Developing a Transition Metal-Free Green Protocol for the Electrophilic Hydrazination of Silyl Enol Ethers using Diazo Electrophiles with EtOH-H_2O as a Safe Solvent

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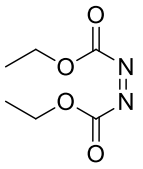
(a) Numbering of azodicarboxylates and azodicarboxamides.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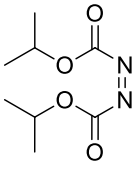
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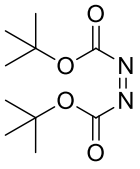
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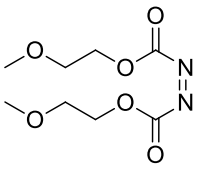
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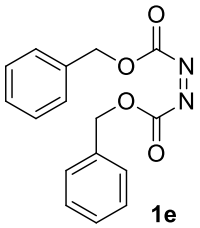
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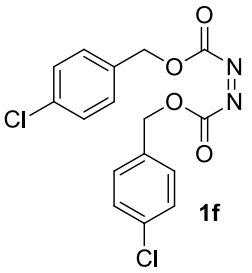
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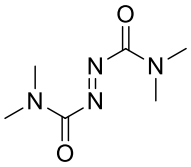
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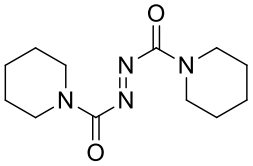
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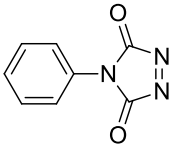
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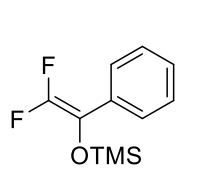
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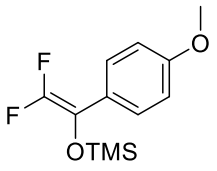
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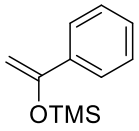
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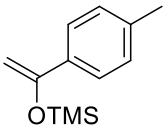
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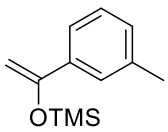
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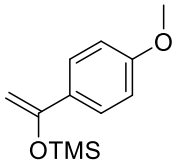
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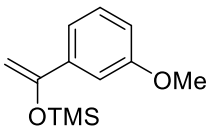
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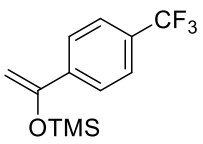
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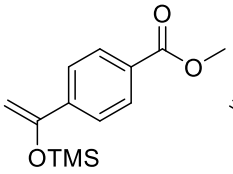
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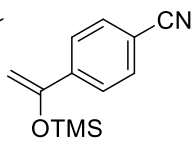
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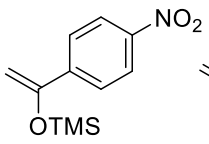
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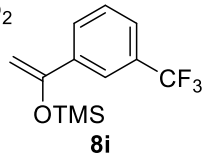
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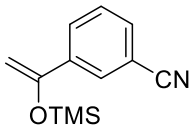
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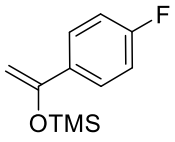
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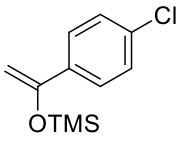
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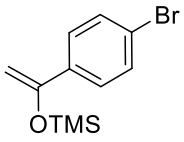
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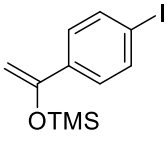
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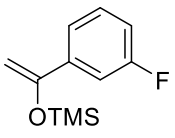
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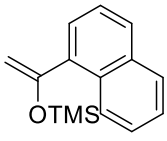
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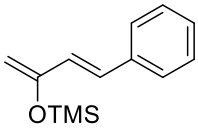
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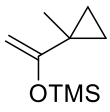
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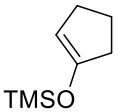
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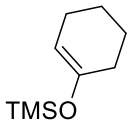
10d

2. Experimental Section

Materials and general methods

All anhydrous reactions were performed under an atmosphere of N_2 or Ar gas with magnetic stirring. Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC). TLC was performed using E. Merck pre-coated silica plates (60F-254) with 0.25 mm thickness and visualized using short-wave UV light or developing agents ($KMnO_4$, phosphomolybdic acid or *p*-anisaldehyde). Purifications were performed using flash column chromatography with 60-120 mesh silica gel as the stationary phase and a gradient of ethyl acetate in petroleum ether as the mobile phase.

Known compounds were characterized by comparing their ^{1}H NMR spectra to the previously reported data. New compounds were characterized by ^{1}H NMR, ^{13}C NMR and MS and copies of proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C-NMR) spectra have been included at the end of the supporting information. ^{1}H-NMR spectra were recorded on Bruker 300 and 400 MHz instruments and chemical shifts are reported in ppm (δ) relative to the internal standard tetramethylsilane (TMS, δ 0.00 ppm). ^{13}C NMR chemical shifts are reported in ppm with respect to solvent resonance as the internal standard (for example, $CDCl_3$ at 77.0 ppm). NMR data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), and broad singlet (br. s)], coupling constant [Hz] and integration). For LC/MS characterization of the purified compounds, reversed phase analytical HPLC/MS experiments were performed on an Agilent 1200 Series system coupled with a single quadrupole instrument using electrospray ionization (ESI) method or Waters Aquity system coupled with a Waters Micromass SQ Mass Spectrometer. High Resolution Mass Spectrometry (HRMS) data were obtained from orbitrap (Thermofisher) mass spectrometer using heated ESI method in positive or negative ion detection mode.

The diazo starting materials **1a**-**1f** and **6a**-**6c** are available commercially. All silyl enol ether starting materials (**2a**,[1] 2b,[1] **2c**,[2] **8a**,[2] **8b**,[2] **8c**,[2] **8d**,[3] **8e**,[4] **8f**,[2] **8g**,[4] **8h**,[2] **8i**,[5] **8j**,[5] **8k**,[2] **8l**,[2] **8m**,[2] **8n**,[2] **8o**[2] and **8p**,[2] and **10a**,[6] **10b**,[2] **10c**[7] and **10d**[7]) are known in the literature and were prepared as per the literature protocols.

Experimental procedures

General method A: the preparation of α-hydrazino ketones using EtOH and water (3a-3g, 4a-4c, 5a-5f, 7a-7c, 9a-9p and **11a-11d)**

To a solution of an azodicarboxylate (0.574 mmol, 1 equiv.) in EtOH (2 mL) and water (1 ml), was added a trimethyl silyl enol ether (0.688 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 2.5 h. After completion of the reaction (monitored by TLC), the solvent was concentrated under vacuum. The crude product was purified by flash column chromatography using a gradient of ethyl acetate and petroleum ether to afford the product.

General method B: the preparation of α-hydrazino ketones under solvent-free condition (3a, 5a, 9a, 9h and **11c)**

A mixture of an azodicarboxylate (0.574 mmol, 1 equiv.) and a trimethyl silyl enol ether (0.688 mmol, 1.2 equiv.) was stirred at room temperature for 2.5 h. After completion of the reaction (monitored by TLC). The reaction mixture was purified by flash column chromatography using a gradient of ethyl acetate and petroleum ether to afford the product.

Diethyl 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3a)[1]

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 156.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of

ethyl acetate and petroleum ether (ratio = 25:75) to afford the title product as a white solid (183.7 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 – 8.19 (m, 2H), 7.65 - 7.62 (m, 1H), 7.54 – 7.50 (m, 2H), 6.87 – 6.72 (m, 1H), 4.35 – 4.30 (m, 2H), 4.17 – 4.11 (m, 2H), 1.37 - 1.34 (m, 3H), 1.13 (br s, 3H); LCMS (ES): *m/z*= 331.0 $[M+H]^+$

The reaction was carried out according to **general method B** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 156.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 25:75) to afford the title product as a white solid (170.4 mg, 90%).

Large scale reaction:
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 5.0 g, 28.7 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 7.8 g, 34.4 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 25:75) to afford the title product as a white solid (8.9 g, 94%).

Diisopropyl 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3b)[8]
The reaction was carried out according to **general method A** using diisopropyl azodicarboxylate (**1b**, 100 mg, 0.495 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 135.4 mg, 0.594 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 25:75) to afford the title product as a white solid (173.6 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 – 8.22 (m, 2H), 7.65 - 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 6.73 – 6.65 (m, 1H), 5.10 – 5.09 (m, 1H), 4.90 – 4.84 (m, 1H), 1.35 - 1.34 (m, 6H), 1.15 – 1.05 (m, 6H); LCMS (ES): *m/z*= 359.0 $[M+H]^+$

Di-tert-butyl 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3c)[8]
The reaction was carried out according to **general method A** using di-tert-butyl azodicarboxylate (**1c**, 100 mg, 0.434 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 118.7 mg, 0.520 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 20:80) to afford the title product as a white solid (164.1 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 – 8.16 (m, 2H), 7.65 - 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 6.56 – 6.37 (m, 1H), 1.57 – 1.55 (m, 9H), 1.29 (s, 9H); LCMS (ES): *m/z*= 385.1 $[M-H]^+$

Bis(2-methoxyethyl) 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3d)
The reaction was carried out according to **general method A** using di-2-Methoxyethyl azodicarboxylate (**1d**, 100 mg, 0.427 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 116.8 mg, 0.512 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 45:55) to afford the title product as a white solid (146.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 – 8.21 (m, 2H), 7.65 - 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 7.32 (br. s, 1H), 4.42 – 4.39 (m, 2H), 4.28 – 4.17 (m, 2H), 3.68 – 3.66 (m, 2H), 3.49 – 3.42 (m, 5H), 3.27 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 181.7 (t, $J_{C\text{-}F}$ = 29.5 Hz), 155.6, 152.7, 134.2 131.9, 129.8, 128.7, 112.7 (t, $J_{C\text{-}F}$ = 258.5 Hz), 70.4, 69.6, 67.0, 65.7, 59.0, 58.8; LCMS (ES): *m/z*= 391.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{21}F_2N_2O_7$ 391.1311; found: 391.1301.

Dibenzyl 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3e)[1]
The reaction was carried out according to **general method A** using dibenzyl azodicarboxylate (**1e**, 100 mg, 0.335 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 91.6 mg, 0.402 mmol, 1.2

equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 20:80) to afford the title product as a white solid (185.2 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 – 8.00 (m, 2H), 7.62 - 7.50 (m, 2H), 7.37 – 7.27 (m, 9H), 7.15 – 7.14 (m, 2H), 6.99 – 6.81 (m, 1H), 5.30 – 5.22 (m, 2H), 5.09 – 507 (m, 2H); LCMS (ES): *m/z*= 453.2 $[M-H]^+$;

Bis(4-chlorobenzyl) 1-(1,1-difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (3f)
The reaction was carried out according to **general method A** using bis(4-chlorobenzyl) diazene-1,2-dicarboxylate (**1f**, 100 mg, 0.273 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 74.6 mg, 0.327 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 20:80) to afford the title product as a white solid (125.4 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 – 7.97 (m, 2H), 7.65 - 7.47 (m, 3H), 7.36 – 7.34 (m, 2H), 7.30 (br. s, 1H), 7.25 – 7.23 (m, 3H), 7.06 – 6.76 (m, 3H), 5.26 – 5.17 (m, 2H), 5.03 (s, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 181.8 (t, J_{C-F} = 27.7 Hz), 155.3, 152.4, 134.8, 134.6, 134.3, 133.6, 132.2, 131.7, 129.7, 129.6, 128.9, 128.8, 128.7, 112.7 (t, J_{C-F} = 258.4 Hz), 68.9, 67.6; LCMS (ES): *m/z*= 521.2 $[M-H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{19}Cl_2F_2N_2O_5$ 523.0634; found: 523.0611.

Diethyl 1-(1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (4a)[8]
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((2,2-difluoro-1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane (**2b**, 177.7 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a colorless liquid (165.1 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 – 8.18 (m, 2H), 7.01 – 6.99 (m, 2H), 6.84 – 6.64 (m, 1H), 4.34 – 4.29 (m, 2H), 4.17 – 4.12 (m, 2H), 3.90 (s, 3H), 1.37 - 1.34 (m, 3H), 1.14 (br. s, 3H); LCMS (ES): *m/z*= 361.0 $[M+H]^+$;

Diisopropyl 1-(1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (4b)
The reaction was carried out according to **general method A** using diisopropyl azodicarboxylate (**1b**, 100 mg, 0.495 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2b**, 153.2 mg, 0.594 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a white solid (172.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 – 8.21 (m, 2H), 7.01 – 6.99 (m, 2H), 6.69 – 6.54 (m, 1H), 5.10 – 5.07 (m, 1H), 4.91 – 4.86 (m, 1H), 3.90 (s, 3H), 1.35 - 1.33 (m, 6H), 1.17 – 1.06 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 180.7 (t, J_{C-F} = 27 Hz), 164.3, 155.5, 152.0 132.4, 124.9, 114.0, 112.8 (t, J_{C-F} = 258 Hz), 73.3, 70.9, 55.5, 22.0, 21.9, 21.4, 21.3; LCMS (ES): *m/z*= 389.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{23}F_2N_2O_6$ 389.1519; found: 389.1513.

Di-tert-butyl 1-(1,1-difluoro-2-(4-methoxyphenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (4c)[1]
The reaction was carried out according to **general method A** using di-tert-butyl azodicarboxylate (**1c**, 100 mg, 0.434 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2b**, 134.3 mg, 0.520 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 20:80) to afford the title product as a white solid (166.1 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 – 8.22 (m, 2H), 7.02 – 6.95 (m, 2H), 6.50 (br. s, 1H), 3.91 (s, 3H), 1.57 – 1.53 (m, 9H), 1.30 (s, 9H); LCMS (ES): *m/z*= 415.2 $[M-H]^+$

Diethyl 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5a)[9]
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 132.2 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate

and petroleum ether (ratio = 35:65) to afford the title product as a white solid (162.0 mg, 96%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.6 Hz, 2H), 7.66 - 7.60 (m, 1H), 7.53 - 7.48 (m, 2H), 7.11 (br. s, 1H), 5.07 – 5.01 (m, 2H), 4.26 – 4.18 (m, 4H), 1.33 - 1.21 (m, 6H); LCMS (ES): *m/z*= 295.2 $[M+H]^+$

The reaction was carried out according to **general method B** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 132.2 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white solid (135.0 mg, 80%; tautomeric/rotameric mixture).

Diisopropyl 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5b)

The reaction was carried out according to **general method A** using diisopropyl azodicarboxylate (**1b**, 100 mg, 0.495 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 114.0 mg, 0.594 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as an off-white solid (143.4 mg, 90%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.93 (m, 2H), 7.64 - 7.61 (m, 1H), 7.54 - 7.48 (m, 2H), 6.94 (br. s, 1H), 5.06 – 4.94 (m, 4H), 1.31 – 1.21 (m, 12H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.8, 194.2, 156.2, 155.8, 155.3, 134.7, 134.6, 134.0, 133.9, 129.0, 128.9, 128.0, 127.9, 71.0, 70.8, 69.9, 69.7, 57.4, 56.1, 22.0, 21.9; LCMS (ES): *m/z*= 323.1 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{23}N_2O_5$ 323.1601; found: 323.1599.

Di-tert-butyl 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5c)

The reaction was carried out according to **general method A** using di-tert-butyl azodicarboxylate (**1c**, 100 mg, 0.434 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 99.9 mg, 0.520 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 20:80) to afford the title product as a white solid (127.5 mg, 84%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.92 (m, 2H), 7.63 - 7.59 (m, 1H), 7.53 - 7.47 (m, 2H), 6.82 – 6.50 (m, 1H), 5.01 – 4.90 (m, 2H), 1.53 – 1.43 (m, 18H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 195.1, 155.6, 154.7, 134.8, 133.9, 133.8, 128.9, 128.8, 127.9, 127.8, 82.2, 81.9, 81.4, 81.1, 57.8, 55.9, 28.2, 28.1, 28.0, 27.9; LCMS (ES): *m/z*= 373.2 $[M+Na]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{26}N_2NaO_5$ 373.1734; found: 373.1738.

Bis(2-methoxyethyl) 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5d)

The reaction was carried out according to **general method A** using di-2-Methoxyethyl azodicarboxylate (**1d**, 100 mg, 0.427 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 98.3 mg, 0.512 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 60:40) to afford the title product as an off-white semi solid (123.9 mg, 82%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.92 (m, 2H), 7.65 - 7.61 (m, 1H), 7.54 - 7.49 (m, 2H), 7.17 – 6.91 (m, 1H), 5.07 – 5.03 (m, 2H), 4.34 – 4.29 (m, 4H), 3.65 – 3.60 (m, 4H), 3.56 – 3.29 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.3, 194.0, 156.4, 155.7, 155.2, 134.5, 134.4, 134.1, 134.0, 128.9, 128.8, 128.0, 70.5, 66.0, 65.9, 65.0, 59.0, 58.9, 58.8, 57.4, 56.1; LCMS (ES): *m/z*= 355.3 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{23}N_2O_7$ 355.1500; found: 355.1526.

Dibenzyl 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5e)[10]

The reaction was carried out according to **general method A** using dibenzyl azodicarboxylate (**1e**, 100 mg, 0.335 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 77.1 mg, 0.402 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate

and petroleum ether (ratio = 30:70) to afford the title product as an off-white solid (120.4 mg, 86%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.25 – 10.03 (m, 1H), 8.00 - 7.96 (m, 2H), 7.68 - 7.66 (m, 1H), 7.57 – 7.53 (m, 2H), 7.36 – 7.28 (m, 10H), 5.25 – 5.01 (m, 6H); LCMS (ES): *m/z*= 419.2 $[M+H]^+$;

Bis(4-chlorobenzyl) 1-(2-oxo-2-phenylethyl)hydrazine-1,2-dicarboxylate (5f)

The reaction was carried out according to **general method A** using bis(4-chlorobenzyl) diazene-1,2-dicarboxylate (**1f**, 100 mg, 0.273 mmol, 1 equiv.) and trimethyl((1-phenylvinyl)oxy)silane (**2c**, 62.8 mg, 0.327 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a white solid (115.4 mg, 87%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.88 (m, 2H), 7.64 (br. s, 1H), 7.52 - 7.50 (m, 2H), 7.31 – 7.02 (m, 9H), 5.30 – 5.01 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.4, 193.9, 156.3, 156.2, 155.7, 155.1, 134.4, 134.2, 134.0, 133.9, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.0, 127.9, 67.9, 67.7, 66.9, 66.8, 57.4, 56.2; LCMS (ES): *m/z*= 487.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{21}Cl_2N_2O_5$ 487.0822; found: 487.0844.

1-(1,1-Difluoro-2-oxo-2-phenylethyl)-N1,N1,N2,N2-tetramethylhydrazine-1,2-dicarboxamide (7a)

The reaction was carried out according to **general method A** using N1,N1,N2,N2-tetramethyldiazene-1,2-dicarboxamide (**6b**, 100 mg, 0.581 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 158.9 mg, 0.697 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 70:30) to afford the title product as a white solid (141.0 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.6 Hz, 2H), 7.62 - 7.59 (m, 1H), 7.52 - 7.49 (m, 2H), 7.05 (br. s, 1H), 2.97 (s, 12H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 182.9 (t, $J_{C\text{-}F}$ = 29.5 Hz), 158.2, 156.7, 134.0, 132.1, 130.0, 128.6, 115.0 (t, $J_{C\text{-}F}$ = 257.5 Hz), 37.8, 36.5; LCMS (ES): *m/z*= 329.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{19}F_2N_4O_3$ 329.1420; found: 329.1435.

1-(1,1-Difluoro-2-oxo-2-phenylethyl)hydrazine-1,2-bis(1-piperidinylcarbonyl) (7b)[1]

The reaction was carried out according to **general method A** using diazene-1,2-diylbis(piperidin-1-ylmethanone) (**6a**, 100 mg, 0.396 mmol, 1 equiv.) and ((2,2-difluoro-1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane (**2a**, 108.3 mg, 0.475 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (126.0 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 7.2 Hz, 2H), 7.62 - 7.58 (m, 1H), 7.52 - 7.48 (m, 2H), 6.99 (br. s, 1H), 3.49 – 3.48 (m, 4H), 3.34 (br. s, 4H), 1.59 – 1.53 (m, 8H), 1.46 (br. s, 4H); LCMS (ES): *m/z*= 409.1 $[M+H]^+$

1-(1,1-Difluoro-2-oxo-2-phenylethyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (7c)[1]

The reaction was carried out according to **general method A** using 4-phenyl-1,2,4-triazole-3,5-dione (**6c**, 100 mg, 0.571 mmol, 1 equiv.) and ((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane (**2a**, 156.2 mg, 0.685 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white solid (151.2 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.70 (m, 1H), 7.58 – 7.54 (m, 2H), 7.52 – 7.49 (m, 4H), 7.46 – 7.43 (m, 1H); LCMS (ES): *m/z*= 332.0 $[M+H]^+$;

Diethyl 1-(2-oxo-2-(p-tolyl)ethyl)hydrazine-1,2-dicarboxylate (9a)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(p-tolyl)vinyl)oxy)silane (**8a**, 141.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white solid (173.2 mg, 98%;

tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.4 Hz, 2H), 7.31 - 7.28 (m, 2H), 7.09 (br. s, 1H), 5.03 – 4.97 (m, 2H), 4.26 – 4.17 (m, 4H), 2.44 (s, 3H), 1.32 – 1.20 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.3, 193.7, 156.6, 156.1, 155.4, 145.1, 145.0, 132.1, 132.0, 129.6, 129.5, 128.1, 128.0, 63.0, 62.1, 57.2, 55.9, 21.8, 14.4; LCMS (ES): *m/z*= 309.1 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{21}N_2O_5$ $(M+H)^+$: 309.1445; found: 309.1469.

The reaction was carried out according to **general method B** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(p-tolyl)vinyl)oxy)silane (**8a**, 141.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white solid (139.6 mg, 79%; tautomeric/rotameric mixture).

Diethyl 1-(2-oxo-2-(m-tolyl)ethyl)hydrazine-1,2-dicarboxylate (9b)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(m-tolyl)vinyl)oxy)silane (**8b**, 141.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white solid (173.2 mg, 98%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 – 7.72 (m, 2H), 7.45 - 7.35 (m, 2H), 7.10 (br. s, 1H), 5.05 – 4.99 (m, 2H), 4.26 – 4.17 (m, 4H), 2.43 (s, 3H), 1.32 – 1.20 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.9, 194.3, 156.5, 156.1, 155.4, 138.9, 138.7, 134.8, 134.7, 134.6, 134.5, 128.8, 128.7, 128.5, 128.4, 125.2, 125.1, 63.1, 63.0, 62.1, 62.0, 57.3, 56.1, 21.3, 14.4; LCMS (ES): *m/z*= 309.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{21}N_2O_5$ $(M+H)^+$: 309.1445; found: 309.1469.

Diethyl 1-(2-(4-methoxyphenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9c)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane (**8c**, 152.7 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as an off-white solid (176.6 mg, 95%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 8.8 Hz, 2H), 7.08 (br. s, 1H), 6.99 – 6.95 (m, 2H), 5.01 – 4.95 (m, 2H), 4.26 – 4.18 (m, 4H), 3.89 (s, 3H), 1.33 – 1.21 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.1, 192.6, 164.2, 156.6, 156.1, 155.4, 130.3, 130.2, 127.6, 127.5, 114.1, 114.0, 63.0, 62.3, 62.0, 56.9, 55.7, 55.5, 14.4; LCMS (ES): *m/z*= 325.4 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{21}N_2O_6$ 325.1394; found: 325.1413.

Diethyl 1-(2-(3-methoxyphenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9d)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(3-methoxyphenyl)vinyl)oxy)trimethylsilane (**8d**, 152.7 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as an off-white solid (174.8 mg, 94%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.90 (m, 2H), 7.12 (br. s, 1H), 6.98 – 6.94 (m, 2H), 5.01 – 4.95 (m, 2H), 4.25 – 4.17 (m, 4H), 3.89 (s, 3H), 1.32 – 1.20 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.1, 192.5, 164.2, 164.1, 156.6, 156.1, 155.4, 130.3, 130.2, 127.6, 127.5, 114.1, 114.0, 62.9, 62.2, 62.0, 56.9, 55.7, 55.5, 14.4; LCMS (ES): *m/z*= 325.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{21}N_2O_6$ 325.1394; found: 325.1413.

Diethyl 1-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)hydrazine-1,2-dicarboxylate (9e)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane (**8e**, 178.8 mg, 0.688

mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a colorless liquid (178.6 mg, 86%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.4 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.05 (br. s, 1H), 5.08 – 5.03 (m, 2H), 4.28 – 4.19 (m, 4H), 1.34 – 1.22 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.0, 193.4, 156.4, 156.2, 156.1, 137.2, 137.1, 135.3 (q, J_{C-F} = 90 Hz), 128.6, 128.4, 126.0, 123.4 (q, J_{C-F} = 270 Hz), 63.2, 62.2, 57.5, 56.3, 14.4; LCMS (ES): *m/z*= 363.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{18}F_3N_2O_5$ 363.1162; found: 363.1187.

Diethyl 1-(2-(4-(methoxycarbonyl)phenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9f)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and methyl 4-(1-((trimethylsilyl)oxy)vinyl)benzoate (**8f**, 172.0 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as an off-white semi solid (181.8 mg, 90%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 – 8.15 (m, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.06 (br. s, 1H), 5.08 – 5.02 (m, 2H), 4.25 – 4.18 (m, 4H), 3.97 (s, 3H), 1.33 – 1.21 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.3, 193.8, 166.0, 156.4, 156.3, 156.1, 137.7, 137.6, 134.8, 134.7, 130.1, 130.0, 127.9, 63.1, 62.3, 62.2, 57.5, 56.3, 52.6, 14.4; LCMS (ES): *m/z*= 353.3 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{21}N_2O_7$ 353.1343; found: 353.1355.

Diethyl 1-(2-(4-cyanophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9g)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and 4-(1-((trimethylsilyl)oxy)vinyl)benzonitrile (**8g**, 149.2 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (157.4 mg, 86%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.03 – 6.54 (m, 1H), 5.06 – 5.01 (m, 2H), 4.27 – 4.18 (m, 4H), 1.33 – 1.23 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.6, 193.0, 156.3, 156.1, 155.4, 137.5, 137.4, 132.8, 132.7, 132.6, 128.6, 128.4, 117.6, 117.3, 63.2, 62.3, 57.5, 56.3, 14.4; LCMS (ES): *m/z*= 320.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{18}N_3O_5$ 320.1241; found: 320.1224.

Diethyl 1-(2-(4-nitrophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9h)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(4-nitrophenyl)vinyl)oxy)silane (**8h**, 163.0 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a pale yellow solid (171.2 mg, 88%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, J = 8.8 Hz, 2H), 8.12 (d, J = 8.0 Hz, 2H), 7.02 – 6.99 (m, 1H), 5.09 – 5.04 (m, 2H), 4.28 – 4.20 (m, 4H), 1.35 – 1.25 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.5, 192.9, 156.3, 156.1, 155.4, 150.9, 138.9, 138.8, 129.1, 124.2, 124.1, 63.3, 62.3, 57.6, 56.5, 14.4; LCMS (ES): *m/z*= 340.3 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}N_3O_7$ 340.1139; found: 340.1153.

The reaction was carried out according to **general method B** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(4-nitrophenyl)vinyl)oxy)silane (**8h**, 163.0 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a pale-yellow solid (157.6 mg, 81%).

Diethyl 1-(2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)hydrazine-1,2-dicarboxylate (9i)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(3-(trifluoromethyl)phenyl)vinyl)oxy)silane (**8i**, 178.8 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as an off-white solid (187.0 mg, 90%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.70 – 7.64 (m, 1H), 7.05 (br. s, 1H), 5.09 – 5.04 (m, 2H), 4.28 – 4.19 (m, 4H), 1.34 - 1.22 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.5, 192.9, 156.4, 156.2, 156.1, 155.4, 135.1, 135.0, 131.6 (q, $J_{C\text{-}F}$ = 100.3 Hz), 130.9, 130.4, 129.7, 129.6, 128.8, 127.5, 124.9, 124.8, 122.1, 63.2, 62.2, 57.3, 56.2, 14.4; LCMS (ES): *m/z*= 363.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{18}F_3N_2O_5$ 363.1162; 363.1187.

Diethyl 1-(2-(3-cyanophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9j)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and 3-(1-((trimethylsilyl)oxy)vinyl)benzonitrile (**8j**, 149.2 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (168.0 mg, 89%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.04 – 6.81 (m, 1H), 5.05 – 5.01 (m, 2H), 4.25 – 4.18 (m, 4H), 1.33 - 1.22 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.0, 192.4, 156.3, 156.1, 155.4, 136.8, 135.4, 135.3, 131.9, 131.7, 130.0, 129.9, 117.6, 113.7, 113.6, 63.2, 62.3, 57.3, 56.2, 14.4; LCMS (ES): *m/z*= 320.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{18}N_3O_5$ 320.1241; 320.1224.

Diethyl 1-(2-(4-fluorophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9k)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane (**8k**, 144.4 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as an off-white solid (162.9 mg, 91%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H), 7.20 – 7.13 (m, 3H), 5.02 – 4.97 (m, 2H), 4.25 – 4.16 (m, 4H), 1.31 – 1.19 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.1, 192.6, 166.2 (d, $J_{C\text{-}F}$ = 254.8 Hz), 156.5, 156.4, 156.1, 155.4, 131.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 130.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 130.7 (d, $J_{C\text{-}F}$ = 9.4 Hz), 130.7 (d, $J_{C\text{-}F}$ = 9.2 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22 Hz), 63.1, 62.1, 57.1, 55.9, 14.4; LCMS (ES): *m/z*= 313.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}FN_2O_5$ 313.1194; found: 313.1195.

Diethyl 1-(2-(4-chlorophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9l)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(4-chlorophenyl)vinyl)oxy)trimethylsilane (**8l**, 155.4 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a white solid (169.4 mg, 90%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.8 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.02 – 6.75 (m, 1H), 5.03 – 4.97 (m, 2H), 4.25 – 4.19 (m, 4H), 1.34 – 1.22 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.6, 193.0, 156.5, 156.4, 156.1, 155.4, 140.7, 140.6, 132.9, 132.8, 129.4, 129.3, 129.2, 129.1, 63.1, 62.1, 57.2, 56.0, 14.4; LCMS (ES): *m/z*= 329.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}ClN_2O_5$ 329.0899; found: 329.0925.

Diethyl 1-(2-(4-bromophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9m)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(4-bromophenyl)vinyl)oxy)trimethylsilane (**8m**, 185.7 mg, 0.688 mmol, 1.2

equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a white solid (196.4 mg, 92%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.75 (m, 2H), 7.68 – 7.59 (m, 2H), 7.03 (br. s, 1H), 5.02 – 4.97 (m, 2H), 4.27 – 4.18 (m, 4H), 1.33 – 1.21 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.8, 193.2, 156.5, 156.3, 156.1, 133.3, 133.2, 132.3, 132.2, 129.4, 63.1, 62.2, 57.2, 56.0, 14.4; LCMS (ES): *m/z*= 375.2 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}BrN_2O_5$ 373.0394; found: 373.0395.

Diethyl 1-(2-(4-iodophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9n)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(4-iodophenyl)vinyl)oxy)trimethylsilane (**8n**, 218.7 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as a white solid (221.7 mg, 92%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 – 7.87 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 6.99 (br. s, 1H), 5.01 – 4.96 (m, 2H), 4.27 – 4.19 (m, 4H), 1.33 – 1.21 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.1, 193.5, 156.4, 156.3, 156.1, 155.4, 138.3, 138.2, 133.8, 133.7, 129.5, 129.2, 102.2, 63.1, 62.9, 62.2, 57.1, 55.9, 14.4; LCMS (ES): *m/z*= 421.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}IN_2O_5$ 421.0255; found: 421.0275.

Diethyl 1-(2-(3-fluorophenyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9o)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and ((1-(3-fluorophenyl)vinyl)oxy)trimethylsilane (**8o**, 144.4 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as an off-white solid (170.1 mg, 95%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.54 – 7.47 (m, 1H), 7.36 – 7.31 (m, 1H), 7.06 (br. s, 1H), 5.04 – 4.98 (m, 2H), 4.27 – 4.18 (m, 4H), 1.33 – 1.22 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 193.6, 193.0, 162.9 (d, $J_{C\text{-}F}$ = 247.7 Hz), 156.4, 156.3, 156.1, 155.4, 136.5 (d, $J_{C\text{-}F}$ = 6.5 Hz), 130.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 123.7 (d, $J_{C\text{-}F}$ = 5.5 Hz), 121.1 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.7 (d, $J_{C\text{-}F}$ = 22.3 Hz), 63.1, 62.2, 57.4, 56.2, 14.4; LCMS (ES): *m/z*= 313.4 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}FN_2O_5$ 313.1194; found: 313.1231.

Diethyl 1-(2-(naphthalen-1-yl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (9p)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane (**8p**, 166.4 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 30:70) to afford the title product as an off-white solid (193.5 mg, 98%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 (s, 1H), 8.07 – 8.05 (m, 1H), 7.91 – 7.89 (m, 2H), 7.64 – 7.53 (m, 3H), 7.16 (br. s, 1H), 5.09 – 5.03 (m, 2H), 4.26 – 4.25 (m, 4H), 1.34 - 1.26 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 198.3, 197.7, 156.6, 156.3, 155.5, 134.0, 132.2, 130.3, 128.6, 128.5, 128.4, 128.2, 126.8, 126.7, 125.6, 125.5, 124.3, 63.1, 63.0, 62.2, 59.4, 58.1, 14.5, 14.4; LCMS (ES): *m/z*= 345.1 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{21}N_2O_5$ 345.1445; found: 345.1473.

Diethyl 1-(2-oxo-4-phenylbut-3-en-1-yl)hydrazine-1,2-dicarboxylate (11a)

The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane (**8a**, 149.9 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as color less liquid (152.4

mg, 83%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 16.4 Hz, 1H), 7.58 – 7.57 (m, 2H), 7.44 – 7.43 (m, 3H), 7.00 (br. s, 1H), 6.76 (d, J = 16 Hz, 1H), 4.74 – 4.66 (m, 2H), 4.24 – 4.21 (m, 4H), 1.33 – 1.24 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 194.6, 194.1, 156.4, 156.1, 155.4, 144.4, 134.0, 131.1, 129.1, 128.5, 122.9, 122.5, 63.0, 62.0, 58.6, 57.2, 14.4; LCMS (ES): *m/z*= 321.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{21}N_2O_5$ 321.1445; found: 321.1470.

Diethyl 1-(2-(1-methylcyclopropyl)-2-oxoethyl)hydrazine-1,2-dicarboxylate (11b)
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and trimethyl((1-(1-methylcyclopropyl)vinyl)oxy)silane (**8d**, 116.9 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (126.4 mg, 81%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94 – 6.68 (m, 1H), 4.51 – 4.45 (m, 2H), 4.21 – 4.16 (m, 4H), 1.39 (s, 3H), 1.31 – 1.23 (m, 8H), 0.81 (s, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 207.0, 206.2, 156.4, 156.1, 155.4, 62.9, 62.0, 61.9, 57.3, 56.2, 25.4, 25.3, 19.3, 19.0, 18.8, 14.5, 14.4; LCMS (ES): *m/z*= 273.0 $[M+H]^+$; HRMS (ESI/Orbitrap) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{21}N_2O_5$ 273.1445; found: 273.1441.

Diethyl 1-(2-oxocyclopentyl)hydrazine-1,2-dicarboxylate (11c)[11]
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and (cyclopent-1-en-1-yloxy)trimethylsilane (**8c**, 107.3 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (131.8 mg, 89%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.70 - 6.30 (m, 1H), 4.62 – 4.52 (m, 1H), 4.26 – 4.18 (m, 4H), 2.39 – 2.32 (m, 2H), 2.20 – 2.01 (m, 3H), 1.86 – 1.78 (m, 1H), 1.35 - 1.31 (m, 6H); LCMS (ES): *m/z*= 259.0 $[M+H]^+$

The reaction was carried out according to **general method B** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and (cyclopent-1-en-1-yloxy)trimethylsilane (**8c**, 107.3 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 40:60) to afford the title product as a white solid (111.0 mg, 75%; tautomeric/rotameric mixture).

Diethyl 1-(2-oxocyclohexyl)hydrazine-1,2-dicarboxylate (11d)[11]
The reaction was carried out according to **general method A** using diethyl azodicarboxylate (**1a**, 100 mg, 0.574 mmol, 1 equiv.) and (cyclohex-1-en-1-yloxy)trimethylsilane (**8b**, 117.1 mg, 0.688 mmol, 1.2 equiv.). The crude product was purified by flash column chromatography using silica gel and a gradient of ethyl acetate and petroleum ether (ratio = 35:65) to afford the title product as a white sold (124.9 mg, 80%; tautomeric/rotameric mixture). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.71 – 6.48 (m, 1H), 4.92 – 4.68 (m, 1H), 4.26 – 4.19 (m, 4H), 2.53 – 2.50 (m, 1H), 2.39 (br. s, 2H), 2.12 – 2.09 (m, 1H), 2.00 (br. s, 1H), 1.94 – 1.78 (m, 2H), 1.60 (br. s, 1H), 1.28 (br. s, 6H); LCMS (ES): *m/z*= 273.0 $[M+H]^+$

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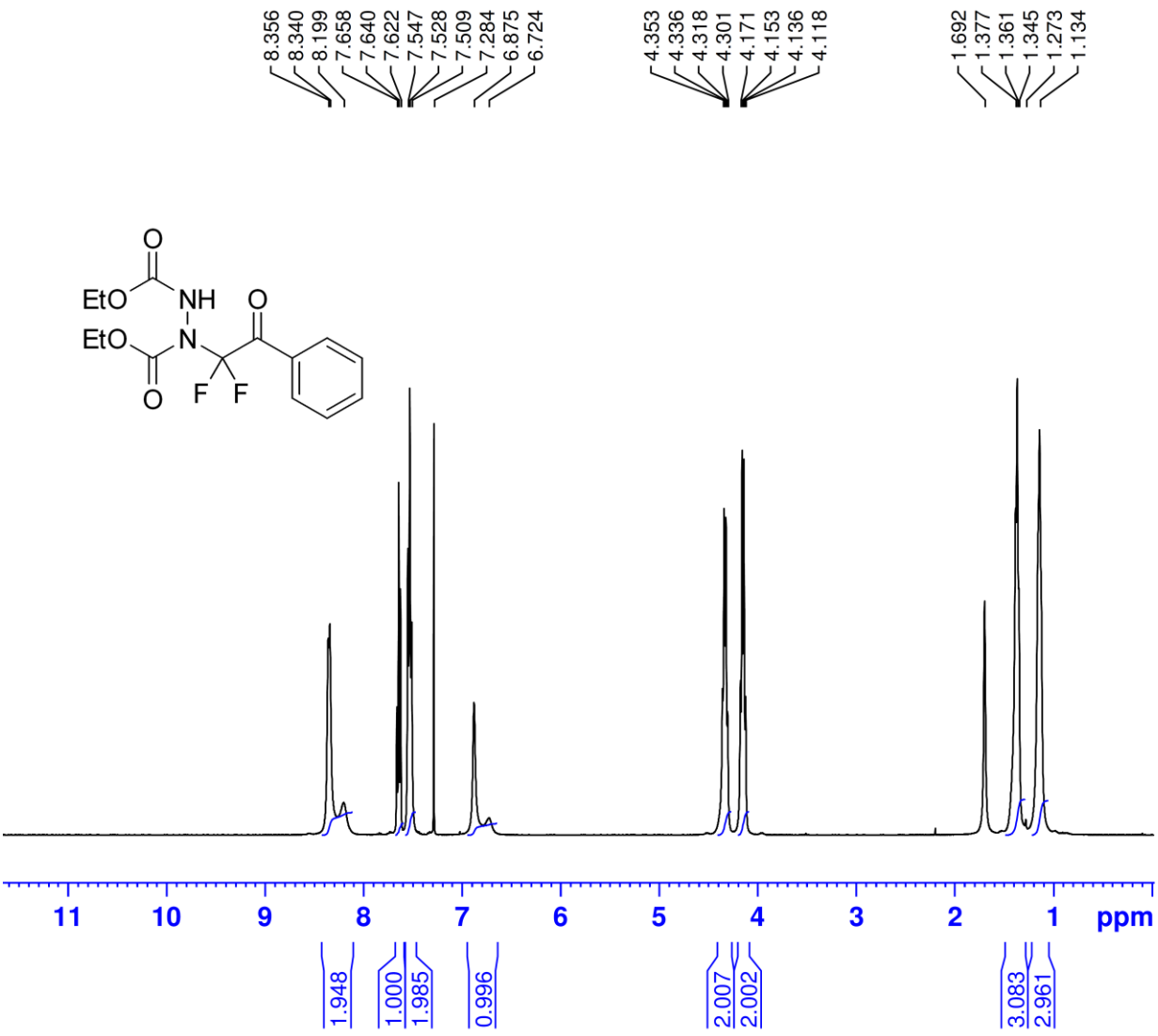
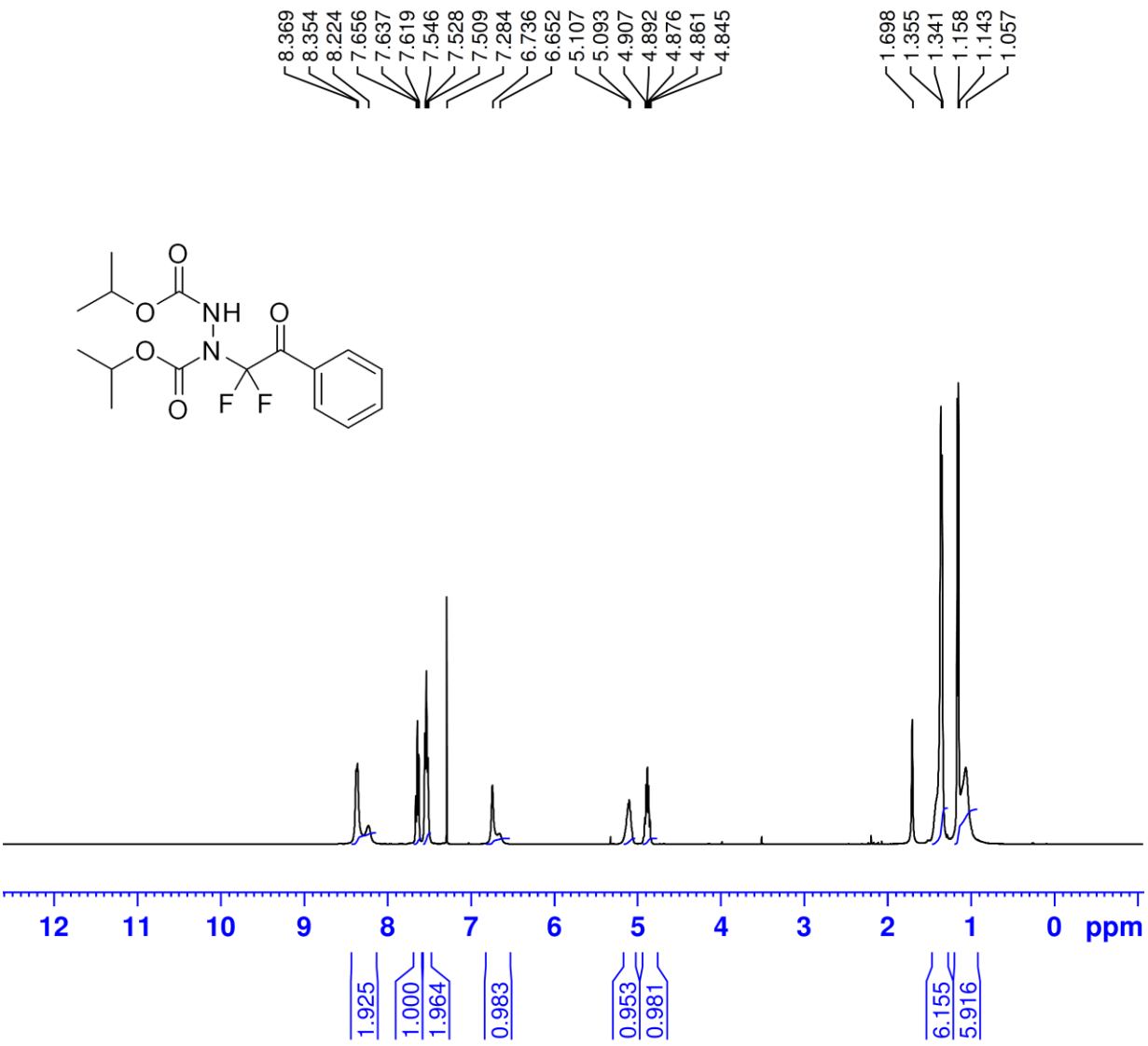
4. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

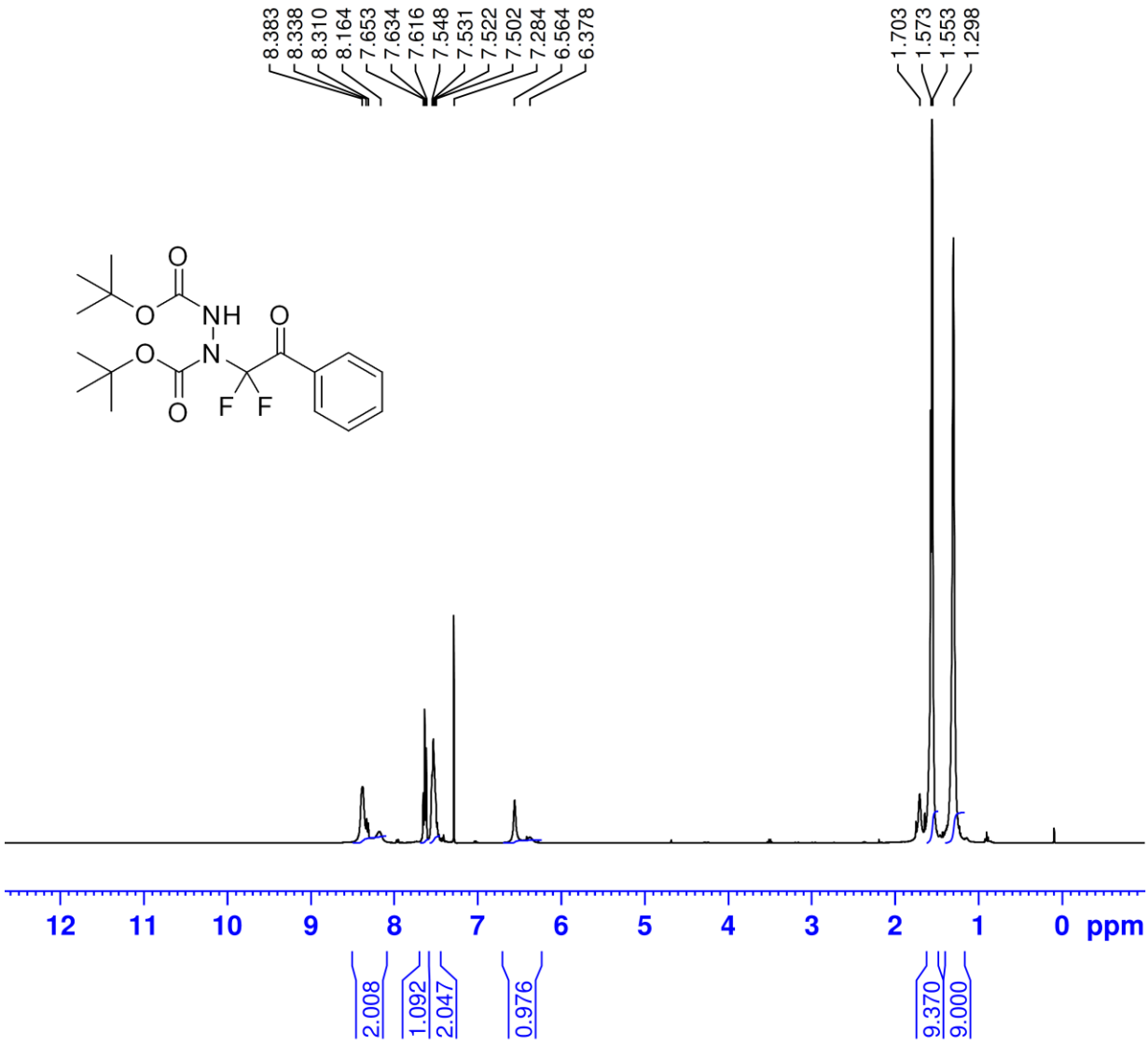
Compound **3a**: ^{1}H NMR (400 MHz, $CDCl_3$)



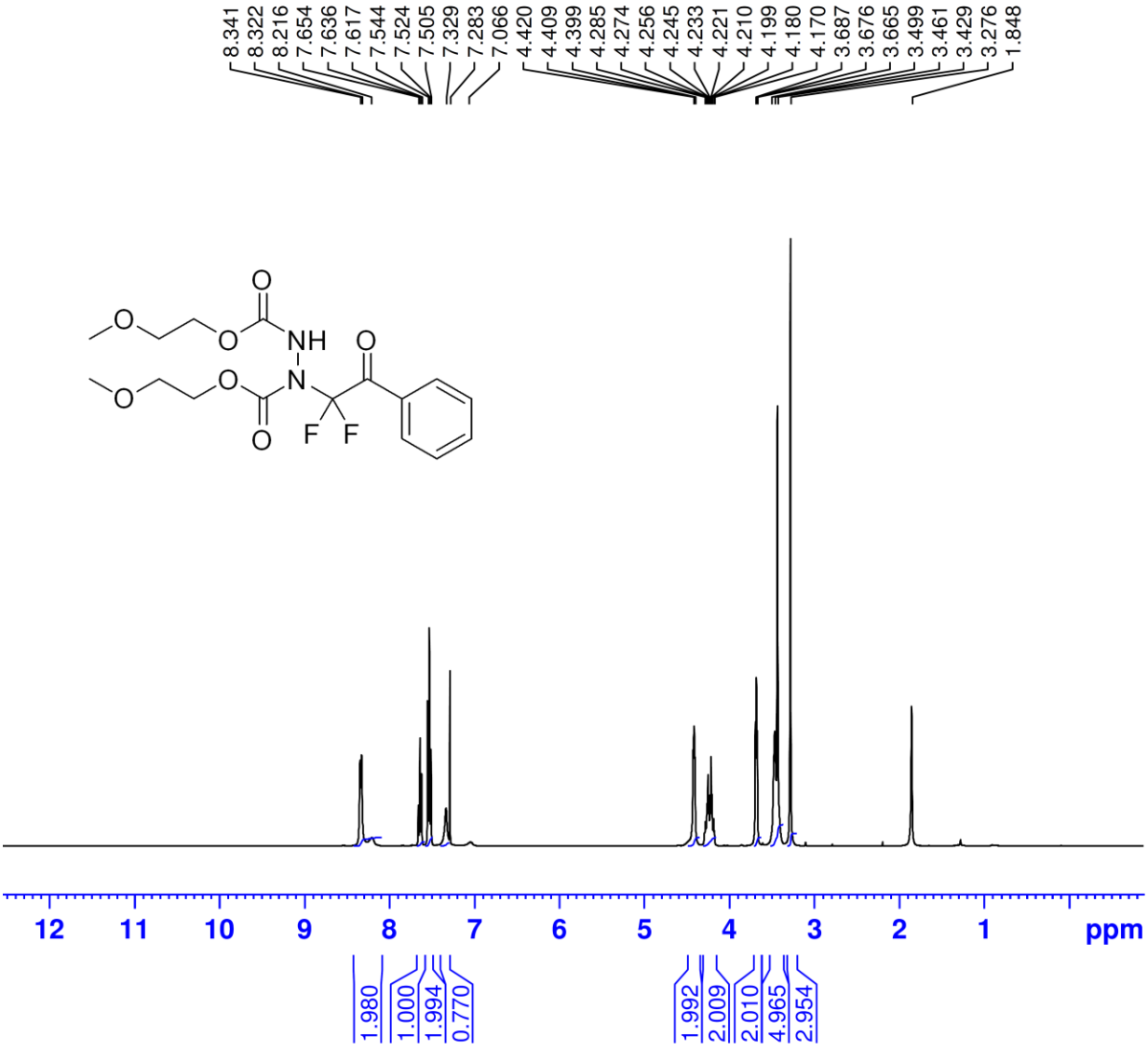
Compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$)



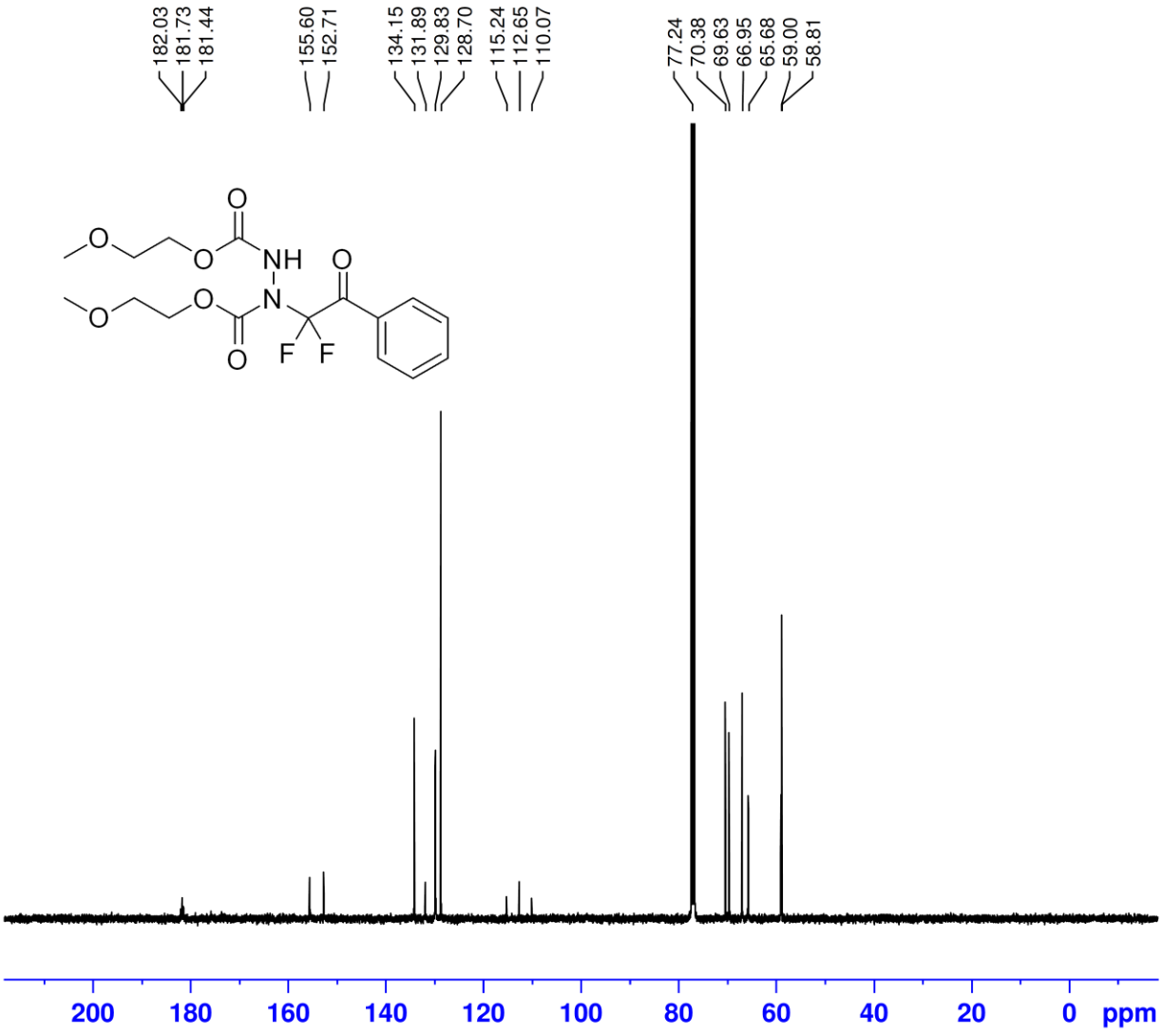
Compound **3c**: ^{1}H NMR (400 MHz, $CDCl_3$)



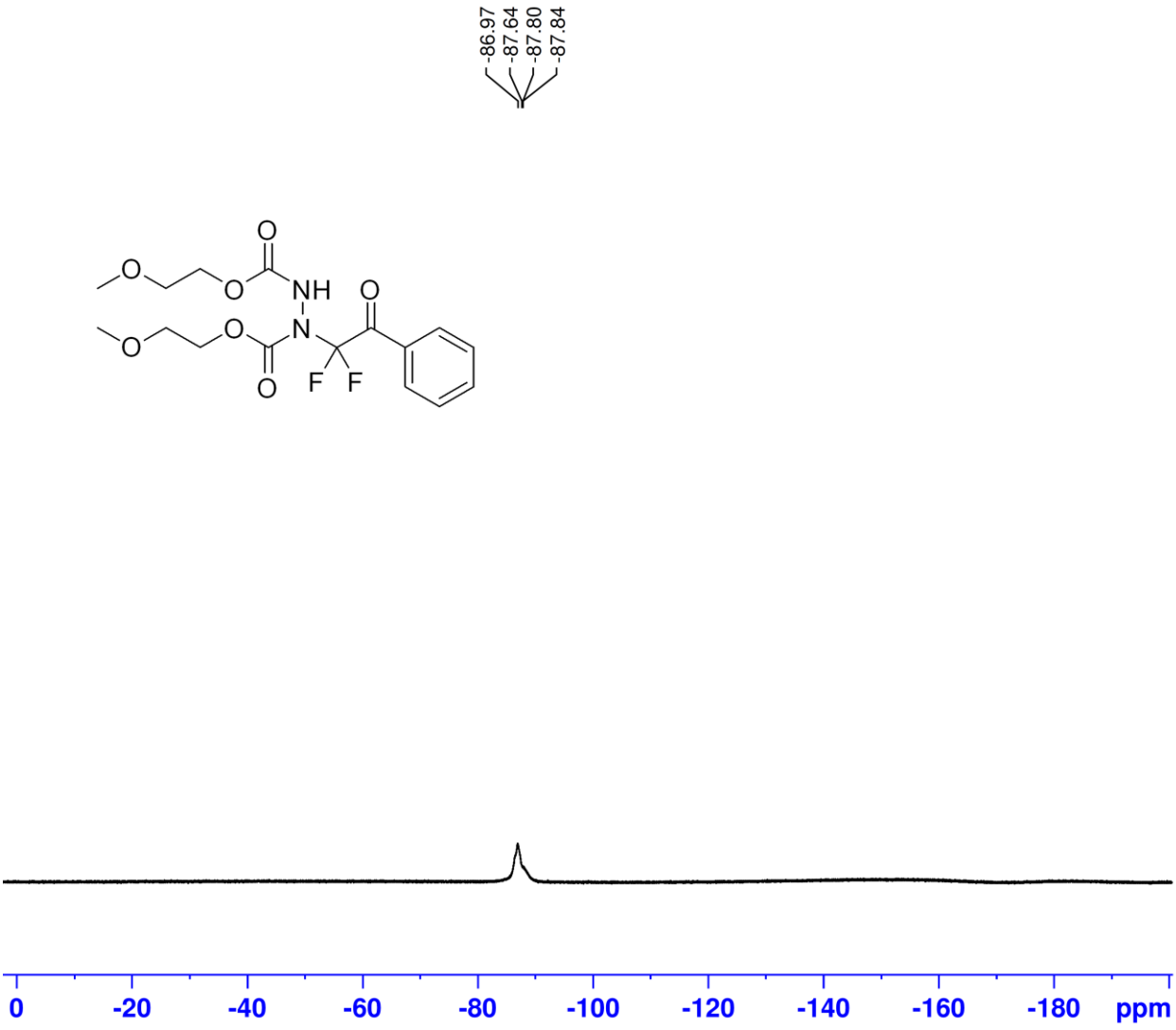
Compound **3d**: ^{1}H NMR (400 MHz, $CDCl_3$)



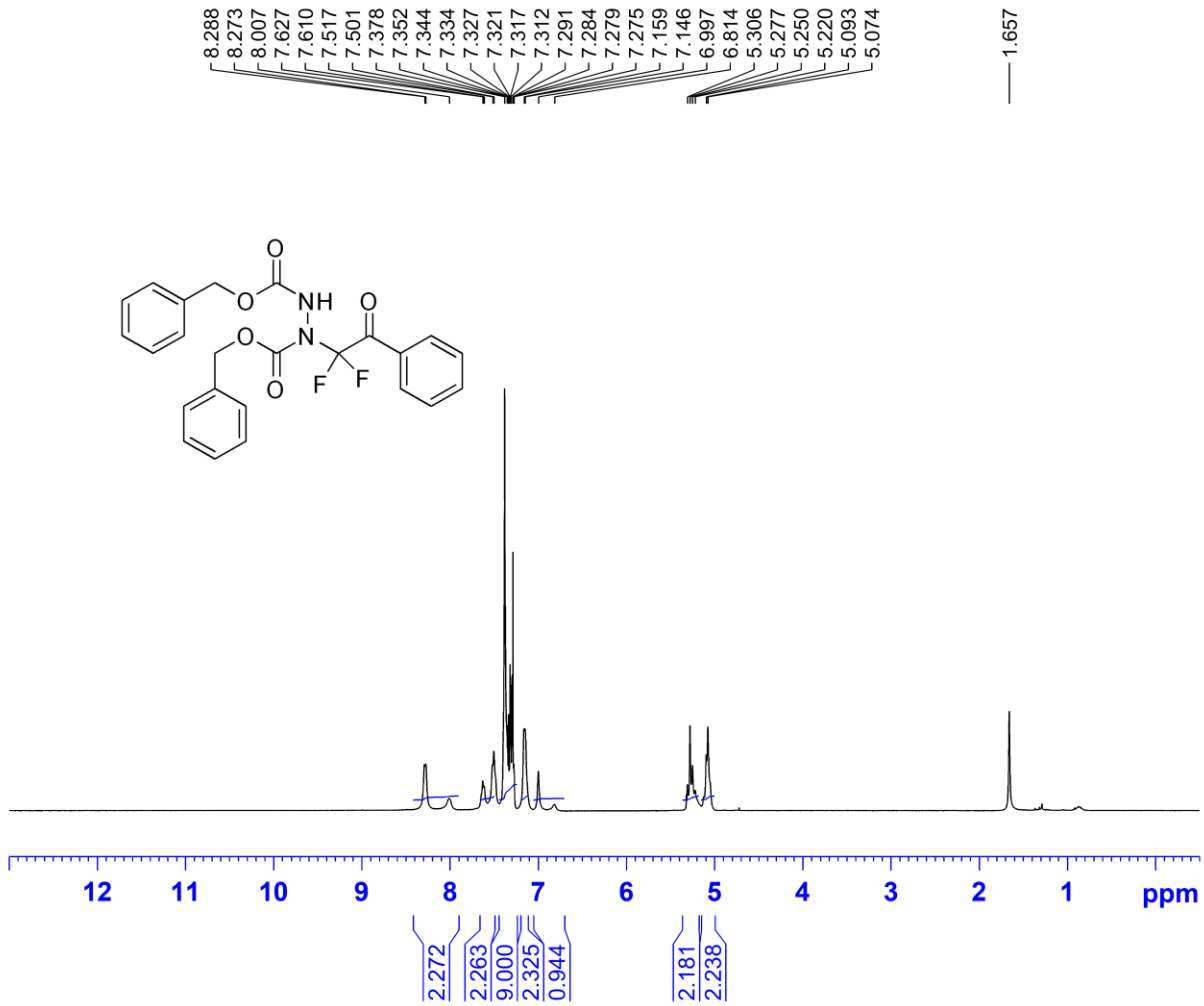
Compound **3d**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



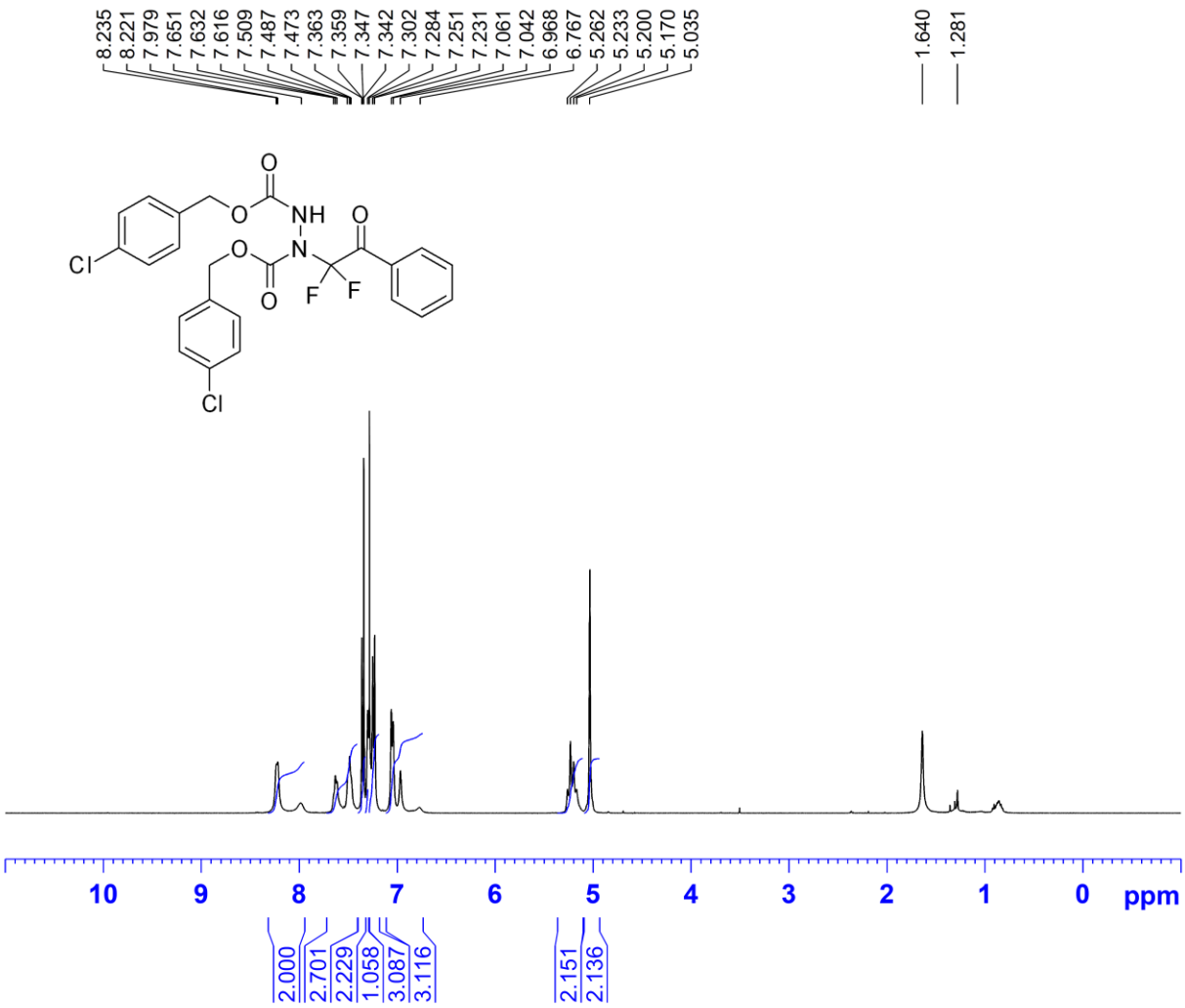
Compound **3d**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



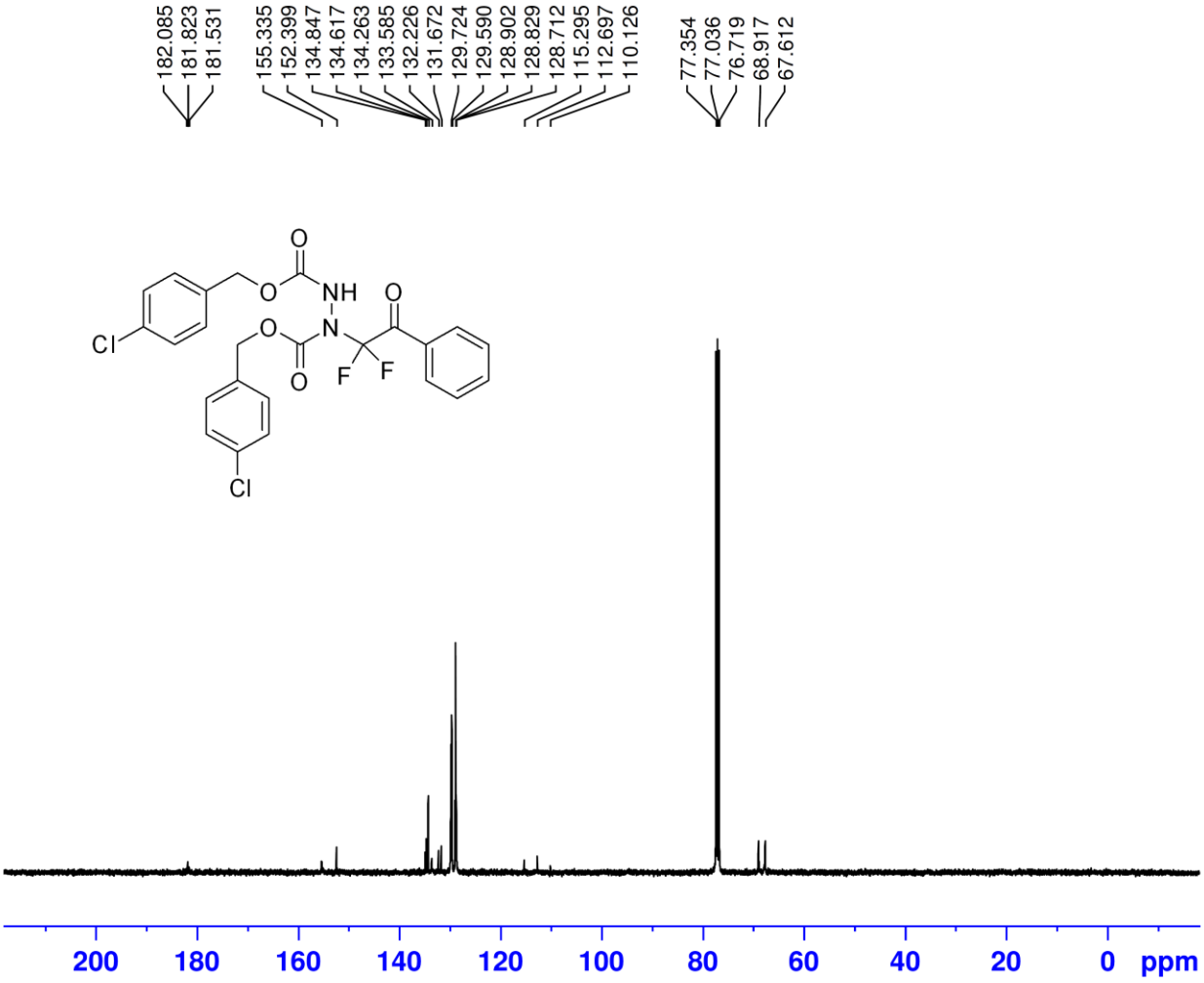
Compound **3e**: ^{1}H NMR (400 MHz, $CDCl_3$)



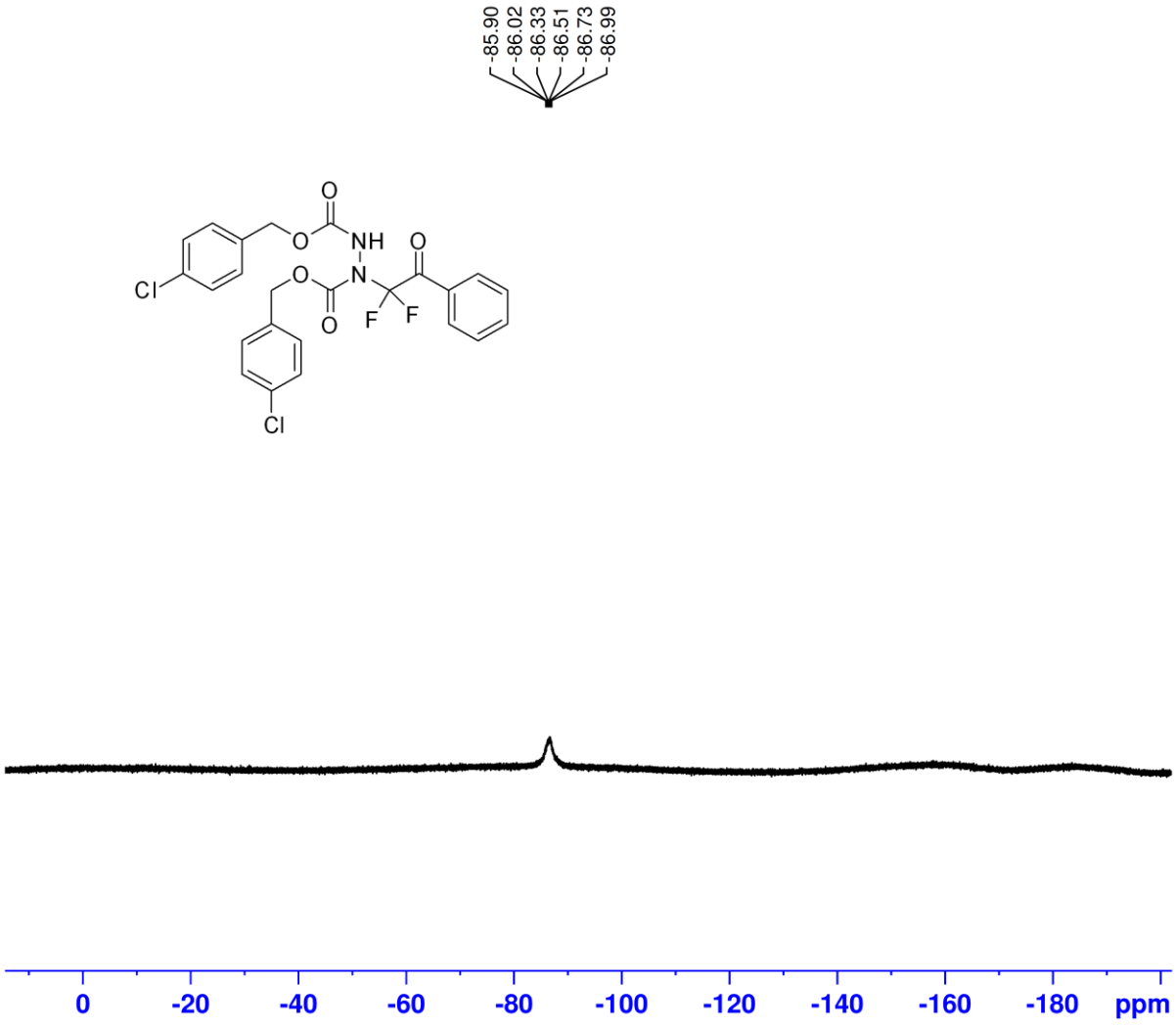
Compound **3f**: ^{1}H NMR (400 MHz, $CDCl_3$)



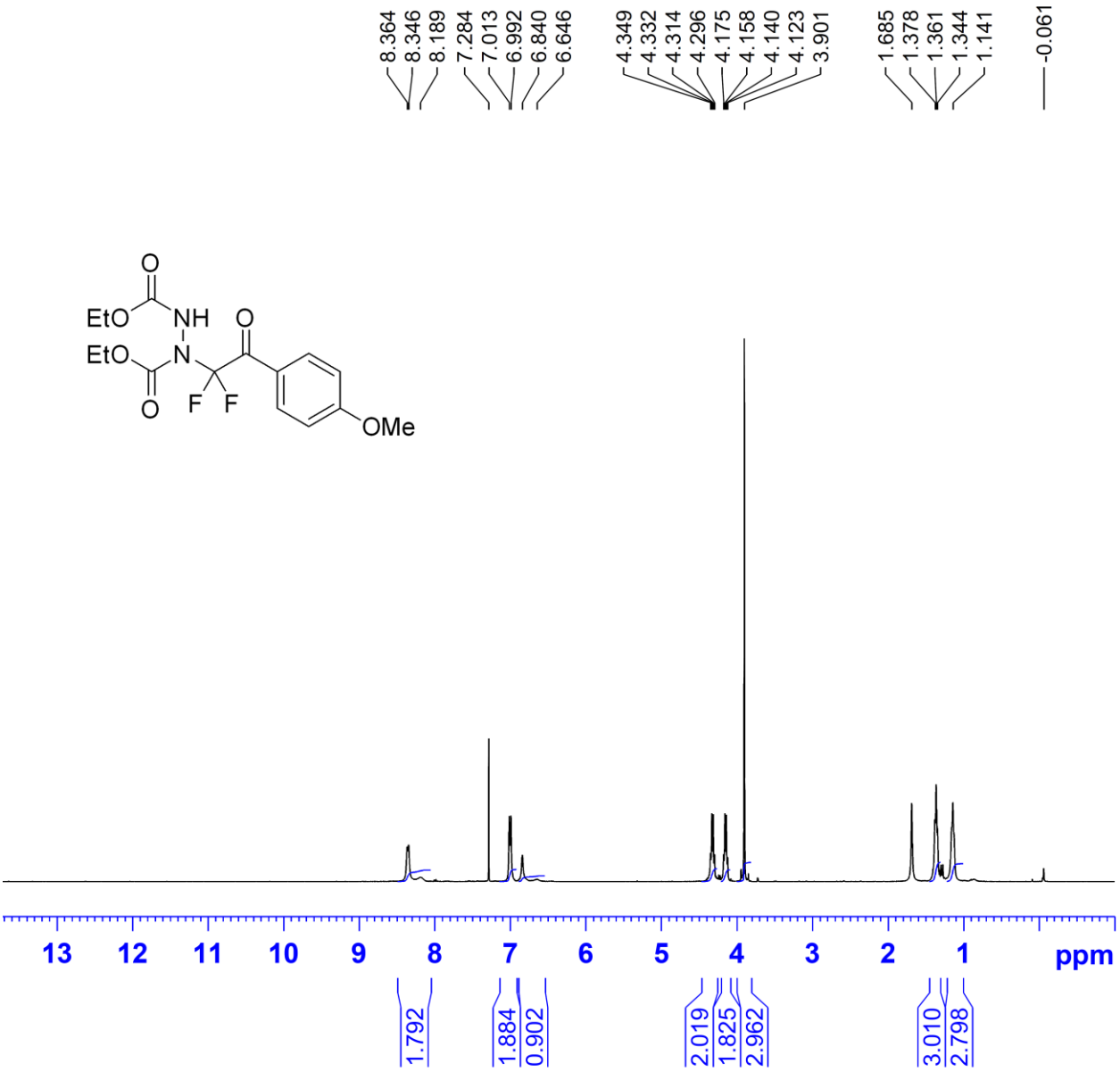
Compound **3f**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



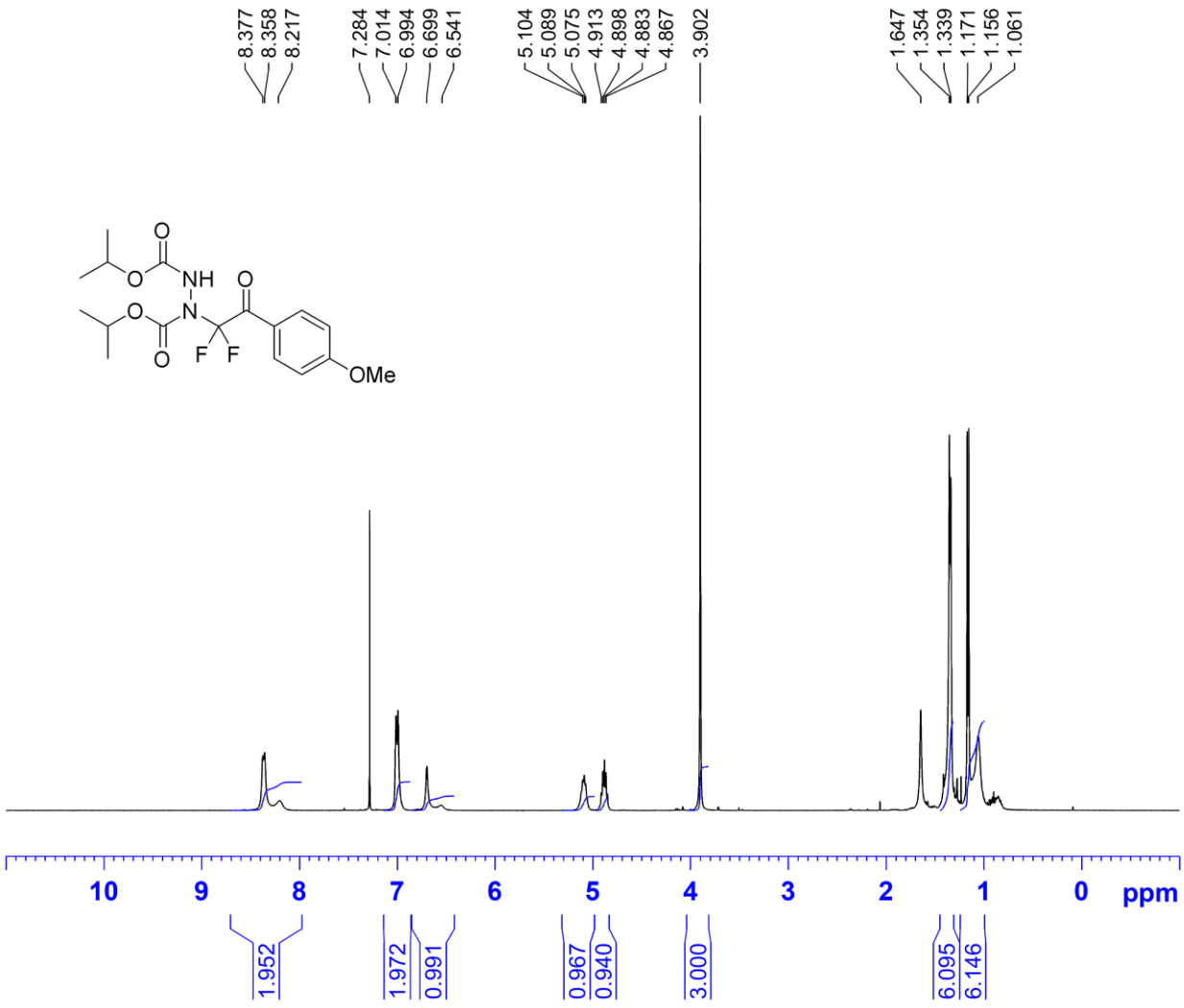
Compound **3f**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



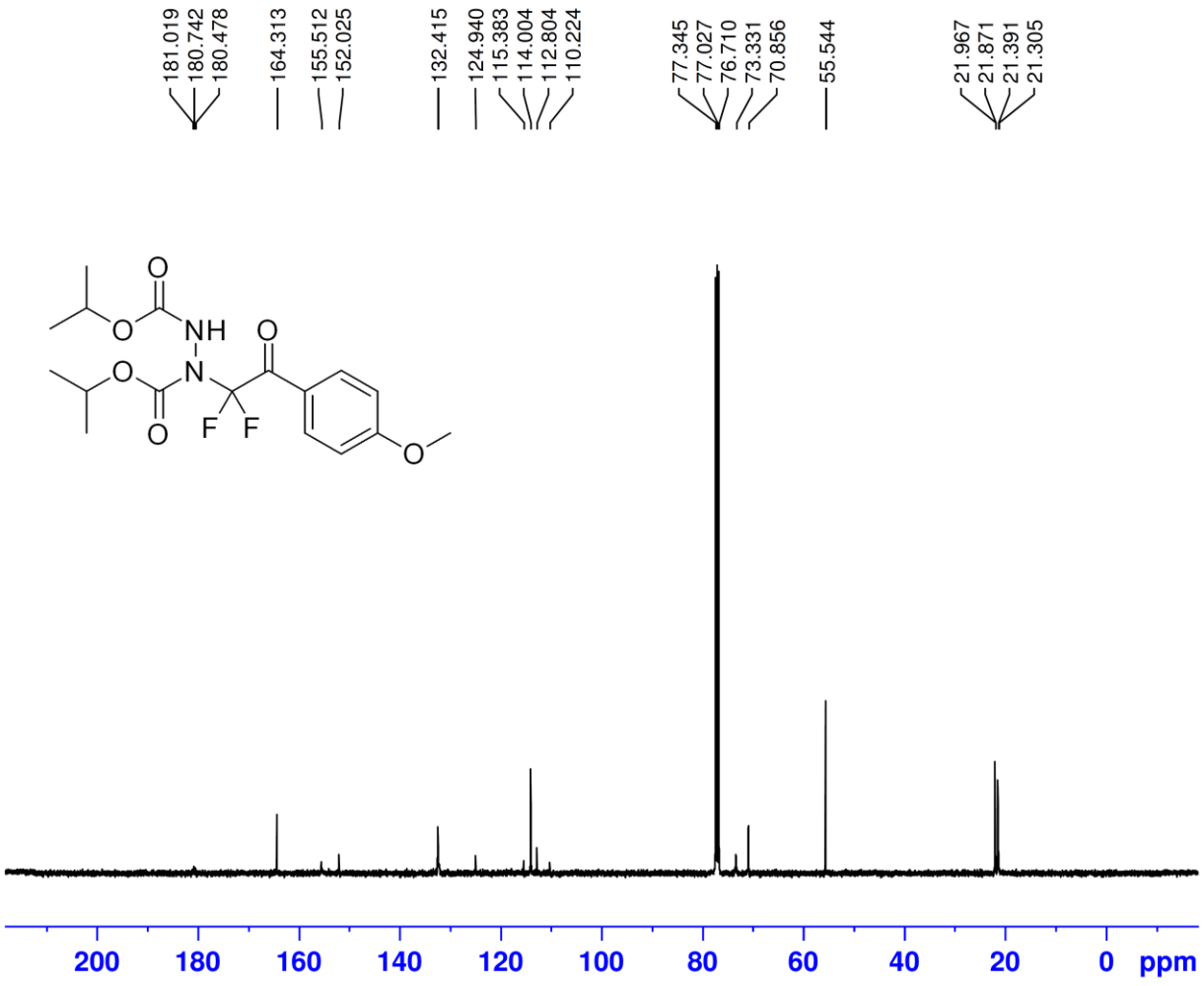
Compound **4a**: ^{1}H NMR (400 MHz, $CDCl_3$)



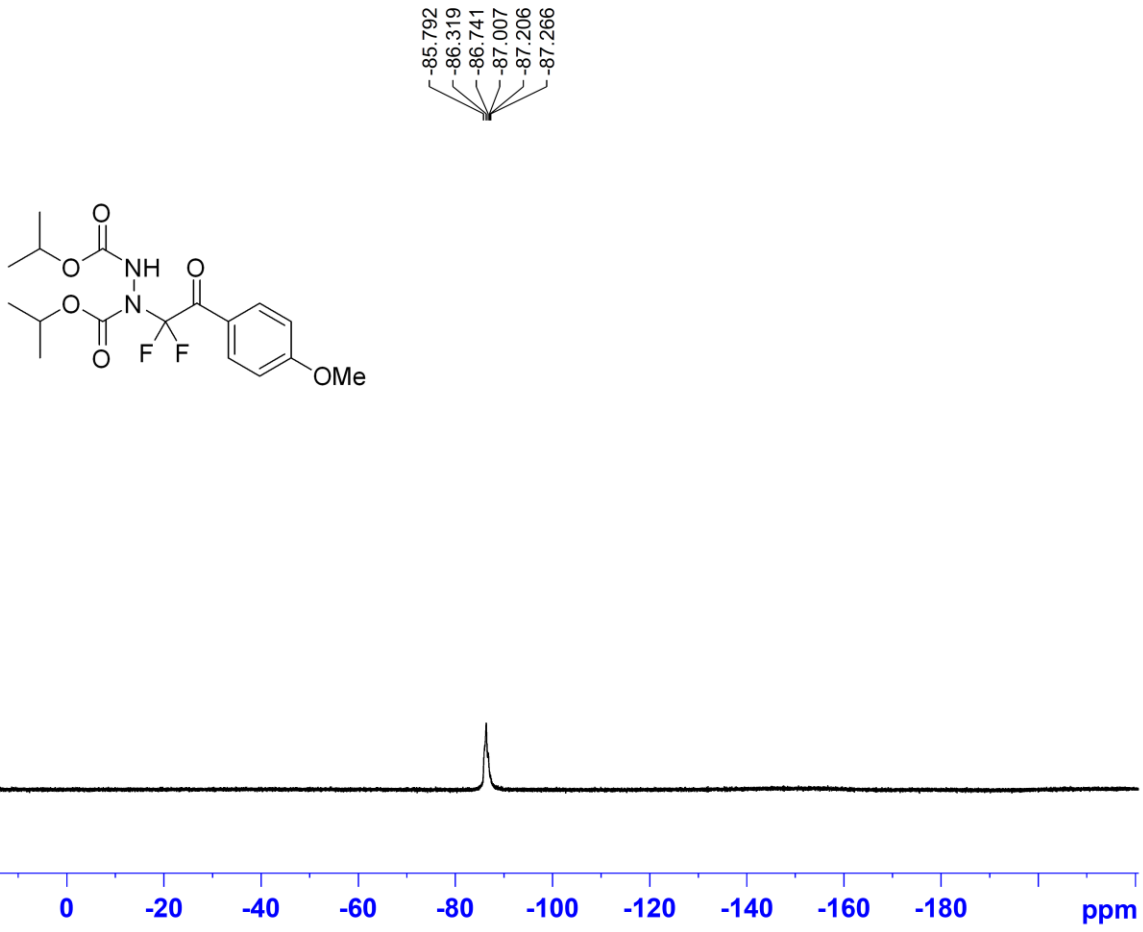
Compound **4b**: ^{1}H NMR (400 MHz, $CDCl_3$)



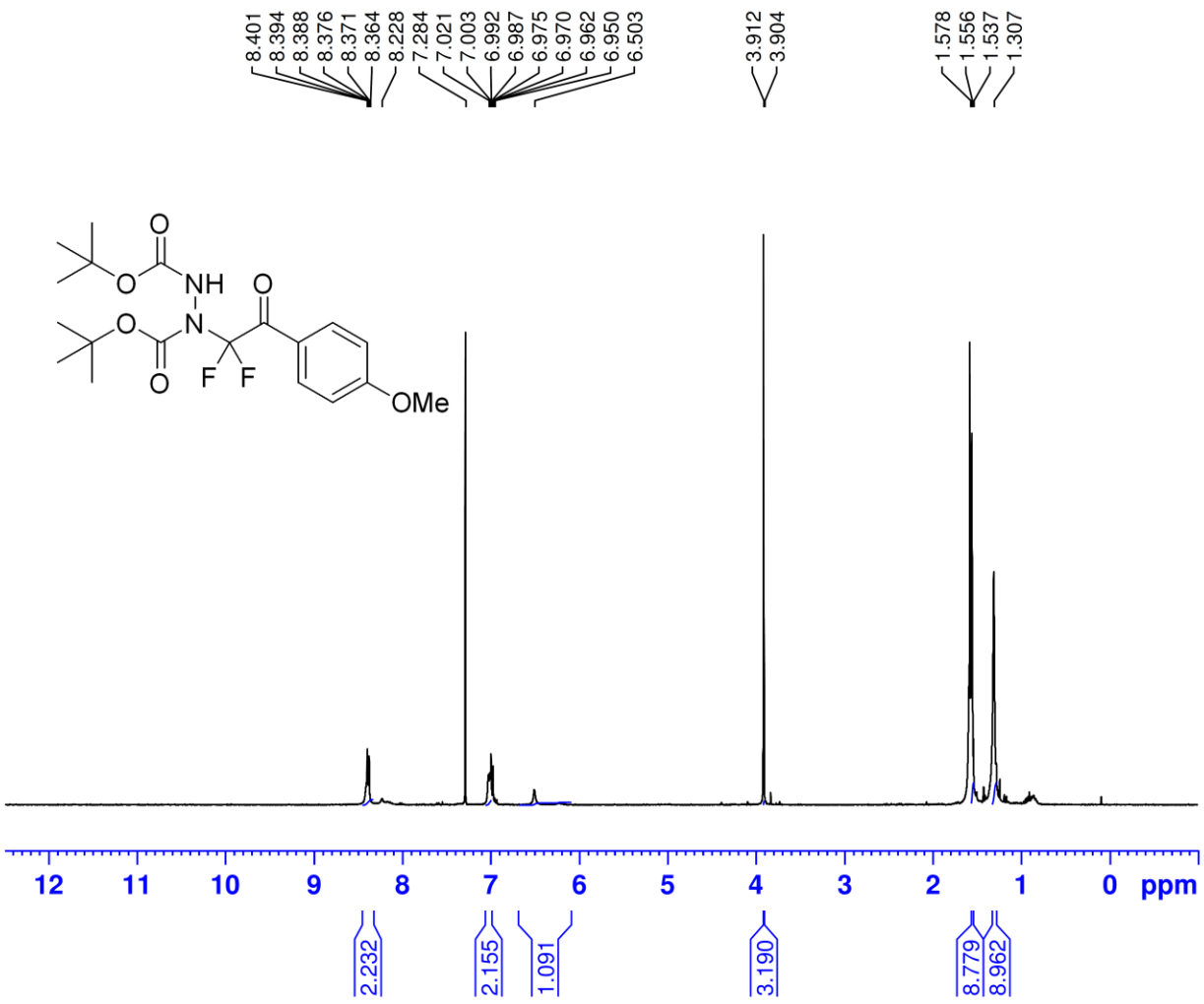
Compound **4b**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



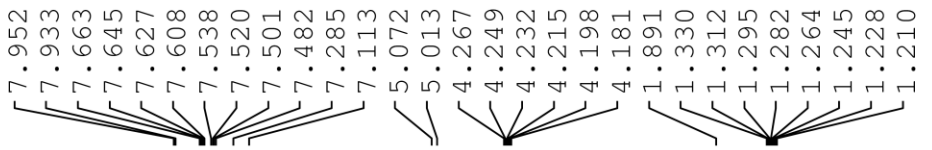
Compound **4b**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

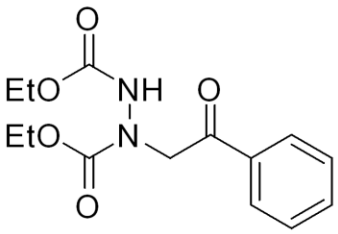


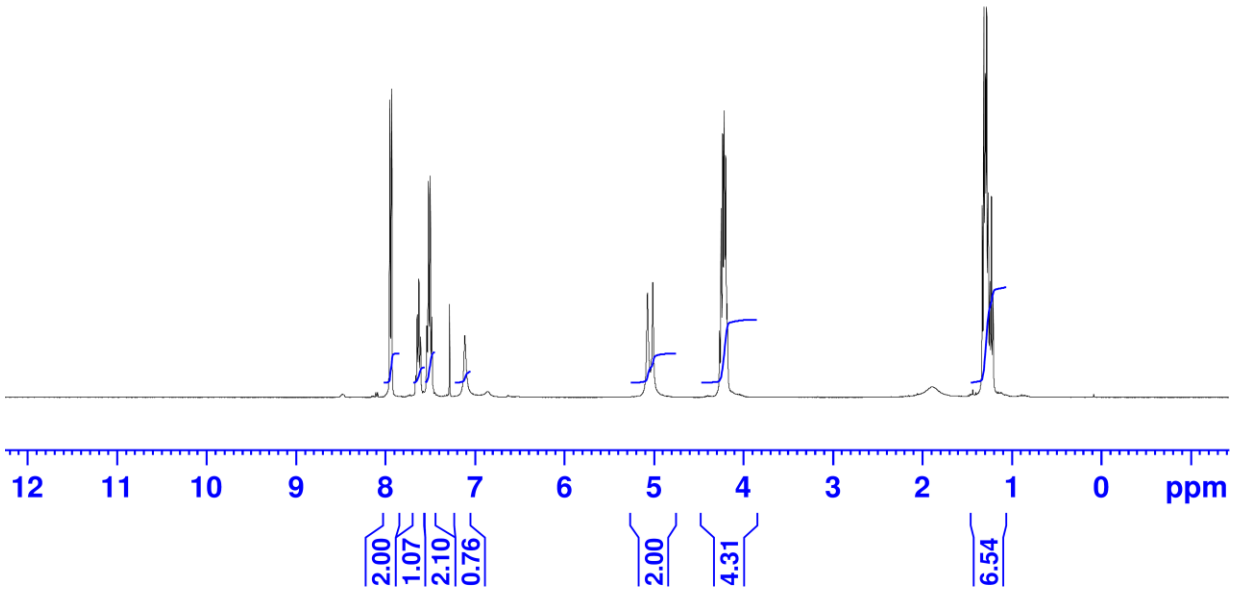
Compound **4c**: ^{1}H NMR (400 MHz, $CDCl_3$)



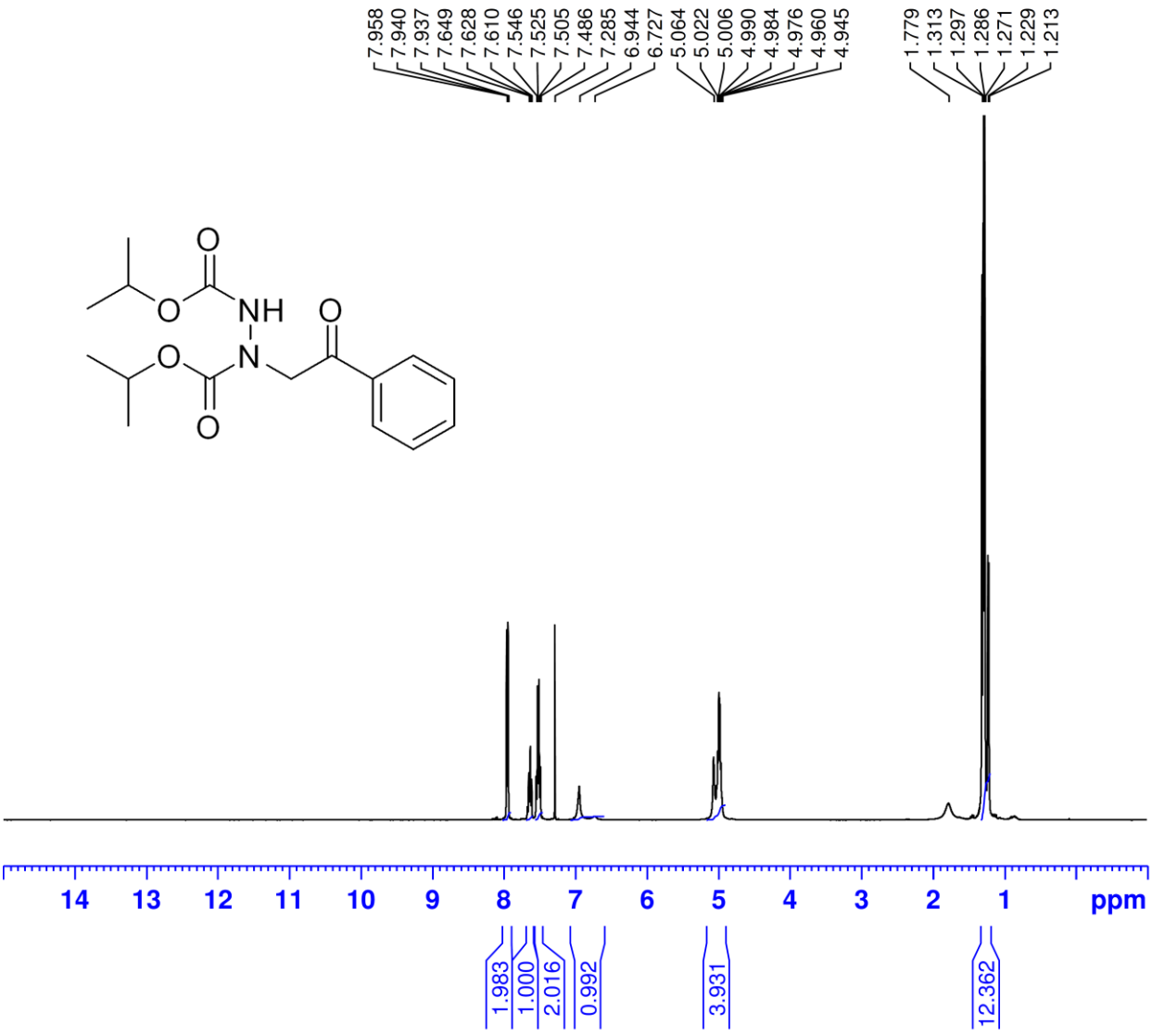
Compound **5a**: ^{1}H NMR (400 MHz, $CDCl_3$)



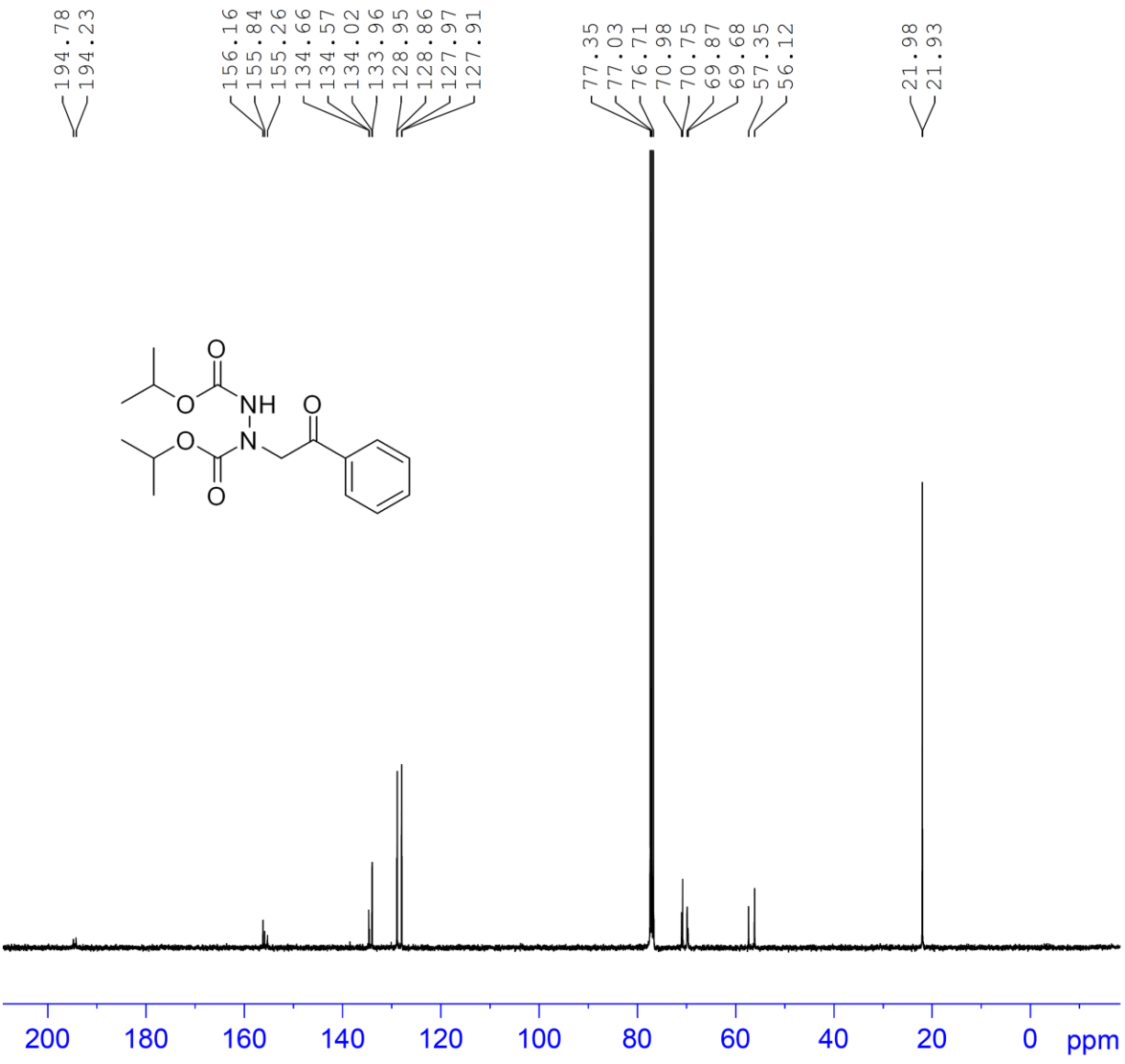




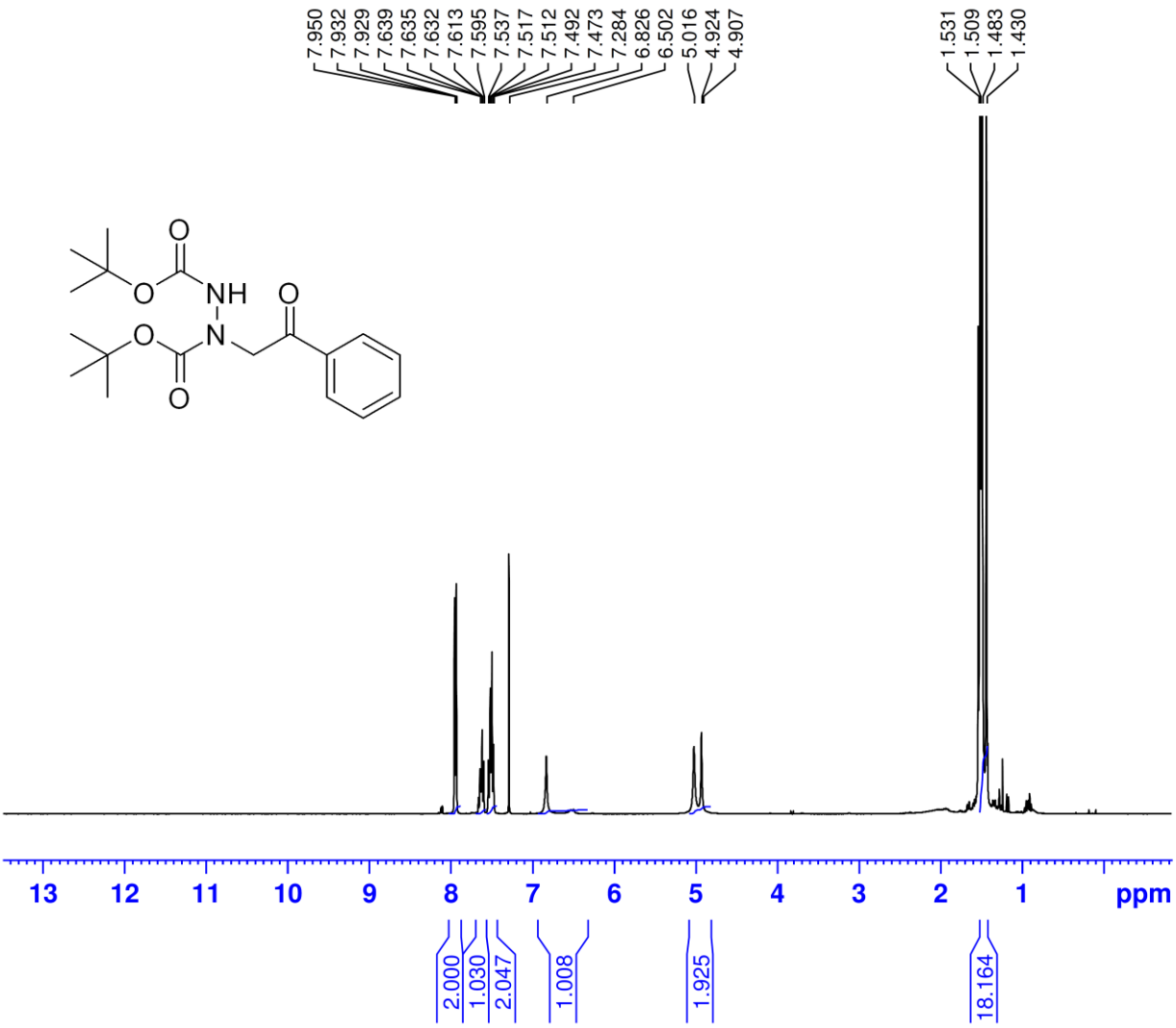
Compound **5b**: ^{1}H NMR (400 MHz, $CDCl_3$)



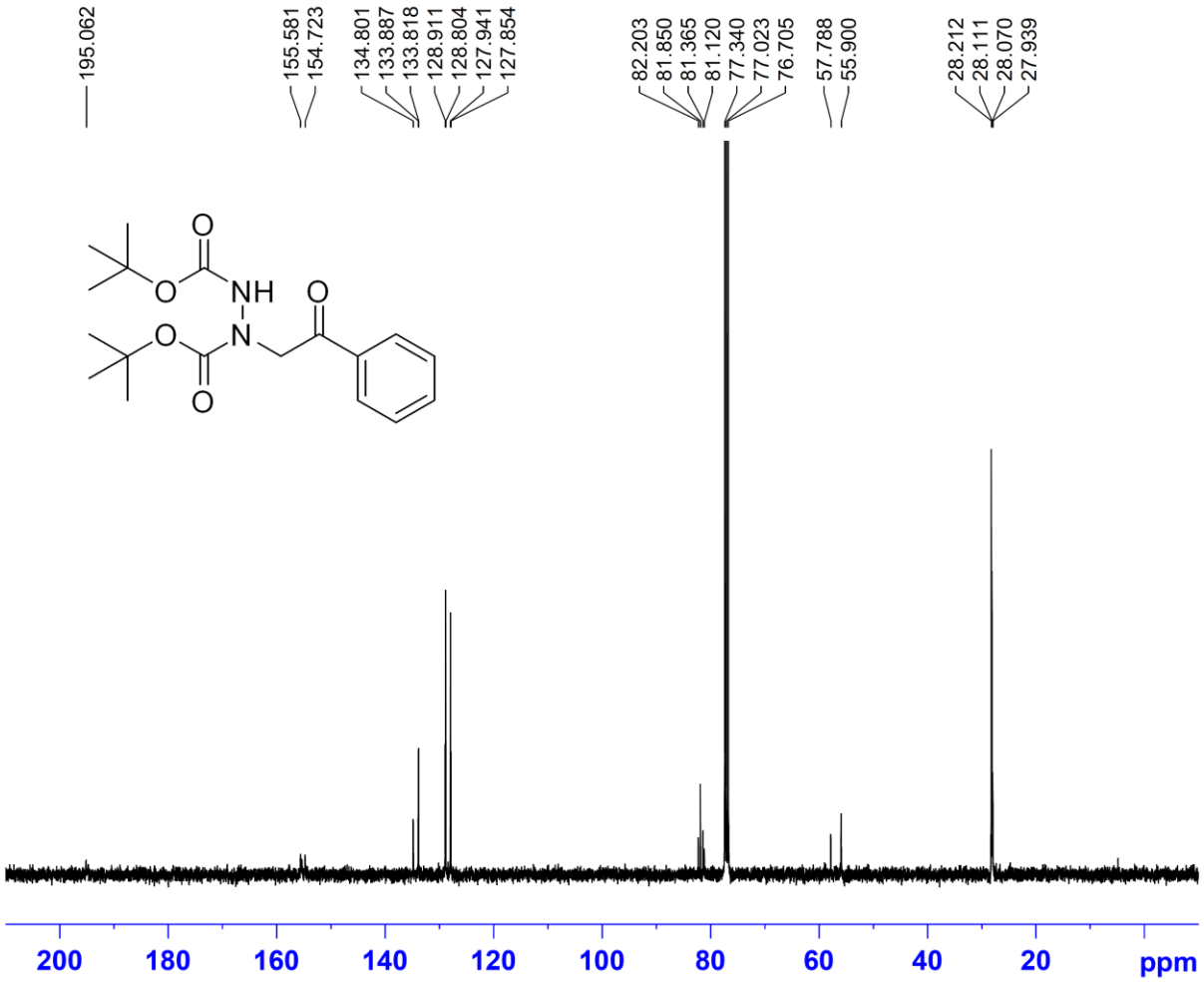
Compound **5b**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



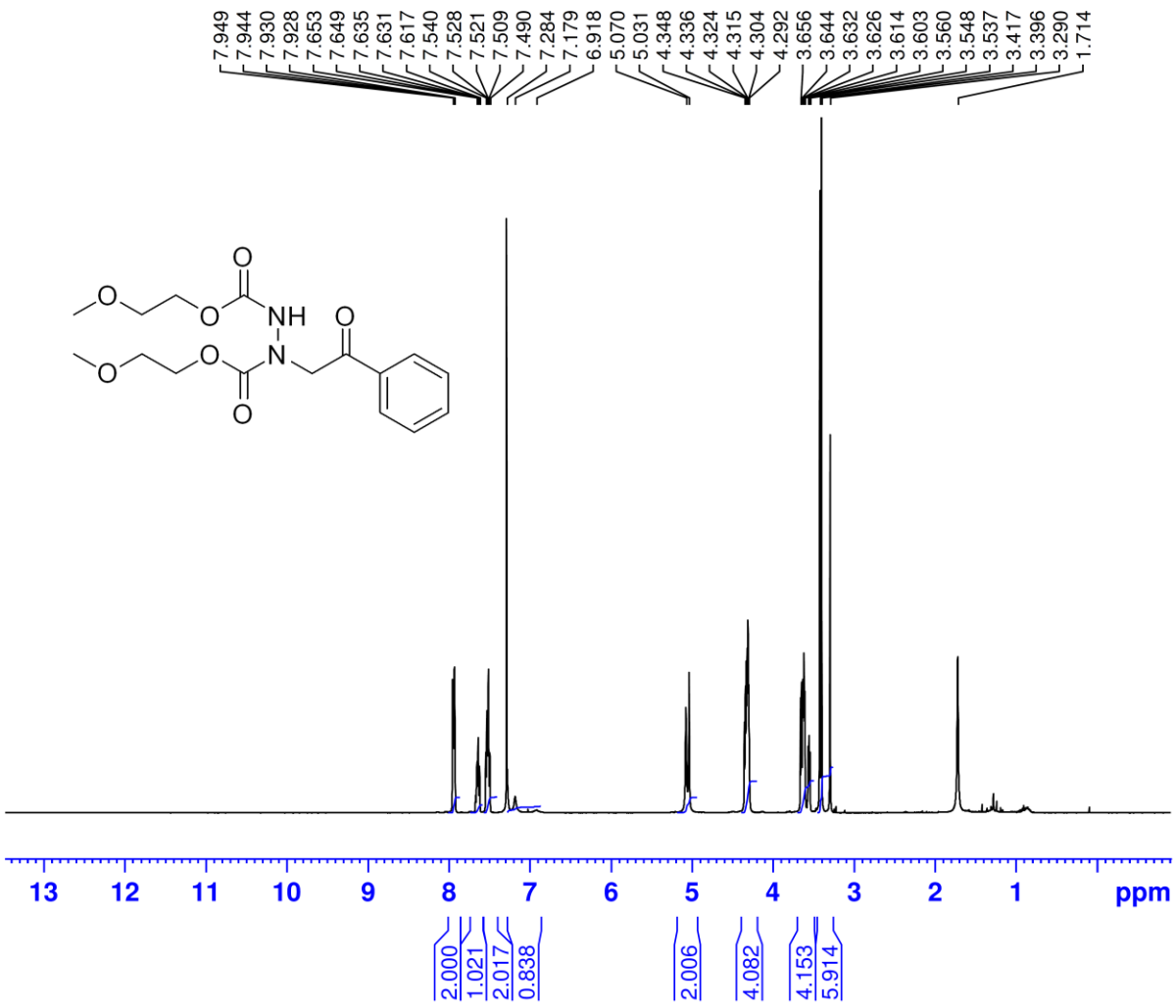
Compound **5c**: ^{1}H NMR (400 MHz, $CDCl_3$)



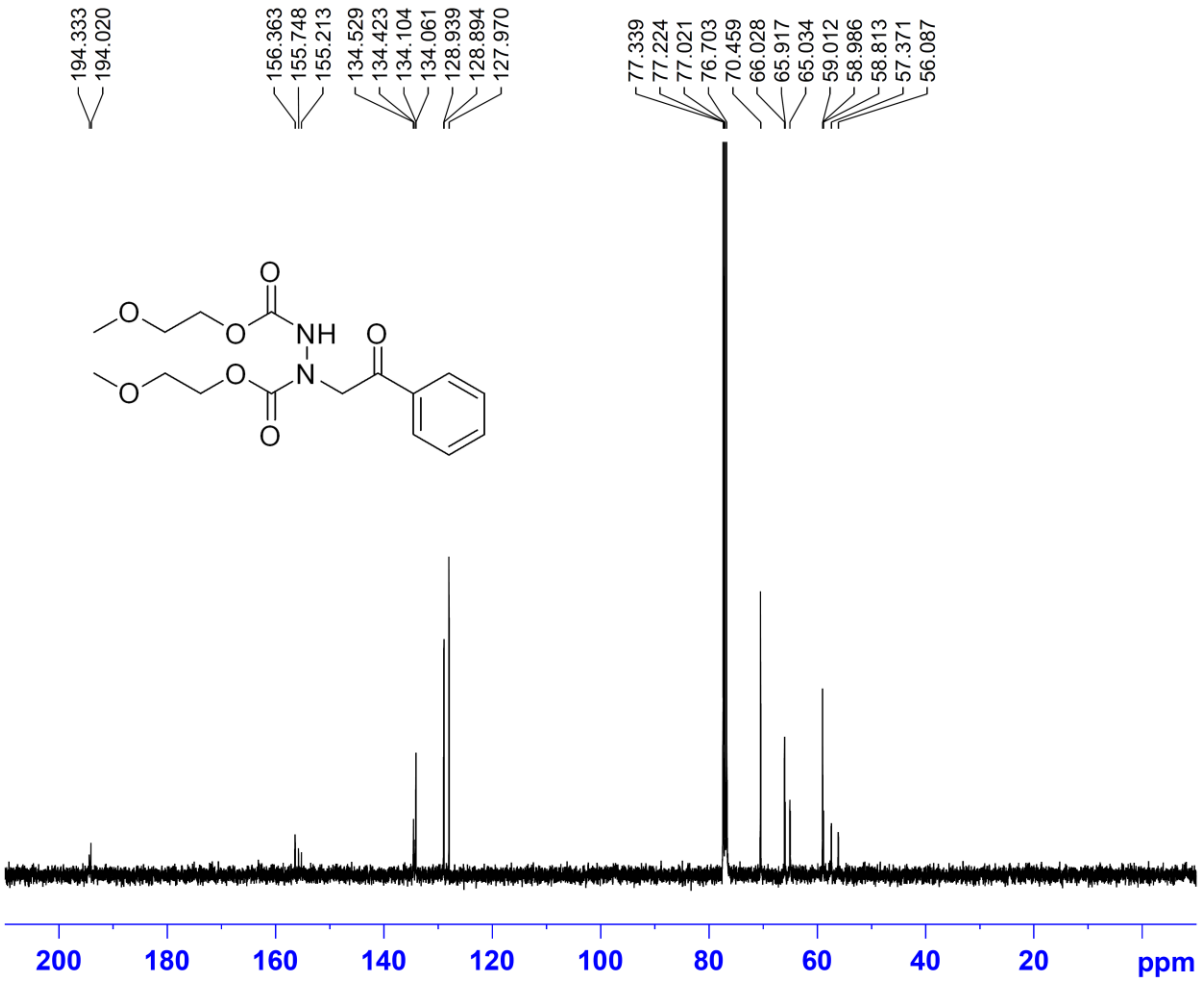
Compound **5c**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



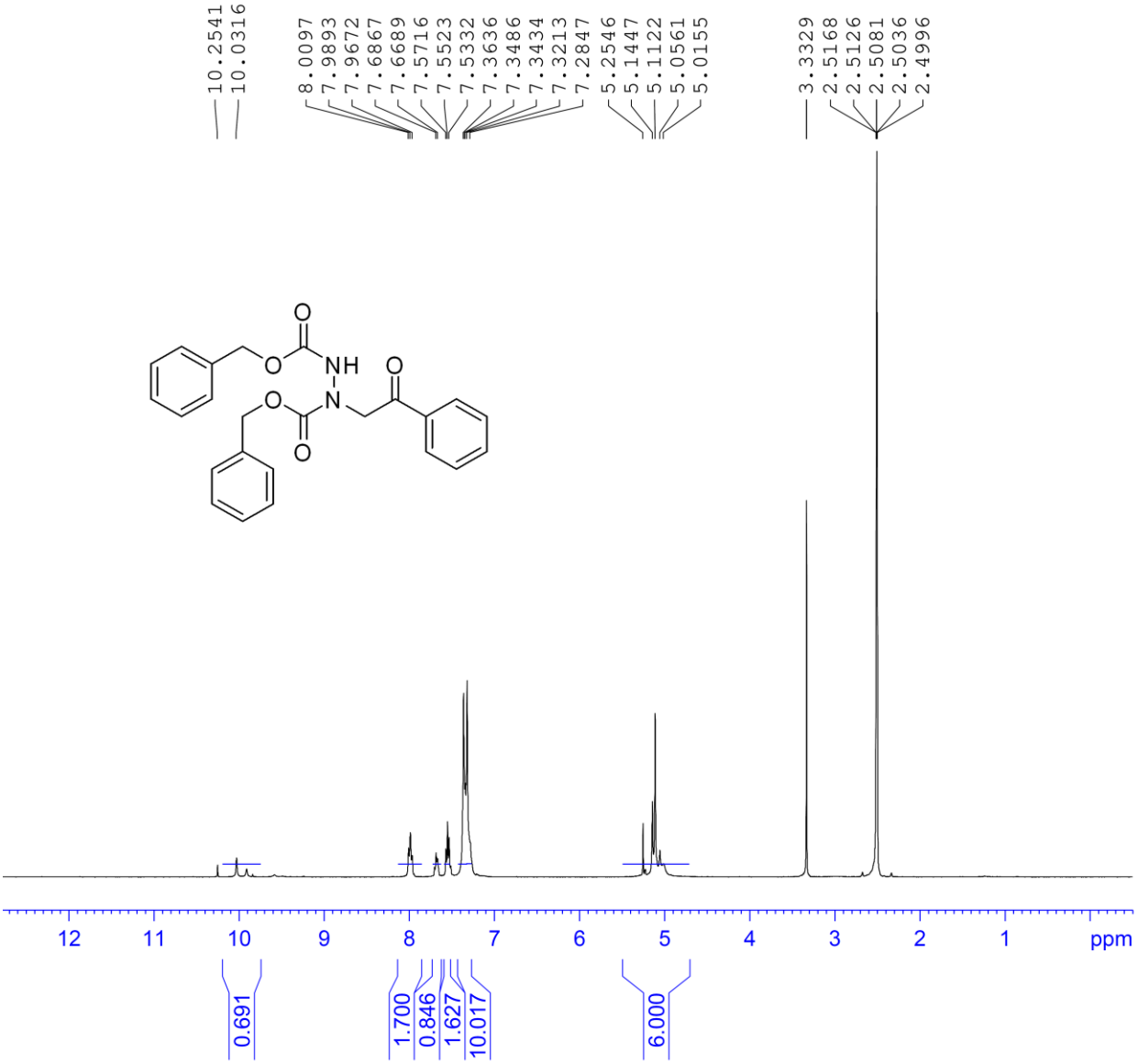
Compound **5d**: ^{1}H NMR (400 MHz, $CDCl_3$)



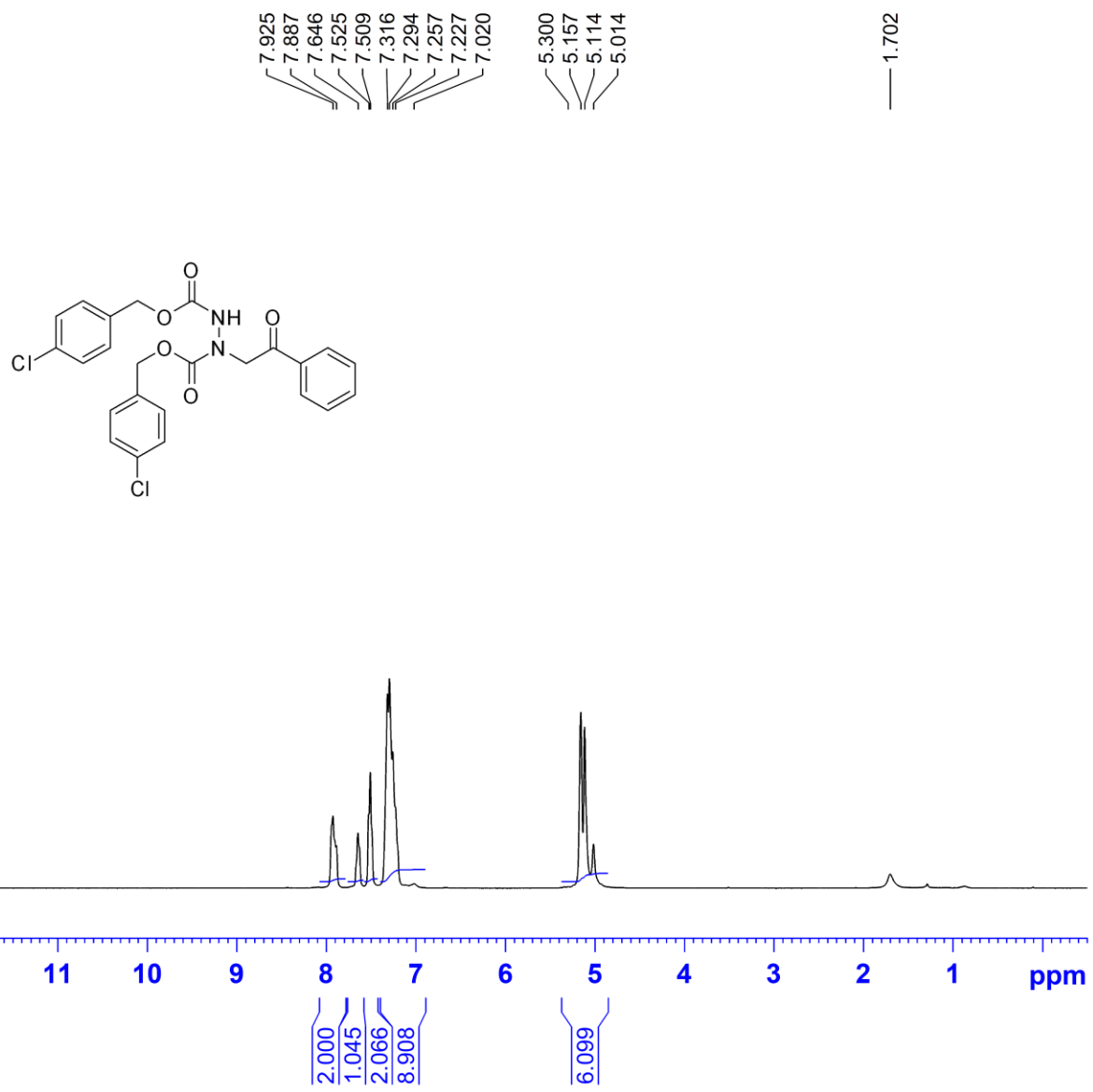
Compound **5d**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



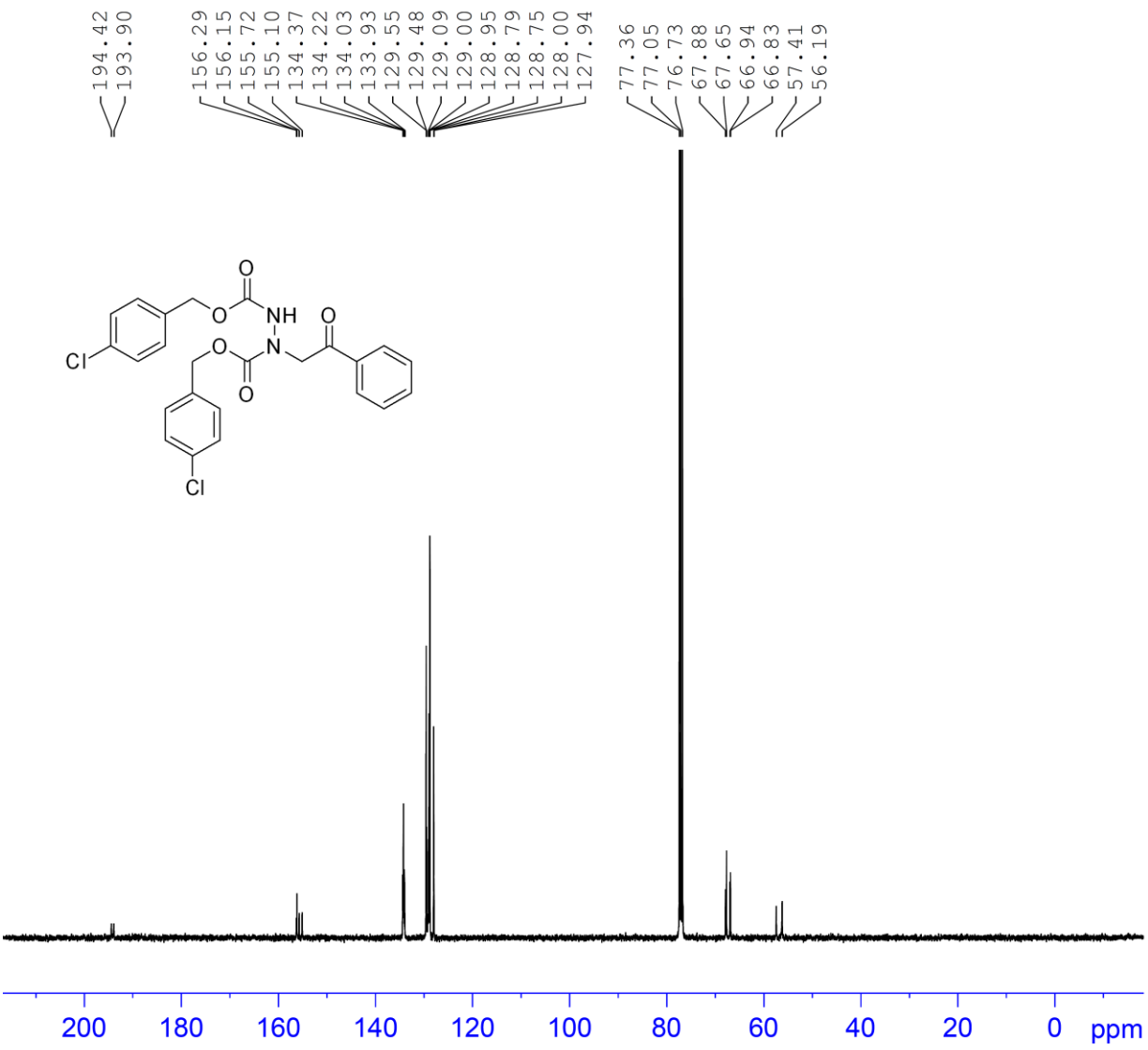
Compound **5e**: ^{1}H NMR (400 MHz, DMSO-d_6)



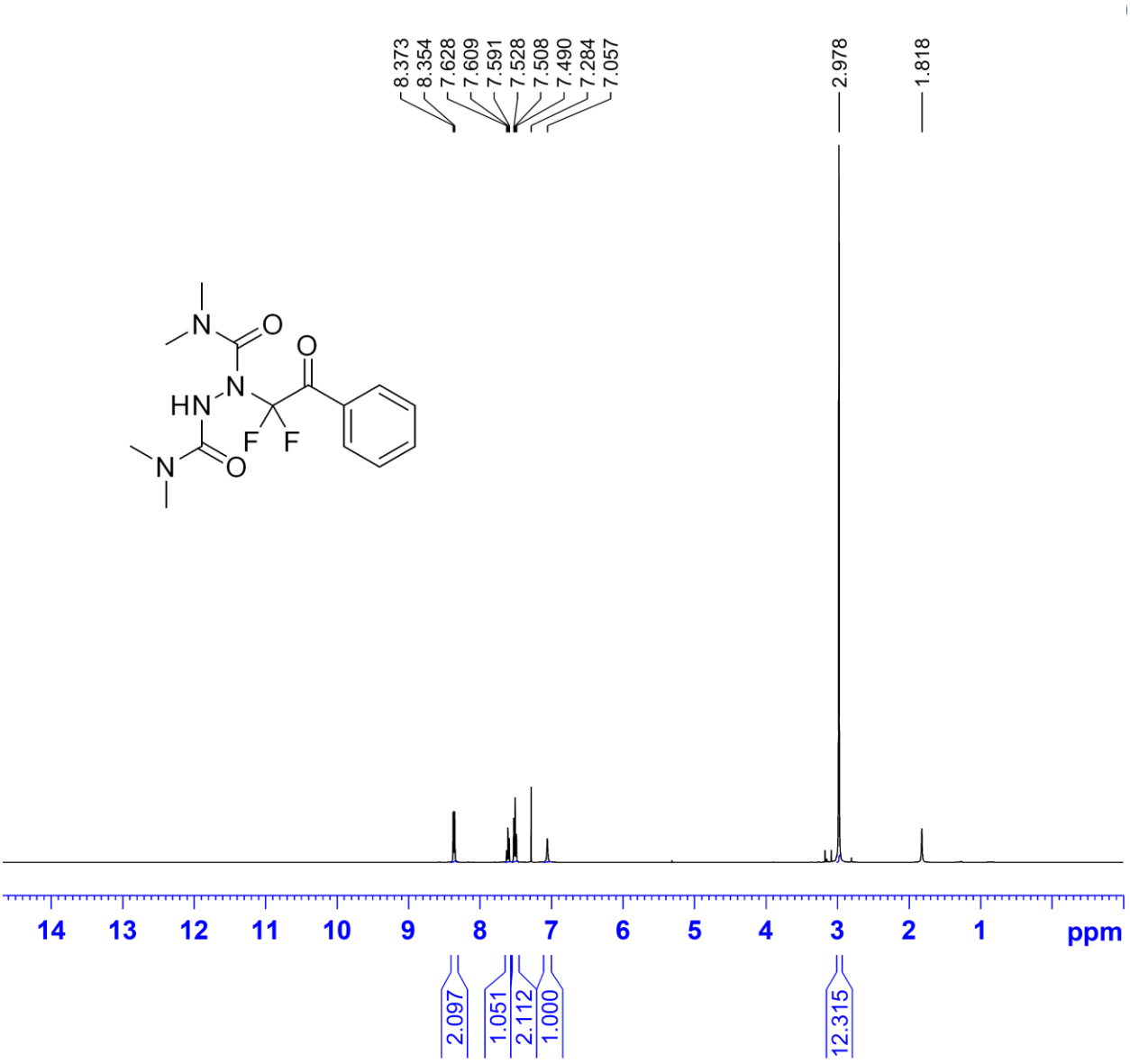
Compound **5f**: ^{1}H NMR (400 MHz, $CDCl_3$)



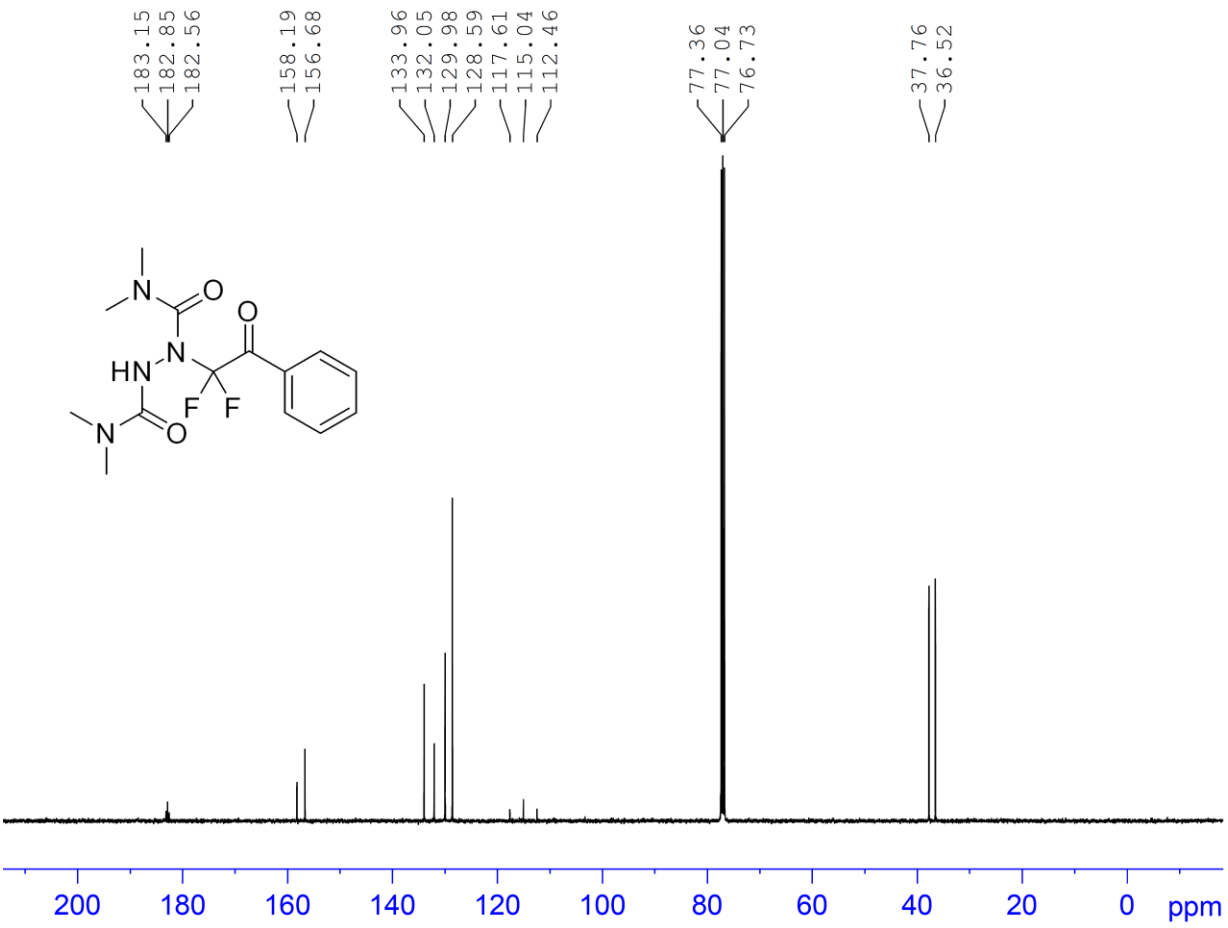
Compound **5f**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



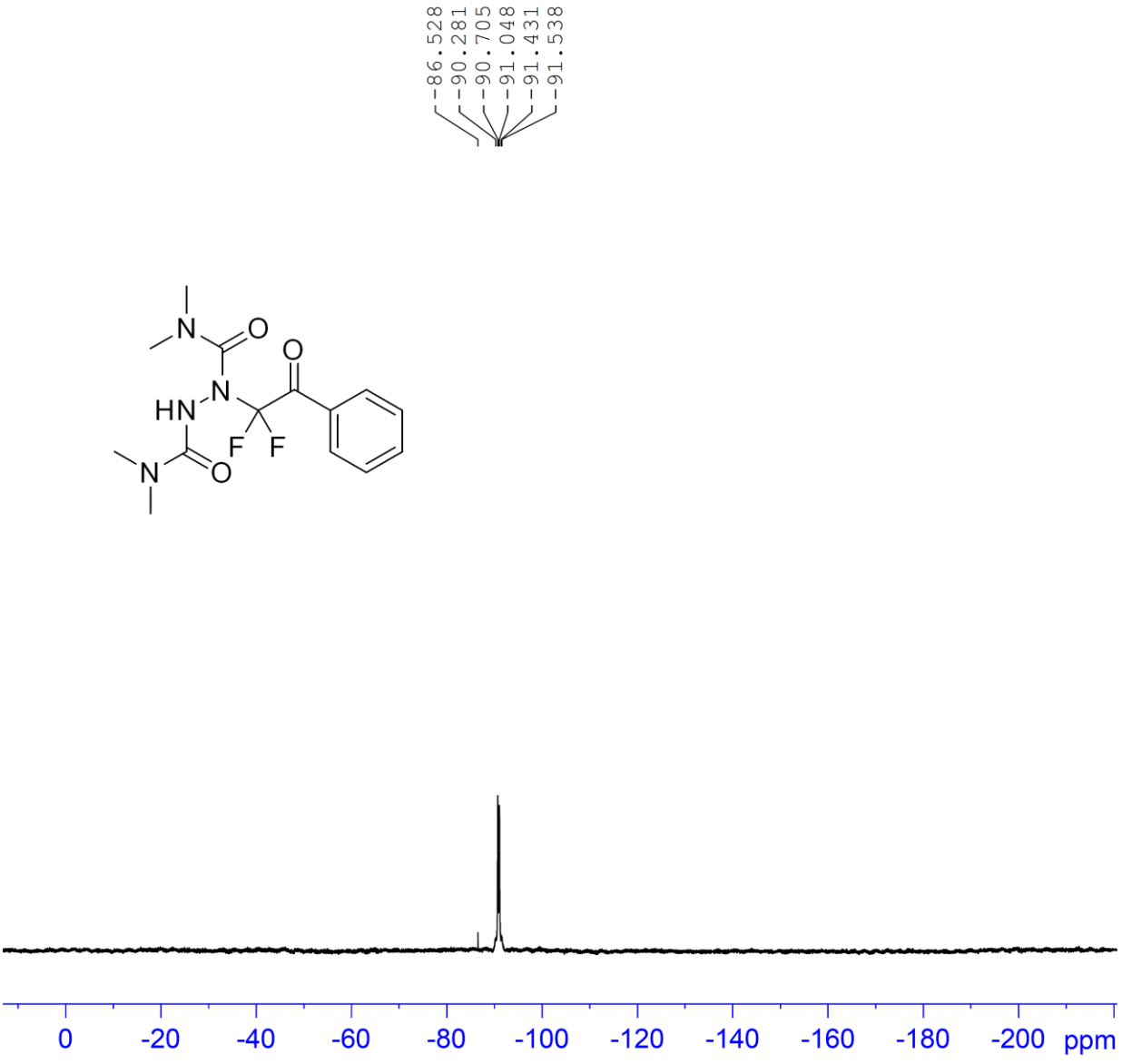
Compound **7a**: ^{1}H NMR (400 MHz, $CDCl_3$)



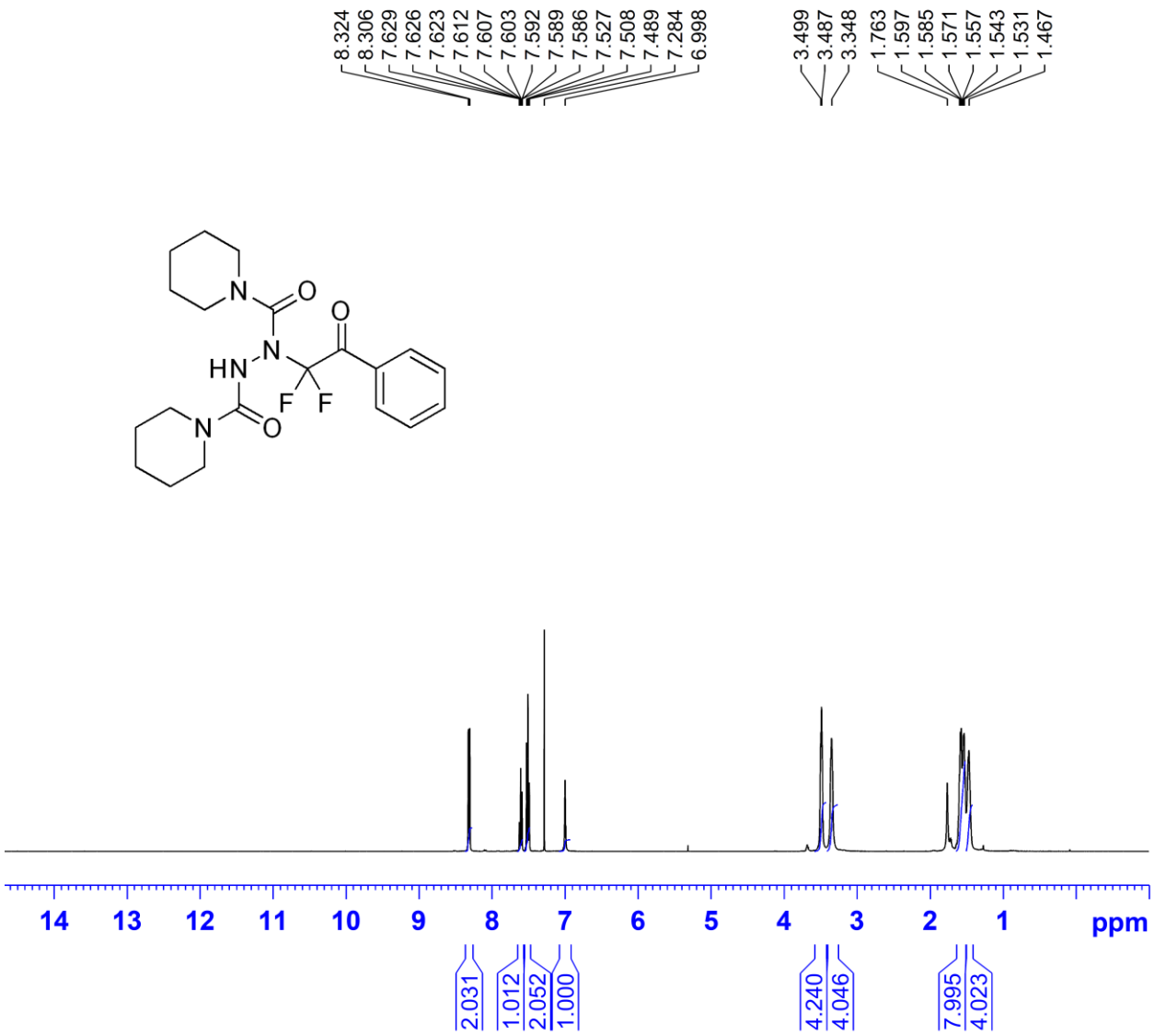
Compound **7a**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



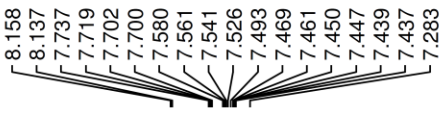
Compound **7a**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

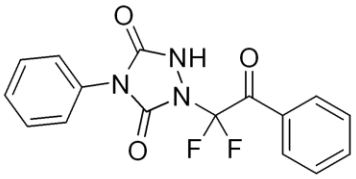


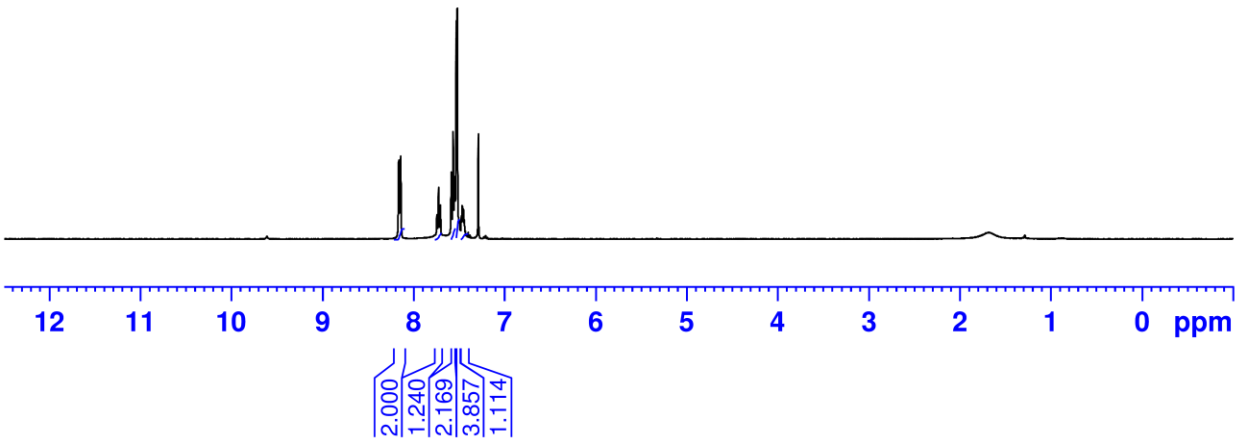
Compound **7b**: ^{1}H NMR (400 MHz, $CDCl_3$)



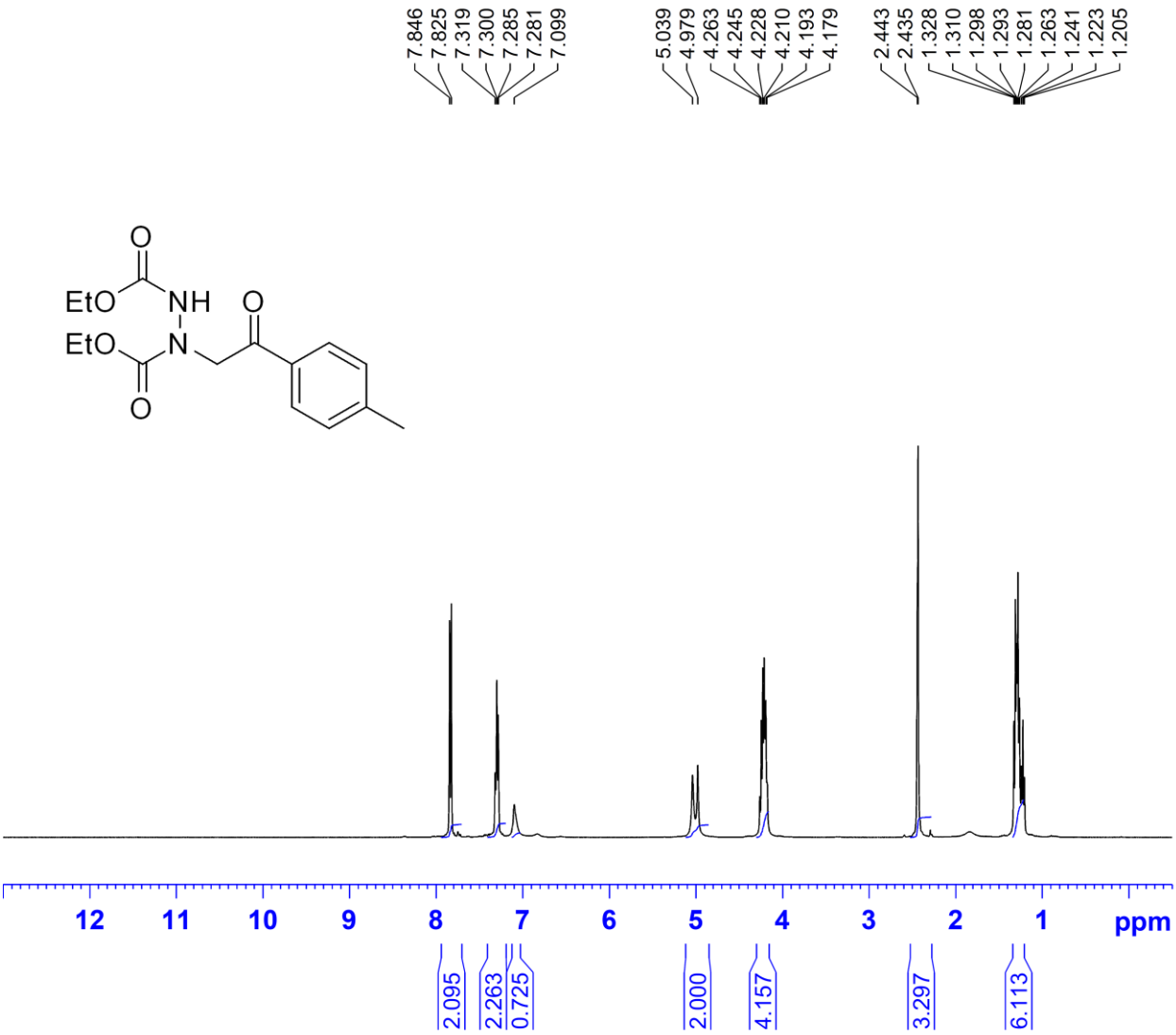
Compound **7c**: ^{1}H NMR (400 MHz, $CDCl_3$)



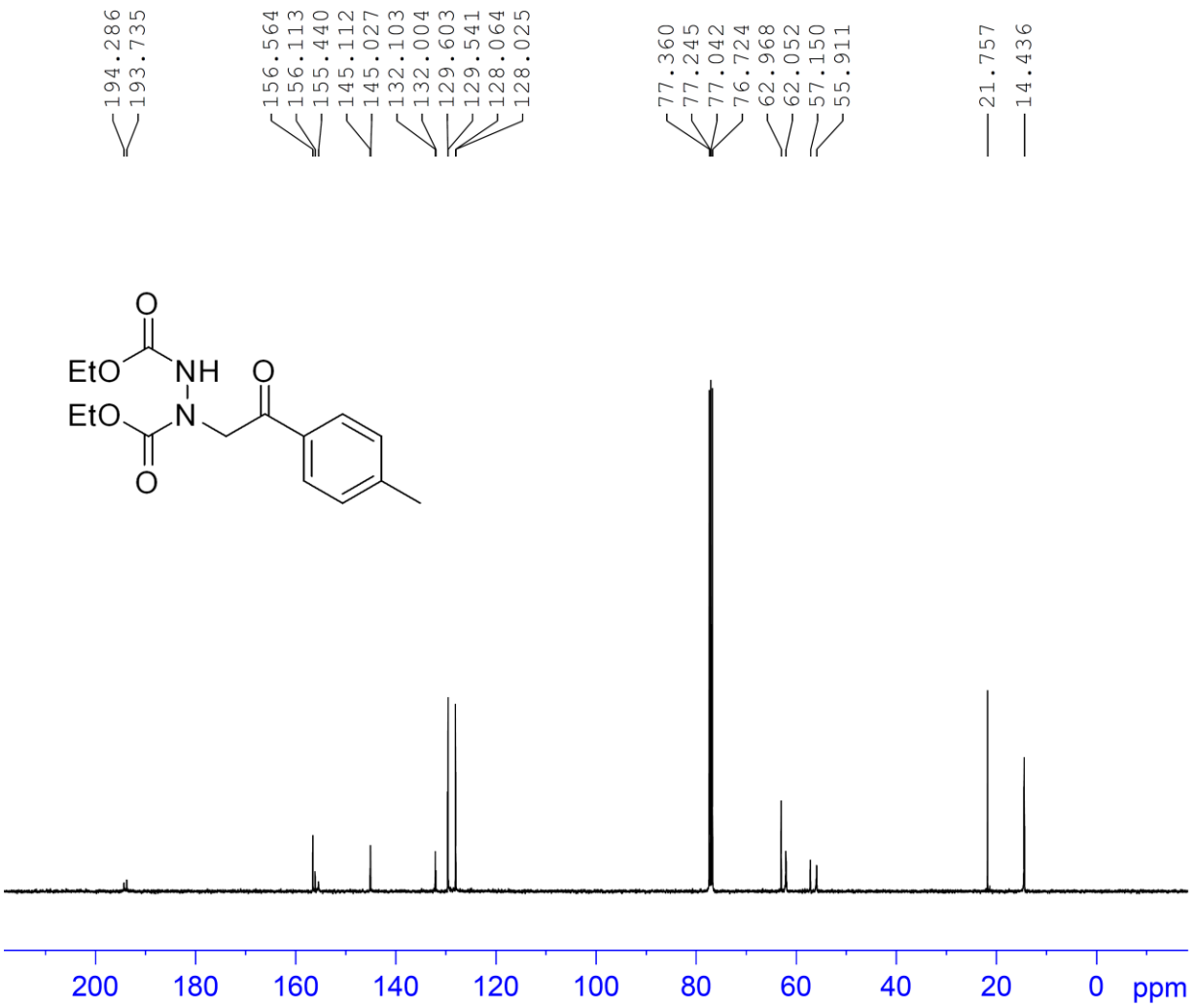




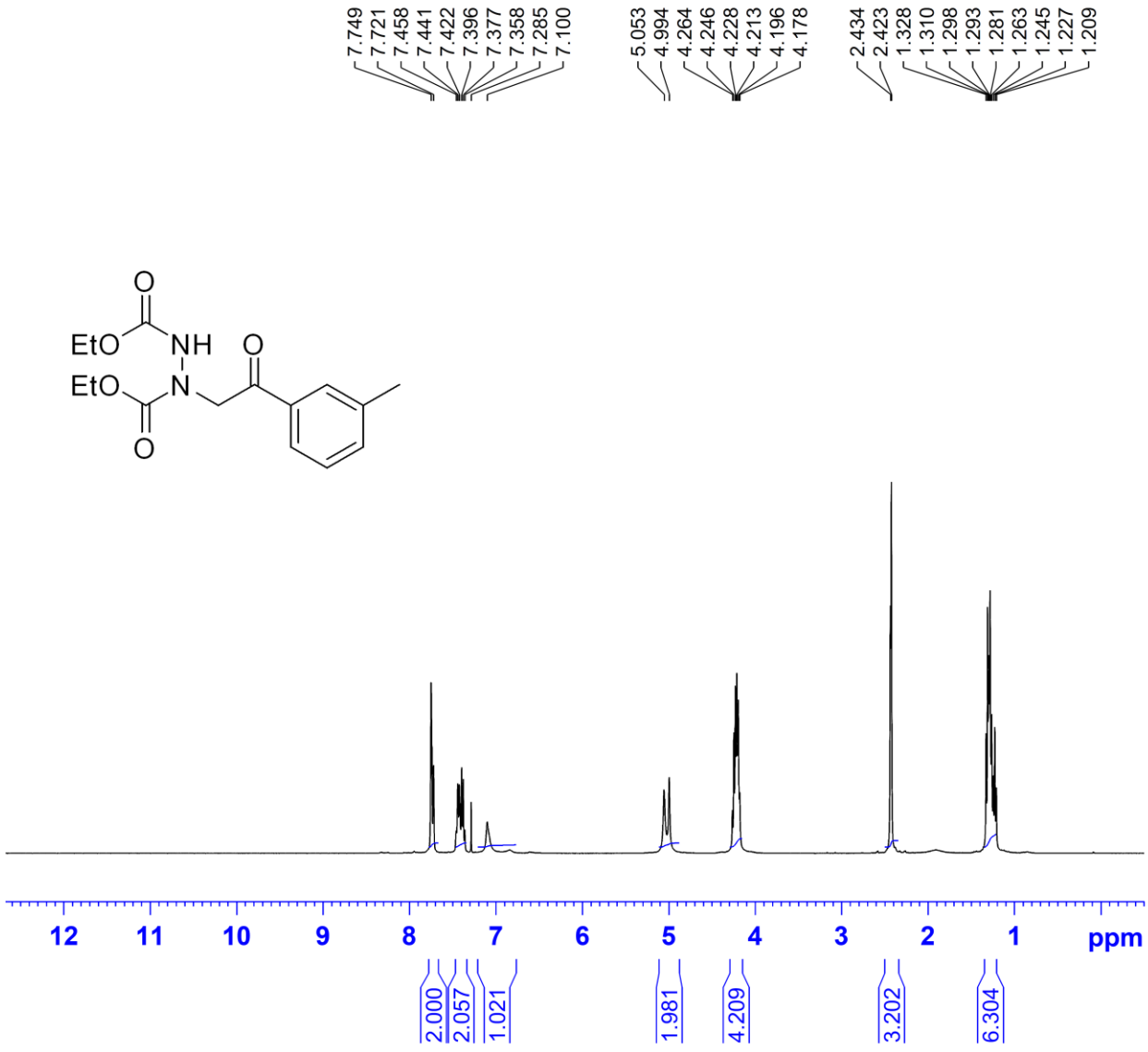
Compound **9a**: ^{1}H NMR (400 MHz, $CDCl_3$)



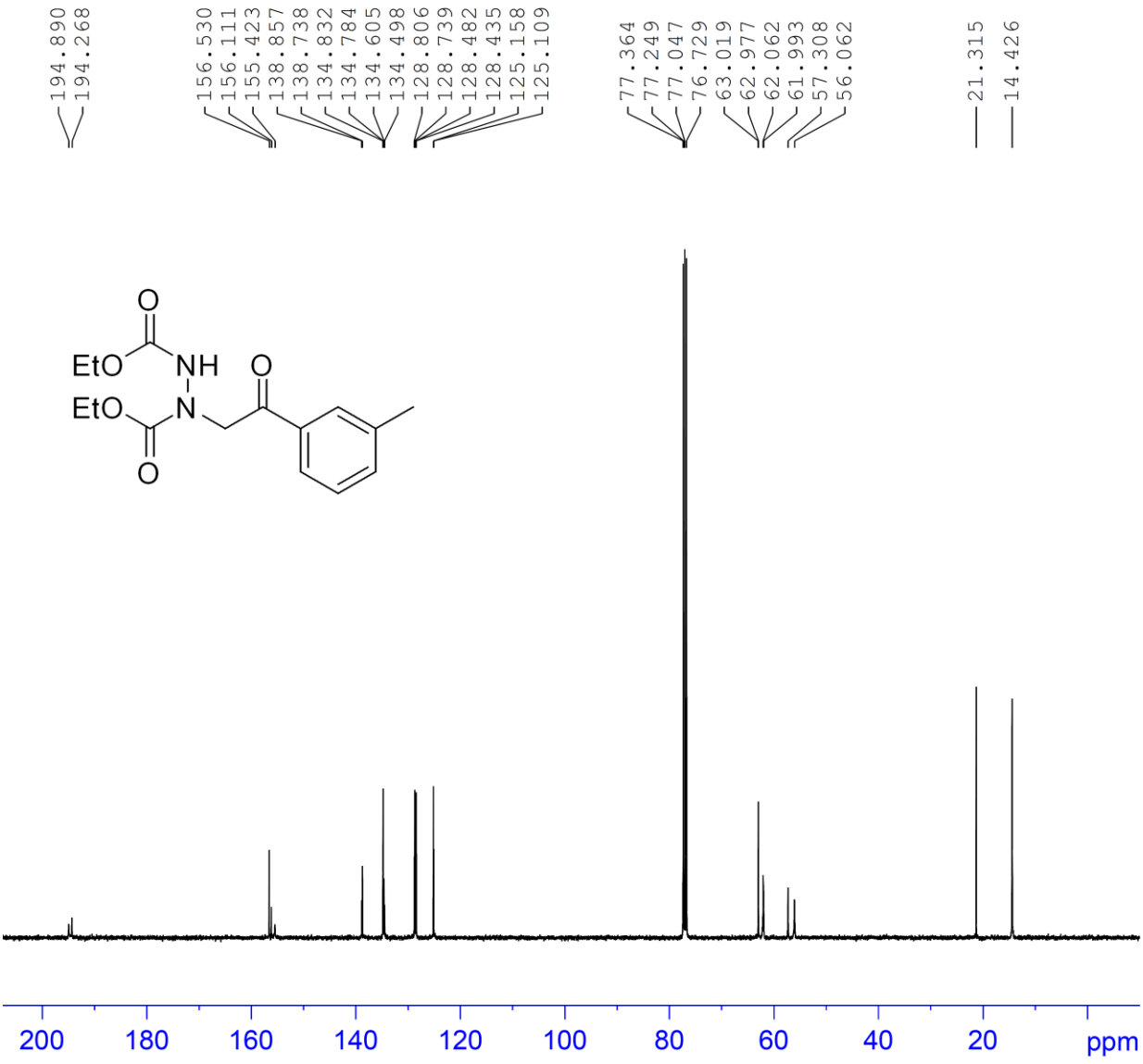
Compound **9a**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



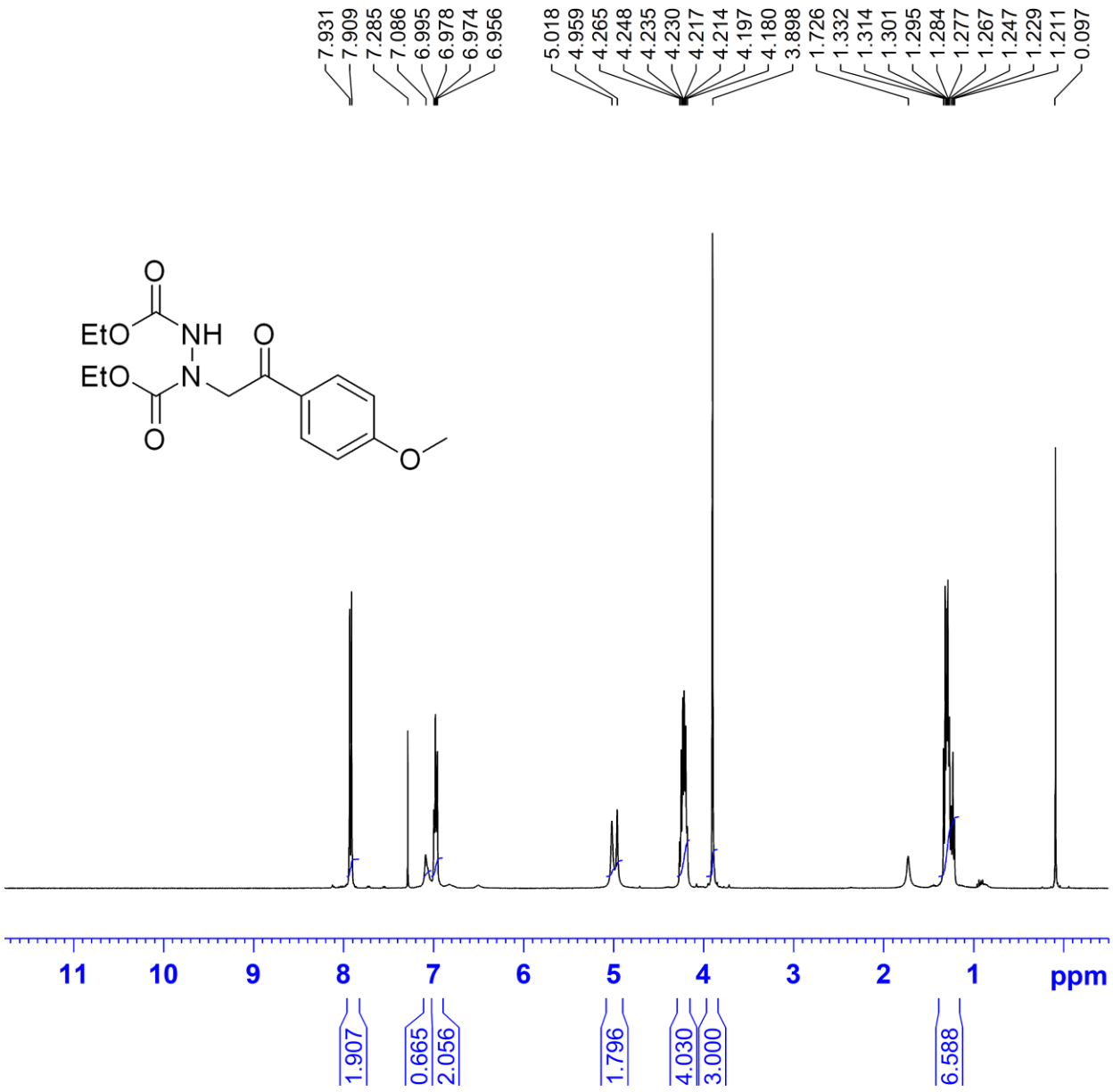
Compound **9b**: ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **9b**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



Compound **9c**: ^{1}H NMR (400 MHz, $CDCl_3$)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4.959
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4.230
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4.214
4.197
4.180
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1.277
1.267
1.247
1.229
1.211
0.097
EtO
NH
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10
9
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6
5
4
3
2
1
ppm
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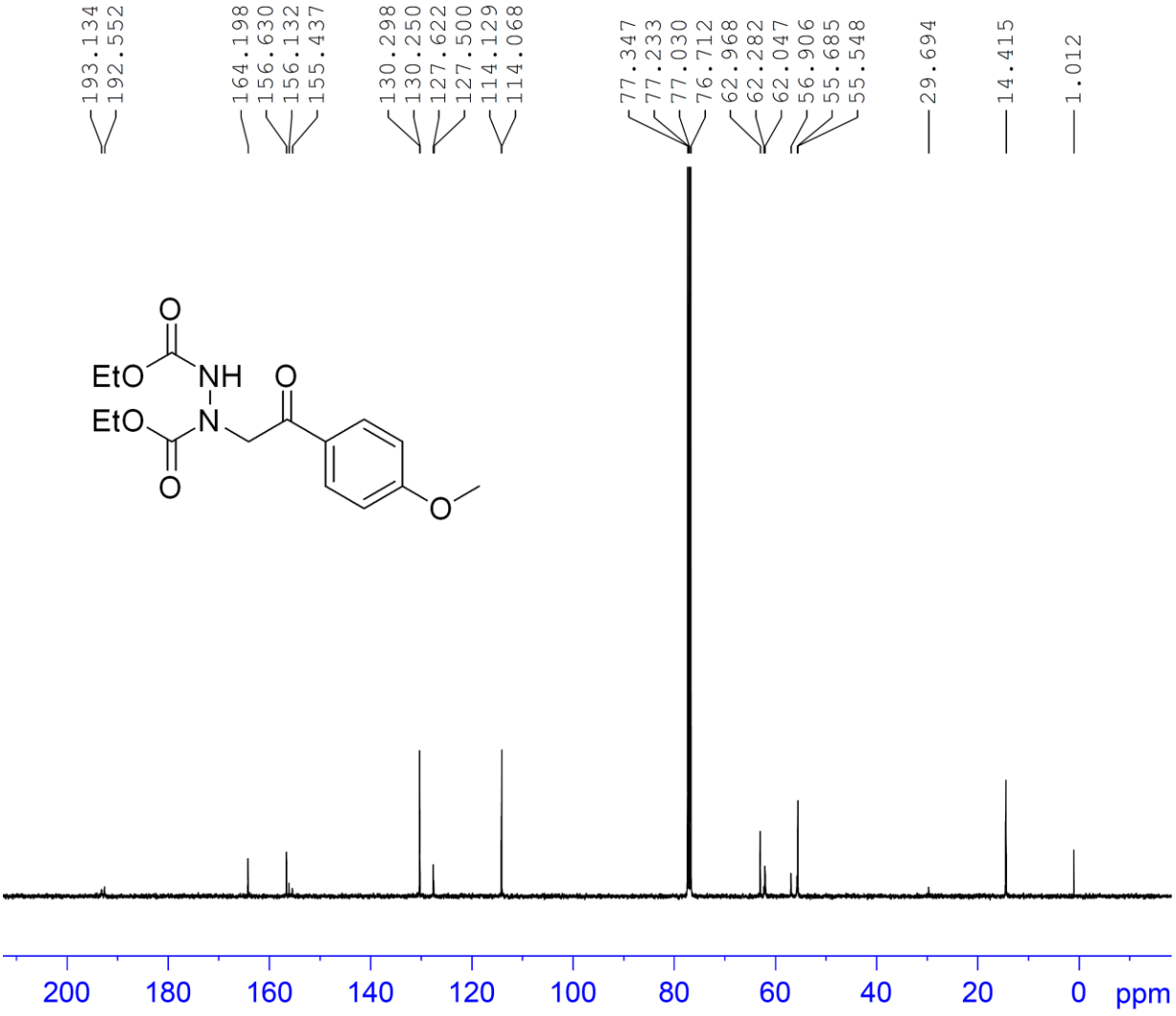
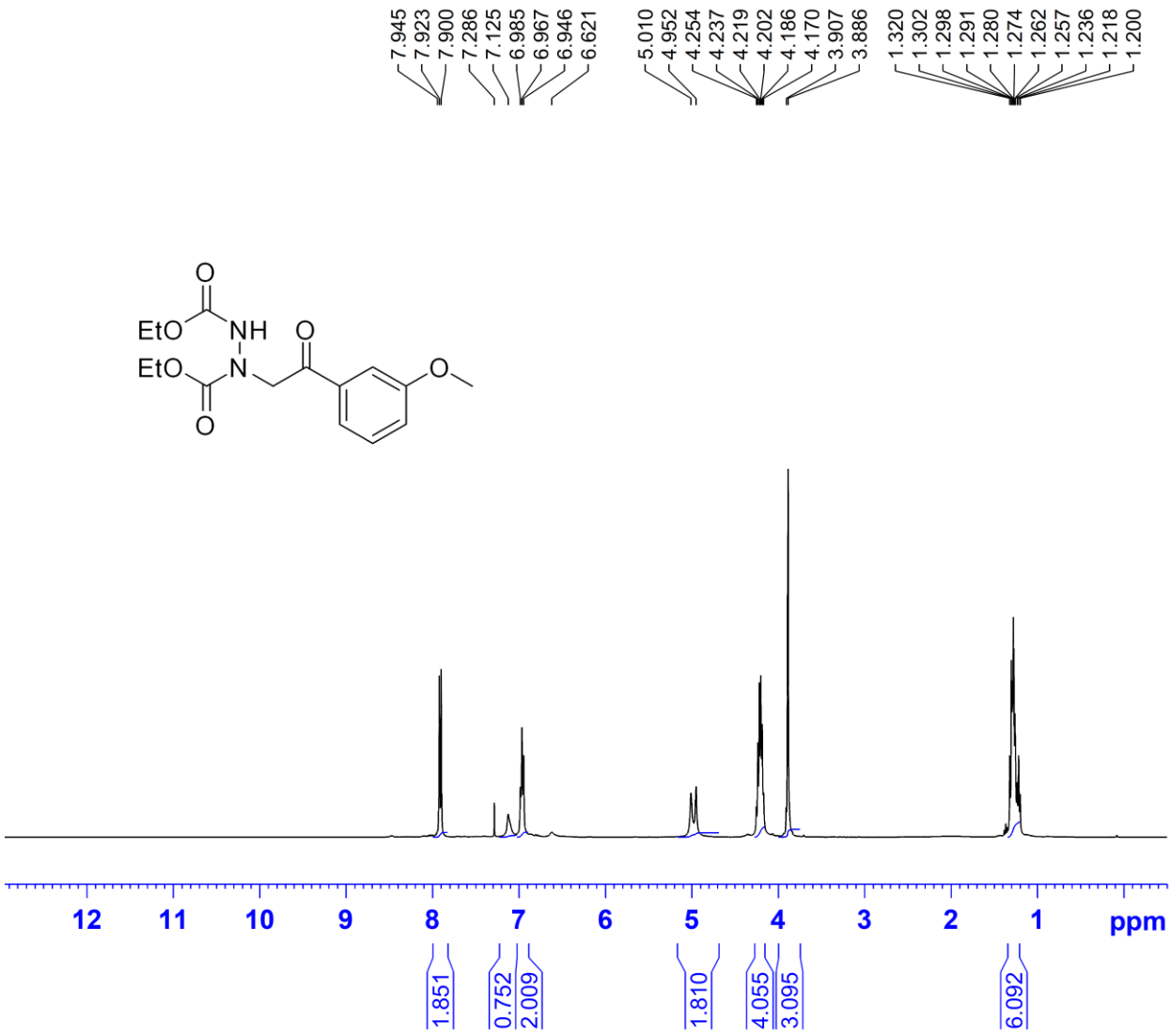
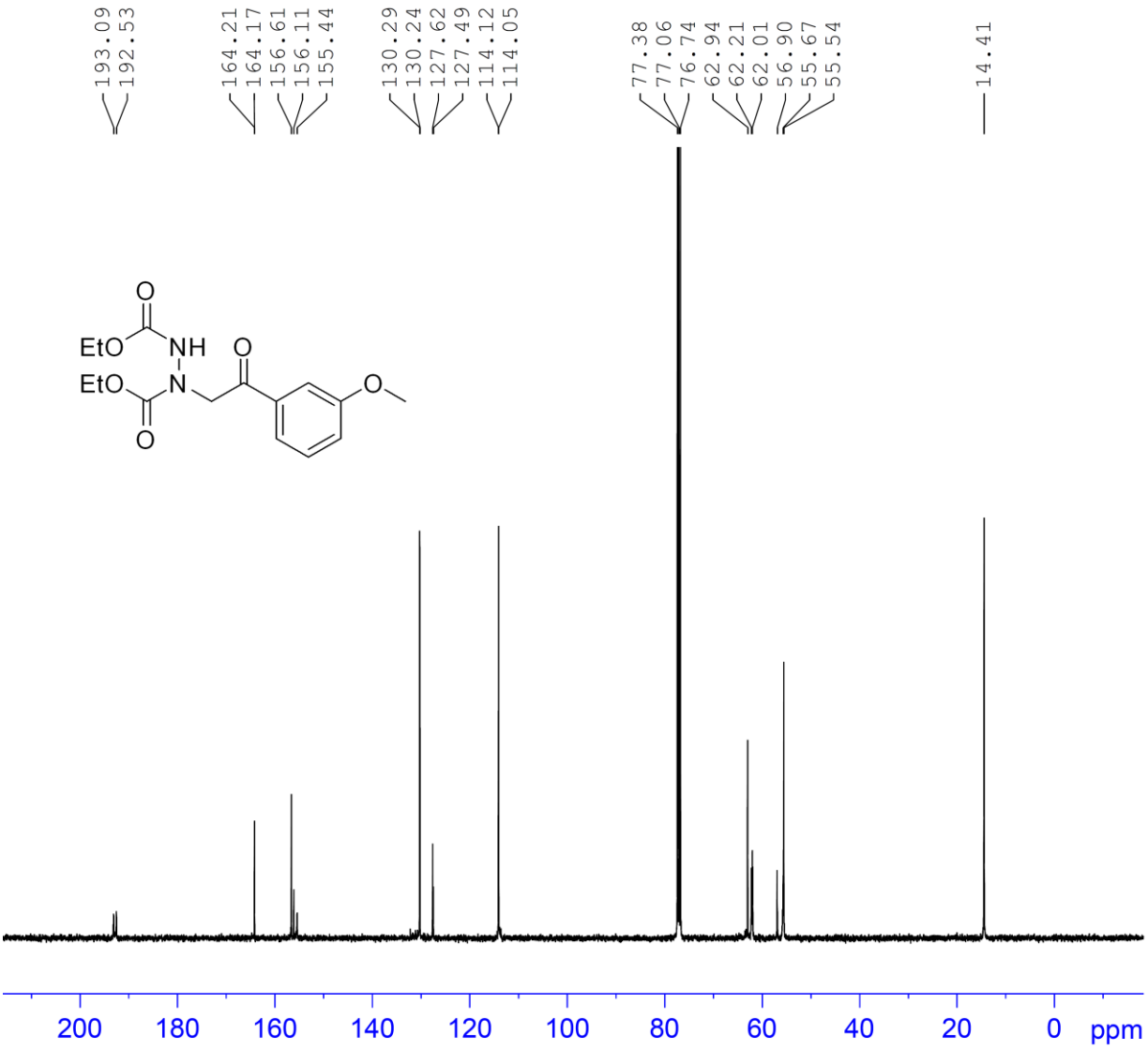
Compound **9c**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



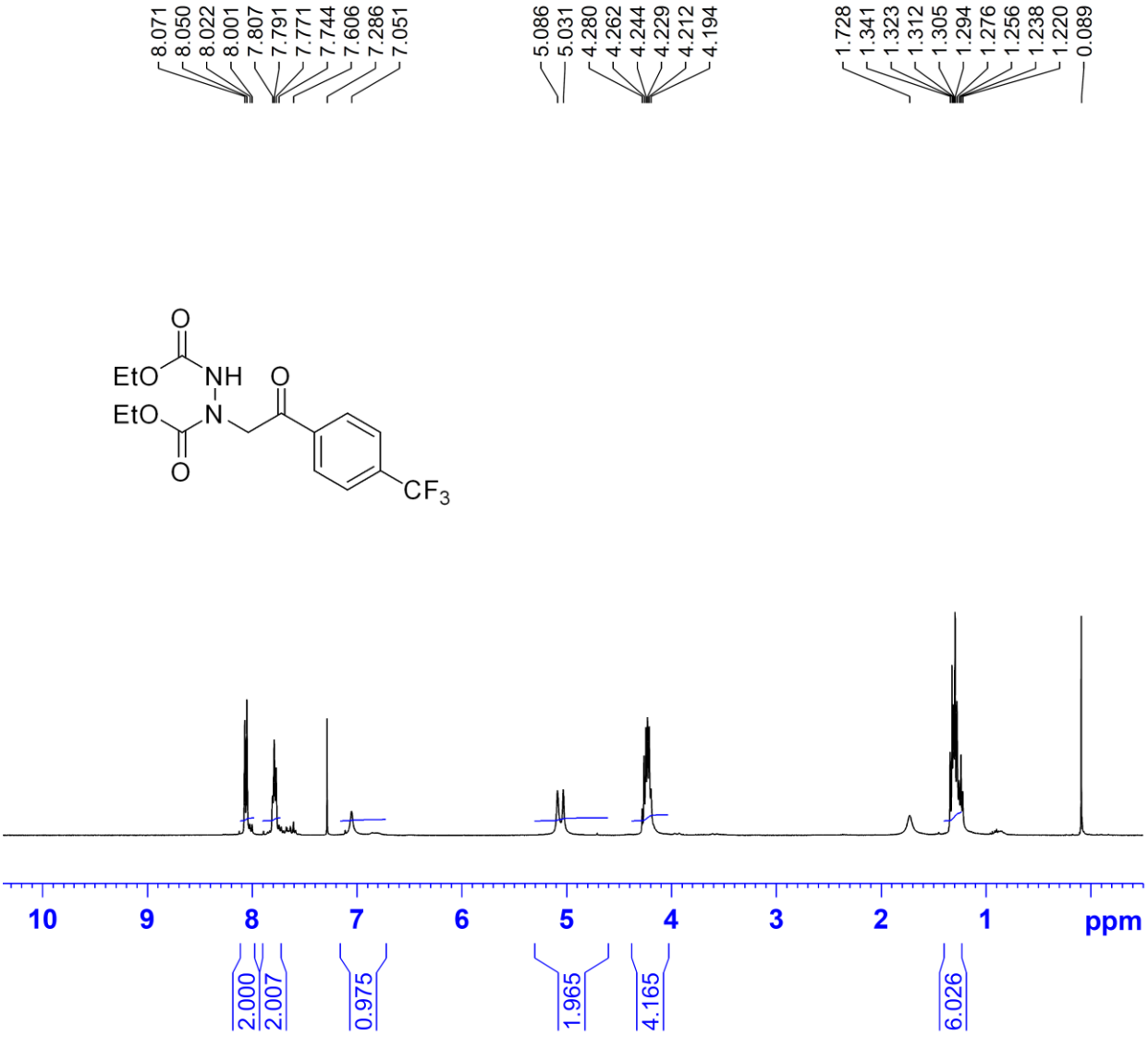
Compound **9d**: ^{1}H NMR (400 MHz, $CDCl_3$)



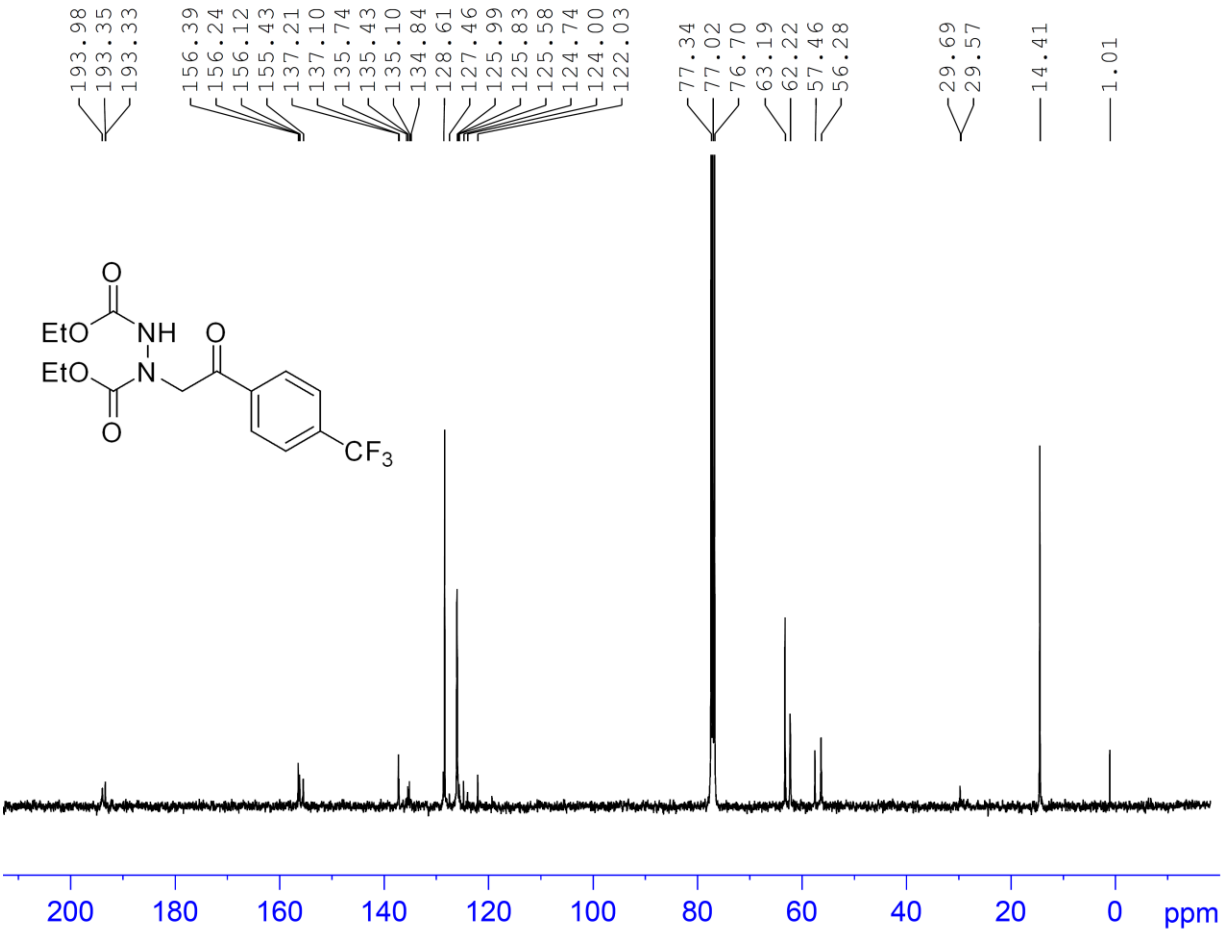
Compound **9d**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



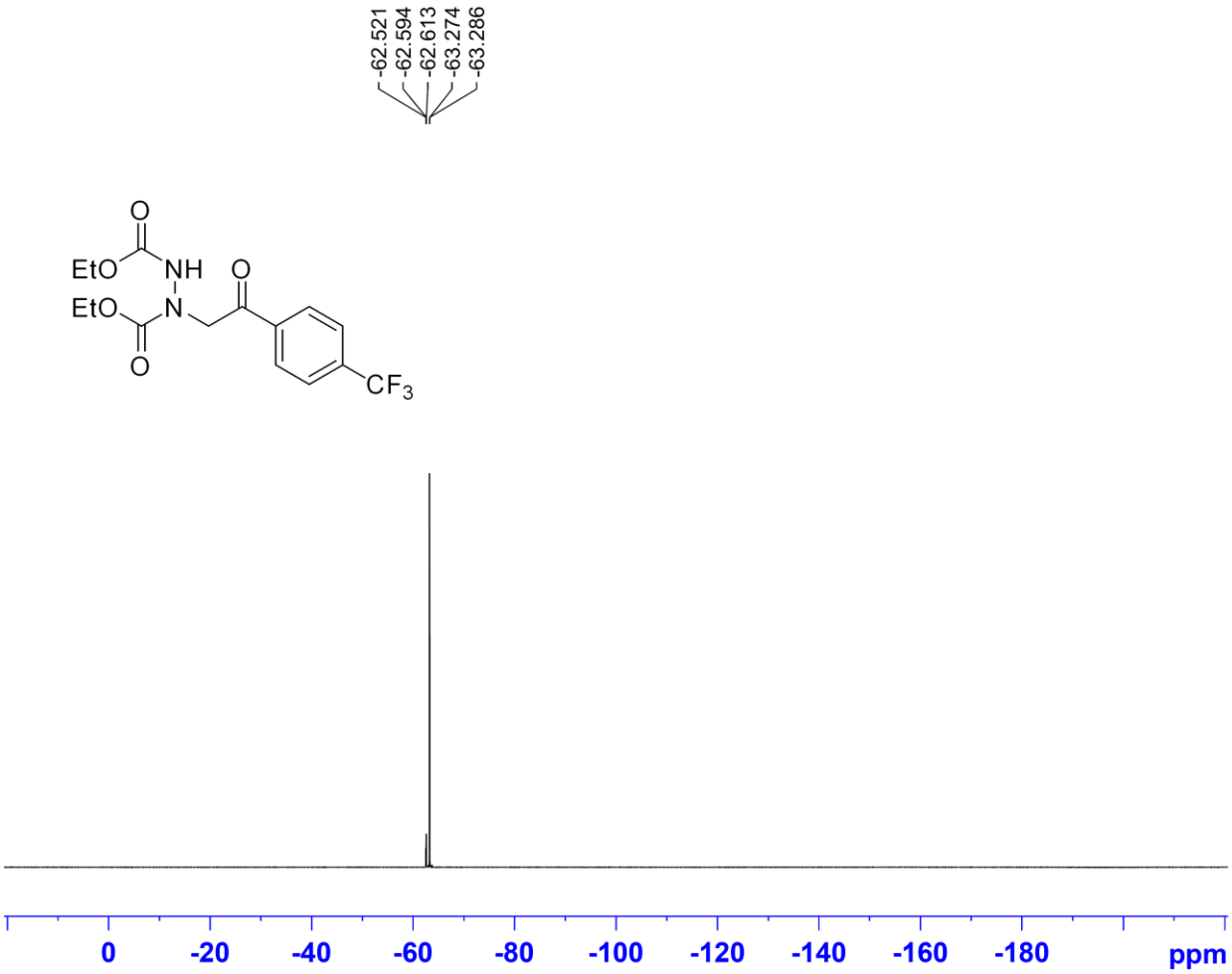
Compound **9e**: ^{1}H NMR (400 MHz, $CDCl_3$)



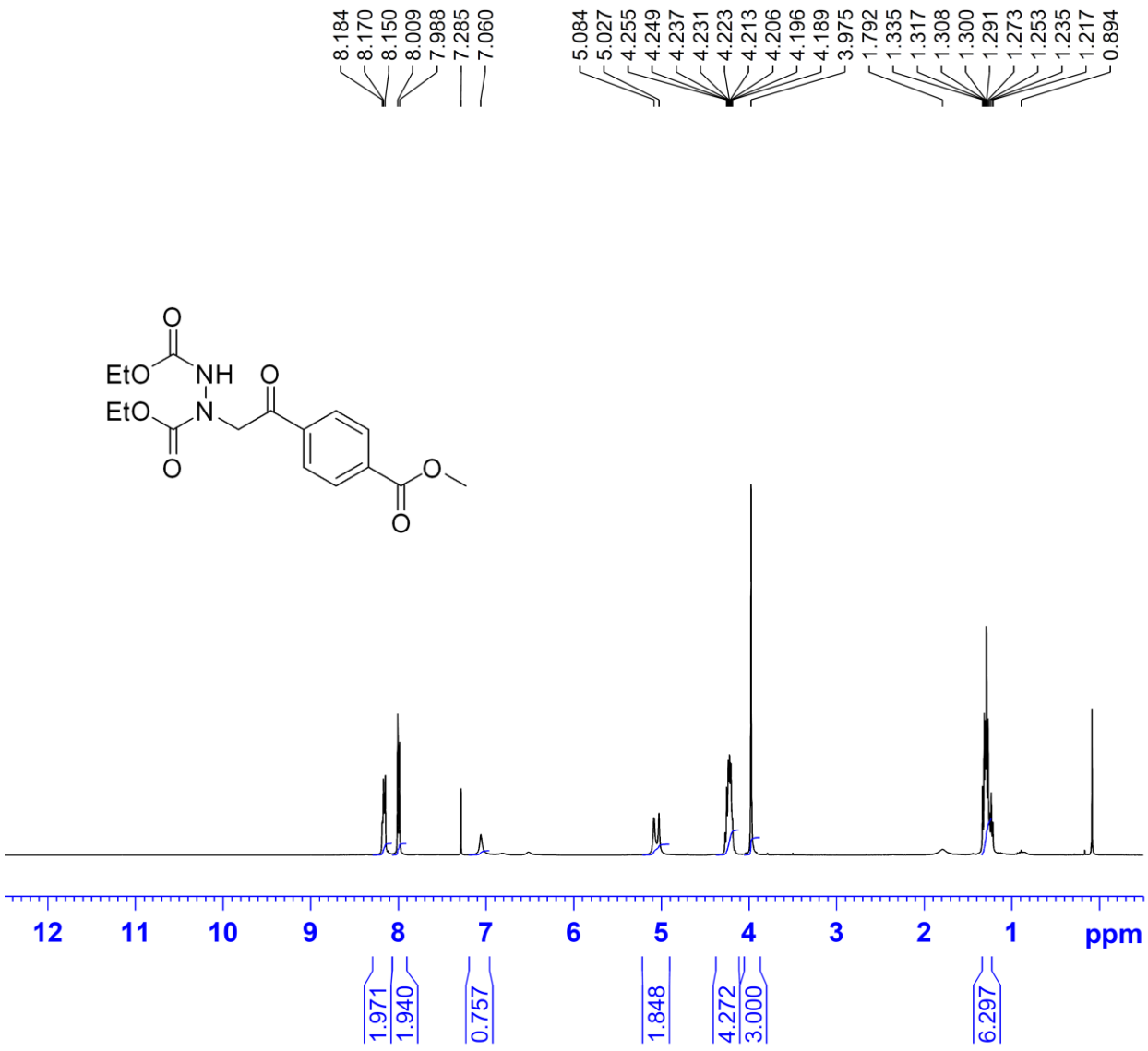
Compound **9e**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



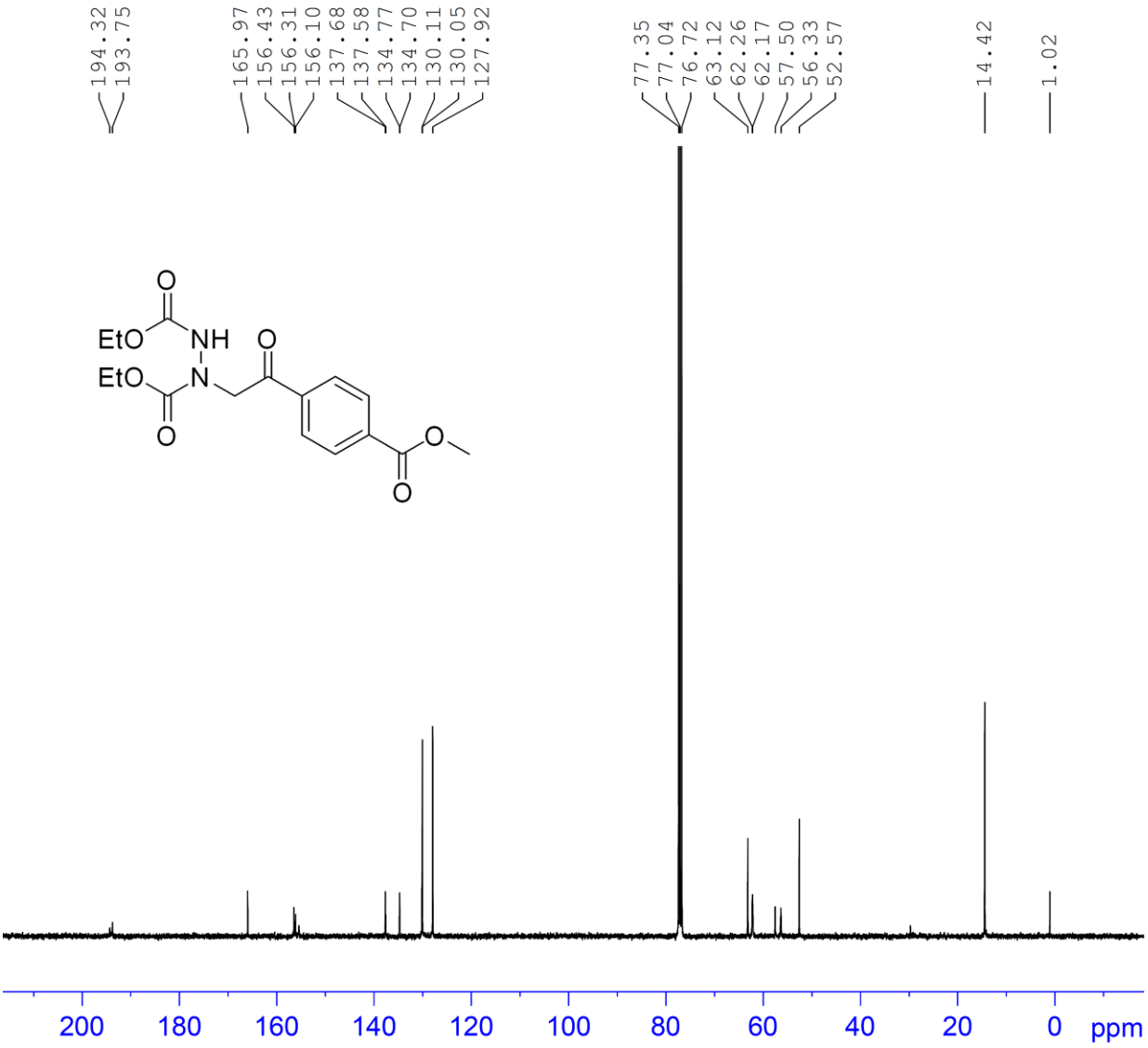
Compound **9e**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



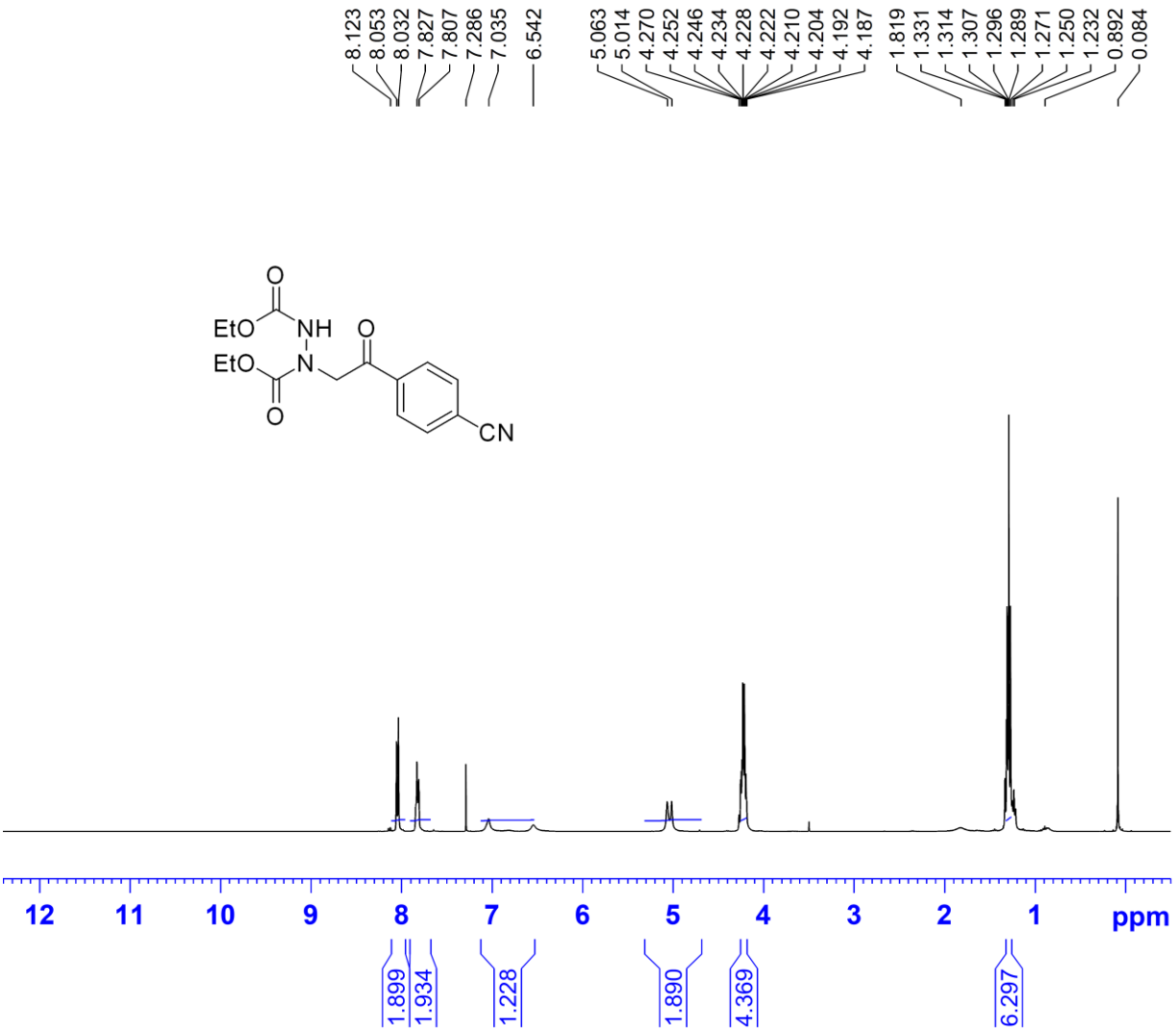
Compound **9f**: ^{1}H NMR (400 MHz, $CDCl_3$)



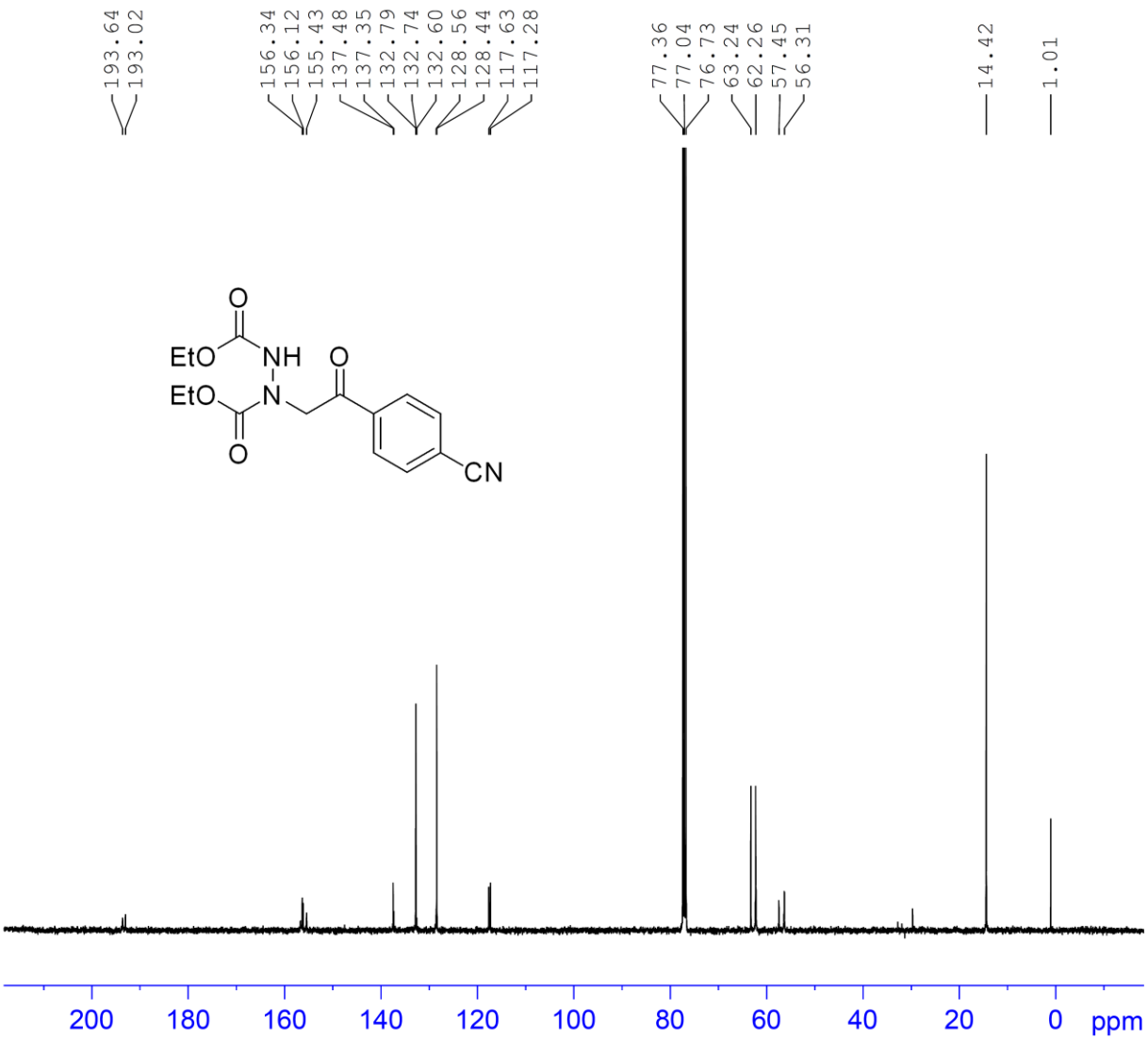
Compound **9f**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



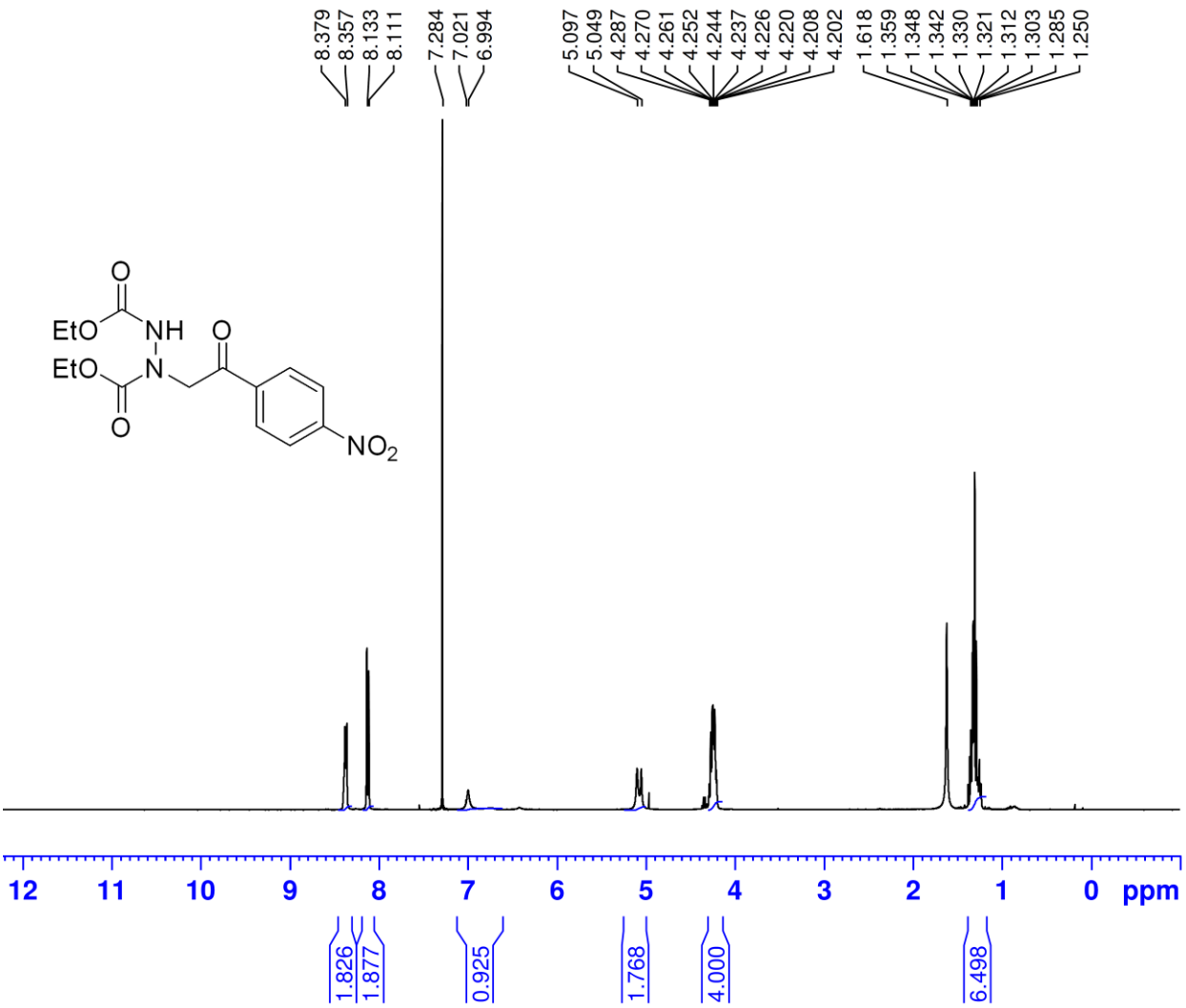
Compound **9g**: ^{1}H NMR (400 MHz, $CDCl_3$)



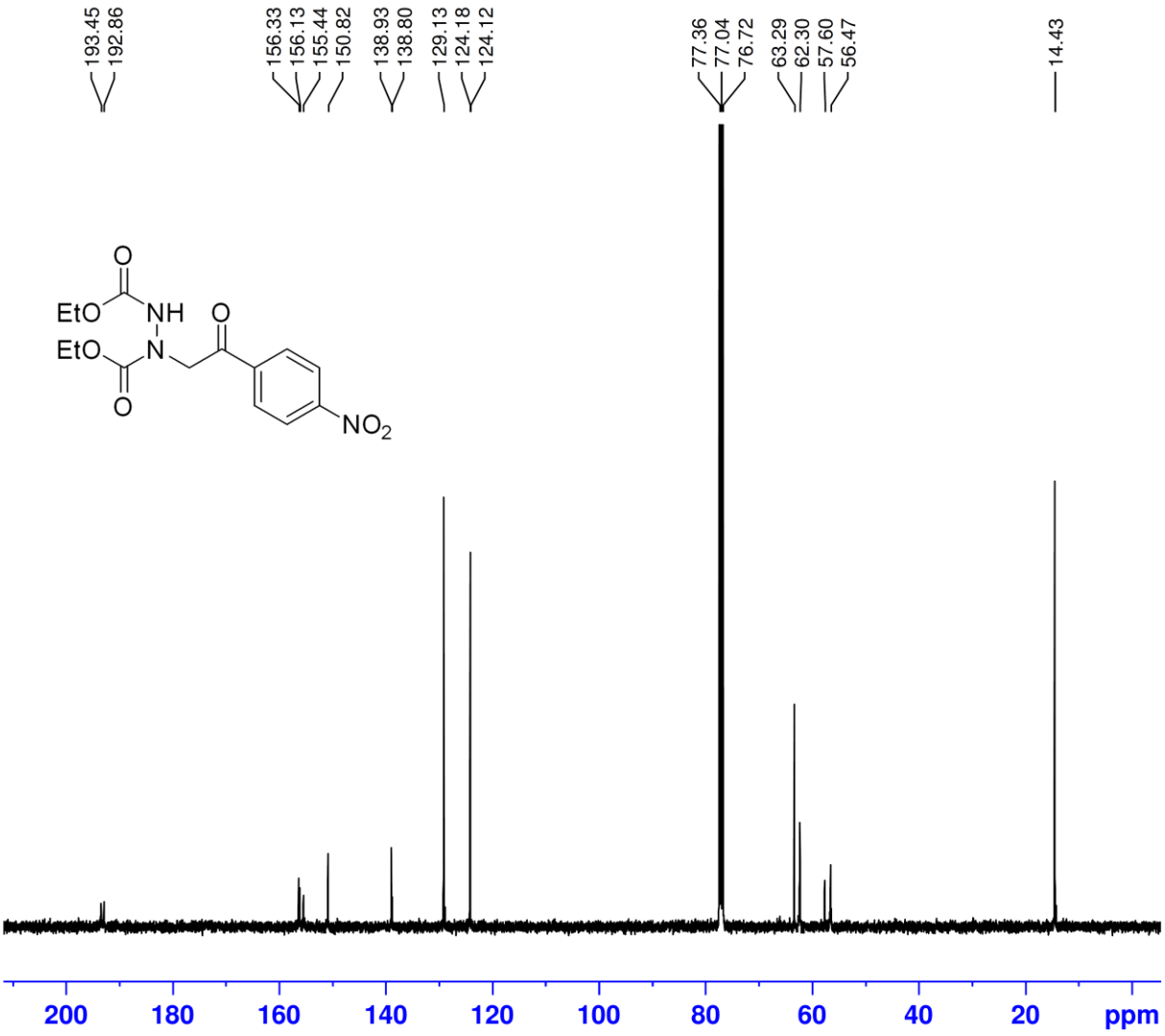
Compound **9g**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



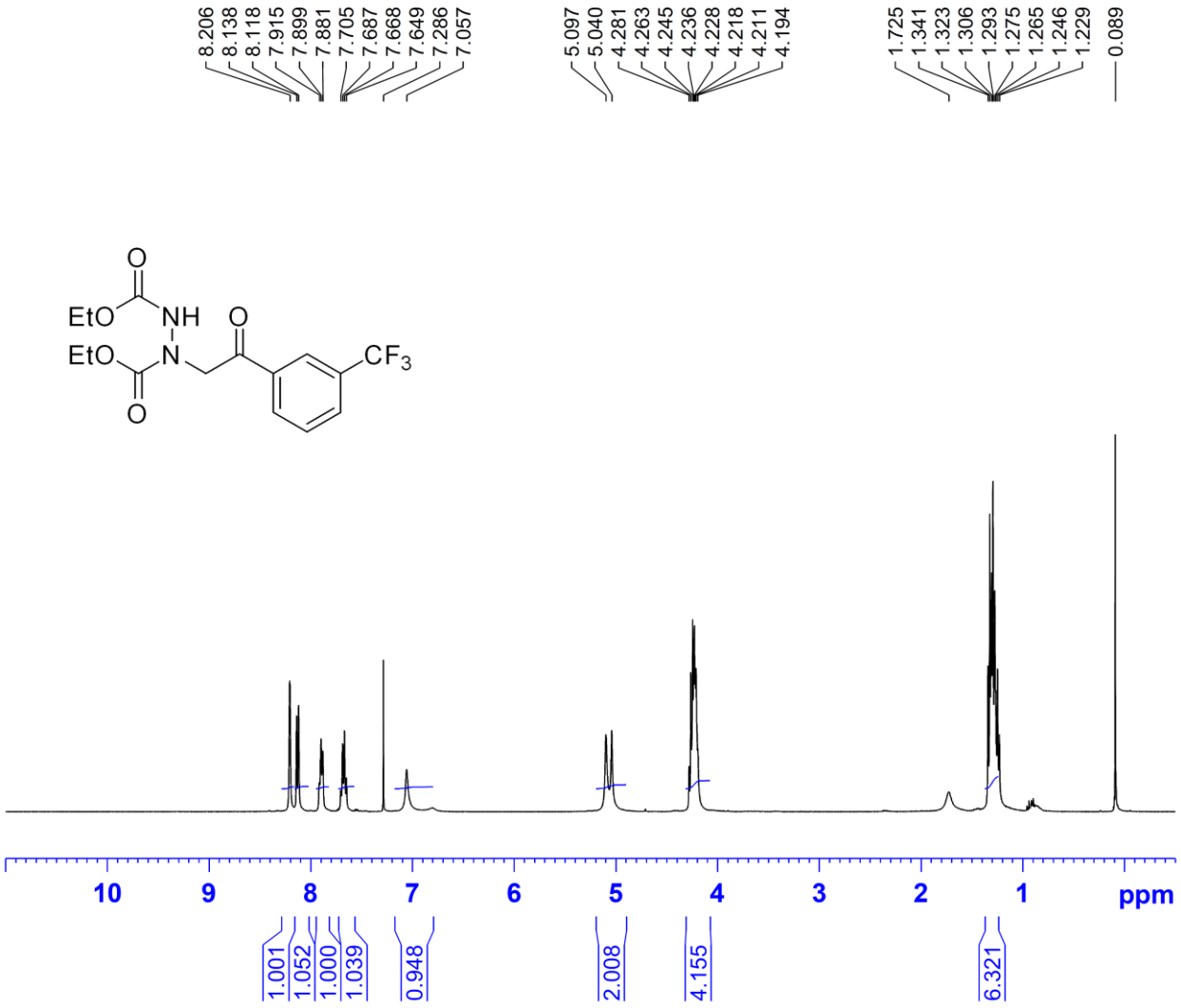
Compound **9h**: ^{1}H NMR (400 MHz, $CDCl_3$)



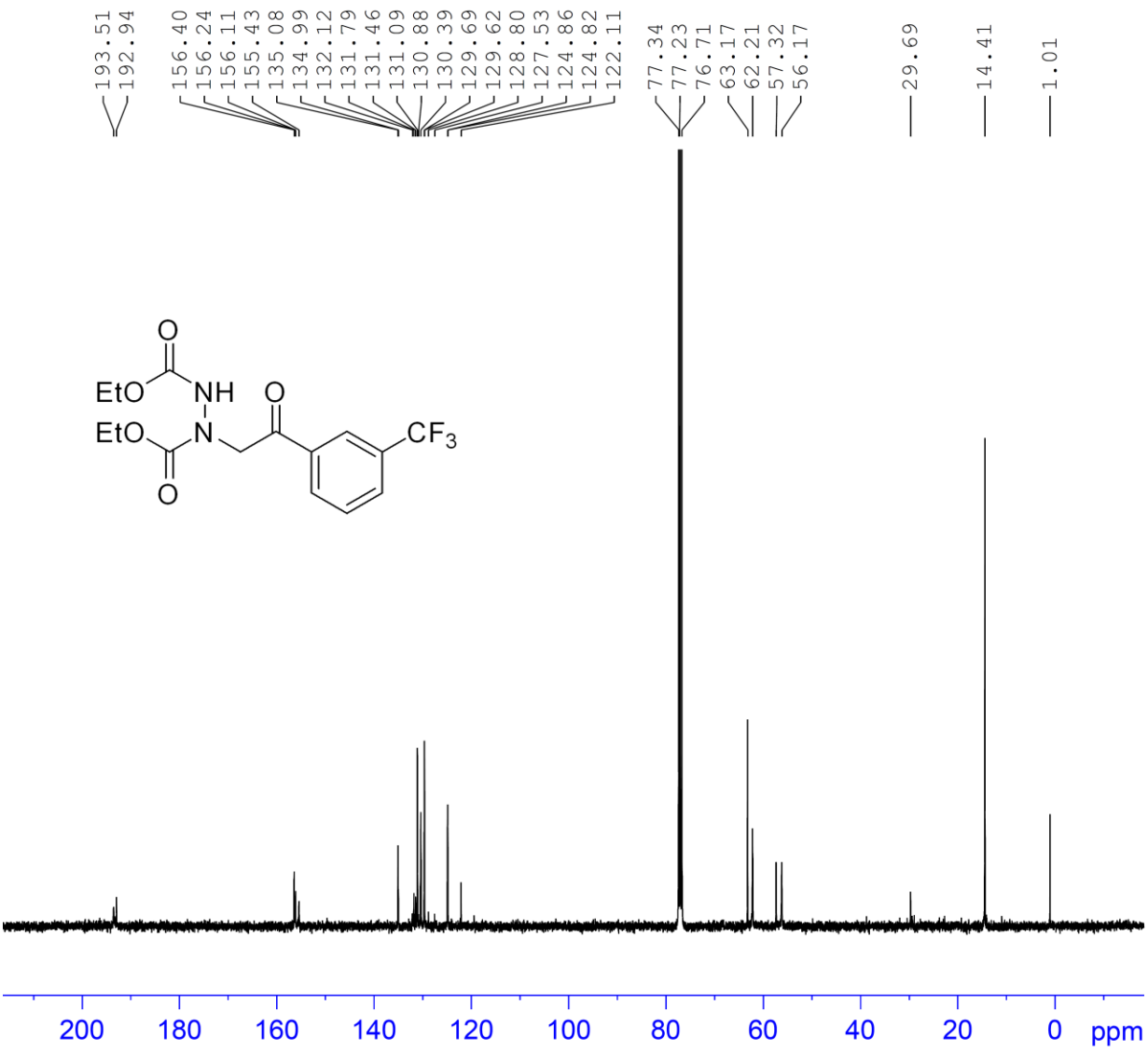
Compound **9h**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



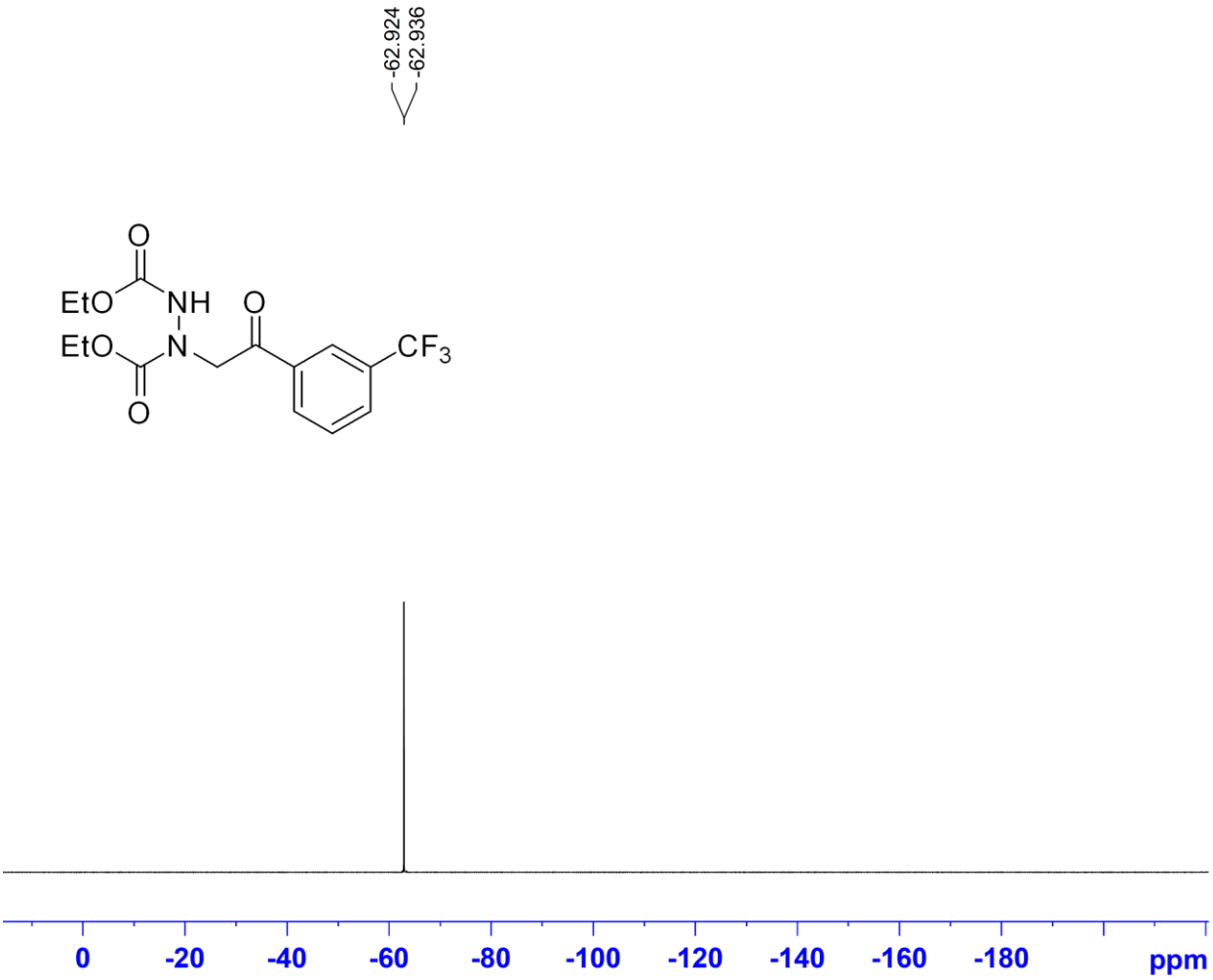
Compound **9i**: ^{1}H NMR (400 MHz, $CDCl_3$)



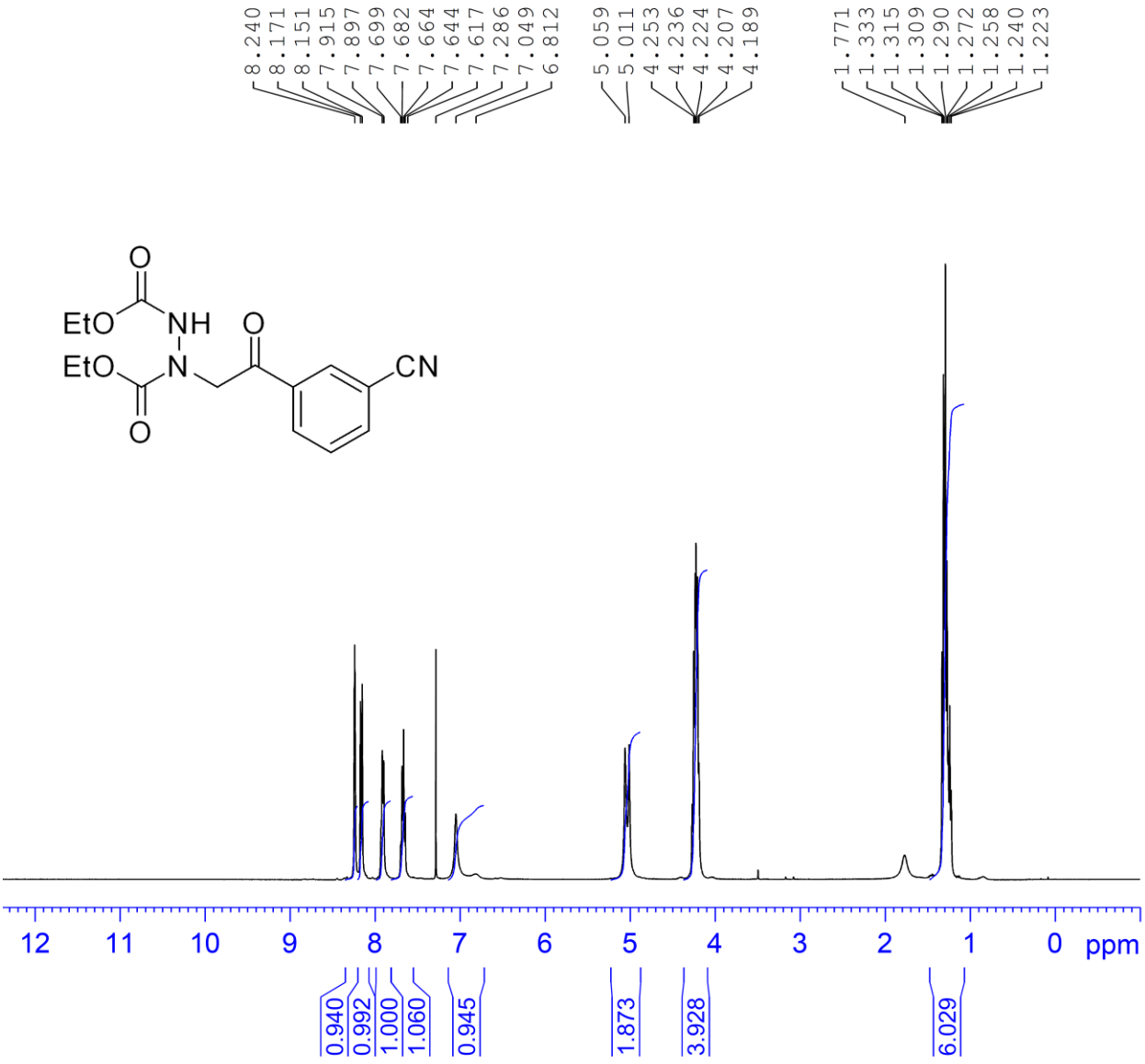
Compound **9i**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



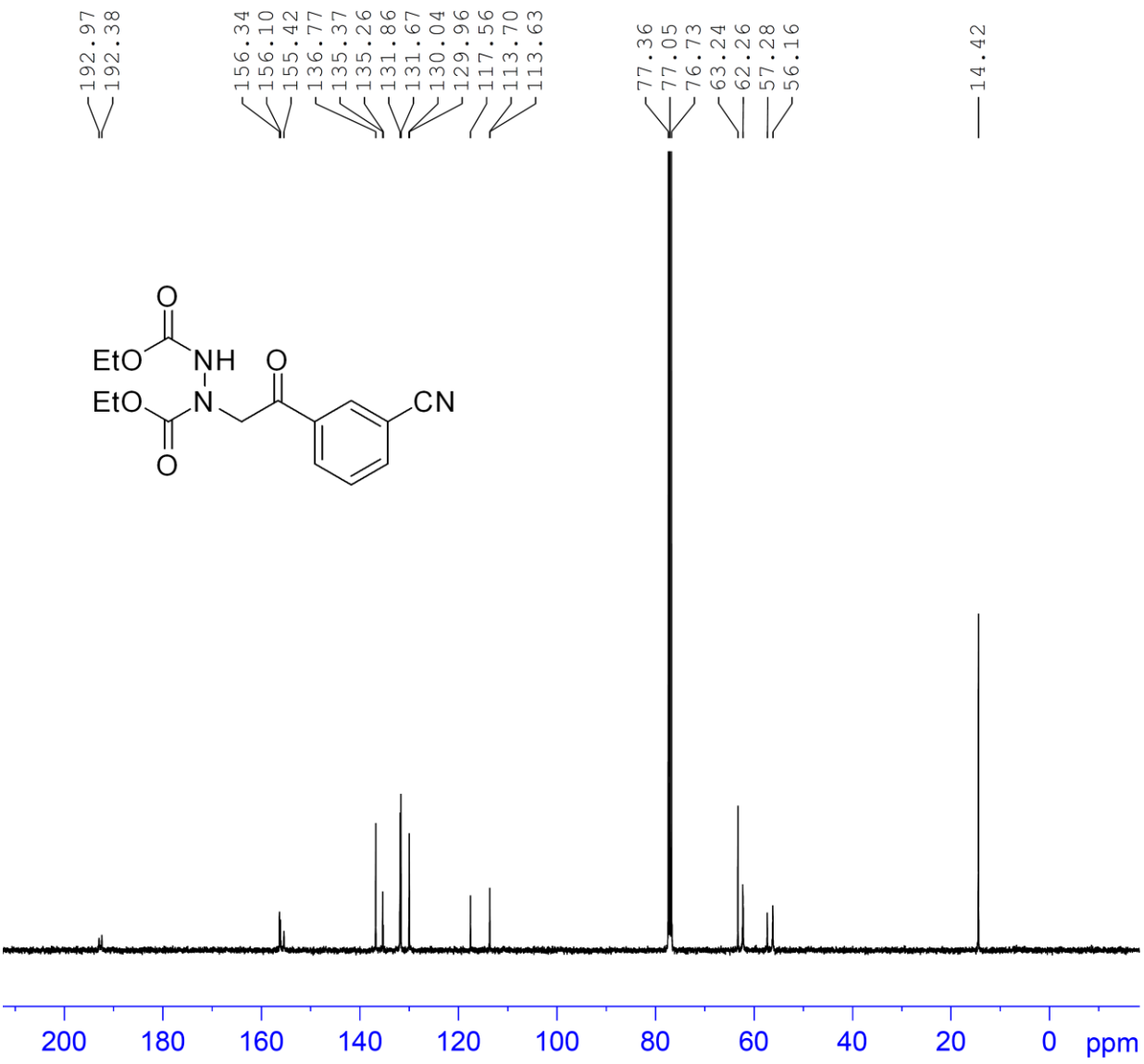
Compound **9i**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



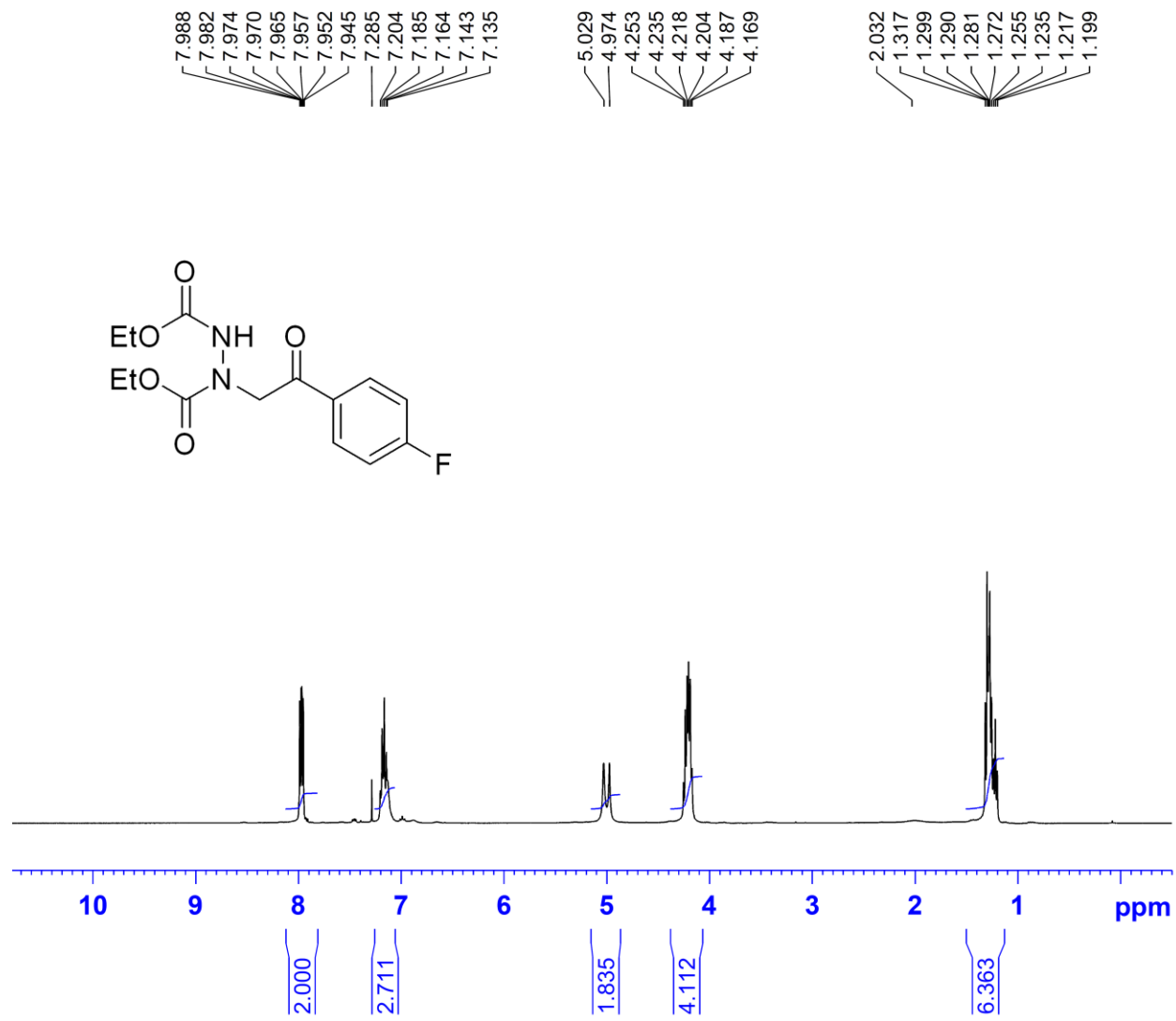
Compound **9j**: ^{1}H NMR (400 MHz, $CDCl_3$)



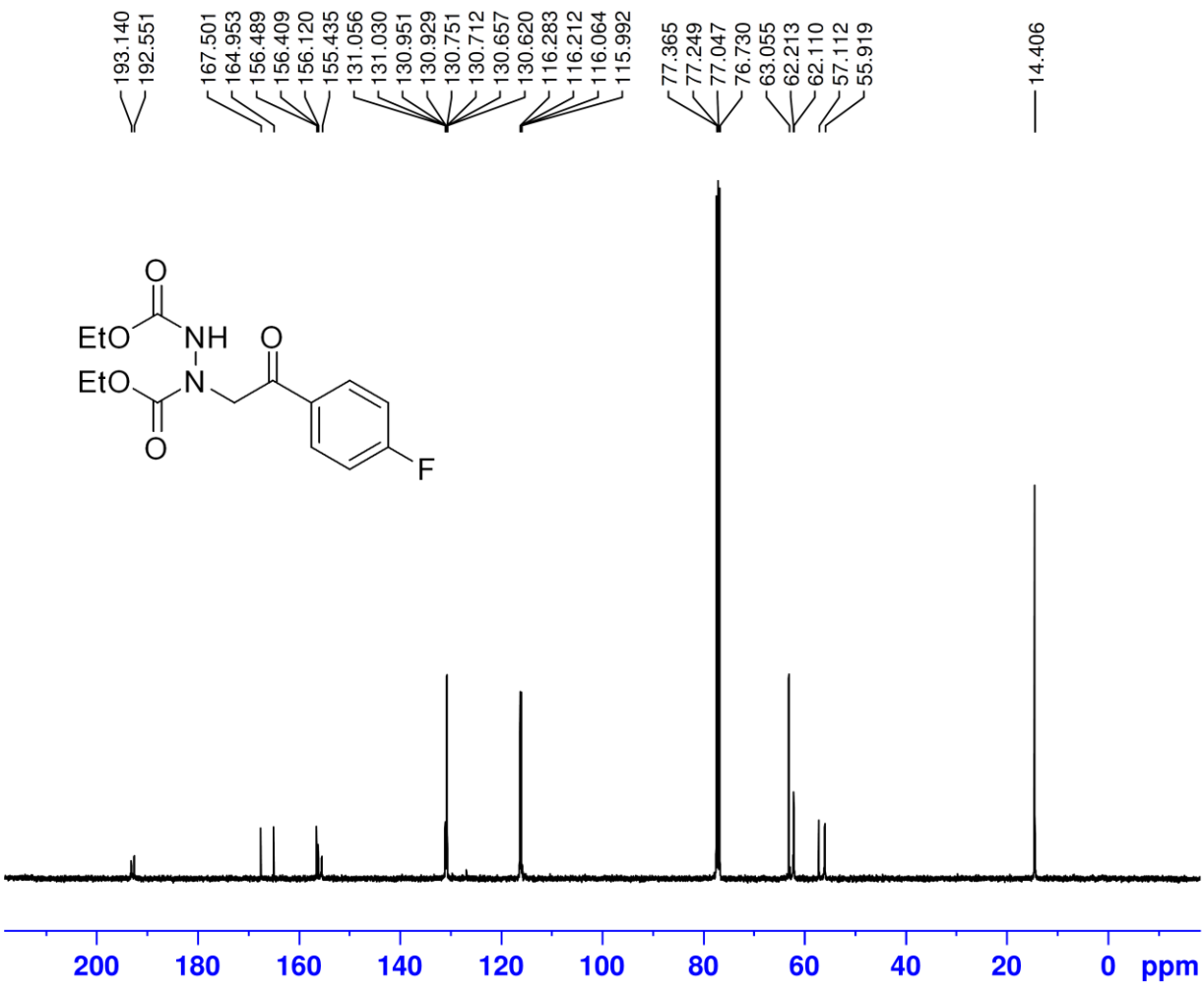
Compound **9j**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



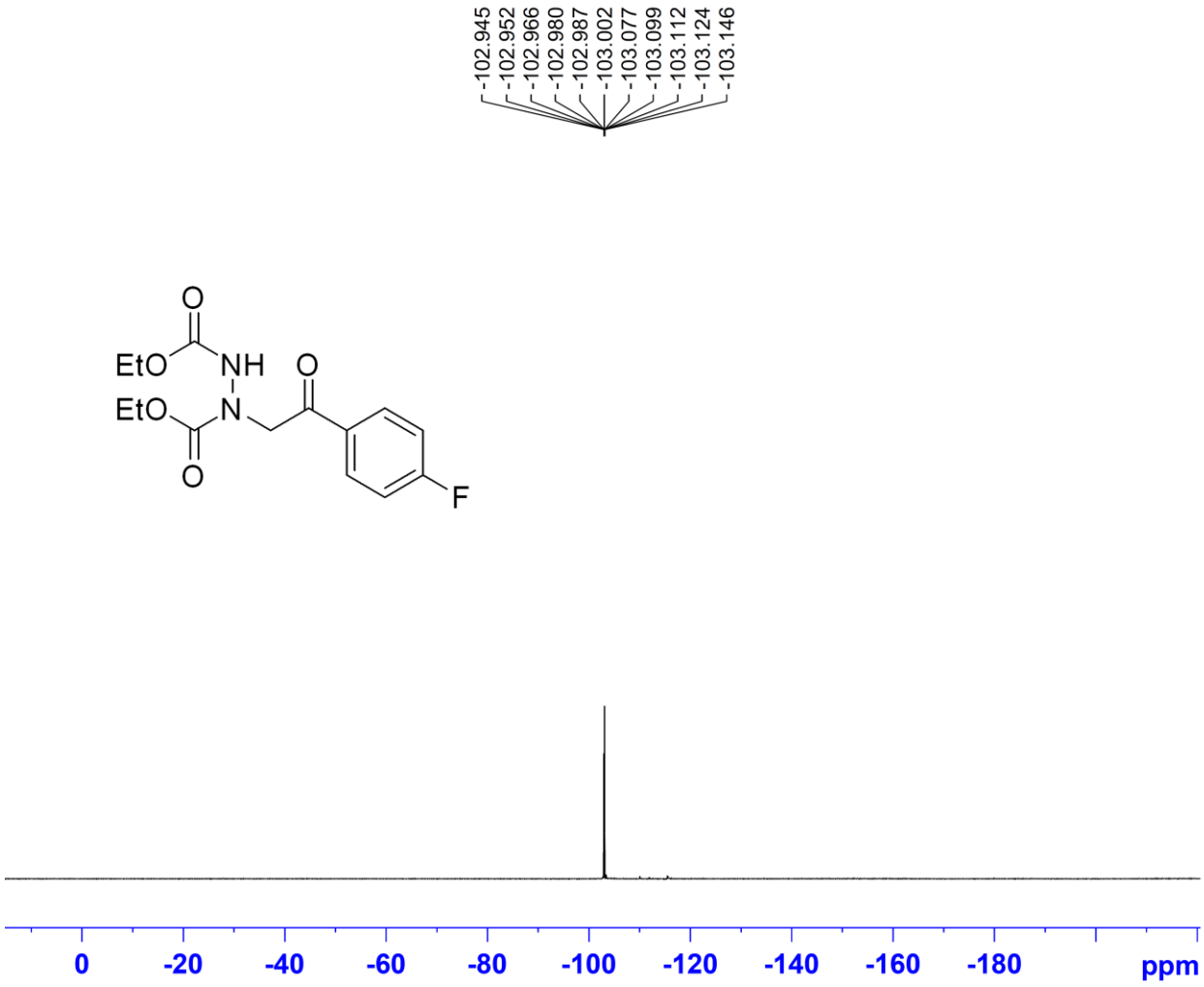
Compound **9k**: ^{1}H NMR (400 MHz, $CDCl_3$)



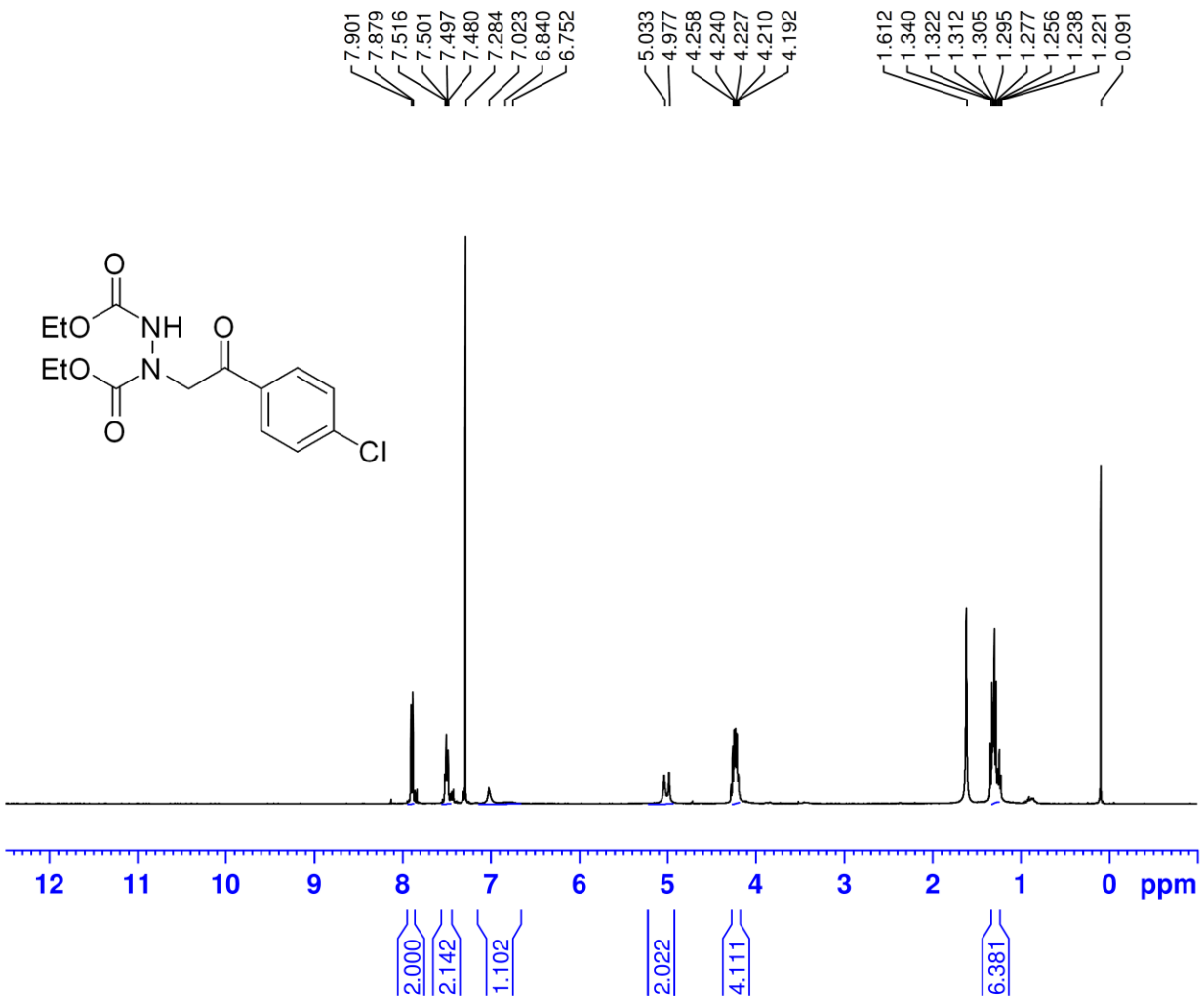
Compound **9k**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



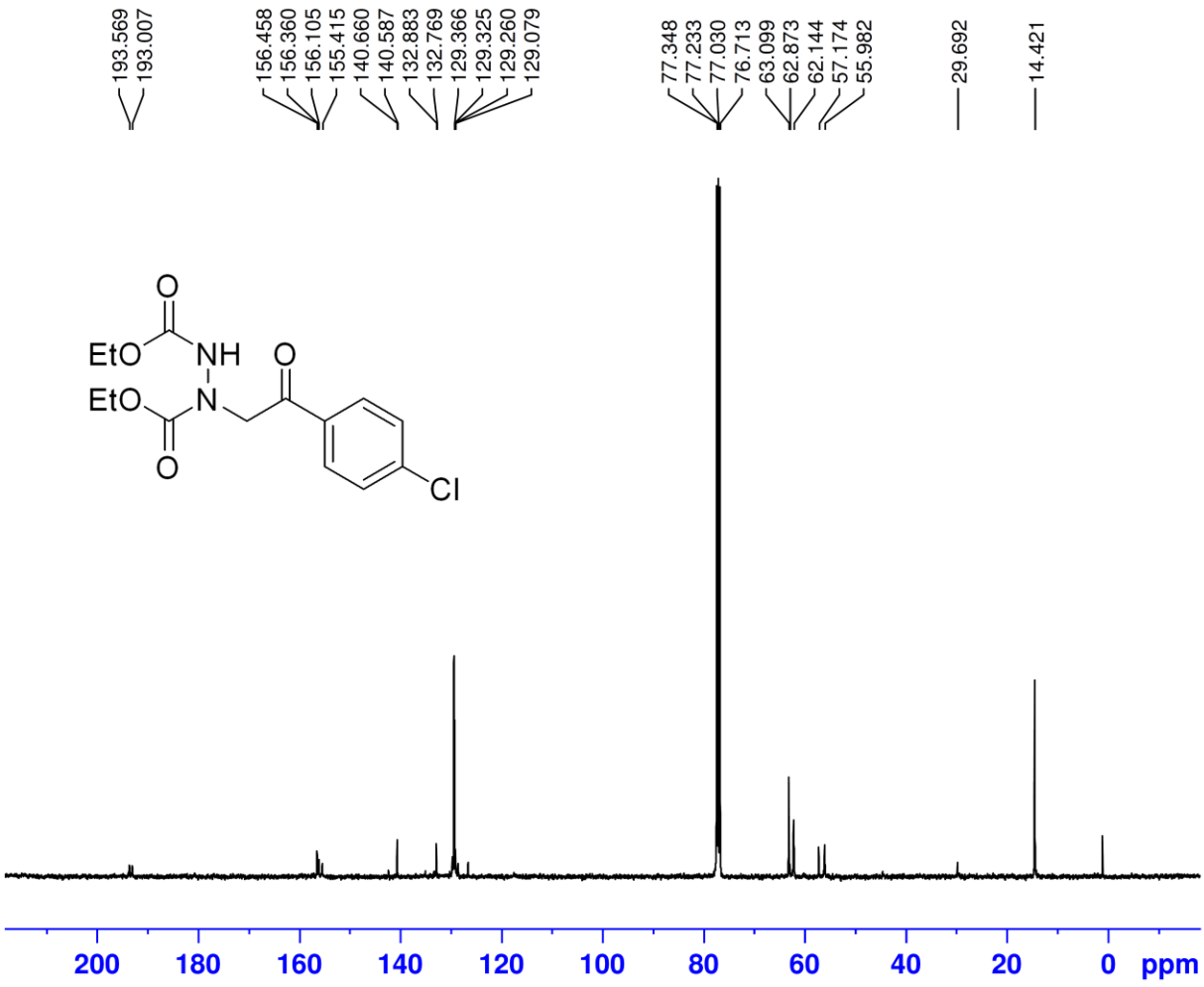
Compound **9k**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



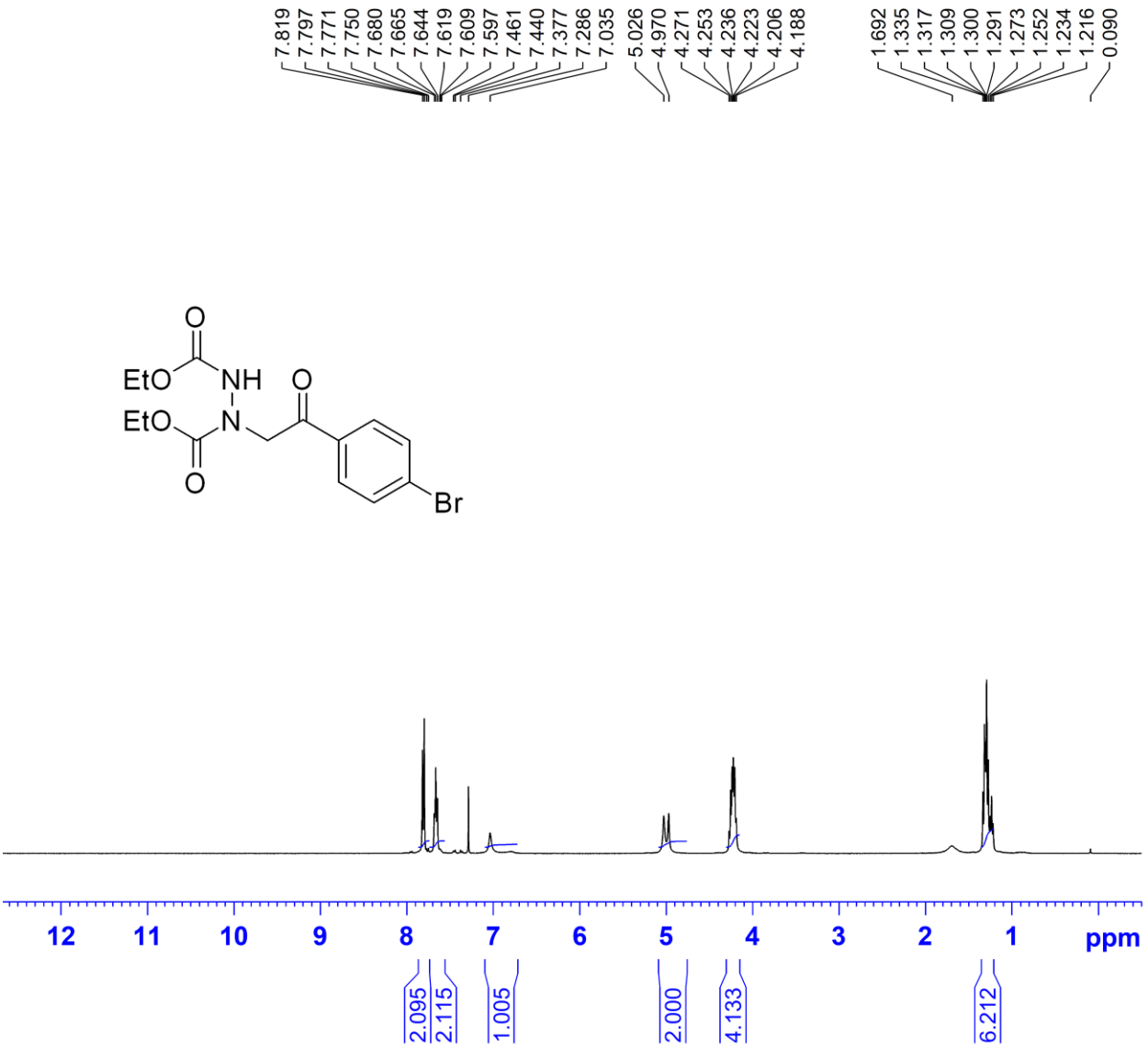
Compound **9l**: ^{1}H NMR (400 MHz, $CDCl_3$)



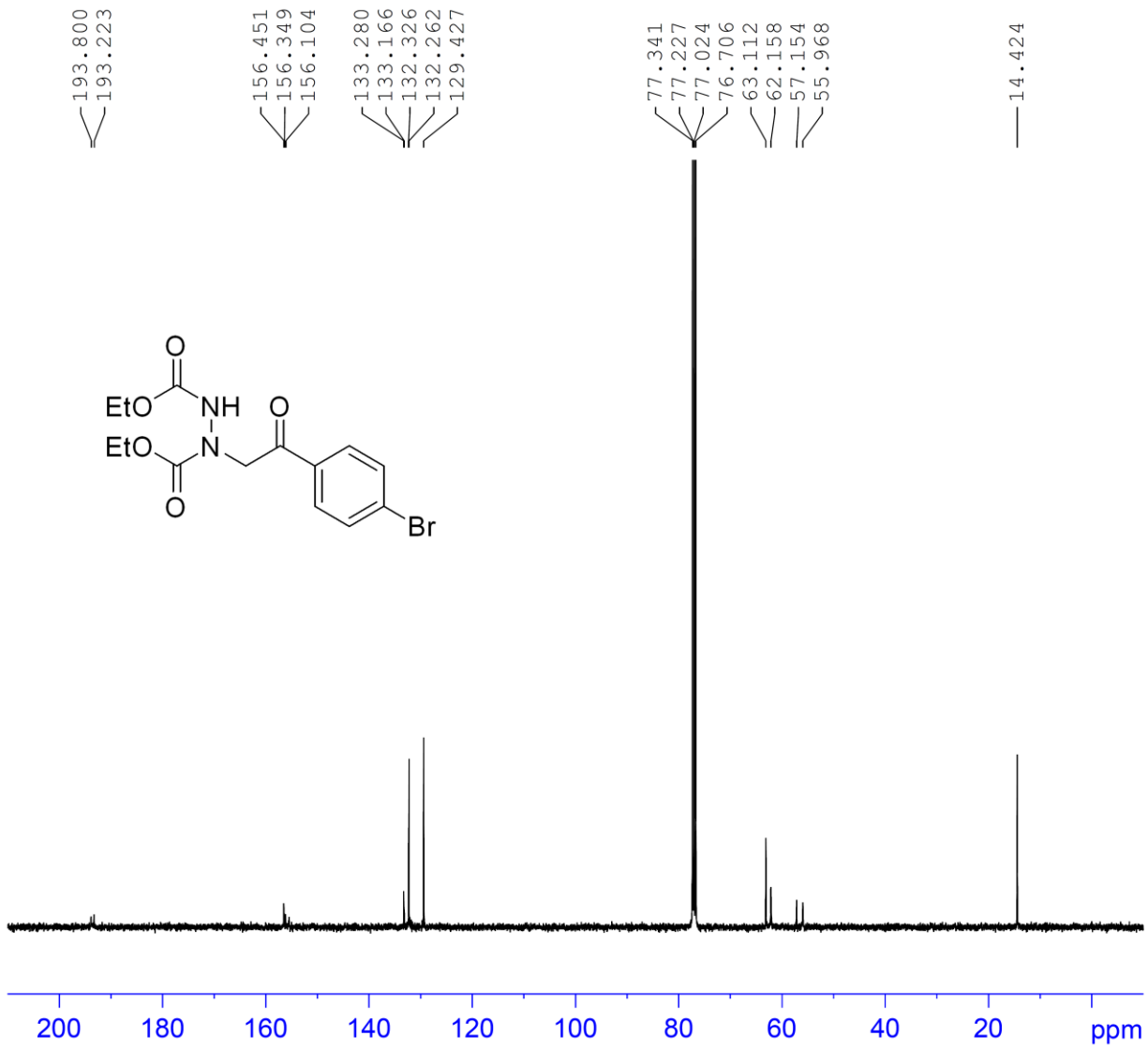
Compound **9l**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



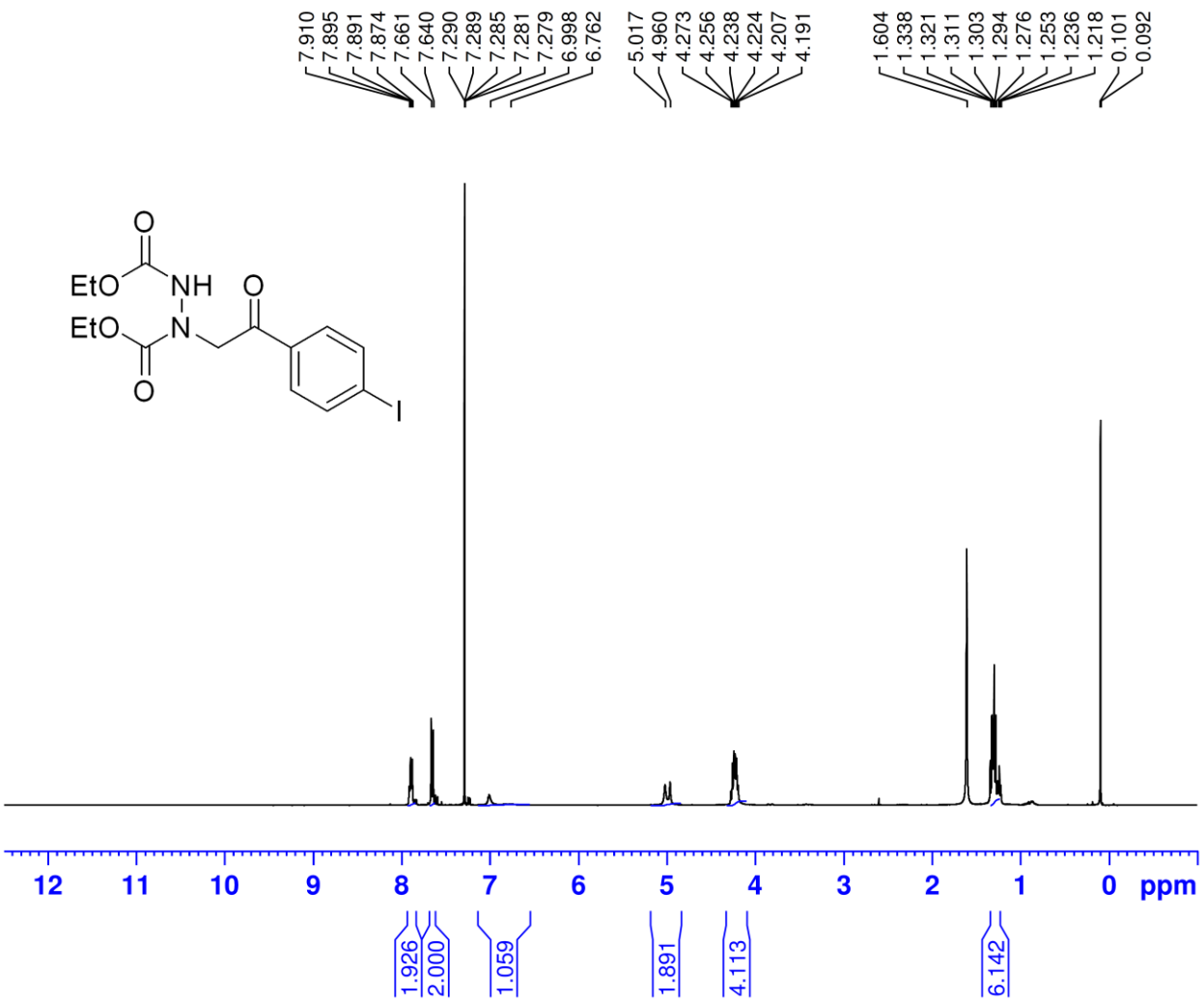
Compound **9m**: ^{1}H NMR (400 MHz, $CDCl_3$)



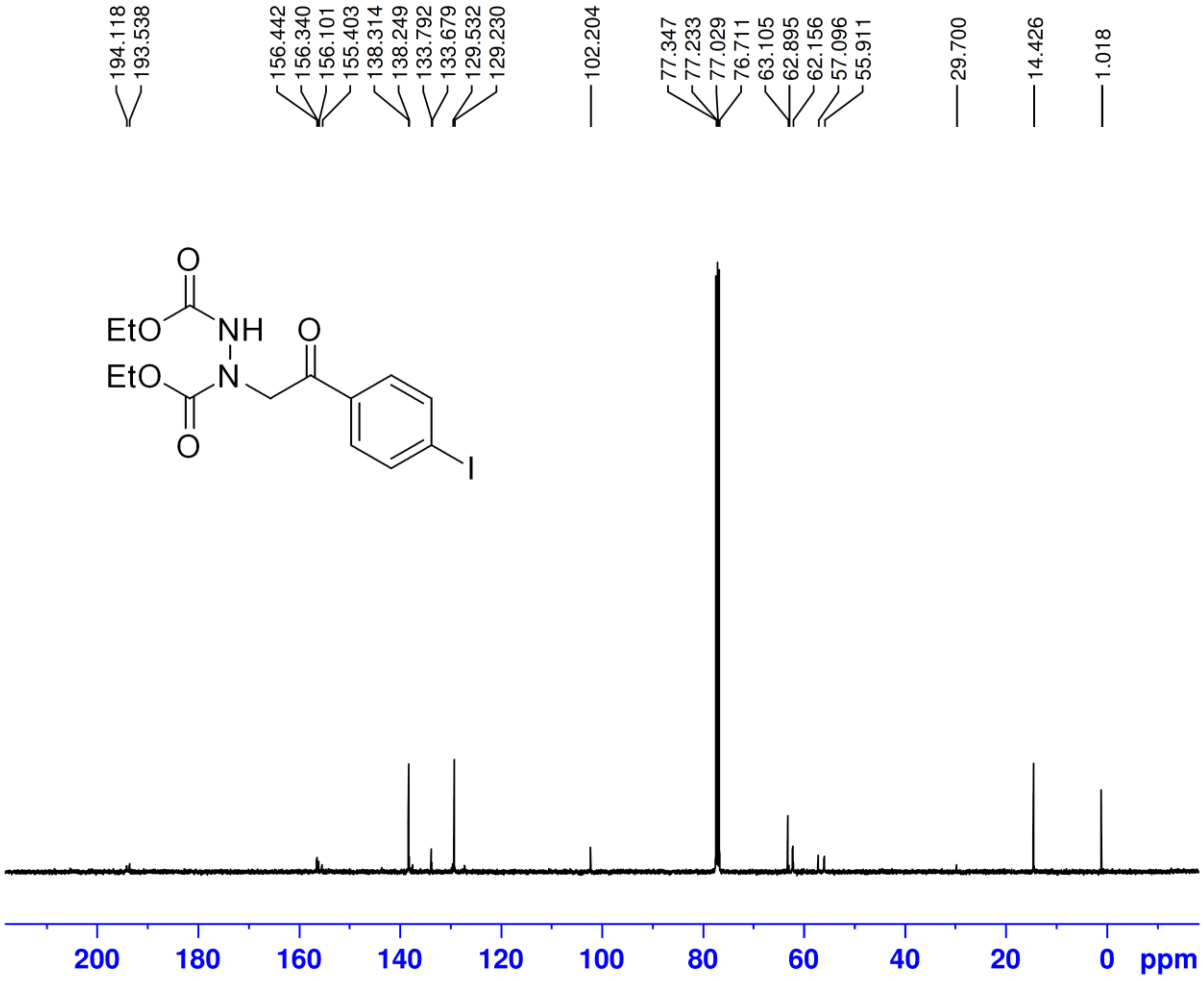
Compound **9m**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


193.800
193.223
156.451
156.349
156.104
133.280
133.166
132.326
132.262
129.427
77.341
77.227
77.024
76.706
63.112
62.158
57.154
55.968
14.424
EtO
NH
O
EtO
N
O
O
Br
200
180
160
140
120
100
80
60
40
20
ppm

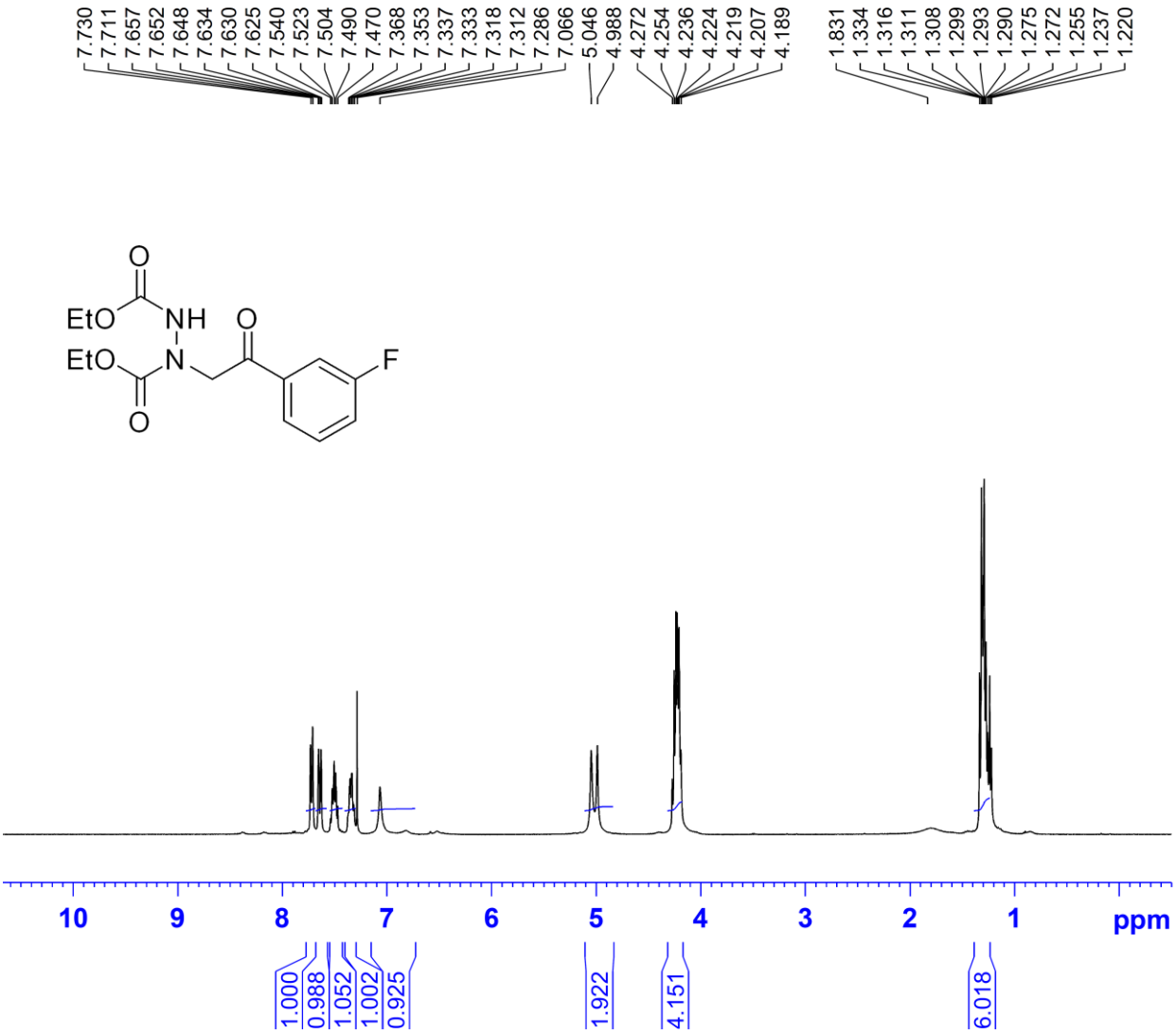
Compound **9n**: ^{1}H NMR (400 MHz, $CDCl_3$)



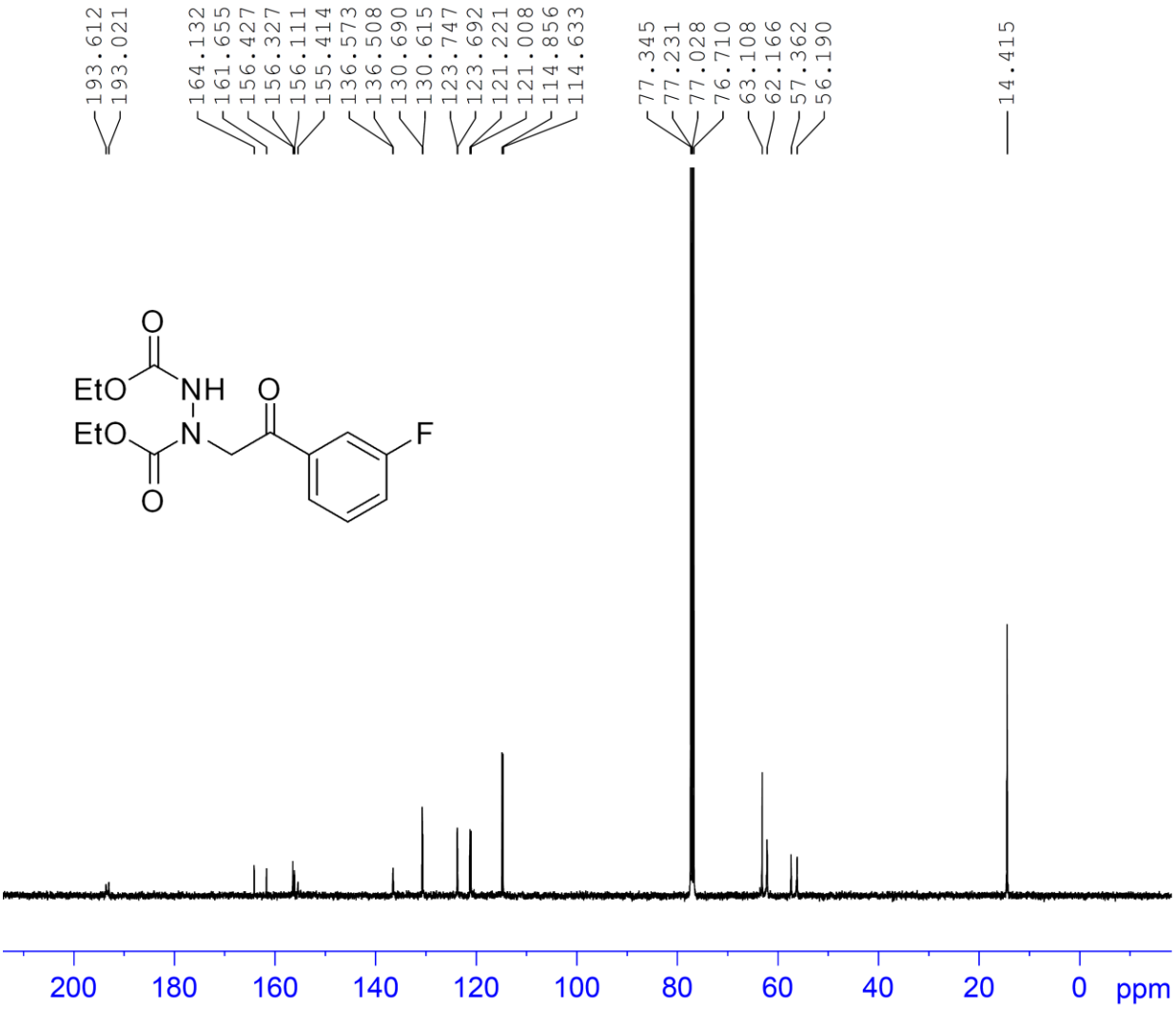
Compound **9n**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



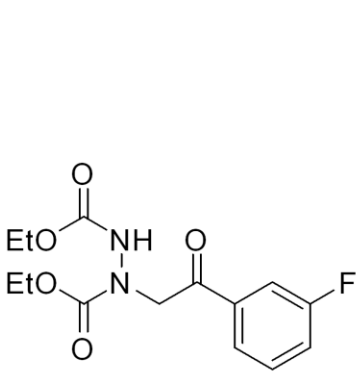
Compound **9o**: ^{1}H NMR (400 MHz, $CDCl_3$)

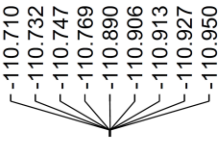


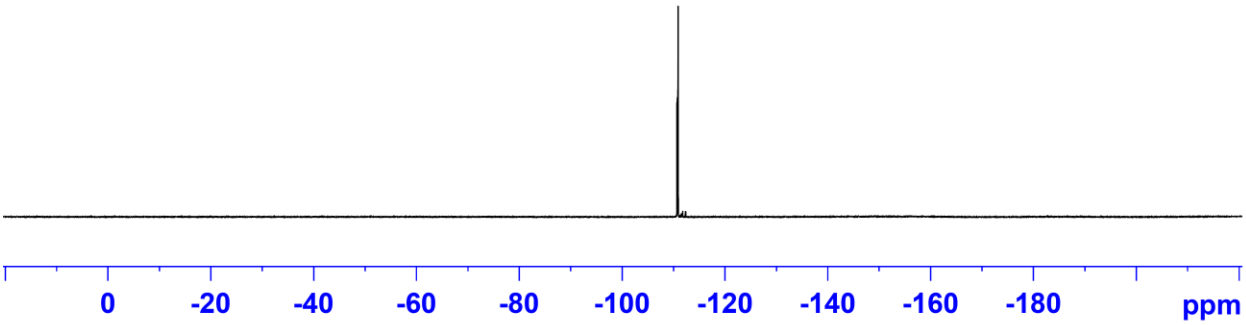
Compound **9o**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



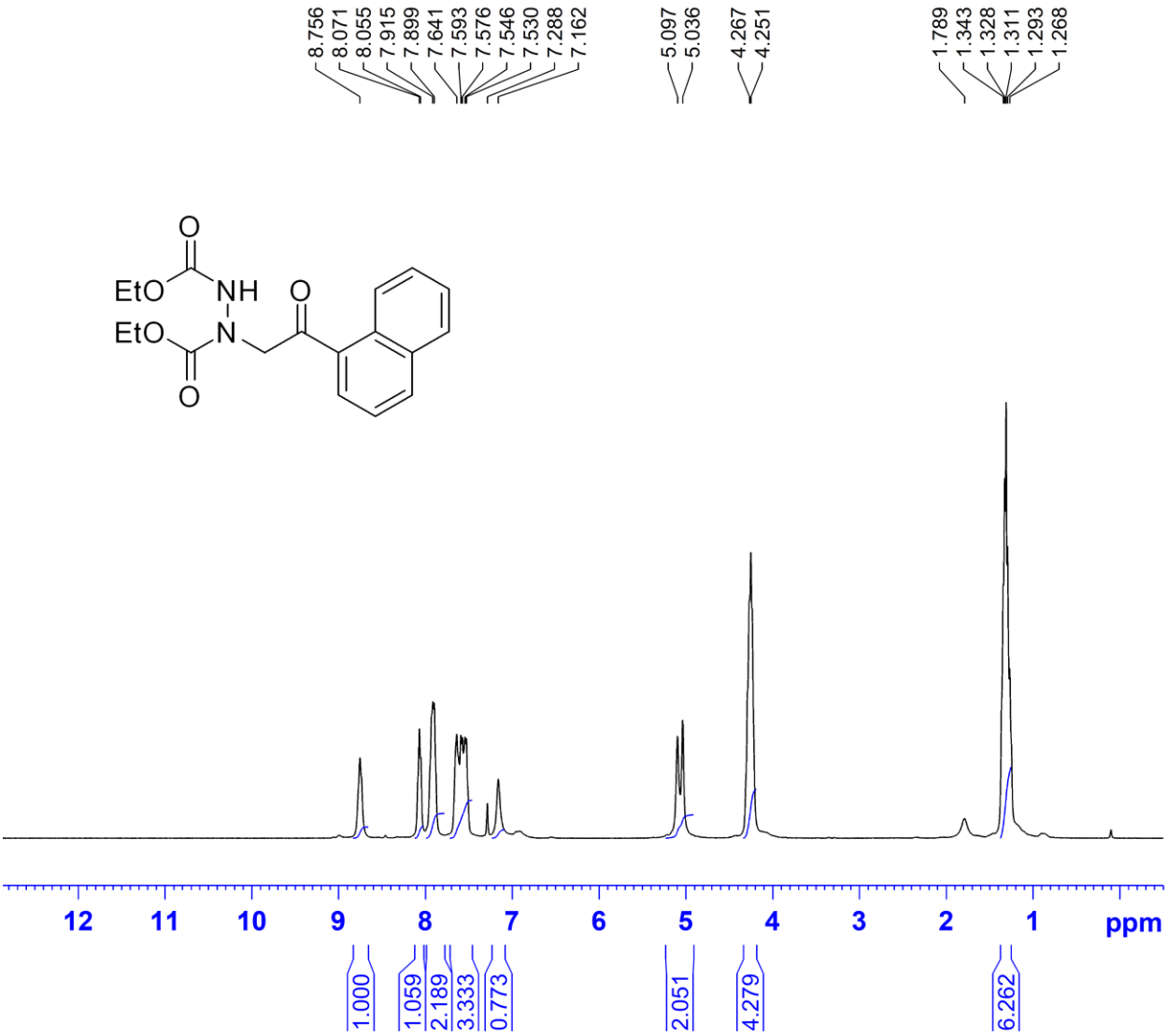
Compound **9o**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



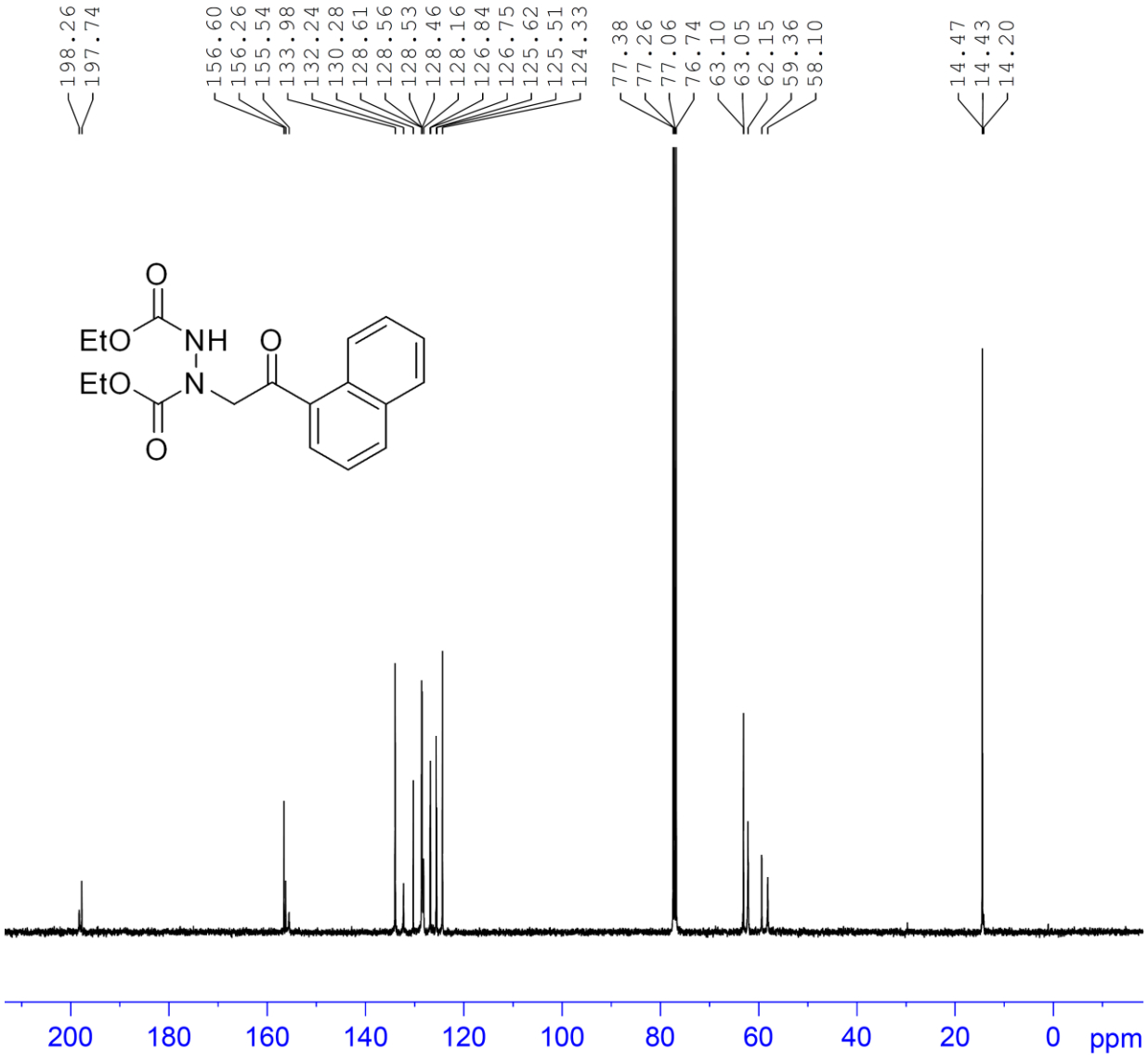




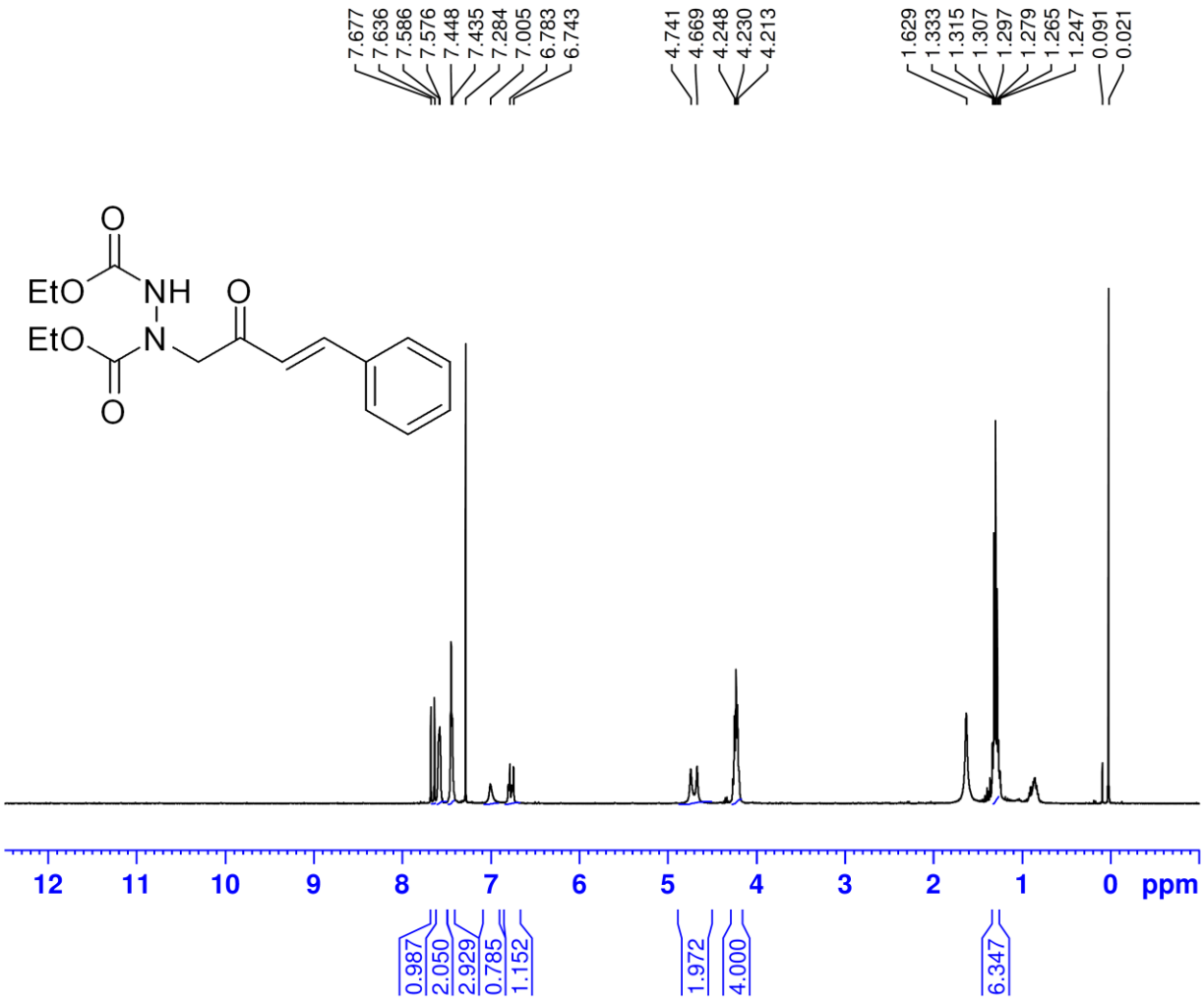
Compound **9p**: ^{1}H NMR (400 MHz, $CDCl_3$)



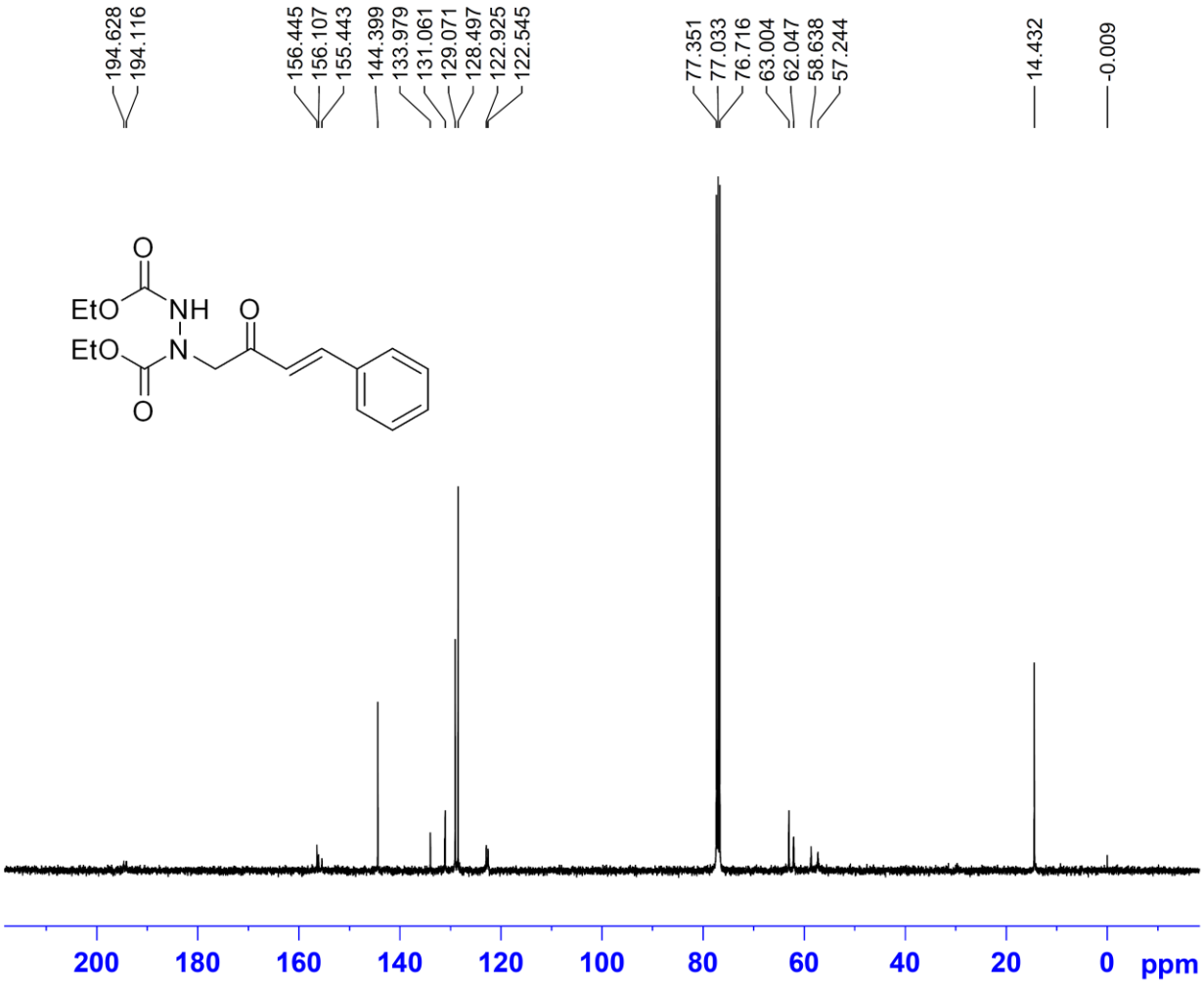
Compound **9p**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



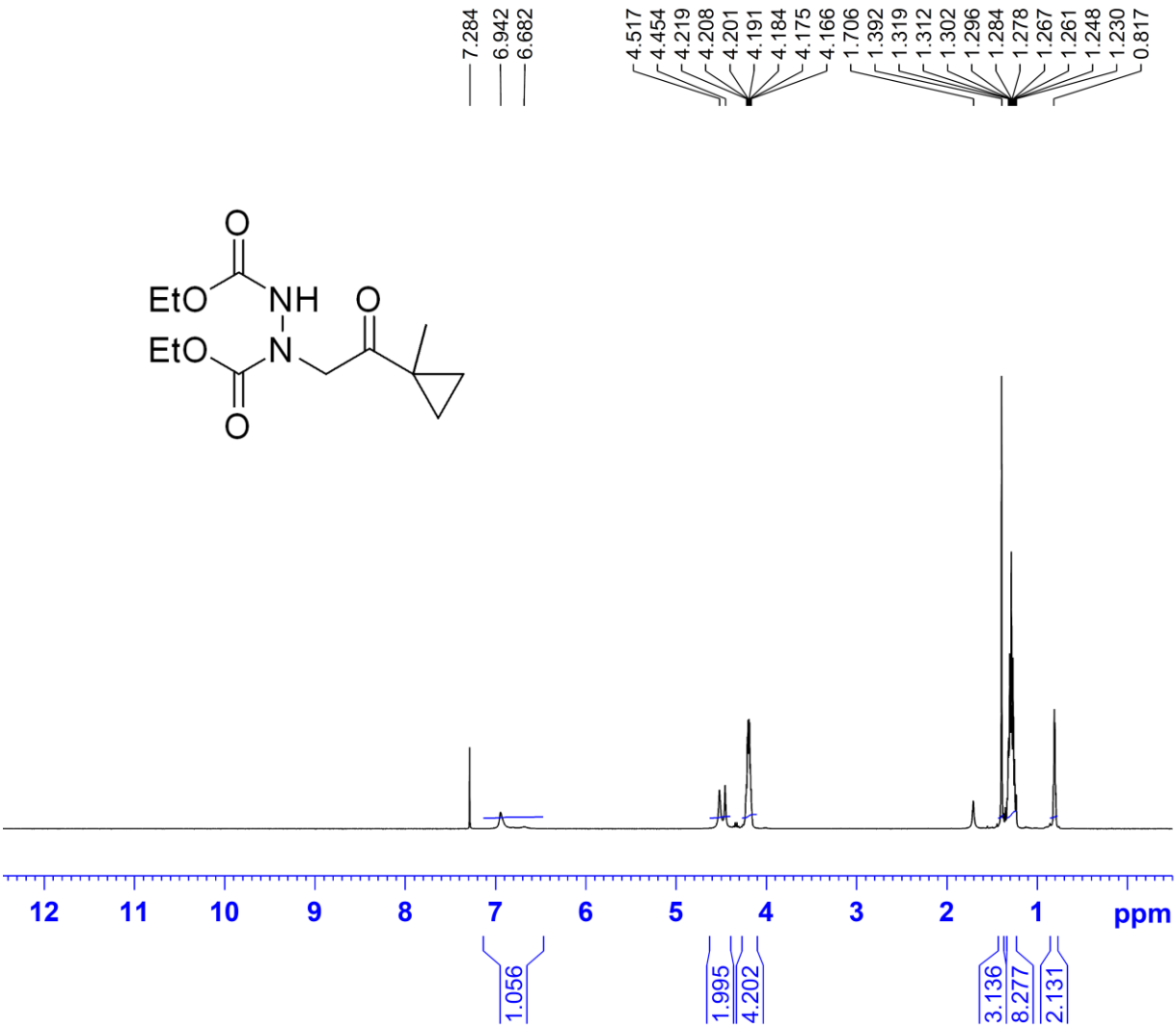
Compound **11a**: ^{1}H NMR (400 MHz, $CDCl_3$)



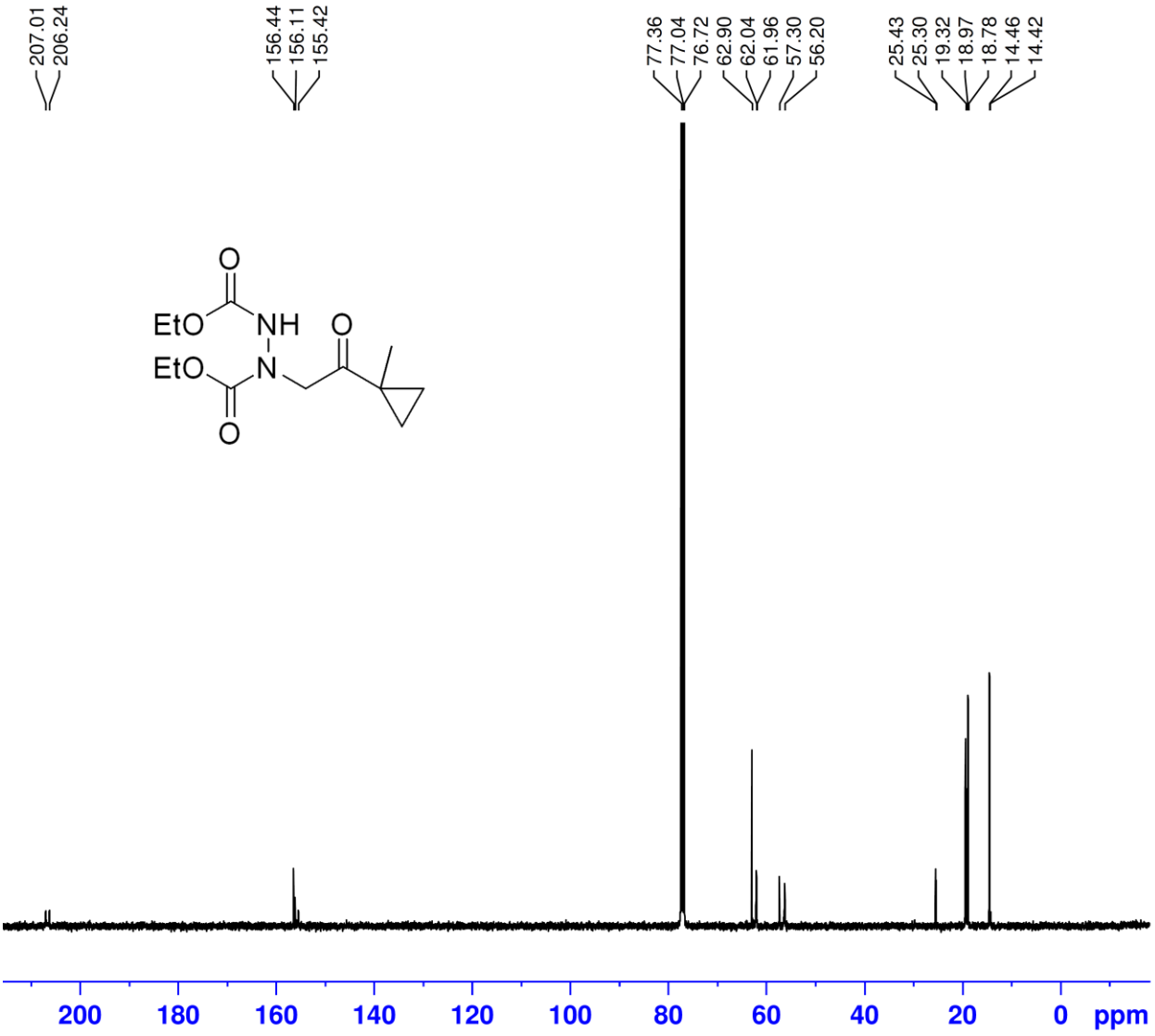
Compound **11a**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



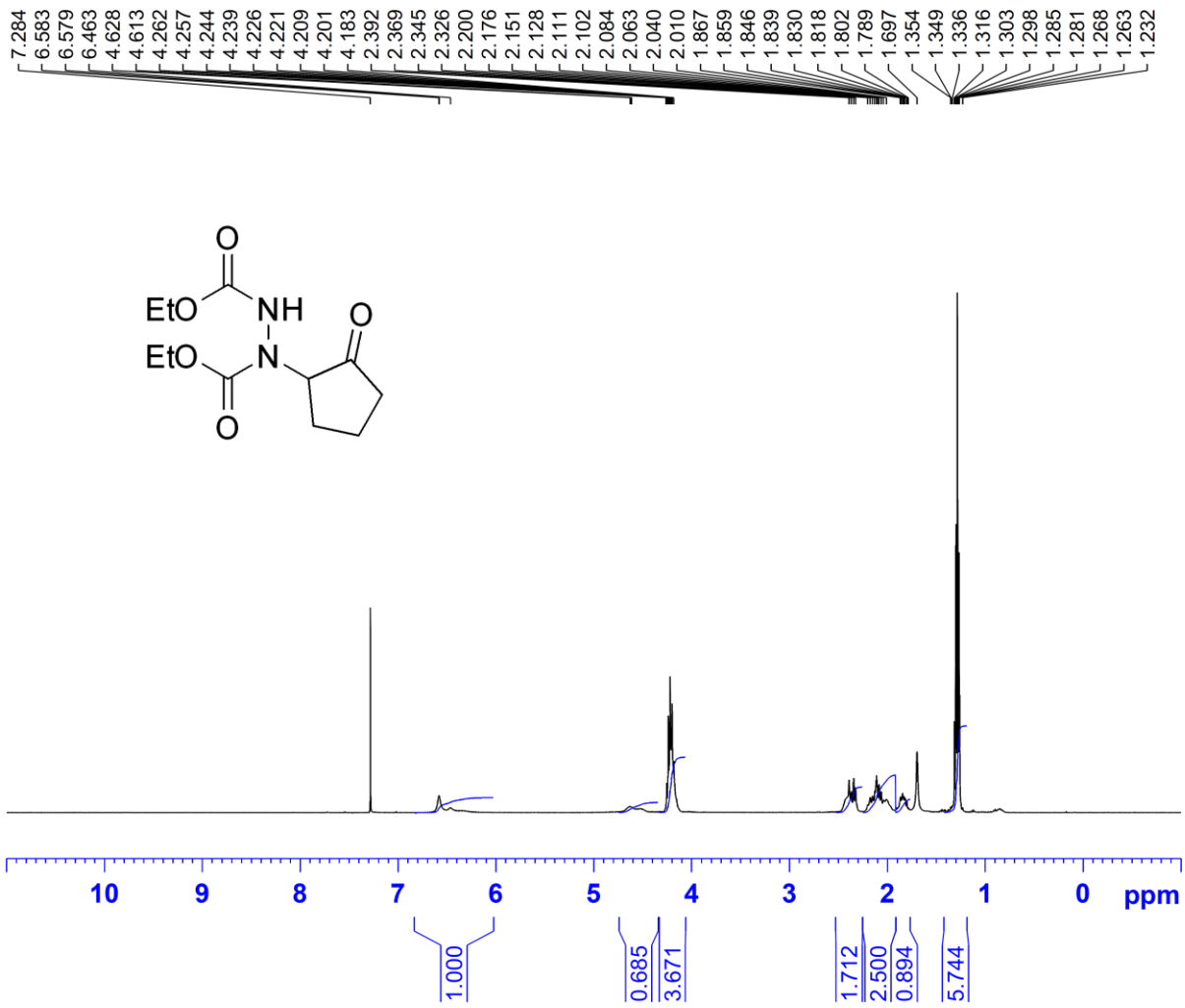
Compound **11b**: ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **11b**: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



Compound **11c**: ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **11d**: ^{1}H NMR (400 MHz, $CDCl_3$)