Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information:

A novel three-component reaction for constructing indolizine-containing aliphatic sulfonyl fluorides

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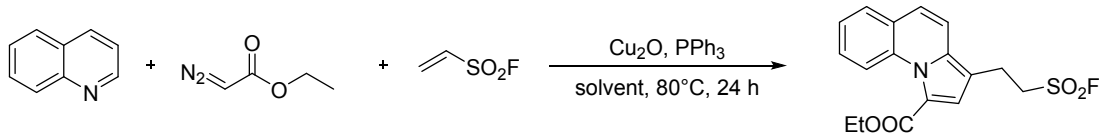
1. General information

All reactions were carried out in dried glassware. All reagents were purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^{1}H), 471 MHz (for ^{19}F), 126 MHz (for ^{13}C) Bruker Avance spectrometer, and were internally referenced to solvent residual signals (note: $CDCl_3$: δ H = 7.264 ppm, δ C = 77.16 ppm). The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. MS experiments were performed on a TOF-Q ESI instrument. Melting points were measured and uncorrected.

2. Optimization of the reaction conditions

Table S1 Screening the Solvent[a]

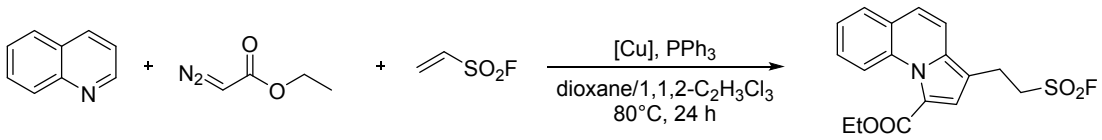


1a **2** **3** **4a**

Entry	Solvent	Yield (**4a**, %)[b]
1	dioxane	15
2	DCE	Trace
3	THF	Trace
4	toluene	17
5	1,1,2-$C_2H_3Cl_3$	12
6	dioxane/toluene (1:1)	22
7	**dioxane/1,1,2-trichloroethane (1:1)**	**34**
8	toluene/1,1,2- trichloroethane (1:1)	15

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), Cu_2O (0.06 mmol, 30 mol%), PPh_3 (0.06 mmol, 30 mol%) and solvent (2 mL, 0.1 M) reacted at 80 °C for 24 h under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

Table S2 Screening the Copper Catalyst[a]

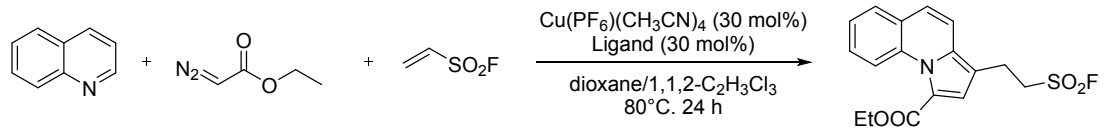


1a **2** **3** **4a**

Entry	[Cu]	Yield (**4a**,%)[b]
1	CuF_2	45
2	$Cu(OTf)_2$	27
3	$Cu(OAc)_2 \cdot H_2O$	32
4	$CuCl_2$	9
5	$CuBr_2$	12
6	CuO	\
7	$CuSO_4$	20
8	CuBr	21
9	CuI	30
10	Cu_2O	34
11	**$Cu(PF_6)(CH_3CN)_4$**	**64**

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), copper catalyst (0.06 mmol, 30 mol%), PPh_3 (0.06 mmol, 30 mol%) and co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 2 mL) reacted at 80 °C for 24 h under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

Table S3 Screening the Ligand[a]

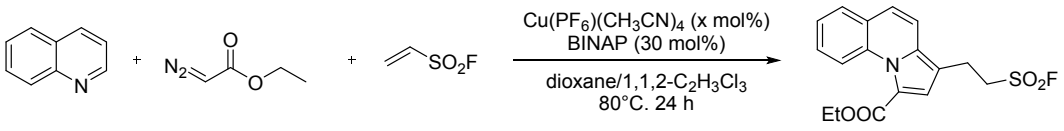


1a 2 3 4a

Entry	Ligand	Yield (**4a**,%)[b]
1	/	46
2	PPh_3	63
3	**BINAP**	**81**
5	xantphos	66
6	*S*-phos	55
7	2-(Diphenylphosphino)-biphenyl	40

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (0.06 mmol, 30 mol%), ligand (0.06 mmol, 30 mol%) and co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 2 mL) reacted at 80 °C for 24 h under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

Table S4 Screening the Loading of [Cu] Catalyst[a]



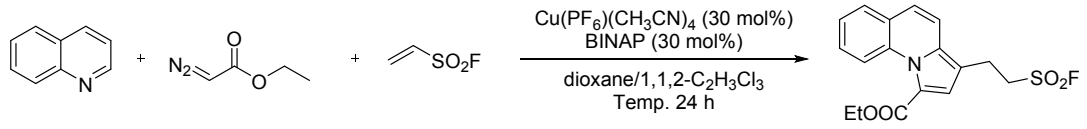
1a 2 3 4a

Entry	[Cu](xmol %)	Yield (**4a**,%)[b]
1	10	41
2	20	63
3	30	81
4	40	79

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (x mol%), BINAP

(0.06 mmol, 30 mol%) and co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 2 mL) reacted at 80 °C for 24 h under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

Table S5 Screening the Reaction Temperature[a]

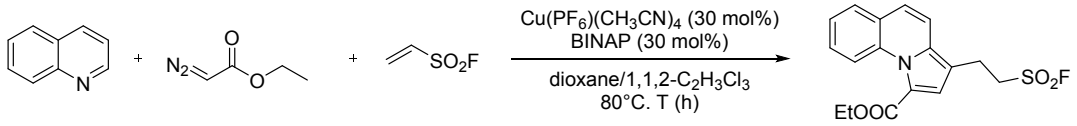


1a **2** **3** **4a**

Entry	Temp (°C)	Yield (**4a**,%)[b]
1	60	54
2	**80**	**81**
3	100	61

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (0.06 mmol, 30 mol%), BINAP (0.06 mmol, 30 mol%) and co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 2 mL) reacted at the corresponding temperature for 24 h under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

Table S6 Screening the Reaction Time[a]



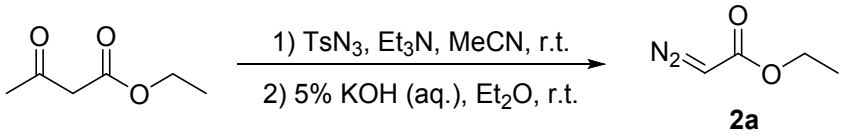
1a 2 3 4a

Entry	Time (h)	Yield (**4a**,%)[b]
1	12	60
2	**24**	**81**
3	36	79

[a]Reaction conditions: a mixture of quinoline (**1a**, 0.2 mmol), ethyl 2-diazoacetate (**2,** 0.2 mmol, 1.0 eq.), ESF (**3** ,0.8 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (0.06 mmol, 30 mol%), BINAP (0.06 mmol, 30 mol%) and co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 2 mL) reacted at 80 °C for the corresponding time under air atmosphere. [b]The yield was determined by HPLC using pure **4a** as the external standard (t_R = 7.7 min, λ_{max} = 254.0 nm, water / methanol = 30 : 70 (v / v)).

3. General procedures

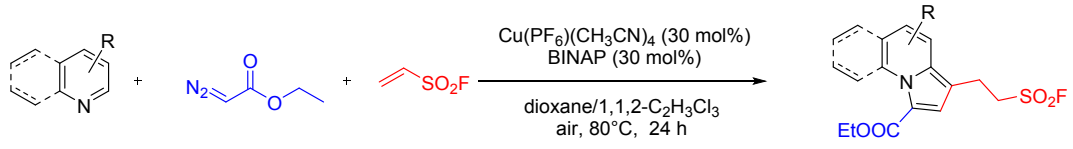
3.1 Procedure for synthesis of 2a[1]



2a

To a solution of ethyl 3-oxobutanoate (1.3 g, 10 mmol) in acetonitrile (12 mL) was added Et_3N (1.31 g, 13 mmol), and then the mixture was cooled in an ice bath before a solution of tosyl azide (2.17 g, 11 mmol) dissolved in acetonitrile (12 mL) was added slowly. After the addition was over, the mixture was warmed to room temperature and the stirring lasted for 10 h. The solvent was removed under reduced pressure and the residue was dissolved in ethyl ether (60 mL) before the addition of 5% KOH (50 mL). Then the reaction mixture was allowed to stir at room temperature for a further 1 h. The organic phase was separated and the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by chromatography over a column of silica gel to provide the desired product as yellow liquid (**2a**, 0.90 g, 79% yield).

3.2 General procedure for synthesis of alkyl sulfonyl fluorides 4 or 6

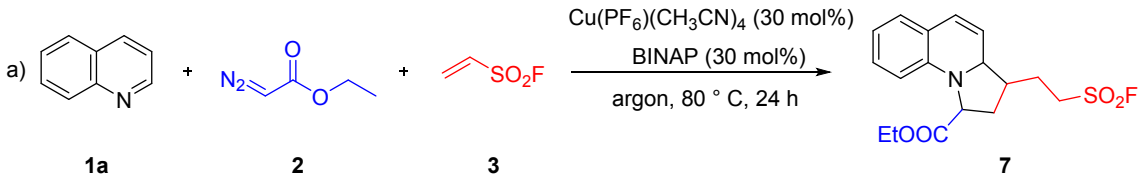


1 or **5** **2** **3** **4** or **6**

A mixture of substituted quinoline or pyridine or isoquinoline (**1** or **5**, 0.5 mmol), ethyl 2-diazoacetate (**2,** 0.5 mmol, 1.0 eq.), ESF (**3**, 2.0 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (30 mol%) and BINAP (30 mol%) in co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 5 mL) reacted at 80 °C for 24 h under air atmosphere. The reaction mixture was cooled to room temperature, then diluted with water (50 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue

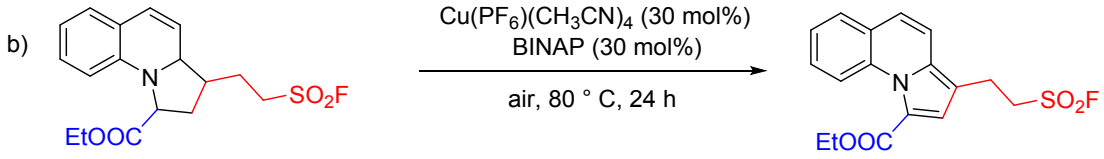
was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford the pure products **4** or **6**.

4. Comparative experiment



A mixture of substituted quinoline (1, 0.5 mmol), ethyl 2-diazoacetate (**2**, 0.5 mmol, 1.0 eq.), ESF (**3**, 2.0 mmol, 4.0 eq.), $Cu(PF_6)(CH_3CN)_4$ (30 mol%) and BINAP (30 mol%) in co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 5 mL) reacted at 80 °C for 24 h under argon atmosphere. The reaction mixture was cooled to room temperature, then diluted with water (50 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford the pure products **7** with 36% yield.

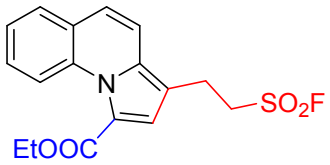
Ethyl-3-(2-(fluorosulfonyl)ethyl)-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-1-carboxylate (**7**). Yellow liquid, 64 mg, 36% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.7 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.56 (t , J = 7.6 Hz,1H), 7.45-7.41(m, 2H), 7.35 (q, J = 8.6 Hz, 2H), 5.36-5.32 (m, 1H), 4.43 (q, J = 7.1 Hz, 2H) , 3.69-3.65 (m, 2H), 3.42-3.39 (m, 2H), 2.22 (t, J = 7.6 Hz, 1H), 2.05-2.00 (m, 2H), 1.46-1.43 (m, 3H). **^{19}F NMR (**471 MHz, $CDCl_3$**)** δ 53.4. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.6, 162.1, 136.0, 128.5, 127.8, 125.6, 125.2, 124.7, 124.1, 120.1, 119.5, 116.1, 109.3, 61.2, 60.8, 14.6, 14.4. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{21}FNO_4S]^+$ ($[M+H]^+$): 354.1097, found: 354.1085.



A mixture of **7** (0.1 mmol), $Cu(PF_6)(CH_3CN)_4$ (30 mol%) and BINAP (30 mol%) in co-solvent dioxane/1,1,2-trichloroethane (1:1, v/v, 0.1 M, 1 mL) reacted at 80 °C for

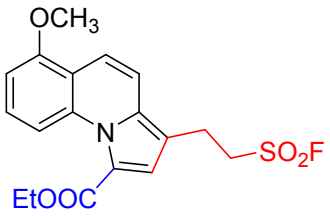
24 h under air atmosphere. And the yield of **4a** (99% yield) was determined by HPLC using pure **4a** as the external standard.

5. Product characterization



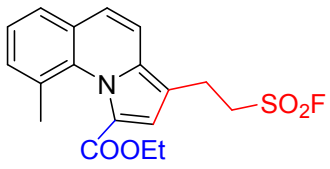
4a

ethyl 3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4a**). Yellow solid, 154 mg, 88% yield. M.p. 104.5-105.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.55 (t , J = 7.9 Hz,1H), 7.43-7.40 (m, 2H), 7.32 (q, J = 8.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H) , 3.68-3.64 (m, 2H), 3.39-3.36(m, 2H),1.44 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.5. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 135.3, 133.9, 128.7, 128.1, 125.1, 125.0, 124.6, 123.9, 120.0, 119.9, 115.1, 110.8, 60.9, 51.6 (d, J = 15.5 Hz), 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{17}FNO_4S]^+$ ($[M+H]^+$): 350.0784, found: 350.0756.



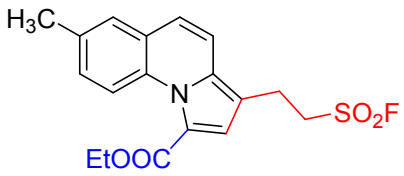
4b

ethyl 3-(2-(fluorosulfonyl)ethyl)-6-methoxypyrrolo[1,2-a]quinoline-1-carboxylate (**4b**). Yellow solid, 152 mg, 80% yield. M.p. 103.4-104.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 9.6 Hz ,1H), 7.48 (t , J = 8.5 Hz, 1H), 7.43 (s,1H), 7.30 (d, J = 9.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.68-3.64 (m, 2H), 3.41-3.37 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.4 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 156.1, 135.5, 134.6, 128.3, 124.1, 119.7, 118.6, 116.2, 113.8, 112.5, 110.3, 105.1, 60.9, 56.1, 51.6 (d, J = 15.4 Hz), 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_5S]^+$ ($[M+H]^+$): 380.0890, found: 380.0961.



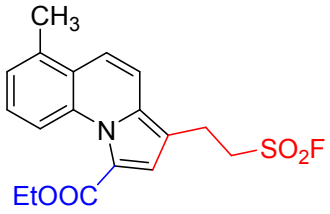
4c

ethyl 3-(2-(fluorosulfonyl)ethyl)-9-methylpyrrolo[1,2-a]quinoline-1-carboxylate (**4c**). Yellow liquid, 125 mg, 69% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (t, J = 4.4 Hz, 1H), 7.35 (d, J = 4.5 Hz, 2H), 7.31 (s, 1H), 7.29 (d, J = 4.7 Hz, 2H) , 4.32 (q, J = 6.9 Hz, 2H), 3.70-3.66 (m, 2H), 3.41 (t, J = 5.5 Hz, 2H), 2.51 (s, 3H), 1.34 (t, J = 6.8 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.4 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 135.8, 134.3, 130.8, 129.5, 126.9, 125.4, 124.8, 124.6, 124.5, 121.5, 114.3, 110.7, 60.7, 51.7(d, J = 14.5 Hz), 20.1, 19.9, 14.5. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_4S]^+$ ($[M+H]^+$): 364.0941, found: 364.0961.



4d

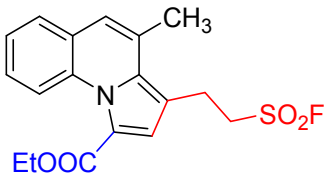
ethyl 3-(2-(fluorosulfonyl)ethyl)-7-methylpyrrolo[1,2-a]quinoline-1-carboxylate (**4d**). Yellow solid, 130 mg, 72% yield. M.p. 100.4-102.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.7 Hz, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.29 (s, 2H), 4.41 (q, J = 7.1 Hz, 2H), 3.67-3.63 (m, 2H), 3.39-3.36 (m, 2H), 2.47 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.4 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 135.1, 134.7, 132.0, 129.3, 128.3, 125.1, 124.5, 123.6, 119.8, 119.6, 114.9, 110.6, 60.8, 51.6 (d, J = 15.4 Hz), 21.0, 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_4S]^+$ ($[M+H]^+$): 364.0941, found: 364.0965.



4e

ethyl 3-(2-(fluorosulfonyl)ethyl)-6-methylpyrrolo[1,2-a]quinoline-1-carboxylate (**4e**). Yellow solid, 138 mg, 76% yield. M.p. 103.4-104.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 9.5 Hz, 1H), 7.45-7.42 (m, 2H), 7.35 (d, J = 9.5 Hz, 1H), 7.27 (d, J = 5.5 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.69-3.65 (m, 2H), 3.42-3.38 (m, 2H), 2.67 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9, 135.5, 135.1, 134.0, 127.5, 126.3,

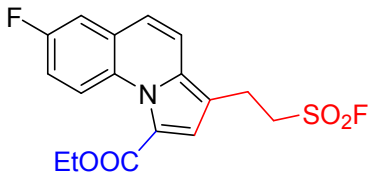
123.95, 123.89, 120.8, 119.9, 118.3, 114.7, 110.5, 60.9, 51.7 (d, J = 15.5 Hz), 29.8, 20.0 (d, J = 2.8 Hz), 14.6. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_4S]^+$ ($[M+H]^+$): 364.0941, found: 364.0971.



4f

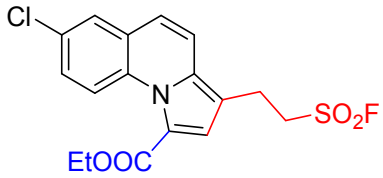
ethyl 3-(2-(fluorosulfonyl)ethyl)-4-methylpyrrolo[1,2-a]quinoline-1-carboxylate (**4f**). Yellow liquid, 145 mg, 80% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.08 (s, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.69-3.66 (m, 2H), 3.63-3.60 (m,2H), 2.65 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9, 135.1, 132.7, 127.5, 127.1, 126.5, 124.99, 124.95, 119.80, 119.86, 111.9, 61.0, 52.6 (d, J = 14.5 Hz), 22.1, 20.1, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_4S]^+$ ($[M+H]^+$): 364.0941, found: 364.0969.

Note: In the ^{13}C NMR spectrum of **4f**, theoretically, there should be eighteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks



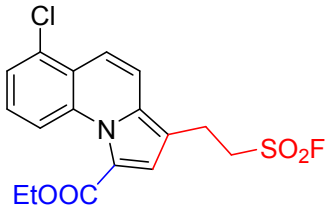
4g

ethyl 7-fluoro-3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4g**). Yellow solid, 110 mg, 60% yield. M.p. 88.0-90.0 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 9.4 Hz, J = 4.7 Hz, 1H), 7.43 (s, 1H), 7.34-7.30 (m, 2H), 7.26-7.22 (m, 2H) , 4.41 (q, J = 7.1 Hz, 2H), 3.68-3.64 (m, 2H), 3.38-3.35 (m, 2H), 1.44 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.7 (s, 1F), 117.2 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7, 134.9, 130.4, 123.8, 123.7, 122.1, 120.1, 116.2, 115.8, 115.6, 113.1, 112.9, 111.2, 61.0, 51.5 (d, J = 14.6 Hz), 19.9, 14.5. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}F_2NO_4S]^+$ ($[M+H]^+$): 368.0690, found: 368.0763.



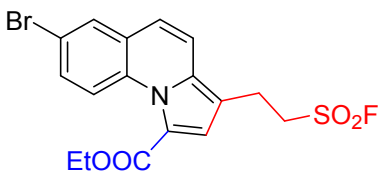
4h

ethyl 7-chloro-3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4h**). Yellow solid, 121 mg, 69% yield. M.p. 145.5-146.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, J = 9.2 Hz, 1H), 7.68 (s, 1H), 7.49 (d, J = 9.3 Hz, 1H), 7.46 (s, 1H) , 7.37 (d, J = 9.2 Hz, 1H), 7.28 (s, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.69-3.65 (m, 2H), 3.41-3.38 (m, 2H), 1.44 (t, J = 7.0 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7, 135.1, 132.4, 130.5, 128.0, 127.5, 126.5, 124.2, 123.5, 121.7, 120.3, 116.4, 111.4, 61.1, 51.6 (d, J = 14.5 Hz), 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}ClFNO_4S]^+$ ($[M+H]^+$): 384.0394, found: 384.0401.



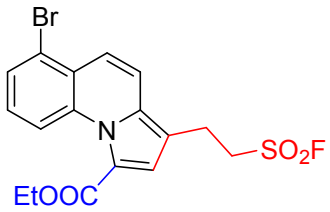
4i

ethyl 6-chloro-3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4i**). Yellow solid, 141 mg, 74% yield. M.p 146.4-148.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 9.6 Hz, 1H), 7.50-7.41 (m, 4H), 4.42 (q, J = 7.1 Hz, 2H), 3.96-3.65 (m, 2H), 3.42-3.38 (m, 2H), 1.44 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7, 135.0, 134.8, 132.4, 127.7, 125.7, 124.5, 123.1, 120.5, 120.4, 119.0, 116.2, 111.3, 61.1, 51.6 (d, J = 14.6 Hz), 19.9, 14.5. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}ClFNO_4S]^+$ ($[M+H]^+$): 384.0394, found: 384.0412.



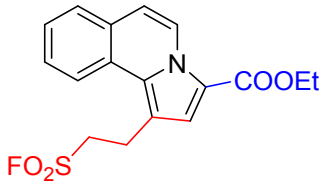
4j

ethyl 7-bromo-3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4j**). Yellow solid, 138 mg, 65% yield. M.p 168.3-170.3 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, J = 9.2 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.62 (dd, J = 2.2 Hz, J = 9.2 Hz, 1H), 7.46 (s, 1H), 7.37 (d, J = 9.1 Hz, 1H), 7.25 (s, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.69-3.65 (m, 2H), 3.41-3.38 (m, 2H), 1.45-1.43 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7, 135.1, 132.9, 130.8, 130.7, 126.9, 124.2, 123.4, 121.9, 120.4, 118.2, 116.3, 111.5, 61.1, 51.6 (d, J = 15.4 Hz), 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}BrFNO_4S^+]^+$ ($[M+H]^+$): 427.9889, found: 427.9954.



4k

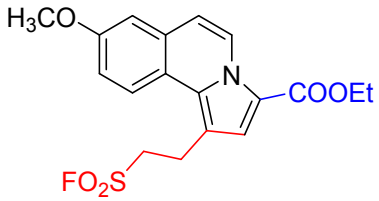
ethyl 7-bromo-3-(2-(fluorosulfonyl)ethyl)pyrrolo[1,2-a]quinoline-1-carboxylate (**4k**). Yellow solid, 139 mg, 65% yield. M.p 165.5-167.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.7 Hz, 1H), 7.82 (dd, J = 0.7 Hz, J = 9.7 Hz, 1H), 7.69 (dd, J = 0.9 Hz, J = 7.8 Hz, 1H), 7.48 (s, 1H), 7.42 (d, J = 9.6 Hz, 1H), 7.40-7.37 (m, 1H), 4.42 (q, J = 7.1 Hz, 2H) , 3.69-3.65 (m, 2H), 3.43-3.40 (m, 2H),1.44 (t, J = 7.1 Hz, 3H).**^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.8. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7, 135.1, 134.9, 129.3, 128.1, 124.6, 124.4, 123.2, 122.9, 120.5, 119.8, 116.5, 111.3, 61.1, 51.6 (d, J = 15.4 Hz), 20.0, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}BrFNO_4S^+]^+$ ($[M+H]^+$): 427.9889, found: 427.9962.



6a

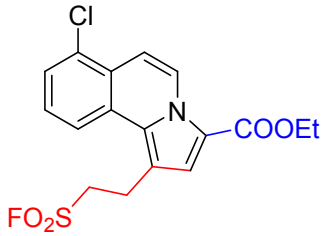
ethyl 1-(2-(fluorosulfonyl)ethyl)pyrrolo[2,1-a]isoquinoline-3-carboxylate (**6a**). Yellow solid, 145 mg, 83% yield. M.p. 104.5-106.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (d, J = 7.5 Hz, 1H), 8.11 (d, J = 8.3 Hz,1H), 7.72 (d, J = 7.8 Hz,1H), 7.62 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.36 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H) , 4.39 (q,

J = 7.1 Hz, 2H) , 3.79-3.73 (m, 4H), 1.42 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 130.7, 128.8, 128.4, 127.7, 127.4, 125.7, 125.0, 122.7, 121.2, 115.5, 113.3, 112.1, 60.4, 50.6 (d, J = 14.5 Hz), 23.4, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{17}FNO_4S]^+$ ($[M+H]^+$): 350.0784, found: 350.0756.



6b

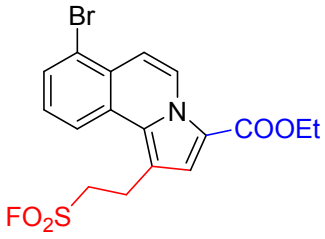
ethyl 1-(2-(fluorosulfonyl)ethyl)-8-methoxypyrrolo[2,1-a]isoquinoline-3-carboxylate (**6b**). Yellow solid, 157 mg, 83% yield. M.p. 106.6 -108.6 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.27 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 9.0 Hz,1H), 7.34 (s, 1H), 7.25 (dd, J = 2.6 Hz, J = 9.0 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H) 3.77-3.68 (m, 4H), 1.42 (t, J = 7.3 Hz, 3H). **^{19}F NMR** (471MHz, $CDCl_3$) δ 53.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 130.7, 130.0, 127.7, 125.5, 124.3, 121.4, 119.8, 117.7, 114.7, 113.0, 110.5, 109.1, 60.3, 55.6, 50.6 (d, J = 14.5 Hz), 23.3, 14.7. **HRMS-ESI** (m/z) calculated for $[C_{18}H_{19}FNO_5S]^+$ ($[M+H]^+$): 380.0890, found: 380.0972.



6c

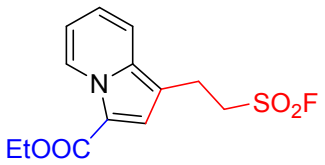
ethyl 7-chloro-1-(2-(fluorosulfonyl)ethyl)pyrrolo[2,1-a]isoquinoline-3-carboxylate (**6c**). Yellow solid, 111 mg, 58% yield. M.p 150.5-151.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (d, J = 7.9 Hz, 1H), 8.03 (d, J = 8.1 Hz,1H), 7.61 (d, J = 7.6 Hz,1H), 7.54 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.39(s, 1H), 4.41 (q, J = 7.1 Hz, 2H), 3.79-3.71 (m, 4H), 1.43 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 132.2, 129.8, 128.5, 127.8, 127.2, 126.6, 126.0, 121.5, 121.4, 115.8, 112.7, 109.2, 60.6, 50.4 (d, J = 15.5 Hz), 23.5, 14.6.

HRMS-ESI (m/z) calculated for $[C_{17}H_{16}ClFNO_4S]^+$ ($[M+H]^+$): 384.0394, found: 384.0385.



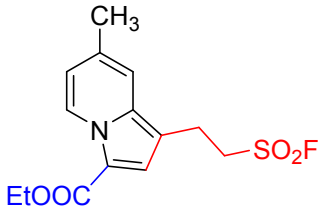
6d

ethyl 7-bromo-1-(2-(fluorosulfonyl)ethyl)pyrrolo[2,1-a]isoquinoline-3-carboxylate (**6d**). Yellow solid, 126 mg, 59% yield. M.p. 167.5-169.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.48-7.45 (m, 1H), 7.40 (s, 1H), 4.41 (q, J = 7.1 Hz, 2H), 3.79-3.71 (m, 4H), 1.44-1.42 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 131.4, 129.8, 128.8, 127.9, 127.2, 126.2, 122.8, 122.1, 121.6, 115.7, 112.7, 111.9, 60.6, 50.4 (d, J = 15.4 Hz), 23.5, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{17}H_{16}BrFNO_4S]^+$ ($[M+H]^+$): 427.9889, found: 427.9923.



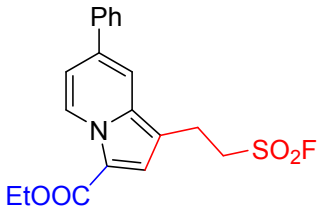
6e

ethyl 1-(2-(fluorosulfonyl)ethyl)indolizine-3-carboxylate (**6e**). Yellow liquid, 111 mg, 89% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, J = 7.1 Hz,1H), 7.47 (d, J = 9.0 Hz, 1H), 7.41 (s, 1H), 7.08 (t, J = 7.0 Hz, 1H), 6.84 (t, J = 6.9 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.68-3.64 (m, 2H) , 3.42-3.39 (m, 2H) , 1.40 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 135.6, 127.7, 122.1, 120.8, 116.2, 113.8, 113.2, 108.4, 60.1, 51.7 (d, J = 15.5 Hz), 20.1, 14.7. **HRMS-ESI** (m/z) calculated for $[C_{13}H_{15}FNO_4S]^+$ ($[M+H]^+$): 300.0628, found: 300.0641.



6f

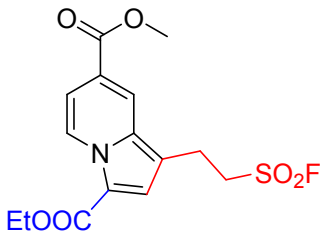
ethyl 1-(2-(fluorosulfonyl)ethyl)-7-methylindolizine-3-carboxylate (**6f**). Yellow liquid, 111 mg, 70% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (d, J = 7.2 Hz,1H), 7.36 (s, 1H), 7.41 (s, 1H), 7.20 (s, 1H), 6.68 (d, J = 7.2 Hz, 1H), 4.54 (q, J = 7.0 Hz, 2H), 3.66-3.62 (m, 2H) , 3.36 (t, J = 8.9 Hz, 2H), 2.40v(s, 3H) 1.39 (t, J = 7.0 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 136.0, 133.0, 127.2, 121.0, 115.9, 114.7, 113.1, 106.9, 59.9, 51.6 (d, J = 14.5 Hz), 22.8, 20.1, 14.3. **HRMS-ESI** (m/z) calculated for $[C_{14}H_{17}FNO_4S]^+$ ($[M+H]^+$): 314.0784, found: 314.0798.



6g

ethyl 1-(2-(fluorosulfonyl)ethyl)-7-phenylindolizine-3-carboxylate (**6g**). Yellow solid, 111 mg, 58% yield. M.p 91.5-93.5 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.46 (dd, J = 0.7 Hz, J = 7.4 Hz, 1H), 7.69-7.68 (m, 1H), 7.67 (s, 1H), 7.64 (q, J = 0.9 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.43 (s, 1H), 7.41-7.40 (m, 1H), 7.14 (dd, J = 1.9 Hz, J = 7.4 Hz,1H), 4.39 (q, J = 7.1 Hz, 2H), 3.72-3.68 (m, 2H), 3.47-3.44 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 130.0, 129.3, 128.5, 127.8, 121.4, 113.04, 112.97, 60.2, 51.7 (d, J = 14.6 Hz), 20.2, 14.7. **HRMS-ESI** (m/z) calculated for $[C_{19}H_{19}FNO_4S]^+$ ($[M+H]^+$): 376.0941, found: 376.0959.

Note: In the ^{13}C NMR spectrum of **6g**, theoretically, there should be seventeen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks



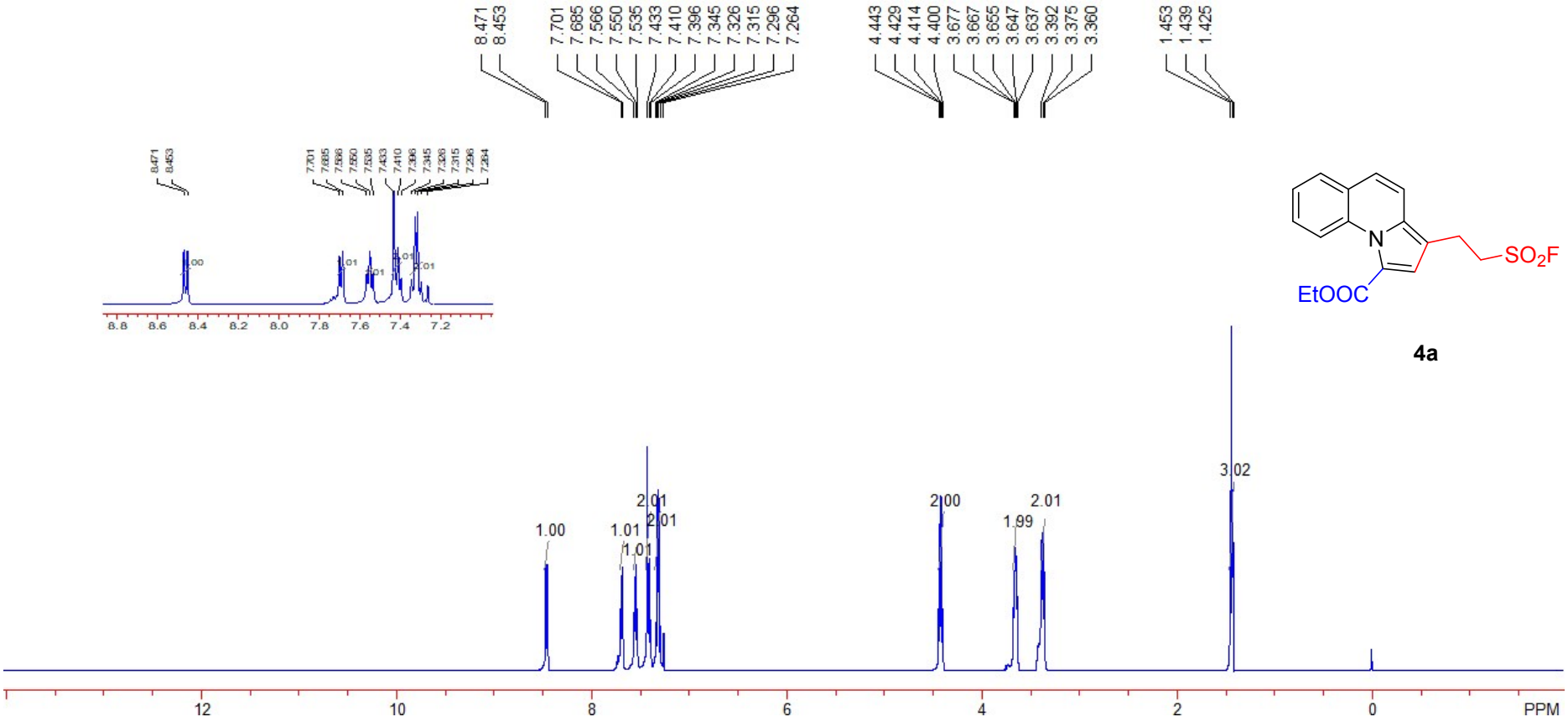
6h

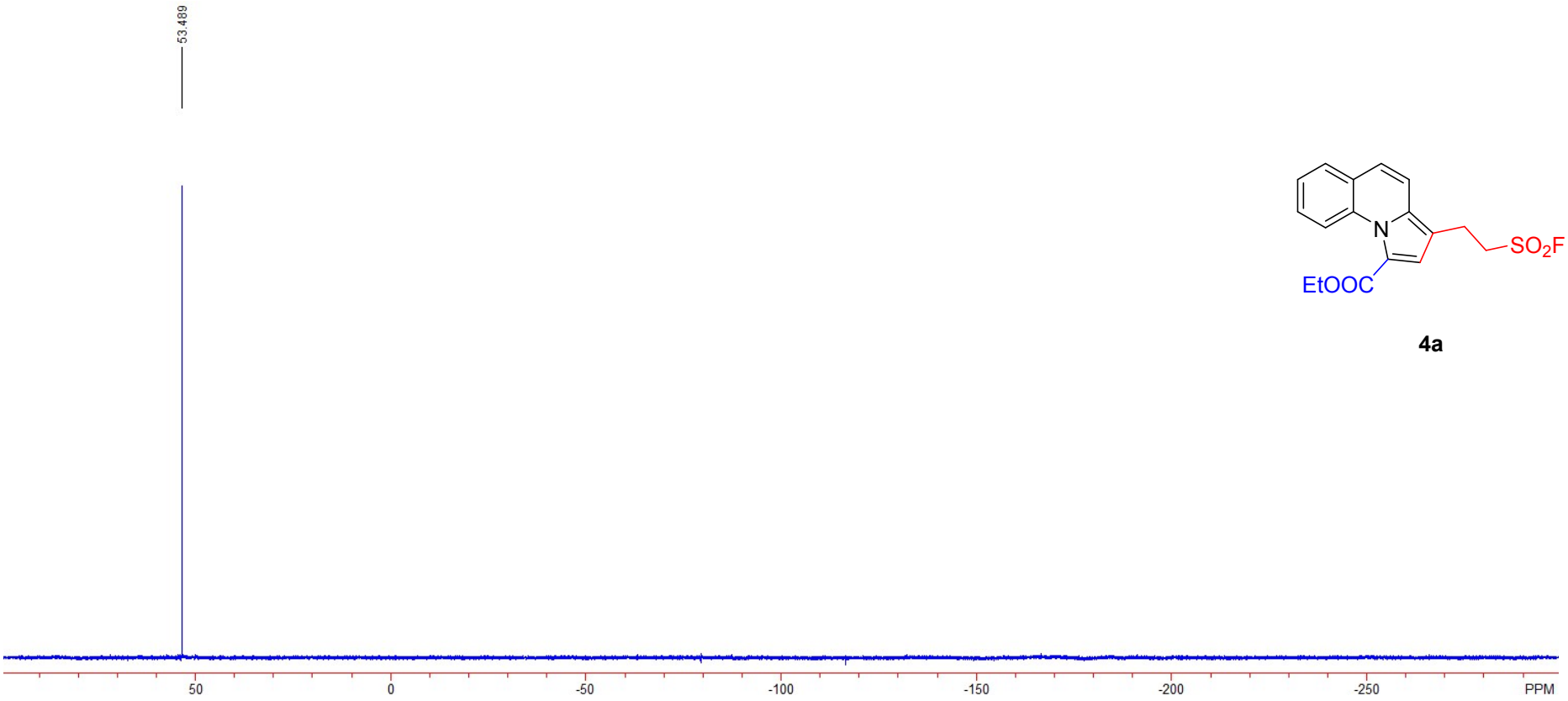
3-ethyl 7-methyl 1-(2-(fluorosulfonyl)ethyl)indolizine-3,7-dicarboxylate (**6h**). Yellow solid, 160 mg, 58% yield. M.p 94.5-96.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 (dd, J = 0.7 Hz, J = 7.4 Hz, 1H), 8.22(s,1H), 7.47 (s, 1H), 7.38 (dd, J = 1.7 Hz, J = 7.5 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 3.71-3.68 (m, 2H) , 3.49-3.46 (m, 2H) , 1.41 (t, J = 7.3 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ 53.9 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.8, 161.0, 134.1, 127.0, 123.0, 121.4, 119.2, 116.1, 112.7, 112.0, 60.6, 52.7, 51.5 (d, J = 15.4 Hz), 20.1, 14.6. **HRMS-ESI** (m/z) calculated for $[C_{15}H_{17}FNO_6S]^+$ ($[M+H]^+$): 358.0682, found: 358.0654.

6. References

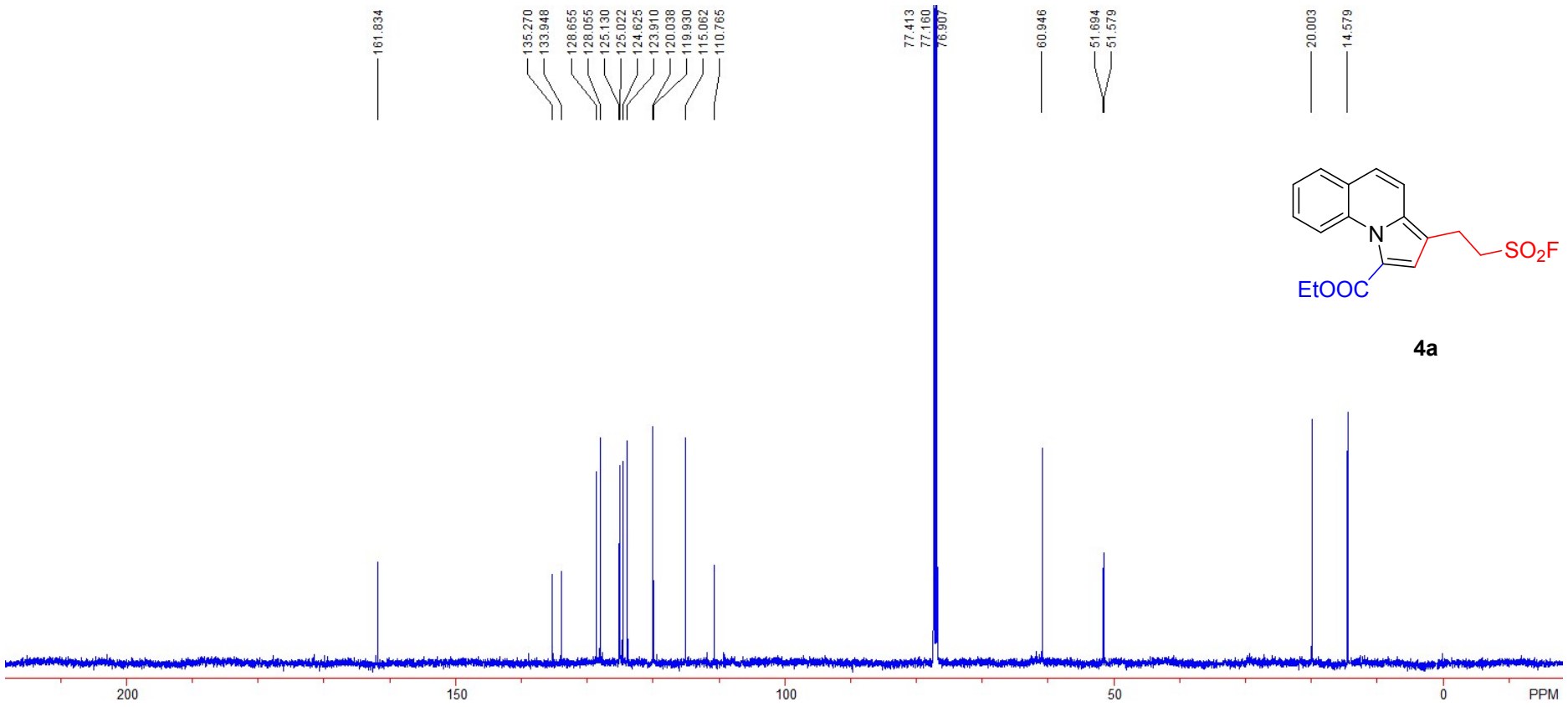
[1] H. Mao, A. Lin, Y. Shi, Z. Mao, X. Zhu, W. Li, H. Hu, Y. Cheng, C. Zhu, Construction of Enantiomerically Enriched Diazo Compounds Using Diazo Esters as Nucleophiles: Chiral Lewis Base Catalysis, *Angew. Chem. Int. Ed.*, 2013, **52**, 6288−6292.

7. NMR spectra.





4a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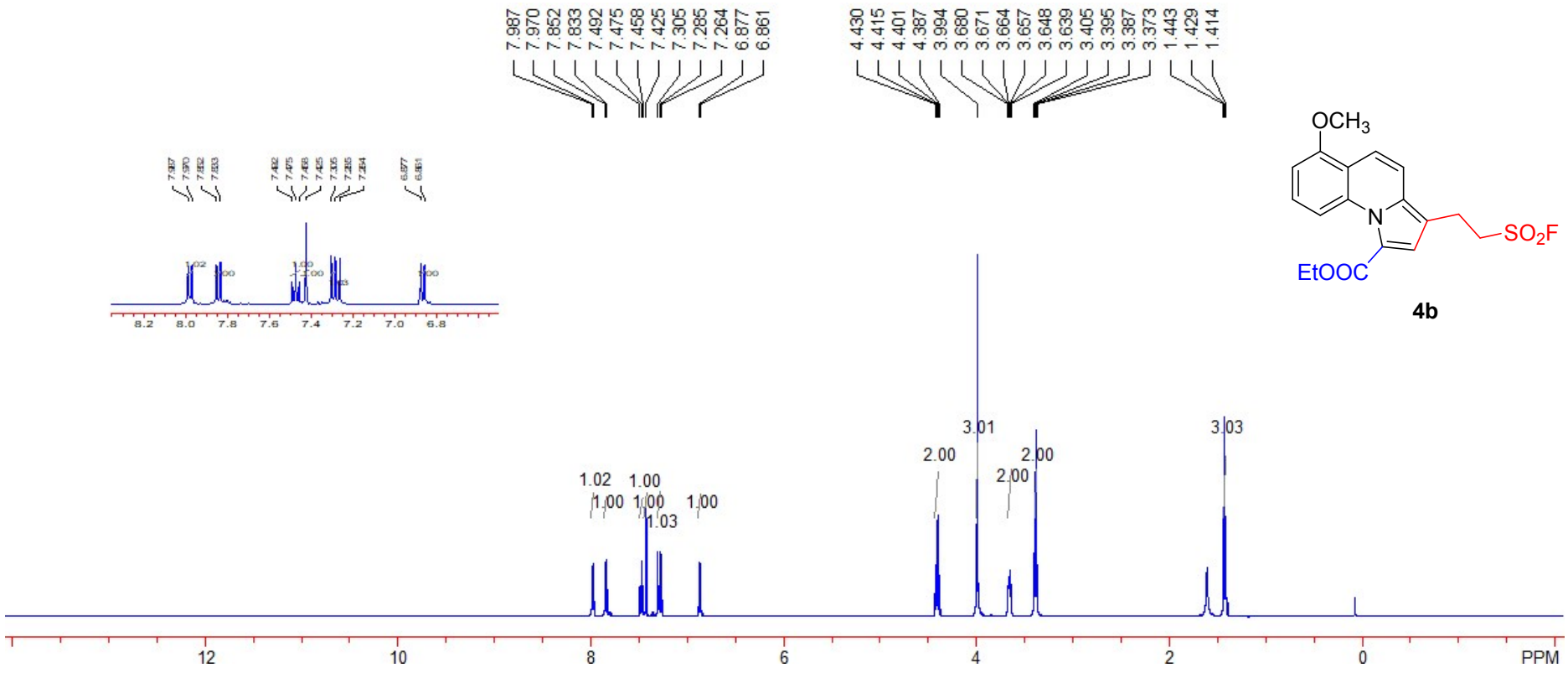
4a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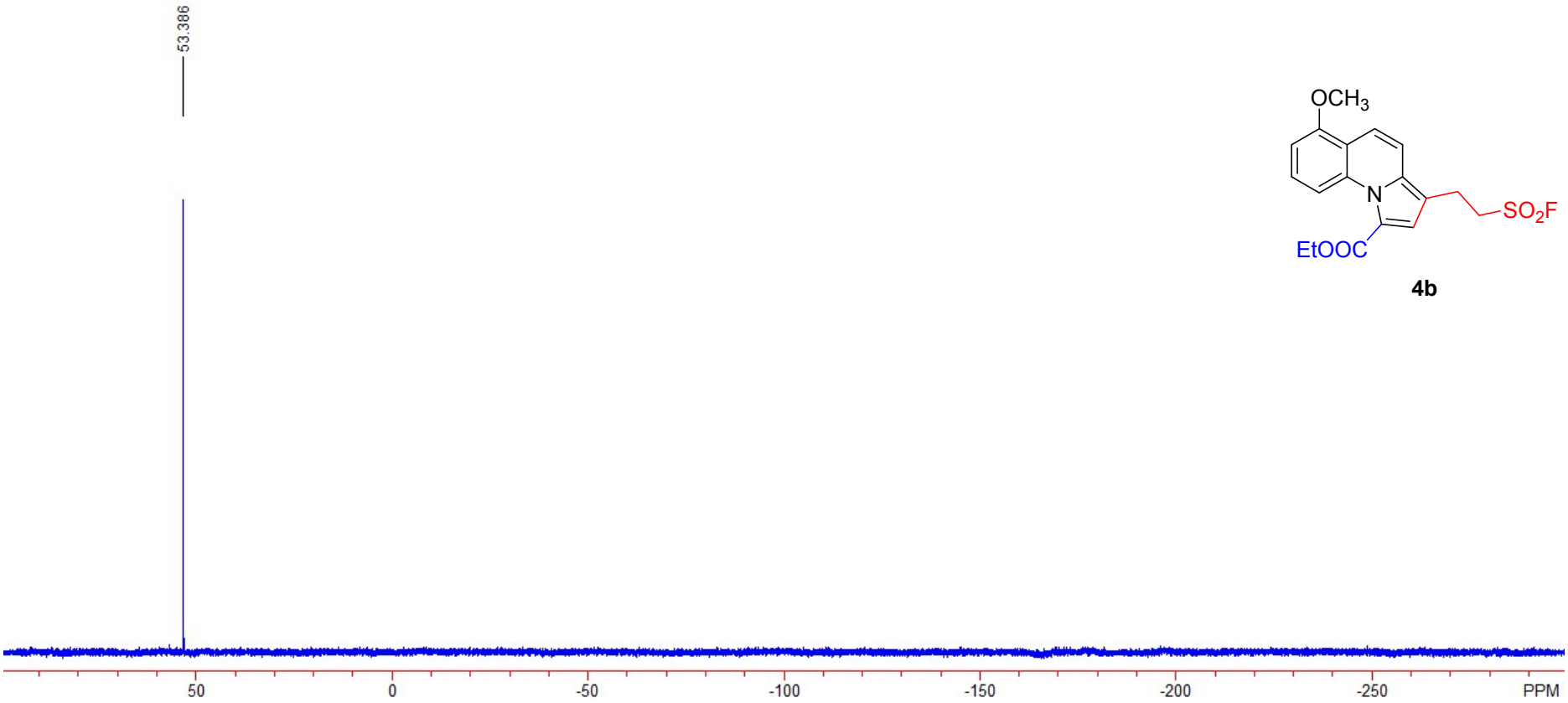
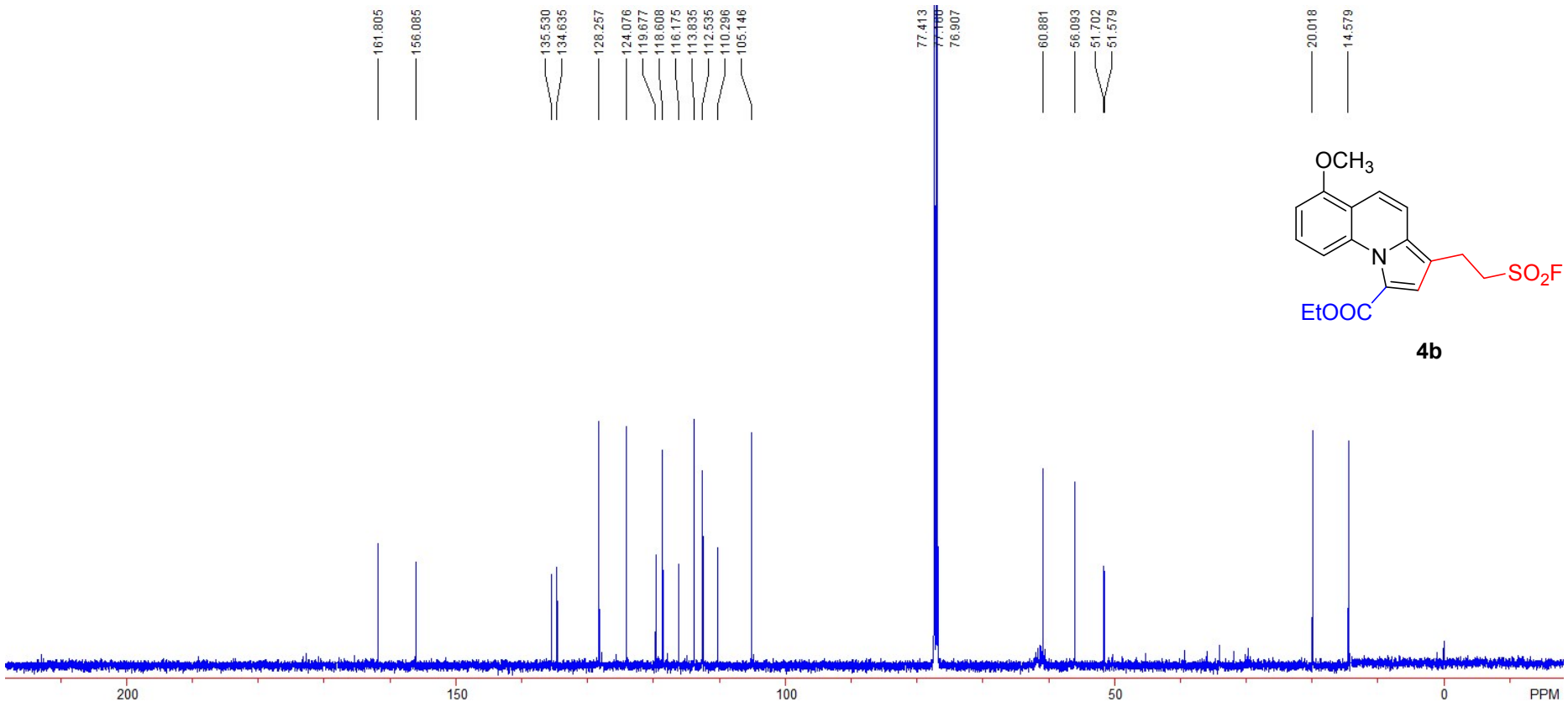


4b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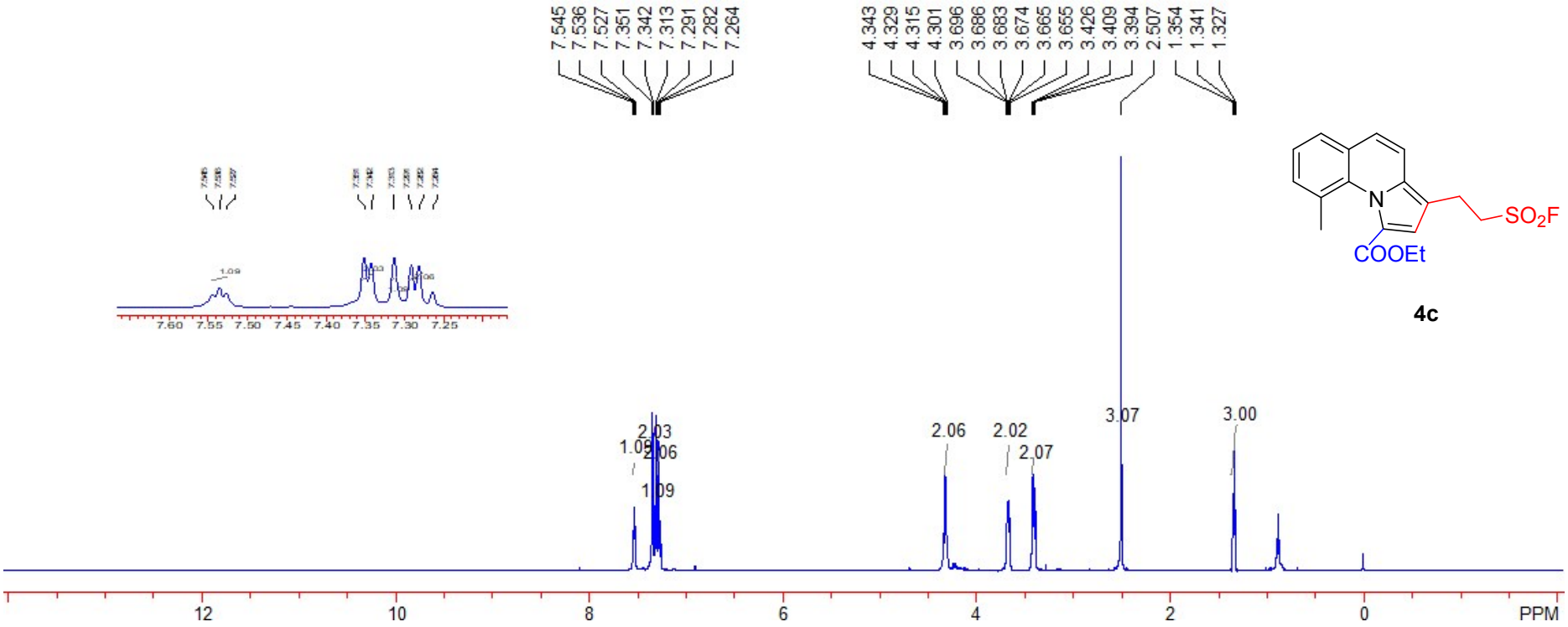
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3.683
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3.655
3.426
3.409
3.394
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1.354
1.341
1.327
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SO2F
COOEt
4c
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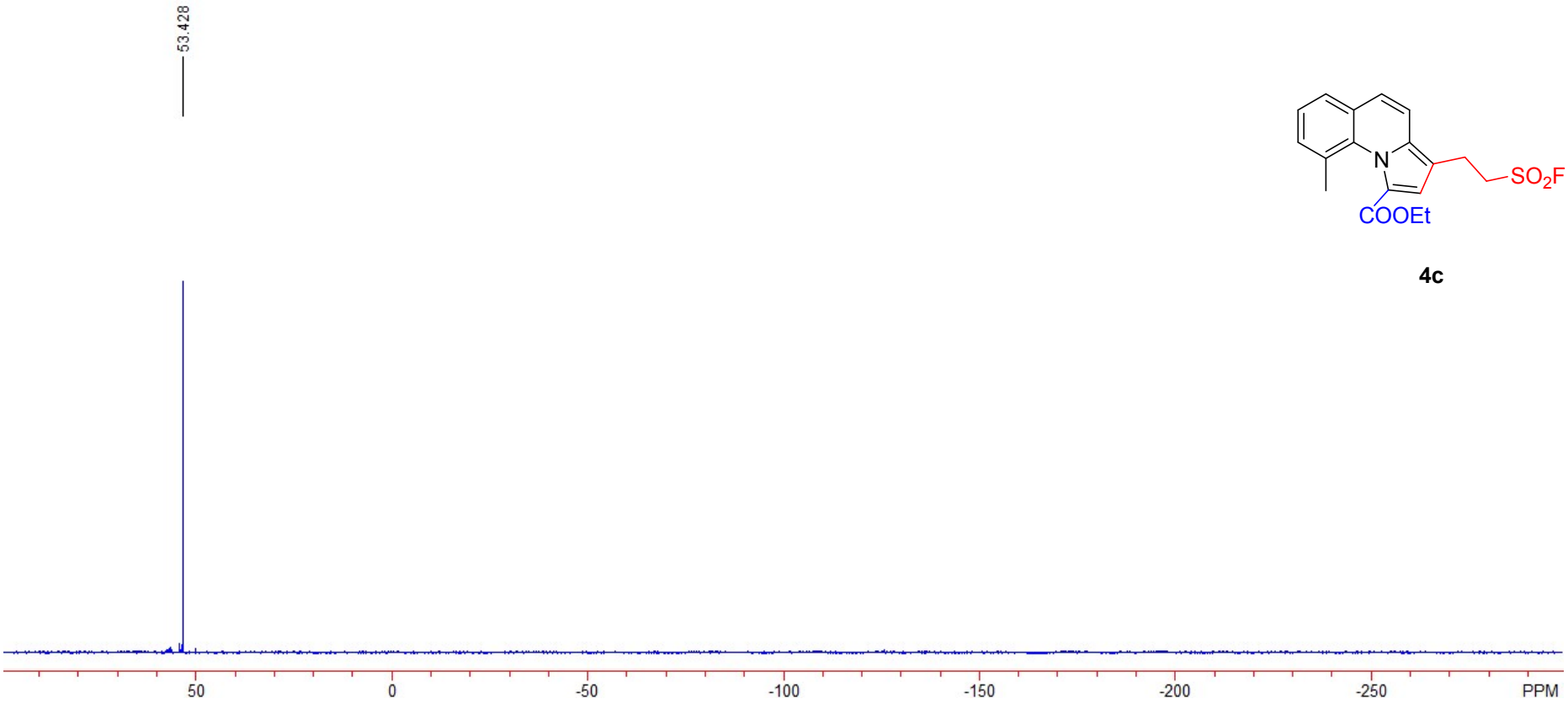

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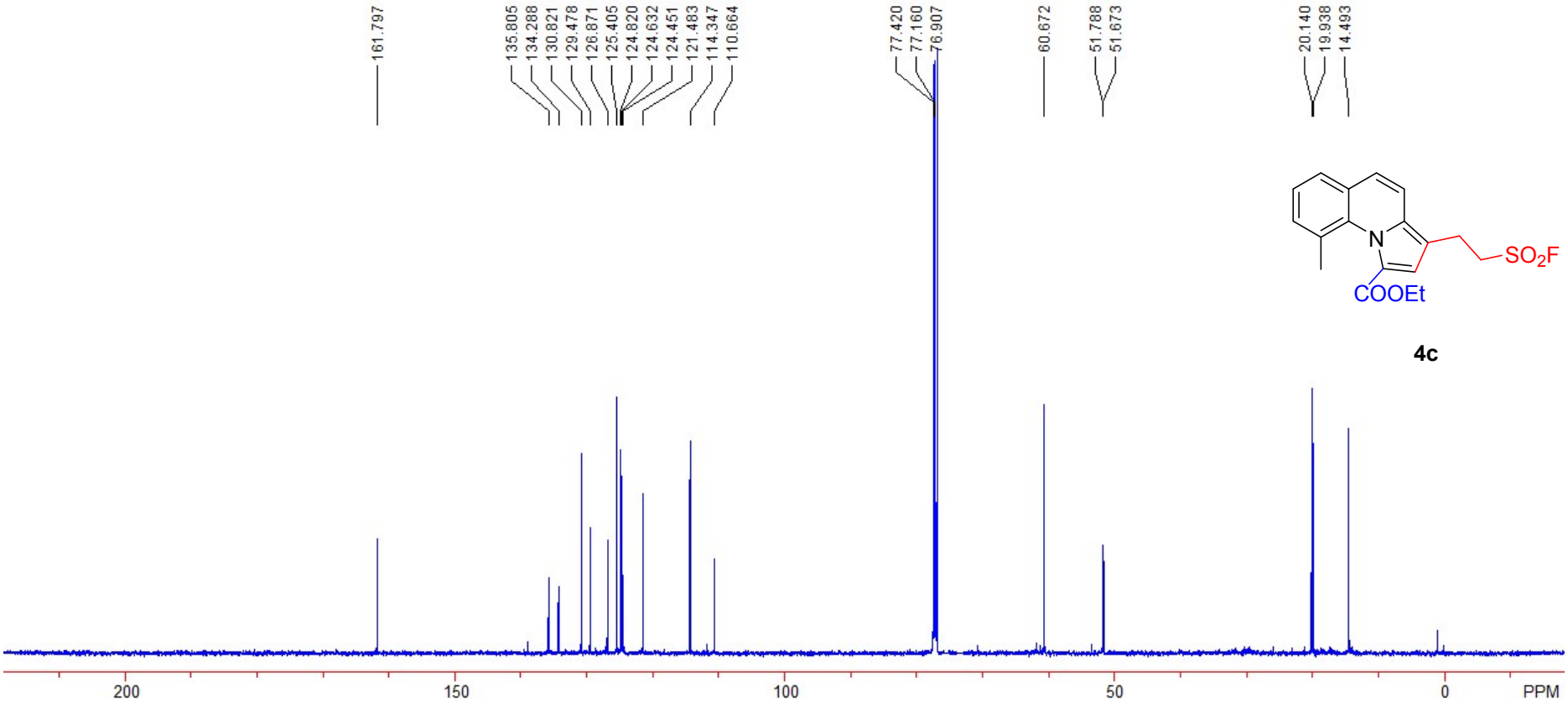
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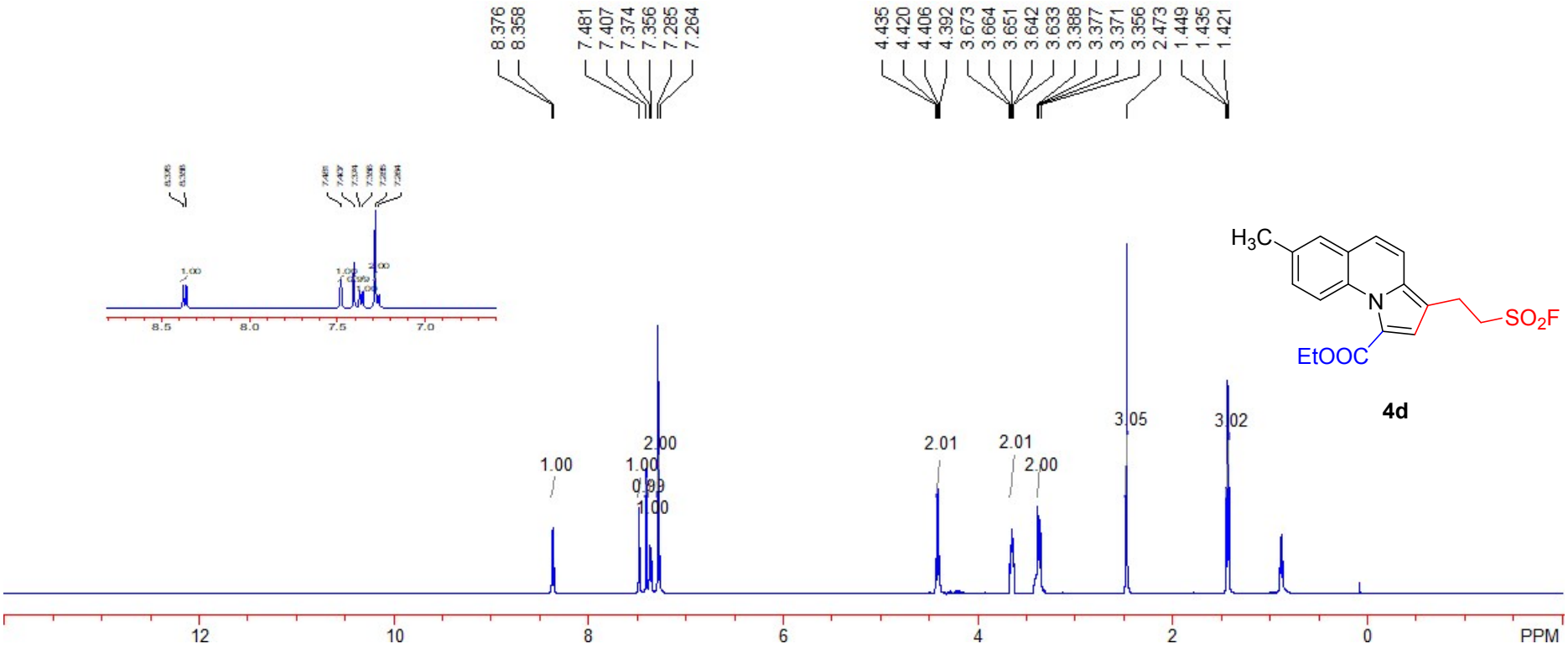
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3.642
3.633
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3.371
3.356
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1.435
1.421
1.00
1.00
2.00
1.00
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1.00
2.01
2.01
2.00
3.05
3.02
12
10
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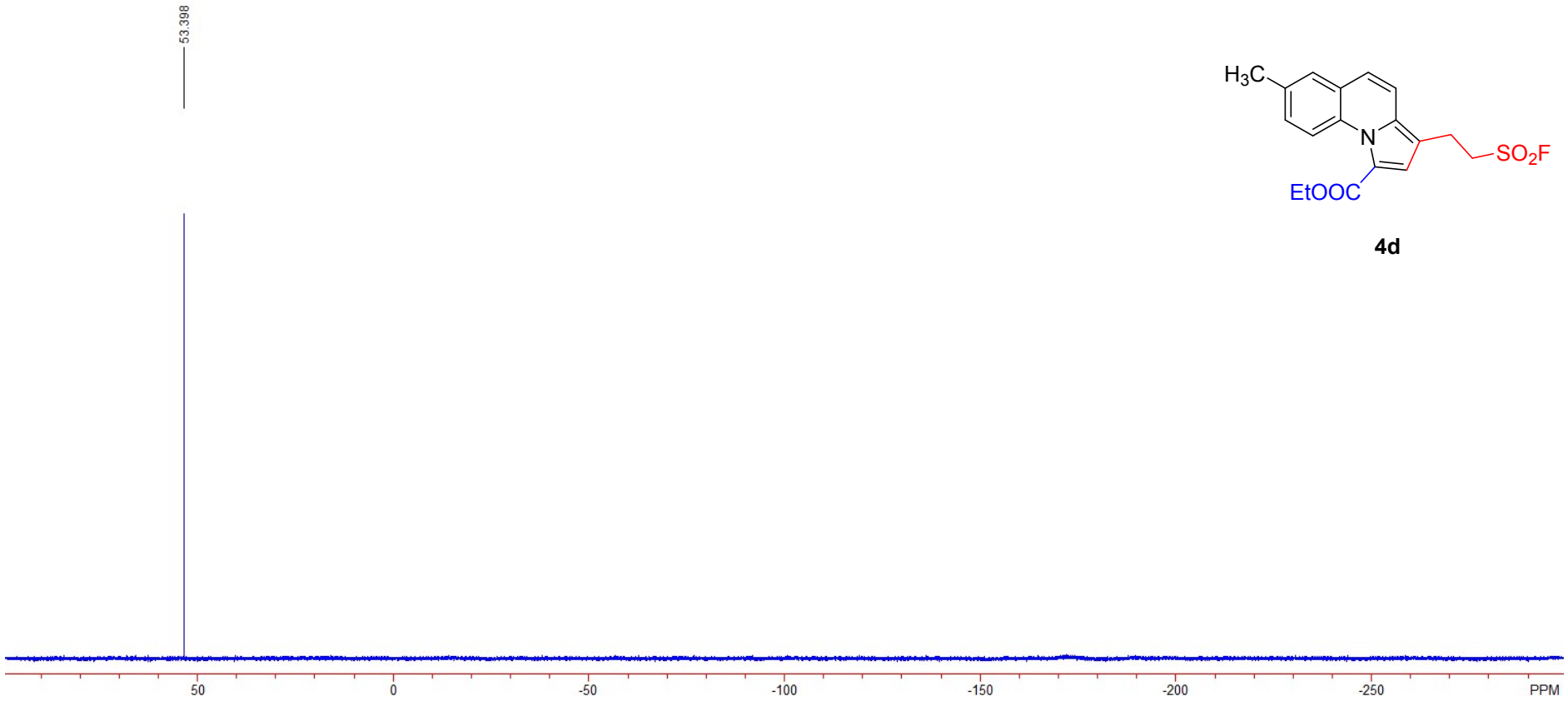
EtOOC
4d



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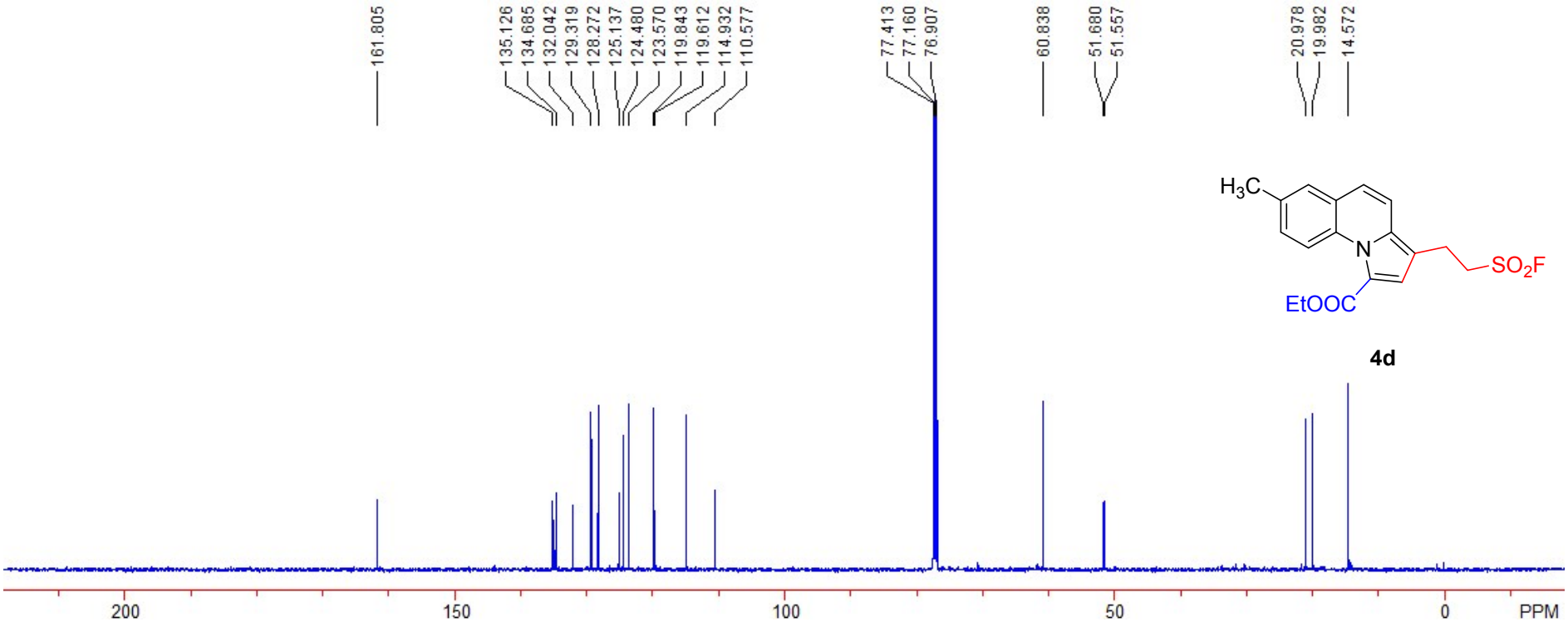
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76.907
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51.680
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4d
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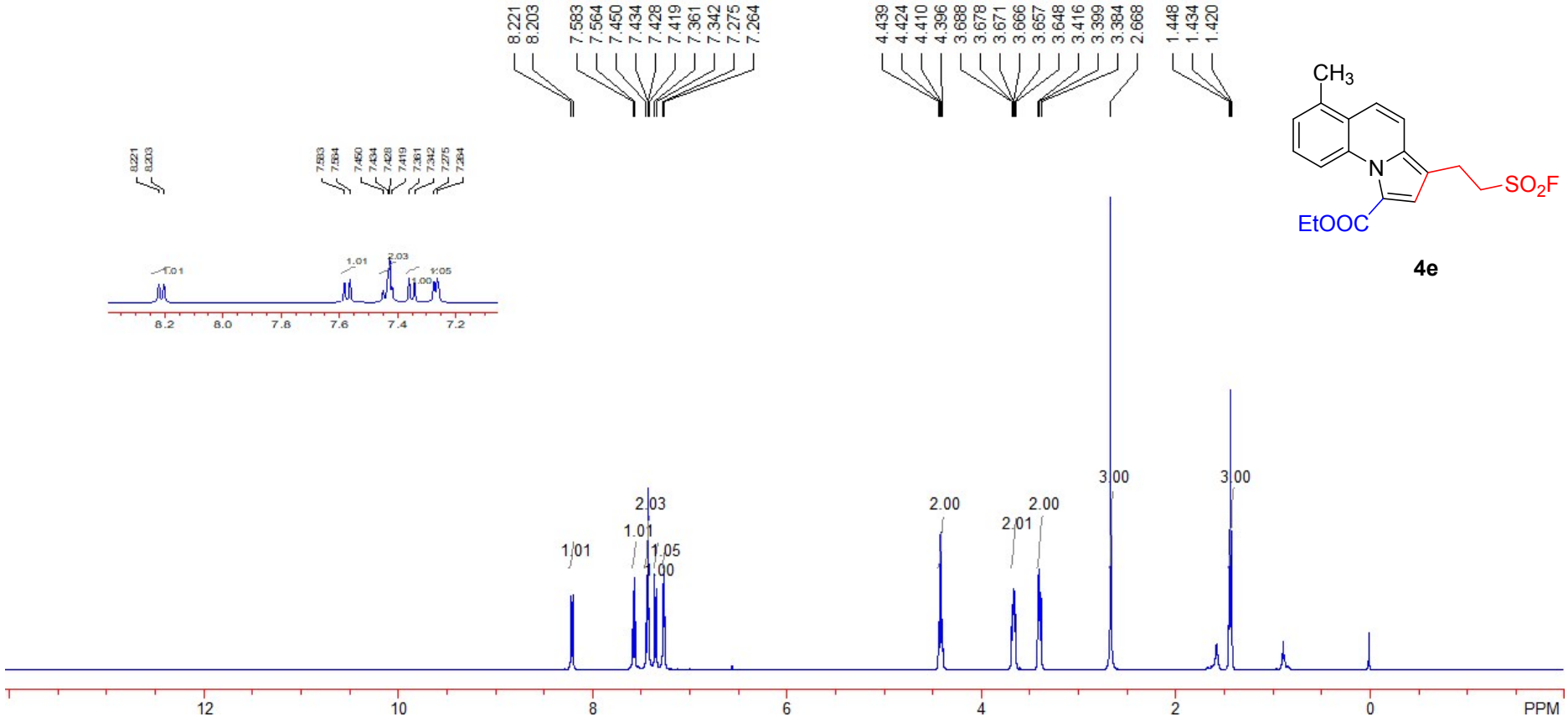
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4.410
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3.666
3.657
3.648
3.416
3.399
3.384
2.668
1.448
1.434
1.420
CH3
N
SO2F
EtOOC
4e
1.01
2.03
1.01
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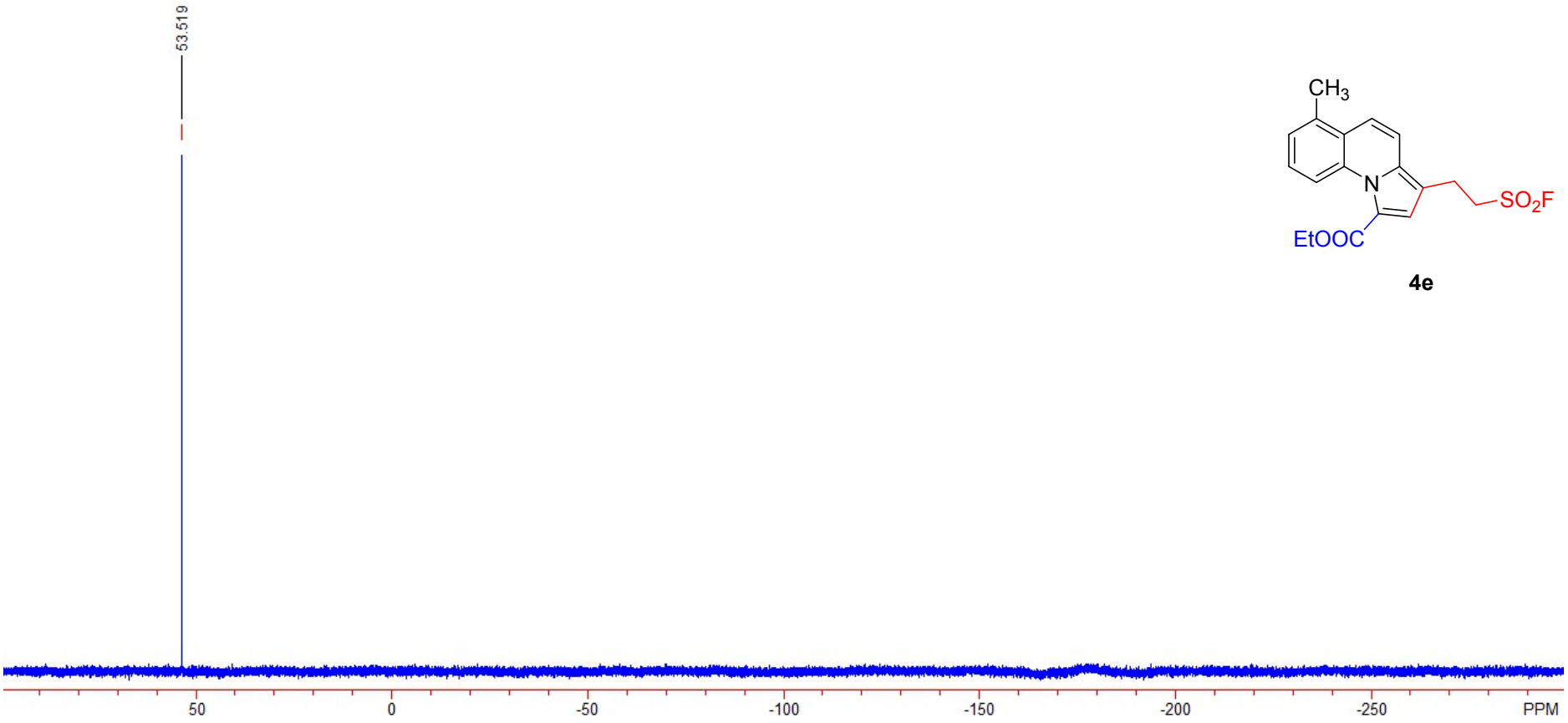

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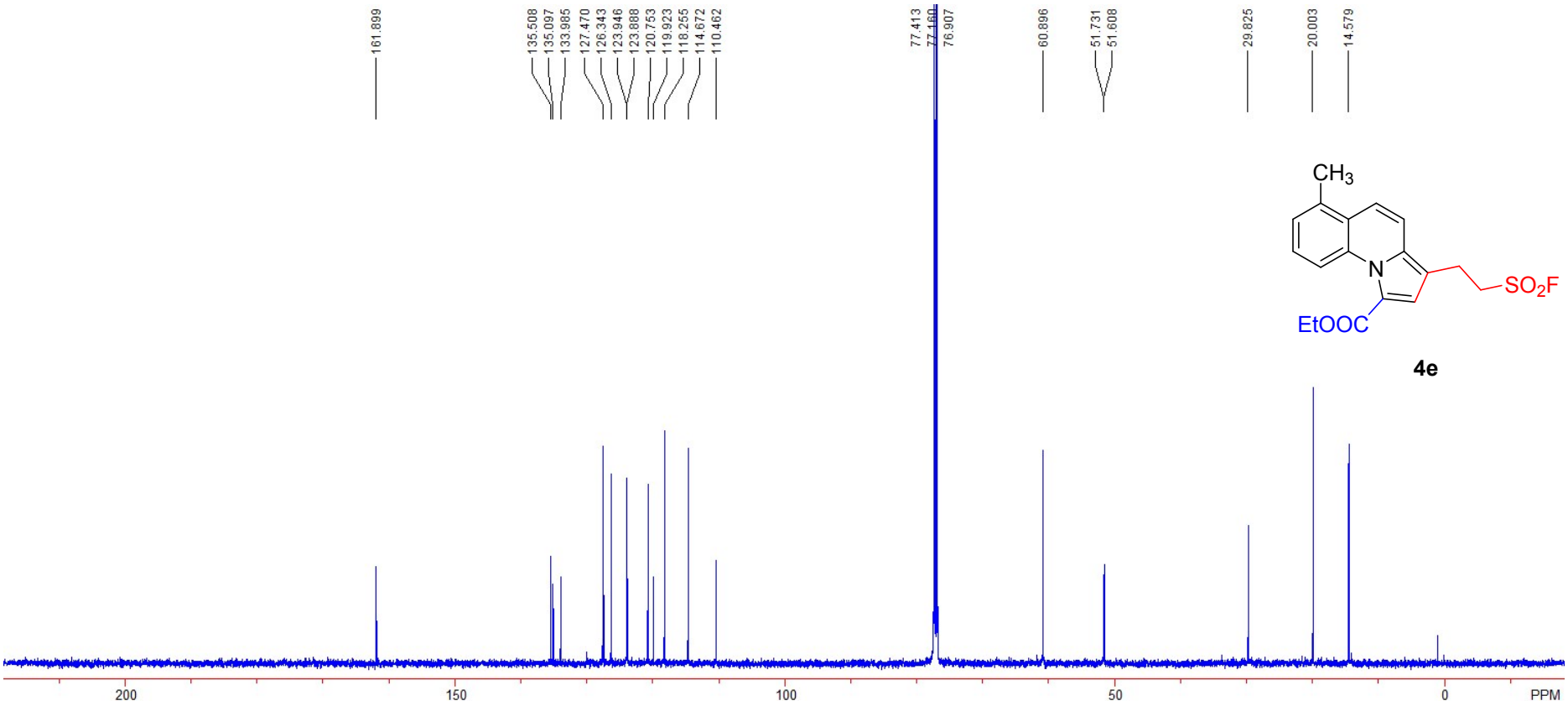
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77.160
76.907
60.896
51.731
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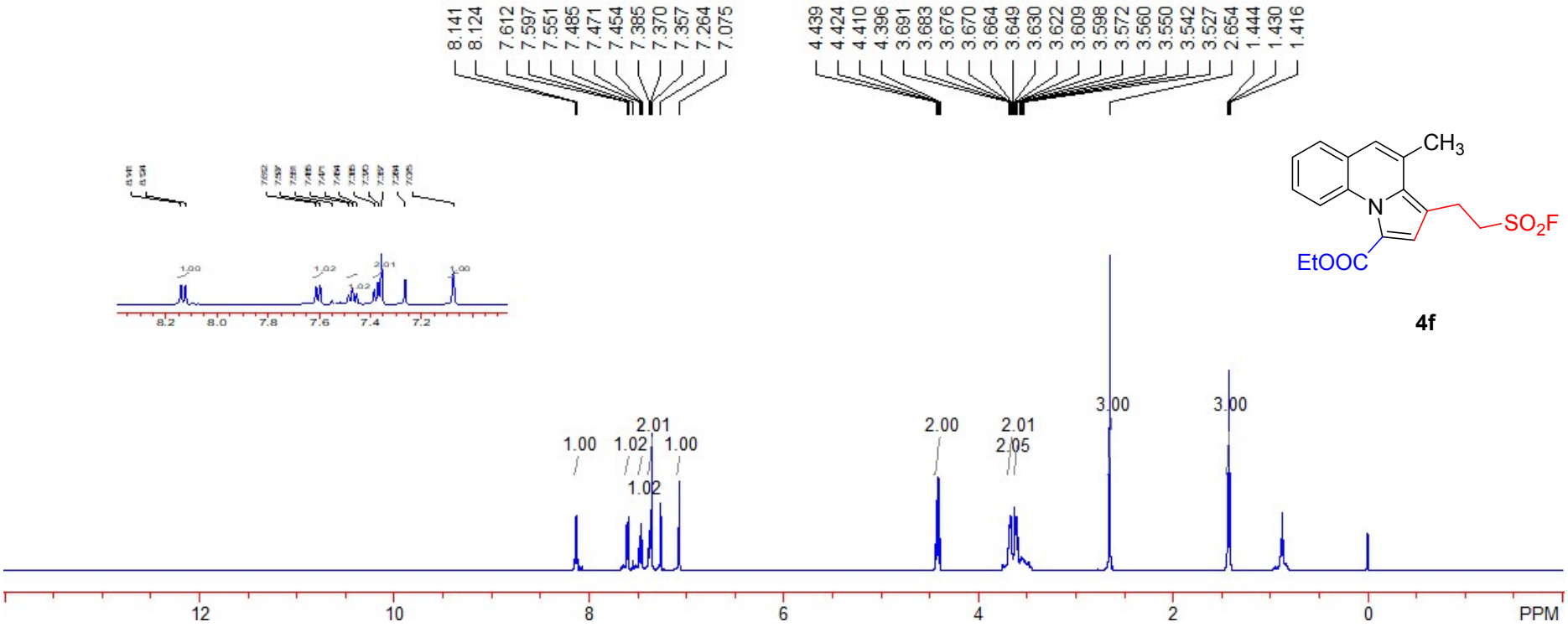
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4.410
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3.676
3.670
3.664
3.649
3.630
3.622
3.609
3.598
3.572
3.560
3.550
3.542
3.527
2.654
1.444
1.430
1.416
CH3
N
SO2F
EtOOC
4f
1.00
1.02
2.01
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3.00
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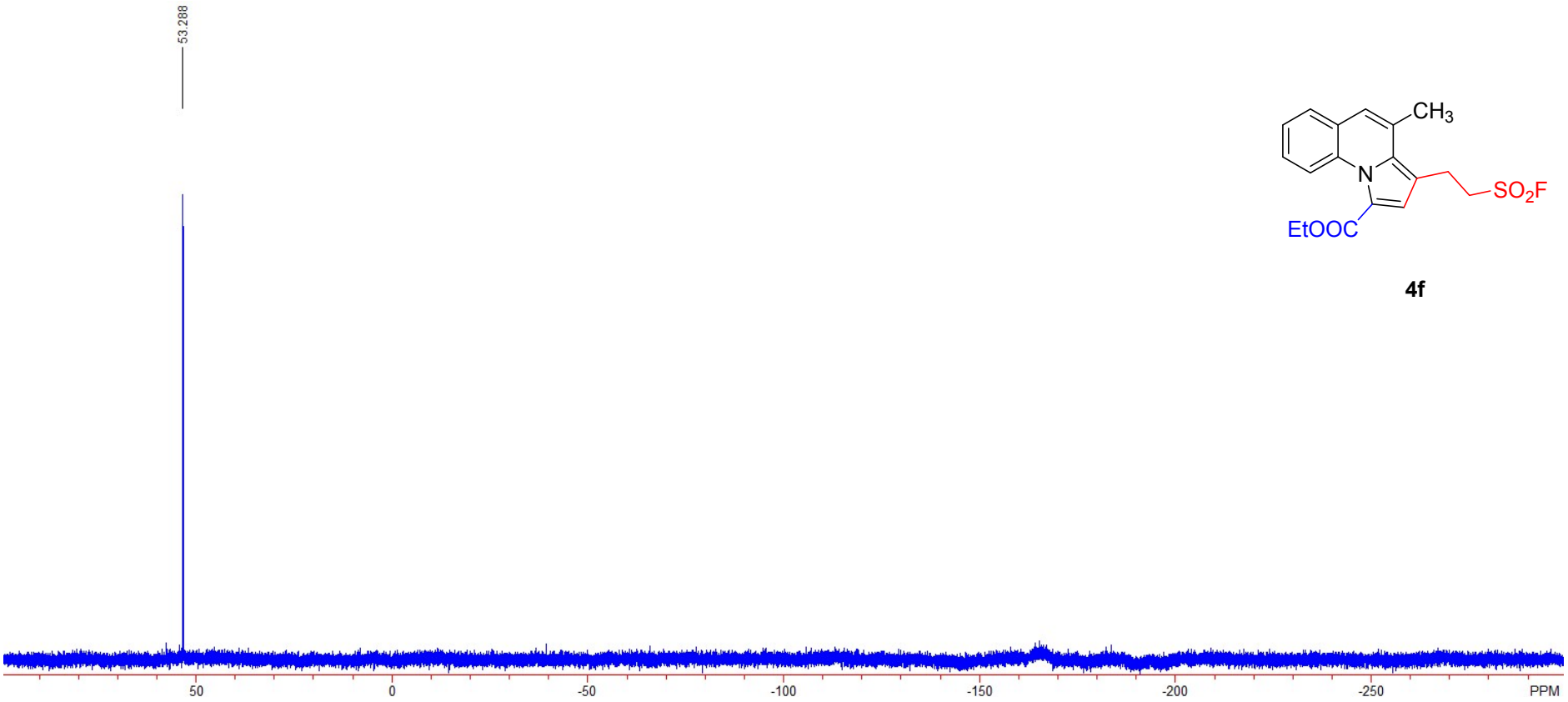

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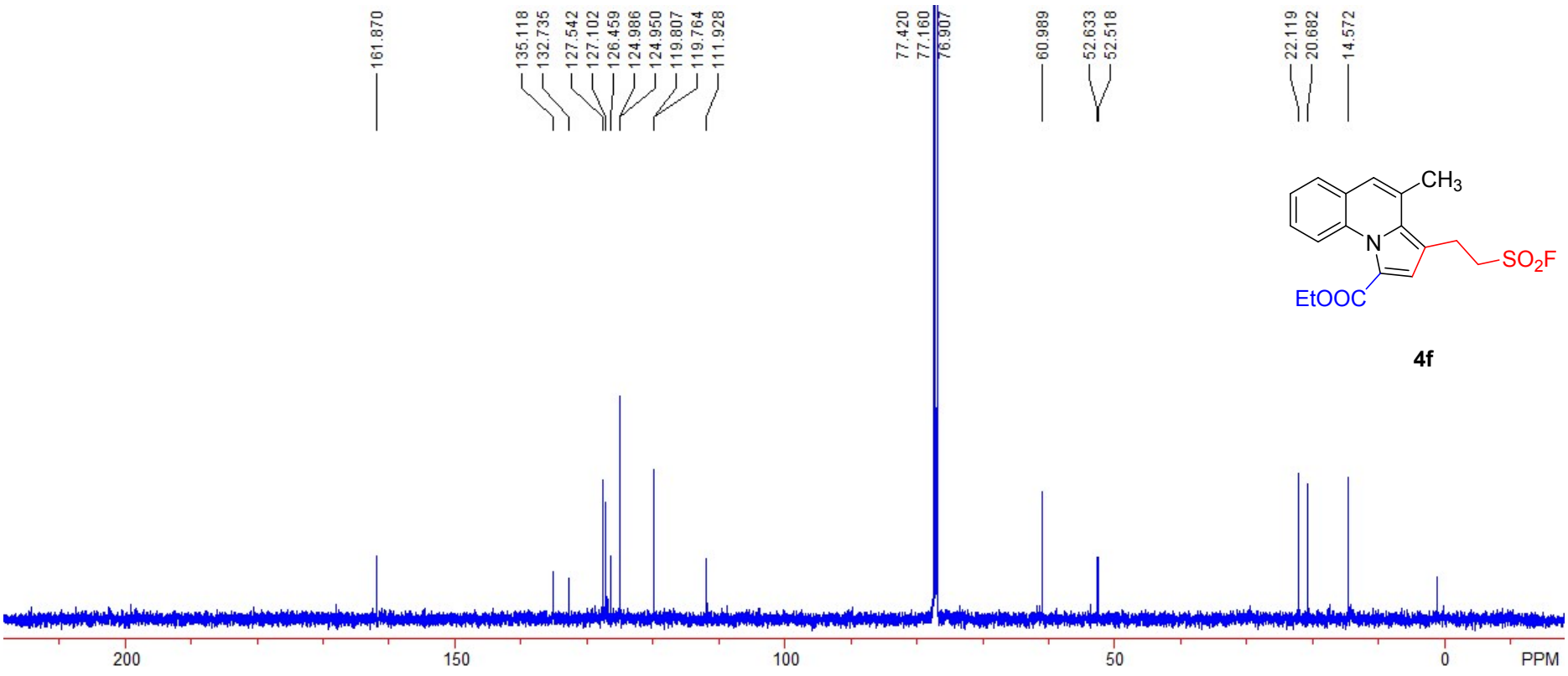
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76.907
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52.633
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14.572
CH3
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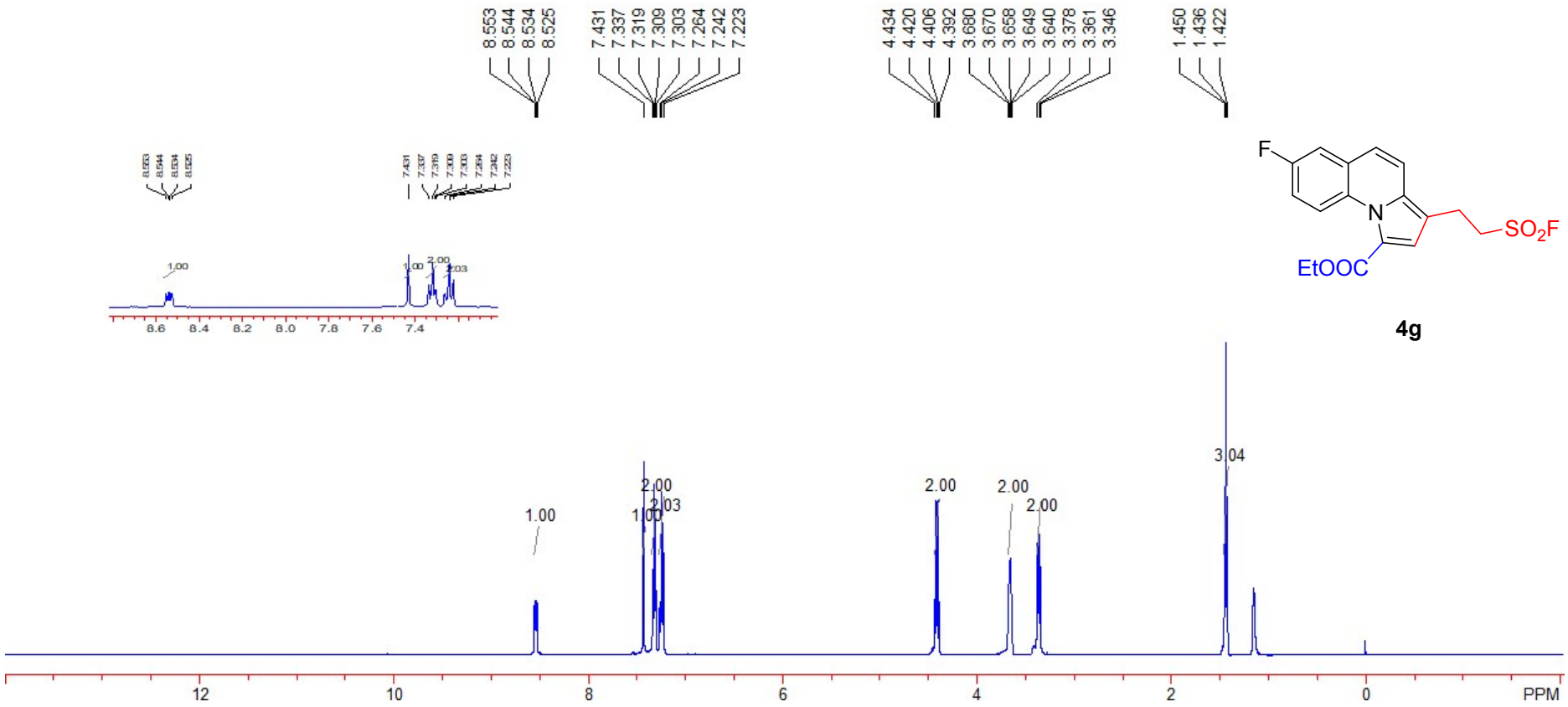
SO2F
EtOOC
200
150
100
50
0
PPM

4f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4.420
4.406
4.392
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3.670
3.658
3.649
3.640
3.378
3.361
3.346
1.450
1.436
1.422
F
N
SO2F
EtOOC
4g
1.00
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3.04
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6
4
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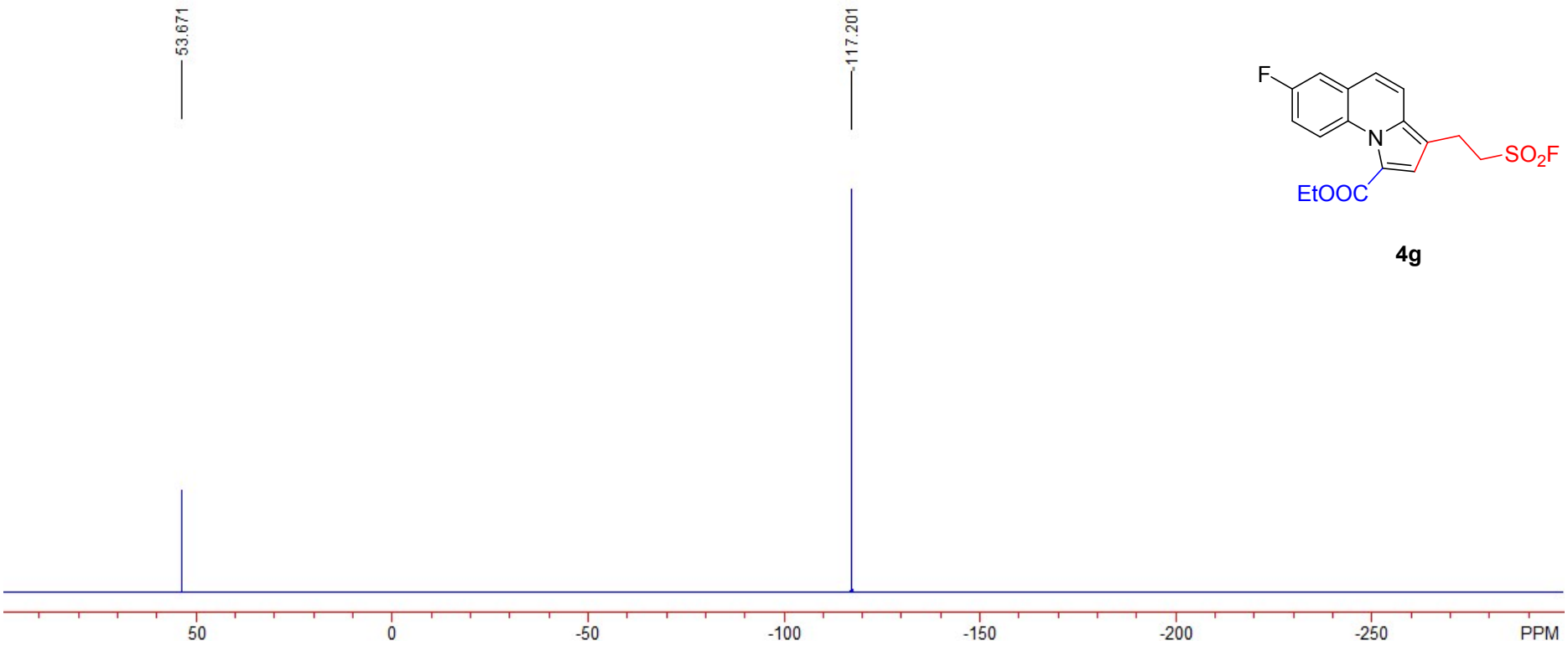

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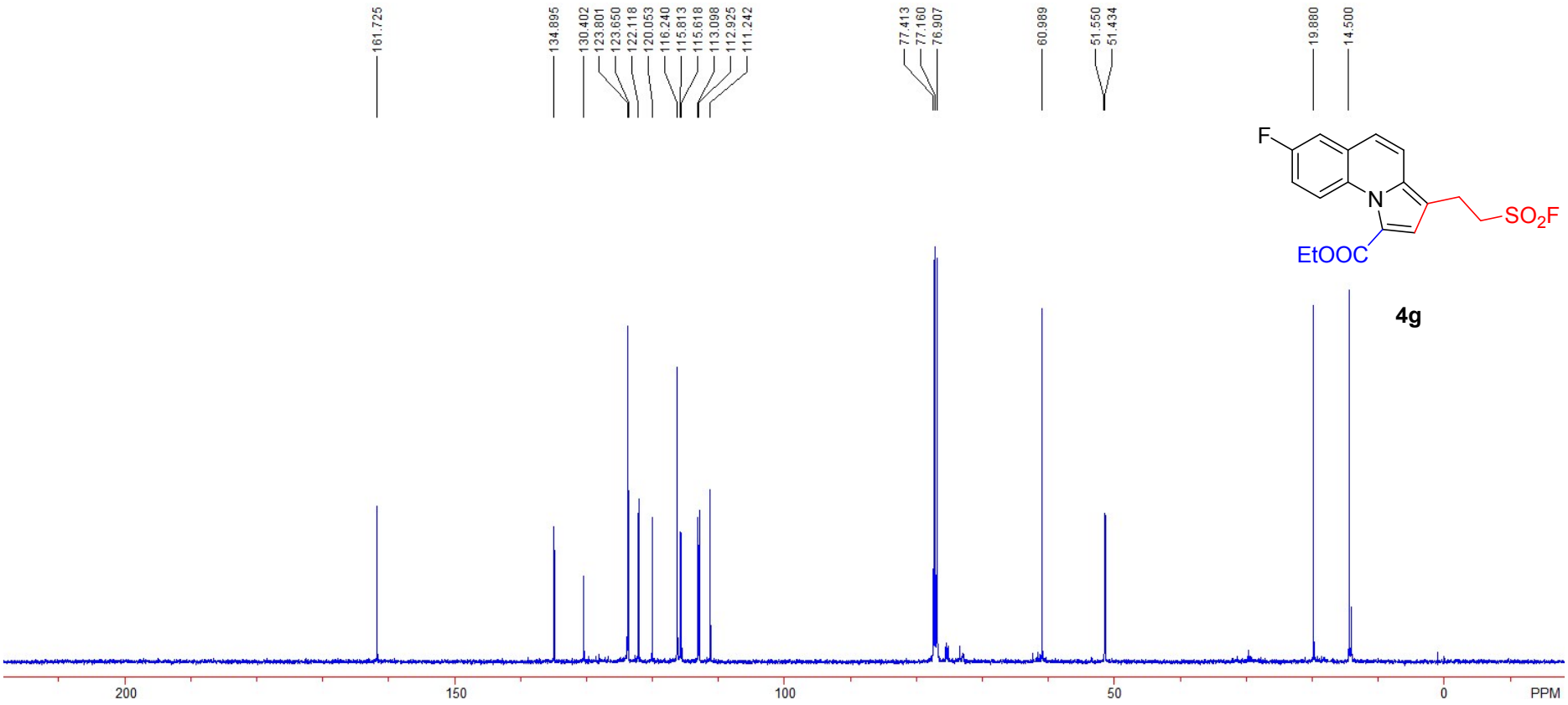
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76.907
60.989
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F
N
SO2F
EtOOC
4g
200
150
100
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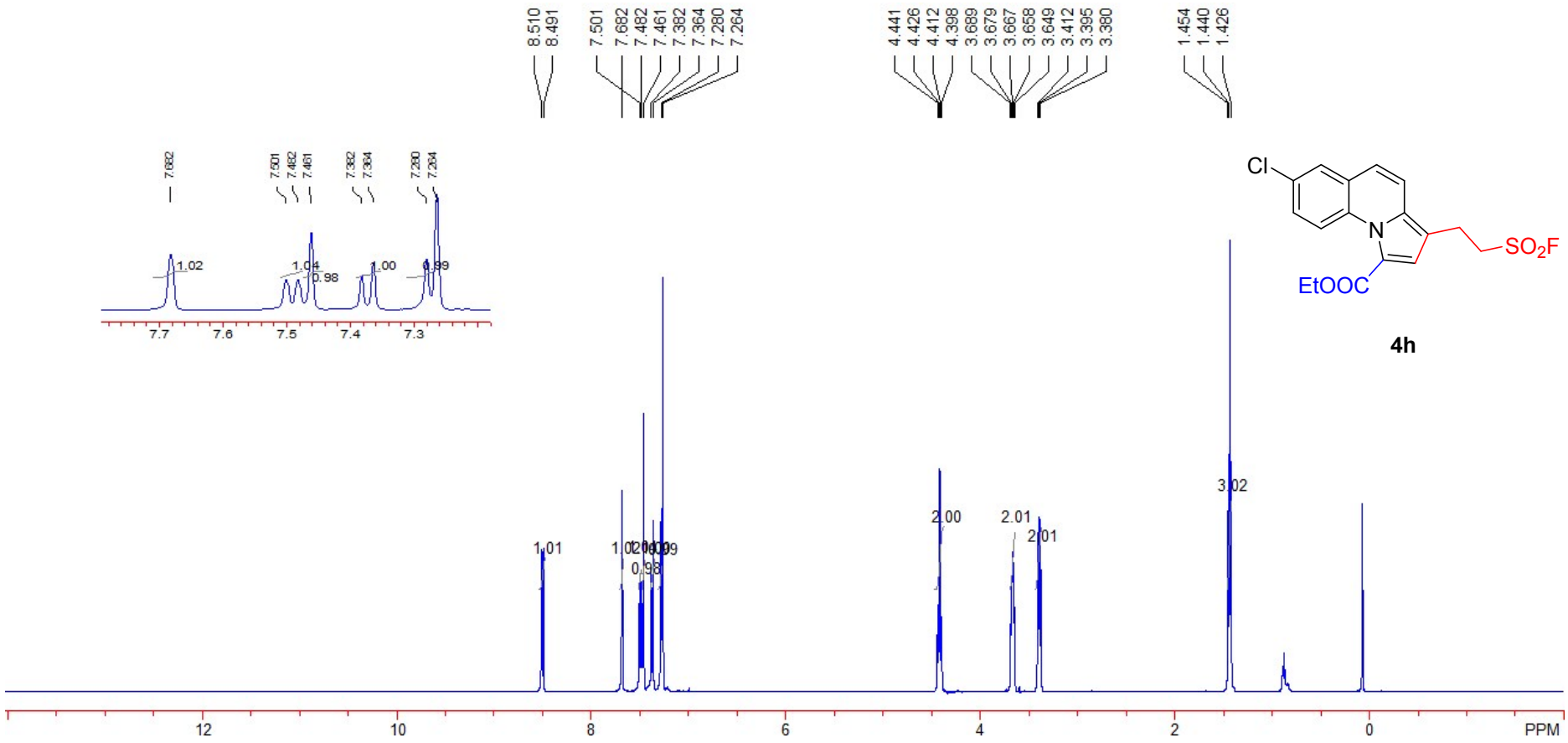
0
PPM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4.412
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1.02
0.98
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6
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2
0
PPM
Cl
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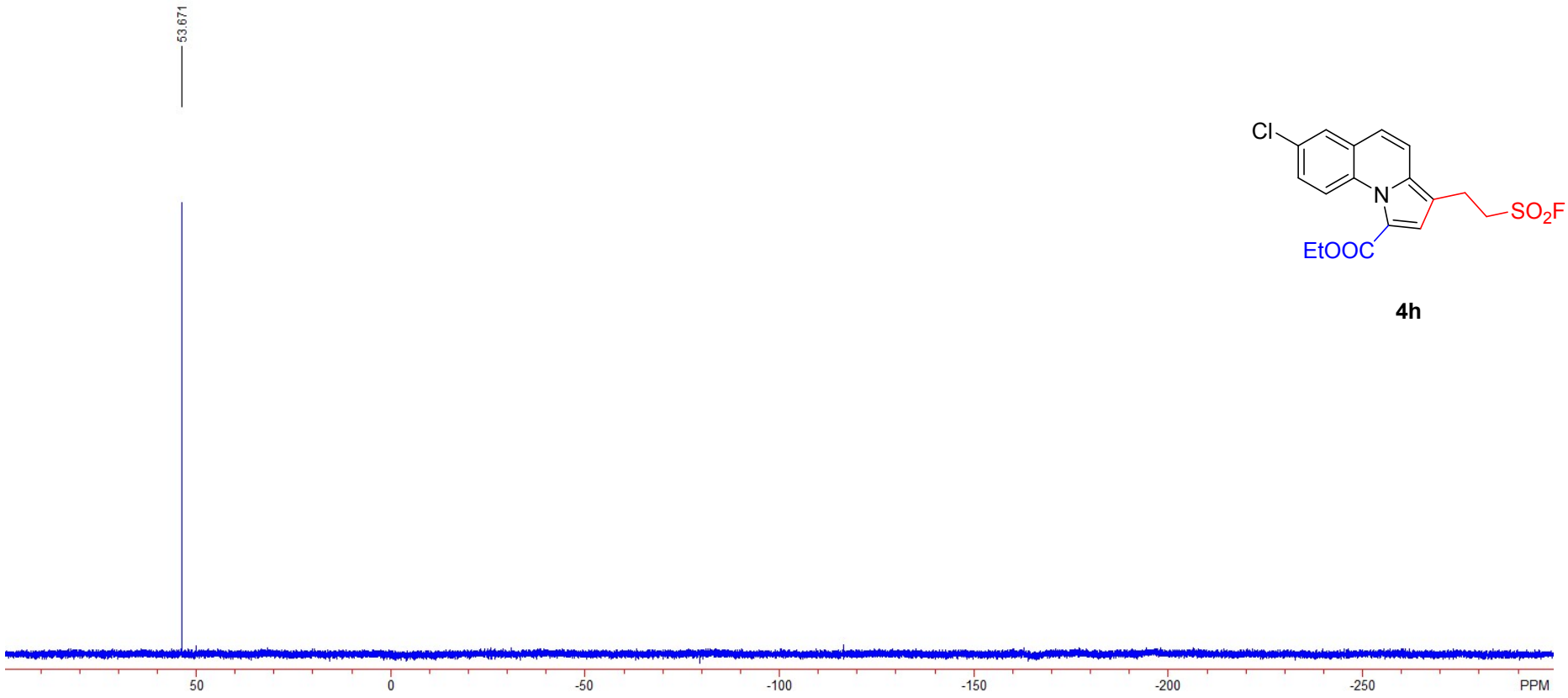
SO2F
EtOOC
4h



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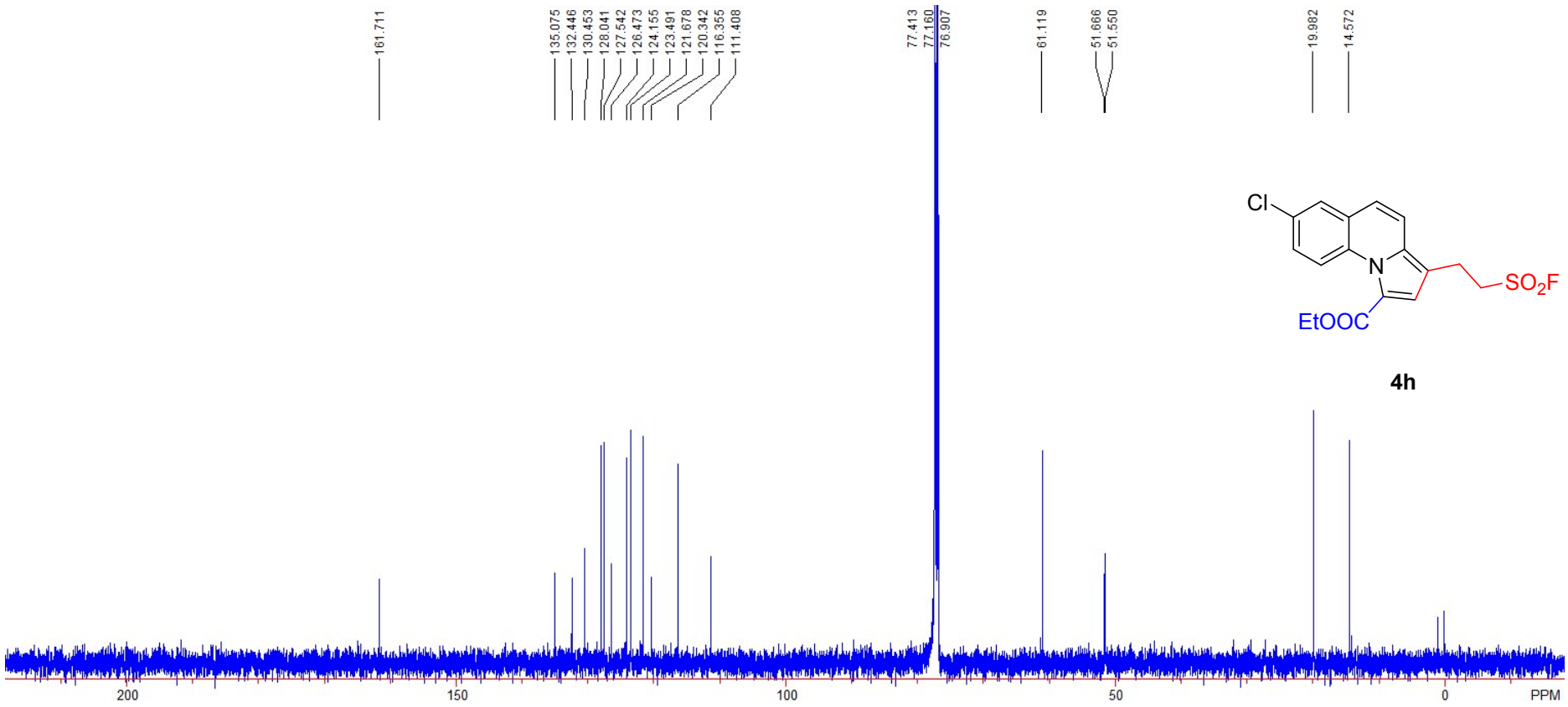
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61.119
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N
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EtOOC
4h
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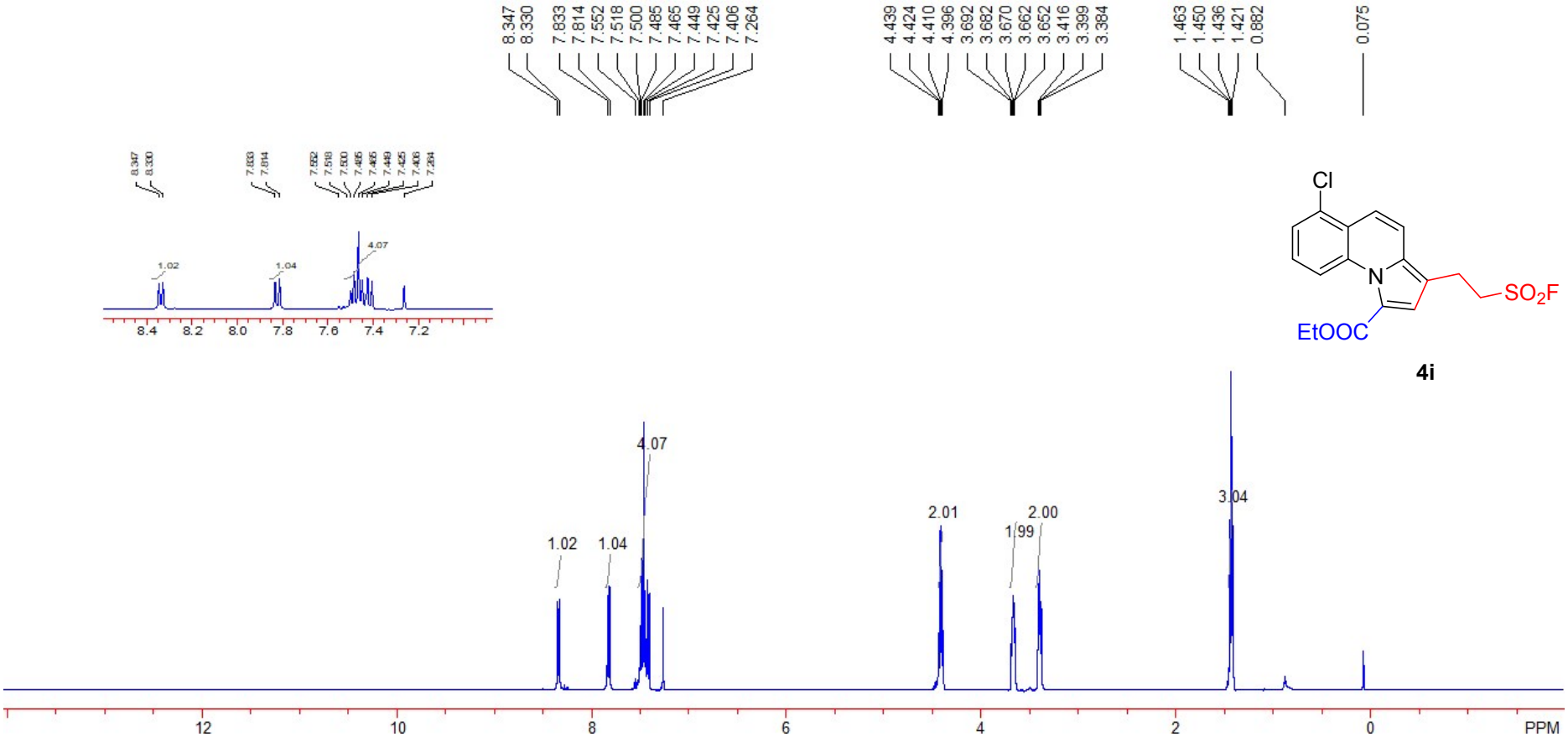
0
PPM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1.04
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8.0
7.8
7.6
7.4
7.2
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SO2F
EtOOC
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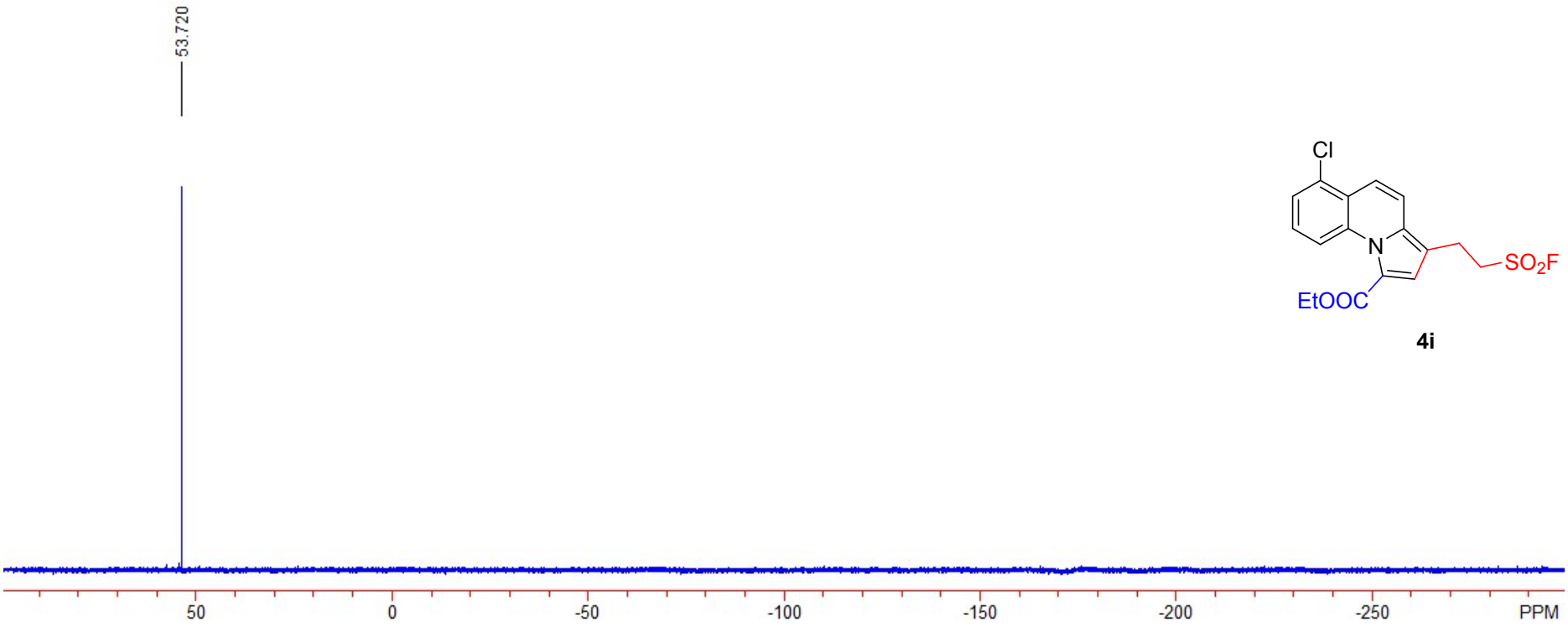

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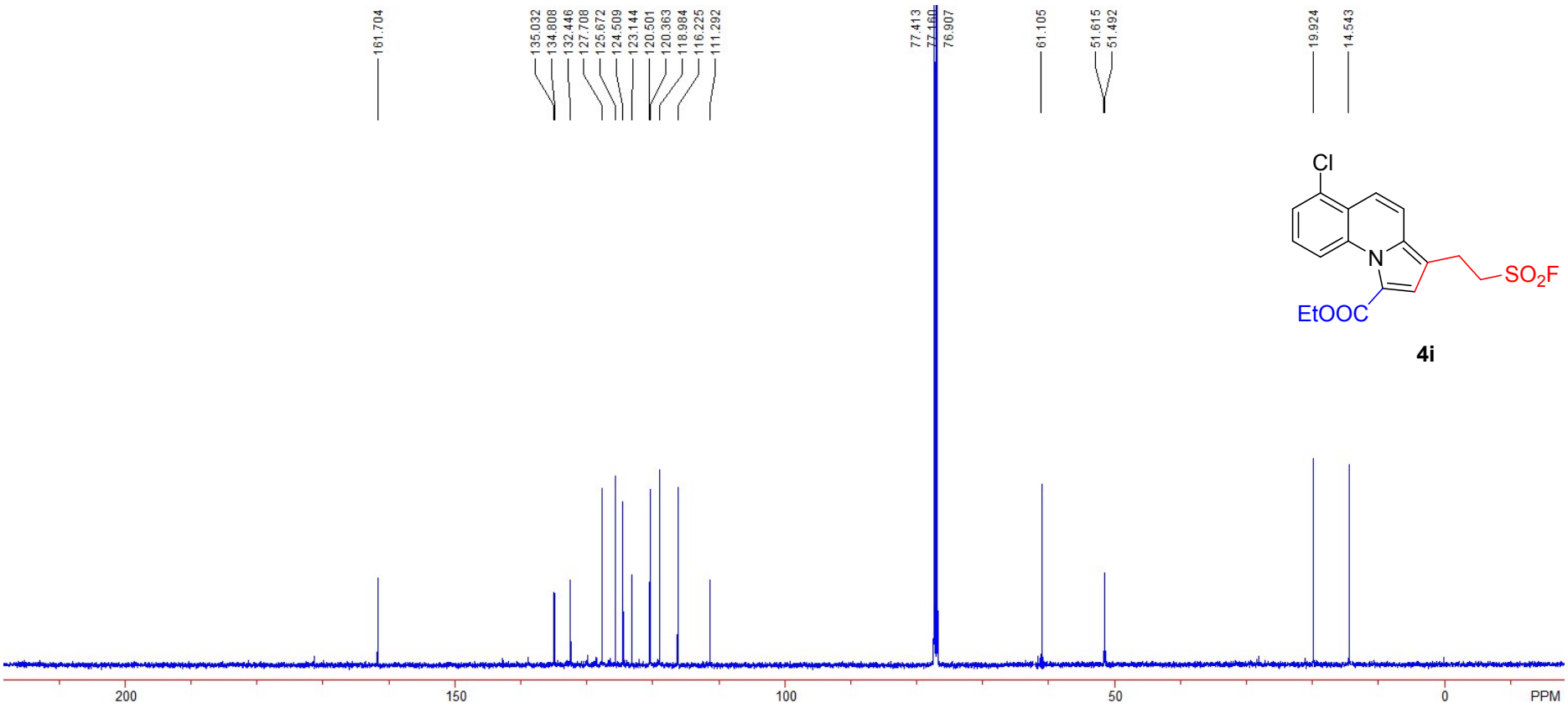
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76.907
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EtOOC
4i
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100
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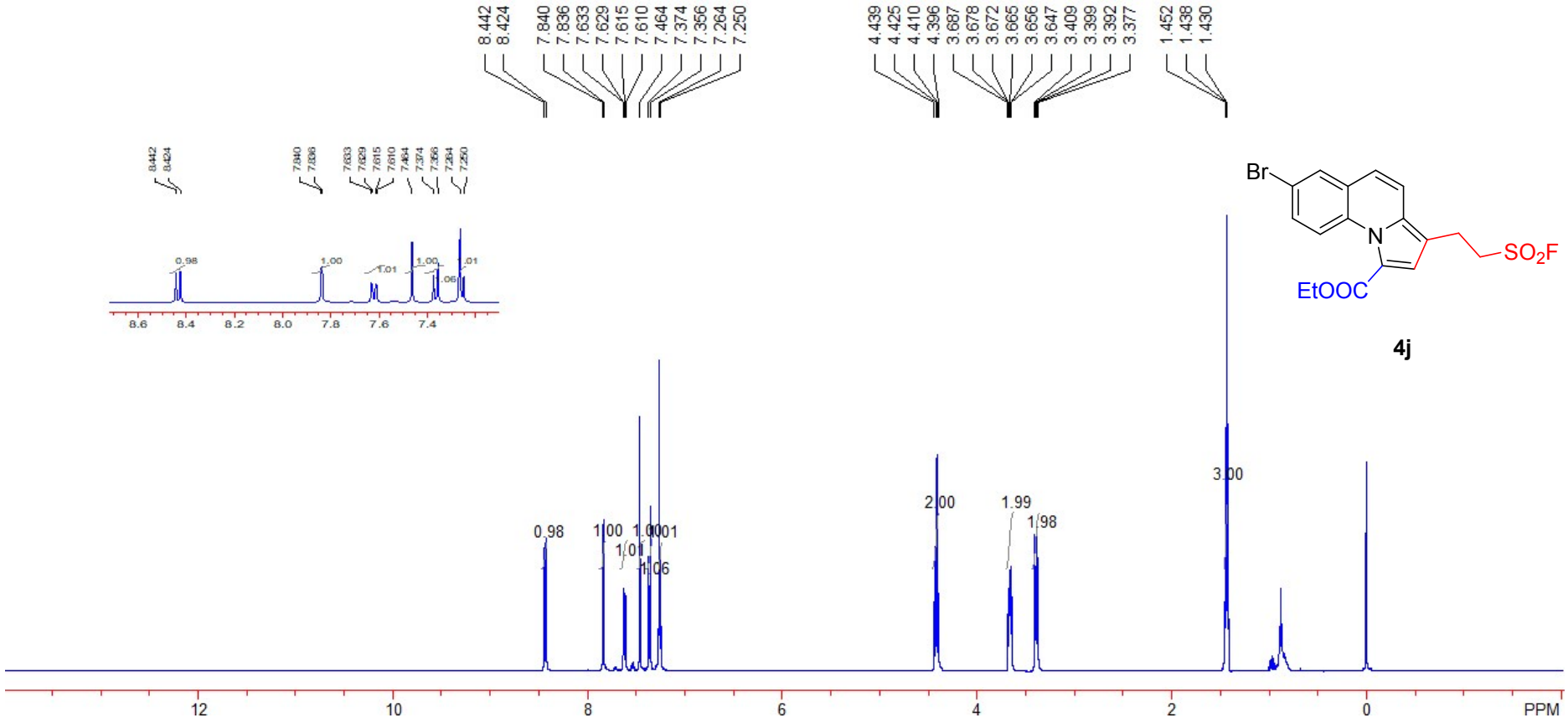
0
PPM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4.410
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3.665
3.656
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3.409
3.399
3.392
3.377
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1.438
1.430
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1.06
2.00
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6
4
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PPM
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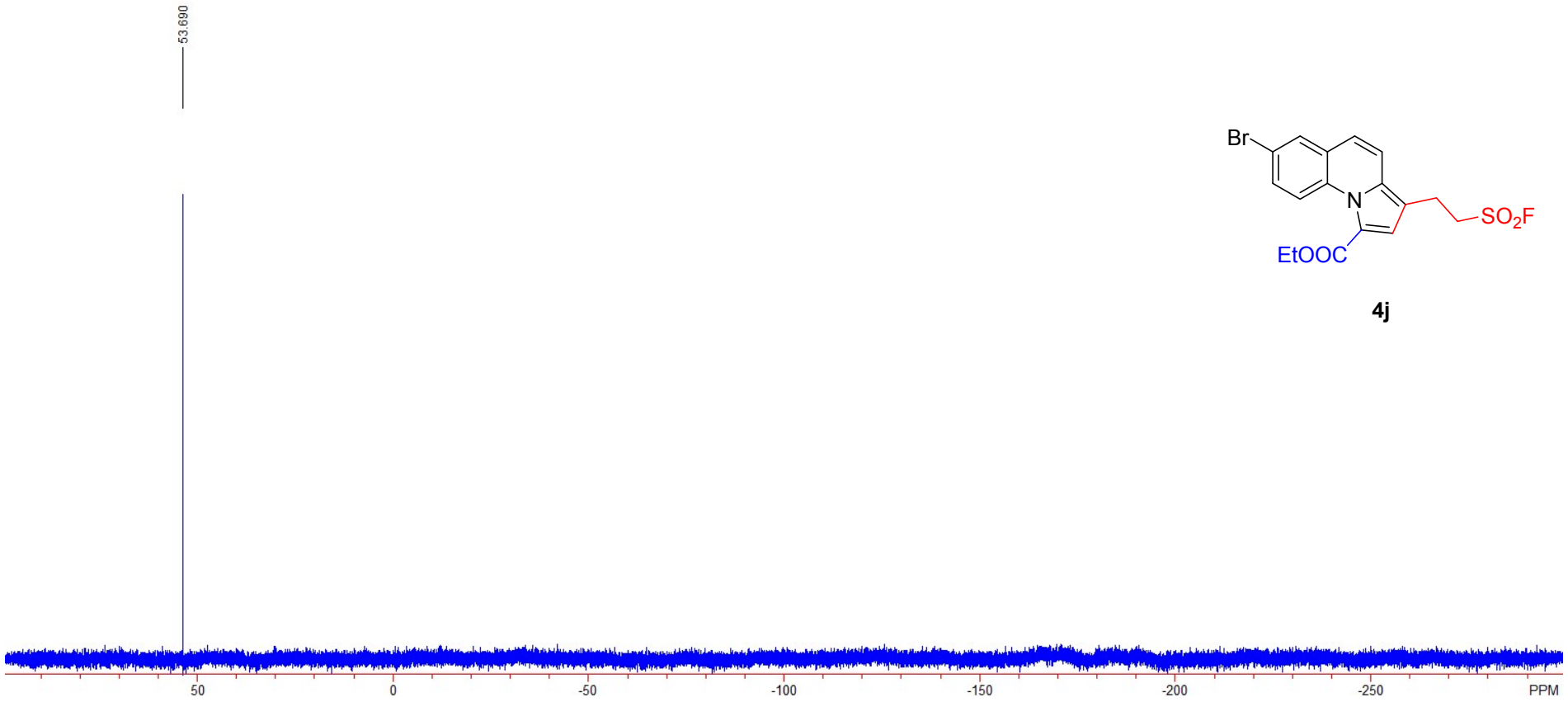
SO2F
EtOOC
4j



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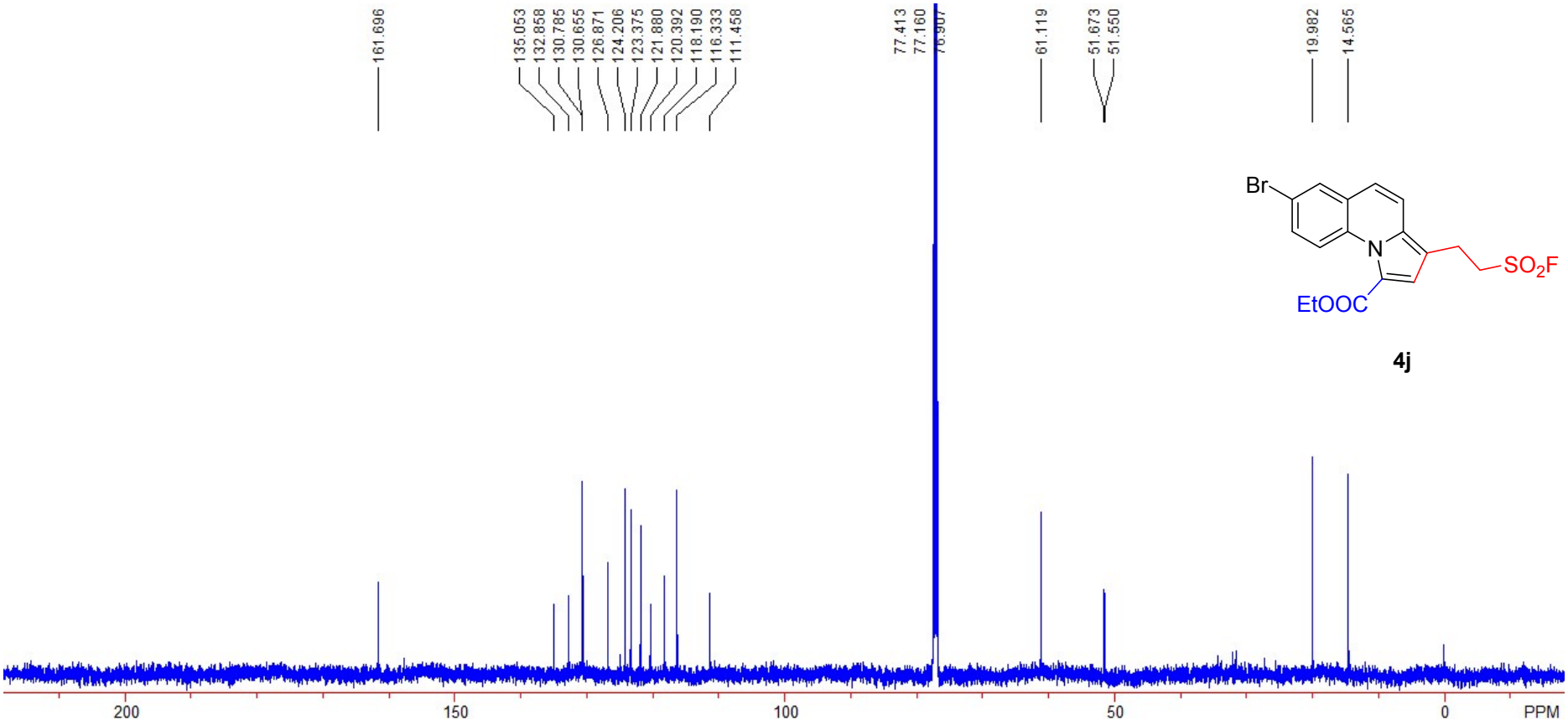
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77.160
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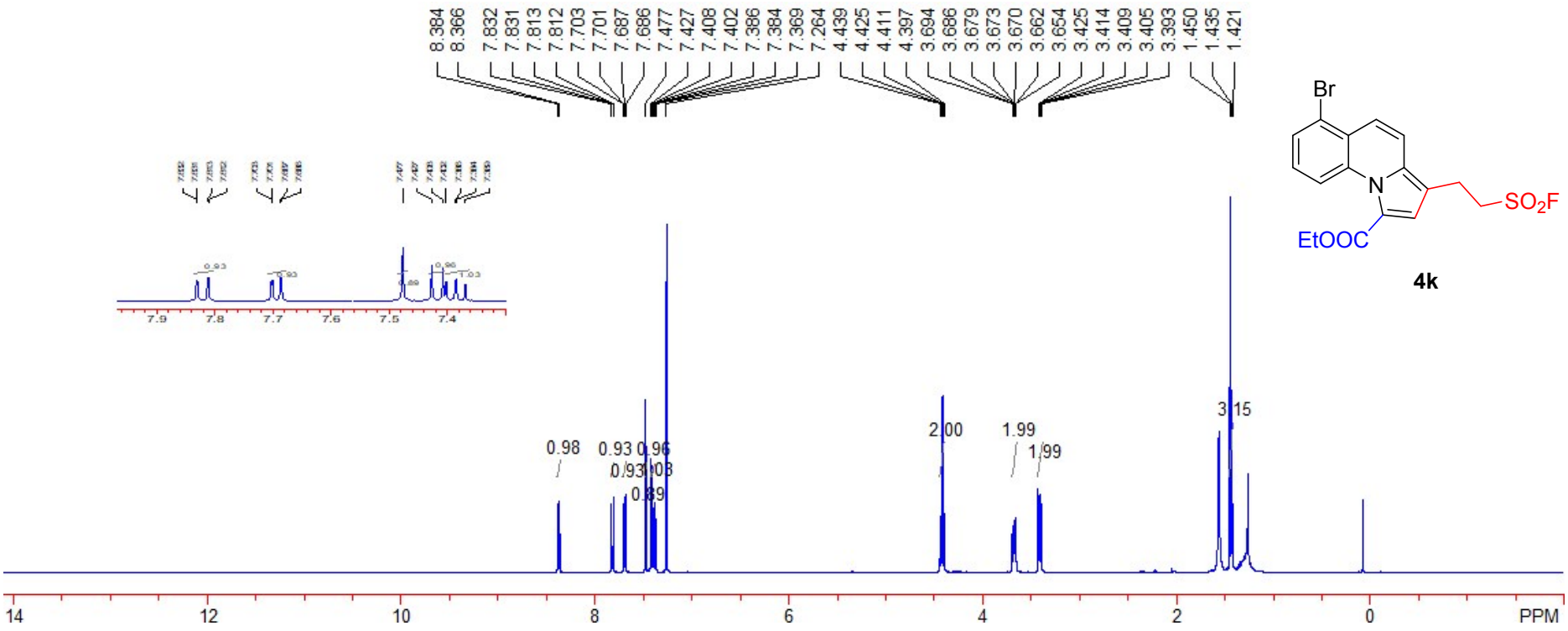
50
0
PPM

4j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1.421
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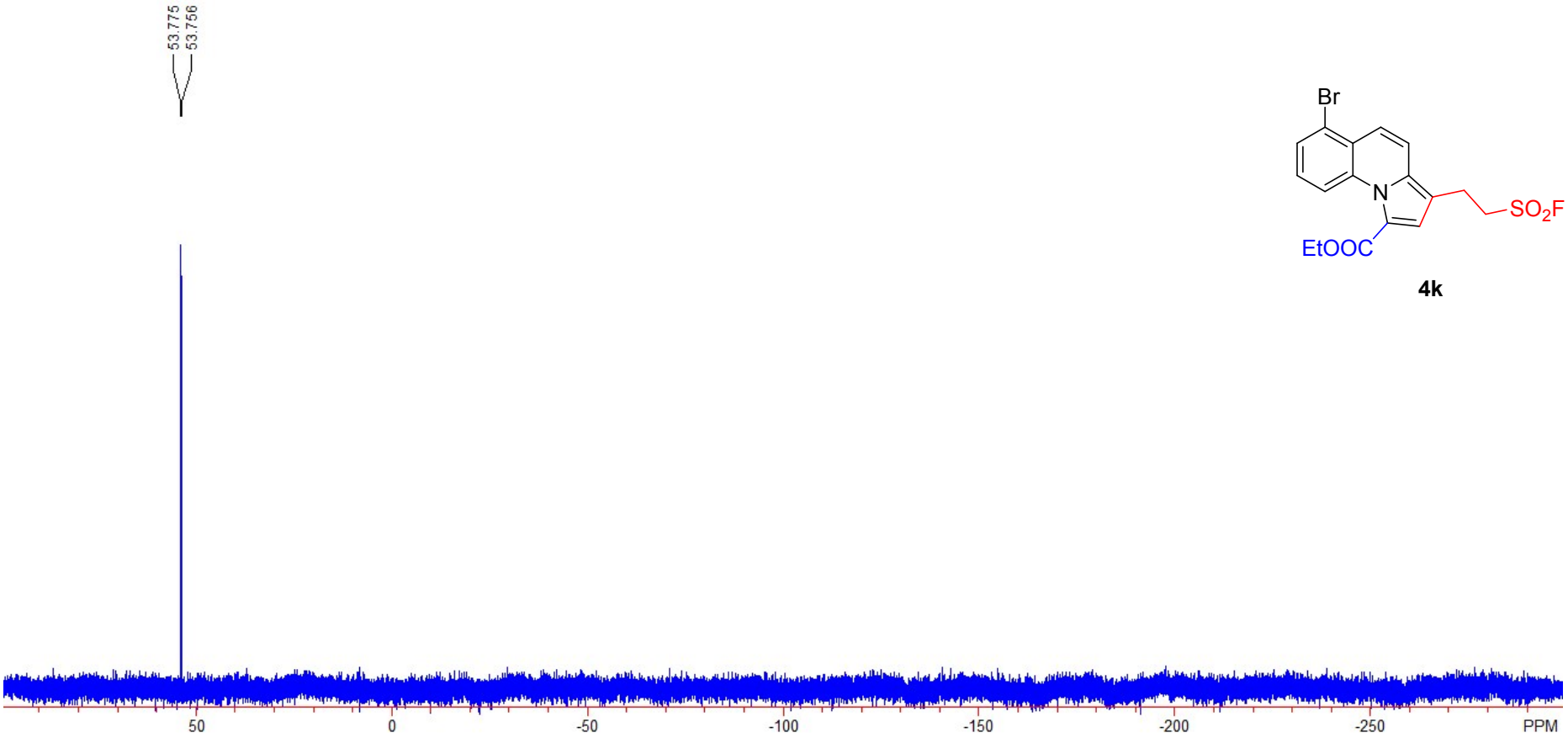

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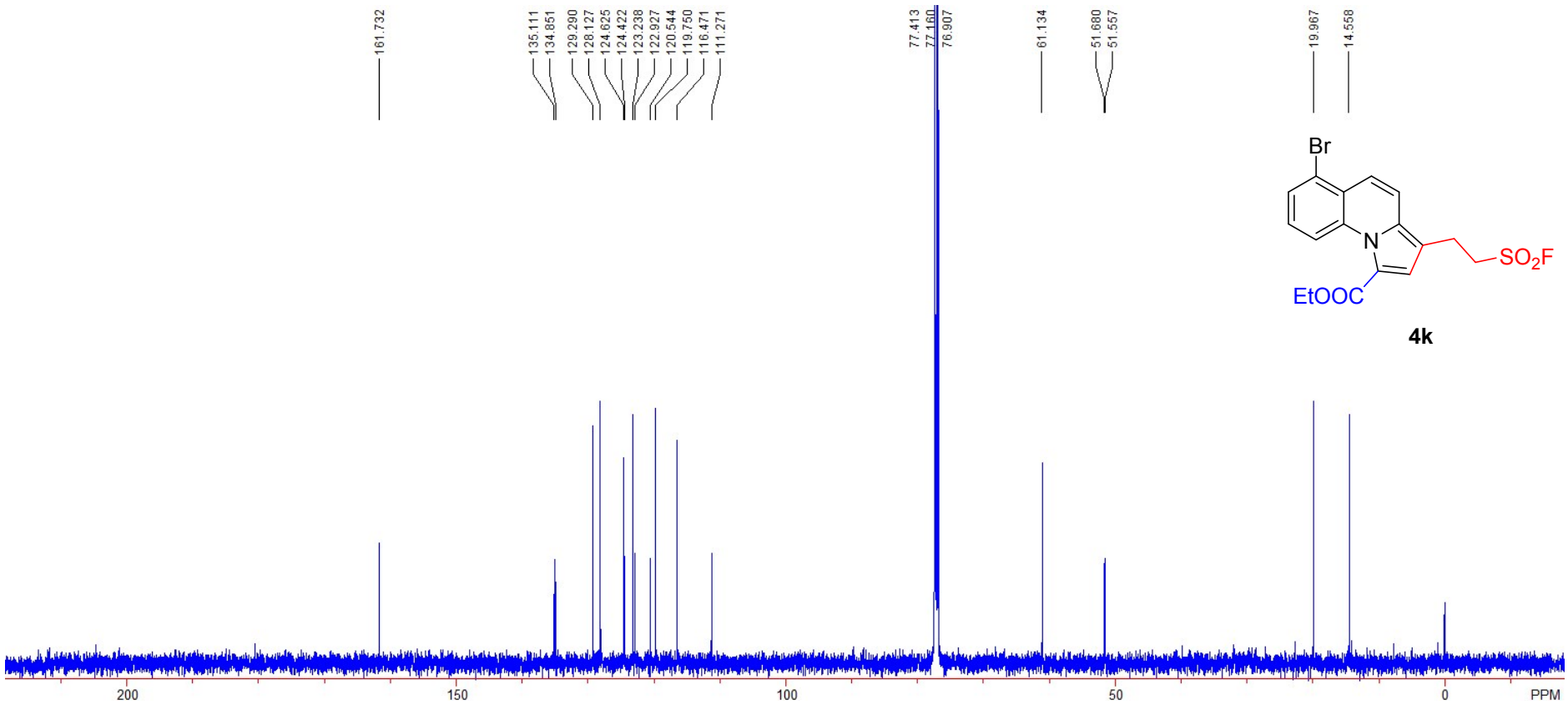
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76.907
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Br
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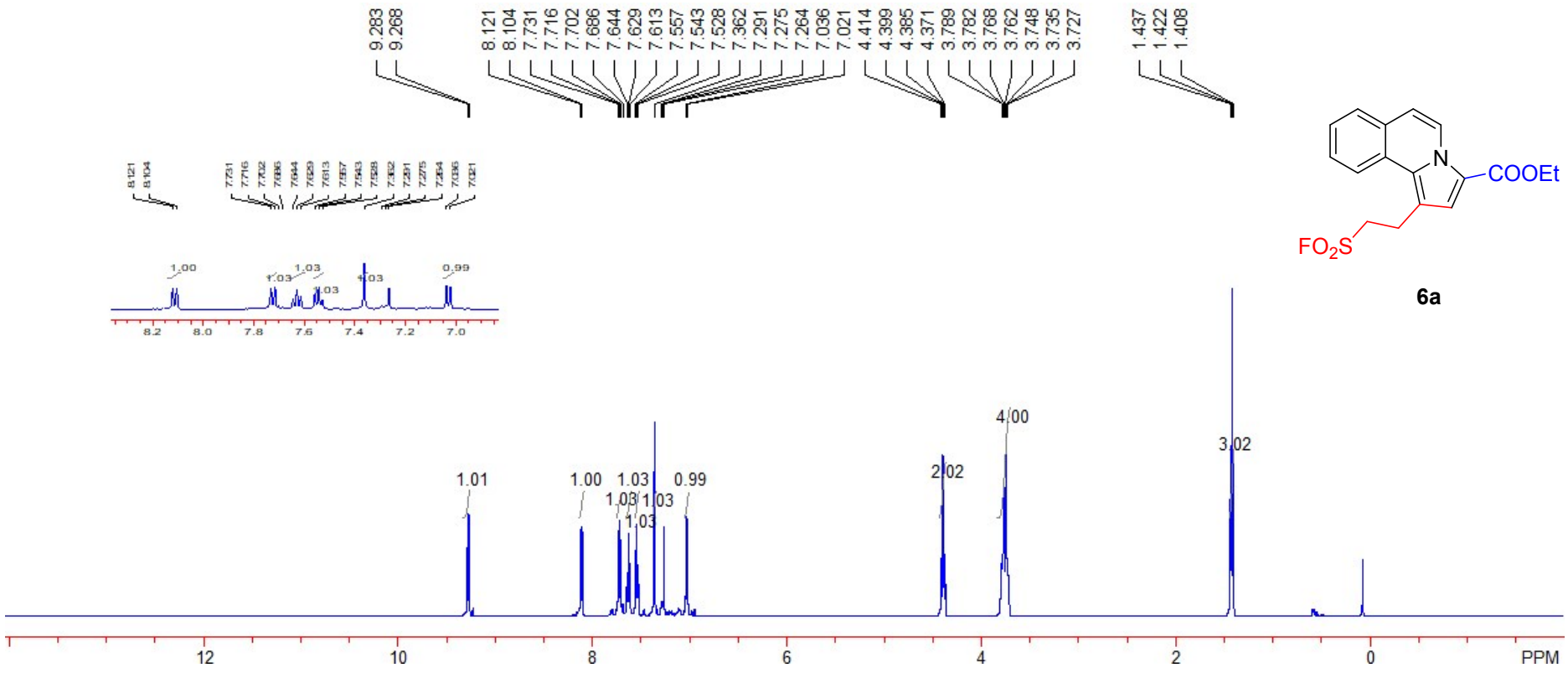
SO2F
EtOOC
200
150
100
50
0
PPM

4k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1.00
1.03
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1.03
1.03
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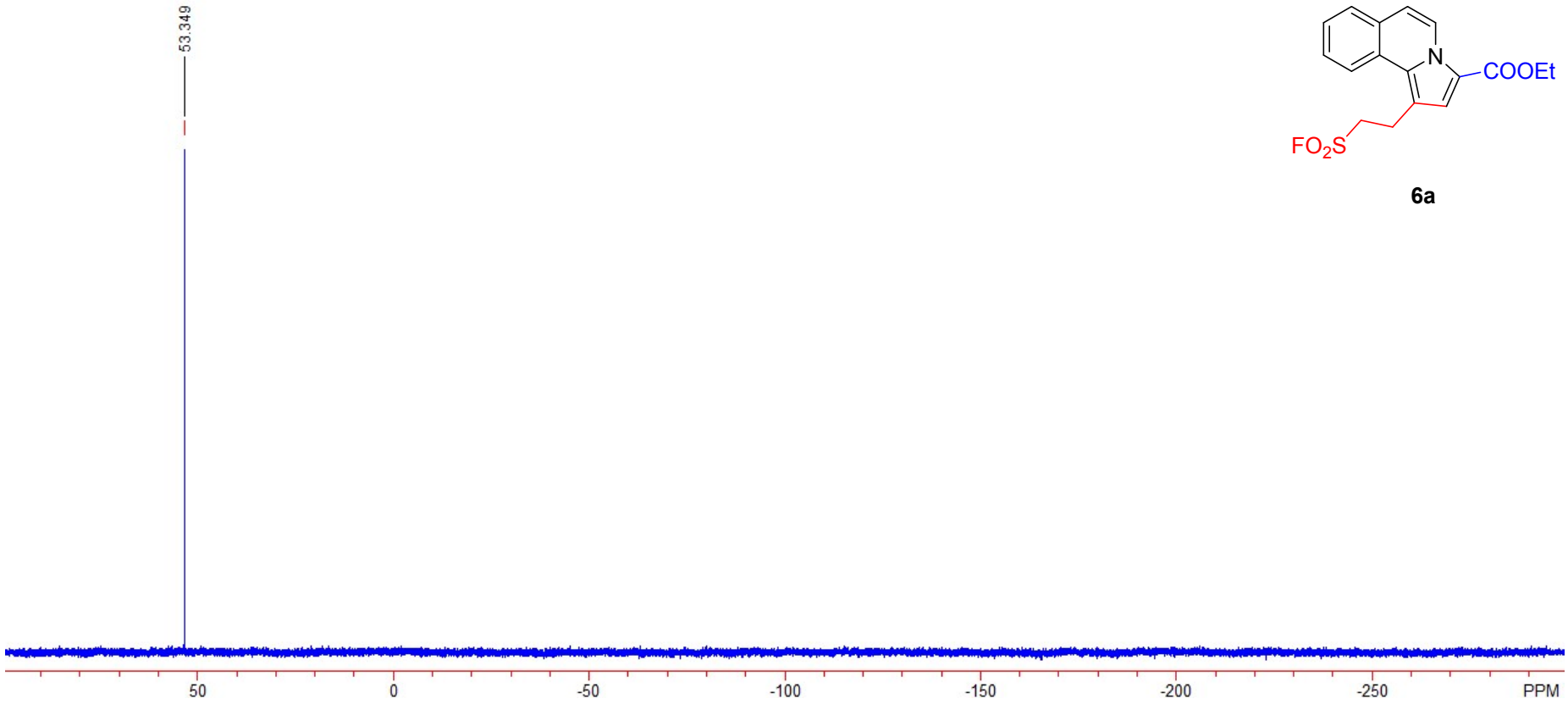
COOEt
FO2S
6a



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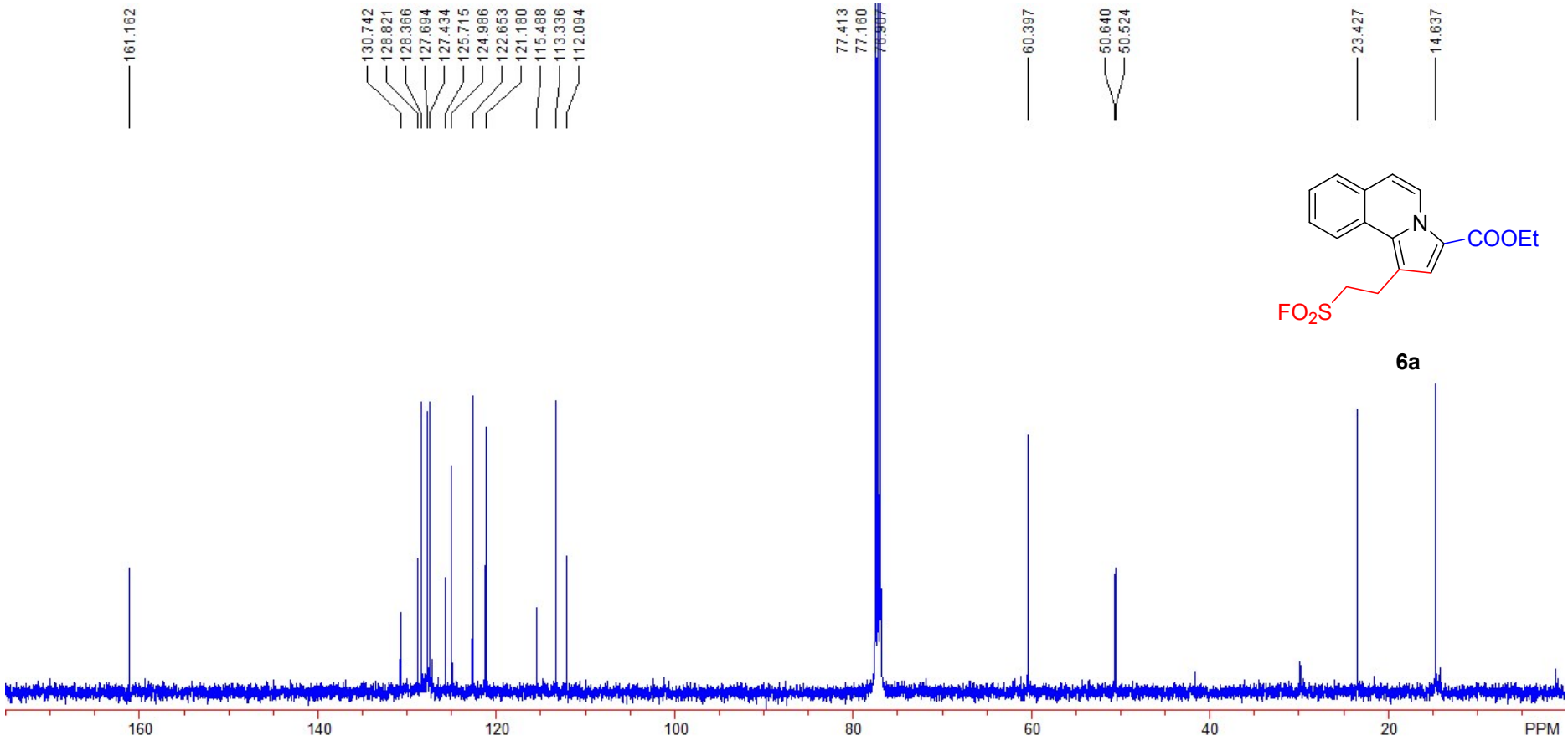
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77.413
77.160
60.397
50.640
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COOEt
FO2S
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120
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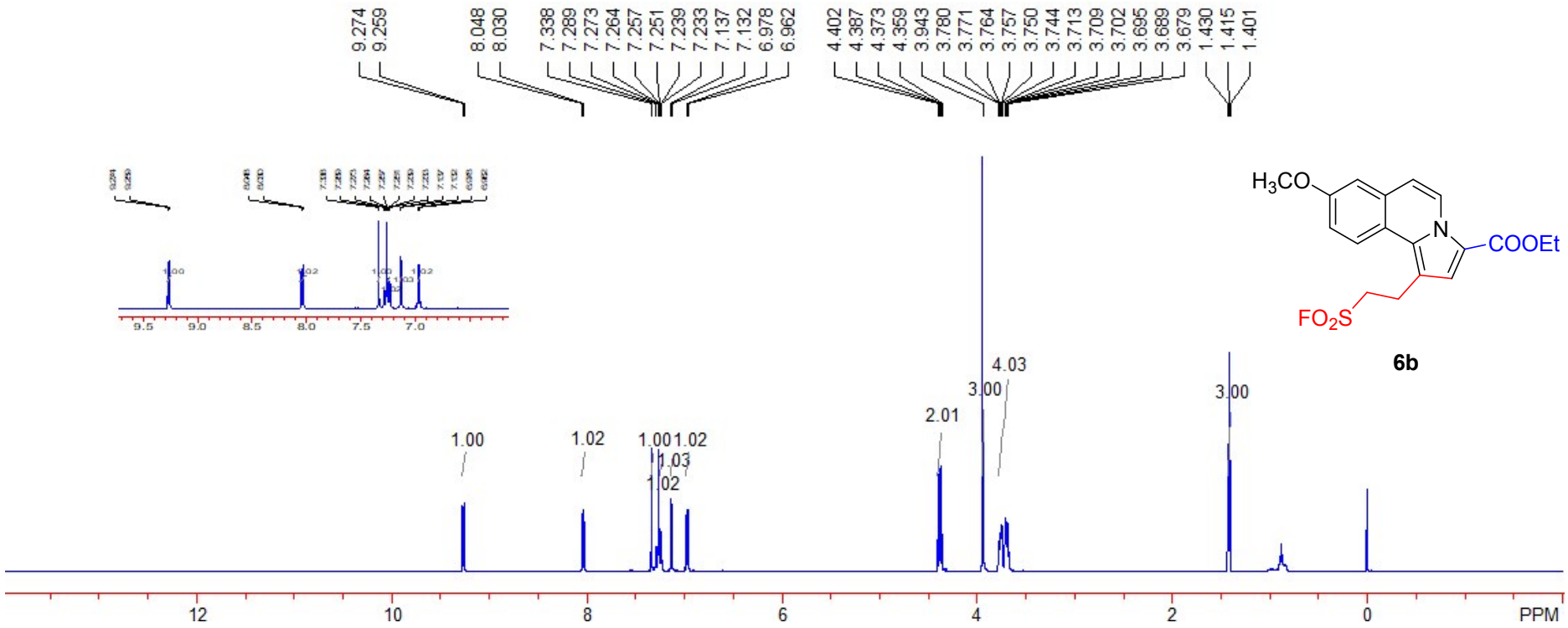
40
20
PPM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3.695
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FO2S
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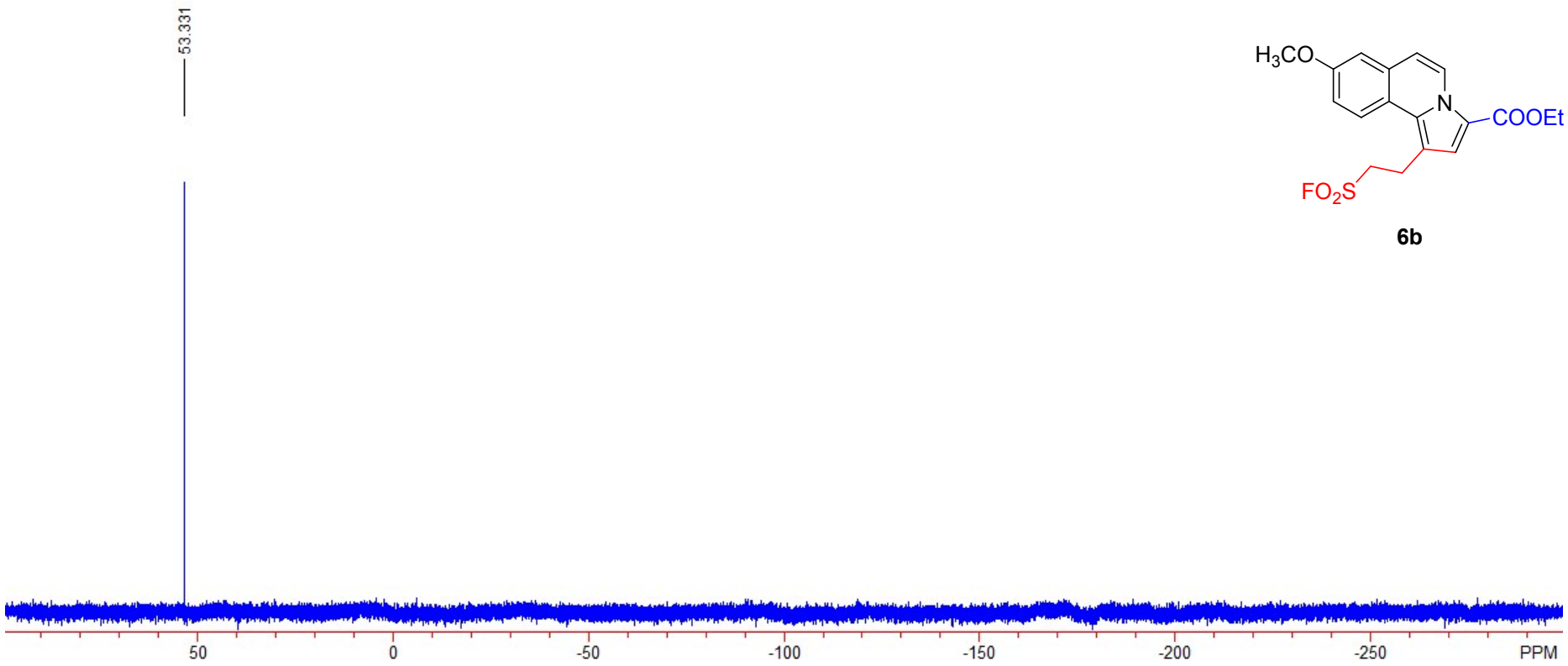

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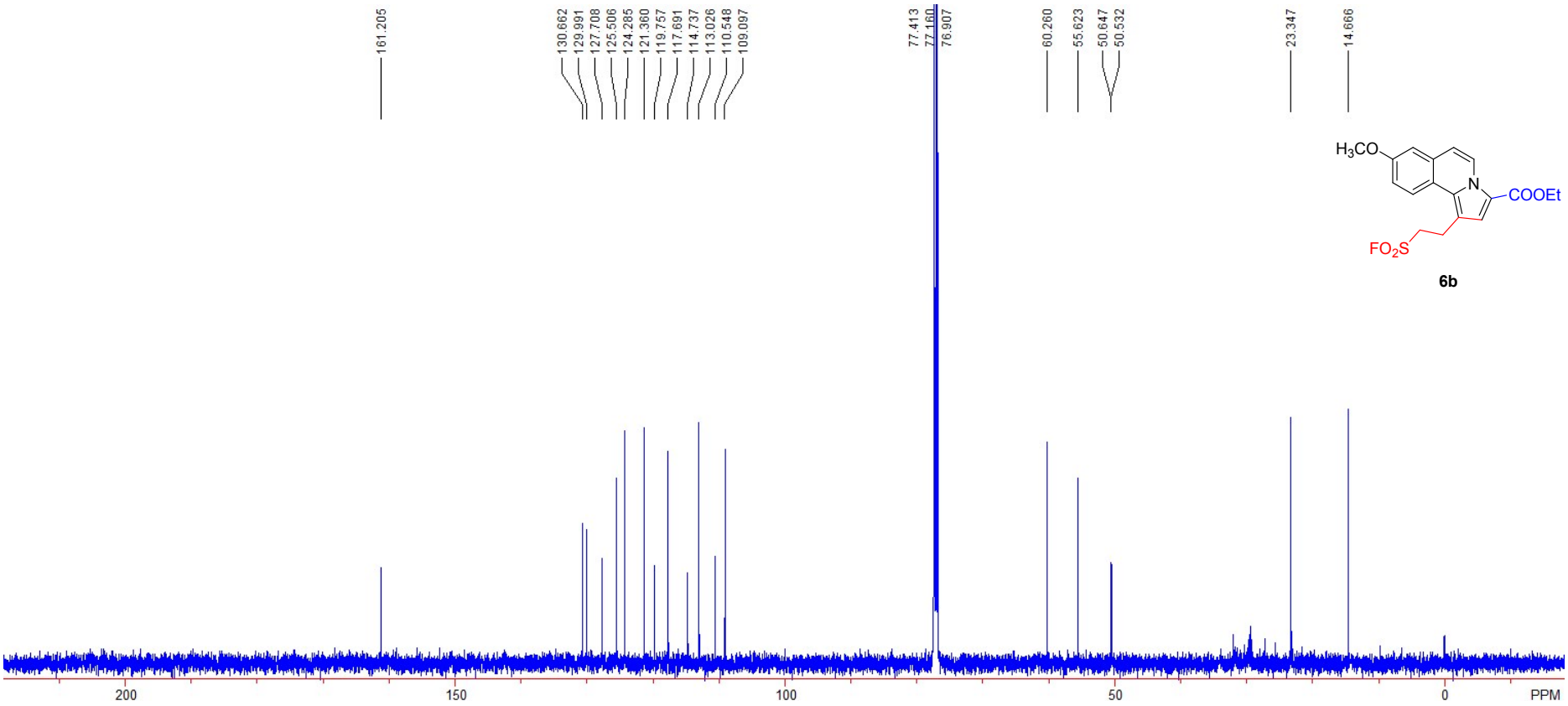
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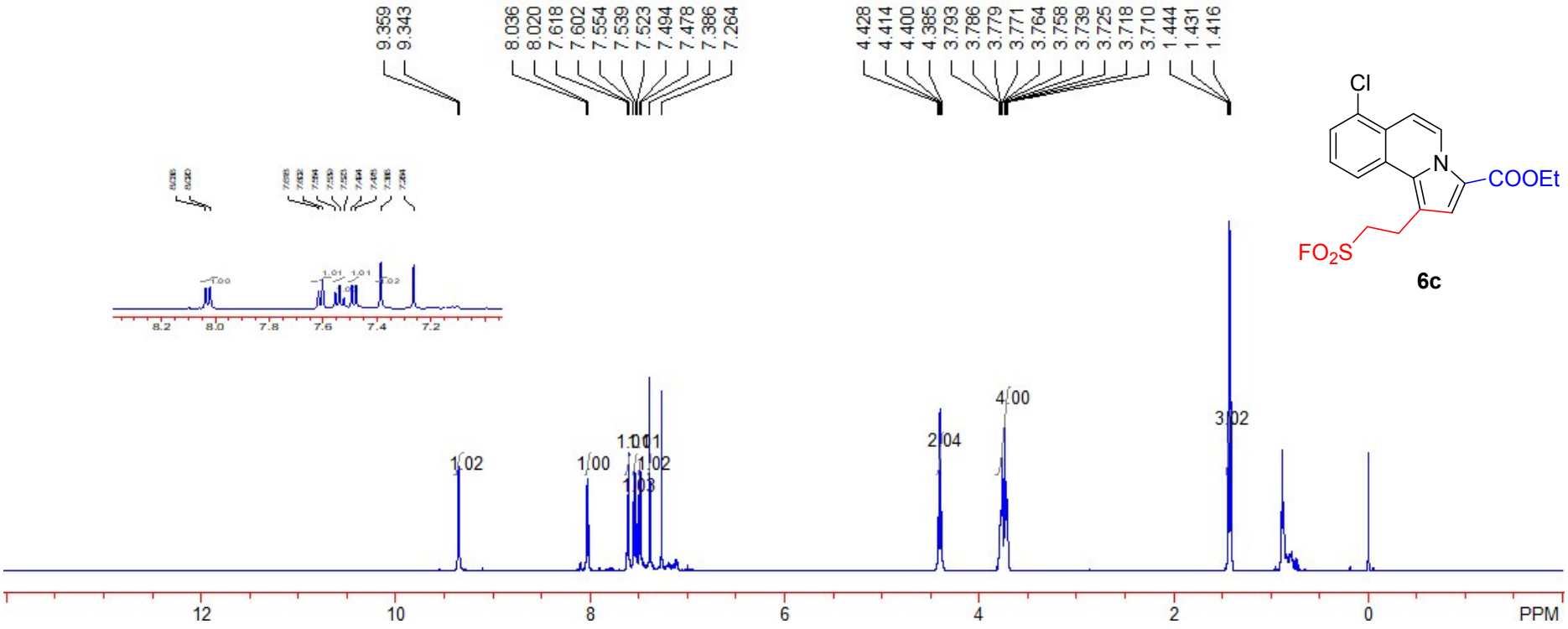
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3.779
3.771
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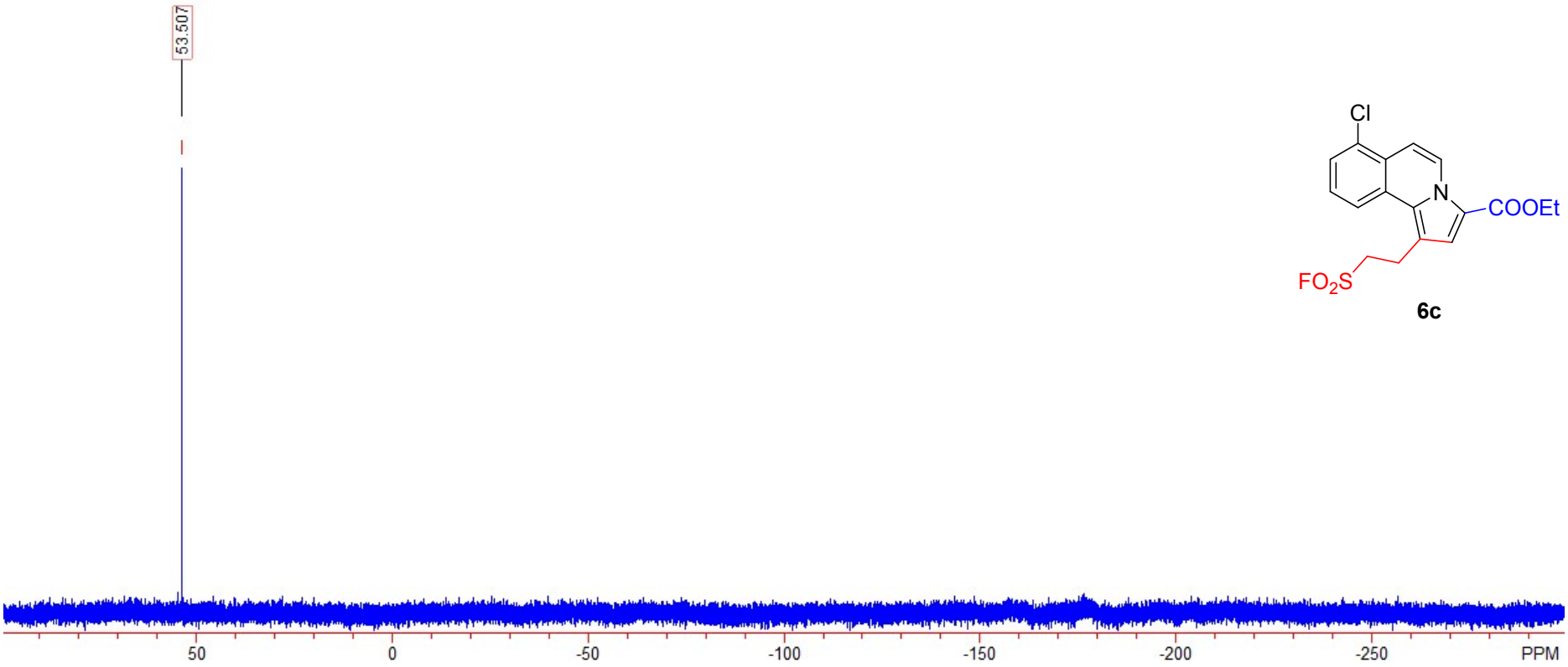

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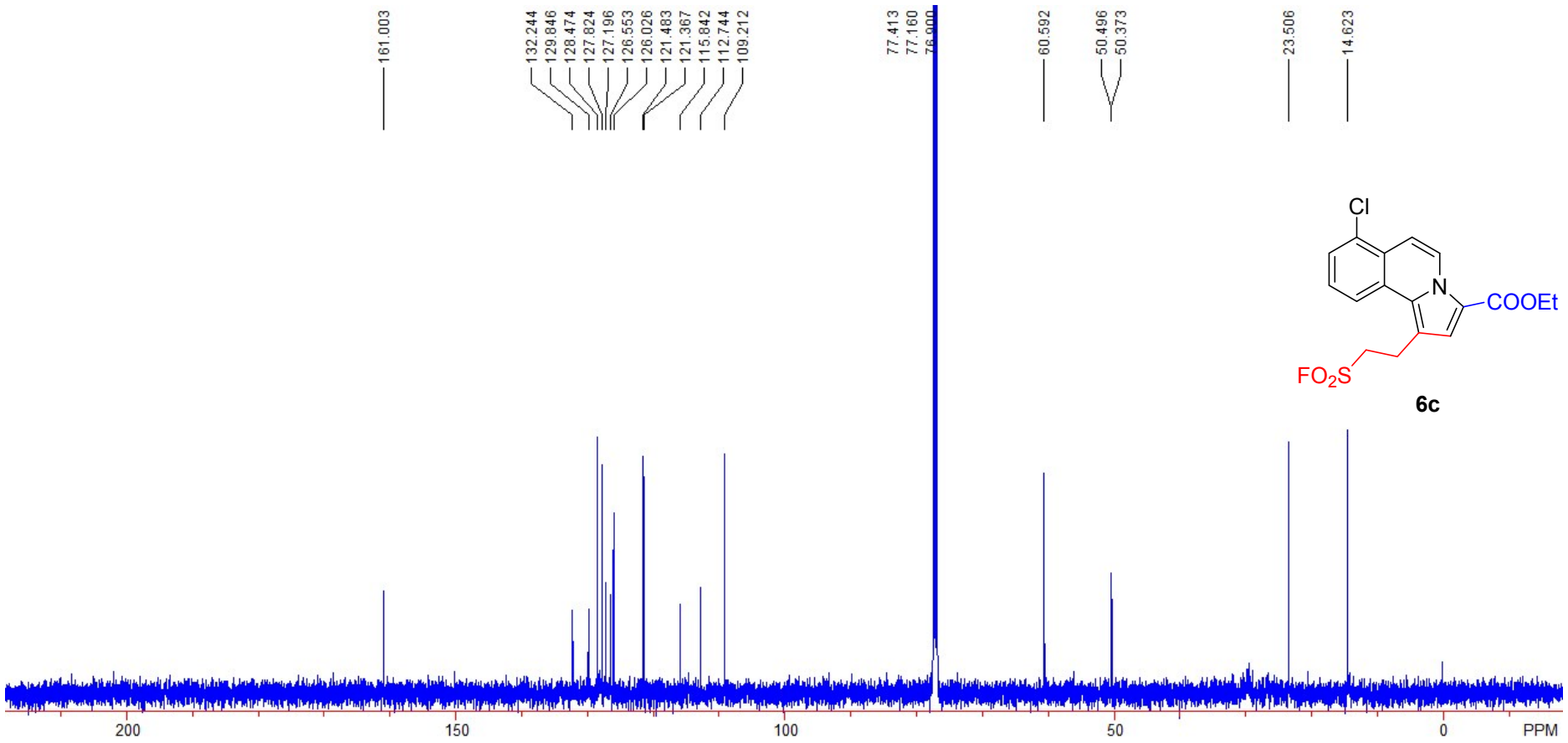
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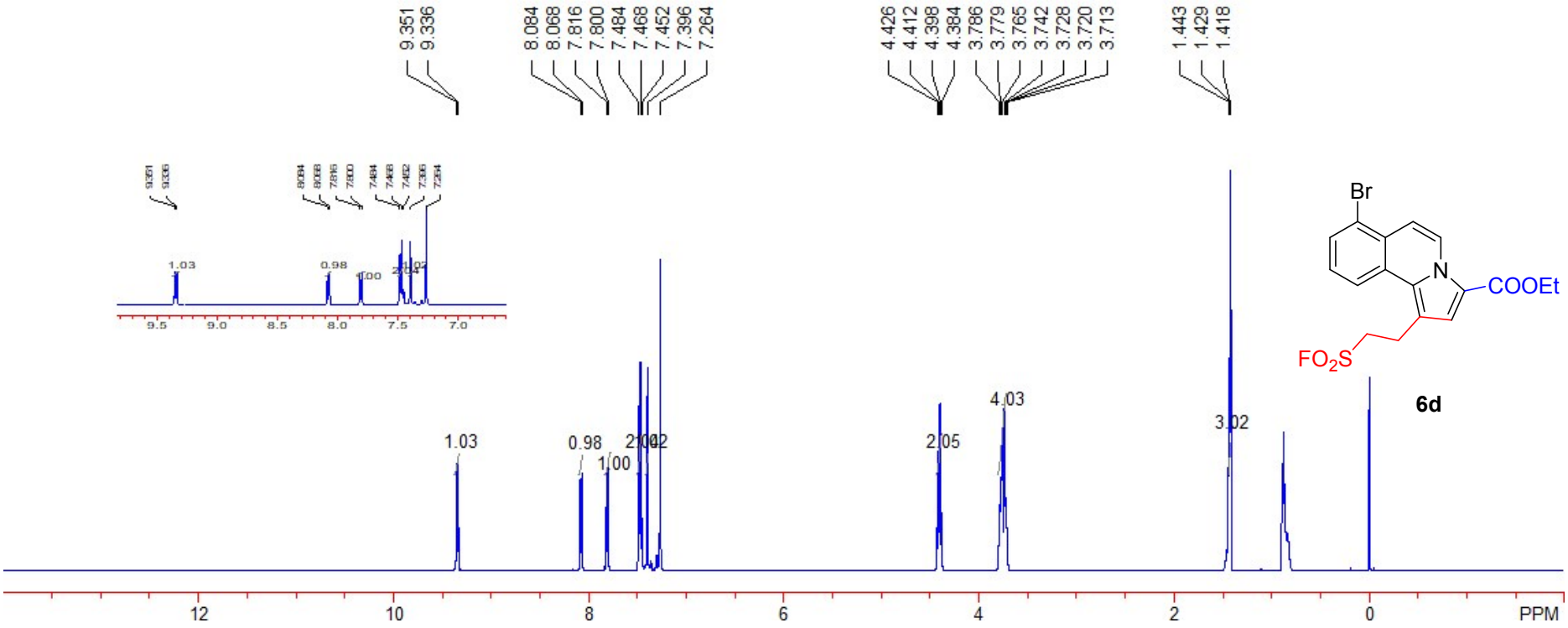
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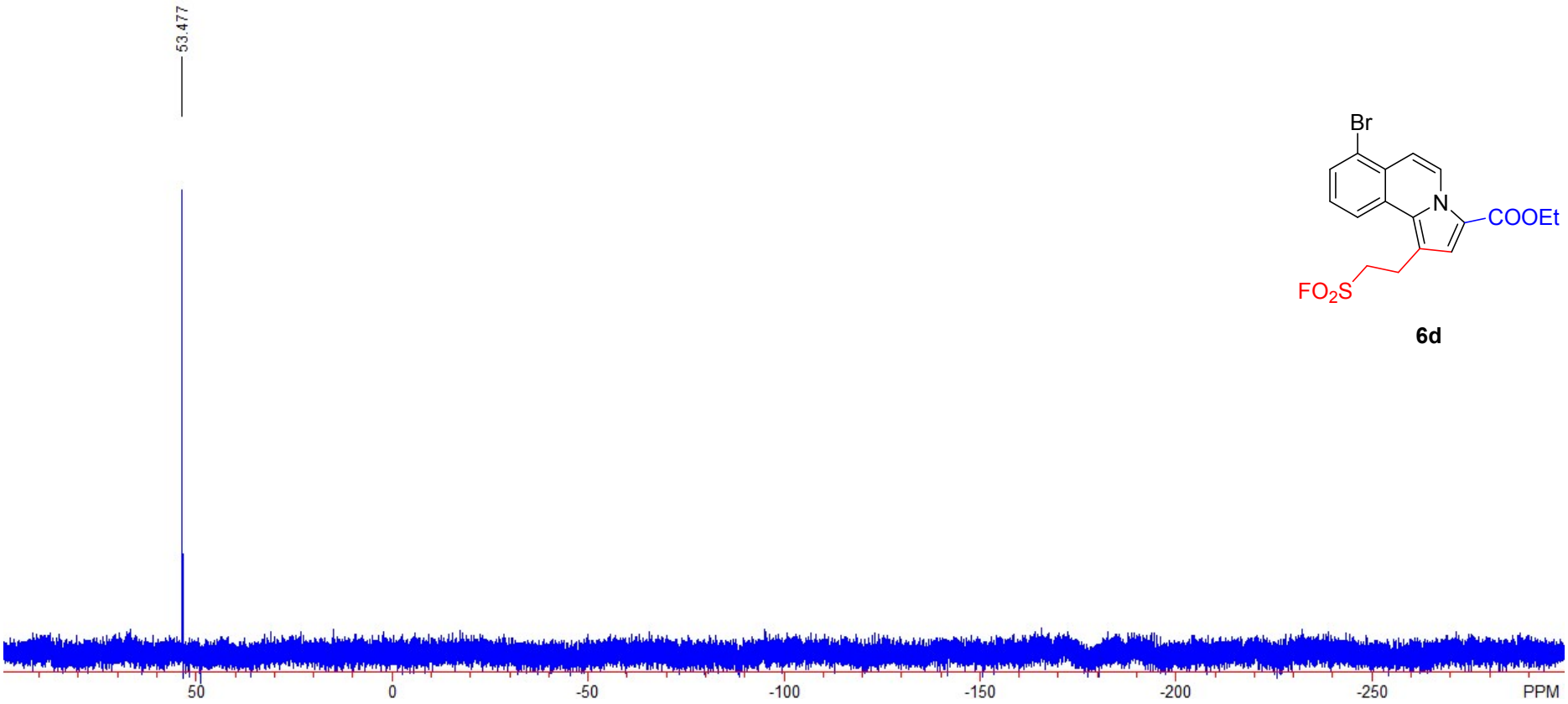

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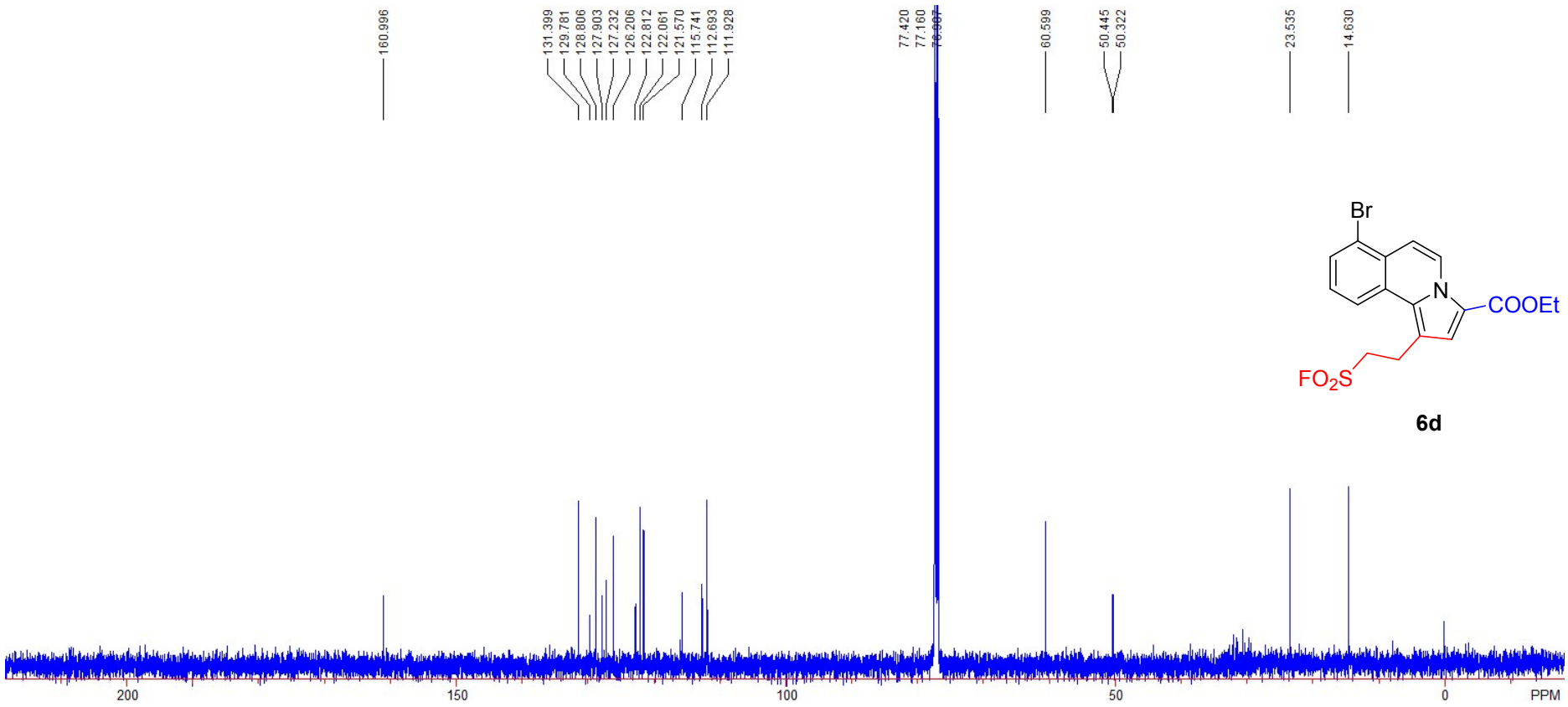
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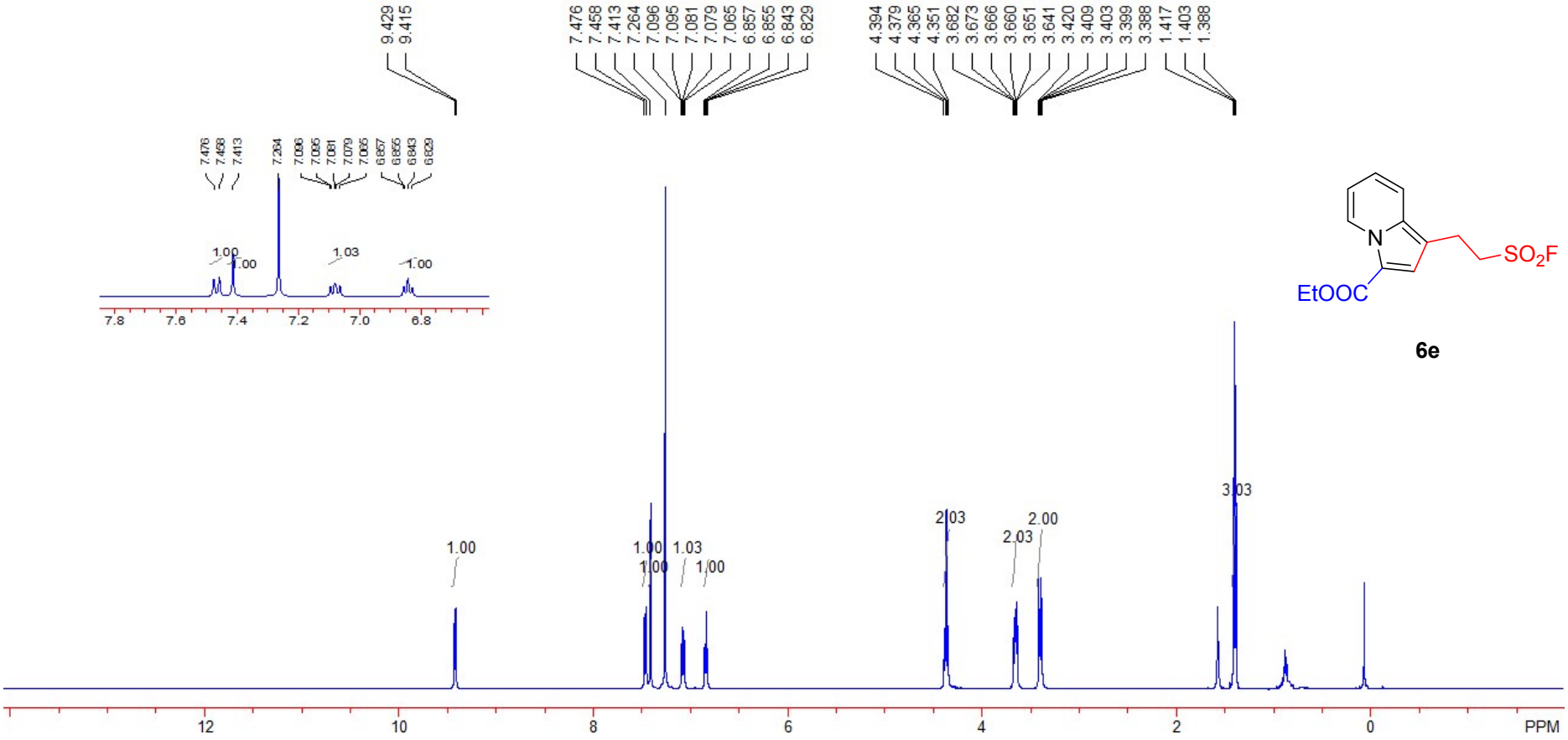
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3.673
3.666
3.660
3.651
3.641
3.420
3.409
3.403
3.399
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1.417
1.403
1.388
1.00
1.00
1.03
1.00
1.00
1.00
1.00
1.03
1.00
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2.03
2.00
3.03
12
10
8
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4
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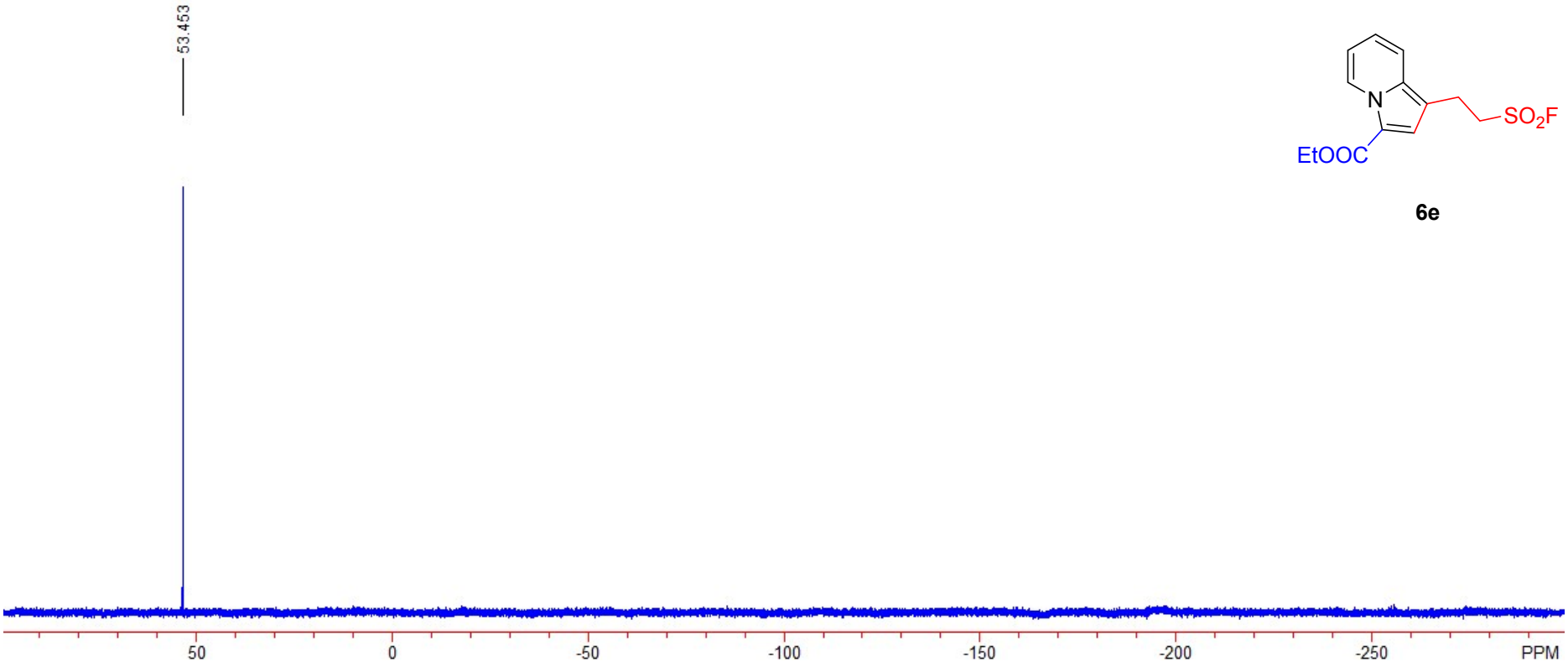
PPM
N
SO2F
EtOOC
6e



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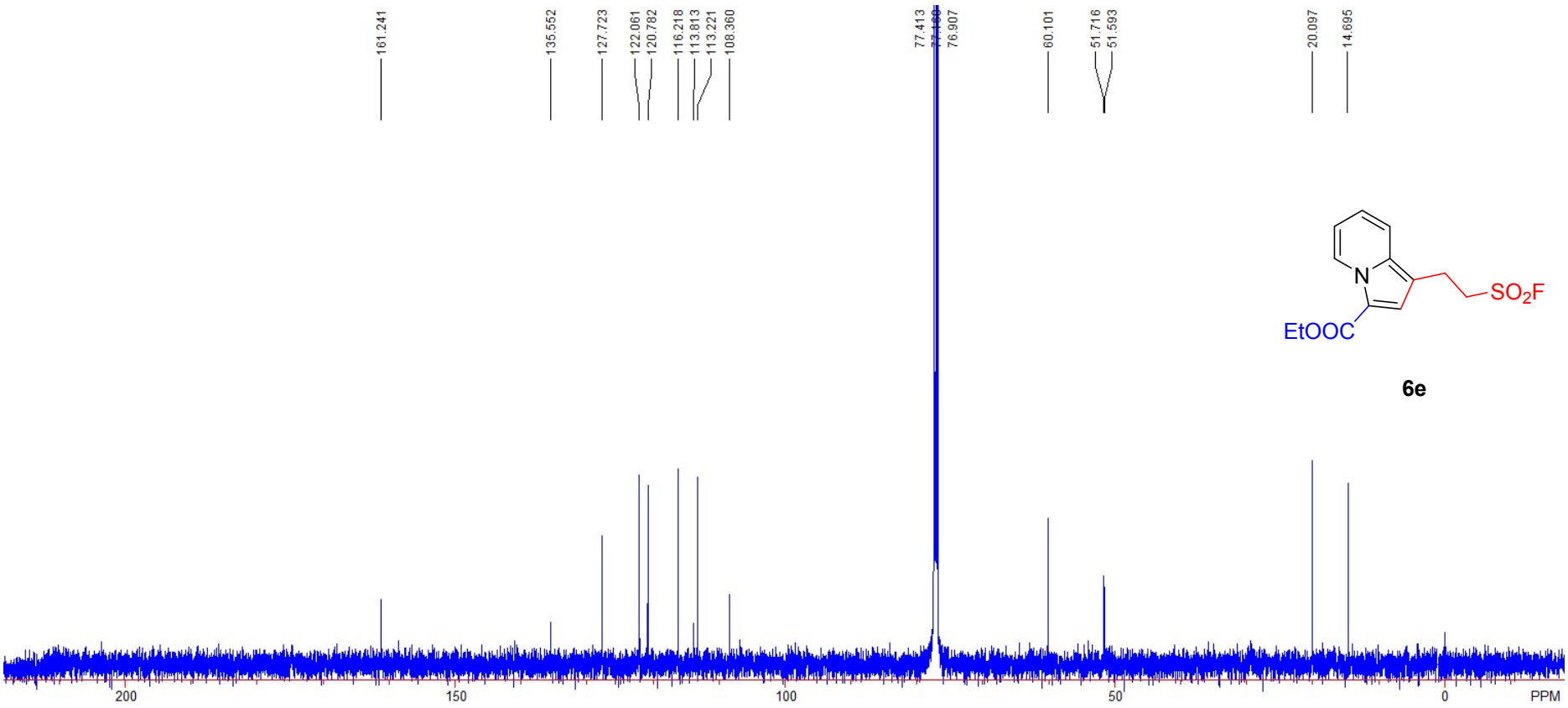
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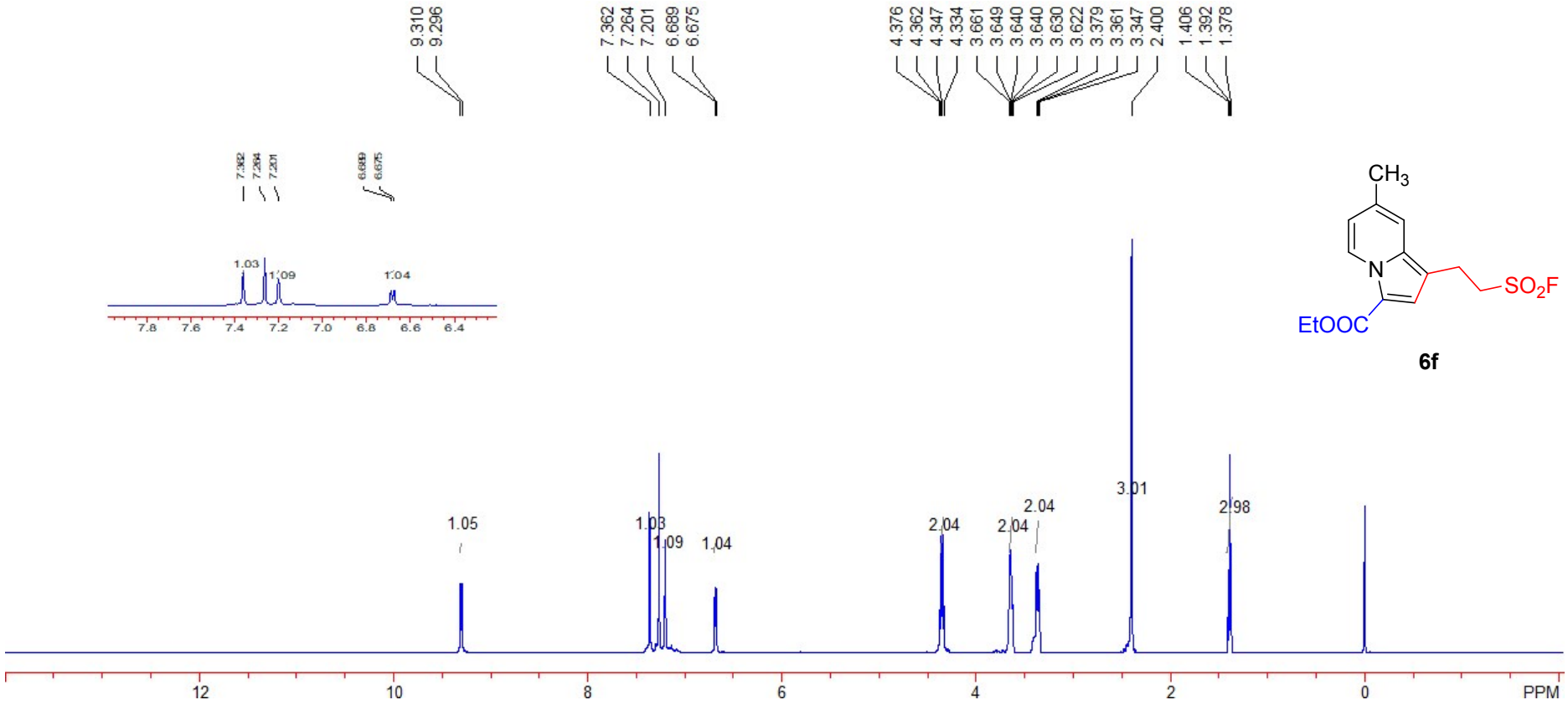
6e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1.09
1.04
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7.6
7.4
7.2
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6.8
6.6
6.4
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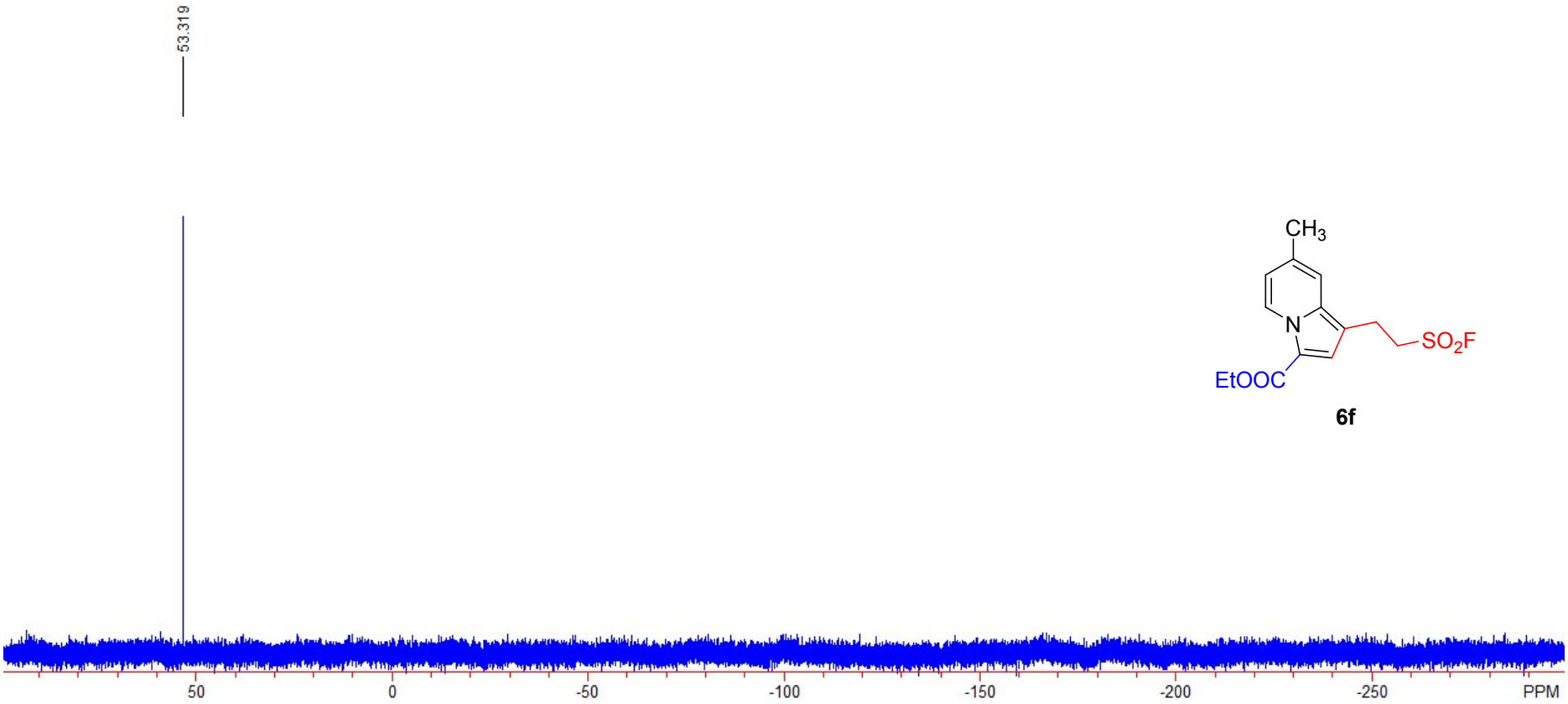

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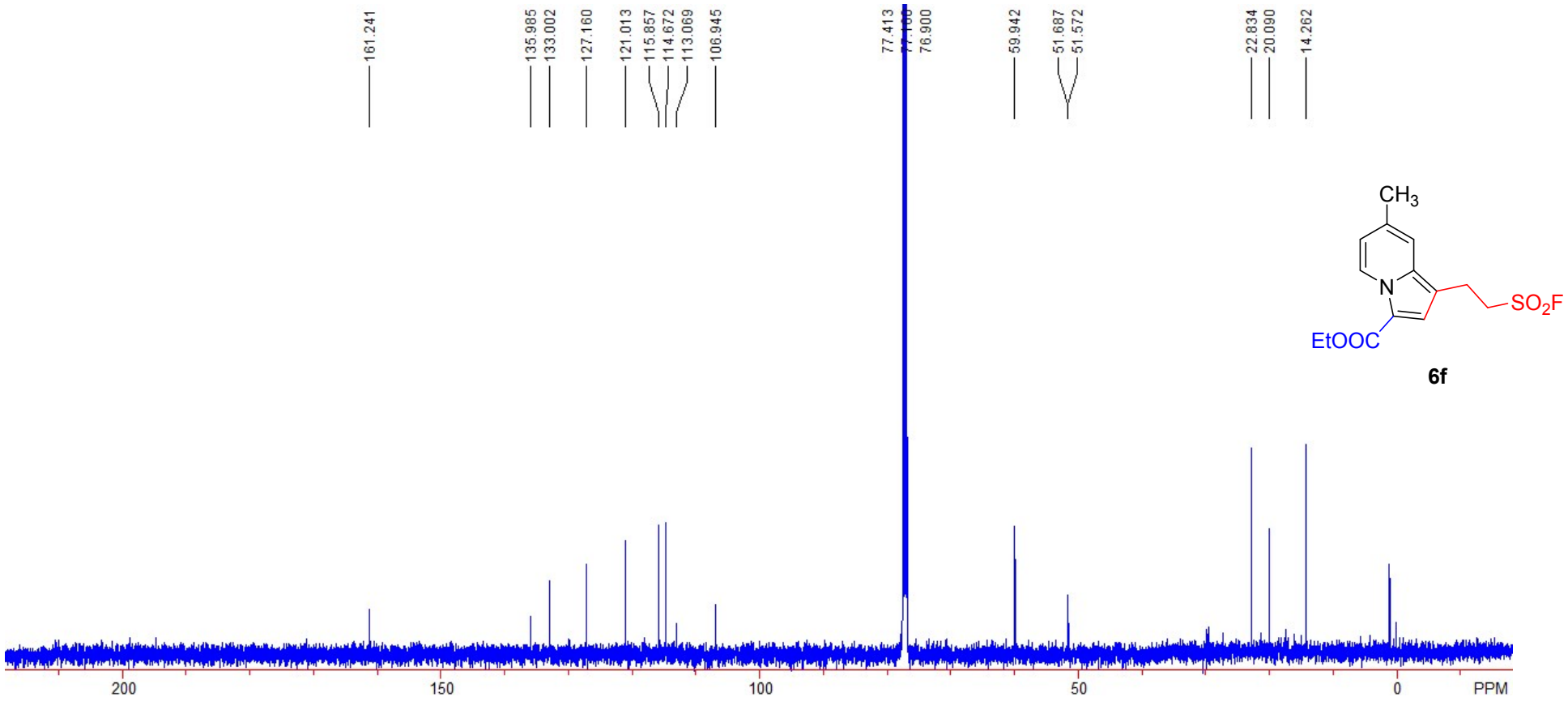
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PPM

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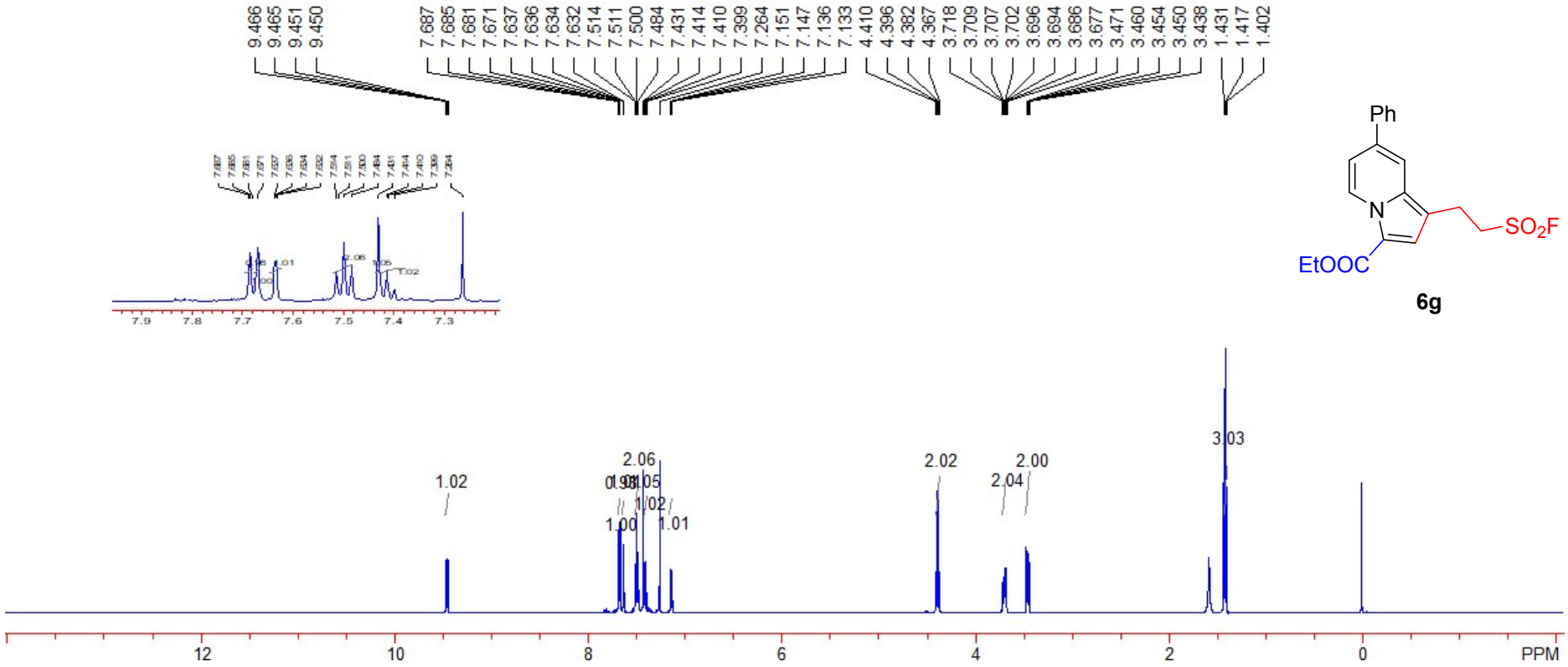
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EtOOC
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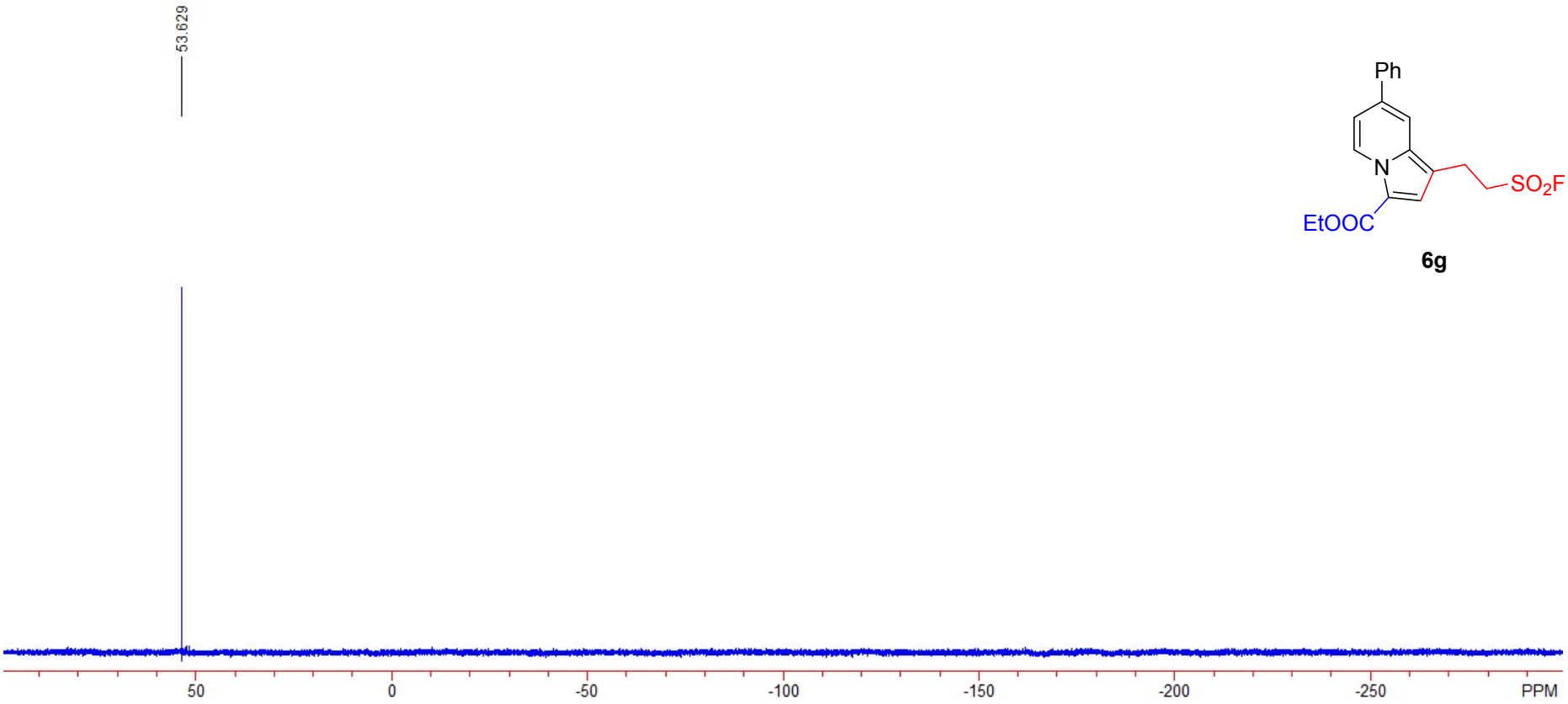
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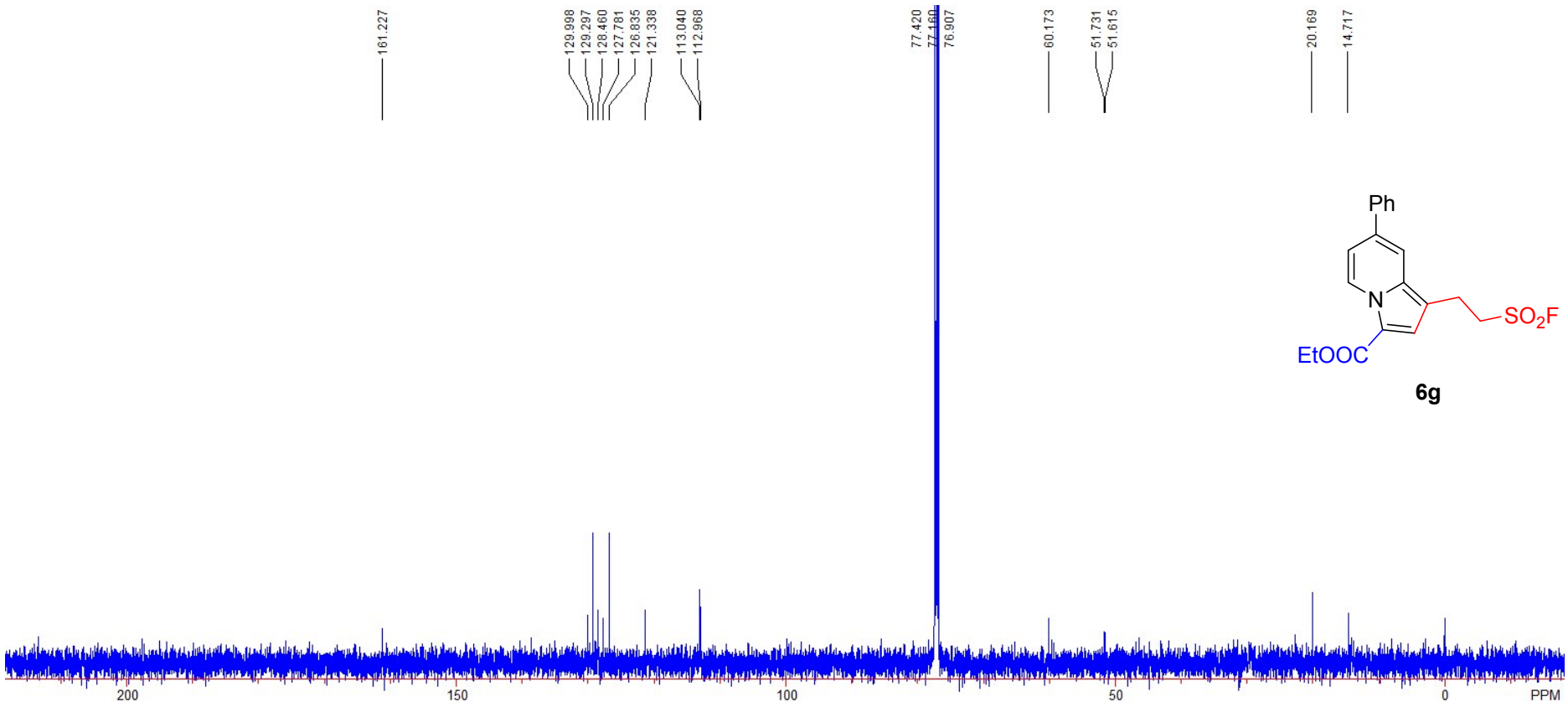
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EtOOC
6g
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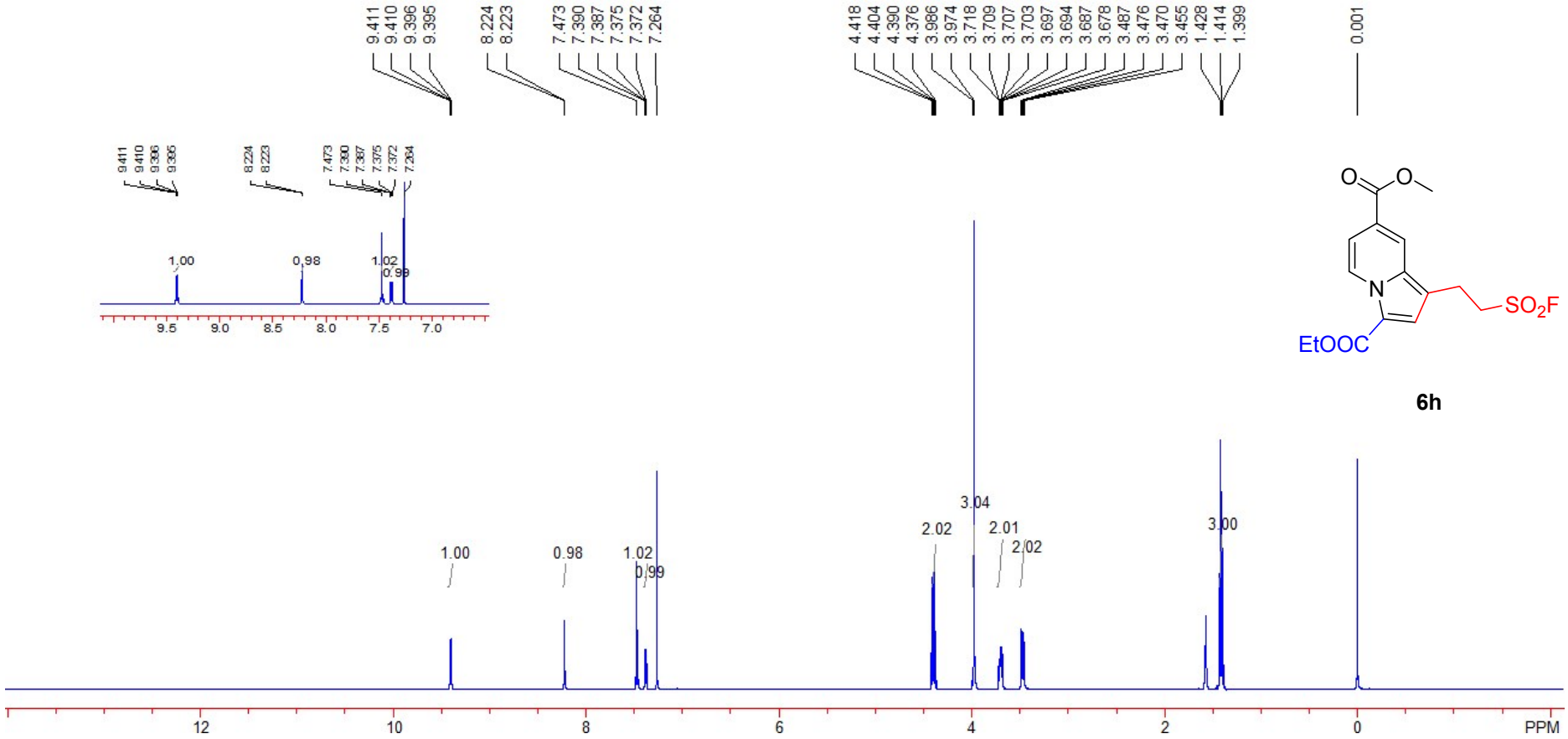
100
50
0
PPM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4
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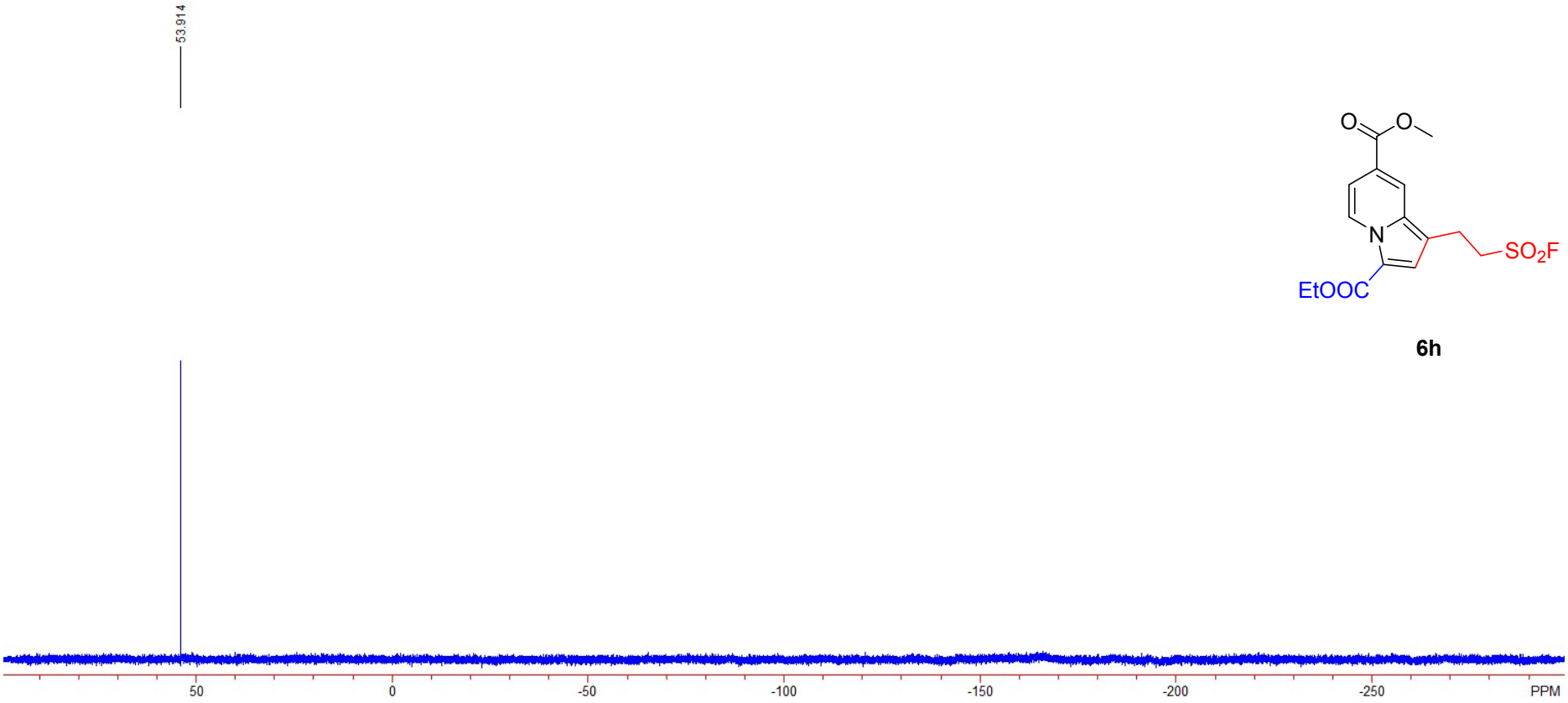
6h



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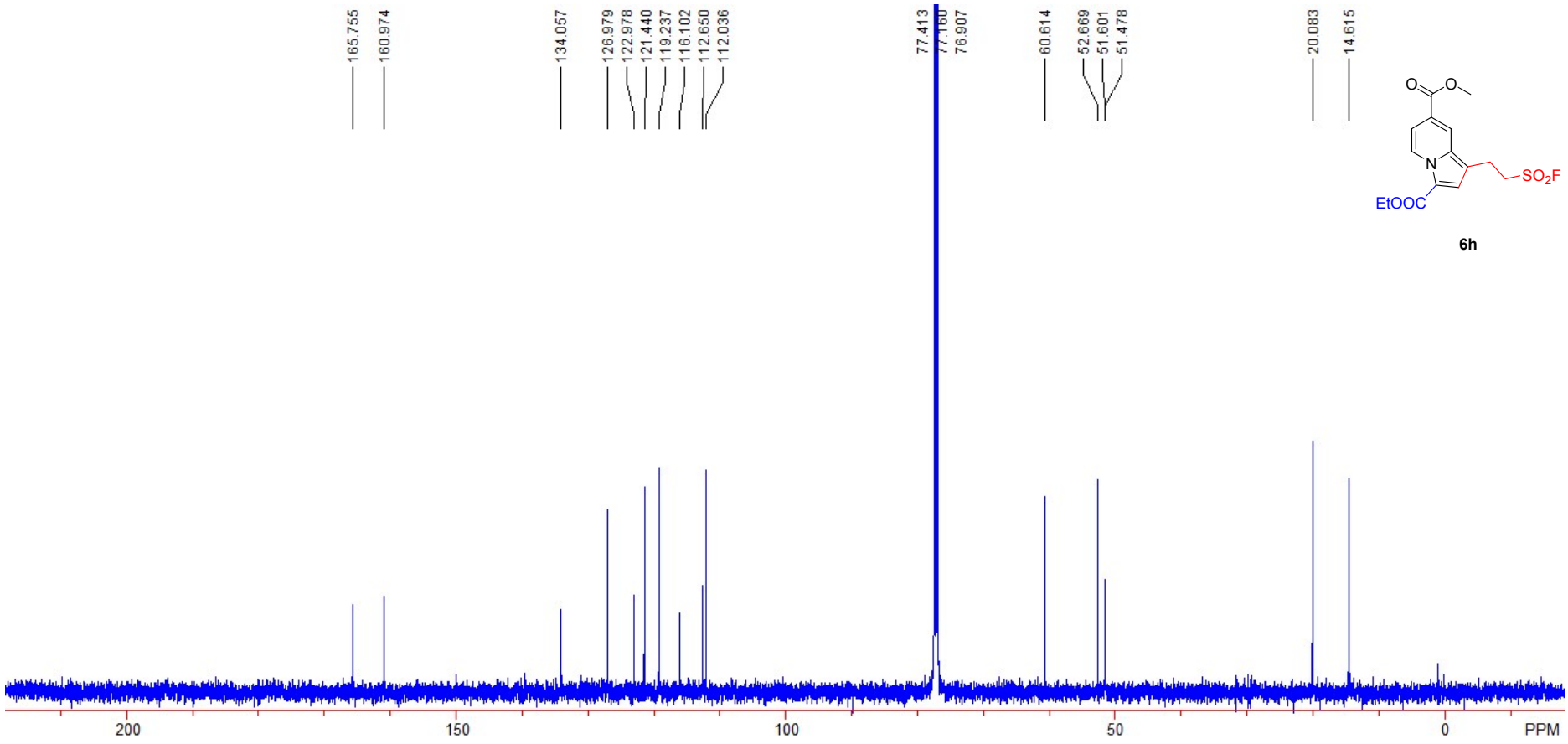
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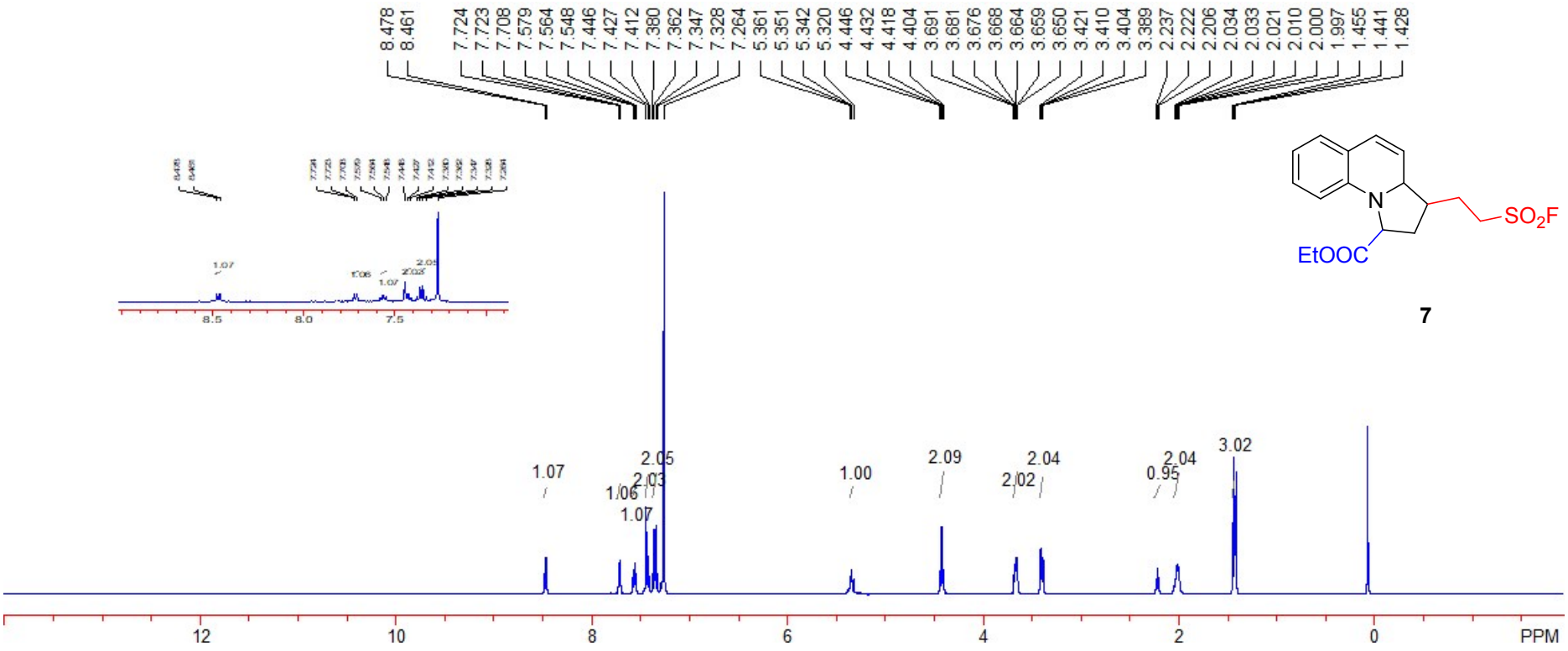
6h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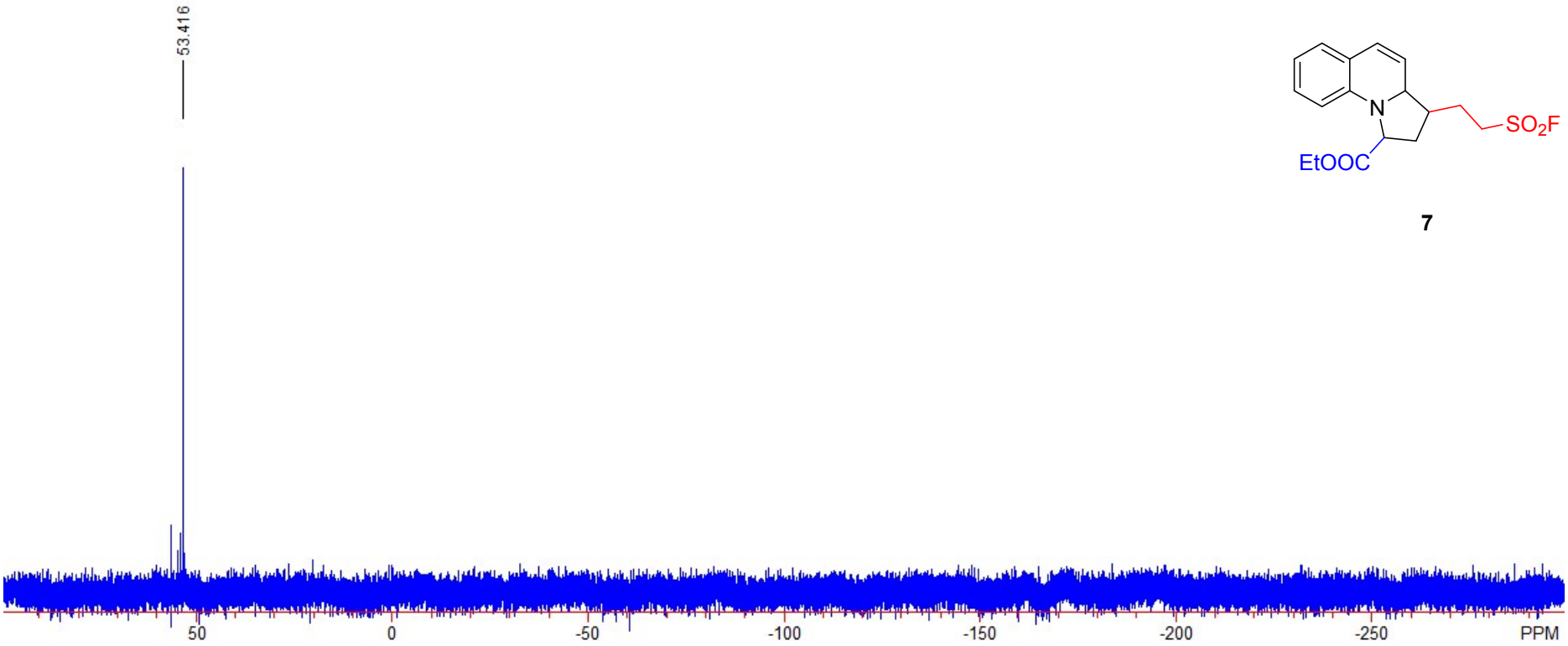

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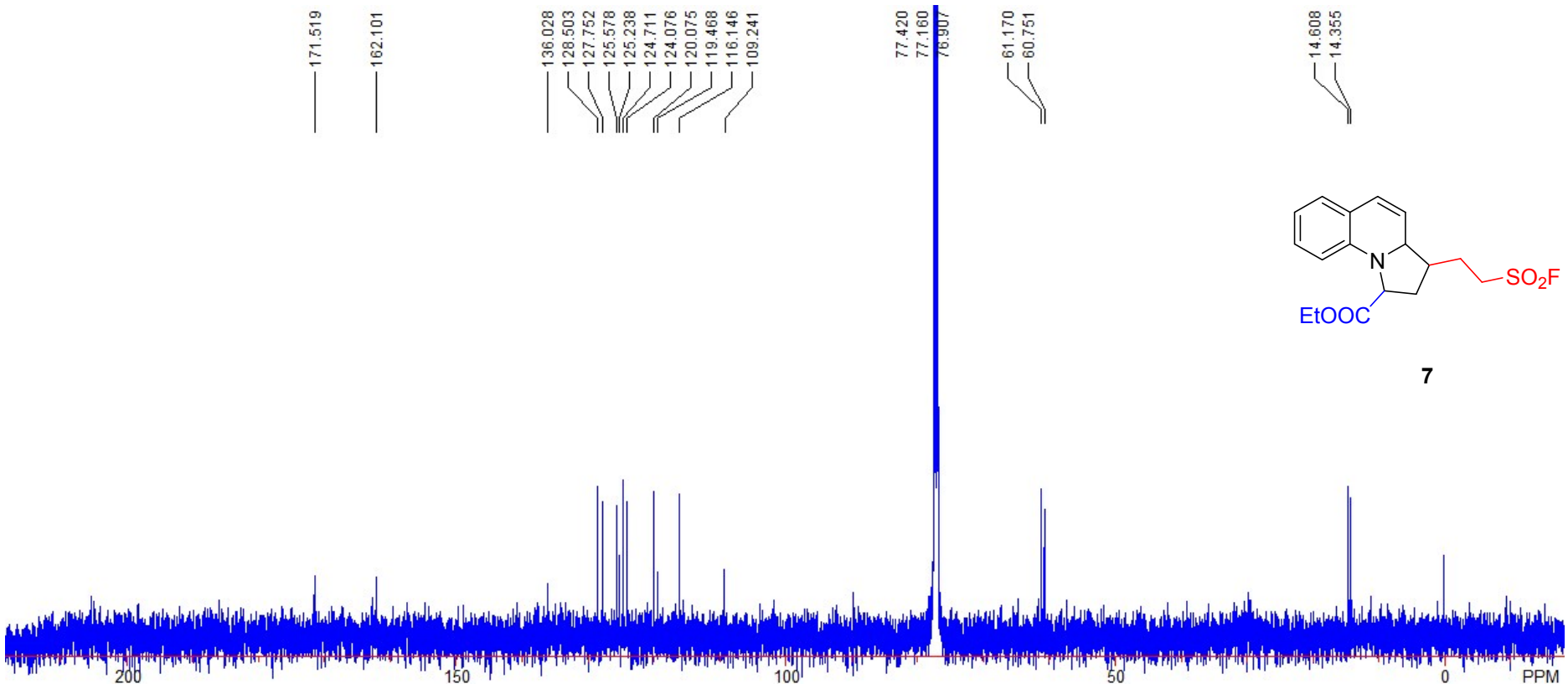
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109.241
77.420
77.160
76.907
61.170
60.751
14.608
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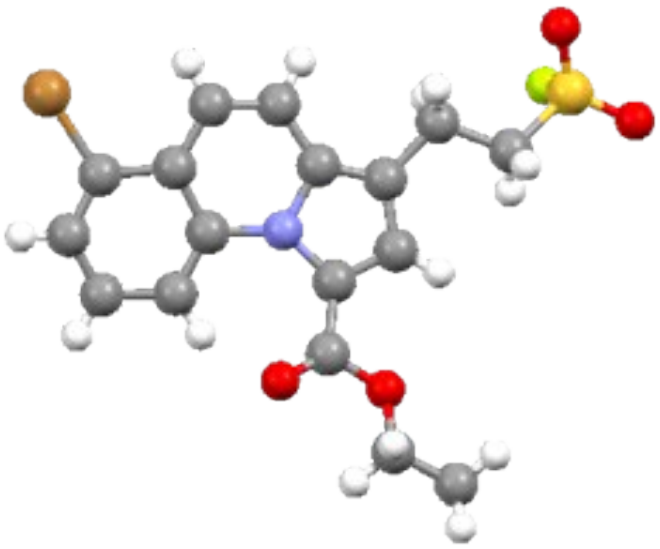
N
SO2F
EtOOC
200
150
100
50
0
PPM

7

8. Data of crystal structure of 4k



The purified compound **4k** about 100 mg is dissolved in diethyl ether and placed in a dark cabinet to slowly evaporate. After several days, a colorless bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart-1000 CDCC diffractometer (graphite-monochromated Mo Kα radiation, λ=0.71073 nm) at 298(2) K. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2043627). The ellipsoid contour probability level in the caption is 50 %.

Table S7. Crystal data and structure refinement for 200731e.

Identification code	200731e	
Empirical formula	C17 H15 Br F N O4 S	
Formula weight	428.27	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9939(12) Å	□= 98.666(3)°.
	b = 10.6492(13) Å	□= 99.199(3)°.
	c = 16.5159(19) Å	□ = 90.008(2)°.
Volume	1714.8(4) $Å^3$	
Z	4	
Density (calculated)	1.659 Mg/m^3	
Absorption coefficient	2.551 mm^{-1}	
F(000)	864	
Crystal size	0.40 x 0.11 x 0.05 mm^3	
Theta range for data collection	1.94 to 25.02°.	

Index ranges	-11<=h<=11, -12<=k<=12, -19<=l<=19
Reflections collected	5865
Independent reflections	5876 [R(int) = 0.0000]
Completeness to theta = 25.02°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8830 and 0.4285
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5876 / 1410 / 456
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.1335, wR2 = 0.2947
R indices (all data)	R1 = 0.2372, wR2 = 0.3387
Extinction coefficient	0.070(6)
Largest diff. peak and hole	1.005 and -1.094 e.$Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 200731e. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	1079(2)	2666(2)	3226(1)	80(1)
Br(2)	6684(2)	3196(2)	3226(1)	80(1)
S(1)	636(6)	6289(5)	9272(3)	69(1)
S(2)	5639(6)	6319(5)	9262(3)	71(1)
F(1)	1430(15)	7347(12)	9078(7)	110(4)
F(2)	6407(14)	7423(10)	9101(7)	101(4)
N(1)	2830(14)	2732(12)	6420(7)	53(2)
N(2)	7847(15)	2748(12)	6387(7)	56(2)
O(1)	5001(13)	1636(11)	8140(7)	75(3)
O(2)	4646(14)	576(12)	6851(7)	82(4)
O(3)	941(17)	6362(13)	10116(7)	102(4)
O(4)	-700(14)	6423(12)	8892(7)	85(4)
O(5)	9500(15)	1191(13)	8073(8)	90(3)
O(6)	10197(15)	1111(12)	6891(7)	87(4)
O(7)	5937(16)	6289(12)	10097(7)	94(4)
O(8)	4293(14)	6457(13)	8864(7)	83(4)
C(1)	4440(20)	1494(17)	7339(10)	62(3)
C(2)	3555(19)	2574(16)	7192(9)	60(3)
C(3)	2993(18)	3257(15)	7789(9)	58(3)
C(4)	1978(18)	3966(16)	7420(9)	54(3)
C(5)	1810(18)	3630(16)	6600(9)	57(3)
C(6)	923(17)	3969(15)	5928(9)	56(3)
C(7)	957(18)	3452(15)	5138(9)	58(3)
C(8)	2029(16)	2697(14)	4955(9)	48(3)
C(9)	3093(18)	2417(14)	5577(9)	49(3)
C(10)	4216(18)	1796(15)	5441(9)	59(3)
C(11)	4395(18)	1411(14)	4603(9)	56(3)
C(12)	3411(17)	1643(15)	3998(10)	55(3)
C(13)	2336(18)	2291(15)	4130(9)	56(3)
C(14)	1072(19)	4908(16)	7832(9)	63(3)
C(15)	1351(19)	5005(15)	8761(9)	59(3)
C(16)	5580(20)	570(18)	8403(11)	85(4)
C(17)	6110(20)	800(20)	9254(12)	107(7)

C(18)	9460(20)	1489(18)	7296(11)	66(3)
C(19)	8271(19)	2360(16)	7150(10)	64(3)
C(20)	7756(18)	3095(15)	7745(10)	60(3)
C(21)	7071(19)	4012(16)	7383(9)	59(3)
C(22)	7090(18)	3869(15)	6568(9)	56(3)
C(23)	6584(16)	4489(14)	5904(9)	53(3)
C(24)	6704(17)	4123(15)	5158(9)	56(3)
C(25)	7301(18)	2917(15)	4915(9)	57(3)
C(26)	7884(19)	2232(15)	5537(9)	57(3)
C(27)	8337(18)	992(15)	5356(9)	59(3)
C(28)	8424(18)	543(15)	4565(10)	63(3)
C(29)	8033(17)	1192(15)	3930(9)	54(3)
C(30)	7529(18)	2382(16)	4113(9)	58(3)
C(31)	6301(19)	5094(15)	7819(9)	61(3)
C(32)	6398(19)	5048(14)	8736(9)	58(3)
C(33)	10440(20)	390(20)	8369(12)	92(5)
C(34)	11000(20)	820(20)	9160(14)	123(7)

Table S9. Bond lengths [Å] and angles [°] for 200731e.

Br(1)-C(13)	1.883(15)
Br(2)-C(30)	1.898(14)
S(1)-O(3)	1.369(12)
S(1)-O(4)	1.399(14)
S(1)-F(1)	1.480(13)
S(1)-C(15)	1.714(16)
S(2)-O(7)	1.369(12)
S(2)-O(8)	1.417(14)
S(2)-F(2)	1.483(13)
S(2)-C(32)	1.737(15)
N(1)-C(2)	1.396(18)
N(1)-C(5)	1.433(19)
N(1)-C(9)	1.448(17)
N(2)-C(19)	1.387(18)
N(2)-C(22)	1.433(18)
N(2)-C(26)	1.435(18)
O(1)-C(1)	1.338(17)
O(1)-C(16)	1.373(18)
O(2)-C(1)	1.210(19)
O(5)-C(33)	1.357(19)
O(5)-C(18)	1.362(19)
O(6)-C(18)	1.11(2)
C(1)-C(2)	1.48(2)
C(2)-C(3)	1.33(2)
C(3)-C(4)	1.38(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.331(19)
C(4)-C(14)	1.51(2)
C(5)-C(6)	1.398(19)
C(6)-C(7)	1.343(19)
C(6)-H(6)	0.9300
C(7)-C(8)	1.38(2)
C(7)-H(7)	0.9300
C(8)-C(9)	1.42(2)
C(8)-C(13)	1.45(2)
C(9)-C(10)	1.34(2)

C(10)-C(11)	1.422(19)
C(10)-H(10)	0.9300
C(11)-C(12)	1.34(2)
C(11)-H(11)	0.9300
C(12)-C(13)	1.31(2)
C(12)-H(12)	0.9300
C(14)-C(15)	1.503(18)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.40(2)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.52(2)
C(19)-C(20)	1.33(2)
C(20)-C(21)	1.35(2)
C(20)-H(20)	0.9300
C(21)-C(22)	1.335(19)
C(21)-C(31)	1.54(2)
C(22)-C(23)	1.392(19)
C(23)-C(24)	1.260(19)
C(23)-H(23)	0.9300
C(24)-C(25)	1.44(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.401(19)
C(25)-C(30)	1.41(2)
C(26)-C(27)	1.401(19)
C(27)-C(28)	1.337(19)
C(27)-H(27)	0.9300
C(28)-C(29)	1.348(19)
C(28)-H(28)	0.9300
C(29)-C(30)	1.37(2)
C(29)-H(29)	0.9300
C(31)-C(32)	1.509(18)

C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(34)	1.35(2)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600

O(3)-S(1)-O(4)	120.3(9)
O(3)-S(1)-F(1)	104.6(9)
O(4)-S(1)-F(1)	106.0(8)
O(3)-S(1)-C(15)	112.2(8)
O(4)-S(1)-C(15)	110.5(8)
F(1)-S(1)-C(15)	100.9(8)
O(7)-S(2)-O(8)	121.6(9)
O(7)-S(2)-F(2)	106.5(9)
O(8)-S(2)-F(2)	104.9(8)
O(7)-S(2)-C(32)	109.1(7)
O(8)-S(2)-C(32)	110.7(8)
F(2)-S(2)-C(32)	102.1(8)
C(2)-N(1)-C(5)	105.2(12)
C(2)-N(1)-C(9)	133.5(14)
C(5)-N(1)-C(9)	119.6(12)
C(19)-N(2)-C(22)	105.0(12)
C(19)-N(2)-C(26)	135.6(13)
C(22)-N(2)-C(26)	119.0(12)
C(1)-O(1)-C(16)	115.3(13)
C(33)-O(5)-C(18)	120.3(16)
O(2)-C(1)-O(1)	121.9(15)
O(2)-C(1)-C(2)	128.6(15)
O(1)-C(1)-C(2)	109.5(14)
C(3)-C(2)-N(1)	109.2(15)
C(3)-C(2)-C(1)	122.9(15)
N(1)-C(2)-C(1)	124.4(14)
C(2)-C(3)-C(4)	108.3(14)

C(2)-C(3)-H(3)	125.8
C(4)-C(3)-H(3)	125.8
C(5)-C(4)-C(3)	109.3(15)
C(5)-C(4)-C(14)	122.0(15)
C(3)-C(4)-C(14)	128.5(13)
C(4)-C(5)-C(6)	135.0(17)
C(4)-C(5)-N(1)	107.6(14)
C(6)-C(5)-N(1)	117.5(14)
C(7)-C(6)-C(5)	122.9(16)
C(7)-C(6)-H(6)	118.6
C(5)-C(6)-H(6)	118.6
C(6)-C(7)-C(8)	119.5(15)
C(6)-C(7)-H(7)	120.3
C(8)-C(7)-H(7)	120.3
C(7)-C(8)-C(9)	122.5(14)
C(7)-C(8)-C(13)	125.1(13)
C(9)-C(8)-C(13)	111.6(14)
C(10)-C(9)-C(8)	125.7(15)
C(10)-C(9)-N(1)	119.0(13)
C(8)-C(9)-N(1)	115.0(14)
C(9)-C(10)-C(11)	117.8(15)
C(9)-C(10)-H(10)	121.1
C(11)-C(10)-H(10)	121.1
C(12)-C(11)-C(10)	118.5(16)
C(12)-C(11)-H(11)	120.8
C(10)-C(11)-H(11)	120.8
C(13)-C(12)-C(11)	123.6(16)
C(13)-C(12)-H(12)	118.2
C(11)-C(12)-H(12)	118.2
C(12)-C(13)-C(8)	122.5(15)
C(12)-C(13)-Br(1)	120.0(13)
C(8)-C(13)-Br(1)	117.5(12)
C(15)-C(14)-C(4)	111.8(13)
C(15)-C(14)-H(14A)	109.3
C(4)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(4)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	107.9

C(14)-C(15)-S(1)	114.0(11)
C(14)-C(15)-H(15A)	108.8
S(1)-C(15)-H(15A)	108.8
C(14)-C(15)-H(15B)	108.8
S(1)-C(15)-H(15B)	108.8
H(15A)-C(15)-H(15B)	107.7
O(1)-C(16)-C(17)	111.2(15)
O(1)-C(16)-H(16A)	109.4
C(17)-C(16)-H(16A)	109.4
O(1)-C(16)-H(16B)	109.4
C(17)-C(16)-H(16B)	109.4
H(16A)-C(16)-H(16B)	108.0
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(6)-C(18)-O(5)	122.1(19)
O(6)-C(18)-C(19)	131.2(18)
O(5)-C(18)-C(19)	106.8(16)
C(20)-C(19)-N(2)	110.5(14)
C(20)-C(19)-C(18)	125.0(15)
N(2)-C(19)-C(18)	122.3(15)
C(19)-C(20)-C(21)	106.6(15)
C(19)-C(20)-H(20)	126.7
C(21)-C(20)-H(20)	126.7
C(22)-C(21)-C(20)	112.2(15)
C(22)-C(21)-C(31)	121.6(14)
C(20)-C(21)-C(31)	126.2(14)
C(21)-C(22)-C(23)	137.5(16)
C(21)-C(22)-N(2)	105.6(13)
C(23)-C(22)-N(2)	116.9(14)
C(24)-C(23)-C(22)	125.3(16)
C(24)-C(23)-H(23)	117.3
C(22)-C(23)-H(23)	117.3
C(23)-C(24)-C(25)	120.7(15)
C(23)-C(24)-H(24)	119.6

C(25)-C(24)-H(24)	119.6
C(26)-C(25)-C(30)	113.3(15)
C(26)-C(25)-C(24)	118.5(14)
C(30)-C(25)-C(24)	127.7(14)
C(25)-C(26)-C(27)	122.1(15)
C(25)-C(26)-N(2)	118.7(14)
C(27)-C(26)-N(2)	118.6(13)
C(28)-C(27)-C(26)	118.0(14)
C(28)-C(27)-H(27)	121.0
C(26)-C(27)-H(27)	121.0
C(27)-C(28)-C(29)	123.6(16)
C(27)-C(28)-H(28)	118.2
C(29)-C(28)-H(28)	118.2
C(28)-C(29)-C(30)	117.7(15)
C(28)-C(29)-H(29)	121.2
C(30)-C(29)-H(29)	121.2
C(29)-C(30)-C(25)	123.6(14)
C(29)-C(30)-Br(2)	118.5(11)
C(25)-C(30)-Br(2)	116.0(12)
C(32)-C(31)-C(21)	112.2(12)
C(32)-C(31)-H(31A)	109.2
C(21)-C(31)-H(31A)	109.2
C(32)-C(31)-H(31B)	109.2
C(21)-C(31)-H(31B)	109.2
H(31A)-C(31)-H(31B)	107.9
C(31)-C(32)-S(2)	113.4(10)
C(31)-C(32)-H(32A)	108.9
S(2)-C(32)-H(32A)	108.9
C(31)-C(32)-H(32B)	108.9
S(2)-C(32)-H(32B)	108.9
H(32A)-C(32)-H(32B)	107.7
C(34)-C(33)-O(5)	111.2(18)
C(34)-C(33)-H(33A)	109.4
O(5)-C(33)-H(33A)	109.4
C(34)-C(33)-H(33B)	109.4
O(5)-C(33)-H(33B)	109.4
H(33A)-C(33)-H(33B)	108.0
C(33)-C(34)-H(34A)	109.5

C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$x 10^3) for 200731e. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	96(2)	94(2)	40(1)	3(1)	-7(1)	29(1)
Br(2)	103(2)	95(2)	44(1)	24(1)	9(1)	29(2)
S(1)	81(3)	82(3)	40(3)	0(2)	8(3)	21(3)
S(2)	88(4)	76(3)	46(3)	-4(2)	15(3)	20(3)
F(1)	132(9)	102(8)	95(8)	4(7)	24(7)	-12(8)
F(2)	122(9)	75(7)	102(8)	-18(6)	38(7)	2(7)
N(1)	66(5)	59(5)	34(4)	2(4)	11(4)	32(4)
N(2)	73(5)	59(4)	34(4)	0(4)	8(4)	34(4)
O(1)	93(6)	76(5)	47(5)	3(5)	-7(5)	53(5)
O(2)	103(8)	77(7)	60(7)	1(6)	1(7)	52(7)
O(3)	145(11)	116(9)	41(7)	-8(6)	20(8)	36(9)
O(4)	84(9)	94(9)	63(8)	-13(6)	-1(7)	14(8)
O(5)	109(7)	100(7)	57(6)	11(5)	6(6)	50(6)
O(6)	106(8)	95(8)	53(7)	-9(6)	7(7)	46(8)
O(7)	124(10)	90(8)	54(8)	-20(6)	-3(7)	60(8)
O(8)	81(7)	100(8)	56(7)	-20(6)	4(6)	24(7)
C(1)	74(6)	64(5)	42(5)	2(5)	-2(5)	28(5)
C(2)	77(5)	64(5)	37(5)	3(4)	6(5)	31(5)
C(3)	73(6)	64(5)	35(5)	-1(5)	10(5)	26(5)
C(4)	70(6)	61(5)	31(5)	1(5)	14(5)	22(5)
C(5)	70(5)	62(5)	40(5)	7(5)	9(5)	25(5)
C(6)	66(6)	69(6)	34(5)	2(5)	10(5)	33(5)
C(7)	67(6)	72(6)	35(5)	3(5)	12(5)	28(5)
C(8)	55(5)	57(5)	33(5)	8(5)	9(5)	29(5)
C(9)	64(5)	54(5)	31(5)	10(4)	11(5)	26(5)
C(10)	72(5)	62(5)	40(4)	3(4)	6(4)	27(4)
C(11)	65(6)	61(5)	40(5)	-1(5)	12(5)	26(5)
C(12)	63(7)	60(6)	42(6)	0(6)	15(6)	27(6)
C(13)	69(6)	58(6)	37(5)	0(5)	4(5)	27(6)
C(14)	77(6)	72(6)	39(5)	0(5)	18(5)	26(6)
C(15)	68(7)	70(7)	39(6)	4(6)	11(6)	17(6)
C(16)	103(9)	79(8)	62(8)	-2(7)	-6(8)	38(8)
C(17)	111(15)	111(13)	82(13)	11(11)	-32(12)	37(13)

C(18)	78(6)	69(6)	46(6)	-1(5)	6(6)	23(6)
C(19)	79(5)	70(5)	41(5)	1(5)	5(5)	38(5)
C(20)	76(5)	65(5)	36(5)	1(5)	9(5)	30(5)
C(21)	74(5)	62(5)	36(5)	-6(5)	8(5)	28(5)
C(22)	70(5)	57(5)	38(5)	0(5)	8(5)	25(5)
C(23)	66(5)	55(5)	38(5)	3(5)	10(5)	30(5)
C(24)	72(6)	56(5)	40(5)	3(5)	9(5)	25(5)
C(25)	72(5)	60(5)	38(5)	3(5)	10(5)	33(5)
C(26)	73(5)	61(5)	34(4)	3(4)	2(4)	29(5)
C(27)	74(6)	63(5)	37(5)	0(5)	7(5)	25(5)
C(28)	76(7)	57(6)	49(6)	-3(6)	3(6)	30(6)
C(29)	73(7)	63(7)	29(6)	5(6)	16(6)	26(6)
C(30)	71(6)	62(6)	37(5)	0(5)	6(5)	28(6)
C(31)	80(6)	61(6)	38(5)	-7(5)	8(5)	32(5)
C(32)	74(7)	59(6)	41(6)	-1(6)	16(6)	20(6)
C(33)	98(9)	103(9)	68(8)	3(8)	0(8)	43(9)
C(34)	89(13)	131(14)	122(14)	-23(12)	-29(12)	52(12)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 200731e.

	x	y	z	U(eq)
H(3)	3241	3257	8356	70
H(6)	282	4580	6032	68
H(7)	267	3601	4717	70
H(10)	4860	1621	5880	70
H(11)	5179	1008	4479	67
H(12)	3496	1325	3453	66
H(14A)	1212	5736	7678	75
H(14B)	132	4648	7633	75
H(15A)	2325	5055	8943	71
H(15B)	1012	4236	8915	71
H(16A)	6308	308	8091	102
H(16B)	4912	-117	8298	102
H(17A)	6796	1465	9357	161
H(17B)	6506	40	9423	161
H(17C)	5397	1055	9564	161
H(20)	7850	2996	8301	72
H(23)	6120	5234	6020	64
H(24)	6406	4635	4759	67
H(27)	8570	496	5772	71
H(28)	8773	-261	4447	75
H(29)	8103	846	3388	65
H(31A)	6669	5904	7744	73
H(31B)	5354	5037	7564	73
H(32A)	7346	5038	8981	70
H(32B)	5971	4263	8808	70
H(33A)	10019	-444	8341	111
H(33B)	11147	290	8025	111
H(34A)	11606	1522	9172	185
H(34B)	11492	152	9397	185
H(34C)	10296	1091	9476	185

Table S12. Torsion angles [°] for 200731e.

C(16)-O(1)-C(1)-O(2)	-13(3)
C(16)-O(1)-C(1)-C(2)	165.3(17)
C(5)-N(1)-C(2)-C(3)	2.9(19)
C(9)-N(1)-C(2)-C(3)	167.5(17)
C(5)-N(1)-C(2)-C(1)	161.9(17)
C(9)-N(1)-C(2)-C(1)	-33(3)
O(2)-C(1)-C(2)-C(3)	153(2)
O(1)-C(1)-C(2)-C(3)	-25(3)
O(2)-C(1)-C(2)-N(1)	-3(3)
O(1)-C(1)-C(2)-N(1)	179.0(17)
N(1)-C(2)-C(3)-C(4)	-6(2)
C(1)-C(2)-C(3)-C(4)	-165.1(17)
C(2)-C(3)-C(4)-C(5)	6(2)
C(2)-C(3)-C(4)-C(14)	-178.4(18)
C(3)-C(4)-C(5)-C(6)	177(2)
C(14)-C(4)-C(5)-C(6)	1(3)
C(3)-C(4)-C(5)-N(1)	-5(2)
C(14)-C(4)-C(5)-N(1)	179.9(15)
C(2)-N(1)-C(5)-C(4)	1.1(19)
C(9)-N(1)-C(5)-C(4)	-166.1(15)
C(2)-N(1)-C(5)-C(6)	179.9(16)
C(9)-N(1)-C(5)-C(6)	13(2)
C(4)-C(5)-C(6)-C(7)	-179(2)
N(1)-C(5)-C(6)-C(7)	3(3)
C(5)-C(6)-C(7)-C(8)	-10(3)
C(6)-C(7)-C(8)-C(9)	1(3)
C(6)-C(7)-C(8)-C(13)	-167.1(17)
C(7)-C(8)-C(9)-C(10)	-173.5(17)
C(13)-C(8)-C(9)-C(10)	-4(2)
C(7)-C(8)-C(9)-N(1)	13(2)
C(13)-C(8)-C(9)-N(1)	-176.8(13)
C(2)-N(1)-C(9)-C(10)	3(3)
C(5)-N(1)-C(9)-C(10)	166.2(16)
C(2)-N(1)-C(9)-C(8)	177.1(16)
C(5)-N(1)-C(9)-C(8)	-20(2)
C(8)-C(9)-C(10)-C(11)	2(3)

N(1)-C(9)-C(10)-C(11)	175.2(14)
C(9)-C(10)-C(11)-C(12)	-3(2)
C(10)-C(11)-C(12)-C(13)	5(3)
C(11)-C(12)-C(13)-C(8)	-7(3)
C(11)-C(12)-C(13)-Br(1)	175.3(13)
C(7)-C(8)-C(13)-C(12)	175.6(18)
C(9)-C(8)-C(13)-C(12)	6(2)
C(7)-C(8)-C(13)-Br(1)	-7(2)
C(9)-C(8)-C(13)-Br(1)	-176.7(11)
C(5)-C(4)-C(14)-C(15)	172.8(18)
C(3)-C(4)-C(14)-C(15)	-2(3)
C(4)-C(14)-C(15)-S(1)	166.4(13)
O(3)-S(1)-C(15)-C(14)	-178.5(14)
O(4)-S(1)-C(15)-C(14)	44.3(17)
F(1)-S(1)-C(15)-C(14)	-67.6(15)
C(1)-O(1)-C(16)-C(17)	-178(2)
C(33)-O(5)-C(18)-O(6)	-2(3)
C(33)-O(5)-C(18)-C(19)	177.9(17)
C(22)-N(2)-C(19)-C(20)	4(2)
C(26)-N(2)-C(19)-C(20)	-168.1(19)
C(22)-N(2)-C(19)-C(18)	-159.4(16)
C(26)-N(2)-C(19)-C(18)	28(3)
O(6)-C(18)-C(19)-C(20)	-155(2)
O(5)-C(18)-C(19)-C(20)	25(3)
O(6)-C(18)-C(19)-N(2)	6(3)
O(5)-C(18)-C(19)-N(2)	-173.4(17)
N(2)-C(19)-C(20)-C(21)	-4(2)
C(18)-C(19)-C(20)-C(21)	159.2(18)
C(19)-C(20)-C(21)-C(22)	2(2)
C(19)-C(20)-C(21)-C(31)	-179.8(19)
C(20)-C(21)-C(22)-C(23)	180(2)
C(31)-C(21)-C(22)-C(23)	2(4)
C(20)-C(21)-C(22)-N(2)	1(2)
C(31)-C(21)-C(22)-N(2)	-177.7(15)
C(19)-N(2)-C(22)-C(21)	-3(2)
C(26)-N(2)-C(22)-C(21)	171.0(16)
C(19)-N(2)-C(22)-C(23)	177.6(16)
C(26)-N(2)-C(22)-C(23)	-8(2)

C(21)-C(22)-C(23)-C(24)	-177(2)
N(2)-C(22)-C(23)-C(24)	2(3)
C(22)-C(23)-C(24)-C(25)	6(3)
C(23)-C(24)-C(25)-C(26)	-7(3)
C(23)-C(24)-C(25)-C(30)	-178.8(19)
C(30)-C(25)-C(26)-C(27)	-15(3)
C(24)-C(25)-C(26)-C(27)	172.2(17)
C(30)-C(25)-C(26)-N(2)	173.5(16)
C(24)-C(25)-C(26)-N(2)	1(3)
C(19)-N(2)-C(26)-C(25)	178(2)
C(22)-N(2)-C(26)-C(25)	7(2)
C(19)-N(2)-C(26)-C(27)	7(3)
C(22)-N(2)-C(26)-C(27)	-164.9(16)
C(25)-C(26)-C(27)-C(28)	12(3)
N(2)-C(26)-C(27)-C(28)	-177.0(16)
C(26)-C(27)-C(28)-C(29)	-4(3)
C(27)-C(28)-C(29)-C(30)	0(3)
C(28)-C(29)-C(30)-C(25)	-5(3)
C(28)-C(29)-C(30)-Br(2)	-169.2(14)
C(26)-C(25)-C(30)-C(29)	12(3)
C(24)-C(25)-C(30)-C(29)	-176.1(18)
C(26)-C(25)-C(30)-Br(2)	176.5(13)
C(24)-C(25)-C(30)-Br(2)	-12(3)
C(22)-C(21)-C(31)-C(32)	178.8(18)
C(20)-C(21)-C(31)-C(32)	1(3)
C(21)-C(31)-C(32)-S(2)	175.8(13)
O(7)-S(2)-C(32)-C(31)	-171.8(14)
O(8)-S(2)-C(32)-C(31)	51.9(17)
F(2)-S(2)-C(32)-C(31)	-59.4(15)
C(18)-O(5)-C(33)-C(34)	136(2)

Symmetry transformations used to generate equivalent atoms:

Table S13. Hydrogen bonds for 200731e [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)