

Supporting Information

Copper-Promoted Conjugate Addition of Carboxylic Acids to Ethenesulfonyl Fluoride (ESF) for Constructing Aliphatic Sulfonyl Fluorides

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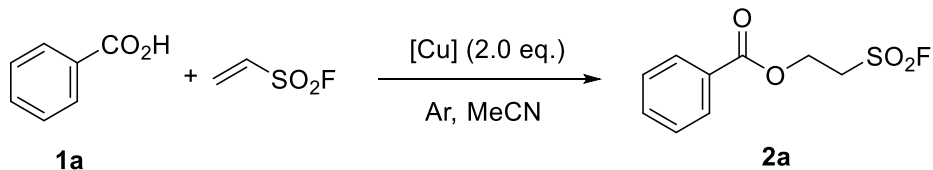
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1. Screening the Optimized Reaction Conditions.

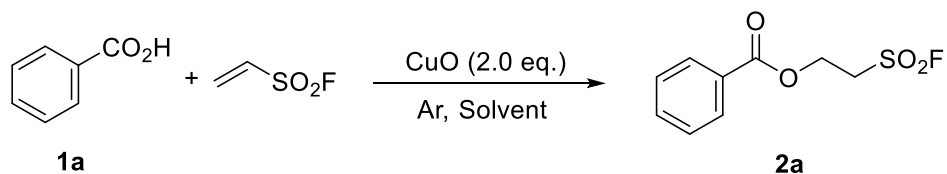
Table S1 Screening the [Cu] Catalyst^a



Entry	Catalyst	Conversion (1a , %)	Yield (2a , %) ^b
1 ^c	Cu(OAc) ₂	90	17
2	Cu(OAc) ₂	93	32
3	CuBr ₂	99	\
4	CuF ₂	99	33
5	Cu(OTf) ₂	41	\
6	Cu(acac) ₂	36	\
7	Cu(CF ₃ CO) ₂	98	27
8	CuSO ₄	98	46
9	CuO	99	74
10	Cu ₂ O	\	\

^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), [Cu] catalyst (2.0 eq.), undried CH₃CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2a** as the external standard ($t_R = 7.5$ min, $\lambda_{max} = 229.9$ nm, water / acetonitrile = 50 : 50 (v / v)). ^cIn the air.

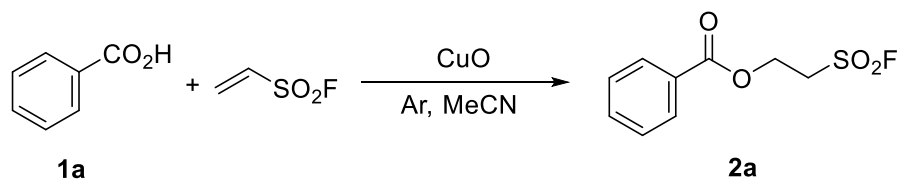
Table S2 Screening of the Solvent ^a



Entry	Solvent (2 mL)	Conversion (1a , %)	Yield (2a , %) ^b
1	CH ₃ CN	97	76
2 ^c	anhydrous CH ₃ CN	83	20
3	anhydrous CH₃CN	98	89
4	Toluene	13	N.D.
5	DMF	2	N.D.
6	1,4-dioxane	1	N.D.
7	DMA	39	34
8	DMSO	\	N.D.
9	Trifluorotoluene	3	N.D.
10	DCE	2	N.D.
11	Acetone	5	N.D.
12	THF	\	N.D.

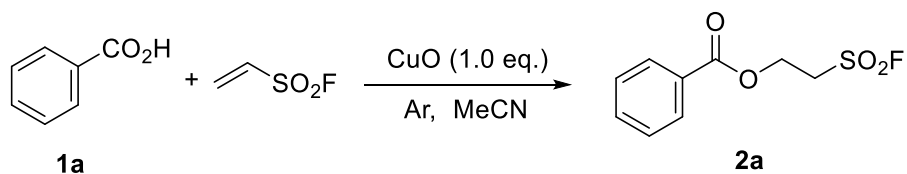
^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO (2.0 eq., 16 mg), solvent (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2a** as the external standard ($t_R = 7.5$ min, $\lambda_{max} = 229.9$ nm, water / acetonitrile = 50 : 50 (v / v)). ^cIn the air.

N.D. means not detected.

Table S3 Screening of CuO Loading ^a

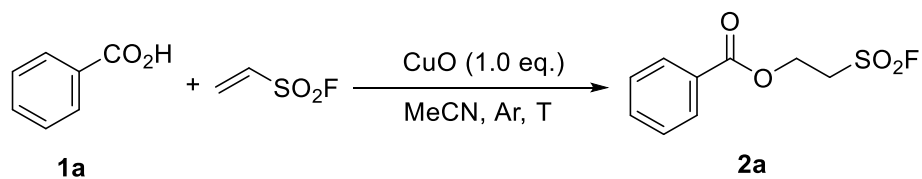
Entry	CuO (X equiv.)	Conversion (1a , %)	Yield (2a , %) ^b
1	2.0	96	87
2	1.5	97	76
3	1.0	99	91
4	0.5	97	74
5	0.2	97	65
6	\	0	trace

^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO, anhydrous CH₃CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2a** as the external standard (*t_R* = 7.5 min, λ_{max} = 229.9 nm, water / acetonitrile = 50 : 50 (v / v)).

Table S4 Screening of ESF Loading ^a

Entry	ESF (equiv.)	Conversion (1a , %)	Yield (2a , %) ^b
1	4.0	90	73
2	2.0	96	88
3	1.5	84	70
4	1.2	83	69
5	1.0	75	57

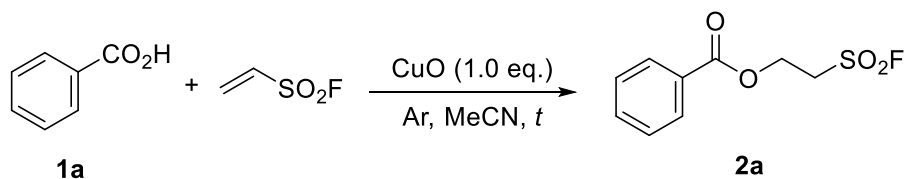
^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO (1.0 eq., 8 mg), anhydrous CH₃CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2a** as the external standard ($t_R = 7.5$ min, $\lambda_{max} = 229.9$ nm, water / acetonitrile = 50 : 50 (v / v)).

Table S5 Screening of Temperature ^a

Entry	T (°C)	Conversion (1a , %)	Yield (2a , %) ^b
1	25	90	4
2	40	93	5
3	50	91	11
4	60	90	51
5	70	95	80
6	80	96	91
7	90	94	87
8	100	94	85
9	110	90	76

^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO (1.0 eq., 8 mg), anhydrous CH_3CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at corresponding temperature for 20 h.

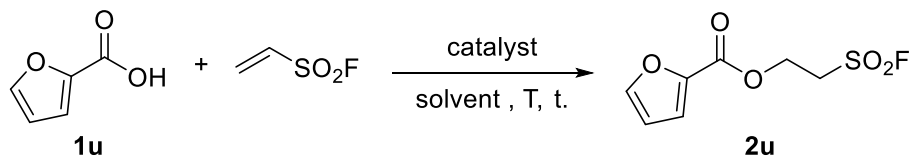
^bThe yields were determined by HPLC using **2a** as the external standard ($t_R = 7.5$ min, $\lambda_{\text{max}} = 229.9$ nm, water / acetonitrile = 50 : 50 (v / v)).

Table S6 Screening of Reaction Time ^a

Entry	Time (h)	Conversion (1a , %)	Yield (2a , %) ^b
1	5	20	N.D.
2	8	33	17
3	15	81	73
4	18	94	84
5	20	95	90
6	24	96	88
7	36	94	85
8	48	90	89

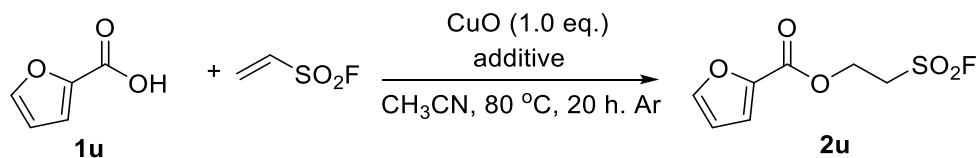
^aReaction condition: Benzoic acid (**1a**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO (1.0 eq., 8 mg), anhydrous CH_3CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for corresponding reaction time.

^bThe yields were determined by HPLC using **2a** as the external standard ($t_R = 7.5$ min, $\lambda_{\text{max}} = 229.9$ nm, water / acetonitrile = 50 : 50 (v / v)).

Table S7 Reaction Optimization ^a

Entry	Catalyst (X eq.)	Solvent	Conversion (1u , %)	Yield (2u , %) ^b
1	CuO (1.0)	MeCN	80	56
2	CuO (1.0)	DMA	0	0
3	CuF ₂ (1.0)	MeCN	19	11
4 ^c	CuO (1.0)	MeCN	34	23
5	CuSO ₄ (1.0)	MeCN	0	0
6	CuO (1.5)	MeCN	39	34
7 ^d	CuO (1.0)	MeCN	12	10
8 ^e	CuO (1.0)	DMA	4	2

^aReaction condition: Furan-2-carboxylic acid (**1u**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), [Cu] catalyst, anhydrous solvent (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2u** as the external standard ($t_R = 4.9$ min, $\lambda_{max} = 254.7$ nm, water / acetonitrile = 50 : 50 (v / v)). ^cReacted for 24 h. ^dESF 1.2 eq., 0.12 mmol, ^eReacted at 100 °C.

Table S8 Reaction Optimization^a

Entry	Additive	(mol%)	Conversion (1u , %)	Yield (2u , %) ^b
1	A	10	80	66
2	B	10	84	76
3	C	10	84	53
4	B	15	87	77
5	B	5	89	78
6	B	2	85	65
7	B	0	79	57

^aReaction condition: Furan-2-carboxylic acid (**1u**, 0.1 mmol), ESF (2.0 eq., 0.2 mmol), CuO (1.0 eq., 8 mg), additive (mol%), anhydrous CH₃CN (2 mL) were added in a sealed tube (20 mL) under argon atmosphere and the reaction mixture was stirred at 80 °C for 20 h. ^bThe yields were determined by HPLC using **2u** as the external standard (*t_R* = 4.9 min, λ_{max} = 254.7 nm, water / acetonitrile = 50 : 50 (v / v)). **A** = [RuCl₂(p-cymene)]₂, **B** = Ru(bpy)₃(PF₆)₂, **C** = Ru(bpy)₃Cl₂.

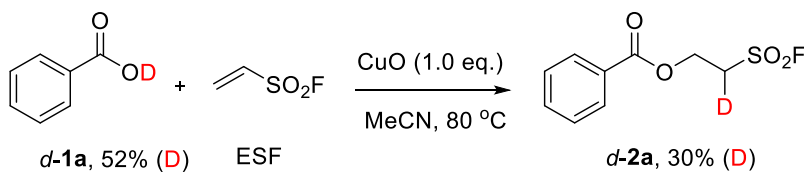
2. Deuterated experiment

The starting material deuterated benzoic acid (*d-1a*) was synthesized according to the previous literature report.^[1]

(carboxy-d)benzene (*d-1a*). Off-white solid, ¹H NMR (500 MHz, CDCl₃) δ 11.47 (br s, 0.48 H), 8.14 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H).

2-(fluorosulfonyl)ethyl-2-d benzoate (*d-2a*). Procedure A was followed, petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 4.81 (t, *J* = 5.1 Hz, 2H), 3.85 (q, *J* = 4.9 Hz, 1.4 H). ¹⁹F NMR (471 MHz, CDCl₃) δ 59.05 (s), 59.01 (s).

The starting material benzoic acid with deuteration rate of 52% (*d-1a*) was carried out in control experiment, which observed the deuteration rate of 30% in isolated product (*d-2a*). Subsequent results were also verified by ¹H-NMR and ¹⁹F-NMR. The deuterated experiment also proved this type reaction was oxa-Michael addition.



[1] C.; Empel, T. V.; Nguyen, Rene M. Koenigs, Tropylium-Catalyzed O-H insertion reactions of diazoalkanes with carboxylic acids, *Org. Lett.* **2021**, 23, 548.

3. NMR spectra

2a, ^1H NMR, 500 MHz, CDCl_3

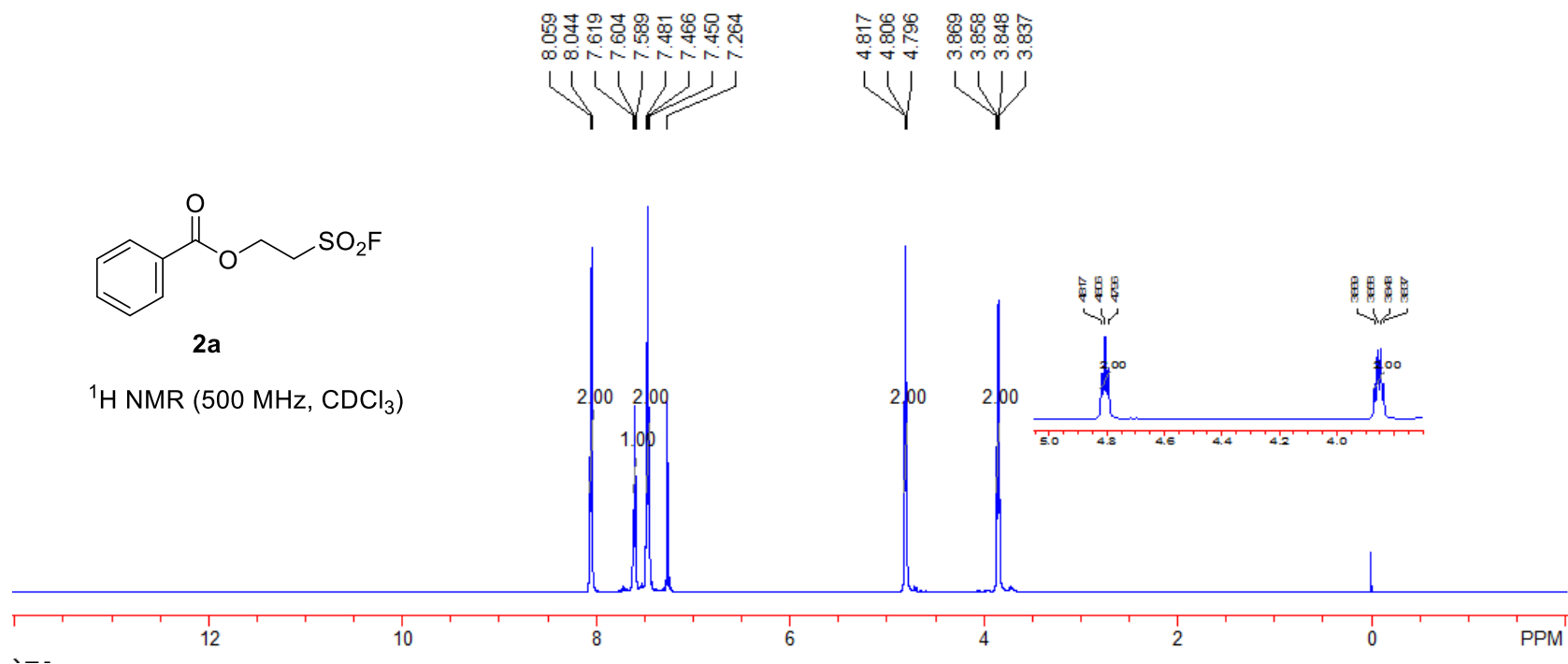


Figure S1. The ^1H NMR spectrum of **2a**

2a, ^{13}C NMR, 126 MHz, CDCl_3

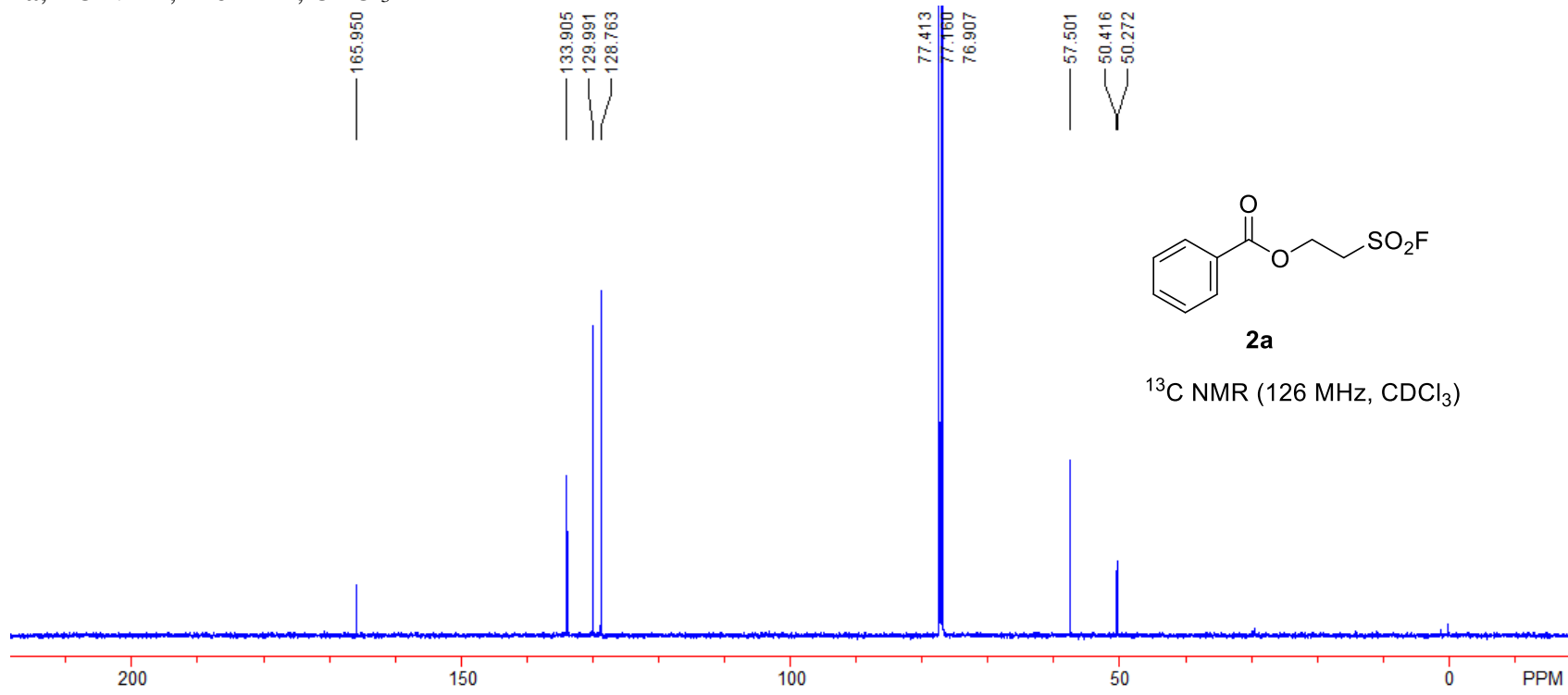


Figure S2. The ^{13}C NMR spectrum of **2a**

2a, ^{19}F NMR, 471 MHz, CDCl_3

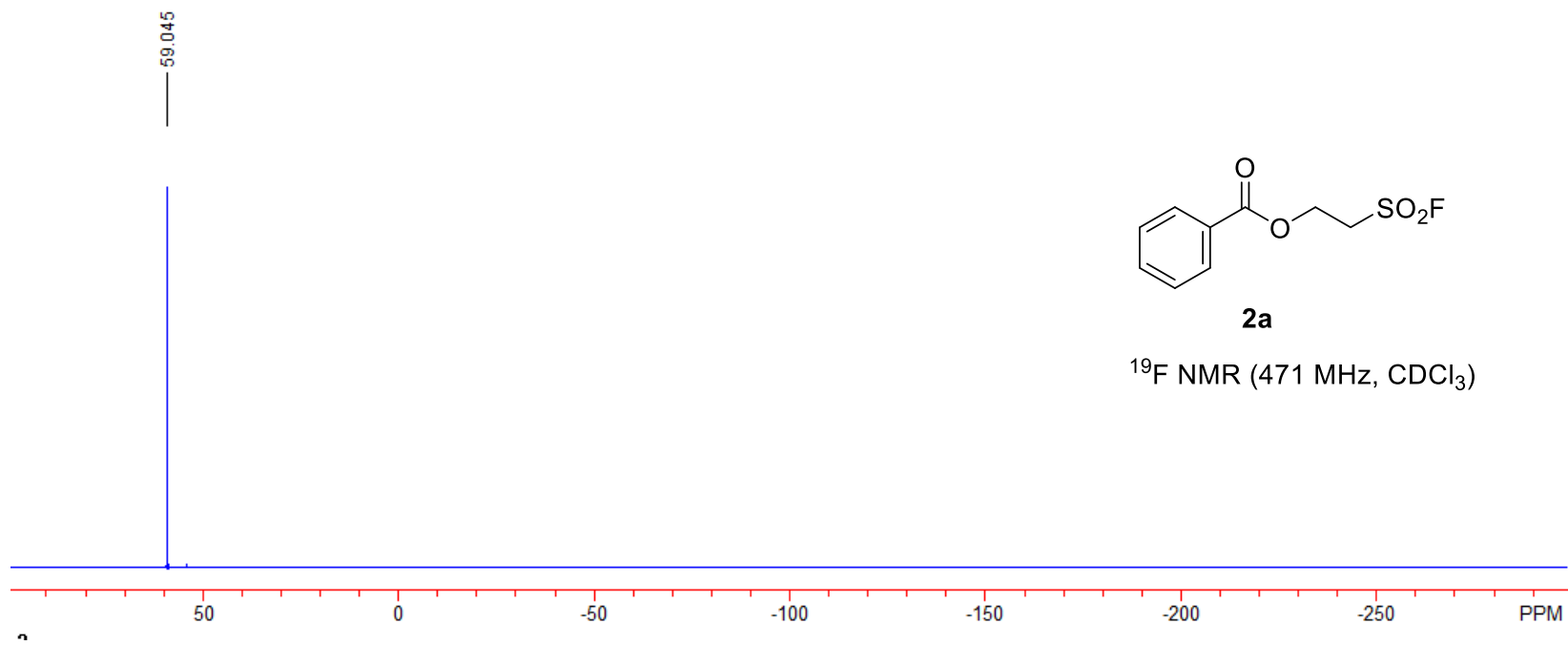


Figure S3. The ^{19}F NMR spectrum of **2a**

2b, ^1H NMR, 500 MHz, CDCl_3

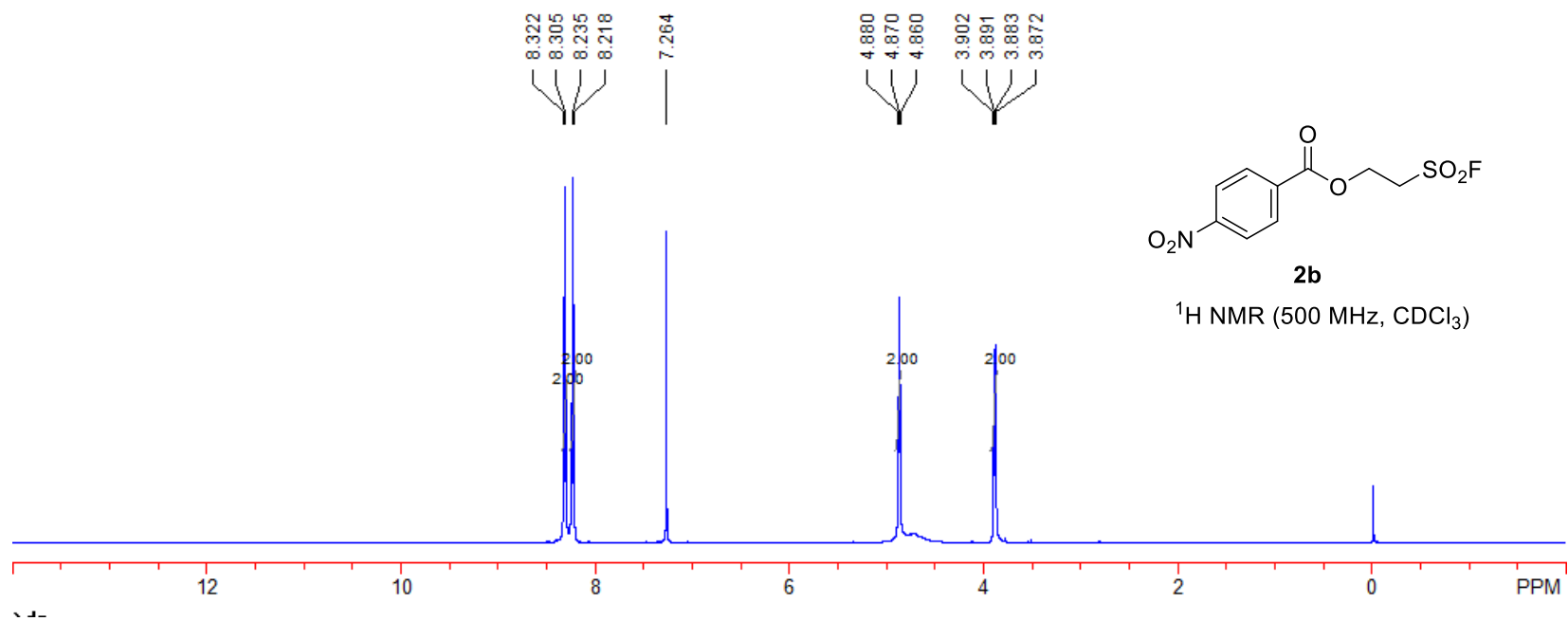


Figure S4. The ^1H NMR spectrum of **2b**

2b, ^{13}C NMR, 126 MHz, CDCl_3

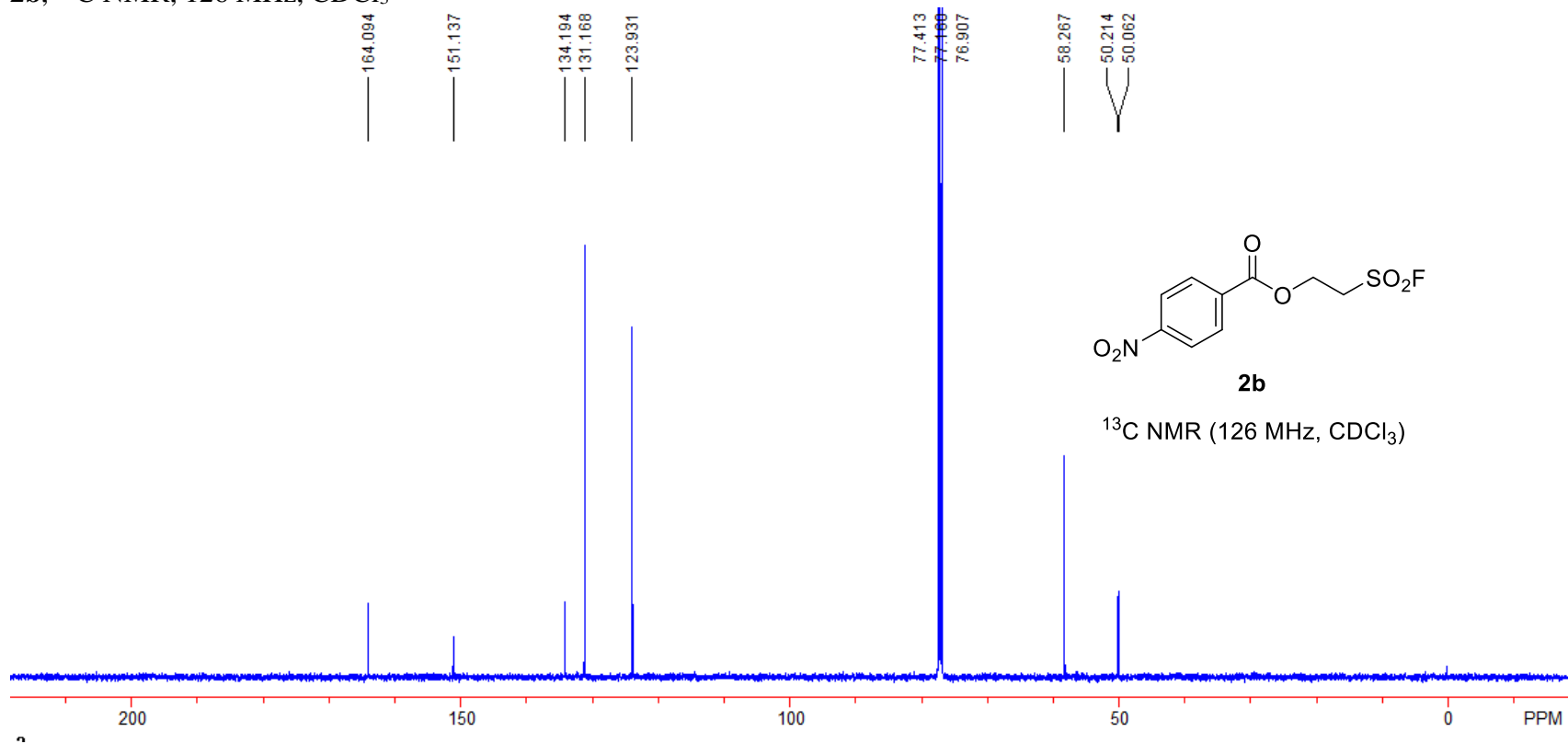


Figure S5. The ^{13}C NMR spectrum of **2b**

2b, ^{19}F NMR, 471 MHz, CDCl_3

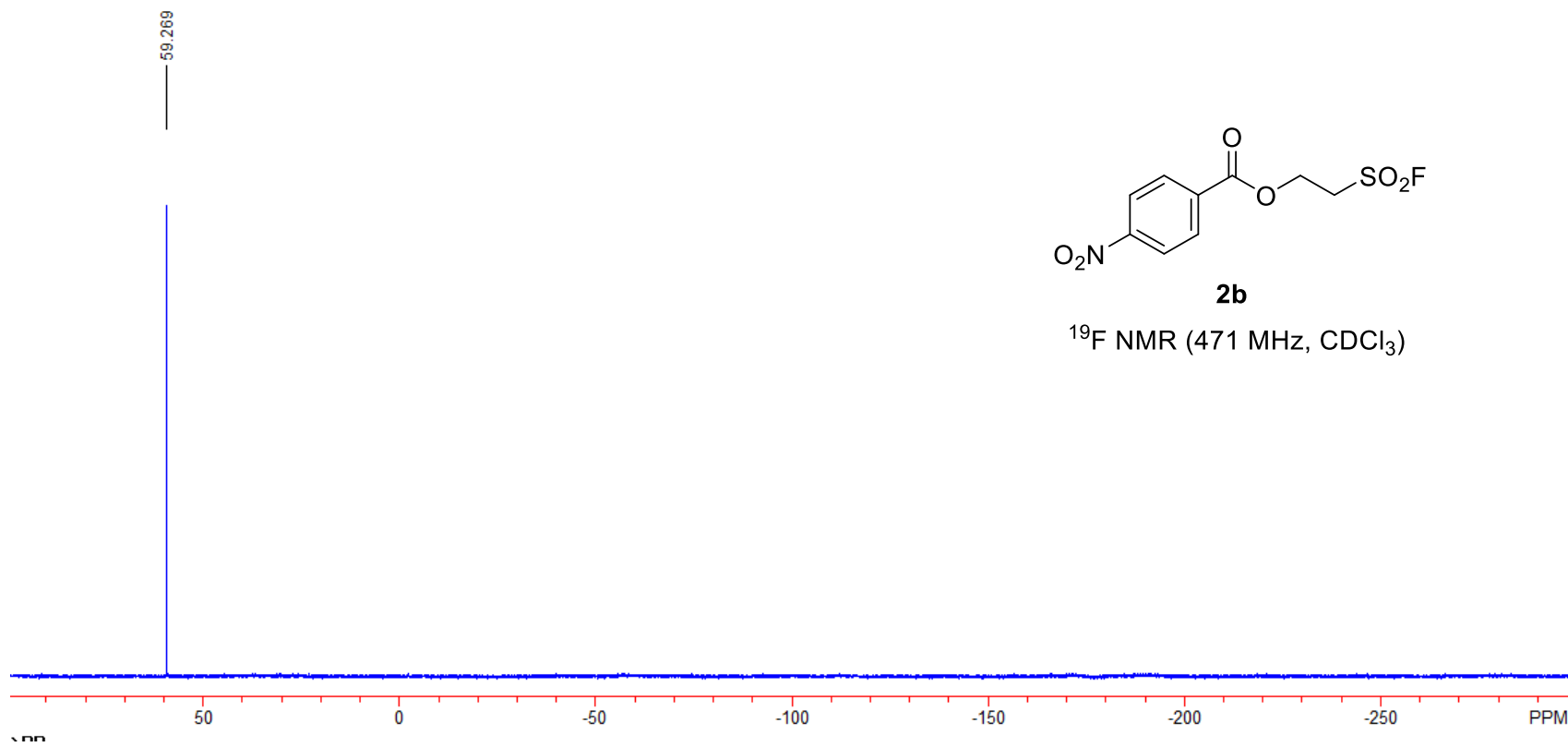


Figure S6. The ^{19}F NMR spectrum of **2b**

2c, ^1H NMR, 500 MHz, CDCl_3

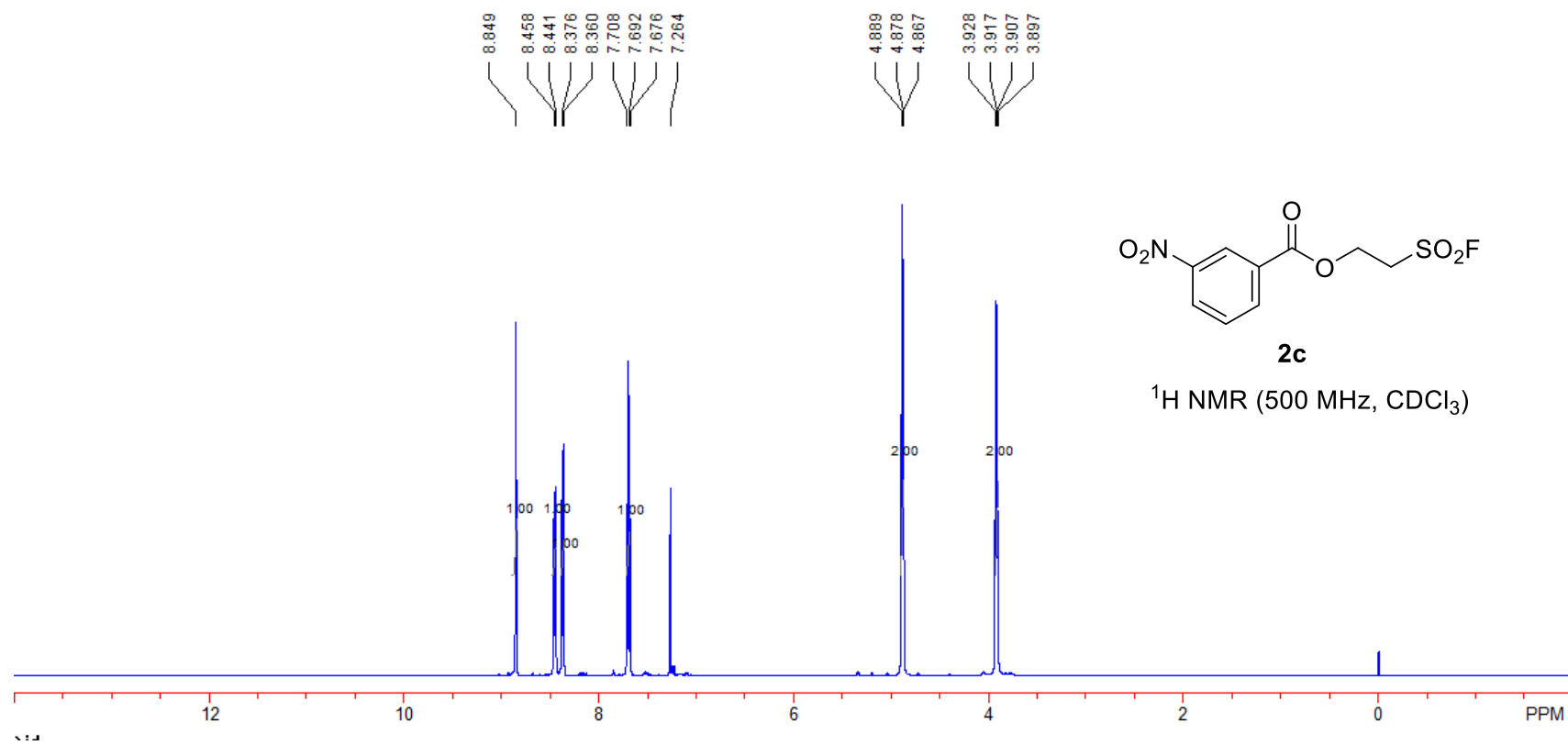


Figure S7. The ^1H NMR spectrum of **2c**

2c, ^{13}C NMR, 126 MHz, CDCl_3

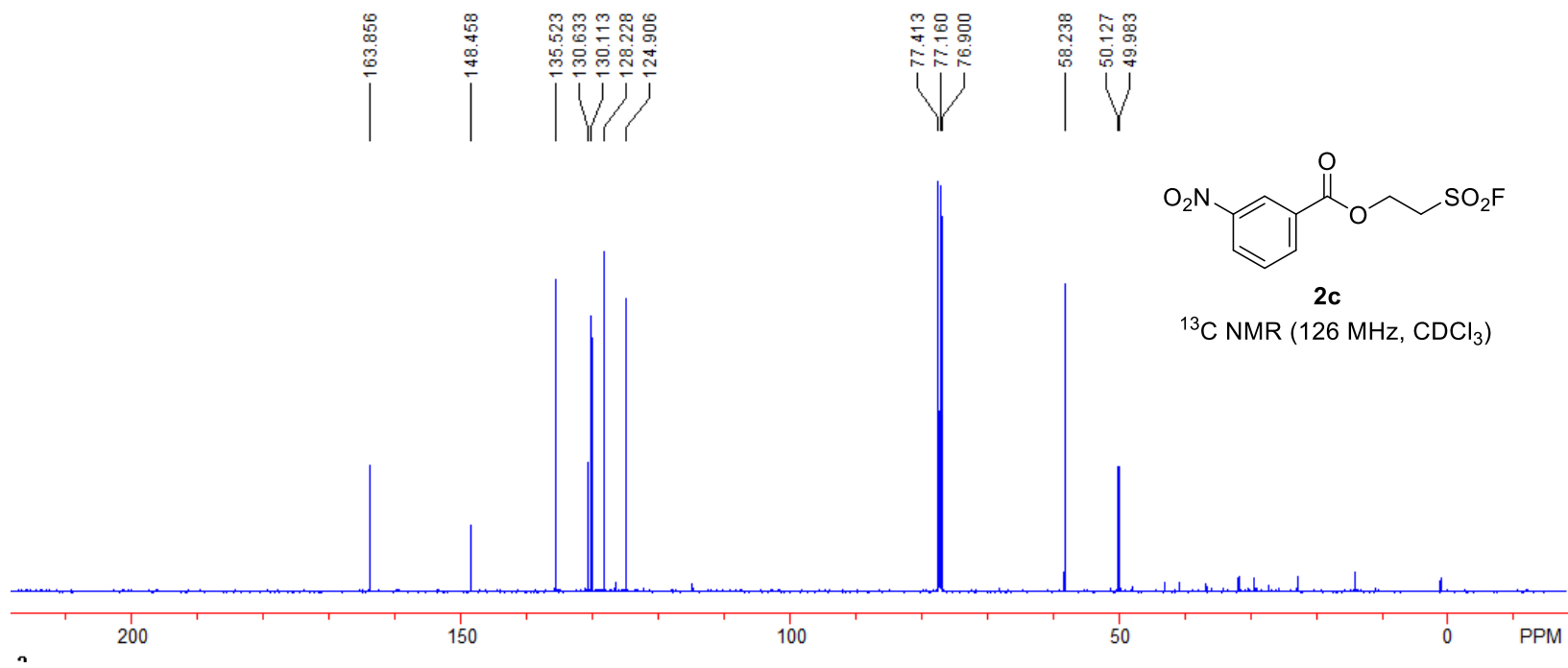


Figure S8. The ^{13}C NMR spectrum of **2c**

2c, ^{19}F NMR, 471 MHz, CDCl_3

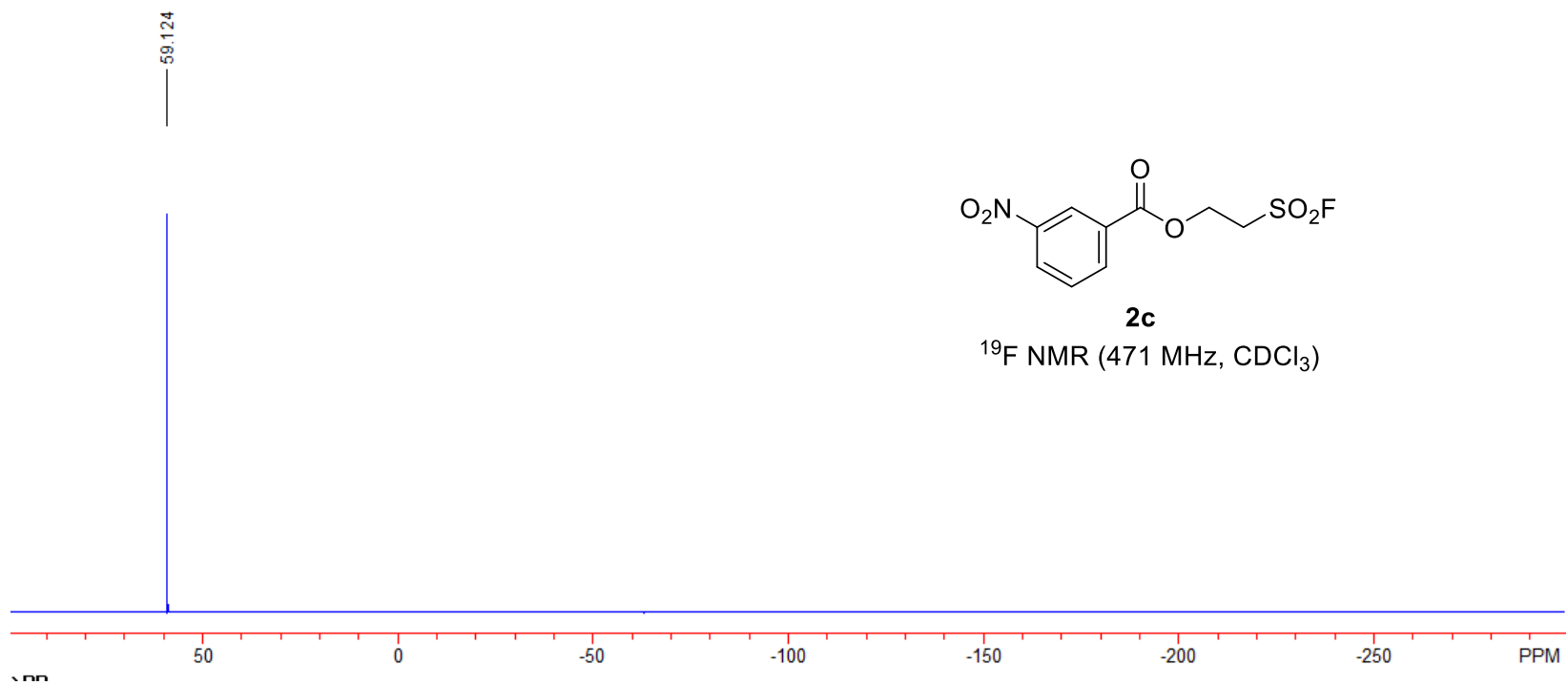


Figure S9. The ^{19}F NMR spectrum of **2c**

2d, ^1H NMR, 500 MHz, CDCl_3

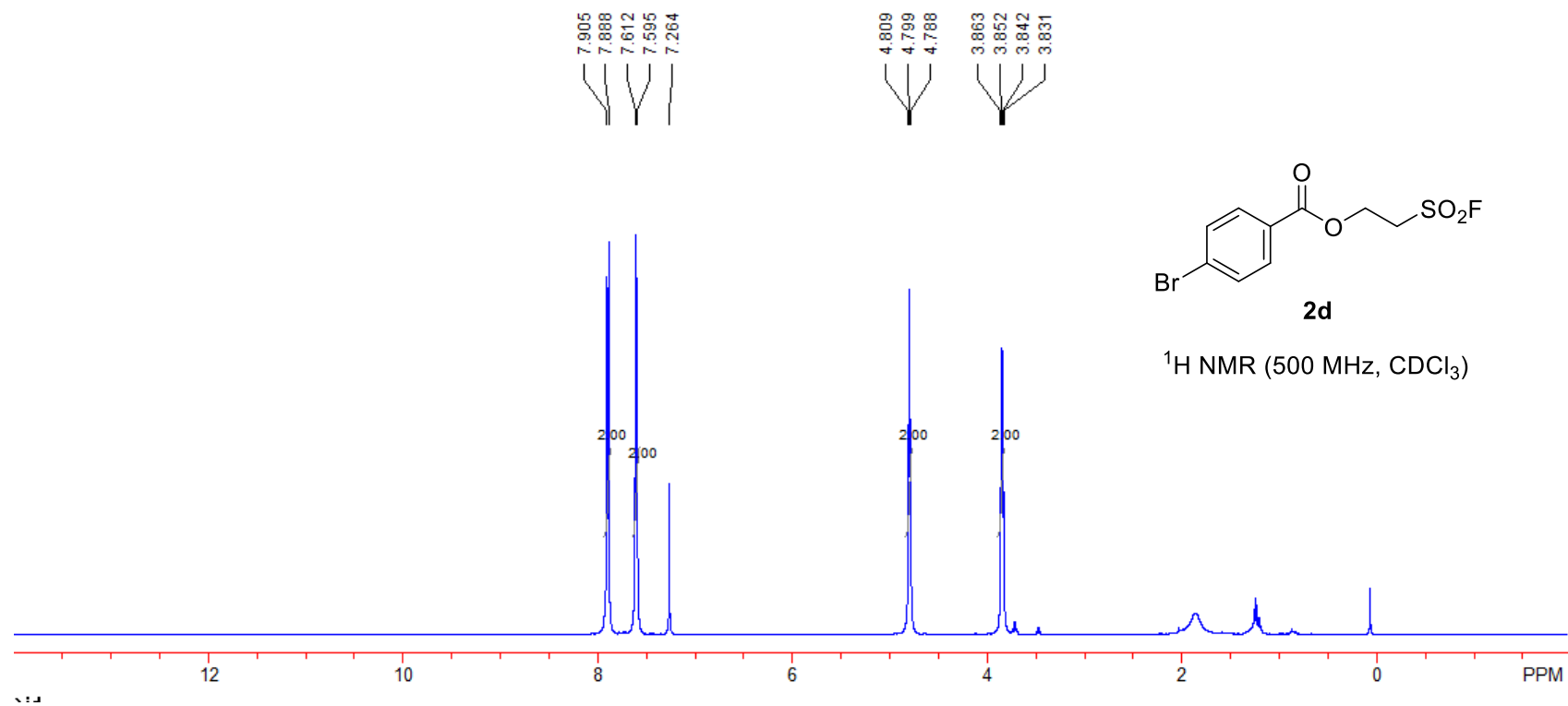


Figure S10. The ^1H NMR spectrum of **2d**

2d, ^{13}C NMR, 126 MHz, CDCl_3

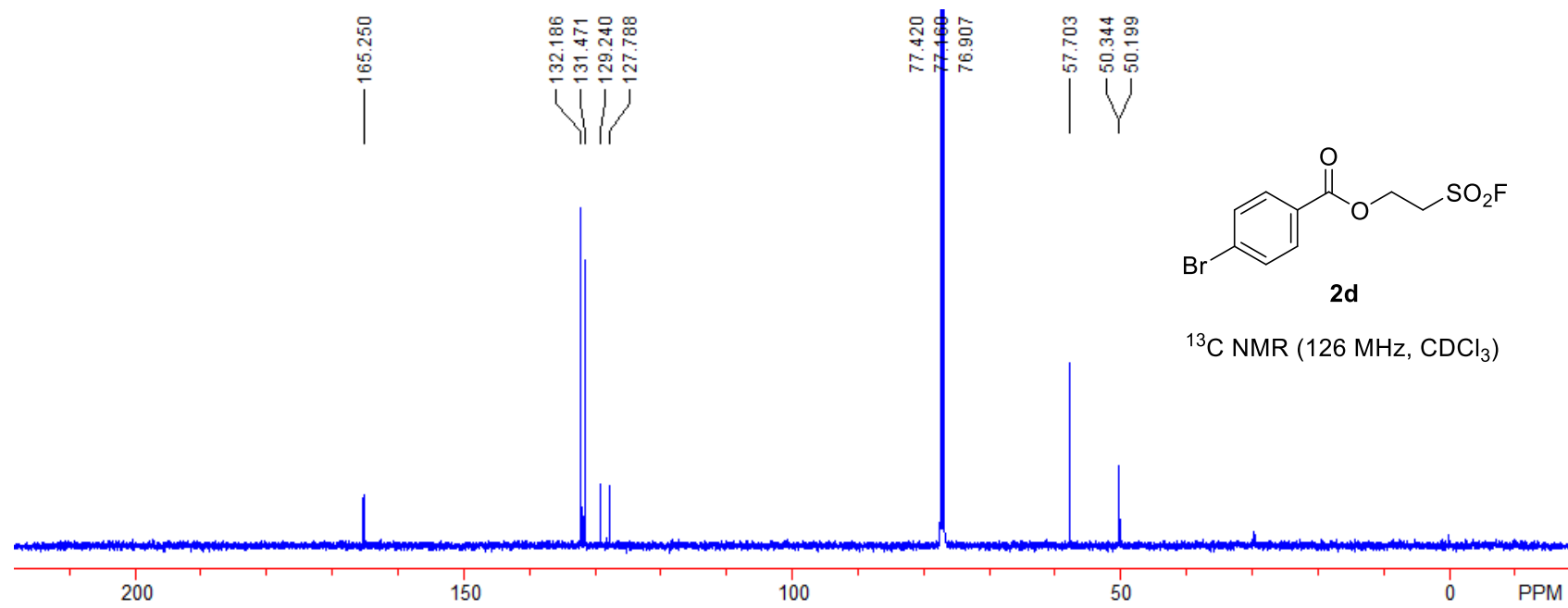


Figure S11. The ^{13}C NMR spectrum of **2d**

2d, ^{19}F NMR, 471 MHz, CDCl_3

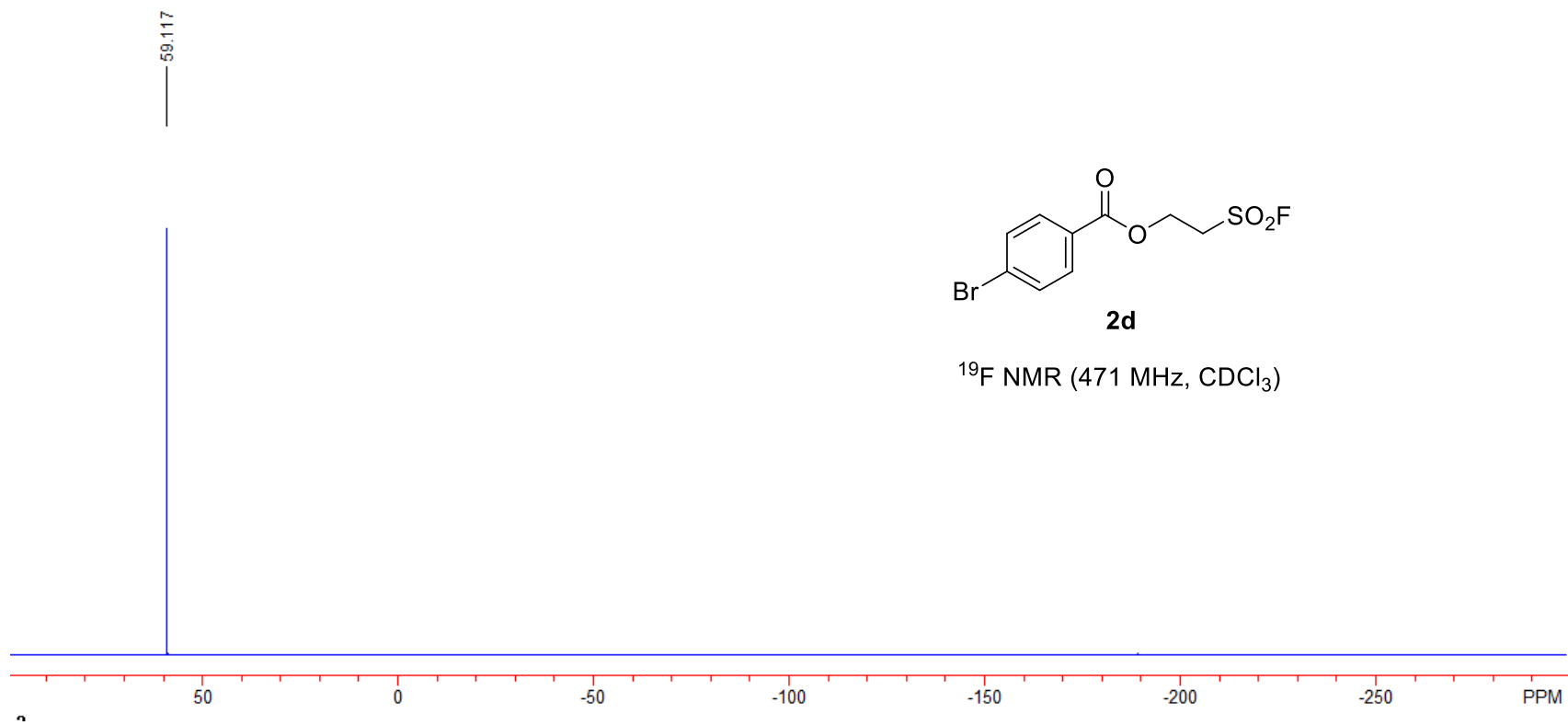


Figure S12. The ^{19}F NMR spectrum of **2d**

2e, ^1H NMR, 500 MHz, CDCl_3

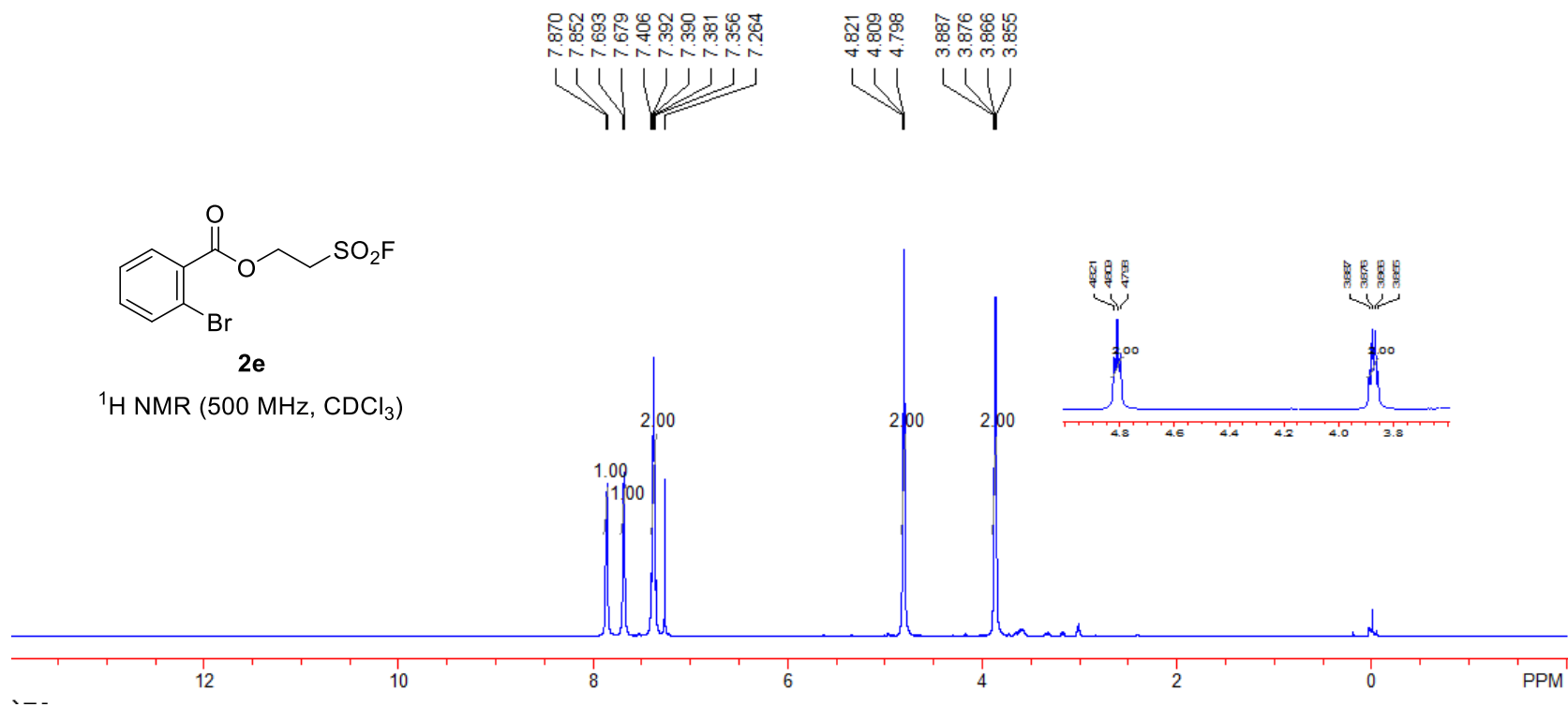


Figure S13. The ^1H NMR spectrum of **2e**

2e, ^{13}C NMR, 126 MHz, CDCl_3

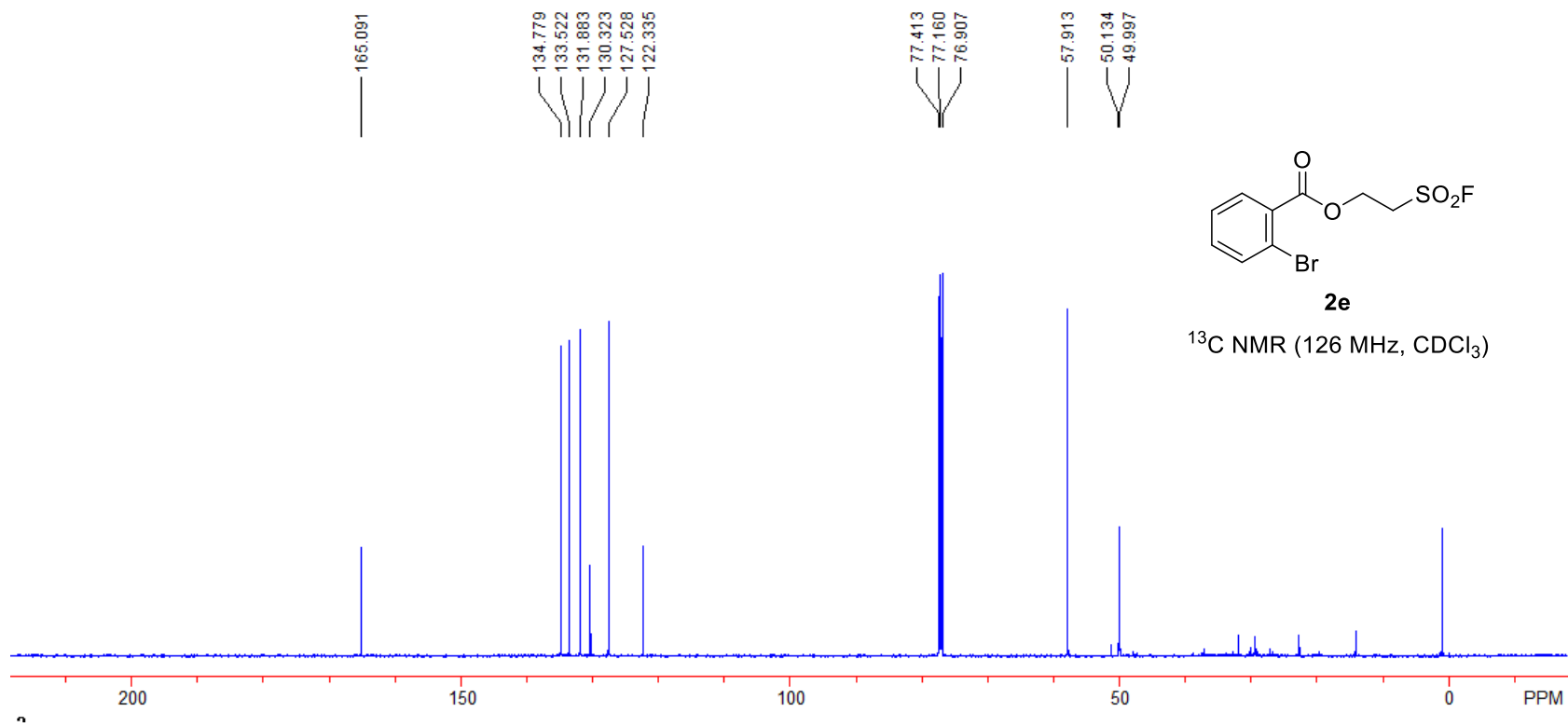


Figure S14. The ^{13}C NMR spectrum of **2e**

2e, ^{19}F NMR, 471 MHz, CDCl_3

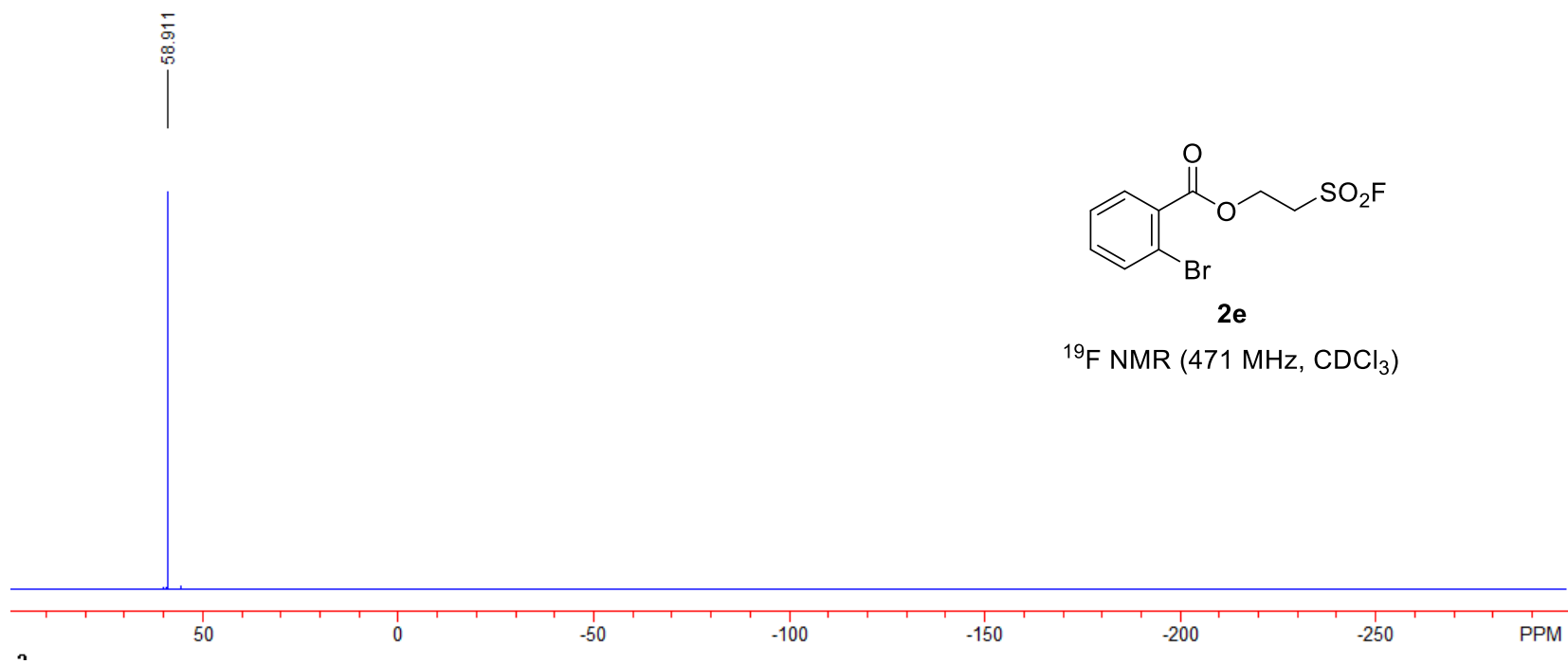


Figure S15. The ^{19}F NMR spectrum of **2e**

2f, ^1H NMR, 500 MHz, CDCl_3

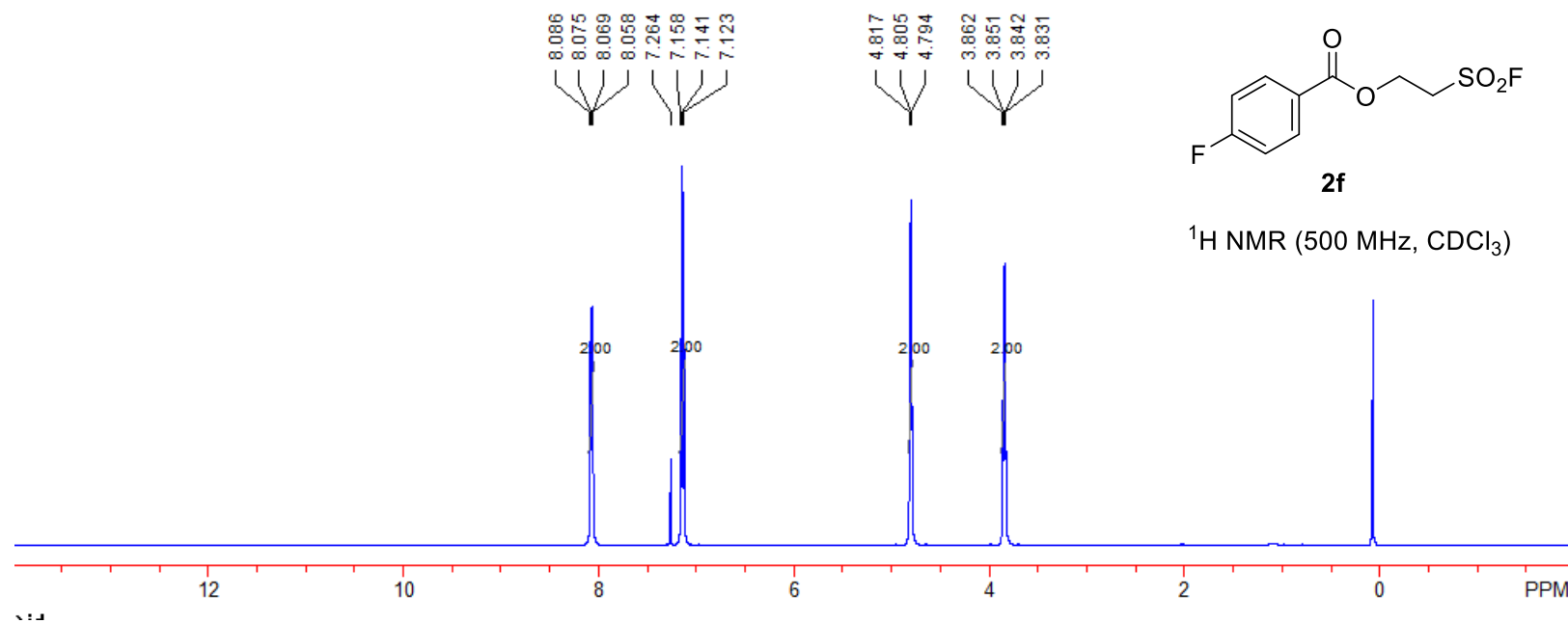


Figure S16. The ^1H NMR spectrum of **2f**

2f, ^{13}C NMR, 126 MHz, CDCl_3

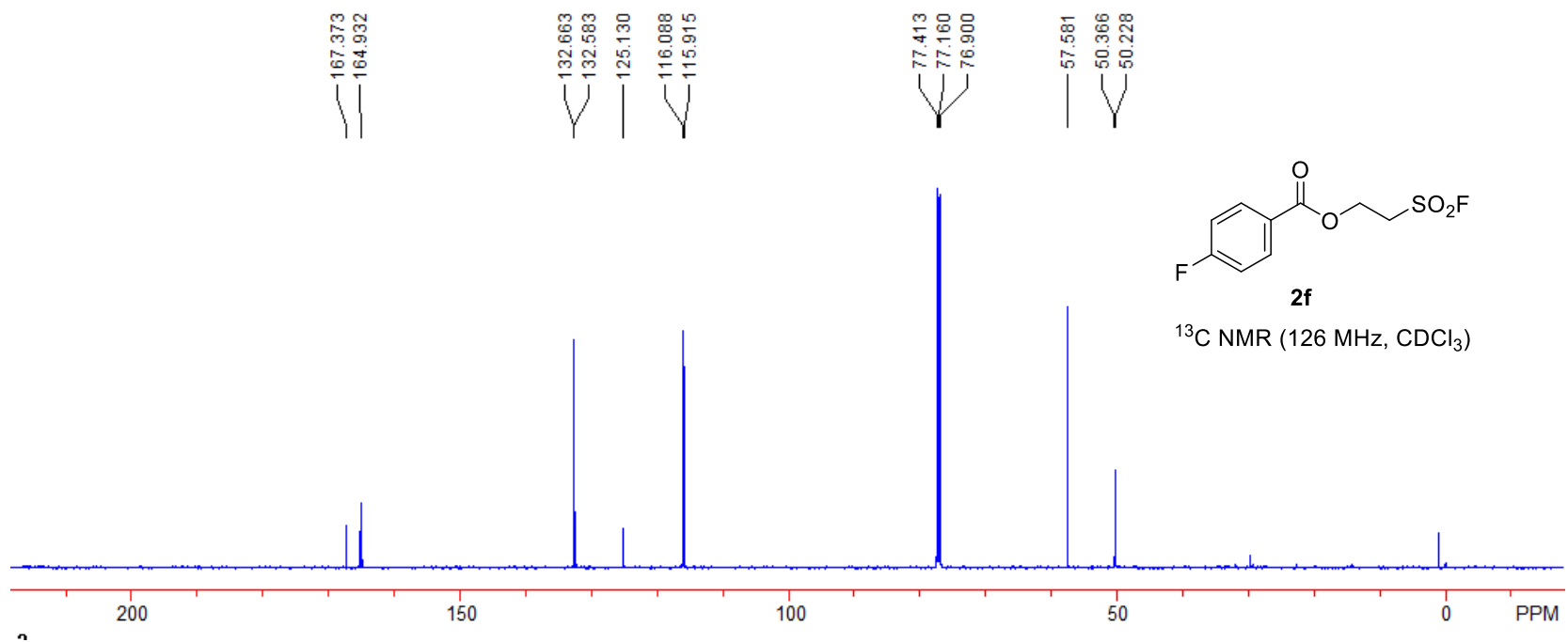


Figure S17. The ^{13}C NMR spectrum of **2f**

2f, ^{19}F NMR, 471 MHz, CDCl_3

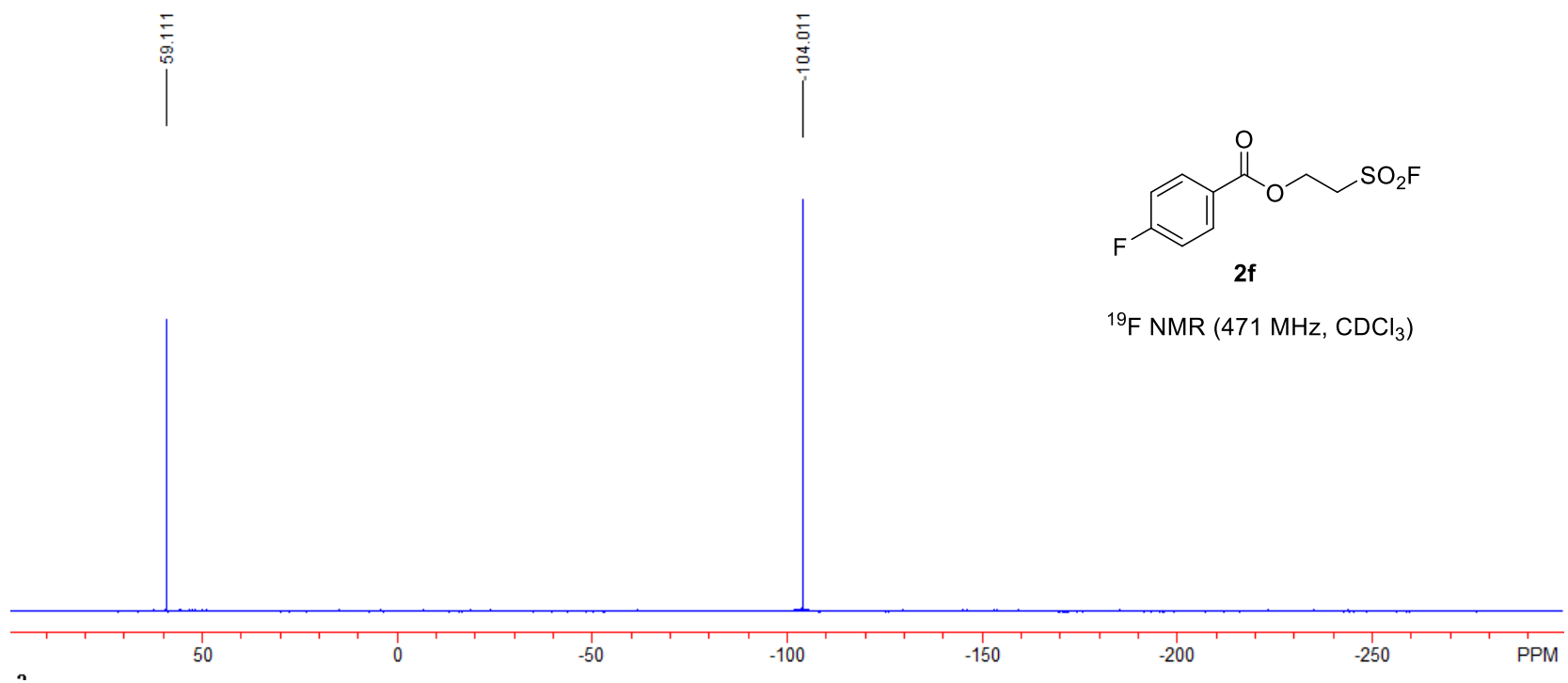


Figure S18. The ^{19}F NMR spectrum of **2f**

2g, ^1H NMR, 500 MHz, CDCl_3

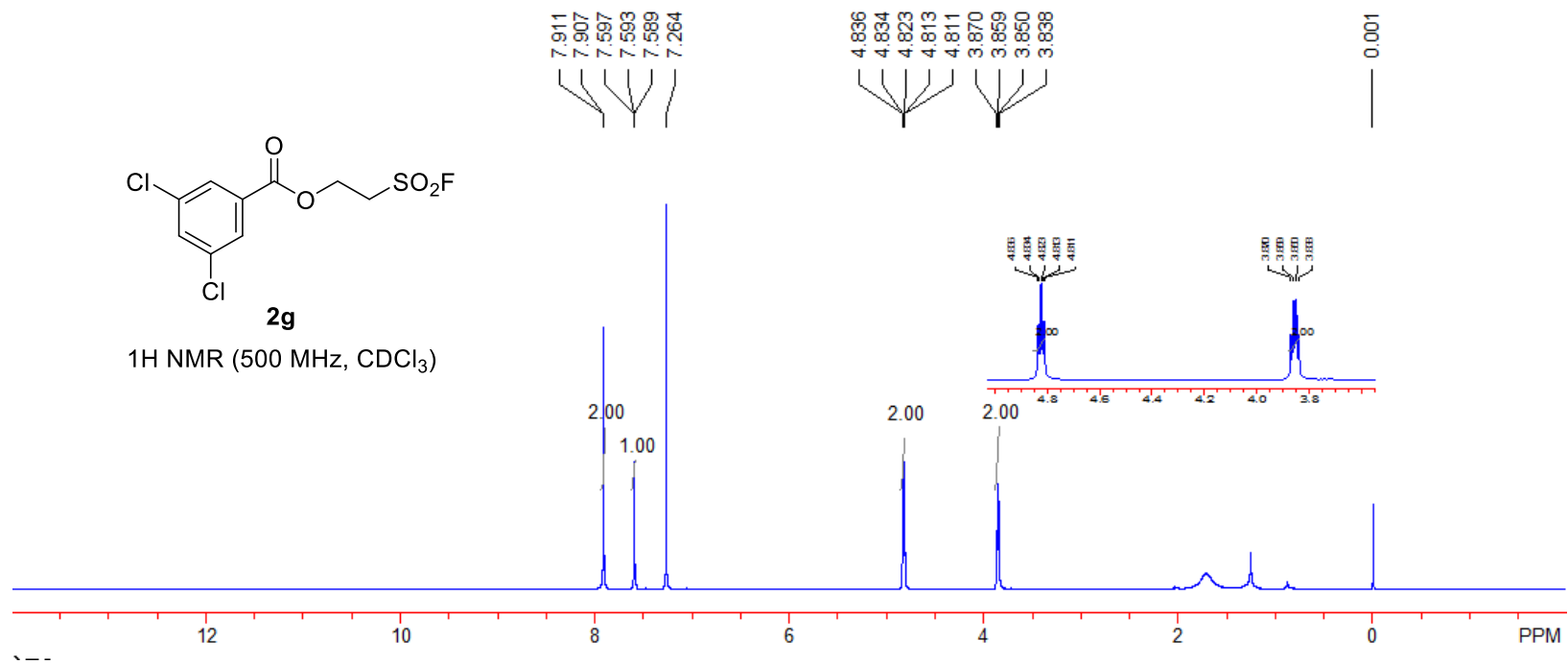


Figure S19. The ^1H NMR spectrum of **2g**

2g, ^{13}C NMR, 126 MHz, CDCl_3

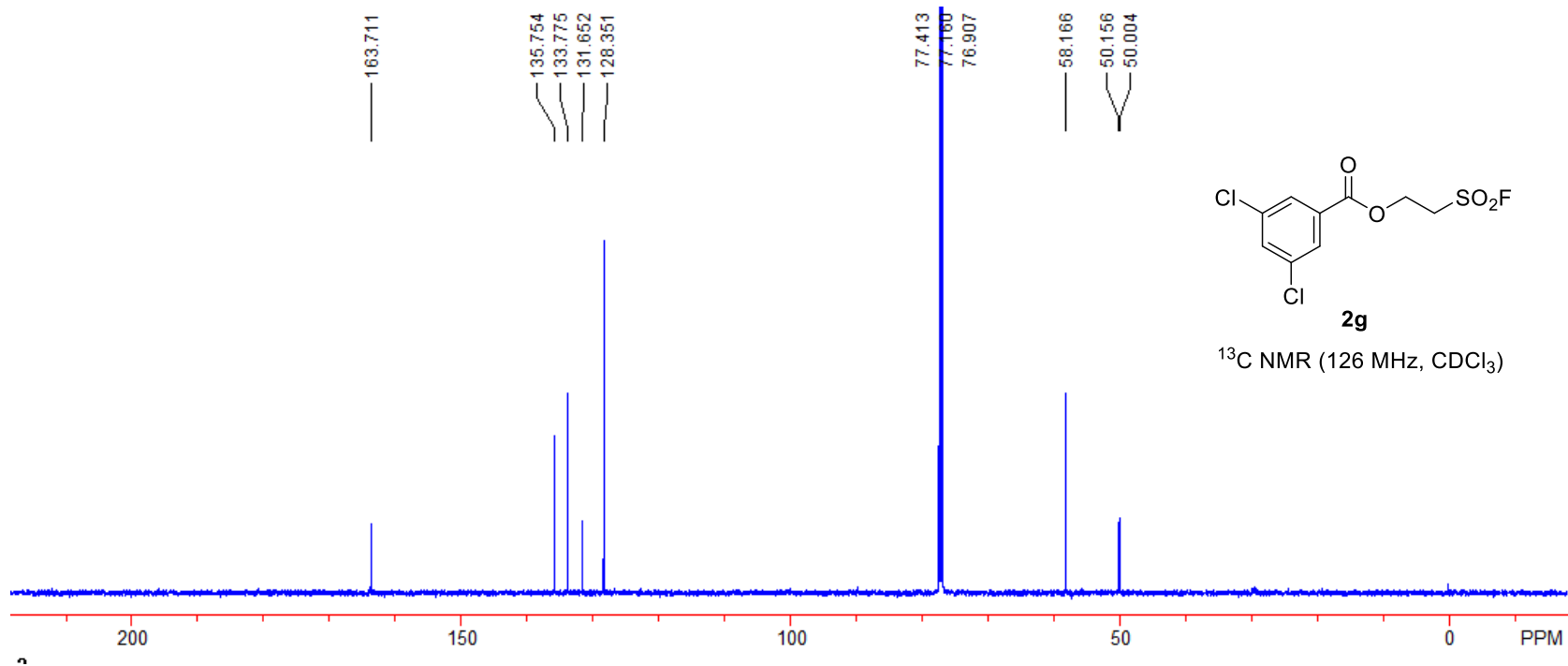


Figure S20. The ^{13}C NMR spectrum of **2g**

2g, ^{19}F NMR, 471 MHz, CDCl_3

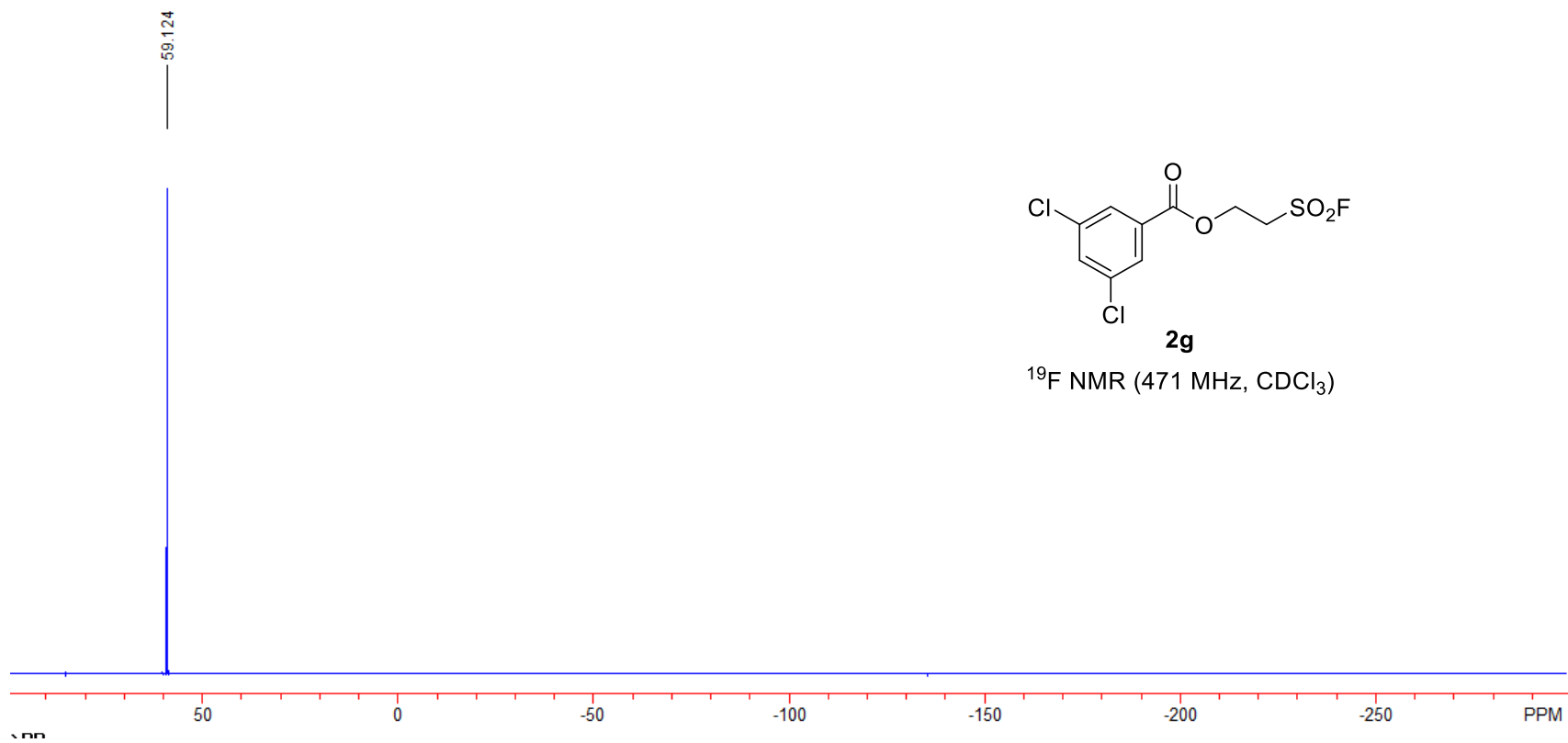


Figure S21. The ^{19}F NMR spectrum of **2g**

2h, ^1H NMR, 500 MHz, CDCl_3

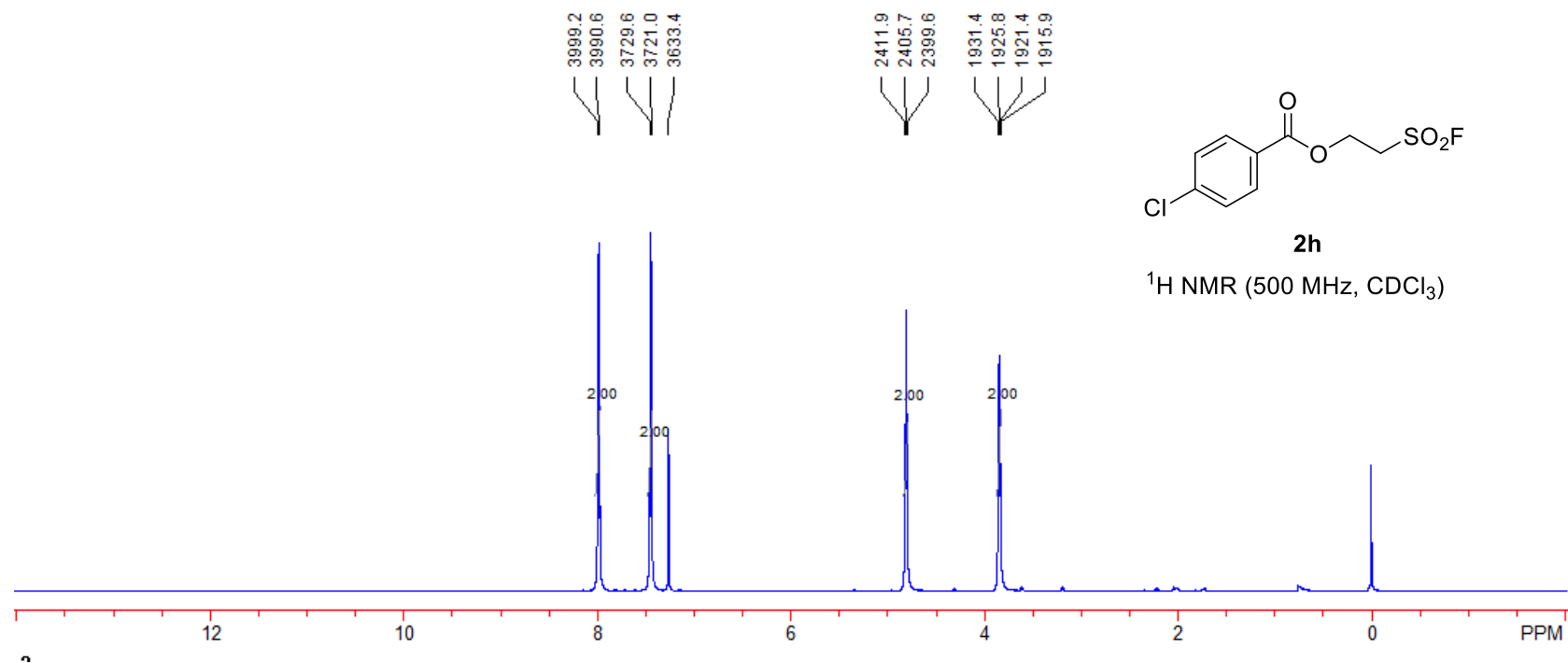


Figure S22. The ^1H NMR spectrum of **2h**

2h, ^{13}C NMR, 126 MHz, CDCl_3

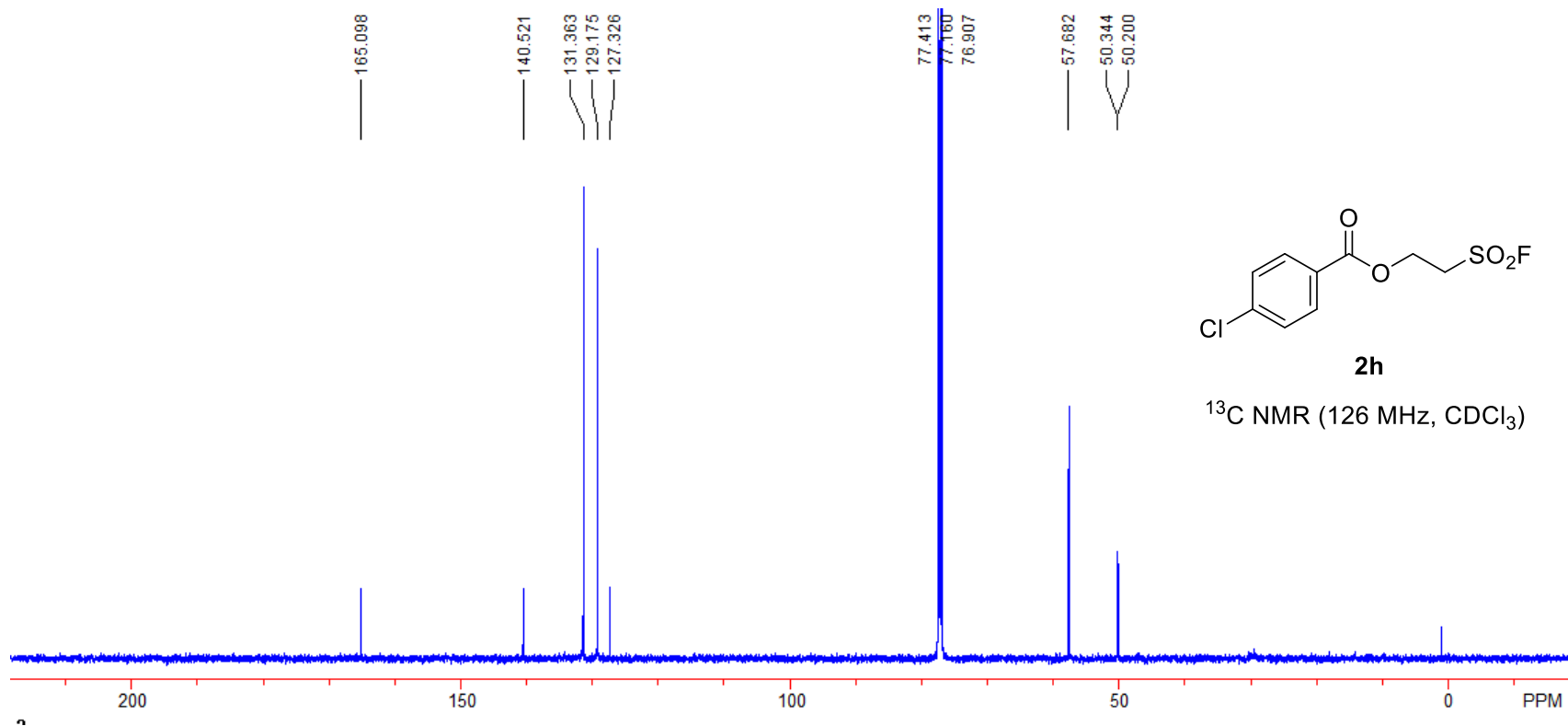


Figure S23. The ^{13}C NMR spectrum of **2h**

2h, ^{19}F NMR, 471 MHz, CDCl_3

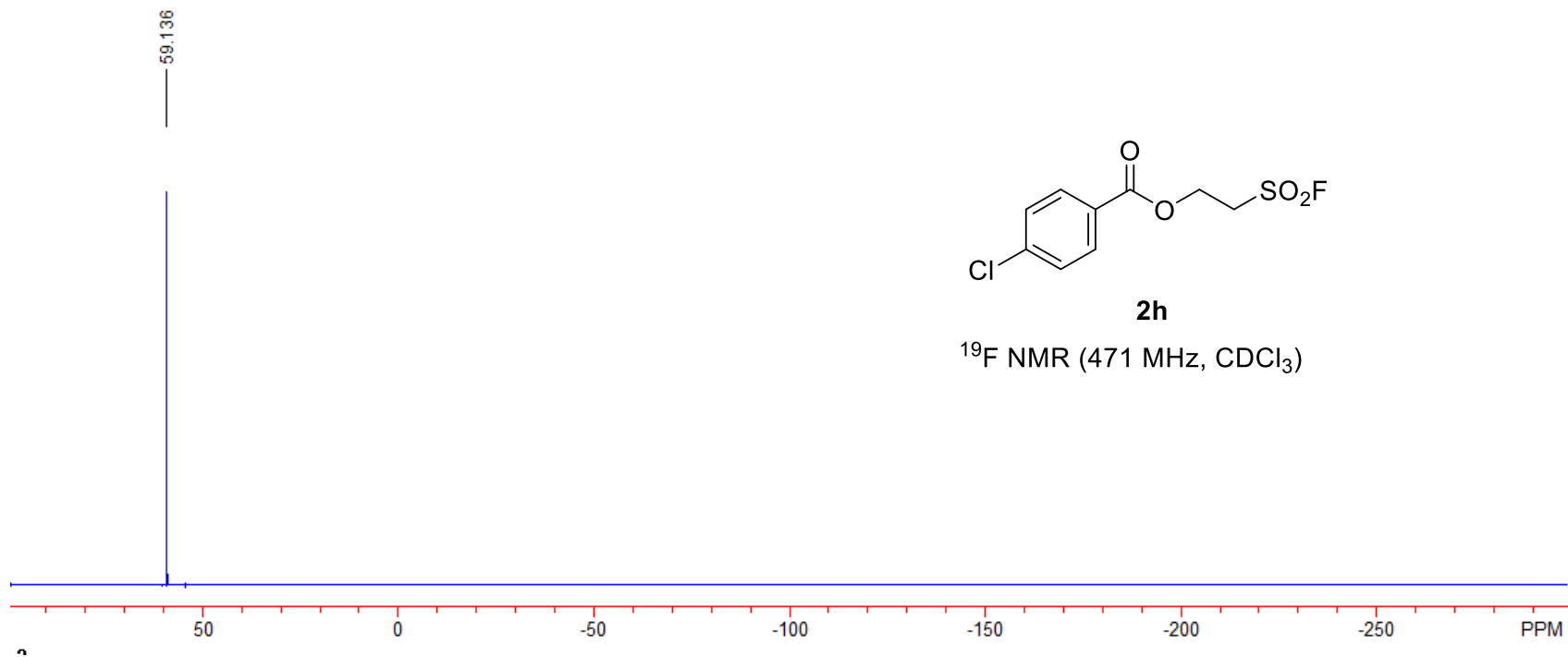


Figure S24. The ^{19}F NMR spectrum of **2h**

2i, ^1H NMR, 500 MHz, CDCl_3

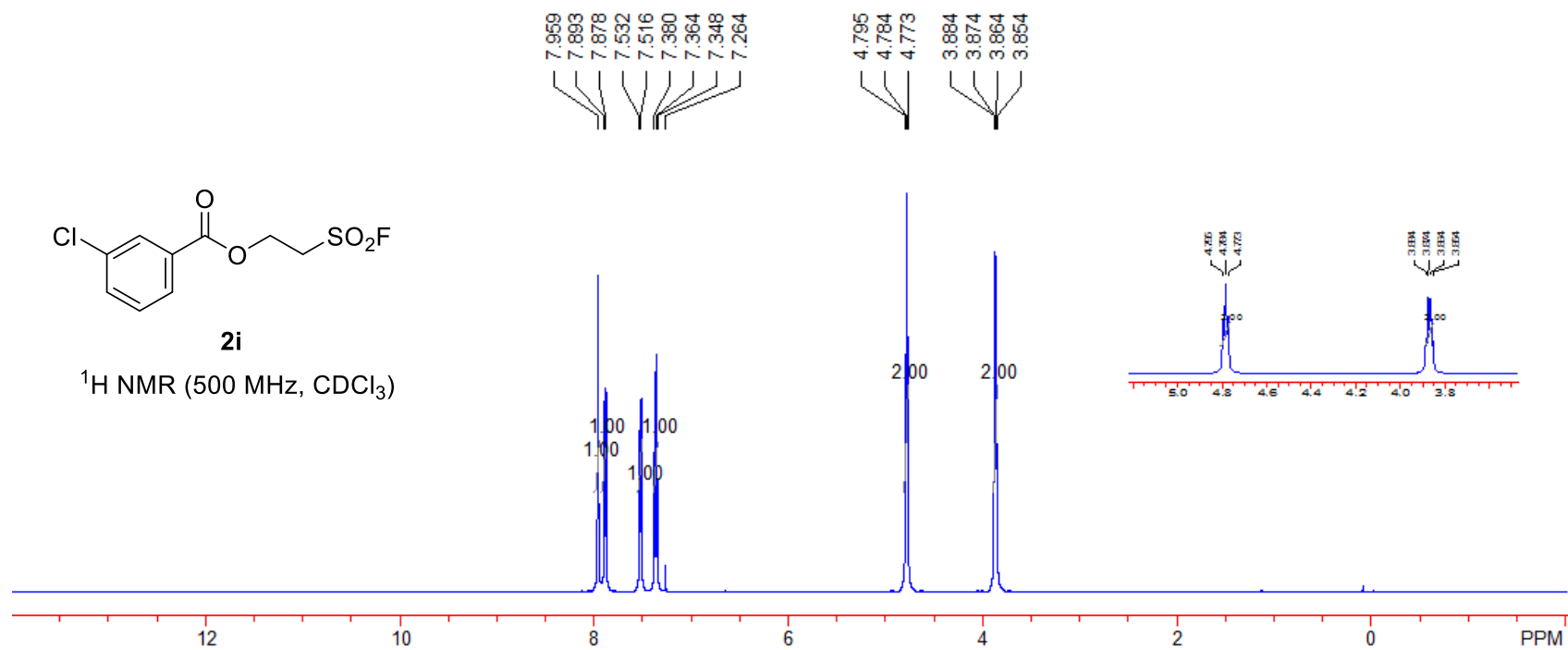


Figure S25. The ^1H NMR spectrum of **2i**

2i, ^{13}C NMR, 126 MHz, CDCl_3

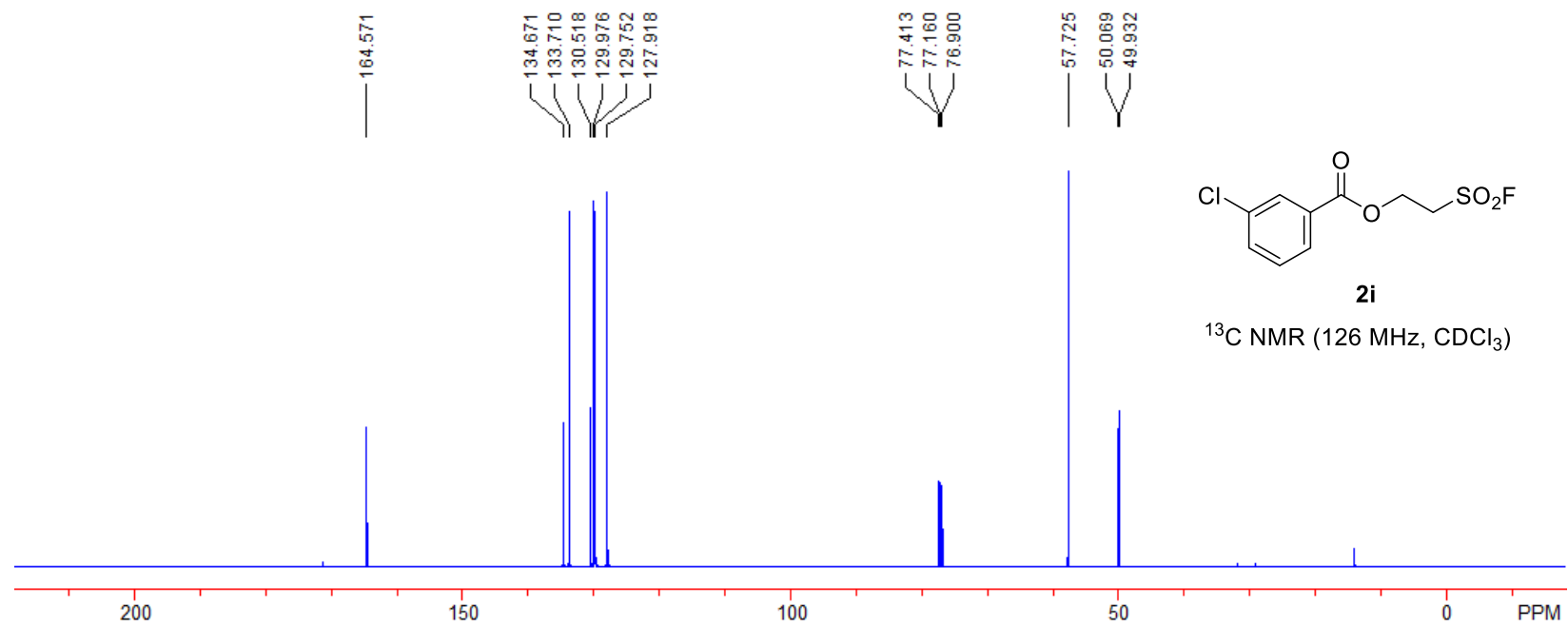


Figure S26. The ^{13}C NMR spectrum of **2i**

2i, ^{19}F NMR, 471 MHz, CDCl_3

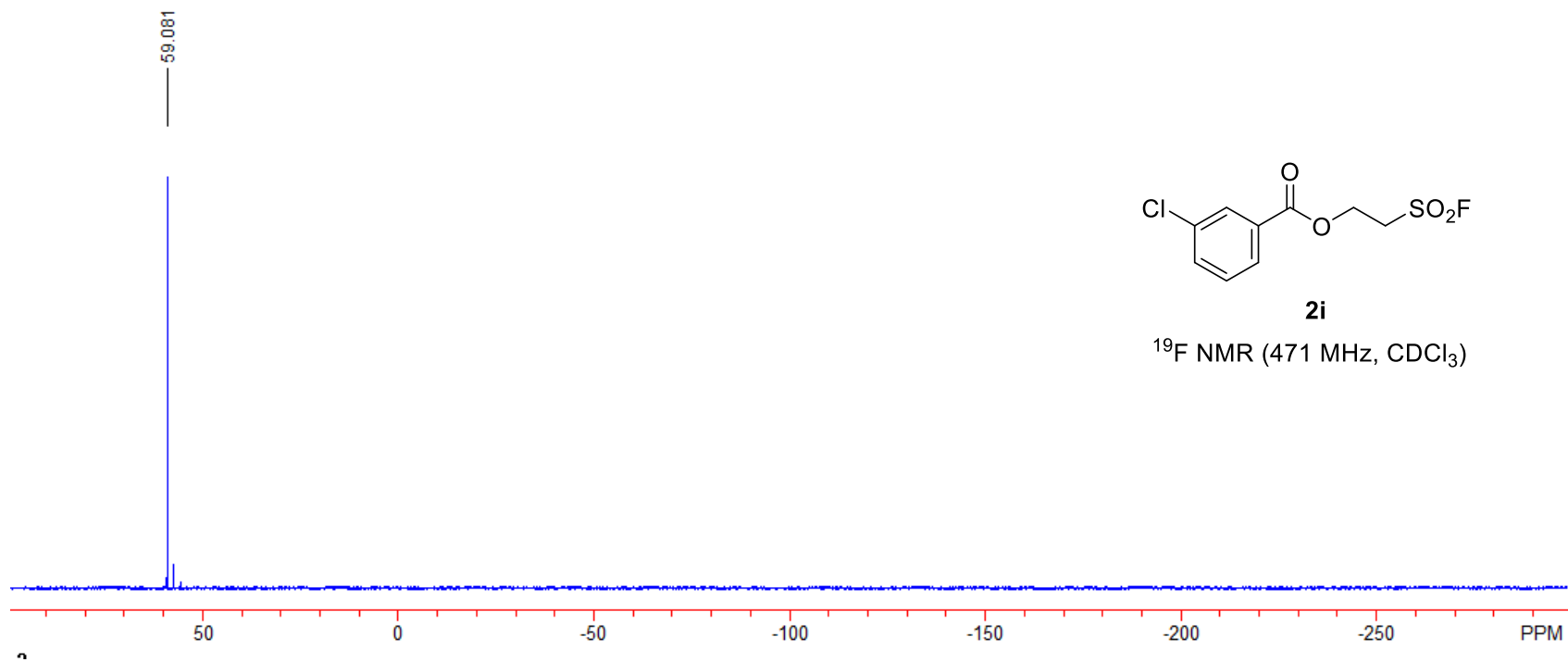


Figure S27. The ^{19}F NMR spectrum of **2i**

2j, ^1H NMR, 500 MHz, CDCl_3

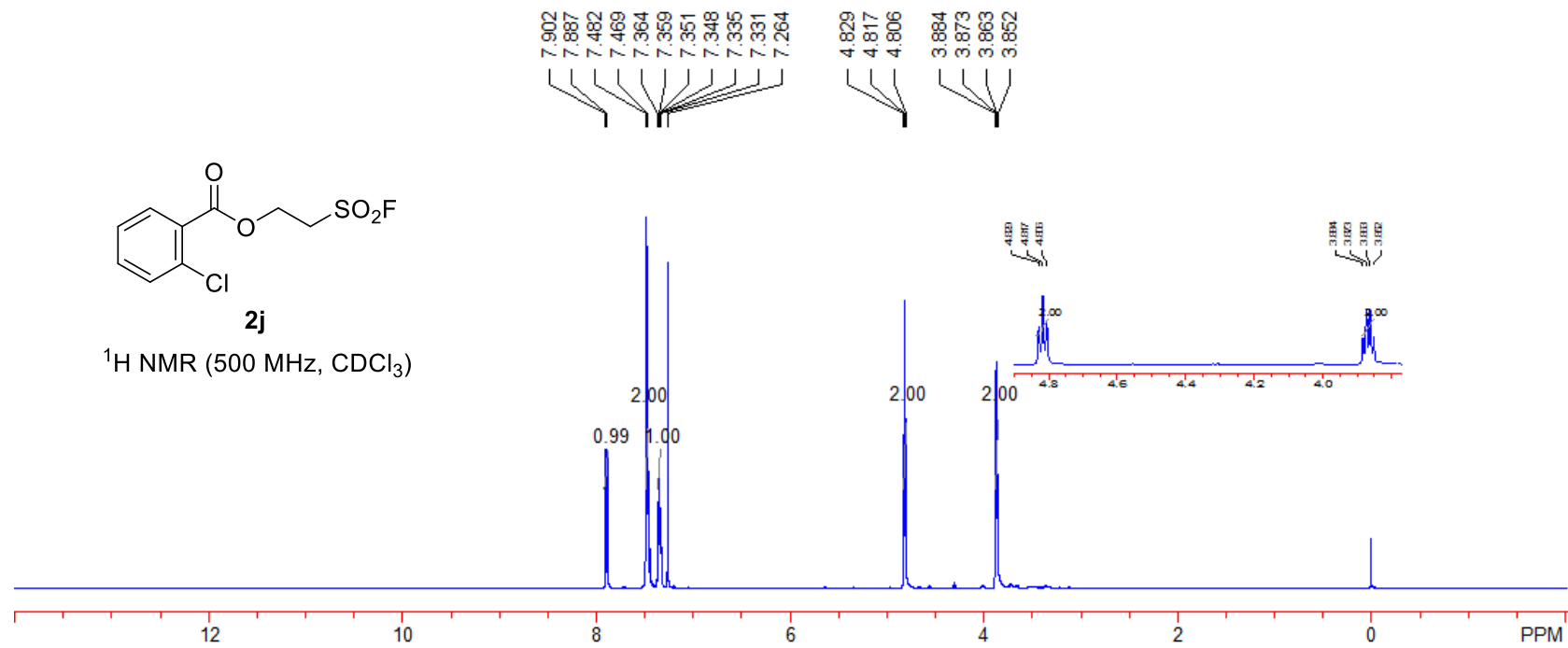


Figure S28. The ^1H NMR spectrum of **2j**

2j, ^{13}C NMR, 126 MHz, CDCl_3

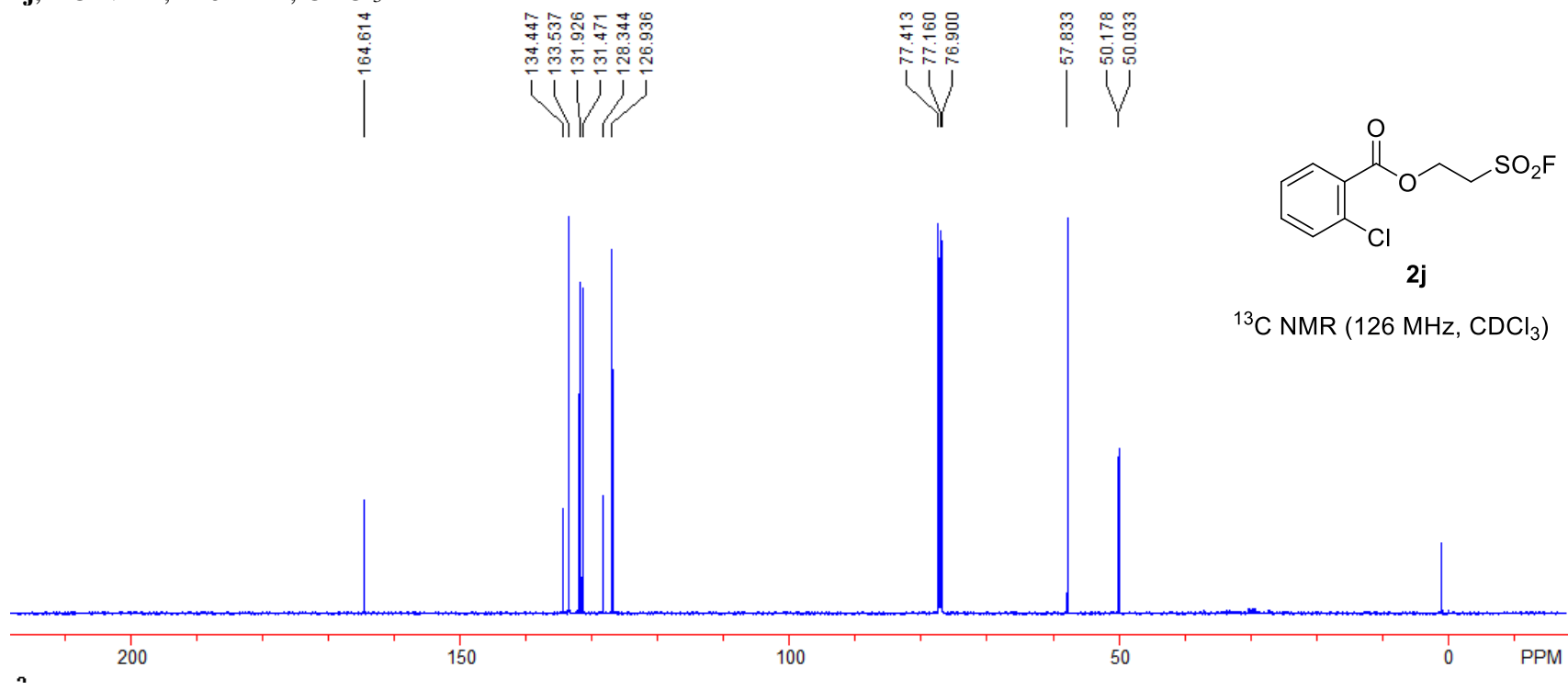


Figure S29. The ^{13}C NMR spectrum of **2j**

2j, ^{19}F NMR, 471 MHz, CDCl_3

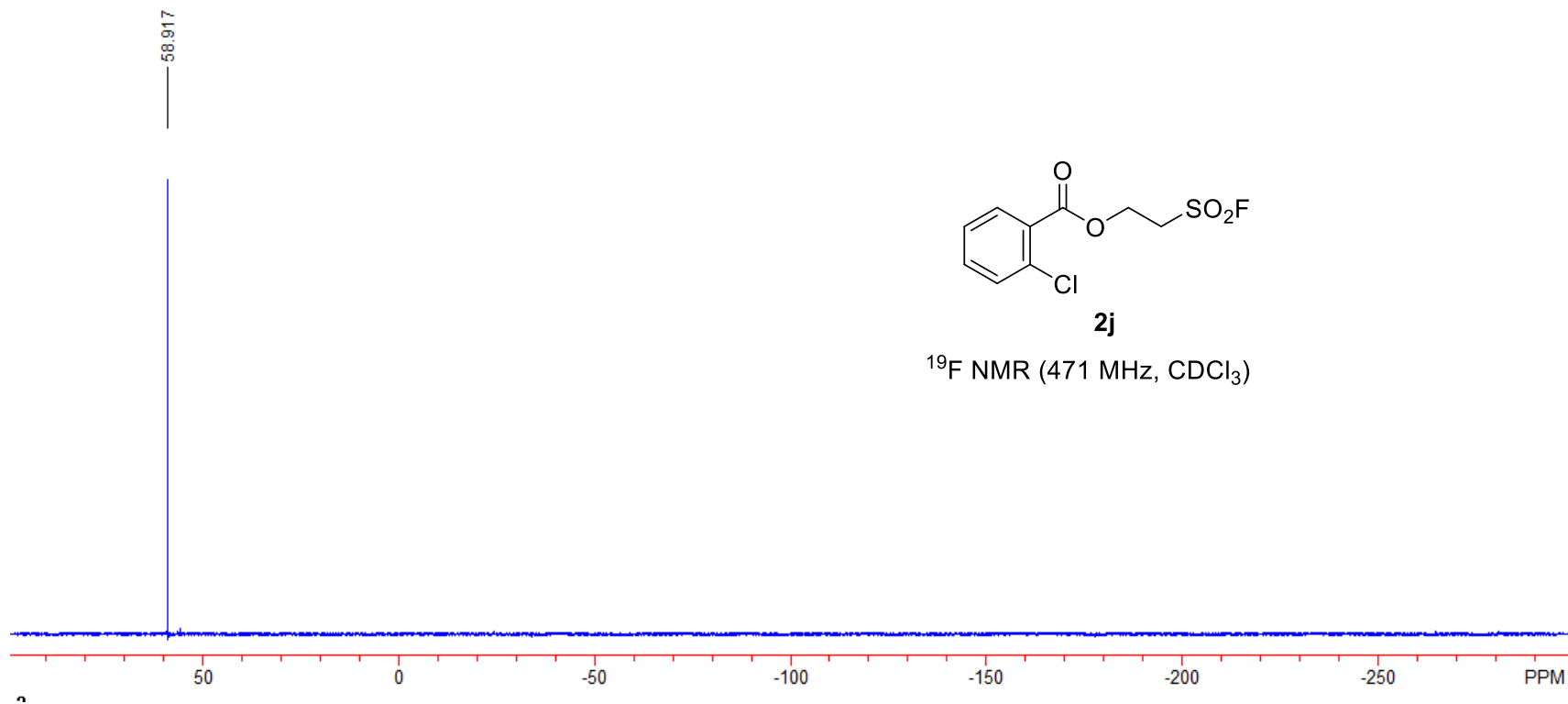


Figure S30. The ^{19}F NMR spectrum of **2j**

2k, ^{13}C NMR, 126 MHz, CDCl_3

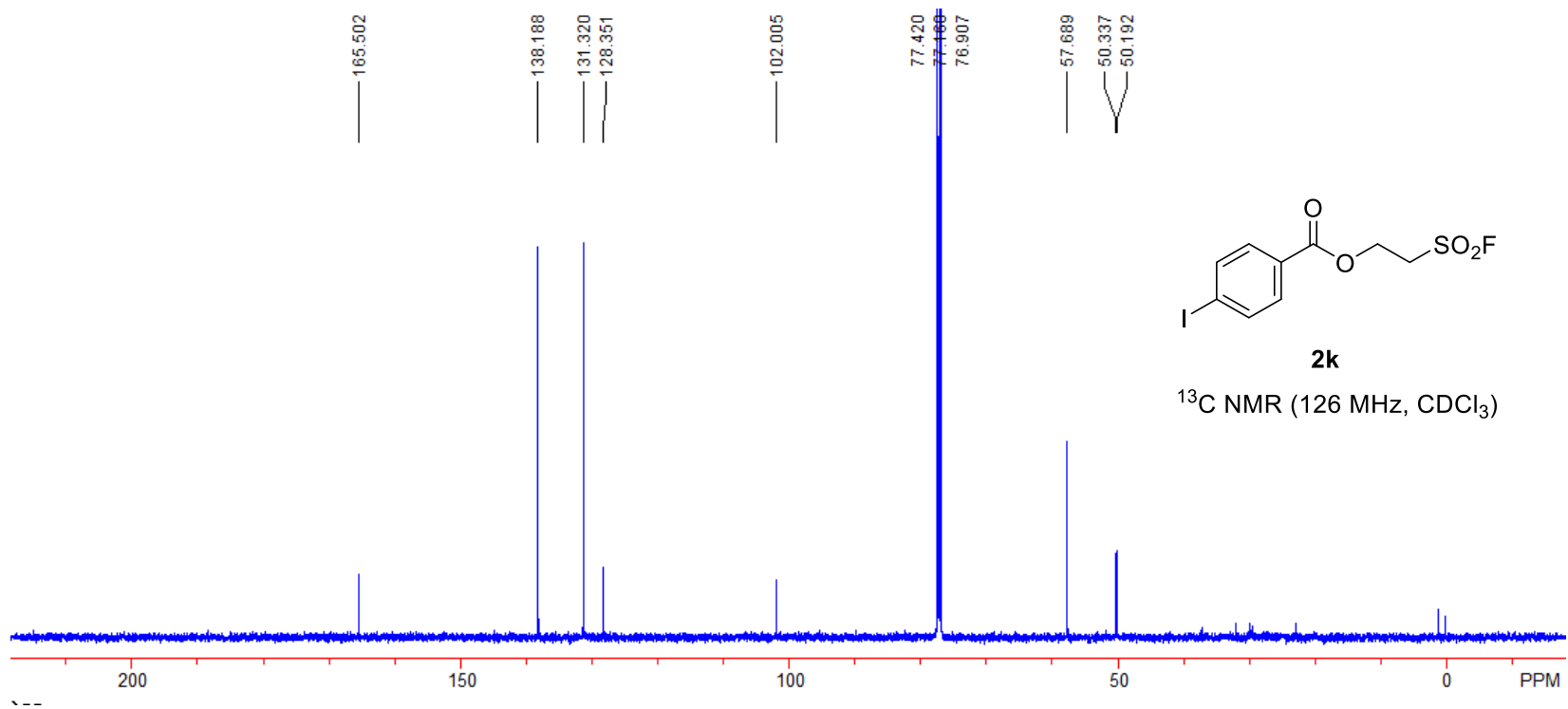


Figure S32. The ^{13}C NMR spectrum of **2k**

2k, ^{19}F NMR, 471 MHz, CDCl_3

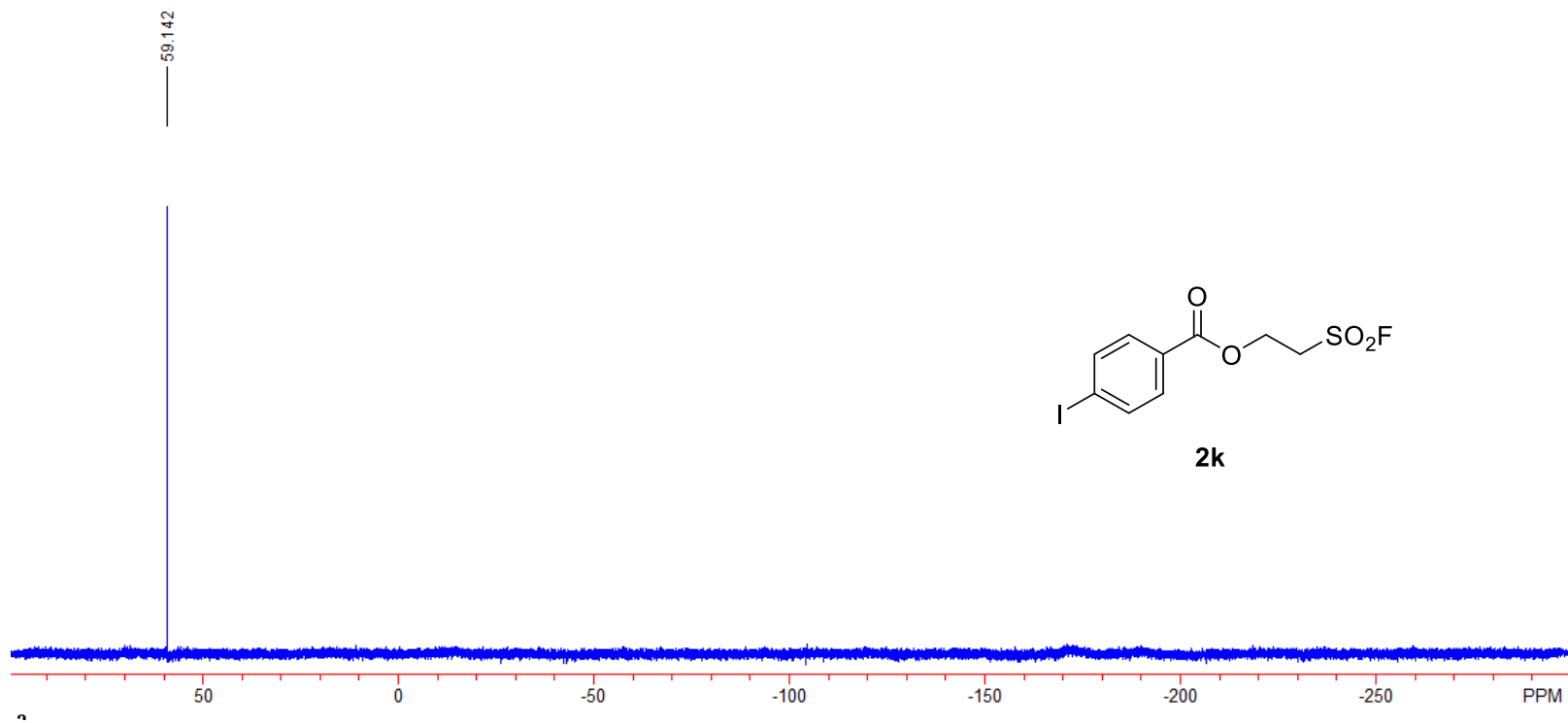
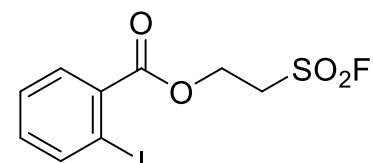


Figure S33. The ^{19}F NMR spectrum of **2k**

21, ^1H NMR, 500 MHz, CDCl_3



21

^1H NMR (500 MHz, CDCl_3)

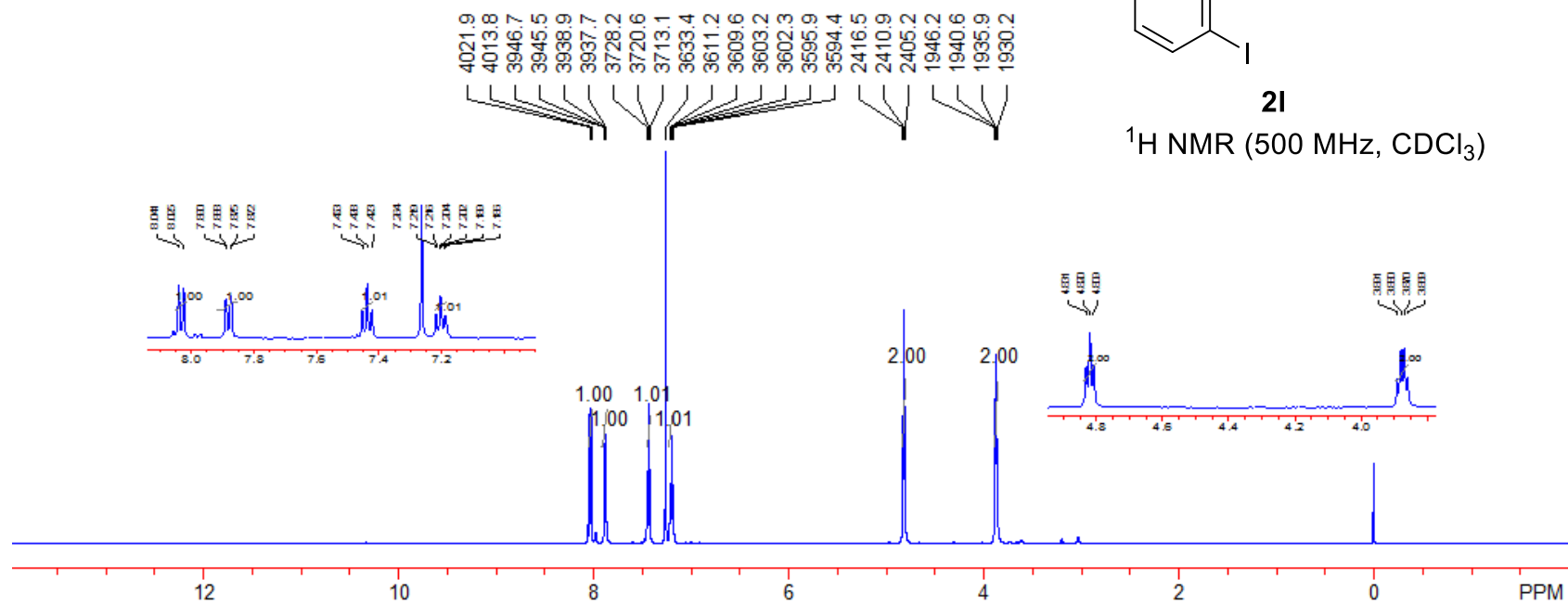


Figure S34. The ^1H NMR spectrum of **21**

2l, ^{13}C NMR, 126 MHz, CDCl_3

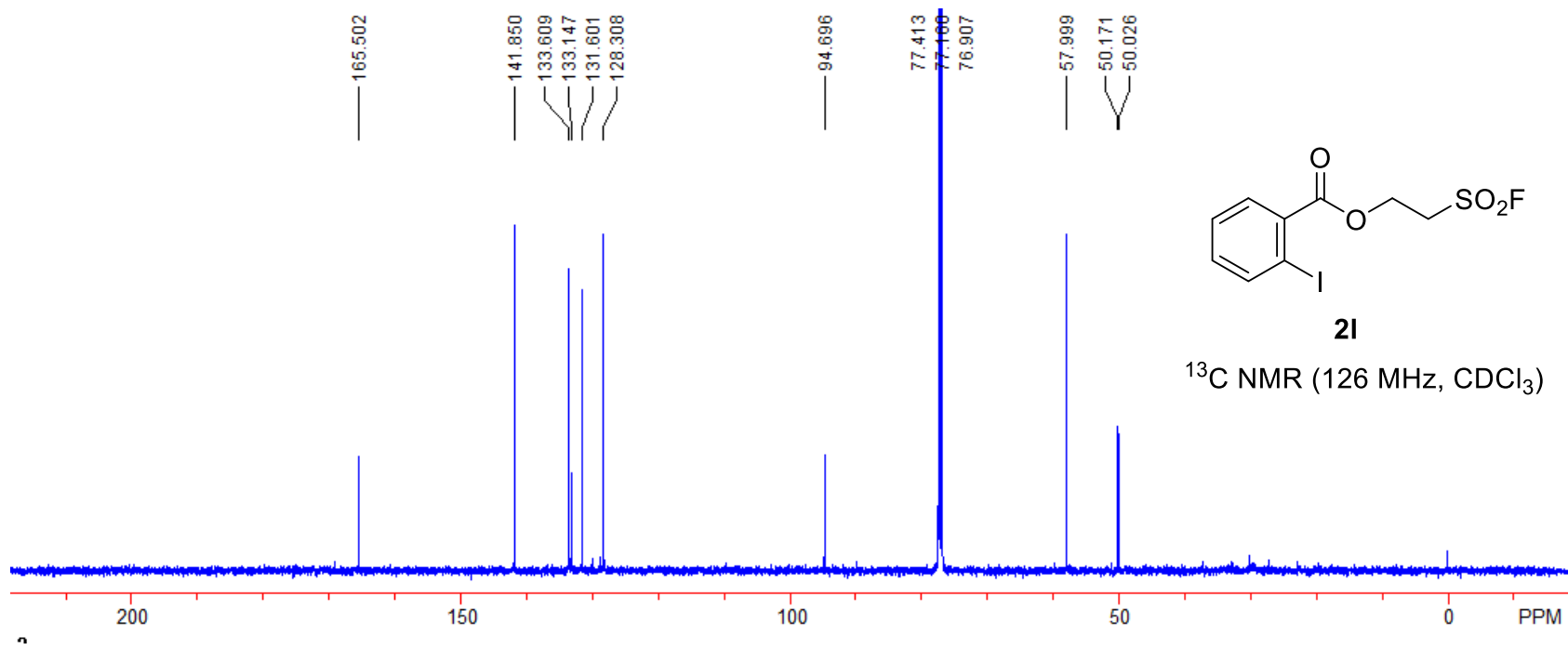


Figure S35. The ^{13}C NMR spectrum of **2l**

21, ^{19}F NMR, 471 MHz, CDCl_3

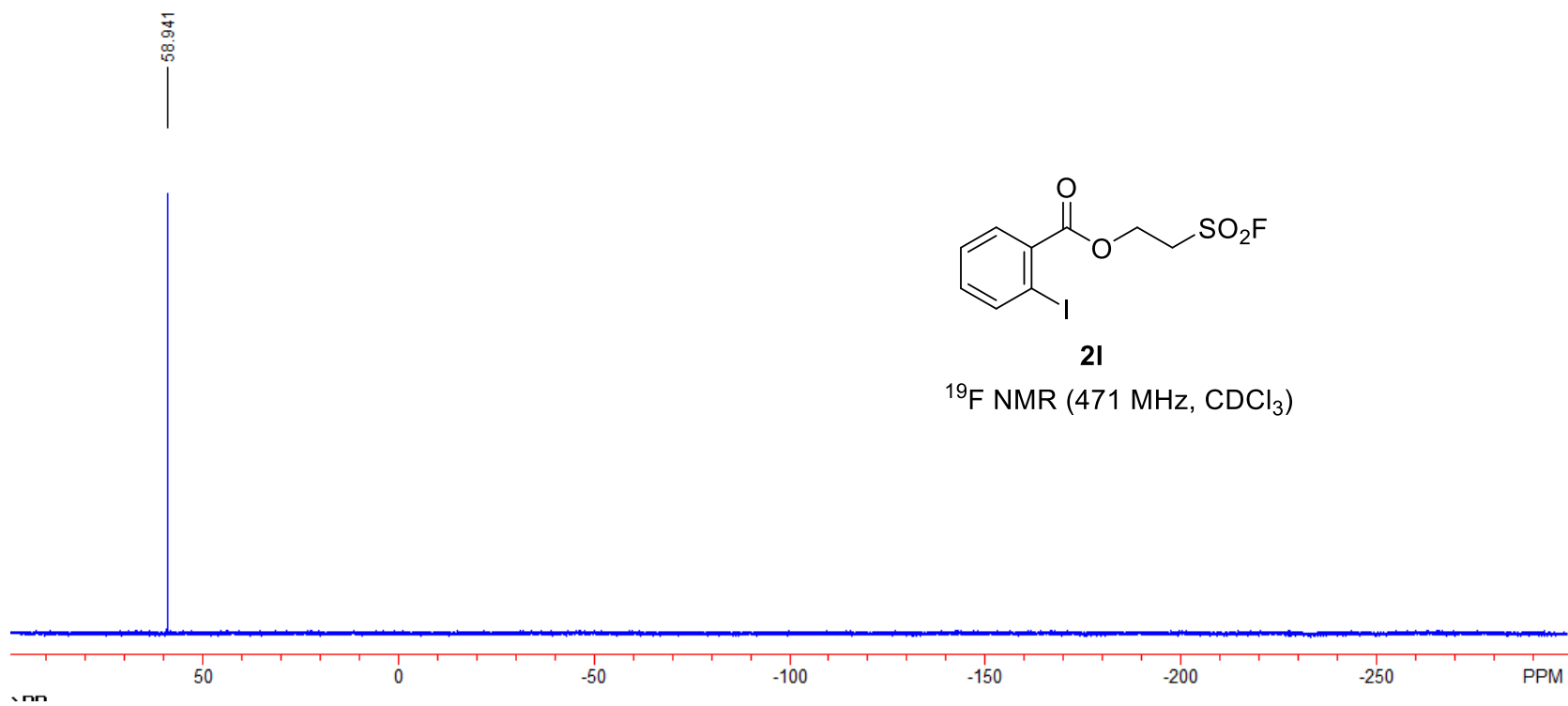


Figure S36. The ^{19}F NMR spectrum of **21**

2m, ^1H NMR, 500 MHz, CDCl_3

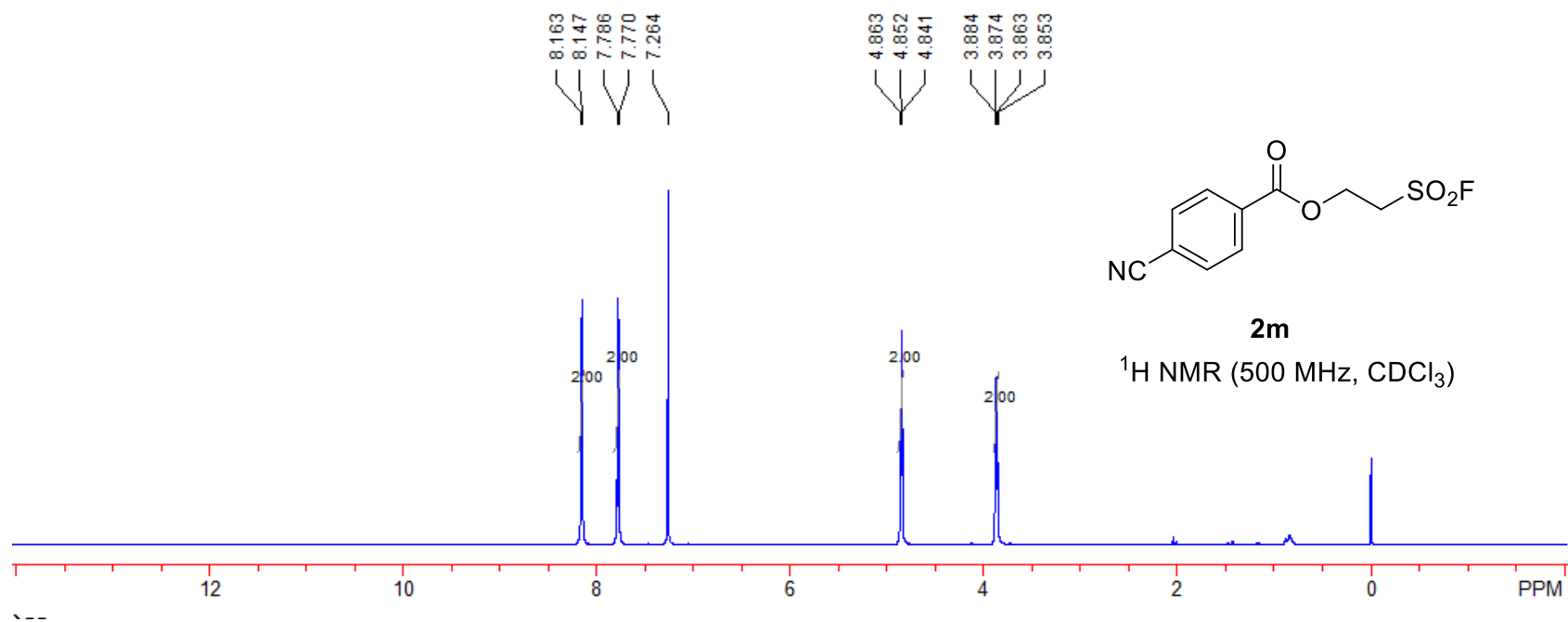


Figure S37. The ^1H NMR spectrum of **2m**

2m, ^{13}C NMR, 126 MHz, CDCl_3

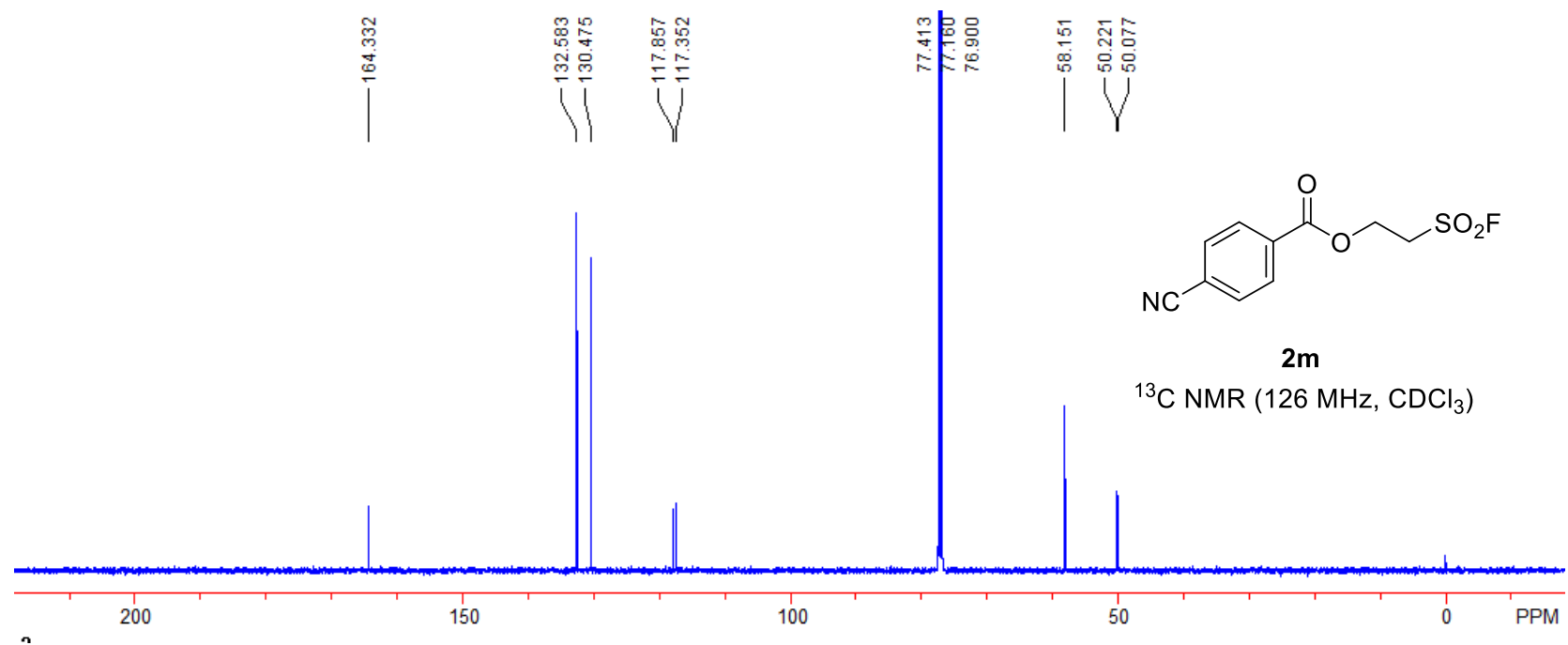


Figure S38. The ^{13}C NMR spectrum of **2m**

2m, ^{19}F NMR, 471 MHz, CDCl_3

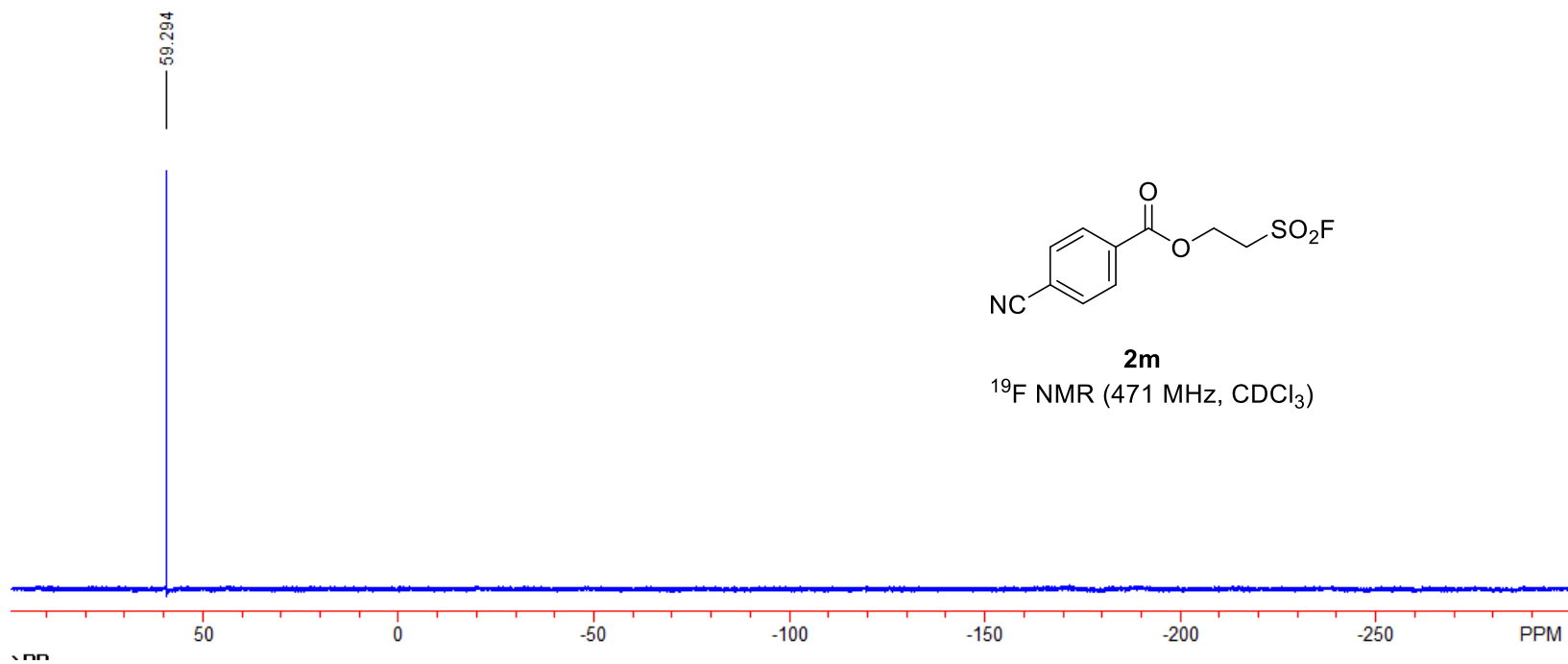


Figure S39. The ^{19}F NMR spectrum of **2m**

2n, ^{13}C NMR, 126 MHz, CDCl_3

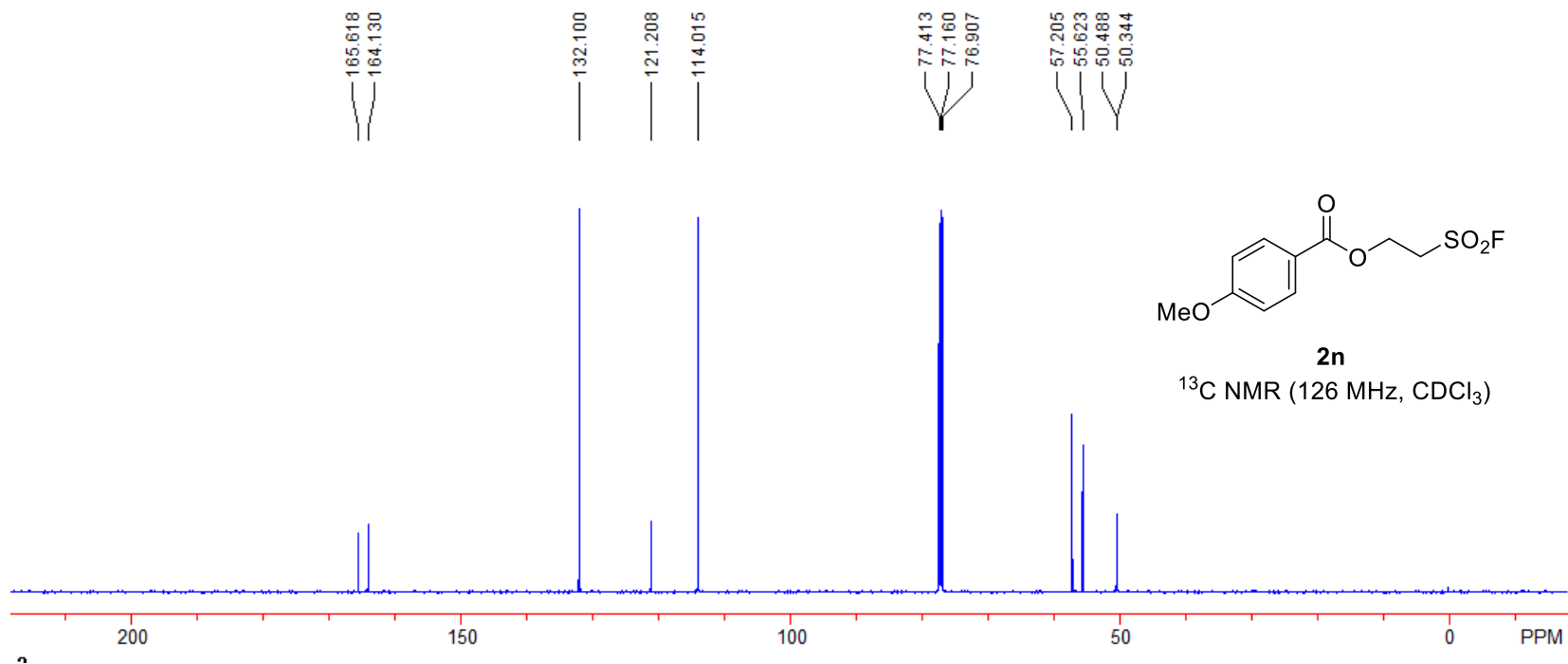


Figure S41. The ^{13}C NMR spectrum of **2n**

2n, ^{19}F NMR, 471 MHz, CDCl_3

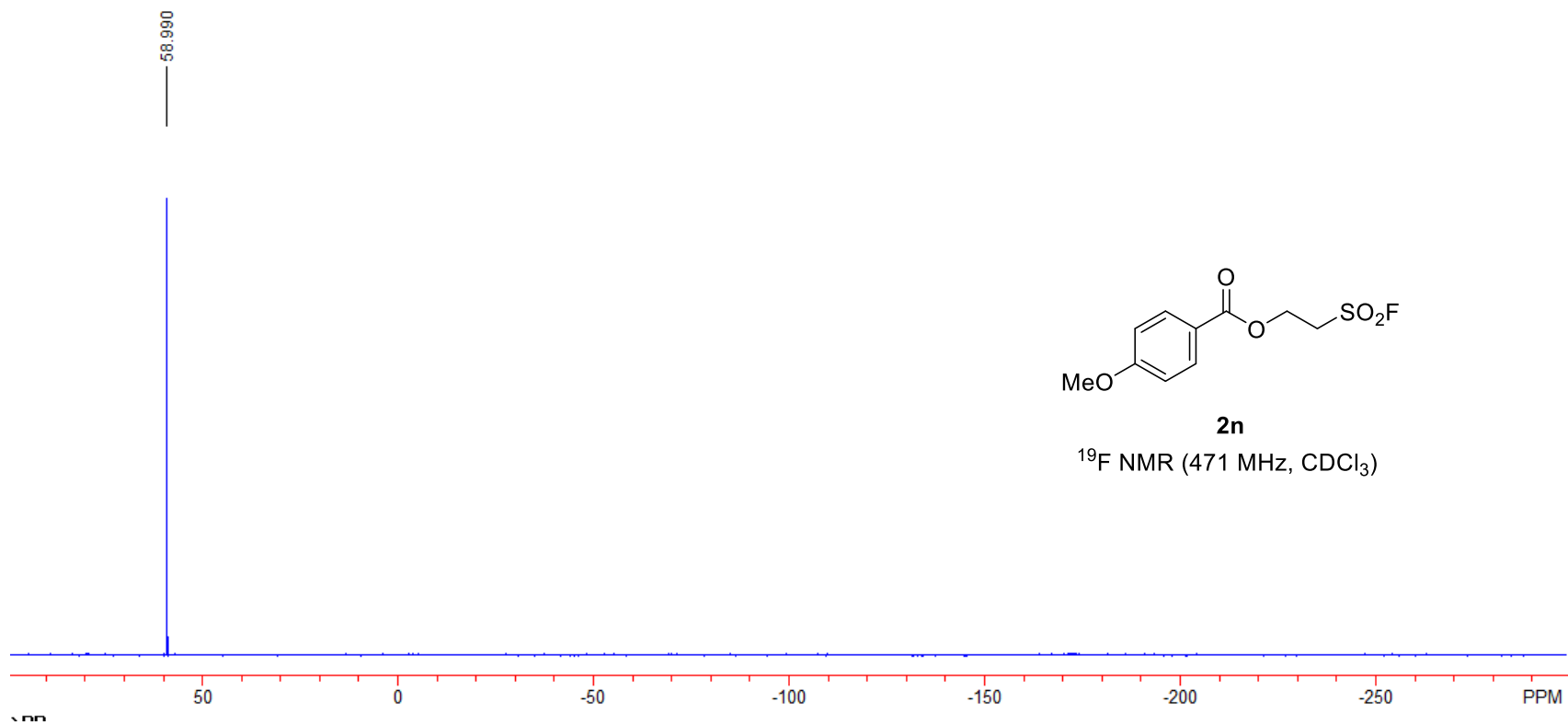


Figure S42. The ^{19}F NMR spectrum of **2n**

2o, ^1H NMR, 500 MHz, CDCl_3

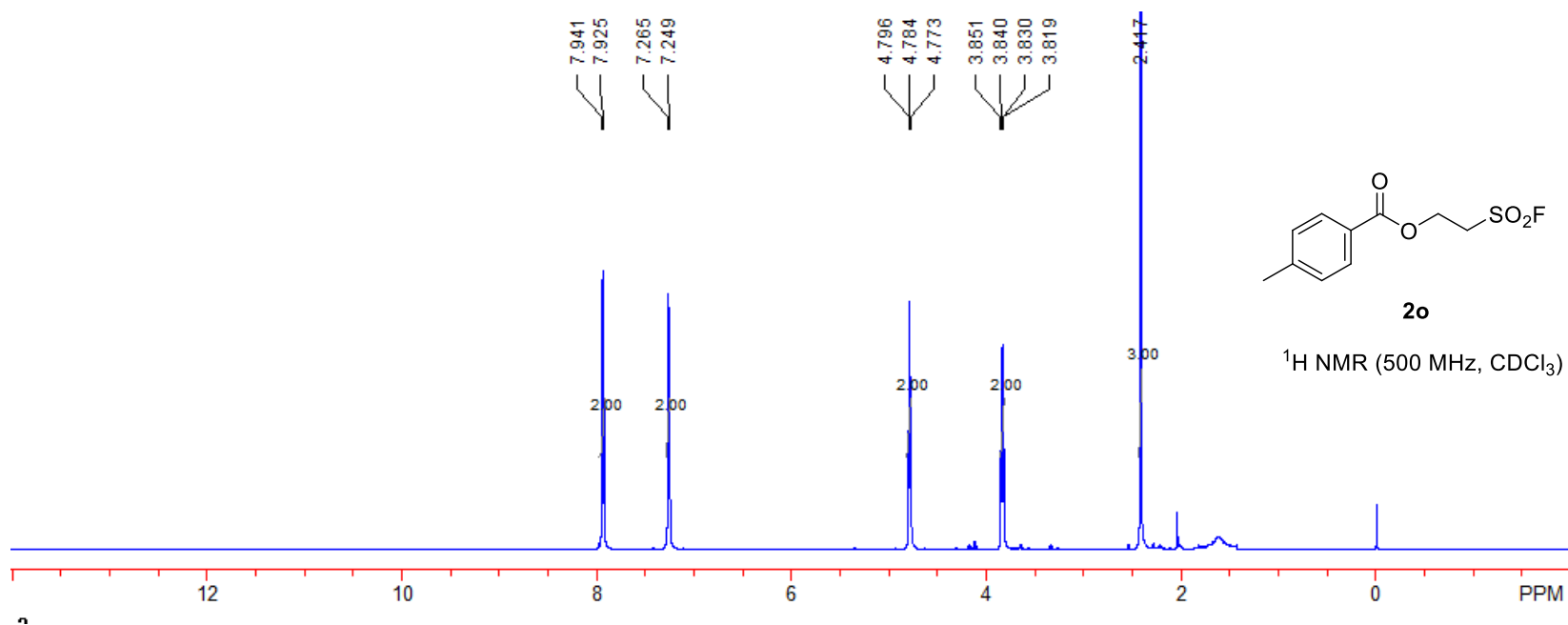


Figure S43. The ^1H NMR spectrum of **2o**

2o, ^{13}C NMR, 126 MHz, CDCl_3

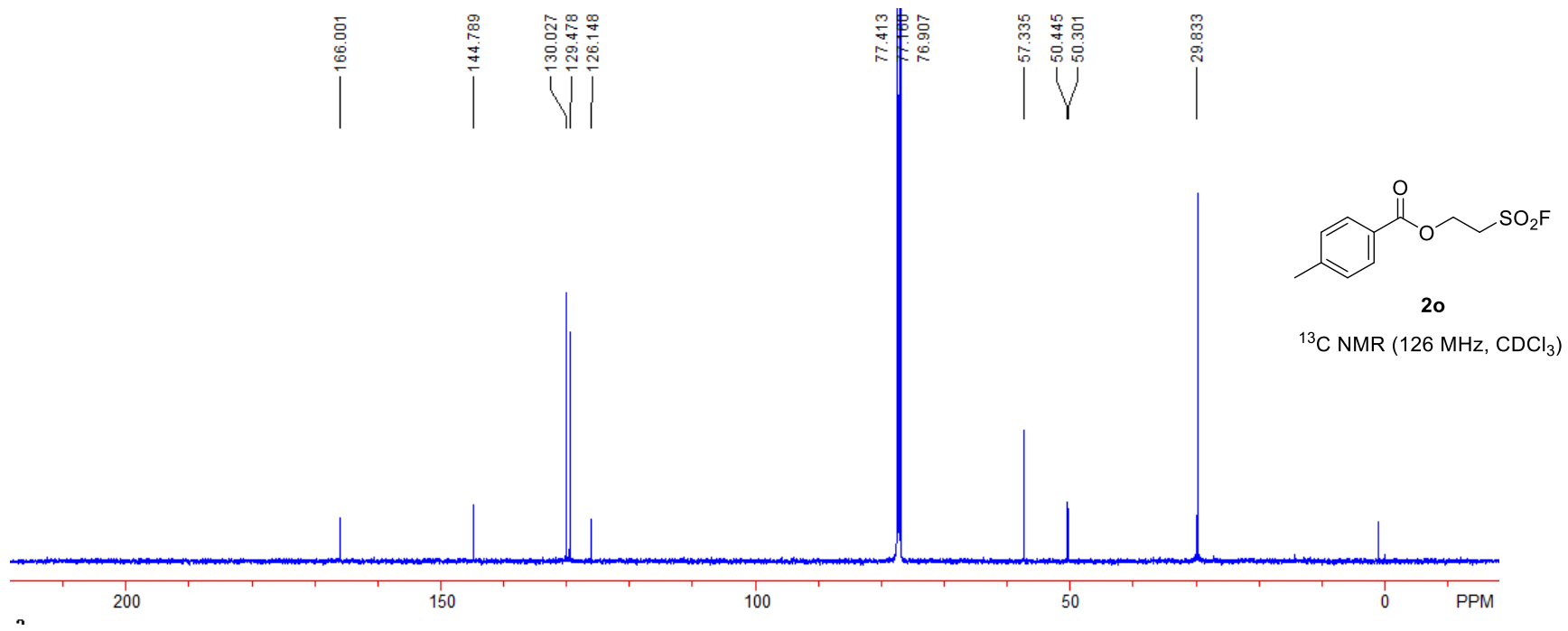


Figure S44. The ^{13}C NMR spectrum of **2o**

2o, ^{19}F NMR, 471 MHz, CDCl_3

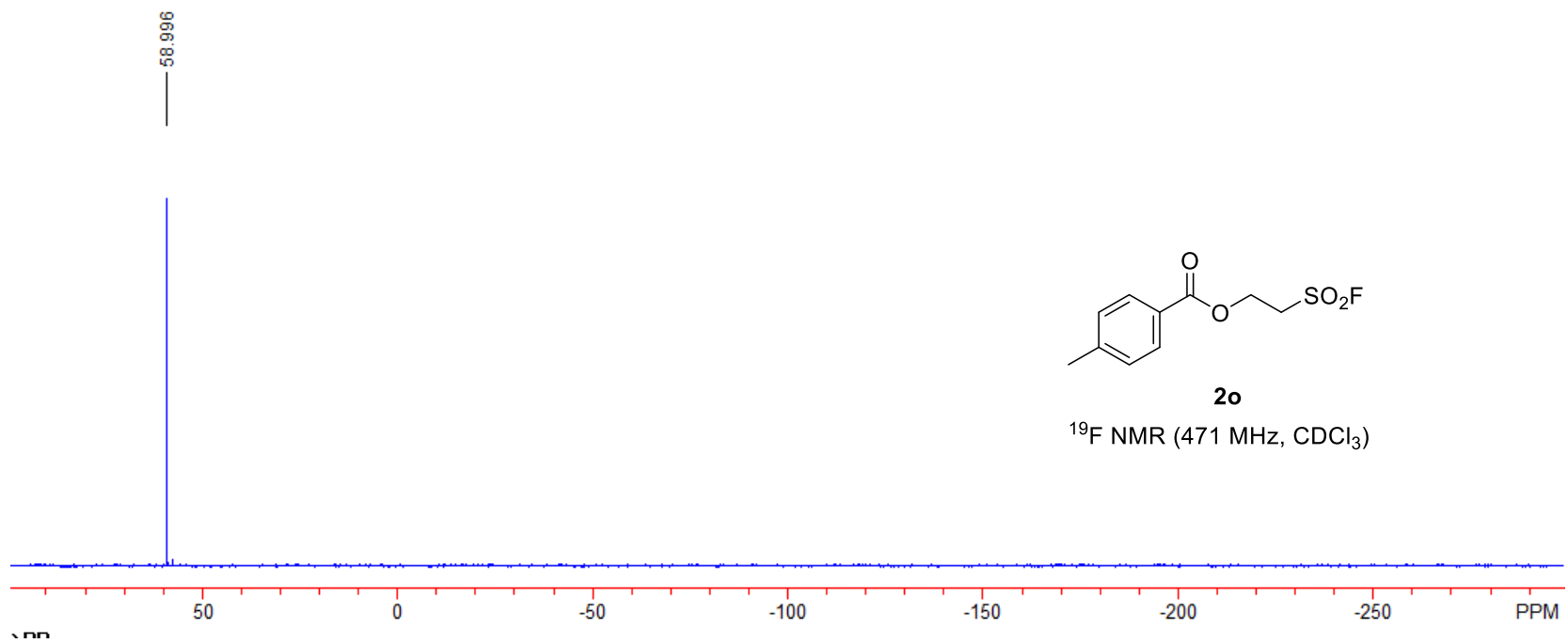


Figure S45. The ^{19}F NMR spectrum of **2o**

2p, ^1H NMR, 500 MHz, CDCl_3

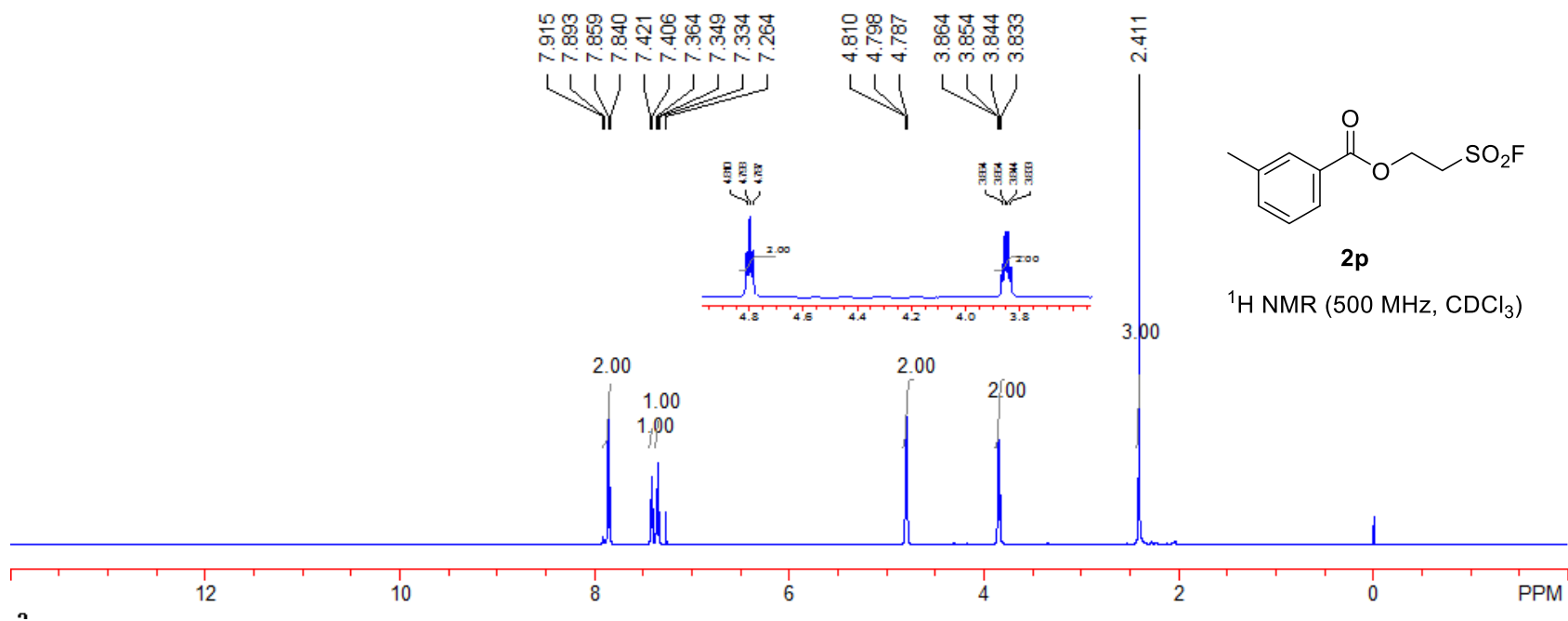


Figure S46. The ^1H NMR spectrum of **2p**

2p, ^{13}C NMR, 126 MHz, CDCl_3

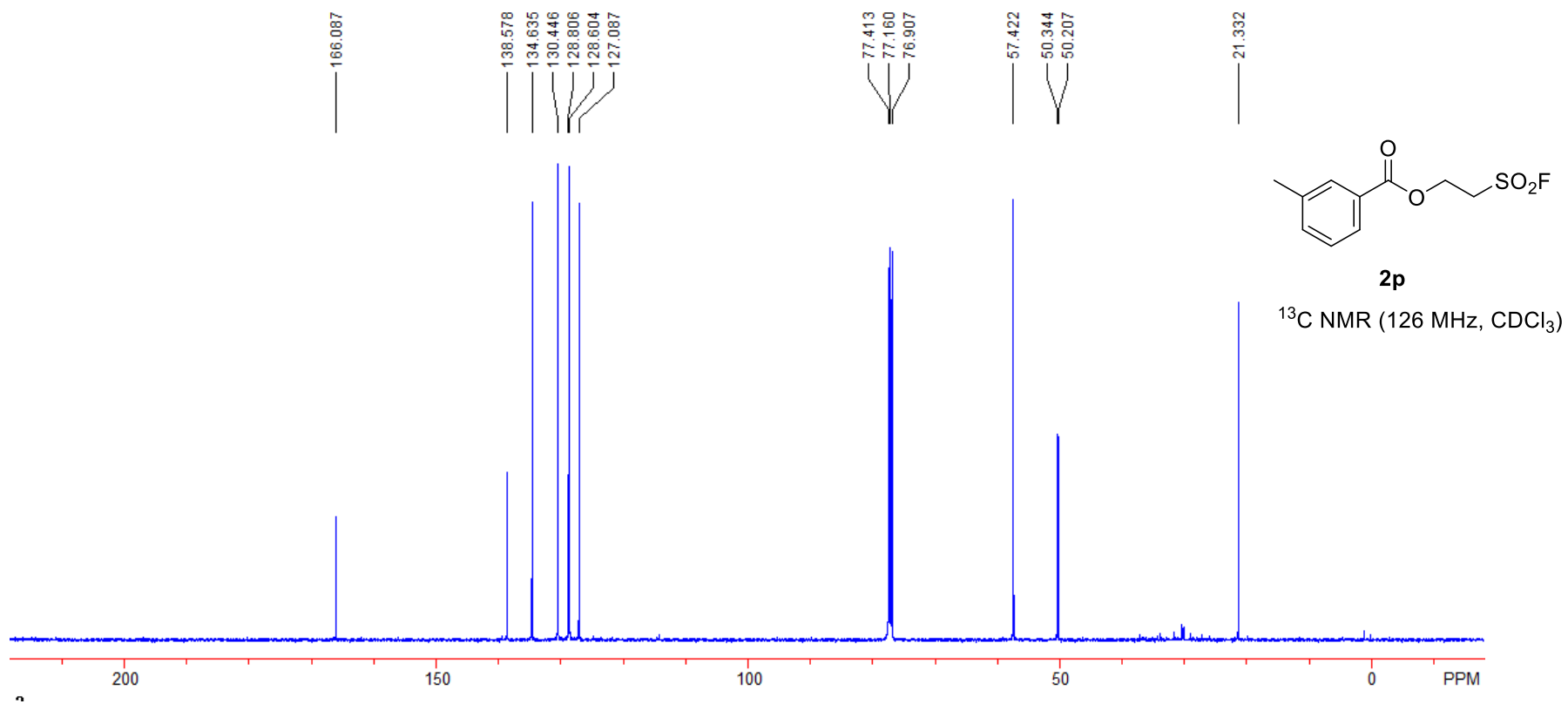


Figure S47. The ^{13}C NMR spectrum of **2p**

2p, ^{19}F NMR, 471 MHz, CDCl_3

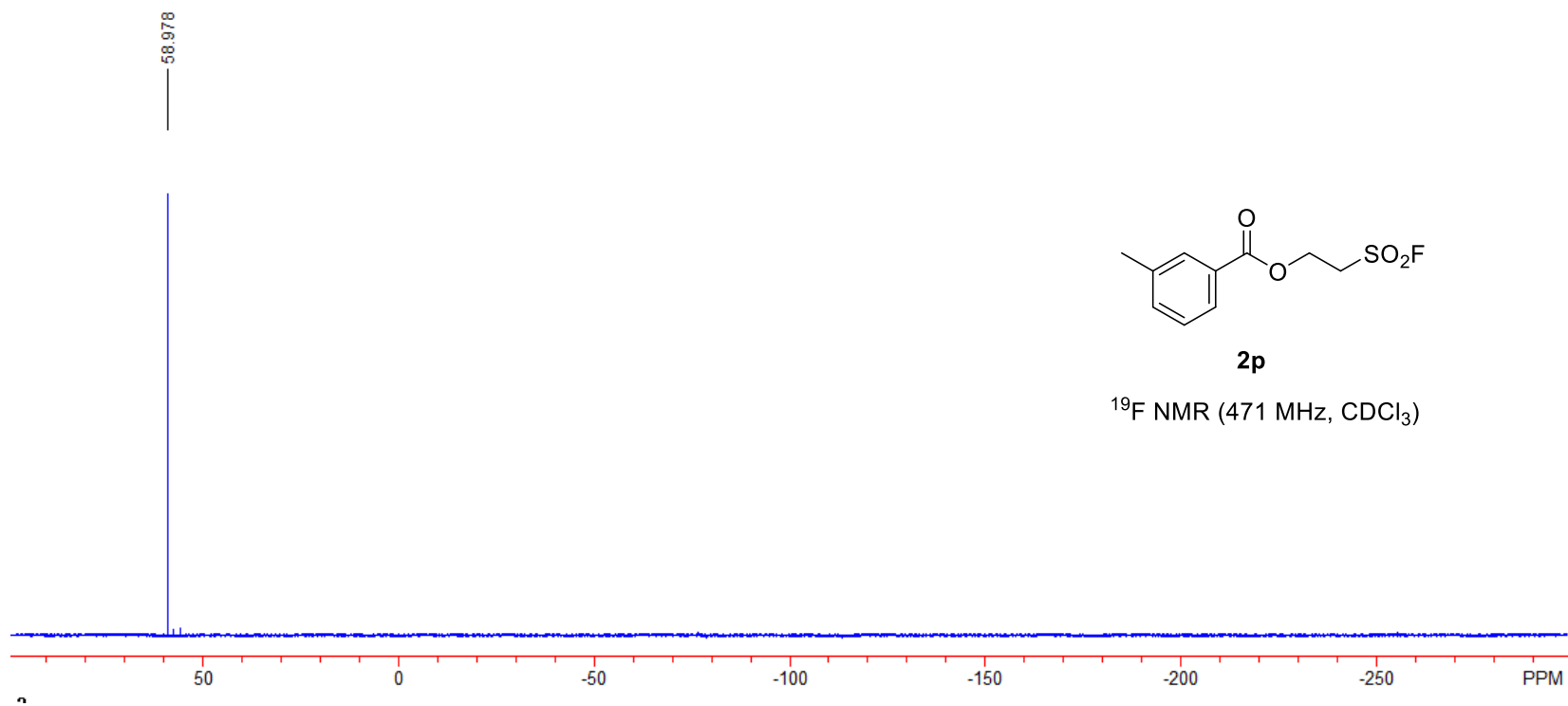


Figure S48. The ^{19}F NMR spectrum of **2p**

2q, ^1H NMR, 500 MHz, CDCl_3

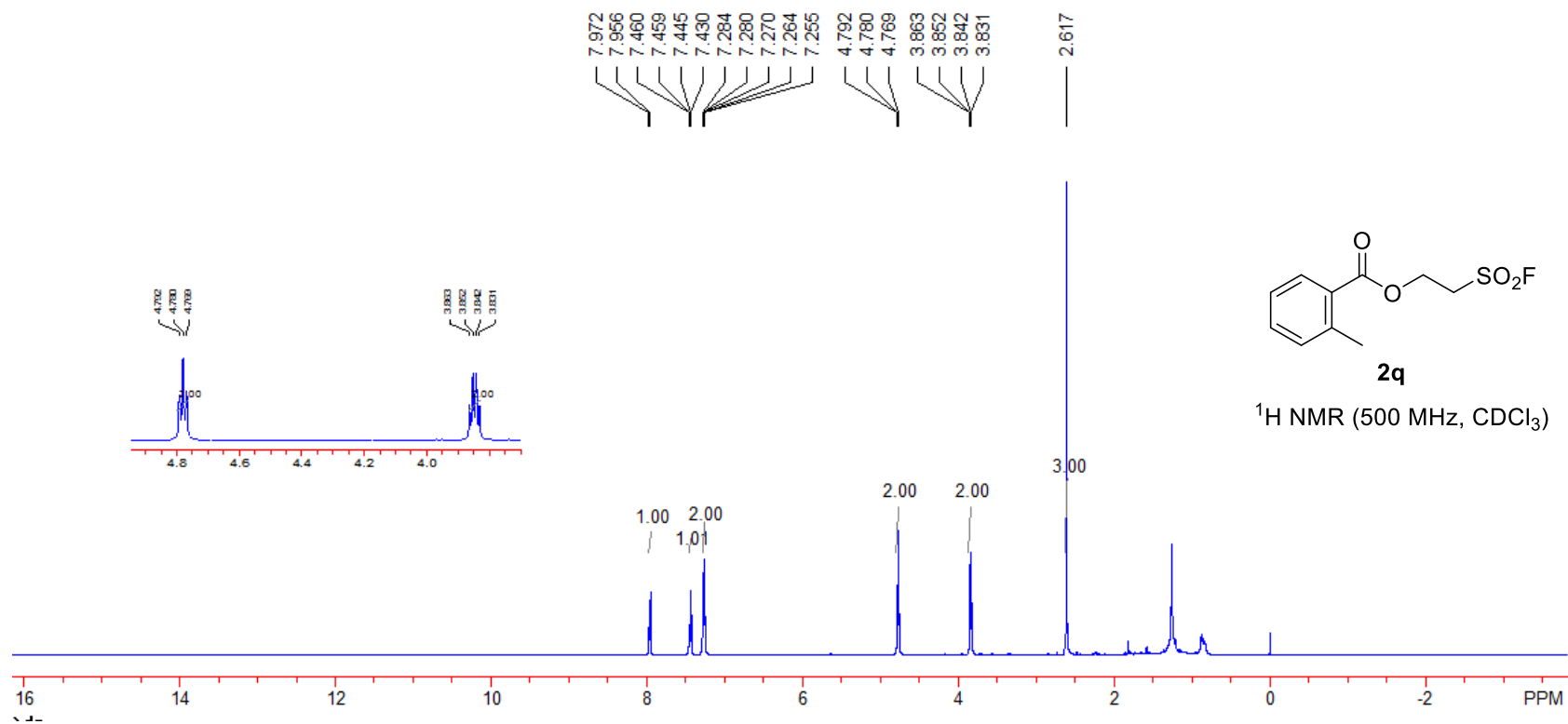


Figure S49. The ^1H NMR spectrum of **2q**

2q, ^{13}C NMR, 126 MHz, CDCl_3

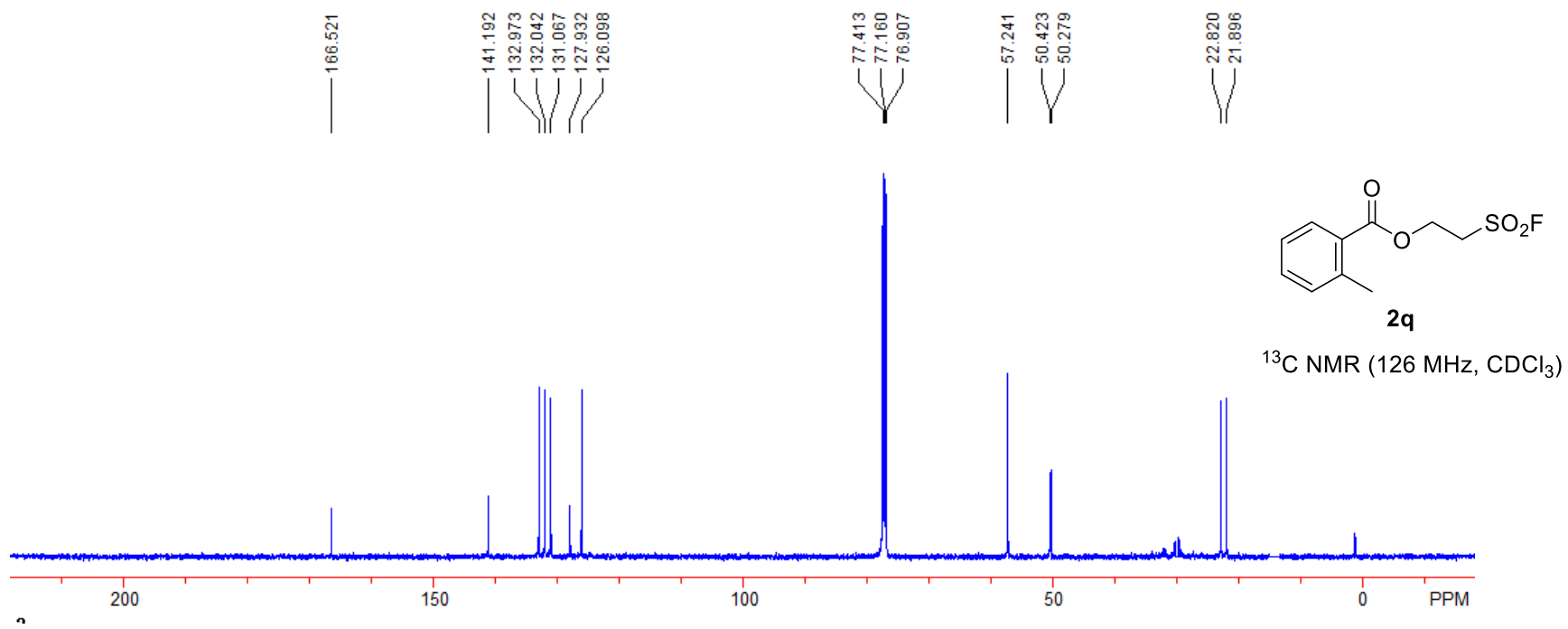


Figure S50. The ^{13}C NMR spectrum of **2q**

2q, ^{19}F NMR, 471 MHz, CDCl_3

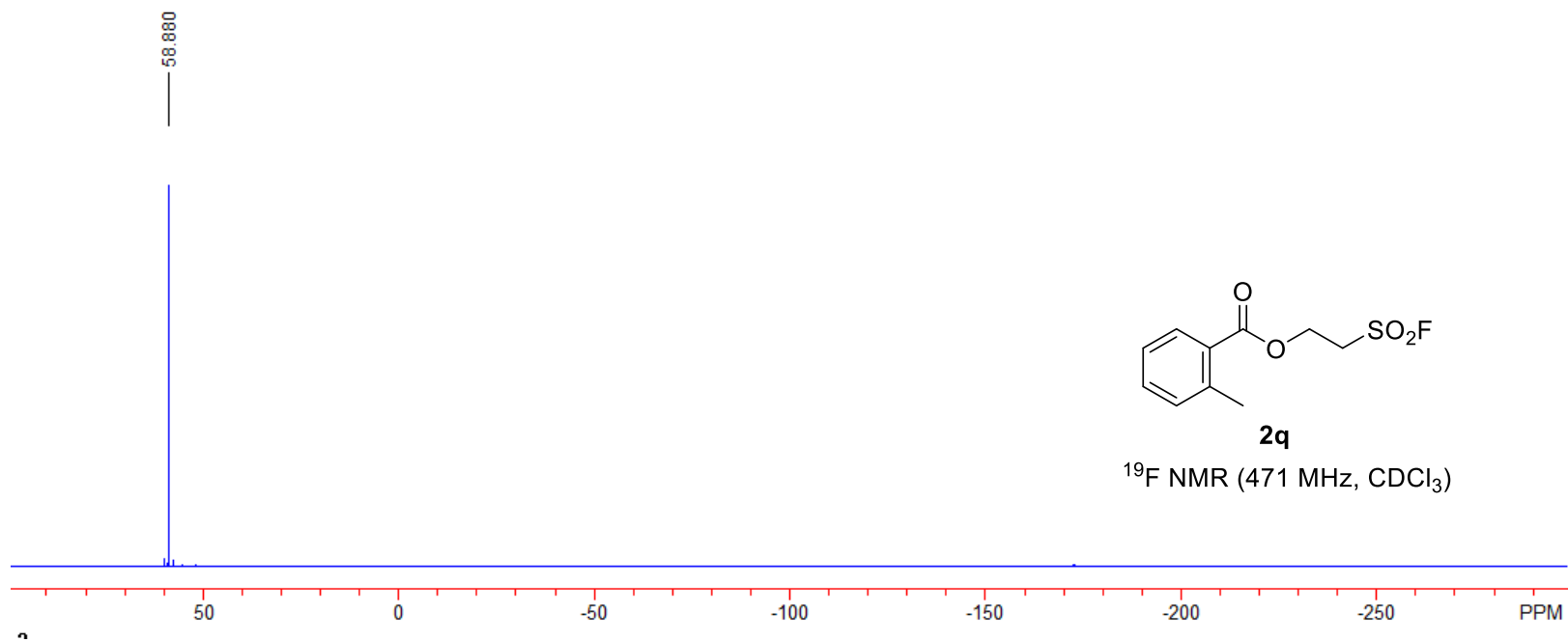


Figure S51. The ^{19}F NMR spectrum of **2q**

2r, ^1H NMR, 500 MHz, CDCl_3

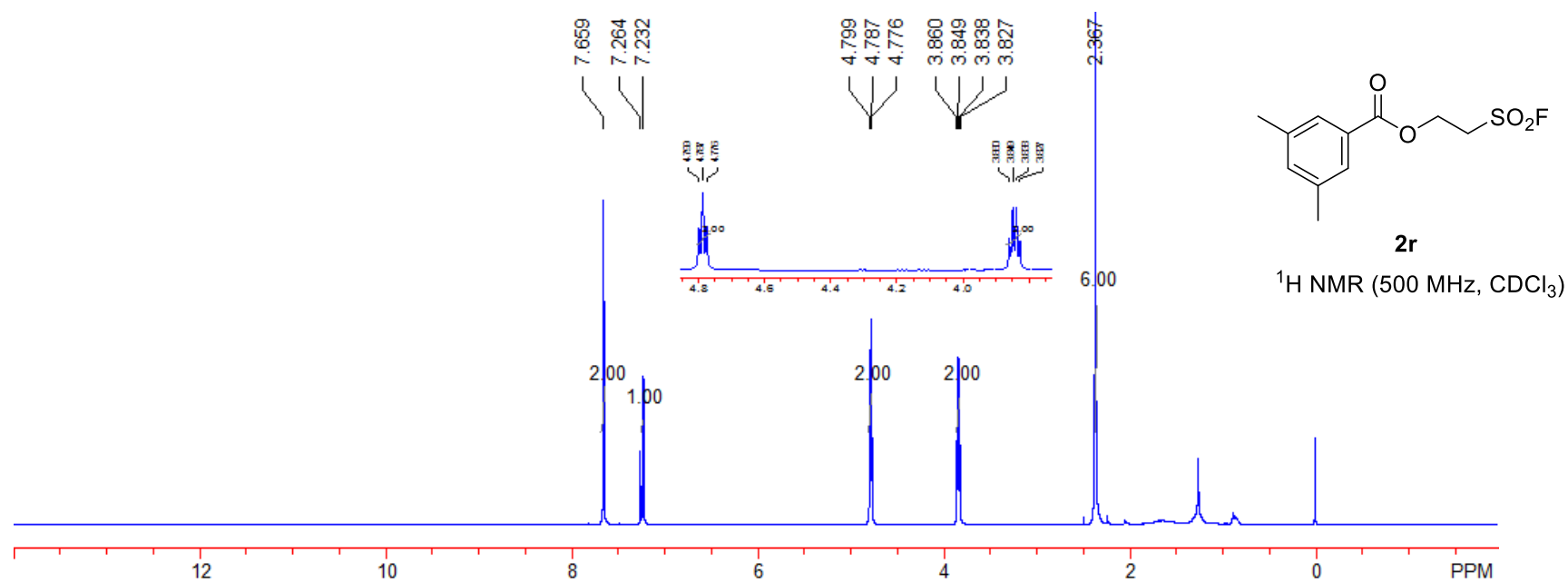


Figure S52. The ^1H NMR spectrum of **2r**

2r, ^{13}C NMR, 126 MHz, CDCl_3

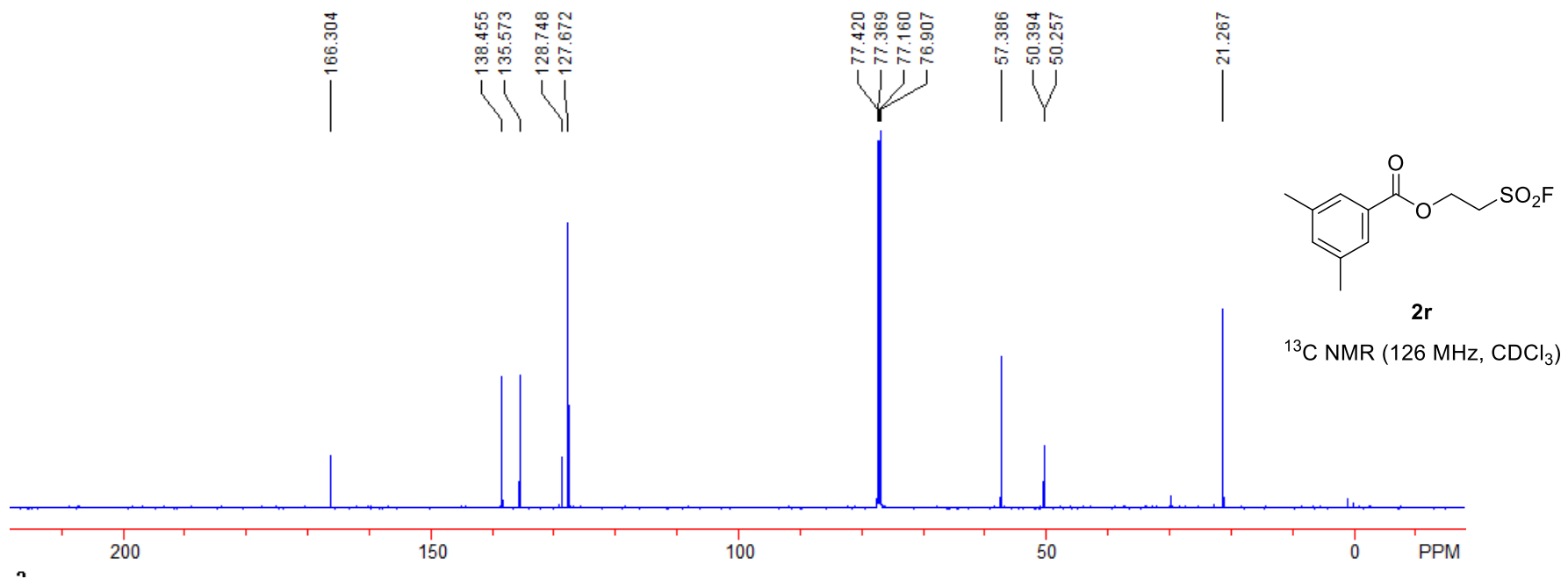


Figure S53. The ^{13}C NMR spectrum of **2r**

2r, ^{19}F NMR, 471 MHz, CDCl_3

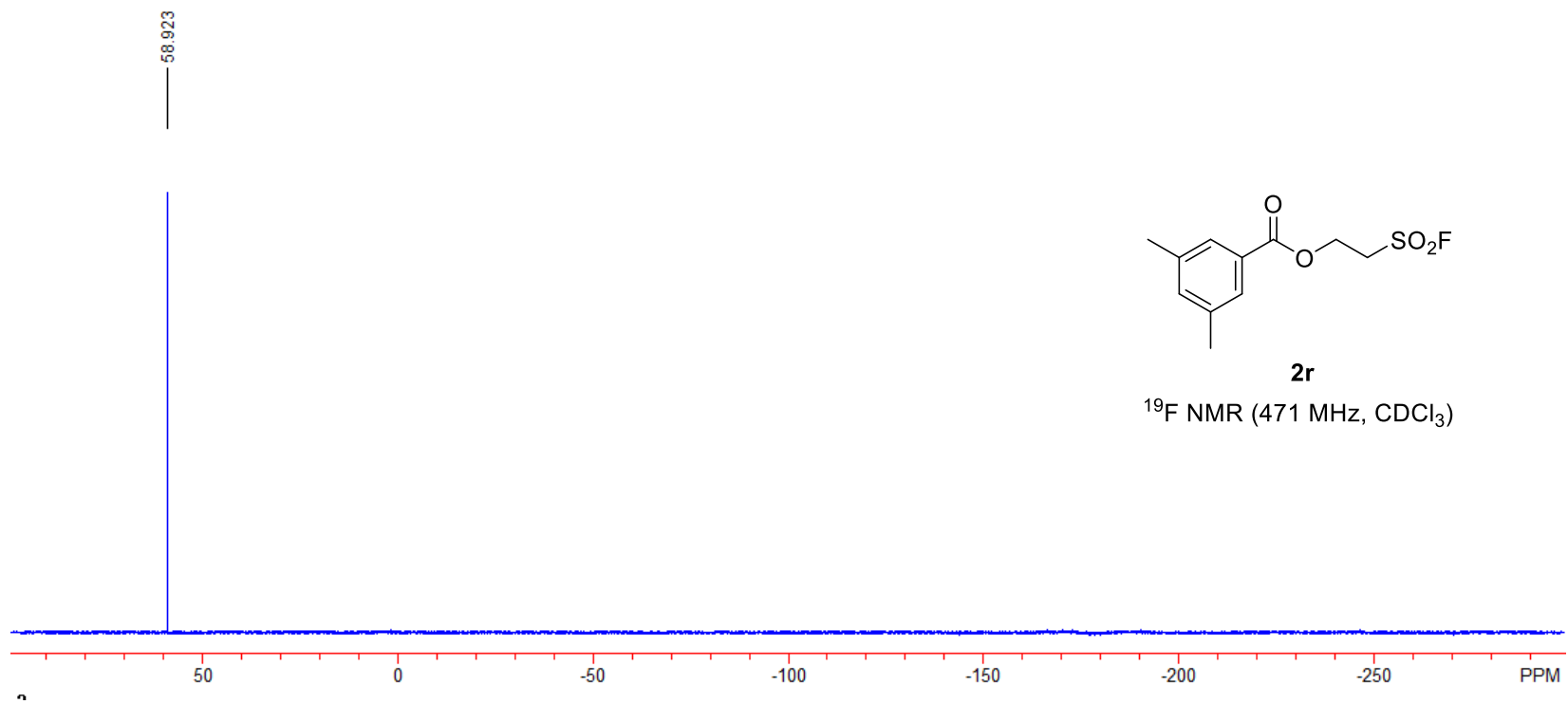


Figure S54. The ^{19}F NMR spectrum of **2r**

2s, ^1H NMR, 500 MHz, CDCl_3

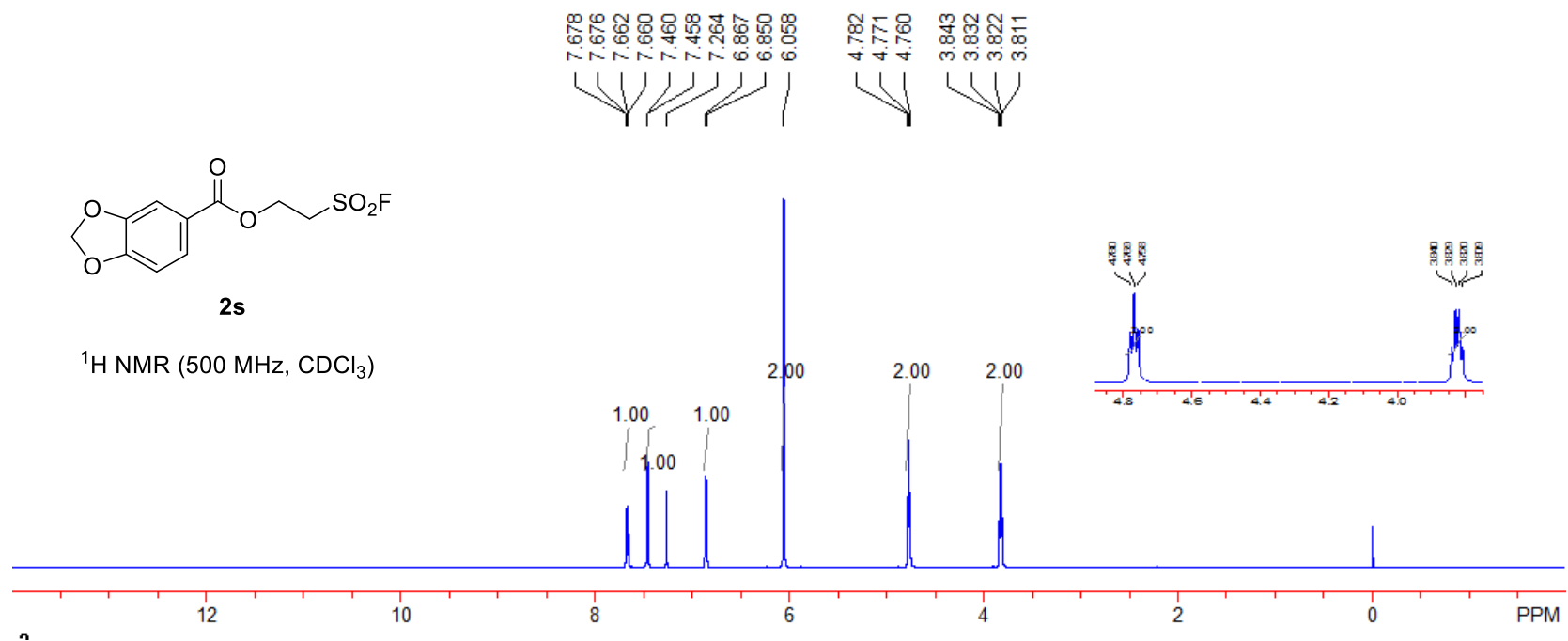


Figure S55. The ^1H NMR spectrum of **2s**

2s, ^{13}C NMR, 126 MHz, CDCl_3

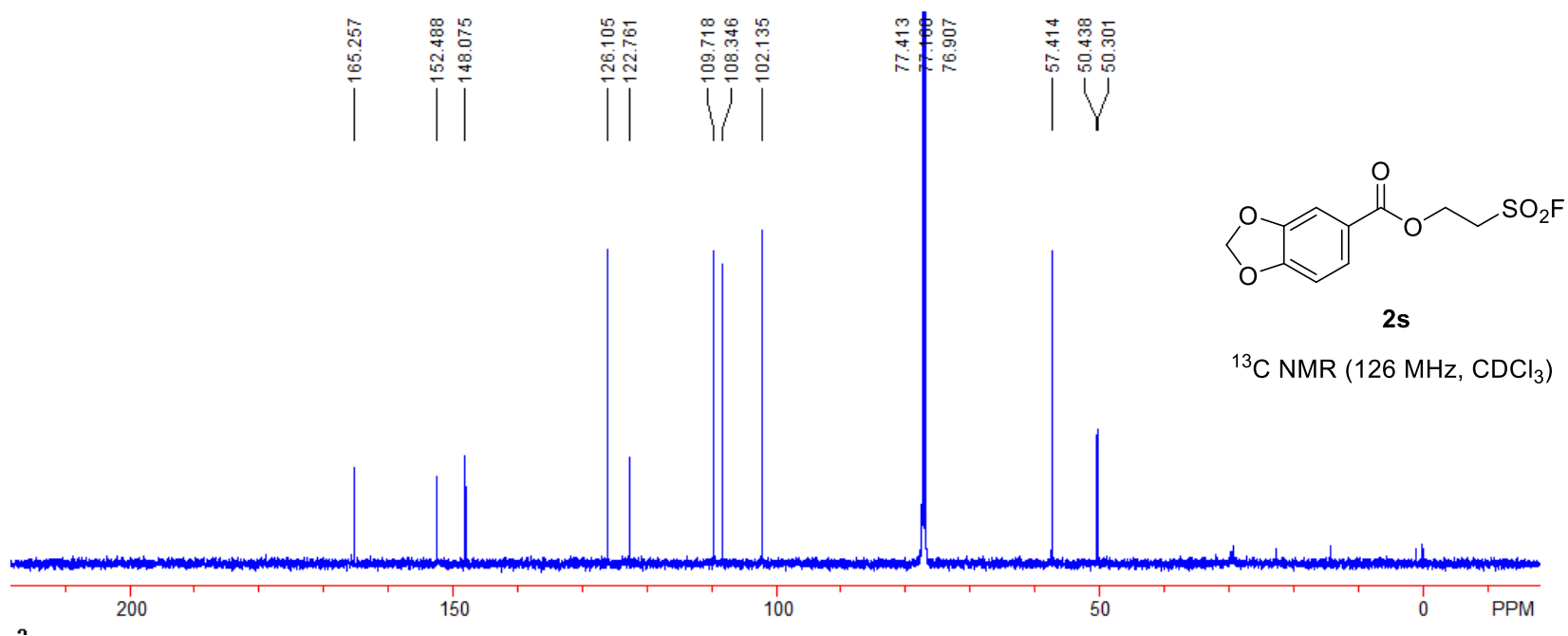


Figure S56. The ^{13}C NMR spectrum of **2s**

2s, ^{19}F NMR, 471 MHz, CDCl_3

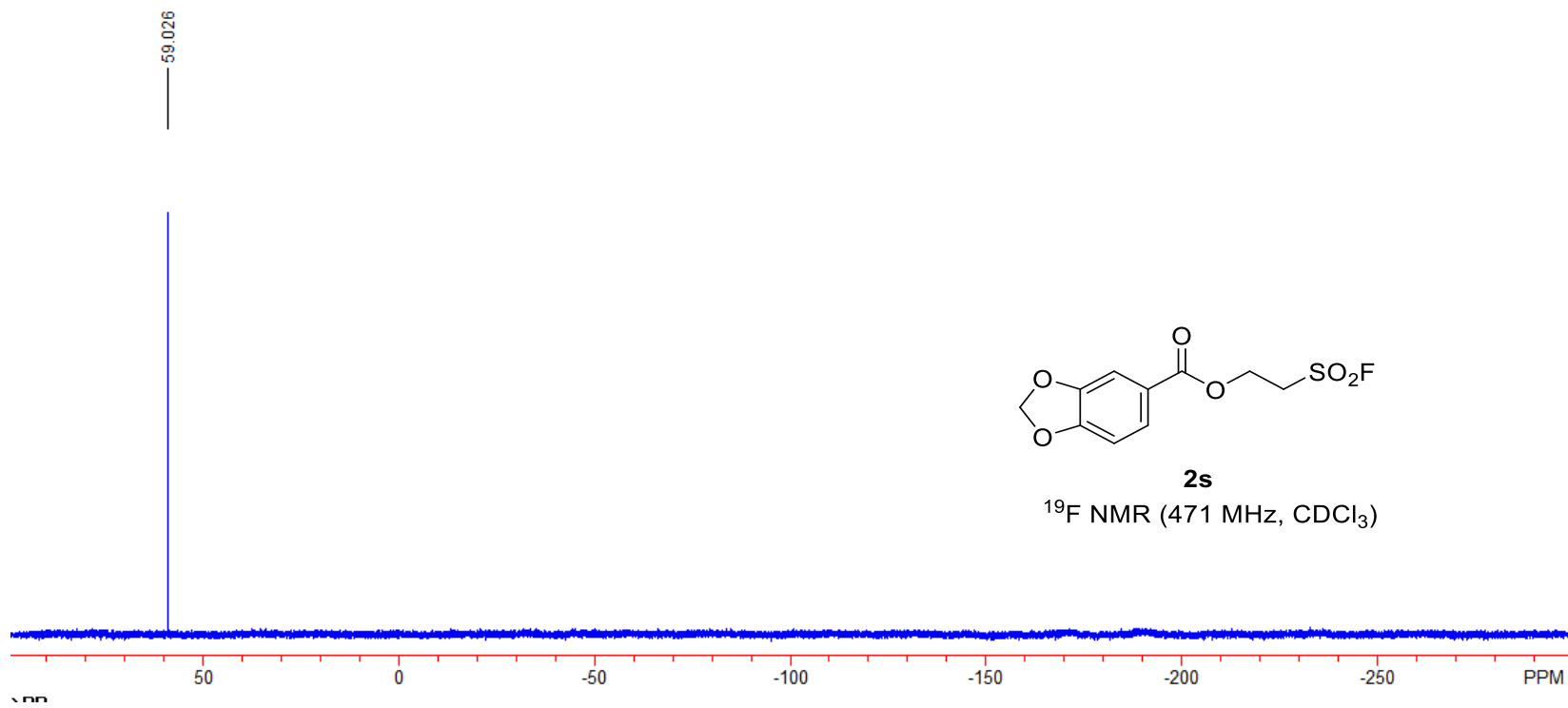


Figure S57. The ^{19}F NMR spectrum of **2s**

2t, ^1H NMR, 500 MHz, CDCl_3

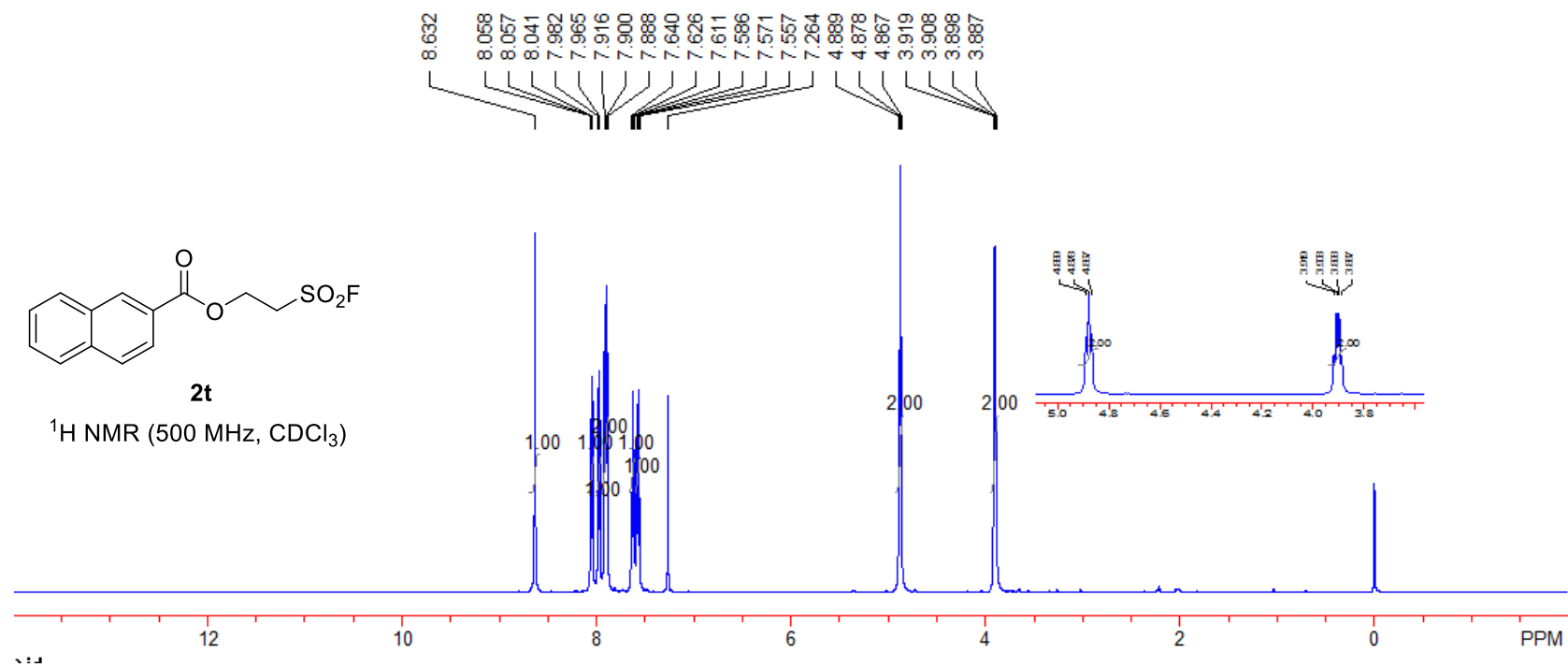


Figure S58. The ^1H NMR spectrum of **2t**

2t, ^{13}C NMR, 126 MHz, CDCl_3

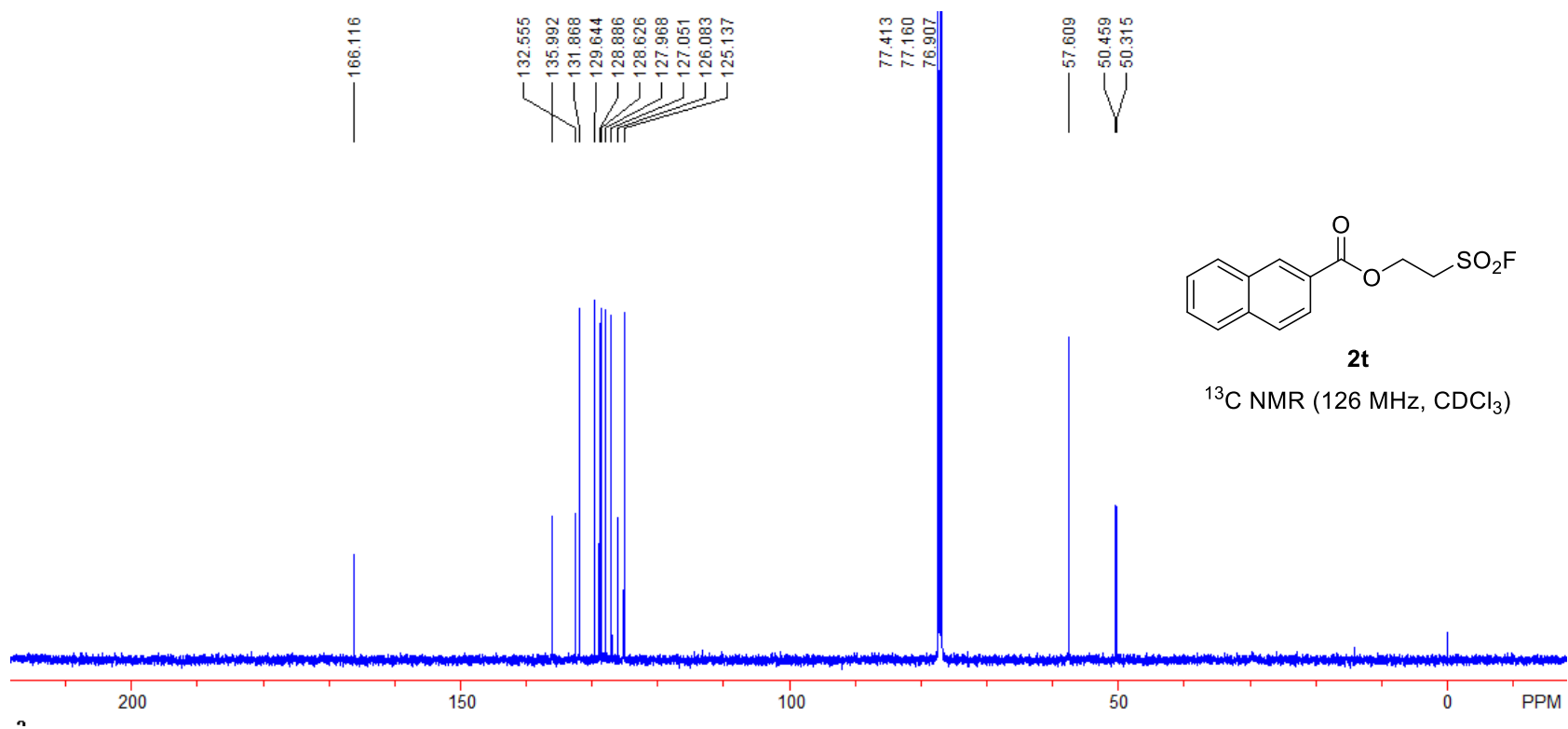


Figure S59. The ^{13}C NMR spectrum of **2t**

2t, ^{19}F NMR, 471 MHz, CDCl_3

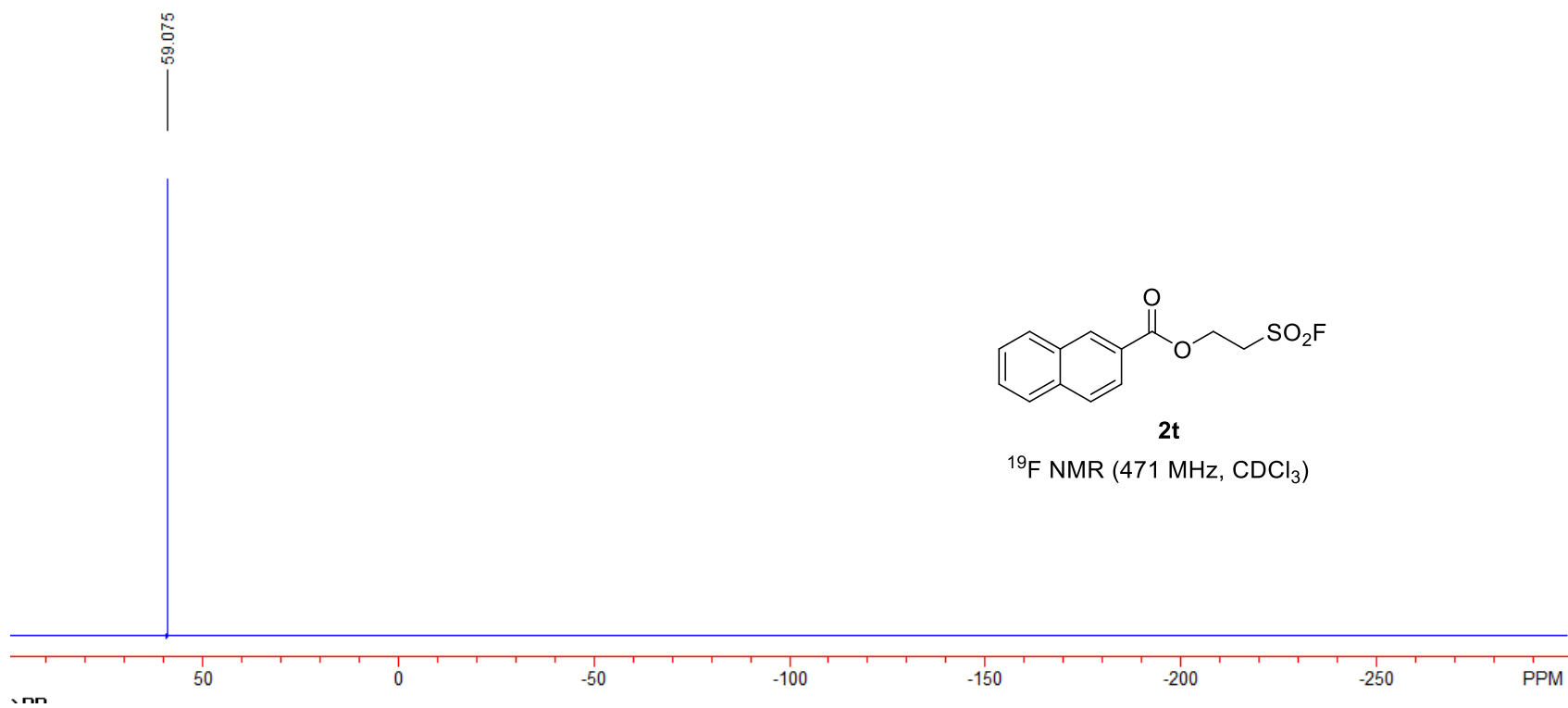


Figure S60. The ^{19}F NMR spectrum of **2t**

2u, ^1H NMR, 500 MHz, CDCl_3

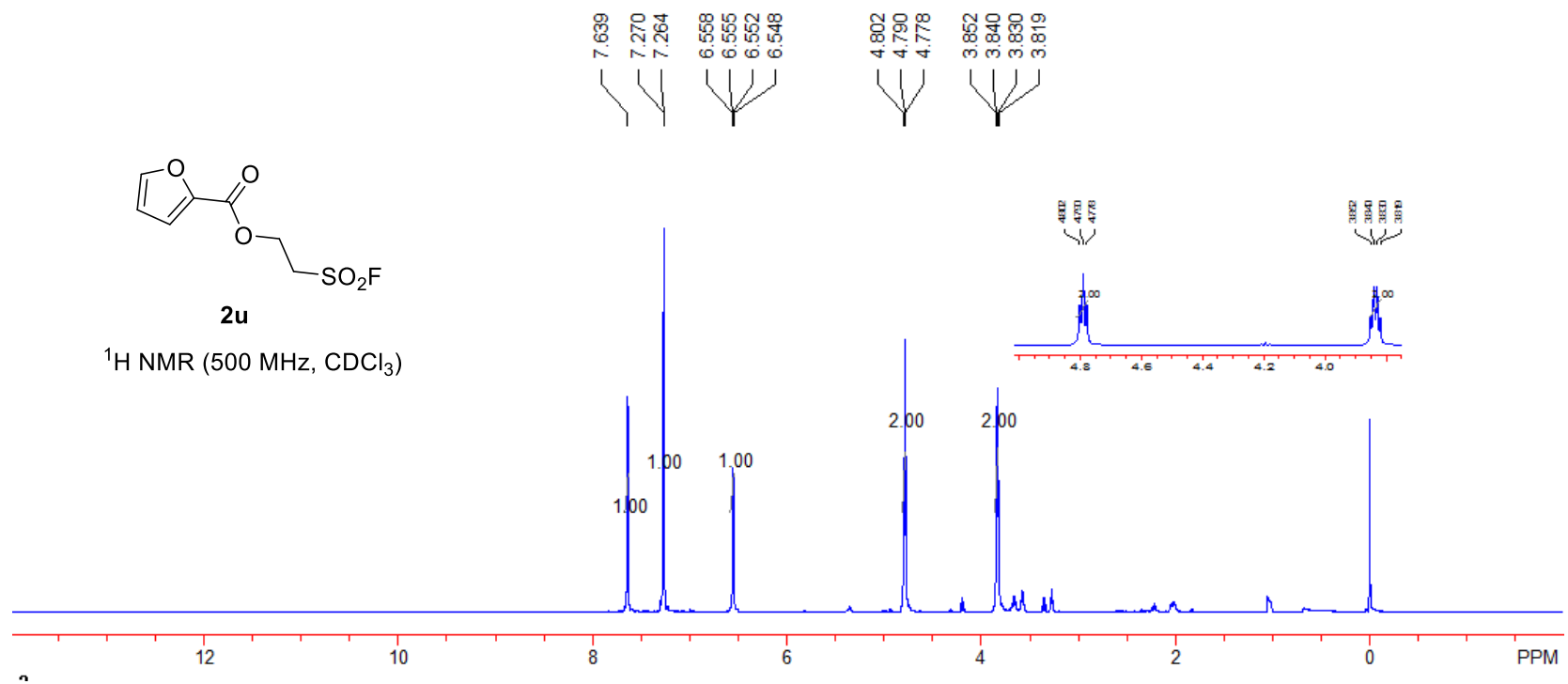


Figure S61. The ^1H NMR spectrum of **2u**

2u, ^{13}C NMR, 126 MHz, CDCl_3

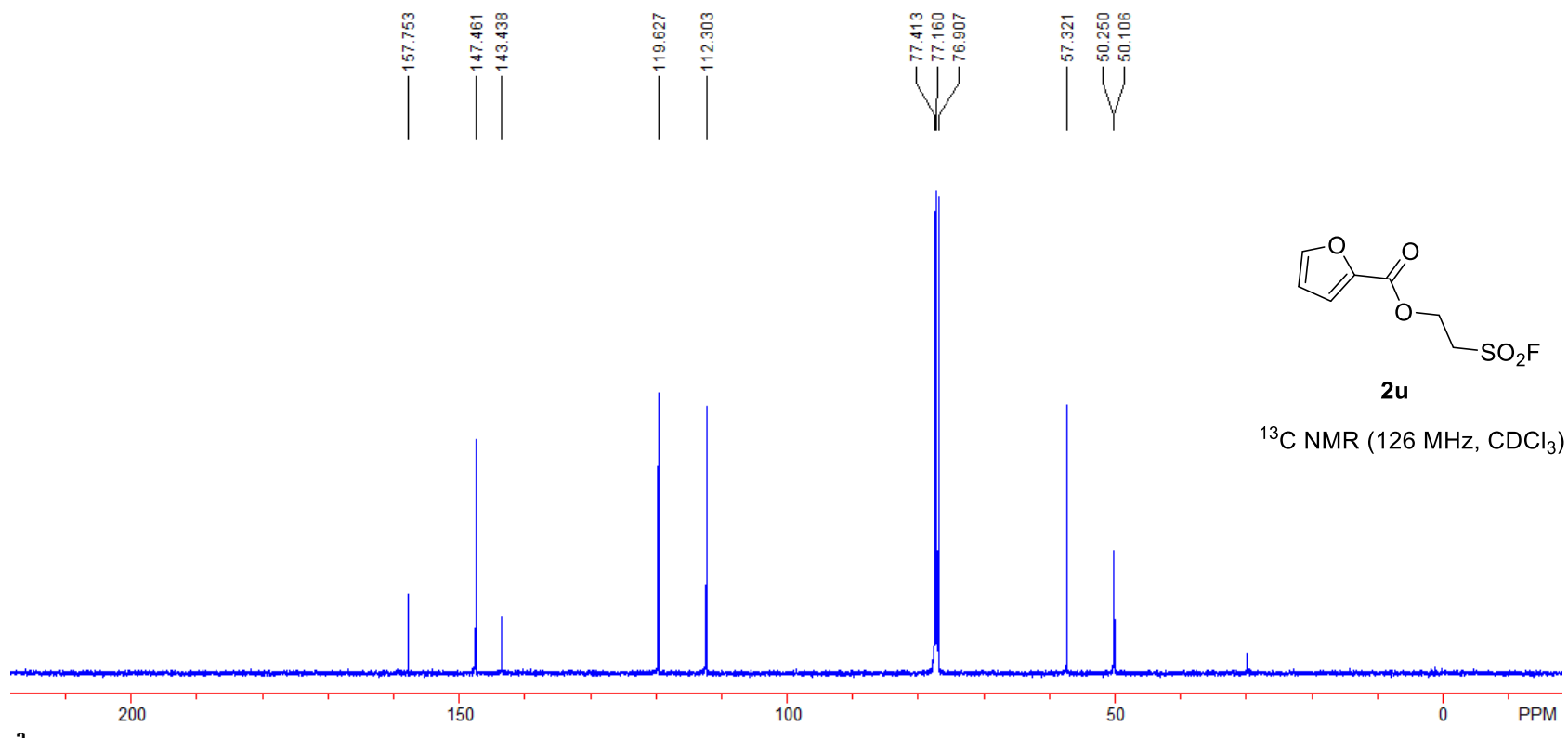


Figure S62. The ^{13}C NMR spectrum of **2u**

2u, ^{19}F NMR, 471 MHz, CDCl_3

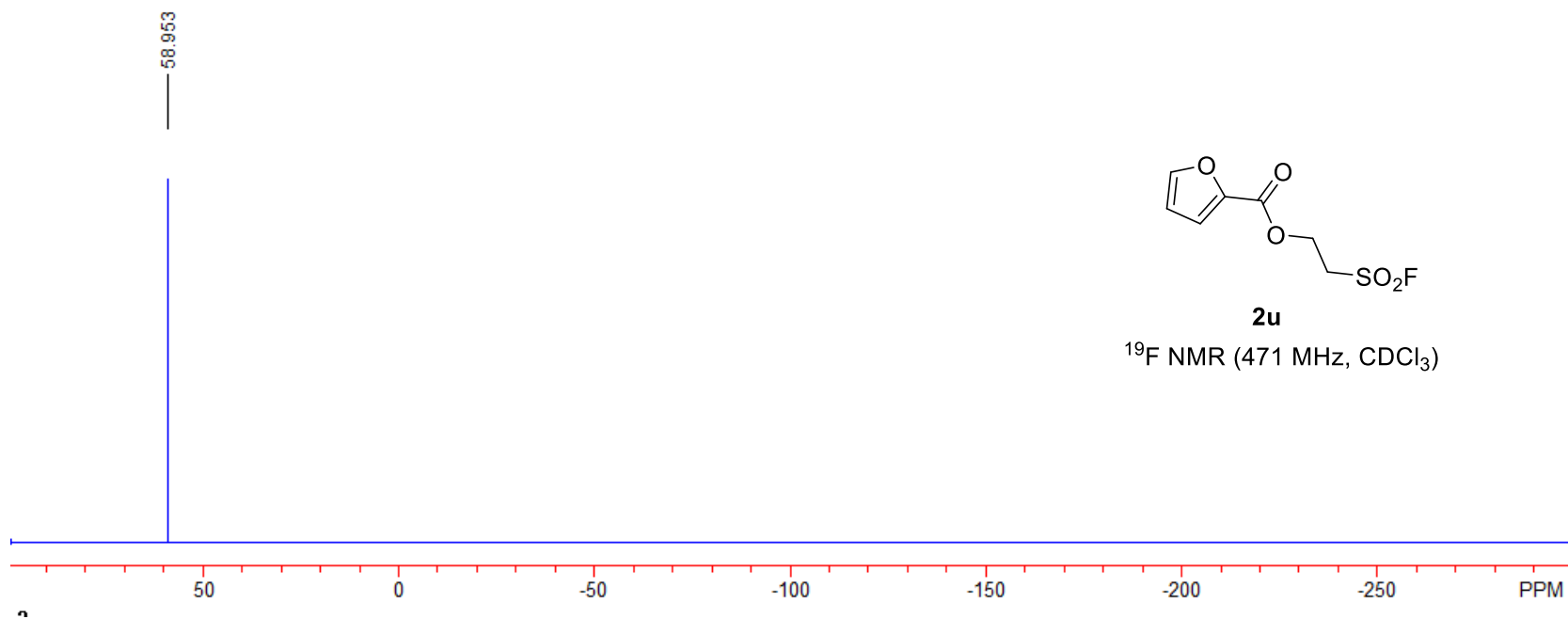


Figure S63. The ^{19}F NMR spectrum of **2u**

2v, ^1H NMR, 500 MHz, CDCl_3

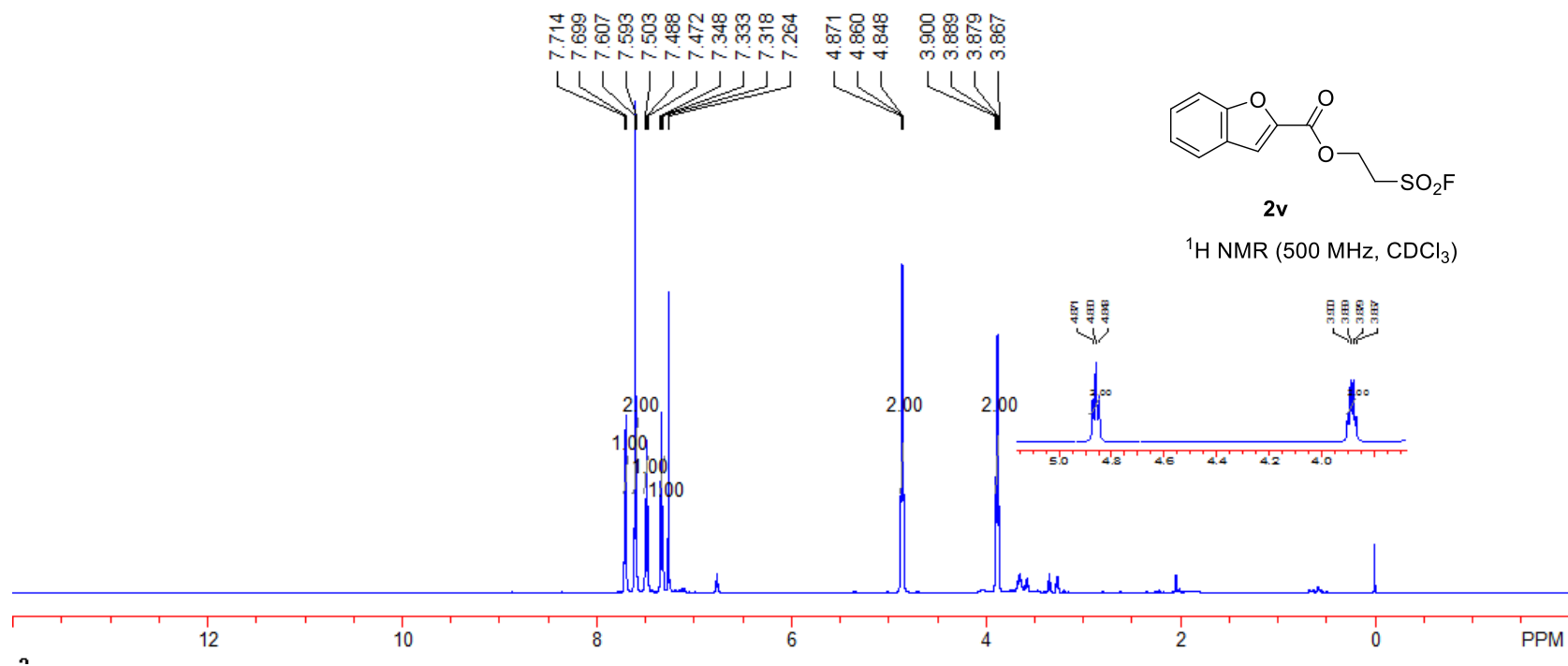


Figure S64. The ^1H NMR spectrum of **2v**

2v, ^{13}C NMR, 126 MHz, CDCl_3

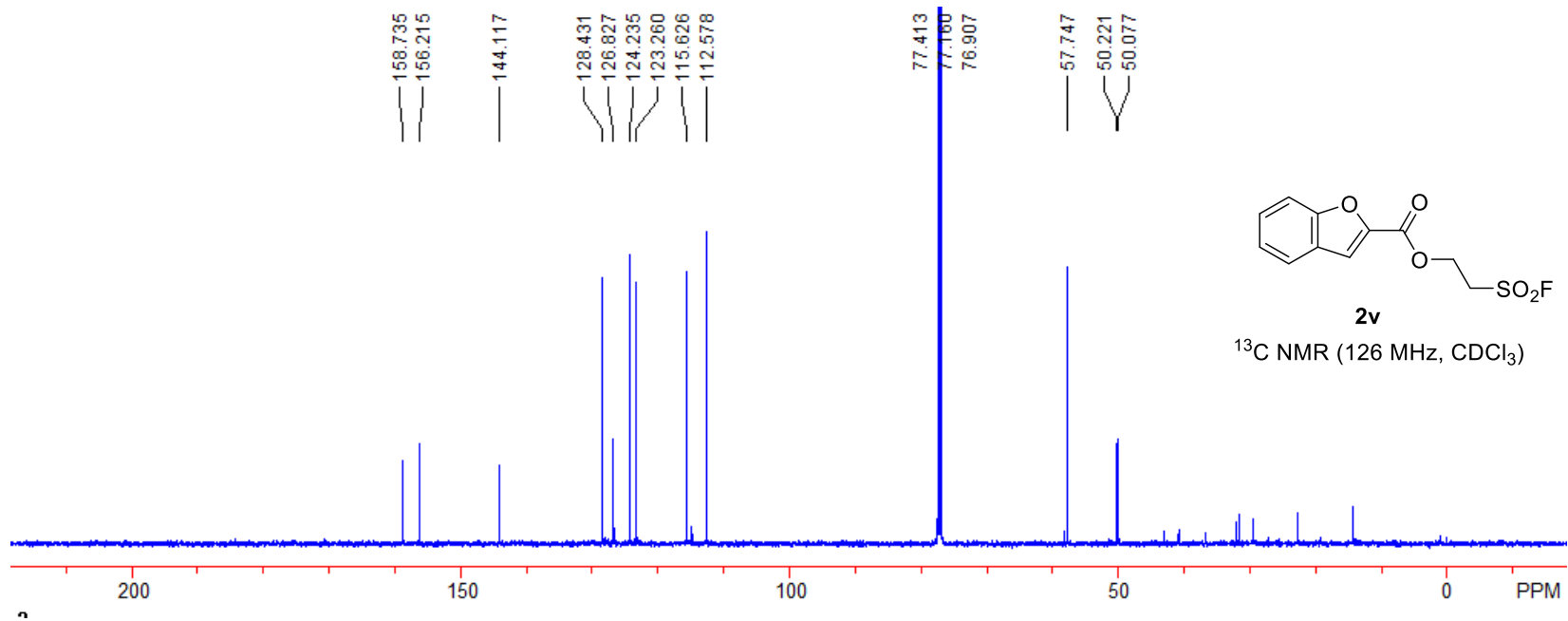


Figure S65. The ^{13}C NMR spectrum of **2v**

2v, ^{19}F NMR, 471 MHz, CDCl_3

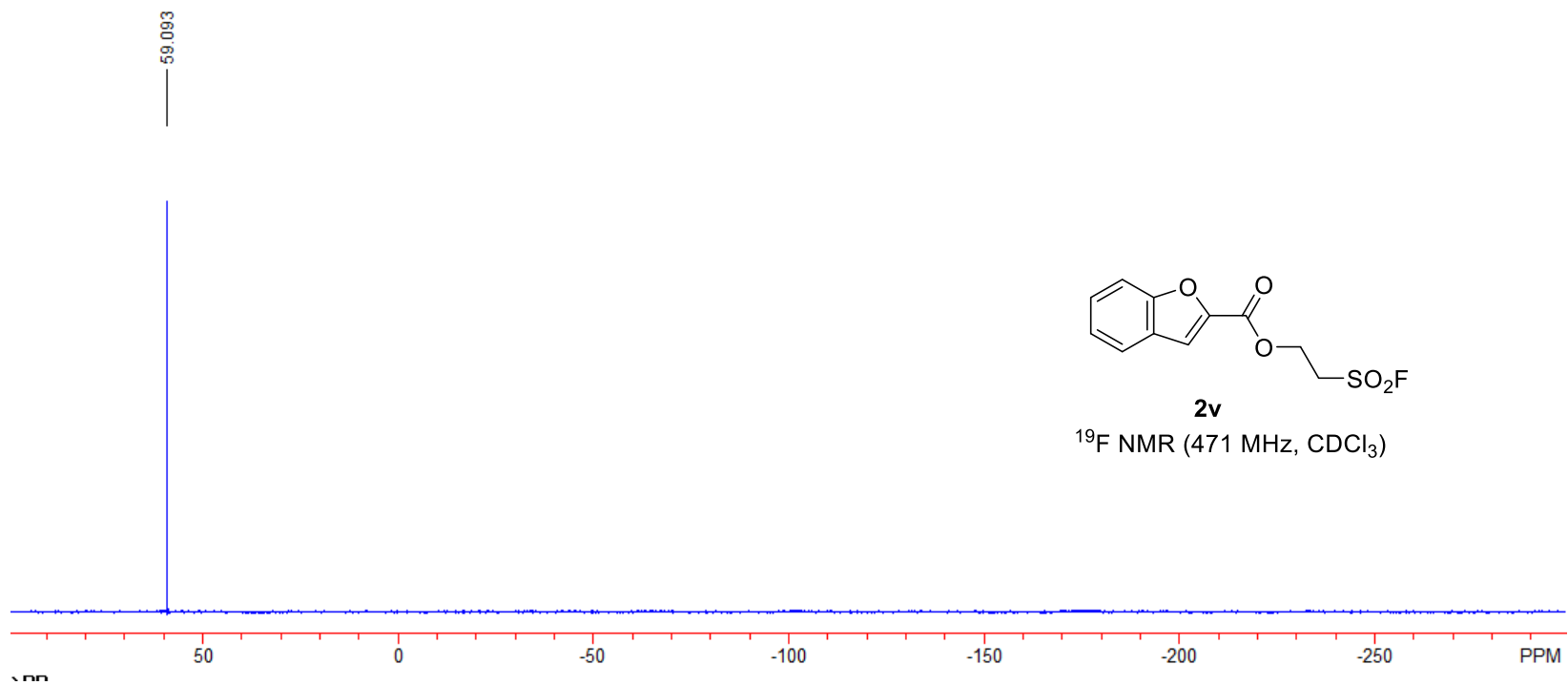


Figure S66. The ^{19}F NMR spectrum of **2v**

2w, ^1H NMR, 500 MHz, CDCl_3

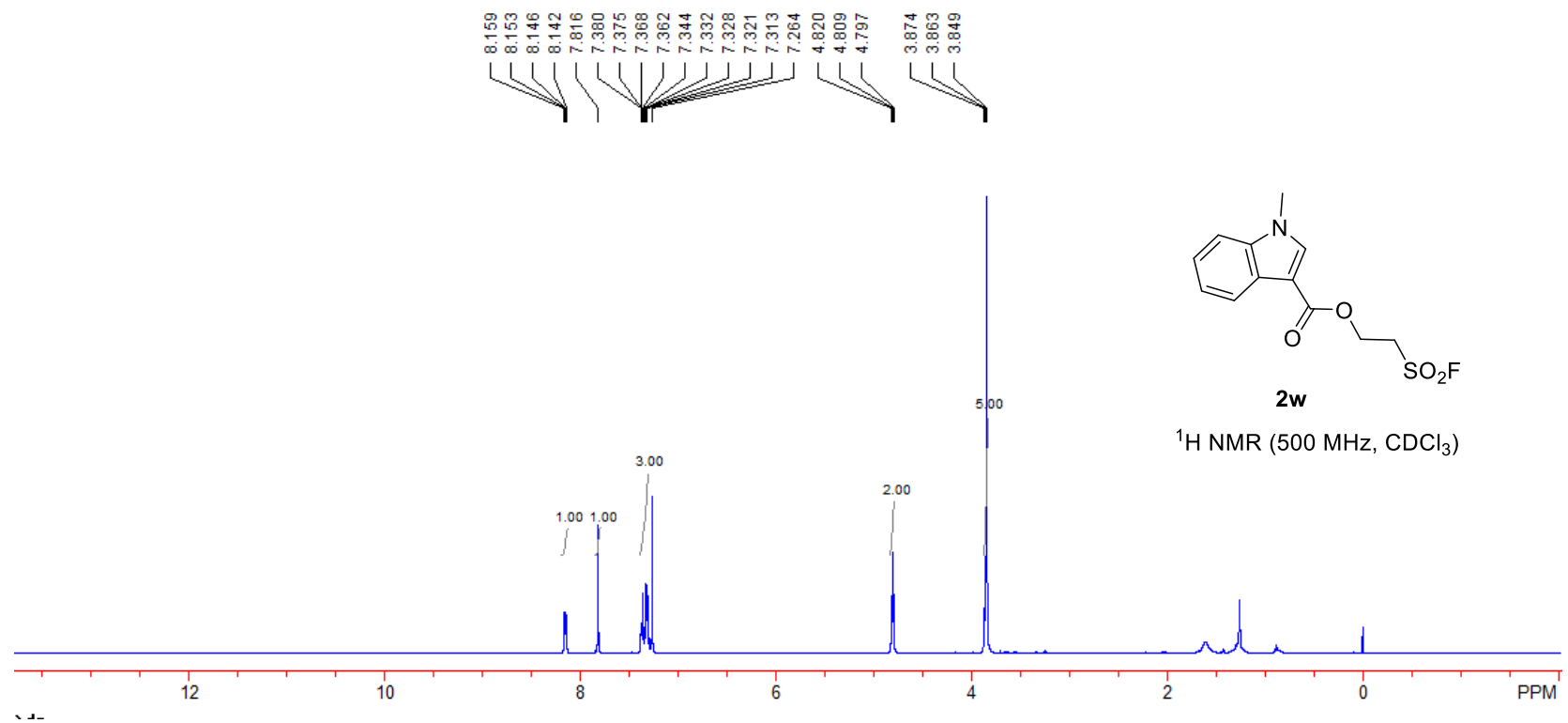


Figure S67. The ^1H NMR spectrum of **2w**

2w, ^{13}C NMR, 126 MHz, CDCl_3

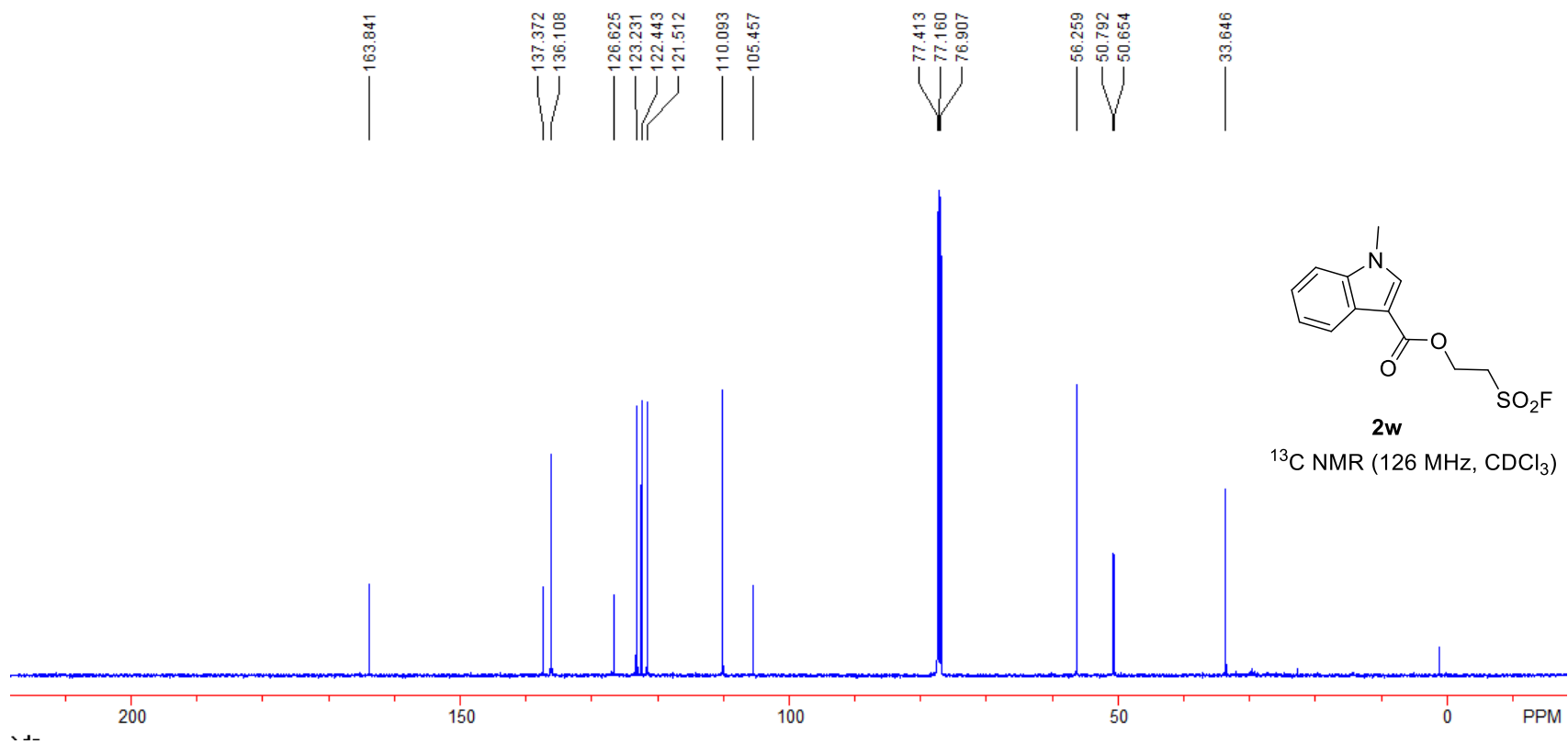


Figure S68. The ^{13}C NMR spectrum of **2w**

2w, ^{19}F NMR, 471 MHz, CDCl_3

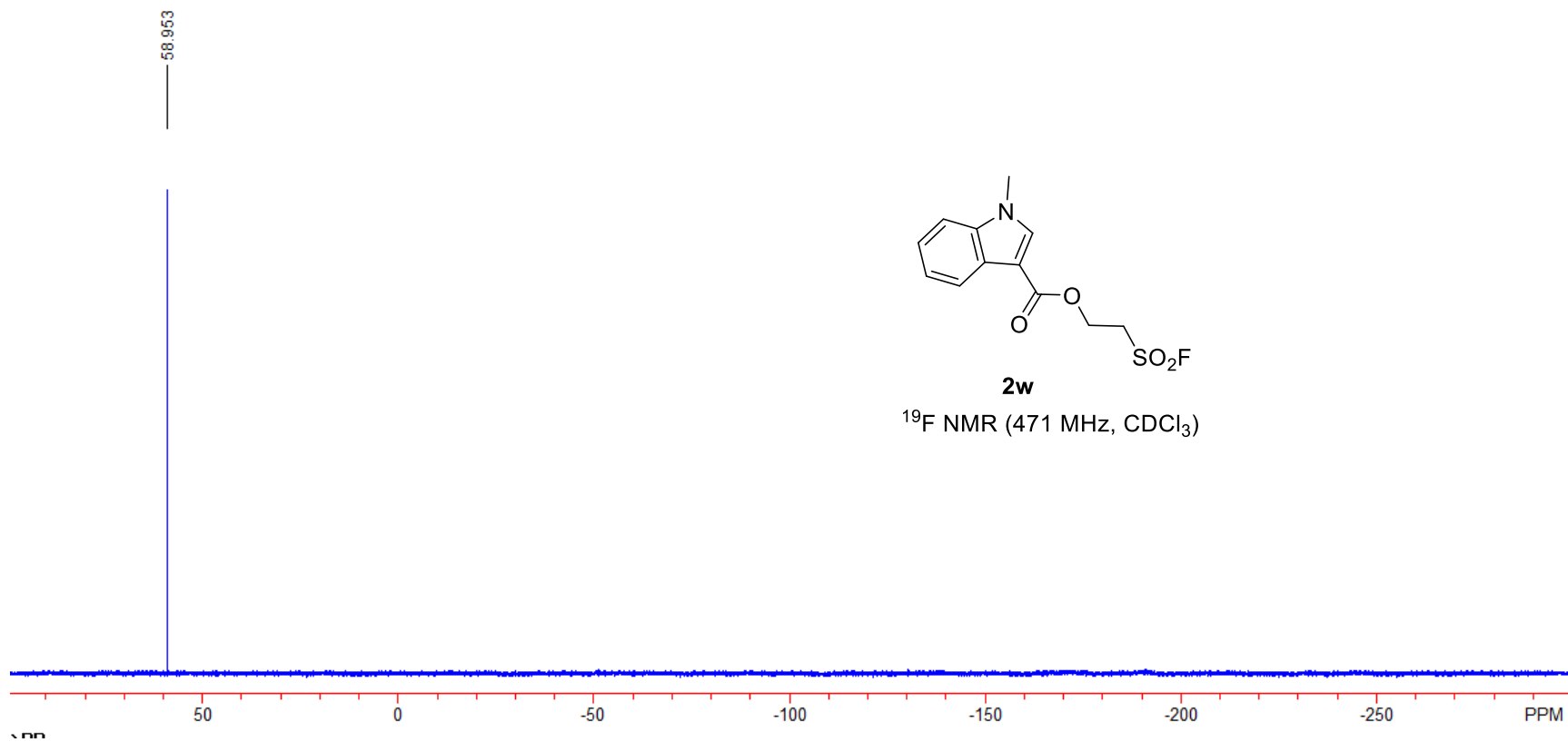


Figure S69. The ^{19}F NMR spectrum of **2w**

2x, ^1H NMR, 500 MHz, CDCl_3

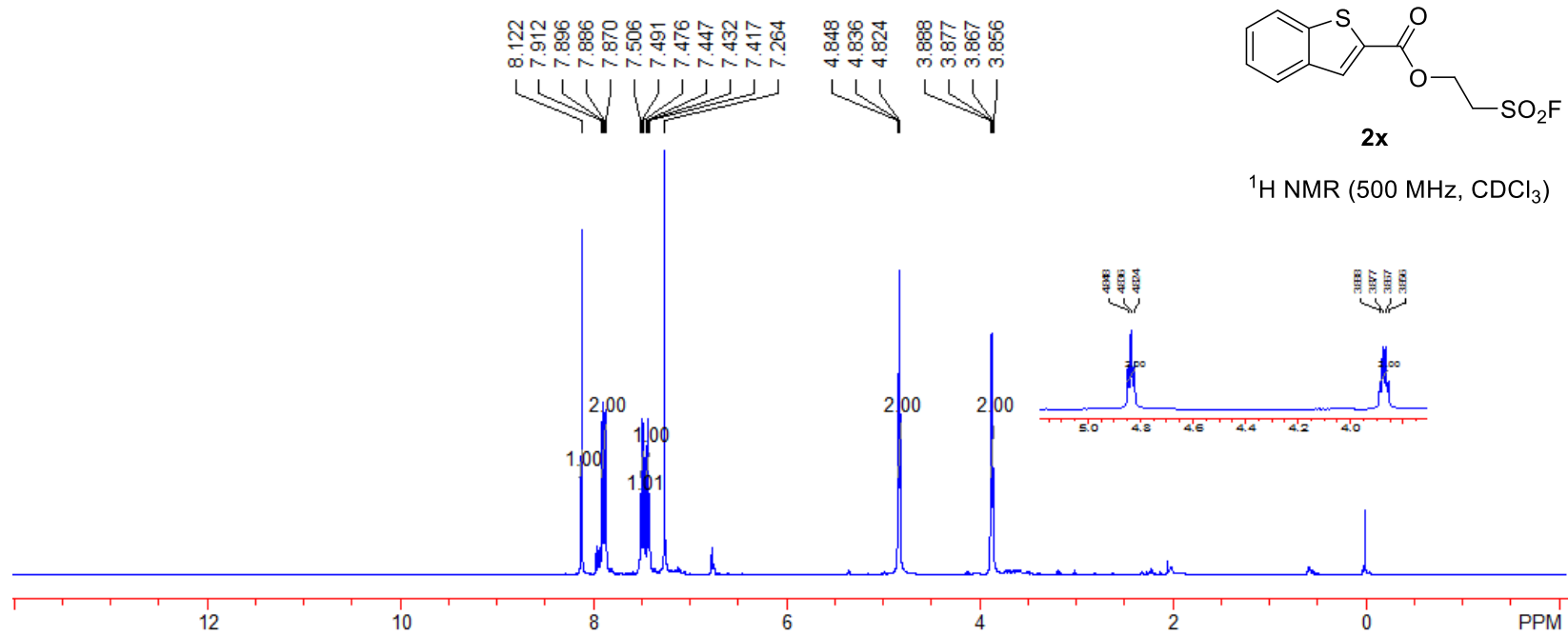


Figure S70. The ^1H NMR spectrum of **2x**

2x, ^{13}C NMR, 126 MHz, CDCl_3

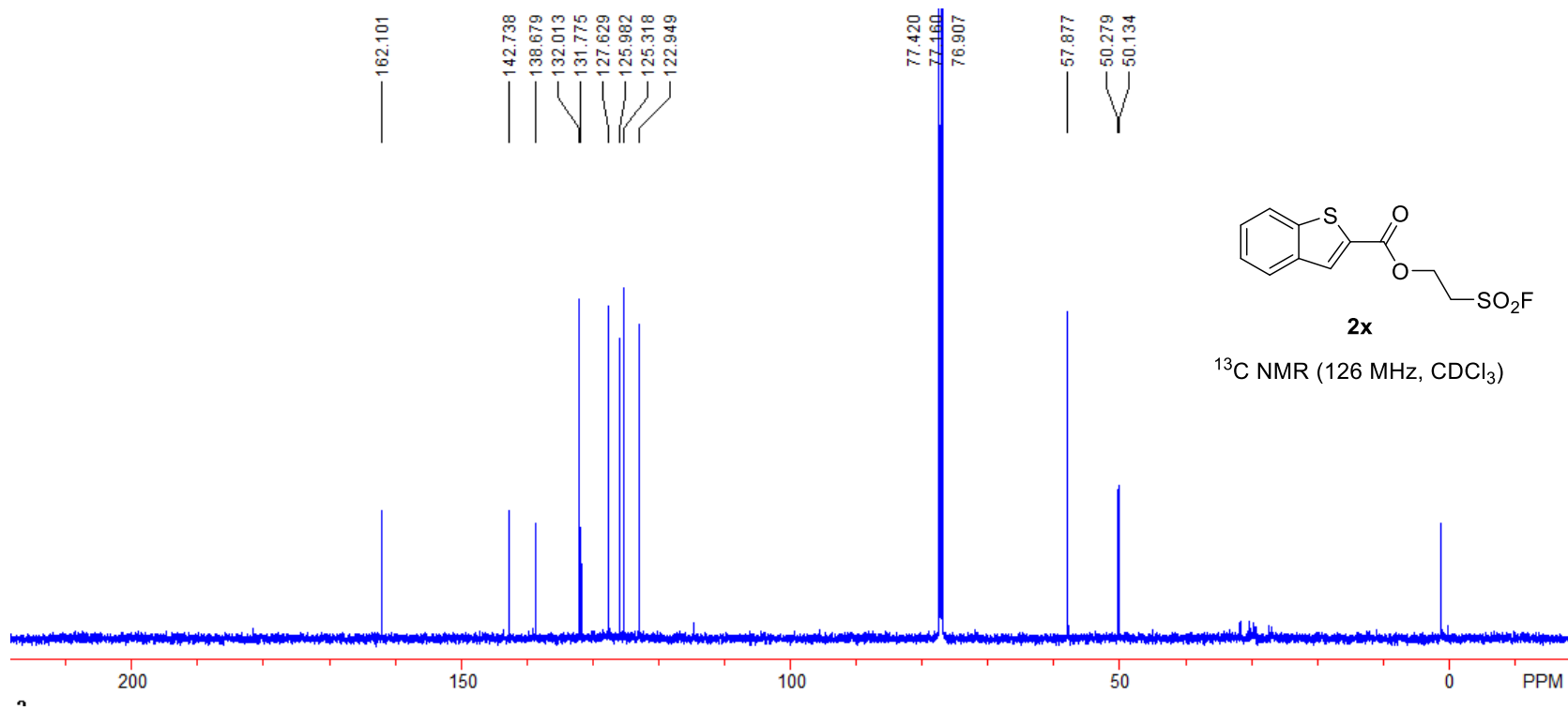


Figure S71. The ^{13}C NMR spectrum of **2x**

2x, ^{19}F NMR, 471 MHz, CDCl_3

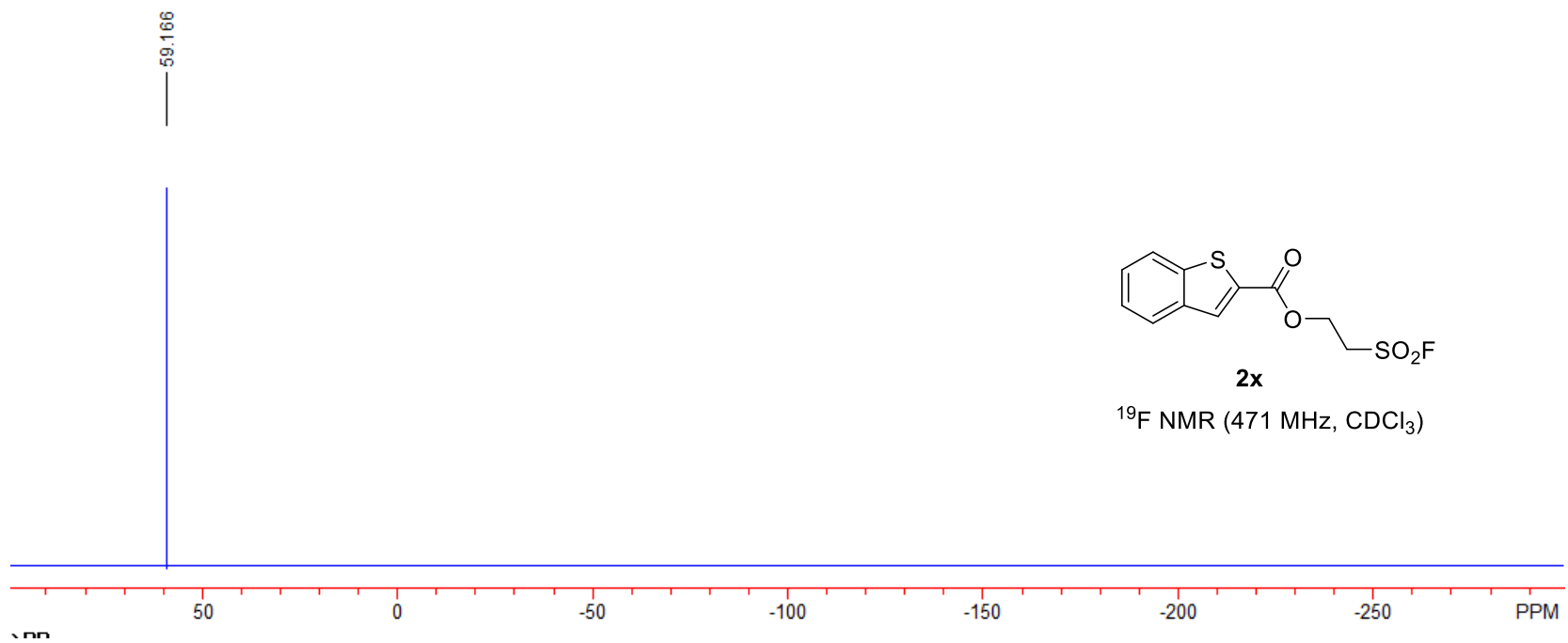


Figure S72. The ^{19}F NMR spectrum of **2x**

2y, ^1H NMR, 500 MHz, CDCl_3

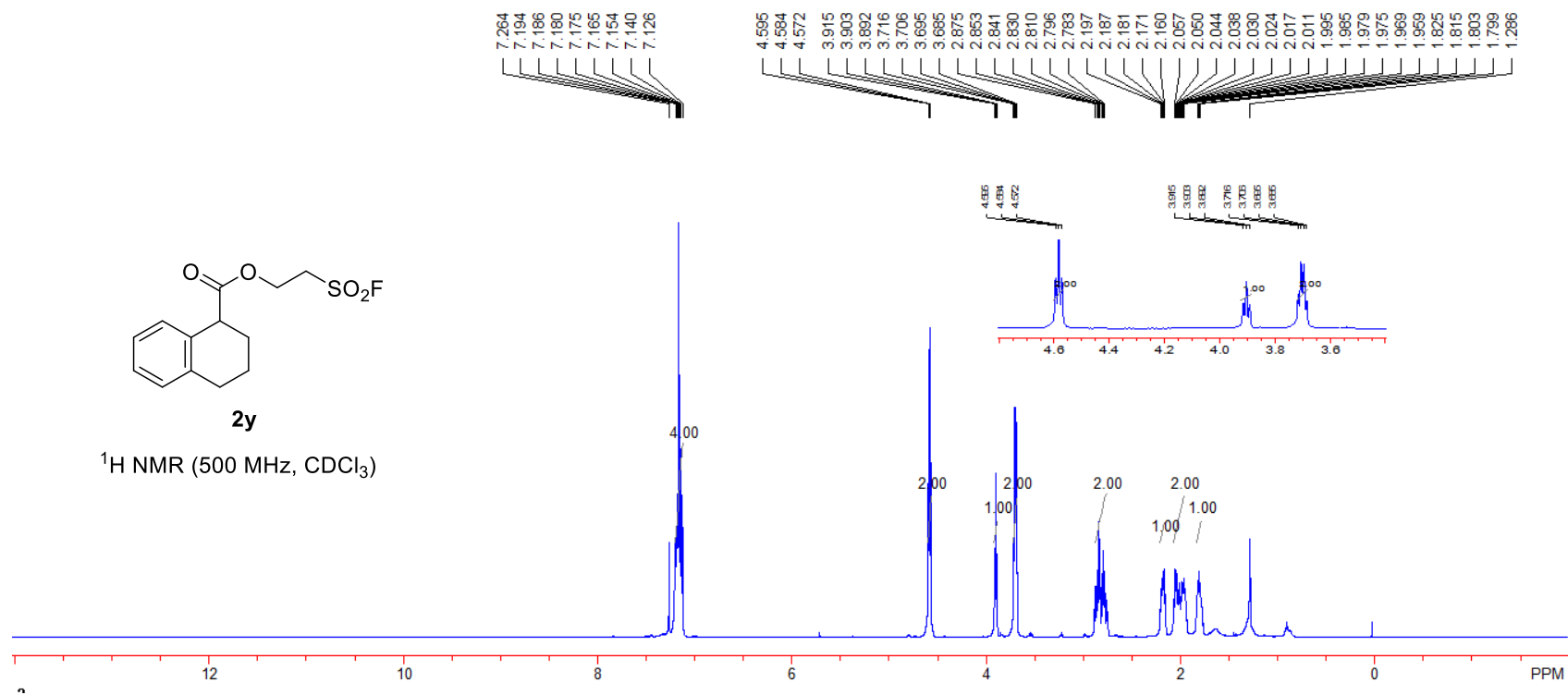


Figure S73. The ^1H NMR spectrum of **2y**

2y, ^{13}C NMR, 126 MHz, CDCl_3

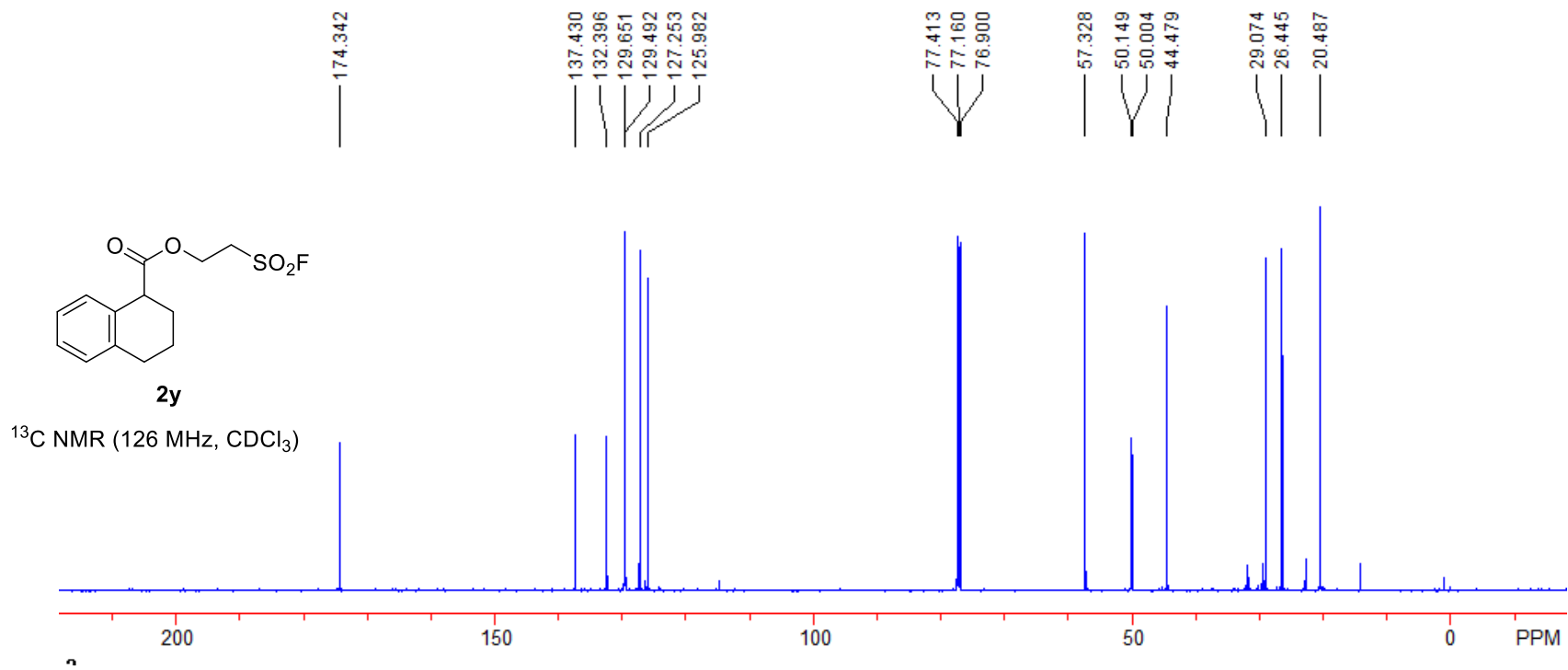


Figure S74. The ^{13}C NMR spectrum of **2y**

2y, ^{19}F NMR, 471 MHz, CDCl_3

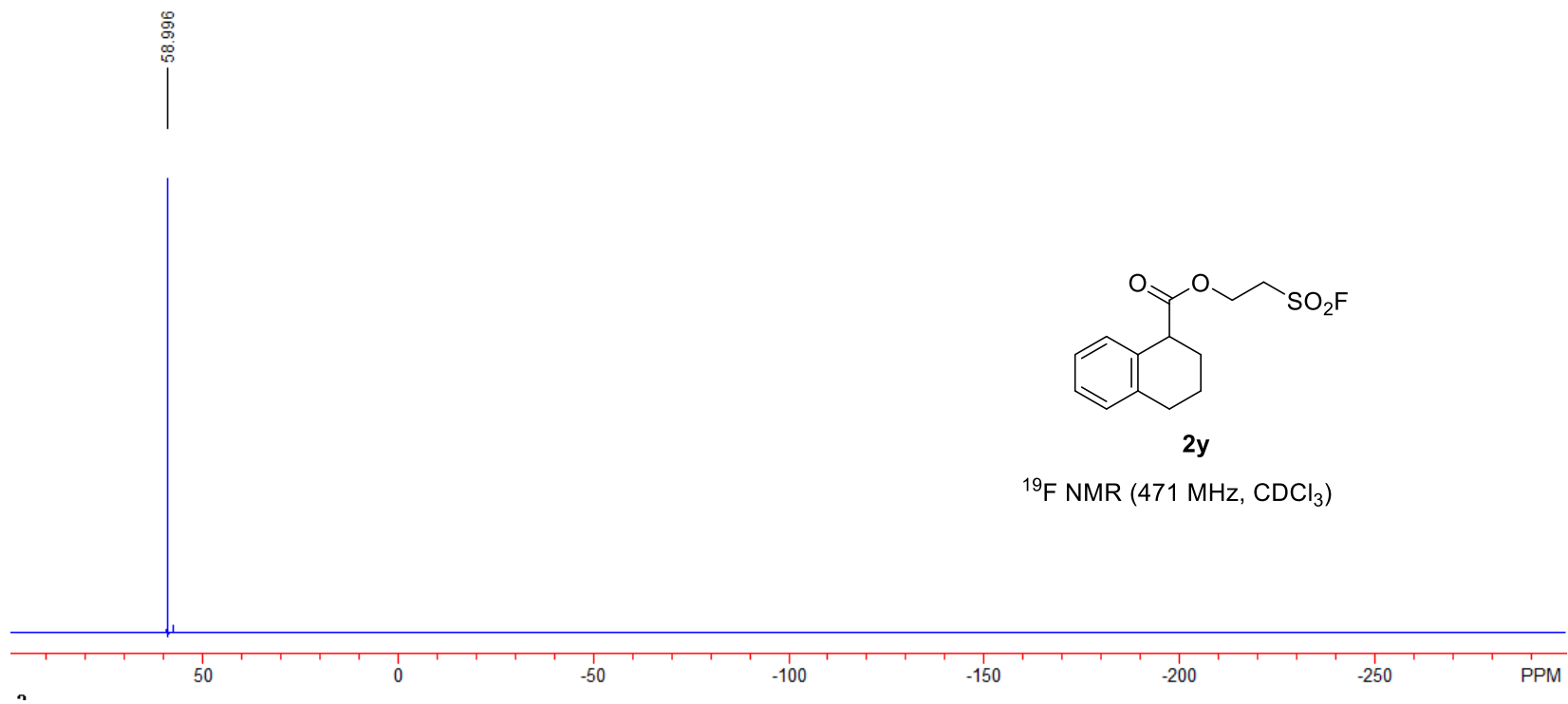


Figure S75. The ^{19}F NMR spectrum of **2y**

2z, ^1H NMR, 500 MHz, CDCl_3

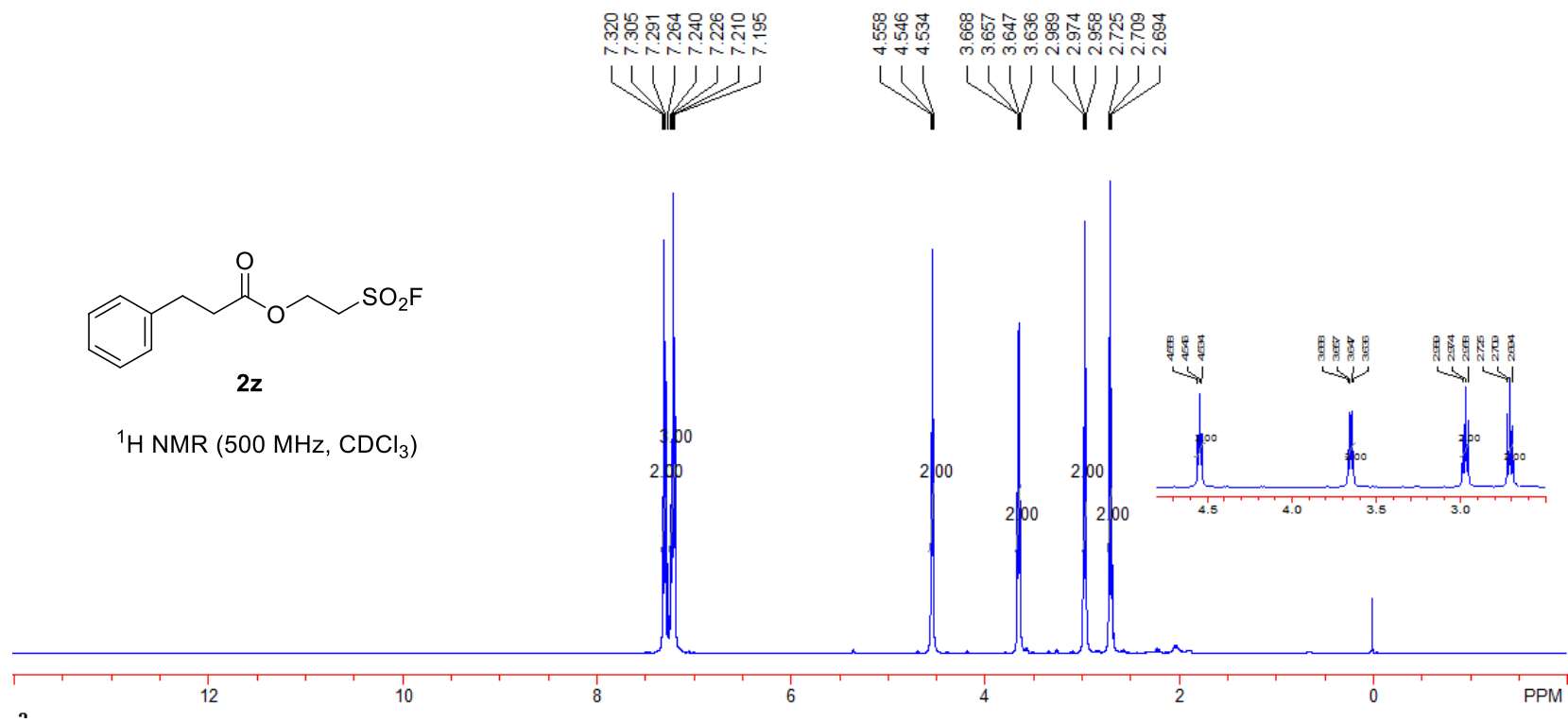


Figure S76. The ^1H NMR spectrum of **2z**

2z, ^{13}C NMR, 126 MHz, CDCl_3

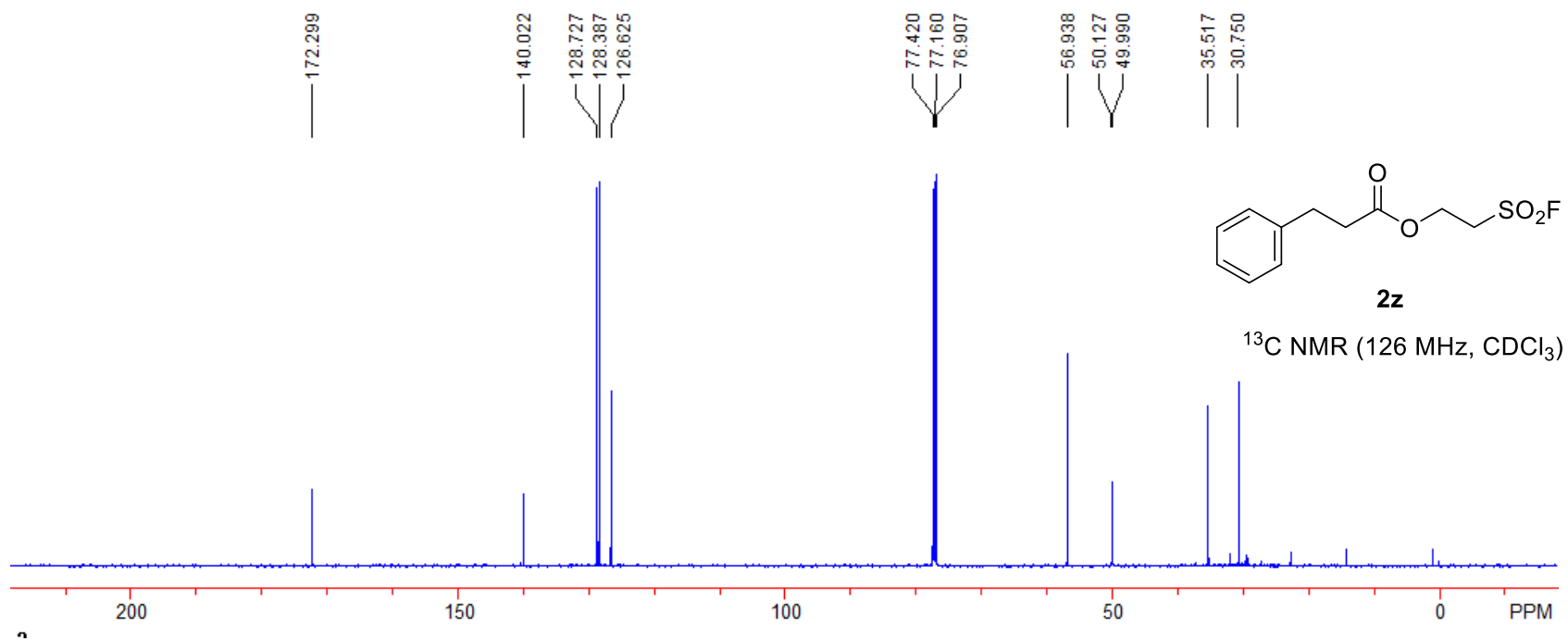


Figure S77. The ^{13}C NMR spectrum of **2z**

2z, ^{19}F NMR, 471 MHz, CDCl_3

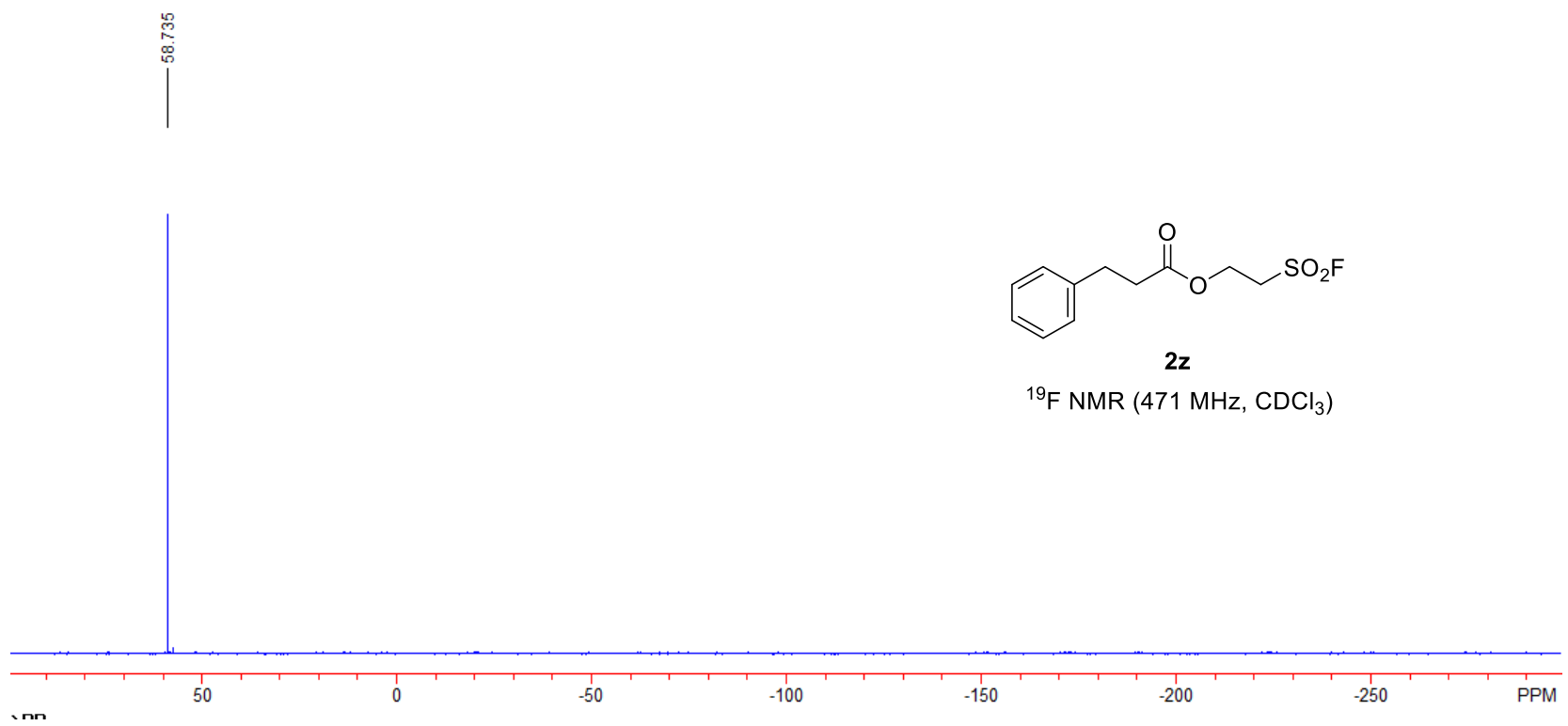


Figure S78. The ^{19}F NMR spectrum of **2z**

2aa, ^1H NMR, 500 MHz, CDCl_3

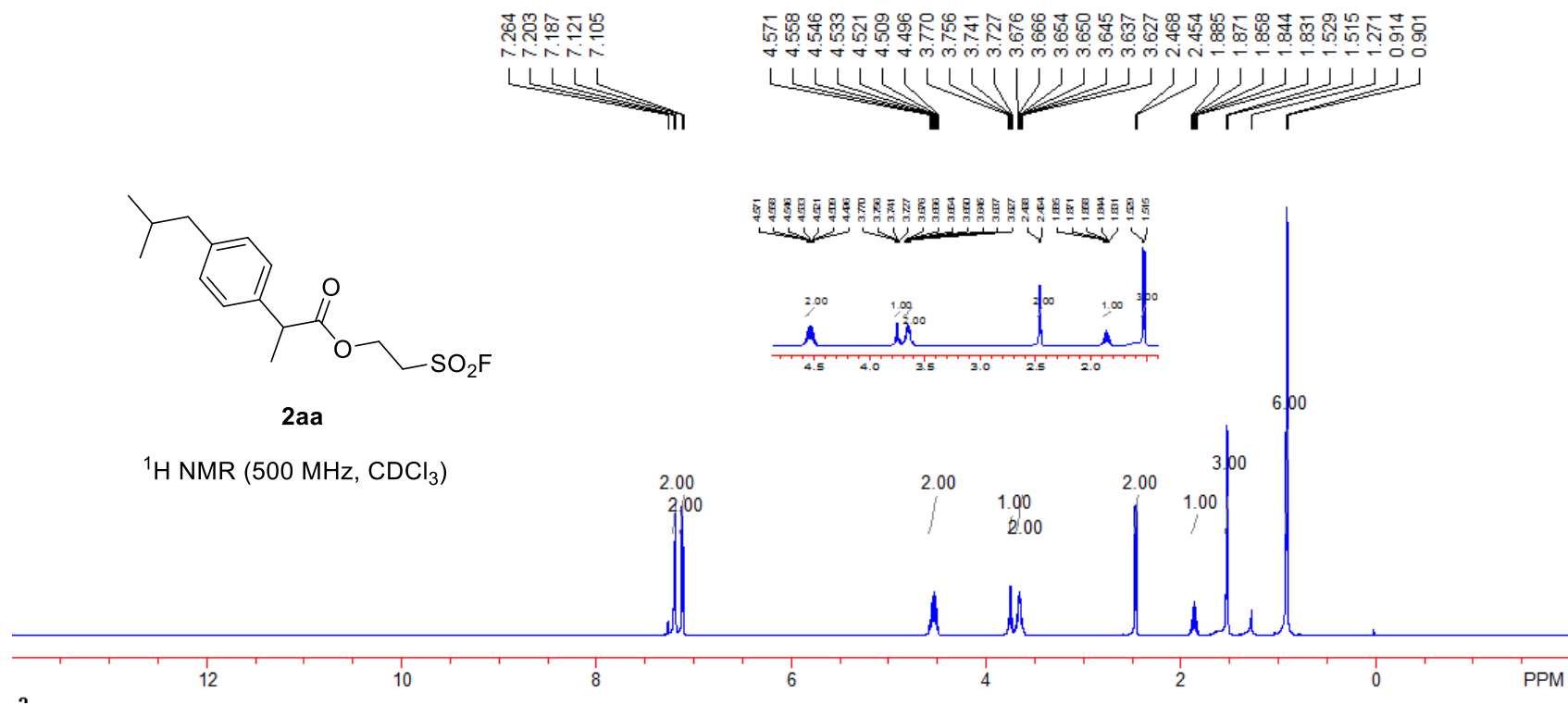


Figure S79. The ^1H NMR spectrum of **2aa**

2aa, ^{13}C NMR, 126 MHz, CDCl_3

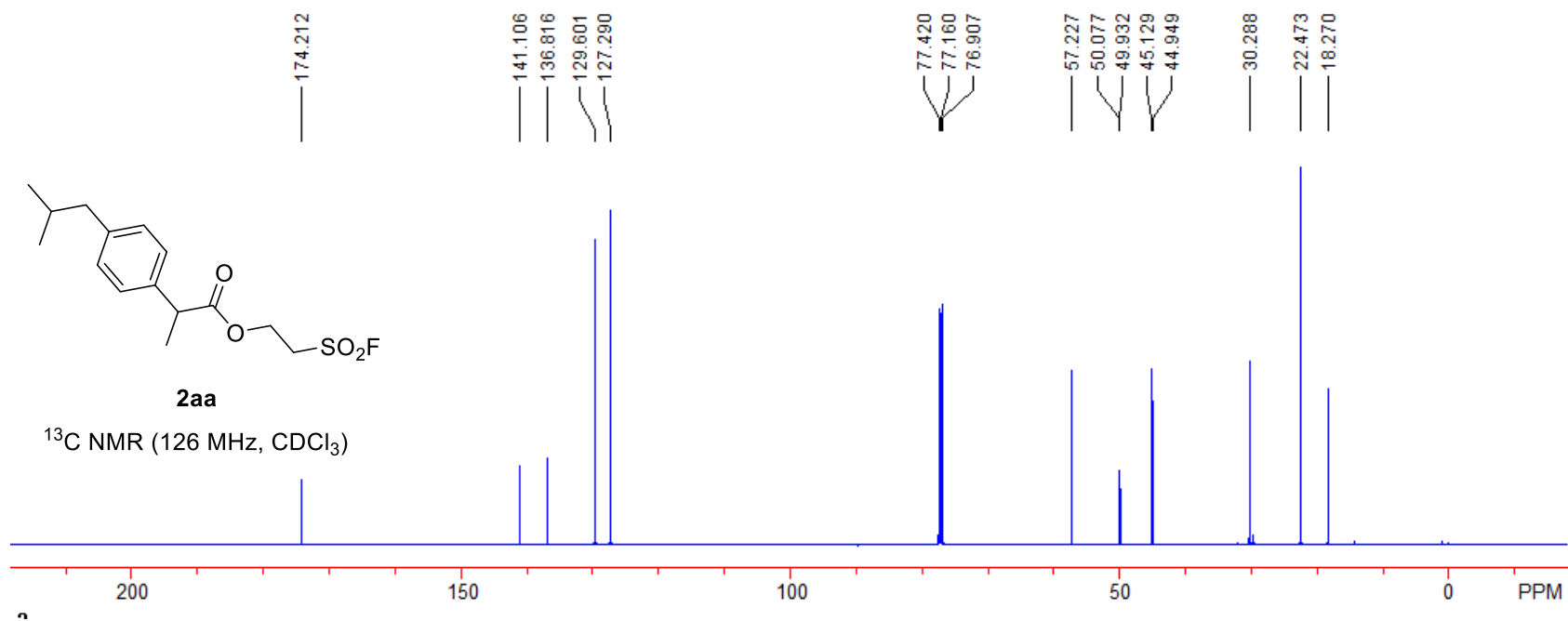


Figure S80. The ^{13}C NMR spectrum of **2aa**

2aa, ^{19}F NMR, 471 MHz, CDCl_3

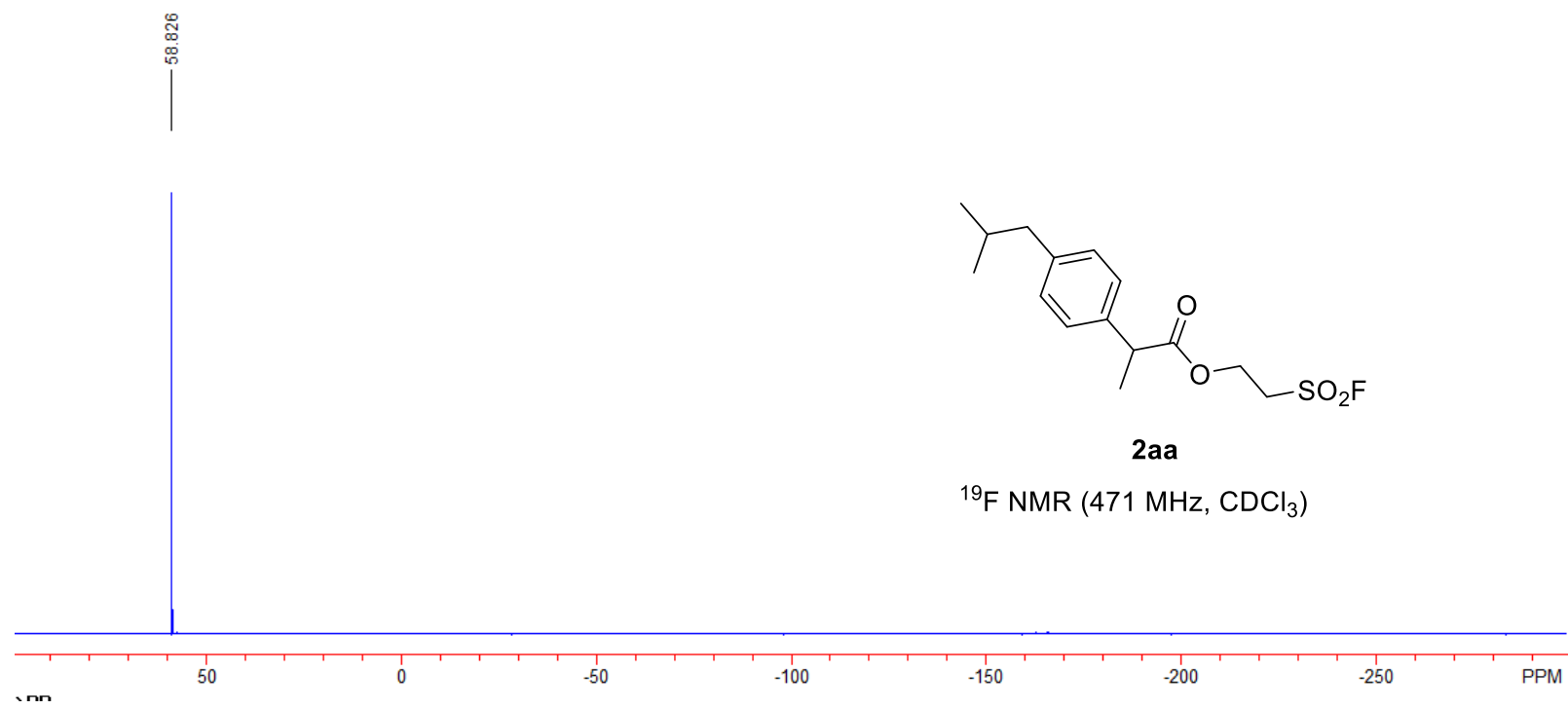


Figure S81. The ^{19}F NMR spectrum of **2aa**

2ab, ^1H NMR, 500 MHz, CDCl_3

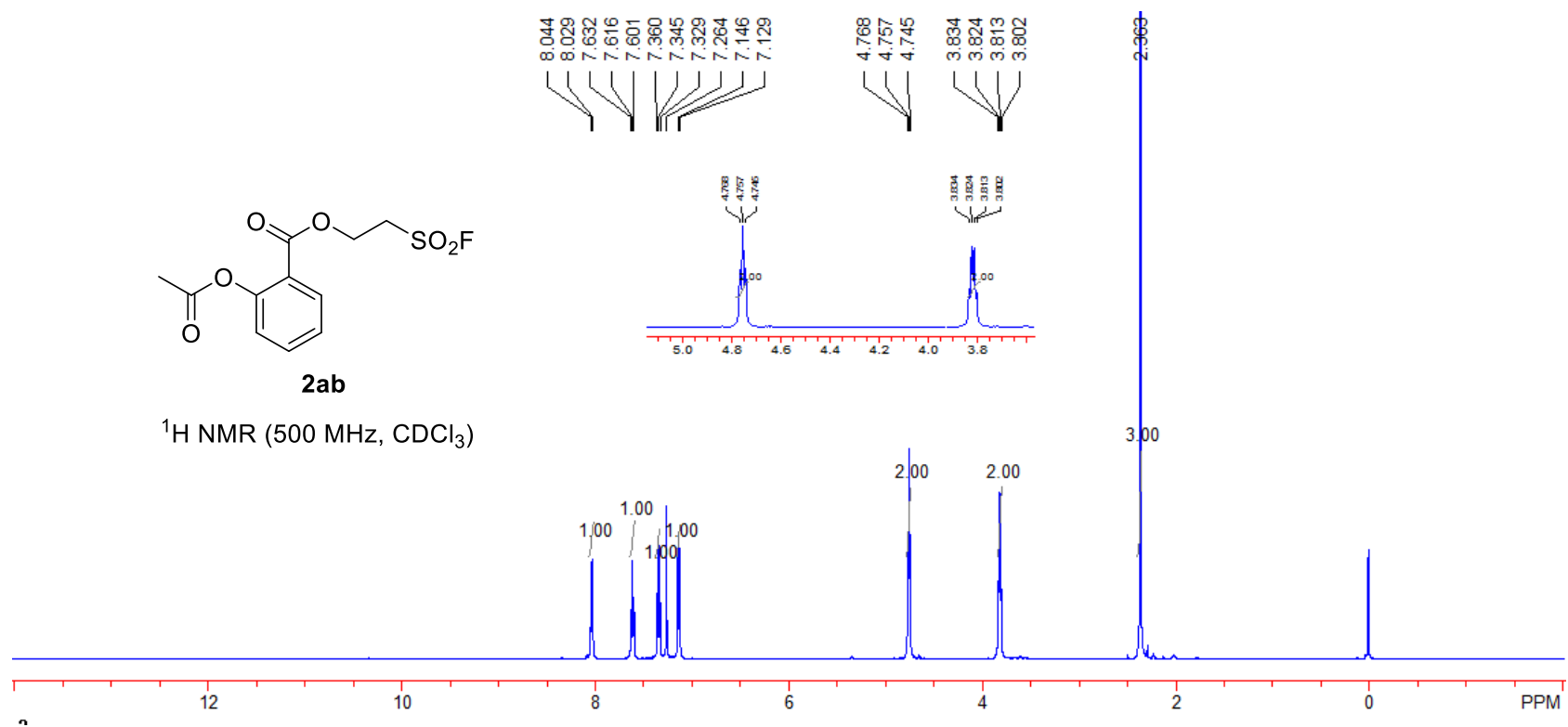


Figure S82. The ^1H NMR spectrum of **2ab**

2ab, ^{13}C NMR, 126 MHz, CDCl_3

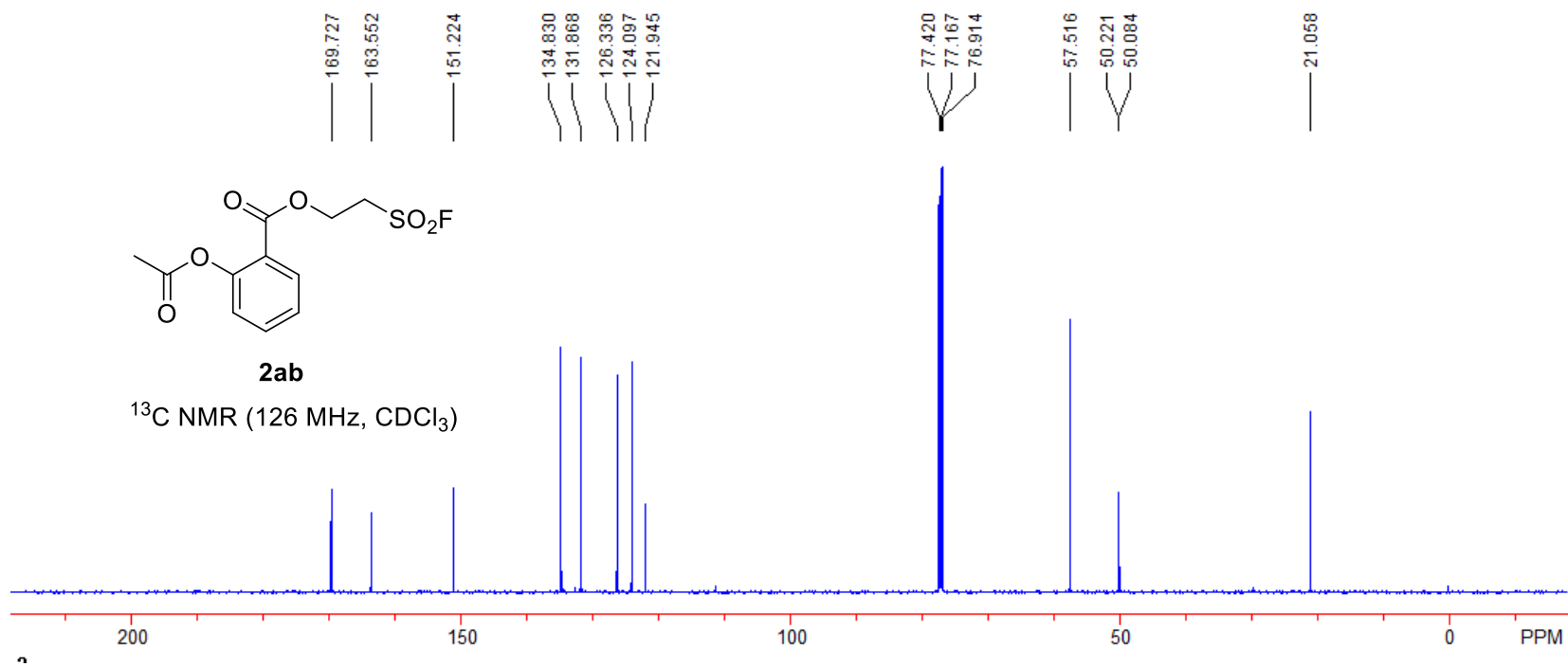


Figure S83. The ^{13}C NMR spectrum of **2ab**

2ab, ^{19}F NMR, 471 MHz, CDCl_3

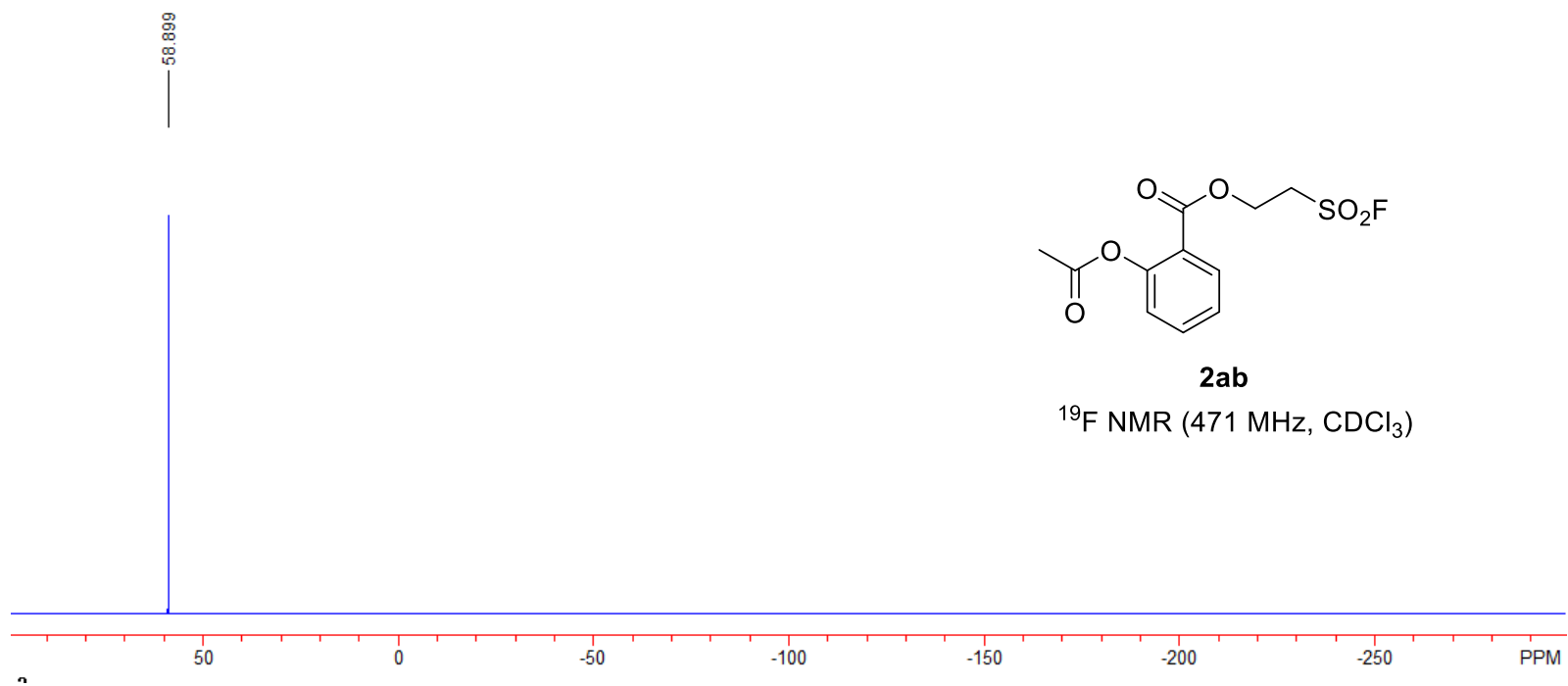


Figure S84. The ^{19}F NMR spectrum of **2ab**

d-1a, ^1H NMR, 500 MHz, CDCl_3

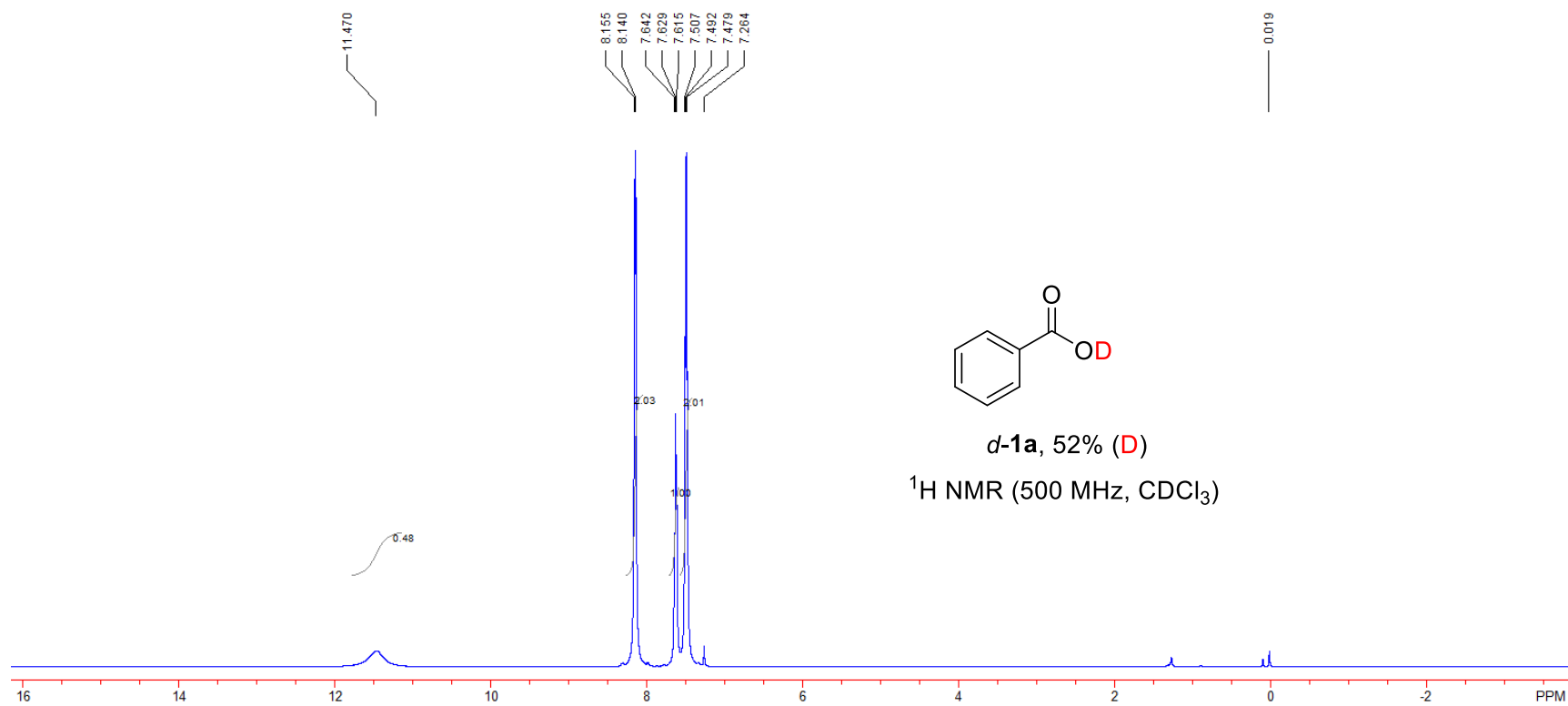


Figure S85. The ^1H NMR spectrum of *d-1a*

d-2a, ^1H NMR, 500 MHz, CDCl_3

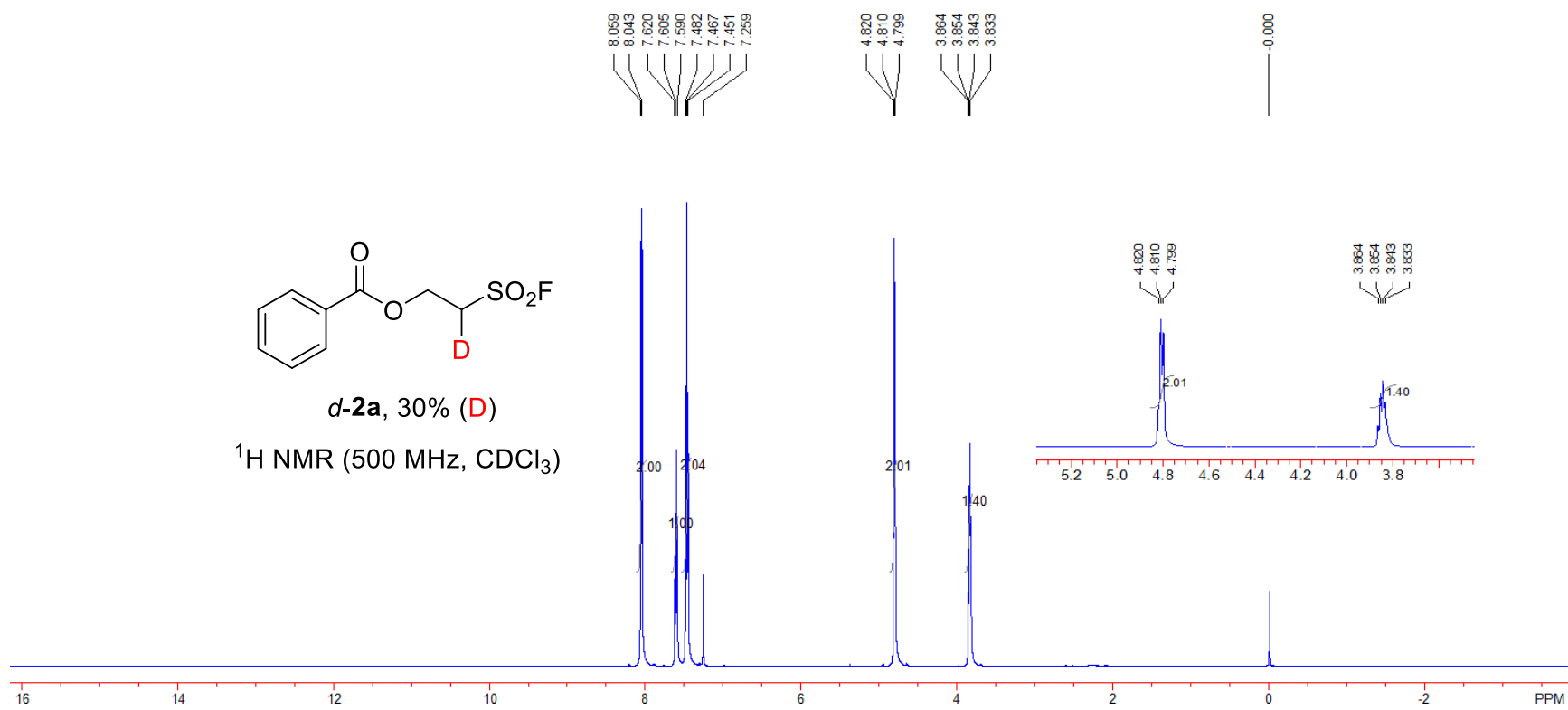
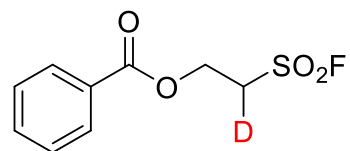
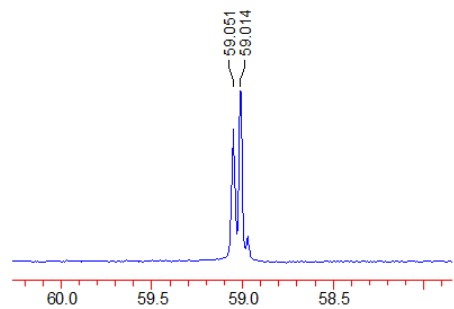


Figure S86. The ^1H NMR spectrum of *d-2a*

d-2a, ^{19}F NMR, 471 MHz, CDCl_3

59.051
59.014



d-2a, 30% (D)

^{19}F NMR (471 MHz, CDCl_3)

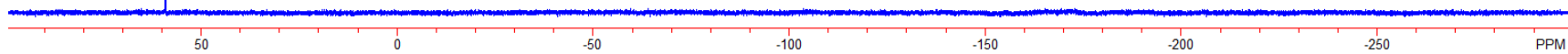


Figure S87. The ^{19}F NMR spectrum of *d-2a*