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Supporting Information

Visible light photocatalytic decarboxylative monofluoroalkenylation of α-amino acids with *gem*-difluoroalkenes

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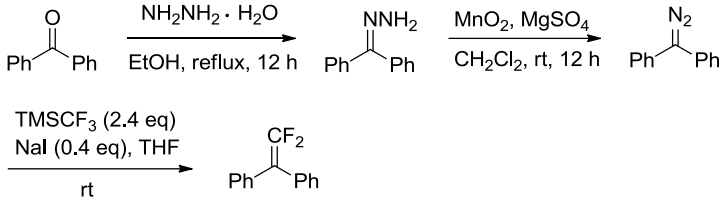
1. General procedures

All reactions were carried out in dry solvents under an atmosphere of argon unless otherwise indicated. Reagents including carbonyl compounds and *N*-protected amino acids (*N*-Boc-proline, *N*-Cbz-proline, *N*-Boc-glycine, *N*-Boc-alanine, *N*-Boc-phenylalanine, *N*-Boc-serine) were purchased from commercial sources. 1,1-Difluoroalkenes were prepared according to the previous procedures. *N*-Boc-pipecolinic acid and *N*-Boc-methionine were prepared according to the reported procedures. The reactions were monitored by thin layer chromatography (TLC) and the products were isolated by column chromatography on silica gel. High resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-IT/TOF quadrupole-time of flight mass spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on JNM-ECS 400 using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm).

2. General procedures for synthesis of 1,1-difluoroalkenes

Method A[1]



To a mixture of benzophenone (10 mmol, 1.82 g) and hydrazine monohydrate (80%, 6 mL, 100 mmol) in ethanol (20 mL) was added HOAc (0.2 mL), and the mixture was heated at reflux for 12 h. After cooling to room temperature, ethanol in the resulting solution was removed, and the residue was dissolved in ethyl acetate (50 mL). The separated organic phase was dried over anhydrous Na_2SO_4 and concentrated to give benzophenone hydrazone as a white solid.

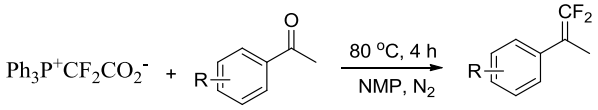
Mixed solution of benzophenone hydrazone (10 mmol, 1.96 g), anhydrous $MgSO_4$ (1.0 g) and CH_2Cl_2 (30 mL) was cooled to 0 ^{o}C. To this rapidly stirring mixture was added activated MnO_2 (21.5 mmol, 3.5 g) in one portion. The reaction mixture was

warmed to room temperature and kept stirring for 12 h, then the solid was filtered off and washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (pretreated with petroleum ether (PE) and Et_3N (PE/Et_3N = 10:1), final purification with PE/Et_3N = 20:1) to afford diphenyldiazomethane as a purple solid, which was kept at - 20 °C.

To a mixture of diphenyldiazomethane (5 mmol, 0.97 g) and NaI (2 mmol, 0.3 g) in THF (50 mL) under Ar was added $TMSCF_3$ (12 mmol, 1.77 mL) at room temperature, and the reaction mixture was stirred for 18 h until color of the reaction mixture was changed from purple to light yellow. Then ethyl acetate (50 mL) was added, and the mixture was washed with H_2O (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated, and the residue was purified by silica gel column chromatography.

1,1-Difluoroalkenes **2a**, **2i**, **2j**, **2m** and **2n** were prepared according to Method A.

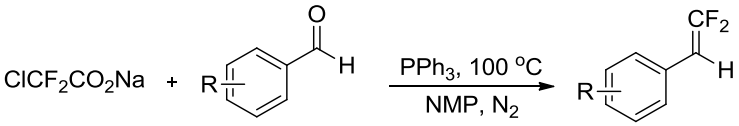
Method B[2]



To a 50 mL flask, (triphenylphosphonio)difluoroacetate (6 mmol, 2.14 g) and acetophenone (3 mmol) were mixed with NMP (6 mL). The mixture was degassed and filled with N_2. Then the reaction mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the reaction mixture was treated with 30% H_2O_2 (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated, and the residue was purified by silica gel column chromatography.

1,1-Difluoroalkenes **2o**, **2p** and **2ab** were prepared according to Method B.

Method C[3]



To a mixture of benzaldehyde (3 mmol) and triphenylphosphine (3.6 mmol, 0.94 mg) in *N*-methylpyrrolidone (6 mL) was added solid $ClCF_2CO_2Na$ (4.5 mmol, 0.68 mg)

slowly at 100 ºC under an argon atmosphere, and the reaction mixture was stirred at the same temperature for about 3 h. After completion of the reaction, the reaction mixture was treated with 30% H_2O_2 (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated, and the residue was purified by silica gel column chromatography.

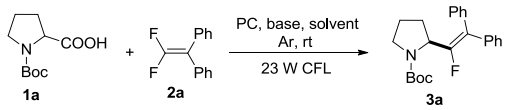
1,1-Difluoroalkenes **2q**-**2aa** were prepared according to Method C.

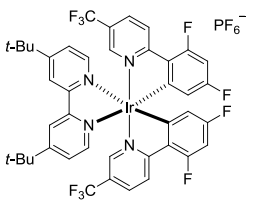
Preparation of 1-(*tert*-butoxycarbonyl)piperidine-2-carboxylic acid (2c) and 2-(*tert*-butoxycarbonyl)amino-4-(methylthio)butanoic acid (2h)[4]

To a mixture of α-amino acid (5 mmol) in dioxane (4 mL) and aqueous 1.25 M NaOH (4 mL) was added Boc_2O (5.25 mmol, 1.14 g) in dioxane (3 mL) at 0 ℃ in an ice bath under N_2. The mixture was stirred at room temperature for 18 h, and then the organic phase was evaporated in vacuo. The remaining aqueous layer was diluted with aqueous 1 M $KHSO_4$ (10 mL), and the solution was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to get product **2c** or **2h**.

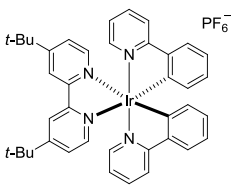
3. Optimization of conditions for photocatalytic decarboxylative monofluoroalkenylation

Table S1 Optimization of conditions for photocatalytic decarboxylative monofluoroalkenylation of *N*-Boc-proline (**1a**) with 1-(2,2-difluoro-1-phenylethenyl)benzene (**2a**)[a]





Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**A**)



Ir(ppy)$_2$(dtbbpy)PF$_6$ (**B**)

Entry	PC	Base.	Solvent	Yield (%)[b]

1	A	Cs_2CO_3	DMSO	33
2	A	Na_2CO_3	DMSO	59
3	A	$NaHCO_3$	DMSO	65
4	A	Li_2CO_3	DMSO	83
5	A	K_2CO_3	DMSO	44
6	A	K_3PO_4	DMSO	63
7	A	K_2HPO_4	DMSO	74
8	A	KH_2PO_4	DMSO	14
9	A	LiOH	DMSO	60
10	A	LiBr	DMSO	NR
11	A	^tBuOLi	DMSO	55
12	A	-	DMSO	NR
13	A	Li_2CO_3	DMF	70
14	A	Li_2CO_3	THF	7
15	A	Li_2CO_3	CH_2Cl_2	NR
16	A	Li_2CO_3	MeCN	NR
17	A	Li_2CO_3	toluene	NR
18	B	Li_2CO_3	DMSO	31
19	$Ir(ppy)_3$	Li_2CO_3	DMSO	5
20	$Ru(ppy)_3Cl_2$	Li_2CO_3	DMSO	NR
21	-	Li_2CO_3	DMSO	NR
22	A	Li_2CO_3	DMSO	75[c]
23	A	Li_2CO_3	DMSO	76[d]
24	A	Li_2CO_3	DMSO	74[e]
25	A	Li_2CO_3	DMSO	20[f]
26	A	Li_2CO_3	DMSO	NR[g]

[a] Reaction conditions: argon atmosphere and irradiation of visible light with 23 W CFL, *N*-Boc-proline (**1a**) (0.4 mmol), 1-(2,2-difluoro-1-phenylethenyl)benzene (**2a**) (0.2 mmol), photocatalyst (PC) (4 μmol), base (0.6 mmol), solvent (2 mL), temperature (rt, ~25 °C), time (36 h) in a sealed Schlenk tube. [b] Isolated yield. [c] PC (2 μmol). [d] Base (0.4 mmol). [e] Time (24 h). [f] The reaction was performed in air. [g] The reaction was carried out in the dark. DMSO = dimethyl sulfoxide. DMF = *N*,*N*-dimethylformamide. THF = tetrahydrofuran, *N*-Boc = *N*-*tert*-butoxycarbonyl. CFL = compact fluorescent light. NR = no reaction.

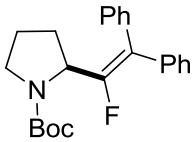
We started our investigation of the proposed reaction starting with *N*-tertbutoxycarbonyl proline (*N*-Boc-Pro) (**1a**) and 1-(2,2-difluoro-1-phenylethenyl) benzene (**2a**) under irradiation of visible light with photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)$ (**A**) and Cs_2CO_3 as base (Table 1). To our delight, we found that the decarboxylative monofluoroalkenylation of **1a** with *gem*-difluoroalkenes was feasible under this catalytic system, generating the target product **3a** in 33% yield (entry 1). To optimize the reaction conditions, a series of factors including bases,

photocatalysts and solvents were tested. Among various bases examined (entries 1-11), Li_2CO_3 provided a prominent increase in yield of the decarboxylative monofluoroalkenylation (entry 4, 83% yield). Indeed, literature suggests that the lithium ion is beneficial for the departure of the fluorine atom in related transformations.[5] No reaction occurred in the absence of base (entry 12). Next, the effect of solvents on the reaction was investigated (entries 13-17), showing that dimethylsulfoxide and dimethyl formamide (entries 4 and 10) were favourable to the progress of the reaction. However, the reaction did not work in dichloromethane, MeCN or toluene (entries 15-17). Other photocatalysts, $Ir(ppy)_2(dtbbpy)PF_6$ (**B**), $Ir(ppy)_3$ and $Ru(ppy)_3Cl_2$, were screened and gave poor results (entries 18-20). No reaction was observed in the absence of photocatalyst (entry 21). Yields decreased when the amount of photocatalyst **A** (entry 22) or base Li_2CO_3 (entry 23) was reduced. Shortening the reaction time led to a lower yield (entry 24). A poor result was obtained when the reaction was performed in air (entry 25) or in the absence of light (entry 26).

4. General procedures for synthesis of compounds 3a-ac

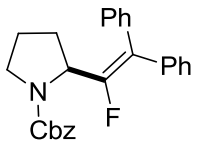
N-Protected α-amino acid **(1)** (0.4 mmol), substituted *gem*-difluoroalkene **(2)** (0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)$ (**A**) (4 μmol, 4.5 mg), Li_2CO_3 (0.6 mmol, 44 mg), DMSO (2.0 mL) were added to a 25-mL Schlenk tube. The tube was filled with argon and then sealed, and irradiated with a 23 W fluorescent lamp (approximately 2 cm away from the light source). After the complete conversion of the substrates (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product (**3a-ac**).

5. Characterization data of compounds 3a-ac and 7



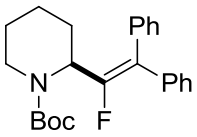
3a

***tert*-Butyl 2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxylate (3a):** Eluent: petroleum ether (PE)/ethyl acetate (EA) (20:1). Yield (61 mg, 83%). White solid, mp 125 - 126 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.36 – 7.21 (m, 10H), 4.46 - 4.39 (m, 1H), 3.53 – 3.46 (m, 2H), 2.22 – 2.16 (m, 2H), 2.05 – 1.95 (m, 1H), 1.81 – 1.73 (m, 1H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 156.67 (d, J = 264.54 Hz), 154.22, 137.90, 137.50, 130.65 (d, J = 1.92 Hz), 129.72 (d, J = 4.79 Hz), 128.37, 128.10, 127.60, 127.20, 119.99 (d, J = 14.38 Hz), 79.84 (79.20), 55.56 (d, J = 24.92 Hz), 47.37, 33.23 (31.78), 28.72, (24.38) 23.80; ^{19}F NMR ($CDCl_3$, 564 MHz) rotameric mixture: δ -122.07 (d, J = 26.31 Hz) (major), -122.75 (d, J = 23.02 Hz) (minor); HRMS (ESI): Calculated for $C_{23}H_{26}NNaO_2F$, $[M+Na]^+$ m/z 390.1840. Found 390.1843.



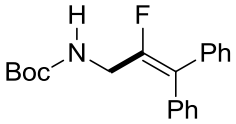
3b

Benzyl 2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxylate (3b): Eluent: PE/EA (20:1). Yield (60 mg, 75%). White solid, mp 87 – 88 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture. δ 7.41 - 7.17 (m, 14H), 6.92 (d, J = 6.87 Hz, 1H), 5.21 – 4.99 (m, 2H), 4.61 – 4.39 (m, 1H), 3.65 – 3.51 (m, 2H), 2.17 – 2.01 (m, 3H), 1.84 – 1.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 156.00 (d, J = 261.66 Hz) (major), 155.71 (d, J = 261.66 Hz) (minor), 154.70, 137.84 (major), 137.76 (minor), 137.01, 136.71, 130.55 (major), 130.32 (minor), 129.62 (major), 129.57 (minor), 128.60 (minor), 128.52 (major), 128.35, 128.10, 127.99, 127.73, 127.46, 127.19, 121.16 (d, J = 13.42 Hz) (minor), 120.58 (d, J = 12.46 Hz) (major), 67.14 (major), 66.78 (minor), 56.24 (d, J = 24.92 Hz) (minor), 55.54 (d, J = 24.92 Hz) (major), 47.73 (major), 47.24 (minor), 32.20 (major), 31.20 (minor), 24.60 (minor), 23.97 (major); ^{19}F NMR ($CDCl_3$, 564 MHz): rotameric mixture, δ -124.13 (d, J = 26.31 Hz) (major), -124.25 (d, J = 29.60 Hz) (minor); HRMS (ESI): Calculated for $C_{26}H_{25}FNO_2$, $[M+H]^+$ m/z 402.1864. Found 402.1864.



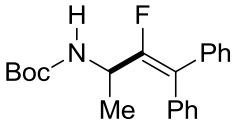
3c

***tert*-Butyl 2-(1-fluoro-2,2-diphenylvinyl)piperidine-1-carboxylate (3c):** Eluent: PE/EA (20:1). Yield (54 mg, 71%). White solid, mp 86 -87 ^{o}C.^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 – 7.20 (m, 10H), 5.10 – 5.02 (m, 1H), 4.02 (dd, J = 9.62 Hz, J = 3.21 Hz, 1H), 3.21 (tt, J = 12.82 Hz, J = 3.21 Hz, 1H), 1.97 – 1.92 (m, 1H), 1.78 – 1.66 (m, 4H), 1.47 – 1.41 (m, 1H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.14 (d, J = 270.29 Hz), 155.06, 137.92 (d, J = 7.67 Hz), 137.63, 130.27 (d, J = 1.92 Hz), 129.80 (d, J = 4.79 Hz), 128.49, 128.04, 127.54, 127.17, 120.96 (d, J = 15.34 Hz), 79.77, 49.22 (d, J = 22.04 Hz), 41.78 (d, J = 4.79 Hz), 29.69, 28.38, 24.91, 20.43; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -108.65; HRMS (ESI): Calculated for $C_{24}H_{28}FNNaO_2$, $[M+Na]^+$ m/z 404.1996. Found 404.1995.



3d

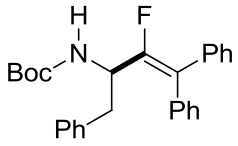
***tert*-Butyl (2-fluoro-3,3-diphenylallyl)carbamate (3d):** Eluent: PE/EA (20:1). Yield (39 mg, 60%). White solid, mp 76 - 77 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) 7.38 – 7.31 (m, 3H), 7.29 – 7.23 (m, 5H), 7.20 – 7.18 (m, 2H), 4.75 (brs, 1H), 4.00 (dd, J = 19.23 Hz, J = 5.50 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.54, 153.30 (d, J = 261.66 Hz), 137.64 (d, J = 6.71 Hz), 136.84, 130.25 (d, J = 2.88 Hz), 129.72 (d, J = 4.79 Hz), 128.68, 128.14, 127.91, 127.52, 122.94 (d, J = 13.42 Hz), 79.85, 40.14 (d, J = 27.80 Hz), 28.46; ^{19}F NMR ($CDCl_3$, 564 MHz): δ -113.47 (t, J = 19.51 Hz); HRMS (ESI): Calculated for $C_{20}H_{22}NNaO_2F$, $[M+Na]^+$ m/z 350.1527. Found 350.1529.



3e

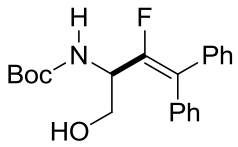
***tert*-Butyl (3-fluoro-4,4-diphenylbut-3-en-2-yl)carbamate (3e):** Eluent: PE/EA

(20:1). Yield (51 mg, 75%). White solid, mp 89 - 90 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 – 7.23 (m, 10H), 4.84 (brs, 1H), 4.61 – 4.50 (m, 1H), 1.44 (s, 9H), 1.35 (d, J = 6.87 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.17 (d, J = 262.62 Hz), 154.51, 137.46, 137.05, 130.25 (d, J = 2.88 Hz), 129.72 (d, J = 4.79 Hz), 128.66, 128.11, 127.82, 127.37, 120.45 (d, J = 14.38 Hz), 79.59, 45.84 (d, J = 27.80 Hz), 28.47, 19.64; ^{19}F NMR ($CDCl_3$, 564 MHz): δ -125.42 (d, J = 26.31 Hz); HRMS (ESI): Calculated for $C_{21}H_{24}NNaO_2F$, $[M+Na]^+$ m/z 364.1683. Found 364.1682.



3f

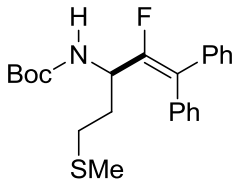
***tert*-Butyl (3-fluoro-1,4,4-triphenylbut-3-en-2-yl)carbamate (3f):** Eluent: PE/EA (20:1). Yield (70 mg, 84%). White solid, mp 85 - 86 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) rotameric mixture: δ 7.30 – 7.18 (m, 11H), 7.11 – 7.10 (m, 2H), 6.77 (m, 2H), 5.00 (brs, 1H), 4.70 – 4.61 (m, 1H), 2.97 – 2.94 (m, 2H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.46, 153.82 (d, J = 263.58 Hz), 137.02, 130.06 (d, J = 1.92 Hz), 129.64, 129.45 (d, J = 4.79 Hz), 128.46, 128.29, 128.06, 127.58, 127.37, 126.76, 122.60 (d, J = 12.46 Hz), 79.75, 51.73 (d, J = 25.88 Hz), 39.75, 28.44; ^{19}F NMR ($CDCl_3$, 564 MHz): δ -125.06 (d, J = 28.18 Hz); ESI: Calculated for $C_{27}H_{28}FNNaO_2$, $[M+Na]^+$ m/z 440.21. Found 440.25.



3g

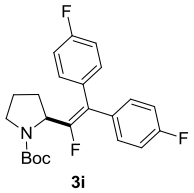
***tert*-Butyl (3-fluoro-1-hydroxy-4,4-diphenylbut-3-en-2-yl)carbamate (3g):** Eluent: PE/EA (2:1). Yield (53 mg, 82%). White solid, mp 129 - 130 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 – 7.23 (m, 10H), 5.08 (brs, 1H), 4.62 – 4.54 (m, 1H), 3.76 – 3.68 (m, 2H), 2.40 (m, 1H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.43, 153.47 (d, J = 261.66 Hz), 137.21, 136.72, 130.28 (d, J = 2.88 Hz), 129.70 (d, J = 4.79 Hz), 128.74, 128.15, 128.00, 127.62, 123.37 (d, J = 13.42 Hz), 80.25, 63.96, 52.11 (d, J = 23 Hz), 28.41; ^{19}F NMR ($CDCl_3$, 564 MHz): δ -122.29 (d, J = 23.84 Hz); ESI:

Calculated for $C_{21}H_{24}FNNaO_3$, $[M+Na]^+$ m/z 380.17. Found 380.15.



3h

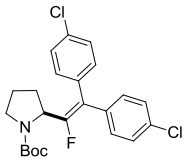
***tert*-Butyl (3-fluoro-1-(methylthio)-4,4-diphenylbut-3-en-2-yl)carbamate (3h):** Eluent: PE/EA (20:1). Yield (60 mg, 75%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 – 7.21 (m, 10H), 4.92 – 4.90 (m, 1H), 4.66 – 4.53 (m, 1H), 2.50 – 2.43 (m, 2H), 2.02 (s, 3H), 2.00 – 1.91 (m, 2H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.78 (d, J = 264.54 Hz), 154.64, 137.19, 136.89, 130.30 (d, J = 1.92 Hz), 129.65 (d, J = 5.75 Hz), 128.68, 128.14, 127.92, 127.51, 122.05 (d, J = 16.29 Hz), 79.79, 49.53 (d, J = 24.92 Hz), 33.43, 30.38, 28.43, 15.54; ^{19}F NMR ($CDCl_3$, 564 MHz): δ 123.96 (d, J = 30.34 Hz). ESI: Calculated for $C_{23}H_{28}FNNaO_2S$, $[M+Na]^+$ m/z 424.18. Found 424.15.



3i

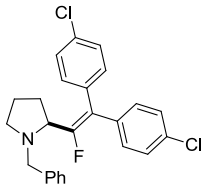
***tert*-Butyl 2-(1-fluoro-2,2-bis(4-fluorophenyl)vinyl)pyrrolidine-1-carboxylate (3i):** Eluent: PE/EA (20:1). Yield (73 mg, 91%). White solid, mp 134 -135 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.34 – 7.16 (m, 4H), 7.05 (t, J = 8.70 Hz, 2H), 7.00 – 6.96 (m, 2H), 4.41 – 4.35 (m, 1H), 3.54 – 3.44 (m, 2H), 2.21 – 2.13 (m, 2H), 2.04 – 1.95 (m, 1H), 1.81 – 1.75 (m, 1H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 162.33 (d, J = 247.03 Hz), 161.85 (d, J = 247.03 Hz), 156.84 (d, J = 266.20 Hz), 154.06, 133.67, 133.28, 132.27, 131.32 (dd, J = 7.67 Hz, J = 5.37 Hz), 118.17 (d, J = 15.34 Hz), 115.54 (d, J = 21.48 Hz), 115.15 (d, J = 20.71 Hz), 79.89 (79.34), 55.49 (d, J = 24.55 Hz), 47.40, 33.13 (31.55), 28.71, (24.46) 23.80; ^{19}F NMR ($CDCl_3$, 564 MHz): rotameric mixture, δ -113.83 (s) (major), -114.62 (s) (minor), -114.28 (s) (major), -114.80 (s) (minor), -121,58 (d, J = 24.66 Hz) (major), -122.62 (d, J = 24.66 Hz) (minor); ESI: Calculated for $C_{23}H_{25}F_3NO_2$, $[M+H]^+$ m/z

404.18. Found 404.10.



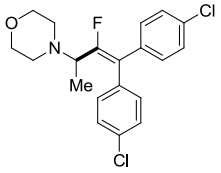
3j

***tert*-Butyl 2-(2,2-bis(4-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate (3j):** Eluent: PE/EA (20:1). Yield (84 mg, 96%). White solid, mp 99 - 100 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.34 - 7.22 (m, 5H), 7.16 – 7.12 (m, 3H), 4.39 – 4.33 (m, 1H), 3.53 – 3.43 (m, 2H), 2.20 – 1.94 (m, 3H), 1.80 – 1.73 (m, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 157.30 (d, J = 269.33 Hz), 153.99, 135.83, 135.46, 133.92, 133.25, 131.90, 130.95 (d, J = 5.75 Hz), 128.81, 128.43, 118.04 (d, J = 15.34 Hz), 79.98 (79.42), 55.50 (d, J = 23.96 Hz), 47.40, 33.12 (31.46), 28.69, (24.52) 23.79; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -119.98 (d, J = 26.01 Hz) (major), -121.09 (d, J = 26.01 Hz) (minor); ESI: Calculated for $C_{23}H_{25}Cl_2FNO_2$, $[M+H]^+$ m/z 436.12. Found 436.10.



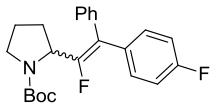
3k

1-Benzyl-2-(2,2-bis(4-chlorophenyl)-1-fluorovinyl)pyrrolidine (3k): Eluent: PE/EA (20:1). Yield (38 mg, 45%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, J = 8.70 Hz, 2H), 7.30 – 7.21 (m, 7H), 7.08 (d, J = 8.70 Hz, 2H), 7.00 (d, J = 8.24 Hz, 2H), 3.84 (d, J = 13.28 Hz, 1H), 3.36 (d, J = 13.28 Hz, 1H), 3.28 (dt, J = 28.39 Hz, J = 8.24 Hz, 1H), 3.04 – 3.00 (m, 1H), 2.28 – 2.22 (m, 1H), 2.12 – 2.08 (m, 1H), 2.03 – 1.90 (m, 2H), 1.77 – 1.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.17 (d, J = 267.41 Hz), 139.11, 136.35 (d, J = 7.67 Hz), 135.47, 133.82, 133.18, 131.87 (d, J = 2.88 Hz), 131.00 (d, J = 4.79 Hz), 128.87 (d, J = 3.83 Hz), 128.29 (d, J = 1.92 Hz), 127.12, 120.89 (d, J = 15.34 Hz), 62.04 (d, J = 23.00 Hz), 58.26, 54.02, 29.14, 23.19; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -119.76 (d, J = 26.01 Hz); HRMS (ESI): Calculated for $C_{25}H_{23}Cl_2FN$, $[M+H]^+$ m/z 426.1186. Found 426.1188.



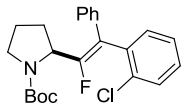
3l

4-(4,4-Bis(4-chlorophenyl)-3-fluorobut-3-en-2-yl)morpholine (3l): Eluent: PE/EA (10:1). Yield (36.6 mg, 48%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, J = 8.24 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.18 – 7.16 (m, 2H), 7.10 (d, J = 8.24 Hz, 2H), 3.72 – 3.62 (m, 4H), 3.30 (dq, J = 31.60 Hz, J = 6.87 Hz, 1H), 2.62 – 2.59 (m, 2H), 2.42 – 2.39 (m, 2H), 1.32 (d, J = 6.87 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.89 (d, J = 273.16 Hz), 136.41 (d, J = 8.63 Hz), 135.13, 133.98, 133.38, 131.70 (d, J = 2.88 Hz), 130.96 (d, J = 5.75 Hz), 129.05, 128.42, 67.39, 58.22 (d, J = 23.00 Hz), 50.50, 14.87; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -114.82 (d, J = 26.00 Hz); HRMS (ESI): Calculated for $C_{20}H_{21}Cl_2FNO$, $[M+H]^+$ m/z 380.0979. Found 380.0981.



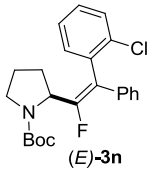
3m

***tert*-Butyl 2-(1-fluoro-2-(4-fluorophenyl)-2-phenylvinyl)pyrrolidine-1-carboxylate (3m):** *Z*/*E* = 2:3. Eluent: PE/EA (20:1). Yield (66 mg, 86%). White solid, mp 107 – 108 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 4H), 7.04 (t, J = 8.70 Hz, 1H), 6.99 – 6.95 (m, 1H), 4.44 – 4.37 (m, 1H), 3.53 – 3.45 (m, 2H), 2.21 – 2.14 (m, 2H), 2.03 – 1.94 (m, 1H), 1.79 – 1.73 (m, 1H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 162.26 (d, J = 247.28 Hz), 161.78 (d, J = 247.28 Hz), 156.82 (d, J = 265.50 Hz), 156.70 (d, J = 269.33 Hz), 154.12, 137.60, 137.30, 133.87, 133.47, 132.30, 131.45 – 131.32 (m), 130.58 (d, J = 2.88 Hz), 129.64 (d, J = 4.79 Hz), 128.48, 128.18, 127.75, 127.34, 119.12, 115.41 (d, J = 21.09 Hz), 115.04 (d, J = 21.09 Hz), 79.85, 55.54 (d, J = 23.96 Hz), 47.38, 33.20, 28.72, 23.80; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -114.11 (major), -114.56 (major), -114.89 (minor), -115.07 (minor), -121.42 (d, J = 26.31 Hz) (major), -122.26 (d, J = 26.31 Hz, 1H), -123.06 (d, J = 26.31 Hz) (minor); ESI: Calculated for $C_{23}H_{26}F_2NO_2$, $[M+H]^+$ m/z 386.19. Found 386.10.



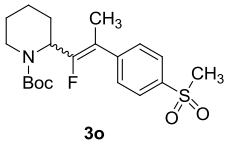
(*Z*)-**3n**

***cis-tert*-Butyl 2-(2-(2-chlorophenyl)-1-fluoro-2-phenylvinyl)pyrrolidine-1-Carboxylate ((*Z*)-3n):** Eluent: PE/EA (20:1). Yield (18 mg, 22%). White solid, mp 117 – 118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.77 – 7.21 (m, 9H), 4.40 – 4.12 (m, 1H), 3.54 – 3.27 (m, 2H), 2.08 – 1.96 (m, 3H), 1.72 – 1.62 (m, 1H), 1.46 – 1.43 (m, 9H); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ – 120.90 (d, *J* = 19.73 Hz) (minor), – 123.25 (d, *J* = 24.66 Hz) (major); HRMS (ESI): Calculated for $C_{23}H_{25}ClFNNaO_2$, $[M+Na]^+$ m/z 424.1450. Found 424.1455.



(*E*)-**3n**

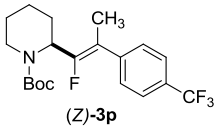
***trans-tert*-Butyl 2-(2-(2-chlorophenyl)-1-fluoro-2-phenylvinyl)pyrrolidine-1-Carboxylate ((*E*)-3n):** Eluent: PE/EA (20:1). Yield (57 mg, 71%). White solid, mp 96 – 97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.44 – 7.38 (m, 2H), 7.32 – 7.23 (m, 7H), 4.74 (dt, *J* = 27.02 Hz, *J* = 6.41 Hz, 1H), 3.53 – 3.44 (m, 2H), 2.27 – 2.14 (m, 2H), 2.05 – 2.00 (m, 1H), 1.83 – 1.81 (m, 1H), 1.51 – 1.39 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 157.58 (d, *J* = 256.87 Hz), 154.20, 136.66, 136.49, 134.12, 131.65, 129.90, 129.76, 128.92, 128.28, 127.46, 126.68, 118.04 (d, *J* = 26.84 Hz), 79.94 (79.23), 54.74 (d, *J* = 23.96 Hz), 47.27, 32.75 (major), 31.26 (minor), 28.69, (24.43) 23.81; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -114.52 (major), -115.10 (minor); HRMS (ESI): Calculated for $C_{23}H_{25}ClFNNaO_2$, $[M+Na]^+$ m/z 424.1450. Found 424.1455.



3o

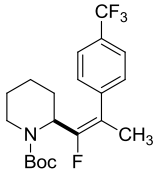
(*E/Z*)**-tert-Butyl 2-(1-fluoro-2-(4-(methylsulfonyl)phenyl)prop-1-en-1-yl)piperidine-1-carboxylate (3o):** *Z/E* = 1:1. Eluent: PE/EA (20:1). Yield (72 mg, 91%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (t, *J* = 8.24 Hz, 2H), 7.46 (d, *J* =

8.24 Hz, 1H), 7.39 (d, *J* = 8.24 Hz, 1H), 5.13 (dd, *J* = 29.31 Hz, *J* = 5.04 Hz, 0.5H), 4.81 (d, *J* = 28.39 Hz, 0.5H), 3.95 (dd, *J* = 13.17 Hz, *J* = 2.99 Hz, 0.5H), 3.84 (d, *J* = 10.53 Hz, 0.5H), 3.04 – 2.94 (m, 4H), 1.98 (d, *J* = 2.75 Hz, 1.5H), 1.90 (d, *J* = 3.66 Hz, 1.5H), 1.81 – 1.69 (m, 1H), 1.60 – 1.56 (m, 4H), 1.45 – 1.36 (m, 5.5H), 1.24 – 1.17 (m, 4.5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.99 (d, *J* = 263.58 Hz), 158.50 (d, *J* = 265.50 Hz), 154.82, 154.48, 145.08 (d, *J* = 9.58 Hz), 144.03, 139.01, 138.55, 129.27 (d, *J* = 2.88 Hz), 129.08 (d, *J* = 4.79 Hz), 127.43, 127.03, 114.06 (d, *J* = 21.09 Hz), 111.89 (d, *J* = 11.50 Hz), 79.85, 79.55, 48.16 (d, *J* = 23.00 Hz), 44.37 (d, *J* = 5.75 Hz), 41.54, 29.17, 28.35, 28.13, 28.04, 24.65, 20.20, 20.15, 16.36, 16.25; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -107.03 – -108.19 (m), -109.80 (d, *J* = 26.01 Hz); HRMS (ESI): Calculated for $C_{20}H_{28}FNNaO_4S$, $[M+Na]^+$ m/z 420.1615. Found 420.1615.



(*Z*)-**3p**

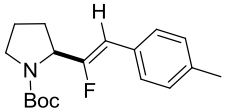
***cis-tert*-Butyl 2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)piperidine-1-carboxylate ((*Z*)-3p):** Eluent: PE/EA (20:1). Yield (15.4 mg, 20%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 – 7.56 (m, 2H), 7.44 – 7.42 (m, 2H), 5.24 – 5.16 (m, 1H), 4.04 – 4.01 (m, 1H), 3.09 – 3.02 (m, 1H), 2.05 – 2.02 (m, 3H), 1.90 – 1.67 (m, 6H), 1.48 – 1.47 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.18 (d, *J* = 263.58 Hz), 155.12, 142.18, 129.03 (q, *J* = 32.59 Hz), 128.69 (d, *J* = 3.83 Hz), 125.10 (d, *J* = 2.88 Hz), 124.31 (q, *J* = 271.25 Hz), 112.44 (d, *J* = 12.46 Hz), 80.07, 48.39 (d, *J* = 23.00 Hz), 41.80, 28.61, 28.37, 24.95, 20.44, 16.70 (d, *J* = 3.83 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ -62.44 (s, 3H), -110.79 (d, *J* = 34.68 Hz, 1H); ESI: Calculated for $C_{20}H_{26}F_4NO_2$, $[M+H]^+$ m/z 388.18. Found 388.10.



(*E*)-**3p**

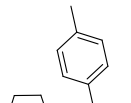
***trans-tert*-Butyl 2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)piperidine-1-carboxylate ((*E*)-3p):** Eluent: PE/EA (20:1). Yield (41.5 mg, 54%). White solid, mp 68 – 69 ^{o}C ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.33 Hz, 2H), 7.34 (d,

J = 7.33 Hz, 2H), 4.89 (d, *J* = 31.14 Hz, 1H), 3.92 (d, *J* = 12.82 Hz, 1H), 3.11 – 3.05 (m, 1H), 1.96 – 1.94 (m, 3H), 1.80 – 1.62 (m, 5H), 1.38 – 1.35 (m, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.90 (d, *J* = 262.62 Hz), 154.76, 143.25 (d, *J* = 8.63 Hz), 129.35 (q, *J* = 32.59 Hz), 128.83 (d, *J* = 2.88 Hz), 125.47 (d, *J* = 2.88 Hz), 124.26 (q, *J* = 272.20 Hz), 114.57 (d, *J* = 21.09 Hz), 79.72, 48.40 (d, *J* = 23 Hz), 41.68 (d, *J* = 3.83 Hz), 29.44, 28.27, 24.96, 20.52, 16.55 (d, *J* = 8.63 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ -62.54 (s, 3H), -108.68 – -109.75 (m, 1H); ESI: Calculated for $C_{20}H_{26}F_4NO_2$, $[M+H]^+$ m/z 388.18. Found 388.10.



(*Z*)-**3q**

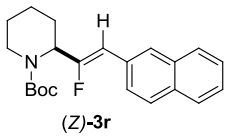
***cis-tert*-Butyl 2-(1-fluoro-2-(*p*-tolyl)vinyl)pyrrolidine-1-carboxylate ((*Z*)-3q):** Eluent: PE/EA (20:1). Yield (24 mg, 39%). White solid, mp 78 – 79 ^{o}C ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.36 (d, *J* = 7.79 Hz, 2H), 7.13 (d, *J* = 6.87 Hz, 2H), 5.52 (d, *J* = 38.93 Hz, 1H), 4.52 – 4.34 (m, 1H), 3.50 – 3.49 (m, 2H), 2.33 (s, 3H), 2.09 – 1.98 (m, 3H), 1.90 – 1.84 (m, 1H), 1.47 – 1.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 159.09 (d, *J* = 267.41 Hz), 154.43, 136.94, 130.46, 129.30, 128.47, 105.60, 79.92, 58.30 (d, *J* = 32.59 Hz), (46.82) 46.48, 30.61 (29.85), 28.52, (24.06) 23.24, 21.32; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -116.85 (dd, *J* = 39.01 Hz, *J* = 17.34 Hz); ESI: Calculated for $C_{18}H_{24}FNNaO_2$, $[M+Na]^+$ m/z 328.18. Found 328.15.



(*E*)-**3q**

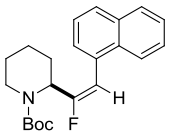
***trans-tert*-Butyl 2-(1-fluoro-2-(*p*-tolyl)vinyl)pyrrolidine-1-carboxylate ((*E*)-3q):** Eluent: PE/EA (20:1). Yield (19 mg, 31%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.29 – 7.11 (m, 4H), 6.18 (d, *J* = 21.52 Hz, 1H), 4.78 – 4.71 (m, 1H), 3.52 – 3.43 (m, 2H), 2.33 (s, 3H), 2.25 – 1.96 (m, 3H), 1.85 – 1.79 (m, 1H), 1.46 – 1.25 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 160.70 (d, *J* = 261.66 Hz), 154.21, 136.72, 130.50 (d, *J* = 12.46 Hz), 129.21, 128.70, 108.13 (d, *J* =

28.75 Hz), 79.92 (79.47), 54.24 (d, *J* = 24.92 Hz), 47.46 (minor), 47.10 (major), 32.26 (major), 31.51 (minor), 28.50, 24.45 (minor), 23.95 (major), 21.26; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -116.70 – -116.87 (m) (minor), -117.47 – -117.64 (m) (major); ESI: Calculated for $C_{18}H_{24}FNNaO_2$, $[M+Na]^+$ m/z 328.18. Found 328.15.



(*Z*)-**3r**

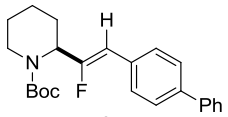
***cis-tert*-Butyl 2-(1-fluoro-2-(naphthalen-2-yl)vinyl)piperidine-1-carboxylate ((*Z*)-3r):** Eluent: PE/EA (20:1). Yield (38 mg, 54%). White solid, mp 82 – 83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (s, 1H), 7.83 – 7.80 (m, 3H), 7.69 – 7.67 (m, 1H), 7.49 – 7.45 (m, 2H), 5.73 (d, *J* = 39.84 Hz, 1H), 5.15 – 5.07 (m, 1H), 4.12 (d, *J* = 12.36 Hz, 1H), 3.03 (t, *J* = 12.82 Hz, 1H), 2.16 (d, *J* = 13.28 Hz, 1H), 1.75 – 1.61 (m, 4H), 1.52 – 1.49 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.75 (d, *J* = 273.16 Hz), 155.30, 133.54, 132.49, 130.81, 128.06 (d, *J* = 3.83 Hz), 127.61, 127.53, 126.65 (d, *J* = 7.67 Hz), 126.22, 126.00, 107.03 (d, *J* = 7.67 Hz), 80.18, 51.80 (d, *J* = 24.92 Hz), 40.63, 28.50, 26.26, 25.27, 19.96; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -109.37 (d, *J* = 43.35 Hz,); ESI : Calculated for $C_{22}H_{26}FNNaO_2$, $[M+Na]^+$ m/z 378.19. Found 378.20.



(*E*)-**3r**

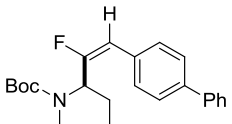
***trans-tert*-Butyl 2-(1-fluoro-2-(naphthalen-2-yl)vinyl)piperidine-1-carboxylate ((*E*)-3r):** Eluent: PE/EA (20:1). Yield (25 mg, 35%). White solid, mp 99 – 100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 – 7.79 (m, 3H), 7.68 (s, 1H), 7.50 – 7.43 (m, 2H), 7.37 (d, *J* = 8.24 Hz, 1H), 6.36 (d, *J* = 23.81 Hz, 1H), 5.36 (dd, *J* = 30.22 Hz, *J* = 4.58 Hz, 1H), 4.00 (dd, *J* = 13.05 Hz, *J* = 2.75 Hz, 1H), 3.15 (tt, *J* = 13.28 Hz, *J* = 3.21 Hz, 1H), 2.04 – 2.00 (m, 1H), 1.88 – 1.81 (m, 1H), 1.79 – 1.71 (m, 3H), 1.51 – 1.42 (m, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.52 (d, *J* = 263.58 Hz), 155.12, 133.49, 132.40, 131.00, 128.18, 127.92, 127.66, 127.36 (d, *J* = 2.88 Hz), 126.82 (d, *J* = 1.92 Hz), 126.34, 126.00, 108.77 (d, *J* = 27.80 Hz), 79.85, 48.30 (d, *J* = 23.00 Hz), 41.87, 29.12, 28.16, 24.88, 20.43; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -102.24 (t, *J* =

26.01 Hz); ESI: Calculated for $C_{22}H_{26}FNNaO_2$, $[M+Na]^+$ m/z 378.19. Found 378.20.



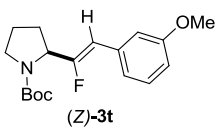
(*Z*)-**3s**

***cis-tert*-Butyl 2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)piperidine-1-carboxylate ((*Z*)-3s):** Eluent: PE/EA (20:1). Yield (40 mg, 52%). White solid, mp 119 – 120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 – 7.57 (m, 6H), 7.46 (t, J = 7.23 Hz, 2H), 7.36 (t, J = 7.33 Hz, 1H), 5.62 (dd, J = 40.30 Hz, J = 0.92 Hz, 1H), 5.11 – 5.06 (m, 1H), 4.11 (d, J = 12.82 Hz, 1H), 3.00 (t, J = 12.82 Hz, 1H), 2.14 (d, J = 13.28 Hz, 1H), 1.74 – 1.59 (m, 4H), 1.54 – 1.48 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.64 (d, J = 273.11 Hz), 155.27, 140.74, 139.87, 132.33, 129.02 (d, J = 7.67 Hz), 128.87, 127.40, 127.19, 127.02, 106.56 (d, J = 7.67 Hz), 80.16, 51.75 (d, J = 33.75 Hz), 40.59, 28.49, 26.23, 25.26, 19.95; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -109.30 (d, J = 34.68 Hz); ESI: Calculated for $C_{24}H_{29}FNO_2$, $[M+H]^+$ m/z 382.21. Found 382.10.



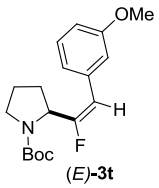
(*E*)-**3s**

***trans-tert*-Butyl 2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)piperidine-1-carboxylate ((*E*)-3s):** Eluent: PE/EA (20:1). Yield (31 mg, 41%). White solid, mp 99 – 100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 – 7.56 (m, 4H), 7.44 (t, J = 7.33 Hz, 2H), 7.37 – 7.29 (m, 3H), 6.24 (d, J = 23.36 Hz, 1H), 5.32 (dd, J = 31.14 Hz, J = 4.58 Hz, 1H), 4.02 (dd, J = 11.22 Hz, J = 3.21 Hz, 1H), 3.14 (tt, J = 12.82 Hz, J = 2.75 Hz, 1H), 2.01 – 1.98 (m, 1H), 1.89 – 1.72 (m, 4H), 1.50 – 1.42 (m, 1H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.49 (d, J = 263.58 Hz), 155.09, 140.75, 139.92, 132.50 (d, J = 13.42 Hz), 129.01 (d, J = 2.88 Hz), 128.90, 127.44, 127.30, 127.02, 108.33 (d, J = 27.80 Hz), 79.88, 48.09 (d, J = 22.04 Hz), 41.78, 29.12, 28.17, 24.87, 20.41; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -102.27 (t, J = 26.01 Hz); ESI: Calculated for $C_{24}H_{29}FNO_2$, $[M+H]^+$ m/z 382.21. Found 382.10.



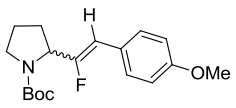
(*Z*)-**3t**

***cis-tert*-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate ((*Z*)-3t):** Eluent: PE/EA (20:1). Yield (28 mg, 43.5%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.25 – 7.20 (m, 1H), 7.03 – 7.01 (m, 2H), 6.78 – 6.77 (m, 1H), 5.51 (d, J = 38.47 Hz, 1H), 4.47 – 4.37 (m, 1H), 3.79 (s, 3H), 3.49 – 3.48 (m, 2H), 2.20 – 1.99 (m, 3H), 1.88 – 1.85 (m, 1H), 1.46 – 1.41 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 159.83 (d, J = 279.87 Hz), 159.69, 154.39, 134.56, 129.50, 121.18, 113.86 (d, J = 7.67 Hz), 112.98, 105.65, 79.98, 58.28 (d, J = 31.63 Hz), 55.28, 46.79 (minor), 46.48 (major), 30.60 (major), 29.65 (minor), 28.52, 24.00 (minor), 23.22 (major); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -114.99 (dd, J = 39.01 Hz, J = 13.00 Hz); ESI: Calculated for $C_{18}H_{24}FNNaO_3$, $[M+Na]^+$ m/z 344.17. Found 344.20.



(*E*)-3t

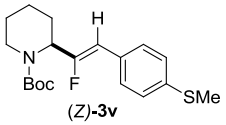
***trans-tert*-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate ((*E*)-3t):** Eluent: PE/EA (20:1). Yield (28 mg, 43.5%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) rotameric mixture: δ 7.26 – 7.22 (m, 1H), 7.14 – 6.97 (m, 1H), 6.80 – 6.75 (m, 2H), 6.19 (d, J = 21.52 Hz, 1H), 4.81 – 4.74 (m, 1H), 3.80 (s, 3H), 3.53 – 3.44 (m, 2H), 2.26 – 1.98 (m, 3H), 1.86 – 1.82 (m, 1H), 1.46 – 1.31 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 161.36 (d, J = 264.54 Hz), 159.62, 154.18, 134.85 (d. J = 12.46 Hz), 129.47, 121.35, 114.78, 112.19, 108.15 (d, J = 26.84 Hz), 79.96 (79.52), 55.32, 54.23 (d, J = 23.00 Hz), 47.39 (minor), 47.09 (major), 32.24 (major), 31.28 (minor), 28.49, 24.54 (minor), 23.94 (major); ^{19}F NMR ($CDCl_3$, 282 MHz) rotameric mixture: δ -116.83 (m) (minor), -116.38 (m) (major); ESI: Calculated for $C_{18}H_{24}FNNaO_3$, $[M+Na]^+$ m/z 344.17. Found 344.20.



3u

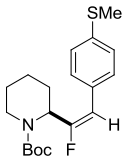
***tert*-Butyl 2-(1-fluoro-2-(4-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate (3u):** *Z*/*E* = 3:2. Eluent: PE/EA (20:1). Yield (43 mg, 67%). Colorless oil. ^{1}H NMR ($CDCl_3$,

400 MHz): rotameric mixture, δ 7.40 – 7.38 (d, J = 8.7 Hz, 2.5H), 7.13 – 7.11 (m, 0.67H), 6.85 (d, J = 8.7 Hz, 3.5H), 6.15 (d, J = 21.52 Hz, 0.66H), 5.47 (d, J = 38.75 Hz, 1H), 4.76 – 4.69 (m, 0.68H), 4.49 – 4.32 (m, 1H), 3.79 (s, 5H), 3.48 – 3.44 (m, 3.33H), 2.23 – 1.97 (m, 5H), 1.88 – 1.80 (m, 1.69H), 1.47 – 1.29 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 158.63, 158.28 (d, J = 270.29 Hz), 154.45, 154.21, 129.94, 129.81, 126.02, 125.90, 113.98, 107.74 (d, J = 35.46 Hz), 105.23, 79.88, 58.29 (d, J = 27.80 Hz), 55.35, 54.15 (d, J = 14.38 Hz), 47.09, 46.48, 32.21, 30.61, 28.53, 23.96, 23.25; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -117.62 – -117.81 (m) (minor), -118.42 – -118.59 (m) (major), -118.84 (dd, J = 39.01 Hz, J = 13.00 Hz); ESI: Calculated for $C_{18}H_{24}FNNaO_3$, $[M+Na]^+$ m/z 344.17. Found 344.20.



(*Z*)-**3v**

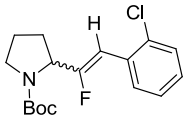
***cis-tert*-Butyl 2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)piperidine-1-carboxylate ((*Z*)-3v):** Eluent: PE/EA (20:1). Yield (29 mg, 41%). White solid, mp 79 – 80 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.40 (d, J = 8.24 Hz, 2H), 7.20 (d, J = 8.24 Hz, 2H), 5.49 (d, J = 39.84 Hz, 1H), 5.05 – 4.97 (m, 1H), 4.05 (d, J = 12.82 Hz, 1H), 2.94 (t, J = 12.82 Hz, 1H), 2.47 (s, 3H), 2.10 – 2.07 (m, 1H), 1.72 – 1.65 (m, 4H), 1.57 – 1.50 (m, 1H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.29 (d, J = 272.20 Hz), 155.27, 137.36, 130.14, 128.98 (d, J = 7.67 Hz), 126.60, 106.38 (d, J = 7.67 Hz), 80.15, 40.58 (d, J = 29.71 Hz), 40.58, 28.49, 26.21, 25.25, 19.93, 15.86; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -109.86 (d, J = 43.35 Hz); ESI: Calculated for $C_{19}H_{27}FNO_2S$, $[M+H]^+$ m/z 352.17. Found 352.10.



(*E*)-**3v**

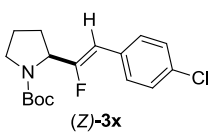
***trans-tert*-Butyl 2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)piperidine-1-carboxylate ((*E*)-3v):** Eluent: PE/EA (20:1). Yield (23 mg, 33%). White solid, mp 83 – 84 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.21 (d, J = 8.24 Hz, 2H), 7.14 (d, J = 8.24 Hz, 2H), 6.14 (d, J

= 23.81 Hz, 1H), 5.21 (dd, *J* = 30.68 Hz, *J* = 4.12 Hz, 1H), 3.97 (dd, *J* = 13.28 Hz, *J* = 3.66 Hz, 1H), 3.08 (tt, *J* = 12.82 Hz, *J* = 2.75 Hz, 1H), 2.46 (s, 3H), 1.94 – 1.91 (m, 1H), 1.82 – 1.75 (m, 1H), 1.71 – 1.68 (m, 3H), 1.48 – 1.40 (m, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.14 (d, *J* = 258.79 Hz), 155.08, 137.30, 130.30 (d, *J* = 13.42 Hz), 129.01 (d, *J* = 1.92 Hz), 126.87, 108.17 (d, *J* = 27.80 Hz), 79.89, 48.14 (d, *J* = 22.04 Hz), 41.80, 29.04, 28.22, 24.85, 20.39, 16.03; ^{19}F NMR ($CDCl_3$, 282 MHz) : δ -102.91 (t, *J* = 26.01 Hz); ESI: Calculated for $C_{19}H_{27}FNO_2S$, $[M+H]^+$ m/z 352.17. Found 352.10.



3w

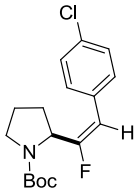
***tert*-Butyl 2-(2-(2-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate (3w):** *Z/E* = 2:3. Eluent: PE/EA (20:1). Yield (38 mg, 58%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.89 – 7.74 (m, 1H), 7.37 – 7.33 (m, 1.68H), 7.25 – 7.14 (m, 4H), 6.32 (d, *J* = 20.61 Hz, 1H), 5.98 (d, *J* = 38.01 Hz, 1H), 4.73 – 4.63 (m, 1H), 4.54 – 4.41 (m, 0.66H), 3.51 – 3.42 (m, 3.41H), 2.23 – 1.82 (m, 6.79H), 1.50 – 1.43 (m, 9H), 1.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 161.93 (d, *J* = 258.79 Hz), 160.85 (d, *J* = 273.16 Hz), 154.28, 154.08, 134.13, 132,71, 131.83 (d, *J* = 14.38 Hz), 131.14, 130.34, 130.12, 129.64, 129.47, 128.51, 128.24, 126.76, 126.64, 105.81 (d, *J* = 30.67 Hz), 101.49 (d, *J* = 29.71 Hz), 80.05 (major), 79.53 (minor), 58.29 (d, *J* = 32.59 Hz), 53.94 (d, *J* = 24.92 Hz), 47.29 (minor), 47.04 (major), 46.70(minor), 46.46 (major), 32.11 (major), 31.18 (minor), 30.67 (major), 29.74 (minor), 28.46, 28.30, 24.42 (minor), 23.78 (major), 23.18; ^{19}F NMR ($CDCl_3$, 282 MHz) rotameric mixture: -113.21 – -113.40 (m), -113.98 – -114.29 (m), -115.12 – -115.27 (m); ESI: Calculated for $C_{17}H_{22}ClFNO_2$, $[M+H]^+$ m/z 326.12. Found 326.10.



(*Z*)**-3x**

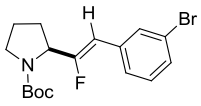
***cis-tert*-Butyl 2-(2-(4-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate**

((*Z*)-3x): Eluent: PE/EA (20:1). Yield (27 mg, 42%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.38 (d, J = 8.24 Hz, 2H), 7.28 – 7.25 (m, 2H), 5.61 – 5.45 (m, 1H), 4.49 – 4.35 (m, 1H), 3.48 – 3.38 (m, 2H), 2.08 – 1.88 (m, 3H), 1.87 – 1.86 (m, 1H), 1.46 – 1.40 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 160.18 (d, J = 278.91 Hz), 154.35, 132.75, 131.76, 129.74, 128.77, 104.72, 79.99, 58.24 (d, J = 31.63 Hz), 46.95 (minor), 46.50 (major), 30.61 (major), 29.80 (minor), 28.52, 24.05 (minor), 23.25 (major); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -114.72 – -114.81 (m); ESI: Calculated for $C_{17}H_{22}ClFNO_2$, $[M+H]^+$ m/z 326.12. Found 326.10.



(*E*)-3x

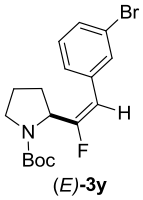
***trans-tert*-Butyl 2-(2-(4-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((*E*)-3x):** Eluent: PE/EA (20:1). Yield (25 mg, 38%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.36 – 7.25 (m, 3H), 7.13 (m, 1H), 6.15 (d, J = 21.07 Hz, 1H), 4.72 – 4.65 (m, 1H), 3.52 – 3.42 (m, 2H), 2.24 – 1.99 (m, 3H), 1.83 – 1.82 (m, 1H), 1.44 – 1.24 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 161.53 (d, J = 254.95 Hz), 154.08, 132.84, 131.97 (d, J = 13.42 Hz), 130.03, 128.69, 107.26 (d, J = 28.75 Hz), 80.02 (major), 79.63 (minor), 54.09 (d, J = 23.00 Hz), 47.37 (minor), 47.08 (major), 32.17 (major), 31.30 (minor), 28.48, 24.54 (minor), 23.92 (major); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -115.05 – -115.24 (m); ESI: Calculated for $C_{17}H_{22}ClFNO_2$, $[M+H]^+$ m/z 326.12. Found 326.10.



(*Z*)-3y

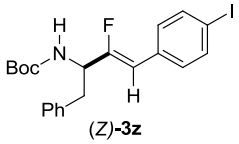
***cis-tert*-Butyl 2-(2-(3-bromophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((*Z*)-3y):** Eluent: PE/EA (20:1). Yield (32 mg, 43%). White solid, mp 84 – 85 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.63 (s, 1H), 7.36 – 7.34 (m, 2H), 7.19 – 7.17 (m, 1H), 5.60 – 5.44 (m, 1H), 4.47 – 4.36 (m, 1H), 3.48 – 3.40 (m, 2H), 2.07 –

1.96 (m, 3H), 1.90 – 1.86 (m, 1H), 1.46 – 1.41 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) rotameric mixture: δ 160.79 (d, J = 273.16 Hz), 154.30, 135.28, 131.27, 130.07, 127.05, 122.68, 104.49, 80.04, 58.18 (d, J = 31.63 Hz), 46.92 (minor), 46.48 (major), 30.61 (major), 29.78 (minor), 28.50, 24.03 (minor), 23.20 (major); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -113.09 – -113.41 (m); ESI: Calculated for $C_{17}H_{22}BrFNO_2$, $[M+H]^+$ m/z 370.07. Found 370.00.



(*E*)-**3y**

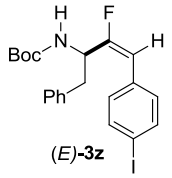
***trans-tert*-Butyl 2-(2-(3-bromophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((*E*)-3y):** Eluent : PE/EA (20:1). Yield (30 mg, 41%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.53 – 7.35 (m, 2H), 7.21 – 7.13 (m, 2H), 6.14 (d, J = 20.61 Hz, 1H), 4.73 – 4.66 (m, 1H), 3.53 – 3.42 (m, 2H), 2.24 – 1.99 (m, 3H), 1.86 – 1.82 (m, 1H), 1.45 – 1.31 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 162.03 (d, J = 260.70 Hz), 154.03, 135.61 (d, J = 12.46 Hz), (131.90) 131.63, 130.00, (127.68) 127.40, 122.48, 107.06 (d, J = 28.75 Hz), 80.12 (79.62), 54.02 (d, J = 23.96 Hz), 47.35 (minor) 47.10 (major), 32.14 (major), 31.33 (minor), 28.45, 24.52 (minor) 23.88 (major); ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -113.93 – -114.40 (m); ESI: Calculated for $C_{17}H_{22}BrFNO_2$, $[M+H]^+$ m/z 370.07. Found 370.00.



(*Z*)-**3z**

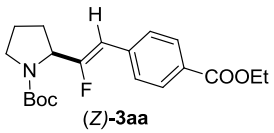
***cis-tert*-Butyl (3-fluoro-4-(4-iodophenyl)-1-phenylbut-3-en-2-yl)carbamate ((*Z*)-3z):** Eluent: PE/EA (20:1). Yield (27 mg, 29%). White solid, mp 137 – 138 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, J = 8.24 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 7.13 (d, J = 8.24 Hz, 2H), 5.44 (d, J = 38.93 Hz, 1H), 5.00 – 4.55 (m, 2H), 3.02 – 3.00 (m, 2H), 1.43 – 1.40 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.32 (d, J = 264.67 Hz), 154.85, 137.63, 136.46, 132.37, 130.47 (d, J = 6.90 Hz), 129.46, 128.92, 128.64, 126.99, 106.64, 92.75, 80.23, 53.85 (d, J = 32.22 Hz), 38.78, 28.42; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ -114.08 – -115.43 (m); ESI:

Calculated for $C_{21}H_{23}FINNaO_2$, $[M+Na]^+$ m/z 490.08. Found 490.40.



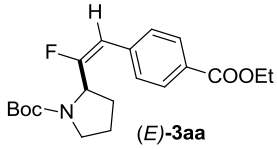
(*E*)-**3z**

***trans-tert*-Butyl (3-fluoro-4-(4-iodophenyl)-1-phenylbut-3-en-2-yl)carbamate ((*E*)-3z):** Eluent: PE/EA (20:1). Yield (32 mg, 34%). White solid, mp 70 – 71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 7.79 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.12 – 7.10 (m, 2H), 6.61 (d, J = 7.79 Hz, 2H), 6.10 (d, J = 21.07 Hz, 1H), 4.93 – 4.80 (m, 2H), 3.00 – 2.87 (m, 2H), 1.42 (s, 9H); δ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.45 (d, J = 253.99 Hz), 154.60, 137.52, 136.50, 131.99 (d, J = 13.42 Hz), 130.40, 129.48, 129.26, 128.90, 128.51, 126.92, 109.47 (d, J = 26.84 Hz), 92.81, 80.02, 50.26 (d, J = 23.96 Hz), 39.24, 28.40; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -117.36 (t, J = 26.01 Hz); ESI: Calculated for $C_{21}H_{23}FINNaO_2$, $[M+Na]^+$ m/z 490.08. Found 490.40.



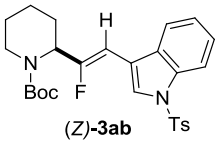
(*Z*)-**3aa**

***cis-tert*-Butyl 2-(2-(4-(ethoxycarbonyl)phenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((*Z*)-3aa):** Eluent: PE/EA (20:1). Yield (25.7mg, 36%). White solid, mp 72 – 73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.99 – 7.98 (m, 2H), 7.51 (d, J = 8.24 Hz, 2H), 5.65 – 5.55 (m, 1H), 4.52 – 4.33 (m, 3H), 3.49 – 3.40 (m, 2H), 2.10 – 1.98 (m, 3H), 1.93 – 1.86 (m, 1H), 1.47 – 1.36 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 166.45, 161.45 (d, J = 275.00 Hz) (major), 161.03 (d, J = 277.00 Hz) (minor), 154.30, 137.74, 129.85, 128.90, 128.30, 105.15, 80.06, 60.98, 58.30 (d, J = 31.63 Hz), 46.94 (minor), 46.52 (major), 30.66 (major), 29.78 (minor), 28.49, 24.07 (minor), 23.27 (major), 14.42; ^{19}F NMR ($CDCl_3$, 282 MHz) rotameric mixture: δ -111.78 (dd, J = 39.01 Hz, J = 13.00 Hz); ESI: Calculated for $C_{20}H_{27}FNO_4$, $[M+H]^+$ m/z 364.18. Found 364.10.



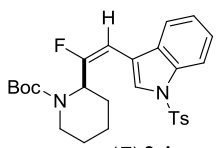
(*E*)-**3aa**

***trans-tert*-Butyl 2-(2-(4-(ethoxycarbonyl)phenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((*E*)-3aa):** Eluent: PE/EA (20:1). Yield (32.8 mg, 45%).Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): rotameric mixture, δ 7.98 (d, J = 8.24 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.26 – 7.25 (m, 1H), 6.22 (d, J = 21.07 Hz, 1H), 4.76 – 4.69 (m, 1H), 4.35 (q, J = 7.28 Hz, 2H), 3.52 – 3.42 (m, 2H), 2.26 – 2.00 (m, 3H), 1.99 – 1.82 (m, 1H), 1.43 – 1.35 (m, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): rotameric mixture, δ 166.38, 162.40 (d, J = 260.70 Hz), 154.05, 138.23 (d, J = 12.46 Hz), 129.77, 128.98, 128.64, 107.83 (d, J = 27.80 Hz), 80.07 (79.58), 61.04 (d, J = 10.54 Hz), 54.20 (d, J = 23.96 Hz), 47.39 (minor), 47.10 (major), 32.18 (major), 31.32 (minor), 28.45, 24.57 (minor), 23.95 (major), 14.43; ^{19}F NMR ($CDCl_3$, 282 MHz) rotameric mixture: δ [-111.69 – -111.87 (m)] -112.82 – -112.99 (m); ESI: Calculated for $C_{20}H_{27}FNO_4$, $[M+H]^+$ m/z 364.18. Found 364.10.



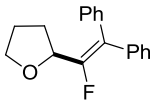
(*Z*)-3ab

***cis-tert*-Butyl 2-(1-fluoro-2-(1-tosyl-1*H*-indol-3-yl)vinyl)piperidine-1-carboxylate ((*Z*)-3ab):** Eluent : PE/EA (20:1). Yield (26 mg, 26%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 8.24 Hz, 1H), 7.87 (s, 1H), 7.77 (d, J = 8.24 Hz, 2H), 7.49 (d, J = 7.79 Hz, 1H), 7.31 (t, J = 7.79 Hz, 1H), 7.26 – 7.19 (m, 3H), 5.71 (d, J = 39.38 Hz, 1H), 5.12 – 5.04 (m, 1H), 4.06 (d, J = 12.82 Hz, 1H), 2.98 – 2.95 (m, 1H), 2.31 (s, 3H), 2.13 – 2.10 (m, 1H), 1.76 – 1.59 (m, 4H), 1.55 – 1.44 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ; ^{19}F NMR ($CDCl_3$, 282 MHz): rotameric mixture, δ 159.54 (d, J = 273.16 Hz), 155.24, 145.05, 135.28, 134.48, 129.99, 129.66, 126.95, 125.07, 124.93, 123.33, 119.06, 114.30, 113.70, 96.75 (d, J = 11.50 Hz), 80.24, 51.53 (d, J = 21.09 Hz), 40.68, 28.49, 26.18, 25.23, 21.64, 19.98; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -101.98 (d, J = 43.35 Hz); HRMS (ESI): Calculated for $C_{27}H_{31}FN_2NaO_4S$, $[M+Na]^+$ m/z 521.1881. Found 521.1884.



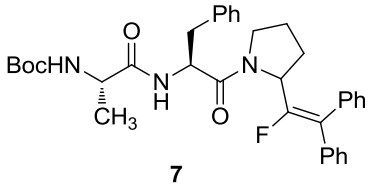
(*E*)-3ab

***trans-tert*-Butyl 2-(1-fluoro-2-(1-tosyl-1H-indol-3-yl)vinyl)piperidine-1-carboxylate ((*E*)-3ab):** Eluent: PE/EA (20:1). Yield (30 mg, 30%). Yellow solid, mp 154 – 155 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 – 7.96 (m, 1H), 7.80 (d, J = 8.24 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.44 (d, J = 7.79 Hz, 1H), 7.32 (t, J = 11.50 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.09 (d, J = 21.07 Hz, 1H), 5.18 (dd, J = 30.68 Hz, J = 4.12 Hz, 1H), 4.00 (dd, J = 13.51 Hz, J = 4.12 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.31 (s, 3H), 1.92 – 1.81 (m, 2H), 1.72 – 1.70 (m, 3H), 1.50 – 1.45 (m, 1H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.49 (d, J = 265.50 Hz), 155.10, 145.09, 135.27, 134.85, 130.74, 130.00, 127.05, 125.20, 123.50, 123.22, 119.46, 115.14 (d, J = 13.42 Hz), 113.76, 98.01 (d, J = 29.71 Hz), 79.92, 48.45 (d, J = 21.09 Hz), 41.97, 28.96, 28.06, 24.83, 21.65, 20.46; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -100.83 (t, J = 26.01 Hz); HRMS (ESI): Calculated for $C_{27}H_{31}FN_2NaO_4S$, $[M+Na]^+$ m/z 521.1881. Found 521.1880.



3ac

2-(1-Fluoro-2,2-diphenylvinyl)tetrahydrofuran (3ac): Eluent: PE/EA (20:1). Yield (42 mg, 78%). White solid, mp 91 – 92 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 – 7.22 (m, 10H), 4.56 (dt, J = 29.31 Hz, J = 7.33 Hz, 1H), 4.01 – 3.96 (m, 1H), 3.84 – 3.80 (m, 1H), 2.19 – 2.02 (m, 3H), 2.01 – 1.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.93 (d, J = 265.50 Hz), 137.94 (d, J = 7.67 Hz), 137.16, 130.57 (d, J = 2.88 Hz), 129.88 (d, J = 4.79 Hz), 128.45, 128.06, 127.70, 127.44, 123.30 (d, J = 14.38 Hz), 75.02 (d, J = 25.88 Hz), 69.33, 28.97, 26.95; ^{19}F NMR ($CDCl_3$, 282 MHz) :δ -126.31 (d, J = 29.60 Hz); ESI: Calculated for $C_{18}H_{18}FO$, $[M+H]^+$ m/z 269.13. Found 269.10.



7

***tert*-Butyl ((2S)-1-(((2S)-1-(2-(1-fluoro-2,2-diphenylvinyl)pyrrolidin-1-yl)-1-oxo-3-phenylpropan-2-yl)amino)-1-oxopropan-2-yl)carbamate (7)** Eluent: PE/EA (2:1). Yield (84 mg, 72%). Waxy solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 - 7.33 (m, 5H), 7.24 - 7.04 (m, 10H), 6.82 (brs, 1H), 4.99 - 4.91 (m, 2H), 4.68 - 4.46 (m, 1H), 4.14 -

4.08 (m, 1H), 3.54 - 3.39 (m, 1H), 3.03 - 2.92 (m, 2H), 2.82 - 2.76 (m, 1H), 1.93 - 1.86 (m, 4H), 1.44 - 1.30 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): 172.00, 169.34, 155.27 (d, *J* = 264.54 Hz), 155.18, 138.05 (d, *J* = 7.67 Hz), 137.20, 136.37, 130.57, 129.62, 129.54, 128.52 (d, *J* = 5.75 Hz), 128.36, 128.23, 127.94, 127.52, 127.06 (d, *J* = 6.71 Hz), 120.43 (d, *J* = 11.50 Hz), 80.02, 56.27 (d, *J* = 24.92 Hz), 52.49, 50.35, 47.46, 39.69, 30.63, 28.37, 24.49, 18.78; ^{19}F NMR ($CDCl_3$, 282 MHz) : δ -119.92 (d, *J* = 26.01Hz) (minor), -123.26 (d, *J* = 26.01Hz) (major); ESI: Calculated for $C_{35}H_{41}FN_3O_4$, $[M+H]^+$ m/z 586.30. Found 586.00.

6. References

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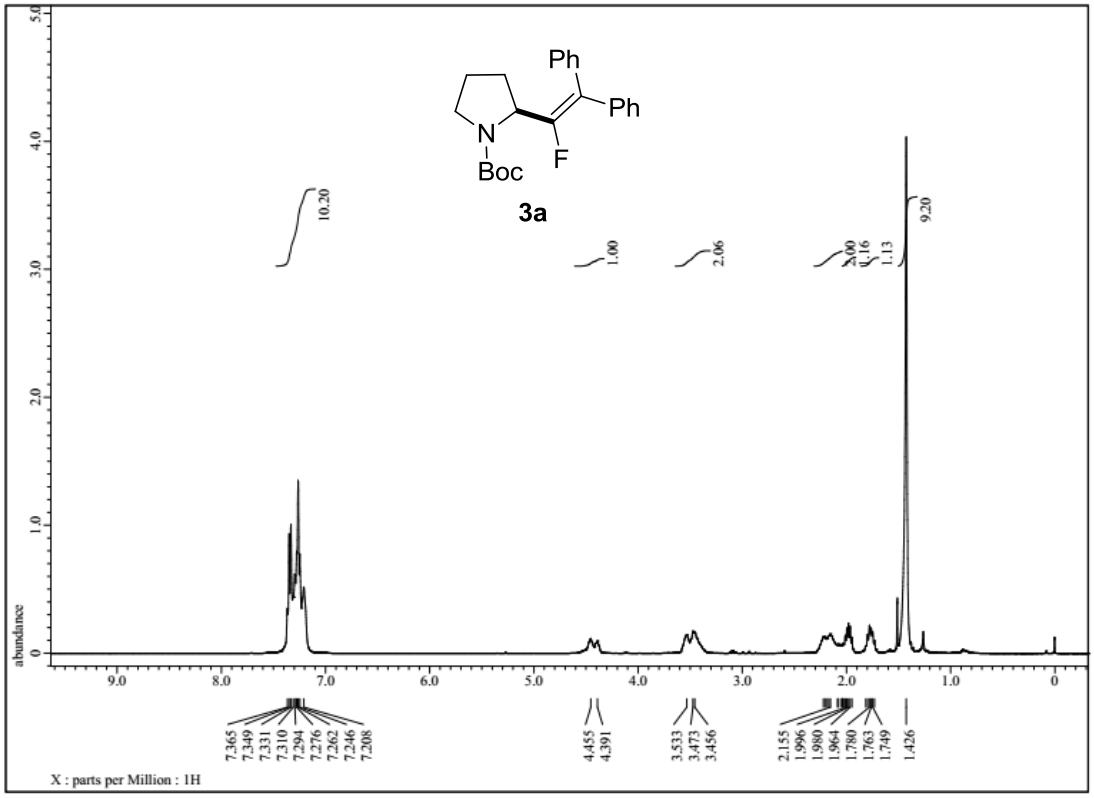
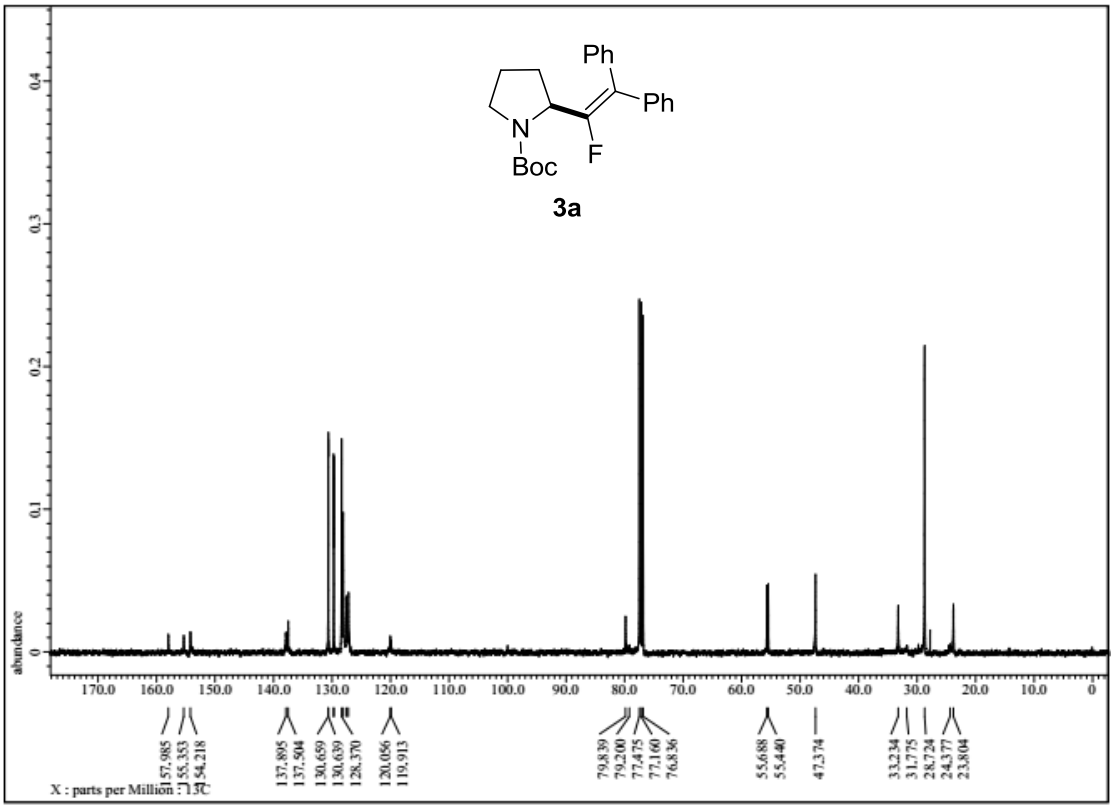
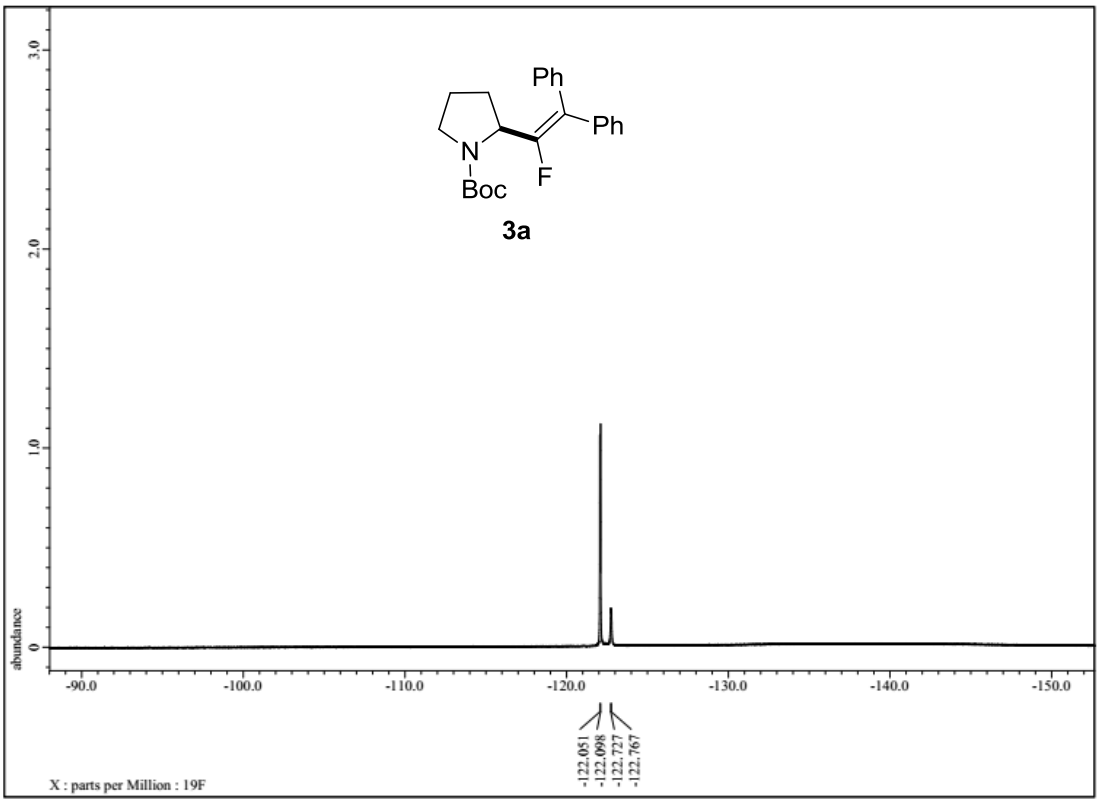
7. ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds 3a-ac and 7



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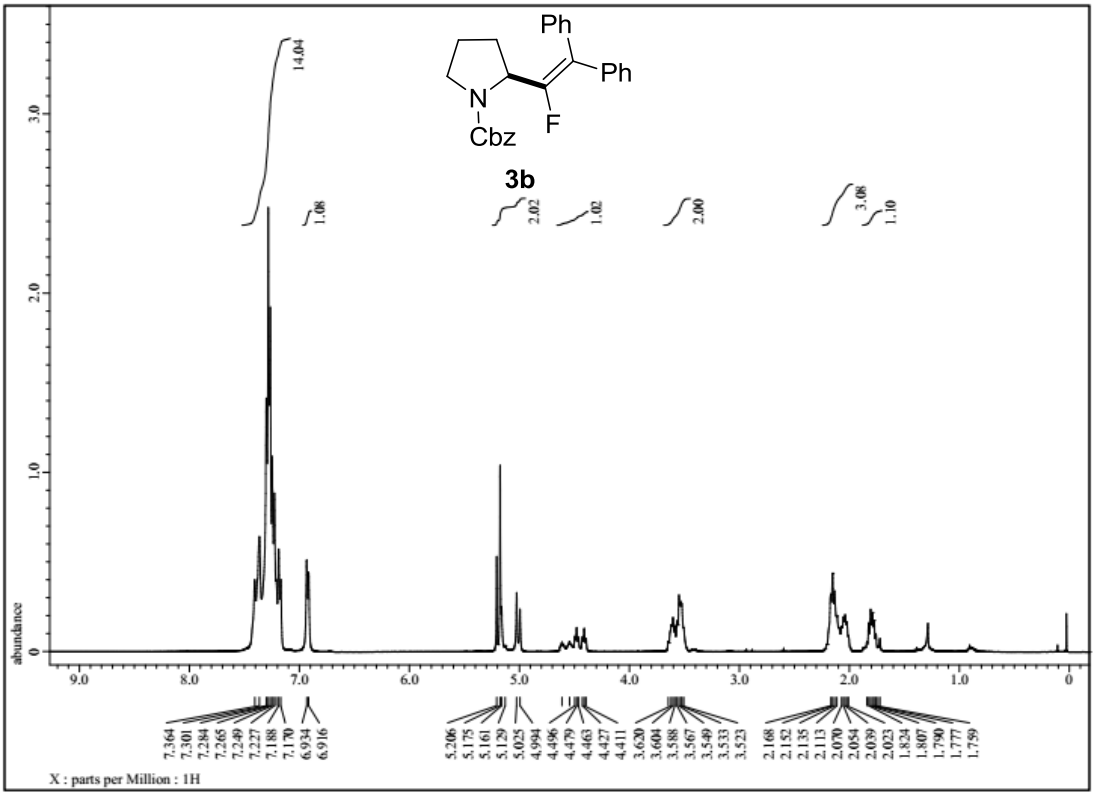
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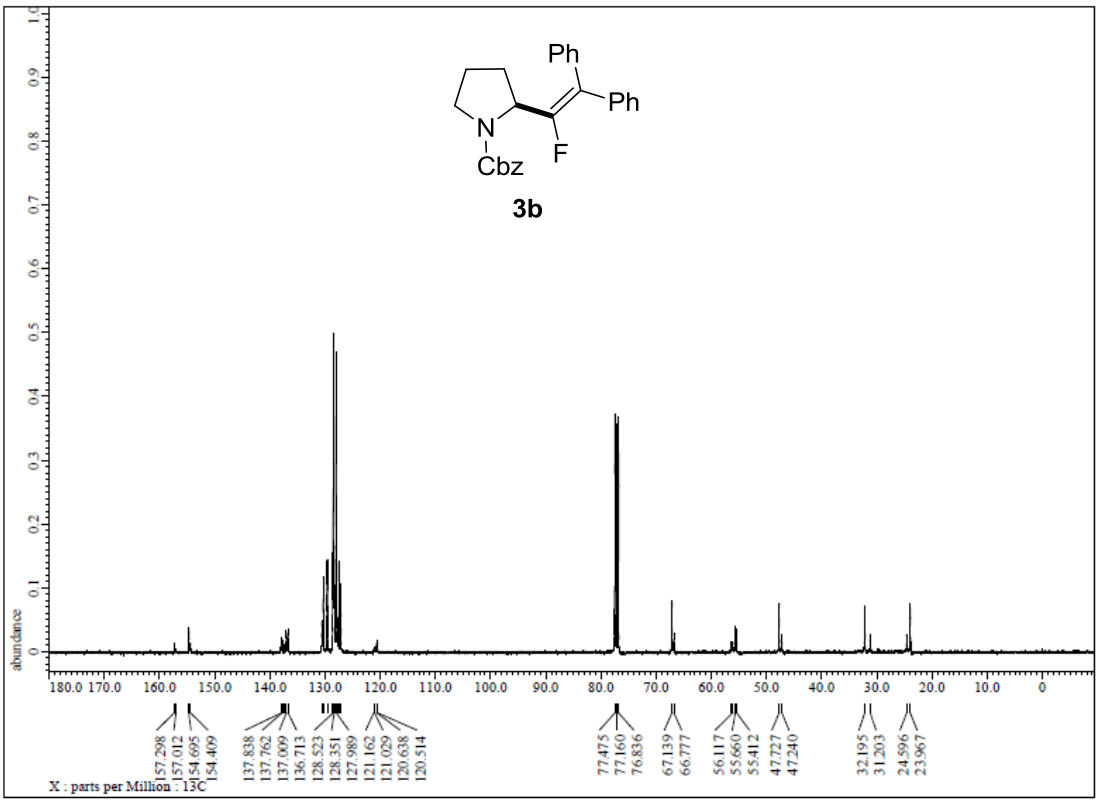
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abundance
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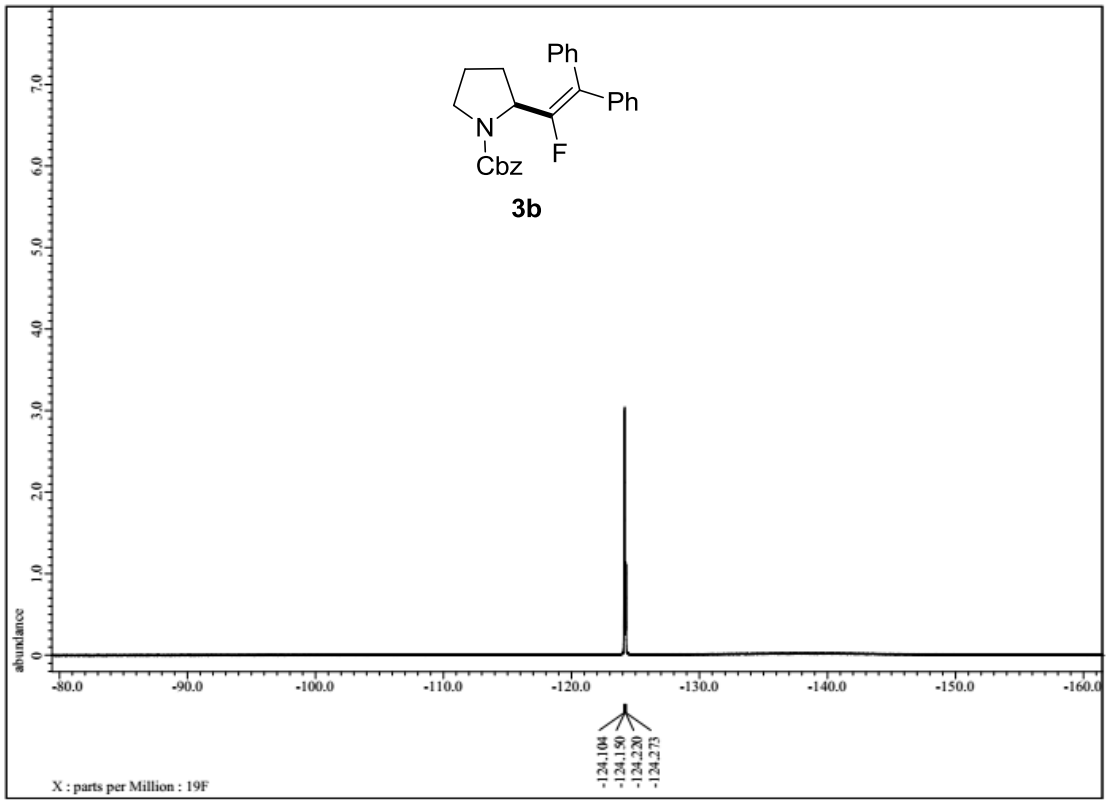
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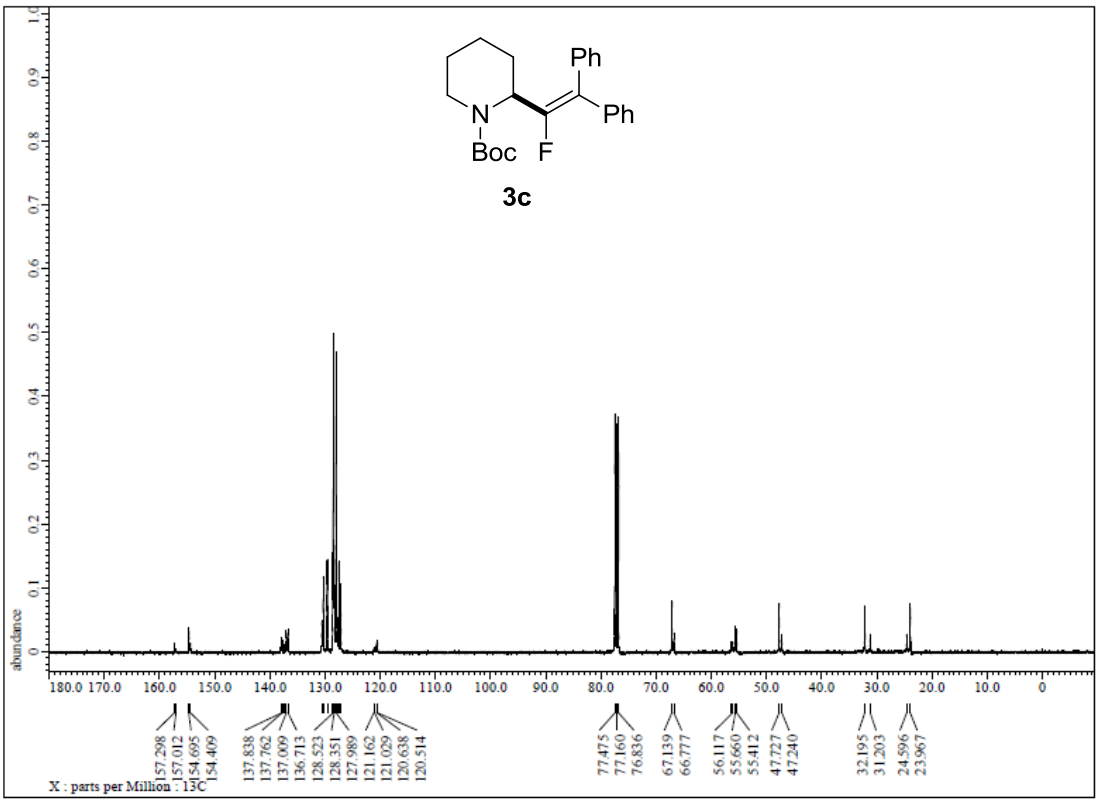
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abundance
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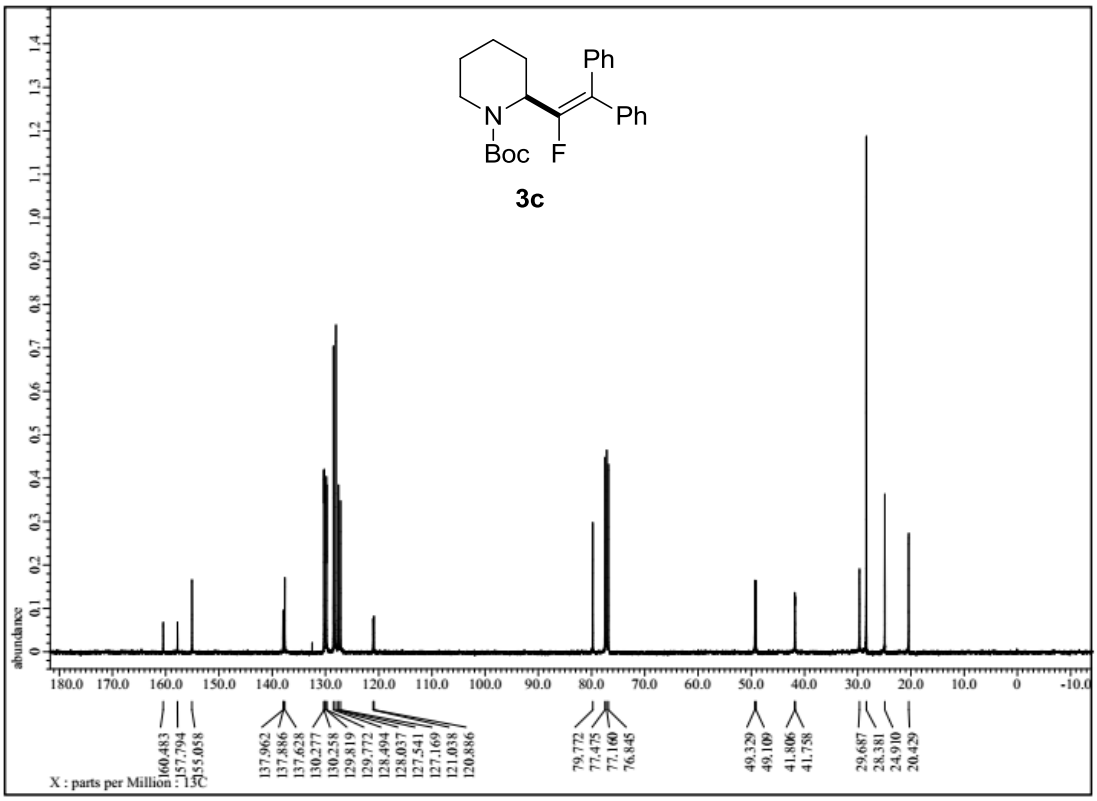
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abundance
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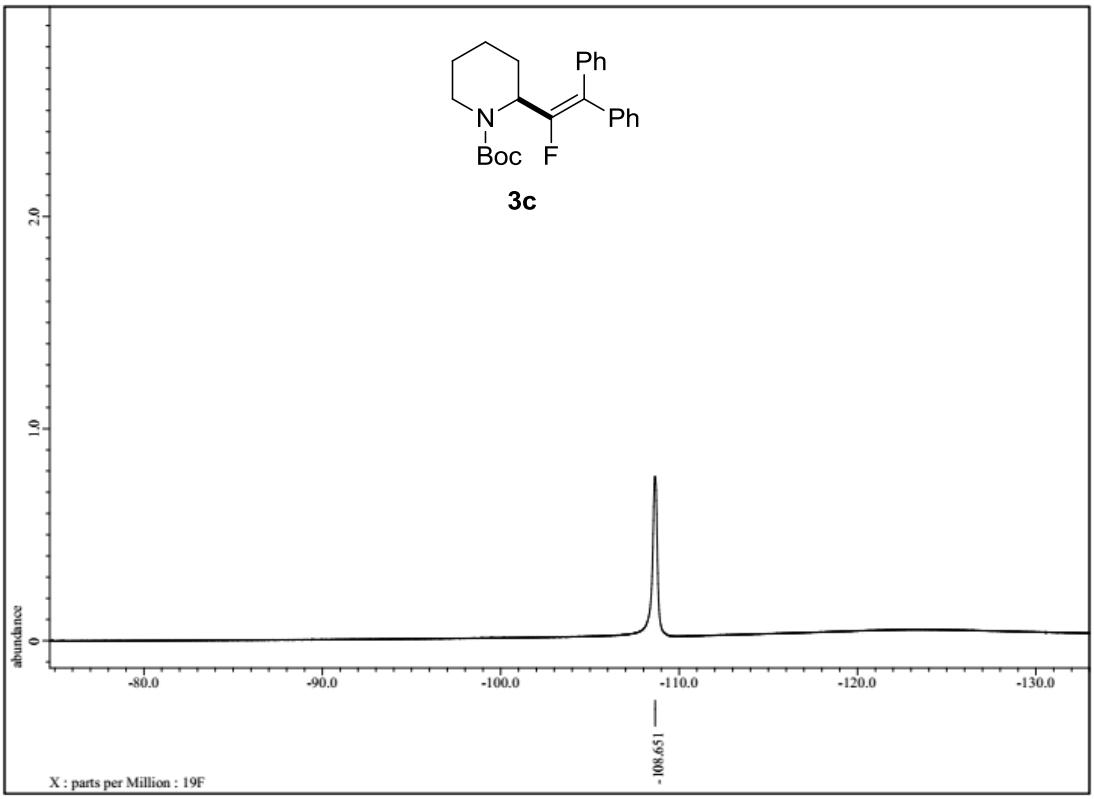
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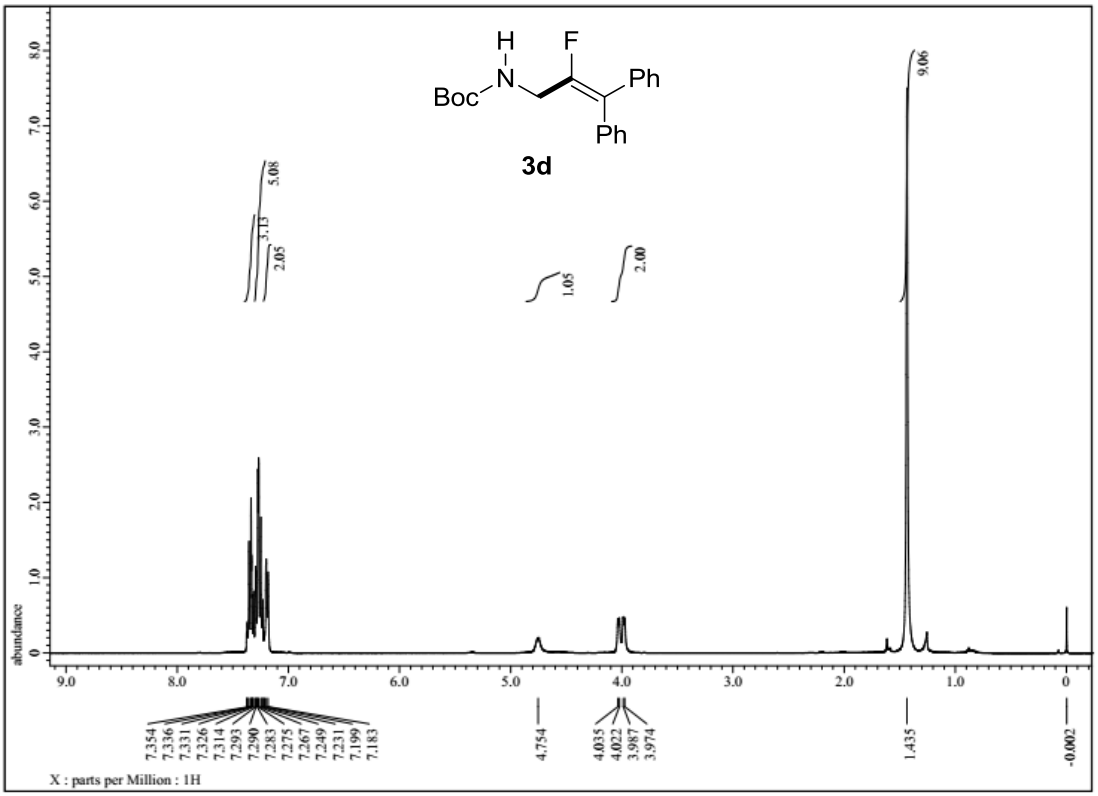
X : parts per Million : 19F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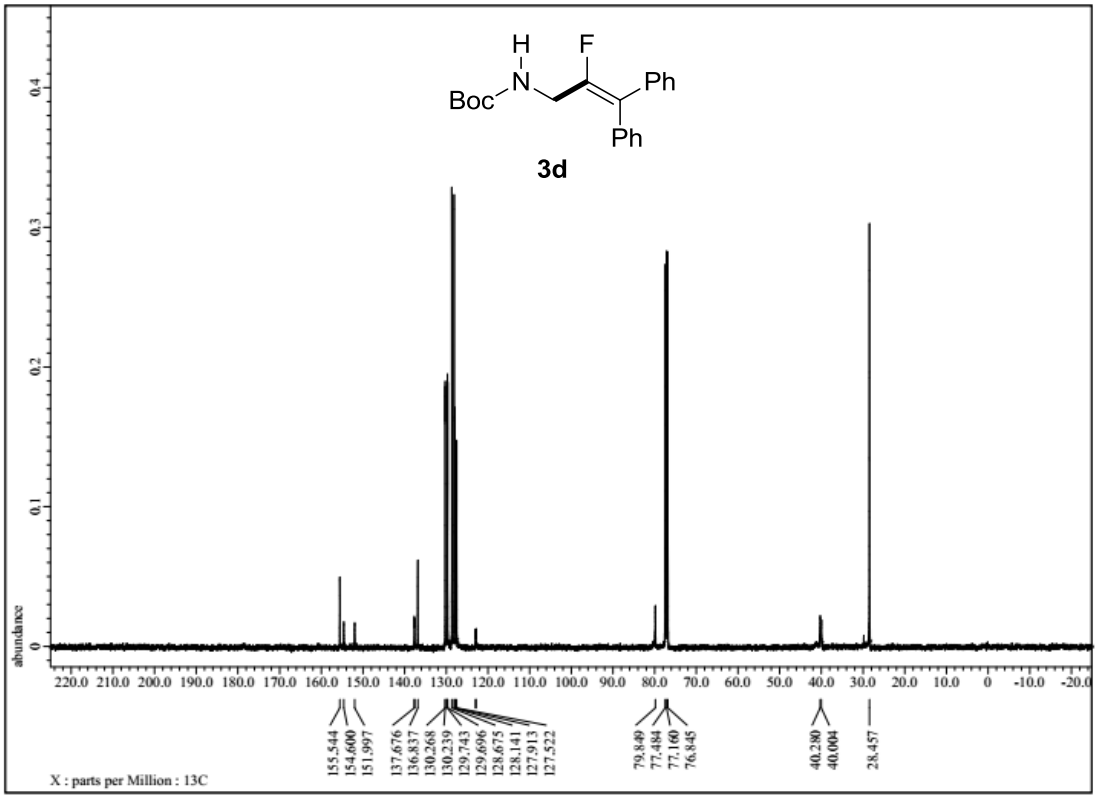
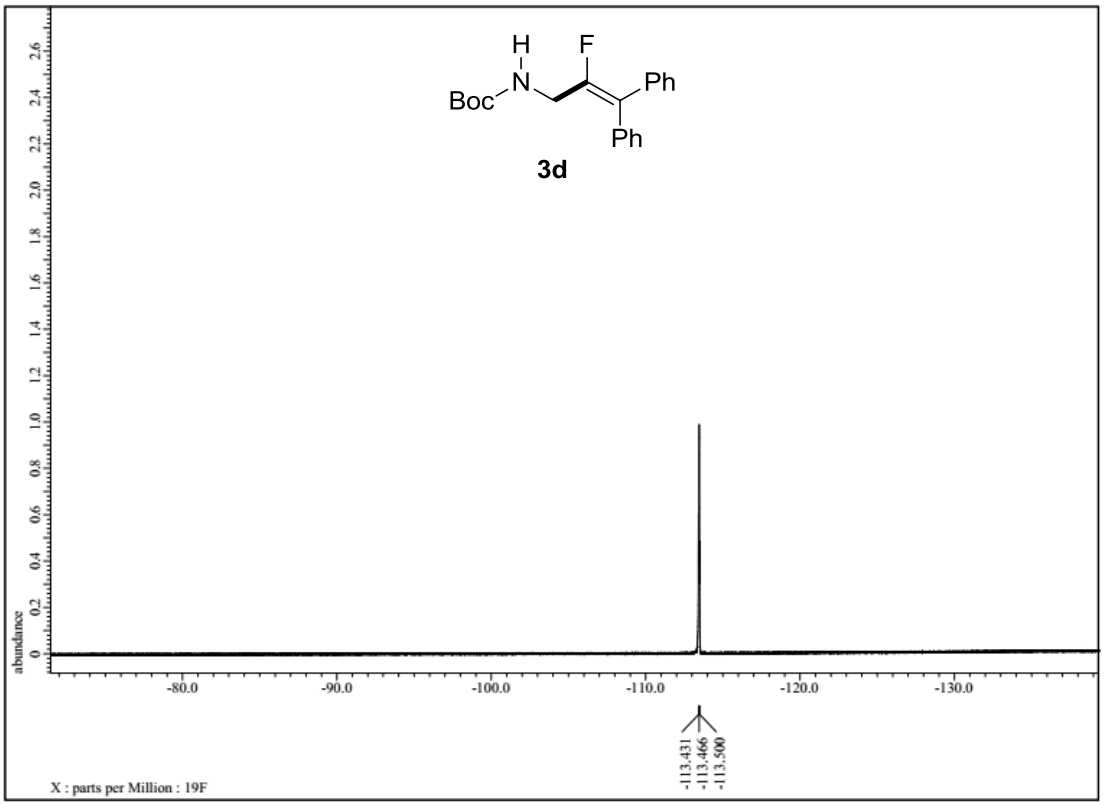
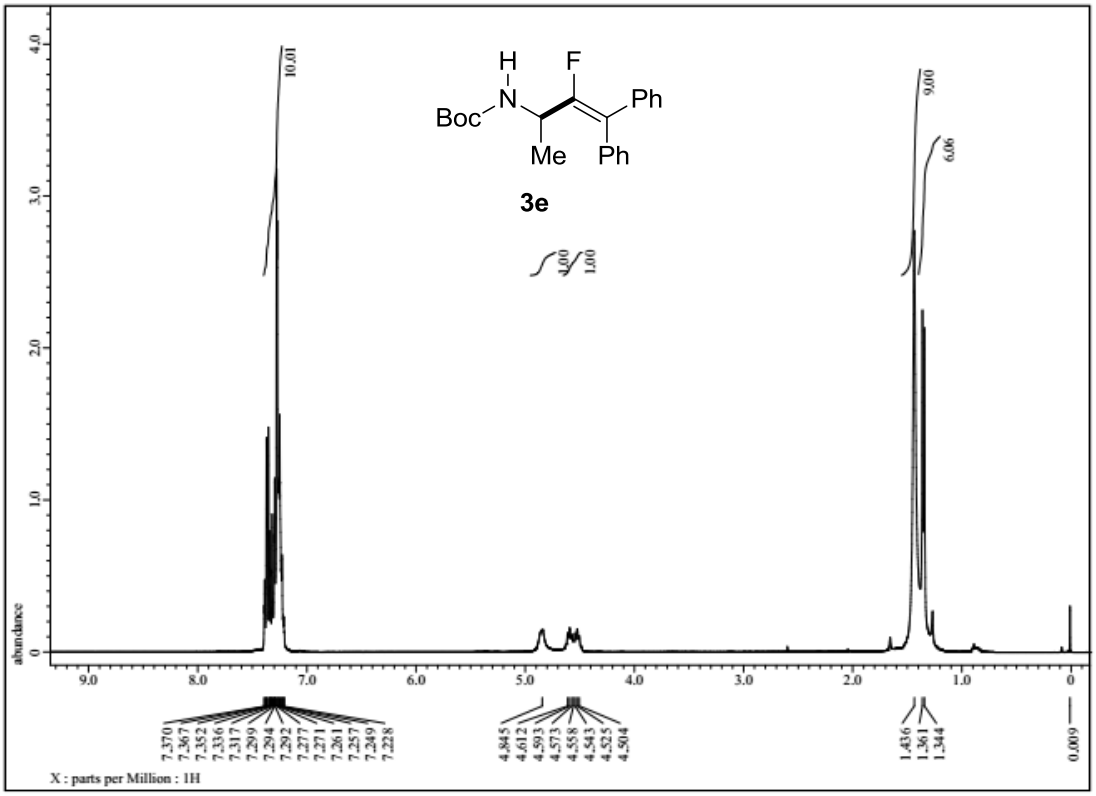
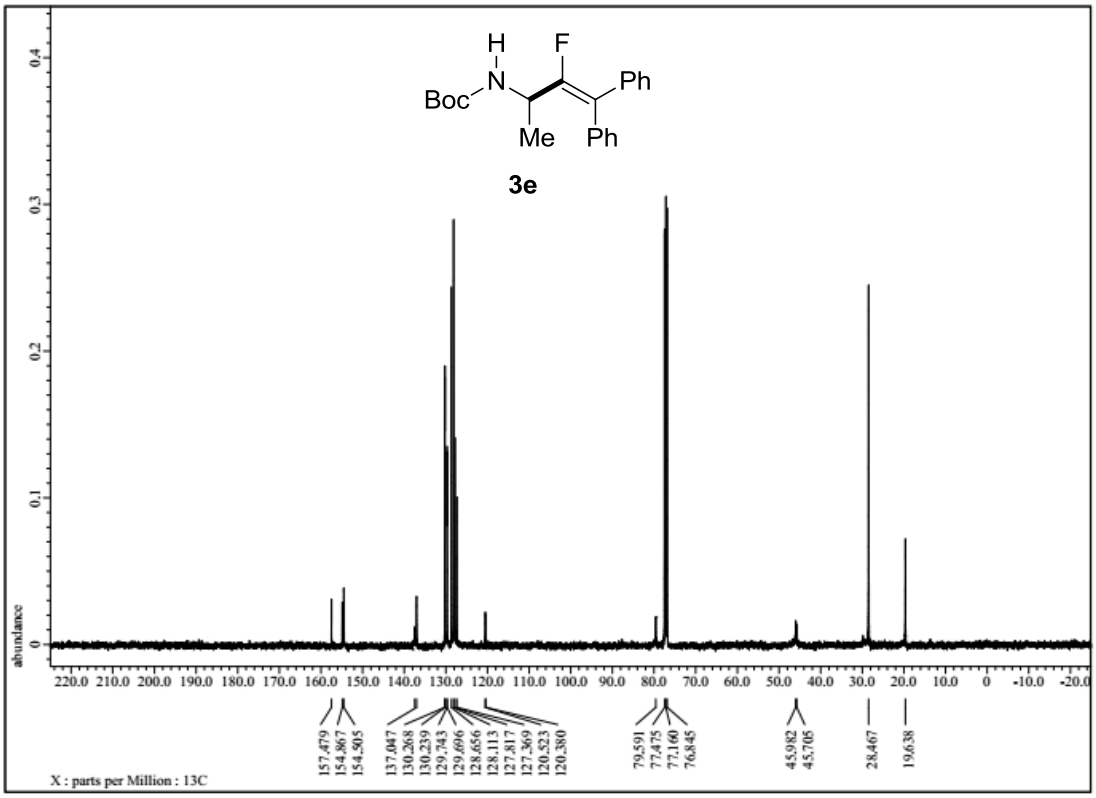
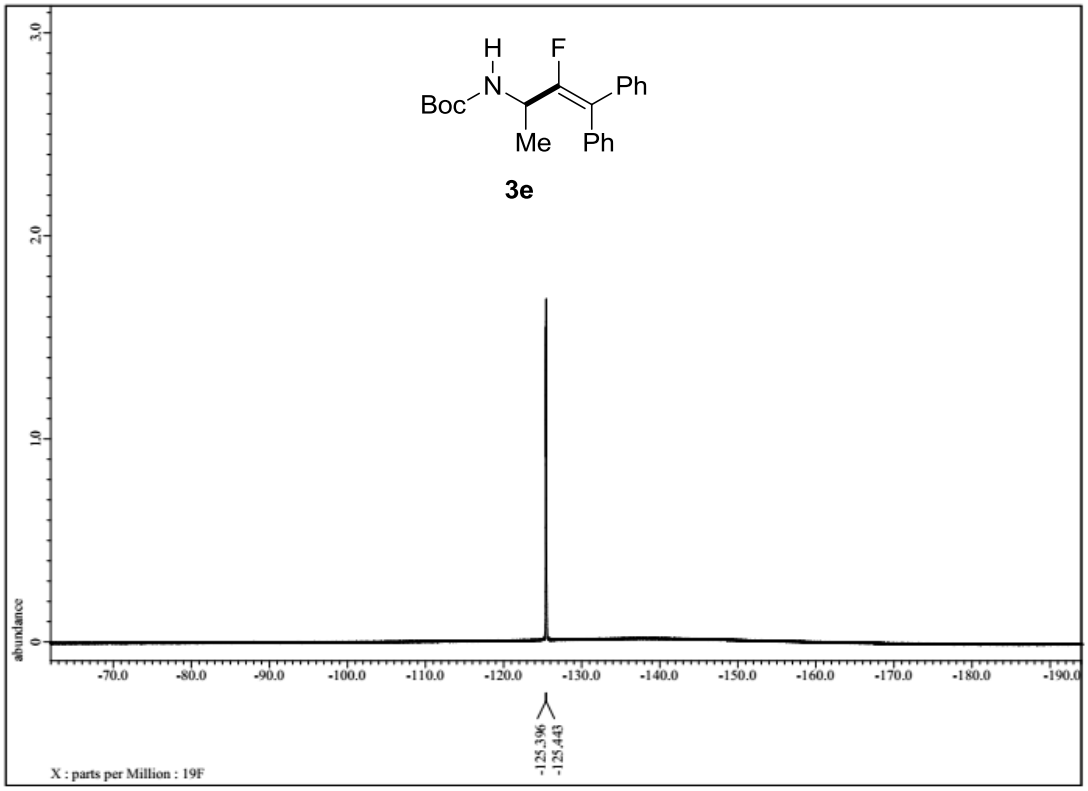
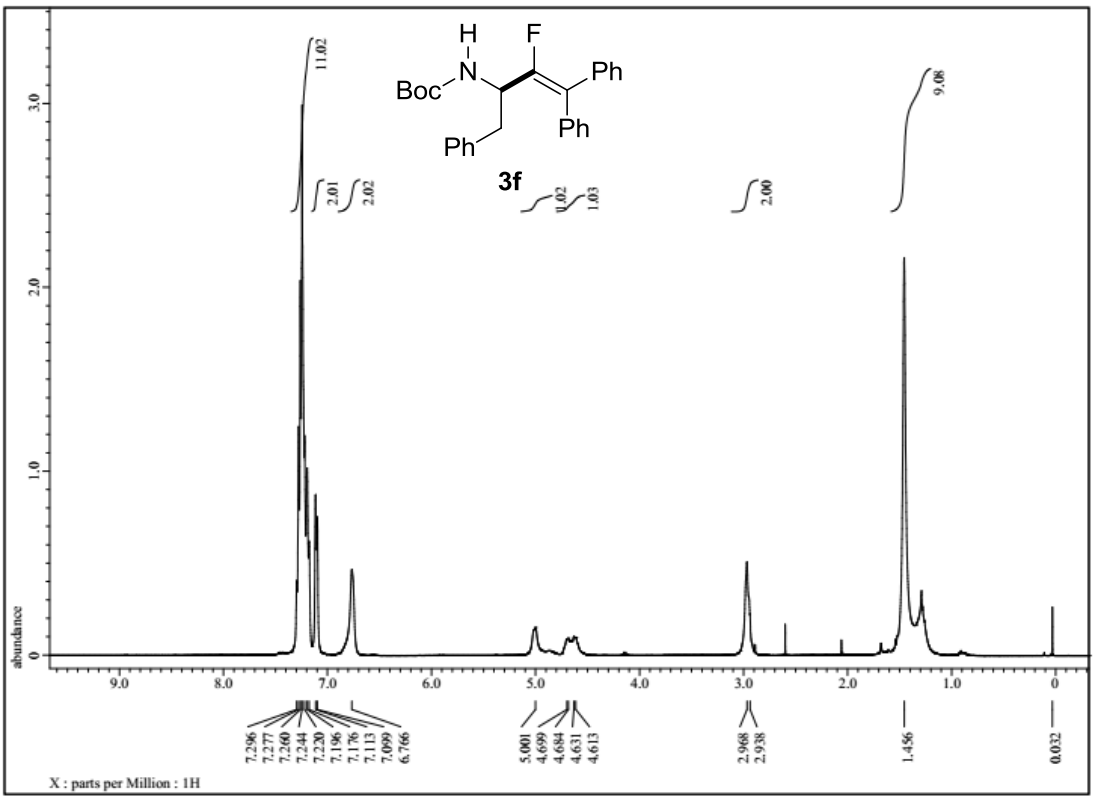

H
F
N
Boc
Ph
Ph
3d
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
155.544
154.600
151.997
137.676
136.837
130.268
130.239
129.743
129.696
128.675
128.141
127.913
127.522
79.849
77.484
77.160
76.845
40.280
40.004
28.457
X : parts per Million : 13C

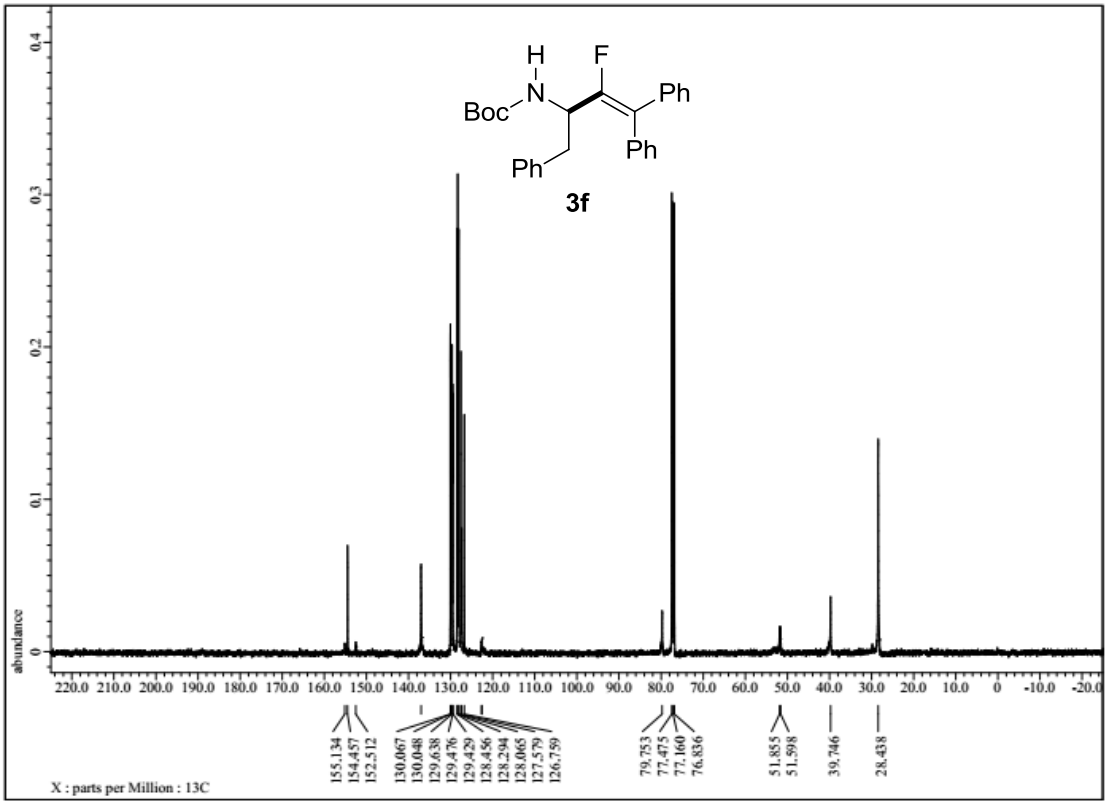

H
F
N
Boc
Ph
Ph
3d
abundance
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-113.431
-113.466
-113.500
X : parts per Million : 19F

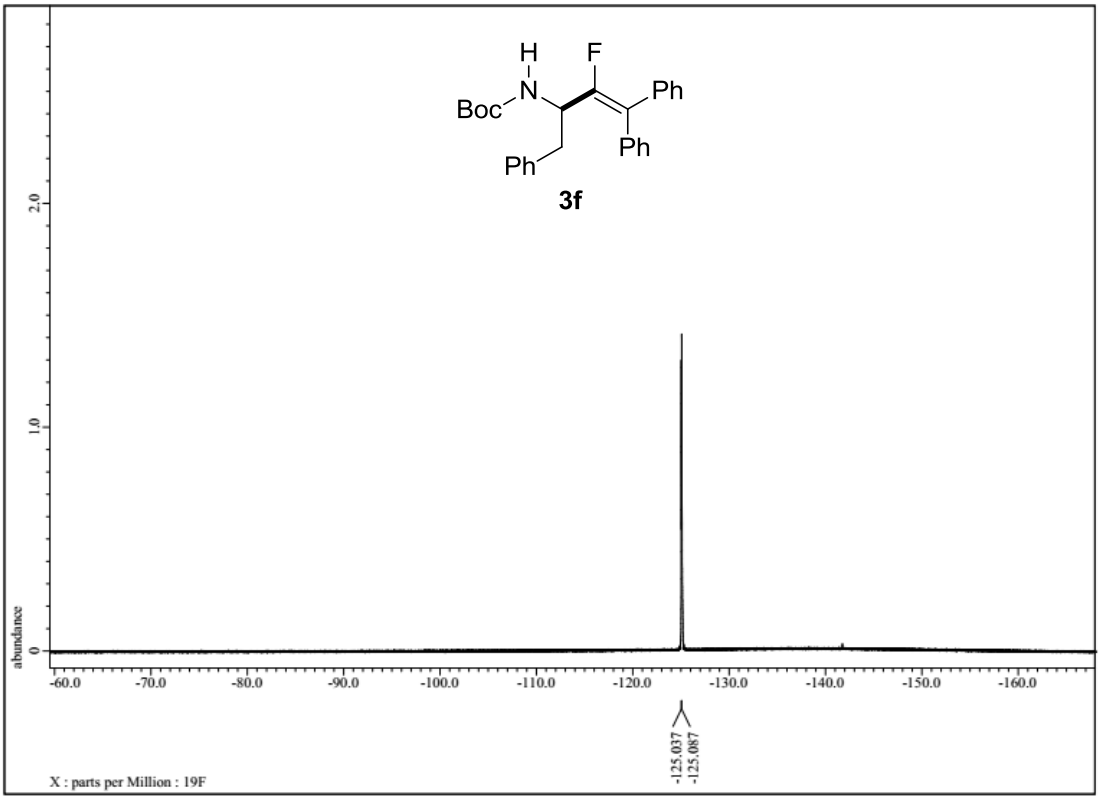

H
F
N
Boc
Ph
Me
Ph
3e
10.01
9.00
6.06
4.00
1.00
abundance
X : parts per Million : 1H

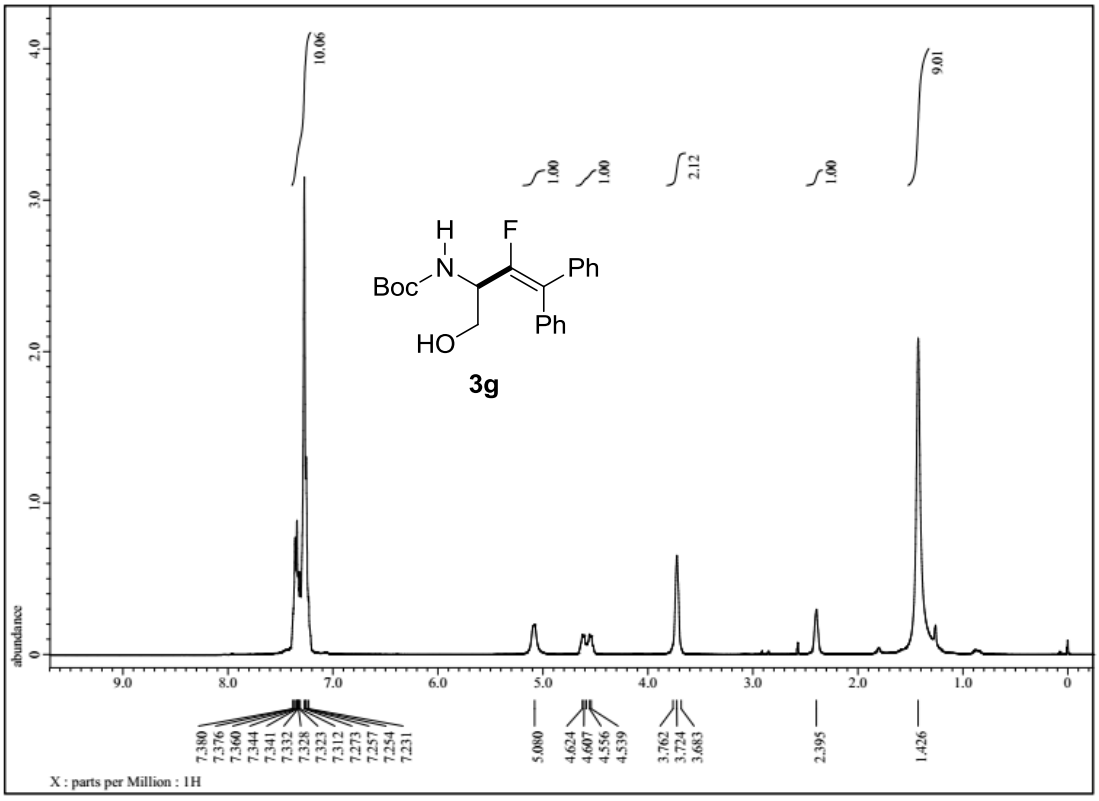

H
F
N
Boc
Ph
Me
Ph
3e
abundance
X : parts per Million : 13C

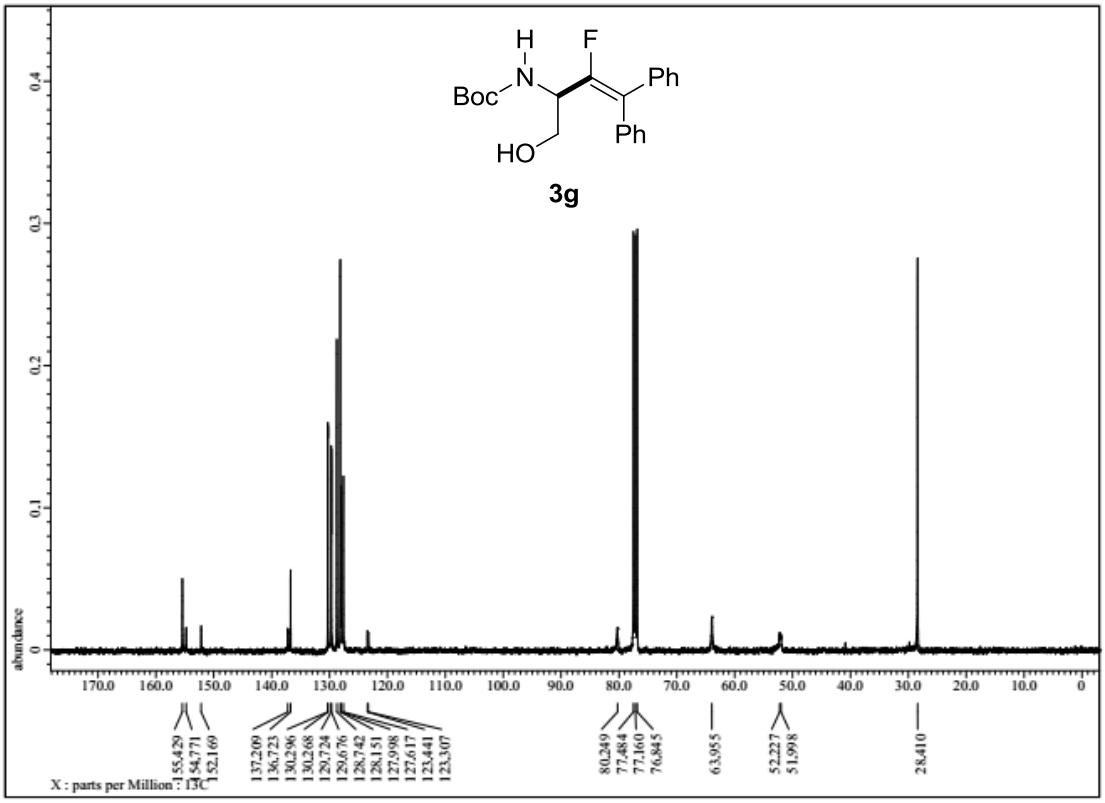

H
F
N
Boc
Ph
Me
Ph
3e
abundance
-125.396
-125.443
X : parts per Million : 19F

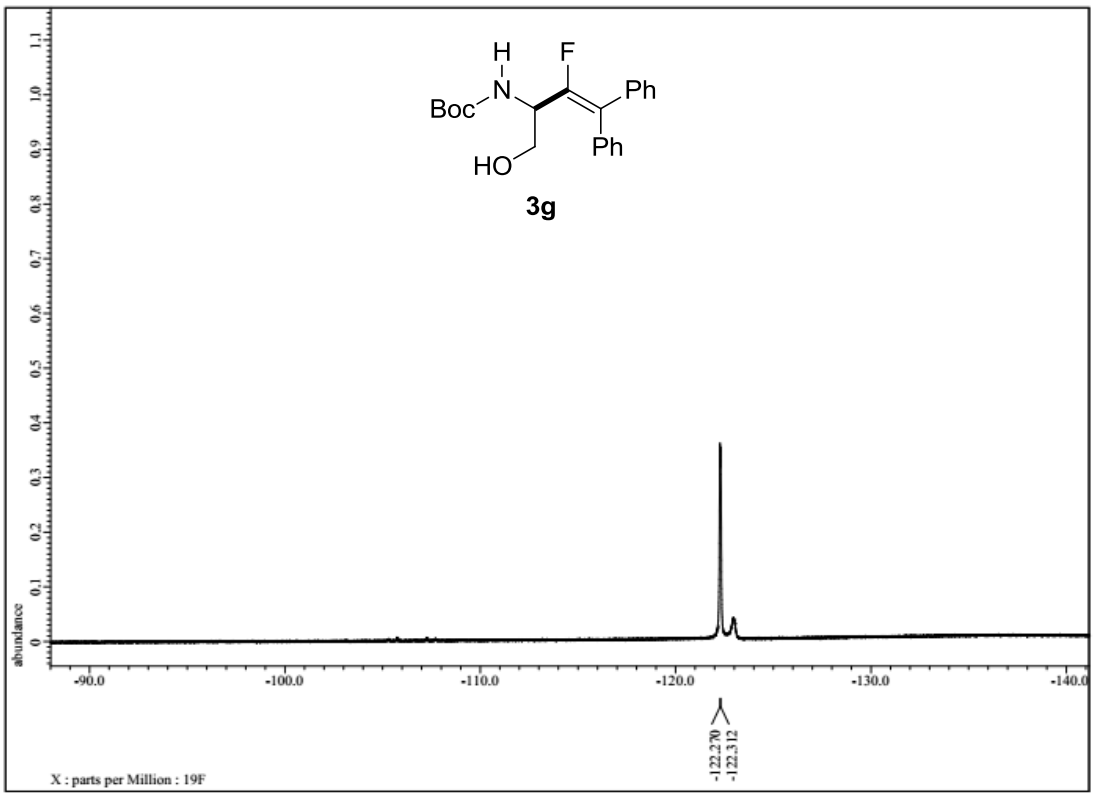

H
F
N
Boc
Ph
Ph
Ph
3f
11.02
2.01
2.02
1.02
1.03
2.00
9.08
abundance
7.296
7.277
7.260
7.244
7.220
7.196
7.176
7.113
7.099
6.766
5.001
4.699
4.684
4.631
4.613
2.968
2.938
1.456
0.032
X : parts per Million : 1H

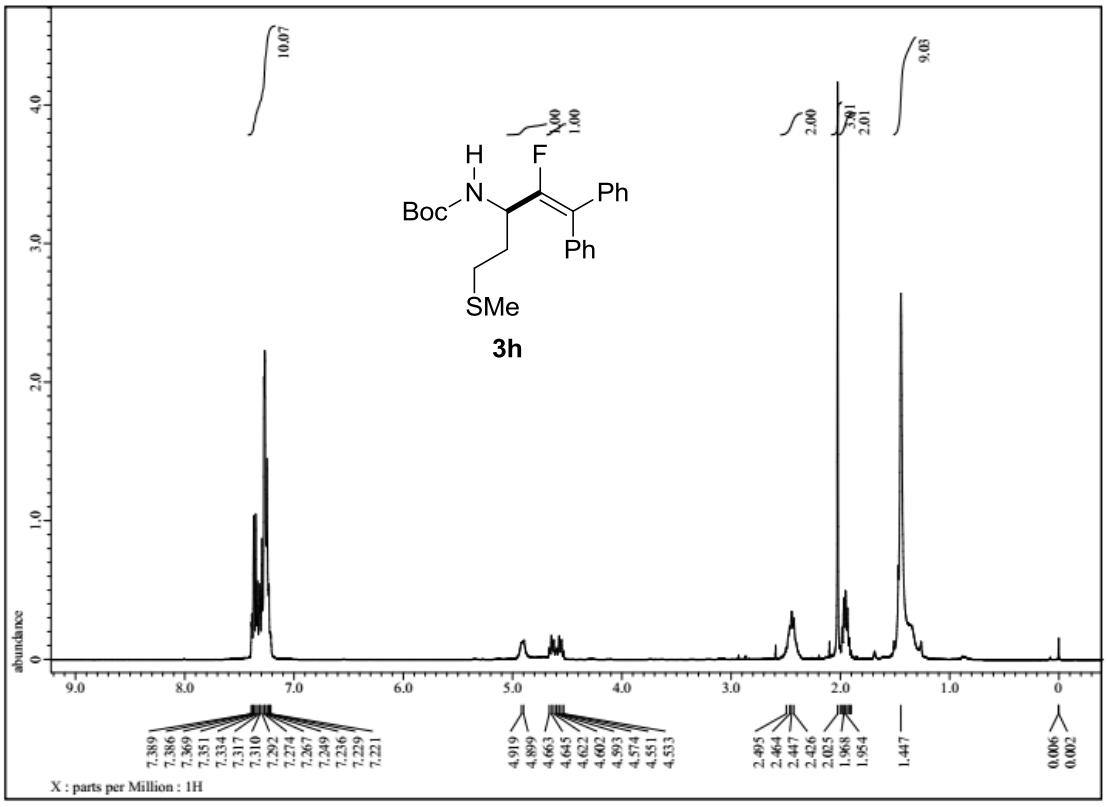

H
N
F
Boc
Ph
Ph
Ph
3f
abundance
155.134
154.457
152.512
130.067
130.048
129.638
129.476
129.429
128.456
128.294
128.065
127.579
126.759
79.753
77.475
77.160
76.836
51.855
51.598
39.746
28.438
X : parts per Million : 13C

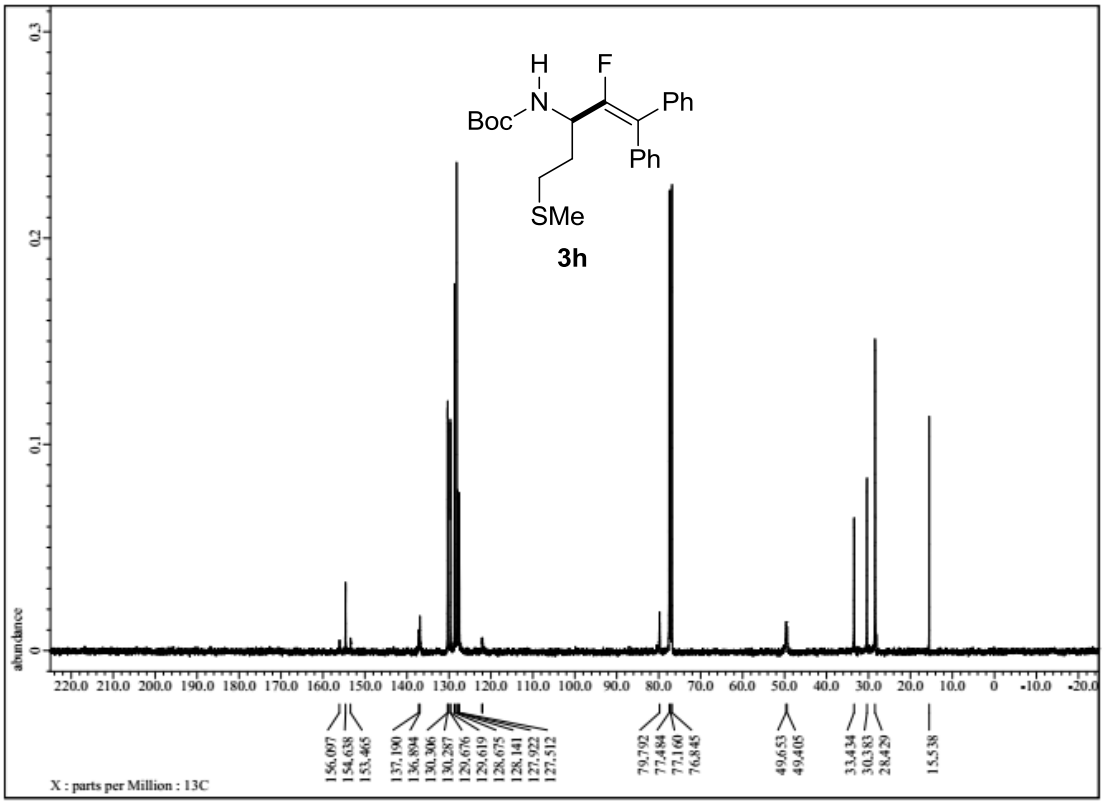

H
N
F
Boc
Ph
Ph
Ph
3f
abundance
-125.037
-125.087
X : parts per Million : 19F

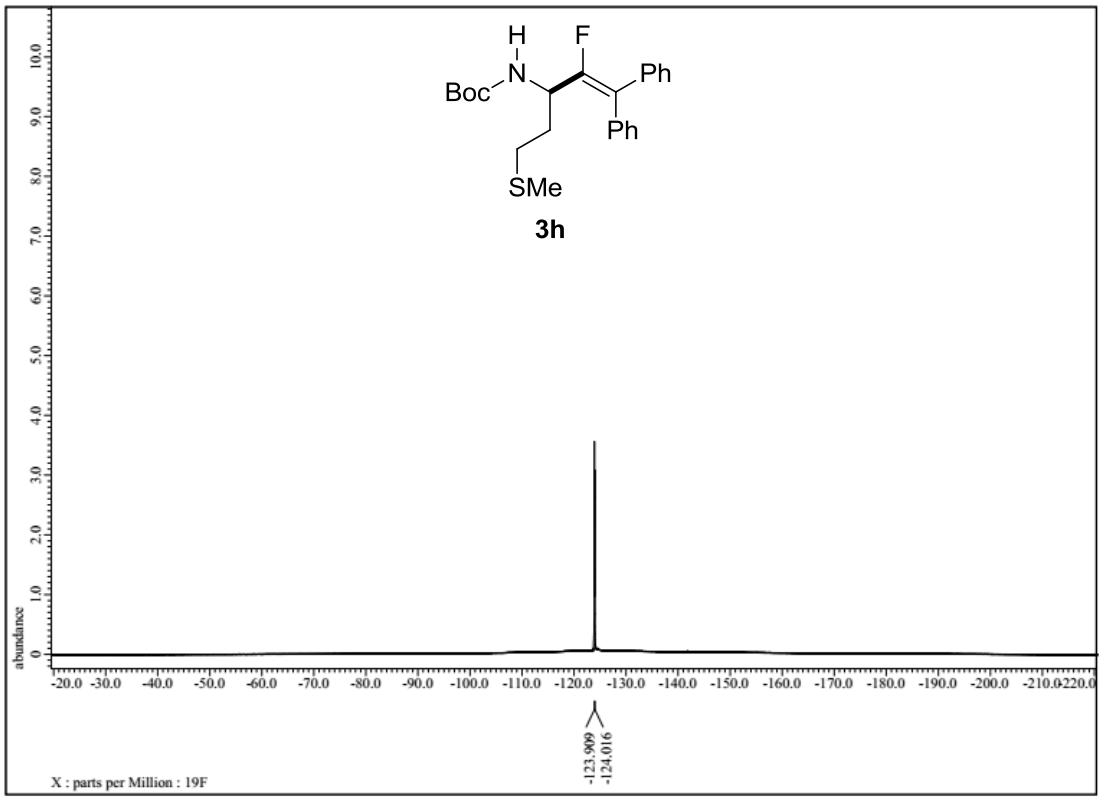

10.06
1.00
1.00
2.12
1.00
9.01
H
F
N
Boc
Ph
Ph
HO
3g
abundance
7.380
7.376
7.360
7.344
7.341
7.332
7.328
7.323
7.312
7.273
7.257
7.254
7.231
5.080
4.624
4.607
4.556
4.539
3.762
3.724
3.683
2.395
1.426
X : parts per Million : 1H

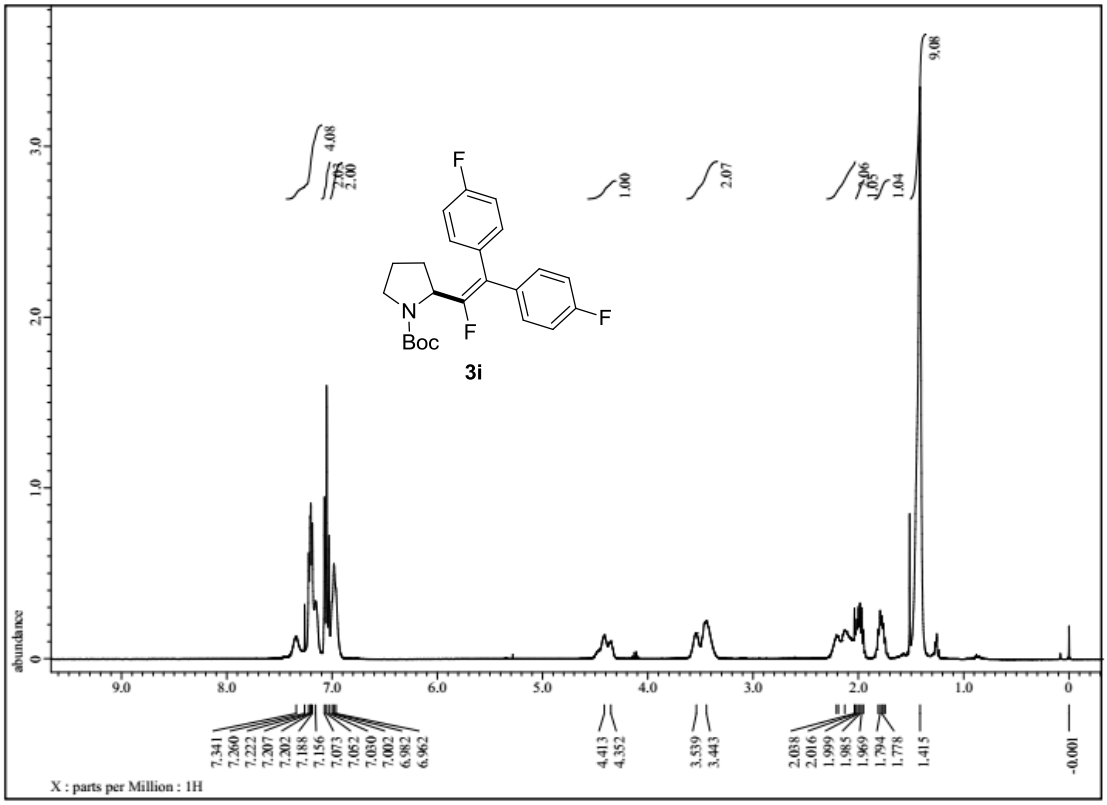

H
F
N
Boc
Ph
Ph
HO
3g
abundance
155.429
154.771
152.169
137.209
136.723
130.296
130.268
129.724
129.676
128.742
128.151
127.998
127.617
123.441
123.307
80.249
77.484
77.160
76.845
63.955
52.227
51.998
28.410
X : parts per Million : 13C

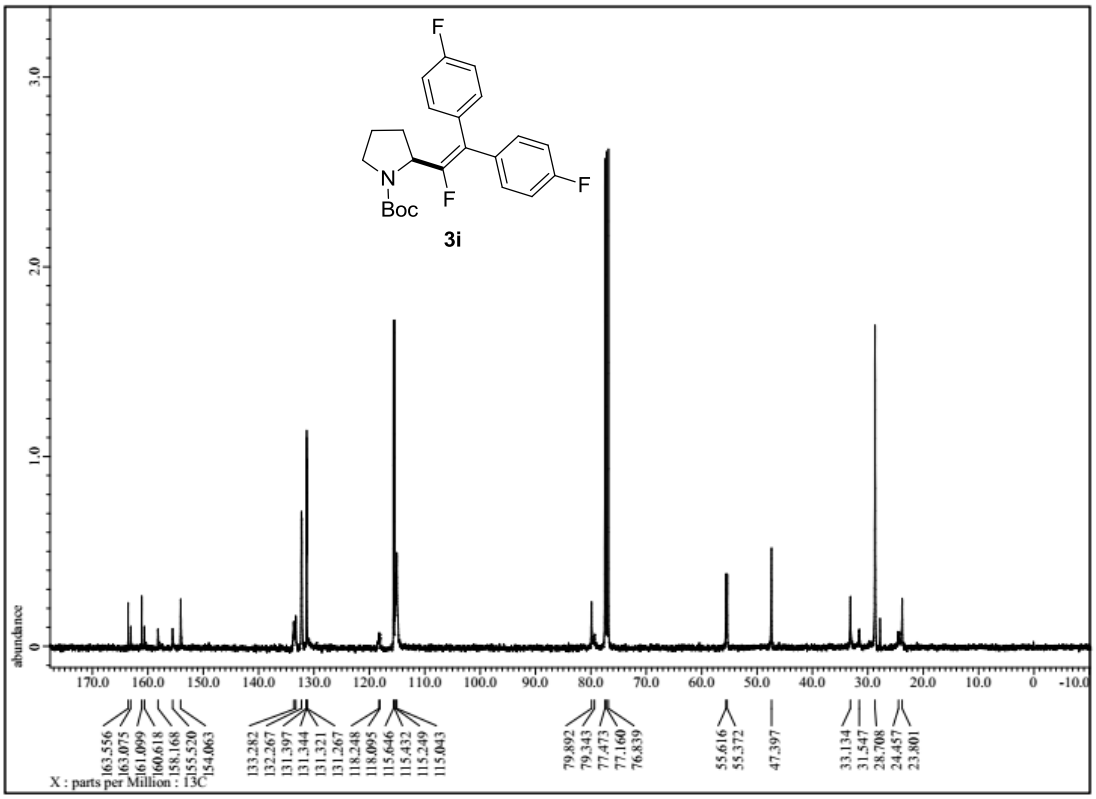

H
N
F
Ph
Boc
Ph
HO
3g
abundance
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-122.270
-122.312
X : parts per Million : 19F

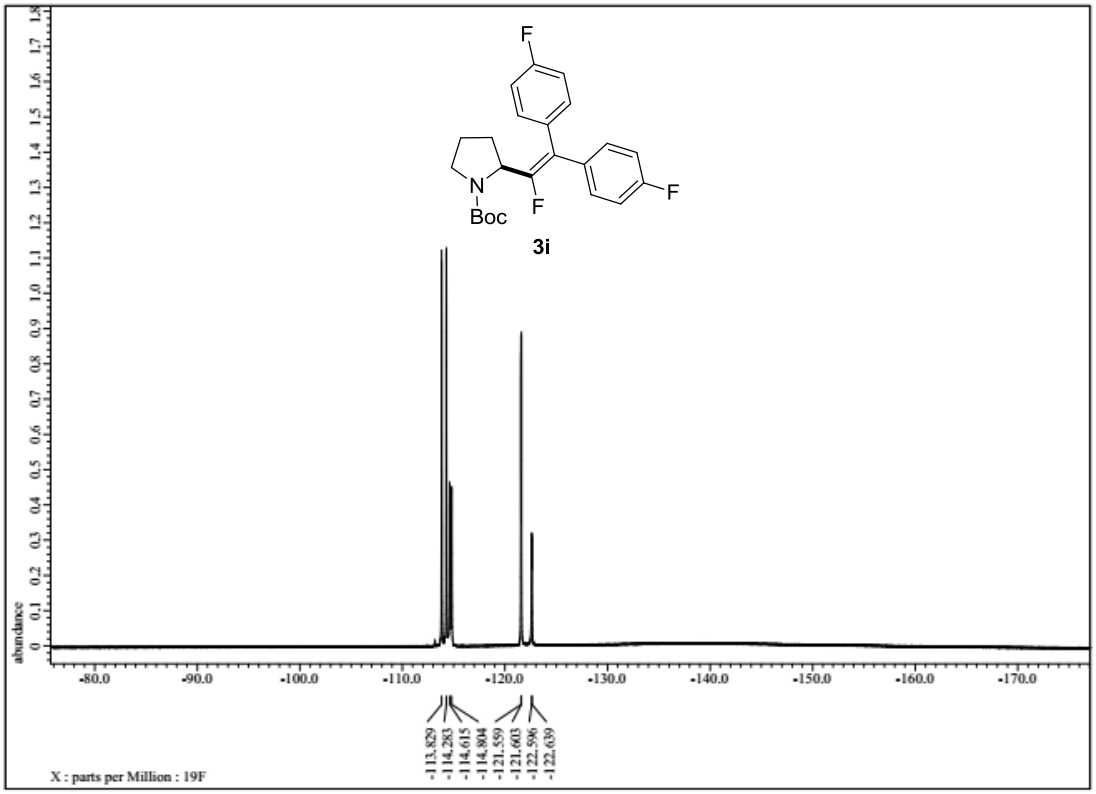

10.07
1.00
1.00
2.00
2.01
2.01
9.03
H
N
F
Ph
Boc
Ph
SMe
3h
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.389
7.386
7.369
7.351
7.334
7.317
7.310
7.292
7.274
7.267
7.249
7.236
7.229
7.221
4.919
4.899
4.663
4.645
4.622
4.602
4.593
4.574
4.551
4.533
2.495
2.464
2.447
2.426
2.025
1.968
1.954
1.447
0.006
0.002
X : parts per Million : 1H

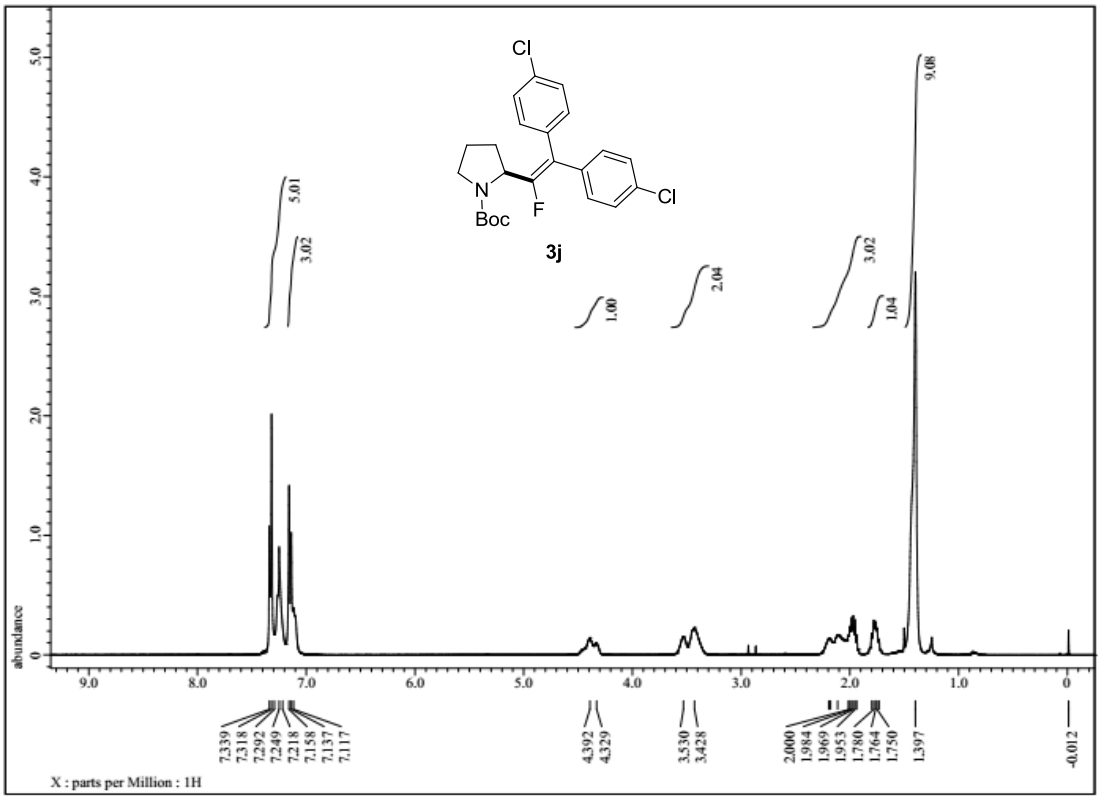

H
N
F
Boc
Ph
Ph
SMe
3h
abundance
X : parts per Million : 13C
156.097
154.638
153.465
137.190
136.894
130.306
130.287
129.676
129.619
128.675
128.141
127.922
127.512
79.792
77.484
77.160
76.845
49.653
49.405
33.434
30.383
28.429
15.538

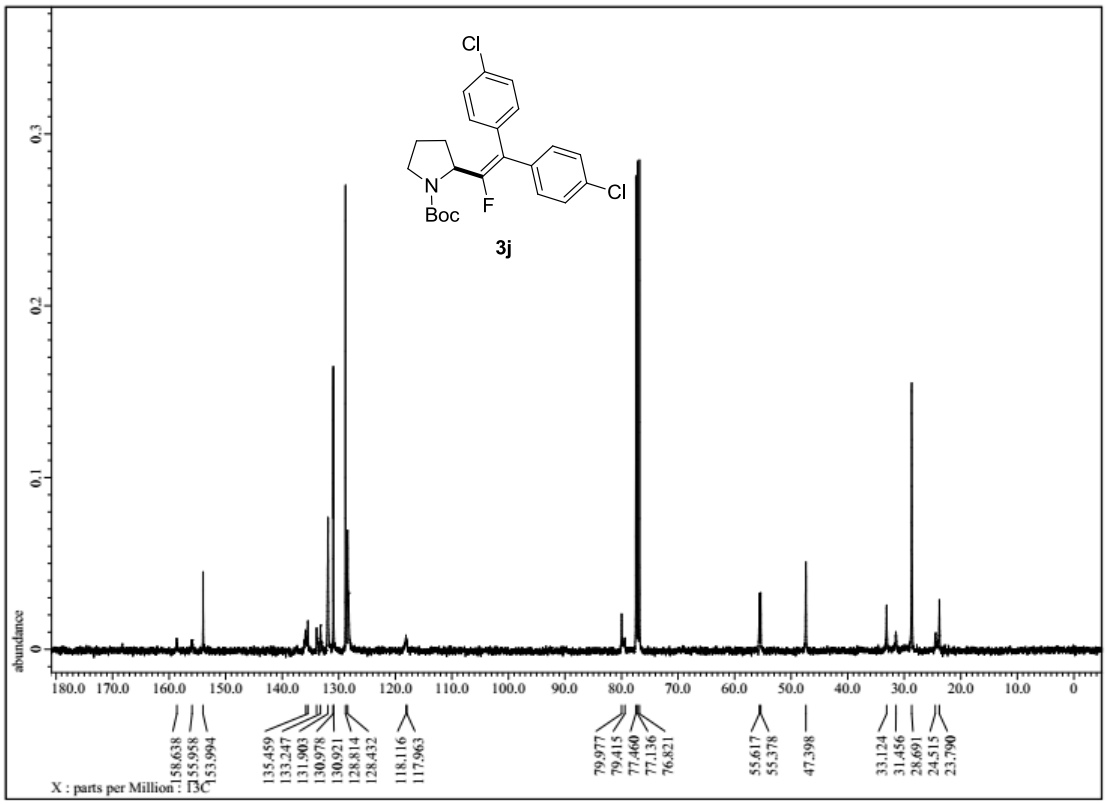

H
N
F
Boc
Ph
Ph
SMe
3h
abundance
X : parts per Million : 19F
-123.909
-124.016

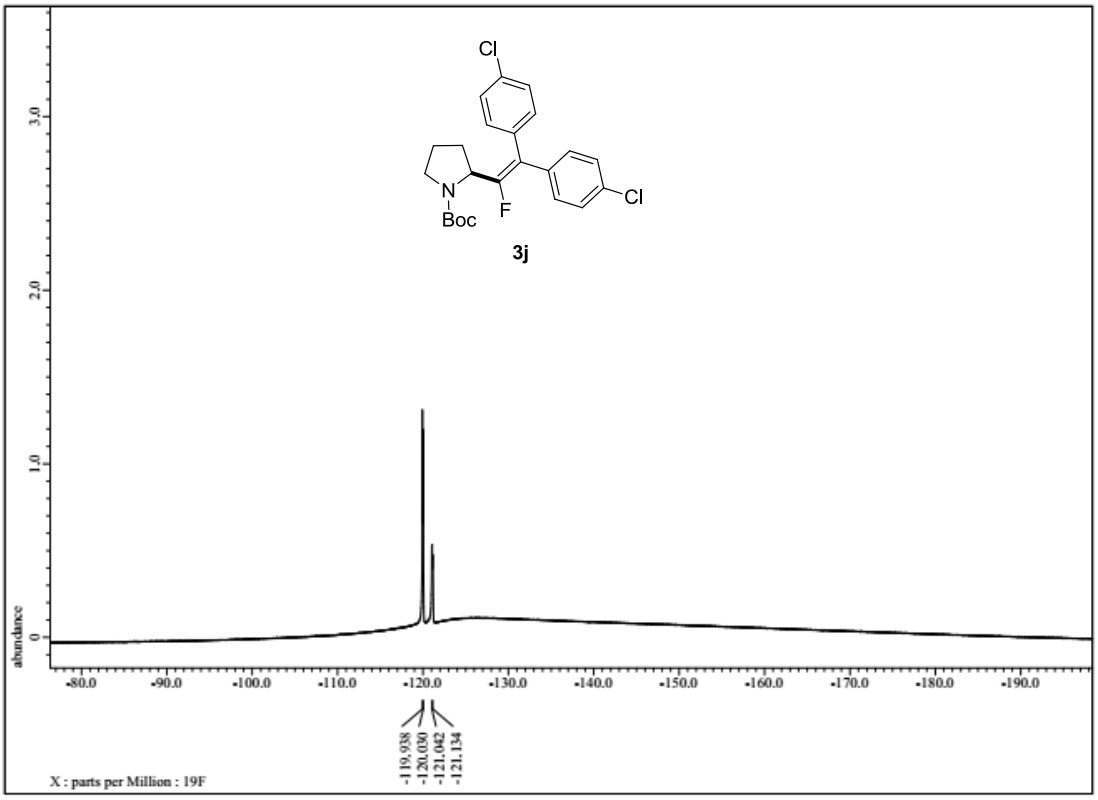

3i
X : parts per Million : 1H

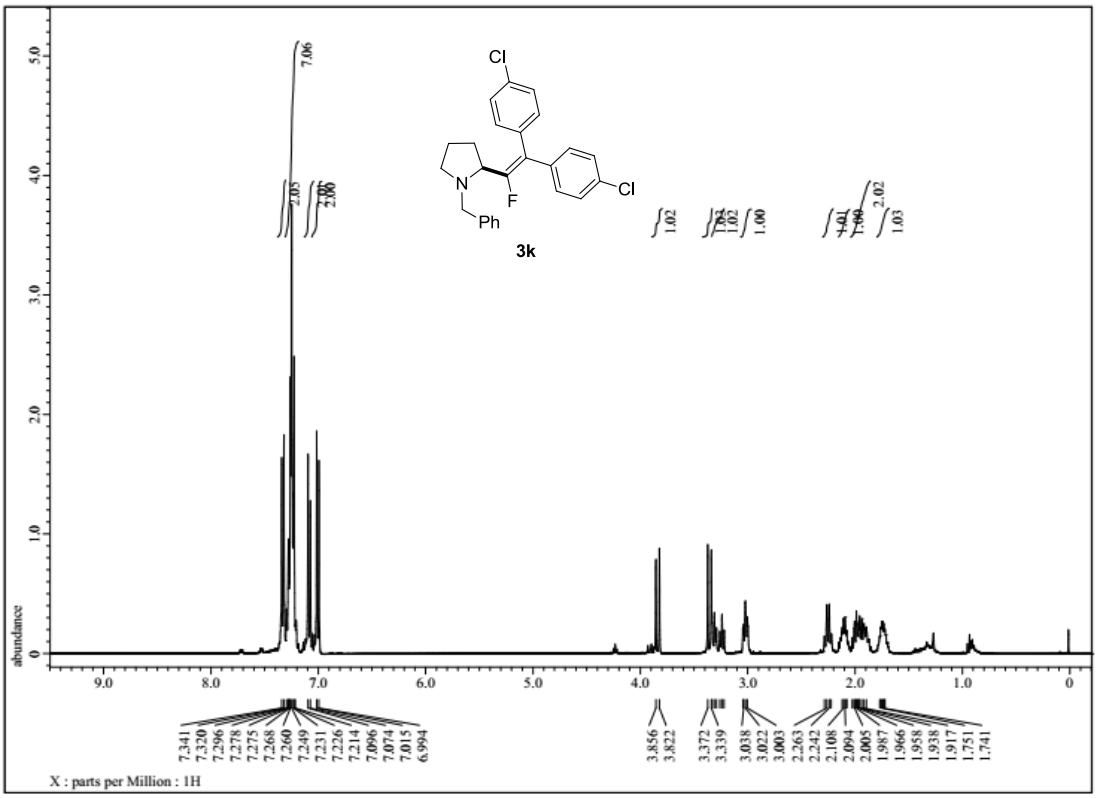

3i
X : parts per Million : 13C

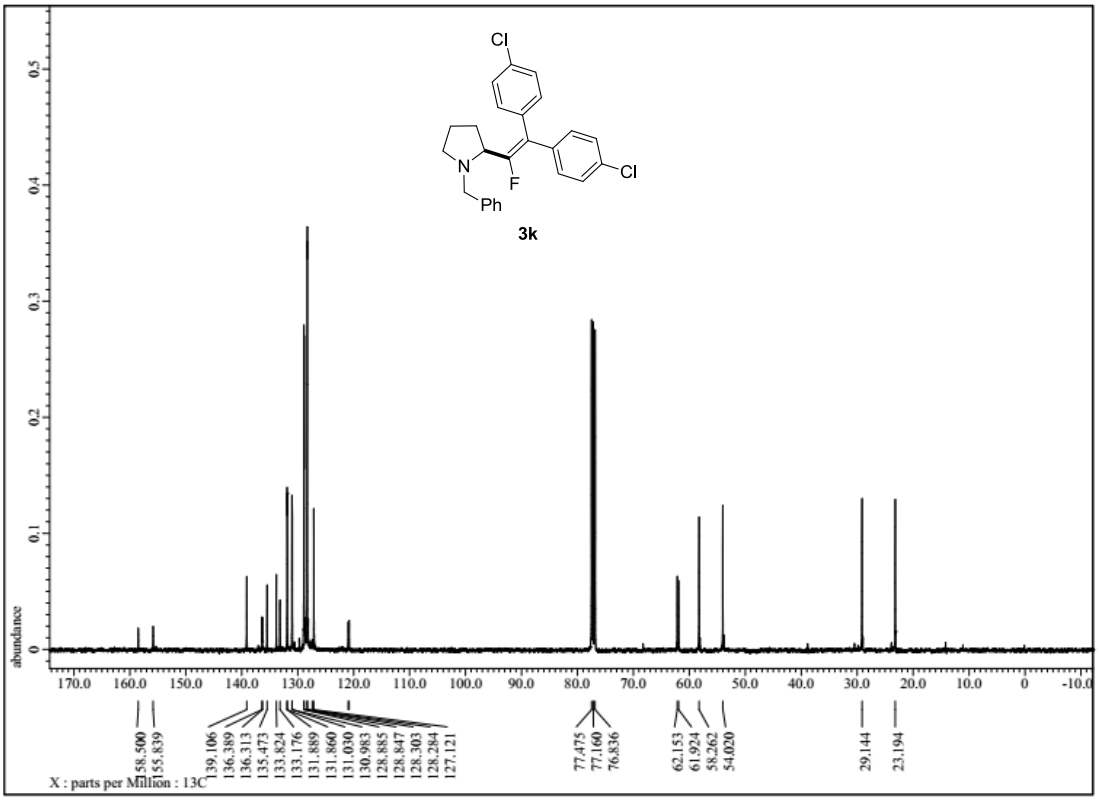

F
N
Boc
F
F
3i
abundance
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-113.829
-114.283
-114.615
-114.804
-121.559
-121.603
-122.596
-122.639
X : parts per Million : 19F

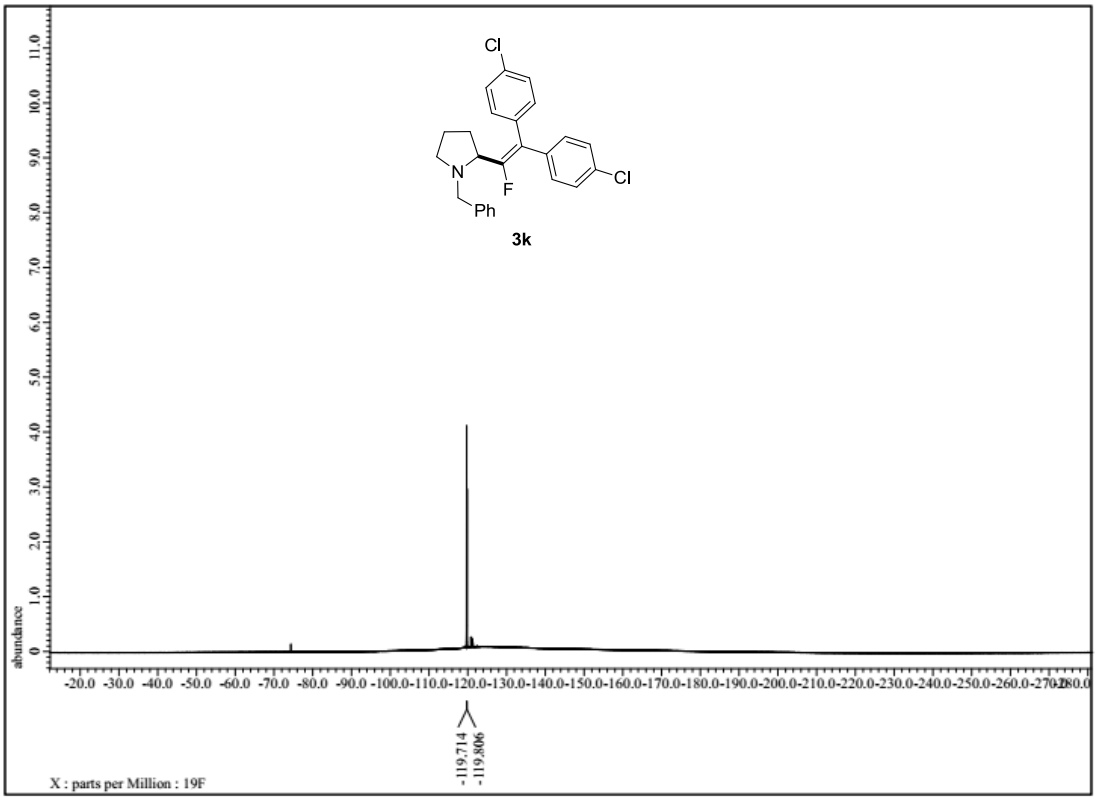

Cl
N
Boc
F
Cl
3j
5.01
3.02
1.00
2.04
3.02
1.04
9.08
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.339
7.318
7.292
7.249
7.218
7.158
7.137
7.117
4.392
4.329
3.530
3.428
2.000
1.984
1.969
1.953
1.780
1.764
1.750
1.397
-0.012
X : parts per Million : 1H

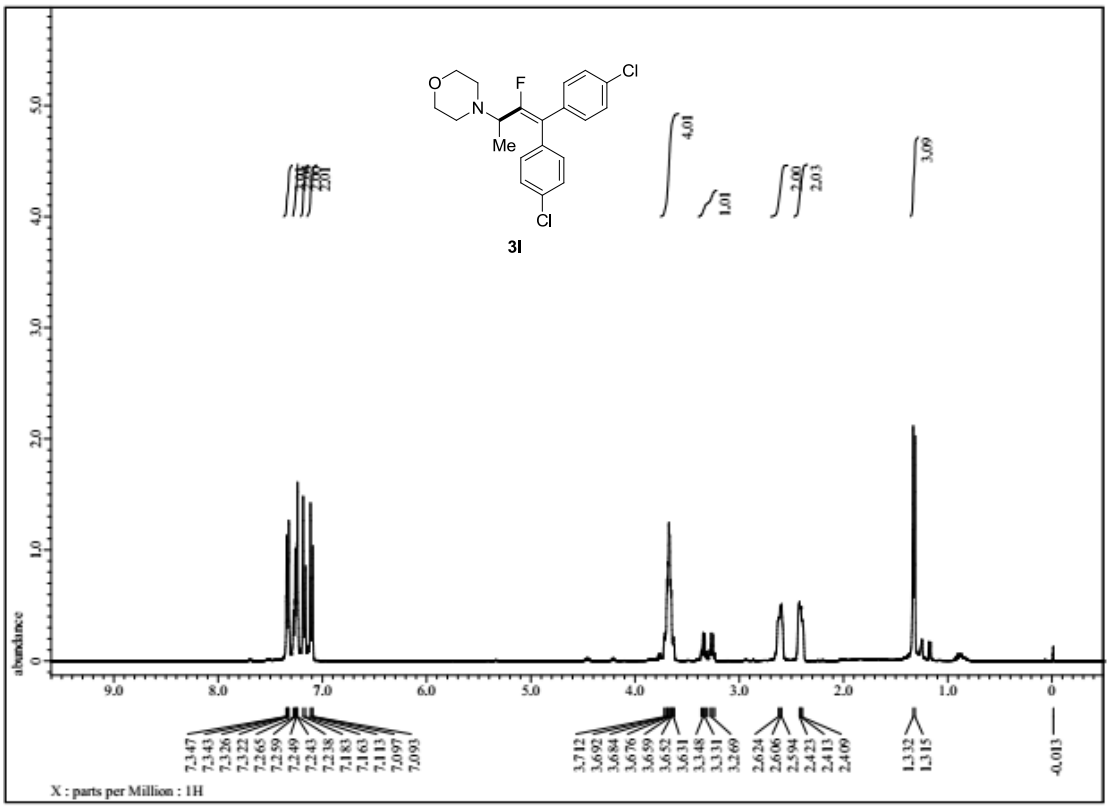

Cl
N
Boc
F
Cl
3j
abundance
0.3
0.2
0.1
0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
158.638
155.958
153.994
135.459
133.247
131.903
130.978
130.921
128.814
128.432
118.116
117.963
79.977
79.415
77.460
77.136
76.821
55.617
55.378
47.398
33.124
31.456
28.691
24.515
23.790
X : parts per Million : 13C

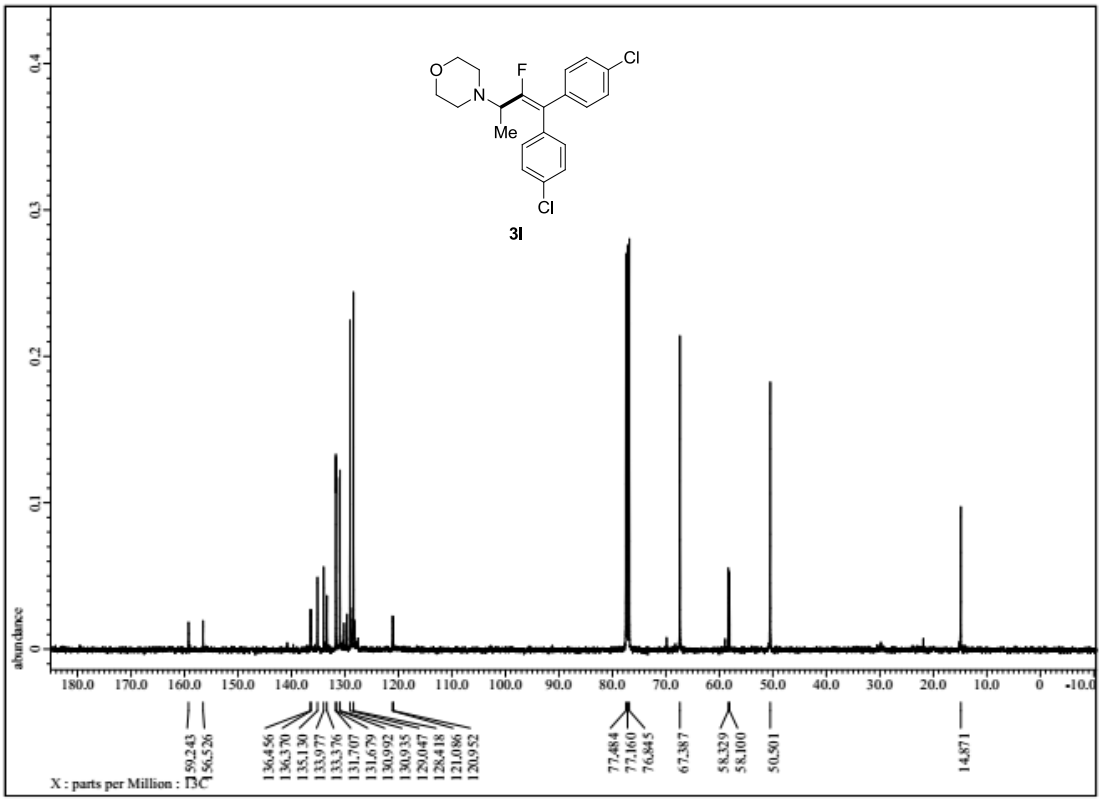

Cl
N
Boc
F
Cl
3j
abundance
3.0
2.0
1.0
0
-80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-119.938
-120.030
-121.042
-121.134
X : parts per Million : 19F

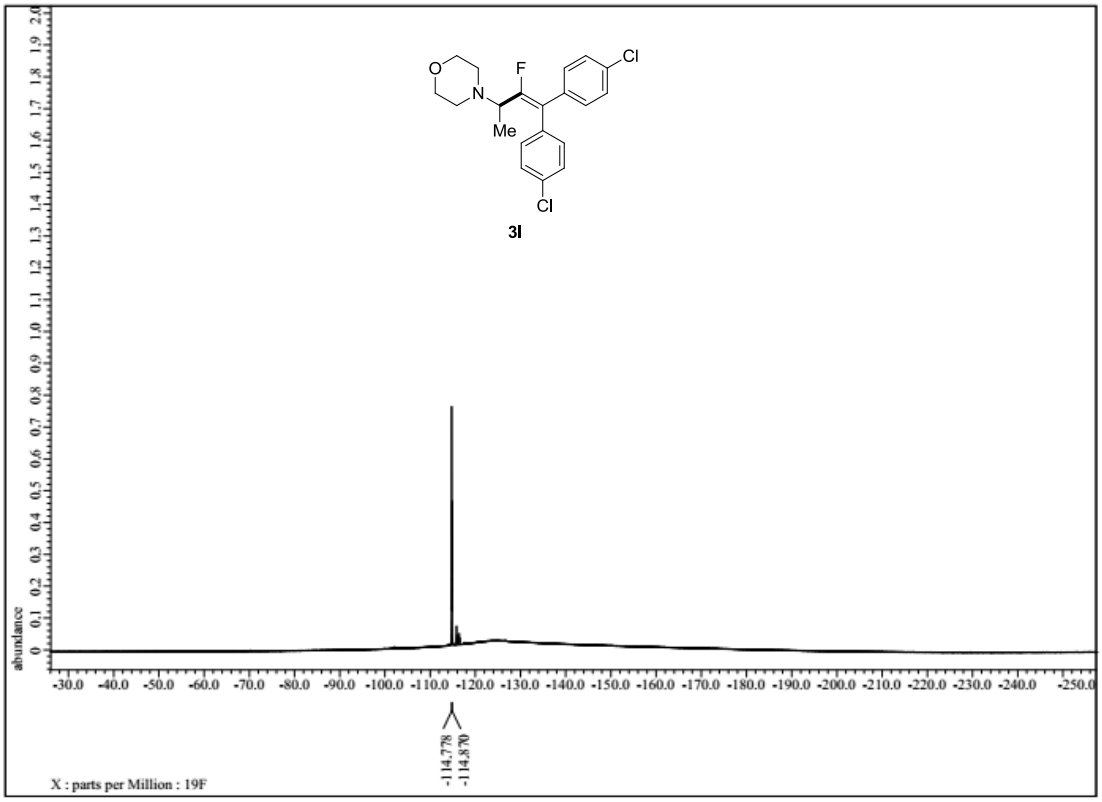

Cl
N
F
Ph
Cl
3k
abundance
X : parts per Million : 1H

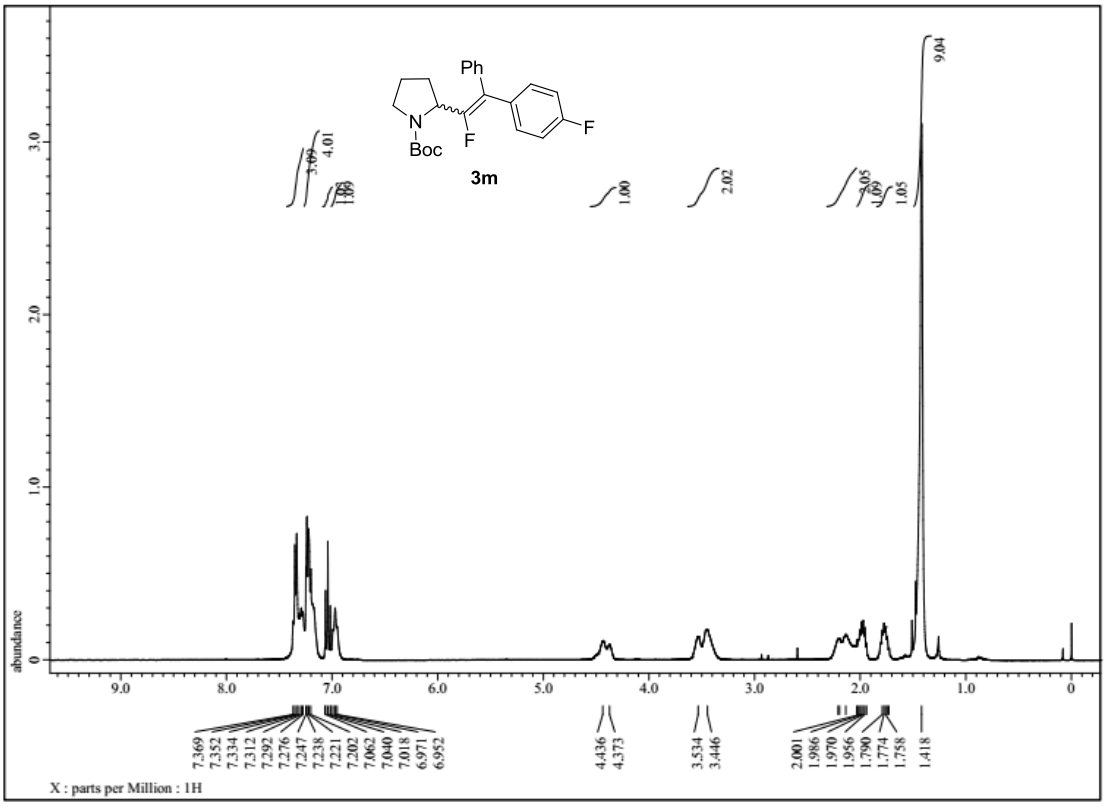

Cl
N
F
Ph
Cl
3k
abundance
X : parts per Million : 13C

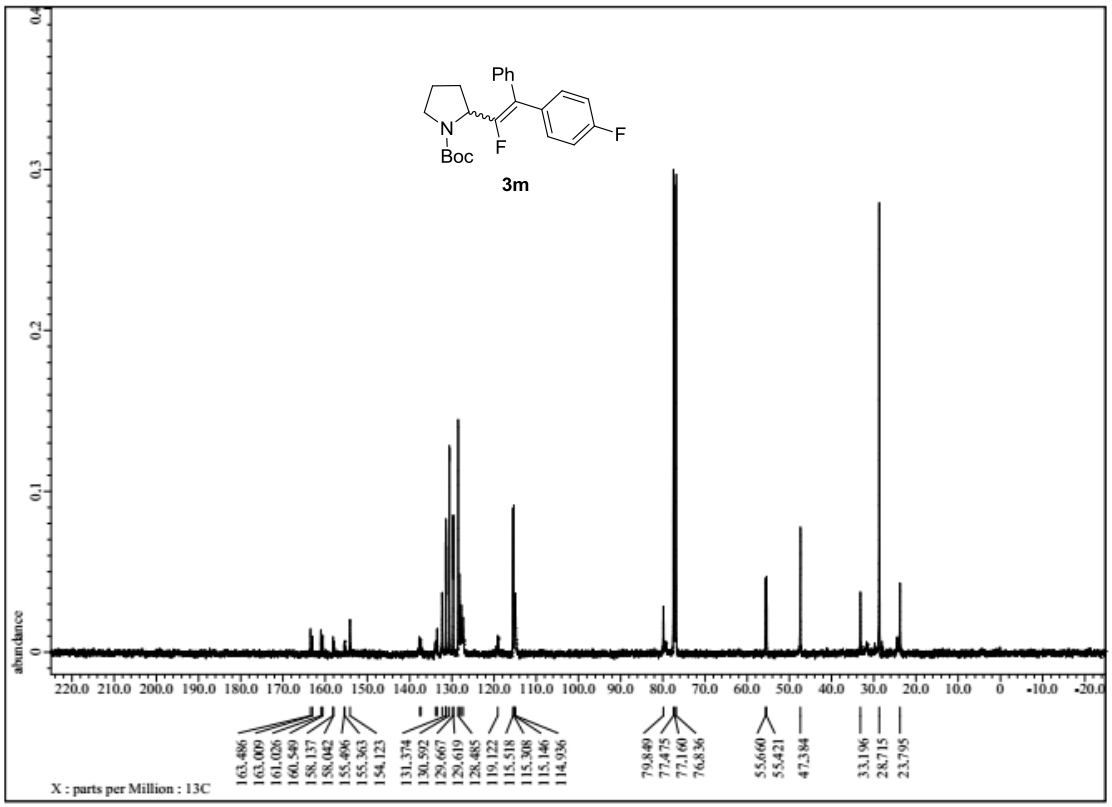

Cl
N
F
Cl
Ph
3k
abundance
-119.714
-119.806
X : parts per Million : 19F

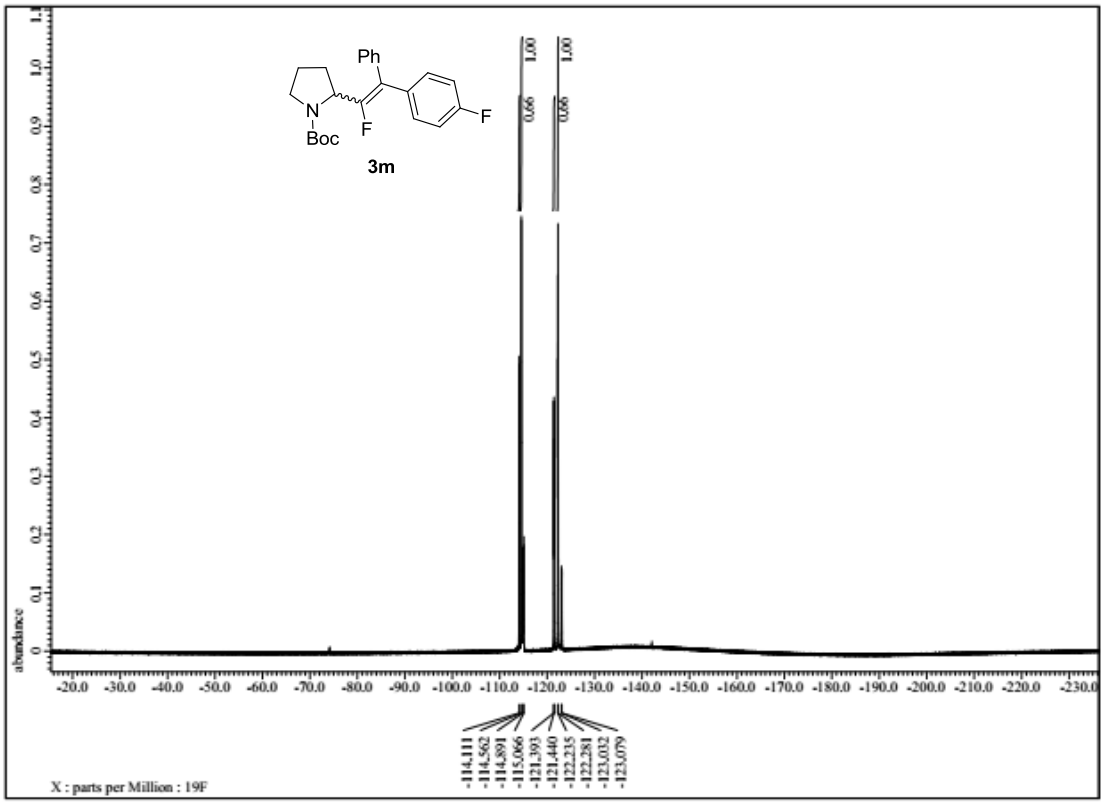

O
N
F
Cl
Me
Cl
3l
4.01
1.01
2.00
2.03
3.09
abundance
X : parts per Million : 1H

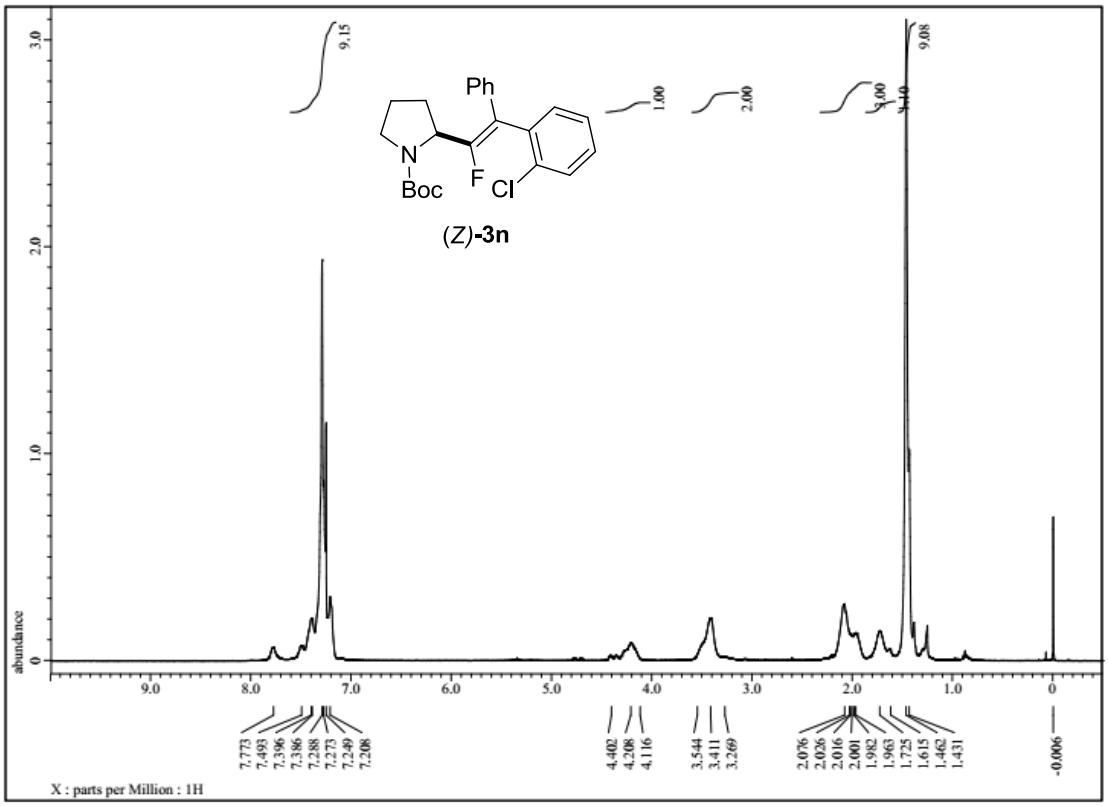

O
N
F
Cl
Me
Cl
3l
abundance
X : parts per Million : 13C

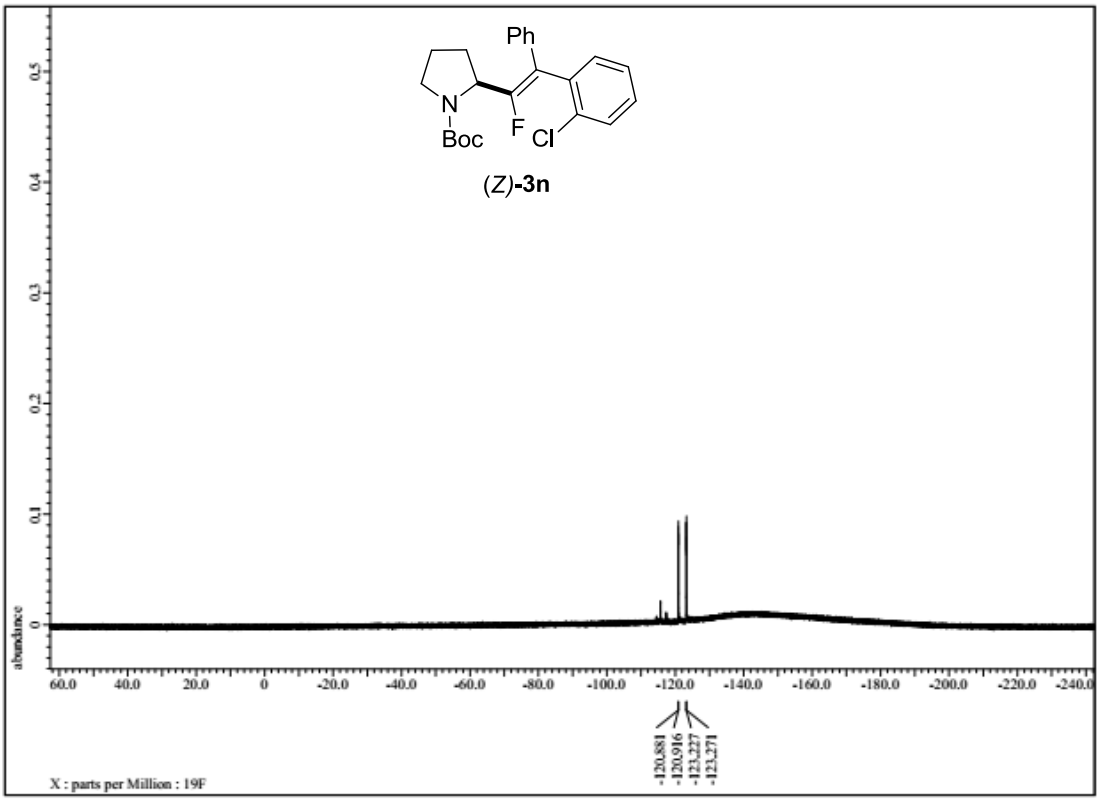

O
N
F
Cl
Me
Cl
3l
abundance
X : parts per Million : 19F

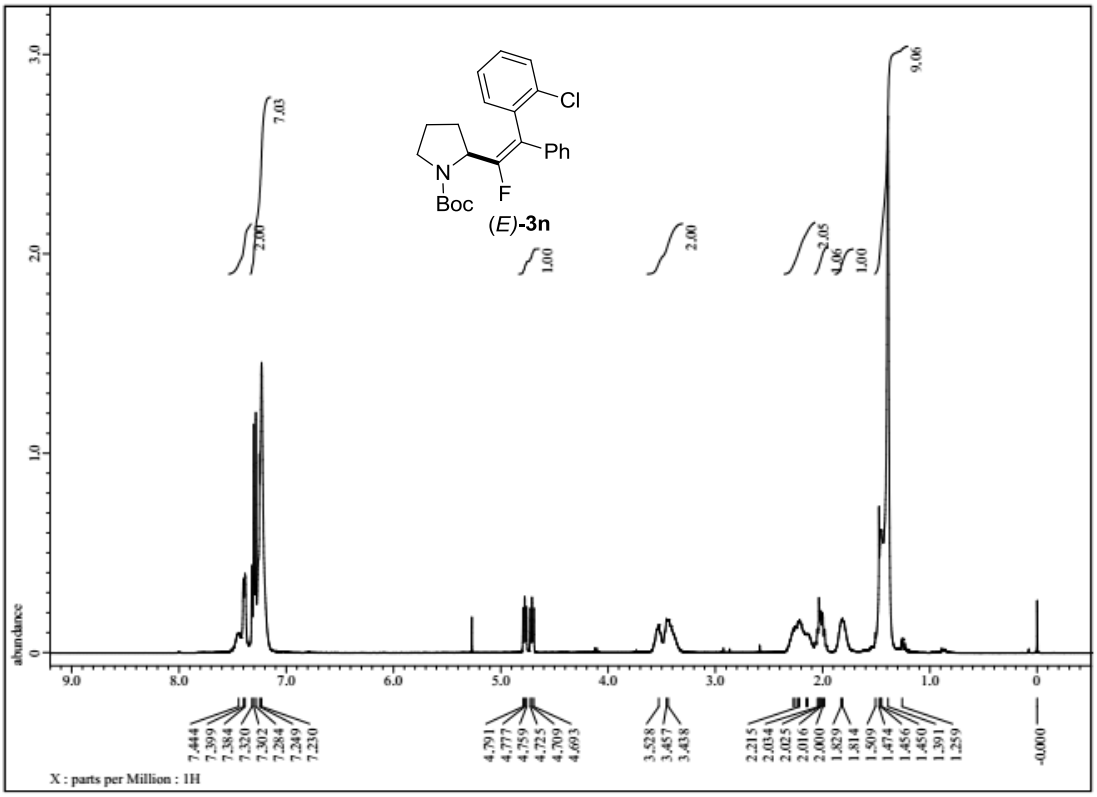

Ph
N
Boc
F
F
3m
9.04
4.01
2.02
1.05
abundance
X : parts per Million : 1H

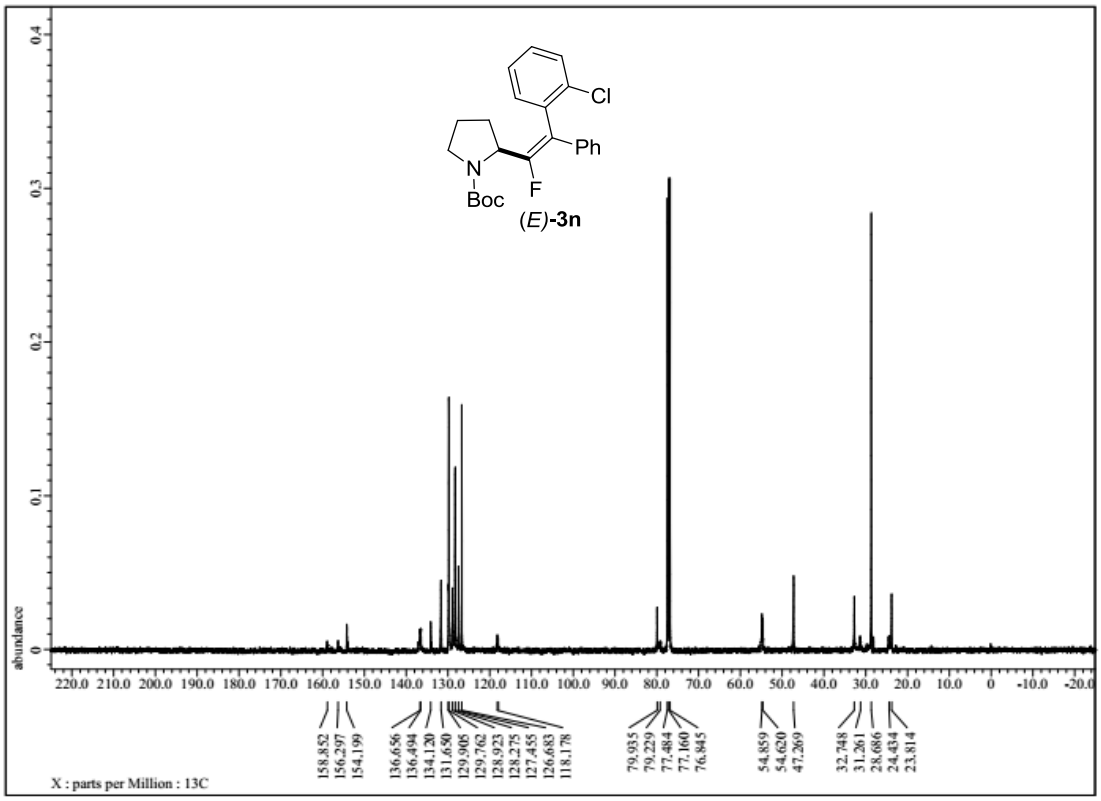

Ph
N
Boc
F
F
3m
abundance
X : parts per Million : 13C

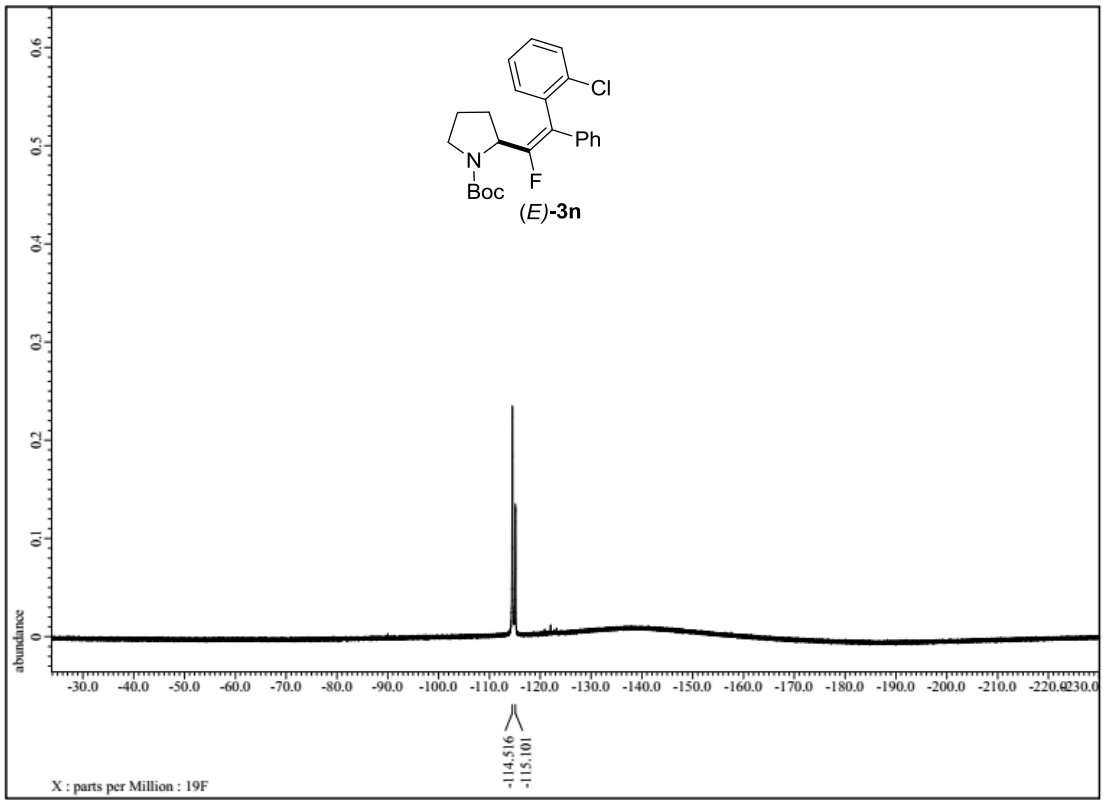

Ph
N
Boc
F
F
3m
1.00
1.00
0.66
0.66
abundance
-20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0 -210.0 -220.0 -230.0
-114.111
-114.562
-114.891
-115.066
-121.393
-121.440
-122.235
-122.281
-123.032
-123.079
X : parts per Million : 19F

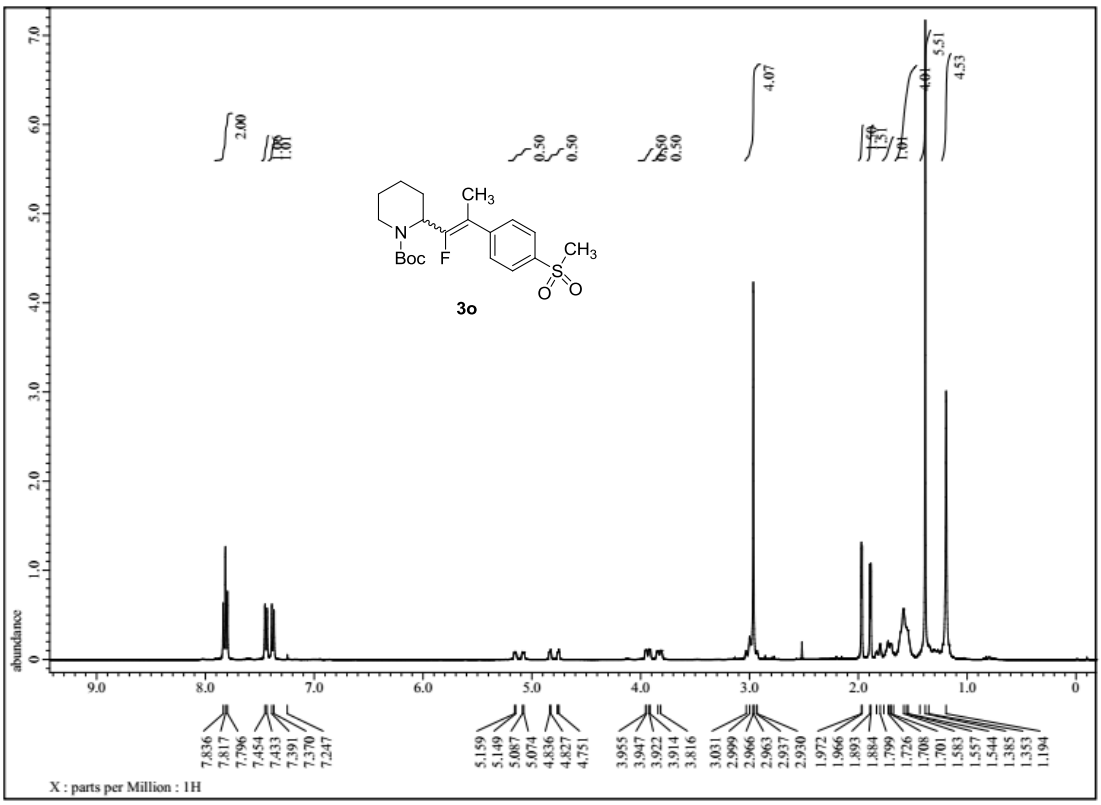

9.15
1.00
2.00
3.00
3.10
9.08
Ph
N
Boc
F
Cl
(Z)-3n
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.773
7.493
7.396
7.386
7.288
7.273
7.249
7.208
4.402
4.208
4.116
3.544
3.411
3.269
2.076
2.026
2.016
2.001
1.982
1.963
1.725
1.615
1.462
1.431
-0.006
X : parts per Million : 1H

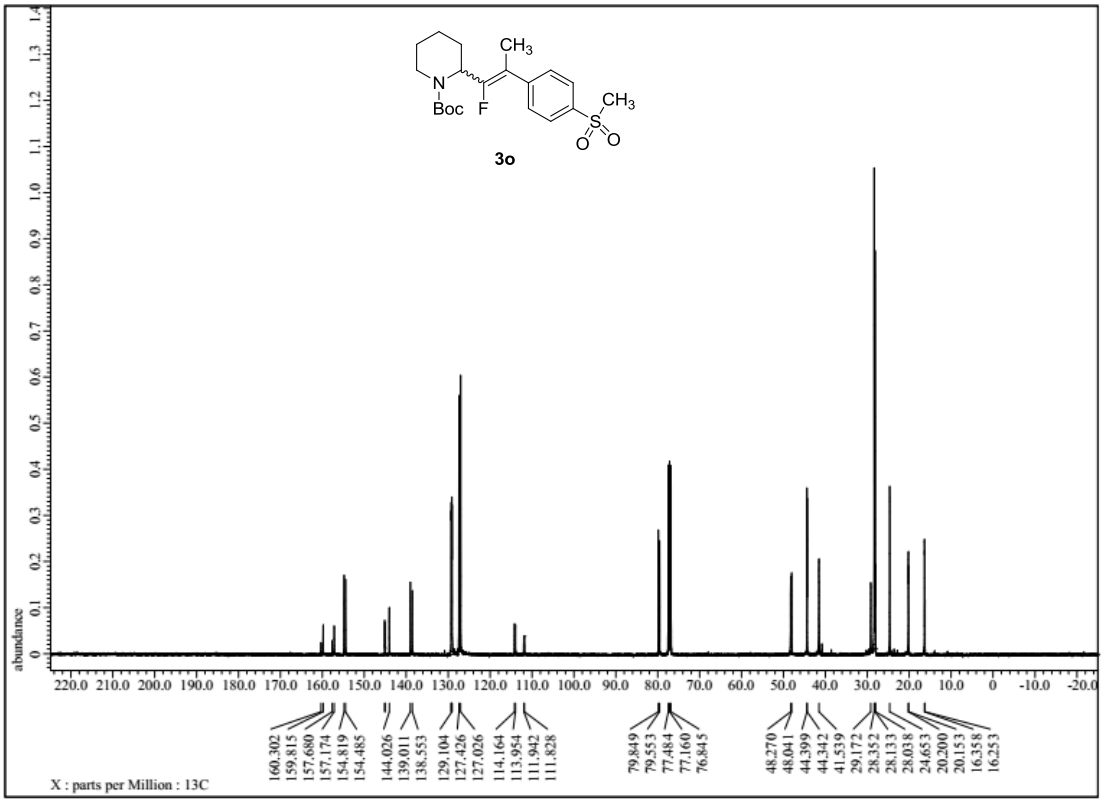

Ph
N
Boc
F
Cl
(Z)-3n
abundance
60.0
40.0
20.0
0
-20.0
-40.0
-60.0
-80.0
-100.0
-120.0
-140.0
-160.0
-180.0
-200.0
-220.0
-240.0
-120.881
-120.916
-123.227
-123.271
X : parts per Million : 19F

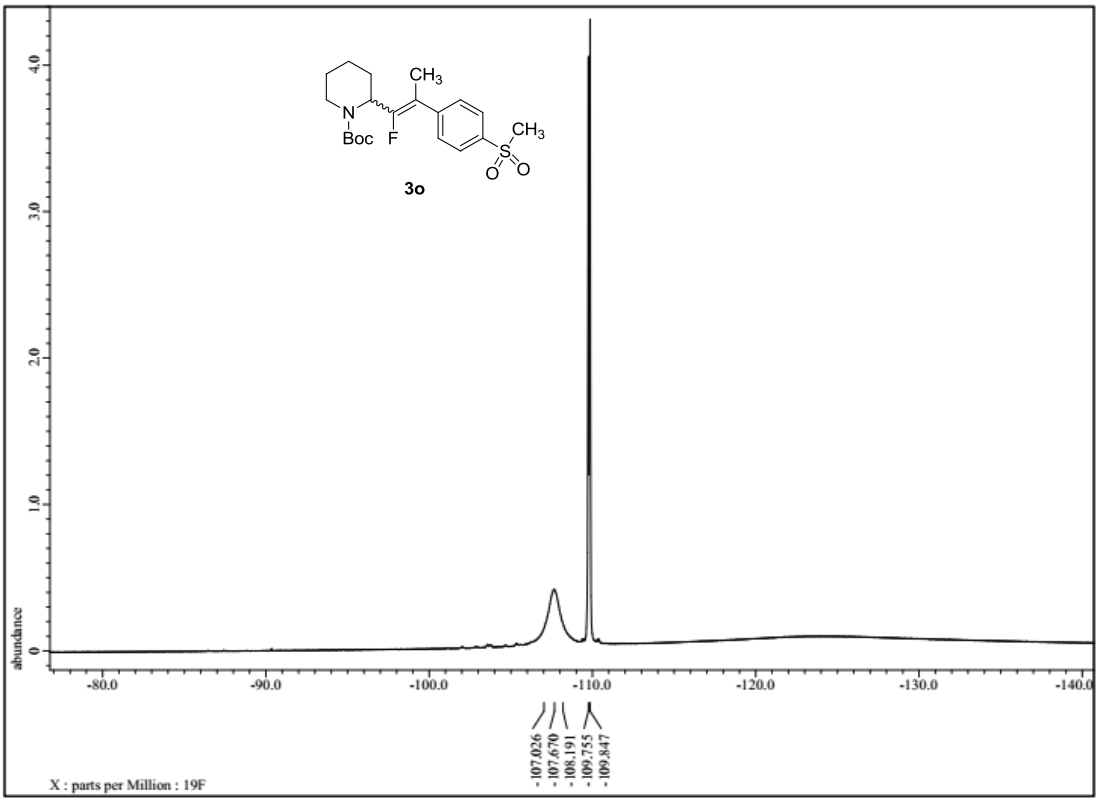

Cl
Ph
N
Boc
F
(E)-3n
7.03
2.00
1.00
2.00
2.05
4.06
1.00
9.06
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.444
7.399
7.384
7.320
7.302
7.284
7.249
7.230
4.791
4.777
4.759
4.725
4.709
4.693
3.528
3.457
3.438
2.215
2.034
2.025
2.016
2.000
1.829
1.814
1.509
1.474
1.456
1.450
1.391
1.259
-0.000
X : parts per Million : 1H

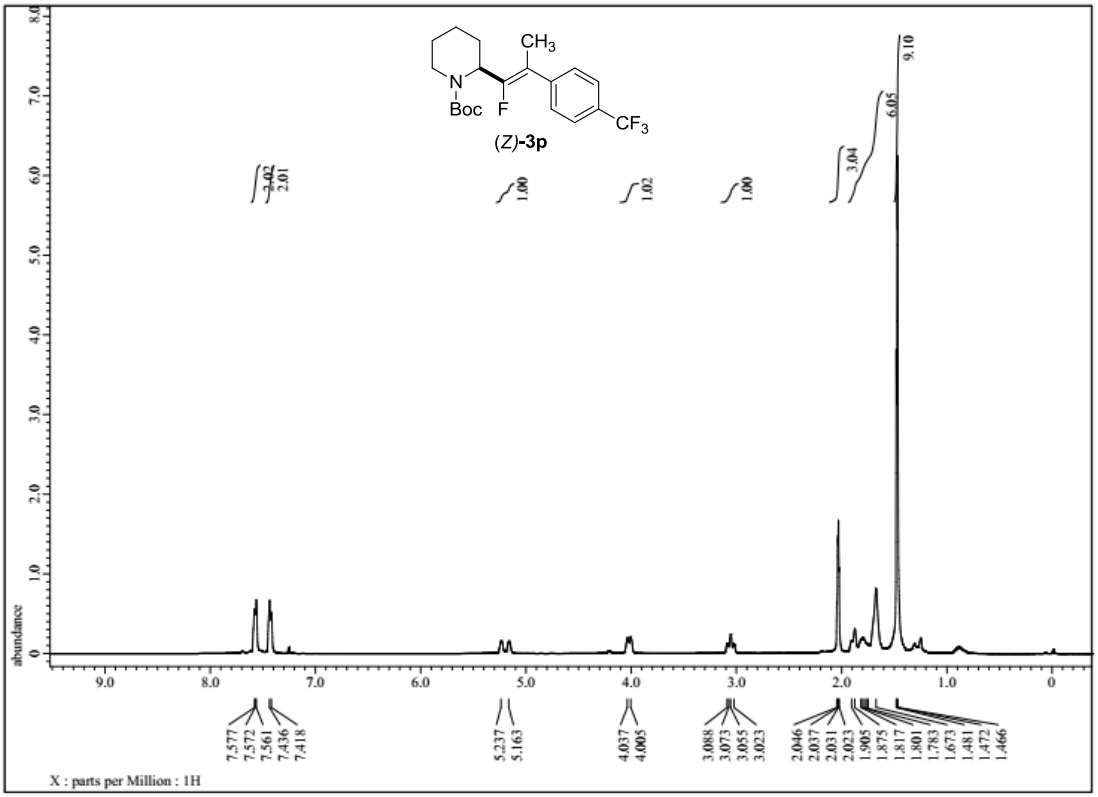

Cl
Ph
N
Boc
F
(E)-3n
abundance
158.852
156.297
154.199
136.656
136.494
134.120
131.650
129.908
129.762
128.923
128.275
127.455
126.683
118.178
79.935
79.229
77.484
77.160
76.845
54.859
54.620
47.269
32.748
31.261
28.686
24.434
23.814
X : parts per Million : 13C

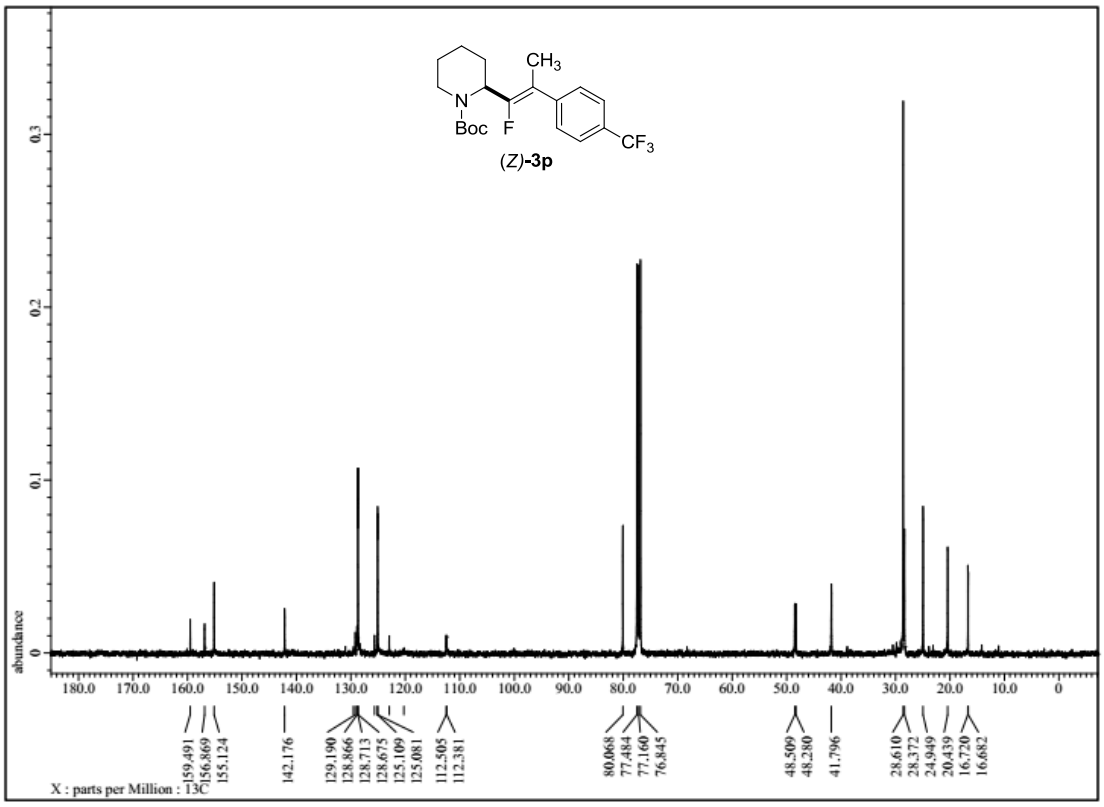

Cl
Ph
N
Boc
F
(E)-3n
abundance
-114.516
-115.101
X : parts per Million : 19F

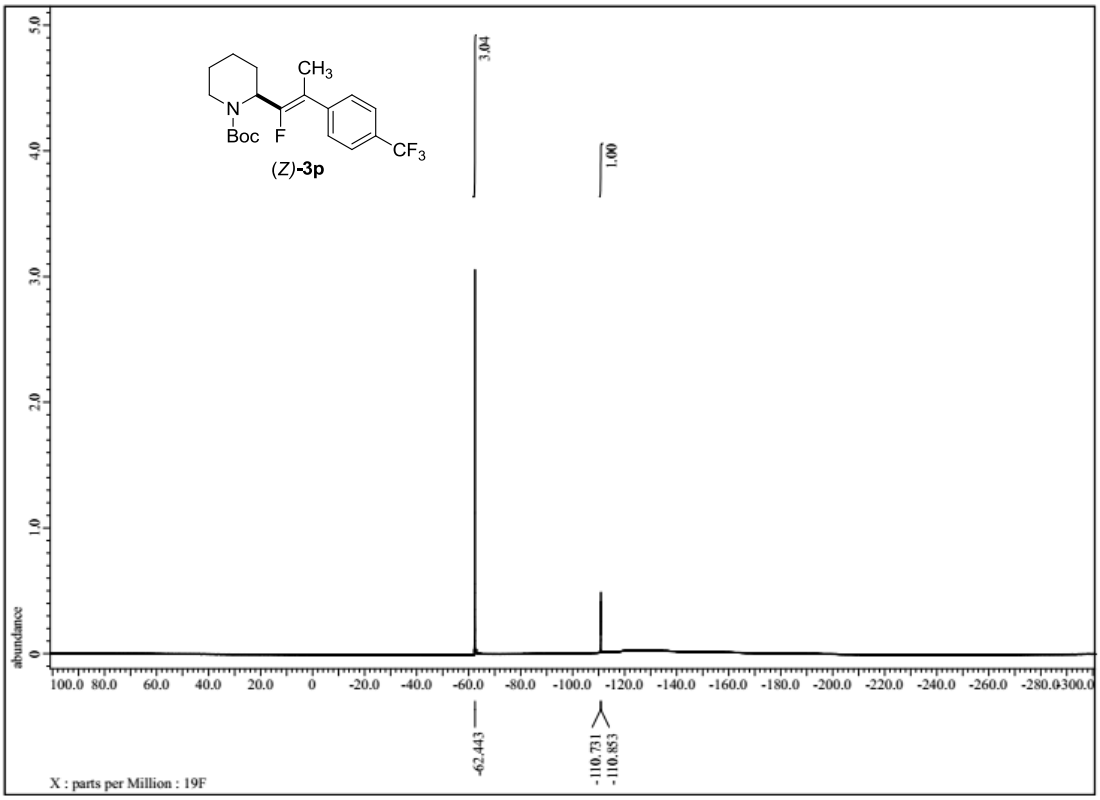

3o
abundance
X : parts per Million : 1H

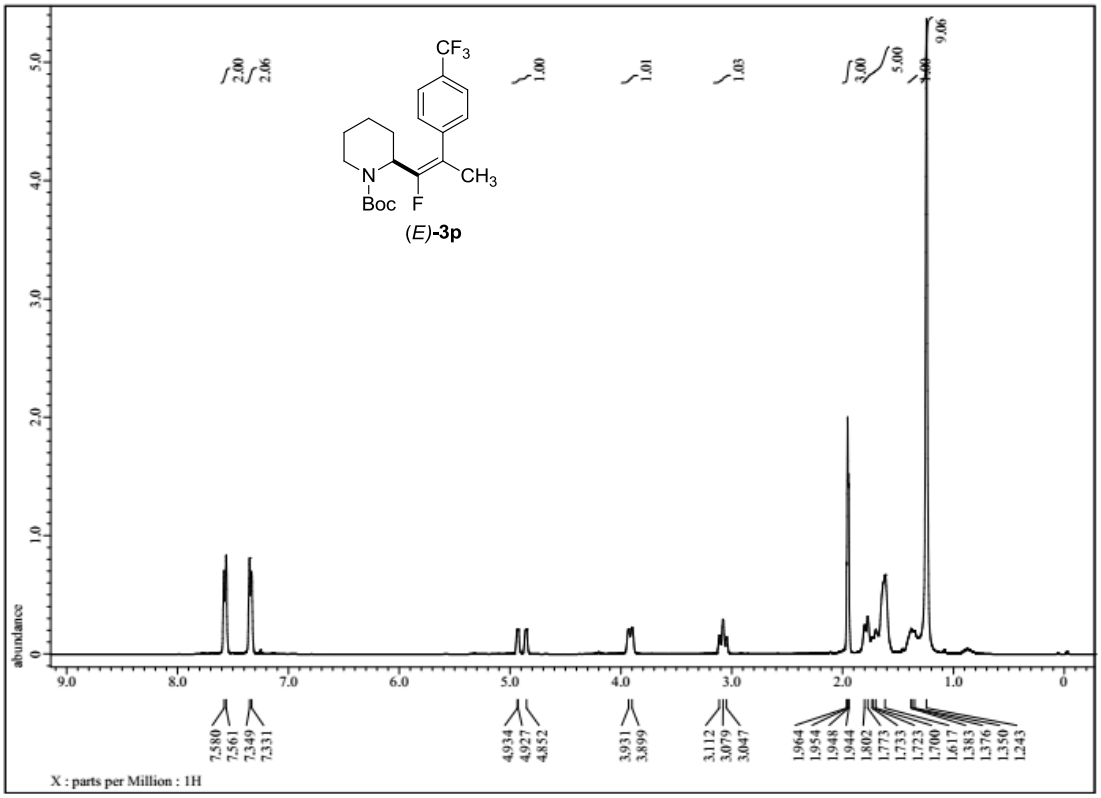

3o
abundance
X : parts per Million : 13C

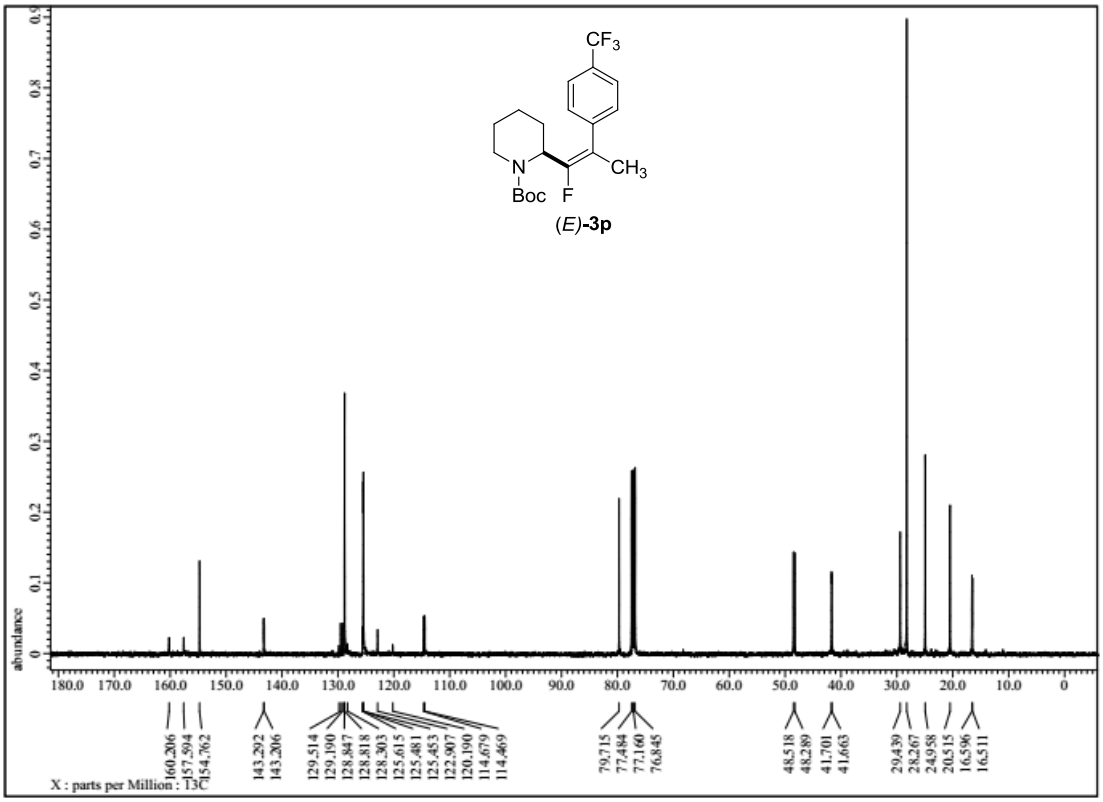

CH3
N
Boc
F
CH3
S
O
O
3o
abundance
4.0
3.0
2.0
1.0
0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-107.026
-107.670
-108.191
-109.755
-109.847
X : parts per Million : 19F

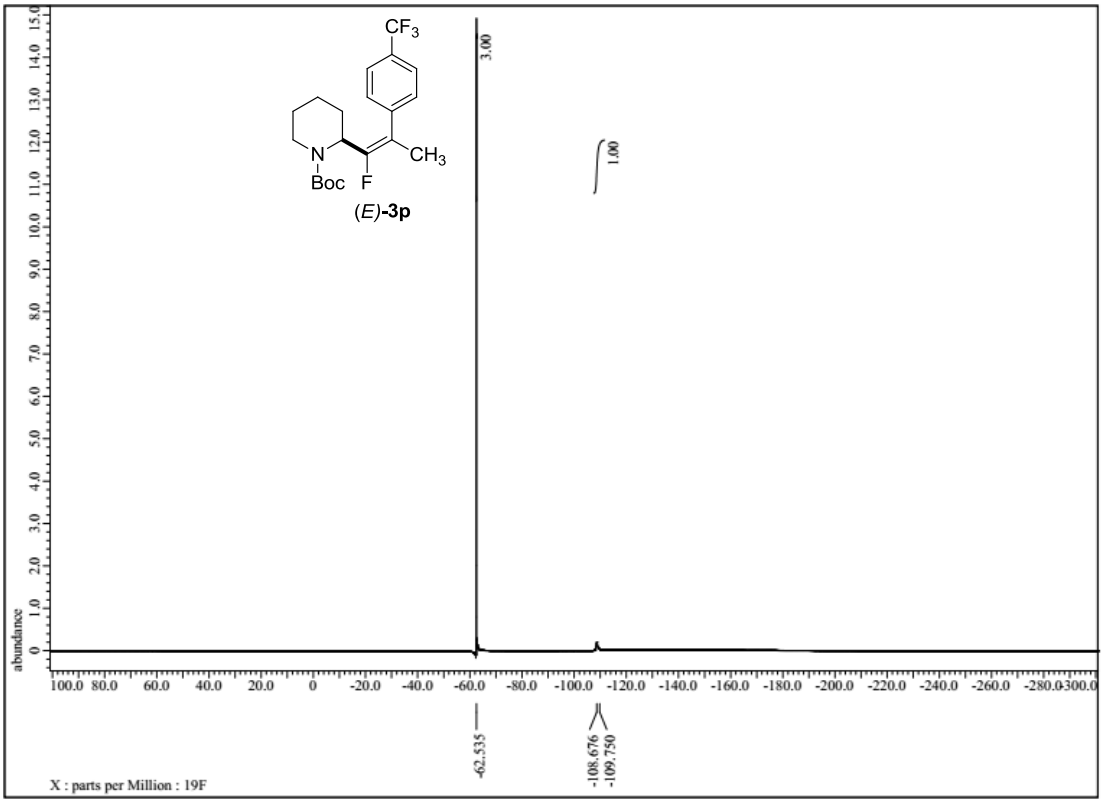

CH3
N
Boc
F
CF3
(Z)-3p
2.02
2.01
1.00
1.02
1.00
3.04
6.05
9.10
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.577
7.572
7.561
7.436
7.418
5.237
5.163
4.037
4.005
3.088
3.073
3.055
3.023
2.046
2.037
2.031
2.023
1.905
1.875
1.817
1.801
1.783
1.673
1.481
1.472
1.466
X : parts per Million : 1H

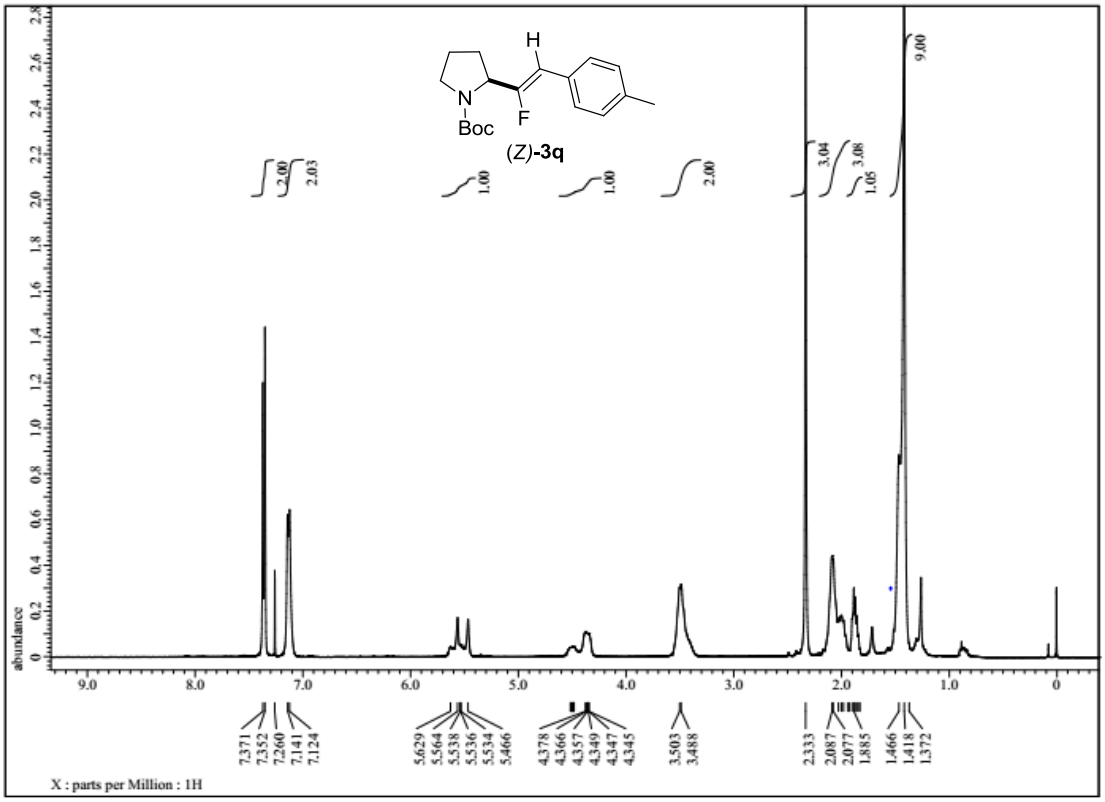

CH3
N
Boc
F
CF3
(Z)-3p
abundance
X : parts per Million : 13C
159.491
156.869
155.124
142.176
129.190
128.866
128.713
128.675
125.109
125.081
112.505
112.381
80.068
77.484
77.160
76.845
48.509
48.280
41.796
28.610
28.372
24.949
20.439
16.720
16.682

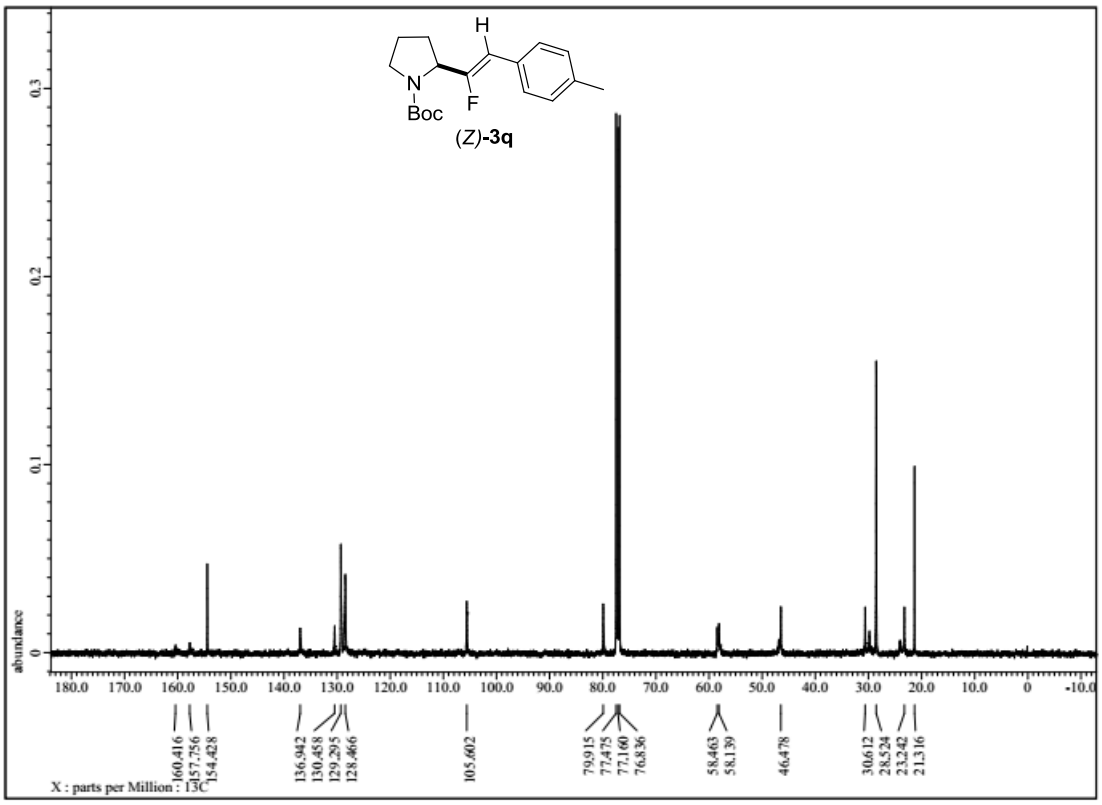

CH3
N
Boc
F
CF3
(Z)-3p
3.04
1.00
abundance
X : parts per Million : 19F
-62.443
-110.731
-110.853

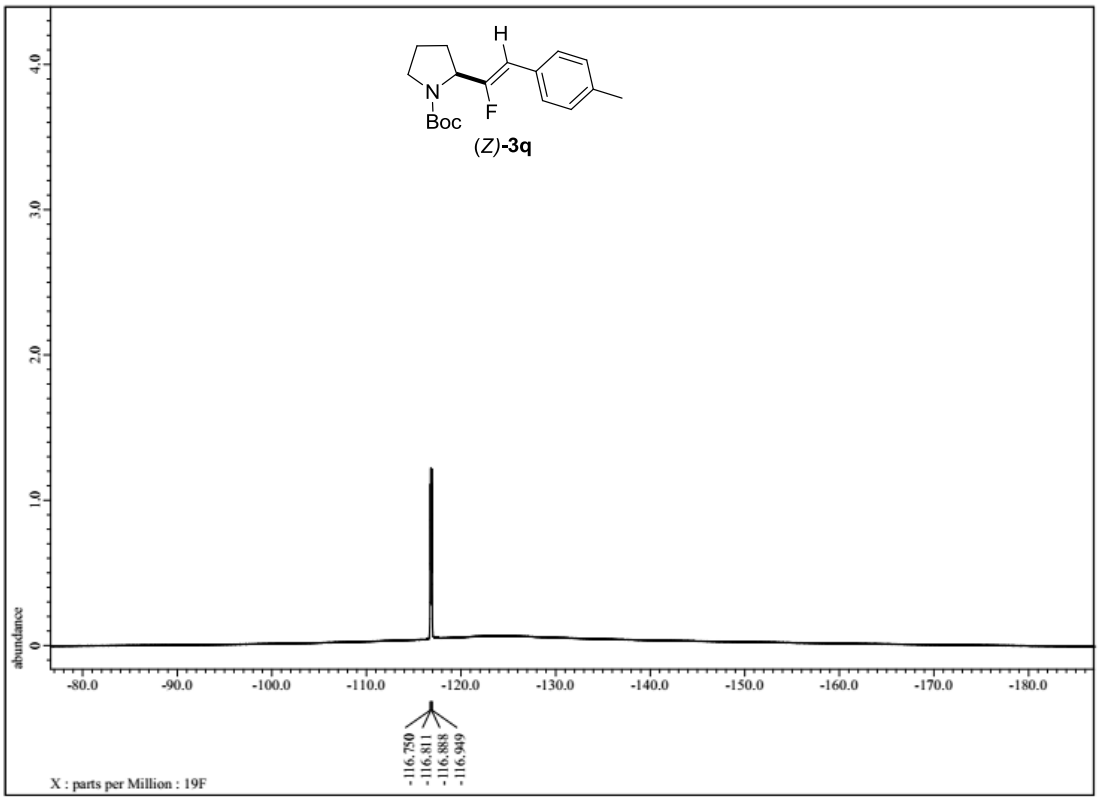

CF3
N
Boc
F
CH3
(E)-3p
abundance
X : parts per Million : 1H

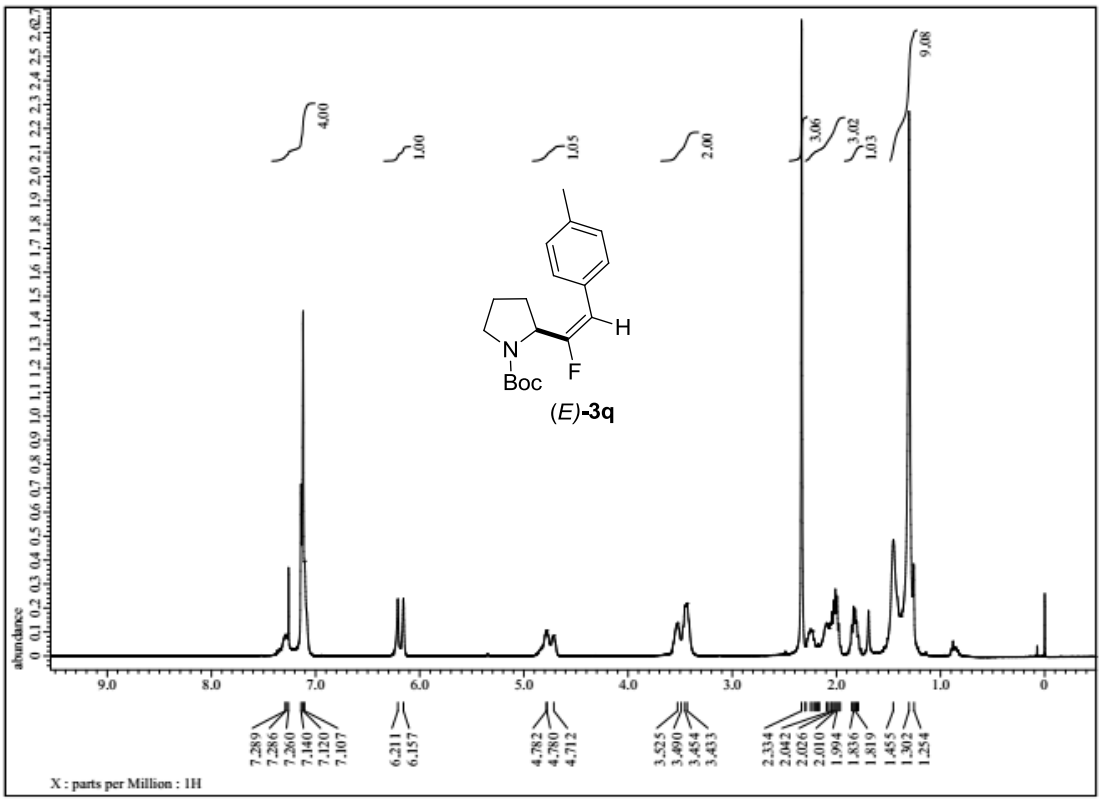

CF3
N
Boc
F
CH3
(E)-3p
abundance
X : parts per Million : 13C

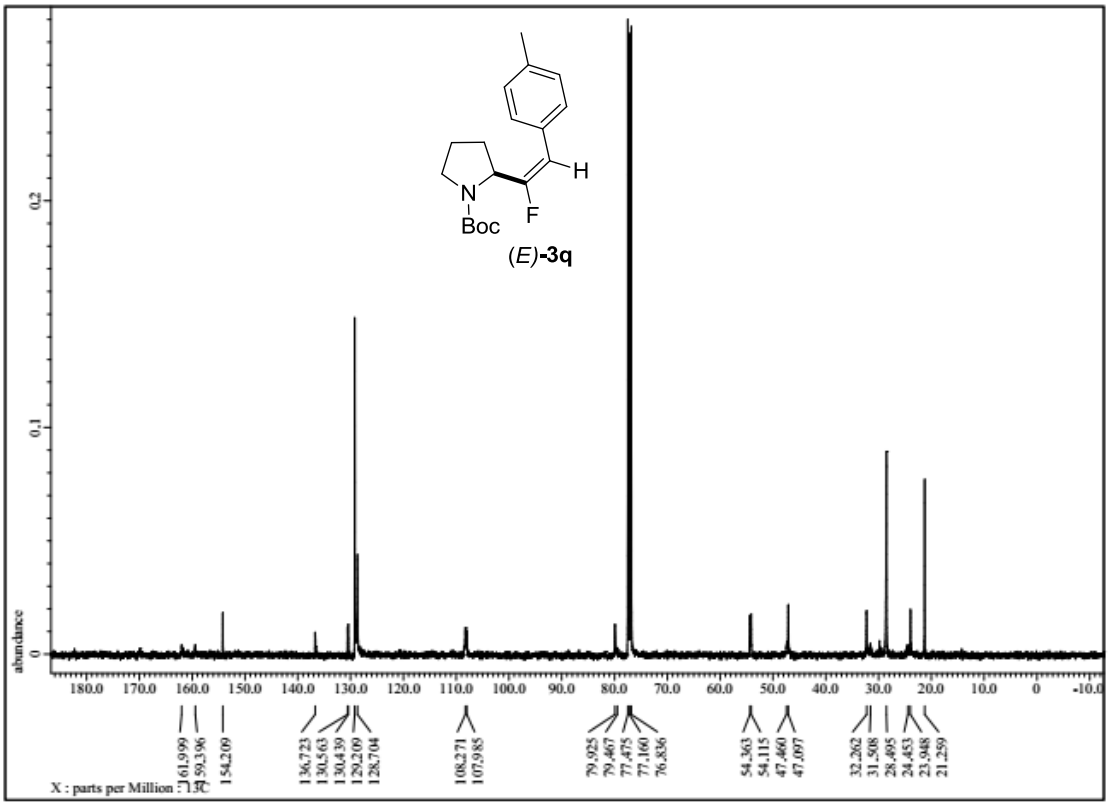

CF3
CH3
N
Boc
F
(E)-3p
3.00
1.00
abundance
-62.535
-108.676
-109.750
X : parts per Million : 19F

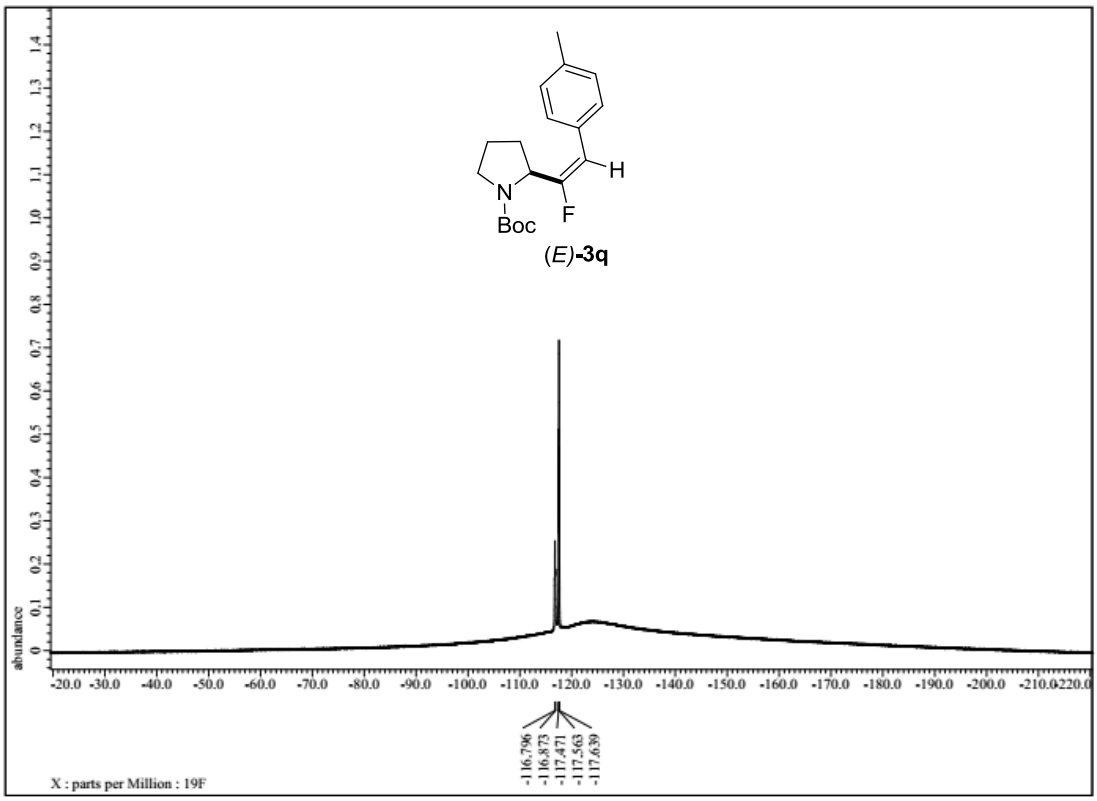

H
N
Boc
F
(Z)-3q
2.00
2.03
1.00
1.00
2.00
3.04
3.08
1.05
9.00
abundance
7.371
7.352
7.260
7.141
7.124
5.629
5.564
5.538
5.536
5.534
5.466
4.378
4.366
4.357
4.349
4.347
4.345
3.503
3.488
2.333
2.087
2.077
1.885
1.466
1.418
1.372
X : parts per Million : 1H

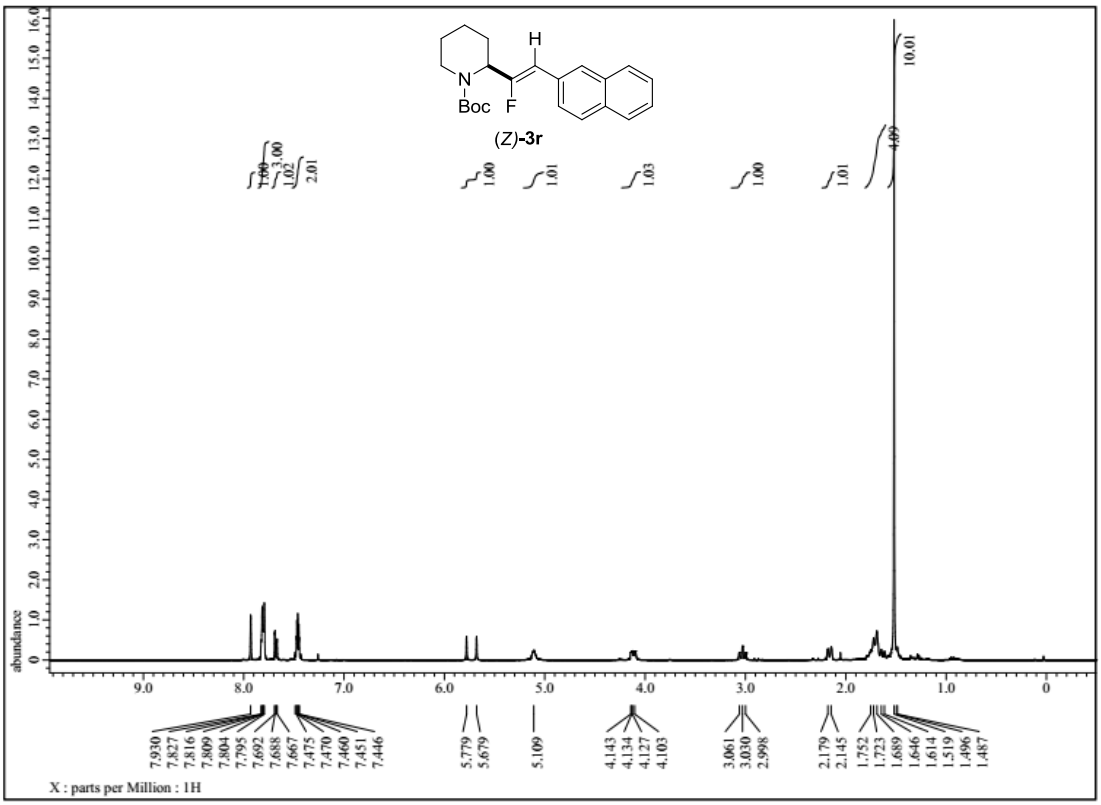

H
N
Boc
F
(Z)-3q
abundance
X : parts per Million : 13C
160.416
157.756
154.428
136.942
130.458
129.295
128.466
105.602
79.915
77.475
77.160
76.836
58.463
58.139
46.478
30.612
28.524
23.242
21.316

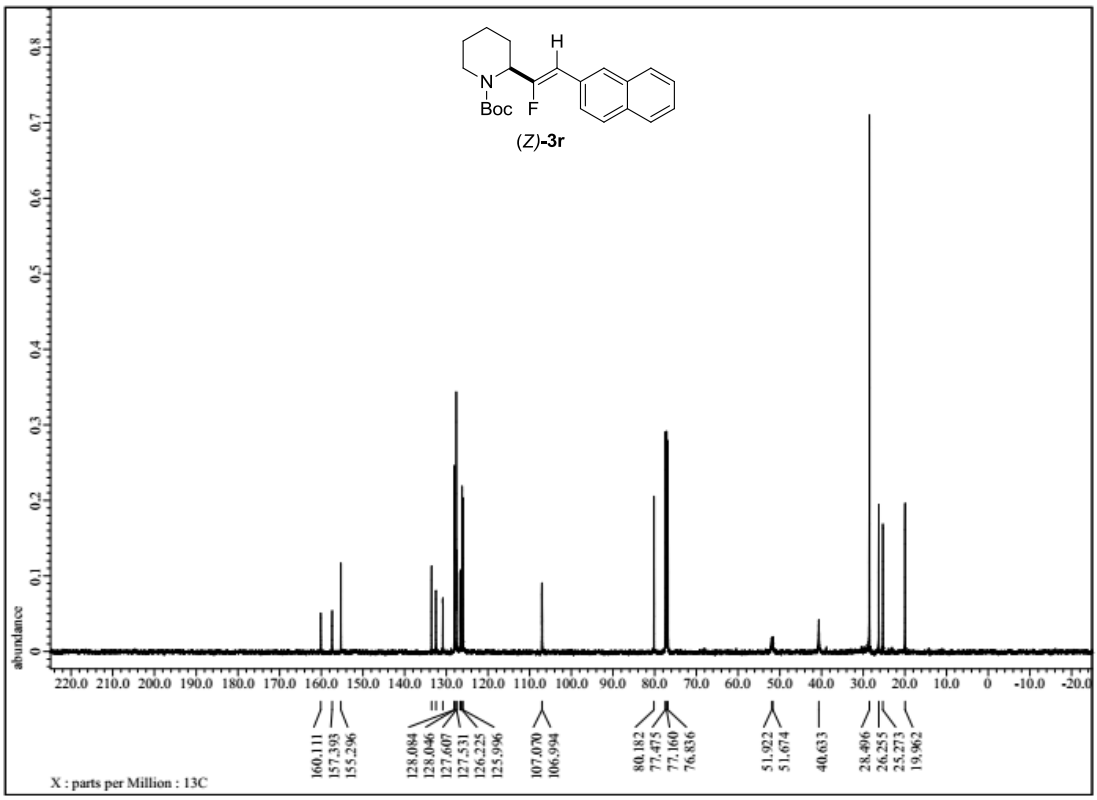

H
N
Boc
F
(Z)-3q
abundance
X : parts per Million : 19F
-116.750
-116.811
-116.888
-116.949

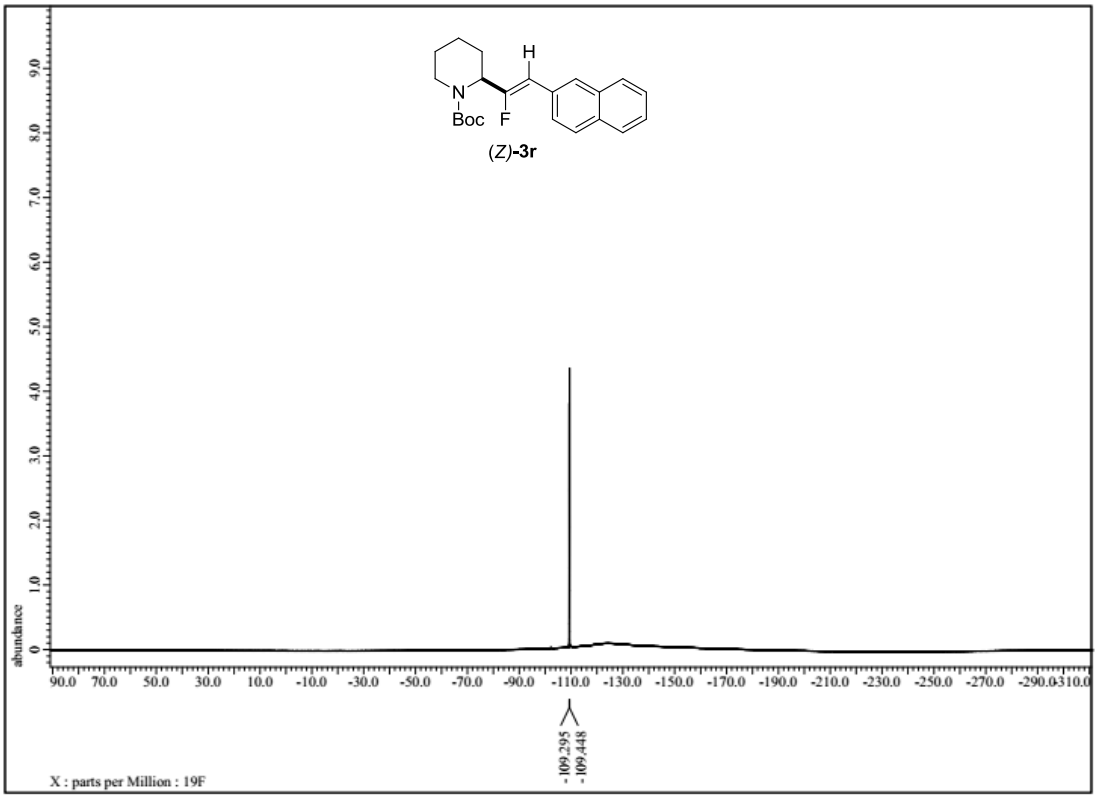

(E)-3q
X : parts per Million : 1H

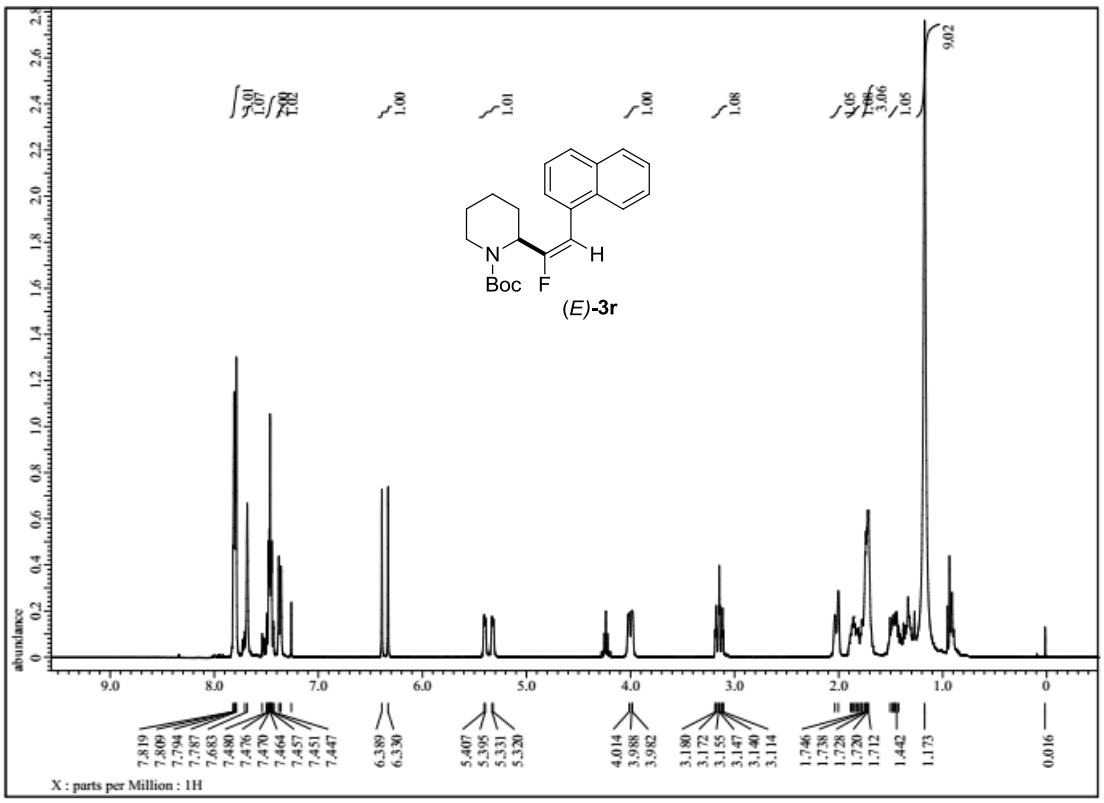

(E)-3q
X : parts per Million : 13C

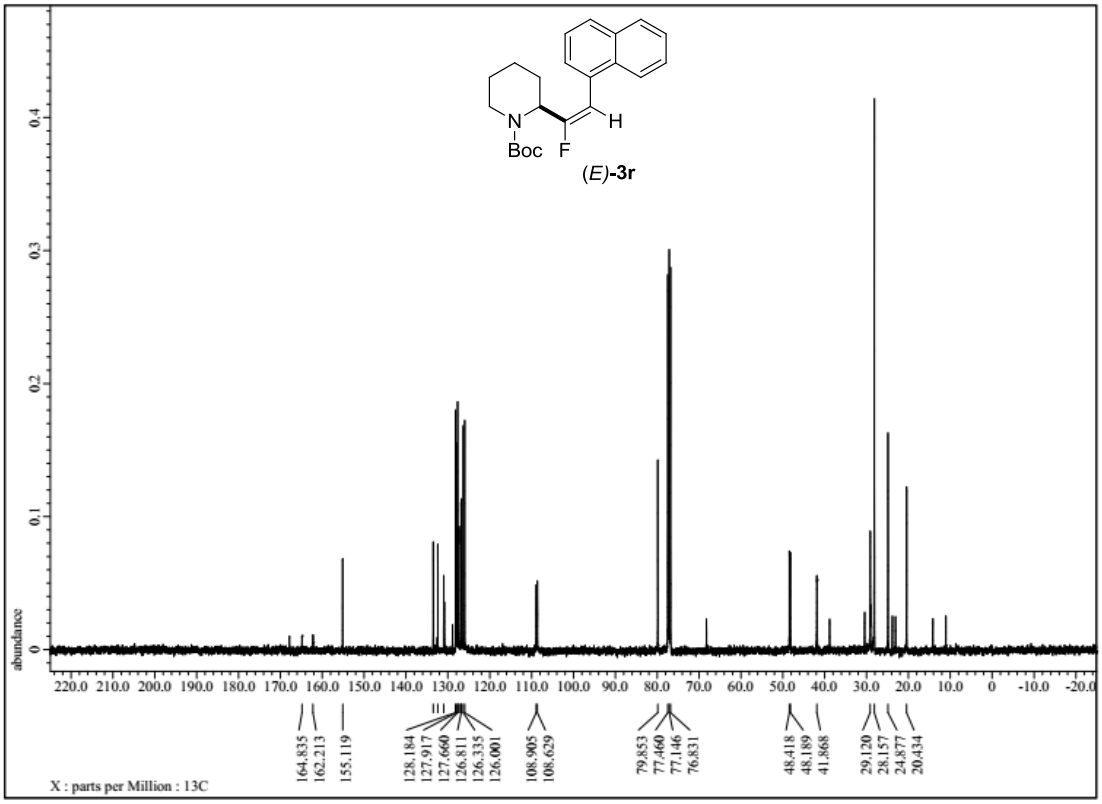

(E)-3q
abundance
X : parts per Million : 19F
-116.796
-116.873
-117.471
-117.563
-117.639

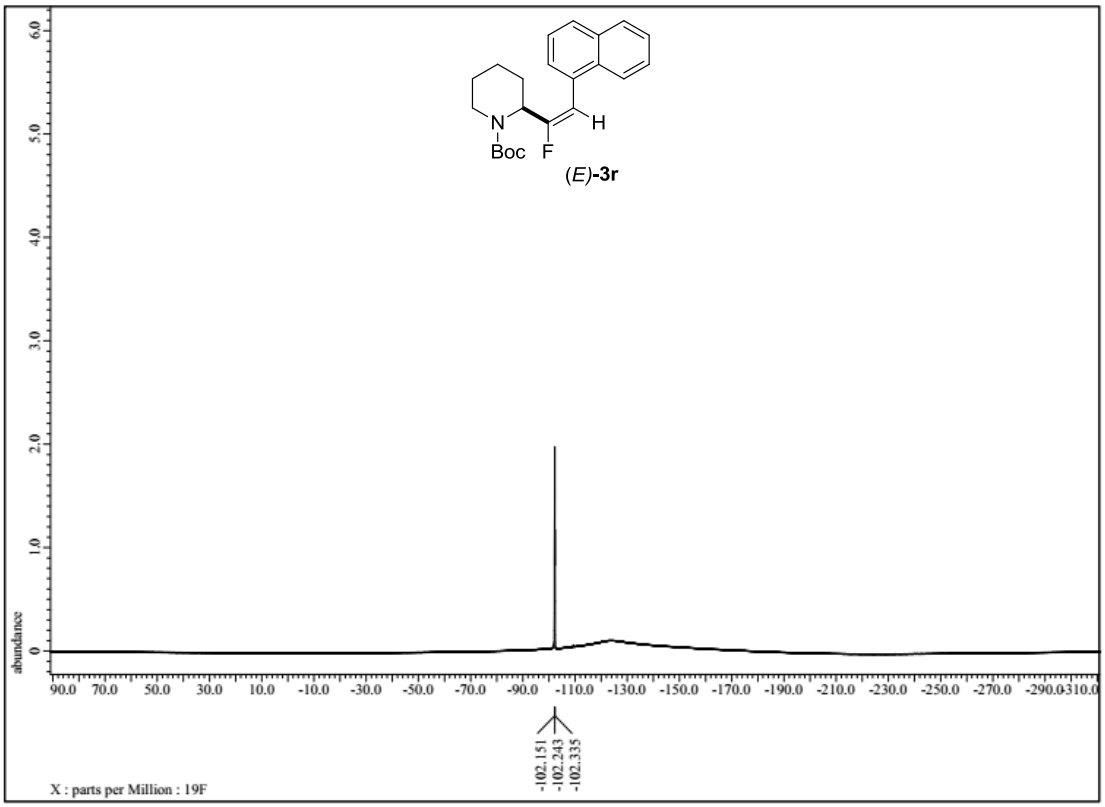

(Z)-3r
abundance
X : parts per Million : 1H
7.930
7.827
7.816
7.809
7.804
7.795
7.692
7.688
7.667
7.475
7.470
7.460
7.451
7.446
5.779
5.679
5.109
4.143
4.134
4.127
4.103
3.061
3.030
2.998
2.179
2.145
1.752
1.723
1.689
1.646
1.614
1.519
1.496
1.487

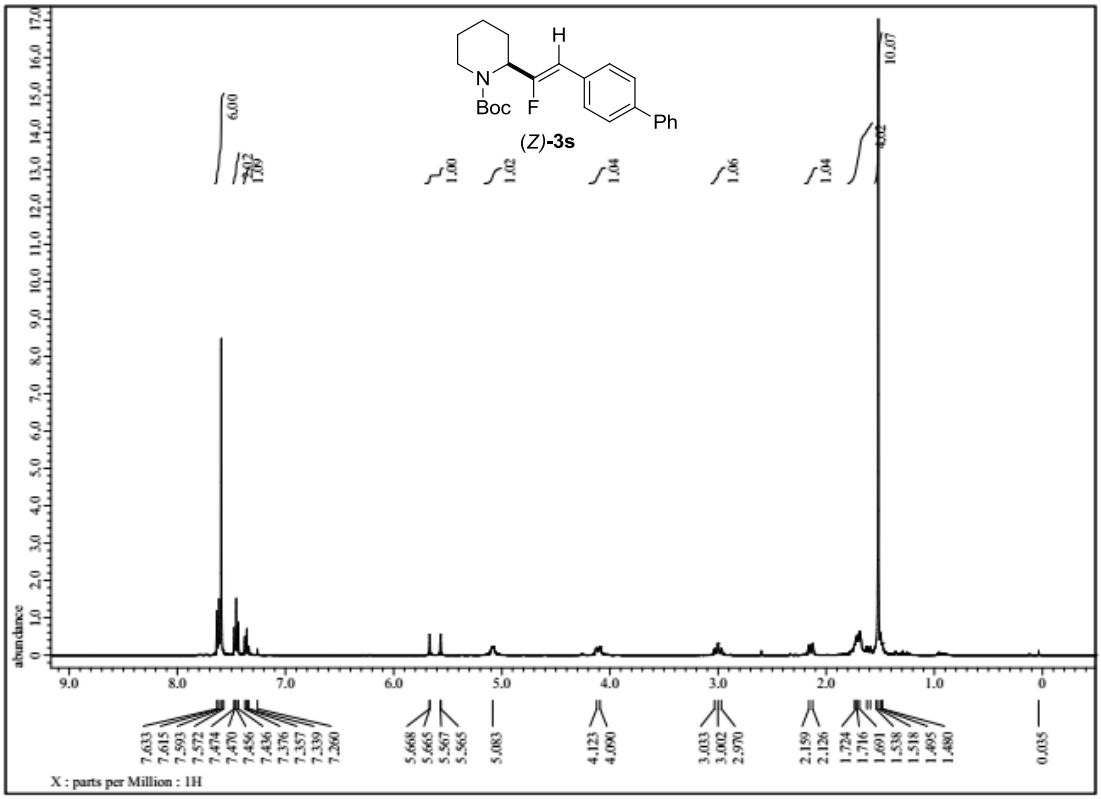

(Z)-3r
abundance
X : parts per Million : 13C
160.111
157.393
155.296
128.084
128.046
127.607
127.531
126.225
125.996
107.070
106.994
80.182
77.475
77.160
76.836
51.922
51.674
40.633
28.496
26.255
25.273
19.962

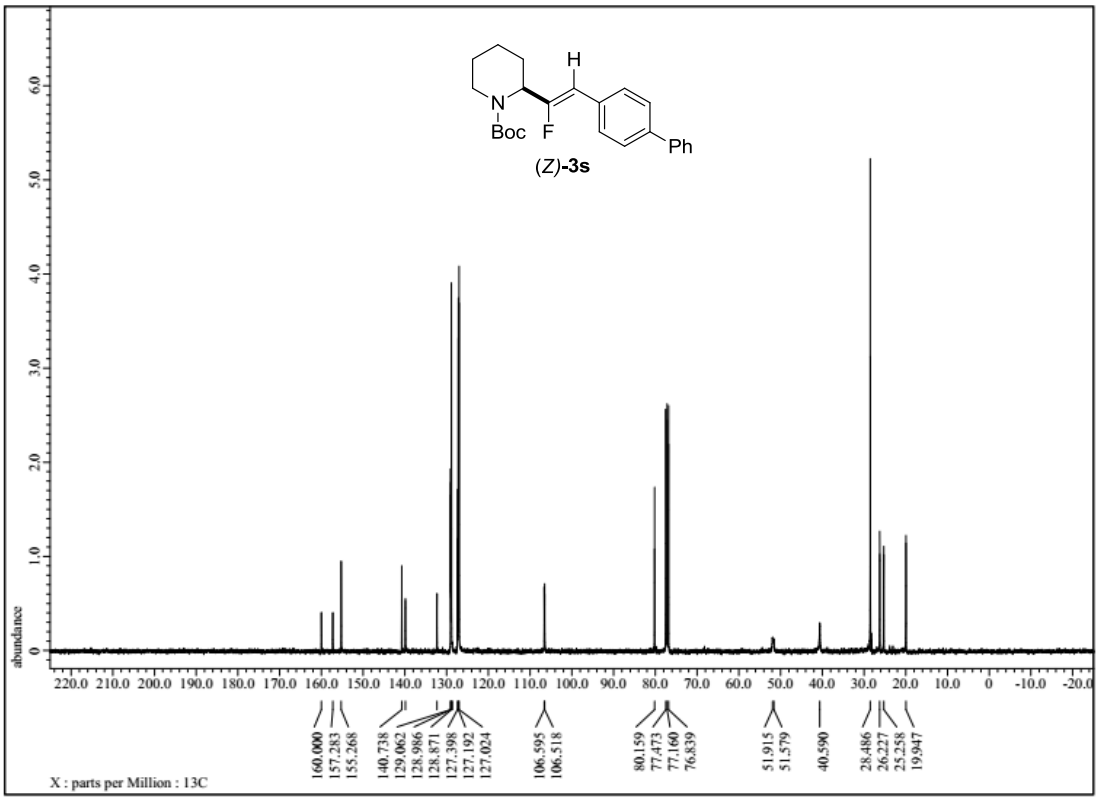

(Z)-3r
abundance
X : parts per Million : 19F
-109.295
-109.448

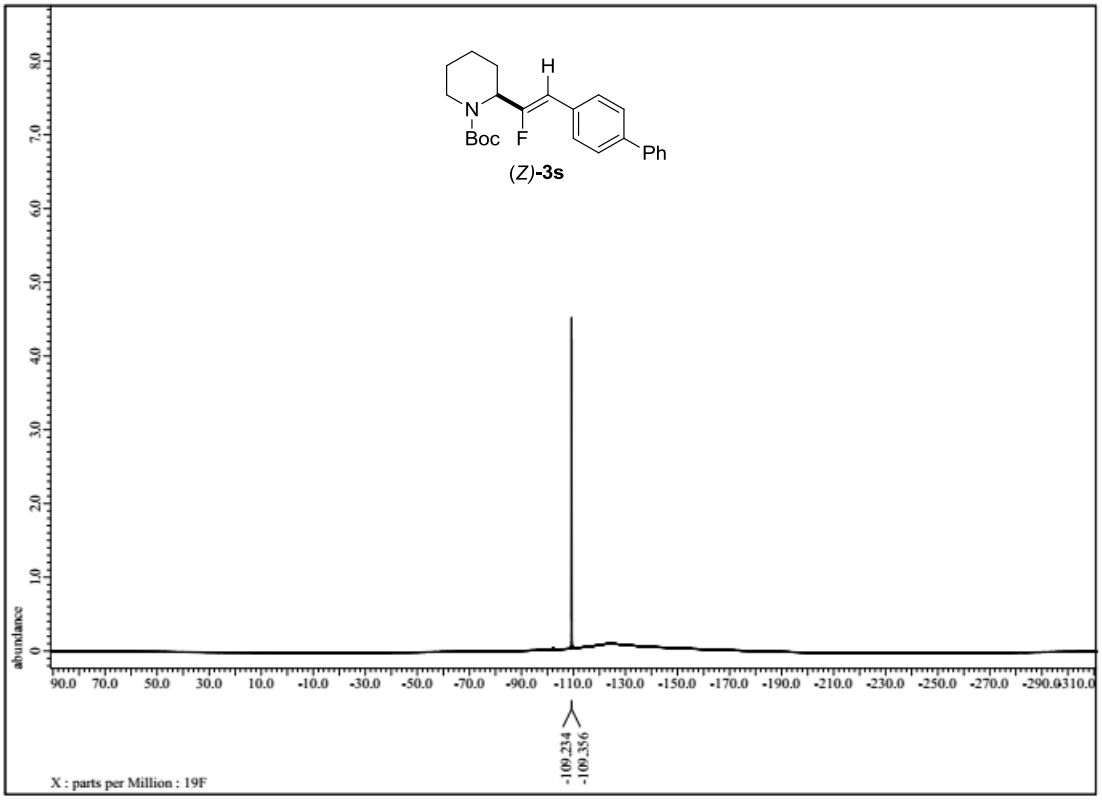

(E)-3r
X : parts per Million : 1H

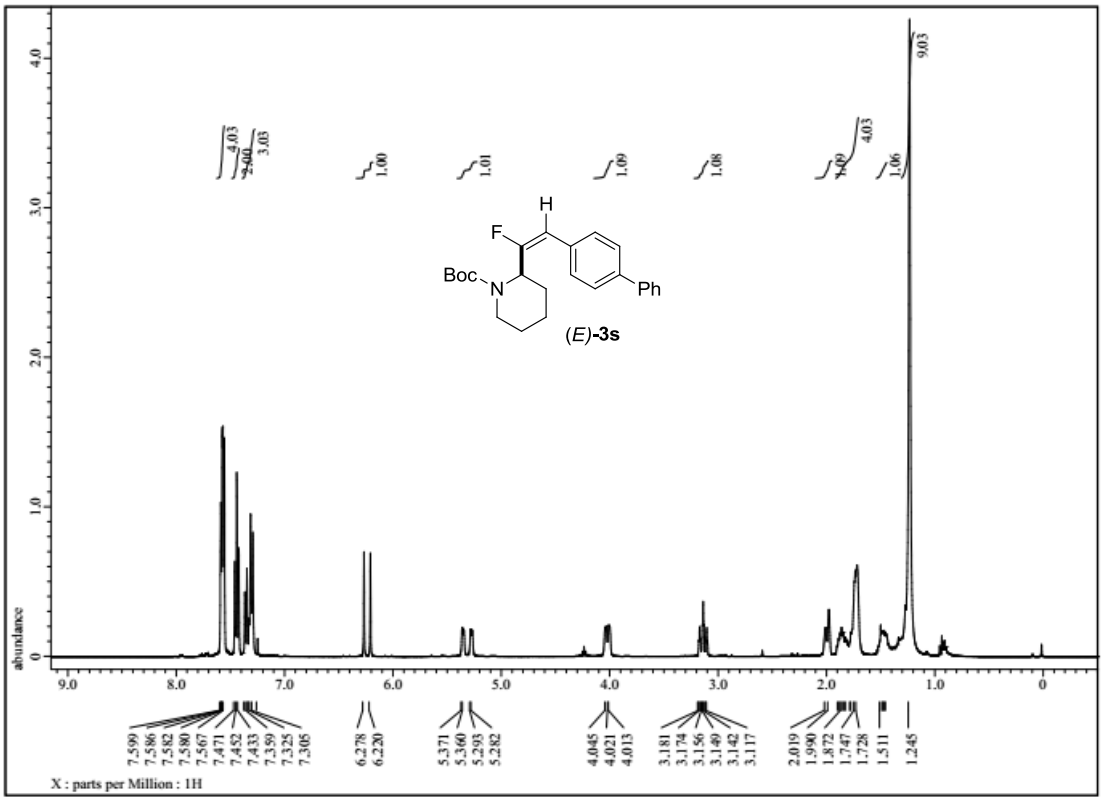

(E)-3r
X : parts per Million : 13C

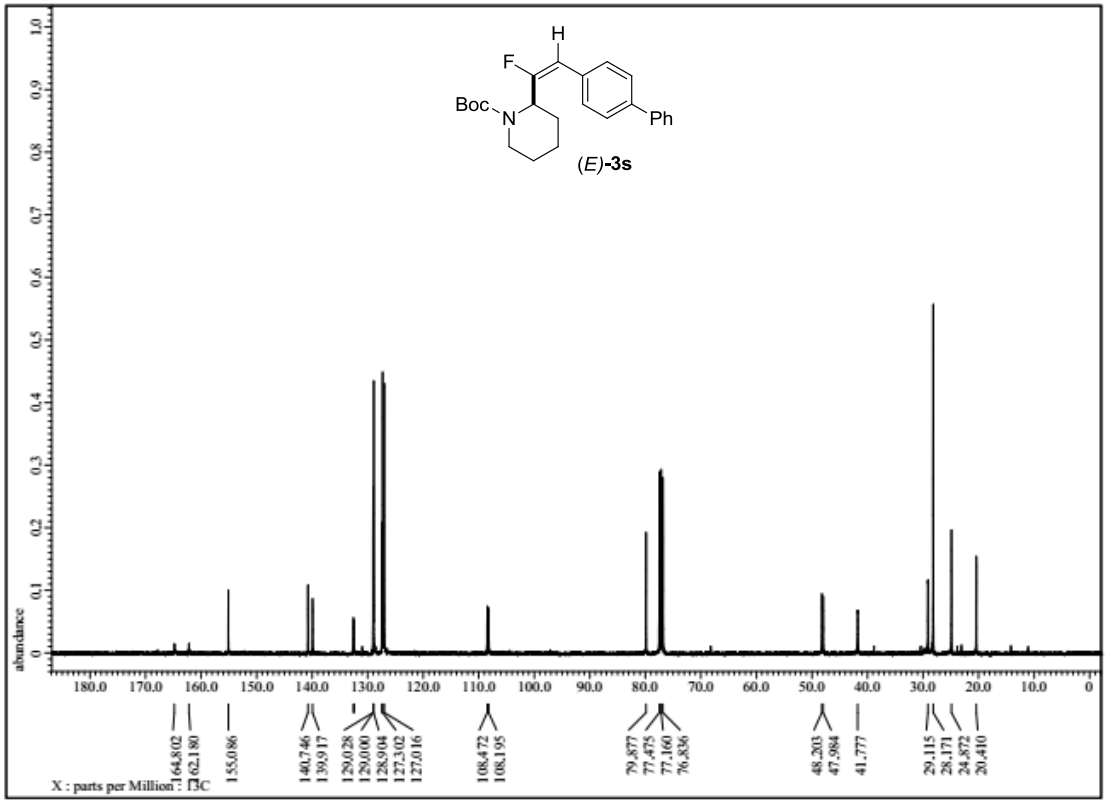

N
Boc
F
H
(E)-3r
abundance
X : parts per Million : 19F
-102.151
-102.243
-102.335

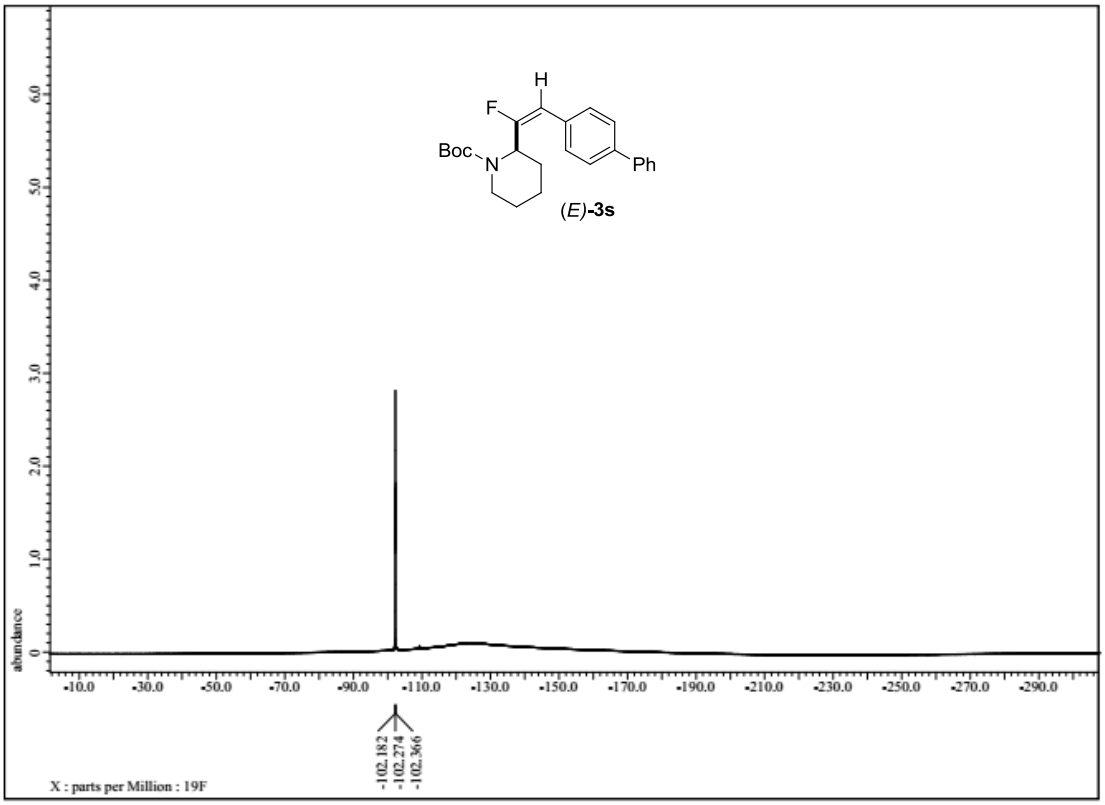

N
Boc
F
H
Ph
(Z)-3s
abundance
X : parts per Million : 1H

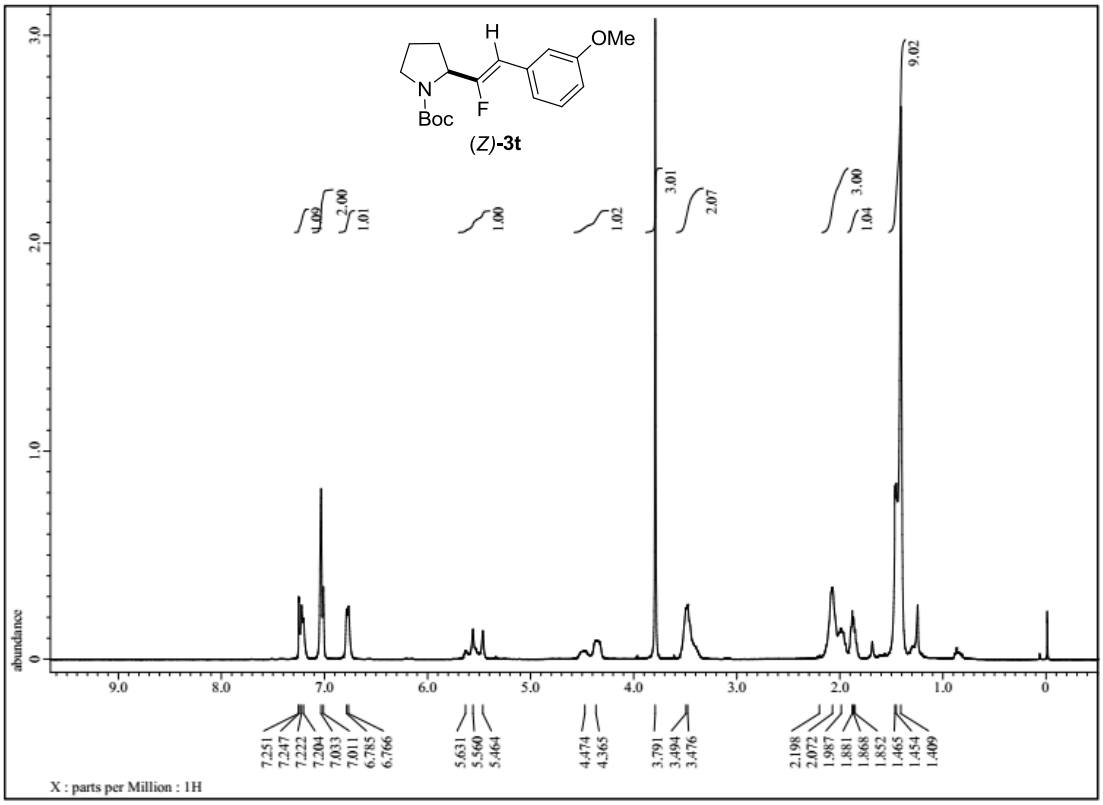

H
N
Boc
F
Ph
(Z)-3s
abundance
X : parts per Million : 13C
160.000
157.283
155.268
140.738
129.062
128.986
128.871
127.398
127.192
127.024
106.595
106.518
80.159
77.473
77.160
76.839
51.915
51.579
40.590
28.486
26.227
25.258
19.947

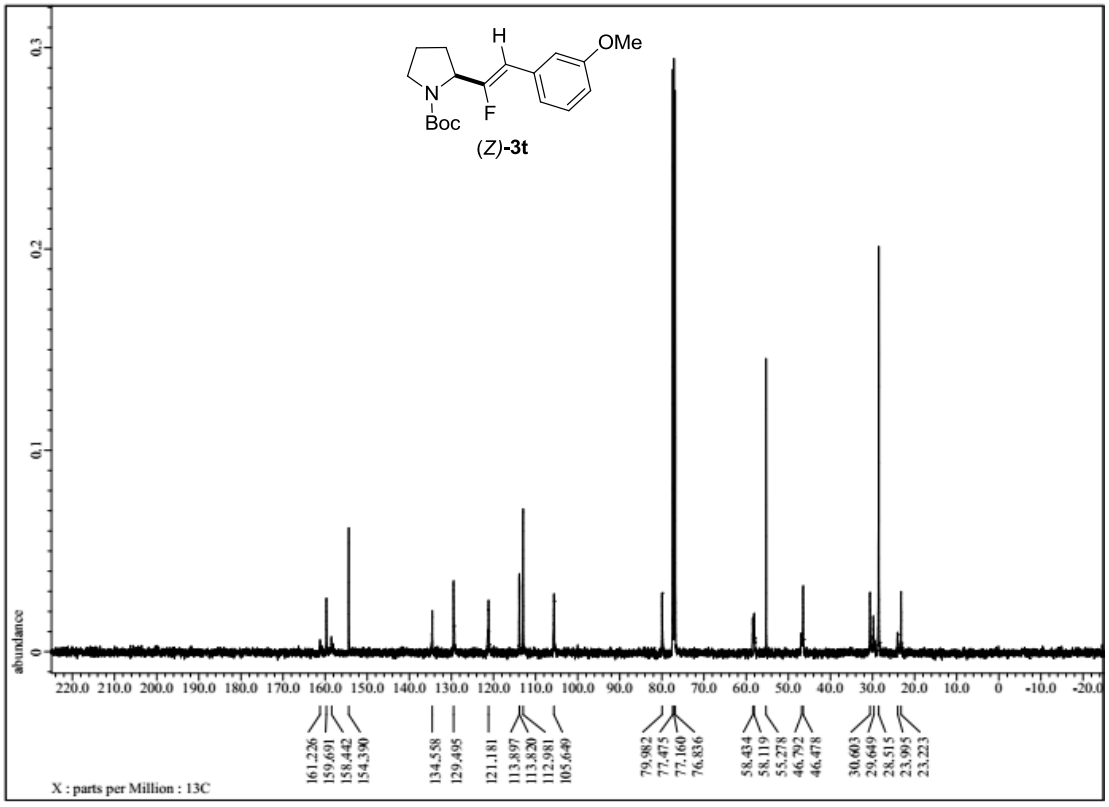

H
N
Boc
F
Ph
(Z)-3s
abundance
X : parts per Million : 19F
-109.234
-109.356

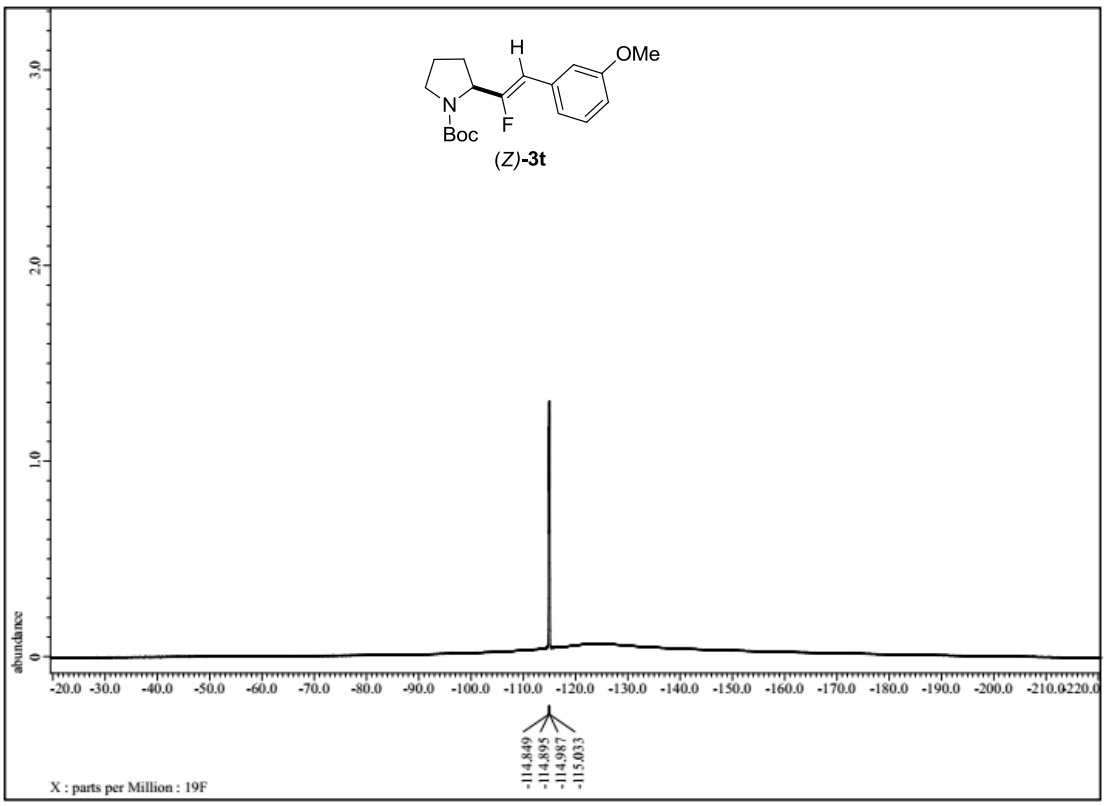

H
F
Boc
N
Ph
(E)-3s
abundance
X : parts per Million : 1H

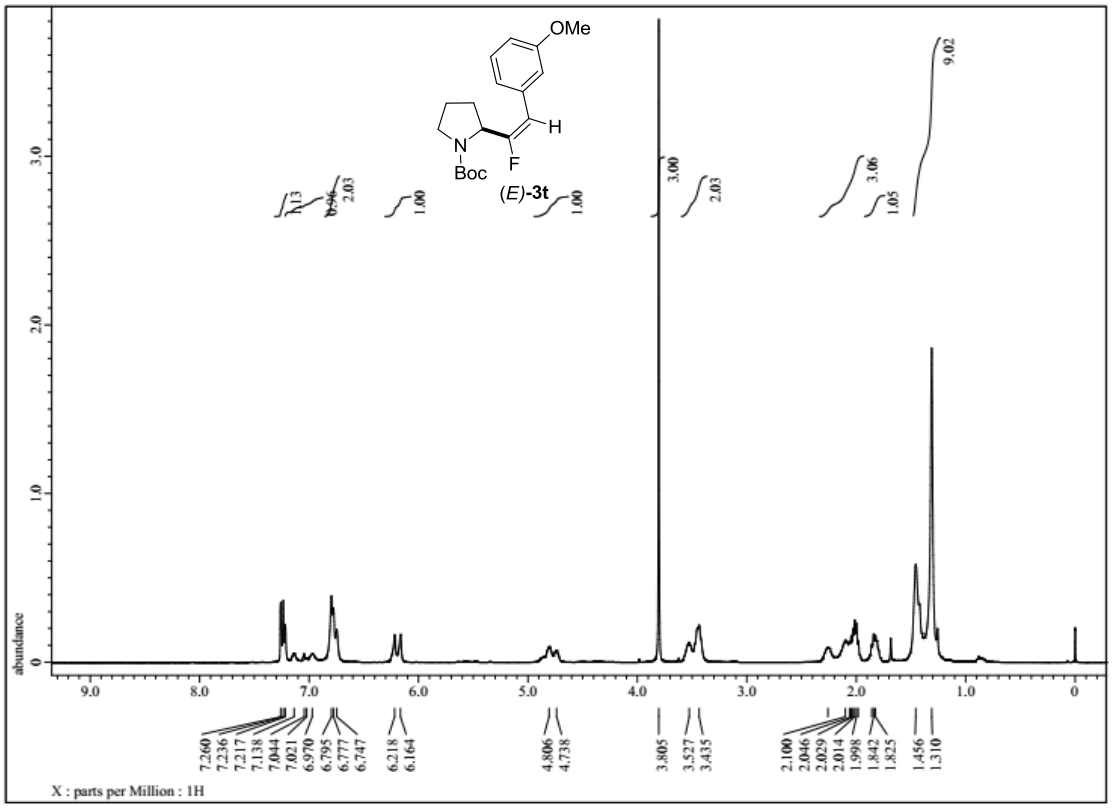

H
F
Boc
N
Ph
(E)-3s
abundance
X : parts per Million : 13C

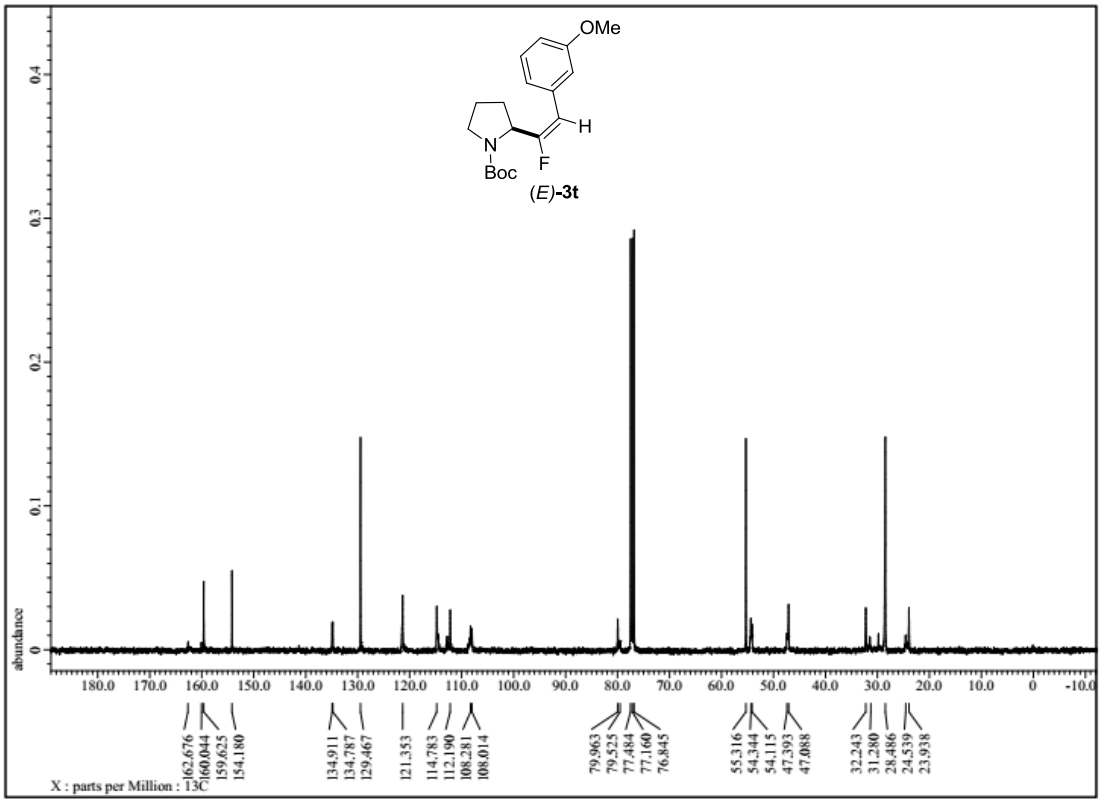

H
F
Boc
N
Ph
(E)-3s
abundance
-102.182
-102.274
-102.366
X : parts per Million : 19F

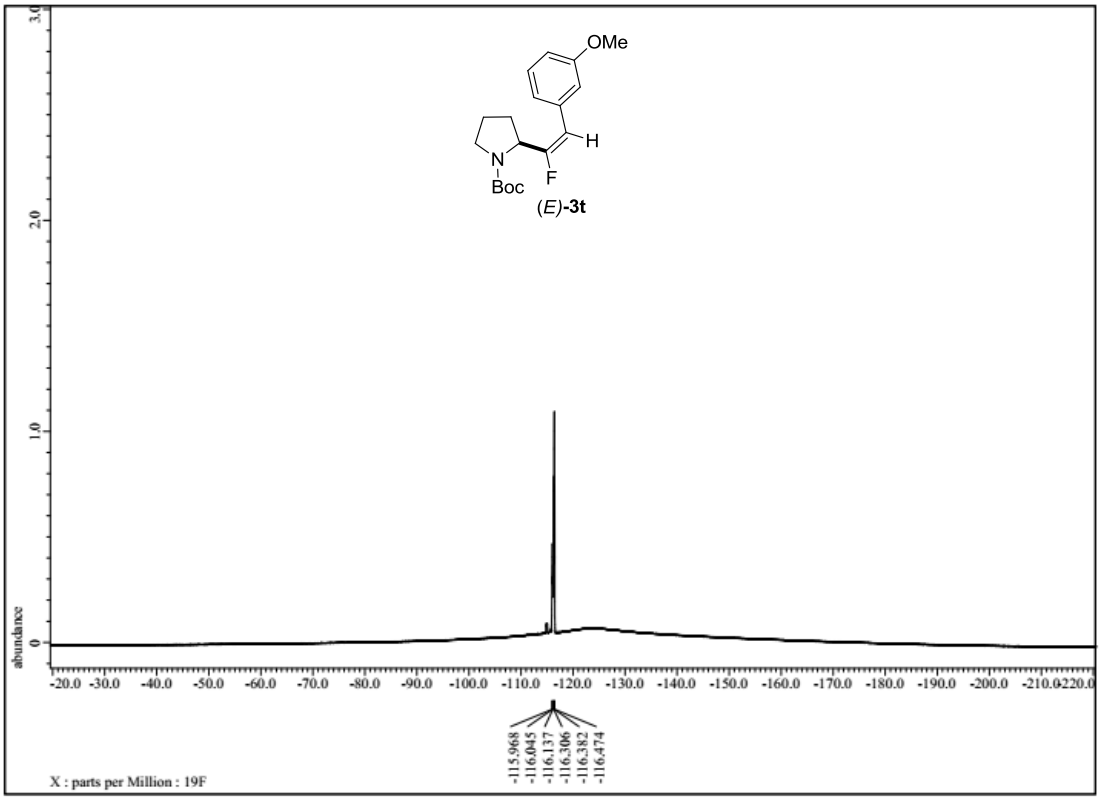

H
OMe
N
Boc
F
(Z)-3t
9.02
3.01
2.07
3.00
2.00
1.04
1.02
1.01
1.00
abundance
7.251
7.247
7.222
7.204
7.033
7.011
6.785
6.766
5.631
5.560
5.464
4.474
4.365
3.791
3.494
3.476
2.198
2.072
1.987
1.881
1.868
1.852
1.465
1.454
1.409
X : parts per Million : 1H

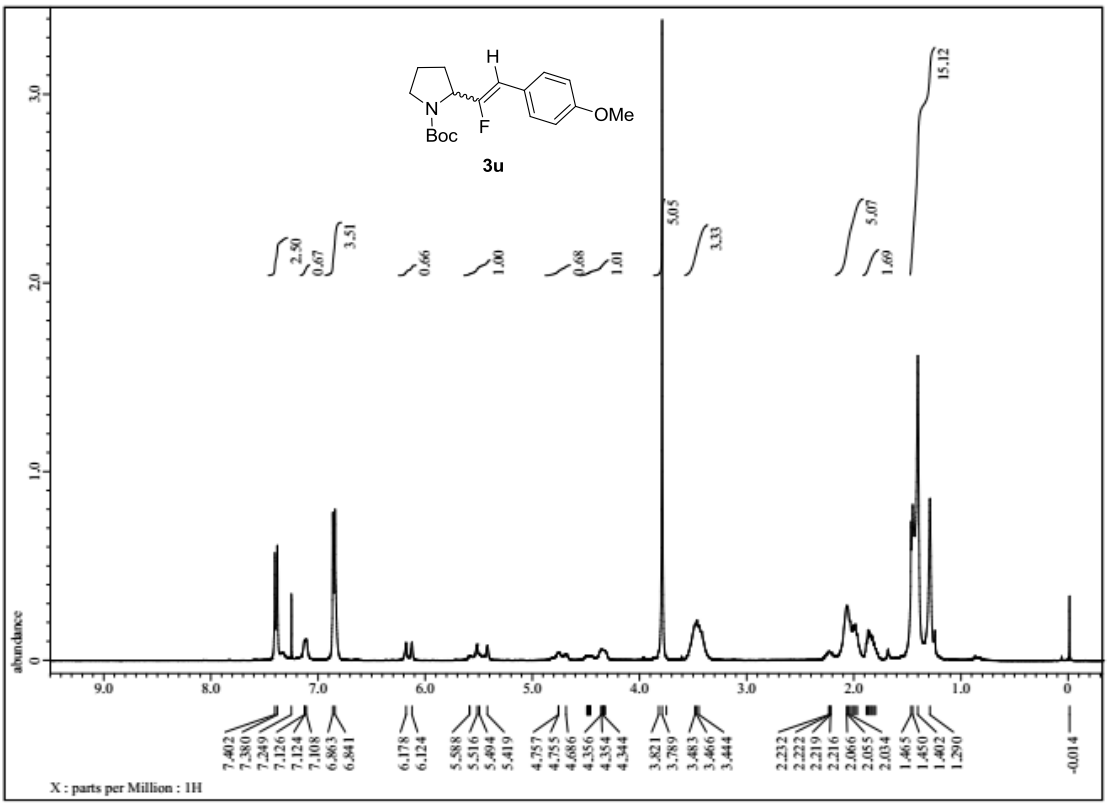

H
OMe
N
Boc
F
(Z)-3t
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
161.226
159.691
158.442
154.390
134.558
129.495
121.181
113.897
113.820
112.981
105.649
79.982
77.475
77.160
76.836
58.434
58.119
55.278
46.792
46.478
30.603
29.649
28.515
23.995
23.223
X : parts per Million : 13C

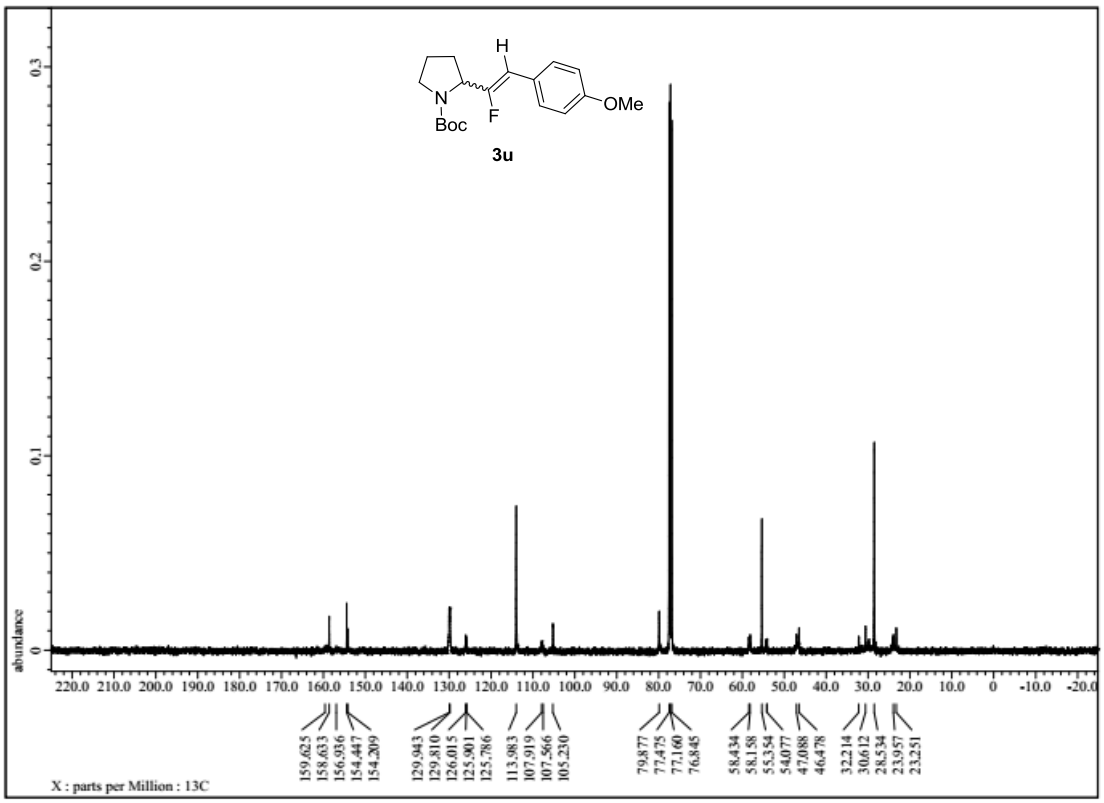

H
OMe
N
Boc
F
(Z)-3t
abundance
3.0
2.0
1.0
0
-20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0 -210.0 -220.0
-114.849
-114.895
-114.987
-115.033
X : parts per Million : 19F

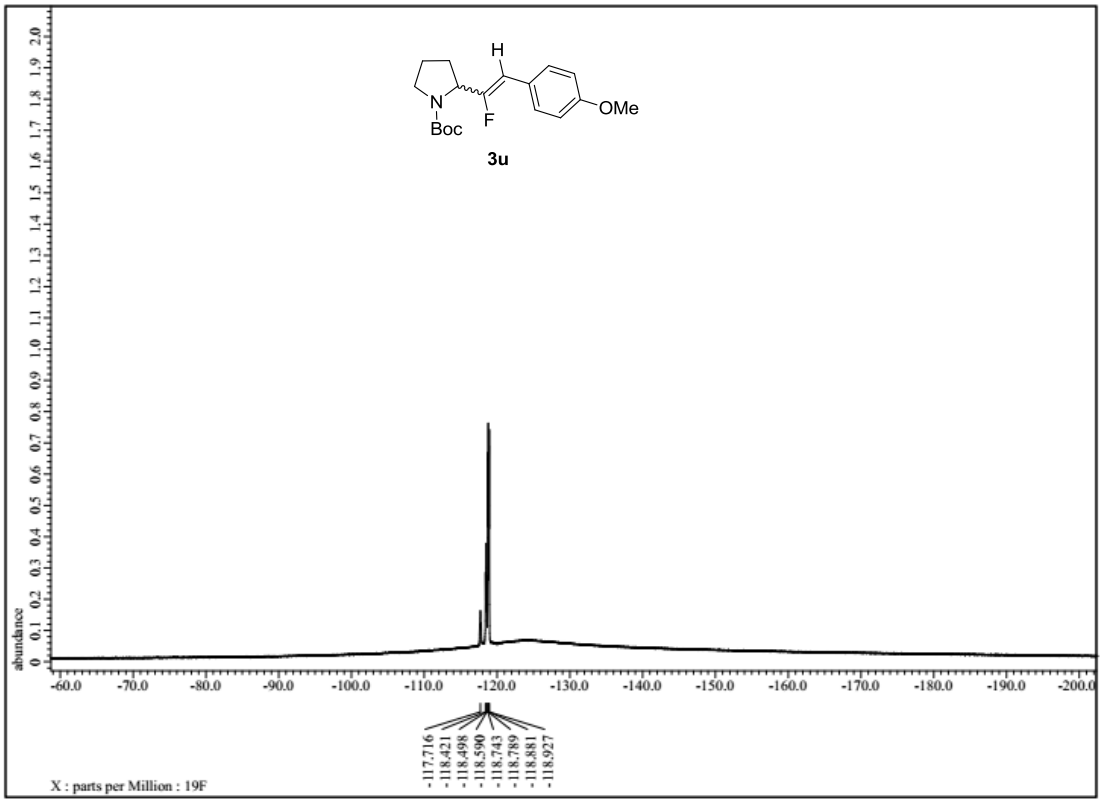

OMe
H
N
Boc
F
(E)-3t
abundance
X : parts per Million : 1H

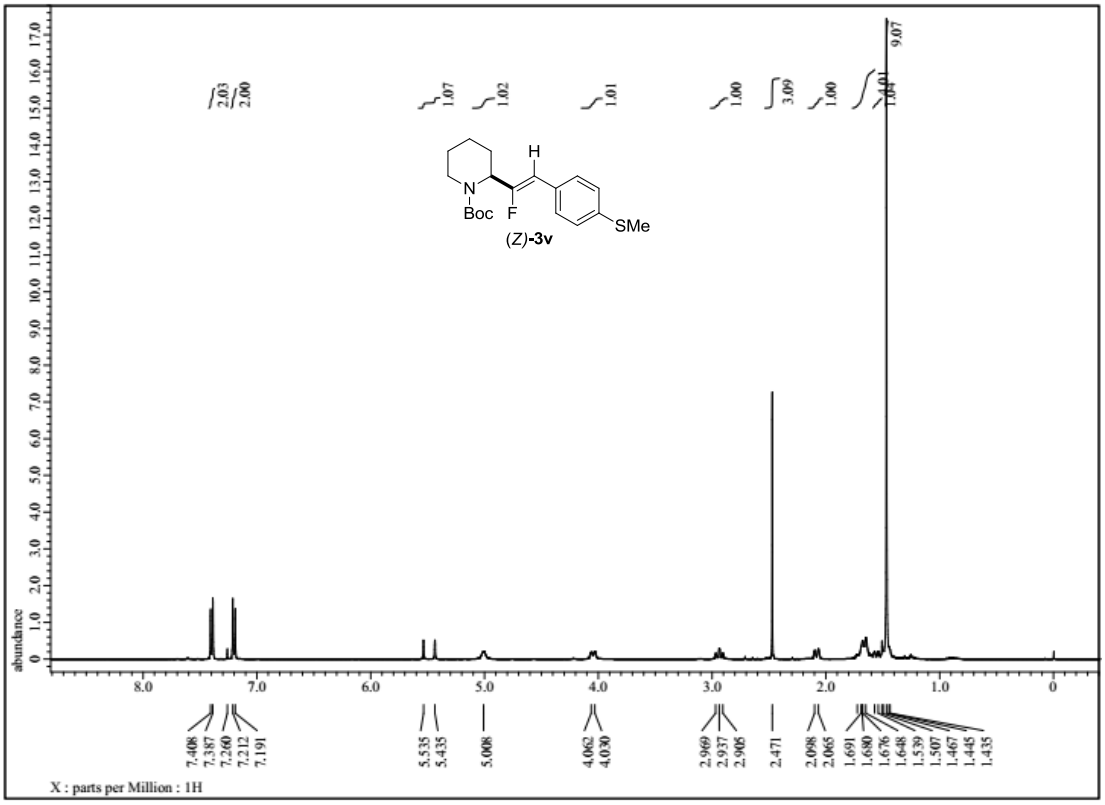

OMe
H
N
Boc
F
(E)-3t
abundance
X : parts per Million : 13C

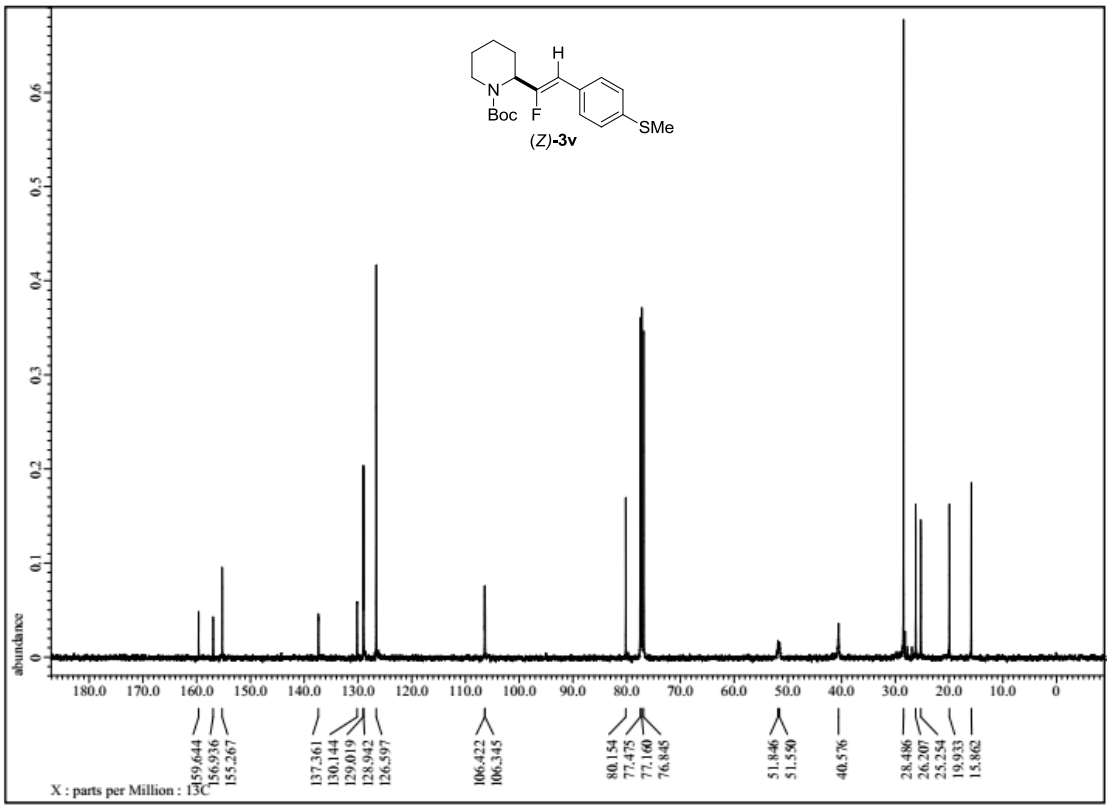

OMe
H
N
Boc
F
(E)-3t
abundance
-20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0 -210.0 -220.0
-115.968
-116.045
-116.137
-116.306
-116.382
-116.474
X : parts per Million : 19F

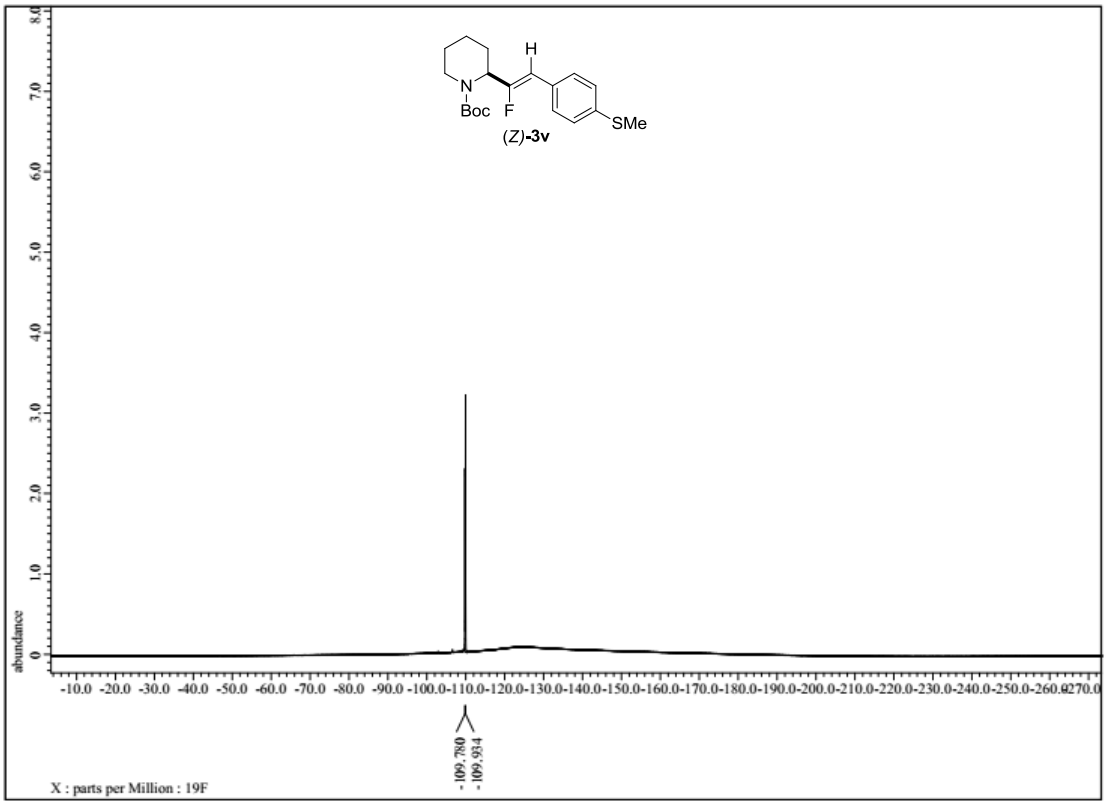

H
N
Boc
F
OMe
3u
2.50
0.67
3.51
0.66
1.00
0.68
1.01
5.05
3.33
5.07
1.69
15.12
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.402
7.380
7.249
7.126
7.124
7.108
6.863
6.841
6.178
6.124
5.588
5.516
5.494
5.419
4.757
4.755
4.686
4.356
4.354
4.344
3.821
3.789
3.483
3.466
3.444
2.232
2.222
2.219
2.216
2.066
2.055
2.034
1.465
1.450
1.402
1.290
-0.014
X : parts per Million : 1H

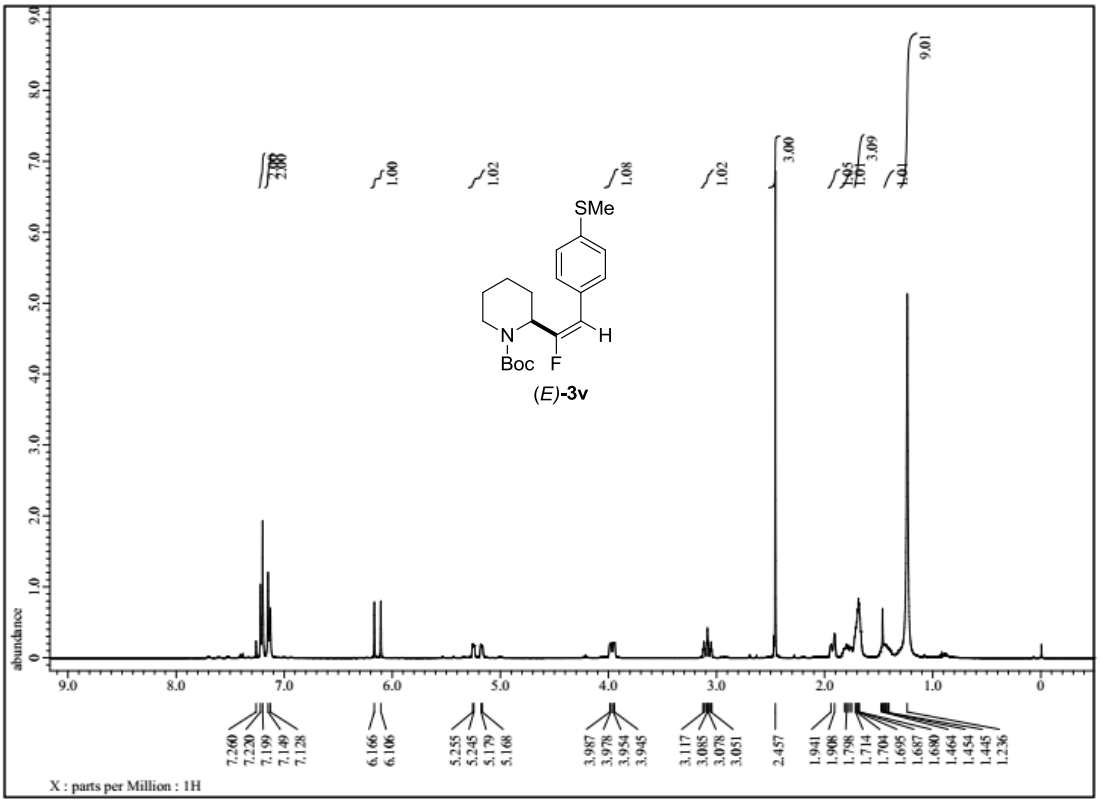

H
N
Boc
F
OMe
3u
abundance
X : parts per Million : 13C
159.625
158.633
156.936
154.447
154.209
129.943
129.810
126.015
125.901
125.786
113.983
107.919
107.566
105.230
79.877
77.475
77.160
76.845
58.434
58.158
55.354
54.077
47.088
46.478
32.214
30.612
28.534
23.957
23.251

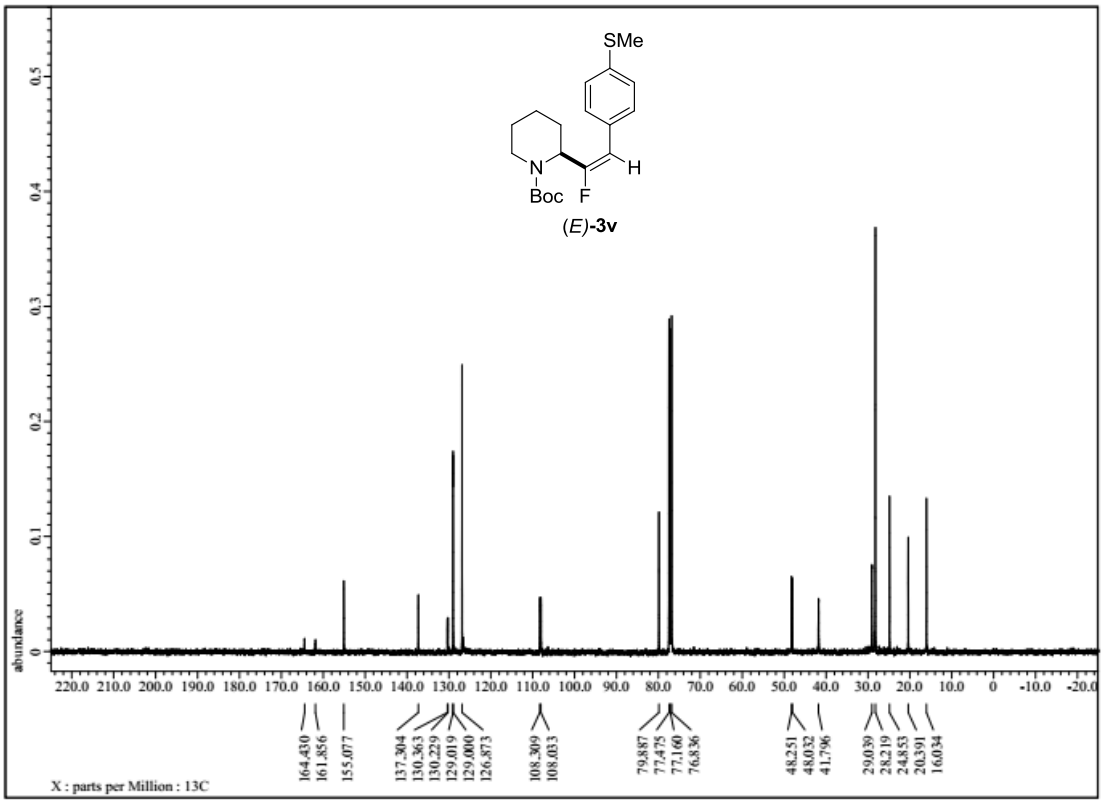

H
N
Boc
F
OMe
3u
abundance
X : parts per Million : 19F
-117.716
-118.421
-118.498
-118.590
-118.743
-118.789
-118.881
-118.927

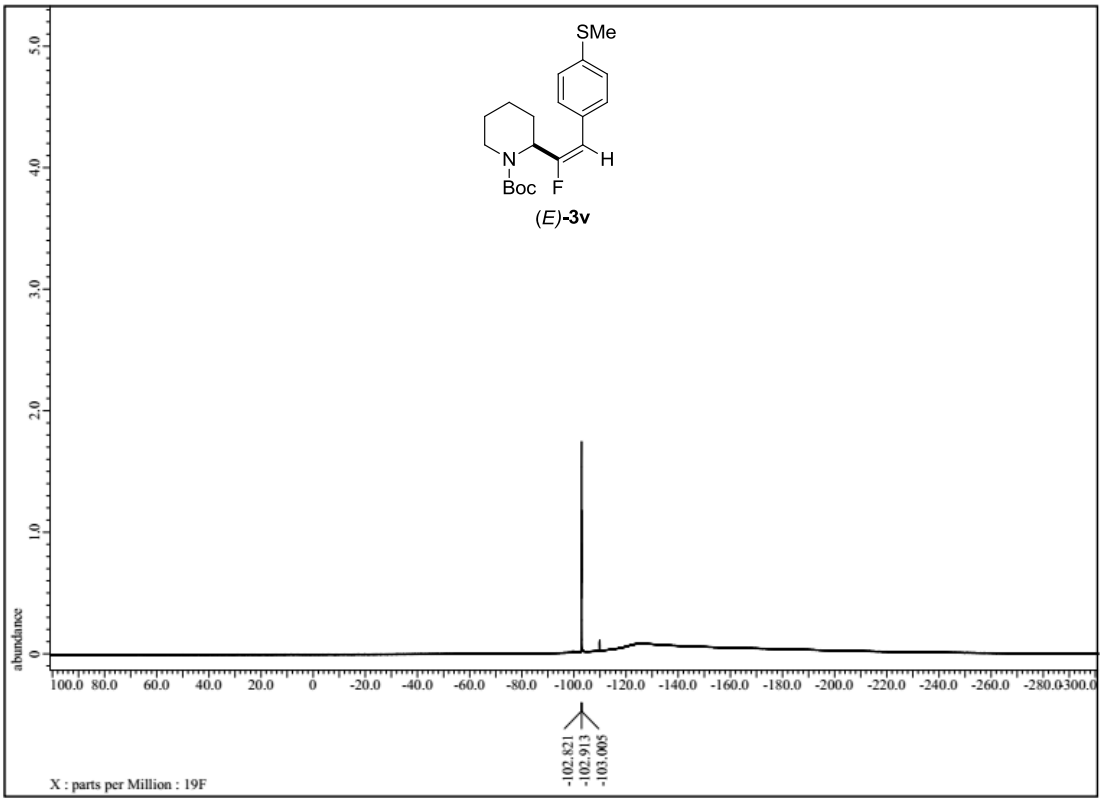

(Z)-3v
abundance
X : parts per Million : 1H

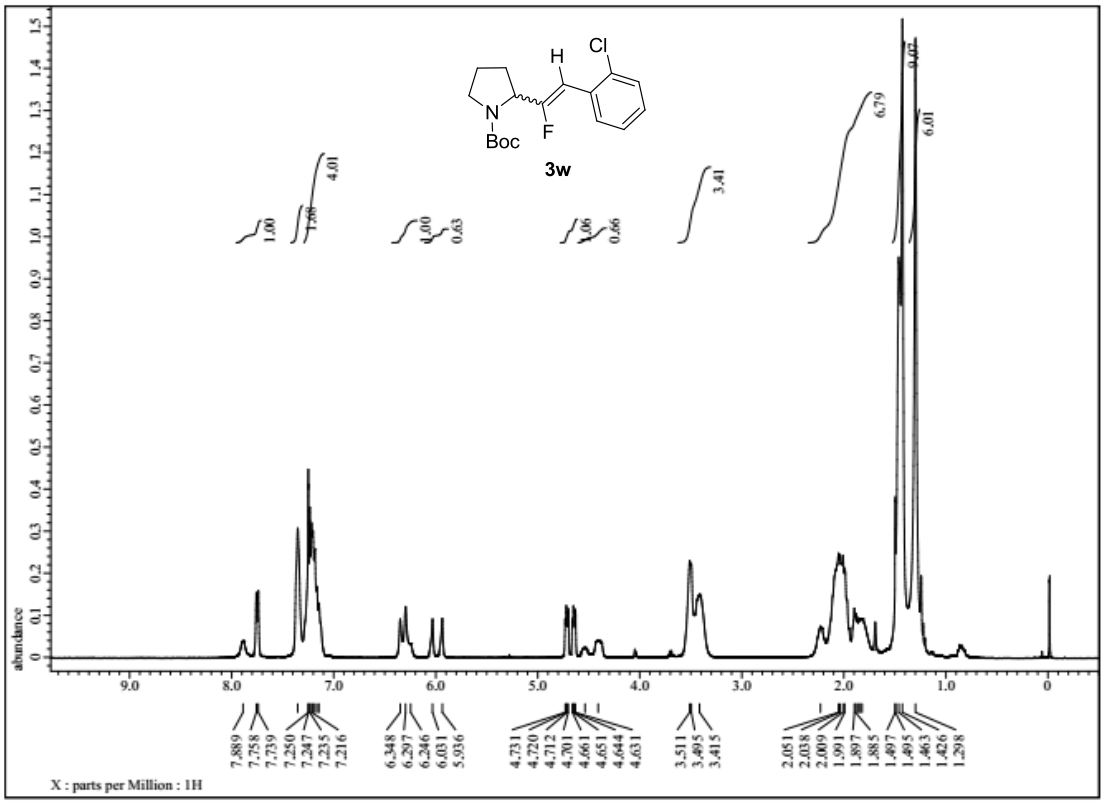

(Z)-3v
abundance
X : parts per Million : 13C

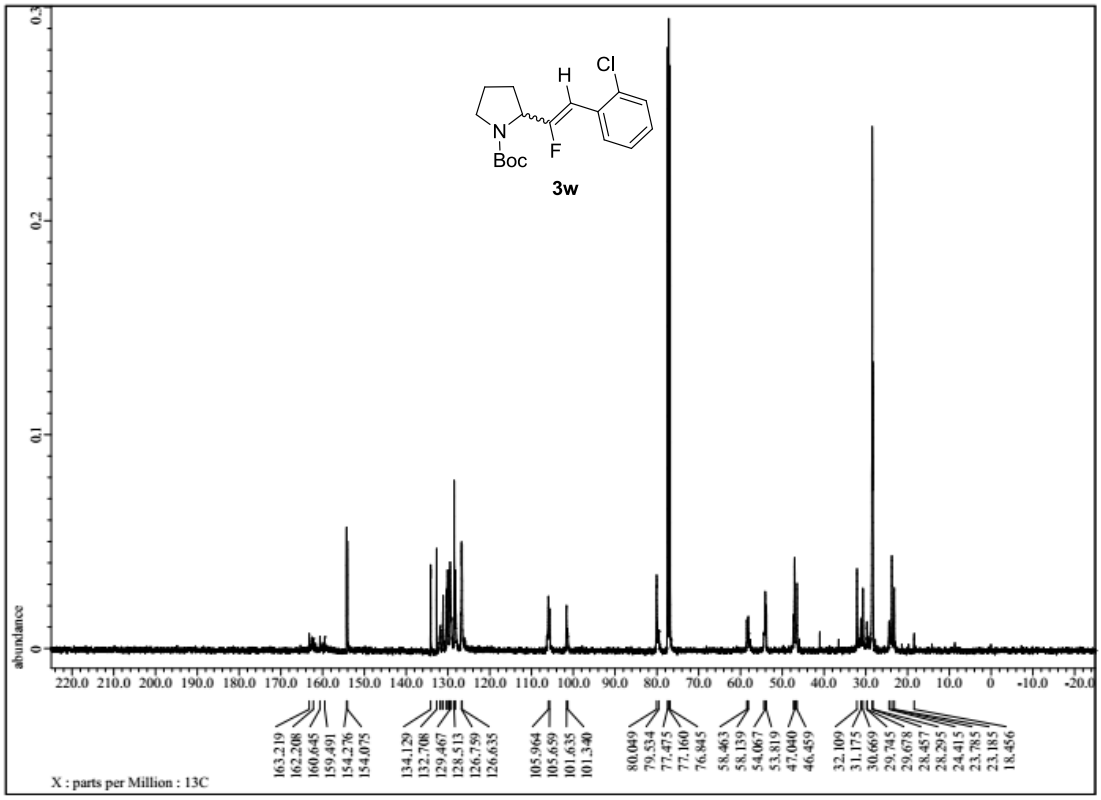

(Z)-3v
abundance
-109.780
-109.934
X : parts per Million : 19F

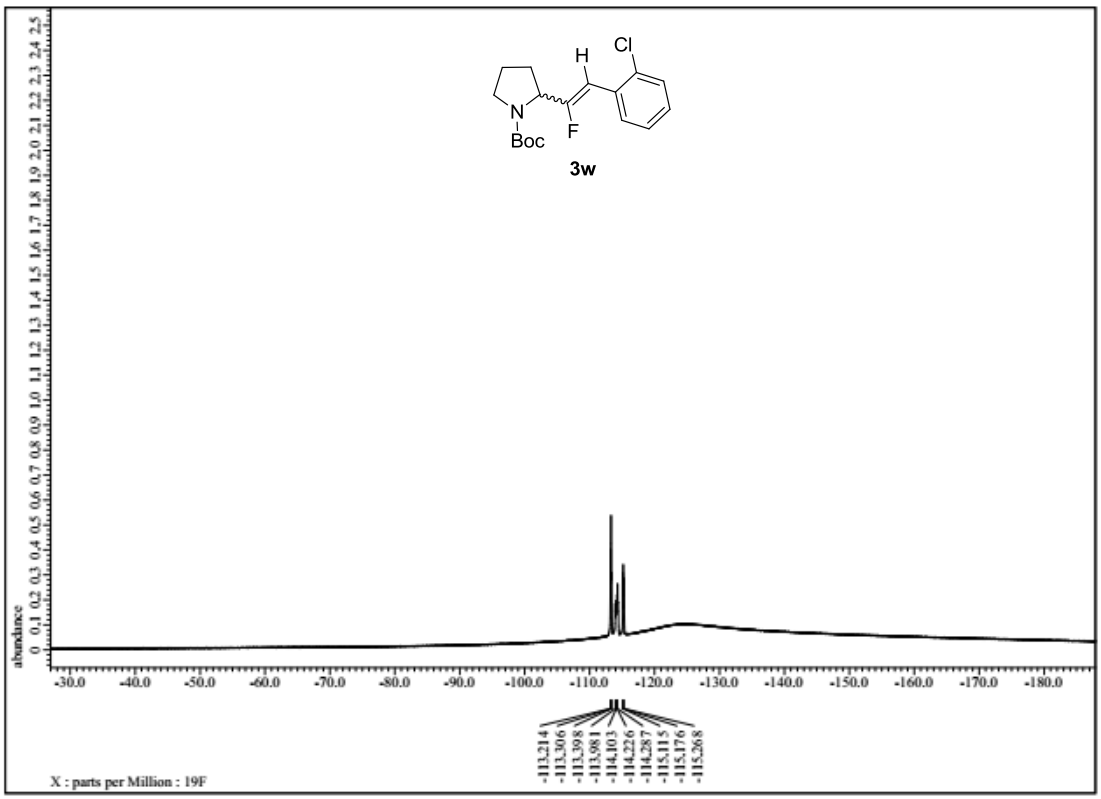

(E)-3v
abundance
X : parts per Million : 1H

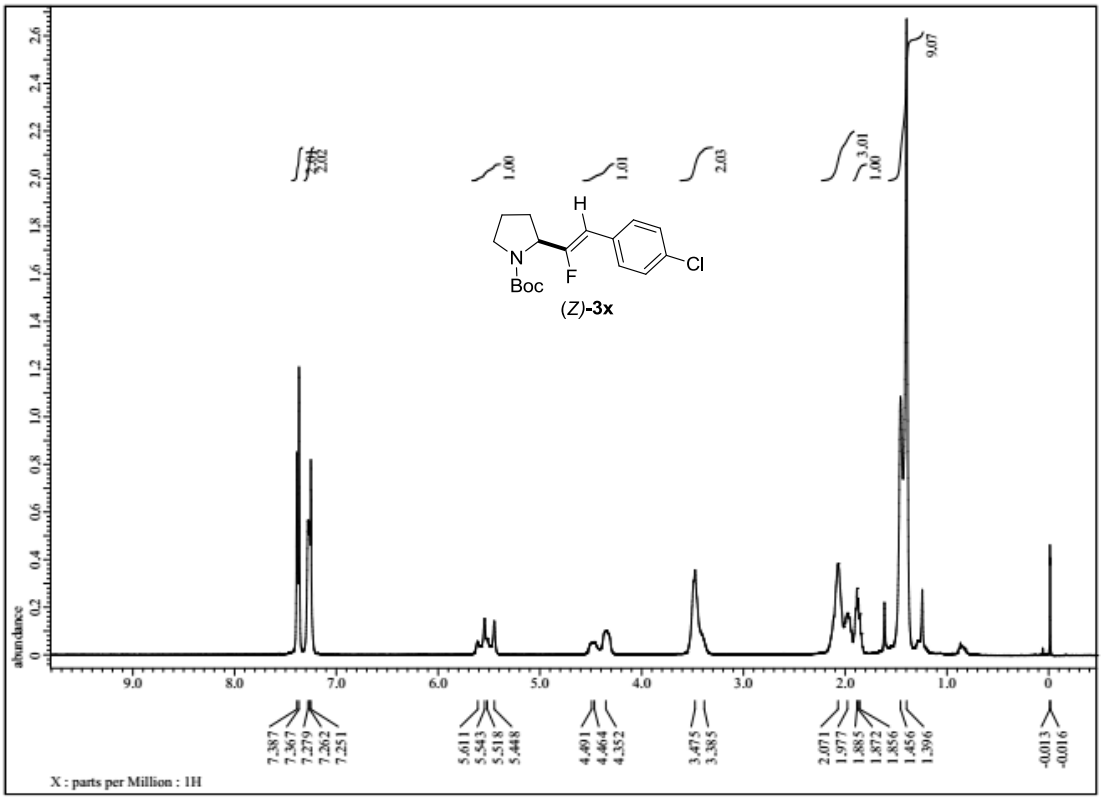

SMe
N
Boc
F
H
(E)-3v
abundance
X : parts per Million : 13C
164.430
161.856
155.077
137.304
130.363
130.229
129.019
129.000
126.873
108.309
108.033
79.887
77.475
77.160
76.836
48.251
48.032
41.796
29.039
28.219
24.853
20.391
16.034

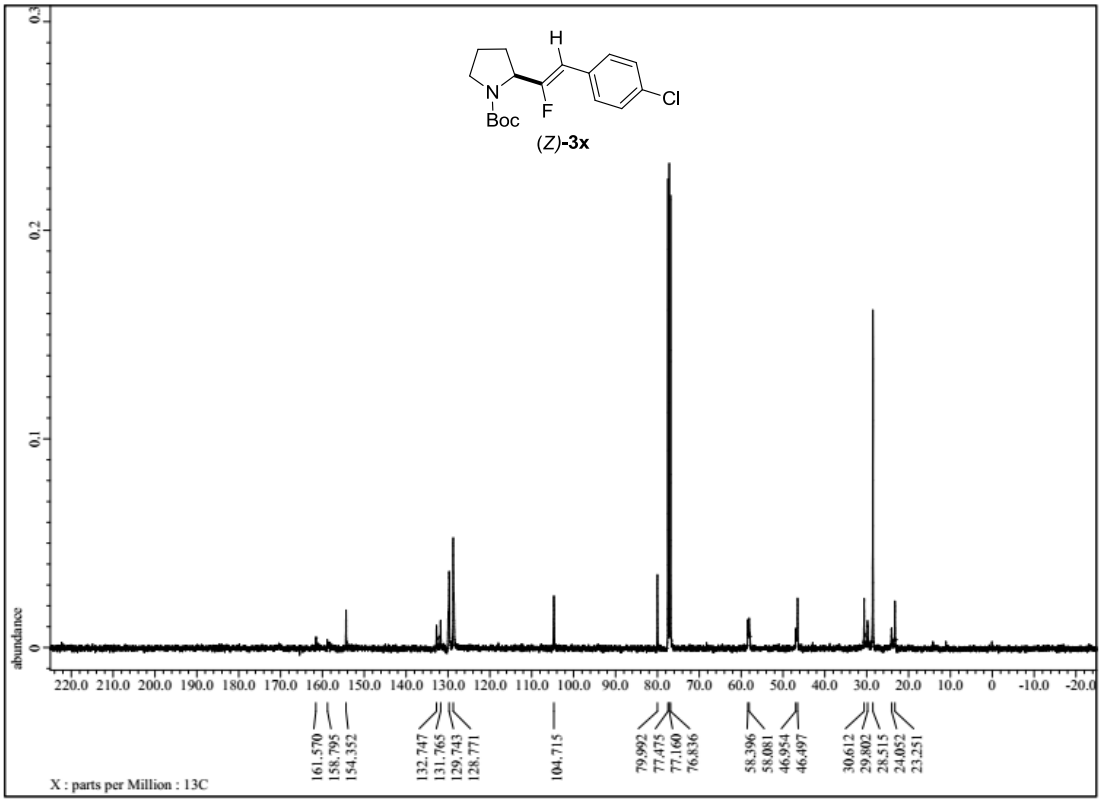

SMe
N
Boc
F
H
(E)-3v
abundance
X : parts per Million : 19F
-102.821
-102.913
-103.005

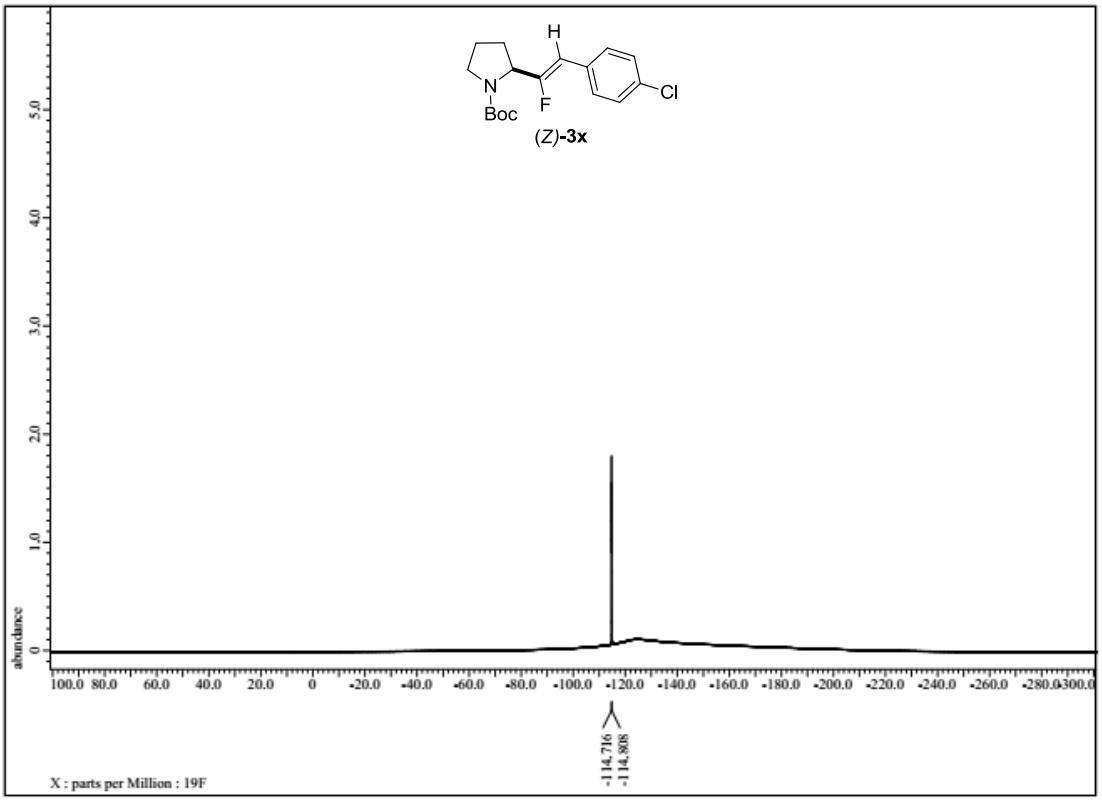

H
Cl
N
Boc
F
3w
abundance
X : parts per Million : 1H

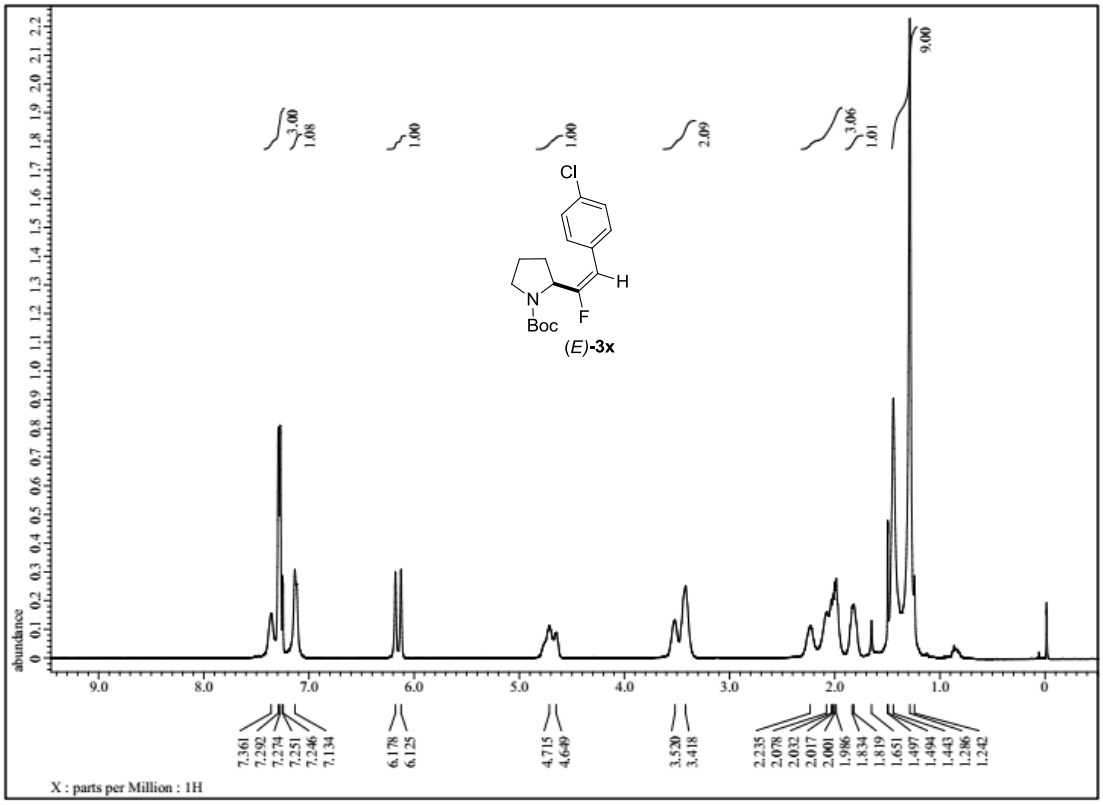

H
Cl
N
Boc
F
3w
abundance
X : parts per Million : 13C

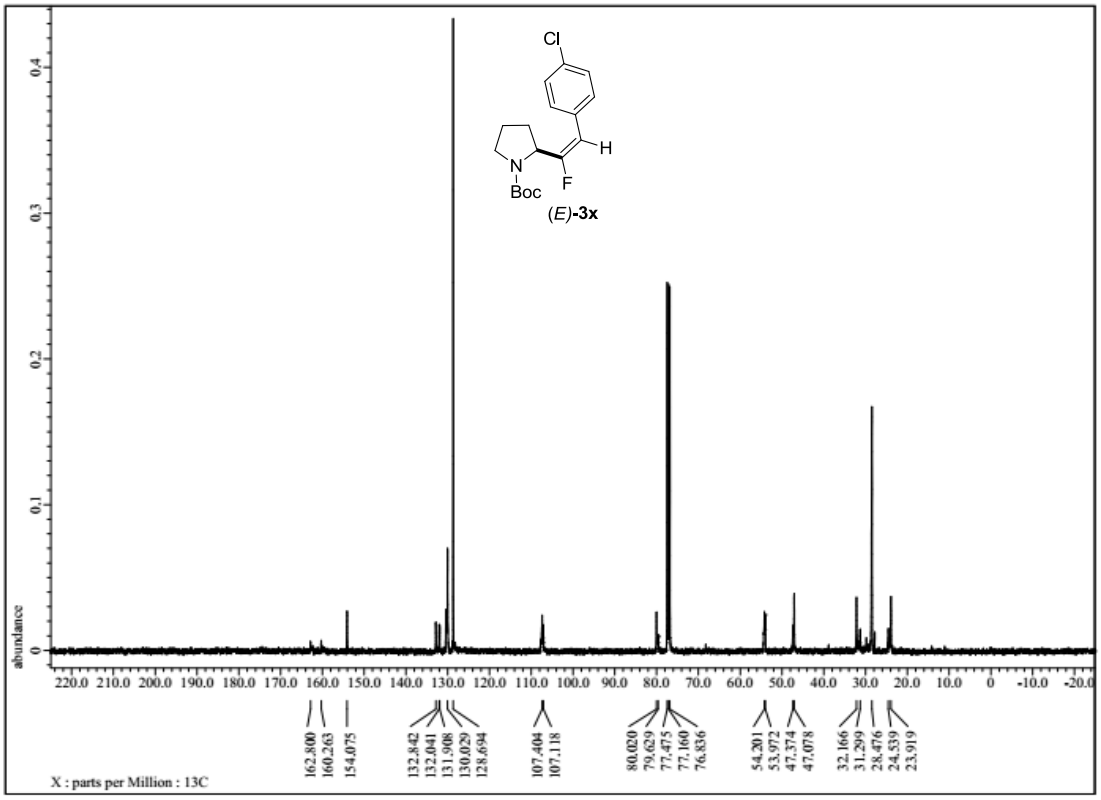

Cl
H
N
Boc
F
3w
abundance
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-113.214
-113.306
-113.398
-113.981
-114.103
-114.226
-114.287
-115.115
-115.176
-115.268
X : parts per Million : 19F

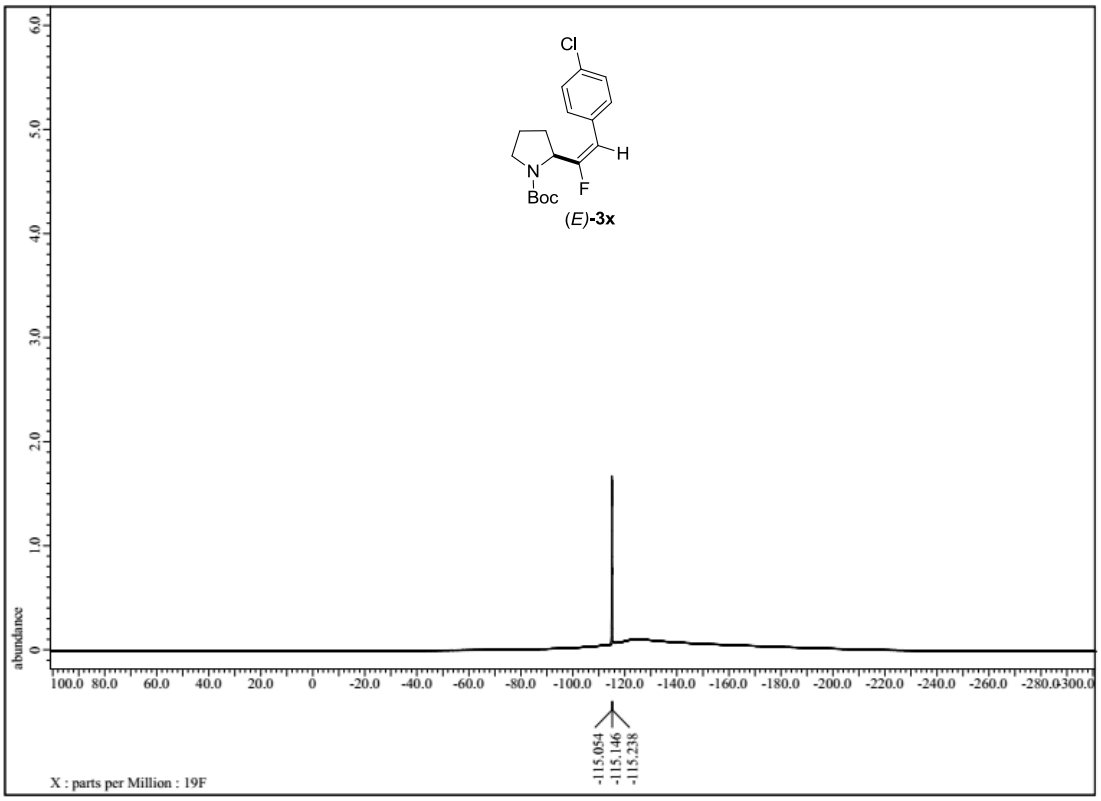

2.02
1.00
1.01
2.03
3.01
1.00
9.07
H
N
Boc
F
Cl
(Z)-3x
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.387
7.367
7.279
7.262
7.251
5.611
5.543
5.518
5.448
4.491
4.464
4.352
3.475
3.385
2.071
1.977
1.885
1.872
1.856
1.456
1.396
-0.013
-0.016
X : parts per Million : 1H

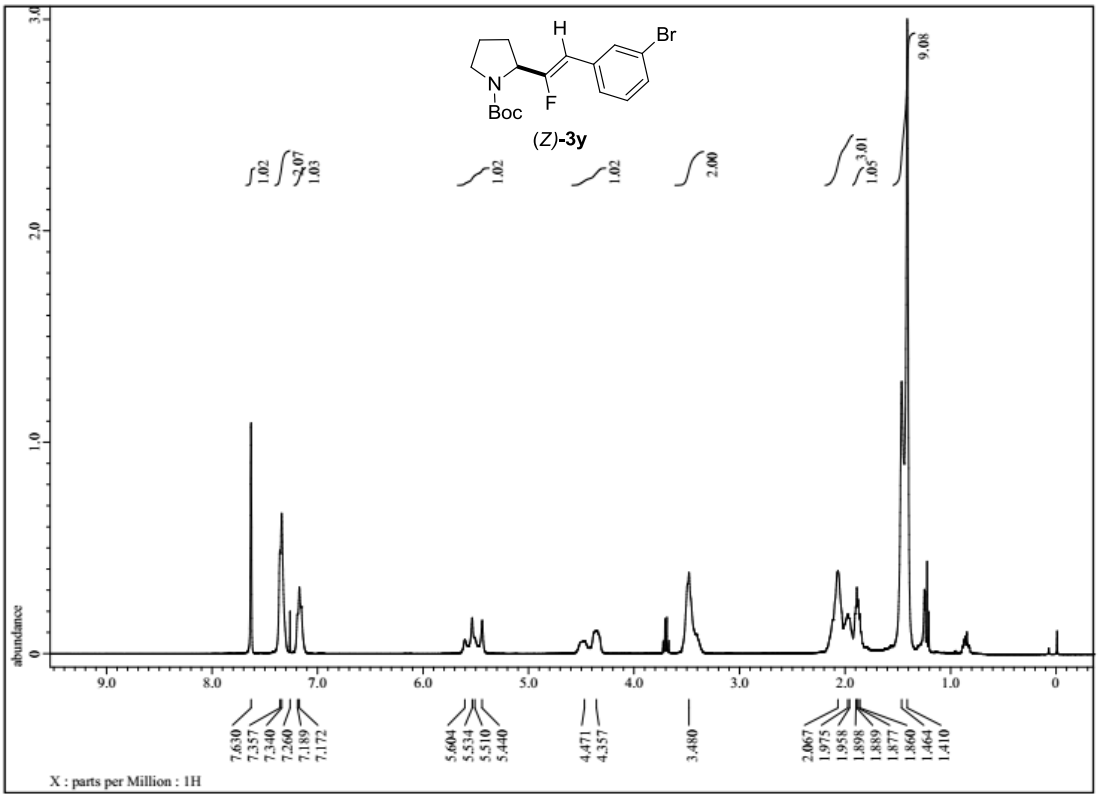

(Z)-3x
abundance
X : parts per Million : 13C
161.570
158.795
154.352
132.747
131.765
129.743
128.771
104.715
79.992
77.475
77.160
76.836
58.396
58.081
46.954
46.497
30.612
29.802
28.515
24.052
23.251

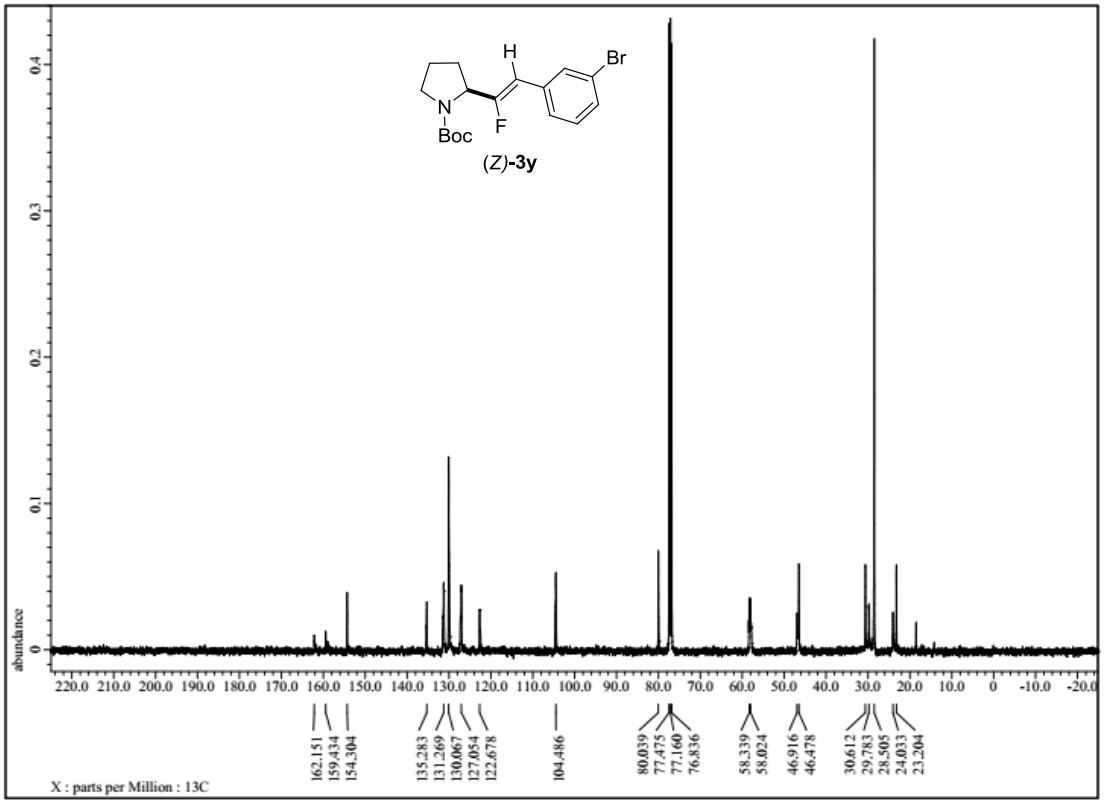

(Z)-3x
abundance
X : parts per Million : 19F
-114.716
-114.808

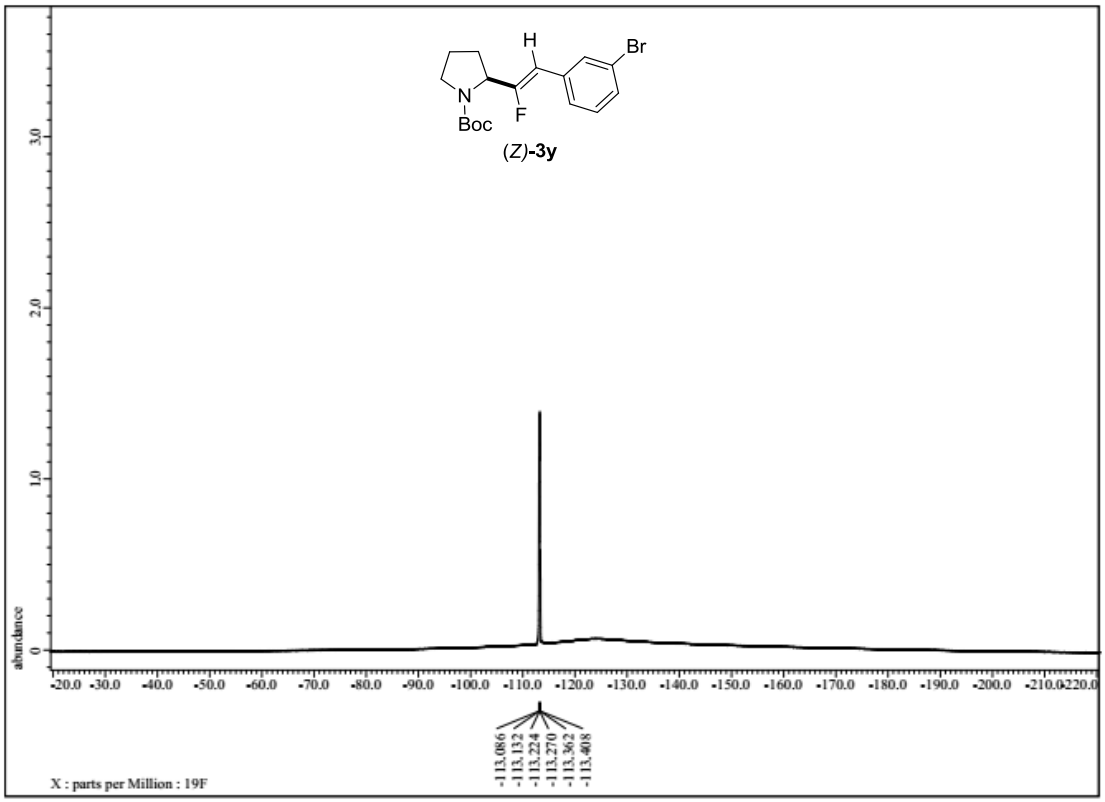

(E)-3x
X : parts per Million : 1H

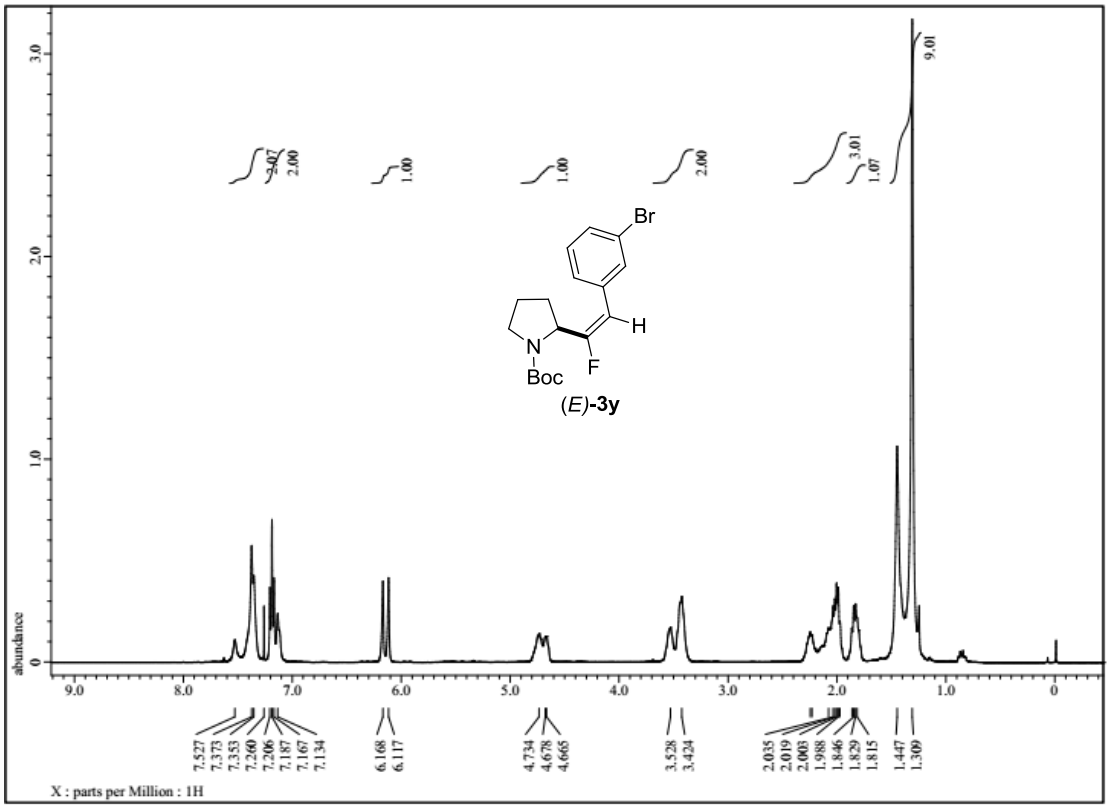

(E)-3x
X : parts per Million : 13C

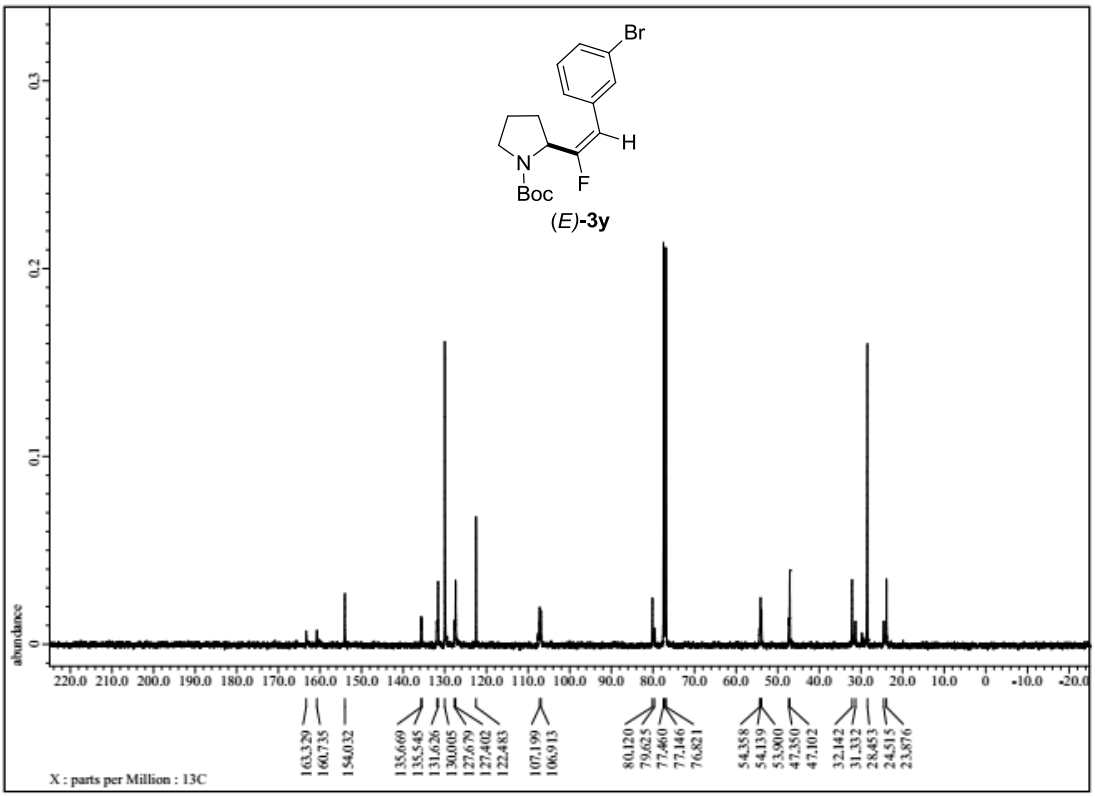

Cl
H
N
Boc
F
(E)-3x
abundance
X : parts per Million : 19F
-115.054
-115.146
-115.238

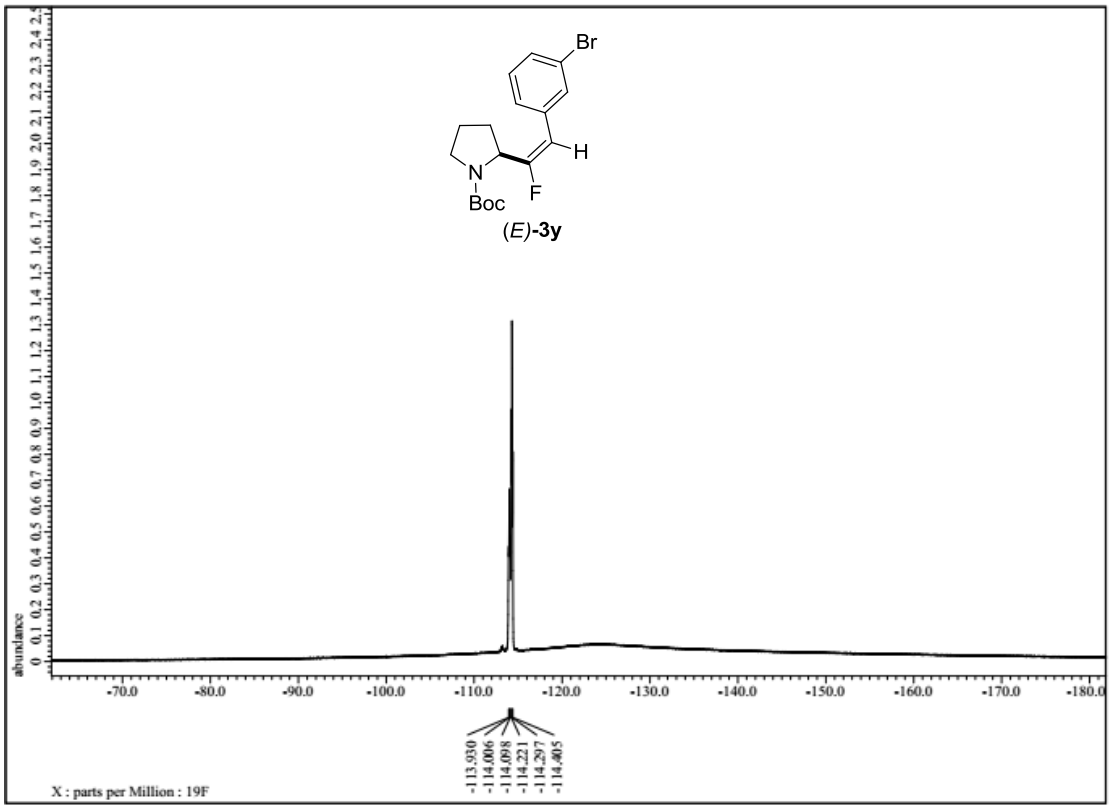

H
Br
N
Boc
F
(Z)-3y
1.02
2.07
1.03
1.02
1.02
2.00
3.01
1.05
9.08
abundance
X : parts per Million : 1H
7.630
7.357
7.340
7.260
7.189
7.172
5.604
5.534
5.510
5.440
4.471
4.357
3.480
2.067
1.975
1.958
1.898
1.889
1.877
1.860
1.464
1.410

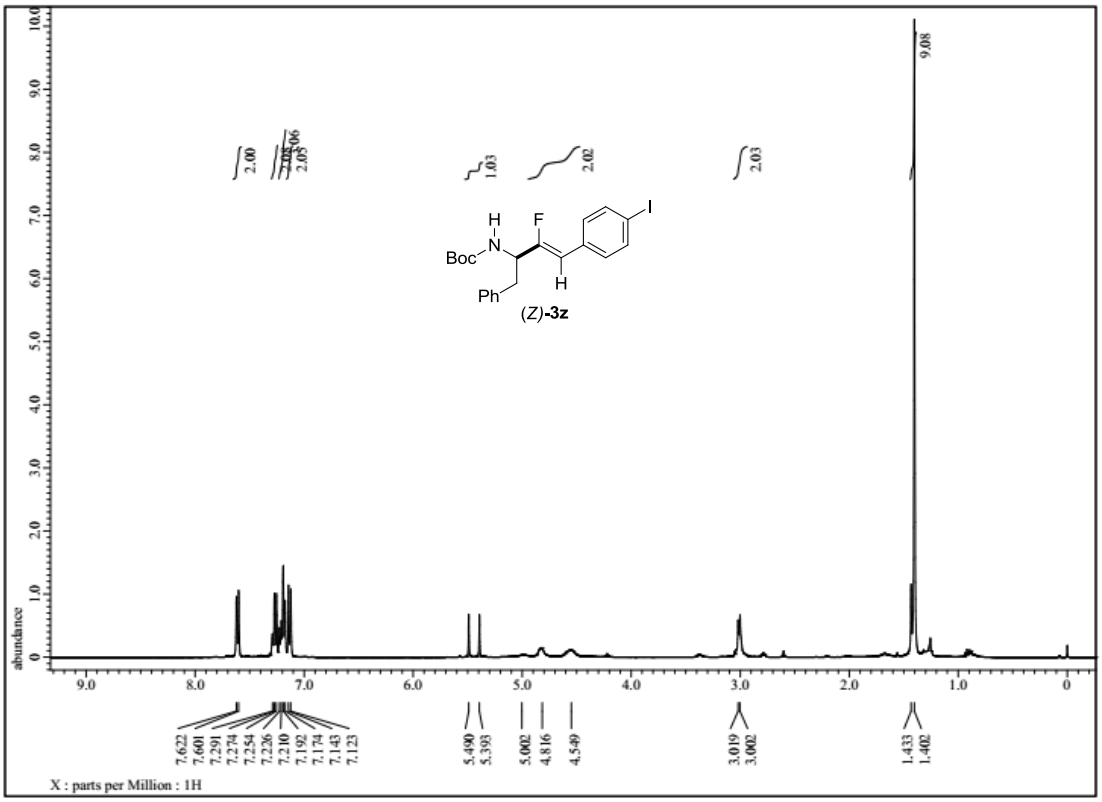

H
Br
N
F
Boc
(Z)-3y
abundance
X : parts per Million : 13C
162.151
159.434
154.304
135.283
131.269
130.067
127.054
122.678
104.486
80.039
77.475
77.160
76.836
58.339
58.024
46.916
46.478
30.612
29.783
28.505
24.033
23.204

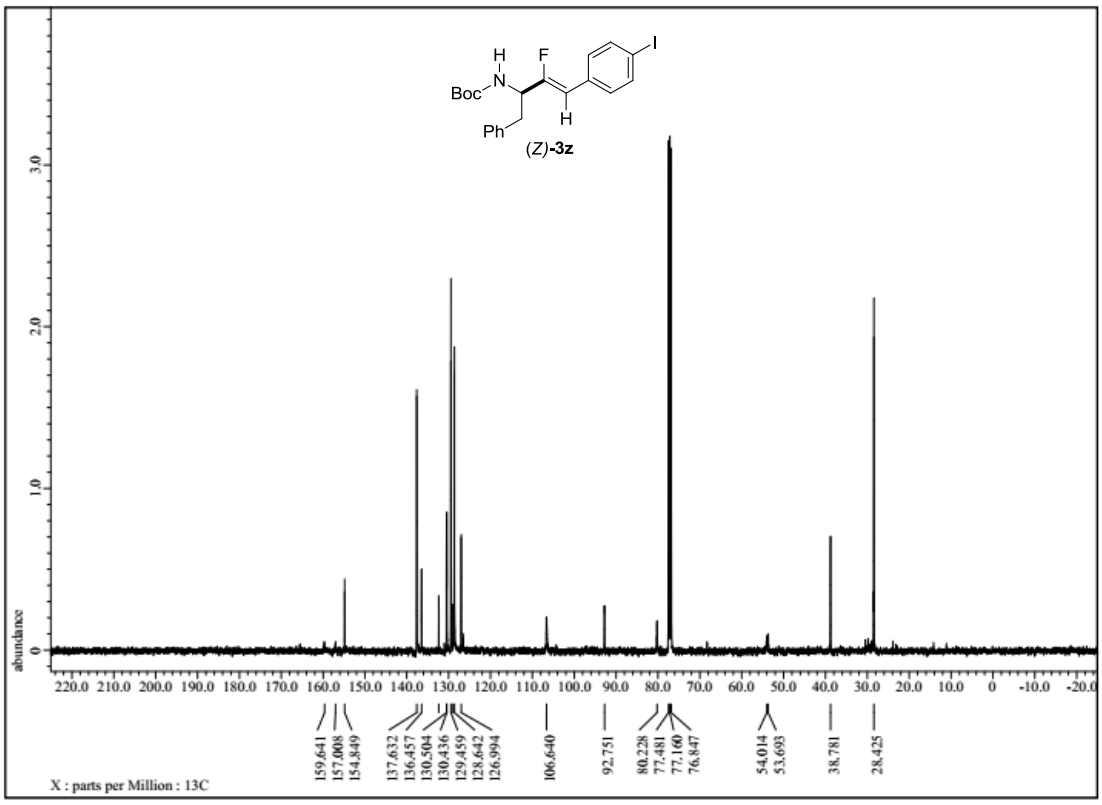

H
Br
N
F
Boc
(Z)-3y
abundance
X : parts per Million : 19F
-113.086
-113.132
-113.224
-113.270
-113.362
-113.408

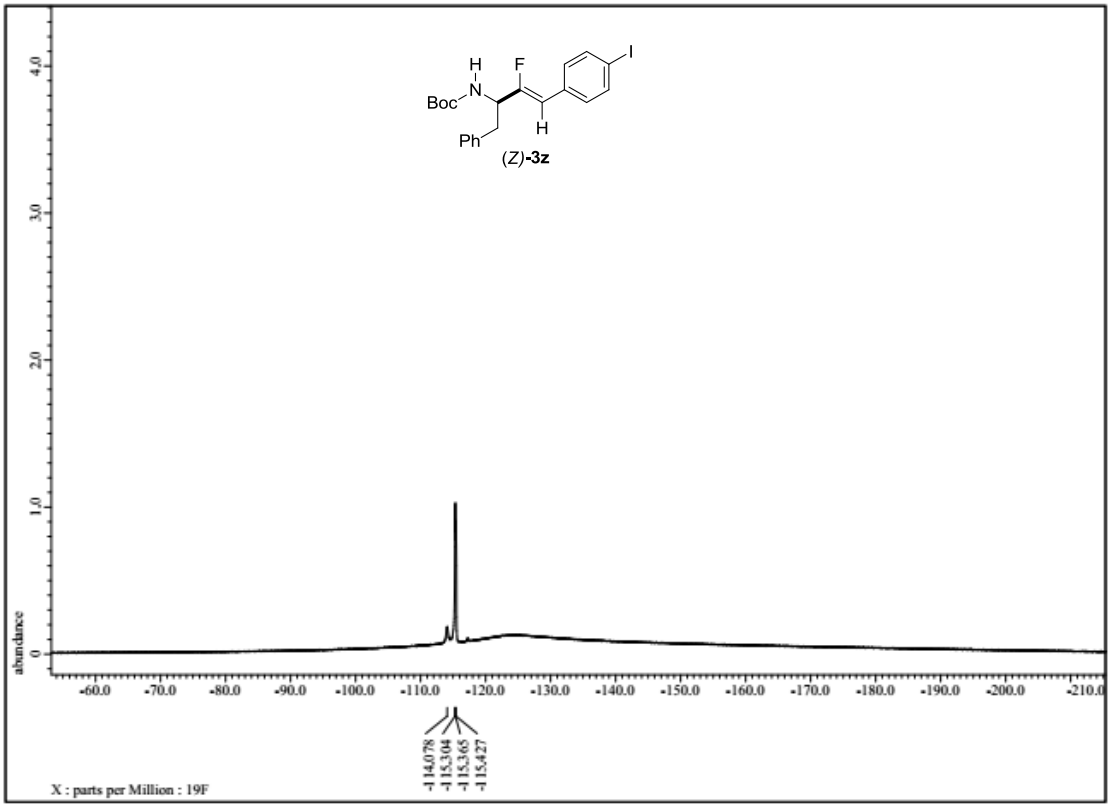

Br
H
N
Boc
F
(E)-3y
abundance
X : parts per Million : 1H

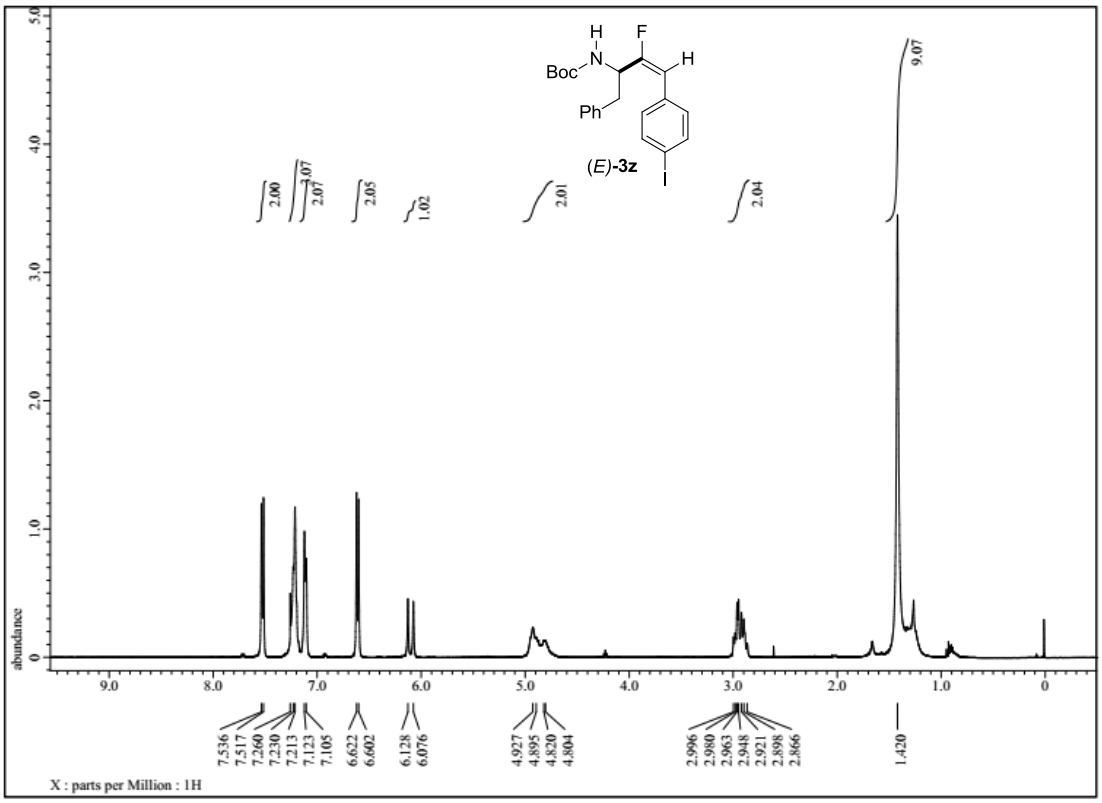

Br
H
N
Boc
F
(E)-3y
abundance
X : parts per Million : 13C

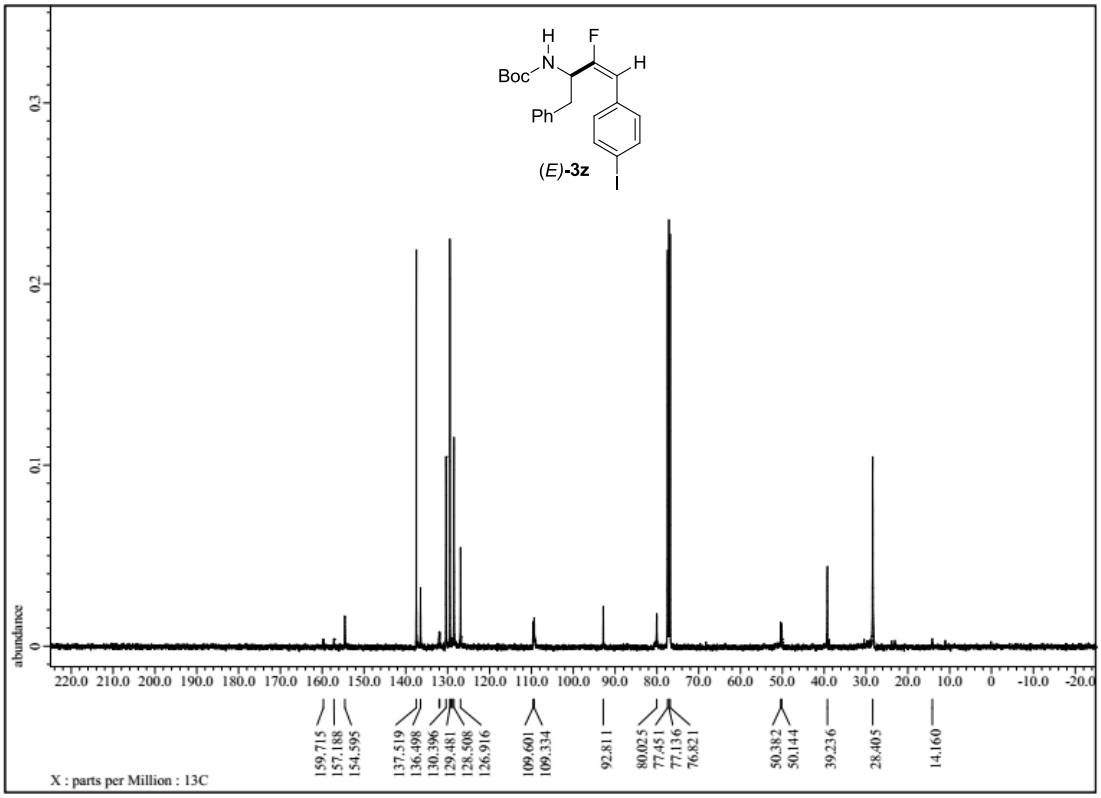

Br
H
N
Boc
F
(E)-3y
abundance
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-113.930
-114.006
-114.098
-114.221
-114.297
-114.405
X : parts per Million : 19F

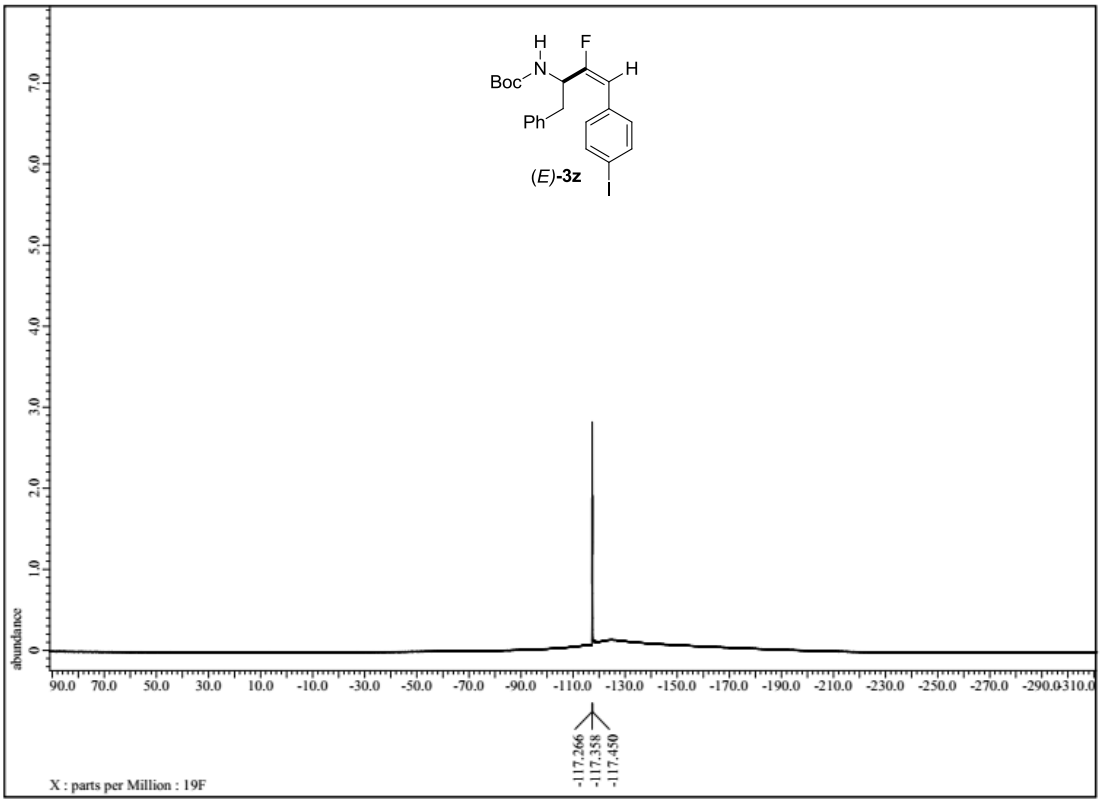

2.00
2.06
2.05
1.03
2.02
2.03
9.08
H
N
Boc
F
I
H
Ph
(Z)-3z
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.622
7.601
7.291
7.274
7.254
7.226
7.210
7.192
7.174
7.143
7.123
5.490
5.393
5.002
4.816
4.549
3.019
3.002
1.433
1.402
X : parts per Million : 1H

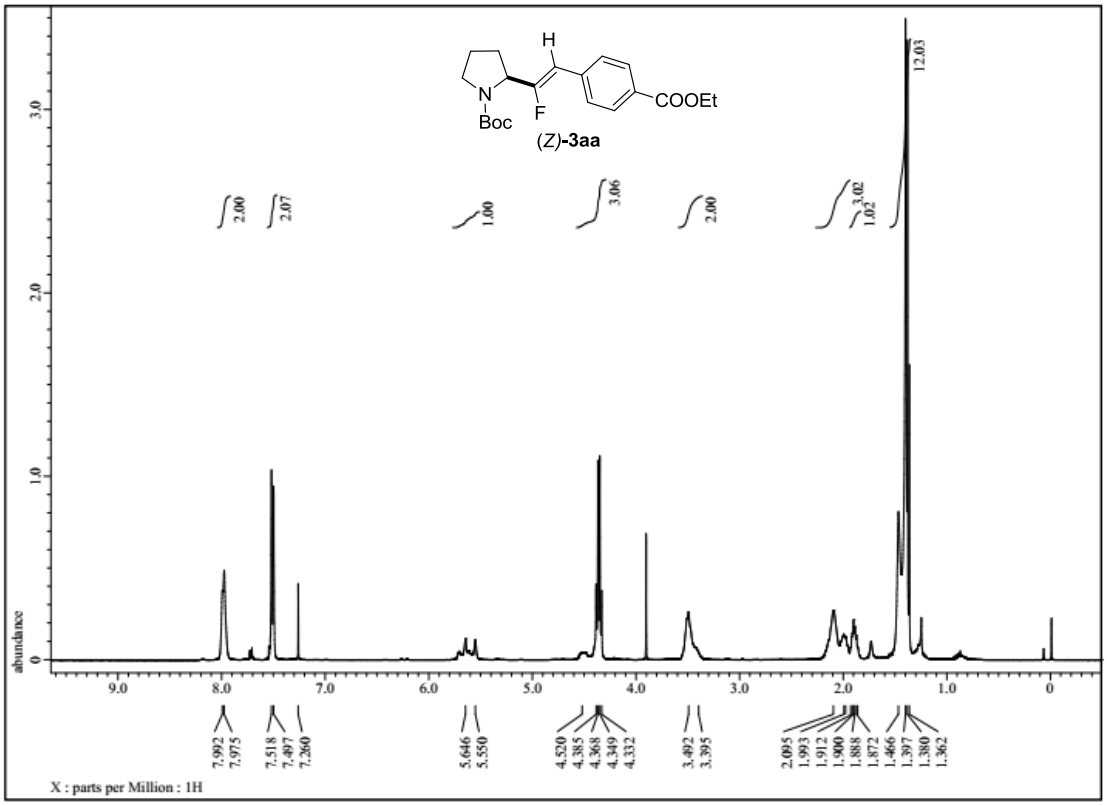

(Z)-3z
abundance
X : parts per Million : 13C
159.641
157.008
154.849
137.632
136.457
130.504
130.436
129.459
128.642
126.994
106.640
92.751
80.228
77.481
77.160
76.847
54.014
53.693
38.781
28.425

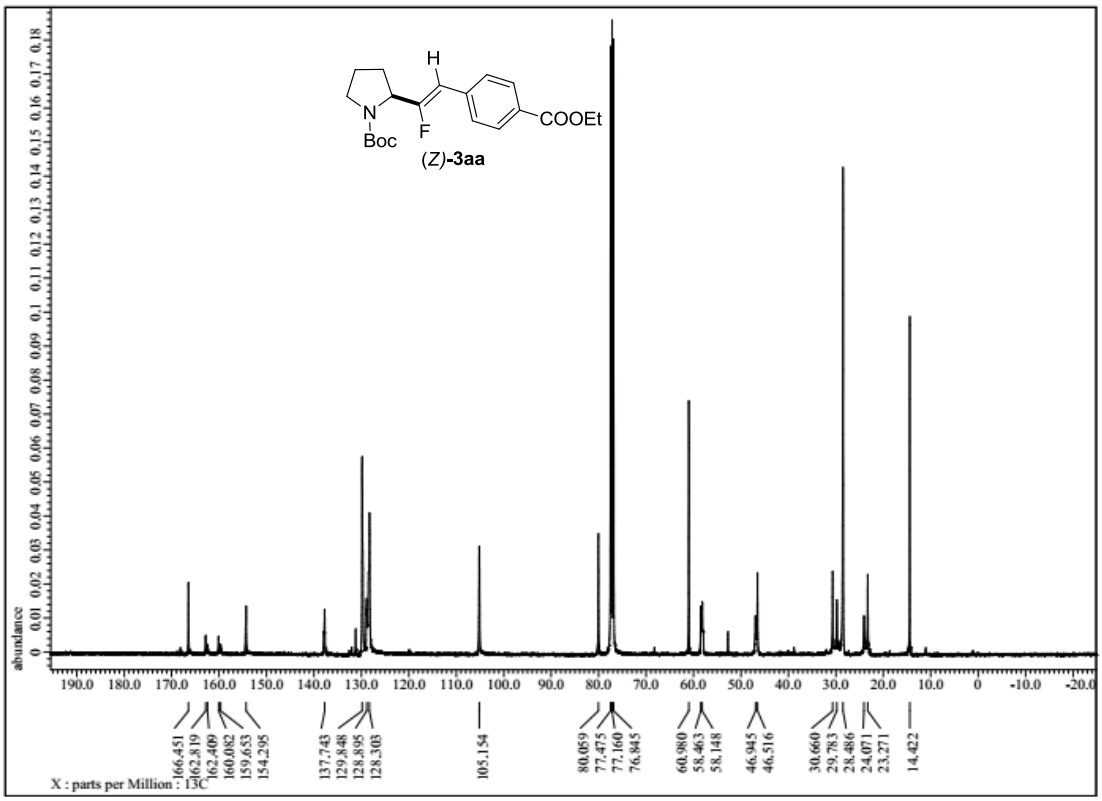

(Z)-3z
abundance
X : parts per Million : 19F
-114.078
-115.304
-115.365
-115.427

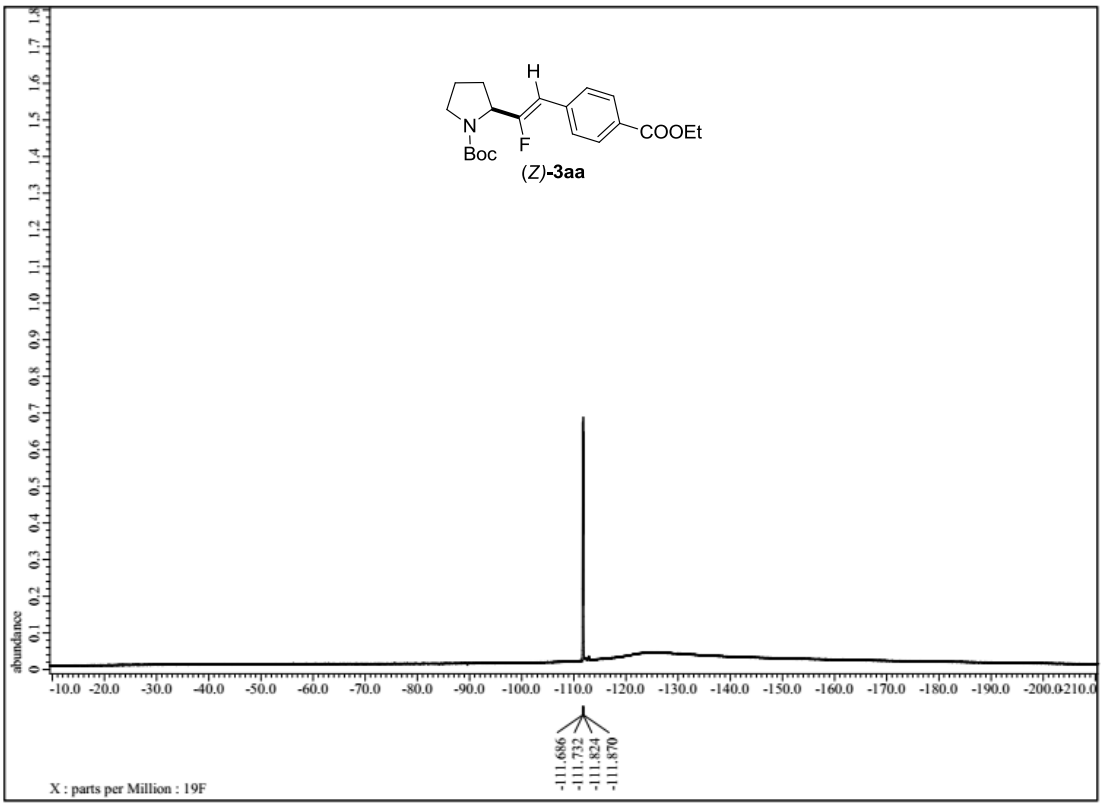

(E)-3z
abundance
X : parts per Million : 1H

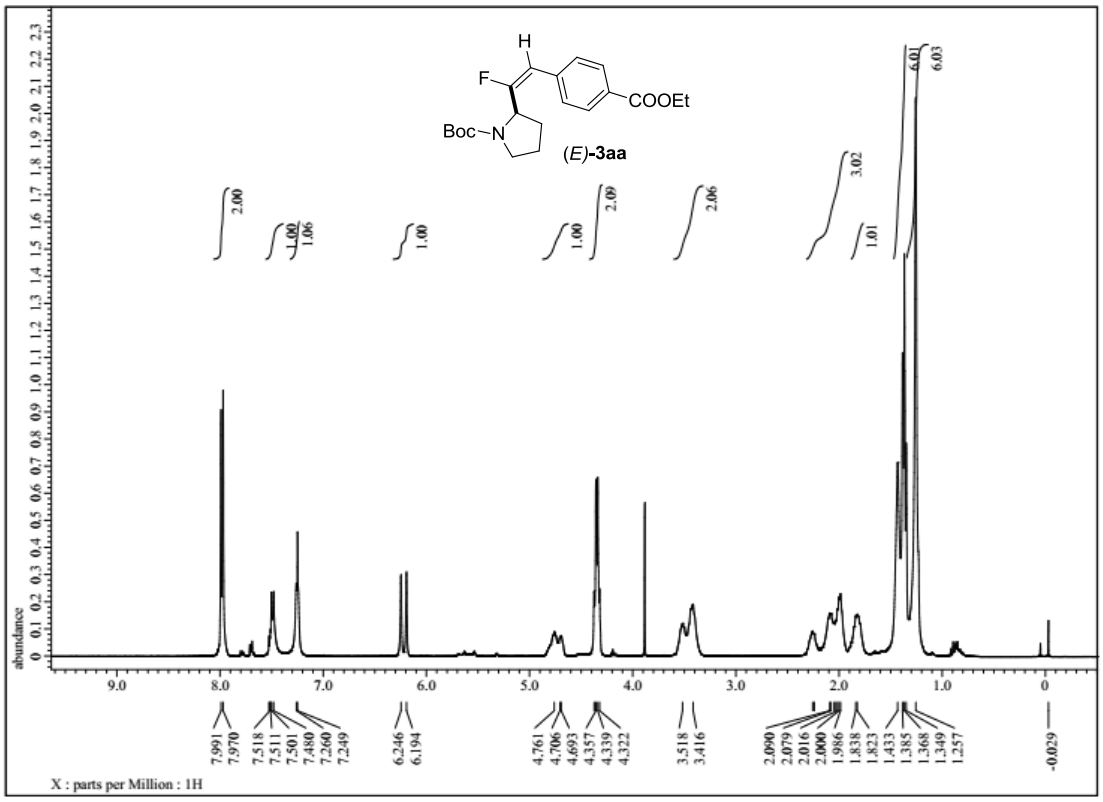

(E)-3z
abundance
X : parts per Million : 13C

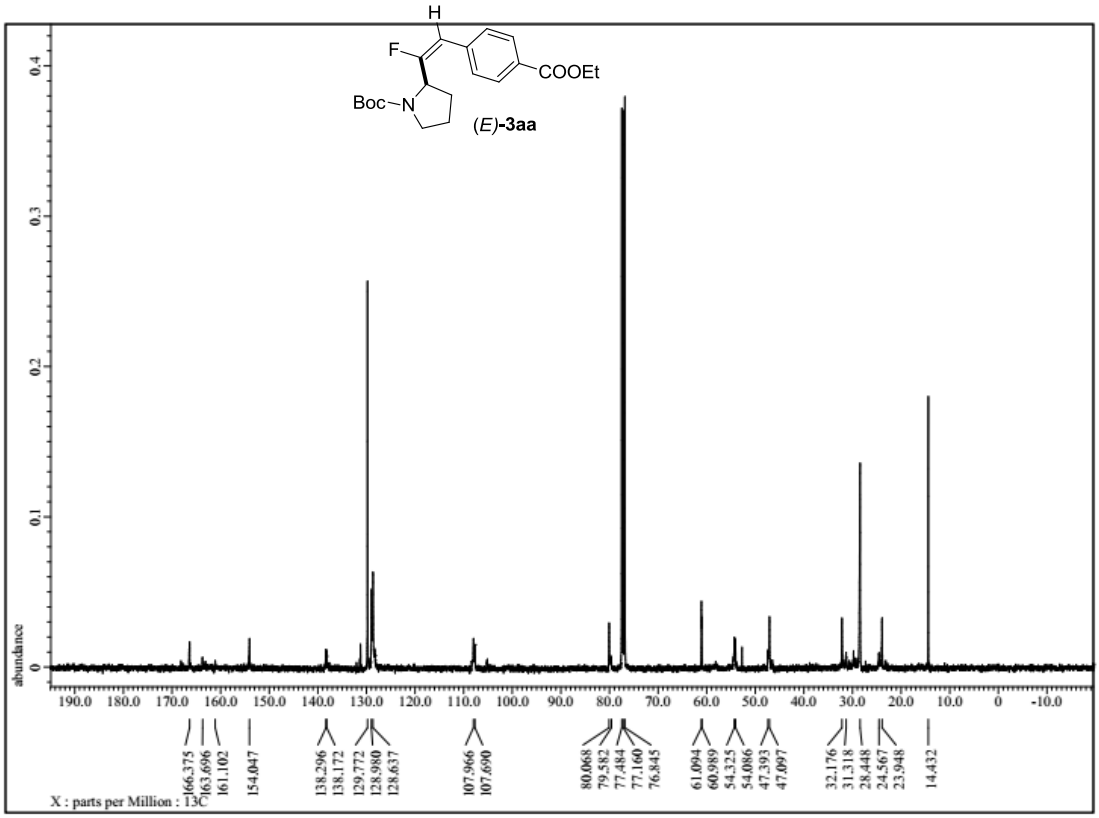

H
F
N
Boc
H
Ph
I
(E)-3z
abundance
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0 -310.0
-117.266
-117.358
-117.450
X : parts per Million : 19F

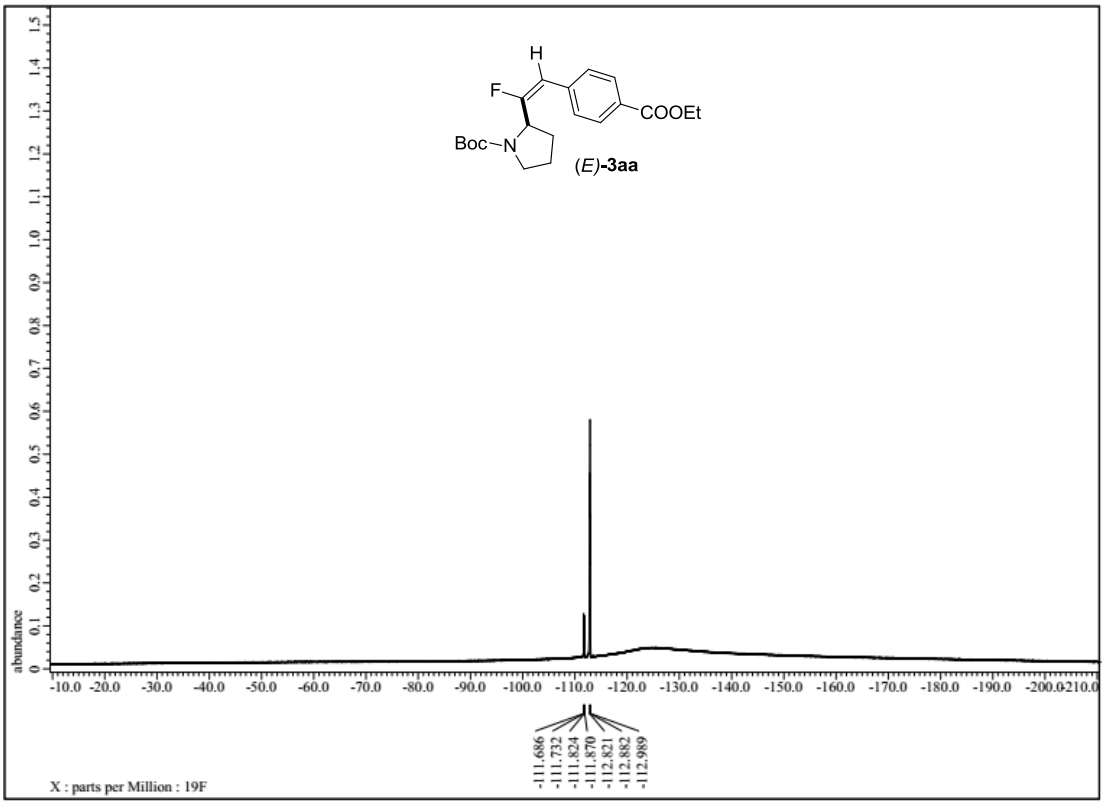

H
N
Boc
F
COOEt
(Z)-3aa
2.00
2.07
1.00
3.06
2.00
3.02
1.02
12.03
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.992
7.975
7.518
7.497
7.260
5.646
5.550
4.520
4.385
4.368
4.349
4.332
3.492
3.395
2.095
1.993
1.912
1.900
1.888
1.872
1.466
1.397
1.380
1.362
X : parts per Million : 1H

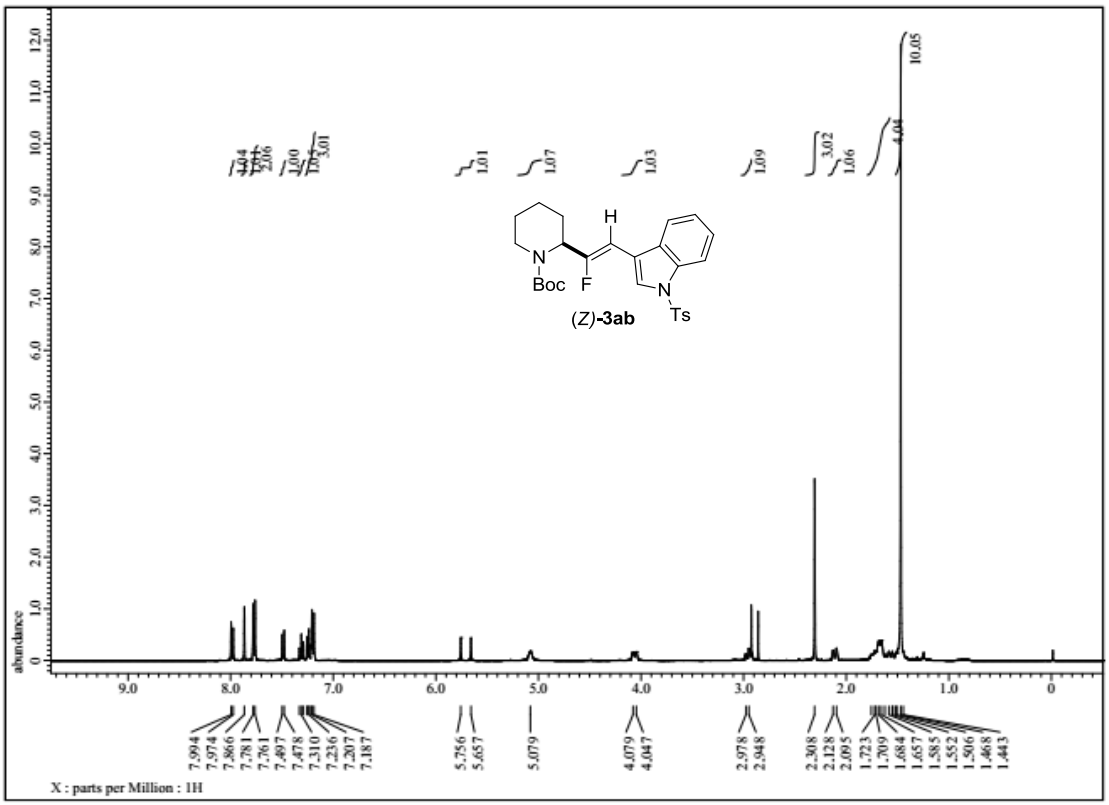

H
N
Boc
F
COOEt
(Z)-3aa
abundance
X : parts per Million : 13C
166.451
162.819
162.409
160.082
159.653
154.295
137.743
129.848
128.895
128.303
105.154
80.059
77.475
77.160
76.845
60.980
58.463
58.148
46.945
46.516
30.660
29.783
28.486
24.071
23.271
14.422

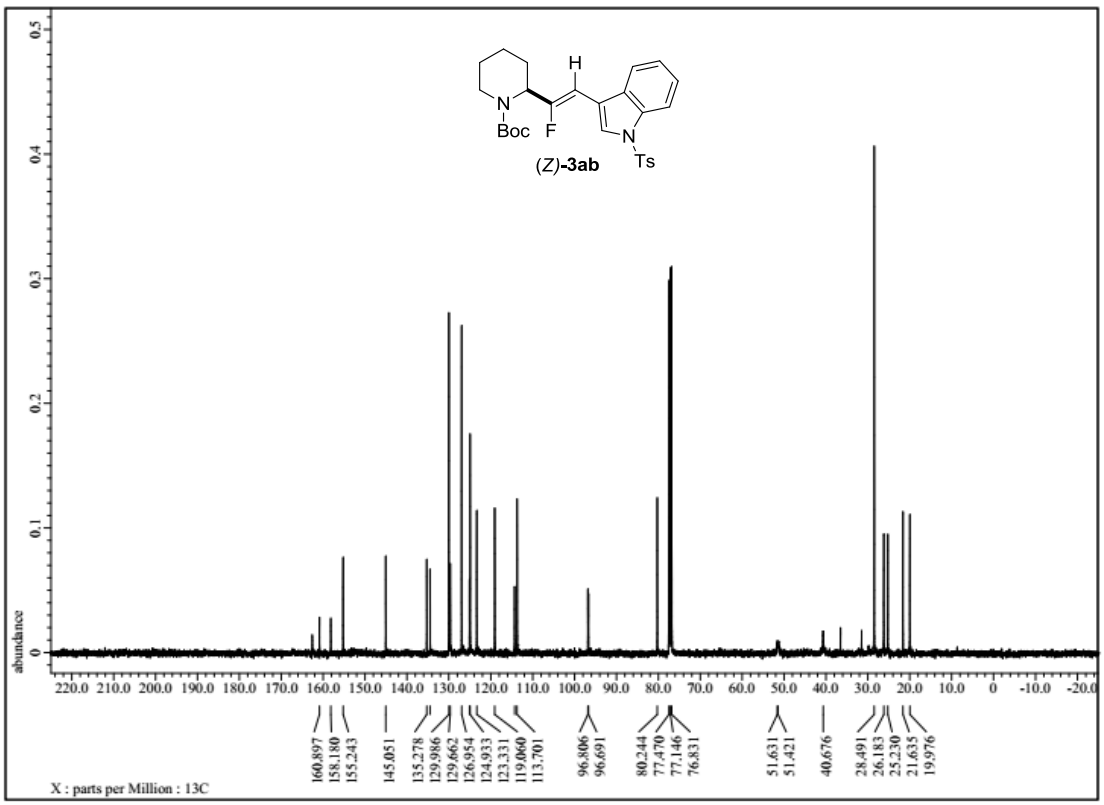

H
N
Boc
F
COOEt
(Z)-3aa
abundance
X : parts per Million : 19F
-111.686
-111.732
-111.824
-111.870

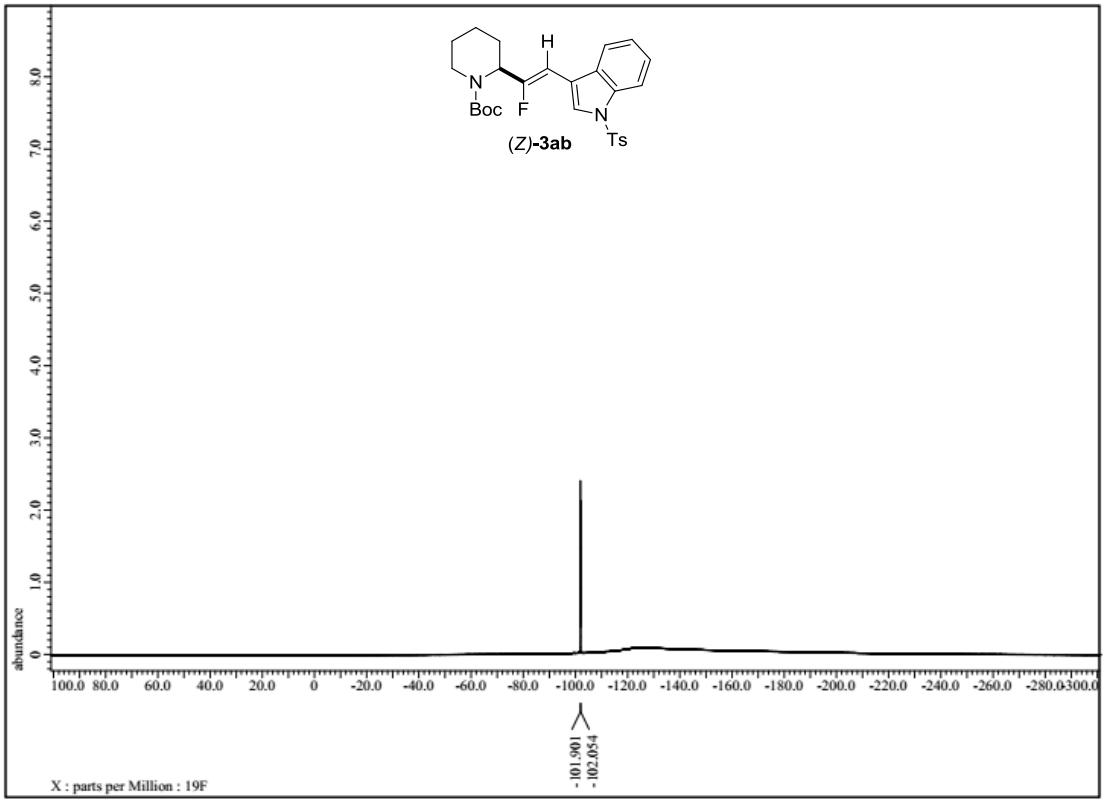

H
F
COOEt
Boc–N
(E)-3aa
abundance
X : parts per Million : 1H

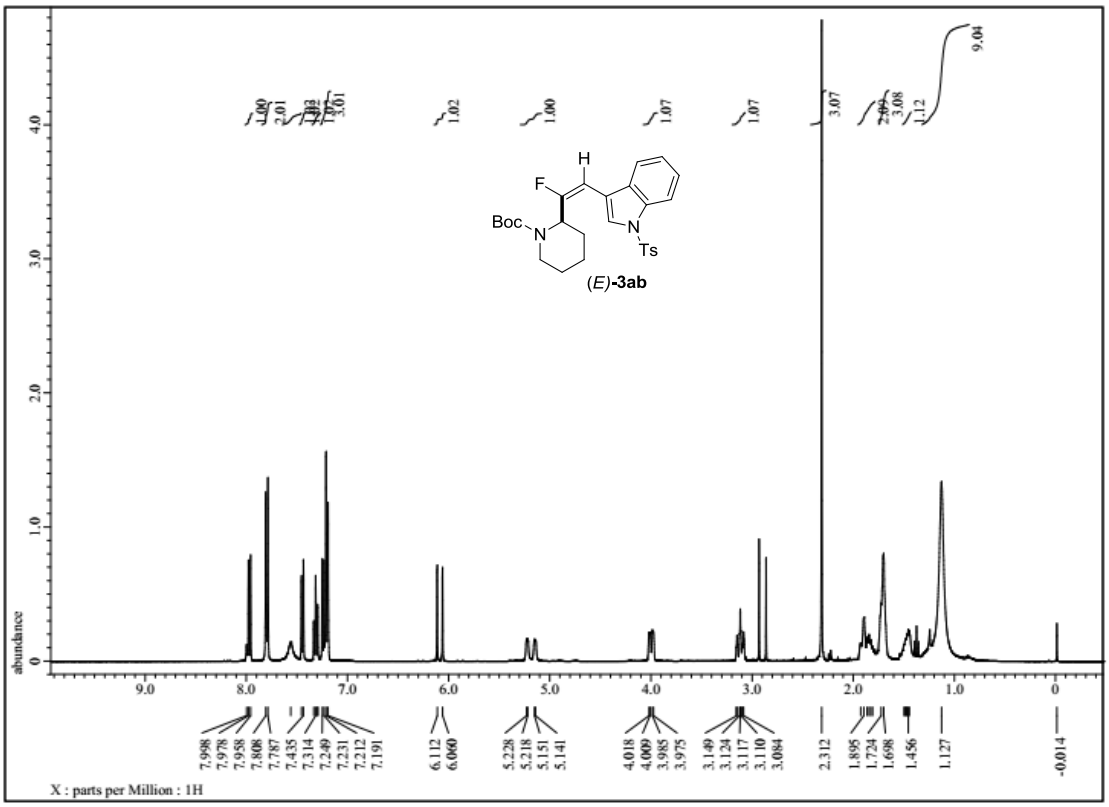

H
F
COOEt
Boc–N
(E)-3aa
abundance
X : parts per Million : 13C

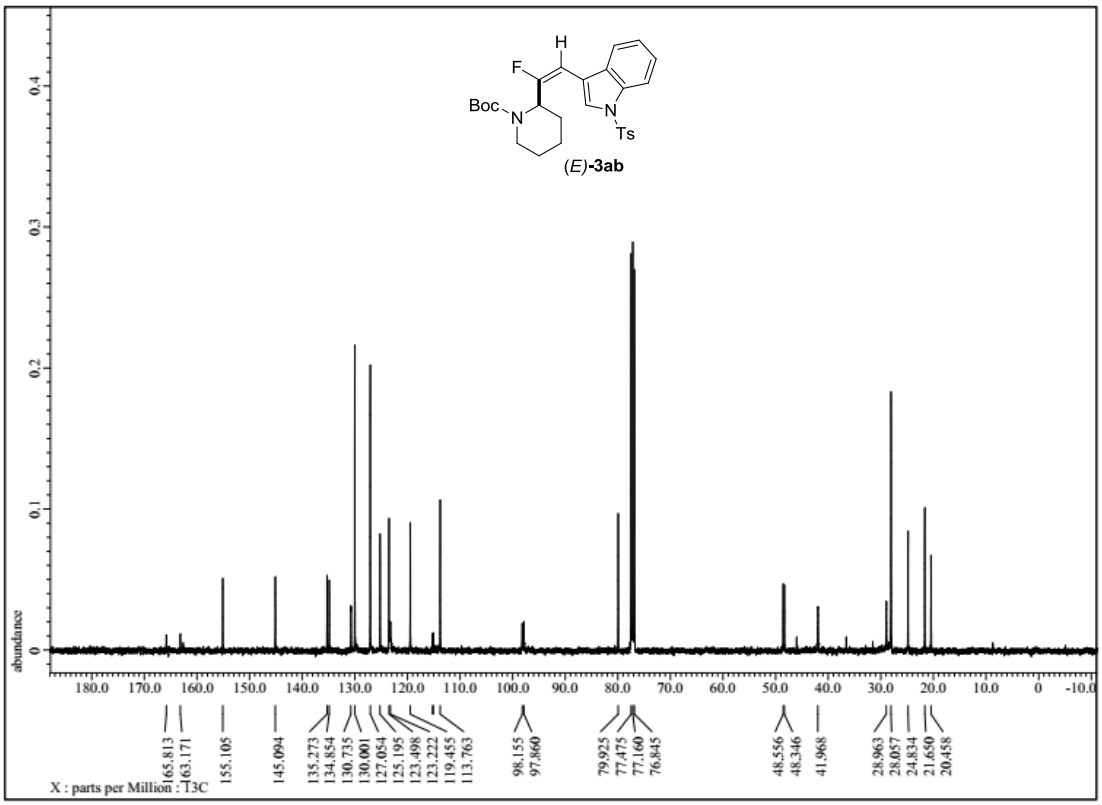

H
F
COOEt
Boc
N
(E)-3aa
abundance
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0 -210.0
-111.686
-111.732
-111.824
-111.870
-112.821
-112.882
-112.989
X : parts per Million : 19F

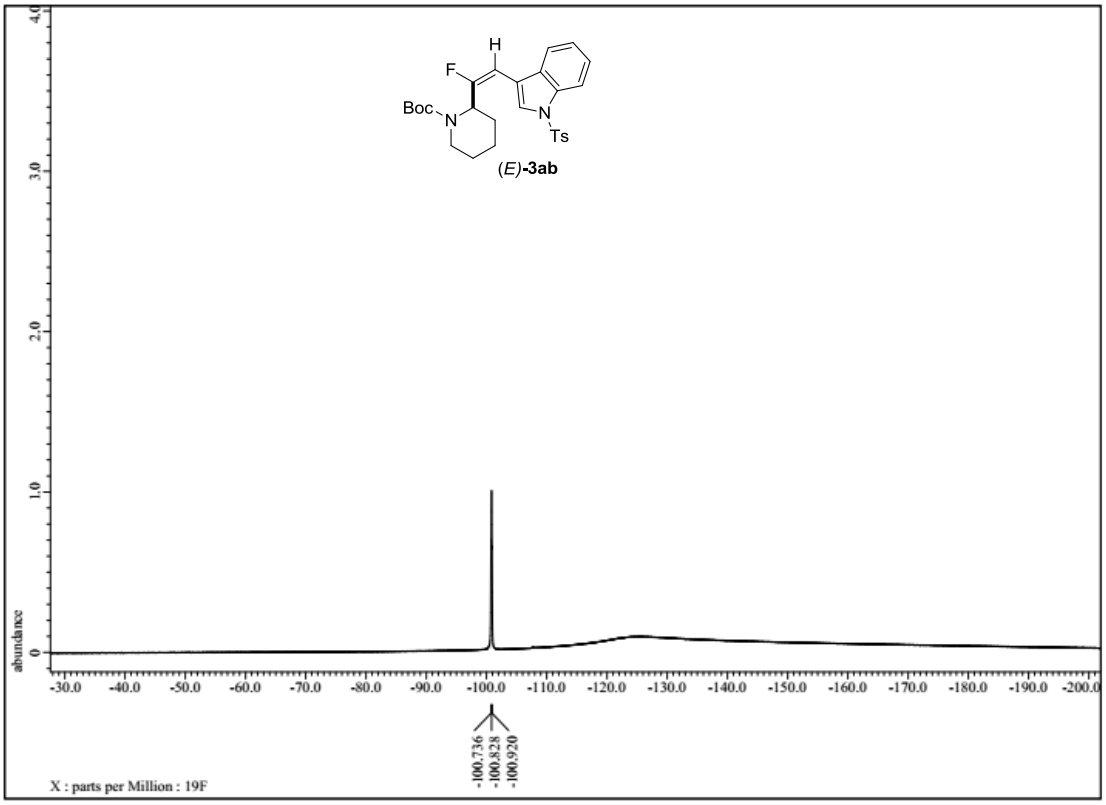

10.05
4.04
3.02
1.06
1.09
1.03
1.07
1.01
H
N
Boc
F
N
Ts
(Z)-3ab
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.994
7.974
7.866
7.781
7.761
7.497
7.478
7.310
7.236
7.207
7.187
5.756
5.657
5.079
4.079
4.047
2.978
2.948
2.308
2.128
2.095
1.723
1.709
1.684
1.657
1.585
1.552
1.506
1.468
1.443
X : parts per Million : 1H

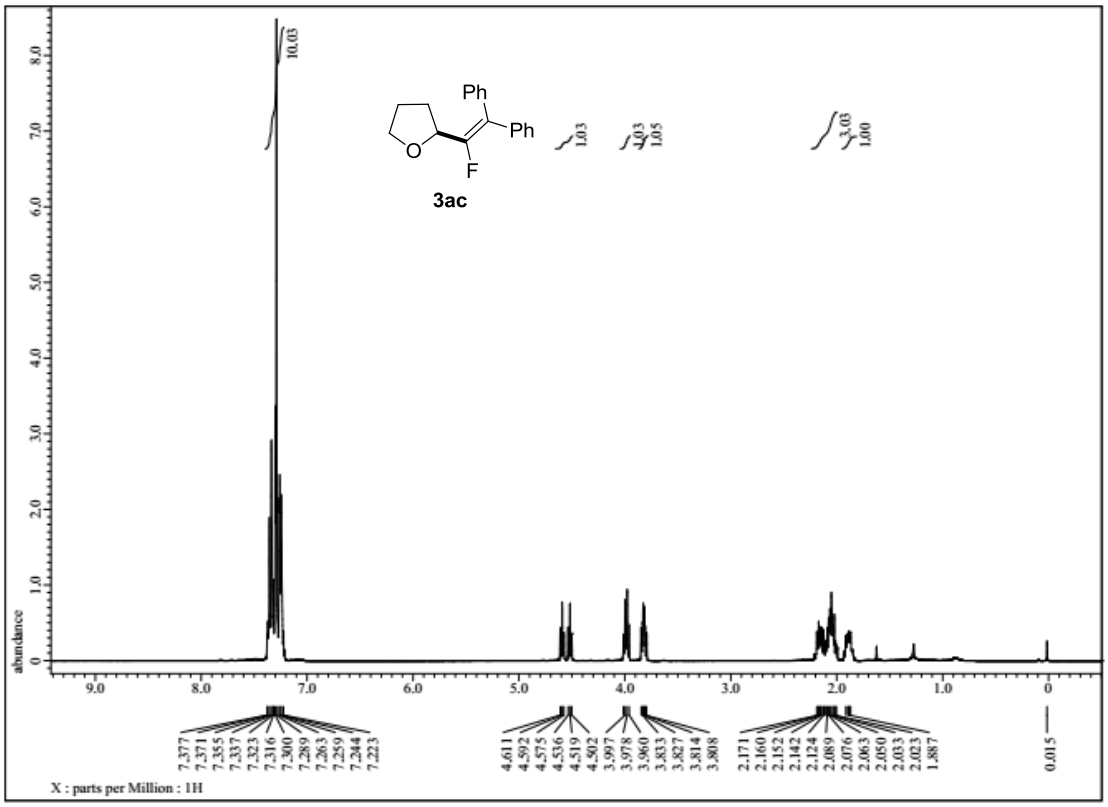

(Z)-3ab
abundance
X : parts per Million : 13C
160.897
158.180
155.243
145.051
135.278
129.986
129.662
126.954
124.933
123.331
119.060
113.701
96.806
96.691
80.244
77.470
77.146
76.831
51.631
51.421
40.676
28.491
26.183
25.230
21.635
19.976

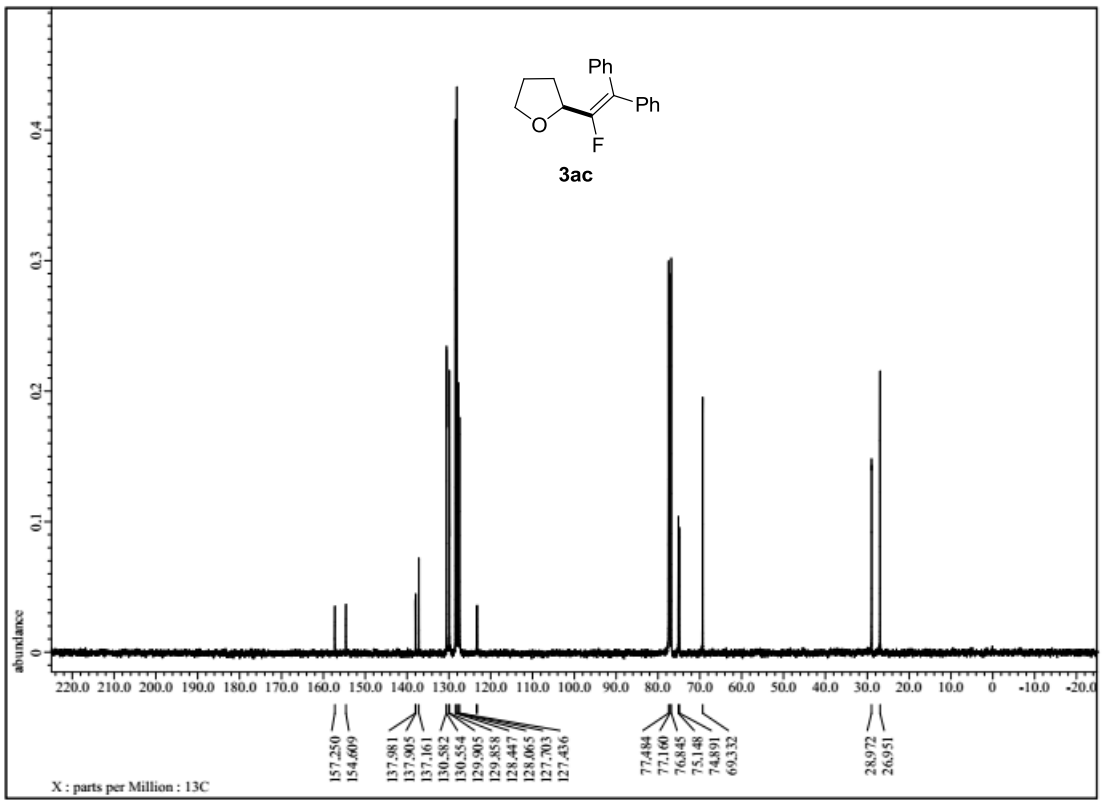

(Z)-3ab
abundance
X : parts per Million : 19F
-101.901
-102.054

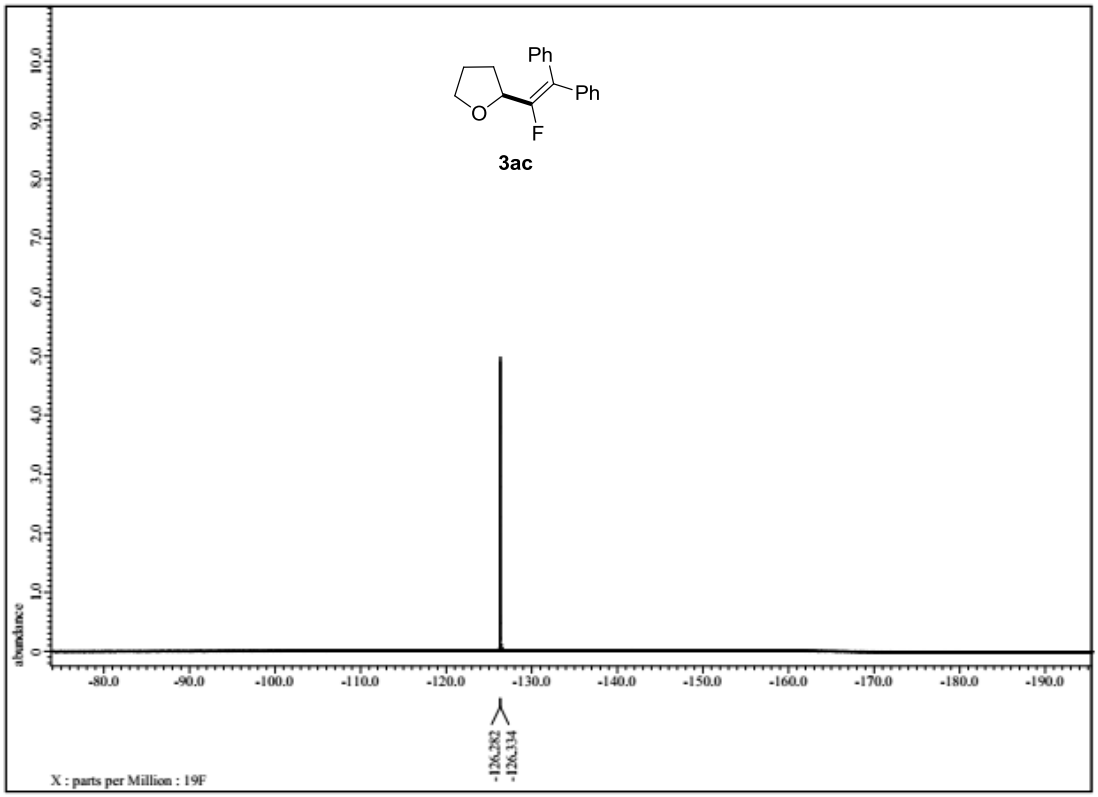

(E)-3ab
abundance
X : parts per Million : 1H

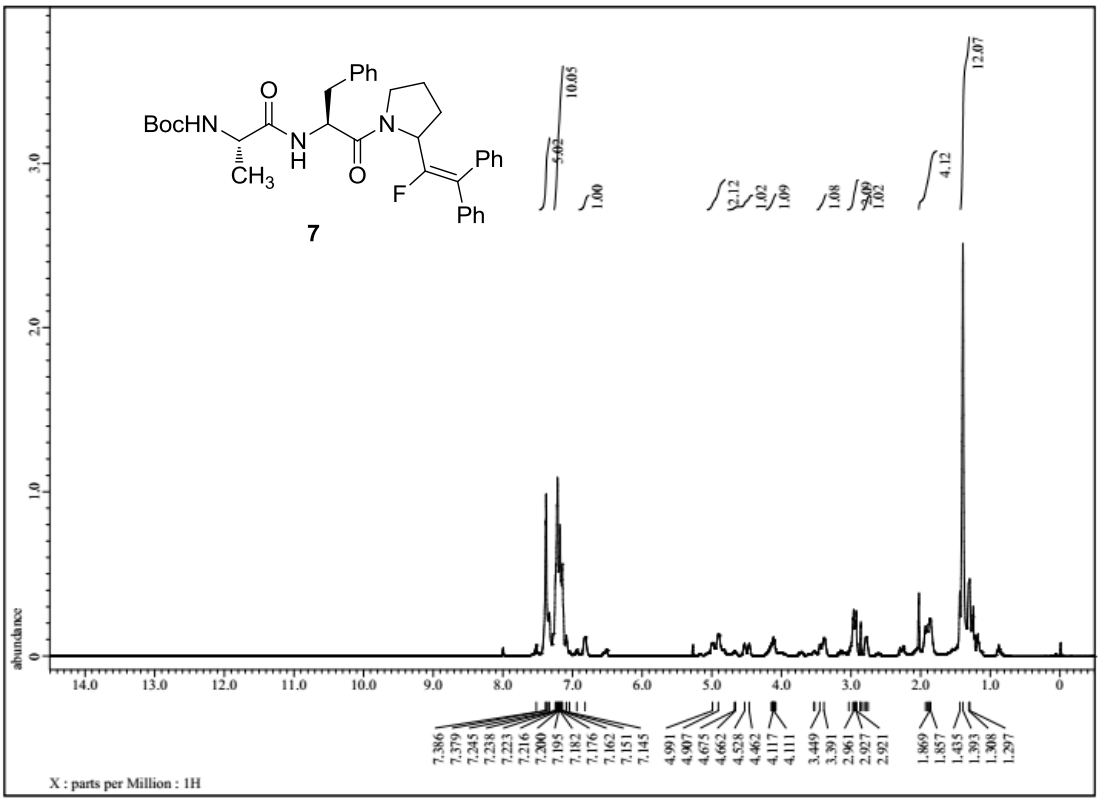

(E)-3ab
abundance
X : parts per Million : 13C

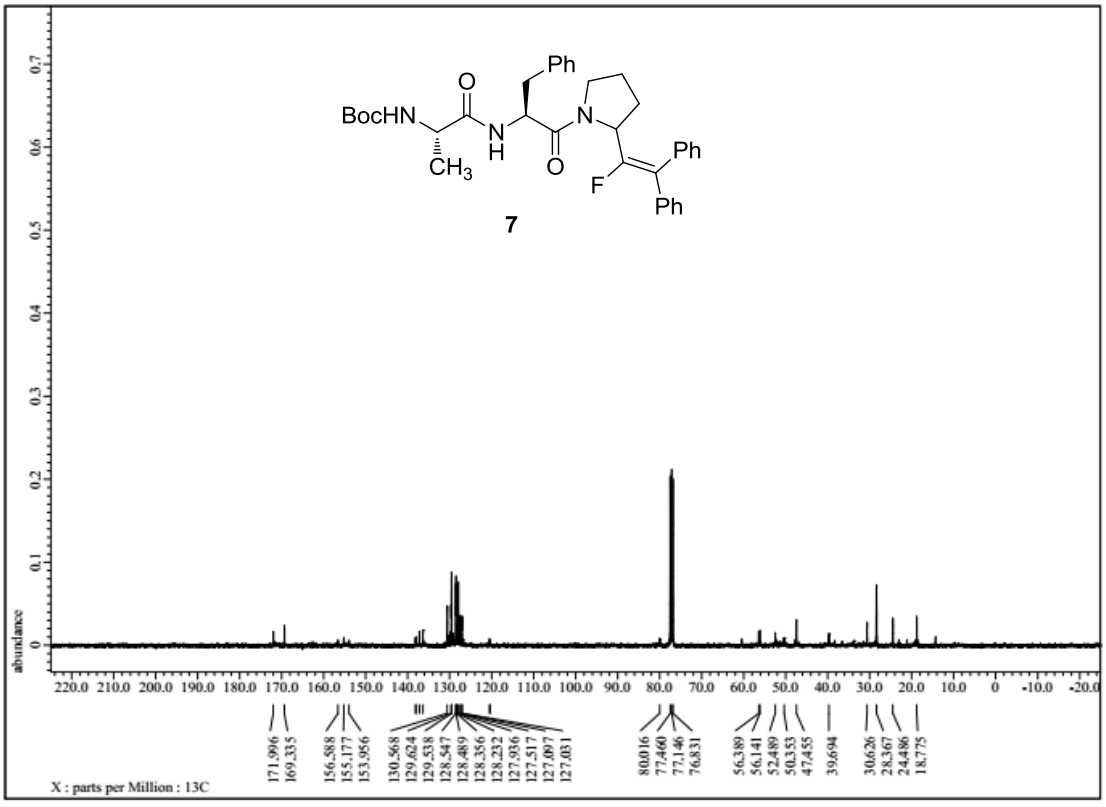

(E)-3ab
abundance
X : parts per Million : 19F
-100.736
-100.828
-100.920

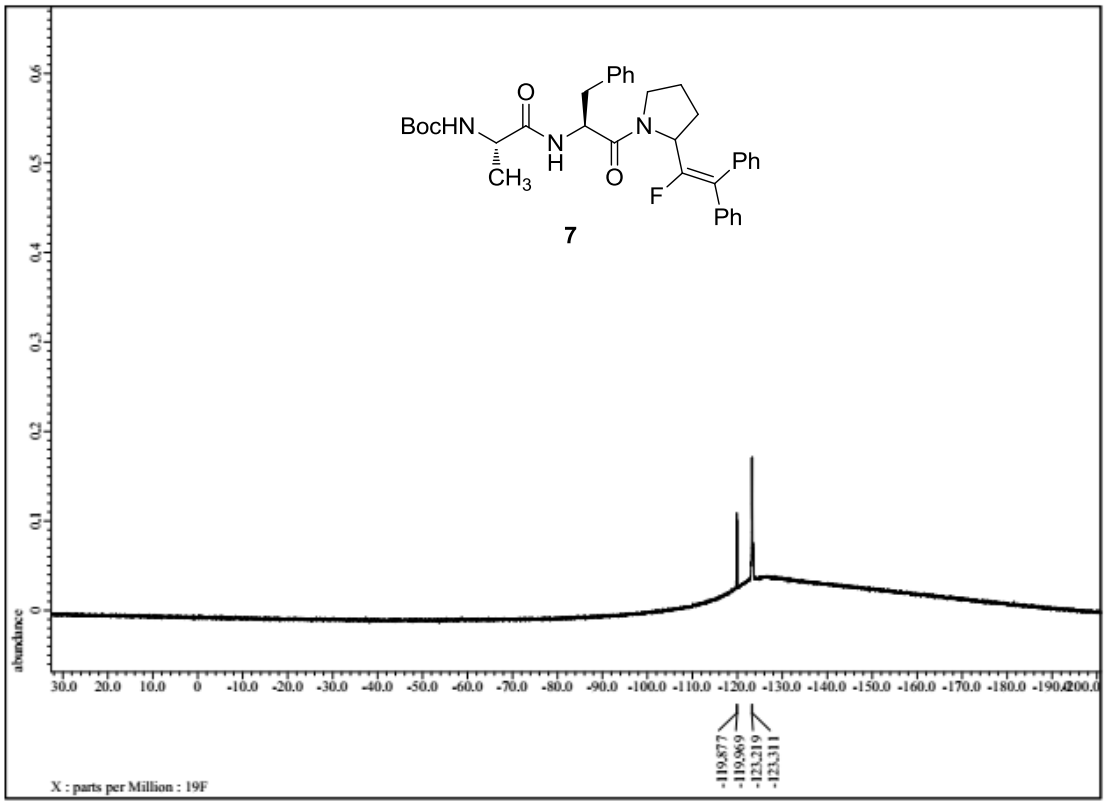

3ac
abundance
X : parts per Million : 1H
10.03
1.03
1.05
3.03
1.00
0.015


Ph
Ph
O
F
3ac
abundance
0
0.1
0.2
0.3
0.4
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
157.250
154.609
137.981
137.905
137.161
130.582
130.554
129.905
129.858
128.447
128.065
127.703
127.436
77.484
77.160
76.845
75.148
74.891
69.332
28.972
26.951
X : parts per Million : 13C


Ph
Ph
O
F
3ac
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
-80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-126.282
-126.334
X : parts per Million : 19F


BocHN
O
N
H
CH3
O
Ph
N
F
Ph
Ph
7
10.05
5.03
1.00
2.12
1.02
1.09
1.08
3.09
1.02
4.12
12.07
abundance
X : parts per Million : 1H


BocHN
O
N
H
CH3
O
Ph
N
F
Ph
Ph
7
abundance
X : parts per Million : 13C


Ph
O
BocHN
N
H
CH3
O
N
Ph
F
Ph
7
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0 -200.0
-119.877
-119.969
-123.219
-123.311
X : parts per Million : 19F