.24 20.20 20.05 20.01 14.45
13C NMR
125.7 MHz
CDCl3
f1 (ppm)

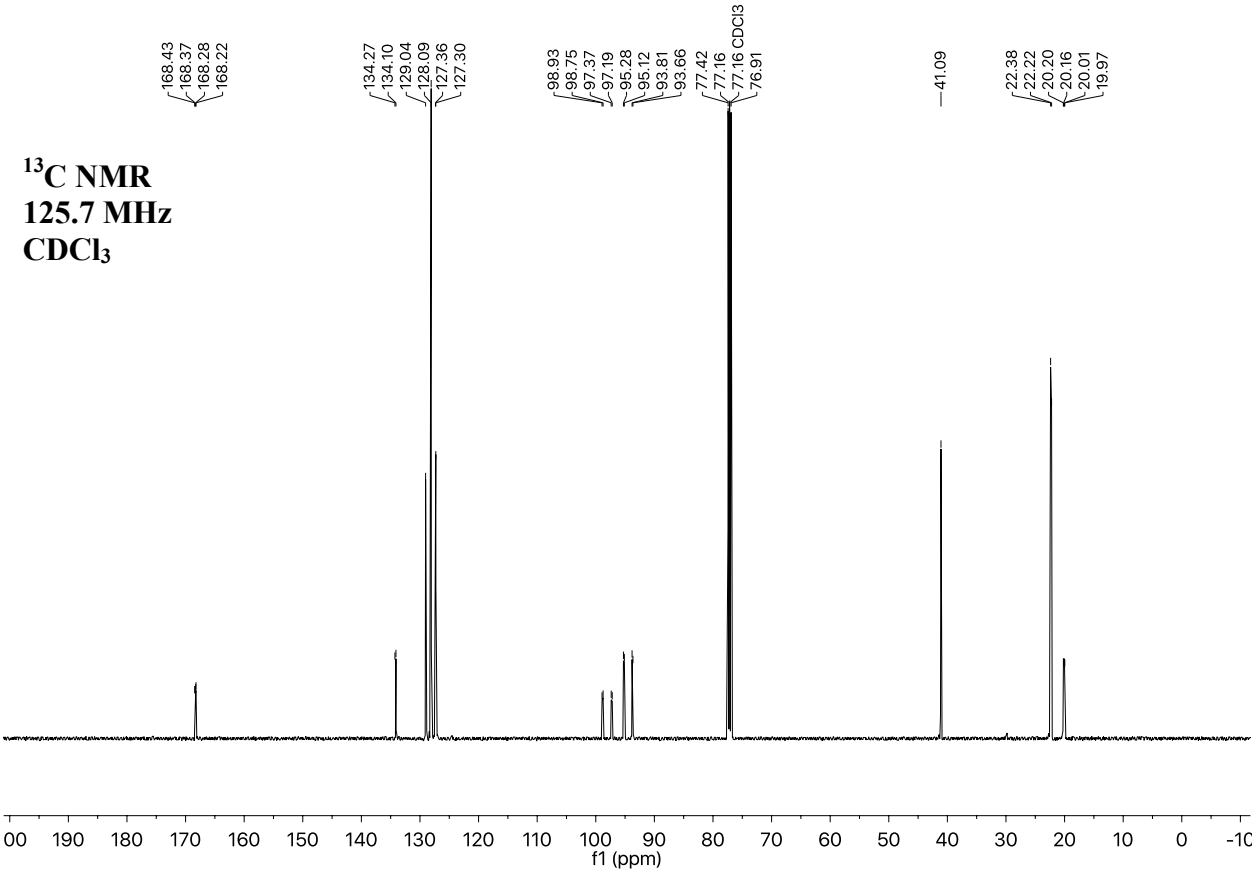

19F NMR
470.4 MHz
CDCl3
f1 (ppm)

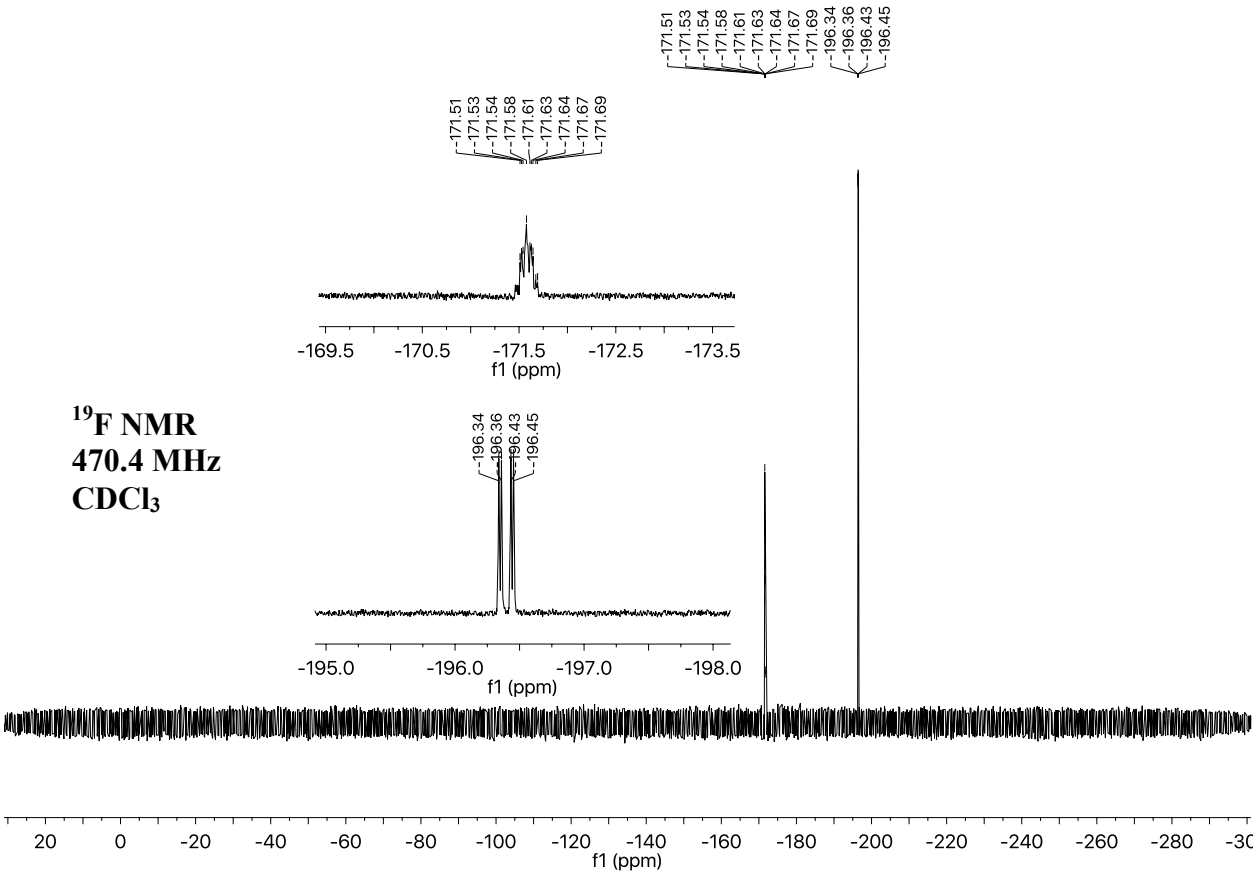
^{1}H NMR
500 MHz
$CDCl_3$



3d

^{13}C NMR
125.7 MHz
$CDCl_3$




-171.51
-171.53
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-171.61
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-171.64
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-196.34
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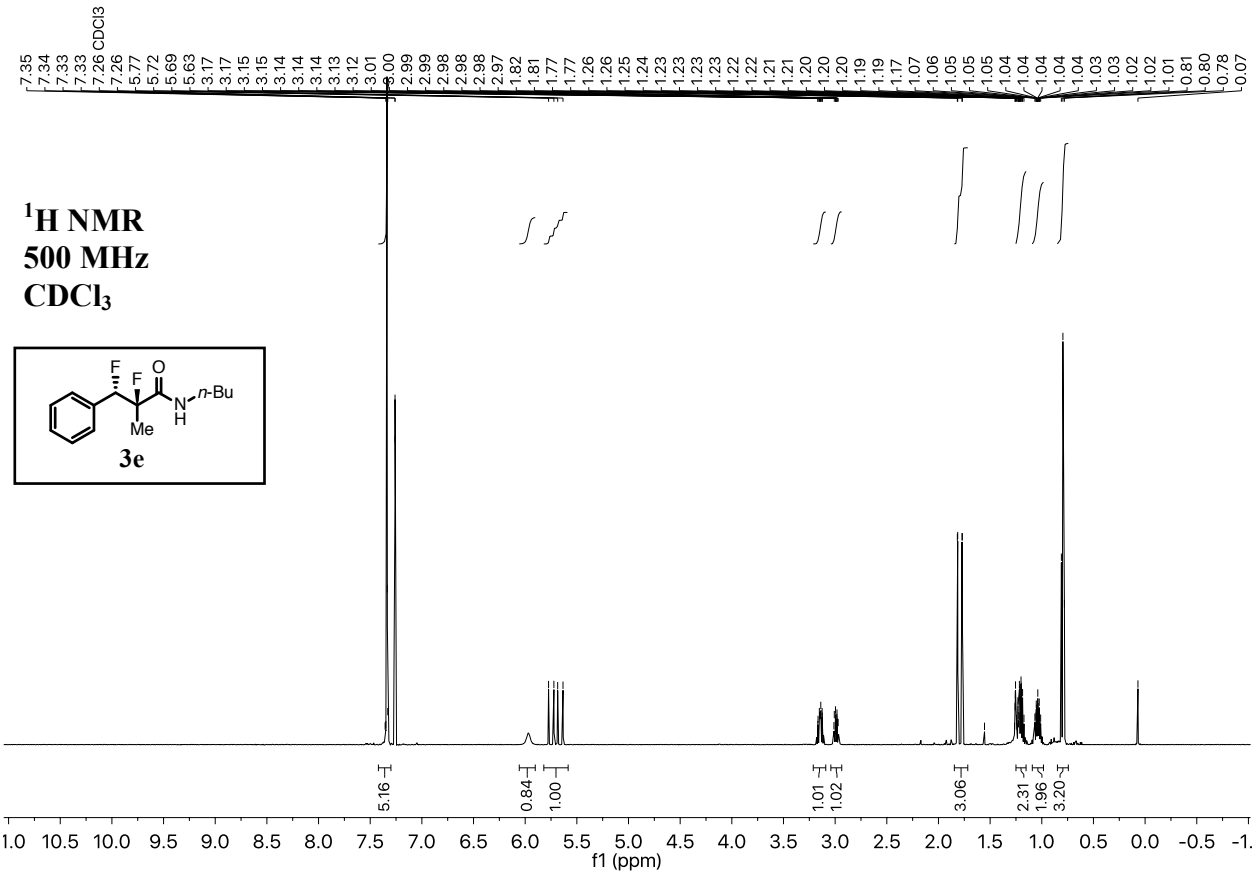
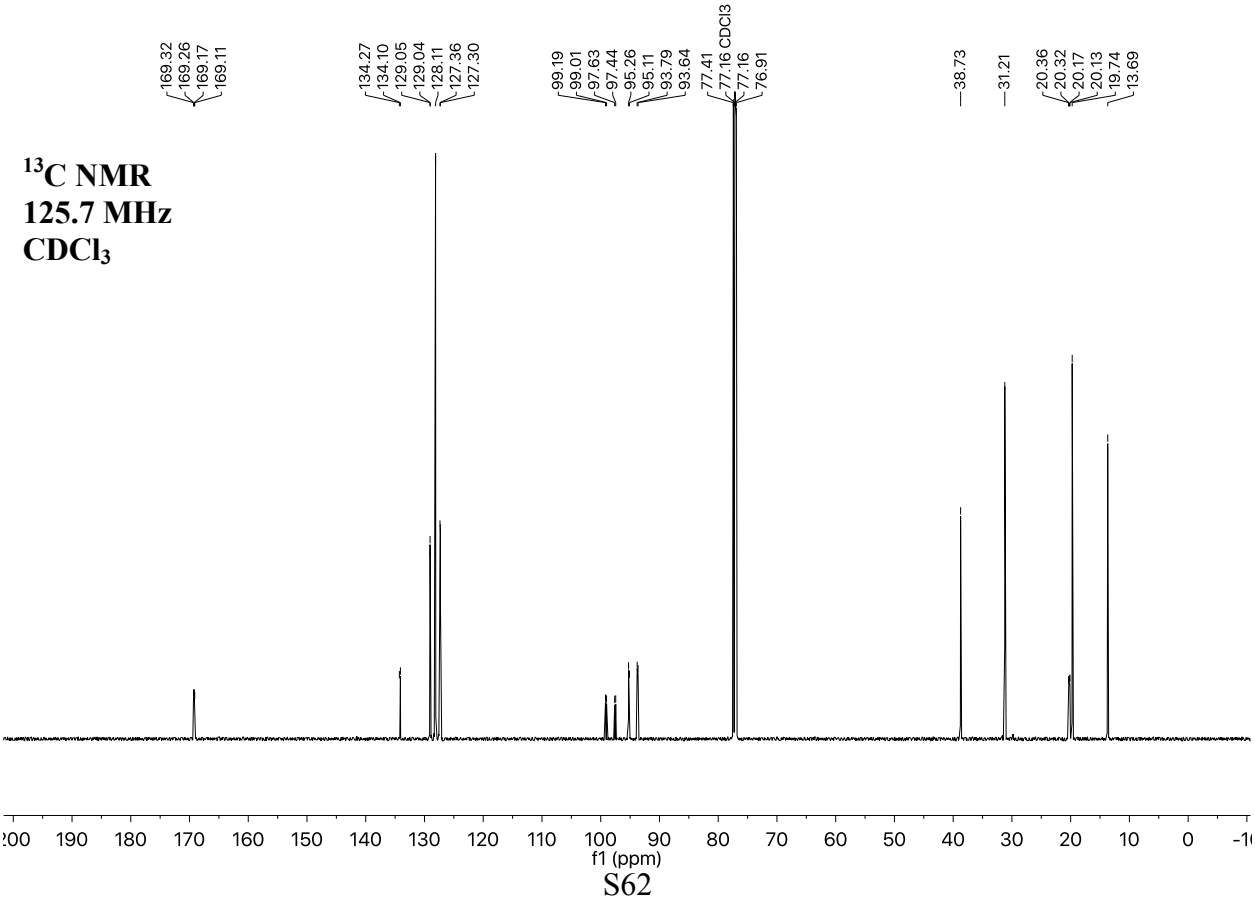
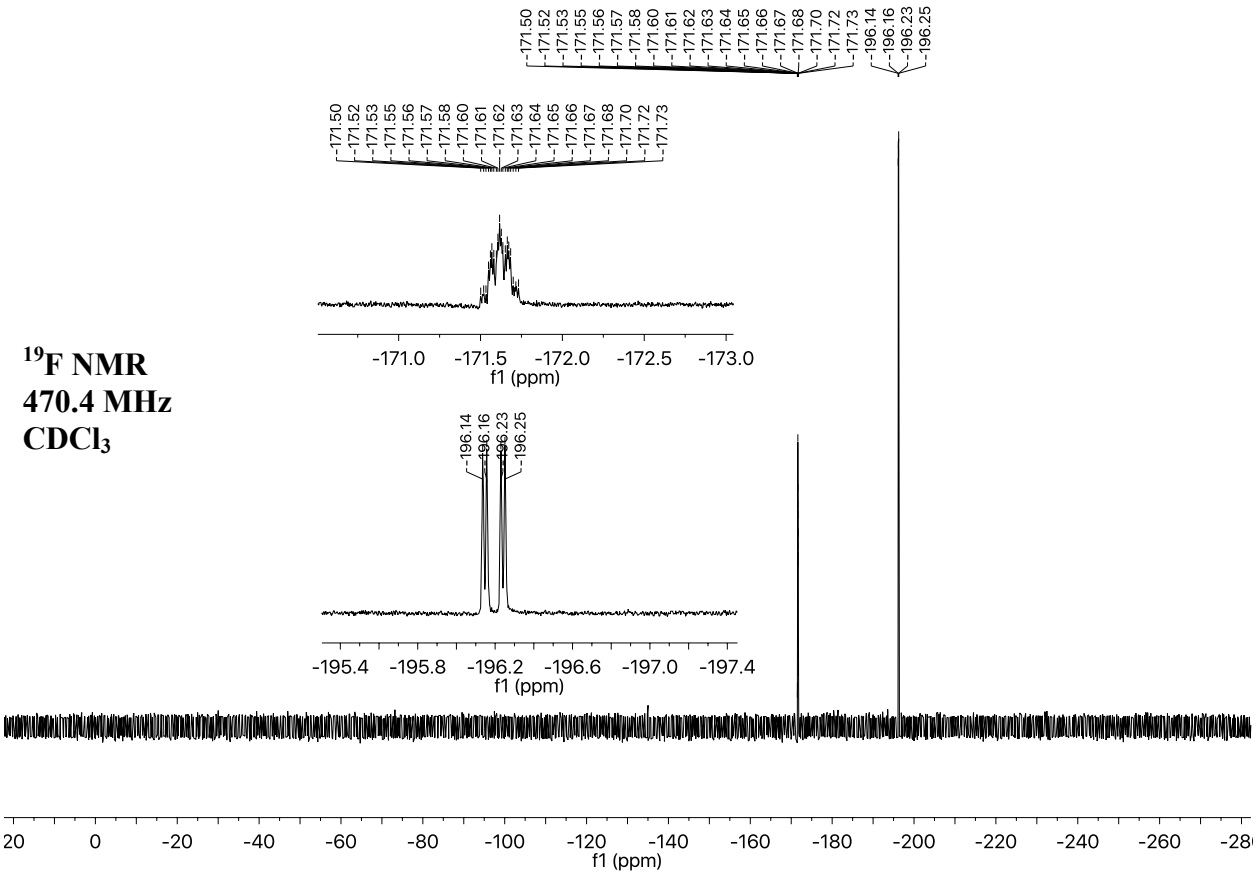
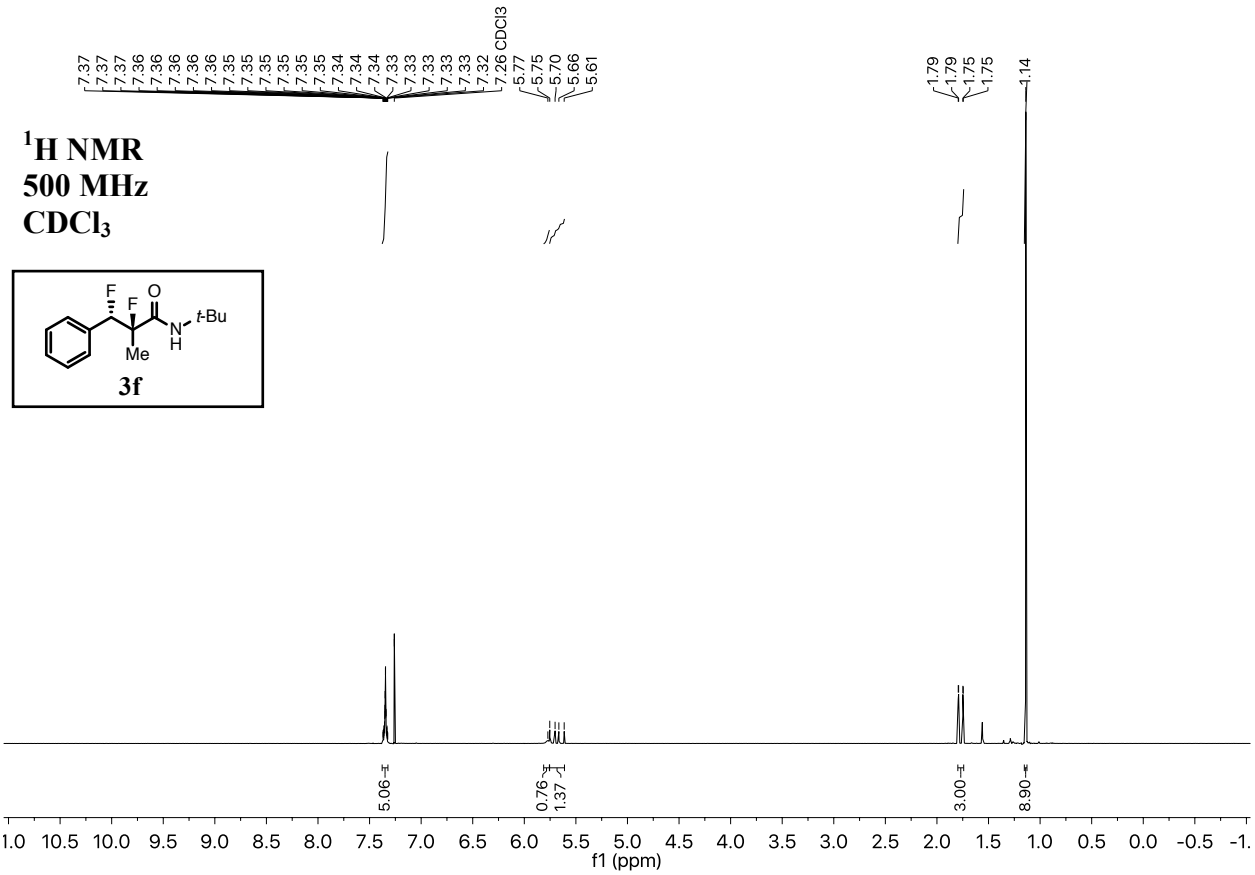
-196.43
-196.45
-169.5
-170.5
-171.5
-172.5
-173.5
f1 (ppm)
-195.0
-196.0
-197.0
-198.0
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)


7.35 7.34 7.33 7.33 7.26 CDCl3 7.26 5.77 5.72 5.69 5.63 3.17 3.17 3.15 3.15 3.14 3.14 3.14 3.13 3.12 3.01 3.00 2.99 2.99 2.98 2.98 2.98 2.97 1.82 1.81 1.77 1.77 1.26 1.26 1.25 1.24 1.23 1.23 1.23 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.20 1.19 1.19 1.17 1.07 1.06 1.05 1.05 1.05 1.04 1.04 1.04 1.04 1.04 1.03 1.03 1.02 1.02 1.01 0.81 0.80 0.78 0.07
1H NMR
500 MHz
CDCl3
F F O
n-Bu
N
H
Me
3e
5.16 0.84 1.00 1.01 1.02 3.06 2.31 1.96 3.20
f1 (ppm)

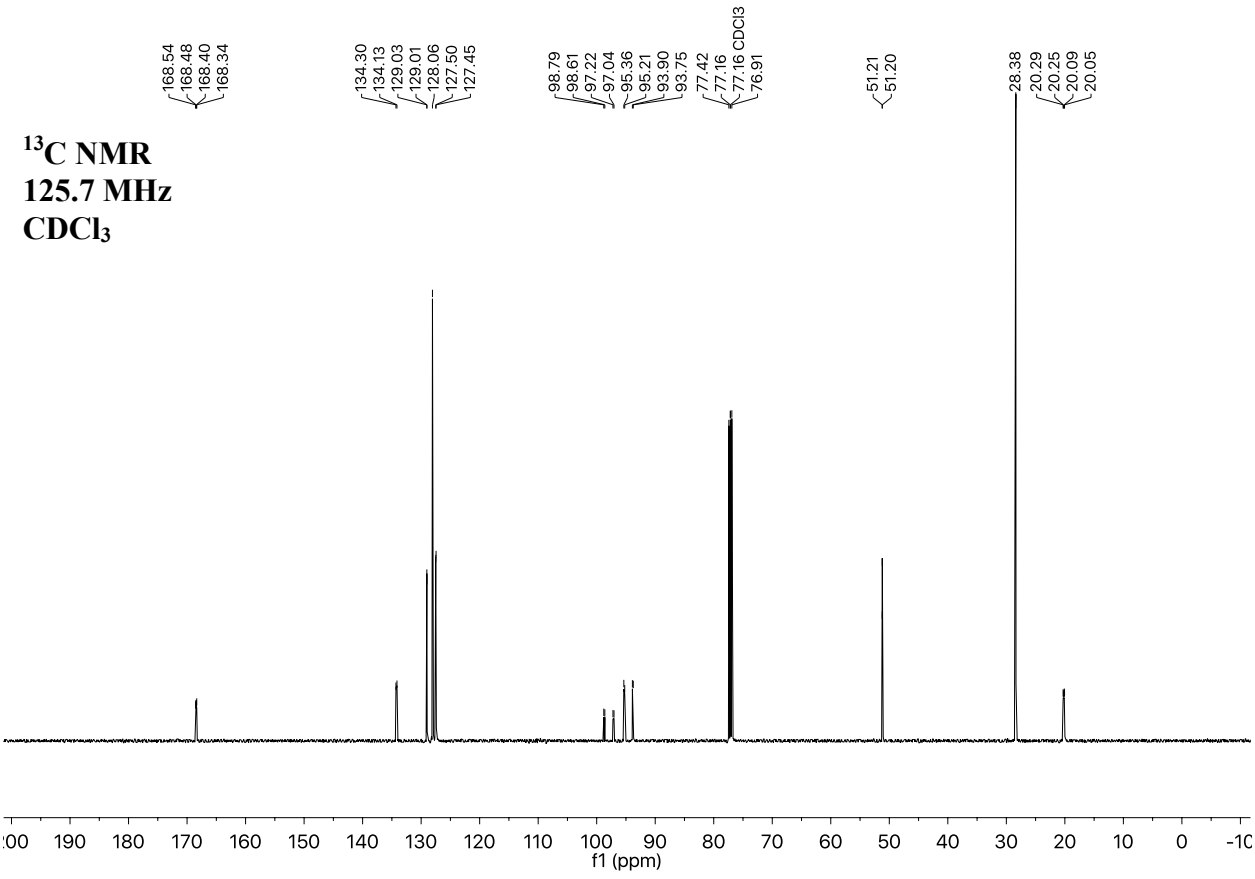

169.32 169.26 169.17 169.11 134.27 134.10 129.05 129.04 128.11 127.36 127.30 99.19 99.01 97.63 97.44 95.26 95.11 93.79 93.64 77.41 77.16 CDCl3 77.16 76.91 38.73 31.21 20.36 20.32 20.17 20.13 19.74 13.69
13C NMR
125.7 MHz
CDCl3
f1 (ppm)


19F NMR
470.4 MHz
CDCl3
f1 (ppm)

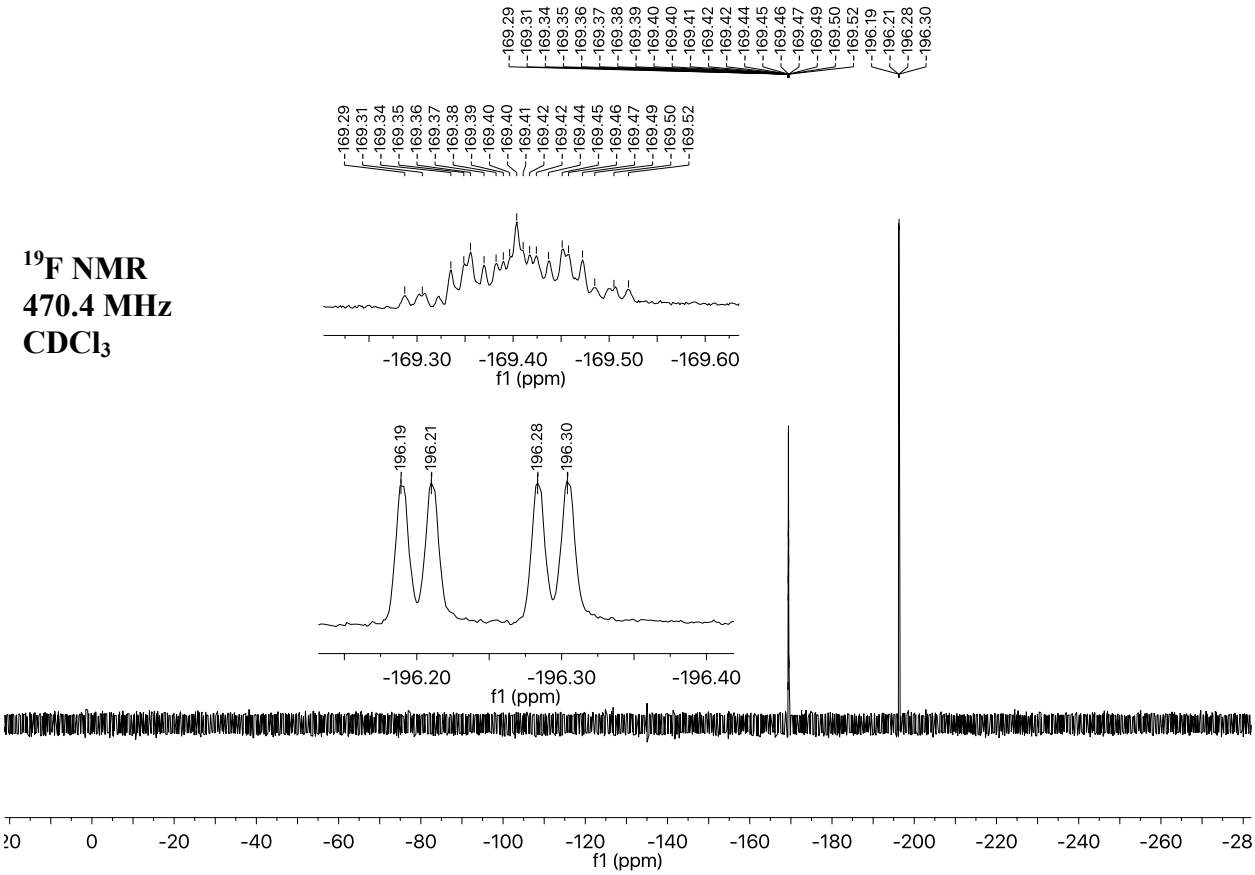


^{1}H NMR
500 MHz
$CDCl_3$

3f



^{13}C NMR
125.7 MHz
$CDCl_3$


169.29
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169.35
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169.39
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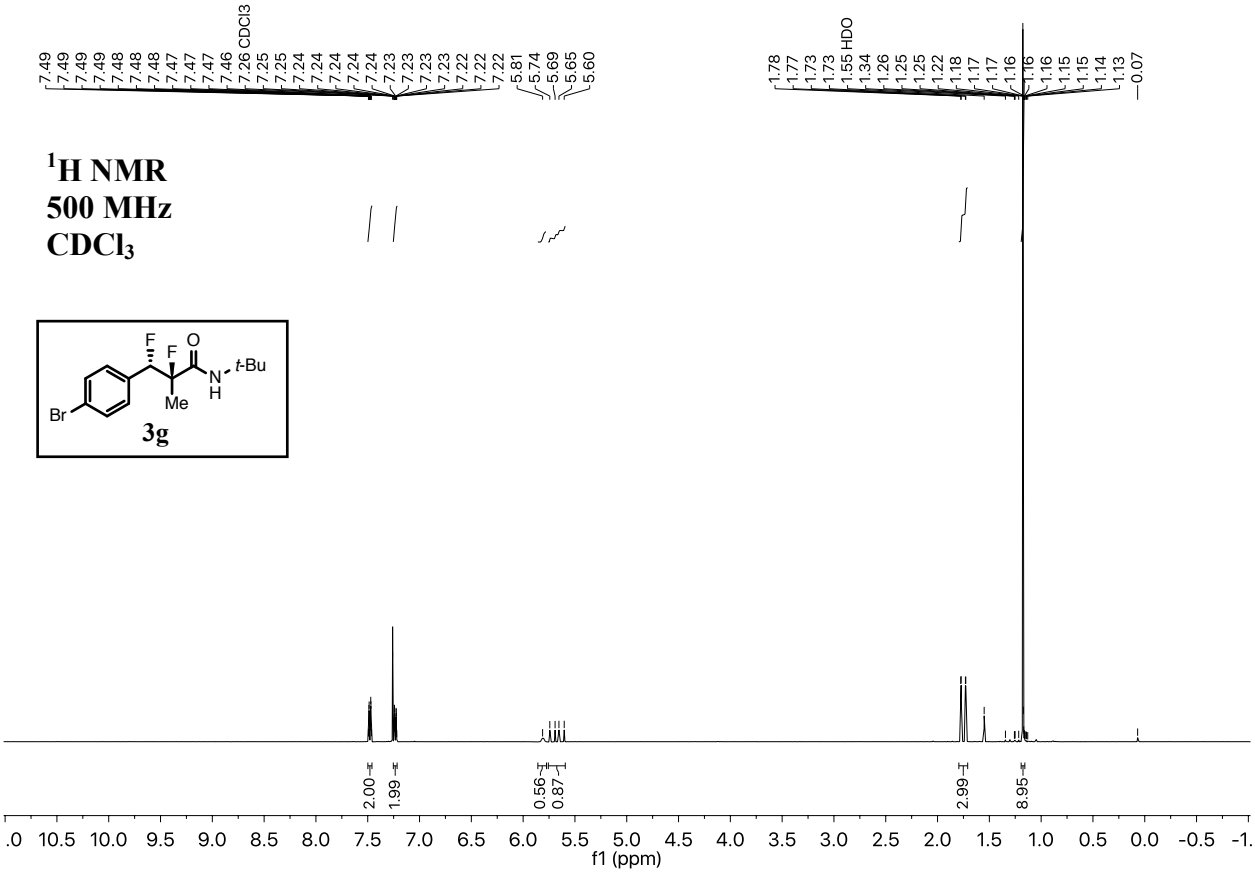
169.41
169.42
169.42
169.44
169.45
169.46
169.47
169.49
169.50
169.52
196.19
196.21
196.28
196.30
19F NMR
470.4 MHz
CDCl3
-169.30
-169.40
-169.50
-169.60
f1 (ppm)
-196.20
-196.30
-196.40
f1 (ppm)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-28
f1 (ppm)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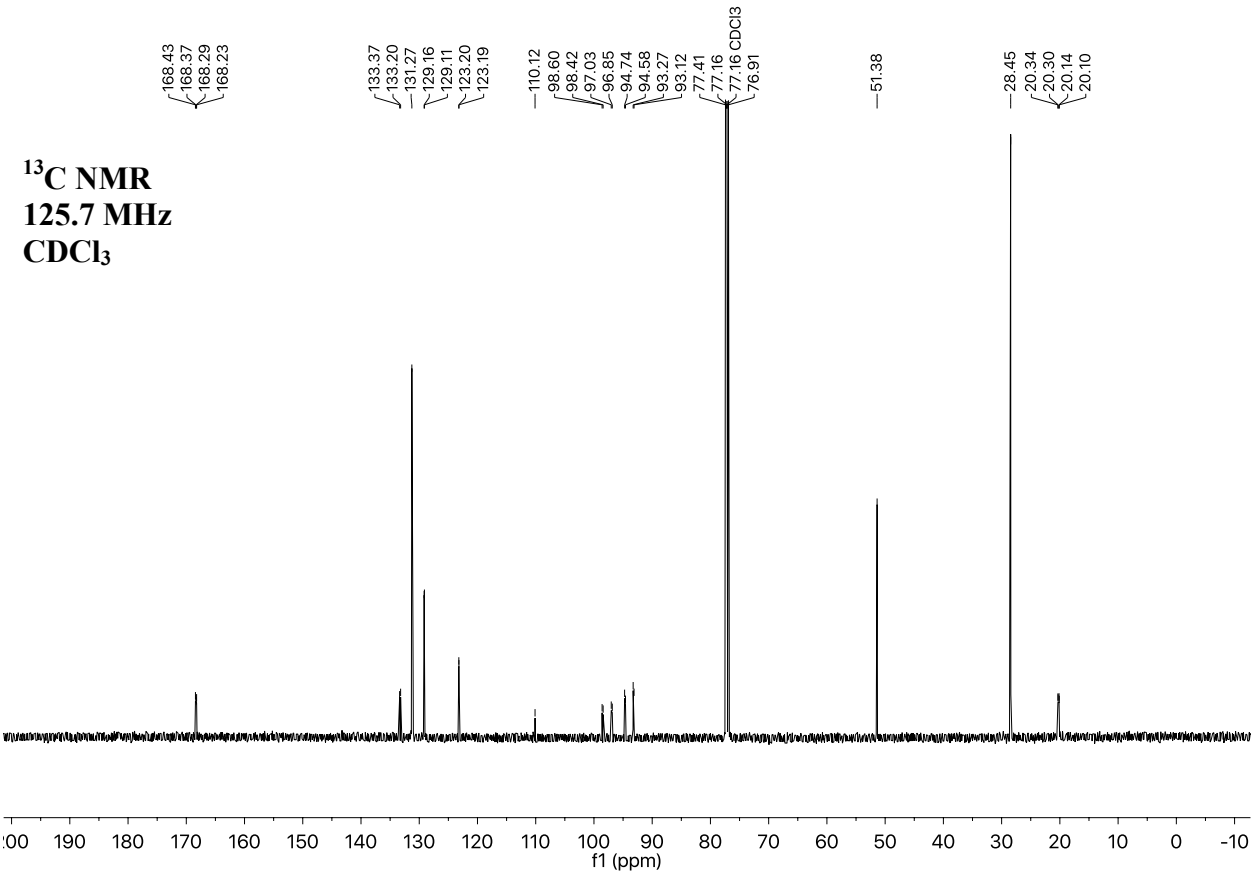
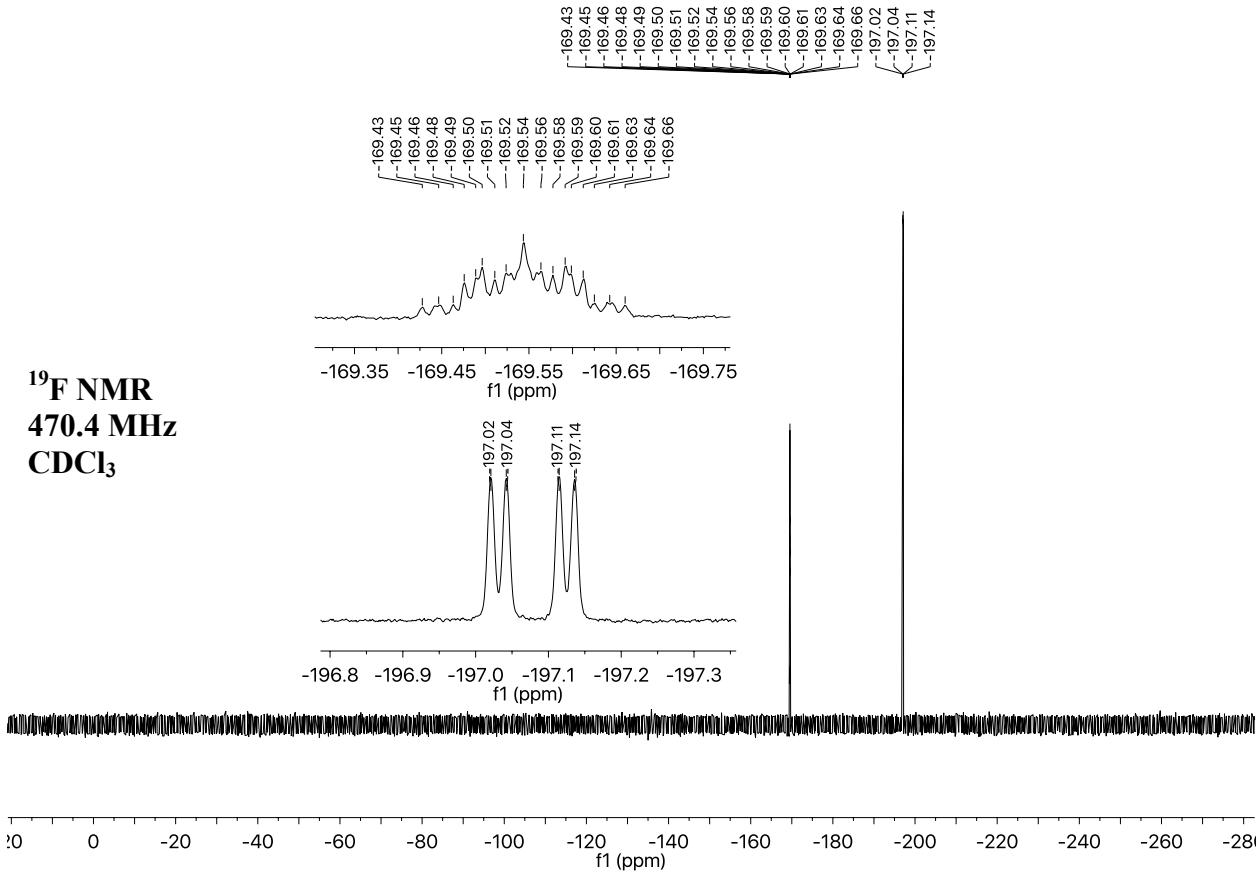
5.81 5.74 5.69 5.65 5.60
1.78 1.77 1.73 1.73 1.55 HDO 1.34 1.26 1.25 1.25 1.22 1.18 1.17 1.17 1.16 1.16 1.16 1.15 1.15 1.14 1.13 0.07
1H NMR
500 MHz
CDCl3
F F O
N t-Bu
H
Me
Br
3g
2.00 1.99 0.56 0.87 2.99 8.95
f1 (ppm)


168.43 168.37 168.29 168.23
133.37 133.20 131.27 129.16 129.11 123.20 123.19
110.12 98.60 98.42 97.03 96.85 94.74 94.58 93.27 93.12 77.41 77.16 77.16 CDCl3 76.91
51.38
28.45 20.34 20.30 20.14 20.10
13C NMR
125.7 MHz
CDCl3
f1 (ppm)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169.52
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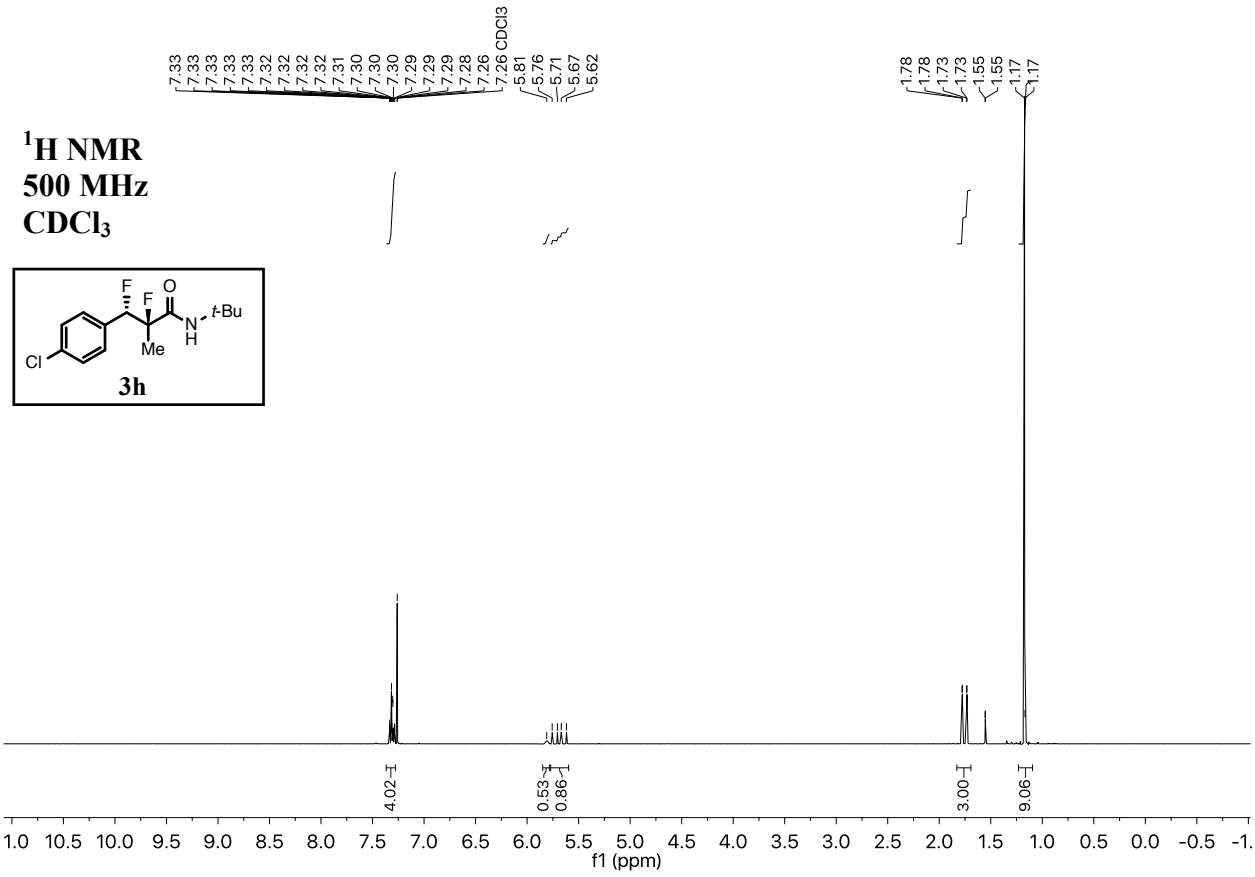
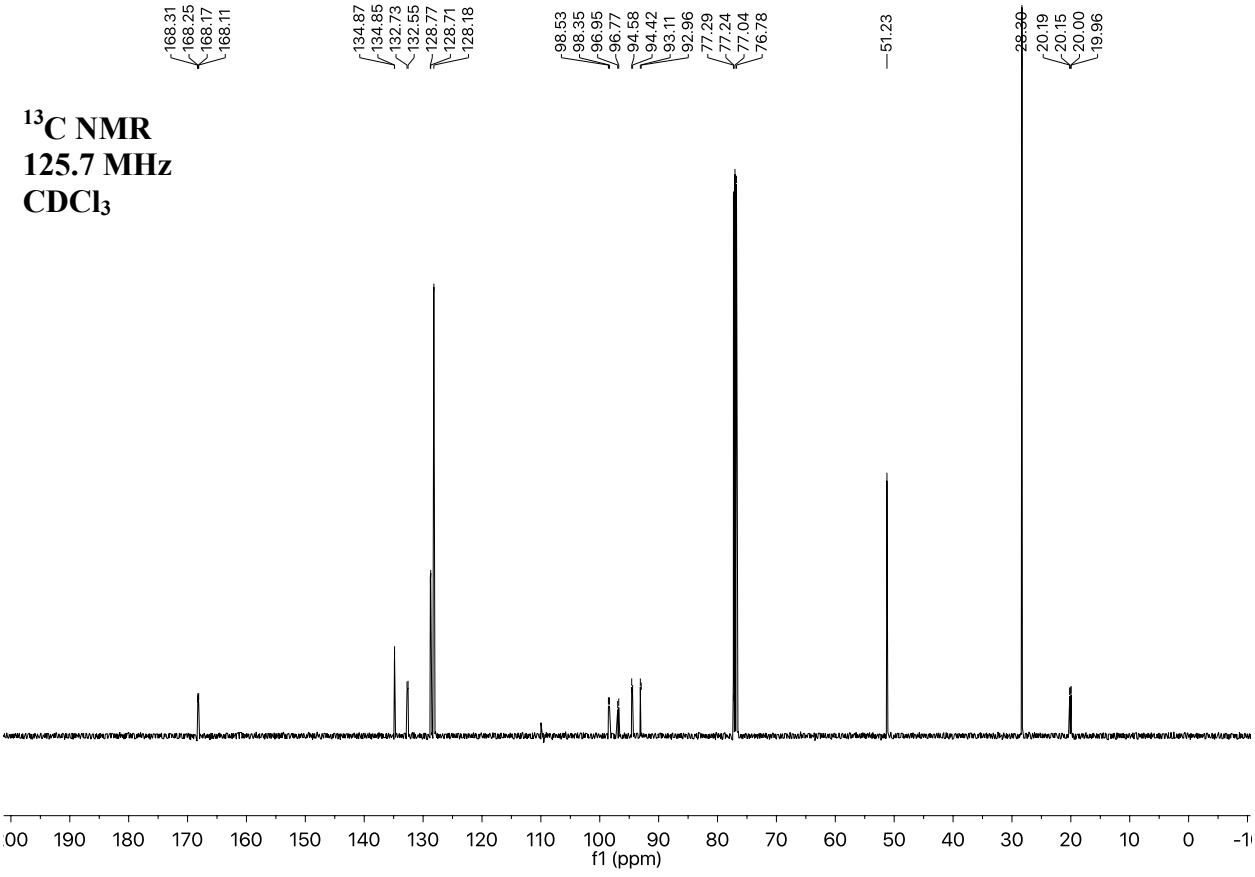
169.58
169.59
169.60
169.61
169.63
169.64
169.66
197.02
197.04
197.11
197.14
-169.35 -169.45 -169.55 -169.65 -169.75
f1 (ppm)
-196.8 -196.9 -197.0 -197.1 -197.2 -197.3
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

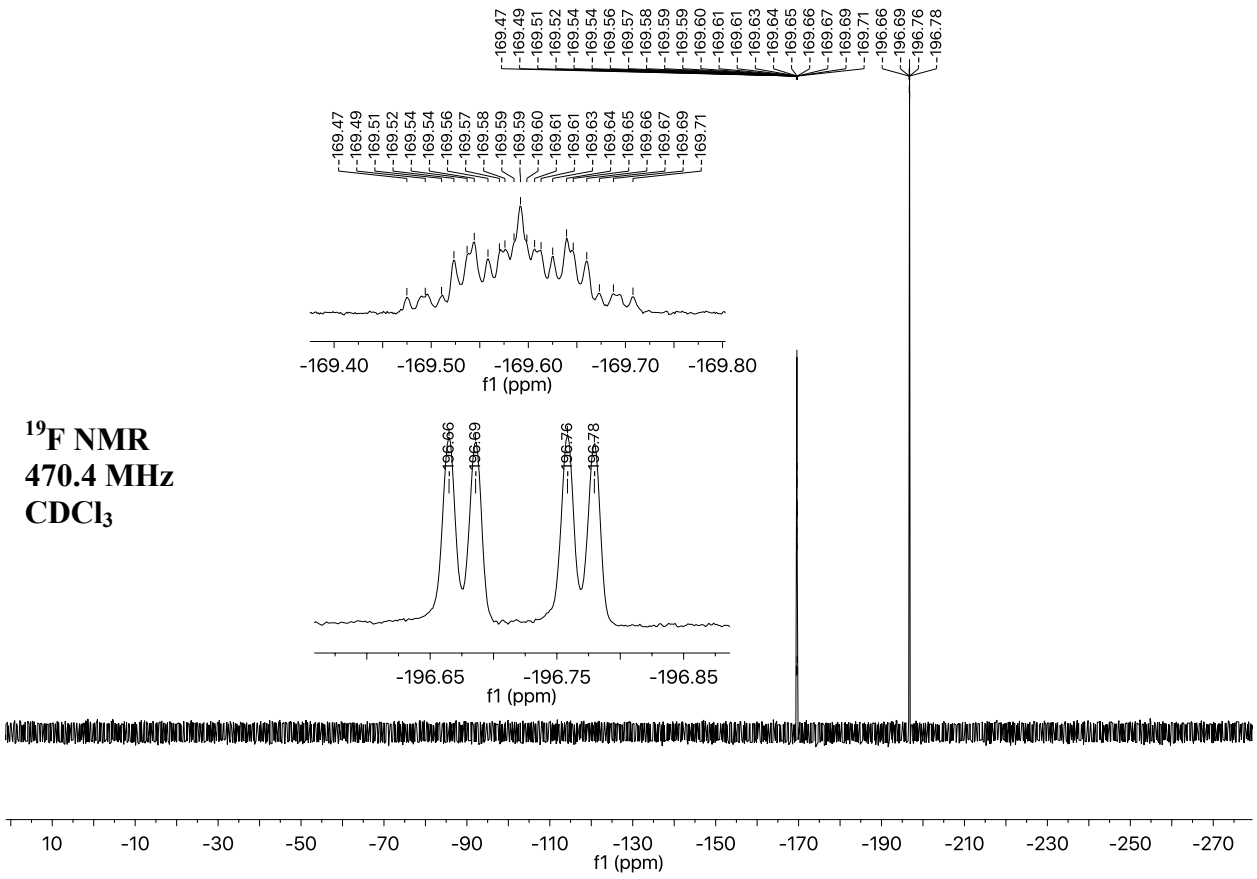


^{1}H NMR
500 MHz
$CDCl_3$

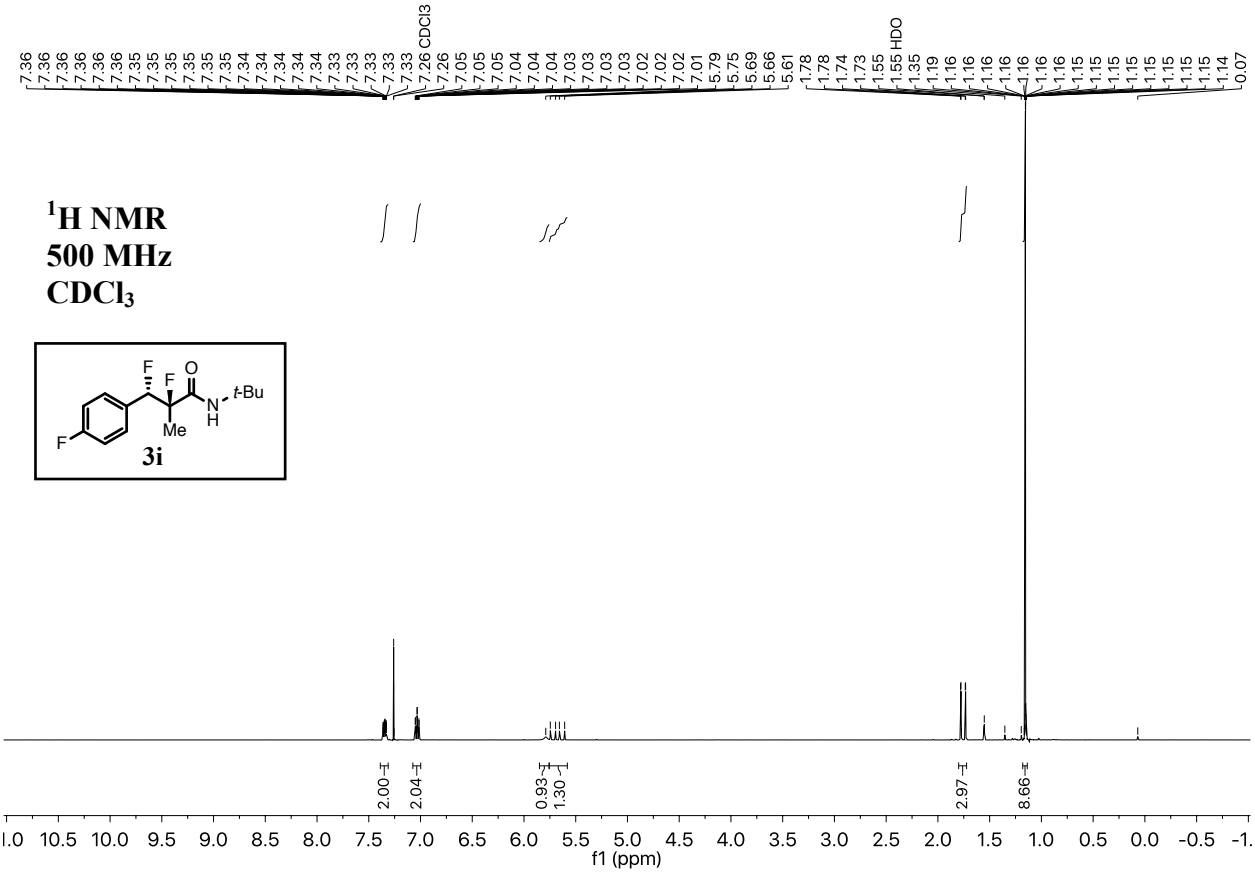
3h

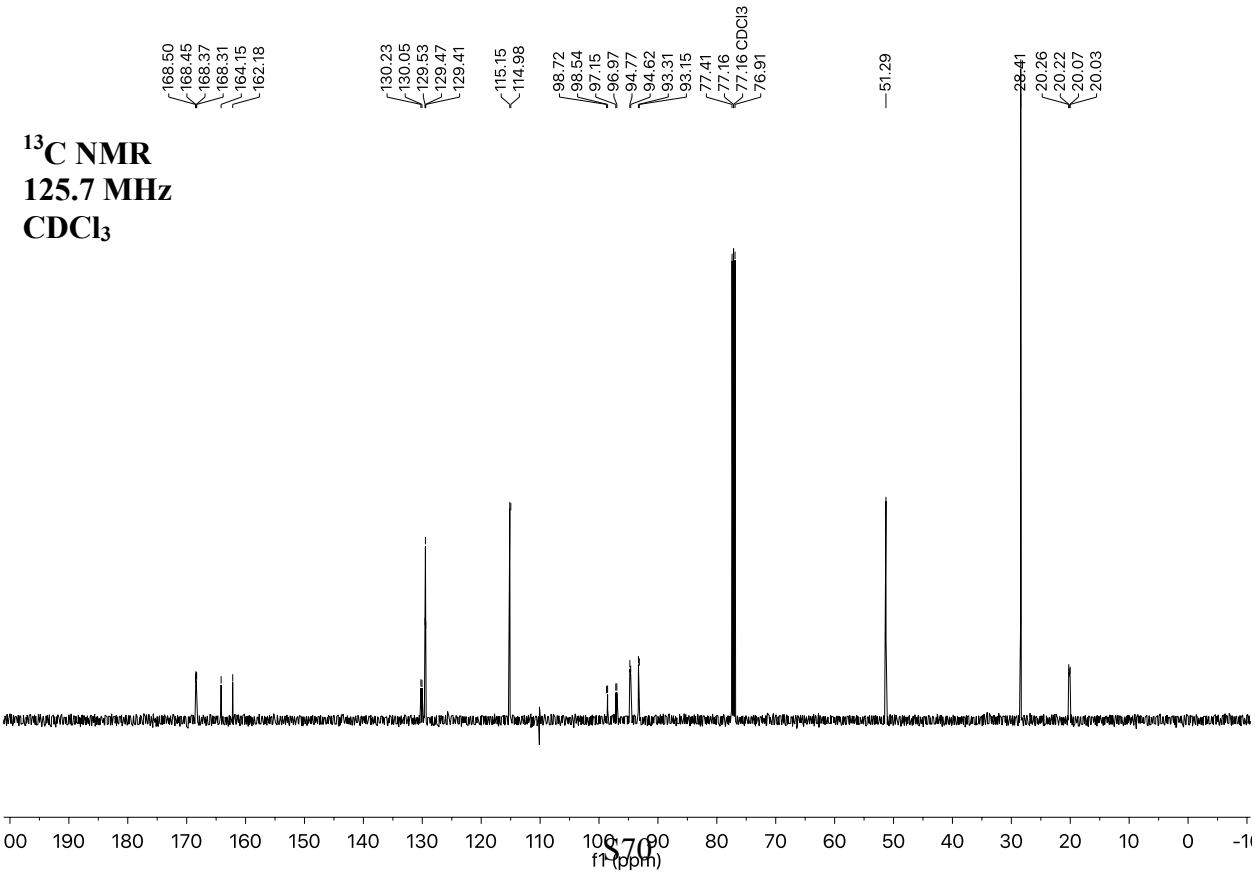


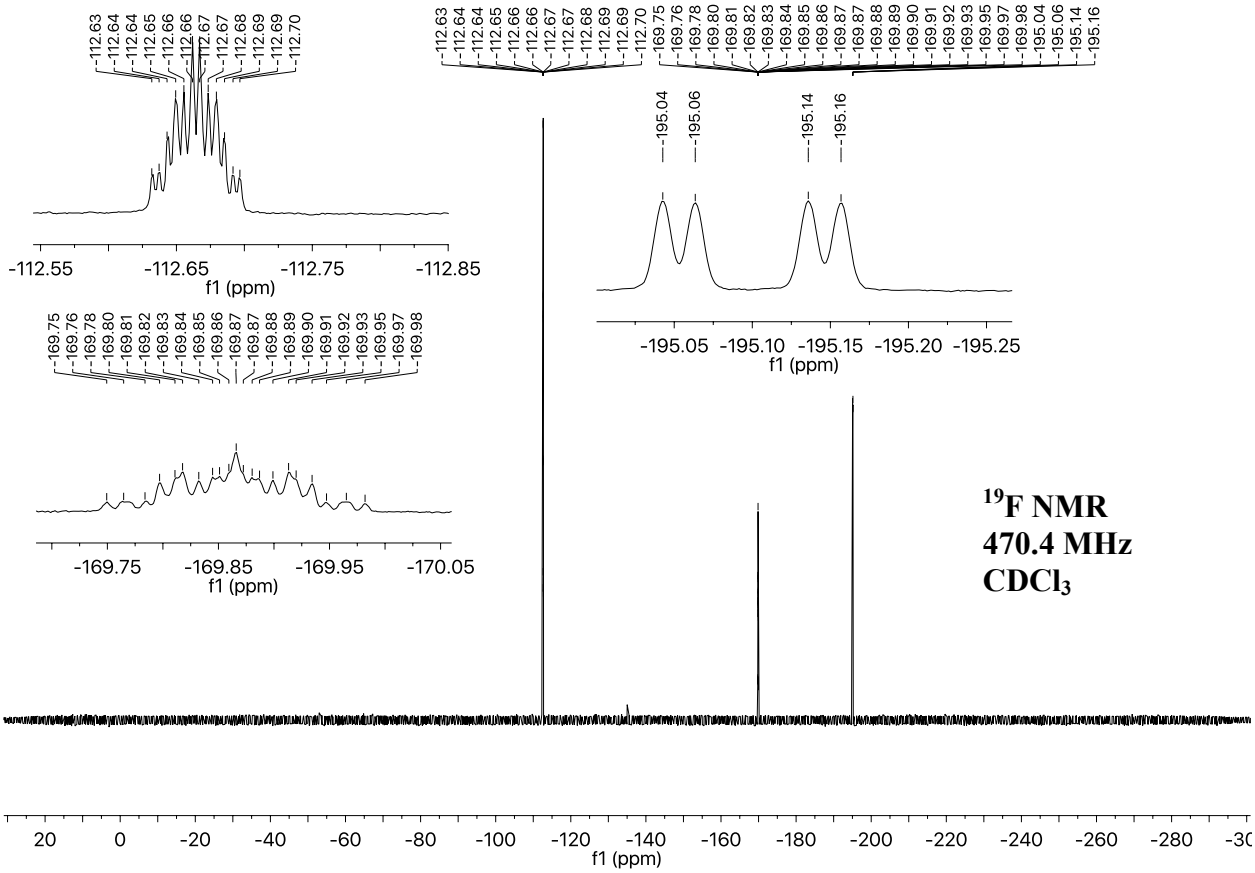
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$


7.36 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.26 CDCl3 7.26 7.05 7.05 7.04 7.04 7.04 7.03 7.03 7.03 7.02 7.02 7.02 7.01 5.79 5.75 5.69 5.66 5.61 1.78 1.78 1.74 1.73 1.55 1.55 HDO 1.35 1.19 1.16 1.16 1.16 1.16 1.16 1.16 1.15 1.15 1.15 1.15 1.15 1.15 1.15 1.14 0.07
1H NMR
500 MHz
CDCl3
F
F
O
N
H
t-Bu
Me
F
3i
2.00
2.04
0.93
1.30
2.97
8.66
f1 (ppm)


168.50 168.45 168.37 168.31 164.15 162.18 130.23 130.05 129.53 129.47 129.41 115.15 114.98 98.72 98.54 97.15 96.97 94.77 94.62 93.31 93.15 77.41 77.16 77.16 CDCl3 76.91 51.29 28.41 20.26 20.22 20.07 20.03
13C NMR
125.7 MHz
CDCl3
f1 (ppm)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-112.69
-112.70
-112.55
-112.65
-112.75
-112.85
f1 (ppm)
-169.75
-169.76
-169.78
-169.80
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-169.93
-169.95
-169.97
-169.98
-169.75
-169.85
-169.95
-170.05
f1 (ppm)
-112.63
-112.64
-112.64
-112.65
-112.66
-112.66
-112.67
-112.67
-112.68
-112.69
-112.69
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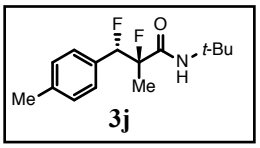
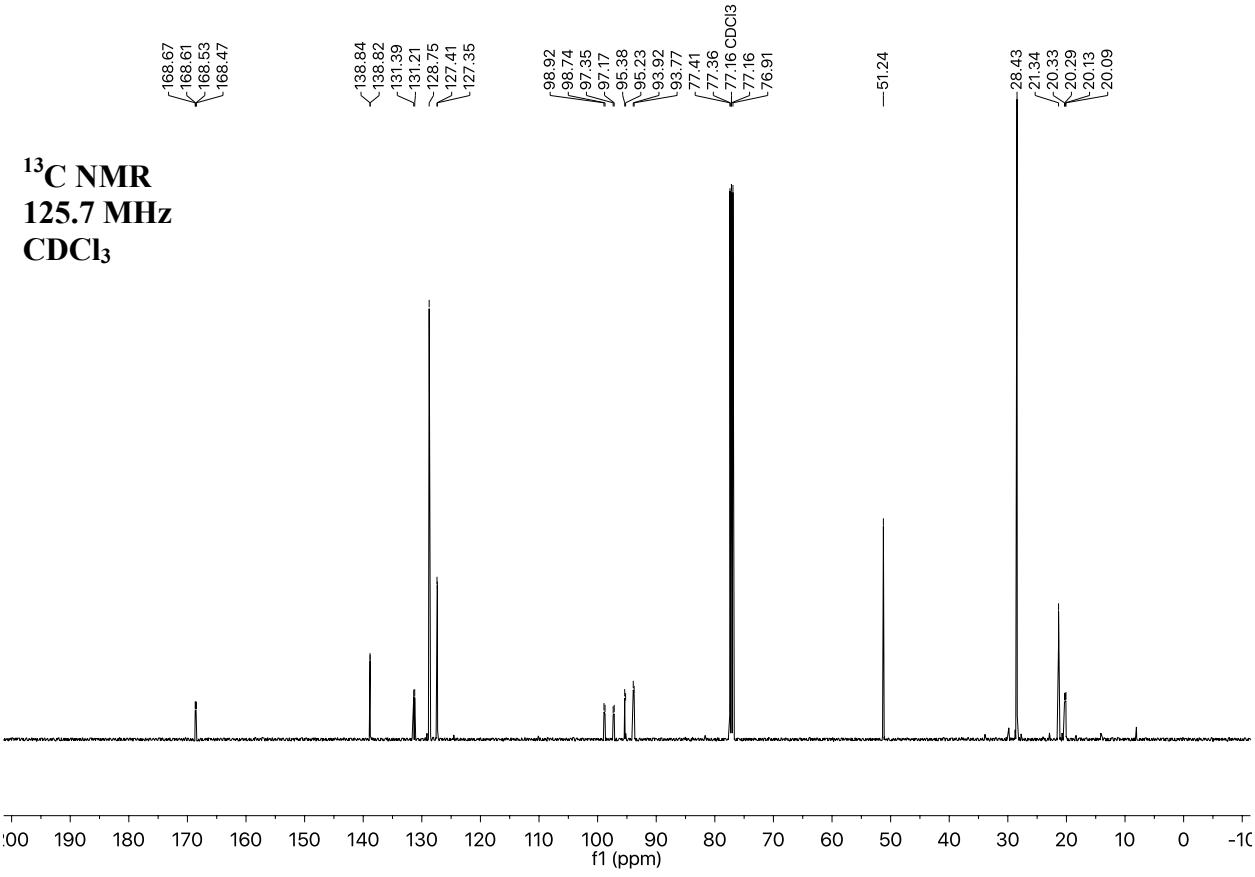
-169.95
-169.97
-169.98
-195.04
-195.06
-195.14
-195.16
-195.05
-195.10
-195.15
-195.20
-195.25
f1 (ppm)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)
19F NMR
470.4 MHz
CDCl3

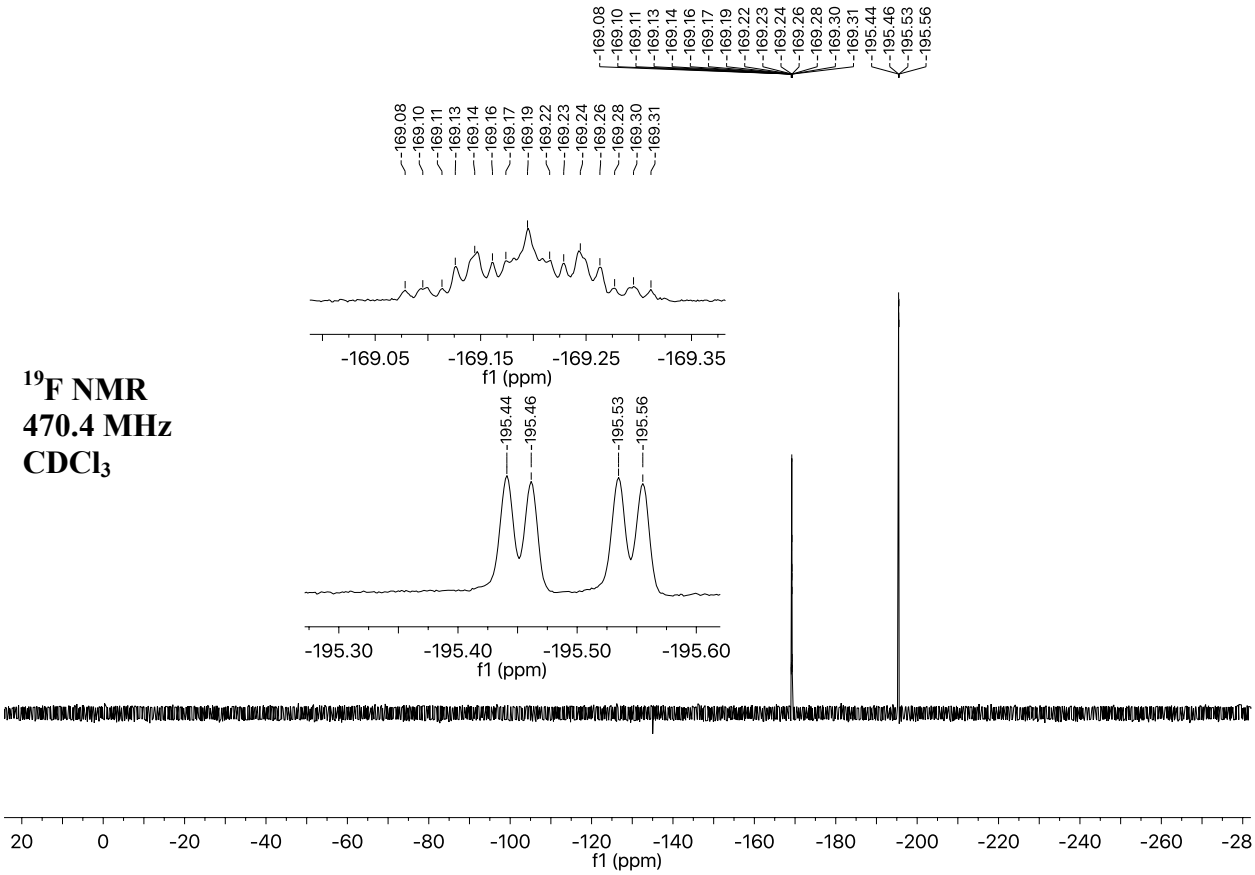
^{1}H NMR
500 MHz
$CDCl_3$



3j

^{13}C NMR
125.7 MHz
$CDCl_3$

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169.17
169.19
169.22
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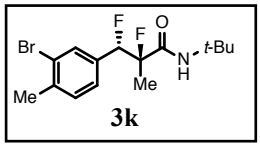
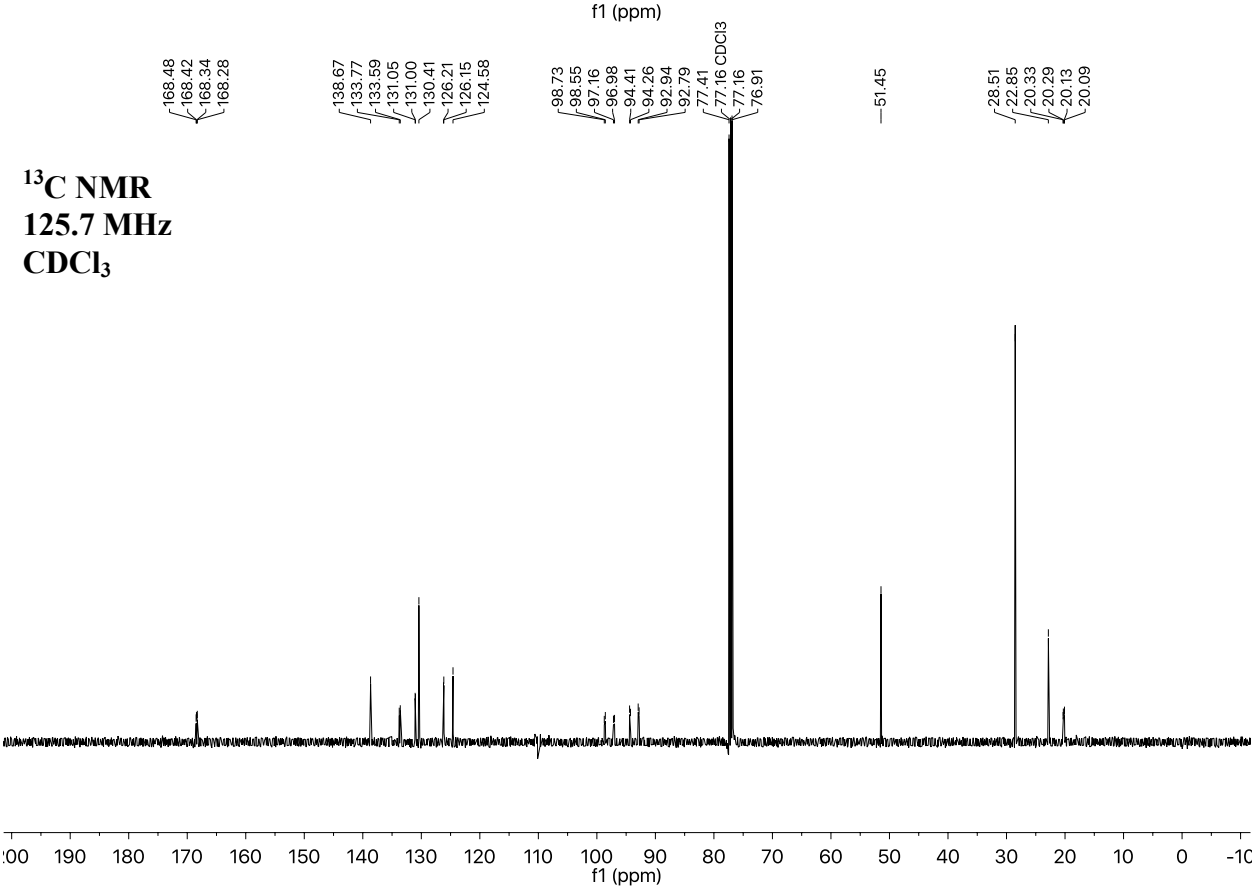
169.24
169.26
169.28
169.30
169.31
195.44
195.46
195.53
195.56
-169.05
-169.15
-169.25
-169.35
f1 (ppm)
-195.30
-195.40
-195.50
-195.60
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-28
f1 (ppm)

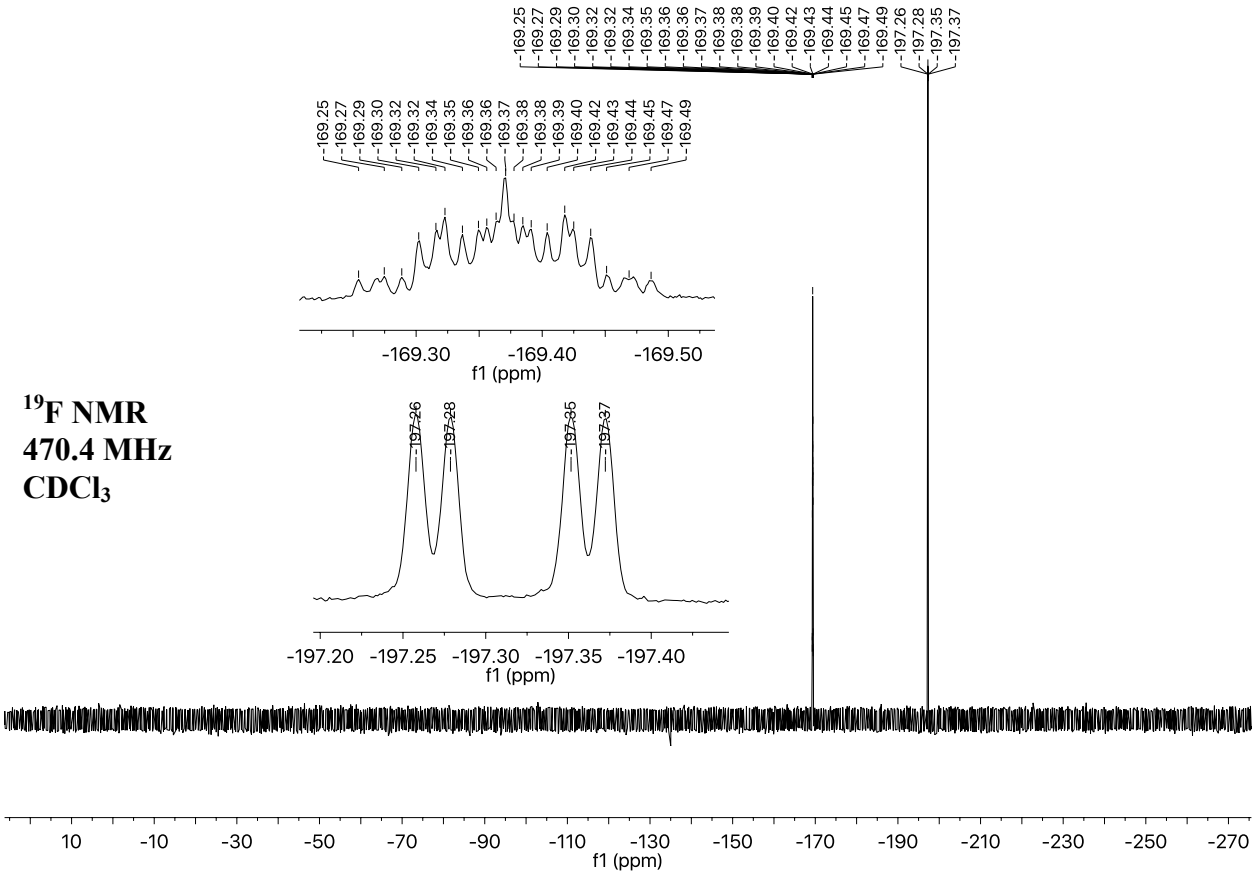
^{1}H NMR
500 MHz
$CDCl_3$

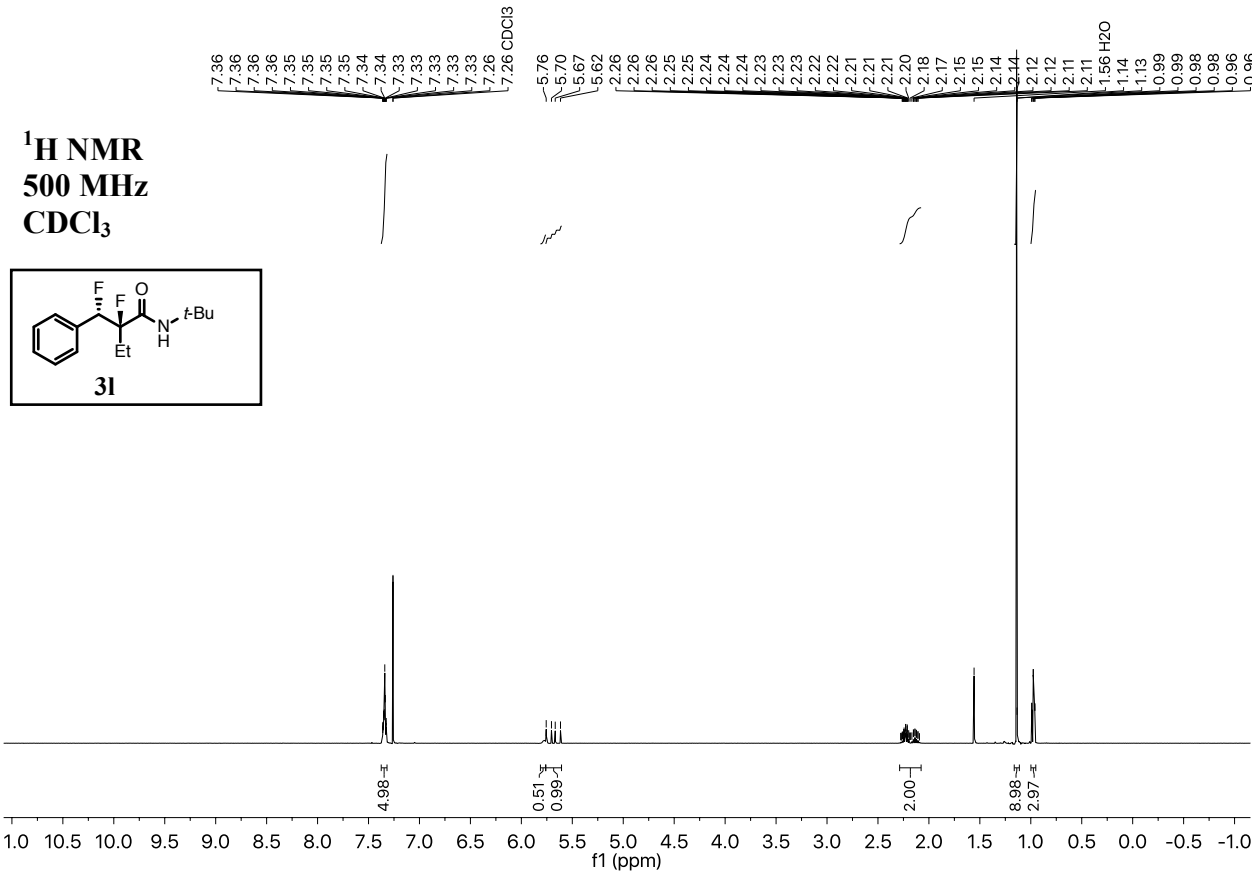


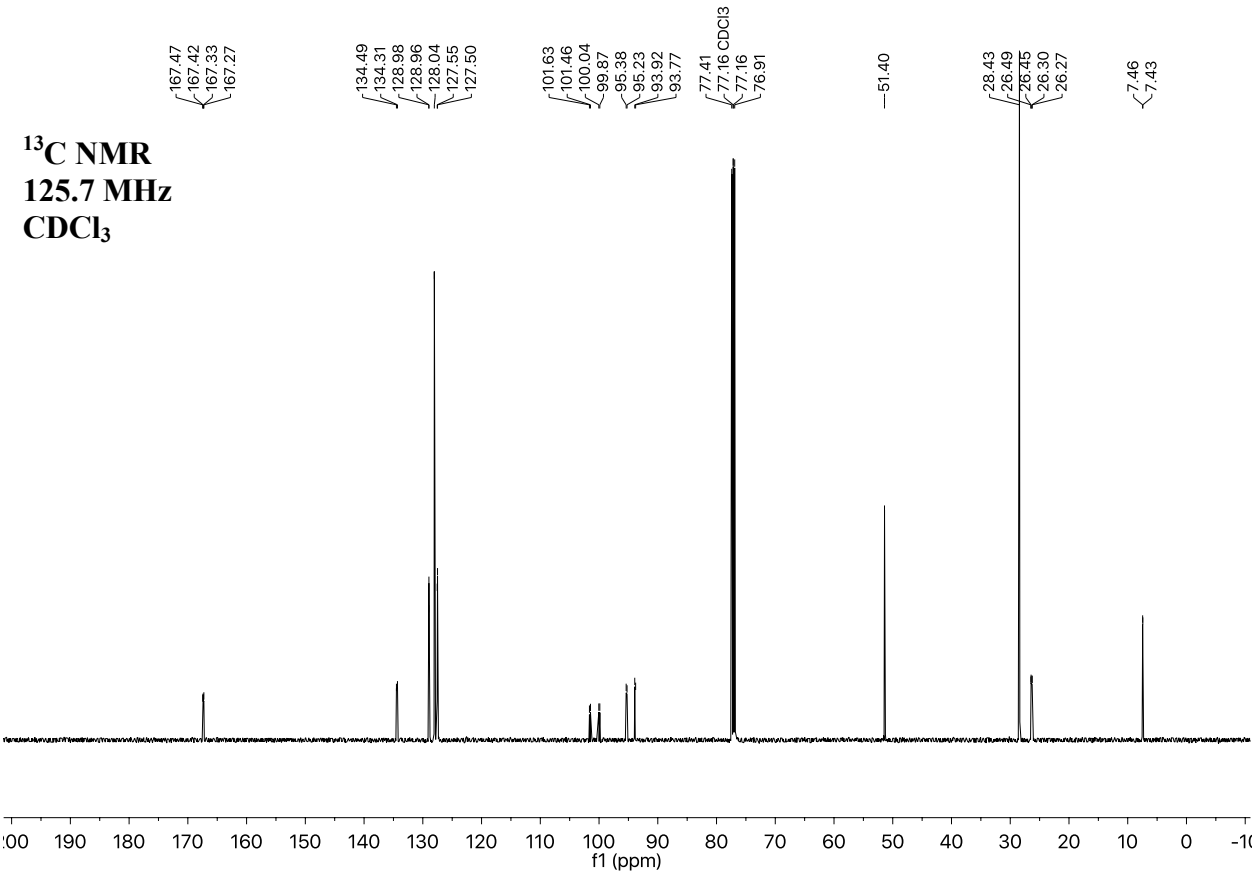
3k

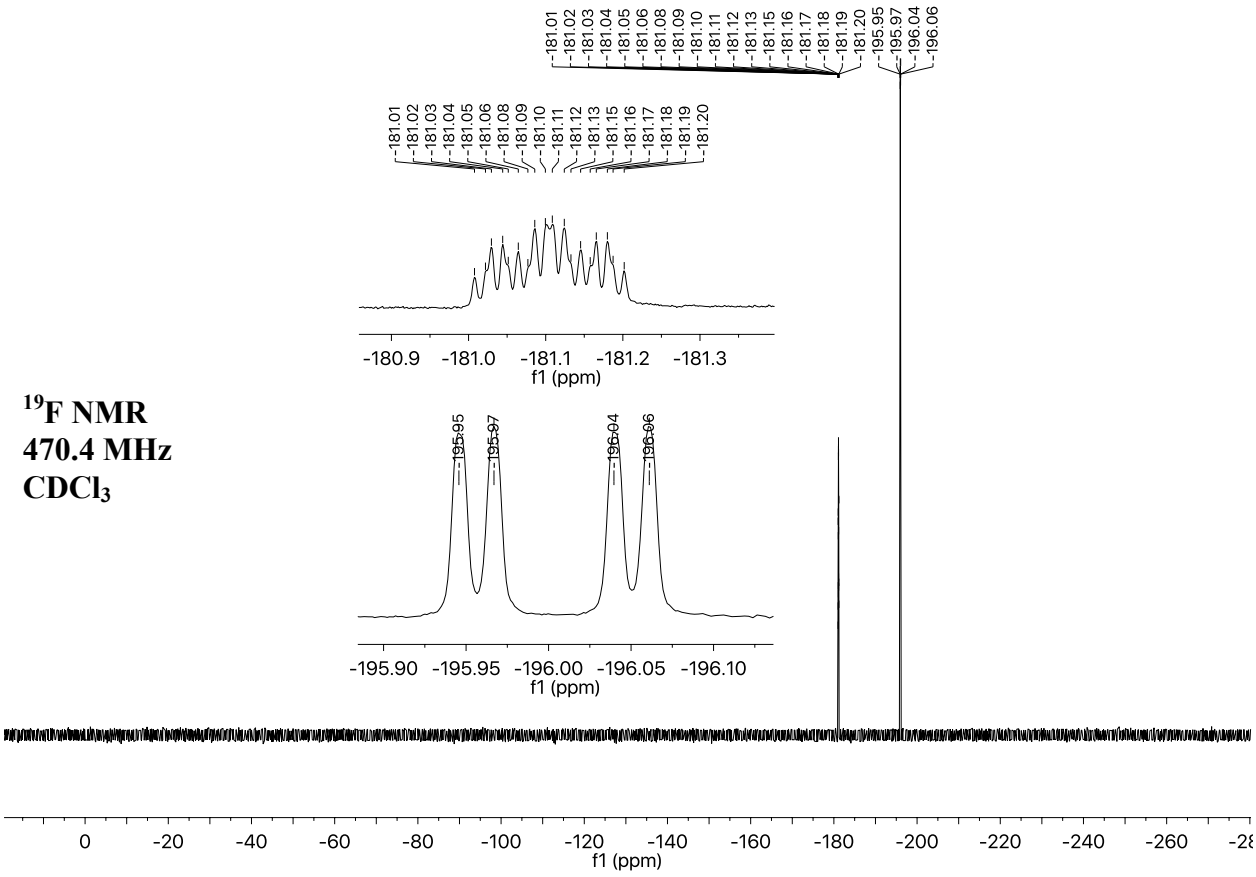
^{13}C NMR
125.7 MHz
$CDCl_3$



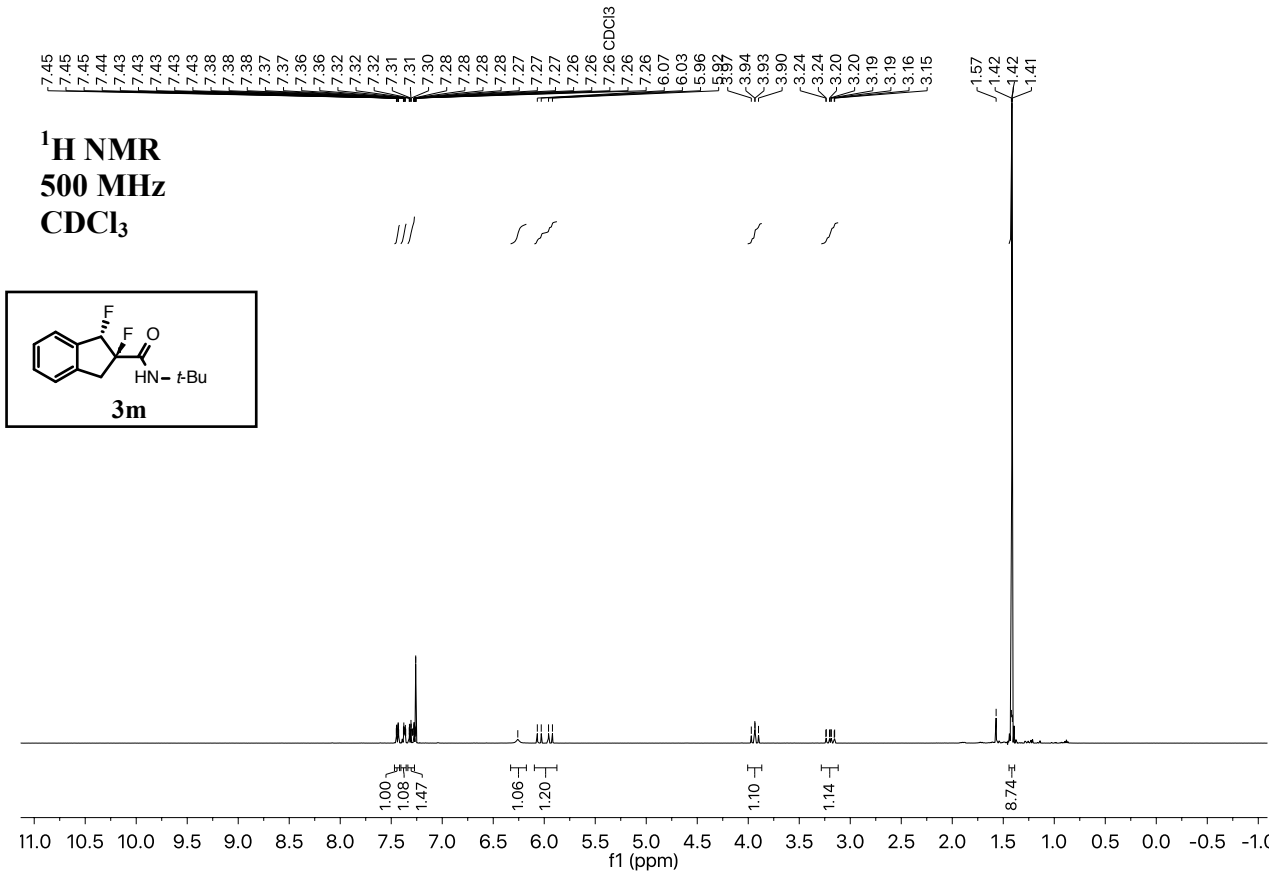

169.25
169.27
169.29
169.30
169.32
169.32
169.34
169.35
169.36
169.36
169.37
169.38
169.38
169.39
169.40
169.42
169.43
169.44
169.45
169.47
169.49
197.26
197.28
197.35
197.37
-169.30
-169.40
-169.50
f1 (ppm)
19F NMR
470.4 MHz
CDCl3
-197.20
-197.25
-197.30
-197.35
-197.40
f1 (ppm)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)

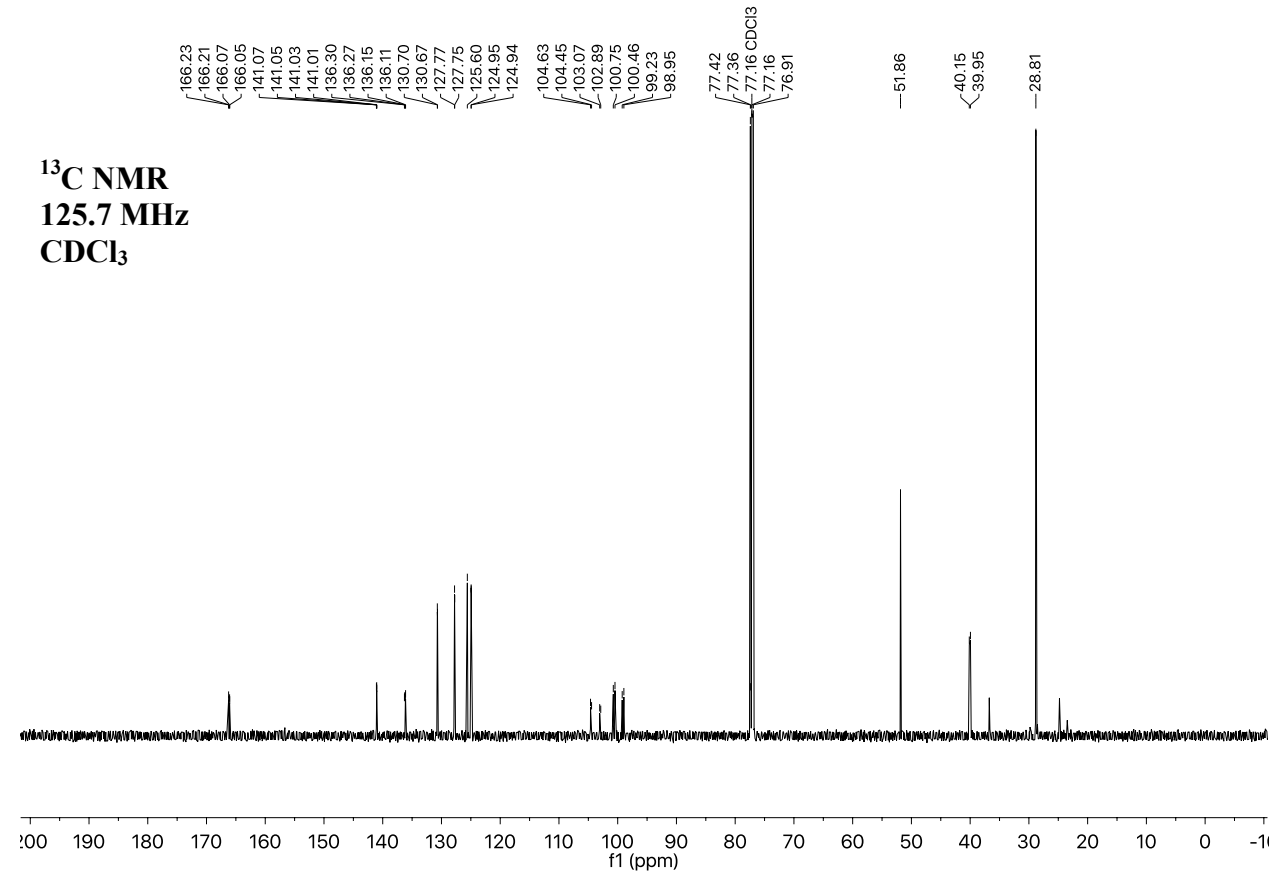

1H NMR
500 MHz
CDCl3
F
F
O
N
H
t-Bu
Et
3l
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.33
7.26
7.26 CDCl3
5.76
5.70
5.67
5.62
2.26
2.26
2.25
2.25
2.24
2.24
2.24
2.23
2.23
2.23
2.22
2.22
2.21
2.21
2.21
2.20
2.18
2.17
2.15
2.15
2.14
2.14
2.12
2.12
2.11
2.11
1.56 H2O
1.14
1.13
0.99
0.99
0.98
0.98
0.96
4.98
0.51
0.99
2.00
8.98
2.97
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

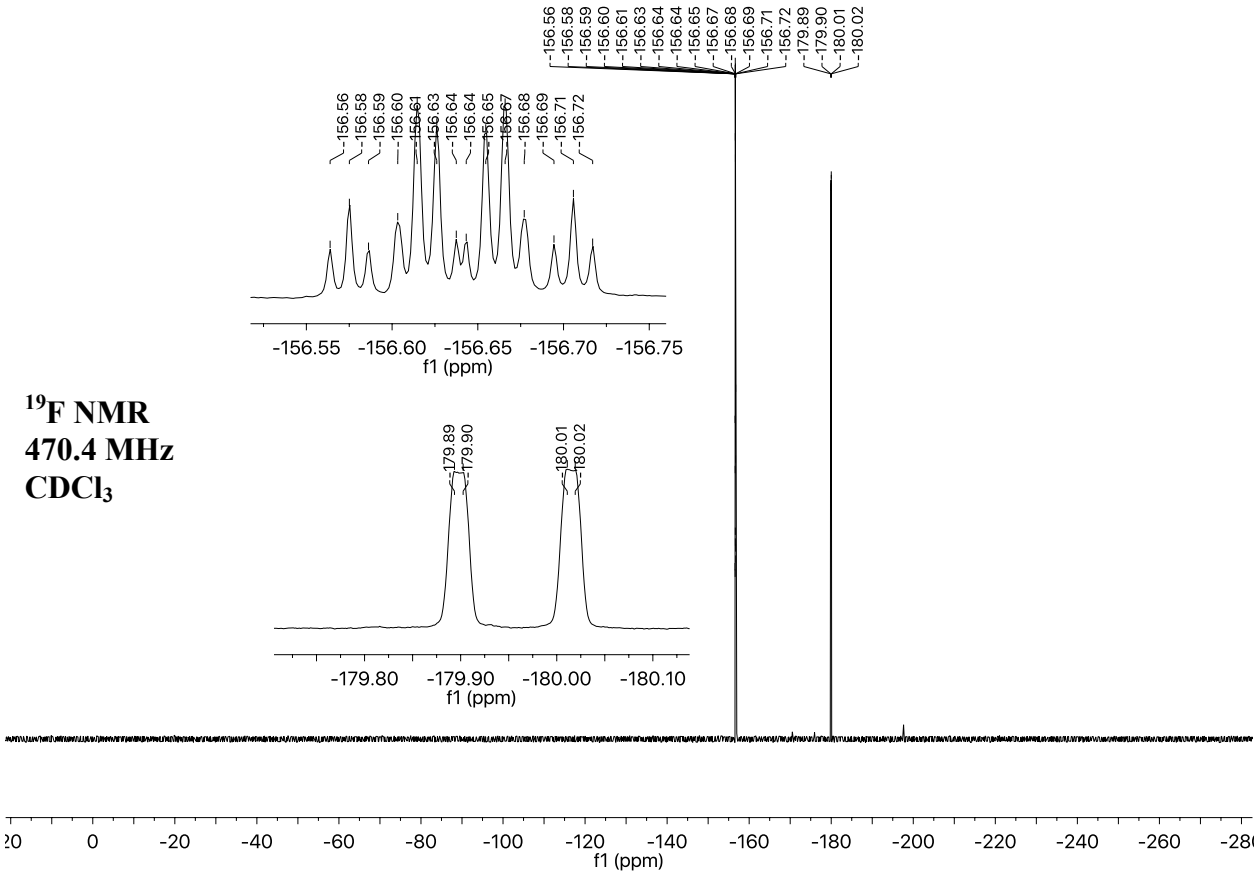

13C NMR
125.7 MHz
CDCl3
167.47
167.42
167.33
167.27
134.49
134.31
128.98
128.96
128.04
127.55
127.50
101.63
101.46
100.04
99.87
95.38
95.23
93.92
93.77
77.41
77.16 CDCl3
77.16
76.91
51.40
28.43
26.49
26.45
26.30
26.27
7.46
7.43
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{19}F NMR
470.4 MHz
$CDCl_3$

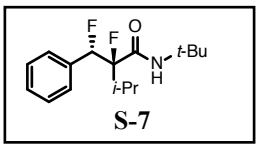

7.45 7.45 7.45 7.44 7.43 7.43 7.43 7.43 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.32 7.32 7.32 7.31 7.31 7.30 7.28 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26 CDCl3 7.26 7.26 6.07 6.03 5.96 5.92 3.97 3.94 3.93 3.90 3.24 3.24 3.20 3.20 3.19 3.19 3.16 3.15 1.57 1.42 1.42 1.41
1H NMR
500 MHz
CDCl3
F
F O
HN– t-Bu
3m
1.00 1.08 1.47 1.06 1.20 1.10 1.14 8.74
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.23 166.21 166.07 166.05 141.07 141.05 141.03 141.01 136.30 136.27 136.15 136.11 130.70 130.67 127.77 127.75 125.60 124.95 124.94 104.63 104.45 103.07 102.89 100.75 100.46 99.23 98.95 77.42 77.36 77.16 CDCl3 77.16 76.91 51.86 40.15 39.95 28.81
13C NMR
125.7 MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



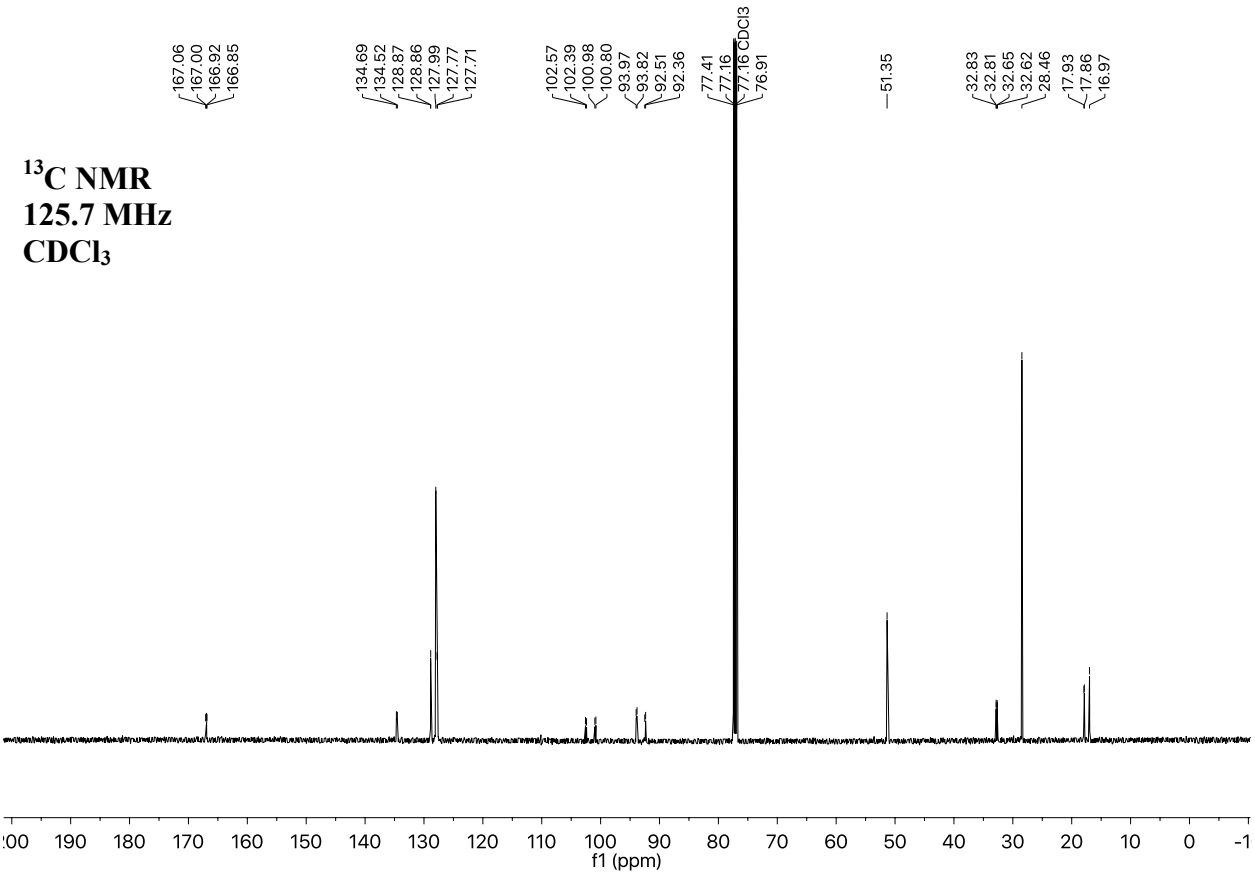
^{19}F NMR
470.4 MHz
$CDCl_3$

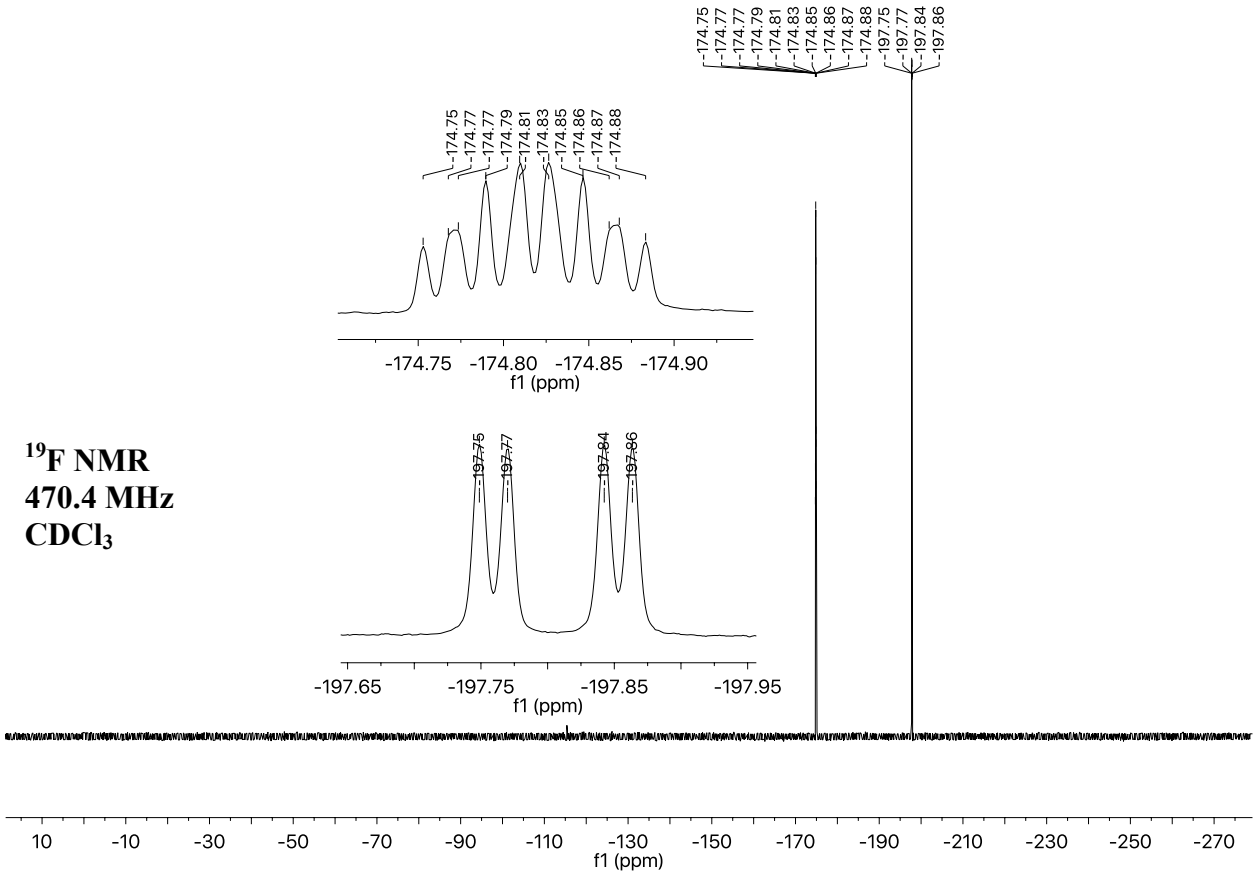
^{1}H NMR
500 MHz
$CDCl_3$



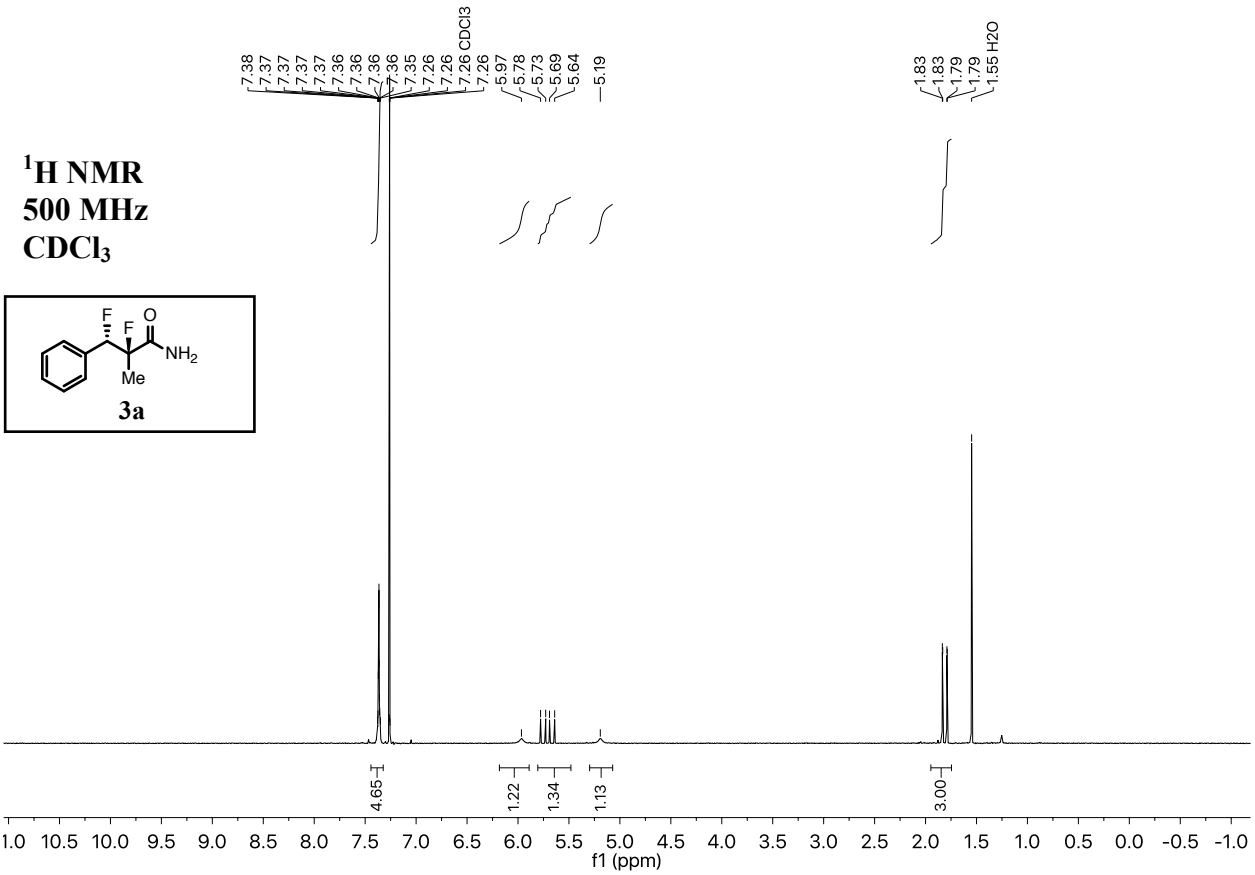
S-7

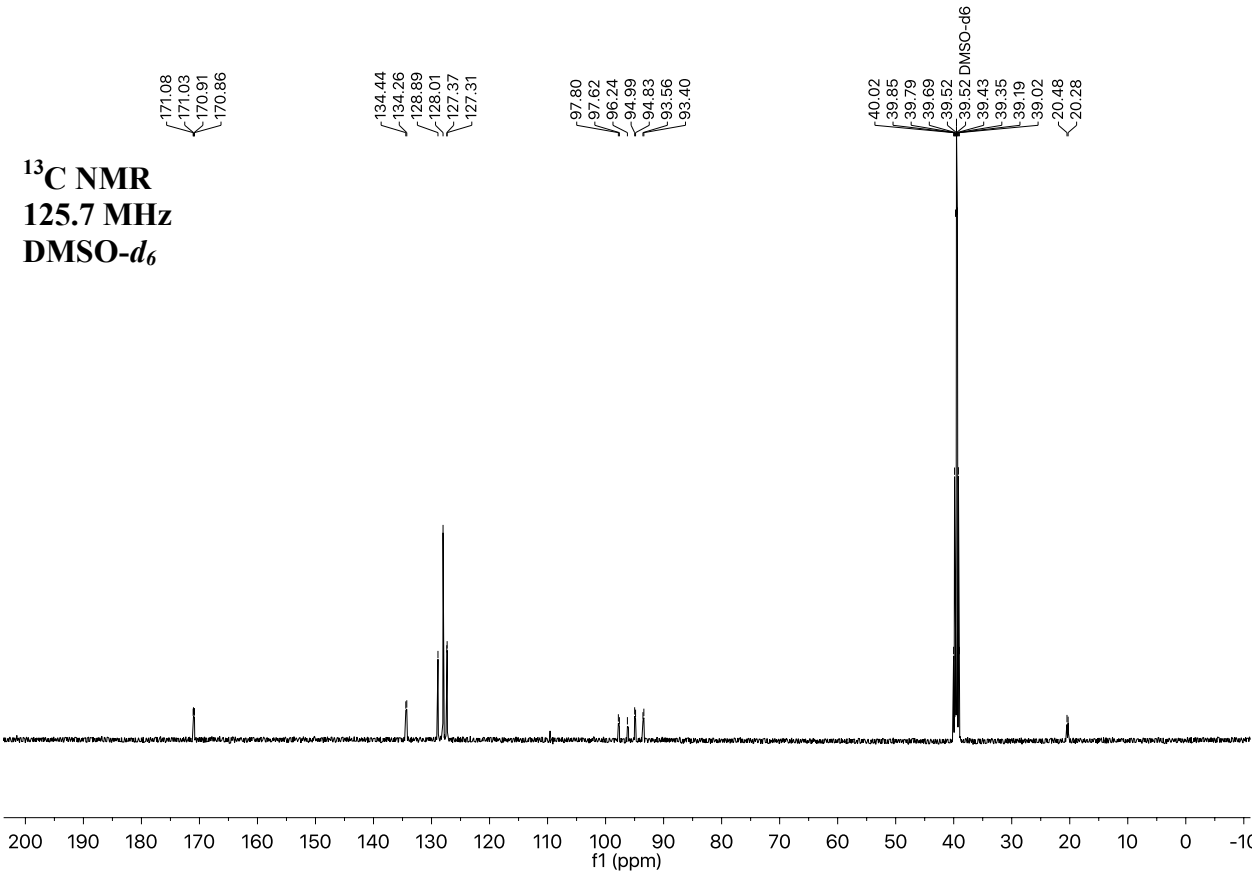
^{13}C NMR
125.7 MHz
$CDCl_3$

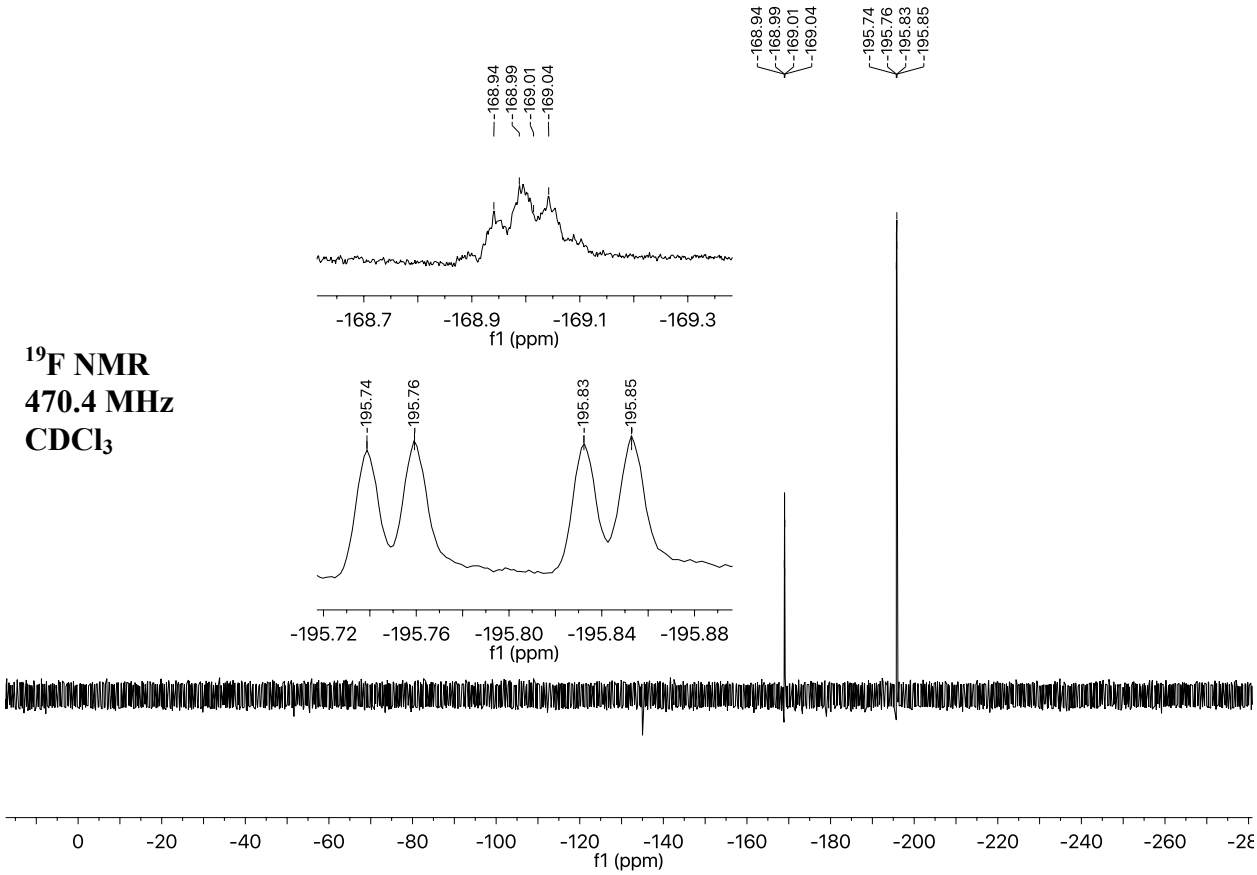




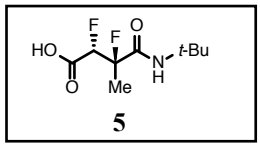
^{19}F NMR
470.4 MHz
$CDCl_3$


7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.26
7.26
7.26 CDCl3
7.26
5.97
5.78
5.73
5.69
5.64
5.19
1.83
1.83
1.79
1.79
1.55 H2O
1H NMR
500 MHz
CDCl3
F
F
O
NH2
Me
3a
4.65
1.22
1.34
1.13
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


171.08
171.03
170.91
170.86
134.44
134.26
128.89
128.01
127.37
127.31
97.80
97.62
96.24
94.99
94.83
93.56
93.40
40.02
39.85
39.79
39.69
39.52
39.52 DMSO-d6
39.43
39.35
39.19
39.02
20.48
20.28
13C NMR
125.7 MHz
DMSO-d6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

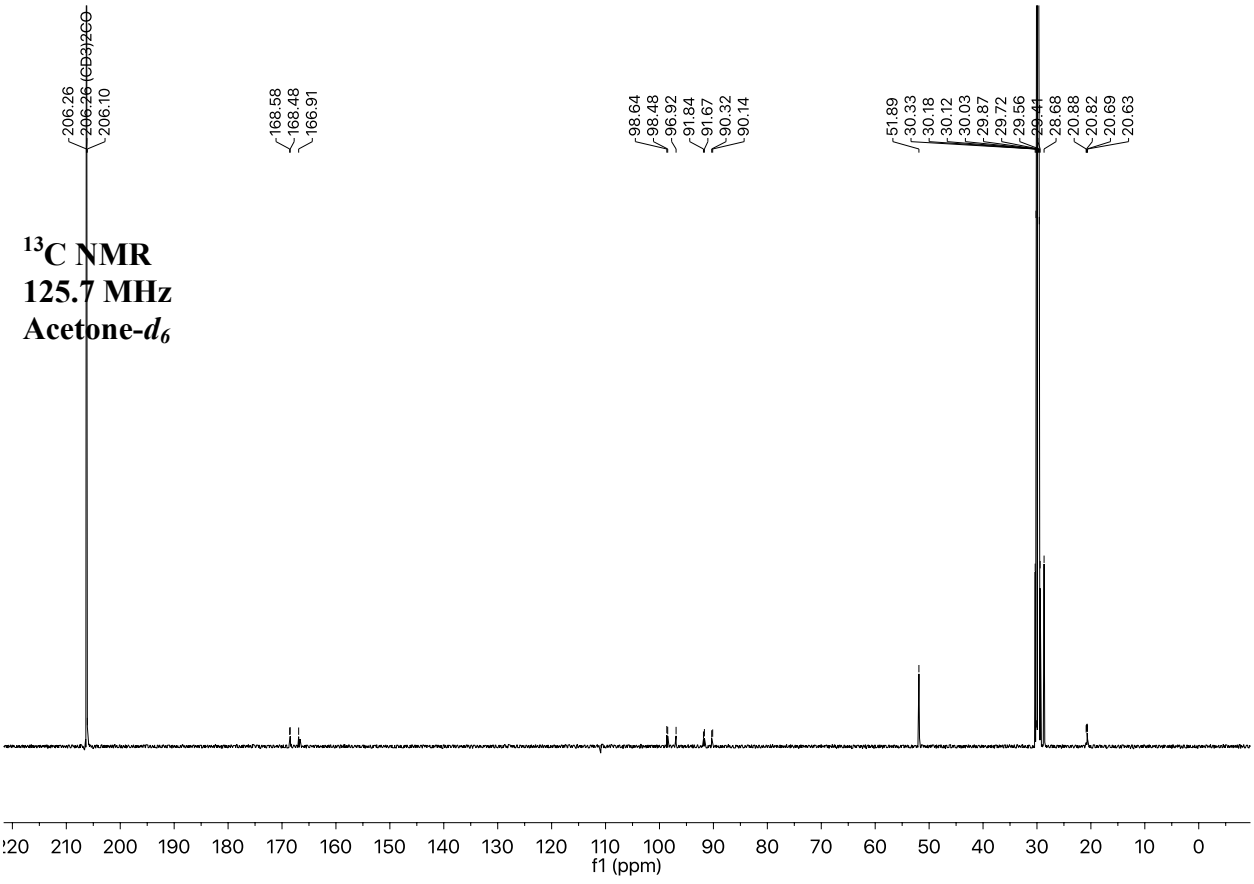

19F NMR
470.4 MHz
CDCl3
-168.94
-168.99
-169.01
-169.04
-195.74
-195.76
-195.83
-195.85
-168.7
-168.9
-169.1
-169.3
f1 (ppm)
-195.72
-195.76
-195.80
-195.84
-195.88
f1 (ppm)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

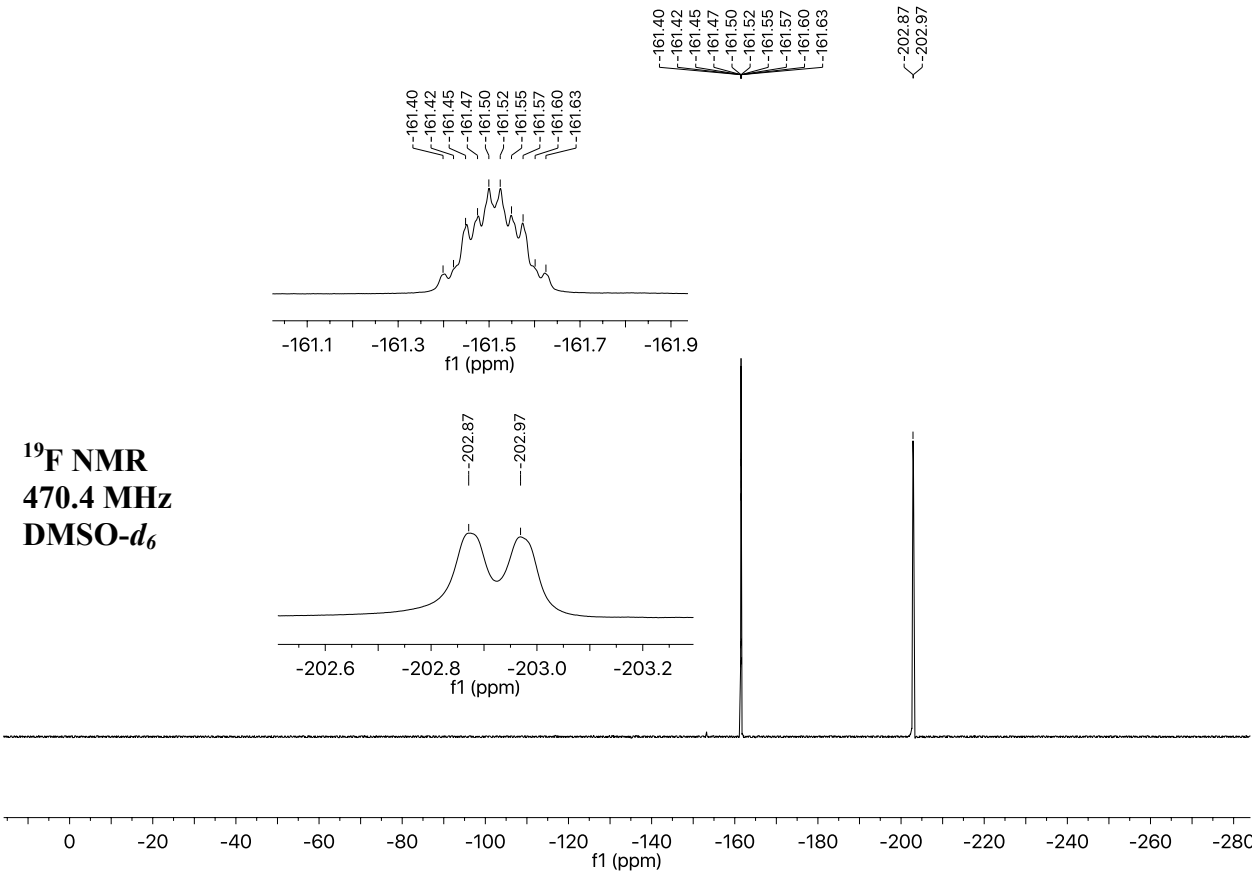
^{1}H NMR
500 MHz
$CDCl_3$



5

^{13}C NMR
125.7 MHz
Acetone-*d_6*





^{19}F NMR
470.4 MHz
DMSO-*d*$_6$