SUPPLEMENTARY INFORMATION

Tandem Intramolecular Cyclisation / 1,3-Aryl Shift in N-(4,4-Diethoxybutyl)-1-Arylmethanimines (Kazan Reaction): Synthesis of 3-Benzylidene-1-Pyrrolines

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General Methods

The ESI-TOF mass spectra were recorded on a AmazonX (Bruker Daltonik GmbH) instrument. IR spectra were obtained with a Bruker Vector 22 spectrometer. Elemental analysis was performed on Carlo Erba EA 1108 instrument. Melting points were determined in glass capillaries with a Stuart SMP 10 apparatus. All solvents were purified and dried according to standard procedures.

NMR Spectroscopy

All NMR experiments were performed with Bruker AVANCE-600, AVANCE-500 and AVANCE-400 spectrometers. Frequencies are 600.1 MHz in ^{1}H NMR, 150.9 MHz in ^{13}C NMR NMR experiments for AVANCE-600, 500.1 MHz in ^{1}H NMR, 128.8 MHz in ^{13}C NMR, and 400.1 MHz in ^{1}H NMR and 100.6 MHz in ^{13}C NMR experiments for Avance 400. Samples (ca. 1 mg) were prepared by dissolving in 0.6 mL of the corresponding solvent and were placed in standard NMR tubes (Norell, USA).

General method of synthesis of *N*-(4,4-diethoxybutyl)imines 1a-r*

To the solution of appropriate aldehyde (8.39 mmol) in dry chloroform (10 ml) 4,4-diethoxybutane-1-amine (1.35 g, 8.39 mmol) was added. Reaction mixture was stirred at room temperature for 6 hours. Solvent was removed in vacuum to give crude **1**, which was used without further purification.

N-(4,4-diethoxybutyl)-1-phenylmethanimine (1a)

Yield: 96%; ^{1}H-NMR ($CDCl_3$) δ: 1.22 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.66-1.75 (2H, m, CH_2), 1.77-1.84 (2H, m, CH_2), 3.47-3.55 (2H, m, CH_2), 3.63-3.70 (4H, m, CH_2), 4.56 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 7.39-7.44 (3H, m, arom.), 7.71-7.76 (2H, m, arom.), 8.29 8.16 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.30, 26.13, 31.40, 60.89, 61.29, 102.78, 127.97, 128.45, 130.38, 136.30, 160.77.

N-(4,4-diethoxybutyl)-1-(4-methoxyphenyl)methanimine (1b)

Yield: 89%; ^{1}H-NMR ($CDCl_3$) δ: 1.17 (6H, t, $^{3}J_{HH}$ 6.9 Hz, CH_3), 1.62-1.70 (2H, m, CH_2), 1.70-1.81 (2H, m, CH_2), 3.41-3.52 (2H, m, CH_2), 3.53-3.67 (4H, m, CH_2), 3.78 (3H, s, CH_3), 4.50 (1H, t, $^{3}J_{HH}$ 5.3 Hz,

* (4,4-diethoxybutyl)imine **1n** could not be obtained by this procedure, starting compounds were isolated regardless of the reaction time and temperature. Attempt to synthesize compound **1n** by refluxing 4,4-diethoxybutane-1-amine and benzaldehyde derivative in benzene with Dean-Stark apparatus resulted in the formation of pyrroline **2n**.

CH), 6.87 д (2H, $^{3}J_{HH}$ 8.8 Hz, arom.), 7.63 д (2H, $^{3}J_{HH}$ 8.7 Hz, arom.), 8.16 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.31, 26.24, 31.43, 55.23, 60.94, 61.22, 102.84, 113.91, 129.25, 129.52, 160.23, 161.50.

4,4-diethoxy-*N*-(4-(prop-2-yn-1-yloxy)benzylidene)butan-1-amine (1c)

Yield: 98%; ^{1}H-NMR ($CDCl_3$) δ: 1.13 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.57-1.64 (2H, m, CH_2), 2.47 (1H, t, $^{3}J_{HH}$ 2.4 Hz, CH), 3.37-3.48 (2H, m, CH_2), 3.50-3.63 (2H, m, CH_2), 4.42-4.49 (1H, m, CH), 4.64 (2H, d, $^{3}J_{HH}$ 2.4 Hz, CH_2), 6.92 (2H, d, $^{3}J_{HH}$ 8.9 Hz, arom.), 7.60 (2H, d, $^{3}J_{HH}$ 8.8 Hz, arom.), 8.13 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.33, 26.22, 31.43, 55.80, 60.97, 61.24, 75.82, 78.19, 102.84, 114.89, 129.50, 130.08, 159.37, 160.11.

1-(4-bromophenyl)-*N*-(4,4-diethoxybutyl)methanimine (1d)

Yield: 93%; ^{1}H-NMR ($CDCl_3$) δ: 1.19 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.64-1.71 (2H, m, CH_2), 1.72-1.82 (2H, m, CH_2), 3.44-3.54 (2H, m, CH_2), 3.58-3.69 (4H, m, CH_2), 4.53 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH_3), 7.52 (2H, d, $^{3}J_{HH}$ 8.5 Hz, arom.), 7.58 (2H, d, $^{3}J_{HH}$ 8.6 Hz, arom.), 8.20 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.33, 26.06, 31.43, 61.02, 61.30, 102.79, 124.82, 129.44, 131.75, 135.19, 159.66.

N-(4-chlorobenzylidene)-4,4-diethoxybutan-1-amine (1e)

Yield: 81%; ^{1}H-NMR ($CDCl_3$) δ: 1.22 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.66-1.74 (2H, m, CH_2), 1.75-1.84 (2H, m, CH_2), 3.45-3.56 (2H, m, CH_2), 3.60-3.72 (4H, m, CH_2), 4.55 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 7.35-7.43 (2H, m, arom.), 7.64-7.72 (2H, m, arom.), 8.25 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 14.33, 25.60, 31.18, 60.54, 61.26, 102.96, 128.61, 129.28, 134.56, 136.49, 161.19.

4-(((4,4-diethoxybutyl)imino)methyl)phenol (1f)

Yield: 89%; ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.63-1.70 (2H, m, CH_2), 1.73-1.83 (2H, m, CH_2), 3.43-3.53 (2H, m, CH_2), 3.58-3.67 (4H, m,CH_2), 4.50 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 6.73 (2H, d, $^{3}J_{HH}$ 8.7 Hz, arom.), 7.52 (2H, d, $^{3}J_{HH}$ 8.7 Hz, arom.), 8.16 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.28, 25.93, 31.31, 60.37, 61.26, 102.84, 116.10, 126.35, 130.39, 160.63, 162.65.

4,4-diethoxy-N-(4-nitrobenzylidene)butan-1-amine (1g)

Yield: 89%; ^{1}H-NMR ($CDCl_3$) δ: 1.08 (6H, t, $^{3}J_{HH}$ 7.2 Hz, CH_3), 1.55-1.63 (2H, m, CH_2), 1.64-1.75 (2H, m, CH_2), 3.34-3.43 (2H, m, CH_2), 3.49-3.61 (4H, m, CH_2), 4.43 (1H, t, $^{3}J_{HH}$ 5.5 Hz, CH); 7.77 (2H, d, $^{3}J_{HH}$ 8.9 Hz, arom.), 8.10 (2H, d, $^{3}J_{HH}$ 8.8 Hz, arom.), 8.25 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.23, 25.87, 31.35, 60.97, 61.33, 102.66, 123.61, 128.58, 141.73, 148.78, 158.46.

4-(((4,4-diethoxybutyl)imino)methyl)-N,N-dimethylaniline (1h)

Yield: 89%; ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.62-1.70 (2H, m, CH_2), 1.71-1.80 (2H, m, CH_2), 2.96 (6H, s, CH_3), 3.43-3.51 (2H, m, CH_2), 3.52-3.58 (2H, m, CH_2), 3.59-3.67 (2H, m, CH_2), 4.51 (1H, t, $^{3}J_{HH}$ 5.4 Hz, CH), 6.66 (2H, d, $^{3}J_{HH}$ 8.6 Hz, arom.), 7.28 (1H, s, CH), 7.58 (2H, d, $^{3}J_{HH}$ 8.6 Hz, arom.), 8.11 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.34, 26.41, 31.45, 40.15, 60.92, 61.21, 102.90, 111.59, 124.47, 129.43, 151.98, 160.84.

N-(4,4-diethoxybutyl)-1-(3-fluorophenyl)methanimine (1i)

Yield: 90%; ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.64-1.72 (2H, m, CH_2), 1.74-1.81 (2H, m, CH_2), 3.44-3.55 (2H, m, CH_2), 3.59-3.70 (4H, m, CH_2), 4.51 (1H, t, $^{3}J_{HH}$ 5.7 Hz, CH), 7.03-7.10 (1H, m, arom.), 7.30-7.38 (1H, m, arom.), 7.41-7.49 (2H, m, arom.), 8.21 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.31, 15.33, 26.07, 31.44, 61.03, 61.20, 102.82, 114.08 (q, J_{CF} 22.1 Hz), 117.36 (q, J_{CF} 21.6 Hz), 124.11 (q, J_{CF} 2.5 Hz), 130.03 (q, J_{CF} 8.0 Hz), 138.70 (q, J_{CF} 7.2 Hz), 159.56 (q, J_{CF} 2.5 Hz), 163.06 (q, J_{CF} 246.3 Hz).

4,4-diethoxy-N-(3-iodobenzylidene)butan-1-amine (1j)

Yield: 89%; ^{1}H-NMR ($CDCl_3$) δ: 1.17 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.61-1.71 (2H, m, CH_2), 1.71-1.80 (2H, m, CH_2), 3.42-3.52 (2H, m, CH_2), 3.57-3.67 (4H, m, CH_2), 4.50 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 7.09 (1H, t, $^{3}J_{HH}$ 7.8 Hz, arom.), 7.57-7.61 (1H, m, arom.), 7.66-7.70 (1H, m, arom.), 8.07 (1H, t, $^{3}J_{HH}$ 1.6 Hz, CH), 8.13 (1H, s, arom.). ^{13}C-NMR ($CDCl_3$) δ: 15.36, 26.06, 31.42, 61.02, 61.26, 94.51, 102.77, 127.44, 130.18, 136.55, 138.28, 139.24, 159.16.

2-(((4,4-diethoxybutyl)imino)methyl)phenol (1k)

Yield: 96%; ^{1}H-NMR ($CDCl_3$) δ: 1.21 (6H, t, $^{3}J_{HH}$ 6.9 Hz, CH_3), 1.65- 1.75 (2H, m, CH_2), 1.76-1.86 (2H, m, CH_2), 3.45-3.57 (2H, m, CH_2), 3.60-3.71 (4H, m, CH_2), 4.52 (1H, t, $^{3}J_{HH}$ 5.7 Hz, CH), 6.86 (1H, t, $^{3}J_{HH}$ 6.9 Hz, arom.), 6.95 (1H, d, $^{3}J_{HH}$ 8.1 Hz, arom.), 7.23 (1H, dd, $^{3}J_{HH}$ 7.6 Hz, $^{4}J_{HH}$ 1.4 Hz, arom.), 7.27-7.31 (1H, m, arom.), 8.33 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.34, 15.36, 26.12, 31.29, 59.36, 61.19, 102.71, 117.01, 118.44, 118.82, 131.16, 132.09, 161.33, 164.85.

4-chloro-2-(((4,4-diethoxybutyl)imino)methyl)phenol (1l)

Yield: 63%; ^{1}H-NMR ($CDCl_3$) δ: 1.22 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.68-1.74 (2H, m, CH_2), 1.77-1.83 (2H, m, CH_2), 3.47-3.55 (2H, m, CH_2), 3.61-3.69 (4H, m, CH_2), 4.53 (1H, t, $^{3}J_{HH}$ 5.5 Hz, CH), 6.91 (1H, d,

$^{3}J_{HH}$ 8.8 Hz, arom.), 7.20-7.29 (2H, m, arom.), 8.28 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.31, 25.98, 31.21, 59.32, 61.20, 102.61, 118.58, 119.49, 123.00, 130.25, 131.94, 159.93, 163.66.

4,4-diethoxy-N-(naphthalen-1-ylmethylene)butan-1-amine (1m)

Yield: 95%; ^{1}H-NMR ($CDCl_3$) δ: 1.24 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.79-1.85 (2H, m, CH_2), 1.88-1.95 (2H, m, CH_2), 3.50-3.58 (2H, m, CH_2), 3.65-3.73 (2H, m, CH_2), 3.77 (2H, t, $^{3}J_{HH}$ 6.5 Hz, CH_2), 4.60 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 7.46-7.55 (2H, m, arom.), 7.59 (1H, t, $^{3}J_{HH}$ 7.2 Hz, arom.), 7.85-7.93 (3H, m, arom.), 8.92 (1H, s, CH), 8.95 (1H, d, $^{3}J_{HH}$ 8.6 Hz, arom.). ^{13}C-NMR ($CDCl_3$) δ: 15.43, 26.42, 31.60, 61.17, 62.37, 103.01, 124.49, 125.27, 126.01, 127.07, 128.62, 128.73, 130.85, 131.36, 131.80, 133.90, 160.65.

2,6-di-tert-butyl-4-(((4,4-diethoxybutyl)imino)methyl)phenol (1o)

Yield: 98%; ^{1}H-NMR ($CDCl_3$) δ: 1.21 (6H, t, $^{3}J_{HH}$ 6.9 Hz, CH_3), 1.46 (18H, s, CH_3), 1.67-1.73 (2H, m, CH_2), 1.74-1.81 (2H, m, CH_2), 3.48-3.54 (2H, m, CH_2), 3.56-3.62 (2H, m, CH_2), 3.64-3.72 (2H, m, CH_2), 4.52-4.58 (2H, m, CH), 7.53 (2H, br.s, arom.), 8.17 уш.с. (2H, br.s, CH). ^{13}C-NMR ($CDCl_3$) δ: 15.38, 26.31, 30.19, 31.42, 34.42, 61.08 (2C), 102.89, 125.23, 127.66, 136.12, 156.20, 161.54.

N-(anthracen-9-ylmethylene)-4,4-diethoxybutan-1-amine (1p)

Yield: 95%; ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.87-1.95 (2H, m, CH_2), 1.99-2.09 (2H, m, CH_2), 3.46-3.57 (2H, m, CH_2), 3.53-3.64 (2H, m, CH_2), 3.68-3.77 (2H, m, CH_2), 4.66 (1H, t, $^{3}J_{HH}$ 5.6 Hz, CH), 7.41-7.49 (4H, m, arom.), 7.92-7.98 (2H, m, arom.), 8.18-8.27 (2H, m, arom.), 8.40 (1H, s, arom.), 9.46 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 14.41, 25.79, 31.36, 61.31, 61.52, 103.02, 124.29, 125.02, 126.29, 128.06, 128.57, 128.90, 129.47, 131.19, 162.23.

4,4-diethoxy-N-(pyridin-4-ylmethylene)butan-1-amine (1q)

Yield: 67%; ^{1}H-NMR ($CDCl_3$) δ: 1.17 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.64-1.72 (2H, m, CH_2), 1.73-1.82 (2H, m, CH_2), 3.45-3.55 (2H, m, CH_2), 3.60-3.75 (4H, m, CH_2), 4.50 (1H, t, $^{3}J_{HH}$ 5.5 Hz, CH), 7.49 (2H, d, $^{3}J_{HH}$ 4.9 Hz, arom.), 8.64 (2H, d, $^{3}J_{HH}$ 4.8 Hz, arom.), 8.21 (1H, s, CH). ^{13}C-NMR ($CDCl_3$) δ: 14.51, 14.53, 25.61, 31.27, 60.85, 61.19, 102.90, 122.19, 143.78, 149.64, 159.82.

4,4-diethoxy-N-(pyridin-3-ylmethylene)butan-1-amine (1r)

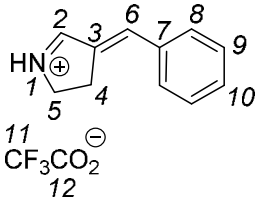
Yield: 81%; ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.63-1.72 (2H, m, CH_2), 1.74-1.82 (2H, m, CH_2), 3.48-3.55 (2H, m, CH_2), 3.63-3.70 (4H, m, CH_2), 4.56 (1H, t, $^{3}J_{HH}$ 5.5 Hz, CH), 7.48-7.52 (1H, m, $^{3}J_{HH}$ 5.5 Hz, arom.), 8.20 (1H, dt, $^{3}J_{HH}$ 8.0 Hz, $^{4}J_{HH}$ 1.9 Hz, arom.), 8.43 (1H, s, CH); 8.60 (1H, dd,

$^{3}J_{HH}$ 4.9 Hz, $^{4}J_{HH}$ 1.7 Hz, arom.), 8.87 (1H, d, $^{4}J_{HH}$ 1.5 Hz, arom.). ^{13}C-NMR ($CDCl_3$) δ: 14.32, 25.56, 31.18, 60.77, 61.24, 102.94, 124.05, 132.16, 135.31, 148.98, 150.56, 159.24.

General method of synthesis of pyrrolines 2a-r[†]

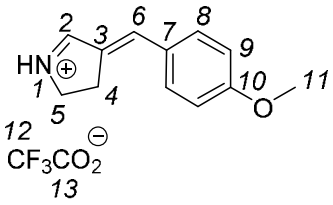
To the solution of *N*-(4,4-diethoxybutyl)imine **1** (4.76 mmol) in dry chloroform (5 ml) trifluoroacetic acid (0.54 g, 4.76 mmol) was added. Reaction mixture was stirred at room temperature for 6 hours. Solvent was removed, residue was washed with diethyl ether (2x20 ml) and dried in vacuum (r.t., 2 h, 0.01 torr).

(*E*)-4-benzylidene-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2a)



Yield: 56%; m.p. 155-156°C. IR (KBr): 1593, 2529, 2598 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.30-3.35 (2H, m, C^{4}H), 4.32-4.38 (2H, m, C^{5}H), 7.50-7.56 (3H, m, $C^{8,10}$H), 7.65-7.71 (2H, m, C^{9}H), 7.76 (1H, t, $^{3}J_{HH}$ 2.7 Hz, C^{6}H), 8.87 (1H, t, $^{3}J_{HH}$ 1.5 Hz, C^{2}H). ^{13}C-NMR (CD_3OD) δ: 25.82 (C^{4}), 54.01 (C^{5}), 116.81 (q, J_{CF} 292.6 Hz, C^{11}), 128.97 (C^{8}), 130.69 (C^{9}), 131.28 (C^{6}), 134.27 (C^{10}), 137.36 (C^{3}), 144.64 (C^{7}), 161.52 (q, J_{CF} 34.7 Hz, C^{12}), 173.88 (C^{2}). Anal. Calcd. for $C_{13}H_{12}F_3NO_2$: C, 57.57; H, 4.46; N, 5.16. Found: C, 57.68; H, 4.33; N, 5.31. ESI-TOF: *m/z* for $C_{13}H_{12}F_3NO_2$ $[M+H]^+$ calcd.: 271, found: 158 $[M\text{-}CF_3CO_2^-]^+$.

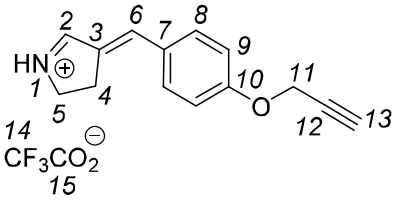
(*E*)-4-(4-methoxybenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2b)



[†] Except pyrroline **2n**, which was obtained according to the following procedure: The solution of appropriate aldehyde (8.39 mmol) and 4,4-diethoxybutane-1-amine (1.35 g, 8.39 mmol) in dry benzene (10 ml) was refluxed with Dean-Stark apparatus for 12 h. Solvent was removed, residue was washed with diethyl ether (2x20 ml) and dried in vacuum (r.t., 2 h, 0.01 torr) to give **2n**.

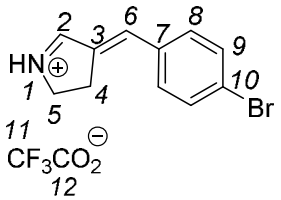
Yield: 50%; m.p. 110-111°C. IR (KBr): 1597, 2514, 2623 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.30-3.36 (2H, m, C^4H), 3.91 (3H, s, $C^{11}H$), 4.31-4.39 (2H, m, C^5H), 7.12 (2H, d, $^3J_{HH}$ 8.9 Hz, C^9H), 7.69 (2H, d, $^3J_{HH}$ 8.9 Hz, C^8H), 7.76 (1H, t, $^3J_{HH}$ 2.6 Hz, C^6H), 8.83 (1H, t, $^3J_{HH}$ 1.5 Hz, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.77 (C^4), 53.38 (C^5), 54.76 (C^{11}), 114.60 (C^9), 116.81 (q, J_{CF} 293.1 Hz, C^{12}), 127.00 (C^3), 133.19 (C^8), 134.21 (C^6), 145.38 (C^7), 161.54 (q, J_{CF} 34.5 Hz, C^{13}), 162.92 (C^{10}), 173.48 (C^2). Anal. Calcd. for $C_{14}H_{14}F_3NO_3$: C, 55.82; H, 4.68; N, 4.65. Found: C, 55.61; H, 4.91; N, 4.77. ESI-TOF: *m/z* for $C_{14}H_{14}F_3NO_3$ $[M+H]^+$ calcd.: 301, found: 188 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(4-(prop-2-yn-1-yloxy)benzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2c)



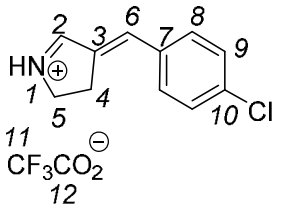
Yield: 43%; m.p. 92-93°C. IR (KBr): 1594, 2637 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.02 (1H, t, $^3J_{HH}$ 2.19 Hz, $C^{13}H$), 3.31-3.39 (2H, m, C^4H), 4.31-4.40 (2H, m, C^5H), 4.86 (2H, d, $^3J_{HH}$ 2.19 Hz, $C^{11}H$), 7.18 (2H, d, $^3J_{HH}$ 8.8 Hz, C^9H), 7.70 (2H, d, $^3J_{HH}$ 8.8 Hz, C^8H), 7.75 (1H, br.s, C^6H), 8.83 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.80 (C^4), 53.58 (C^{11}), 55.53 (C^5), 76.11 (C^{13}), 77.67 (C^{12}), 115.52 (C^9), 116.89 (q, J_{CF} 299.9 Hz, C^{14}), 127.71 (C^3), 132.98 (C^8), 134.80 (C^6), 144.94 (C^7), 160.66 (C^{10}), 161.14-162.15 (m, C^{15}), 173.56 (C^2). Anal. Calcd. for $C_{16}H_{14}F_3NO_3$: C, 59.08; H, 4.34; N, 4.31. Found: C, 58.86; H, 4.48; N, 4.21. ESI-TOF: *m/z* for $C_{16}H_{14}F_3NO_3$ $[M+H]^+$ calcd.: 325, found: 212 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(4-bromobenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2d)



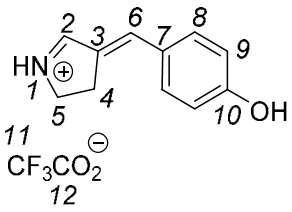
Yield: 26%; m.p. 172-173°C. IR (KBr): 1596, 2536, 2617 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.28-3.38 (2H, m, C^4H), 4.33-4.42 (2H, m, C^5H), 7.71 (2H, d, $^3J_{HH}$ 8.5 Hz, C^8H), 7.71 (2H, d, $^3J_{HH}$ 8.6 Hz, C^9H), 7.72 (1H, br.s, C^6H), 8.90 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.80 (C^4), 54.23 (C^5), 116.79 (q, J_{CF} 292.8 Hz, C^{11}), 125.56 (C^3), 132.07 (C^8), 132.21 (C^9), 133.31 (C^6), 138.19 (C^{10}), 142.78 (C^7), 161.49 (q, J_{CF} 34.7 Hz, C^{12}), 173.75 (C^2). Anal. Calcd. for $C_{13}H_{11}BrF_3NO_2$: C, 44.73; H, 3.09; Br, 22.96; N 3.91. Found: C, 44.73; H, 3.09; Br, 22.96; N, 3.91. ESI-TOF: *m/z* for $C_{13}H_{11}BrF_3NO_2$ $[M+H]^+$ calcd.: 350, found: 237 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(4-clorobenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2e)



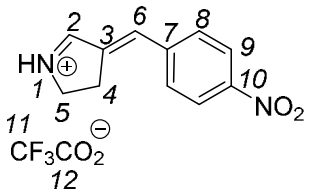
Yield: 40%; m.p. 170-171°C. IR (KBr): 1562, 2523, 2601 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.25-3.30 (2H, m, C^4H), 4.40-4.44 (2H, m, C^5H), 7.57 (2H, d, $^3J_{HH}$ 8.6 Hz, C^8H), 7.69 (2H, d, $^3J_{HH}$ 8.6 Hz, C^9H), 7.71 (1H, br.s, C^6H), 8.84 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.85 (C^4), 54.58 (C^5), 125.01 (C^3), 129.15 (C^8), 131.88 (C^9), 133.05 (C^6), 138.33 (C^{10}), 141.95 (C^7), 173.52 (C^2). Anal. Calcd. for $C_{13}H_{11}ClF_3NO_2$: C, 51.08; H, 3.63; Cl, 11.60; N, 4.58. Found: C, 50.88; H, 3.80; Cl, 11.71; N, 4.79. ESI-TOF: *m/z* for $C_{13}H_{11}ClF_3NO_2$ $[M+H]^+$ calcd.: 306, found: 192 $[M-CF_3CO_2^-]^+$.

(*E*)-4-(4-hydroxybenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2f)



Yield: 70%; m.p. 152-153°C. IR (KBr): 1580, 2453, 2578 cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$) δ: 3.26-3.31 (2H, m, C^4H), 4.29-4.36 (2H, m, C^5H), 6.76 (2H, d, $^3J_{HH}$ 8.7 Hz, C^8H), 7.60 (2H, d, $^3J_{HH}$ 8.7 Hz, C^9H), 7.72 (1H, br.s, C^6H), 8.77 (1H, br.s, C^2H). ^{13}C-NMR ($(CD_3)_2SO$) δ: 25.78 (C^4), 53.24 (C^5), 116.06 (C^9), 125.85 (C^3), 133.21 (C^6), 133.56 (C^8), 145.93 (C^7), 161.60 (C^{10}), 173.31 (C^2). Anal. Calcd. for $C_{13}H_{12}F_3NO_3$: C, 54.36; H, 4.21; N, 4.88. Found: C, 54.41; H, 4.18; N, 4.90. ESI-TOF: *m/z* for $C_{13}H_{12}F_3NO_3$ $[M+H]^+$ calcd.: 287, found: 192 $[M-CF_3CO_2^-]^+$.

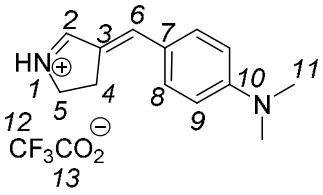
(*E*)-4-(4-nitrobenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2g)



Yield: 37%; m.p. 131-133°C. IR (KBr): 1587, 2342 cm^{-1}. ^{1}H-NMR (CD_3OD : $(CD_3)_2SO$ =9:1) δ: 3.28-3.37 (2H, m, C^4H), 4.37-4.44 (2H, m, C^5H), 7.70 (1H, br.s, C^6H), 7.91 (2H, d, $^3J_{HH}$ 8.7 Hz, C^8H), 8.37 (2H, d, $^3J_{HH}$ 8.7 Hz, C^9H), 8.81 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD : $(CD_3)_2SO$ =9:1) δ: 26.39 (C^4), 56.19

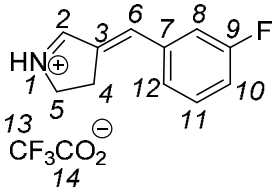
(C^5), 116.88 (q, J_{CF} 294.2 Hz, C^{11}), 123.56 (C^3), 123.80 (C^9), 130.89 (C^8), 137.40 (C^6), 142.79 (C^7), 148.17 (C^{10}), 161.2 (q, J_{CF} 34.5 Hz, C^{12}), 172.65 (C^2). Anal. Calcd. for $C_{13}H_{11}F_3N_2O_4$: C, 49.38; H, 3.51; N, 8.86. Found: C, 49.53; H, 3.73; N, 9.02. ESI-TOF: *m/z* for $C_{13}H_{11}F_3N_2O_4$ $[M+H]^+$ calcd.: 316, found: 203 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(4-(dimethylamino)benzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2h)



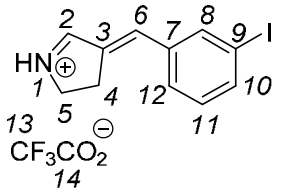
Yield: 19%; m.p. 121-123°C. IR (KBr): 1583, 2358 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.13 (6H, s, $C^{11}H$), 3.27-3.38 (2H, m, C^4H), 4.25-4.35 (2H, m, C^5H), 6.87 (2H, d, $^3J_{HH}$ 8.9 Hz, C^9H), 7.59 (2H, d, $^3J_{HH}$ 8.9 Hz, C^8H), 7.68 (1H, s, C^6H), 8.63 c (1H, s, C^2H). ^{13}C-NMR (CD_3OD) δ: 26.12 (C^4), 38.71 (C^{11}), 52.48 (C^5), 111.76 (C^9), 116.83 (q, J_{CF} 289.9 Hz, C^{12}), 121.93 (C^3), 129.90 (C^6), 133.82 (C^8), 147.13 (C^7), 153.24 (C^{10}), 161.52 (q, J_{CF} 34.3 Hz, C^{13}), 171.83 (C^2). Anal. Calcd. for $C_{15}H_{17}F_3N_2O_2$: C, 57.32; H, 5.45; N, 8.91. Found: C, 57.11; H, 5.69; N, 9.12. ESI-TOF: *m/z* for $C_{15}H_{17}F_3N_2O_2$ $[M+H]^+$ calcd.: 314, found: 201 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(3-fluorobenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2i)



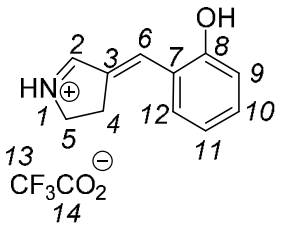
Yield: 42%; m.p. 127-128°C. IR (KBr): 1582, 2462, 2600, 2806 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.52-2.59 (2H, m, C^4H), 3.55-3.59 (2H, m, C^5H), 6.47 (1H, td, $^3J_{HH}$ 8.3 Hz, $^3J_{HH}$ 2.0 Hz, $C^{11}H$), 6.62 (1H, d, $^3J_{HH}$ 9.8 Hz, $C^{12}H$), 6.71 (1H, d, $^3J_{HH}$ 7.8 Hz, $C^{12}H$), 6.74-6.79 (1H, m, $C^{10}H$), 6.93 (1H, br.s, C^6H), 8.10 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.00 (C^4), 53.61 (C^5), 115.69 (d, J_{CF} 22.6 Hz, C^8), 115.98 (q, J_{CF} 292.7 Hz, C^{13}), 116.94 (d, J_{CF} 21.6 Hz, C^{10}), 125.76 (C^3), 129.99 (d, J_{CF} 8.1 Hz, C^7), 135.70 (d, J_{CF} 7.6 Hz, C^{11}), 138.14 (C^6), 141.59 (C^{12}), 160.70 (q, J_{CF} 34.6 Hz, C^{14}), 162.17 (d, J_{CF} 246.2 Hz, C^9), 172.96 (C^2). Anal. Calcd. for $C_{13}H_{11}F_4NO_2$: C, 53.99; H, 3.83; N, 4.84. Found: C, 54.17; H, 3.77; N, 4.95. ESI-TOF: *m/z* for $C_{13}H_{11}F_4NO_2$ $[M+H]^+$ calcd.: 289, found: 176 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(3-iodobenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2j)



Yield: 41%; m.p. 134-136°C. IR (KBr): 1570, 2428, 2528, 2586 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.28-3.31 (2H, m, C^4H), 4.34-4.38 (2H, m, C^5H), 7.32 (1H, d, $^3J_{HH}$ 7.8 Hz, $C^{11}H$), 7.62 (1H, t, $^3J_{HH}$ 2.8 Hz, C^6H), 7.70 (1H, d, $^3J_{HH}$ 8.3 Hz, $C^{12}H$), 7.88 (1H, d, $^3J_{HH}$ 8.3 Hz, $C^{10}H$), 8.03 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.00 (C^4), 53.61 (C^5), 93.96 (C^9), 129.15 (C^3), 130.53 (C^6), 136.52 (C^{12}), 139.11 (C^{11}), 139.21 (C^7), 139.63 (C^8), 140.99 (C^{10}), 173.37 (C^2). Anal. Calcd. for $C_{13}H_{11}F_3INO_2$: C, 39.32; H, 2.79; N, 3.53. Found: C, 39.08; H, 2.95; N, 3.37. ESI-TOF: *m/z* for $C_{13}H_{11}F_3INO_2$ $[M+H]^+$ calcd.: 397, found: 284 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(2-hydroxybenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2k)

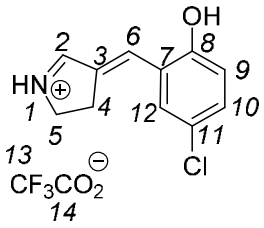


Yield: 19%; m.p. 163-164°C. IR (KBr): 1598, 2647, 2737, 3071 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.24-3.32 (2H, m, C^4H), 4.29-4.38 (2H, m, C^5H), 6.93-7.01 (2H, m, $C^{9,10}H$), 7.36 (1H, t, $^3J_{HH}$ 7.6 Hz, $C^{11}H$), 7.60 (1H, d, $^3J_{HH}$ 7.8 Hz, $C^{12}H$), 8.22 (1H, s, C^6H), 8.87 (1H, s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.81 (C^4), 53.60 (C^5), 115.71 (C^{10}), 116.85 (q, J_{CF} 292.9 Hz, C^{13}), 119.56 (C^{11}), 121.47 (C^3), 129.22 (C^{12}), 133.33 (C^9), 135.41 (C^7), 139.73 (C^6), 158.25 (C^8), 161 (q, J_{CF} 34.6 Hz, C^{14}), 173.79 (C^2). Anal. Calcd. for $C_{13}H_{12}F_3NO_3$: C, 54.36; H, 4.21; N, 4.88. Found: C, 54.15; H, 4.32; N, 5.01. ESI-TOF: *m/z* for $C_{13}H_{12}F_3NO_3$ $[M+H]^+$ calcd.: 287, found: 174 $[M\text{-}CF_3CO_2^-]^+$.

(*Z*)-4-(2-hydroxybenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2k)

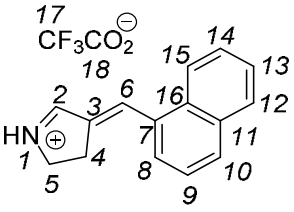
^{1}H-NMR (CD_3OD) δ: 2.60-2.70 (2H, m, C^4H), 3.12-3.24 (2H, m, C^5H), 5.53 (1H, s, C^6H), 6.66 (1H, s, C^2H), 6.96-7.01 (2H, m, $C^{9,10}H$), 7.17 (1H, dd, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.4 Hz $C^{12}H$), 7.22 (1H, td, $^3J_{HH}$ 7.9 Hz, $^4J_{HH}$ 1.4 Hz $C^{11}H$). ^{13}C-NMR (CD_3OD) δ: 30.58 (C^4), 38.06 (C^5), 98.11 (C^6), 115.92 (C^{10}), 116.87 (q, J_{CF} 293.1 Hz, C^{13}), 120.80 (C^3), 121.48 (C^{11}), 124.31 (C^2), 126.38 (C^{12}), 127.53 (C^7), 128.86 (C^9), 161.71 (q, J_{CF} 34.4 Hz, C^{14}), 150.19 (C^8).

(*E*)-4-(5-chloro-2-hydroxybenzylidene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2l)



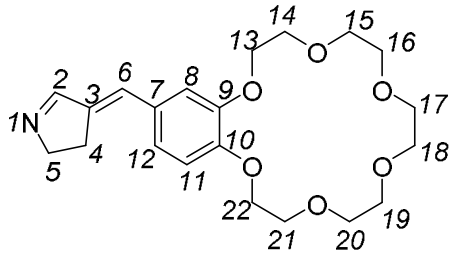
Yield: 15%; m.p. 194-195°C. IR (KBr): 1582, 2460, 2527, 2586 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.25-3.31 (2H, m, C^4H), 4.33-4.38 (2H, m, C^5H), 6.94 (1H, d, $^3J_{HH}$ 8.8 Hz, C^9H), 7.34 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^4J_{HH}$ 2.6 Hz, $C^{10}H$), 7.56 (1H, d, $^3J_{HH}$ 2.5 Hz, $C^{12}H$), 8.07 (1H, t, $^3J_{HH}$ 2.6 Hz, C^6H), 8.86 (1H, br.s, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.71 (C^4), 54.26 (C^5), 117.05 (C^7), 122.86 (C^9), 124.24 (C^3), 128.13 (C^{12}), 132.36 (C^{11}), 137.08 (C^{10}), 137.17 (C^6), 156.63 (C^8), 173.65 (C^2). Anal. Calcd. for $C_{13}H_{11}ClF_3NO_3$: C, 48.54; H, 3.45; Cl, 11.02; N, 4.35. Found: C, 48.70; H, 3.24; Cl, 10.89; N, 4.19. ESI-TOF: *m/z* for $C_{13}H_{11}ClF_3NO_3$ $[M+H]^+$ calcd.: 322, found: 208 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-(naphthalen-1-ylmethylene)-3,4-dihydro-2H-pyrrol-1-ium trifluoroacetate (2m)



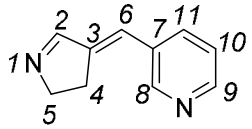
Yield: 31%; m.p. 138-149°C. IR (KBr): 1568, 2424, 2522, 2594 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.34-3.38 (2H, m, C^4H), 4.33-4.39 (2H, m, C^5H), 7.60-7.70 (3H, m, $C^{9,13,14}H$), 7.93 (1H, d, $^3J_{HH}$ 7.2 Hz, C^8H), 8.00 (1H, d, $^3J_{HH}$ 7.4 Hz, $C^{15}H$), 8.07 (1H, d, $^3J_{HH}$ 8.2 Hz, $C^{10}H$), 8.28 (1H, d, $^3J_{HH}$ 8.6 Hz, $C^{12}H$), 8.62 (1H, t, $^3J_{HH}$ 2.8 Hz, C^6H), 9.00 (1H, t, $^3J_{HH}$ 1.6 Hz, C^2H). ^{13}C-NMR (CD_3OD) δ: 25.92 (C^4), 54.06 (C^5), 122.68 (C^9), 125.00 (C^8), 126.36 (C^3), 127.24 (C^{13}), 127.44 (C^{14}), 128.81 (C^{12}), 130.52 (C^{15}), 131.73(C^{10}), 131.86 (C^6), 133.92 (C^{16}), 139.27 (C^{11}), 140.19 (C^7), 173.46 (C^2). Anal. Calcd. for $C_{17}H_{14}F_3NO_2$: C, 63.55; H, 3.39; N, 4.36. Found: C, 63.71; H, 3.23; N, 4.18. ESI-TOF: *m/z* for $C_{17}H_{14}F_3NO_2$ $[M+H]^+$ calcd.: 321, found: 208 $[M\text{-}CF_3CO_2^-]^+$.

(*E*)-4-((2,3,5,6,8,9,11,12,14,15-decahydrobenzo[b][1,4,7,10,13,16]hexaoxacyclooctadecin-18-yl)methylene)-3,4-dihydro-2H-pyrrole (2n)



Yield: 97%; m.p. 112-113°C. IR (KBr): 1580, 2453, 2533 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.85-2.91 (2H, m, C^4H), 3.69-3.73 (10H, m, $C^{5,16,17,18,19}H$), 3.75-3.77 (4H, m, $C^{15,20}H$), 3.89-3.92 (4H, m, $C^{14,21}H$), 4.18-4.21 (4H, m, $C^{13,22}H$), 7.01 (1H, d, $^3J_{HH}$ 6.8 Hz, $C^{11}H$), 7.03 (1H, s, C^6H), 7.08 (1H, d, $^3J_{HH}$ 1.3 Hz, C^8H), 7.12 (1H, d, $^3J_{HH}$ 8.4 Hz, $C^{12}H$), 8.10 (1H, s, C^2H). ^{13}C-NMR (CD_3OD) δ: 26.91 (C^4), 59.37 (C^5), 68.44 (C^{13}), 68.58 (C^{22}), 69.17 (C^{14}), 69.28 (C^{21}), 70.08 ($C^{16,17,18,19}$), 70.26 (C^{15}), 70.31 (C^{20}), 112.94 (C^8), 114.27 (C^{11}), 123.34 (C^{12}), 129.56 (C^3), 131.75 (C^6), 139.76 (C^7), 148.42 (C^9), 149.48 (C^{10}), 170.02 (C^2). Anal. Calcd. for $C_{21}H_{29}NO_6$: C, 64.43; H, 7.47; N, 3.58. Found: C, 64.15; H, 7.64; N, 3.79. ESI-TOF: *m/z* for $C_{21}H_{29}NO_6$ $[M+H]^+$ calcd.: 392, found: 392.

(*E*)-3-((2H-pyrrol-4(3H)-ylidene)methyl)pyridine (2r)

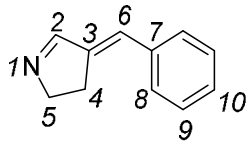


Yield: 84%; m.p. 162-163°C. IR (KBr): 1598, 2445, 2524 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.86-3.00 (2H, m, C^4H), 4.15-4.27 (2H, m, C^5H), 7.03 (1H, t, $^3J_{HH}$ 2.7 Hz, C^6H), 7.47-7.53 (1H, m, $C^{10}H$), 7.99 (1H, t, $^3J_{HH}$ 2.3 Hz, C^2H), 8.02 (1H, d, $^3J_{HH}$ 7.9 Hz, $C^{11}H$), 8.46 (1H, dd, $^3J_{HH}$ 4.9 Hz, $^4J_{HH}$ 1.3 Hz, C^9H), 8.69 (1H, d, $^3J_{HH}$ 1.7 Hz, C^8H). ^{13}C-NMR (CD_3OD) δ: 27.37 (C^4), 61.29 (C^5), 123.92 (C^{10}), 124.00 (C^3), 133.17 (C^6), 135.83 (C^7), 145.84 (C^{11}), 147.68 (C^8), 149.32 (C^9), 168.37 (C^2). Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.16; H, 6.25; N, 17.97. ESI-TOF: *m/z* for $C_{10}H_{10}N_2$ $[M+H]^+$ calcd.: 158, found: 159.

Obtaining free bases from trifluoroacetate salts of pyrrolines 2a,d

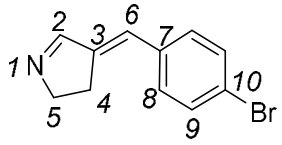
To the mixture of water (5 ml) and chloroform (5 ml) pyrroline **2** trifluoroacetate (1.27 mmol) and potassium carbonate (1.76 g, 12.7 mmol) was added. Mixture was stirred vigorously at room temperature for 12 h. Organic phase was separated, dried over $MgSO_4$ and solvent was removed in vacuum. The residue was dried in vacuum (r.t., 2 h, 0.01 torr) to give free base **2**.

(*E*)-4-benzylidene-3,4-dihydro-2H-pyrrole (2a)[1]



Yield: 52%; m.p. 64-65°C. IR (KBr): 1570 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.82-2.89 (2H, m, C^4H), 4.11-4.17 (2H, m, C^5H), 6.96 (1H, t, $^{3}J_{HH}$ 2.8 Hz, C^6H), 7.31 (1H, t, $^{3}J_{HH}$ 7.4 Hz, C^6H), 7.40 (2H, t, $^{3}J_{HH}$ 7.7 Hz, $C^{10}H$), 7.50 (2H, d, $^{3}J_{HH}$ 7.6 Hz, C^8H), 7.90 (1H, t, $^{4}J_{HH}$ 2.2 Hz, C^2H). ^{13}C-NMR (CD_3OD) δ: 27.36 (C^4), 61.09 (C^5), 127.99 (C^{10}), 128.51 (C^9), 128.51 (C^6), 128.73 (C^8), 136.53 (C^3), 143.01 (C^7), 169.01 (C^2). Anal. Calcd. for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.20; H, 6.95; N, 9.11. ESI-TOF: *m/z* for $C_{11}H_{11}N$ $[M+H]^+$ calcd.: 158, found: 158.

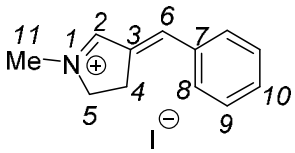
(*E*)-4-(4-bromobenzylidene)-3,4-dihydro-2H-pyrrole (2d)



Yield: 68%; m.p. 77-78°C. IR (KBr): 1598 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.83-2.89 (2H, m, C^4H), 4.13-4.20 (2H, m, C^5H), 6.95 (1H, t, $^{3}J_{HH}$ 2.8 Hz, C^6H), 7.44 (2H, d, $^{3}J_{HH}$ 8.5 Hz, C^8H), 7.57 (2H, d, $^{3}J_{HH}$ 8.6 Hz, C^9H), 7.93 (1H, t, $^{4}J_{HH}$ 2.8 Hz, C^2H). ^{13}C-NMR (CD_3OD) δ: 27.31 (C^4), 61.16 (C^5), 121.69 (C^{10}), 127.10 (C^6), 130.29 (C^8), 131.50 (C^9), 135.64 (C^3), 143.85 (C^7), 168.79 (C^2).

Anal. Calcd. for $C_{11}H_{10}BrN$: C, 55.96; H, 4.27; Br, 33.84; N, 5.93. Found: C, 56.11; H, 4.39; Br, 34.04; N, 5.76. ESI-TOF: *m/z* for $C_{11}H_{10}BrN$ $[M+H]^+$ calcd.: 236, found: 236.

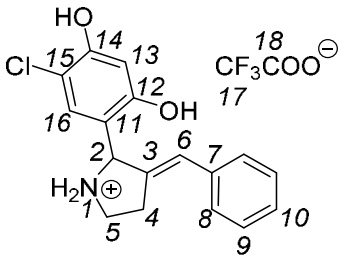
(*E*)-4-benzylidene-1-methyl-3,4-dihydro-2H-pyrrol-1-ium iodide (4)



The solution of N-(4,4-diethoxybutyl)-1-phenylmethanimine **1a** (0.5 g, 2 mmol) and methyl iodide (0.29 g, 2 mmol) in dry acetonitrile (5 ml) was stirred at room temperature for 12 hours. The solvent was removed in vacuum and the residue washed with diethyl ether (2x5 ml) and dried in vacuum (r.t., 2 h, 0.01 torr) to give target compound **4**. Yield: 99%; m.p. 115-116°C. IR (KBr): 1597, 1643 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.33-3.40 (2H, m, C^4H), 3.88 (3H, s, $C^{11}H$), 4.45-4.51 (2H, m, C^5H), 7.38-7.46 (3H, m, $C^{9,10}H$), 7.49-7.54 (2H, m, C^8H), 7.86 (1H, s, C^6H), 9.77 (1H, s, C^2H). ^{13}C-NMR ($CDCl_3$) δ: 27.55 (C^4), 41,43 (C^{11}), 60.61 (C^5), 129.31 (C^8), 131.06 (C^9),131.82 (C^{10}), 133.78 (C^3), 135.54 (C^7), 145.64 (C^6),

173.25 (C^2).). Anal. Calcd. for $C_{12}H_{14}IN$: C, 48.18; H, 4.72; I, 42.42; N, 4.68. Found: C, 48.00; H, 4.51; I, 42.26; N, 4.89. ESI-TOF: m/z for $C_{12}H_{14}IN$ $[M+H]^+$ calcd.: 299, found: 172 $[M-I^-]^+$.

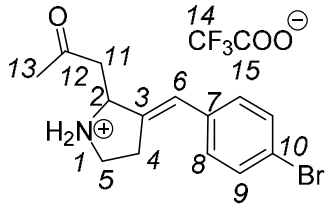
(*E*)-3-benzylidene-2-(5-chloro-2,4-dihydroxyphenyl)pyrrolidin-1-ium trifluoroacetate (5)



The solution of pyrroline **2a** trifluoroacetate (0.3 g, 1.11 mmol) and 4-chlororesorcinol (0.16 g, 1.11 mmol) in dry chloroform (5 ml) was refluxed for 12 h. Precipitate was filtered off, wased with diethyl ether (5 ml) and dried in vacuum (r.t., 2 h, 0.01 torr) to give compound **5**. Yield: 65%; m.p. 193-194°C. IR (KBr): 1597, 2437, 2509, 2546 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.09-3.23 (2H, m, C^4H), 3.44-3.51 (1H, m, C^5H), 3.61-3.67 (1H, m, C^5H'), 5.45 (1H, s, C^2H), 6.28 (1H, s, C^6H), 6.62 (1H, s, $C^{13}H$), 7.26 (1H, s, $C^{16}H$), 7.27 (1H, t, $^3J_{HH}$ 7.1 Hz, $C^{10}H$), 7.33-7.40 (4H, m, $C^{8,9}H$). ^{13}C-NMR (CD_3OD) δ: 28.59 (C^4), 44.40 (C^5), 62.88 (C^2), 103.68 (C^{13}), 111.21 (C^{15}), 113.24 (C^{11}), 116.68 (q, J_{CF} 292.2 Hz, C^{17}), 125.65 (C^6),127.22 (C^{10}), 128.11 (C^8), 128.23 (C^9), 130.57 (C^{16}), 136.29 (C^3), 136.34 (C^7), 155.27 (C^{14}), 155.64 (C^{12}), 161.70 (q, J_{CF} 34.2 Hz, C^{18}). Anal. Calcd. for $C_{19}H_{17}ClF_3NO_4$: C, 54.88; H, 4.12; Cl, 8.53; N, 3.37. Found: C, 55.01; H, 3.91; Cl, 8.70; N, 3.55.

ESI-TOF: *m/z* for $C_{19}H_{18}ClF_3NO_4$ $[M+H]^+$ calcd.: 417, found: 302 $[M-CF_3CO_2^-]^+$

(*E*)-3-(4-bromobenzylidene)-2-(2-oxopropyl)pyrrolidin-1-ium trifluoroacetate (6)



The solution of pyrroline **2d** trifluoroacetate (0.39 g, 1.11 mmol) in acetone (5 ml) was stirred at room temperature for 12 h. The precipitate was filtered off, washed with diethyl ether (5 ml) and dried in vacuum (r.t., 2h, 0.01 torr) to give compound **6**. Yield: 73%; m.p. 165-166°C. IR (KBr): 1598, 1658 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.29 (3H, s, $C^{13}H$), 2.98-3.05 (2H, m, C^4H), 3.10-3.19 (1H, m, $C^{11}H$), 3.38 (1H, m, $C^{11}H`$), 3.42-3.46 (1H, m, $C^5H$), 3.54-3.62 (1H, m, $C^5H`$), 4.56-4.62 (1H, m, C^2H), 6.55-6.57 (1H, m, C^6H), 7.30 (2H, d, $^3J_{HH}$ 8.5 Hz, C^8H), 7.55 (2H, d, $^3J_{HH}$ 8.5 Hz, C^9H). ^{13}C-NMR (CD_3OD) δ: 27.75 (C^4), 28.34 (C^{13}), 44.37 (C^5), 44.59 (C^{11}), 58.44 (C^2), 121.04 (C^{10}), 123.26 (C^6), 129.91 (C^8), 131.35 (C^9),

135.32 (C^7), 137.42 (C^3), 206.20 (C^{12}). Anal. Calcd. for $C_{16}H_{17}BrF_3NO_3$: C, 47.08; H, 4.20; Br, 19.57; N, 3.43. Found: C, 46.89; H, 4.41; Br, 19.65; N, 3.49. ESI-TOF: *m/z* for $C_{16}H_{18}BrF_3NO_3$ $[M+H]^+$ calcd.: 409, found: 295 $[M\text{-}CF_3CO_2^-]^+$.

X-ray experiments.

Crystals of compounds **2a,b,i** were obtained by recrystallization from methanol. Crystals of compound **6** were obtained by recrystallization from methanol/hydrochloric acid mixture. The X-ray diffraction data for the crystals of **2a**, **2b**, **2i**, and chloride **6** were collected on a Smart Apex II (**2b**, **2i**, **6**) and KAPPA Apex (**2a**) automatic diffractometer using graphite monochromated radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXL97[2] program. All the non-hydrogen atoms and H(N) were refined with anisotropic atomic displacement parameters. All figures were made using the program OLEX2.[3] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center (1544114-1544117).

	2a	**2b**	**2i**	**6**
Chemical formula	$C_{13}H_{12}F_3NO_2$	$C_{14}H_{14}F_3NO_3$	$C_{13}H_{11}F_4NO_2$	$C_{14}H_{17}BrClNO$
Formula Mass	271.24	301.26	289.23	330.65
Temperature/K	296(2)	296(2)	296(2)	296(2)
Crystal class	monoclinic	triclinic	orthorhombic	monoclinic
Space group	P 21/c	P -1	P na21	P 21/n
No. of formula units per unit cell, *Z*	4	2	4	4
Crystal system	a=13.578(3) b=10.2118(19) c=9.1356(17) β=97.423(4)	a=7.961(5) b=10.047(7) c=10.047(7) α=115.086(7) β=106.138(8) γ=90.896(8)	a=23.90(4) b=5.288(9) c=10.524(19)	a= 5.038(2) b= 24.005(11) c= 12.287(6) β= 99.804(6)
Unit cell volume/Å	1256.1(4)	690.8(8)	1330(4)	1464.2(11)
F(000)	560	312	592	672
ρ_{calc}/g cm^{-1}	1.434	1.448	1.444	1.500
Absorption coefficient, μ/mm	0.126	0.128	0.134	2.978

θ/deg	2.50<θ<26.00	2.27<θ<29.06	3.41<θ<19.77	2.39<θ<22.71
No. of reflections measured	13498	6307	9514	15113
No. of independent reflections	2458	2698	2621	2879
Number of parameters	*205*	*194*	*181*	*172*
Reflections [I>2σ]	*1189*	*1901*	*1519*	*2206*
R_{int}	*0.0710*	*0.0224*	*0.0544*	*0.0394*
Flack parameter				
R_1/ $wR(F^2)$, [$I>2\sigma$]	0.0430/0.0890	0.0560/0.1688	0.0647/0.1684	0.0381/0.0628
R_1/ $wR(F^2)$, (all data)	0.1230/0.1166	0.0777/0.1884	0.1116/0.2017	0.0578/0.0647
Goodness of fit on F^2	1.060	1.264	0.967	1.893
ρ_{max}/ρ_{min} /eÅ^{-3}	0.120/-0.136	0.312/-0.335	0.360/-0.246	0.519/-0.387
CCDC number	1544114	1544115	1544116	1544117

H-bonds in crystals of compounds **2a,b,i** and **6**.

H-bond	**Symmetry operation**	**D- H**	**H...A**	**D...A**	**D- H...A**
		2a			
N(1)-H(1)...F(1)	1-x,1/2+y,3/2-z	1.07(3)	2.47(3)	3.058(8)	113.7(16)
N(1)-H(1)...O(2)	1-x,1/2+y,3/2-z	1.07(3)	1.64(3)	2.698(3)	169(2)
C(2)-H(2)...O(2)	x,3/2-y,1/2+z	0.93	2.39	3.247(3)	154
C(10)-H(10)...F(1A)	-x,1/2+y,1/2-z	0.93	2.43	3.32(3)	160
C(4)-H(42)...O(1)	x,y,1+z	0.97	2.53	3.356(3)	143
		2b			
N(1)-H(1)...O(17)	x,1+y,z	0.88(3)	1.81(3)	2.694(4)	178(4)
C(5)-H(51)...O(18)	1-x,2-y,2-z	0.97	2.57	3.349(4)	137
		2i			
N(1)-H(1)...O(2)	-1/2+x,-1/2-y,	0.86	1.83	2.688(9)	177
C(2)-H(2)...O(1)	1-x,-y,-1/2+z	0.93	2.19	3.106(10)	168
		6			

N(1)-H(1A)...Cl(18)	-1/2+x,3/2-y,1/2+z	0.86(2)	2.19(2)	3.051(3)	177(3)
N(1)-H(1B)...O(17)		0.87(2)	2.39(2)	2.878(3)	115.8(18)
N(1)-H(1B)...Cl(18)	1/2+x,3/2-y,1/2+z	0.87(2)	2.46(2)	3.171(3)	138.7(18)

References

(1) Mandal, S.; Mahato, S.; Jana, C. K. *Org. Lett.* **2015**, *17*, 3762–3765.

(2) Sheldrick, G. M. SHELXTL v.6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

Copies of NMR spectra

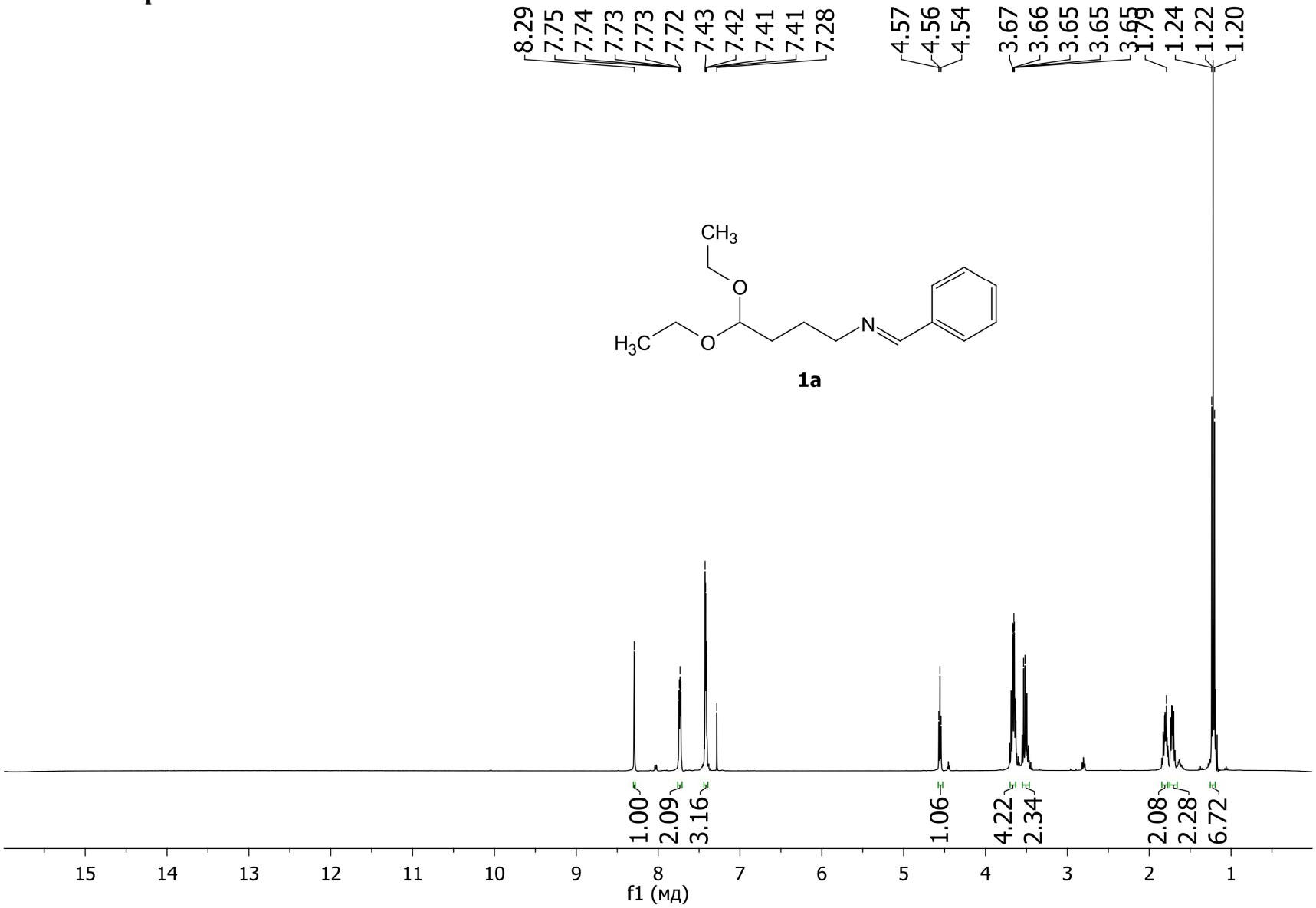


Figure S1: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1a**

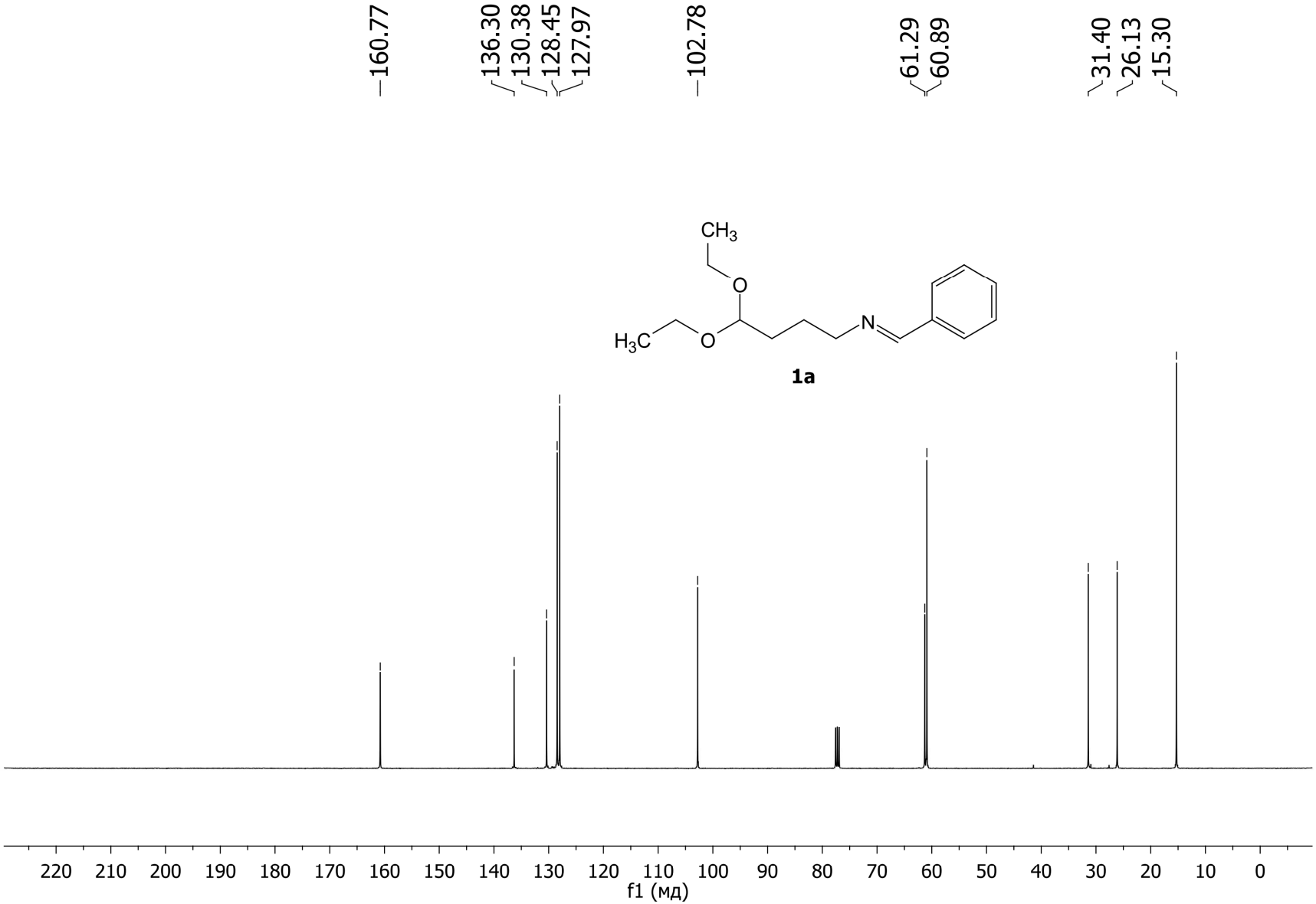


Figure S2: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1a**

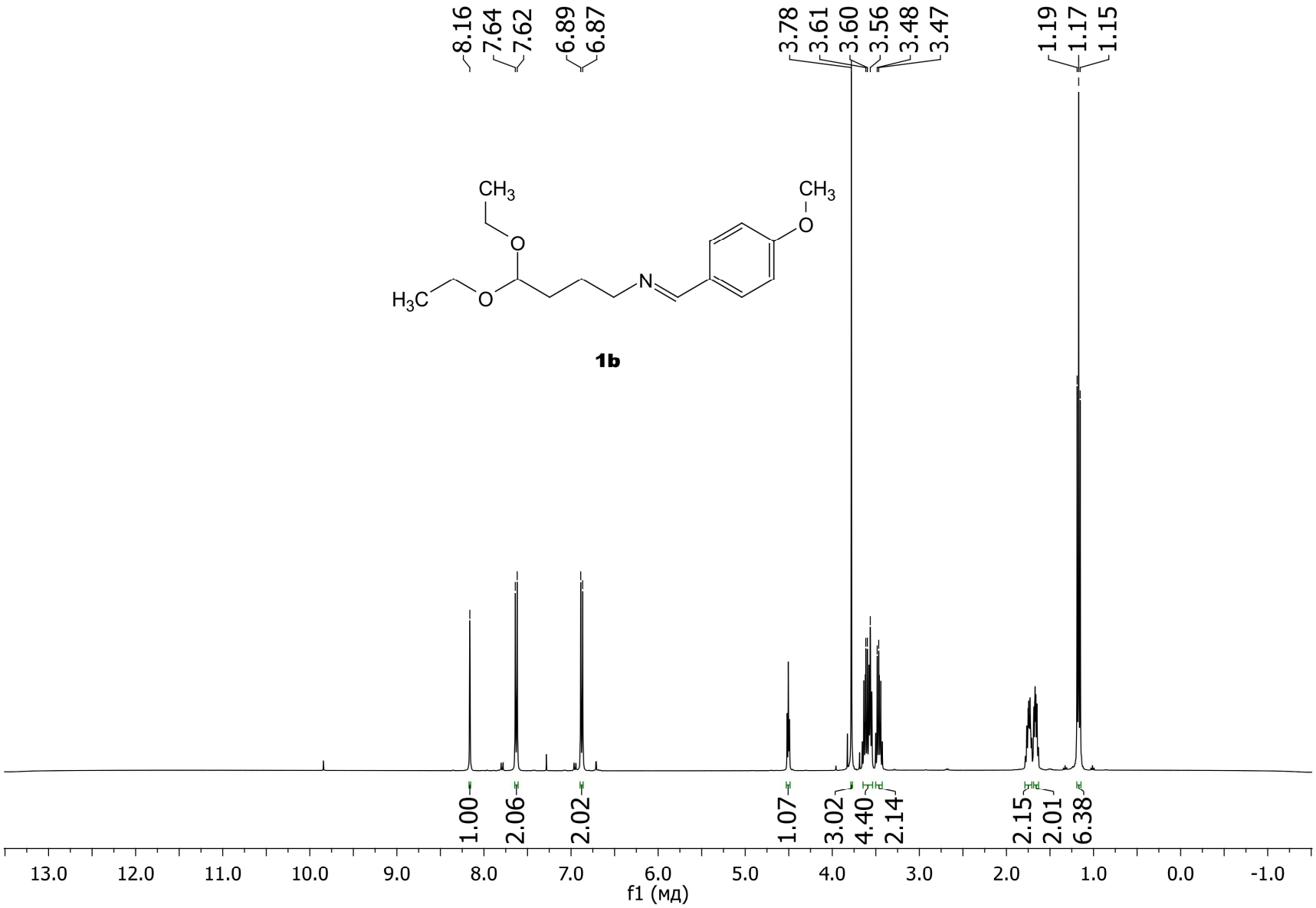


Figure S3: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1b**

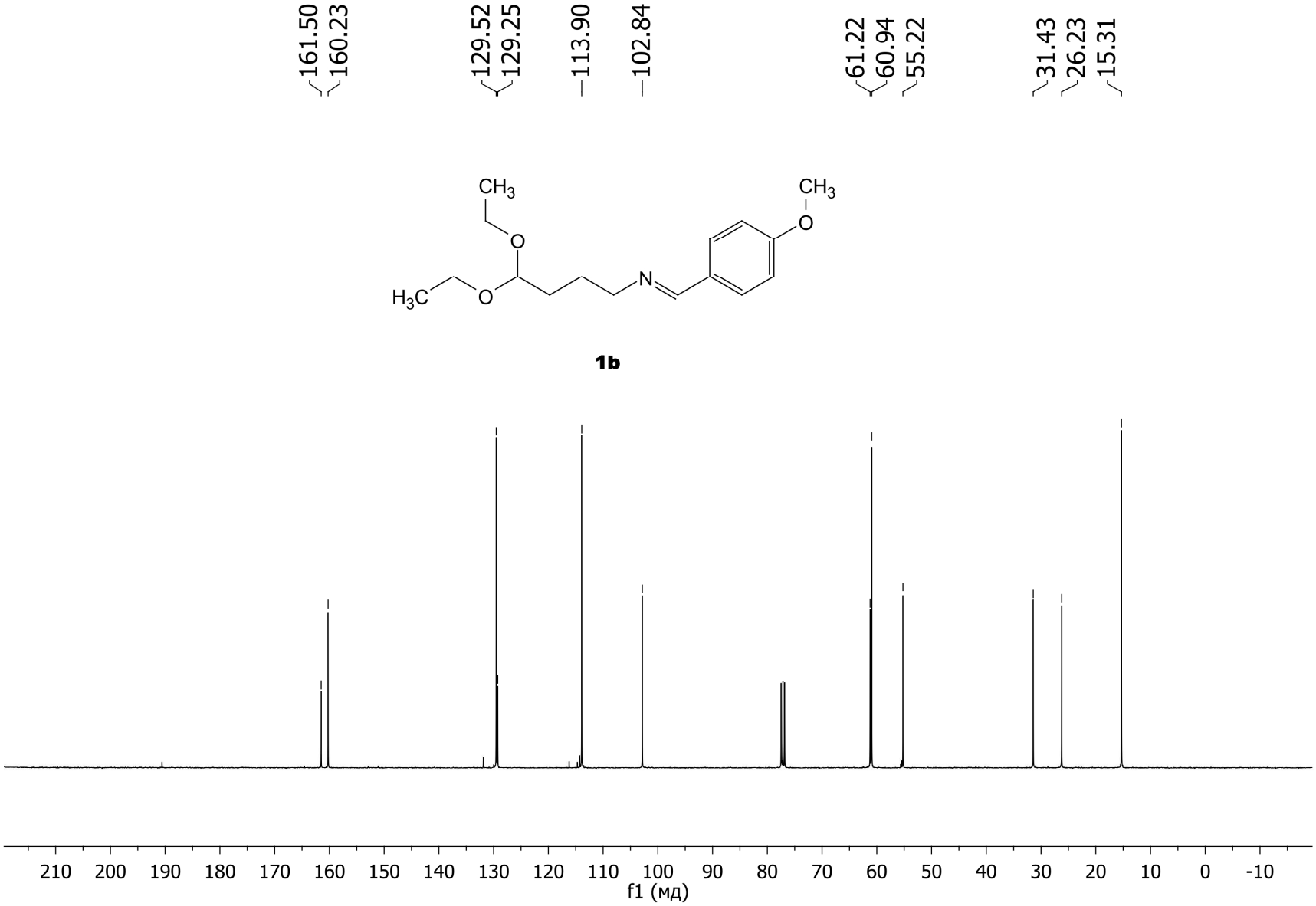


Figure S4: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1b**

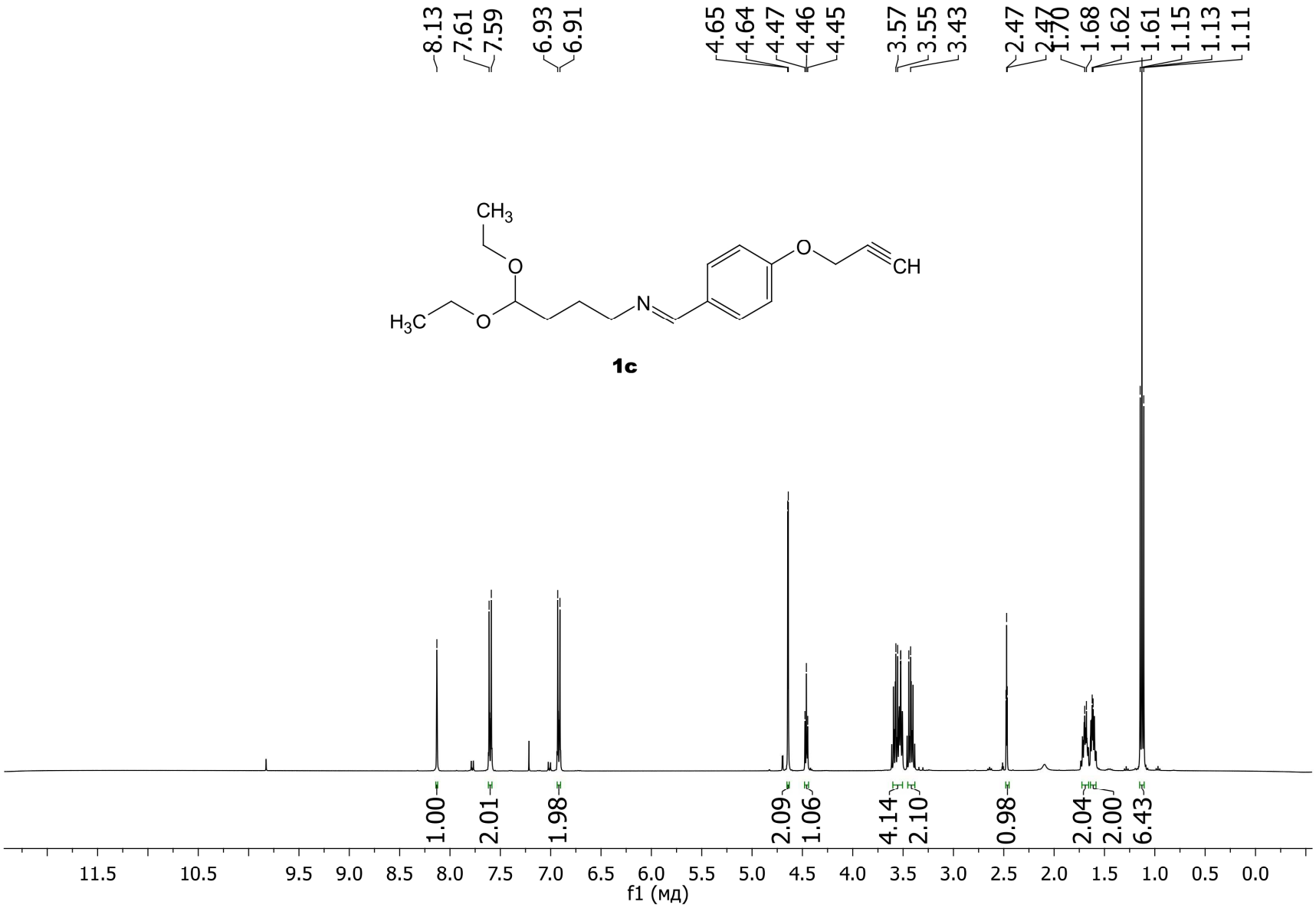


Figure S5: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1c**

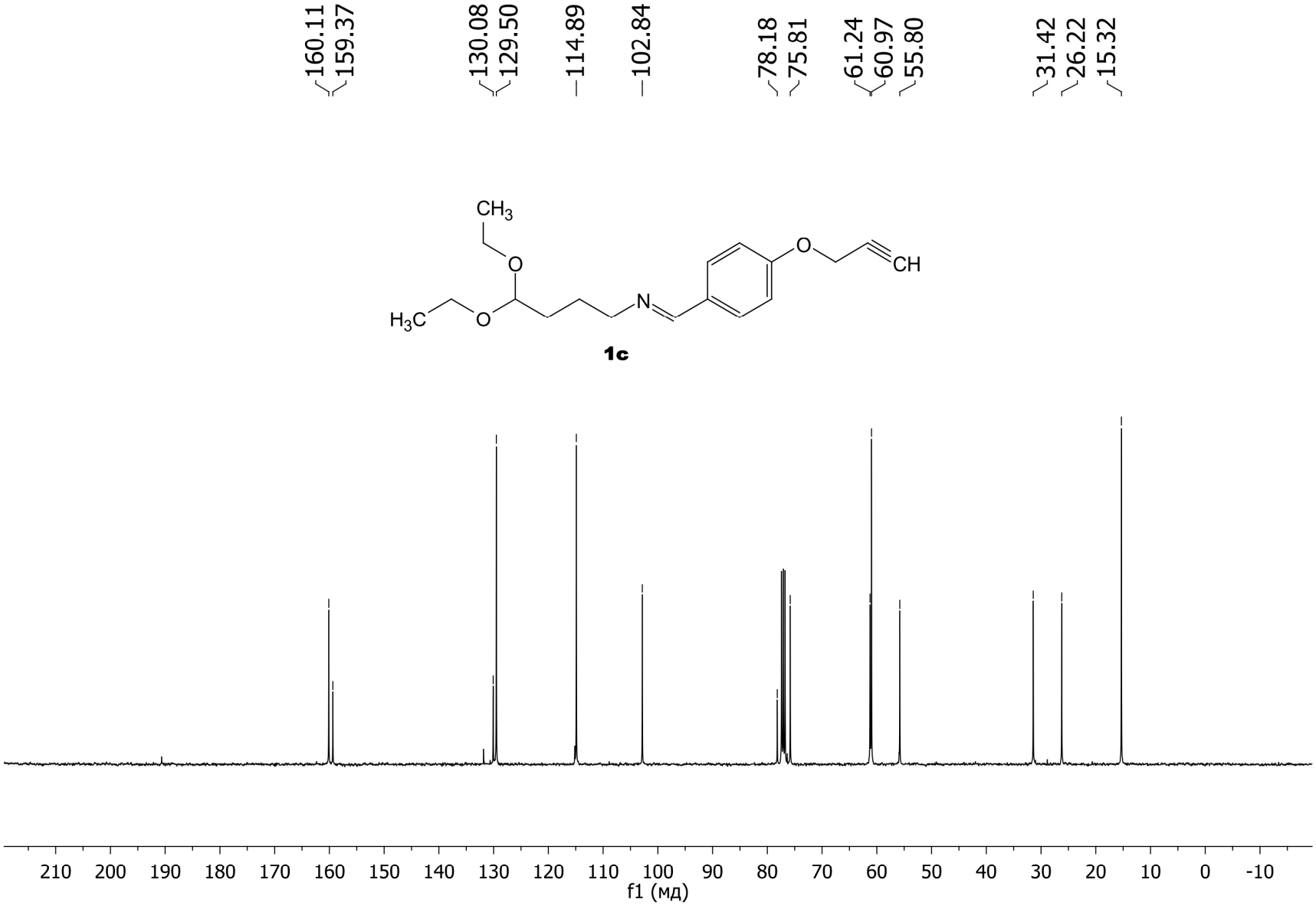


Figure S6: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1c**

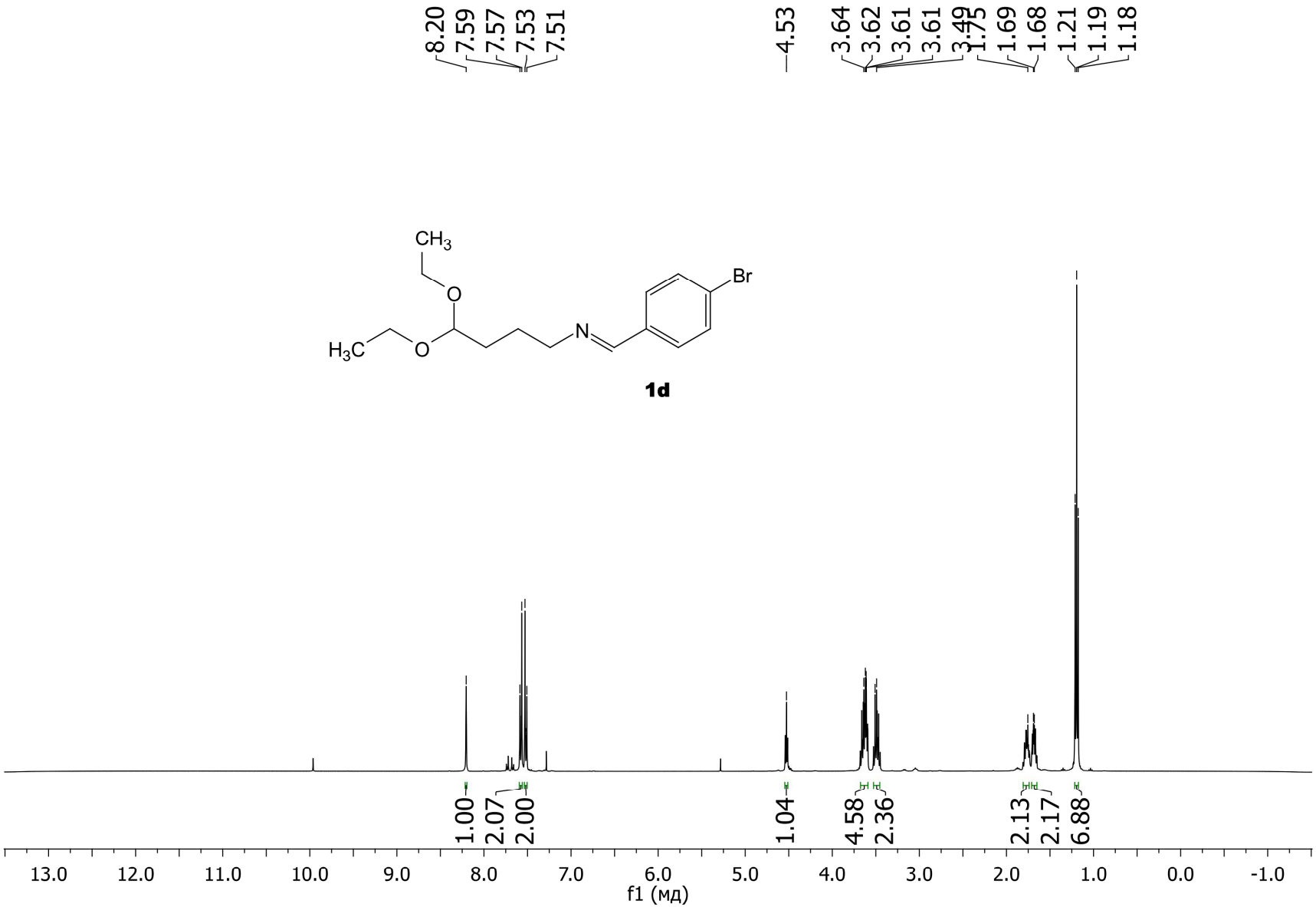


Figure S7: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1d**

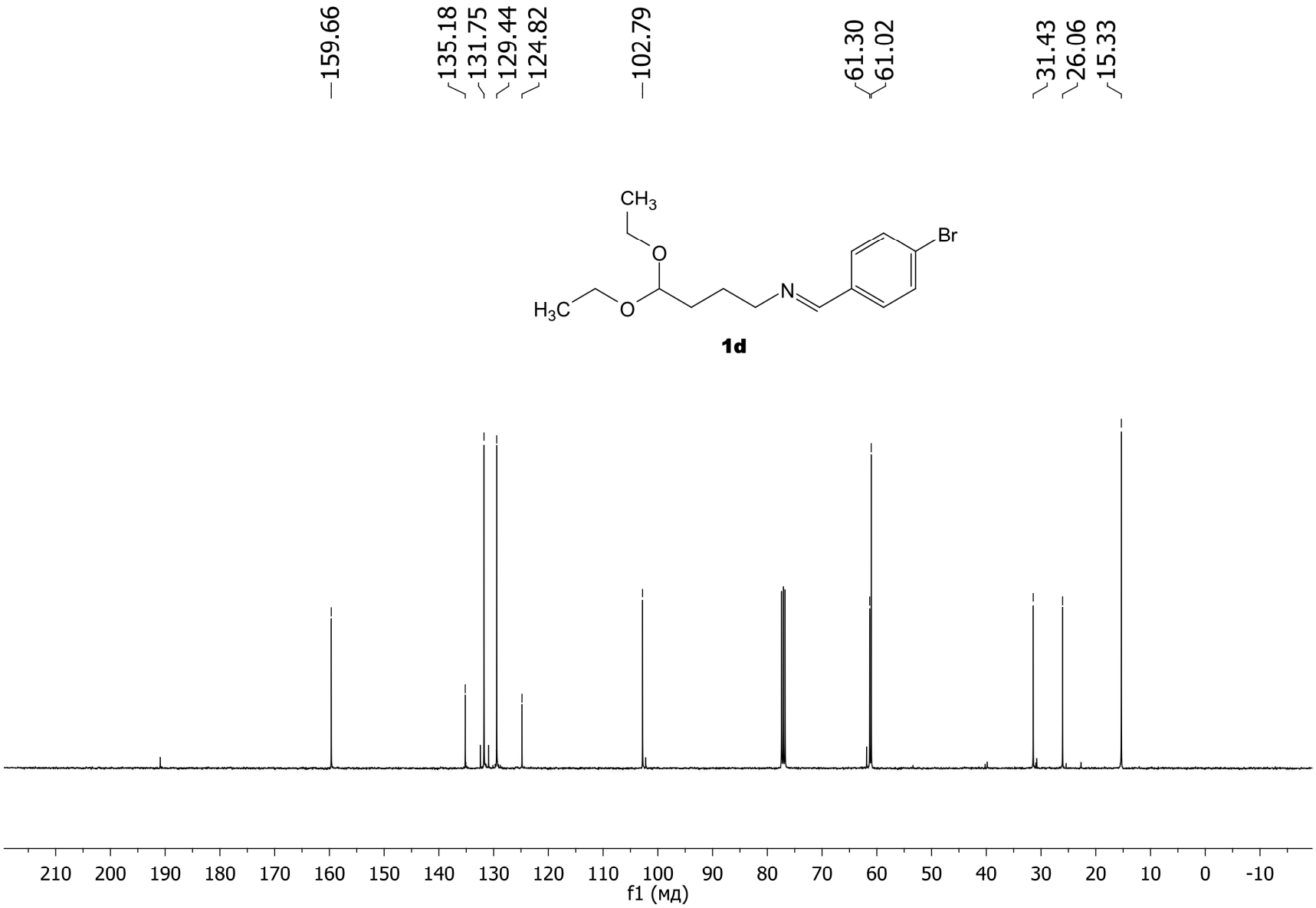


Figure S8: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1d**

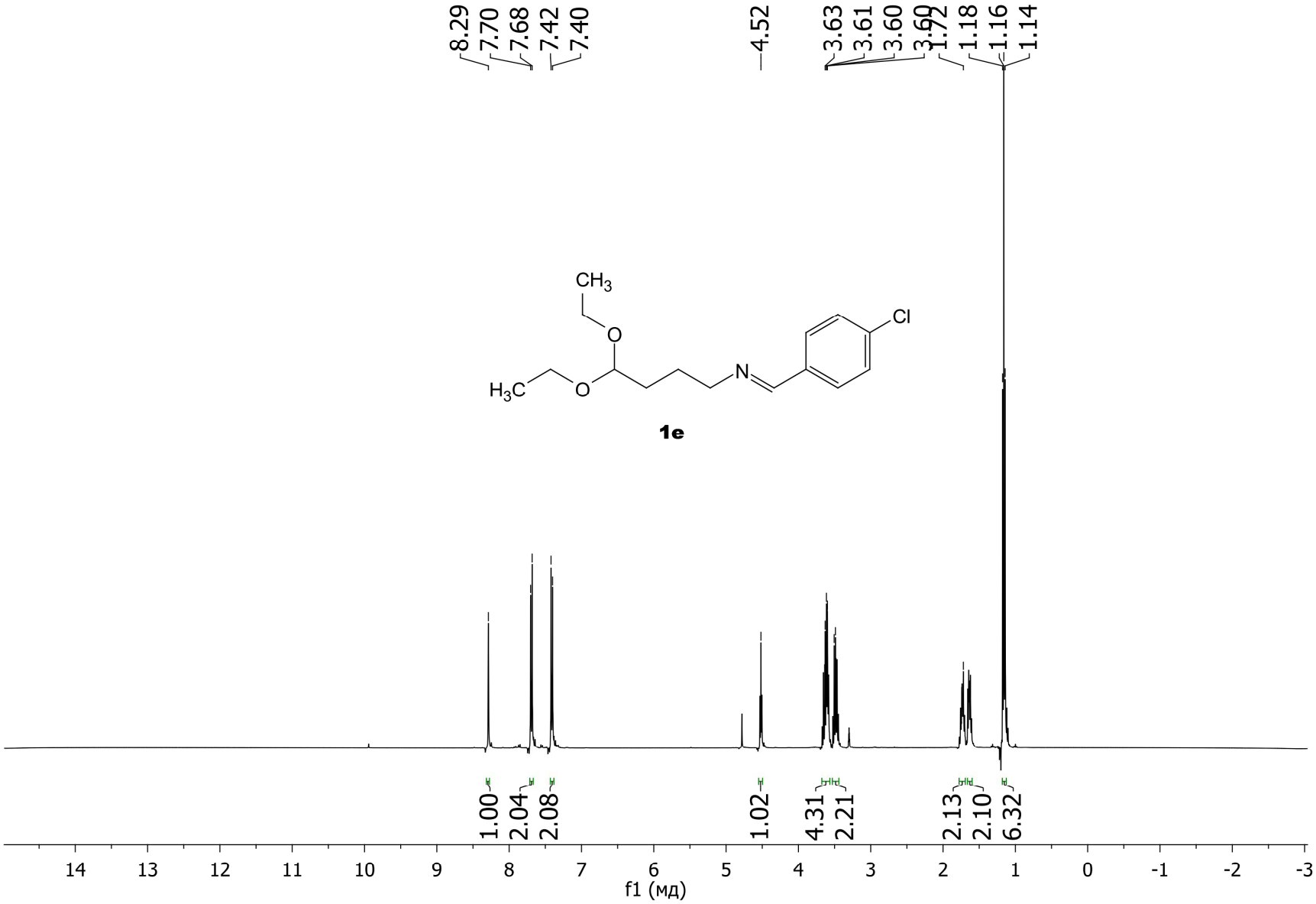


Figure S9: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1e**

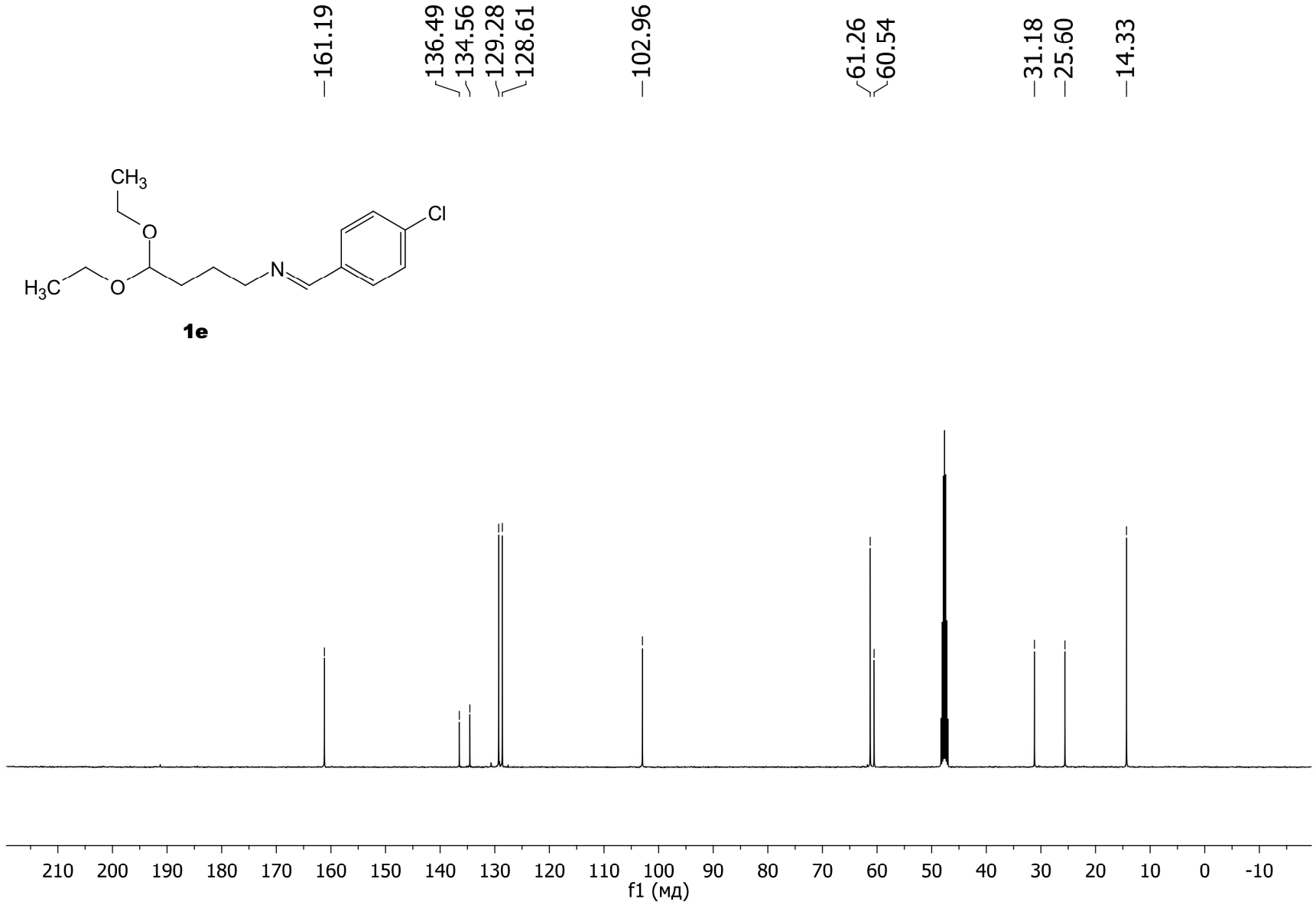


Figure S10: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1e**

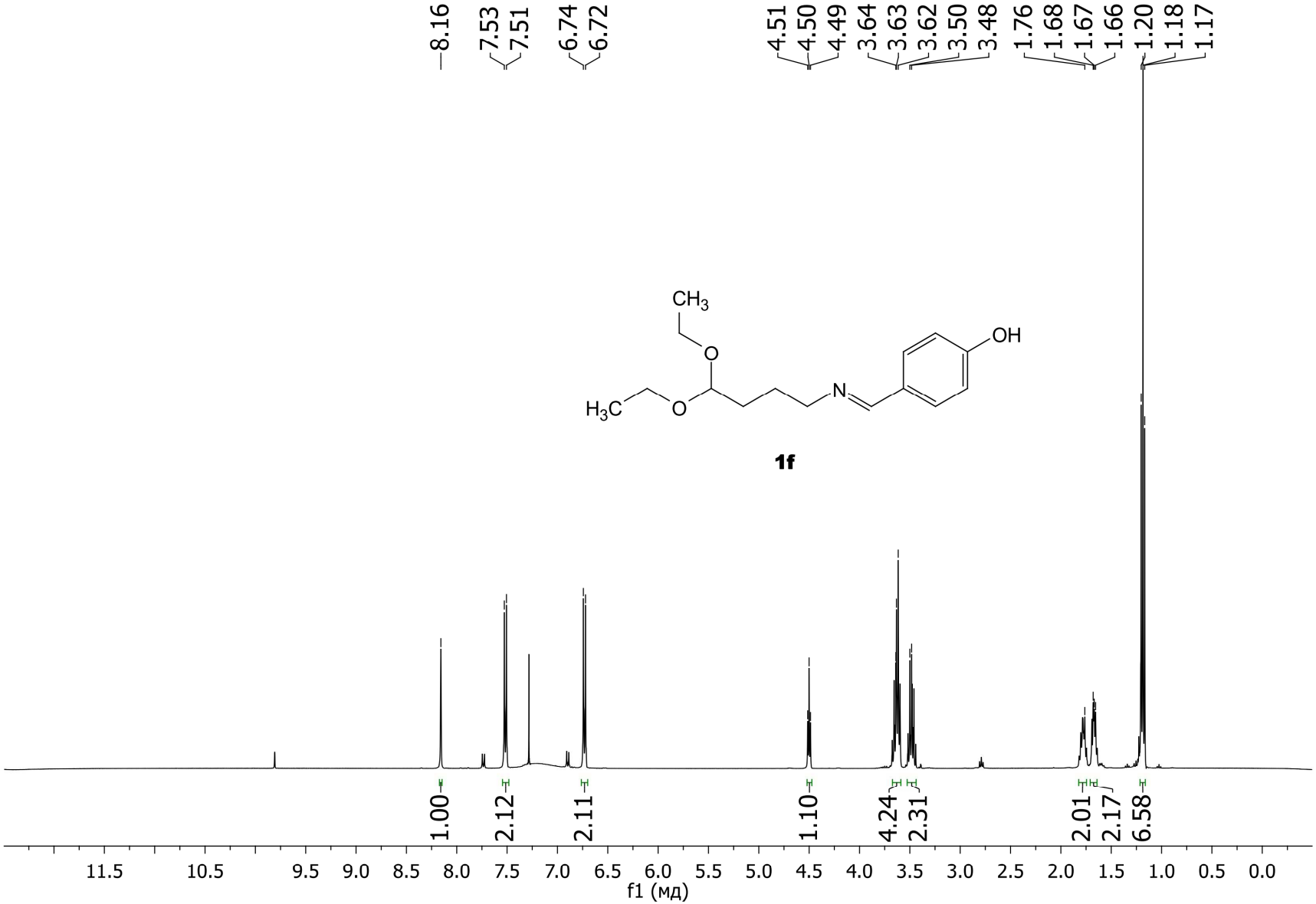


Figure S11: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1f**

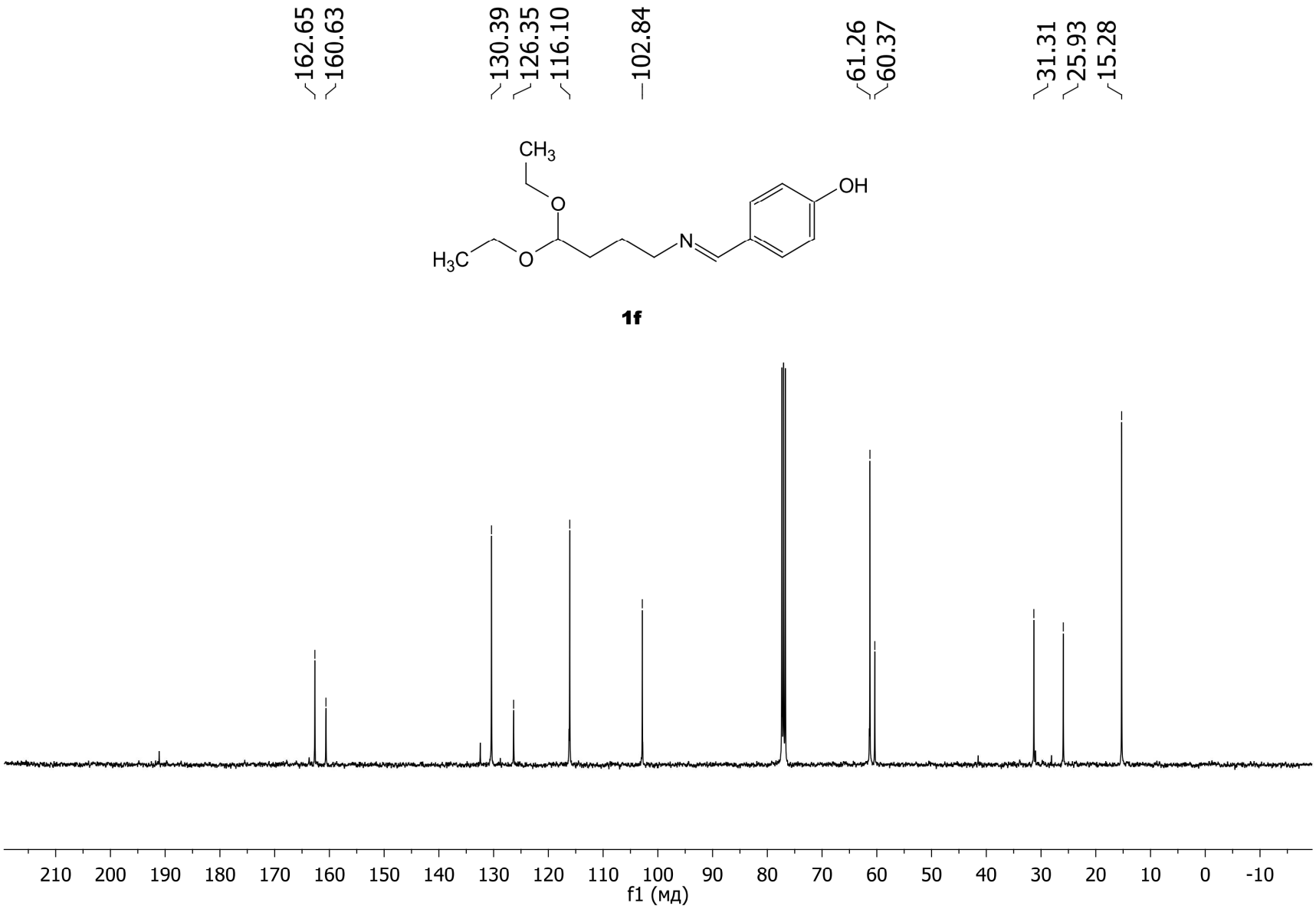


Figure S12: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1f**

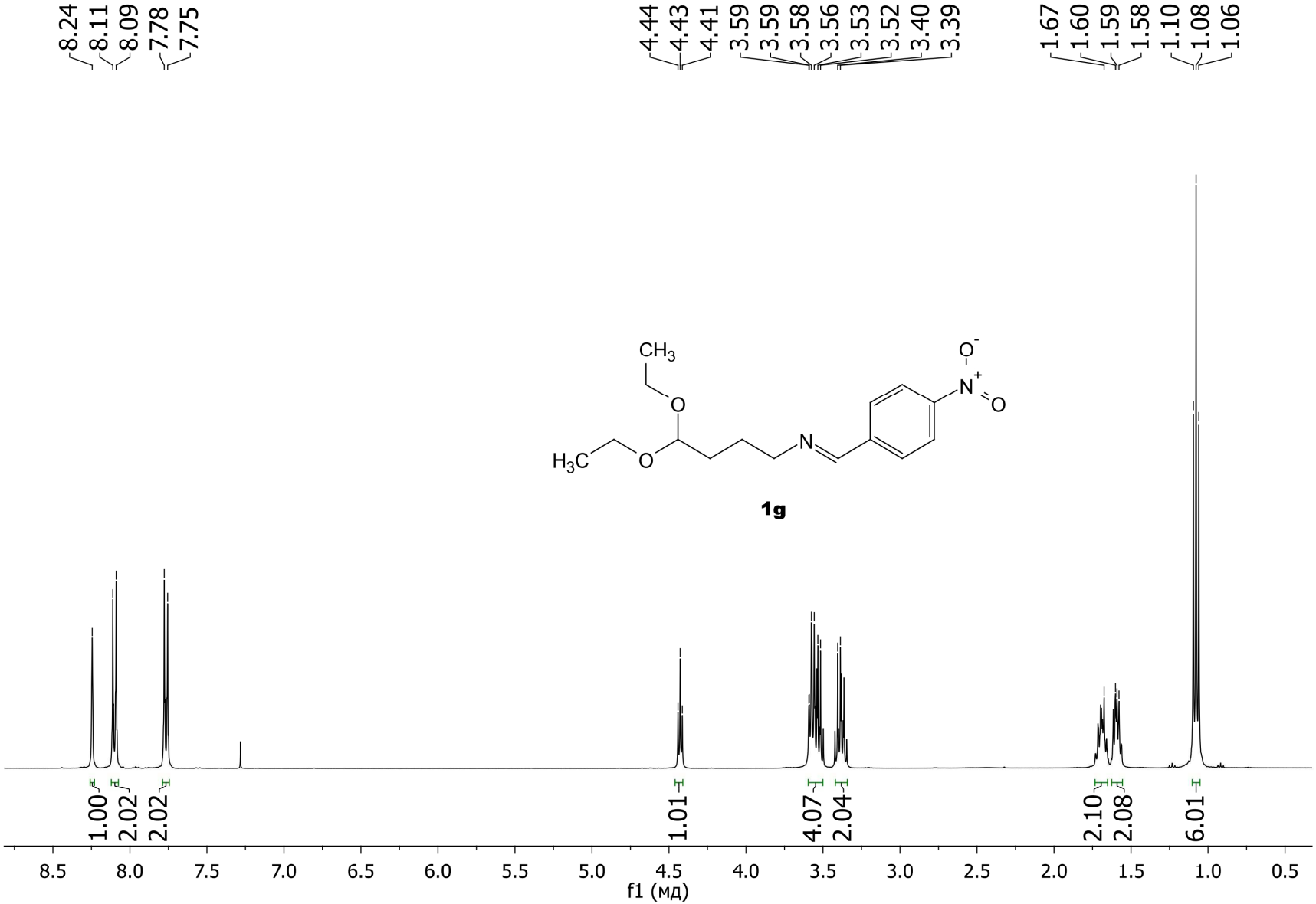


Figure S13: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1g**

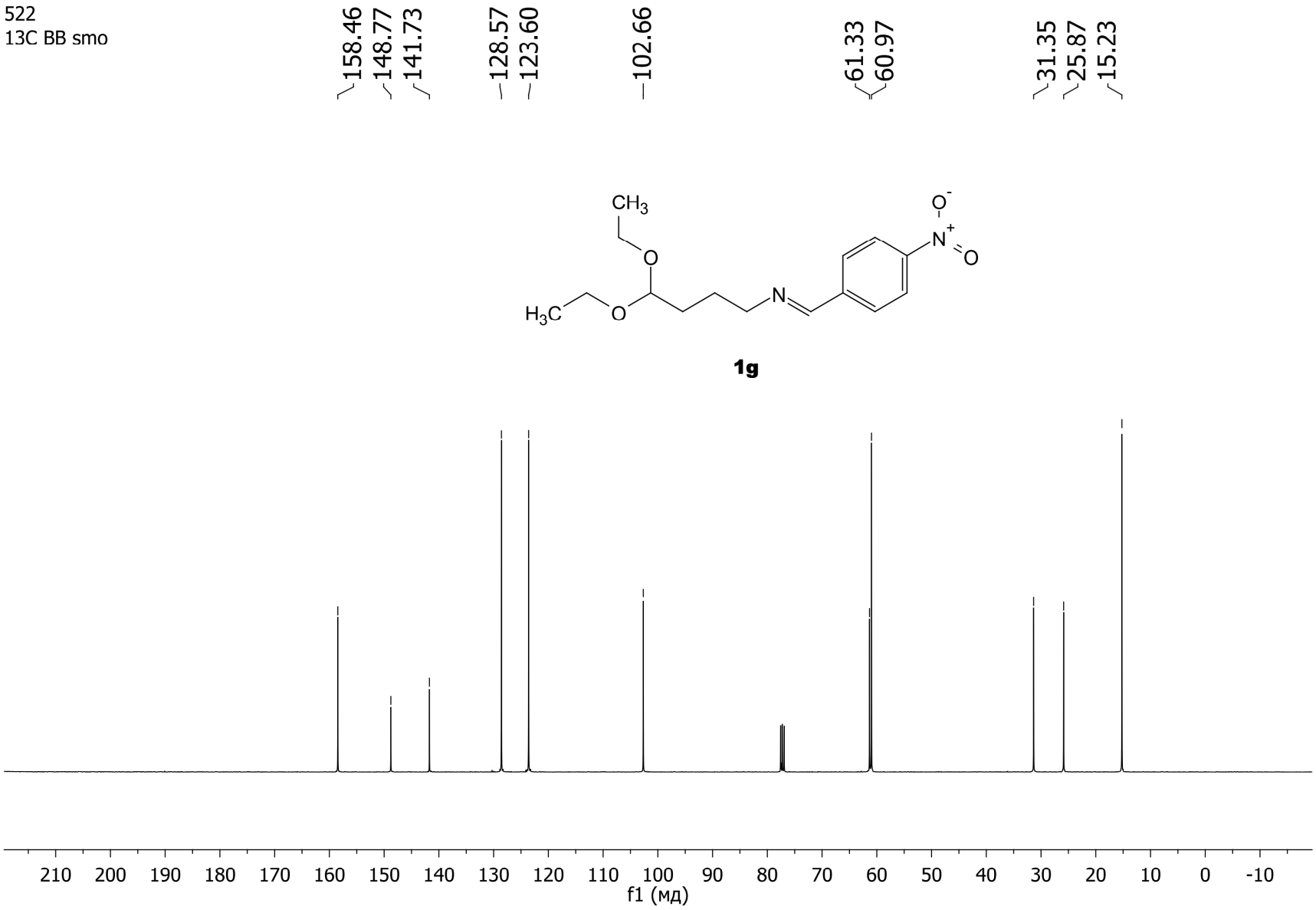


Figure S14: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1g**

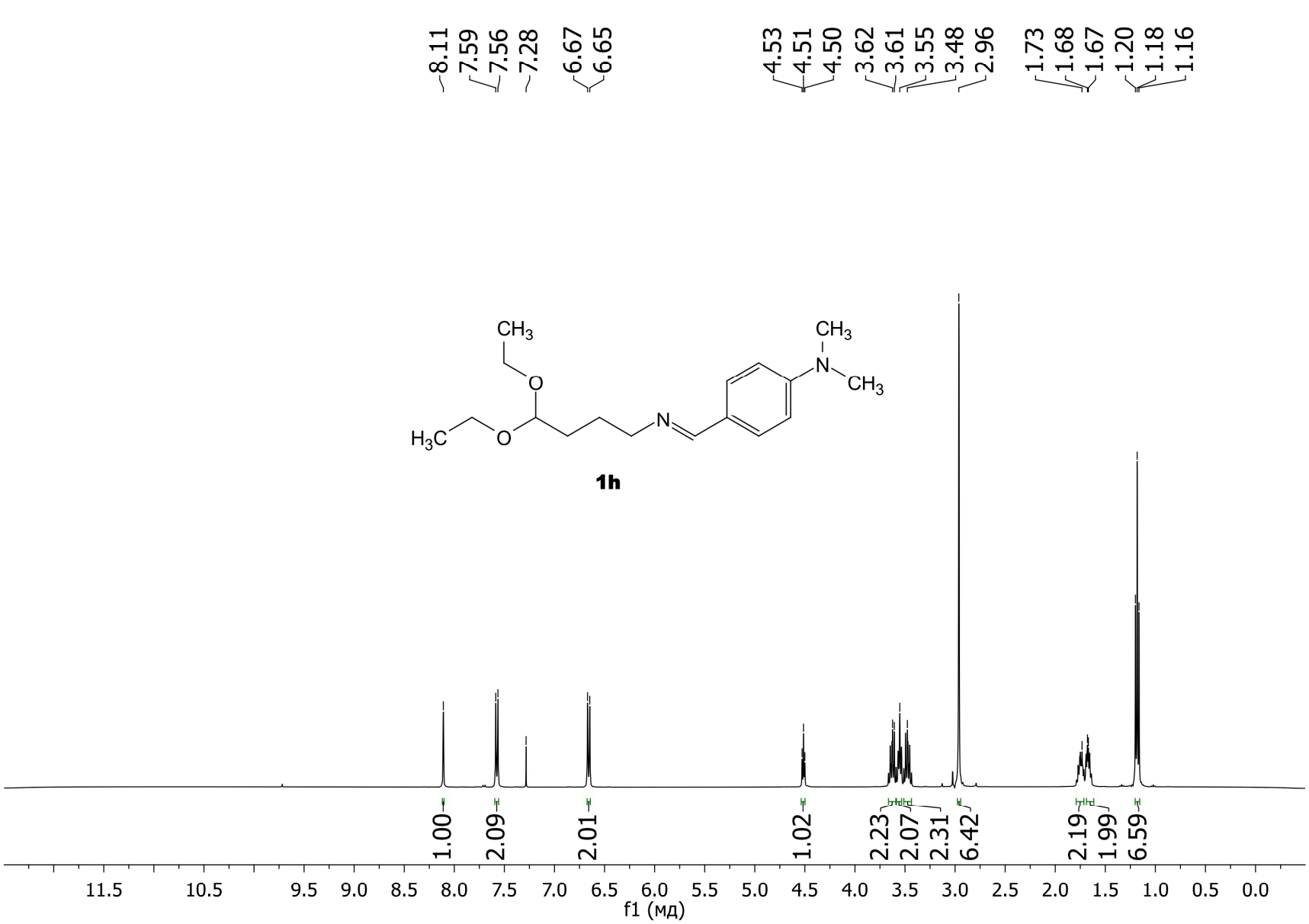


Figure S15: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1h**

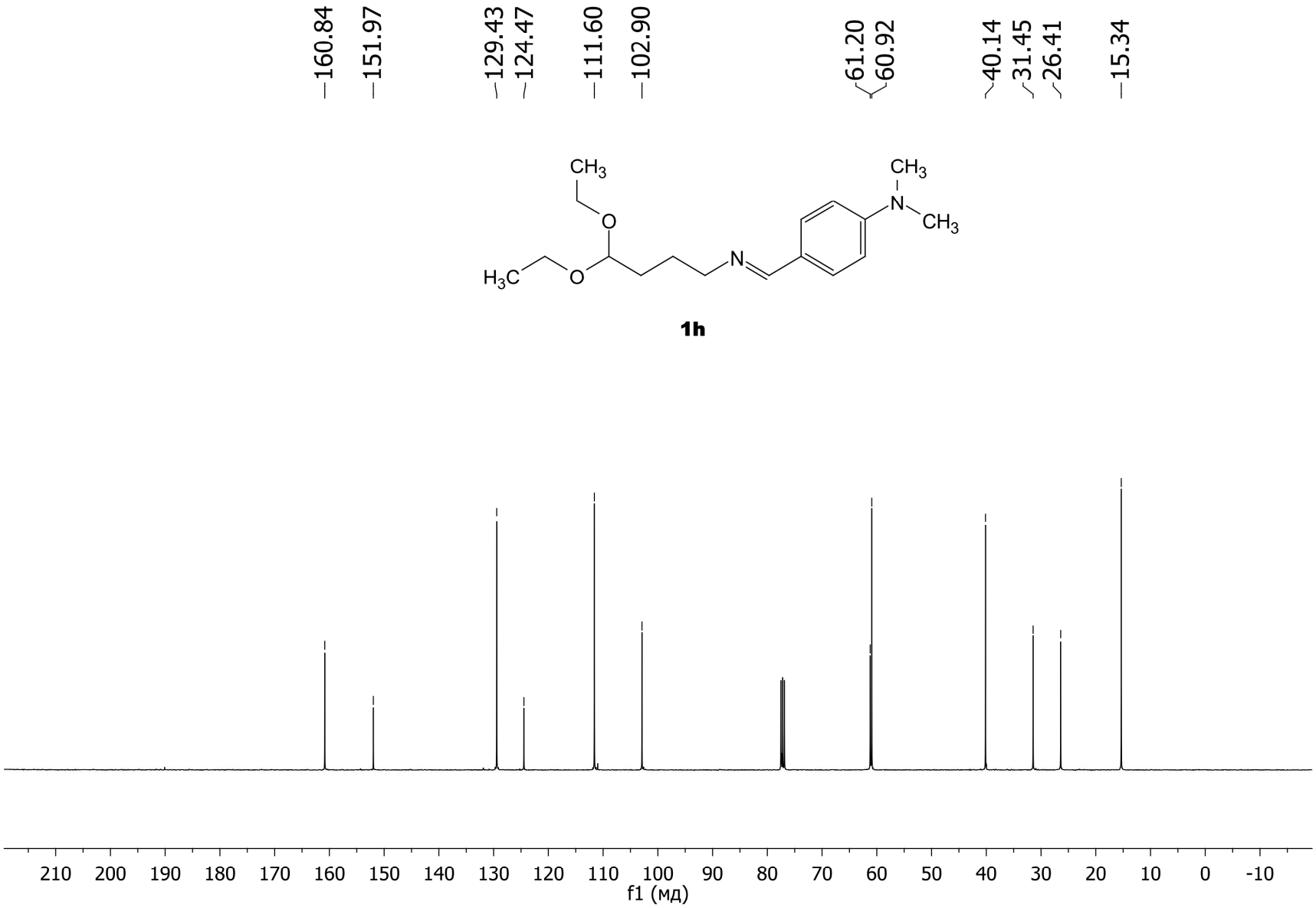


Figure S16: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1h**

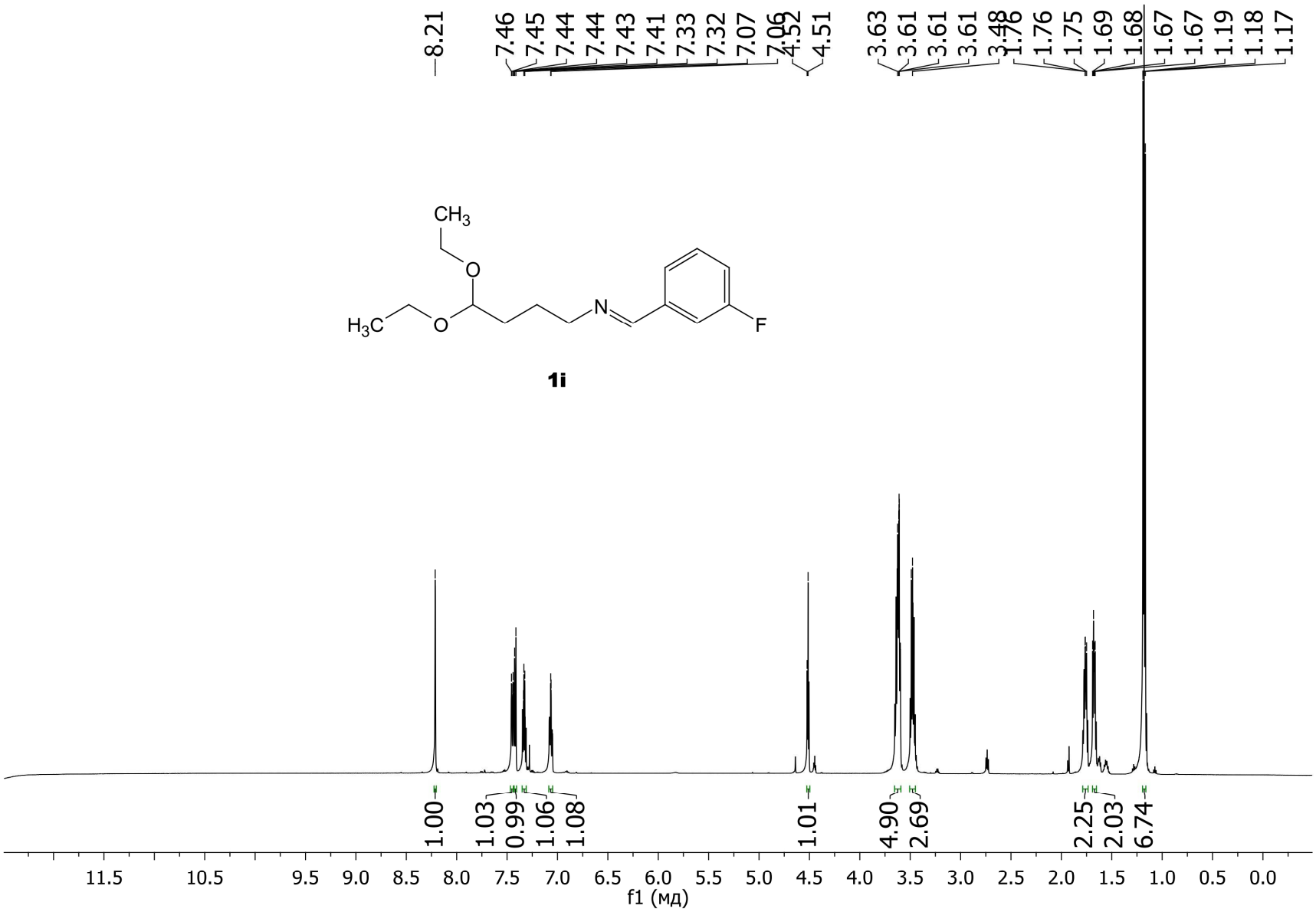


Figure S17: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1i**

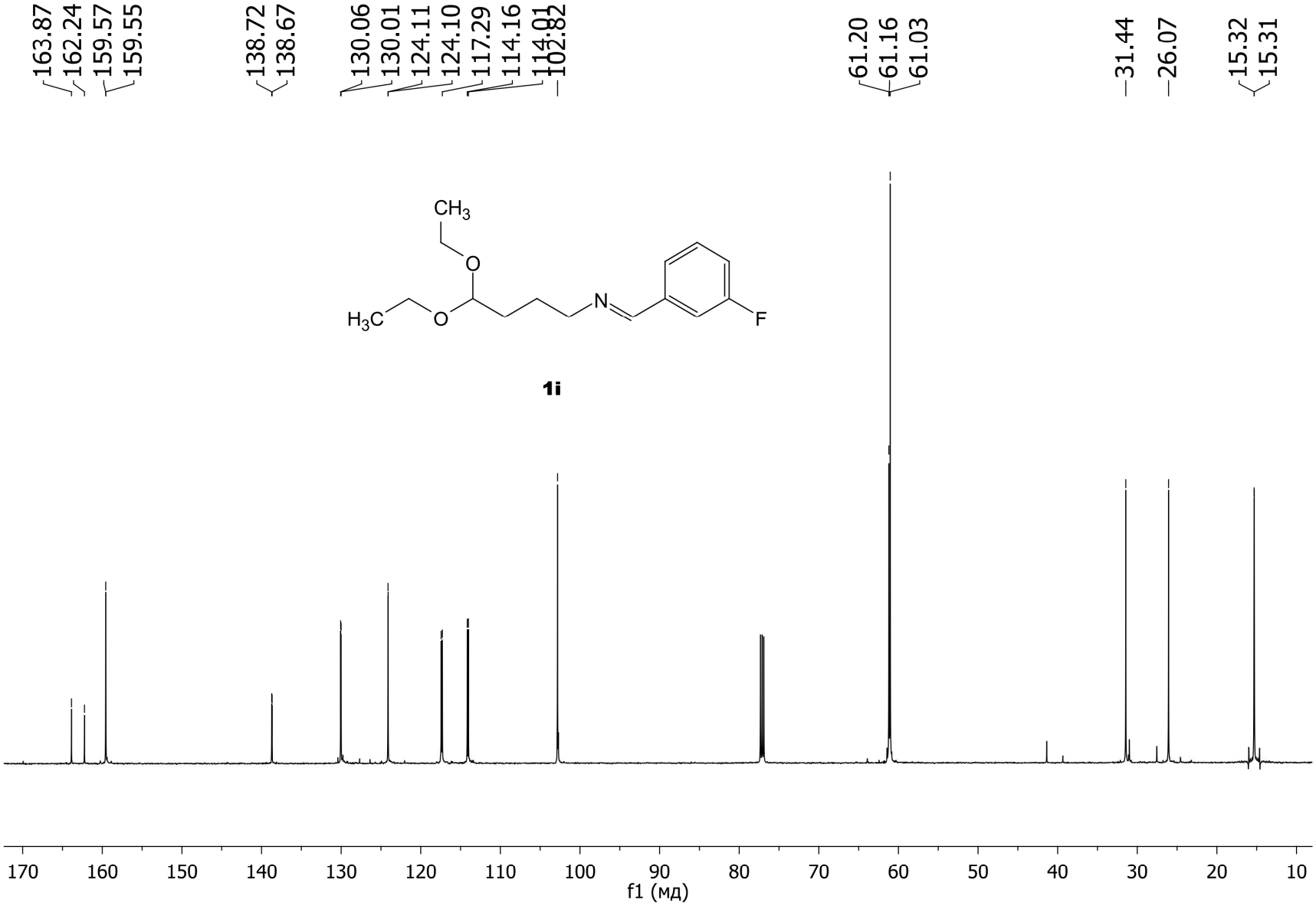


Figure S18: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1i**

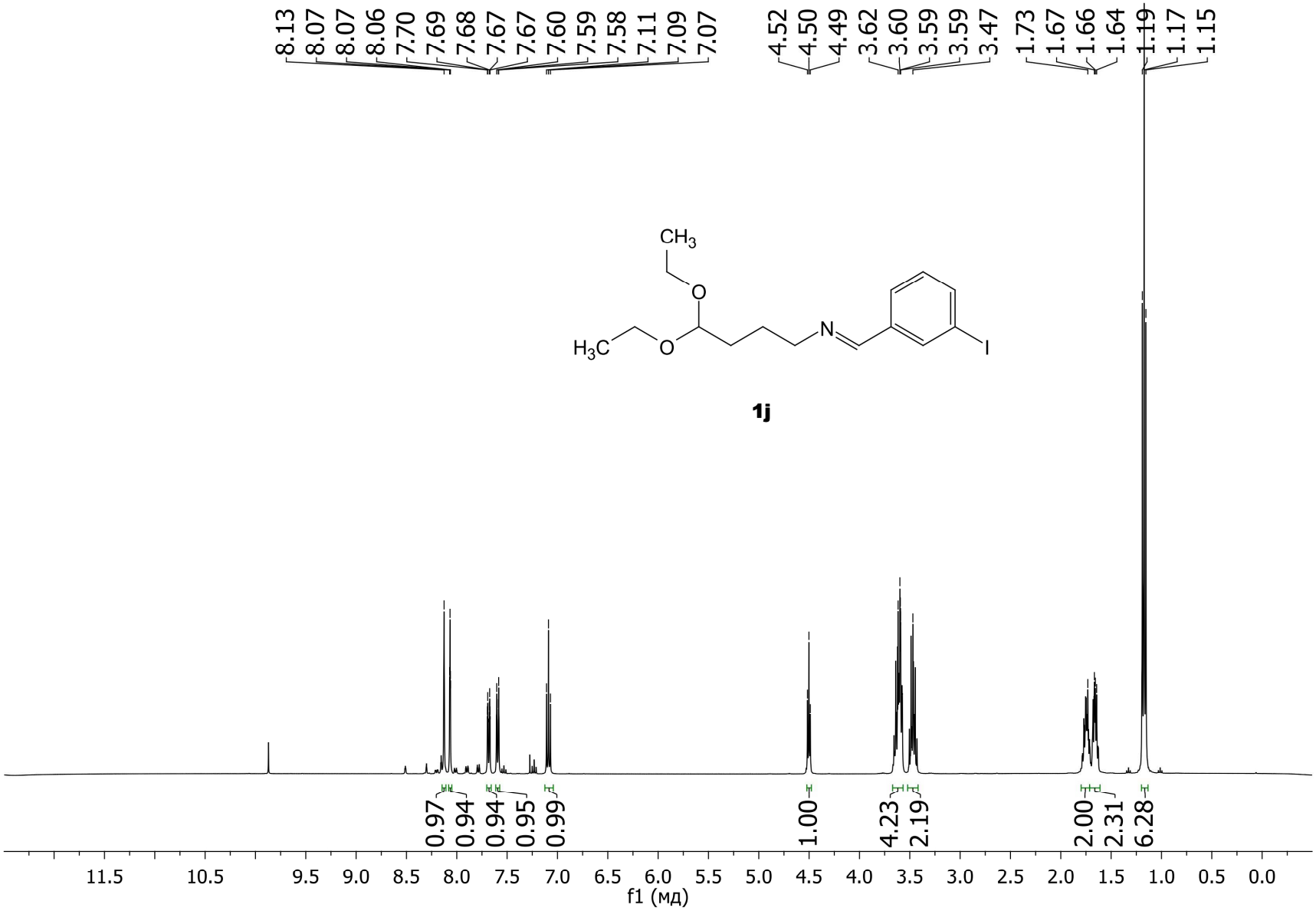


Figure S19: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1j**

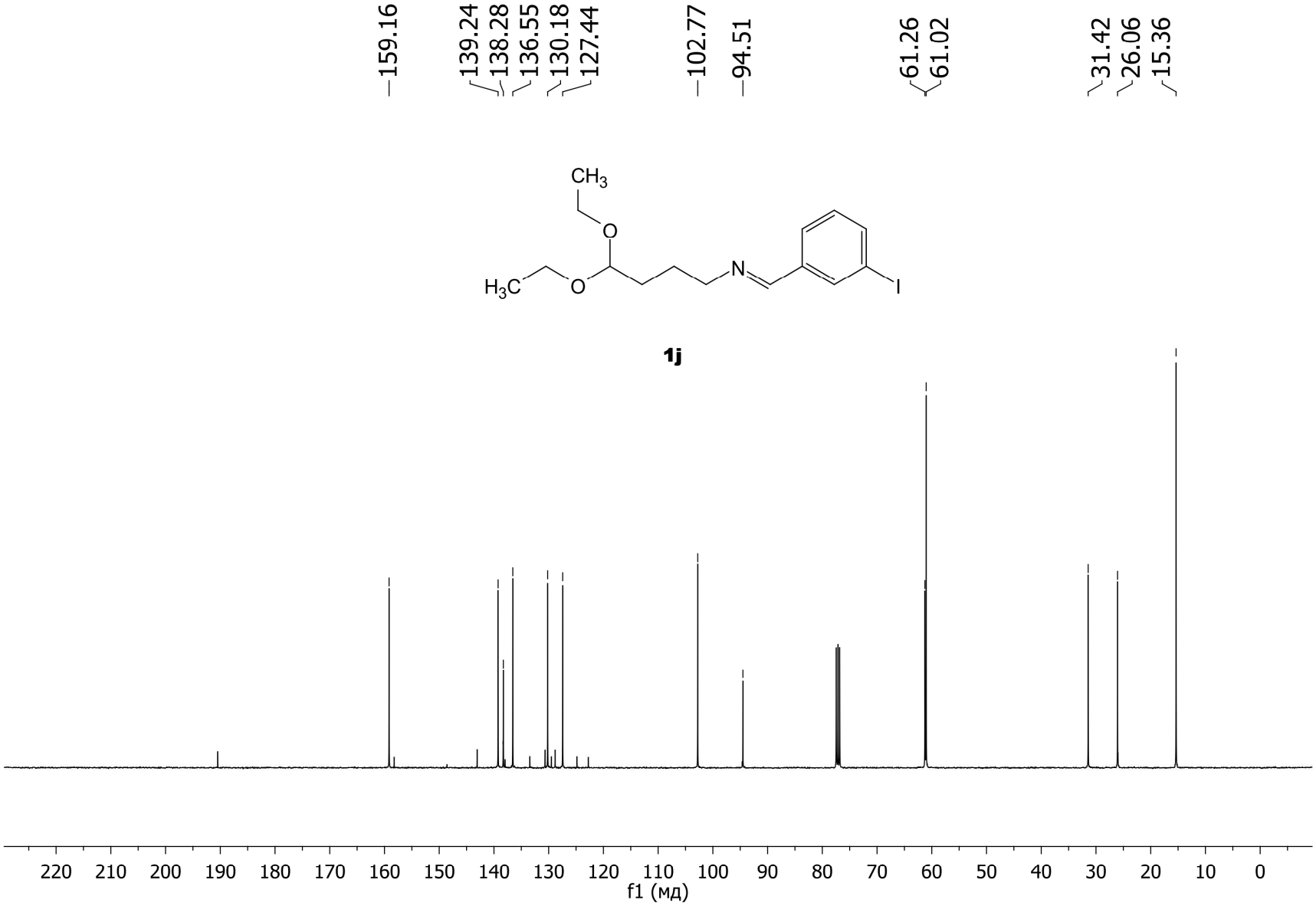


Figure S20: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1j**

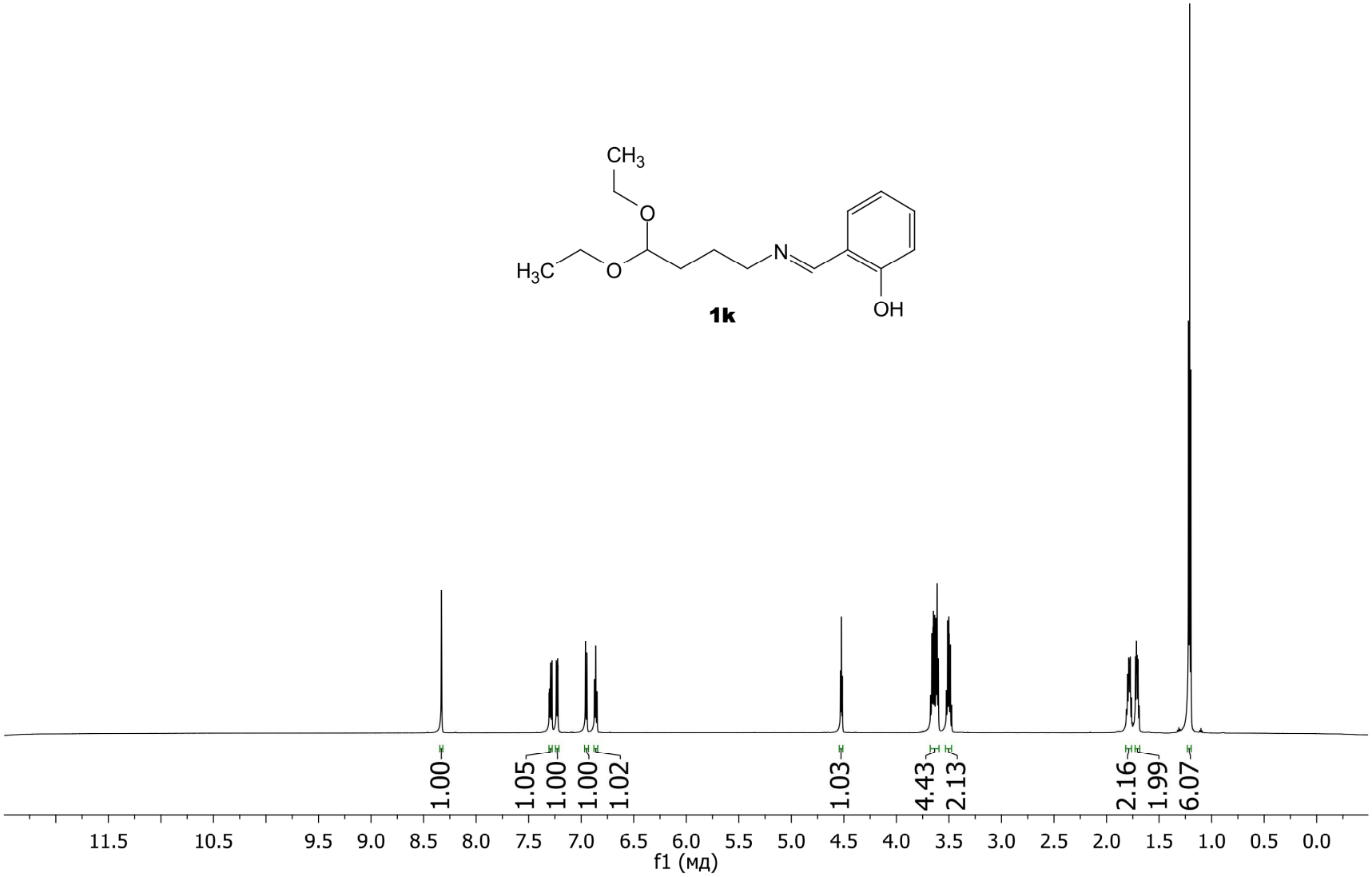


Figure S21: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1k**

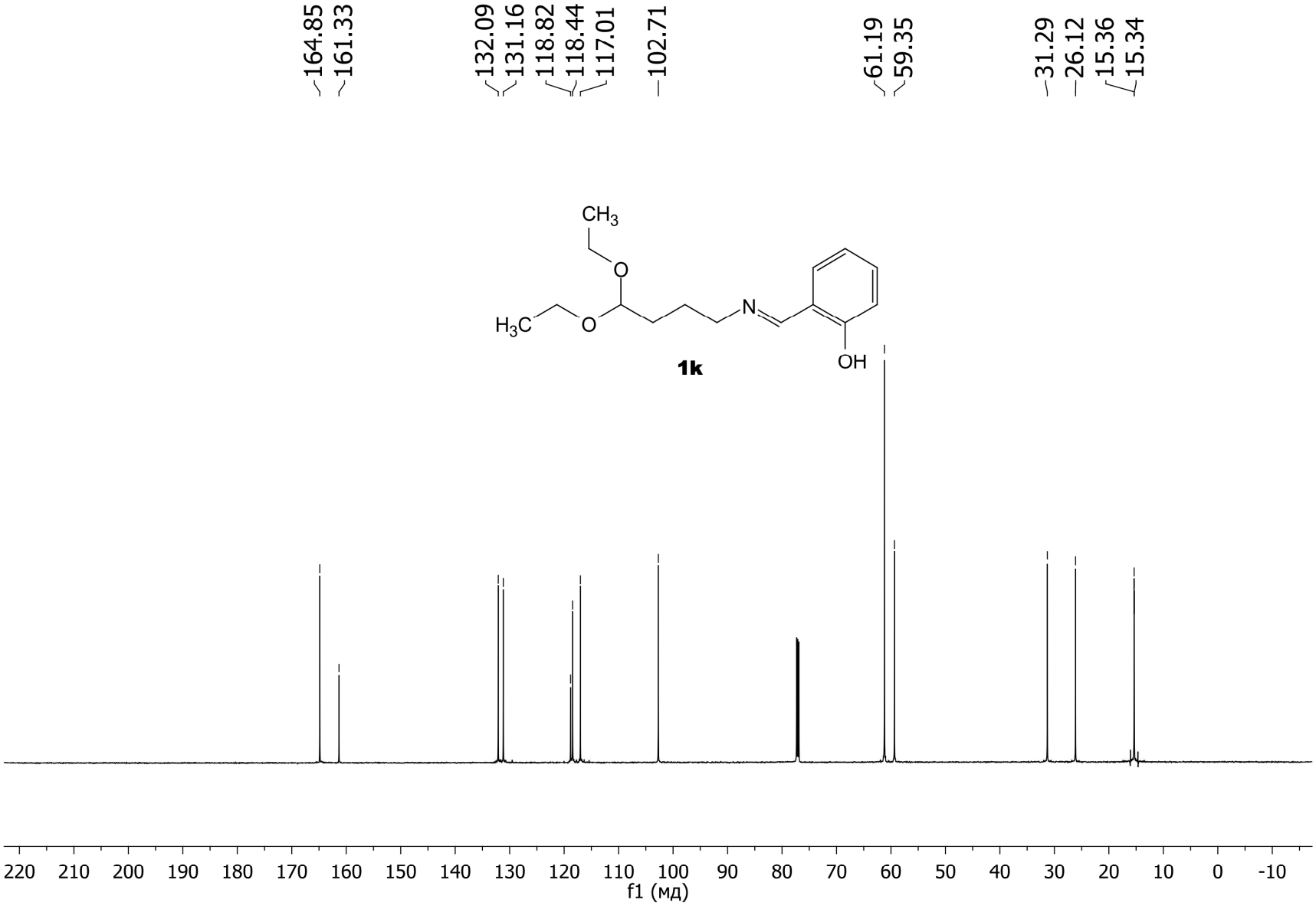


Figure S22: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1k**

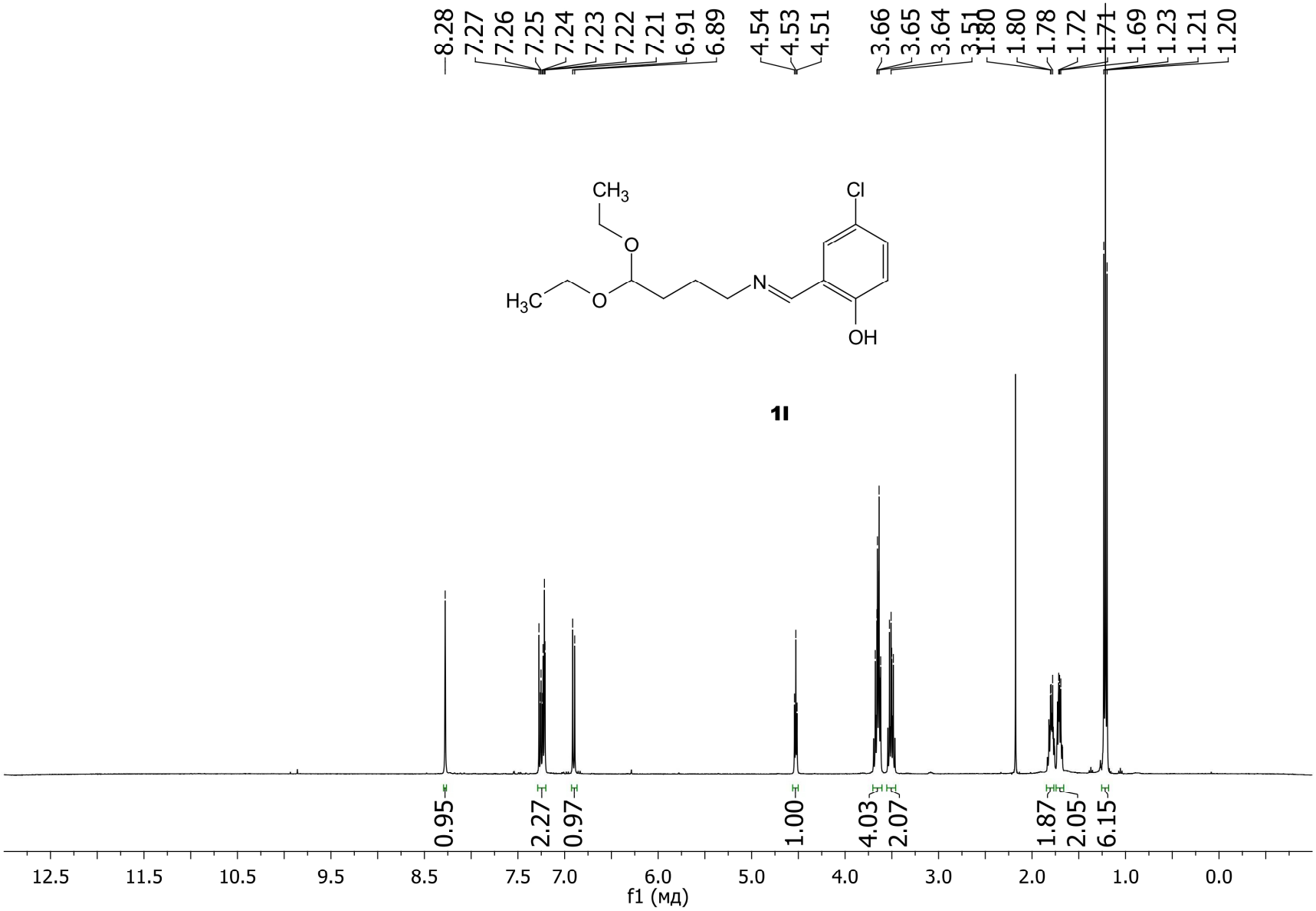


Figure S23: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1l**

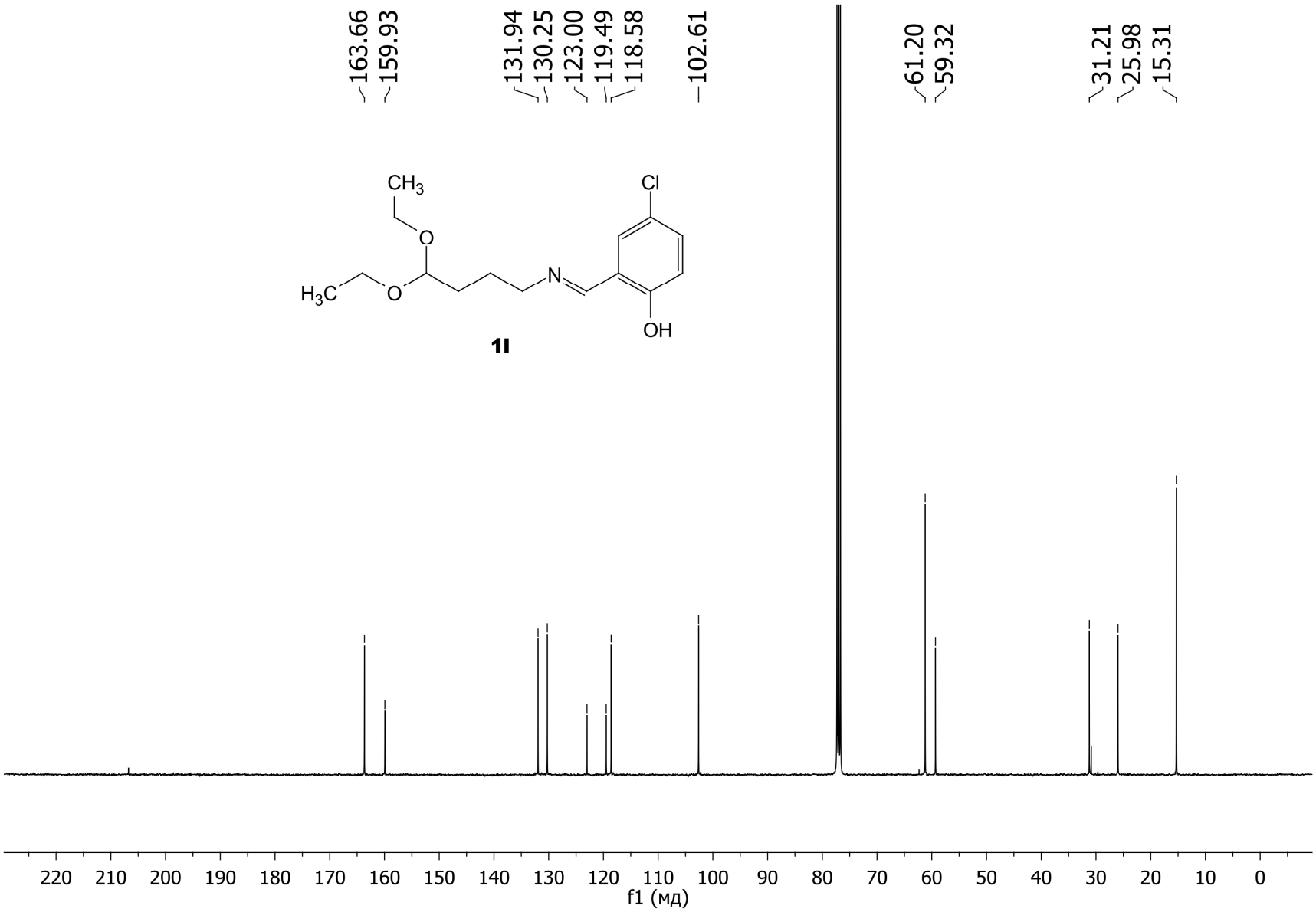


Figure S24: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1l**

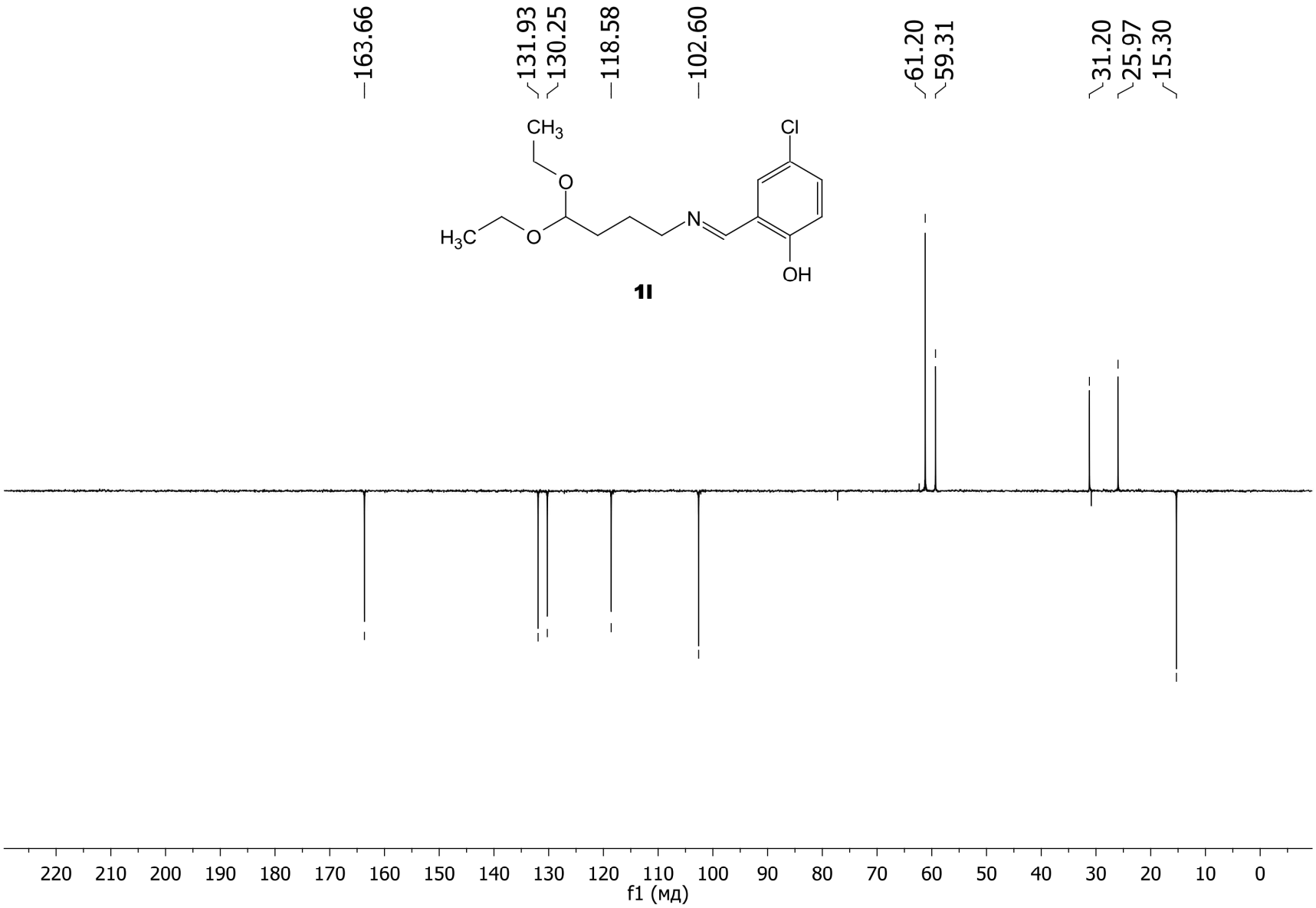


Figure S25: NMR $^{13}C\{^{1}H\}$ DEPT spectrum ($CDCl_3$, 400MHz, 135° pulse) of the compound **1l**

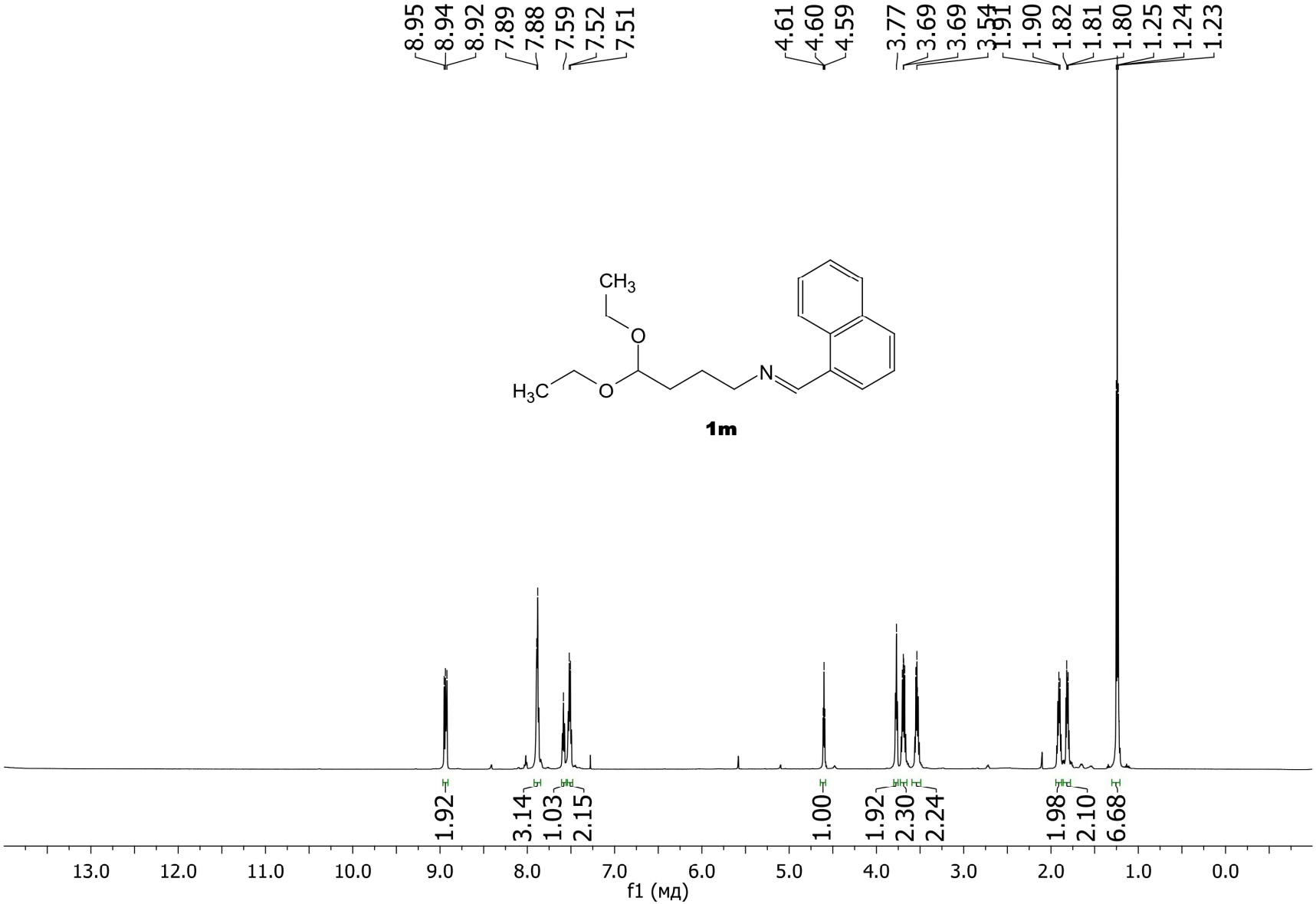


Figure S26: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1m**

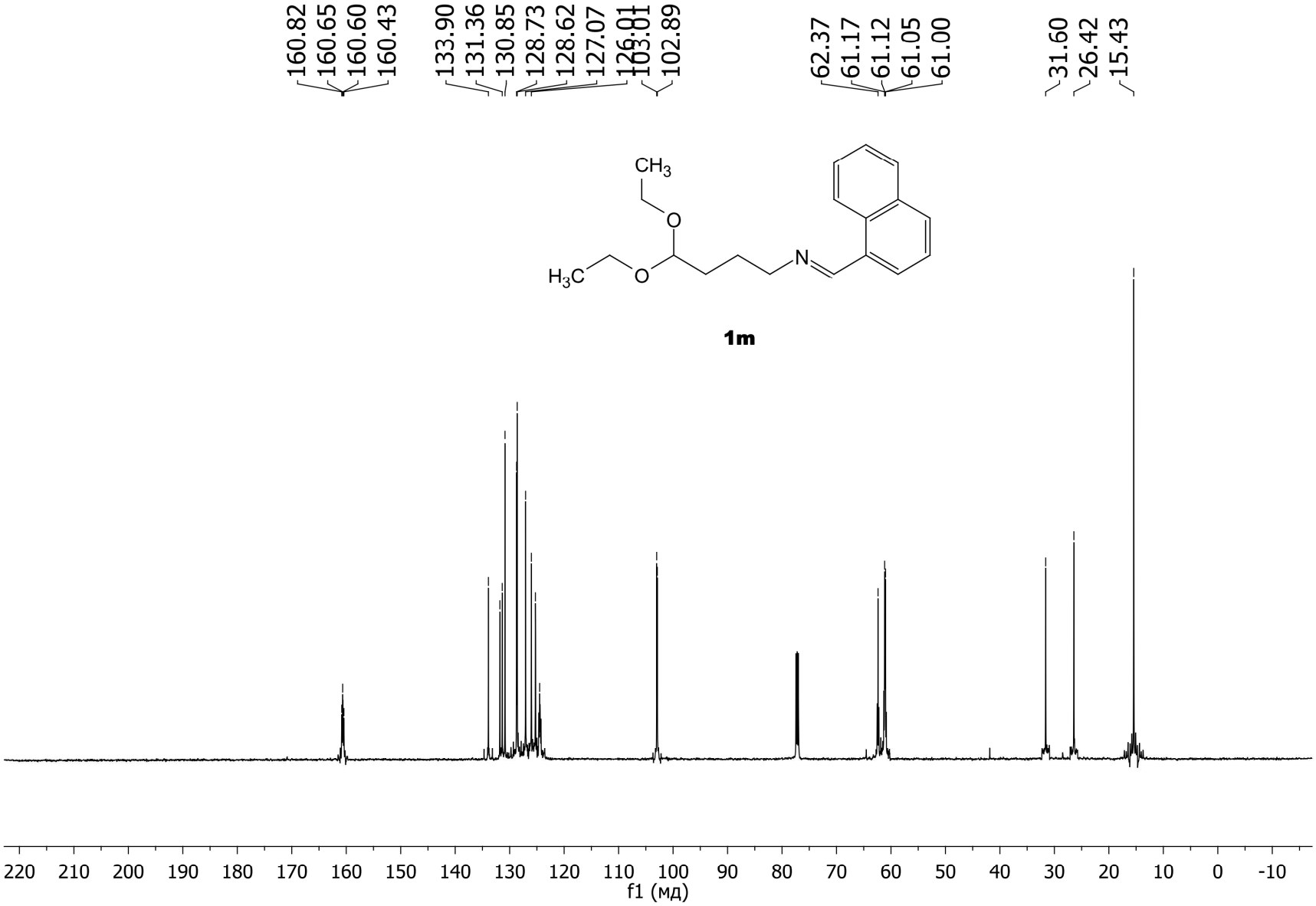


Figure S27: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1m**

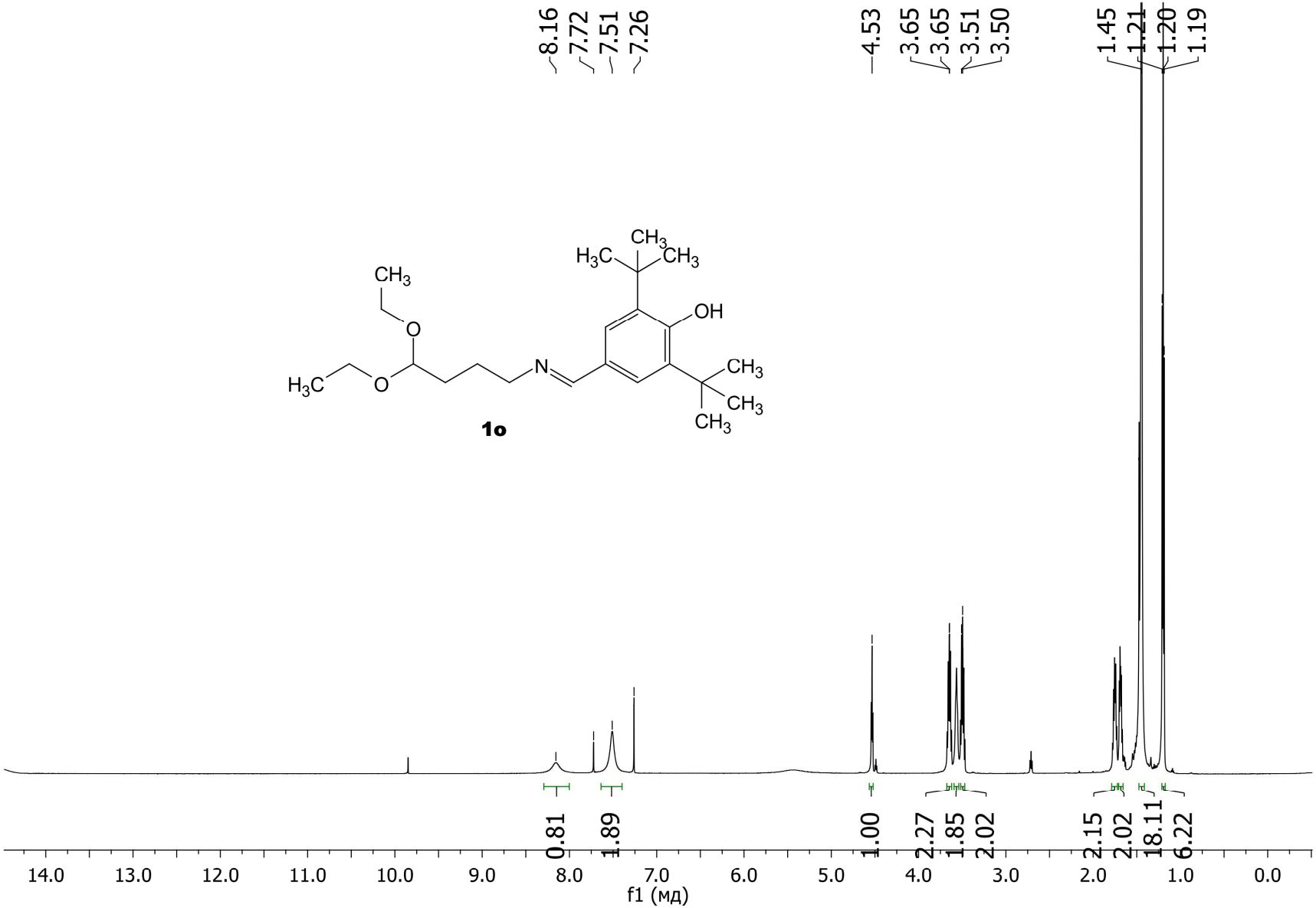


Figure S28: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1o**

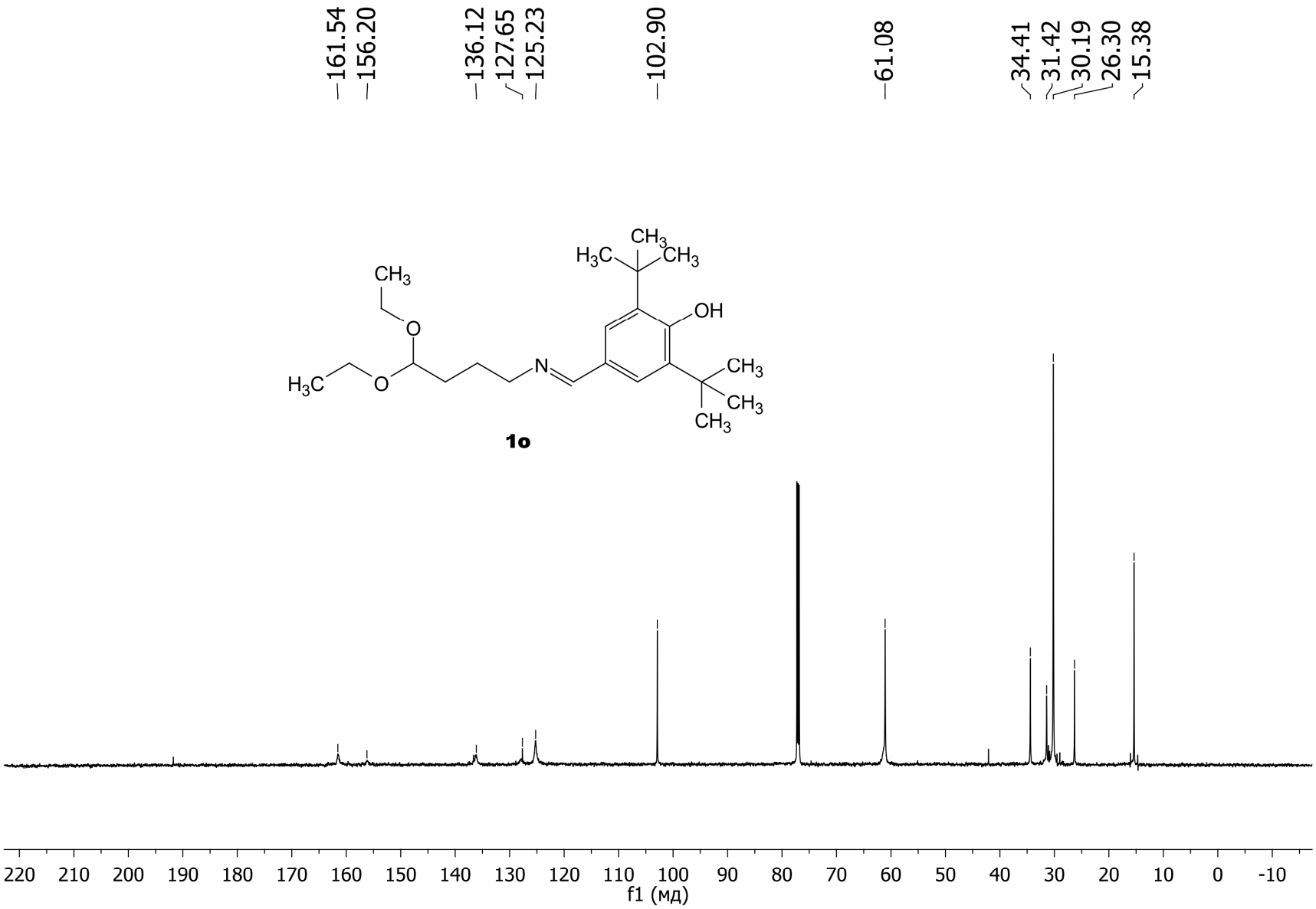


Figure S29: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1o**

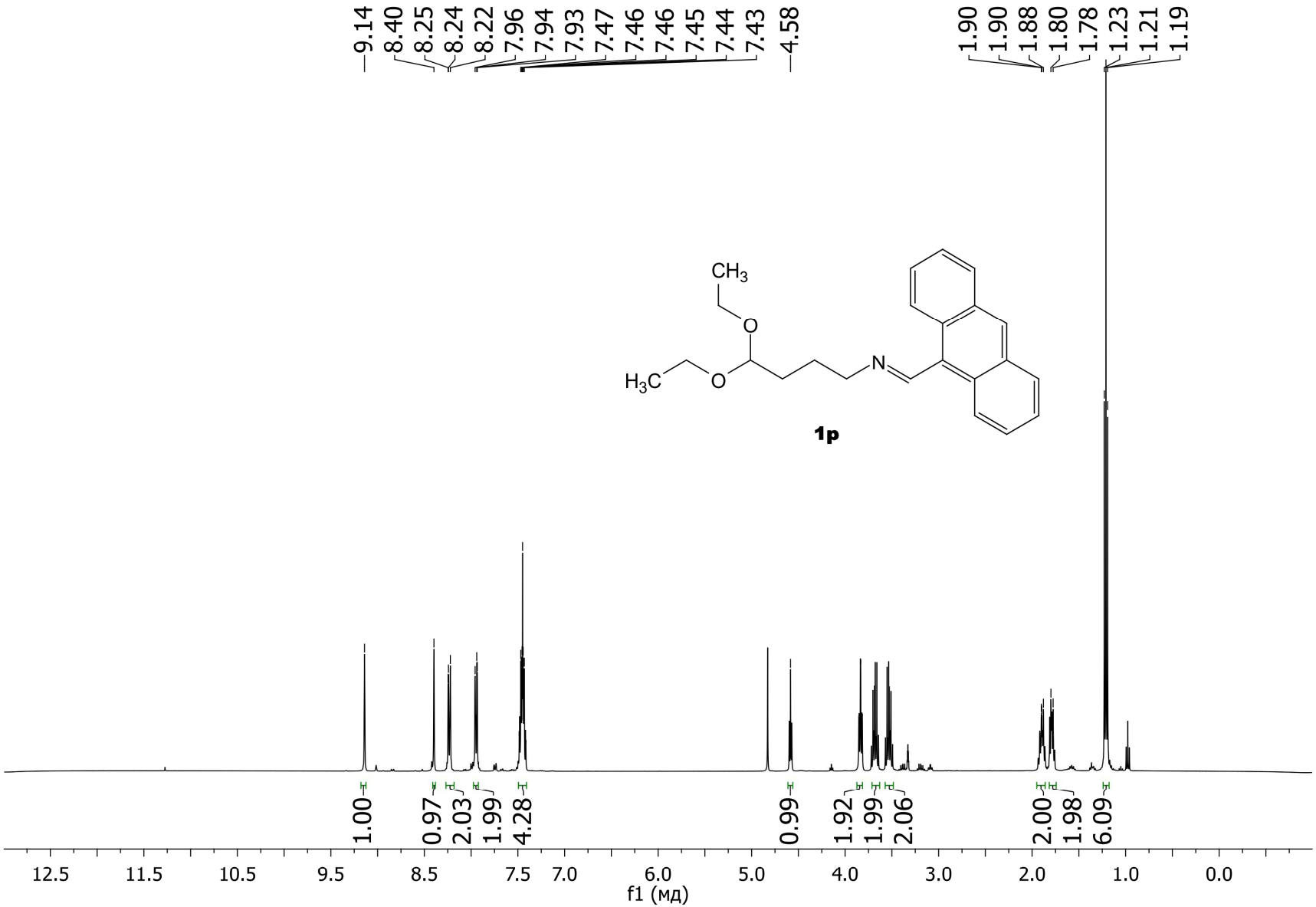


Figure S30: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1p**

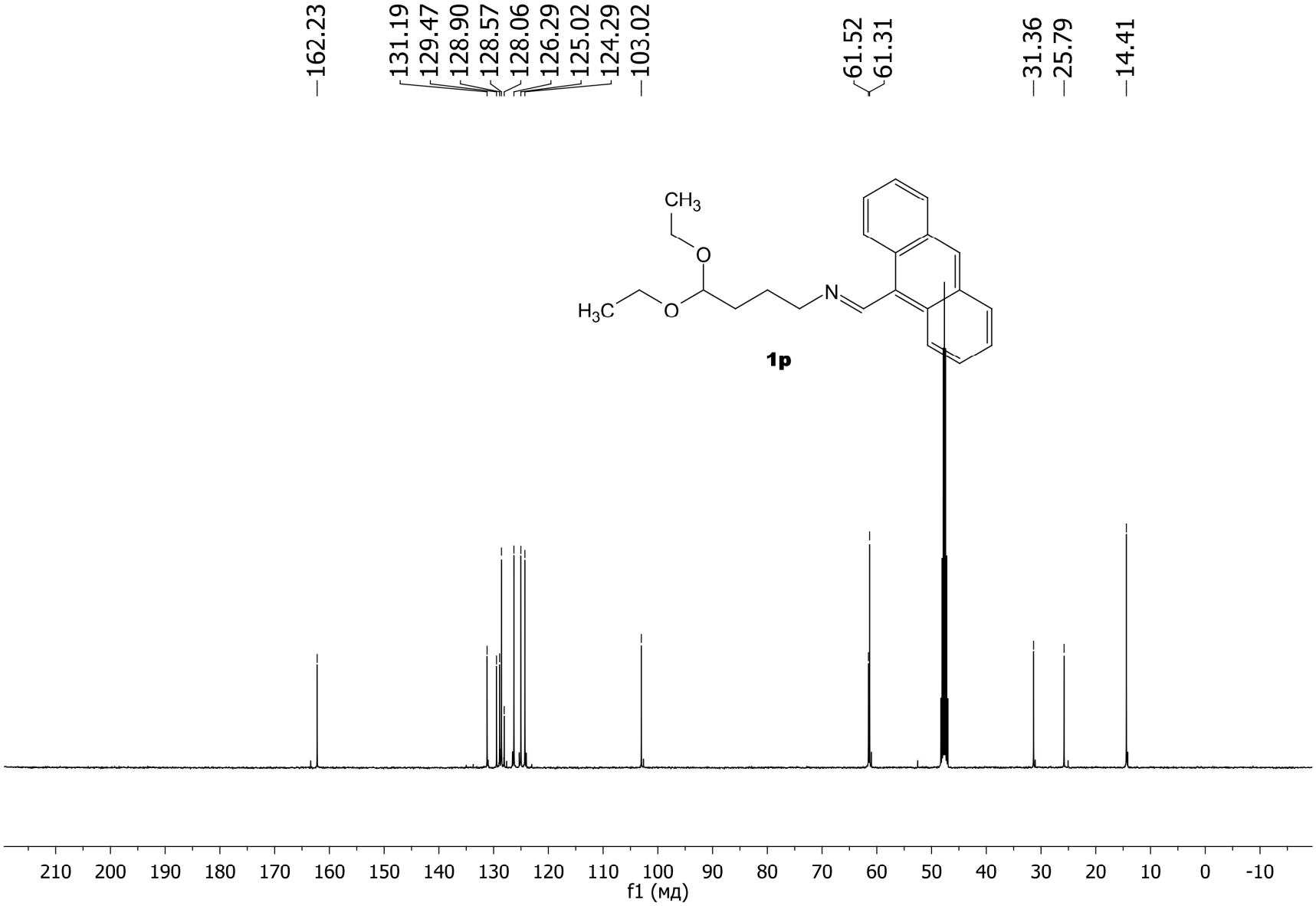


Figure S31: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1p**

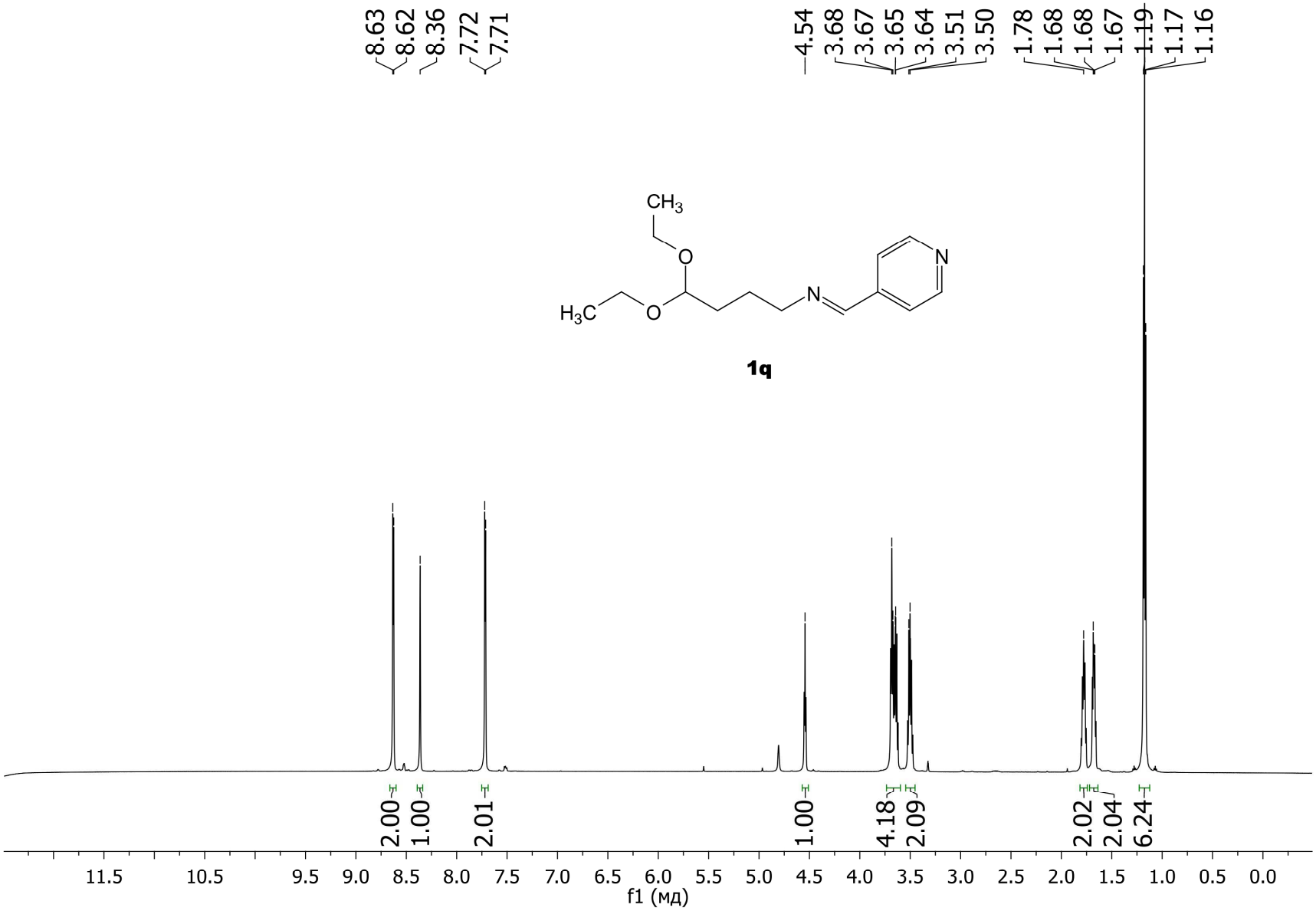


Figure S32: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1q**

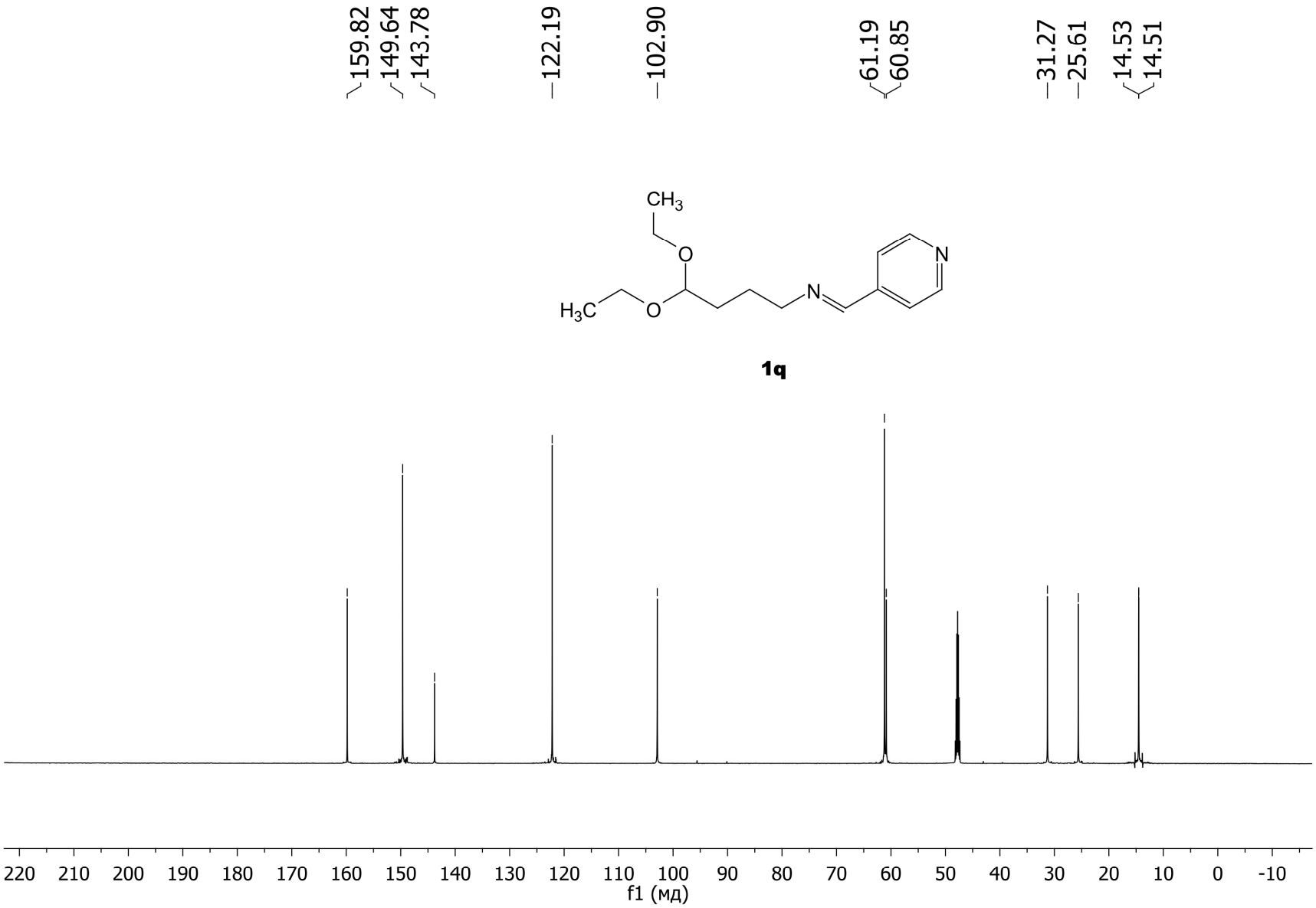


Figure S33: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1q**

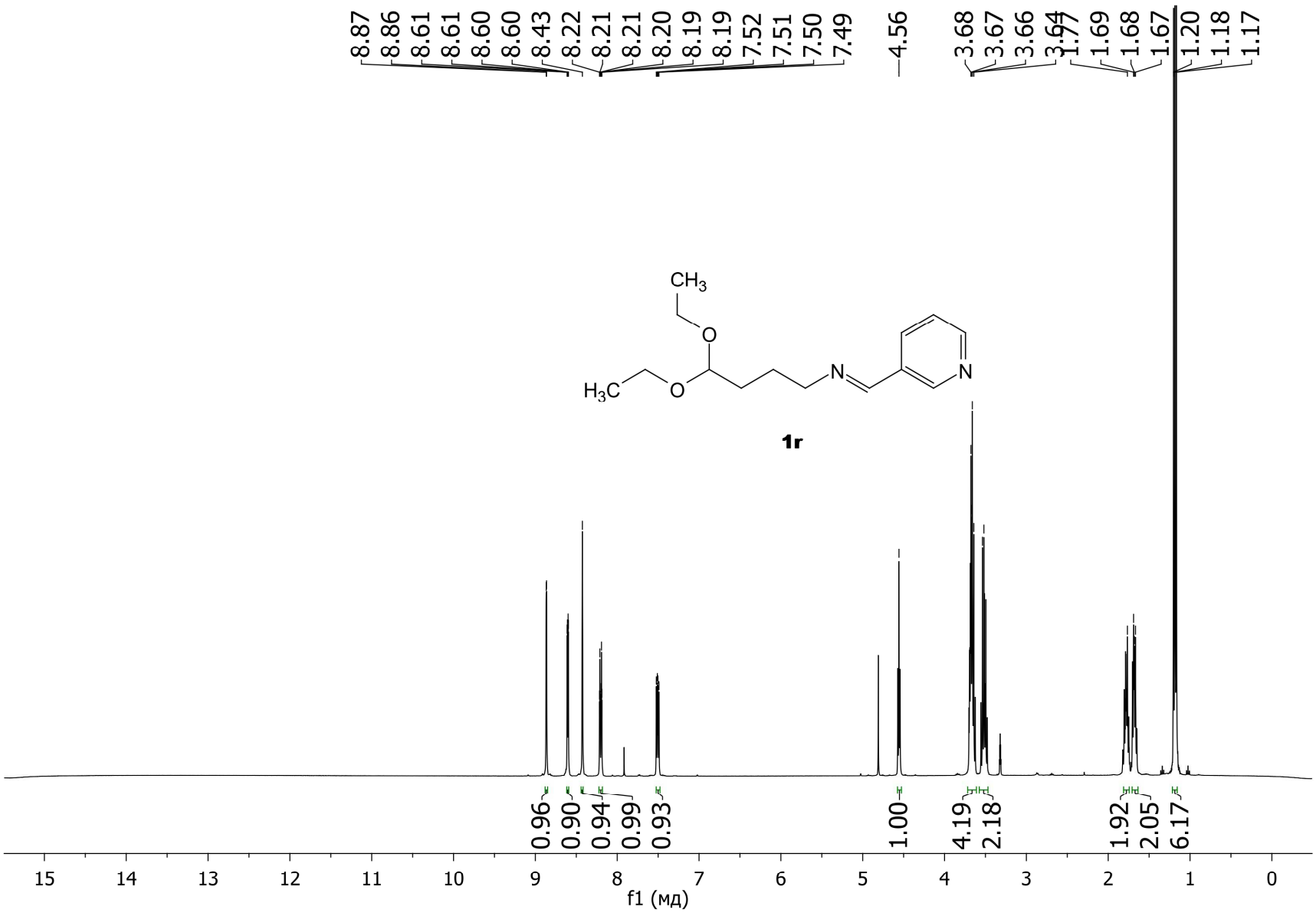


Figure S34: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **1r**

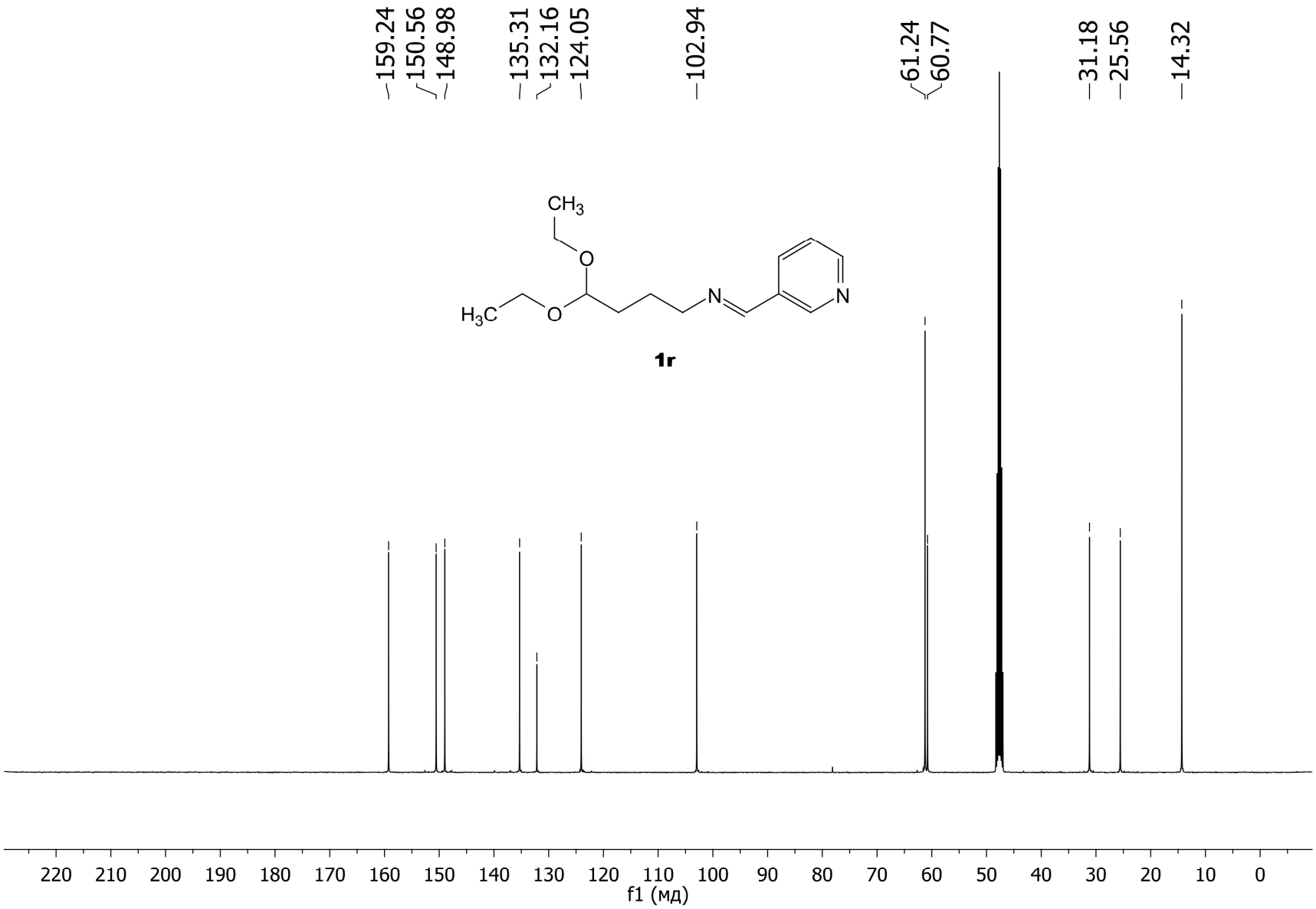


Figure S35: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **1r**

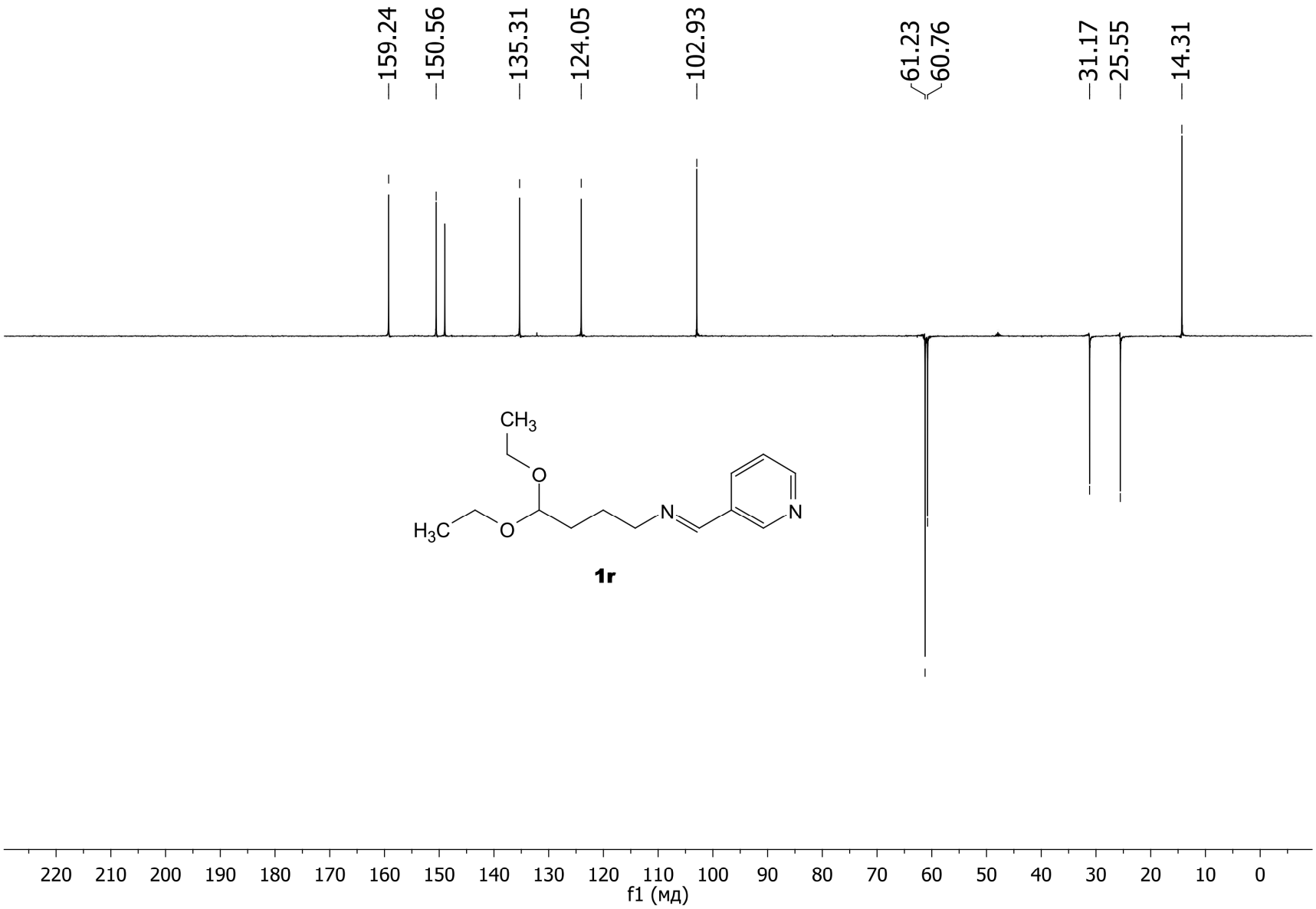


Figure S36: NMR $^{13}C\{^{1}H\}$ DEPT spectrum ($CDCl_3$, 400MHz, 135° pulse) of the compound **1r**

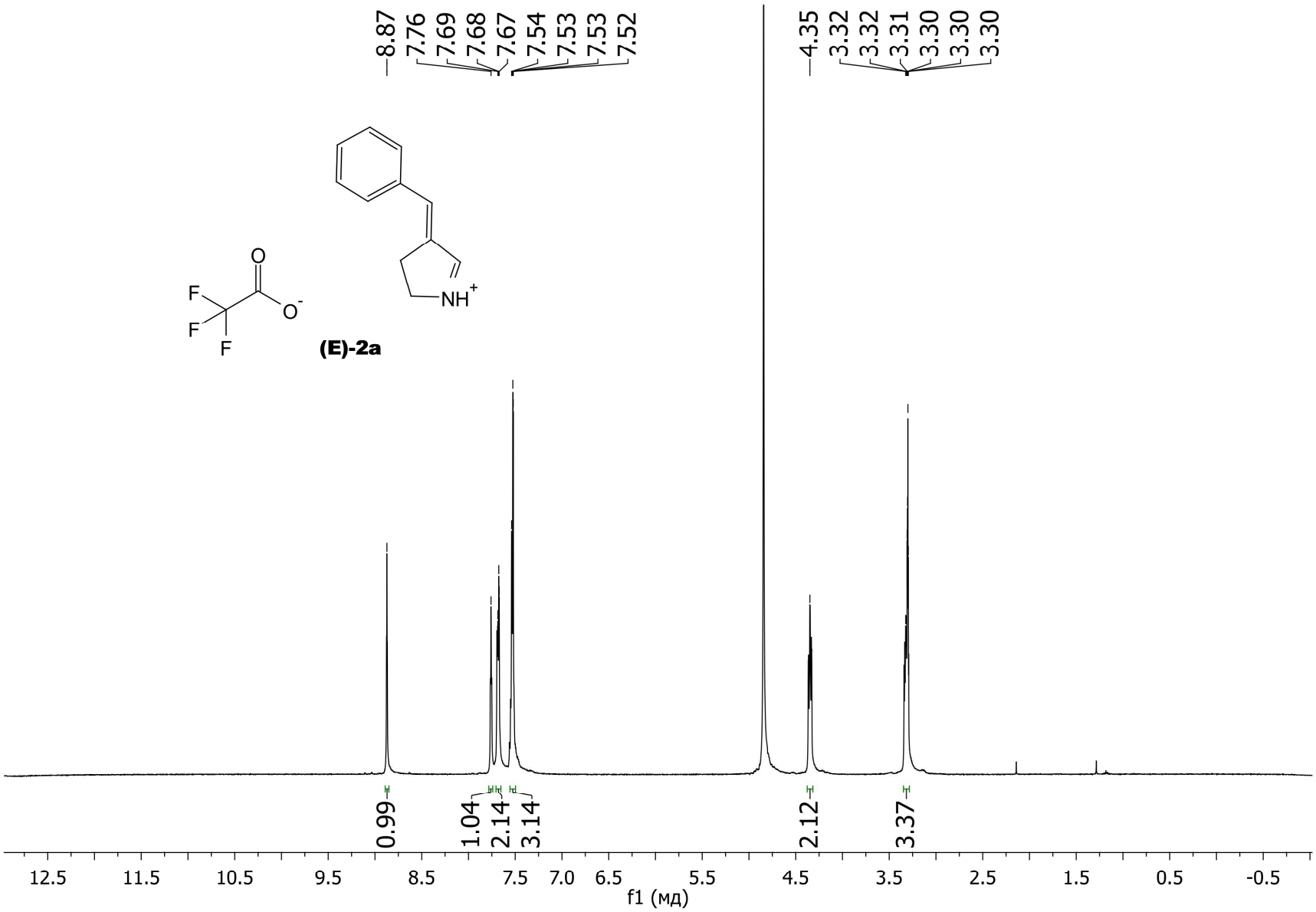


Figure S37: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2a**

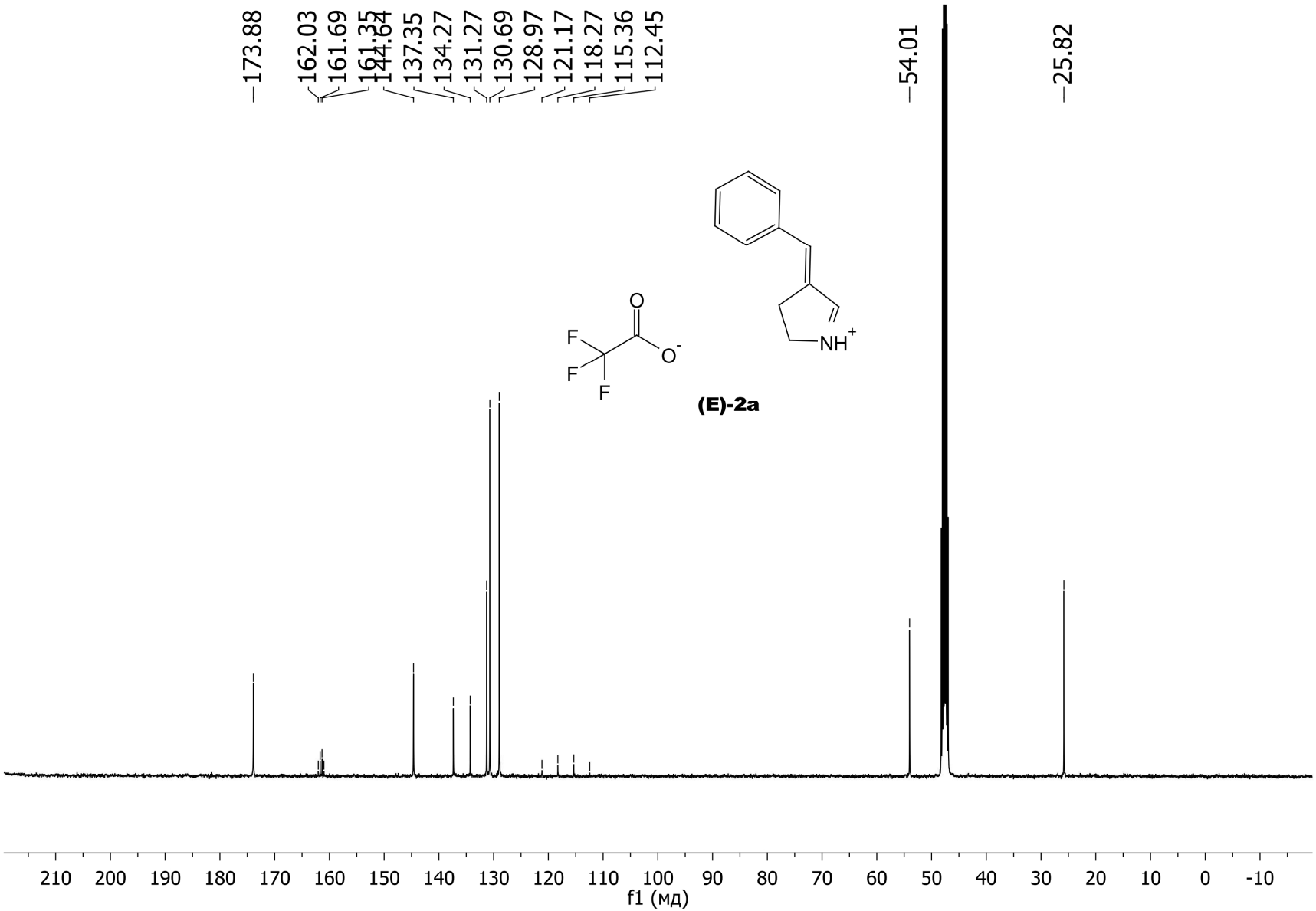


Figure S38: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2a**

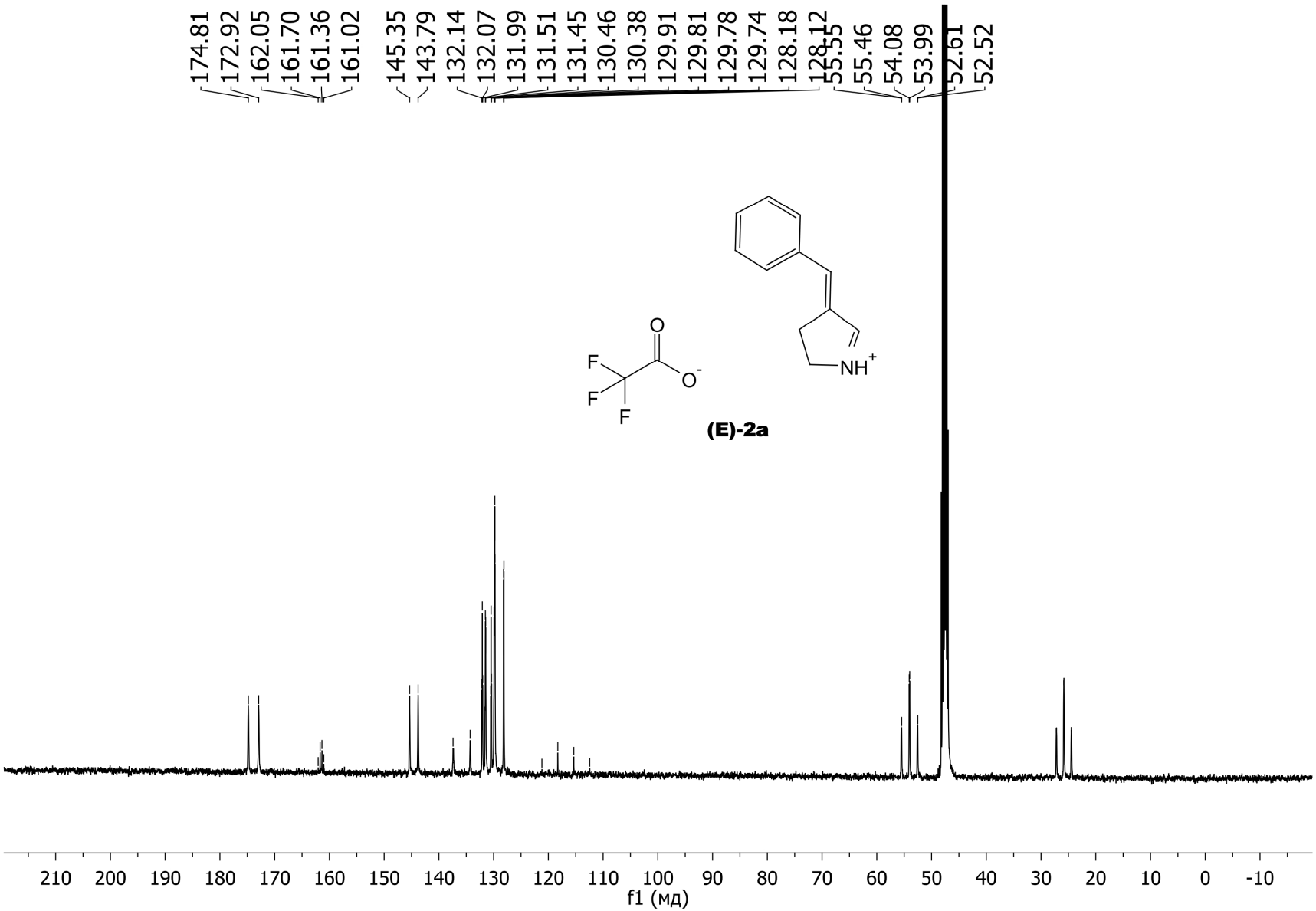


Figure S39: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2a**

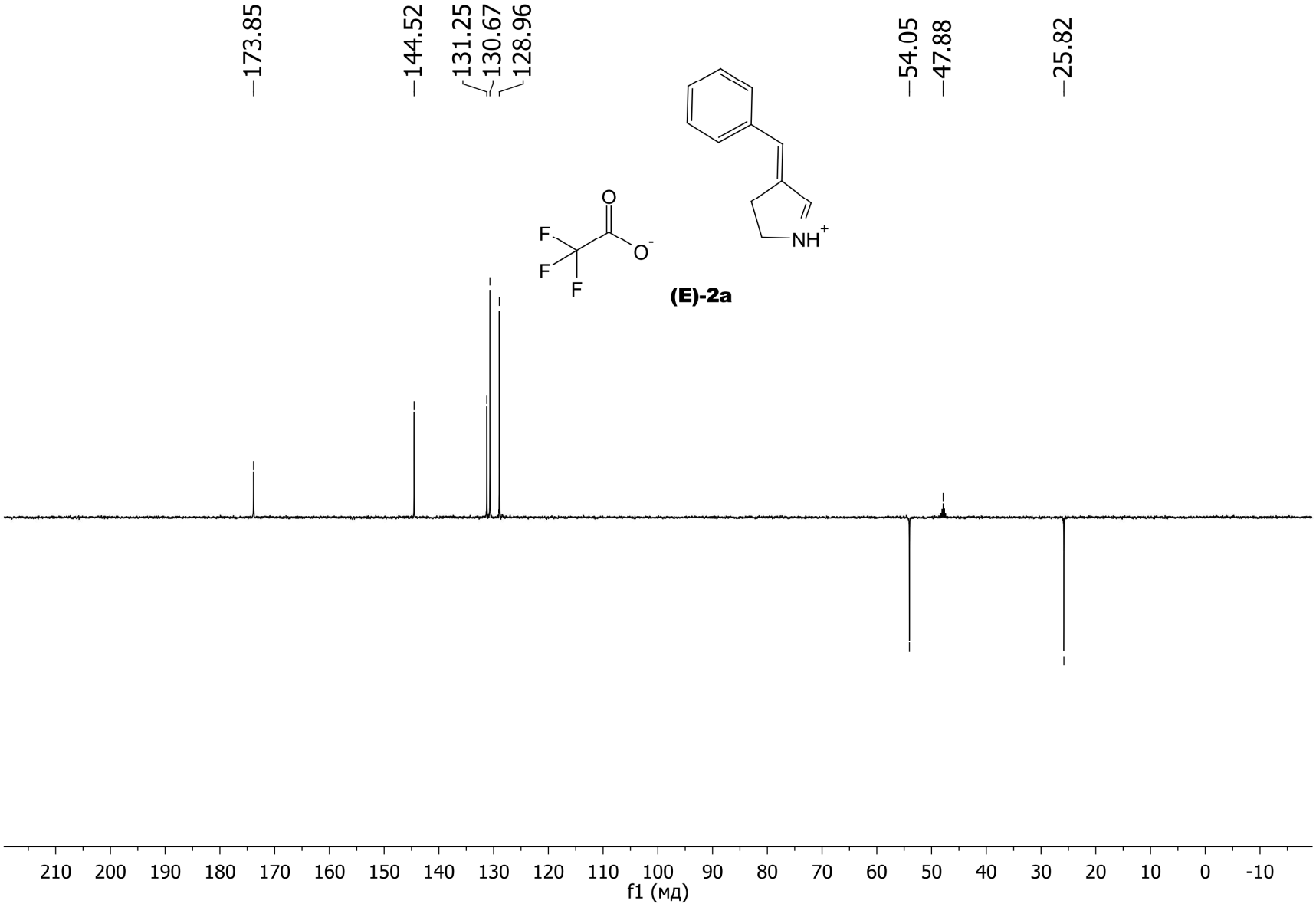


Figure S40: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2a**

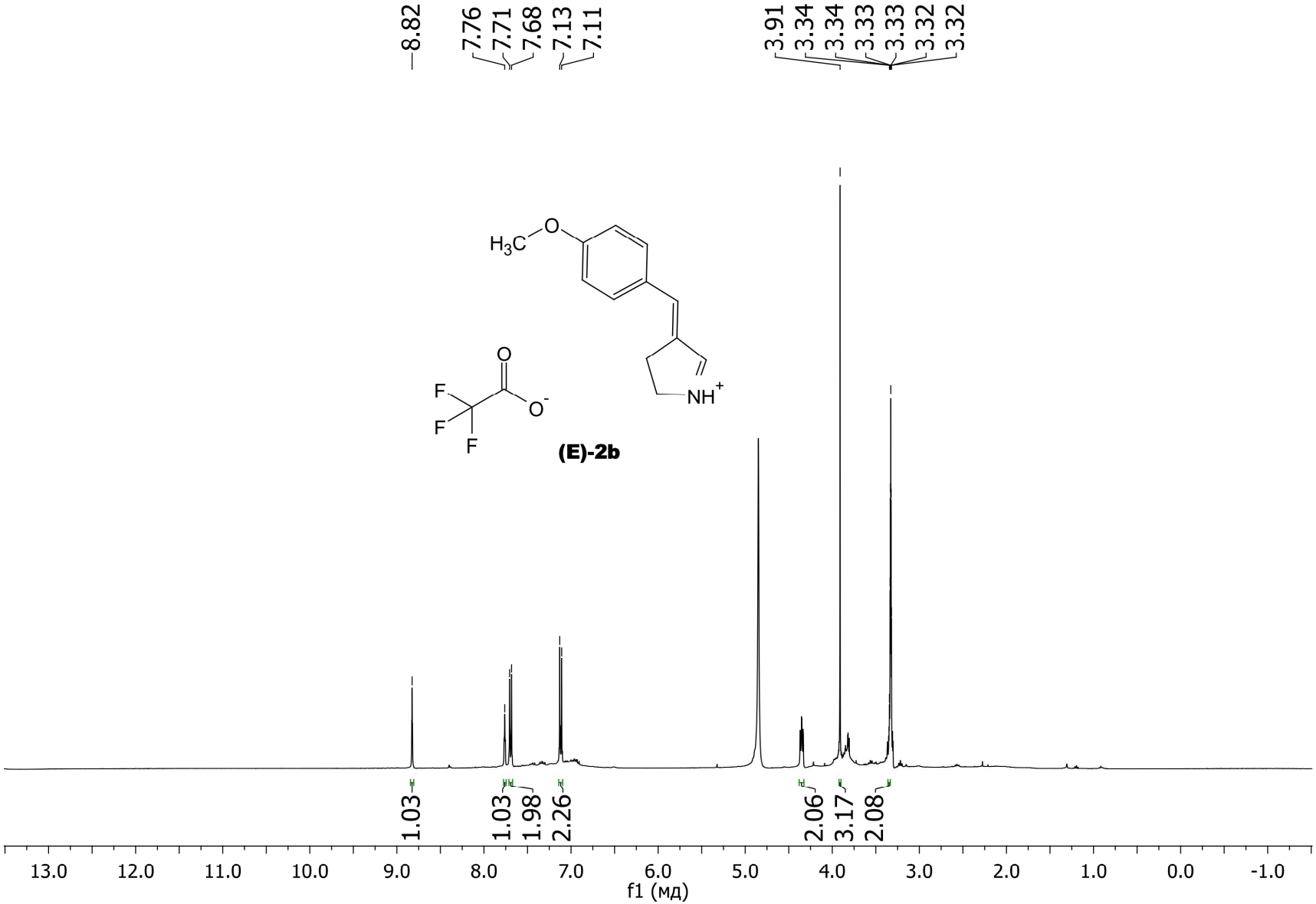


Figure S41: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2b**

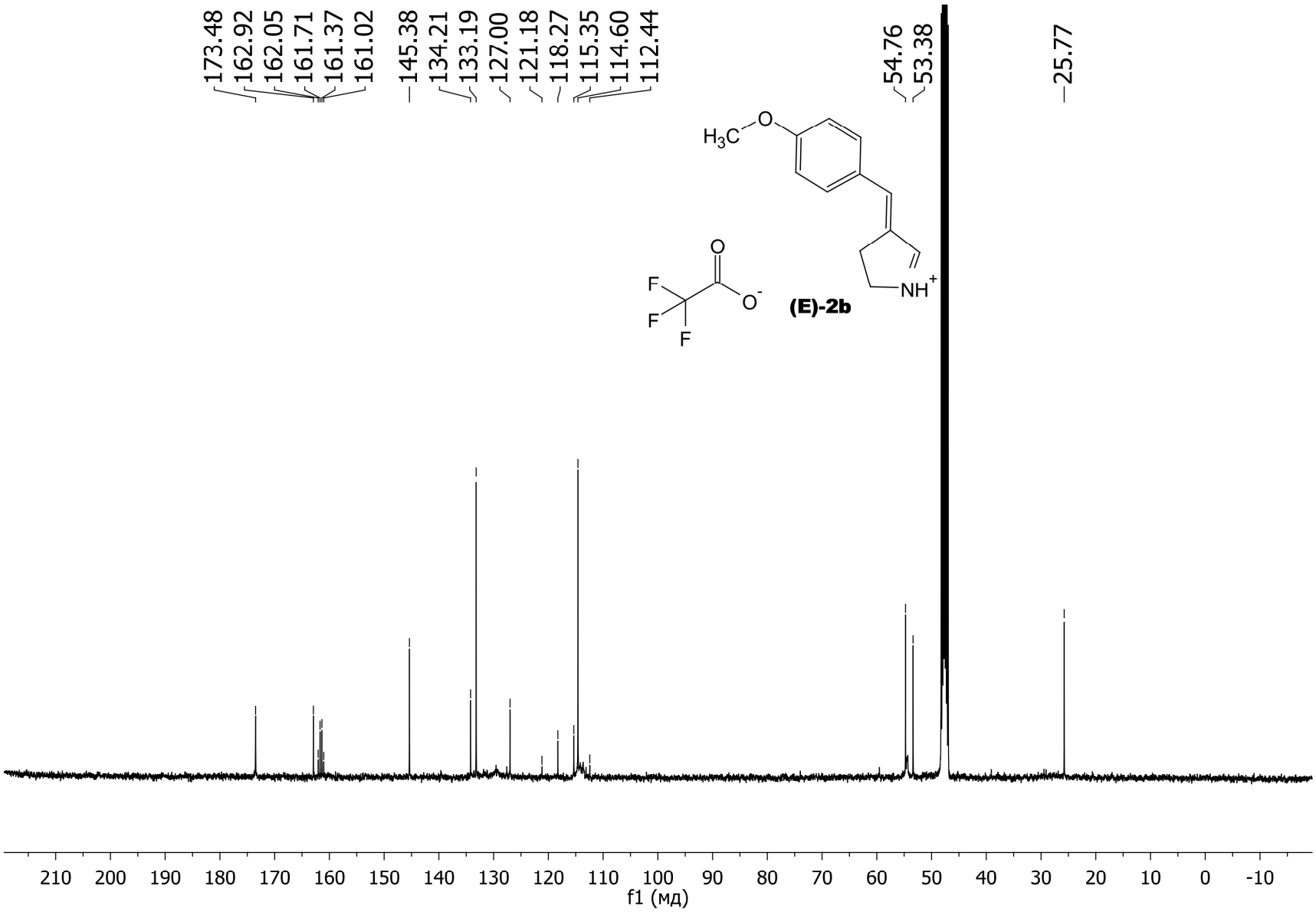


Figure S42: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2b**

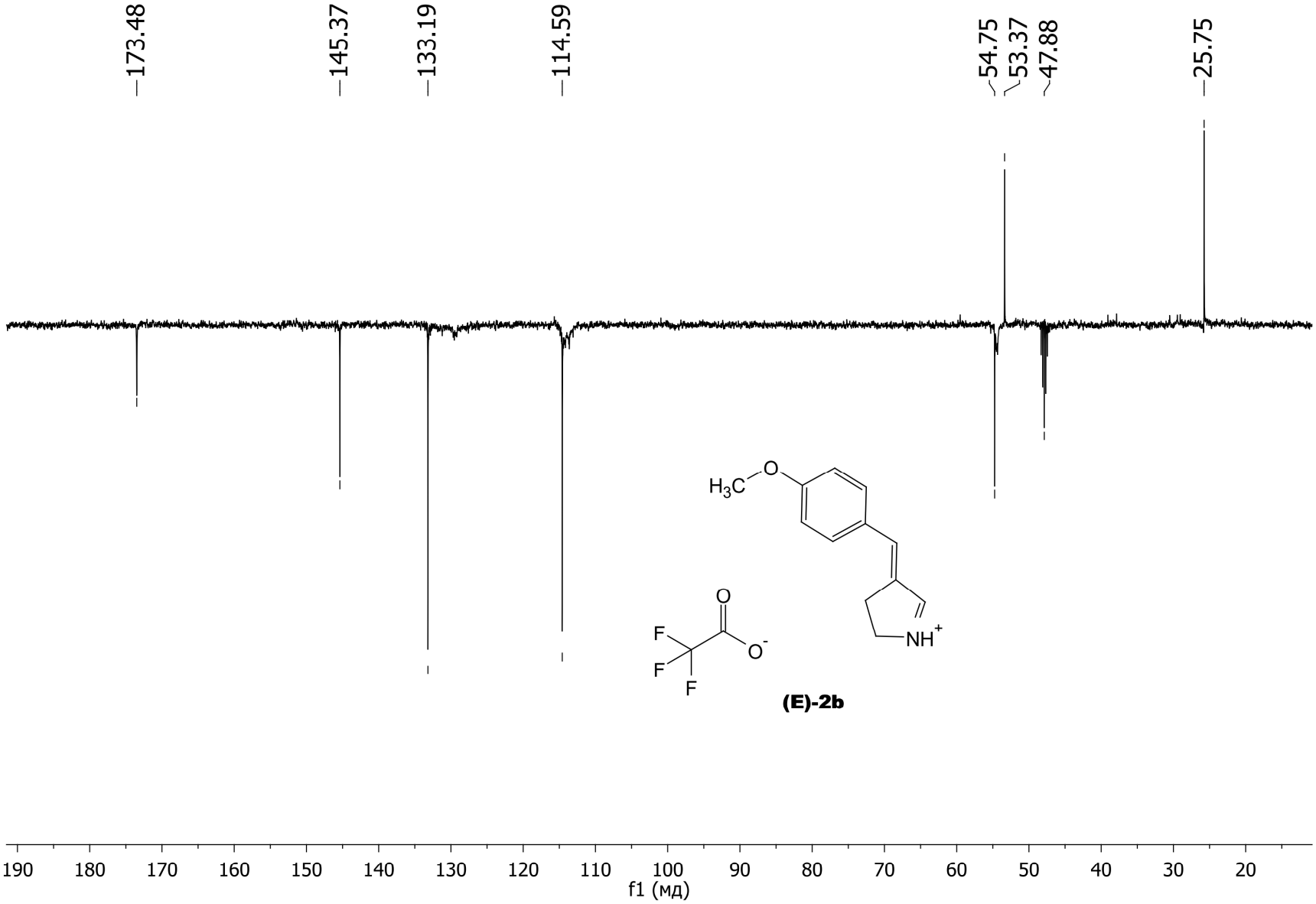


Figure S43: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2b**

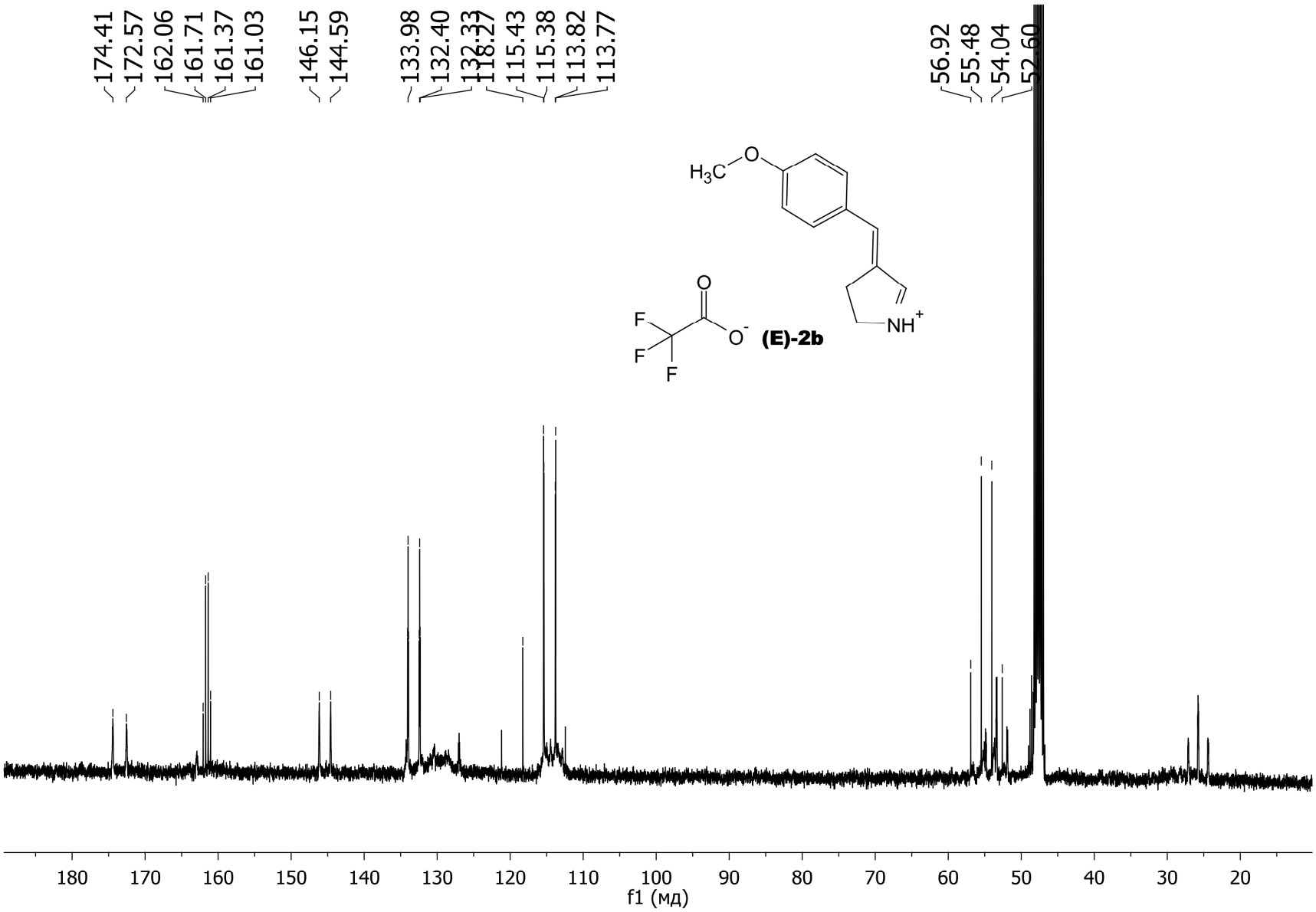


Figure S44: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2b**

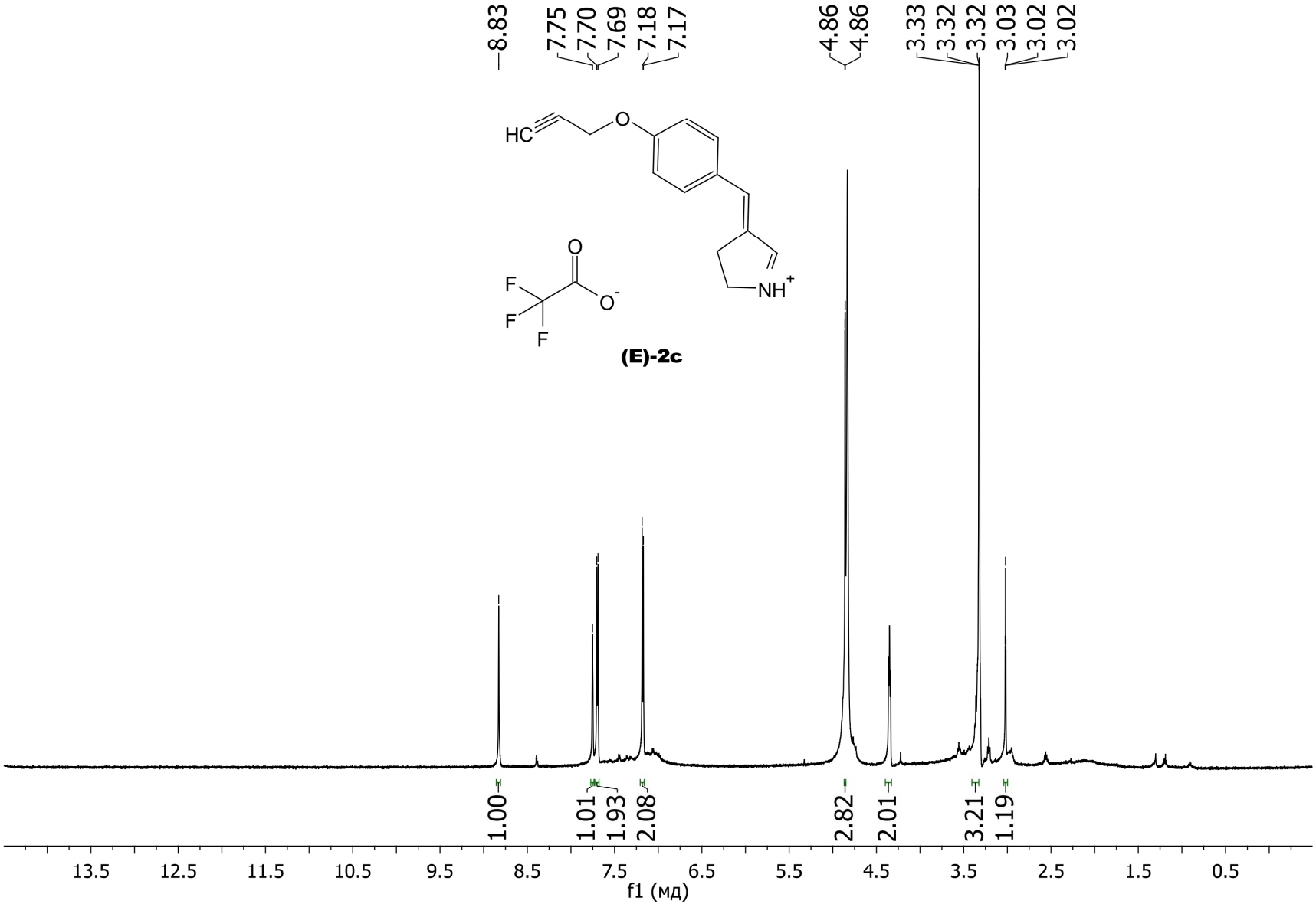


Figure S45: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2c**

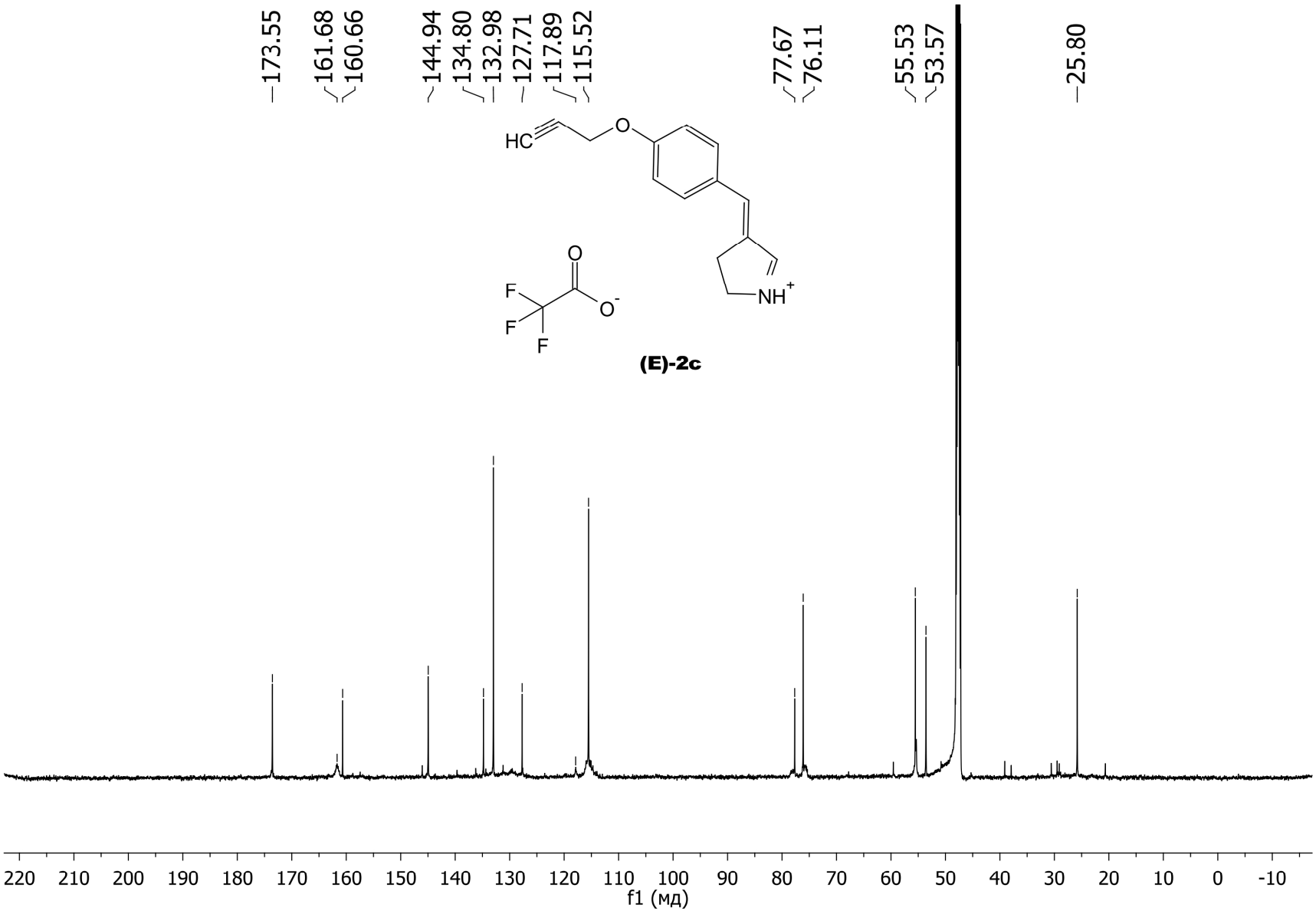


Figure S46: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2c**

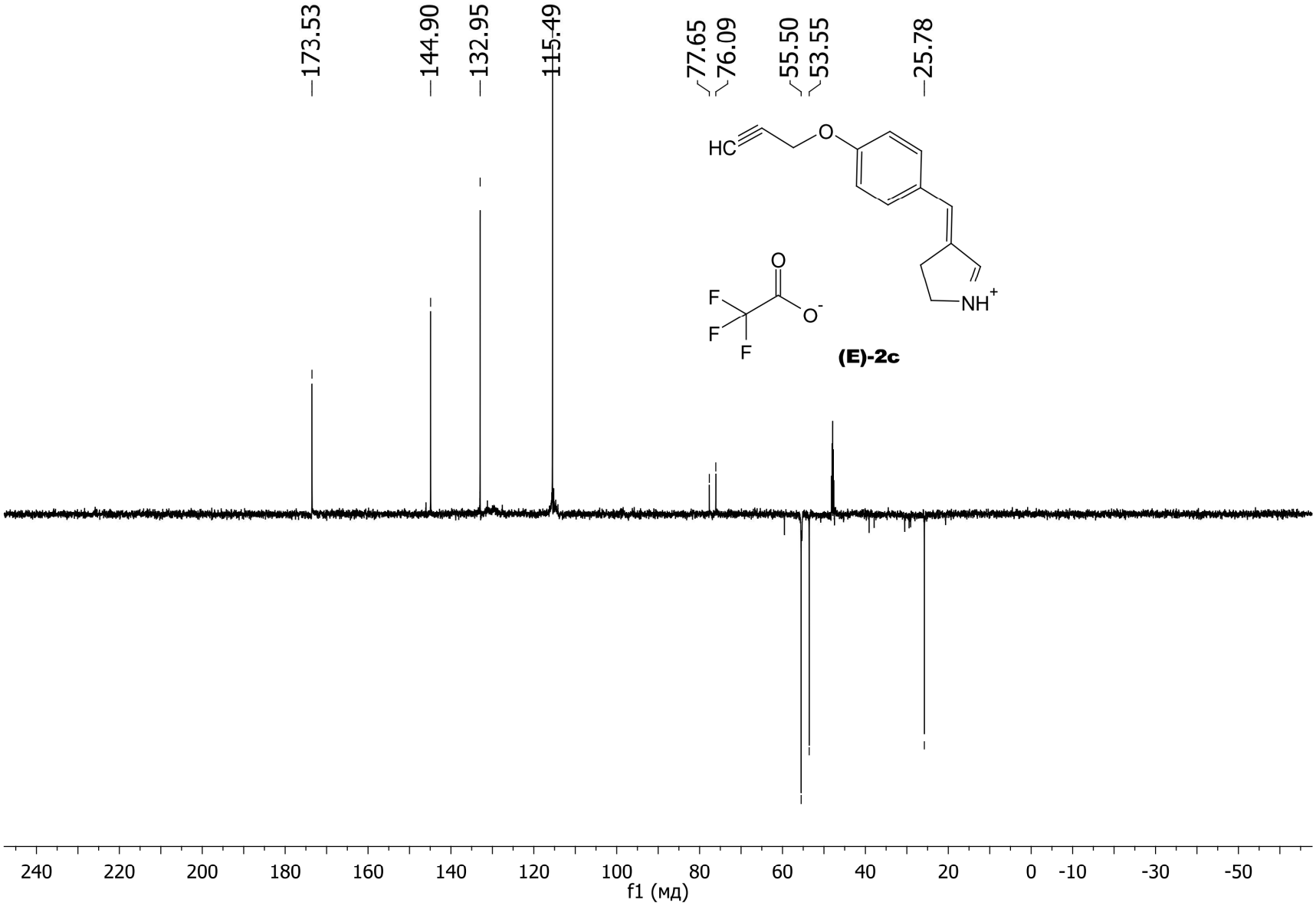


Figure S47: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2c**

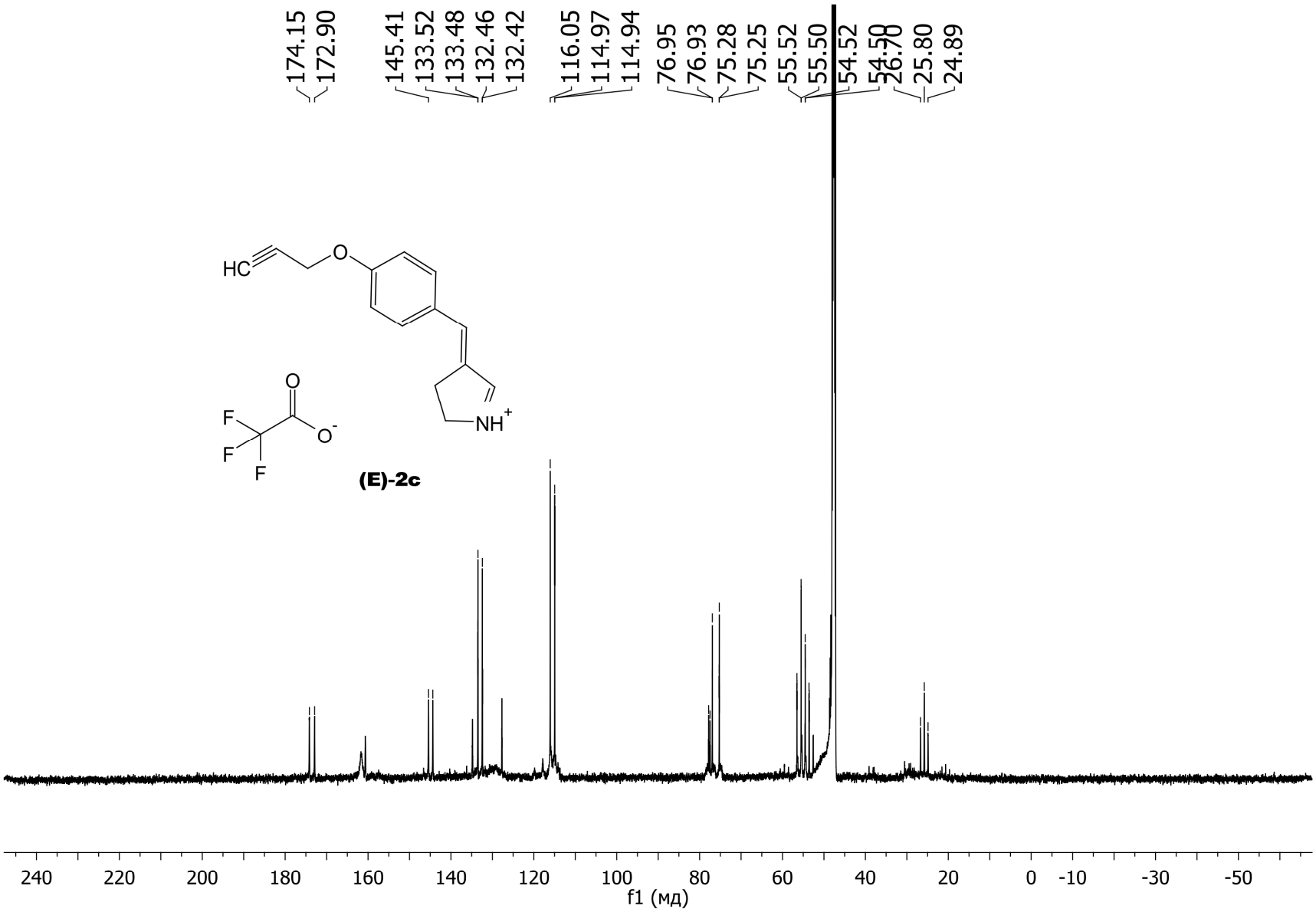


Figure S48: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2c**

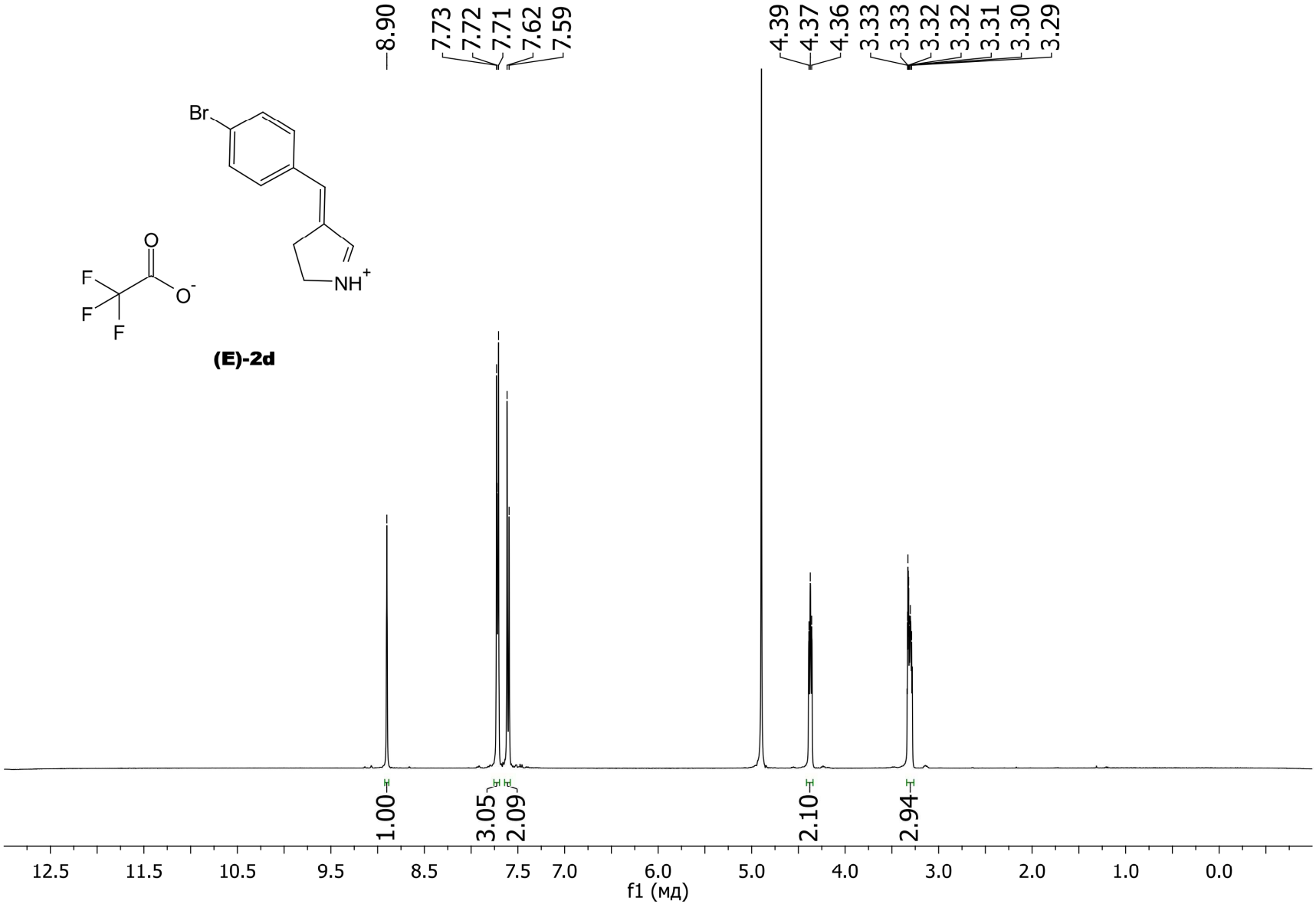


Figure S49: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2d**

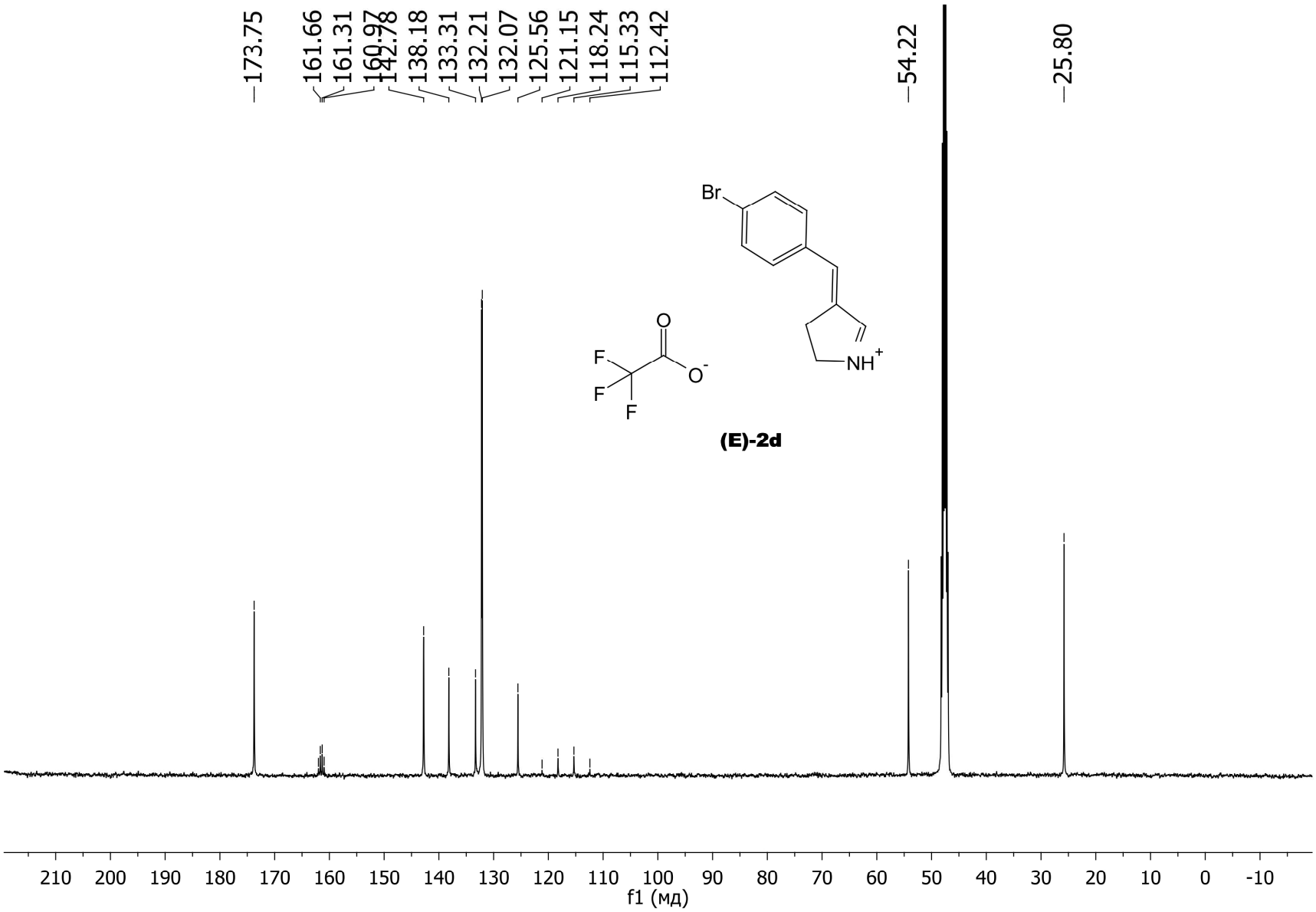


Figure S50: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2d**

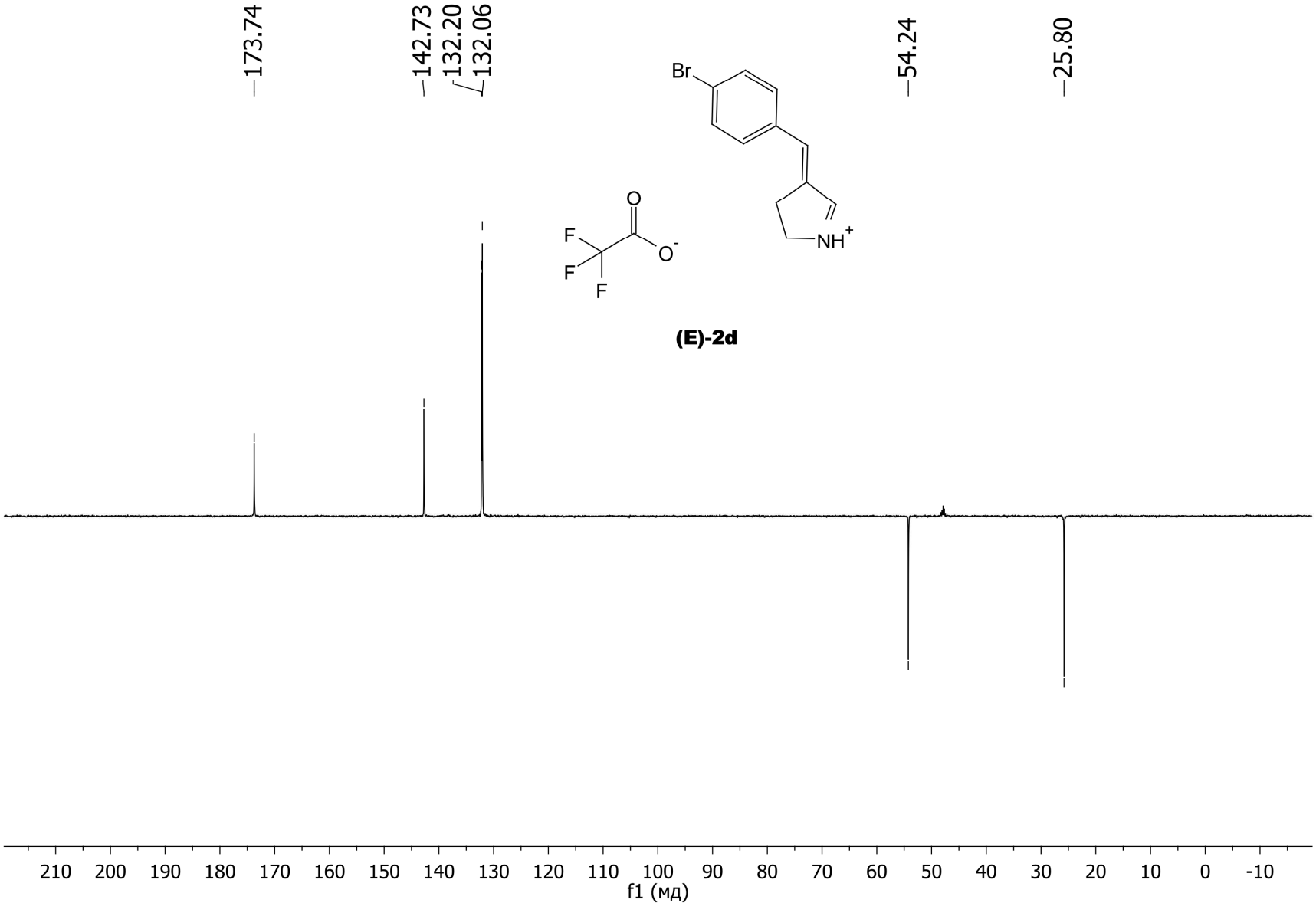


Figure S51: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2d**

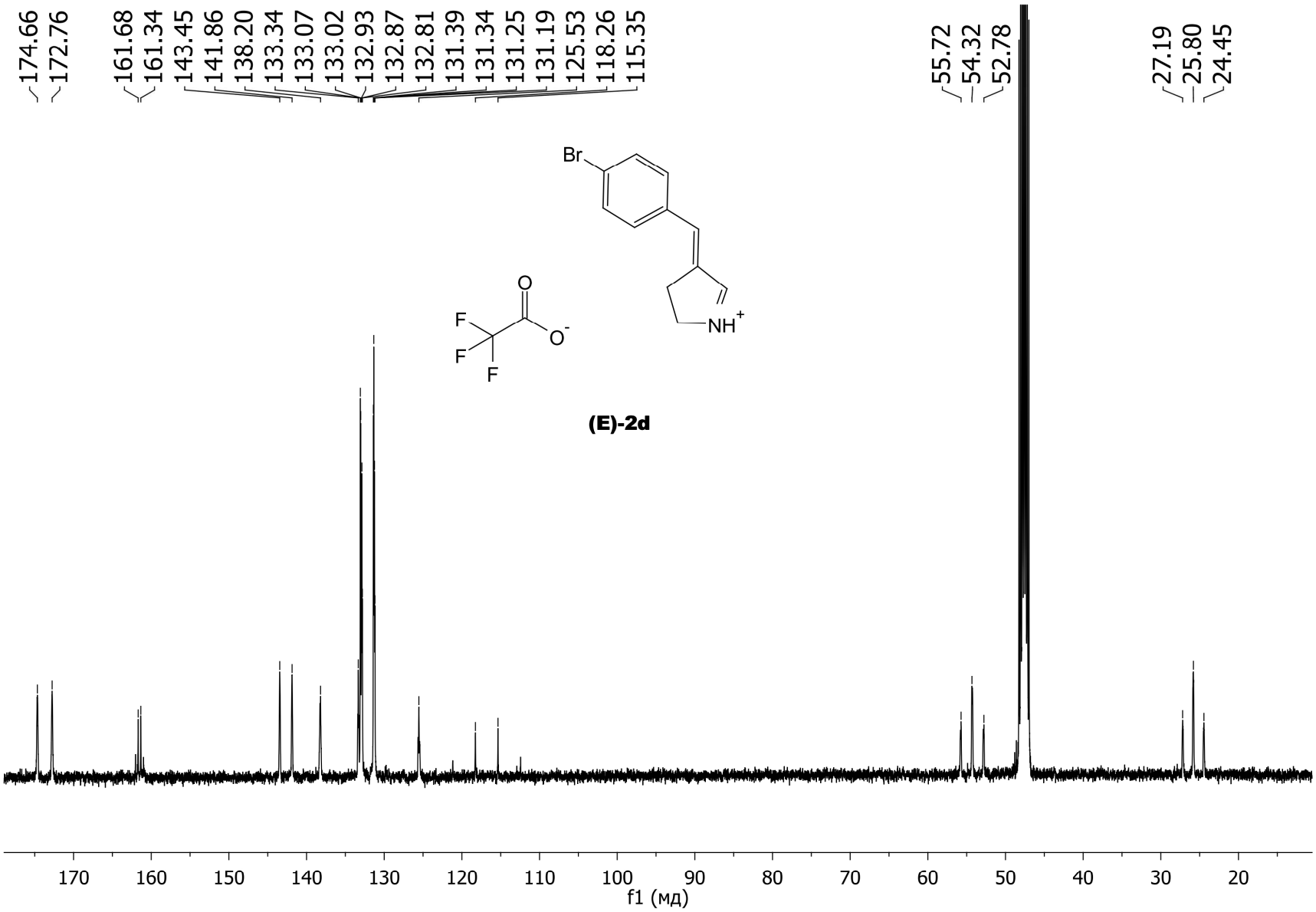


Figure S52: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2d**

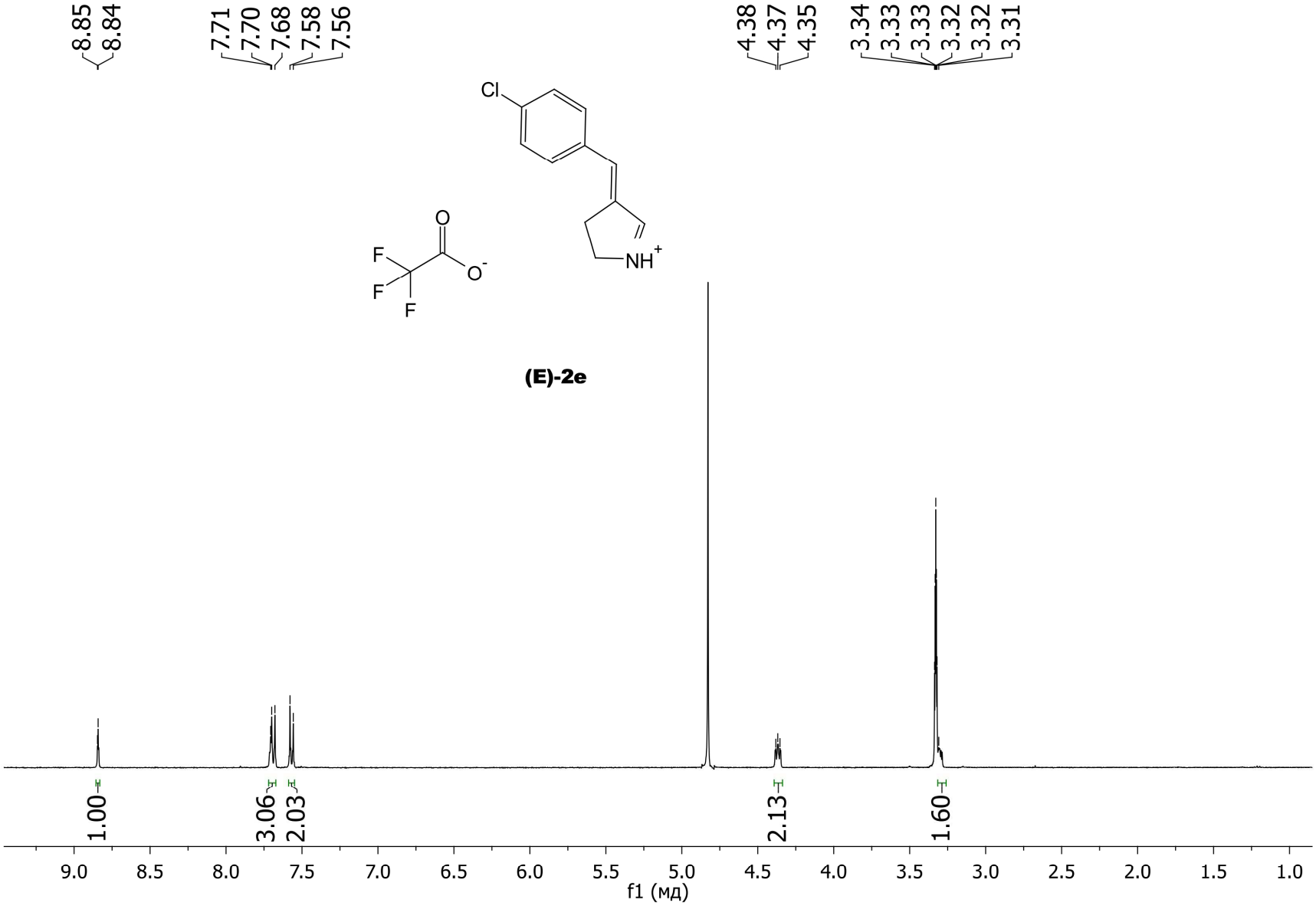


Figure S53: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2e**

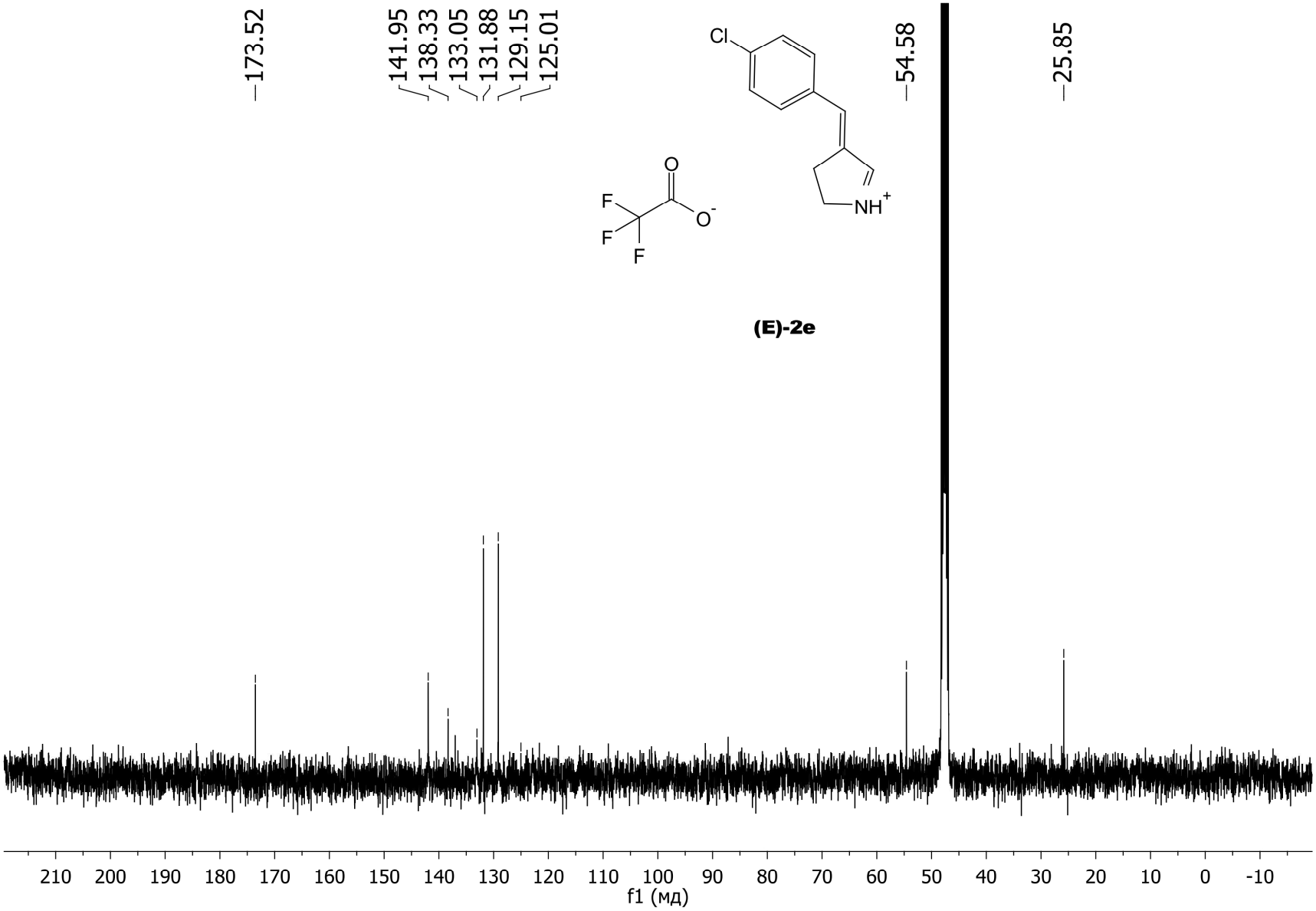


Figure S54: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2e**

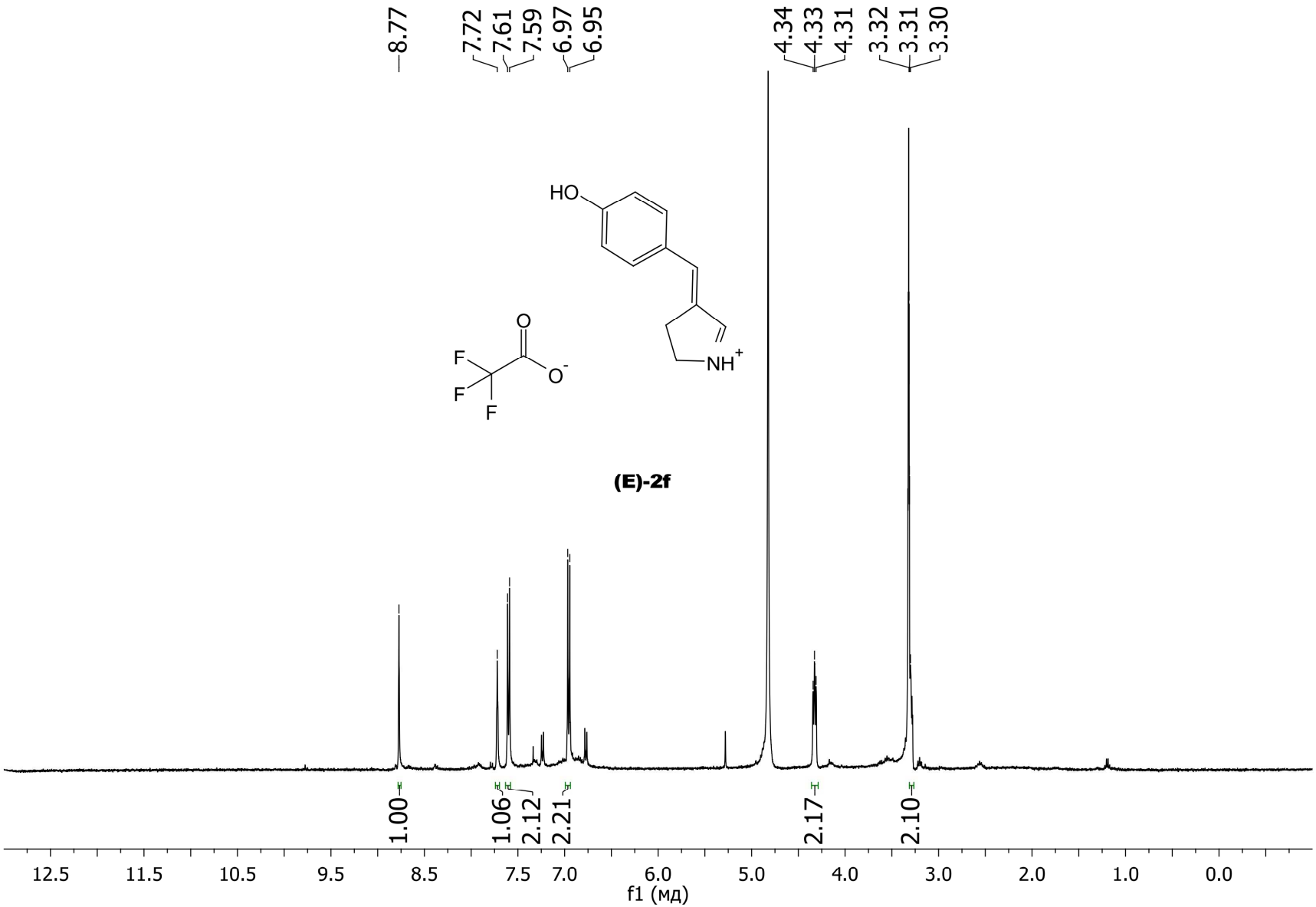


Figure S55: NMR ^{1}H spectrum ($(CD_3)_2SO$, 600MHz) of the compound (*E*)-**2f**

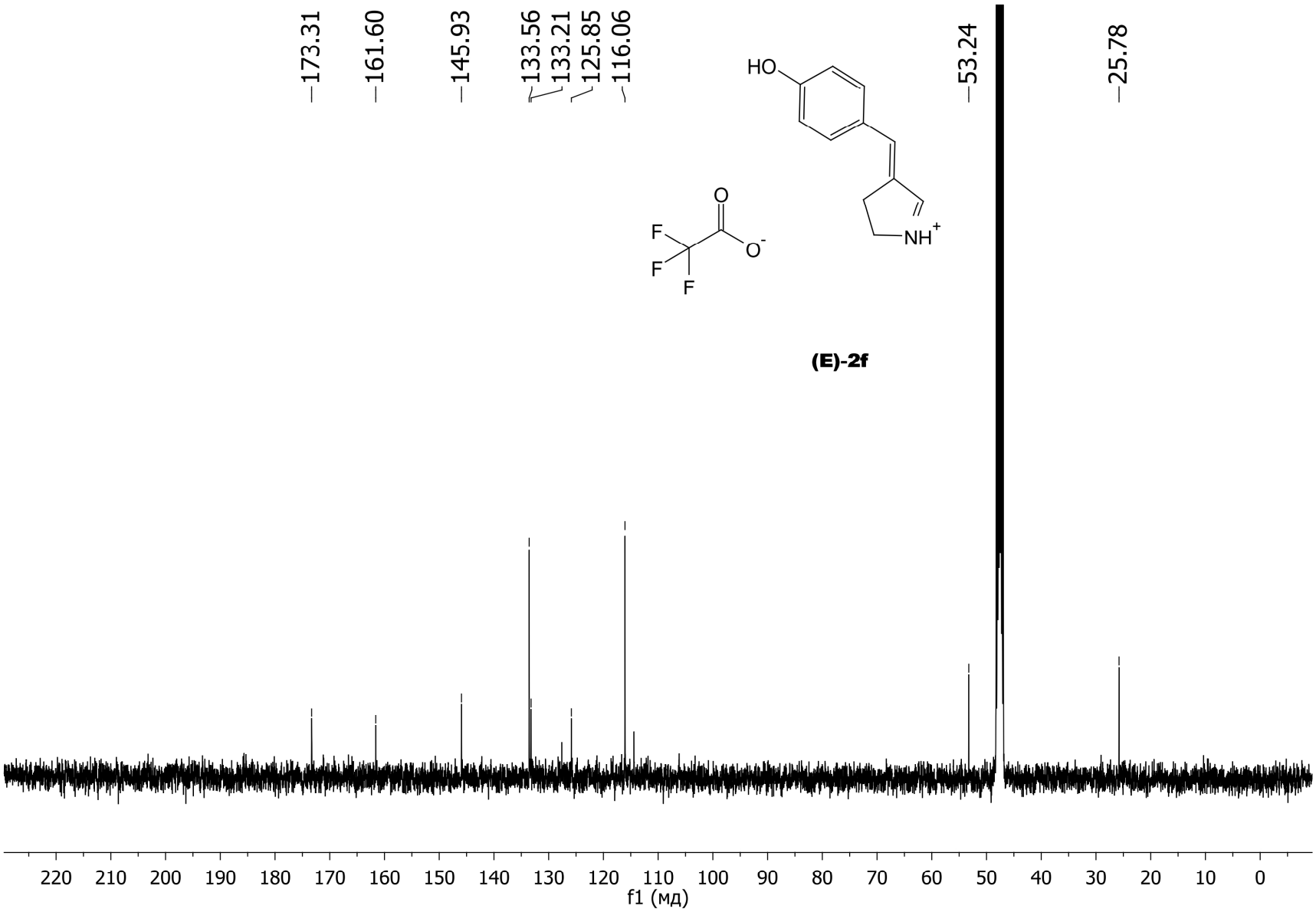


Figure S56: NMR $^{13}C\{^{1}H\}$ spectrum ($(CD_3)_2SO$, 600MHz) of the compound (*E*)-**2f**

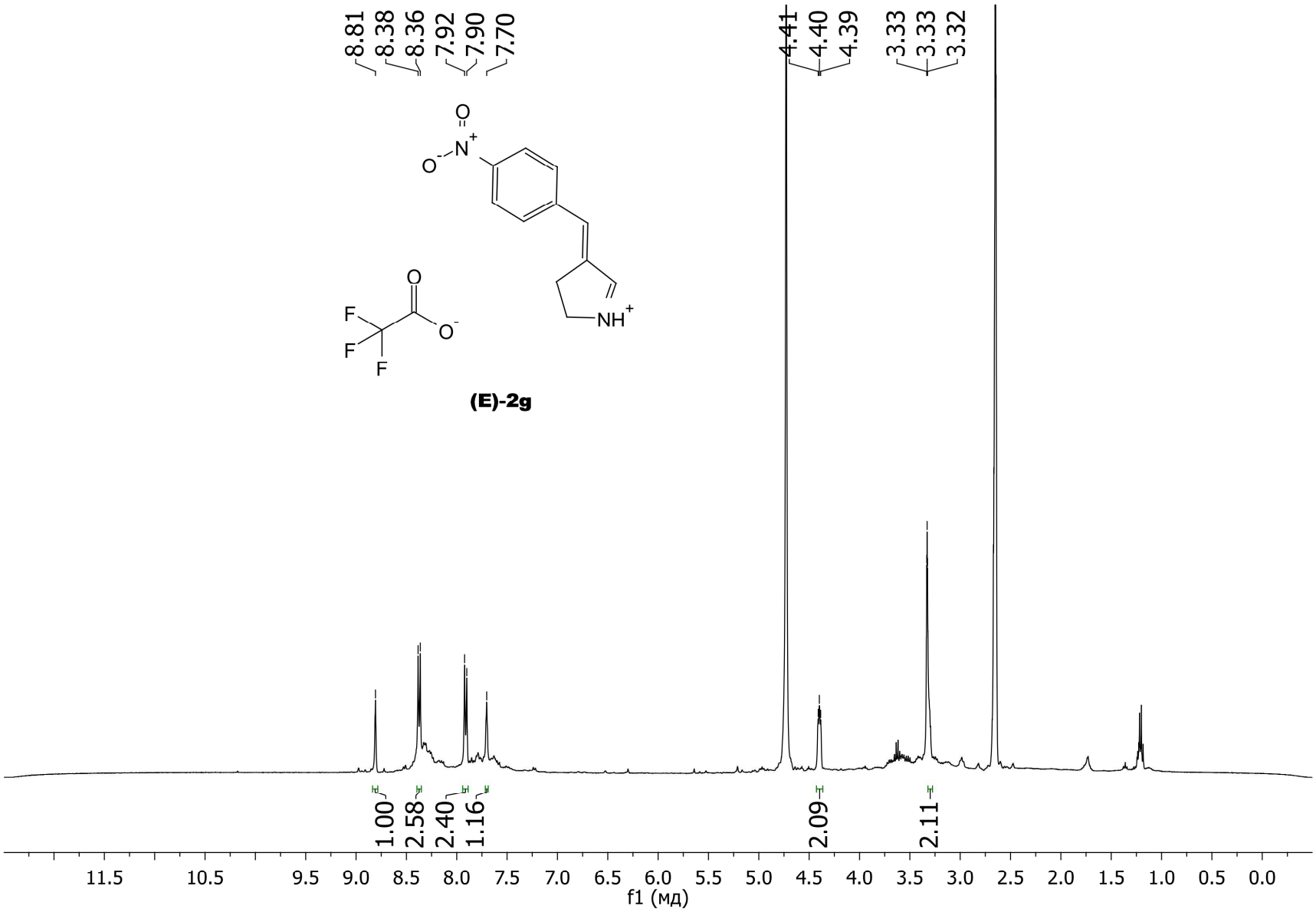


Figure S57: NMR ^{1}H spectrum ($(CD_3)_2SO$, 600MHz) of the compound (*E*)-**2g**

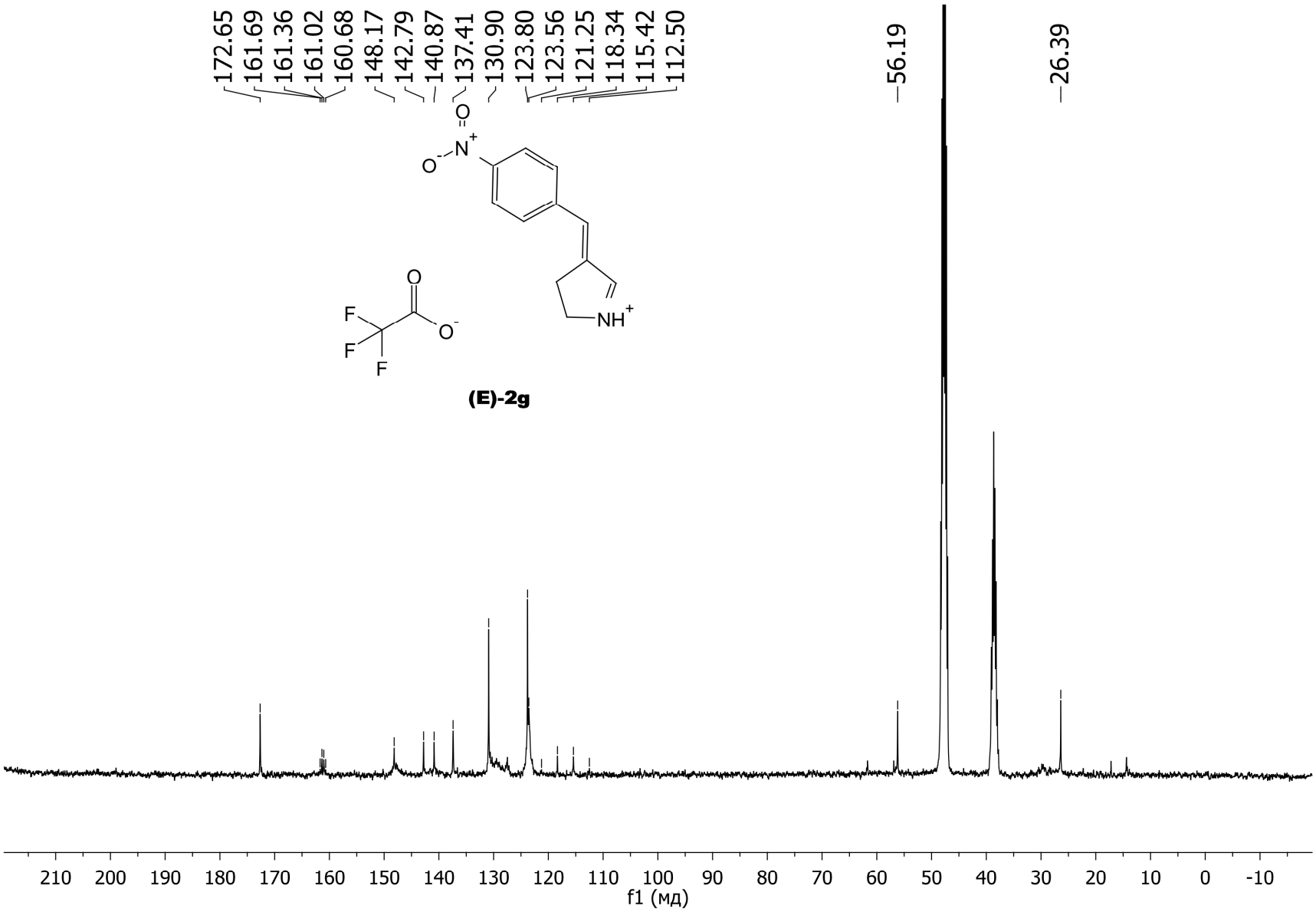


Figure S58: NMR $^{13}C\{^{1}H\}$ spectrum ($(CD_3)_2SO$, 600MHz) of the compound (*E*)-**2g**

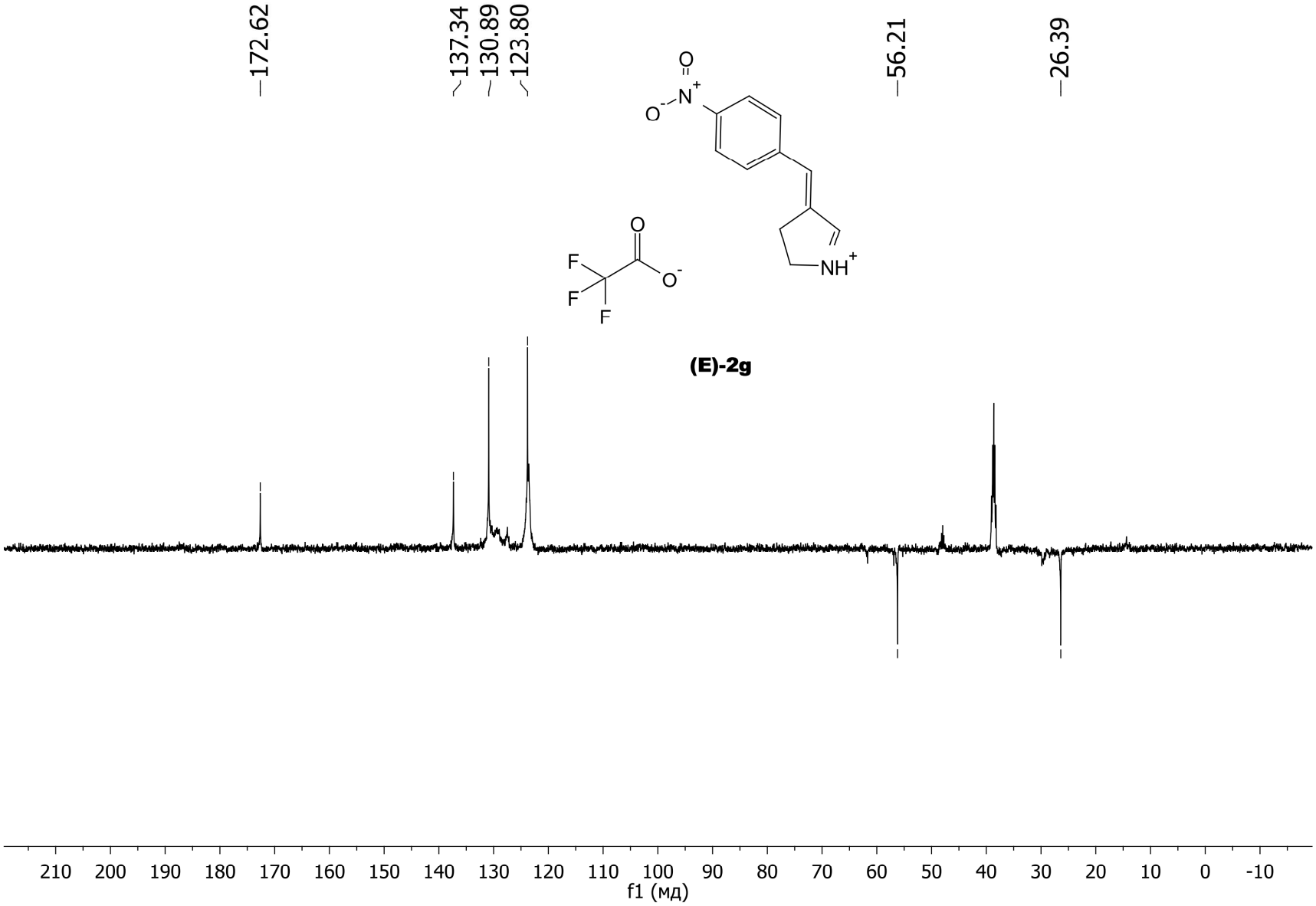


Figure S59: NMR ^{13}C DEPT spectrum ($(CD_3)_2SO$, 600MHz, 135° pulse) of the compound (*E*)-**2g**

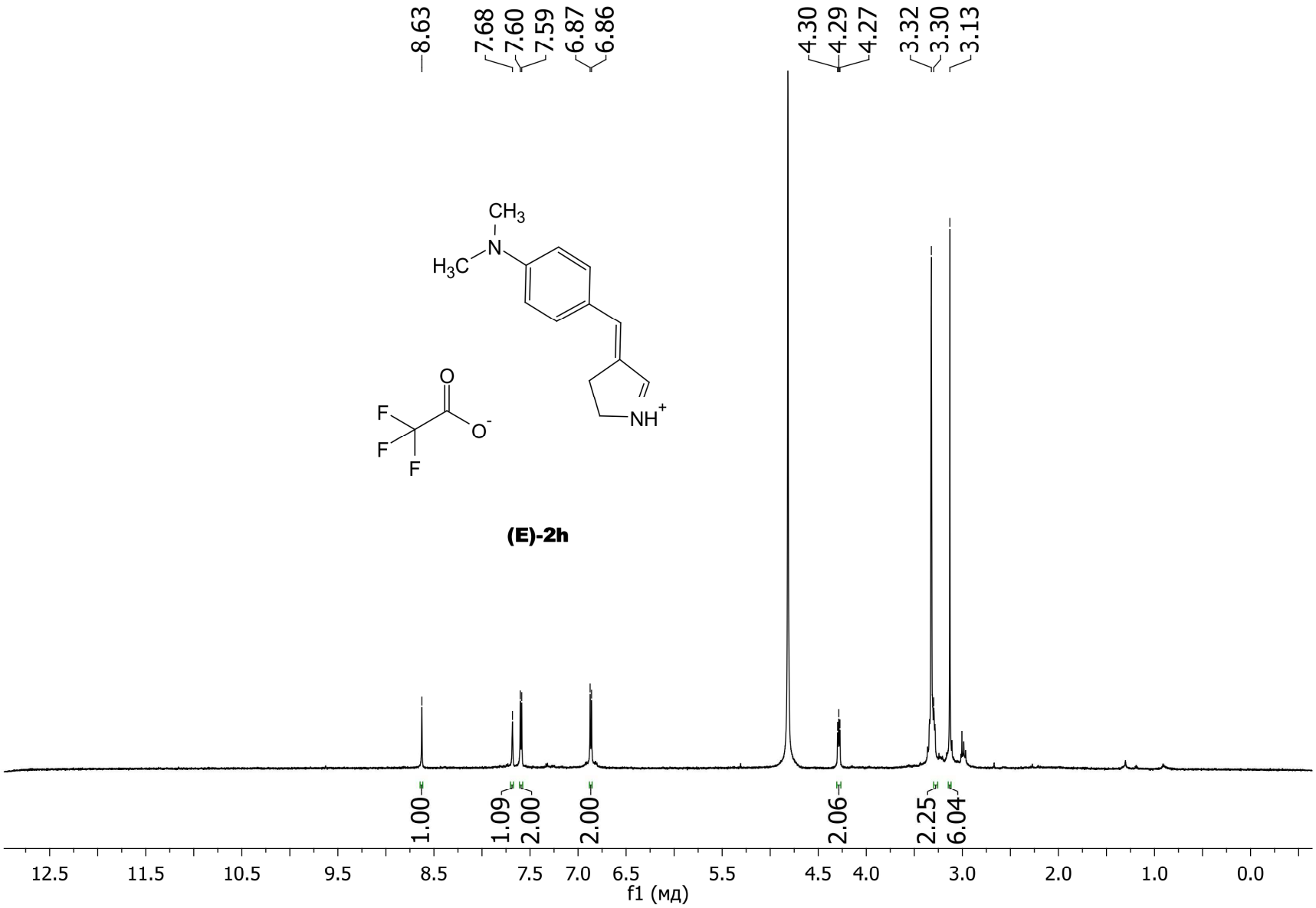


Figure S60: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2h**

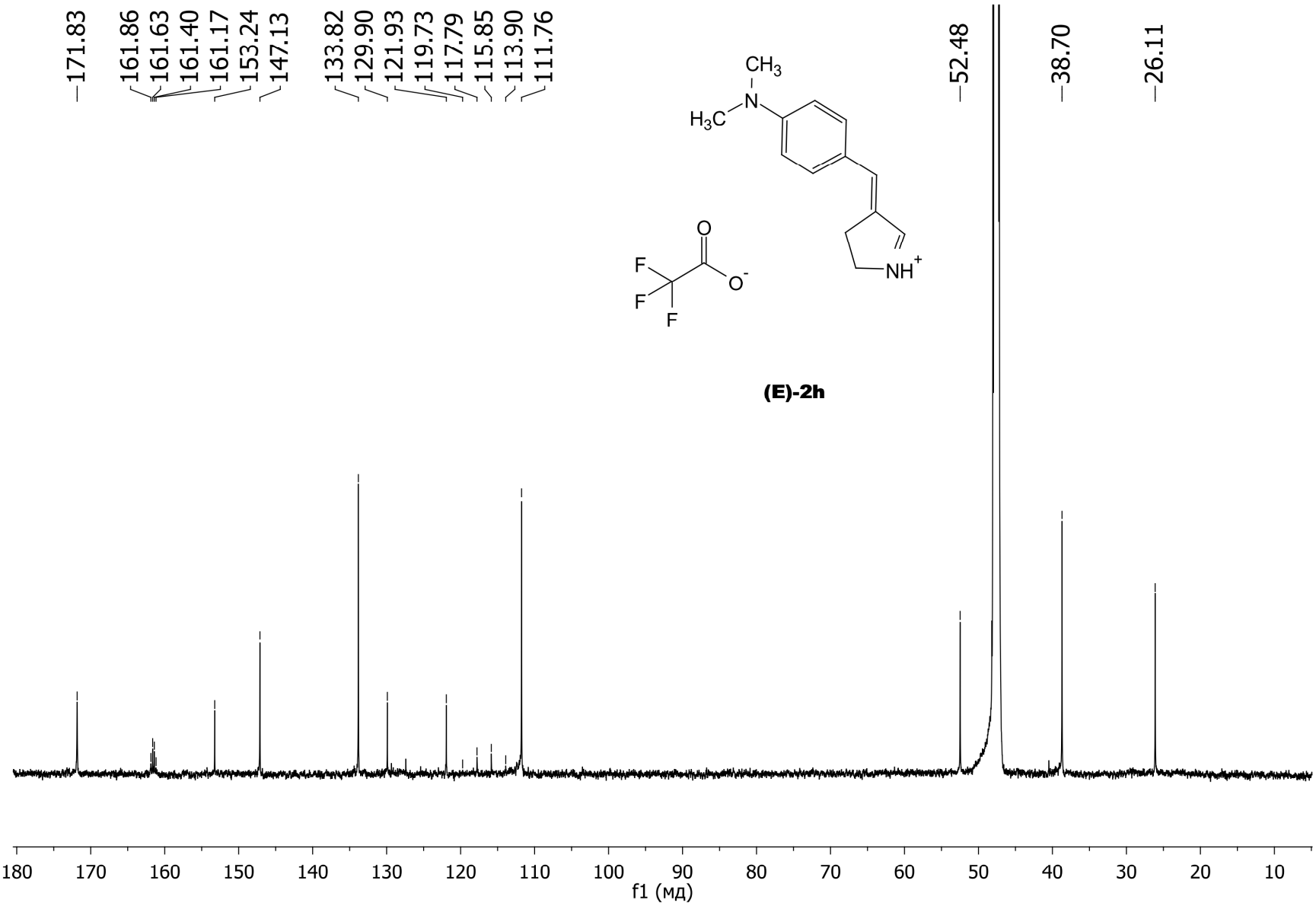


Figure S61: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2h**

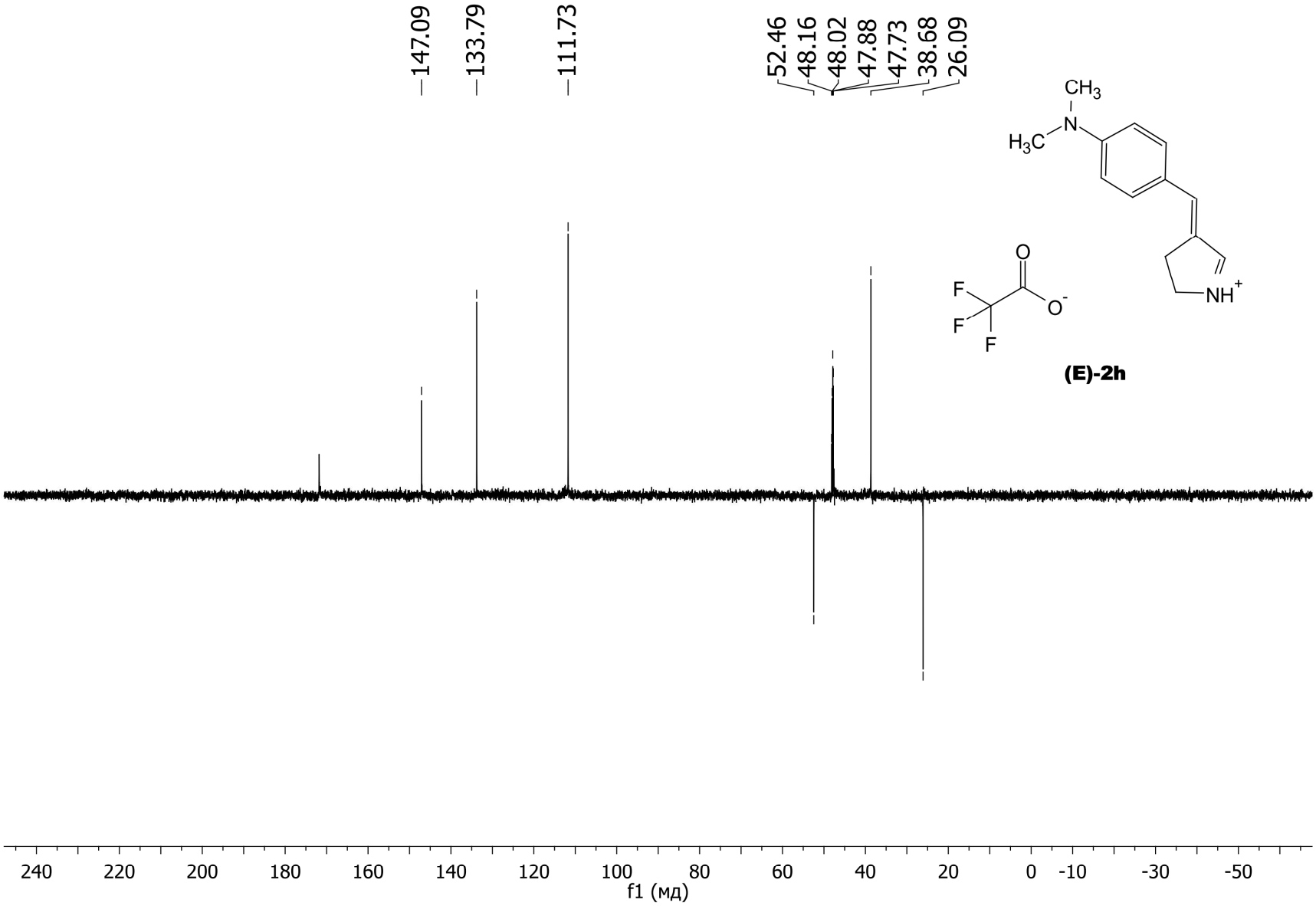


Figure S62: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2h**

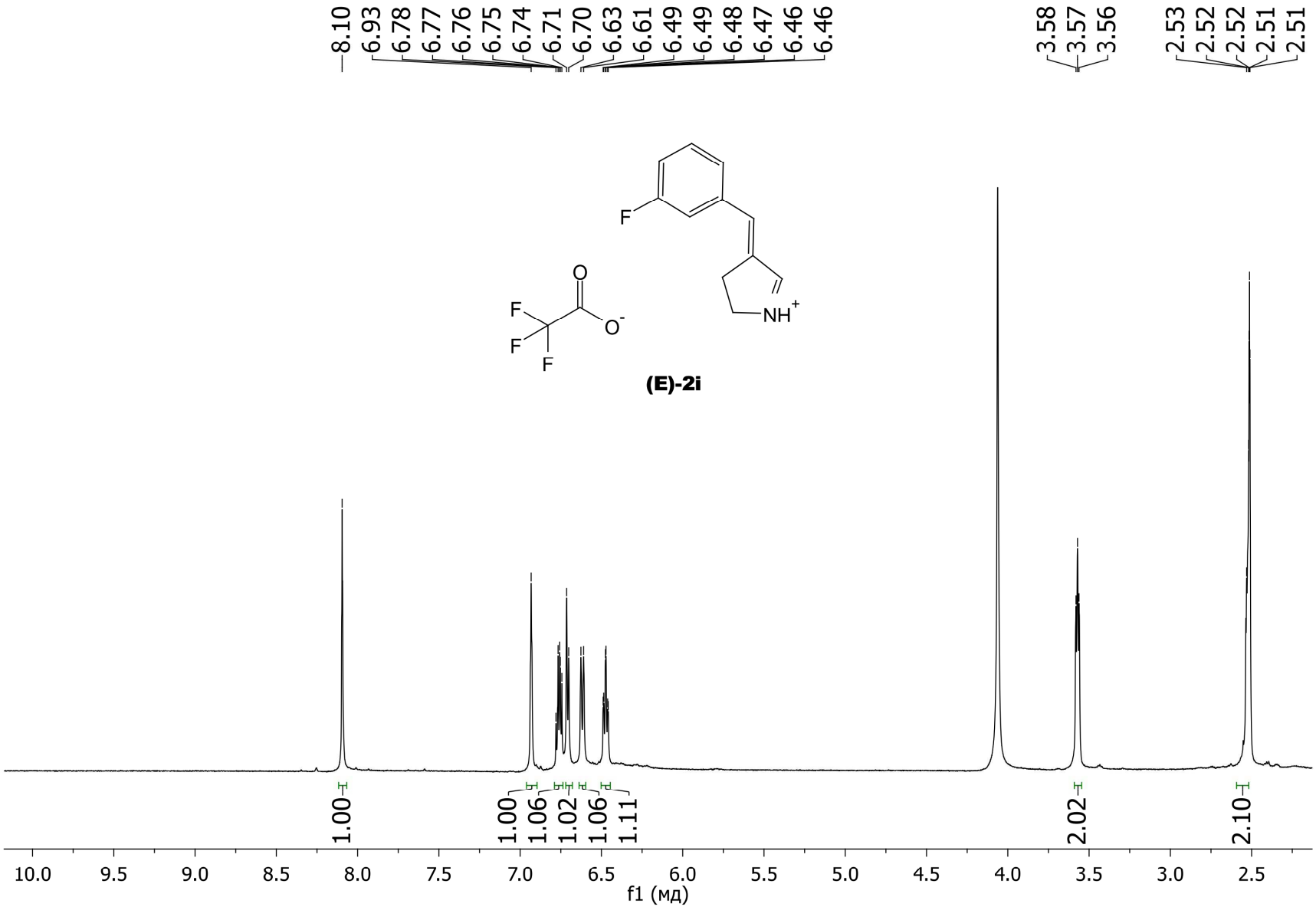


Figure S63: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2i**

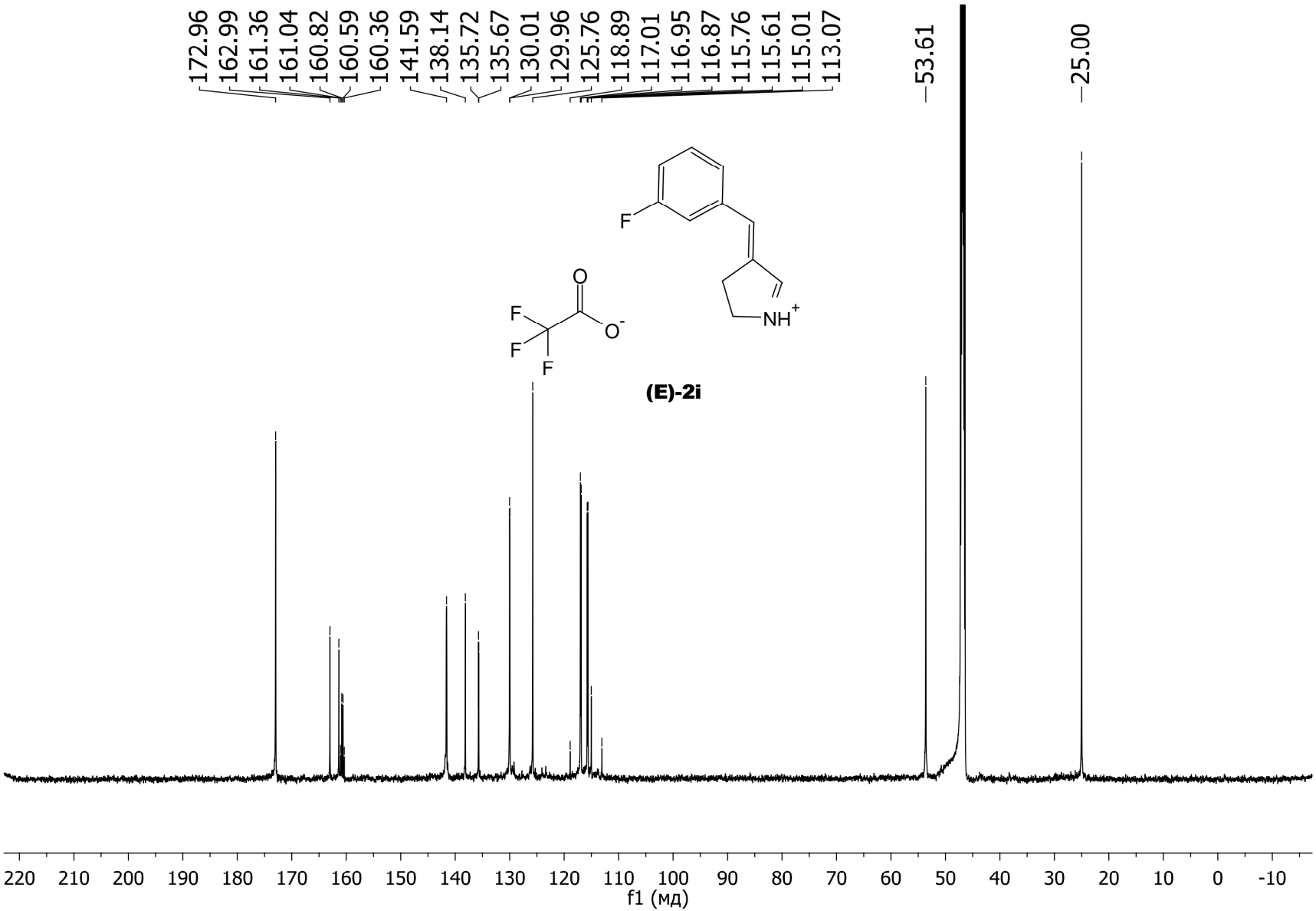


Figure S64: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2i**

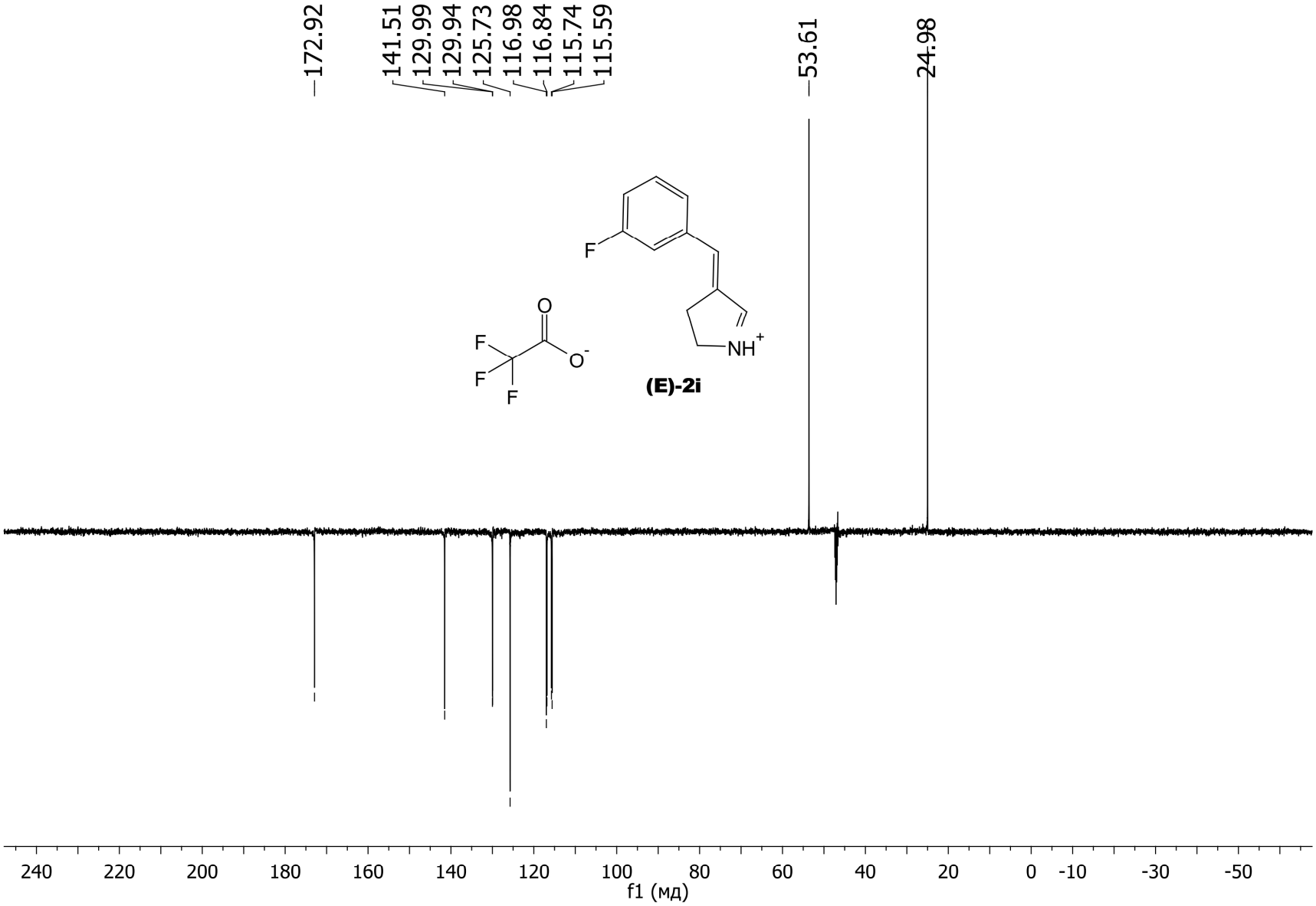


Figure S65: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2i**

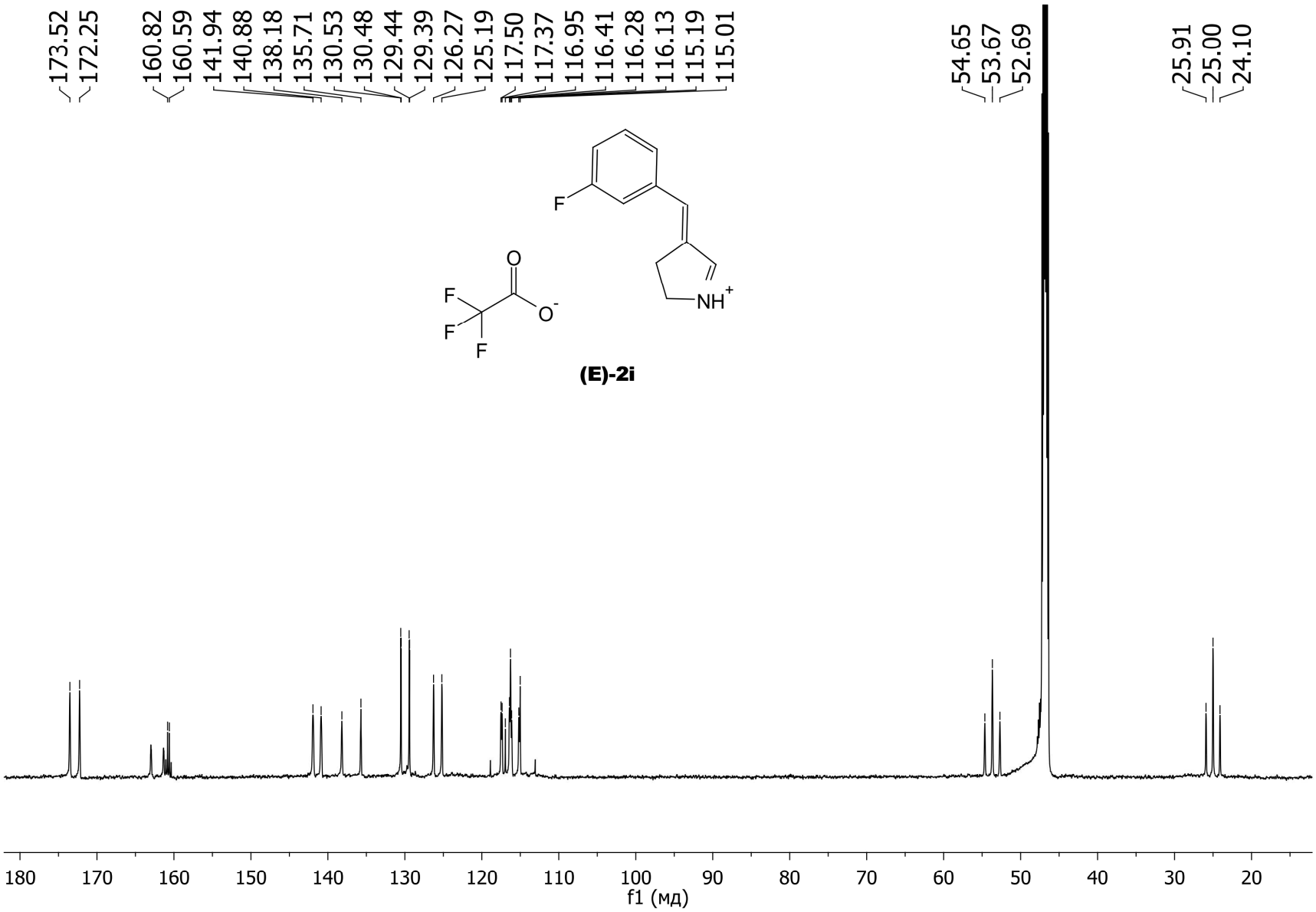


Figure S66: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2i**

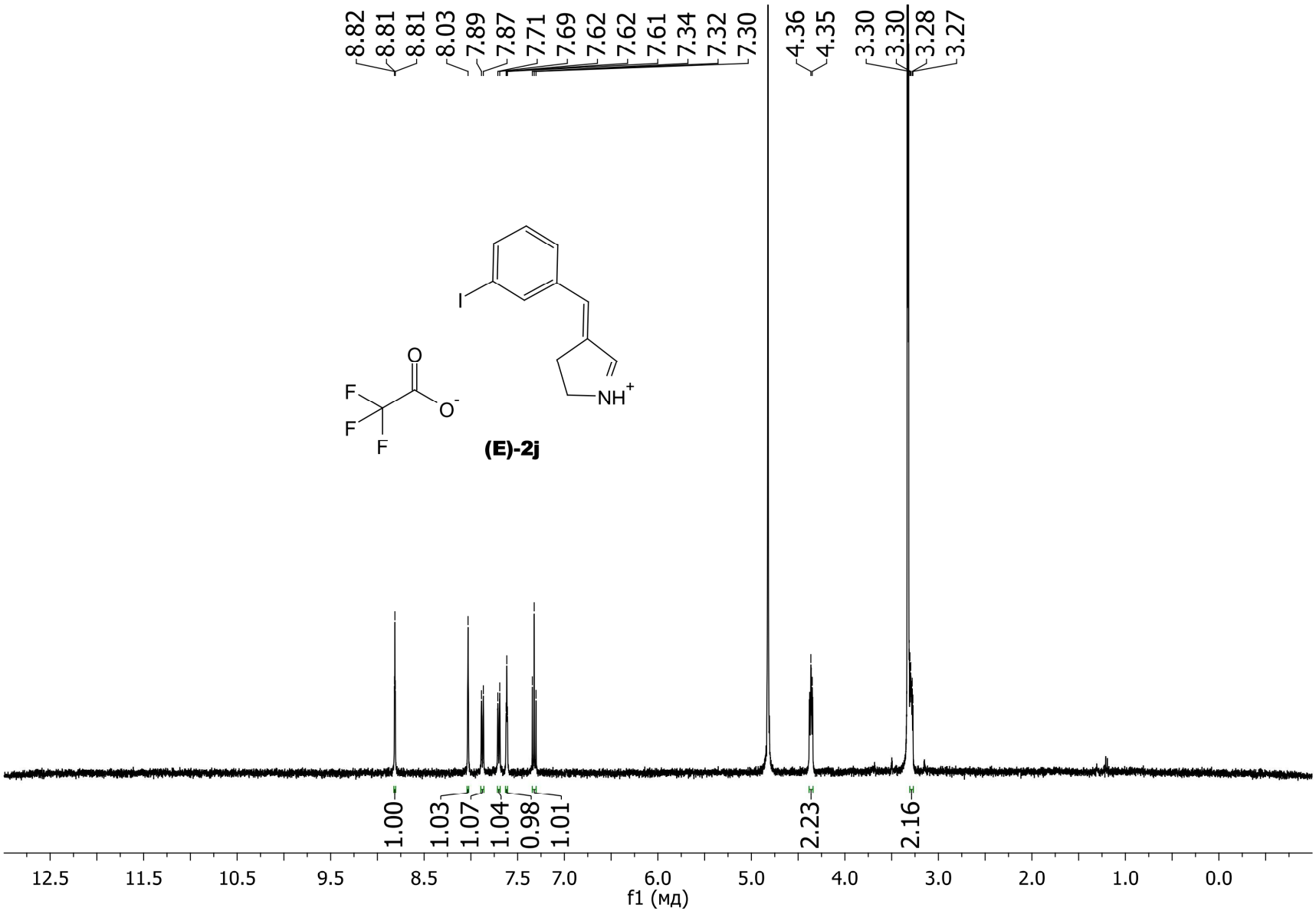


Figure S67: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2j**

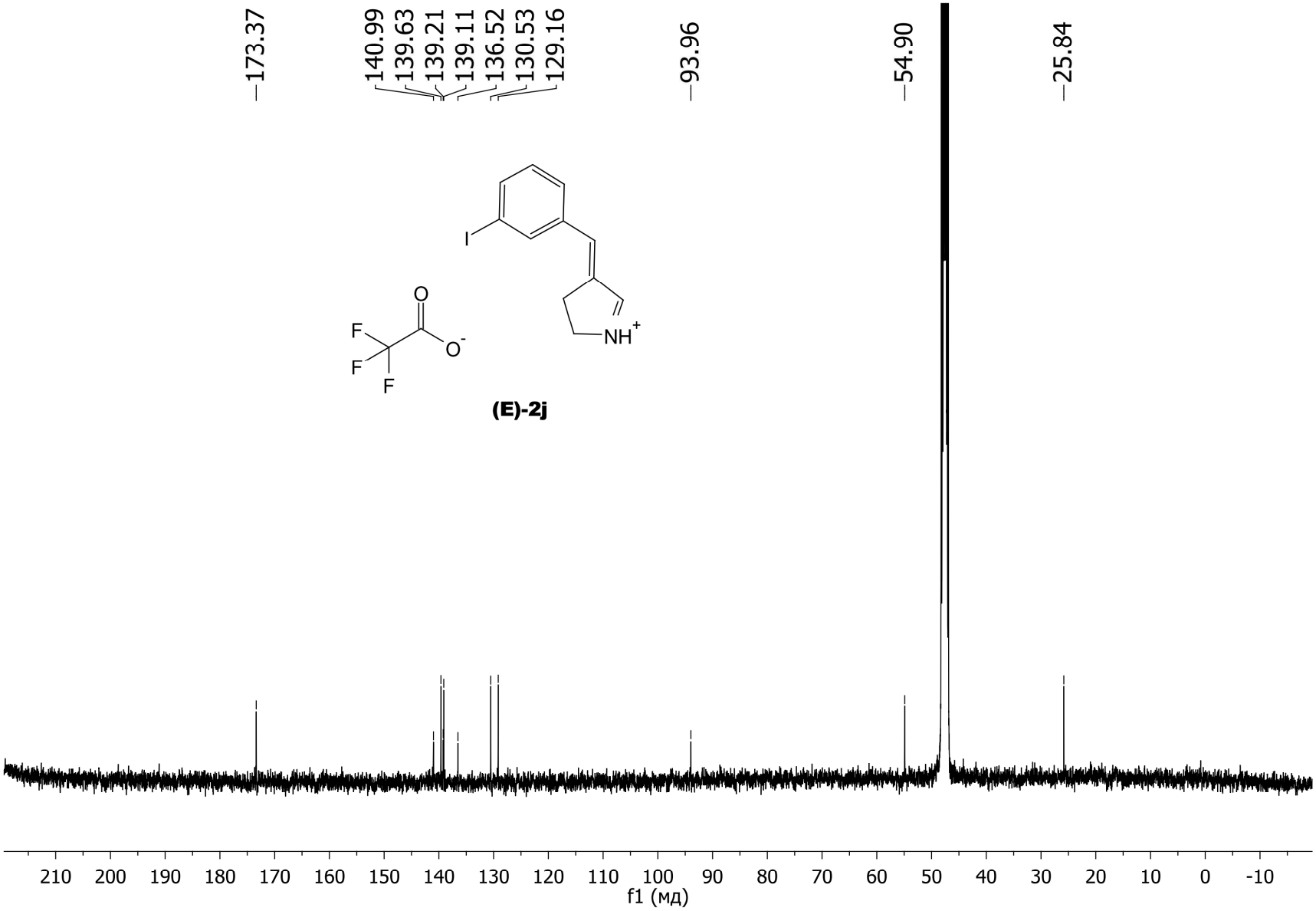


Figure S68: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2j**

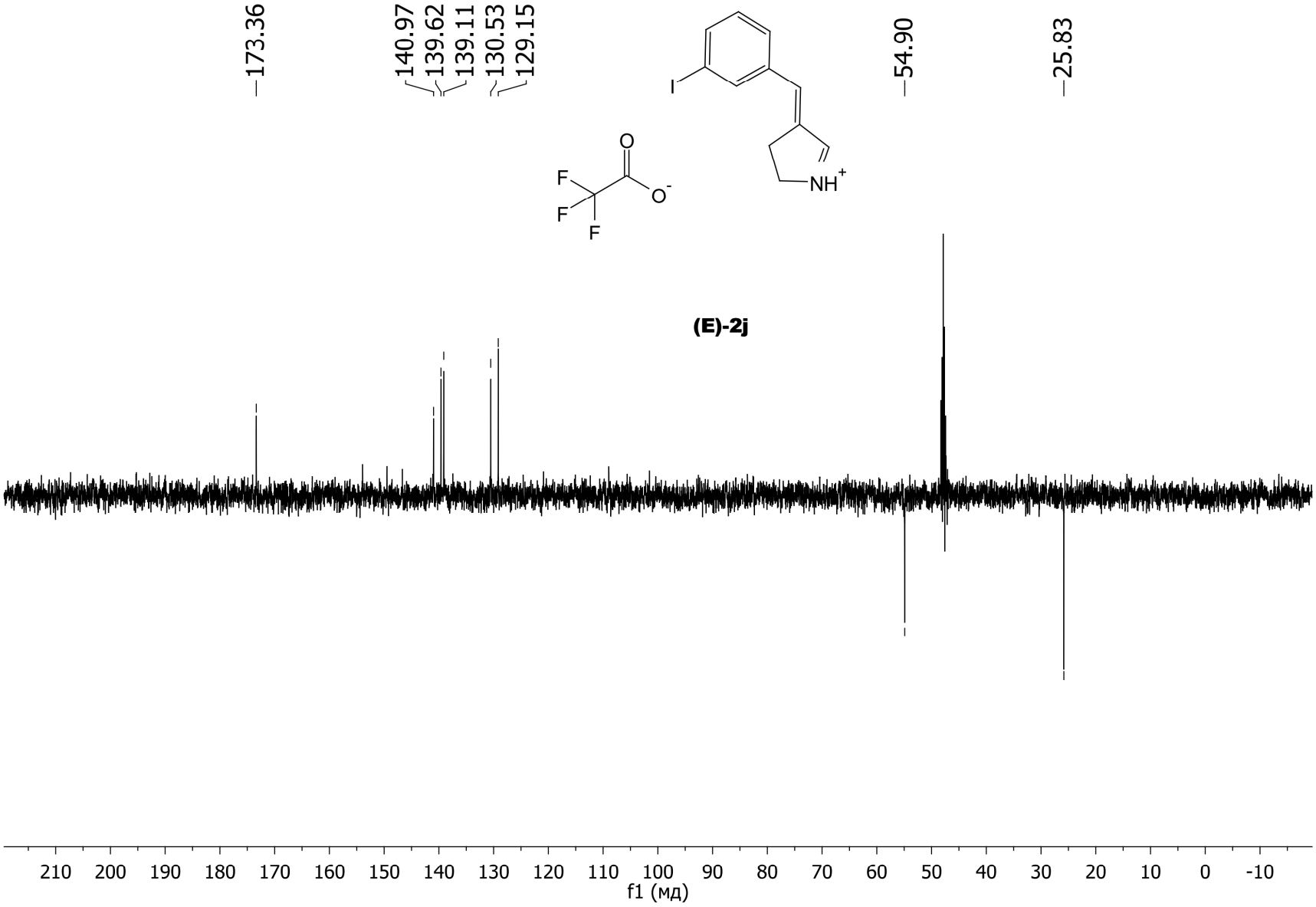


Figure S69: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2j**

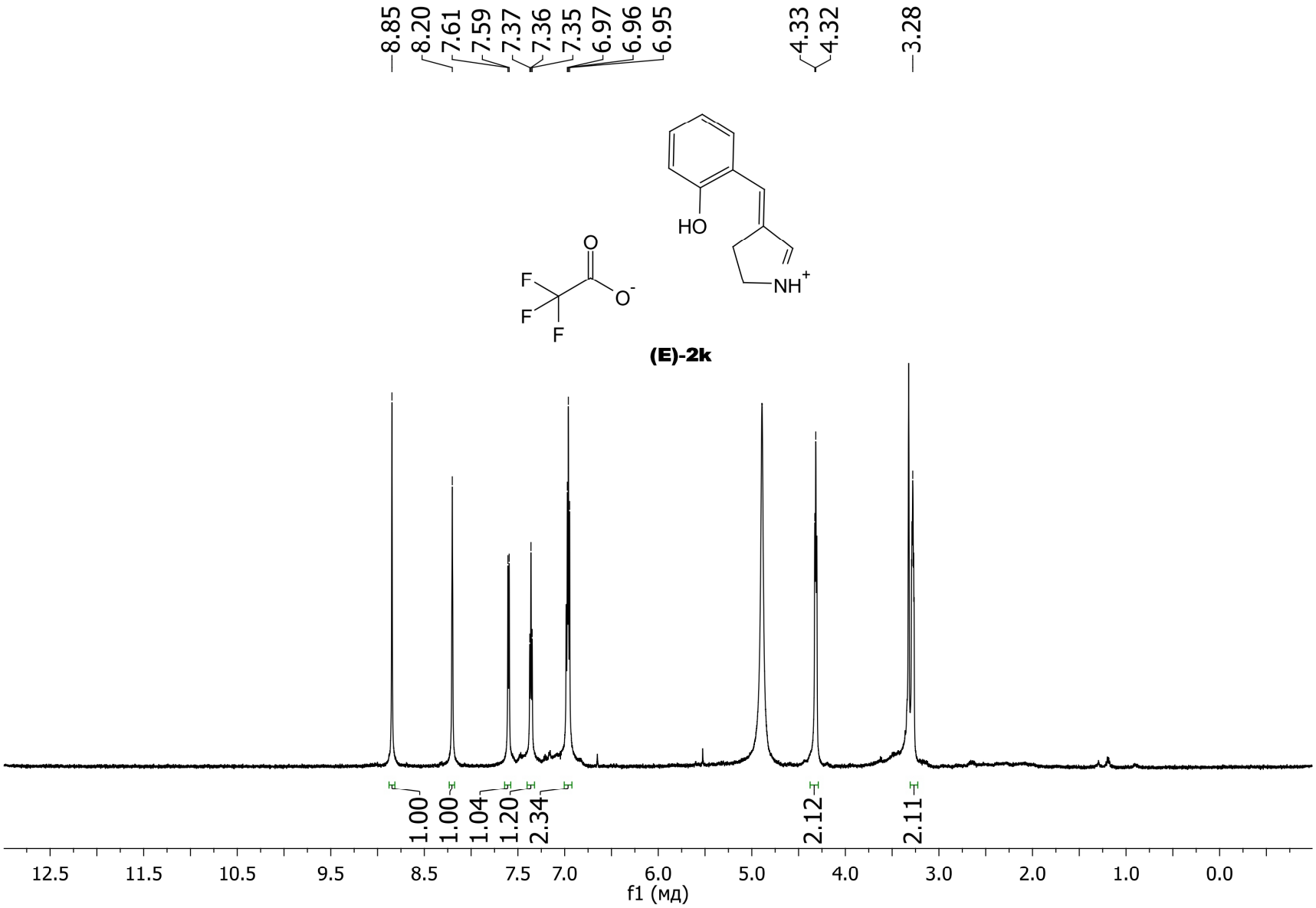


Figure S70: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2k**

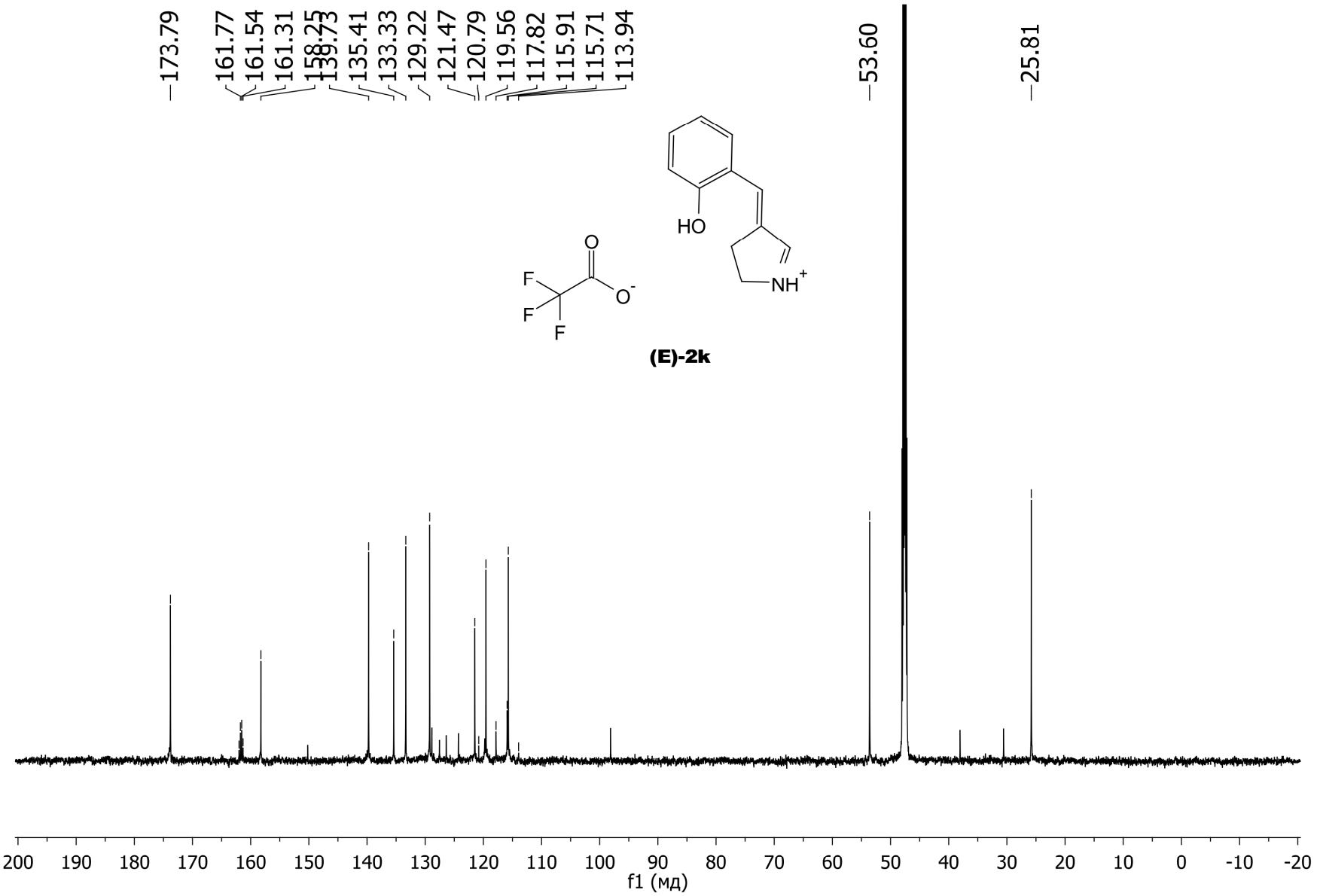


Figure S71: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2k**

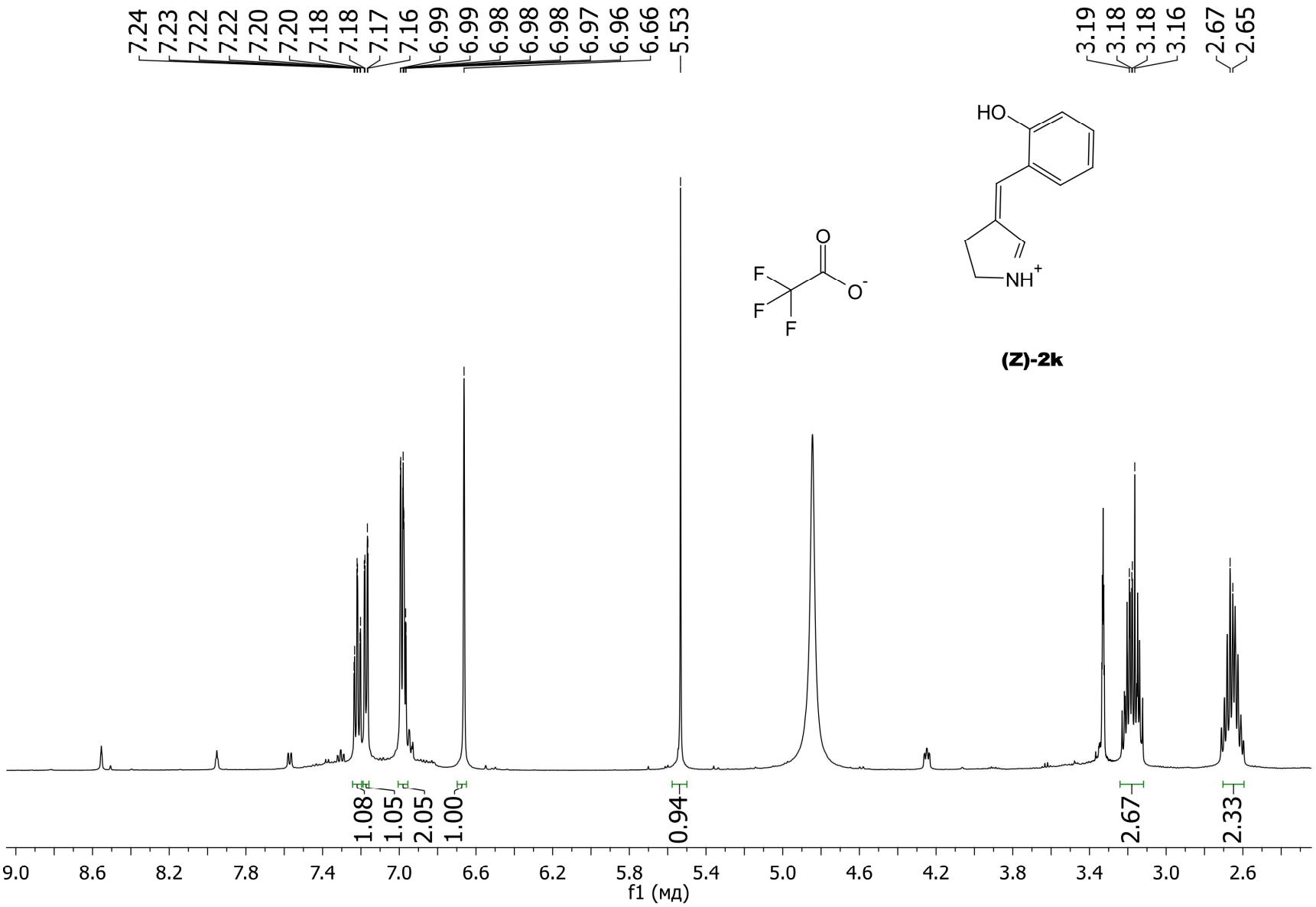


Figure S72: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*Z*)-**2k**

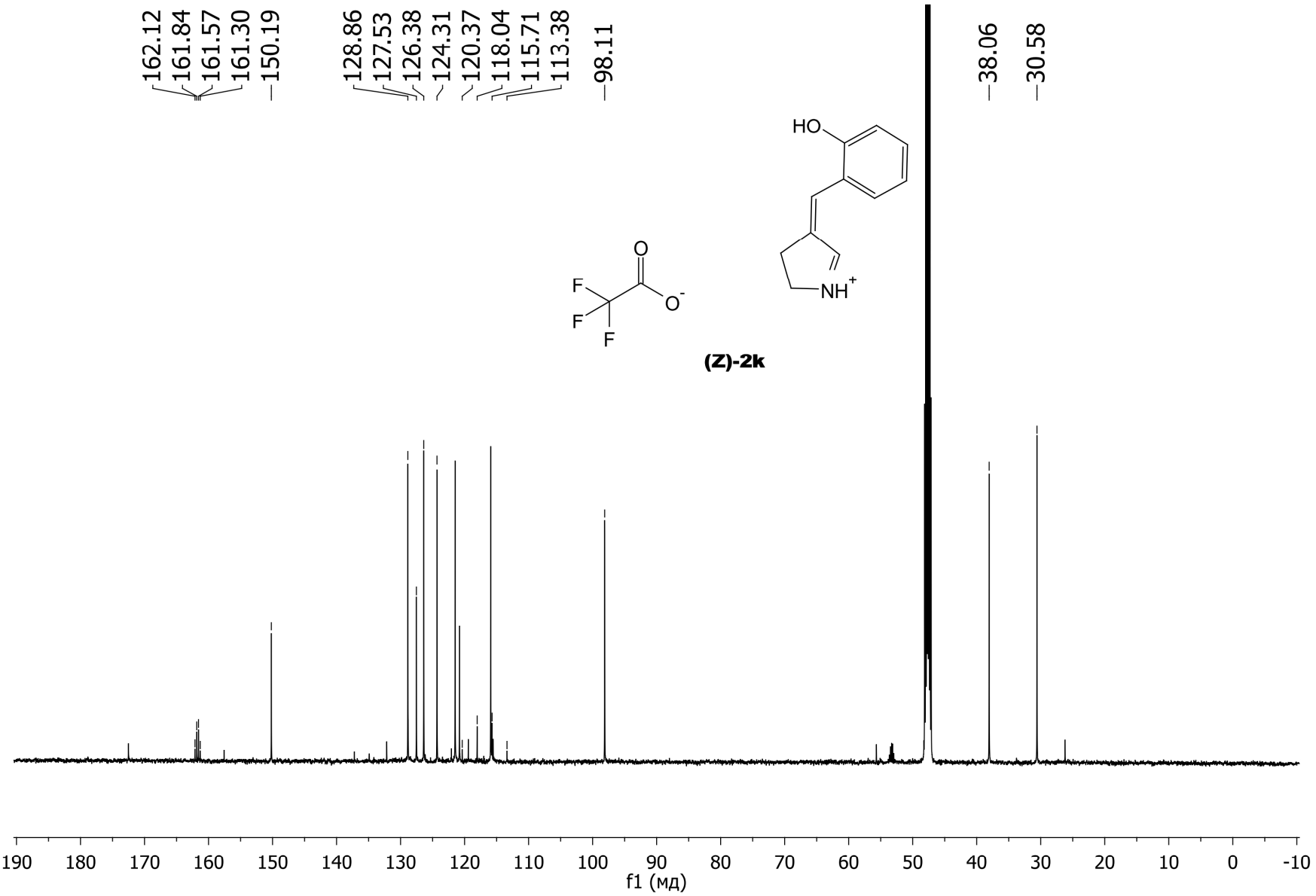


Figure S73: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*Z*)-**2k**

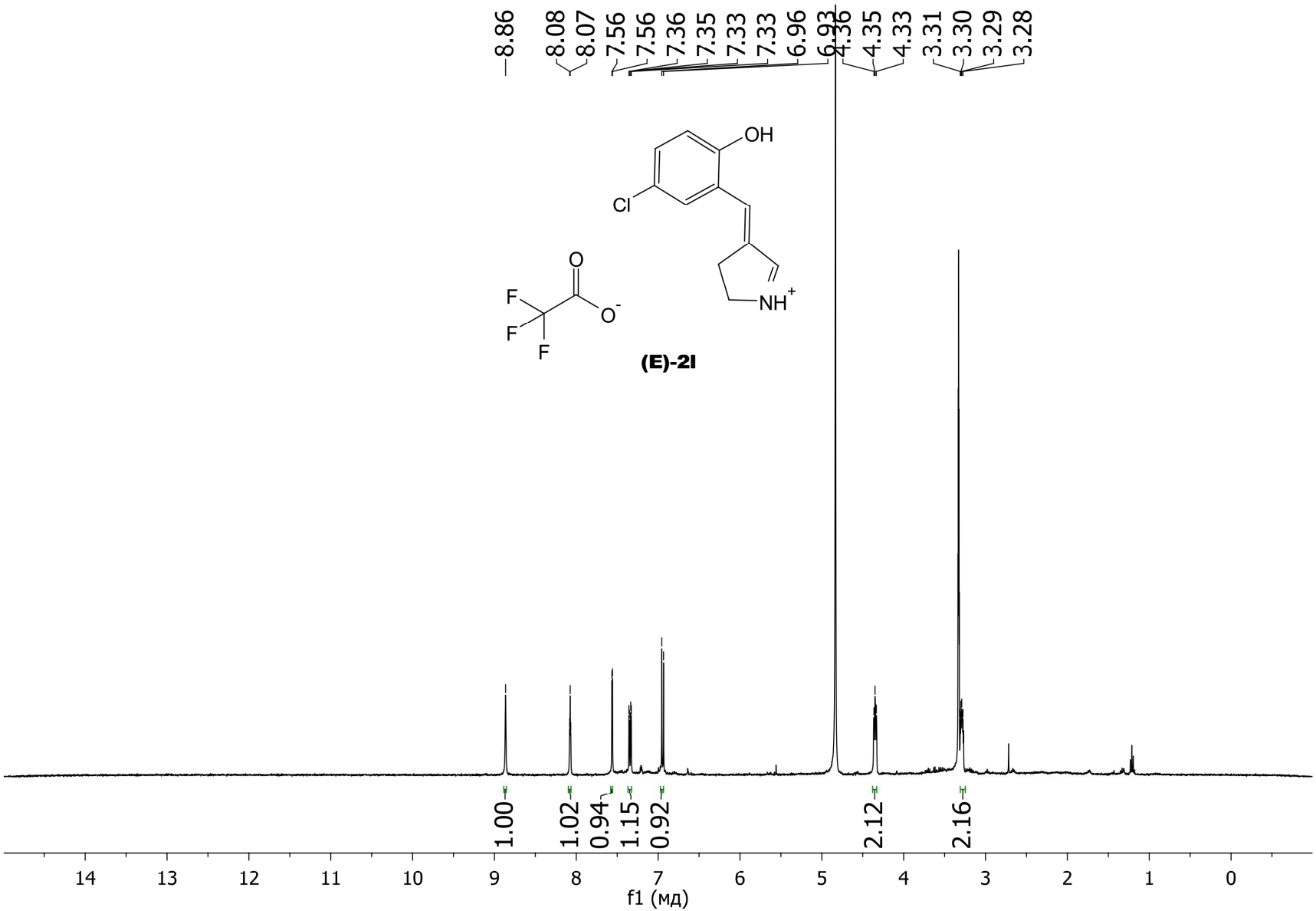


Figure S74: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2l**

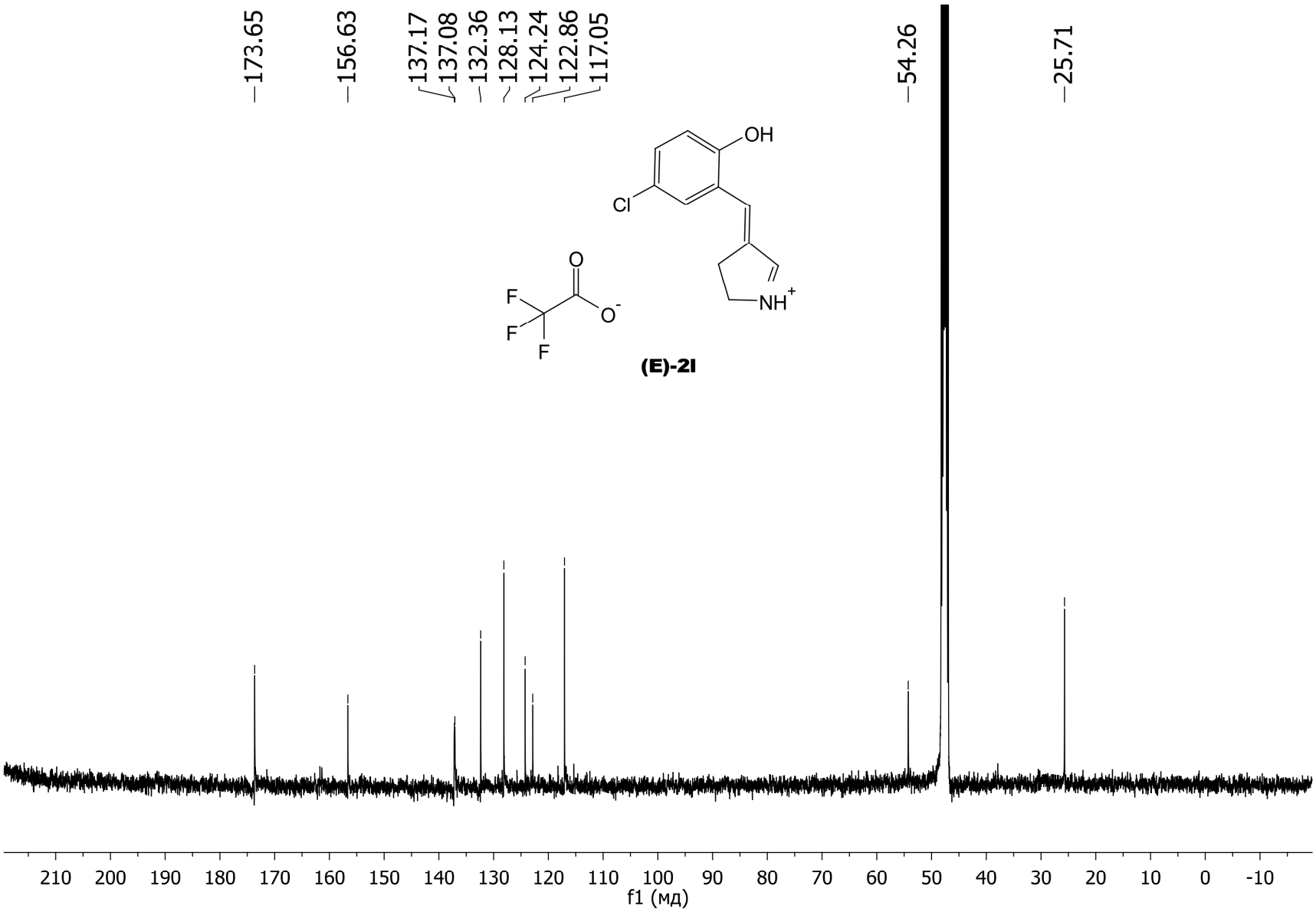


Figure S75: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2l**

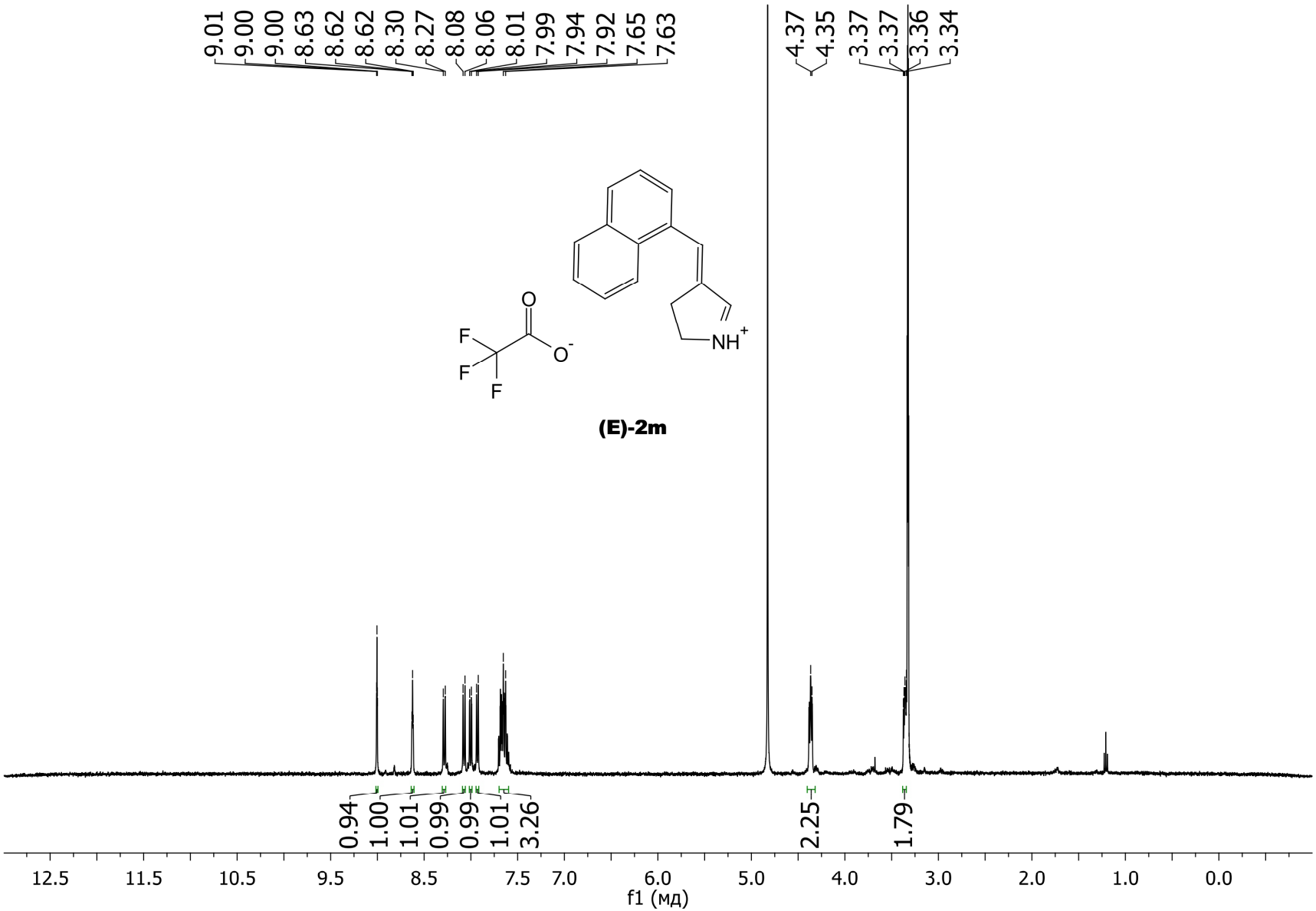


Figure S76: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2m**

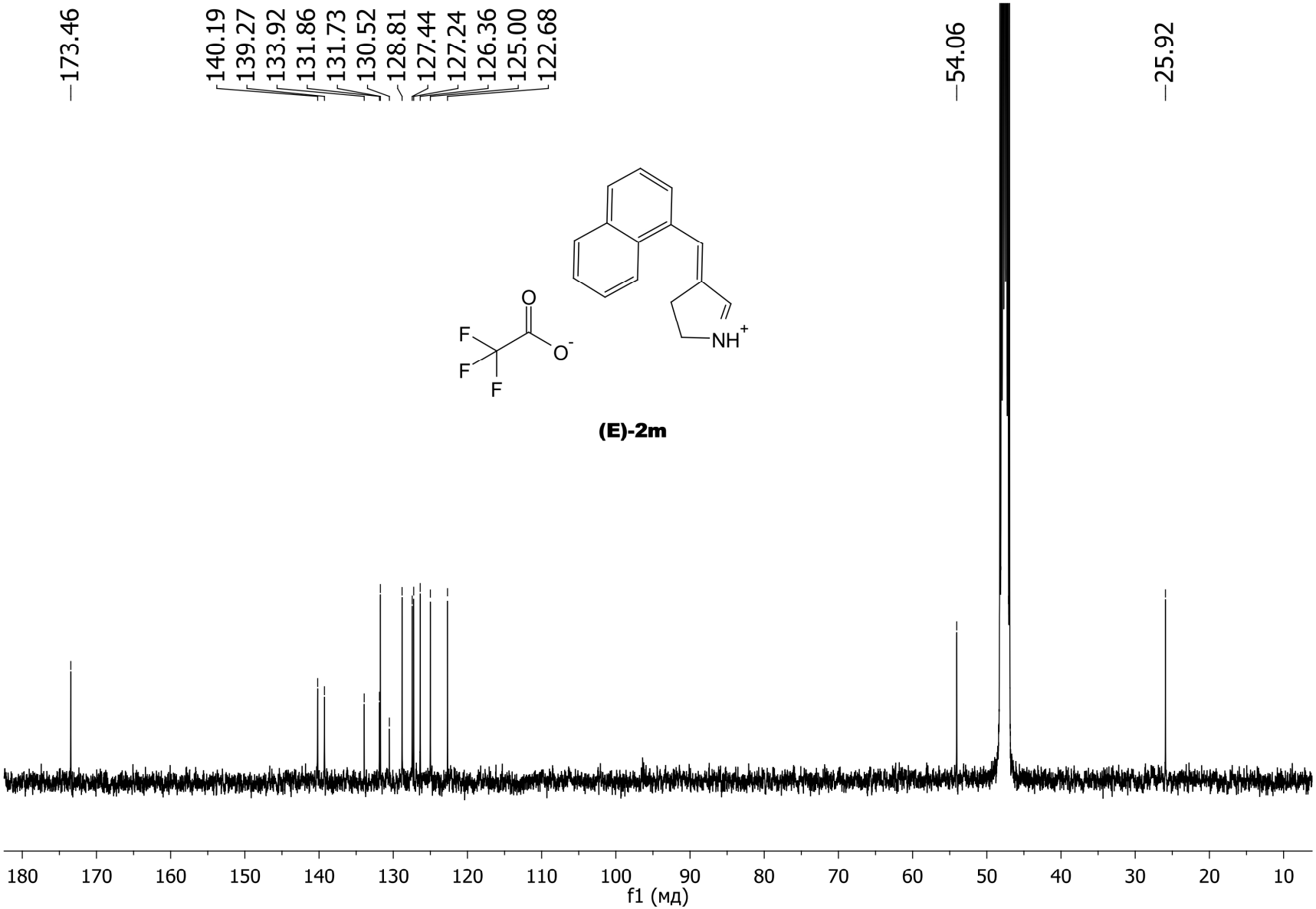


Figure S77: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2m**

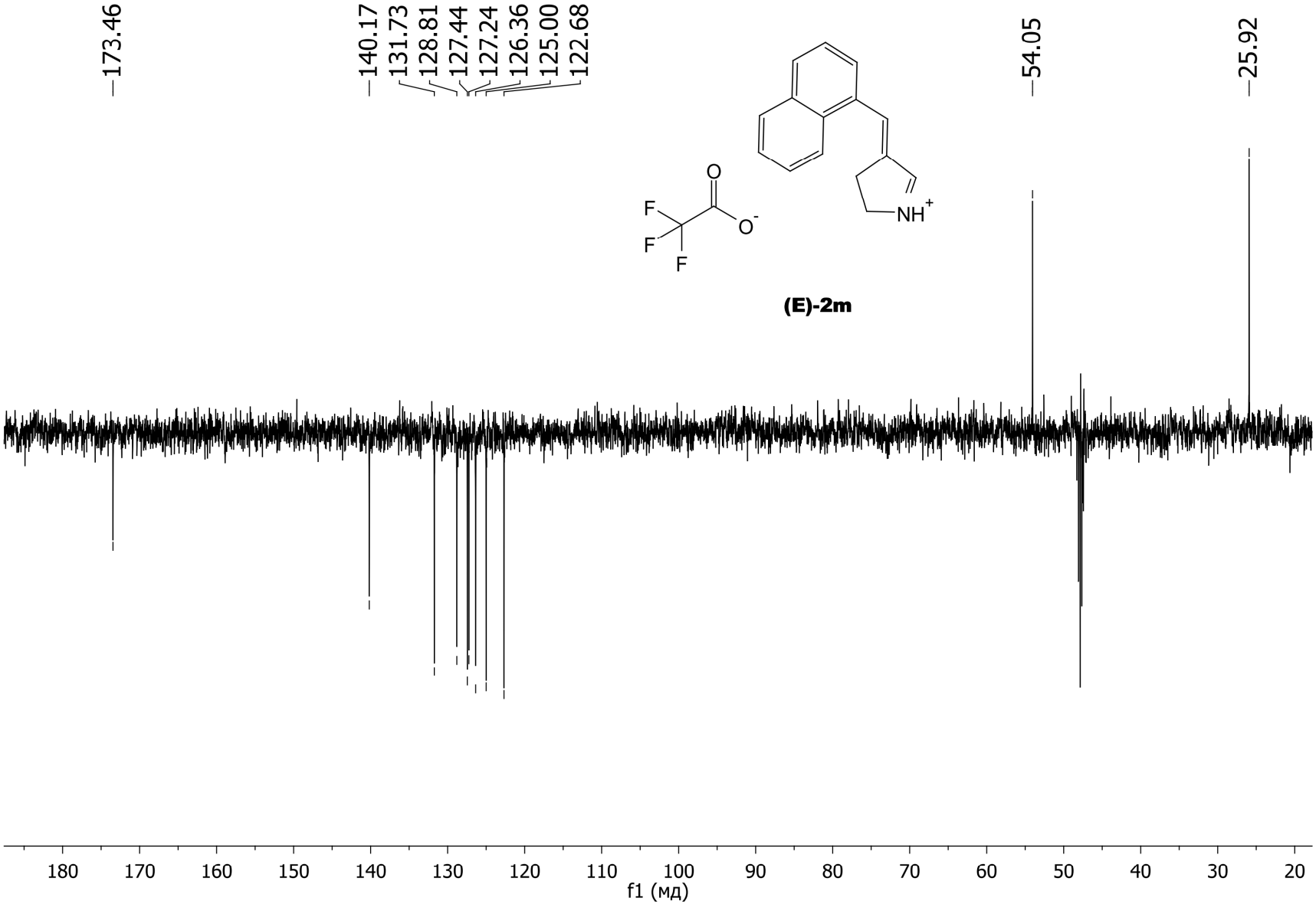


Figure S78: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2m**

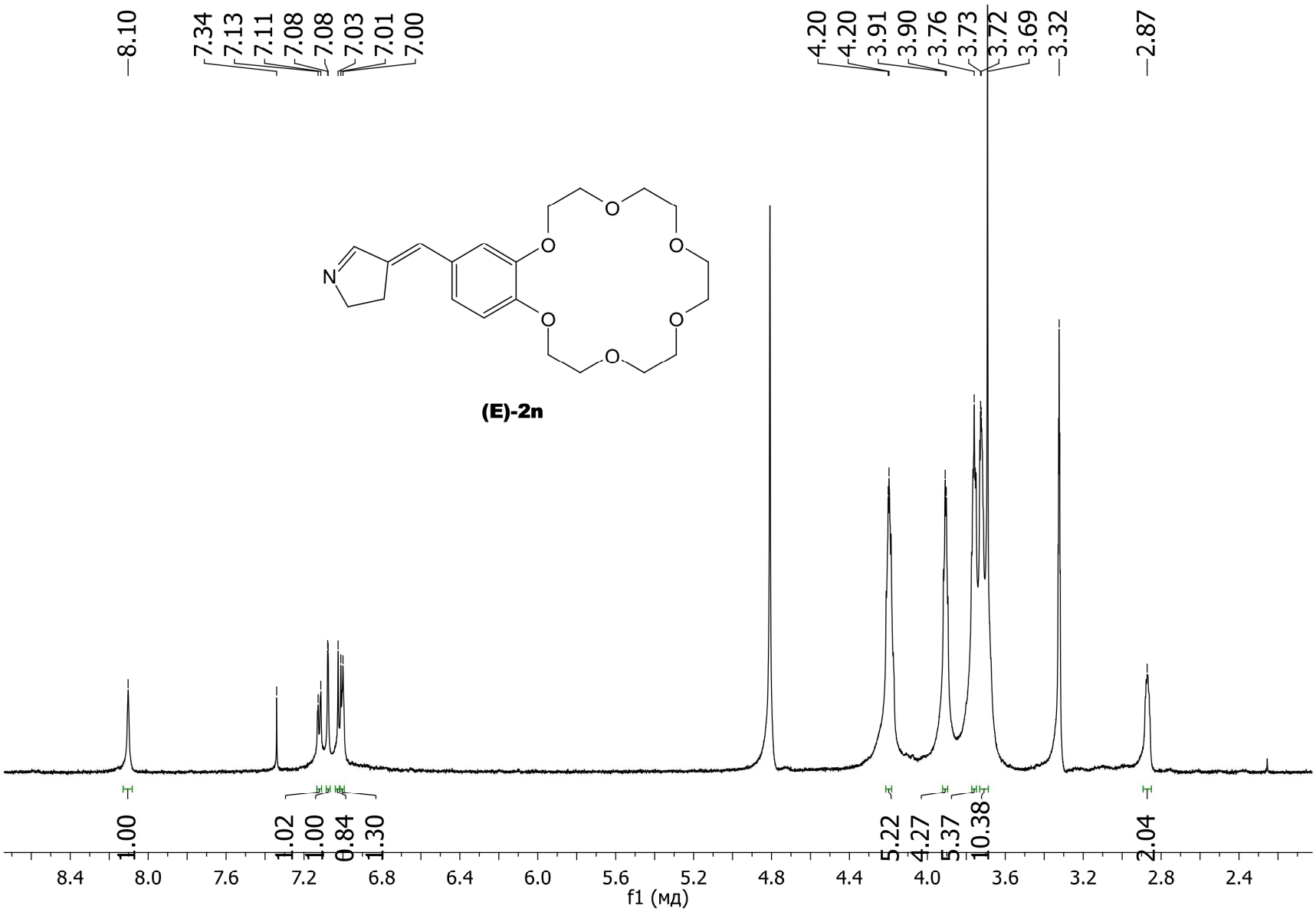


Figure S79: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2n**

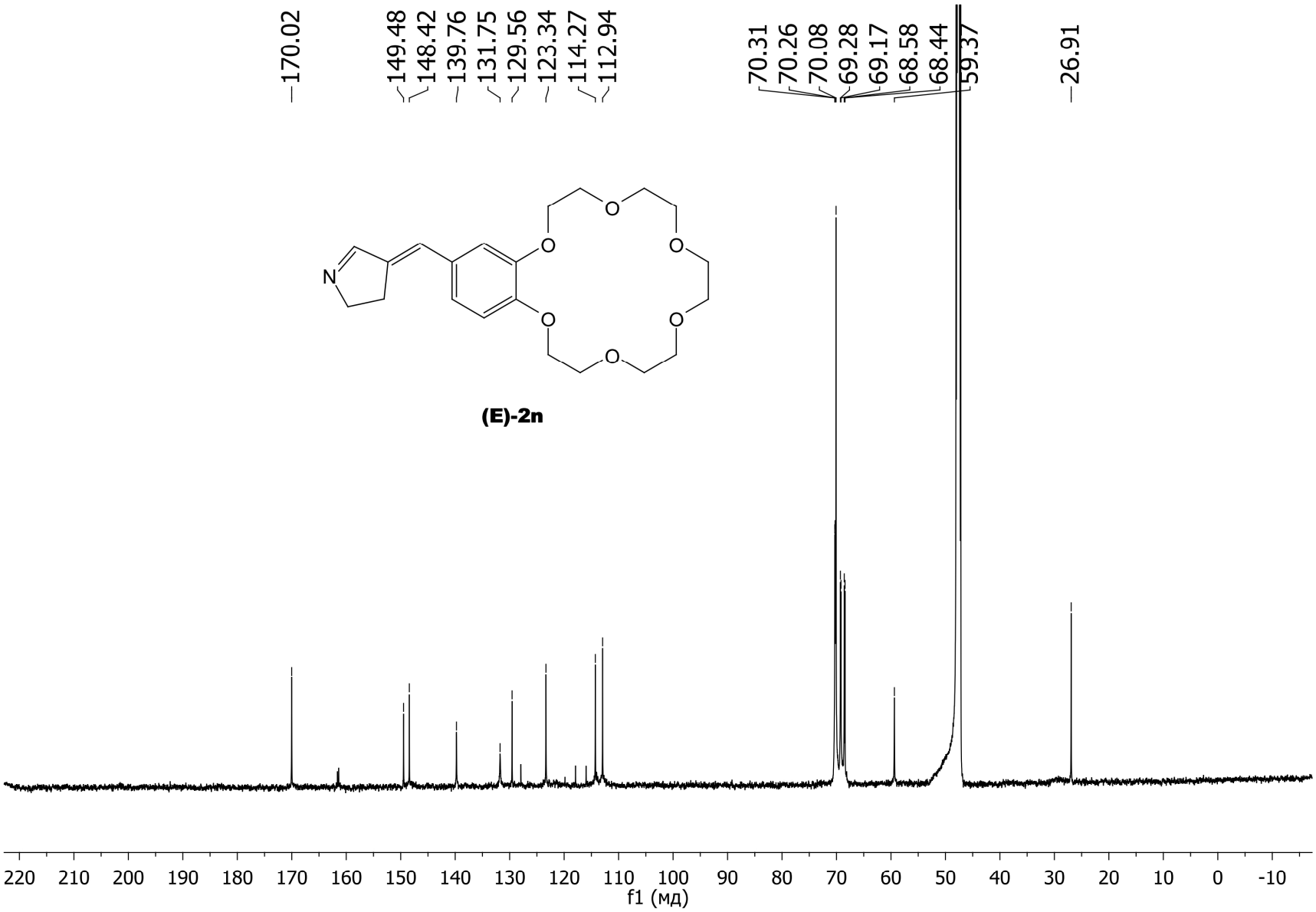


Figure S80: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2n**

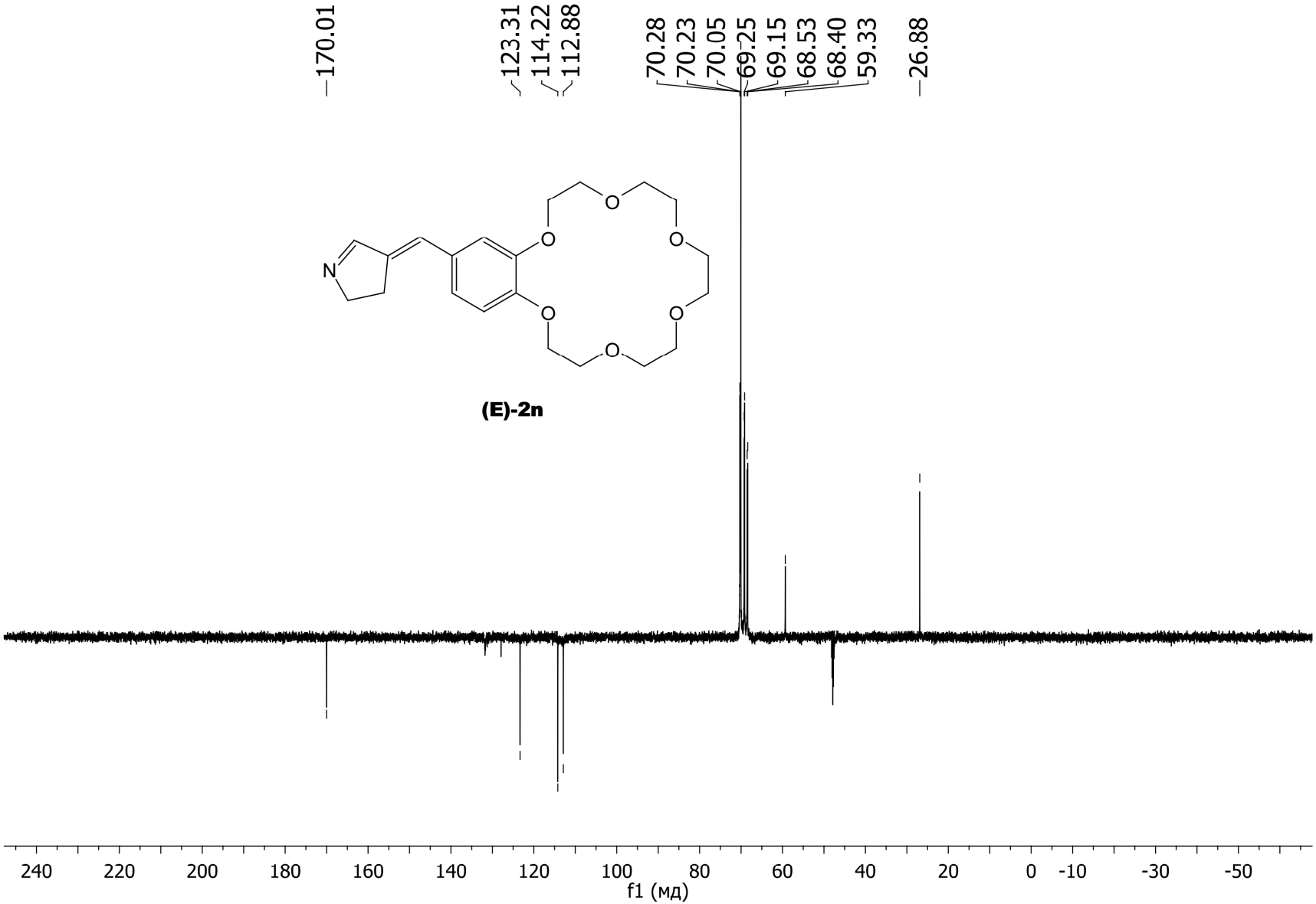


Figure S81: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2n**

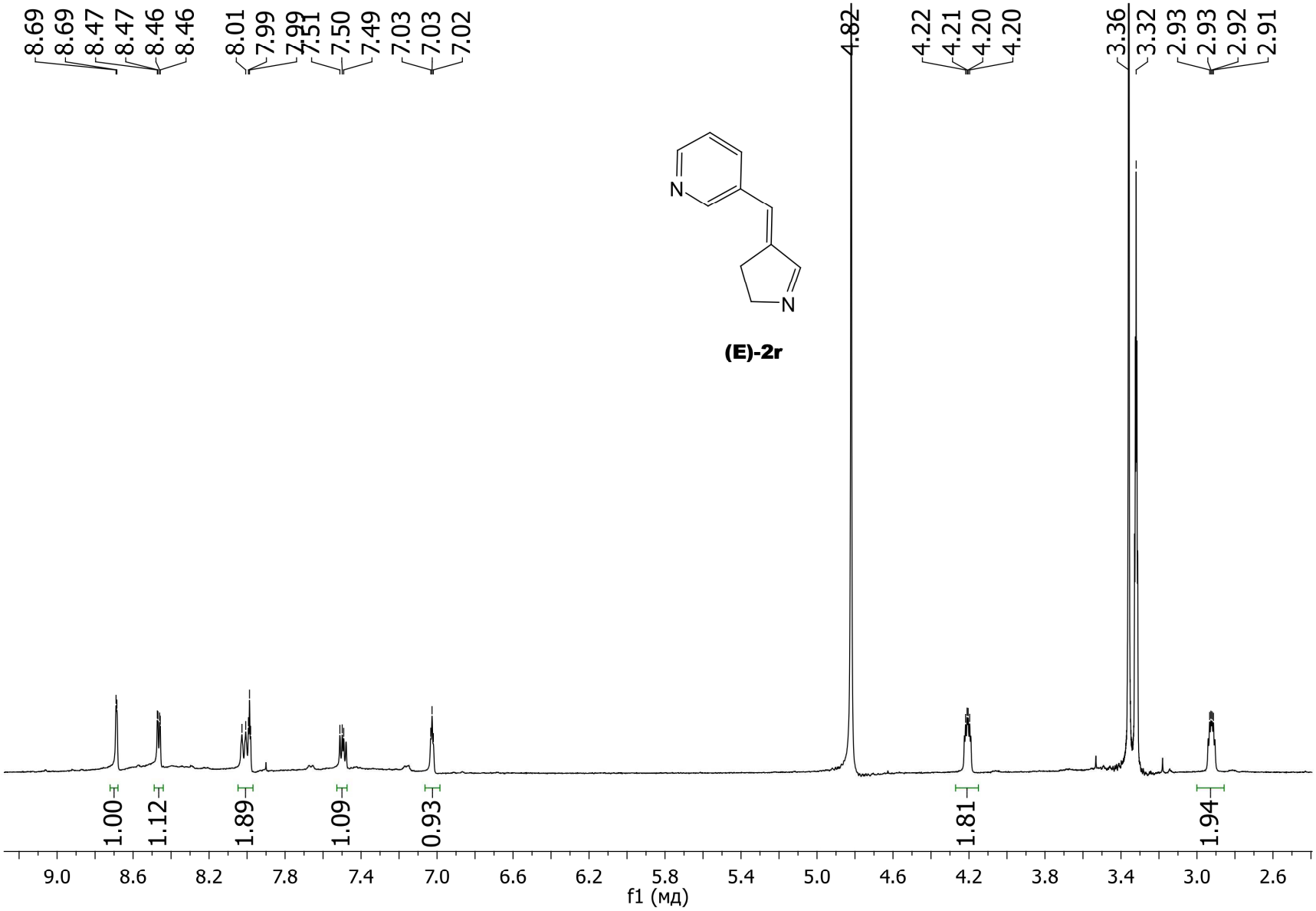


Figure S82: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2r**

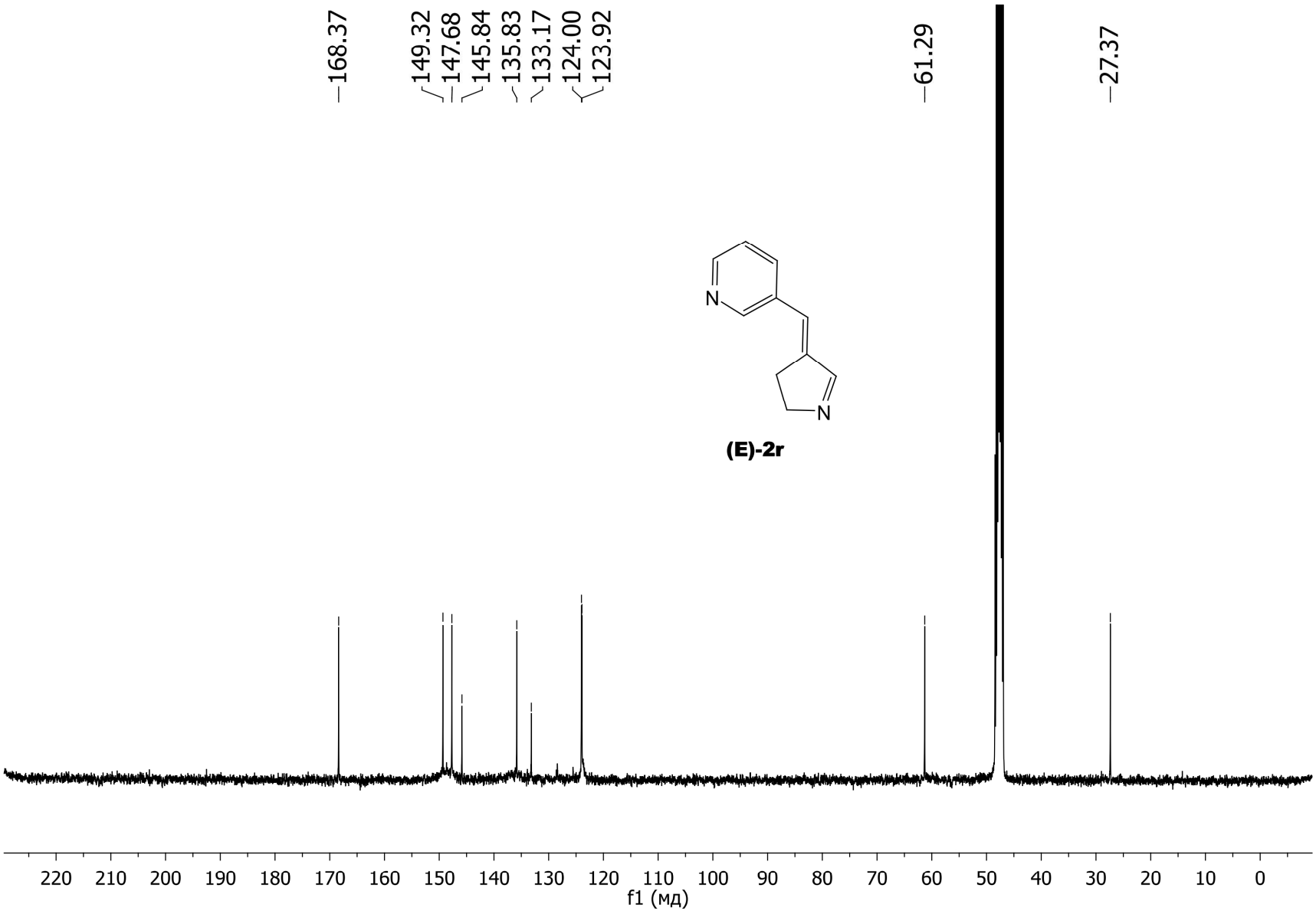


Figure S83: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound (*E*)-**2r**

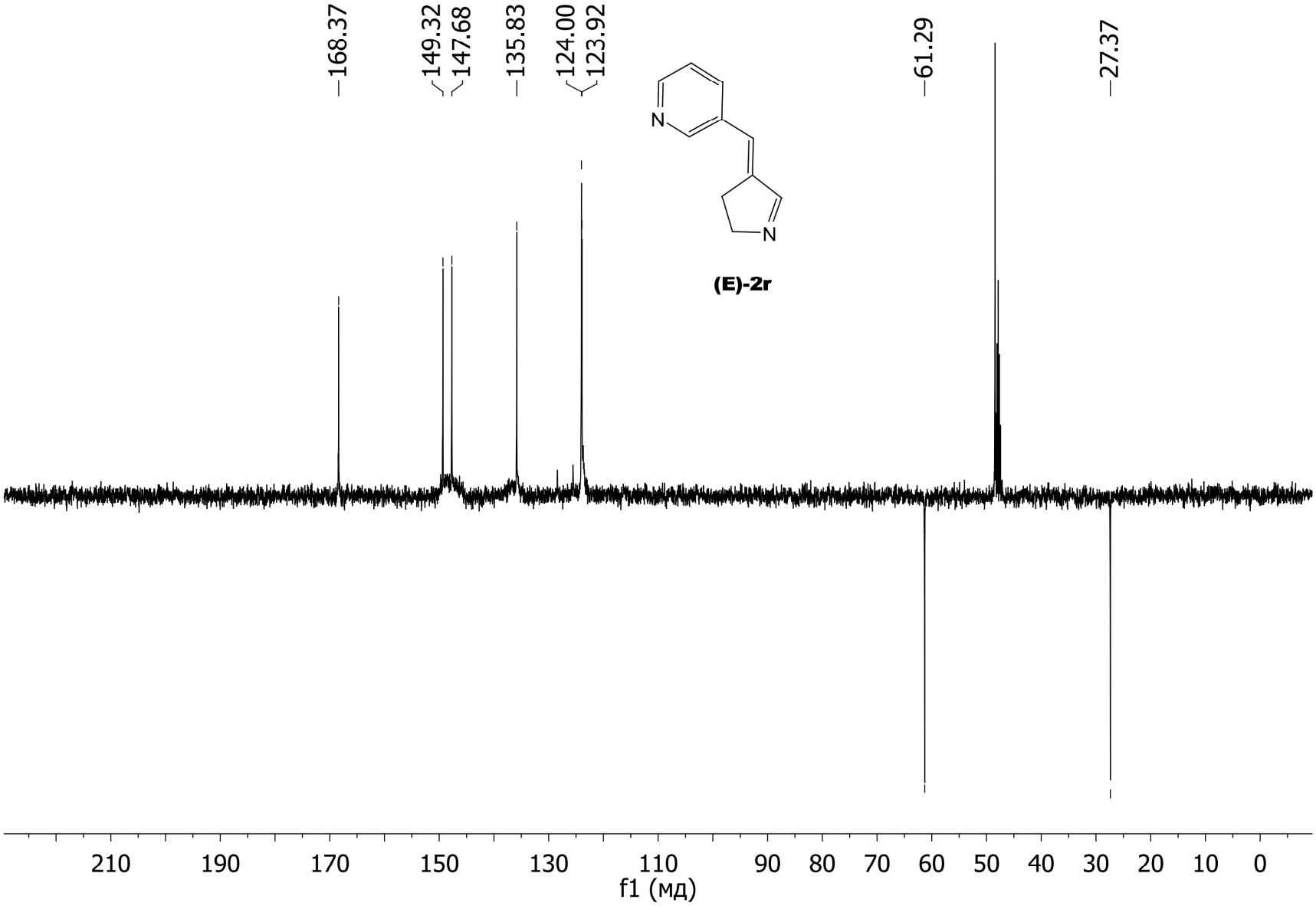


Figure S84: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound (*E*)-**2r**

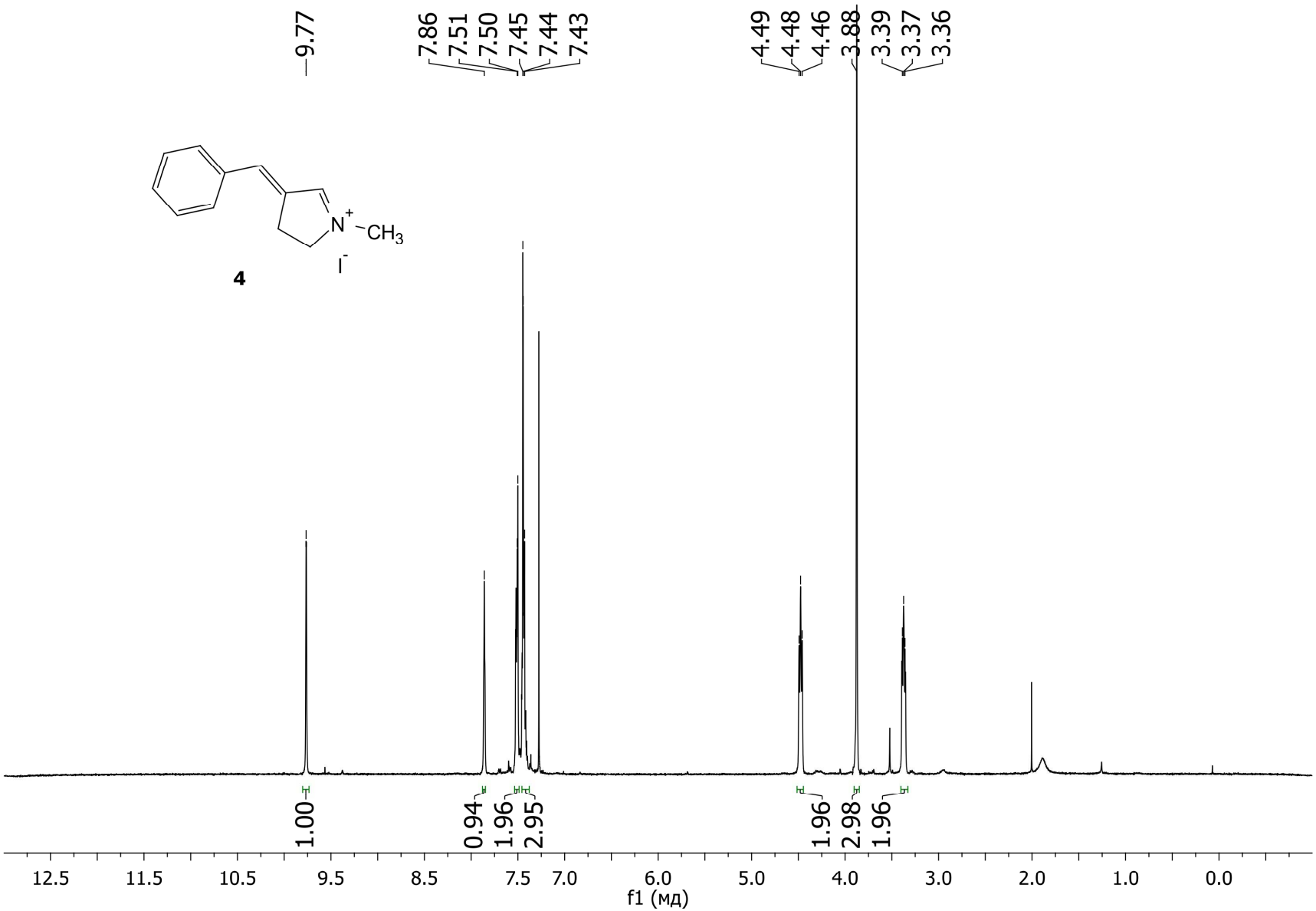


Figure S85: NMR ^{1}H spectrum ($CDCl_3$, 400MHz) of the compound **4**

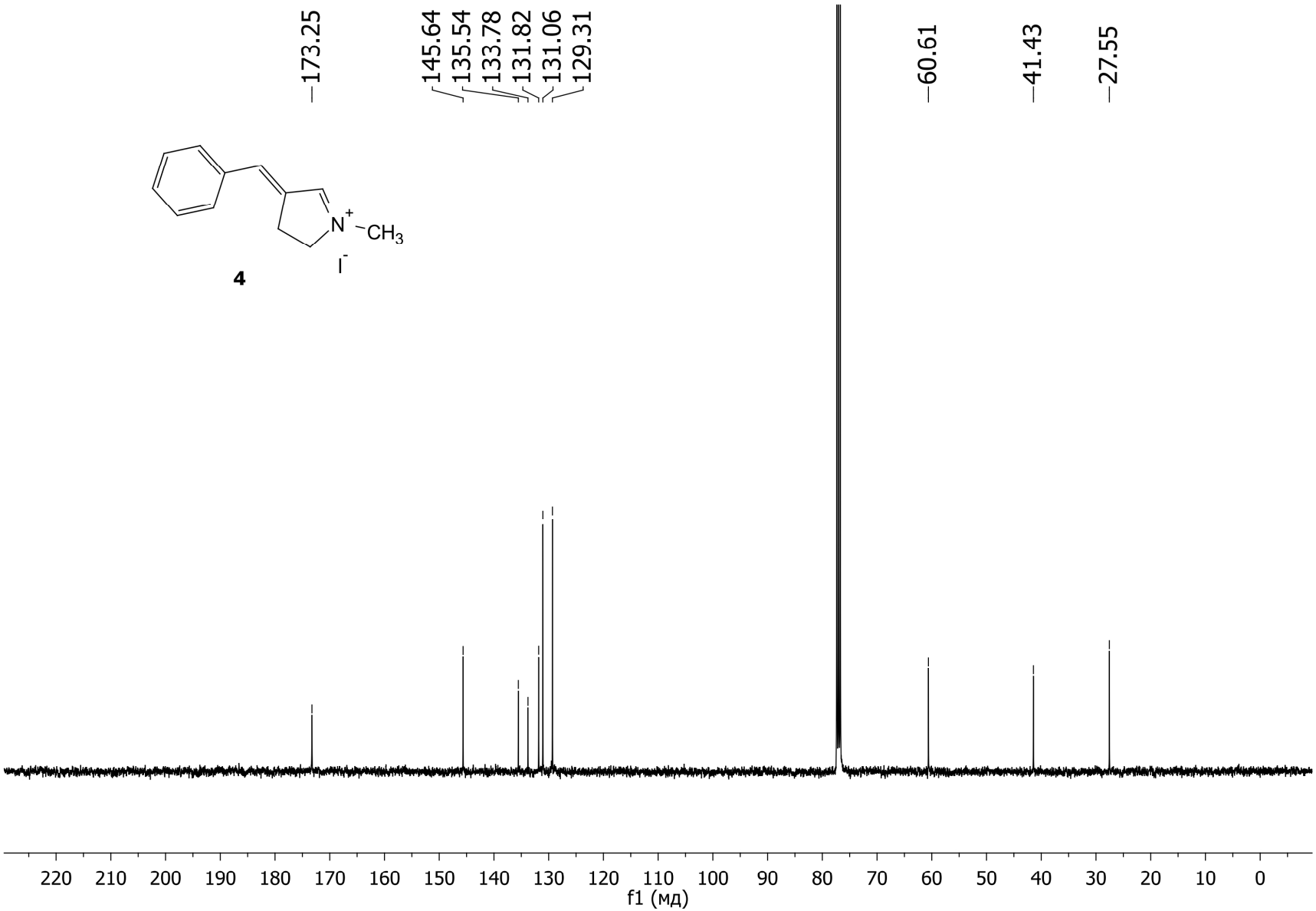


Figure S86: NMR $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 400MHz) of the compound **4**

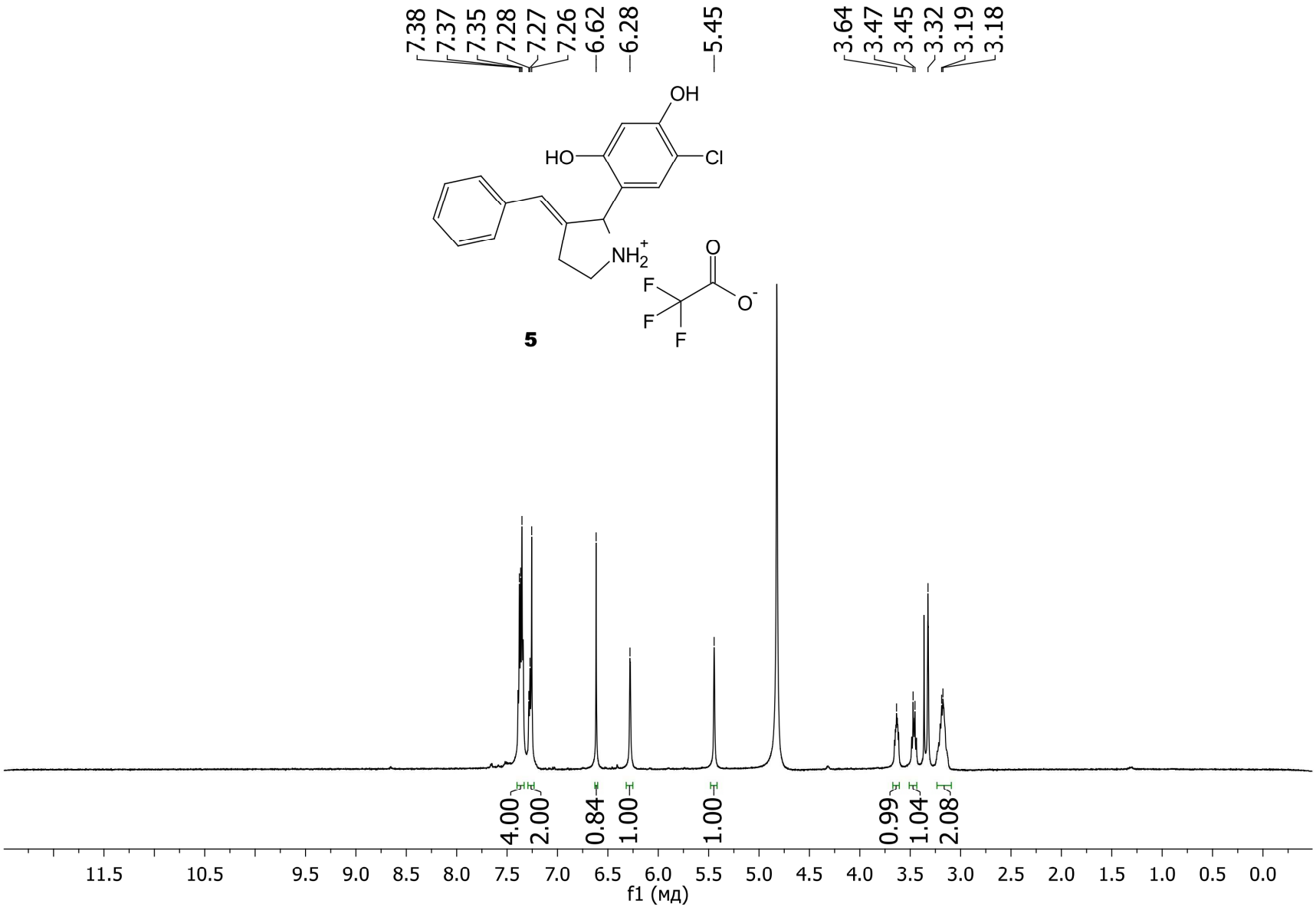


Figure S87: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound **5**

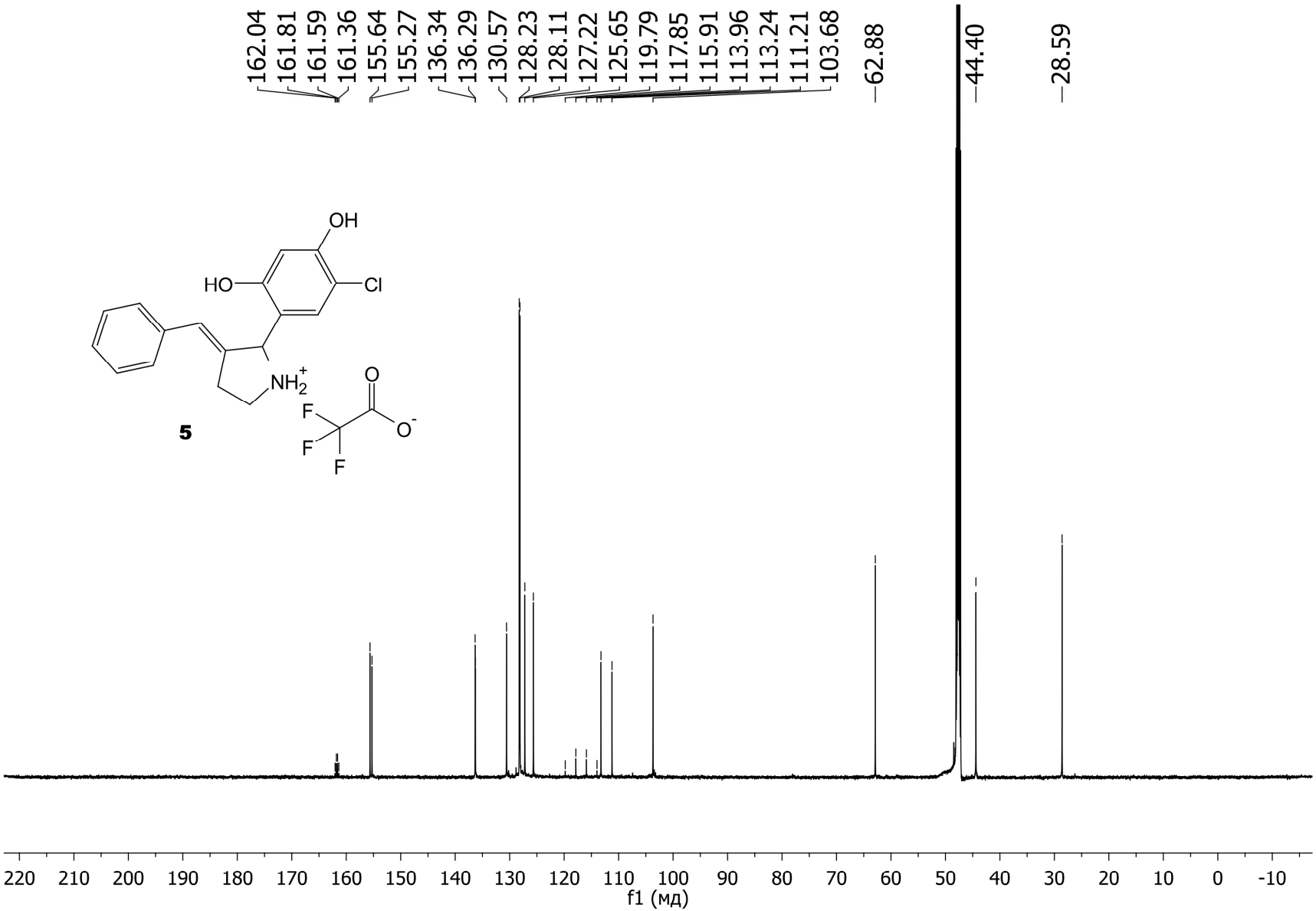


Figure S88: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound **5**

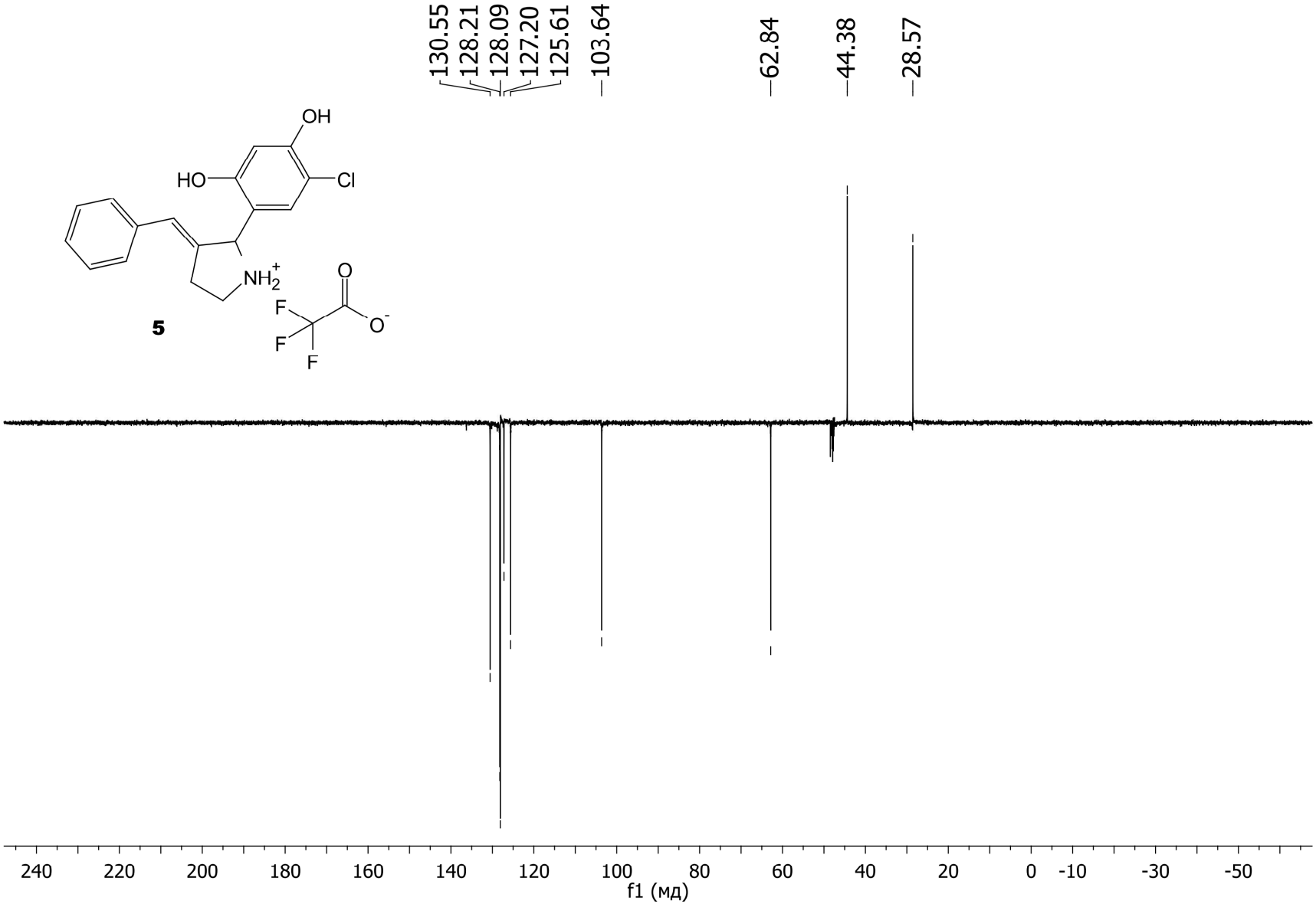


Figure S89: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound **5**

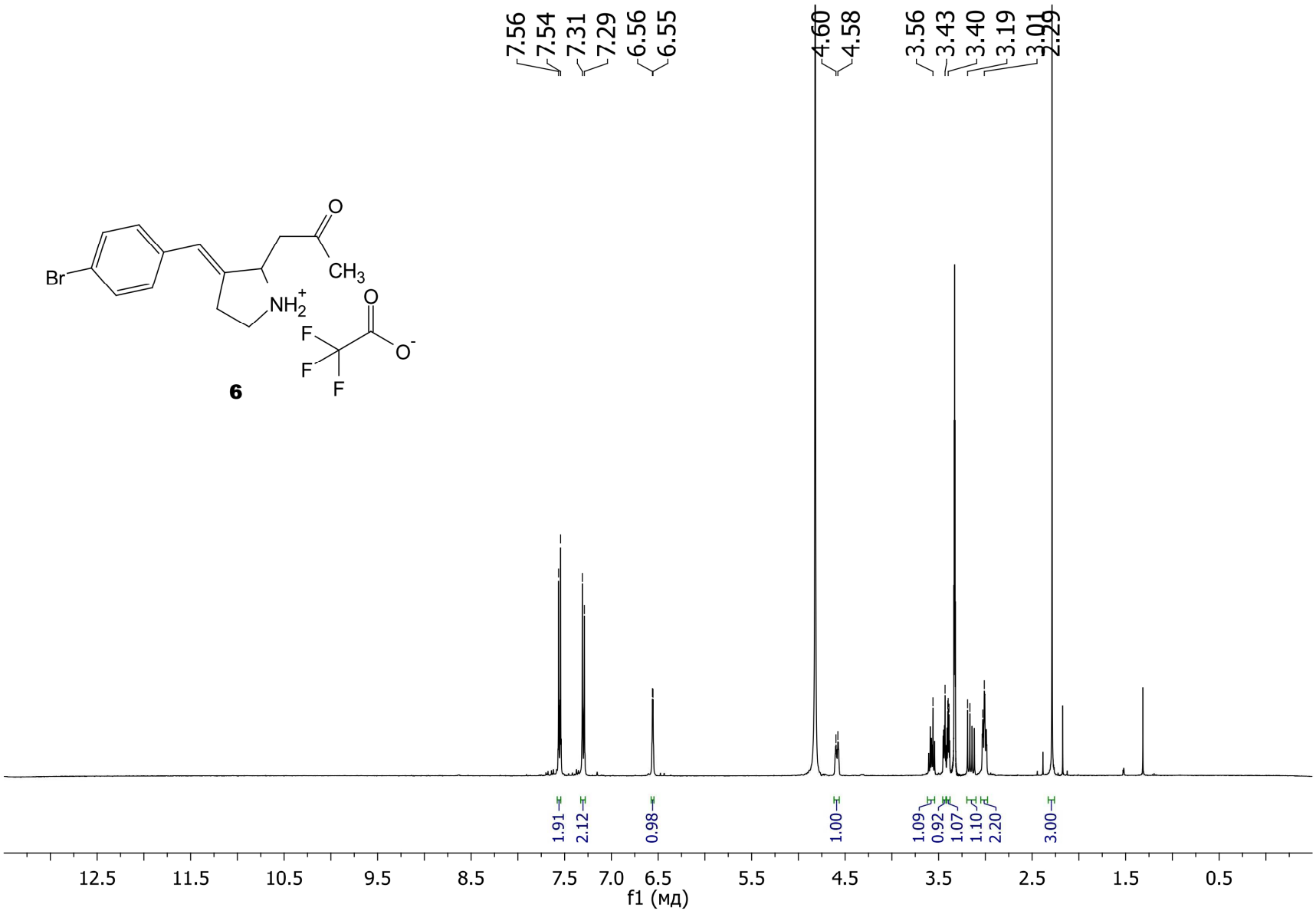


Figure S90: NMR ^{1}H spectrum (CD_3OD, 600MHz) of the compound **6**

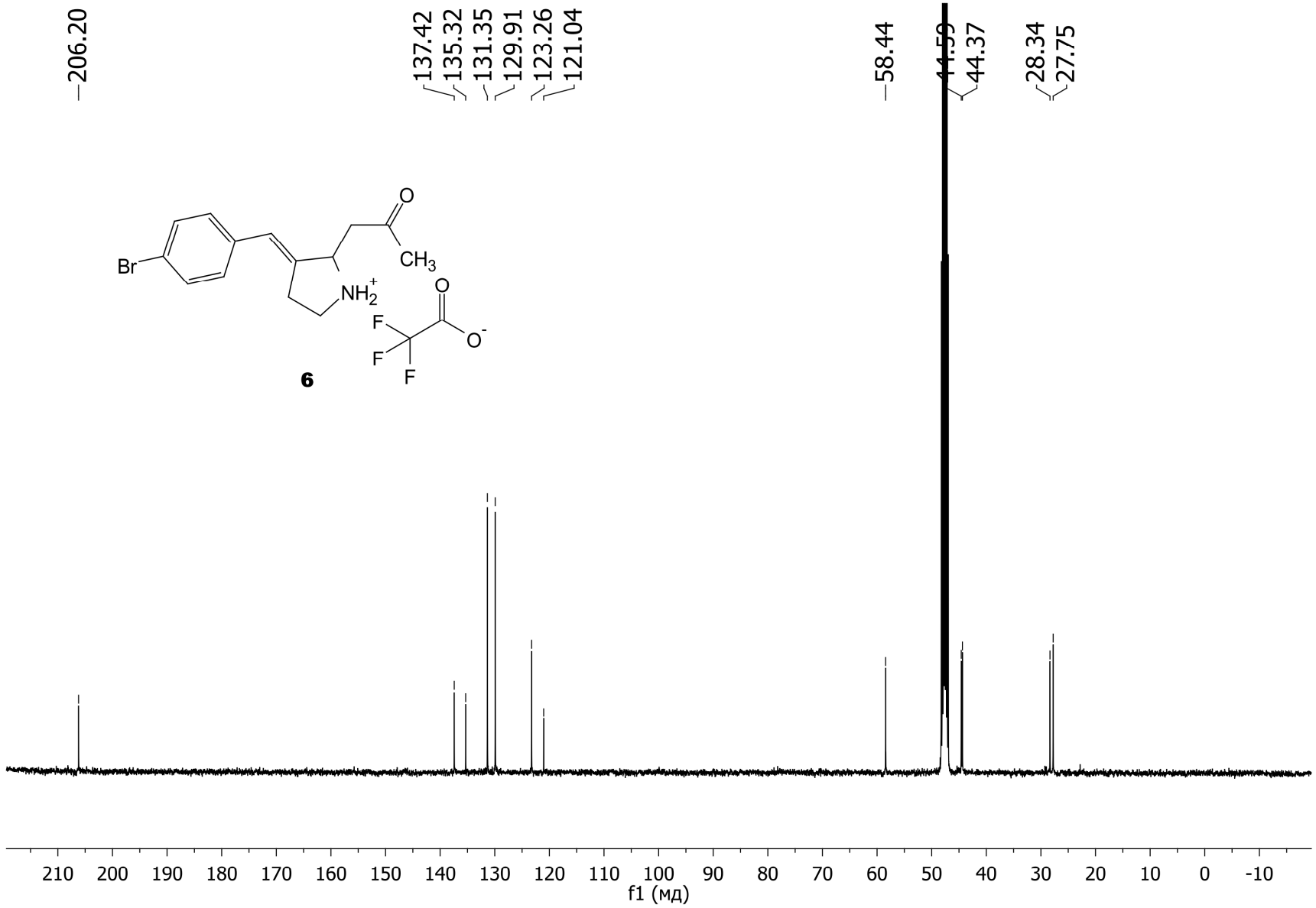


Figure S91: NMR $^{13}C\{^{1}H\}$ spectrum (CD_3OD, 600MHz) of the compound **6**

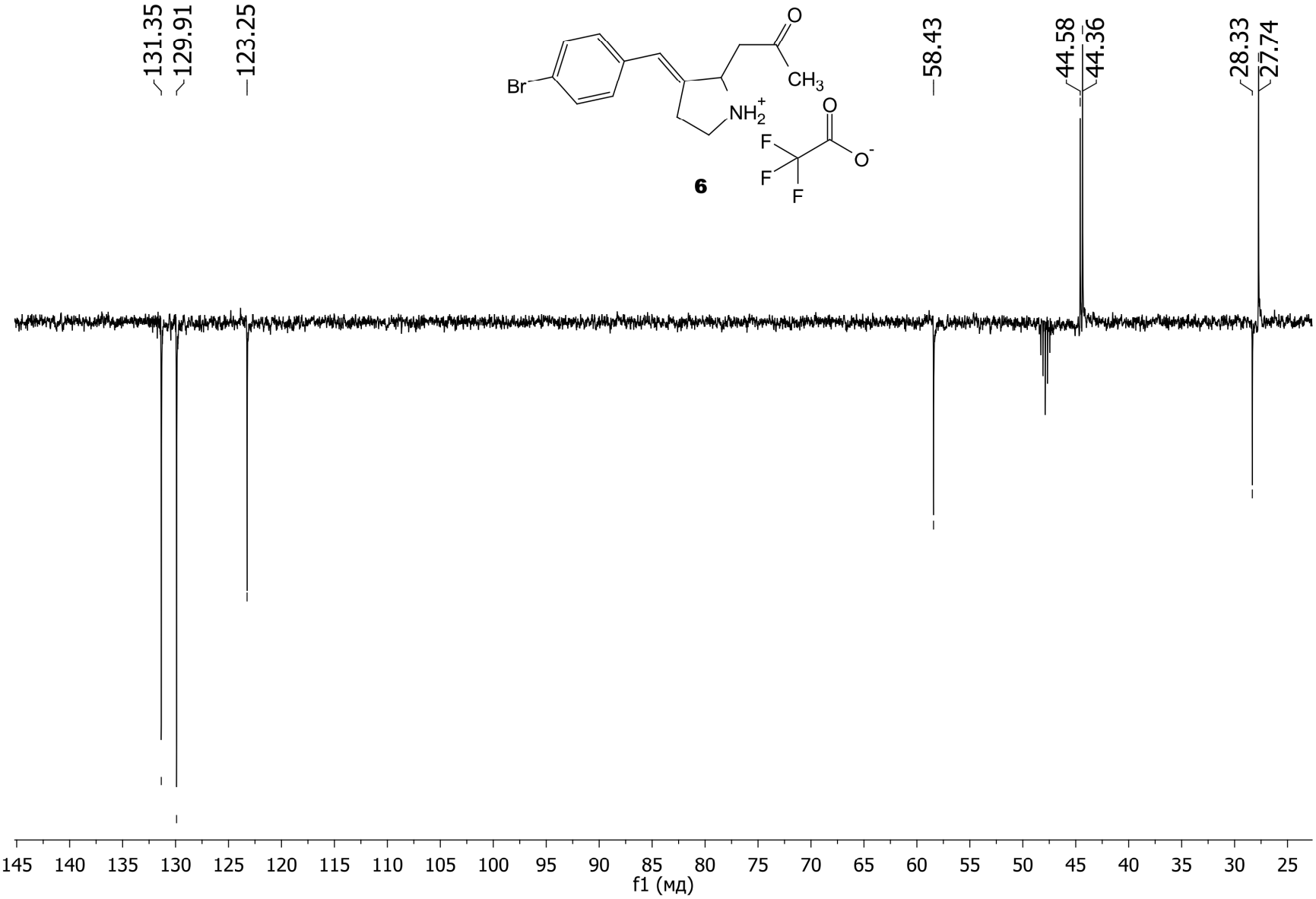


Figure S92: NMR ^{13}C DEPT spectrum (CD_3OD, 600MHz, 135° pulse) of the compound **6**

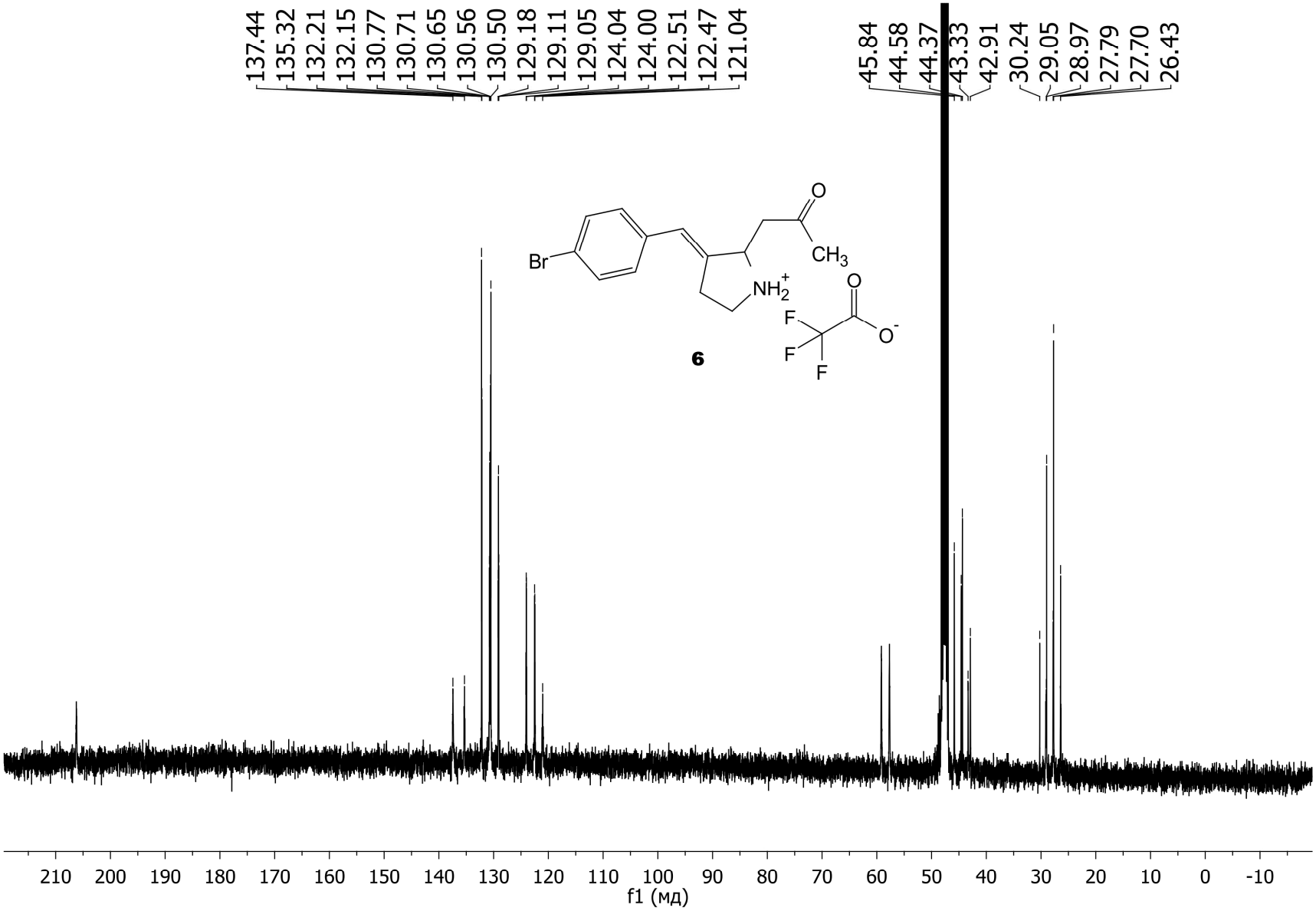


Figure S93: NMR ^{13}C spectrum (CD_3OD, 600MHz) of the compound **6**