Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ruthenium(II)-catalyzed Selective C-H Difluoroalkylation of Aniline Derivatives with Pyrimidyl Auxiliaries

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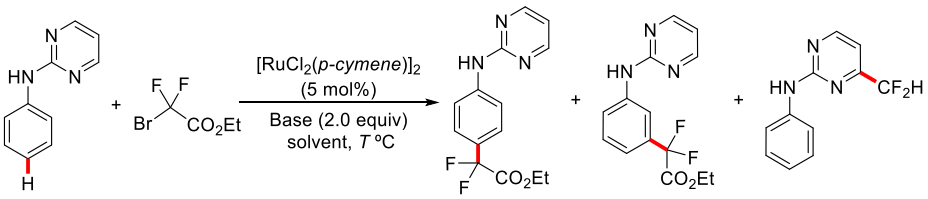
Table of Contents

1. General Remarks

Catalytic reactions were performed under Ar atmosphere using pre-dried glassware and standard Schlenk techniques. 1,4-Dioxane and toluene were dried with CaH_2 and freshly distilled, DCE was dried with P_2O_5 and freshly distilled. The substrates **1**,[1] bromodifluoroamides **2z**, **2aa**,[2] **13**,[3] [$Ru(O_2CMes)_2$(*p-cymene*)],[4] and [$Ru(OAc)_2$(*p-cymene*)][5] were synthesized according to previously described methods. Other chemicals were obtained from commercial sources and were used without further purification. For Column chromatography, 200-300 mesh silica gel and preparative TLC (PTLC) was employed. Analytical TLC was performed with silica gel GF254 plates. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) were recorded in $CDCl_3$ using TMS as internal standard. All products were further characterized by high resolution mass spectra (HRMS, FTMS, ESI full ms [100-2000]), copies of their ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were provided. If not otherwise specified, chemical shifts (δ) are given in ppm.

2. Optimization Studies

Table S1. Testing of Bases, Solvents and Temperature.[a]

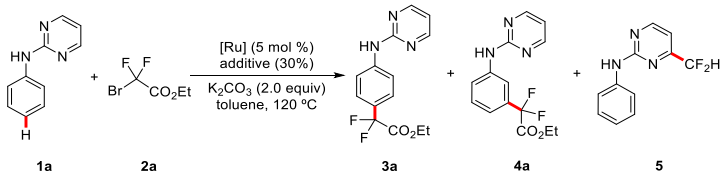


1a **2a** **3a** **4a** **5**

Entry	Base	*T* [℃]	Solvent	Yield [%]		
				3a	**4a**	**5**
1	K_2CO_3	120	1,4-dioxane	-	-	-
2	K_2CO_3	120	DCE	<5	-	-
3	K_2CO_3	120	TCE	-	-	-
4	K_2CO_3	120	TBME	16	-	-
5	K_2CO_3	120	DME	-	-	-
6	K_2CO_3	120	MeCN	-	-	67[b]
7	**K_2CO_3**	**120**	**toluene**	**39**	**-**	**-**
8	K_2CO_3	120	$PhCF_3$	28	-	-
9	K_2CO_3	120	*o*-xylene	30	-	-
10	K_2CO_3	120	*m*-xylene	27	-	-
11	K_2CO_3	120	*p*-xylene	26	-	-
12	K_2CO_3	120	Mesitylene	21	-	-
13	K_2CO_3	100	toluene	-	-	-
14	K_2CO_3	140	toluene	35	13	
15	K_2CO_3	120	toluene			
16	**Na_2CO_3**	**120**	**toluene**	**41**	**8**	
17	Cs_2CO_3	120	toluene	29[b]	-	
18	K_3PO_4	120	toluene	-	-	
19	NaOAc	120	toluene	13[b]	11[b]	
20	KOAc	120	toluene	21[b]	18[b]	
21	CsOAc	120	toluene	15[b]	13[b]	
22	TMEDA	-	toluene	-	-	

[a]Standard reaction conditions: aniline derivative (0.2 mmol), bromodifluoroacetate (0.6 mmol), $[RuCl_2(p\text{-}cymene)]_2$ (0.01 mmol), base (0.4 mmol), and solvent (1 mL) under argon atmosphere, yields of isolated products. [b]Yield was determined by GC-MS spectroscopy using diphenyl oxide as the internal standard. DCE = 1,2-dichloromethane, TCE = 1,1,2-trichloromethane, DME = 1,2-dimethoxyethane. TMEDA = *N,N'*-tetramethylethylenediamine

Table S2. Optimization of Ruthenium(II)-Catalyzed C–H Difluoromethylation.[a]

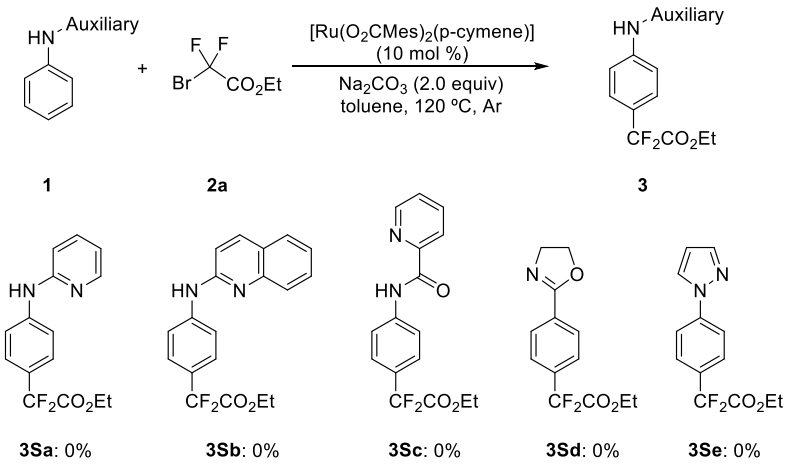


1a **2a** **3a** **4a** **5**

Entry	Catalyst	Additive	Yield [%]		
			3a	**4a**	**5**
1	$[RuCl_2(p\text{-}cymene)]_2$	NaOAc	25	13[b]	-
2	$[RuCl_2(p\text{-}cymene)]_2$	KOAc	28	19[b]	-
3	$[RuCl_2(p\text{-}cymene)]_2$	Piv-OH	22[b]	31[b]	-
4	$[RuCl_2(p\text{-}cymene)]_2$	1-AdCOOH	18[b]	34[b]	-
5	$[RuCl_2(p\text{-}cymene)]_2$	$MesCO_2H$	25[b](23)	40[b]	-
6	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Ac-L-Val	28[b]	35[b]	
7	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Ac-L-Phe	24[b]	38[b]	-
8	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Ac-L-Ile	27[b]	41[b]	-
9	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Ac-L-Gly	25[b]	36[b]	-
10	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Ac-L-Cys	18[b]	38[b]	-
11	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Piv-Val	25[b]	39[b]	-
12	$[RuCl_2(p\text{-}cymene)]_2$	*N*-Piv-Leu	21[b]	33[b]	-
13	$[RuCl_2(p\text{-}cymene)]_2$	PPh_3	-	-	78
14	$[RuCl_2(p\text{-}cymene)]_2$	$AgNTf_2$	28[b]	8[b]	-
15	$[RuCl_2(p\text{-}cymene)]_2$	$AgBH_4$	27[b]	7[b]	
16	$[RuCl_2(p\text{-}cymene)]_2$	$AgSbF_6$	30[b]	-	-
17	$[RuCl_2(p\text{-}cymene)]_2$	$AgNO_3$	36[b]	9[b]	-
18	$[RuCl_2(p\text{-}cymene)]_2$	AgOAc	29[b]	21[b]	
19	$[RuCl_2(p\text{-}cymene)]_2$	AgTFA	19[b]	14[b]	-
20	$[RuCl_2(p\text{-}cymene)]_2$	Ag_2CO_3	35[b]	<5	-
21	$[RuCl_2(p\text{-}cymene)]_2$	$AgNTf_2$+*N*-Ac-L-Ile	20[b]	46[b]	-
22	$[RuCl_2(p\text{-}cymene)]_2$	$AgNTf_2$+$MesCO_2H$	14[b]	54[b]	-
23	$[RuCl_2(p\text{-}cymene)]_2$	$AgNTf_2$+*N*-Piv-Val	33[b]	26[b]	-
24	$Ru_3(CO)_{12}$	-	-	-	-
25	$RuCl_2(PPh_3)_3$	-	-	-	59[b]
26	$RuCl_2$(COD)	-	-	-	-
27	$[Ru(OAc)_2(p\text{-}cymene)]$	-	27	<5	-
28	$[Ru(O_2CMes)_2(p\text{-}cymene)]$	-	58	<5	-
29[c]	**$[Ru(O_2CMes)_2(p\text{-}cymene)]$**	-	**65**	**15**	
30	$[Ru(O_2CMes)_2(p\text{-}cymene)]$	$MesCO_2H$	34[b]	30[b]	
31	$[Ru(O_2CMes)_2(p\text{-}cymene)]$	*N*-Ac-L-Ile	25[b]	39[b]	

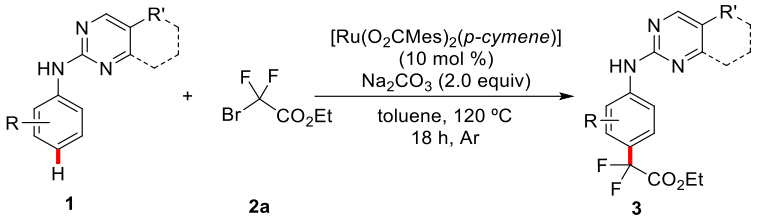
[a] Standard reaction conditions: aniline derivative (0.2 mmol), bromodifluoroacetate (0.6 mmol), $[Ru(O_2CMes)_2(p\text{-}cymene)]$ (0.02 mmol), base (0.4 mmol), and solvent (1 mL) under argon atmosphere, yields of isolated products. [b] GC yield. [c] Na_2CO_3 (0.4 mmol) was used. $MesCO_2H$ = 2,4,6-trimethylbenzoic acid.

Scheme S1. Optimization of auxiliary

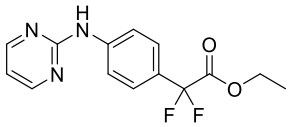


No better results were achieved by changing other *N*-substituted auxiliaries.

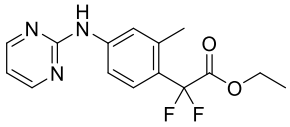
2. General Procedure for Ruthenium(II)-Catalyzed site-selective Difluoromethylation



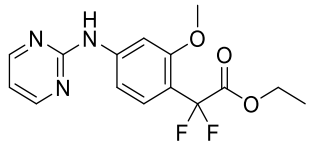
General Procedure : A mixture of **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), [Ru(O_2CMes)$_2$(*p-cymene*)] (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ºC for 18 hours. The reaction mixture cooled to room temperature and concentrated in *vacuo*. The resulting residue was purified by column chromatography (PE/EA) on silica gel to give the product **3** or **4**.



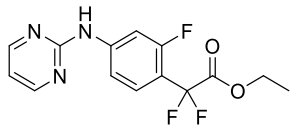
ethyl 2,2-difluoro-2-(4-(pyrimidin-2-ylamino)phenyl)acetate (3a)
amorphous yellow solid, 65% (38 mg), M.p. (from $CHCl_3$): 56-62 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.7 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.62 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 4.7 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.37 (t, *J* = 35.9 Hz), 158.00, 141.96, 128.93, 126.40 (t, *J* = 6.1 Hz), 126.23, 118.63, 113.48 (t, *J* = 251.7 Hz), 113.28, 63.01, 13.88.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.0 .
HRMS(ESI) Calcd for $C_{14}H_{13}F_2N_3O_2$ [M+H$^+$]: 294.1049, found: 294.1042.



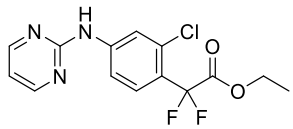
ethyl 2,2-difluoro-2-(2-methyl-4-(pyrimidin-2-ylamino)phenyl)acetate (3b)
amorphous yellow solid, 68% (41.7 mg), M.p. (from $CHCl_3$): 70-74 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 4.8 Hz, 2H), 7.62 – 7.51 (m, 3H), 7.50 (s, 1H), 6.80 (t, *J* = 4.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3 (t, *J* = 35.6 Hz), 159.8 , 158.0 141.6, 137.5 (t, *J* = 3.0 Hz), 127.2 (t, *J* = 8.8 Hz), 124.7 (t, *J* = 23.8 Hz), 121.6 , 116.0 , 114.3 (t, *J* = 249.5 Hz), 113.1, 63.0, 19.9 (t, *J* = 2.6 Hz), 13.9.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.4.
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_2$ [M+H$^+$]: 308.1205, found: 308.1202.



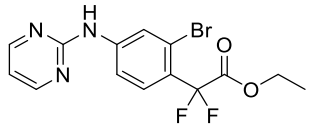
ethyl 2,2-difluoro-2-(2-methoxy-4-(pyrimidin-2-ylamino)phenyl)acetate (3c)
amorphous yellow solid, 52% (33.5 mg), M.p. (from $CHCl_3$): 86-90 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 4.8 Hz, 2H), 7.84 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.80 (t, *J* = 4.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3 (t, *J* = 34.5 Hz), 159.8, 158.0, 157.5, 143.5, 126.9 (t, *J* = 7.3 Hz), 115.5 (t, *J* = 24.7 Hz), 113.3, 112.5 (t, *J* = 247.5 Hz), 110.4, 102.1, 62.6, 55.7, 14.0.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.51.
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_3$ [M+H$^+$]: 324.1154, found: 324.1158.



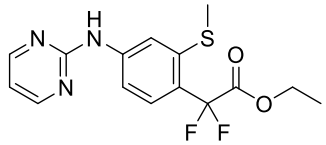
ethyl 2,2-difluoro-2-(2-fluoro-4-(pyrimidin-2-ylamino)phenyl)acetate (3d)
yellow solid, 39% (24.3 mg), M.p. (from $CHCl_3$): 130-136 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 13.5 Hz, 1H), 7.81 (s, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.86 (t, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (t, *J* = 34.6 Hz), 161.6 (t, *J* = 4.8 Hz), 159.4, 159.1 (t, *J* = 4.7 Hz), 158.1, 144.0 (d, *J* = 11.5 Hz), 127.4 (td, *J* = 6.8, 3.8 Hz), 113.9, 113.8 (d, *J* = 2.9 Hz), 111.8 (t, *J* = 250.3 Hz), 106.2 (d, *J* = 26.7 Hz), 63.3, 13.9.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.0 (d, *J* = 7.8 Hz), -112.7 (t, *J* = 7.6 Hz).
HRMS(ESI) Calcd for $C_{14}H_{12}F_3N_3O_2$ [M+H$^+$]: 312.0954, found: 312.0947.



ethyl 2-(2-chloro-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3e)
amorphous yellow oil, 45% (29.4 mg), M.p. (from $CHCl_3$): 68-74°C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 4.0 Hz, 2H), 8.04 (s, 1H), 7.87 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.50 (m, *J* = 8.6, 2.1 Hz, 1H), 6.85 (t, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, *J* = 34.6 Hz), 159.4, 158.0, 142.8, 132.5 (t, *J* = 4.4 Hz), 127.7 (t, *J* = 8.4 Hz), 124.1 (t, *J* = 24.8 Hz), 119.9, 116.4, 113.7, 112.3 (t, *J* = 250.1 Hz), 63.3, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.2.
HRMS(ESI) Calcd for $C_{14}H_{12}ClF_2N_3O_2$ [M+H$^+$]: 328.0659, found: 328.0653.

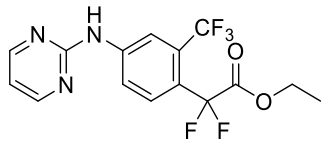


ethyl 2-(2-bromo-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3f)
amorphous yellow solid, 43% (31.8 mg), M.p. (from $CHCl_3$): 115-120 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 4.8 Hz, 2H), 8.18 (s, 1H), 8.05 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 6.85 (t, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4 (t, *J* = 34.6 Hz), 159.4 , 158.1 , 142.8 , 128.1 (t, *J* = 8.8 Hz), 125.8 (t, *J* = 24.6 Hz), 123.3 , 120.8 (t, *J* = 4.2 Hz), 117.0 , 113.8 , 113.0 (t, *J* = 248.7 Hz), 63.4 , 13.9 .
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.6.
HRMS(ESI) Calcd for $C_{14}H_{12}BrF_2N_3O_2$ [M+H$^+$]: 372.0154, found: 372.0159.

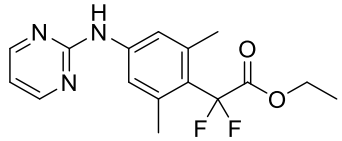


ethyl 2,2-difluoro-2-(2-(methylthio)-4-(pyrimidin-2-ylamino)phenyl)acetate (3g)
amorphous yellow solid, 40% (27.2 mg), M.p. (from $CHCl_3$): 98-102 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.95 (s, 1H), 7.73 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1 (t, *J* = 34.8 Hz), 159.6, 158.0, 142.1, 137.5 (t, *J* = 4.2 Hz), 127.1 (t, *J* = 9.1 Hz), 126.3 (t, *J* = 23.6 Hz), 120.0, 116.1, 113.4, 113.2 (t, *J* = 248.0 Hz), 63.0, 18.2, 13.8.

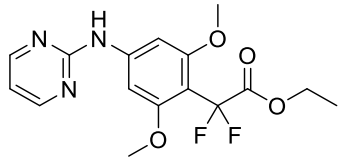
^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.3.
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_2S$ [M+H$^+$]: 340.0926, found: 340.0922.



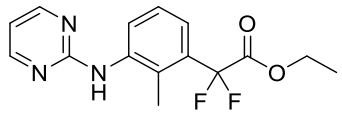
ethyl 2,2-difluoro-2-(4-(pyrimidin-2-ylamino)-2-(trifluoromethyl)phenyl)acetate (3h)
yellow solid, 23% (16.6 mg), M.p. (from $CHCl_3$): 98-100 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 4.9 Hz, 2H), 8.17 – 8.14 (m, 1H), 8.08 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 6.88 (t, *J* = 4.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5 (t, *J* = 35.1 Hz), 159.4, 158.1, 142.2, 129.2 (t, *J* = 10.1 Hz), 128.5 (d, *J* = 32.7 Hz), 123.4 (t, *J* = 26.2 Hz), 123.3 (q, *J* = 273.9 Hz), 120.7, 117.3 (q, *J* = 6.2 Hz), 114.0, 113.0 (t, *J* = 252.2 Hz), 63.3, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.6 (t, *J* = 11.3 Hz), -98.0 (q, *J* = 11.1, 10.4 Hz).
HRMS(ESI) Calcd for $C_{15}H_{12}F_5N_3O_2$ [M+H$^+$]: 362.0922, found: 362.0915.



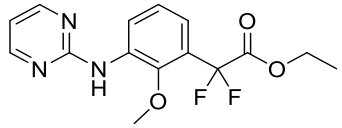
ethyl 2-(2,6-dimethyl-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3j)
amorphous yellow solid, 51% (32.7 mg), M.p. (from $CHCl_3$): 65-70 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.75 – 7.52 (m, 1H), 7.36 (s, 2H), 6.78 (t, *J* = 4.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 4.3 Hz, 6H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6 (t, *J* = 35.9 Hz), 159.8, 158.0, 140.5, 138.9 (t, *J* = 3.2 Hz), 123.5 (t, *J* = 22.8 Hz), 120.9, 120.1, 116.1 (t, *J* = 253.0 Hz), 113.0, 63.0, 22.0 (t, *J* = 5.9 Hz), 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.3.
HRMS(ESI) Calcd for $C_{16}H_{17}F_2N_3O_2$ [M+H$^+$]: 322.1362, found: 322.1360.



ethyl 2-(2,6-dimethoxy-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3k)
amorphous yellow solid, 41% (28.9 mg), M.p. (from $CHCl_3$): 104-110 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.75 (s, 1H), 7.03 (s, 2H), 6.81 (t, *J* = 4.8 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8 (t, *J* = 33.3 Hz), 159.7, 159.6 (t, *J* = 2.6 Hz), 157.9, 143.6, 113.3, 113.3 (t, *J* = 247.6 Hz), 103.4 (t, *J* = 24.0 Hz), 95.3, 62.4, 56.1, 14.0.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.4.
HRMS(ESI) Calcd for $C_{16}H_{17}F_2N_3O_4$ [M+H$^+$]: 354.1260, found: 354.1255.

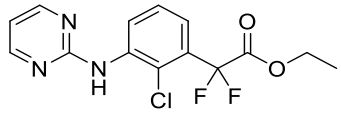


ethyl 2,2-difluoro-2-(3-methyl-4-(pyrimidin-2-ylamino)phenyl)acetate (3l)
amorphous yellow solid, 56% (34.3 mg), M.p. (from $CHCl_3$): 64-68 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 4.4 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 6.72 (t, *J* = 4.0 Hz, 1H), 4.32 (q, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3 (t, *J* = 35.0 Hz), 160.7 , 158.2 , 138.4 , 132.2 (t, *J* = 23.0 Hz), 128.8 (t, *J* = 3.0 Hz), 126.3 , 126.0 , 122.4 (t, *J* = 9.0 Hz), 114.0 (t, *J* = 250.0Hz), 112.7 , 63.3 , 14.0 (t, *J* = 3.0 Hz), 13. 9 .
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.8 .
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_2$ [M+H$^+$]: 308.1205, found: 308.1206.

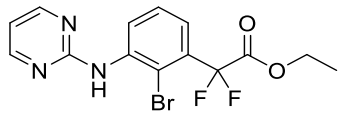


ethyl 2,2-difluoro-2-(3-methoxy-4-(pyrimidin-2-ylamino)phenyl)acetate (3m)
amorphous yellow solid, 40% (25.8 mg), M.p. (from $CHCl_3$): 75-82 °C.

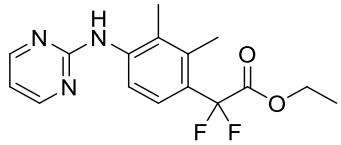
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.57 (m, 1H), 8.47 (d, *J* = 4.8 Hz, 2H), 7.61 (s, 1H), 7.34 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.79 (t, *J* = 4.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7 (t, *J* = 33.7 Hz), 159.7, 158.1, 146.5 (t, *J* = 5.3 Hz), 133.3, 127.1 (t, *J* = 25.2 Hz), 124.7, 122.9, 119.2 (t, *J* = 7.2 Hz), 113.2, 112.0 (t, *J* = 248.3 Hz), 62.9, 62.0, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.0.
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_3$ [M+H$^+$]: 324.1154, found: 324.1161.



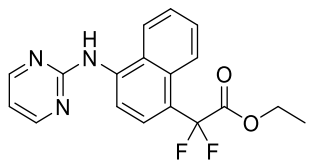
ethyl 2-(3-chloro-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3o)
amorphous yellow solid, 37% (24.2 mg), M.p. (from $CHCl_3$): 68-71 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (t, *J* = 5.0 Hz, 1H), 8.48 (d, *J* = 4.8 Hz, 2H), 7.70 (s, 1H), 7.43 (d, *J* = 5.0 Hz, 2H), 6.84 (t, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2 (t, *J* = 33.9 Hz), 159.4, 158.0, 137.0, 131.4 (t, *J* = 24.4 Hz), 127.2, 122.7, 120.3 (t, *J* = 8.9 Hz), 119.8 (t, *J* = 4.3 Hz), 113.8, 112.2 (t, *J* = 250.7 Hz), 63.4, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.01.
HRMS(ESI) Calcd for $C_{14}H_{12}ClF_2N_3O_2$ [M+H$^+$]: 328.0659, found: 328.0654.



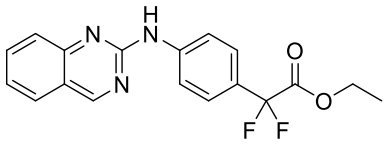
ethyl 2-(3-bromo-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3p)
amorphous yellow solid, 32% (23.7 mg), M.p. (from $CHCl_3$): 79-84 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (dd, *J* = 7.8, 2.0 Hz, 1H), 8.48 (d, *J* = 4.8 Hz, 2H), 7.75 (s, 1H), 7.51 – 7.40 (m, 2H), 6.84 (t, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1 (t, *J* = 33.9 Hz), 159.5, 158.0, 138.1, 133.4 (t, *J* = 24.2 Hz), 127.9, 123.1, 121.2 (t, *J* = 9.5 Hz), 113.8, 112.8 (d, *J* = 249.2 Hz), 111.2 (d, *J* = 4.0 Hz), 63.4, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.2.
HRMS(ESI) Calcd for $C_{14}H_{12}BrF_2N_3O_2$ [M+H$^+$]: 372.0154, found: 372.0161.



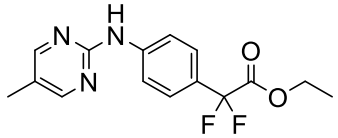
ethyl 2-(2,3-dimethyl-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetate (3q)
amorphous yellow solid, 46% (29.6 mg), M.p. (from $CHCl_3$): 62-66 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 4.8 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.08 (s, 1H), 6.74 (t, *J* = 4.8 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.25 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7 (t, *J* = 35.4 Hz), 160.6, 158.3, 139.5, 136.0 (t, *J* = 2.0 Hz), 129.7, 127.2, 124.3 (t, *J* = 9.6 Hz), 119.9, 113.2 (t, *J* = 250.0 Hz), 112.9, 63.2, 16.8, 14.2, 14.0.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.11.
HRMS(ESI) Calcd for $C_{16}H_{17}F_2N_3O_2$ [M+H$^+$]: 322.1362, found: 322.1361.



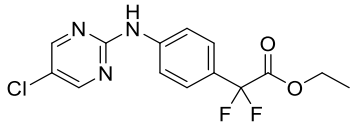
ethyl 2,2-difluoro-2-(4-(pyrimidin-2-ylamino)naphthalen-1-yl)acetate (3r)
yellow solid, 53% (36.3 mg), M.p. (from $CHCl_3$): 155-158 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.36 (d, *J* = 4.9 Hz, 2H), 8.27 (d, *J* = 8.1 Hz, 1H), 8.19 (dd, *J* = 8.1, 4.0 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.58 (dddd, *J* = 17.4, 8.1, 6.8, 1.4 Hz, 2H), 6.72 (t, *J* = 4.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5 (t, *J* = 35.2 Hz), 160.7, 158.2, 137.6, 130.4, 127.4, 127.3, 126.2, 125.4 (t, *J* = 9.6 Hz), 125.0 (t, *J* = 3.1 Hz), 123.9 (t, *J* = 23.6 Hz), 121.9, 117.1, 114.4 (t, *J* = 251.3 Hz), 113.0, 63.2, 13.8.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.4.
HRMS(ESI) Calcd for $C_{18}H_{15}F_2N_3O_2$ [M+H$^+$]: 344.1205, found: 344.1211.



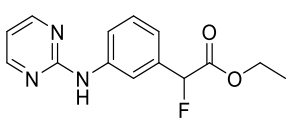
ethyl 2,2-difluoro-2-(4-(quinazolin-2-ylamino)phenyl)acetate (3s)
yellow solid, 51% (35 mg), M.p. (from $CHCl_3$): 132-138 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.69 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.58 (s, 1H), 7.42 – 7.36 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 164.5 (t, *J* = 39.3 Hz), 161.96, 156.35, 151.26, 142.15, 134.63, 128.97, 127.49, 126.5 (t, *J* = 5.7 Hz), 126.13, 124.37, 121.08, 118.36, 113.56 (t, *J* = 251.9 Hz), 63.05, 13.93.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.0.
HRMS(ESI) Calcd for $C_{18}H_{15}F_2N_3O_2$ [M+H$^+$]: 344.1205, found: 344.1208.



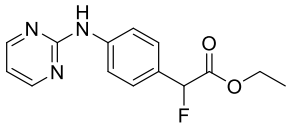
ethyl 2,2-difluoro-2-(4-((5-methylpyrimidin-2-yl)amino)phenyl)acetate (3t)
amorphous yellow solid, 45% (27.5 mg), M.p. (from $CHCl_3$): 58-64 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.24 (t, *J* = 35.9 Hz), 158.05, 157.92, 142.29, 136.25, 126.40 (t, *J* = 6.1 Hz), 125.73, 122.02, 118.13, 113.53 (t, *J* = 251.4 Hz), 62.99, 14.86, 13.89.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.0.
HRMS(ESI) Calcd for $C_{15}H_{15}F_2N_3O_2$ [M+H$^+$]: 308.1205, found: 308.1202.



ethyl 2-(4-((5-chloropyrimidin-2-yl)amino)phenyl)-2,2-difluoroacetate (3u)
amorphous yellow solid, 41% (26.8 mg), M.p. (from $CHCl_3$): 54-58 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.4 (s, 2H), 7.7 (d, *J* = 8.4 Hz, 2H), 7.6 (d, *J* = 8.4 Hz, 2H), 7.4 (s, 1H), 4.3 (q, *J* = 7.2 Hz, 2H), 1.3 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1 (t, *J* = 35.3 Hz), 157.9, 156.3, 139.4, 133.6 (t, *J* = 25.6 Hz), 129.4, 121.5, 121.5, 119.7 (t, *J* = 6.1 Hz), 116.1 (t, *J* = 6.5 Hz), 113.2 (t, *J* = 252.4 Hz), 63.2, 13.9.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.2.
HRMS(ESI) Calcd for $C_{14}H_{12}ClF_2N_3O_2$ [M+H$^+$]: 328.0659, found: 328.0653.

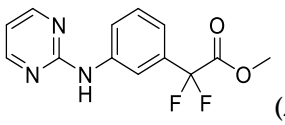


(4w)

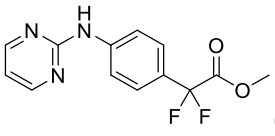


(3w)

ethyl 2-fluoro-2-(3-(pyrimidin-2-ylamino)phenyl)acetate (4w)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 4.8 Hz, 2H), 7.77 (s, 1H), 7.74 (s, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 5.79 (d, *J* = 47.8 Hz, 1H), 4.25 (dd, *J* = 19.9, 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -180.1.
ethyl 2-fluoro-2-(4-(pyrimidin-2-ylamino)phenyl)acetate (3w)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 4.5 Hz, 2H), 7.74 (s, 1H), 7.68 (d, *J* = 4.8 Hz, 2H), 7.43 (d, 2H), 6.77 (s, *J* = 4.8 Hz, 1H), 5.74 (d, *J* = 47.8 Hz, 1H), 4.26 – 4.18 (m, 2H), 1.26 (t, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -175.9.
Mixture (**4w**:**3w** = 5:1) yellow oil, 37% (20.3 mg).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 168.4, 159.9 (d, *J* = 8.1 Hz), 158.0, 139.9, 135.1, 134.9, 129.3, 127.8 (d, *J* = 5.5 Hz), 120.6, 120.6, 120.3, 120.3, 119.2, 117.3, 117.2, 112.9, 89.3 (d, *J* = 185.7 Hz), 89.2 (d, *J* = 184.6 Hz), 61.9, 61.8, 14.0.
HRMS(ESI) Calcd for $C_{14}H_{14}FN_3O_2$ [M+H$^+$]: 276.1143, found: 276.1149.

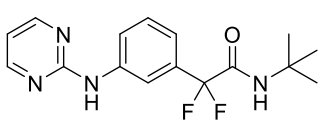


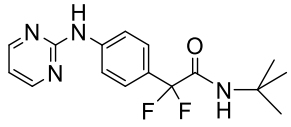
(4x)



(3x)

methyl 2,2-difluoro-2-(3-(pyrimidin-2-ylamino)phenyl)acetate (4x)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.8 Hz, 2H), 8.01 (s, 1H), 7.88 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.26 (s, 1H), 6.78 (t, *J* = 4.8 Hz, 1H), 3.85 (s, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.9.
methyl 2,2-difluoro-2-(4-(pyrimidin-2-ylamino)phenyl)acetate (3x)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.9 Hz, 2H), 8.01 (s, 3H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 6.82 (t, *J* = 4.8 Hz, 1H), 3.87 (s, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.1.
Mixture (**4x**:**3x** = 10:1) yellow oil, 55% (30.6 mg).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7 (t, *J* = 35.7 Hz), 159.8, 158.0, 140.0, 136.2, 133.3 (t, *J* = 25.4 Hz), 129.3, 128.6, 126.4 (t, *J* = 5.9 Hz), 121.8, 119.2 (t, *J* = 6.2 Hz), 118.8, 116.1 (t, *J* = 6.4 Hz), 115.8, 113.3, 113.1, 110.8, 53.6.
HRMS(ESI) Calcd for $C_{13}H_{11}F_2N_3O_2$ [M+H$^+$]: 280.0892, found: 280.0894.

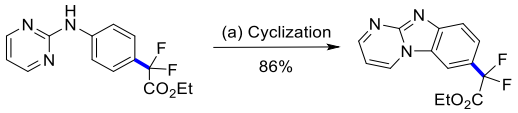

(4y)


(3y)

N-(tert-butyl)-2,2-difluoro-2-(3-(pyrimidin-2-ylamino)phenyl)acetamide (4y)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.90 (s, 1H), 7.88 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.4 Hz, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 6.31 (s, 1H), 1.40 (s, 9H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.8.
N-(tert-butyl)-2,2-difluoro-2-(4-(pyrimidin-2-ylamino)phenyl)acetamide (3y)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.42 (s, 1H), 6.79 (t, *J* = 4.8 Hz, 1H), 6.25 (s, 1H), 1.40 (s, 9H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.8.
Mixture (**4y**:**3y** = 1:1) white solid, 41% (26.2 mg).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 163.13, 159.92, 159.81, 158.17, 158.04, 145.37, 141.83, 139.88, 134.07 (t, *J* = 25.4 Hz), 133.34, 133.25, 129.39, 129.25, 126.61, 126.54, 121.60, 118.77, 117.67, 116.46, 116.39, 114.81, 114.58, 113.98, 113.87, 113.31, 113.24, 113.09, 113.03, 52.21, 52.13, 28.57, 28.49.
HRMS(ESI) Calcd for $C_{16}H_{18}F_2N_4O$ [M+H$^+$]: 321.1521, found: 321.1526.

3. Difluoromethylated aniline derivatives diversified transformations

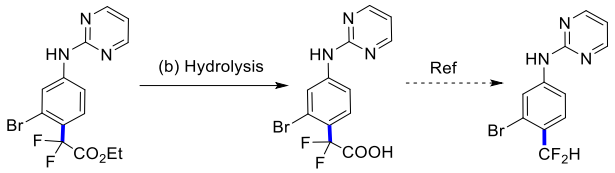
(a) Cyclization (synthesis of difluoromethyl modified imidazo[1,2-*a*]pyrimidine 6)



3a **6**

To an oven-dried flask containing substrates **3a** (0.3 mmol, 88 mg) and PIFA (0.45 mmol, 1.5 equiv.), MeCN (1.5 mL) was added. The reaction mixture was stirred at room temperature, which was monitored by TLC. Upon completion, the mixture was extracted with ethyl acetate (3*10 mL). The combined organic phase was washed with brine and dried with Na_2SO_4. After that, the solid was filtered off through a thin pad of *Celite*, and the filtrate was evaporated in vacuo to give the crude product, which was purified by column chromatography on silica gel (ethyl acetate) to give ethyl 2-(benzo[4,5]imidazo[1,2-a]pyrimidin-7-yl)-2,2-difluoroacetate **6** as light yellow solid (75 mg, 86%), M.p.:218-222 °C.
ethyl 2-(benzo[4,5]imidazo[1,2-a]pyrimidin-7-yl)-2,2-difluoroacetate (6)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 (dd, *J* = 6.8, 2.2 Hz, 1H), 8.89 (dd, *J* = 4.1, 2.1 Hz, 1H), 8.24 (d, *J* = 1.6 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.80 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.06 (dd, *J* = 6.8, 4.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.35 (t, *J* = 36.0 Hz), 156.84, 151.93, 145.92, 133.91, 126.57, 126.49 (t, *J* = 26.2 Hz), 123.66 (t, *J* = 5.4 Hz), 121.04, 112.42 (t, *J* = 251.8 Hz), 109.1 (t, *J* = 7.0 Hz), 107.52, 63.48, 13.98.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.27.
HRMS(ESI) Calcd for $C_{14}H_{11}F_2N_3O_2$ [M+H$^+$]: 292.0892, found: 292.0896.

(b) Hydrolysis (procedure of hydrolysis of ethyl ester 7)



3f 7

To a solution of **3f** (37.2 mg, 0.1 mmol) in MeOH (1 mL) was added K_2CO_3 (1 mL, 1N) at 23 °C. The mixture was stirred at 23 °C for 20 min and poured into 5% HCl (1 mL), and successively extracted with EtOAc (5 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvents in vacuo, the residue was purified by column chromatography (CH_2Cl_2/MeOH = 5/1) to give **7** (34 mg, 98%) as colorless solid.

2-(2-Bromo-4-(pyrimidin-2-ylamino)phenyl)-2,2-difluoroacetic acid (7):

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (d, *J* = 1.6 Hz, 1H), 8.55 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 2.1 Hz, 1H), 7.75 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 6.92 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.69 (t, *J* = 34.6 Hz), 158.25, 142.26, 129.34, 129.08, 128.18 (t, *J* = 8.3 Hz), 122.77, 119.71 (t, *J* = 3.5 Hz), 116.46, 115.60 (t, *J* = 248.7 Hz), 113.33.

^{19}F NMR (376 MHz, DMSO-d_6) δ -96.36.

HRMS(ESI) Calcd for C12H8BrF2N3O2 [M+H$^+$]: 343.9841, found: 343.9846.

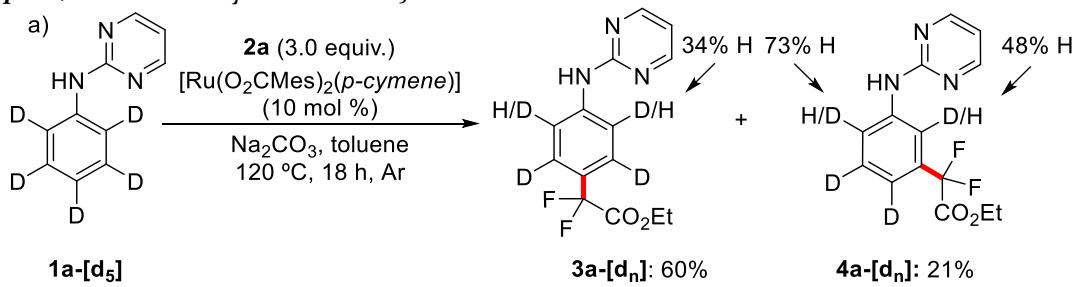
4. Mechanistic Studies

(a) H/D Scrambling

Synthesis[2] of **1a-[*d*$_5$]**:

To a 250 mL three-necked round bottomed flask was charged 2-amino-4-chloroaminopyrimidine (1.42 g, 11 mmol), copper iodide (952 mg, 5 mmol, 50 mol%) and potassium carbonate (2.76 g, 20 mmol). A condenser was equipped and the flask was evacuated and refilled with nitrogen three times. d_5-bromobenzene (1.05 mL, 1.62 mL, 10 mmol), *N,N'*-dimethylethylenediamine (538 μL, 441 mg, 5 mmol, 50 mol%) and 1,4-dioxane (40 mL) were then added *via* septum. The reaction mixture was heated to 100 °C for 72 h. After this time, the reaction mixture was allowed to cool to room temperature and concentrated ammonia solution (20 mL) and brine (80 mL) were added and extracted with EtOAc (3 x 100 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified *via* silica gel column chromatography (EtOAc/Hexanes, 5:95 v:v) to give pure white solid, 33% (706 mg).

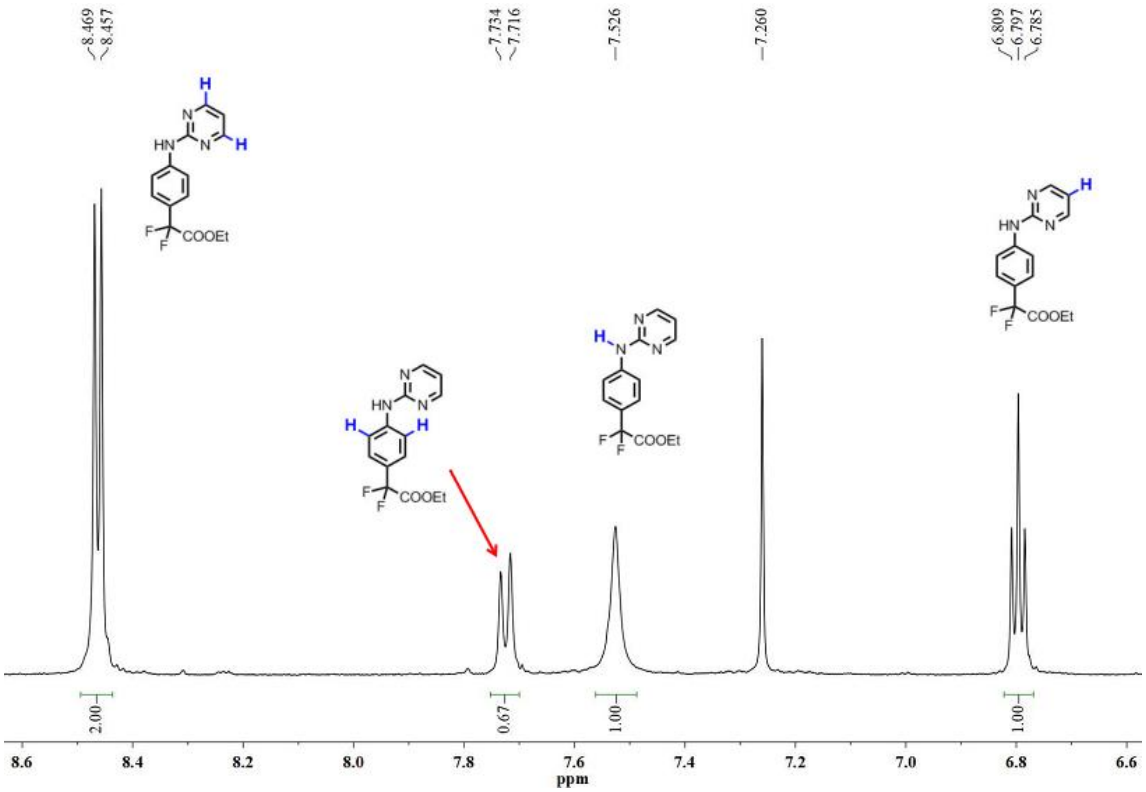
***para*/*meta* C-H Alkylation of 1a-d$_5$**



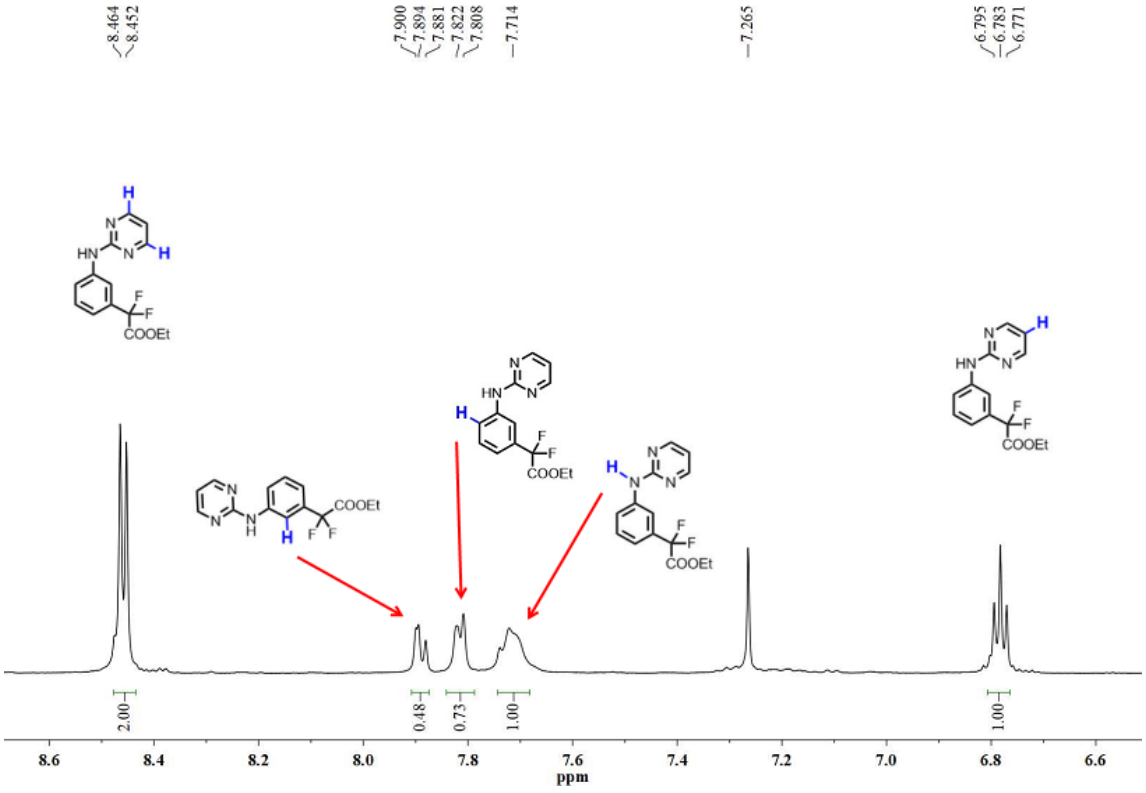
1a-[d$_5$] **3a-[d$_n$]**: 60% **4a-[d$_n$]**: 21%

1a-[*d*$_5$] (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), [Ru(O_2CMes)$_2$(*p-cymene*)] (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) were placed in a 10 mL glass tube sealed under argon atmosphere was heated at 120 °C for 18 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE/EA) on silica gel to give the product **3a-[*d*$_n$]** and **4a-[*d*$_n$]** The D incorporation was determined by ^{1}H-NMR spectroscopy.

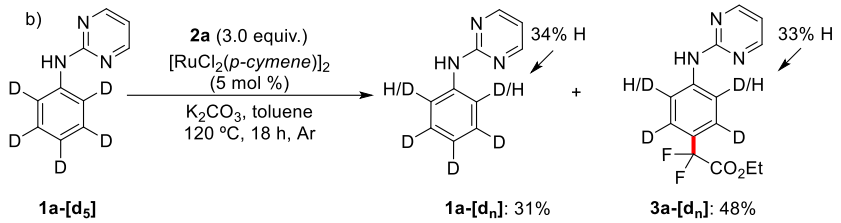
3a-[*d*$_n$] – 34% H in each *ortho* position



4a-[d_n] – 48% and 73% H in *ortho* position

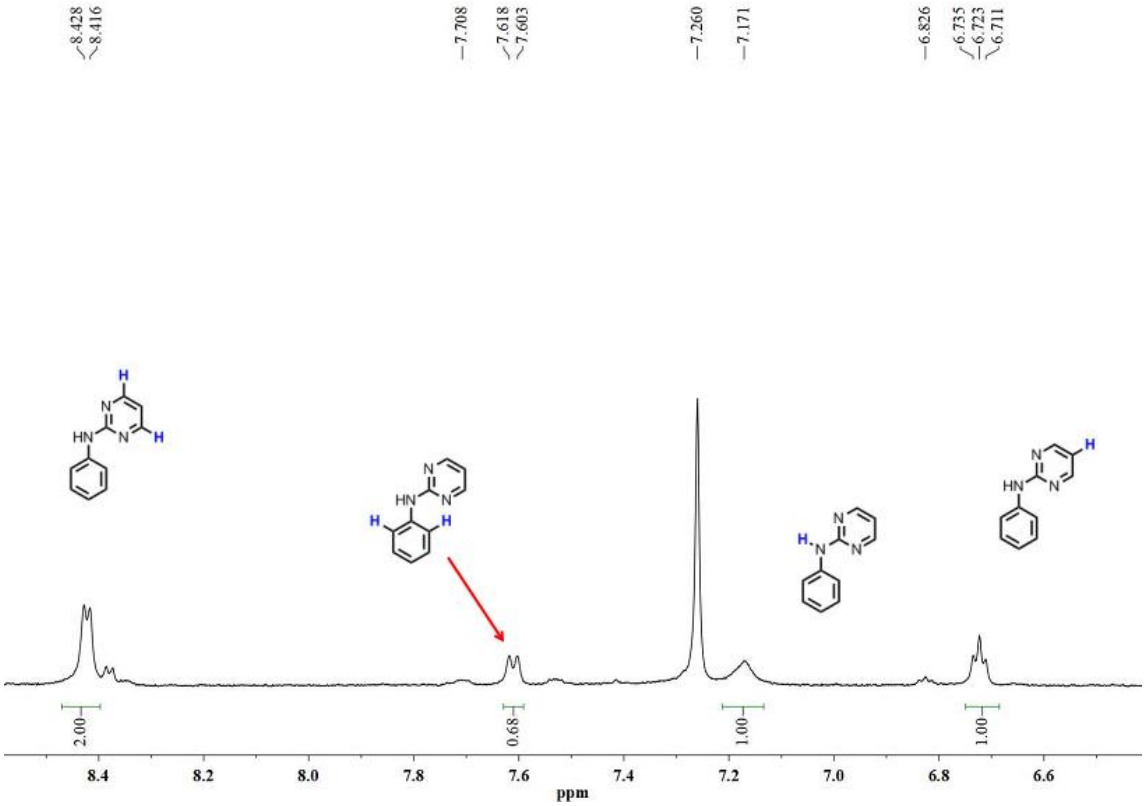


***para*-selective C-H Alkylation of 1a-d_5**

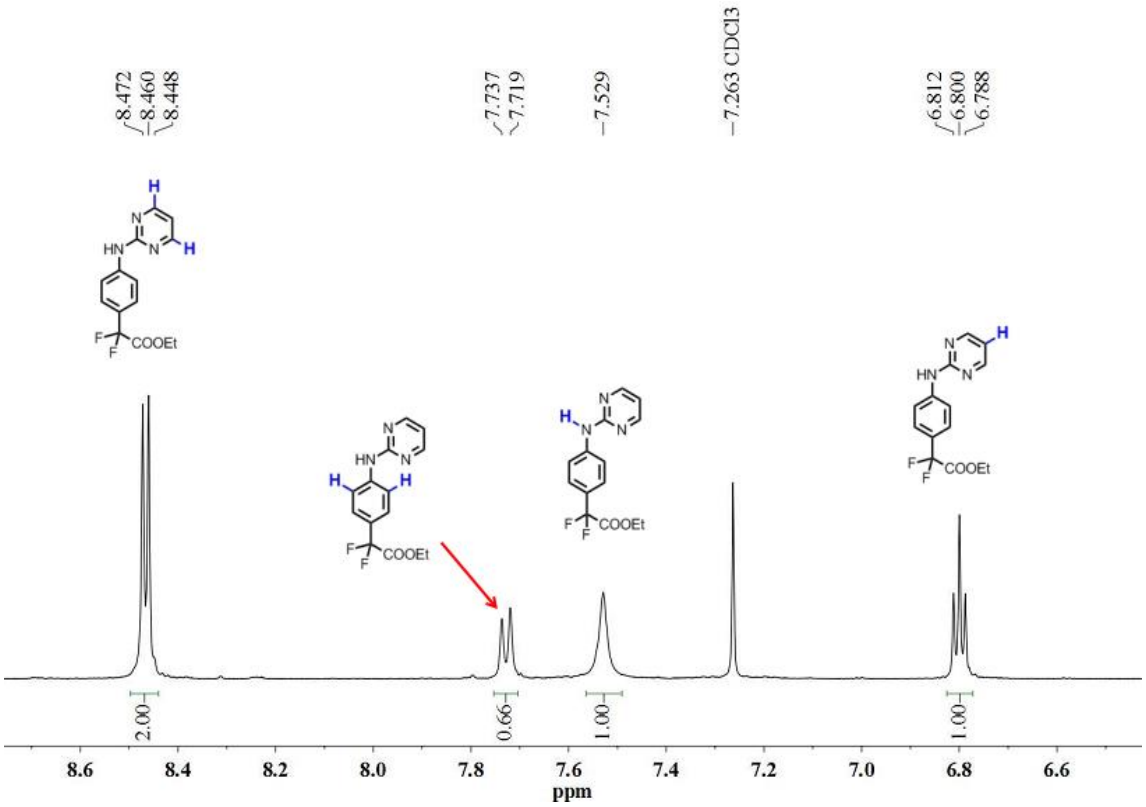


1a-[d_5] (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5 mol %), K_2CO_3 (27.8 mg, 2 equiv.), and toluene (1 mL) were placed in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 18 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE/EA) on silica gel to give **1a-[d_n]** and the product **3a-[d_n]**. The D incorporation was determined by ^{1}H-NMR spectroscopy.

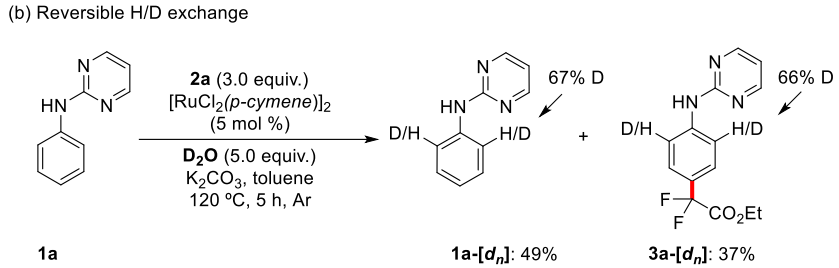
1a-[d_n] – 34% H in each *ortho* position



3a-[d_n] – 34% H in each *ortho* position

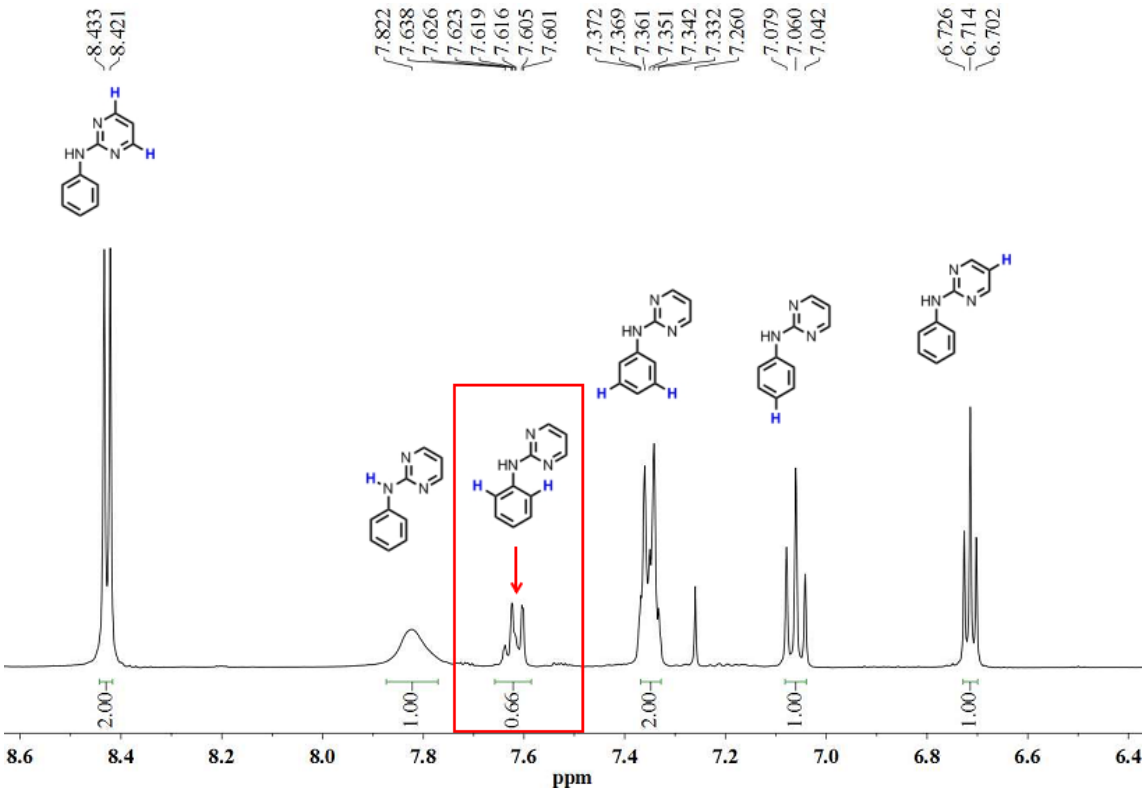


(b) Reversible H/D exchange

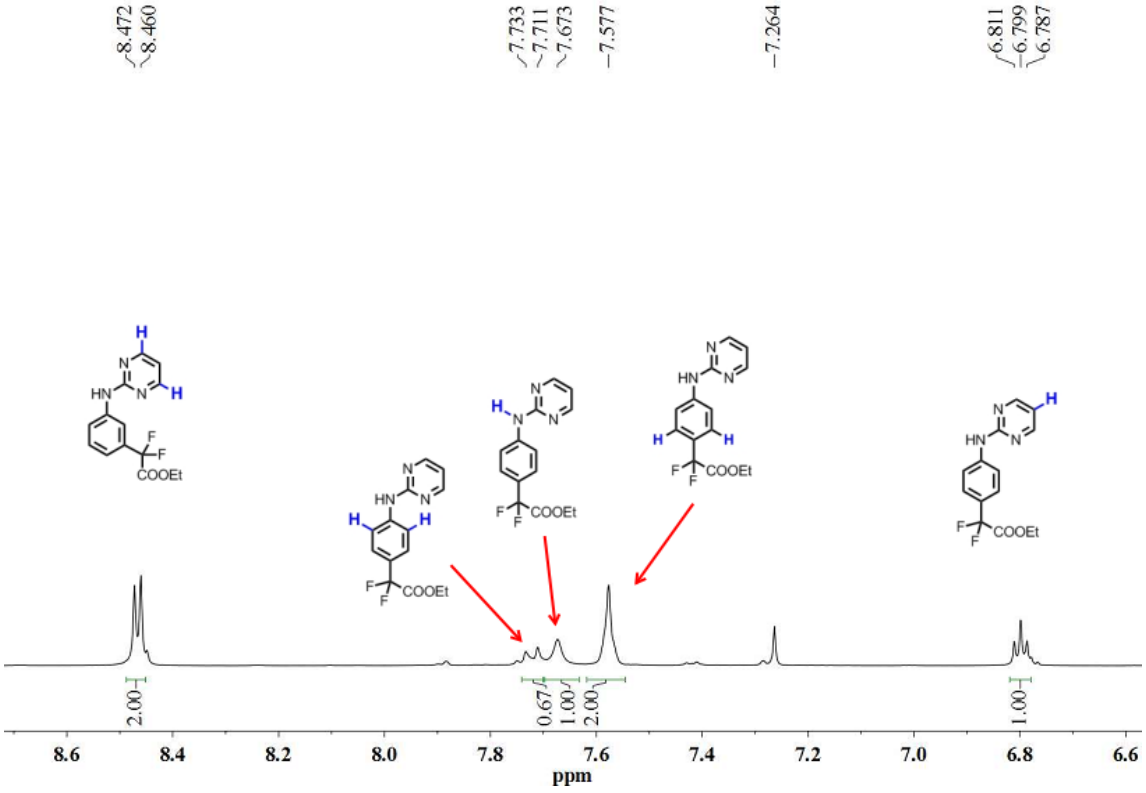


1a (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5 mol %), K_2CO_3 (27.8 mg, 2 equiv.), D_2O (50 μL) and toluene (1 mL) were placed in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 5 hours. At ambient temperature, the reaction mixture was diluted with H_2O (5 mL) and extracted with EtOAc (3*10 mL). The combined organic layer was dried with Na_2SO_4 and concentrated underreduced pressure. The resulting residue was purified by column chromatography (PE/EA) on silica gel to give**1a**-[d_n] and the product **3a**-[d_n]. The D incorporation was determined by ^{1}H-NMR spectroscopy.

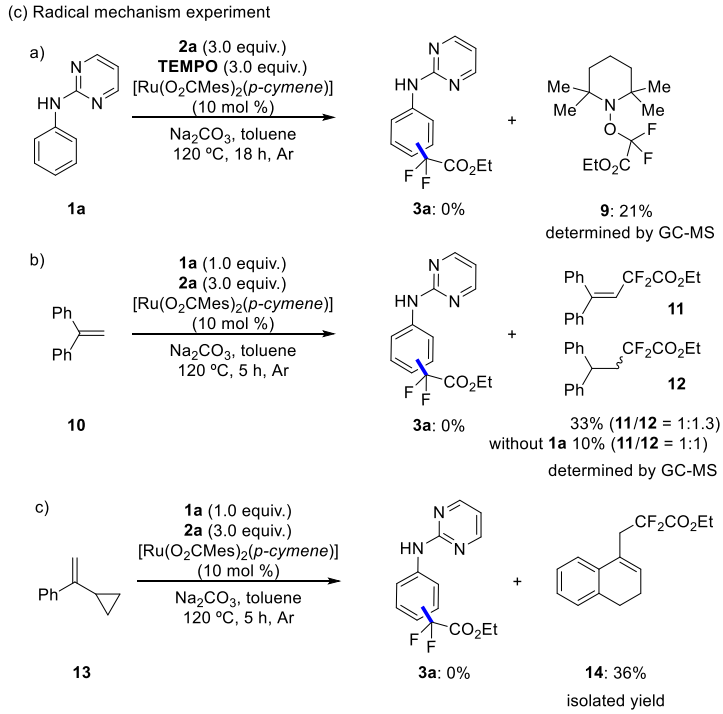
1a-[d_n] – 67% D incorporation in each *ortho* position



3a-[d_n] – 66% D incorporation in each *ortho* position



(c) Radical mechanism experiment



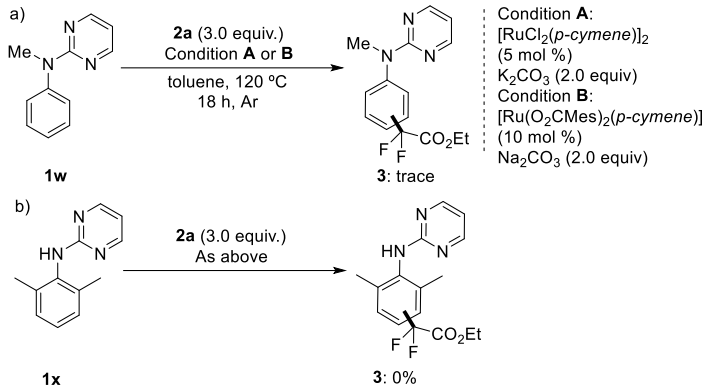
a) A mixture of **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), TEMPO (93.7 mg, 0.6 mmol), $[Ru(O_2CMes)_2(p\text{-}cymene)]$ (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 18 hours. After completion of the reaction, GC-MS was employed to detect the result.

b) A mixture of **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), **10** (34.2 μL, 0.2 mmol), $[Ru(O_2CMes)_2(p\text{-}cymene)]$ (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 5 hours. After completion of the reaction, **11, 12** and the ratio was determined by GC-MS.

c) A mixture of **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), **13** (34.2 μL, 0.2 mmol), $[Ru(O_2CMes)_2(p\text{-}cymene)]$ (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 18 hours. After completion of the reaction, The resulting residue was purified by column chromatography (PE/EA) on silica gel to give the product **14**.
ethyl 3-(3,4-dihydronaphthalen-1-yl)-2,2-difluoropropanoate (14):
colorless oil, 36%.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.09 (m, 4H), 6.06 (t, *J* = 4.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.22 (t, *J* = 15.9 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.25 (td, *J* = 8.0, 4.7 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.03 (t, *J* = 32.7 Hz), 136.29, 133.84, 131.56, 127.58, 127.32 (t, *J* = 4.4 Hz), 127.12, 126.28, 122.81, 115.48 (t, *J* = 252.2 Hz), 62.63, 37.28 (t, *J* = 24.2 Hz), 27.99, 23.16, 13.70.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.25.
Spectra data was consist with the literature.[6]

(d) Control experiment

(d) Control experiments

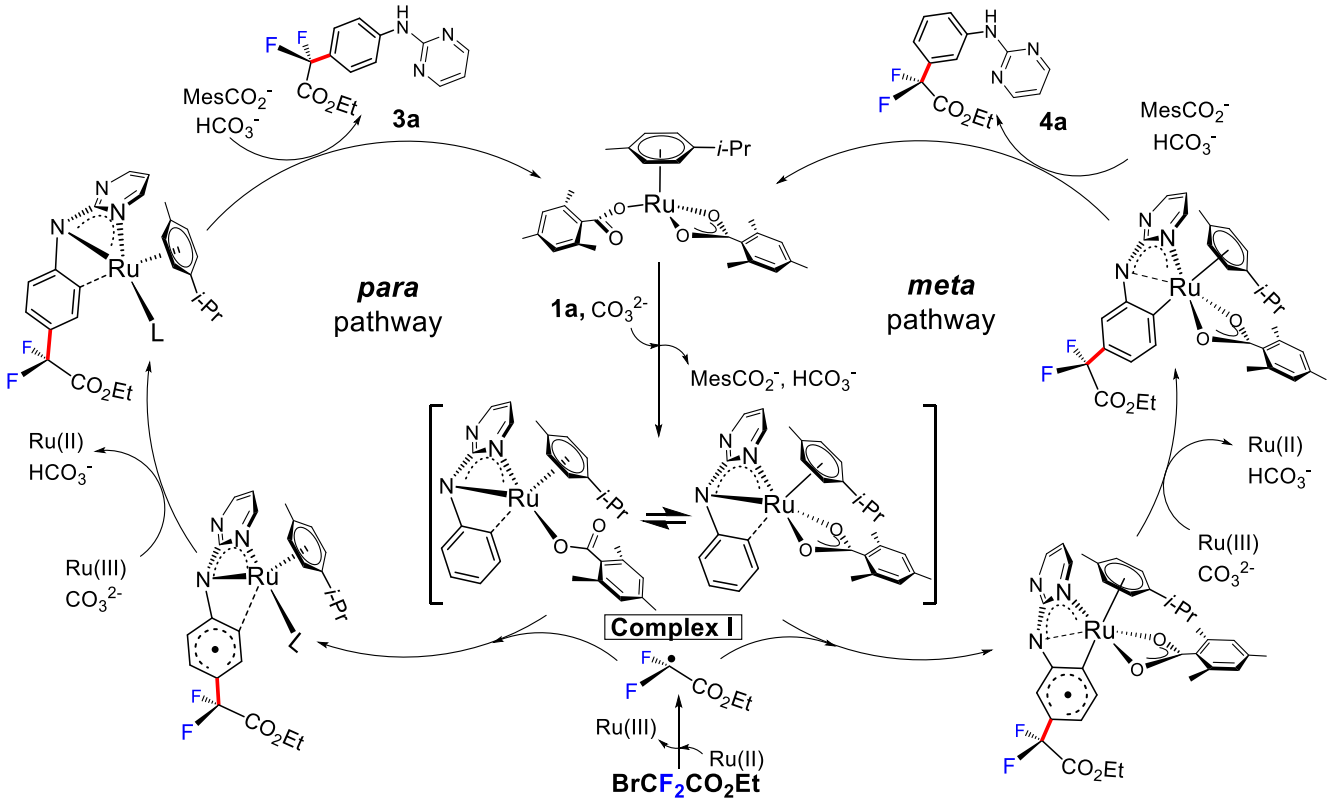


General procedure :

Condition **A**: **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), $[Ru(O_2CMes)_2(p\text{-}cymene)]$ (5.6 mg, 10 mol %), Na_2CO_3 (42.4 mg, 2 equiv.), and toluene (1 mL) were placed in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 18 hours.

Condition **B**: **1** (0.2 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (80 μL, 121.8 mg, 3 equiv.), $[RuCl_2(p\text{-}cymene)]_2$ (6.1 mg, 5 mol %), K_2CO_3 (27.8 mg, 2 equiv.), and toluene (1 mL) were placed in a 10 mL glass tube sealed under argon atmosphere was heated at 120 ℃ for 18 hours.

5. Proposed mechanism



6. Computational Data

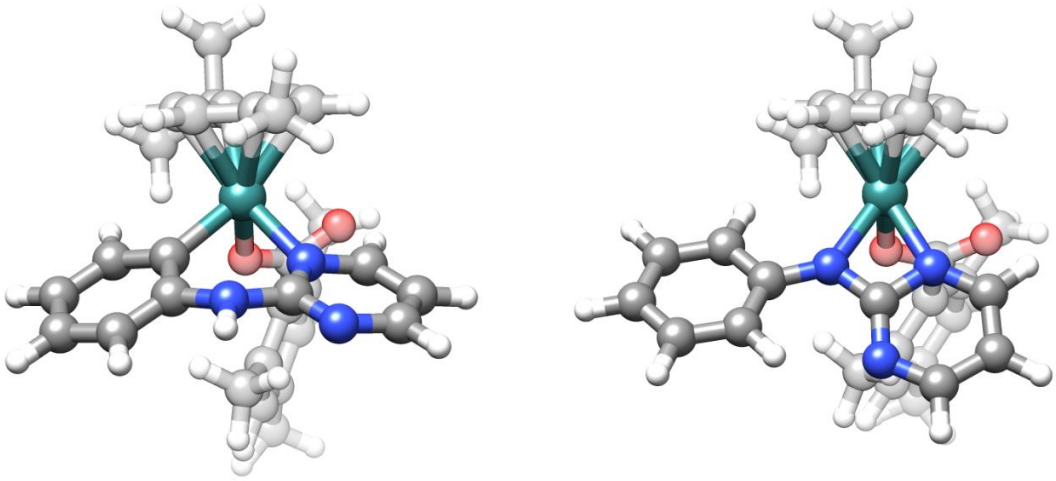
a) Computational Methods[7]

The density functional theory (DFT) calculations are performed by Gaussian 09 program. All geometries are optimized at the B3LYP level with 6-31G(d) basis set (lanl2dz basis set for Ru). Harmonic frequency calculations are performed for stationary points and transition states. Local minima are confirmed without imaginary frequency. Transition states are verified with one imaginary frequency.

b) Results

Regionselecvity

Based on our experimental finds, we speculated that there are two active Ru intermediate isomers A_C and A_N shown in the Figure S1. For A_C, the carbon atom on the phenyl group bonds to the metal center. While, For A_N, the nitrogen atom between the phenyl group and pyrimidine group bonds to the metal center. A_N is 3.6 kcal/mol lower than A_C. Then, we paid attention to the radical addition step, which is consider as the step that determines the regionselecvity. Both the radical addition of $\cdot CF_2CO_2Et$ to A_C and A_N were taken into account. As shown in Figure S2 and Figure S3, four possible transition states and products were located. Reactant B_N is lower than the Reactant B_C. TS_*para*_B_N and *Para*_B_N are the lowest energy transition state and product in respectively. At the same time, B_N, TS_*para*_B_N and *Para*_B_N constitute a reaction pathway in Figure S2. It means the radical addition of $\cdot CF_2CO_2Et$ to the A_N via transition state TS_*para*_B_N leads to the *para*-product *Para*_B_N kinetically and thermodynamically favorable. This consists with the experimental results.



(a) (b)

Figure S1. a) Structure of A_C; b) Structure of A_N.

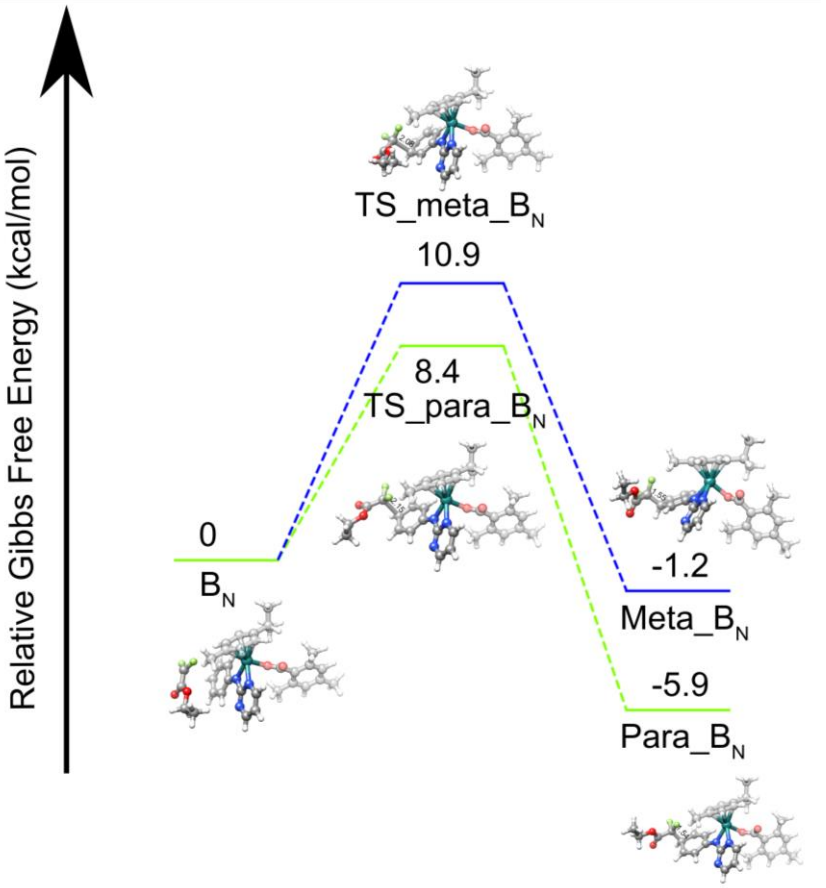


Figure S2. free energy surface of the radical addition of $\cdot CF_2CO_2Et$ to A_N

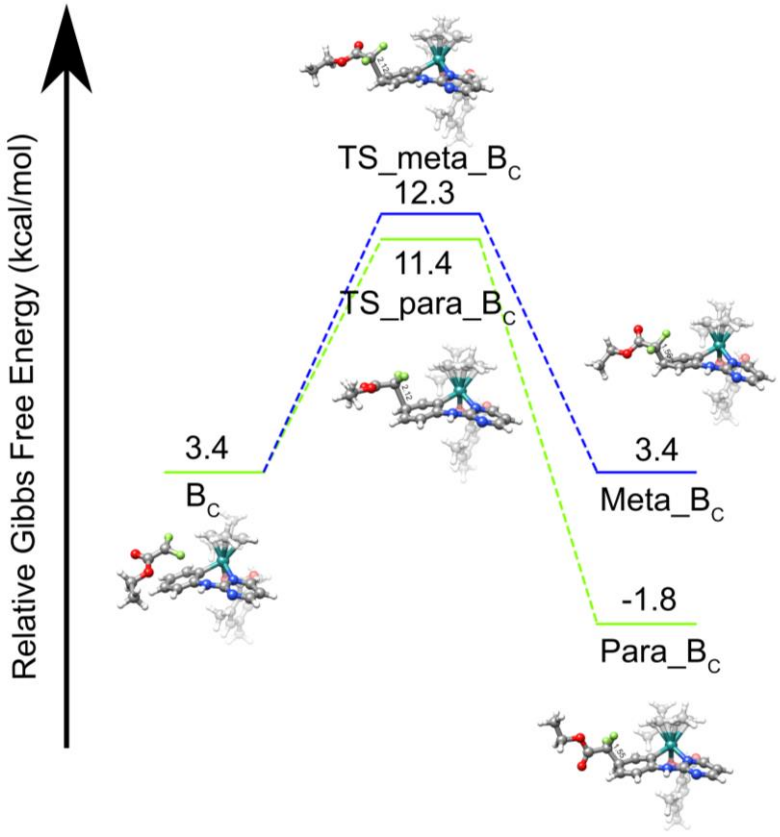
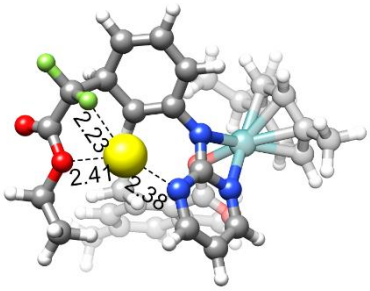


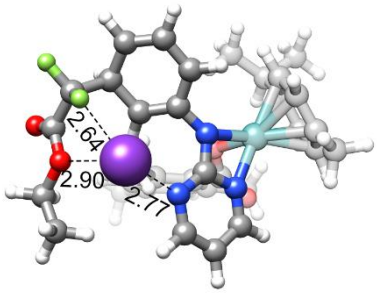
Figure S3. free energy surface of the radical addition of $\cdot CF_2CO_2Et$ to A_C

Yield of *meta*-production

The yield of *meta*-production in presence of Na_2CO_3 is bigger than the yield in the presence of K_2CO_3. We find the cation can interact with the *Meta*_B_N forming a more stable structure shown in the Figure S3. The binding energy of Na^+ is 20.7 kcal/mol bigger than the binding energy of K^+. *Meta*_B_N binding with Na^+ is more stable intermediate.



Binding energy: -61.3 kcal/mol
(a)



Binding energy: -40.6 kcal/mol
(b)

Figure S4 a) Structure of Meta_B_N binding with Na^+; b) Structure of Meta_B_N binding with K^+,

c) Results Optimized Cartesian coordinates at B3LYP/6-31G level of theory

A_C

Atom	X	Y	Z
C	0.727400	2.793700	0.136100
C	1.710200	2.441300	1.085700
C	2.912700	1.785300	0.668300
C	3.173700	1.528600	-0.697400
C	2.201700	1.984200	-1.658200
C	1.021300	2.606400	-1.263100
H	1.530400	2.585100	2.143900
H	3.622800	1.454600	1.419500
H	2.370600	1.777300	-2.711900
H	0.262200	2.847900	-1.997100
C	-0.583100	3.467600	0.512100
H	-1.308300	3.165600	-0.252800
C	4.456700	0.879800	-1.150900
H	5.177600	1.639200	-1.482300
H	4.918600	0.307500	-0.341400
H	4.284400	0.201000	-1.992700
C	-1.145600	3.049000	1.877100
H	-0.498500	3.368000	2.703600
H	-2.121900	3.521400	2.033600

H	-1.279000	1.964800	1.928100
C	-0.412000	4.999700	0.422200
H	-0.050500	5.309900	-0.564800
H	-1.370600	5.499000	0.603300
H	0.303700	5.359000	1.171700
u	1.209100	0.525000	-0.047000
C	-4.575500	-2.008300	0.505700
C	-3.273300	-1.575500	0.225700
C	-3.089200	-0.322000	-0.401600
C	-4.216000	0.466800	-0.735800
C	-5.493300	-0.000300	-0.412300
C	-5.698600	-1.237600	0.204100
H	-4.711300	-2.978600	0.979800
H	-6.353800	0.620900	-0.655200
C	-2.126500	-2.491300	0.599100
H	-1.556700	-2.097300	1.445200
H	-2.508000	-3.483400	0.864400
H	-1.412400	-2.609300	-0.222300
C	-7.093600	-1.733500	0.507600
H	-7.578800	-2.138700	-0.390800
H	-7.080400	-2.530200	1.259000
H	-7.734300	-0.926400	0.881500
C	-4.098800	1.811700	-1.420600
H	-3.655100	1.712500	-2.414200
H	-5.085400	2.278200	-1.512700
H	-3.453800	2.499800	-0.861300
C	-1.698000	0.178400	-0.742700
O	-1.475300	0.721900	-1.839800
O	-0.821400	-0.013800	0.193700
N	2.807400	-2.360400	0.286900
H	3.406900	-3.173700	0.354700
C	2.256000	-1.886600	1.507700
C	1.476500	-0.717900	1.567900
C	2.537800	-2.650900	2.651000
C	0.938800	-0.398200	2.826100
C	2.018700	-2.281400	3.888200
H	3.153800	-3.545100	2.562800

C	1.201300	-1.153500	3.972600
H	0.293100	0.470900	2.912900
H	2.239300	-2.877700	4.769200
H	0.768700	-0.860200	4.926100
C	2.302100	-2.219500	-0.965000
C	2.200400	-3.080200	-3.079700
C	0.869400	-1.218100	-2.474600
C	1.213100	-2.155900	-3.435700
H	2.568200	-3.816200	-3.793100
H	0.127600	-0.441100	-2.640600
H	0.749500	-2.151100	-4.414800
N	1.439000	-1.210300	-1.248100
N	2.734900	-3.128000	-1.866100

A_N

Atom	X	Y	Z
C	-0.605900	2.770500	-0.789100
C	-1.798000	2.229900	-1.317200
C	-2.902900	1.914700	-0.458100
C	-2.872400	2.184800	0.929200
C	-1.637700	2.696100	1.455200
C	-0.537700	3.004500	0.624400
H	-1.868300	1.987400	-2.369800
H	-3.772200	1.424700	-0.885700
H	-1.530300	2.810200	2.529900
H	0.399800	3.307500	1.073400
C	0.600300	3.091900	-1.655400
H	1.476800	3.032600	-0.998600
C	-4.047700	1.899300	1.826300
H	-4.641900	2.809100	1.983000
H	-4.703900	1.140600	1.389700
H	-3.720000	1.543000	2.808100
C	0.824800	2.106800	-2.811600
H	0.020200	2.155600	-3.555800
H	1.756900	2.357200	-3.330000
H	0.903800	1.082900	-2.436100
C	0.486800	4.546400	-2.160500

H	0.373200	5.255600	-1.332700
H	1.386900	4.821300	-2.721500
H	-0.376000	4.664000	-2.827100
Ru	-1.122400	0.830000	0.359900
C	4.391500	-2.155000	-0.583600
C	3.150900	-1.641900	-0.190400
C	3.079800	-0.306600	0.270600
C	4.252300	0.481300	0.327500
C	5.464000	-0.072100	-0.100900
C	5.559400	-1.388900	-0.554300
H	4.442700	-3.186300	-0.928300
H	6.359900	0.545500	-0.072600
C	1.945700	-2.555400	-0.259400
H	1.245600	-2.242100	-1.038700
H	2.261800	-3.583000	-0.467600
H	1.381400	-2.561200	0.678800
C	6.886600	-1.978100	-0.973000
H	7.339400	-2.560300	-0.158800
H	6.774100	-2.654700	-1.827800
H	7.602200	-1.196900	-1.251200
C	4.255700	1.909900	0.828500
H	4.045400	1.952600	1.900700
H	5.228000	2.376800	0.638400
H	3.485700	2.520200	0.342700
C	1.767000	0.301700	0.720900
O	1.704600	0.998900	1.740100
O	0.763700	0.039400	-0.075800
N	-1.821700	-1.165100	0.009400
C	-2.324200	-1.890600	-1.072500
C	-2.995400	-3.125500	-0.939100
C	-2.185000	-1.344600	-2.363200
C	-3.507900	-3.768900	-2.064200
H	-3.093800	-3.572600	0.041300
C	-2.701500	-1.999200	-3.478900
H	-1.643300	-0.411100	-2.475200
C	-3.372000	-3.216300	-3.339800
H	-4.021700	-4.719000	-1.937200

H	-2.572200	-1.556700	-4.463900
H	-3.775700	-3.727300	-4.209400
C	-1.542200	-1.602000	1.240600
C	-0.616200	-0.685800	3.192800
C	-1.234900	-2.976600	3.021400
C	-0.701600	-1.939200	3.797900
H	-0.184500	0.182900	3.678700
H	-1.326700	-3.977800	3.441700
H	-0.362500	-2.101700	4.813700
N	-1.643400	-2.843100	1.759500
N	-1.069200	-0.519700	1.955600

B_N

Atom	X	Y	Z
C	1.240900	3.072700	-0.298600
C	0.014400	2.864100	-0.978400
C	-1.196800	2.663200	-0.245700
C	-1.242500	2.725900	1.170800
C	0.014300	2.890700	1.834600
C	1.227700	3.092500	1.127900
H	-0.003900	2.787600	-2.058000
H	-2.100800	2.415200	-0.791000
H	0.046500	2.825300	2.918600
H	2.162500	3.140200	1.672100
C	2.559500	3.252900	-1.030600
H	3.335400	2.867000	-0.358600
C	-2.527800	2.544100	1.935200
H	-2.997200	3.515700	2.139000
H	-3.239300	1.935600	1.370800
H	-2.345200	2.053900	2.896900
C	2.656100	2.475300	-2.351300
H	1.971900	2.872300	-3.111500
H	3.670600	2.564200	-2.755000
H	2.439100	1.415200	-2.193700
C	2.819500	4.760300	-1.240800
H	2.803000	5.310800	-0.293400
H	3.801100	4.910700	-1.703700

H	2.063400	5.200700	-1.901900
Ru	0.254000	1.135700	0.500000
C	4.779400	-3.020600	-1.047300
C	3.734200	-2.223000	-0.566900
C	4.041000	-0.966600	0.006300
C	5.388400	-0.539500	0.079600
C	6.392300	-1.364600	-0.437200
C	6.113500	-2.612800	-0.998200
H	4.537800	-3.991200	-1.476600
H	7.424500	-1.021600	-0.392200
C	2.324800	-2.767100	-0.667100
H	1.717100	-2.189500	-1.368400
H	2.346400	-3.810300	-0.999200
H	1.803200	-2.732300	0.294900
C	7.222600	-3.504800	-1.505400
H	7.611900	-4.150400	-0.706100
H	6.874000	-4.161200	-2.310300
H	8.066400	-2.919000	-1.886600
C	5.799600	0.784400	0.688500
H	5.587900	0.809900	1.760400
H	6.869500	0.957500	0.531100
H	5.254200	1.627000	0.247700
C	2.955200	-0.074400	0.574500
O	3.126100	0.532100	1.639200
O	1.878100	-0.006700	-0.164200
N	-0.915300	-0.600900	0.024100
C	-1.630900	-1.063200	-1.080000
C	-2.483000	-2.189900	-1.051000
C	-1.520600	-0.346800	-2.288300
C	-3.200100	-2.557100	-2.189700
H	-2.561300	-2.770800	-0.141700
C	-2.241700	-0.725500	-3.418100
H	-0.843900	0.500400	-2.328100
C	-3.095100	-1.830500	-3.378200
H	-3.856200	-3.422500	-2.141500
H	-2.132300	-0.153300	-4.336300
H	-3.663300	-2.123300	-4.256200

C	-0.677000	-1.220300	1.183200
C	0.572800	-0.767400	3.118100
C	-0.609600	-2.807800	2.809200
C	0.221200	-2.022300	3.617000
H	1.236400	-0.083300	3.636700
H	-0.924800	-3.793800	3.149800
H	0.578900	-2.370000	4.578400
N	-1.058800	-2.444500	1.605900
N	0.095500	-0.367300	1.946300
C	-5.667600	-0.645400	-0.554700
O	-6.442900	-1.475800	-0.993500
O	-5.174600	-0.600100	0.700300
C	-5.220000	0.499500	-1.330800
C	-5.602200	-1.679700	1.565900
C	-4.814200	-1.570800	2.856800
H	-5.422300	-2.629500	1.054600
H	-6.681500	-1.585700	1.729100
H	-5.137400	-2.354700	3.550700
H	-3.743800	-1.697100	2.667300
H	-4.976900	-0.599800	3.336300
F	-4.236500	1.290900	-0.922300
F	-5.405500	0.533100	-2.630100

TS_meta_B_N

Atom	X	Y	Z
C	-1.270800	3.025900	0.251600
C	-0.116000	2.771300	1.041000
C	1.138100	2.490200	0.418700
C	1.305100	2.508000	-0.991500
C	0.118400	2.712600	-1.762200
C	-1.138300	3.006500	-1.166200
H	-0.191600	2.717800	2.119300
H	1.979700	2.201300	1.041500
H	0.172800	2.612800	-2.842700
H	-2.020300	3.092900	-1.788300
C	-2.634300	3.296000	0.864200
H	-3.369500	2.891800	0.157800

C	2.641200	2.237400	-1.632400
H	3.172700	3.178600	-1.826200
H	3.273800	1.620000	-0.987800
H	2.519800	1.720400	-2.589800
C	-2.862200	2.612600	2.220200
H	-2.223000	3.036600	3.004500
H	-3.900200	2.764200	2.535700
H	-2.677400	1.537000	2.150700
C	-2.852700	4.821700	0.959500
H	-2.747700	5.308800	-0.016400
H	-3.859000	5.033500	1.337800
H	-2.130900	5.280100	1.646300
u	-0.321600	1.021200	-0.399400
C	-4.989900	-3.022000	0.990700
C	-3.914900	-2.247700	0.539700
C	-4.174600	-0.970900	-0.009200
C	-5.506100	-0.502100	-0.096300
C	-6.542700	-1.305300	0.390000
C	-6.309500	-2.568500	0.938400
H	-4.785100	-4.011500	1.395600
H	-7.564000	-0.933600	0.328500
C	-2.523100	-2.836400	0.630700
H	-1.892900	-2.277900	1.327500
H	-2.573700	-3.879400	0.960300
H	-2.009100	-2.816300	-0.336500
C	-7.445700	-3.408200	1.474200
H	-7.629500	-3.199300	2.537100
H	-8.380400	-3.207500	0.939000
H	-7.228700	-4.478600	1.388200
C	-5.861500	0.841800	-0.695500
H	-5.592600	0.886700	-1.753700
H	-6.934500	1.033700	-0.589800
H	-5.325500	1.662800	-0.204200
C	-3.049600	-0.107800	-0.546400
O	-3.158300	0.475300	-1.631900
O	-2.009000	-0.041000	0.242300
N	0.782300	-0.710700	0.173600

C	1.652200	-0.995000	1.222800
C	2.797200	-1.783400	1.091600
C	1.372100	-0.403000	2.479300
C	3.762000	-1.832000	2.145400
H	2.994900	-2.286900	0.154500
C	2.233100	-0.585300	3.567700
H	0.455100	0.168200	2.585100
C	3.403400	-1.312900	3.432500
H	4.509200	-2.624000	2.113000
H	1.966600	-0.159800	4.532200
H	4.080600	-1.442200	4.270200
C	0.626300	-1.354400	-0.985800
C	-0.583700	-1.003400	-2.962200
C	0.679900	-2.981700	-2.565200
C	-0.173300	-2.260400	-3.409700
H	-1.254300	-0.358100	-3.520500
H	1.051800	-3.958500	-2.873500
H	-0.495600	-2.653100	-4.366200
N	1.086200	-2.564200	-1.363600
N	-0.151000	-0.548700	-1.792600
C	5.884900	-1.004100	0.380500
O	6.825300	-1.763600	0.505700
O	5.270600	-0.706900	-0.782700
C	5.164100	-0.414900	1.541100
C	5.786200	-1.391400	-1.950700
C	4.817000	-1.143900	-3.091000
H	5.886600	-2.455200	-1.716900
H	6.786800	-1.002300	-2.167400
H	5.176500	-1.644600	-3.996800
H	3.824600	-1.537000	-2.847700
H	4.726000	-0.073700	-3.303800
F	4.462500	0.706800	1.289200
F	5.946500	-0.235100	2.612300

Meta_B_N

Atom	X	Y	Z
C	1.622100	3.049500	-0.478700

C	0.607700	2.707700	-1.428100
C	-0.741100	2.551500	-1.016700
C	-1.155600	2.760300	0.333600
C	-0.120100	3.029800	1.269800
C	1.241100	3.213800	0.874200
H	0.871400	2.504200	-2.457700
H	-1.473700	2.209600	-1.741700
H	-0.368100	3.077100	2.326500
H	2.001500	3.375900	1.628700
C	3.080400	3.222200	-0.868700
H	3.664700	2.837700	-0.024800
C	-2.599300	2.620200	0.741300
H	-3.125000	3.577000	0.622800
H	-3.121500	1.876200	0.131500
H	-2.684700	2.323100	1.791600
C	3.494300	2.441700	-2.124900
H	3.024300	2.846600	-3.030000
H	4.578000	2.521100	-2.264200
H	3.237400	1.382500	-2.036800
C	3.388300	4.727400	-1.025800
H	3.155100	5.287300	-0.113400
H	4.451200	4.871600	-1.249800
H	2.808800	5.163900	-1.848500
Ru	0.470600	1.160600	0.231200
C	4.852600	-3.324400	-0.604200
C	3.832400	-2.429300	-0.262800
C	4.179700	-1.125900	0.164300
C	5.543200	-0.754700	0.242700
C	6.522700	-1.680500	-0.131600
C	6.202700	-2.972500	-0.553100
H	4.579000	-4.328500	-0.923200
H	7.568300	-1.381300	-0.085800
C	2.402400	-2.919400	-0.345700
H	1.844300	-2.408000	-1.134200
H	2.383400	-3.996300	-0.543700
H	1.854800	-2.739900	0.585400
C	7.283000	-3.966900	-0.910200

H	7.584100	-4.560000	-0.035700
H	6.942600	-4.672000	-1.676700
H	8.181700	-3.465100	-1.285600
C	5.997800	0.612900	0.706100
H	5.715300	0.792500	1.746200
H	7.084900	0.703800	0.609300
H	5.540700	1.417000	0.118100
C	3.115700	-0.121600	0.564300
O	3.265600	0.603000	1.556600
O	2.082200	-0.095200	-0.235000
N	-0.738800	-0.566200	-0.061800
C	-1.674300	-0.933400	-1.031100
C	-2.893300	-1.500200	-0.733500
C	-1.334300	-0.652300	-2.391400
C	-3.945500	-1.736900	-1.780300
H	-3.124800	-1.769800	0.290400
C	-2.240200	-0.953900	-3.432700
H	-0.349700	-0.250800	-2.606400
C	-3.480700	-1.472500	-3.184200
H	-4.335900	-2.766500	-1.700400
H	-1.932600	-0.773700	-4.460500
H	-4.172800	-1.684600	-3.992200
C	-0.604900	-1.035100	1.181600
C	0.646000	-0.465500	3.079100
C	-0.729400	-2.406800	2.981700
C	0.170500	-1.616200	3.708900
H	1.358000	0.215400	3.533700
H	-1.150200	-3.305600	3.431800
H	0.480300	-1.880200	4.712700
N	-1.124800	-2.148700	1.733900
N	0.225500	-0.164400	1.855700
C	-5.837200	-1.222100	-0.115800
O	-6.263500	-2.332700	0.105600
O	-5.841200	-0.199800	0.745300
C	-5.191600	-0.861000	-1.468000
C	-6.424200	-0.481700	2.044700
C	-6.339600	0.789900	2.866300

H	-5.871000	-1.309000	2.499800
H	-7.456900	-0.811800	1.896400
H	-6.773300	0.618000	3.857500
H	-5.298700	1.103700	2.995600
H	-6.890000	1.604400	2.385000
F	-4.870700	0.464800	-1.511300
F	-6.150500	-1.073800	-2.425100

TS_para_B_N

Atom	X	Y	Z
C	-1.418600	2.930800	0.267700
C	-0.159300	2.589000	0.827700
C	0.969600	2.350400	-0.014700
C	0.901500	2.490400	-1.425000
C	-0.391500	2.768600	-1.969800
C	-1.524400	3.022100	-1.150400
H	-0.056900	2.446800	1.895700
H	1.896500	2.005400	0.434200
H	-0.518400	2.762700	-3.048900
H	-2.494300	3.171900	-1.607900
C	-2.647800	3.184700	1.123500
H	-3.512800	2.899100	0.512700
C	2.109300	2.271700	-2.298000
H	2.604400	3.226700	-2.517700
H	2.837400	1.623500	-1.801400
H	1.831900	1.812700	-3.252400
C	-2.697000	2.362800	2.419500
H	-1.911700	2.662700	3.124200
H	-3.657300	2.527800	2.920400
H	-2.598200	1.294700	2.208100
C	-2.752100	4.698600	1.412000
H	-2.772200	5.287300	0.488200
H	-3.670500	4.911000	1.970400
H	-1.903300	5.043100	2.014900
u	-0.646700	0.970100	-0.702400
C	-5.250500	-2.909400	1.258900
C	-4.210300	-2.186100	0.665200

C	-4.487400	-0.907600	0.125900
C	-5.801100	-0.386900	0.194500
C	-6.799300	-1.141200	0.820600
C	-6.550000	-2.406900	1.354500
H	-5.033300	-3.896800	1.662700
H	-7.803400	-0.726200	0.886200
C	-2.839900	-2.827800	0.612900
H	-2.122400	-2.299500	1.246200
H	-2.898900	-3.870100	0.943600
H	-2.421900	-2.819900	-0.399300
C	-7.655000	-3.219600	1.988300
H	-8.110500	-3.907600	1.262900
H	-7.280100	-3.828700	2.818400
H	-8.455000	-2.577800	2.373000
C	-6.181500	0.963700	-0.374200
H	-6.095100	0.972600	-1.463800
H	-7.210300	1.215900	-0.096000
H	-5.527400	1.763700	-0.009000
C	-3.405900	-0.084500	-0.544700
O	-3.637500	0.546500	-1.582800
O	-2.260200	-0.097800	0.086400
N	0.464700	-0.835500	-0.434800
C	1.475500	-1.219400	0.421500
C	2.538900	-2.087400	0.052900
C	1.484700	-0.663600	1.726600
C	3.612300	-2.266400	0.899400
H	2.491100	-2.603700	-0.897900
C	2.550700	-0.857800	2.578200
H	0.616200	-0.093500	2.043000
C	3.721200	-1.539500	2.125100
H	4.424500	-2.922200	0.597400
H	2.537400	-0.426000	3.574400
H	4.456700	-1.856200	2.860700
C	0.089300	-1.387300	-1.599200
C	-1.359900	-0.821100	-3.348100
C	-0.197900	-2.898500	-3.263700
C	-1.099600	-2.061400	-3.932800

H	-2.059100	-0.100700	-3.759200
H	0.052800	-3.873400	-3.680100
H	-1.576200	-2.360300	-4.858400
N	0.394500	-2.595500	-2.106500
N	-0.739000	-0.482000	-2.224100
C	6.285700	-0.320300	1.319100
O	7.113300	-0.525700	2.188200
O	6.427400	-0.647900	0.015700
C	4.921200	0.170500	1.602300
C	7.678700	-1.284800	-0.327800
C	7.624300	-1.626600	-1.805100
H	7.806900	-2.174200	0.297800
H	8.499400	-0.598200	-0.095200
H	8.559100	-2.110400	-2.109000
H	6.796200	-2.310200	-2.018100
H	7.489900	-0.724400	-2.410400
F	4.263900	0.748100	0.575900
F	4.832000	0.943000	2.694300

Para_B_N

Atom	X	Y	Z
C	1.234200	2.985600	-0.359000
C	0.063900	2.499800	-1.018100
C	-1.105500	2.184500	-0.274100
C	-1.179200	2.368700	1.137000
C	0.022500	2.781100	1.779700
C	1.198700	3.128300	1.050400
H	0.075700	2.312800	-2.083900
H	-1.954000	1.740600	-0.787000
H	0.050400	2.818000	2.865200
H	2.101300	3.400400	1.584200
C	2.504800	3.340900	-1.111700
H	3.335500	3.100300	-0.438200
C	-2.439900	2.060900	1.902400
H	-3.052900	2.965100	2.012500
H	-3.042600	1.312100	1.380000
H	-2.214200	1.686900	2.906400

C	2.707700	2.551900	-2.413900
H	1.968600	2.826800	-3.176700
H	3.695700	2.779100	-2.829000
H	2.648500	1.474400	-2.236400
C	2.525800	4.862900	-1.374600
H	2.440200	5.436500	-0.445000
H	3.465000	5.146000	-1.862800
H	1.700700	5.160000	-2.033300
Ru	0.555100	0.976700	0.602500
C	5.222100	-2.923000	-1.138800
C	4.194100	-2.158600	-0.574000
C	4.436600	-0.797600	-0.279200
C	5.706700	-0.236700	-0.551600
C	6.692000	-1.037100	-1.137700
C	6.474800	-2.384600	-1.436000
H	5.031900	-3.972600	-1.355400
H	7.660500	-0.593300	-1.361700
C	2.876100	-2.842700	-0.280600
H	2.067000	-2.443800	-0.897500
H	2.959200	-3.919300	-0.462400
H	2.570100	-2.703100	0.761900
C	7.571600	-3.236300	-2.032000
H	8.262100	-3.597500	-1.257700
H	7.163900	-4.116200	-2.540900
H	8.169200	-2.672000	-2.757300
C	6.046000	1.206200	-0.244400
H	5.990500	1.405500	0.828700
H	7.053600	1.443800	-0.601200
H	5.347900	1.900900	-0.726100
C	3.363300	0.070300	0.350400
O	3.628100	0.828600	1.291100
O	2.187900	-0.056000	-0.206400
N	-0.444900	-0.907000	0.505600
C	-1.492300	-1.364600	-0.253300
C	-2.561400	-2.179000	0.253500
C	-1.553400	-0.960700	-1.629300
C	-3.693800	-2.380500	-0.470900

H	-2.434800	-2.654100	1.220100
C	-2.660100	-1.153800	-2.390700
H	-0.658200	-0.516700	-2.057900
C	-3.934800	-1.693800	-1.793600
H	-4.480000	-3.027700	-0.091600
H	-2.671500	-0.867300	-3.437700
H	-4.436900	-2.379900	-2.490300
C	-0.000600	-1.346800	1.693700
C	1.495400	-0.594800	3.327800
C	0.411400	-2.714200	3.452400
C	1.312600	-1.798500	4.012700
H	2.177600	0.182200	3.656900
H	0.214900	-3.661100	3.954100
H	1.841700	-2.009900	4.933800
N	-0.244700	-2.521000	2.307000
N	0.816900	-0.365000	2.210400
C	-6.321400	-0.993200	-1.099100
O	-6.837500	-2.023200	-1.473000
O	-6.857700	-0.123000	-0.240600
C	-4.945500	-0.532500	-1.622600
C	-8.178600	-0.463000	0.256900
C	-8.607000	0.644400	1.199800
H	-8.119900	-1.435100	0.756100
H	-8.854300	-0.566500	-0.597700
H	-9.603700	0.424700	1.597600
H	-7.911800	0.733700	2.040500
H	-8.647200	1.606900	0.680100
F	-4.432900	0.441400	-0.809800
F	-5.179400	0.057100	-2.843300

B_C

Atom	X	Y	Z
C	-1.294800	-2.851100	-0.920100
C	0.016900	-2.629100	-1.392900
C	1.121400	-2.632900	-0.482400
C	0.938900	-2.910800	0.892100
C	-0.393500	-3.231600	1.335200

C	-1.477500	-3.217100	0.461900
H	0.193000	-2.373400	-2.430500
H	2.111300	-2.385000	-0.849300
H	-0.560500	-3.426800	2.391400
H	-2.481900	-3.365800	0.839300
C	-2.514900	-2.833200	-1.827300
H	-3.356800	-2.528500	-1.194400
C	2.101500	-2.950700	1.851500
H	2.444800	-3.983400	2.000500
H	2.943800	-2.364400	1.475700
H	1.821400	-2.553000	2.833000
C	-2.423600	-1.838000	-2.992100
H	-1.639200	-2.114500	-3.707500
H	-3.371000	-1.826800	-3.542900
H	-2.229400	-0.826500	-2.624600
C	-2.795500	-4.264700	-2.333500
H	-2.904200	-4.973600	-1.504900
H	-3.721600	-4.284500	-2.919200
H	-1.980900	-4.619800	-2.976400
u	-0.327400	-1.098700	0.265200
C	-4.594800	3.541900	-0.439700
C	-3.652700	2.562800	-0.101500
C	-4.055900	1.208400	-0.069200
C	-5.393000	0.867000	-0.380600
C	-6.288600	1.880100	-0.736200
C	-5.914500	3.226100	-0.765100
H	-4.281400	4.584400	-0.451900
H	-7.311100	1.607700	-0.992100
C	-2.245400	3.013800	0.229200
H	-1.537300	2.724700	-0.552400
H	-2.215800	4.102900	0.344600
H	-1.877900	2.563200	1.156900
C	-6.915300	4.305400	-1.108000
H	-7.507200	4.595500	-0.228900
H	-6.419000	5.209100	-1.478000
H	-7.622500	3.968900	-1.874700
C	-5.895900	-0.560600	-0.360300

H	-5.835800	-0.986700	0.644100
H	-6.933800	-0.603700	-0.707300
H	-5.298900	-1.211800	-1.010100
C	-3.078800	0.118200	0.329800
O	-3.429300	-0.779000	1.117700
O	-1.906900	0.228000	-0.214500
N	1.982500	0.902500	1.539700
H	2.775600	1.374500	1.955500
C	1.806000	1.079500	0.142400
C	0.826700	0.375000	-0.579400
C	2.671700	1.994600	-0.479400
C	0.718700	0.689000	-1.944900
C	2.559400	2.251100	-1.843600
H	3.426600	2.508500	0.113600
C	1.565700	1.602300	-2.578300
H	-0.053000	0.200500	-2.532800
H	3.230500	2.959600	-2.321200
H	1.451200	1.803100	-3.640600
C	1.045900	0.579900	2.466300
C	0.431100	0.689200	4.664400
C	-1.049400	-0.200500	3.045300
C	-0.831600	0.168400	4.363700
H	0.704800	0.950700	5.685600
H	-1.983100	-0.633800	2.696200
H	-1.598600	0.035600	5.117100
N	-0.101600	-0.043500	2.093700
N	1.357500	0.906600	3.739500
C	5.755400	0.481300	-1.357600
O	5.986700	0.522800	-2.551600
O	6.181500	1.366200	-0.431900
C	5.039400	-0.620700	-0.729700
C	6.992900	2.450000	-0.947200
C	7.425400	3.296100	0.234800
H	6.397700	3.020200	-1.667600
H	7.845800	2.023000	-1.484400
H	8.045400	4.128300	-0.115400
H	6.558800	3.710600	0.759900

H	8.010800	2.705000	0.946300
F	4.596900	-0.561400	0.515800
F	4.362600	-1.468400	-1.479500

TS_meta_B_C

Atom	X	Y	Z
C	0.946500	-1.141800	2.710900
C	-0.445800	-1.019400	2.516700
C	-1.157100	-1.999200	1.753500
C	-0.501600	-3.132000	1.219000
C	0.901000	-3.286500	1.509200
C	1.605100	-2.334200	2.240200
H	-0.978900	-0.146800	2.873400
H	-2.210400	-1.839900	1.547500
H	1.430300	-4.139800	1.092800
H	2.677500	-2.425600	2.361900
C	1.763500	-0.128200	3.497100
H	2.781600	-0.180300	3.093200
C	-1.249500	-4.189400	0.447300
H	-1.521000	-5.026900	1.103700
H	-2.170500	-3.786500	0.016700
H	-0.639700	-4.594400	-0.367300
C	1.282200	1.322700	3.358800
H	0.282400	1.468000	3.785900
H	1.962800	1.988400	3.901500
H	1.268200	1.631700	2.309700
C	1.818200	-0.560600	4.978600
H	2.202100	-1.581100	5.089600
H	2.474100	0.111000	5.544100
H	0.821500	-0.523400	5.434800
Ru	0.466700	-1.201800	0.421000
C	4.232900	3.385200	-1.825800
C	3.470000	2.264400	-1.479300
C	3.845000	1.504200	-0.346800
C	4.974900	1.888300	0.412000
C	5.689400	3.031200	0.037400
C	5.342200	3.791600	-1.081300

H	3.944800	3.959400	-2.704800
H	6.547000	3.330900	0.637100
C	2.285300	1.912600	-2.354400
H	1.337900	2.084200	-1.836000
H	2.299900	2.514800	-3.269400
H	2.289900	0.856400	-2.643600
C	6.157300	4.995900	-1.492100
H	5.530400	5.766300	-1.954900
H	6.669100	5.445600	-0.634300
H	6.929300	4.724300	-2.225200
C	5.439700	1.120400	1.630800
H	5.737400	0.102700	1.367400
H	6.285700	1.630900	2.103200
H	4.645100	1.027700	2.380800
C	3.066200	0.263500	0.047100
O	3.664400	-0.774500	0.383500
O	1.777800	0.403900	-0.005600
N	-1.256500	-1.561800	-2.389200
H	-1.837700	-1.789400	-3.186400
C	-1.654700	-0.436600	-1.626500
C	-0.938700	-0.032600	-0.473200
C	-2.786300	0.241100	-2.066600
C	-1.351400	1.182800	0.121000
C	-3.314600	1.326200	-1.311000
H	-3.324400	-0.105300	-2.946400
C	-2.480000	1.870200	-0.286200
H	-0.762000	1.582400	0.940800
H	-4.046000	1.970900	-1.793600
H	-2.776500	2.784300	0.220400
C	-0.026000	-2.129700	-2.488100
C	1.370000	-3.414900	-3.762300
C	2.139100	-2.439600	-1.747200
C	2.428500	-3.187400	-2.877600
H	1.498300	-4.032600	-4.649800
H	2.877600	-2.206200	-0.984700
H	3.422200	-3.583800	-3.047700
N	0.903400	-1.939800	-1.517600

N	0.163500	-2.890500	-3.587200
C	-5.546100	1.337900	0.596100
O	-5.198100	1.630400	1.724900
O	-6.499700	1.979200	-0.116400
C	-4.851300	0.334600	-0.240200
C	-7.147600	3.077400	0.564000
C	-8.186400	3.648800	-0.382800
H	-6.389500	3.817700	0.841000
H	-7.596800	2.703500	1.489700
H	-8.704000	4.487300	0.096100
H	-7.719300	4.012200	-1.303900
H	-8.929700	2.890800	-0.649600
F	-5.579900	-0.230900	-1.219900
F	-4.218900	-0.615600	0.466700

Meta_B_C

Atom	X	Y	Z
C	0.971200	-1.180000	2.700200
C	-0.423400	-1.080000	2.506800
C	-1.118100	-2.073800	1.746900
C	-0.445300	-3.198700	1.216400
C	0.960900	-3.324800	1.500300
C	1.649900	-2.360500	2.231400
H	-0.969900	-0.214000	2.859300
H	-2.173700	-1.930800	1.538500
H	1.504200	-4.169200	1.083500
H	2.723700	-2.433600	2.353500
C	1.773300	-0.150800	3.481100
H	2.784600	-0.172300	3.058400
C	-1.177700	-4.274300	0.454900
H	-1.440900	-5.107100	1.120700
H	-2.102000	-3.888100	0.016700
H	-0.560000	-4.681300	-0.352700
C	1.250000	1.287600	3.365600
H	0.255300	1.401500	3.813400
H	1.923000	1.966600	3.901200
H	1.206200	1.606200	2.320300

C	1.864900	-0.593900	4.957700
H	2.277300	-1.604700	5.053400
H	2.512300	0.090200	5.518000
H	0.875200	-0.586800	5.430600
Ru	0.486500	-1.254400	0.407000
C	4.068300	3.486700	-1.827100
C	3.353800	2.333200	-1.485300
C	3.750900	1.593100	-0.346800
C	4.855900	2.028900	0.420900
C	5.521500	3.202200	0.050200
C	5.150800	3.944500	-1.073000
H	3.763100	4.045300	-2.710300
H	6.359500	3.541200	0.656600
C	2.196500	1.925300	-2.372900
H	1.236900	2.040300	-1.861800
H	2.186400	2.534900	-3.283100
H	2.261200	0.873400	-2.670900
C	5.914300	5.184000	-1.478300
H	6.699100	4.947800	-2.210100
H	5.256200	5.928100	-1.940800
H	6.404000	5.652800	-0.617800
C	5.345200	1.284800	1.644800
H	5.681100	0.277500	1.387300
H	6.170100	1.828900	2.116900
H	4.552500	1.166600	2.393200
C	3.022000	0.321300	0.045000
O	3.660100	-0.689400	0.391100
O	1.729400	0.405600	-0.020500
N	-1.266300	-1.756800	-2.355200
H	-1.847100	-2.034400	-3.137000
C	-1.738800	-0.663700	-1.585900
C	-0.959300	-0.158800	-0.498200
C	-2.951100	-0.130800	-1.942100
C	-1.390000	1.089900	0.045000
C	-3.590500	0.957900	-1.130900
H	-3.519200	-0.542800	-2.772700
C	-2.593100	1.661000	-0.249900

H	-0.717300	1.602200	0.728300
H	-4.097200	1.678600	-1.790500
H	-2.875000	2.617000	0.185100
C	0.006100	-2.217200	-2.488900
C	1.470000	-3.379800	-3.805700
C	2.201900	-2.381400	-1.788500
C	2.524300	-3.092100	-2.934100
H	1.626700	-3.972900	-4.705400
H	2.934300	-2.113600	-1.031400
H	3.539900	-3.417300	-3.124400
N	0.938800	-1.971700	-1.533200
N	0.232200	-2.946100	-3.602500
C	-5.485700	1.383200	0.602300
O	-5.443600	1.397100	1.809100
O	-6.139000	2.268000	-0.166200
C	-4.753300	0.357100	-0.282400
C	-6.865500	3.304400	0.542100
C	-7.534300	4.183500	-0.496800
H	-6.158200	3.861400	1.164700
H	-7.589800	2.825000	1.207800
H	-8.096700	4.980600	0.001400
H	-6.792400	4.645500	-1.156000
H	-8.229300	3.602900	-1.111500
F	-5.675400	-0.211400	-1.128100
F	-4.292700	-0.631900	0.532600

TS_para_B_C

Atom	X	Y	Z
C	-0.915100	-2.684700	-0.804200
C	0.449300	-2.367000	-0.972400
C	1.352100	-2.457100	0.134400
C	0.919500	-2.911400	1.400900
C	-0.456600	-3.317200	1.527900
C	-1.346800	-3.221000	0.462100
H	0.819600	-1.974900	-1.911500
H	2.377600	-2.130400	-0.002100
H	-0.817400	-3.649100	2.498100

H	-2.396200	-3.446300	0.608900
C	-1.928700	-2.597200	-1.934400
H	-2.903000	-2.432300	-1.458500
C	1.873500	-3.046800	2.560600
H	2.235600	-4.080200	2.645400
H	2.742800	-2.395300	2.434200
H	1.389300	-2.790100	3.509000
C	-1.689600	-1.439900	-2.914300
H	-0.749600	-1.555800	-3.467200
H	-2.497100	-1.413000	-3.654500
H	-1.675900	-0.481600	-2.387500
C	-1.985000	-3.953500	-2.670400
H	-2.196900	-4.780000	-1.982400
H	-2.771900	-3.937500	-3.432900
H	-1.032800	-4.166600	-3.171000
Ru	-0.291200	-1.059800	0.755600
C	-4.574000	3.484300	-0.390300
C	-3.664400	2.520100	0.060000
C	-3.988600	1.152300	-0.086600
C	-5.218700	0.782500	-0.678900
C	-6.082000	1.783800	-1.134300
C	-5.781200	3.141600	-1.001700
H	-4.326400	4.536200	-0.259200
H	-7.021900	1.491200	-1.599200
C	-2.381500	2.997800	0.707300
H	-1.515500	2.811700	0.065700
H	-2.440200	4.072100	0.913900
H	-2.180600	2.480000	1.651000
C	-6.723400	4.202400	-1.521900
H	-6.609100	5.144200	-0.974200
H	-6.534400	4.418500	-2.582400
H	-7.769500	3.886500	-1.438800
C	-5.641600	-0.661100	-0.848600
H	-5.753000	-1.157300	0.118600
H	-6.590000	-0.718500	-1.393200
H	-4.898000	-1.239200	-1.410300
C	-3.048700	0.075200	0.420000

O	-3.492000	-0.893800	1.061400
O	-1.801900	0.272400	0.119000
N	1.643500	0.866700	2.652800
H	2.300800	1.333000	3.266300
C	1.769200	1.136600	1.277100
C	0.956800	0.502600	0.308500
C	2.745900	2.094400	0.918700
C	1.125600	0.919600	-1.008200
C	2.944100	2.437100	-0.400400
H	3.326700	2.582400	1.700600
C	2.192600	1.776800	-1.421000
H	0.480300	0.511300	-1.778400
H	3.693600	3.176800	-0.664400
H	2.131300	2.237400	-2.405600
C	0.559600	0.412700	3.340900
C	-0.464200	0.286500	5.379200
C	-1.553000	-0.509800	3.432300
C	-1.609500	-0.263800	4.795400
H	-0.405800	0.465000	6.451700
H	-2.378400	-0.940100	2.871400
H	-2.494900	-0.504800	5.371200
N	-0.455600	-0.216400	2.697100
N	0.603600	0.633500	4.671300
C	4.601700	1.029800	-2.922100
O	4.473500	1.389300	-4.077600
O	5.638400	1.347300	-2.117500
C	3.539700	0.317200	-2.174300
C	6.660000	2.172200	-2.723500
C	7.719500	2.431900	-1.669100
H	6.198800	3.098100	-3.083200
H	7.066500	1.647100	-3.593800
H	8.517600	3.053000	-2.090400
H	7.294000	2.954900	-0.806500
H	8.160500	1.493100	-1.319200
F	3.935600	-0.387700	-1.098800
F	2.758300	-0.448700	-2.957700

Para_B_C

Atom	X	Y	Z
C	0.472400	-0.609200	2.792200
C	-0.869500	-0.724800	2.375300
C	-1.333900	-1.932500	1.763200
C	-0.483400	-3.051200	1.611400
C	0.853200	-2.951500	2.141700
C	1.319500	-1.774700	2.717800
H	-1.542100	0.122500	2.426500
H	-2.347300	-1.964600	1.376300
H	1.529100	-3.794200	2.022100
H	2.357300	-1.690600	3.016100
C	1.035200	0.651500	3.429800
H	2.111500	0.643900	3.219200
C	-0.973300	-4.342200	1.005800
H	-1.245800	-5.058700	1.792300
H	-1.856700	-4.177400	0.382000
H	-0.200800	-4.811900	0.387600
C	0.462200	1.959600	2.867200
H	-0.609100	2.063800	3.077100
H	0.966400	2.812700	3.335100
H	0.619400	2.020100	1.786700
C	0.853500	0.571900	4.961100
H	1.296400	-0.341100	5.375400
H	1.333400	1.430400	5.444500
H	-0.209800	0.583000	5.230200
Ru	0.406600	-1.221100	0.543000
C	4.165400	3.175600	-2.064200
C	3.429900	2.077200	-1.604600
C	3.684300	1.577800	-0.305900
C	4.668000	2.194700	0.501600
C	5.357800	3.305400	0.004400
C	5.129600	3.809200	-1.277900
H	3.972300	3.548800	-3.068500
H	6.100300	3.786200	0.639000
C	2.404900	1.466700	-2.537300
H	1.385400	1.646100	-2.184800

H	2.511300	1.888400	-3.542700
H	2.516000	0.379600	-2.610600
C	5.922000	4.981500	-1.808700
H	6.827800	4.646700	-2.332800
H	5.336200	5.572300	-2.521700
H	6.243900	5.647400	-1.000400
C	5.001400	1.712200	1.897200
H	5.420100	0.703000	1.877600
H	5.719700	2.389400	2.371800
H	4.111800	1.665000	2.536400
C	2.932300	0.371100	0.222900
O	3.536500	-0.520500	0.846100
O	1.661100	0.381600	-0.033900
N	-0.746100	-2.238700	-2.426300
H	-1.149600	-2.666300	-3.251400
C	-1.369500	-1.081400	-1.950500
C	-0.936200	-0.395100	-0.773500
C	-2.455100	-0.591300	-2.739100
C	-1.558400	0.787200	-0.473600
C	-3.140300	0.533900	-2.406800
H	-2.721900	-1.128200	-3.650100
C	-2.787600	1.317700	-1.173700
H	-1.224700	1.370500	0.376900
H	-3.945200	0.899700	-3.036300
H	-2.664300	2.382200	-1.433100
C	0.480400	-2.755800	-2.152500
C	2.112800	-4.196500	-2.845500
C	2.472200	-2.769700	-0.987900
C	2.984100	-3.719100	-1.858100
H	2.418100	-4.979900	-3.537600
H	3.051000	-2.331000	-0.179700
H	4.001400	-4.078000	-1.760100
N	1.205100	-2.307500	-1.094200
N	0.884700	-3.724200	-3.004900
C	-5.252300	1.980000	-0.689100
O	-5.258800	2.796300	-1.584200
O	-6.323000	1.574900	-0.002300

C	-3.961400	1.313500	-0.166200
C	-7.582500	2.196100	-0.368200
C	-8.651000	1.625800	0.544100
H	-7.779500	1.982300	-1.423400
H	-7.478700	3.280200	-0.260700
H	-9.621700	2.069800	0.297700
H	-8.727500	0.540300	0.426500
H	-8.427100	1.845100	1.592800
F	-4.241100	0.041600	0.245500
F	-3.605600	2.023300	0.962200

Structure of Meta_B_N binding with Na^+

Atom	X	Y	Z
C	3.233500	1.652500	-1.365300
C	2.325200	2.720700	-1.507700
C	2.077600	3.633900	-0.426400
C	2.723300	3.502500	0.818600
C	3.604800	2.376700	0.978700
C	3.868200	1.490300	-0.083700
H	1.764900	2.837700	-2.427600
H	1.346200	4.424000	-0.563300
H	4.046000	2.177800	1.950300
H	4.483500	0.618600	0.102100
C	3.540200	0.662800	-2.475300
H	3.775500	-0.289600	-1.984500
C	2.485200	4.465700	1.950600
H	3.300200	5.198800	1.999400
H	1.548200	5.014400	1.818600
H	2.450300	3.947400	2.914000
C	2.370400	0.405600	-3.434400
H	2.110000	1.297000	-4.018000
H	2.651600	-0.374100	-4.149500
H	1.485500	0.063200	-2.889400
C	4.802100	1.132600	-3.232200
H	5.653900	1.270900	-2.557200
H	5.085200	0.388900	-3.984400
H	4.620300	2.083100	-3.747600

Ru	1.655400	1.523700	0.303600
C	0.776300	-4.755300	-0.492700
C	0.803700	-3.410900	-0.110100
C	2.042600	-2.800200	0.182700
C	3.235600	-3.554800	0.076900
C	3.158100	-4.888900	-0.335600
C	1.941700	-5.515000	-0.617600
H	-0.184100	-5.220700	-0.706300
H	4.080200	-5.458000	-0.432700
C	-0.512800	-2.669500	-0.023700
H	-0.608600	-1.953900	-0.846400
H	-1.347100	-3.378500	-0.079100
H	-0.603700	-2.099300	0.907800
C	1.886700	-6.970200	-1.017600
H	1.809900	-7.620200	-0.135700
H	1.019300	-7.180300	-1.652400
H	2.787600	-7.270400	-1.562800
C	4.603100	-2.979800	0.378200
H	4.713700	-2.755200	1.442400
H	5.384800	-3.686700	0.083800
H	4.782600	-2.040100	-0.157600
C	2.132800	-1.357800	0.630000
O	2.874800	-1.029000	1.560900
O	1.397800	-0.518400	-0.065600
N	-0.523800	1.586900	0.382500
C	-1.566000	1.686400	-0.550100
C	-2.345100	0.611000	-0.920800
C	-1.756700	2.956500	-1.185100
C	-3.415600	0.713000	-1.982600
H	-2.100500	-0.372900	-0.531300
C	-2.709600	3.108200	-2.217000
H	-1.143200	3.791900	-0.867300
C	-3.503900	2.071600	-2.624400
H	-3.232000	-0.049700	-2.761500
H	-2.808500	4.075500	-2.702700
H	-4.227800	2.202200	-3.421400
C	-0.590500	1.123400	1.626700

C	0.919200	0.592500	3.340900
C	-1.430000	0.399800	3.632300
C	-0.158400	0.269600	4.175400
H	1.955100	0.481500	3.641400
H	-2.303200	0.162100	4.238300
H	-0.005500	-0.075800	5.189900
N	-1.682300	0.797500	2.368600
N	0.695800	1.045400	2.118100
C	-4.872800	-1.128400	-0.882700
O	-4.995500	-2.080700	-1.603500
O	-4.716500	-1.173600	0.462000
C	-4.809300	0.313700	-1.425000
C	-4.741700	-2.522400	1.051500
C	-4.613600	-2.371800	2.552800
H	-3.916600	-3.089700	0.614500
H	-5.682500	-2.991400	0.756100
H	-4.648100	-3.361700	3.019000
H	-3.657000	-1.913000	2.829800
H	-5.439200	-1.781900	2.967200
F	-5.156300	1.198400	-0.391900
F	-5.756300	0.441700	-2.373900
Na	-3.864700	0.885900	1.401200

Structure of Meta_B_N binding with K^+

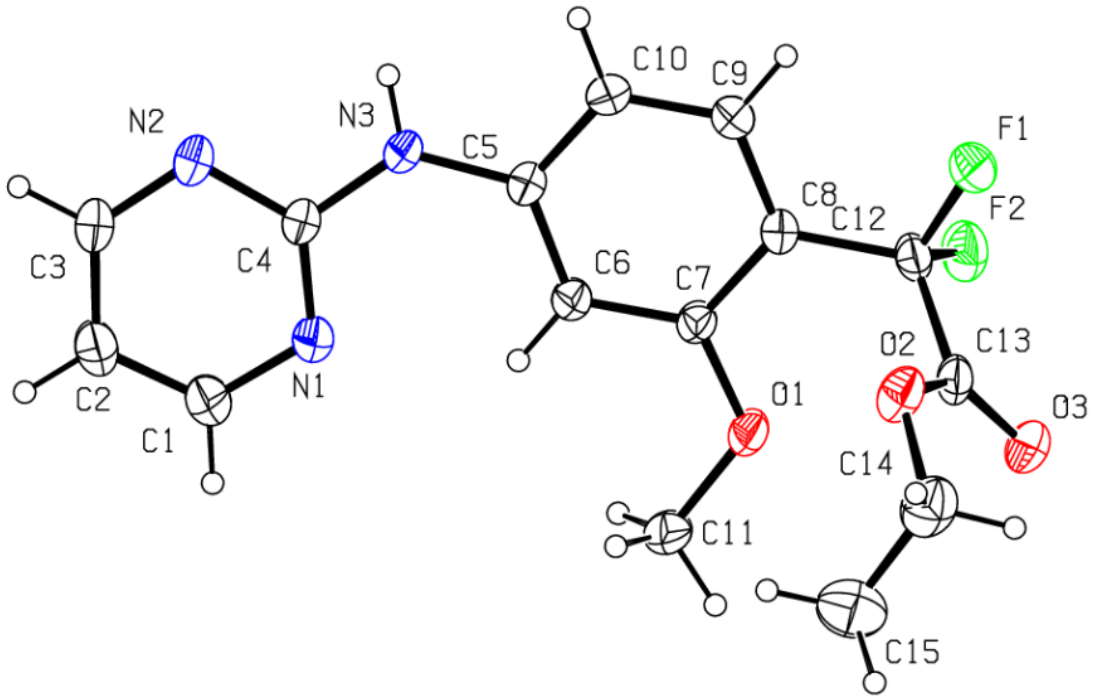
Atom	X	Y	Z
C	-3.410000	2.054800	1.196600
C	-2.291100	2.743400	1.715100
C	-1.545600	3.657100	0.897500
C	-1.904400	3.933500	-0.439300
C	-2.996400	3.169700	-0.973900
C	-3.745200	2.266200	-0.183400
H	-1.962500	2.556600	2.730200
H	-0.670200	4.144000	1.317800
H	-3.237000	3.262100	-2.029200
H	-4.517900	1.665700	-0.647300
C	-4.233600	1.084500	2.023900
H	-4.641600	0.347100	1.322000

C	-1.163500	4.939100	-1.286300
H	-1.721800	5.883000	-1.334000
H	-0.174900	5.157600	-0.870200
H	-1.034900	4.579800	-2.314400
C	-3.431500	0.317200	3.084200
H	-3.055900	0.977000	3.876000
H	-4.081000	-0.421600	3.565300
H	-2.590300	-0.212900	2.629000
C	-5.421100	1.848900	2.650400
H	-6.025100	2.357900	1.890700
H	-6.071000	1.149000	3.186500
H	-5.070300	2.601500	3.366700
u	-1.589000	1.652000	-0.177600
C	-2.136500	-4.677000	0.088700
C	-1.873300	-3.326200	-0.159900
C	-2.949000	-2.464800	-0.474100
C	-4.267100	-2.978100	-0.531800
C	-4.478800	-4.330900	-0.249300
C	-3.430400	-5.202000	0.056400
H	-1.303300	-5.338400	0.318300
H	-5.496200	-4.715700	-0.276400
C	-0.434200	-2.859500	-0.104400
H	-0.259500	-2.190300	0.742600
H	0.237200	-3.720200	-0.014100
H	-0.151400	-2.305700	-1.007400
C	-3.686500	-6.668100	0.313600
H	-3.730700	-7.232900	-0.627200
H	-2.894300	-7.113400	0.924300
H	-4.641100	-6.823700	0.827900
C	-5.469200	-2.127900	-0.883700
H	-5.456600	-1.842700	-1.939800
H	-6.394000	-2.677200	-0.681000
H	-5.499900	-1.192800	-0.313700
C	-2.727700	-1.001900	-0.779400
O	-3.313700	-0.447000	-1.714900
O	-1.902000	-0.395100	0.044400
N	0.533600	1.047400	-0.171900

C	1.421700	0.631300	0.826300
C	2.348100	-0.397400	0.730800
C	1.263100	1.308400	2.084100
C	3.237100	-0.793100	1.894500
H	2.344600	-1.045000	-0.142500
C	1.933700	0.869500	3.240800
H	0.548300	2.119500	2.136700
C	2.844100	-0.150800	3.199000
H	3.230300	-1.889600	2.007300
H	1.704100	1.342100	4.192400
H	3.344700	-0.490400	4.098200
C	0.539200	0.758000	-1.474800
C	-1.004100	0.846500	-3.242000
C	1.209300	0.047200	-3.543700
C	-0.037100	0.311900	-4.099600
H	-2.020000	1.060300	-3.554200
H	2.001400	-0.364100	-4.169100
H	-0.255100	0.105300	-5.139800
N	1.529000	0.250400	-2.251200
N	-0.699300	1.092900	-1.977000
C	5.505700	-1.390900	0.667900
O	5.583900	-2.576200	0.852200
O	6.094100	-0.700900	-0.341100
C	4.738300	-0.449100	1.633300
C	7.176900	-1.343800	-1.098900
C	8.313700	-0.340000	-1.199400
H	6.770400	-1.614500	-2.078600
H	7.459600	-2.260200	-0.579100
H	9.088700	-0.721000	-1.871800
H	7.972500	0.627000	-1.590900
H	8.765200	-0.167200	-0.218200
F	4.838700	0.852900	1.181800
F	5.450500	-0.518000	2.792100
K	4.115500	0.694900	-1.530700

7. Crystallographic Details

Crystals were grown from a mixture of CH_2Cl_2 and n-hexane.

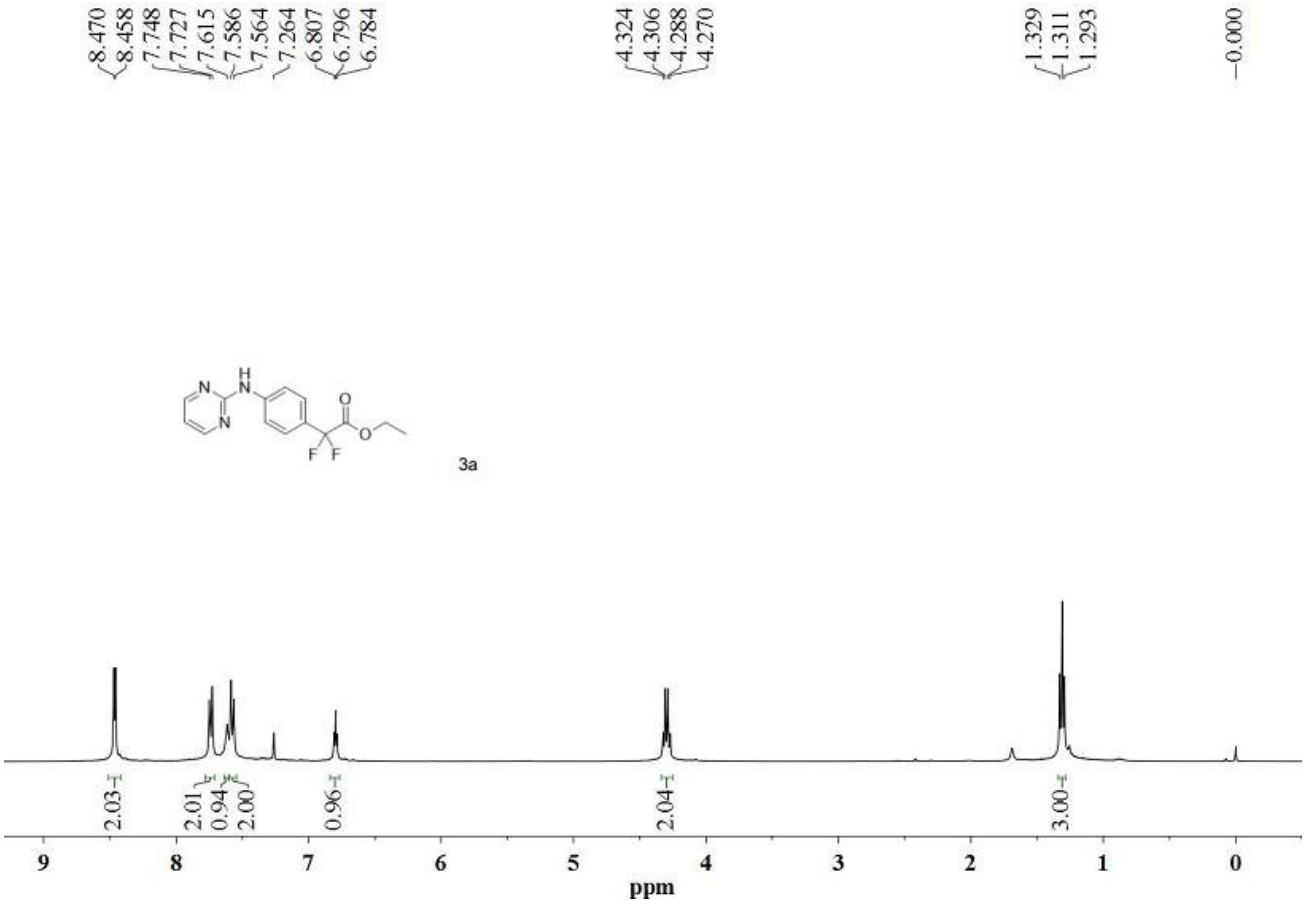


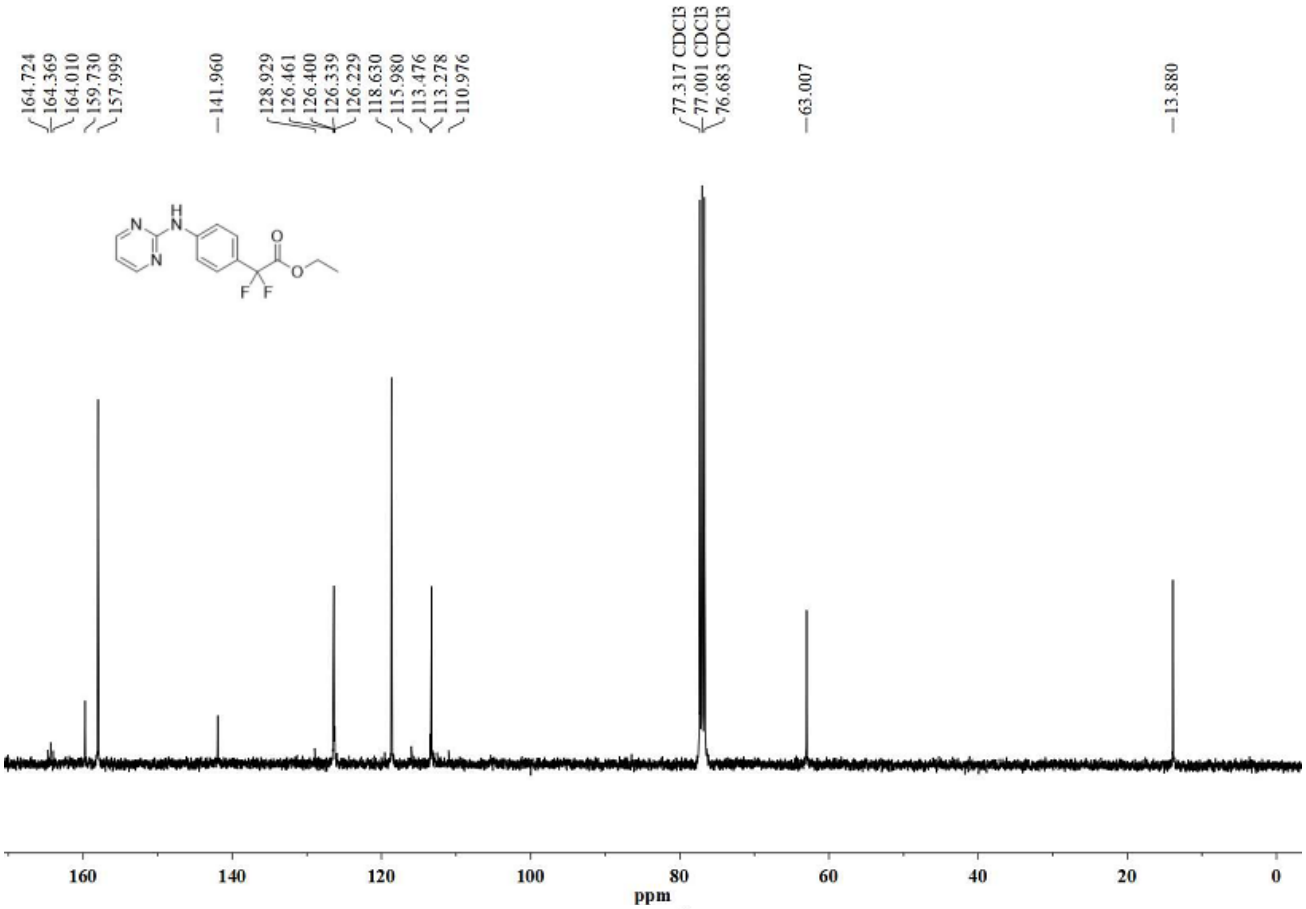
Molecular structure of compound **3c**. The ellipsoid contour percent probability level is 30% in the caption of the thermal ellipsoid plot. (CCDC 1827733)

Table S3.Crystal data and structure refinement for 3c.	
Identification code	3c
Empirical formula	$C_{15}H_{15}F_2N_3O_3$
Formula weight	323.30
Temperature/K	289.7(5)
Crystal system	triclinic
Space group	P-1
a/Å	12.5999(8)
b/Å	12.8512(7)
c/Å	13.5479(9)
α/°	63.165(6)
β/°	62.666(7)
γ/°	64.519(6)
Volume/Å^3	1668.7(2)
Z	4
ρ_{calc}g/cm^3	1.287
μ/mm^{-1}	0.907
F(000)	672.0
Crystal size/mm^3	0.23 × 0.21 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.744 to 139.966

Index ranges	-15 ≤ h ≤ 14, -15 ≤ k ≤ 11, -16 ≤ l ≤ 12
Reflections collected	10134
Independent reflections	6075 [R_{int} = 0.0531, R_{sigma} = 0.0583]
Data/restraints/parameters	6075/18/419
Goodness-of-fit on F^2	1.169
Final R indexes [I>=2σ (I)]	R_1 = 0.0789, wR_2 = 0.2500
Final R indexes [all data]	R_1 = 0.0990, wR_2 = 0.3102
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.44

8. NMR spectra

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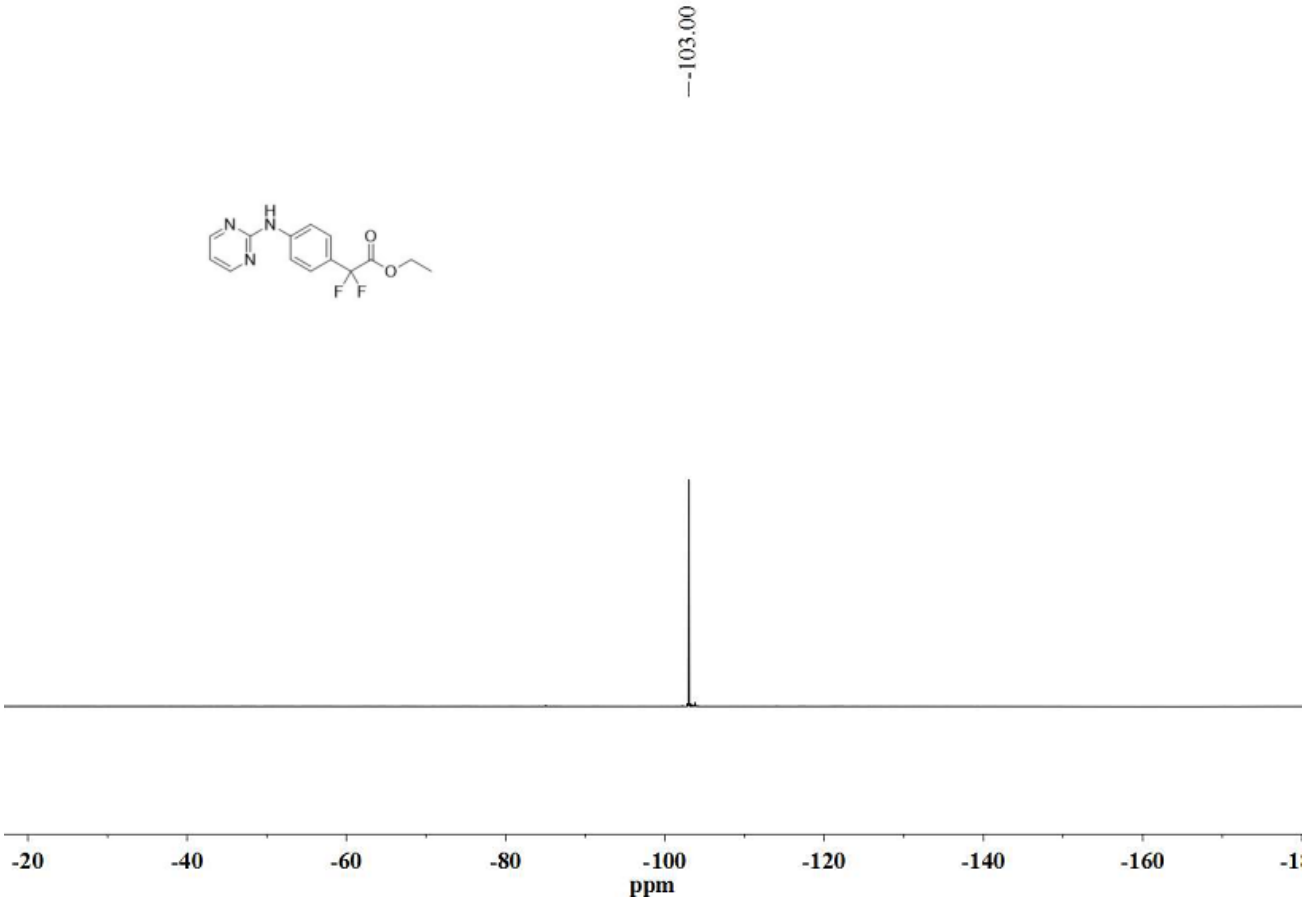
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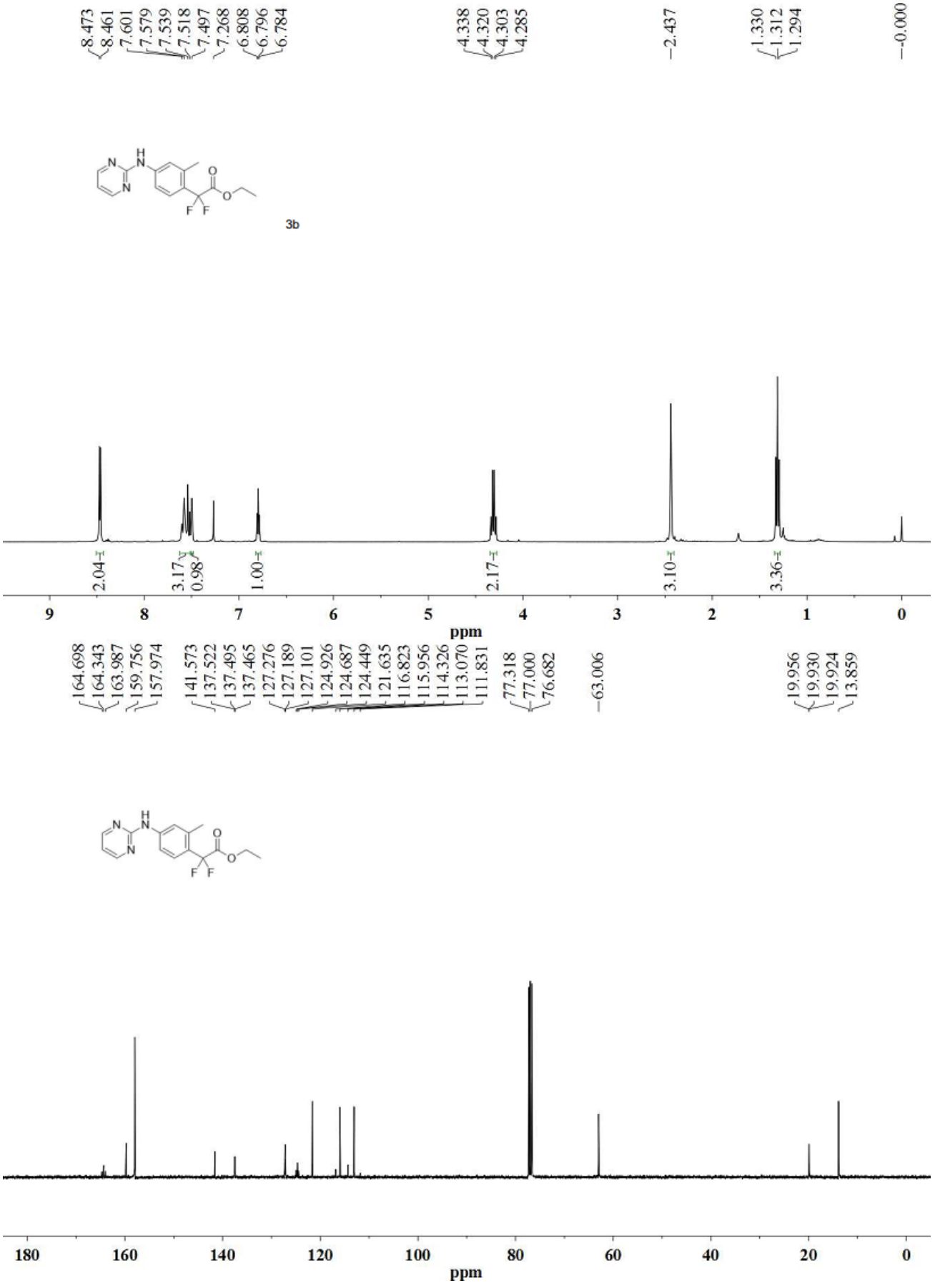
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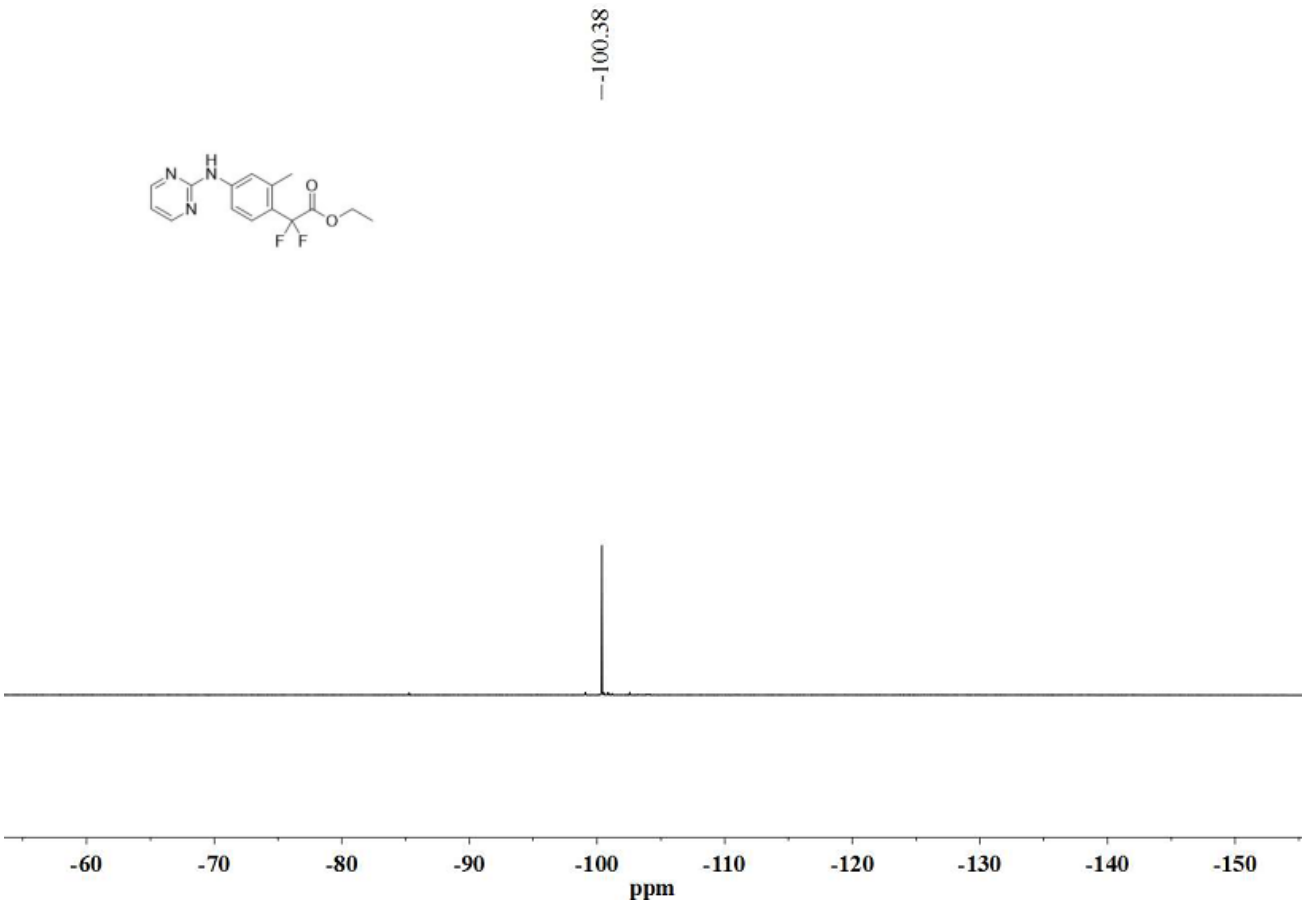
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-150
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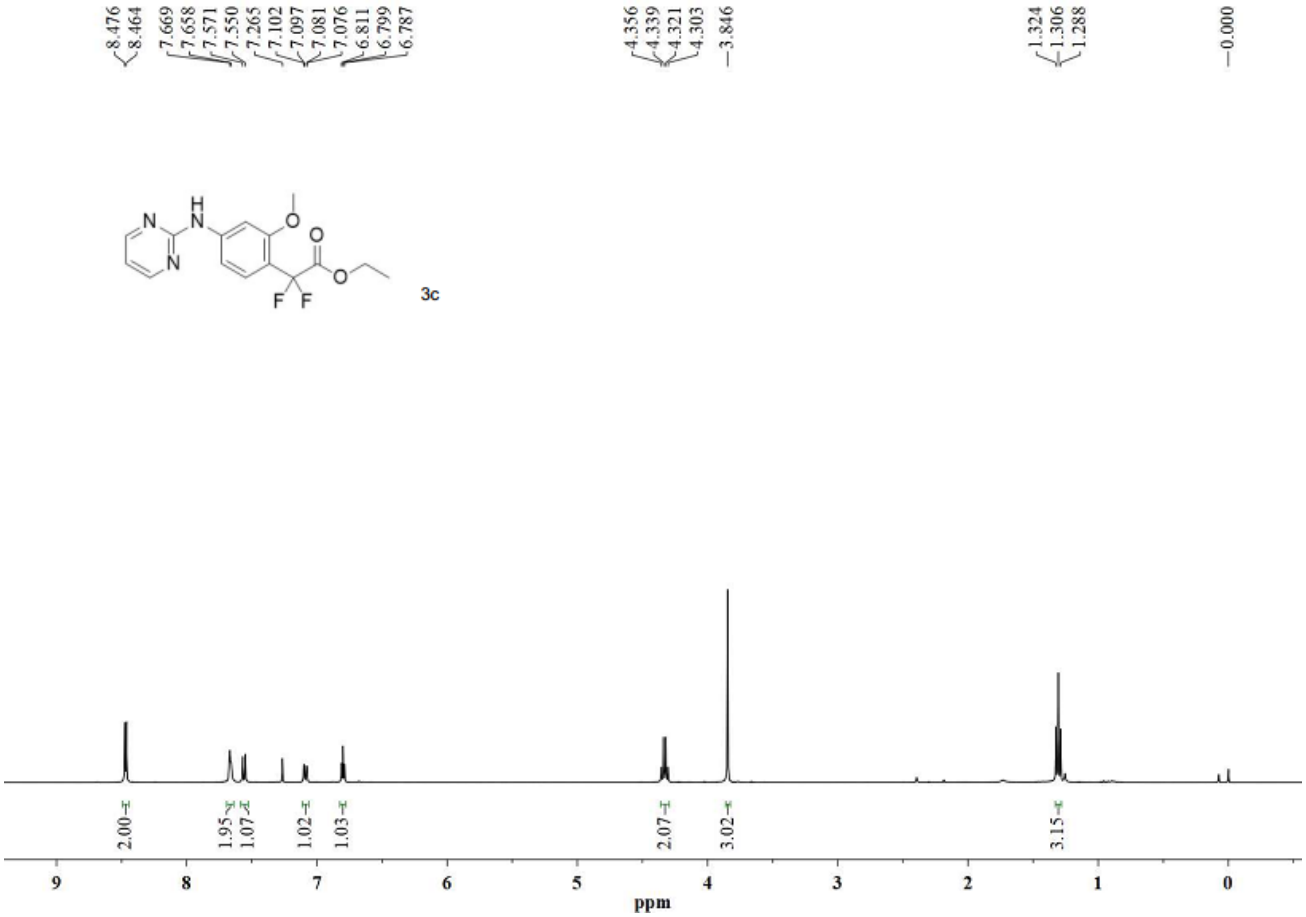
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7.550
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7.102
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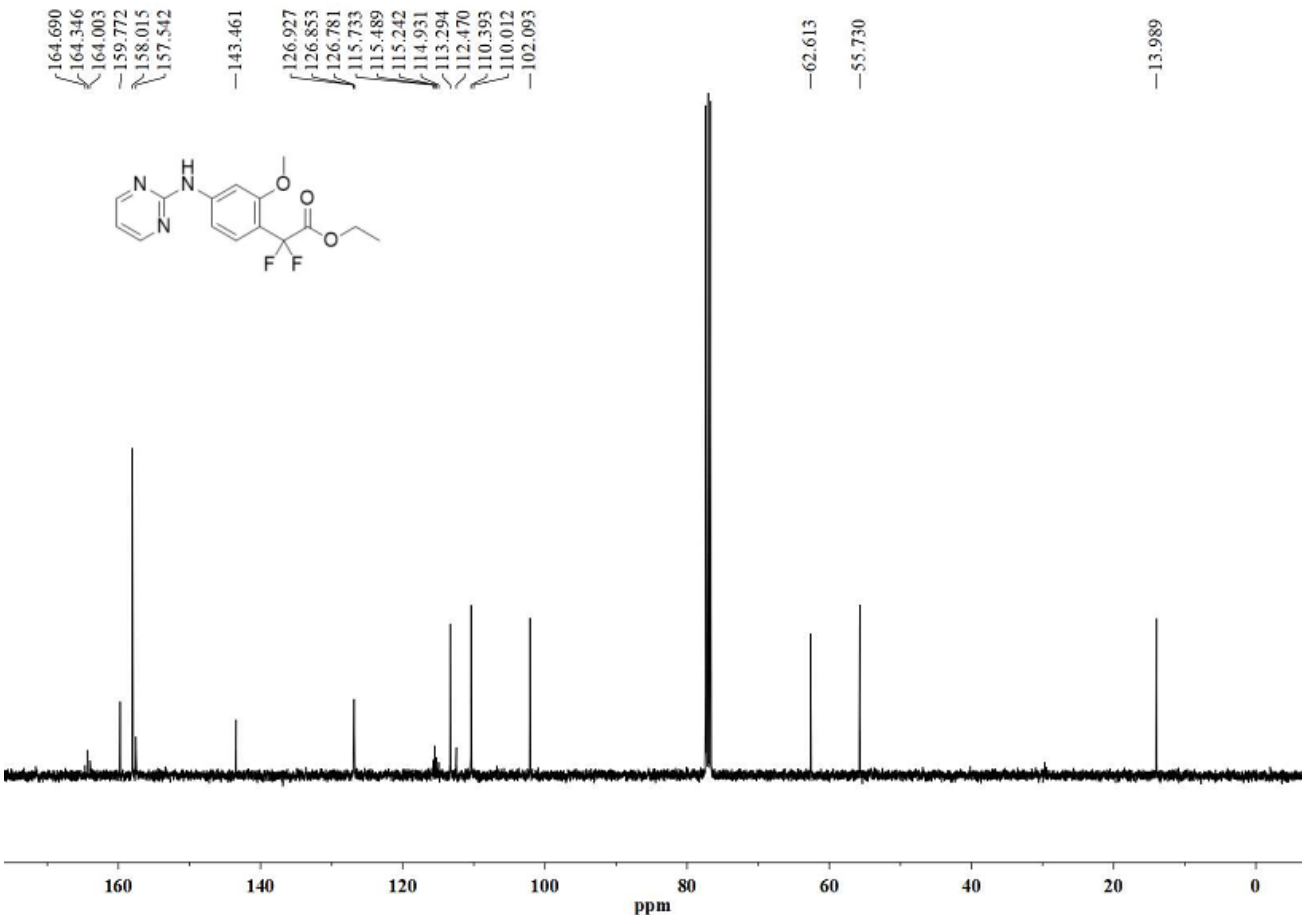
7.081
7.076
6.811
6.799
6.787
4.356
4.339
4.321
4.303
3.846
1.324
1.306
1.288
0.000
2.00
1.95
1.07
1.02
1.03
2.07
3.02
3.15
9
8
7
6
5
4
3
2
1
0
ppm

3c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157.542
143.461
126.927
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115.733
115.489
115.242
114.931
113.294
112.470
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13.989
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120
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80
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40
20
0
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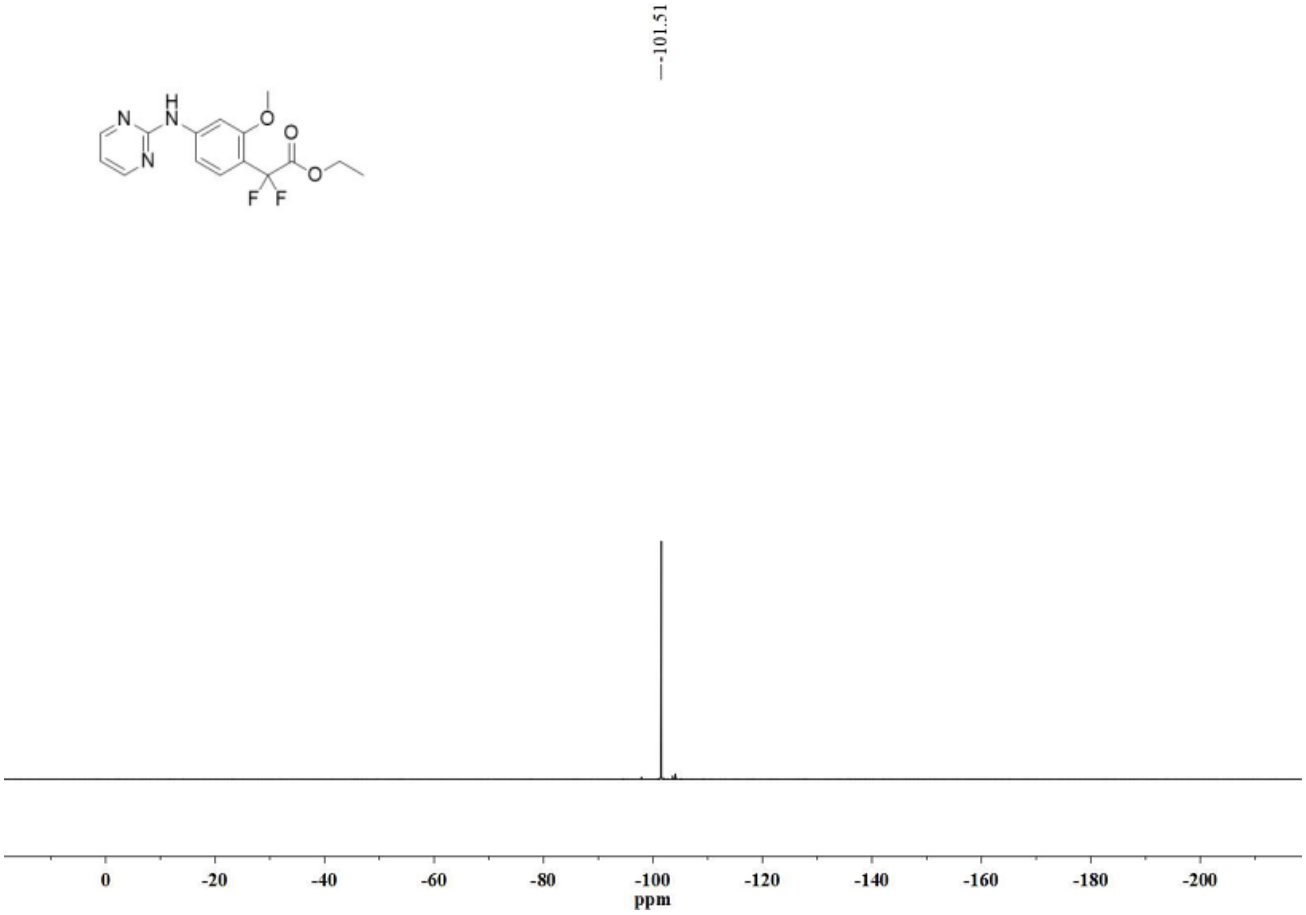
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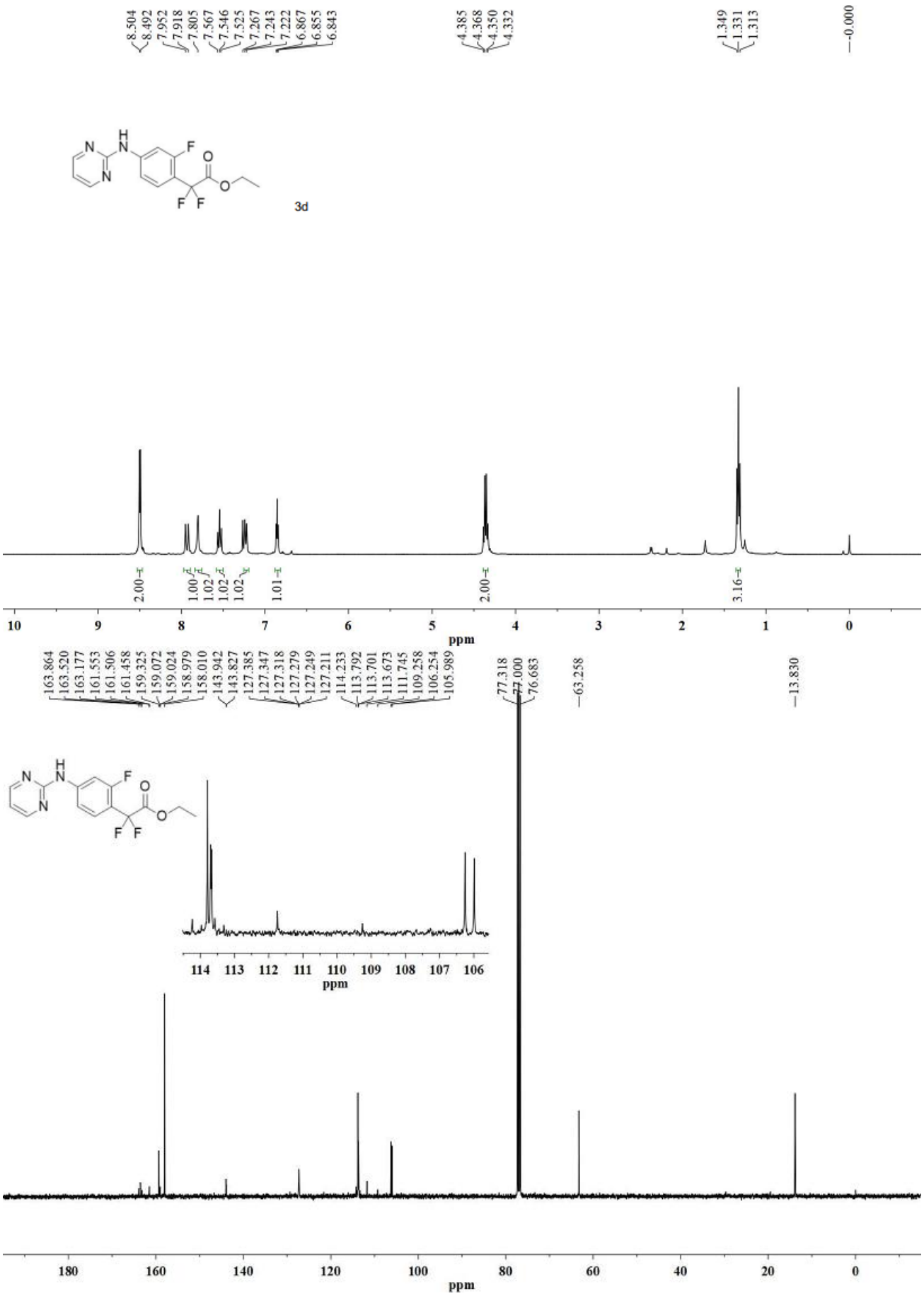
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7.952
7.918
7.805
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7.546
7.525
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7.243
7.222
6.867
6.855
6.843
4.385
4.368
4.350
4.332
1.349
1.331
1.313
0.000
3d
2.00
1.00
1.02
1.02
1.02
1.01
2.00
3.16
ppm
163.864
163.520
163.177
161.553
161.506
161.458
159.325
159.072
159.024
158.979
158.010
143.942
143.827
127.385
127.347
127.318
127.279
127.249
127.211
114.233
113.792
113.701
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105.989
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77.000
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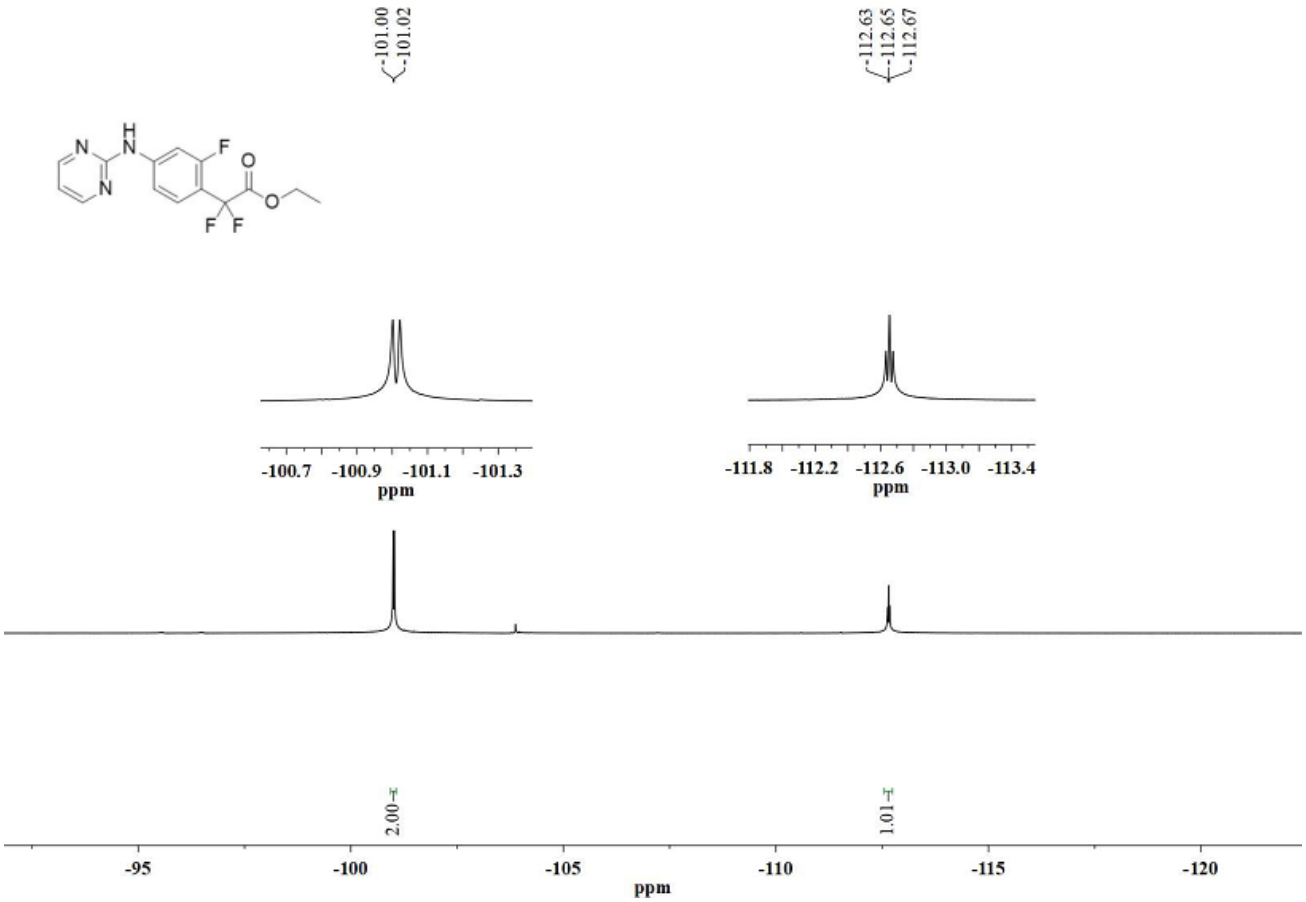
63.258
13.830
ppm
ppm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-101.02
-112.63
-112.65
-112.67
-100.7 -100.9 -101.1 -101.3
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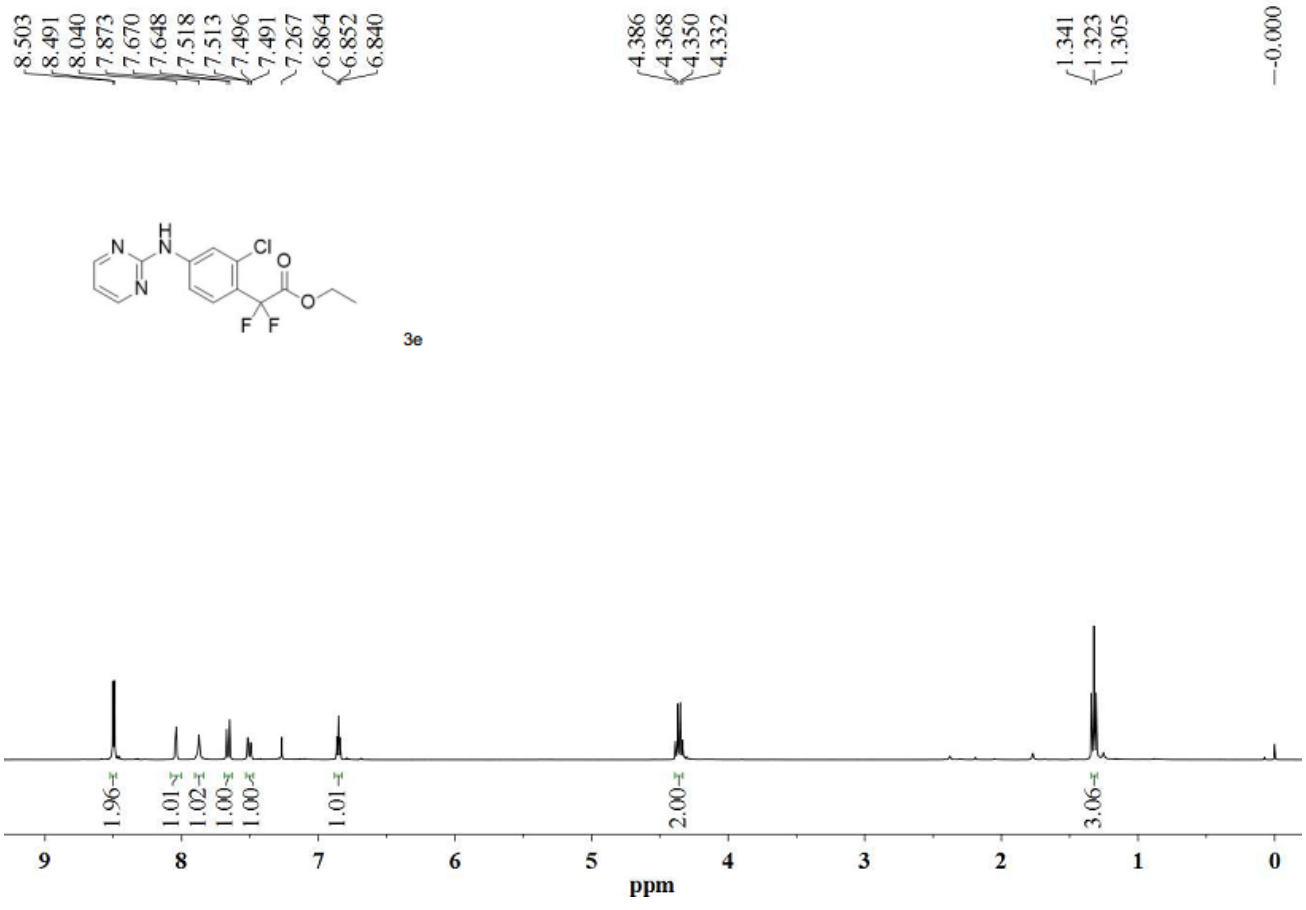
ppm
2.00
1.01
-95 -100 -105 -110 -115 -120
ppm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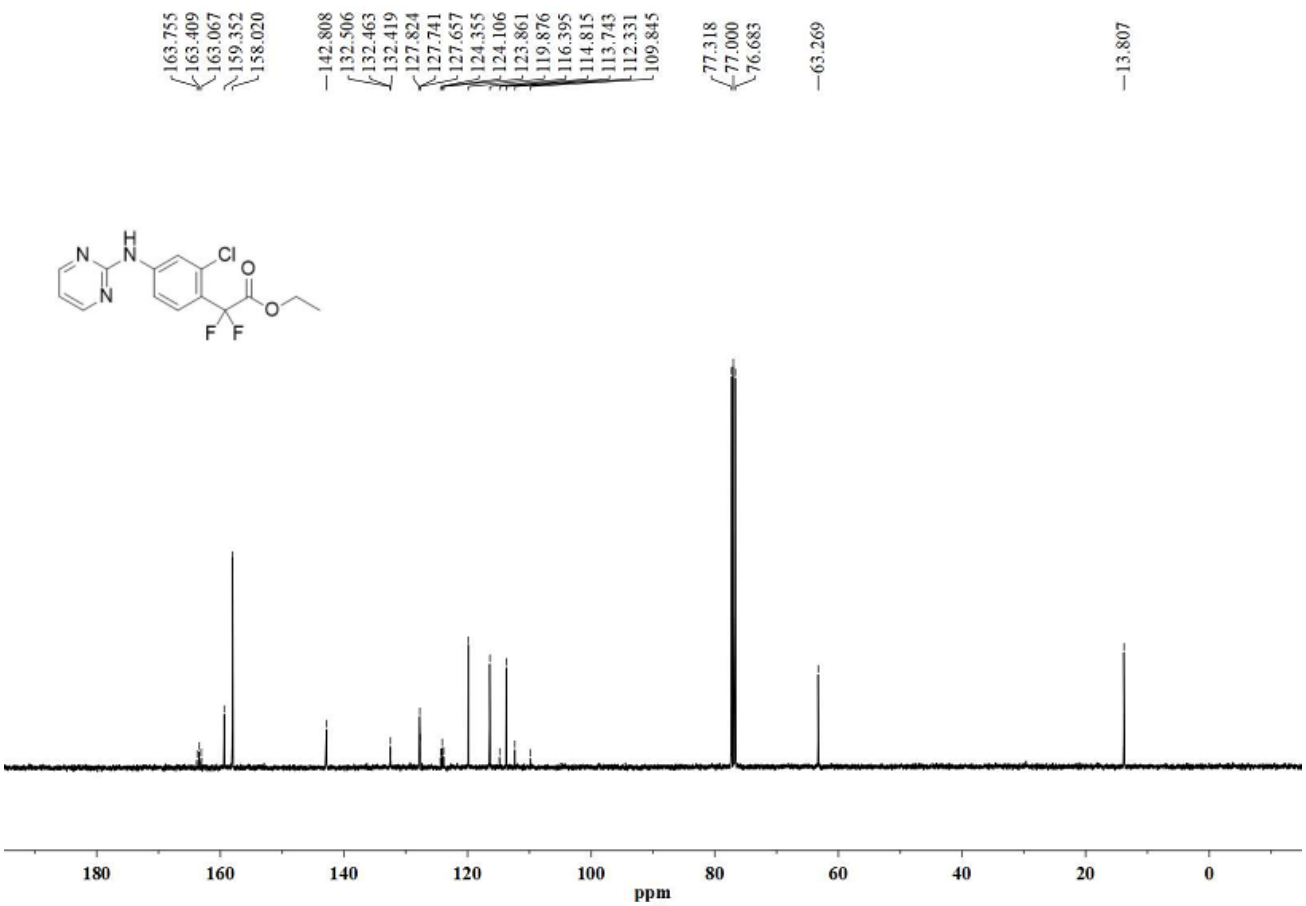
8.491
8.040
7.873
7.670
7.648
7.518
7.513
7.496
7.491
7.267
6.864
6.852
6.840
4.386
4.368
4.350
4.332
1.341
1.323
1.305
0.000
3e
1.96
1.01
1.02
1.00
1.00
1.01
2.00
3.06
9 8 7 6 5 4 3 2 1 0
ppm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142.808
132.506
132.463
132.419
127.824
127.741
127.657
124.355
124.106
123.861
119.876
116.395
114.815
113.743
112.331
109.845
77.318
77.000
76.683
63.269
13.807
N
H
N
Cl
O
O
F
F
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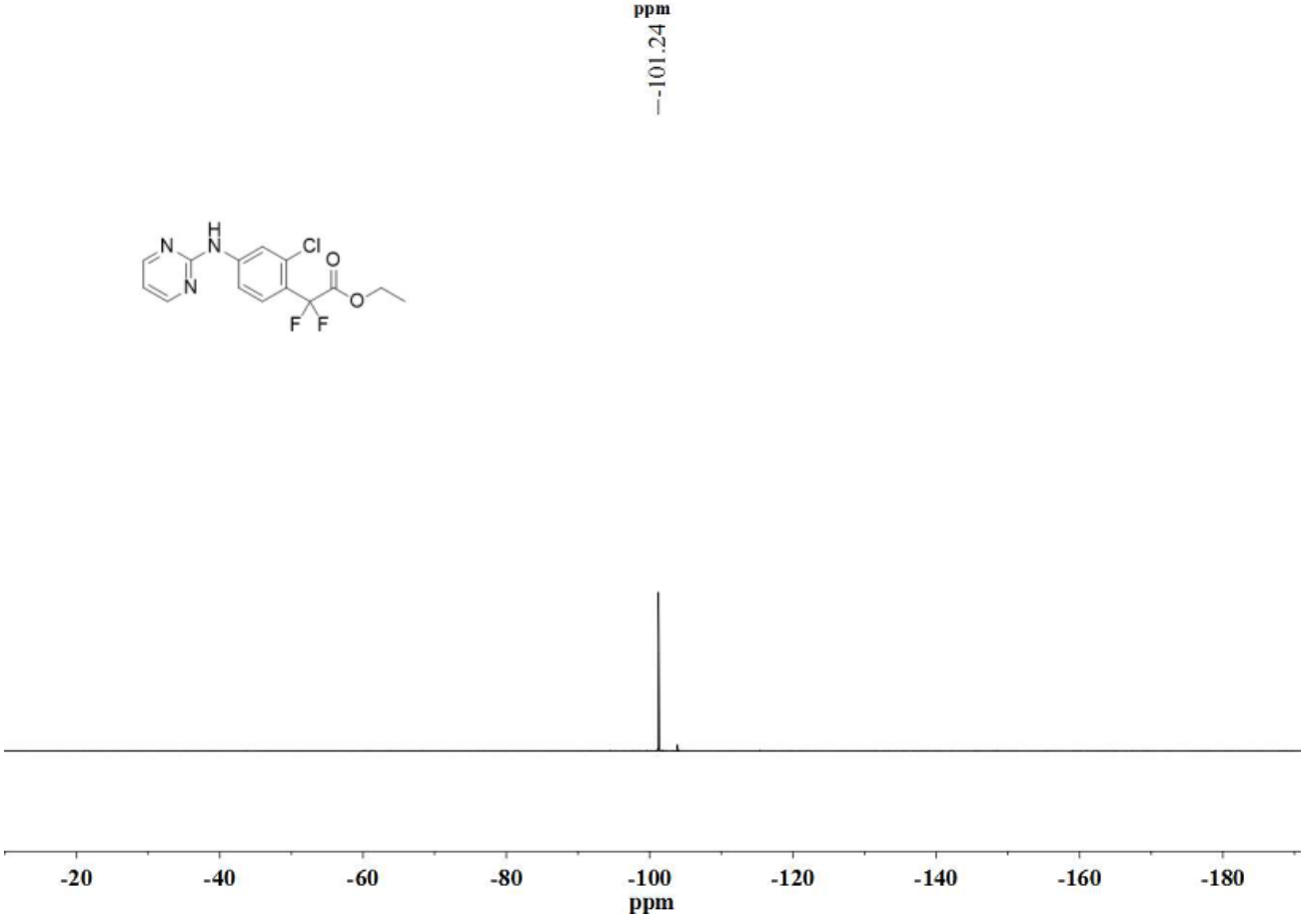
160
140
120
100
80
60
40
20
0
ppm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O
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-60
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-100
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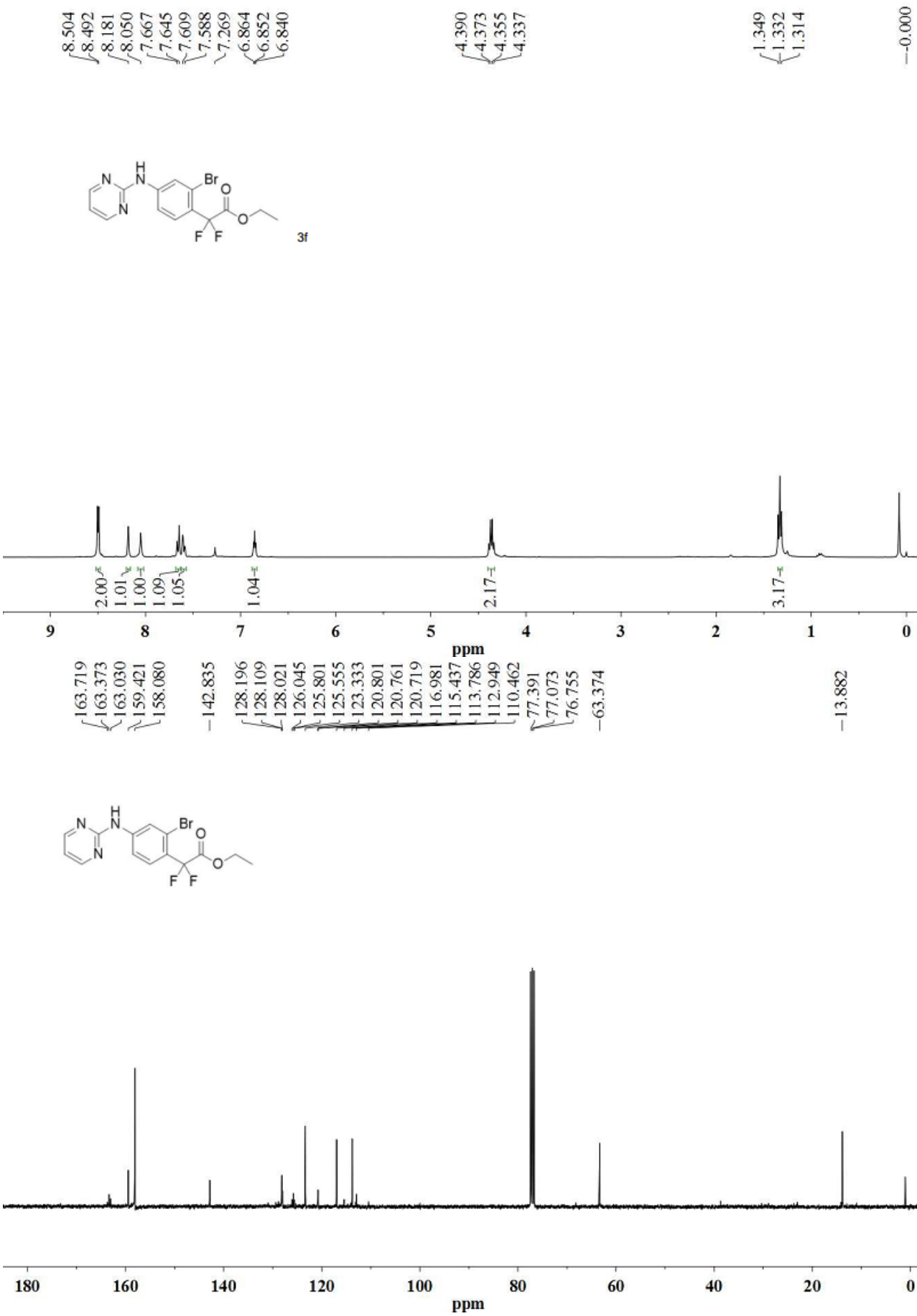
-140
-160
-180
ppm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8.492
8.181
8.050
7.667
7.645
7.609
7.588
7.269
6.864
6.852
6.840
4.390
4.373
4.355
4.337
1.349
1.332
1.314
0.000
3f
2.00
1.01
1.00
1.09
1.05
1.04
2.17
3.17
ppm
163.719
163.373
163.030
159.421
158.080
142.835
128.196
128.109
128.021
126.045
125.801
125.555
123.333
120.801
120.761
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113.786
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77.073
76.755
63.374
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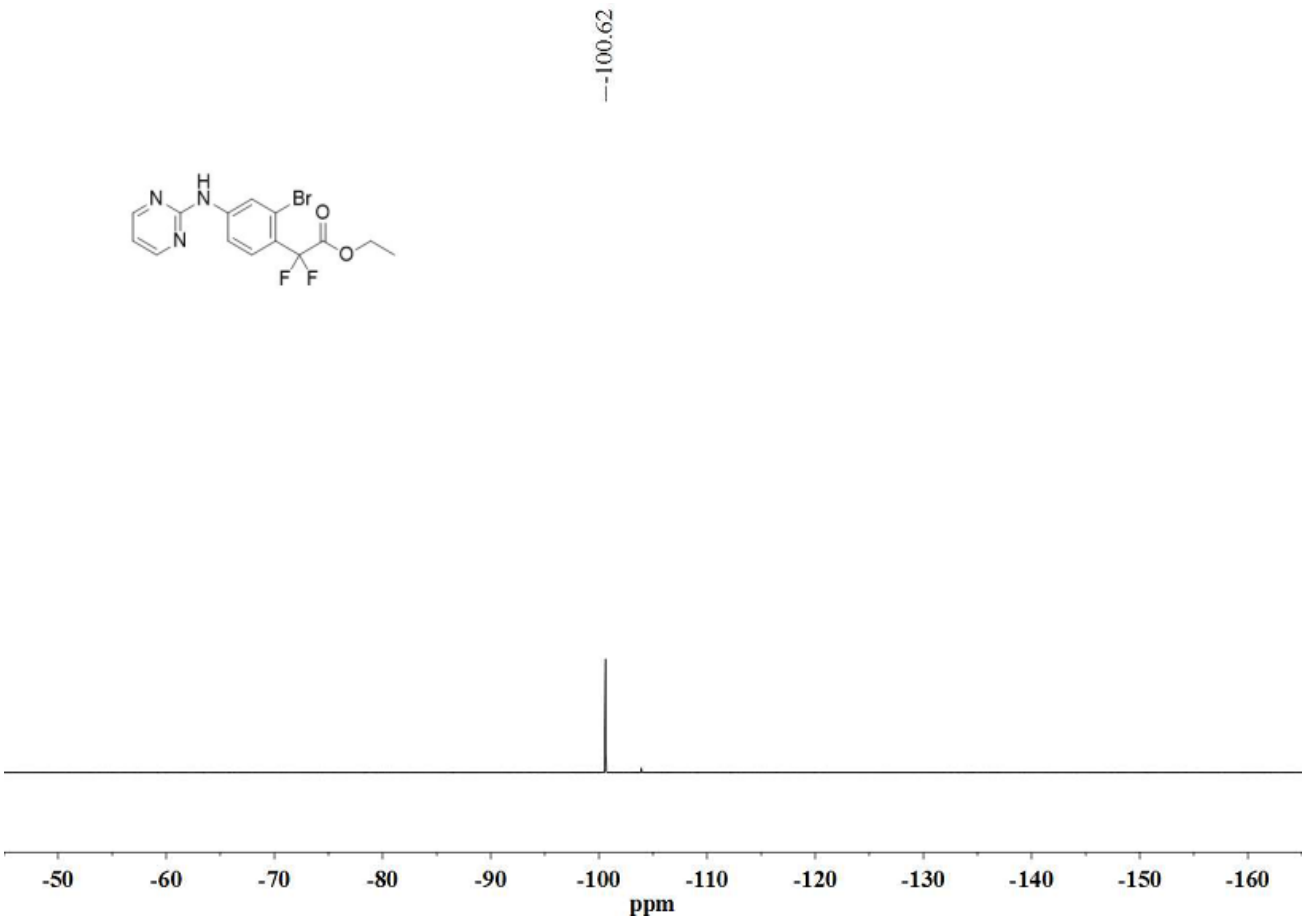
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Br
O
O
F F
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
ppm
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8.474
7.946
7.731
7.636
7.615
7.519
7.498
7.269
6.832
6.820
6.808
4.375
4.357
4.339
4.322
2.467
1.343
1.325
1.307
0.000
S
O
O
F F
2.00
1.02
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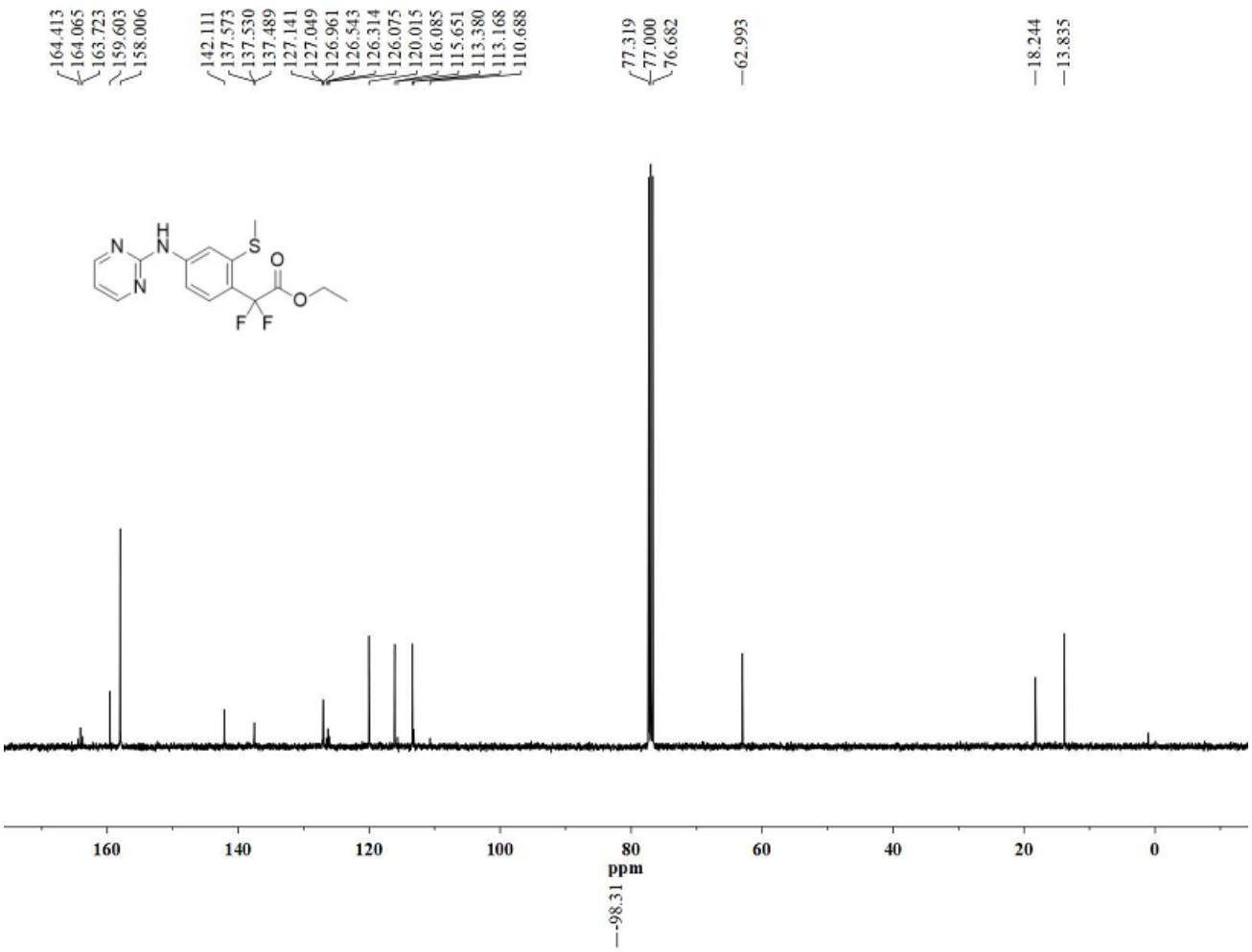
1.03
1.04
1.05
2.18
3.08
3.07
9 8 7 6 5 4 3 2 1 0
ppm

3g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158.006
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137.573
137.530
137.489
127.141
127.049
126.961
126.543
126.314
126.075
120.015
116.085
115.651
113.380
113.168
110.688
77.319
77.000
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62.993
18.244
13.835
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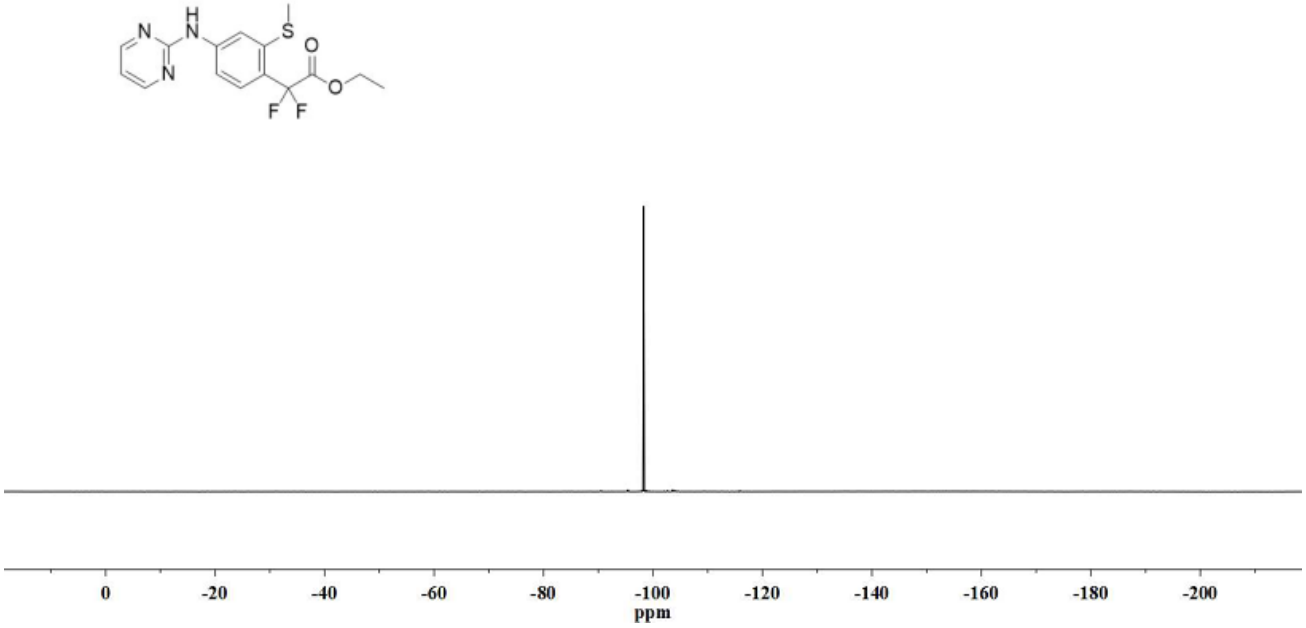
140
120
100
80
60
40
20
0
ppm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-160
-180
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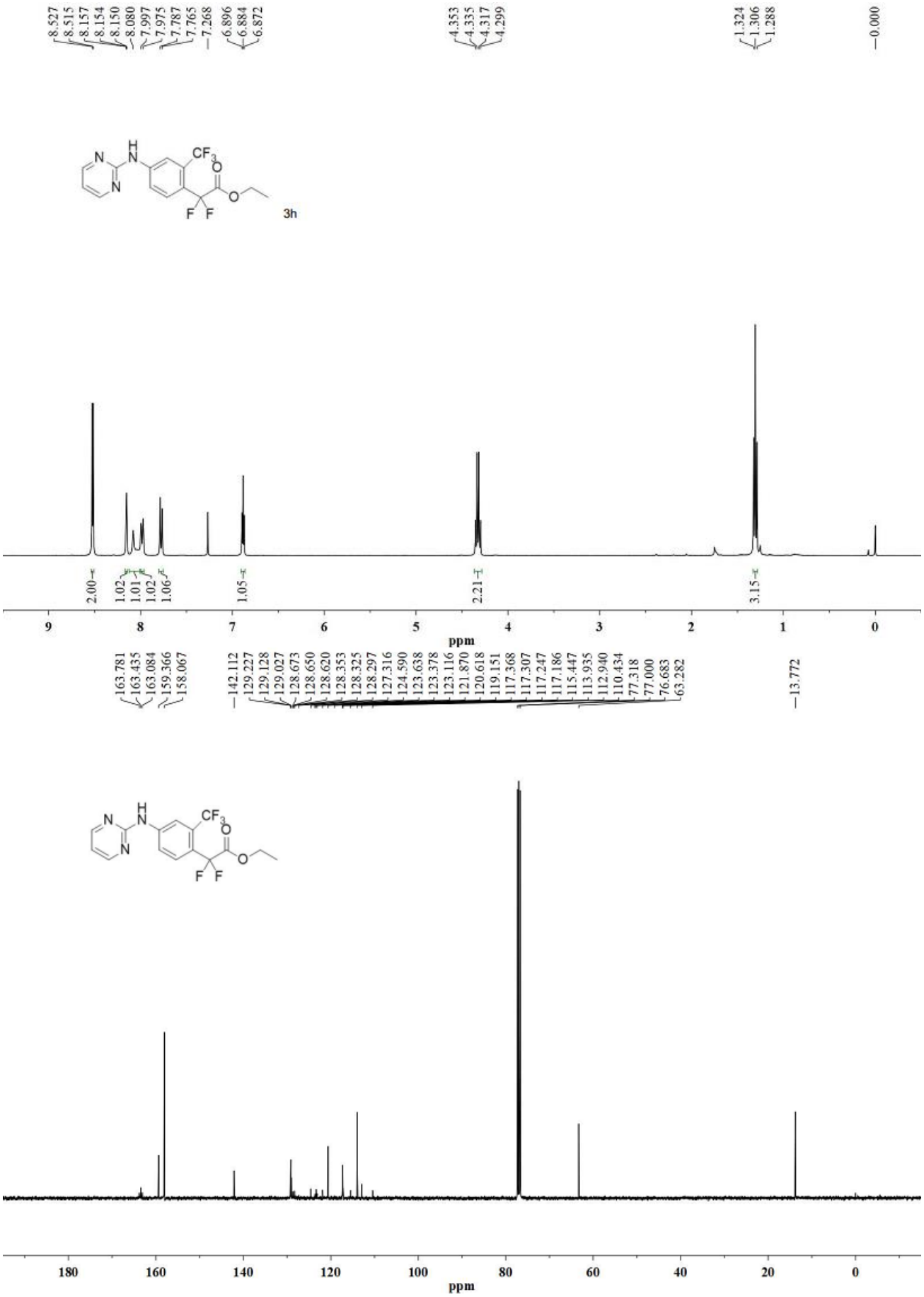
ppm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8.157
8.154
8.150
8.080
7.997
7.975
7.787
7.765
7.268
6.896
6.884
6.872
4.353
4.335
4.317
4.299
1.324
1.306
1.288
0.000
3h
2.00
1.02
1.01
1.02
1.06
1.05
2.21
3.15
ppm
163.781
163.435
163.084
159.366
158.067
142.112
129.227
129.128
129.027
128.673
128.650
128.620
128.353
128.325
128.297
127.316
124.590
123.638
123.378
123.116
121.870
120.618
119.151
117.368
117.307
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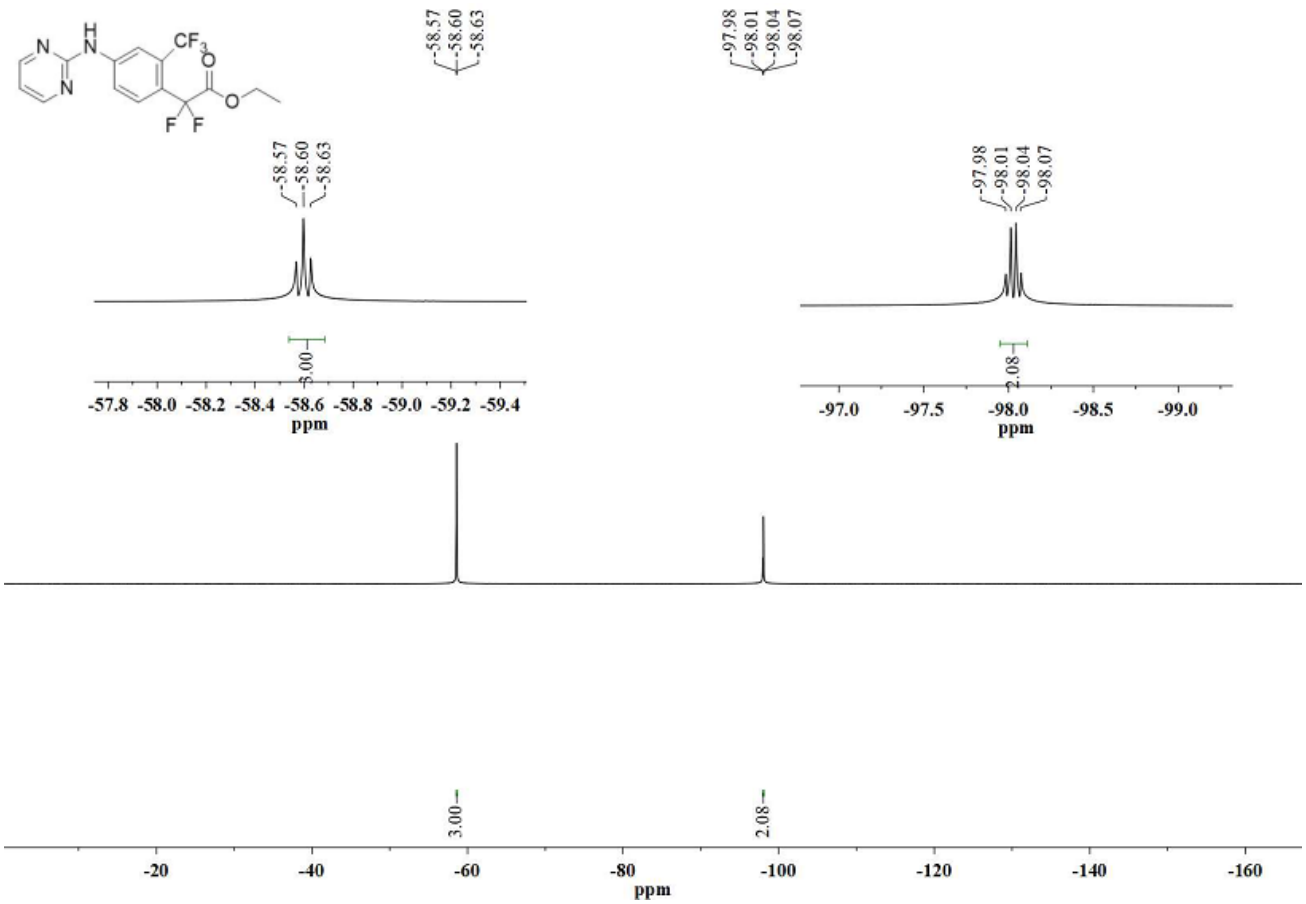
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-58.60
-58.63
-97.98
-98.01
-98.04
-98.07
3.00
2.08
-57.8 -58.0 -58.2 -58.4 -58.6 -58.8 -59.0 -59.2 -59.4
-97.0 -97.5 -98.0 -98.5 -99.0
ppm
-20 -40 -60 -80 -100 -120 -140 -160
ppm


8.465
8.453
7.727
7.718
7.704
7.703
7.662
7.586
7.550
7.542
7.536
7.527
7.355
7.267
6.791
6.779
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4.295
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2.469
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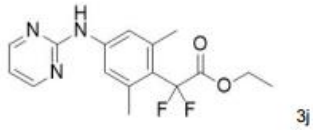
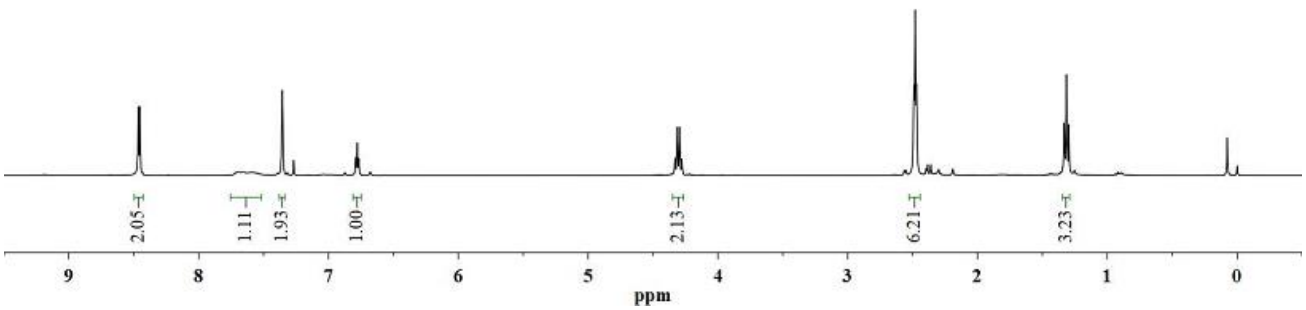
1.314
1.296
0.000



3j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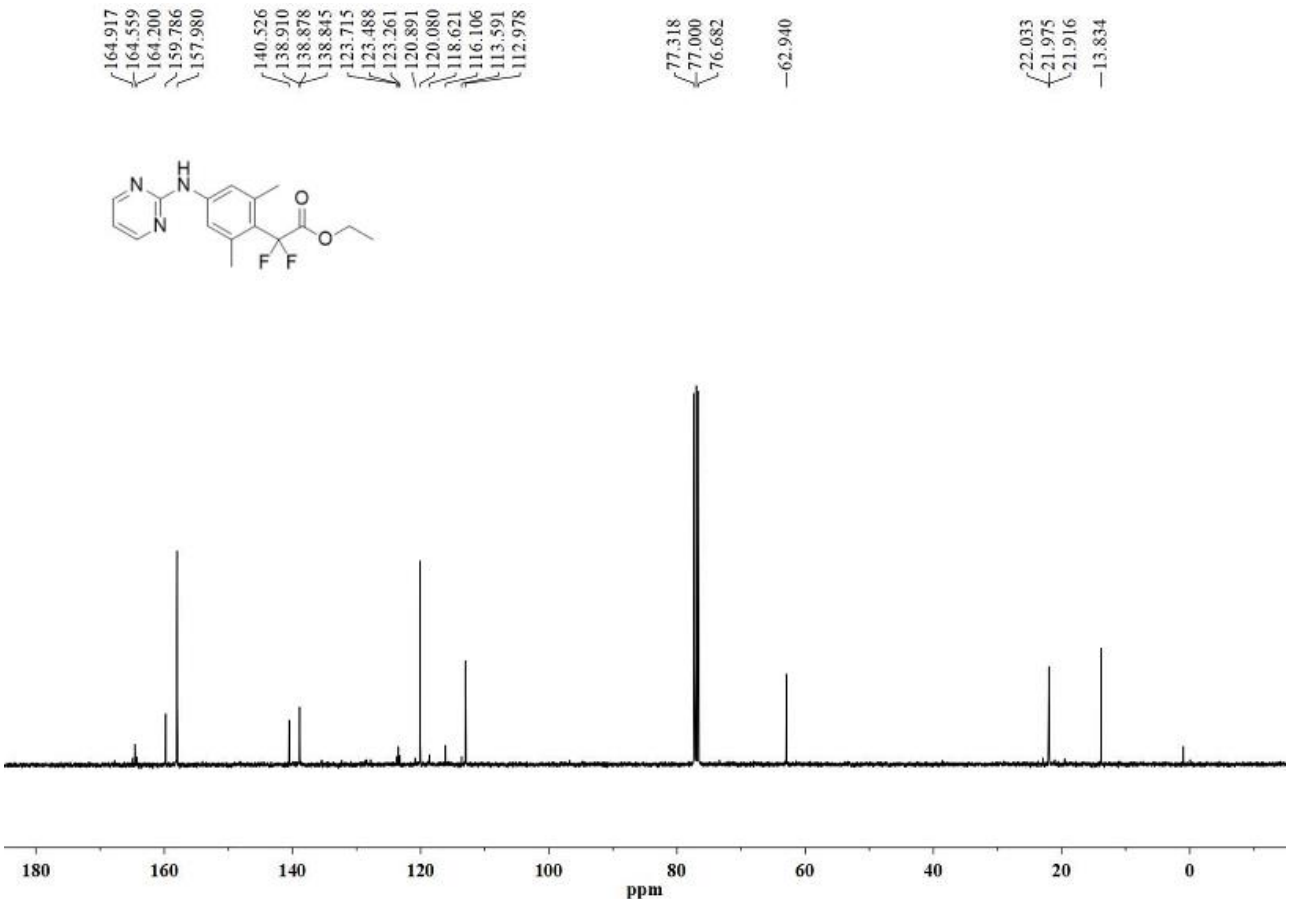
1.11
1.93
1.00
2.13
6.21
3.23
9 8 7 6 5 4 3 2 1 0
ppm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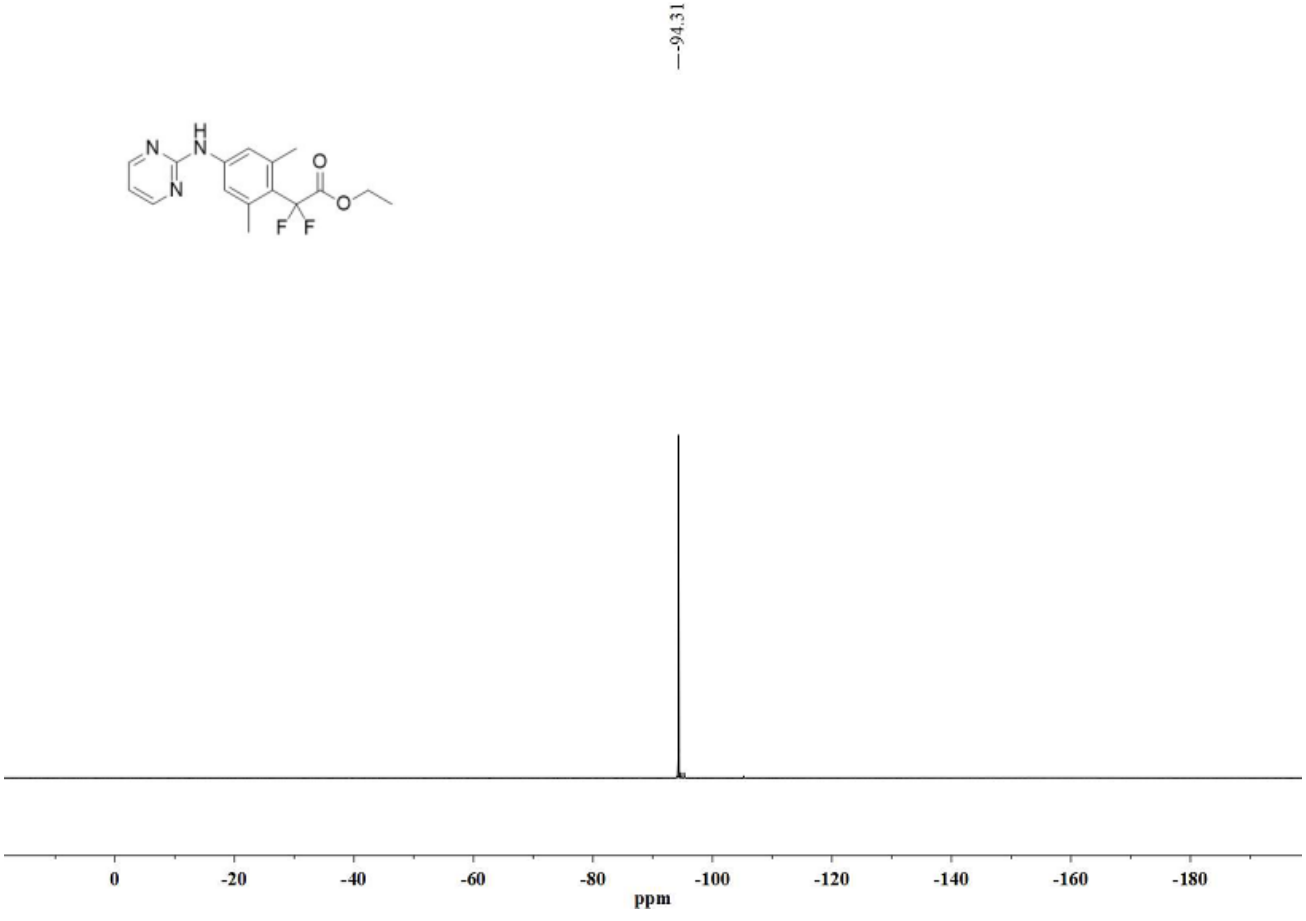
159.786
157.980
140.526
138.910
138.878
138.845
123.715
123.488
123.261
120.891
120.080
118.621
116.106
113.591
112.978
77.318
77.000
76.682
62.940
22.033
21.975
21.916
13.834
N
H
N
O
O
F
F
180
160
140
120
100
80
60
40
20
0
ppm


94.31
N
H
N
O
O
F
F
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-20
-40
-60
-80
-100
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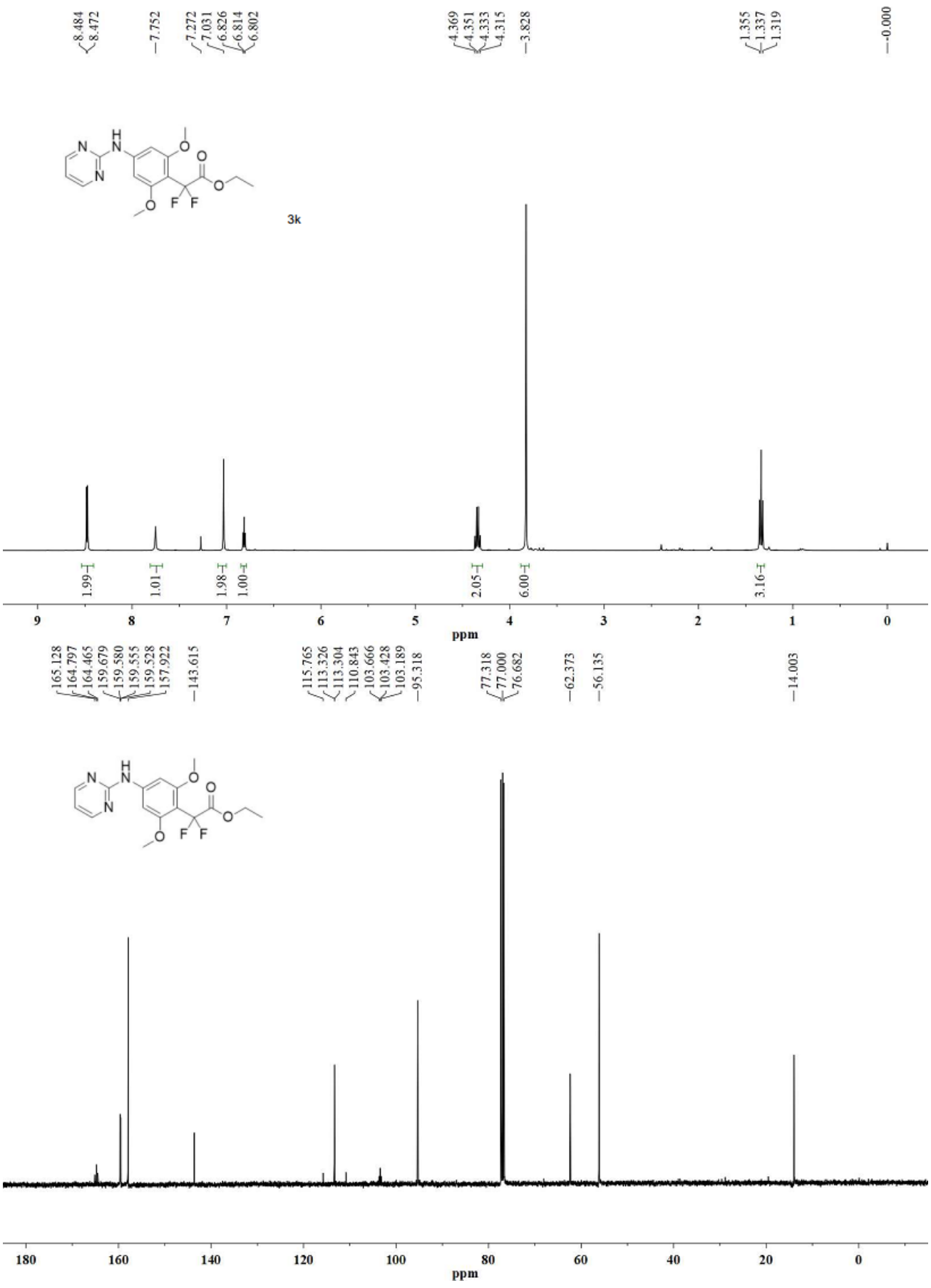
-140
-160
-180
ppm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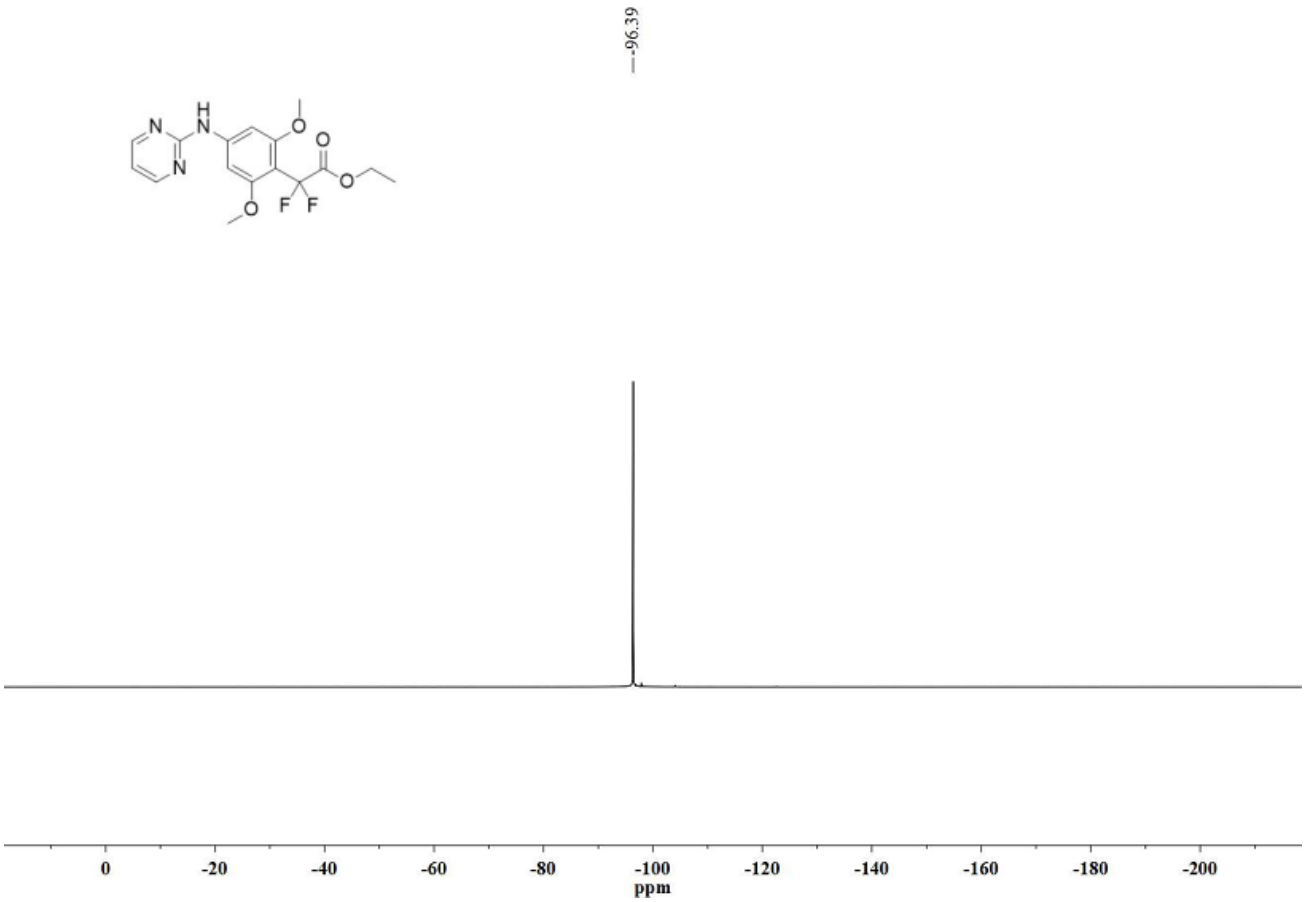
6.802
4.369
4.351
4.333
4.315
3.828
1.355
1.337
1.319
0.000
3k
1.99
1.01
1.98
1.00
2.05
6.00
3.16
ppm
165.128
164.797
164.465
159.679
159.580
159.555
159.528
157.922
143.615
115.765
113.326
113.304
110.843
103.666
103.428
103.189
95.318
77.318
77.000
76.682
62.373
56.135
14.003
ppm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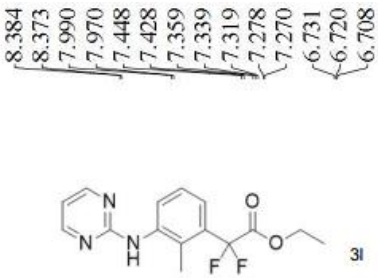
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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7.448
7.428
7.359
7.339
7.319
7.278
7.270
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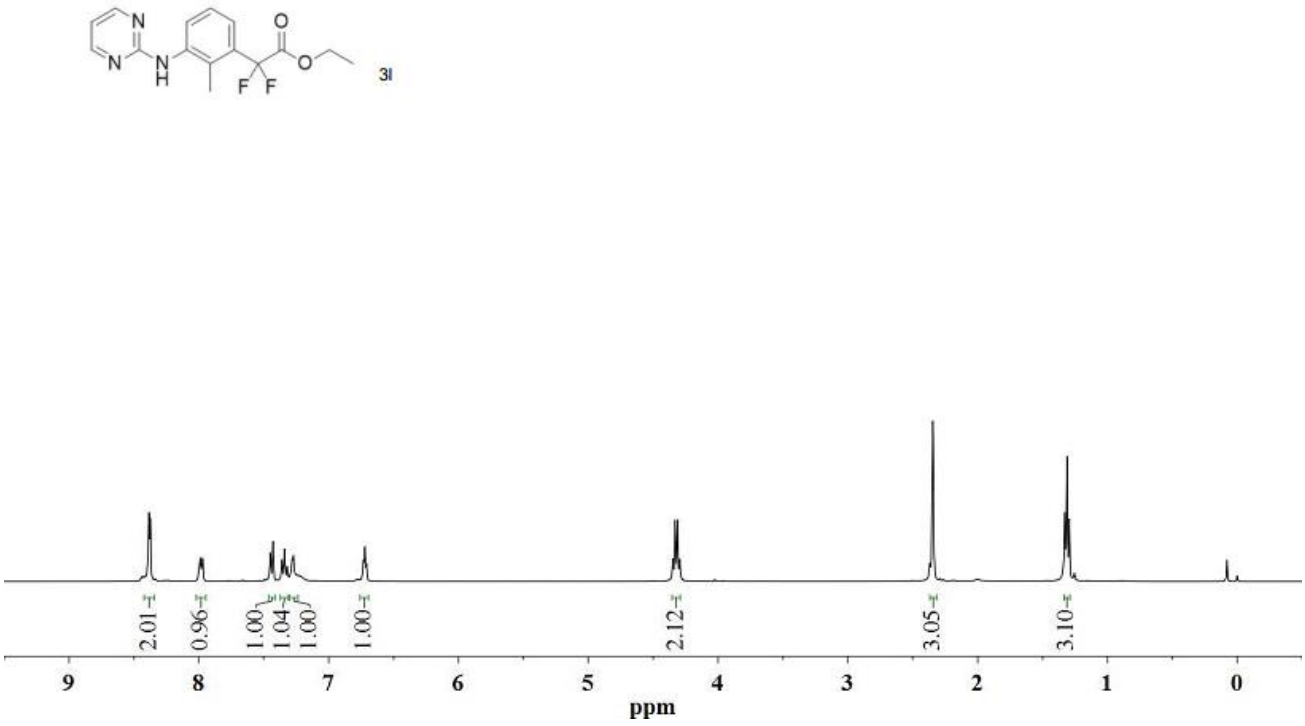
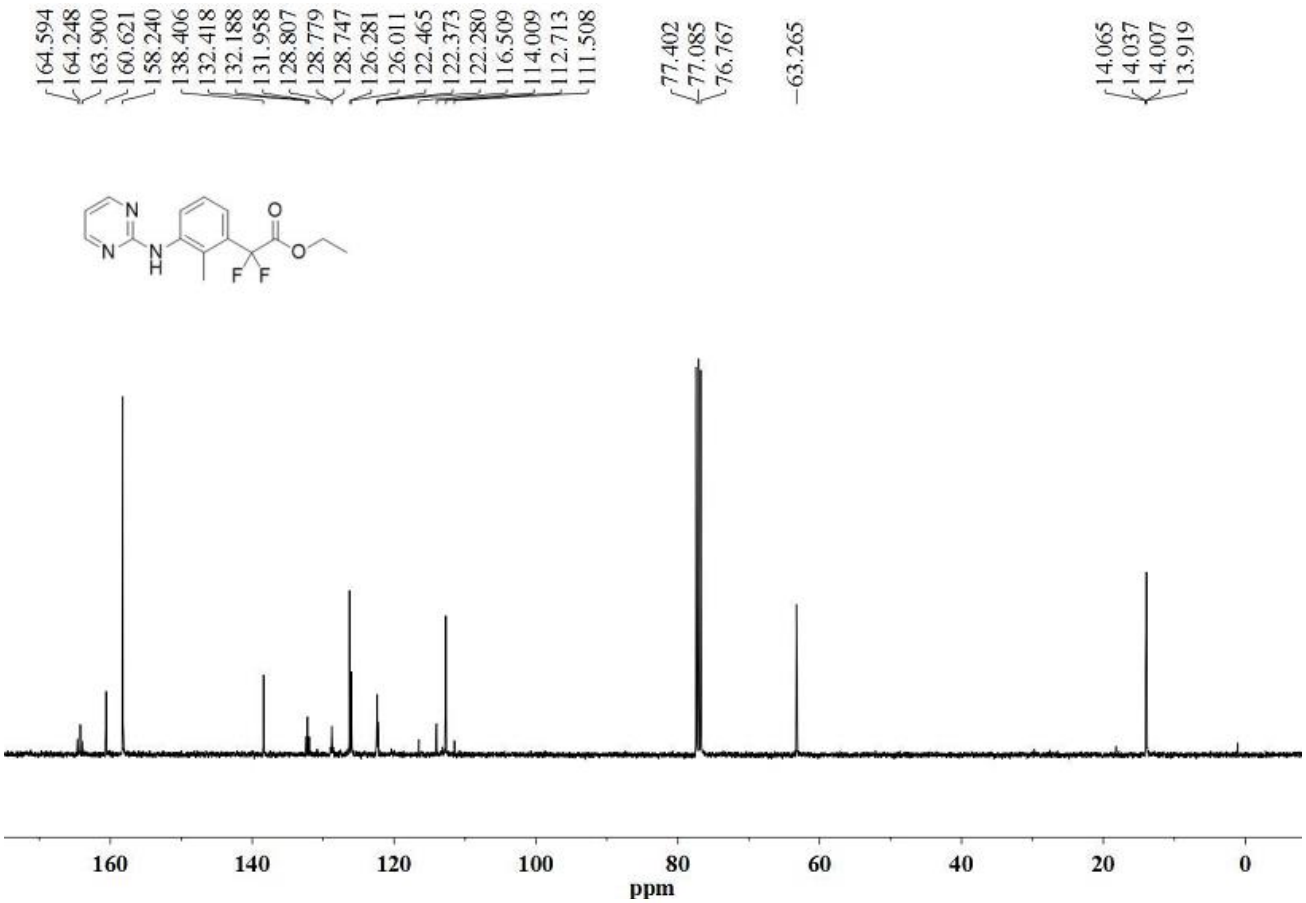
6.708
4.348
4.330
4.312
4.294
2.344
1.329
1.311
1.293
0.000


2.01
0.96
1.00
1.04
1.00
1.00
2.12
3.05
3.10
9
8
7
6
5
4
3
2
1
0
ppm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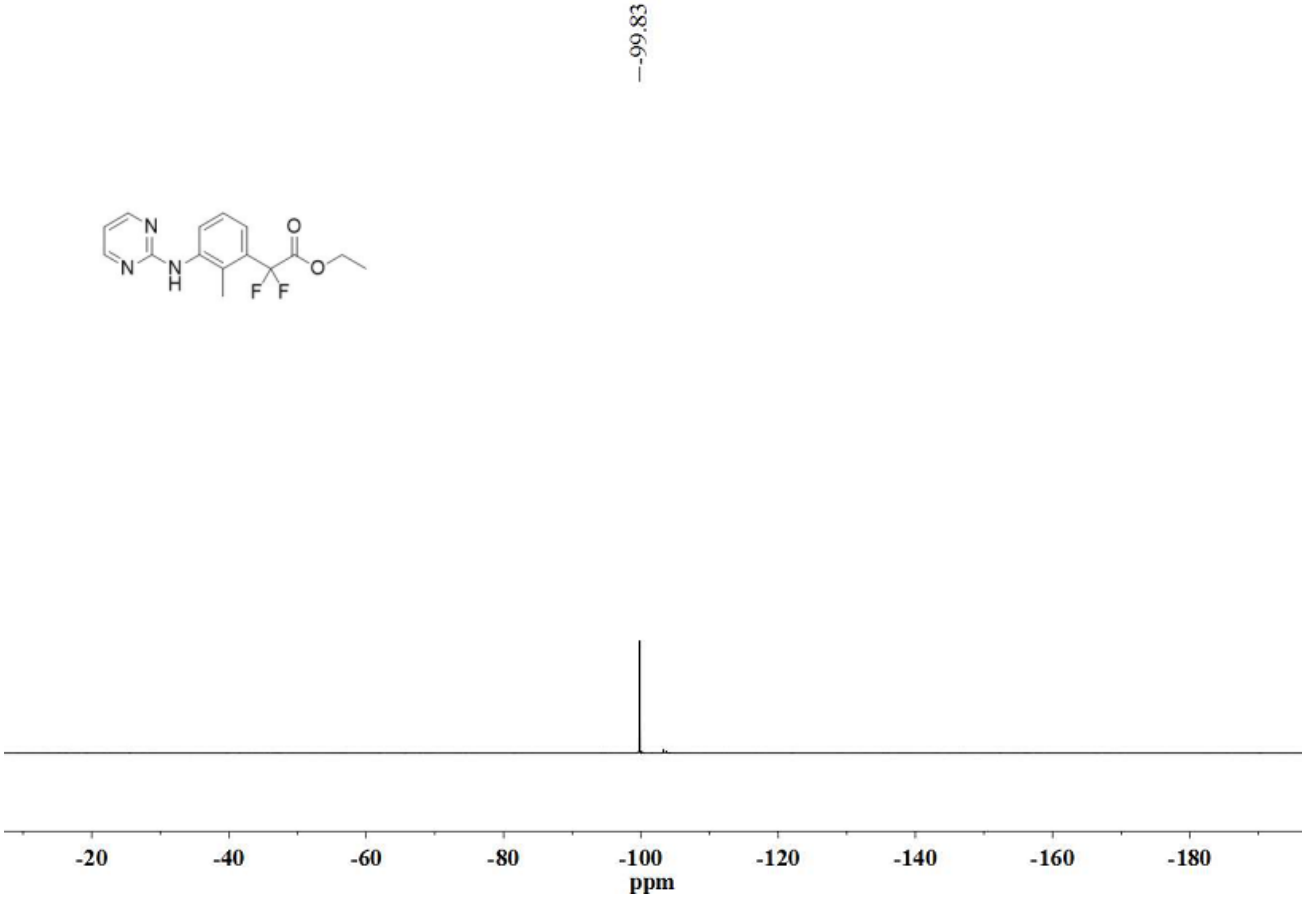
132.188
131.958
128.807
128.779
128.747
126.281
126.011
122.465
122.373
122.280
116.509
114.009
112.713
111.508
77.402
77.085
76.767
63.265
14.065
14.037
14.007
13.919
160
140
120
100
80
60
40
20
0
ppm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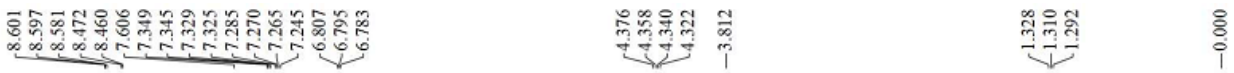
-160
-180
ppm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8.581
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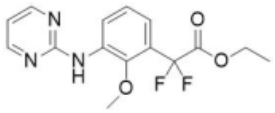
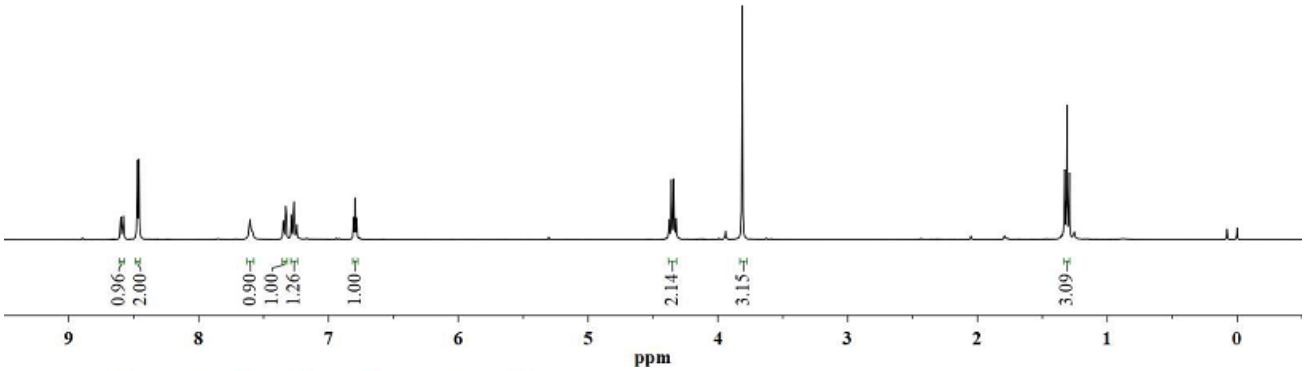
8.460
7.606
7.349
7.345
7.329
7.325
7.285
7.270
7.265
7.245
6.807
6.795
6.783
4.376
4.358
4.340
4.322
3.812
1.328
1.310
1.292
0.000


N
N
H
O
F F
O
O

3m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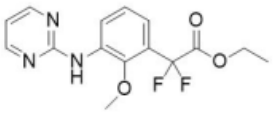
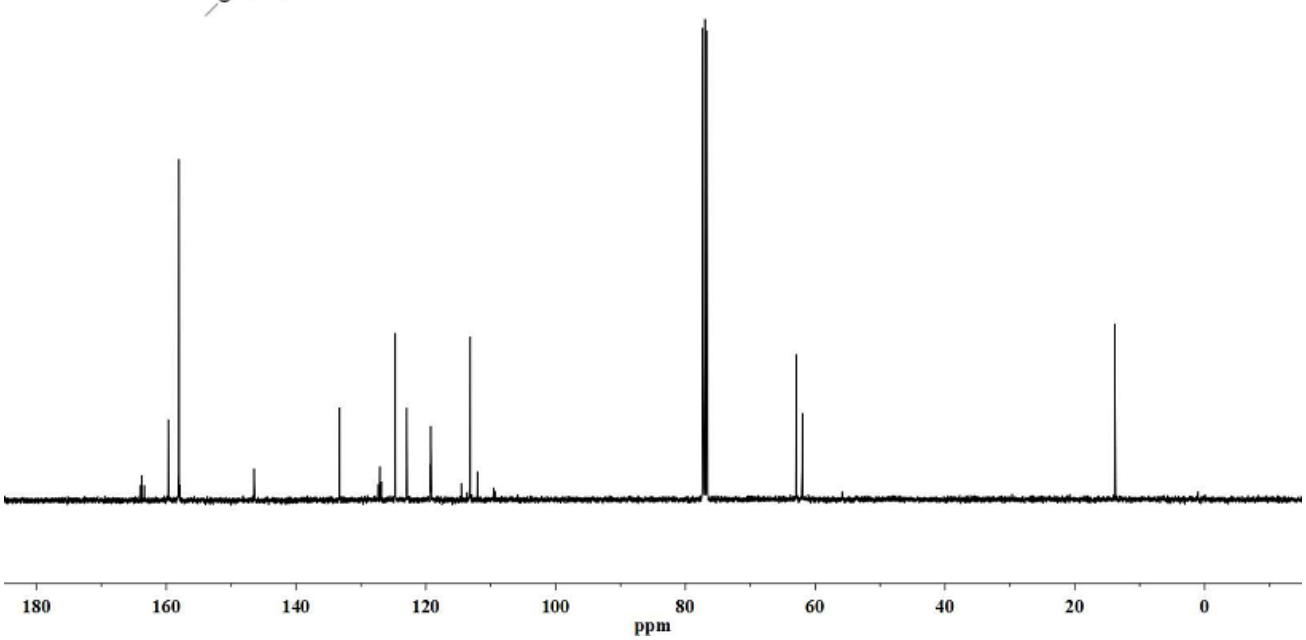
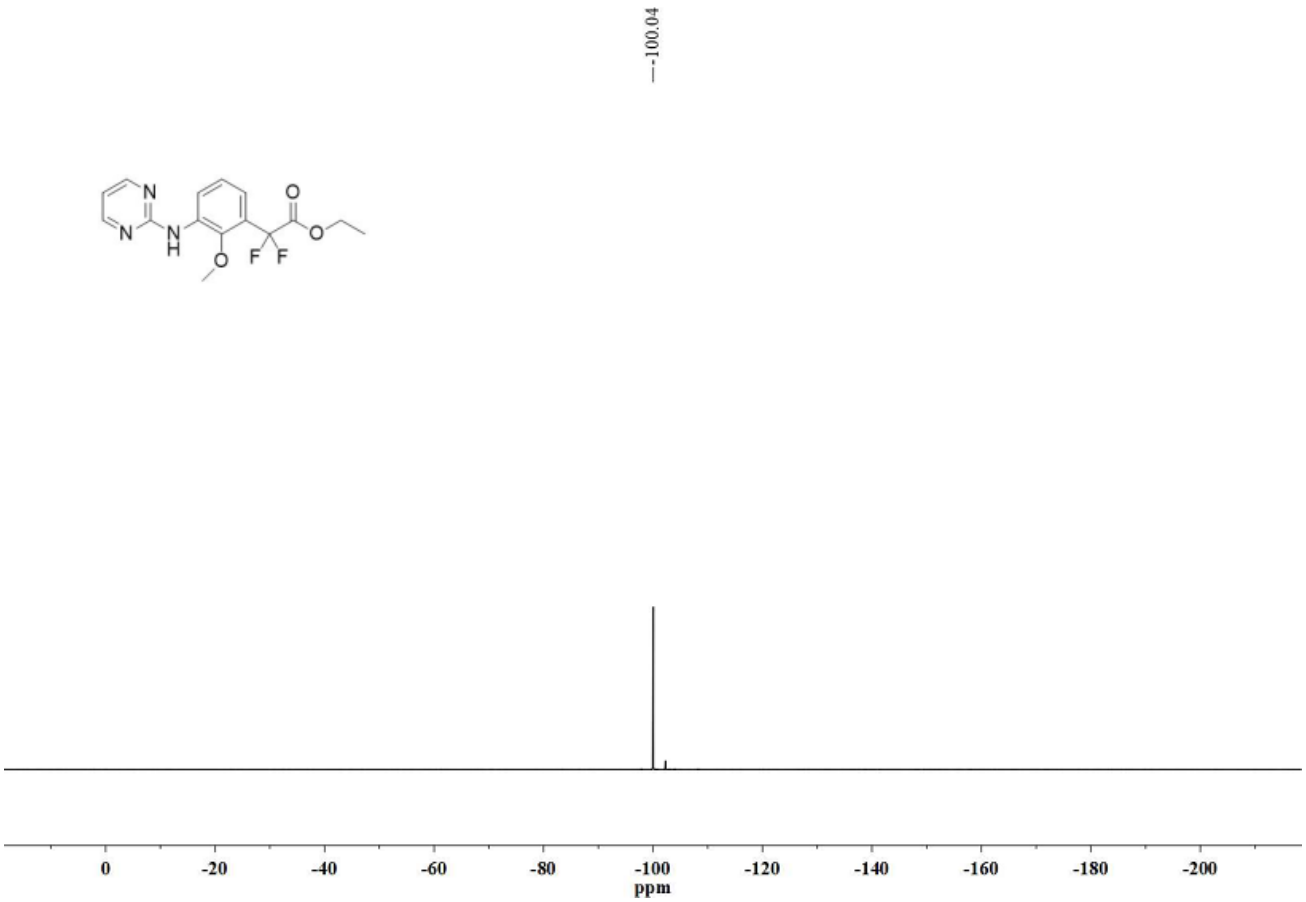
2.00
0.90
1.00
1.26
1.00
2.14
3.15
3.09
9
8
7
6
5
4
3
2
1
0
ppm


164.051
163.716
163.380
159.691
158.068
146.509
146.457
146.404
133.318
127.357
127.106
126.856
124.709
122.930
119.316
119.244
119.173
114.489
113.192
112.021
109.553
77.318
77.001
76.683
62.921
61.990
13.841


N
N
H
O
F F
O
O


180
160
140
120
100
80
60
40
20
0
ppm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-80
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-160
-180
-200
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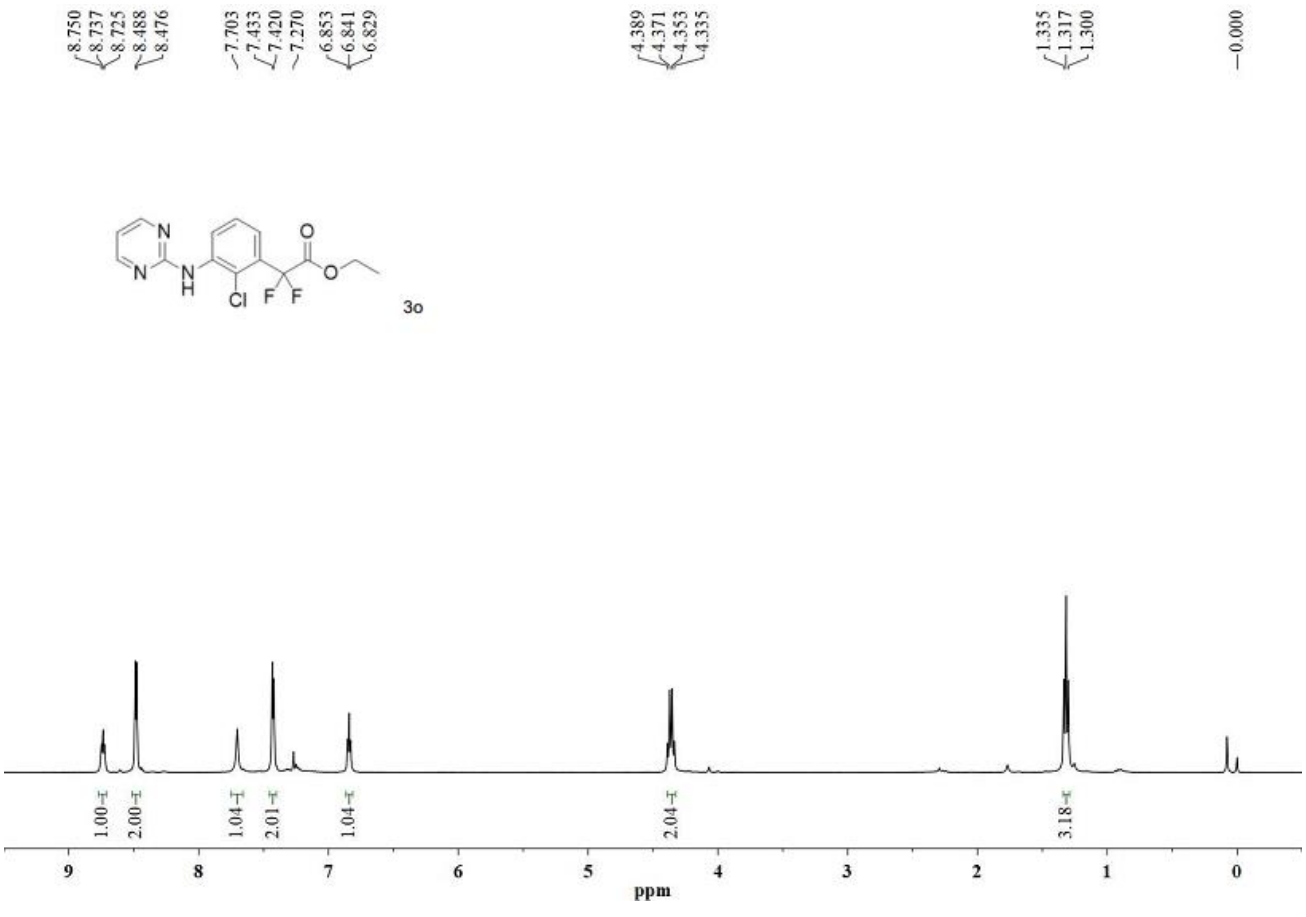
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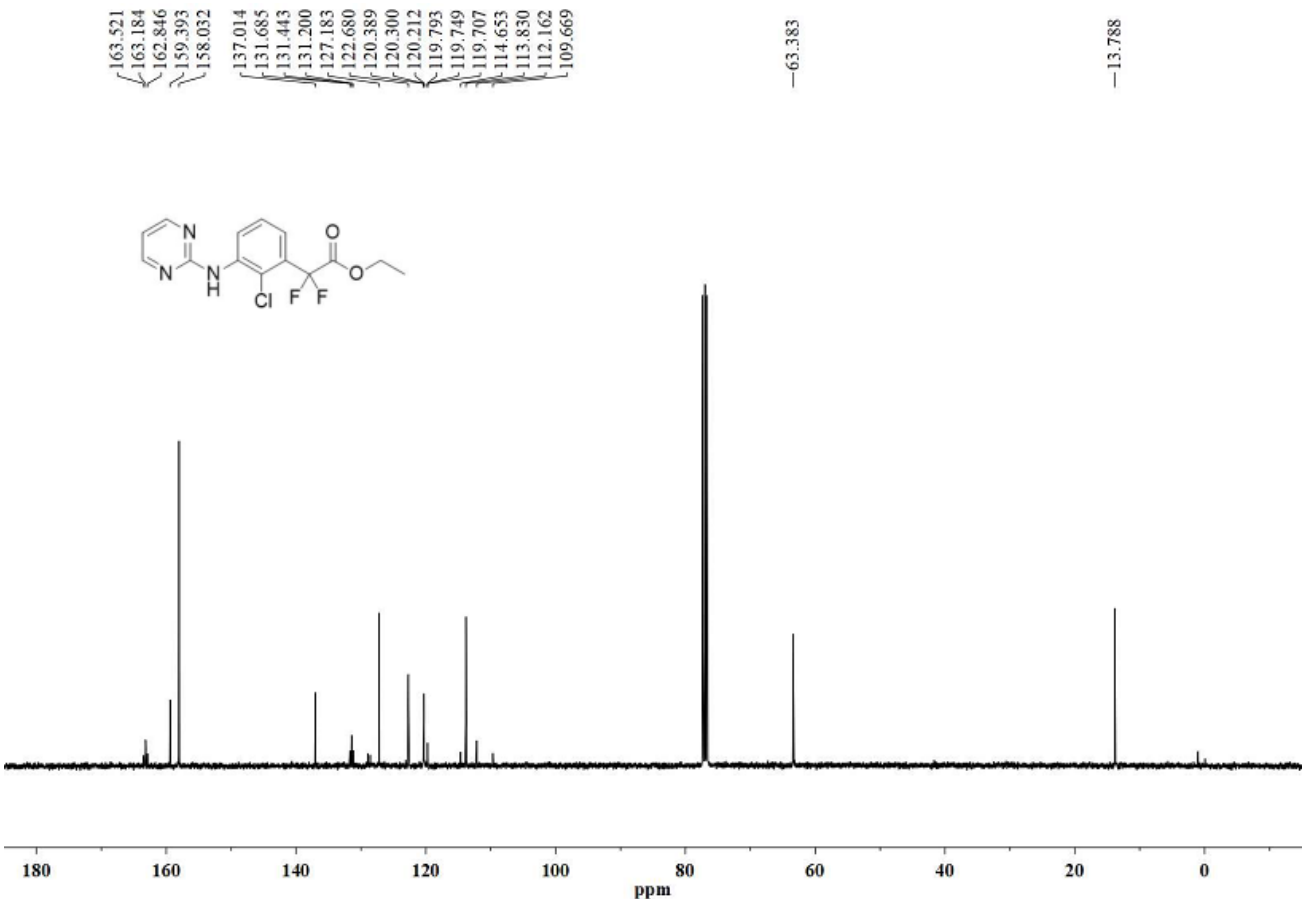
6.841
6.829
4.389
4.371
4.353
4.335
1.335
1.317
1.300
0.000
1.00
2.00
1.04
2.01
1.04
2.04
3.18
9
8
7
6
5
4
3
2
1
0
ppm

3o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158.032
137.014
131.685
131.443
131.200
127.183
122.680
120.389
120.300
120.212
119.793
119.749
119.707
114.653
113.830
112.162
109.669
63.383
13.788
N
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H
Cl
F
F
O
O
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160
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120
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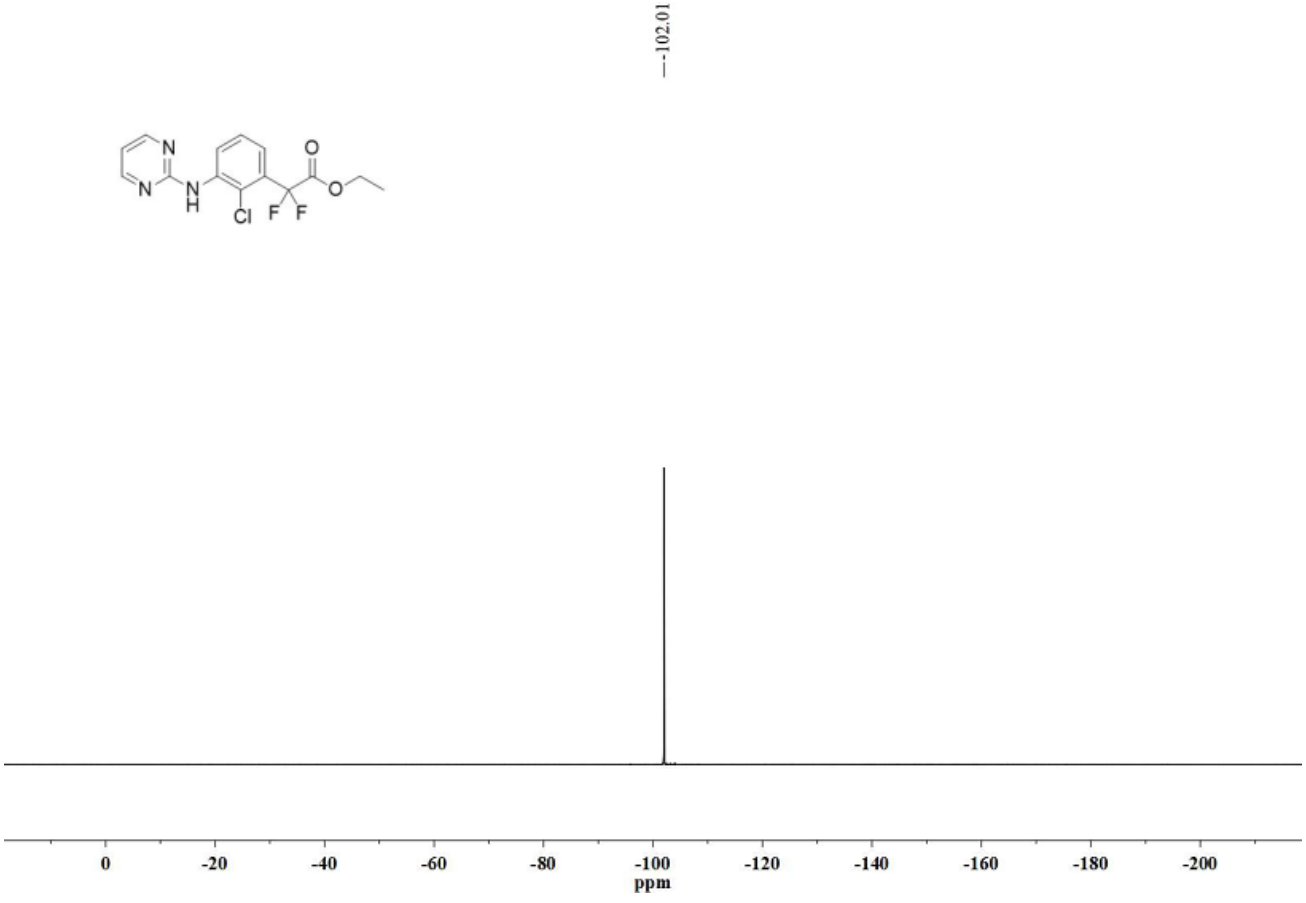
40
20
0
ppm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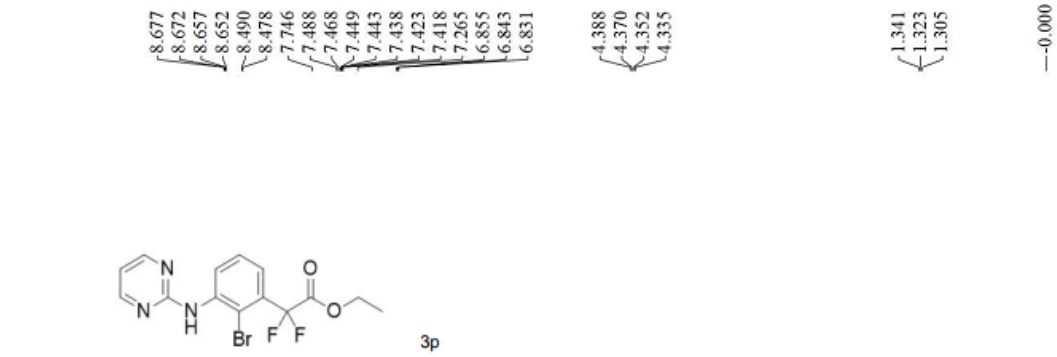
-200
ppm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8.478
7.746
7.488
7.468
7.449
7.443
7.438
7.423
7.418
7.265
6.855
6.843
6.831
4.388
4.370
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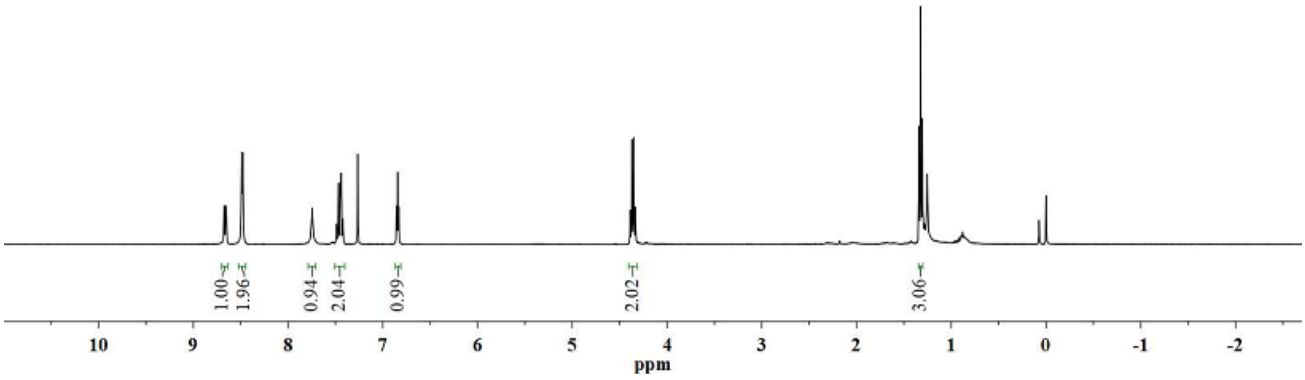
4.335
1.341
1.323
1.305
0.000

N
N
H
Br
F
F
O
O

3p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1.96
0.94
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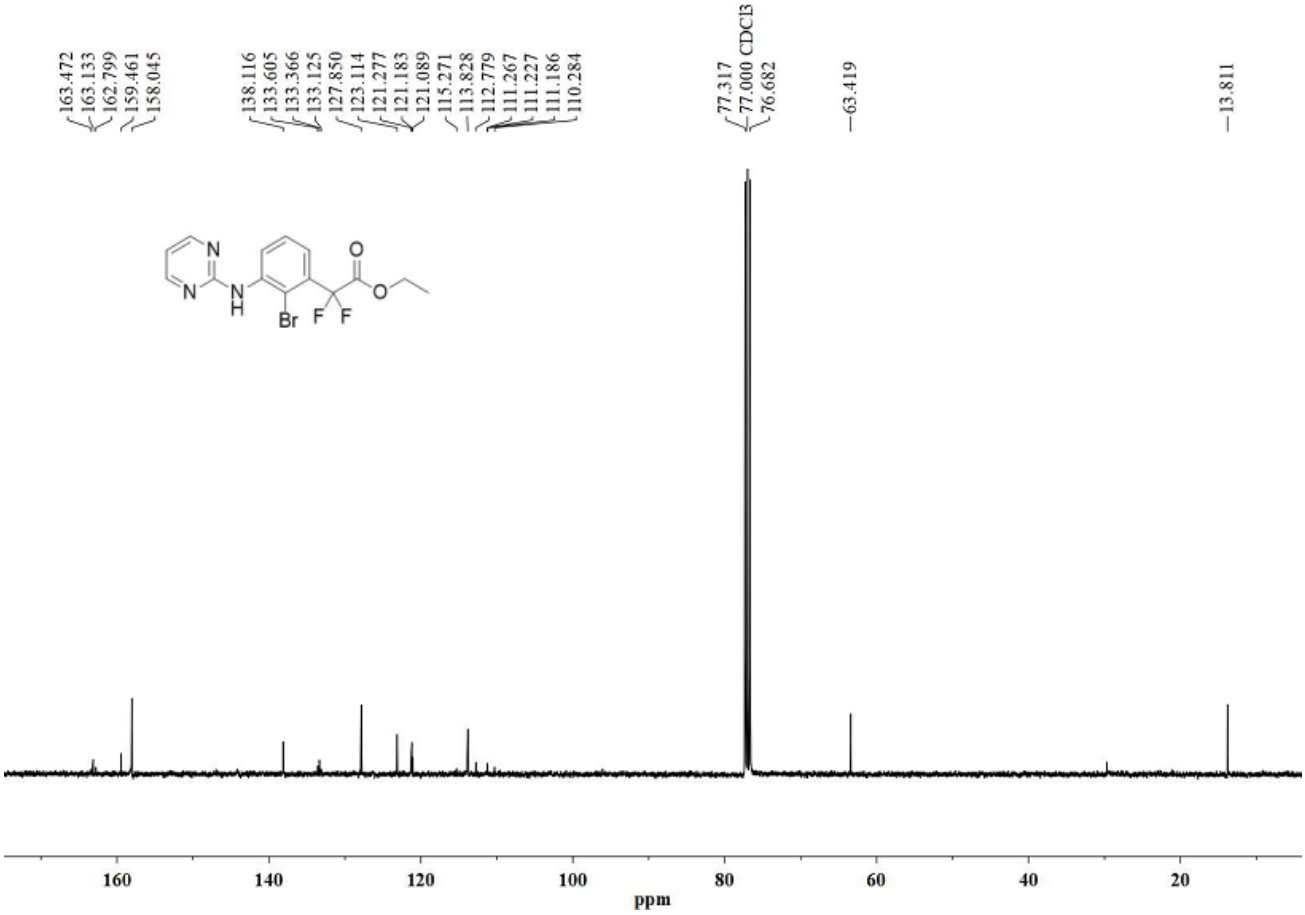
3.06
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm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158.045
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133.605
133.366
133.125
127.850
123.114
121.277
121.183
121.089
115.271
113.828
112.779
111.267
111.227
111.186
110.284
77.317
77.000 CDCl3
76.682
63.419
13.811
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140
120
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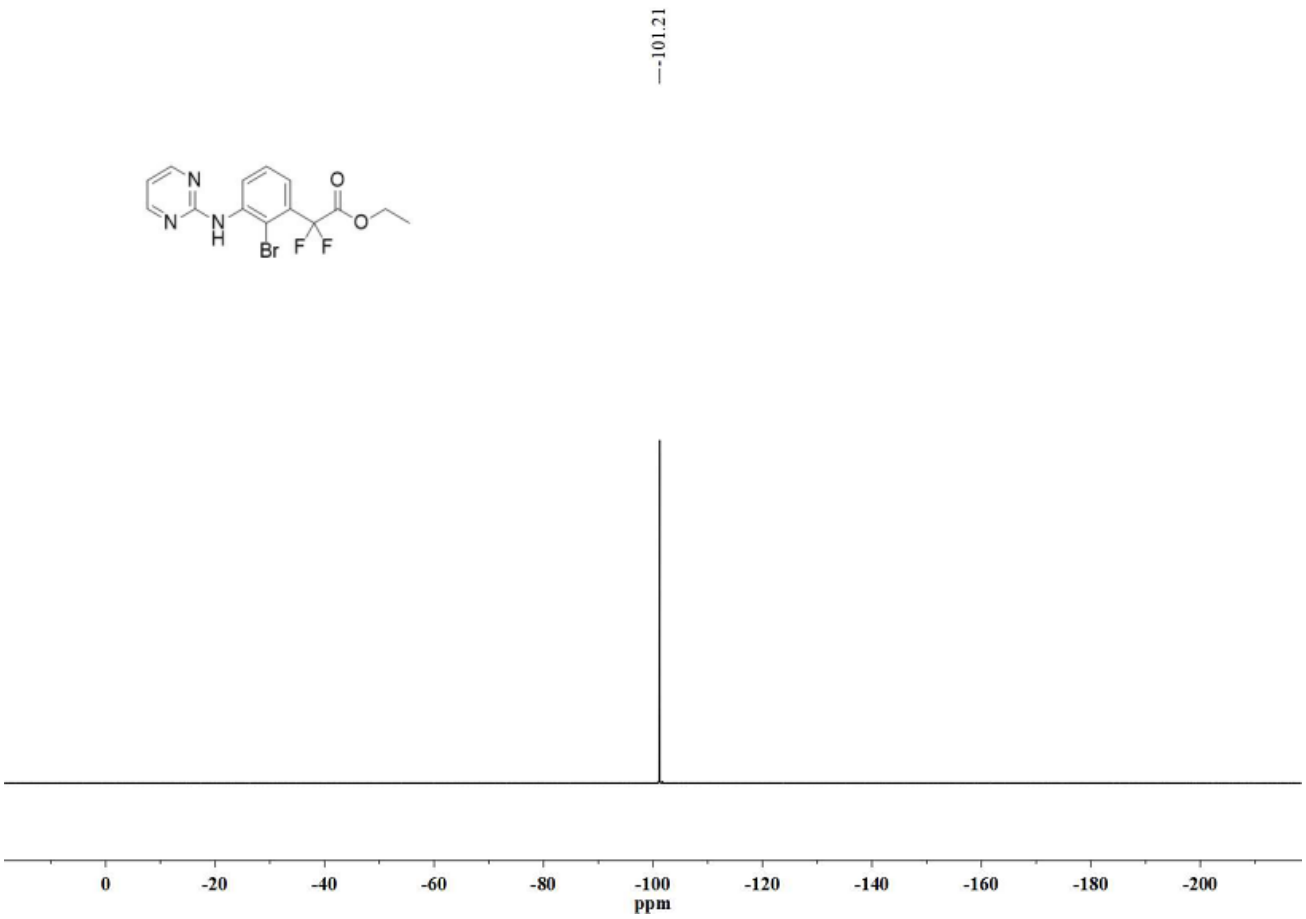
80
60
40
20
ppm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Br
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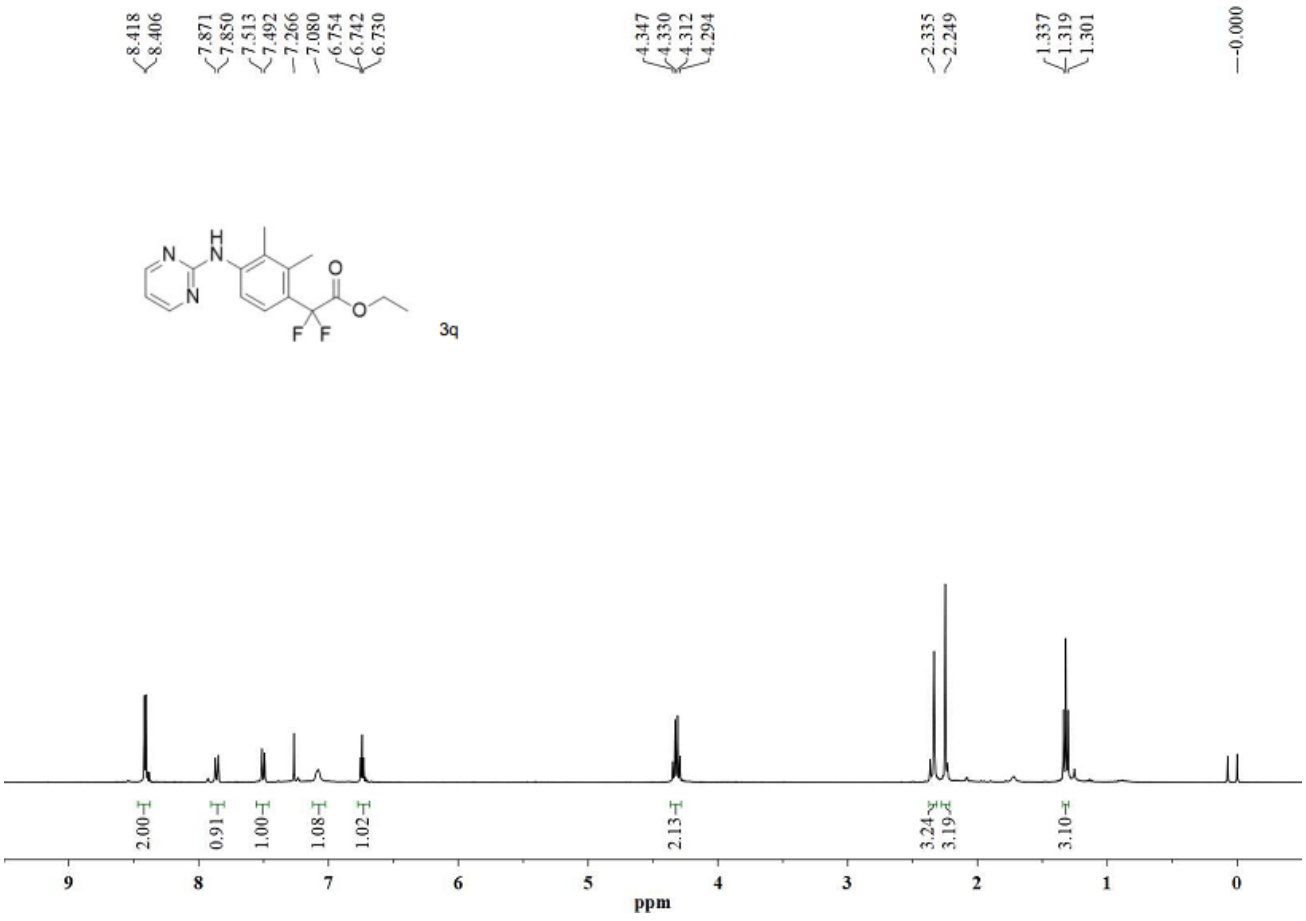
ppm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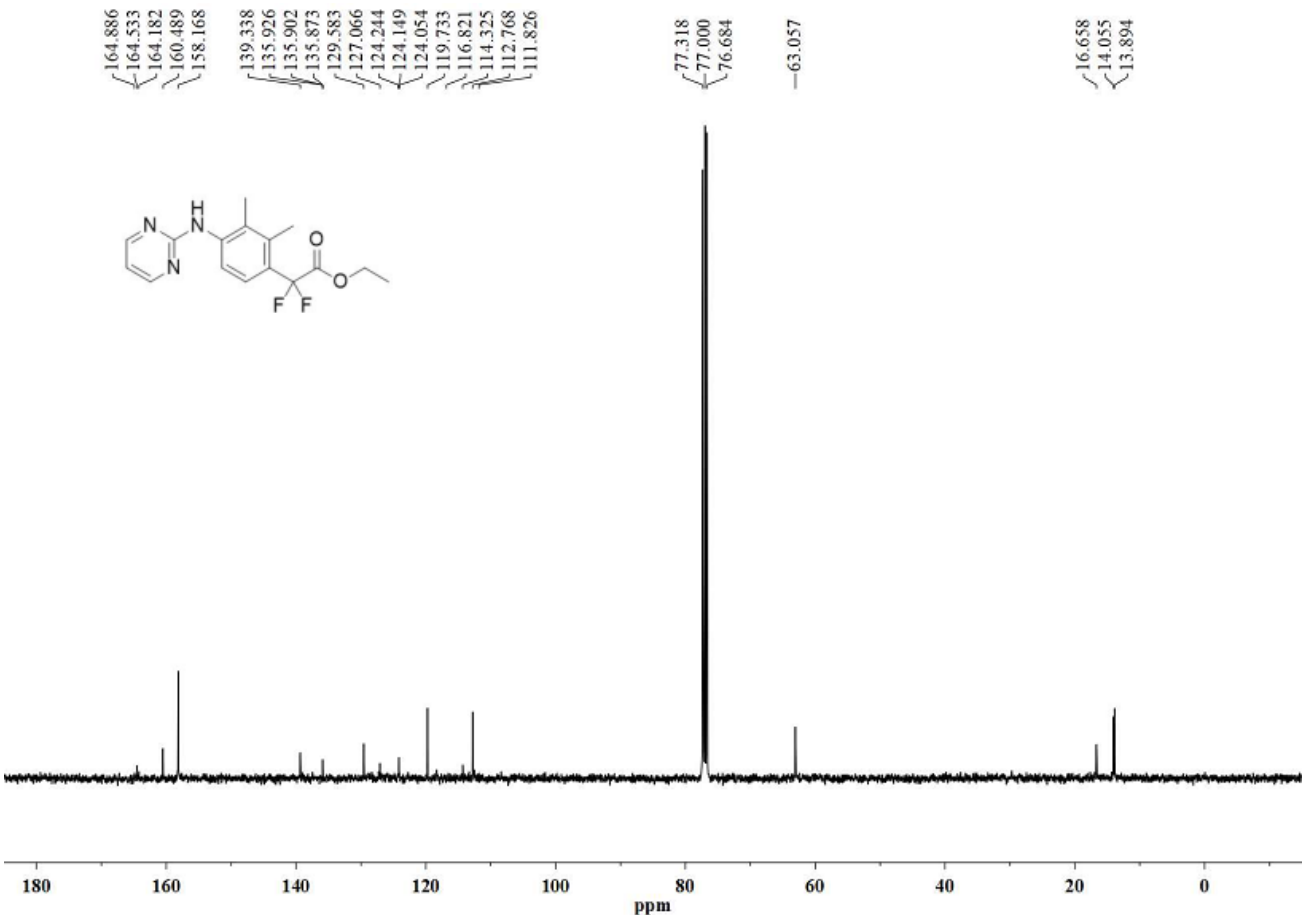
7.871
7.850
7.513
7.492
7.266
7.080
6.754
6.742
6.730
4.347
4.330
4.312
4.294
2.335
2.249
1.337
1.319
1.301
0.000
N
H
N
O
O
F
F
2.00
0.91
1.00
1.08
1.02
2.13
3.24
3.19
3.10
9
8
7
6
5
4
3
2
1
0
ppm

3q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164.182
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158.168
139.338
135.926
135.902
135.873
129.583
127.066
124.244
124.149
124.054
119.733
116.821
114.325
112.768
111.826
77.318
77.000
76.684
63.057
16.658
14.055
13.894
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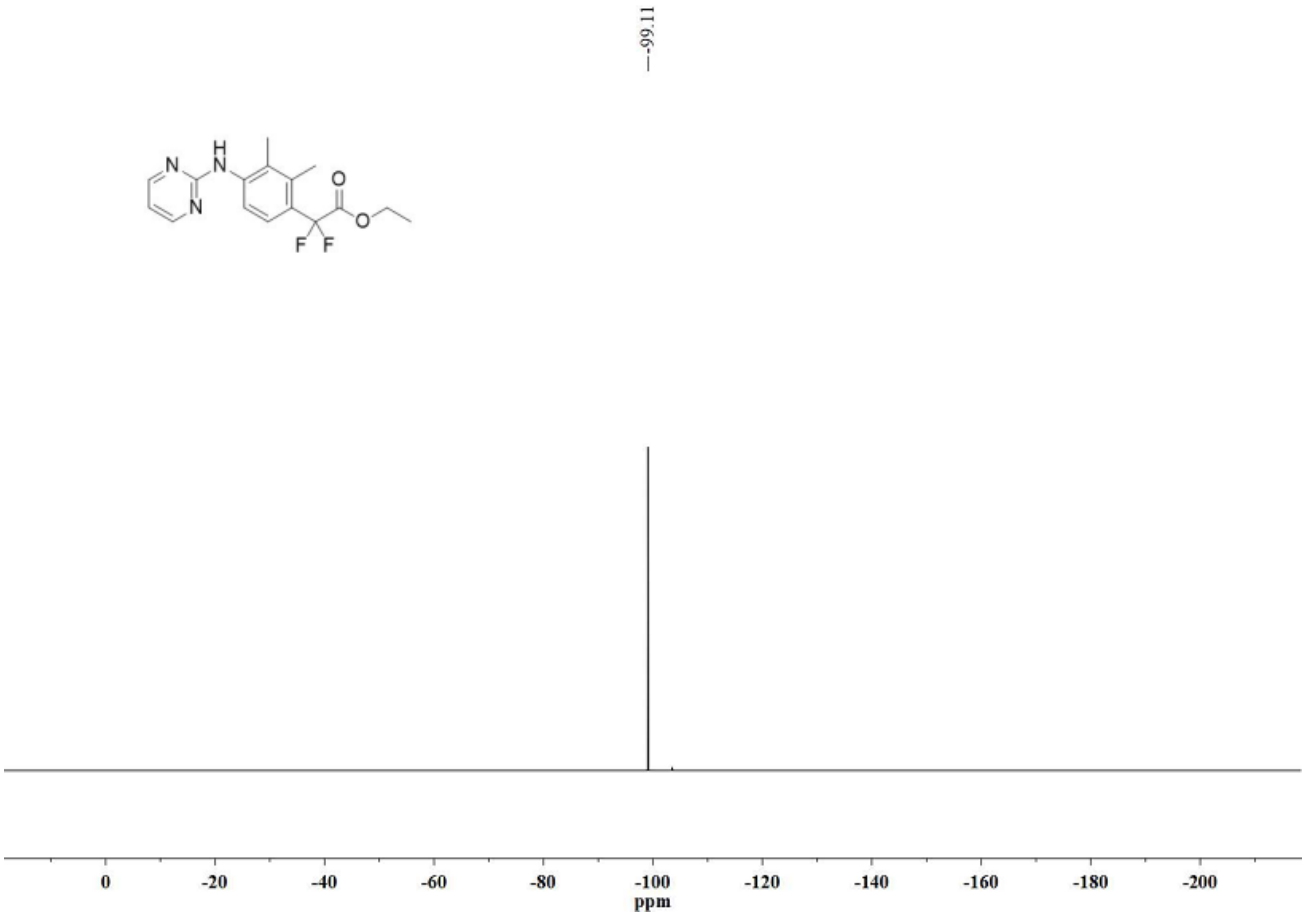
160
140
120
100
80
60
40
20
0
ppm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-60
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-120
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-160
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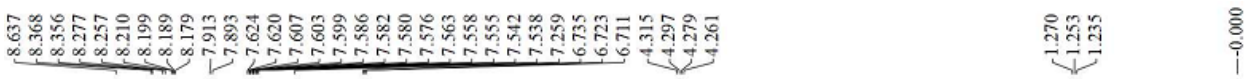
ppm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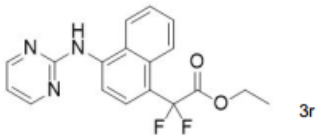
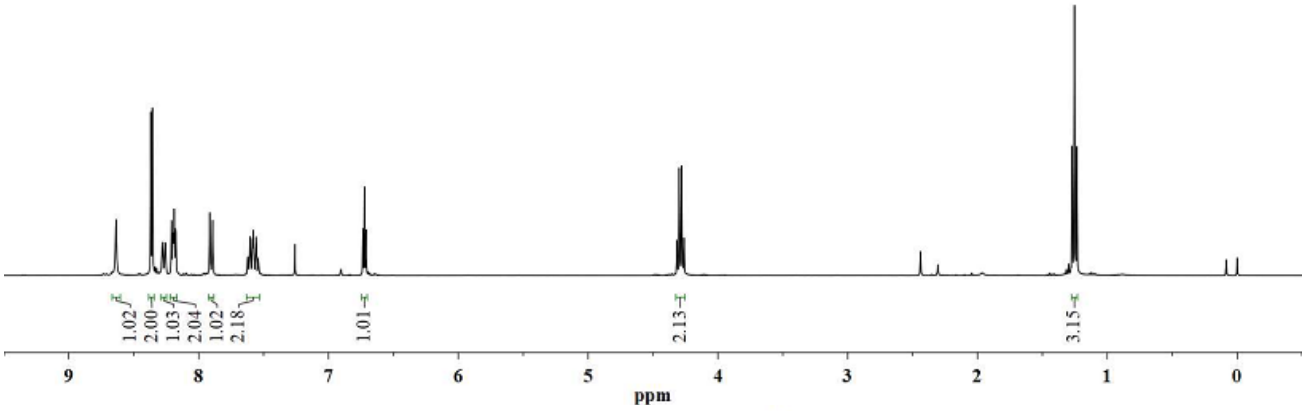
8.368
8.356
8.277
8.257
8.210
8.199
8.189
8.179
7.913
7.893
7.624
7.620
7.607
7.603
7.599
7.586
7.582
7.580
7.576
7.563
7.558
7.555
7.542
7.538
7.259
6.735
6.723
6.711
4.315
4.297
4.279
4.261
1.270
1.253
1.235
0.000


N
H
N
O
O
F F

3r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2.00
1.03
2.04
1.02
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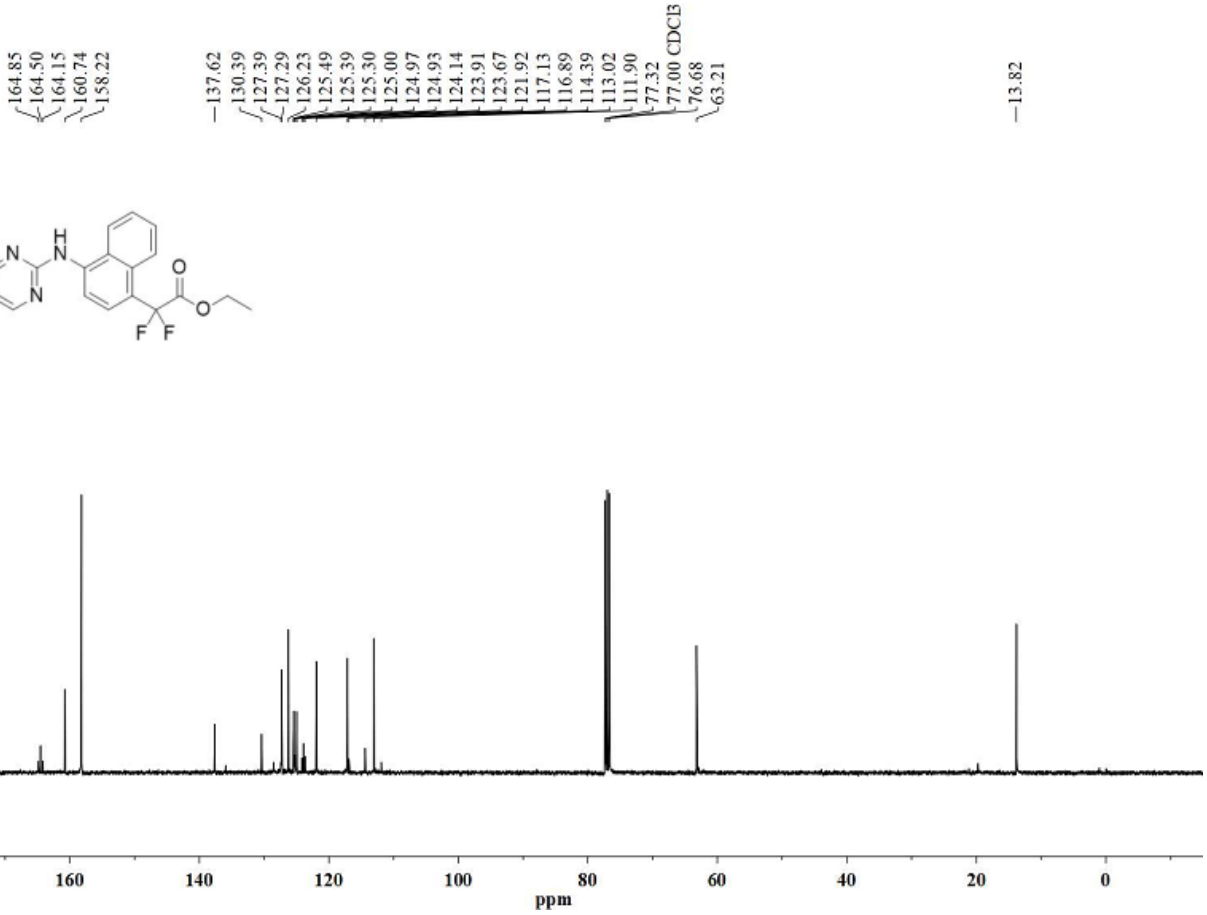
1.01
2.13
3.15
9
8
7
6
5
4
3
2
1
0
ppm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164.50
164.15
160.74
158.22
137.62
130.39
127.39
127.29
126.23
125.49
125.39
125.30
125.00
124.97
124.93
124.14
123.91
123.67
121.92
117.13
116.89
114.39
113.02
111.90
77.32
77.00 CDCl3
76.68
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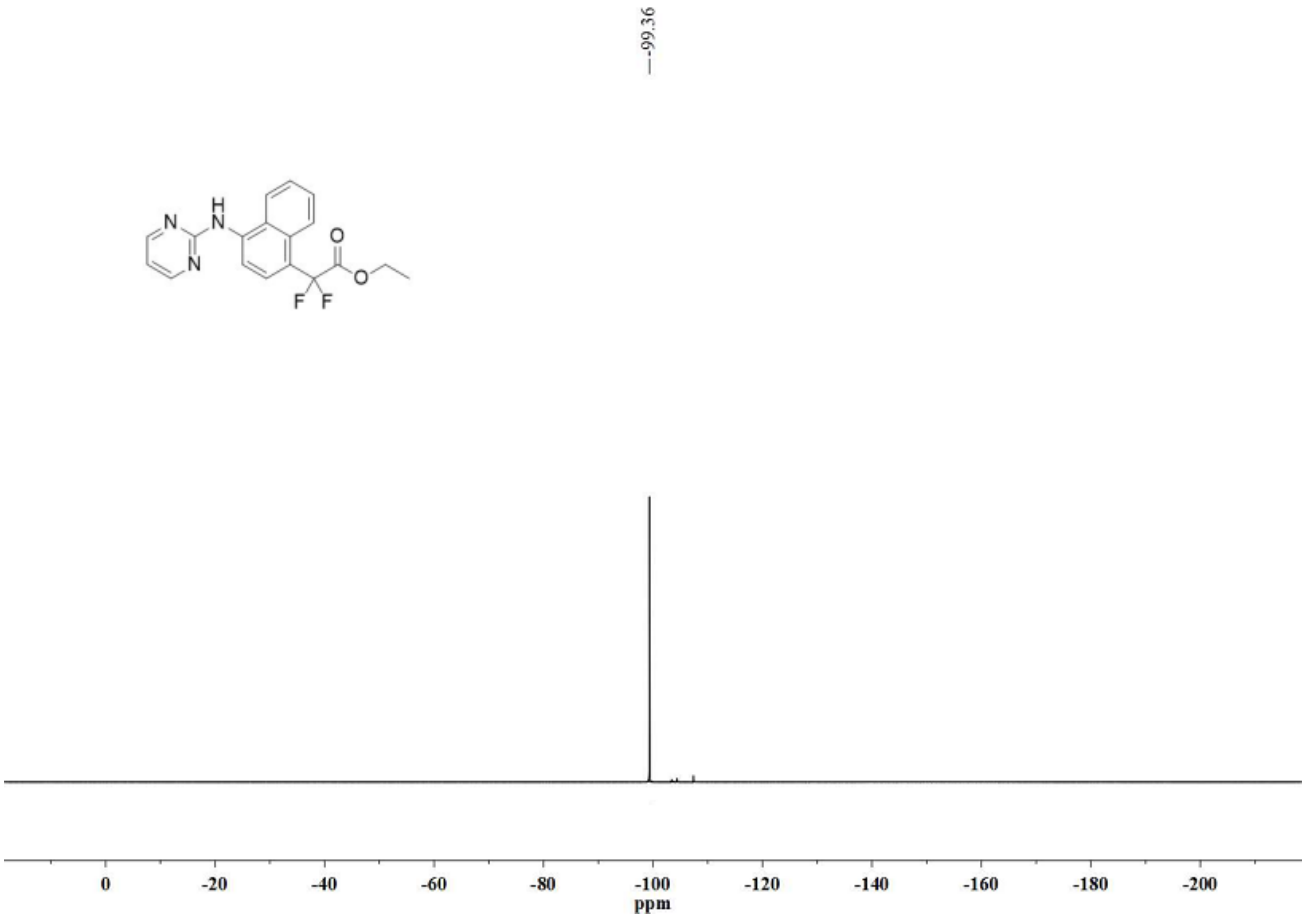
160
140
120
100
80
60
40
20
0
ppm

N
H
N
O
O
F F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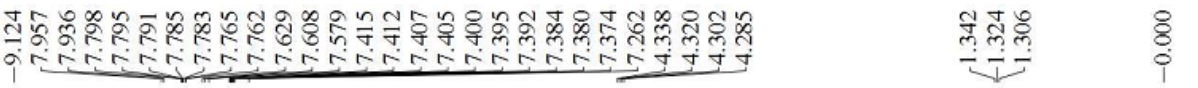
-200
ppm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7.957
7.936
7.798
7.795
7.791
7.785
7.783
7.765
7.762
7.629
7.608
7.579
7.415
7.412
7.407
7.405
7.400
7.395
7.392
7.384
7.380
7.374
7.262
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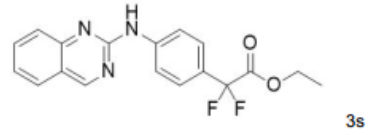
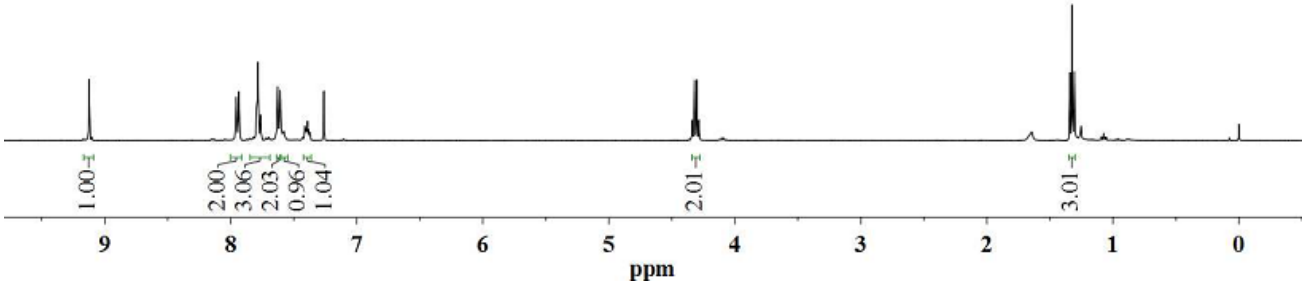
1.324
1.306
0.000



3s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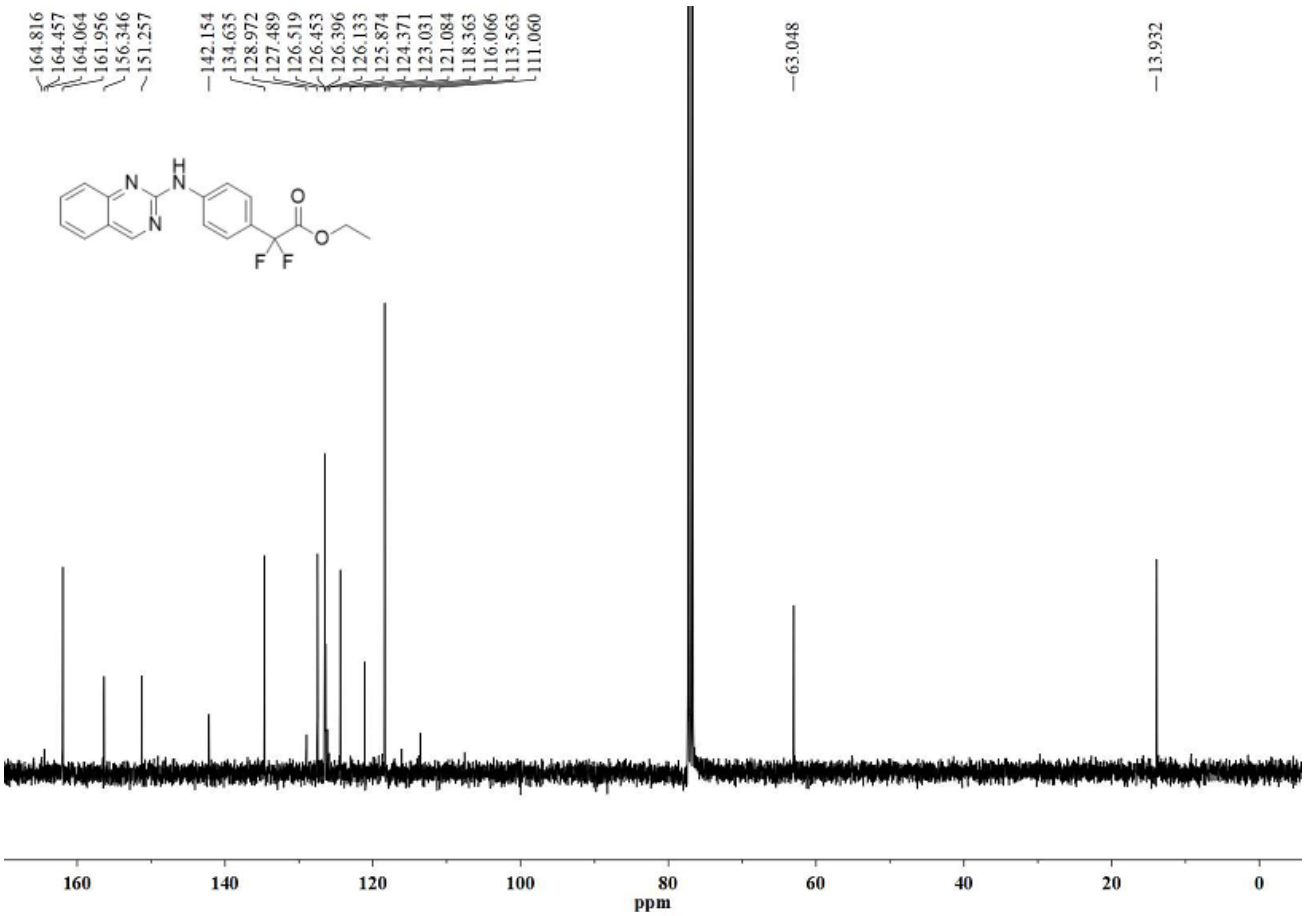
1.04
2.01
3.01
9
8
7
6
5
4
3
2
1
0
ppm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164.064
161.956
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151.257
142.154
134.635
128.972
127.489
126.519
126.453
126.396
126.133
125.874
124.371
123.031
121.084
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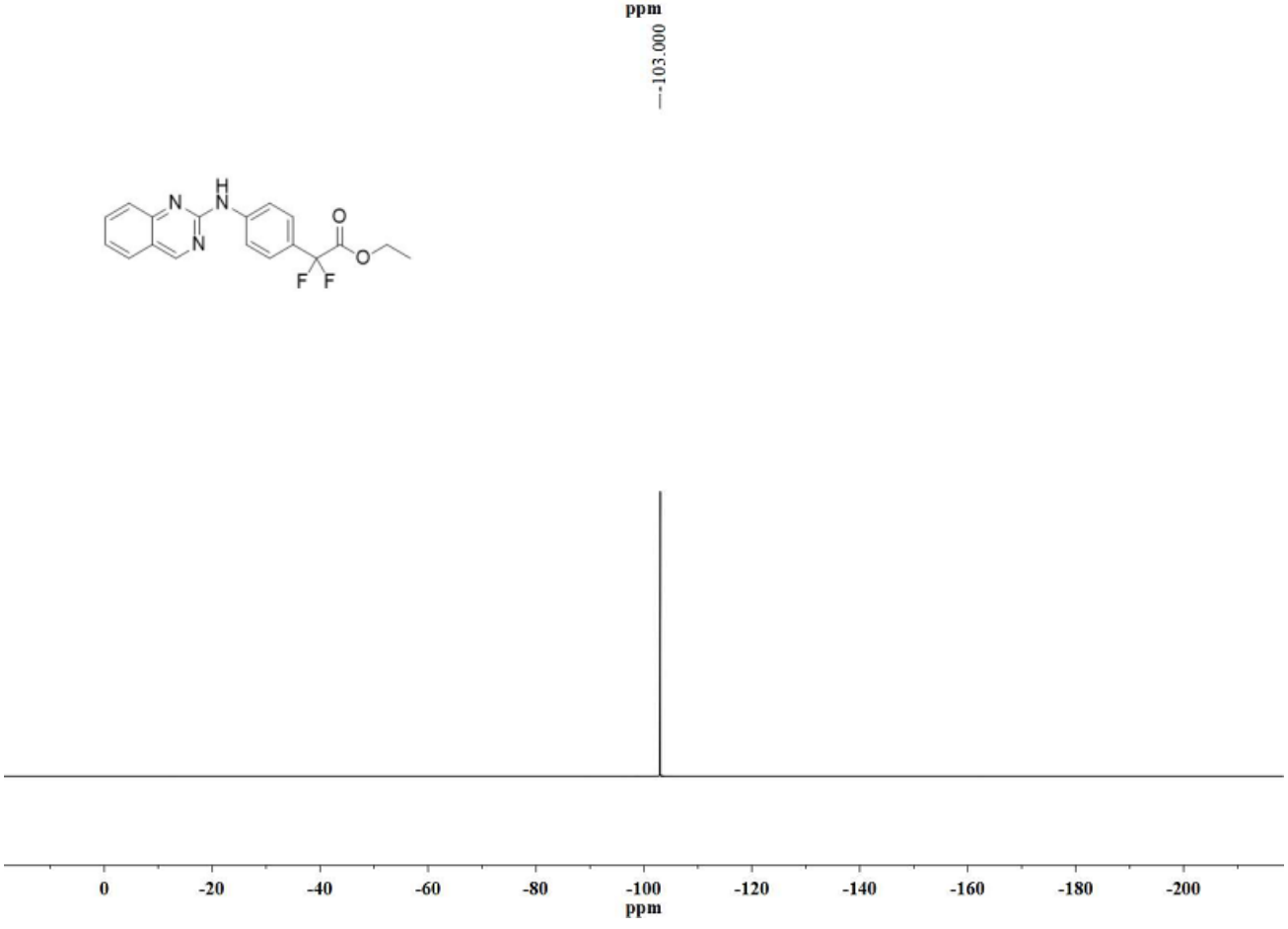
111.060
63.048
13.932
160
140
120
100
80
60
40
20
0
ppm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-180
-200
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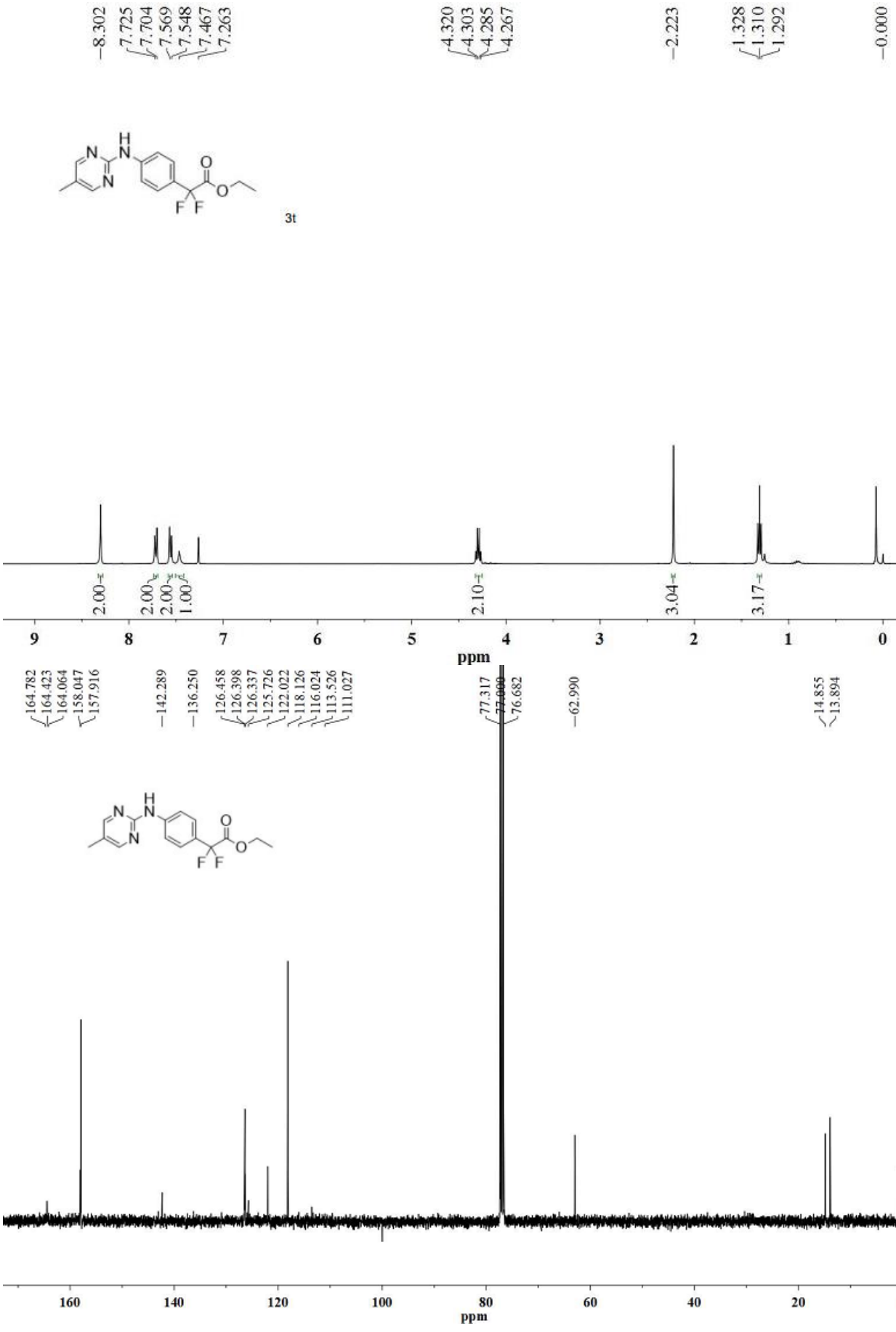
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7.467
7.263
4.320
4.303
4.285
4.267
2.223
1.328
1.310
1.292
0.000
3t
2.00
2.00
2.00
1.00
2.10
3.04
3.17
ppm
164.782
164.423
164.064
158.047
157.916
142.289
136.250
126.458
126.398
126.337
125.726
122.022
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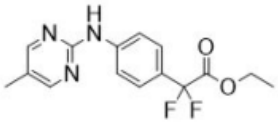
116.024
113.526
111.027
77.317
77.000
76.682
62.990
14.855
13.894
ppm



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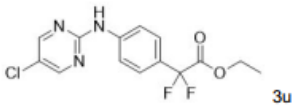
3u

8.404
7.708
7.687
7.596
7.575
7.448
7.267
4.328
4.311
4.293
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1.318
1.300
0.000
9
8
7
6
5
4
3
2
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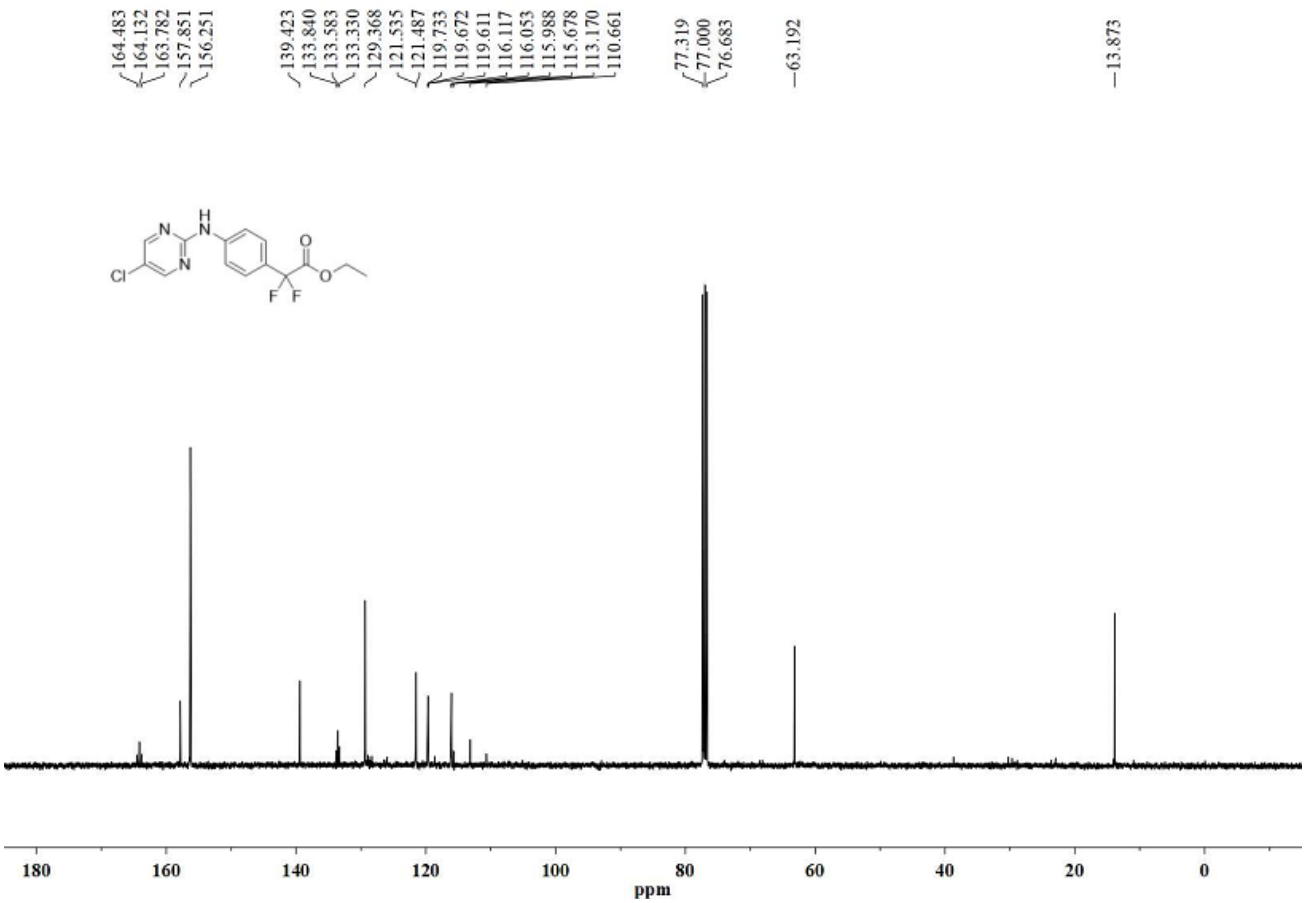
0
ppm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157.851
156.251
139.423
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133.583
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129.368
121.535
121.487
119.733
119.672
119.611
116.117
116.053
115.988
115.678
113.170
110.661
77.319
77.000
76.683
63.192
13.873
Cl
N
H
O
F F
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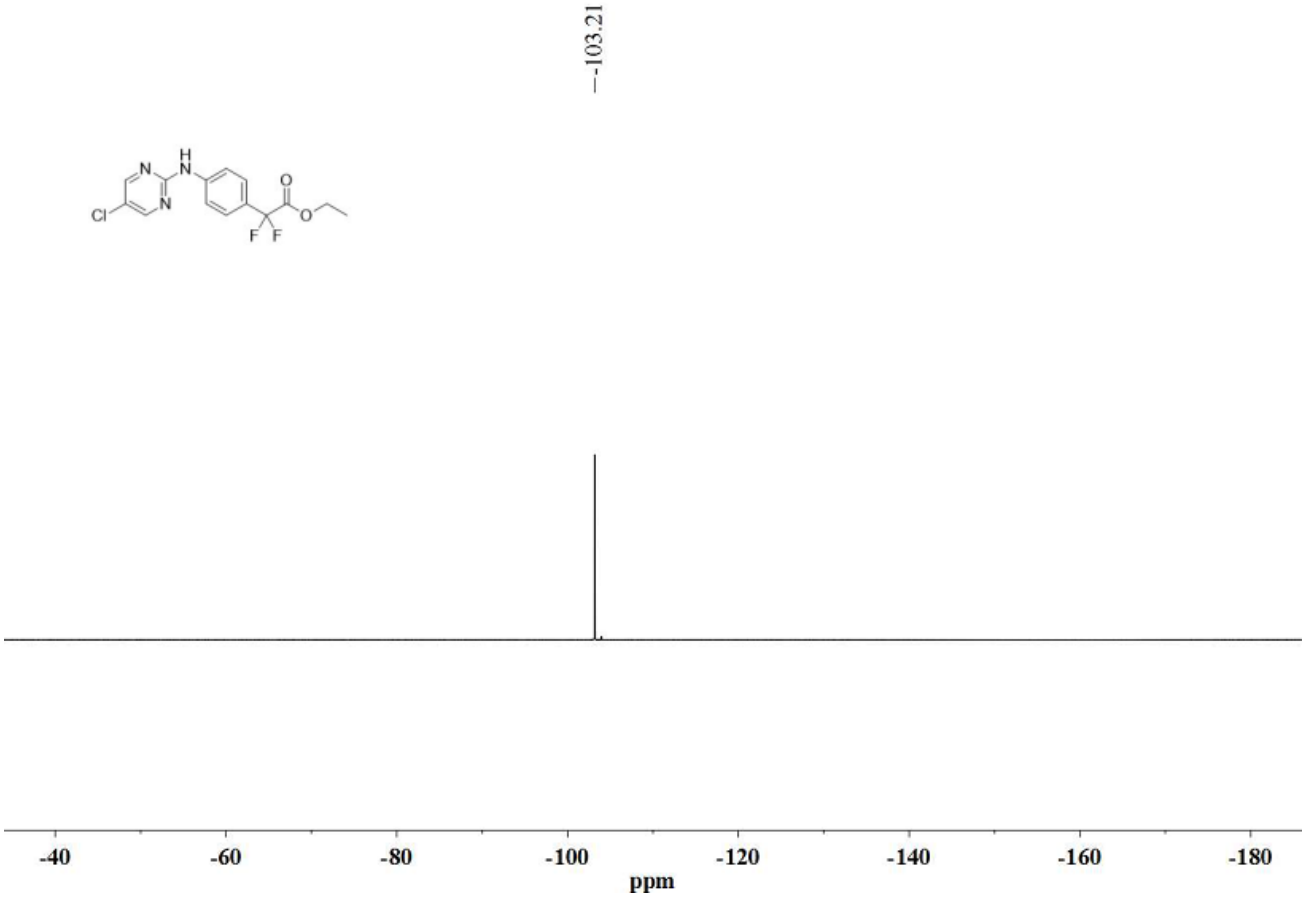
160
140
120
100
80
60
40
20
0
ppm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Cl
N
H
O
F F
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-60
-80
-100
-120
-140
-160
-180
ppm


8.816
8.810
8.804
8.798
8.132
8.097
8.094
8.070
8.053
8.036
7.804
7.785
7.753
7.734
7.714
7.620
7.506
7.488
7.143
7.131
7.119
7.107
6.209
6.158
6.090
6.039
4.689
4.671
4.663
4.654
4.645
4.638
4.636
4.627
4.621
4.613
4.609
4.603
4.595
4.586
4.577
4.568
4.559
4.550
4.533
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1.640
1.630
1.623
1.612
1.605
0.353
4w
3w
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0.41
1.00
0.98
1.18
1.20
2.46
4.03
ppm
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168.402
159.886
159.805
158.000
139.899
135.050
134.846
129.341
127.847
127.793
120.618
120.556
120.334
120.315
119.173
117.306
117.241
112.870
90.180
90.064
88.334
88.229
77.317
77.000
76.682
61.875
61.772
14.036
ppm


-175.89
-180.06
-168
-170
-172
-174
-176
-178
-180
-182
-184
-186
-188
ppm


8.471
8.459
8.446
8.434
8.015
7.990
7.887
7.850
7.829
7.753
7.731
7.586
7.564
7.448
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7.408
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7.265
6.816
6.804
6.796
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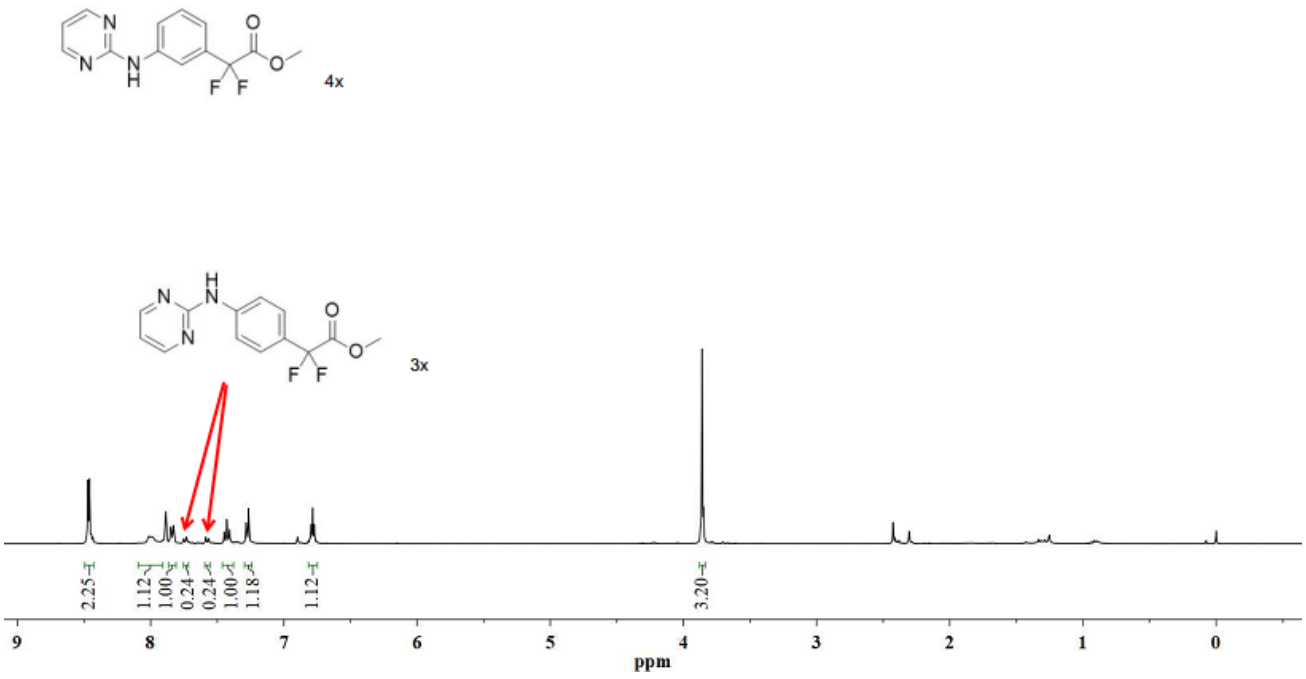
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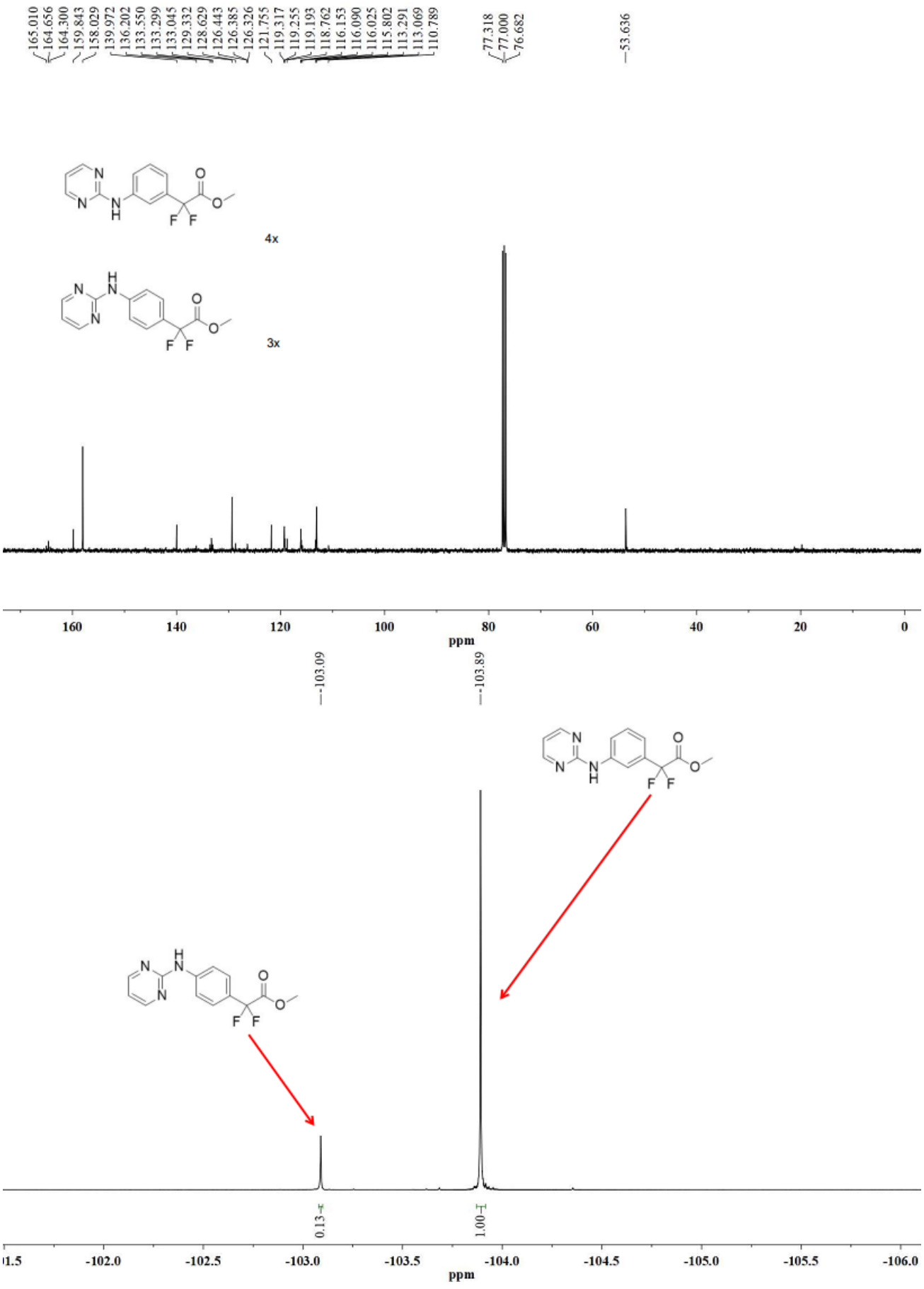
1.18
1.12
3.20
9
8
7
6
5
4
3
2
1
0
ppm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158.029
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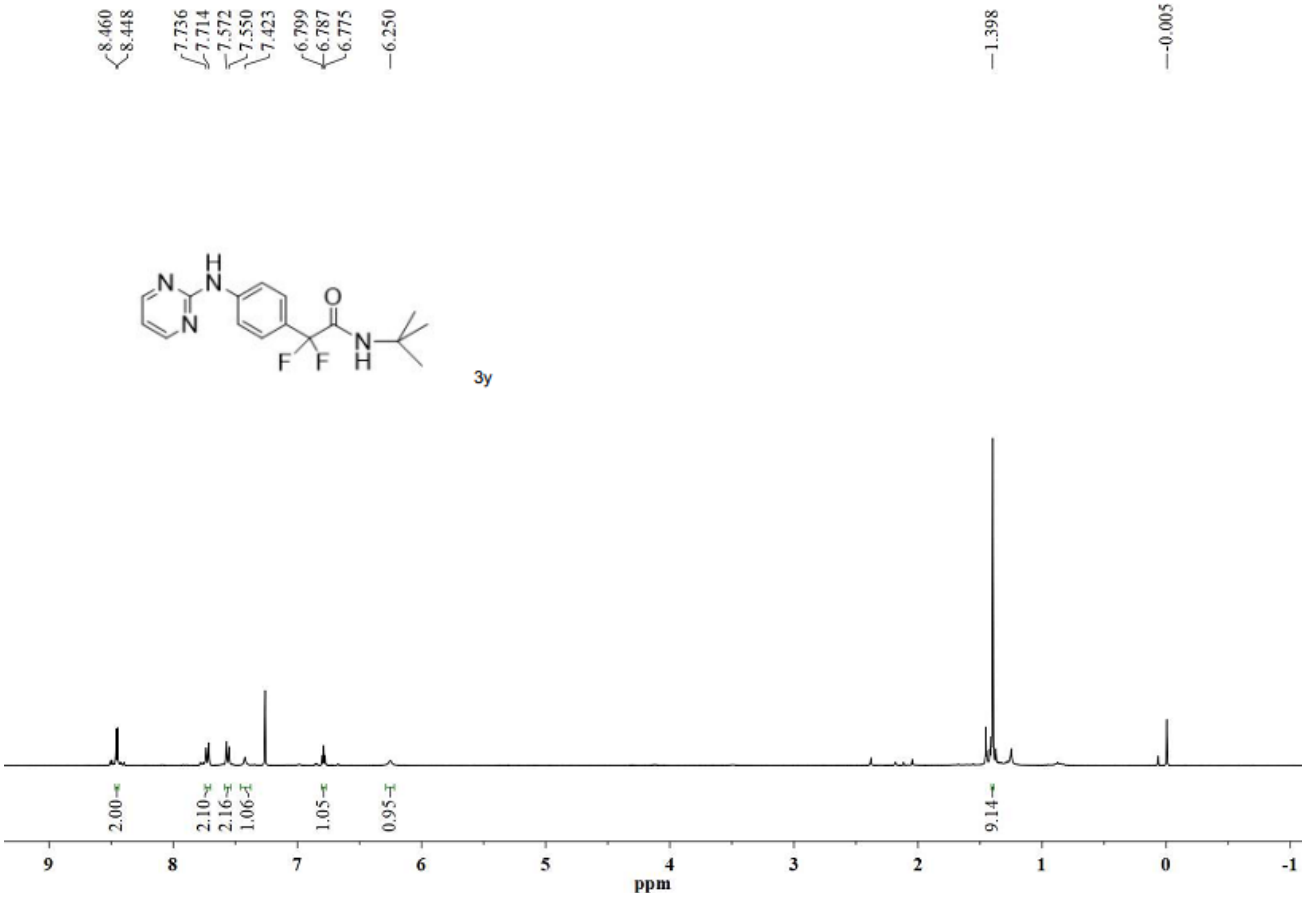
133.550
133.299
133.045
129.332
128.629
126.443
126.385
126.326
121.755
119.317
119.255
119.193
118.762
116.153
116.090
116.025
115.802
113.291
113.069
110.789
77.318
77.000
76.682
53.636
4x
3x
160
140
120
100
80
60
40
20
0
ppm
-103.09
-103.89
0.13
1.00
-102.0
-102.5
-103.0
-103.5
-104.0
-104.5
-105.0
-105.5
-106.0
ppm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7.550
7.423
6.799
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3y
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1.06
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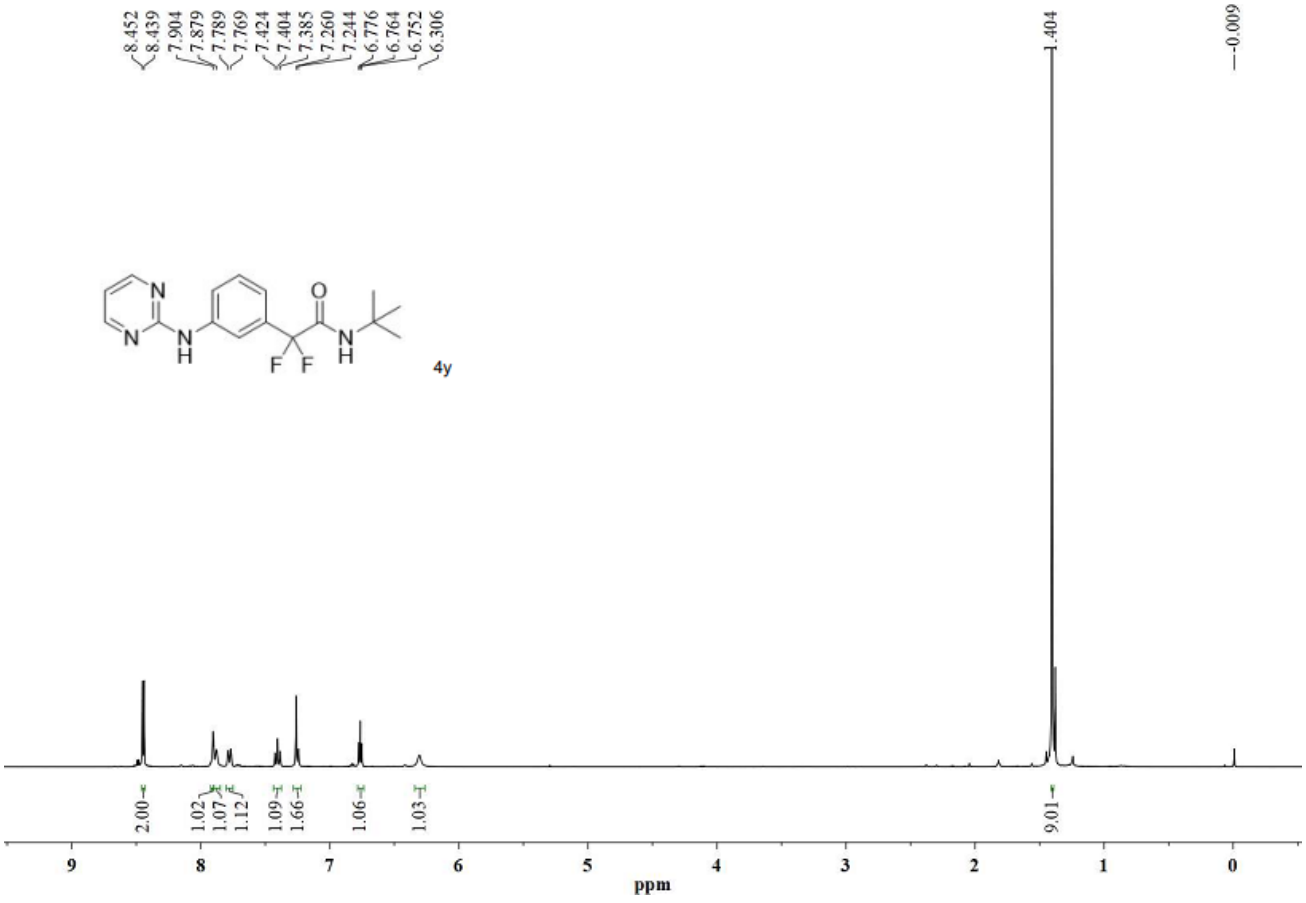
ppm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6.776
6.764
6.752
6.306
1.404
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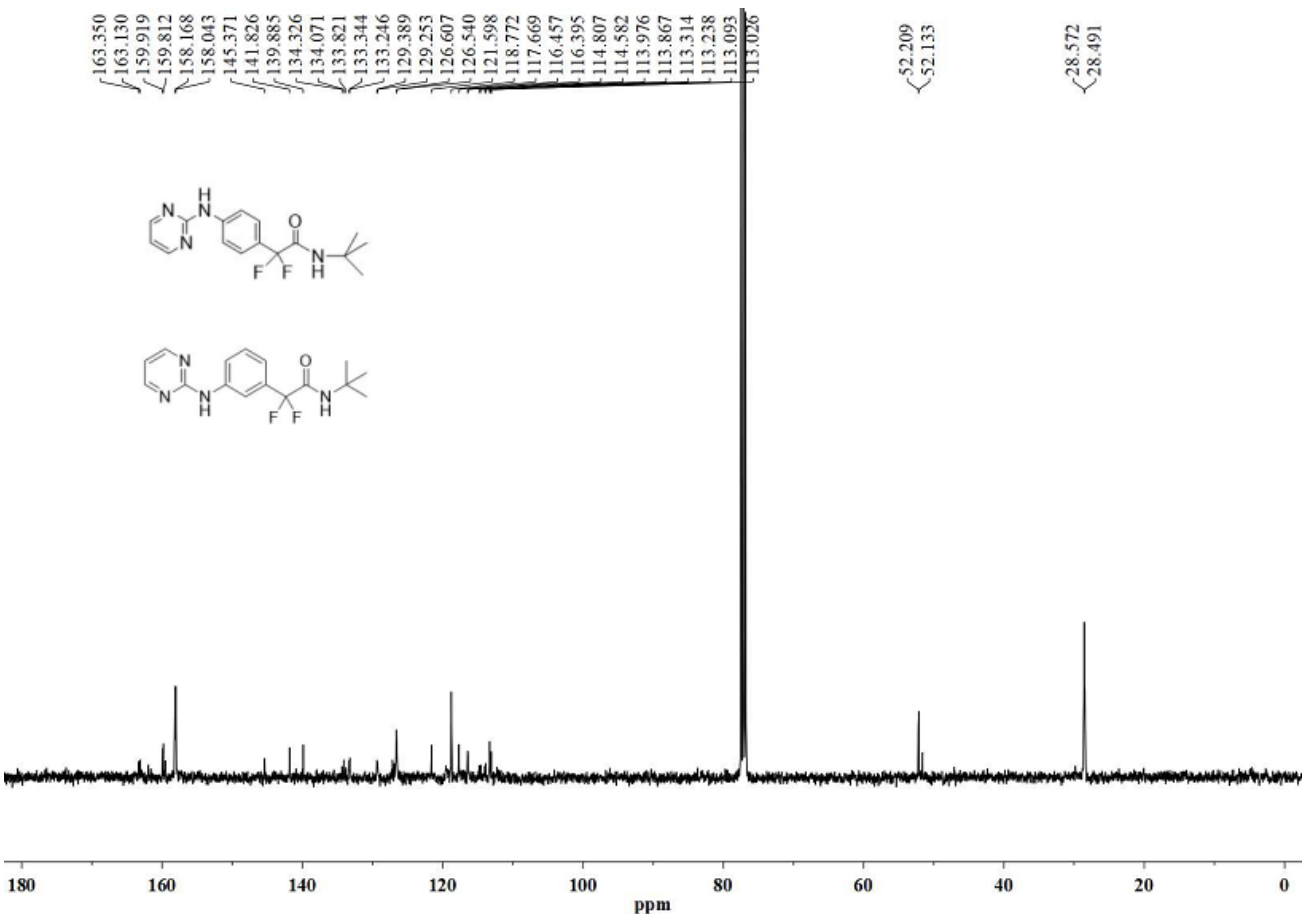
1.02
1.07
1.12
1.09
1.66
1.06
1.03
9.01
ppm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134.071
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133.344
133.246
129.389
129.253
126.607
126.540
121.598
118.772
117.669
116.457
116.395
114.807
114.582
113.976
113.867
113.314
113.238
113.093
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52.133
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28.491
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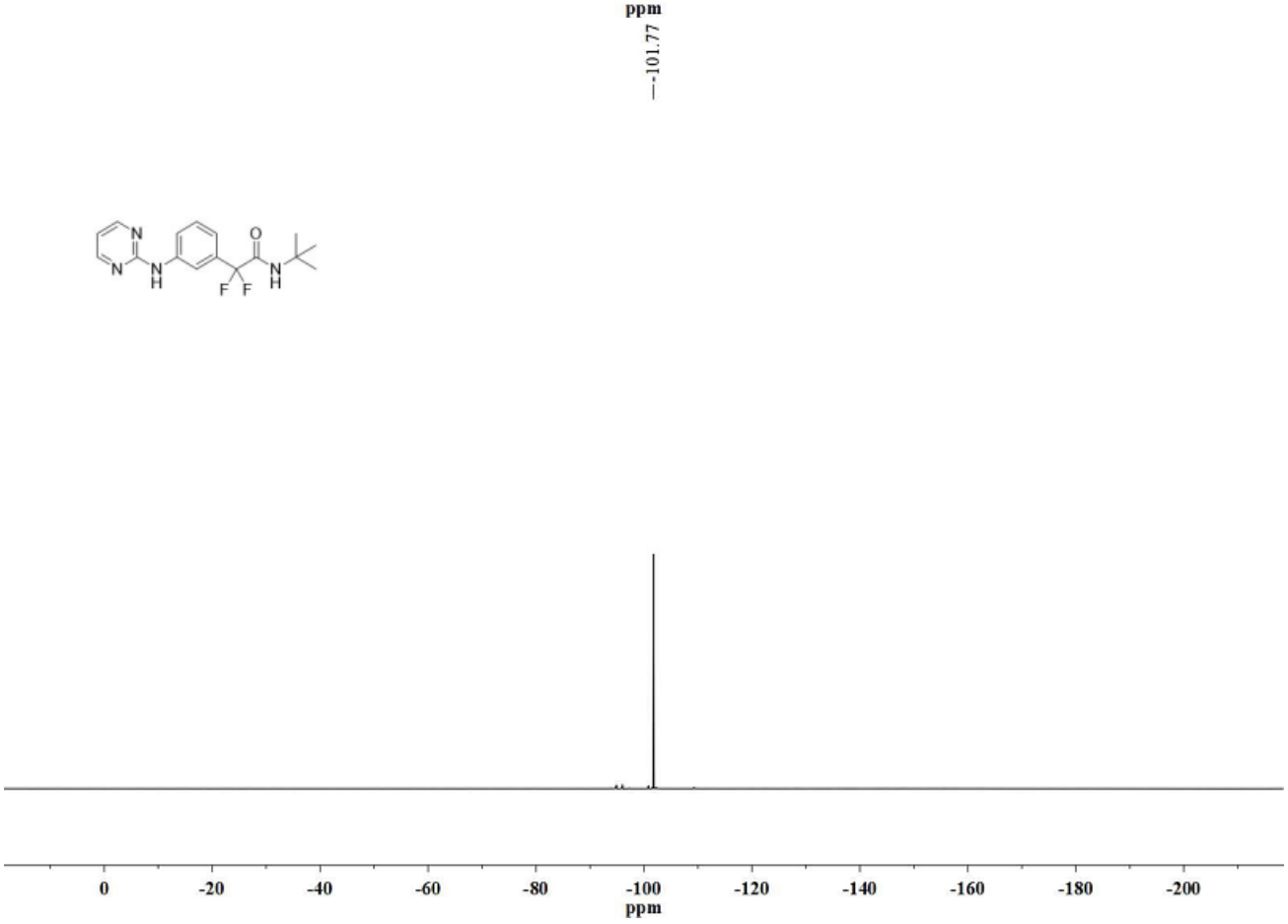
140
120
100
80
60
40
20
0
ppm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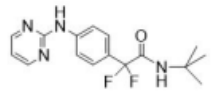
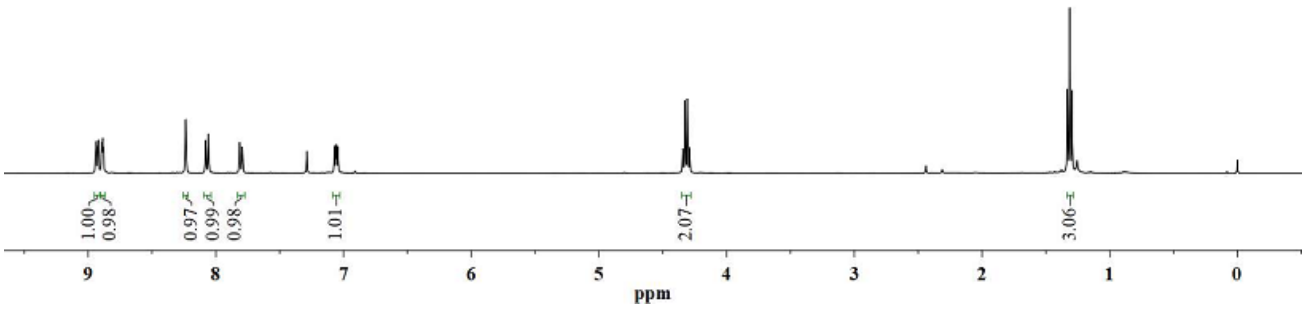
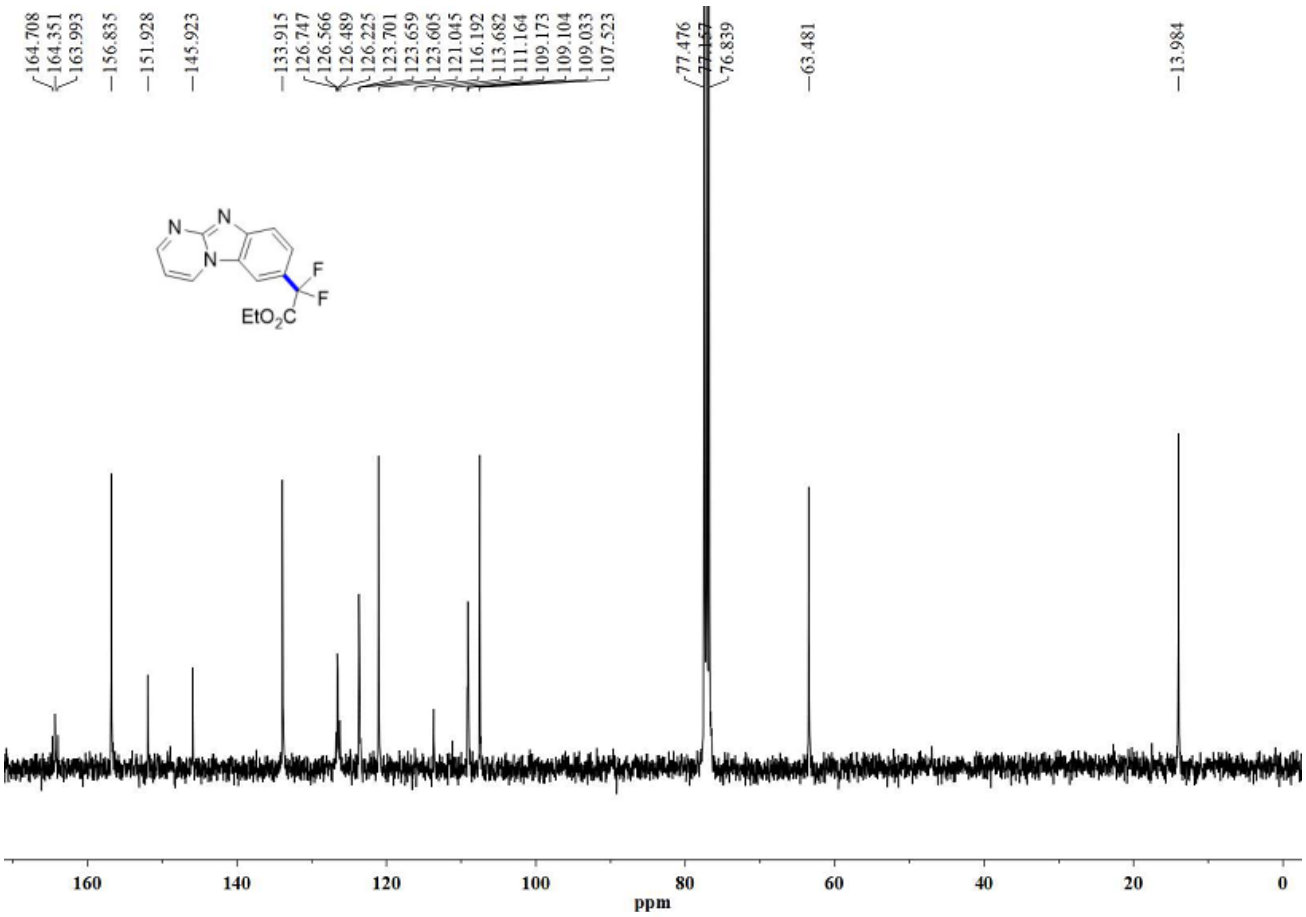


8.936
8.925
8.919
8.896
8.891
8.886
8.234
8.080
8.058
7.816
7.811
7.794
7.790
7.287
7.071
7.061
7.054
7.044
4.343
4.325
4.307
4.289
1.331
1.313
1.295
0.000

6

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123.659
123.605
121.045
116.192
113.682
111.164
109.173
109.104
109.033
107.523
77.476
77.163
76.839
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N
N
F
F
EtO2C
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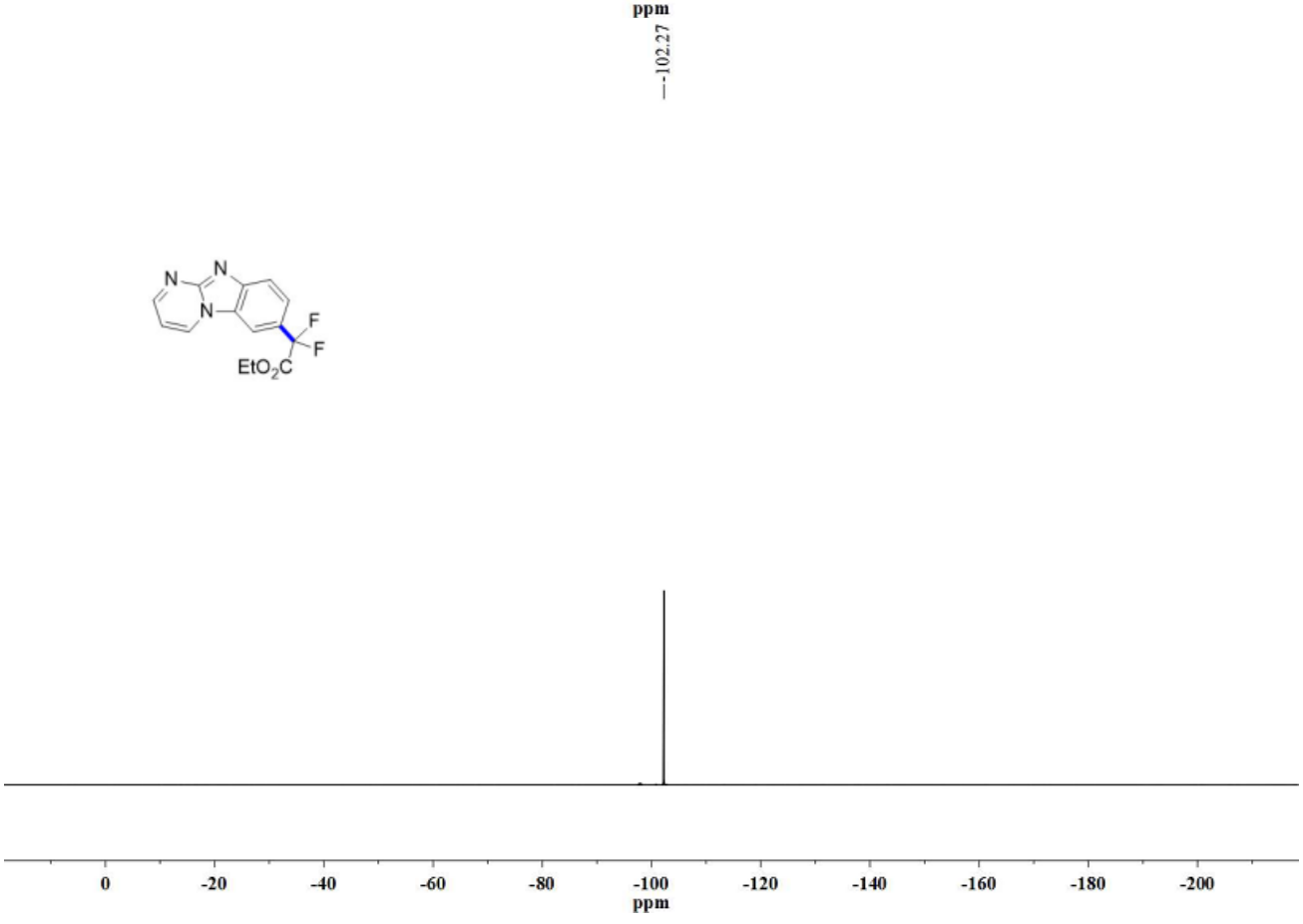
120
100
80
60
40
20
0
ppm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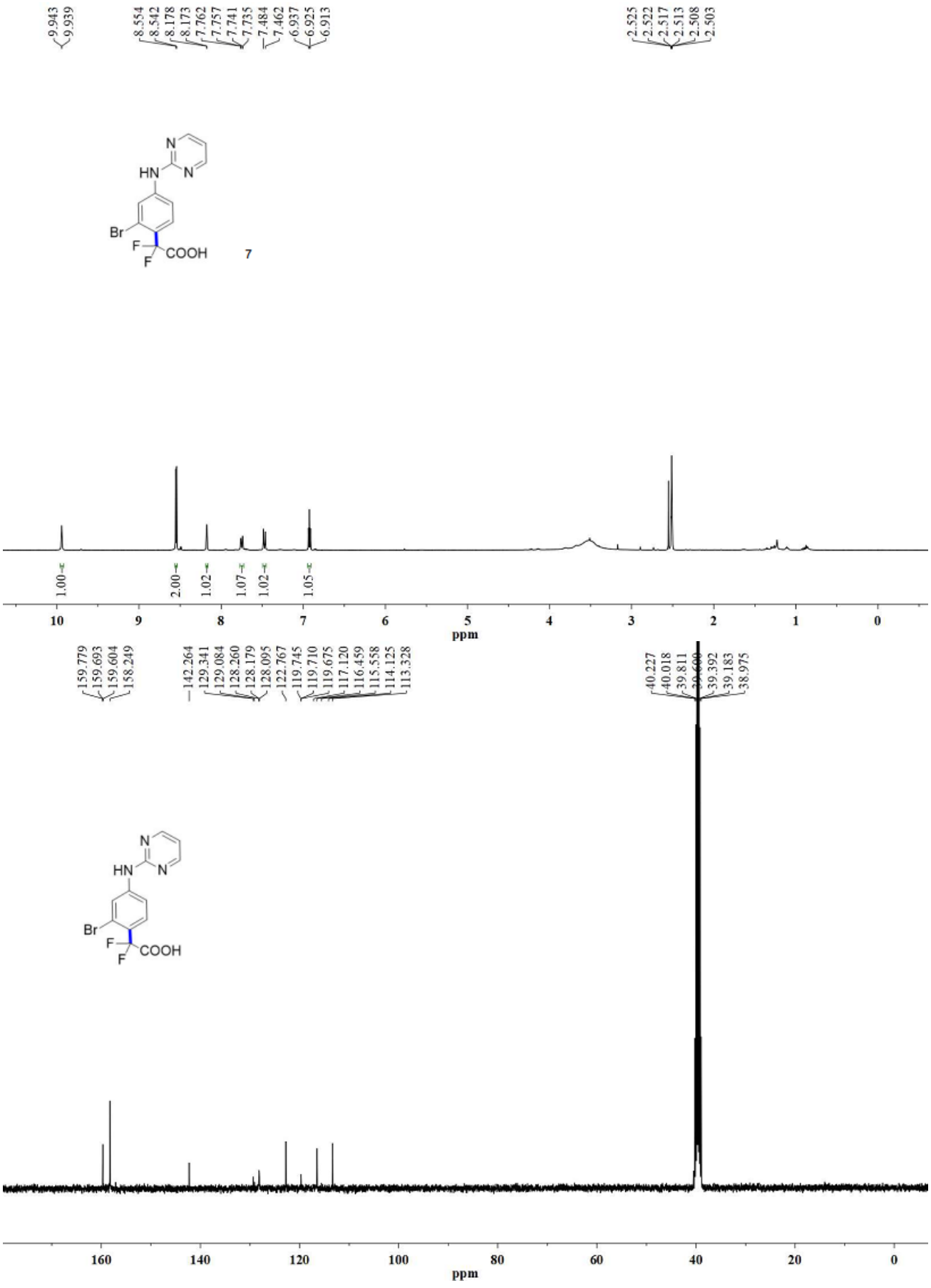
-200
ppm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7.757
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7.735
7.484
7.462
6.937
6.925
6.913
2.525
2.522
2.517
2.513
2.508
2.503
HN
N
N
Br
F
F
COOH
7
1.00
2.00
1.02
1.07
1.02
1.05
ppm
159.779
159.693
159.604
158.249
142.264
129.341
129.084
128.260
128.179
128.095
122.767
119.745
119.710
119.675
117.120
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114.125
113.328
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39.811
39.600
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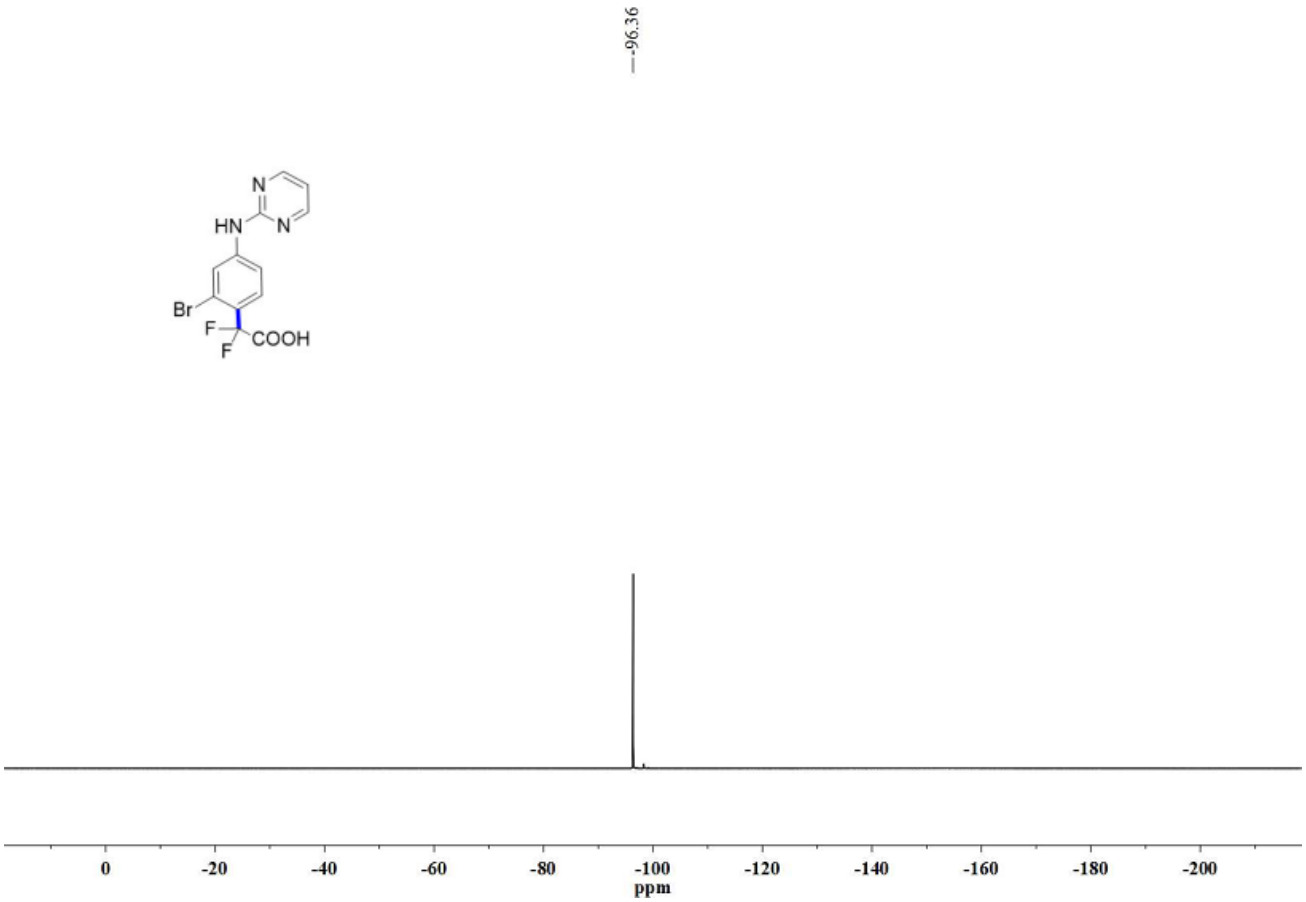
39.183
38.975
ppm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N
Br
F
F
COOH
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-40
-60
-80
-100
-120
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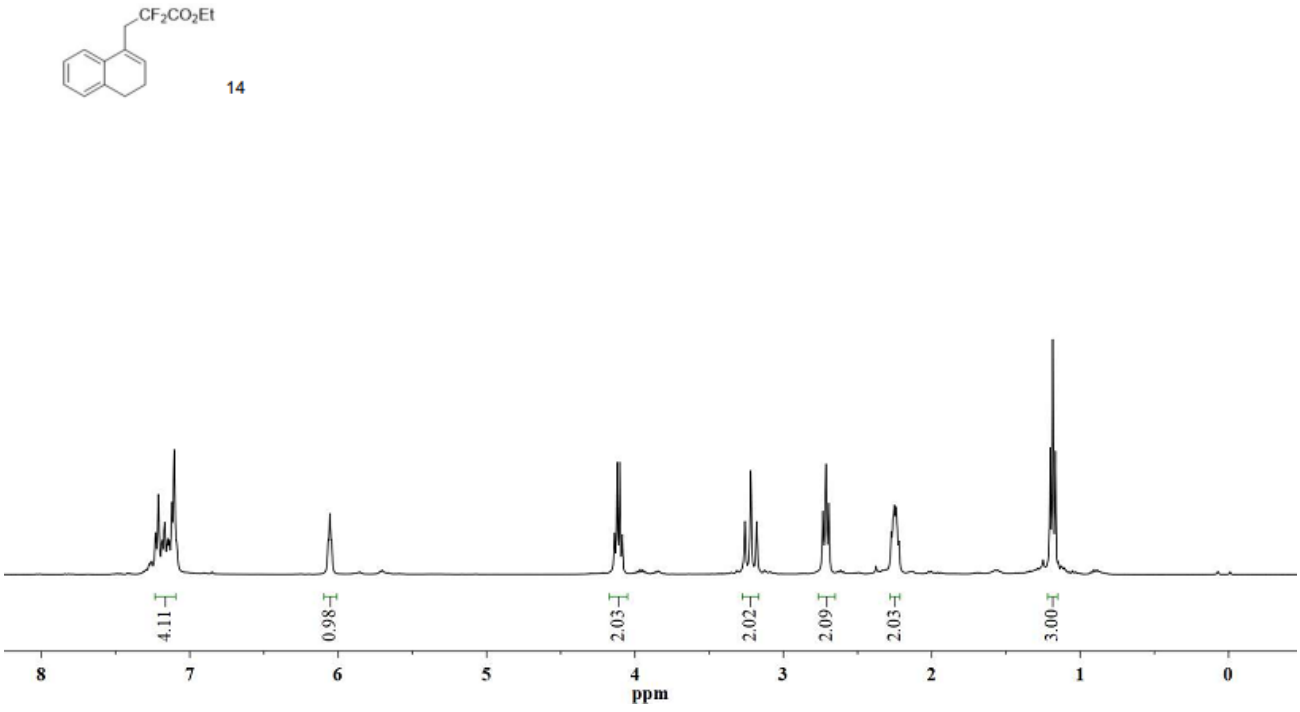
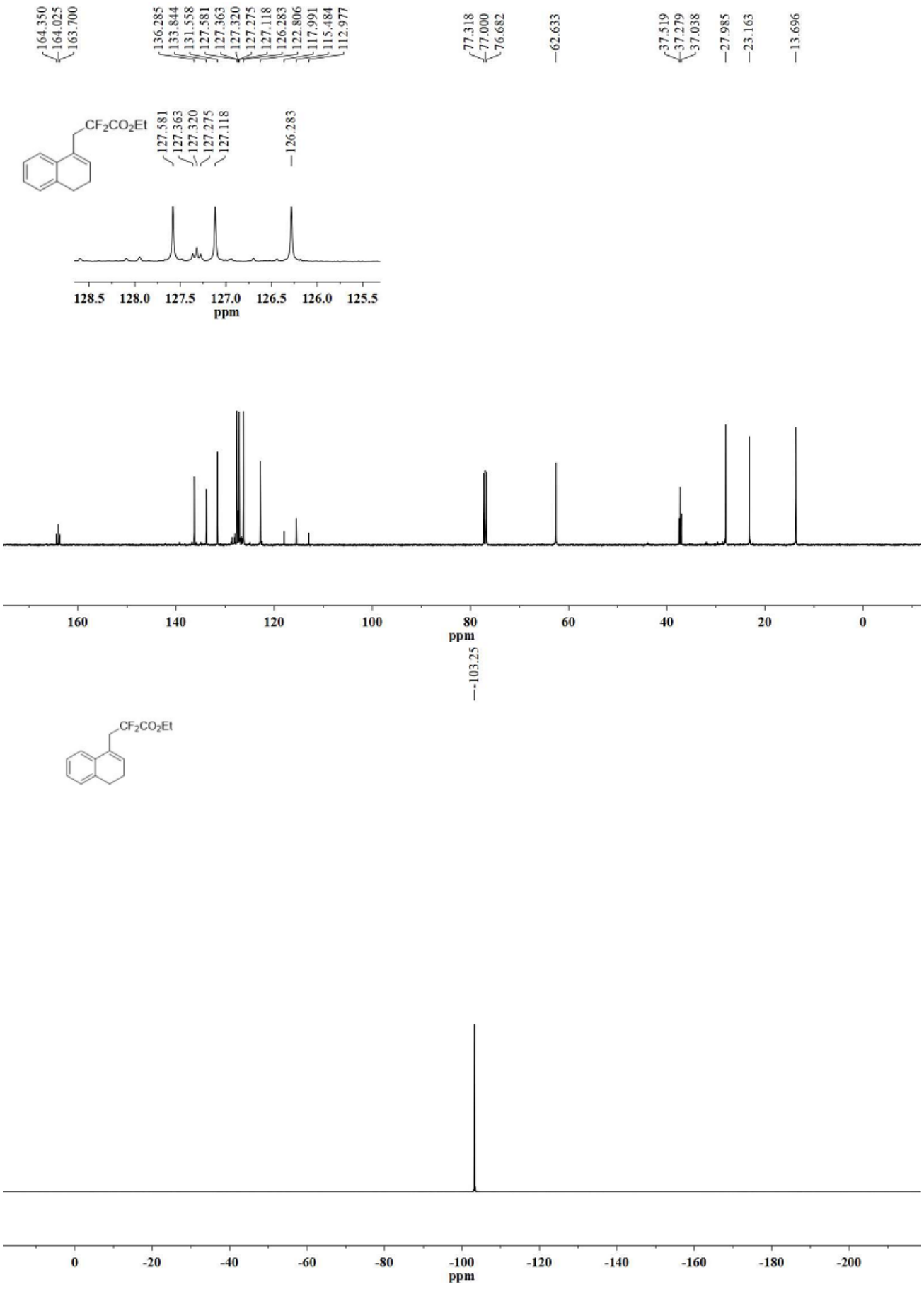
-160
-180
-200
ppm
7.261
7.230
7.211
7.190
7.184
7.173
7.168
7.155
7.149
7.141
7.137
7.122
7.119
7.107
7.102
7.088
6.067
6.055
6.044
4.138
4.121
4.103
4.085
3.259
3.219
3.179
2.733
2.713
2.693
2.272
2.261
2.252
2.240
2.232
2.220
1.202
1.184
1.166
-0.010


CF2CO2Et
14
4.11
0.98
2.03
2.02
2.09
2.03
3.00
8
7
6
5
4
3
2
1
0
ppm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127.363
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127.275
127.118
126.283
122.806
117.991
115.484
112.977
77.318
77.000
76.682
62.633
37.519
37.279
37.038
27.985
23.163
13.696
CF2CO2Et
127.581
127.363
127.320
127.275
127.118
126.283
128.5 128.0 127.5 127.0 126.5 126.0 125.5
ppm
160 140 120 100 80 60 40 20 0
ppm
-103.25
CF2CO2Et
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
ppm

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