SUPPORTING INFORMATION

Successive C-C bond cleavage, fluorination, trifluoromethylthio- or pentafluorophenylthiolation under metal-free conditions to provide compounds with dual fluoro-functionalization

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1. Experimental Section

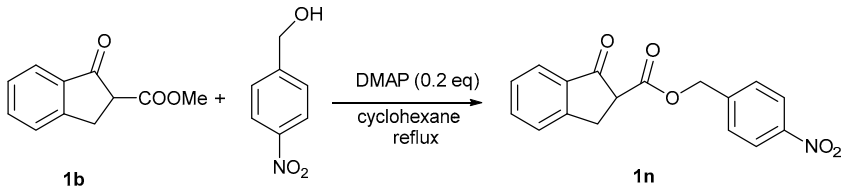
1.1 General Methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63—210 μm. The ^{1}H-NMR (500 MHz or 400 MHz), ^{19}F-NMR (282 MHz), ^{13}C-NMR (125.7 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 500, Buruker Avance 400 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00). The C_6F_6 [δ = −162.2 ($CDCl_3$)] was used as internal standard for ^{19}F NMR. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020 (ESI-MS). High resolution mass spectrometry were recorded on a Waters Synapt G2 HDMS (ESI-MS). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting point were recorded on a BUCHI M-565. The balance used is ATX-224 (Shimadzu Corporation); Minimum Display 0.1 mg; Repeatability (Standard Deviation); 0.1 mg; Linearity error ±0.2 mg. All solvents were dried and distilled before use. Chemist Plaza CP-170 (SIBATA SCIENTIFIC TECHNOLOGY LTD.) for heating and cooling was used for all the reaction.

DAST [(Diethylamino)sulfur Trifluoride] (Purity: >90.0%, Product Number; D1868), Methoxy-DAST [Bis(2-methoxyethyl)aminosulfur Trifluoride] (Purity: >90.0%, Product Number; B2440) and Morph-DAST (Morpholinosulfur Trifluoride) (Purity: >93.0%, Product Number; M1573) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Methyl-DAST (Dimethylaminosulfur trifluoride) was purchased from Aldrich, USA. (Purity: >95.0%, Product Number; 248215).

The *β*-keto esters **1a—m** and **1o—1q** are known compounds, and all these compounds were synthesized according to the literature procedures. [1—5]

1.2 Preparation of 4-nitrobenzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1n);

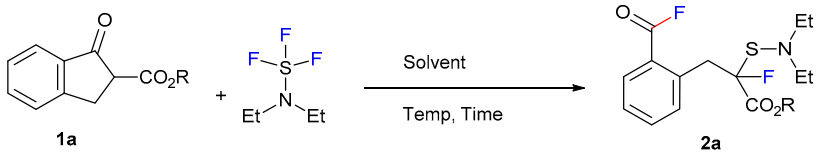


1b **1n**

To a flask equipped with a Dean-Stark trap and reflux condenser was added methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1b** (0.5 g, 2.6 mmol), (4-nitrophenyl)methanol (0.6 g, 3.9 mmol), DMAP (0.06 g, 0.52 mmol) and cyclohexane (4 mL). The mixture was heated to reflux, distilling the methanol formed during the reaction. The mixture was refluxed until complete conversion was observed by TLC, then concentrated under reduced pressure and the crude product was purified by flash column chromatography (Hex: AcOEt = 8:1—3:1) to provide the title compound **1n** as a white solid in 45% yield (0.36 g). This compound was observed as a mixture of two isomers (keto- and enol forms) in the NMR. mp: 97.9—99.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.22—8.27 (m, 4H), 7.79 (d, 1H, *J* = 8.4 Hz), 7.63—7.68 (m, 2H), 7.57—7.59 (m, 4H), 7.50—7.53 (m, 1H), 7.40—7.48 (m, 4H), 5.26—5.40 (m, 4H), 3.83 (dd, 1H, *J* = 8.4, J = 4.0 Hz), 3.57—3.62 (m, 3H), 3.41 (dd, 1H, *J* = 17.2, J = 8.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 199.0, 168.7, 153.5, 147.7, 143.5, 142.9, 136.6, 135.7, 135.0, 129.9, 128.2, 128.0, 127.0, 126.6, 124.9, 124.8, 123.9, 121.0, 101.1, 65.7, 64.2, 53.2, 32.5, 30.1; IR (KBr): 3283, 1658, 1573, 1514, 1341, 1270, 1218, 1180, 759 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{13}NNaO_5$ $[M+H]^+$: 334.0691; Found: 334.0696.

2. Optimization of ring-opening reaction condition (mono-fluorination)

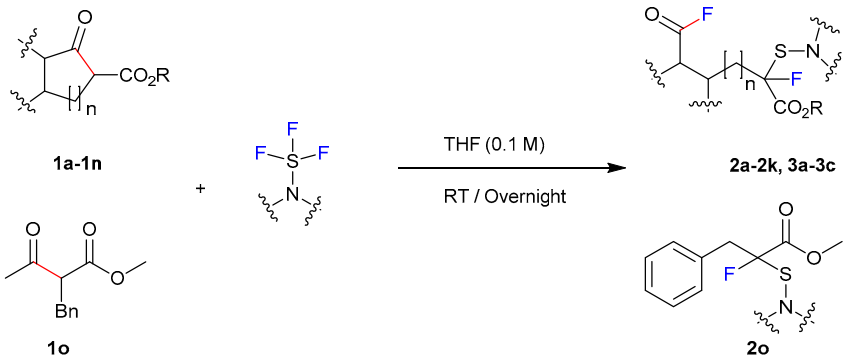
Table S1. Optimization of ring-opening reaction condition[a]



Entry	Solvent	DAST (eq)	Temp (°C)	Time	**2a** (%)[b]
1	DMF	2.0	RT	Overnight	54
2	DMF	1.0	RT	Overnight	30
3	DMF	3.0	RT	Overnight	50
4	DMF	4.0	RT	Overnight	54
5	DMF	2.0	50	Overnight	36
6	CH_2Cl_2	2.0	RT	Overnight	31
7	toluene	2.0	RT	Overnight	14
8	**THF**	**2.0**	RT	**Overnight**	**85**
9	EtOH	2.0	RT	Overnight	NR
10	**CH_3CN**	**2.0**	RT	**Overnight**	**85**
11	THF	1.5	RT	Overnight	71
12	CH_3CN	1.5	RT	Overnight	66
13[c]	THF	2.0	RT	Overnight	60

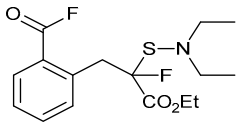
[a]The reaction of **1a** with DAST was carried out in different solvents and at different temperature. For detailed reaction conditions, see the table S1. [b] Yield was determined by ^{19}F NMR spectroscopy with an internal standard as C_6H_5F. [c] Following the general procedure, and use 1.0 eq of base (DIEA).

3. General procedure and product characterization data for 2a—2k, 2o and 3a—3c;



A flame-dried vessel was successively charged, under nitrogen, with *β*-keto esters **1a—1k** and **1o** (0.1 mmol, 1.0 equiv) and anhydrous THF (1.0 mL). The solution was cooled to 0 °C and the DAST (0.2 mmol, 2.0 equiv) was added slowly by syringe. Then the reaction mixture was stirred at room temperature for overnight, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography to provide the title compound **2a—2k, 2o and 3a—3c**.

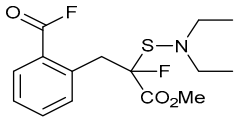
3.1 Ethyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (2a);



Following the general procedure, using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **1a** (20.4 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **2a** as a yellow oil in 85% yield (29.6 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.96 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 7.54—7.58 (m, 1H), 7.38—7.42 (m, 2H), 4.12—4.23 (m, 2H), 3.94 (dd, 1H, J = 15.0 Hz, J = 11.0 Hz), 3.79 (dd, 1H, J = 25.5 Hz, J = 14.5 Hz), 3.02—3.08 (m, 4H), 1.25 (t, 3H, J = 7.2 Hz), 1.10 (t, 6H, J = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.3 (s, 1F), –140.1 (dd, 1F, J = 25.6 Hz, J = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.3 (d, J = 31.3 Hz), 156.9 (d, J = 346.6 Hz), 137.8 (d, J = 6.0 Hz), 134.2,

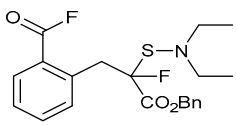
132.7 (d, J = 3.0 Hz), 132.4 (d, J = 1.2 Hz), 127.9, 125.7 (d, J = 57.3 Hz), 107.2 (d, J = 234.8 Hz), 62.3, 52.3, 36.8 (d, J = 21.8 Hz), 14.1, 13.7; IR (NaCl): 2985, 2924, 2854, 1725, 1696, 1450, 1261, 715, 531 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{22}F_2NO_3S$ $[M+H]^+$: 346.1288; Found: 346.1291.

3.2 Methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (2b);



Following the general procedure, using methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1b** (19.0 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **2b** as a yellow oil in 78% yield (25.8 mg). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.96 (dd, 1H, J = 8.5 Hz, J = 1.5 Hz), 7.55—7.58 (m, 1H), 7.39—7.42 (m, 2H), 3.94 (dd, 1H, J = 14.5 Hz, J = 10.5 Hz), 3.79 (dd, 1H, J = 25.0 Hz, J = 14.5 Hz), 3.74 (s, 3H), 2.96—3.03 (m, 4H), 1.09 (t, 6H, J = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.4 (s, 1F), –140.4 (dd, 1F, J = 23.6 Hz, J = 9.5 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.7 (d, J = 31.4 Hz), 156.9 (d, J = 346.9 Hz), 137.7 (d, J = 6.2 Hz), 134.3, 132.7 (d, J = 3.7 Hz), 132.4 (d, J = 1.2 Hz), 127.9, 125.7 (d, J = 57.8 Hz), 107.3 (d, J = 235.0 Hz), 52.9, 52.3, 36.8 (d, J = 22.6 Hz), 13.7; IR (NaCl): 2973, 2931, 2858, 1812, 1758, 1237, 1119, 756, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{15}H_{19}F_2NNaO_3S$ $[M+Na]^+$: 354.0951; Found: 354.0955.

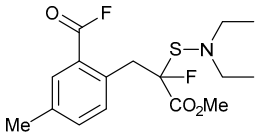
3.3 Benzyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (2c);



Following the general procedure, using benzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1c** (26.6 mg, 0.1 mmol, 1.0 equiv) and

DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **2c** as a yellow oil in 69% yield (28.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.92 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.39—7.43 (m, 1H), 7.29—7.36 (m, 6H), 7.23—7.26 (m, 1H), 5.20, 5.11 (AB quartet, *J*=12.5 Hz, 2H), 3.98 (dd, 1H, *J* = 14.5 Hz, *J* = 10.0 Hz), 3.73 (dd, 1H, *J* = 25.5 Hz, *J* = 14.5 Hz), 2.83—3.06 (m, 4H), 1.04 (s, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.1 (s, 1F), –140.4 (dd, 1F, *J* = 25.6 Hz, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.2 (d, *J* = 31.4 Hz), 156.8 (d, *J* = 346.9 Hz), 137.7 (d, *J* = 6.2 Hz), 134.9, 134.3, 132.6 (d, *J* = 3.7 Hz), 132.4 (d, *J* = 1.2 Hz), 128.9, 128.7, 128.6, 127.8, 125.6 (d, *J* = 57.8 Hz), 107.2 (d, *J* = 235.0 Hz), 67.8, 52.3, 36.8 (d, *J* = 21.3 Hz), 13.7; IR (NaCl): 2970, 2935, 2873, 1811, 1749, 1236, 1002, 741, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{21}H_{23}F_2NNaO_3S$ $[M+Na]^+$: 430.1264; Found: 430.1257.

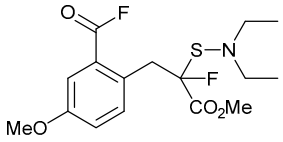
3.4 Methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)-4-methylphenyl)propanoate (2d);



Following the general procedure, using methyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1d** (20.2 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **2d** as a yellow oil in 70% yield (24.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.76 (d, 1H, *J* = 1.5 Hz), 7.36 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.26—7.28 (m, 1H), 3.88 (dd, 1H, *J* = 14.5 Hz, *J* = 11.0 Hz), 3.70—3.78 (m, 4H), 2.97—3.02 (m, 4H), 2.37 (s, 3H), 1.09 (t, 6H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.3 (s, 1F), –140.3 (dd, 1F, *J* = 24.5 Hz, *J* = 10.8 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.8 (d, *J* = 31.6 Hz), 157.1

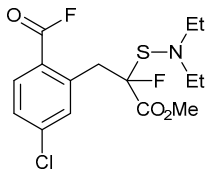
(d, J = 346.9 Hz), 137.9, 135.1, 134.5 (d, J = 5.0 Hz), 132.9, 132.6 (d, J = 3.7 Hz), 125.4 (d, J = 56.5 Hz), 107.4 (d, J = 234.3 Hz), 52.9, 52.3, 36.5 (d, J = 21.8 Hz), 20.9, 13.7; IR (NaCl): 2973, 2927, 2870, 1817, 1756, 1259, 1175, 1015, 764, 728 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{21}F_2NNaO_3S$ $[M+Na]^+$: 368.1108; Found: 368.1100.

3.5 Methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)-4-methoxyphenyl)propanoate (2e);



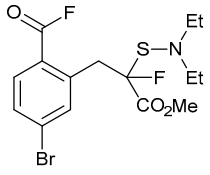
Following the general procedure, using methyl 6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1e** (22.0 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **2e** as a yellow oil in 80% yield (28.9 mg). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.44 (d, 1H, J = 2.5 Hz), 7.29 (d, 1H, J = 8.5 Hz), 7.09 (dd, 1H, J = 8.5 Hz, J = 2.5 Hz), 3.82—3.87 (m, 4H), 3.67—3.75 (m, 4H), 2.95—3.06 (m, 4H), 1.09 (t, 6H, J = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.3 (s, 1F), –140.3 (dd, 1F, J = 24.8 Hz, J = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.8 (d, J = 31.6 Hz), 158.8, 156.7 (d, J = 347.4 Hz), 133.9 (d, J = 3.7 Hz), 129.3 (d, J = 5.0 Hz), 126.4 (d, J = 56.5 Hz), 120.3, 117.0, 107.5 (d, J = 234.0 Hz), 55.6, 52.8, 52.3, 36.5 (dd, J = 21.7 Hz, J = 1.2 Hz), 13.7; IR (NaCl): 2970, 2931, 2858, 1813, 1755, 1507, 1267, 1004, 760, 724 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{21}F_2NNaO_4S$ $[M+Na]^+$: 384.1057; Found: 384.1071.

3.6 Methyl 3-(4-chloro-2-(fluorocarbonyl)phenyl)-2-((diethylamino)thio)-2-fluoropropanoate (2f);



Following the general procedure, using methyl 6-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1f** (22.6 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **2f** as a yellow oil in 67% yield (24.5 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.90 (d, 1H, *J* = 8.5 Hz), 7.38—7.40 (m, 2H), 3.91 (dd, 1H, *J* = 14.5 Hz, *J* = 11.0 Hz), 3.72—3.80 (m, 4H), 2.97—3.03 (m, 4H), 1.10 (t, 6H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.4 (s, 1F), –140.3 (dd, 1F, *J* = 23.6 Hz, *J* = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.5 (d, *J* = 31.1 Hz), 156.1 (d, *J* = 345.8 Hz), 140.9, 139.7 (d, *J* = 6.2 Hz), 133.6, 132.9 (d, *J* = 2.7 Hz), 128.3, 124.0 (d, *J* = 58.8 Hz), 107.0 (d, *J* = 235.0 Hz), 53.0, 52.3, 36.6 (d, *J* = 21.7 Hz), 13.7; IR (NaCl): 2973, 2933, 2868, 1815, 1757, 1236, 1005, 769, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{15}H_{18}ClF_2NNaO_3S$ $[M+Na]^+$: 388.0562; Found: 388.0574.

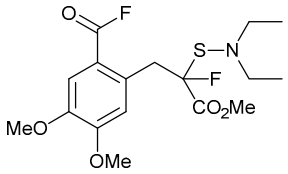
3.7 Methyl 3-(4-bromo-2-(fluorocarbonyl)phenyl)-2-((diethylamino)thio)-2-fluoropropanoate (2g);



Following the general procedure, using methyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1g** (26.9 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **2g**

as a yellow oil in 71% yield (29.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.81 (d, 1H, *J* = 8.0 Hz), 7.54—7.56 (m, 2H), 3.91 (dd, 1H, *J* = 14.5 Hz, *J* = 10.5 Hz), 3.70—3.78 (m, 4H), 2.97—3.03 (m, 4H), 1.10 (t, 6H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.4 (s, 1F), –140.3 (dd, 1F, *J* = 24.5 Hz, *J* = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.3 (d, *J* = 31.1 Hz), 156.3 (d, *J* = 345.9 Hz), 139.5 (d, *J* = 6.2 Hz), 135.7 (d, *J* = 2.4 Hz), 133.4, 131.2, 129.4, 124.4 (d, *J* = 58.9 Hz), 106.9 (d, *J* = 235.0 Hz), 52.9, 52.1, 36.4 (d, *J* = 21.7 Hz), 13.6; IR (NaCl): 2972, 2931, 2867, 1815, 1757, 1238, 1004, 767, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{15}H_{18}BrF_2NNaO_3S$ $[M+Na]^+$: 432.0057; Found: 432.0049.

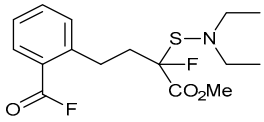
3.8 Methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)-4,5-dimethoxyphenyl)propanoate (2h);



Following the general procedure, using methyl 5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1h** (25.0 mg, 0.1 mmol, 1.0 equiv) and DAST (30 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1—3:1) to provide the title compound **2h** as a white solid in 54% yield (21.2 mg); mp: 102—103 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.42 (s, 1H), 6.87 (s, 1H), 3.93 (s, 3H), 3.86—3.92 (m, 4H), 3.74—3.82 (m, 4H), 2.96—3.06 (m, 4H), 1.09 (t, 6H, *J* = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.6 (s, 1F), –140.0 (dd, 1F, *J* = 24.5 Hz, *J* = 12.6 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.8 (d, *J* = 31.4 Hz), 156.4 (d, *J* = 342.1 Hz), 153.5, 147.8, 132.8 (d, *J* = 6.2 Hz), 116.7 (d, *J* = 57.6 Hz), 114.8 (d, *J* = 1.8 Hz), 114.3 (d, *J* = 1.4 Hz), 107.3 (d, *J* = 234.4 Hz), 56.1, 56.0, 52.8, 52.1, 36.5 (d, *J* = 21.7 Hz), 13.6; IR (NaCl): 2961, 2918, 2853, 1802, 1523, 1275, 1130, 1048, 800, 717, 592 cm^{-1};

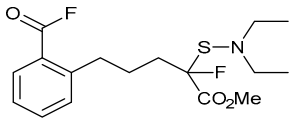
HRMS (ESI): Calcd. for $C_{17}H_{23}F_2NNaO_5S$ $[M+Na]^+$: 414.1163; Found: 414.1189.

3.9 Methyl 2-((diethylamino)thio)-2-fluoro-4-(2-(fluorocarbonyl)phenyl)butanoate (2i);



Following the general procedure, using methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate **1i** (40.8 mg, 0.2 mmol, 1.0 equiv) and DAST (60 μL, 0.4 mmol, 2.0 equiv) in THF (2 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1—12:1) to provide the title compound **2i** as a yellow oil in 30% yield (20.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.99 (dd, 1H, *J* = 7.0 Hz, *J* = 1.0 Hz), 7.56—7.59 (m, 1H), 7.34—7.38 (m, 2H), 3.73 (s, 3H), 3.18—3.24 (m, 1H), 2.94—3.10 (m, 5H), 2.36—2.47 (m, 1H), 2.13—2.20 (m, 1H), 1.09 (s, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.7 (s, 1F), –142.3 (dd, 1F, *J* = 19.4 Hz, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.0 (d, *J* = 32.5 Hz), 156.3 (d, *J* = 345.8 Hz), 145.6 (d, *J* = 7.5 Hz), 135.0, 132.9 (d, *J* = 1.2 Hz), 132.3 (d, *J* = 4.2 Hz), 127.2, 123.4 (d, *J* = 56.5 Hz), 107.7 (d, *J* = 230.2 Hz), 52.7, 52.2, 35.0 (d, *J* = 21.9 Hz), 28.9 (d, *J* = 3.2 Hz), 13.7; IR (NaCl): 2973, 2935, 2868, 1809, 1754, 1233, 1001, 928, 742, 695 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{21}F_2NNaO_3S$ $[M+Na]^+$: 368.1108; Found: 368.1105.

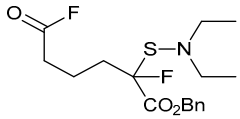
3.10 Methyl 2-((diethylamino)thio)-2-fluoro-5-(2-(fluorocarbonyl)phenyl)pentanoate (2j);



Following the general procedure, using methyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate **1j** (43.6 mg, 0.2 mmol, 1.0 equiv) and DAST (60 μL, 0.4 mmol, 2.0 equiv) in THF (2 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was

purified by flash column chromatography (Hex: AcOEt = 15:1—12:1) to provide the title compound **2j** as a yellow oil in 39% yield (28.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.99 (dd, 1H, *J* = 7.5 Hz, *J* = 1.0 Hz), 7.56—7.59 (m, 1H), 7.31—7.36 (m, 2 H), 3.80 (s, 3H), 2.93—3.05 (m, 6H), 2.08—2.19 (m, 1H), 1.95—2.03 (m, 1H), 1.79—1.84 (m, 1H), 1.62—1.68 (m, 1H), 1.08 (t, 6H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +29.3 (s, 1F), –141.9 (dd, 1F, *J* = 25.6 Hz, *J* = 11.8 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.4 (d, *J* = 31.9 Hz), 156.4 (d, *J* = 345.6 Hz), 147.0 (d, *J* = 7.4 Hz), 134.9, 132.9 (d, *J* = 1.5 Hz), 131.6 (d, *J* = 4.2 Hz), 126.8, 123.2 (d, *J* = 56.3 Hz), 108.2 (d, *J* = 230.0 Hz), 52.8, 52.2, 34.0 (d, *J* = 22.3 Hz), 33.9, 25.0 (d, *J* = 2.2 Hz), 13.7; IR (NaCl): 2971, 2930, 2870, 1808, 1749, 1229, 999, 743, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{23}F_2NNaO_3S$ $[M+Na]^+$: 382.1264; Found: 382.1260.

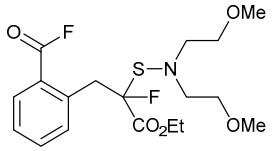
3.11 Benzyl 2-((diethylamino)thio)-2,6-difluoro-6-oxohexanoate (2k);



Following the general procedure, using benzyl 2-oxocyclopentanecarboxylate **2k** (43.6 mg, 0.2 mmol, 1.0 equiv) and DAST (60 μL, 0.4 mmol, 2.0 equiv) in THF (2 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1—5:1) to provide the title compound **2k** as a yellow oil in 39% yield (28.1 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32—7.42 (m, 5H), 5.29, 5.18 (AB quartet, *J*=12.0 Hz, 2H), 3.90—3.00 (m, 4H), 2.47—2.51 (m, 2H), 2.10—2.44 (m, 1H), 1.92—2.08 (m, 1H), 1.78—1.89 (m, 1H), 1.63—1.73 (m, 1H), 1.04—1.10 (m, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +44.9 (s, 1F),–142.0 (dd, 1F, *J* = 24.2 Hz, *J* = 9.5 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.5 (d, *J* = 31.8 Hz), 162.8 (d, *J* = 360.1 Hz), 134.9, 128.8, 128.7, 107.8 (d, *J* = 230.7 Hz), 67.9, 52.2, 32.9 (d, *J* = 22.3 Hz), 31.6 (d, *J* = 51.5 Hz), 18.3, 13.6; IR (NaCl): 2974, 2938, 2866, 1847, 1748, 1119, 1264, 1001, 753, 698, 669 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{24}F_2NO_3S$ $[M+H]^+$: 360.1445; Found: 360.1444.

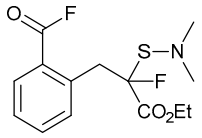
3.12 Ethyl

2-((bis(2-methoxyethyl)amino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (3a);



Following the general procedure, using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **1a** (20.4 mg, 0.1 mmol, 1.0 equiv) and Methoxy-DAST [Bis(2-methoxyethyl)aminosulfur Trifluoride] (41 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **3a** as a yellow oil in 77% yield (31.4 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.97 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.55—7.58 (m, 1H), 7.39—7.42 (m, 2 H), 4.17—4.22 (m, 2H), 3.91 (dd, 1H, *J* = 14.5 Hz, *J* = 10.5 Hz), 3.80 (dd, 1H, *J* = 25.5 Hz, *J* = 14.5 Hz), 3.51 (s, 4H), 3.33 (s, 6H), 3.22 (s, 4H), 1.26 (t, 3H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.2 (s, 1F), –140.7 (dd, 1F, *J* = 24.5 Hz, *J* = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.1 (d, *J* = 31.4 Hz), 156.8 (d, *J* = 346.6 Hz), 137.7 (d, *J* = 6.2 Hz), 134.3, 132.7 (d, *J* = 2.5 Hz), 132.4, 127.9, 125.6 (d, *J* = 57.3 Hz), 107.2 (d, *J* = 234.3 Hz), 71.3, 71.0, 62.4, 58.8, 58.2, 36.5 (d, *J* = 21.4 Hz), 14.1; IR (NaCl): 2981, 2927, 1812, 1751, 1449, 1237, 1004, 741, 703 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{25}F_2NNaO_5S$ $[M+Na]^+$: 428.1319; Found: 428.1324.

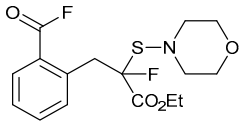
3.13 Ethyl 2-((dimethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (3b);



Following the general procedure, using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **1a** (20.4 mg, 0.1 mmol, 1.0 equiv) and Methyl-DAST (Dimethylaminosulfur trifluoride) (22 μL, 0.2 mmol, 2.0 equiv) in

THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 15:1) to provide the title compound **3b** as a yellow oil in 51% yield (16.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.97 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.55—7.58 (m, 1H), 7.39—7.42 (m, 2H), 4.19—4.23 (m, 2H), 3.92 (dd, 1H, *J* = 14.5 Hz, *J* = 11.5 Hz), 3.80 (dd, 1H, *J* = 25.0 Hz, *J* = 14.5 Hz), 2.86 (s, 6H), 1.27 (t, 3H, *J* = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.2 (s, 1F), –140.4 (dd, 1F, *J* = 24.5 Hz, *J* = 11.5 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.6 (d, *J* = 31.1 Hz), 156.8 (d, *J* = 346.6 Hz), 137.6 (d, *J* = 6.4 Hz), 134.3, 132.8 (d, *J* = 3.2 Hz), 132.4, 128.0, 125.6 (d, *J* = 57.3 Hz), 107.1 (d, *J* = 234.0 Hz), 62.4, 49.3, 36.8 (d, *J* = 20.7 Hz), 14.1; IR (NaCl): 2986, 2937, 2791, 1811, 1749, 1237, 1003, 755, 742, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{17}F_2NNaO_3S$ $[M+Na]^+$: 340.0795; Found: 340.0789.

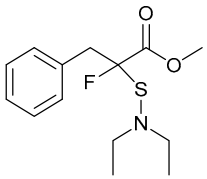
3.14 Ethyl 2-fluoro-3-(2-(fluorocarbonyl)phenyl)-2-(morpholinothio)propanoate (3c);



Following the general procedure, using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **1a** (20.4 mg, 0.1 mmol, 1.0 equiv) and Morph-DAST (Morpholinosulfur Trifluoride) (27 μL, 0.2 mmol, 2.0 equiv) in THF (1 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **3c** as a yellow oil in 72% yield (25.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.99 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.56—7.59 (m, 1H), 7.39—7.44 (m, 2H), 4.19—4.24 (m, 2H), 4.00 (dd, 1H, *J* = 14.5 Hz, *J* = 12.0 Hz), 3.79 (dd, 1H, *J* = 24.5 Hz, *J* = 14.5 Hz), 3.58—3.65 (m, 4H), 3.05—3.12 (m, 4H), 1.27 (t, 3H, *J* = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +31.2 (s, 1F), –138.6 (dd, 1F, *J* = 23.6 Hz, *J* = 11.8 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.0 (d, *J* = 30.9 Hz), 156.8 (d, *J* = 346.5 Hz), 137.4 (d, *J* = 6.2 Hz), 134.3, 132.8 (d, *J* = 3.2 Hz), 132.5,

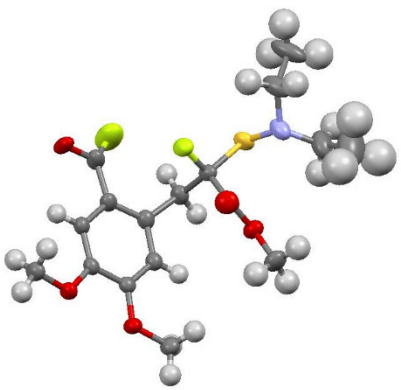
128.1, 125.5 (d, J = 57.4 Hz), 107.6 (d, J = 235.3 Hz), 67.8, 62.5, 57.3, 37.0 (d, J = 21.6 Hz), 14.2; IR (NaCl): 2961, 2913, 2853, 1811, 1750, 1237, 1113, 1003, 742, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{19}F_2NNaO_4S$ $[M+Na]^+$: 382.0901; Found: 382.0894.

Methyl 2-((diethylamino)thio)-2-fluoro-3-phenylpropanoate (2o);



Following the general procedure, using methyl 2-benzyl-3-oxobutanoate **1o** (41.2 mg, 0.2 mmol, 1.0 equiv) and DAST (60 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL), the reaction mixture was stirred at 50 °C for overnight. After cooling to room temperature, the reaction was quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1—10:1) to provide the title compound **2o** as a yellow oil in 45% yield (25.6 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.21—7.29 (m, 5H), 3.73 (s, 3H), 3.33 (dd, 1H, J = 28.0 Hz, J = 14.5 Hz), 3.21 (t, 1H, J = 14.0 Hz), 2.95—3.02 (m, 4H), 1.10 (t, 6H, J = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –140.2 (dd, 1F, J = 26.7 Hz, J = 12.9 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.9 (d, J = 31.6 Hz), 133.6, 130.2, 128.4, 127.4, 107.9 (d, J = 233.1 Hz), 52.7, 52.3, 40.3 (d, J = 21.7 Hz), 13.7; IR (NaCl): 2970, 2920, 2861, 1584, 1237, 1167, 1082, 913, 785, 708, 609 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{20}FNNaO_2S$ $[M+Na]^+$: 308.1096; Found: 308.1079.

4. X-ray crystallography data for the 2h (CCDC 1415530)



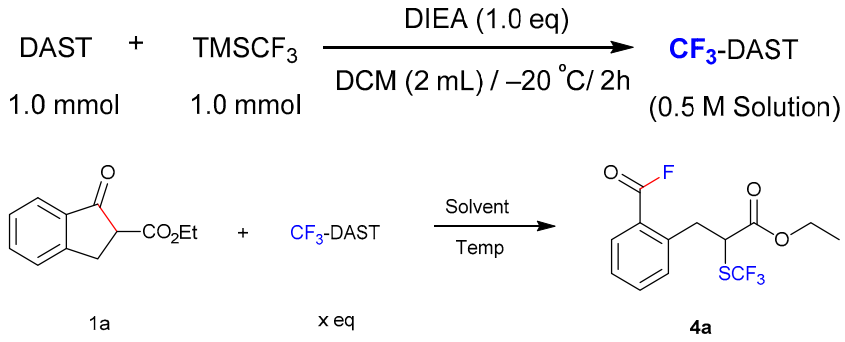
EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{17}H_{23}F_2NO_5S$
Formula Weight	391.43
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.200 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 38.0429(9) Å b = 5.9645(2) Å c = 19.5829(5) Å β = 120.9238(7) ^{o} V = 3811.8(2) $Å^3$
Space Group	C2/c (#15)
Z value	8
D_{calc}	1.364 g/cm^3
F_{000}	1648.00
μ(MoKα)	2.153 cm^{-1}

5. Optimization of ring-opening reaction condition (SCF_3)

Table S2. Optimization of ring-opening reaction condition[a]

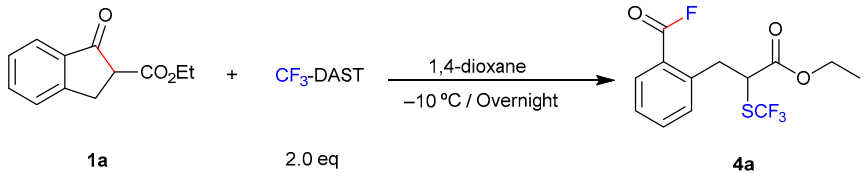


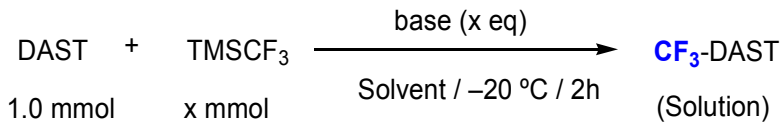
Entry	Solvent	CF_3-DAST (eq)	Temp(°C)	Time	**4a** (%)[b]
1	THF	2.0	RT	Overnight	28
2	THF	2.0	50	Overnight	18
3	THF	2.0	0	Overnight	17
4	THF	2.0	–20	Overnight	22
5	DMF	2.0	RT	Overnight	24
6	DCM	2.0	RT	Overnight	14
7	CH_3CN	2.0	RT	Overnight	3
8	MeOH	2.0	RT	Overnight	0
9	Toluene	2.0	RT	Overnight	18
10	Et_2O	2.0	RT	Overnight	34
11	dioxane	2.0	RT	Overnight	49
12	Benzene	2.0	RT	Overnight	17
13	$CHCl_3$	2.0	RT	Overnight	30
14	Pridine	2.0	RT	Overnight	32
15	dioxane	2.0	50	Overnight	38

16	dioxane	2.0	0	Overnight	67
17	**dioxane**	**2.0**	**–10**	**Overnight**	**78**
18	dioxane	1.0	–10	Overnight	52
19	dioxane	1.5	–10	Overnight	61

[a]The reaction of **1a** with 2.0 equivalents of CF_3-DAST (0.5 M mixture in DCM) was carried out in different solvents and at different temperature. For detailed reaction conditions, see the table S2. [b]Yield was determined by ^{19}F NMR spectroscopy with an internal standard as $C_6H_5CF_3$.

Table S3. Optimization of ring-opening reaction condition[a]





Entry	Solvent	Base (eq)	$TMSCF_3$	Concentration	**4a** (%)[b]	
					Time	yield
1	THF	DIEA (1.0)	1.0	0.5	Overnight	46
2	Et_2O	DIEA (1.0)	1.0	0.5	Overnight	40
3	$CHCl_3$	DIEA (1.0)	1.0	0.5	Overnight	0
4	dioxane	DIEA (1.0)	1.0	0.5	Overnight	5
5	DCM	TEA (1.0)	1.0	0.5	Overnight	54
6	DCM	DBU (1.0)	1.0	0.5	Overnight	trace
7	DCM	DIEA (1.0)	2.0	0.5	Overnight	61
8	DCM	DIEA (1.0)	3.0	0.5	Overnight	38
9	DCM	DIEA (1.0)	1.0	1.0	Overnight	66
10	DCM	DIEA (0.5)	1.0	0.5	Overnight	53
11	DCM	DIEA (1.5)	1.0	0.5	Overnight	72
12	DCM	DIEA (1.0)	1.0	0.5	30 min	42
13	DCM	DIEA (1.0)	1.0	0.5	1 h	47

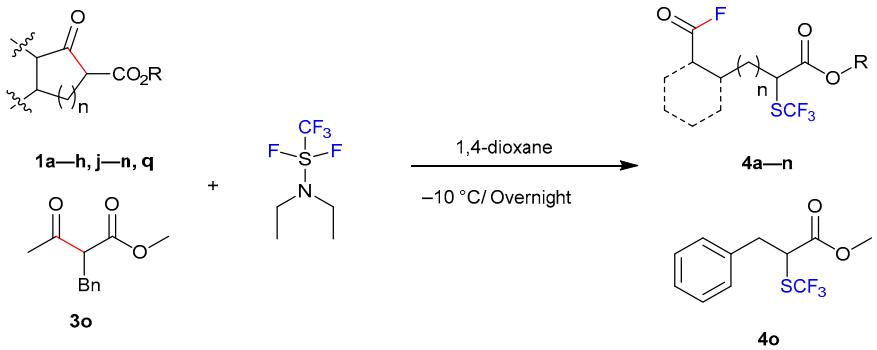
14	DCM	DIEA (1.0)	1.0	0.5	3 h	58
15	DCM	---------	1.0	0.5	Overnight	6
16	DCM	DIEA (0.1)	1.0	0.5	Overnight	19

[a]The reaction of**1a** with 2.0 equivalents of CF_3-DAST (0.5 M mixture in DCM) was carried out in different solvents and different bases. For detailed reaction conditions, see the table S3. [b] Yield was determined by ^{19}F NMR spectroscopy with an internal standard as $C_6H_5CF_3$.

6. Typical procedure preparation of CF_3-DAST reagents

A flame-dried vessel was successively charged, under nitrogen, with diisopropylethylamine (0.17 mL, 1.0 mmol) and anhydrous dichloromethane (2 mL). The resulting mixture was cooled to –20 °C, the diethylaminosulfurtrifluoride (0.15 mL, 1.0 mmol) was added slowly by syringe, stirred for 15 min at same temperature, then the trimethylsilyltrifluoromethane (0.16 mL, 1.0 mmol) was added slowly by syringe, and stirring for two hours under the same reaction temperature. After two hours, the solution was directly used for next step without purification. See below.

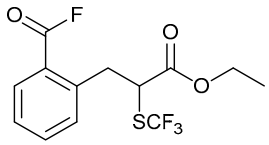
7. General procedure and product characterization data for 4a—4o;



A flame-dried vessel was successively charged, under nitrogen, with *β*-keto esters **1a—h, j—n, q and 1o** (0.1 mmol, 1.0 equiv) and anhydrous 1,4-dioxane (1.0 mL). The solution was cooled to –10 °C and the 0.5M solution of CF_3-DAST (0.2 mmol, 2.0 equiv, 0.45 mL taken from the solution above mentioned) or (0.4 mmol, 4.0 equiv,

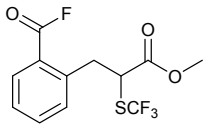
0.9 mL taken from the solution above mentioned) in CH_2Cl_2 was added slowly by syringe. Then the reaction mixture was stirred at –10 °C or room temperature for overnight, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography to provide the title compound **4a—4n** and **4o**.

7.1 Ethyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4a);



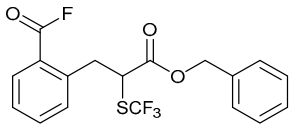
Following the general procedure, using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **1a** (20.4 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 8:1:1) to provide the title compound **4a** as a yellow oil in 61% yield (19.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.00 (dd, 1H, *J* = 7.5 Hz, *J* = 1.0 Hz), 7.54—7.57 (m, 1H), 7.37—7.40 (m, 1H), 7.30 (d, 1H, *J* = 7.5 Hz), 4.05—4.10 (m, 2H), 3.98—4.04 (m, 1H), 3.53 (dd, 1H, *J* = 13.5 Hz, *J* = 7.0 Hz), 3.47 (dd, 1H, *J* = 13.5 Hz, *J* = 9.0 Hz), 1.09 (t, 3 H, *J* = 7.2 Hz; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.9 (s, 1F), –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.3, 156.4 (d, *J* = 345.5 Hz), 141.2 (d, *J* = 8.2 Hz), 135.1, 133.3 (d, *J* = 4.2 Hz), 133.2, 130.0 (q, *J* = 307.4 Hz), 128.4, 123.7 (d, *J* = 56.9 Hz), 62.1, 46.3, 37.0, 13.9; IR (NaCl): 2986, 2942, 1806, 1740, 1238, 1112, 1009, 757, 742, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{12}F_4NaO_3S$ $[M+Na]^+$: 347.0341; Found: 347.0326.

7.2 Methyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4b);



Following the general procedure, using methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1b** (19.1 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 8:1:1) to provide the title compound **4b** as a yellow oil in 35% yield (10.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.00 (dd, 1H, *J* = 7.5 Hz, *J* = 1.0 Hz), 7.55—7.58 (m, 1H), 7.38—7.41 (m, 1H), 7.29 (d, 1H, *J* = 8.0 Hz), 4.08—4.11 (m, 1H), 3.61 (s, 3H), 3.48—3.54 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.9 (s, 1F), –40.9 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.8, 156.5 (d, *J* = 345.6 Hz), 141.1 (d, *J* = 8.2 Hz), 135.1, 133.2 (d, *J* = 4.0 Hz), 133.2, 129.9 (q, *J* = 307.7 Hz), 128.5, 123.7 (d, *J* = 56.9 Hz), 53.0, 46.1, 37.0; IR (NaCl): 2957, 1806, 1745, 1237, 1110, 1008, 757, 742, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{12}H_{10}F_4NaO_3S$ $[M+Na]^+$: 333.0184; Found: 333.0193.

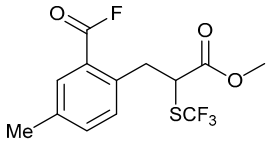
7.3 Benzyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4c);



Following the general procedure, using benzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1c** (26.7 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 10:1:1) to provide the title compound **4c** as a yellow oil in 64% yield (24.7 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.96 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.43—7.46 (m, 1H), 7.32—7.36 (m, 1H), 7.24—7.26 (m, 3H), 7.18—7.20 (m, 1H), 7.13—7.15 (m, 2H), 4.98—5.04 (m, 2H), 4.12—4.15 (m, 1H),

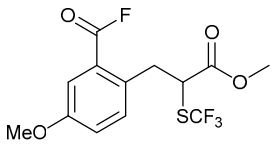
3.55 (dd, 1H, J = 13.5 Hz, J = 7.0 Hz), 3.45 (dd, 1H, J = 13.5 Hz, J = 9.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.8 (s, 1F), –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.2, 156.4 (d, J = 345.5 Hz), 141.0 (d, J = 8.2 Hz), 135.1, 134.9, 133.2 (d, J = 3.6 Hz), 129.9 (q, J = 307.8 Hz), 128.7, 128.6, 128.5, 128.4, 123.7 (d, J = 56.8 Hz), 67.8, 46.2, 37.1; IR (NaCl): 3068, 3035, 2959, 1804, 1741, 1238, 1161, 1110, 1007, 741, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{14}F_4NaO_3S$ $[M+Na]^+$: 409.0497; Found: 409.0486.

7.4 Methyl 3-(2-(fluorocarbonyl)-4-methylphenyl)-2-((trifluoromethyl)thio)propanoate (4d);



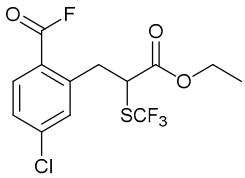
Following the general procedure, using methyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1d** (20.4 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 10:1:1) to provide the title compound **4d** as a yellow oil in 59% yield (19.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.79 (d, 1H, J = 1.5 Hz), 7.35 (dd, 1H, J = 7.5 Hz, J = 1.0 Hz), 7.15—7.17 (m, 1H), 4.06—4.09 (m, 1H), 3.61 (s, 3H), 3.41—3.49 (m, 2H), 2.33 (s, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.6 (s, 1F), —40.8 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.9, 156.6 (d, J = 345.5 Hz), 138.5, 138.0 (d, J = 7.9 Hz), 135.9, 133.7, 133.1 (d, J = 4.3 Hz), 129.9 (q, J = 307.3 Hz), 123.4 (d, J = 55.9 Hz), 53.0, 46.2, 36.5, 21.0; IR (NaCl): 2957, 1803, 1746, 1501, 1439, 1261, 1165, 1111, 1019, 758, 730, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{12}F_4NaO_3S$ $[M+Na]^+$: 347.0341; Found: 347.0336.

7.5 Methyl 3-(2-(fluorocarbonyl)-4-methoxyphenyl)-2-((trifluoromethyl)thio)propanoate (4e);



Following the general procedure, using methyl 6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1e** (22.0 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 10:1:1) to provide the title compound **4e** as a yellow oil in 48% yield (16.3 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.47 (d, 1H, *J* = 2.5 Hz), 7.18—7.20 (m, 1H), 7.08 (dd, 1H, *J* = 8.5 Hz, *J* = 3.0 Hz), 4.04—4.07 (m, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 3.37—3.44 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.8 (s, 1F), –40.8 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.9, 159.1, 156.3 (d, *J* = 346.0 Hz), 134.4 (d, *J* = 4.5 Hz), 132.9 (d, *J* = 7.5 Hz), 130.0 (q, *J* = 307.2 Hz), 124.5 (d, *J* = 56.4 Hz), 121.1, 117.7, 55.7, 53.0, 46.3, 36.2; IR (NaCl): 3009, 2956, 2844, 1807, 1744, 1504, 1165, 1111, 1010, 758, 731, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{12}F_4NaO_4S$ $[M+Na]^+$: 363.0290; Found: 363.0296.

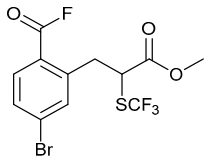
7.6 Ethyl 3-(5-chloro-2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4f);



Following the general procedure, using ethyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1f** (23.9 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 10:1:1) to provide the title compound **4f** as a yellow oil in 45% yield (16.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.93 (d, 1H, *J* = 8.5 Hz), 7.37 (dd, 1H, *J* = 8.5 Hz, *J* = 2.0 Hz), 7.30 (s, 1H), 4.02—4.12 (m, 3H), 3.51 (dd, 1H, *J* = 13.5 Hz, *J* = 7.0 Hz), 3.44 (dd, 1H, *J* = 13.5 Hz, *J* = 9.0 Hz), 1.13 (t, 3H,

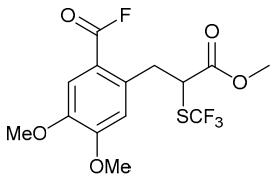
J = 7.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.2 (s, 1F), –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.0, 155.7 (d, J = 344.7 Hz), 143.1 (d, J = 8.2 Hz), 141.8, 134.4, 133.4 (d, J = 4.1 Hz), 129.9 (q, J = 307.5 Hz), 128.7, 122.1 (d, J = 58.1 Hz), 62.4, 46.0, 36.8, 13.9; IR (NaCl): 2984, 2943, 1809, 1740, 1595, 1566, 1236, 1111, 1010, 768, 758, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{11}ClF_4NaO_3S$ $[M+Na]^+$: 380.9951; Found: 380.9955.

7.7 Methyl 3-(5-bromo-2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4g);



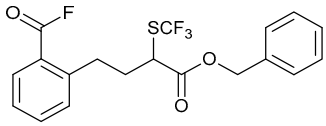
Following the general procedure, using methyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1g** (26.9 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 10:1:1) to provide the title compound **4g** as a yellow oil in 49% yield (19.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.84 (d, 1H, J = 8.5 Hz), 7.54 (dd, 1H, J = 8.5 Hz, J = 2.0 Hz), 7.47 (s, 1H), 4.04—4.07 (m, 1H), 3.64 (s, 3H), 3.46—3.49 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.2 (s, 1F), –40.8 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.4, 155.9 (d, J = 344.9 Hz), 142.9 (d, J = 8.1 Hz), 136.3 (d, J = 4.1 Hz), 134.3, 131.8, 130.6, 129.8 (q, J = 307.8 Hz), 122.5 (d, J = 58.0 Hz), 53.2, 45.9, 36.7; IR (NaCl): 3022, 2956, 1807, 1742, 1589, 1561, 1239, 1111, 1011, 758, 689, 669 cm^{-1}; HRMS (ESI): Calcd. for $C_{12}H_9BrF_4NaO_3S$ $[M+Na]^+$: 410.9290; Found: 410.9261.

7.8 Methyl 3-(2-(fluorocarbonyl)-4,5-dimethoxyphenyl)-2-((trifluoromethyl)thio)propanoate (4h);



Following the general procedure, using methyl 5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1h** (25.0 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 5:1:1) to provide the title compound **4h** as a white solid in 40% yield (14.7 mg). mp: 89.7—90.9. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.40 (s, 1H), 6.72 (s, 1H), 4.06—4.10 (m, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.62 (s, 3H), 3.49 (dd, 1H, *J* = 13.5 Hz, *J* = 7.0 Hz), 3.41 (dd, 1H, *J* = 13.5 Hz, *J* = 8.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +25.5 (s, 1F), –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 171.0, 156.2 (d, *J* = 341.2 Hz), 154.2, 148.2, 136.4 (d, *J* = 8.2 Hz), 129.9 (q, *J* = 307.6 Hz), 115.5 (d, *J* = 4.3 Hz), 115.0 (d, *J* = 57.4 Hz), 114.7, 56.4, 56.2, 53.0, 46.0, 36.9; IR (NaCl): 2944, 2850, 1794, 1741, 1576, 1526, 1277, 1214, 1127, 962, 878, 768, 720, 651 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{14}F_4NaO_5S$ $[M+Na]^+$: 393.0396; Found: 393.0386.

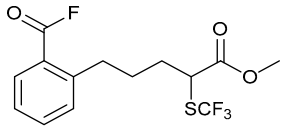
7.9 Benzyl 4-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)butanoate (4i);



Following the general procedure, using benzyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate **1q** (56.1 mg, 0.2 mmol, 1.0 equiv) and CF_3-DAST (1.8 mL, 4.0 equiv) in dioxane (2 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **4i** as a yellow oil in 27% yield (21.6 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.01 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.55—7.59 (m, 1H), 7.34—7.39 (m, 6H), 7.26 (d, 1H, *J* = 6.0 Hz), 5.21 (s, 2H), 3.90—3.93 (m, 1H), 3.14—3.20 (m, 1H), 3.01—3.06 (m, 1H),

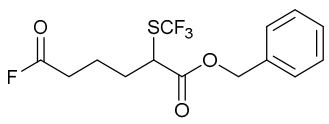
2.21—2.29 (m, 1H), 2.12—2.19 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.6 (s, 1F), –40.8 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.4, 156.3 (d, *J* = 345.2 Hz), 145.3 (d, *J* = 8.0 Hz), 135.2, 135.0, 133.1, 131.9 (d, *J* = 4.2 Hz), 130.1 (q, *J* = 307.5 Hz), 128.8, 128.7, 128.6, 127.4, 123.2 (d, *J* = 56.4 Hz), 68.0, 46.3, 33.1, 31.8; IR (NaCl): 3068, 3034, 2960, 1806, 1740, 1231, 1113, 1003, 756, 696, 646 cm^{-1}; HRMS (ESI): Calcd. for $C_{19}H_{16}F_4NaO_3S$ $[M+Na]^+$: 423.0654; Found: 423.0652.

7.10 Methyl 5-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)pentanoate (4j);



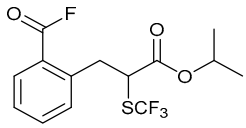
Following the general procedure, using methyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate **1j** (43.7 mg, 0.2 mmol, 1.0 equiv) and CF_3-DAST (1.8 mL, 4.0 equiv) in dioxane (2 mL), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **4j** as a yellow oil in 53% yield (36.2 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.94 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 7.50—7.54 (m, 1H), 7.25—7.31 (m, 2H), 3.74—3.77 (m, 1H), 3.70 (s, 3H), 2.91—3.02 (m, 2H), 1.94—2.01 (m, 1H), 1.81—1.89 (m, 1H), 1.69—1.74 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +29.1 (s, 1F), –41.1 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 171.3, 156.4 (d, *J* = 345.2 Hz), 146.8 (d, *J* = 8.0 Hz), 135.0, 133.0 (d, *J* = 1.4 Hz), 131.7 (d, *J* = 4.2 Hz), 130.1 (q, *J* = 306.9 Hz), 127.0, 123.2 (d, *J* = 56.5 Hz), 53.1, 46.1 (d, *J* = 1.5 Hz), 33.9, 31.8, 28.3; IR (NaCl): 2956, 2870, 1807, 1744, 1449, 1231, 1115, 1000, 758, 742, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{14}F_4NaO_3S$ $[M+Na]^+$: 361.0497; Found: 361.0481.

7.11 Benzyl 6-fluoro-6-oxo-2-((trifluoromethyl)thio)hexanoate (4k);



Following the general procedure, using methyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate **1k** (43.7 mg, 0.2 mmol, 1.0 equiv) and CF_3-DAST (0.9 mL, 2.0 equiv) in dioxane (2 mL), the reaction mixture was stirred at room temperature for overnight. Target product **4k** is too unstable to be isolated under purification, so **4k** was ascertained only by ^{19}F NMR of the crude product and yield was also decided by ^{19}F NMR, in 26% yield. ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +44.5 (s, 1F), –40.8 (s, 3F);

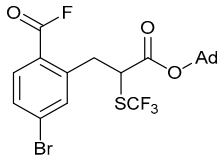
7.12 Isopropyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4l);



Following the general procedure, using isopropyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1l** (21.8 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 8:1:1) to provide the title compound **4l** as a yellow oil in 56% yield (18.9 mg). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.00 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 7.53—7.56 (m, 1H), 7.37—7.40 (m, 1H), 7.30 (d, 1H, J = 8.0 Hz), 4.83—4.91 (m, 1H), 4.03—4.06 (m, 1H), 3.54 (dd, 1H, J = 13.5 Hz, J = 7.0 Hz), 3.43 (dd, 1H, J = 13.5 Hz, J = 9.0 Hz), 1.13 (d, 3H, J = 6.5 Hz), 0.97 (d, 3H, J = 6.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.9 (s, 1F), —40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.9, 156.4 (d, J = 345.5 Hz), 141.2 (d, J = 8.0 Hz), 135.1, 133.3 (d, J = 4.0 Hz), 133.2, 130.0 (q, J = 307.5 Hz), 128.4, 123.7 (d, J = 56.5 Hz), 69.9, 46.4, 37.0, 21.5, 21.4; IR (NaCl): 2985, 2938, 1807, 1736, 1237, 1169, 1100, 1008, 757, 741, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{14}F_4NaO_3S$ $[M+Na]^+$: 361.0497; Found: 361.0500.

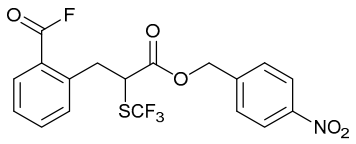
7.13 Adamantan-1-yl

3-(5-bromo-2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4m);



Following the general procedure, using adamantan-1-yl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1m** (38.9 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 8:1:1) to provide the title compound **4m** as a yellow oil in 37% yield (18.8 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.84 (d, 1H, *J* = 8.5 Hz), 7.53 (dd, 1H, *J* = 8.5 Hz, *J* = 2.0 Hz), 7.48 (s, 1H), 3.92—3.95 (m, 1H), 3.54 (dd, 1H, *J* = 13.5 Hz, *J* = 6.5 Hz), 3.30 (dd, 1H, *J* = 13.5 Hz, *J* = 10.0 Hz), 2.08 (s, 3H), 1.89—1.94 (m, 6H), 1.56 (t, 6H, *J* = 2.7 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.2 (s, 1F), –40.5 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.8, 155.8 (d, *J* = 344.6 Hz), 143.3 (d, *J* = 8.0 Hz), 136.4 (d, *J* = 4.0 Hz), 134.3, 131.6, 130.6, 130.0 (q, *J* = 307.3 Hz), 122.6 (d, *J* = 58.1 Hz), 83.4, 47.1, 41.0, 36.9, 36.1, 30.9; IR (NaCl): 2913, 2855, 1809, 1732, 1589, 1239, 1159, 1111, 1007, 768, 758, 690 cm^{-1}; HRMS (ESI): Calcd. for $C_{21}H_{21}BrF_4NaO_3S$ $[M+Na]^+$: 531.0229; Found: 531.0237.

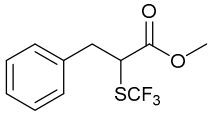
7.14 4-nitrobenzyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (4n);



Following the general procedure, using 4-nitrobenzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate **1n** (31.1 mg, 0.1 mmol, 1.0 equiv) and CF_3-DAST (0.45 mL, 2.0 equiv) in dioxane (1 mL), the reaction mixture was stirred at –10 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt: DCM = 8:1:1) to provide the title compound **4n** as a yellow oil in 36% yield (15.5 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.10—8.13 (m,

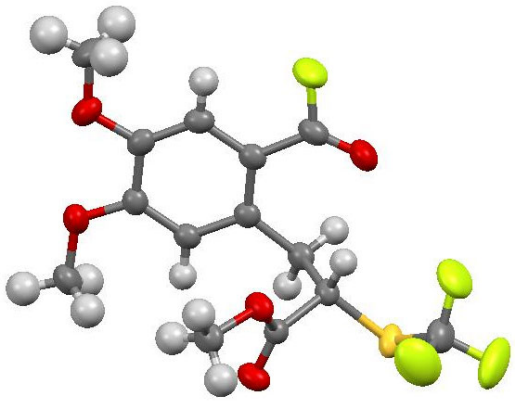
2H), 8.00 (dd, 1H, J = 7.5 Hz, J = 1.0 Hz), 7.48—7.52 (m, 1H), 7.37—7.40 (m, 1H), 7.31 (d, 2H, J = 9.0 Hz), 7.25 (d, 1H, J = 7.5 Hz), 5.09—5.15 (m, 2H), 4.15—4.18 (m, 1H), 3.47—3.55 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +27.9 (s, 1F), –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.1, 156.5 (d, J = 345.8 Hz), 147.9, 142.0, 140.8 (d, J = 8.4 Hz), 135.2, 133.4 (d, J = 4.2 Hz), 133.3, 129.8 (q, J = 307.7 Hz), 128.6, 123.9, 123.7 (d, J = 60.7 Hz), 66.2, 46.0, 36.8; IR (NaCl): 2924, 2861, 1803, 1746, 1523, 1348, 1237, 1160, 1107, 1008, 740, 696, 647 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{13}F_4NNaO_5S$ $[M+Na]^+$: 454.0348; Found: 454.0340.

7.15 Methyl 3-phenyl-2-((trifluoromethyl)thio)propanoate (4o);



Following the general procedure, using methyl 2-benzyl-3-oxobutanoate **1o** (41.2 mg, 0.2 mmol, 1.0 equiv) and CF_3-DAST (1.8 mL, 4.0 equiv) in DMF (2 mL), the reaction mixture was stirred at 50 °C for overnight. After cooling to room temperature, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =10:1) to provide the title compound **4o** as a yellow oil in 19% yield (10.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.31—7.33 (m, 2H), 7.26—7.28 (m, 1H), 7.17—7.19 (m, 2H), 4.01—4.04 (m, 1H), 3.68 (s, 3H), 3.23 (dd, 1H, J = 14.0 Hz, J = 9.5 Hz), 3.12 (dd, 1H, J = 14.0 Hz, J = 6.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –41.0 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.8, 136.1, 130.1 (q, J = 307.0 Hz), 129.1, 128.8, 127.6, 53.0, 47.5, 38.4; IR (NaCl): 3032, 2955, 1747, 1438, 1162, 1110, 845, 747, 699 cm^{-1}; HRMS (ESI): Calcd. For $C_{11}H_{11}F_3NaO_2S$ $[M+Na]^+$: 287.0330; Found: 287.0332.

8**. X-ray crystallography data for the 4h (CCDC 1415531)**

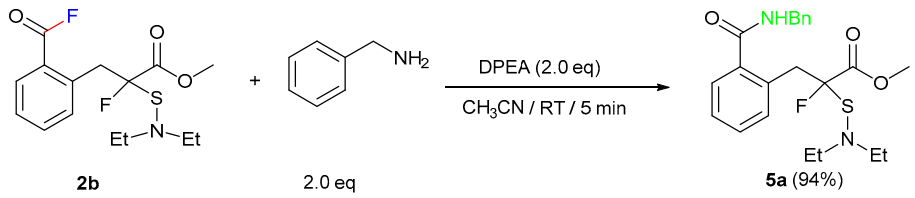


EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{14}H_{14}F_4O_5S$
Formula Weight	370.32
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.300 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.1328(3) Å b = 19.0087(6) Å c = 10.7270(4) Å β = 104.6528(9) ^{o} V = 1604.4(1) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.533 g/cm^3
F_{000}	760.00
μ(MoKα)	2.665 cm^{-1}

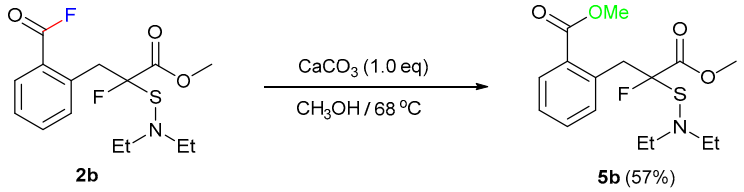
9. General procedure and product characterization data for 5a;



2b 2.0 eq **5a** (94%)

A flame-dried vessel was successively charged, under nitrogen, with methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (**2b**) (66.2 mg, 0.2 mmol) and anhydrous acetonitrile (2.0 mL), stirred at room temperature for 5 min, then benzylamine (44 μL, 0.4 mmol, 2.0 equiv) and diisopropylethylamine (68 μL, 0.4 mmol, 2.0 equiv) were added slowly by syringe. The reaction mixture was stirred at room temperature for 5 min, quenched with water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4, concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =5:1—3:1) to provide the target product **5a** as a colourless oil in 94% yield (78.6 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.39—7.41 (m, 3H), 7.31—7.36 (m, 2H), 7.29—7.30 (m, 1H), 7.24—7.27 (m, 3H), 6.49 (s, 1H), 4.58—4.66 (m, 2H), 3.71—3.76 (m, 4H), 3.53 (dd, 1H, J = 27.2 Hz, J = 15.0 Hz), 2.92—2.98 (m, 4H), 1.07 (t, 6H, J = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –137.9 (dd, 1F, J = 26.7 Hz, J = 12.8 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.8, 169.0 (d, J = 31.8 Hz), 138.1, 131.8, 131.1, 130.0, 128.8, 128.1, 127.7, 127.6, 127.5, 108.6 (d, J = 232.6 Hz), 52.8, 52.2, 44.2, 36.3 (d, J = 21.9 Hz), 13.7; IR (NaCl): 3307, 2971, 2931, 2360, 2341, 1749, 1652, 1539, 1268, 911, 731 cm^{-1}; HRMS (ESI): Calcd. For $C_{22}H_{27}FN_2NaO_3S$ $[M+Na]^+$: 441.1624; Found: 441.1621.

10. General procedure and product characterization data for 5b;

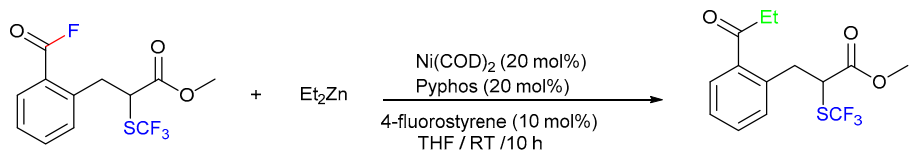


2b **5b** (57%)

A flame-dried vessel was successively charged, under nitrogen, with methanol (2.0

mL) and $CaCO_3$ (20.0 mg, 0.2 mmol, 1.0 equiv), stirred at 45 °C for 10 min, the solution of methyl 2-((diethylamino)thio)-2-fluoro-3-(2-(fluorocarbonyl)phenyl)propanoate (**2b**) (66.2 mg, 0.2 mmol) in methanol (1.0 mL) was added slowly by syringe at same temperature. Then the reaction mixture was stirred at 68 °C for 24 hours. The mixture was cooled to room temperature for filtration and concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =10:1—6:1) to provide the target product **5b** as a colourless oil in 57% yield (39.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.80 (dd, 1H, *J* = 8.5 Hz, *J* = 1.5 Hz), 7.38—7.42 (m, 1H), 7.28—7.32 (m, 2H), 3.88—3.93 (m, 4H), 3.76 (dd, 1H, *J* = 26.5 Hz, *J* = 14.5 Hz), 3.70 (s, 3H), 2.95—3.04 (m, 4H), 1.07 (t, 6H, *J* = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –140.4 (dd, 1F, *J* = 24.8 Hz, *J* = 11.8 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.0 (d, *J* = 31.8 Hz), 168.4, 134.4, 132.2, 131.8, 131.6, 130.5, 127.4, 107.7 (d, *J* = 234.1 Hz), 52.7, 52.2, 36.8 (d, *J* = 21.4 Hz), 13.7; IR (NaCl): 2971, 2952, 2360, 2341, 1719, 1435, 1256, 1085, 668 cm^{-1}; HRMS (ESI): Calcd. for $C_{16}H_{22}FNNaO_4S$ $[M+Na]^+$: 366.1151 Found: 366.1155.

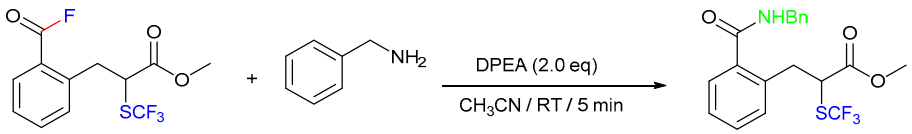
11. General procedure and product characterization data for 6a;



A flame-dried round bottom flask was charged with $Ni(COD)_2$ (5.5 mg, 0.02 mmol, 20 mol%) and pyphos (7.0 mg, 24 mol%) in an inert atmosphere (N_2) glove box. Upon removal from the glove box, anhydrous THF (0.5 mL) was added via syringe under an atmosphere of argon and stirred at ambient temperature for 15 minutes. 4-fluorostyrene (2.4μL, 0.02 mmol, 20 mol%) was introduced via syringe followed by a solution of diethylzinc (0.1 mL,1.0 equiv, 1M solution in Hexane). Then the solution of methyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (**4b**)

(31.0 mg, 0.1 mmol) in THF (0.5 mL) was added. The reaction mixture was stirred at the room temperature for 12 hours, quenched with 1M HCl (4 mL), extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =10:1) to provide the target product **6a** as a colourless oil in 59% yield (18.8 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78 (dd, 1H, *J* = 7.6 Hz, *J* = 1.6 Hz), 7.42—7.46 (m, 1H), 7.35—7.40 (m, 1H), 7.25 (dd, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz), 4.28 (dd, 1H, *J* = 8.2 Hz, *J* = 7.4 Hz), 3.67 (s, 3H), 3.32—3.42 (m, 2H), 2.91—3.01 (m, 2H), 1.21 (t, 3H, *J* = 7.4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –40.8 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 204.3, 171.4, 137.4, 136.5, 132.9, 131.8, 130.1 (q, *J* = 307.6 Hz), 129.6, 127.7, 52.8, 47.0, 36.8, 34.4, 8.6; IR (NaCl): 2940, 1744, 1686, 1438, 1159, 1112, 1032, 952, 756 cm^{-1}; HRMS (ESI): Calcd. for $C_{14}H_{15}F_3NaO_3S$ $[M+Na]^+$: 343.0592; Found: 343.0603.

12. General procedure and product characterization data for 6b;

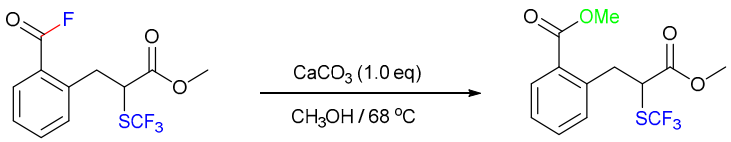


4b 2.0 eq **6b** (73%)

A flame-dried vessel was successively charged, under nitrogen, with methyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (**4b**) (31.0 mg, 0.1 mmol) and anhydrous acetonitrile (1.0 mL), stirred at room temperature for 5 min, then the benzylamine (22 μL, 0.2 mmol, 2.0 equiv) and diisopropylethylamine (34 μL, 0.2 mmol, 2.0 equiv) was added slowly by syringe. The reaction mixture was stirred at room temperature for 5 min, quenched with water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4, concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =20:1—10:1) to provide the target product **6b** as a colourless oil in 73% yield (28.9 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.42 (dd, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz), 7.33—7.39 (m, 5H),

7.26—7.32 (m, 2H), 7.24 (dd, 1H, J = 7.6 Hz, J = 1.2Hz), 6.29 (s, 1H), 4.57—4.66 (m, 2H), 4.37 (dd, 1H, J = 8.4 Hz, J = 7.6 Hz), 3.66 (s, 3H), 3.42 (dd, 1H, J = 14.0 Hz, J = 8.8 Hz), 3.42 (dd, 1H, J = 13.6 Hz, J = 7.6 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –40.7 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 171.3, 169.1, 138.0, 136.2, 135.2, 131.6, 130.4, 130.0 (q, J = 307.4 Hz), 128.9, 128.0, 127.8, 127.7, 127.3, 52.9, 47.0, 44.2, 35.7; IR (NaCl): 3298, 3064, 3031, 2953, 1743, 1641, 1529, 1156, 1112, 752, 699, 660 cm^{-1}; HRMS (ESI): Calcd. for $C_{19}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 420.0857; Found: 420.0848.

13. General procedure and product characterization data for 6c;



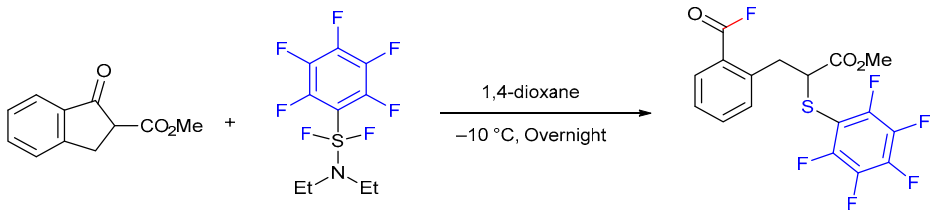
4b **6c** (72%)

A flame-dried vessel was successively charged, under nitrogen, with methanol (1.0 mL) and $CaCO_3$ (10.0 mg, 0.1 mmol, 1.0 equiv), stirred at 45 °C for 10 min, the solution of methyl 3-(2-(fluorocarbonyl)phenyl)-2-((trifluoromethyl)thio)propanoate (**4b**) (31.0 mg, 0.1 mmol) in methanol (0.5 mL) was added slowly by syringe at same temperature. Then the reaction mixture was stirred at 68 °C for 24 hours. Which was cooled to room temperature, filtration, concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt =20:1) to provide the target product **6c** as a colourless oil in 72% yield (23.1 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (dd, 1H, J = 7.6 Hz, J = 1.2 Hz), 7.44—7.48 (m, 1H), 7.33—7.38 (m, 1H), 7.24 (dd, 1H, J = 7.6 Hz, J = 0.8 Hz), 4.28 (dd, 1H, J = 8.4 Hz, J = 7.0 Hz), 3.92 (s, 3H), 3.66 (s, 3H), 3.45—3.56 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –40.9 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 171.3, 167.4, 138.1, 132.6, 132.5, 131.6, 130.1 (q, J = 307.2 Hz), 129.5, 127.8, 52.9, 52.4, 46.9, 37.1; IR (NaCl): 3003, 2956, 2845, 1745, 1720, 1437, 1269, 1113, 844, 751, 707, 664 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{13}F_3NaO_4S$ $[M+Na]^+$: 345.0384 Found: 345.0370.

14. Typical procedure preparation of C_6F_5-DAST reagents

A flame-dried vessel was successively charged, under nitrogen, with diisopropylethylamine (0.17 mL, 1.0 mmol) and anhydrous dichloromethane (2 mL). The resulting mixture was cooled to –10 °C, the diethylaminosulfurtrifluoride (0.15 mL, 1.0 mmol) was added slowly by syringe, stirred for 15 min at same temperature, then the trimethyl(perfluorophenyl)silane (0.19 mL, 1.0 mmol) was added slowly by syringe, and stirring for two hours under the same reaction temperature, after two hours directly use for next step reactions without purifacation.

15. General procedure and product characterization data for 7b;

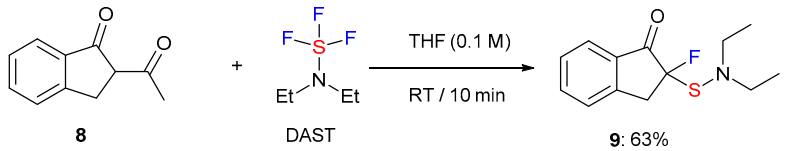


1b **7b**

A flame-dried vessel was successively charged, under nitrogen, with *β*-keto esters **1b** (19.0 mg, 0.1 mmol, 1.0 equiv) and anhydrous 1,4-dioxane (1.0 mL). The solution was cooled to –10 °C and the 0.5M solution of C_6F_5-DAST (0.2 mmol, 2.0 equiv, 0.46 mL) in CH_2Cl_2 was added slowly by syringe. Then the reaction mixture was stirred at –10 °C or room temperature for overnight, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt = 12:1) to provide the title compound **7b** as a colourless oil in 53% yield (21.6 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.03 (dd, 1H, *J* = 8.0 Hz, *J* = 1.6 Hz), 7.58—7.62 (m, 1H), 7.38—7.45 (m, 2H), 3.91—3.94 (m, 1H), 3.62 (s, 3H), 3.44—3.58 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: +28.0 (s, 1F), –

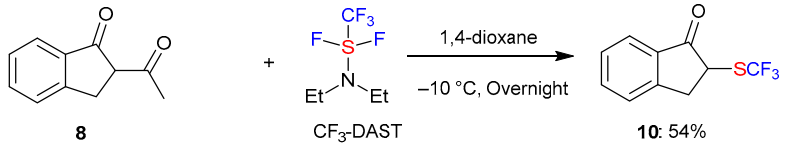
131.01— –131.08 (m, 2F), –149.94— –150.09 (m, 1F), –160.84— –160.97 (m, 2F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 170.7, 156.4 (d, J = 345.5 Hz), 149.3, 147.3, 141.8 (d, J = 8.1 Hz), 141.6, 138.7, 136.8, 135.1, 133.2, 133.0 (d, J = 4.1 Hz), 128.2, 123.4 (d, J = 56.5 Hz), 106.2, 52.7, 50.0, 36.8; IR (NaCl): 2956, 2920, 2862, 1804, 1738, 1515, 1489, 1237, 1093, 1008, 863, 756, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{10}F_6NaO_3S$ $[M+Na]^+$: 431.0153; Found: 431.0155.

16. General procedure and product characterization data for 9;



A flame-dried vessel was successively charged, under nitrogen, with 2-acetyl-2,3-dihydro-1H-inden-1-one **8** (34.8 mg, 0.2 mmol, 1.0 equiv) and anhydrous THF (2.0 mL). The solution was cooled to 0 °C and the DAST (0.4 mmol, 2.0 equiv) was added slowly by syringe. Then the reaction mixture was stirred at room temperature for 10 min, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt = 5:1) to provide the title compound **9** as a yellow oil in 63% yield (31.9 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.81 (d, 1H, J = 7.5 Hz), 7.61—7.64 (m, 1H), 7.43 (t, 1H, J = 7.5 Hz), 7.37 (d, 1H, J = 7.5 Hz), 3.26—3.39 (m, 2H), 3.04 (s, 4H), 1.08 (s, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –147.0 (d, 1F, J = 12.9 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 1195.4 (d, J = 24.8 Hz), 147.2 (d, J = 4.5 Hz), 135.7, 133.6 (d, J = 2.7 Hz), 128.6, 126.4, 125.3, 108.3 (d, J = 241.7 Hz), 52.4 (d, J = 17.8 Hz), 36.7 (d, J = 23.5 Hz), 14.1; IR (NaCl): 2969, 2930, 2360, 2341, 1732, 1717, 1558, 1540, 1084, 668 cm^{-1}; HRMS (ESI): Calcd. for $C_{13}H_{17}FNOS$ $[M+H]^+$: 254.1015; Found: 254.1035. This compound is not so stable under column chromatography on silica-gel.

17. General procedure and product characterization data for 10;



A flame-dried vessel was successively charged, under nitrogen, with 2-acetyl-2,3-dihydro-1H-inden-1-one **8** (34.8 mg, 0.2 mmol, 1.0 equiv) and anhydrous 1,4-dioxane (2.0 mL). The solution was cooled to –10 °C and the 0.5M solution of CF_3-DAST (0.4 mmol, 2.0 equiv, 0.90 mL taken from the solution above mentioned) in CH_2Cl_2 was added slowly by syringe. Then the reaction mixture was stirred at –10 °C or room temperature for overnight, quenched by addition of water (10 mL), extracted with ethyl acetate (3 x 20 mL), dried over with Na_2SO_4 and then concentrated in vacuo. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **10** as a yellow oil in 54% yield (25.1 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.82 (d, 1H, J = 8.0 Hz), 7.66—7.69 (m, 1H), 7.47—7.49 (m, 1H), 7.42—7.45 (m, 1H), 4.24 (dd, 1H, J = 8.0 Hz, J = 4.5 Hz), 3.79 (dd, 1H, J = 17.5 Hz, J = 8.0 Hz), 3.37 (dd, 1H, J = 17.5 Hz, J = 4.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –40.0 (s, 3F); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 199.3, 151.5, 134.6, 130.7 (q, J = 307.4 Hz), 128.4, 126.5, 124.9,47.5, 36.4; IR (NaCl): 2925, 2360, 2341, 1732, 1717, 1540, 1507, 1110, 668 cm^{-1}; MS (ESI, m/z): 231 $[M-H]^-$. The NMR data are consistent with those reported in the literature. [6]

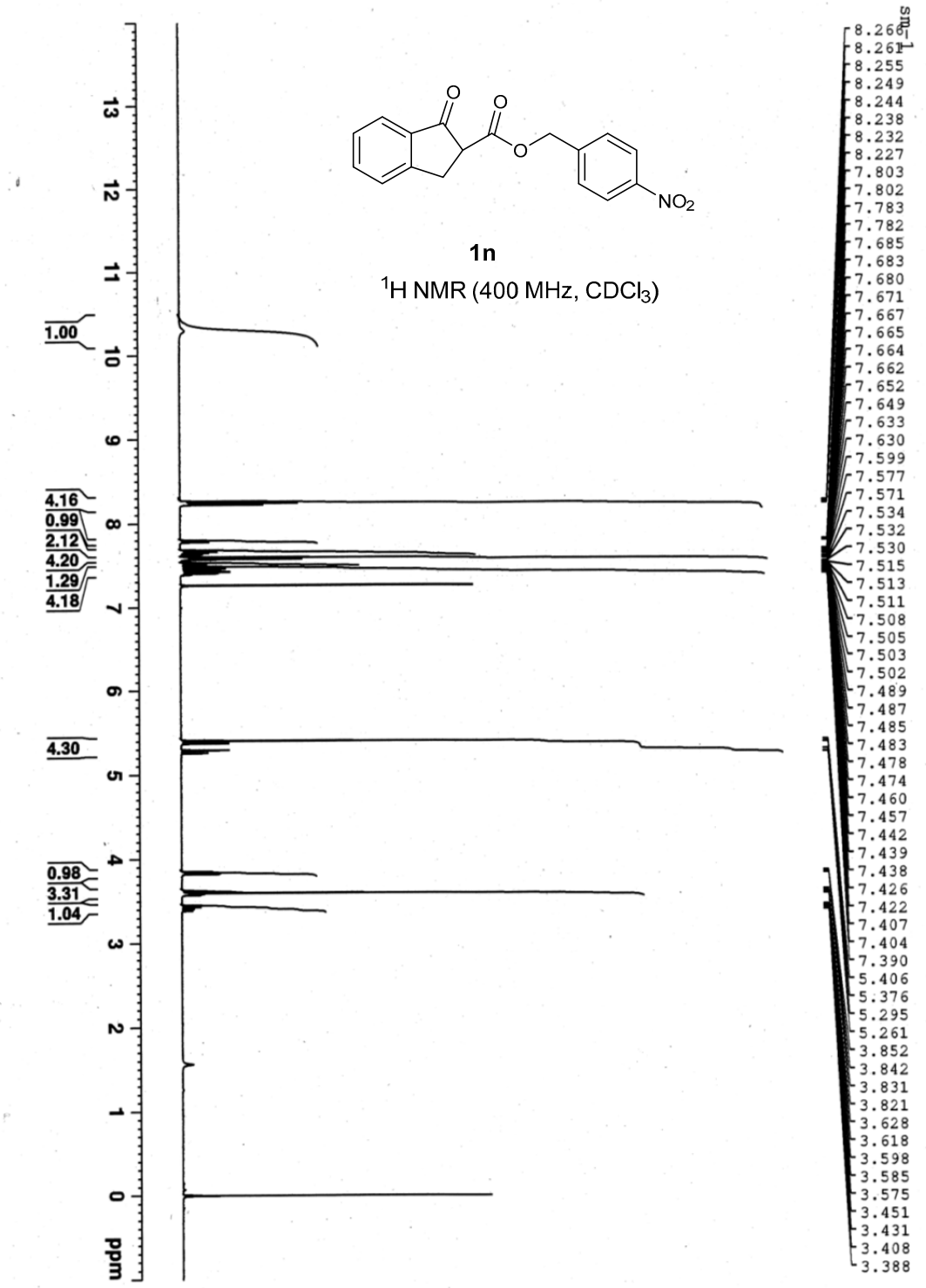
18. References

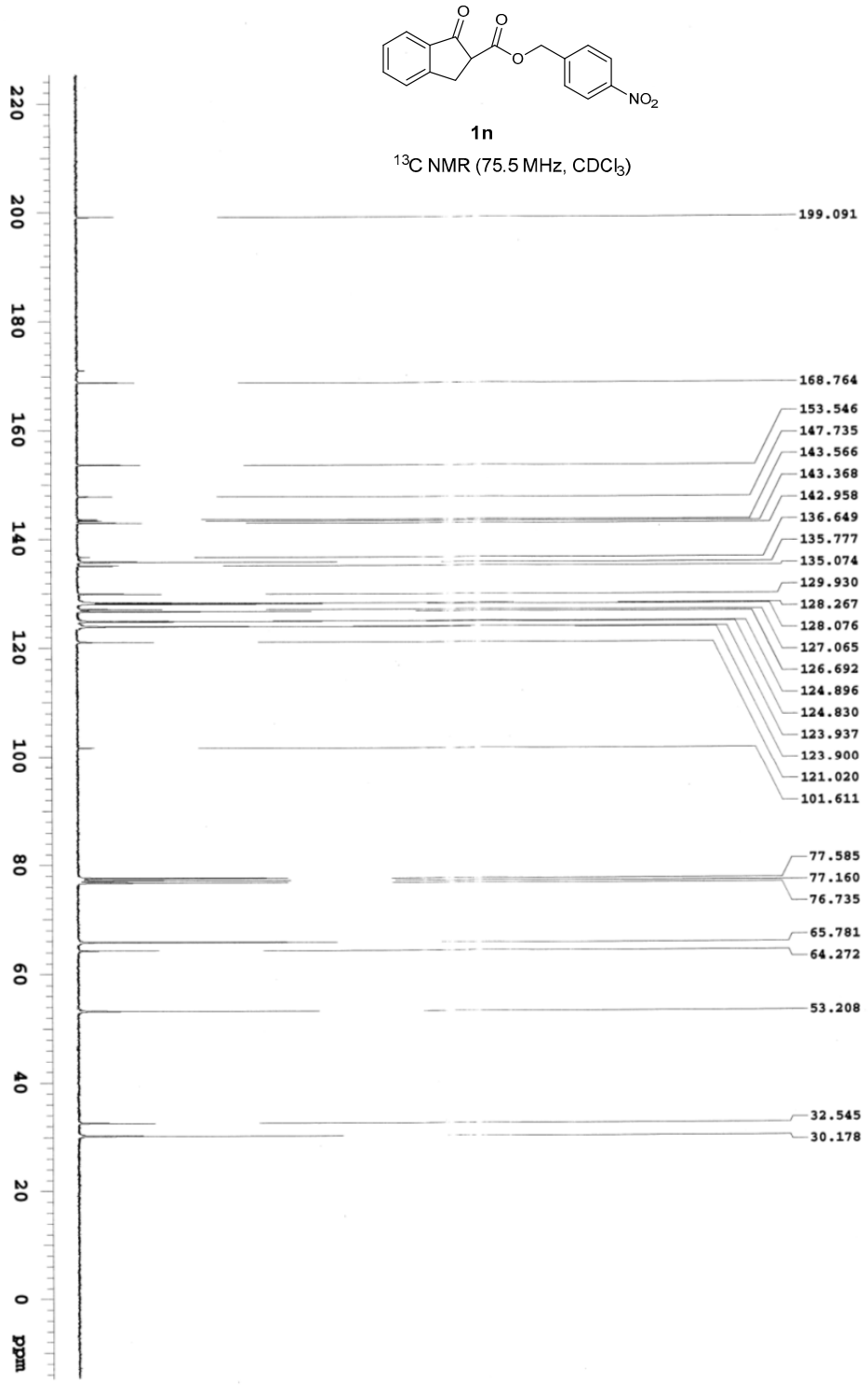
1. Cordova, A.; Janda, K. D. *J. Org. Chem.* **2001,** *66***,** 1906.
2. Nieman, J. A.; Keay, B. A. *Tetrahedron Asymmetry* **1995**, *6*, 1575.
3. Smith, A. M. R.; Rzepa, H. S.; White, A. J. P.; Billen, D.; Hii, K. K. *J. Org. Chem.* **2010**, *75*, 3085.
4. Nakajima, M.; Yamamoto, S.; Yamaguchi, Y.; Nakamura, S.; Hashimoto, S.

Tetrahedron **2003**, *59*, 7307.

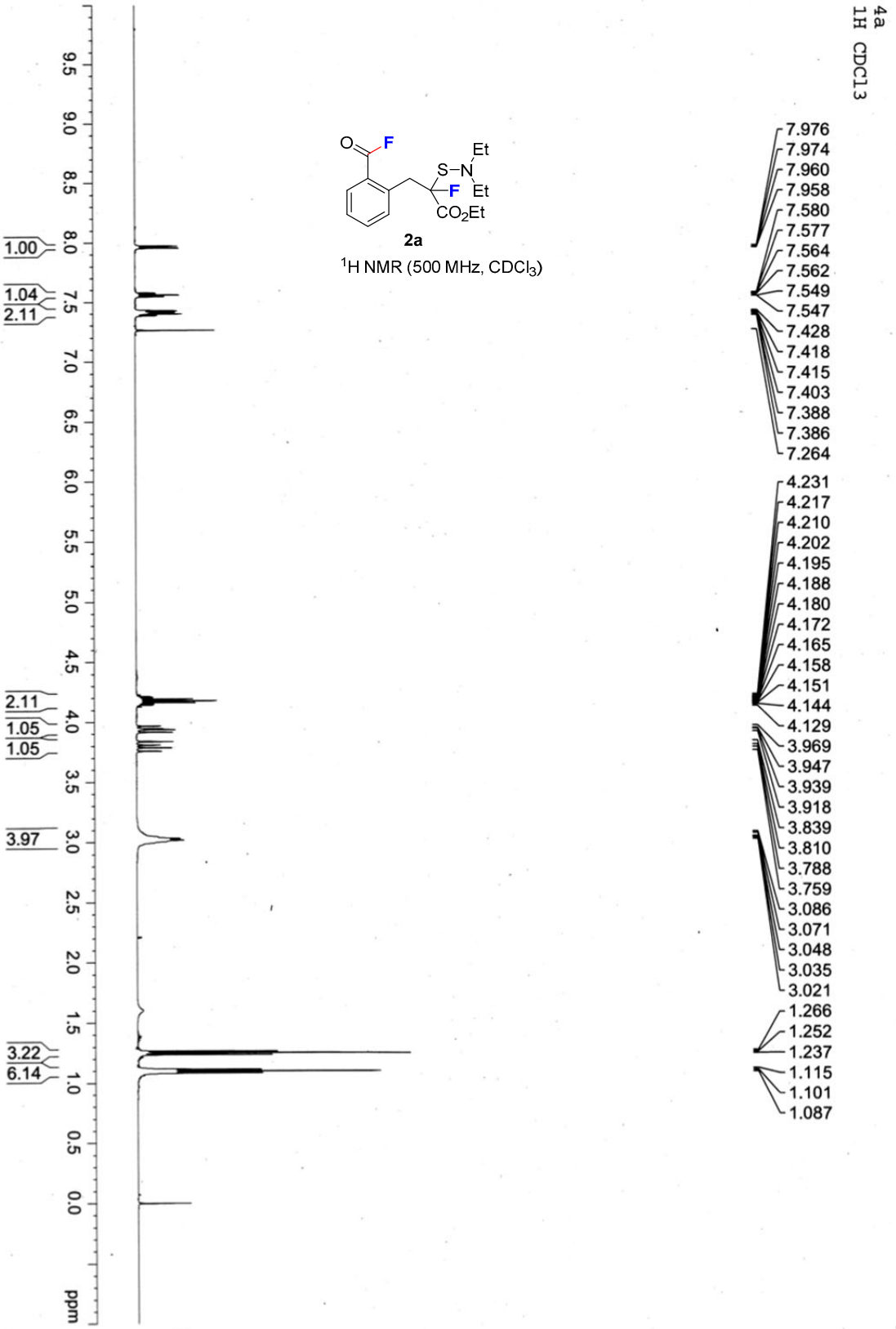
5. Lian, M.; Li, Z.; Du, J.; Meng, Q.; Gao, Z. *Eur. J. Org. Chem.* **2010***,* 6525.
6. Alazet, S.; Zimmer, L.; Billard, T. *Chem. Eur. J.* **2014**, *20*, 8589.

19. ^{1}H NMR **and** ^{13}C **NMR spectra for** starting material **1n**;



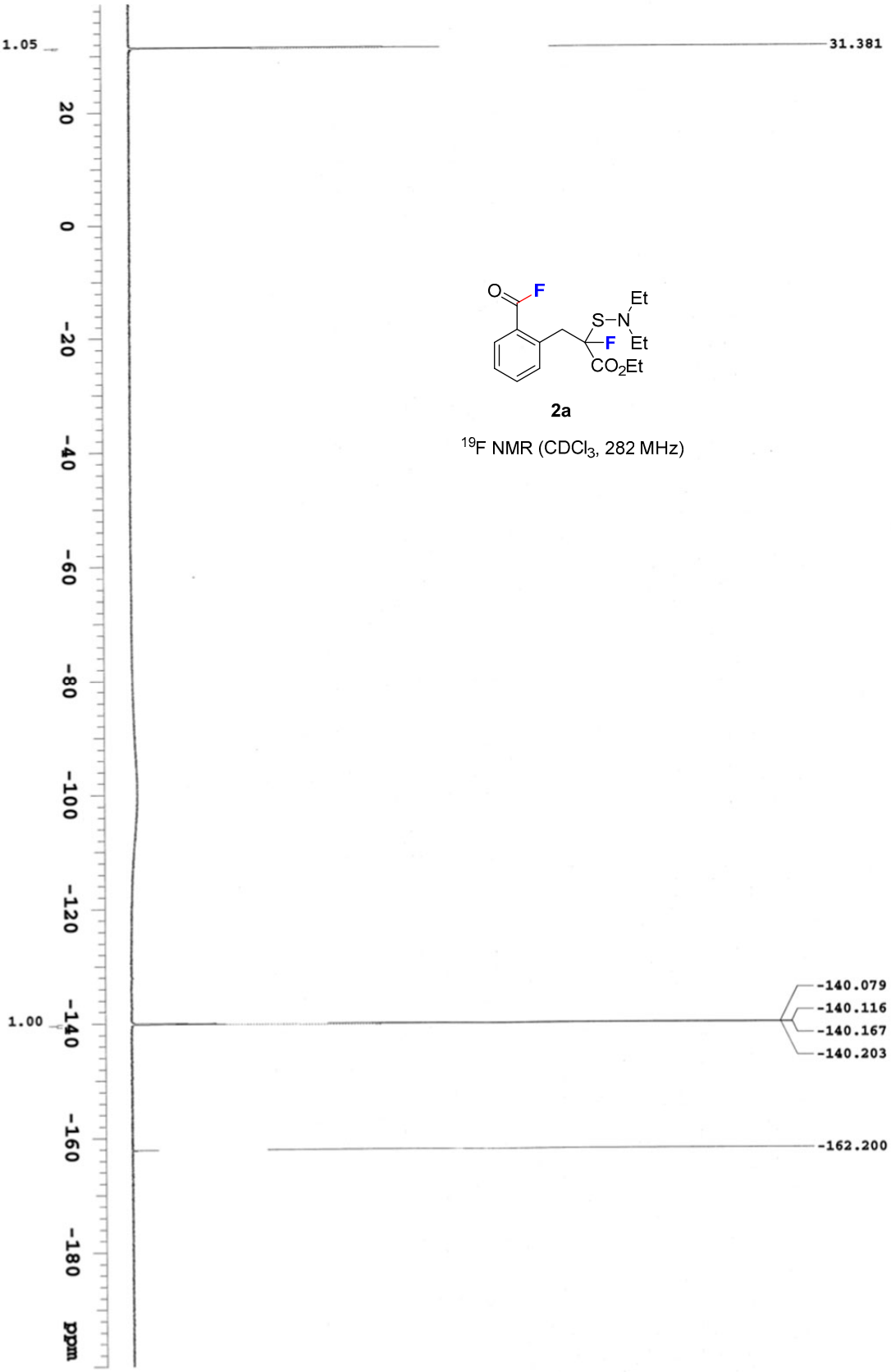

O
O
O
NO2
1n
13C NMR (75.5 MHz, CDCl3)
199.091
168.764
153.546
147.735
143.566
143.368
142.958
136.649
135.777
135.074
129.930
128.267
128.076
127.065
126.692
124.896
124.830
123.937
123.900
121.020
101.611
77.585
77.160
76.735
65.781
64.272
53.208
32.545
30.178
220
200
180
160
140
120
100
80
60
40
20
0
ppm

20. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for doubly fluoro-functionalization compounds 2a—2k, 2o and 3a—3c (Table 1)



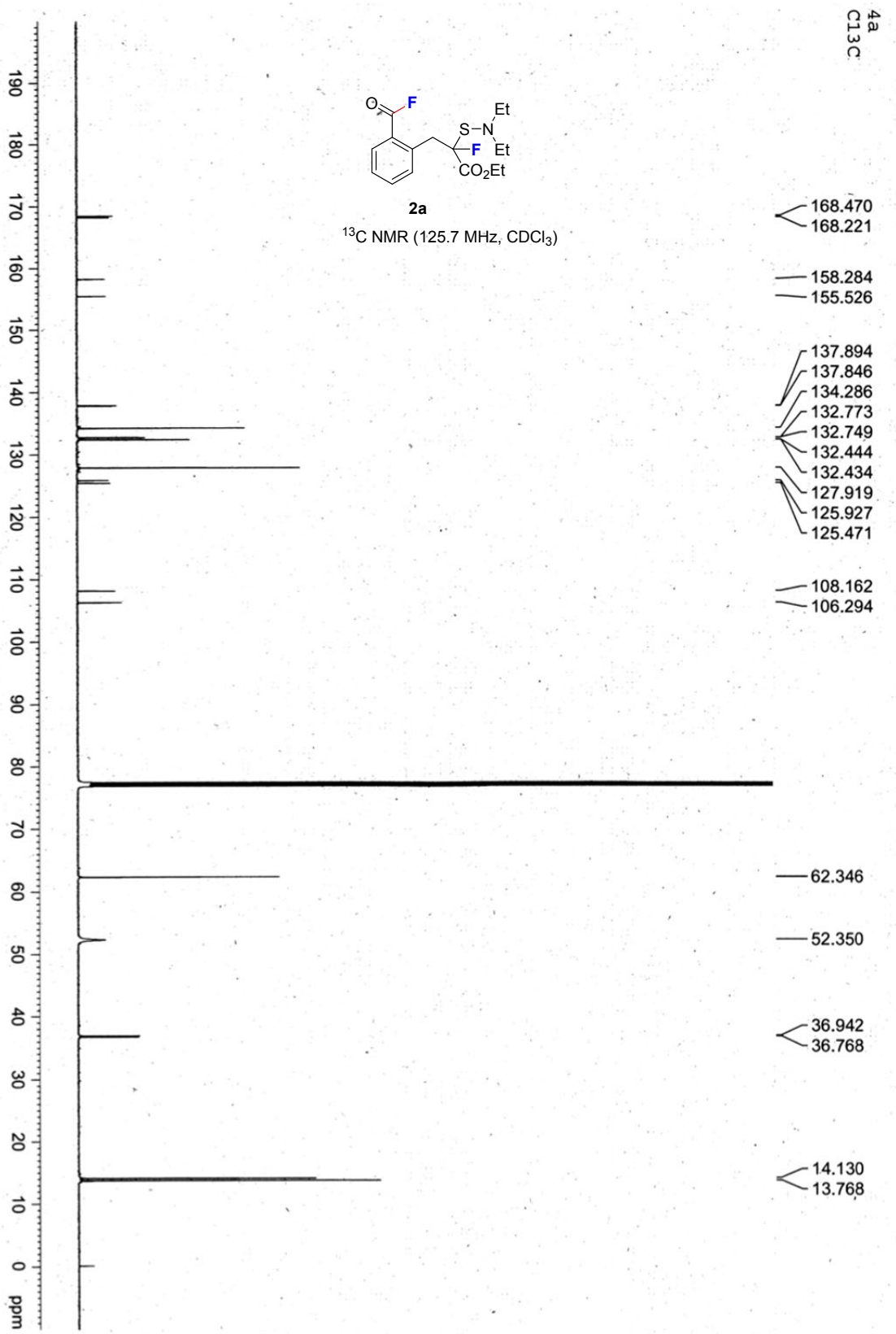
2a

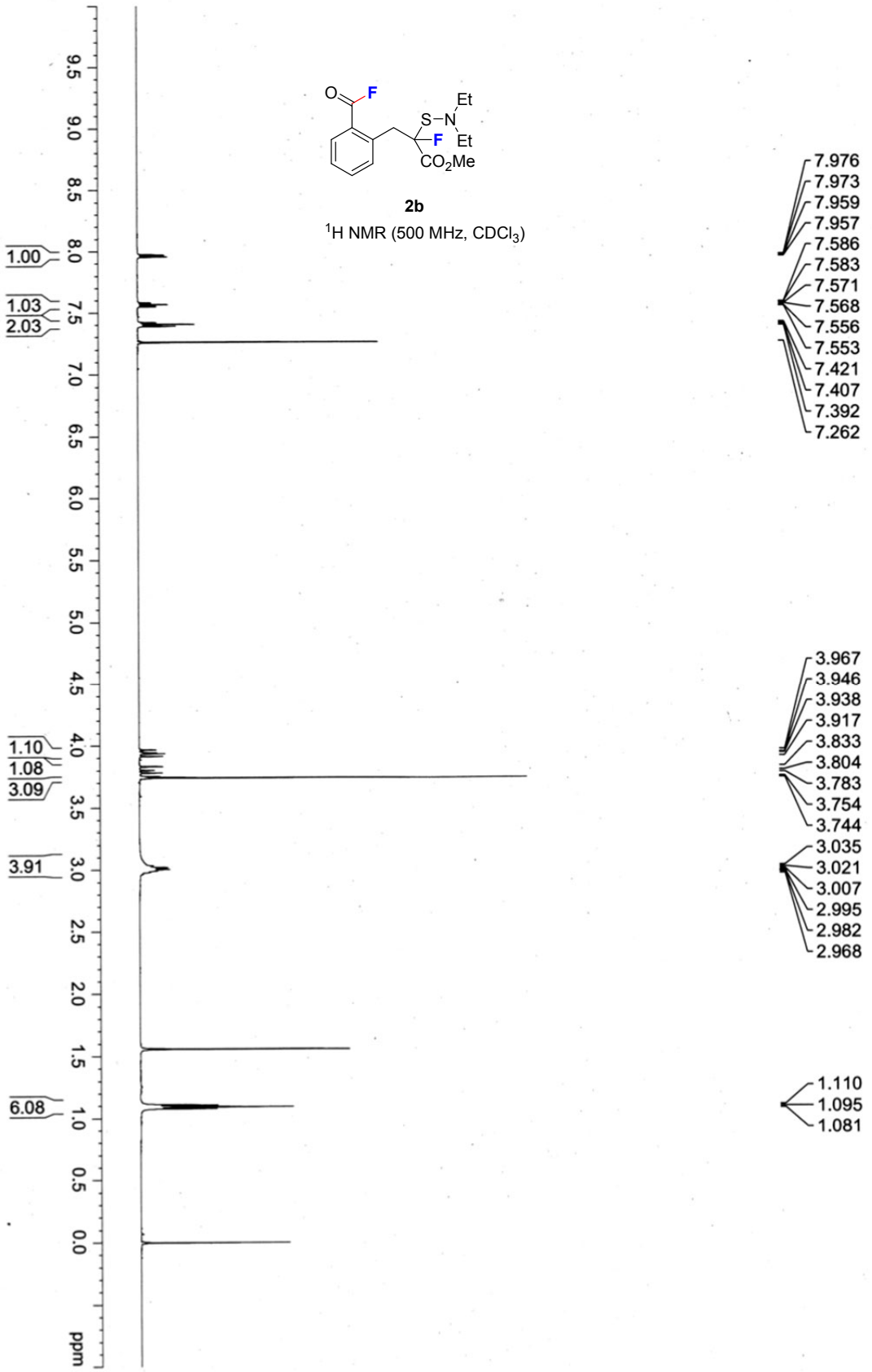
^{1}H NMR (500 MHz, $CDCl_3$)

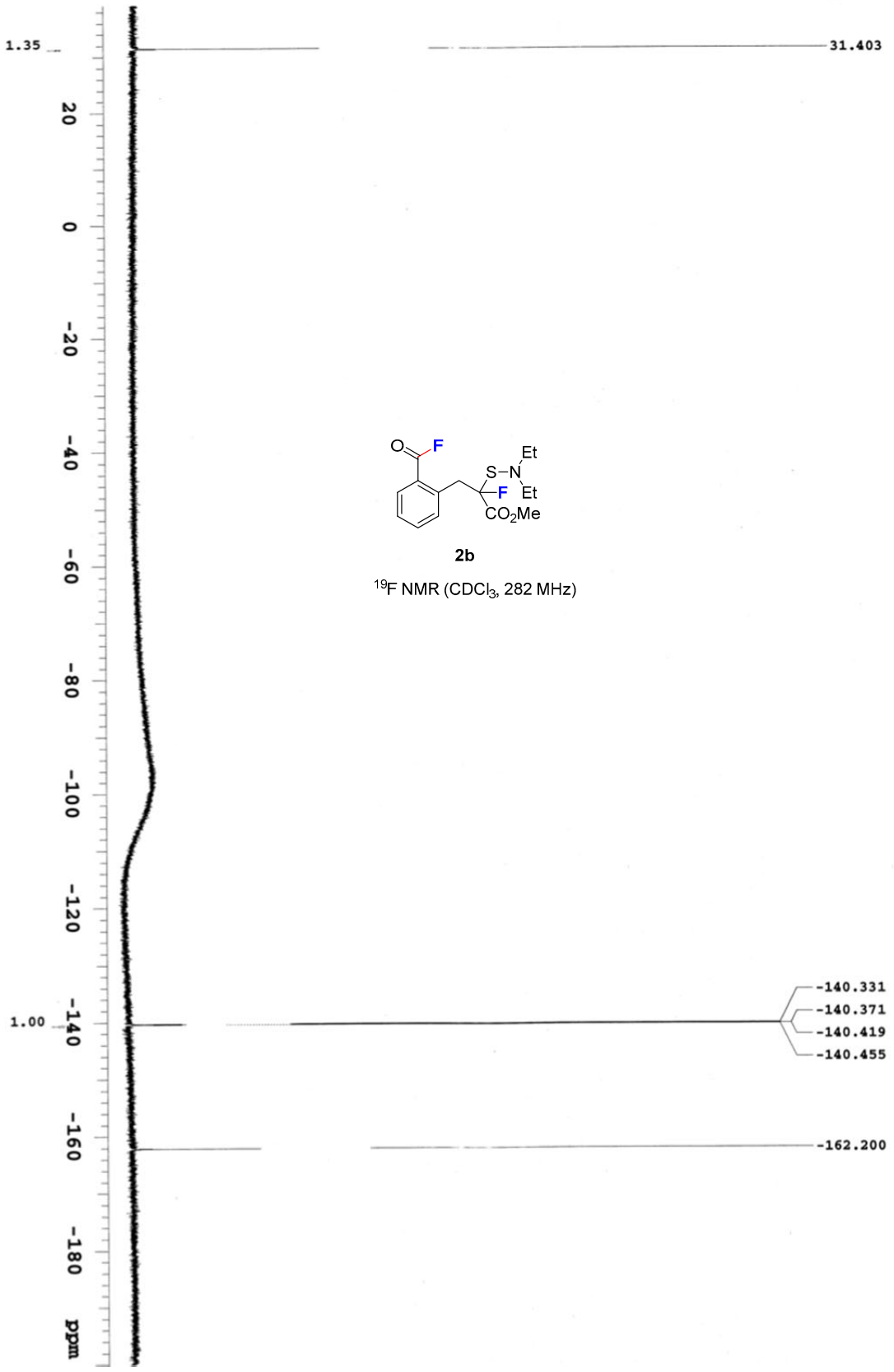


2a

^{19}F NMR ($CDCl_3$, 282 MHz)

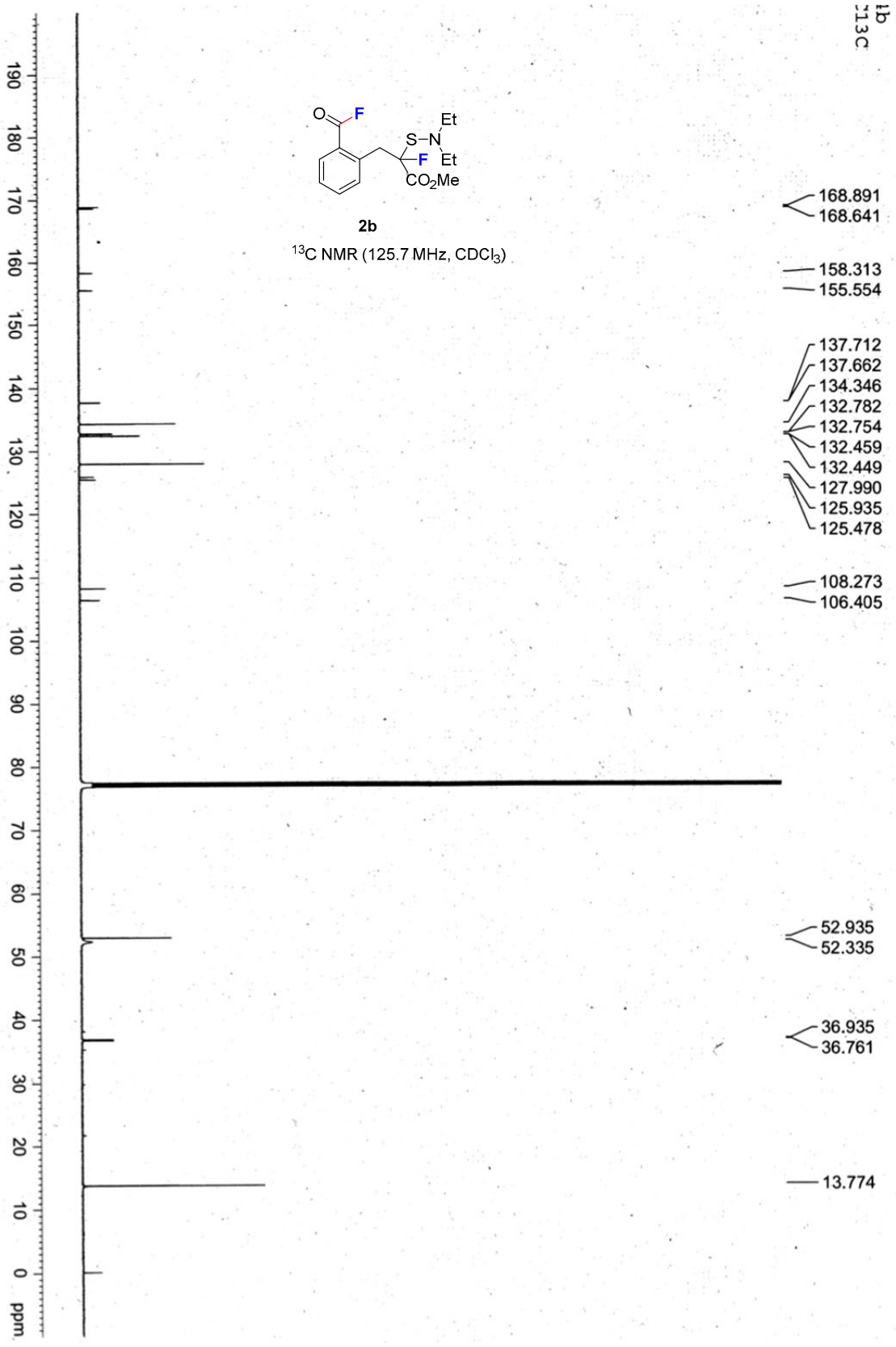

4a
C13C
O
F
Et
S–N
F
Et
CO2Et
2a
13C NMR (125.7 MHz, CDCl3)
168.470
168.221
158.284
155.526
137.894
137.846
134.286
132.773
132.749
132.444
132.434
127.919
125.927
125.471
108.162
106.294
62.346
52.350
36.942
36.768
14.130
13.768
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

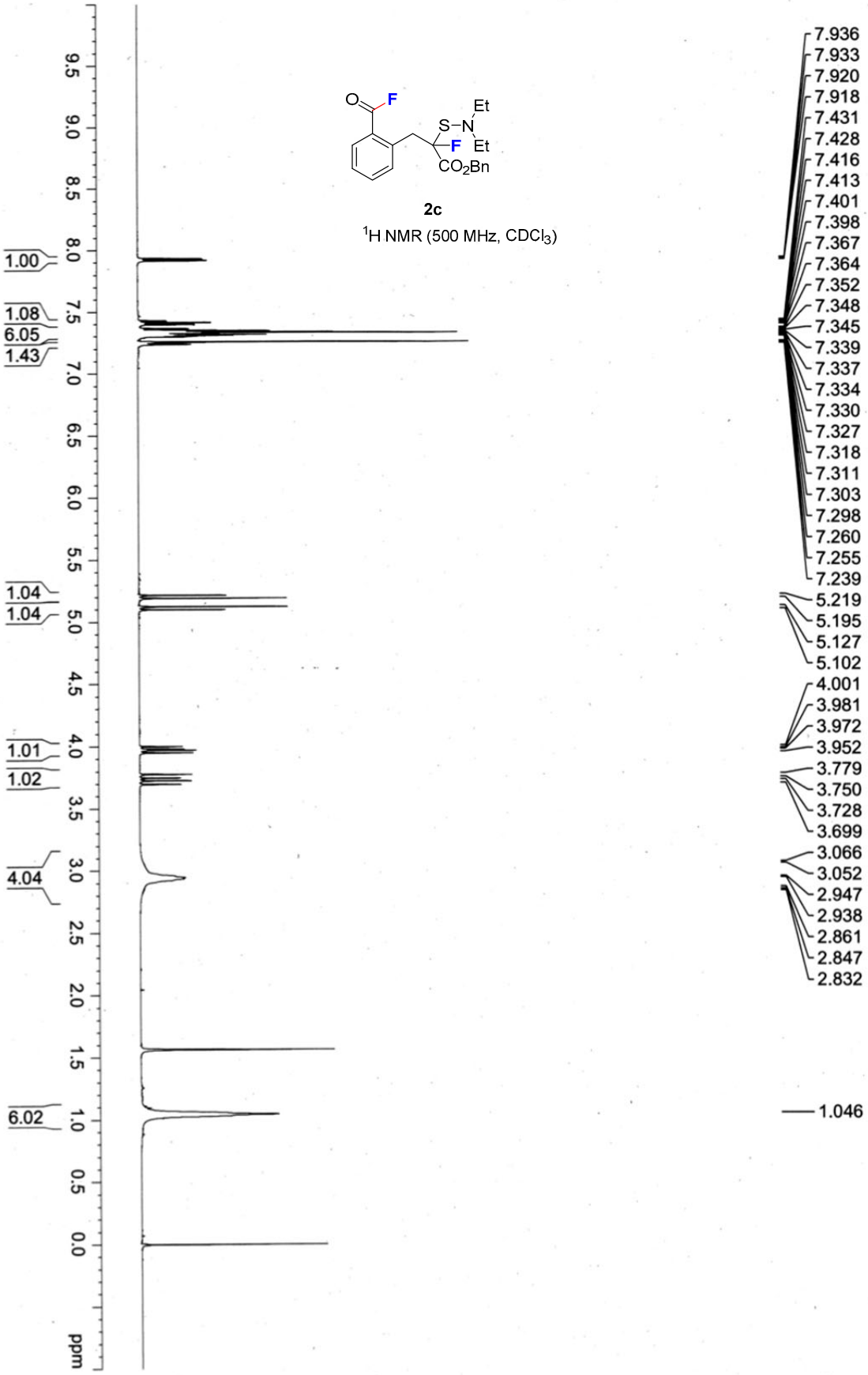

O
F
Et
S–N
F
Et
CO2Me
2b
1H NMR (500 MHz, CDCl3)
7.976
7.973
7.959
7.957
7.586
7.583
7.571
7.568
7.556
7.553
7.421
7.407
7.392
7.262
3.967
3.946
3.938
3.917
3.833
3.804
3.783
3.754
3.744
3.035
3.021
3.007
2.995
2.982
2.968
1.110
1.095
1.081
1.00
1.03
2.03
1.10
1.08
3.09
3.91
6.08
ppm

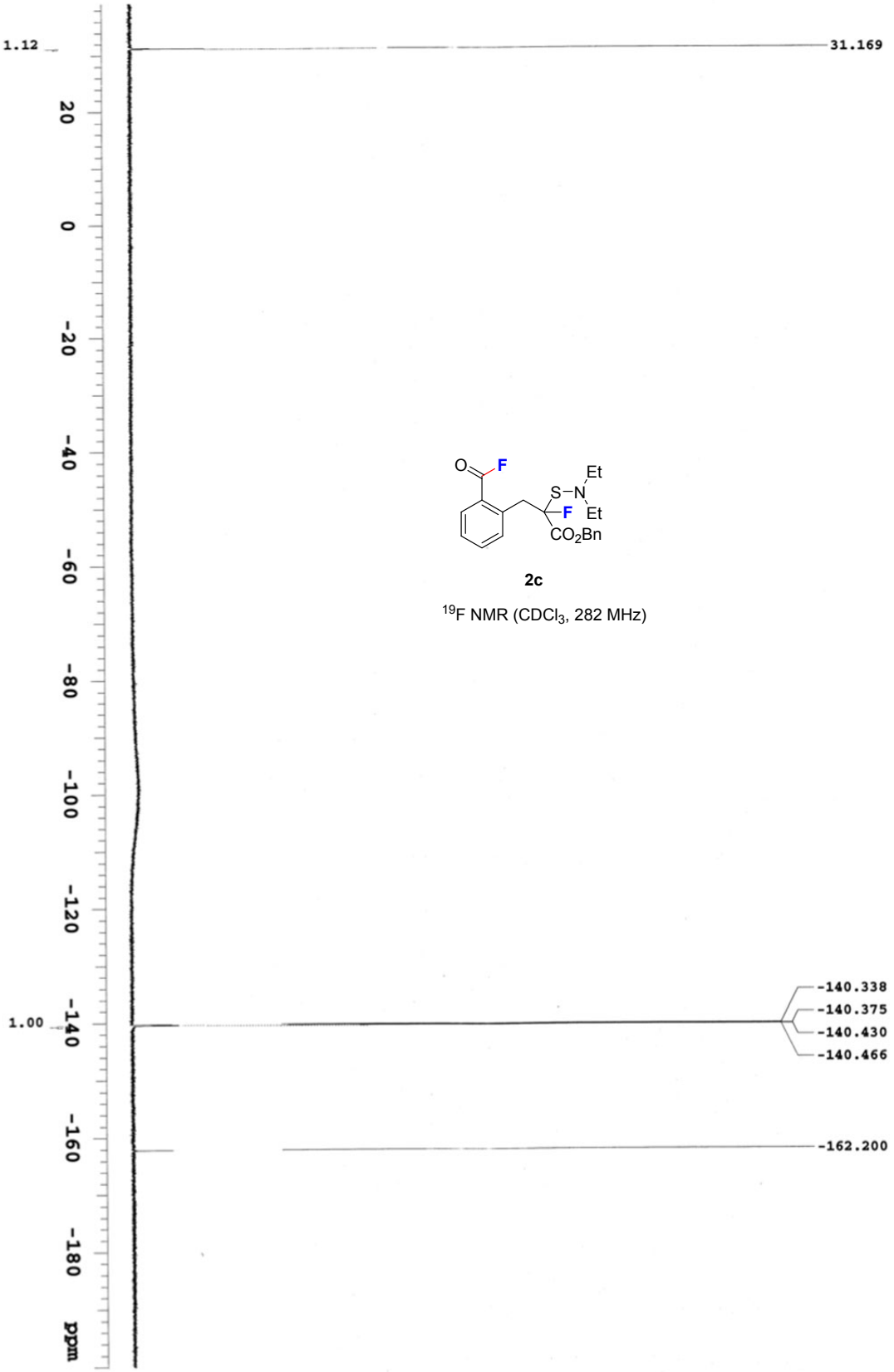


2b

^{19}F NMR ($CDCl_3$, 282 MHz)

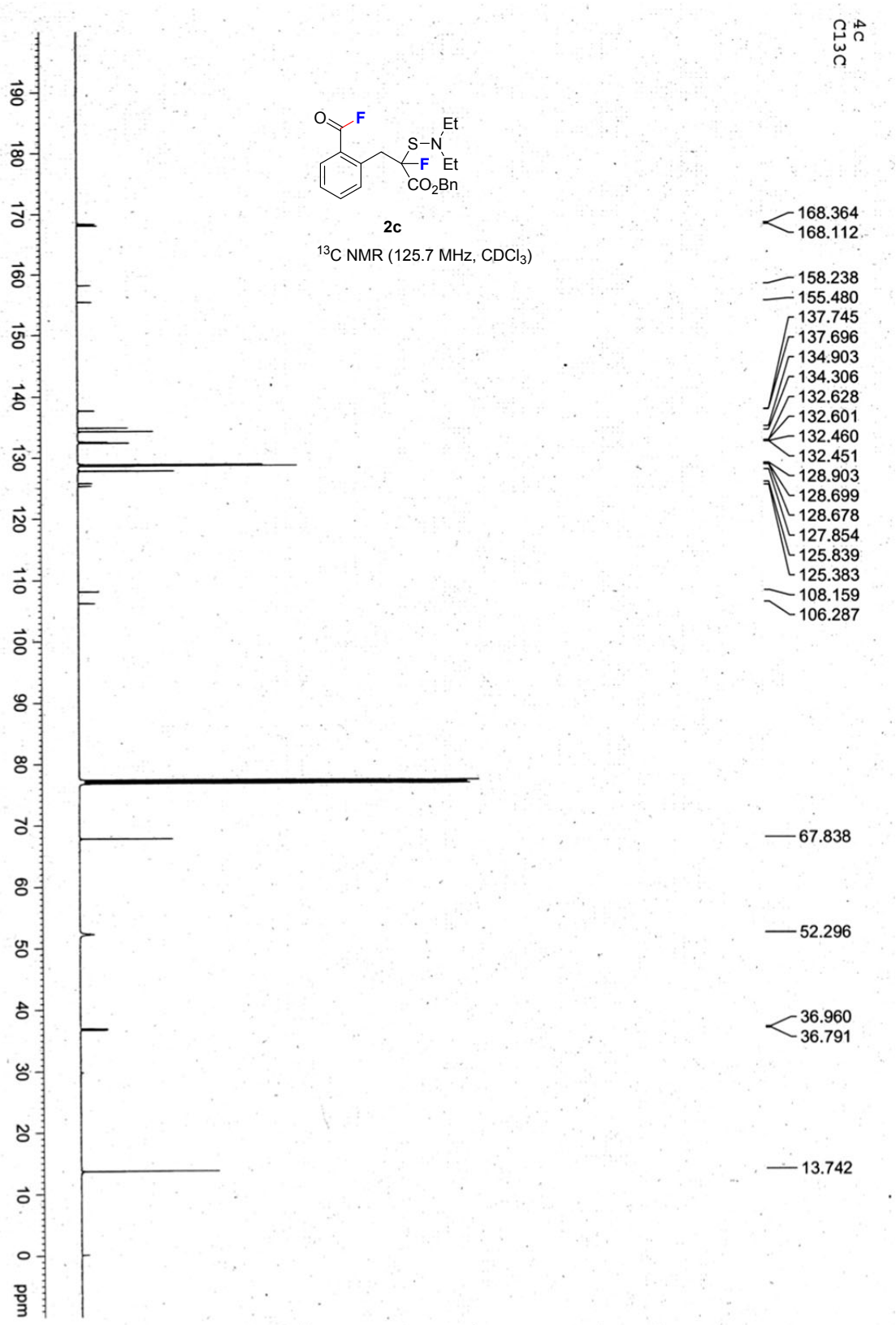

2b
13C NMR (125.7 MHz, CDCl3)
168.891
168.641
158.313
155.554
137.712
137.662
134.346
132.782
132.754
132.459
132.449
127.990
125.935
125.478
108.273
106.405
52.935
52.335
36.935
36.761
13.774
ppm

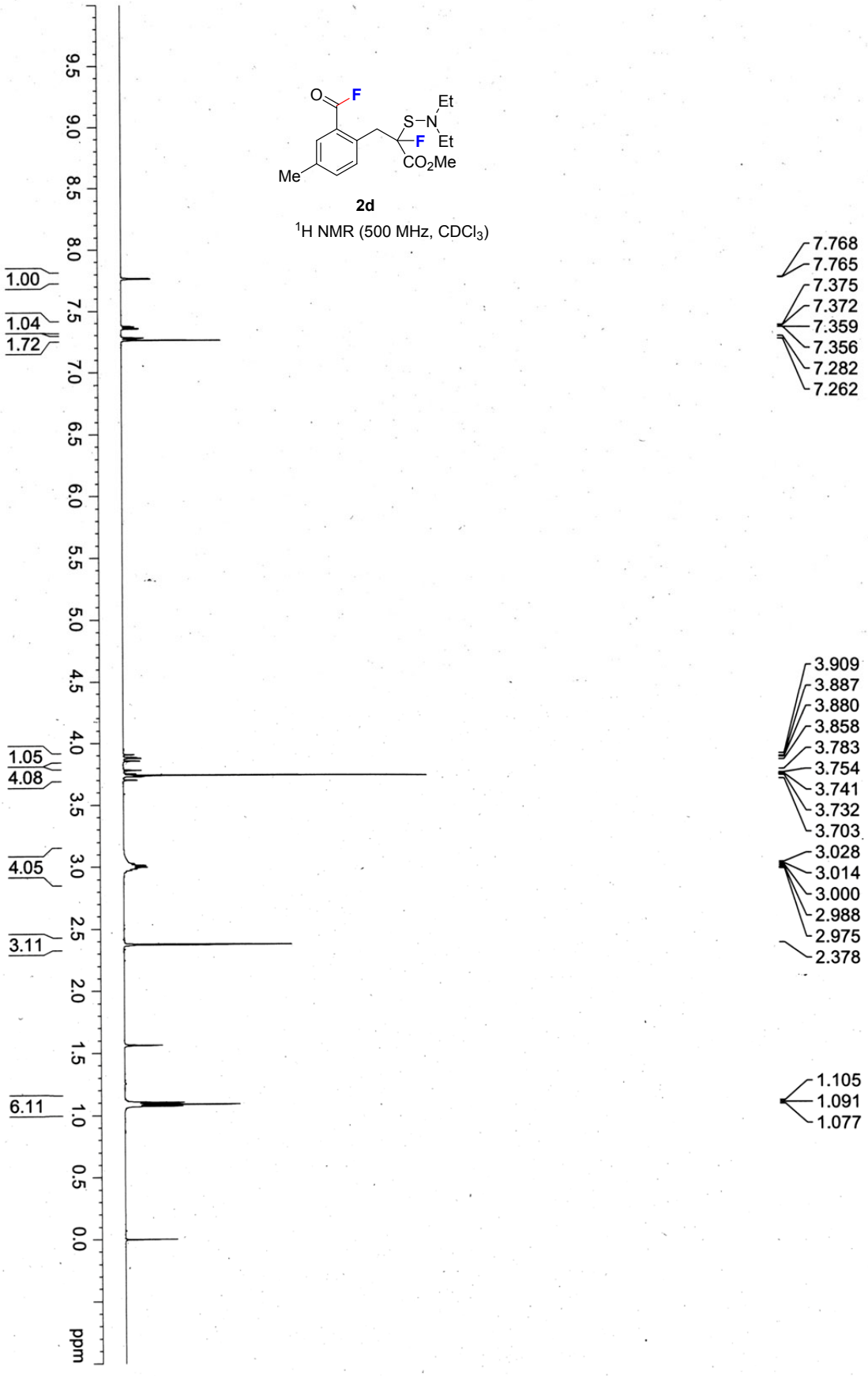

O
F
Et
S–N
F
Et
CO2Bn
2c
1H NMR (500 MHz, CDCl3)
1.00
1.08
6.05
1.43
1.04
1.04
1.01
1.02
4.04
6.02
ppm
7.936
7.933
7.920
7.918
7.431
7.428
7.416
7.413
7.401
7.398
7.367
7.364
7.352
7.348
7.345
7.339
7.337
7.334
7.330
7.327
7.318
7.311
7.303
7.298
7.260
7.255
7.239
5.219
5.195
5.127
5.102
4.001
3.981
3.972
3.952
3.779
3.750
3.728
3.699
3.066
3.052
2.947
2.938
2.861
2.847
2.832
1.046

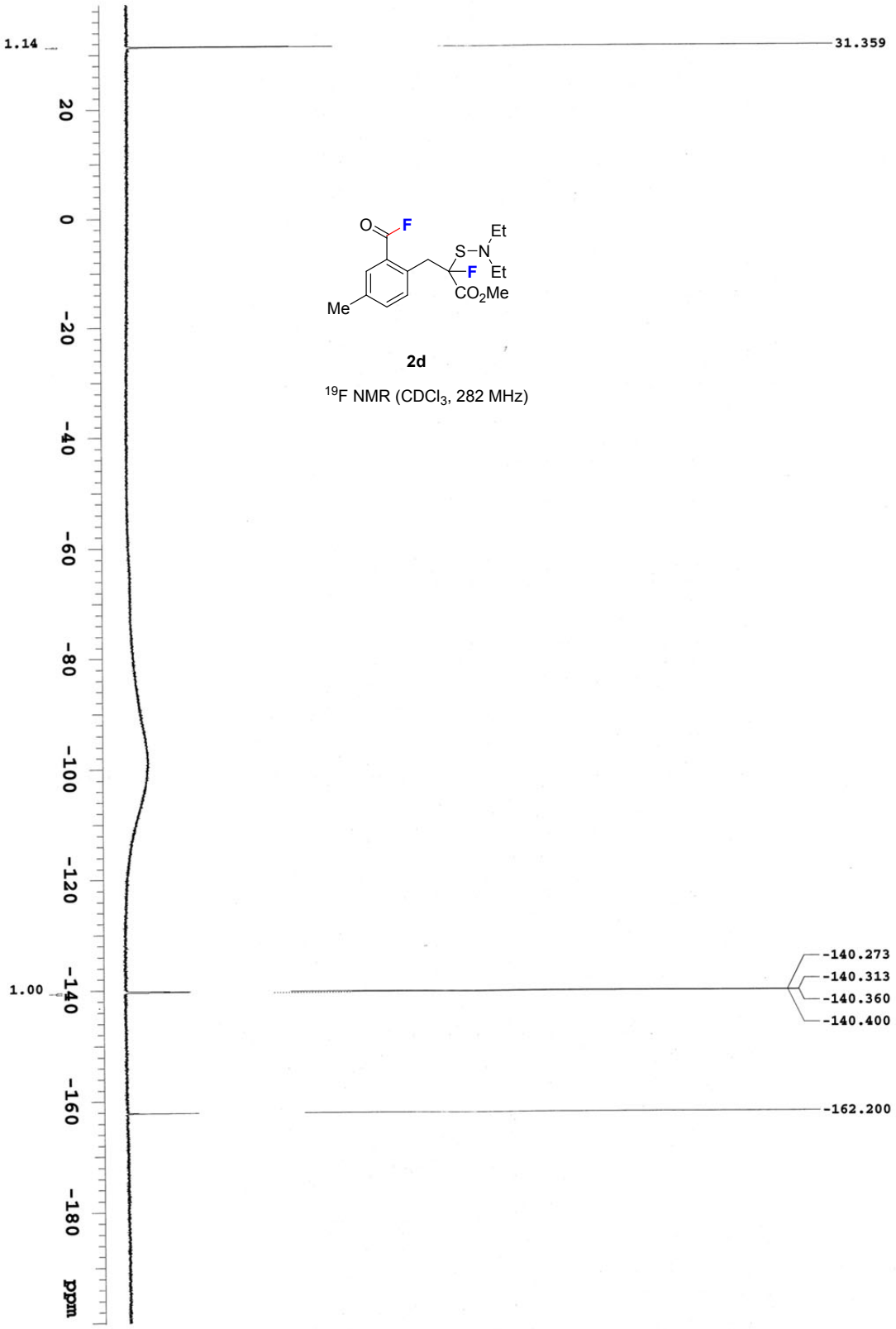


2c

^{19}F NMR ($CDCl_3$, 282 MHz)

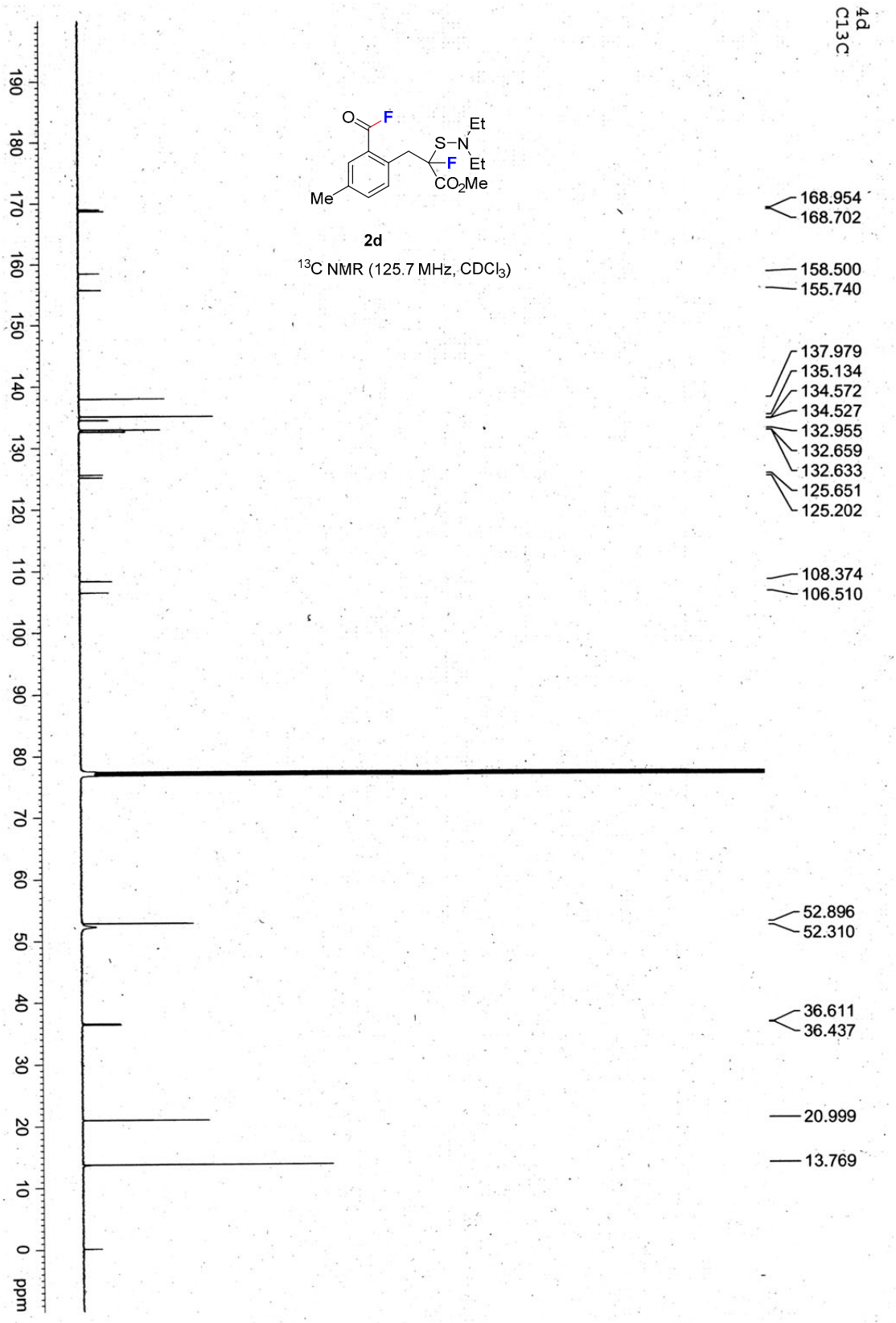

4c
C13C
O
F
Et
S–N
F
Et
CO2Bn
2c
13C NMR (125.7 MHz, CDCl3)
168.364
168.112
158.238
155.480
137.745
137.696
134.903
134.306
132.628
132.601
132.460
132.451
128.903
128.699
128.678
127.854
125.839
125.383
108.159
106.287
67.838
52.296
36.960
36.791
13.742
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

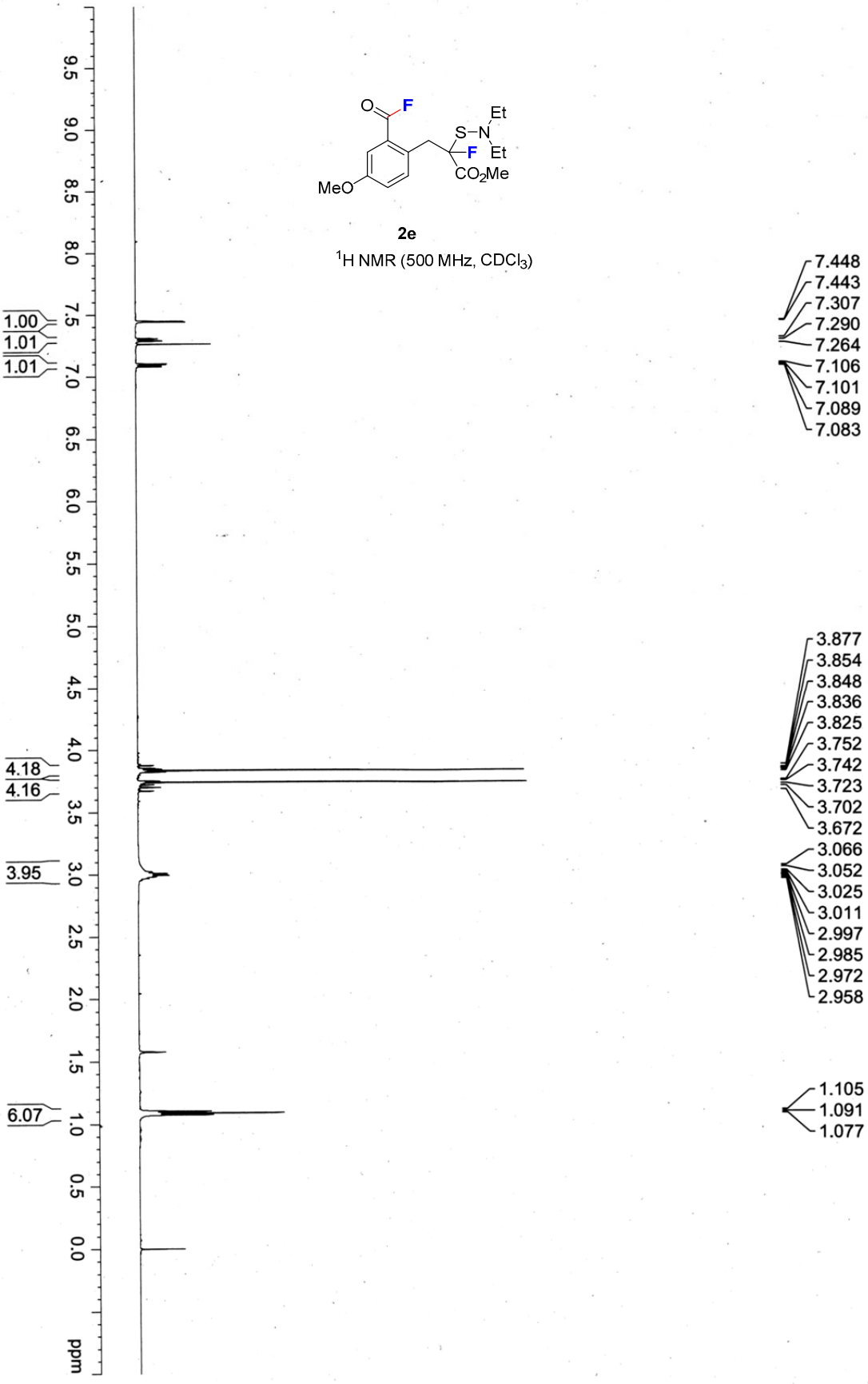

O
F
Et
S−N
F
Et
CO2Me
Me
2d
1H NMR (500 MHz, CDCl3)
7.768
7.765
7.375
7.372
7.359
7.356
7.282
7.262
3.909
3.887
3.880
3.858
3.783
3.754
3.741
3.732
3.703
3.028
3.014
3.000
2.988
2.975
2.378
1.105
1.091
1.077
1.00
1.04
1.72
1.05
4.08
4.05
3.11
6.11
ppm

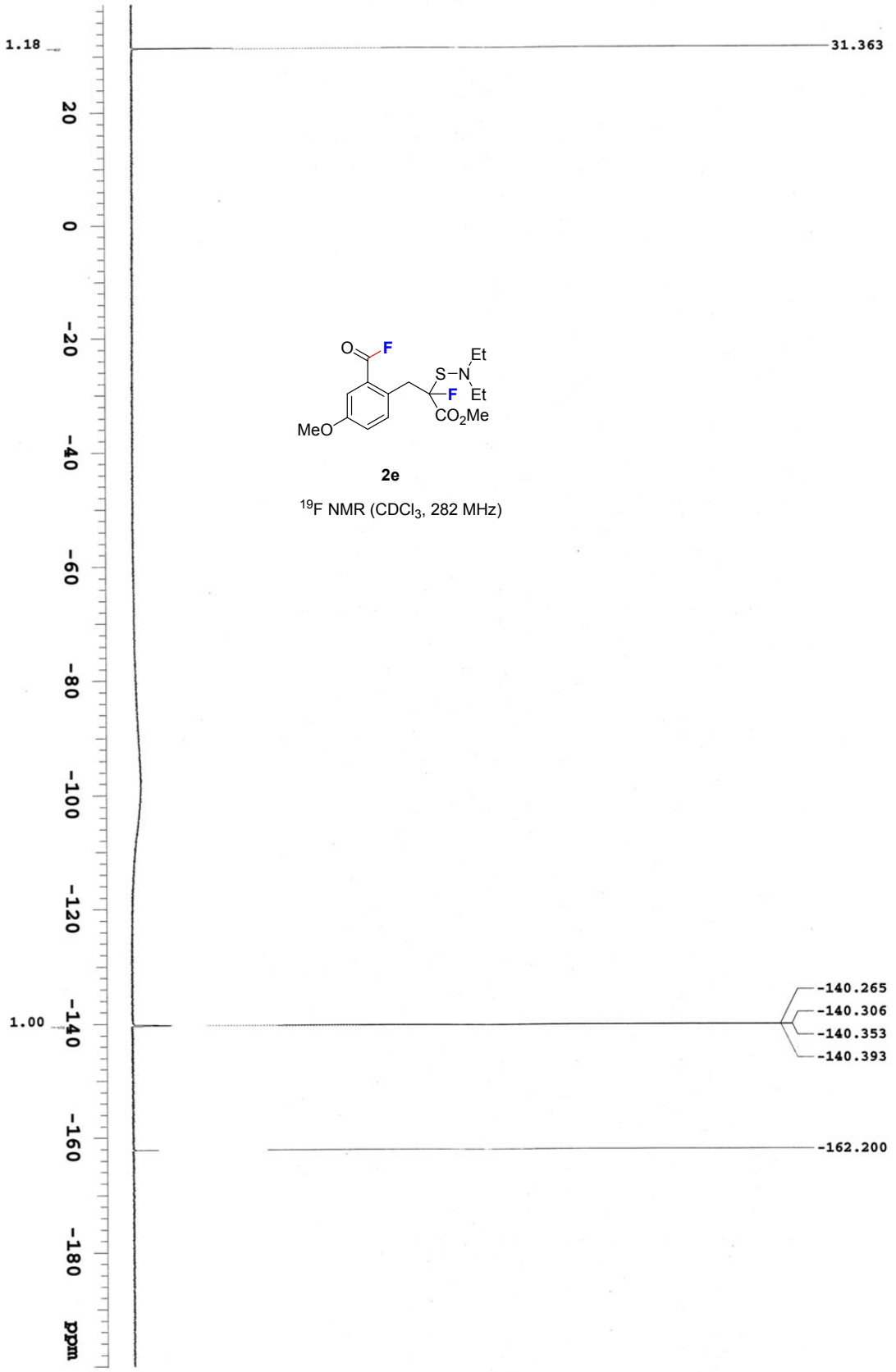


2d

^{19}F NMR ($CDCl_3$, 282 MHz)

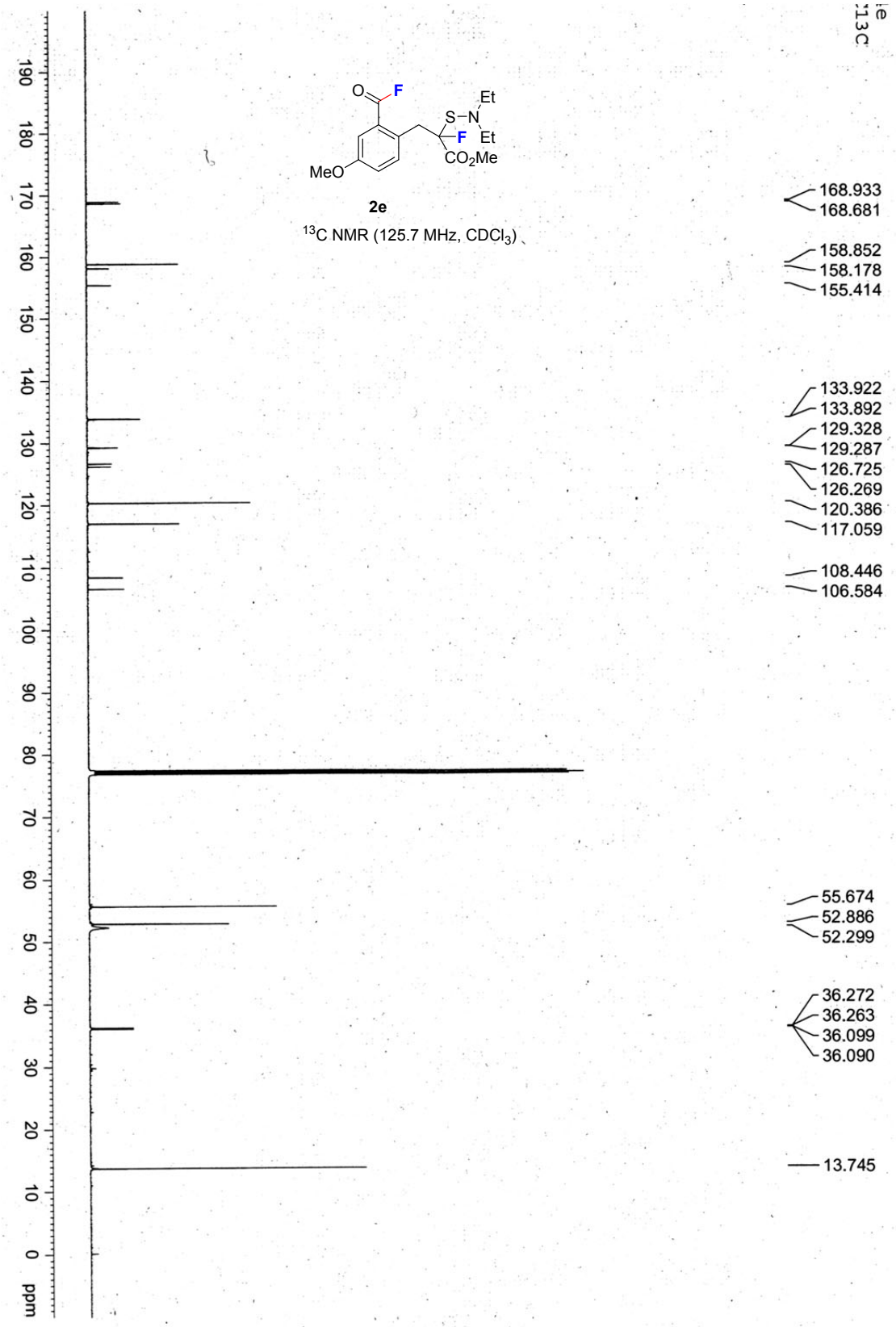

4d
C13C
O
F
Et
S–N
F
Et
CO2Me
Me
2d
13C NMR (125.7 MHz, CDCl3)
168.954
168.702
158.500
155.740
137.979
135.134
134.572
134.527
132.955
132.659
132.633
125.651
125.202
108.374
106.510
52.896
52.310
36.611
36.437
20.999
13.769
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

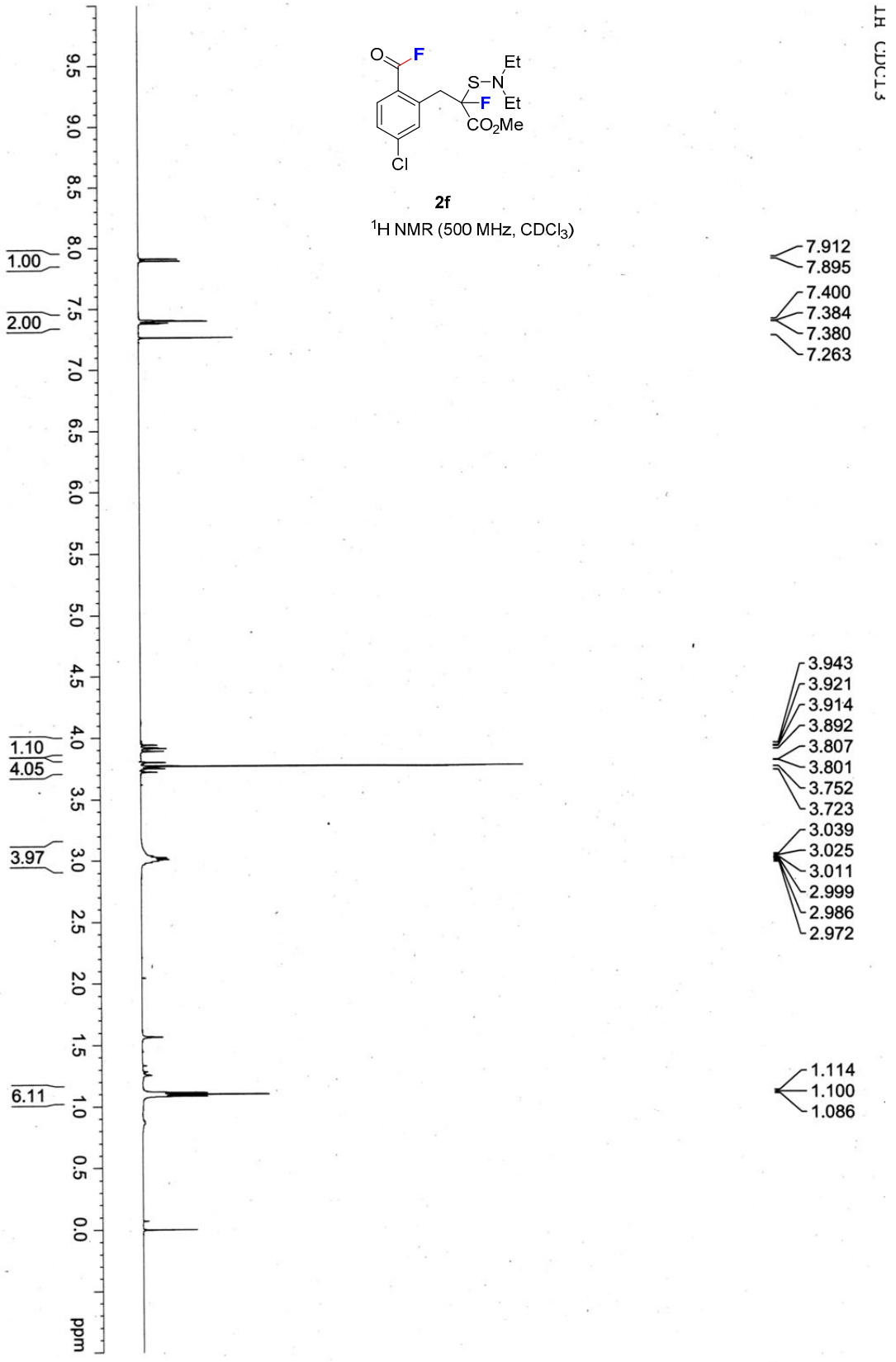

O
F
Et
S–N
F
Et
CO2Me
MeO
2e
1H NMR (500 MHz, CDCl3)
7.448
7.443
7.307
7.290
7.264
7.106
7.101
7.089
7.083
3.877
3.854
3.848
3.836
3.825
3.752
3.742
3.723
3.702
3.672
3.066
3.052
3.025
3.011
2.997
2.985
2.972
2.958
1.105
1.091
1.077
1.00
1.01
1.01
4.18
4.16
3.95
6.07
ppm

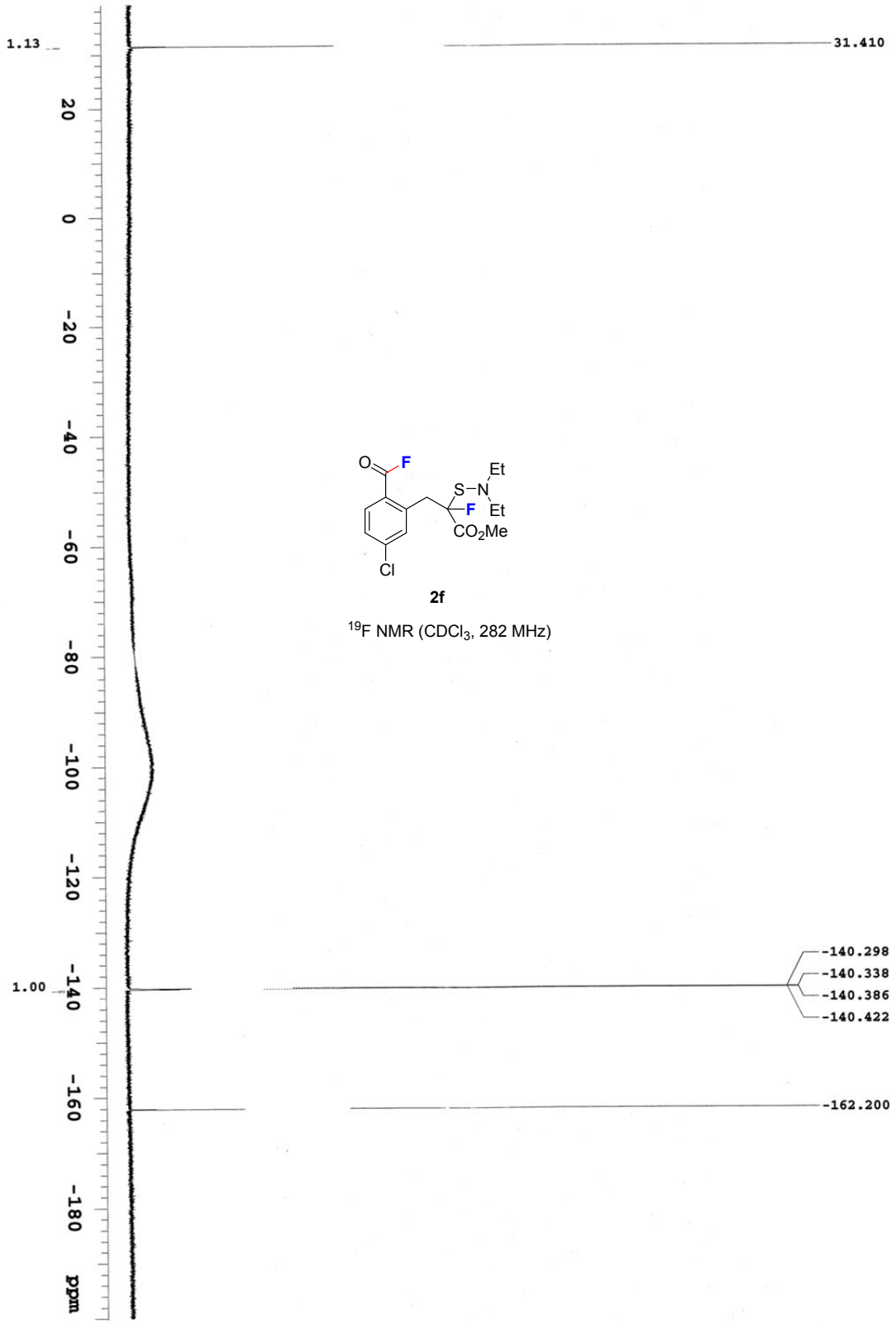


2e

^{19}F NMR ($CDCl_3$, 282 MHz)

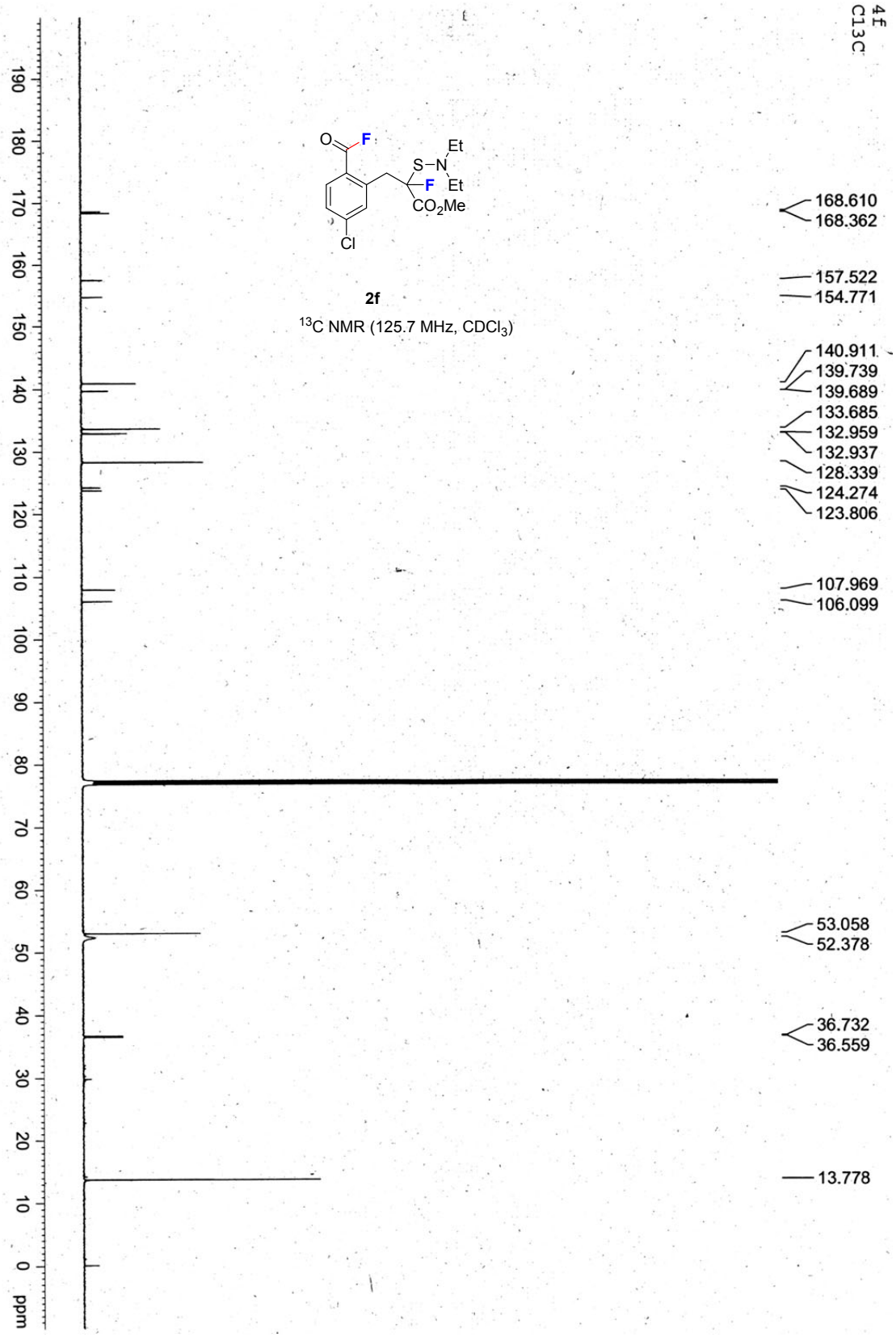

O
F
Et
S–N
F
Et
CO2Me
MeO
2e
13C NMR (125.7 MHz, CDCl3)
168.933
168.681
158.852
158.178
155.414
133.922
133.892
129.328
129.287
126.725
126.269
120.386
117.059
108.446
106.584
55.674
52.886
52.299
36.272
36.263
36.099
36.090
13.745
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


1H CDCl3
O
F
S–N
Et
Et
F
CO2Me
Cl
2f
1H NMR (500 MHz, CDCl3)
7.912
7.895
7.400
7.384
7.380
7.263
3.943
3.921
3.914
3.892
3.807
3.801
3.752
3.723
3.039
3.025
3.011
2.999
2.986
2.972
1.114
1.100
1.086
1.00
2.00
1.10
4.05
3.97
6.11
ppm



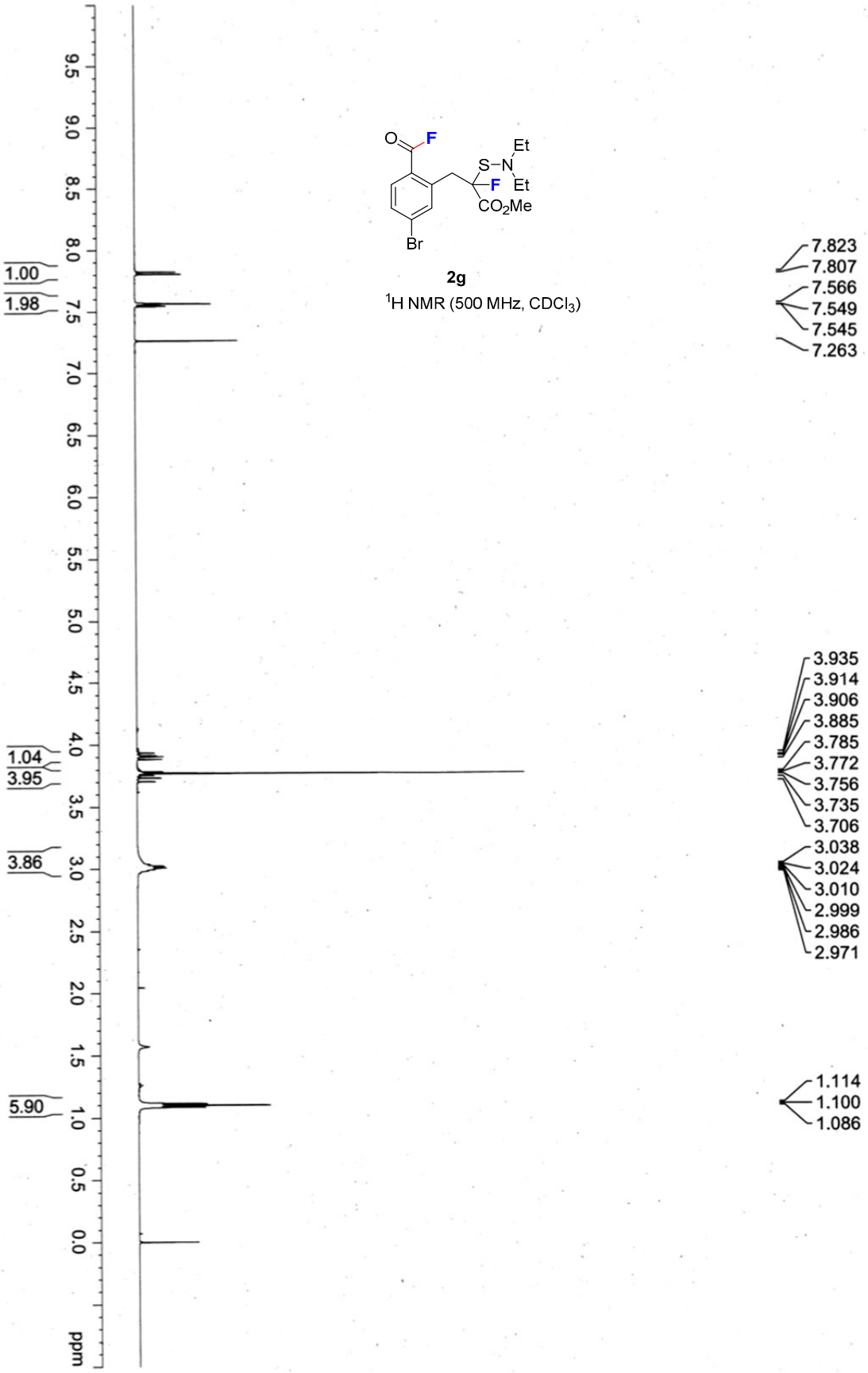
2f

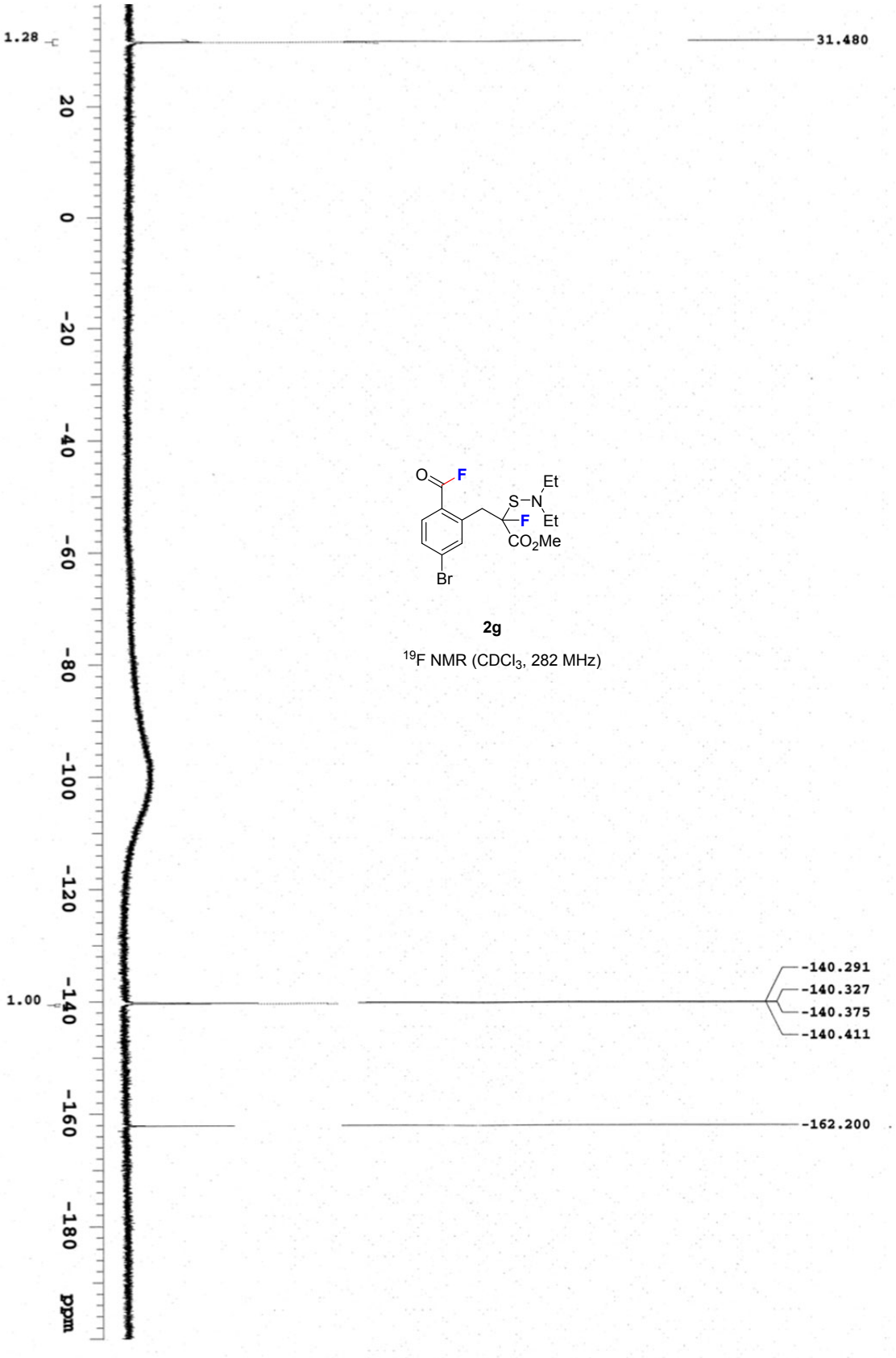
^{19}F NMR ($CDCl_3$, 282 MHz)



2f

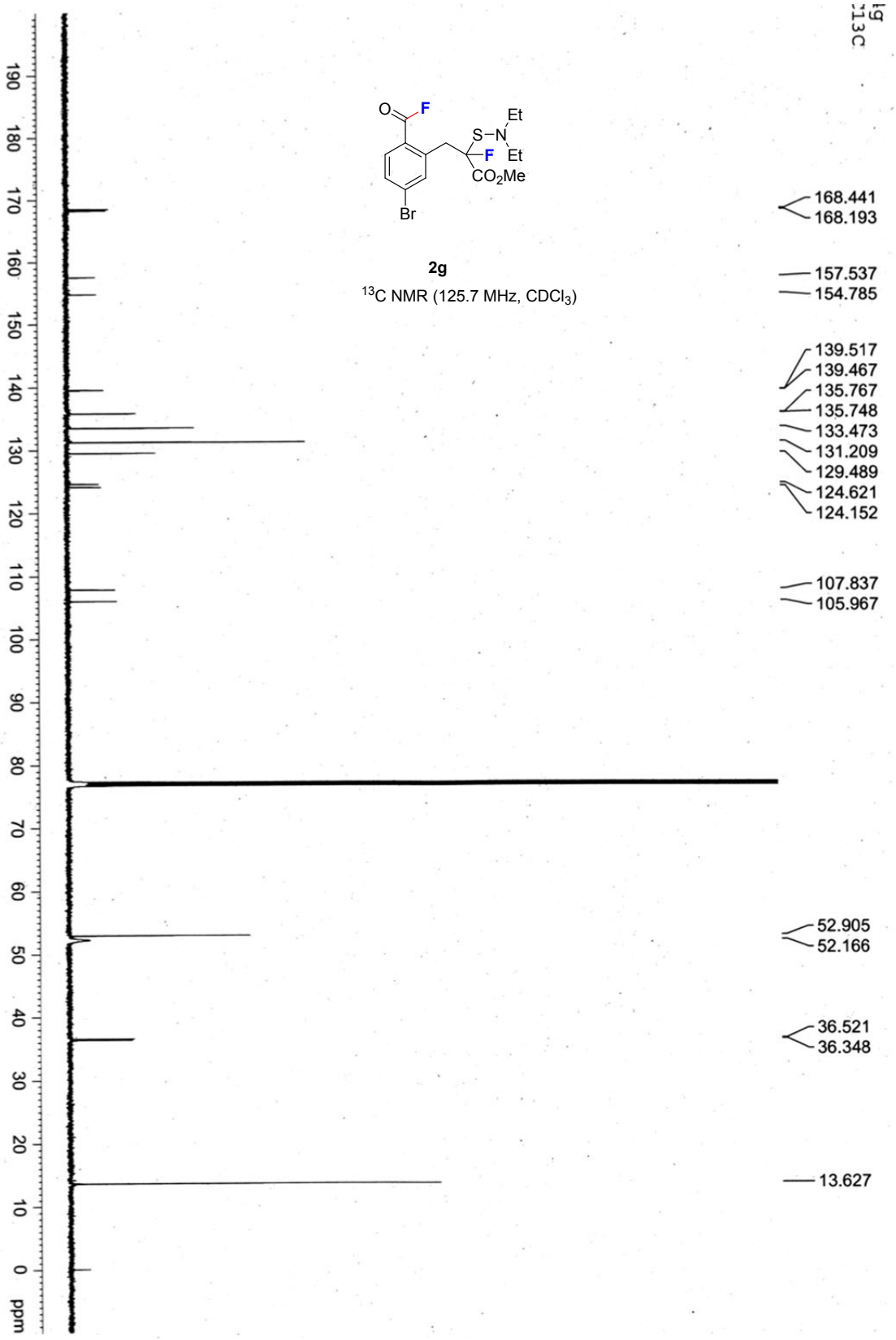
^{13}C NMR (125.7 MHz, $CDCl_3$)

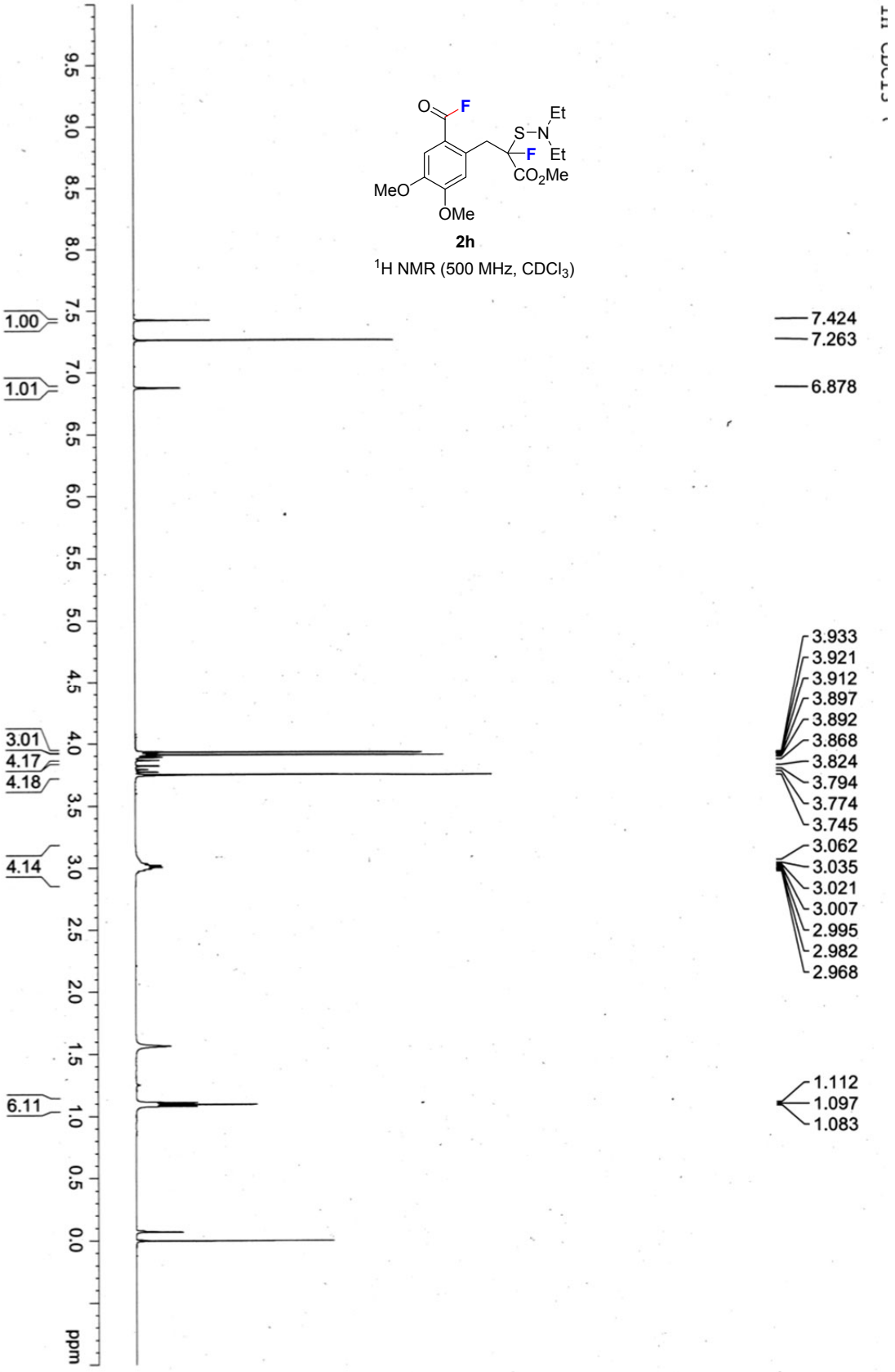

O
F
S–N
Et
F
Et
CO2Me
Br
2g
1H NMR (500 MHz, CDCl3)
7.823
7.807
7.566
7.549
7.545
7.263
3.935
3.914
3.906
3.885
3.785
3.772
3.756
3.735
3.706
3.038
3.024
3.010
2.999
2.986
2.971
1.114
1.100
1.086
1.00
1.98
1.04
3.95
3.86
5.90
ppm

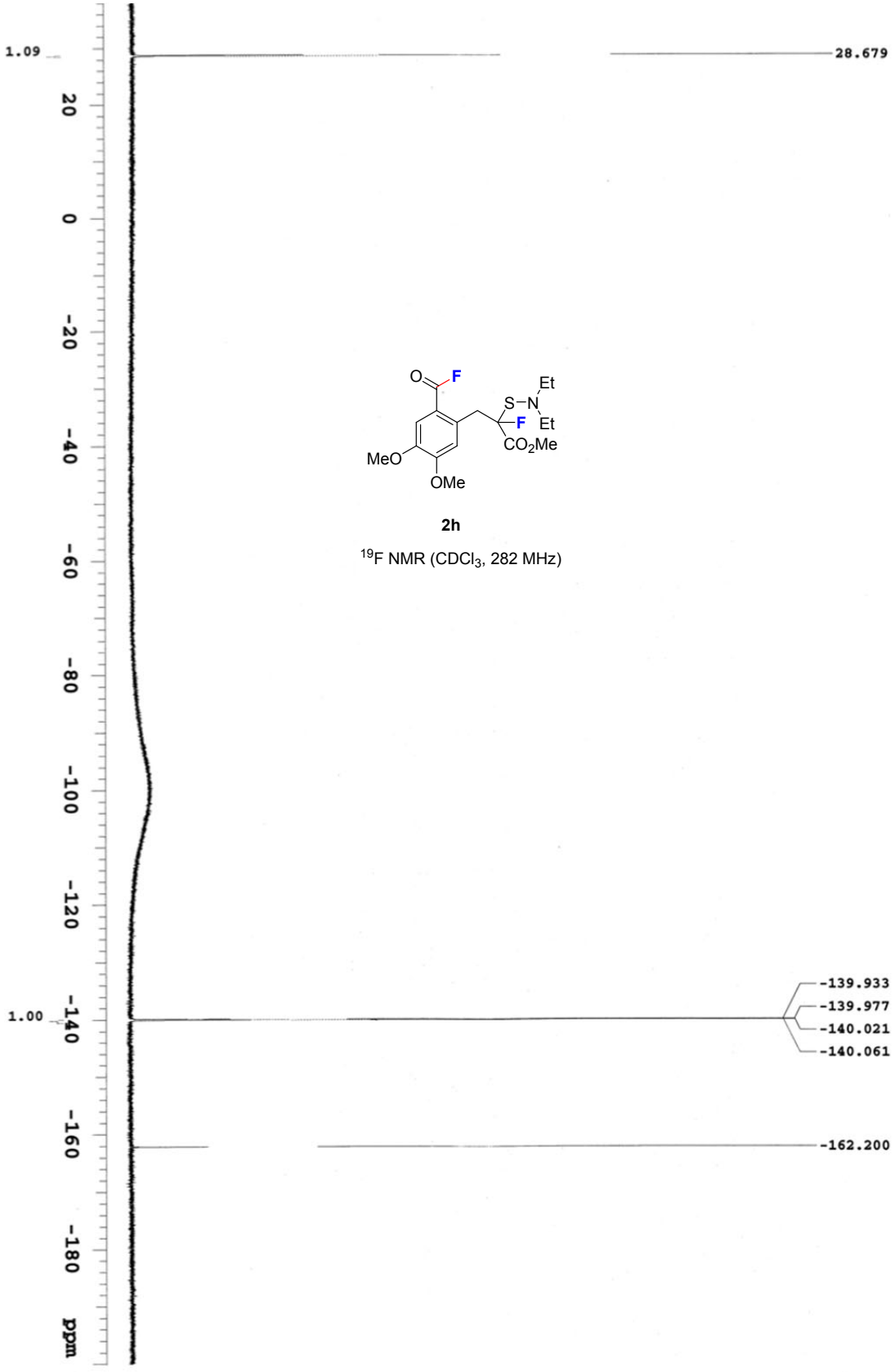


2g

^{19}F NMR ($CDCl_3$, 282 MHz)

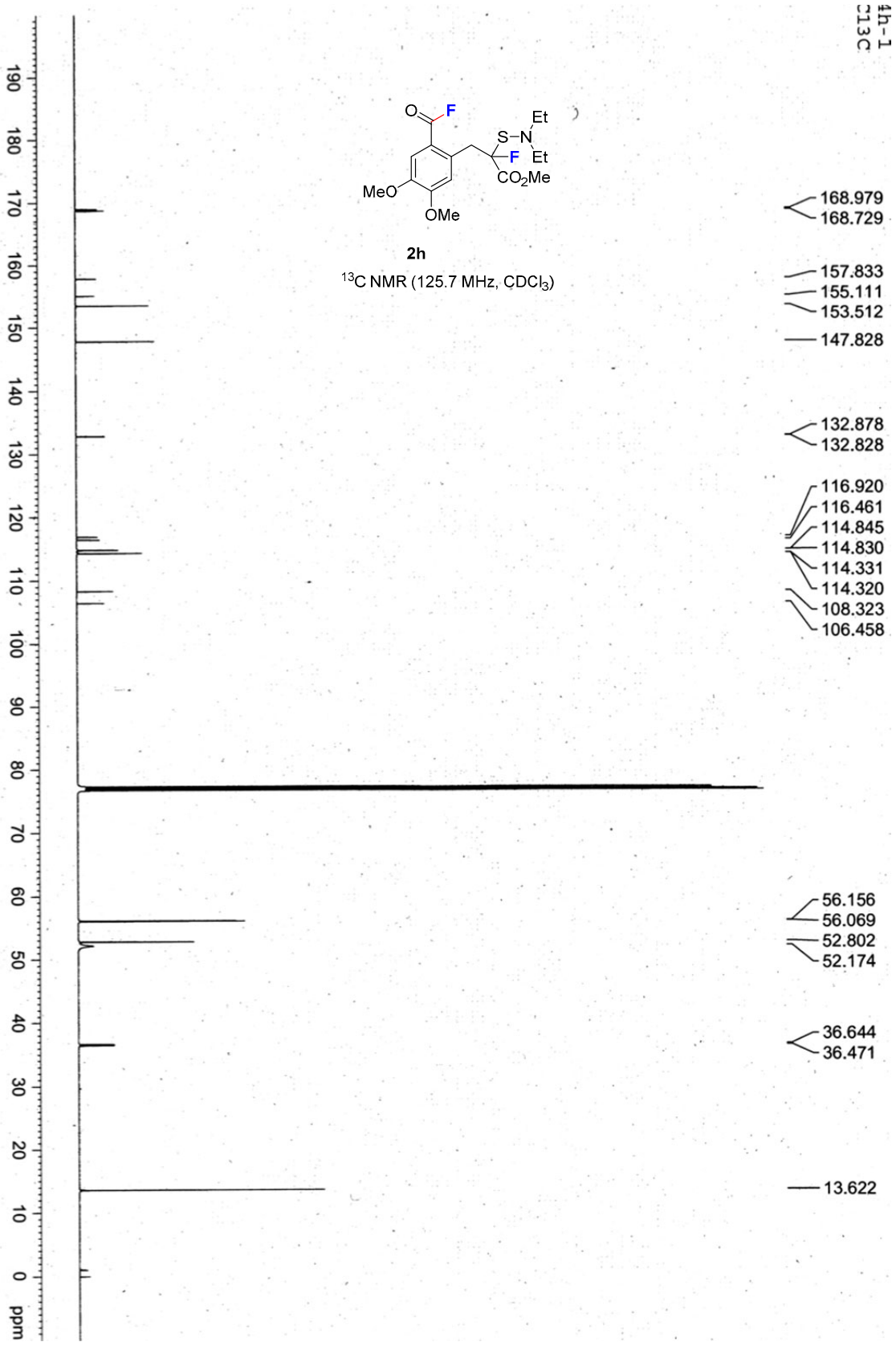

2g
13C
O
F
Et
S–N
F
Et
CO2Me
Br
2g
13C NMR (125.7 MHz, CDCl3)
168.441
168.193
157.537
154.785
139.517
139.467
135.767
135.748
133.473
131.209
129.489
124.621
124.152
107.837
105.967
52.905
52.166
36.521
36.348
13.627
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

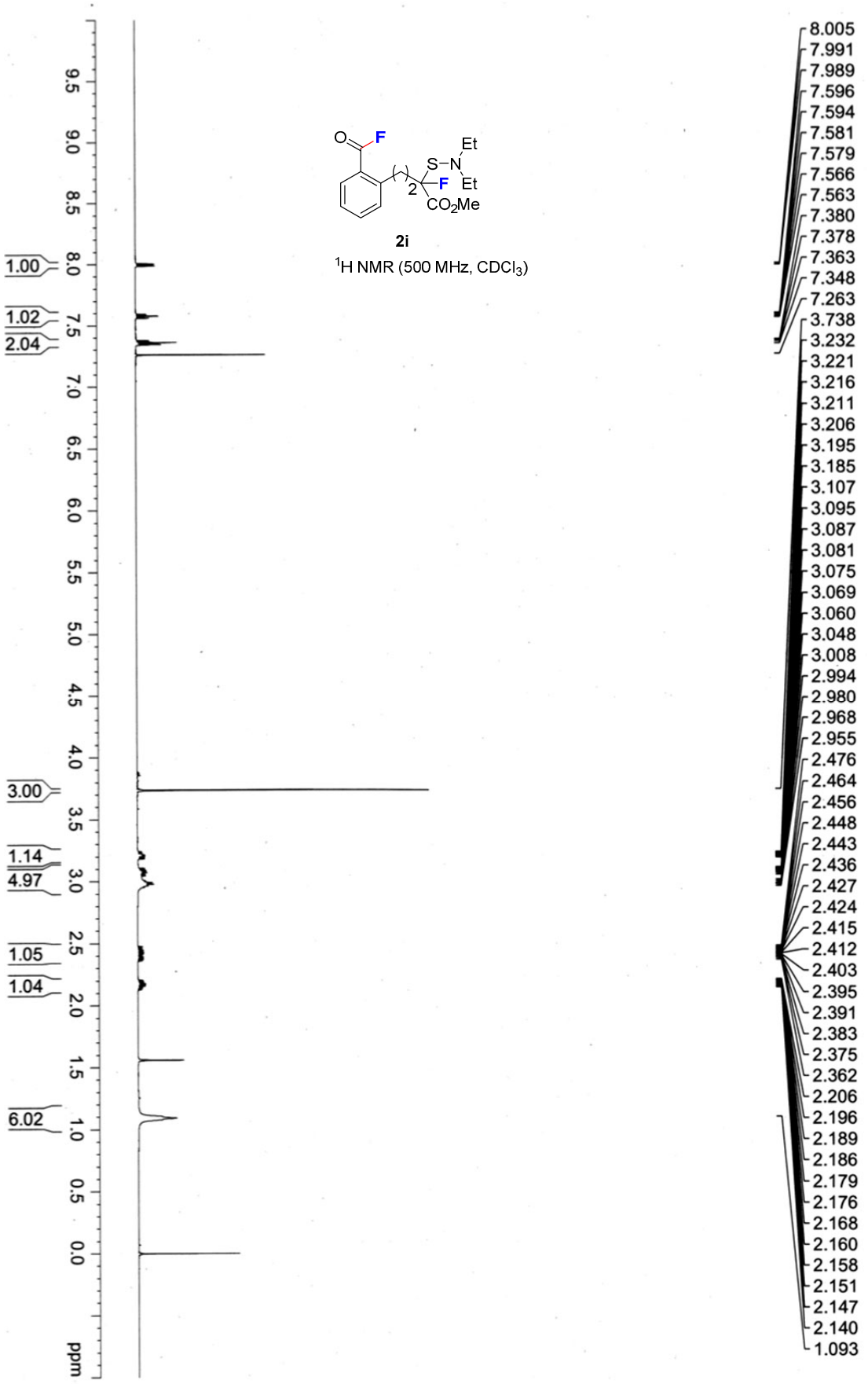

O
F
Et
S–N
Et
F
CO2Me
MeO
OMe
2h
1H NMR (500 MHz, CDCl3)
1.00
1.01
3.01
4.17
4.18
4.14
6.11
7.424
7.263
6.878
3.933
3.921
3.912
3.897
3.892
3.868
3.824
3.794
3.774
3.745
3.062
3.035
3.021
3.007
2.995
2.982
2.968
1.112
1.097
1.083
ppm

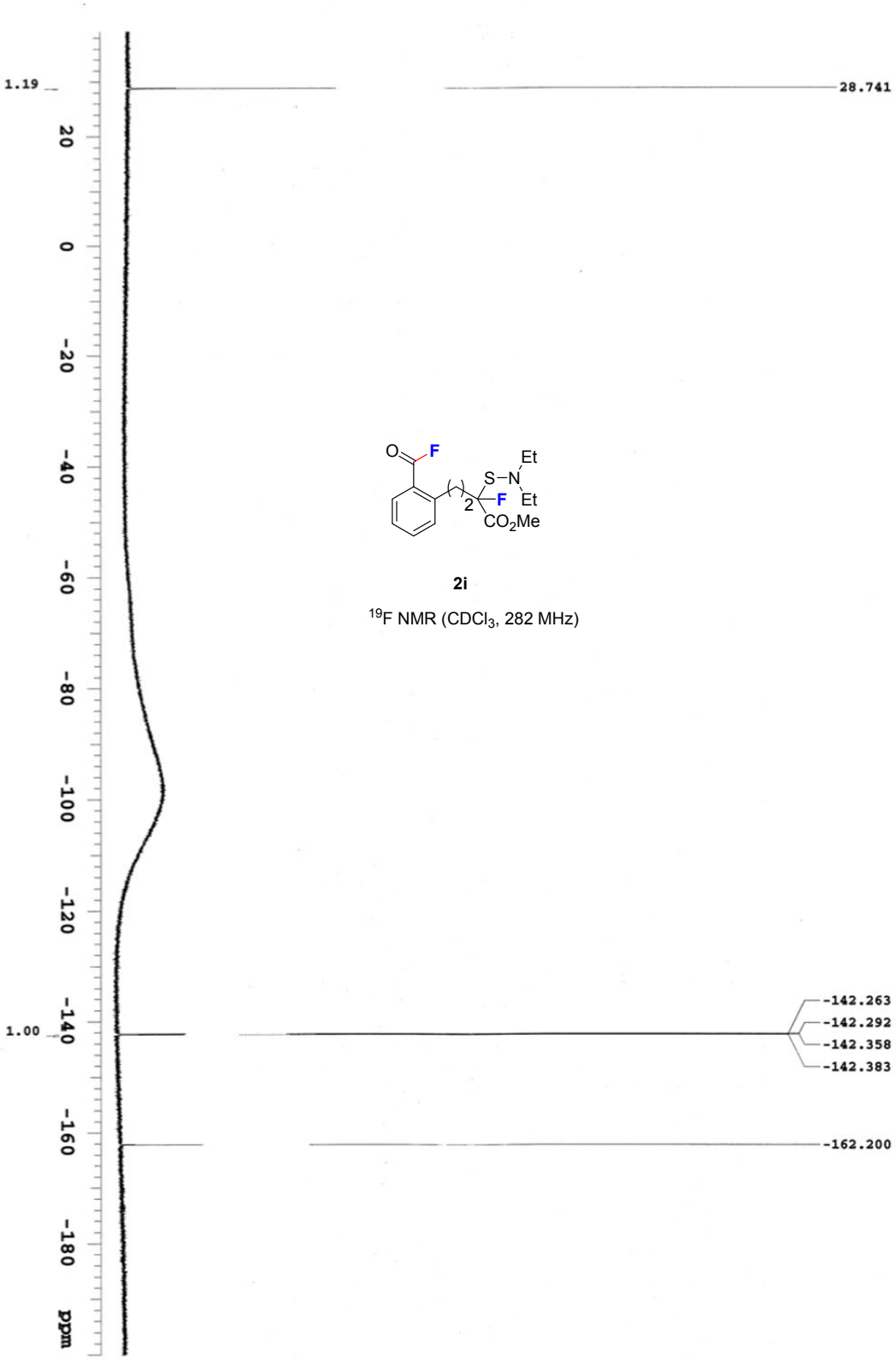


2h

^{19}F NMR ($CDCl_3$, 282 MHz)

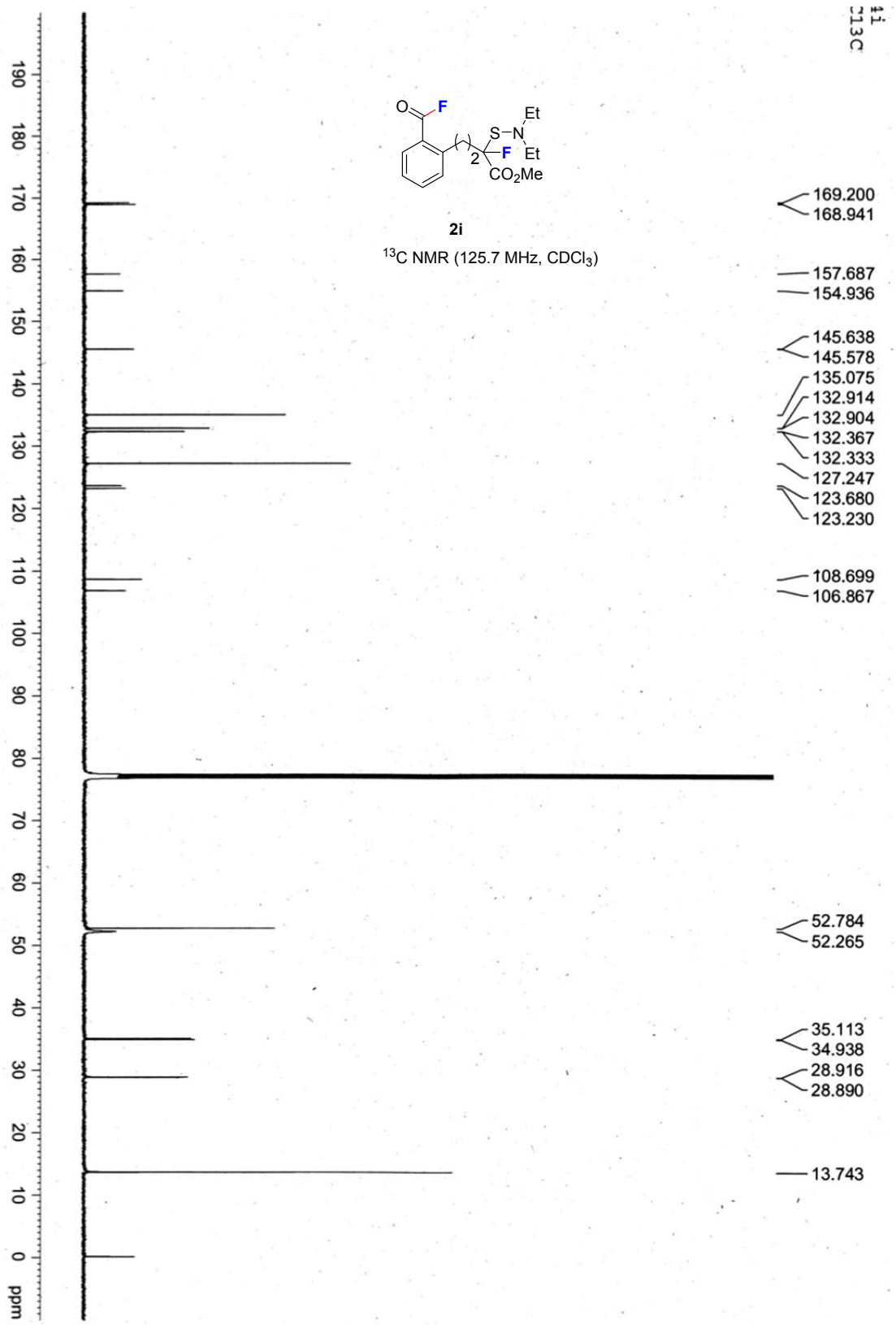

4h-1
C13C
O
F
Et
S–N
F
Et
CO2Me
MeO
OMe
2h
13C NMR (125.7 MHz, CDCl3)
168.979
168.729
157.833
155.111
153.512
147.828
132.878
132.828
116.920
116.461
114.845
114.830
114.331
114.320
108.323
106.458
56.156
56.069
52.802
52.174
36.644
36.471
13.622
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

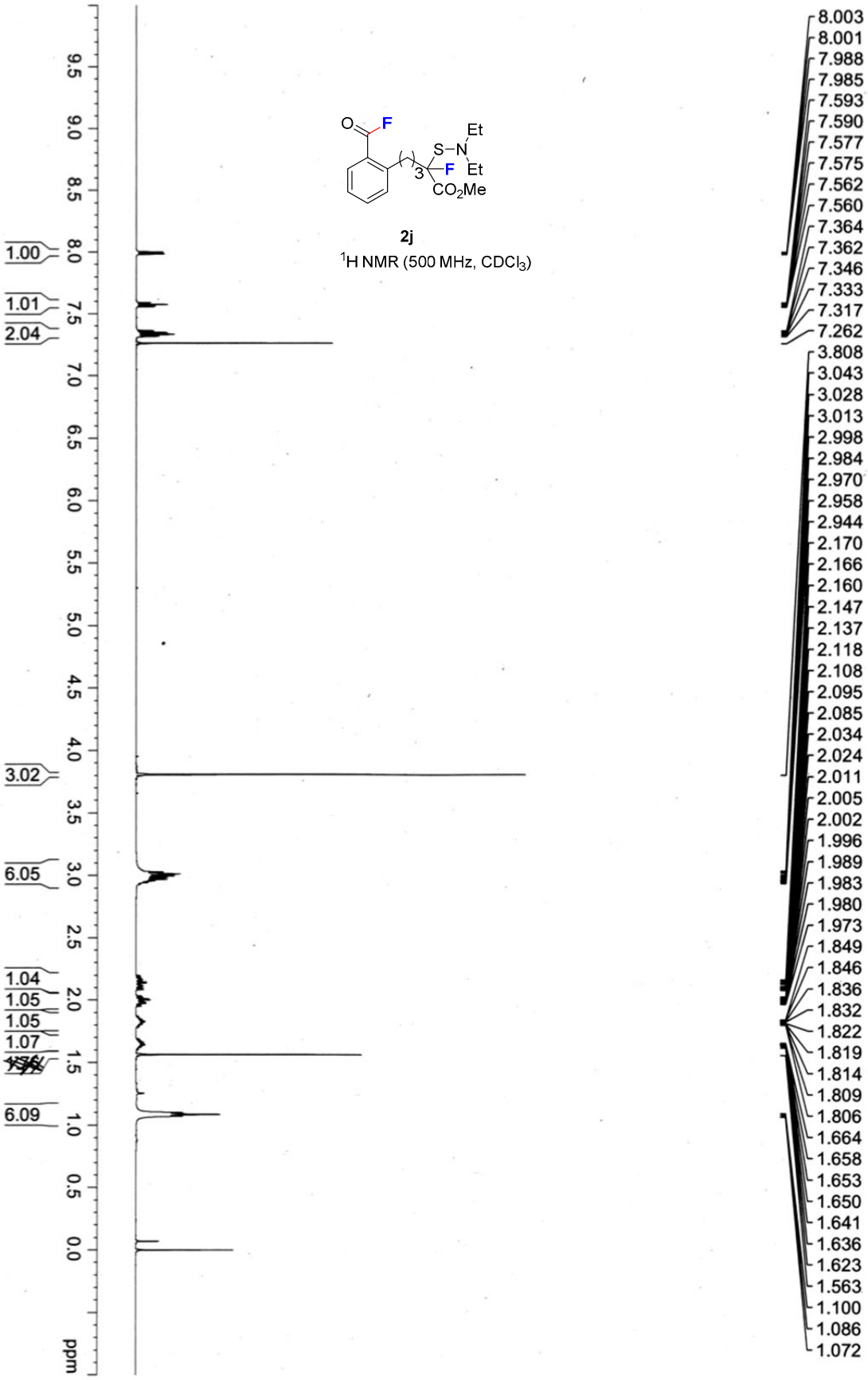

O
F
Et
S–N
Et
2
F
CO2Me
2i
1H NMR (500 MHz, CDCl3)
1.00
1.02
2.04
3.00
1.14
4.97
1.05
1.04
6.02
ppm
8.005
7.991
7.989
7.596
7.594
7.581
7.579
7.566
7.563
7.380
7.378
7.363
7.348
7.263
3.738
3.232
3.221
3.216
3.211
3.206
3.195
3.185
3.107
3.095
3.087
3.081
3.075
3.069
3.060
3.048
3.008
2.994
2.980
2.968
2.955
2.476
2.464
2.456
2.448
2.443
2.436
2.427
2.424
2.415
2.412
2.403
2.395
2.391
2.383
2.375
2.362
2.206
2.196
2.189
2.186
2.179
2.176
2.168
2.160
2.158
2.151
2.147
2.140
1.093

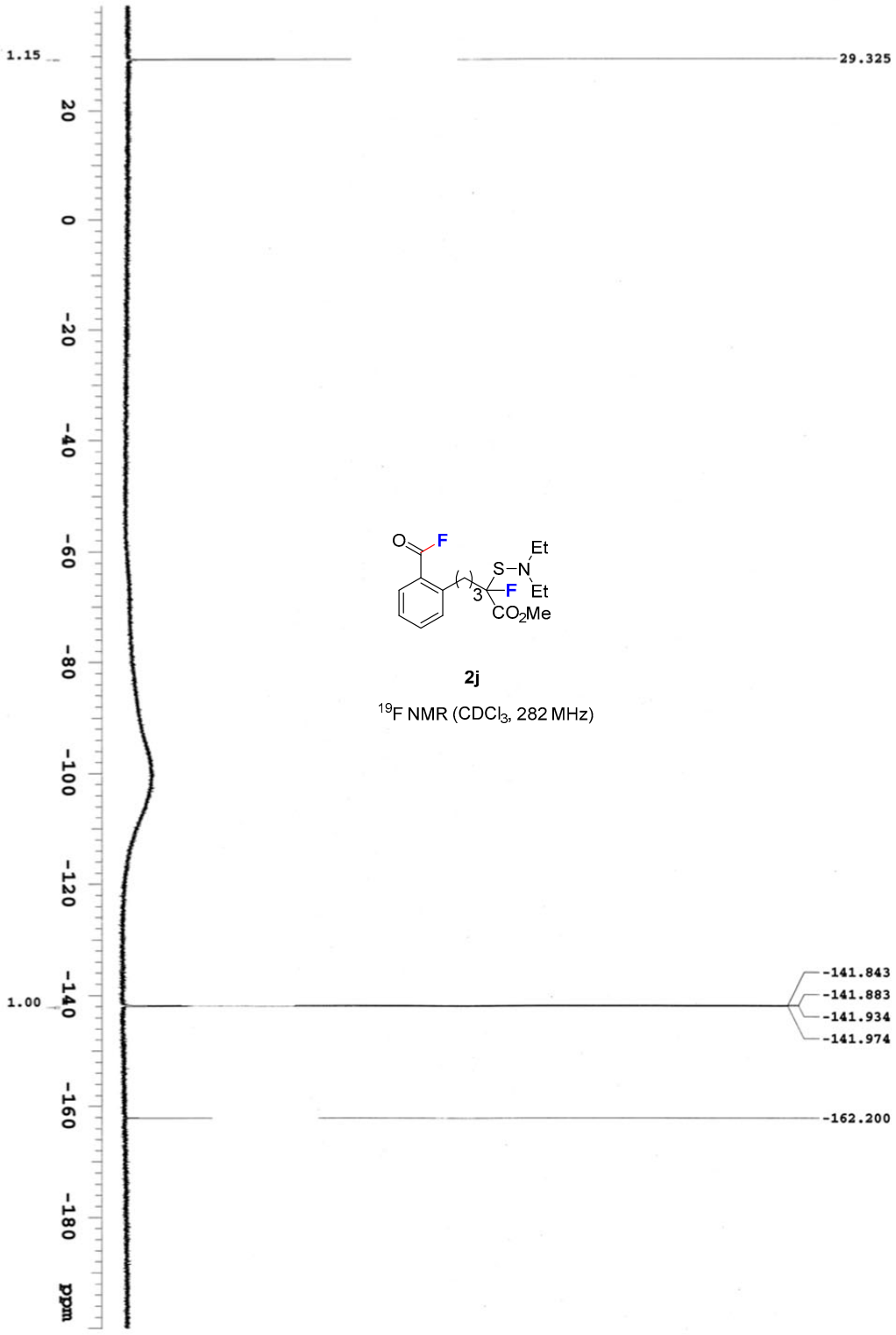


2i

^{19}F NMR ($CDCl_3$, 282 MHz)

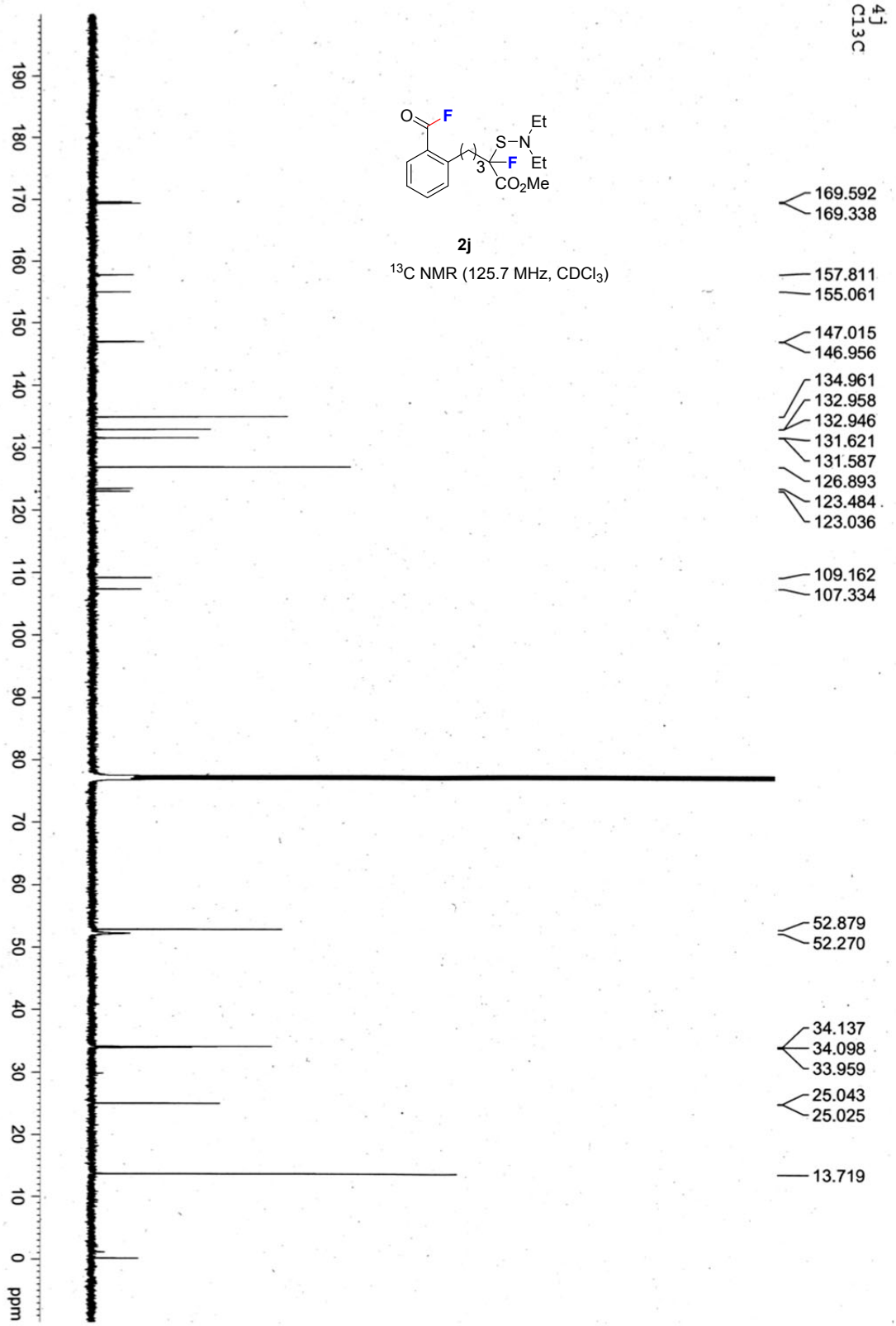

41
213C
O
F
Et
S–N
Et
F
2
CO2Me
2i
13C NMR (125.7 MHz, CDCl3)
169.200
168.941
157.687
154.936
145.638
145.578
135.075
132.914
132.904
132.367
132.333
127.247
123.680
123.230
108.699
106.867
52.784
52.265
35.113
34.938
28.916
28.890
13.743
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

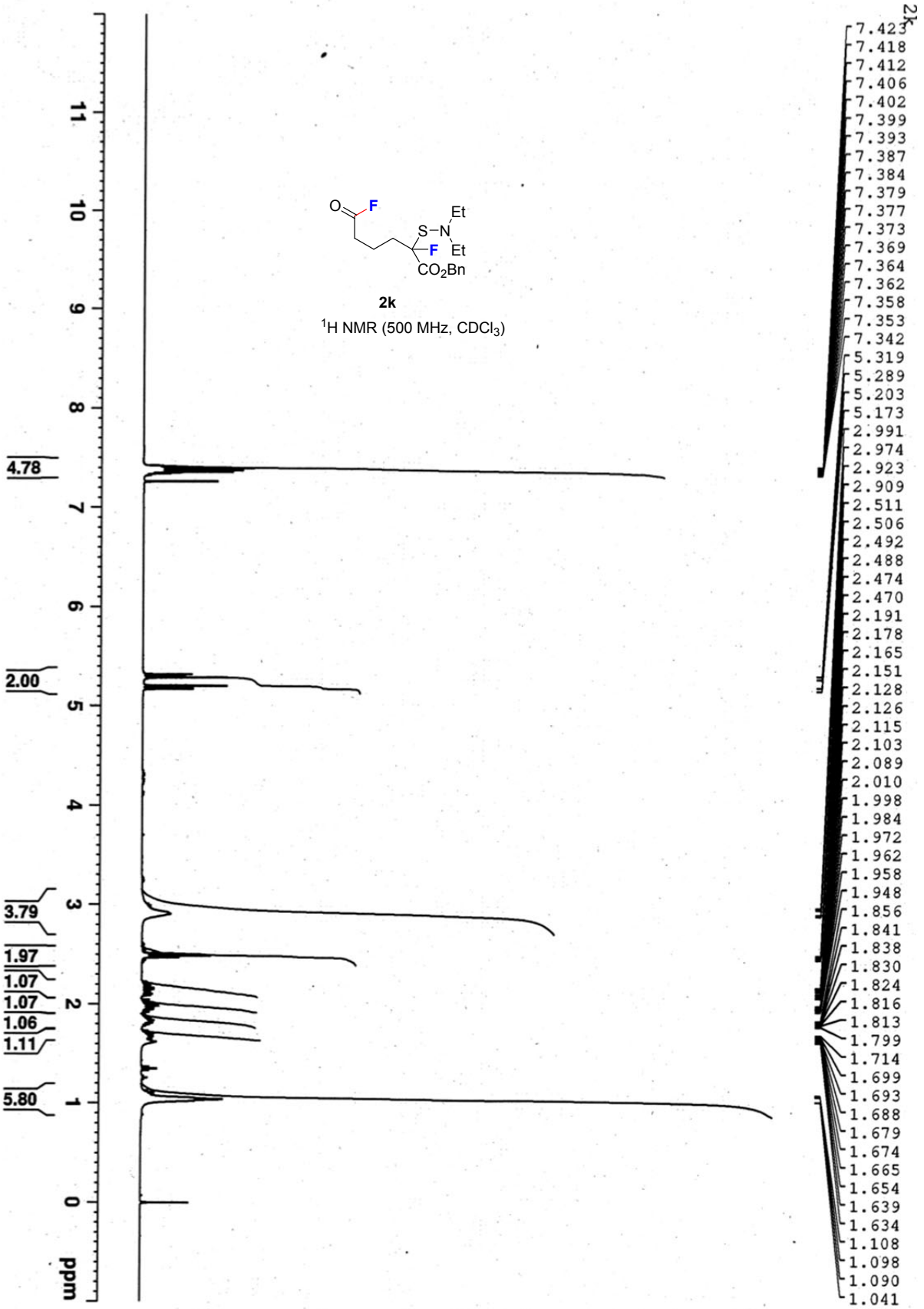

O
F
Et
S–N
Et
F
3
CO2Me
2j
1H NMR (500 MHz, CDCl3)
1.00
1.01
2.04
3.02
6.05
1.04
1.05
1.05
1.07
6.09
ppm
8.003
8.001
7.988
7.985
7.593
7.590
7.577
7.575
7.562
7.560
7.364
7.362
7.346
7.333
7.317
7.262
3.808
3.043
3.028
3.013
2.998
2.984
2.970
2.958
2.944
2.170
2.166
2.160
2.147
2.137
2.118
2.108
2.095
2.085
2.034
2.024
2.011
2.005
2.002
1.996
1.989
1.983
1.980
1.973
1.849
1.846
1.836
1.832
1.822
1.819
1.814
1.809
1.806
1.664
1.658
1.653
1.650
1.641
1.636
1.623
1.563
1.100
1.086
1.072



2j

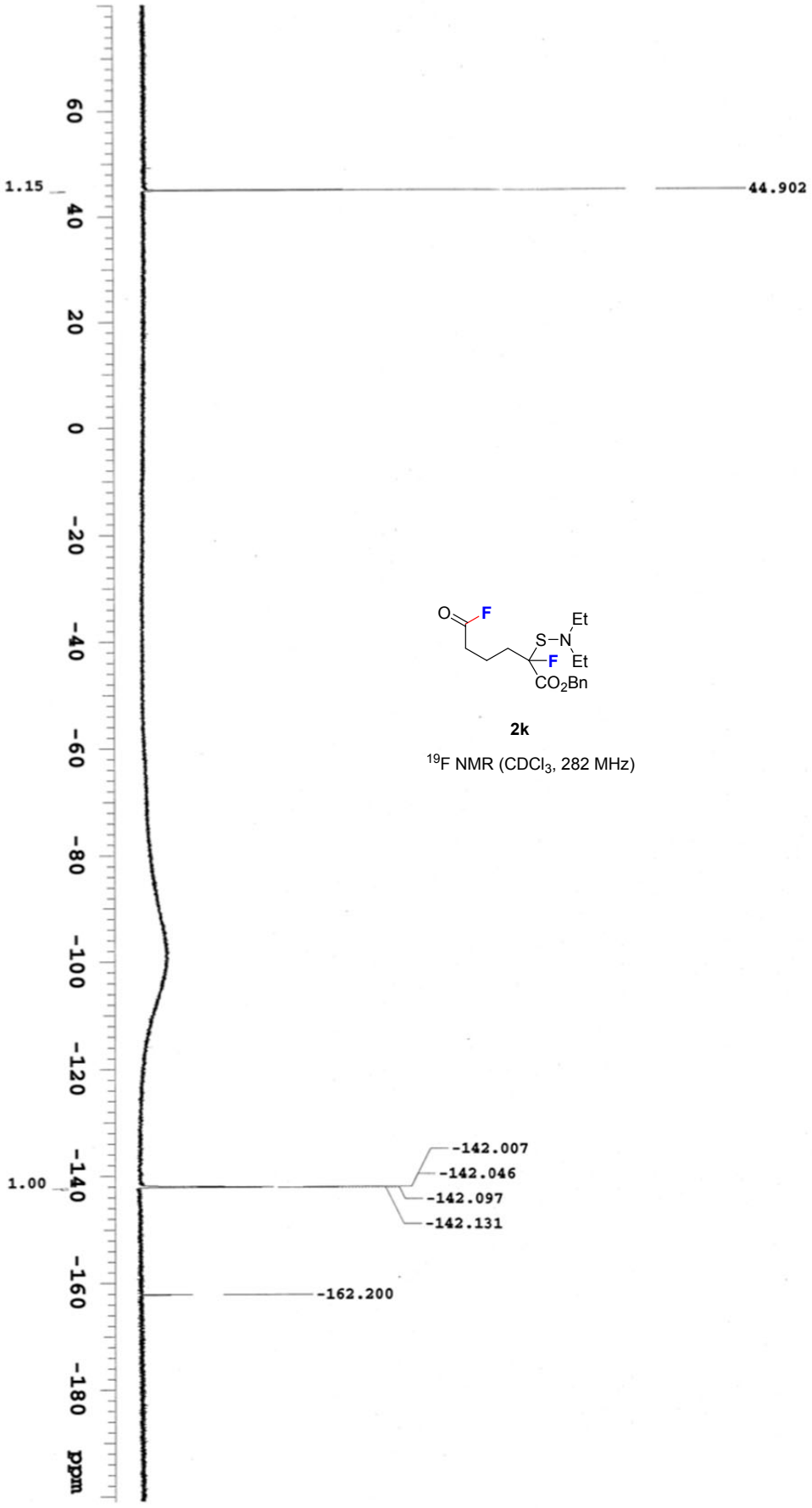
^{19}F NMR ($CDCl_3$, 282 MHz)


4j
C13C
O
F
Et
S–N
Et
F
3
CO2Me
2j
13C NMR (125.7 MHz, CDCl3)
169.592
169.338
157.811
155.061
147.015
146.956
134.961
132.958
132.946
131.621
131.587
126.893
123.484
123.036
109.162
107.334
52.879
52.270
34.137
34.098
33.959
25.043
25.025
13.719
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



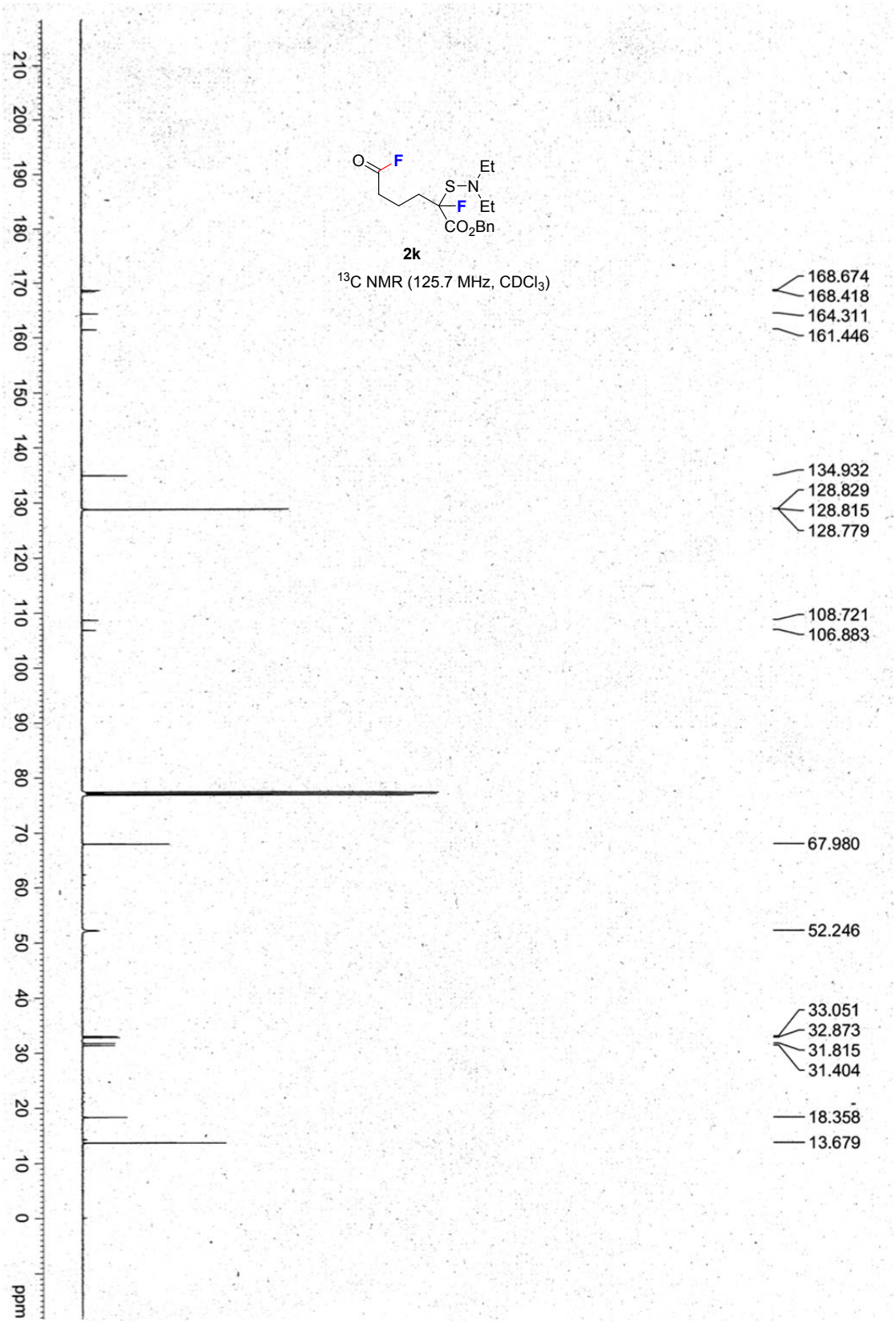
2k

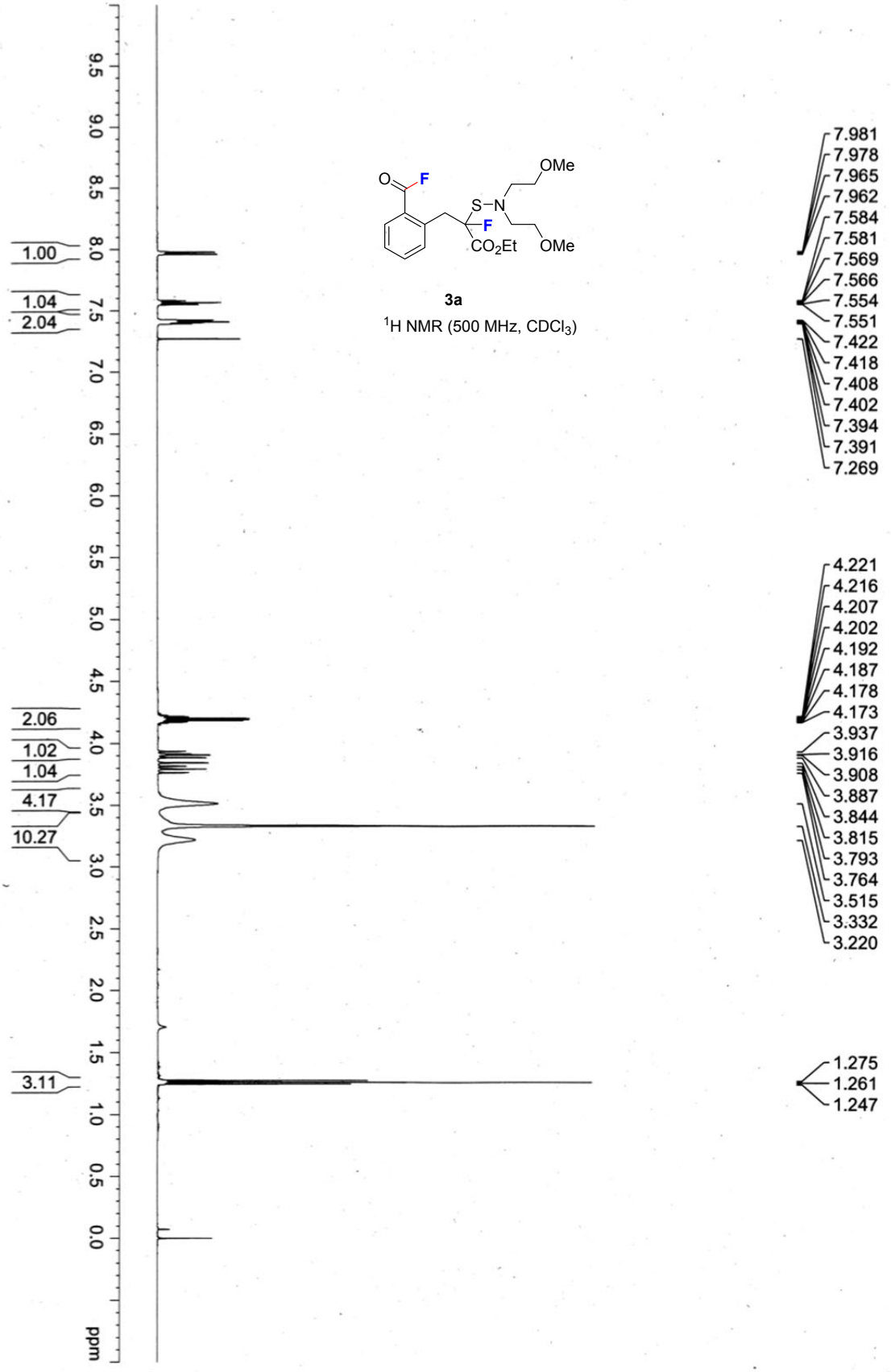
^{1}H NMR (500 MHz, $CDCl_3$)

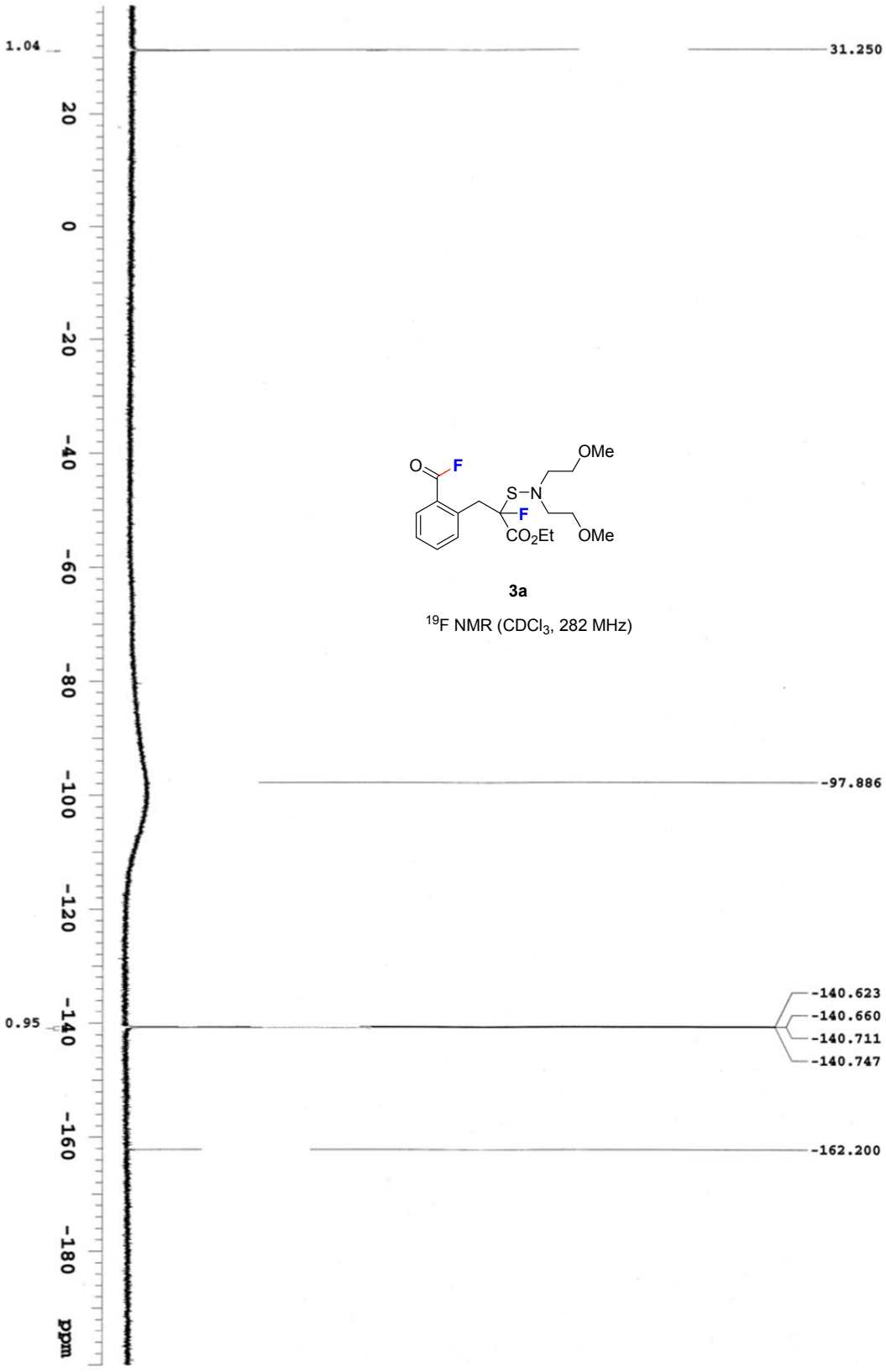


2k

^{19}F NMR ($CDCl_3$, 282 MHz)

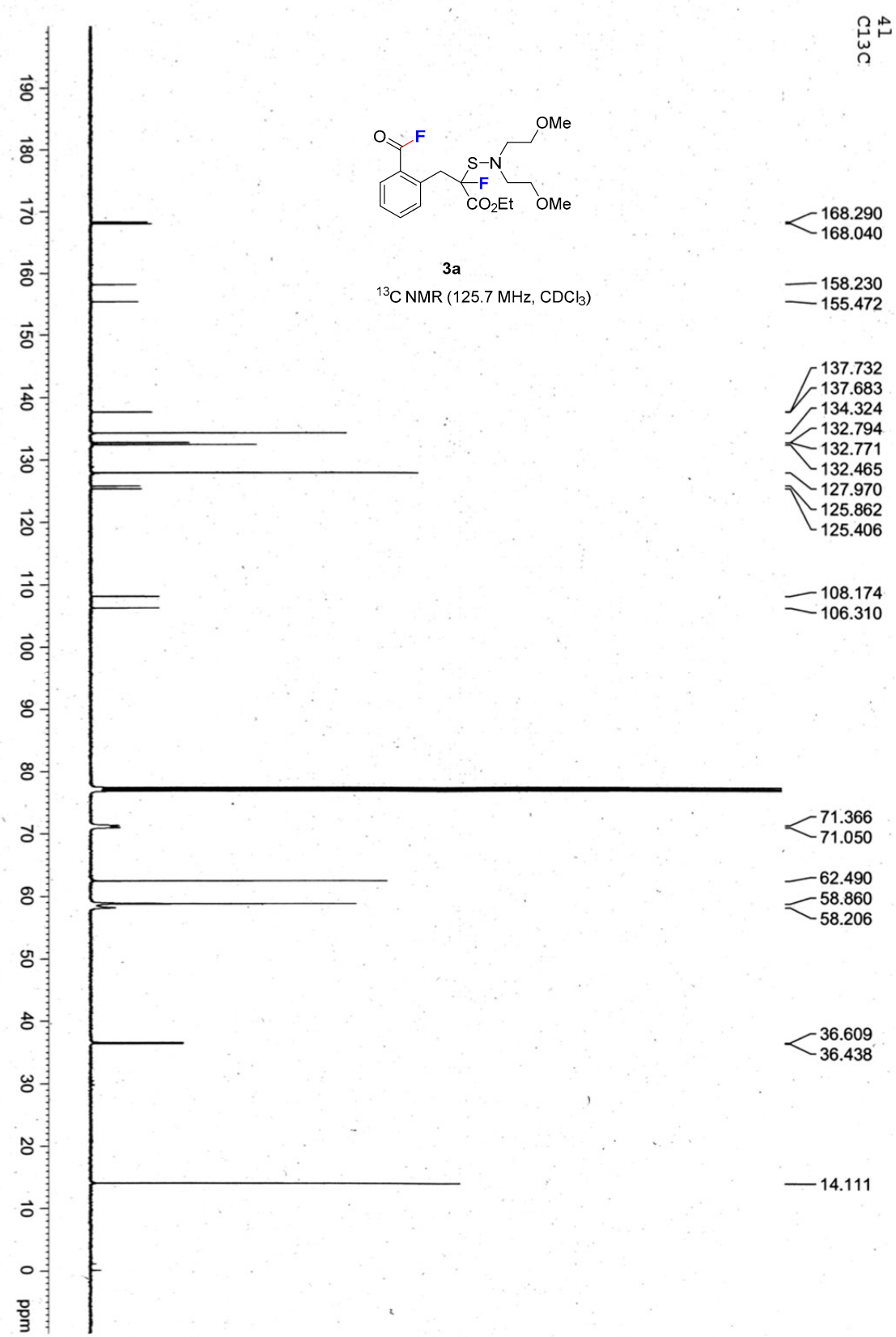

O
F
Et
S–N
F
Et
CO2Bn
2k
13C NMR (125.7 MHz, CDCl3)
168.674
168.418
164.311
161.446
134.932
128.829
128.815
128.779
108.721
106.883
67.980
52.246
33.051
32.873
31.815
31.404
18.358
13.679
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

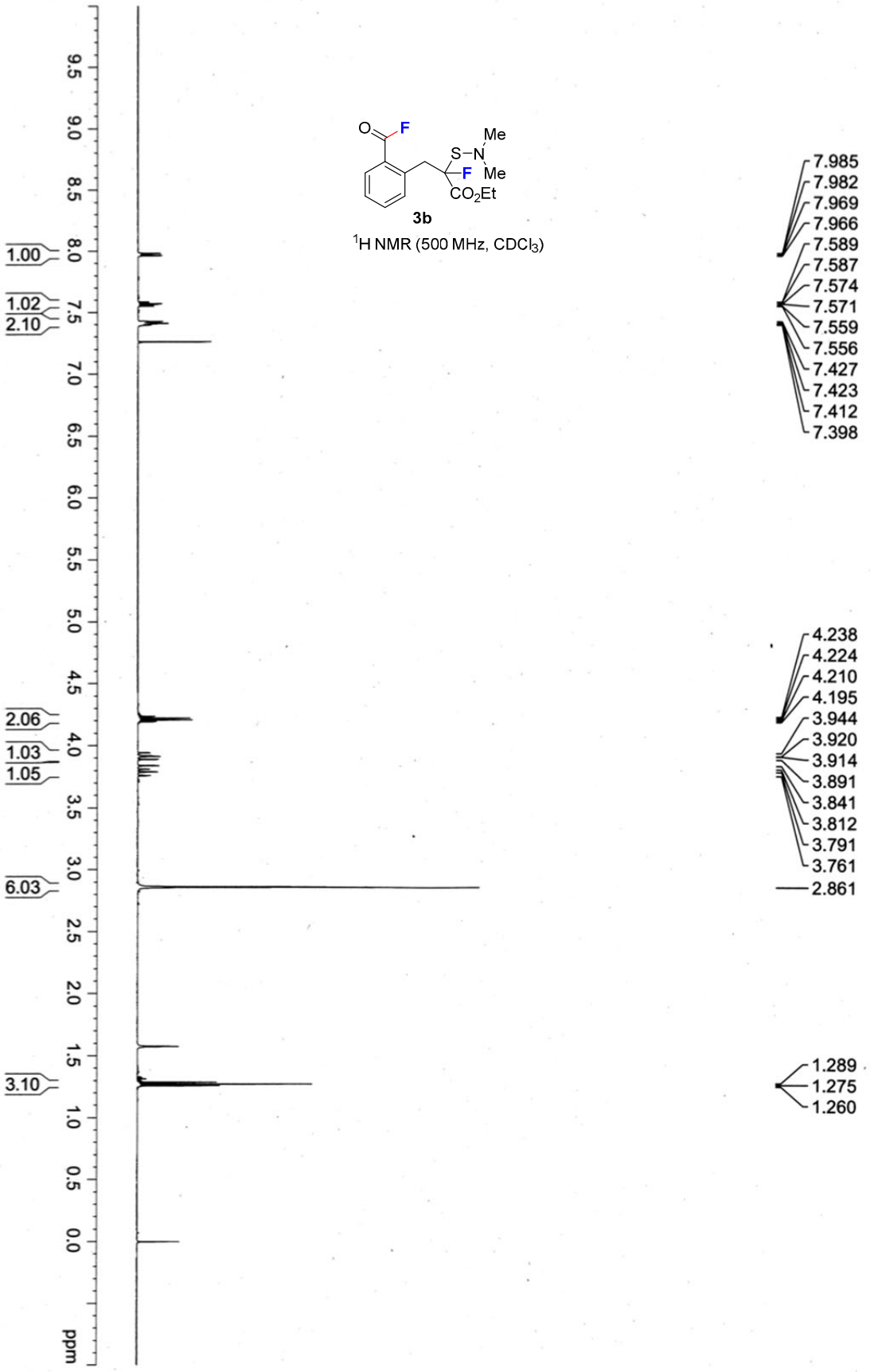

O
F
S–N
F
CO2Et
OMe
OMe
3a
1H NMR (500 MHz, CDCl3)
1.00
1.04
2.04
2.06
1.02
1.04
4.17
10.27
3.11
7.981
7.978
7.965
7.962
7.584
7.581
7.569
7.566
7.554
7.551
7.422
7.418
7.408
7.402
7.394
7.391
7.269
4.221
4.216
4.207
4.202
4.192
4.187
4.178
4.173
3.937
3.916
3.908
3.887
3.844
3.815
3.793
3.764
3.515
3.332
3.220
1.275
1.261
1.247
ppm

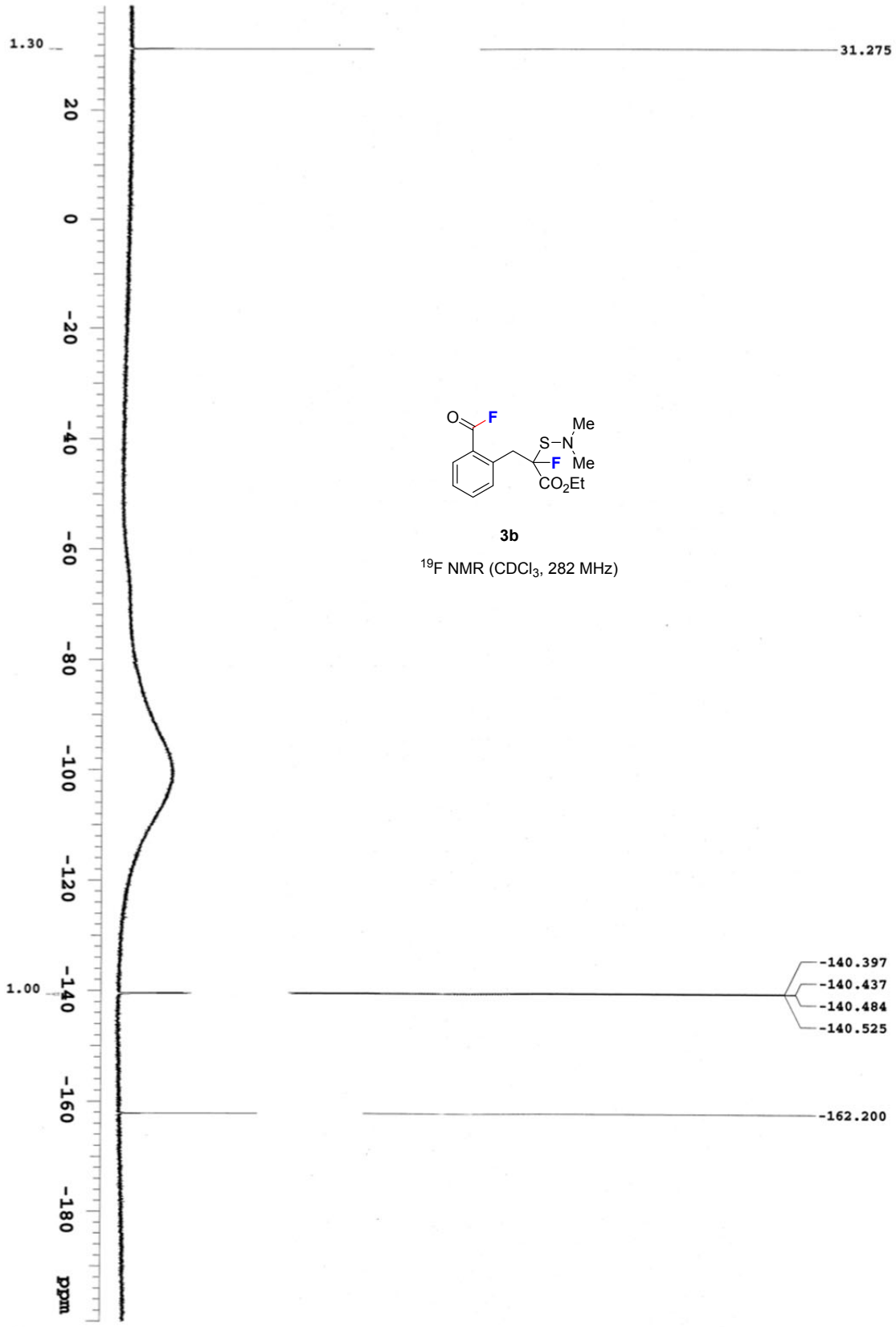


3a

^{19}F NMR ($CDCl_3$, 282 MHz)

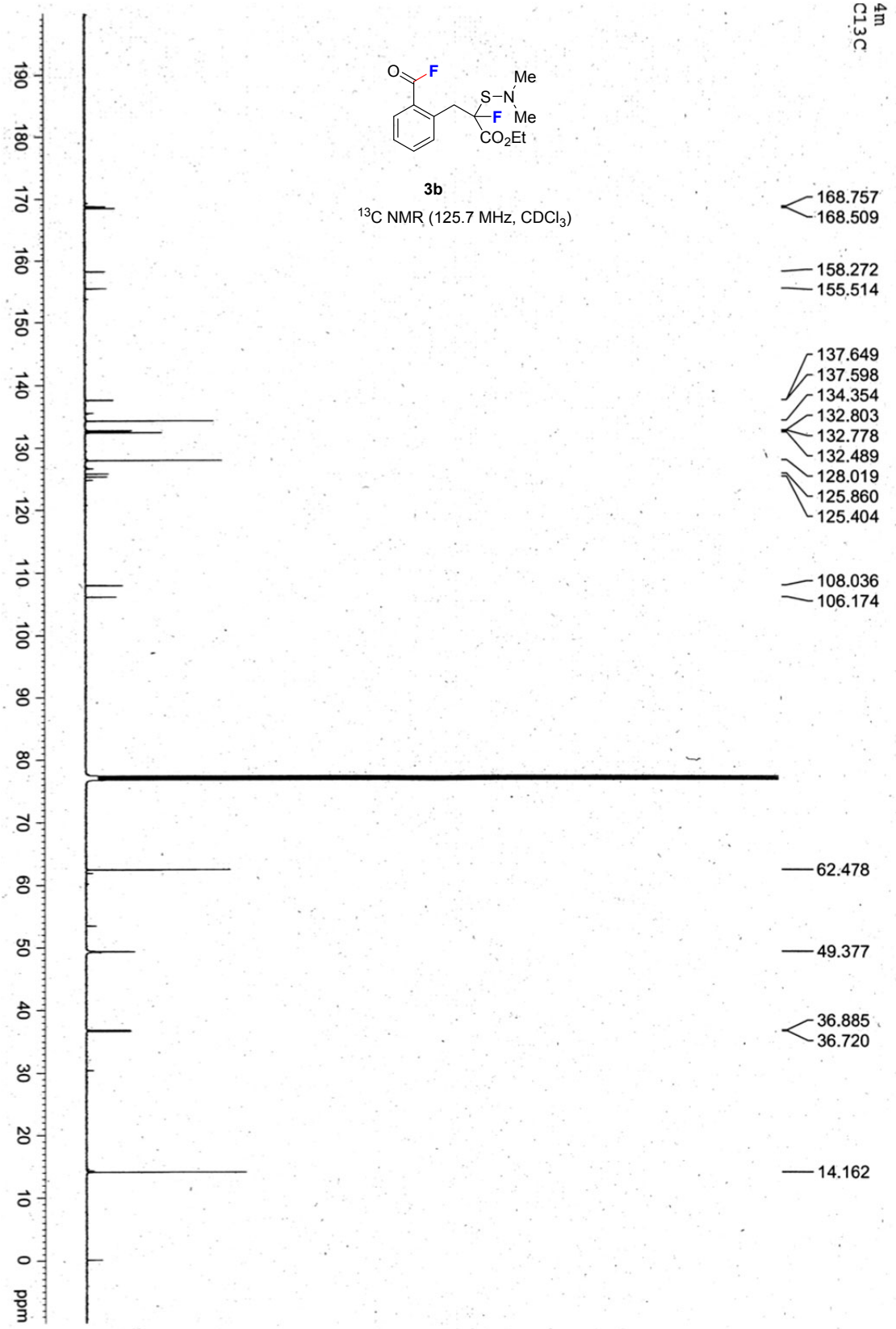

41
C13C
O
F
S–N
F
CO2Et
OMe
OMe
3a
13C NMR (125.7 MHz, CDCl3)
168.290
168.040
158.230
155.472
137.732
137.683
134.324
132.794
132.771
132.465
127.970
125.862
125.406
108.174
106.310
71.366
71.050
62.490
58.860
58.206
36.609
36.438
14.111
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

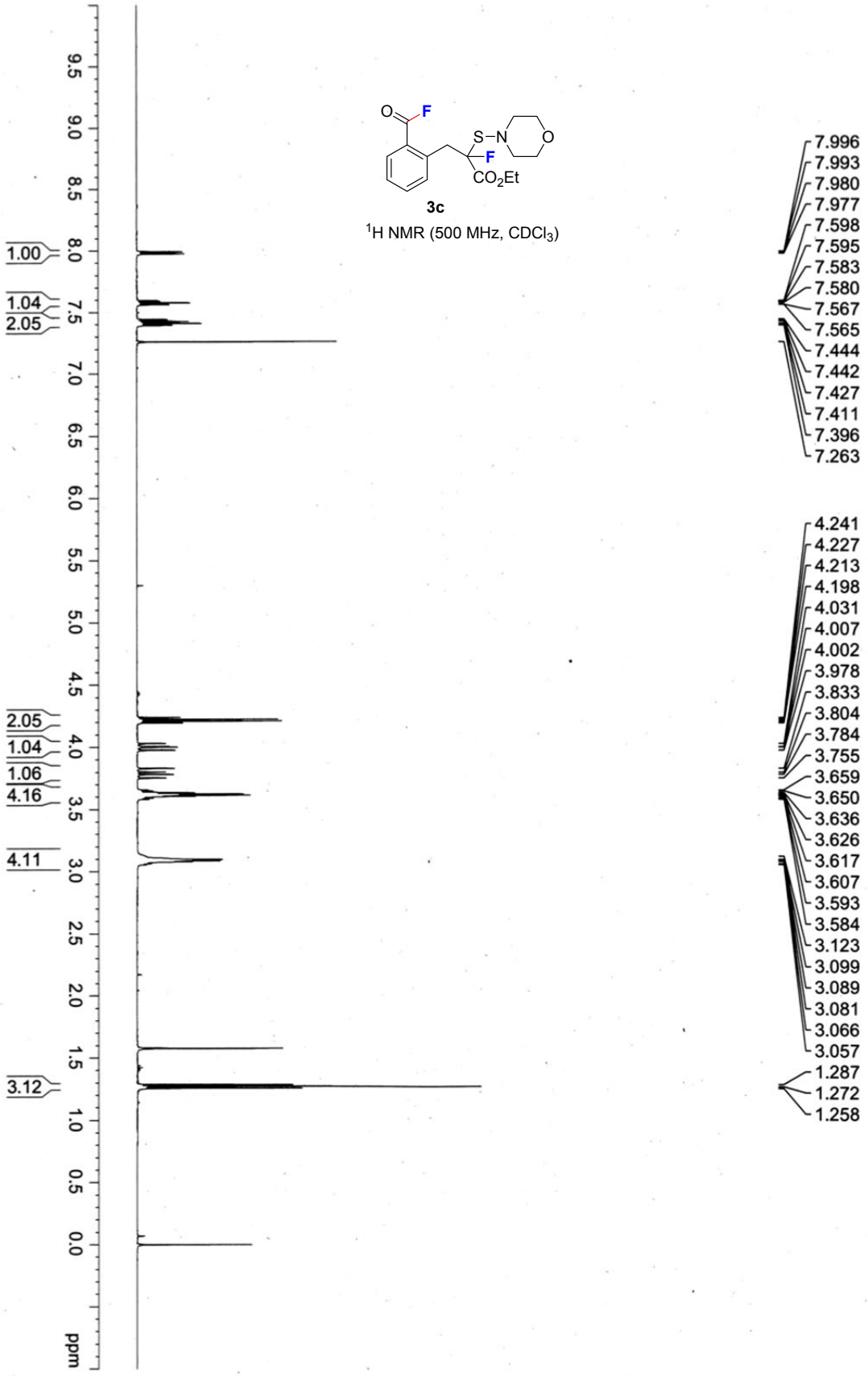

3b
1H NMR (500 MHz, CDCl3)
1.00
1.02
2.10
2.06
1.03
1.05
6.03
3.10
7.985
7.982
7.969
7.966
7.589
7.587
7.574
7.571
7.559
7.556
7.427
7.423
7.412
7.398
4.238
4.224
4.210
4.195
3.944
3.920
3.914
3.891
3.841
3.812
3.791
3.761
2.861
1.289
1.275
1.260
ppm

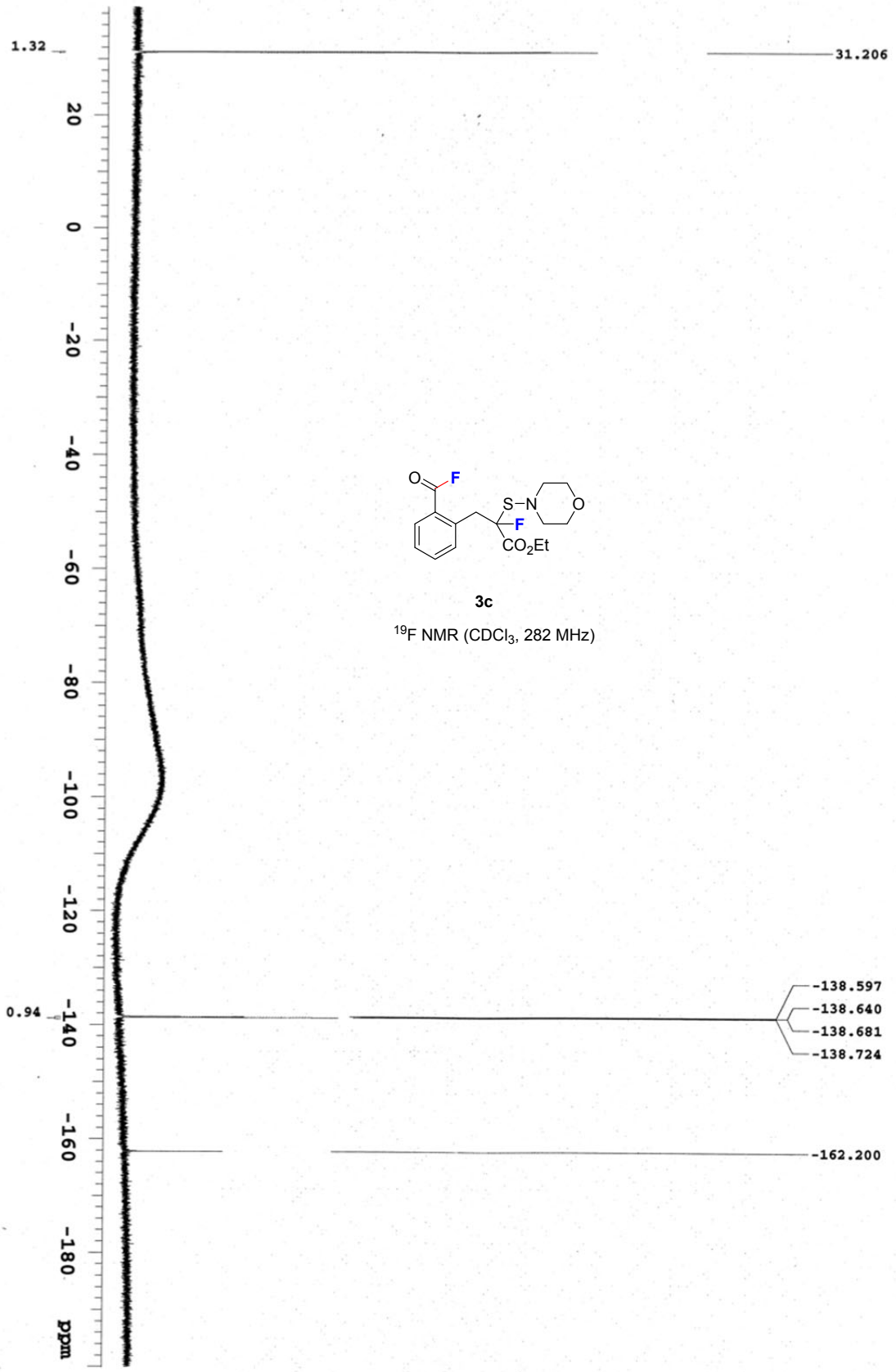


3b

^{19}F NMR ($CDCl_3$, 282 MHz)

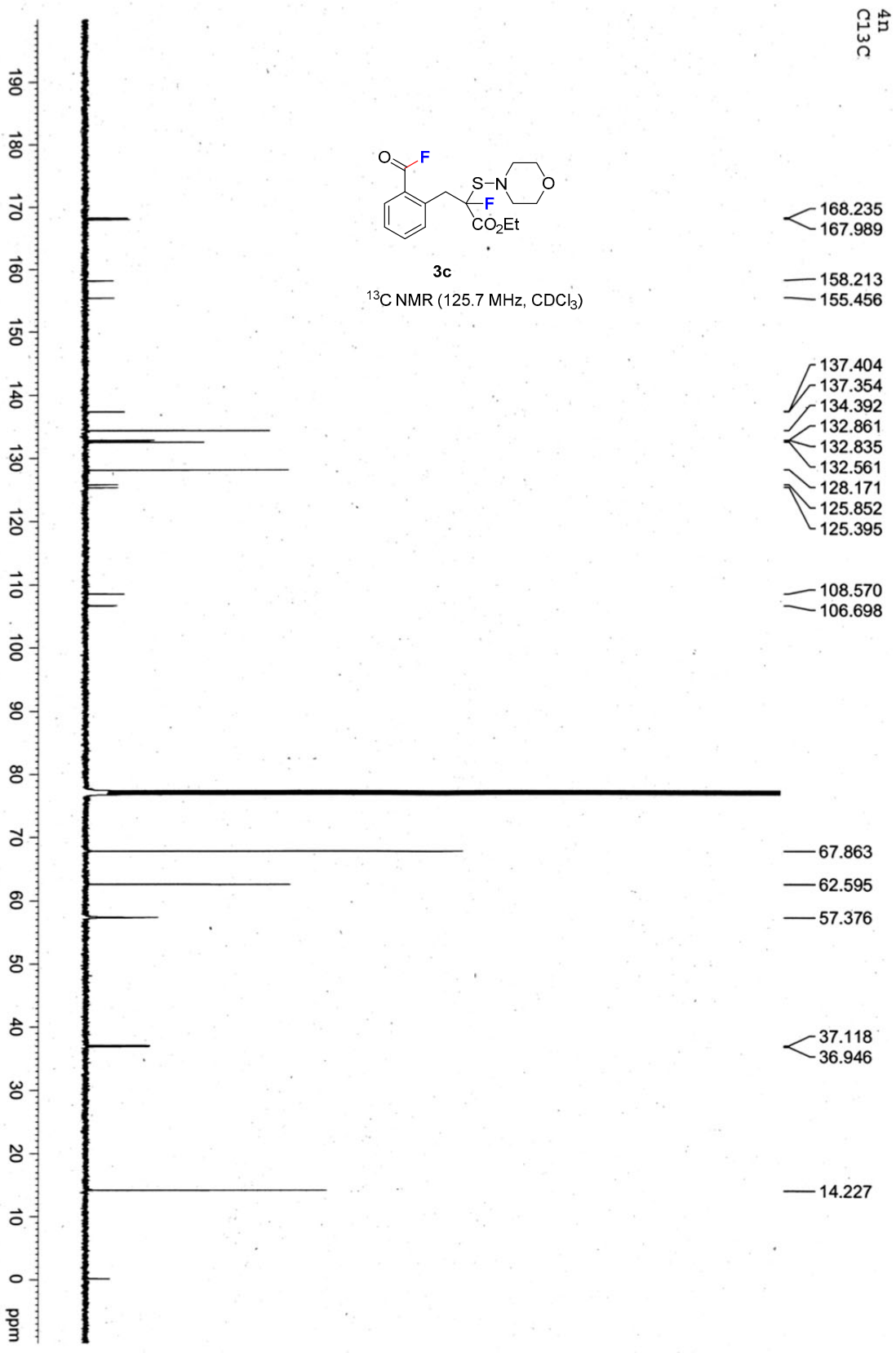

4m
C13C
O
F
Me
S–N
F
Me
CO2Et
3b
13C NMR (125.7 MHz, CDCl3)
168.757
168.509
158.272
155.514
137.649
137.598
134.354
132.803
132.778
132.489
128.019
125.860
125.404
108.036
106.174
62.478
49.377
36.885
36.720
14.162
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

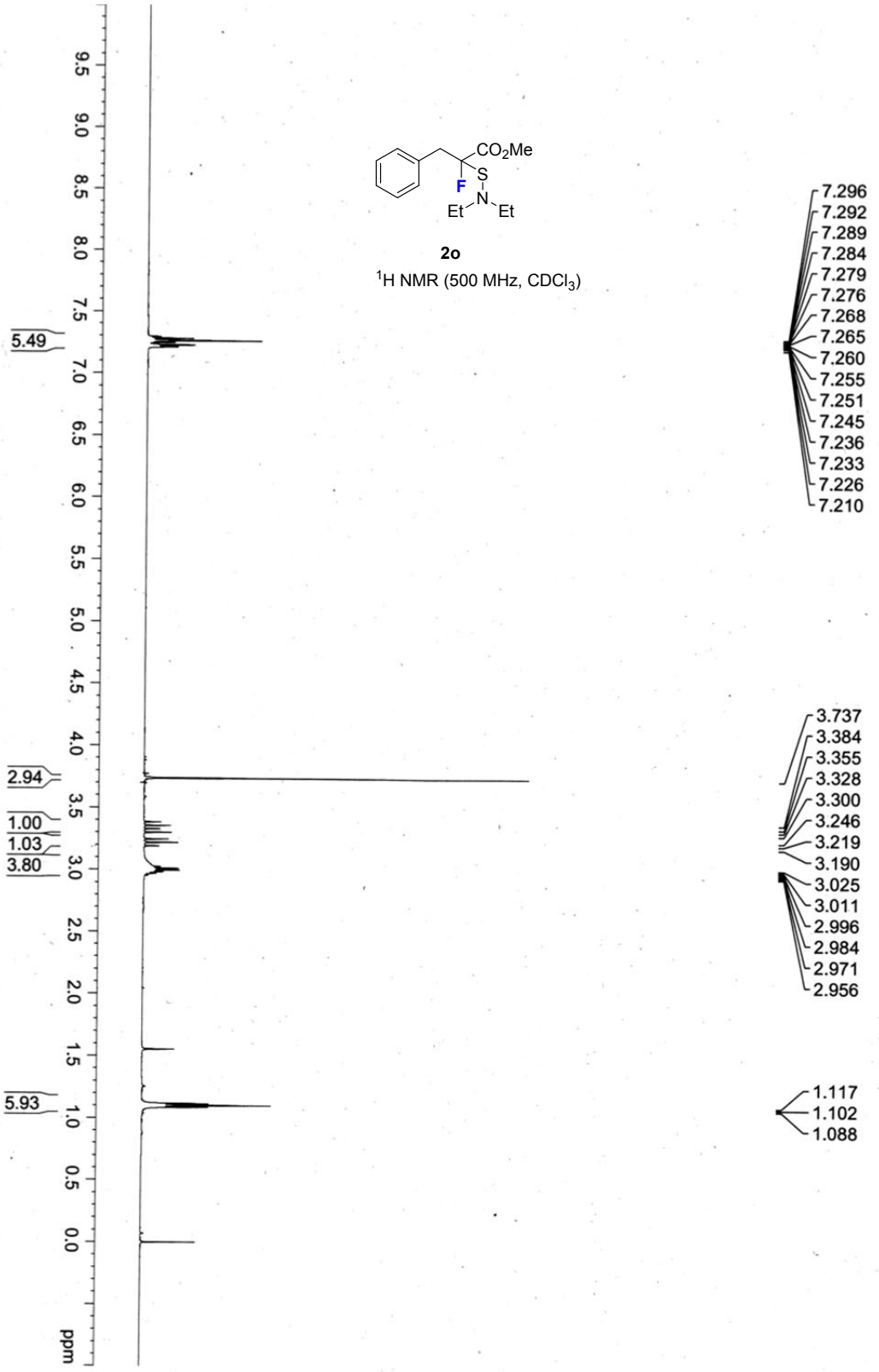

O
F
S–N
O
F
CO2Et
3c
1H NMR (500 MHz, CDCl3)
1.00
1.04
2.05
2.05
1.04
1.06
4.16
4.11
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
7.996
7.993
7.980
7.977
7.598
7.595
7.583
7.580
7.567
7.565
7.444
7.442
7.427
7.411
7.396
7.263
4.241
4.227
4.213
4.198
4.031
4.007
4.002
3.978
3.833
3.804
3.784
3.755
3.659
3.650
3.636
3.626
3.617
3.607
3.593
3.584
3.123
3.099
3.089
3.081
3.066
3.057
1.287
1.272
1.258

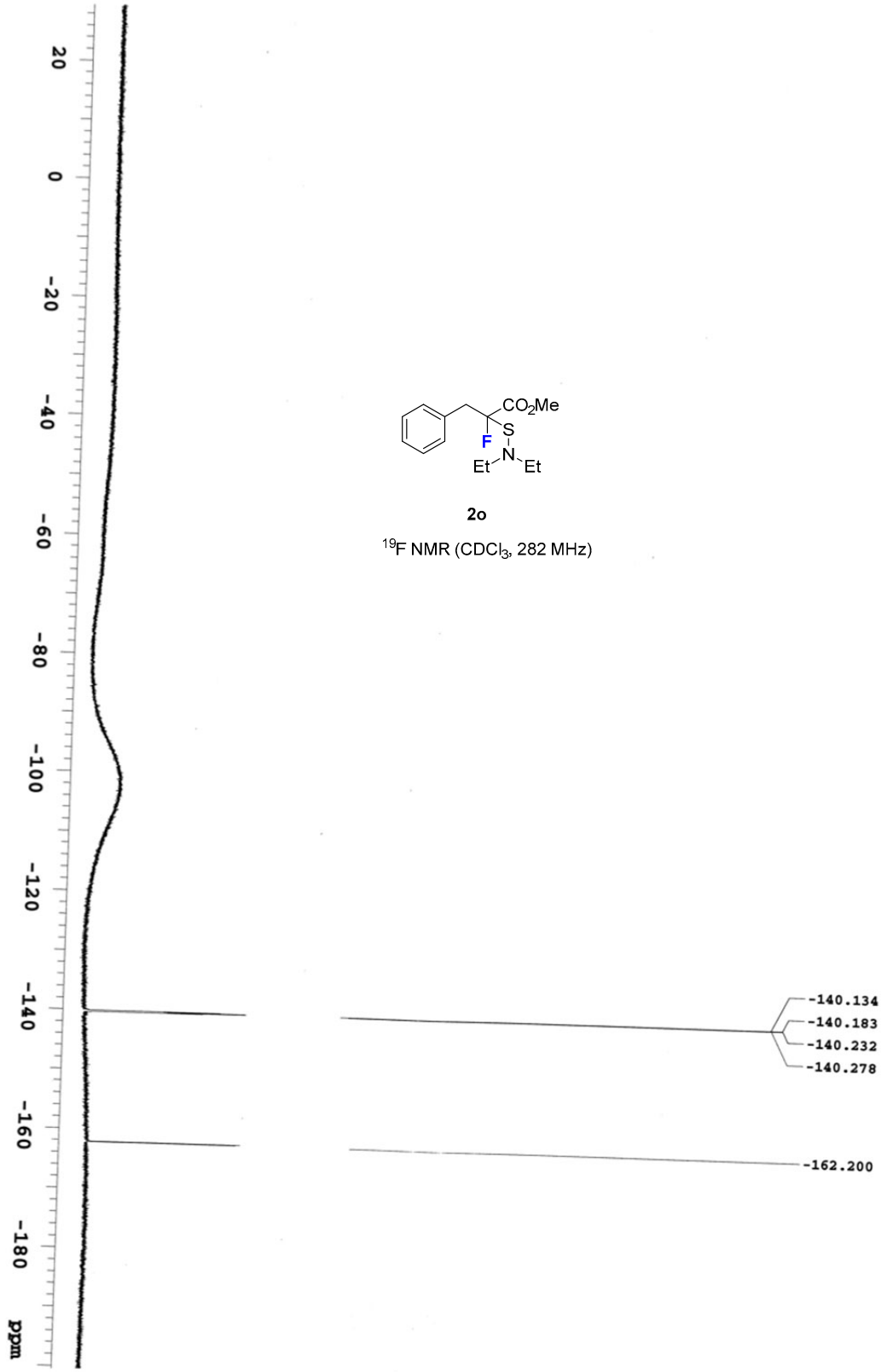


3c

^{19}F NMR ($CDCl_3$, 282 MHz)

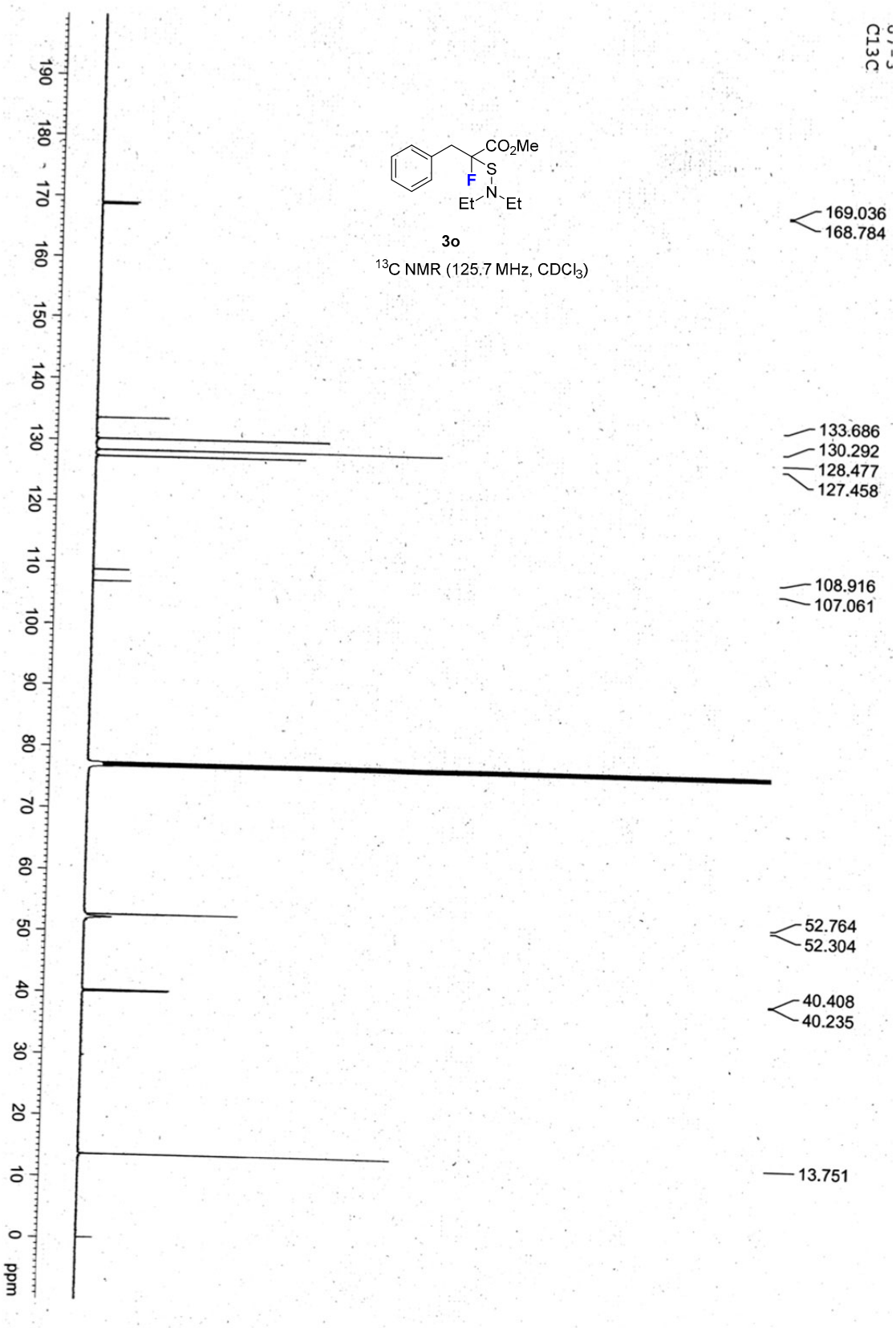

4n
C13C
O
F
S–N
O
F
CO2Et
3c
13C NMR (125.7 MHz, CDCl3)
168.235
167.989
158.213
155.456
137.404
137.354
134.392
132.861
132.835
132.561
128.171
125.852
125.395
108.570
106.698
67.863
62.595
57.376
37.118
36.946
14.227
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CO2Me
S
F
N
Et
Et
2o
1H NMR (500 MHz, CDCl3)
7.296
7.292
7.289
7.284
7.279
7.276
7.268
7.265
7.260
7.255
7.251
7.245
7.236
7.233
7.226
7.210
3.737
3.384
3.355
3.328
3.300
3.246
3.219
3.190
3.025
3.011
2.996
2.984
2.971
2.956
1.117
1.102
1.088
5.49
2.94
1.00
1.03
3.80
5.93
ppm



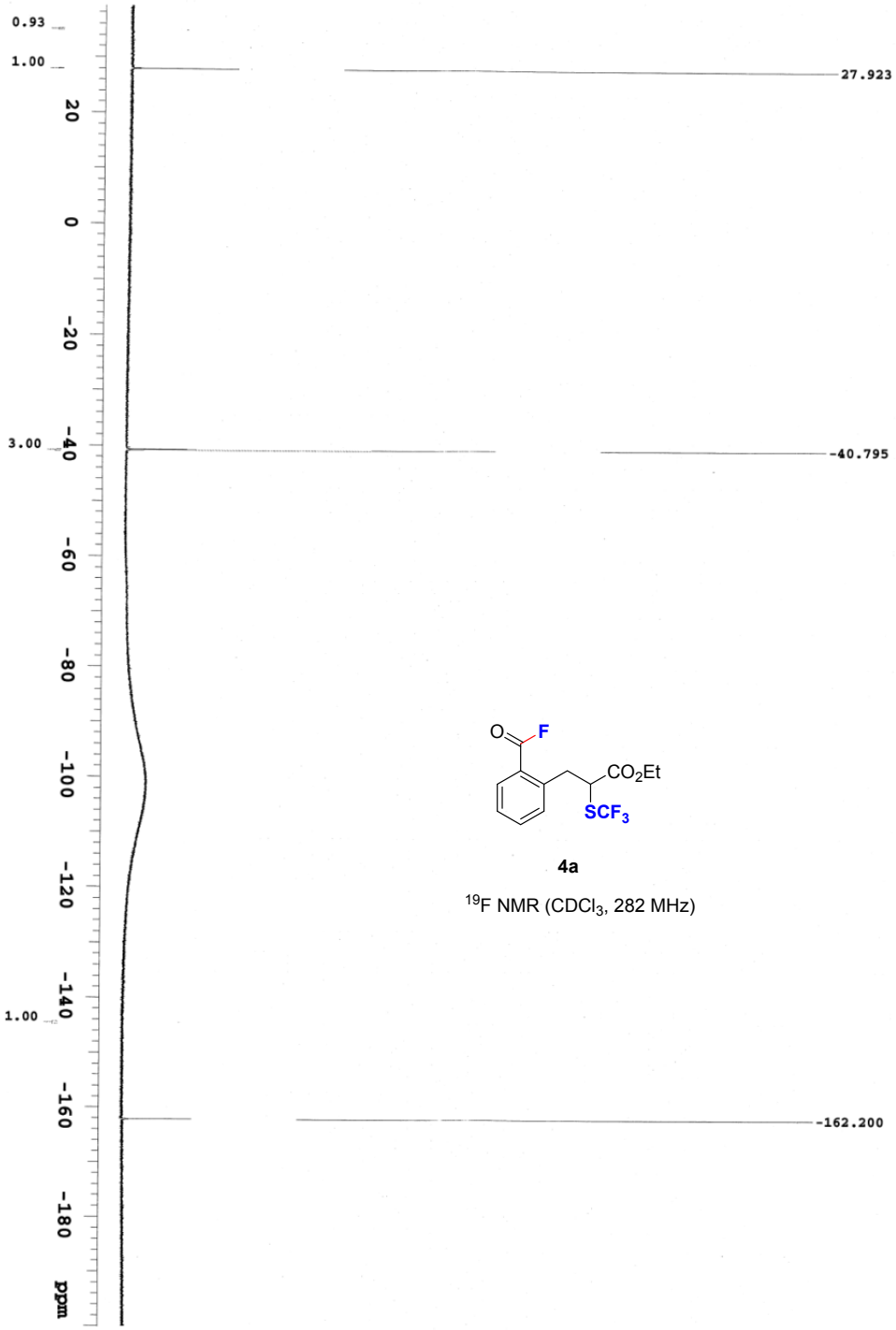
2o

^{19}F NMR ($CDCl_3$, 282 MHz)


C13C
CO2Me
S
F
N
Et
Et
3o
13C NMR (125.7 MHz, CDCl3)
169.036
168.784
133.686
130.292
128.477
127.458
108.916
107.061
52.764
52.304
40.408
40.235
13.751
ppm

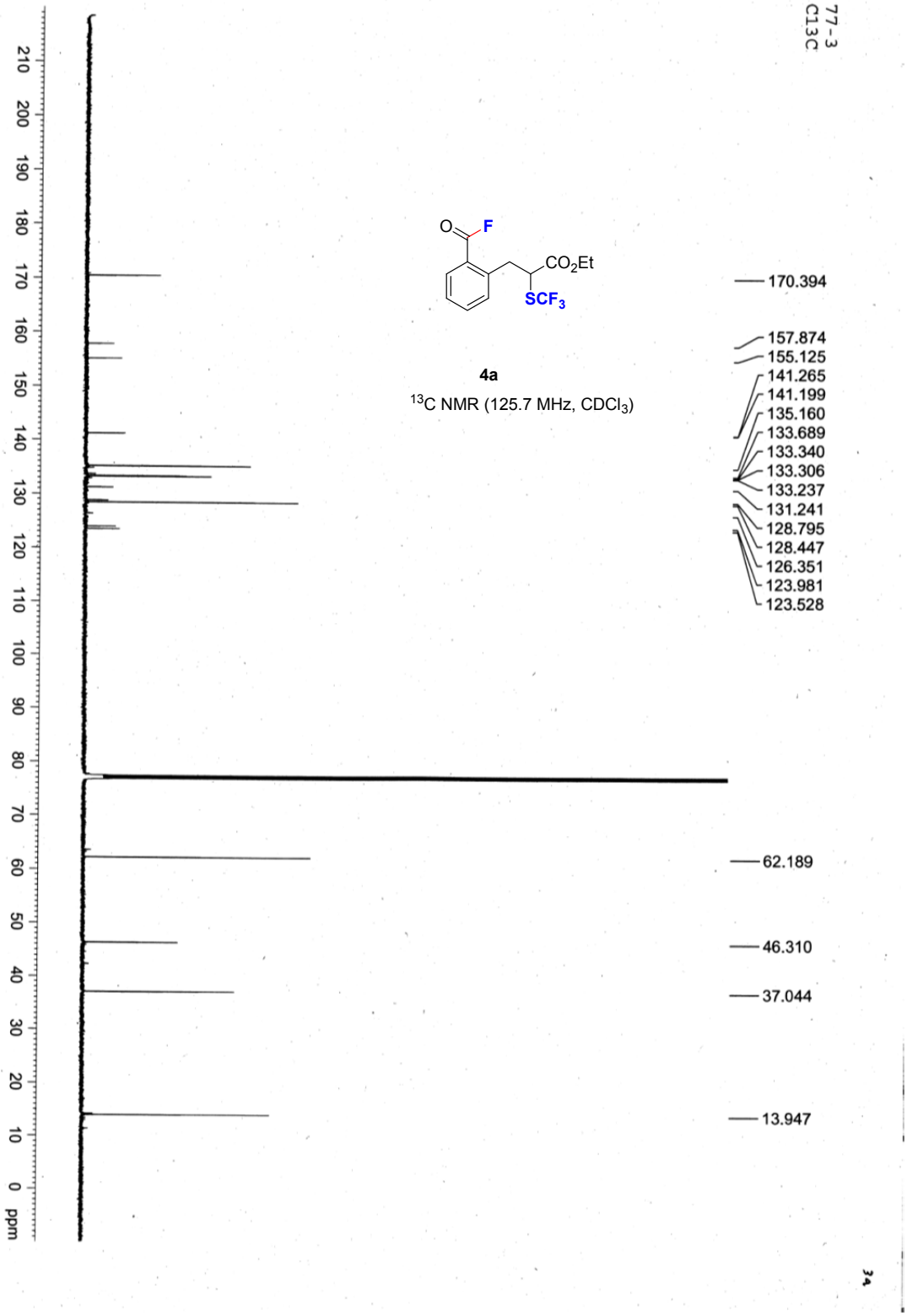
21. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for doubly fluoro-functionalization compounds 4a—4o (Table 2)

77-3
1H CDCl3 (
O
F
CO2Et
SCF3
4a
1H NMR (500 MHz, CDCl3)
8.010
8.008
7.995
7.992
7.575
7.572
7.560
7.557
7.545
7.542
7.409
7.406
7.393
7.391
7.378
7.376
7.307
7.292
4.106
4.096
4.092
4.085
4.081
4.078
4.070
4.064
4.056
4.054
4.042
4.039
4.032
4.025
4.018
4.011
4.003
3.989
3.557
3.543
3.530
3.516
3.494
3.476
3.467
3.449
1.109
1.094
1.080
1.00
1.06
1.10
1.01
2.03
1.04
2.07
3.06
ppm



4a

^{19}F NMR ($CDCl_3$, 282 MHz)


77-3
C13C
O
F
CO2Et
SCF3
4a
13C NMR (125.7 MHz, CDCl3)
170.394
157.874
155.125
141.265
141.199
135.160
133.689
133.340
133.306
133.237
131.241
128.795
128.447
126.351
123.981
123.528
62.189
46.310
37.044
13.947
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

79-4
1H CDCl3 (

4b

^{1}H NMR (500 MHz, $CDCl_3$)

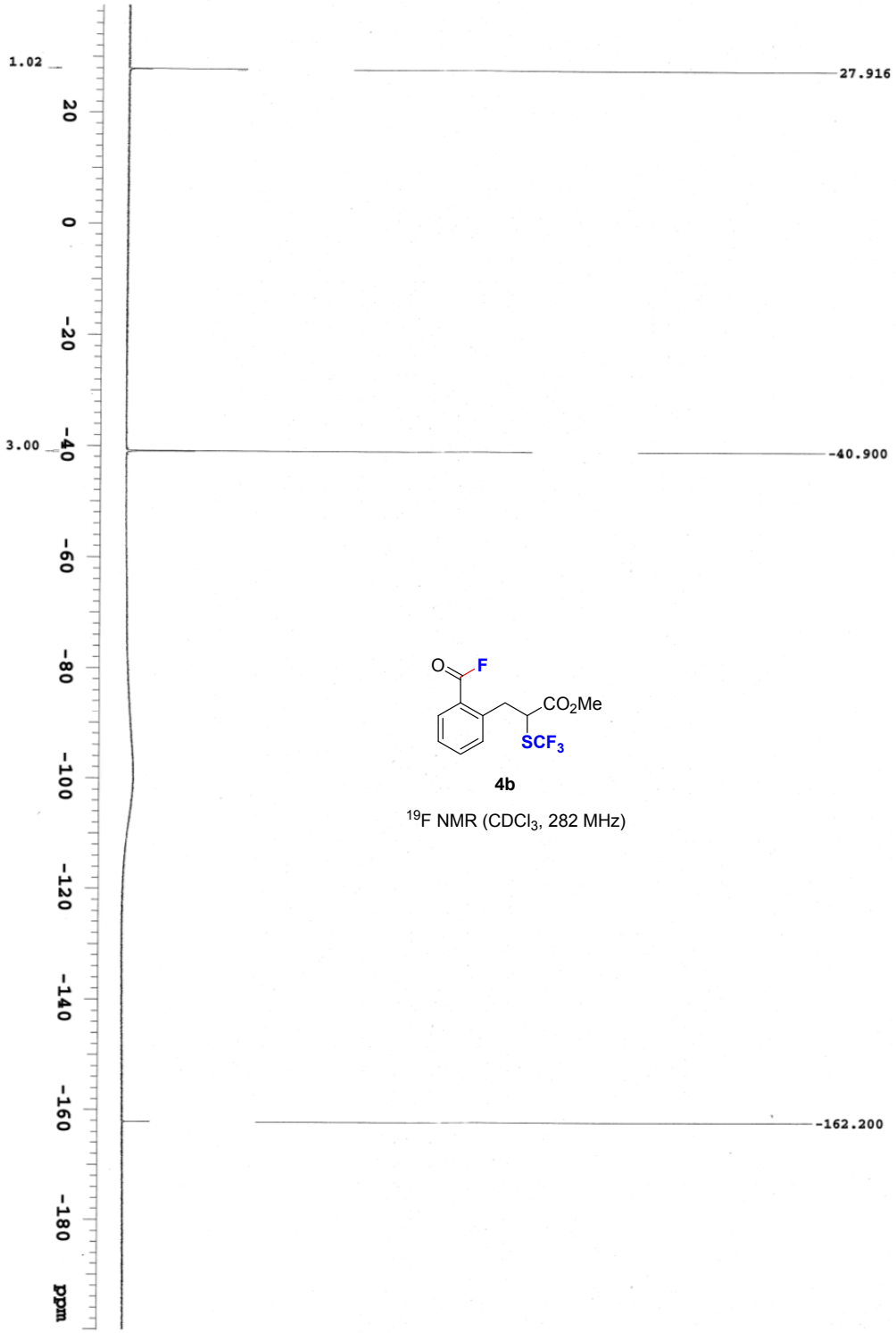
8.011
8.009
7.996
7.993
7.583
7.580
7.568
7.565
7.553
7.550
7.413
7.410
7.397
7.395
7.382
7.380
7.303
7.287

4.117
4.101
4.100
4.085
3.611
3.546
3.531
3.519
3.512
3.504
3.495
3.485

1.00
1.03
1.03
1.01
1.00
3.02
1.97

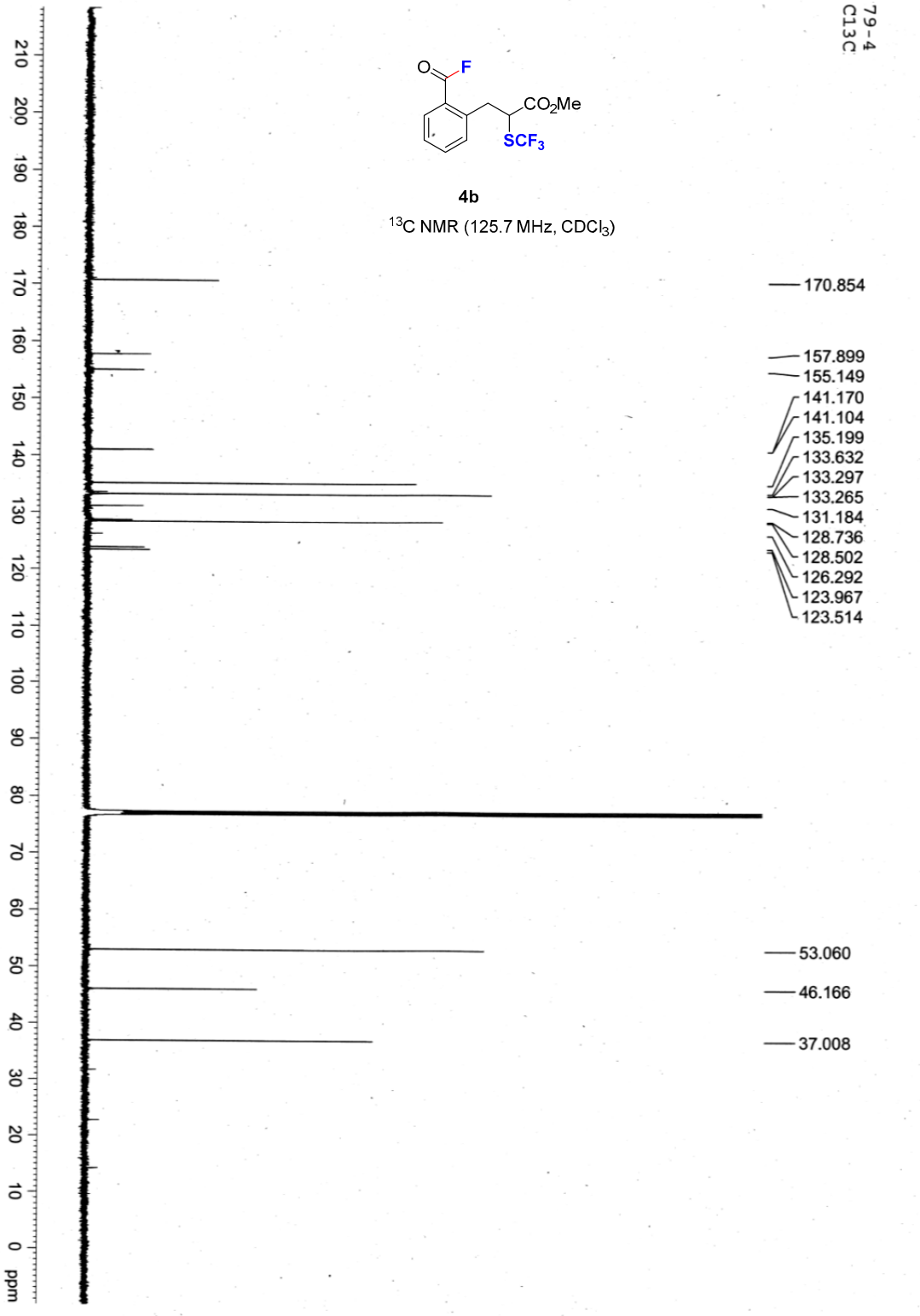
11 10 9 8 7 6 5 4 3 2 1 0 ppm

66
34



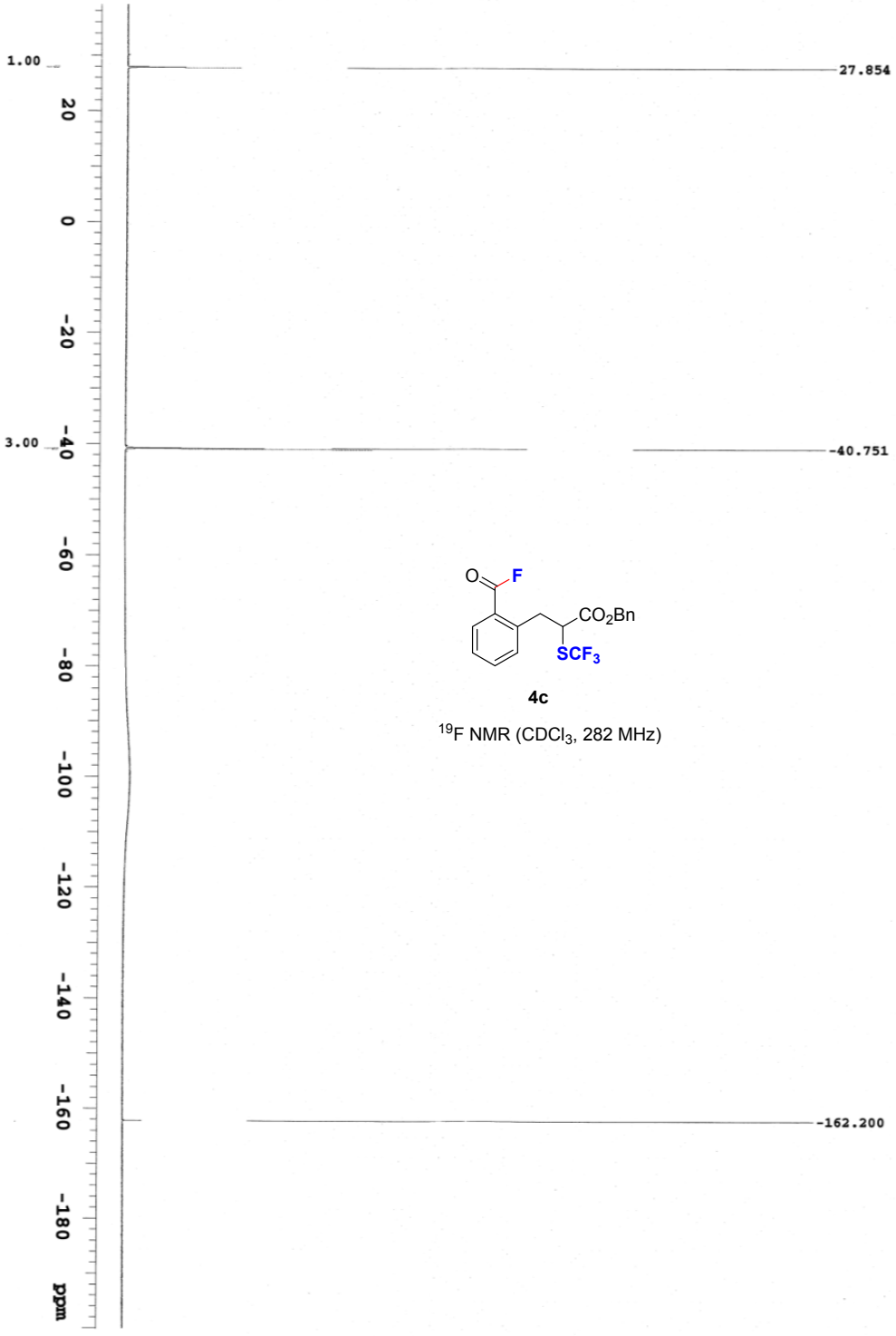
4b

^{19}F NMR ($CDCl_3$, 282 MHz)


79-4
C13C
O
F
CO2Me
SCF3
4b
13C NMR (125.7 MHz, CDCl3)
170.854
157.899
155.149
141.170
141.104
135.199
133.632
133.297
133.265
131.184
128.736
128.502
126.292
123.967
123.514
53.060
46.166
37.008
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7b

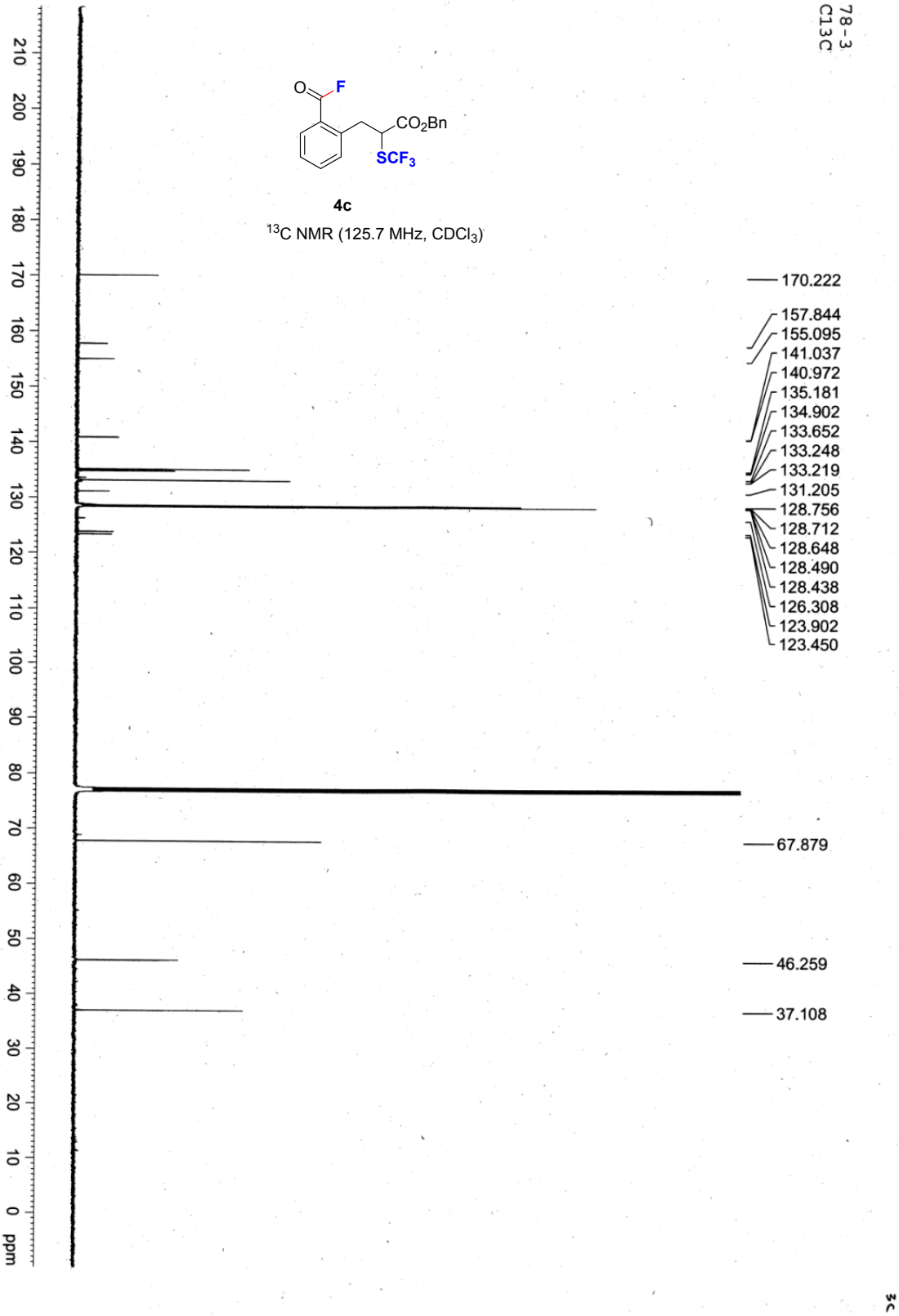
4c

^{1}H NMR (500 MHz, $CDCl_3$)



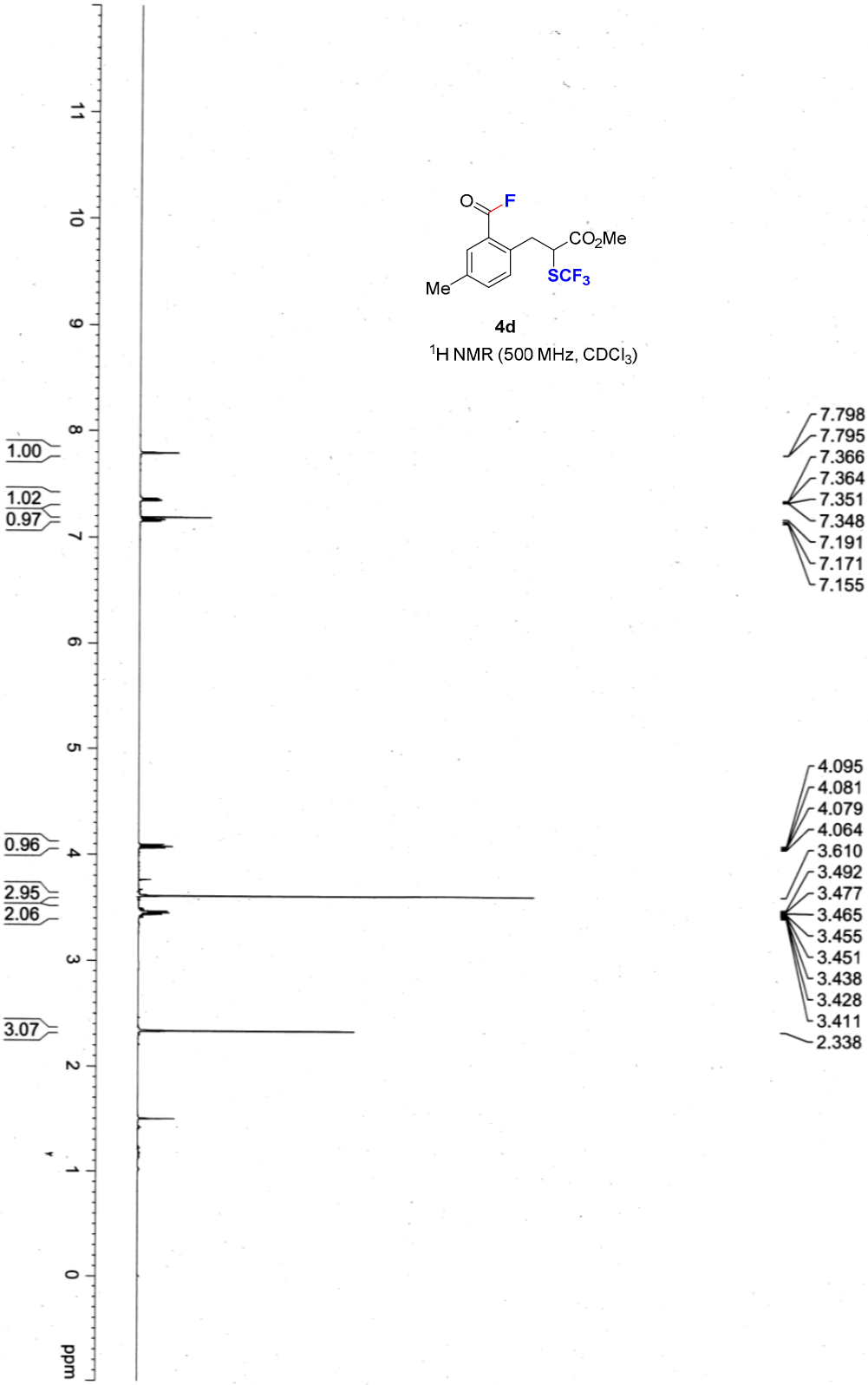
4c

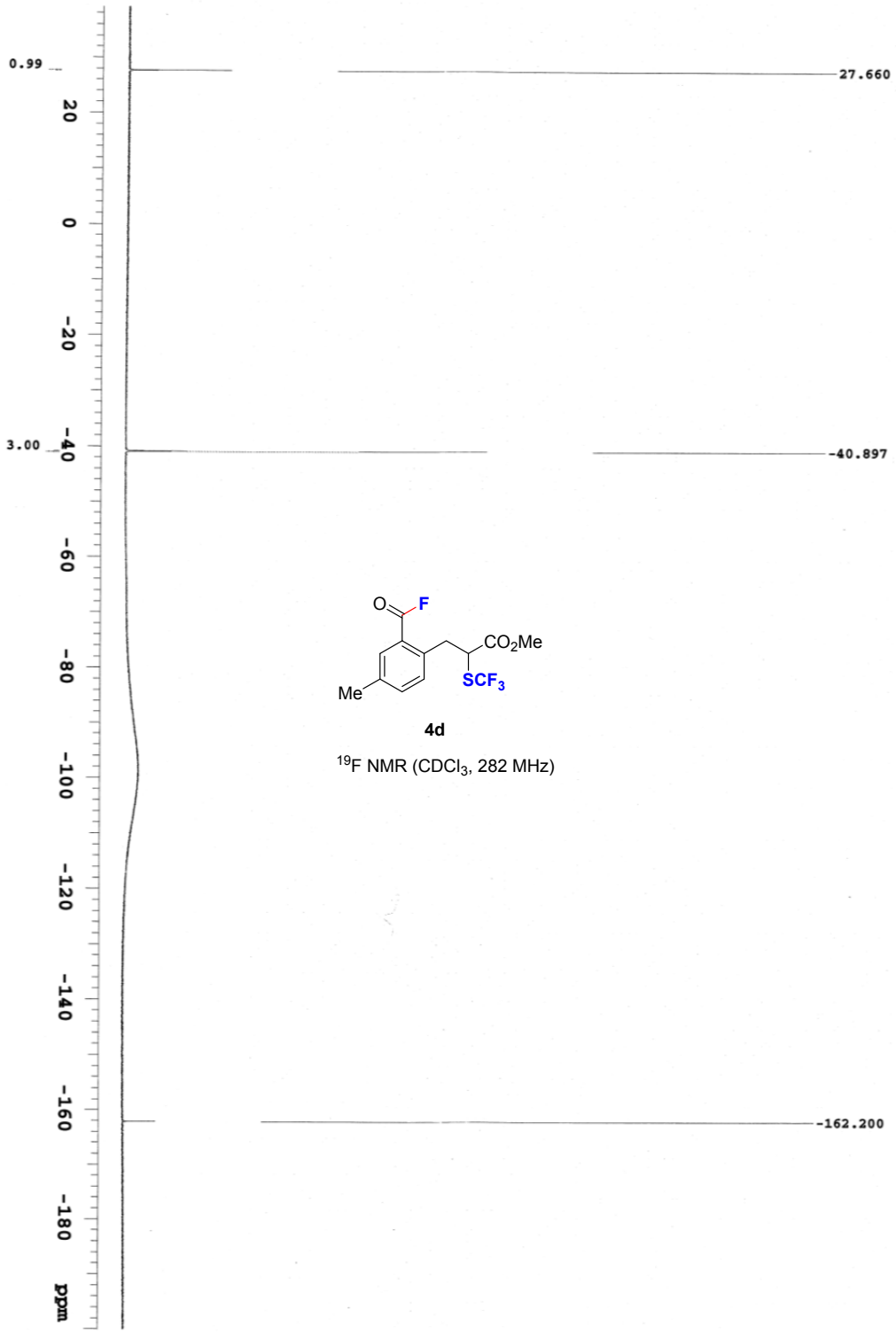
^{19}F NMR ($CDCl_3$, 282 MHz)



4c

^{13}C NMR (125.7 MHz, $CDCl_3$)

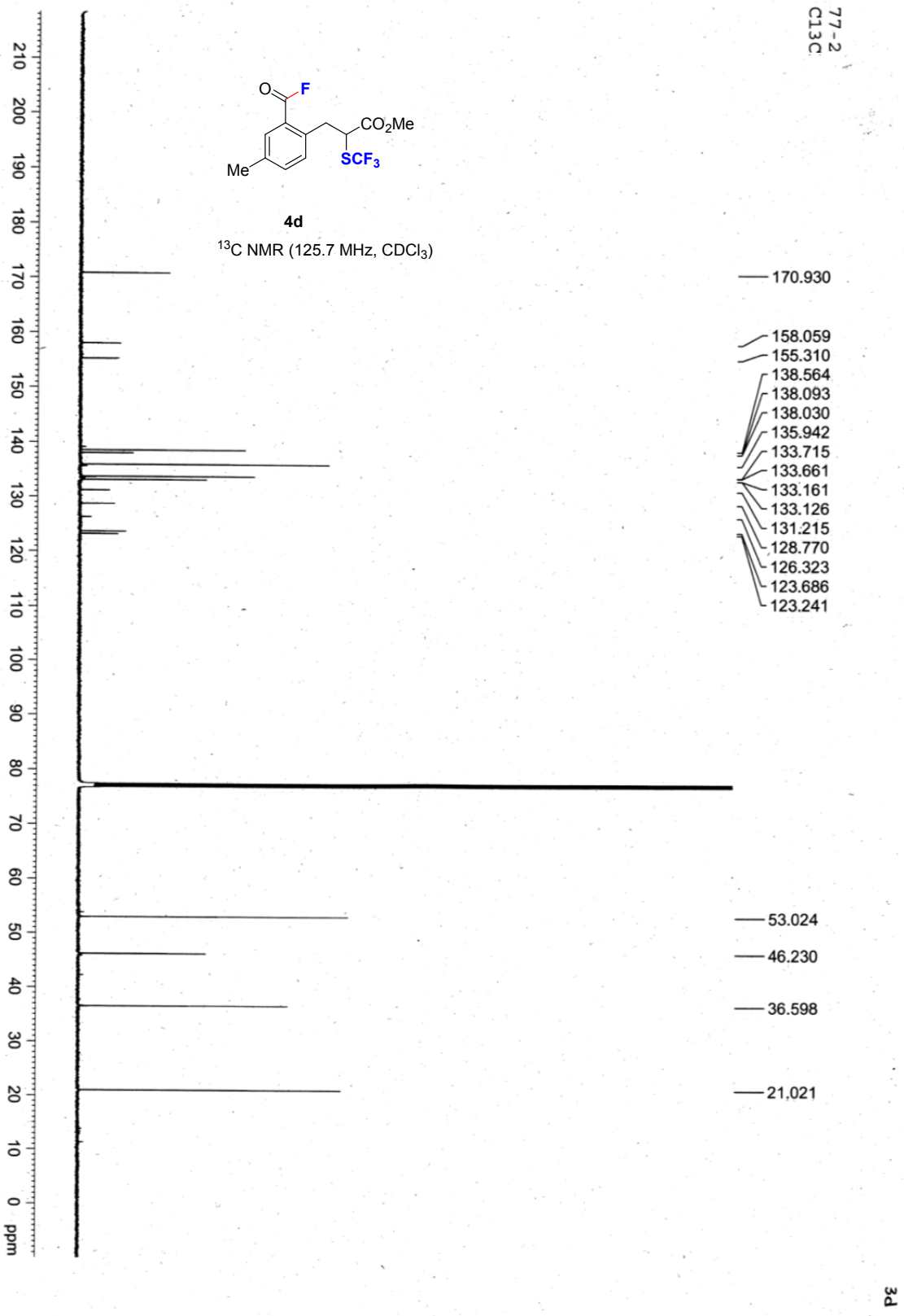

77-2
1H CDCl3
O
F
CO2Me
SCF3
Me
4d
1H NMR (500 MHz, CDCl3)
7.798
7.795
7.366
7.364
7.351
7.348
7.191
7.171
7.155
4.095
4.081
4.079
4.064
3.610
3.492
3.477
3.465
3.455
3.451
3.438
3.428
3.411
2.338
1.00
1.02
0.97
0.96
2.95
2.06
3.07
ppm
3d

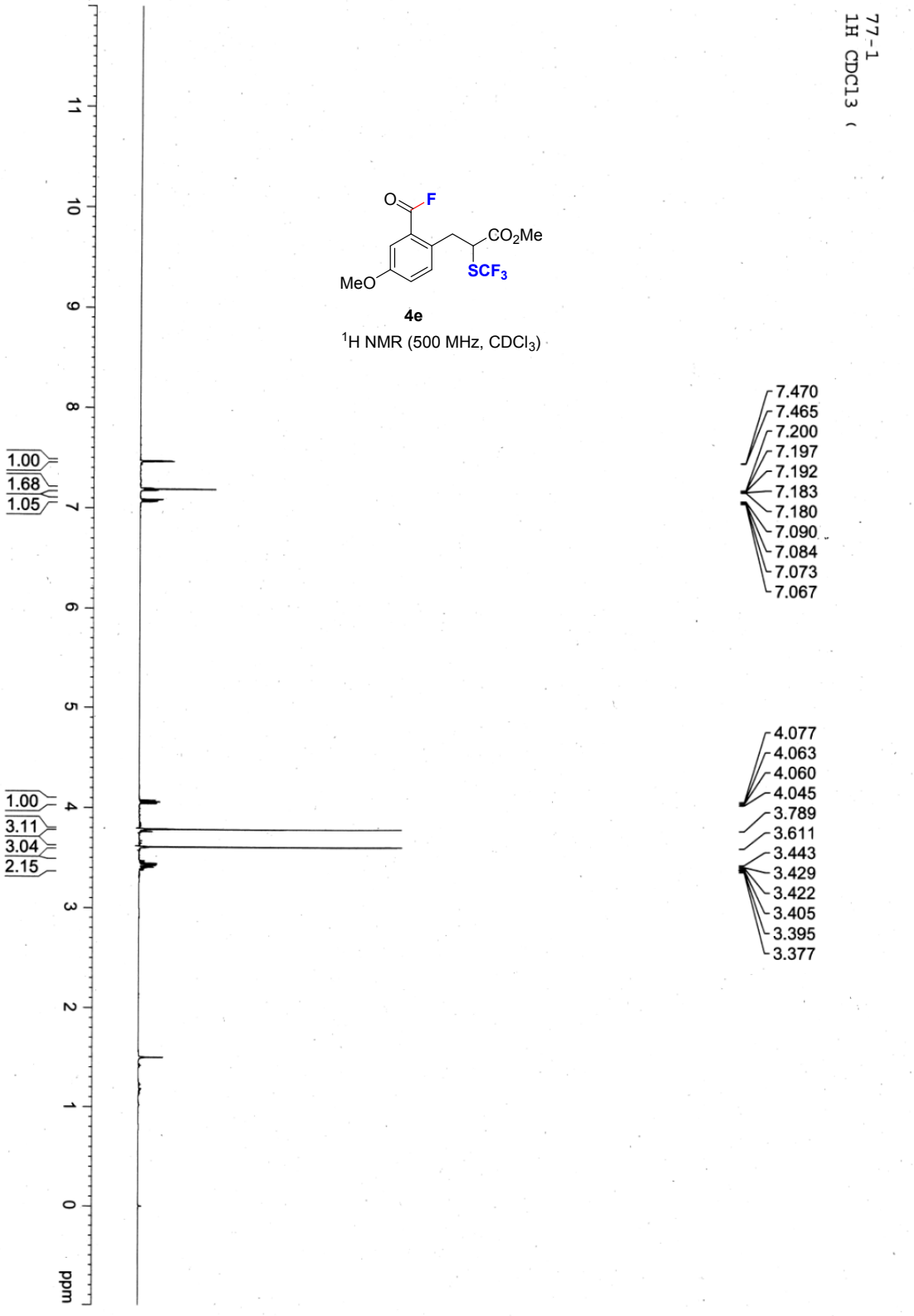


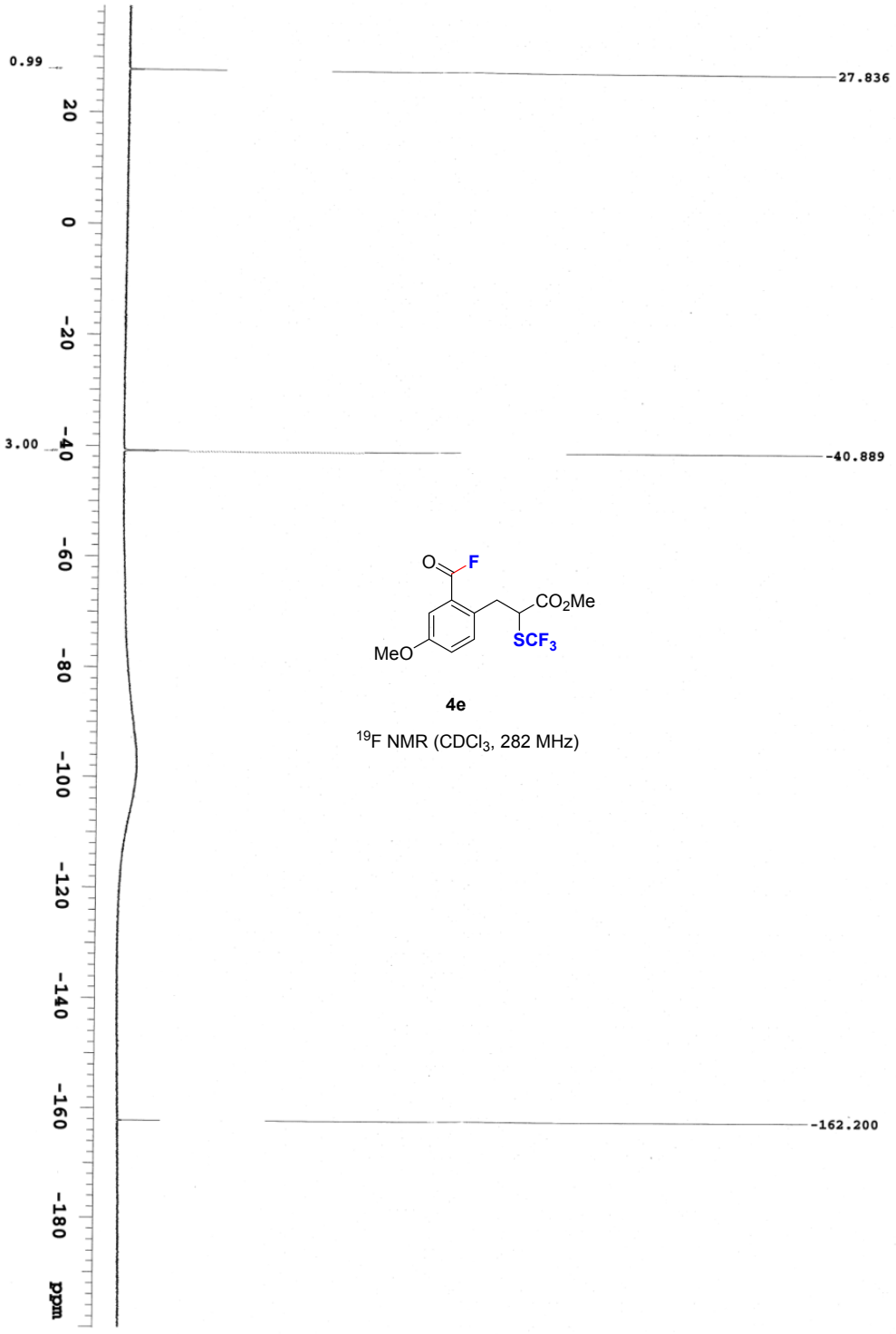
4d

^{19}F NMR ($CDCl_3$, 282 MHz)

3d


77-2
C13C
O
F
CO2Me
Me
SCF3
4d
13C NMR (125.7 MHz, CDCl3)
170.930
158.059
155.310
138.564
138.093
138.030
135.942
133.715
133.661
133.161
133.126
131.215
128.770
126.323
123.686
123.241
53.024
46.230
36.598
21.021
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
3d

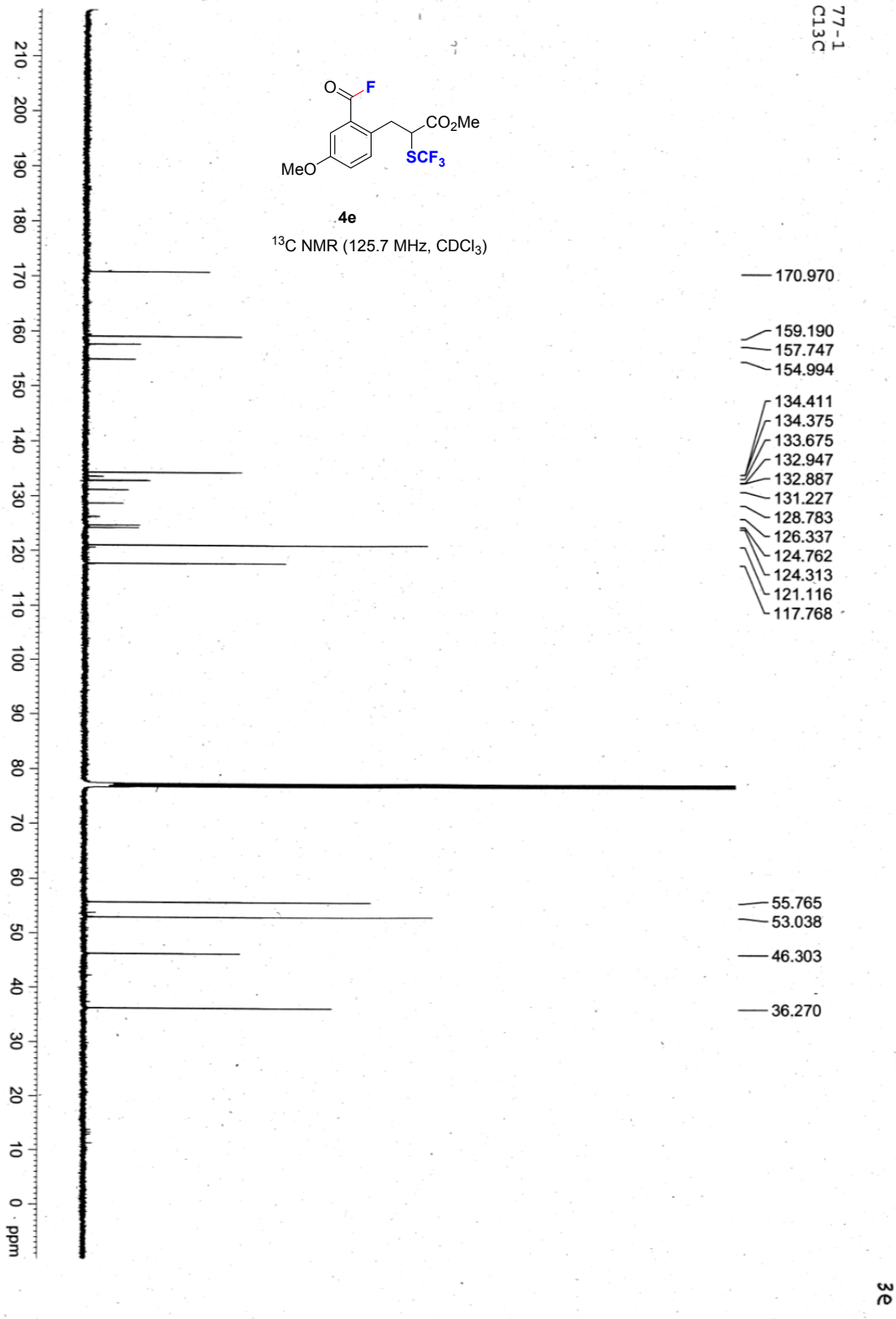

77-1
1H CDCl3 (
O
F
CO2Me
SCF3
MeO
4e
1H NMR (500 MHz, CDCl3)
7.470
7.465
7.200
7.197
7.192
7.183
7.180
7.090
7.084
7.073
7.067
4.077
4.063
4.060
4.045
3.789
3.611
3.443
3.429
3.422
3.405
3.395
3.377
1.00
1.68
1.05
1.00
3.11
3.04
2.15
ppm
3e

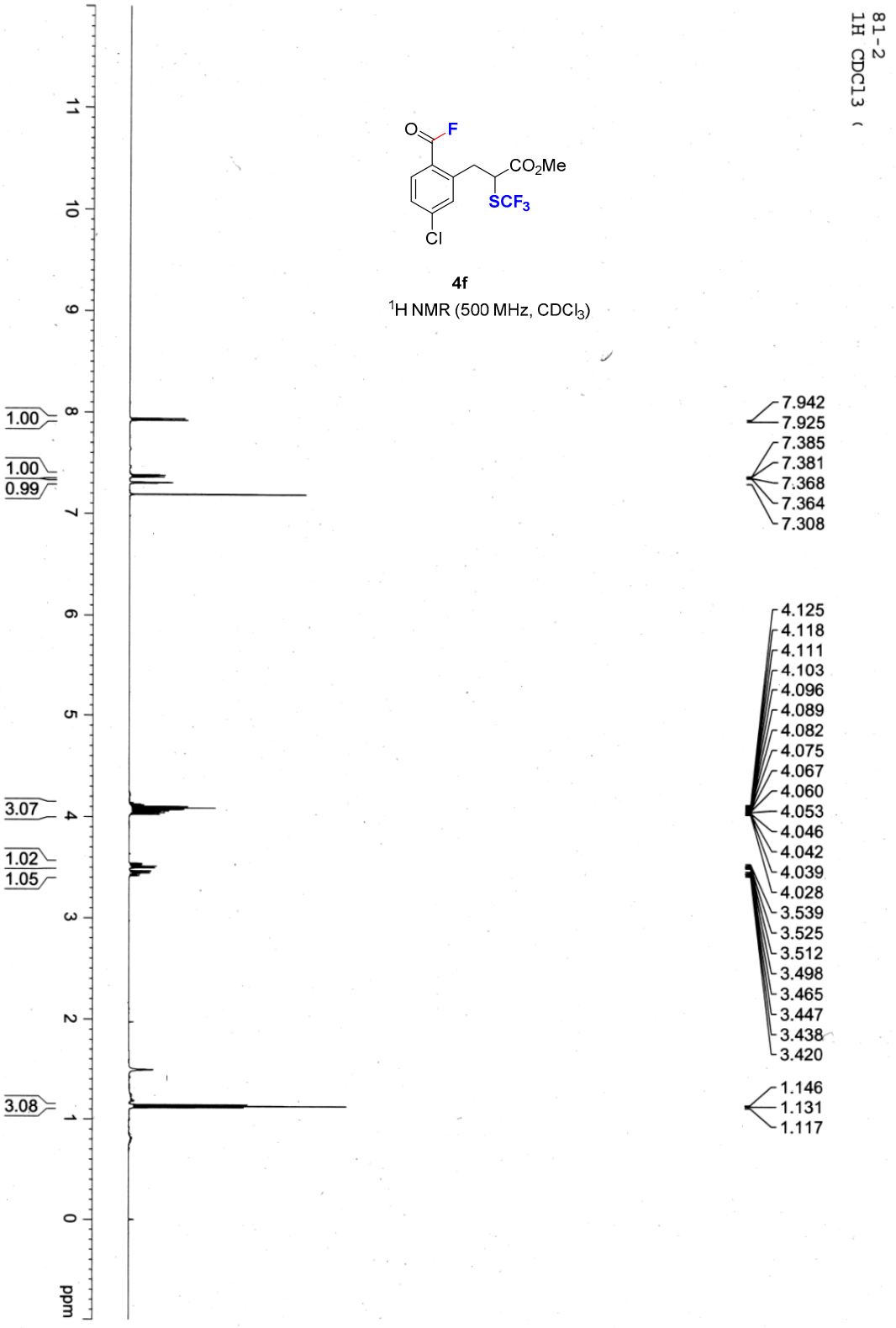


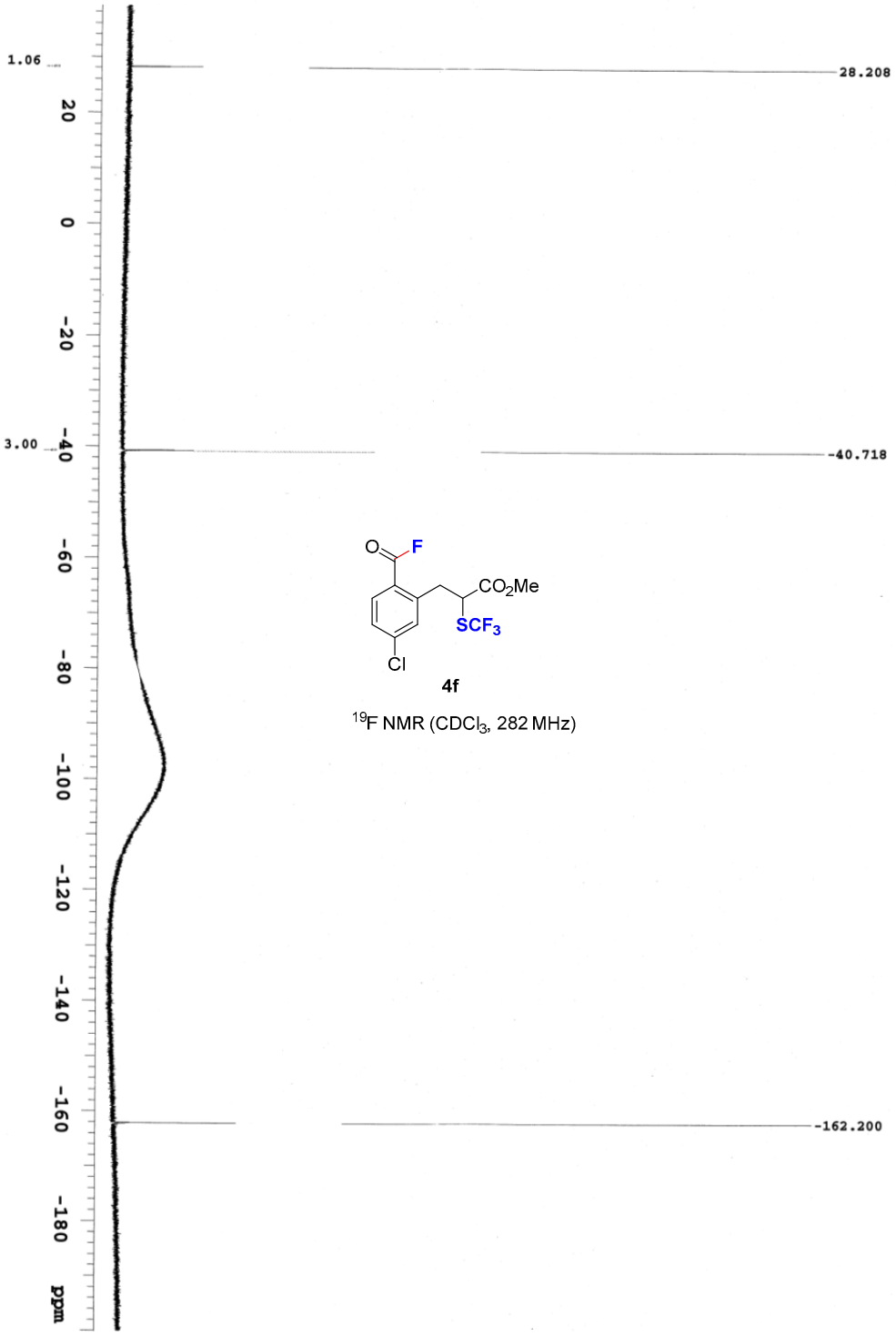
4e

^{19}F NMR ($CDCl_3$, 282 MHz)

3e


77-1
C13C
O
F
CO2Me
SCF3
MeO
4e
13C NMR (125.7 MHz, CDCl3)
170.970
159.190
157.747
154.994
134.411
134.375
133.675
132.947
132.887
131.227
128.783
126.337
124.762
124.313
121.116
117.768
55.765
53.038
46.303
36.270
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
3e

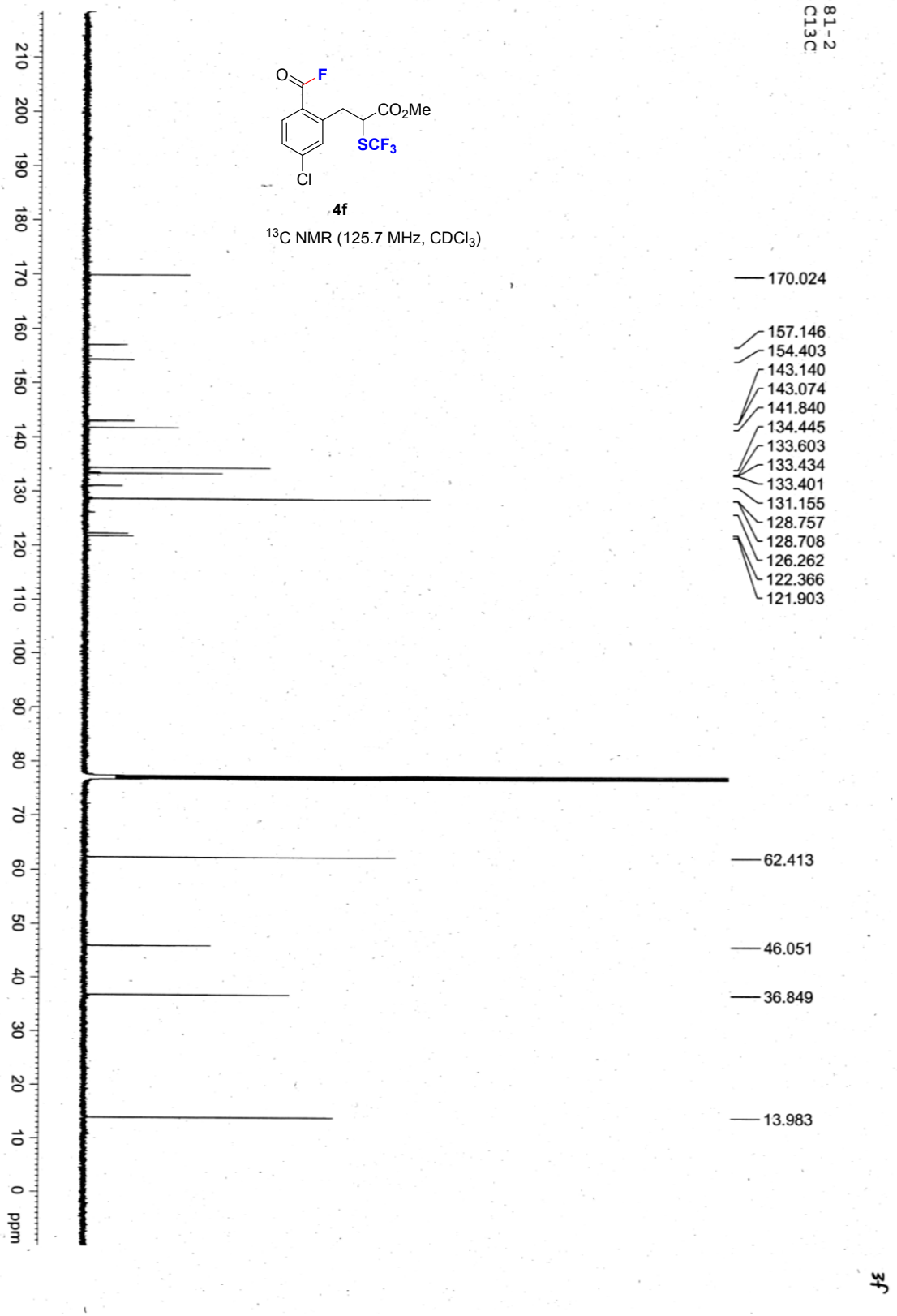

81-2
1H CDCl3 (
O
F
CO2Me
SCF3
Cl
4f
1H NMR (500 MHz, CDCl3)
7.942
7.925
7.385
7.381
7.368
7.364
7.308
4.125
4.118
4.111
4.103
4.096
4.089
4.082
4.075
4.067
4.060
4.053
4.046
4.042
4.039
4.028
3.539
3.525
3.512
3.498
3.465
3.447
3.438
3.420
1.146
1.131
1.117
1.00
1.00
0.99
3.07
1.02
1.05
3.08
ppm
3f

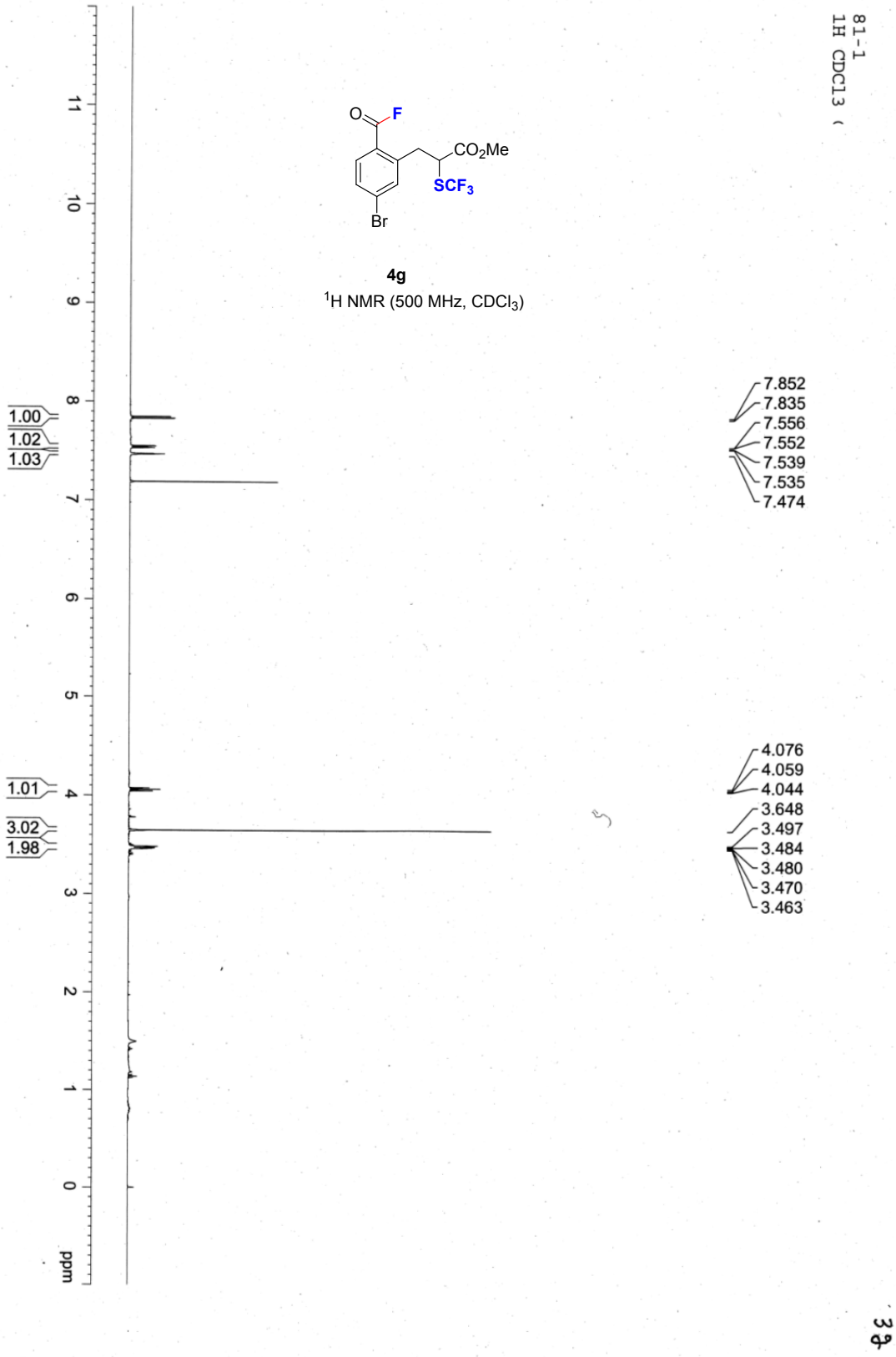


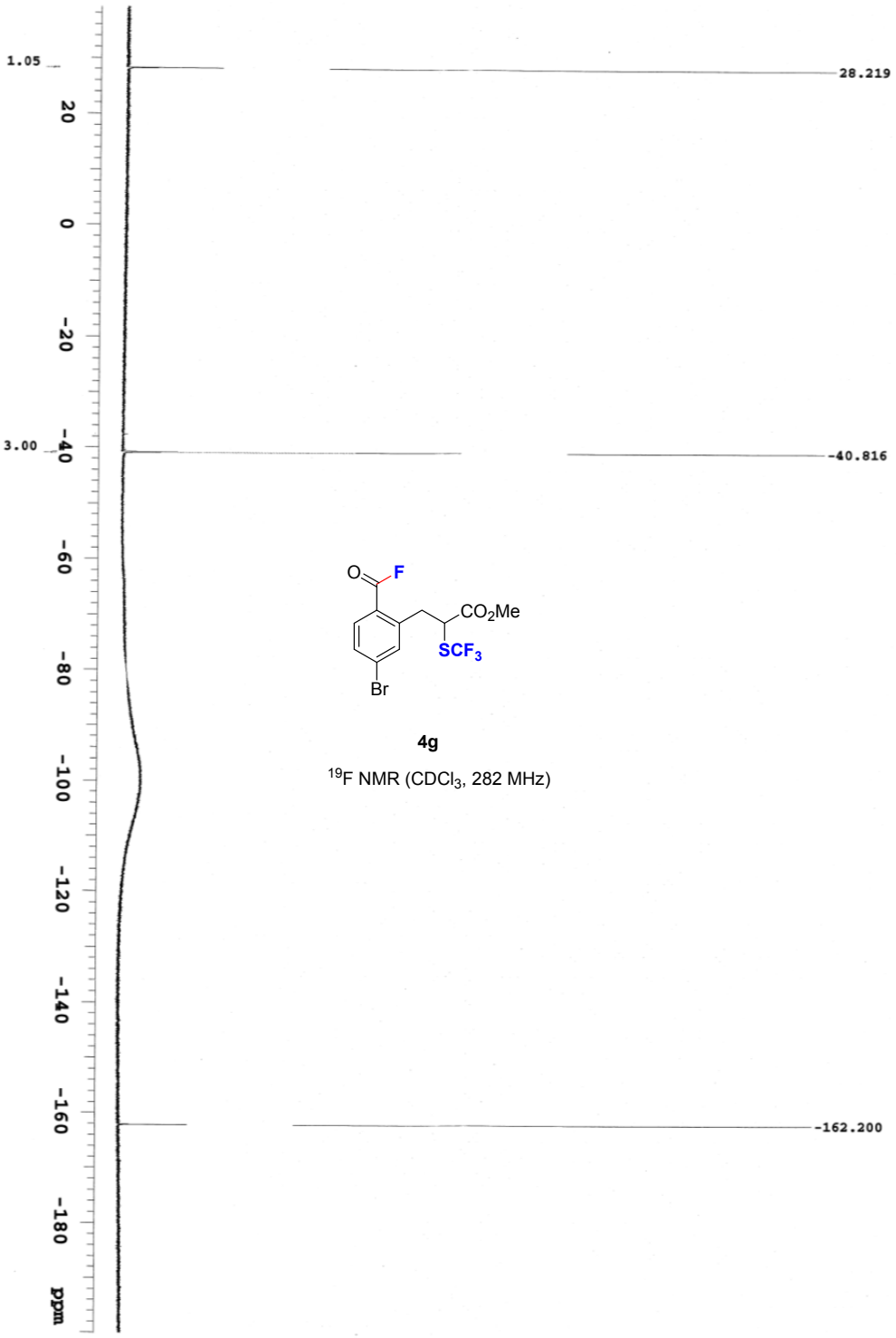
4f

^{19}F NMR ($CDCl_3$, 282 MHz)

3f

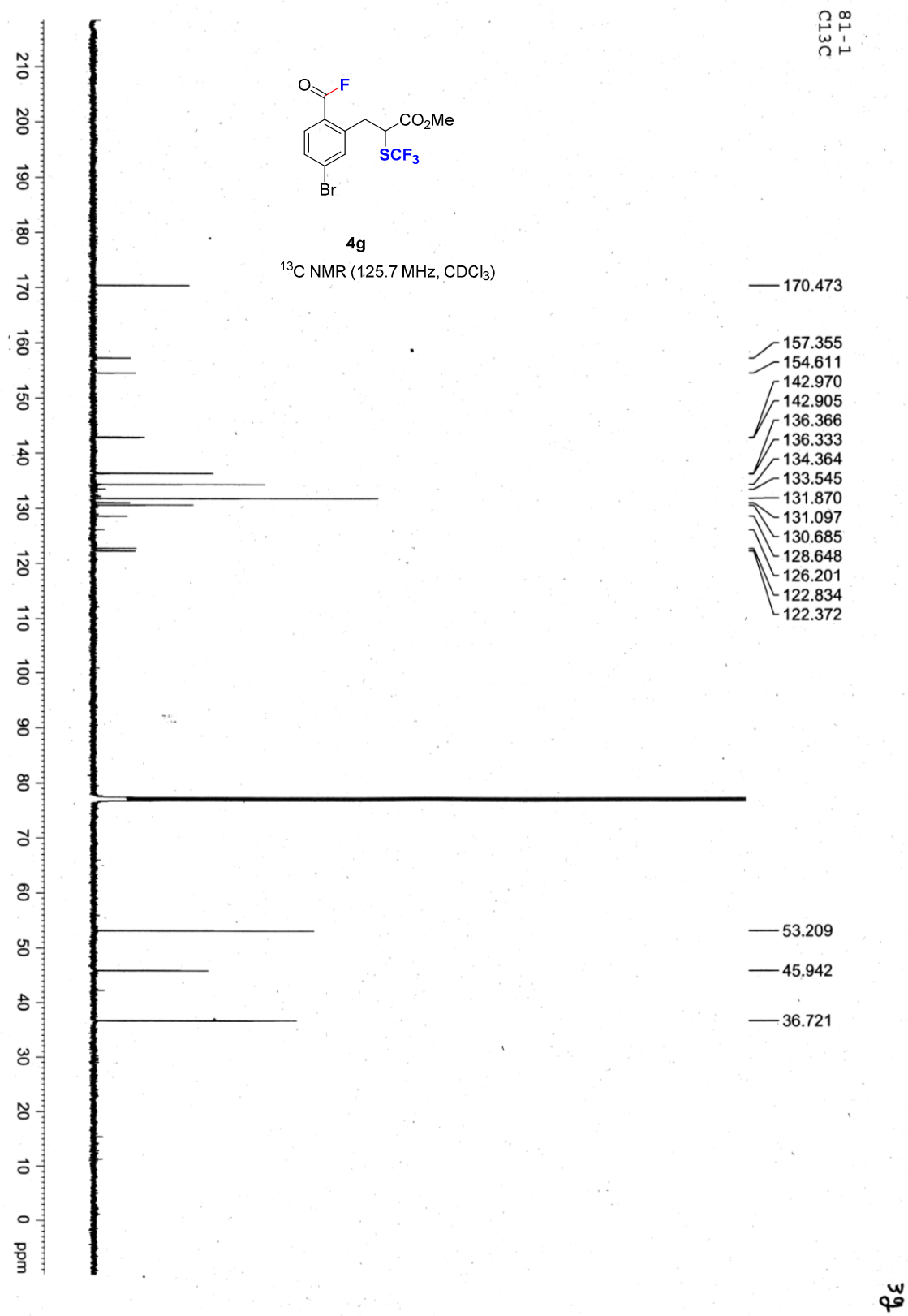

81-2
C13C
O
F
CO2Me
SCF3
Cl
4f
13C NMR (125.7 MHz, CDCl3)
170.024
157.146
154.403
143.140
143.074
141.840
134.445
133.603
133.434
133.401
131.155
128.757
128.708
126.262
122.366
121.903
62.413
46.051
36.849
13.983
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
4f

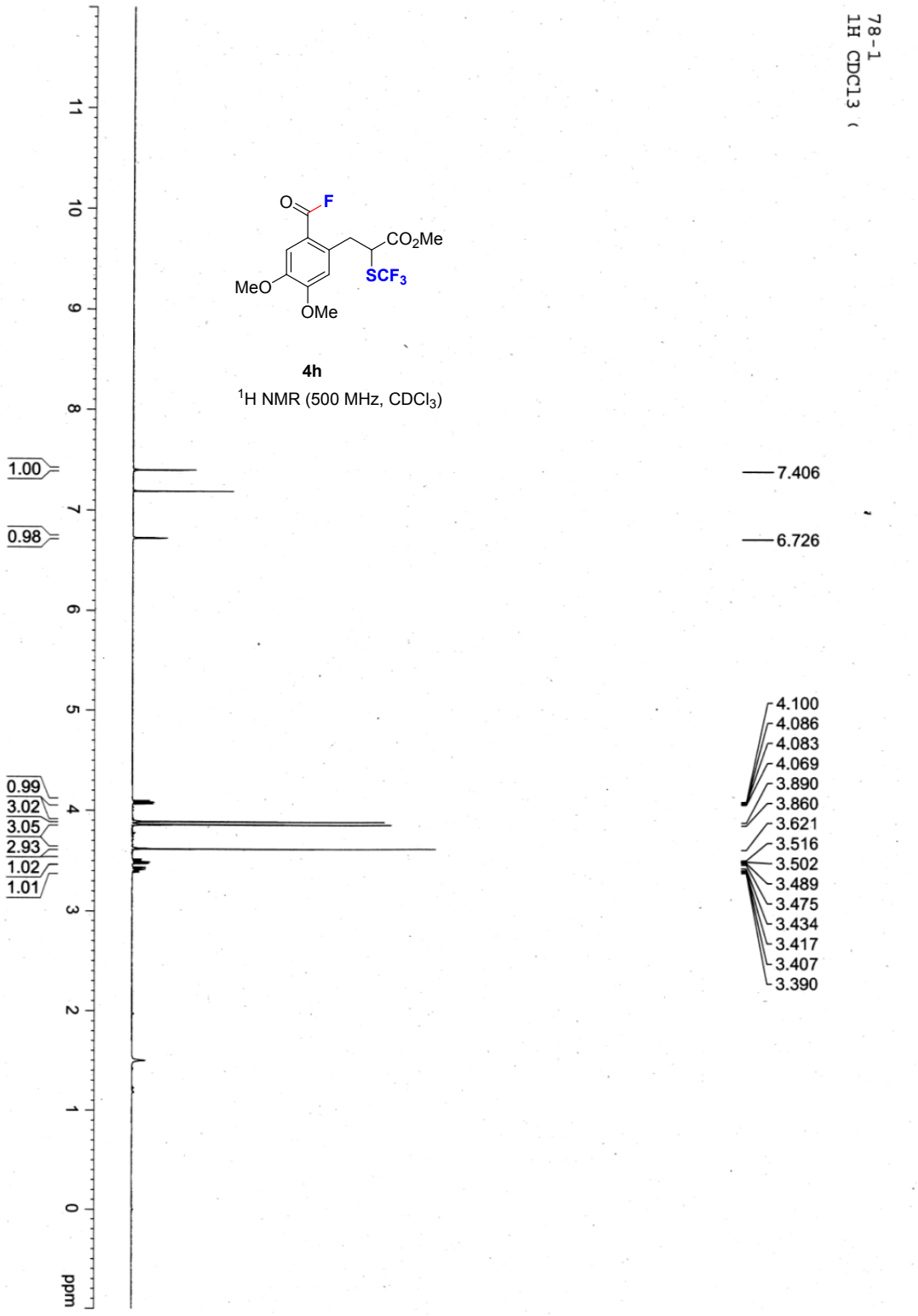

81-1
1H CDCl3
O
F
CO2Me
SCF3
Br
4g
1H NMR (500 MHz, CDCl3)
7.852
7.835
7.556
7.552
7.539
7.535
7.474
4.076
4.059
4.044
3.648
3.497
3.484
3.480
3.470
3.463
1.00
1.02
1.03
1.01
3.02
1.98
ppm

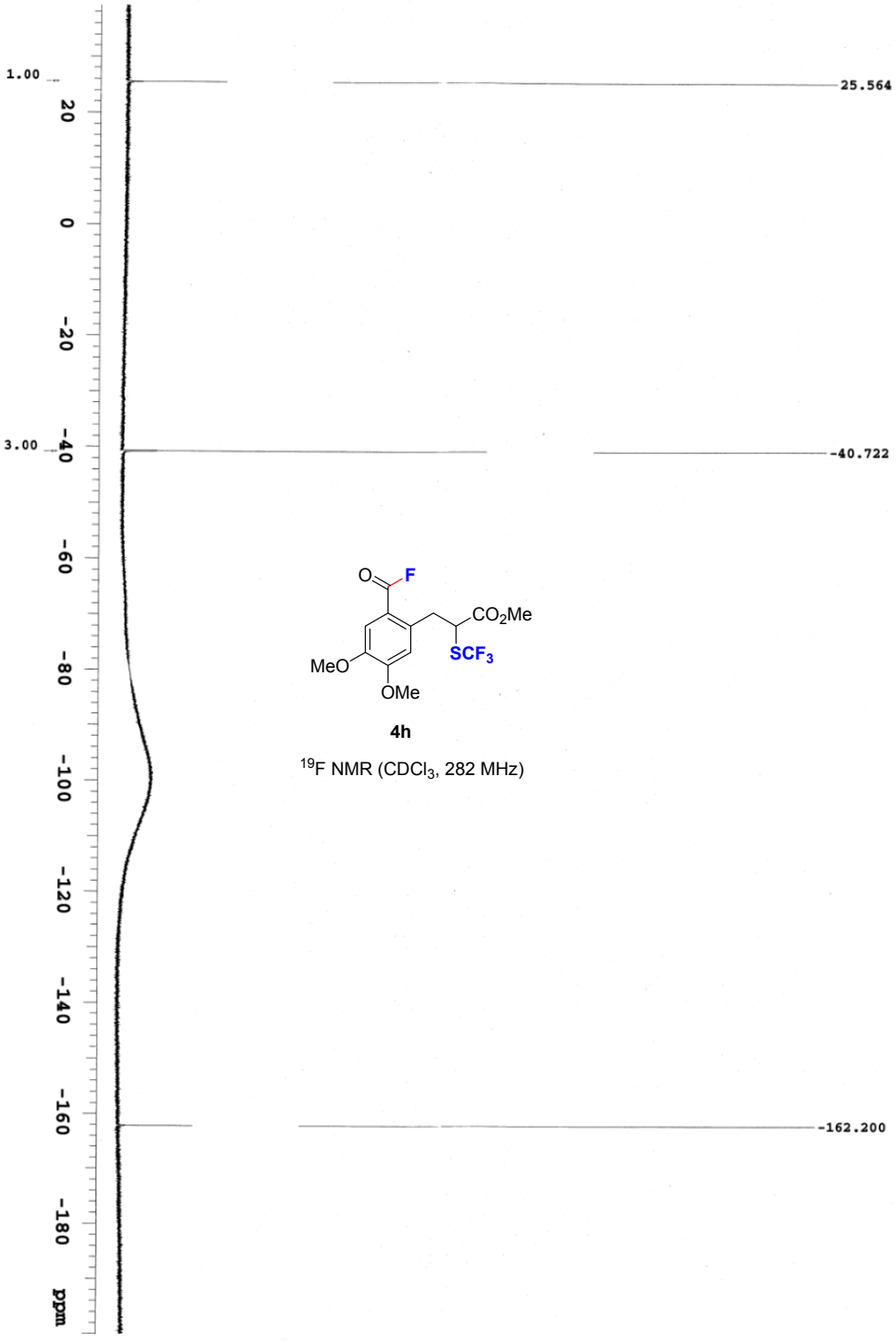


4g

^{19}F NMR ($CDCl_3$, 282 MHz)

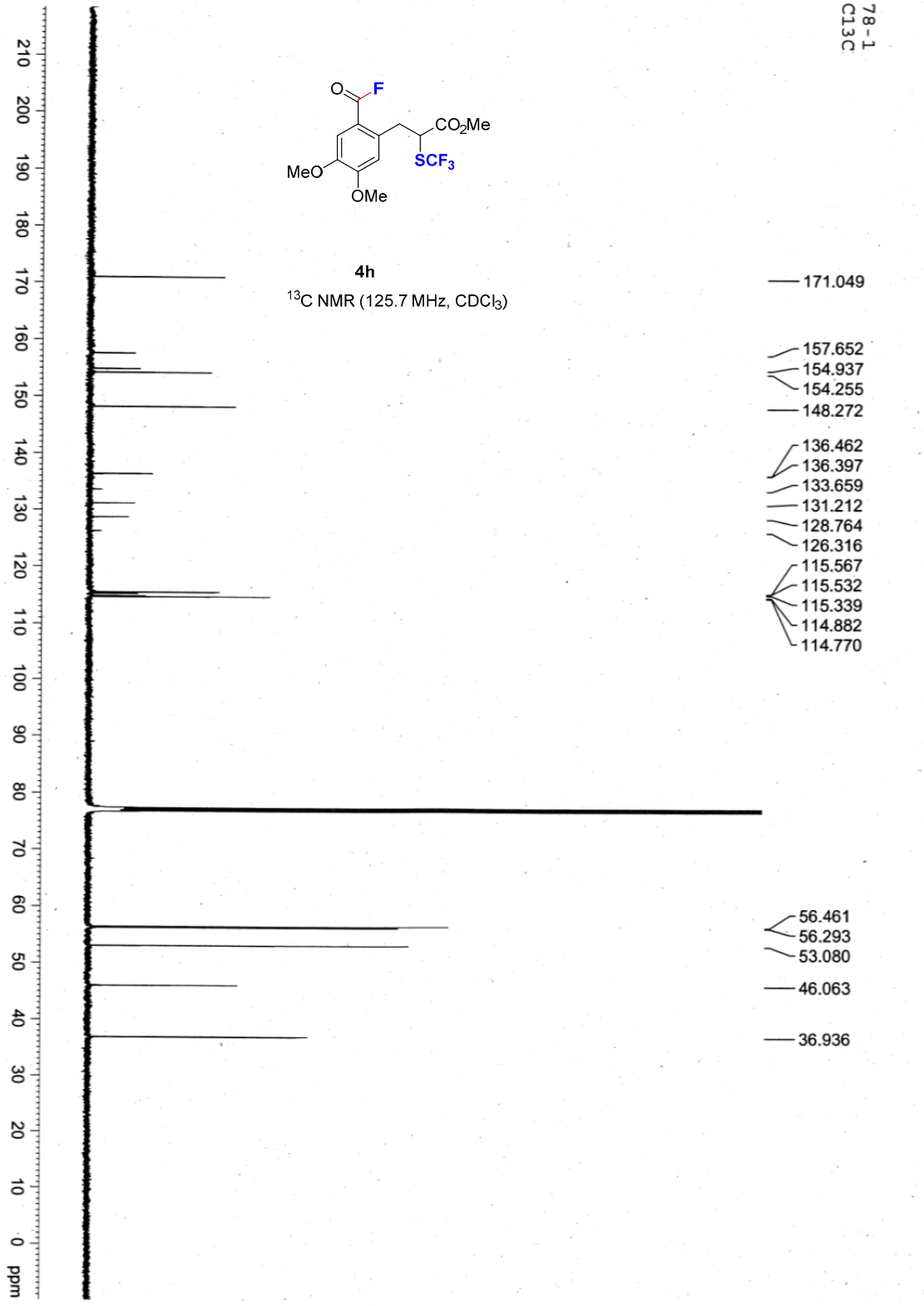

81-1
C13C
O
F
CO2Me
SCF3
Br
4g
13C NMR (125.7 MHz, CDCl3)
170.473
157.355
154.611
142.970
142.905
136.366
136.333
134.364
133.545
131.870
131.097
130.685
128.648
126.201
122.834
122.372
53.209
45.942
36.721
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


78-1
1H CDCl3
O
F
CO2Me
SCF3
MeO
OMe
4h
1H NMR (500 MHz, CDCl3)
1.00
0.98
0.99
3.02
3.05
2.93
1.02
1.01
7.406
6.726
4.100
4.086
4.083
4.069
3.890
3.860
3.621
3.516
3.502
3.489
3.475
3.434
3.417
3.407
3.390
ppm
3h



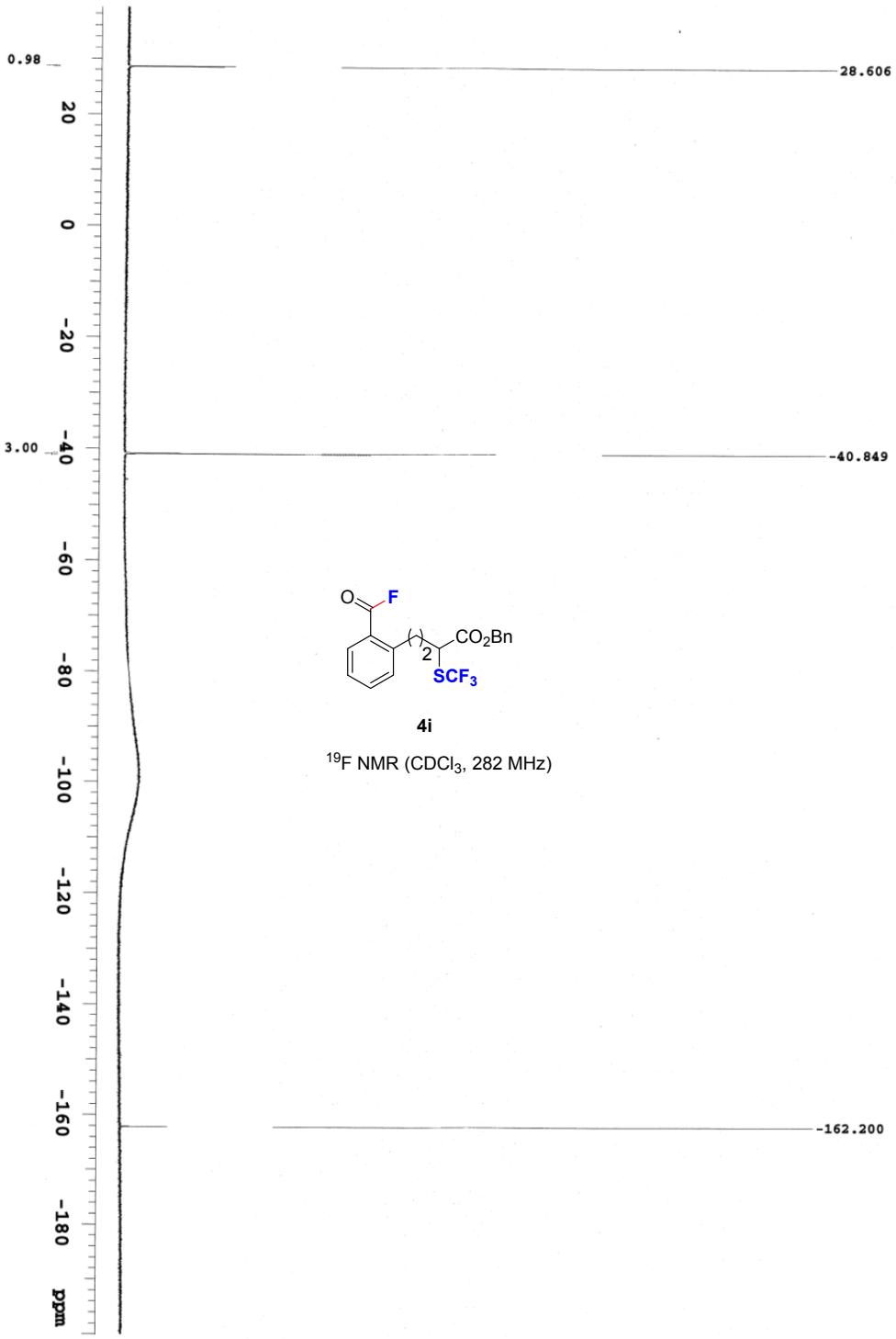
4h

^{19}F NMR ($CDCl_3$, 282 MHz)


78-1
C13C
O
F
CO2Me
SCF3
MeO
OMe
4h
13C NMR (125.7 MHz, CDCl3)
171.049
157.652
154.937
154.255
148.272
136.462
136.397
133.659
131.212
128.764
126.316
115.567
115.532
115.339
114.882
114.770
56.461
56.293
53.080
46.063
36.936
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
3h

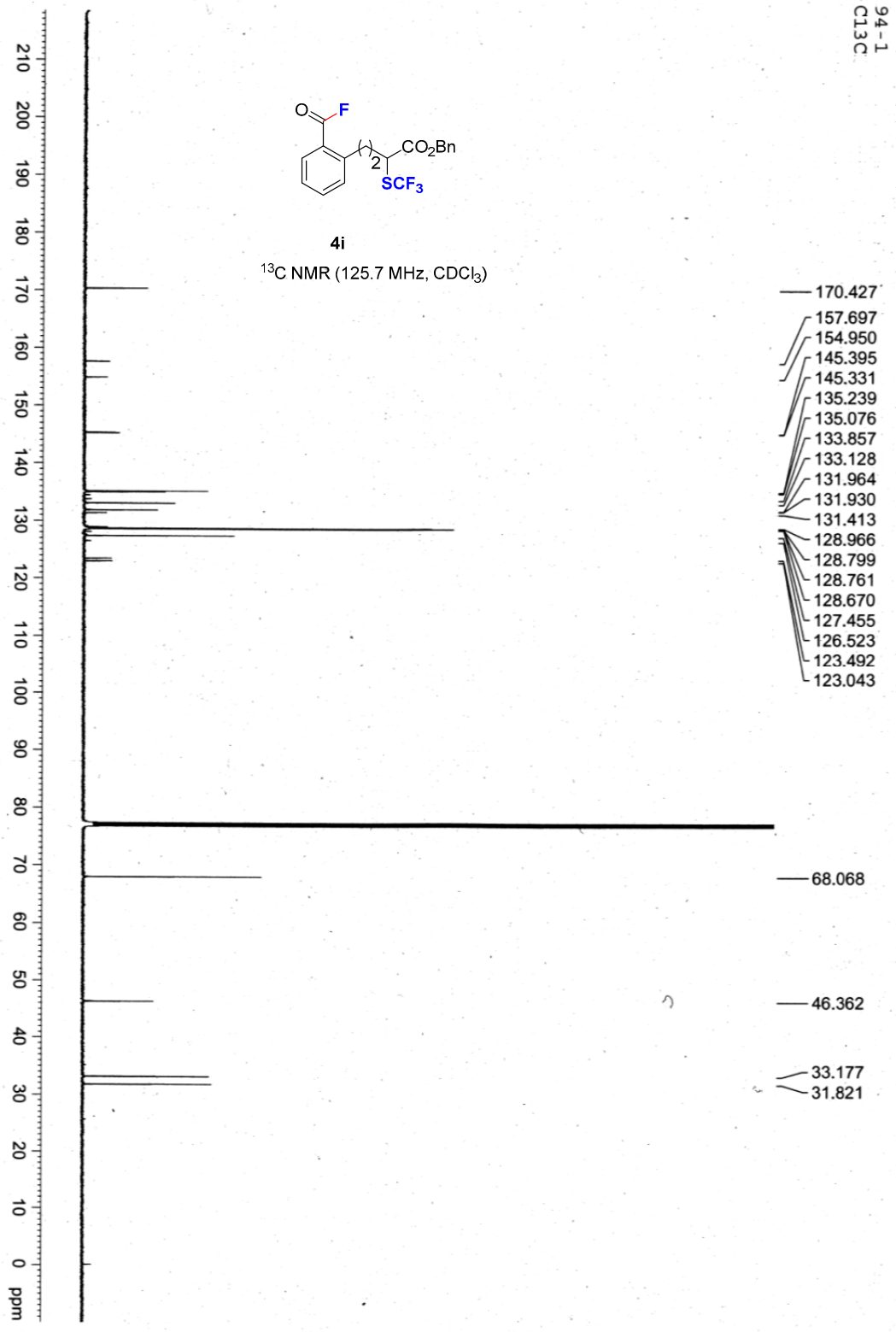
4i

^{1}H NMR (500 MHz, $CDCl_3$)



4i

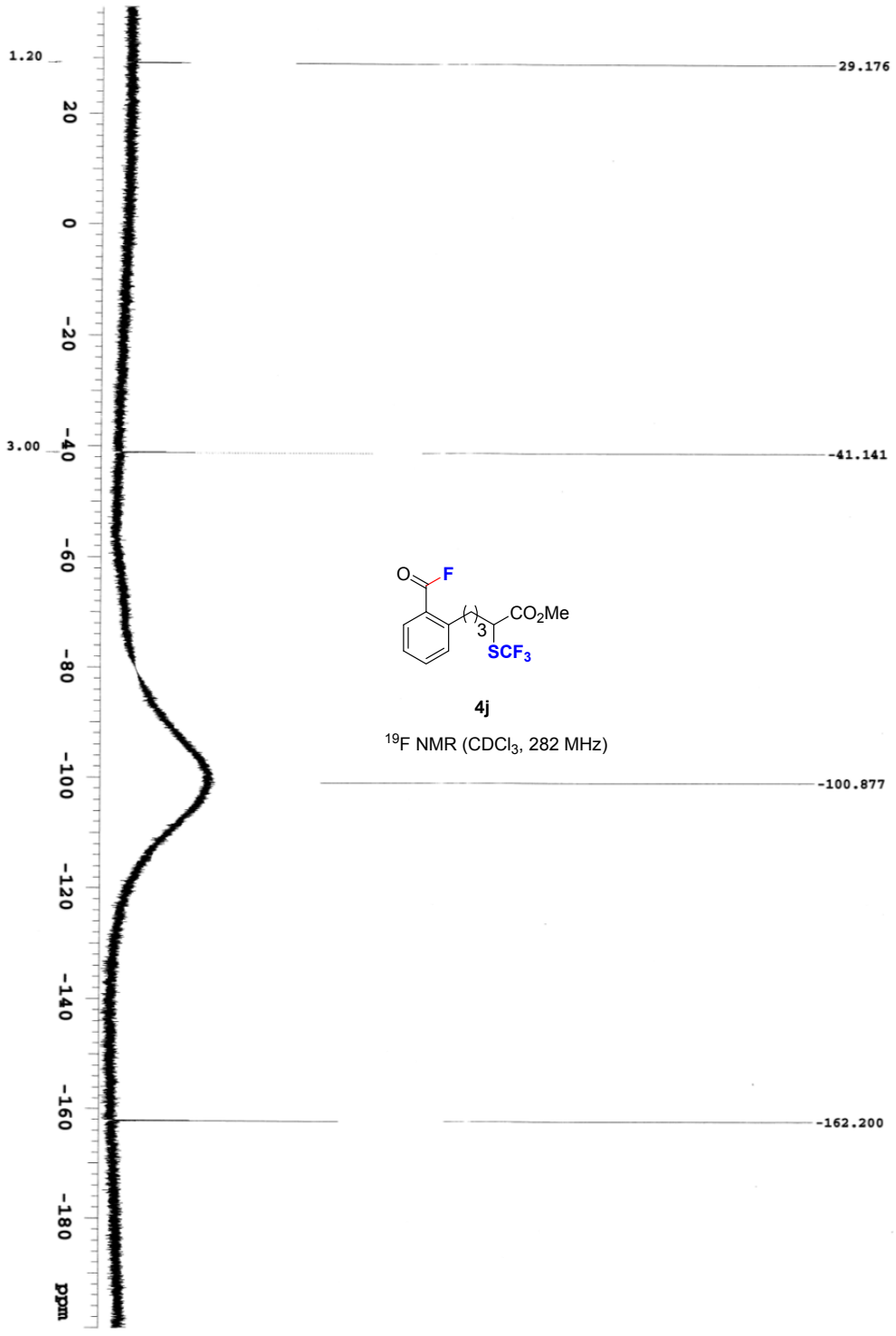
^{19}F NMR ($CDCl_3$, 282 MHz)


94-1
C13C
O
F
CO2Bn
2
SCF3
4i
13C NMR (125.7 MHz, CDCl3)
170.427
157.697
154.950
145.395
145.331
135.239
135.076
133.857
133.128
131.964
131.930
131.413
128.966
128.799
128.761
128.670
127.455
126.523
123.492
123.043
68.068
46.362
33.177
31.821
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4j

^{1}H NMR (500 MHz, $CDCl_3$)

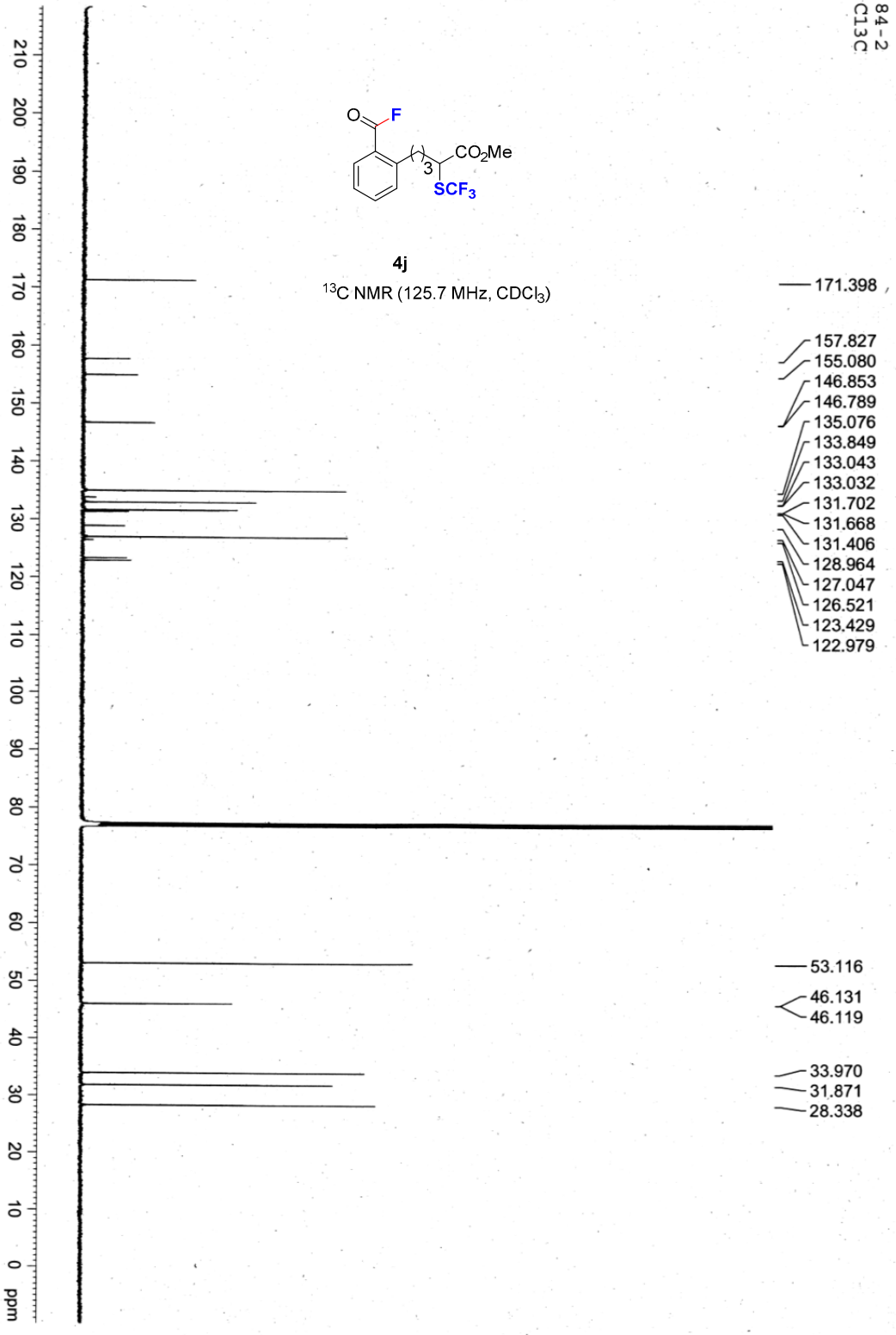
3D

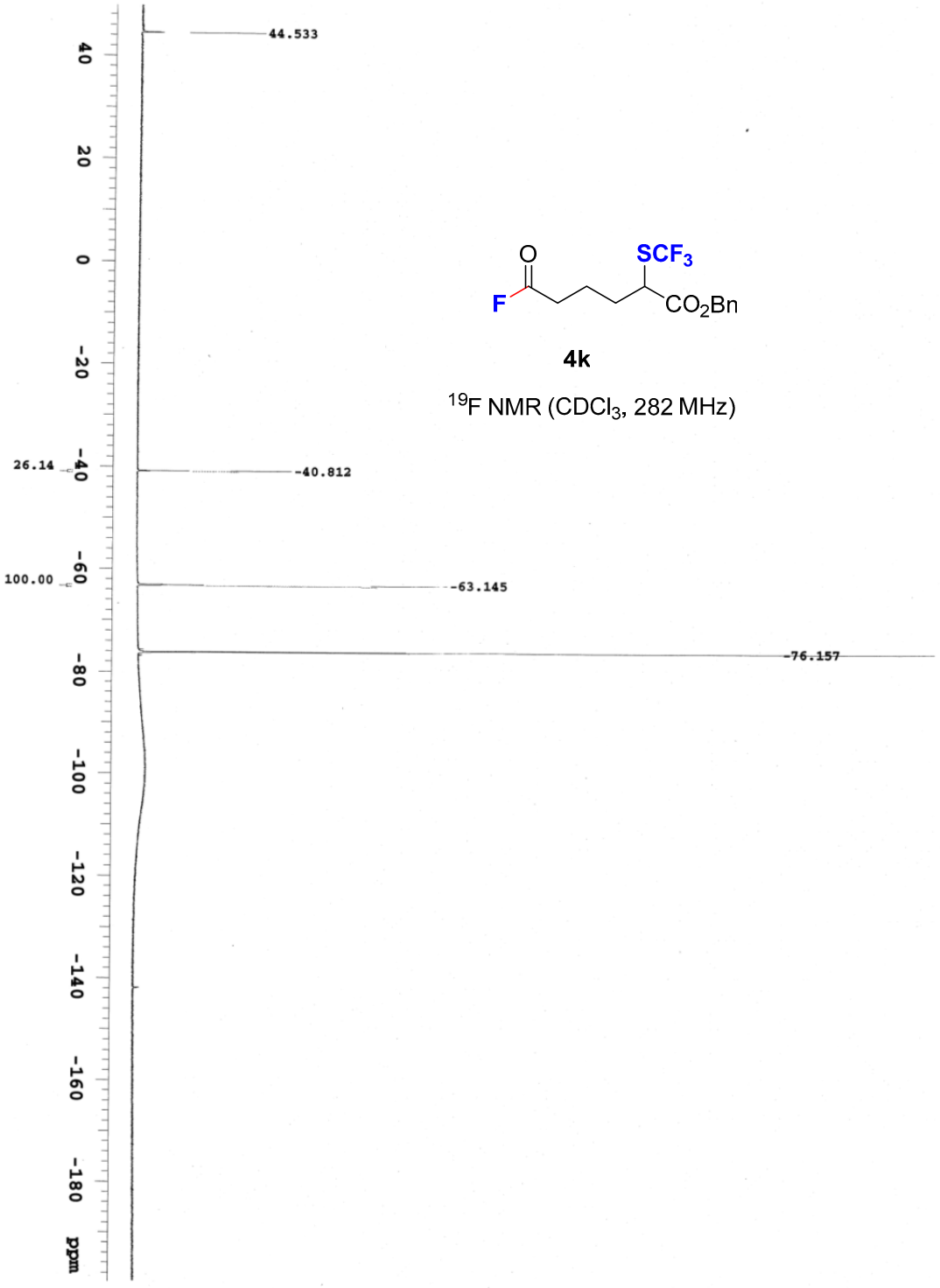


4j

^{19}F NMR ($CDCl_3$, 282 MHz)

3J

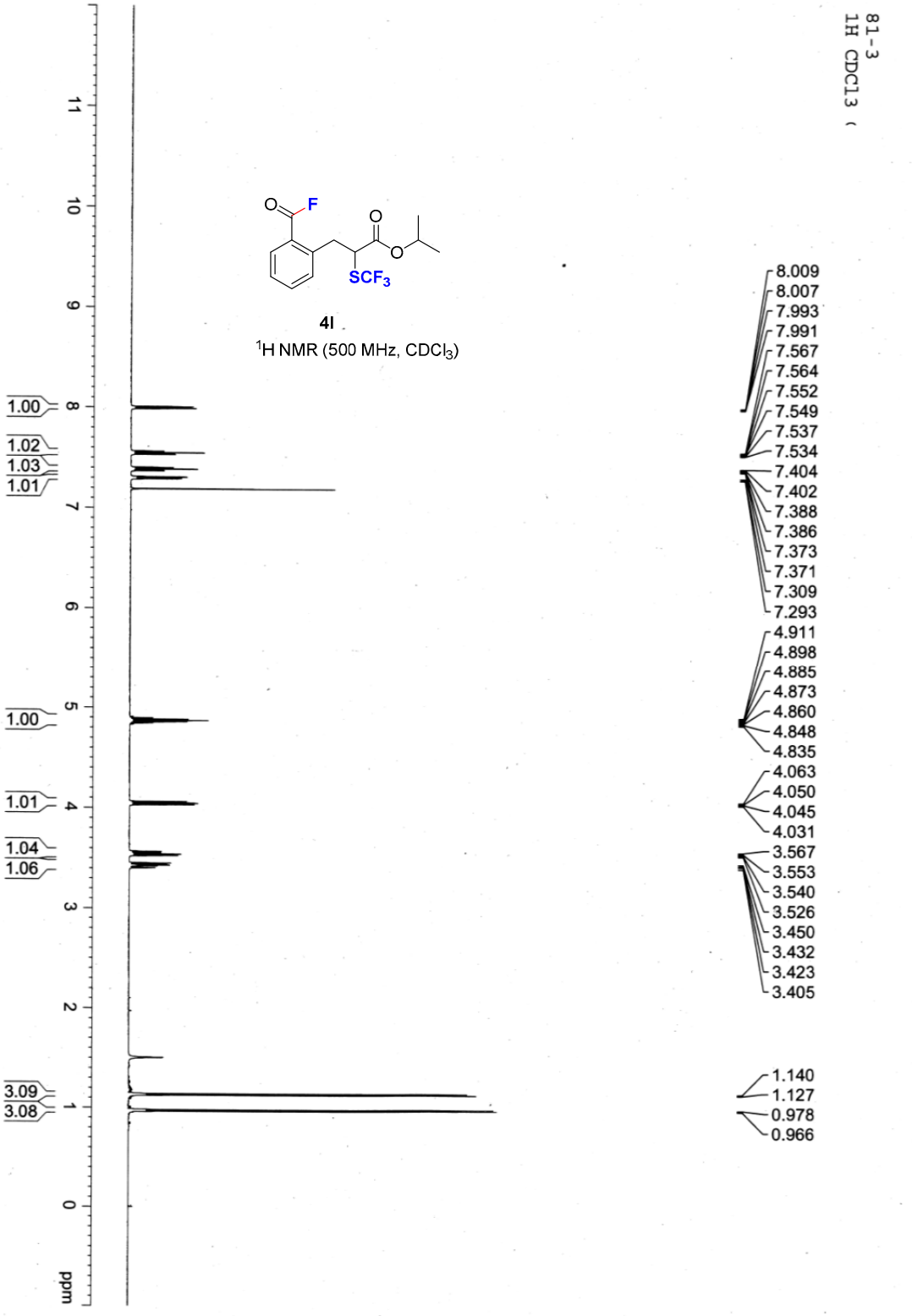

84-2
C13C
O
F
CO2Me
3
SCF3
4j
13C NMR (125.7 MHz, CDCl3)
171.398
157.827
155.080
146.853
146.789
135.076
133.849
133.043
133.032
131.702
131.668
131.406
128.964
127.047
126.521
123.429
122.979
53.116
46.131
46.119
33.970
31.871
28.338
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



4k

^{19}F NMR ($CDCl_3$, 282 MHz)

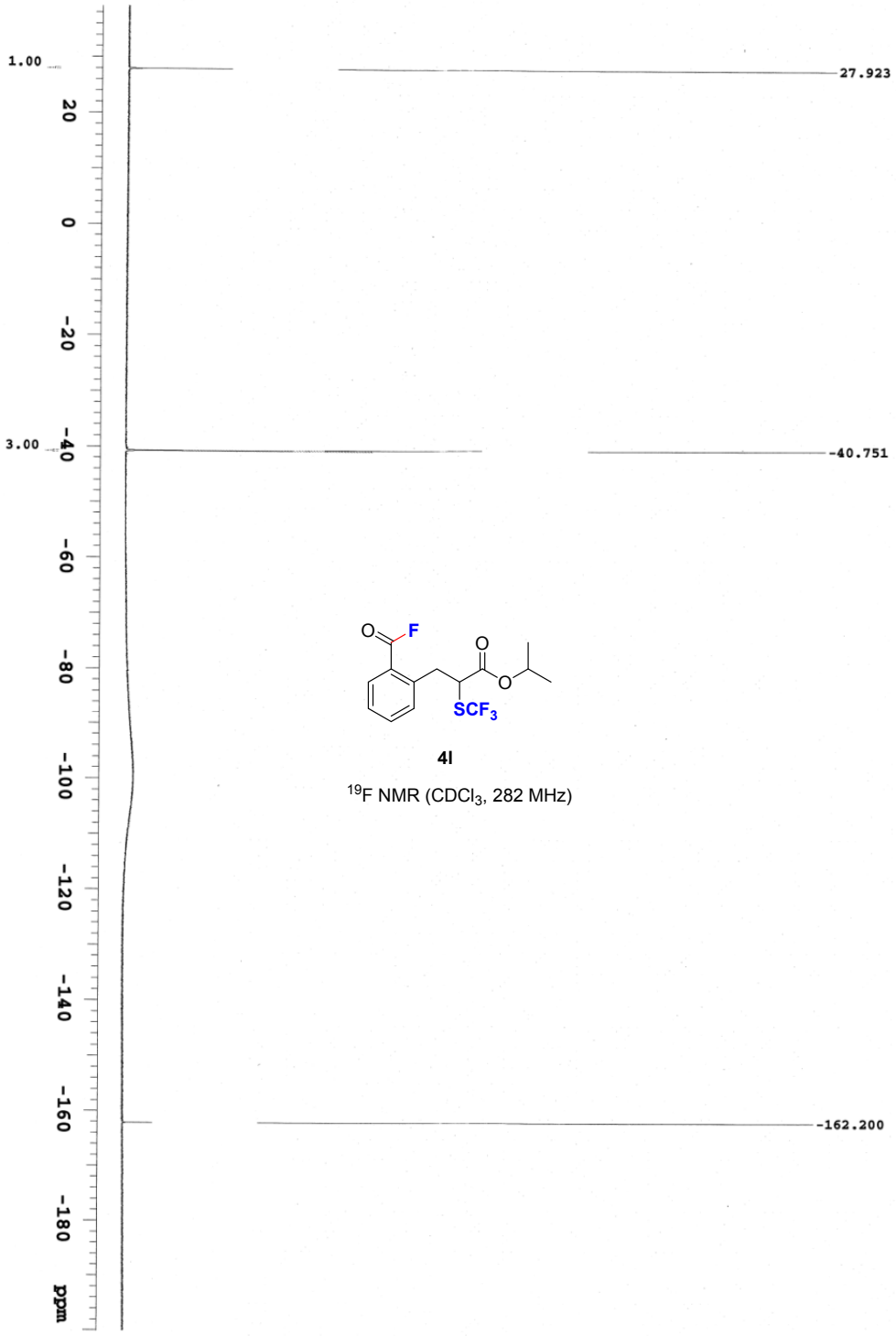
3k



4l

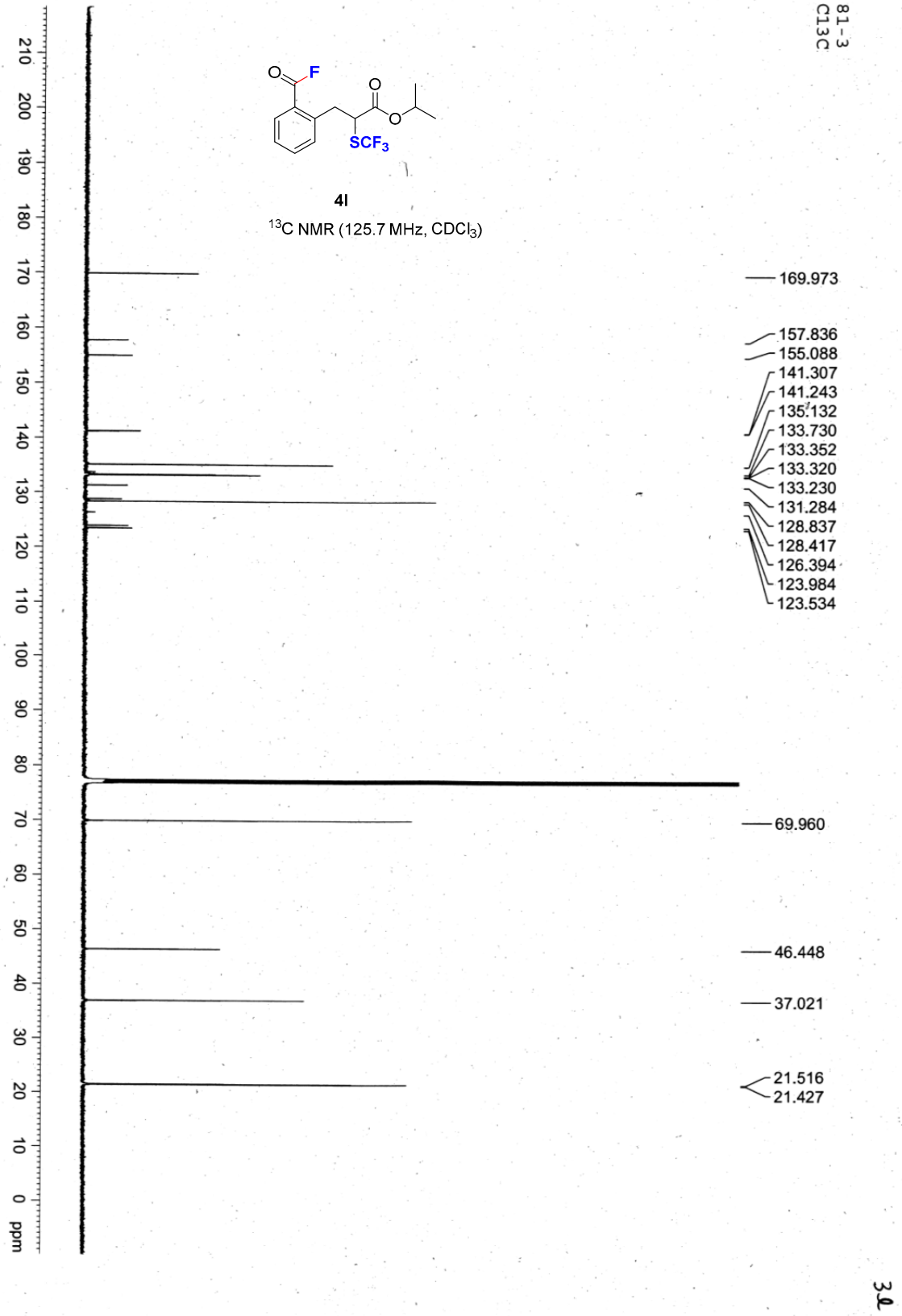
^{1}H NMR (500 MHz, $CDCl_3$)

3l

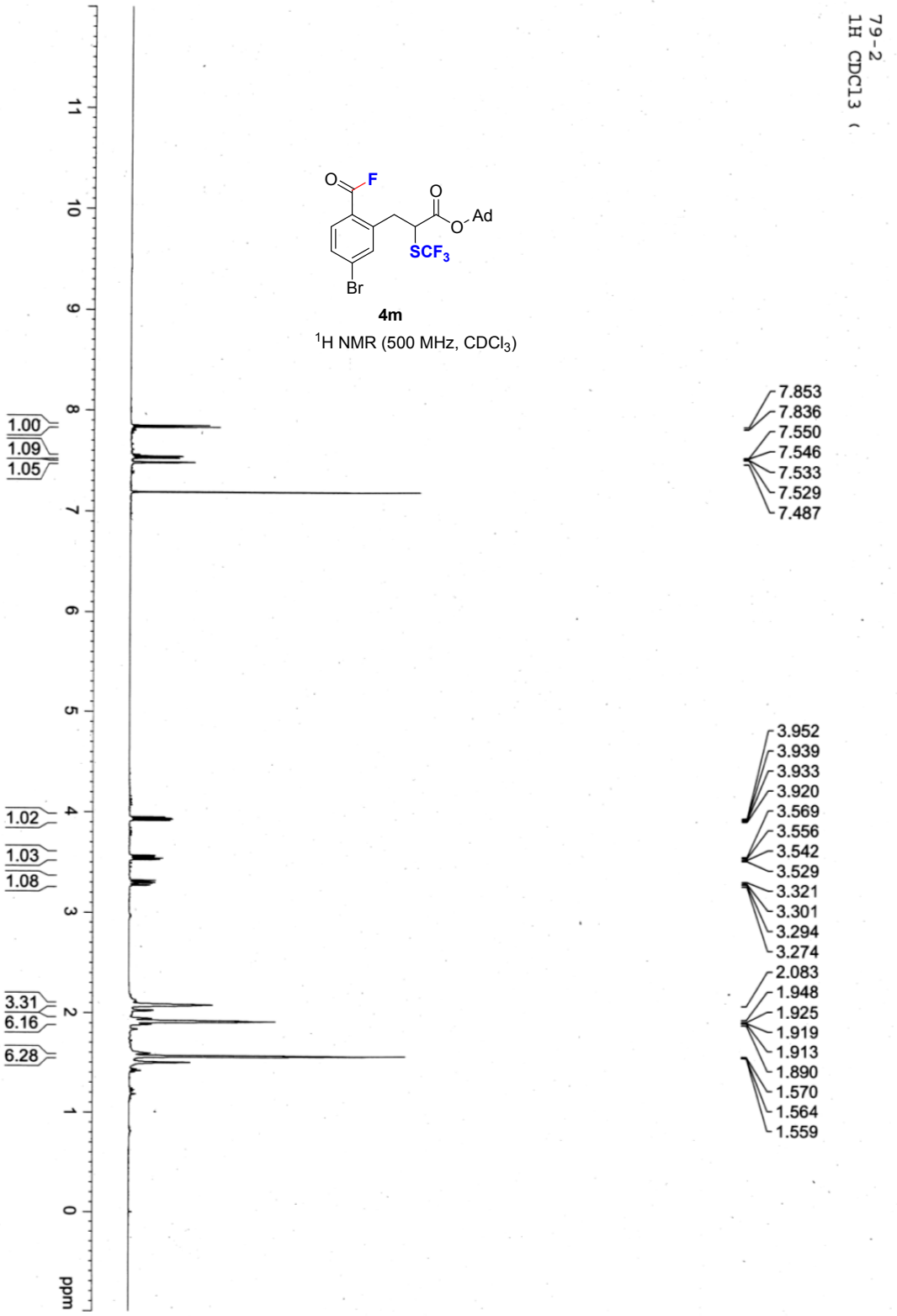


4l

^{19}F NMR ($CDCl_3$, 282 MHz)

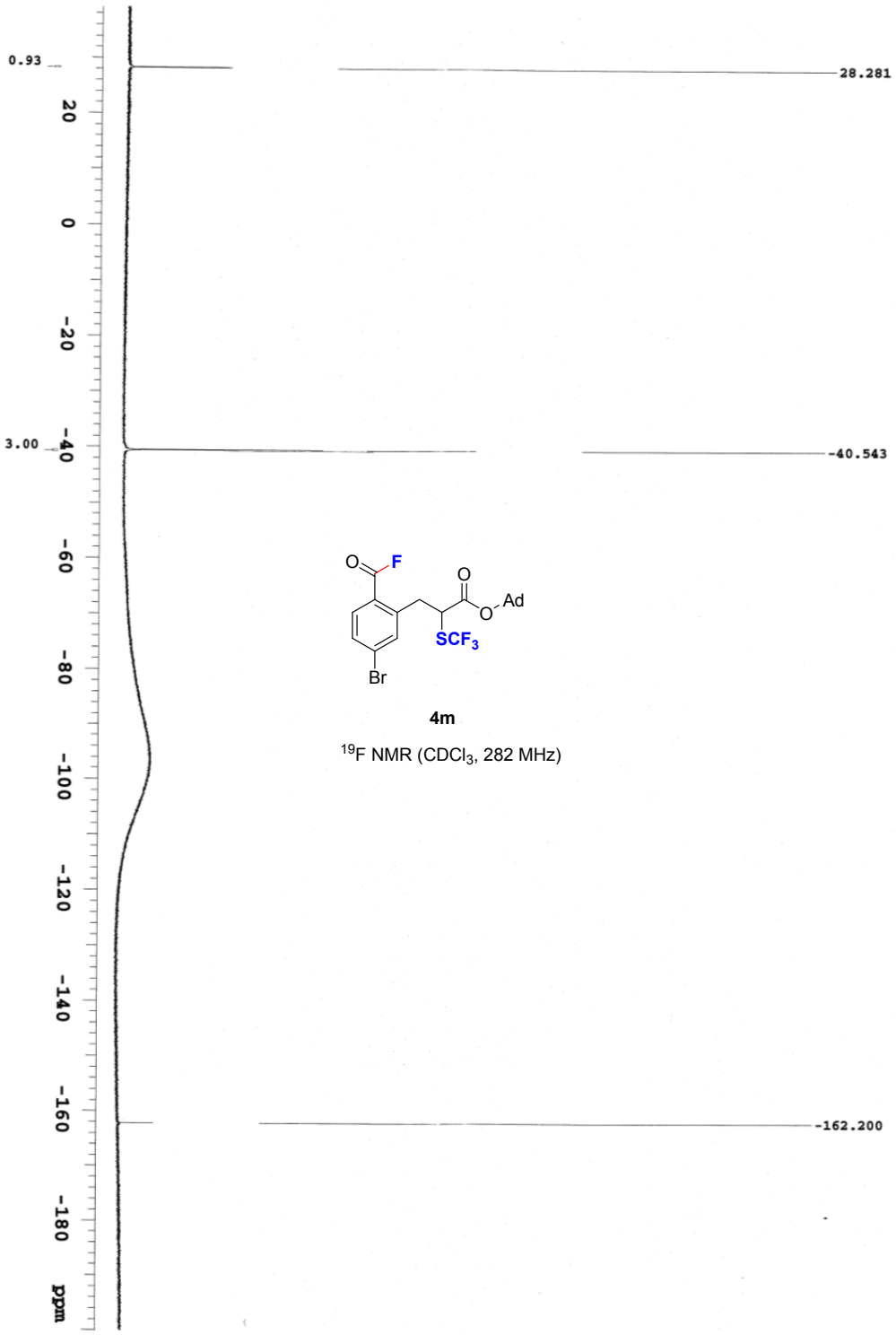

81-3
C13C
O
F
O
O
SCF3
4l
13C NMR (125.7 MHz, CDCl3)
169.973
157.836
155.088
141.307
141.243
135.132
133.730
133.352
133.320
133.230
131.284
128.837
128.417
126.394
123.984
123.534
69.960
46.448
37.021
21.516
21.427
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3.0



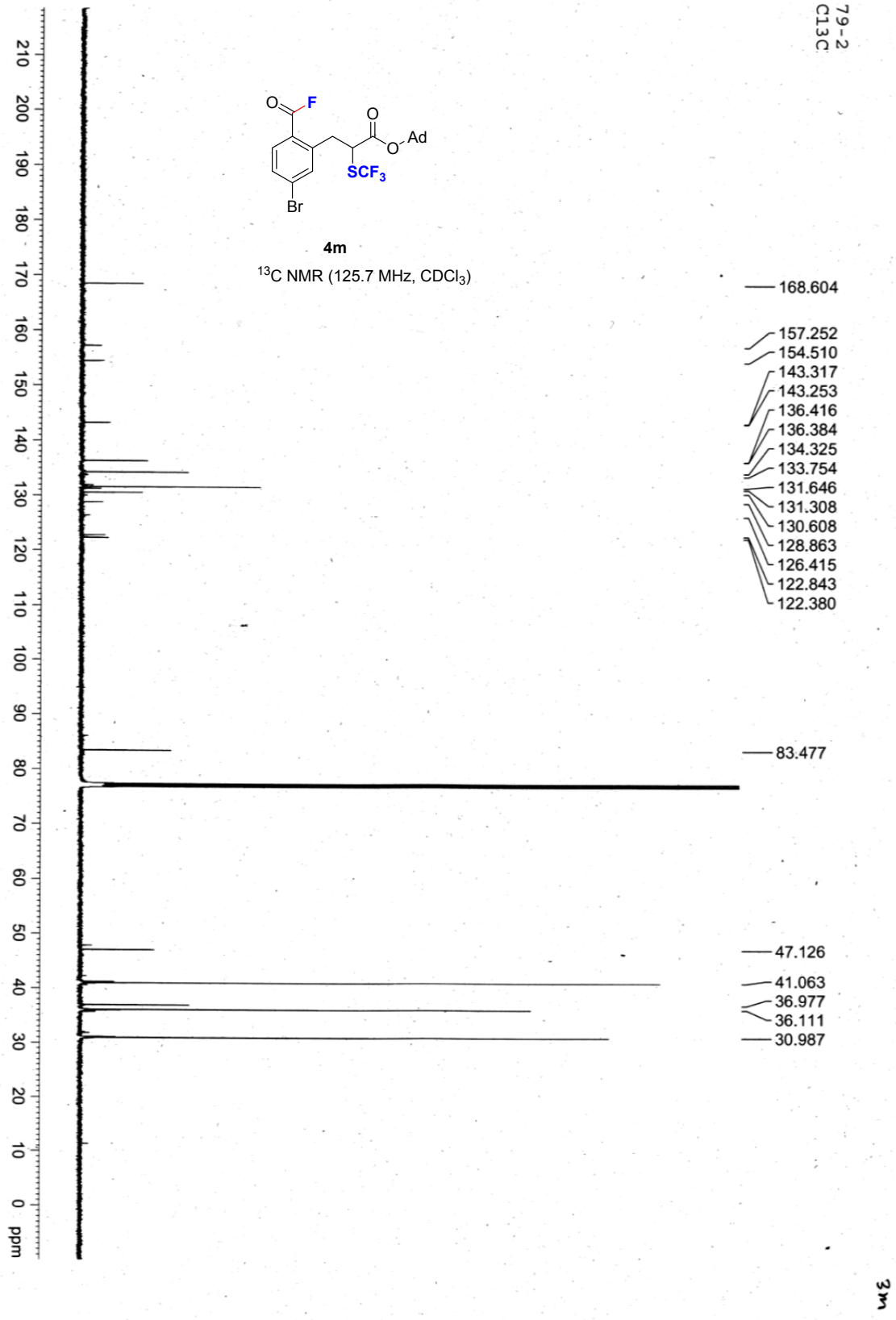
4m

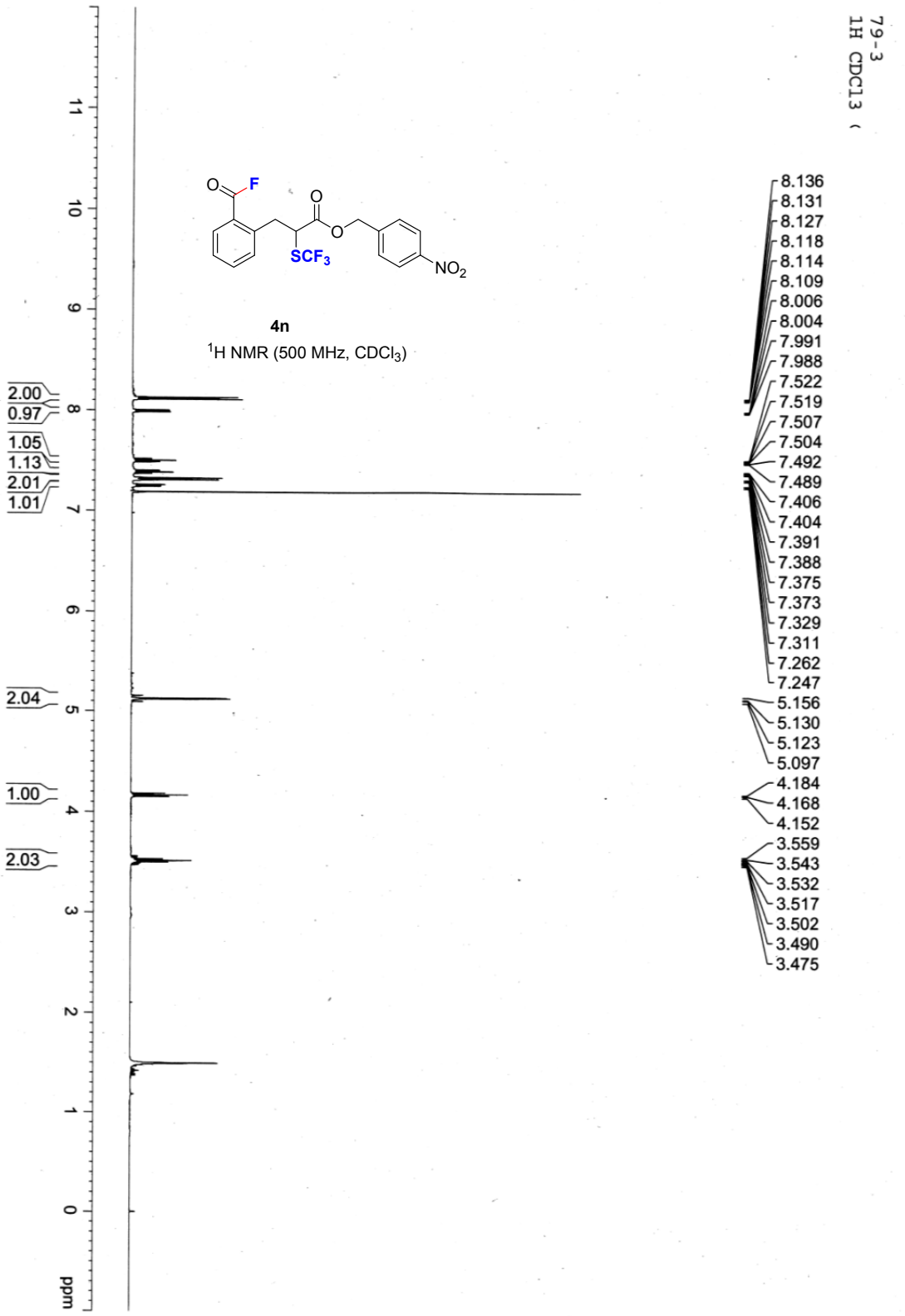
^{1}H NMR (500 MHz, $CDCl_3$)

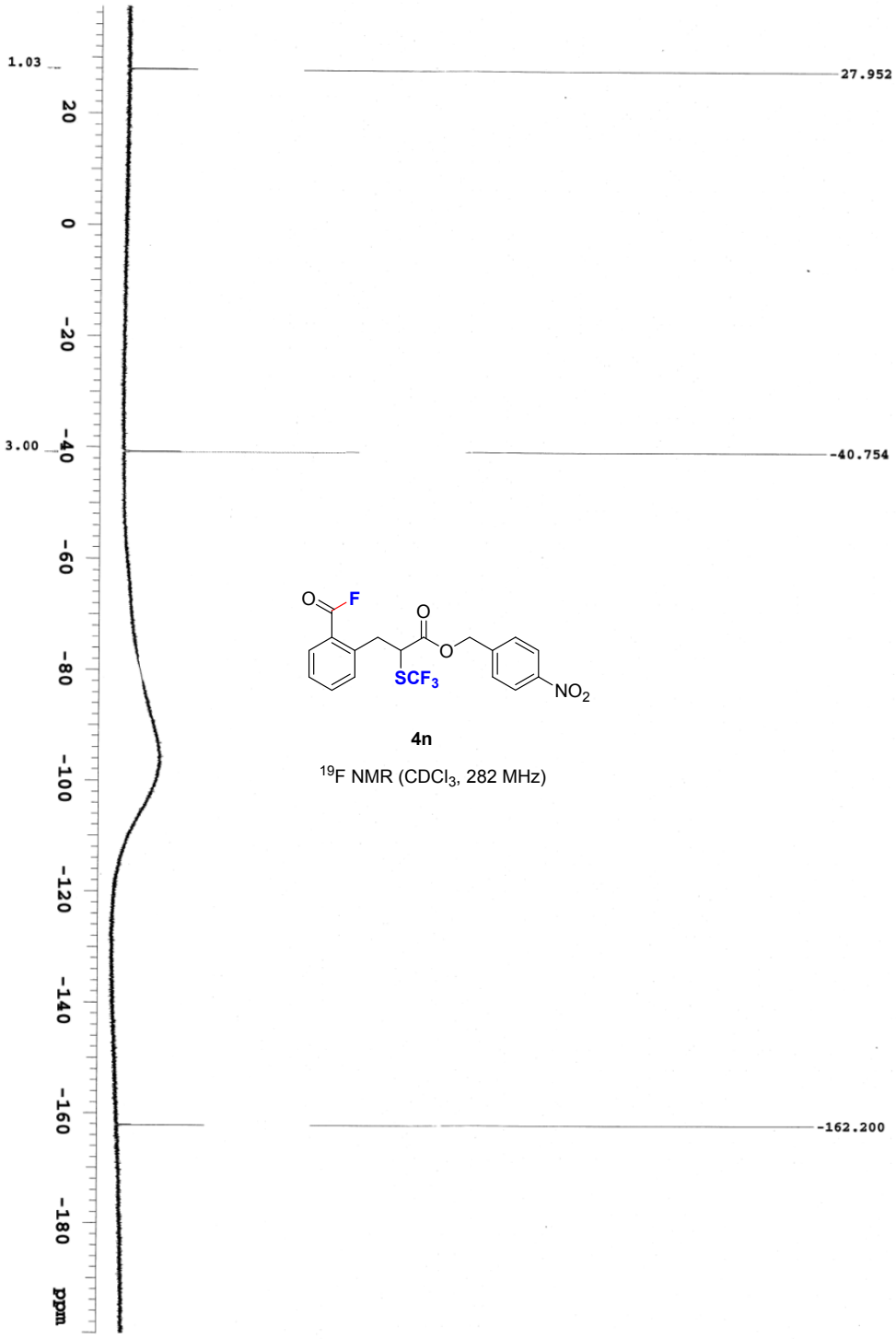


4m

^{19}F NMR ($CDCl_3$, 282 MHz)

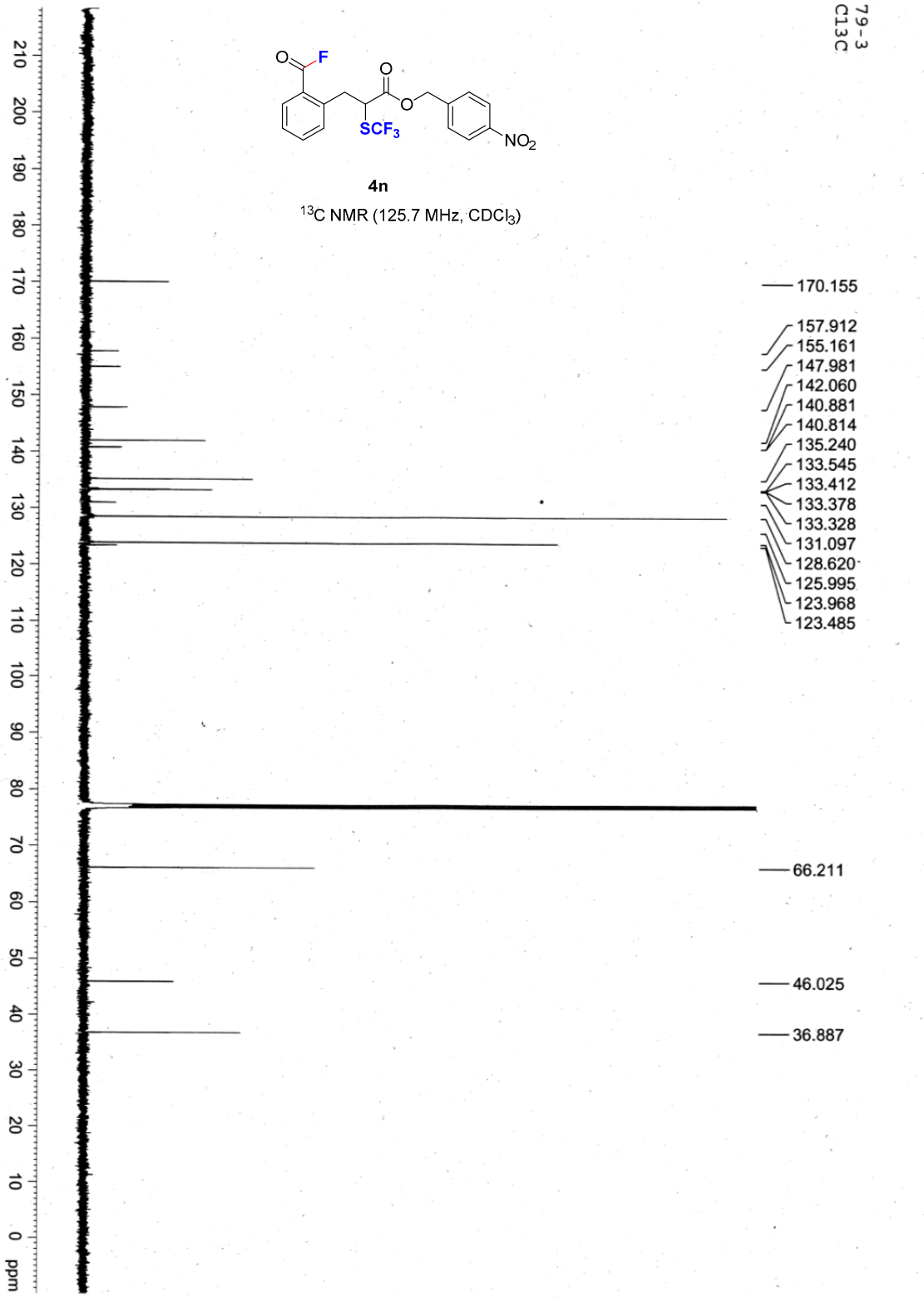

79-2
C13C
O
F
O
O
Ad
SCF3
Br
4m
13C NMR (125.7 MHz, CDCl3)
168.604
157.252
154.510
143.317
143.253
136.416
136.384
134.325
133.754
131.646
131.308
130.608
128.863
126.415
122.843
122.380
83.477
47.126
41.063
36.977
36.111
30.987
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
3m


79-3
1H CDCl3
8.136
8.131
8.127
8.118
8.114
8.109
8.006
8.004
7.991
7.988
7.522
7.519
7.507
7.504
7.492
7.489
7.406
7.404
7.391
7.388
7.375
7.373
7.329
7.311
7.262
7.247
5.156
5.130
5.123
5.097
4.184
4.168
4.152
3.559
3.543
3.532
3.517
3.502
3.490
3.475
2.00
0.97
1.05
1.13
2.01
1.01
2.04
1.00
2.03
ppm
O
F
O
O
SCF3
NO2
4n
1H NMR (500 MHz, CDCl3)
3n



4n

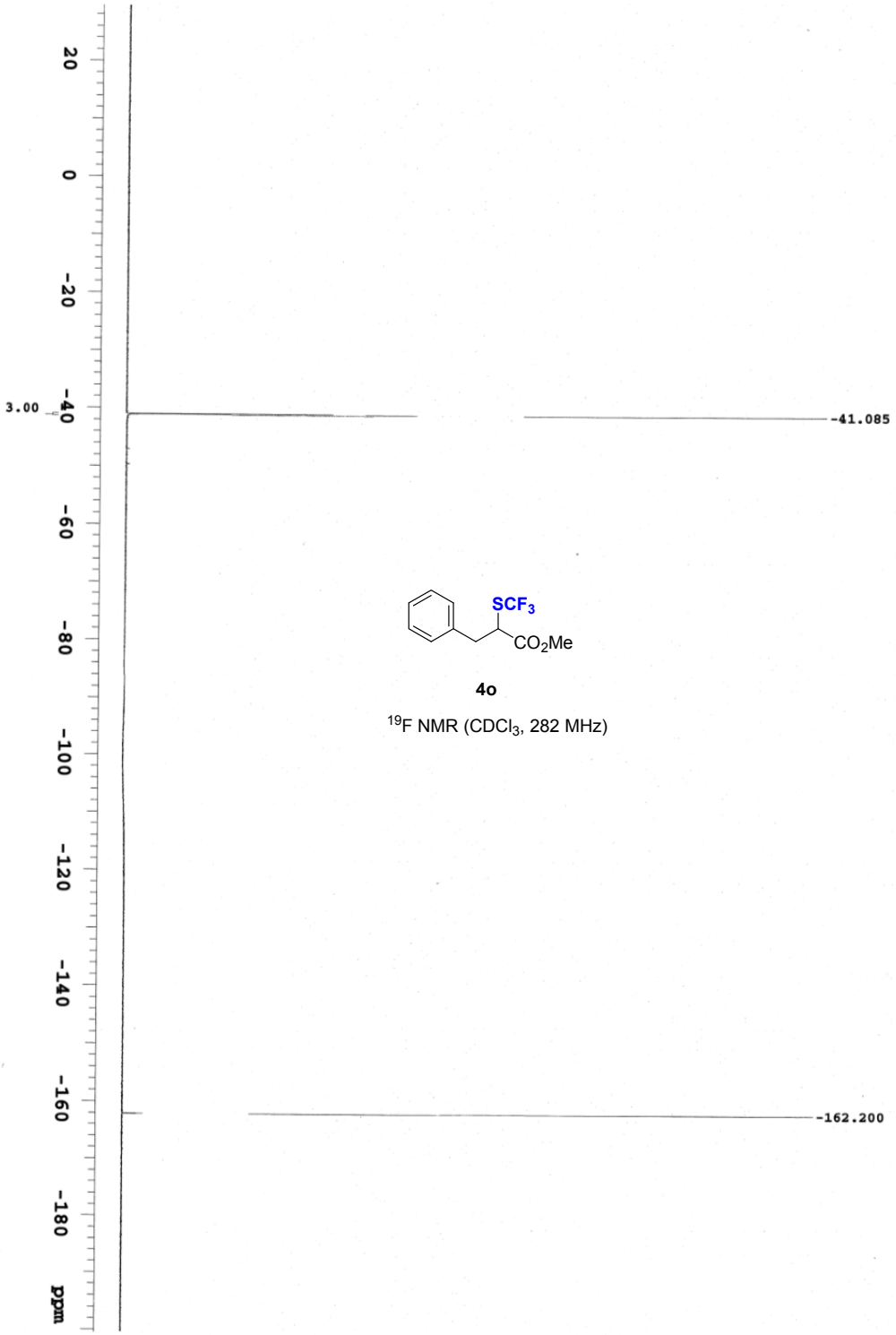
^{19}F NMR ($CDCl_3$, 282 MHz)


79-3
C13C
F
O
O
O
SCF3
NO2
4n
13C NMR (125.7 MHz, CDCl3)
170.155
157.912
155.161
147.981
142.060
140.881
140.814
135.240
133.545
133.412
133.378
133.328
131.097
128.620
125.995
123.968
123.485
66.211
46.025
36.887
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3n

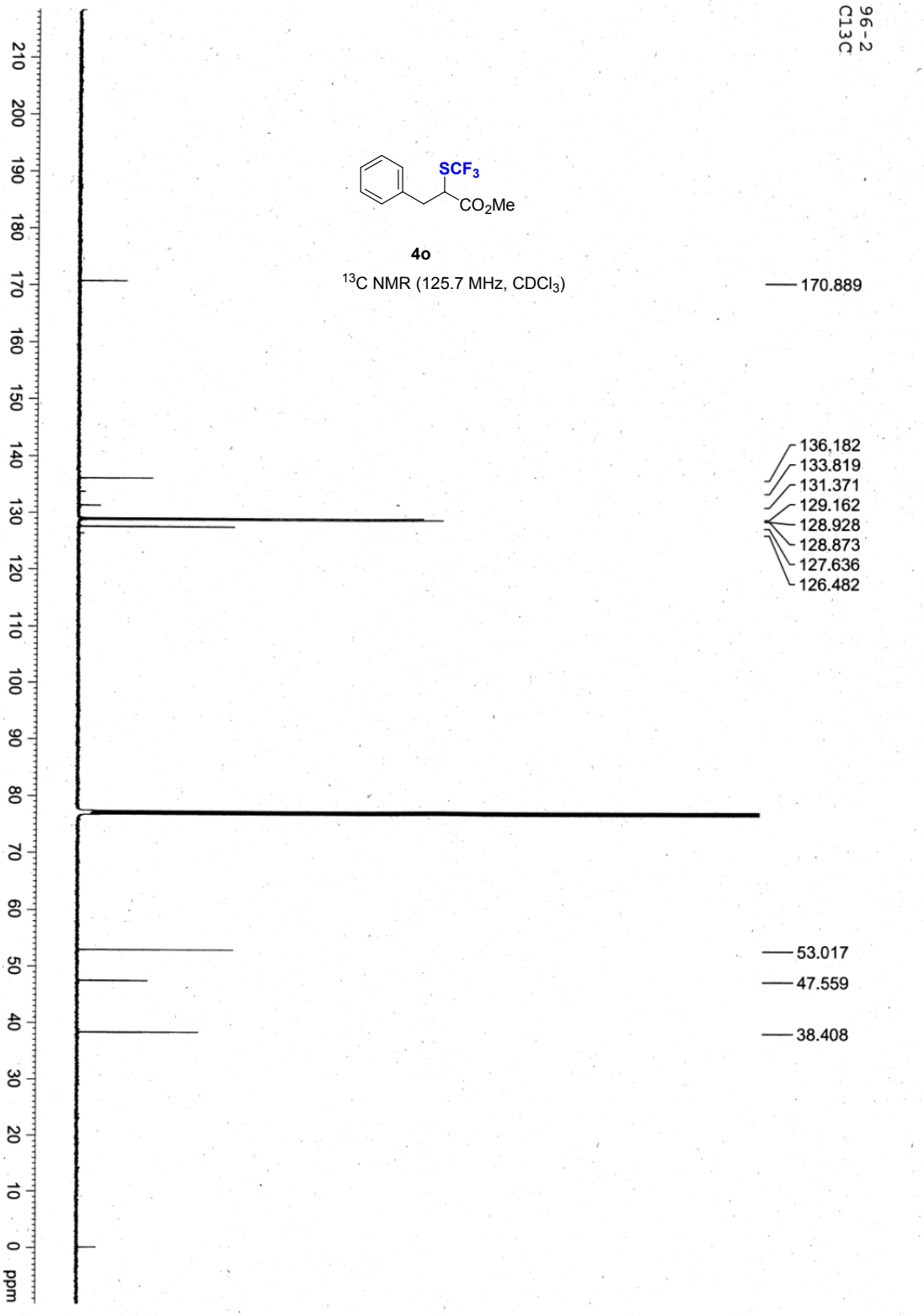
96-2
1H CDCl3 (
SCF3
CO2Me
4o
1H NMR (500 MHz, CDCl3)
7.333
7.330
7.327
7.321
7.317
7.314
7.305
7.302
7.298
7.286
7.283
7.281
7.274
7.269
7.260
7.254
7.194
7.191
7.187
7.177
4.049
4.037
4.031
4.018
3.682
3.264
3.245
3.236
3.217
3.152
3.139
3.124
3.111
2.01
0.87
2.00
1.00
3.06
1.06
1.06
ppm

30



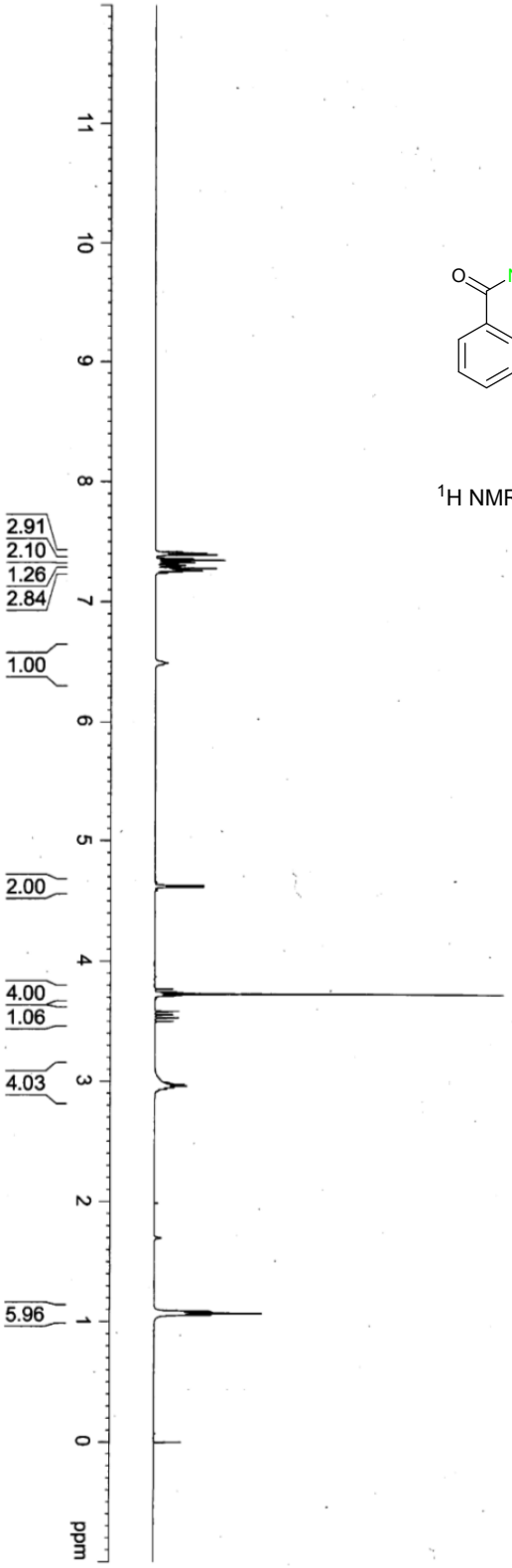
4o

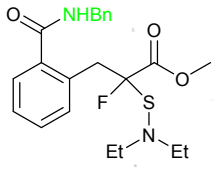
^{19}F NMR ($CDCl_3$, 282 MHz)


96-2
C13C
SCF3
CO2Me
4o
13C NMR (125.7 MHz, CDCl3)
170.889
136.182
133.819
131.371
129.162
128.928
128.873
127.636
126.482
53.017
47.559
38.408
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

30

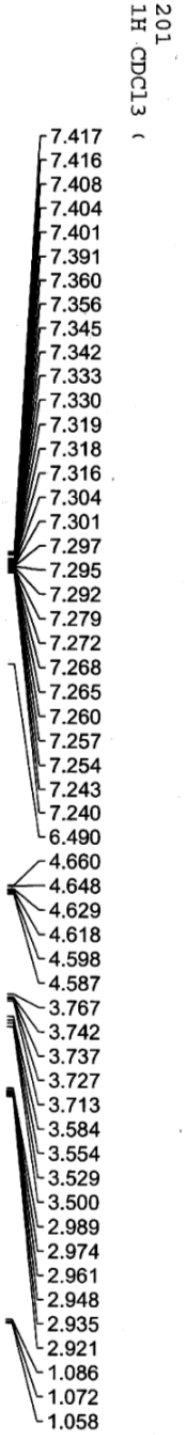
22. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for transformation of acid fluorides 2b and 4b to ketones 5a, 6a amides 5b, 6b and ester 6c (Scheme 2);

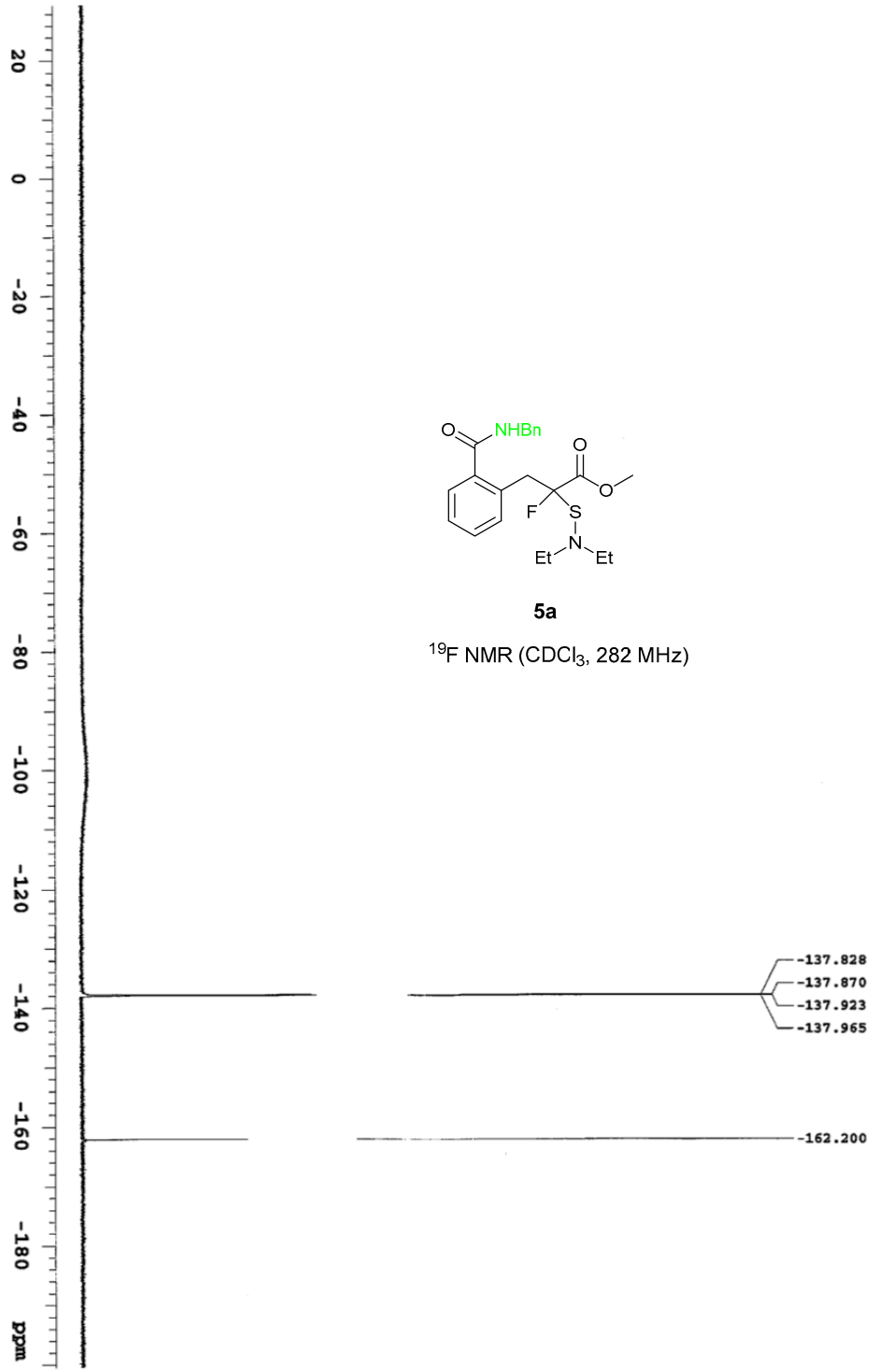




5a

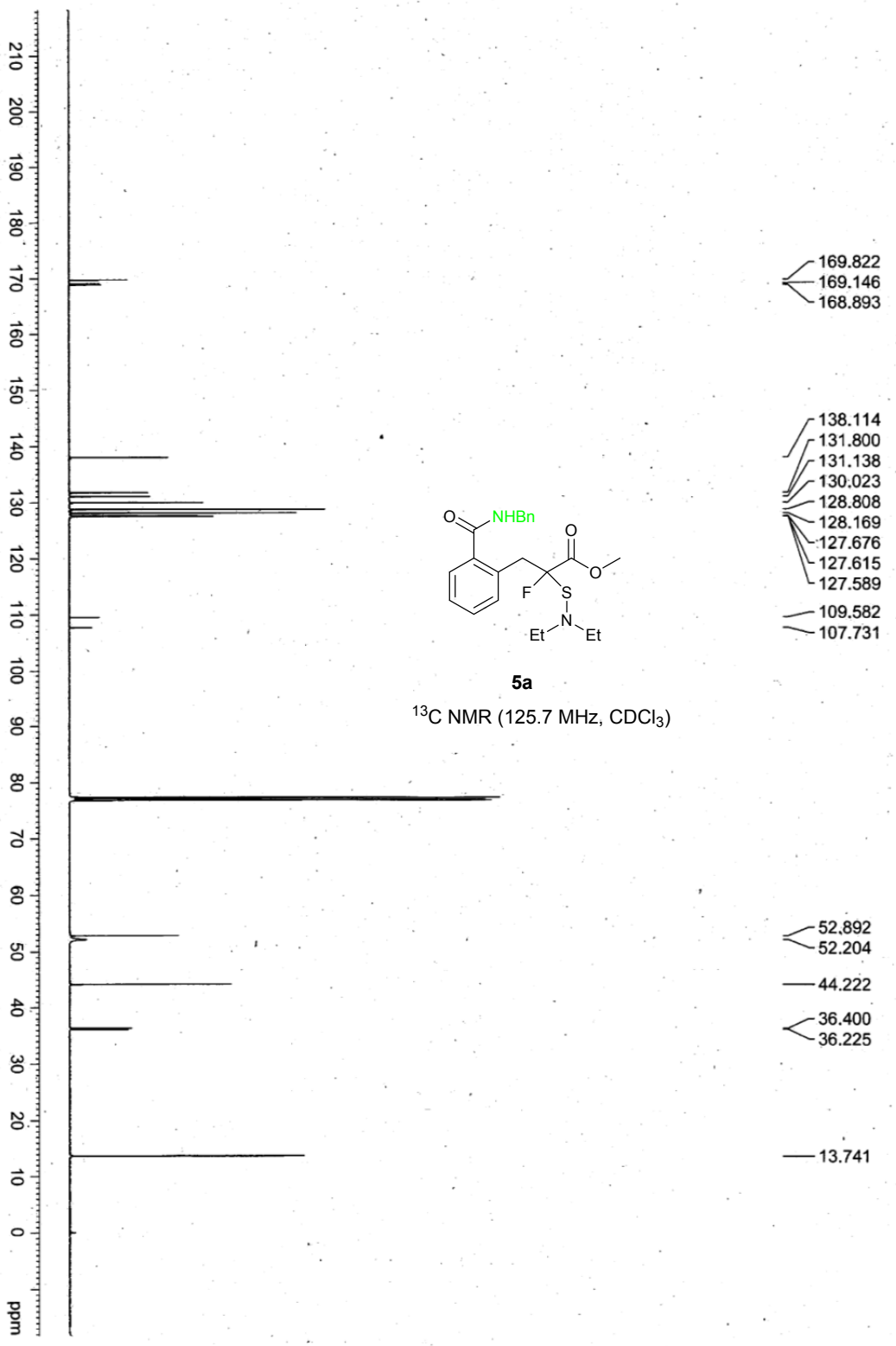
^{1}H NMR (500 MHz, $CDCl_3$)





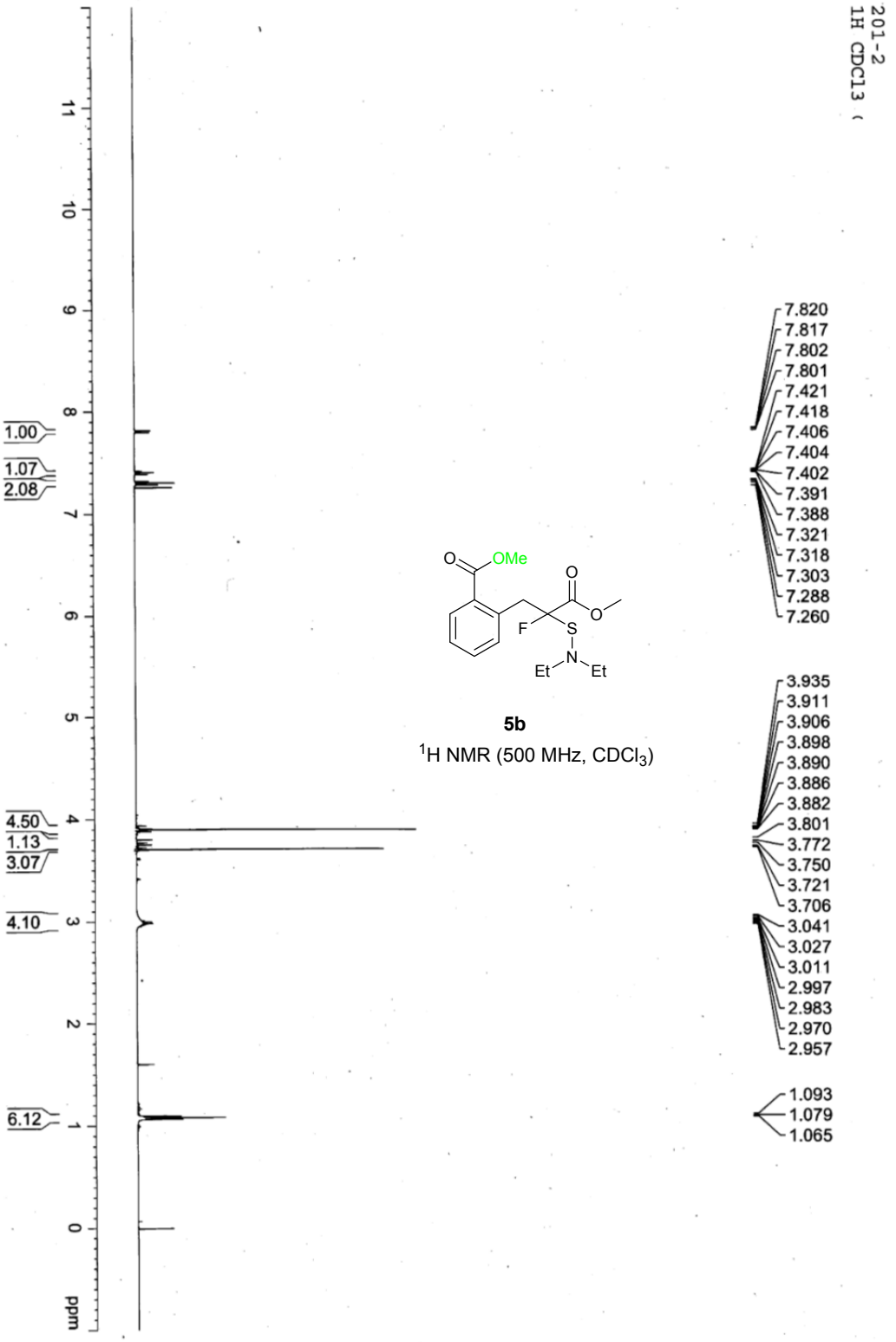
5a

^{19}F NMR ($CDCl_3$, 282 MHz)



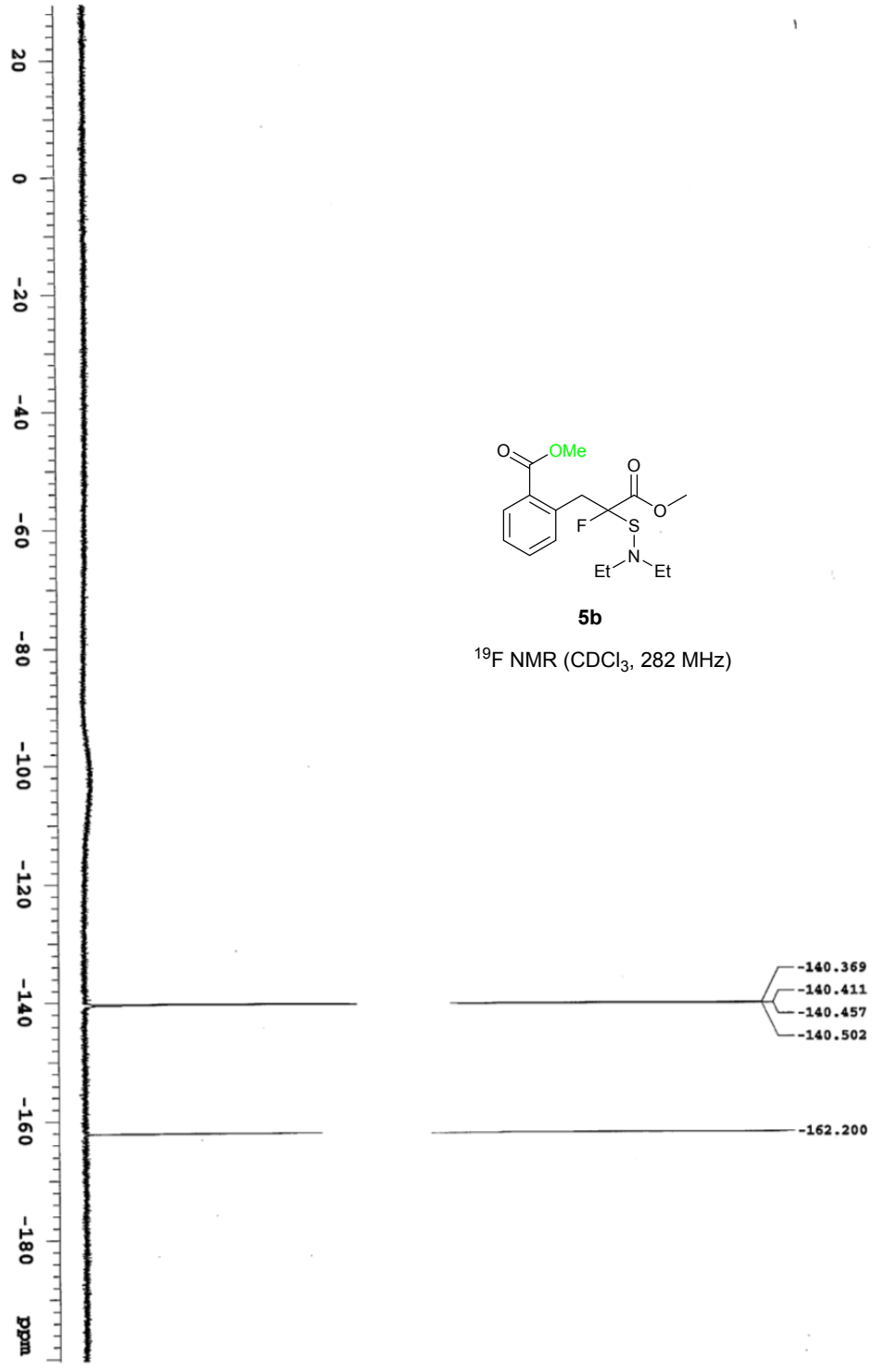
5a

^{13}C NMR (125.7 MHz, $CDCl_3$)



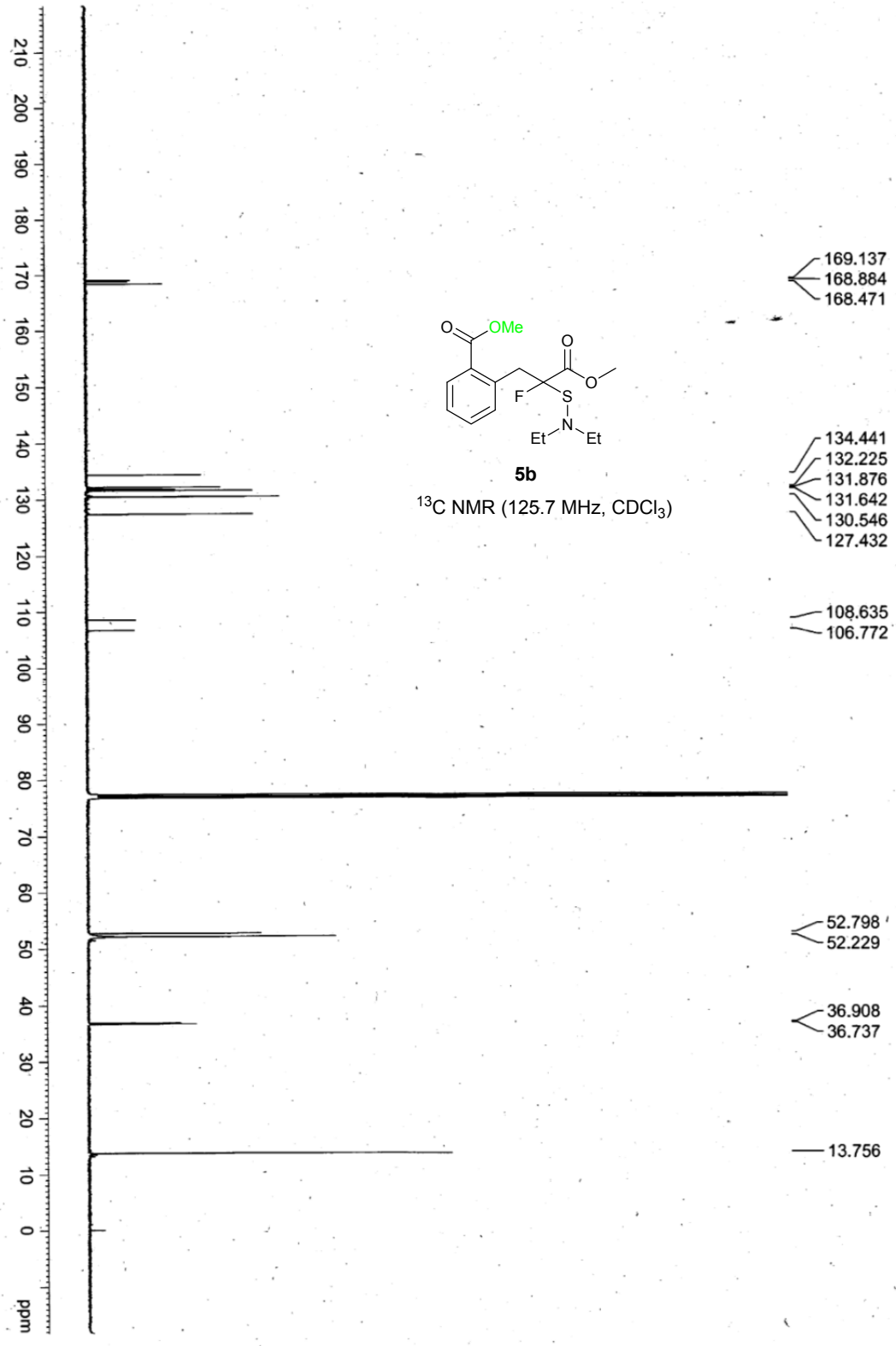
5b

^{1}H NMR (500 MHz, $CDCl_3$)



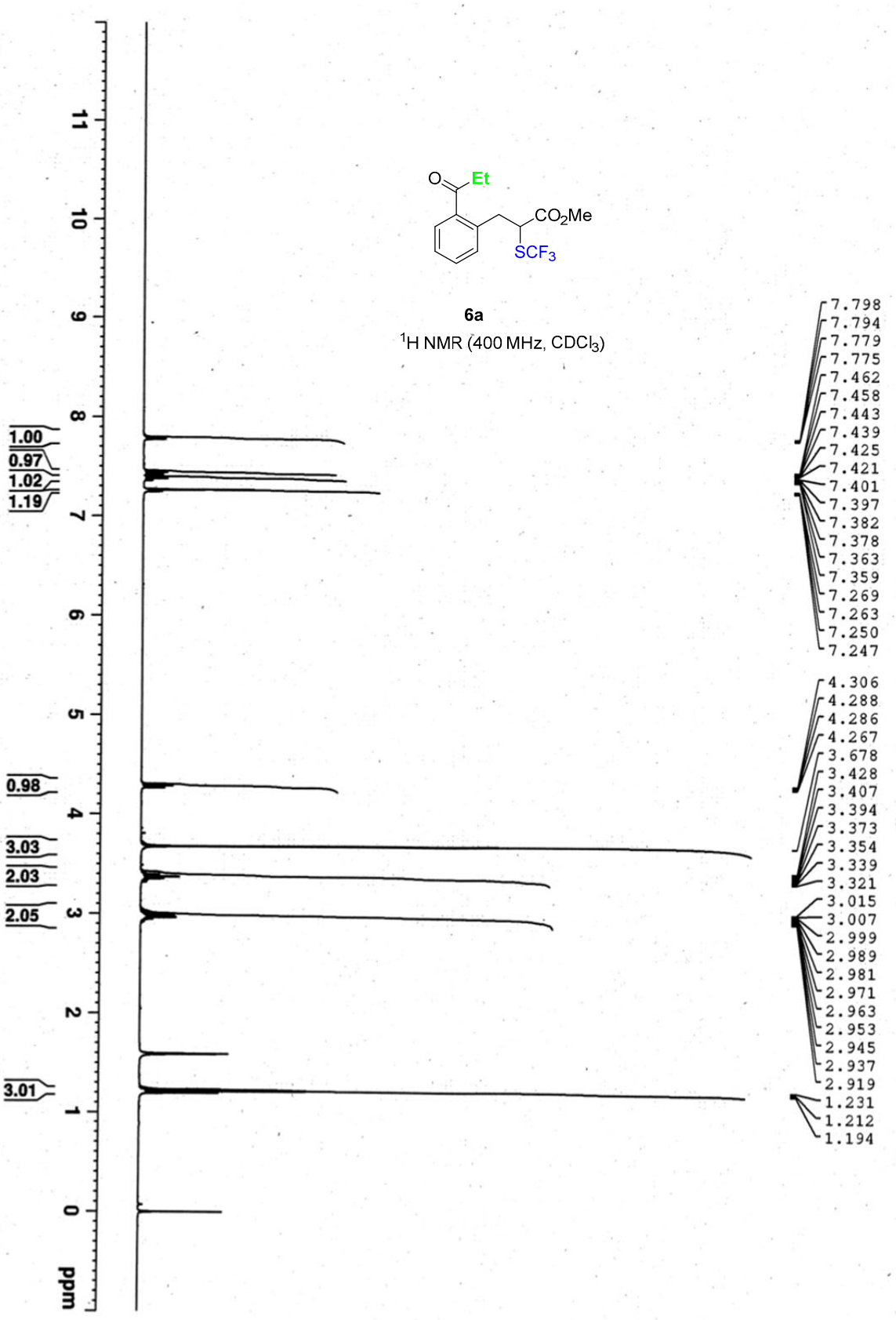
5b

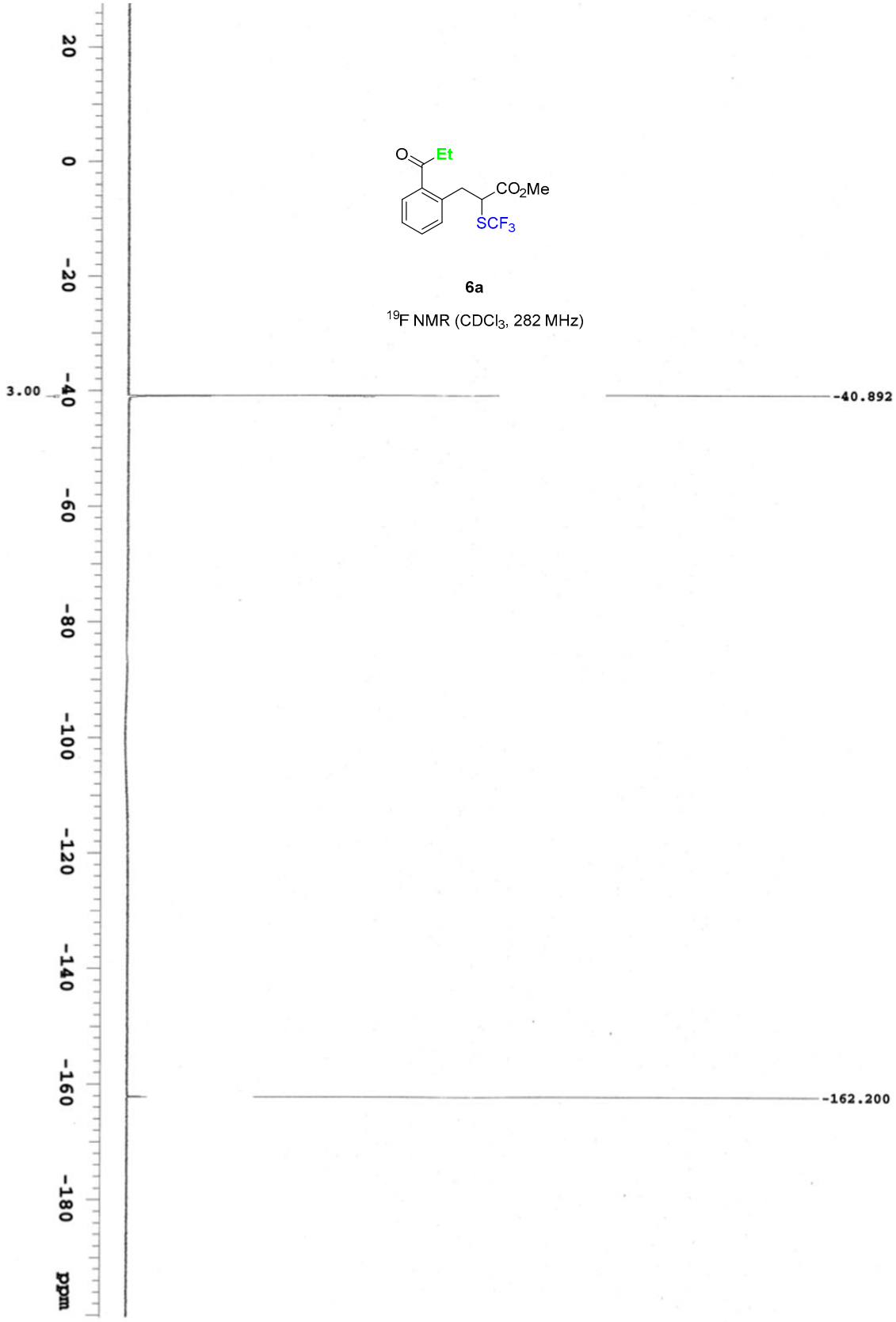
^{19}F NMR ($CDCl_3$, 282 MHz)



5b

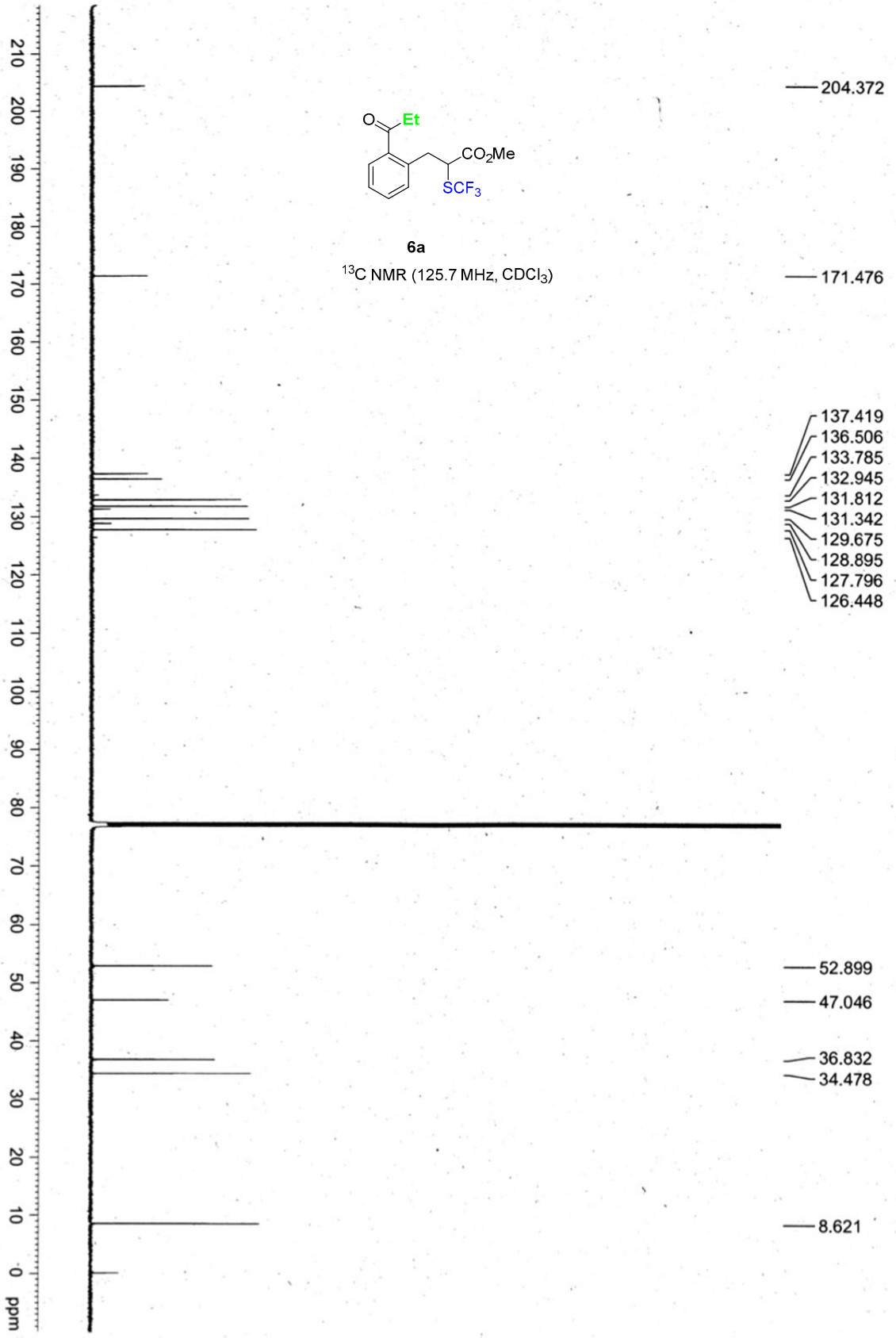
^{13}C NMR (125.7 MHz, $CDCl_3$)

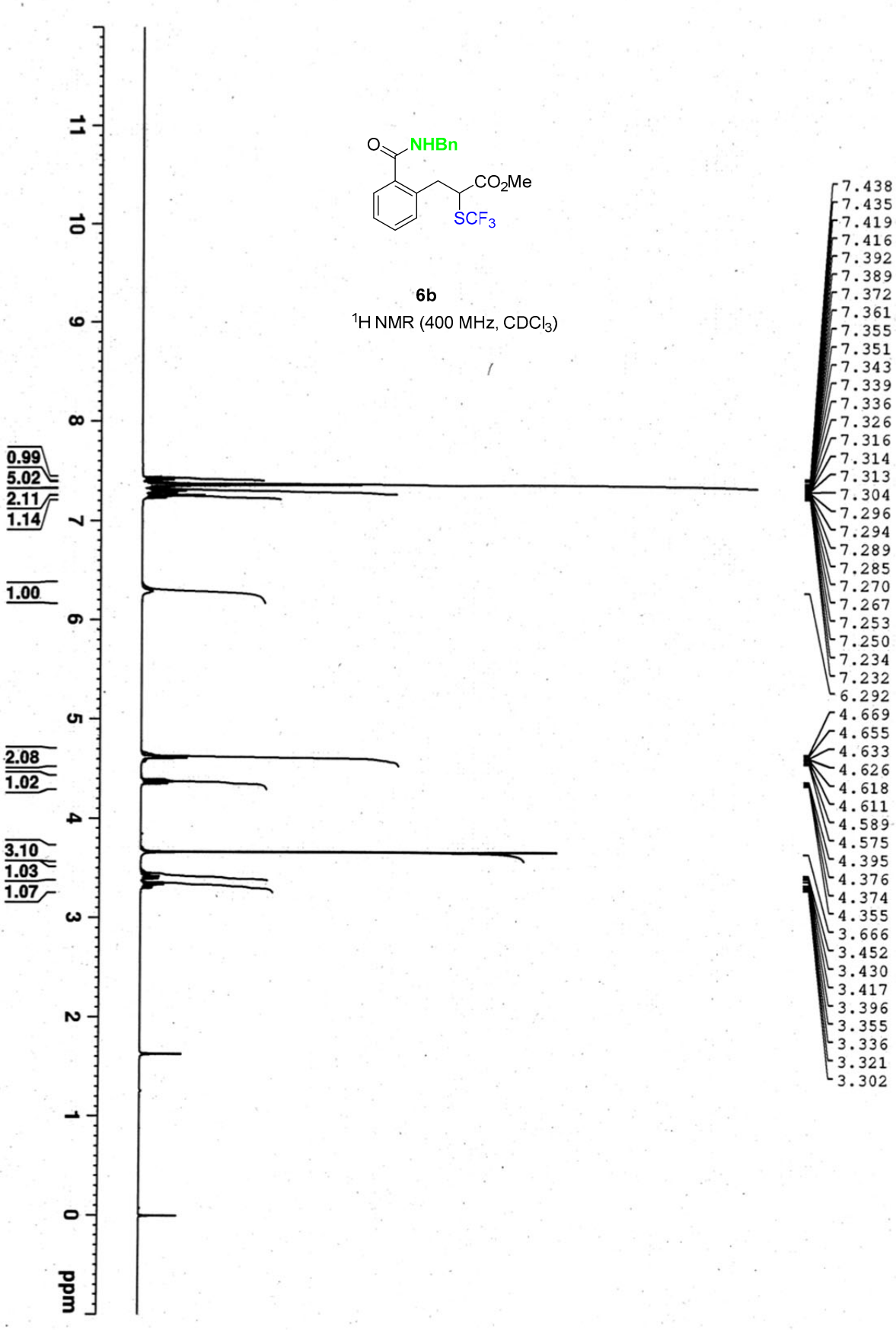

O
Et
CO2Me
SCF3
6a
1H NMR (400 MHz, CDCl3)
7.798
7.794
7.779
7.775
7.462
7.458
7.443
7.439
7.425
7.421
7.401
7.397
7.382
7.378
7.363
7.359
7.269
7.263
7.250
7.247
4.306
4.288
4.286
4.267
3.678
3.428
3.407
3.394
3.373
3.354
3.339
3.321
3.015
3.007
2.999
2.989
2.981
2.971
2.963
2.953
2.945
2.937
2.919
1.231
1.212
1.194
1.00
0.97
1.02
1.19
0.98
3.03
2.03
2.05
3.01
ppm

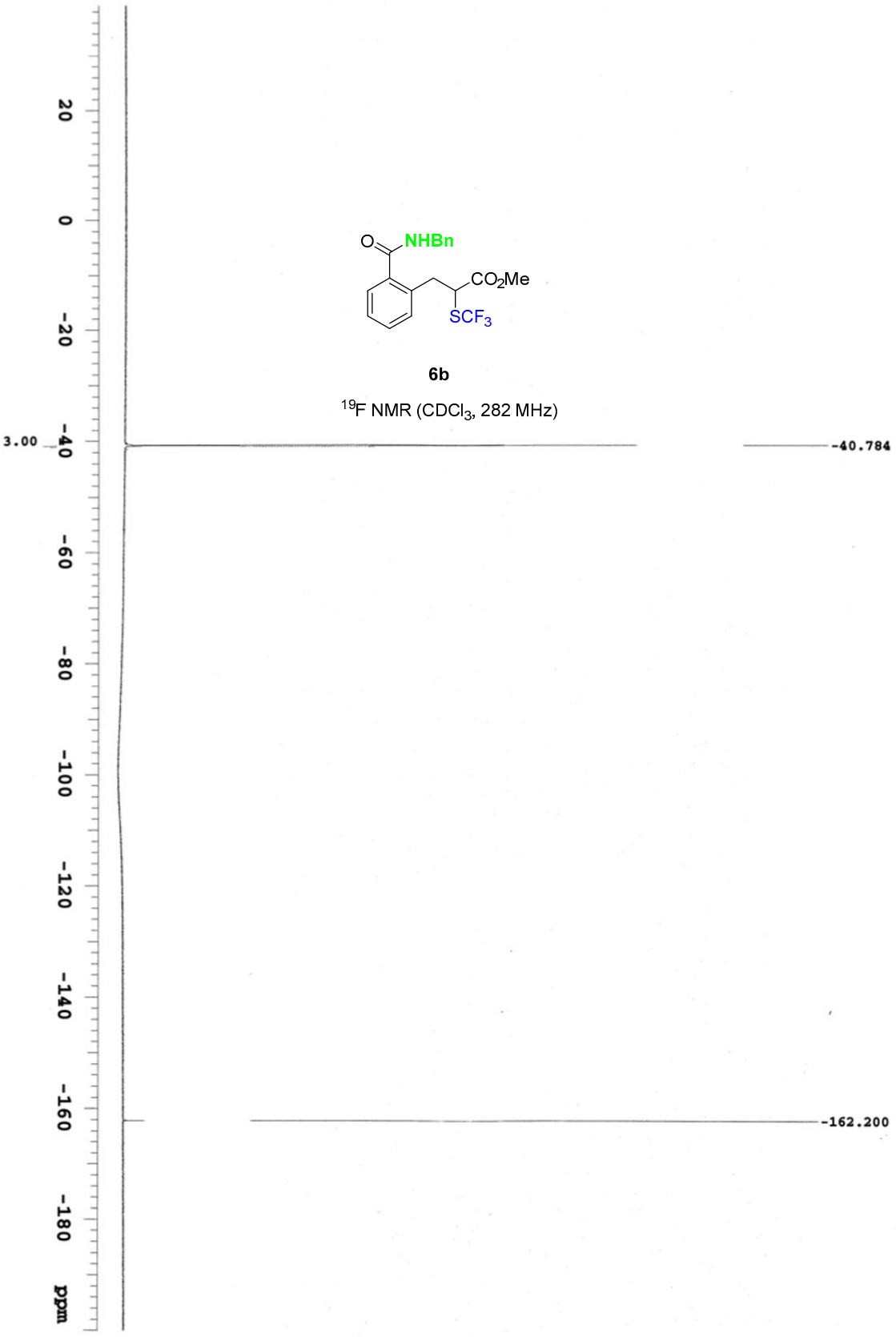


6a

^{19}F NMR ($CDCl_3$, 282 MHz)

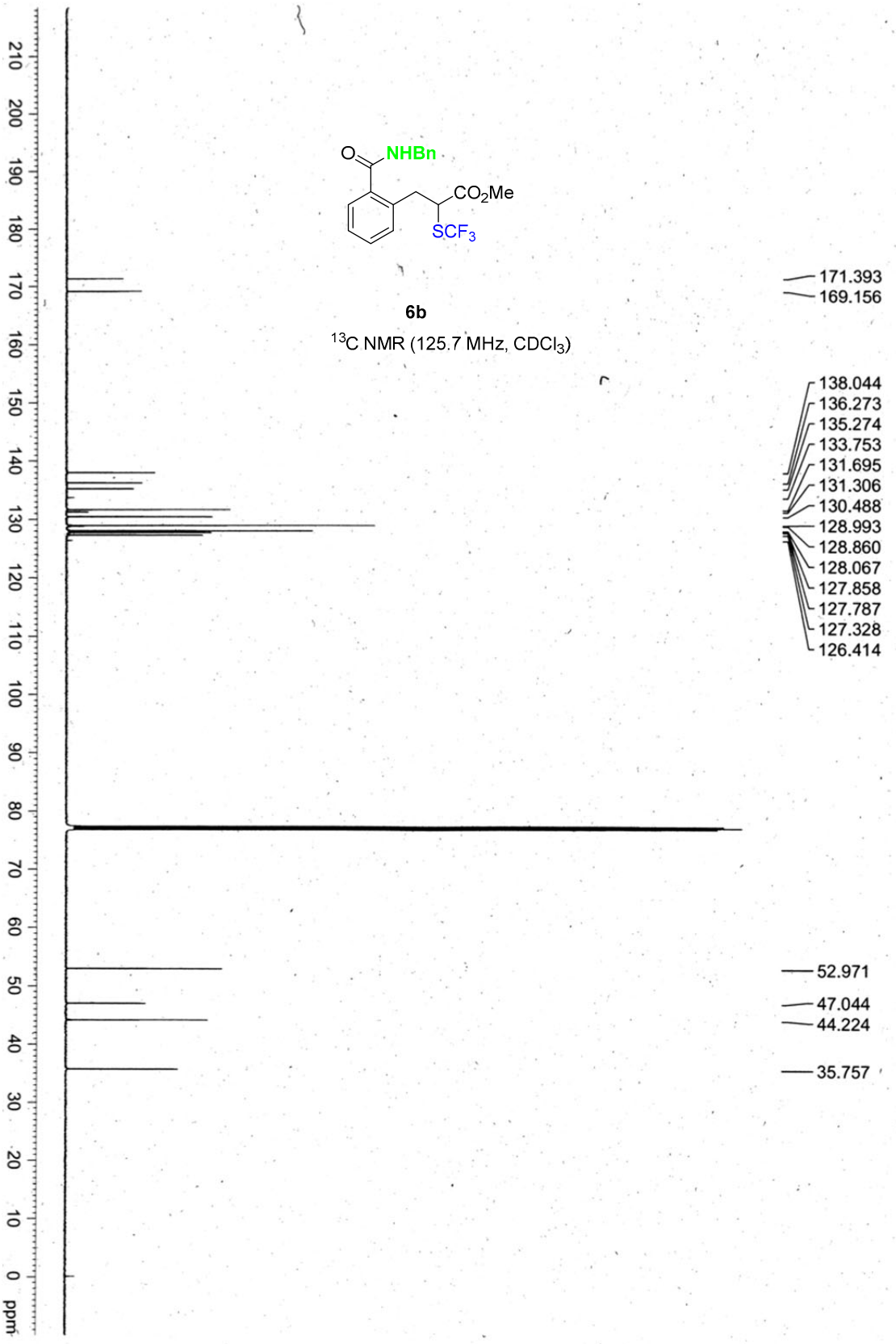

O
Et
CO2Me
SCF3
6a
13C NMR (125.7 MHz, CDCl3)
204.372
171.476
137.419
136.506
133.785
132.945
131.812
131.342
129.675
128.895
127.796
126.448
52.899
47.046
36.832
34.478
8.621
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

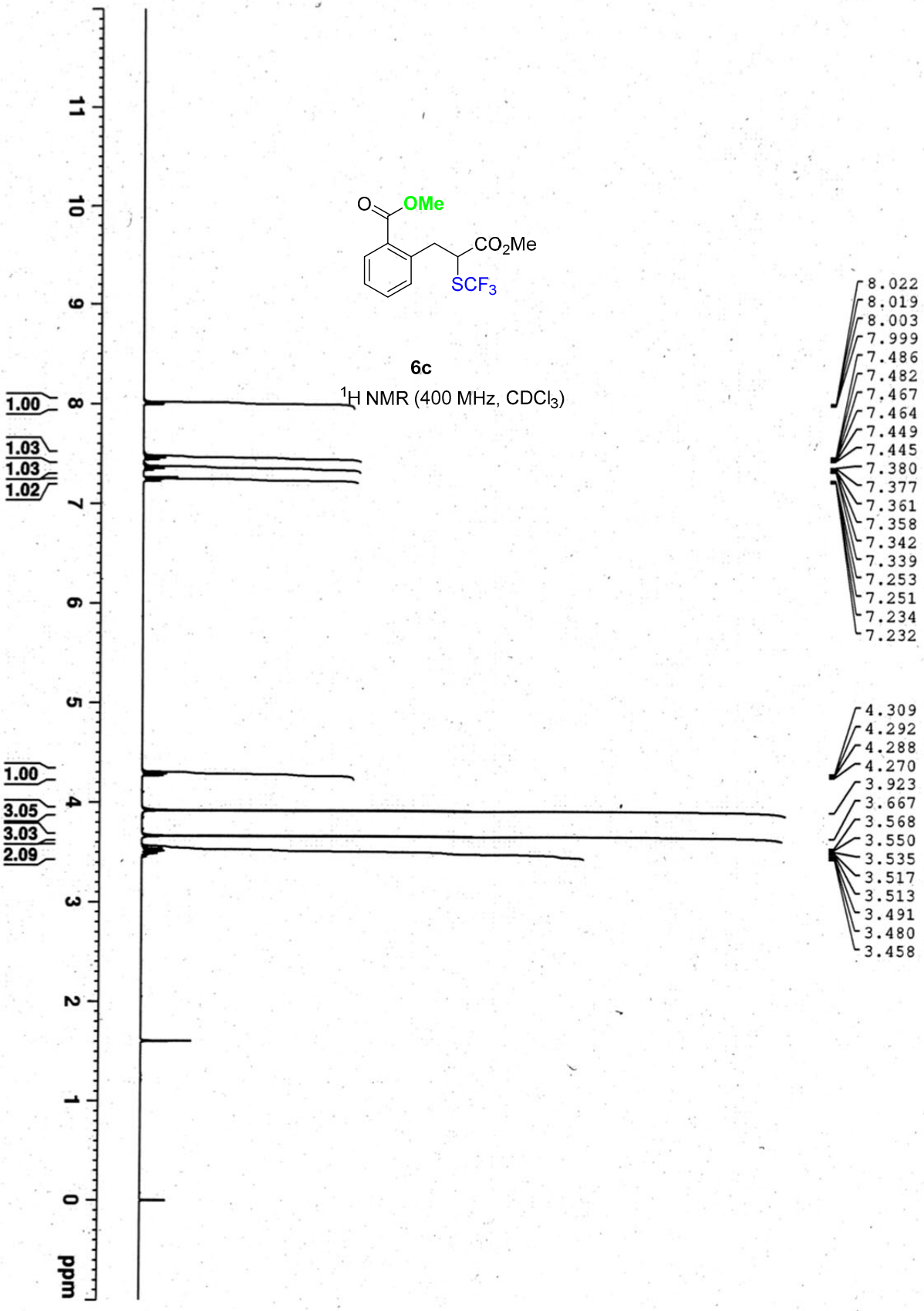

O
NHBn
CO2Me
SCF3
6b
1H NMR (400 MHz, CDCl3)
0.99
5.02
2.11
1.14
1.00
2.08
1.02
3.10
1.03
1.07
ppm
7.438
7.435
7.419
7.416
7.392
7.389
7.372
7.361
7.355
7.351
7.343
7.339
7.336
7.326
7.316
7.314
7.313
7.304
7.296
7.294
7.289
7.285
7.270
7.267
7.253
7.250
7.234
7.232
6.292
4.669
4.655
4.633
4.626
4.618
4.611
4.589
4.575
4.395
4.376
4.374
4.355
3.666
3.452
3.430
3.417
3.396
3.355
3.336
3.321
3.302

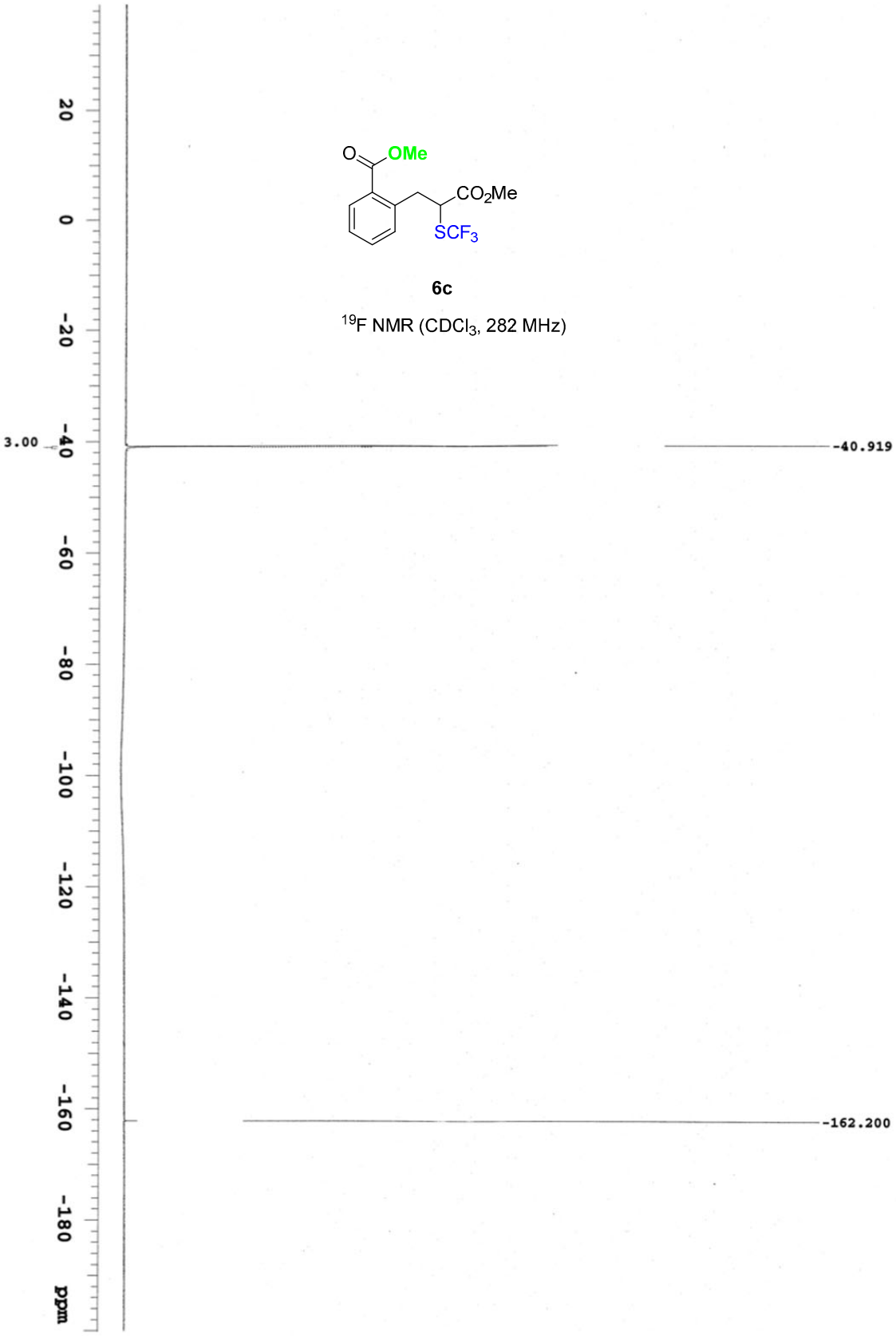


6b

^{19}F NMR ($CDCl_3$, 282 MHz)

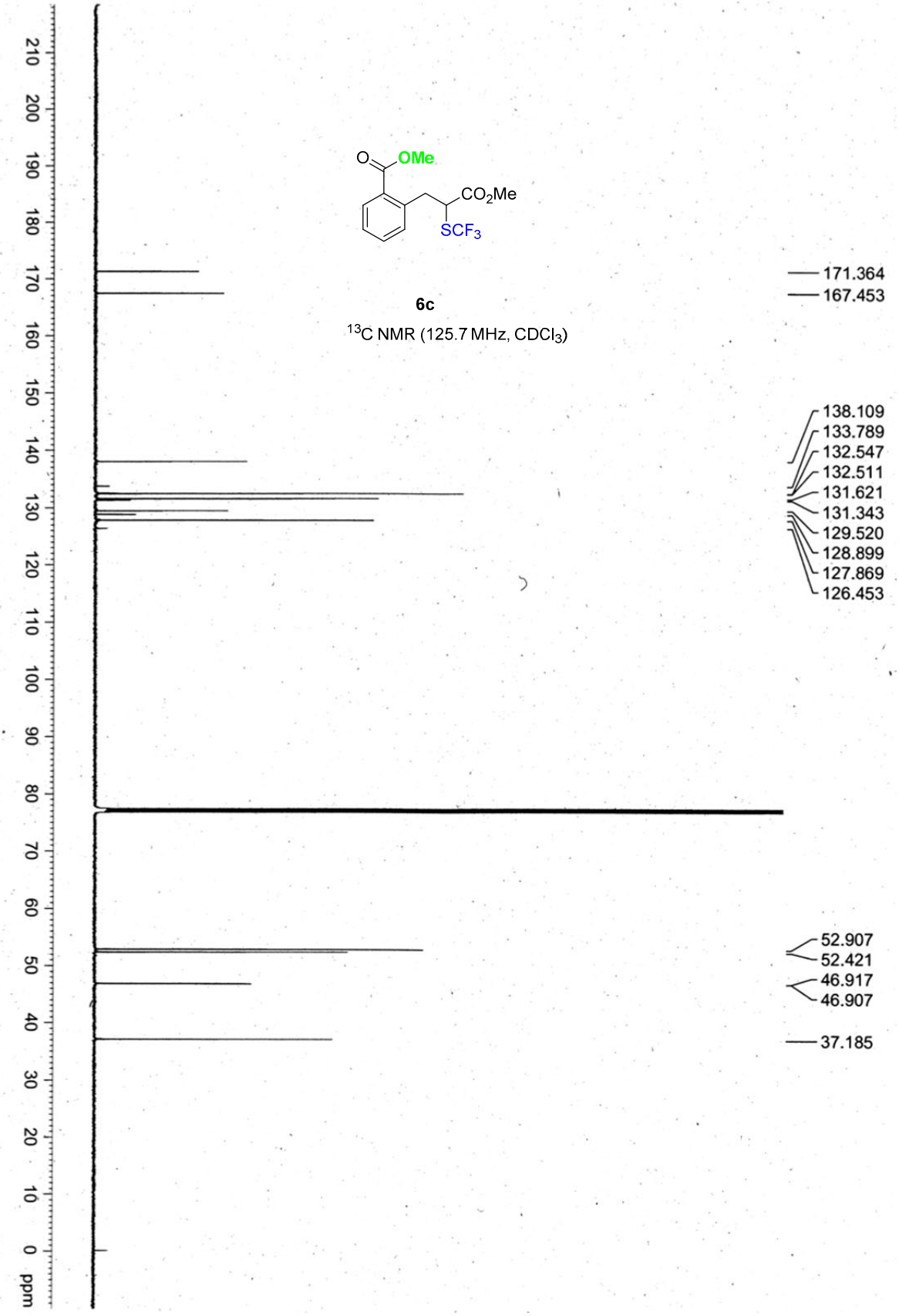

O
NHBn
CO2Me
SCF3
6b
13C NMR (125.7 MHz, CDCl3)
171.393
169.156
138.044
136.273
135.274
133.753
131.695
131.306
130.488
128.993
128.860
128.067
127.858
127.787
127.328
126.414
52.971
47.044
44.224
35.757
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OMe
CO2Me
SCF3
6c
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.03
1.02
1.00
3.05
3.03
2.09
8.022
8.019
8.003
7.999
7.486
7.482
7.467
7.464
7.449
7.445
7.380
7.377
7.361
7.358
7.342
7.339
7.253
7.251
7.234
7.232
4.309
4.292
4.288
4.270
3.923
3.667
3.568
3.550
3.535
3.517
3.513
3.491
3.480
3.458
ppm

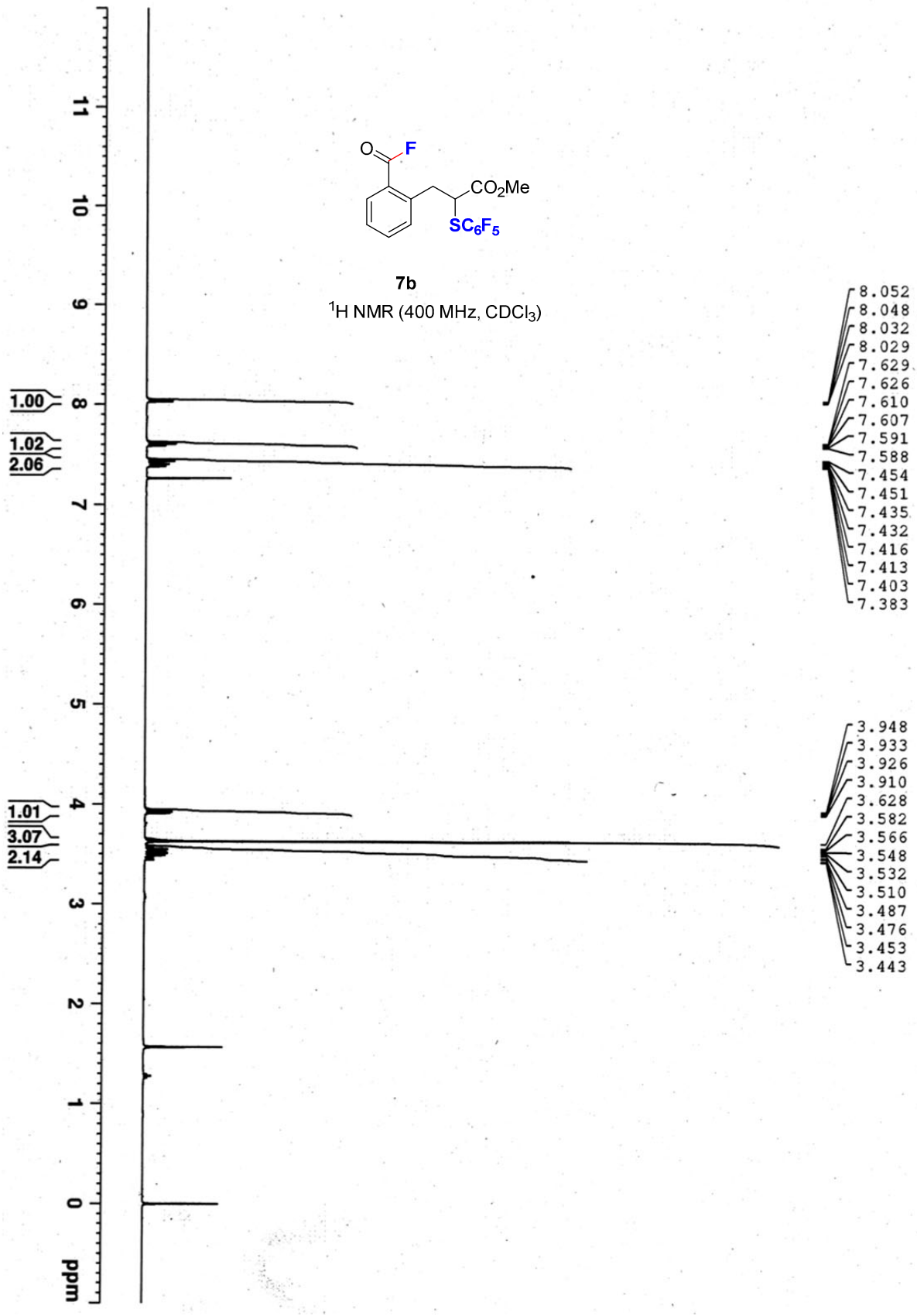


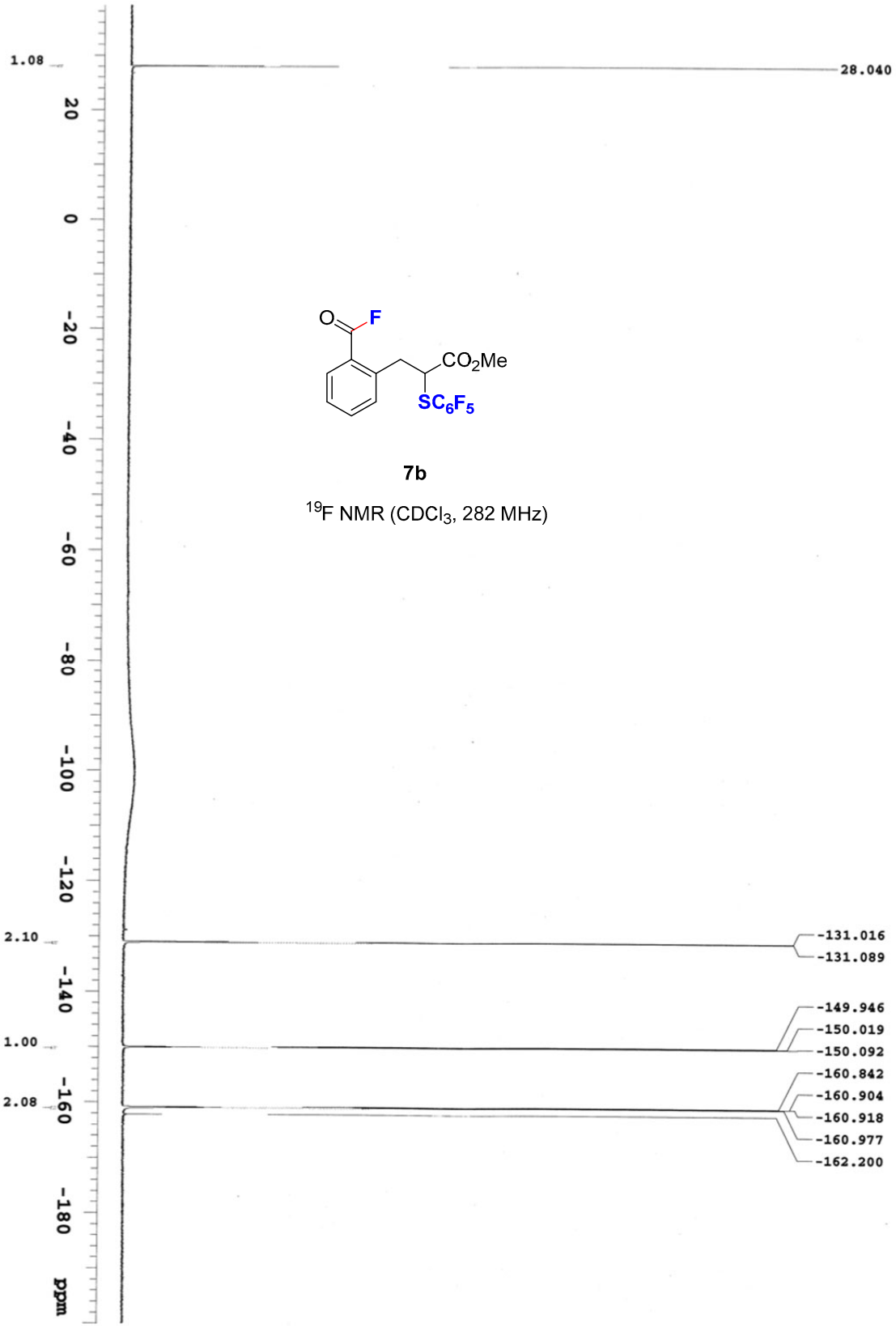
6c

^{19}F NMR ($CDCl_3$, 282 MHz)


O
OMe
CO2Me
SCF3
6c
13C NMR (125.7 MHz, CDCl3)
171.364
167.453
138.109
133.789
132.547
132.511
131.621
131.343
129.520
128.899
127.869
126.453
52.907
52.421
46.917
46.907
37.185
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

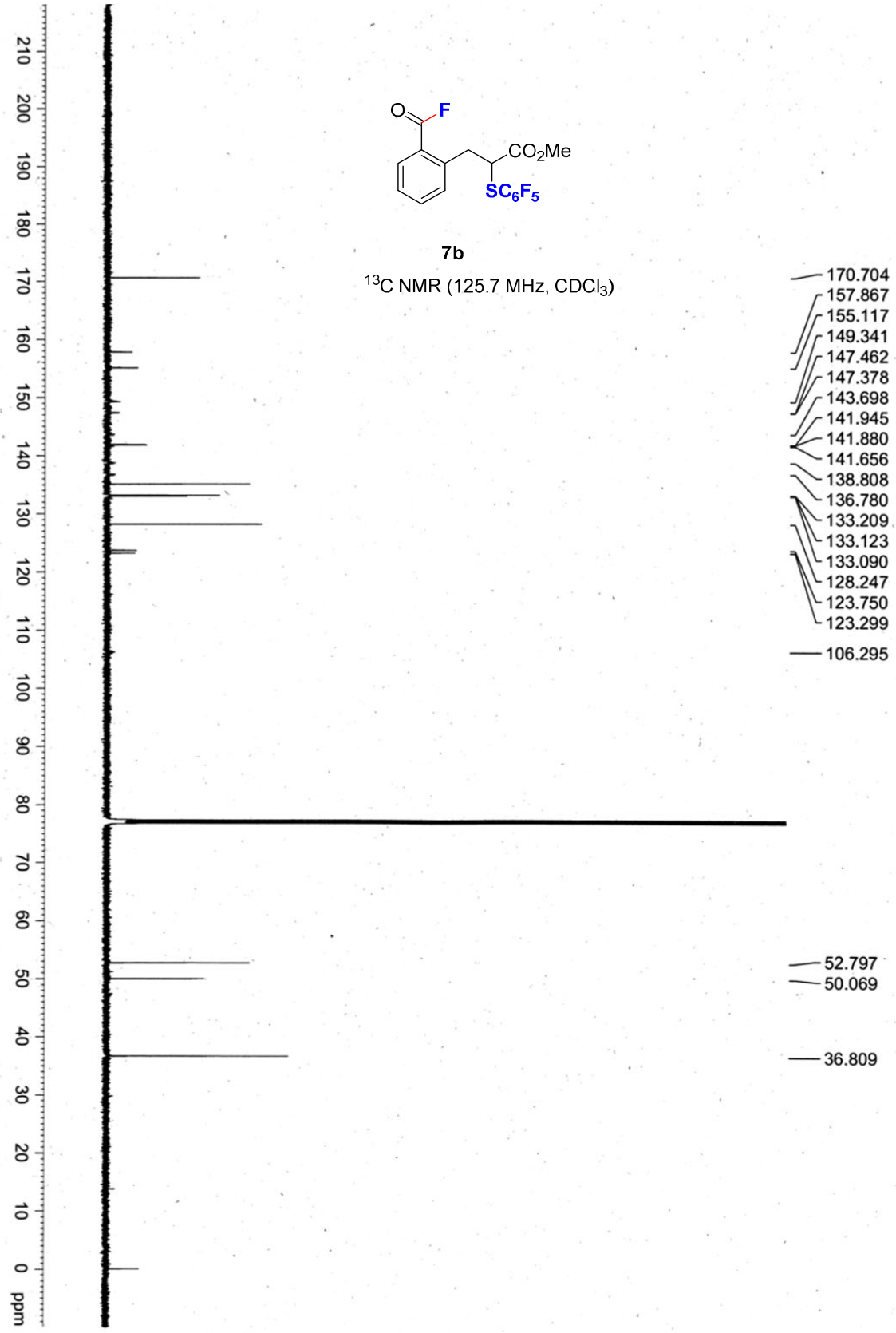
23. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for product 7b (Scheme 3)



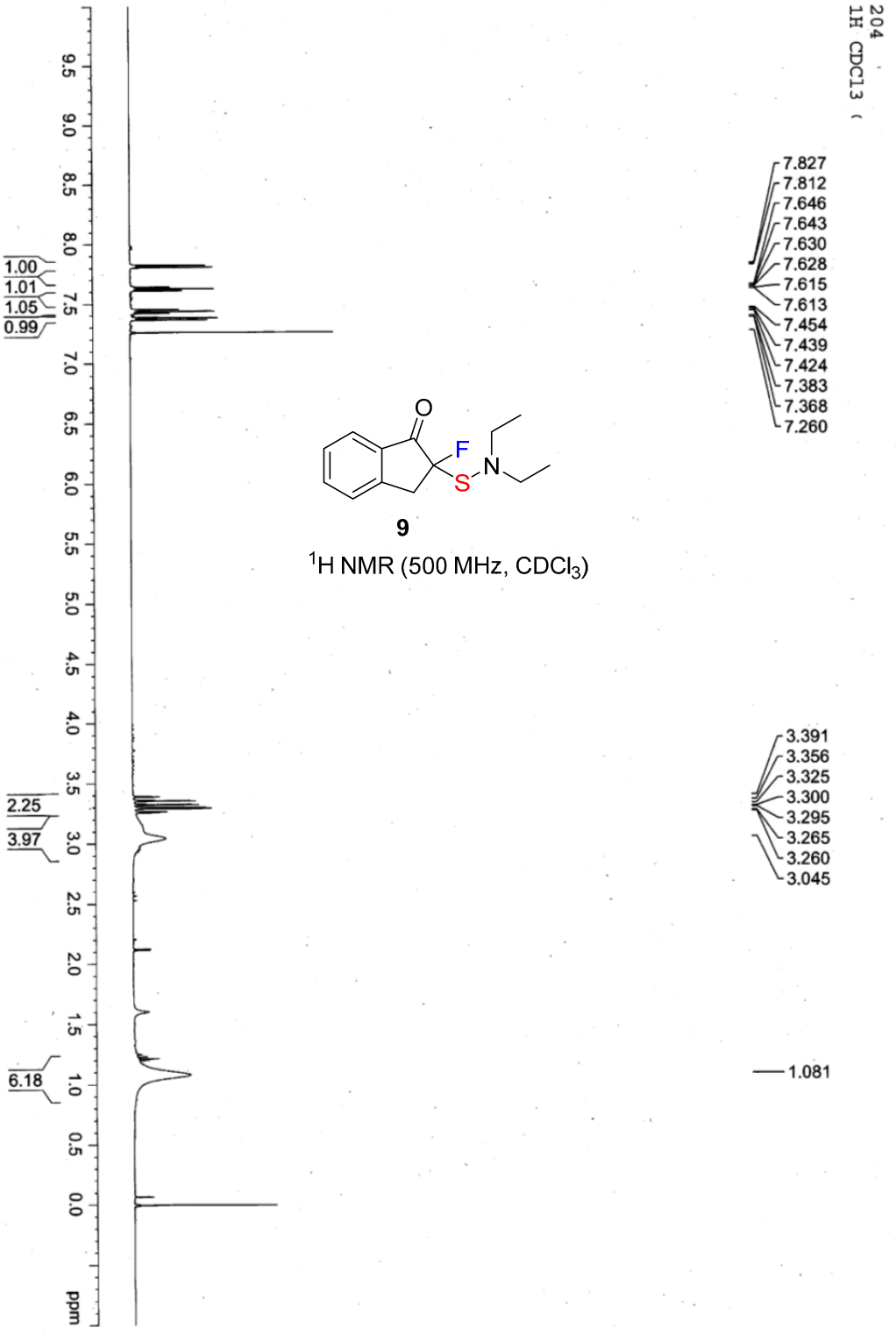


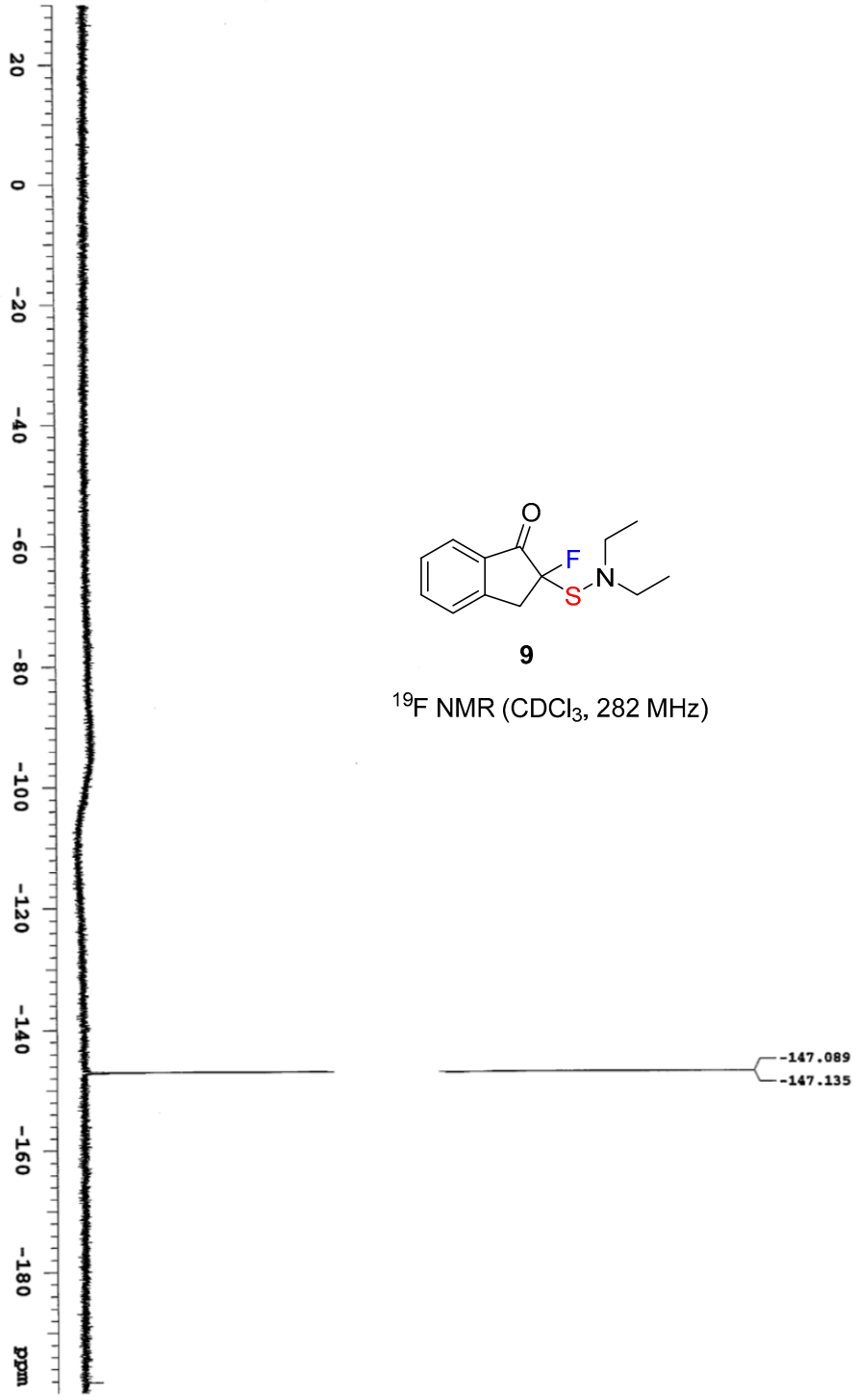
7b

^{19}F NMR ($CDCl_3$, 282 MHz)


O
F
CO2Me
SC6F5
7b
13C NMR (125.7 MHz, CDCl3)
170.704
157.867
155.117
149.341
147.462
147.378
143.698
141.945
141.880
141.656
138.808
136.780
133.209
133.123
133.090
128.247
123.750
123.299
106.295
52.797
50.069
36.809
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

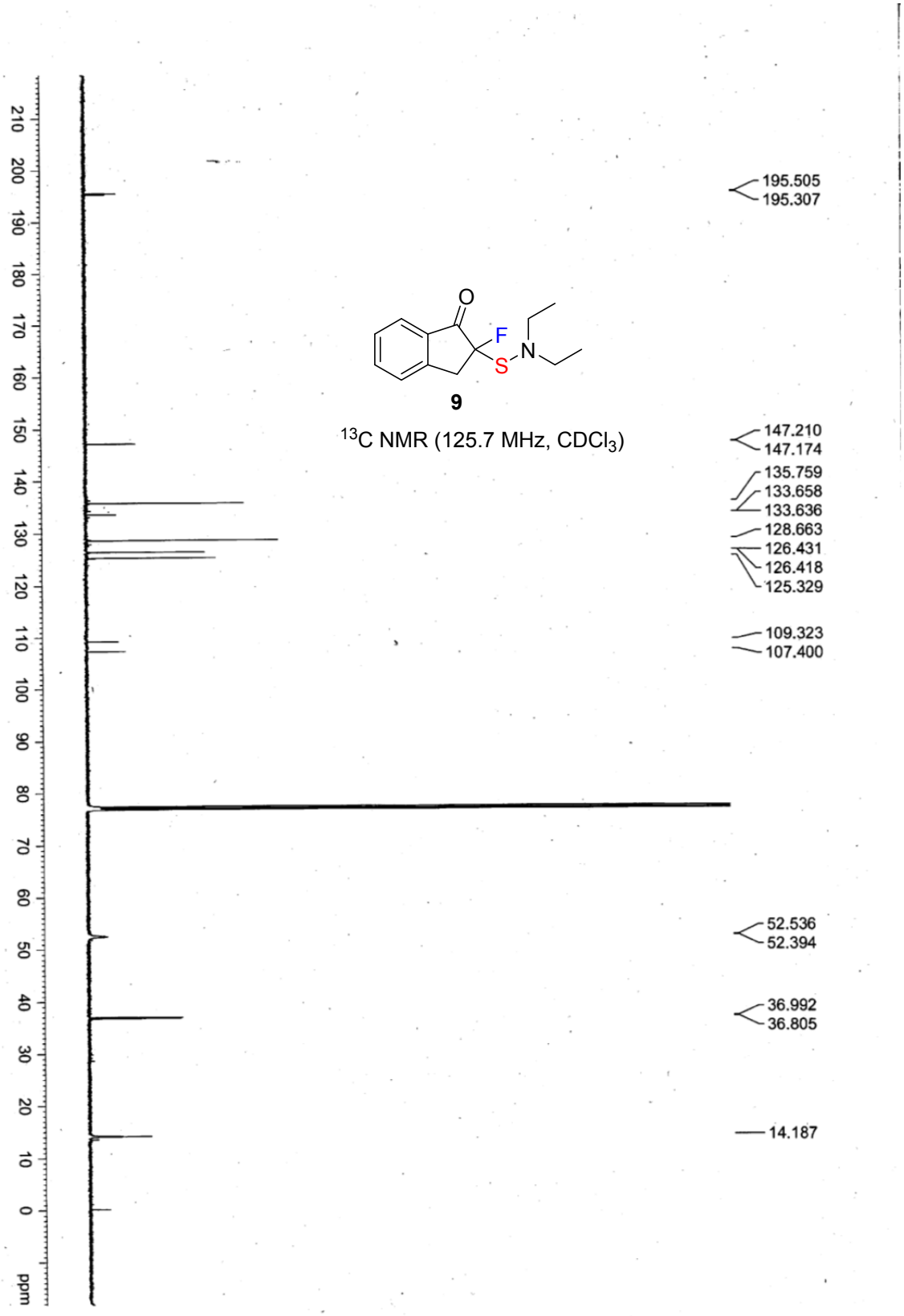
24. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for product 9 and 10 (Scheme 4);

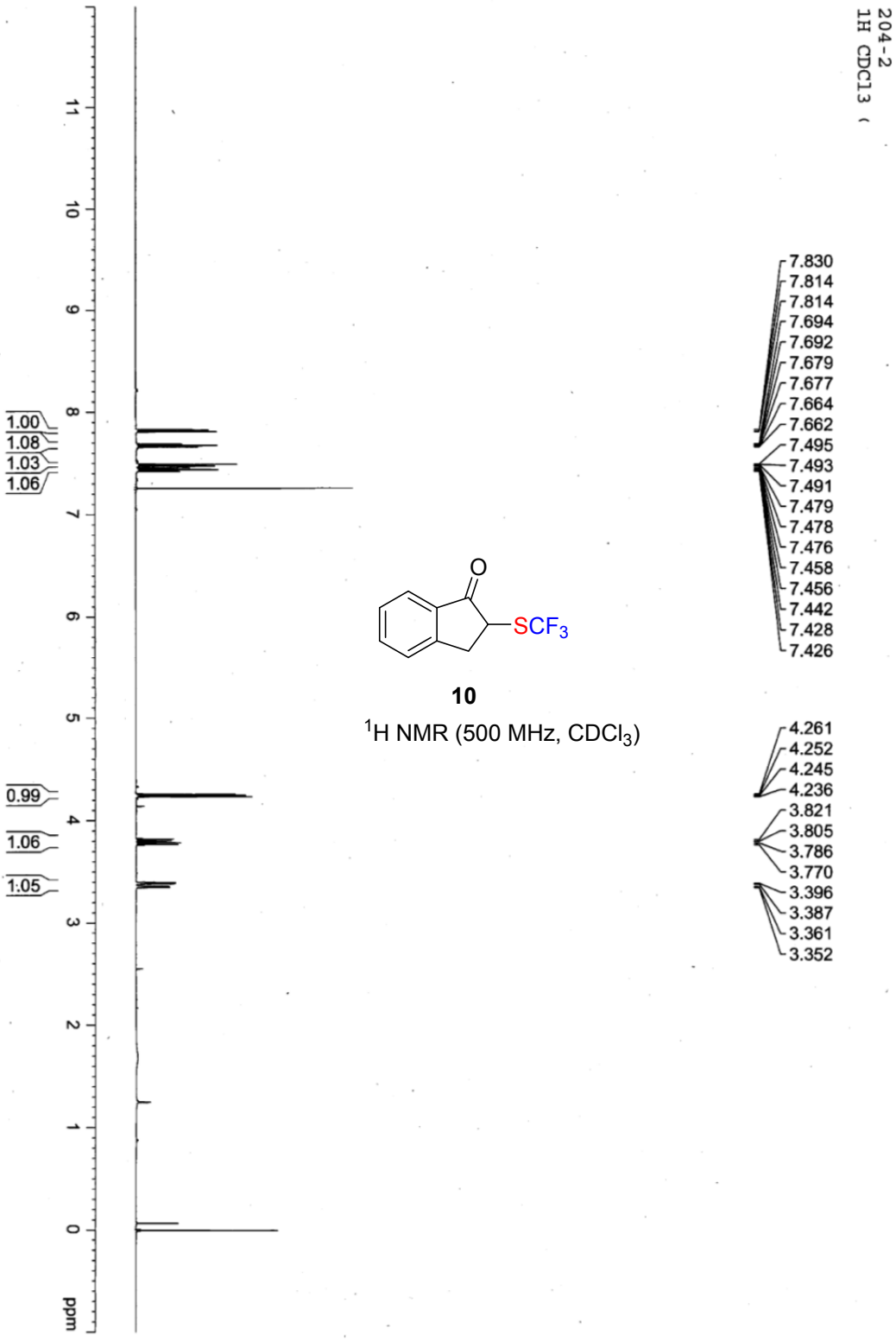




9

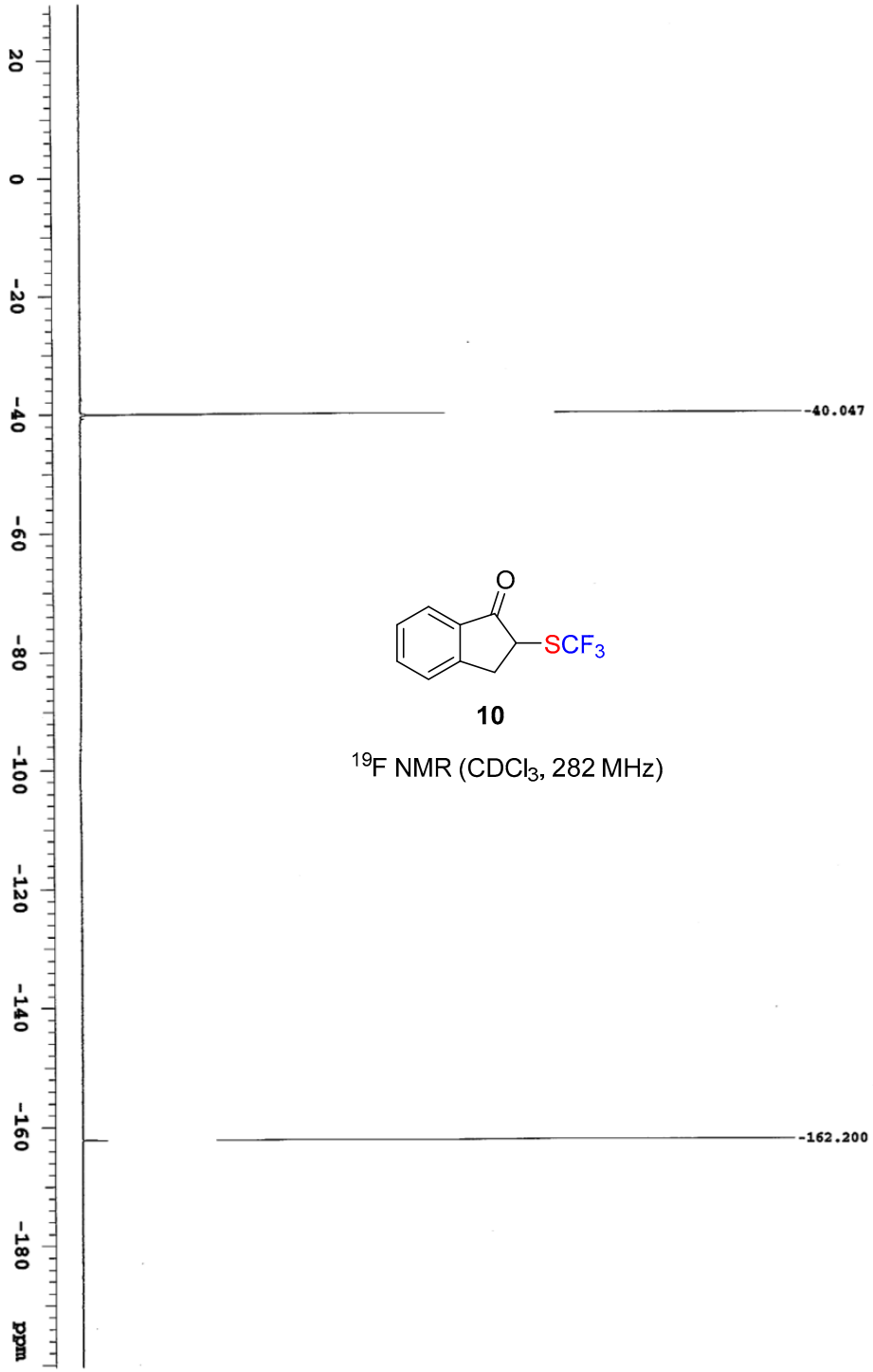
^{19}F NMR ($CDCl_3$, 282 MHz)


O
F
S
N
9
13C NMR (125.7 MHz, CDCl3)
195.505
195.307
147.210
147.174
135.759
133.658
133.636
128.663
126.431
126.418
125.329
109.323
107.400
52.536
52.394
36.992
36.805
14.187
ppm



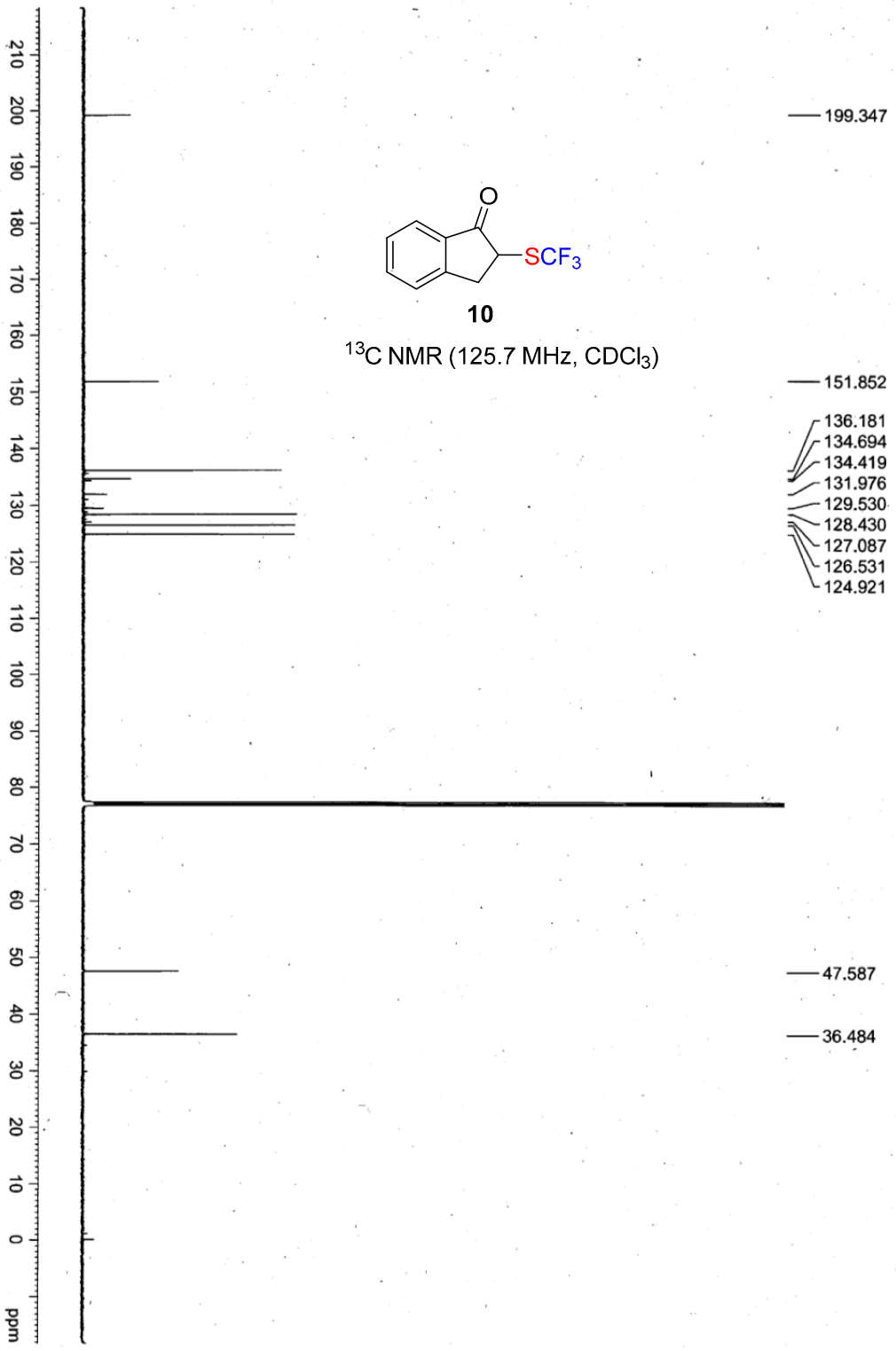
10

^{1}H NMR (500 MHz, $CDCl_3$)



10

^{19}F NMR ($CDCl_3$, 282 MHz)



10

^{13}C NMR (125.7 MHz, $CDCl_3$)