Eliminative Deoxofluorination using XtalFluor-E: A One-Step Synthesis of Monofluoroalkenes From Cyclohexanone Derivatives

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1. General information

The following includes additional optimization results, general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. All reactions were carried out under an argon atmosphere with dry solvents. Et_2O, THF, CH_3CN, CH_2Cl_2 and toluene were purified using a Vacuum Atmospheres Inc. Solvent Purification System. All other commercially available compounds were used as received. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Silicycle silica gel 60 Å F254 TLC plates, and visualized under UV or by staining with potassium permanganate. Flash column chromatography was carried out on Silicycle silica gel 60 Å, 230–400 mesh. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ at ambient temperature using

Agilent DD2 500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield of tetramethylsilane and are respectively referenced to tetramethylsilane (δ = 0.00 ppm) and residual solvent (δ = 77.16 ppm for $CDCl_3$). For ^{19}F NMR, $CFCl_3$ is used as the external standard. High-resolution mass spectra were obtained on a LC/MS–TOF Agilent 6210 using electrospray ionization (ESI). Infrared spectra were recorded using a Thermo Scientific Nicolet 380 FT-IR spectrometer. Melting points were recorded on a Stanford Research System OptiMelt capillary melting point apparatus and are uncorrected. Benzyl 4-oxopiperidine-1-carboxylate (**4a**),[1] *tert*-butyl 4-oxopiperidine-1-carboxylate (**4b**),[2] 1-tosyl-piperidin-4-one (**4c**),[3] 4-methyl-*N*-(4-oxo-cyclohexyl)benzenesulfonamide (**4g**),[4] 4-oxocyclohexyl benzoate (**4h**),[5] 4-(benzyloxy)-cyclohexan-1-one (**4i**),[6] and ethyl 3-oxocyclohexane-1-carboxylate (**4k**)[7] were prepared according to literature procedures.

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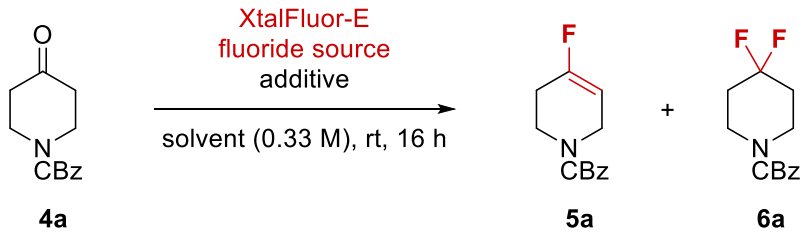
[1] Masse, J.; Langlois, N. *Heterocycles* **2009**, *77*, 417–432.
[2] Wang, Z.; Miller, E. J.; Scalia, S. J. *Org. Lett.* **2011**, *13*, 6540–6543.
[3] Jiang, Z.; Zhao, J.; Gao, B.; Chen, S.; Qu, W.; Mei, X.; Rui, C.; Ning, J.; She, D. *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, *188*, 1026–1037.
[4] Tsuchiya, D. ; Moriyama, K. ; Togo, H. *Synlett* **2011**, 2701–2704.
[5] Kamijo, S.; Amaoka, Y.; Inoue, M. *Synthesis* **2010**, 2475–2489.
[6] Dibble, D. J.; Ziller, J. W.; Woerpel, K. A. *J. Org. Chem.* **2011**, *76*, 7706–7719.
[7] De Lucca, G. V. *et al. J. Med. Chem.* **2016**, *59*, 7915–7935.

2. Additional optimization results

Table S1. Additional Optimization Results for the Eliminative Deoxofluorination of **4a** using XtalFluor-E



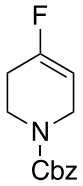
4a **5a** **6a**

entry	XtalFluor-E (equiv)	fluoride source (equiv)[a]	solvent	additive (equiv)	conversion (%)[b]	ratio **5a**/**6a**[b]	yield (%)[c]
1	1.5	$Et_3N{\cdot}2HF$ (3)	DCE[d]	-	100	1:3.2	14
2	1.5	$Et_3N{\cdot}2HF$ (3)	DME[e]	-	59	1:1.9	8
3	1.5	$Et_3N{\cdot}2HF$ (3)	TFE	-	48	-	0
4	1.5	$Et_3N{\cdot}2HF$ (3)	HFIP	-	31	-	0
5	3	$Et_3N{\cdot}2HF$ (3)	NMP		90	6:1	42
6	3	$Et_3N{\cdot}2HF$ (3)	DMPU	-	80	13:1	39
7[f]	3	$Et_3N{\cdot}2HF$ (3)	DMA	-	52	18:1	18
8	3	$Et_3N{\cdot}2HF$ (3)	CH_2Cl_2/DMA (9:1)	-	100	1:2.4	25
9	3	$Et_3N{\cdot}2HF$ (3)	CH_2Cl_2/DMA (1:1)	-	100	2.2:1	55
10	3	$Et_3N{\cdot}2HF$ (3)	CH_2Cl_2/DMA (1:9)	-	100	5.3:1	64
11	3	TBAF[g] (3)	DMA	-	97	-	0
12	3	$TBAF{\cdot}3H_2O$ (3)	DMA	-	71	-	0
13	3	DMPU·HF (3)[h]	DMA	-	28	2.7:1	16
14[i]	3	$Et_3N{\cdot}2HF$ (3)	DMA	-	80	5.8:1	46
15	3	$Et_3N{\cdot}2HF$ (3)	DMA	NaOAc (1)	79	8.4:1	42
16	3	$Et_3N{\cdot}2HF$ (3)	DMA	NH_4OAc (1)	1	-	0
17	3	$Et_3N{\cdot}2HF$ (3)	DMA	AgOTf (1)	93	8:1	80
18	3	$Et_3N{\cdot}2HF$ (3)	DMA	LiOTf (1)	91	10.4:1	73
19	3	$Et_3N{\cdot}2HF$ (3)	DMA	$AgOCOCF_3$ (1)	88	6.6:1	53
20	3	$Et_3N{\cdot}2HF$ (3)	DMA	AcOH (1 drop)	79	6.8:1	56
21	3	$Et_3N{\cdot}2HF$ (3)	DMA	AcOH (1)	67	9.4:1	15
22	3	$Et_3N{\cdot}2HF$ (3)	DMA	TFA (1 drop)	88	7.6:1	55
23	3	$Et_3N{\cdot}2HF$ (3)	DMA	TFA (1)	90	9.5:1	38
24	3	$Et_3N{\cdot}2HF$ (3)	DMA	conc. H_2SO_4 (1 drop)	89	7.8:1	52
25	3	$Et_3N{\cdot}2HF$ (3)	DMA	conc. H_2SO_4 (1)	81	12:1	31

[a] $Et_3N{\cdot}2HF$ is generated *in situ* by adding Et_3N (1 equiv) to $Et_3N{\cdot}3HF$ (2 equiv). [b] Determined by ^{19}F NMR analysis of the crude mixture after workup. [c] Yield of **5a** determined by ^{19}F NMR analysis of the crude mixture after workup. [d] 1,2-Dichloroethane. [e] 1,2-Dimethoxyethane. F Reaction was performed at 0.1 M concentration. [g] A 1 M solution in THF was used. [h] 3 Equiv. of Et_3N was also added. [i] XtalFluor-M was used instead of XtalFluor-E.

3. Synthesis of monofluoroalkenes from cyclohexanone derivatives

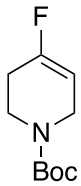
General procedure - To a solution of $Et_3N{\cdot}3HF$ (218 μL, 1.33 mmol, 2 equiv) in DMA (2 mL) were successively added triethylamine (94 μL, 0.67 mmol, 1 equiv), XtalFluor-E (460 mg, 2.00 mmol, 3 equiv) and the ketone (0.67 mmol, 1 equiv). After 16 hours stirring at room temperature under inert atmosphere, the reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic layers were washed with brine and water, dried over Na_2SO_4 and filtered through a pad of silica gel. Solvents were evaporated, and the resulting crude material was purified by silica gel flash chromatography.



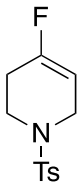
Benzyl 4-fluoro-3,6-dihydropyridine-1(*2H*)-carboxylate (5a). Using the general procedure on benzyl 4-oxopiperidine-1-carboxylate (0.67 mmol), fluoroalkene **5a** was obtained as a colorless oil (124 mg, 79%) after purification by flash chromatography using hexane/EtOAc (85:15) as the eluent. The title compound was contaminated with benzyl 4,4-difluoropiperidine-1-carboxylate in a 5.9:1 ratio. Major compound: IR (ATR, ZnSe) ν = 2941, 1697, 1425, 1234, 1210, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 5.21-5.12 (m, 3H), 4.00 (bs, 2H), 3.68 (bs, 2H), 2.31 (bs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0 (d, *J* = 258.3 Hz), 155.3, 136.5, 128.5 (2C), 128.1, 128.0 (2C), 99.5 (d, *J* = 15.9 Hz), 67.4, 41.1, 40.5, 25.9 (d, *J* = 22.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -101.6 (s, 1F); HRMS-ESI calcd for $C_{13}H_{15}FNO_2$ $[M+H]^+$ 236.1081, found 236.1098.

Procedure for the 1 mmol scale of benzyl 4-oxopiperidine-1-carboxylate. To a solution of $Et_3N{\cdot}3HF$ (326 μL, 2.00 mmol, 2 equiv) in DMA (3 mL) were successively added triethylamine

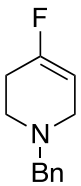
(139 μL, 1.00 mmol, 1 equiv), XtalFluor-E (690 mg, 3.00 mmol, 3 equiv) and benzyl 4-oxopiperidine-1-carboxylate (233 mg, 1.00 mmol, 1 equiv). After 16 hours stirring at room temperature under inert atmosphere, the reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic layers were washed with brine and water, dried over Na_2SO_4 and filtered through a pad of silica gel. Solvents were evaporated, and the resulting crude material was purified by silica gel flash chromatography using hexane/EtOAc (85:15) as the eluent. Benzyl 4-fluoro-3,6-dihydropyridine-1(*2H*)-carboxylate (**5a**) was obtained as a colorless oil (177 mg, 75%) and was contaminated with benzyl 4,4-difluoropiperidine-1-carboxylate in a 6.1:1 ratio. Spectral data for **5a** were identical to those described above.



***tert*-Butyl 4-fluoro-3,6-dihydropyridine-1(*2H*)-carboxylate (5b).** Using the general procedure on *tert*-butyl 4-oxopiperidine-1-carboxylate (0.67 mmol), fluoroalkene **5b** was obtained as a colorless oil (60 mg, 66%) after purification by flash chromatography using hexane/EtOAc (9:1) as the eluent. The title compound was contaminated with *tert*-butyl 4,4-difluoropiperidine-1-carboxylate in a 4.5:1 ratio. Major compound: IR (ATR, ZnSe) ν = 2977, 2934, 1724, 1670, 1597, 1302 1147 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19 (d, *J* = 14.9 Hz, 1H), 3.92 (bs, 2H), 3.60 (bs, 2H), 2.29 (bs, 2H), 1.47 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0 (d, *J* = 251.9 Hz), 154.6, 100.0 (d, *J* = 39.6 Hz), 80.0, 41.0, 40.6, 28.4 (3C), 26.1 (d, *J* = 14.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.1 (s, 1F); HRMS-ESI calcd for $C_{10}H_{16}FNNaO_2$ $[M+Na]^+$ 224.1057, found 224.1082.

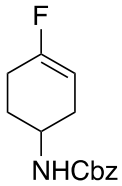


4-Fluoro-1-tosyl-1,2,3,6-tetrahydropyridine (5c). Using the general procedure on 1-tosyl-piperidin-4-one (0.67 mmol), fluoroalkene **5c** was obtained as a white solid (128 mg, 75%) after purification by flash chromatography using hexane/EtOAc (9:1) as the eluent. The title compound was contaminated with 4,4-difluoro-1-tosylpiperidine in a 19:1 ratio. Major compound: mp: 85-86 °C; IR (ATR, ZnSe) ν = 3044, 2924, 2857, 1712, 1596, 1462, 1337, 1145 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.35-7.32 (m, 2H), 5.17 (dtt, *J* = 14.8, 3.5, 1.3 Hz, 1H), 3.64 (ddt, *J* = 5.3, 3.6, 2.6 Hz, 2H), 3.31 (td, *J* = 5.9, 1.8 Hz, 2H), 2.43 (s, 3H), 2.37-2.33 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4 (d, *J* = 258.2 Hz), 143.9, 133.4, 129.8 (2C), 127.5 (2C), 98.8 (d, *J* = 17.9 Hz), 42.8 (d, *J* = 3.3 Hz), 42.7 (d, *J* = 4.1 Hz), 26.0 (d, *J* = 24.2 Hz), 21.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.2 (d, *J* = 14.8 Hz, 1F); HRMS-ESI calcd for $C_{12}H_{14}FNNaO_2S$ $[M+Na]^+$ 278.0621, found 278.0634.

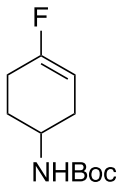


1-Benzyl-4-fluoro-1,2,3,6-tetrahydropyridine (5d). Using the general procedure on 1-benzylpiperidine-4-one (0.67 mmol), fluoroalkene **5d** was obtained as a colorless oil (18 mg, 14%) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. The title compound was contaminated with 1-benzyl-4,4-difluoropiperidine in a 1.6:1 ratio. Spectral data for **5d** were identical to those previously reported.[8]

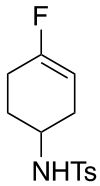
[8] Yang, M.-H.; Matikonda, S. S.; Altman, R. A. *Org. Lett.* **2013**, *15*, 3894–3897.



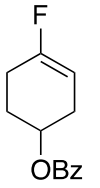
Benzyl (4-fluorocyclohex-3-en-1-yl)carbamate (5e). Using the general procedure on benzyl (4-oxocyclohexyl)carbamate (0.67 mmol), fluoroalkene **5e** was obtained as a white solid (87 mg, 53%) after purification by flash chromatography using hexane/EtOAc (85:15) as the eluent. mp: 49-50 °C; IR (ATR, ZnSe) ν = 3003, 2950, 2849, 1682, 1541, 1264, 1131 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 5.11-5.06 (m, 3H), 4.90 (bs, 1H), 3.86 (bs, 1H), 2.40-2.19 (m, 3H), 1.95-1.90 (m, 2H), 1.79-1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9 (d, *J* = 255.5 Hz), 155.7, 136.5, 128.5 (3C), 128.2 (2C), 99.4 (d, *J* = 17.0 Hz), 66.7, 45.4, 29.1 (d, *J* = 8.0 Hz), 27.8 (d, *J* = 9.1 Hz), 23.4 (d, *J* = 24.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.1 (d, *J* = 15.6 Hz, 1F); HRMS-ESI calcd for $C_{14}H_{16}FNNaO_2$ $[M+Na]^+$ 272.1057, found 272.1060.



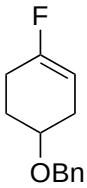
***tert*-Butyl (4-fluorocyclohex-3-en-1-yl)carbamate (5f).** Using the general procedure on *tert*-butyl (4-oxocyclohexyl)carbamate (0.67 mmol), fluoroalkene **5f** was obtained as a white solid (69 mg, 48%) after purification by flash chromatography using hexane/EtOAc (9:1) as the eluent. mp: 79-80 °C; IR (ATR, ZnSe) ν = 3306, 2969, 2930, 1673, 1521, 1364, 1124 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13-5.08 (m, 1H), 4.62 (bs, 1H), 3.79 (bs, 1H), 2.40-2.22 (m, 3H), 1.96-1.92 (m, 2H), 1.78-1.70 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9 (d, *J* = 255.3 Hz), 155.3, 99.5 (d, *J* = 19.0 Hz), 79.3, 44.9, 29.2 (d, *J* = 8.1 Hz), 28.4 (3C), 28.0 (d, *J* = 8.9 Hz), 23.50 (d, *J* = 24.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.4 (d, *J* = 14.4 Hz, 1F); HRMS-ESI calcd for $C_{11}H_{19}FNO_2$ $[M+H]^+$ 216.1394, found 216.1392.



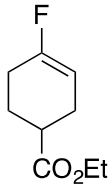
***N*-(4-fluorocyclohex-3-en-1-yl)-4-methylbenzenesulfonamide (5g).** Using the general procedure on 4-methyl-*N*-(4-oxocyclohexyl)benzenesulfonamide (0.329 mmol) scale, fluoroalkene **5g** was obtained as a white solid (45 mg, 51%) after purification by flash chromatography using hexane/EtOAc (8:2) as the eluent. mp: 95-96 °C; IR (ATR, ZnSe) ν = 3235, 2931, 2903, 2845, 1705, 1425, 1322 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.01 (dt, *J* = 16.1, 4.0 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 3.51-3.45 (m, 1H), 2.44 (s, 3H), 2.24-2.21 (m, 3H), 1.91-186 (m, 1H), 1.84-1.79 (m, 1H), 1.75-1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (d, *J* = 256.0 Hz), 143.5, 137.8, 129.8 (2C), 127.0 (2C), 99.1 (d, *J* = 17.5 Hz), 48.0 (d, *J* = 1.9 Hz), 29.6 (d, *J* = 8.1 Hz), 28.5 (d, *J* = 9.3 Hz), 23.3 (d, *J* = 25.0 Hz), 21.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -101.8 (d, *J* = 11.8 Hz, 1F); HRMS-ESI calcd for $C_{13}H_{16}FNNaO_2S$ $[M+Na]^+$ 292.0778, found 292.0777.



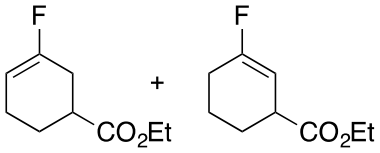
4-Fluorocyclohex-3-en-1-yl benzoate (5h). Using the general procedure on 4-oxocyclohexyl benzoate (0.67 mmol), fluoroalkene **5h** was obtained as a colorless oil (71 mg, 49%) after purification by flash chromatography using hexane/EtOAc (97:3) as the eluent. IR (ATR, ZnSe) ν = 2934, 2851, 1712, 1269, 1109 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7.57-7.54 (m, 1H), 7.45-7.42 (m, 2H), 5.31-5.27 (m, 1H), 5.17-5.12 (m, 1H), 2.53-2.40 (m, 2H), 2.36-2.30 (m, 2H), 2.14-2.06 (m, 1H), 2.05-2.00 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 158.7 (d, *J* = 254.9 Hz), 133.0, 130.4, 129.6 (2C), 128.4 (2C), 98.7 (d, *J* = 17.5 Hz), 68.4, 28.2 (d, *J* = 8.0 Hz), 26.9 (d, *J* = 9.1 Hz), 22.7 (d, *J* = 25.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.2 (d, *J* = 16.0 Hz, 1F); HRMS-ESI calcd for $C_{13}H_{14}FO_2$ $[M+H]^+$ 221.0972, found 221.0972.



(((4-Fluorocyclohex-3-en-1-yl)oxy)methyl)benzene (5i). Using the general procedure on 4-(benzyloxy)cyclohexan-1-one (0.67 mmol), fluoroalkene **5i** was obtained as a colorless oil (38 mg, 27%) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. IR (ATR, ZnSe) ν = 2929, 2850, 1703, 1453, 1373, 1093 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 4H), 7.33-7.29 (m, 1H), 5.10 (dtd, *J* = 16.1, 3.4, 1.7 Hz, 1H), 4.62-4.55 (m, 2H), 3.71-3.67 (m, 1H), 2.41-2.33 (m, 2H), 2.28-2.16 (m, 2H), 2.03-1.97 (m, 1H), 1.94-189 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (d, *J* = 254.8 Hz), 138.7, 128.4 (2C), 127.6, 127.5 (2C), 99.0 (d, *J* = 17.2 Hz), 72.4 (d, *J* = 2.0 Hz), 70.3, 28.6 (d, *J* = 8.1 Hz), 27.3 (d, *J* = 9.4 Hz), 23.4 (d, *J* = 25.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -103.1 (d, *J* = 16.3 Hz, 1F); HRMS-ESI calcd for $C_{13}H_{16}FO$ $[M+H]^+$ 207.1179, found 207.1144.



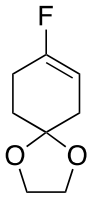
Ethyl 4-fluorocyclohex-3-ene-1-carboxylate (5j). Using the general procedure on ethyl 4-oxocyclohexane-1-carboxylate (0.67 mmol), fluoroalkene **5j** was obtained as a colorless oil (87 mg, 76%) after purification by flash chromatography using hexane/EtOAc (85:15) as the eluent. Spectral data for **5j** were identical to those previously reported.[9]



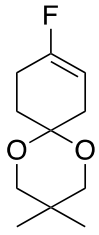
Ethyl 3-fluorocyclohexene-1-carboxylate (5k). Using the general procedure on ethyl 3-oxocyclohexane-1-carboxylate (0.67 mmol), fluoroalkenes **5k** were obtained in a 1.1:1 ratio as a colorless oil (48 mg, 42%) after purification by flash chromatography using hexane/EtOAc (95:5)

[9] Umemoto, T.; Singh, R. P.; Xu, Y.; Saito, N. *J. Am. Chem. Soc.* **2010**, *132*, 18199–18205.

as the eluent. The title compounds were contaminated with traces of unidentified side-products. IR (ATR, ZnSe) ν = 2936, 2853, 1731, 1445, 1368, 1177, 1137 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (ddt, *J* = 16.8, 3.3, 1.5 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1.1H), 4.16 (q, *J* = 7.3 Hz, 2H), 4.15 (q, *J* = 7.3 Hz, 2.2H), 3.16 (bs, 1H), 2.72-2.66 (m, 1.1H), 2.49-1.59 (m, 12.6H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 173.8, 161.3 (d, *J* = 257.4 Hz), 157.9 (d, *J* = 252.8 Hz), 101.5 (d, *J* = 14.9 Hz), 100.9 (d, *J* = 19.2 Hz), 60.7, 60.6, 39.6 (d, *J* = 7.2 Hz), 39.5 (d, *J* = 8.1 Hz), 27.7, 27.5, 25.3, 25.1, 21.6, 21.5, 20.8, 20.7, 14.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.8 (d, *J* = 16.7 Hz, 1F), -102.8 (dd, *J* = 16.7, 5.9 Hz, 1.1F); HRMS-ESI calcd for $C_9H_{14}FO_2$ $[M+H]^+$ 173.0972, found 173.0959.



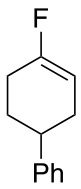
8-Fluoro-1,4-dioxaspiro[4.5]dec-7-ene (5l). Using the general procedure on 1,4-dioxaspiro[4.5]decan-8-one (0.67 mmol), fluoroalkene **5l** was obtained as a colorless oil (80 mg, 76%) after purification by flash chromatography using pentane/Et_2O (9:1) as the eluent. The title compound was contaminated with 8,8-difluoro-1,4-dioxaspiro[4.5]decane in a 20:1 ratio. Spectral data for **5l** were identical to those previously reported.[10]



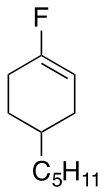
9-Fluoro-3,3-dimethyl-1,5-dioxaspiro[5.5]undec-8-ene (5m). Using the general procedure on 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one (0.67 mmol), fluoroalkene **5m** was obtained as a white solid (82 mg, 62%) after purification by flash chromatography using hexane/EtOAc (9:1) as the eluent. The title compound was

[10] Tius, M. A.; Kawakami, J. K. *Synth. Commun.* **1992**, *22*, 1461–1471.

contaminated with 9,9-difluoro-3,3-dimethyl-1,5-dioxaspiro[5.5]undecane in a 34:1 ratio. Spectral data for **5m** were identical to those previously reported.[11]



4-Fluoro-1,2,3,6-tetrahydro-1,1'-biphenyl (5n). Using the general procedure on 4-phenylcyclohexan-1-one (0.67 mmol), fluoroalkene **5n** was obtained as a colorless oil (44 mg, 38%) after purification by flash chromatography using hexane as the eluent. Spectral data for **5n** were identical to those previously reported.[11]



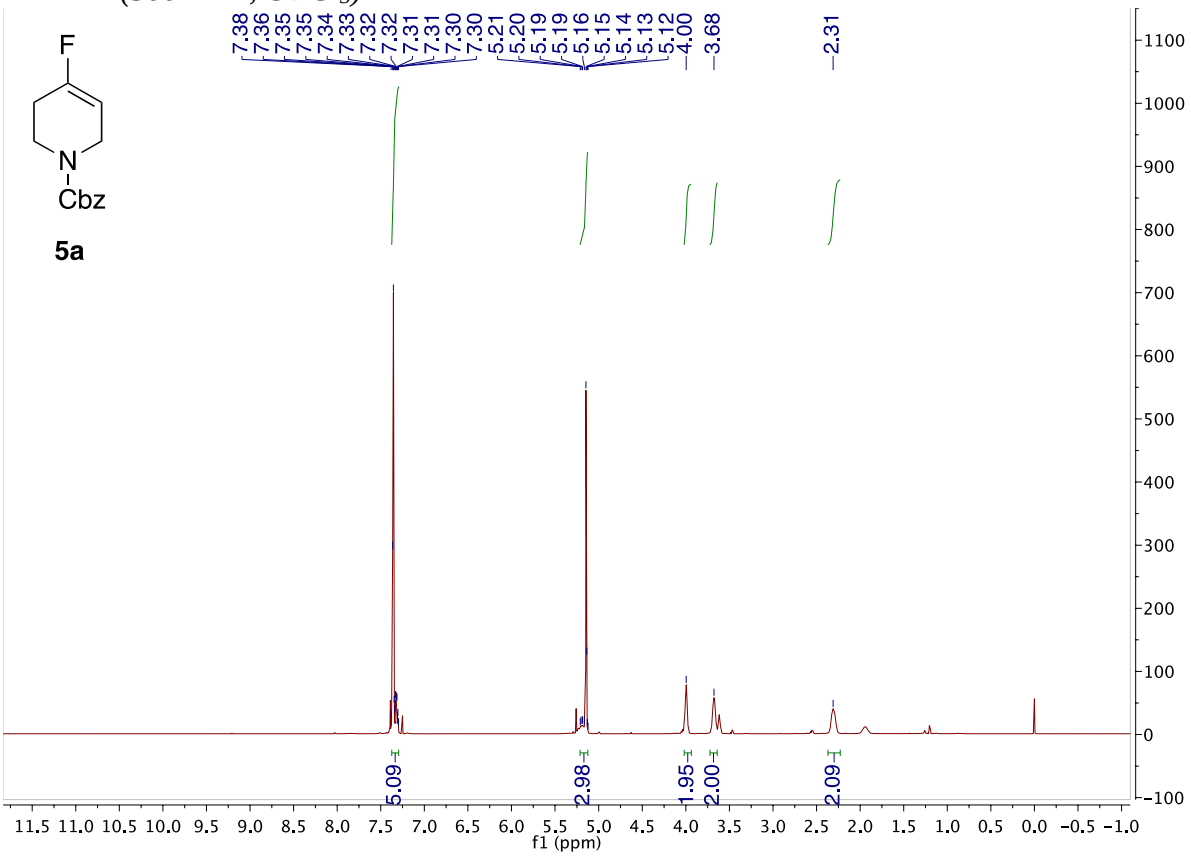
1-Fluoro-4-pentylcyclohex-1-ene (5o). Using the general procedure on 4-pentylcyclohexan-1-one (0.67 mmol), fluoroalkene **5o** was obtained as a colorless oil (16 mg, 14%) after purification by flash chromatography using pentane as the eluent. Spectral data for **5o** were identical to those previously reported.[11]

[11] Ye, Y.; Takada, T.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2016**, *55*, 15559–15563.

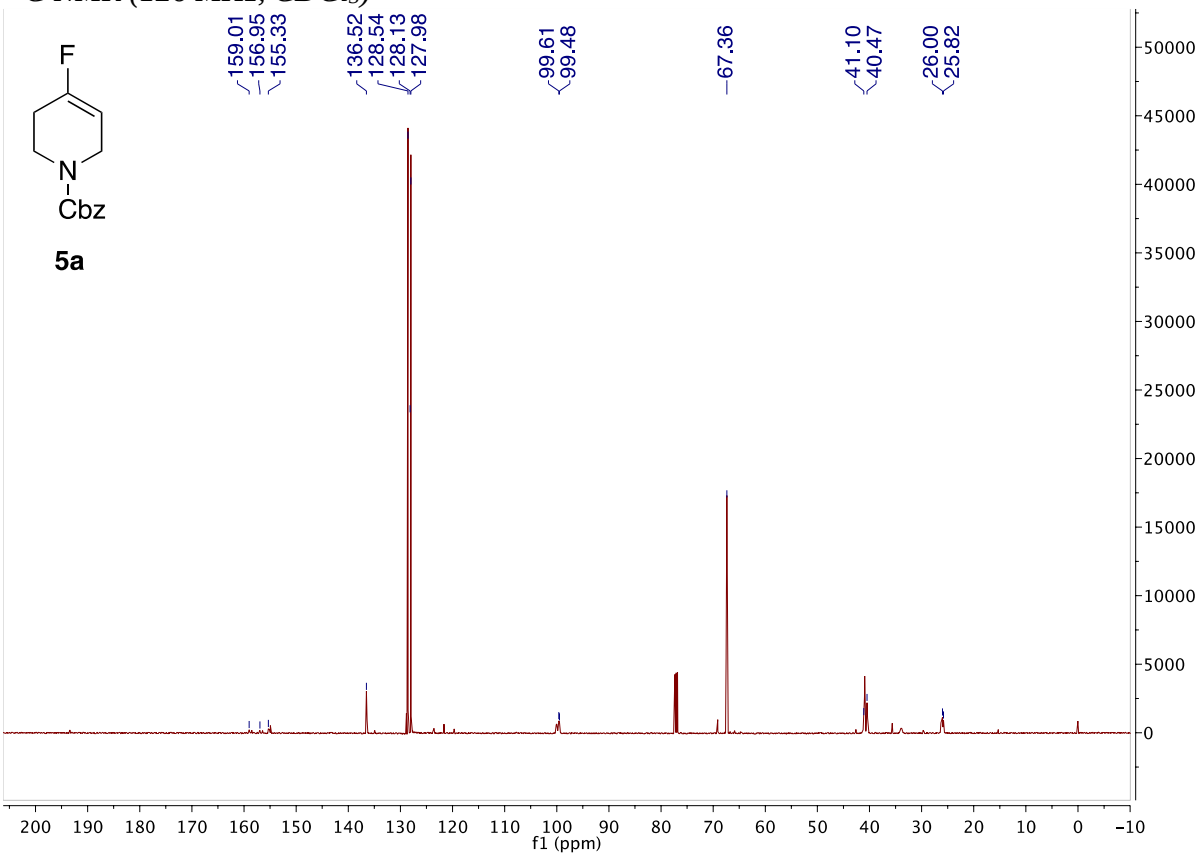
NMR Spectra

Benzyl 4-fluoro-3,6-dihydropyridine-1(*2H*)-carboxylate (5a)

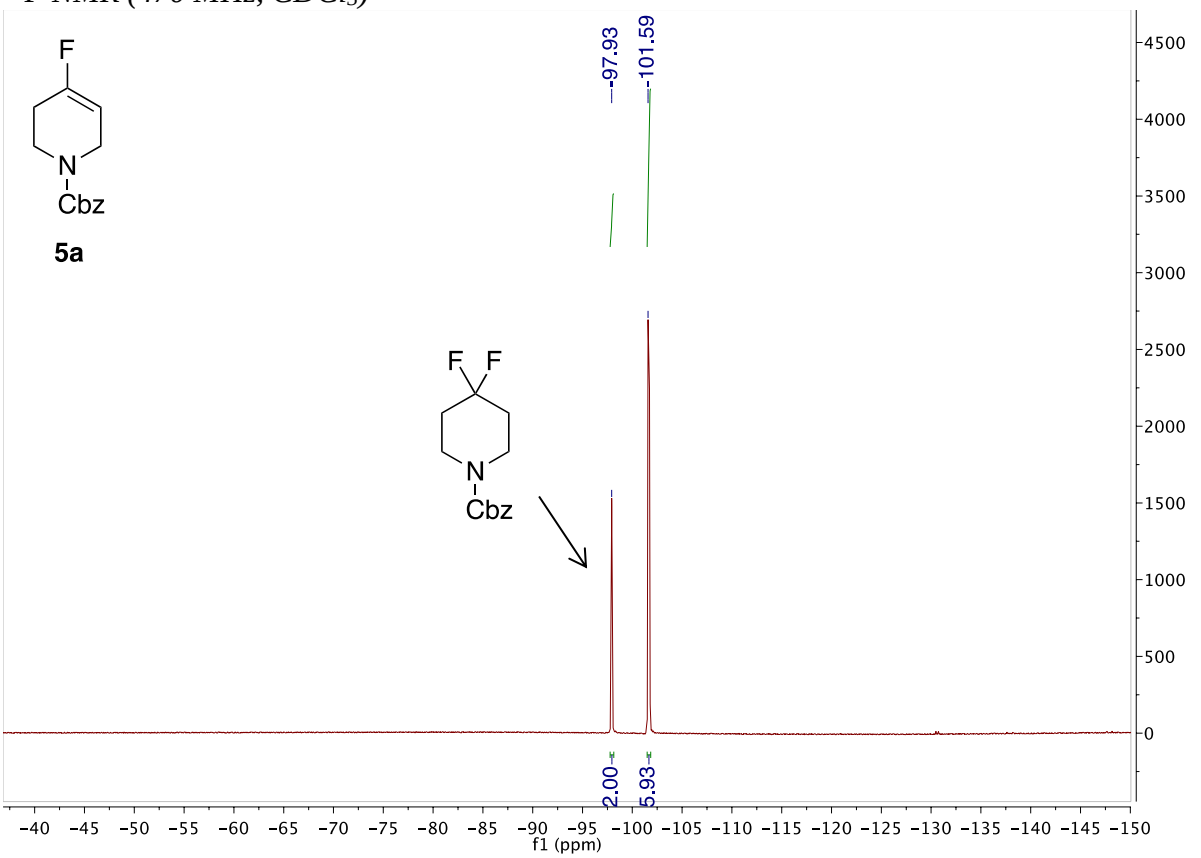
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

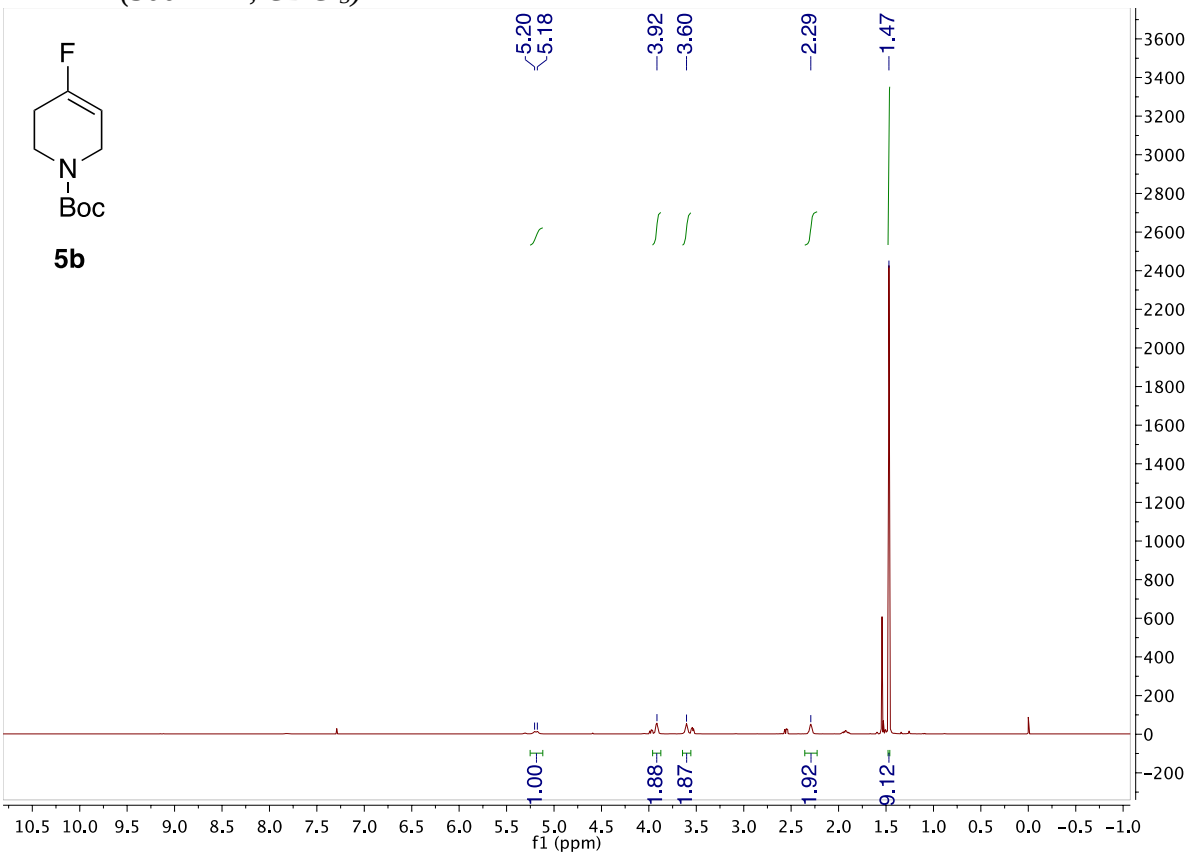


^{19}F NMR (470 MHz, $CDCl_3$)

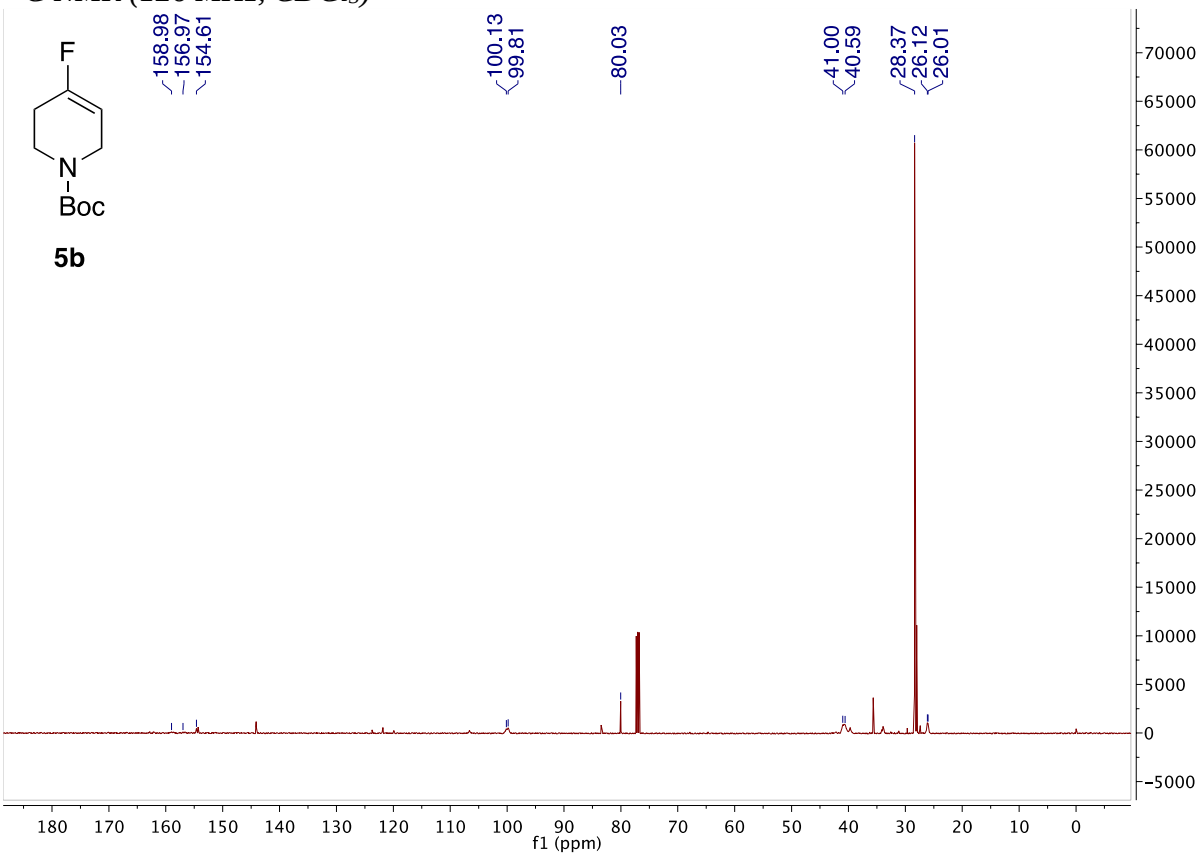


tert-Butyl 4-fluoro-3,6-dihydropyridine-1(_2H_)-carboxylate (5b)

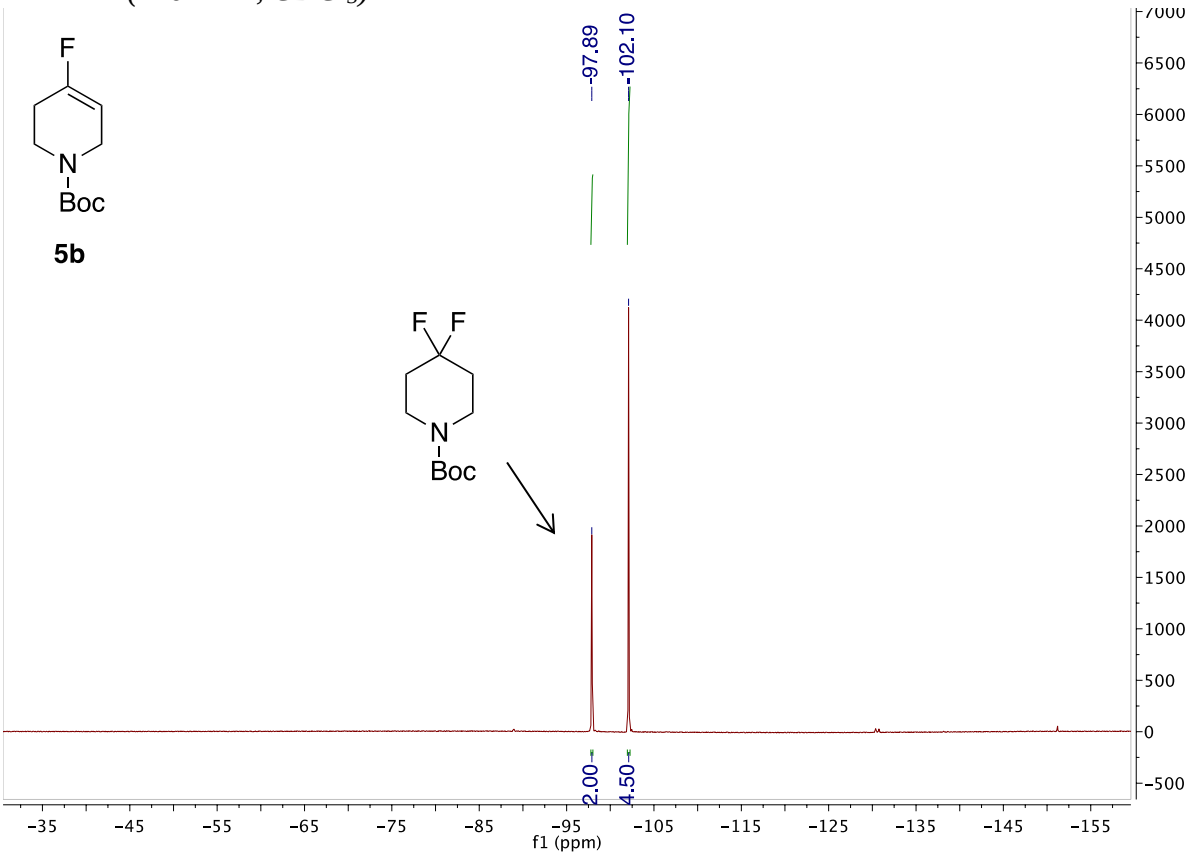
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

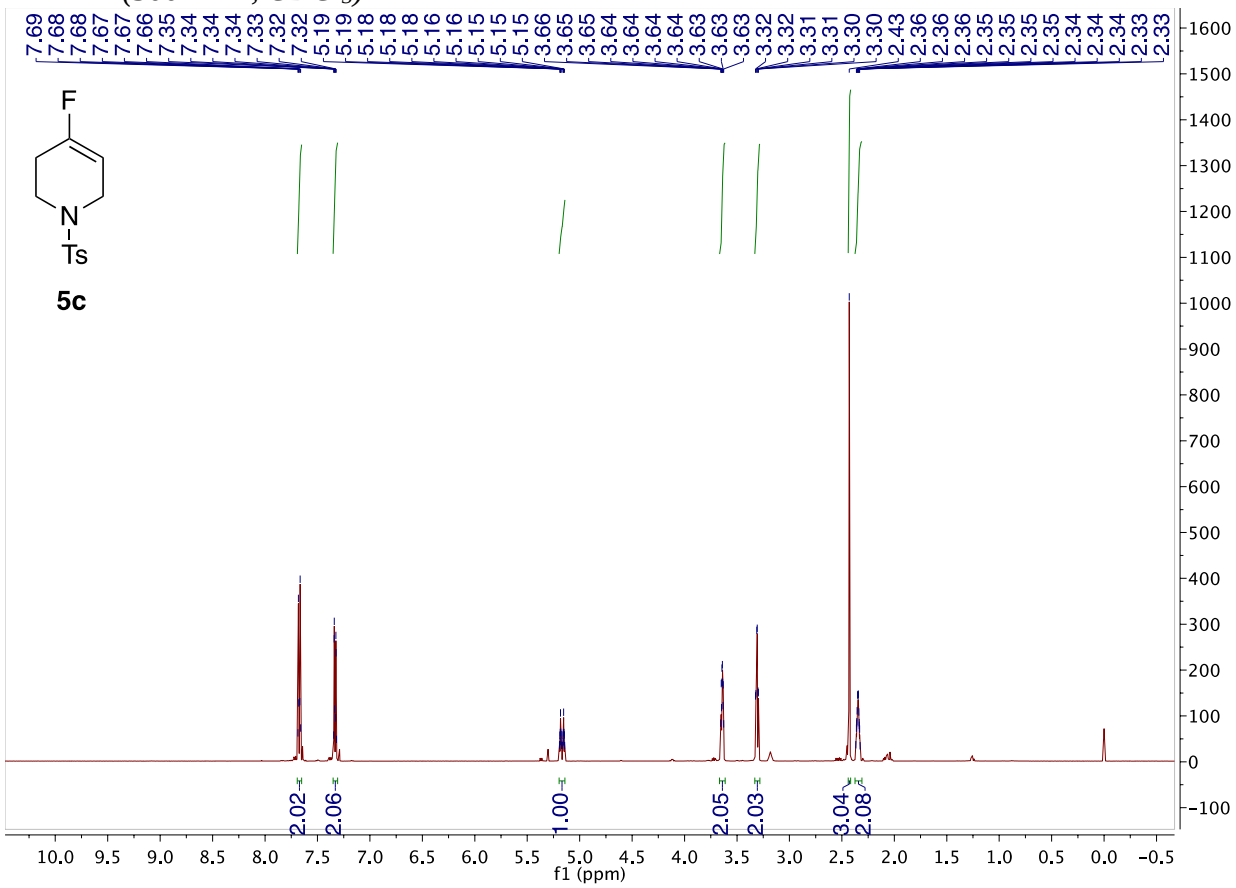


^{19}F NMR (470 MHz, $CDCl_3$)

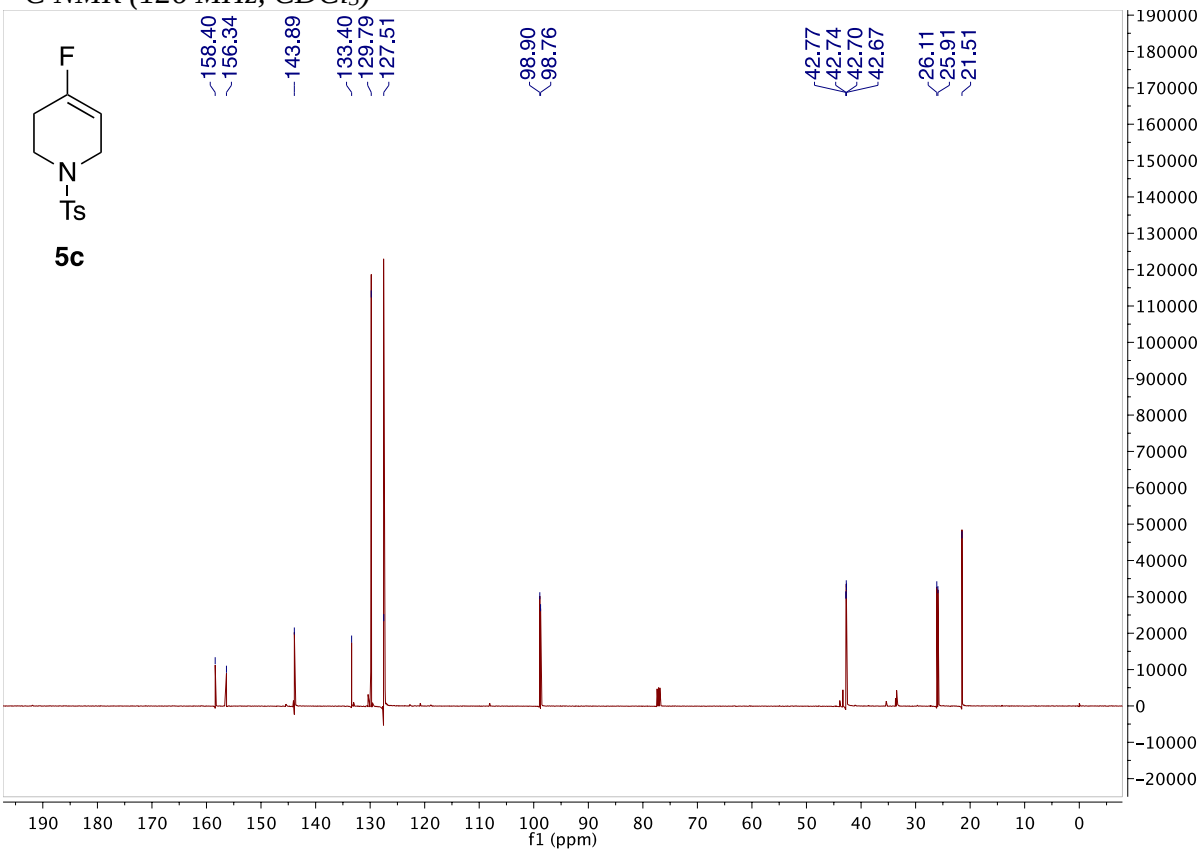


4-Fluoro-1-tosyl-1,2,3,6-tetrahydropyridine (5c)

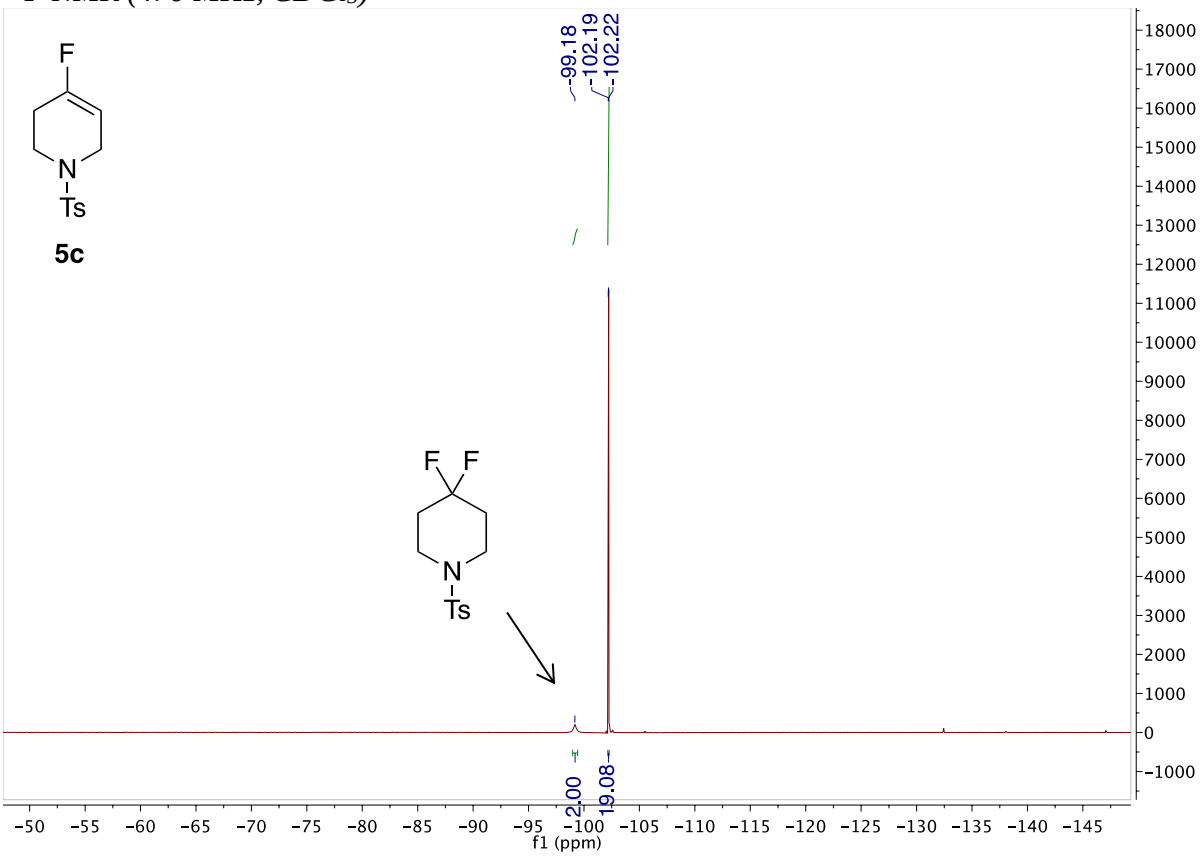
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

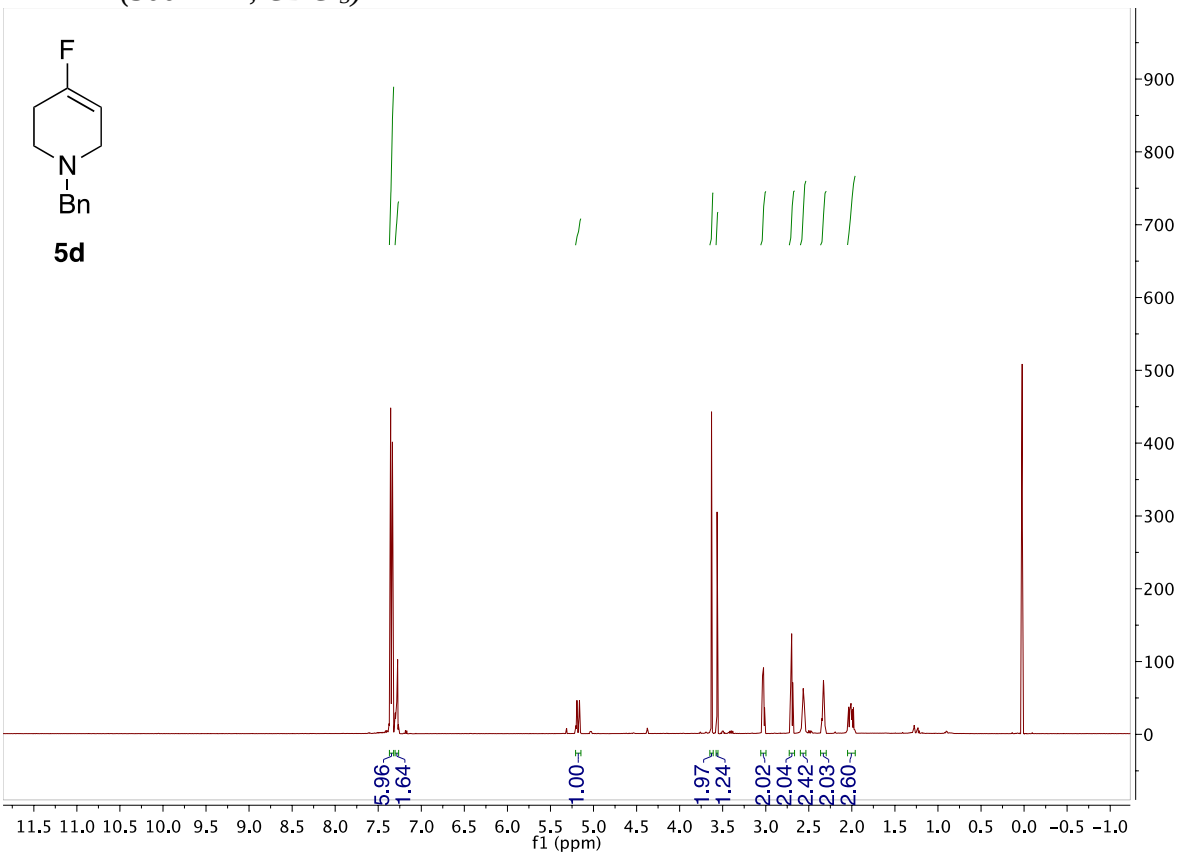


^{19}F NMR (470 MHz, $CDCl_3$)



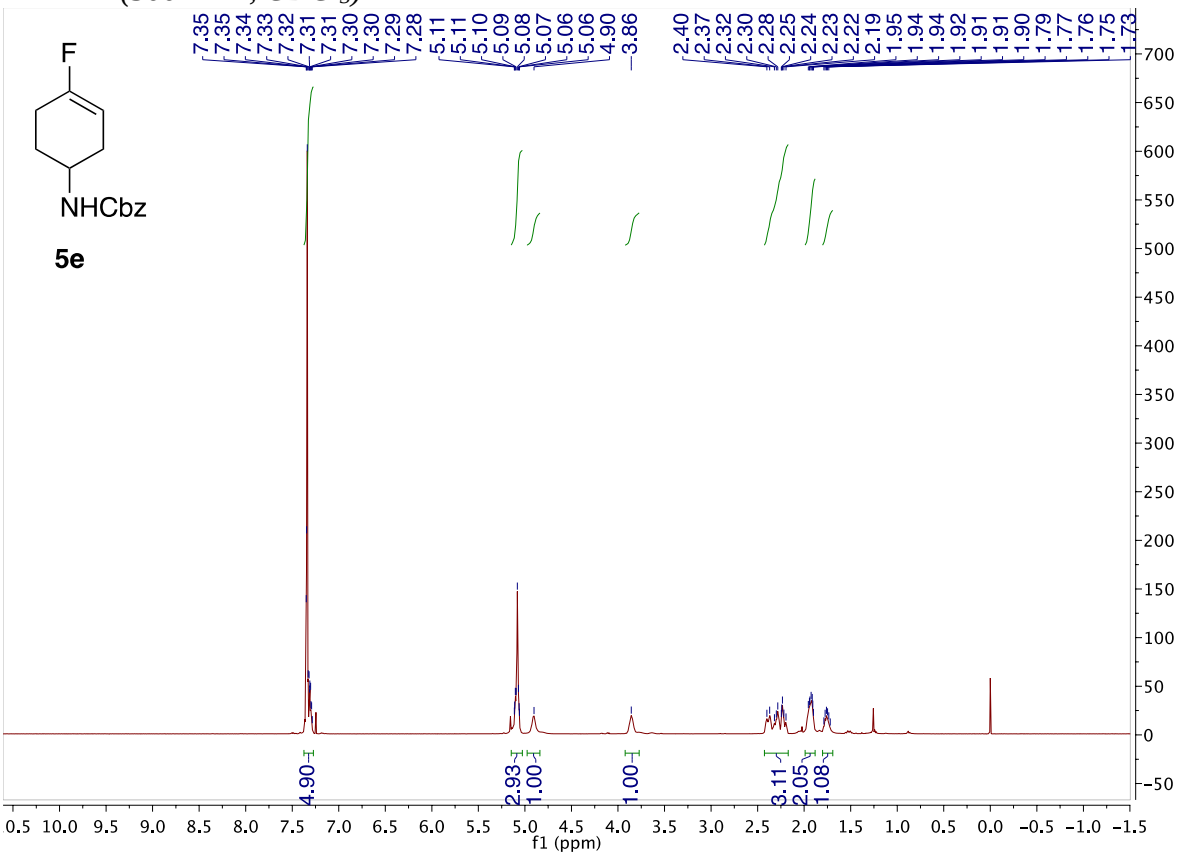
1-Benzyl-4-fluoro-1,2,3,6-tetrahydropyridine (5d)

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

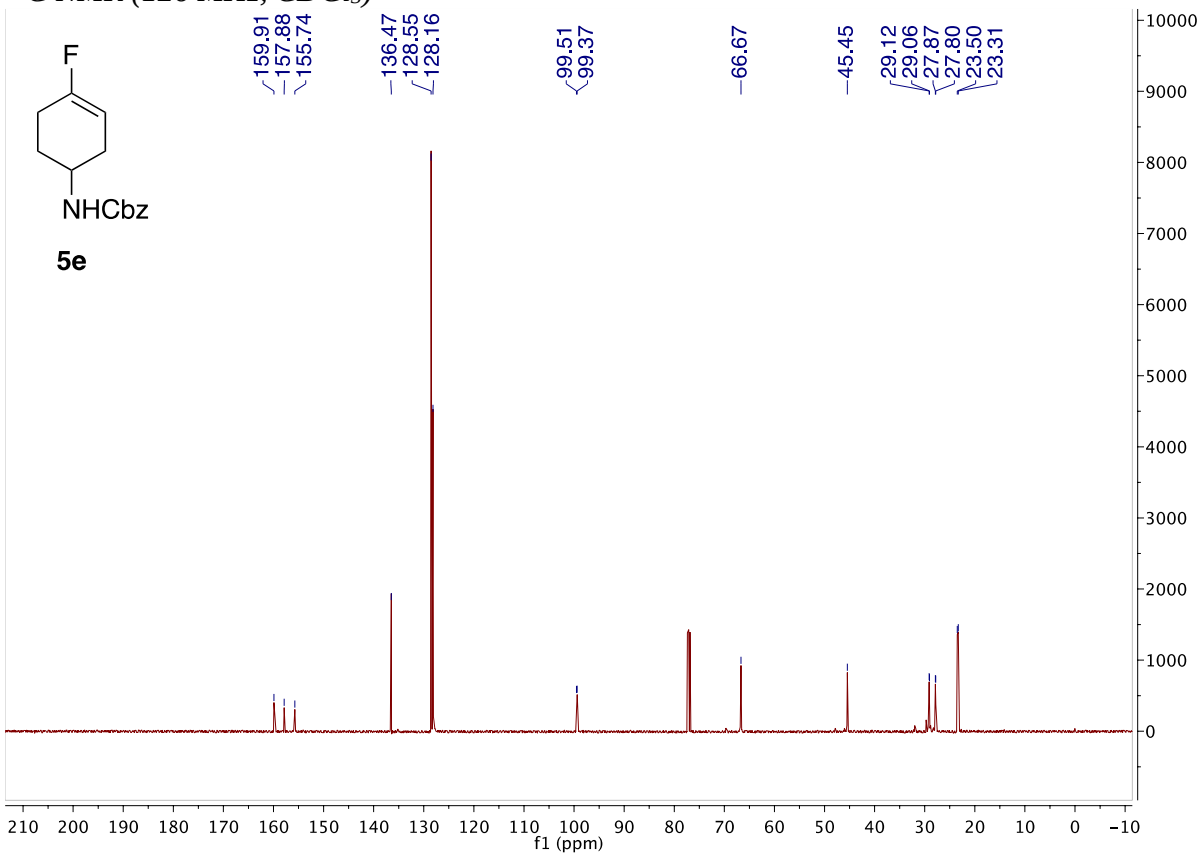


Benzyl (4-fluorocyclohex-3-en-1-yl)carbamate (5e)

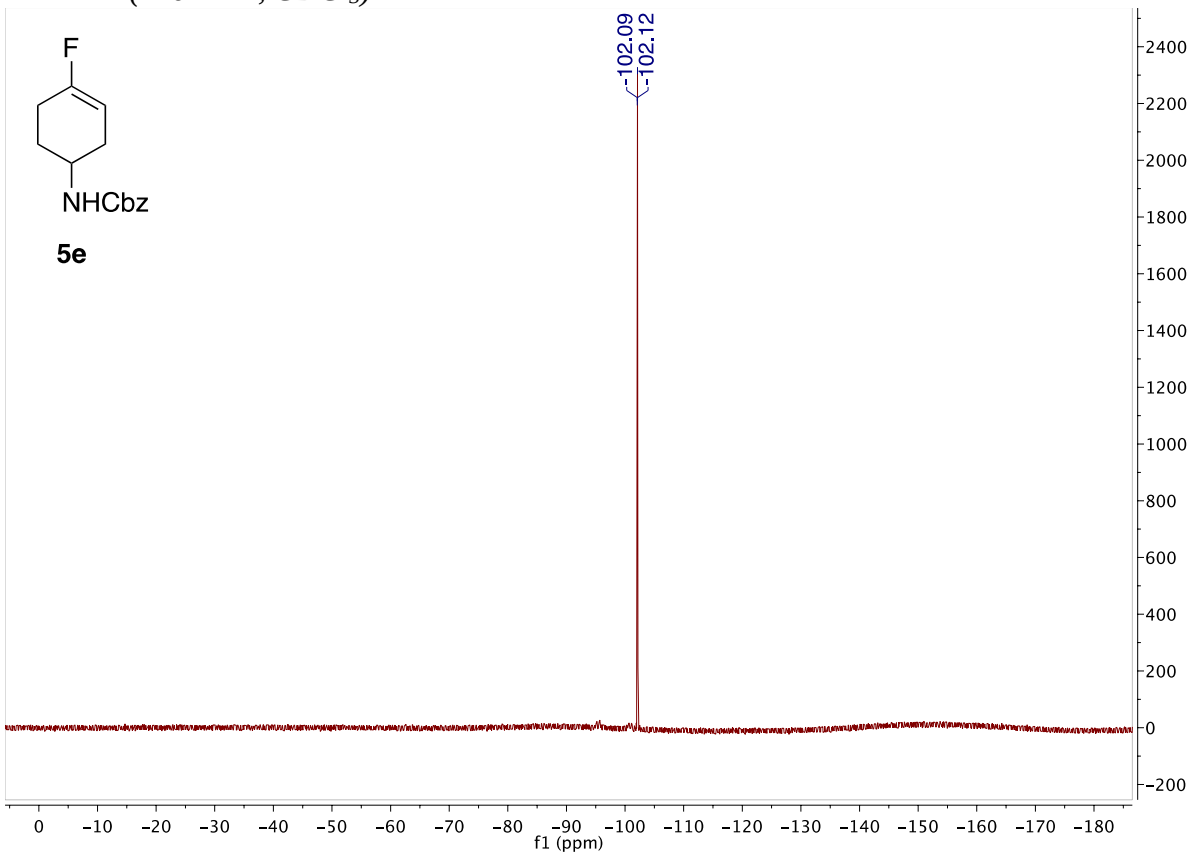
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

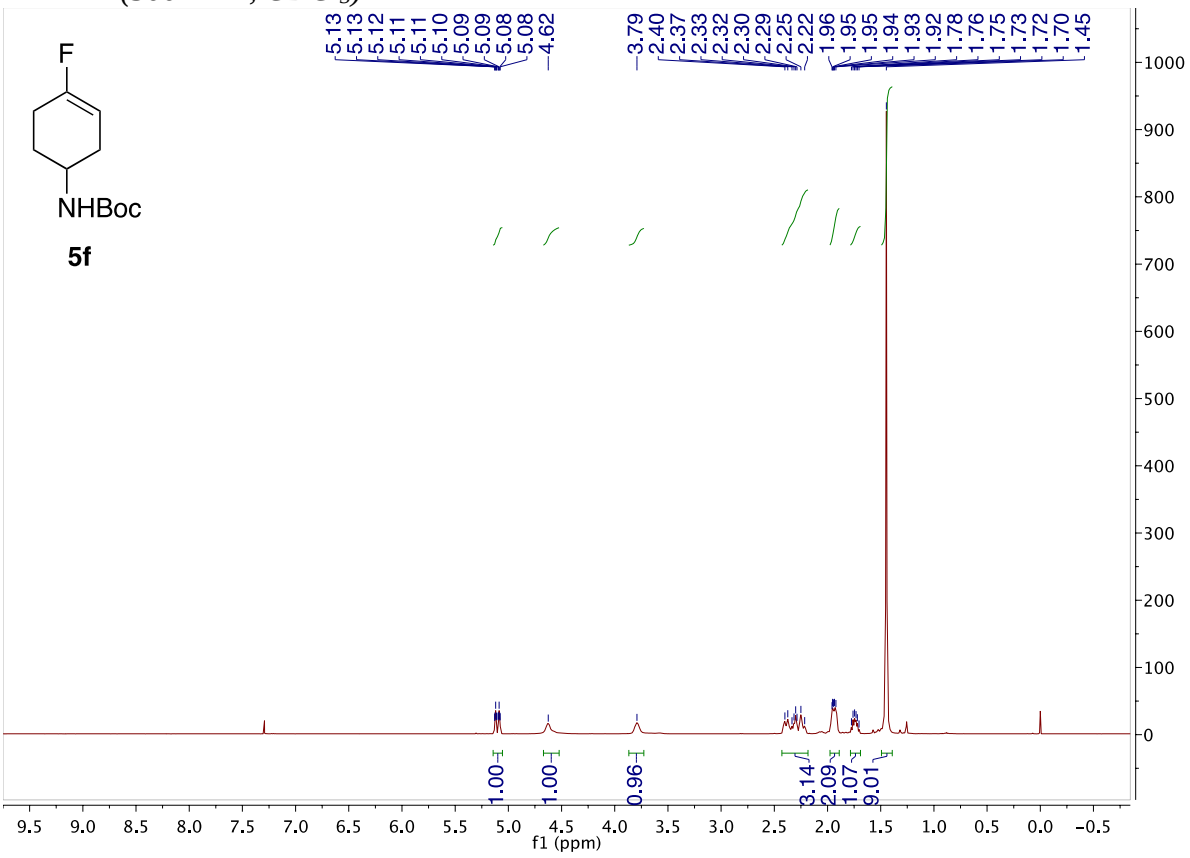


^{19}F NMR (470 MHz, $CDCl_3$)

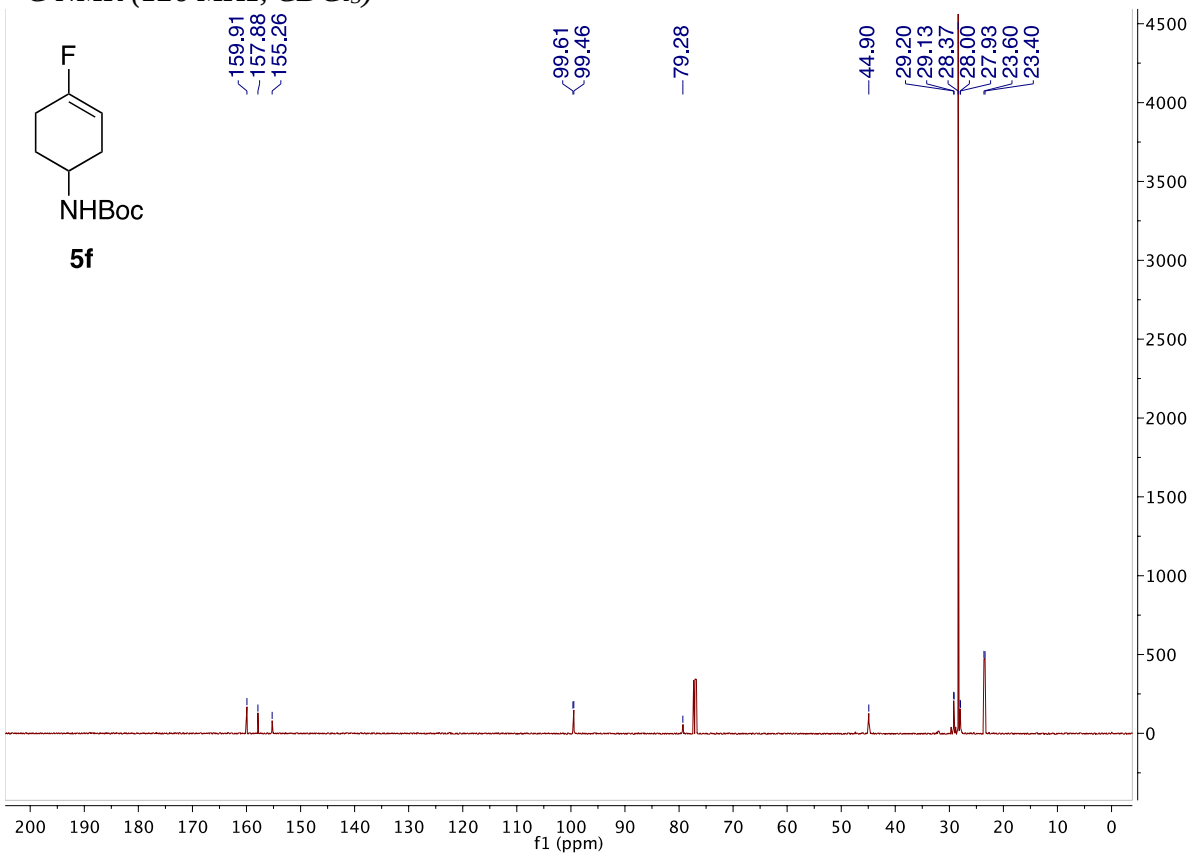


tert-Butyl (4-fluorocyclohex-3-en-1-yl)carbamate (5f)

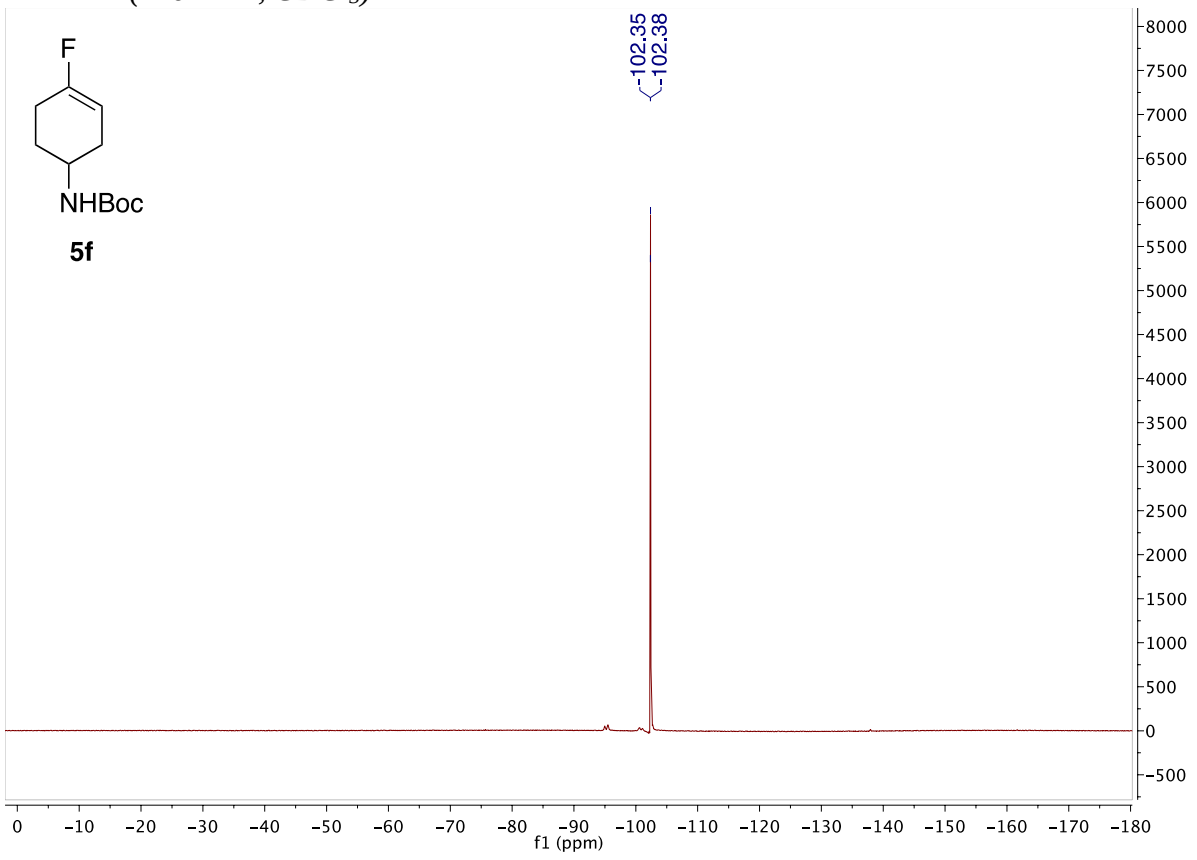
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

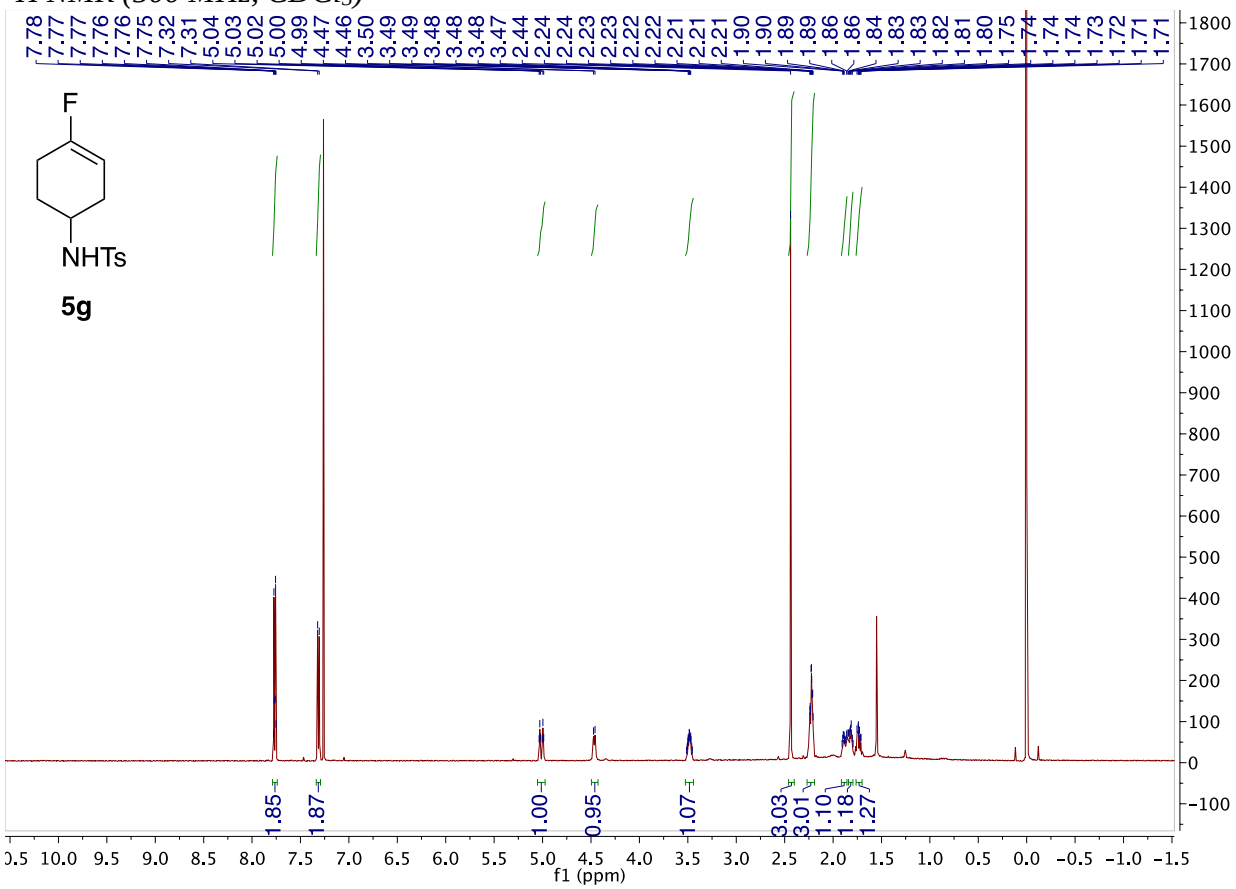


^{19}F NMR (470 MHz, $CDCl_3$)

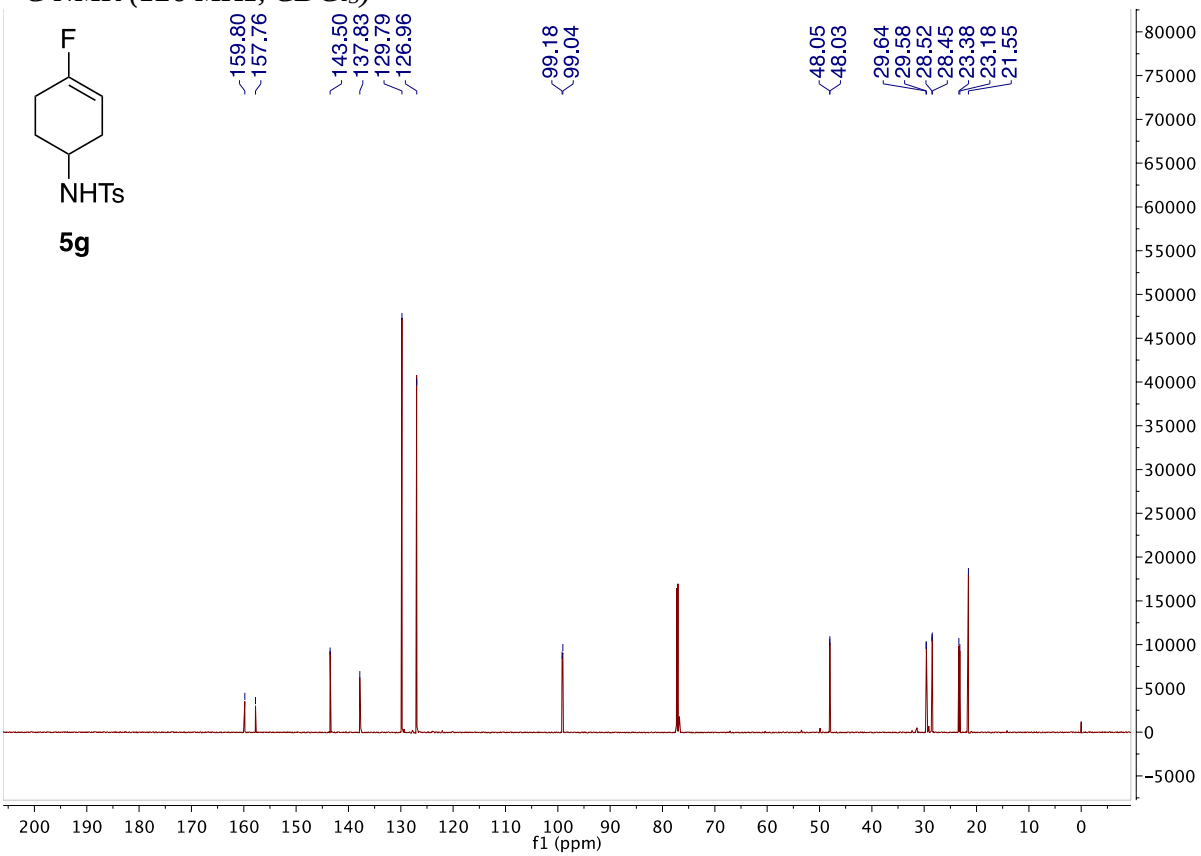


_N_-(4-fluorocyclohex-3-en-1-yl)-4-methylbenzenesulfonamide (5g)

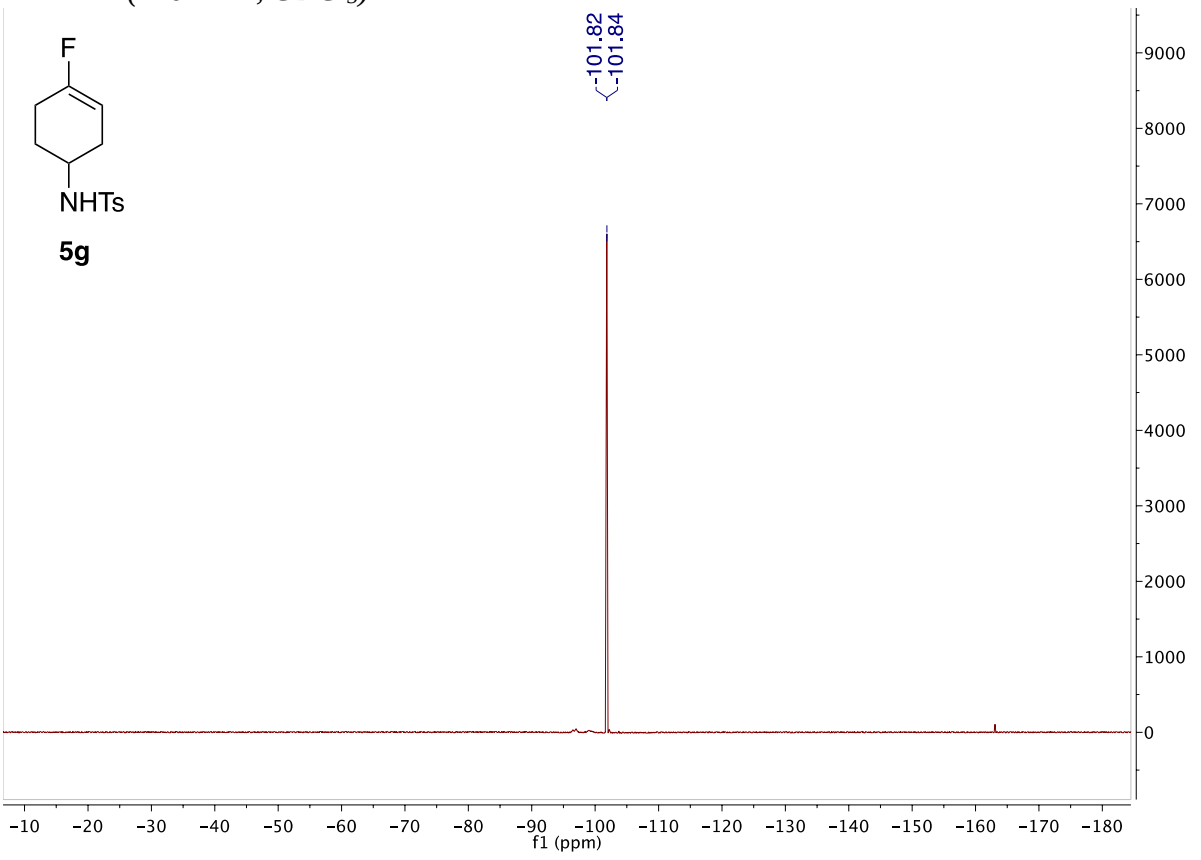
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

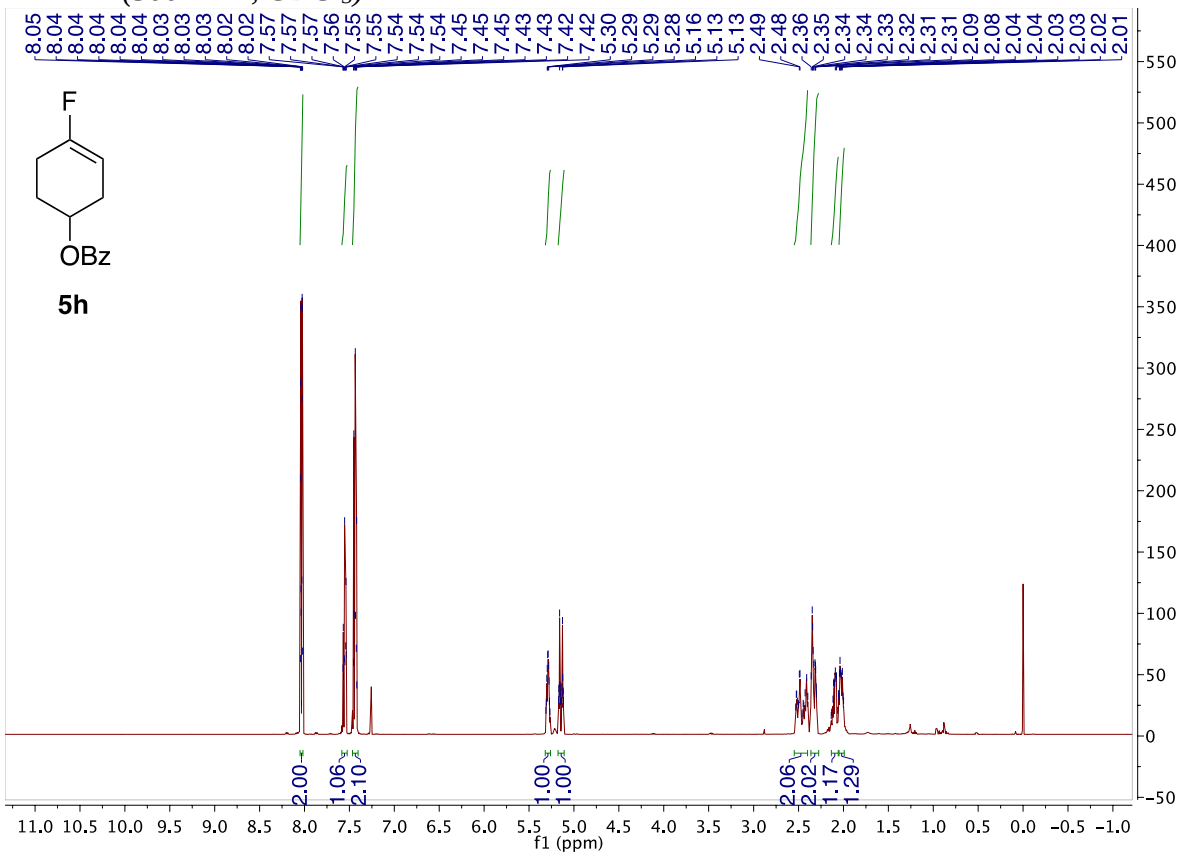


^{19}F NMR (470 MHz, $CDCl_3$)

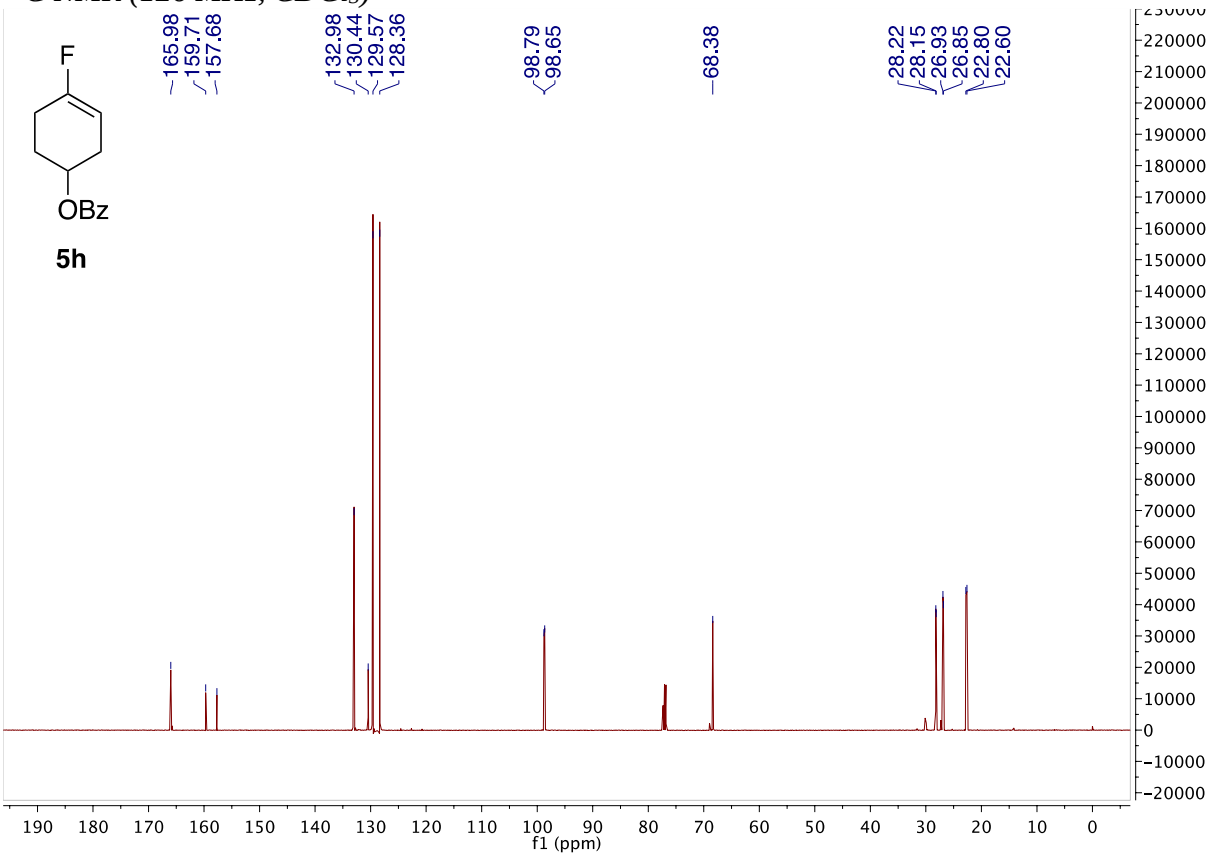


4-Fluorocyclohex-3-en-1-yl benzoate (5h)

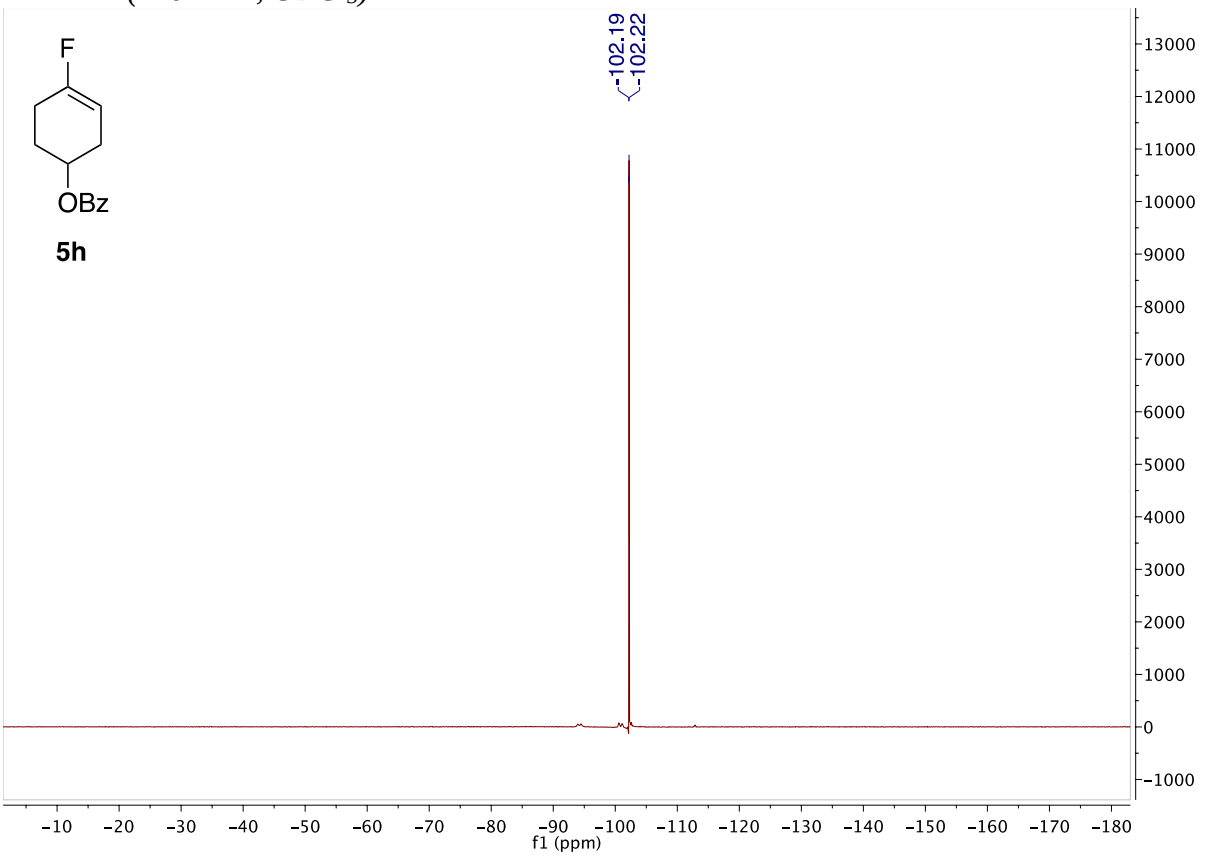
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

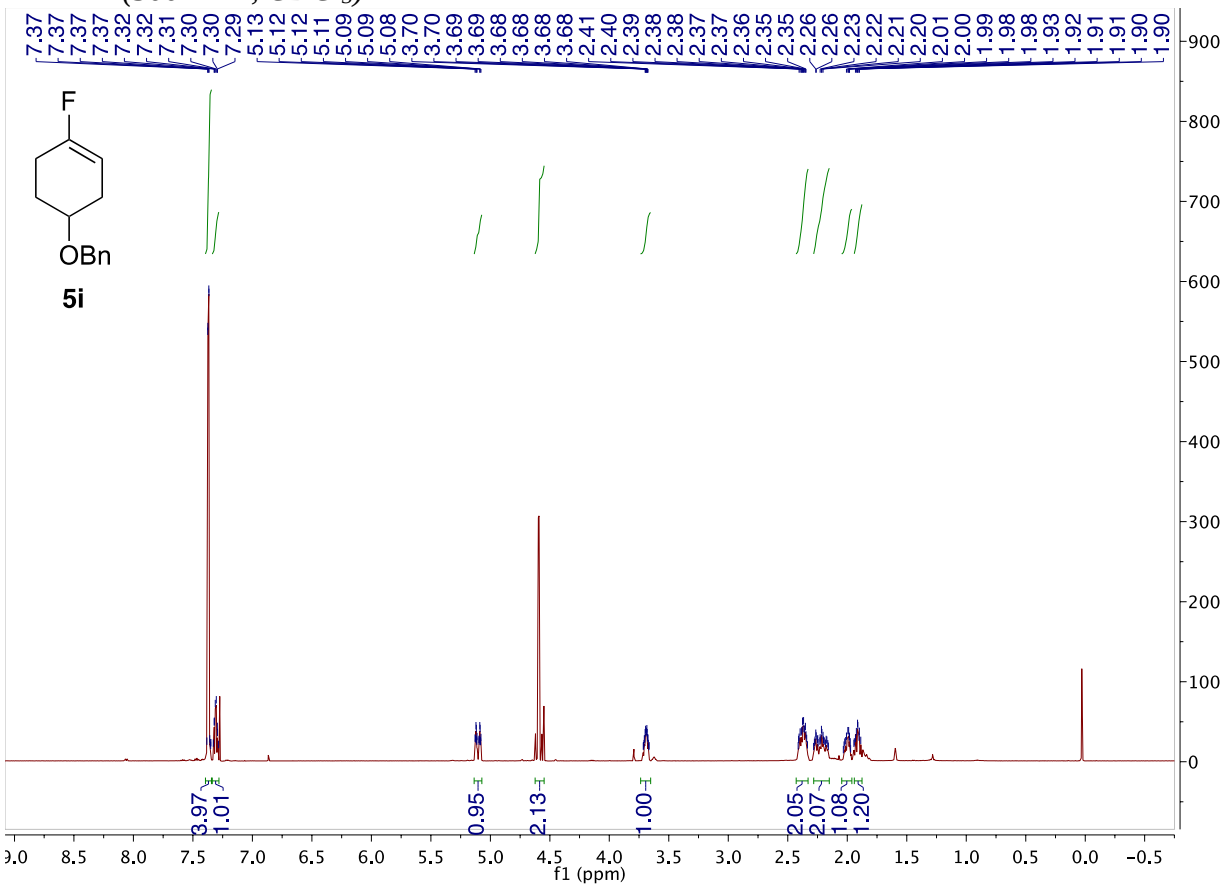


^{19}F NMR (470 MHz, $CDCl_3$)

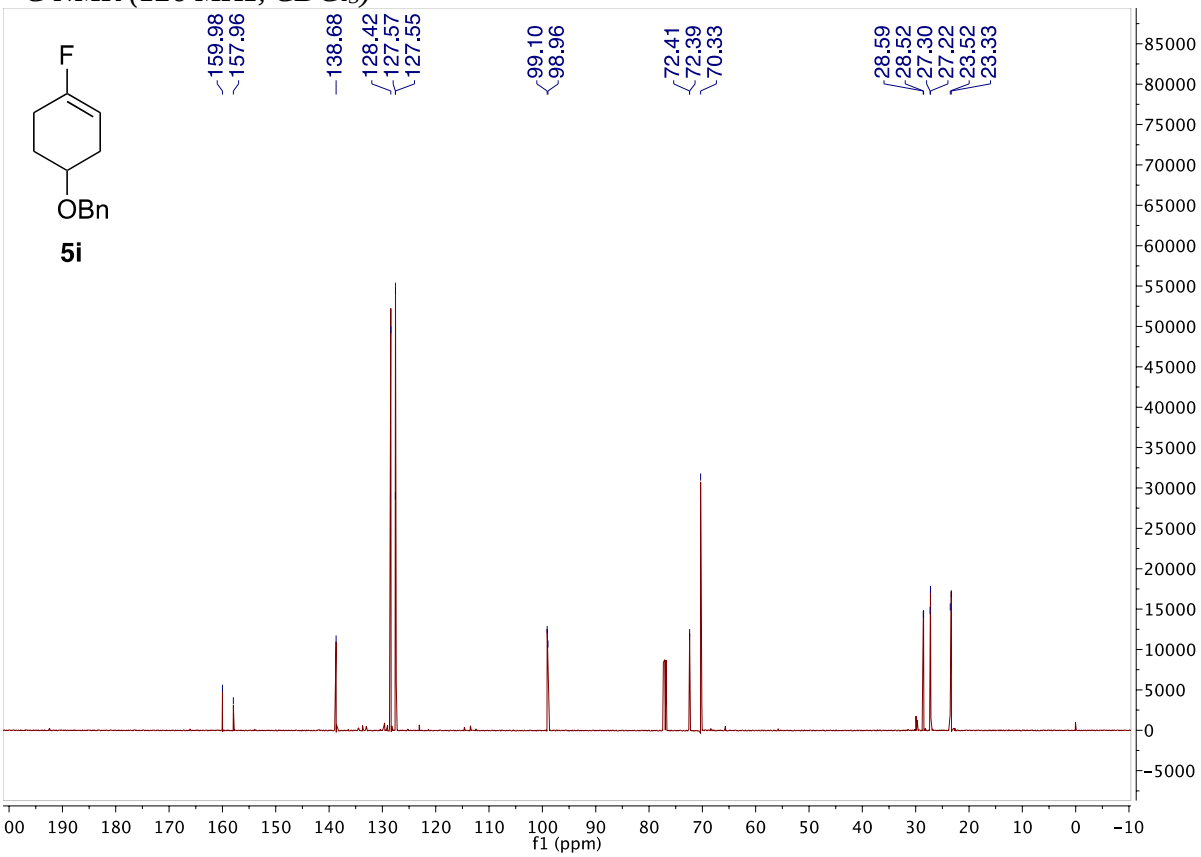


(((4-Fluorocyclohex-3-en-1-yl)oxy)methyl)benzene (5i)

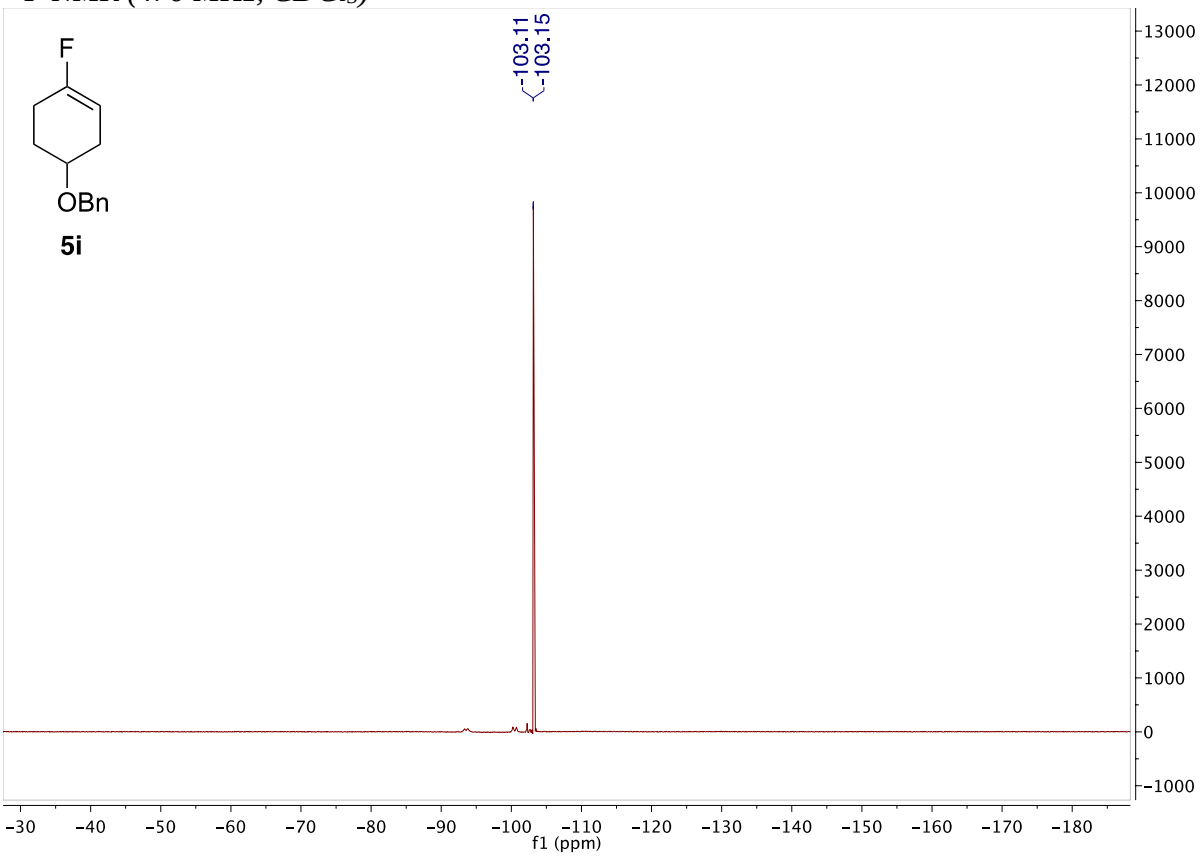
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

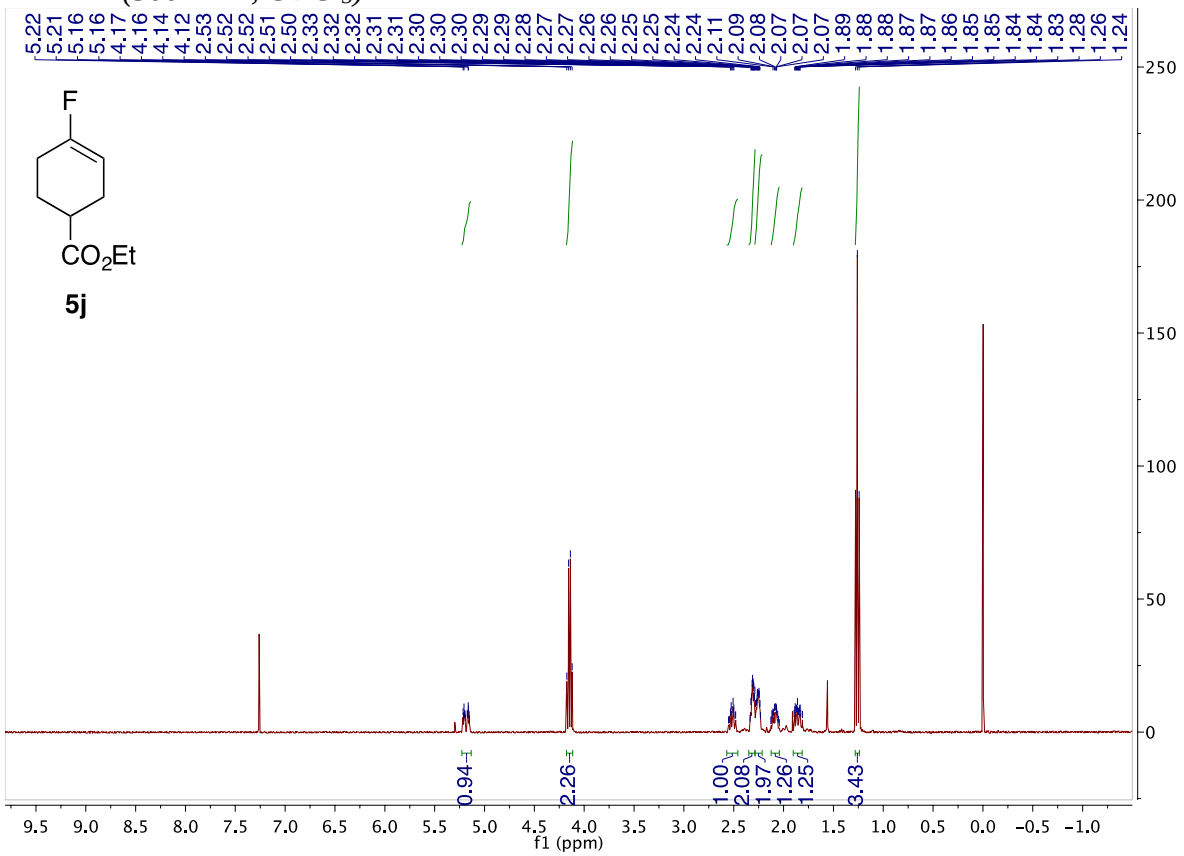


^{19}F NMR (470 MHz, $CDCl_3$)



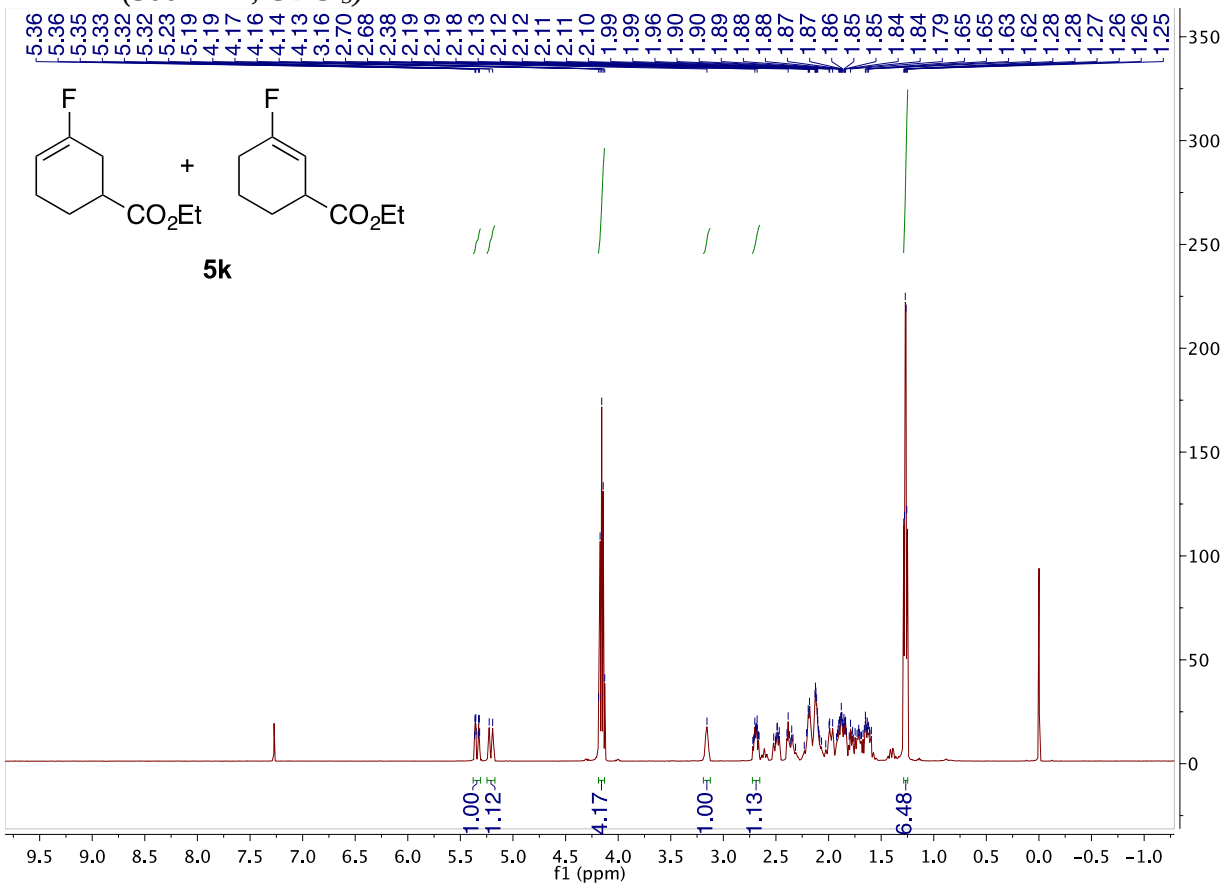
Ethyl 4-fluorocyclohex-3-ene-1-carboxylate (5j)

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

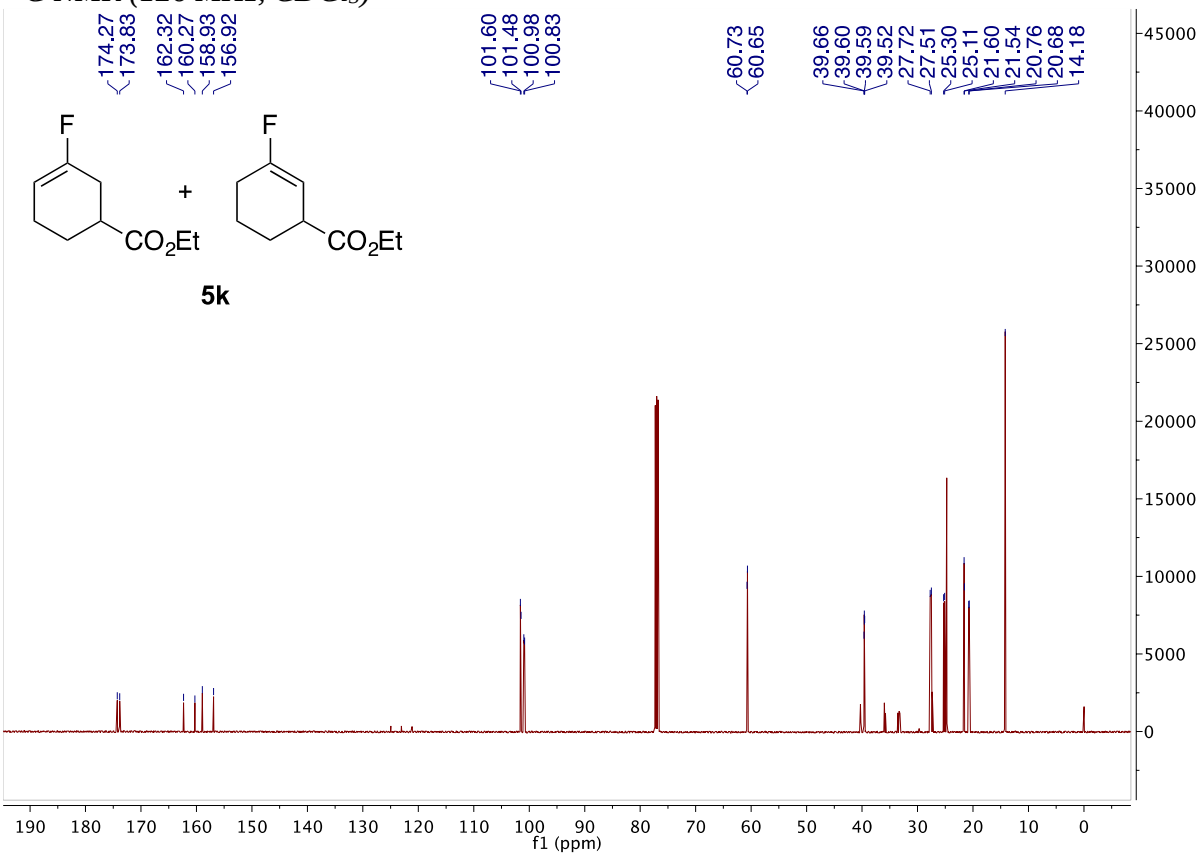


Ethyl 3-fluorocyclohexene-1-carboxylate (5k)

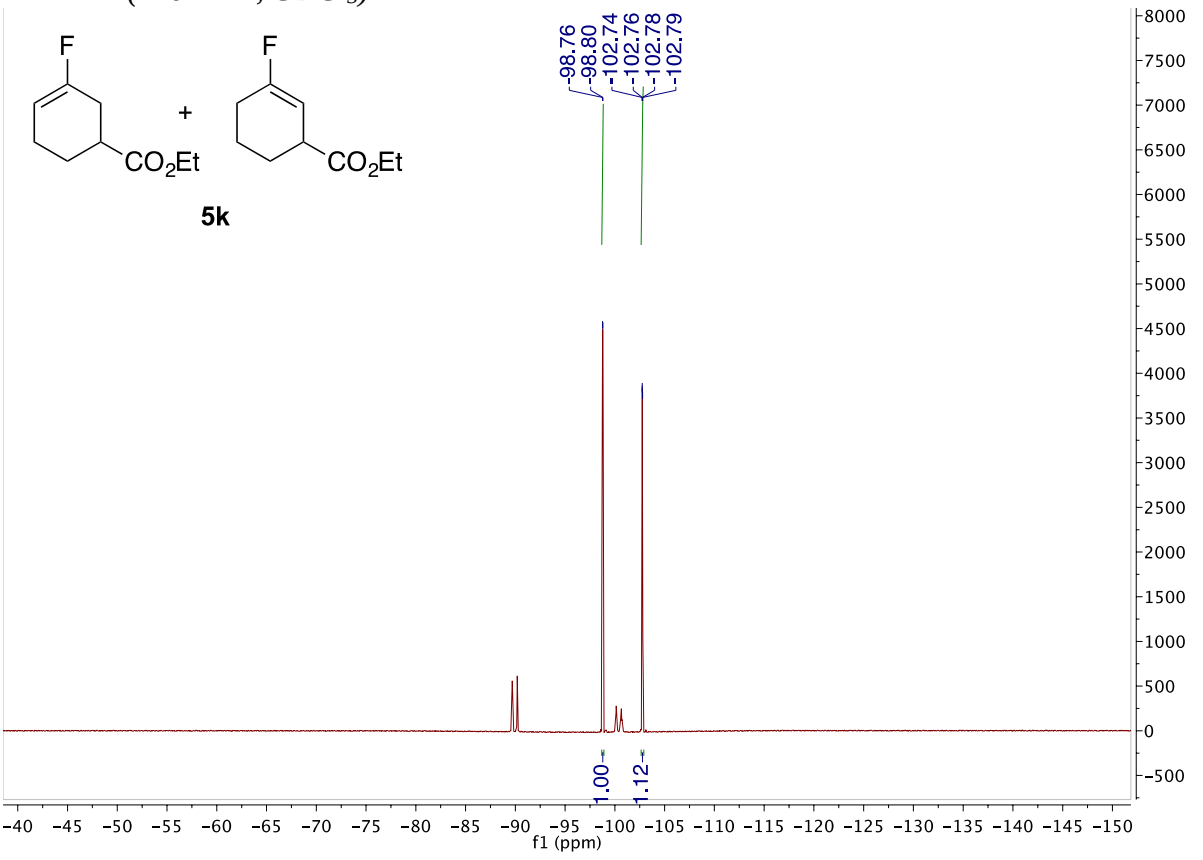
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

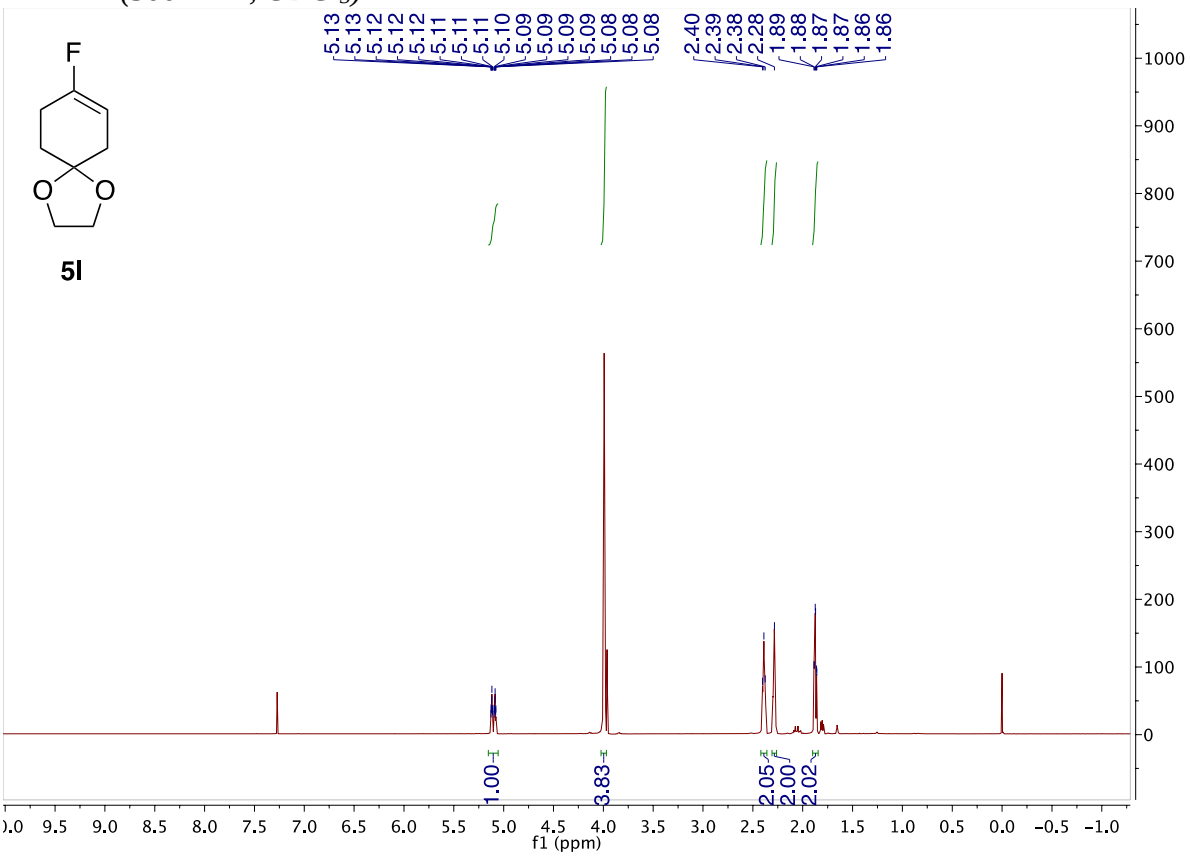


^{19}F NMR (470 MHz, $CDCl_3$)



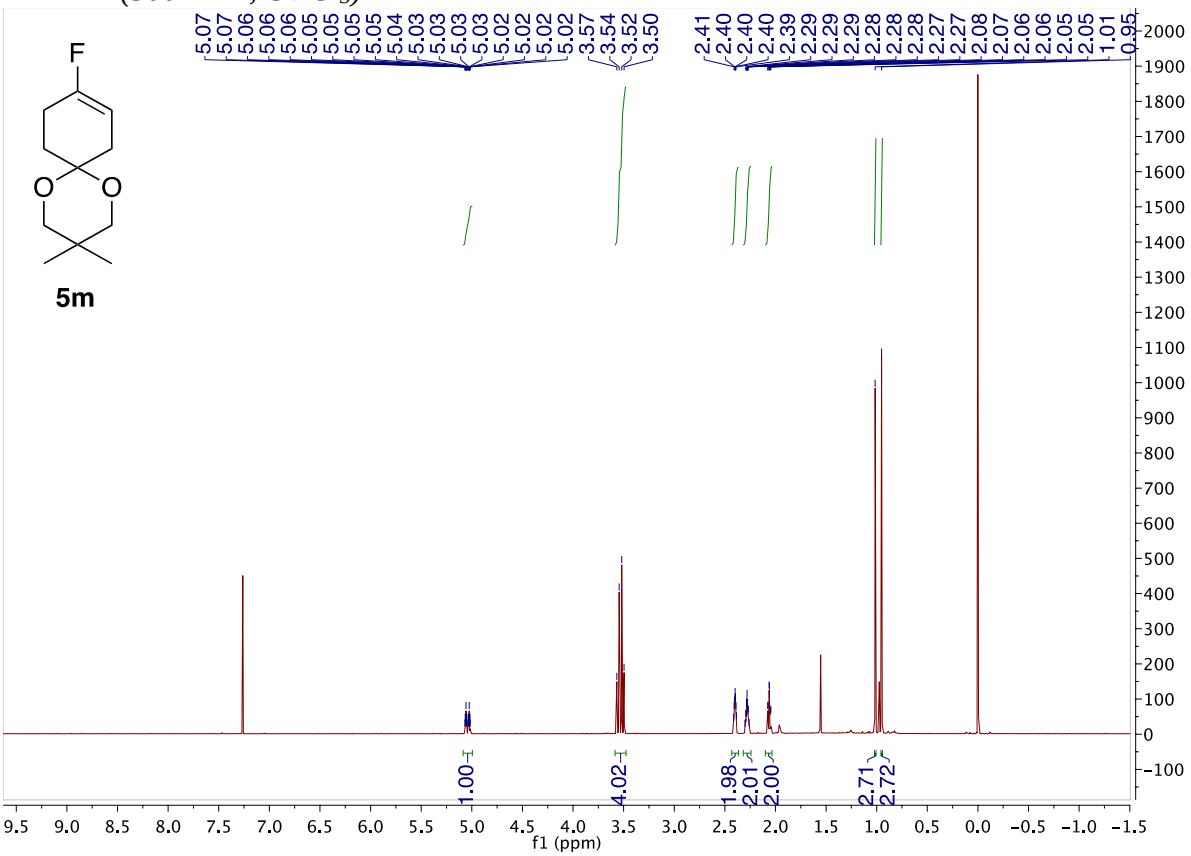
8-Fluoro-1,4-dioxaspiro[4.5]dec-7-ene (5l)

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



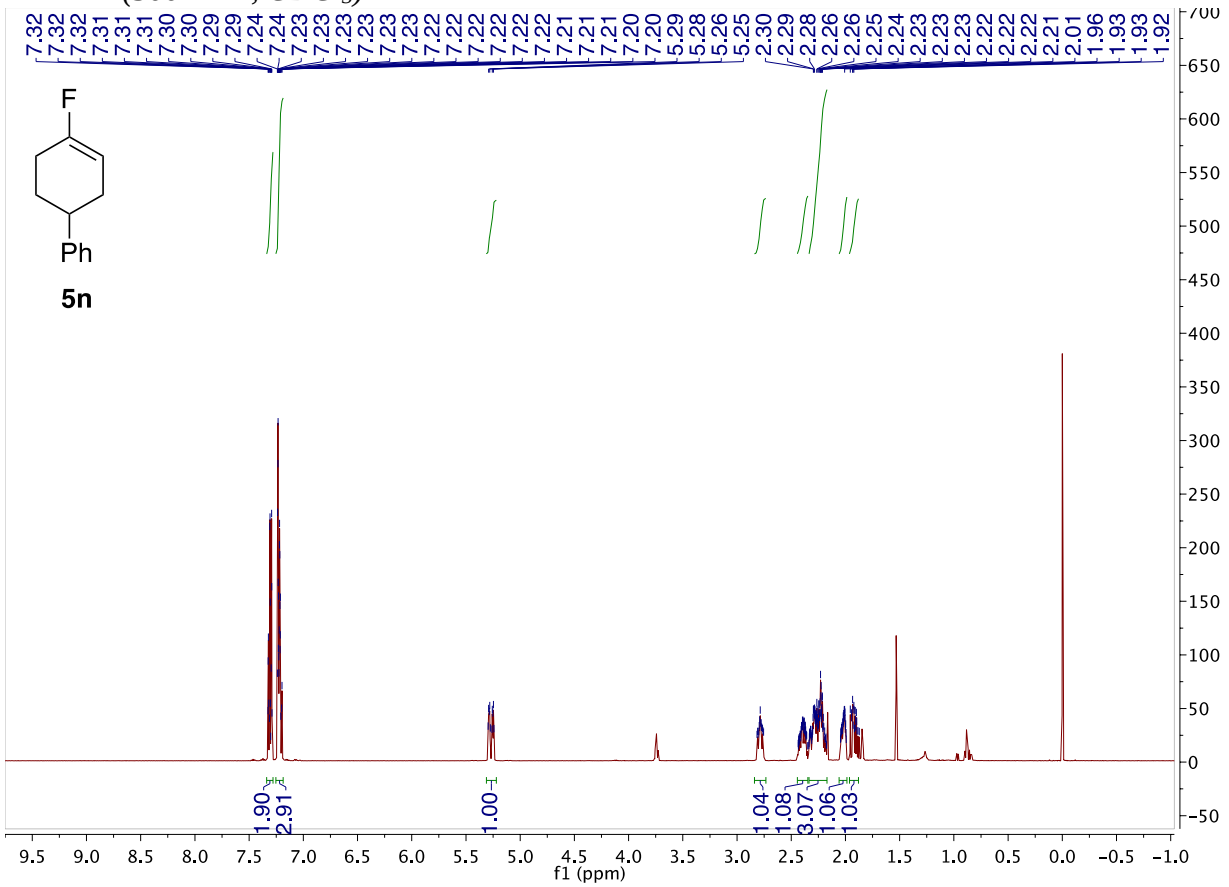
9-Fluoro-3,3-dimethyl-1,5-dioxaspiro[5.5]undec-8-ene (5m)

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



4-Fluoro-1,2,3,6-tetrahydro-1,1'-biphenyl (5n)

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



1-Fluoro-4-pentylcyclohex-1-ene (5o)

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