Supporting Information

5-Chlorocoumaranone-Conjugates as Chemiluminescent Protecting Groups (CLPG) and Precursors to Fluorescent Protecting Groups (FPG)

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Author Contributions

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T.L Conceptualization: Assist, Investigation: Lead

R.H. Investigation: Assist

M.S.W. Conceptualization: Assist

L.S. Methodology: Lead

N.T.F. Methodology: Assist

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1.1 NMR and IR spectra of compound 5A

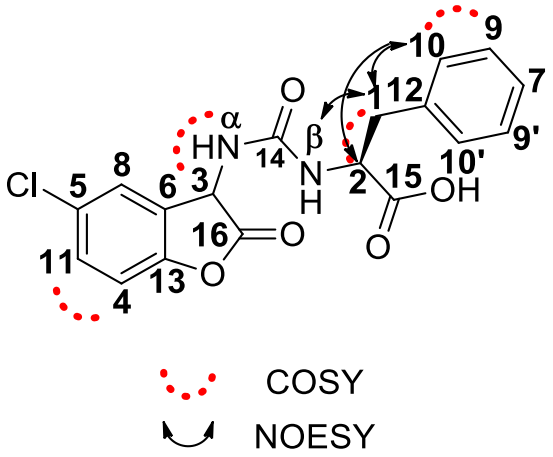
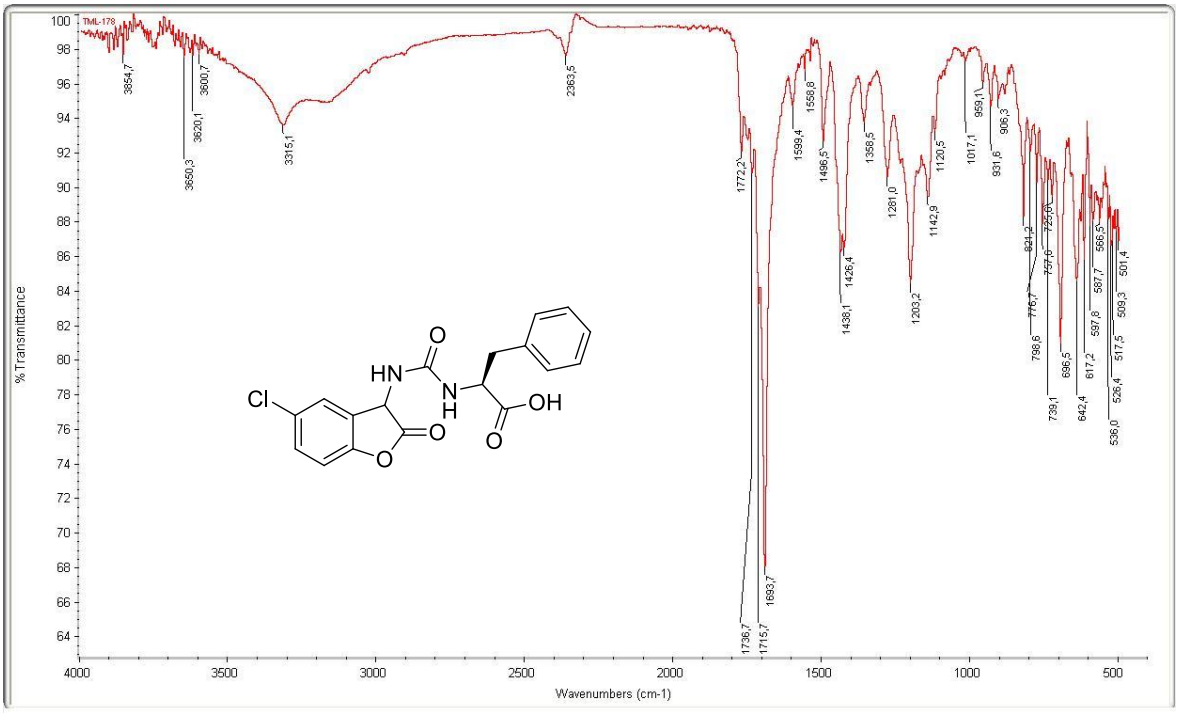


Table S1: 1D and 2D-NMR data of (2*S*)-2-(3-(5-chloro-2-oxo-2,3-dihydrobenzofuran-3-yl)ureido)-3-phenylpropanoic acid (5A) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	3.26+3.36 (2H, m)	33.3+33.4, CH_2	C1→H2(^{2}J), H10(^{3}J)
2	4.83+4.84 (1H, ψt, *J* = 10.9 Hz)	52.92+52.98, CH	C2→H1(^{2}J)
3	5.21+5.30 (1H, s)	54.01+54.04, CH	C3→H4(^{4}J), H8(^{3}J), NH_α(^{2}J)
4	6.84+6.87 (1H, d, *J* = 8.7 Hz)	117.0+117.2, CH_{arom}	C4→NH_β(^{7}J)
5	-	122.42+122.47, C_q	C5→H8(^{2}J), H4(^{3}J), H11(^{2}J)
6	-	123.59+123.60, C_q	C6→H3(^{2}J), H4(^{3}J), NH_β(^{5}J)
7	7.22 (1H, m)	126.6+126.7, CH_{arom}	C7→H10(^{3}J)
8	6.63+6.77 (1H, d, *J* = 2.5 Hz)	127.3+127.4, CH_{arom}	C8→H3(^{3}J), H11(^{3}J)
9	7.27 (2H, m)	128.28+128.31, 2xCH_{arom}	C9→H9(^{3}J)
10	7.15 +7.21 (2H, m)	128.81+128.86, 2xCH_{arom}	C10→H1(^{3}J), H10(^{3}J)
11	7.13+7.19 (1H, m)	129.30+129.33, CH_{arom}	C11→H8(^{3}J)
12		137.34+137.36, C_q	C12→H1(^{2}J), H2(^{3}J), H9(^{3}J)
13		154.6, C_q	C13→H3(^{3}J), H4(^{2}J), H8(^{3}J), H11(^{3}J), NH_β(^{6}J)
14	-	155.96+156.07, C_q	C14→H2(^{3}J), H3(^{3}J), NH_α(^{2}J)
15	-	170.1, C_q	C15→H1(^{3}J), H2(^{2}J)
16	-	171.87+171.95, C_q	C16→H2(^{6}J), H3(^{2}J), NH_α(^{3}J)
NH_α	8.48 (1H, s)	-	-
NH_β	10.19+10.21 (1H, s)	-	-
COOH	13.24 (1H, br)	-	-

Note: The ^{1}H- and ^{13}C-NMR-spectra show a mixture of rotamers.

Chemical Formula:	$C_{18}H_{15}ClN_2O_5$
Molecular Weight:	374.78 g/mol
IR:	$\tilde{\nu}$[cm^{-1}] = 3854 (w), 3650 (w), 3620 (w), 3600 (w), 3315 (br), 2363 (w), 1772 (w), 1737 (w), 1716 (m), 1694 (vs), 1599 (w), 1559 (w), 1497 (m), 1438 (m), 1426 (m), 1359 (w), 1281 (m), 1203 (m), 1143 (w), 1121 (w), 1017 (w), 959 (w), 932 (s), 906 (w), 821 (m).
HR-MS:	Theor. $[M+H]^+$: 375.07422, found: 375.07423. Theor. [M+Na]+: 397.05617, found: 397.05640.
MP:	Decomposition above 190 °C.
R_f:	0.25 (SiO_2, 20:1 DCM:MeOH + 1% AcOH).


TML-178
% Transmittance
Wavenumbers (cm-1)
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3620,1
3600,7
3315,1
2363,5
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1736,7
1715,7
1693,7
1599,4
1558,8
1496,5
1438,1
1426,4
1368,5
1281,0
1203,2
1142,9
1120,5
1017,1
959,1
931,6
906,3
824,2
798,6
776,7
739,1
725,0
696,5
642,4
617,2
597,8
587,7
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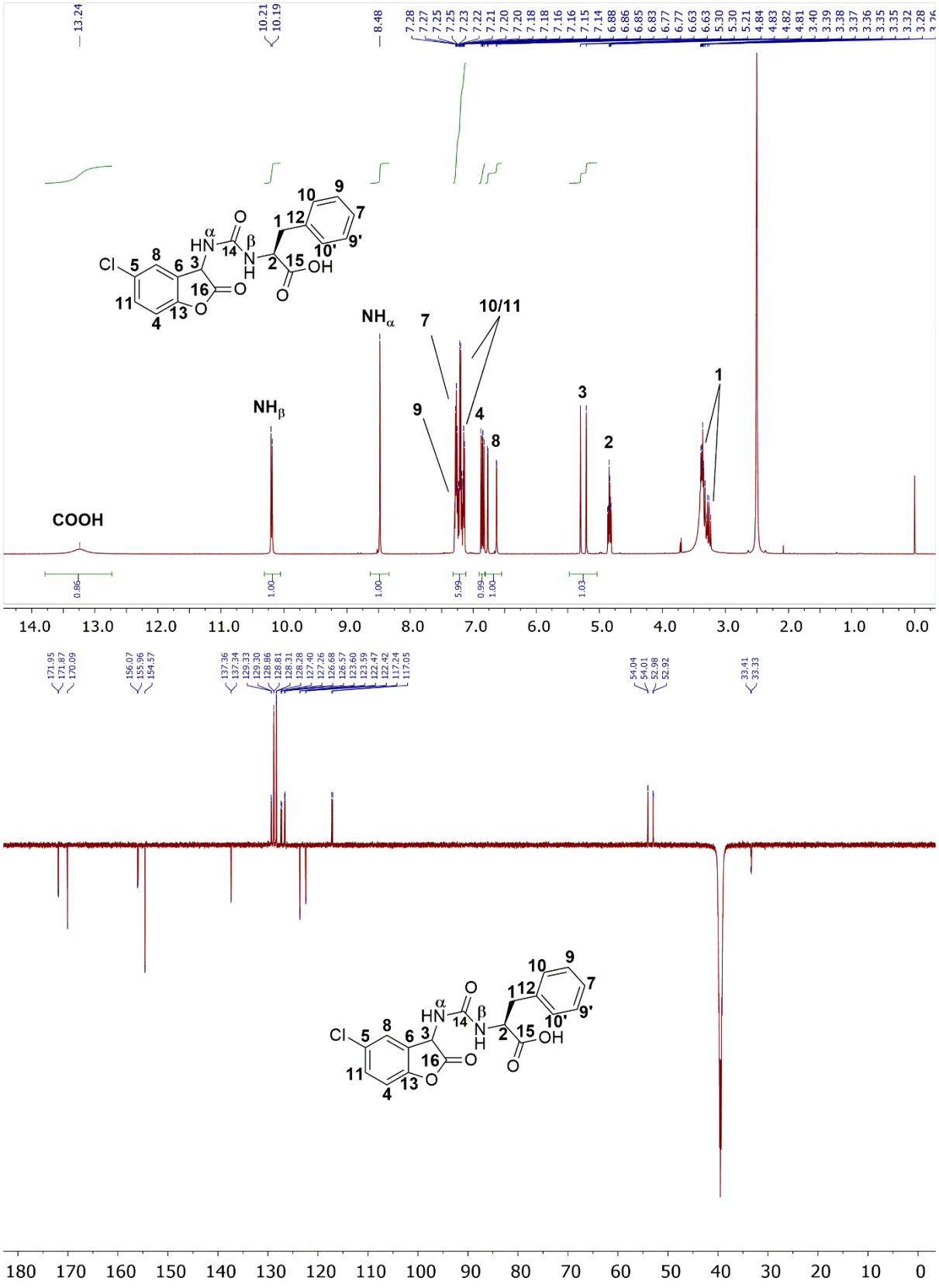
N
H
O
O
O
OH
Cl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10.19
8.48
7.28
7.27
7.25
7.25
7.23
7.22
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7.20
7.18
7.18
7.16
7.16
7.15
7.14
6.88
6.86
6.85
6.83
6.77
6.77
6.63
6.63
5.30
5.30
5.21
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4.83
4.82
4.81
3.40
3.39
3.38
3.37
3.36
3.35
3.35
3.32
3.28
NH$_\alpha$
NH$_\beta$
COOH
10/11
0.86
1.00
1.00
5.99
0.99
1.00
1.03
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
171.95
171.87
170.09
156.07
155.96
154.57
137.36
137.34
129.33
129.30
128.86
128.81
128.31
128.28
127.40
127.26
126.67
123.67
123.60
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52.92
33.41
33.33
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
30
20
10
0

Figure S1: NMR- and IR-spectra of **5A**.

1.2 NMR and IR spectra of compound 5E

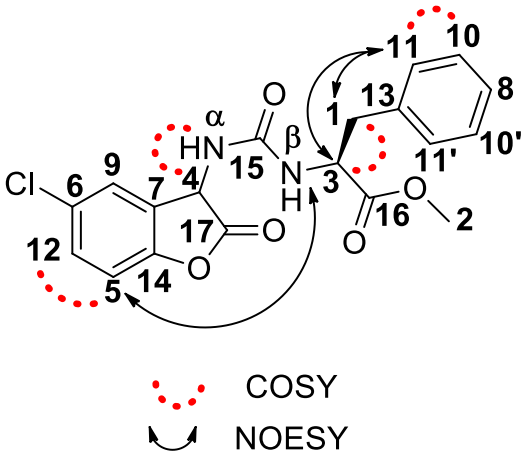
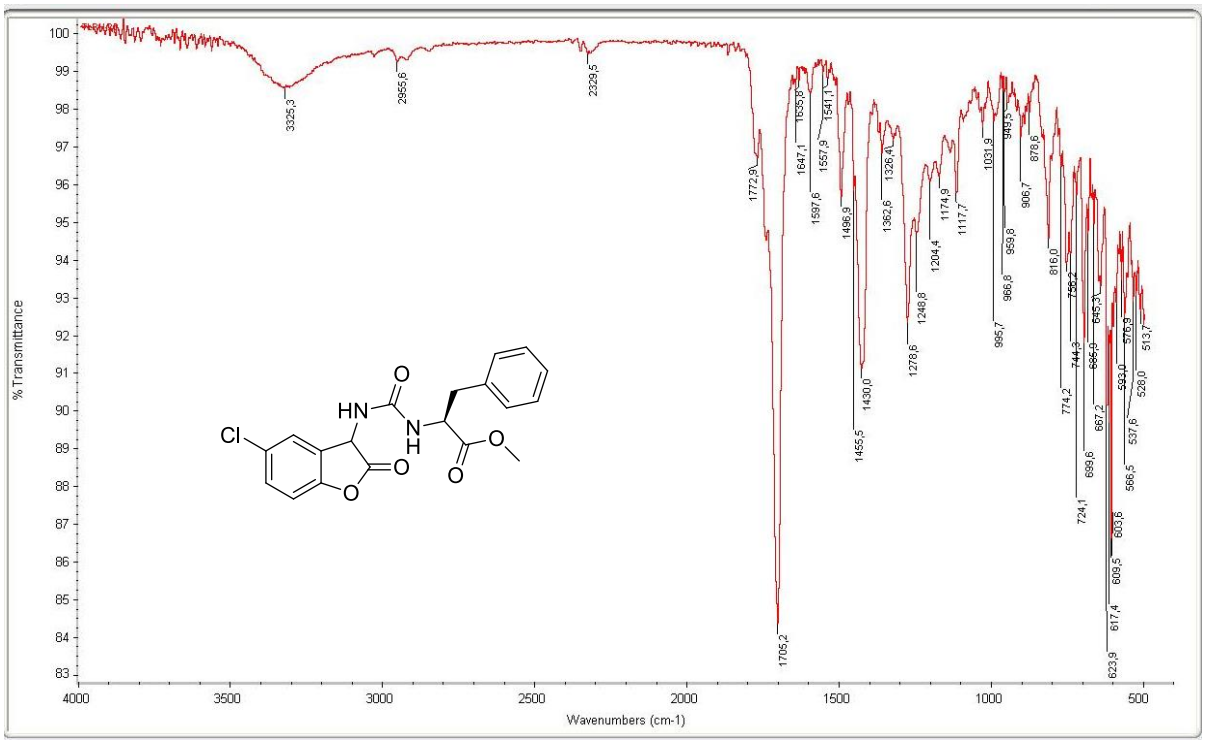


Table S2: 1D and 2D-NMR data of (2*S*)-methyl 2-(3-(5-chloro-2-oxo-2,3-dihydrobenzofuran-3-yl)ureido)-3-phenylpropanoate (5E) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	3.21-3.32 (1H, m) 3.38+3.40 (1H, m)	33.45+33.41, CH_2	C1→H3(^{2}J), H11(^{3}J)
2	3.70+3.72 (3H, s)	52.62+52.56, CH_3	-
3	4.95-5.00 (1H, m)	52.66, CH	C3→H1(^{2}J),
4	5.19+5.30 (1H, d, *J* = 1.1 Hz)	54.5+54.4, CH	C4→H5(^{4}J), H9(^{3}J), NH_α(^{2}J)
5	6.84+6.86 (1H, d, *J* = 8.7 Hz)	117.3+117.1, CH_{arom}	C5→NH_β(^{7}J)
6		122.45+122.42, C_q	C6→H5(^{3}J), H9(^{2}J), H12(^{2}J)
7		123.51+123.50, C_q	C7→H4(^{2}J), H5(^{3}J), NH_β(^{5}J)
8	7.23 (1H, m)	126.8+126.7, CH_{arom}	C8→H11(^{3}J)
9	6.67+6.82 (1H, d, *J* = 2.7 Hz)	127.8+127.6, CH_{arom}	C9→H4(^{3}J), H12(^{3}J)
10	7.27 (2H, m)	128.36+128.35, 2xCH_{arom}	C10→H10(^{3}J)
11	7.16+7.21 (2H, m)	128.97+128.93, 2xCH_{arom}	C11→H1(^{3}J), H11(^{3}J)
12	7.21 (1H, m)	129.45+129.42, CH_{arom}	C12→H9(^{3}J)
13	-	136.92+136.89, C_q	C13→H1(^{2}J), H10(^{3}J)
14	-	154.64+154.63, C_q	C14→H9(^{3}J), H12(^{3}J), NH_β(^{6}J)
15	-	155.9+155.7, C_q	C15→H3(^{3}J), H4(^{3}J), NH_α(^{2}J)
16	-	169.14+169.07, C_q	C16→H1(^{3}J), H2(^{3}J), H3(^{2}J)
17	-	171.9+171.8, C_q	C17→H3(^{6}J), H4(^{2}J), NH_α(^{3}J)
NH_α	8.52 (1H, s)		
NH_β	10.17+10.18 (1H, s)		

Note: The ^{1}H- and ^{13}C-NMR-spectra show a mixture of rotamers.

Chemical Formula:	$C_{19}H_{17}ClN_2O_5$
Molecular Weight:	388.80 g/mol
IR:	$\tilde{\nu}$ [cm^{-1}] = 3325 (w), 2955 (w), 2330 (w), 1773 (w), 1705 (s), 1647 (w), 1635 (w), 1597 (w), 1556 (w), 1541 (w), 1497 (w), 1454 (w), 1430 (m), 1363 (w), 1326 (w), 1279 (m), 1249 (w), 1204 (w), 1175 (w), 1118 (w), 1032 (w), 996 (w), 967 (w), 960 (w), 950 (w), 907 (w), 879 (w), 816 (w).
HR-MS:	Theor. $[M+H]^+$: 398.08987, found: 397.08991. Theor. $[M+Na]^+$: 411.07182, found: 411.07179.
MP:	206 °C.
R_f:	0.35 (SiO_2, 20:1 DCM:MeOH).


% Transmittance
Wavenumbers (cm-1)
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2329,5
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1557,9
1541,1
1496,9
1455,5
1430,0
1362,6
1326,4
1278,6
1248,8
1204,4
1174,9
1117,7
1031,9
995,7
966,8
959,8
906,7
878,6
816,0
774,2
744,3
724,1
699,6
667,2
645,3
623,9
617,4
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H
O
O
O
O

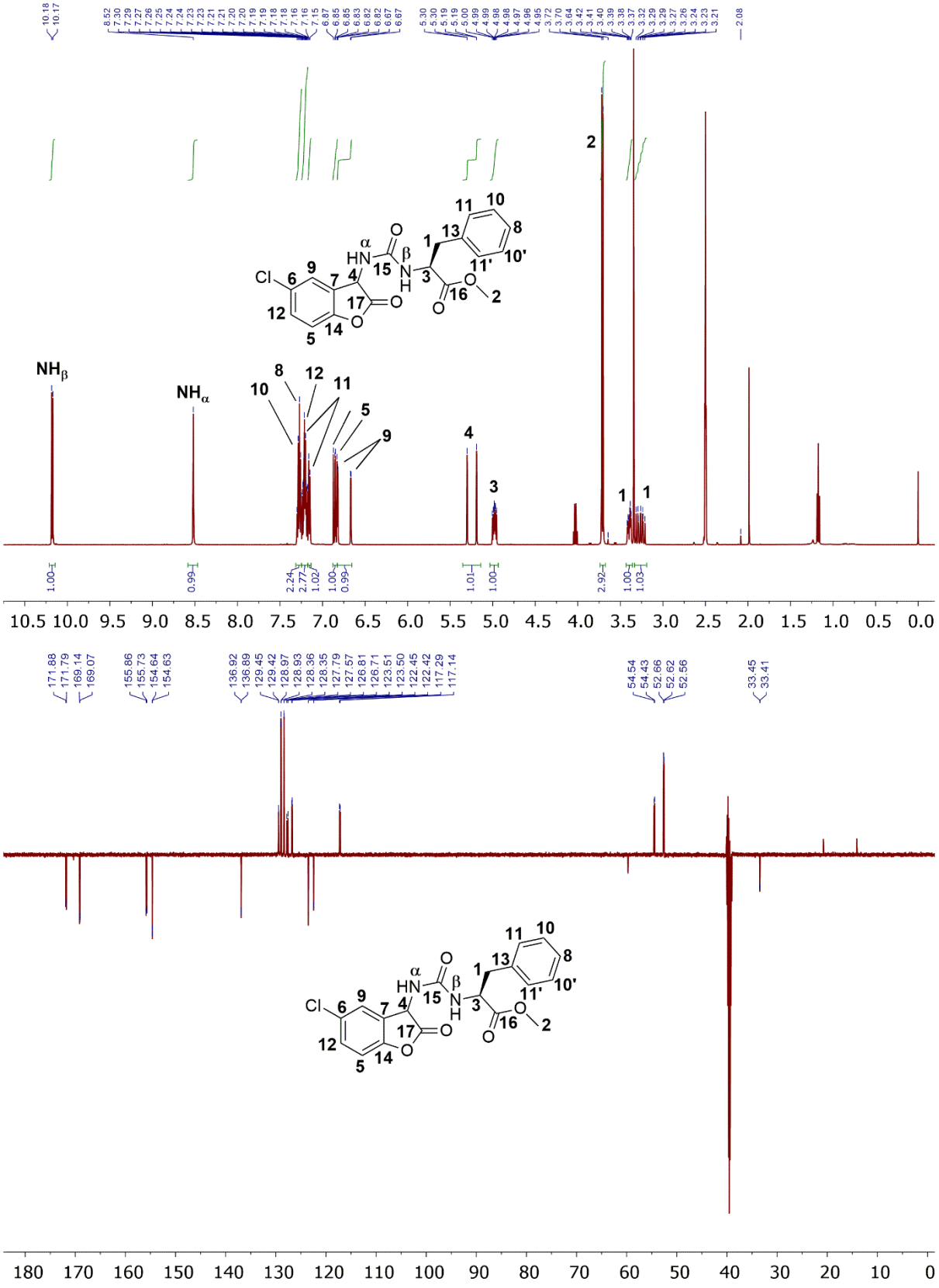

NHβ
NHα
2
1
3
4
5
9
8
10
12
11
Cl
HN
α
β
N
H
O
15
16
17
14
13
11'
10'

Figure S2: NMR- and IR-spectra of **5E**.

1.3 NMR and IR spectra of compound 6

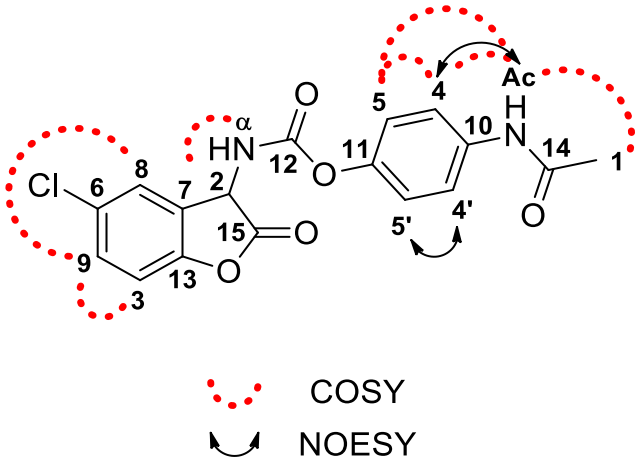


Table 3: 1D and 2D-NMR data of 4-acetamidophenyl (5-chloro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamate (6) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	2.03 (3H, s)	23.9, CH_3	-
2	5.37 (1H, d, *J* = 8.2 Hz)	53.0, CH	C2→H3(^{4}J), H8(^{3}J), NH_α(^{2}J)
3	6.84 (1H, d, *J* = 8.7 Hz)	117.5, CH_{arom}	C3→H8(^{4}J)
4	7.56 (2H, d, *J* = 8.9 Hz)	119.8, 2xCH_{arom}	C4→H4(^{3}J), H5(^{2}J), NH_{Ac}(^{3}J)
5	7.03 (2H, d, *J* = 9.0 Hz)	121.9, 2xCH_{arom}	C5→H4(^{2}J), H5(^{3}J)
6	-	122.2, C_q	C6→H3(^{3}J), H8(^{2}J), H9(^{2}J)
7	-	126.7, C_q	C7→H2(^{2}J), H3(^{3}J)
8	7.27 (1H, d, *J* = 2.7 Hz)	127.1, CH_{arom}	C8→H9(^{3}J)
9	7.16 (1H, dd, *J* = 8.7, 2.7 Hz)	128.3, CH_{arom}	C9→H8(^{3}J)
10	-	136.4, C_q	C10→H4(^{2}J), H5(^{3}J), NH_{Ac}(^{2}J)
11	-	146.2, C_q	C11→H4(^{3}J), H5(^{2}J)
12	-	154.2, C_q	C12→H2(^{3}J), NH_α(^{2}J)
13	-	154.4, C_q	C13→H3(^{2}J), H8(^{3}J), H9(^{3}J)
14	-	168.2, C_q	C14→H1(^{2}J), NH_{Ac}(^{2}J)
15	-	171.71, C_q	C15→H2(^{2}J)
NH_α	8.11 (1H, d, *J* = 8.2 Hz)	-	-
NH_{Ac}	9.97 (1H, s)	-	-

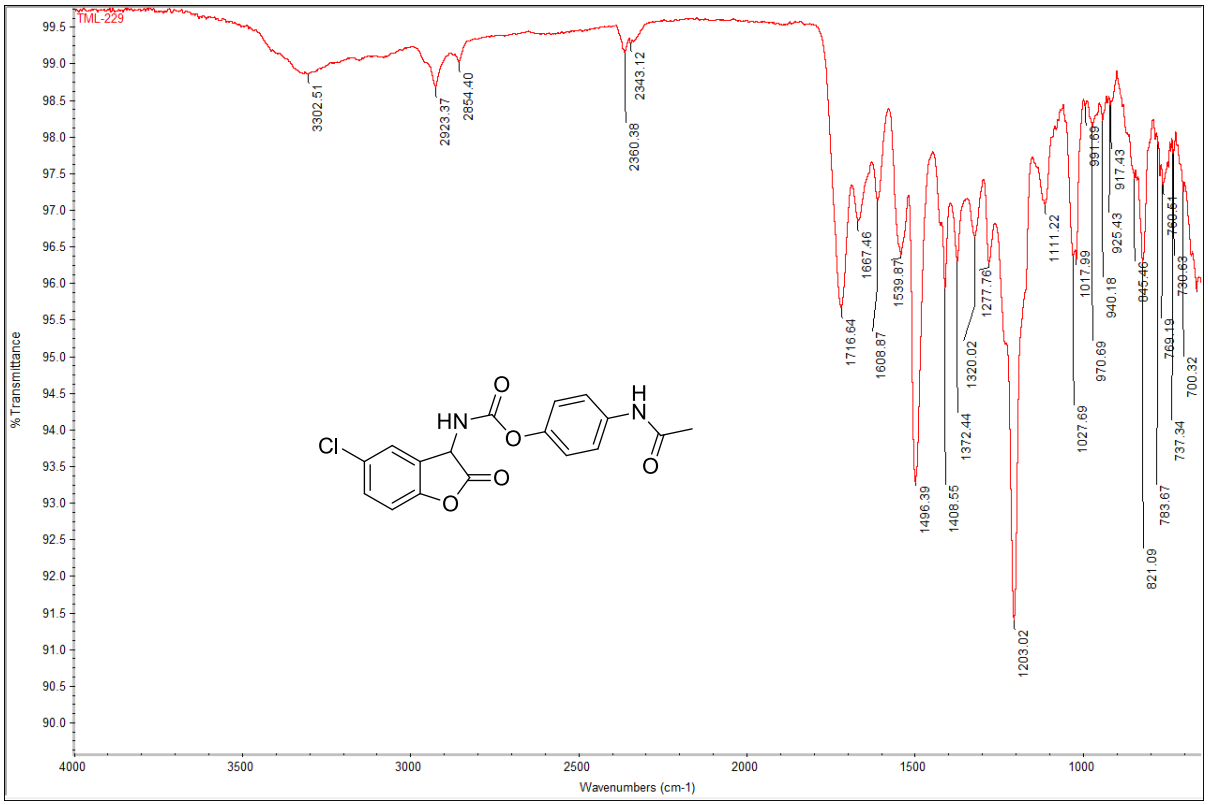
Chemical Formula: $C_{17}H_{13}ClN_2O_5$

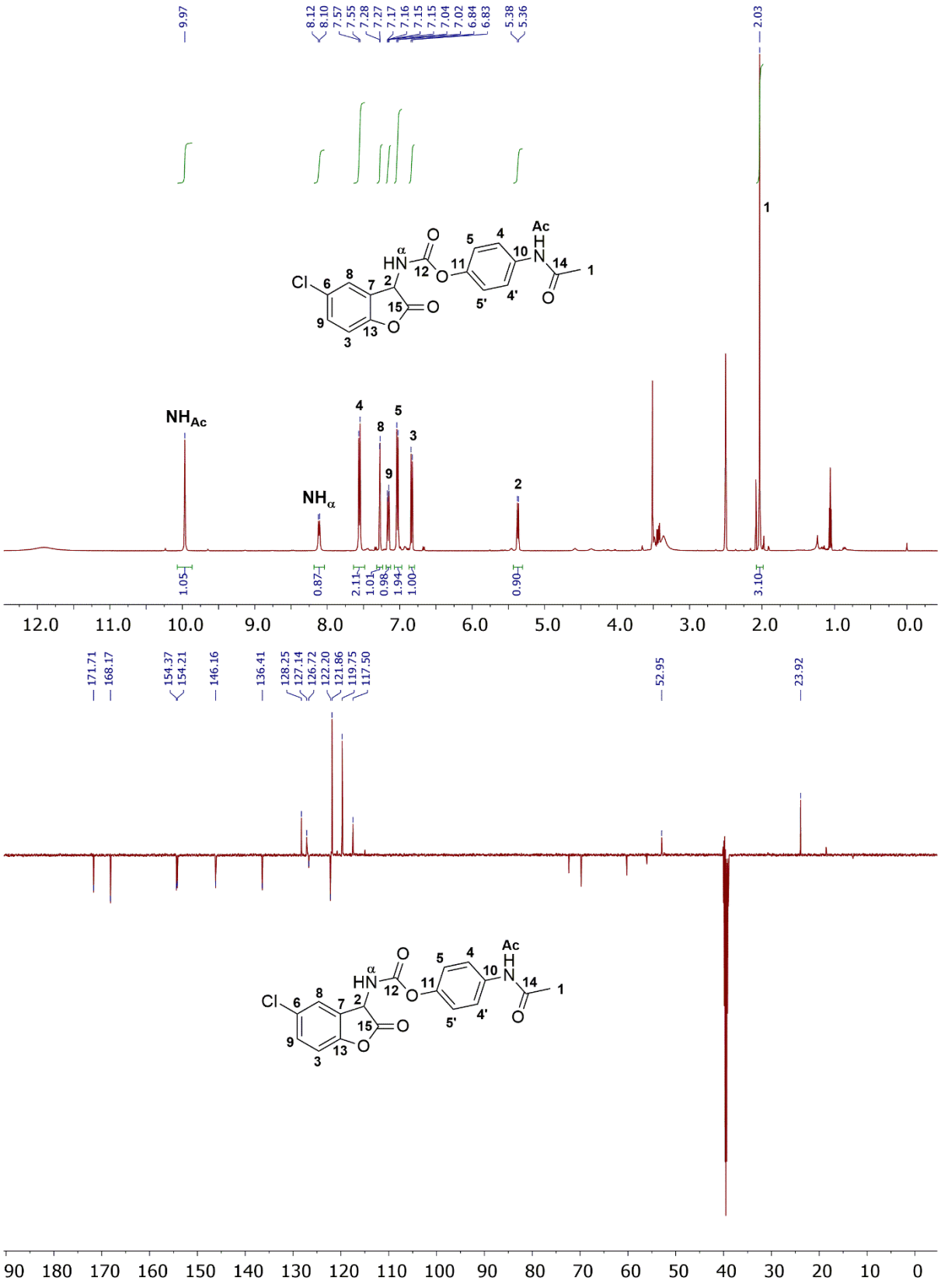
Molecular Weight: 360.75 g/mol

IR: $\tilde{\nu}$ [cm^{-1}] = 3303 (br), 2923 (w), 2854 (w), 2360 (w), 2343 (w), 1717 (m), 1667 (w), 1609 (w), 1540 (w), 1496 (s), 1409 (w), 1372 (w), 1320 (w), 1278 (w), 1203 (vs), 1111 (w), 1028 (m), 1018 (m), 992 (w), 971 (w), 940 (w), 925 (w), 917 (w), 845 (w), 821 (m).

MP: Change of colour: 148 °C; Melting at 175 °C.

R_f: 0.10 (SiO_2, 8:1 DCM:MeOH).




9.97
8.12
8.10
7.57
7.55
7.28
7.27
7.17
7.16
7.15
7.15
7.04
7.02
6.84
6.83
5.38
5.36
2.03
NHAc
NHα
1.05
0.87
2.11
1.01
0.98
1.94
1.00
0.90
3.10
12.0
11.0
10.0
9.0
8.0
7.0
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3.0
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0.0
171.71
168.17
154.37
154.21
146.16
136.41
128.25
127.14
126.72
122.20
121.86
119.75
117.50
52.95
23.92
90
180
170
160
150
140
130
120
110
100
90
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60
50
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Figure S3: NMR- and IR-spectra of **6**.

1.4 NMR and IR spectra of compound 8

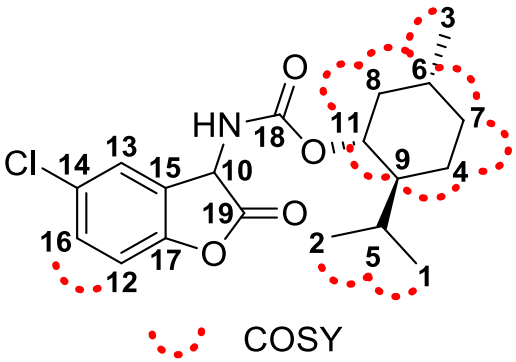
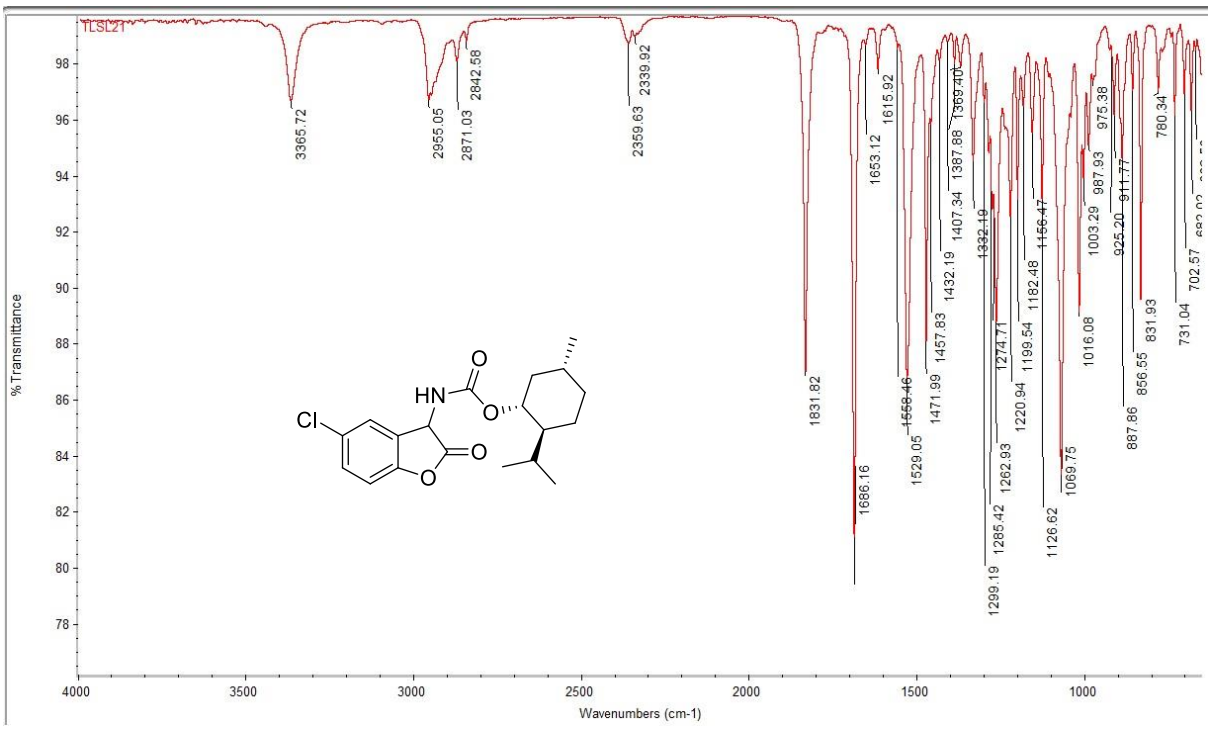


Table S4: 1D and 2D-NMR data of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (5-chloro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamate (8) in $CDCl_3$, at 298 K and 500 MHz for ^1H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^xJ)
1	0.74-0.80 (3H, s)	16.5, CH_3	C1→H2(^3J)
2	0.90 (3H, m)	20.85+20.88, CH_3	C2→H1(^3J)
3	0.89 (3H, m)	22.0, CH_3	C3→H8(^3J)
4	1.04 (1H, m); 1.67 (1H, m)	23.7, CH_2	-
5	1.89 (1H, m)	26.5, CH	C5→H1(^2J), H2(^2J)
6	1.43 (1H, m)	31.5, CH	C6→H3(^2J), H7(^2J), H8(^2J)
7	0.84 (1H, m); 1.65 (1H, m)	34.3, CH_2	C7→H3(^3J), H8(^3J)
8	0.98 (1H, m); 1.99 (1H, m)	41.2, CH_2	C8→H3(^3J)
9	1.33 (1H, m)	47.4+47.5, CH	C9→H1(^3J), H2(^3J)
10	5.20-5.60 (1H, br)	52.4+52.8, CH	C10→H12(^4J), H13(^3J)
11	4.53 (1H, m)	76.9, CH	C11→H8(^2J), H9(^2J)
12	7.05 (1H, d, *J* = 8.3 Hz)	112.3+112.4, CH_{arom}	C12→H13(^4J)
13	7.34 (1H, m)	124.85+124.94, CH_{arom}	C13→H16(^3J)
14	-	126.6, C_q	C14→H12(^3J)
15	-	130.10+130.12, C_q	C15→H12(^3J), H16(^4J)
16	7.33 (1H, m)	130.4, CH_{arom}	C16→H13(^3J)
17	-	152.19+152.24, C_q	C17→H12(^2J), H13(^3J), H16(^3J)
18	-	155.9, C_q	C18→H10(^3J)
19	-	172.9+173.0, C_q	C19→H10(^2J)

Note: The ^1H- and ^{13}C-NMR-spectra show a mixture of rotamers.

Chemical Formula:	$C_{19}H_{24}ClNO_4$
Molecular Weight:	365.85 g/mol
IR:	$\tilde{\nu}$ [cm^{-1}] = 3366 (br), 2955 (w), 2871 (w), 2843 (w), 2360 (w), 2340 (w), 1832 (s), 1686 (vs), 1653 (w), 1616 (w), 1558 (w), 1529 (s), 1472 (s), 1458 (w), 1432 (w), 1388 (w), 1369 (w), 1332 (w), 1299 (w), 1285 (w), 1275 (w), 1263 (m), 1221 (w), 1200 (w), 1183 (w), 1157 (w), 1070 (s), 1016 (m), 1003 (w), 988 (w), 975 (w), 925 (w), 912 (w), 888 (w), 857 (w), 832 (m).
HR-MS:	Theor. $[M+Na]^+$: 388.12860, found: 388.12883.
Melting Point:	172 °C.
R_f:	0.27 (SiO_2, 100:1 Toluene:MeOH + 1% AcOH).


TLSL21
% Transmittance
Wavenumbers (cm-1)
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2359.63
2339.92
1831.82
1686.16
1653.12
1615.92
1558.46
1529.05
1471.99
1457.83
1432.19
1407.34
1387.88
1369.40
1332.19
1299.19
1285.42
1274.71
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925.20
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702.57
Cl
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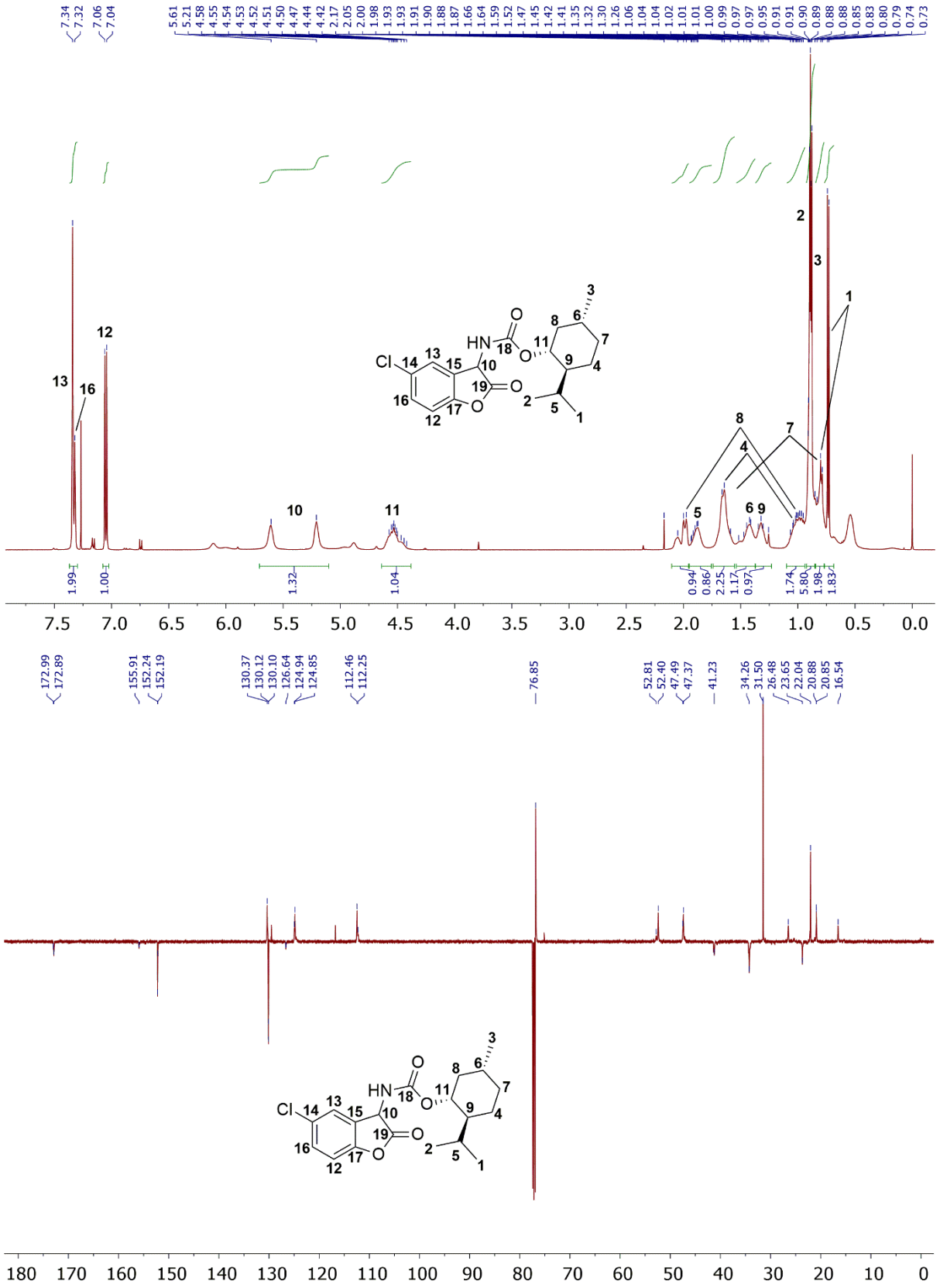
O
O
O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7.04
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5.21
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4.55
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4.50
4.47
4.44
4.42
2.17
2.05
2.00
1.98
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1.90
1.88
1.87
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1.30
1.26
1.06
1.04
1.04
1.02
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0.97
0.97
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0.89
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0.85
0.83
0.80
0.79
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0.73
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1.00
1.32
1.04
0.94
0.86
2.25
1.17
0.97
1.74
5.80
1.98
1.83
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7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
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172.89
155.91
152.24
152.19
130.37
130.12
130.10
126.64
124.94
124.85
112.46
112.25
76.85
52.81
52.40
47.49
47.37
41.23
34.26
31.50
26.48
23.65
22.04
20.88
20.85
16.54
180
170
160
150
140
130
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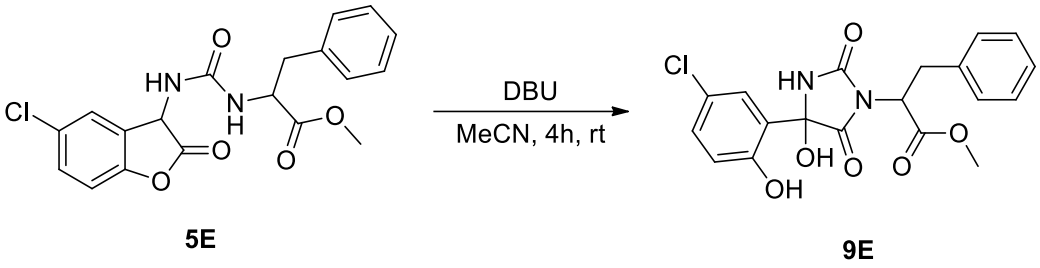
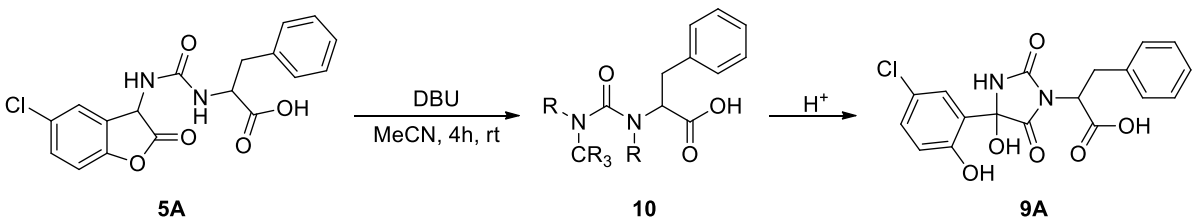
Figure S4: NMR- and IR-spectra of **8**.

2. Decomposition Experiments



5E **9E**

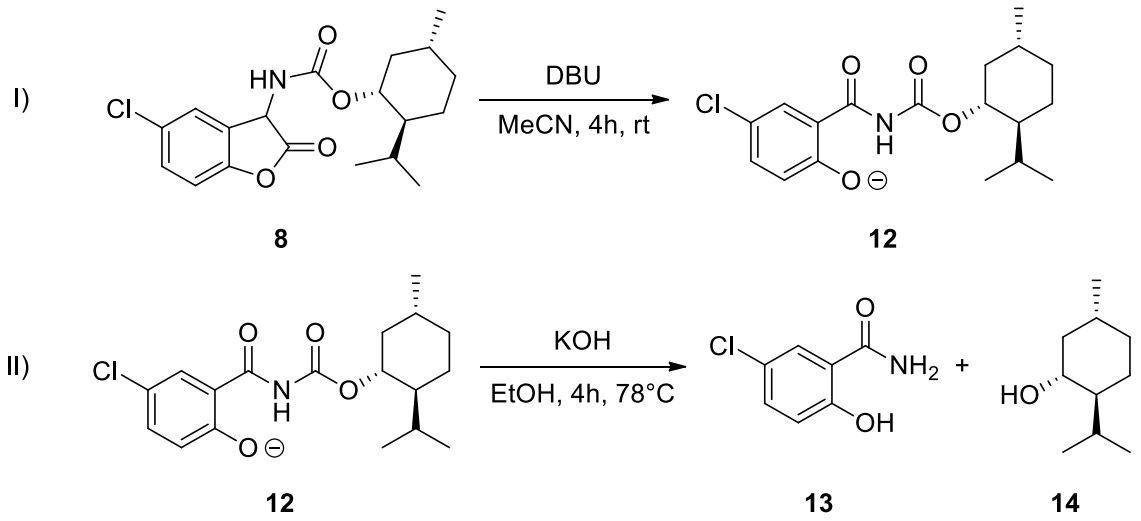
Decomposition experiment 5E-DE: 200 mg (0.51 mmol, 1.0 eq.) of **5E** were dissolved in 10.0 ml MeCN and 0.15 ml (1.03 mmol, 2.0 eq.) of DBU were added. At the begin of the addition a small flash of blue light could be seen and the clear mixture slowly turned orange and then dark brown. After 4 hours 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 ethylacetate (20 ml per extraction) and the combined organic layers were washed four times with water and subsequently dried over sodium sulfate. Finally, the solvent was removed under reduced pressure and 50 mg of a brownish solid were obtained, which were analysed via NMR-spectroscopy and ESI-MS.



5A **10** **9A**

Decomposition experiment 5A-DE: 200 mg (0.53 mmol, 1.0 eq.) of **5A** were dissolved in 10.0 ml MeCN and 0.16 ml (1.07 mmol, 2.0 eq.) of DBU were added. At the begin of the addition a small flash of blue light could be seen and the clear

mixture slowly turned orange and then dark brown. After 4 hours the solvent was removed under reduced pressure. 10 ml of water and 1.0 ml of 2 M HCl solution were added to the crude product, which then changed its colour to orange. The aqueous phase was extracted three times with ethylacetate (20 ml per extraction) and the combined organic layers dried over sodium sulfate. Finally, the solvent was removed under reduced pressure. 22 mg of a brownish, orange solid was obtained, which were analysed via NMR.



Decomposition experiment 8-DE: 50 mg (0.14 mmol, 1.0 eq.) of **6** were dissolved in 5.0 ml MeCN and 42 µl (0.28 mmol, 2.0 eq.) of DBU were added. Over a time period of 20 minutes a strong emission of blue light could be seen and the clear mixture slowly turned yellow, then orange and finally dark red. After 4 hours the solvent was removed under reduced pressure and 10 ml of water and ethylacetate were added to the crude product. The organic phase was washed four times with water and subsequently dried over sodium sulfate. Finally, the solvent was removed under reduced pressure and 45 mg of a colourless solid were obtained, which was analysed via NMR. After compound **12** was verified, it was dissolved in 5 ml EtOH and 24 mg

KOH (0.42 mmol, 3.0 eq.) were added and the solution was refluxed for 4 hours. After that 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 ethylacetate (15 ml per extraction) and the combined organic layers were washed with brine and subsequently dried over sodium sulfate. Finally, the solvent was removed under reduced pressure and 20 mg (0.11 mmol, 79% minus the contamination by 5-chlorosalicylamide **13**) of L-menthol **14** were obtained.

2.1 NMR and ESI-spectra of 5E

Results from Experiment 5E-DE (Mainproduct)

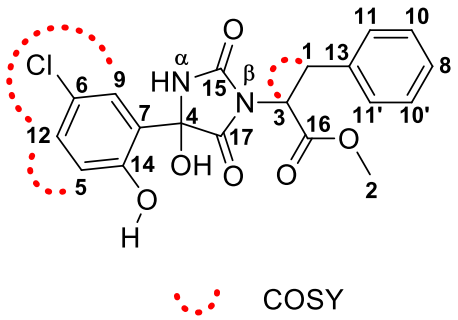


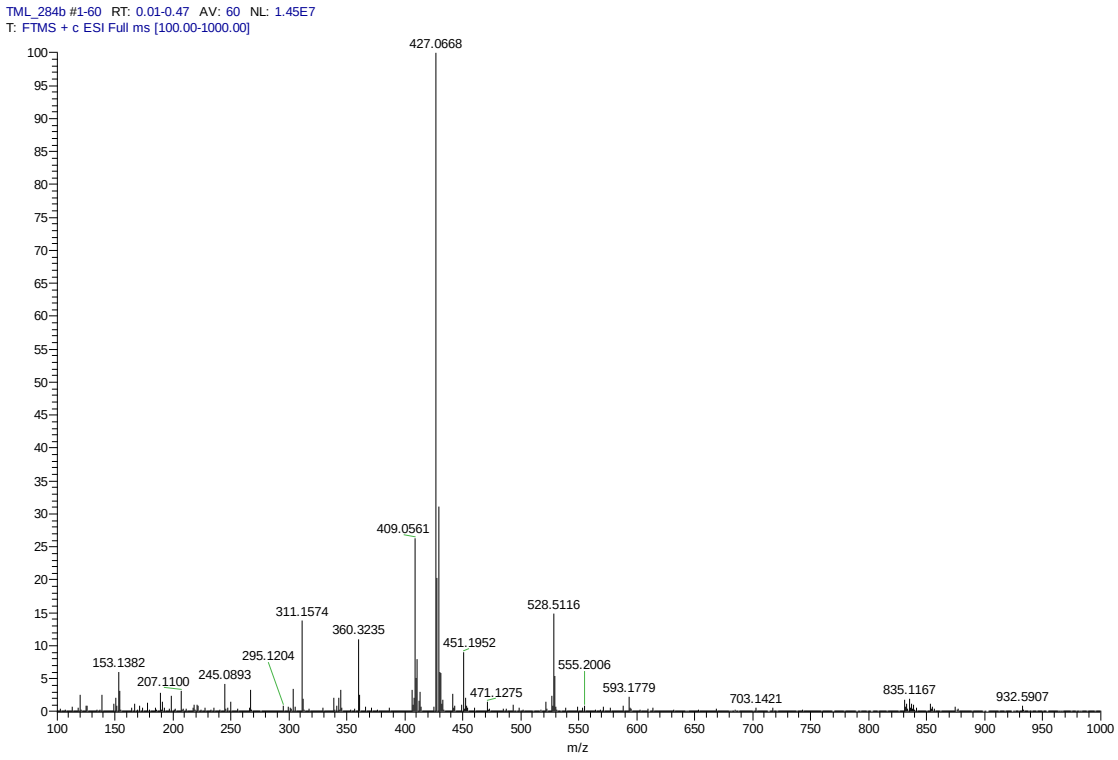
Table S4: 1D and 2D-NMR data of methyl 2-(4-(5-chloro-2-hydroxyphenyl)-4-hydroxy-2,5-dioxoimidazolidin-1-yl)-3-phenylpropanoate (9E) in DMSO-d_6, at 298 K and 499 MHz for ^{1}H and 126 MHz for ^{13}C.

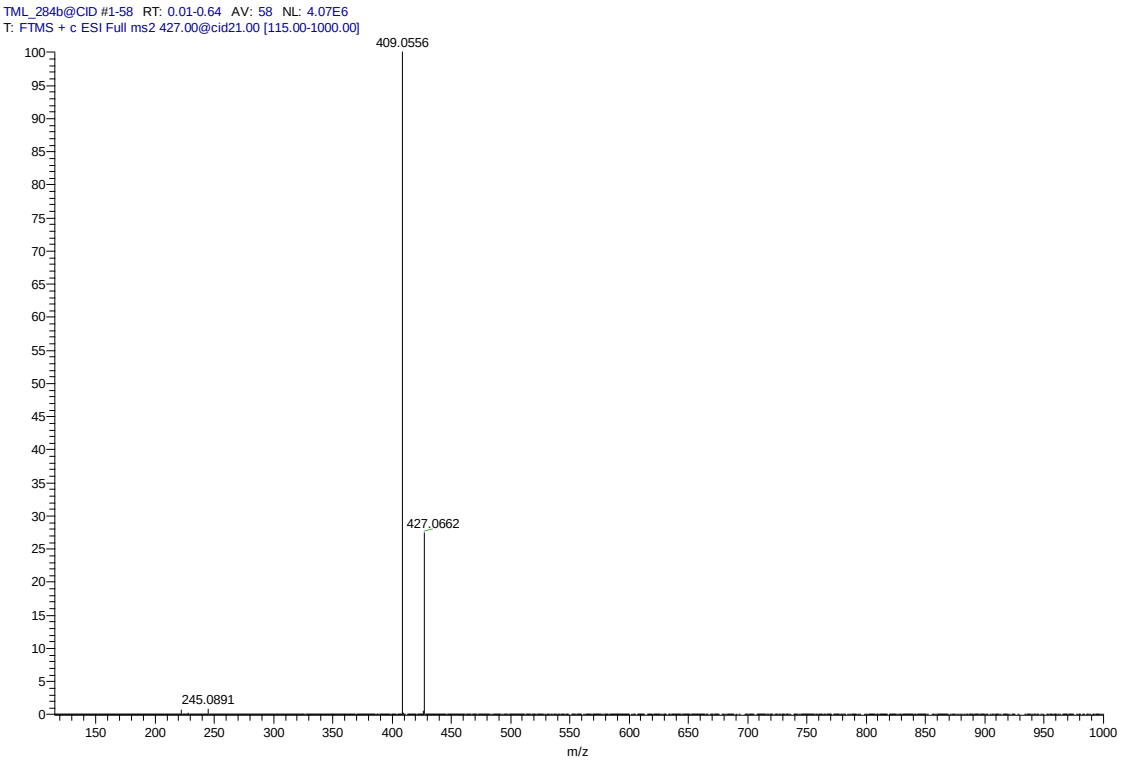
No.	δ_H [ppm], *J* in [Hz]	δ_C, δ_N [ppm], mult.	HMBC (^{x}J)
1	3.04 (1H, dd, *J* = 14.2, 1.6 Hz) +3.45 (1H, dd, *J* = 14.2, 7.2 Hz)	33.38+33.61, CH_2	C1→H3(^{2}J), H11(^{3}J)
2	3.64 (3H, s)	52.30+52.32, CH_3	-
3	4.78 (1H, dd, *J* = 7.8, 1.8 Hz)	52.7, CH	C3→H1(^{2}J),
4	-	81.76+81.92, C_q	C4→H5(^{4}J), H9(^{3}J), NH_α(^{2}J)
5	6.80 (1H, d, *J* = 8.6 Hz)	117.1, CH_{arom}	-
6	-	122.0, C_q	C6→H5(^{3}J), H9(^{2}J), H12(^{2}J)
7	-	126.25+126.33, C_q	C7→H5(^{3}J)
8	7.20 (1H, m)	126.5, CH_{arom}	C8→H11(^{3}J)
9	7.49 (1H, d, *J* = 2.6 Hz)	127.37, CH_{arom}	C9→H12(^{3}J)
10	7.27 (2H, m)	128.31+128.34, 2xCH_{arom}	C10→H10(^{3}J)
11	7.25 (2H, m)	129.02+129.07, 2xCH_{arom}	C11→H1(^{3}J), H8(^{3}J), H11(^{3}J)
12	7.24 (1H, m)	129.5, CH_{arom}	C12→H9(^{3}J)
13	-	137.7, C_q	C13→H1(^{2}J), H10(^{3}J)
14	-	153.48+153.54, C_q	C14→H5(^{2}J), H9(^{3}J), H12(^{3}J)
15	-	154.93+154.97, C_q	C15→H3(^{3}J), NH_α(^{2}J)
16	-	168.92+169.04, C_q	C16→H1(^{3}J), H2(^{3}J), H3(^{2}J)
17	-	172.16+172.29, C_q	C17→H3(^{3}J), NH_α(^{3}J)
NH_α	8.86+8.83 (1H, s)	112.6, NH	-
N_β	-	147.8, NR_3	N_β→H1(^{3}J), H3(^{2}J), NH_α(^{3}J)
Ph-OH	10.13 (1H, br)	-	-

Chemical Formula: $C_{19}H_{17}ClN_2O_6$

Molecular Weight: 404.80 g/mol

MS (ESI): mz (%) 427.0668 [M+Na$^+$] (27), 409.556 [M+Na$^+$-H_2O] (100).





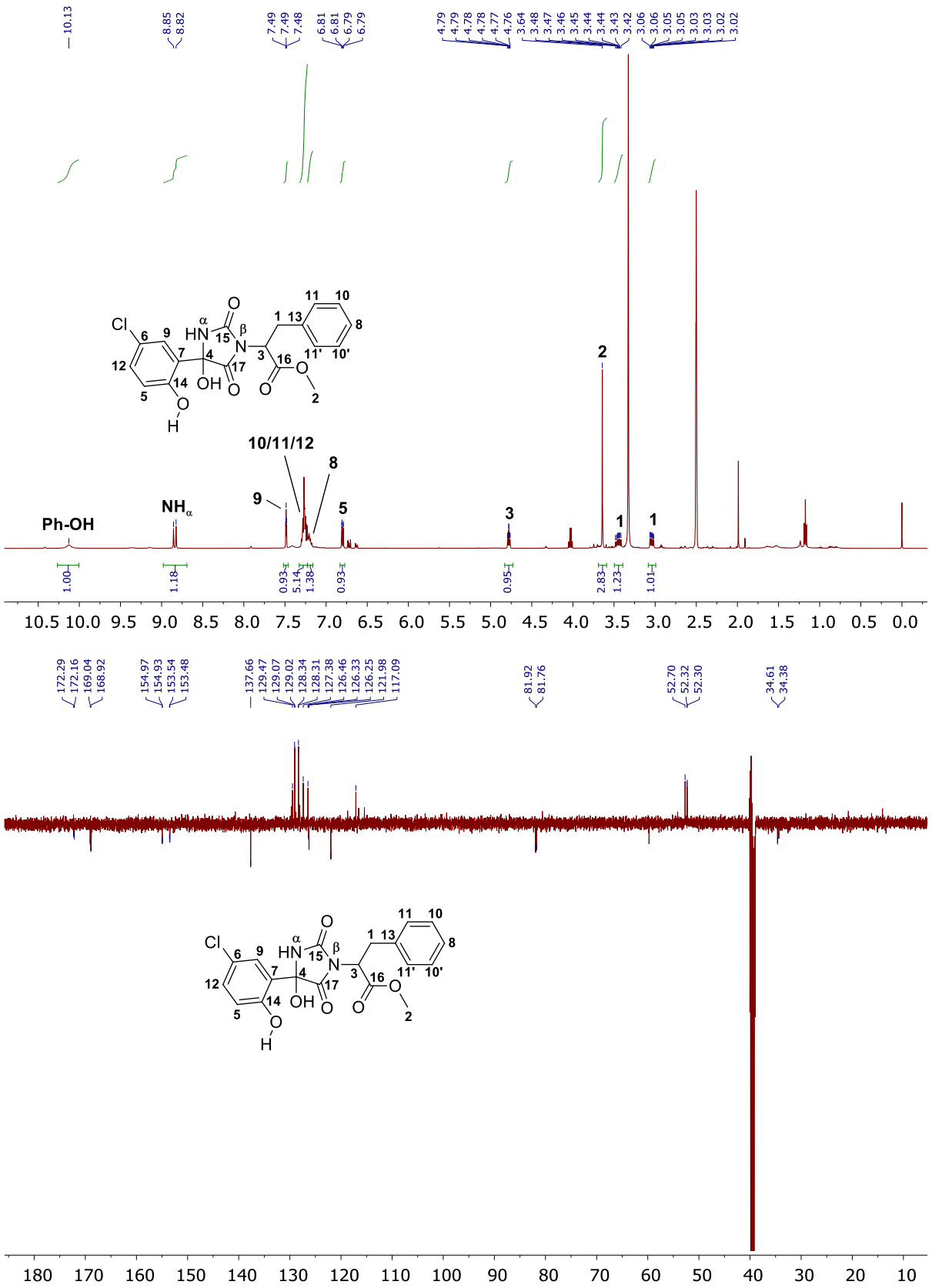


Figure S5: NMR- and ESI-spectra of **9E**.

2.2 NMR-spectra of 5A

Results from Experiment 5A-DE (Product after protonation)

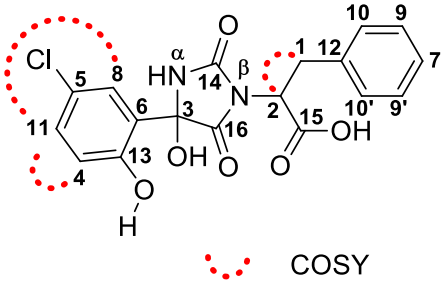
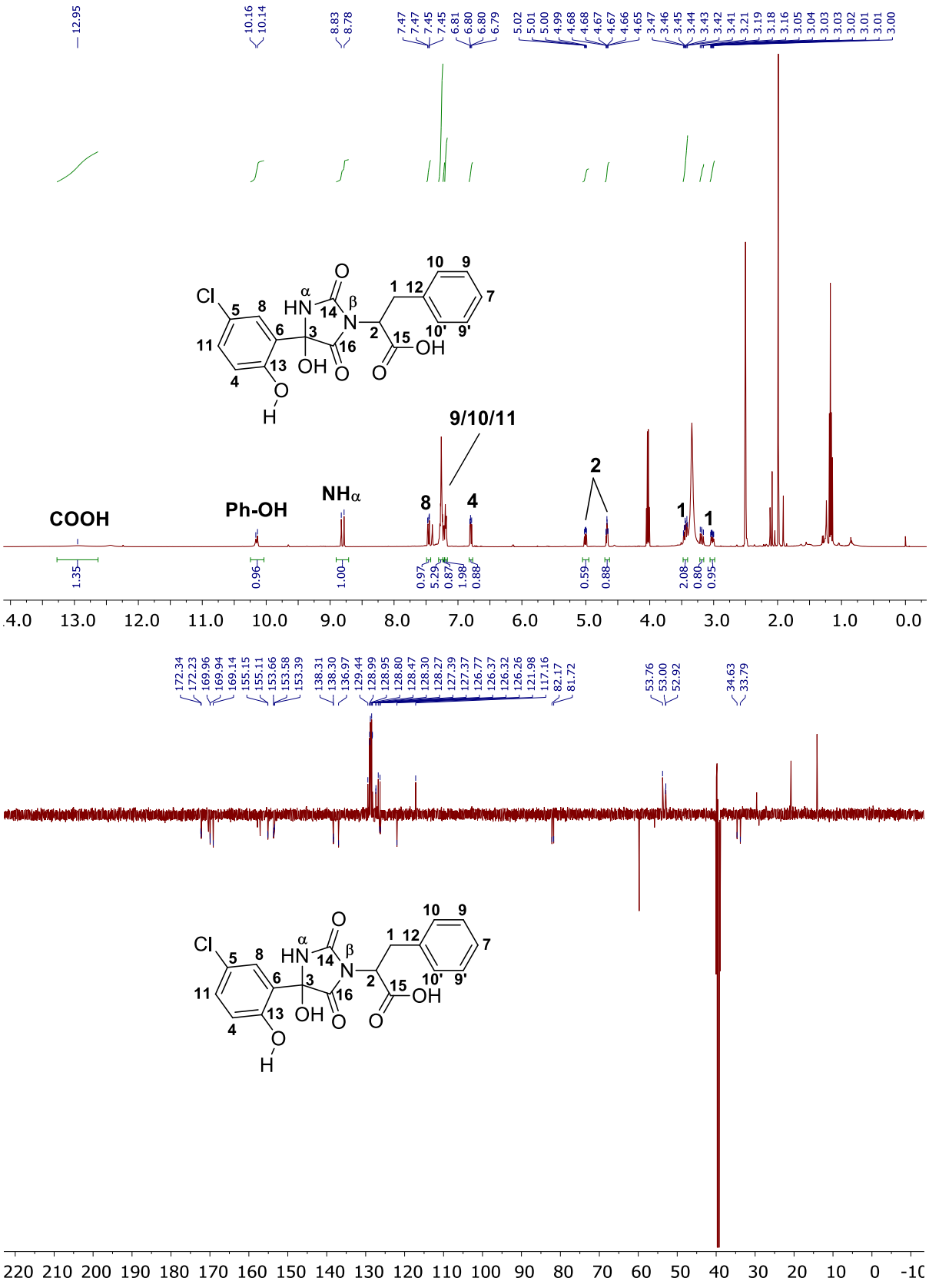


Table S6: 1D and 2D-NMR data of 2-(4-(5-chloro-2-hydroxyphenyl)-4-hydroxy-2,5-dioxoimidazolidin-1-yl)-3-phenylpropanoic acid (9A) in DMSO-d$_6$, at 298 K and 499 MHz for ^{1}H and 126 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C [ppm], mult.	HMBC (^{x}J)
1	3.02 (½ H, dd, *J* = 14.2, 6.6 Hz)/3.18 (½ H dd, *J* = 14.2, 10.8 Hz) + 3.44 (1H, dd, *J* = 14.2, 5.6 Hz)	33.79+34.63, CH_2	C1→H2(^{2}J), H10(^{3}J)
2	4.67 (½ H, m) + 5.01 (½ H, dd. *J* = 10.8, 5.2 Hz)	52.92/53.00+53.76, CH	C2→H1(^{2}J)
3	-	81.72+82.17, C_q	C3→H4(^{4}J), H8(^{3}J), NH_α(^{2}J)
4	6.80 (1H, d, *J* = 8.6 Hz)	117.2, CH_{arom}	-
5	-	122.0, C_q	C5→H4(^{3}J), H8(^{2}J), H11(^{2}J)
6	-	126.26+126.37, C_q	C6→H4(^{3}J), Ph-OH(^{3}J)
7	7.20 (1H, m)	126.32, CH_{arom}	C7→H10(^{3}J)
8	7.46 (1H, d, *J* = 2.7 Hz)	126.8+127.37/127.39, CH_{arom}	C8→H11(^{3}J)
9	7.19 (1H, m) + 7.26 (1H, m)	128.27/128.30+128.47, 2xCH_{arom}	C9→H9(^{3}J)
10	7.19 (1H, m) + 7.25 (1H. m)	128.8+128.95/128.99, 2xCH_{arom}	C10→H1(^{3}J), H7(^{3}J), H10(^{3}J)
11	7.23 (1H, m)	129.4, CH_{arom}	C11→H8(^{3}J)
12	-	137.0+138.30/138.31, C_q	C12→H1(^{2}J), H2(^{3}J), H9(^{3}J)
13	-	153.39+153.58/153.66, C_q	C13→H4(^{3}J), H8(^{3}J), H11(^{3}J)
14	-	155.11+155.15, C_q	C14→H2(^{3}J), NH_α(^{2}J)
15	-	169.14+169.94/169.96, C_q	C15→H1(^{3}J), H2(^{2}J)
16	-	172.23+172.34, C_q	C16→H2(^{3}J), NH_α(^{3}J)
NH_α	8.78+8.83 (1H, s)	-	-
N_β	-	-	-
Ph-OH	10.14 +10.16(1H, br)	-	-
COOH	12.95 (1H, br)	-	-

Chemical Formula: $C_{18}H_{15}ClN_2O_6$

Molecular Weight: 390.06g/mol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6.80
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3.18
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3.01
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3.00
COOH
Ph-OH
NHα
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4
9/10/11
2
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0.87
1.98
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0.80
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10.0
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169.96
169.94
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126.32
126.26
121.98
117.16
82.17
81.72
53.76
53.00
52.92
34.63
33.79
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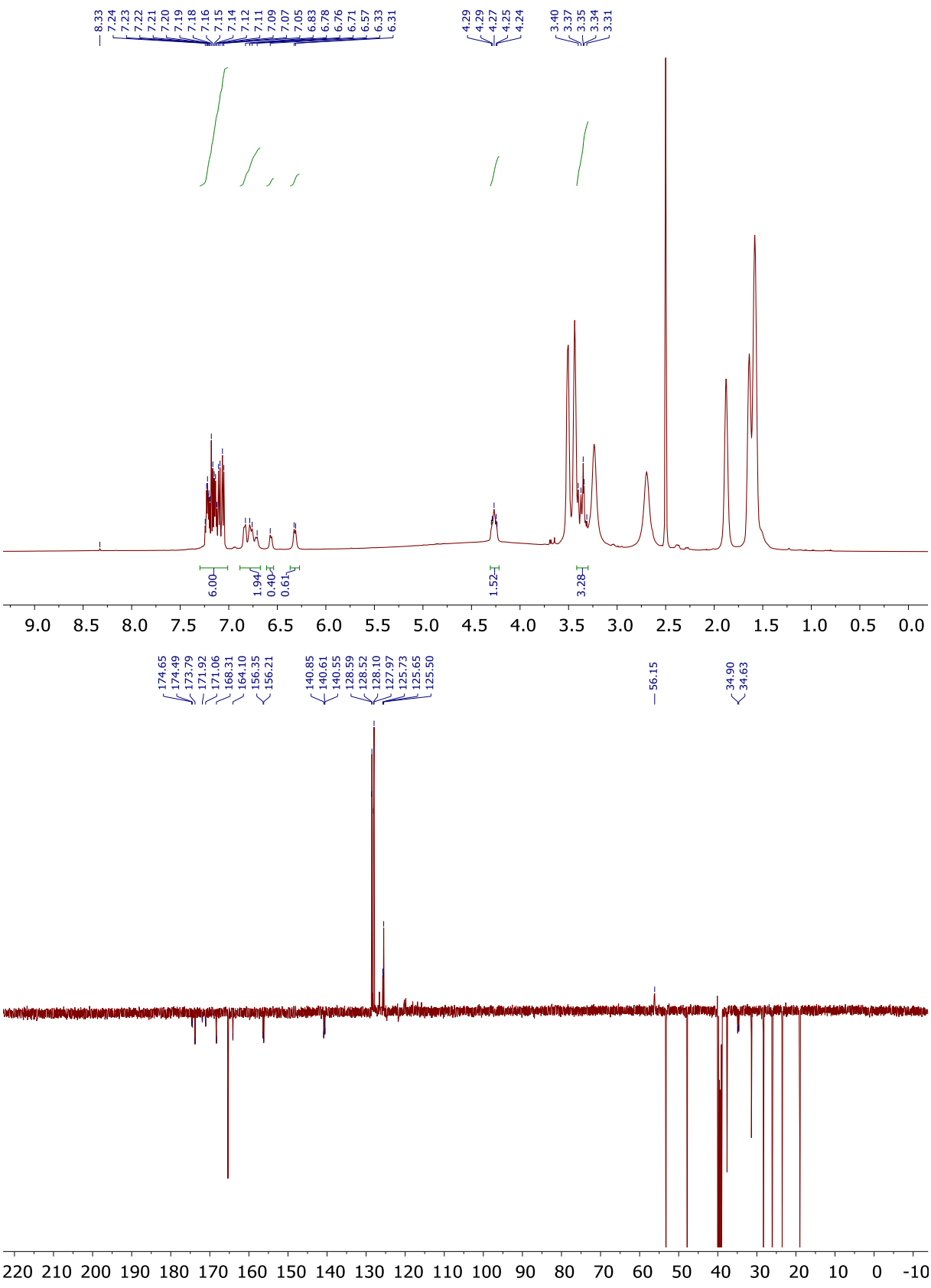
Figure S6: NMR-spectra of **9A**.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7.21
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7.18
7.16
7.15
7.14
7.12
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7.07
7.05
6.83
6.78
6.76
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6.33
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4.29
4.27
4.25
4.24
3.40
3.37
3.35
3.34
3.31
6.00
1.94
0.40
0.61
1.52
3.28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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174.49
173.79
171.92
171.06
168.31
164.10
156.35
156.21
140.85
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140.55
128.59
128.52
128.10
127.97
125.73
125.65
125.50
56.15
34.90
34.63
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Figure S7: NMR-spectra of **5A-DE** before protonation (Contaminated with DBU).

2.3 NMR-spectra of 12

Results from Experiment 8-DE (Product after 1 hour of oxidation)

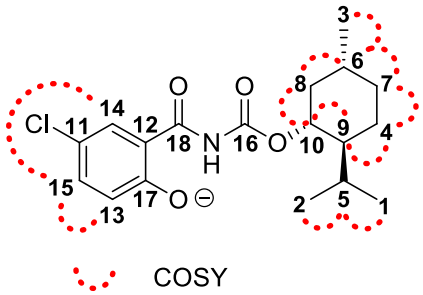

Table S5: 1D and 2D-NMR data of 4-chloro-2-(((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)carbamoyl)phenolate (12) in DMSO-d_6, at 298 K and 500 MHz for ^{1}H and 125 MHz for ^{13}C.

No.	δ_H [ppm], *J* in [Hz]	δ_C, δ_N [ppm], mult.	HMBC (^{x}J)
1	0.75 (3H, d, *J* = 7.0 Hz)	16.3, CH_3	C1→H2(^{3}J), H5(^{2}J)
2	0.87 (3H, m)	20.5, CH_3	C2→H1(^{3}J), H5(^{2}J)
3	0.89 (3H, m)	22.0, CH_3	C3→H8(^{3}J)
4	1.04 (1H, m); 1.62 (1H, m)	23.1, CH_2	C4→H9(^{2}J)
5	1.90 (1H, m)	25.8, CH	C5→H1(^{2}J), H2(^{2}J), H10(^{3}J)
6	1.45 (1H, m)	30.9, CH	C6→H3(^{2}J), H8(^{2}J)
7	0.84 (1H, m); 1.65 (1H, m)	33.8, CH_2	C7→H3(^{3}J), H8(^{3}J)
8	0.98 (1H, m); 1.92 (1H, m)	40.9, CH_2	C8→H3(^{3}J), H10(^{2}J)
9	1.34 (1H, m)	46.6, CH	C9→H1(^{3}J), H2(^{3}J), H4(^{2}J), H5(^{2}J), H7(^{3}J), H8(^{3}J), H10(^{2}J)
10	4.50 (1H, td, *J* = 10.9, 4.3 Hz)	72.9, CH	C10→H4(^{3}J), H8(^{2}J), H9(^{2}J)
11	-	112.5, C_q	C11→H13(^{3}J), H14(^{2}J), H15(^{2}J)
12	-	117.6, C_q	C12→H13(^{3}J)
13	6.34 (1H, d, *J* = 8.9 Hz)	124.0, CH_{arom}	-
14	7.50 (1H, d, *J* = 3.1 Hz)	128.2, CH_{arom}	C14→H15(^{3}J)
15	6.92 (1H, dd, *J* = 9.0, 3.1 Hz)	132.5, CH_{arom}	C15→H14(^{3}J)
16	-	151.8, C_q	C16→H10(^{3}J)
17	-	165.9, C_q	C17→H13(^{2}J), H14(^{3}J)
18	-	170.8, C_q	C18→H13(^{4}J), H14(^{3}J), H15(^{5}J)
NH	15.91 (1H, s)	139.9, NH	-

Chemical Formula: $C_{18}H_{23}ClNO_4^-$

Molecular Weight: 352.83 g/mol

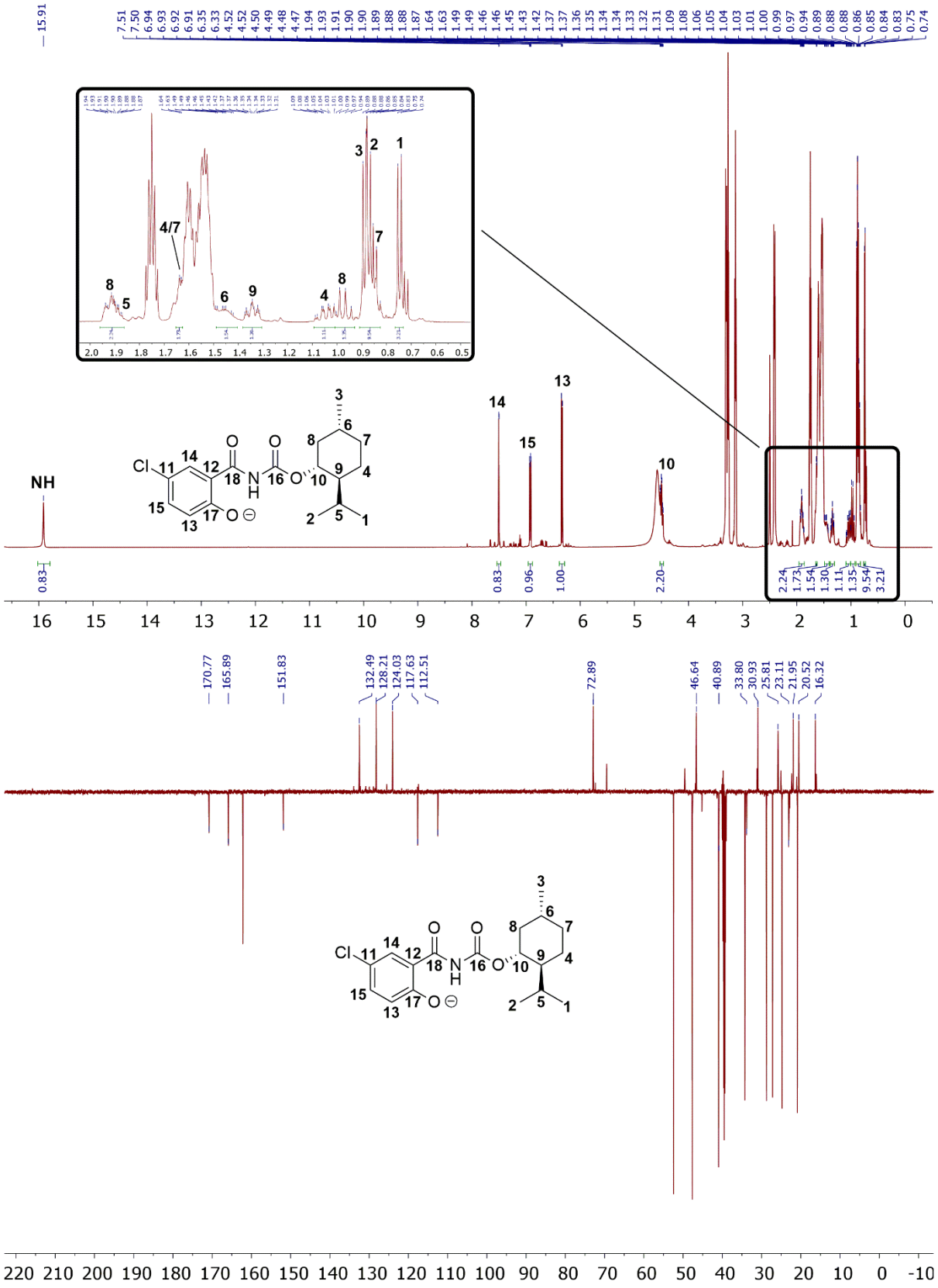

Figure S8: NMR-spectra of **12** (Contaminated with DBU).