Title: Preparation of Imidazolidin-4-ones and Their Evaluation as Hydrolytically Cleavable Precursors for the Slow Release of Bioactive Volatile Carbonyl Derivatives

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General aspects and instrumentation: Demineralised water was obtained from a Millipore Synergy 185 water purifier. IR spectra: Perkin Elmer 1600 FTIR spectrometer, $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded at 25°C on a Bruker 400 MHz DPX or 500 MHz Avance spectrometer, δ in ppm downfield from Me_4Si as internal standard, J in Hz. Standard pulse sequences and parameters were used. High-resolution mass spectra (HR-MS) were recorded in the multi-mode on an Agilent 1200 RR high performance liquid chromatograph, equipped with an Agilent Eclipse Plus C18 column (2.1 × 100 mm i.d.), eluted at 0.5 mL min^{-1} with a gradient of water (containing 0.1% of formic acid)/acetonitrile at 50°C and coupled to an MSD TOF HR G3250A mass spectrometer (multi-mode source, dual mode positive) at 350°C, with the N_2 flow at 5 mL min^{-1}, the nebuliser pressure at 40 psi, the capillary voltage at 3000 V, and the fragmentor voltage at 140 V, or by direct injection into the mass spectrometer.

Additional Figures for the Crystal Structure of (5*S*,6*S*,9*R*)-4a and Calculated log $P_{o/w}$ Values for Precursors 1–11:

Figure S1. View of the molecular structure of (5*S*,6*S*,9*R*)-**4a**; the two occupancy parts are represented in purple (70% of occupancy) and green (30% of occupancy).

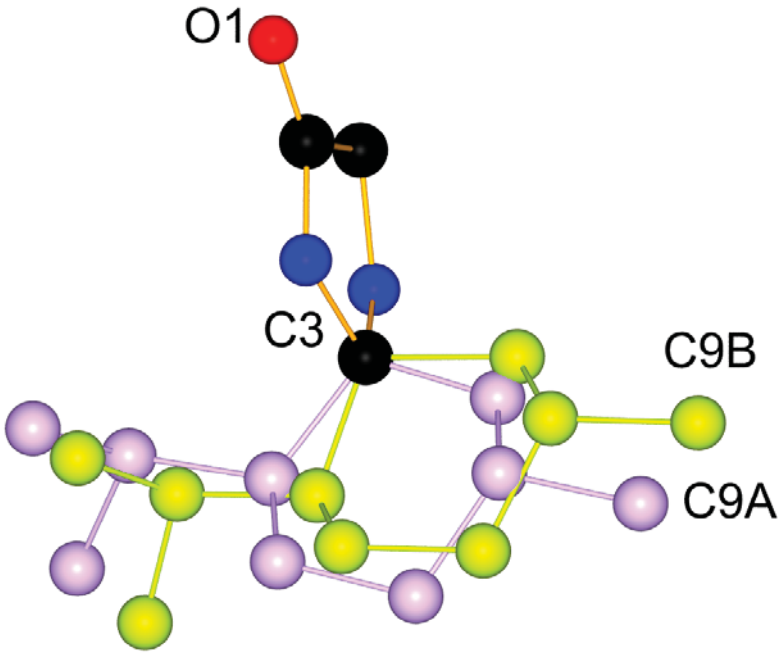


Figure S2. View of the crystal packing of (5*S*,6*S*,9*R*)-**4a** along the *a* axis; hydrogen bonds are drawn as dashed blue lines.

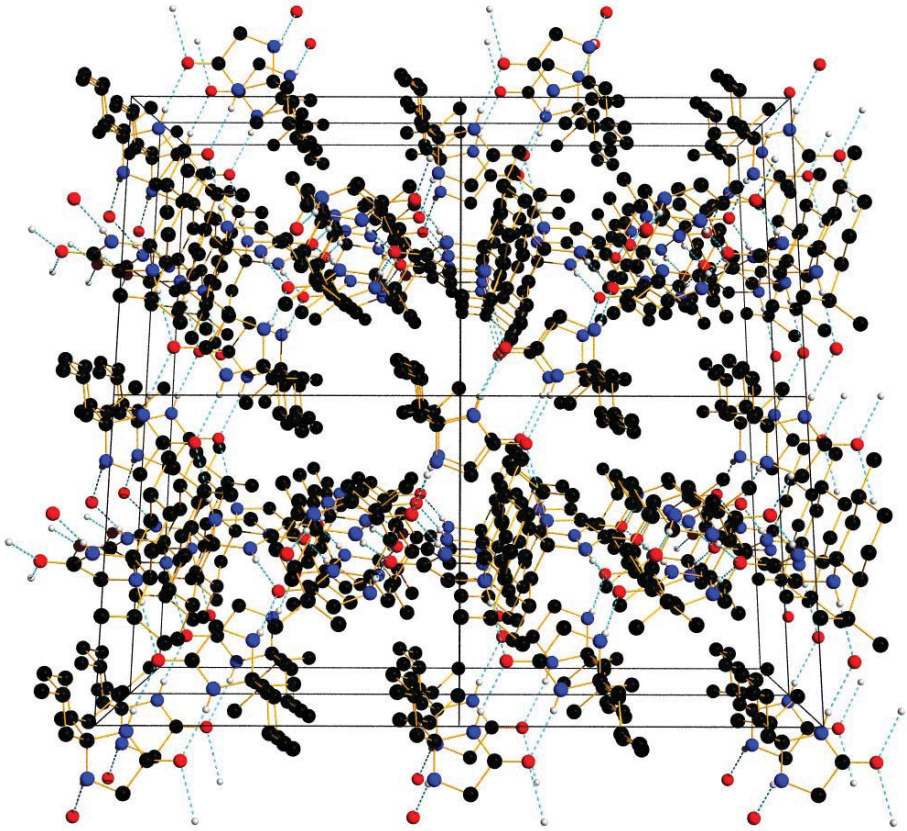


Figure S3. View of the crystal packing of (5*S*,6*S*,9*R*)-**4a** along the *b* axis; hydrogen bonds are drawn as dashed blue lines.

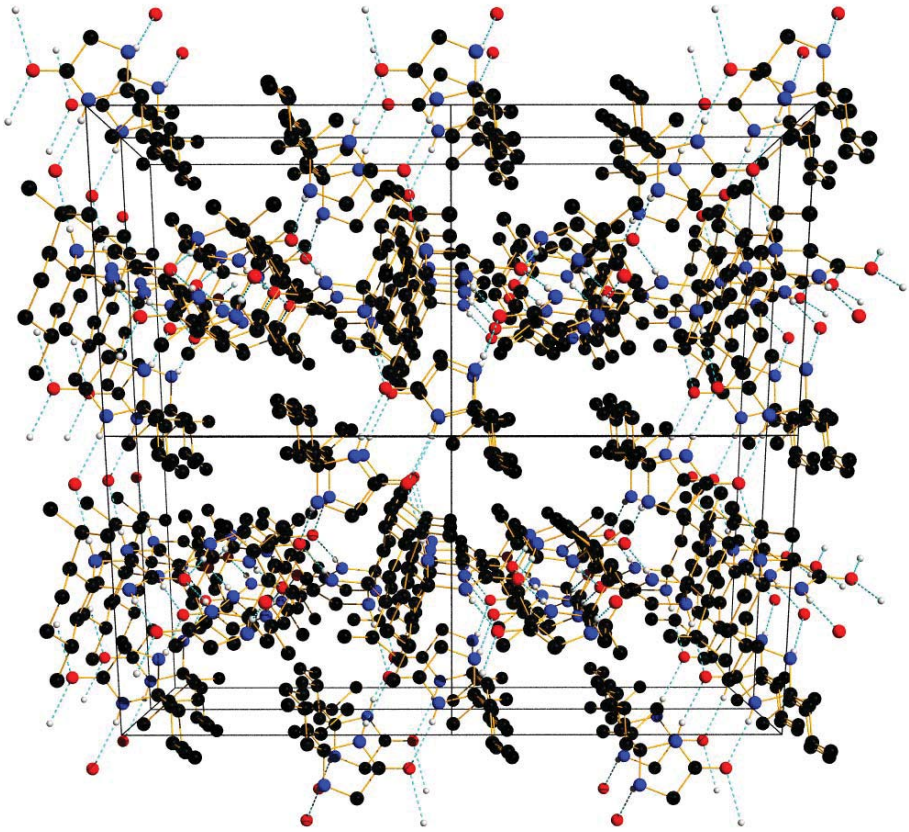


Figure S4. View of the crystal packing of (5*S*,6*S*,9*R*)-**4a** along the *c* axis; hydrogen bonds are drawn as dashed blue lines.

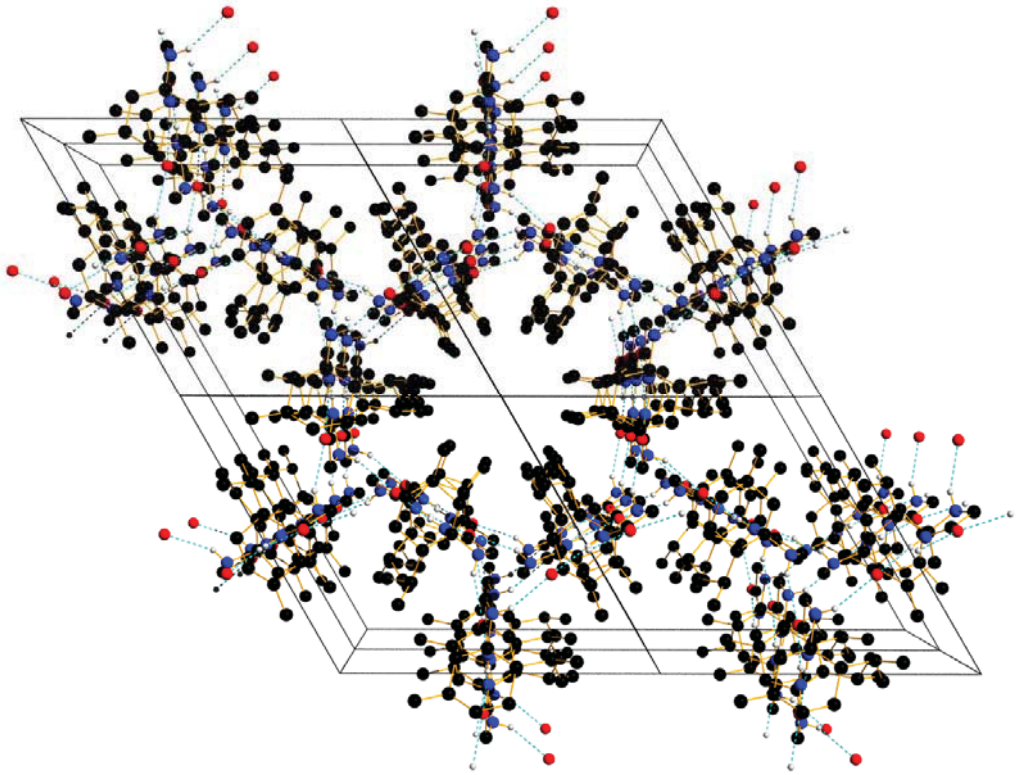


Table S1. Calculated logarithmic octanol/water partition coefficients (log $P_{o/w}$) of imidazolidinones **1**–**9**, oxazolidin-4-one **10**, and oxazolidine **11**.

Precursor	log $P_{o/w}$[a]	Precursor	log $P_{o/w}$[a]
1a	1.12	**1b**	1.55
1c	3.25	**1d**	2.14
2a	1.77	**2b**	2.18
2c	3.89	**2d**	2.77
3a	2.21	**3b**	2.63
4a	2.78	**4b**	3.19
5a	1.64	**5c**	3.76
6a	2.04	**7a**	3.35
8a	0.48	**9a**	1.53
10	2.64	**11**	3.17

[a] values calculated according to ref. [45].

Efficiency of the Heptane Extraction of (±)-3,5,5-trimethylhexanal after 1 h and 240 h:

Figure S5. Efficiency of the heptane extraction of (±)-3,5,5-trimethylhexanal (corresponding to 1, 5, 10, 50, and 100 mol-% of the theoretical amount to be released from **2**) from water/acetonitrile buffer solutions at pH 4.6 (potassium hydrogen phthalate, ●) and 7.3 (sodium/potassium phosphate, ○) after standing for 1 h (solid line) and 240 h (dotted line).

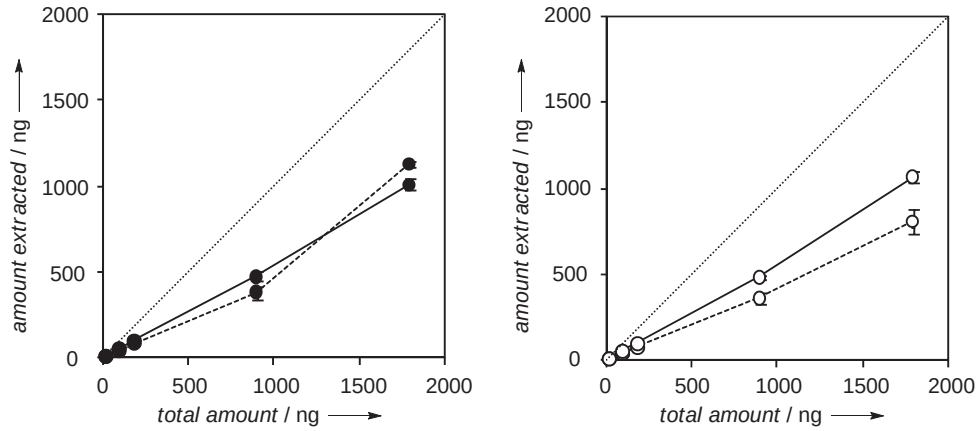


Table S2. Amounts of (±)-3,5,5-trimethylhexanal (corresponding to 1, 5, 10, 50, and 100 mol-% of the theoretical amount to be released from **2**) extracted from water/acetonitrile buffer solutions at pH 4.6 and 7.3 (Figure S5) and an emulsion of a cationic surfactant in water (Figure 7).

Total amount		Amount released from					
		buffer pH 4.6		buffer pH 7.3		emulsion pH 4.4	
		after 1 h	after 240 h	after 1 h	after 240 h	after 1 h	after 240 h
[mol-%]	[ng]	[ng]	[ng]	[ng]	[ng]	[ng]	[ng]
1	17.9	11.5 (±0.3)	9.9 (±1.4)	11.7 (±0.2)	8.0 (±0.3)	10.9 (±0.3)	8.1 (±2.2)
5	89.6	51.2 (±0.8)	41.3 (±4.9)	55.1 (±3.0)	36.0 (±2.7)	48.3 (±4.0)	26.7 (±1.3)
10	179.2	105.1 (±2.3)	84.3 (±11.9)	99.1 (±3.9)	76.8 (±4.5)	95.8 (±6.3)	49.4 (±7.2)
50	895.8	476.2 (±26.7)	383.1 (±38.2)	484.2 (±8.5)	363.4 (±30.6)	463.0 (±33.1)	171.8 (±37.7)
100	1791.7	1007.5 (±33.5)	1129.1 (±15.9)	1065.2 (±30.2)	807.8 (±69.8)	971.9 (±119.0)	358.1 (±108.6)

Efficiency of the Heptane Extraction of Aldehydes and Ketones after 1 h: The efficiency of extraction of the different compounds was verified at concentrations corresponding to 1 [(±)-2-methylundecanal], 3 (Trifernal®, hexanal, and Triplal®), 10 [3,5,5-trimethylhexanal and (*R*)-citronellal], 15 (2-heptanone), 20 [(–)-menthone], or 35 mol-% [(±)-5-methyl-3-heptanone] with respect to the total amount to be released from the corresponding precursor (Table S3). These data were used to correct the absolute values of aldehydes and ketones extracted from the different media (data listed in Tables S4–S6).

Table S3. Amount of different fragrance aldehydes and ketones extracted with heptane from buffered solutions in water/acetonitrile 4:1 at pH 4.6 and 7.3 or a diluted TEA-esterquat emulsion at pH 4.4 after standing for 1 h.

Carbonyl compound	Amount extracted from		
	buffer pH 4.6 [%]	buffer pH 7.3 [%]	emulsion pH 4.4 [%]
3,5,5-Trimethylhexanal	59	55	53
Trifernal®	30	31	23
(*R*)-Citronellal	41	43	29
(–)-Menthone	46	43	36
2-Heptanone	35	34	29
5-Methyl-3-heptanone	43	45	34
2-Methylundecanal	35	29	7
Hexanal	32	29	22
Triplal®	40	42	36

Table S4. Amounts of carbonyl compounds in mol-% and standard deviations (in brackets) of volatile carbonyl compounds extracted from buffered solutions in water/acetonitrile 4:1 at pH 4.6 and 7.3 or a diluted TEA-esterquat emulsion at pH 4.4 after hydrolysis of their corresponding precursors **1**–**9** (numerical data for Figures 8 and S6).

Time [h]	Trifernal® from **1a** buffer pH 4.6 [mol-%]	Trifernal® from **1a** buffer pH 7.3 [mol-%]	Trifernal® from **1a** emulsion pH 4.4 [mol-%]	Trifernal® from **1b** buffer pH 4.6 [mol-%]	Trifernal® from **1b** buffer pH 7.3 [mol-%]	Trifernal® from **1b** emulsion pH 4.4 [mol-%]
1	3.0 (±0.1)	2.6 (±0.2)	2.8 (±0.6)	0.8 (±0.1)	0.7 (±0.0)	1.2 (±0.2)
24	4.9 (±0.6)	3.6 (±0.5)	2.9 (±3.3)	1.3 (±0.1)	1.0 (±0.2)	1.4 (±0.2)
48	6.1 (±1.1)	4.8 (±1.2)	3.4 (±4.6)	1.4 (±0.5)	1.0 (±0.3)	1.3 (±0.7)
72	6.2 (±0.8)	5.3 (±0.8)	1.2 (±1.5)	1.9 (±0.1)	1.3 (±0.2)	0.3 (±0.2)
96	6.8 (±1.0)	6.1 (±1.3)	0.2 (±0.1)	2.2 (±0.4)	1.6 (±0.3)	0.2 (±0.2)
168	6.7 (±0.4)	7.8 (±1.6)	0.3 (±0.1)	2.7 (±0.3)	2.3 (±0.5)	0.2 (±0.1)
192	8.2 (±0.8)	9.2 (±1.8)	0.3 (±0.1)	3.6 (±0.7)	2.8 (±0.8)	0.2 (±0.1)
216	8.7 (±0.7)	9.1 (±1.8)	0.2 (±0.1)	3.2 (±0.2)	3.1 (±0.3)	0.4 (±0.3)
240	8.4 (±0.4)	10.6 (±1.7)	0.3 (±0.0)	2.9 (±0.1)	3.0 (±0.2)	0.3 (±0.1)
Time [h]	Trifernal® from **1c** buffer pH 4.6 [mol-%]	Trifernal® from **1c** buffer pH 7.3 [mol-%]	Trifernal® from **1c** emulsion pH 4.4 [mol-%]	Trifernal® from **1d** buffer pH 4.6 [mol-%]	Trifernal® from **1d** buffer pH 7.3 [mol-%]	Trifernal® from **1d** emulsion pH 4.4 [mol-%]
1	1.0 (±0.2)	0.8 (±0.1)	1.2 (±0.1)	0.6 (±0.1)	0.7 (±0.1)	0.8 (±0.1)
24	1.9 (±0.1)	1.3 (±0.0)	2.1 (±0.1)	1.2 (±0.1)	2.5 (±0.1)	1.4 (±0.9)
48	2.6 (±0.1)	1.4 (±0.0)	3.1 (±0.7)	1.8 (±0.0)	4.0 (±0.3)	1.8 (±2.1)
72	3.1 (±0.3)	1.6 (±0.0)	4.2 (±0.8)	2.2 (±0.3)	4.8 (±0.3)	1.2 (±1.0)
96	3.1 (±0.5)	1.6 (±0.2)	2.8 (±1.0)	2.6 (±0.2)	5.2 (±0.4)	0.3 (±0.0)
168	4.3 (±0.3)	2.3 (±0.0)	0.4 (±0.2)	3.5 (±0.2)	6.0 (±0.4)	0.2 (±0.1)
192	4.3 (±0.2)	2.5 (±0.1)	0.3 (±0.2)	4.5 (±0.8)	7.2 (±0.9)	0.2 (±0.0)
216	4.7 (±0.2)	3.0 (±0.1)	0.3 (±0.1)	4.6 (±0.1)	7.8 (±0.0)	0.3 (±0.2)
240	4.6 (±0.2)	2.6 (±0.0)	0.3 (±0.1)	4.9 (±0.7)	5.6 (±0.9)	0.3 (±0.1)
Time [h]	3,5,5-Trimethylhexanal from **2a** buffer pH 4.6 [mol-%]	3,5,5-Trimethylhexanal from **2a** buffer pH 7.3 [mol-%]	3,5,5-Trimethylhexanal from **2a** emulsion pH 4.4 [mol-%]	3,5,5-Trimethylhexanal from **2b** buffer pH 4.6 [mol-%]	3,5,5-Trimethylhexanal from **2b** buffer pH 7.3 [mol-%]	3,5,5-Trimethylhexanal from **2b** emulsion pH 4.4 [mol-%]
1	3.4 (±1.4)	3.0 (±1.7)	1.9 (±1.3)	0.9 (±0.9)	1.0 (±0.9)	0.8 (±0.5)
24	5.7 (±0.5)	4.8 (±0.4)	1.7 (±0.8)	1.4 (±1.0)	1.6 (±1.2)	1.1 (±1.0)
48	6.9 (±1.2)	6.3 (±0.9)	1.7 (±1.8)	1.4 (±0.9)	1.9 (±1.0)	1.1 (±0.7)
72	7.4 (±1.2)	7.8 (±0.5)	1.2 (±1.4)	1.5 (±1.0)	2.5 (±1.1)	0.5 (±0.2)
96	7.5 (±0.7)	8.8 (±0.3)	0.4 (±0.2)	1.8 (±1.0)	3.1 (±1.4)	0.2 (±0.1)
168	7.9 (±1.4)	11.8 (±0.4)	0.4 (±0.2)	2.4 (±1.1)	5.5 (±1.8)	0.4 (±0.0)
192	9.3 (±0.3)	14.4 (±2.1)	0.4 (±0.2)	2.7 (±1.1)	6.5 (±2.0)	0.3 (±0.0)
216	9.3 (±1.3)	14.9 (±0.1)	0.3 (±0.0)	2.8 (±0.9)	7.0 (±1.3)	0.3 (±0.0)
240	9.2 (±0.6)	15.0 (±2.0)	0.3 (±0.0)	3.1 (±0.9)	6.2 (±3.7)	0.3 (±0.0)

Table S4 (continued).

Time [h]	3,5,5-Trimethylhexanal from **2c** buffer pH 4.6 [mol-%]	3,5,5-Trimethylhexanal from **2c** buffer pH 7.3 [mol-%]	3,5,5-Trimethylhexanal from **2c** emulsion pH 4.4 [mol-%]	3,5,5-Trimethylhexanal from **2d** buffer pH 4.6 [mol-%]	3,5,5-Trimethylhexanal from **2d** buffer pH 7.3 [mol-%]	3,5,5-Trimethylhexanal from **2d** emulsion pH 4.4 [mol-%]
1	1.5 (±0.9)	1.4 (±0.9)	1.1 (±0.6)	1.0 (±0.3)	1.4 (±0.1)	0.8 (±0.3)
24	1.8 (±0.8)	1.4 (±0.6)	0.9 (±0.1)	1.7 (±0.4)	4.8 (±0.1)	1.6 (±0.6)
48	2.5 (±0.6)	2.0 (±0.6)	0.8 (±0.6)	2.5 (±0.1)	6.5 (±0.5)	2.1 (±1.6)
72	2.9 (±0.7)	2.3 (±0.6)	0.7 (±0.6)	2.9 (±0.1)	6.9 (±0.6)	1.7 (±1.4)
96	3.1 (±0.1)	2.4 (±0.1)	0.5 (±0.4)	3.6 (±0.3)	7.7 (±0.8)	0.9 (±0.3)
168	4.0 (±0.8)	3.2 (±0.8)	0.3 (±0.1)	4.5 (±0.2)	8.2 (±0.9)	0.4 (±0.0)
192	4.9 (±0.6)	4.5 (±0.2)	0.3 (±0.1)	5.2 (±0.4)	9.7 (±1.2)	0.3 (±0.1)
216	5.3 (±0.7)	4.9 (±1.1)	0.4 (±0.0)	5.1 (±0.4)	9.6 (±0.2)	0.3 (±0.1)
240	5.2 (±0.2)	4.6 (±0.1)	0.3 (±0.0)	5.7 (±0.1)	10.5 (±1.2)	0.3 (±0.1)
Time [h]	(*R*)-Citronellal from **3a** buffer pH 4.6 [mol-%]	(*R*)-Citronellal from **3a** buffer pH 7.3 [mol-%]	(*R*)-Citronellal from **3a** emulsion pH 4.4 [mol-%]	(*R*)-Citronellal from **3b** buffer pH 4.6 [mol-%]	(*R*)-Citronellal from **3b** buffer pH 7.3 [mol-%]	(*R*)-Citronellal from **3b** emulsion pH 4.4 [mol-%]
1	12.6 (±1.0)	11.1 (±1.6)	16.9 (±0.4)	2.6 (±0.6)	2.9 (±0.3)	2.3 (±0.5)
24	12.4 (±0.5)	15.2 (±0.7)	19.1 (±2.9)	0.6 (±0.1)	3.5 (±0.2)	0.5 (±0.2)
48	9.2 (±2.8)	13.6 (±4.7)	13.9 (±4.8)	0.3 (±0.0)	4.3 (±0.2)	0.5 (±0.4)
72	10.6 (±0.9)	17.6 (±2.4)	16.9 (±1.2)	0.3 (±0.0)	4.6 (±0.1)	0.2 (±0.1)
96	10.3 (±0.6)	17.7 (±1.5)	17.4 (±2.2)	0.3 (±0.0)	5.1 (±0.4)	0.3 (±0.2)
168	10.1 (±0.0)	20.5 (±0.8)	14.9 (±0.4)	0.4 (±0.1)	6.3 (±0.7)	0.3 (±0.2)
192	10.5 (±1.3)	21.4 (±1.8)	15.3 (±2.6)	0.3 (±0.1)	8.4 (±0.0)	0.2 (±0.1)
216	11.0 (±0.1)	22.6 (±1.8)	17.0 (±0.9)	0.3 (±0.0)	8.0 (±0.6)	0.2 (±0.1)
240	11.0 (±0.0)	22.8 (±0.8)	17.0 (±1.0)	0.5 (±0.1)	9.1 (±0.6)	0.2 (±0.1)
Time [h]	(–)-Menthone from **4a** buffer pH 4.6 [mol-%]	(–)-Menthone from **4a** buffer pH 7.3 [mol-%]	(–)-Menthone from **4a** emulsion pH 4.4 [mol-%]	(–)-Menthone from **4b** buffer pH 4.6 [mol-%]	(–)-Menthone from **4b** buffer pH 7.3 [mol-%]	(–)-Menthone from **4b** emulsion pH 4.4 [mol-%]
1	17.3 (±2.6)	20.1 (±2.9)	18.8 (±4.4)	0.9 (±0.7)	0.9 (±0.6)	0.9 (±0.7)
24	18.9 (±4.8)	20.9 (±4.5)	20.2 (±4.0)	1.1 (±0.6)	1.3 (±0.6)	1.3 (±0.4)
48	20.4 (±1.8)	22.9 (±0.5)	21.6 (±2.0)	1.3 (±0.7)	1.5 (±0.9)	1.3 (±0.6)
72	23.0 (±1.6)	26.1 (±0.0)	22.9 (±2.1)	1.6 (±0.7)	2.0 (±0.9)	1.6 (±0.5)
96	22.5 (±2.5)	25.8 (±0.8)	22.4 (±1.2)	1.9 (±1.0)	2.3 (±0.7)	1.6 (±0.5)
168	27.0 (±1.1)	33.5 (±0.1)	26.4 (±2.3)	2.8 (±0.9)	3.5 (±1.3)	2.1 (±0.7)
192	31.2 (±1.5)	38.3 (±1.0)	26.9 (±1.5)	3.4 (±1.7)	4.3 (±1.9)	2.5 (±1.3)
216	31.6 (±2.0)	39.1 (±0.6)	27.1 (±1.4)	3.6 (±0.9)	4.8 (±1.1)	2.9 (±0.4)
240	32.8 (±0.5)	41.6 (±3.2)	27.2 (±1.6)	3.9 (±0.6)	5.0 (±0.4)	2.8 (±0.4)

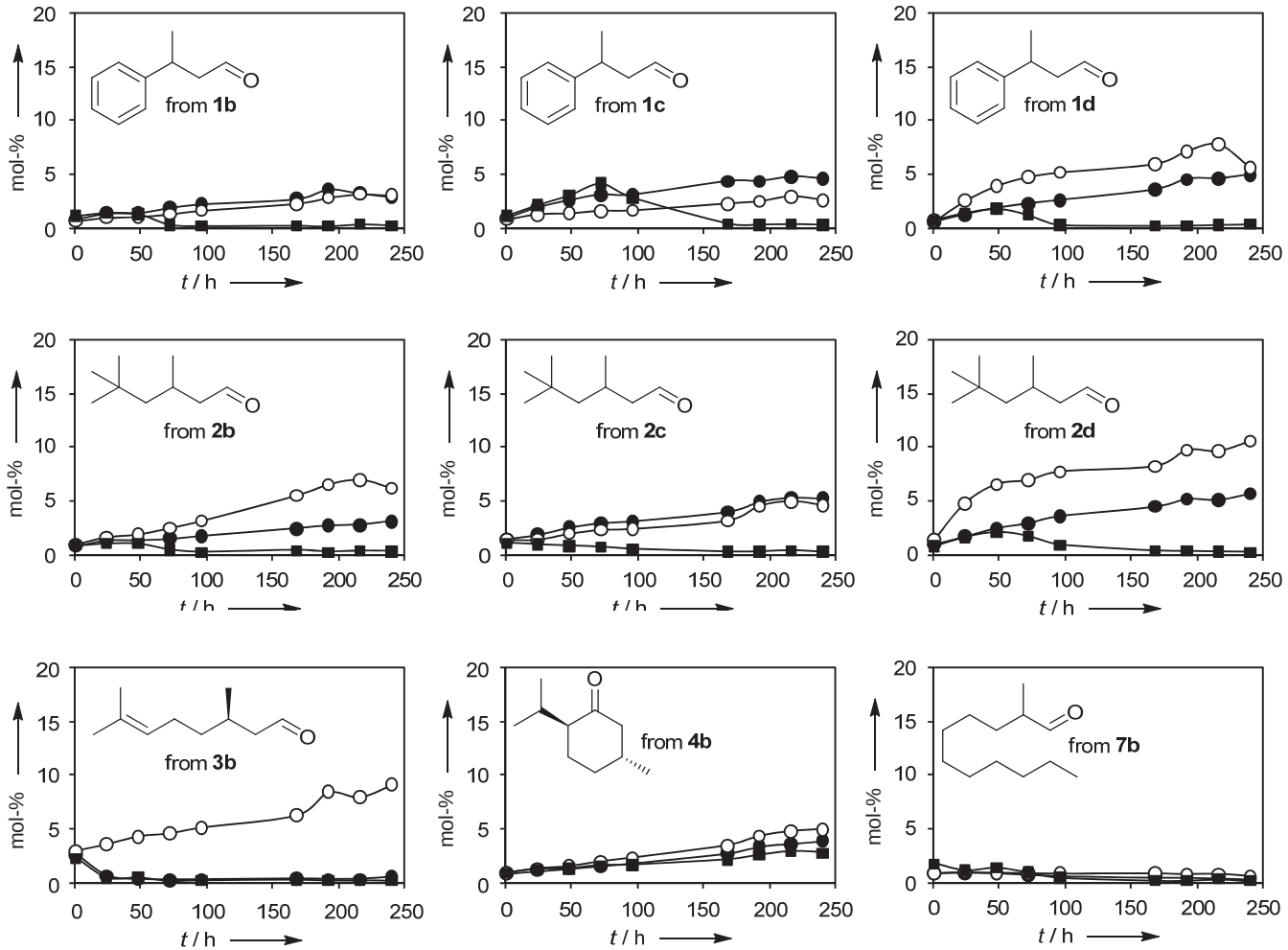
Table S4 (continued)

Time [h]	2-Heptanone from **5a** buffer pH 4.6 [mol-%]	2-Heptanone from **5a** buffer pH 7.3 [mol-%]	2-Heptanone from **5a** emulsion pH 4.4 [mol-%]	5-Methyl-3-heptanone from **6a** buffer pH 4.6 [mol-%]	5-Methyl-3-heptanone from **6a** buffer pH 7.3 [mol-%]	5-Methyl-3-heptanone from **6a** emulsion pH 4.4 [mol-%]
1	16.3 (±6.1)	16.2 (±7.0)	23.1 (±8.4)	41.4 (±23.0)	40.4 (±18.8)	50.9 (±27.2)
24	18.7 (±4.4)	21.0 (±5.4)	28.2 (±3.4)	44.5 (±13.8)	44.7 (±10.6)	59.1 (±9.8)
48	17.7 (±9.9)	21.6 (±11.3)	27.6 (±12.3)	43.9 (±29.2)	44.7 (±26.9)	62.9 (±30.0)
72	20.8 (±6.9)	26.5 (±8.3)	33.4 (±7.4)	52.4 (±20.5)	57.5 (±18.7)	71.2 (±15.0)
96	22.5 (±7.2)	29.4 (±7.0)	31.6 (±7.5)	57.2 (±19.8)	64.2 (±20.4)	72.5 (±23.1)
168	28.1 (±7.7)	41.6 (±8.3)	38.6 (±13.1)	67.9 (±19.5)	84.3 (±5.6)	72.2 (±22.7)
192	30.5 (±7.6)	42.8 (±9.7)	37.4 (±14.9)	75.1 (±15.3)	86.5 (±7.9)	72.4 (±25.1)
216	31.7 (±6.2)	48.4 (±7.6)	46.4 (±6.8)	79.9 (±15.2)	95.4 (±4.2)	95.0 (±5.1)
240	32.9 (±6.0)	49.7 (±5.8)	45.5 (±1.2)	78.8 (±12.4)	98.6 (±6.5)	88.3 (±1.5)

Time [h]	2-Methylundecanal from **7a** buffer pH 4.6 [mol-%]	2-Methylundecanal from **7a** buffer pH 7.3 [mol-%]	2-Methylundecanal from **7a** emulsion pH 4.4 [mol-%]	2-Methylundecanal from **7b** buffer pH 4.6 [mol-%]	2-Methylundecanal from **7b** buffer pH 7.3 [mol-%]	2-Methylundecanal from **7b** emulsion pH 4.4 [mol-%]
1	1.7 (±1.3)	1.2 (±0.9)	1.3 (±0.5)	0.9 (±0.5)	0.8 (±0.5)	1.8 (±0.9)
24	1.4 (±0.6)	1.5 (±0.5)	1.4 (±0.5)	0.9 (±0.2)	0.9 (±0.4)	1.2 (±0.4)
48	1.5 (±0.2)	1.7 (±0.1)	1.3 (±0.4)	0.8 (±0.3)	0.9 (±0.4)	1.4 (±0.7)
72	1.5 (±0.2)	1.8 (±0.0)	1.6 (±1.6)	0.7 (±0.1)	0.9 (±0.2)	0.9 (±0.0)
96	1.4 (±0.1)	1.7 (±0.0)	1.1 (±1.0)	0.6 (±0.2)	0.8 (±0.2)	0.5 (±0.0)
168	1.1 (±0.2)	1.6 (±0.1)	0.7 (±0.4)	0.5 (±0.0)	0.9 (±0.1)	0.2 (±0.0)
192	1.0 (±0.0)	1.6 (±0.2)	0.5 (±0.1)	0.5 (±0.1)	0.8 (±0.0)	0.2 (±0.0)
216	0.8 (±0.1)	1.4 (±0.0)	0.2 (±0.0)	0.5 (±0.0)	0.8 (±0.1)	0.3 (±0.1)
240	0.8 (±0.0)	1.3 (±0.4)	0.3 (±0.0)	0.4 (±0.0)	0.6 (±0.0)	0.2 (±0.0)

Time [h]	Hexanal from **8a** buffer pH 4.6 [mol-%]	Hexanal from **8a** buffer pH 7.3 [mol-%]	Hexanal from **8a** emulsion pH 4.4 [mol-%]	Triplal® from **9a** buffer pH 4.6 [mol-%]	Triplal® from **9a** buffer pH 7.3 [mol-%]	Triplal® from **9a** emulsion pH 4.4 [mol-%]
1	3.7 (±0.0)	2.6 (±0.4)	3.6 (±0.6)	2.8 (±0.5)	2.4 (±0.4)	2.2 (±1.0)
24	5.6 (±0.2)	5.1 (±0.2)	7.2 (±0.8)	3.0 (±0.1)	2.8 (±0.4)	2.0 (±1.2)
48	5.4 (±0.0)	5.8 (±0.2)	6.7 (±0.5)	3.3 (±0.1)	3.3 (±0.1)	1.9 (±2.0)
72	5.9 (±0.2)	6.8 (±0.2)	7.5 (±0.8)	3.6 (±0.1)	3.6 (±0.1)	1.4 (±1.5)
96	5.5 (±0.1)	6.7 (±0.3)	2.9 (±3.2)	4.0 (±0.2)	4.1 (±0.2)	0.5 (±0.3)
168	6.0 (±0.1)	8.7 (±0.1)	0.1 (±0.1)	4.6 (±0.2)	4.4 (±1.8)	0.5 (±0.3)
192	5.8 (±0.6)	8.8 (±0.0)	0.1 (±0.1)	5.1 (±0.0)	6.1 (±0.5)	0.5 (±0.3)
216	5.9 (±0.5)	10.3 (±0.0)	0.2 (±0.0)	5.0 (±0.9)	5.8 (±0.5)	0.4 (±0.3)
240	6.1 (±0.1)	9.1 (±0.9)	0.1 (±0.1)	5.8 (±0.0)	7.0 (±1.1)	0.5 (±0.4)

Figure S6. Comparison of the hydrolysis of imidazolidinones **1b–d**, **2b–d**, **3b**, **4b**, and **7b** releasing different fragrance aldehydes and ketones in buffered solutions of water/acetonitrile 4:1 at pH 4.6 (—●—) and 7.3 (—○—) or in a diluted aqueous TEA-esterquat emulsion at pH 4.4 (—■—). Numerical data: see Table S4.

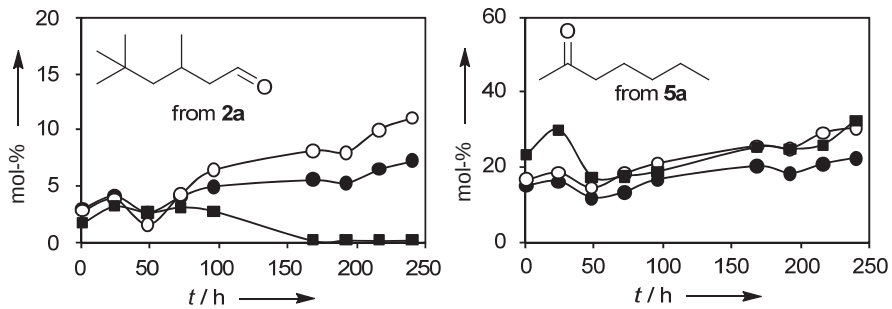


Procedure for the Hydrolysis in Aqueous Media with a Constant Headspace Volume: To verify whether an increasing headspace volume during the experiment had an influence on the amount of fragrance extracted from the different samples, we prepared a series of small individual glass flasks, which were opened only at the moment of the extraction. For the measurements performed with a constant headspace volume above the samples, solutions of imidazolidinones **2a** and **5a** (0.14 mL) were added to the buffer solutions and the cationic surfactant emulsion (70 mL, to give a final concentration of ca. 1.5×10^{-4} mol L^{-1}). The flasks were shaken vigorously (10 times) before aliquots (7 mL) were pipetted into nine small glass flasks (9 mL), which then were closed and left standing at room temperature. After 1 h, the content of the first flask of each series was extracted with heptane (0.42 mL). The heptane phase was decanted (0.10 to 0.15 mL) and analysed by GC as described above. The remaining eight flasks were extracted after 24, 48, 72, 96, 168, 192, 216, and 240 h, respectively. The headspace volume above the sample buffer solutions or the cationic surfactant emulsion thus does not seem to have a strong impact on the recovery of the released carbonyl compounds (see Table S5 and Figure S7).

Table S5. Amounts of carbonyl compounds in mol-% and standard deviations (in brackets) of volatile carbonyl compounds extracted from buffered solutions in water/acetonitrile 4:1 at pH 4.6 and 7.3 or a diluted TEA-esterquat emulsion at pH 4.4 after hydrolysis of their corresponding precursors **2a** and **5a**. The headspace above the samples was kept constant during the experiment (numerical data for Figure S7).

Time [h]	3,5,5-Trimethylhexanal from **2a** buffer pH 4.6 [mol-%]	3,5,5-Trimethylhexanal from **2a** buffer pH 7.3 [mol-%]	3,5,5-Trimethylhexanal from **2a** emulsion pH 4.4 [mol-%]	2-Heptanone from **5a** buffer pH 4.6 [mol-%]	2-Heptanone from **5a** buffer pH 7.3 [mol-%]	2-Heptanone from **5a** emulsion pH 4.4 [mol-%]
1	3.0 (±2.7)	2.8 (±2.9)	1.8 (±0.9)	15.0 (±11.6)	16.6 (±11.0)	23.4 (±21.0)
24	4.1 (±3.3)	3.8 (±3.4)	3.2 (±2.8)	16.1 (±10.3)	18.5 (±11.2)	29.8 (±15.9)
48	2.6 (±1.0)	1.6 (±0.1)	2.7 (±1.6)	11.7 (±5.7)	14.6 (±6.1)	17.4 (±7.5)
72	4.0 (±1.9)	4.2 (±2.3)	3.1 (±1.4)	13.2 (±4.7)	18.3 (±7.0)	17.5 (±5.8)
96	5.0 (±2.7)	6.4 (±3.7)	2.8 (±1.6)	16.6 (±9.7)	21.0 (±9.2)	18.7 (±8.3)
168	5.6 (±1.4)	8.1 (±3.1)	0.2 (±0.0)	20.2 (±8.8)	25.7 (±8.9)	25.2 (±9.6)
192	5.3 (±1.6)	8.0 (±1.4)	0.2 (±0.1)	18.2 (±3.8)	25.0 (±5.8)	24.7 (±7.4)
216	6.5 (±0.4)	10.0 (±0.5)	0.2 (±0.1)	20.8 (±7.8)	29.1 (±6.4)	25.9 (±10.9)
240	7.3 (±3.1)	11.0 (±4.8)	0.2 (±0.0)	22.4 (±11.1)	30.6 (±13.2)	32.4 (±17.9)

Figure S7. Comparison of the hydrolysis of imidazolidinones **2a** and **5a** in buffered solutions of water/acetonitrile 4:1 at pH 4.6 (—●—) and 7.3 (—○—) or in a diluted aqueous TEA-esterquat emulsion at pH 4.4 (—■—) at a constant headspace volume. Numerical data: see Table S5.

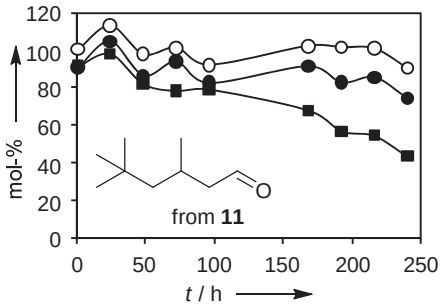


Data for the Hydrolysis of 11 in Aqueous Media (with Increasing Headspace Volume):

Table S6. Amounts of 3,5,5-trimethylhexanal in mol-% and standard deviations (in brackets) of 3,5,5-trimethylhexanal extracted from buffered solutions in water/acetonitrile 4:1 at pH 4.6 and 7.3 or a diluted TEA-esterquat emulsion at pH 4.4 after hydrolysis of oxazolidine **11** (numerical data for Figure S8).

Time [h]	3,5,5-Trimethylhexanal from **11** buffer pH 4.6 [mol-%]		3,5,5-Trimethylhexanal from **11** buffer pH 7.3 [mol-%]		3,5,5-Trimethylhexanal from **11** emulsion pH 4.4 [mol-%]	
1	91.2	(±6.9)	100.7	(±6.2)	91.9	(±5.7)
24	104.8	(±7.4)	113.2	(±8.7)	98.4	(±16.8)
48	86.5	(±0.7)	97.8	(±1.4)	82.3	(±3.5)
72	94.0	(±7.6)	101.4	(±9.5)	78.6	(±4.5)
96	82.7	(±7.3)	92.2	(±9.3)	79.4	(±4.1)
168	91.5	(±2.8)	102.4	(±10.9)	68.2	(±3.4)
192	82.9	(±6.4)	101.6	(±10.6)	57.0	(±4.4)
216	85.7	(±9.2)	100.9	(±9.9)	54.6	(±3.6)
240	74.6	(±3.1)	90.4	(±4.6)	43.4	(±21.9)

Figure S8. Release of 3,5,5-trimethylhexanal from oxazolidine **11** in buffered solutions of water/acetonitrile 4:1 at pH 4.6 (—●—) and 7.3 (—○—) or in a diluted aqueous TEA-esterquat emulsion at pH 4.4 (—■—). Numerical data: see Table S6.



Data for Dynamic Headspace Measurements:

Table S7. Average dynamic headspace concentrations and standard deviations (in brackets) measured for the controlled release of different fragrance aldehydes or ketones from glycinamide-derived imidazolidinones **1a**–**9a**, oxazolidinone **10**, and oxazolidine **11** on dry fabric after drying for three days with respect to the corresponding free fragrance as the reference (numerical data for Figures 9 and 10).

Time [min]	Trifernal® (reference) [ng L^{-1}]	Trifernal® from **1a** [ng L^{-1}]	3,5,5-Tri-methylhexanal (reference) [ng L^{-1}]	3,5,5-Tri-methylhexanal from **2a** [ng L^{-1}]	(*R*)-Citronellal (reference) [ng L^{-1}]	(*R*)-Citronellal from **3a** [ng L^{-1}]
30	3.2 (±5.9)	5.9 (±7.4)	2.2 (±1.4)	15.2 (±4.7)	0.8 (±0.9)	2.2 (±1.2)
90	5.2 (±4.1)	13.6 (±13.5)	3.3 (±1.9)	37.1 (±12.4)	3.6 (±5.5)	13.9 (±9.1)
150	7.5 (±4.8)	19.2 (±15.8)	3.9 (±2.2)	37.0 (±10.5)	4.8 (±5.5)	16.1 (±7.7)
210	7.4 (±4.5)	21.1 (±16.4)	3.5 (±2.5)	33.6 (±6.9)	4.6 (±5.9)	15.3 (±4.8)
270	7.2 (±3.5)	21.2 (±16.3)	3.4 (±2.2)	30.0 (±4.6)	3.3 (±4.1)	13.8 (±2.7)
330	7.2 (±2.7)	20.9 (±15.7)	3.2 (±2.1)	27.2 (±4.3)	3.2 (±3.3)	12.5 (±2.2)
390	6.8 (±2.4)	19.3 (±13.9)	3.2 (±2.2)	24.7 (±4.8)	1.9 (±2.3)	11.6 (±0.8)
450	6.2 (±1.9)	20.2 (±14.3)	2.9 (±2.0)	22.9 (±4.8)	1.4 (±1.5)	10.6 (±0.8)

Time [min]	(–)-Menthone (reference) [ng L^{-1}]	(–)-Menthone from (5*R*,6*S*,9*R*)-**4a** [ng L^{-1}]	(–)-Menthone from (5*S*,6*S*,9*R*)-**4a** [ng L^{-1}]	2-Heptanone (reference) [ng L^{-1}]	2-Heptanone from **5a** [ng L^{-1}]
30	0.2 (±0.1)	12.5 (±3.9)	11.8 (±7.3)	1.3 (±1.1)	21.8 (±14.3)
90	0.4 (±0.2)	34.5 (±22.4)	61.4 (±33.0)	1.4 (±1.4)	54.4 (±40.5)
150	0.5 (±0.3)	39.6 (±19.3)	64.6 (±34.7)	1.9 (±1.4)	52.5 (±38.6)
210	0.5 (±0.4)	37.7 (±23.3)	60.1 (±27.9)	2.4 (±4.1)	32.8 (±20.0)
270	0.4 (±0.3)	28.5 (±17.1)	52.1 (±21.5)	1.6 (±2.7)	17.0 (±6.1)
330	0.4 (±0.2)	26.0 (±16.5)	43.6 (±15.7)	1.0 (±0.9)	12.3 (±1.6)
390	0.3 (±0.2)	23.5 (±16.0)	36.0 (±12.3)	0.8 (±0.7)	11.0 (±0.8)
450	0.2 (±0.1)	21.2 (±15.1)	29.5 (±9.7)	0.7 (±0.4)	10.4 (±0.8)

Time [min]	5-Methyl-3-heptanone (reference) [ng L^{-1}]	5-Methyl-3-heptanone from **6a** [ng L^{-1}]	2-Methyl-undecanal (reference) [ng L^{-1}]	2-Methyl-undecanal from **7a** [ng L^{-1}]	Hexanal (reference) [ng L^{-1}]	Hexanal from **8a** [ng L^{-1}]
30	0.3 (±0.2)	38.5 (±10.2)	0.7 (±0.5)	2.6 (±0.4)	9.3 (±3.2)	10.1 (±4.8)
90	0.7 (±0.2)	111.2 (±40.2)	1.4 (±1.5)	6.8 (±7.2)	13.4 (±4.9)	13.9 (±1.2)
150	0.6 (±0.2)	124.3 (±62.0)	2.3 (±2.7)	9.5 (±12.1)	15.0 (±5.4)	16.7 (±4.1)
210	0.5 (±0.2)	121.3 (±70.8)	2.8 (±3.1)	8.7 (±10.4)	13.4 (±3.5)	15.2 (±2.2)
270	0.4 (±0.2)	96.7 (±49.7)	2.9 (±3.2)	7.0 (±9.1)	10.5 (±1.3)	14.2 (±1.5)
330	0.3 (±0.1)	70.8 (±31.8)	3.8 (±2.9)	6.7 (±6.8)	8.8 (±0.9)	12.1 (±0.5)
390	0.2 (±0.2)	55.0 (±22.8)	5.0 (±4.0)	4.6 (±7.1)	7.8 (±1.0)	10.6 (±0.5)
450	0.1 (±0.1)	44.7 (±16.4)	3.7 (±2.2)	3.9 (±5.7)	6.9 (±1.5)	8.8 (±0.3)

Time [min]	Triplal® (reference) [ng L^{-1}]	Triplal® from **9a** [ng L^{-1}]	3,5,5-Tri-methylhexanal (reference) [ng L^{-1}]	3,5,5-Tri-methylhexanal from **10** [ng L^{-1}]	3,5,5-Tri-methylhexanal from **11** [ng L^{-1}]
30	n.d.[a]	n.d.[a]	2.2 (±1.4)	3.5 (±0.1)	3.0 (±0.7)
90	7.9 (±2.5)	21.3 (±16.6)	3.3 (±1.9)	4.7 (±0.3)	4.0 (±1.4)
150	10.6 (±2.3)	24.1 (±17.9)	3.9 (±2.2)	4.2 (±0.1)	4.3 (±1.6)
210	10.1 (±3.3)	24.8 (±17.5)	3.5 (±2.5)	4.4 (±0.0)	4.7 (±2.3)
270	12.5 (±3.2)	25.7 (±16.3)	3.4 (±2.2)	4.1 (±0.1)	4.2 (±1.5)
330	13.8 (±3.4)	26.1 (±15.4)	3.2 (±2.1)	4.0 (±0.4)	4.1 (±1.5)
390	12.0 (±1.4)	17.4 (±0.4)	3.2 (±2.2)	3.7 (±0.4)	3.8 (±1.3)
450	2.7 (±3.8)	18.1 (±0.6)	2.9 (±2.0)	3.5 (±0.1)	3.5 (±1.0)

[a] not determined.

Table S8. Average dynamic headspace concentrations and standard deviations (in brackets) measured for the controlled release of different fragrance aldehydes or ketones from imidazolidinones **1b**–**1d**, **2b**–**2d**, **3b**, **4b**, **5c**, and **7b** on dry fabric after drying for three days with respect to the corresponding free fragrance as the reference (numerical data for Figures 10 and S9). To facilitate comparison, the headspace data of the reference samples from Table S7 are listed again.

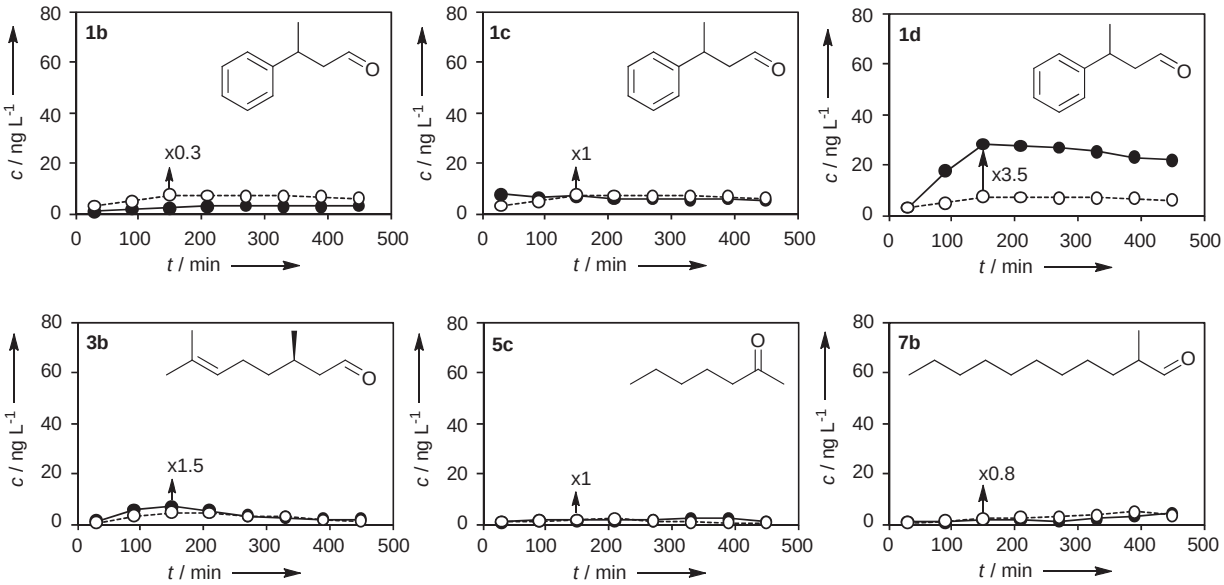
Time [min]	Trifernal® (reference) [ng L^{-1}]	Trifernal® from **1b** [ng L^{-1}]	Trifernal® from **1c** [ng L^{-1}]	Trifernal® from **1d** [ng L^{-1}]	3,5,5-Trimethylhexanal (reference) [ng L^{-1}]	3,5,5-Trimethylhexanal from **2b** [ng L^{-1}]
30	3.2 (±5.9)	1.1 (±0.1)	7.8 (±10.2)	3.3 (±0.4)	2.2 (±1.4)	2.7 (±0.9)
90	5.2 (±4.1)	1.9 (±0.4)	6.4 (±1.1)	17.7 (±1.6)	3.3 (±1.9)	10.3 (±5.6)
150	7.5 (±4.8)	2.3 (±0.2)	7.2 (±2.7)	28.3 (±4.4)	3.9 (±2.2)	10.0 (±5.2)
210	7.4 (±4.5)	3.1 (±1.1)	6.0 (±0.7)	27.7 (±5.4)	3.5 (±2.5)	8.5 (±3.3)
270	7.2 (±3.5)	3.4 (±1.4)	6.0 (±0.3)	27.0 (±5.8)	3.4 (±2.2)	7.3 (±2.3)
330	7.2 (±2.7)	3.1 (±1.0)	5.8 (±0.2)	25.3 (±3.9)	3.2 (±2.1)	6.0 (±1.4)
390	6.8 (±2.4)	3.1 (±1.0)	5.9 (±0.4)	23.0 (±4.2)	3.2 (±2.2)	5.8 (±1.0)
450	6.2 (±1.9)	3.2 (±1.0)	5.4 (±0.6)	22.1 (±3.2)	2.9 (±2.0)	5.1 (±1.2)

Time [min]	3,5,5-Trimethylhexanal from **2c** [ng L^{-1}]	3,5,5-Trimethylhexanal from **2d** [ng L^{-1}]	(*R*)-Citronellal (reference) [ng L^{-1}]	(*R*)-Citronellal from **3b** [ng L^{-1}]	(–)-Menthone (reference) [ng L^{-1}]	(–)-Menthone from **4b**[a] [ng L^{-1}]
30	6.2 (±2.0)	6.9 (±0.0)	0.8 (±0.9)	1.5 (±1.1)	0.2 (±0.1)	7.0
90	11.2 (±2.3)	13.0 (±0.0)	3.6 (±5.5)	5.9 (±6.2)	0.4 (±0.2)	31.5
150	10.6 (±2.7)	15.1 (±0.8)	4.8 (±5.5)	7.1 (±5.0)	0.5 (±0.3)	31.8
210	9.6 (±3.1)	14.5 (±0.6)	4.6 (±5.9)	5.5 (±3.0)	0.5 (±0.4)	30.6
270	8.9 (±3.4)	14.0 (±1.1)	3.3 (±4.1)	3.4 (±1.9)	0.4 (±0.3)	24.9
330	7.7 (±3.1)	13.0 (±0.5)	3.2 (±3.3)	2.8 (±1.3)	0.4 (±0.2)	19.2
390	7.8 (±3.7)	12.0 (±0.6)	1.9 (±2.3)	2.1 (±1.0)	0.3 (±0.2)	14.4
450	7.0 (±3.1)	11.3 (±0.4)	1.4 (±1.5)	2.1 (±0.8)	0.2 (±0.1)	11.1

Time [min]	2-Heptanone (reference) [ng L^{-1}]	2-Heptanone from **5c** [ng L^{-1}]	2-Methyl-undecanal (reference) [ng L^{-1}]	2-Methyl-undecanal from **7b** [ng L^{-1}]
30	1.3 (±1.1)	1.1 (±0.2)	0.7 (±0.5)	1.3 (±1.2)
90	1.4 (±1.4)	1.7 (±0.1)	1.4 (±1.5)	1.1 (±1.1)
150	1.9 (±1.4)	1.6 (±0.1)	2.3 (±2.7)	1.9 (±2.2)
210	2.4 (±4.1)	1.8 (±0.1)	2.8 (±3.1)	1.9 (±1.8)
270	1.6 (±2.7)	1.8 (±0.2)	2.9 (±3.2)	1.3 (±1.4)
330	1.0 (±0.9)	2.3 (±1.2)	3.8 (±2.9)	2.4 (±1.5)
390	0.8 (±0.7)	2.4 (±1.0)	5.0 (±4.0)	3.2 (±3.0)
450	0.7 (±0.4)	1.2 (±0.7)	3.7 (±2.2)	4.4 (±4.8)

[a] single measurement.

Figure S9. Dynamic headspace concentrations of different fragrance aldehydes or ketones (---○---) and the corresponding fragrance aldehydes or ketones released from imidazolidinones **1b**–**1d**, **3b**, **5c**, and **7b** (—●—) measured on dry cotton after drying for three days. Numerical data see Table S8.



Spectra of Compounds 1–11:

Figure S10. ^{1}H- and ^{13}C-NMR spectra of **1a** in $CDCl_3$.

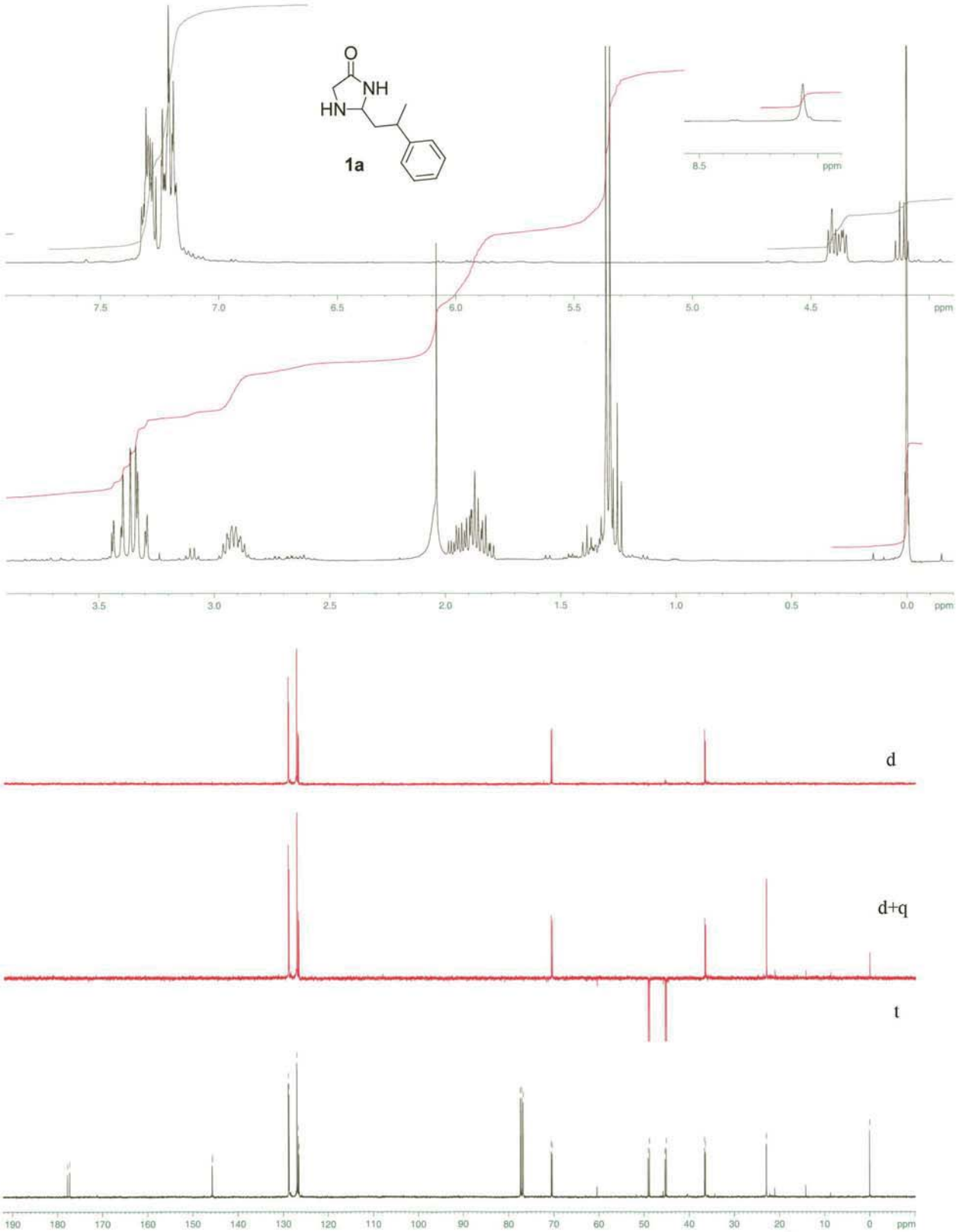


Figure S11. ^{1}H- and ^{13}C-NMR spectra of **1b** in $CDCl_3$.

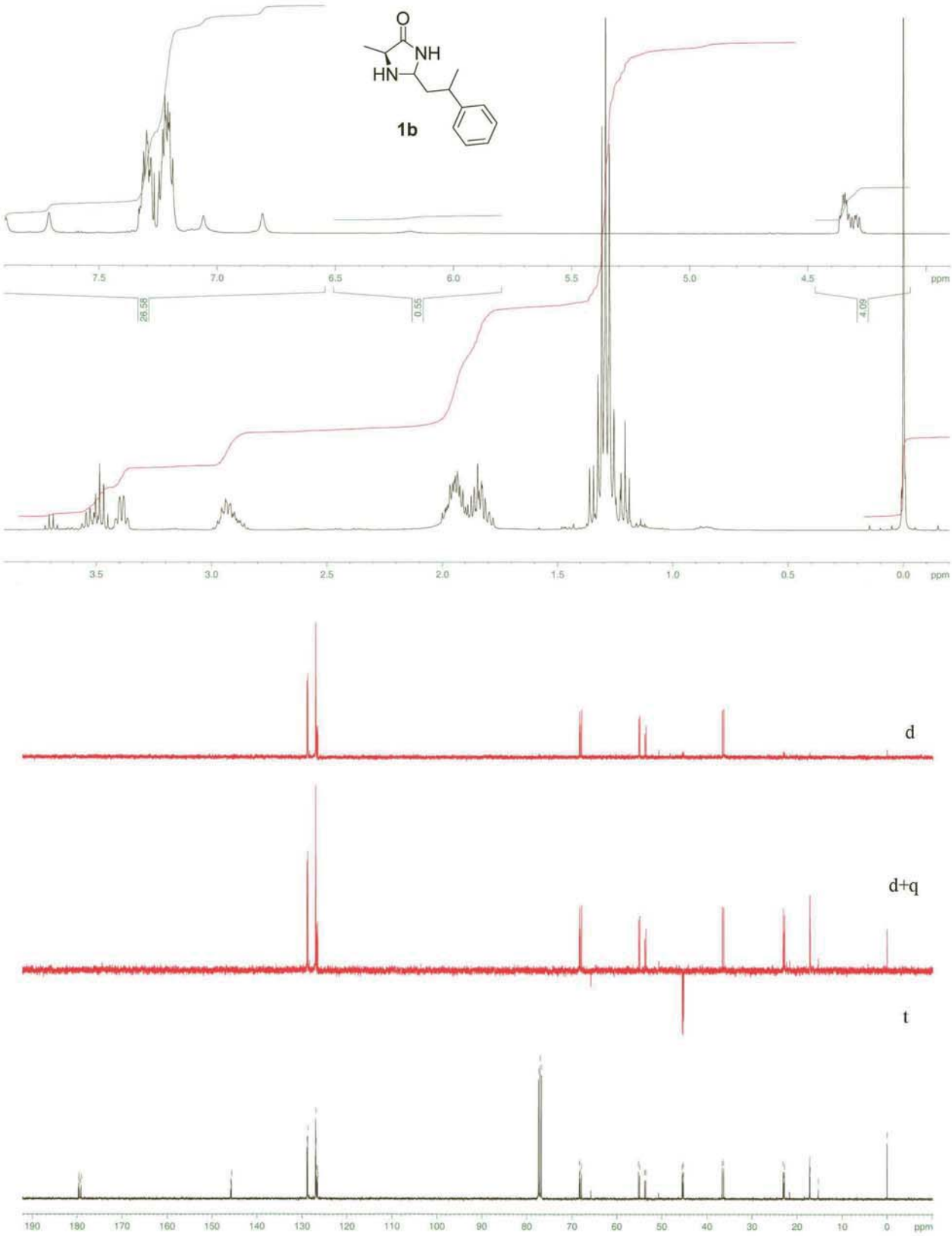


Figure S12. ^{1}H- and ^{13}C-NMR spectra of **1c** in $CDCl_3$.

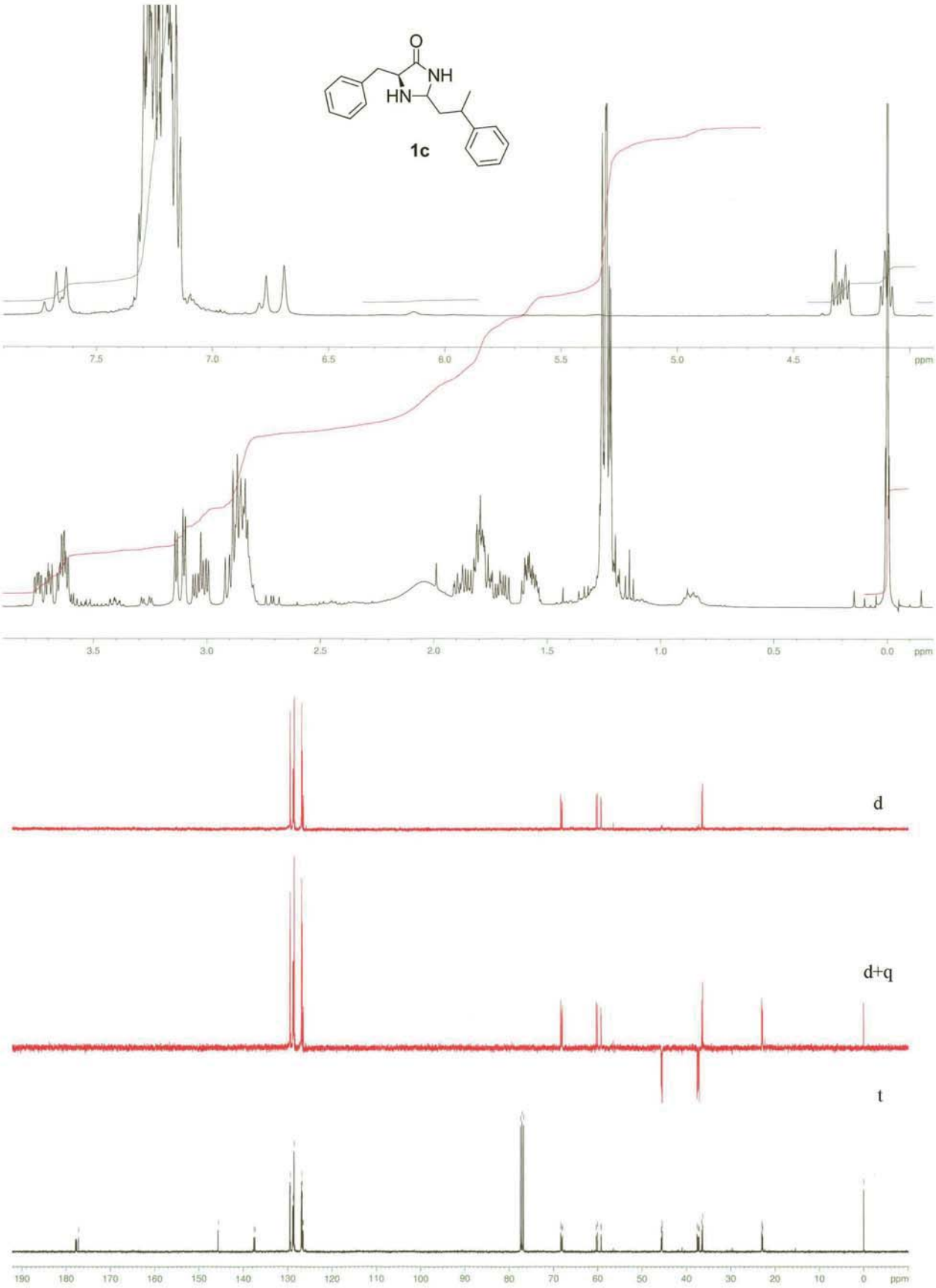


Figure S13. ^{1}H- and ^{13}C-NMR spectra of **1d** in [D_6]DMSO.

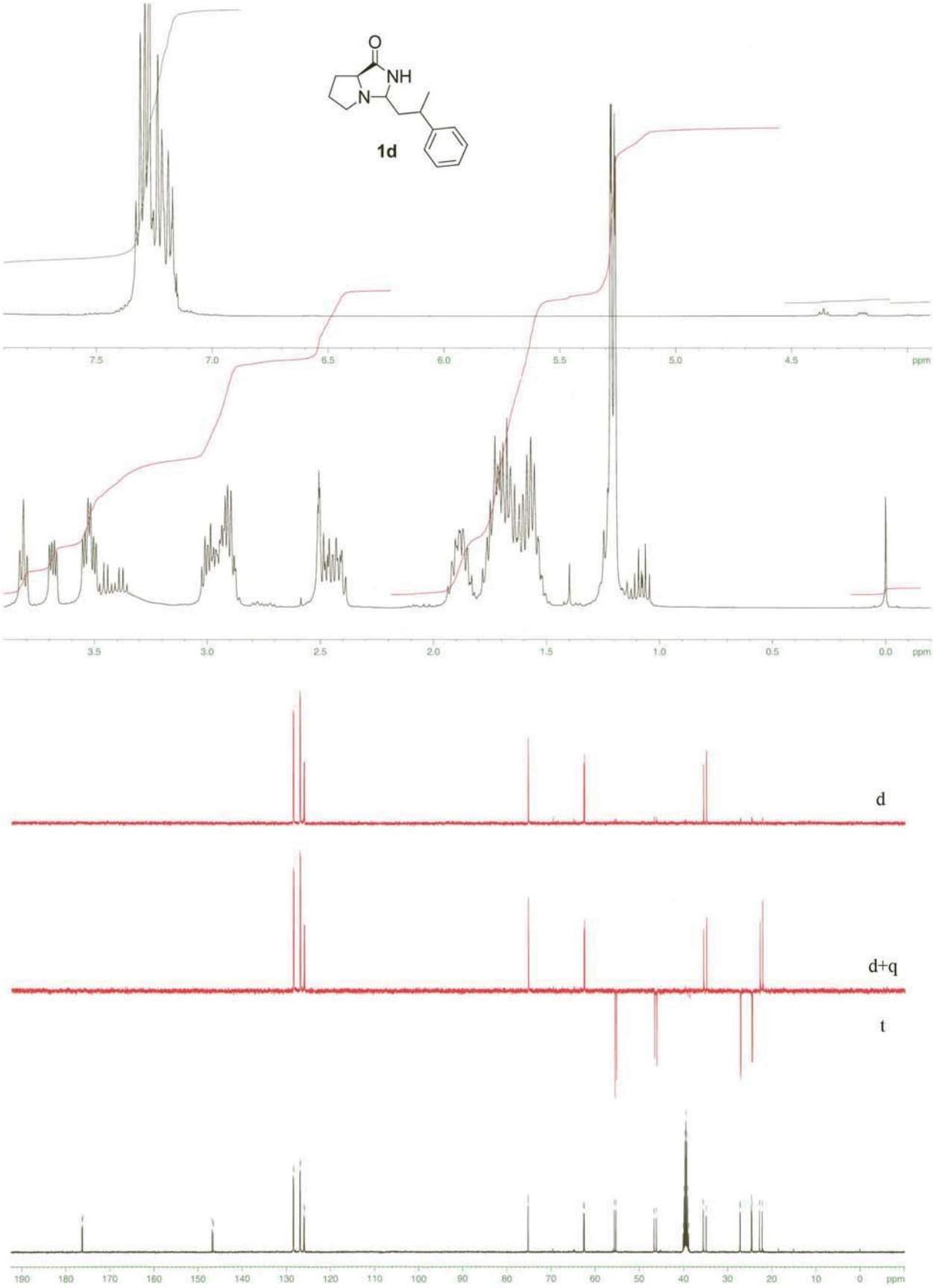


Figure S14. ^{1}H- and ^{13}C-NMR spectra of **2a** in $CDCl_3$.

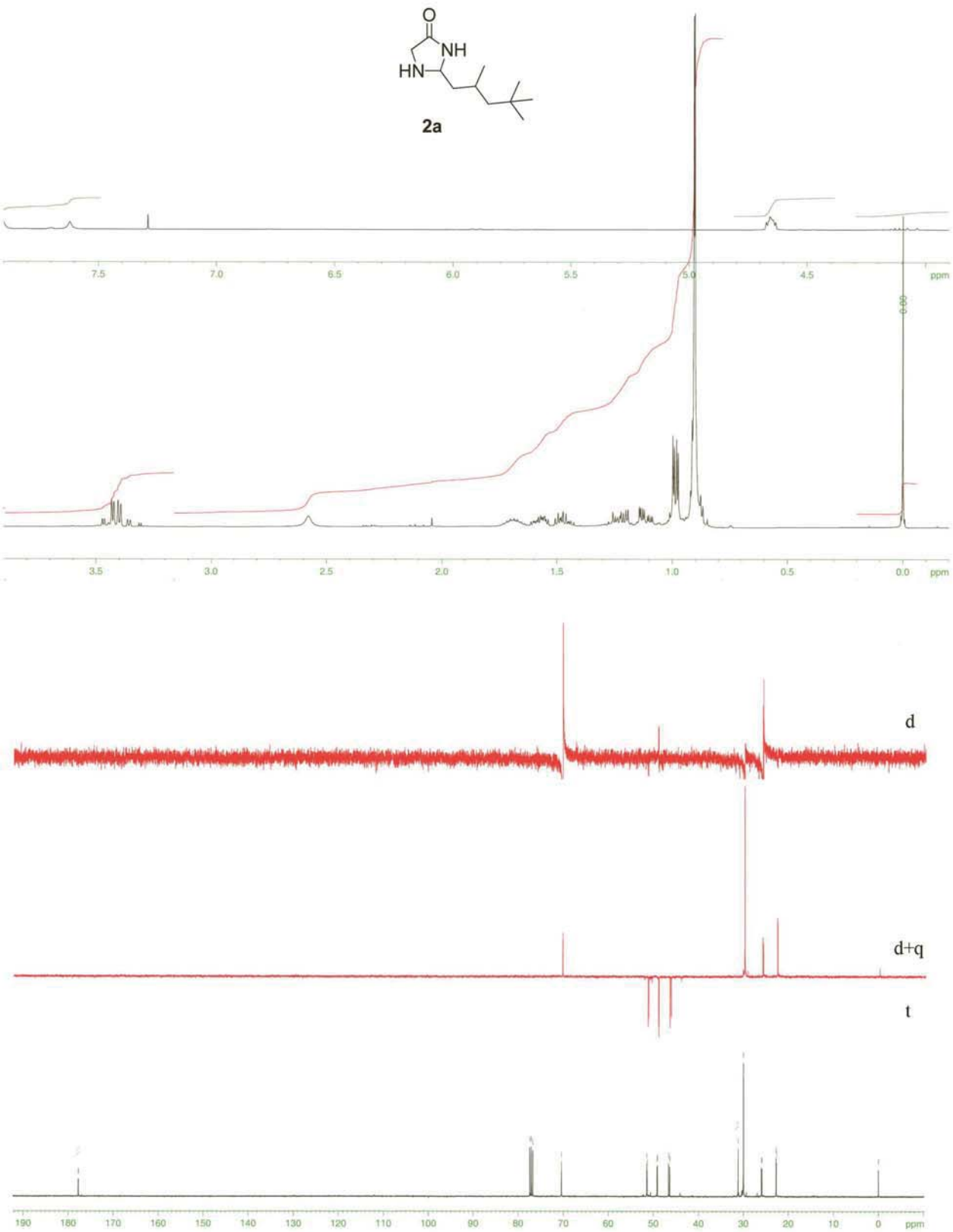


Figure S15. ^{1}H- and ^{13}C-NMR spectra of **2b** in $CDCl_3$.

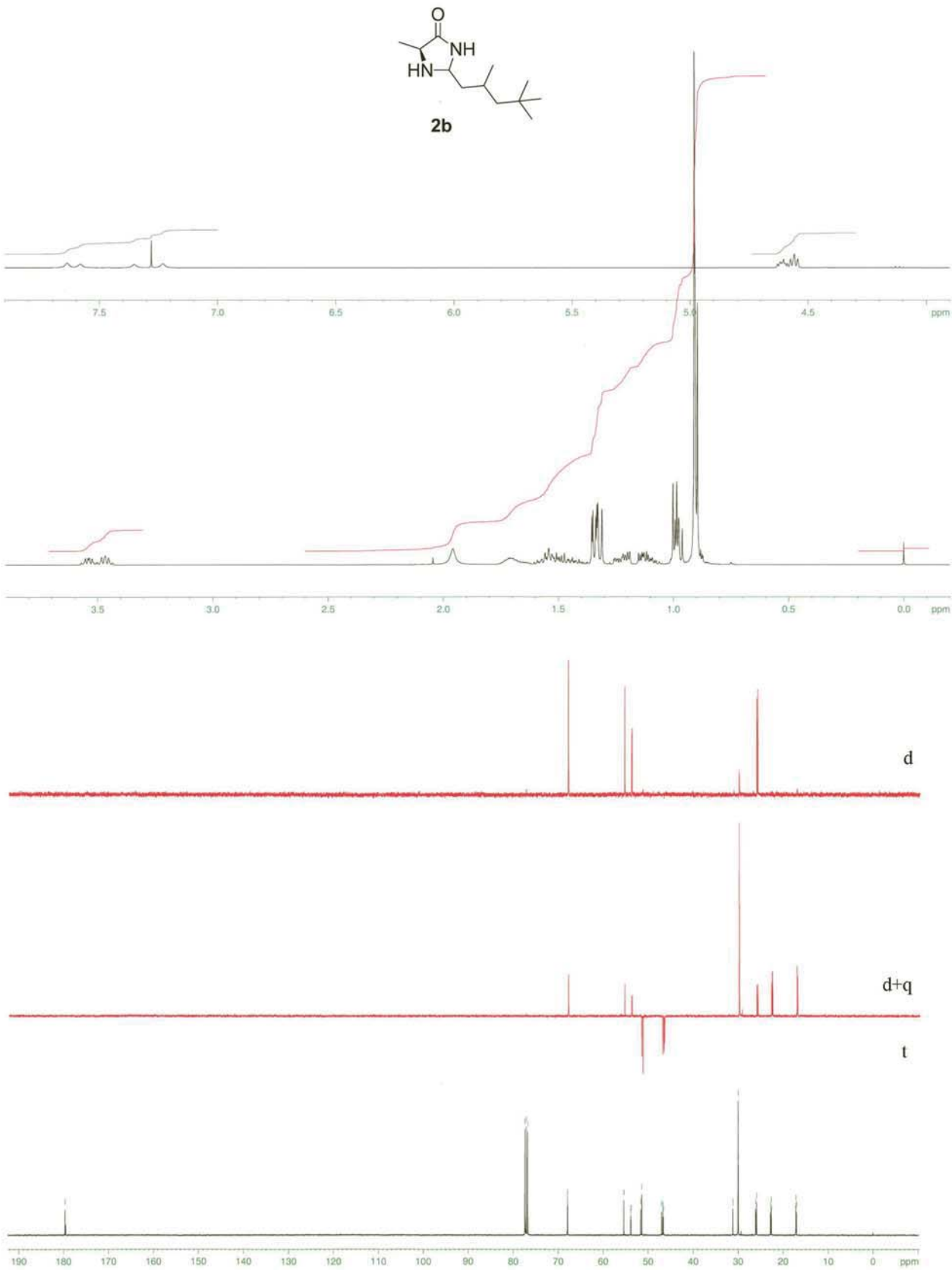


Figure S16. ^{1}H- and ^{13}C-NMR spectra of **2c** in $CDCl_3$.

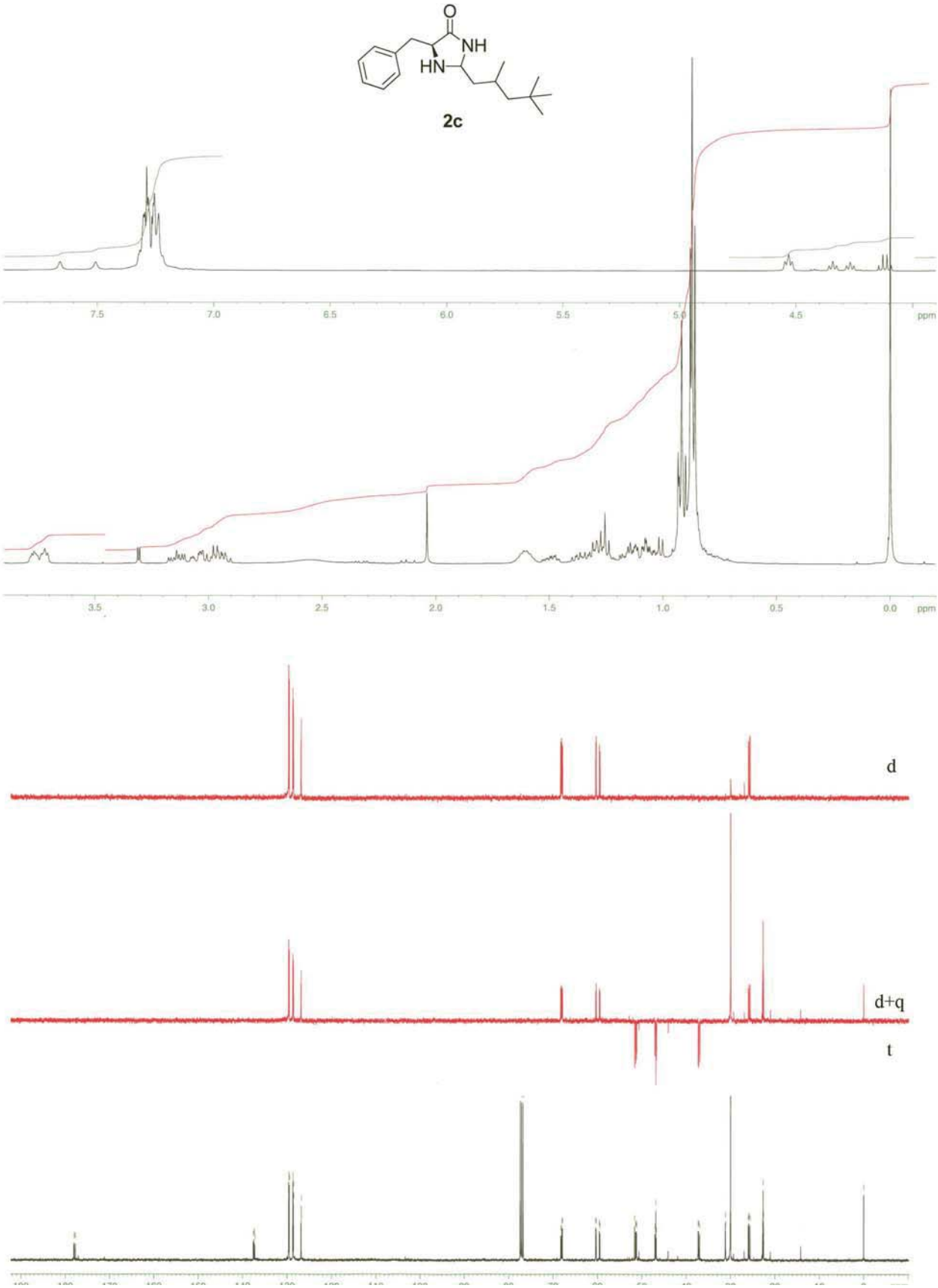


Figure S17. ^{1}H- and ^{13}C-NMR spectra of **2d** in $CDCl_3$.

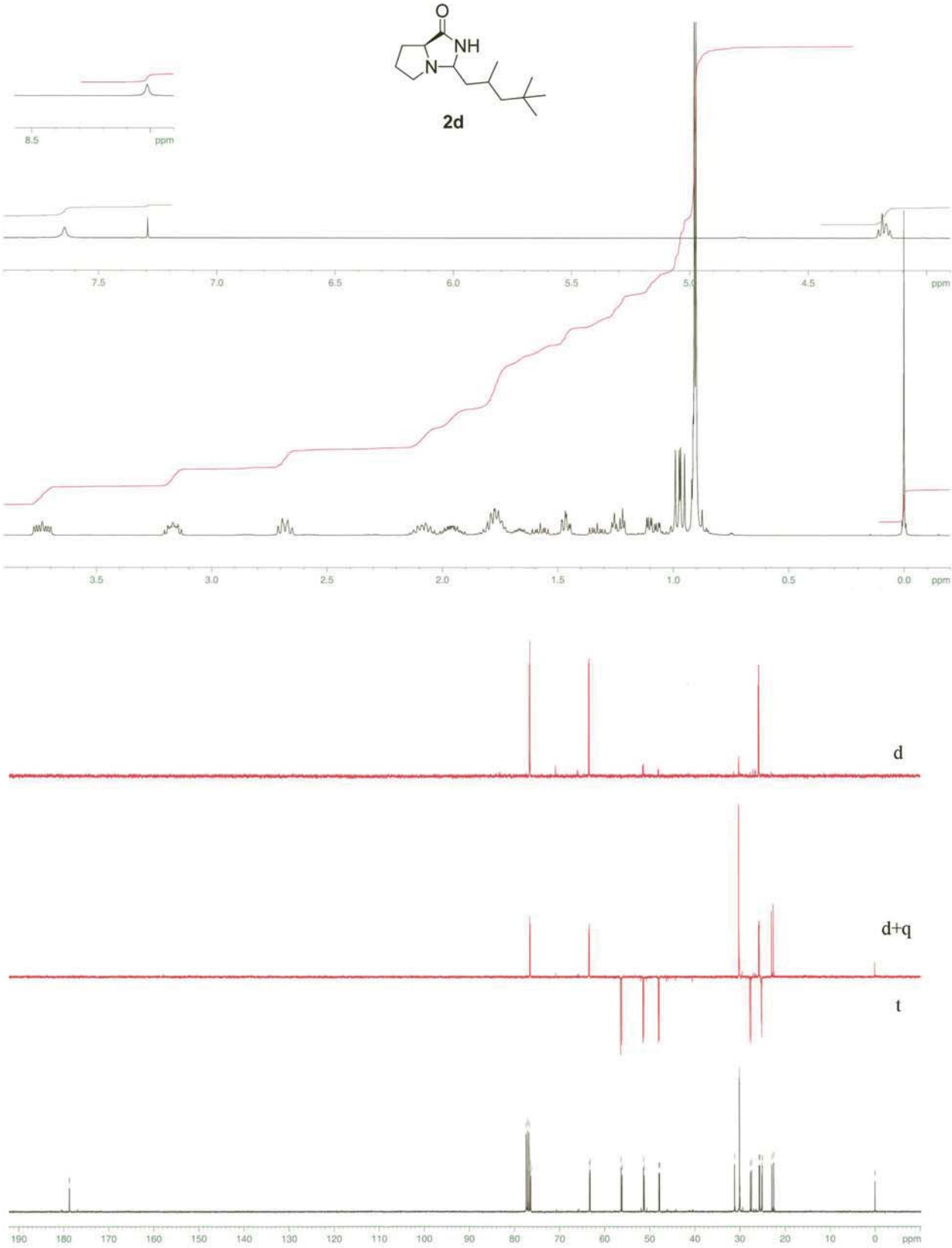


Figure S18. ^{1}H- and ^{13}C-NMR spectra of **3a** in $CDCl_3$.

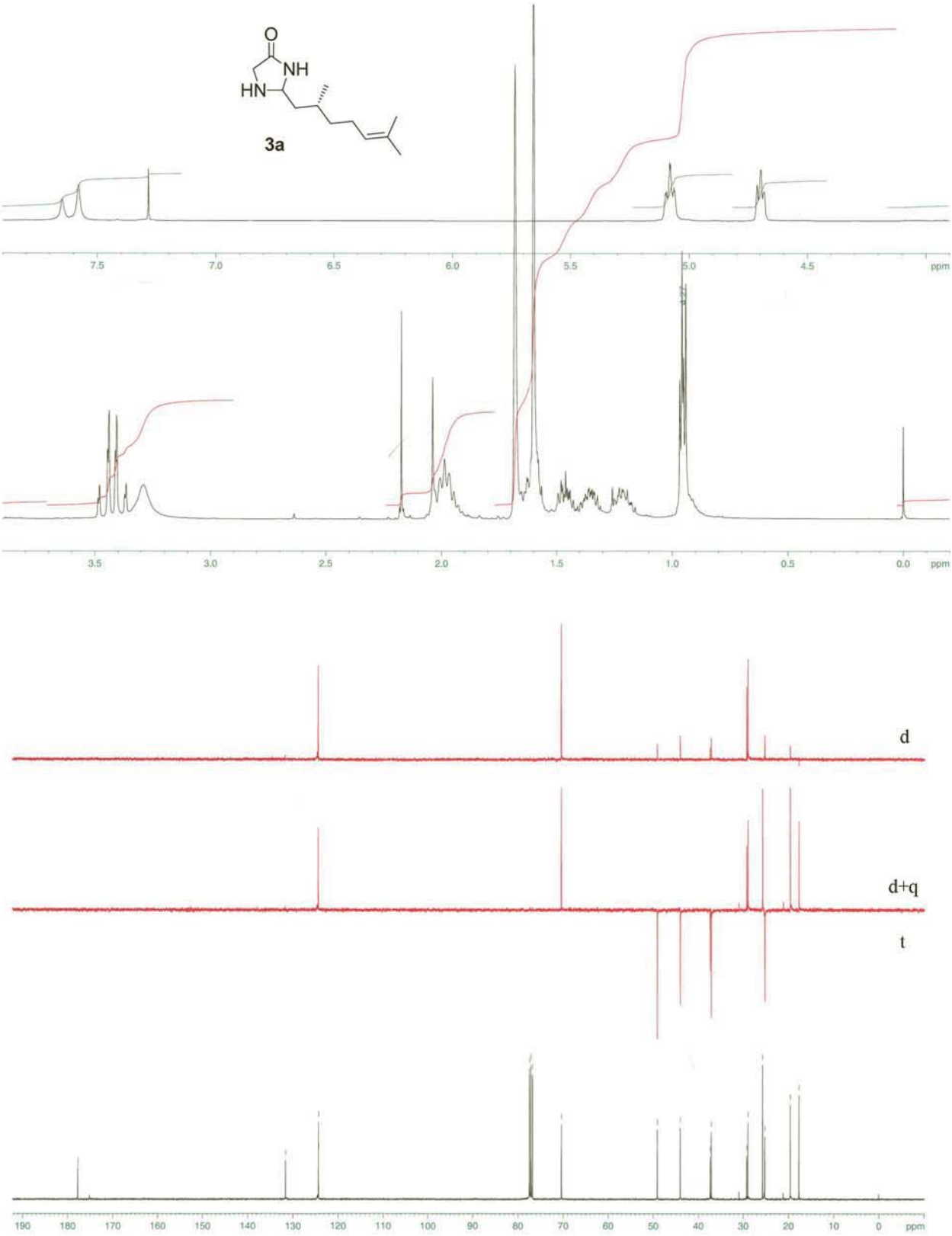


Figure S19. ^{1}H- and ^{13}C-NMR spectra of **3b** in $CDCl_3$.

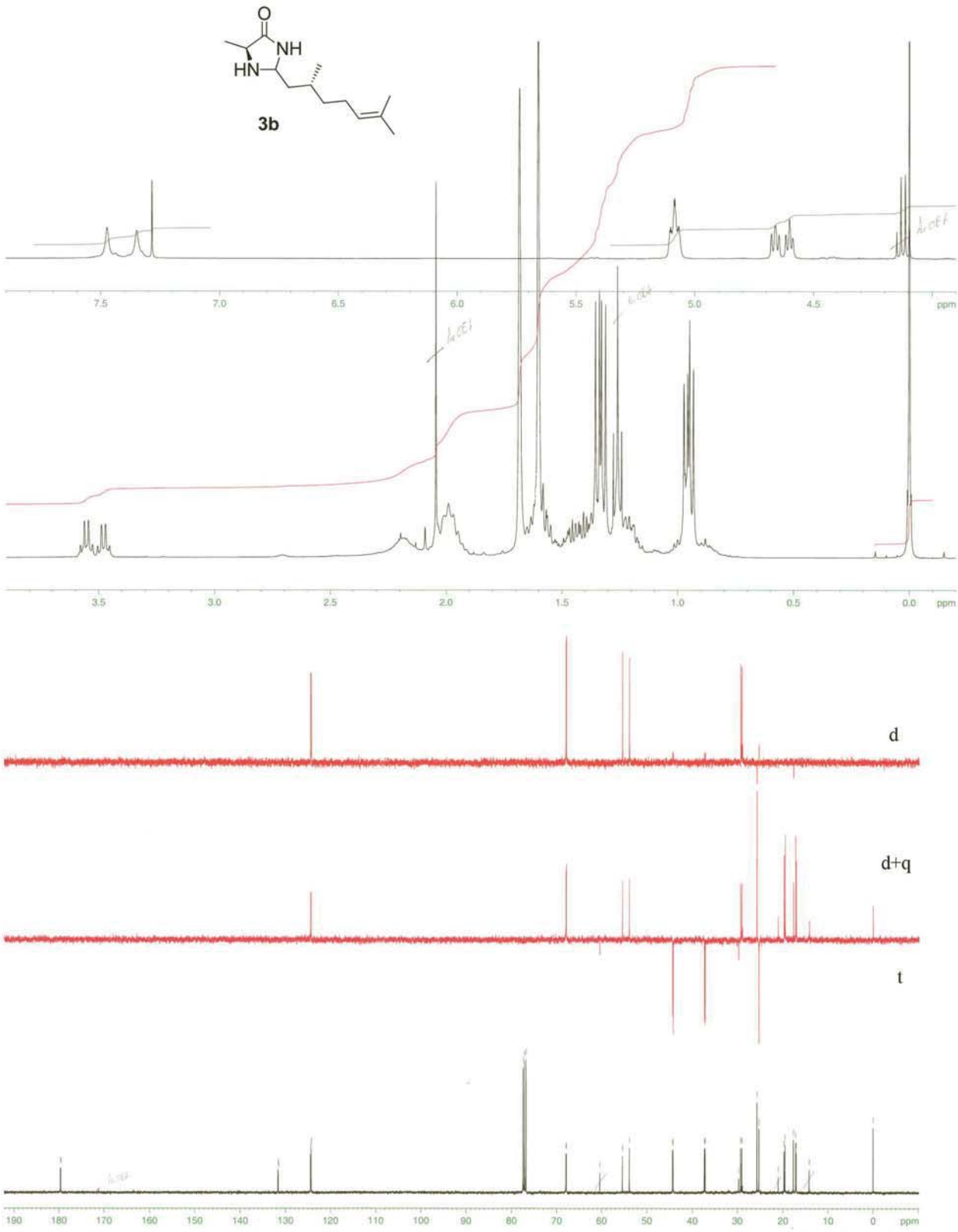


Figure S20. ^{1}H- and ^{13}C-NMR spectra of (5*R*,6*S*,9*R*)-**4a** in $CDCl_3$.

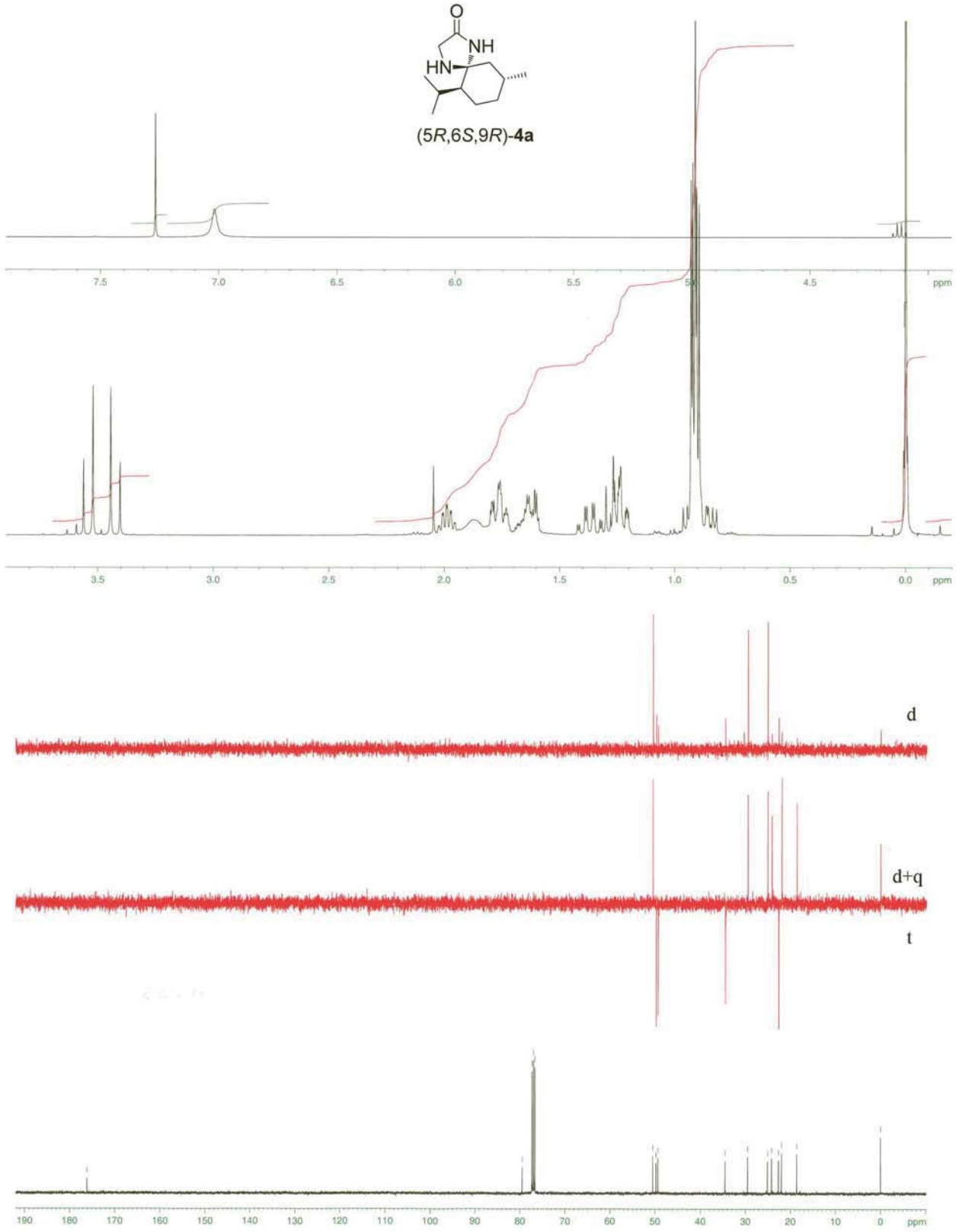


Figure S21. ^{1}H- and ^{13}C-NMR spectra of (5*S*,6*S*,9*R*)-**4a** in $CDCl_3$.

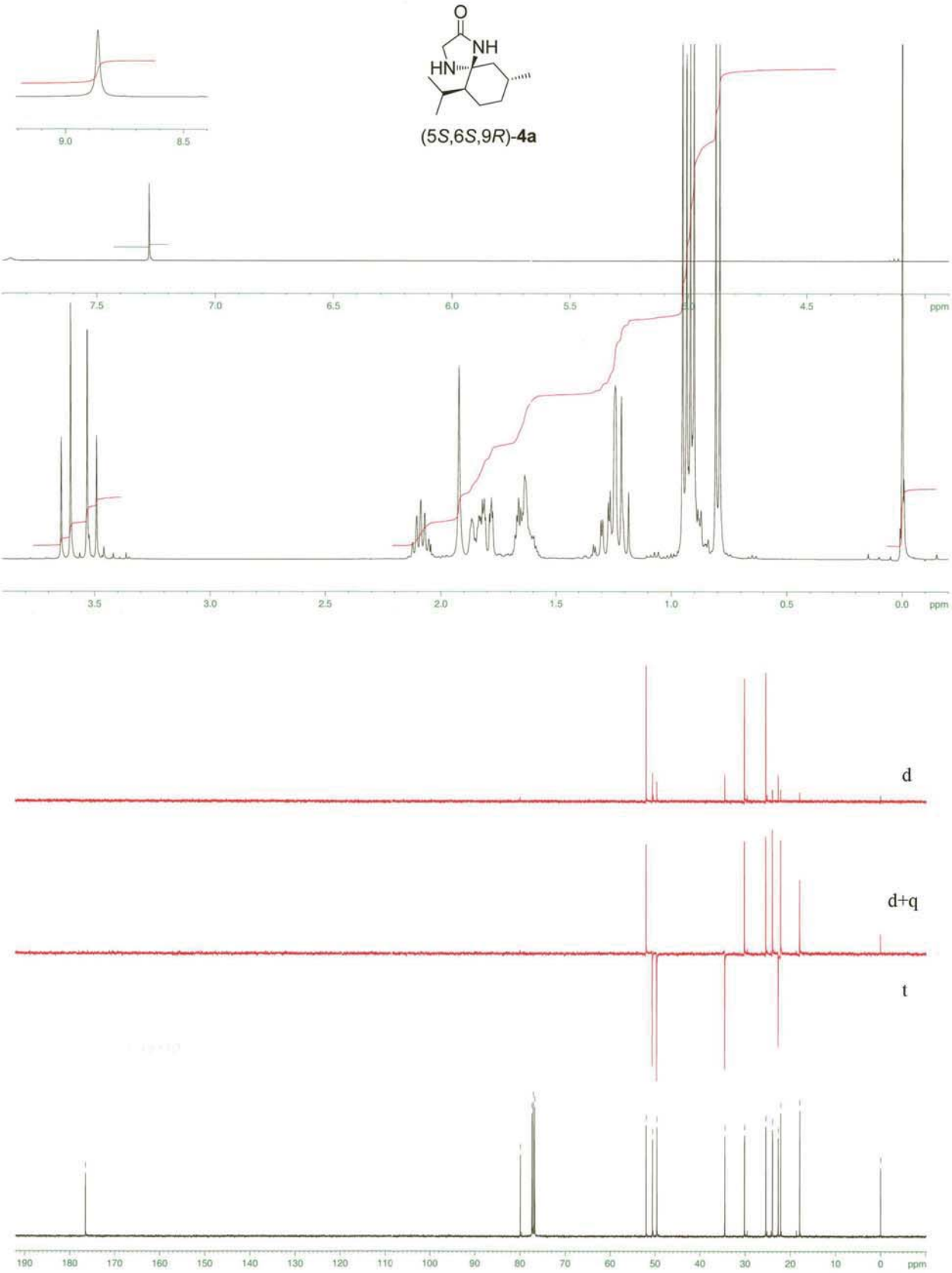


Figure S22. ^{1}H- and ^{13}C-NMR spectra of **4b** in $CDCl_3$.

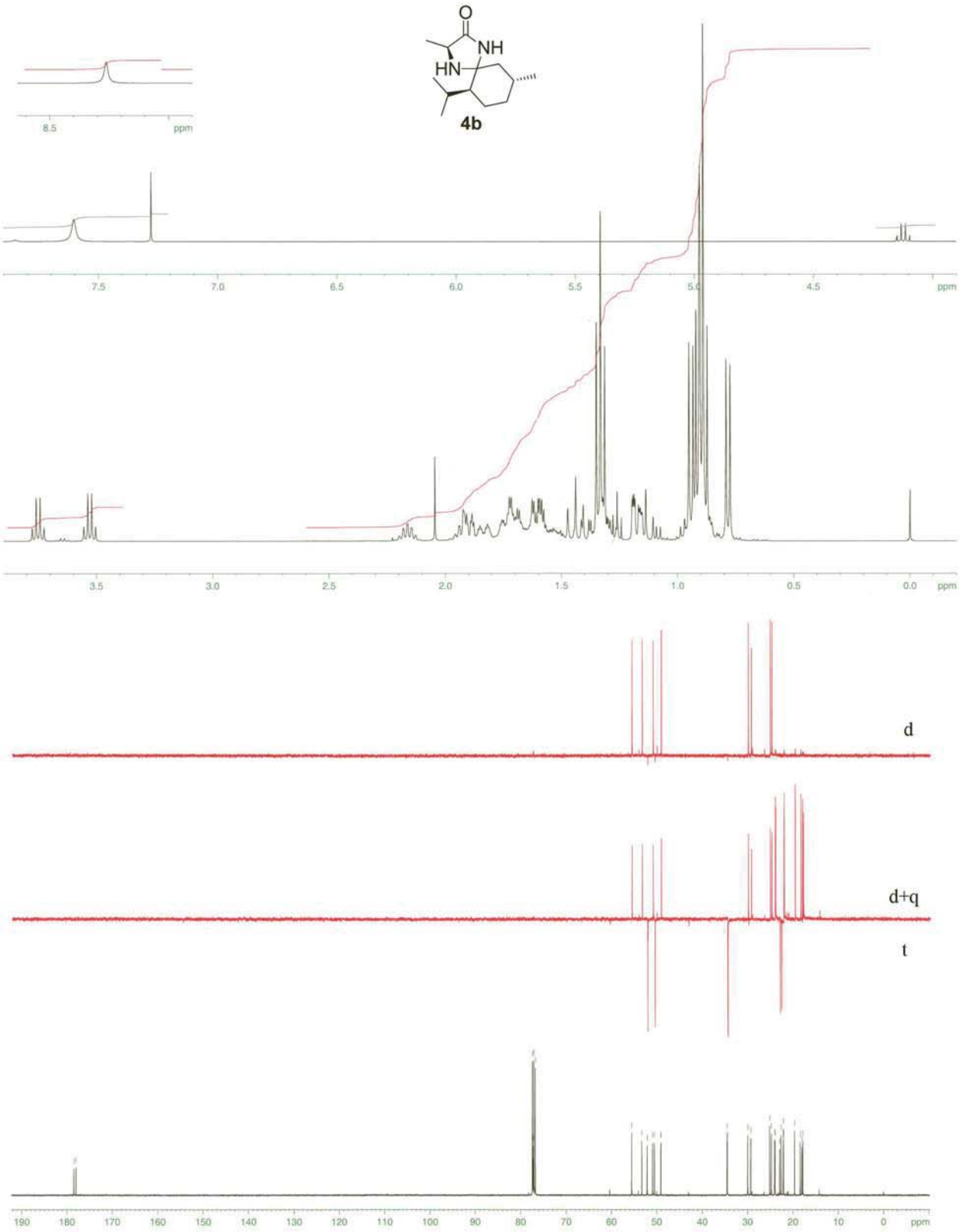


Figure S23. ^{1}H- and ^{13}C-NMR spectra of **5a** in $CDCl_3$.

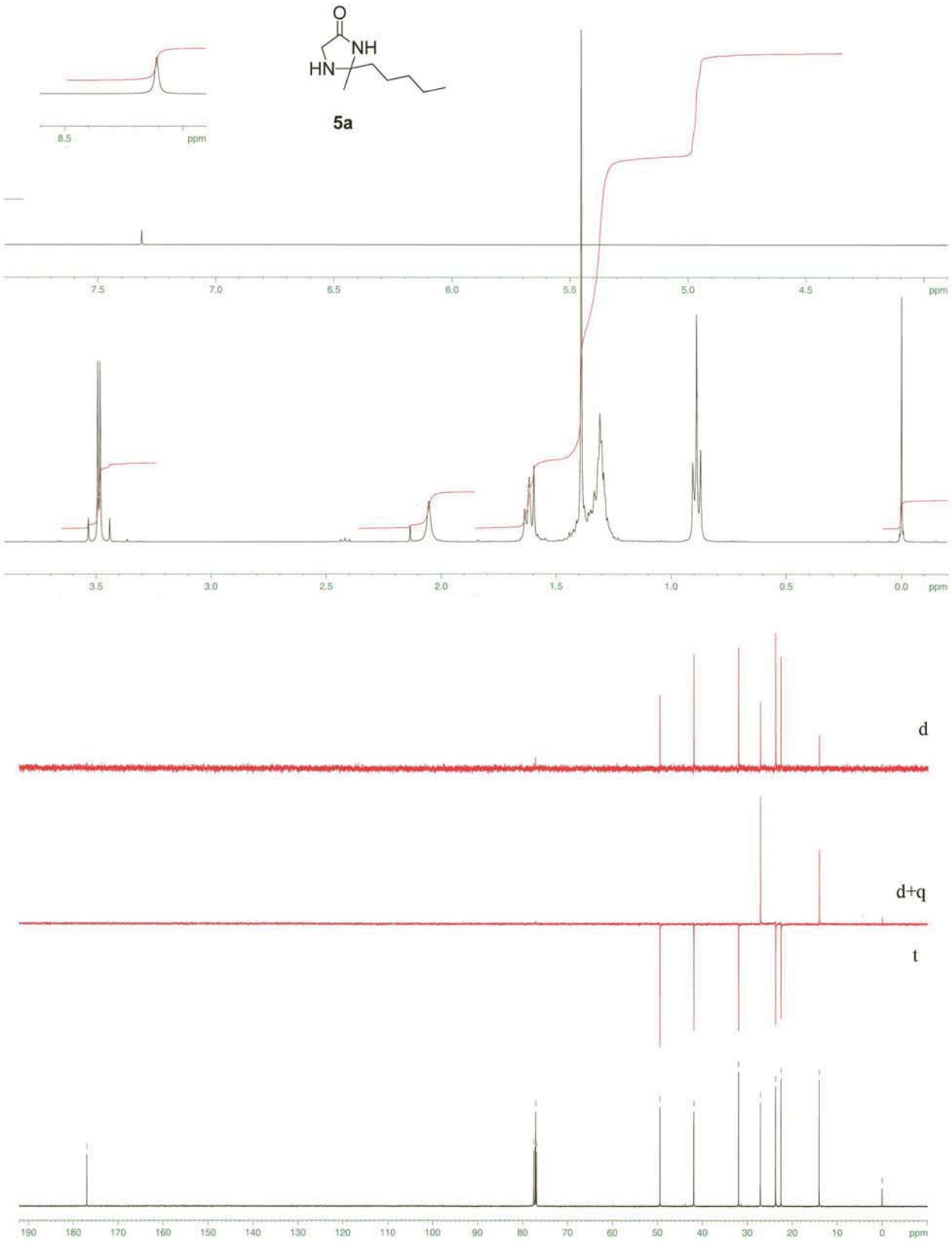


Figure S24. ^{1}H- and ^{13}C-NMR spectra of **5c** in $CDCl_3$.

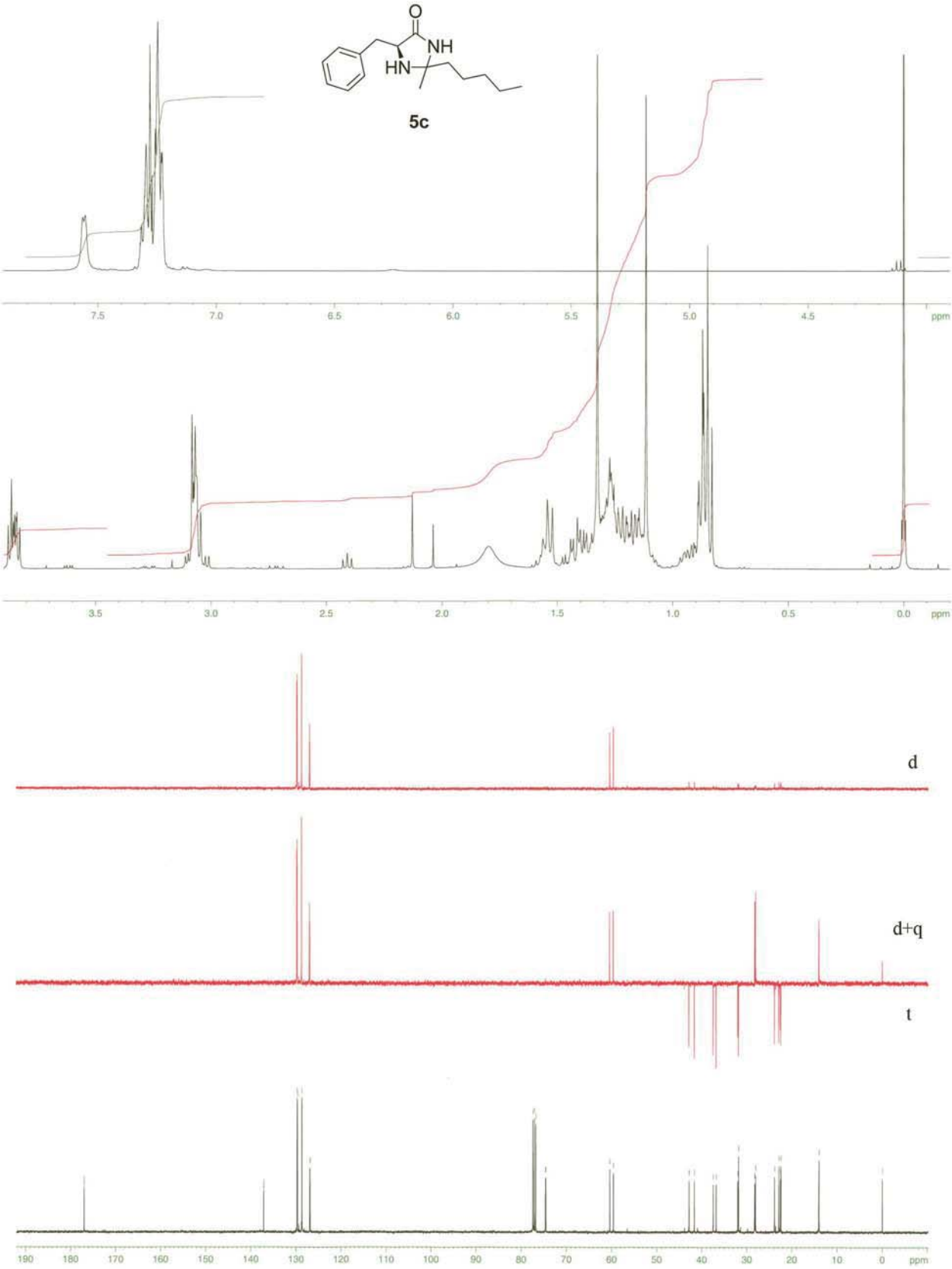


Figure S25. ^{1}H- and ^{13}C-NMR spectra of **6a** in $CDCl_3$.

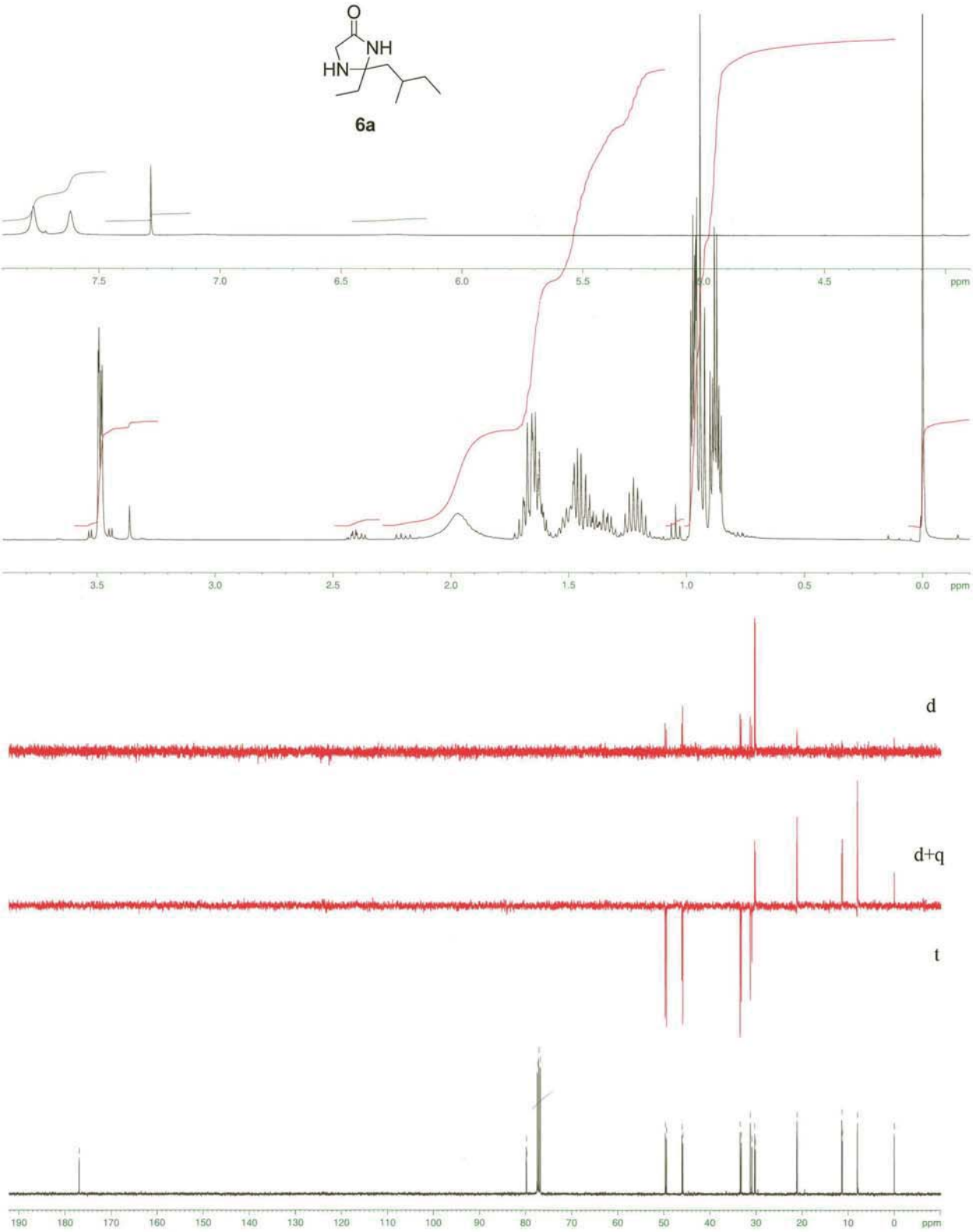


Figure S26. ^{1}H- and ^{13}C-NMR spectra of **7a** in $CDCl_3$.

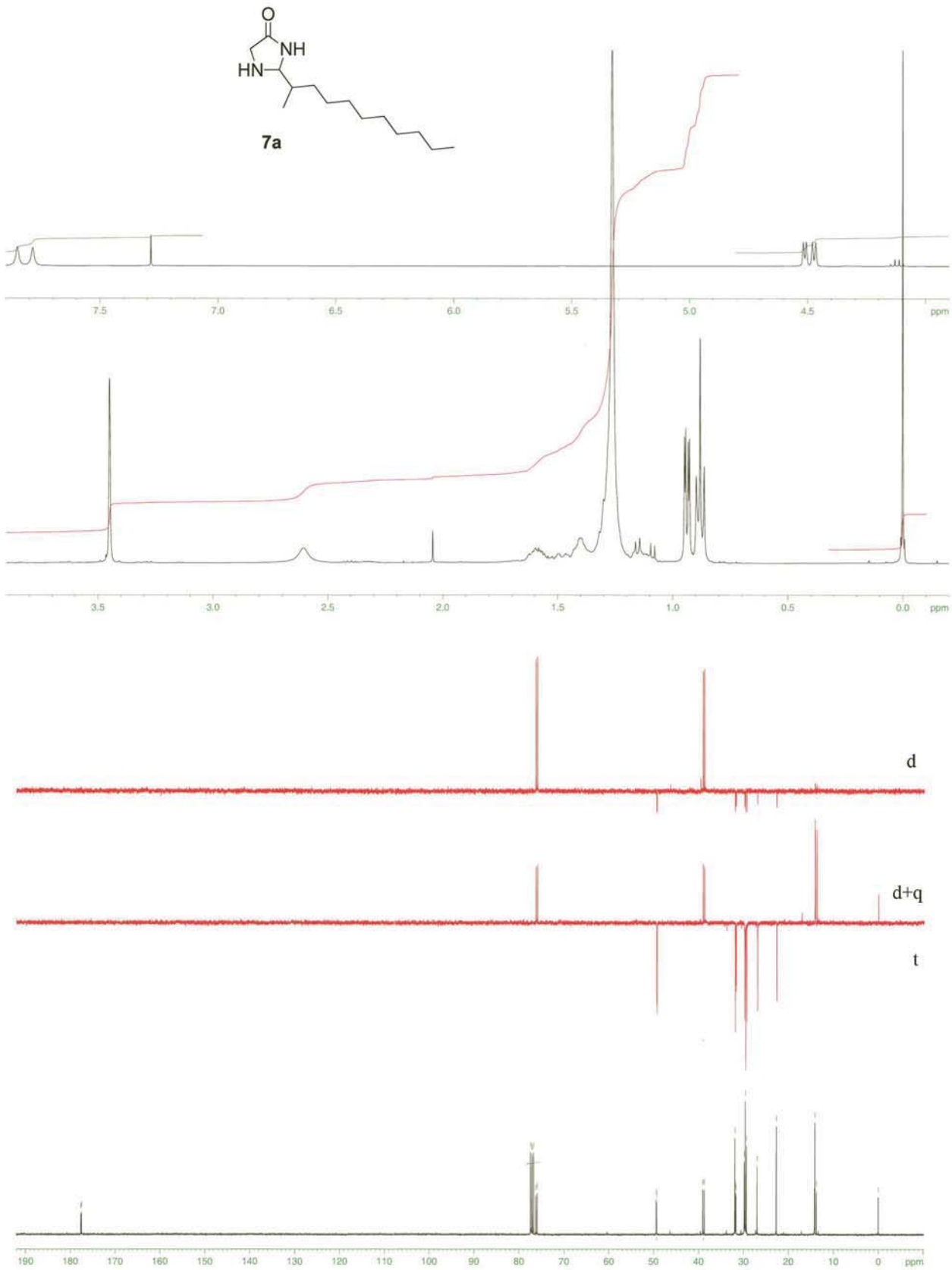


Figure S27. ^{1}H- and ^{13}C-NMR spectra of **7b** in $CDCl_3$.

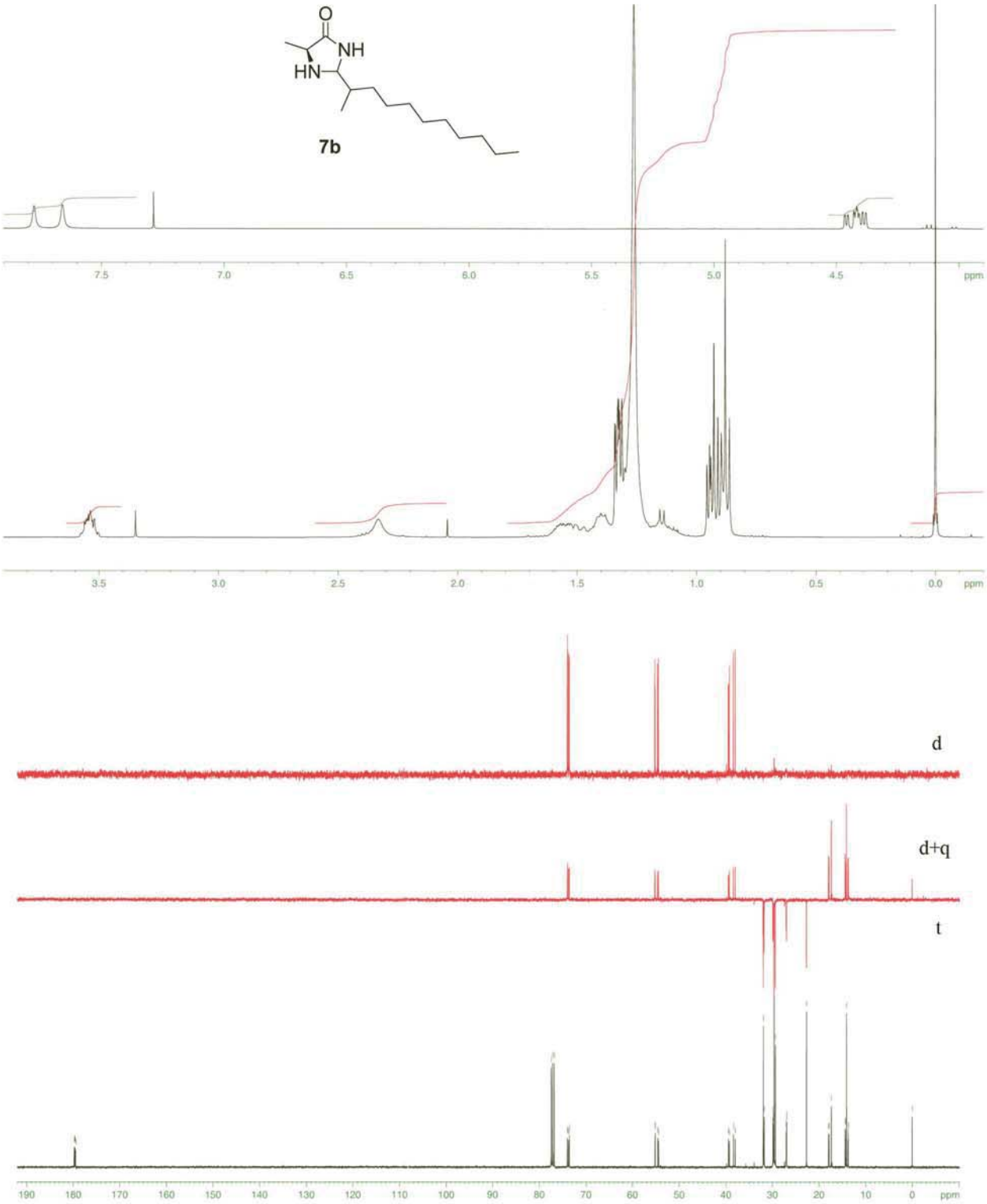


Figure S28. ^{1}H- and ^{13}C-NMR spectra of **8a** in $CDCl_3$.

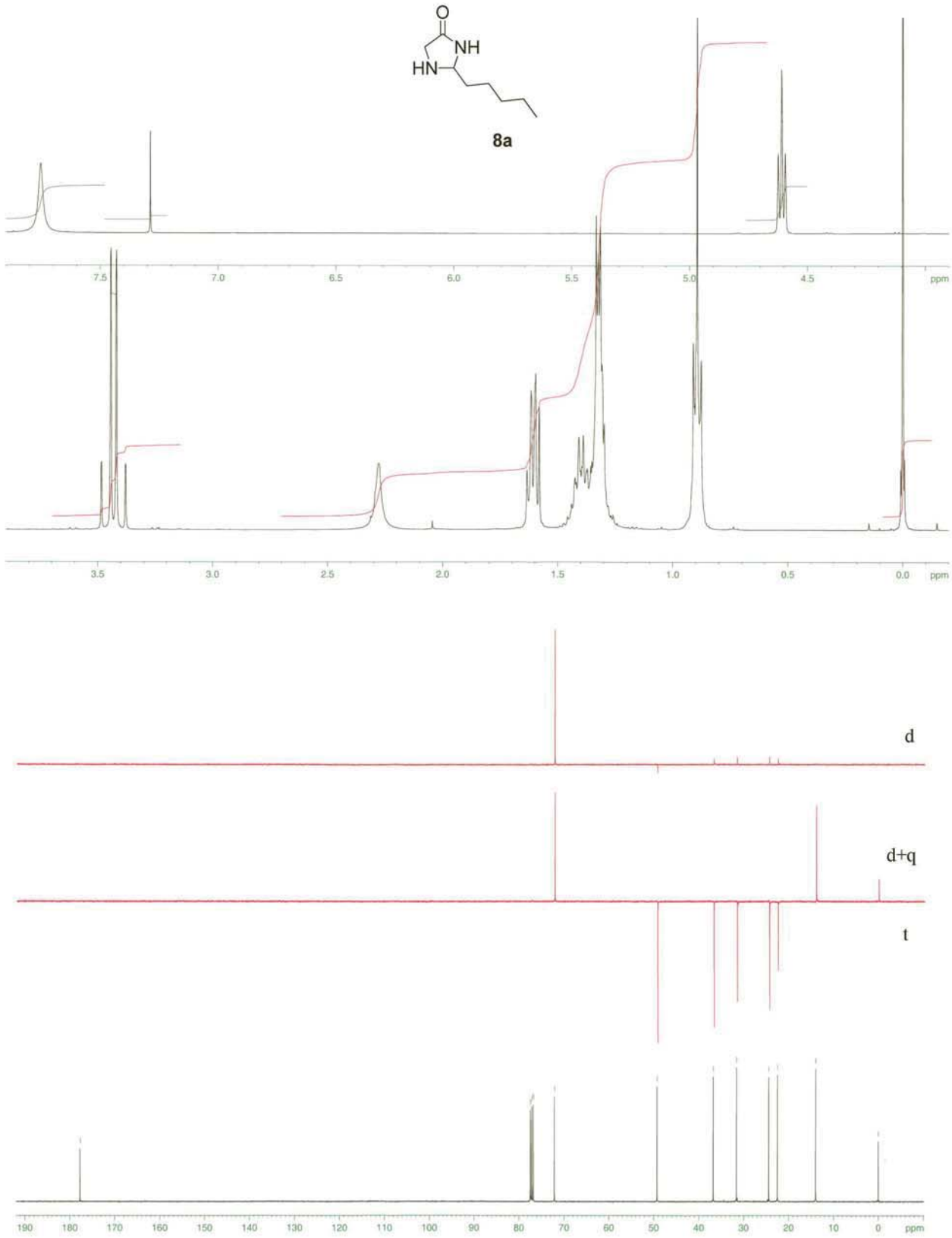


Figure S29. ^{1}H- and ^{13}C-NMR spectra of **9a** in $CDCl_3$.

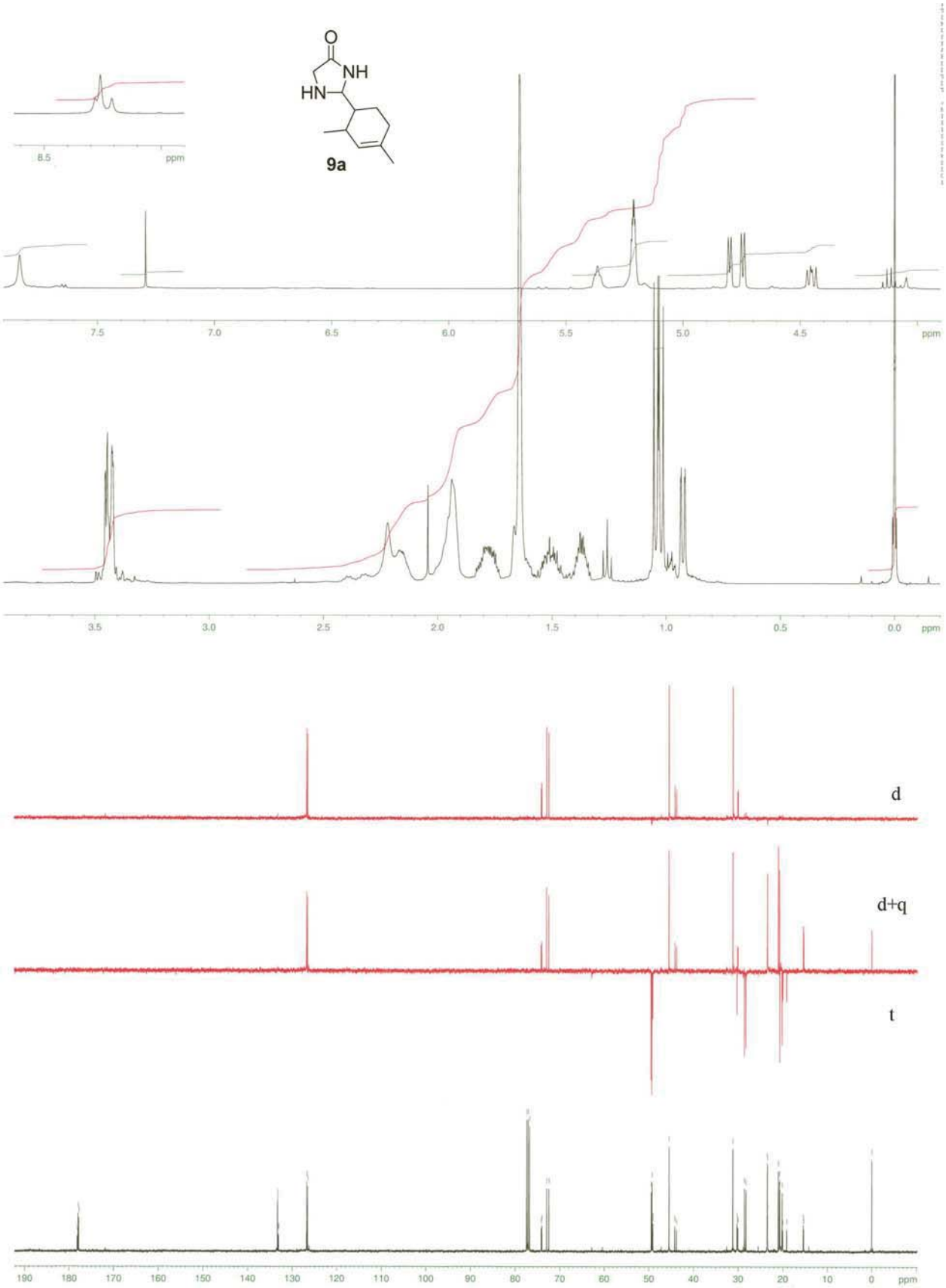


Figure S30. ^{1}H- and ^{13}C-NMR spectra of **10** in $CDCl_3$.

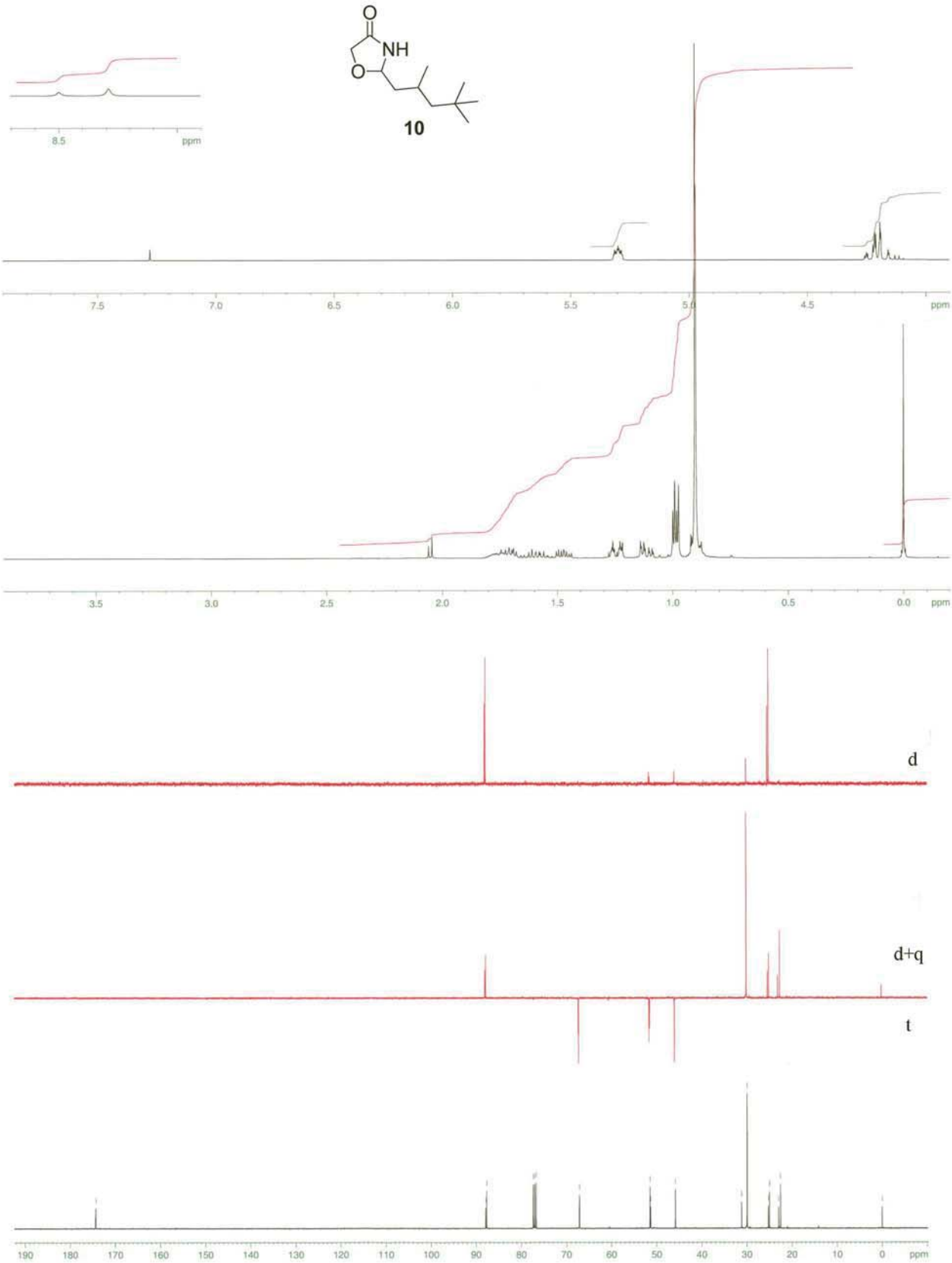


Figure S31. ^{1}H- and ^{13}C-NMR spectra of **11** in $CDCl_3$.