Metal-Free Intramolecular Aminofluorination of Alkenes Mediated by $PhI(OPiv)_2$/ Hydrogen Fluoride-Pyridine System

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General Considerations

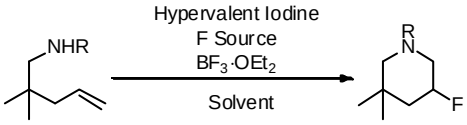
Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. The chemical shifts (δ) are given in parts per million relative to the internal standard TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel (40-63 μm) and eluted with petroleum ether/ethyl acetate. Dichloromethane was dried by refluxing over P_2O_5 for 4h followed by fractional distillation. Compounds **1a-1t**[S1] were synthesized according to the reported procedure.

General Procedure for Aminofluorination of Unactivated Alkenes

To a solution of alkene (0.25 mmol) and PIDP (122 mg, 0.30 mmol) in DCM (2 mL) and HF/Py (65 μL, 2.5 mmol) was added $BF_3{\cdot}OEt_2$ (3.5 μL, 0.025mmol). The reaction mixture was stirred at room temperature for 4 hours. Then the solvent was removed under vacuum, and the residue was purified by flash chromatography to afford the product.

(S1) Michael, F. E.; Cochran, B. M.; *J. Am. Chem. Soc.*, **2006**, *128*, 4246–4247.

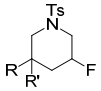
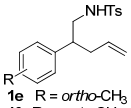
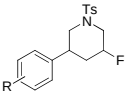
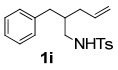
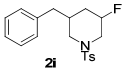
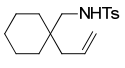
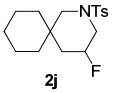
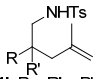
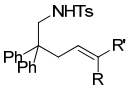
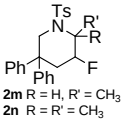
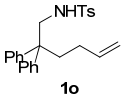
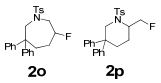
Table 1S. Hypervalent Iodine(III) Mediated Intramolecular Aminofluorination of Alkenes



1a **2a**

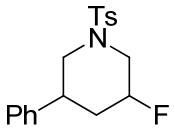
entry	[F] source	solvent	hypervalent iodine(III)	R	yield(%)
1	AgF(2.5 eq)	DCM	PIDA	Ts	18
2	AgF(2.5 eq)	DCM	PIDP	Ts	29
3	AgF(2.5 eq)	DCM	PIDP	Ts	n.r.[a]
4	HF/H_2O(2.5 eq)	DCM	PIDP	Ts	0
5	$KF{\cdot}2H_2O$(2.5 eq)	DCM	PIDP	Ts	0
6	CaF_2(2.5 eq)	DCM	PIDP	Ts	0
7	LiF(2.5 eq)	DCM	PIDP	Ts	0
8	MgF_2(2.5 eq)	DCM	PIDP	Ts	0
9	KF·HF(2.5 eq)	DCM	PIDP	Ts	0
10	NH_4HF_2(2.5 eq)	DCM	PIDP	Ts	0
11	$NEt_3{\cdot}3HF$(2.5 eq)	DCM	PIDP	Ts	0
12	TBAF(2.5 eq)	DCM	PIDP	Ts	n.r.
13	HF/Py(2 eq)	DCM	PIDP	Ts	35
14	HF/Py(3 eq)	DCM	PIDP	Ts	70
15	HF/Py(4 eq)	DCM	PIDP	Ts	76
16	HF/Py(5 eq)	DCM	PIDP	Ts	81
17	HF/Py(10 eq)	DCM	PIDP	Ts	85
18	HF/Py(15 eq)	DCM	PIDP	Ts	85
19	HF/Py(10 eq)	DCM	PIDA	Ts	39
20	HF/Py(10 eq)	DCM	PIFA	Ts	59
21	HF/Py(10 eq)	DMSO	PIDP	Ts	n.r.
22	HF/Py(10 eq)	THF	PIDP	Ts	n.r.
23	HF/Py(10 eq)	MeCN	PIDP	Ts	n.r.
24	HF/Py(10 eq)	DCM	PIDP	Cbz	complex
25	HF/Py(10 eq)	DCM	PIDP	Bz	complex
26	HF/Py(10 eq)	DCM	PIDP	Ac	complex
27	HF/Py(10 eq)	DCM	PIDP	Boc	complex

Table 2S. Hypervalent Iodine(III) Mediated Intramolecular Aminofluorination of Alkenes[a]

entry	alkene	product	yield (%)
1	 **1a**	 **2a**	85
2	 **1b** R = R' = H **1c** R = R' = Ph **1d** R = Ph R' = H	 **2b** R = R' = H **2c** R = R' = Ph **2d** R = Ph R' = H	90
3			81
4			81 (*cis*:*trans* > 99:1)
5	 **1e** R = *ortho*-CH_3 **1f** R = *meta*-CH_3 **1g** R = *para*-CH_3	 **2e** R = *ortho*-CH_3 **2f** R = *meta*-CH_3 **2g** R = *para*-CH_3	78 (*cis*:*trans* > 99:1)
6			75 (*cis*:*trans* > 99:1)
7			64 (*cis*:*trans* > 99:1)
8	 **1h**	 **2h**	89 (*Z*:*E*=1.6:1)[b]
9	 **1i**	 **2i**	63 (*cis*:*trans* > 99:1)
10	 **1j**	 **2j**	80
11	 **1k** R = R' = Ph **1l** R = Ph R' = H	 **2k** R = R' = Ph **2l** R = Ph R = H	59
12			59 (*E*:*Z* > 99:1)
13	 **1m** R = H, R' = CH_3 **1n** R = R' = CH_3	 **2m** R = H, R' = CH_3 **2n** R = R' = CH_3	complex mixture
14			complex mixture
15	 **1o**	 **2o** **2p**	33 (**2o**:**2p**=9.3:1)[c]

[a] Reactions were conducted at 0.25 mmol scale. [b] Isolated yield (the ratio of diastereoselectivity was determined by ^{19}F NMR). The *E* isomer can't be isolated. [c] Products **2o** and **2p** cannot be separated by column chromato-graphy on silica gel.

Characterization of compound 2d



^{1}H-^{1}H COSY and NOESY-1D were used to identify the structures of **2d**.

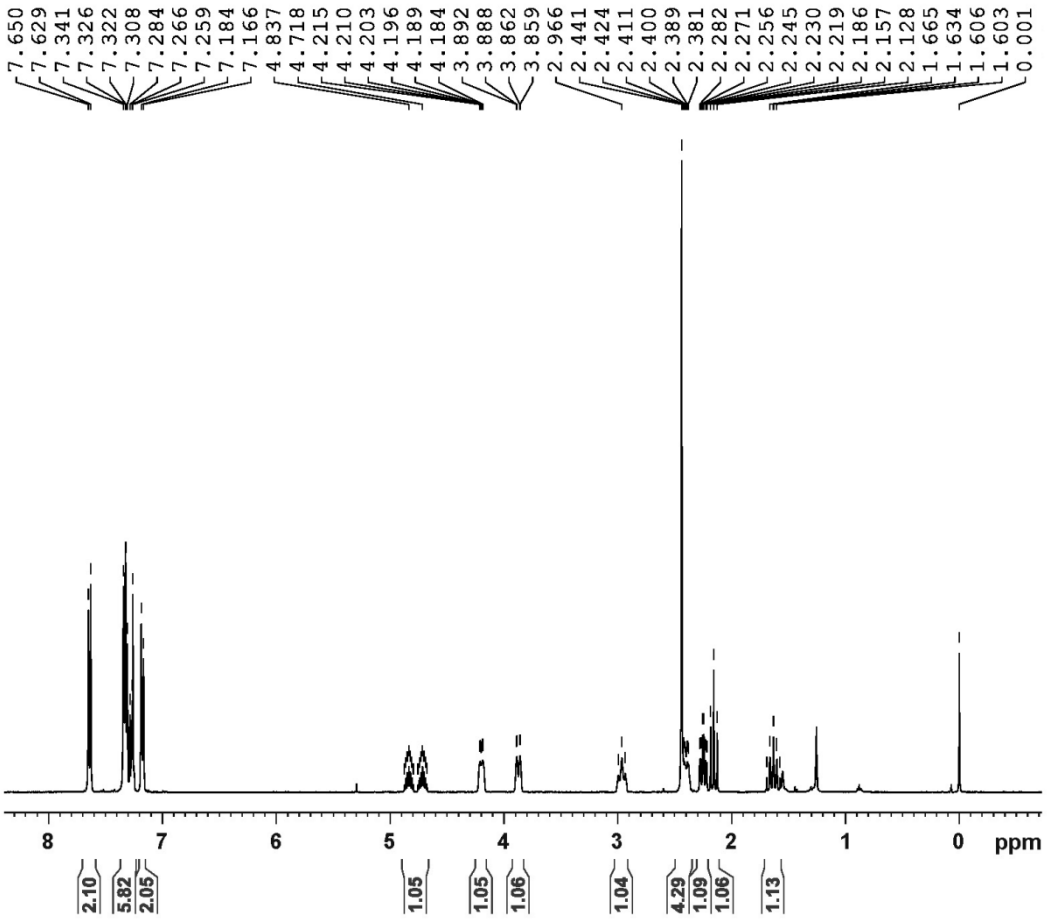


Figure S1. The ^{1}H NMR Spectrum of Compound **2d**

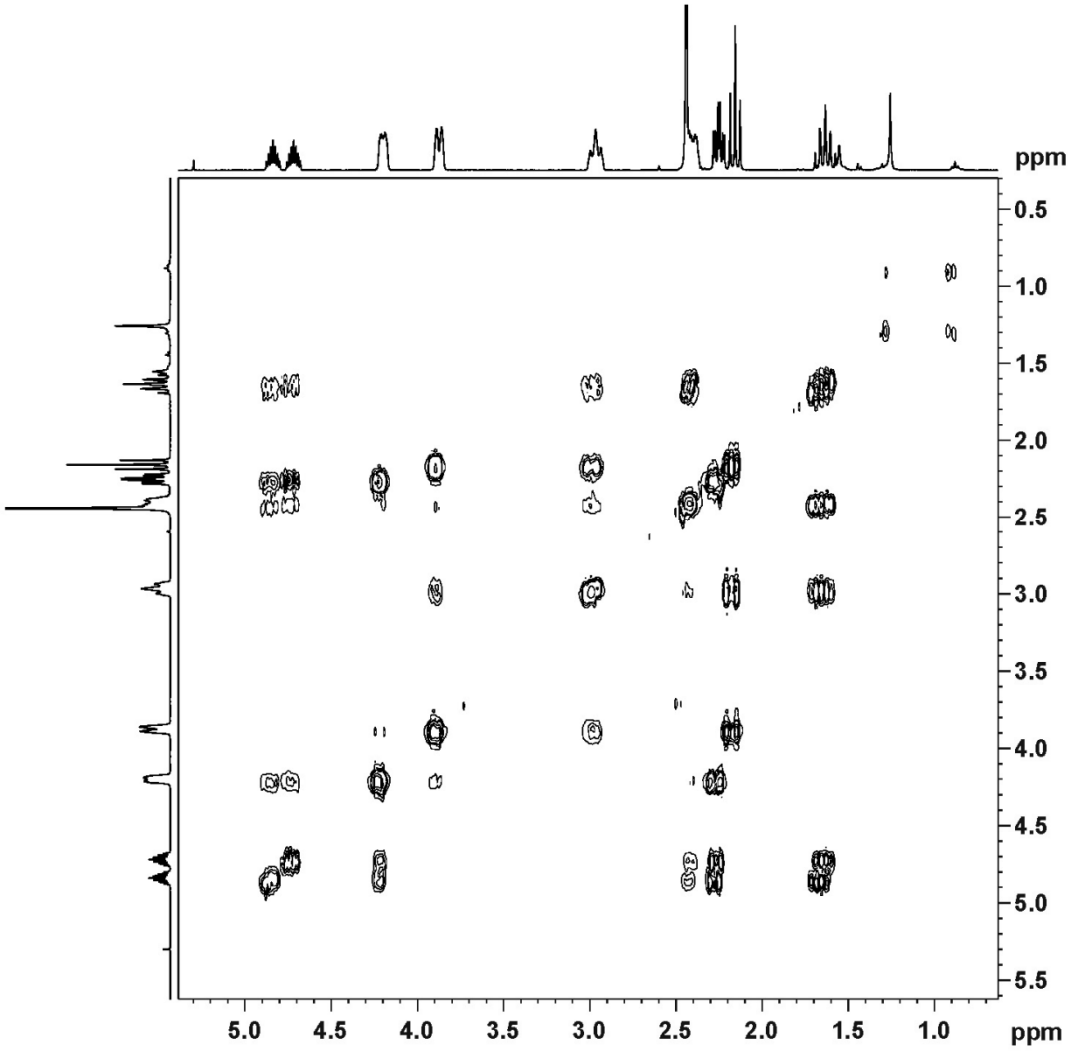


Figure S2. The ^{1}H-^{1}H COSY Spectrum of Compound **2d**

Furthermore, the NOESY spectroscopy shows that there are stronger NOE between Hax1 and Heq1, Hax3 and Heq1, which means Hax1 Heq1 and Hax3 in one side of ring (Scheme S4 and Figure S5). This result supports that **2i** is in *cis*-configuration.

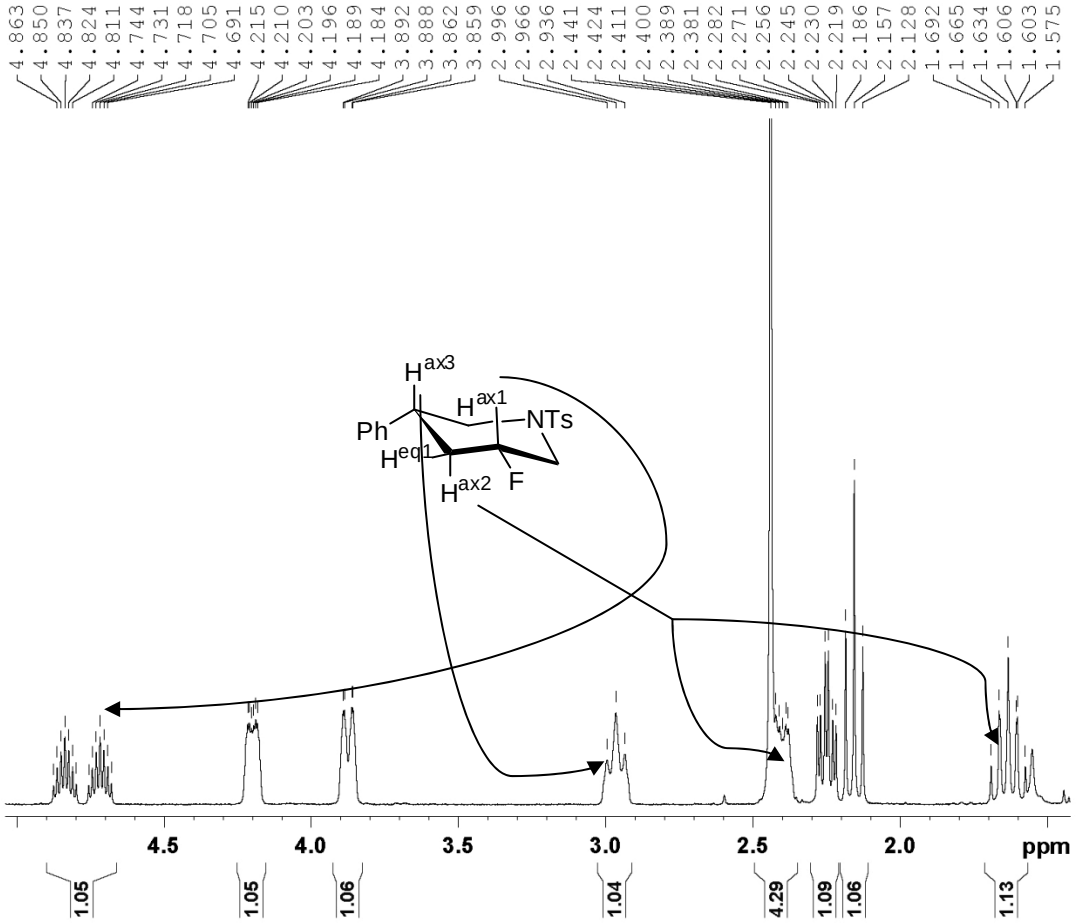


Figure S3. The ^{1}H NMR Spectrum and Assignment of Compound **2d**

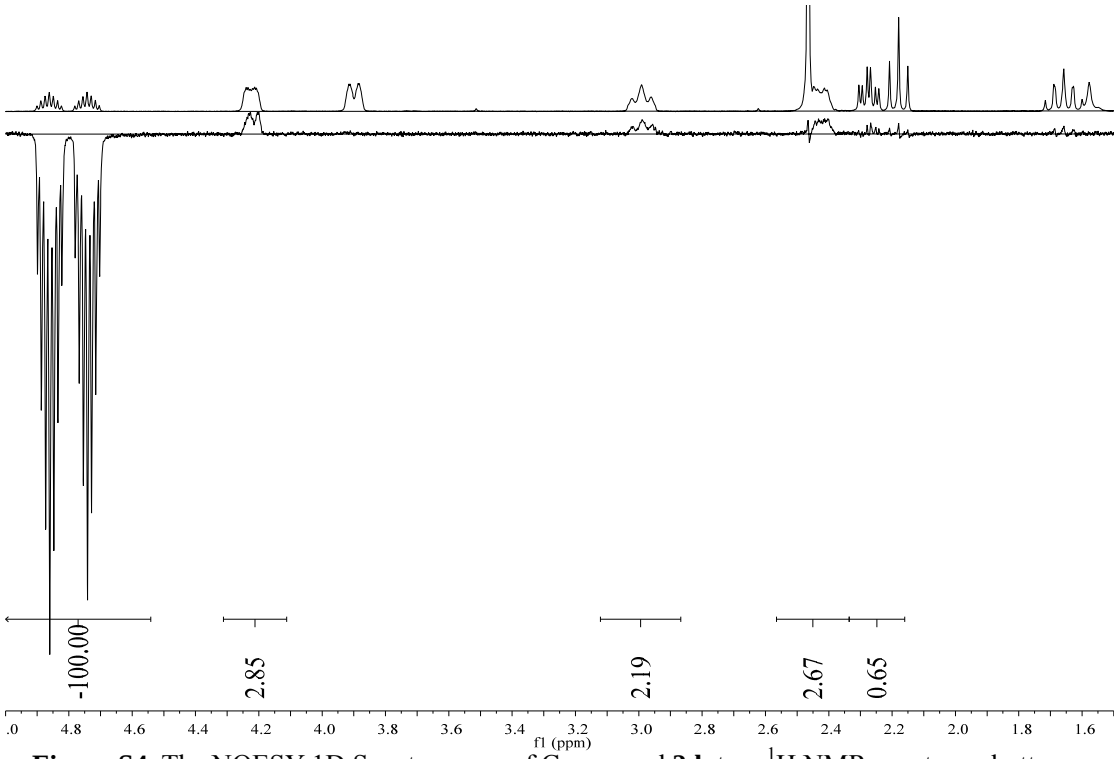


Figure S4. The NOESY-1D Spectroscopy of Compound **2d**: top, ^{1}H NMR spectrum; bottom, NOSEY-1D spectroscopy

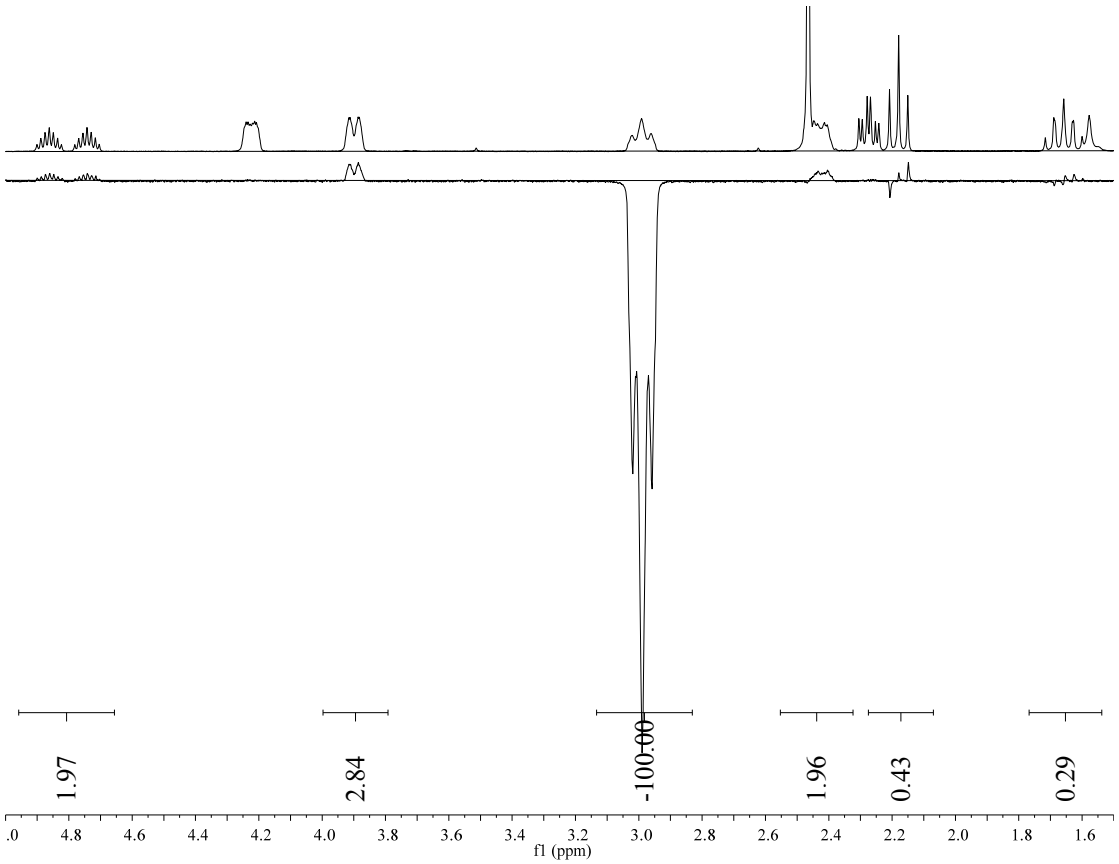
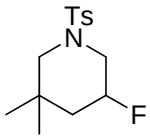


Figure S5. The NOESY-1D Spectroscopy of Compound **2d**: top, ^{1}H NMR spectrum; bottom, NOSEY-1D spectroscopy

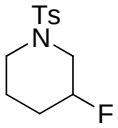
Product Characterization:

5-fluoro-3,3-dimethyl-1-tosylpiperidine (2a)



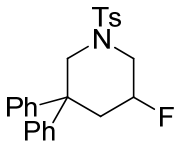
General procedure, compound **2a** was isolated in 85% yield (60.7mg, white amorphous solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.88 – 4.67 (m, 1H), 3.60 (td, *J* = 12.9, 4.3 Hz, 1H), 2.97 (d, *J* = 11.4 Hz, 1H), 2.62 (dt, *J* = 11.2, 7.8 Hz, 1H), 2.44 (s, 3H), 2.38 (d, *J* = 11.5 Hz, 1H), 1.78 – 1.65 (m, 1H), 1.35 (td, *J* = 12.9, 8.8 Hz, 1H), 1.09 – 0.97 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 133.5, 129.7, 127.5, 85.8 (d, *J* = 175.5 Hz), 56.7, 49.7 (d, *J* = 28.7 Hz), 42.7 (d, *J* = 17.5 Hz), 31.9 (d, *J* = 7.2 Hz), 27.8, 25.9, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -183.11.

3-fluoro-1-tosylpiperidine (2b)



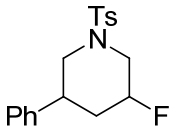
General procedure, compound **2b** was isolated in 90% yield (57.9mg, white amorphous solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 4.67 (dtt, *J* = 47.4, 6.9, 3.5 Hz, 1H), 3.32 (ddd, *J* = 19.7, 11.9, 3.2 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.97 – 2.88 (m, 1H), 2.44 (s, 3H), 1.94 – 1.71 (m, 2H), 1.71 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 133.2, 129.6, 127.5, 85.9 (d, *J* = 176.3 Hz), 49.5 (d, *J* = 26.5 Hz), 45.7, 29.1 (d, *J* = 20.0 Hz), 21.4, 21.0 (d, *J* = 6.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -182.77.

5-fluoro-3,3-diphenyl-1-tosylpiperidine (2c)



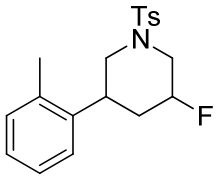
General procedure, compound **2c** was isolated in 81% yield (83.1mg, white amorphous solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.12 (m, 10H), 4.64 – 4.42 (m, 2H), 4.07 – 3.97 (m, 1H), 3.01 – 2.90 (m, 1H), 2.47 – 2.35 (m, 4H), 2.29 (td, *J* = 10.0, 5.5 Hz, 1H), 2.16 (dd, *J* = 20.3, 11.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.1, 143.1, 132.1, 129.9, 128.6, 128.6, 127.7, 127.67, 126.8, 126.5, 126.4, 85.54 (d, *J* = 173.7 Hz), 53.8, 49.79 (d, *J* = 31.1 Hz), 46.40 (d, *J* = 11.0 Hz), 41.01 (d, *J* = 18.8 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -185.51.

3-fluoro-5-phenyl-1-tosylpiperidine (2d)



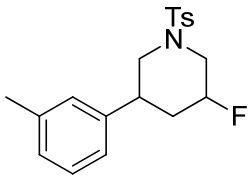
General procedure, compound **2d** was isolated in 81% yield (67.4mg, white amorphous solid) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.17 (d, *J* = 7.1 Hz, 2H), 4.89 – 4.66 (m, 1H), 4.23 – 4.16 (m, 1H), 3.87 (dd, *J* = 11.7, 1.6 Hz, 1H), 2.97 (t, *J* = 12.0 Hz, 1H), 2.49 – 2.35 (m, 4H), 2.25 (td, *J* = 10.5, 4.3 Hz, 1H), 2.16 (t, *J* = 11.6 Hz, 1H), 1.71 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.1, 133.1, 129.8, 128.8, 127.5, 127.4, 127.1, 86.90 (d, *J* = 176.4 Hz), 51.9, 49.45 (d, *J* = 31.4 Hz), 40.02 (d, *J* = 11.0 Hz), 36.95 (d, *J* = 18.3 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -181.19.

3-fluoro-5-(o-tolyl)-1-tosylpiperidine (2e)



General procedure, compound **2e** was isolated in 78% yield (67.9mg, white amorphous solid, mp 165.1 – 165.9 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.11 (m, 3H), 7.09 – 7.01 (m, 1H), 4.91 – 4.68 (m, 1H), 4.27 – 4.17 (m, 1H), 3.86 – 3.75 (m, 1H), 3.22 – 3.08 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 2.35 – 2.25 (m, 2H), 2.14 (t, *J* = 11.5 Hz, 1H), 1.74 – 1.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.2, 136.0, 133.3, 130.9, 129.8, 127.5, 127.1, 126.4, 125.3, 87.0 (d, *J* = 176.8 Hz), 51.1, 49.6 (d, *J* = 31.5 Hz), 36.7 (d, *J* = 18.2 Hz), 35.8 (d, *J* = 10.9 Hz), 21.5, 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.61. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14275.

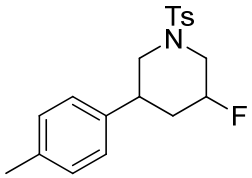
3-fluoro-5-(m-tolyl)-1-tosylpiperidine (2f)



General procedure, compound **2f** was isolated in 75% yield (65.4mg, white amorphous solid, mp 125.1 – 125.9 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.93 (m, 2H), 4.87 – 4.65 (m, 1H), 4.23 – 4.14 (m, 1H), 3.86 (dd, *J* = 11.6, 1.5 Hz, 1H), 2.97 –

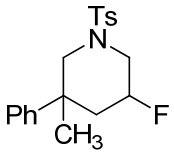
2.86 (m, 1H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.33 (s, 3H), 2.24 (td, *J* = 10.5, 4.3 Hz, 1H), 2.14 (t, *J* = 11.5 Hz, 1H), 1.70 – 1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.1, 138.4, 133.1, 129.8, 128.6, 128.1, 127.9, 127.5, 124.0, 87.0 (d, *J* = 176.5 Hz), 52.0, 49.5 (d, *J* = 31.5 Hz), 40.0 (d, *J* = 10.7 Hz), 36.9 (d, *J* = 18.3 Hz), 21.5, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -181.05. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14279.

3-fluoro-5-(p-tolyl)-1-tosylpiperidine (2g)



General procedure, compound **2g** was isolated in 64% yield (55.3mg, white amorphous solid, mp 185.4 – 186.2 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.88 – 4.64 (m, 1H), 4.27 – 4.14 (m, 1H), 3.85 (dd, *J* = 11.6, 1.5 Hz, 1H), 2.93 (t, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.32 (s, 3H), 2.23 (td, *J* = 10.5, 4.3 Hz, 1H), 2.12 (t, *J* = 11.6 Hz, 1H), 1.67 – 1.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 137.1, 133.1, 129.8, 129.4, 127.6, 126.9, 87.0 (d, *J* = 176.5 Hz), 52.1, 49.5 (d, *J* = 31.3 Hz), 39.6 (d, *J* = 10.6 Hz), 37.0 (d, *J* = 18.2 Hz), 21.5, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -181.08. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14276.

5-fluoro-3-methyl-3-phenyl-1-tosylpiperidine (2h)

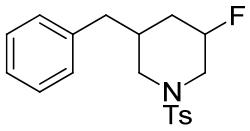


***cis*-Configuration**

General procedure, compound **2h** was isolated in 89% yield (77.3mg, white amorphous solid) (*cis* : *trans* =1.6:1). *cis*-Configuration (white amorphous solid, mp 123.3 – 123.6 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.28 (m, 6H), 7.28 – 7.20 (m, 1H), 4.97 (dtt, *J* = 47.9, 9.9, 4.9 Hz, 1H), 4.06 (dt, *J* = 10.3, 5.0 Hz, 1H), 3.68 (dd, *J* = 11.6, 1.5 Hz, 1H), 2.48 (d, *J* = 11.6 Hz, 1H), 2.42 (s, 3H), 2.36 – 2.25 (m, 2H), 1.78 (dd, *J* = 23.1, 12.6 Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 143.8, 133.2, 129.8, 128.6, 127.4, 126.8, 125.0, 85.8 (d, *J* = 173.9 Hz), 55.4, 49.8 (d, *J* = 30.4 Hz), 41.3 (d, *J* = 17.8 Hz), 38.9 (d, *J* = 10.2 Hz), 25.3, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -184.87. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14230.

trans-configuration can't be separated**.**

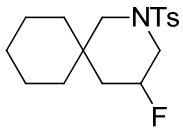
3-benzyl-5-fluoro-1-tosylpiperidine (2i)



General procedure, compound **2i** was isolated in 63% yield (54.7mg, white amorphous solid, mp 110.3 – 111.0 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.19 (m, 5H), 7.10 (d, *J* = 7.1 Hz, 2H), 4.69 – 4.46 (m, 1H), 3.93 (dt, *J* = 10.9, 5.5 Hz, 1H), 3.62 (d, *J* = 10.0 Hz, 1H), 2.67 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.53 – 2.41 (m, 4H), 2.36 – 2.27 (m, 1H), 2.13 – 1.91 (m, 3H), 1.19 – 1.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

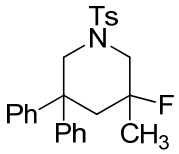
143.8, 138.4, 133.3, 129.8, 128.9, 128.6, 127.6, 126.5, 86.8 (d, J = 176.1 Hz), 50.7, 49.7 (d, J = 30.6 Hz), 39.6, 36.2 (d, J = 18.2 Hz), 35.8 (d, J = 8.9 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.58. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14279.

4-fluoro-2-tosyl-2-azaspiro[5.5]undecane (2j)



General procedure, compound **2j** was isolated in 80% yield (65.3mg, white amorphous solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.89 – 4.66 (m, 1H), 3.60 (td, J = 13.1, 4.3 Hz, 1H), 3.18 (d, J = 11.7 Hz, 1H), 2.67 (dt, J = 11.2, 7.9 Hz, 1H), 2.49 – 2.39 (m, 4H), 1.81 (ddd, J = 17.6, 13.4, 4.3 Hz, 1H), 1.56 – 1.25 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 133.7, 129.7, 127.5, 85.49 (d, J = 175.1 Hz), 54.0, 50.18 (d, J = 28.5 Hz), 40.97 (d, J = 17.8 Hz), 36.2, 34.52 (d, J = 7.1 Hz), 33.9, 26.1, 21.5, 21.4, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -182.40.

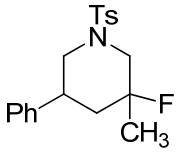
3-fluoro-3-methyl-5,5-diphenyl-1-tosylpiperidine (2k)



General procedure, compound **2k** was isolated in 59% yield (62.5mg, white amorphous solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.30 (ddd, J = 20.4, 17.4, 7.7 Hz, 10H), 7.21 – 7.12 (m, 2H), 3.66 (d, J = 12.4 Hz, 1H), 3.37 (d, J = 12.4 Hz, 1H), 3.15 – 3.03 (m, 1H), 2.96 (t, J = 10.2 Hz, 1H), 2.65 (t, J = 12.7 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.40 (s, 3H),

1.12 (d, *J* = 22.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 145.1, 143.9, 132.4, 129.8, 128.5, 128.3, 127.7, 127.2, 126.9, 126.4, 126.2, 91.5 (d, *J* = 174.1 Hz), 54.5 (d, *J* = 29.1 Hz), 53.8, 45.5 (d, *J* = 6.5 Hz), 44.9 (d, *J* = 20.6 Hz), 25.1 (d, *J* = 23.6 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.76.

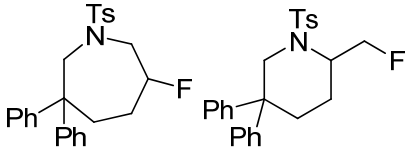
3-fluoro-3-methyl-5-phenyl-1-tosylpiperidine (2l)



General procedure, compound **2l** was isolated in 59% yield (40.7mg, white amorphous solid, mp 148.7 – 149.5 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.22 (m, 5H), 7.21 – 7.13 (m, 2H), 3.90 (dd, *J* = 11.5, 1.6 Hz, 1H), 3.83 (d, *J* = 10.7 Hz, 1H), 3.00 (t, *J* = 12.3 Hz, 1H), 2.43 (s, 3H), 2.35 (dd, *J* = 10.7, 6.7 Hz, 1H), 2.20 – 2.08 (m, 2H), 1.82 (q, *J* = 13.1 Hz, 1H), 1.65 (d, *J* = 23.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.4, 133.1, 129.8, 128.8, 127.6, 127.4, 127.1, 92.3 (d, *J* = 172.2 Hz), 54.2 (d, *J* = 34.8 Hz), 52.5, 42.3 (d, *J* = 20.7 Hz), 40.2 (d, *J* = 11.5 Hz), 23.4 (d, *J* = 24.0 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.50. HRMS: m/z (ESI) Calcd for $C_{19}H_{23}FNO_2S$ 348.14280, found 348.14298.

2-(fluoromethyl)-5,5-diphenyl-1-tosylpiperidine (2o)

6-fluoro-3,3-diphenyl-1-tosylazepane (2p)



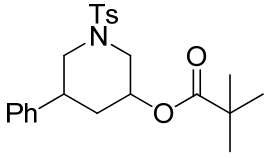
General procedure, compound **2o** and **2p** was isolated in 33% yield (28.8mg, colorless oil) (**2o** : **2p** =9.3:1). Products **2o** and **2p** can not be separated by column chromatography on silica gel.

Major product 2o : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.36 – 7.15 (m, 10H), 4.94 – 4.73 (m, 1H), 4.20 (d, *J* = 13.8 Hz, 1H), 3.68 (td, *J* = 13.8, 5.7 Hz, 1H), 3.31 (d, *J* = 13.7 Hz, 1H), 3.08 (td, *J* = 14.6, 7.2 Hz, 1H), 2.61 (ddd, *J* = 12.1, 6.7, 3.5 Hz, 1H), 2.40 (s, 3H), 2.35 – 2.25 (m, 1H), 1.88 (ddd, *J* = 15.8, 10.0, 4.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 145.6, 143.8, 134.4, 129.9, 128.4, 128.1, 127.6, 127.5, 126.5, 126.4, 90.2 (d, *J* = 171.3 Hz), 61.5, 53.2 (d, *J* = 32.3 Hz), 50.7, 30.6 (d, *J* = 3.6 Hz), 27.8 (d, *J* = 21.3 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.44.

2p: ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 143.5, 136.9, 129.7, 129.6, 128.5, 128.4, 127.9, 127.5, 127.0, 126.5, 126.1, 82.0 (d, *J* = 174.0 Hz), 51.2 (d, *J* = 21.7 Hz), 50.1, 45.8, 42.0, 29.7, 26.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -224.53.

2o and **2p** HRMS: m/z (ESI) Calcd for $C_{25}H_{27}FNO_2S$ 424.17410, found 424.17437.

5-phenyl-1-tosylpiperidin-3-yl pivalate (3)

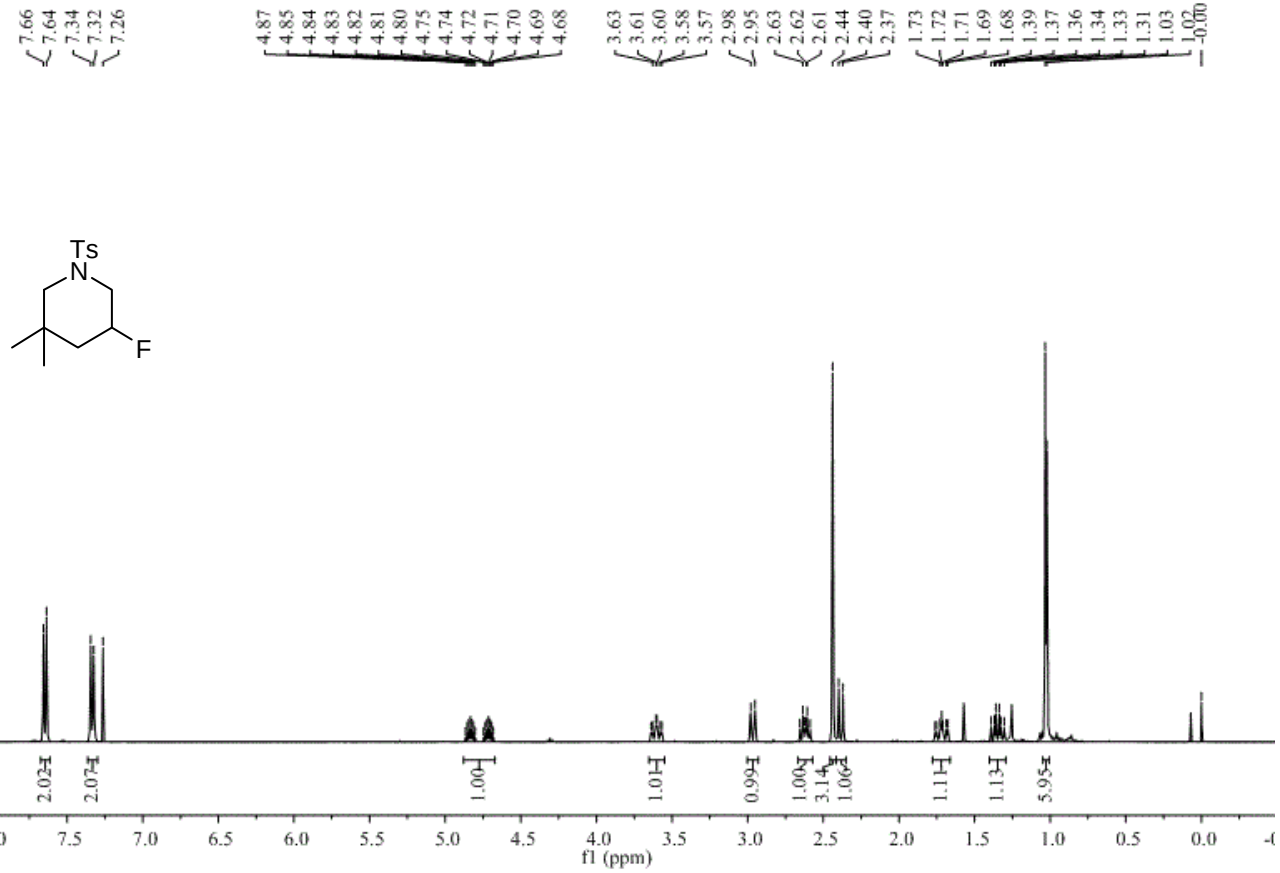


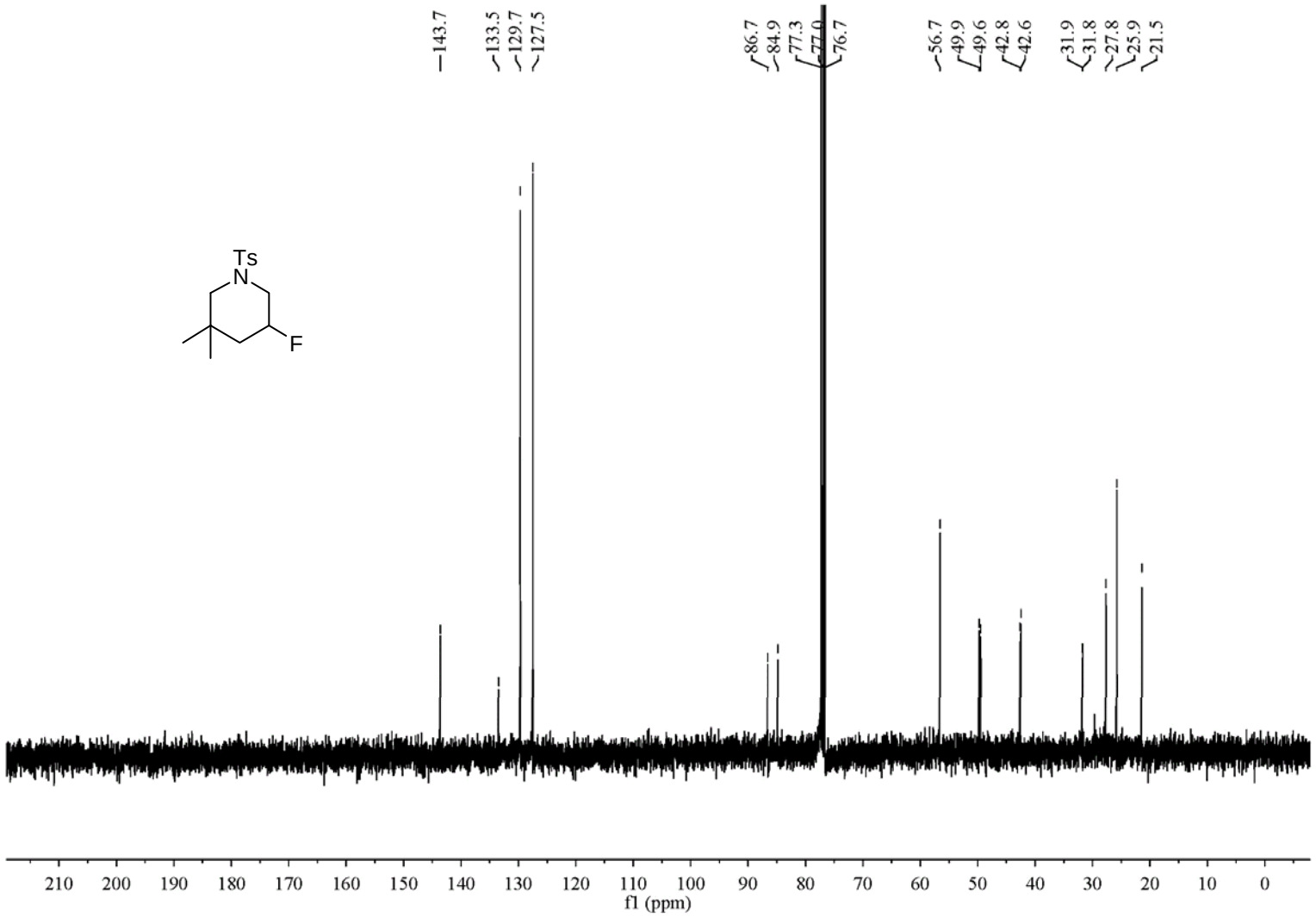
$BF_3 \cdot OEt_2$ (3.5 μL, 0.025mmol) was added to a solution of alkene **1d** (0.25 mmol) and PIDP (122 mg, 0.30 mmol) in DCM (2 mL). The reaction mixture was stirred at room temperature for 4 hours. Then the solvent was removed under vacuum, and the residue was purified by flash chromatography to afford the product. Compound **3** was isolated in 64% yield (67mg,

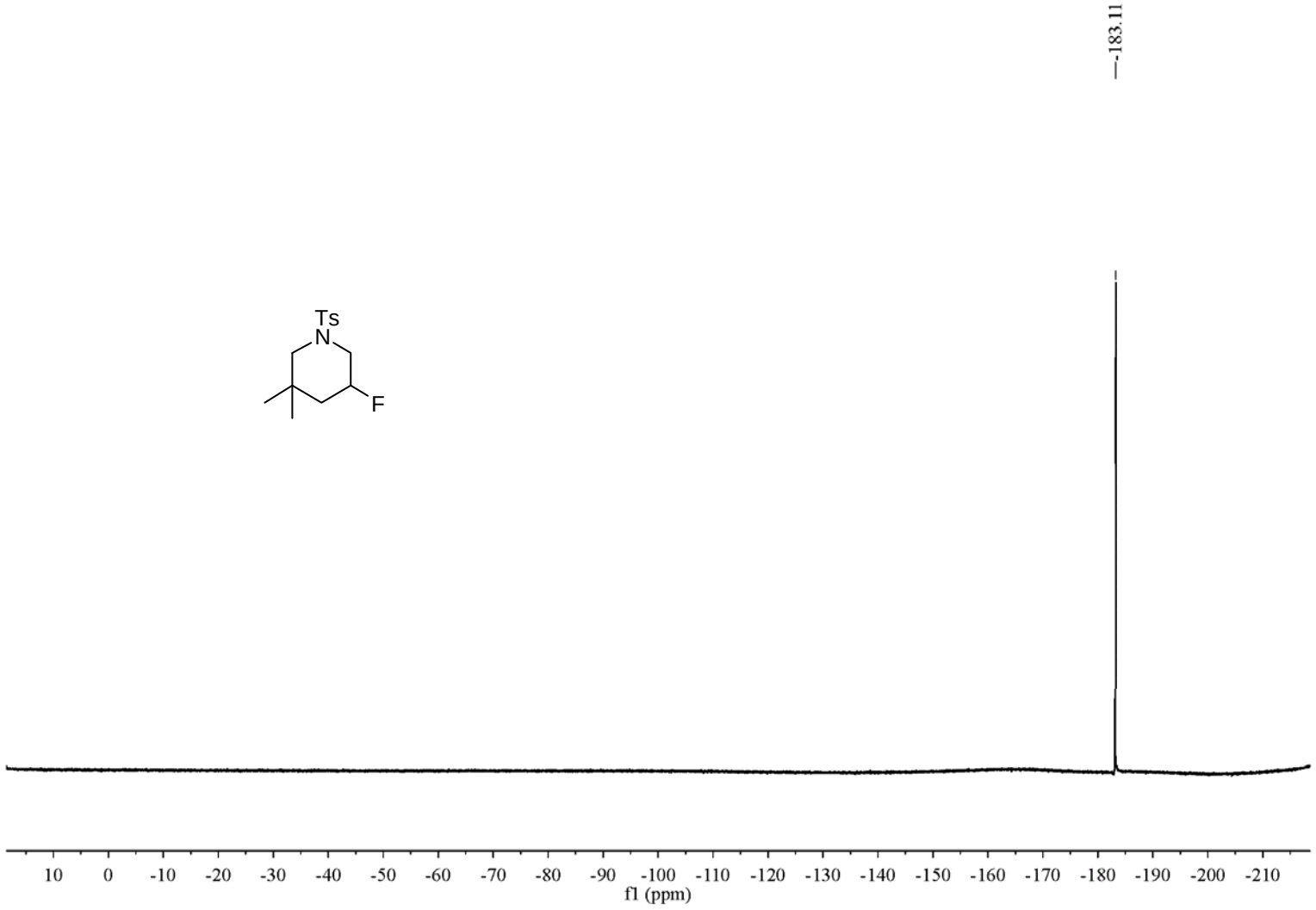
white amorphous solid, mp 150.1 – 150.3 °C) (*cis* : *trans* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.20 (m, 5H), 7.16 (d, *J* = 7.1 Hz, 2H), 5.03 – 4.89 (m, 1H), 4.06 (d, *J* = 6.9 Hz, 1H), 3.89 (d, *J* = 10.9 Hz, 1H), 2.97 (t, *J* = 11.7 Hz, 1H), 2.44 (s, 3H), 2.27 (t, *J* = 10.6 Hz, 3H), 1.48 (q, *J* = 12.0 Hz, 1H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 143.7, 140.6, 133.5, 129.8, 128.7, 127.5, 127.2, 127.0, 68.0, 51.8, 48.7, 40.3, 38.6, 36.2, 27.0, 21.5. HRMS: m/z (ESI) Calcd for $C_{23}H_{30}NO_4S$ 416.18901, found 416.18935.

The Spectrum of Products

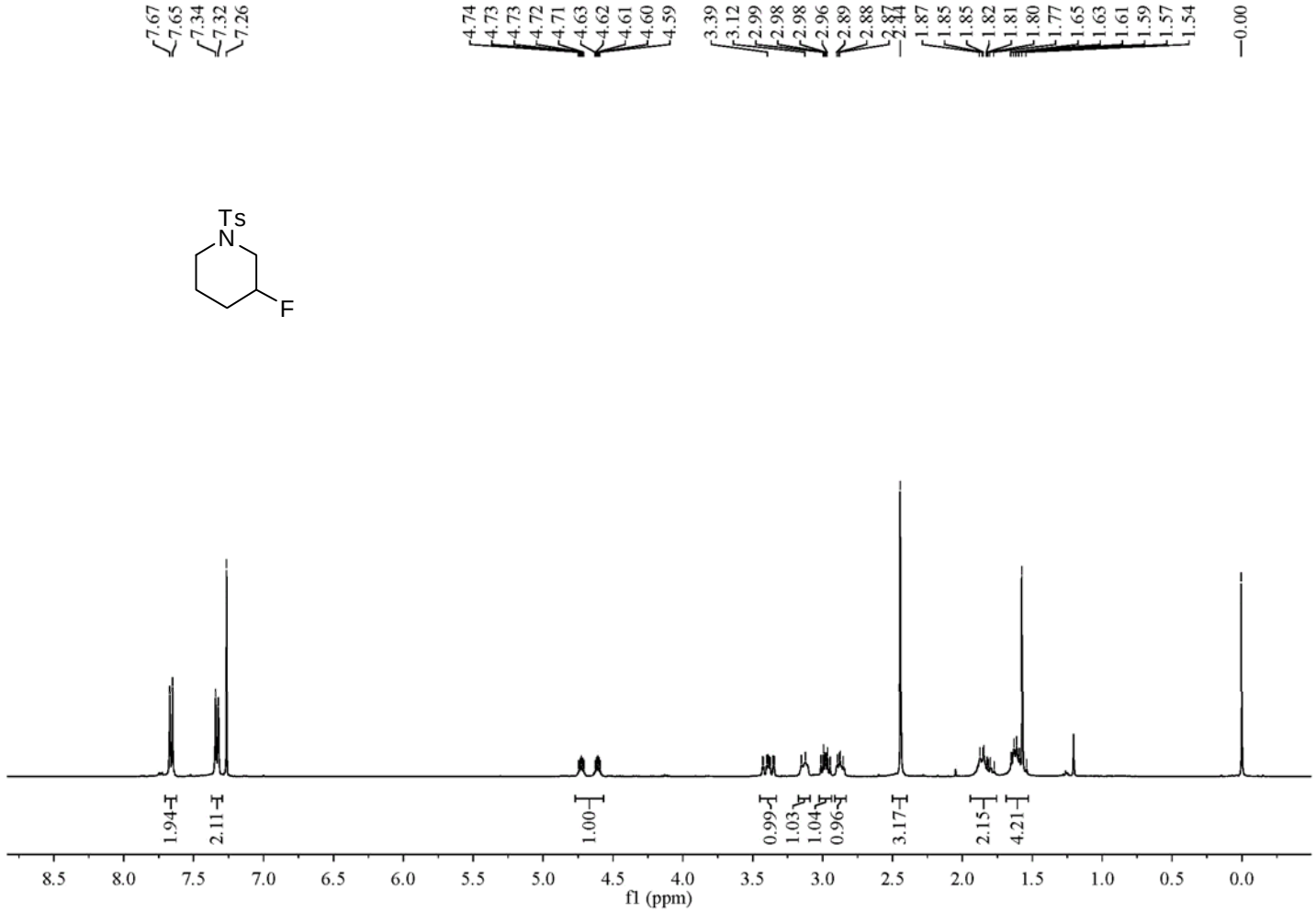
5-fluoro-3,3-dimethyl-1-tosylpiperidine(2a) (400 MHz, $CDCl_3$)

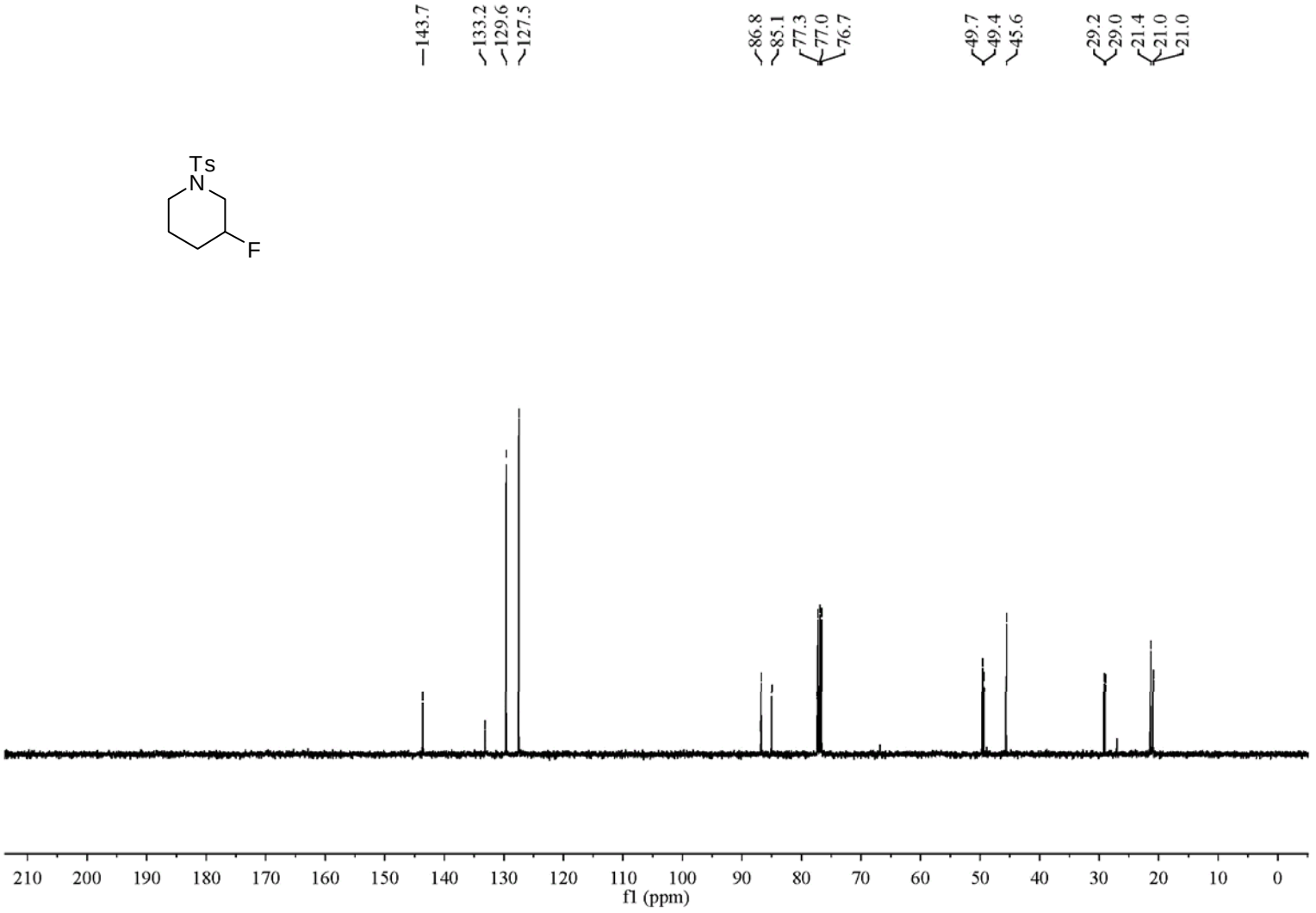


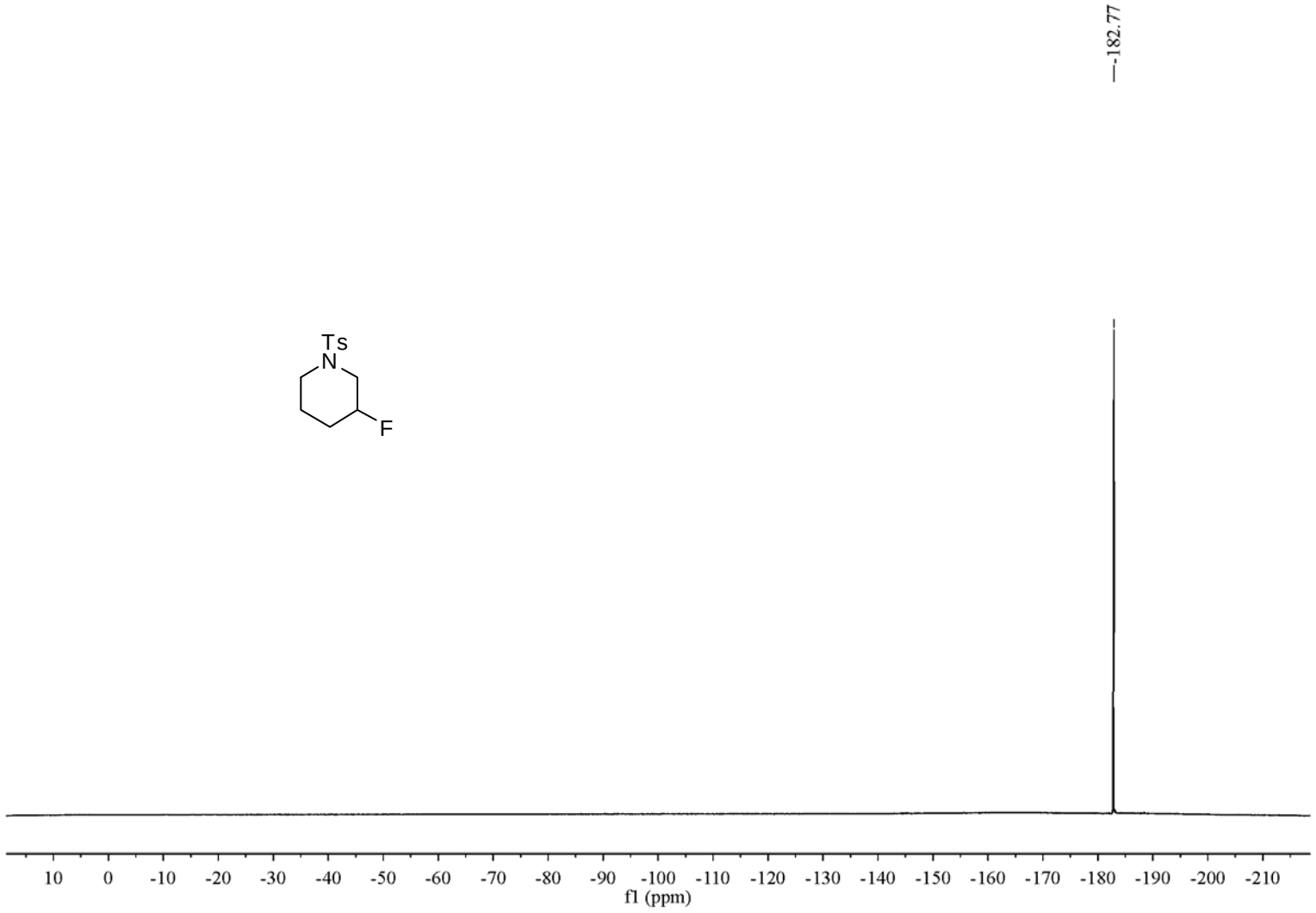




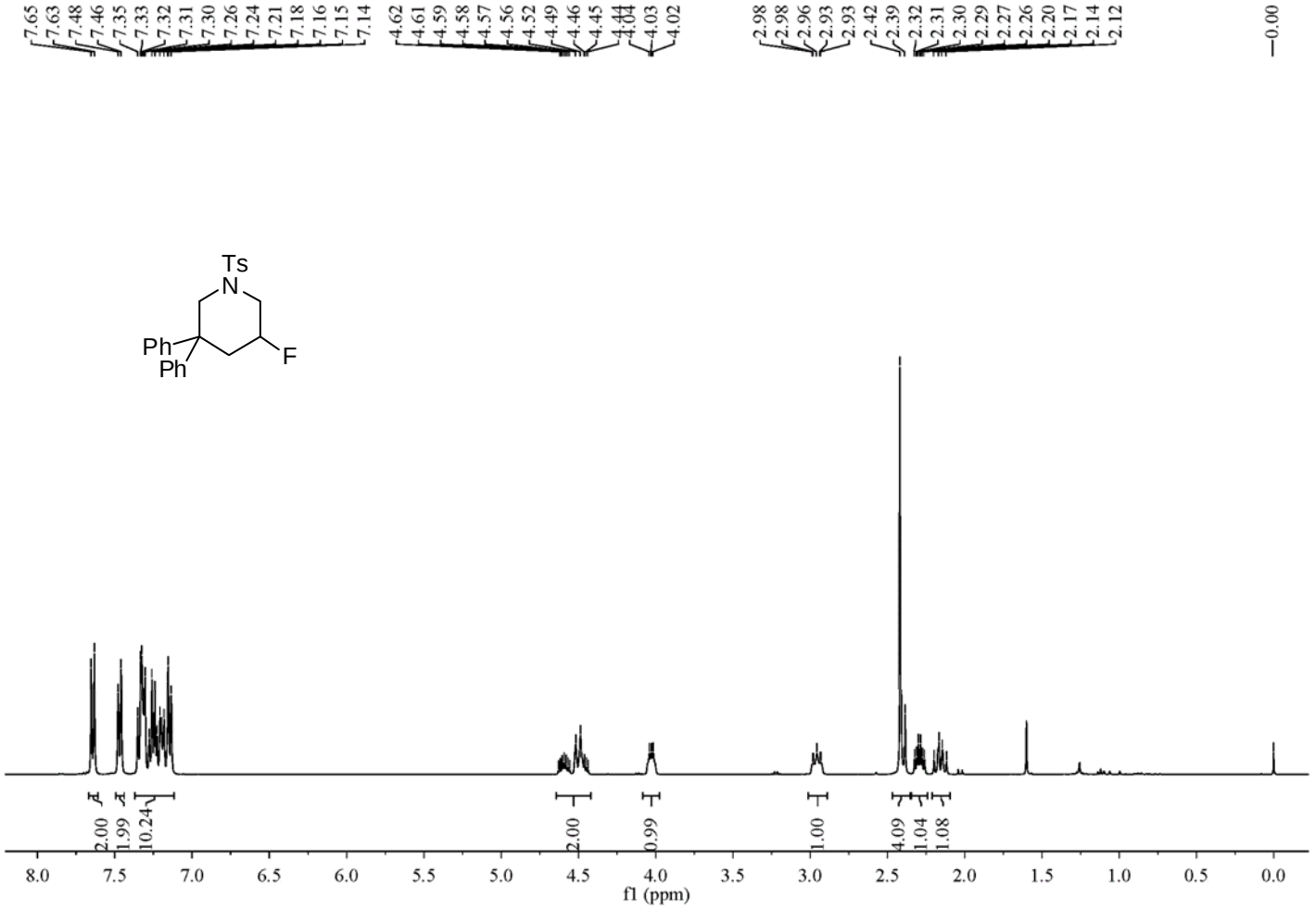
3-fluoro-1-tosylpiperidine(2b) (400 MHz, $CDCl_3$)

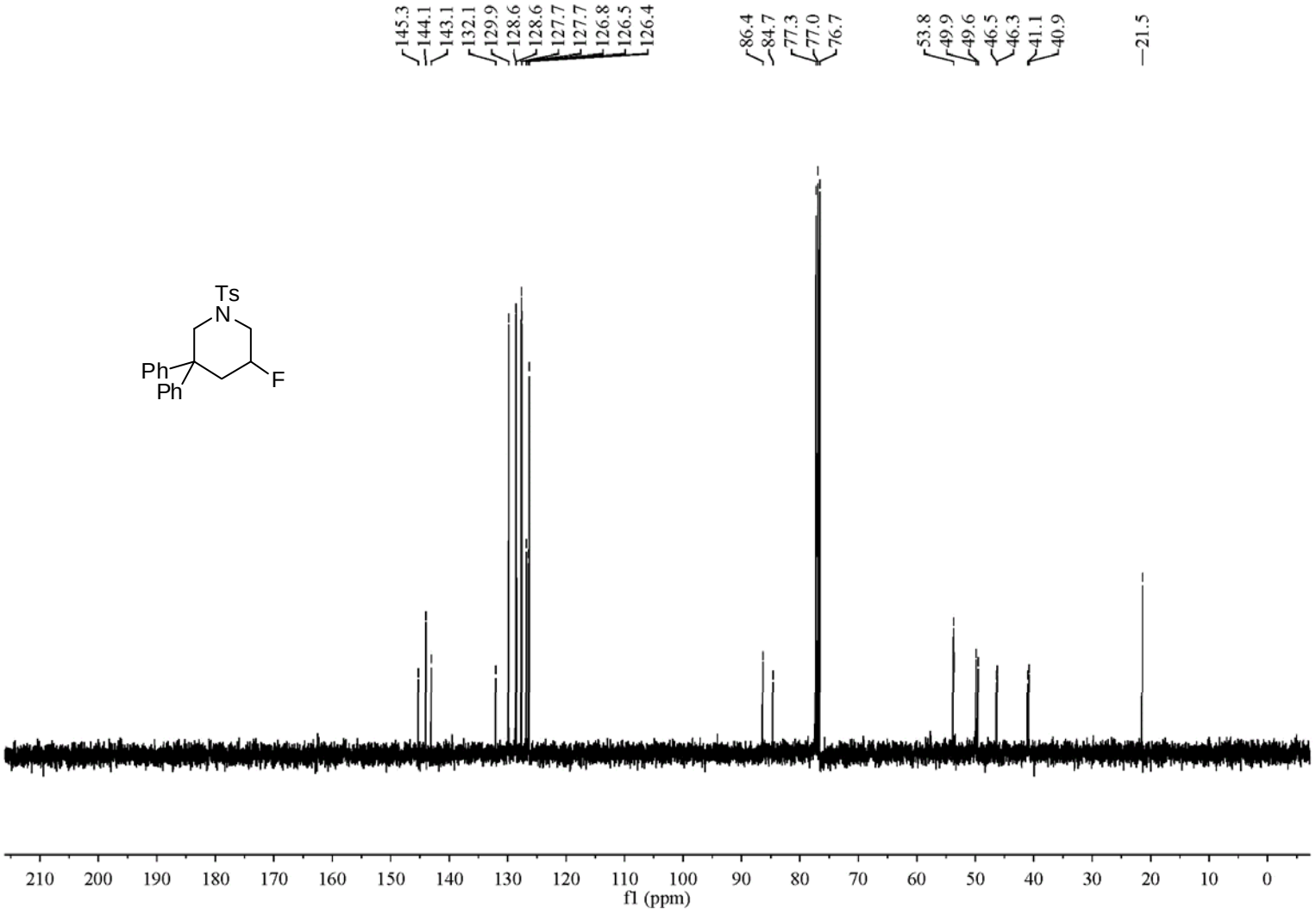


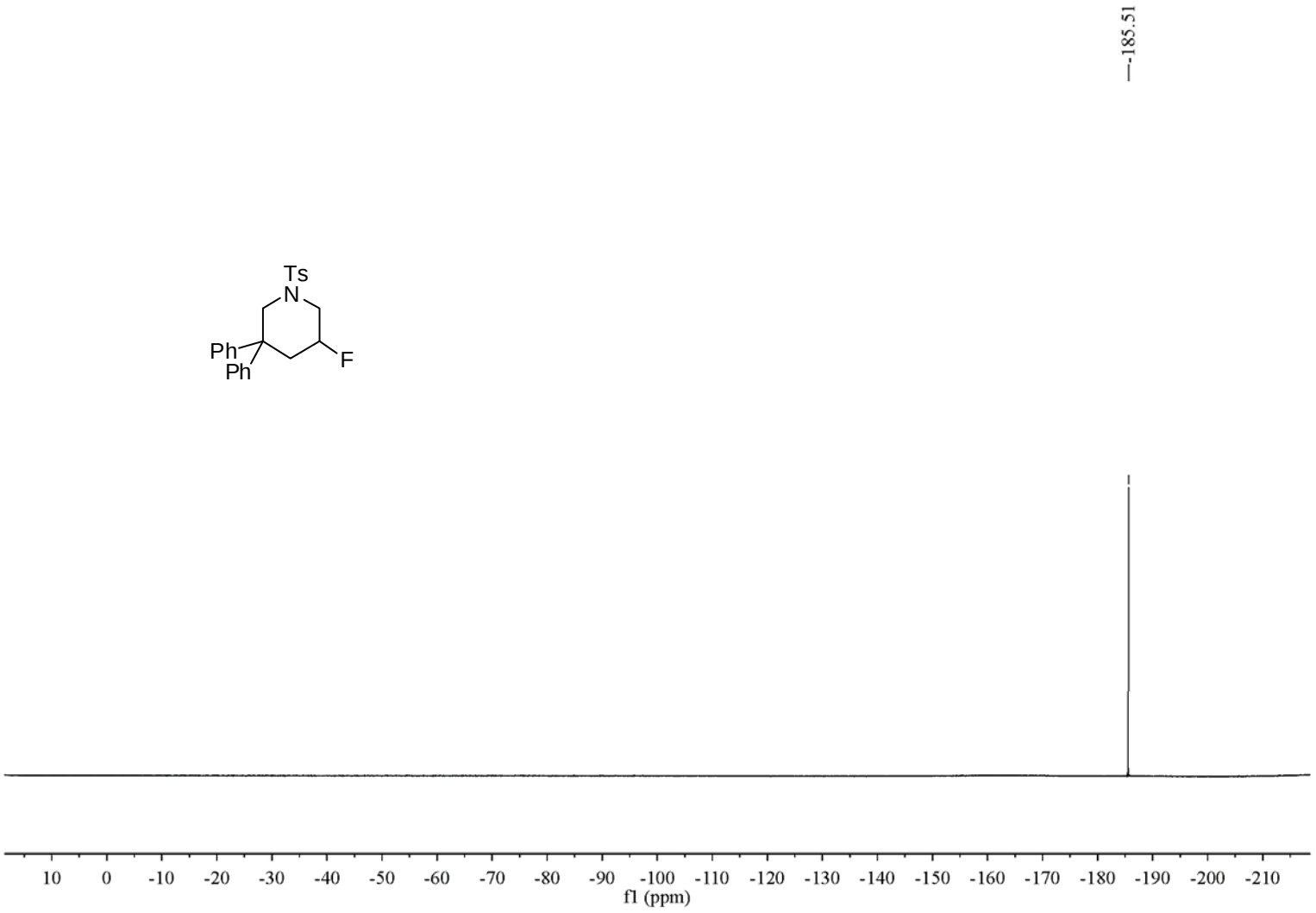




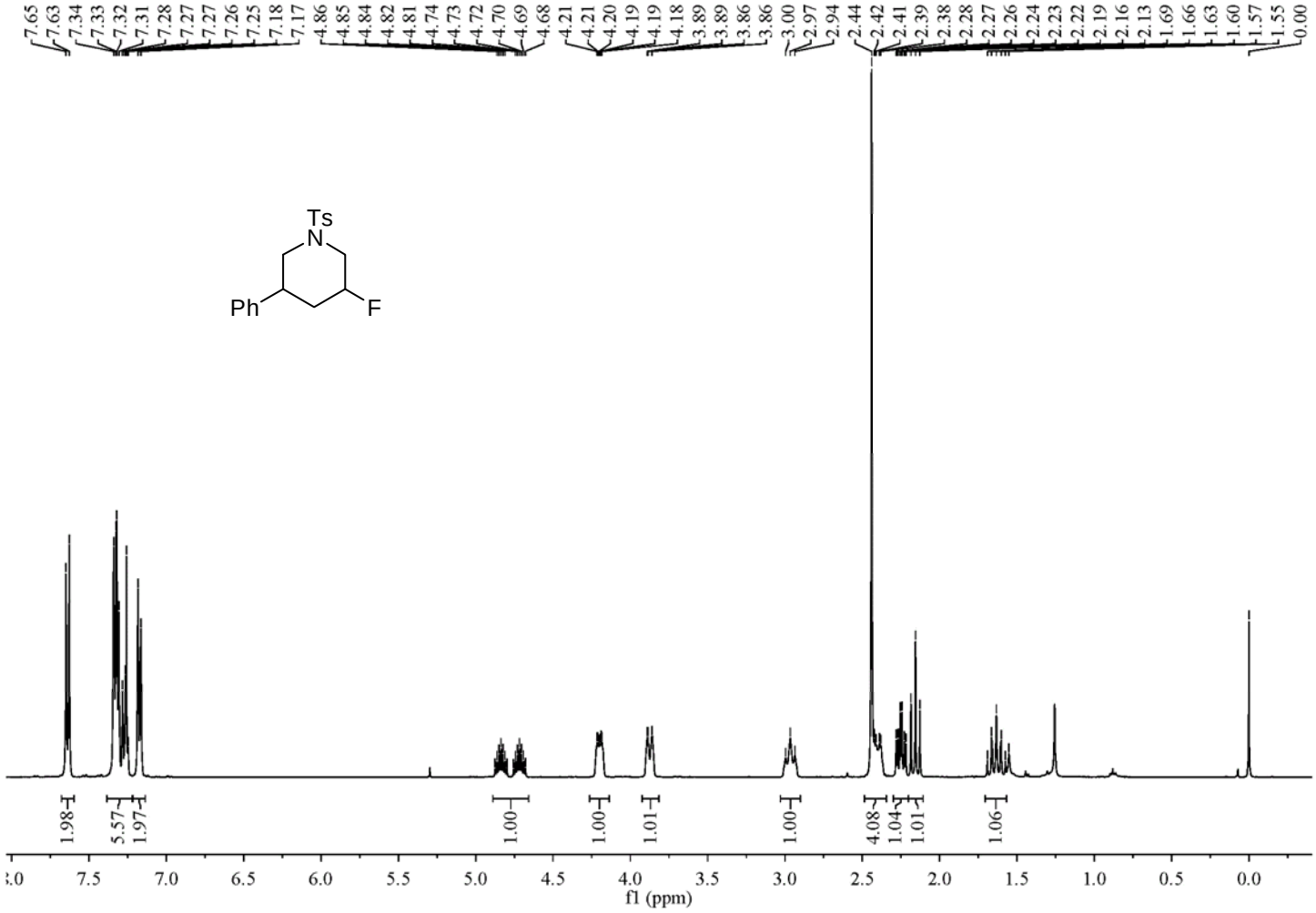
5-fluoro-3,3-diphenyl-1-tosylpiperidine(2c) (400 MHz, $CDCl_3$)

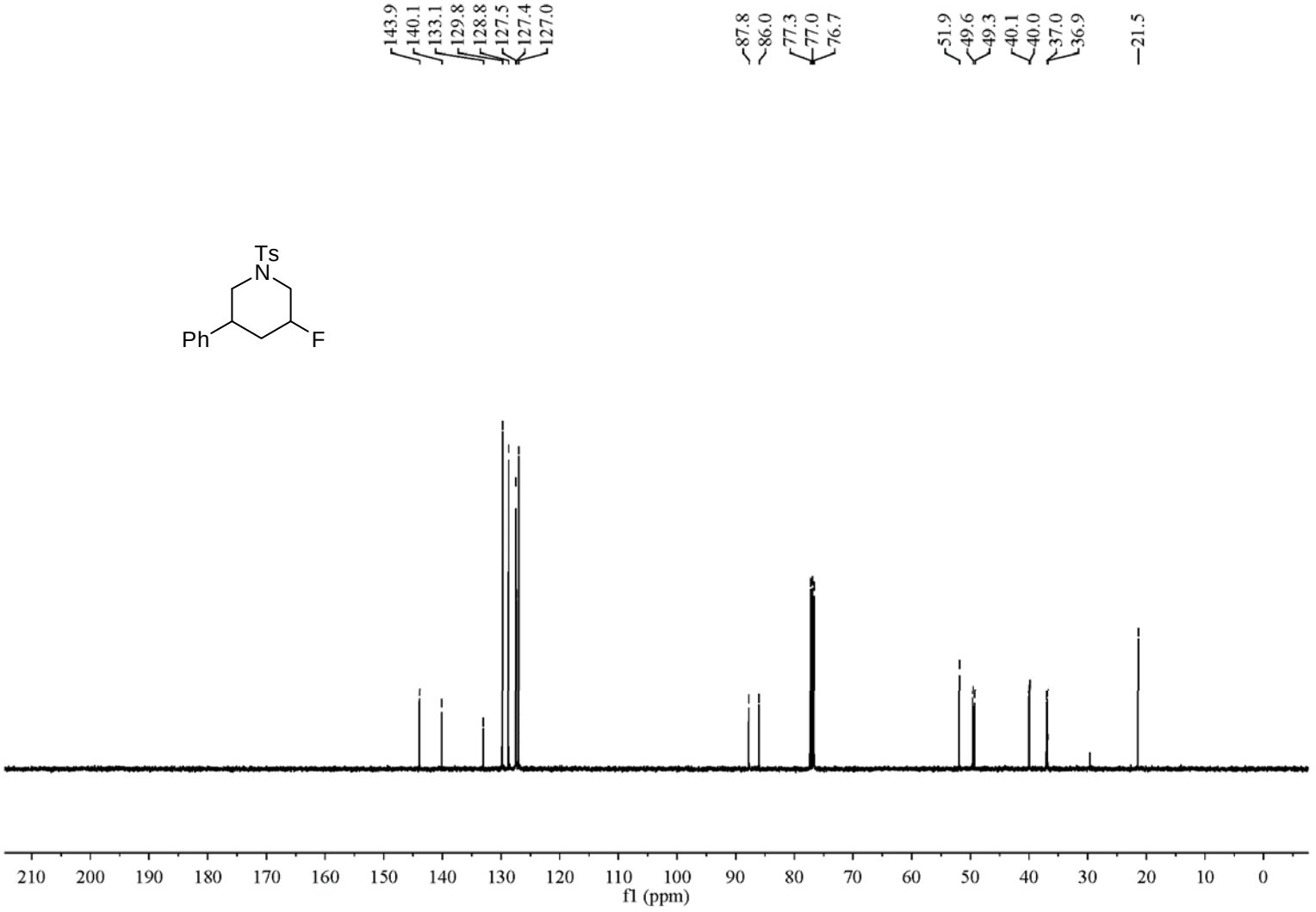


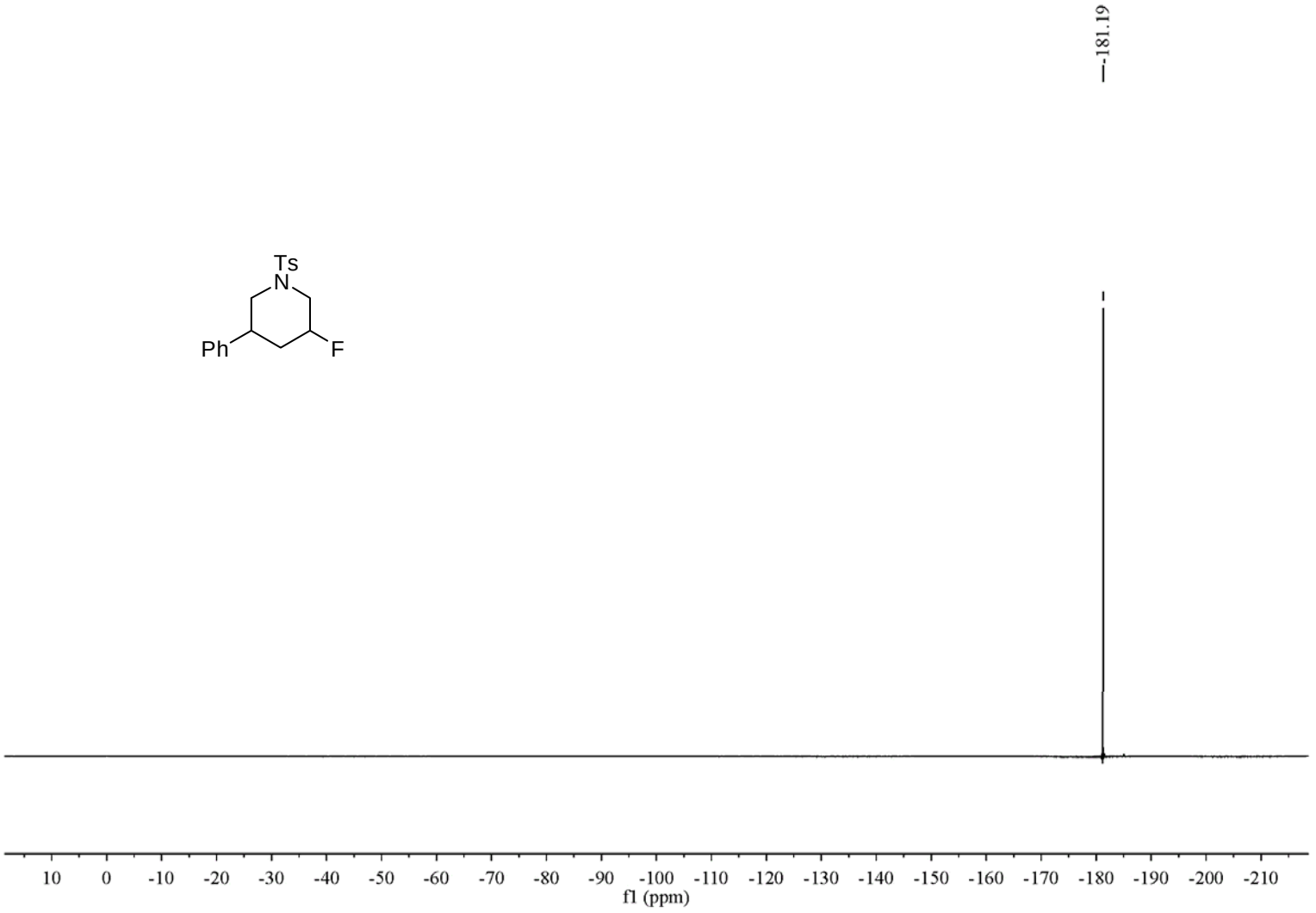




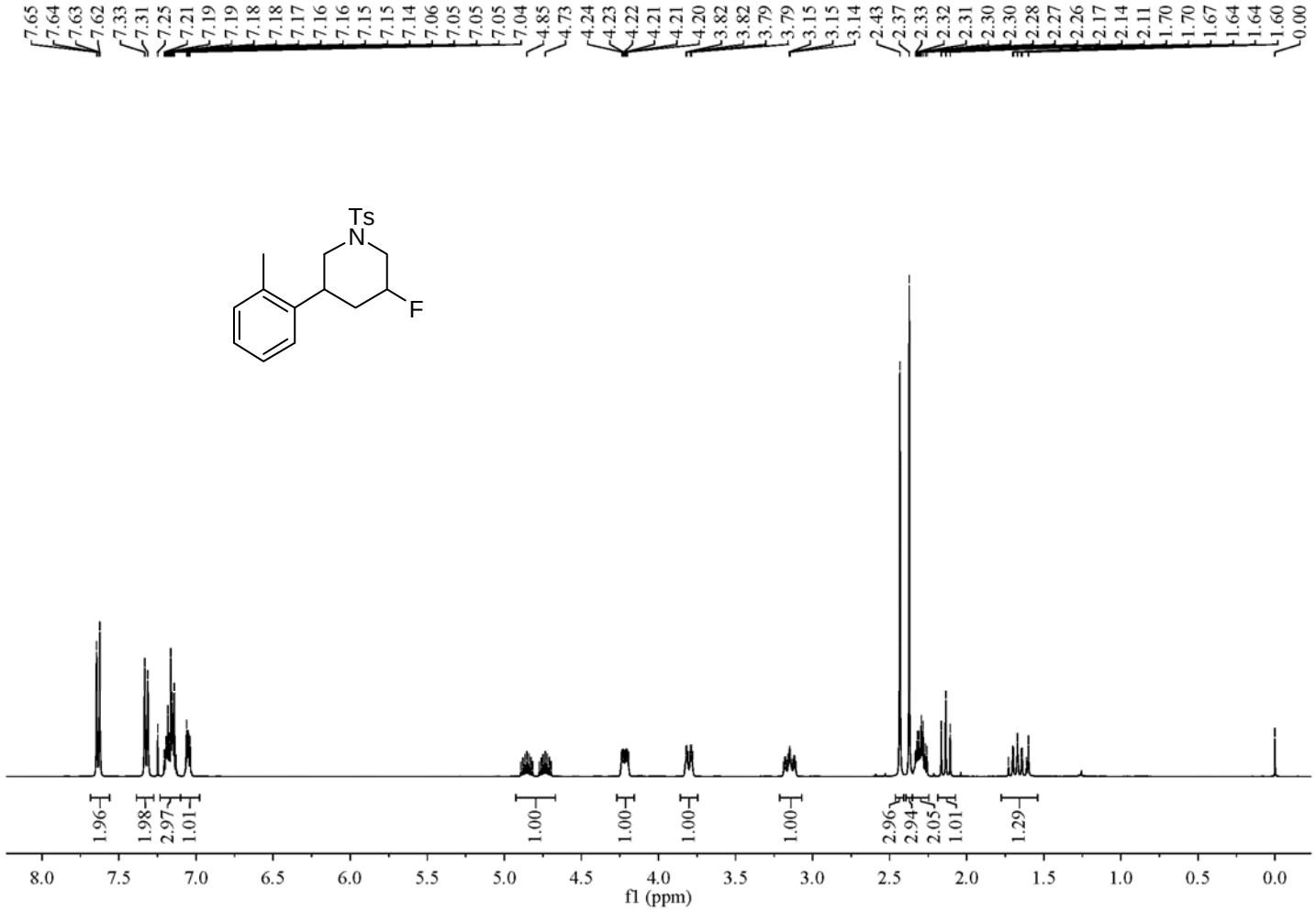
3-fluoro-5-phenyl-1-tosylpiperidine(2d) (400 MHz, $CDCl_3$)

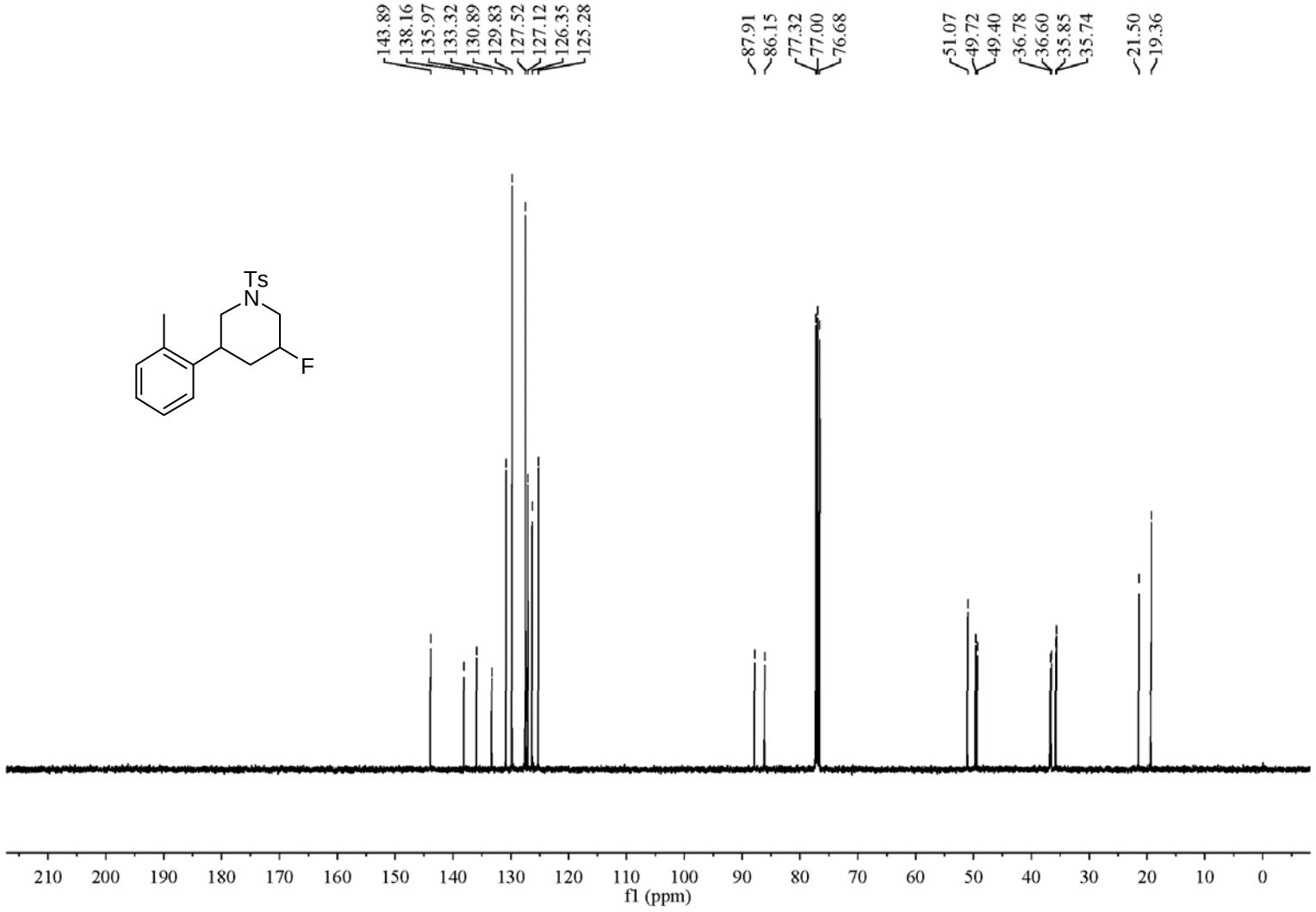


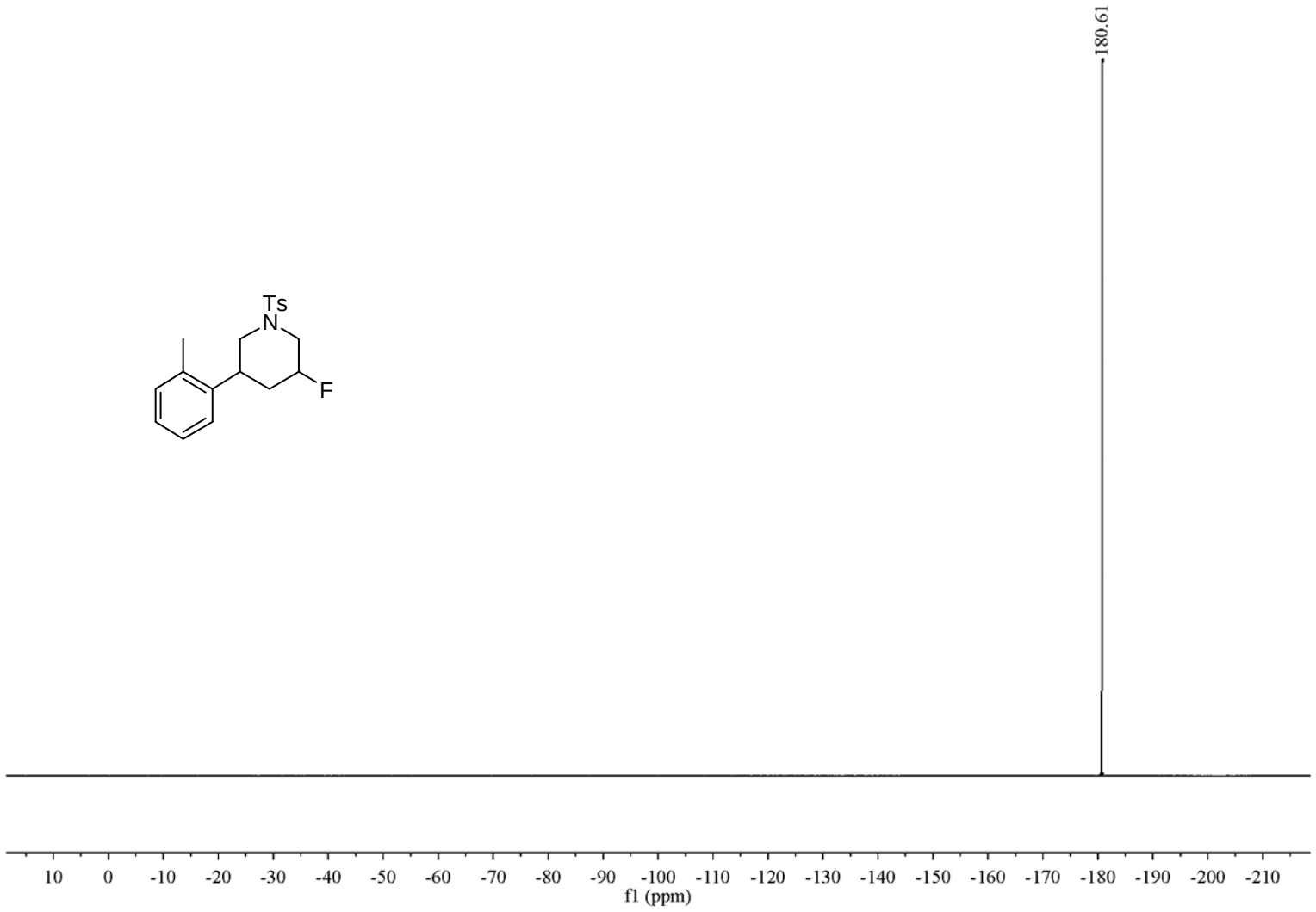




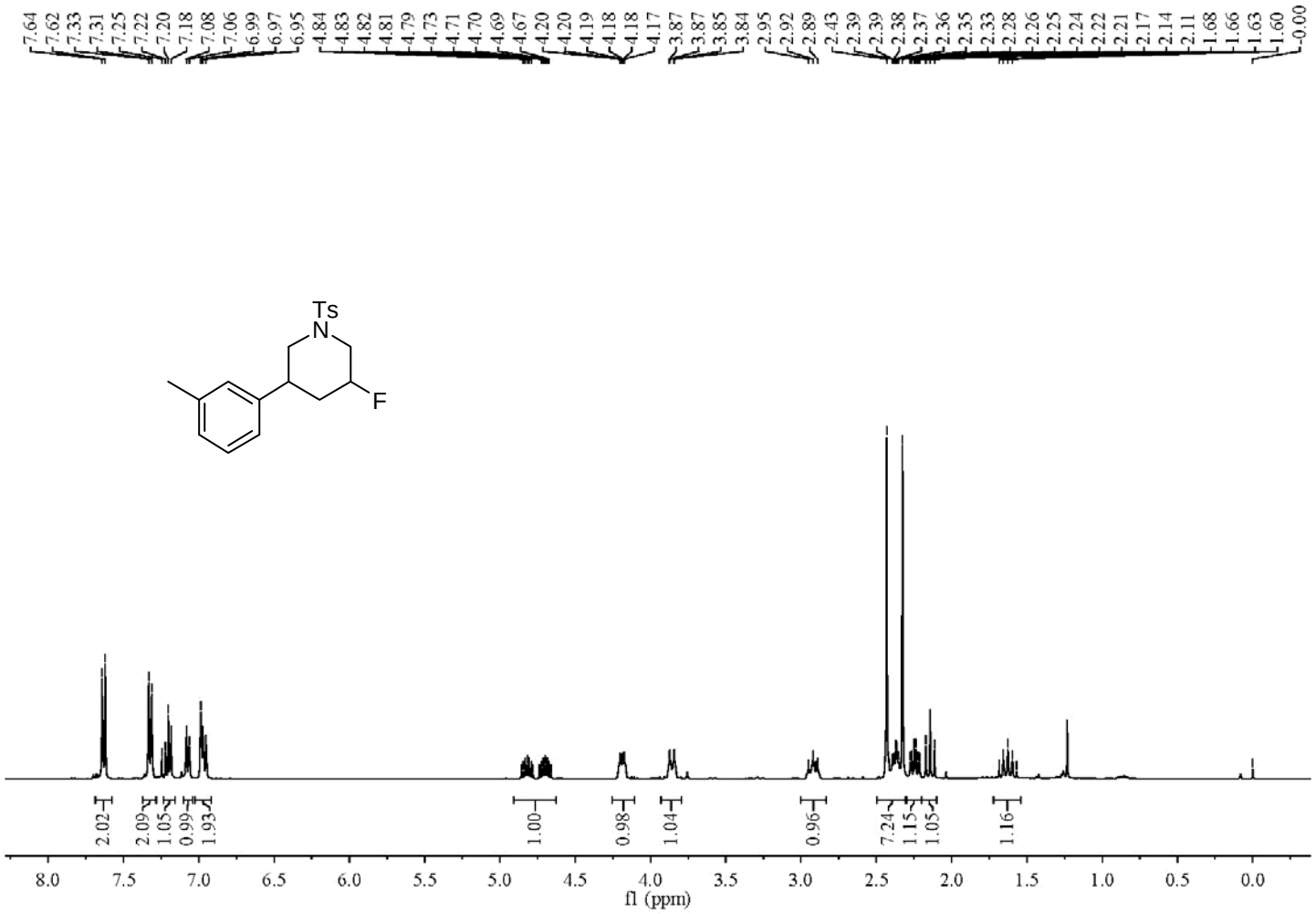
3-fluoro-5-(o-tolyl)-1-tosylpiperidine(2e) (400 MHz, $CDCl_3$)

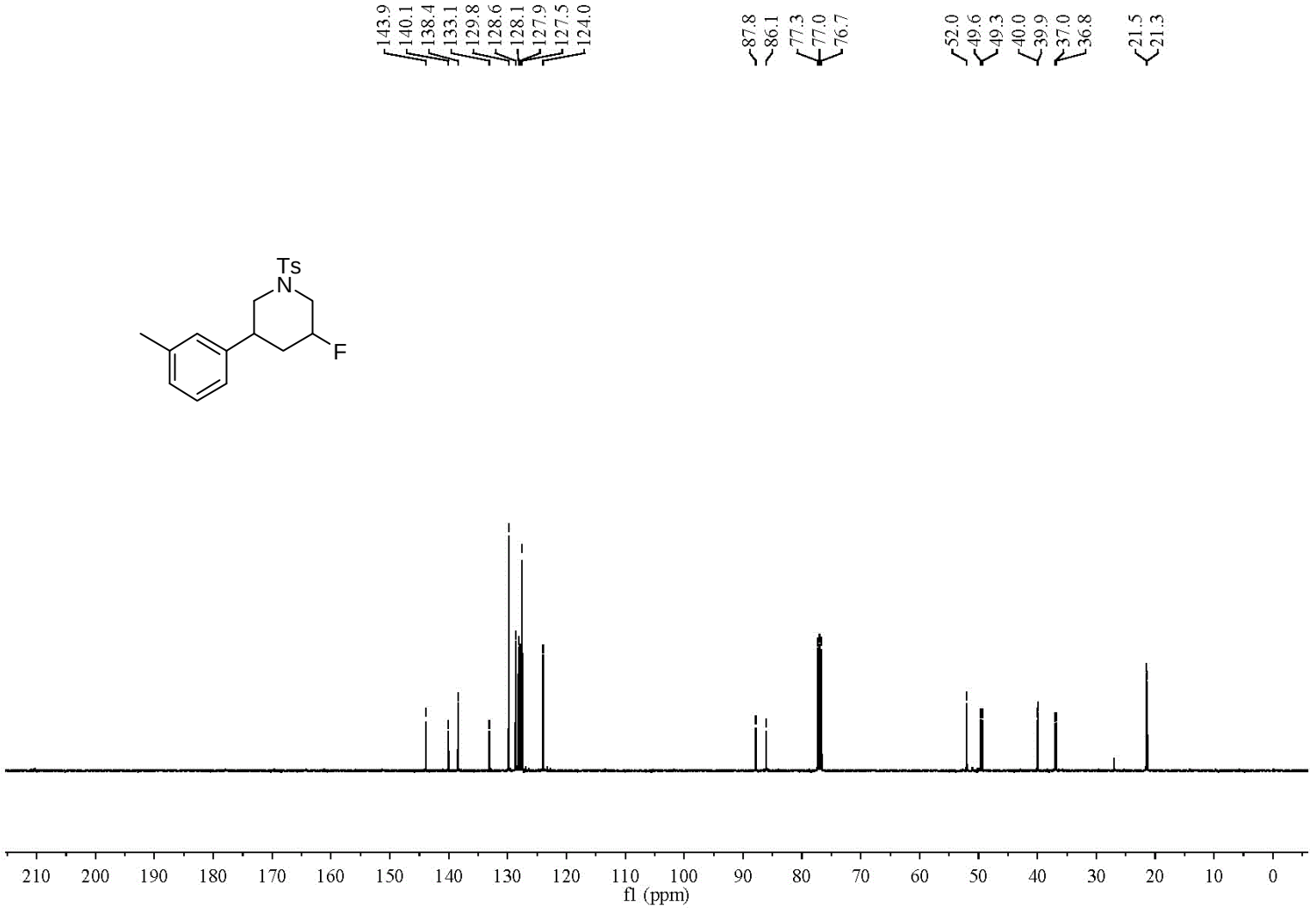


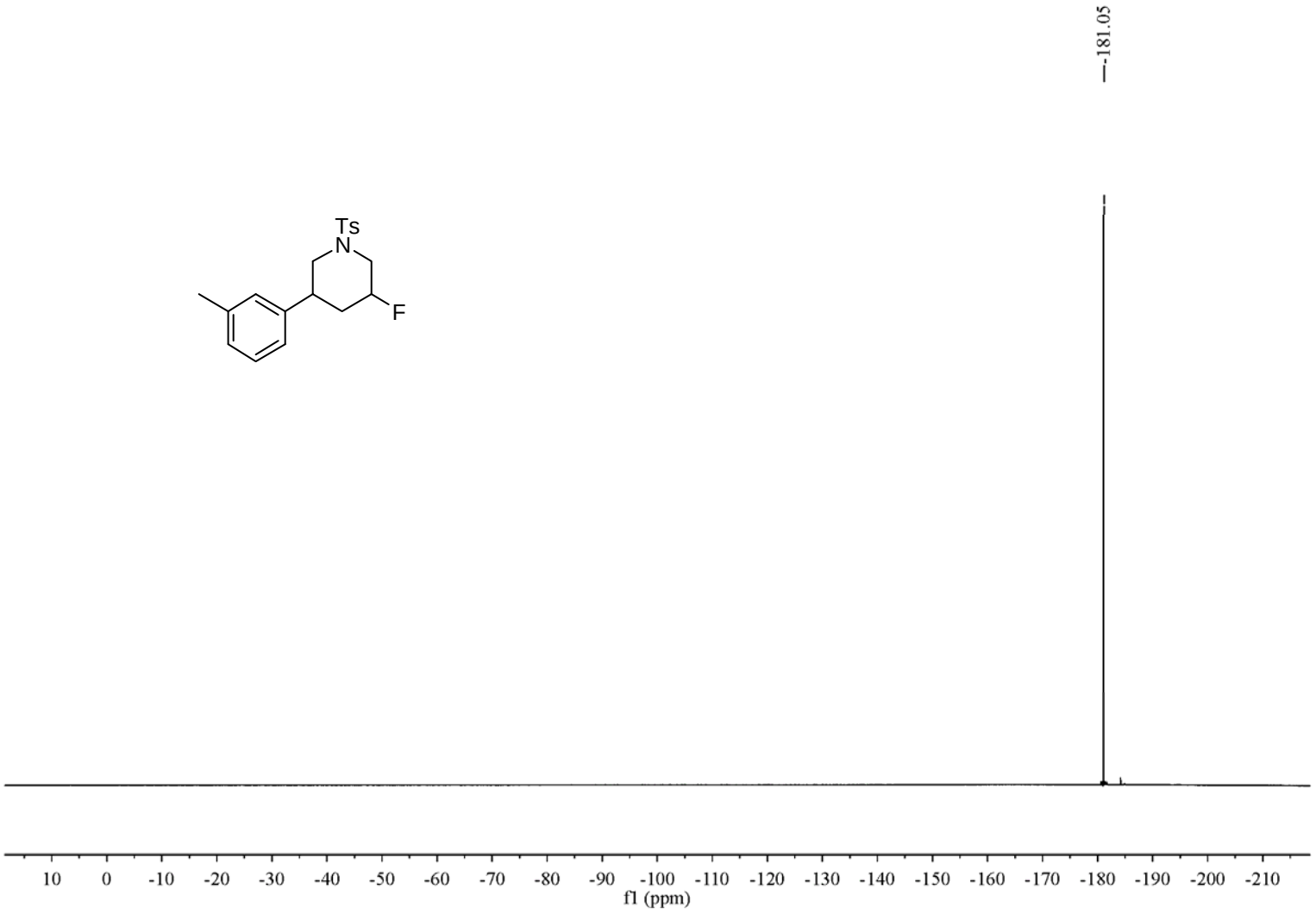




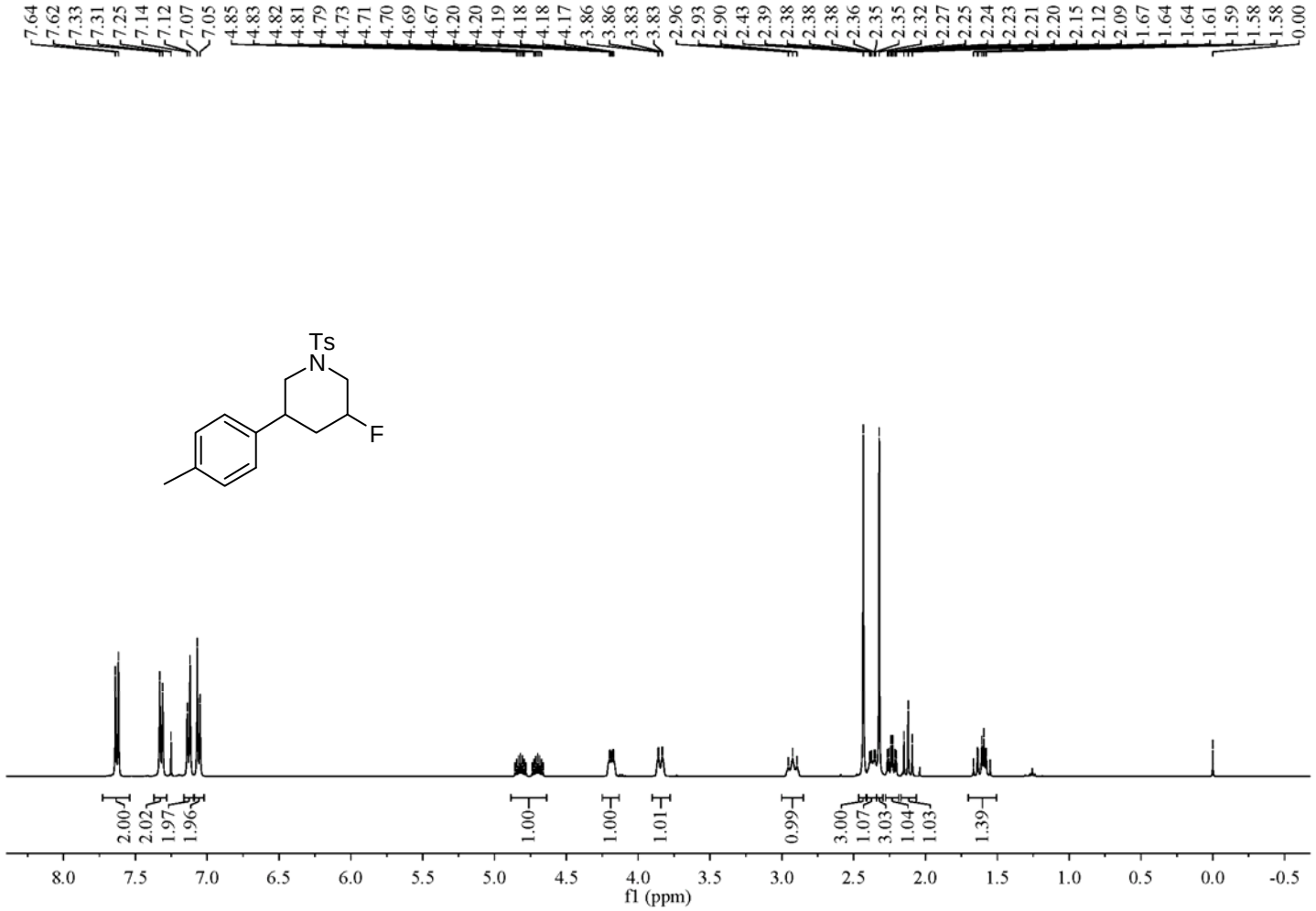
3-fluoro-5-(m-tolyl)-1-tosylpiperidine(2f) (400 MHz, $CDCl_3$)

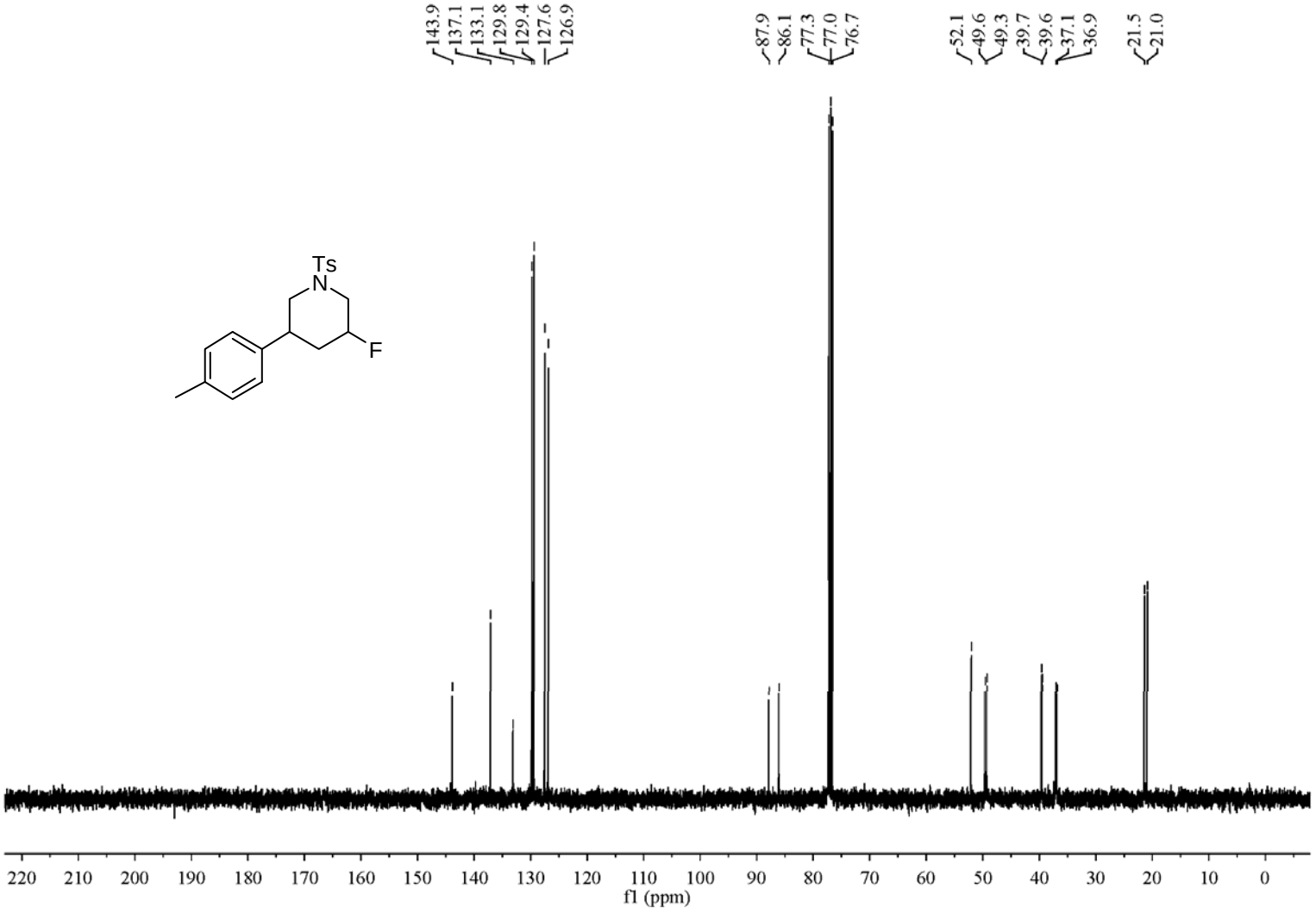


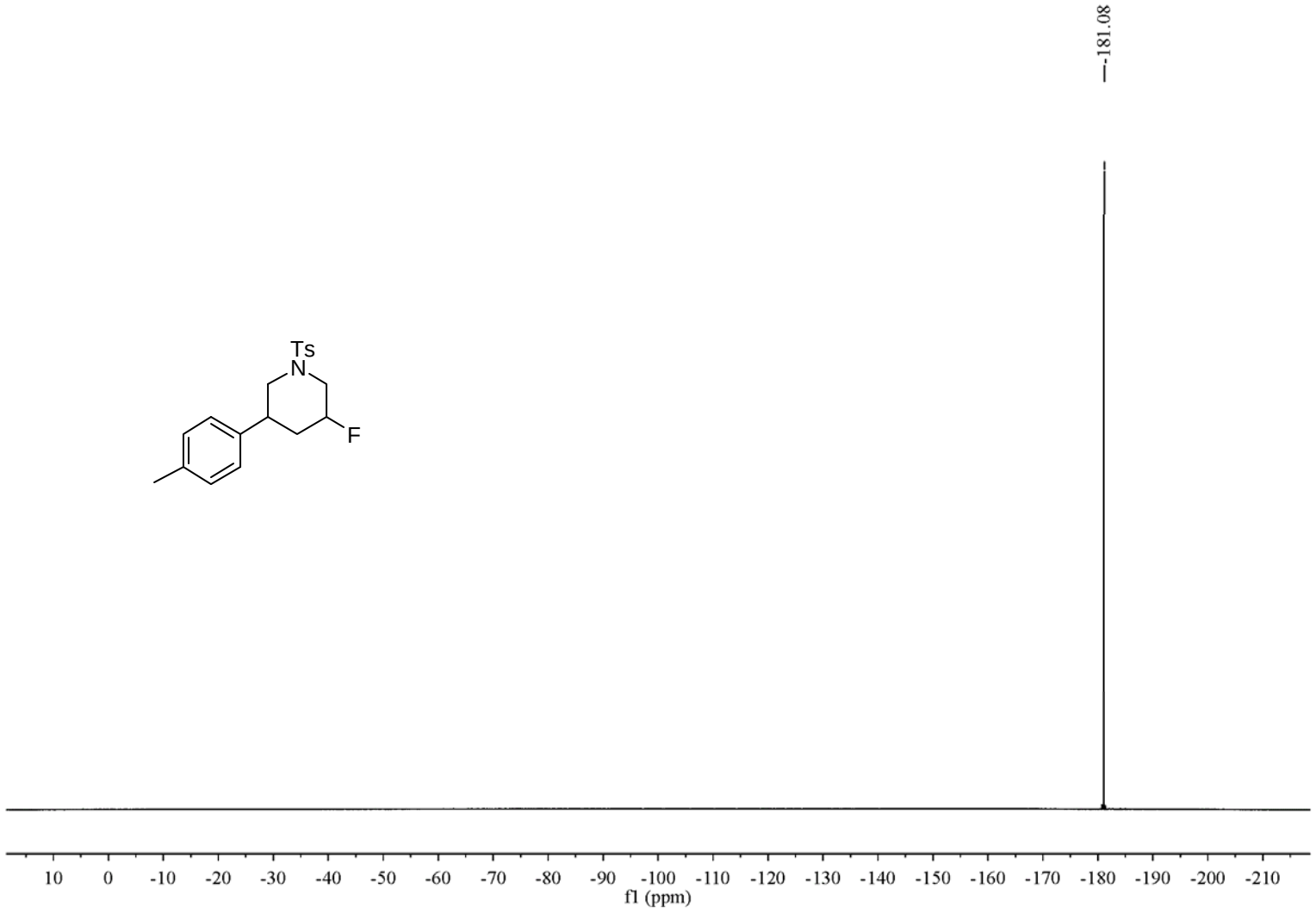




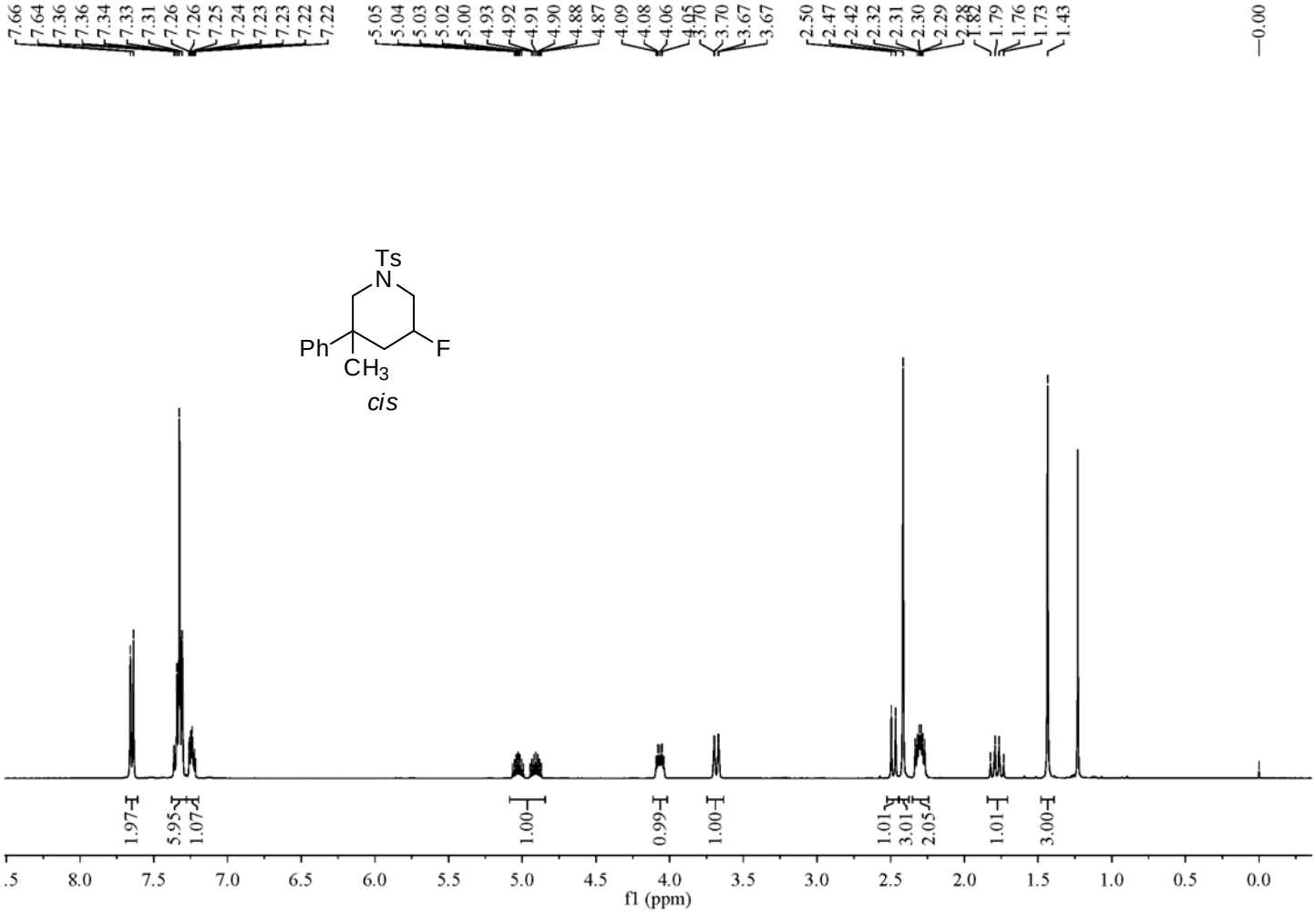
3-fluoro-5-(p-tolyl)-1-tosylpiperidine(2g) (400 MHz, $CDCl_3$)

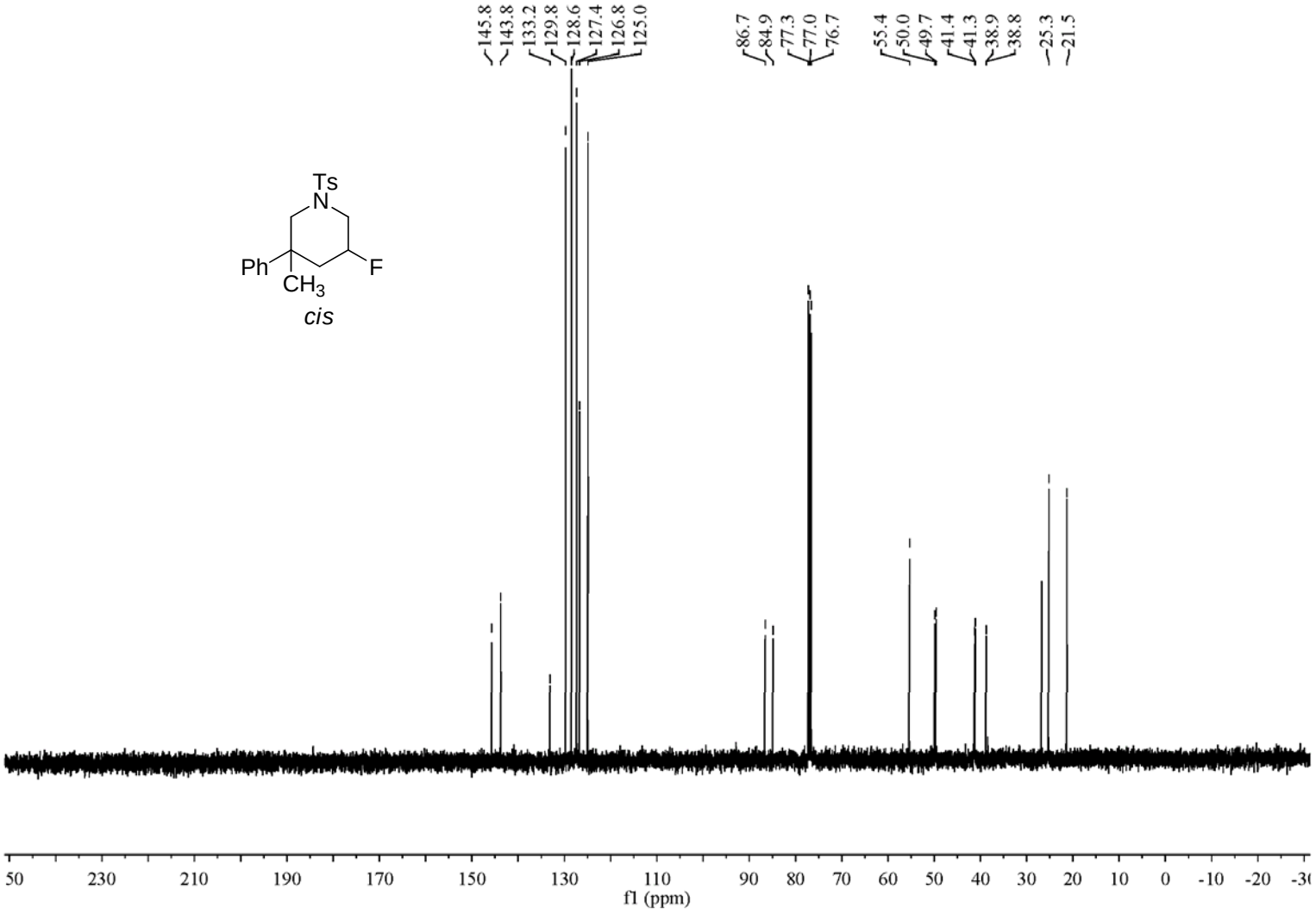




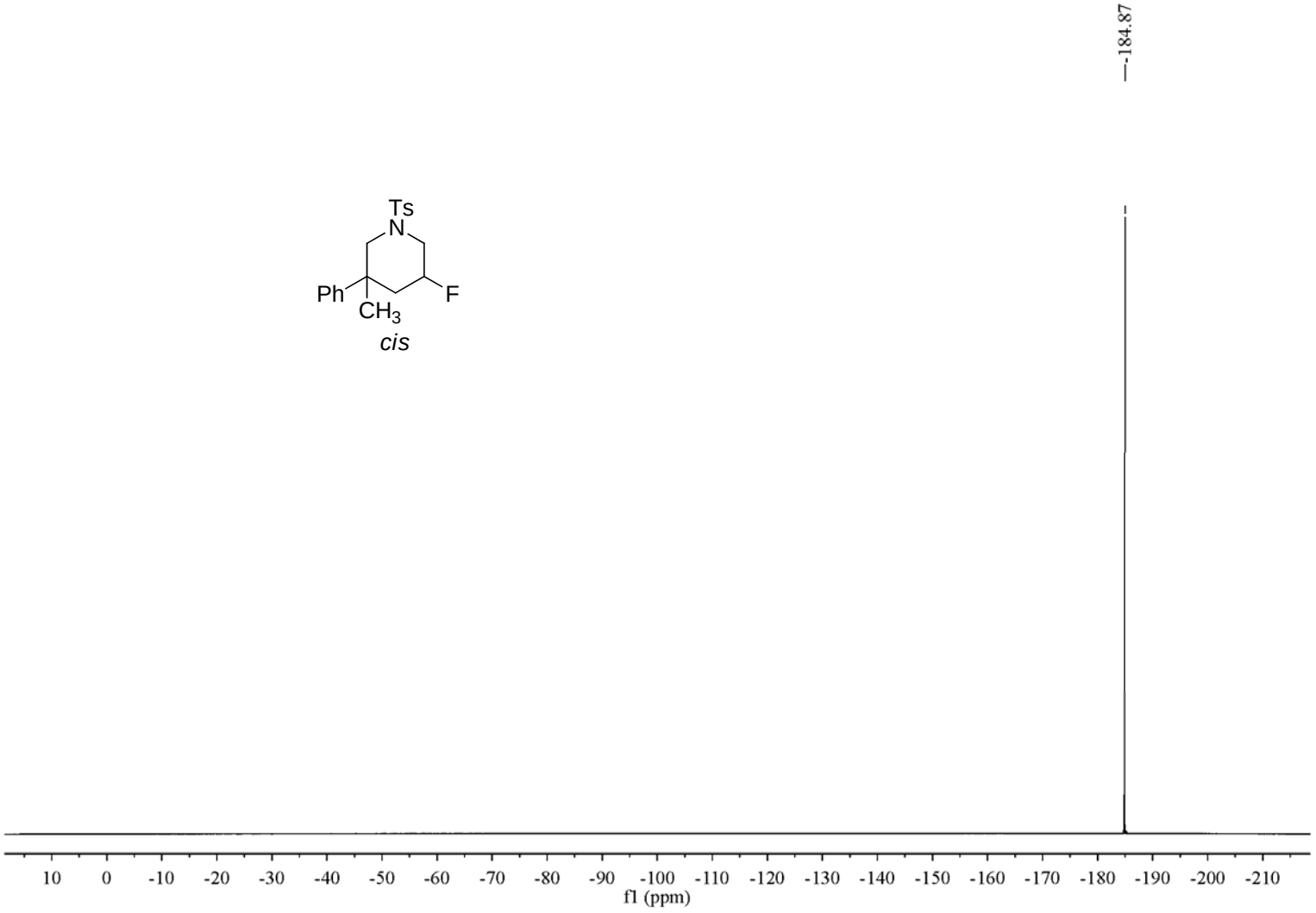


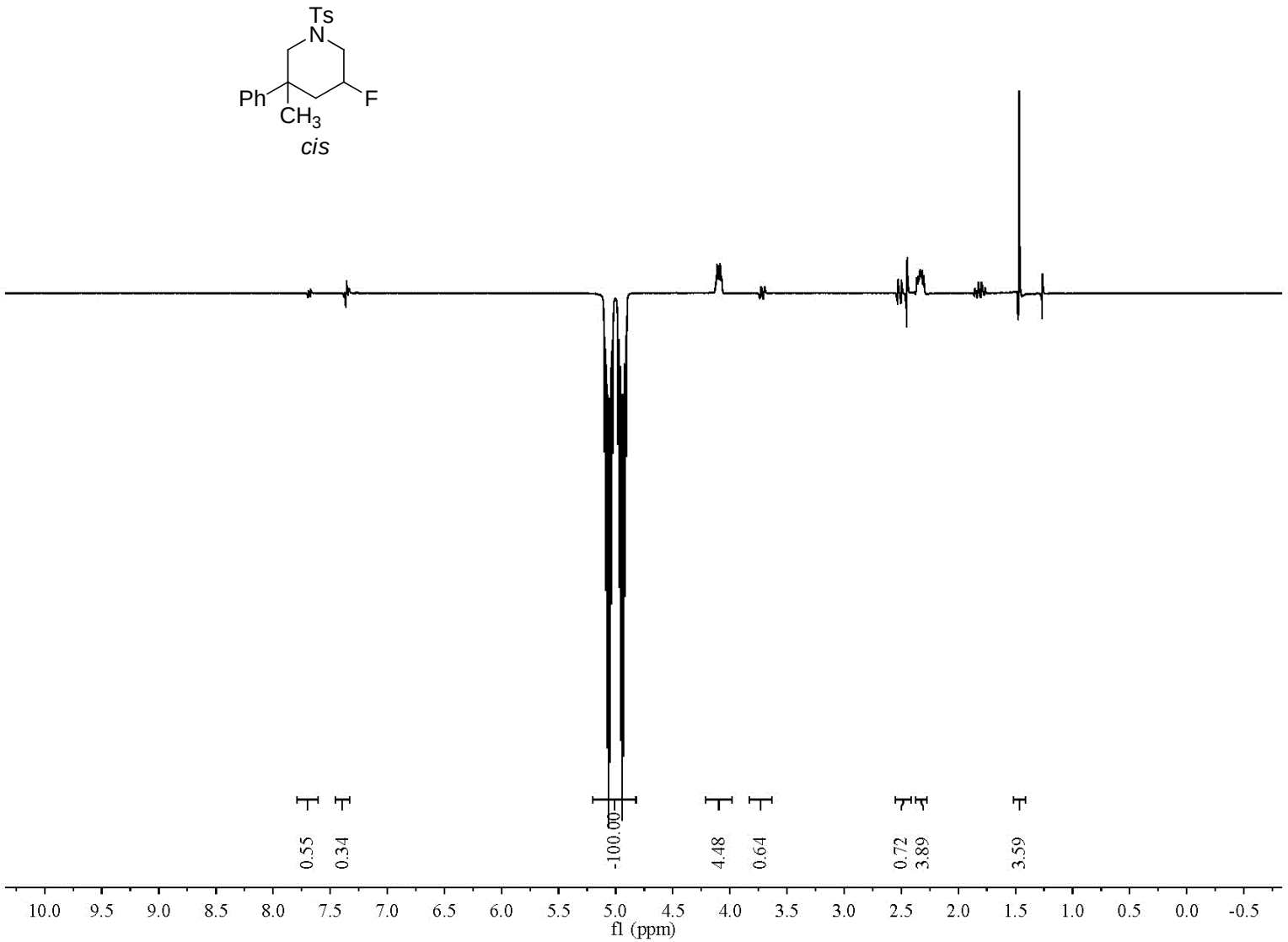
5-fluoro-3-methyl-3-phenyl-1-tosylpiperidine(2h) (400 MHz, $CDCl_3$)

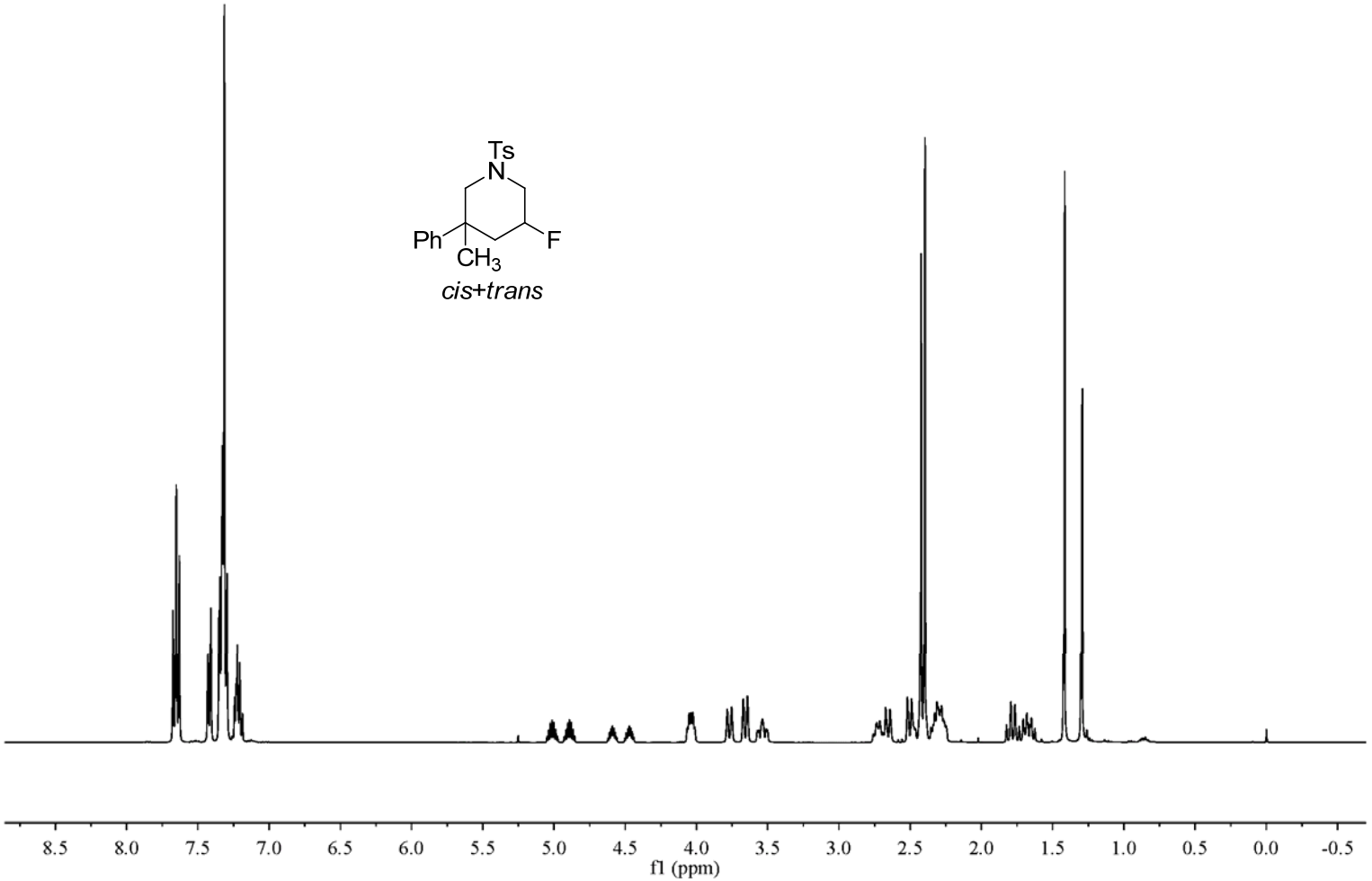


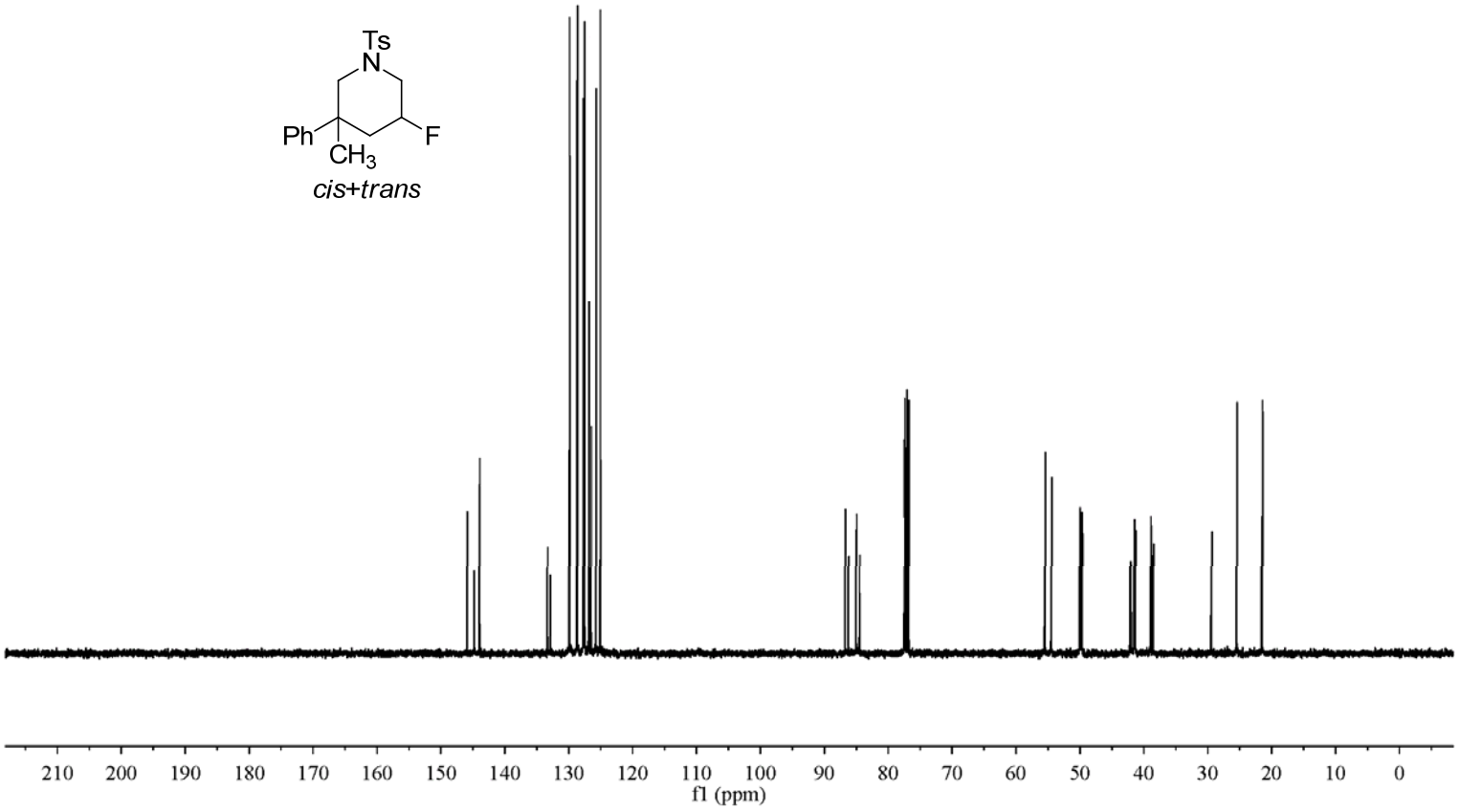


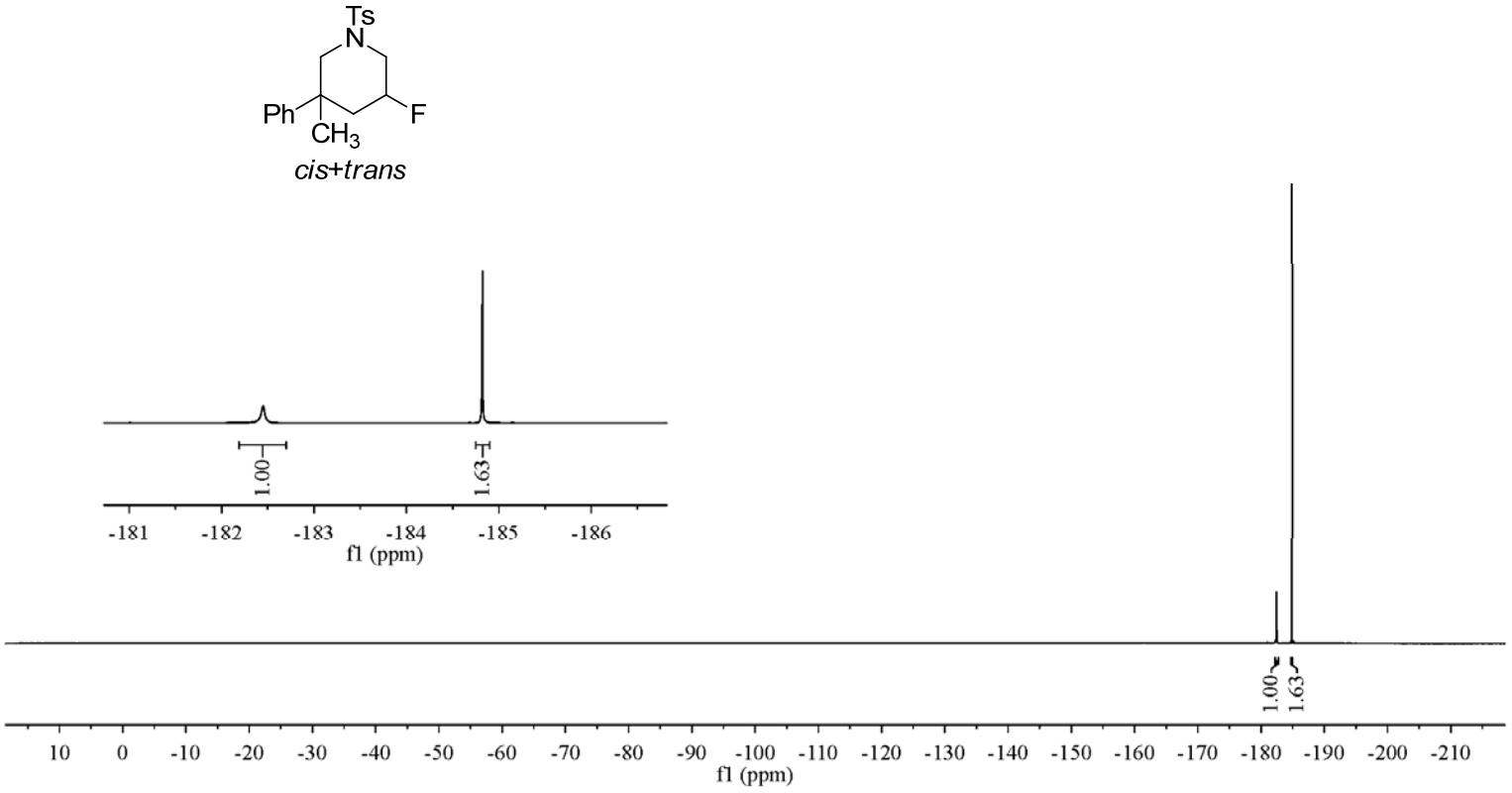
cis



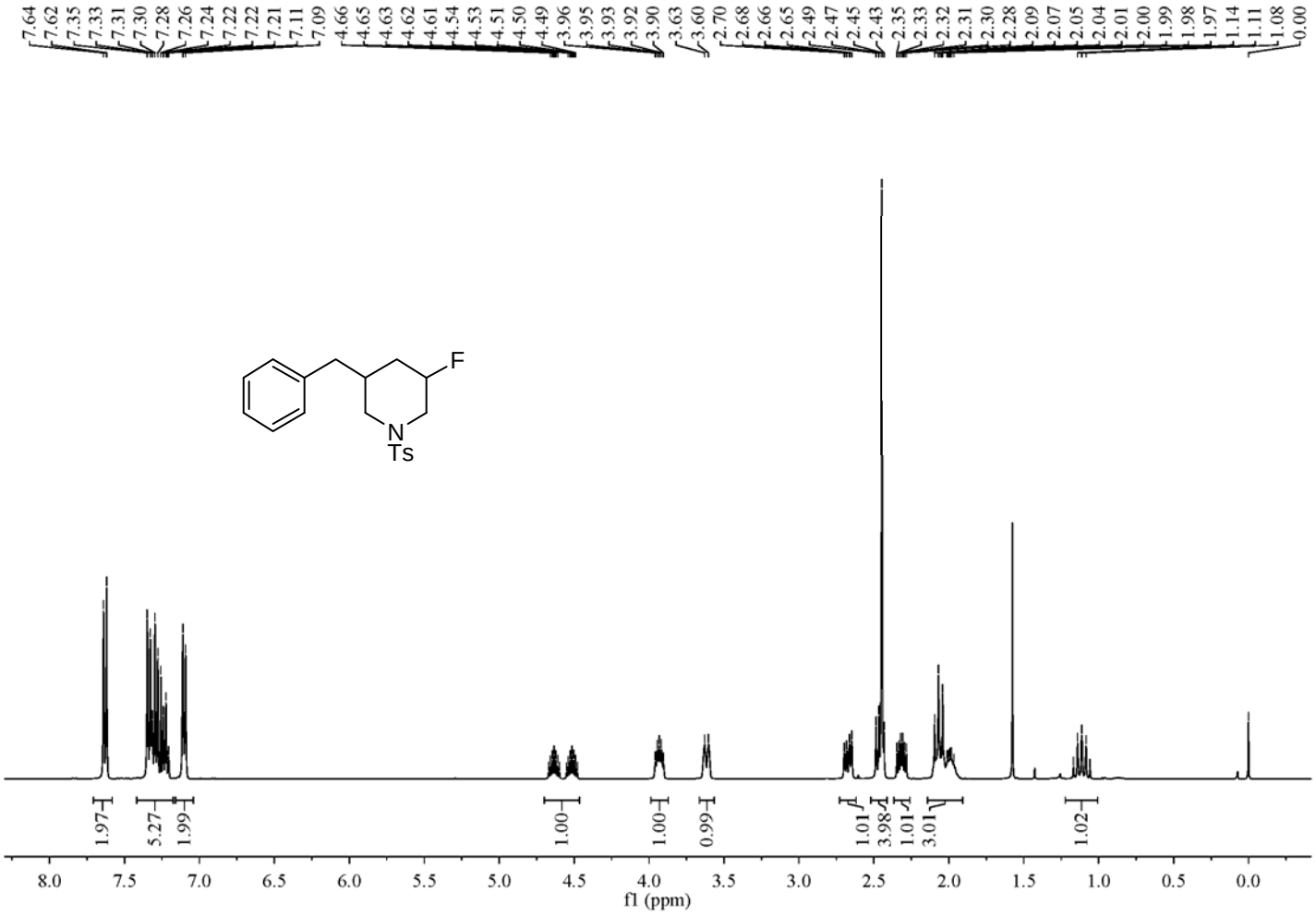


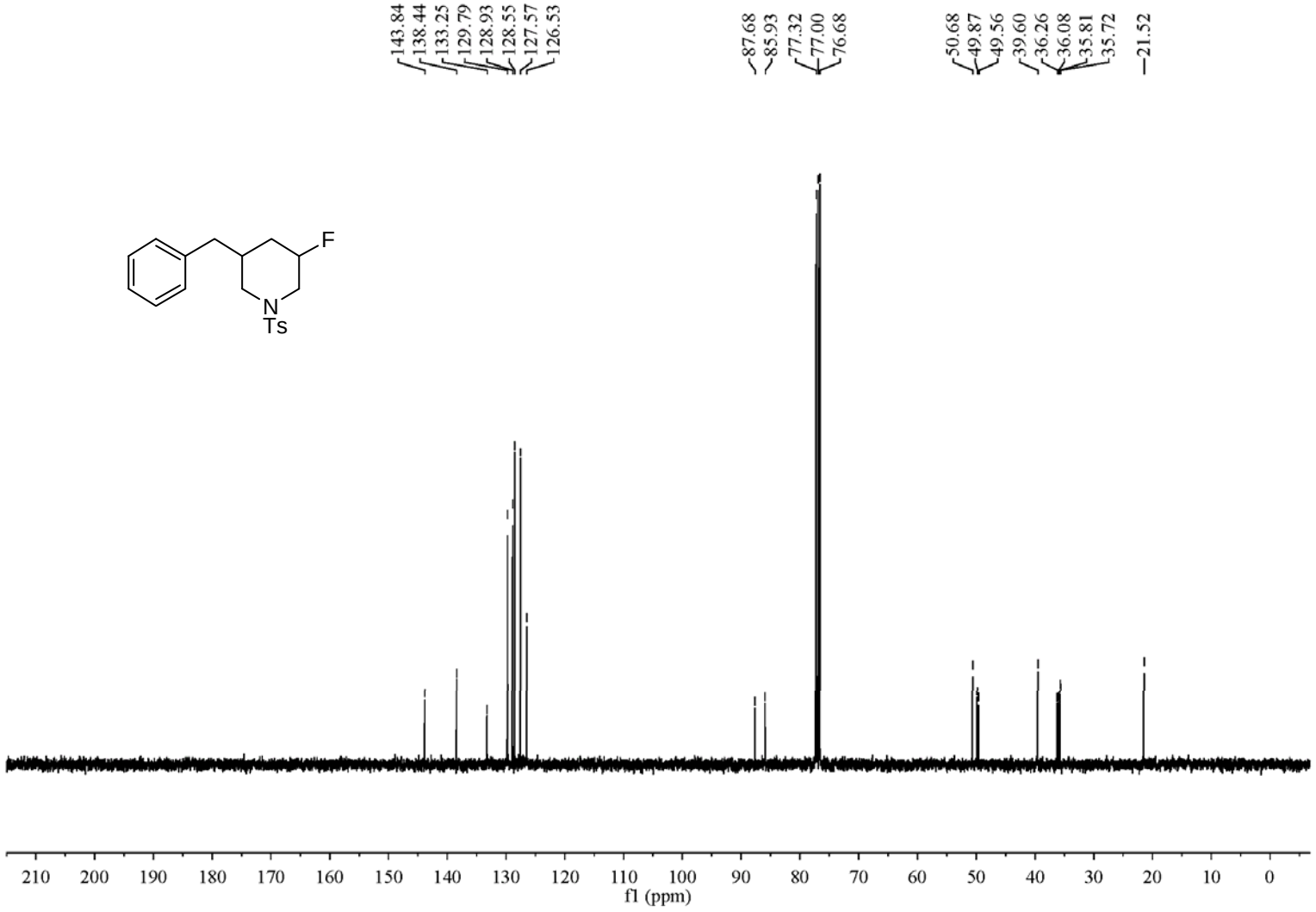


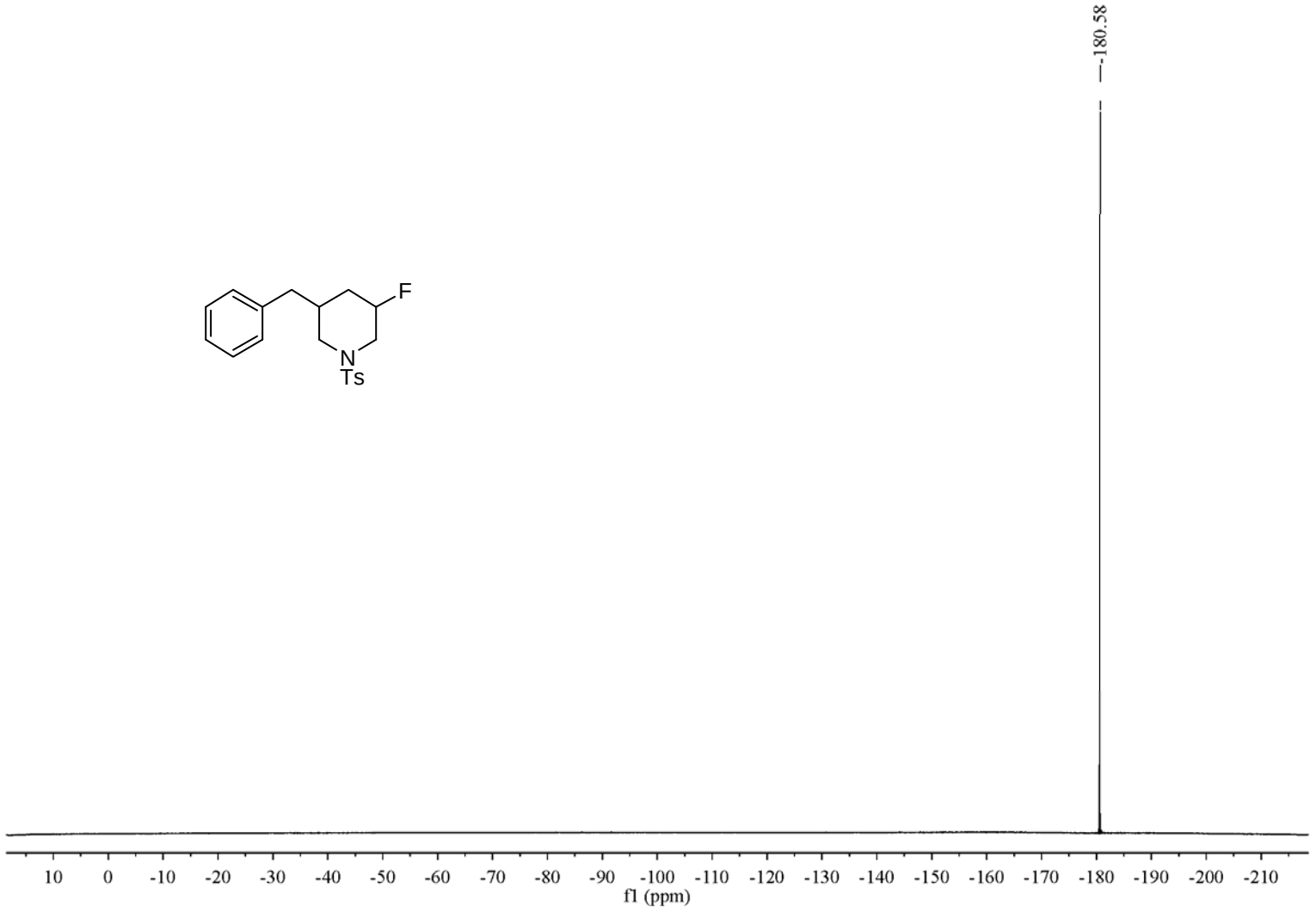




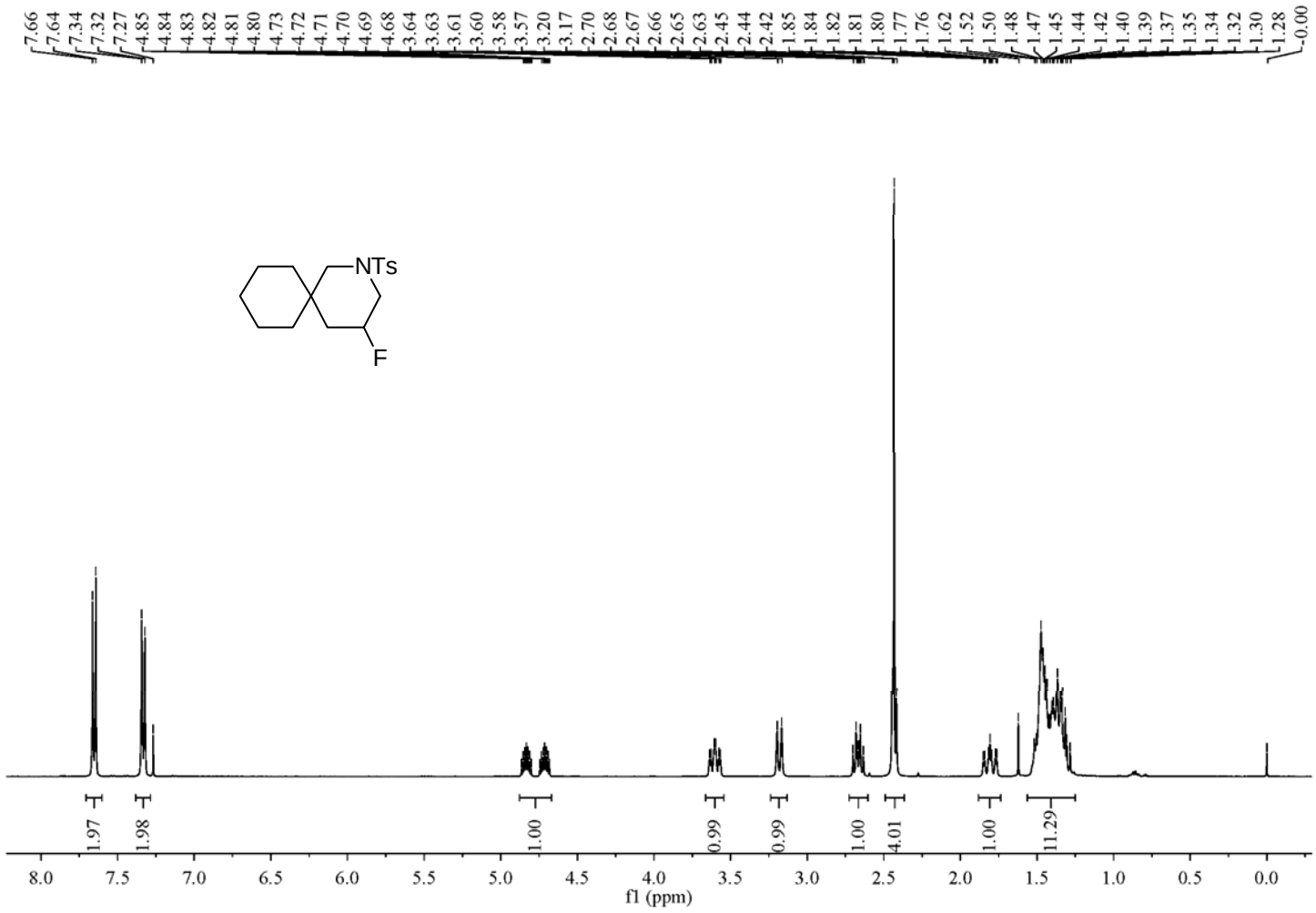
3-benzyl-5-fluoro-1-tosylpiperidine(2i) (400 MHz, $CDCl_3$)

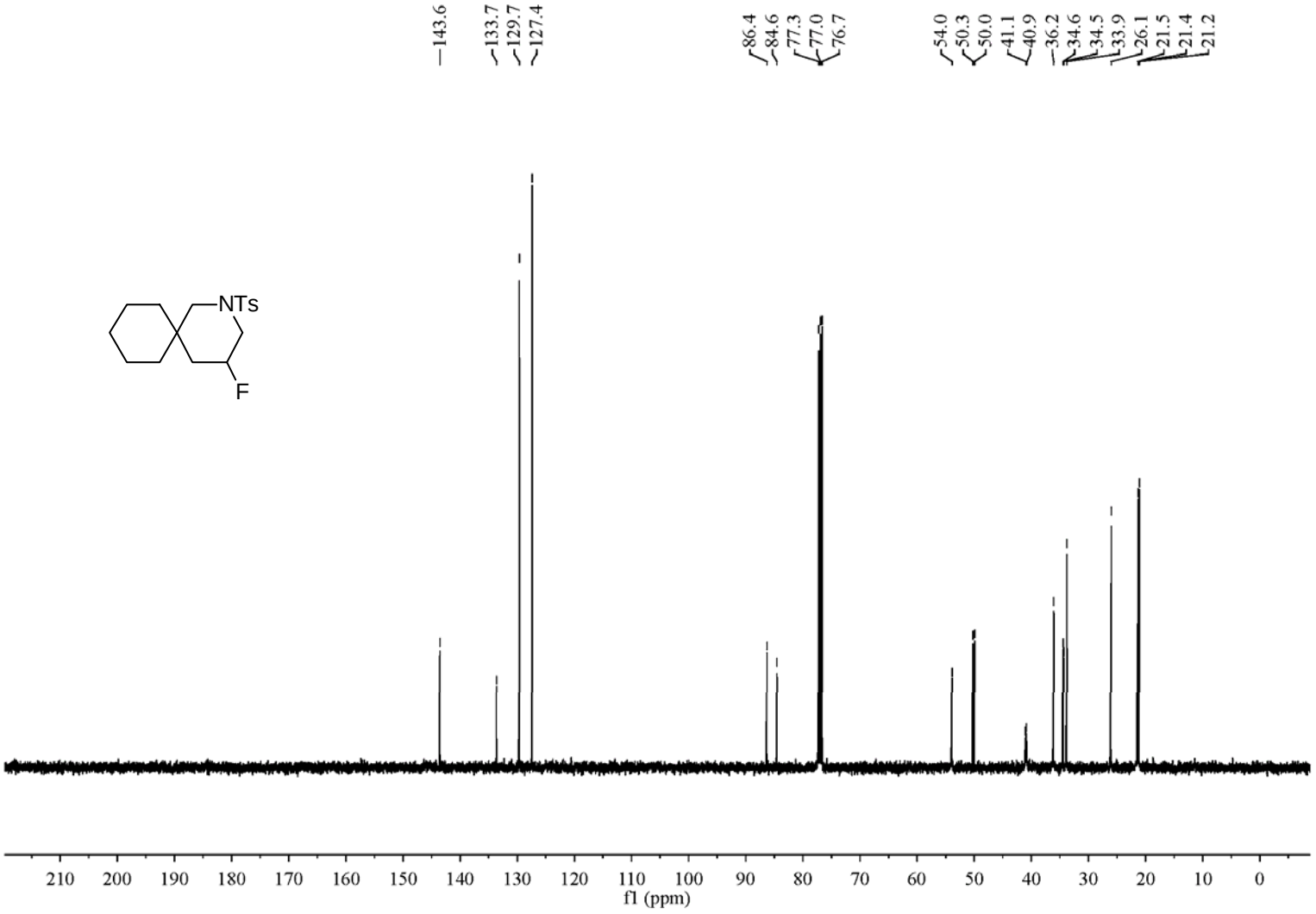




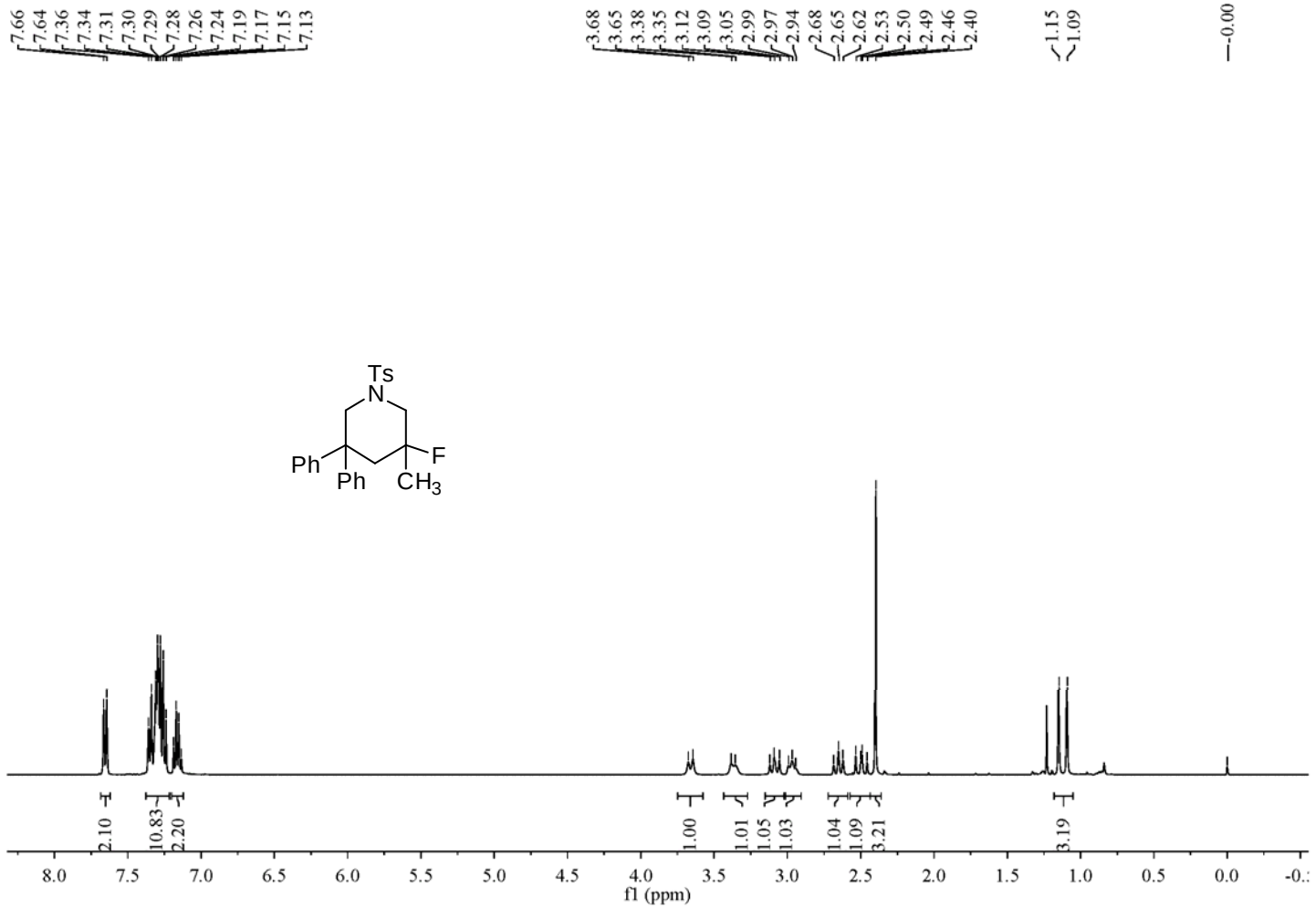


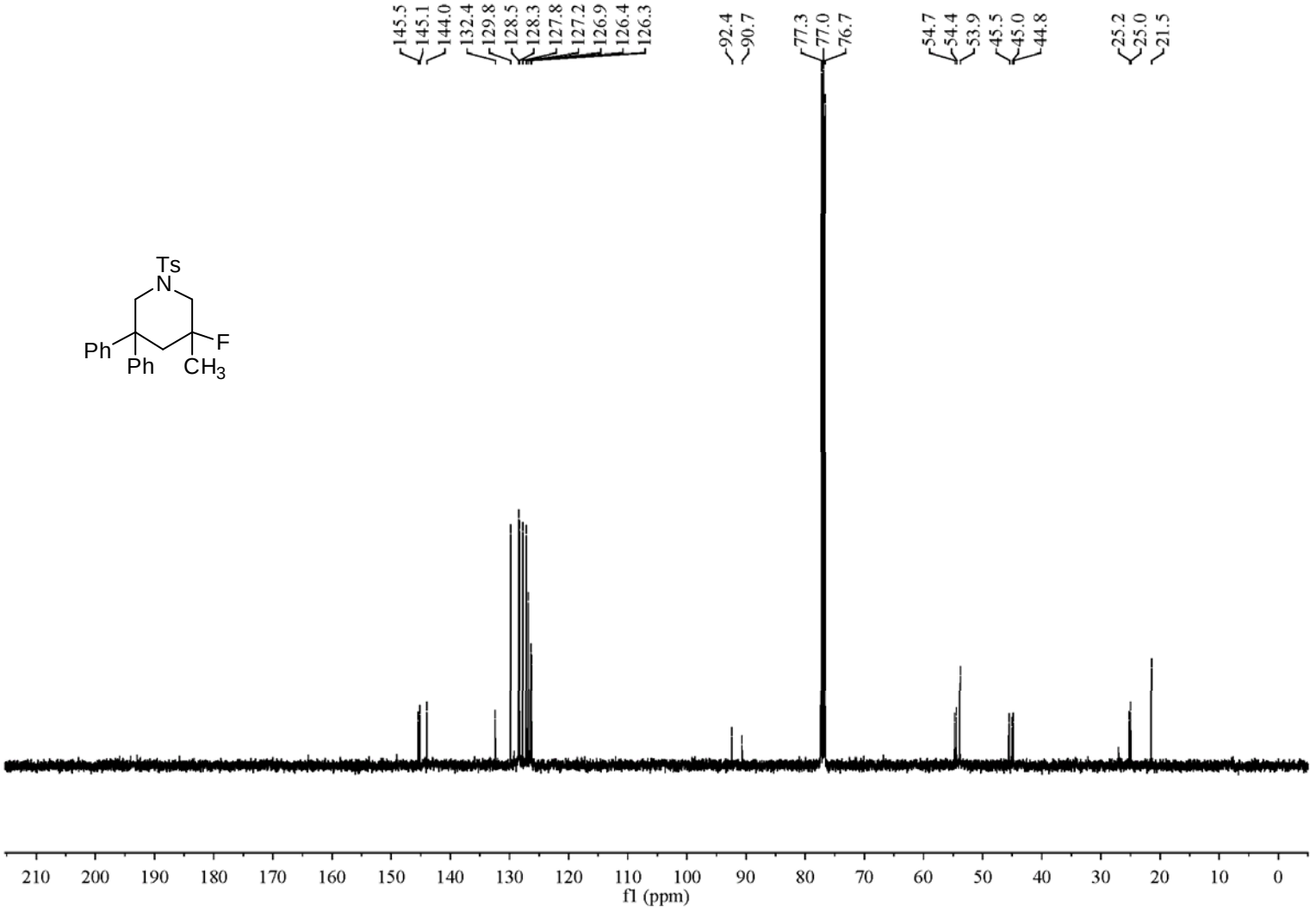
4-fluoro-2-tosyl-2-azaspiro[5.5]undecane (2j) (400 MHz, $CDCl_3$)

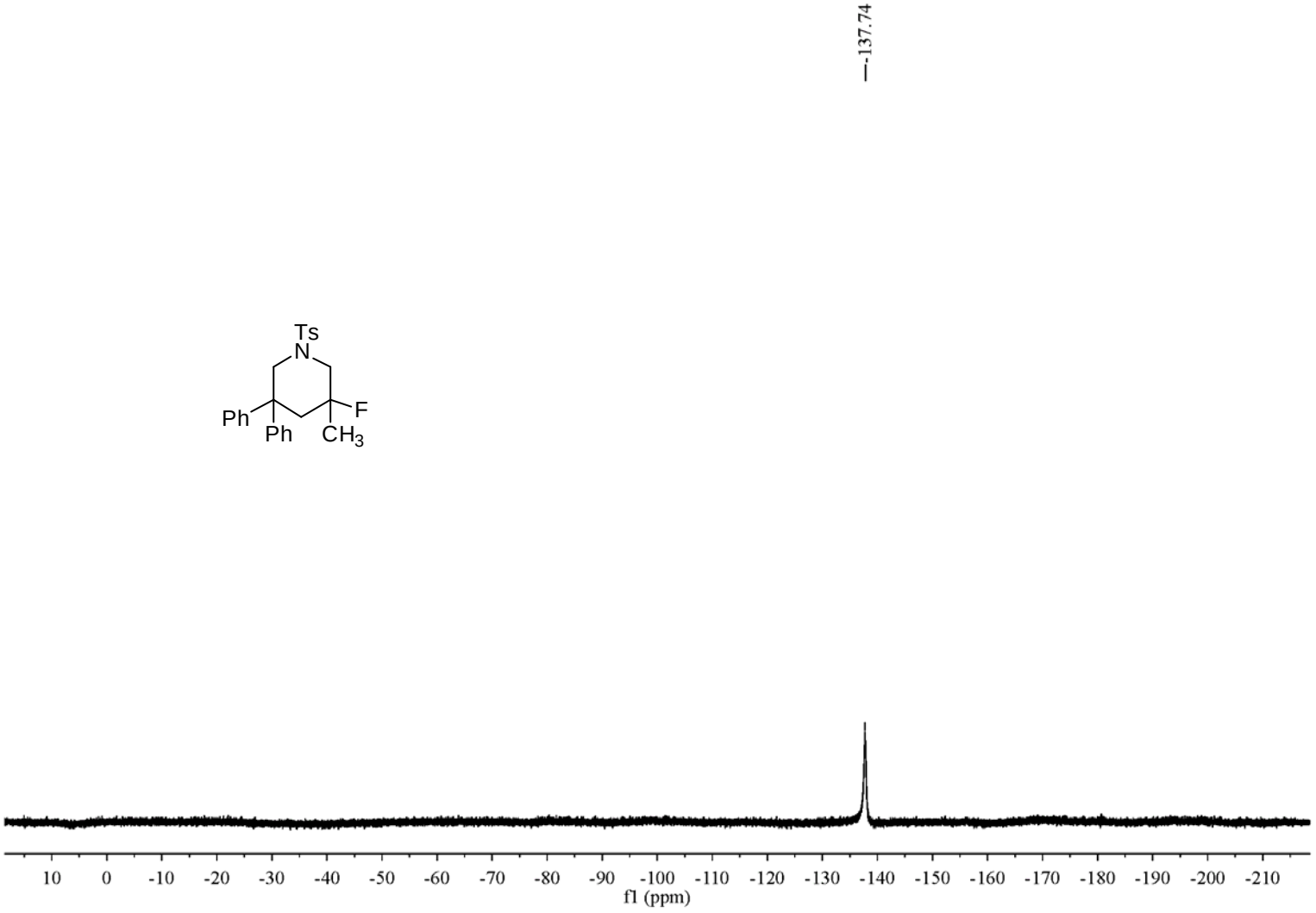




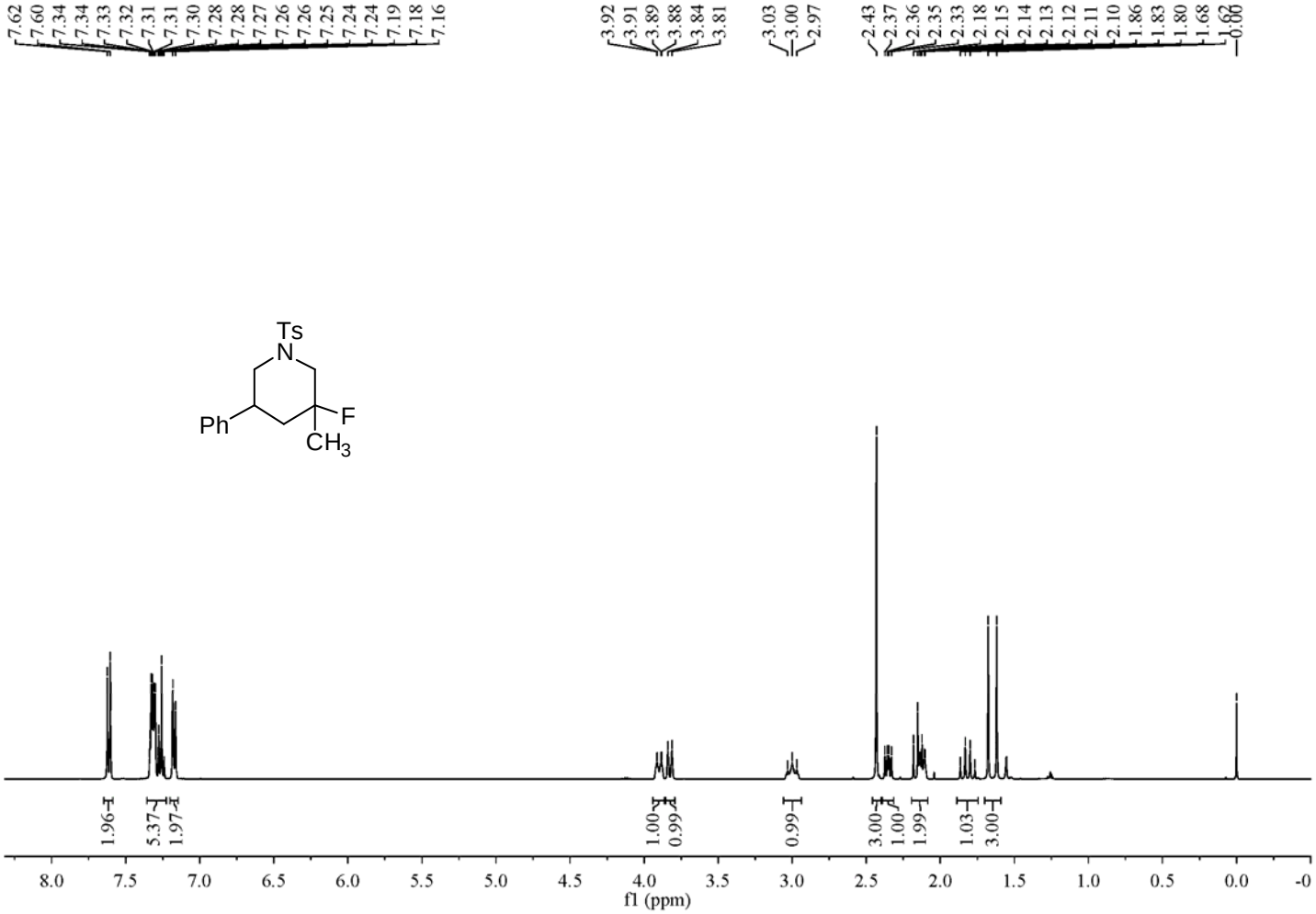
3-fluoro-3-methyl-5,5-diphenyl-1-tosylpiperidine(2k) (400 MHz, $CDCl_3$)

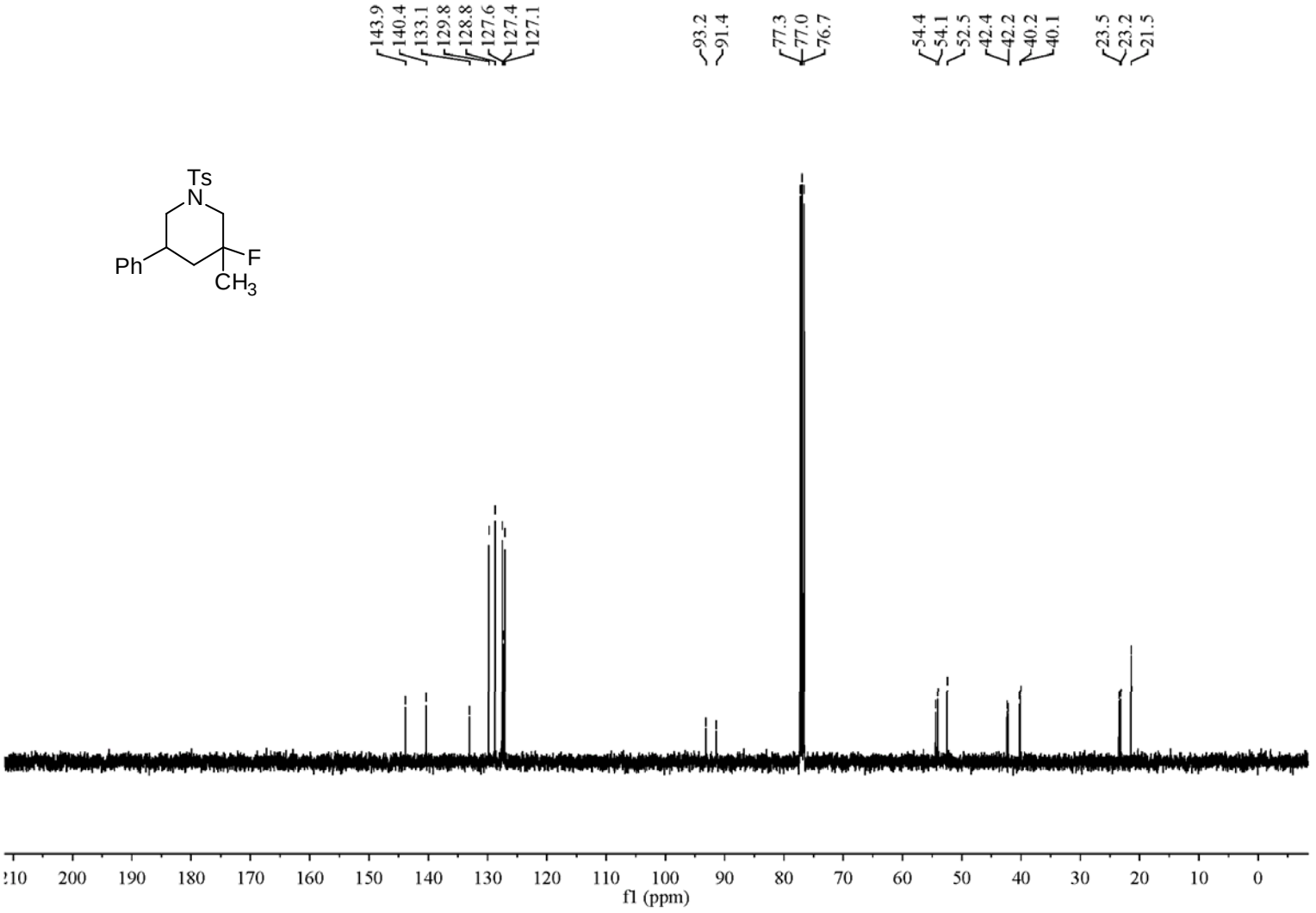


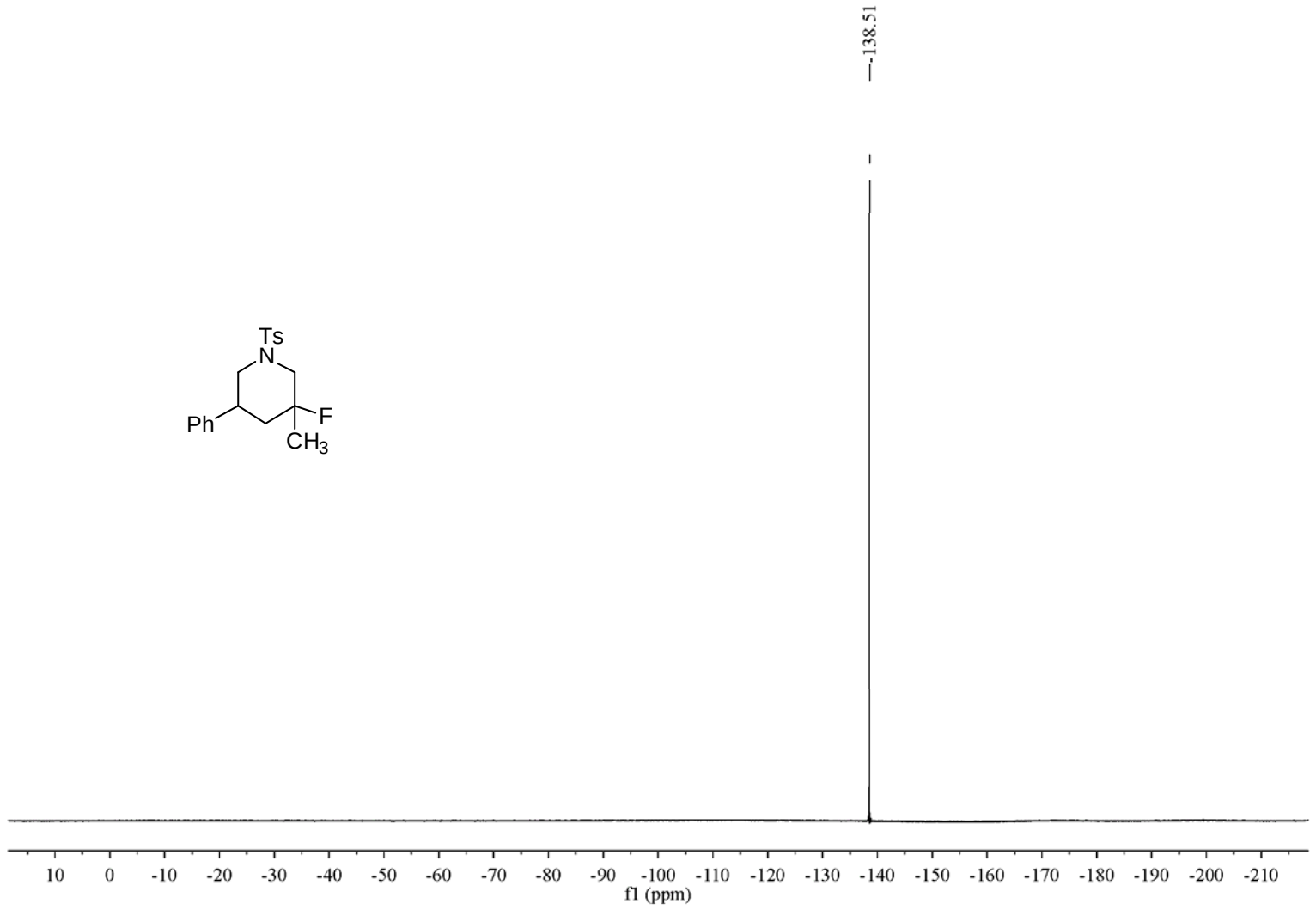




3-fluoro-3-methyl-5-phenyl-1-tosylpiperidine(2l) (400 MHz, $CDCl_3$)

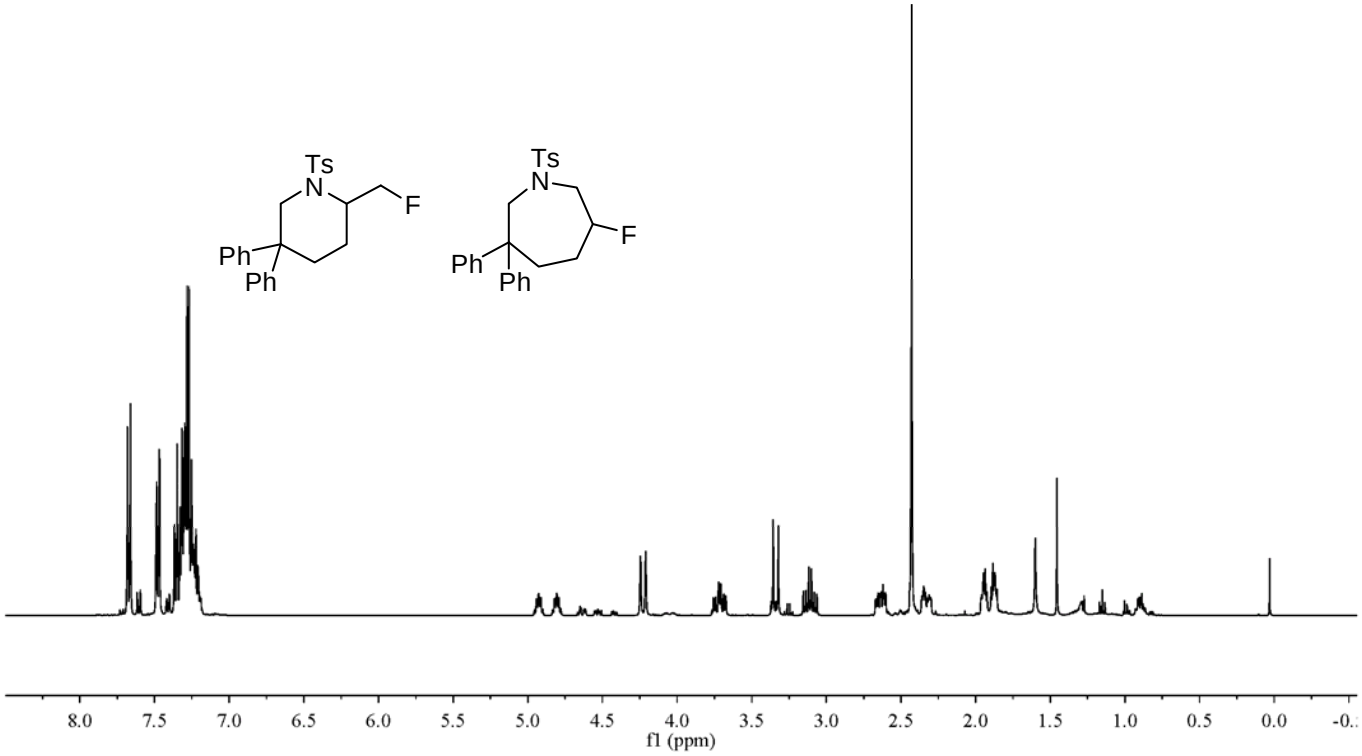


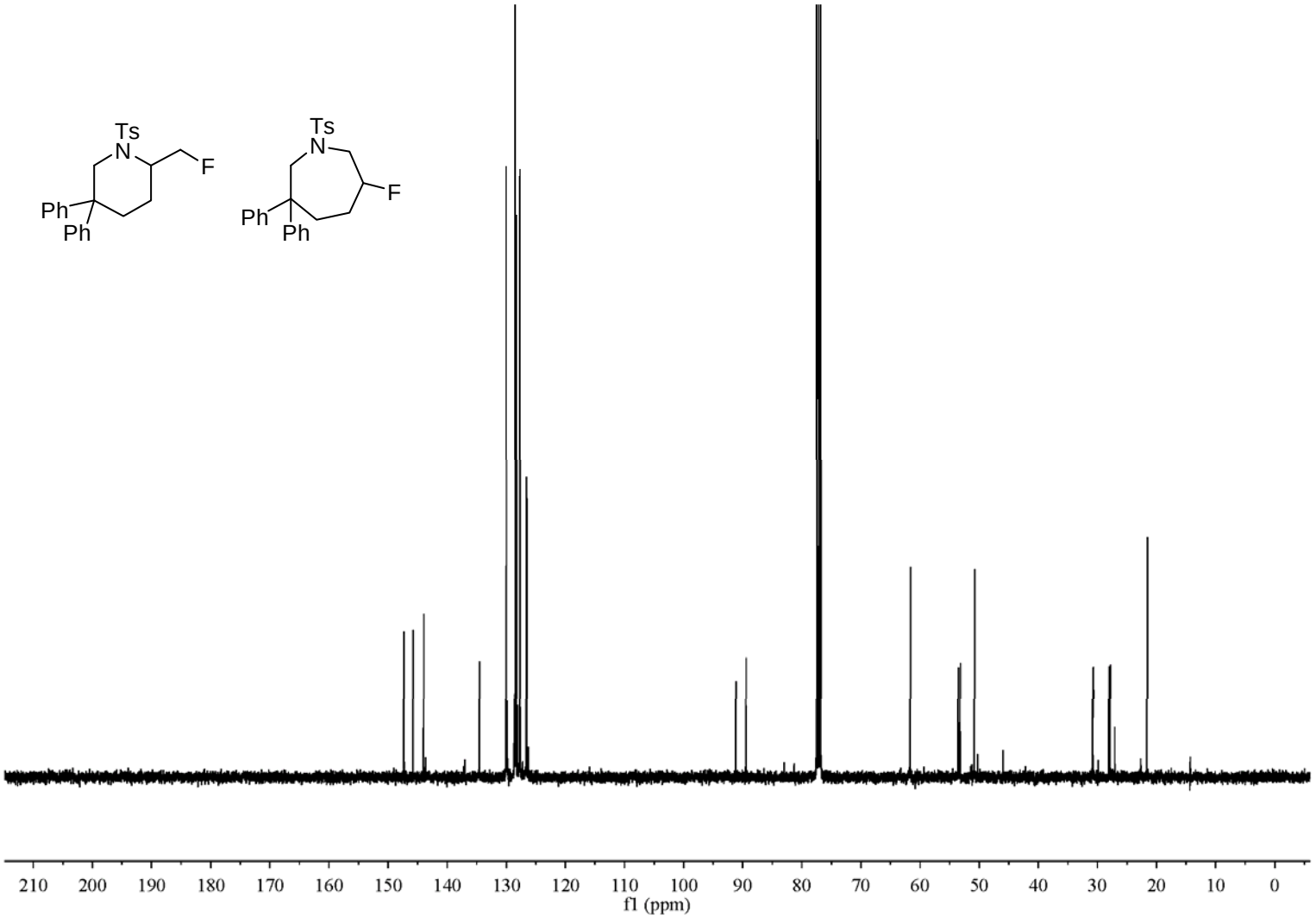


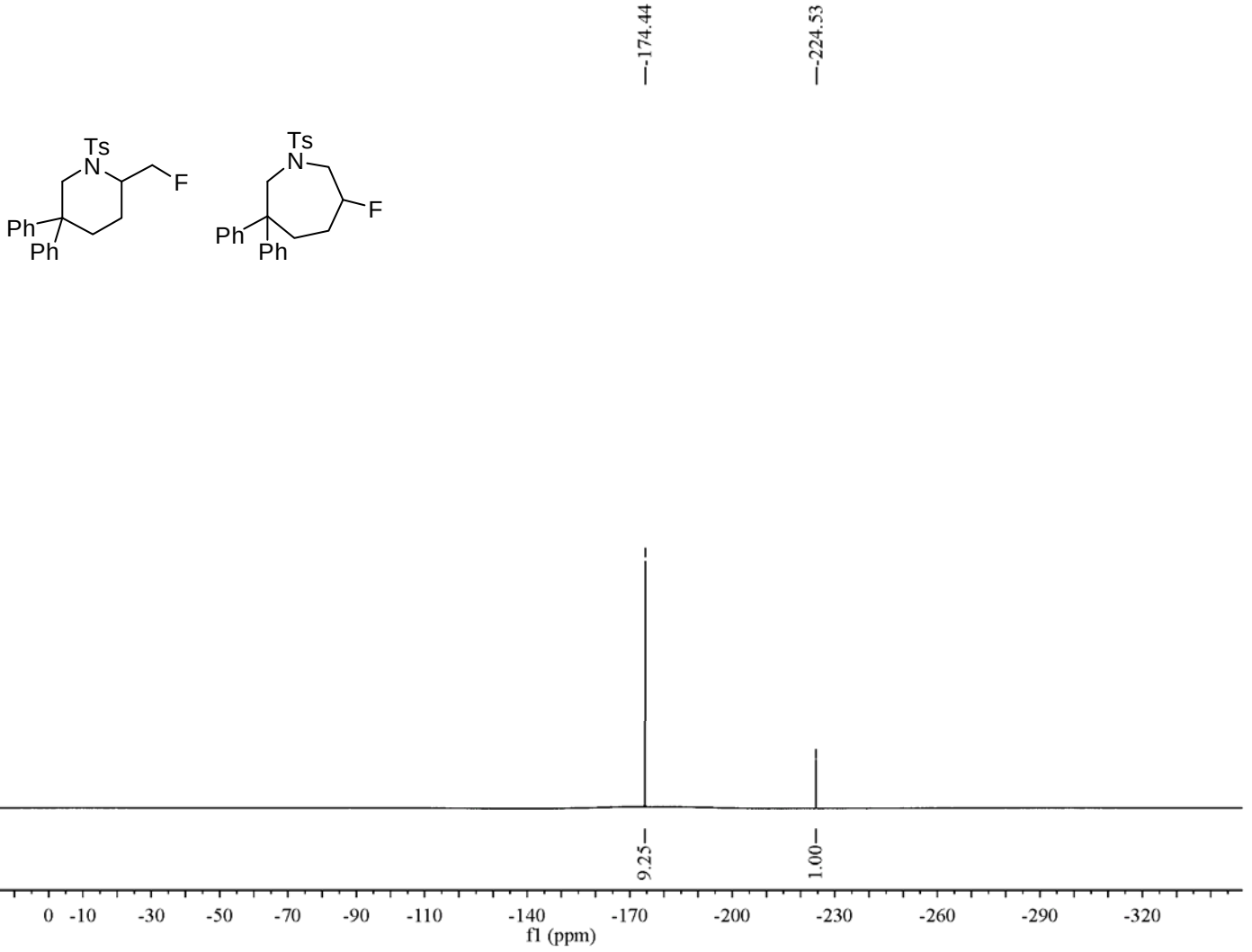


2-(fluoromethyl)-5,5-diphenyl-1-tosylpiperidine(2o)

6-fluoro-3,3-diphenyl-1-tosylazepane(2p) (400 MHz, $CDCl_3$)







5-phenyl-1-tosylpiperidin-3-yl pivalate (3) (400 MHz, $CDCl_3$)