Supporting Information

Thiolate-CLPG (Chemiluminescent Protecting Groups) based on coumaranone thiolcarbamates

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M.W. Conceptualization: Assist

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1. Experimental section

1.1 Analysing methods

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H- and ^{13}C-NMR spectra were recorded at 499, 500 or 600 MHz and 125 or 150 MHz respectively. The measurements were performed on a *Bruker* Avance II+ 600, *Bruker* Avance III 500 and *Bruker* Avance III 499 spectrometer. The chemical shifts δ are reported in ppm downfield of the internal standard of TMS [δ (^{1}H-NMR) = 0.00 ppm, δ (^{13}C-NMR) = 0.00 ppm]. DMSO-d_6 [δ (^{1}H-NMR) = 2.50 ppm, δ (^{13}C-NMR) = 39.5 ppm] was used as solvent. H,H couplings are represented with J (italics) and given in Hz, while H,C interactions in the HMBC spectrum are described with J (not italics). The fine structure is designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sxt (sextet), br (broad), ψ (pseudo) and m (multiplet).
The spectra were evaluated using *MestReNova*. The atom numbering illustrated in the figures does not correspond to the rules of IUPAC. Besides the one-dimensional ^{1}H-NMR and ^{13}C-APT-experiments, 2D-spectra (H,C-HMBC, H,C-HSQC, H,H-COSY, H,H-NOESY) were additionally measured for a suitable structure determination. All relevant data for each compound is summarised in a spread sheet. COSY and NOESY interactions of each molecule are represented by respective arrows.

Luminescence spectroscopy

The chemiluminescence spectra were measured using a FLS980 Photoluminescence Spectrometer (*Edinburgh Instruments*) with a photomultiplier tube-detector and a xenon lamp. Quartz cells with a diameter of 1 cm were used for the measurements. Every stock solution was prepared with a concentration of 10^{-2} mol/l in acetonitrile.

Melting points

Melting points of solid compounds were determined with a MP50 Melting Point System (*Mettler Toledo*). The given temperatures refer to the moment where the sample begins to melt.

Infrared-spectroscopy (IR)

Infrared-spectra were measured using a Nicolet 380 FT-IR, a Nicolet iS20 FTIR (*Thermo Fischer Scientific*) and a UATR Two Instrument (*Perkin Elmer*). The wave numbers are reported from 4000 to 800 cm^{-1}. The signals are listed with the following abbreviations: w (weak), m (medium), s (strong), vs (very strong) and br (broad).

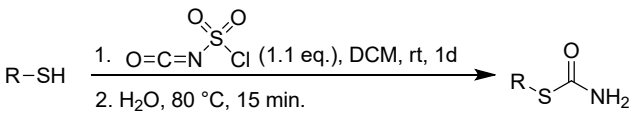
Mass spectrometry and high-resolution mass spectrometry (HR-MS)

High resolution mass spectra were measured with a MAT 900 S (*Finnigan*) and with a LTQ Orbitrap XL (*Thermo Fischer Scientific*) via electron spray ionisation (ESI).

Chemicals and solvents

The applied reagents and solvents were purchased from commercial sources (*Alfa Aesar*, *Fischer Scientific*, *Carbolution*, *Arcos Organics* and *TCI*). The degree of purity of the compounds is at least 95% and they were used without any further treatment.

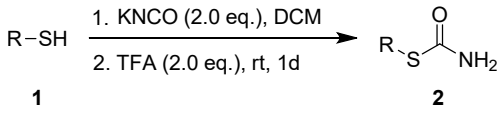
1.2 General Procedures



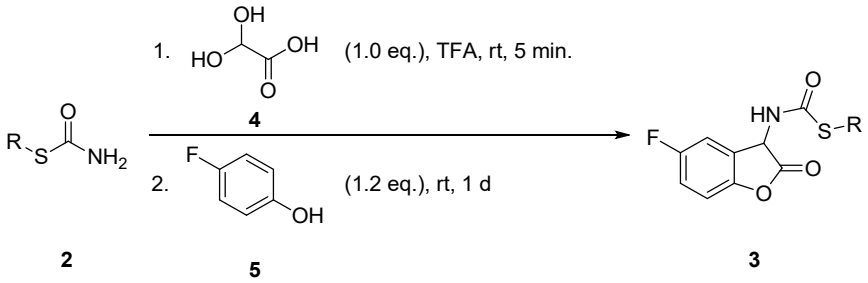
1 **2**

<u>Syntheses of aromatic thiolcarbamates (GP-I):</u> The synthesis protocol of R. Graf was followed with minor modifications.[1] Chlorosulfonyl isocyanate (CSI) (1.1 eq.) was added dropwise at room temperature to a solution of the corresponding thiol **1** (1.0 eq.) dissolved in DCM (7.6 ml per 1 mmol of the alcohol/thiol). The solution in controlled to <40 °C during the addition. Afterwards, the solution is stirred at room temperature for 24 h. The solvent is removed at reduced pressure and ice is added to the residue (5 g per 1 mmol of the alcohol/thiol). The reaction mixture is stirred intensively at room temperature until the ice has completely melted. Hereafter, the aqueous suspension/solution is heated to 80 °C for 15

minutes and then again cooled to room temperature. The resulting precipitate is filtered off, washed with water and finally dried overnight in vacuo over P_2O_5 in a desiccator.



Syntheses of aliphatic thiolcarbamates (GP-II): The synthesis protocol of B. Loev and M. F. Kormendy was followed with minor modifications.[2] The corresponding thiol **1** (1.0 eq.) and KNCO (2.0 eq.) were suspended in DCM (1.8 mL per 1 mmol of the thiol) and stirred at room temperature. Subsequently, trifluoroacetic acid (2.0 eq.) was added dropwise. The suspension was stirred overnight at room temperature. The reaction is then quenched with water (at least 4.0 eq.). The organic phase is separated and dried over Na_2SO_4, filtered off, and the solvent is removed at reduced pressure. If necessary, the aqueous phase was extracted 2-3 times with DCM or EtOAc (1.5 times the volume of the aqueous phase). The combined organic phases were washed with brine (the same volume of the solution), dried over $MgSO_4$, filtered off and the solvent was removed at reduced pressure.



Syntheses of 2-coumaranones with thiolcarbamate-substructures (GP-III): The synthesis protocol of S. Schramm was followed with minor modifications.[3] Glyoxylic acid monohydrate (**4**) (1.00 eq.) and the respective (thiol)carbamate compound **2** (1.00 eq.) were dissolved in trifluoroacetic acid (1.6 mL per 1 mmol (thiol)carbamate compound). After 5 minutes, the *p*-fluorophenol (**5**) (1.20 eq.) was added, and the solution was stirred at room temperature for 1 day. After that the reaction was poured into a beaker with ice water (at least 4 times the volume of the reaction mixture) and the precipitated solid was filtered off, washed with water and dried overnight in vacuo over P_2O_5 in a desiccator. If no precipitation occurred, the solution was

extracted three times with EtOAc or DCM (1.5 times the volume of the aqueous phase). The combined organic phases were dried over Na_2SO_4, filtered off and the solvent was removed at reduced pressure. The raw product was purified by column chromatography on silica gel with (*c*-Hex/Toluene 1:1 + 1% AcOH).

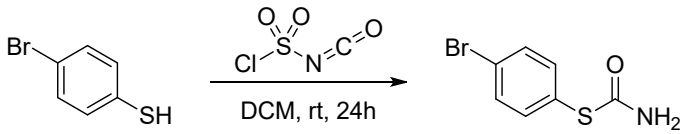
Decomposition experiments (small and large scale) (GP-IV): To follow the rate of decomposition, the coumaranone (1.00 eq.) was dissolved in DMSO-d_6 (0.7 ml) in an NMR tube and DBU (2.00 eq.) was added. At the beginning of the addition, a small flash or a long-lasting emission of blue/blue-greenish light appeared and the colour of the solution changed slowly with time. A ^{1}H-NMR was recorded before the addition of DBU. Then, after addition of the base, a ^{1}H-NMR spectrum was measured again at specific time intervals. Between these measurements, the sample was saturated with oxygen. The reaction was continued until complete oxidation.

Simultaneously for NMR-detection, the coumaranone (1.00 eq.) was dissolved in MeCN (20 ml per 1 mmol of coumaranone) and DBU (2.00 eq.) was added. At the begin of the addition a small flash or a long-lasting emission of blue/blue-greenish light appeared and the colour of the solution slowly changed over time. After 4 hours the solvent was removed under reduced pressure and 10 ml of water were added to the crude product. The aqueous phase was extracted three times with EtOAc (15 ml per extraction) and the combined organic layers were washed four times with water and subsequently dried over Na_2SO_4. Finally, the solvent was removed under reduced pressure and the obtained product was analysed via NMR-spectroscopy.

2. Syntheses

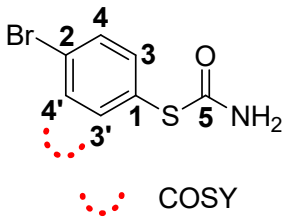
2.1 Syntheses of *S*-organyl thiolcarbamates

2.1.1 Synthesis of *S*-(4-bromophenyl)-carbamothioate (2a)



C_6H_5BrS		C_7H_6BrNOS
189.07 g/mol		232.10 g/mol
2.00 g		2.05 g
1a	**83%**	**2a**

Prepared according to **GP-I** using *p*-bromothiphenol (**1a**) (2.00 g, 10.6 mmol, 1.0 eq.) and CSI (1.01 ml, 11.7 mmol, 1.1 eq.) in 81 ml of DCM. **2a** was obtained as a colourless solid in a yield of 83%.



Yield: 2.05 g (8.83 mmol, 83%).

Appearance: Colourless solid.

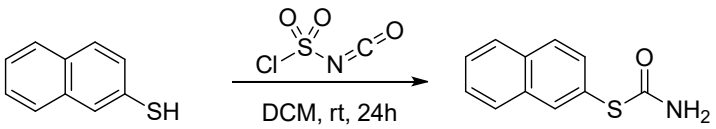
Table 1: 1D and 2D-NMR data of *S*-(4-bromophenyl) carbamothioate (2a) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	-	122.4, C_q	C1→H3(^{2}J), H4(^{3}J)
2	-	128.8, C_q	C2→H3(^{3}J), H4(^{2}J)
3	7.59 (2H, d, *J* = 8.5 Hz)	131.8, 2xCH_{arom}	C3→H3(^{3}J), H4(^{2}J), NH(^{5}J)
4	7.38 (2H, d, *J* = 8.5 Hz)	136.8, 2xCH_{arom}	C4→H3(^{2}J), H4(^{3}J)
5	-	164.3, C_q	-
NH_2	7.67-7.85 (2H, br)	-	-

IR: ν [cm^{-1}] = 3386 (br), 3317 (w), 3289 (w), 3215 (w), 3179 (m), 3075 (w), 2957 (w), 2925 (m), 2873 (w), 2851 (w), 2766 (w), 1915 (w), 1644 (vs), 1609 (s), 1576 (w), 1561 (w), 1469 (m), 1406 (w), 1387 (w), 1312 (s), 1277 (m), 1239 (w), 1201 (w), 1172 (m), 1115 (m), 1091 (w), 1063 (m), 1010 (m), 968 (w), 891 (w), 833 (w), 820 (s).

MP: 185 °C.

2.1.2 Synthesis of *S*-naphthalen-2-yl-carbamothioate (2b)



$C_{10}H_8S$		$C_{11}H_9NOS$
160.24 g/mol		203.26 g/mol
2.00 g		1.71 g
1b	**67%**	**2b**

Prepared according to **GP-I** using naphthalene-2-thiol (**1b**) (2.00 g, 12.5 mmol, 1.0 eq.) and CSI (1.20 ml, 13.8 mmol, 1.1 eq.) in 95 ml of DCM. **2b** was obtained as a beige solid in a yield of 67%.

Yield: 1.71 g (8.40 mmol, 67%).

Appearance: Beige solid.

IR: ν [cm^{-1}] = 3409 (m), 3316 (m), 3296 (m), 3172 (w), 3047 (w), 2112 (w), 1941 (w), 1916 (w), 1860 (w), 1794 (w), 1772 (w), 1646 (s), 1608 (s), 1575 (m), 1497 (w), 1455 (w), 1362 (w), 1343 (w), 1312 (s), 1267 (m), 1237 (m), 1194 (m), 1153 (m), 1132 (m), 1111 (m), 1080 (w), 1070 (w), 1016 (w), 975 (w), 945 (m), 888 (w), 856 (m), 823 (s).

MP: 173 °C.

HR-MS (ESI): Theor.$[M+H]^+$: 204.04776, found: 204.04777.

Theor.$[M+Na]^+$: 226.02970, found: 226.02967.

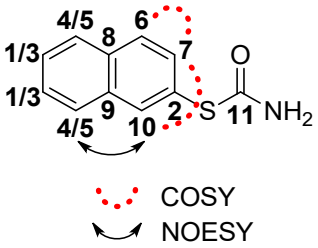
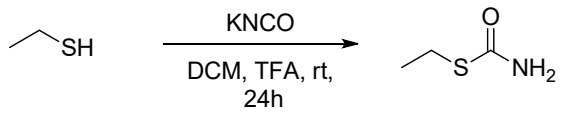


Table 2: **1D and 2D-NMR data of *S*-naphthalen-2-yl carbamothioate (2b) in DMSO-d_6, at 298 K and 600 MHz for ^{1}H and 150 MHz for ^{13}C.**

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	7.57 (1H, m)	126.6, CH_{arom}	C1→H3(^{3}J), H6(^{3}J)
2	-	126.7, C_q	C2→H6(^{3}J)
3	7.57 (1H, m)	127.0, CH_{arom}	C3→H1(^{3}J)
4	7.95 (1H, m)	127.6, CH_{arom}	C4→H10(^{3}J)
5	7.95 (1H, m)	127.7, CH_{arom}	C5→H1/3(^{2}J), H4(^{3}J)
6	7.93 (1H, d, *J* = 8.6 Hz)	128.1, CH_{arom}	-
7	7.52 (1H, dd, *J* = 8.5, 1.8 Hz)	132.0, CH_{arom}	C7→H10(^{3}J)
8	-	132.5, C_q	C8→H7(^{3}J), H10(^{3}J)
9	-	133.0, C_q	C9→H4(^{2}J), H6(^{3}J)
10	8.08 (1H, d, *J* = 1.4 Hz)	134.3, CH_{arom}	C10→H4(^{3}J), H7(^{3}J)
11	-	165.1, C_q	-
NH_2	7.65-7.82 (2H, br)	-	-

Note: C1/C3 and C4/C5 could not be assigned.

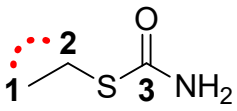
2.1.3 Synthesis of *S*-ethyl carbamothioate (2c)



C_2H_6S		C_3H_7NOS
62.13 g/mol		105.16 g/mol
6.00 ml		2.98 g
1c	**35%**	**2c**

Prepared according to **GP-II** using ethanethiol (**1c**) (6.00 ml, 83.2 mmol, 1.0 eq.), KNCO (13.5 g, 166 mmol, 2.0 eq.) and TFA (12.7 ml, 166 mmol, 2.0 eq.) in 150 ml of DCM. **2c** was obtained as a colourless solid in a yield of 34%.

Yield: 2.98 g (28.3 mmol, 34%).



Appearance: Colourless solid.

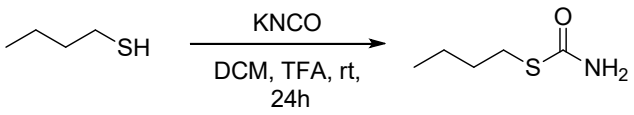
Table 3: **1D and 2D-NMR data of *S*-ethyl carbamothioate (2c) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.**

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	1.17 (3H, t, *J* = 7.3 Hz)	16.0, CH_3	C1→H2(^{2}J)
2	2.72 (2H, q, *J* = 7.3 Hz)	23.1, CH_2	C2→H1(^{2}J)
3	-	167.0, C_q	C3→H2(^{3}J)
NH_2	7.44 (1H, br)	-	-

IR: ν [cm^{-1}] = 3676 (w), 3369 (m), 3284 (m), 3213 (m), 3177 (m), 2985 (w), 2970 (w), 2932 (w), 2871 (w), 2763 (w), 2083 (w), 1638 (s), 1610 (s), 1447 (w), 1440 (w), 1413 (w), 1377 (w), 1299 (s), 1252 (s), 1112 (m), 1057 (w), 977 (w).

MP: 107 °C.

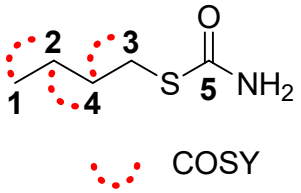
2.1.4. Synthesis of *S*-butyl carbamothioate (2d)



$C_4H_{10}S$		$C_5H_{11}NOS$
90.19 g/mol		133.21 g/mol
6.00 ml		4.09 g
1d	**55%**	**2d**

Prepared according to **GP-II** using butane-1-thiol (**1d**) (6.00 ml, 55.9 mmol, 1.0 eq.), KNCO (9.08 g, 112 mmol, 2.0 eq.) and TFA (8.63 ml, 112 mmol, 2.0 eq.) in 100 ml of DCM. **2d** was obtained as a colourless solid in a yield of 55%.

Yield: 4.09 g (30.7 mmol, 55%).



Appearance: Colourless solid.

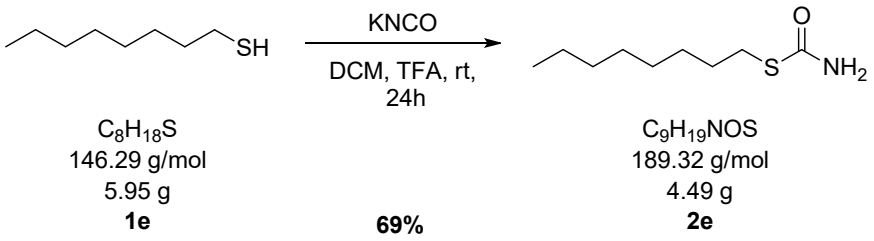
Table 4: 1D and 2D-NMR data of *S*-butyl carbamothioate (2d) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^xJ)
1	0.87 (3H, t, *J* = 7.3 Hz)	13.5, CH_3	C1→H2(^{2}J), H3(^{4}J), H4(^{3}J)
2	1.33 (2H, sxt, *J* = 7.3 Hz)	21.3, CH_2	C2→H1(^{2}J), H3(^{3}J), H4(^{2}J)
3	2.73 (2H, t, *J* = 7.2 Hz)	28.4, CH_2	C3→H2(^{3}J), H4(^{2}J)
4	1.48 (2H, quin, *J* = 7.5 Hz)	32.3, CH_2	C4→H1(^{3}J), H2(^{2}J), H3(^{2}J)
5	-	167.1, C_q	C5→H3(^{3}J)
NH_2	7.43 (2H, br)	-	-

IR: ν [cm^{-1}] = 3661 (w), 3379 (m), 3286 (m), 3216 (m), 3180 (m), 2957 (m), 2929 (m), 2873 (w), 2860 (w), 2764 (w), 1643 (s), 1616 (s), 1464 (w), 1438 (w), 1409 (w), 1377 (w), 1313 (s), 1293 (s), 1269 (s), 1225 (m), 1202 (m), 1113 (m), 1077 (w), 1050 (w), 911 (w), 875 (w).

MP: 100 °C.

2.1.5 Synthesis of *S*-octyl carbamothioate (2e)



$C_8H_{18}S$		$C_9H_{19}NOS$
146.29 g/mol		189.32 g/mol
5.95 g		4.49 g
1e	**69%**	**2e**

Prepared according to **GP-II** using octane-1-thiol (**1e**) (5.95 ml, 34.2 mmol, 1.0 eq.), KNCO (5.54 g, 68.4 mmol, 2.0 eq.) and TFA (5.27 ml, 68.4 mmol, 2.0 eq.) in 62 ml of DCM. **2e** was obtained as a colourless solid in a yield of 69%.

Yield: 4.49 g (23.7 mmol, 69%).

Appearance: Colourless solid.

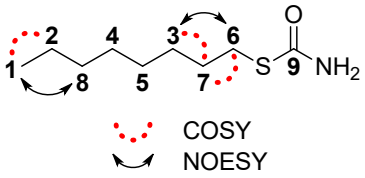


Table 5: 1D and 2D-NMR data of *S*-octyl carbamothioate (2e) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

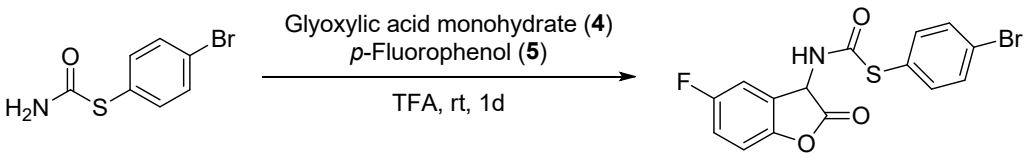
No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	0.85 (3H, t, *J* = 7.1 Hz)	13.8, CH_3	C1→H2(^{2}J), H8(^{3}J)
2	1.27 (2H, m)	22.0, CH_2	C2→H1(^{2}J), H8(^{2}J)
3	1.31 (2H, m)	28.0, CH_2	C3→H6(^{3}J)
4	1.26 (2H, m)	28.4, CH_2	C4→H2(^{3}J)
5	1.26 (2H, m)	28.5, CH_2	C5→H3(^{2}J)
6	2.73 (2H, t, *J* = 7.2 Hz)	28.7, CH_2	C6→H7(^{2}J)
7	1.49 (2H, quin, *J* = 7.3 Hz)	30.1, CH_2	C7→H6(^{2}J)
8	1.25 (2H, m)	31.1, CH_2	C8→H1(^{3}J), H2(^{2}J)
9	-	167.0, C_q	C9→H6(^{3}J)
NH_2	7.38 (2H, br)	-	-

IR: ν [cm^{-1}] = 3381 (m), 3287 (w), 3214 (m), 3180 (m), 2957 (m), 2918 (s), 2873 (w), 2850 (m), 2767 (w), 1645 (vs), 1617 (s), 1463 (w), 1406 (w), 1323 (m), 1297 (s), 1276 (s), 1239 (m), 1200 (m), 1115 (m), 958 (w), 891 (w), 849 (w).

MP: 100 °C.

2.2 Syntheses of Coumaranones with thiolcarbamate structures

2.2.1 Synthesis of *S*-(4-bromophenyl) (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3a)



C_7H_6BrNOS		$C_{15}H_9BrFNO_3S$
232.10 g/mol		382.20 g/mol
0.80 g		0.26 g
2a	**20%**	**3a**

Prepared according to **GP-III** using *S*-(4-bromophenyl) carbamothioate (**2a**) (0.80 g, 3.45 mmol, 1.0 eq.), glyoxylic acid monohydrate (**4**) (0.32 g, 3.45 mmol, 1.0 eq.), *p*-fluorophenol (**5**) (0.46 g, 4.14 mmol, 1.2 eq.) in 6 ml of TFA. **3a** was obtained as a colourless solid in a yield of 20%.

Yield: 0.26 g (0.68 mmol, 20%).

Appearance: Colourless solid.

R_f-Value: 0.10 (SiO_2, *c*-Hex/Toluene 1:1 + 1% AcOH).

IR: ν [cm^{-1}] = 3327 (br), 3087 (w), 2931 (w), 2359 (w), 1814 (s), 1652 (s), 1610 (w), 1563 (w), 1500 (s), 1485 (s), 1477 (s), 1448 (w), 1386 (w), 1323 (w), 1273 (w), 1263 (w), 1250 (w), 1235 (w), 1209 (m), 1191 (w), 1129 (s), 1118 (s), 1089 (vs), 1076 (vs), 1052 (w), 1009 (w), 958 (w), 939 (w), 898 (w), 865 (w), 834 (m), 824 (vs).

MP: 191 °C.

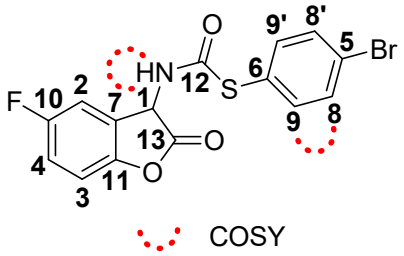
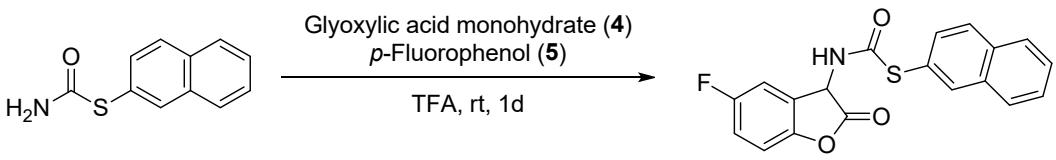


Table 7: 1D and 2D-NMR data of *S*-(4-bromophenyl) (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3a) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	5.54 (1H, d, *J* = 7.3 Hz)	52.5, CH	C1→H2(^{3}J), NH(^{2}J)
2	7.25 (1H, m)	111.46+111.67, CH_{arom}	C2→H4(^{3}J)
3	7.22 (1H, m)	111.78+111.84, CH_{arom}	-
4	7.21 (1H, m)	116.0+116.2, CH_{arom}	C4→H2(^{3}J)
5	-	123.1, C_q	C5→H8(^{2}J), H9(^{3}J)
6	-	126.9, C_q	C6→H8(^{3}J), H9(^{2}J)
7	-	127.1+127.2, C_q	C7→H1(^{2}J), H2(^{2}J), NH(^{3}J)
8	7.60 (2H, d, *J* = 8.5 Hz)	132.1, 2xCH_{arom}	C8→H8(^{3}J)
9	7.38 (2H, d, *J* = 8.5 Hz)	136.9, 2xCH_{arom}	C9→H9(^{3}J)
10	-	149.41+149.43, C_q	C10→H1(^{4}J), H2(^{2}J), H3(^{3}J), H4(^{2}J)
11	-	157.9+159.8, C_q	C11→H2(^{3}J), H4(^{3}J)
12	-	164.6, C_q	C12→H1(^{3}J), H9(^{4}J), NH(^{2}J)
13	-	172.8, C_q	C13→H1(^{2}J), NH(^{3}J)
NH	9.64 (1H, d, *J* = 7.4 Hz)	-	-

2.2.2 Synthesis of *S*-naphthalen-2-yl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3b)



$C_{11}H_9NOS$		$C_{19}H_{12}FNO_3S$
203.26 g/mol		353.37 g/mol
1.00 g		0.20 g
2b	**12%**	**3b**

Prepared according to **GP-III** using *S*-naphthalen-2-yl carbamothioate (**2b**) (1.00 g, 4.91 mmol, 1.0 eq.), glyoxylic acid monohydrate (**4**) (0.45 g, 4.91 mmol, 1.0 eq.), *p*-fluorophenol (**5**) (0.66 g, 5.90 mmol, 1.2 eq.) in 8 ml of TFA. **3b** was obtained as a brownish solid in a yield of 12%.

Yield: 0.20 g (0.57 mmol, 12%).

Appearance: Brownish solid.

R_f-Value: 0.10 (SiO_2, *c*-Hex/Toluene 1:1 + 1% AcOH).

IR: ν [cm^{-1}] = 3326 (br), 3059 (w), 2934 (w), 2361 (w), 2341 (w), 1816 (s), 1716 (w), 1700 (w), 1648 (vs), 1612 (w), 1586 (w), 1559 (w), 1480 (vs), 1449 (w), 1366 (w), 1341 (w), 1318 (m), 1274 (w), 1253 (w), 1233 (w), 1209 (s), 1190 (m), 1131 (s), 1119 (s), 1079 (s), 1066 (s), 1052 (w), 1019 (w), 980 (w), 939 (m), 893 (m), 873 (w), 859 (w), 849 (s), 830 (s), 818 (s), 800 (w).

MP: 175 °C.

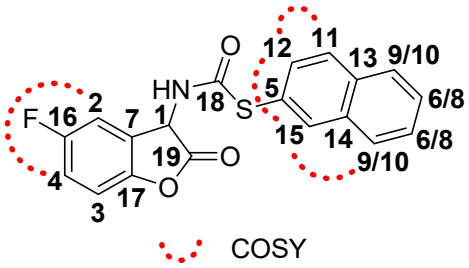
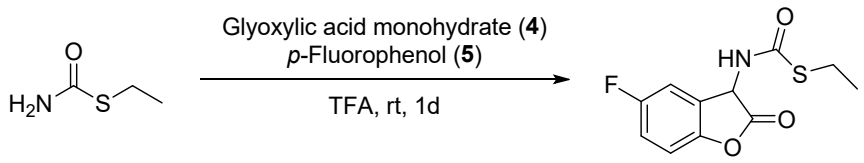


Table 8: 1D and 2D-NMR data of *S*-naphthalen-2-yl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3b) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	5.55 (1H, d, *J* = 7.4 Hz)	52.5, CH	C1→H2(^{3}J), NH(^{2}J)
2	7.27 (1H, m)	111.5+111.6, CH_{arom}	C2→H4(^{3}J)
3	7.21 (1H, m)	111.76+111.81, CH_{arom}	-
4	7.20 (1H, m)	116.0+116.1, CH_{arom}	C4→H2(^{3}J)
5	-	124.7, C_q	C5→H11(^{3}J)
6	7.56 (1H, m)	126.7, CH_{arom}	-
7	-	127.26, C_q	C7→H3(^{3}J)
8	7.58 (1H, m)	127.32, CH_{arom}	-
9	7.95 (1H, m)	127.6, CH_{arom}	-
10	7.95 (1H, m)	127.8, CH_{arom}	-
11	7.93 (1H, m)	128.5, CH_{arom}	C11→H9/10(^{3}J)
12	7.48 (1H, dd, *J* = 8.5, 1.8 Hz)	131.7, CH_{arom}	C12→H11(^{2}J). H15(^{3}J)
13	-	132.8, C_q	C13→H9/H10(^{3}J). H12(^{3}J), H15(^{3}J)
14	-	133.0, C_q	C14→H9/H10(^{3}J), H15(^{2}J)
15	8.10 (1H, d, *J* = 1.4 Hz)	134.7, CH_{arom}	C15→H12(^{3}J)
16	-	149.41+149.42, C_q	C16→H2(^{2}J), H3(^{3}J), H4(^{2}J)
17	-	158.1+159.7, C_q	C17→H2(^{3}J), H3(^{2}J)
18	-	165.3, C_q	C18→H1(^{3}J), NH(^{2}J)
19	-	172.8, C_q	C19→H1(^{2}J), NH(^{3}J)
NH	9.59 (1H, d, *J* = 7.5 Hz)	-	-

Note: C6/C8 and C9/C10 could not be assigned.

2.2.3 Synthesis of *S*-ethyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3c)



C_3H_7NOS		$C_{11}H_{10}FNO_3S$
105.16 g/mol		255.27 g/mol
2.00 g		0.40 g
2c	**8%**	**3c**

Prepared according to **GP-III** using *S*-ethyl carbamothioate (**2c**) (2.00 g, 19.0 mmol, 1.0 eq.), glyoxylic acid monohydrate (**4**) (1.75 g, 19.0 mmol, 1.0 eq.), *p*-fluorophenol (**5**) (2.56 g, 22.8 mmol, 1.2 eq.) in 30 ml of TFA. **3c** was obtained as a colourless solid in a yield of 8%.

Yield: 0.40 g (1.58 mmol, 8%).

Appearance: Colourless solid.

R_f-Value: 0.13 (SiO_2, *c*-Hex/Toluene 1:1 + 1% AcOH).

IR: ν [cm^{-1}] = 3348 (br), 3076 (w), 2976 (w), 2912 (w), 2359 (w), 2341 (w), 1799 (s), 1646 (vs), 1505 (s), 1479 (s), 1457 (w), 1446 (w), 1383 (w), 1321 (m), 1268 (m), 1253 (w), 1233 (w), 1203 (s), 1195 (s), 1119 (s), 1076 (vs), 1047 (w), 955 (w), 947 (w), 899 (m), 885 (m), 822 (s).

MP: 183 °C.

HR-MS (EI): Theor.$[M+H]^+$: 255.0359, found: 255.0361.

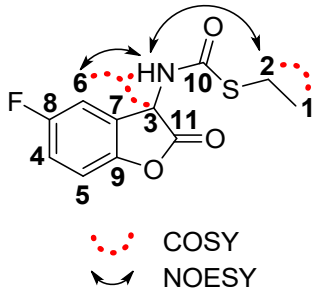
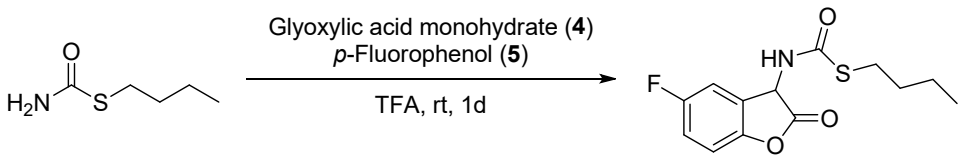


Table 9: **1D and 2D-NMR data of *S*-ethyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3c) in DMSO-d_6, at 298 K and 499 MHz for ^{1}H and 125 MHz for ^{13}C.**

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	1.14 (3H, t, *J* = 7.3 Hz)	15.5, CH_3	C1→H2(^{2}J)
2	2.76 (2H, m)	23.4, CH_2	C2→H1(^{2}J)
3	5.46 (1H, d, *J* = 7.2 Hz)	52.29+52.30, CH	C3→H6(^{3}J), NH(^{2}J)
4	7.19 (1H, m)	111.3+111.5, CH_{arom}	C4→H6(^{3}J)
5	7.25 (1H, m)	111.7+111.8, CH_{arom}	C5→H3(^{4}J), H6(^{4}J)
6	7.21 (1H, m)	116.0+115.8, CH_{arom}	C6→H3(^{3}J), H4(^{3}J)
7	-	127.56+127.63, C_q	C7→H3(^{2}J), H5(^{3}J), NH(^{3}J)
8	-	149.42+149.44, C_q	C8→H3(^{4}J), H4(^{2}J)
9	-	157.9+159.8, C_q	C9→H3(^{3}J), H5(^{2}J), H6(^{3}J)
10	-	167.0, C_q	C10→H2(^{3}J), H3(^{3}J), NH(^{2}J)
11	-	173.0, C_q	C11→H3(^{2}J), NH(^{3}J)
NH	9.37 (1H, d, *J* = 7.4 Hz)	-	-

2.2.4 Synthesis of *S*-butyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3d)



$C_5H_{11}NOS$		$C_{13}H_{14}FNO_3S$
133.21 g/mol		283.32 g/mol
1.50 g		0.14 g
2d	**4%**	**3d**

Prepared according to **GP-III** using *S*-butyl carbamothioate (**2d**) (1.50 g, 11.3 mmol, 1.0 eq.), glyoxylic acid monohydrate (**4**) (1.04 g, 11.3 mmol, 1.0 eq.), *p*-fluorophenol (**5**) (1.51 g, 13.5 mmol, 1.2 eq.) in 18 ml of TFA. **3d** was obtained as a colourless solid in a yield of 4%.

Yield: 0.14 g (0.49 mmol, 4%).

Appearance: Colourless solid.

R_f-Value: 0.13 (SiO_2, *c*-Hex/Toluene 1:1 + 1% AcOH).

IR: ν [cm^{-1}] = 3346 (br), 3076 (w), 2960 (w), 2930 (w), 2873 (w), 2358 (w), 1797 (s), 1649 (vs), 1507 (s), 1480 (s), 1447 (w), 1379 (w), 1324 (m), 1268 (m),1254 (w), 1236 (w), 1203 (s), 1194 (s), 1121 (vs), 1078 (vs), 1053 (w), 956 (w), 947 (w), 918 (w), 902 (w), 887 (s). 821 (s).

MP: 162 °C.

HR-MS (ESI): Theor.$[M+Na]^+$: 306.05706, found: 306.05694.

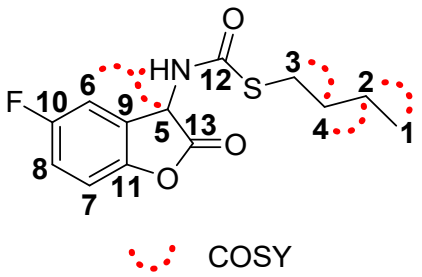
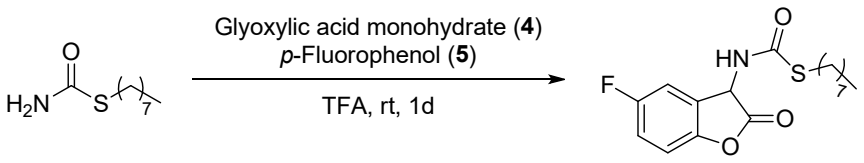


Table 10: **1D and 2D-NMR data of *S*-butyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3d) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.**

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	0.84 (3H, t, *J* = 7.4 Hz)	13.4, CH_3	C1→H2(^{2}J), H4(^{3}J)
2	1.29 (2H, sxt, *J* = 7.3 Hz)	21.2, CH_2	C2→H1(^{2}J), H3(^{3}J), H4(^{2}J)
3	2.76 (2H, m)	28.6, CH_2	C3→H2(^{3}J), H4(^{2}J)
4	1.45 (2H, quin, *J* = 7.3 Hz)	31.9, CH_2	C4→H1(^{3}J), H2(^{2}J), H3(^{2}J)
5	5.45 (1H, d, *J* = 7.2 Hz)	52.3, CH	C5→H6(^{3}J), NH(^{2}J)
6	7.18 (1H, m)	111.3+111.5, CH_{arom}	C6→H5(^{3}J), H8(^{3}J)
7	7.25 (1H, m)	111.7+111.8, CH_{arom}	C7→H5(^{4}J)
8	7.21 (1H, m)	115.8+116.0, CH_{arom}	C8→H6(^{3}J)
9	-	127.55+127.63, C_q	C9→H5(^{2}J), H7(^{3}J), NH(^{3}J)
10	-	149.42+149.43, C_q	C10→H5(^{4}J), H6(^{2}J), H8(^{2}J)
11	-	157.9+159.8, C_q	C11→H5(^{3}J), H7(^{2}J), H8(^{3}J)
12	-	167.0, C_q	C12→H3(^{3}J), H5(^{3}J), NH(^{2}J)
13	-	173.0, C_q	C13→H5(^{2}J), NH(^{3}J)
NH	9.38 (1H, d, *J* = 7.4 Hz)	-	-

2.2.5 Synthesis of *S*-octyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3e)



$C_9H_{19}NOS$		$C_{17}H_{22}FNO_3S$
189.32 g/mol		339.42 g/mol
1.00 g		0.30 g
2e	**17%**	**3e**

Prepared according to **GP-III** using *S*-octyl carbamothioate (**2e**) (1.00 g, 5.28 mmol, 1.0 eq.), glyoxylic acid monohydrate (**4**) (0.49 g, 5.28 mmol, 1.0 eq.), *p*-fluorophenol (**5**) (0.71 g, 6.34 mmol, 1.2 eq.) in 9 ml of TFA. **3e** was obtained as a colourless solid in a yield of 17%.

Yield: 0.30 g (0.88 mmol, 17%).

Appearance: Colourless solid.

R_f-Value: 0.13 (SiO_2, *c*-Hex/Toluene 1:1 + 1% AcOH).

IR: ν [cm^{-1}] = 3342 (m), 3072 (w), 2951 (w), 2921 (br), 2852 (w), 2363 (w), 1799 (s), 1708 (w), 1651 (vs), 1506 (m), 1482 (s), 1467 (m), 1448 (w), 1437 (w), 1381 (w), 1321 (w), 1268 (w), 1254 (s), 1232 (w), 1205 (s), 1194 (s), 1120 (s), 1077 (s), 1006 (w), 955 (w), 946 (w), 900 (w), 886 (w), 824 (m).

MP: 133 °C.

HR-MS (ESI): Theor.$[M+H]^+$: 340.13771, found: 340.13754.

Theor.$[M+Na]^+$: 362.11966, found: 362.11962.

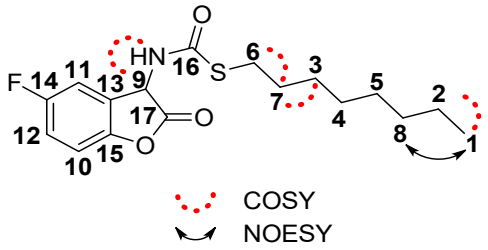
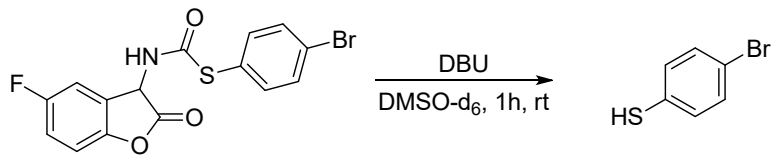


Table 11: **1D and 2D-NMR data of *S*-octyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (3e) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.**

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	0.85 (3H, t, *J* = 7.0 Hz)	13.9, CH_3	C1→H2(^{2}J)
2	1.24 (2H, m)	22.1, CH_2	C2→H1(^{2}J), H8(^{2}J)
3	1.25 (2H, m)	28.0, CH_2	C3→H6(^{3}J)
4	1.22 (2H, m)	28.4, CH_2	C4→H3(^{2}J), H7(^{3}J)
5	1.23 (2H, m)	28.6, CH_2	-
6	2.75 (2H, m)	28.9, CH_2	C6→H7(^{2}J)
7	1.46 (2H, quin, *J* = 7.3 Hz)	29.9, CH_2	C7→H6(^{2}J)
8	1.21 (2H, m)	31.2, CH_2	C8→H1(^{3}J), H2(^{2}J)
9	5.44 (1H, d, *J* = 7.1 Hz)	52.3, CH	C9→H11(^{3}J), NH(^{2}J)
10	7.17 (1H, m)	111.25+111.45, CH_{arom}	C10→H9(^{4}J), H12(^{2}J)
11	7.24 (1H, m)	111.73+111.79, CH_{arom}	C11→H9(^{3}J), H12(^{3}J)
12	7.21 (1H, m)	115.8+116.0, CH_{arom}	C12→H10(^{2}J)
13	-	127.56+127.63, C_q	C13→H9(^{2}J), H11(^{2}J), NH(^{3}J)
14	-	149.42+149.43, C_q	C14→H9(^{4}J), H12(^{2}J), H11(^{2}J), H10(^{2}J)
15	-	159.8+157.9, C_q	C15→H9(^{3}J), H11(^{3}J)
16	-	167.1, C_q	C16→H6(^{3}J), H9(^{3}J), NH(^{2}J)
17	-	173.0, C_q	C17→H9(^{2}J), NH(^{3}J)
NH	9.37 (1H, d, *J* = 7.3 Hz)	-	-

2.3 Decomposition experiments

2.3.1 Decomposition of 3a with DBU



$C_{15}H_9BrFNO_3S$
382.20 g/mol
20 mg
3a

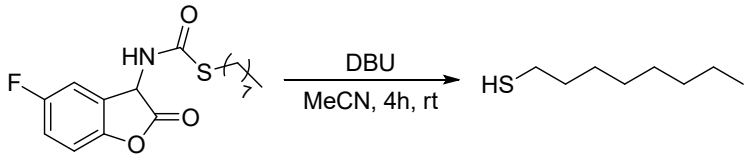
quant.

C_6H_5BrS
189.07 g/mol
1a

Prepared according to **GP-IV**. Only the small scale experiment was done using thiolcarbamate-coumaranone **3a** (0.02 g, 0.05 mmol, 1.0 eq.) and DBU (14.9 µl, 0.10 mmol, 2.0 eq.) in 0.70 ml of DMSO-d_6. During the experiment a strong emission of light green light could be seen over a time period of 10 minutes. **1a** was deprotected in a quantitative yield.

Yield (Small scale): Quantitative.

2.3.2 Decomposition of 3e with DBU



$C_{17}H_{22}FNO_3S$
339.42 g/mol
0.05 g
3e

82%

$C_8H_{18}S$
146.29 g/mol
18.0 mg
1e

Prepared according to **GP-IV**. Small scale experiment: Thiolcarbamate-coumaranone **3e** (0.02 g, 0.06 mmol, 1.0 eq.) and DBU (17.6 µl, 0.12 mmol, 2.0 eq.) in 0.70 ml of DMSO-d_6. Large scale experiment: Thiolcarbamate-coumaranone **3e** (0.05 g, 0.15 mmol, 1.0 eq.) and DBU (0.04 ml, 0.29 mmol, 2.0 eq.) in 10.0 ml of MeCN. During both experiments a strong emission of light blue light could be seen over a time period of 20 and 5 minutes, respectively. **1e** was deprotected in a yield of 82%.

Yield (Large scale): 18.0 mg (0.12 mmol, 82%).

3. NMR-Spectra

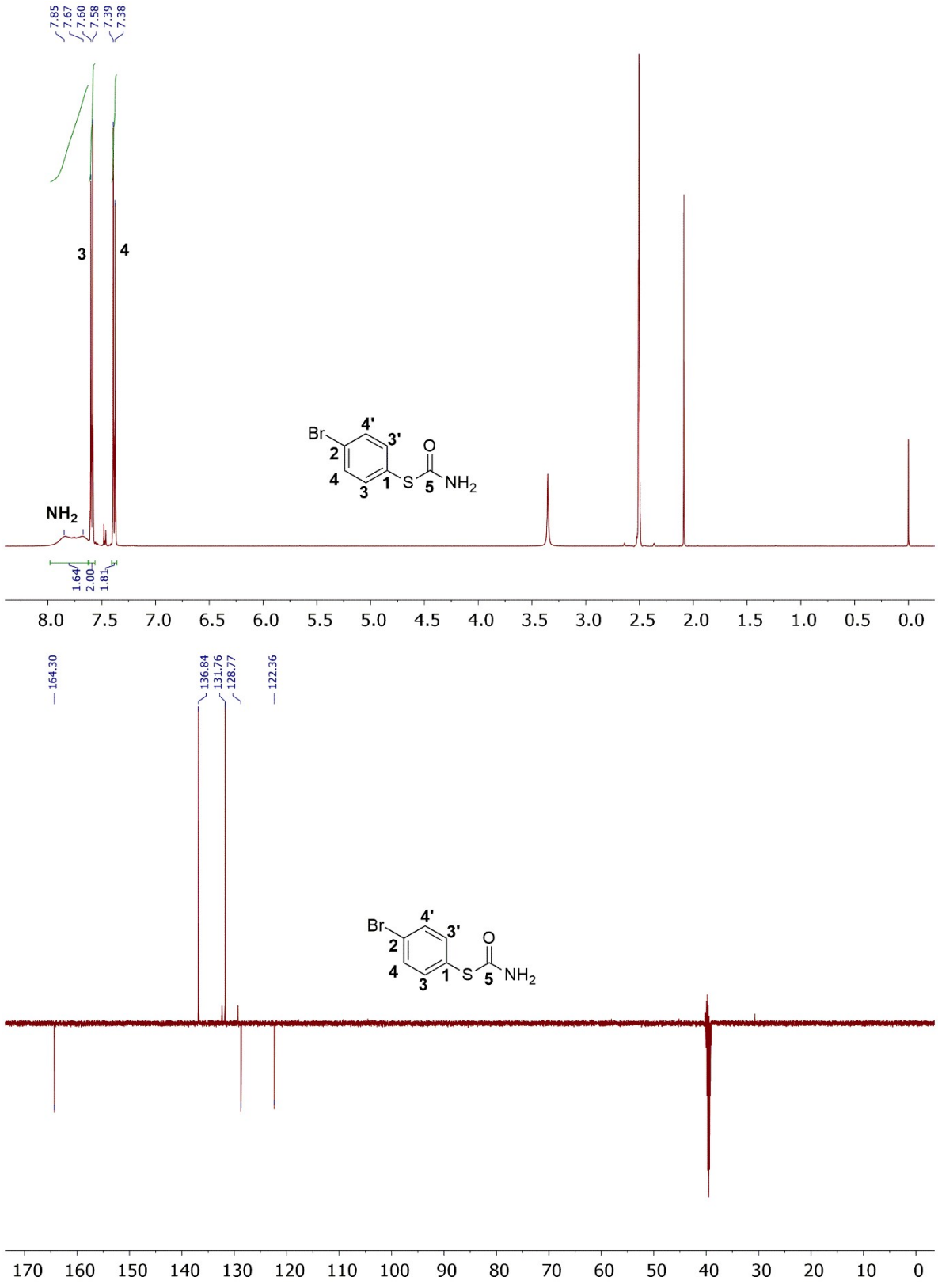


Figure 1: ^{1}H- and ^{13}C-NMR-spectrum of *S*-(4-bromophenyl) carbamothioate (**2a**) in DMSO-d_6.

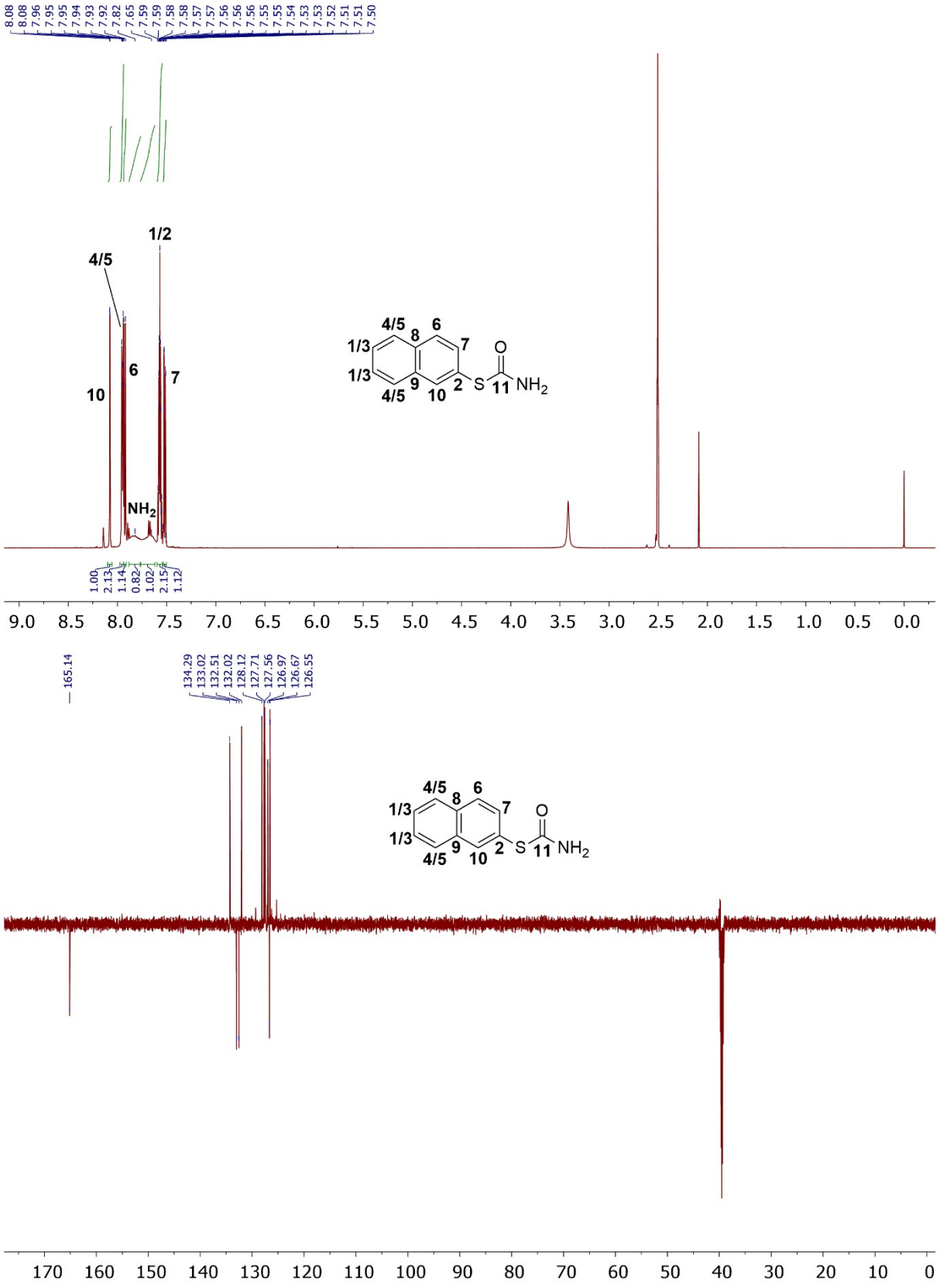


Figure 2: ^{1}H- and ^{13}C-NMR-spectrum of *S*-naphthalen-2-yl carbamothioate (**2b**) in DMSO-d_6.

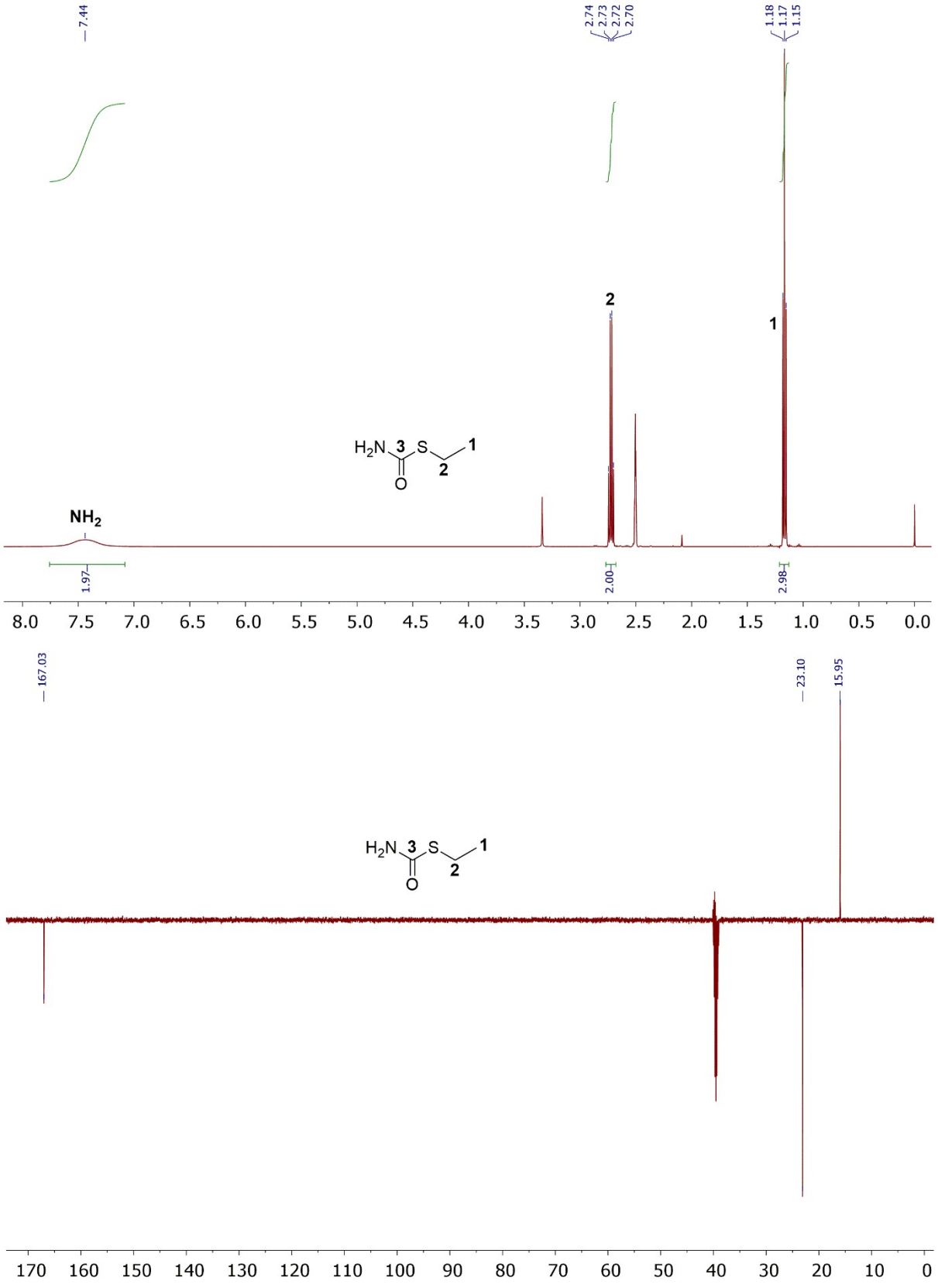


Figure 3: ^{1}H- and ^{13}C-NMR-spectrum of *S*-ethyl carbamothioate (**2c**) in DMSO-d_6.

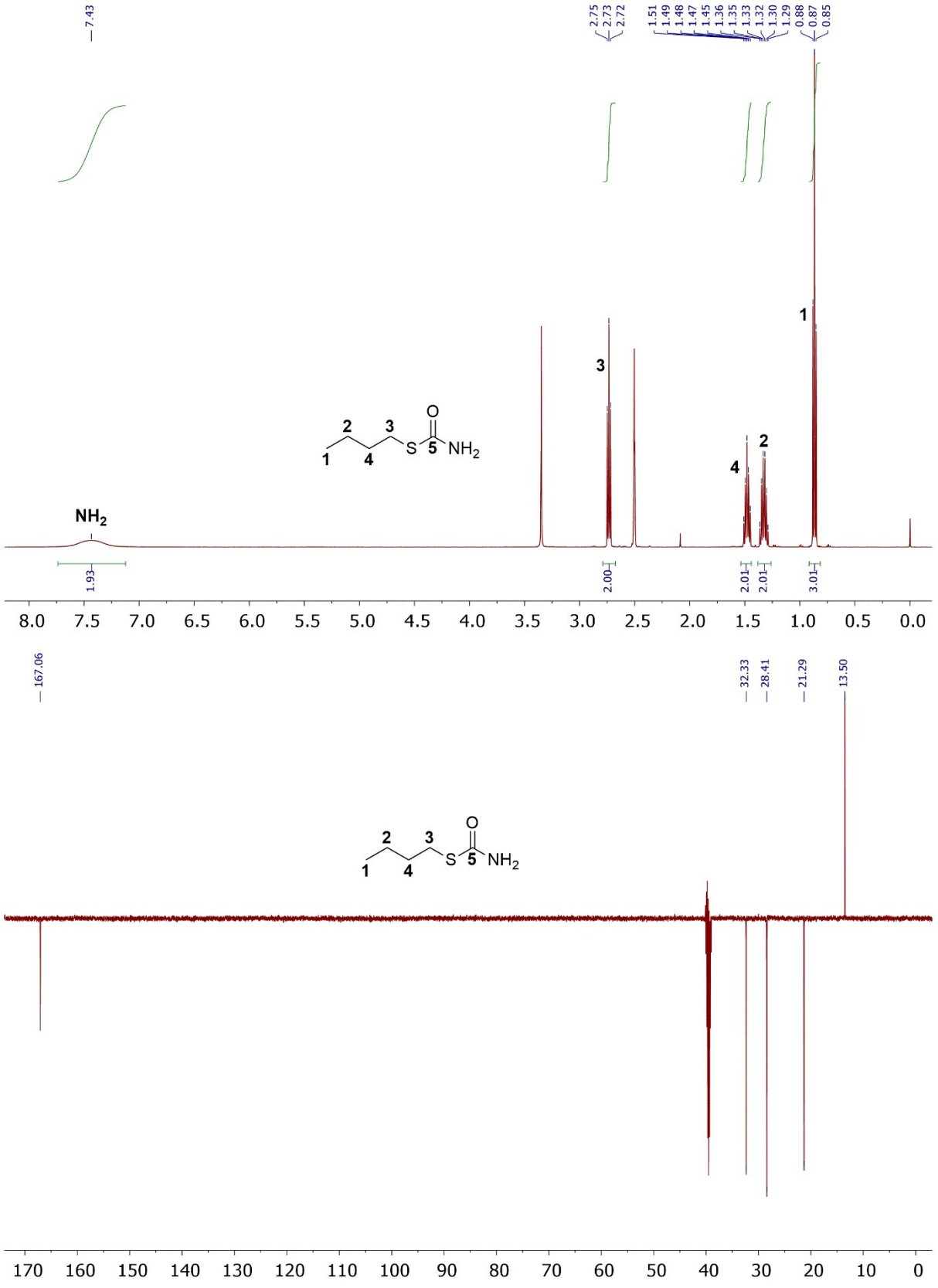


Figure 4: ^{1}H- and ^{13}C-NMR-spectrum of *S*-butyl carbamothioate (**2d**) in DMSO-d_6.

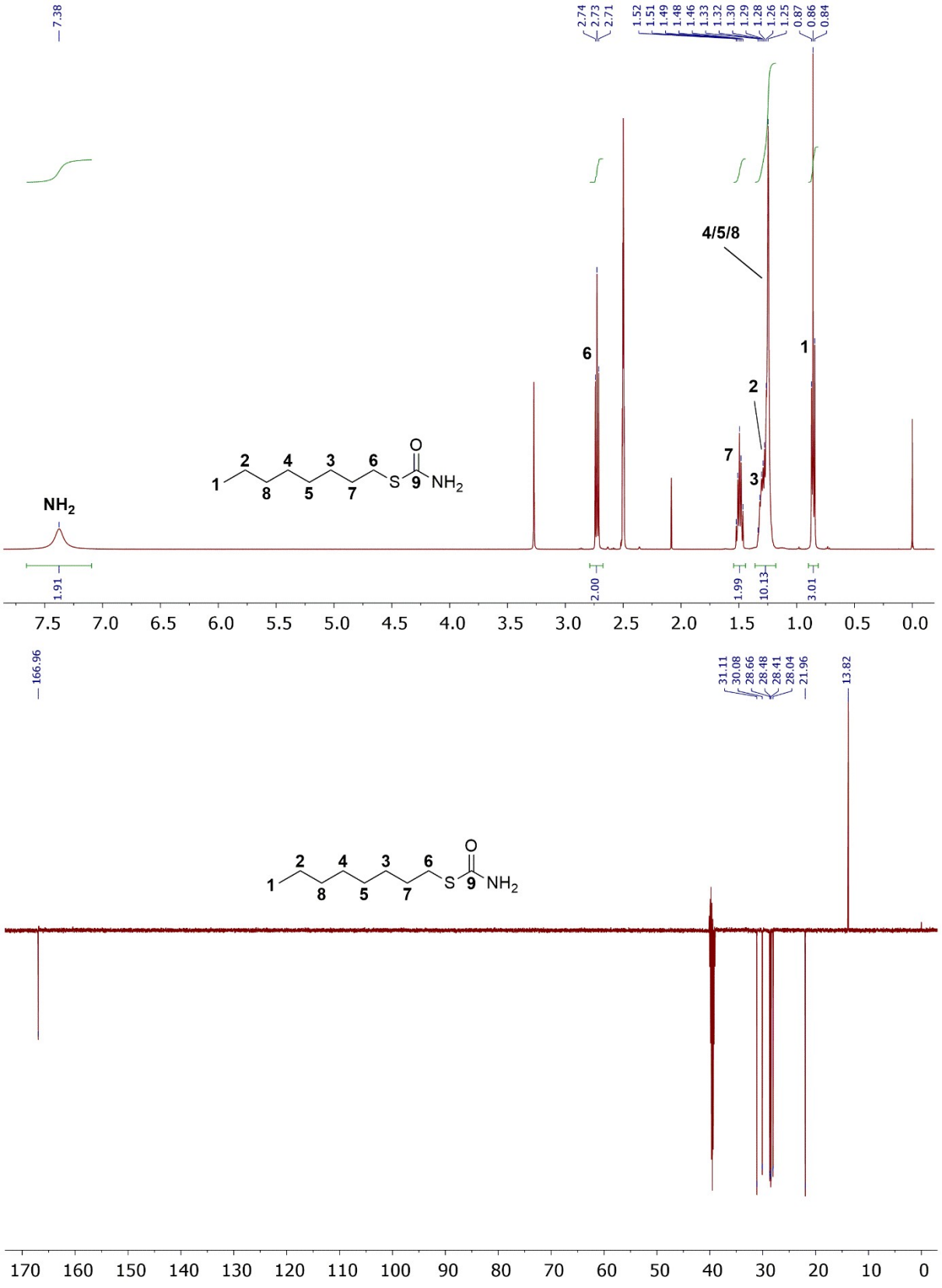


Figure 5: ^{1}H- and ^{13}C-NMR-spectrum of *S*-octyl carbamothioate (**2e**) in DMSO-d_6.

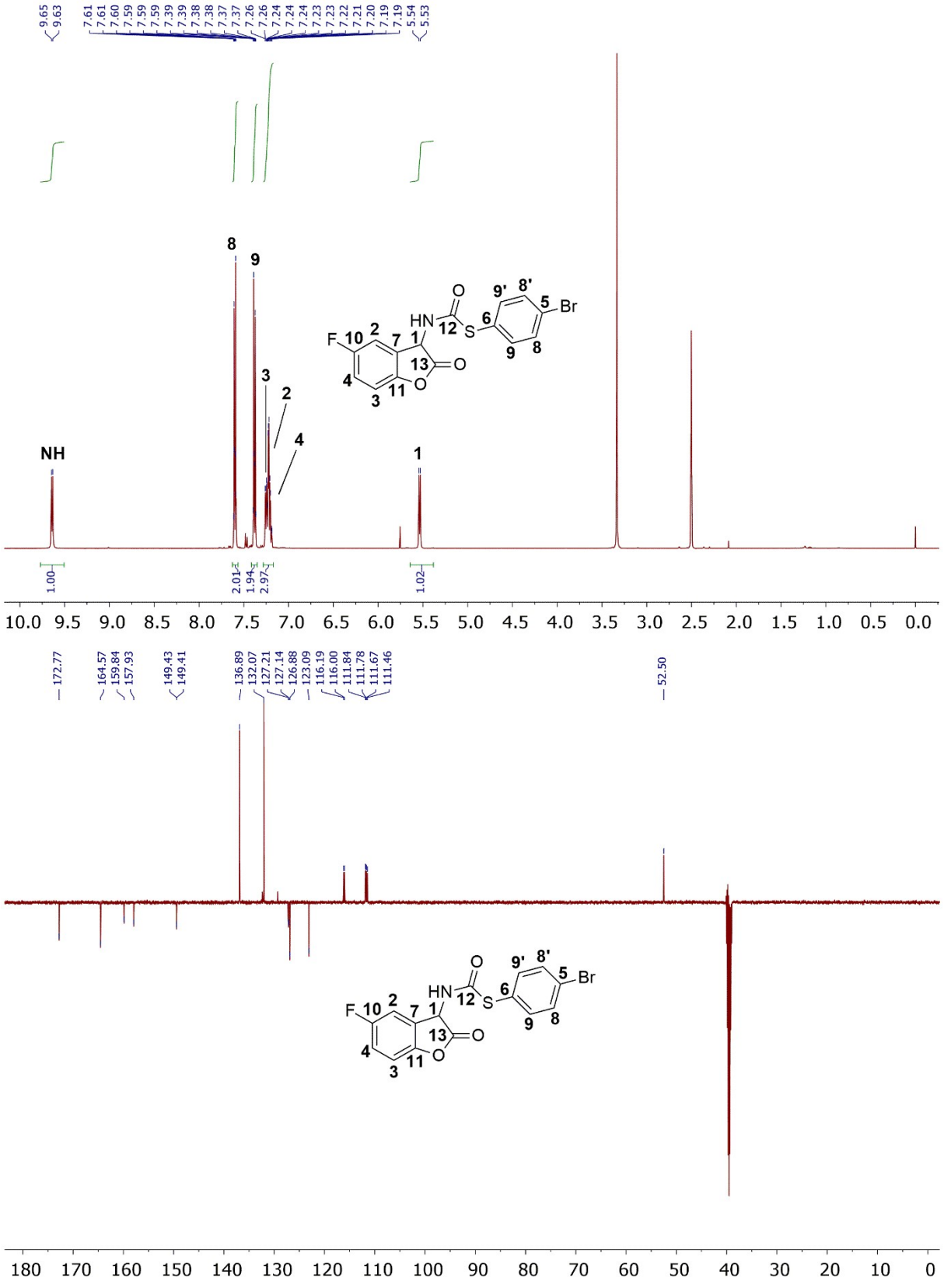


Figure 6: ^{1}H- and ^{13}C-NMR-spectrum of *S*-(4-bromophenyl) (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (**3a**) in DMSO-d_6.

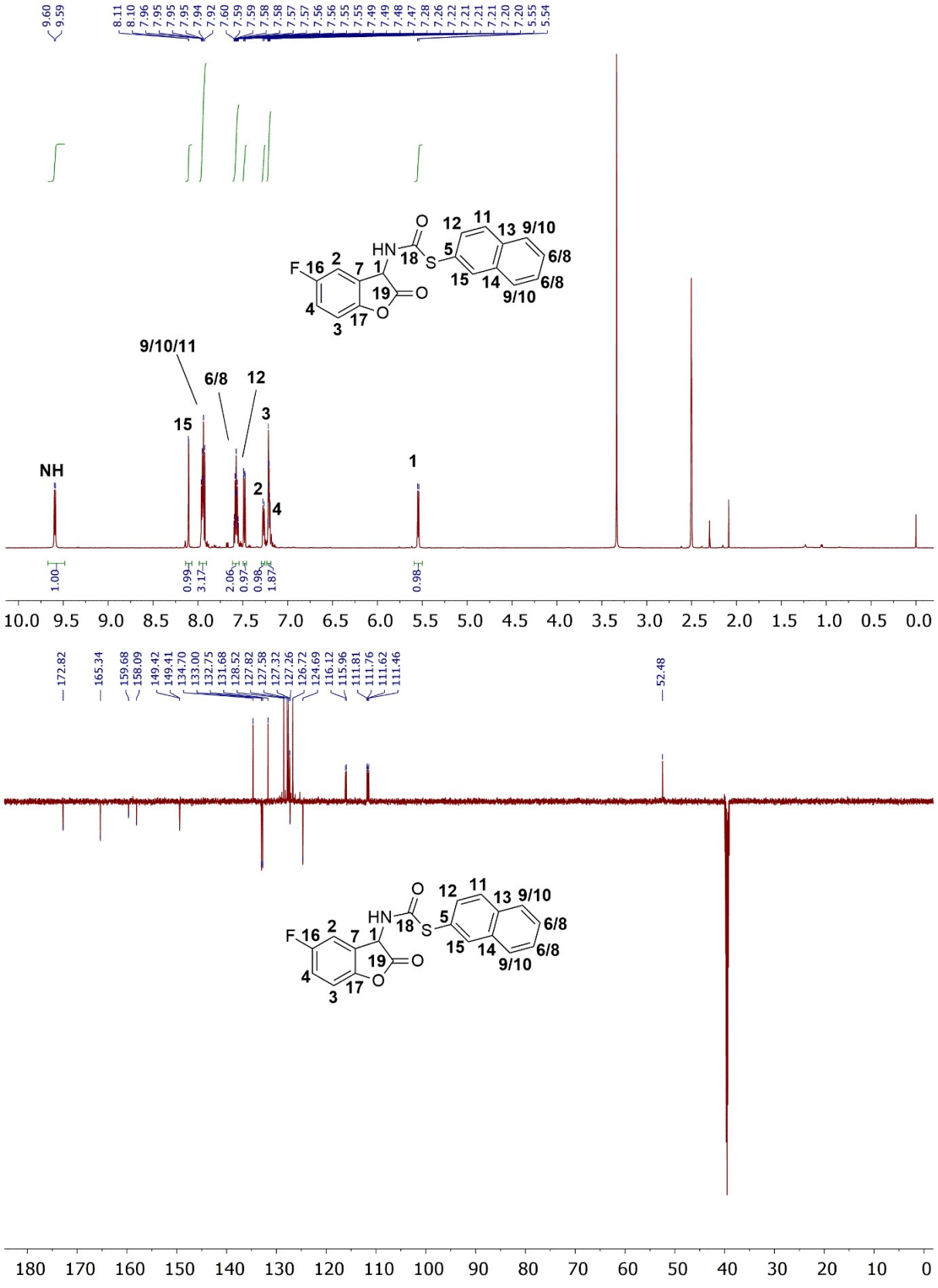


Figure 7: ^{1}H- and ^{13}C-NMR-spectrum of *S*-naphthalen-2-yl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (**3b**) in DMSO-d_6.

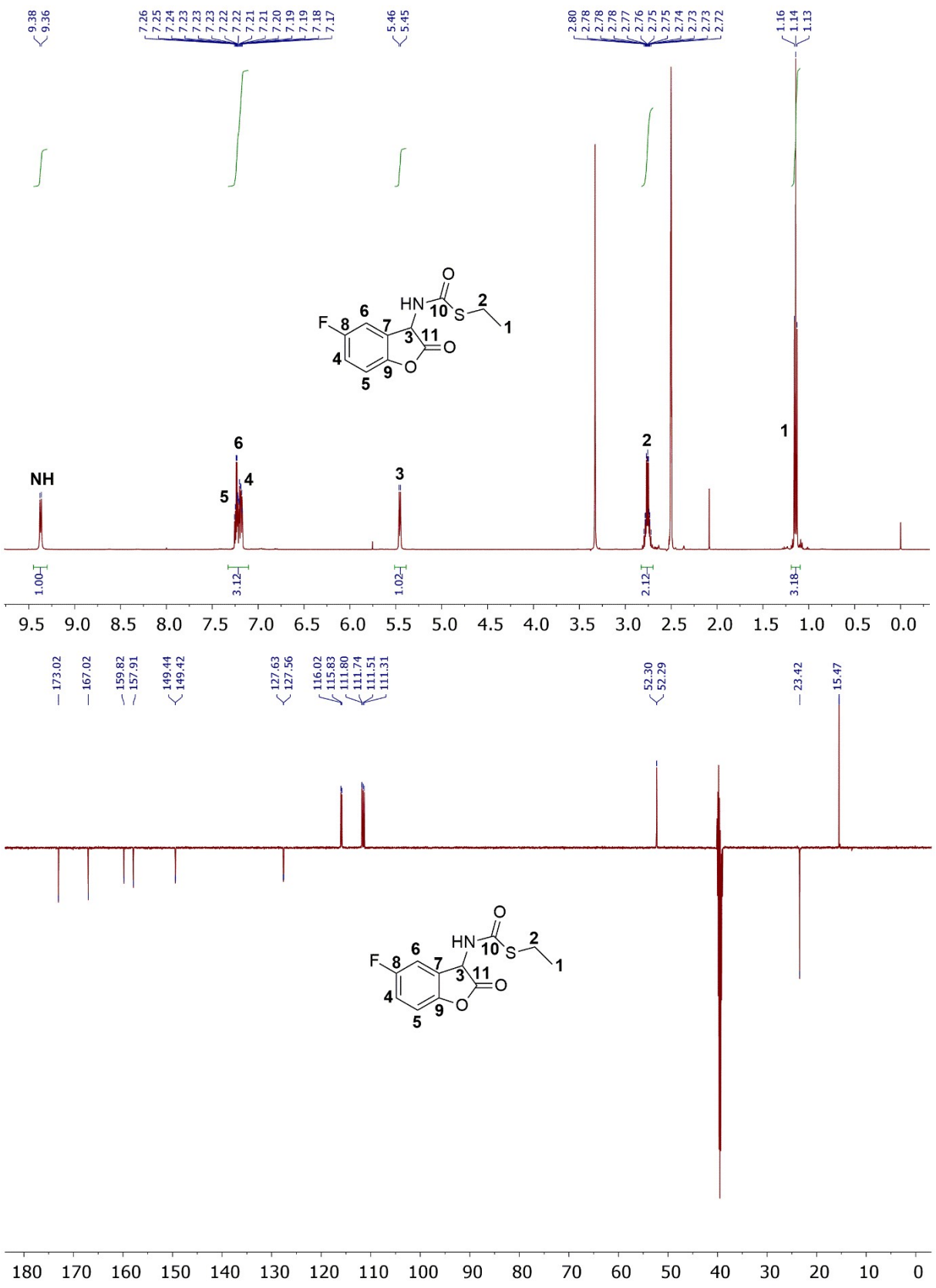


Figure 8: ^{1}H- and ^{13}C-NMR-spectrum of *S*-ethyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (**3c**) in DMSO-d_6.

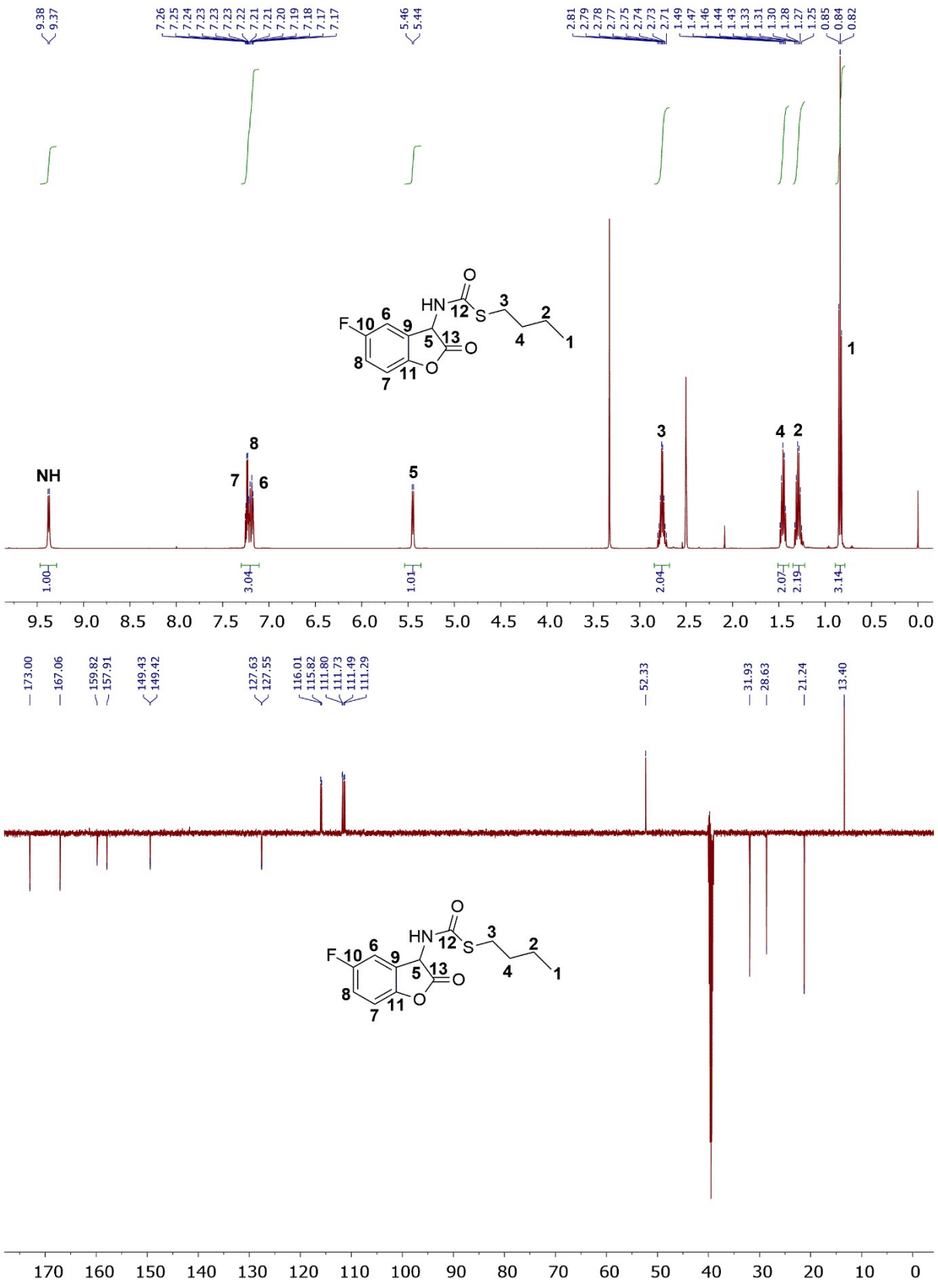


Figure 9: ^{1}H- and ^{13}C-NMR-spectrum of *S*-butyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (**3d**) in DMSO-d_6.

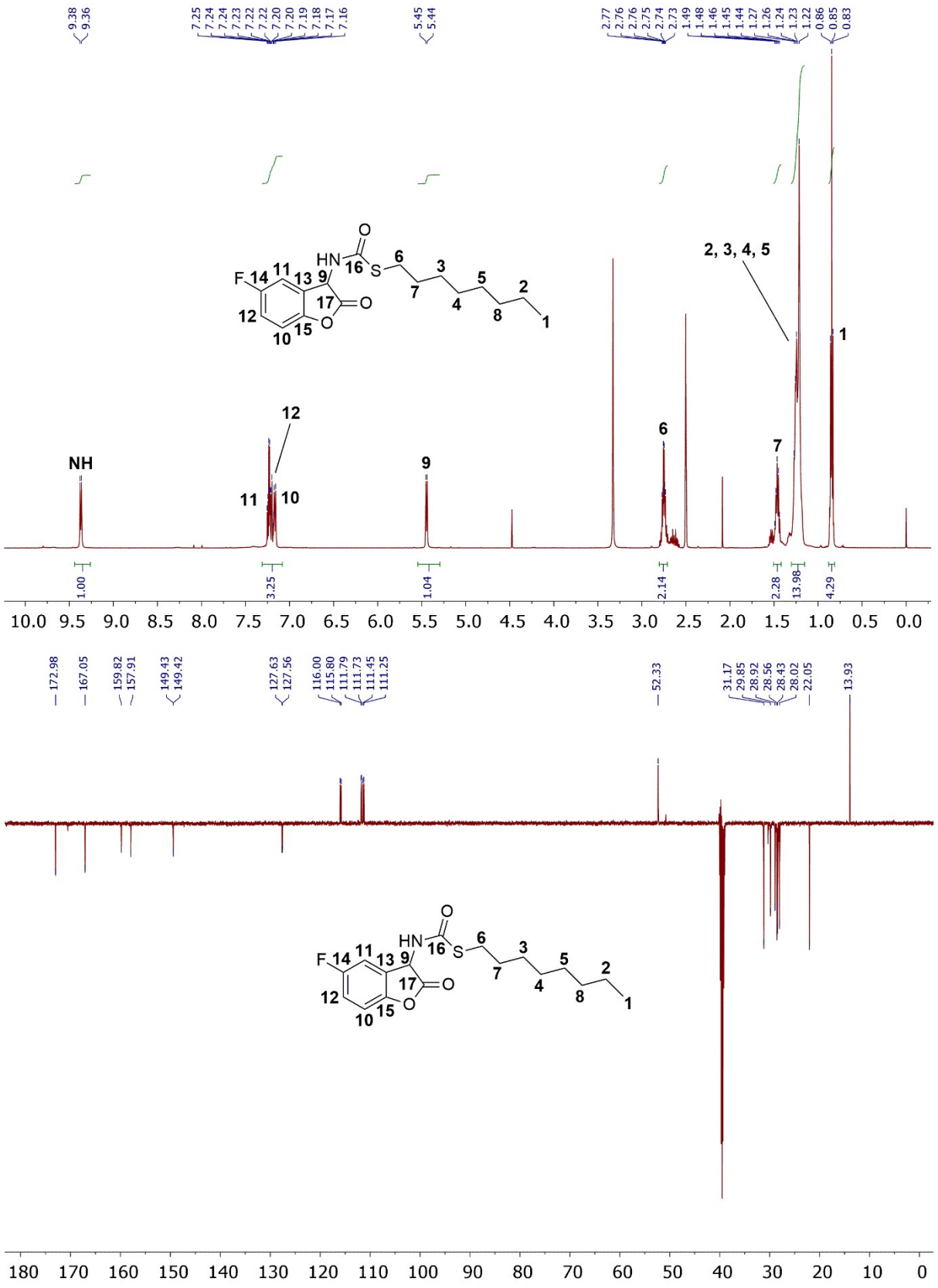


Figure 10: ^{1}H- and ^{13}C-NMR-spectrum of *S*-octyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamothioate (**3e**) in DMSO-d_6.

4. CL and photoluminescence spectra of Coumaranones 3b-3d

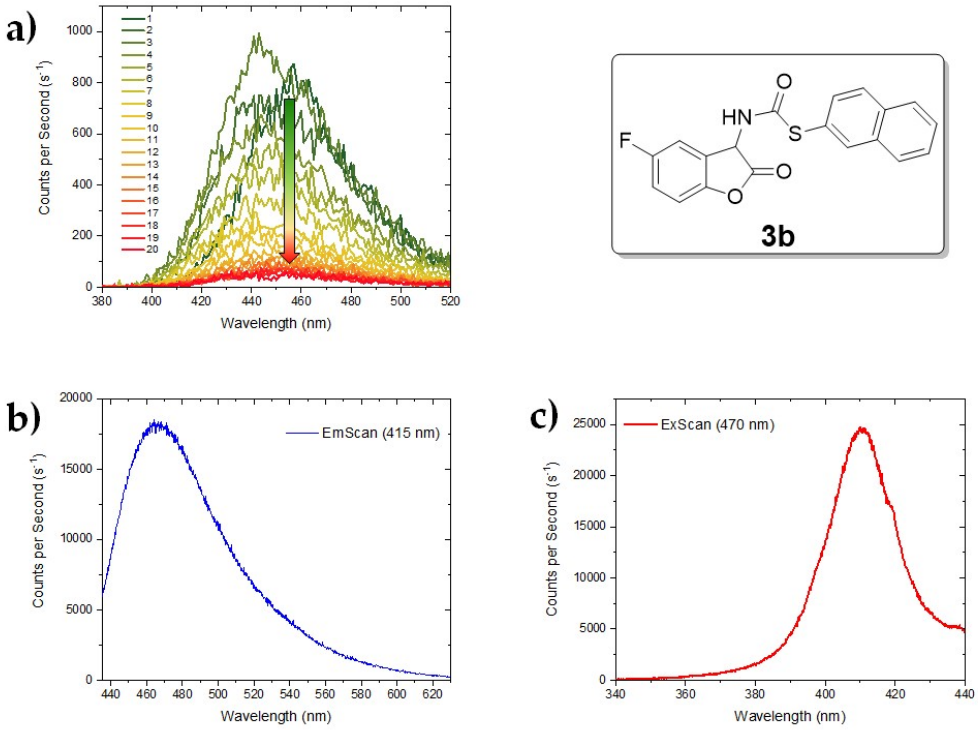


Figure 11: Emission and excitation spectra of **3b** in acetonitrile (every scan took 45 s): (a) emission scans of CL (i.e., without external excitation, Slit: 0.2), the arrow indicates the decrease in the CL; (b) emission scan of **3b** after CL was finished (external excitation λ_{Ex} = 415 nm, Slit: 1.0); (c) excitation scan of **3b** after CL was finished (λ_{Em} = 470 nm, Slit: 1.0).

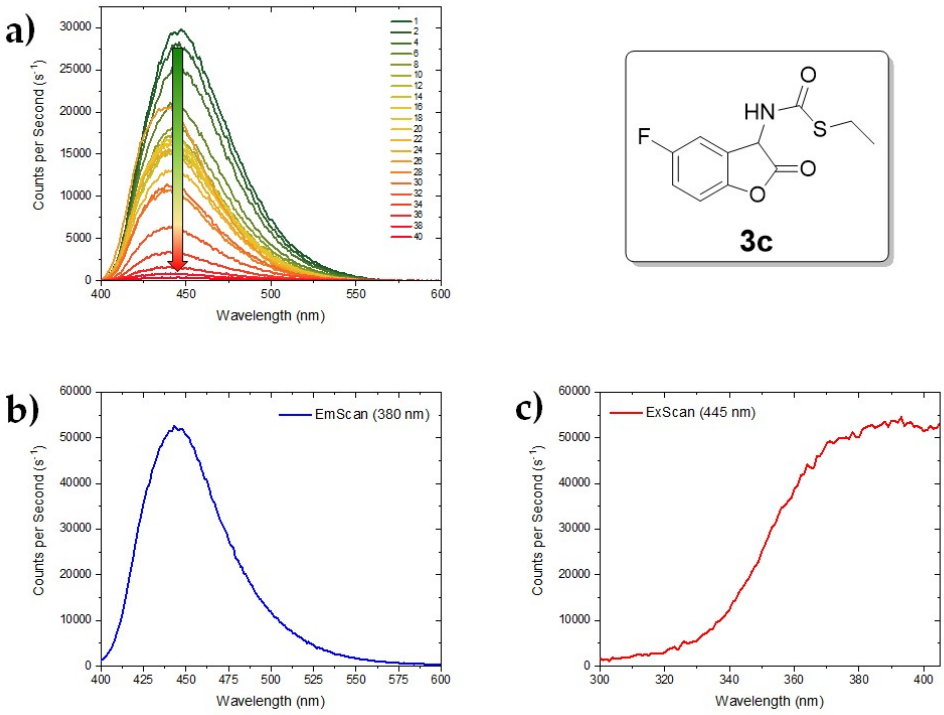


Figure 12: Emission and excitation spectra of **3c** in acetonitrile (every scan took 45 s): (a) emission scans of CL (i.e., without external excitation, Slit: 0.8), the arrow indicates the decrease in the CL; (b) emission scan of **3c** after CL was finished (external excitation λ_{Ex} = 380 nm, Slit: 1.3); (c) excitation scan of **3c** after CL was finished (λ_{Em} = 445 nm, Slit: 1.2).

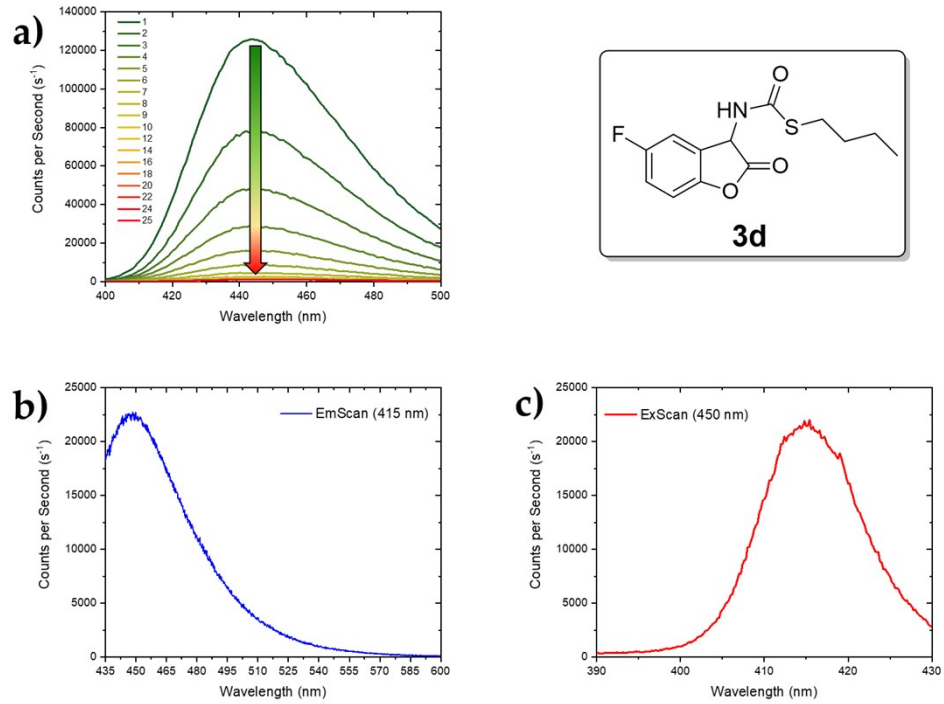
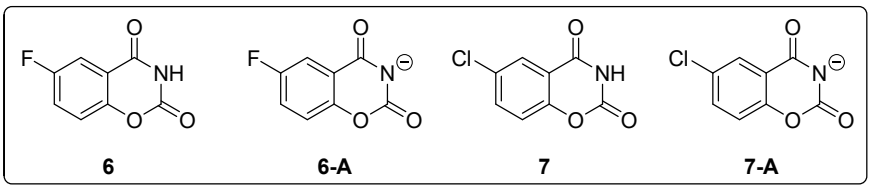


Figure 13: Emission and excitation spectra of **3d** in acetonitrile (every scan took 45 s): (a) emission scans of CL (i.e., without external excitation, Slit: 0.2), the arrow indicates the decrease in the CL; (b) emission scan of **3d** after CL was finished (external excitation λ_{Ex} = 415 nm, Slit: 0.5); (c) excitation scan of **3d** after CL was finished (λ_{Em} = 450 nm, Slit: 0.5).

5. Theoretical calculations

Compound **6-A** is the final product resulting from the decomposition of coumaranone **3e**. Theoretical calculations were conducted for two distinct derivatives in both their protonated and deprotonated forms, as illustrated in Scheme 1.



Scheme 1: Benzoxazinedione derivatives in their protonated and deprotonated states, which were used for theoretical calculations.

Calculations of the photophysical properties of these compounds were performed using DFT and TDDFT respectively in the following approach. First, a geometry optimization in the ground state was performed to obtain an appropriate ground state geometry. Afterwards, the absorption wavelengths and oscillator strengths were computed for the first 10 excited states. This was followed by a geometry optimization in the excited state, from which $E_{ex}(r_{ex})$, the energy of the excited state equilibrium geometry in equilibrium solvation, was obtained. For $E_{gs}(r_{ex})$, a single-point calculation was conducted in the electronic ground state with the equilibrium geometry and solvation of the excited state. This approach assumes that an electronic transition occurs so quickly that neither the molecules nor the surrounding solvation molecules themselves have time to adapt geometrically to the new electronic state. All calculations were carried out using *Gaussian 16* with the B3LYP functional and the 6-31+G(d,p) basis set.[4-6] Input structures were created using Avogadro.[7] The PCM (polarizable continuum model) method was employed for the solvents.[8] Absorption ($S_0 \rightarrow S_1$) and emission ($S_1 \rightarrow S_0$) including the oscillator strength were calculated in acetonitrile, DMF, DMSO, and water for each substrate. The results of these calculations for all four compounds are summarized in Table 1. The obtained values indicate that benzoxazinedione (e.g., compounds **6** and **7** in Scheme 1) needs to be protonated to exhibit efficient fluorescence. Additionally, the calculated wavelengths for the absorption and emission maxima of the GS→S_1 and S_1→GS transitions do not correspond to those of the fluorescent species observed after the oxidation of **3e**. This discrepancy suggests that either further decomposition of **6-A** or alternative

fragmentation reactions, which deviate from the established mechanisms in the literature, may occur and lead to the formation of different fluorescent species.

Table 12: Obtained values of the theoretical calculations of the absorption, emission and oscillator strength of **6**, **6-A**, **7** and **7-A** in acetonitrile, DMF, DMSO and water. The values in bold indicate that the absorption and emission processes are allowed. The absorption and emission values are compared to the obtained maxima after the CL reaction of **3e**.

Entry	Solvent	Absorption ($S_0 \rightarrow S_1$) in [nm] and [eV]	Emission ($S_1 \rightarrow S_0$) in [nm] and [eV]	Oscillator Strength of ($S_0 \rightarrow S_1$) and ($S_1 \rightarrow S_0$)
6	**MeCN**	286.205895 / 4.33193	345.533871 / 3.58814	**0.0578 / 0.1494**
	DMF	286.941808 / 4.32082	345.21926 / 3.59141	**0.0577 / 0.1496**
	DMSO	286.864794 / 4.32198	345.675488 / 3.58667	**0.0577 / 0.1507**
	Water	286.196646 / 4.33207	346.701091 / 3.57606	**0.0577 / 0.1525**
6-A	**MeCN**	267.317498 / 4.63802	399.66343 / 3.10217	0.0000 / 0.0001
	DMF	269.350101 / 4.60302	402.087227 / 3.08347	0.0000 / 0.0001
	DMSO	268.405467 / 4.61922	399.417509 / 3.10408	0.0000 / 0.0001
	Water	265.388036 / 4.67174	400.716189 / 3.09402	0.0000 / 0.0001
7	**MeCN**	294.477502 / 4.21025	366.186688 / 3.38451	**0.0425 / 0.1186**
	DMF	295.813149 / 4.19124	365.570165 / 3.39148	**0.0425 /0.1188**
	DMSO	295.617775 / 4.19401	366.323014 / 3.38451	**0.0425 / 0.1197**
	Water	294.318118 / 4.21253	368.101249 / 3.36816	**0.0425 / 0.1213**
7-A	**MeCN**	266.928445 / 4.64478	399.673737 / 3.10209	0.0000 / 0.0001
	DMF	268.895032 /4.61081	397.272498 / 3.12084	0.0000 / 0.0001
	DMSO	267.964006 / 4.62683	397.096906 / 3.12222	0.0000 / 0.0001
	Water	265.014771 / 4.67832	398.113158 / 3.11425	0.0000 / 0.0001
Entry	**Solvent**	**Absorption λ_{max} [nm]**	**Fluorescence λ_{max} [nm]**	
3e	**MeCN**	407	452	

From the excited state calculations, the oscillator strength of absorption for the first 10 excited states (Table 2) were obtained. It is noteworthy that the $S_0 \rightarrow S_7$ transition of compound **6** shows the highest probability, with oscillator strengths ranging from 0.411 to 0.415, whereas the $S_0 \rightarrow S_4$ transition of compound **7** has even higher values, between 0.697 and 0.705. This indicates that halide substitution significantly impacts the photophysical properties. Conversely, for the deprotonated species **6-A** and **7-A**, the $GS \rightarrow S_2$ and $GS \rightarrow S_3$ transitions are the most likely but exhibit much lower oscillator strengths. However, emission from higher excited states is unlikely since the $GS \rightarrow S_1$ absorption of all four compounds falls within the UV range. Additionally, due to the low pKs values of the phthalimide moiety and the alkaline conditions under which oxidation occurs, the concentration of protonated species is expected to be very low. Consequently, species **6-A** and **7-A** might undergo further reactions via various pathways, leading to the formation of different fluorescent species depending on the potential

nucleofuge or fragmentation reactions. Overall, theoretical calculations indicate that benzoxazinediones can be ruled out as potential fluorescent species.

Table 13: Obtained values of the theoretical calculations for the oscillator strength of the absorption for the first ten excited states of **6**, **6-A**, **7** and **7-A** in acetonitrile, DMF, DMSO and water. The values in bold indicate the most probable transitions ($GS \rightarrow S_x$).

	6				**6-A**			
Excited State	**DMF**	**MeCN**	**DMSO**	**Water**	**DMF**	**MeCN**	**DMSO**	**Water**
S_1	0.0577	0.0578	0.0577	0.0577	0	0	0	0
S_2	0.0001	0.0001	0.0001	0.0001	**0.0745**	**0.0756**	**0.0749**	**0.0759**
S_3	0.0814	0.0805	0.0815	0.0809	**0.0688**	**0.0692**	**0.0689**	**0.0698**
S_4	0.0769	0.0719	0.0774	0.0742	0.0004	0.0004	0.0004	0.0004
S_5	0	0	0	0	0	0	0	0
S_6	**0.1468**	**0.1515**	**0.1473**	**0.1521**	0.0003	0.0005	0.0003	0.022
S_7	**0.4132**	**0.4148**	**0.4118**	**0.4105**	0.0158	0.0194	0.0176	0.0004
S_8	0	0	0	0	0.0042	0.0019	0.0031	0.0011
S_9	0.0004	0.0004	0.0004	0.0004	0	0	0	0
S_{10}	**0.1547**	**0.1546**	**0.1552**	**0.1559**	0.0001	0.0001	0.0001	0.0001

	7				**7-A**			
Excited State	**DMF**	**MeCN**	**DMSO**	**Water**	**DMF**	**MeCN**	**DMSO**	**Water**
S_1	0.0425	0.0425	0.0425	0.0425	0	0	0	0
S_2	0.0001	0.0001	0.0001	0.0001	**0.0604**	**0.0605**	**0.0603**	**0.0603**
S_3	0.0258	0.0255	0.0259	0.0259	**0.0564**	**0.0572**	**0.0567**	**0.058**
S_4	**0.7046**	**0.6982**	**0.7036**	**0.6971**	0.0003	0.0003	0.0003	0.0004
S_5	0.0002	0.0051	0.0002	0.0045	0.0003	0.0003	0.0003	0.0003
S_6	0.0027	0.0002	0.0027	0.0002	0.0041	0.0057	0.0045	0.0077
S_7	**0.096**	**0.1062**	**0.0974**	**0.1072**	0	0	0	0.0098
S_8	0	0	0	0	0.0131	0.0118	0.0127	0
S_9	0	0	0	0	0	0	0	0
S_{10}	0.0253	0.0233	0.025	0.0232	0.0002	0.0002	0.0002	0.0002

6. Literature

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