Supplementary Information

Synthesis of α,ω-polyfluorinated amino acid derivatives and δ,δ-difluoronorvaline

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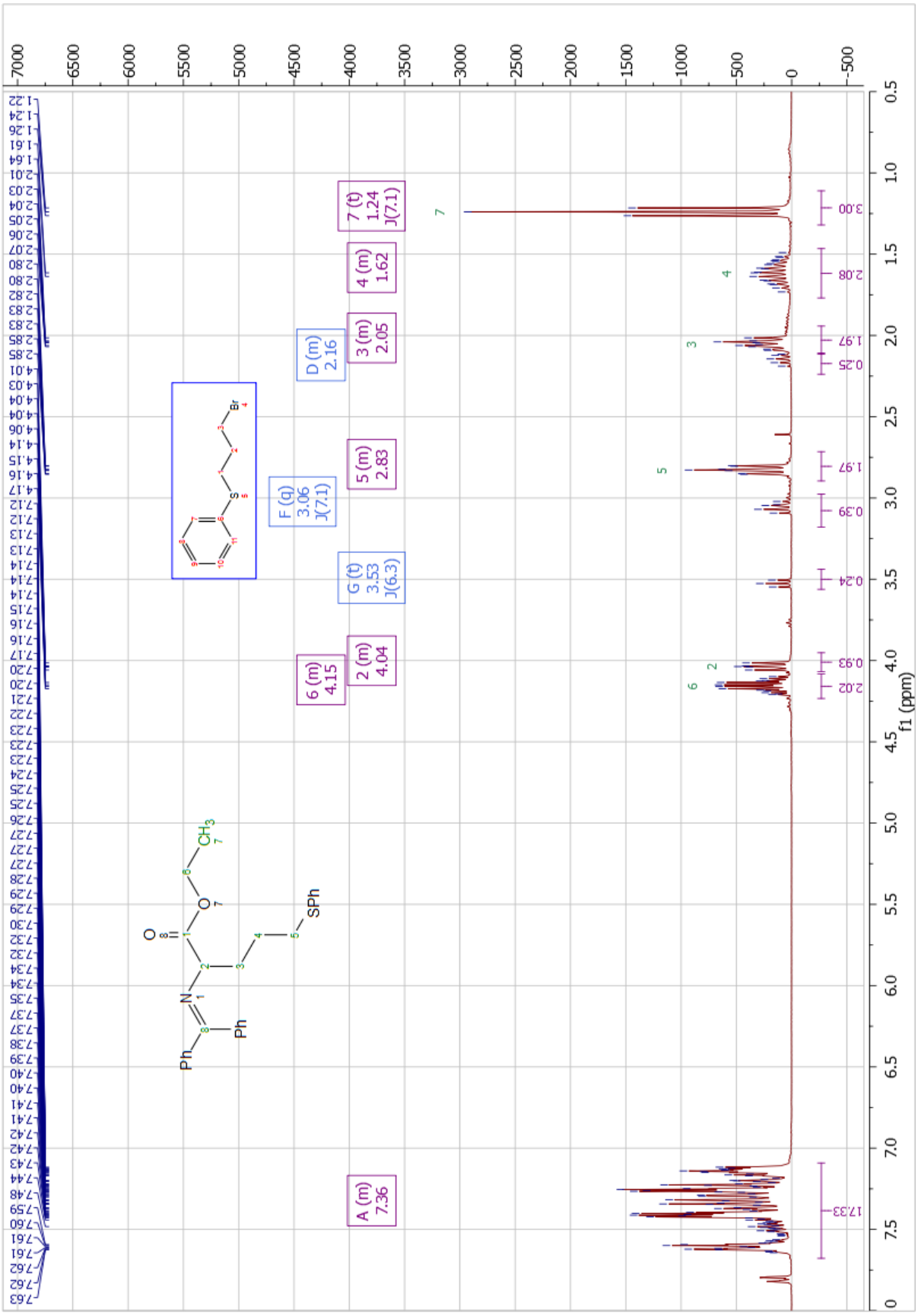
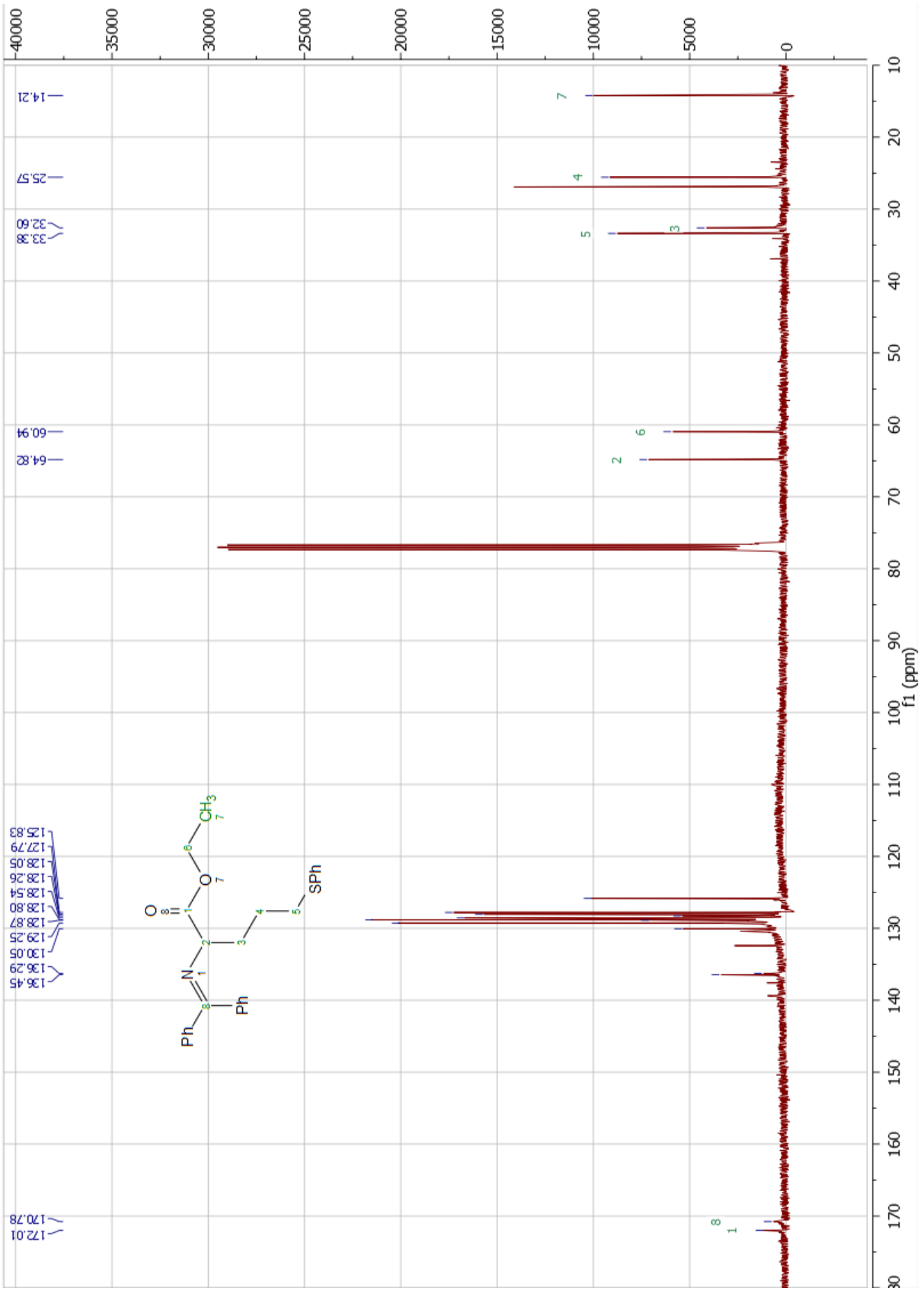
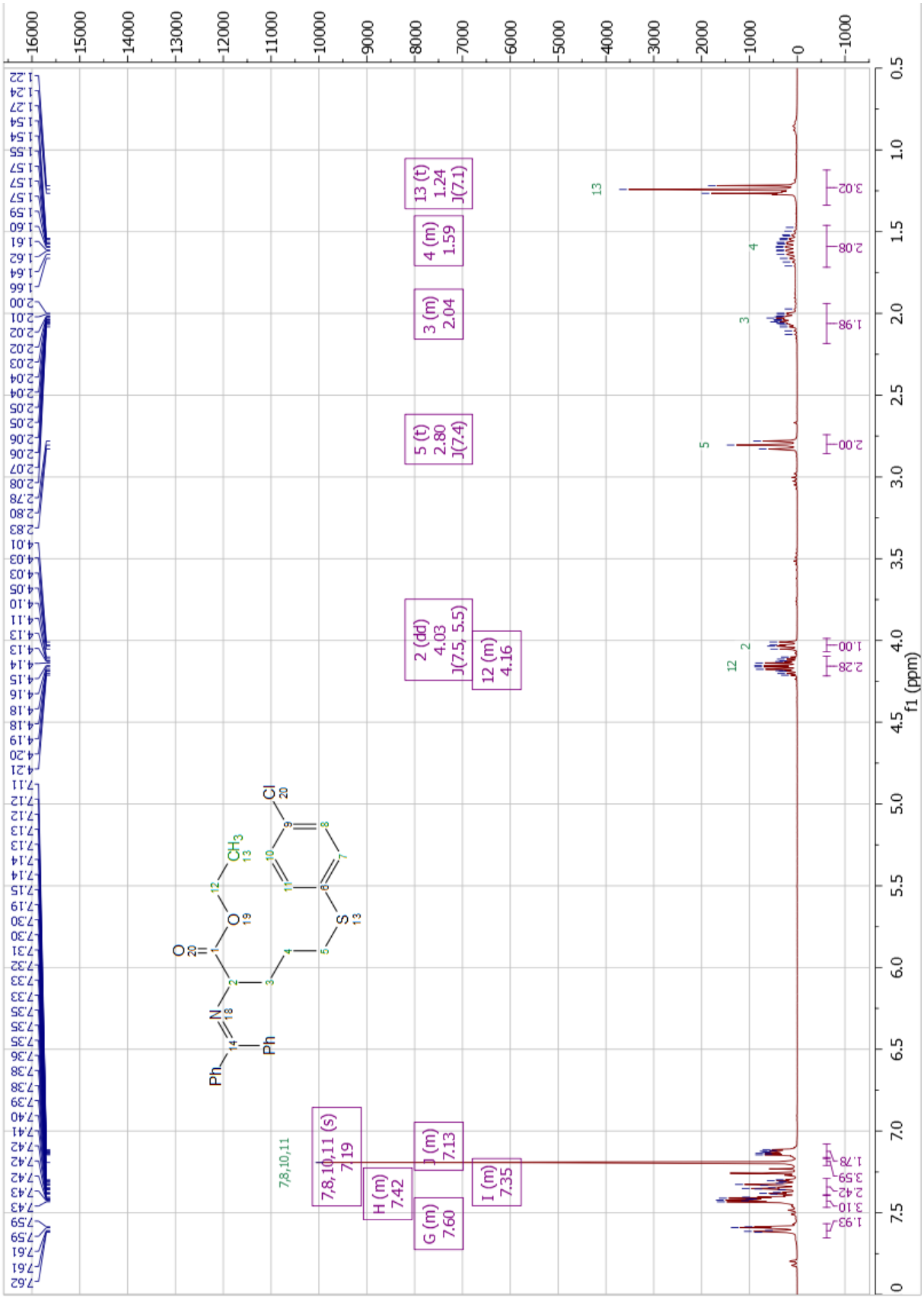
1. Ethyl 5-phenylthio-2-(diphenylmethylene)aminopentanoate (5a)

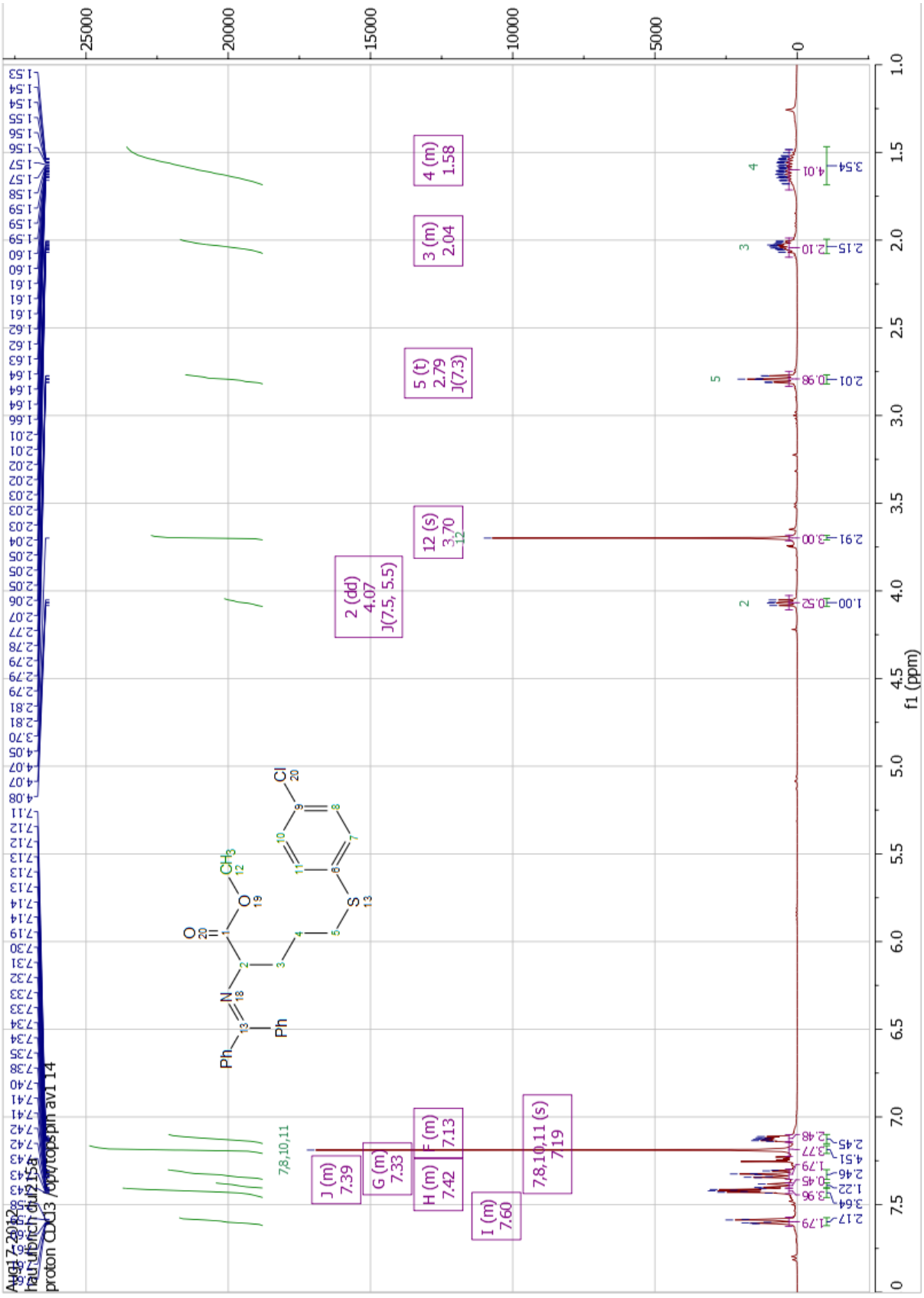


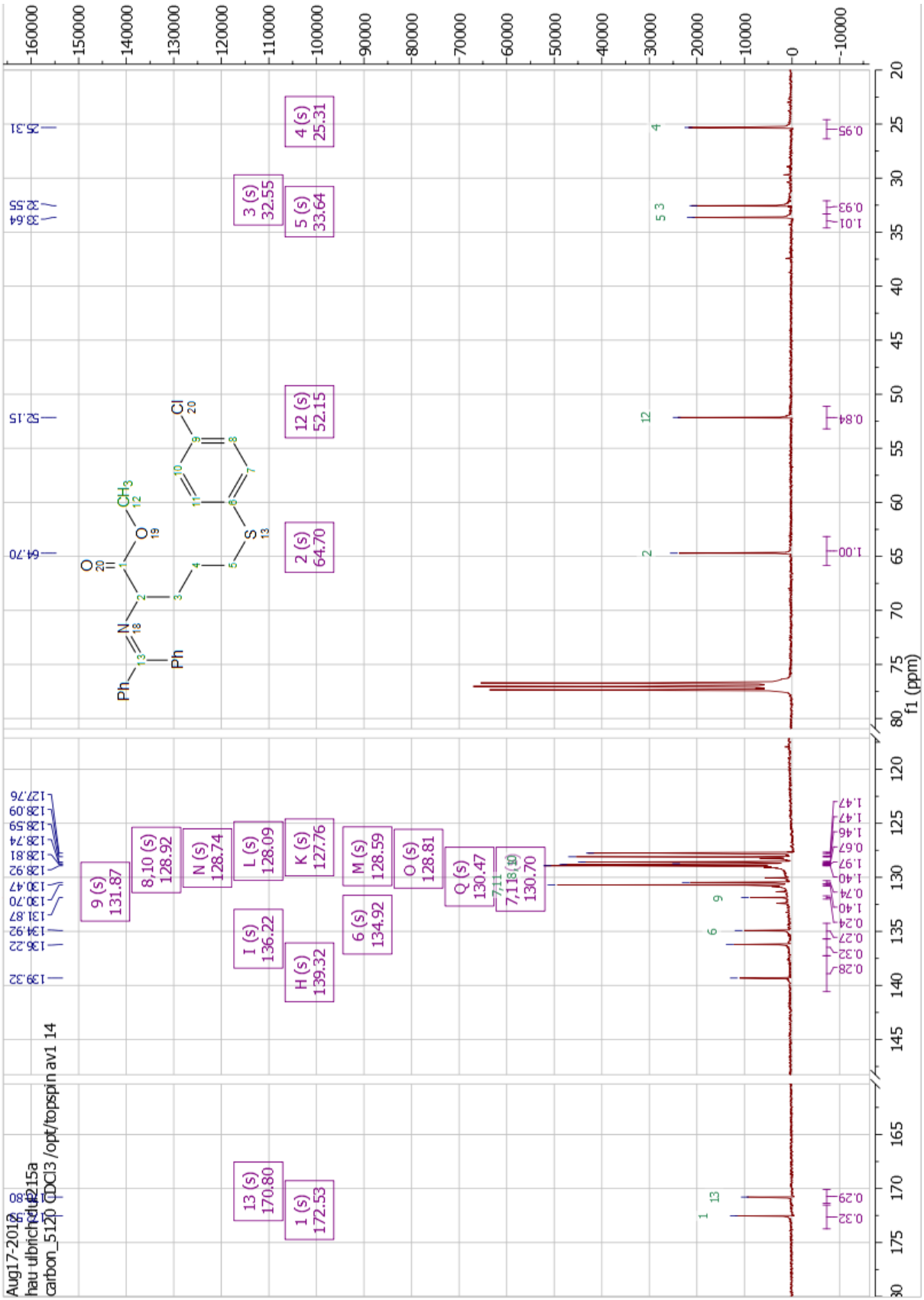

14.21
25.57
32.60
33.38
60.94
64.82
125.83
127.79
128.05
128.26
128.54
128.80
128.87
129.25
130.05
136.29
136.45
170.78
172.01
Ph
N
Ph
O
O
CH3
SPh
f1 (ppm)

2. Ethyl 5-(4-chlorophenyl)thio-2-(diphenylmethylene)aminopentanoate (5b)

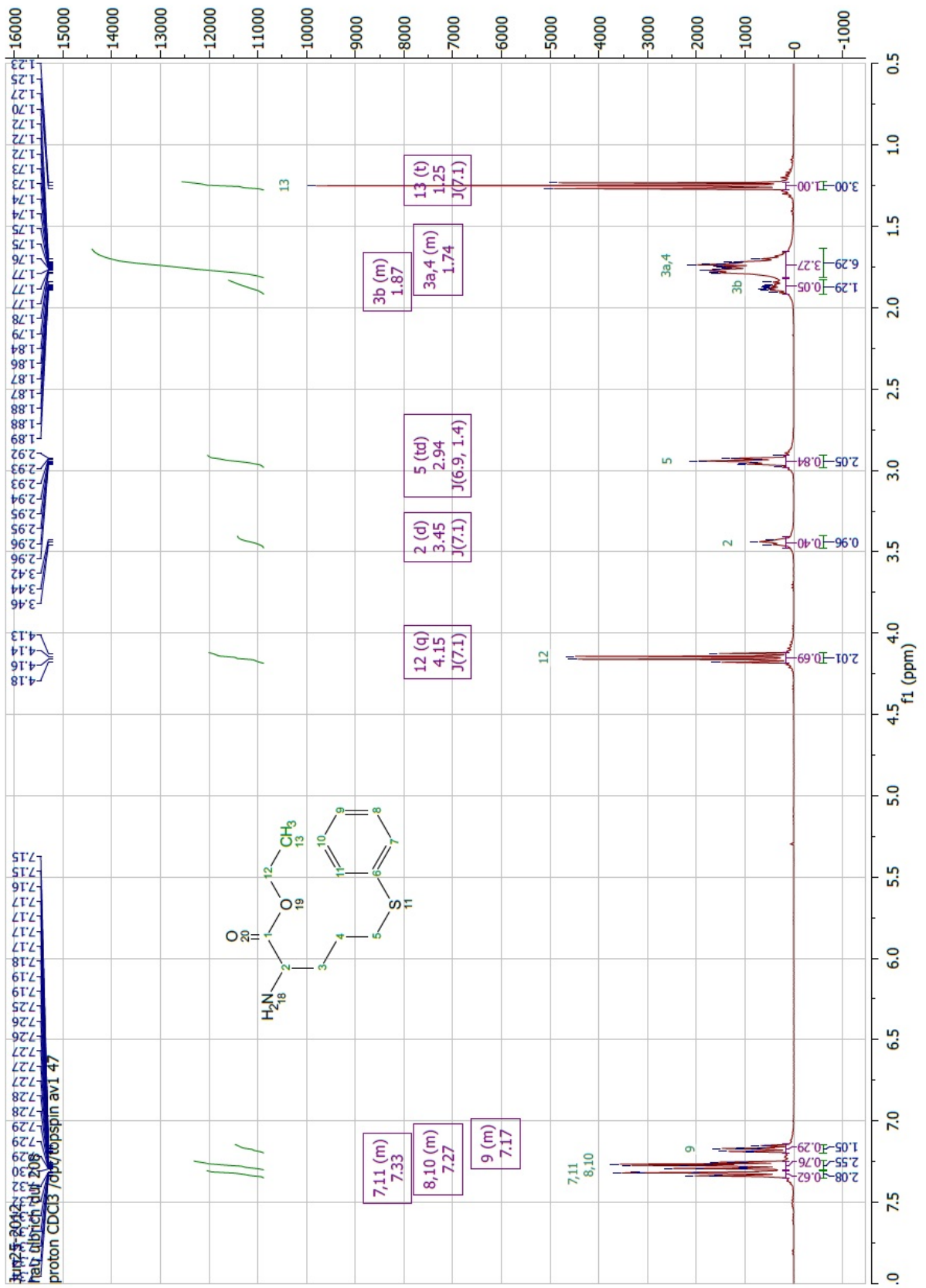


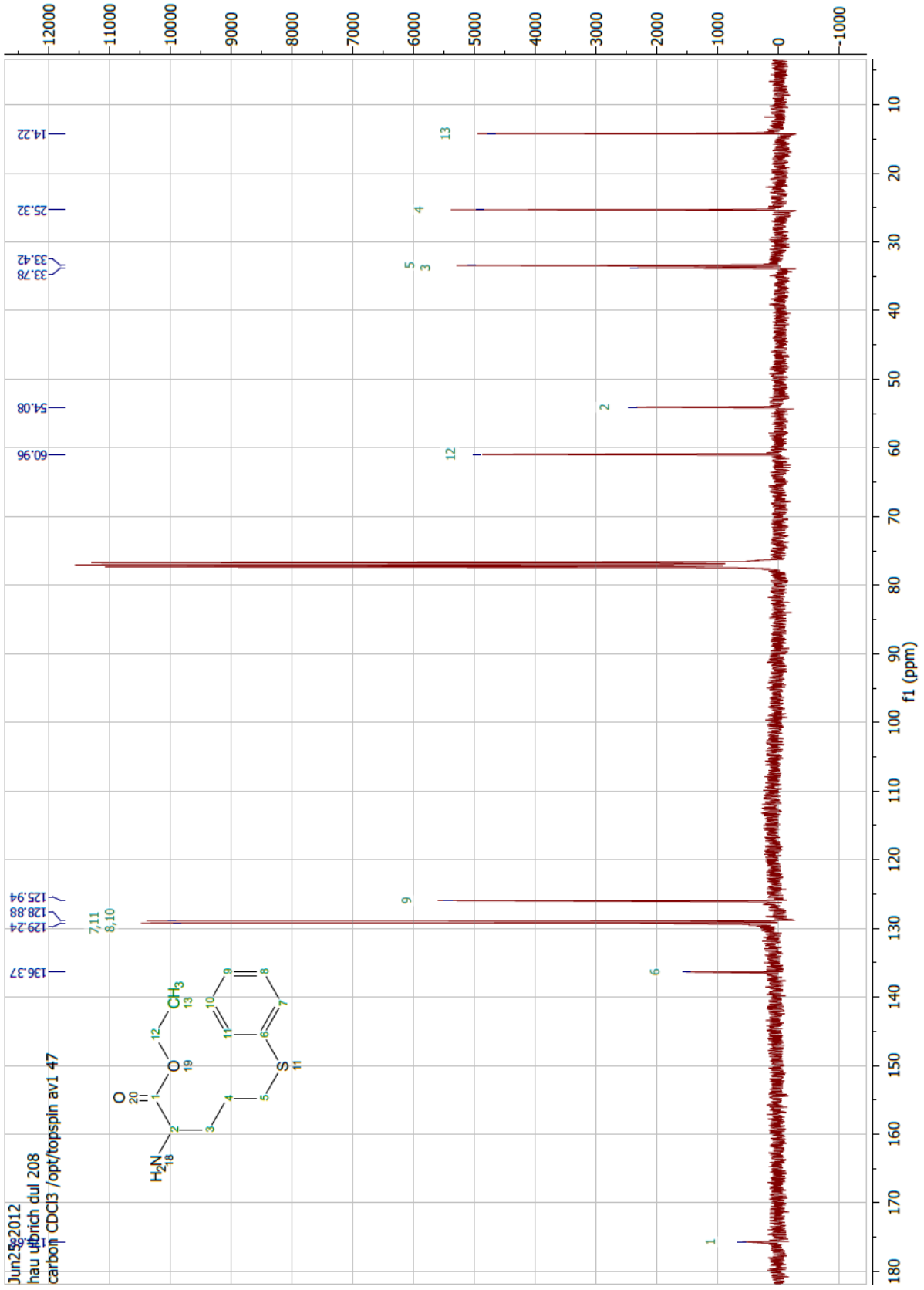
3. Methyl 5-(4-chlorophenyl)thio-2-(diphenylmethylene)aminopentanoate (6b)



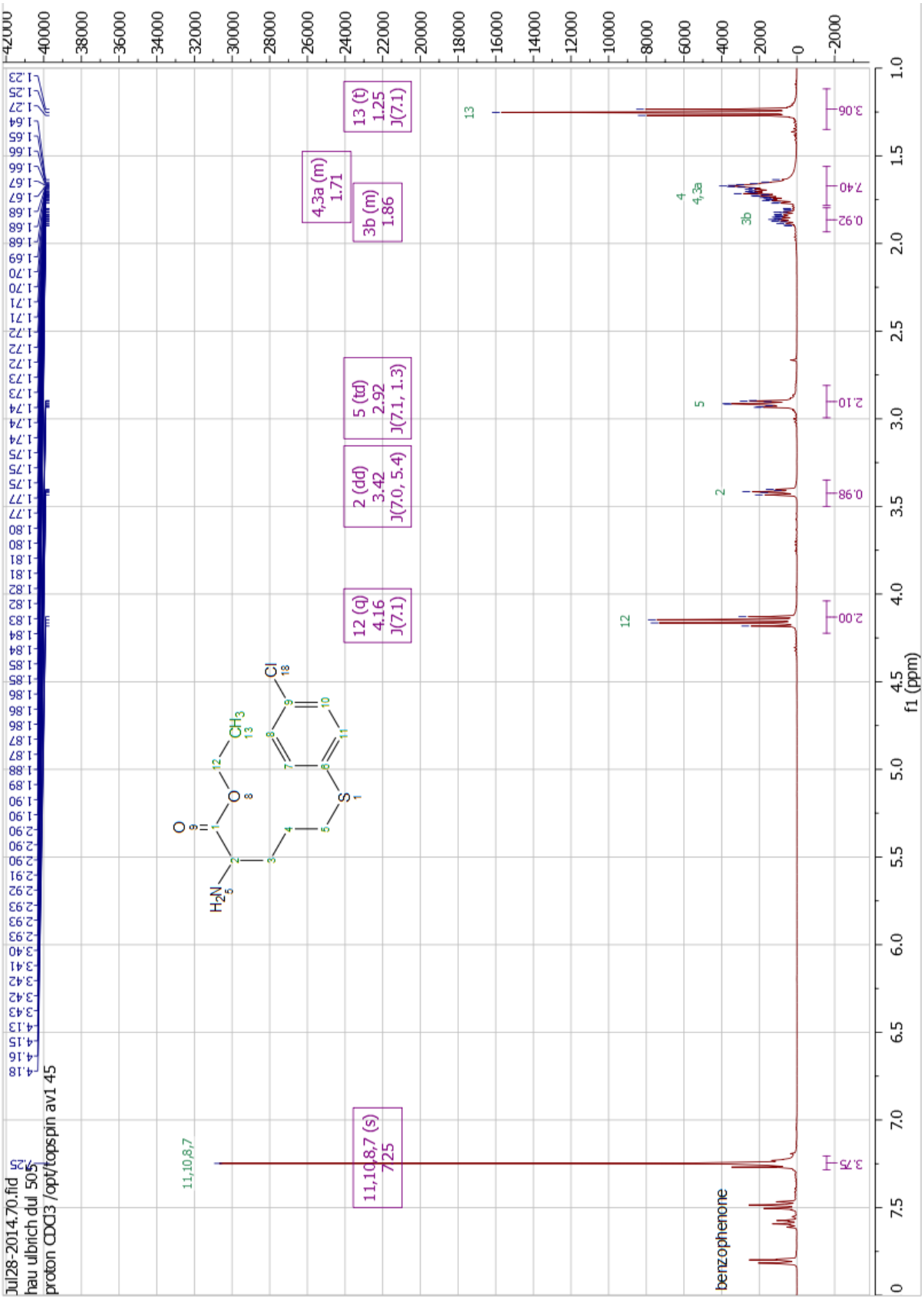

Aug17-2018
hau ulbrich dur215a
carbon_512 CDCl3 /opt/topspin av1 14
f1 (ppm)
Ph
Ph
N
O
O
CH3
S
Cl
1 (s) 172.53
13 (s) 170.80
H (s) 139.32
I (s) 136.22
6 (s) 134.92
M (s) 128.59
K (s) 127.76
L (s) 128.09
N (s) 128.74
8,10 (s) 128.92
9 (s) 131.87
Q (s) 130.47
7,11 (s) 130.70
O (s) 128.81
2 (s) 64.70
12 (s) 52.15
3 (s) 32.55
5 (s) 33.64
4 (s) 25.31

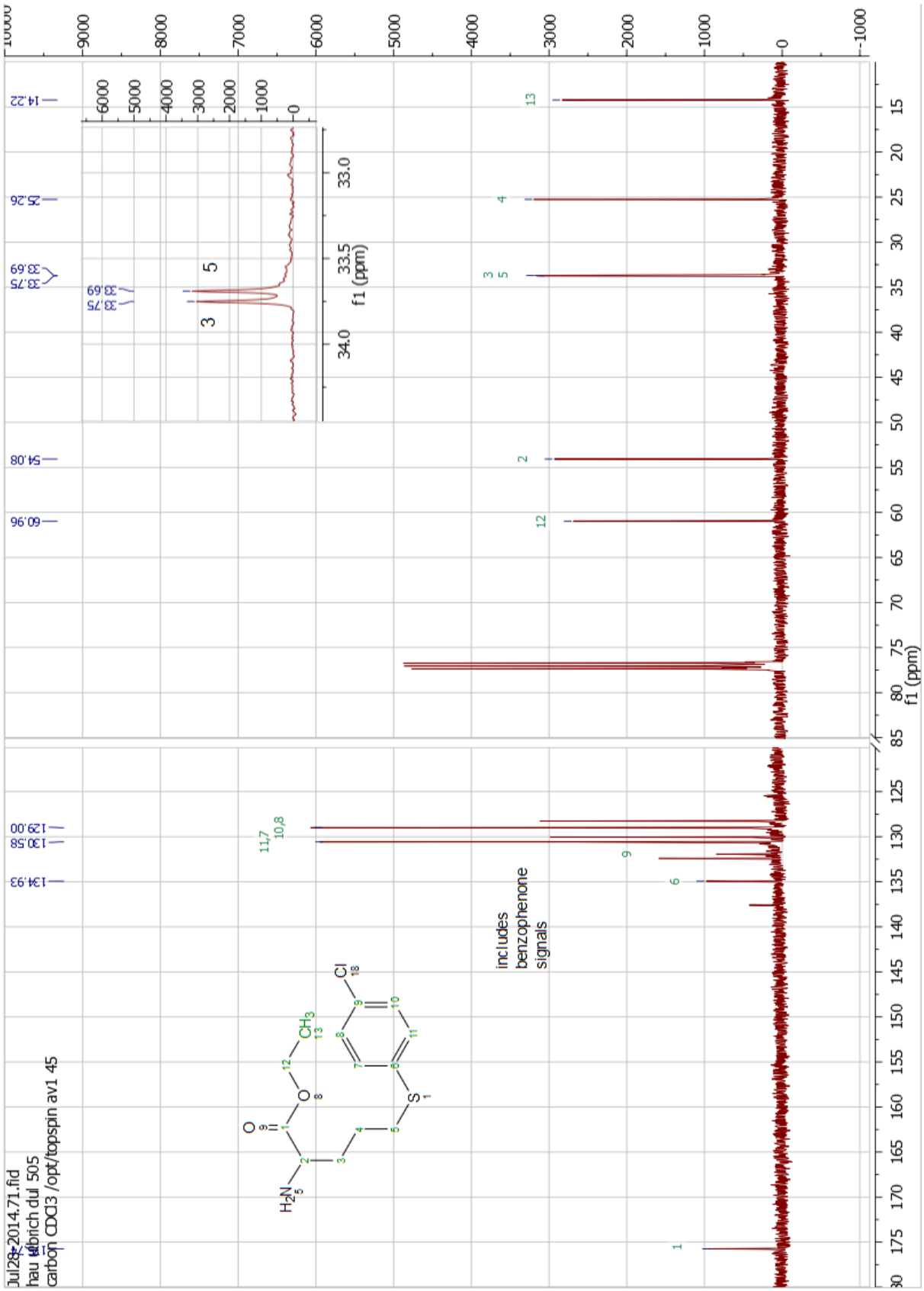
4. Ethyl 2-amino-5-phenylthiopentanoate (7a)



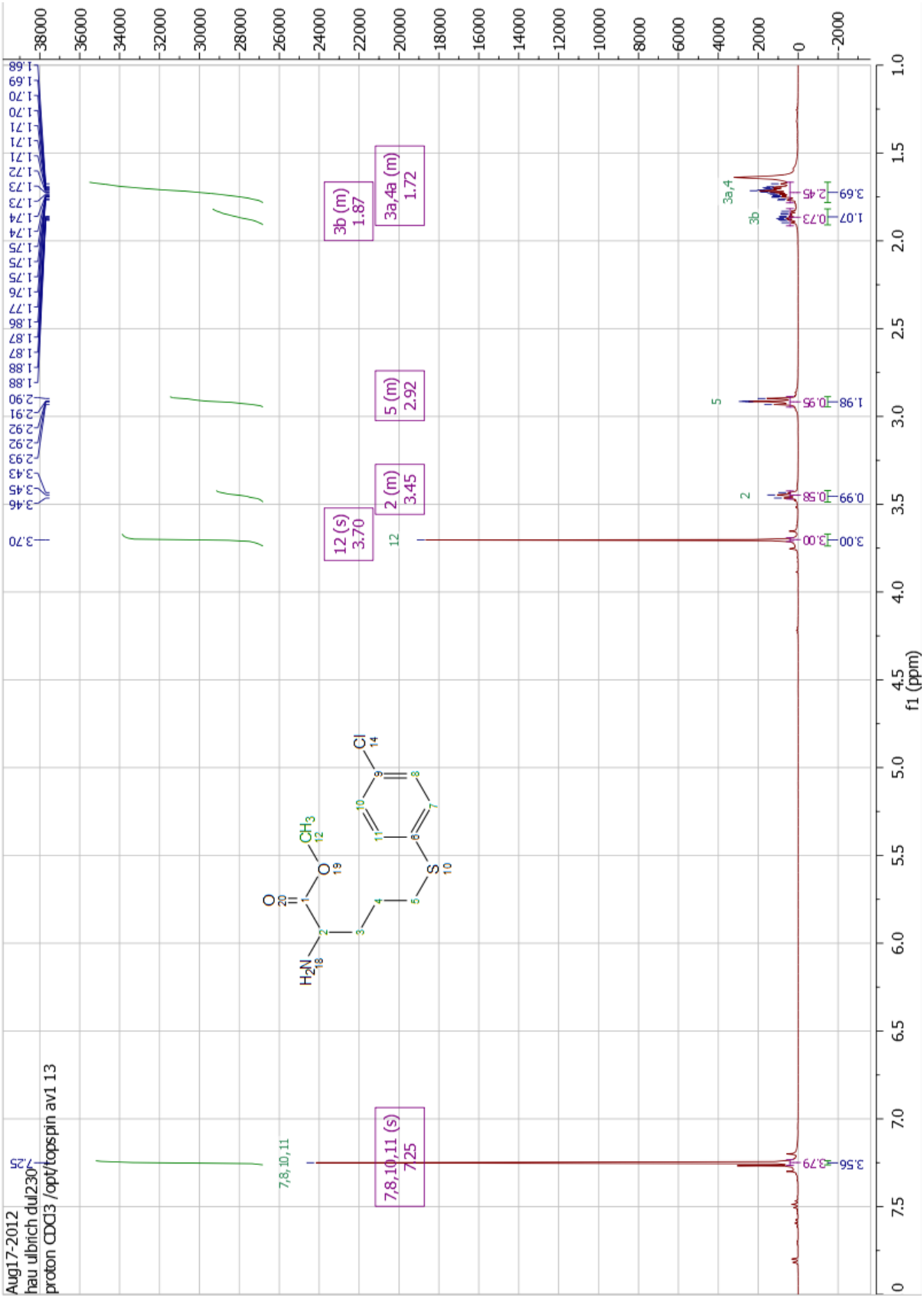

Jun25 2012
hau ulbrich dul 208
carbon CDCl3 /opt/topspin av1 47
f1 (ppm)
14.22
25.32
33.42
33.78
54.08
60.96
125.94
128.88
129.24
136.37
7,11
8,10
1
2
3
4
5
6
9
12
13
O
O
O
S
CH3
H2N

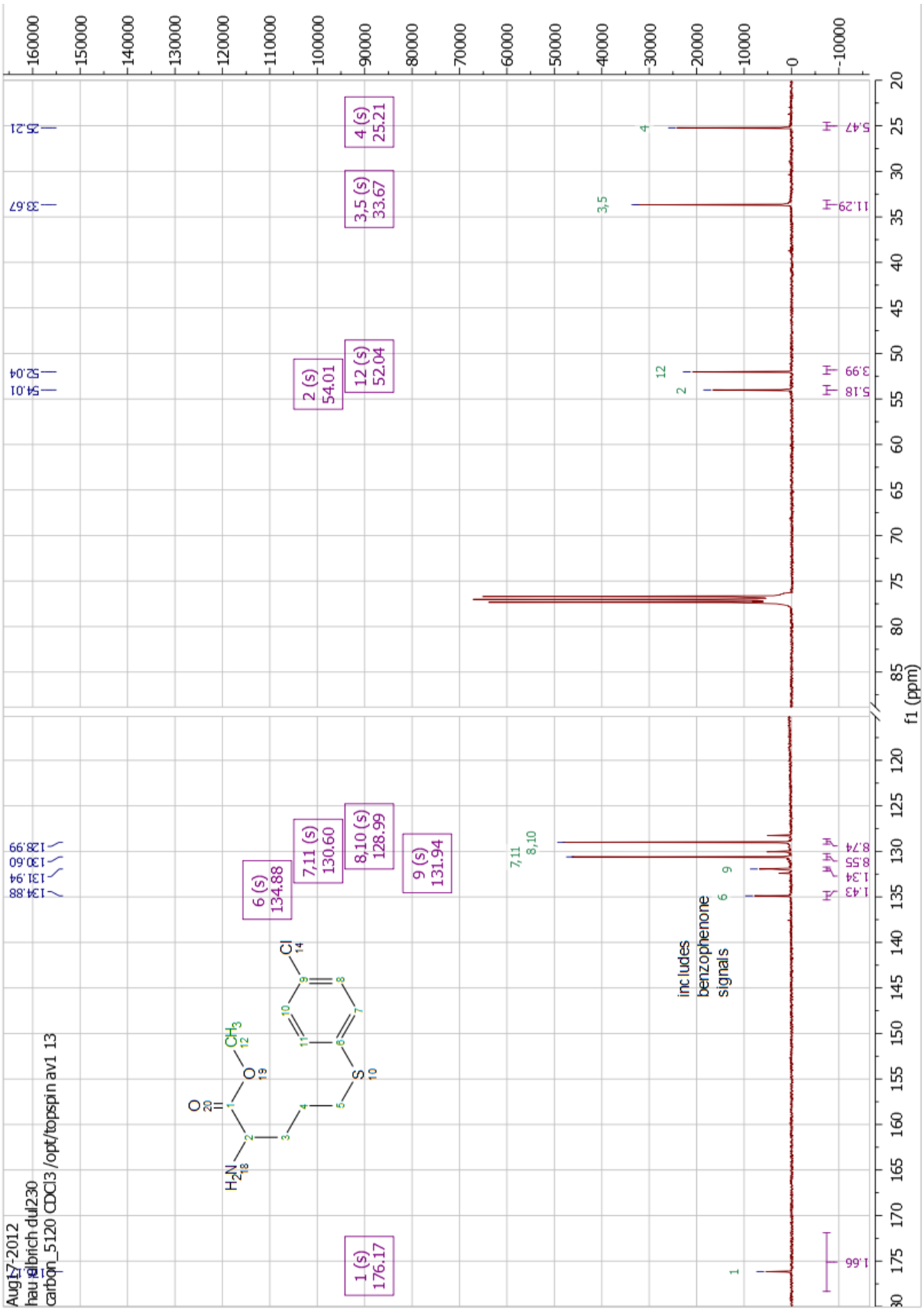
5. Ethyl 2-amino-5-(4-chlorophenyl)thiopentanoate (7b)



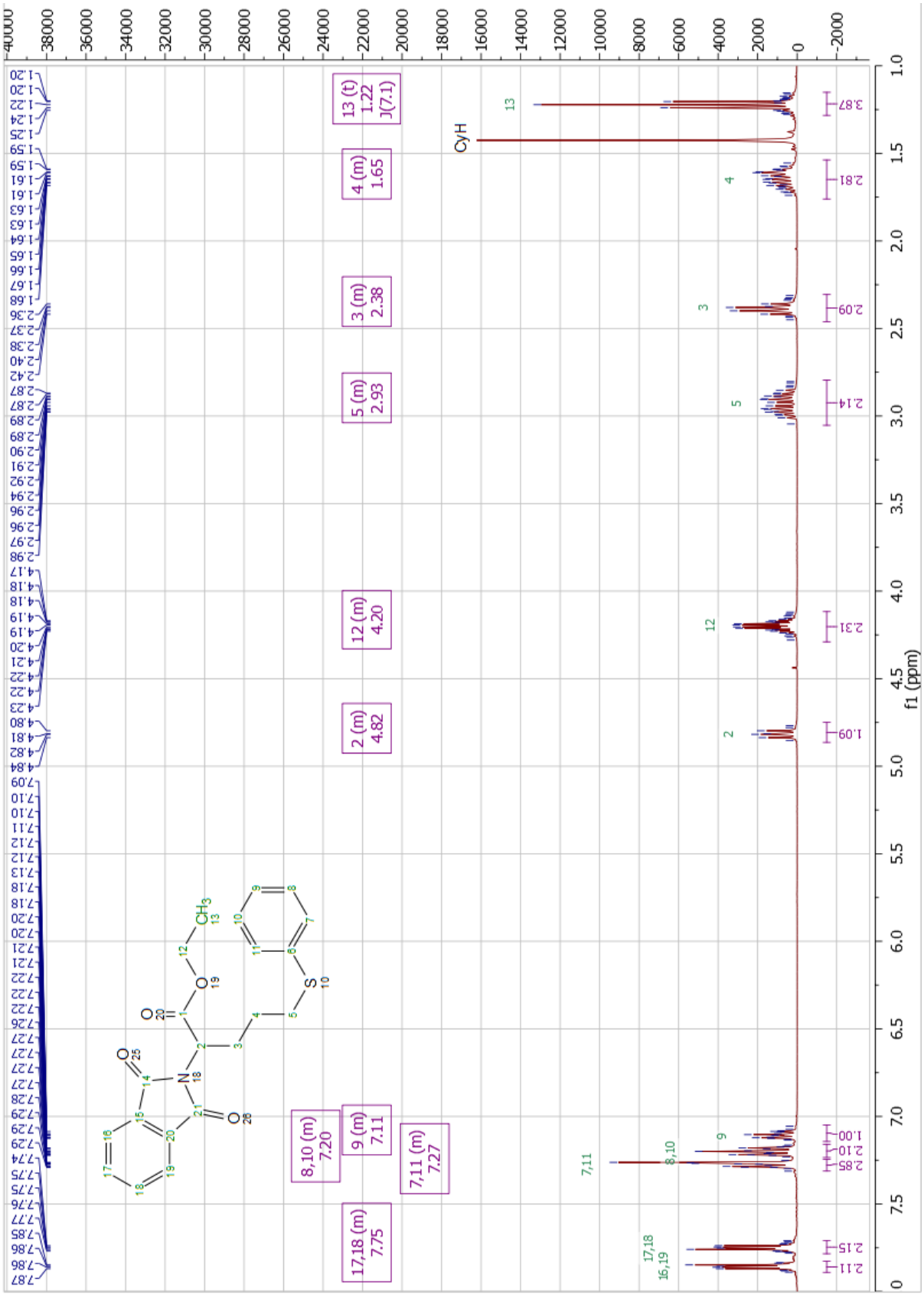

Jul28-2014.71.fid
carbon CDCl3 /opt/topspin av1 45
includes
benzophenone
signals
f1 (ppm)

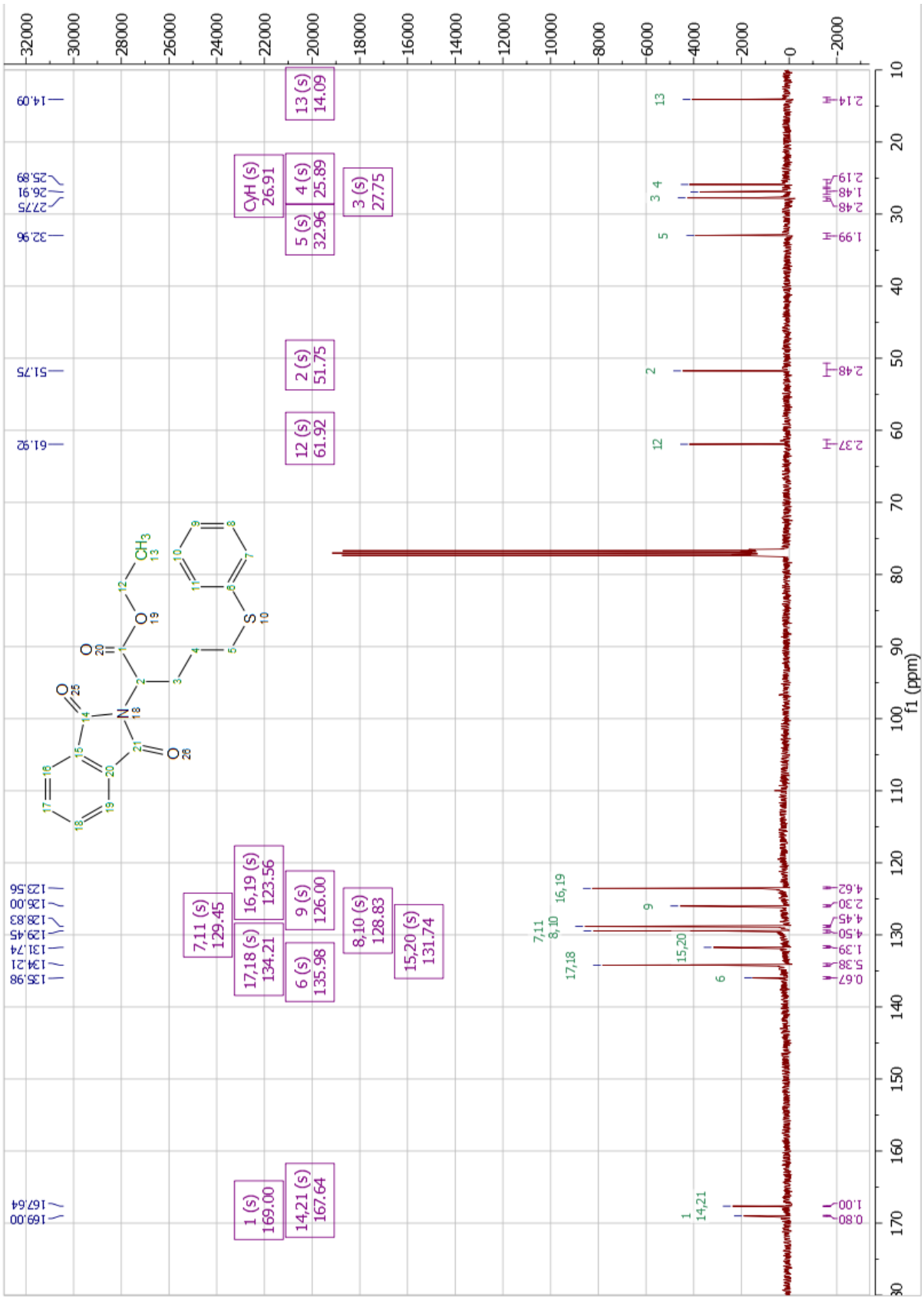
6. Methyl 2-amino-5-(4-chlorophenylthio)pentanoate (8b)



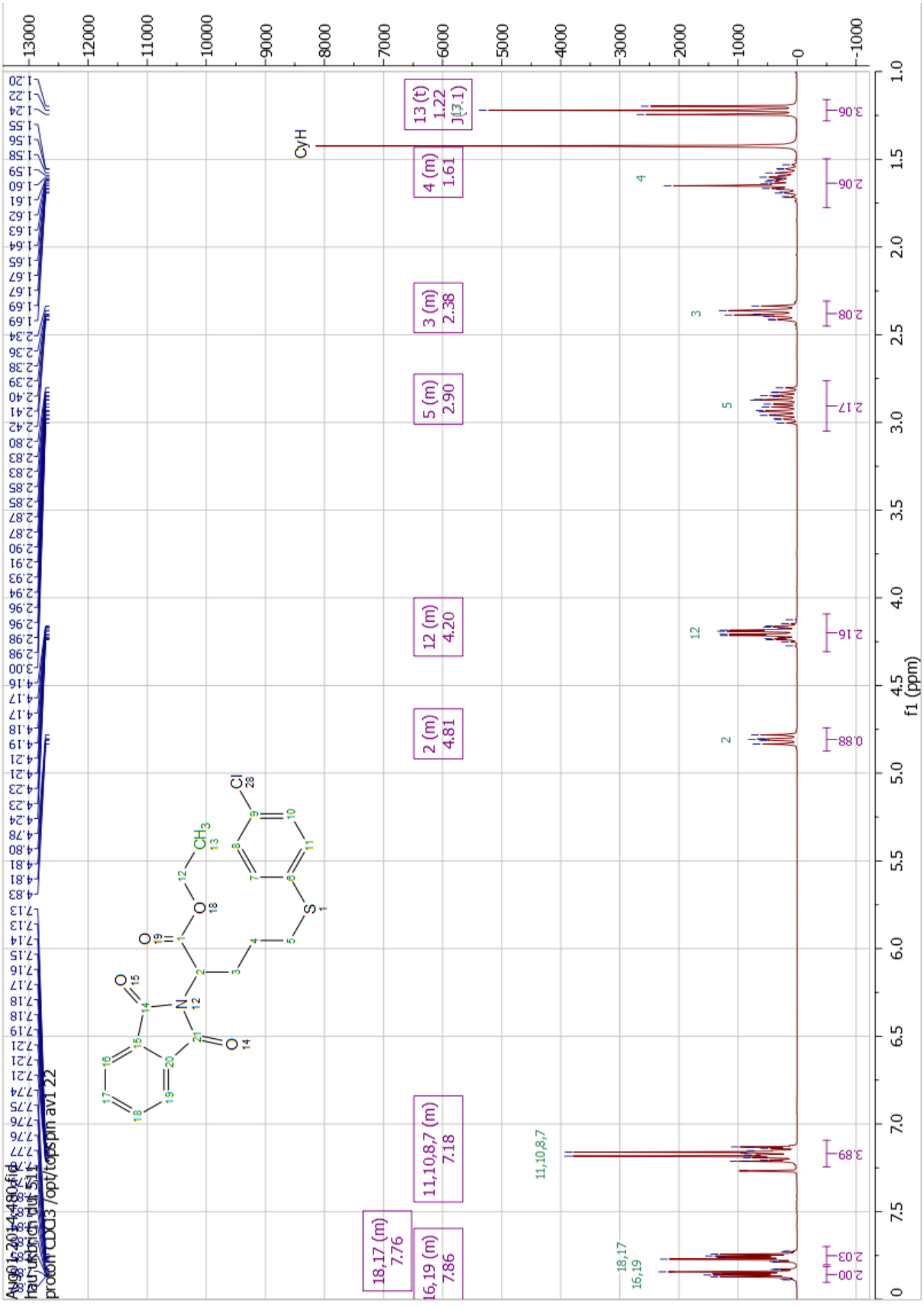

Aug17-2012
hau_albrich dul230
carbon_5120 CDCl3 /opt/topspin av1 13
1 (s) 176.17
6 (s) 134.88
7,11 (s) 130.60
8,10 (s) 128.99
9 (s) 131.94
2 (s) 54.01
12 (s) 52.04
3,5 (s) 33.67
4 (s) 25.21
includes benzophenone signals
f1 (ppm)

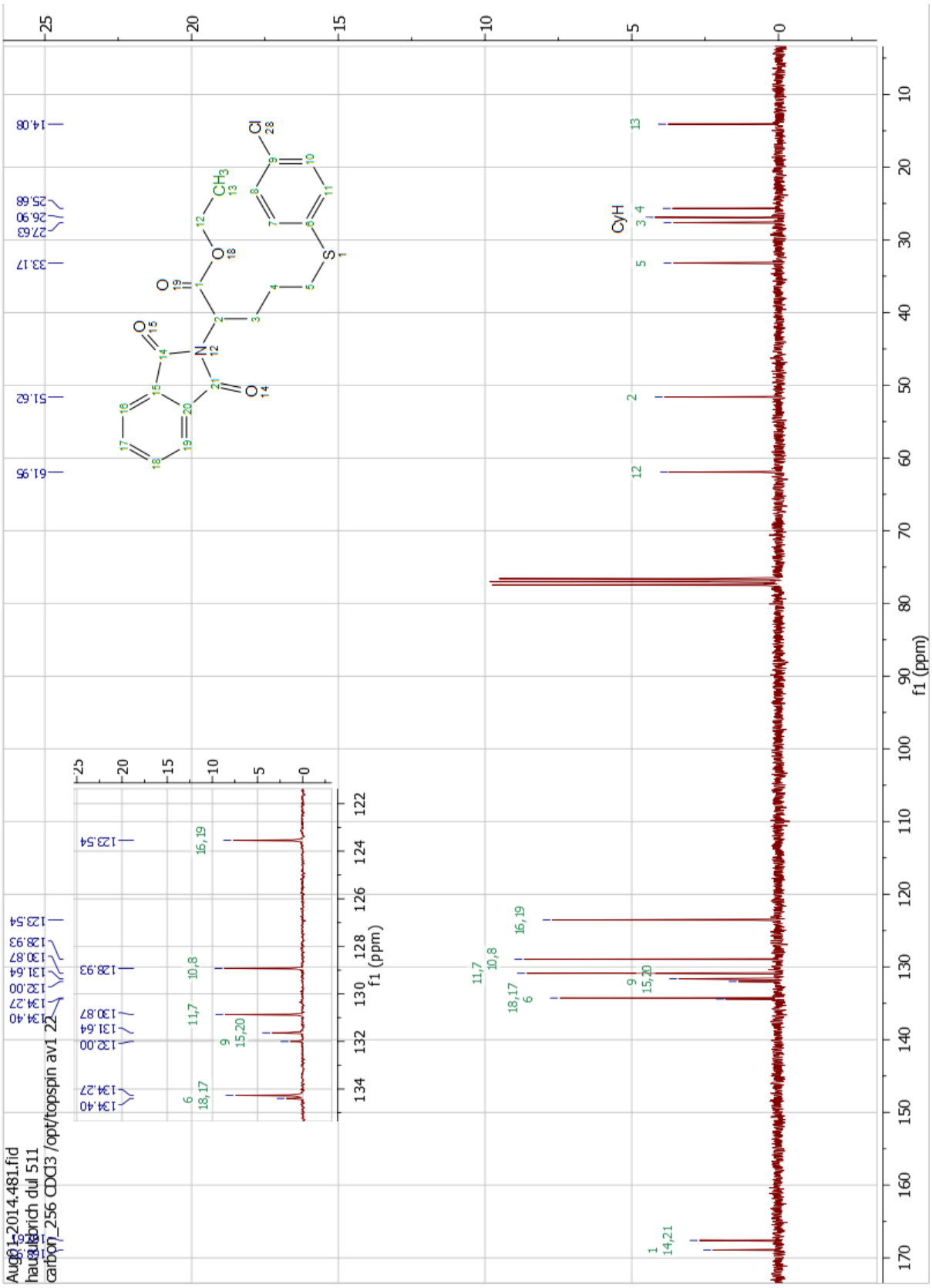
7. Ethyl 5-phenylthio-2-phthalimidopentanoate (9a)



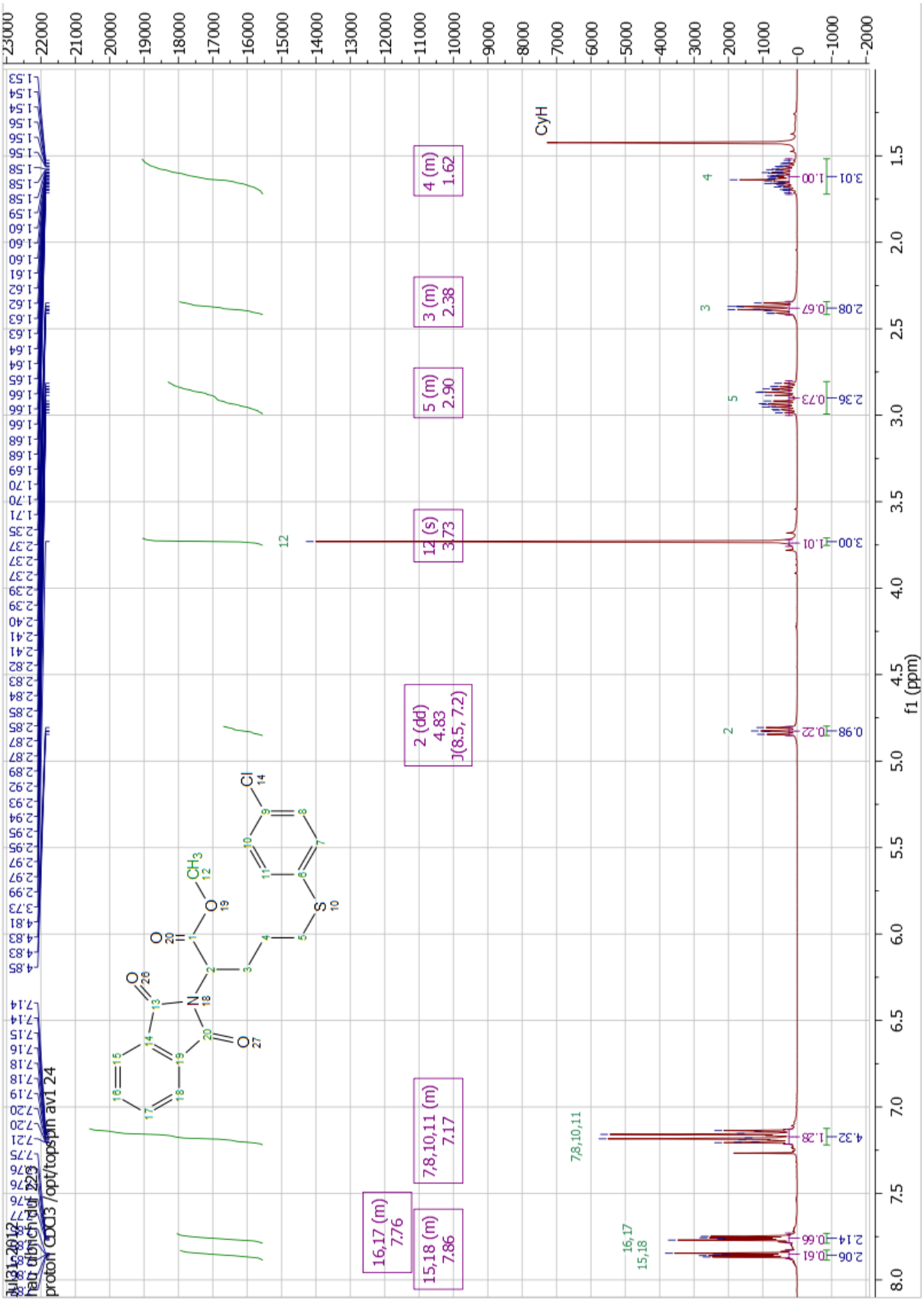

f1 (ppm)
1 (s) 169.00
14,21 (s) 167.64
6 (s) 135.98
17,18 (s) 134.21
9 (s) 126.00
16,19 (s) 123.56
7,11 (s) 129.45
8,10 (s) 128.83
15,20 (s) 131.74
12 (s) 61.92
2 (s) 51.75
5 (s) 32.96
4 (s) 25.89
CyH (s) 26.91
3 (s) 27.75
13 (s) 14.09

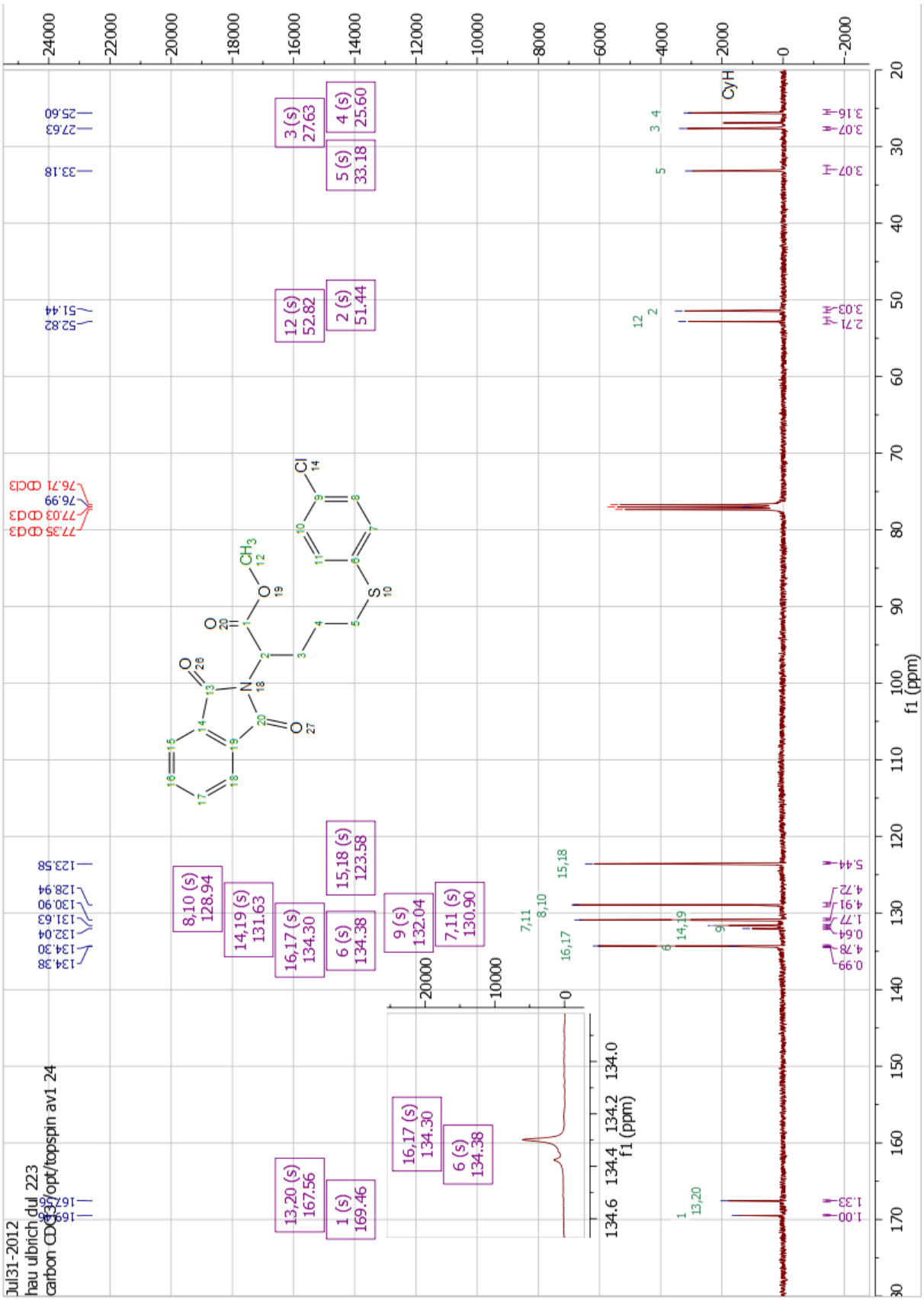
8. Ethyl 5-(4-chlorophenyl)thio-2-phthalimidopentanoate (9b)



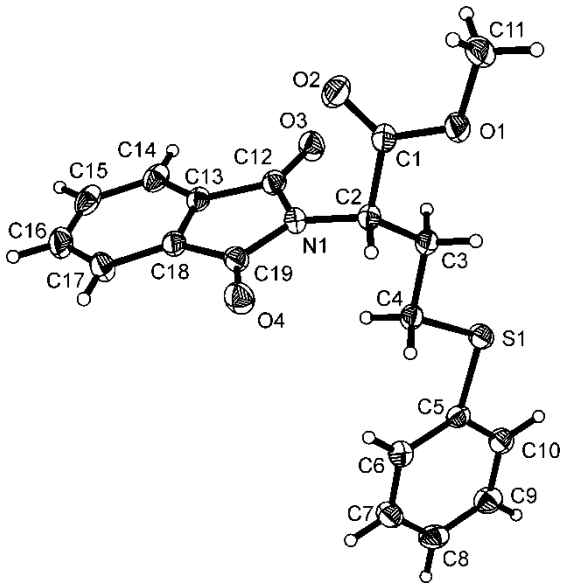

Aug01-2014.481.fid
carbon_256 CDCl3 /opt/topspin av1 22
f1 (ppm)
CyH

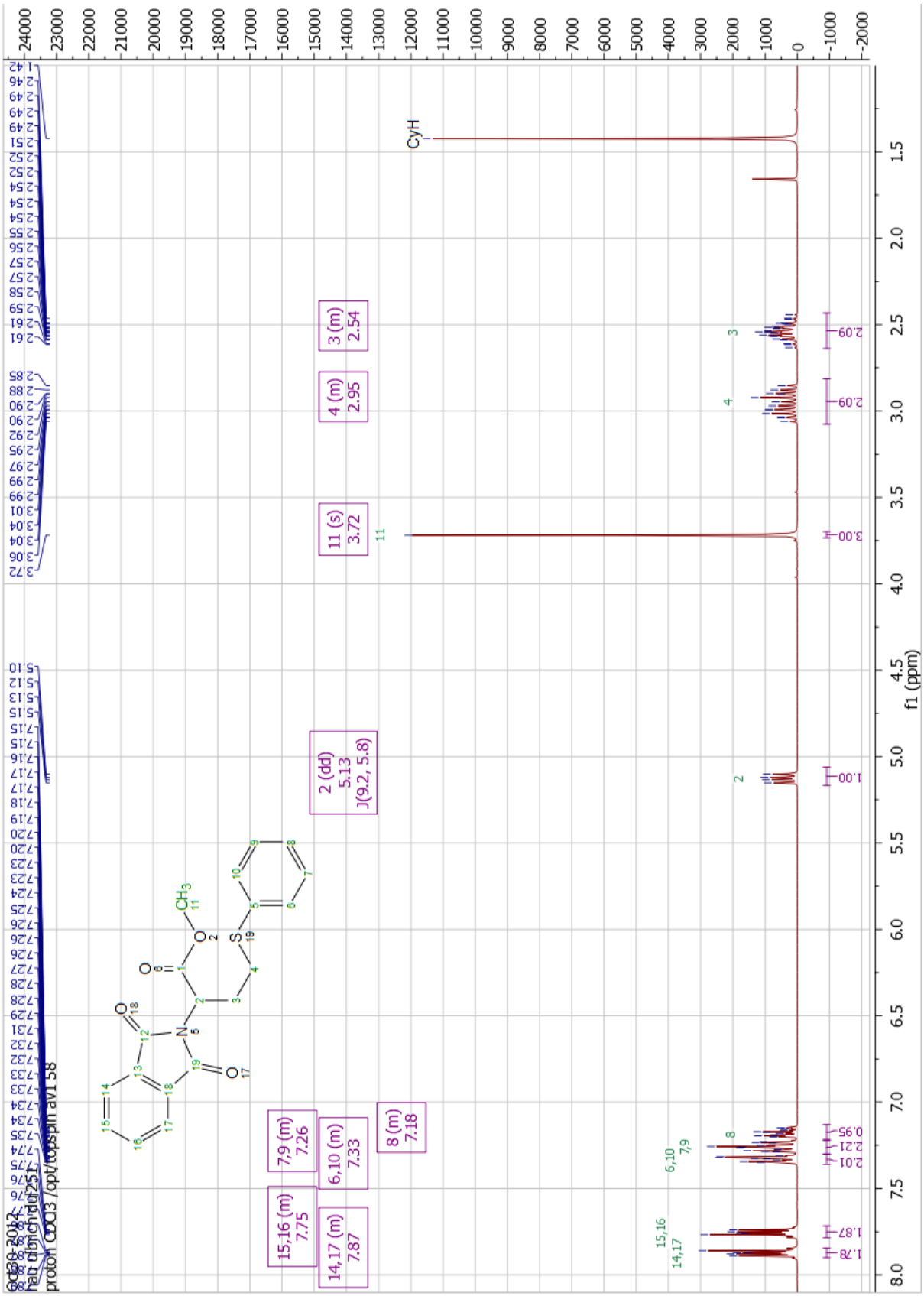
9. Methyl 5-(4-chlorophenyl)thio-2-phthalimidopentanoate (10b)

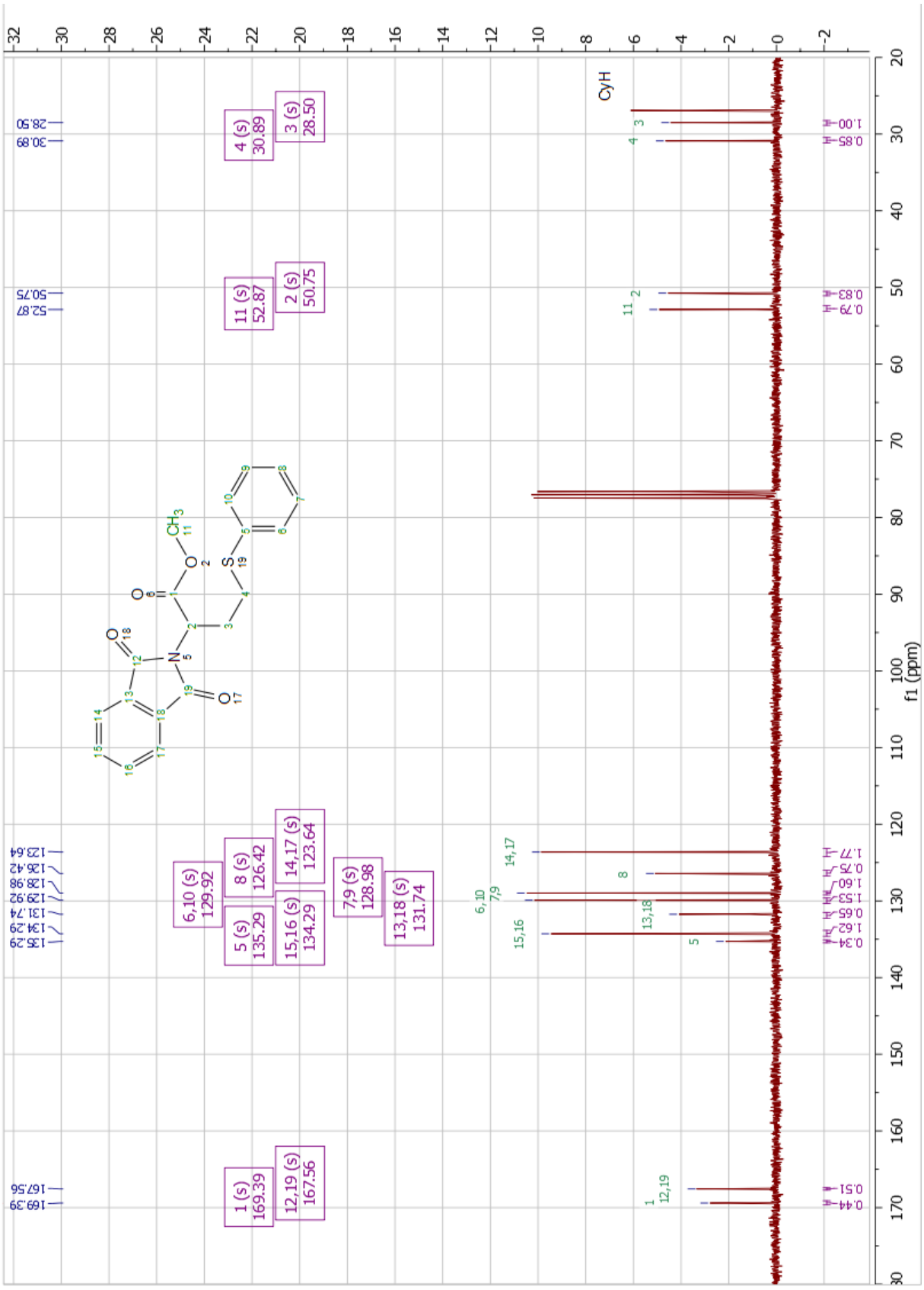



Jul31-2012
hau ulbrich dul 223
carbon CDCl3 /opt/topspin av1 24
f1 (ppm)
CyH
Cl
CH3
O
S
N
1 (s) 169.46
13,20 (s) 167.56
6 (s) 134.38
16,17 (s) 134.30
14,19 (s) 131.63
8,10 (s) 128.94
15,18 (s) 123.58
9 (s) 132.04
7,11 (s) 130.90
2 (s) 51.44
12 (s) 52.82
5 (s) 33.18
3 (s) 27.63
4 (s) 25.60
77,35 CDCl3
77,03 CDCl3
76,99
76,71 CDCl3

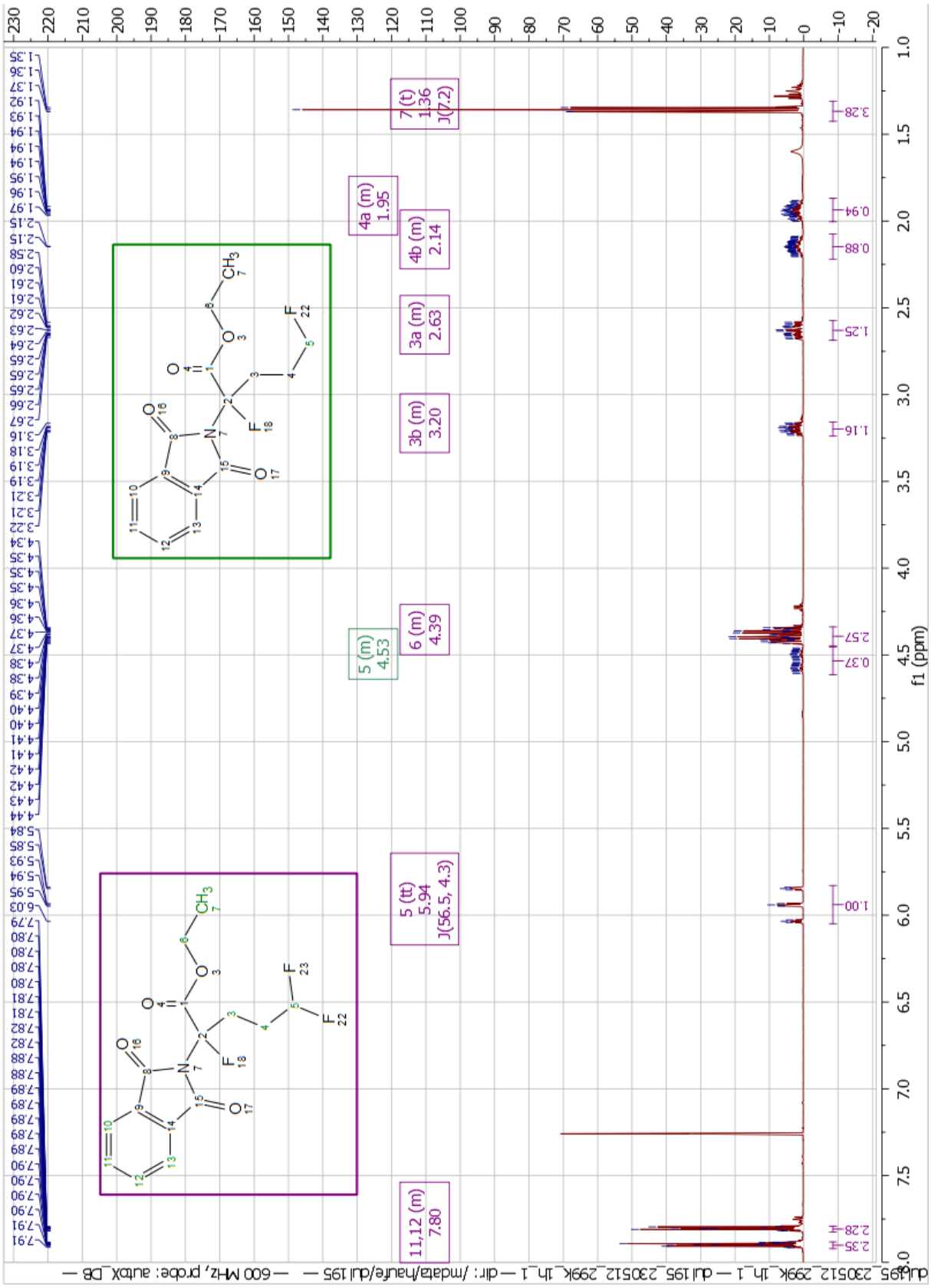
10. Methyl 4-phenylthio-2-phthalimidobutanoate (12)

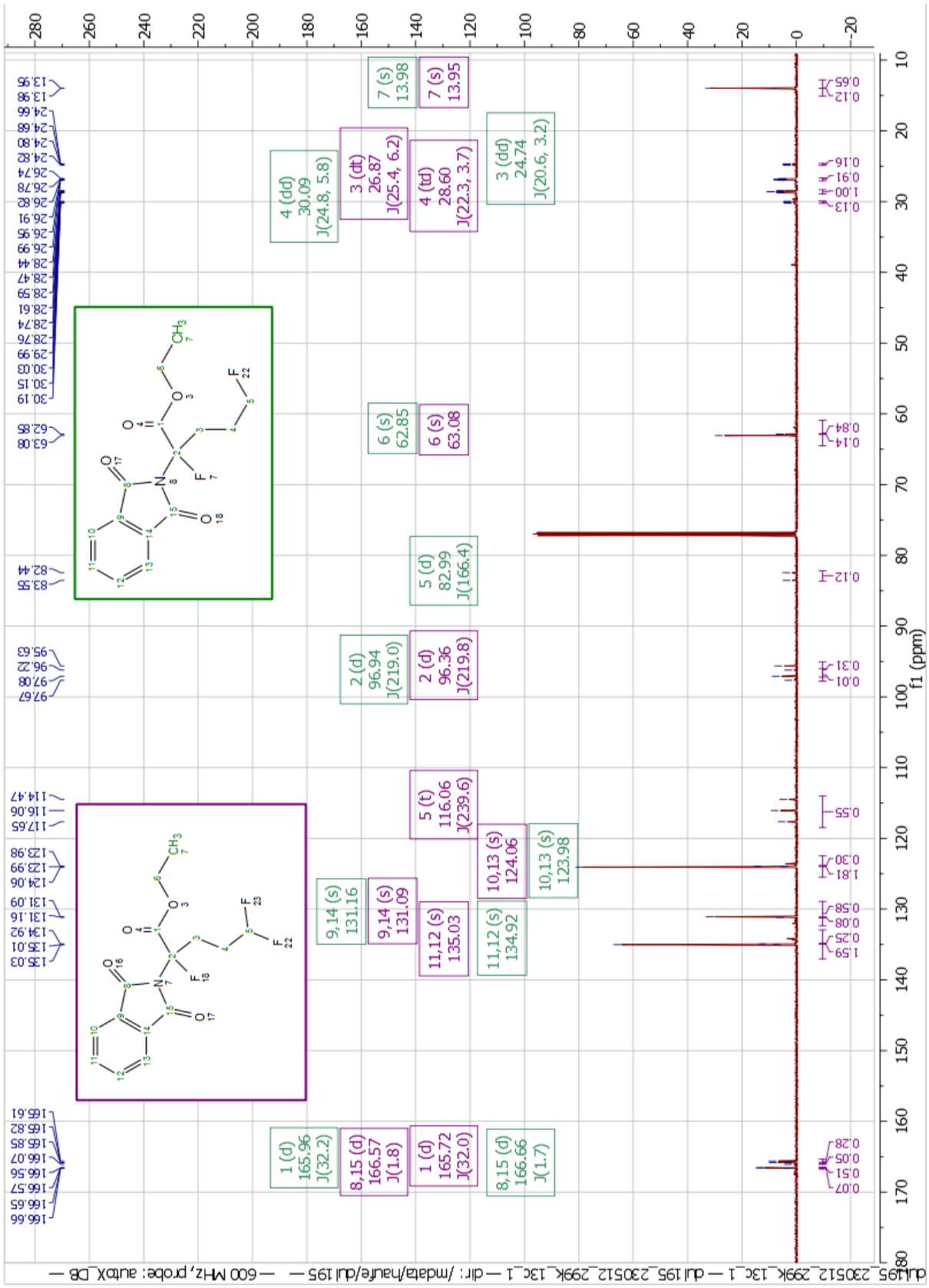


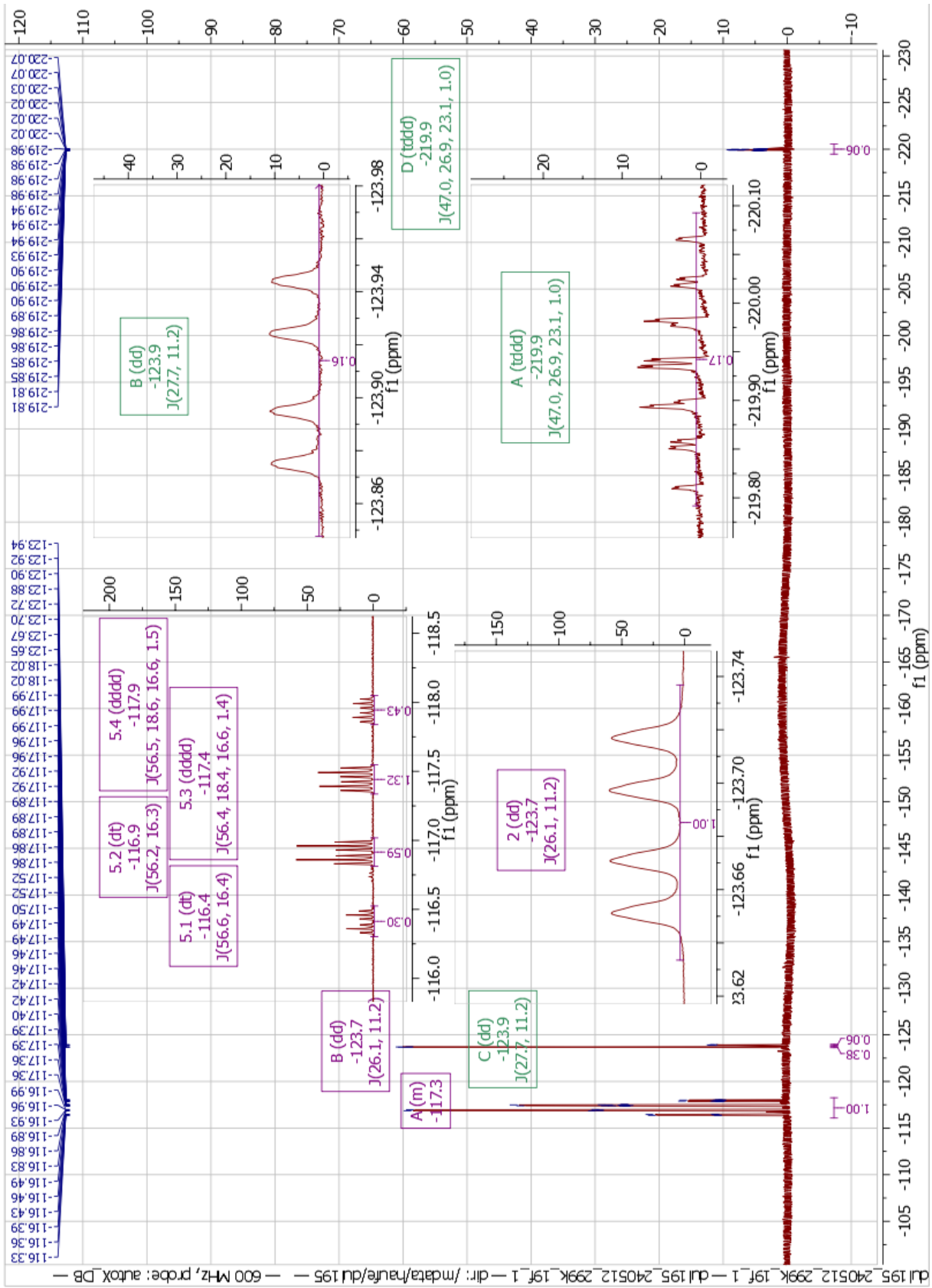

proton CDCl3 /opt/topspin av1 58
15,16 (m) 7.75
14,17 (m) 7.87
7,9 (m) 7.26
6,10 (m) 7.33
8 (m) 7.18
2 (dd) 5.13 J(9.2, 5.8)
11 (s) 3.72
4 (m) 2.95
3 (m) 2.54
CH3
f1 (ppm)

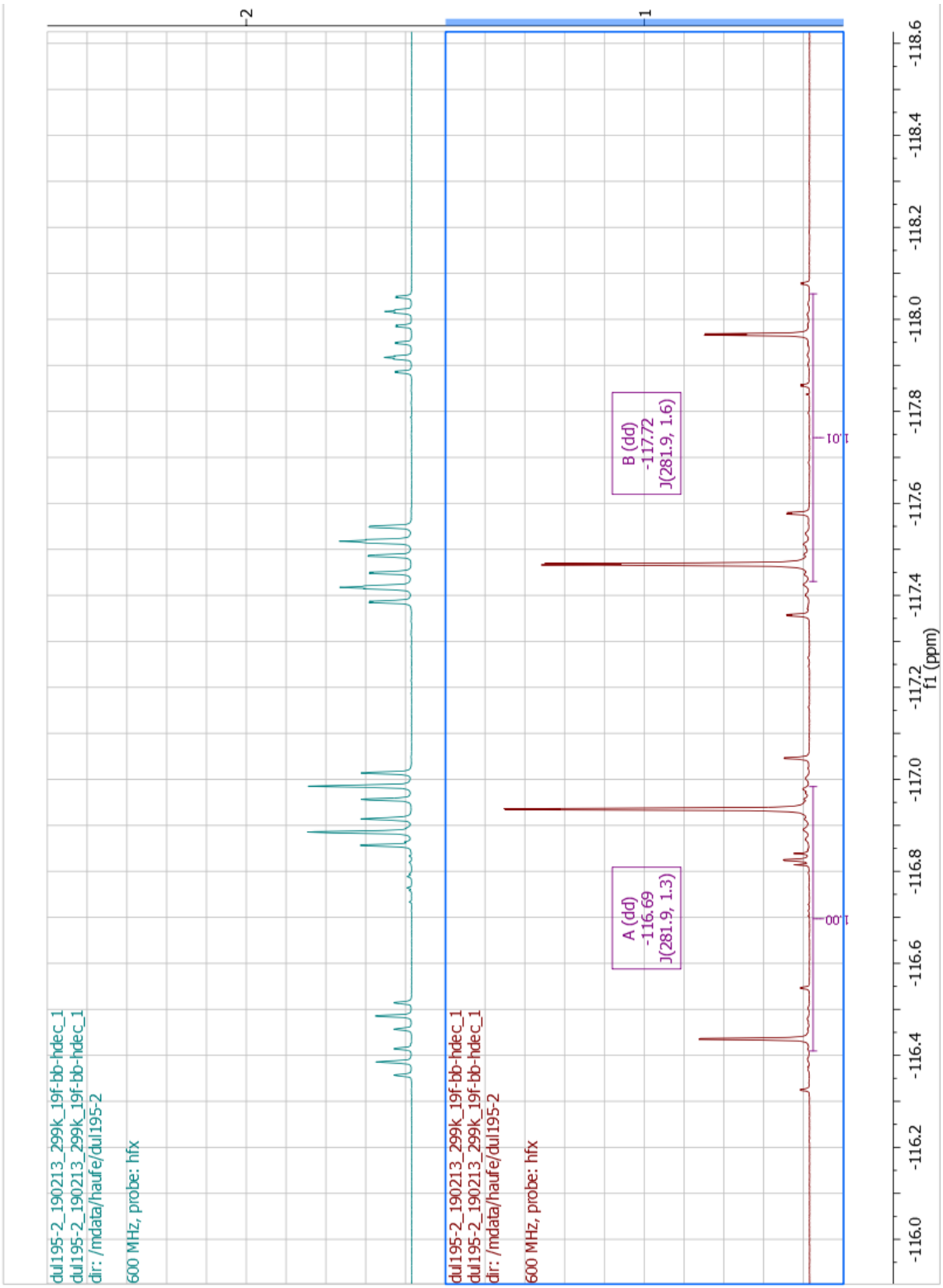

f1 (ppm)
CyH
1 (s) 169.39
12,19 (s) 167.56
5 (s) 135.29
15,16 (s) 134.29
6,10 (s) 129.92
8 (s) 126.42
7,9 (s) 128.98
13,18 (s) 131.74
14,17 (s) 123.64
11 (s) 52.87
2 (s) 50.75
4 (s) 30.89
3 (s) 28.50

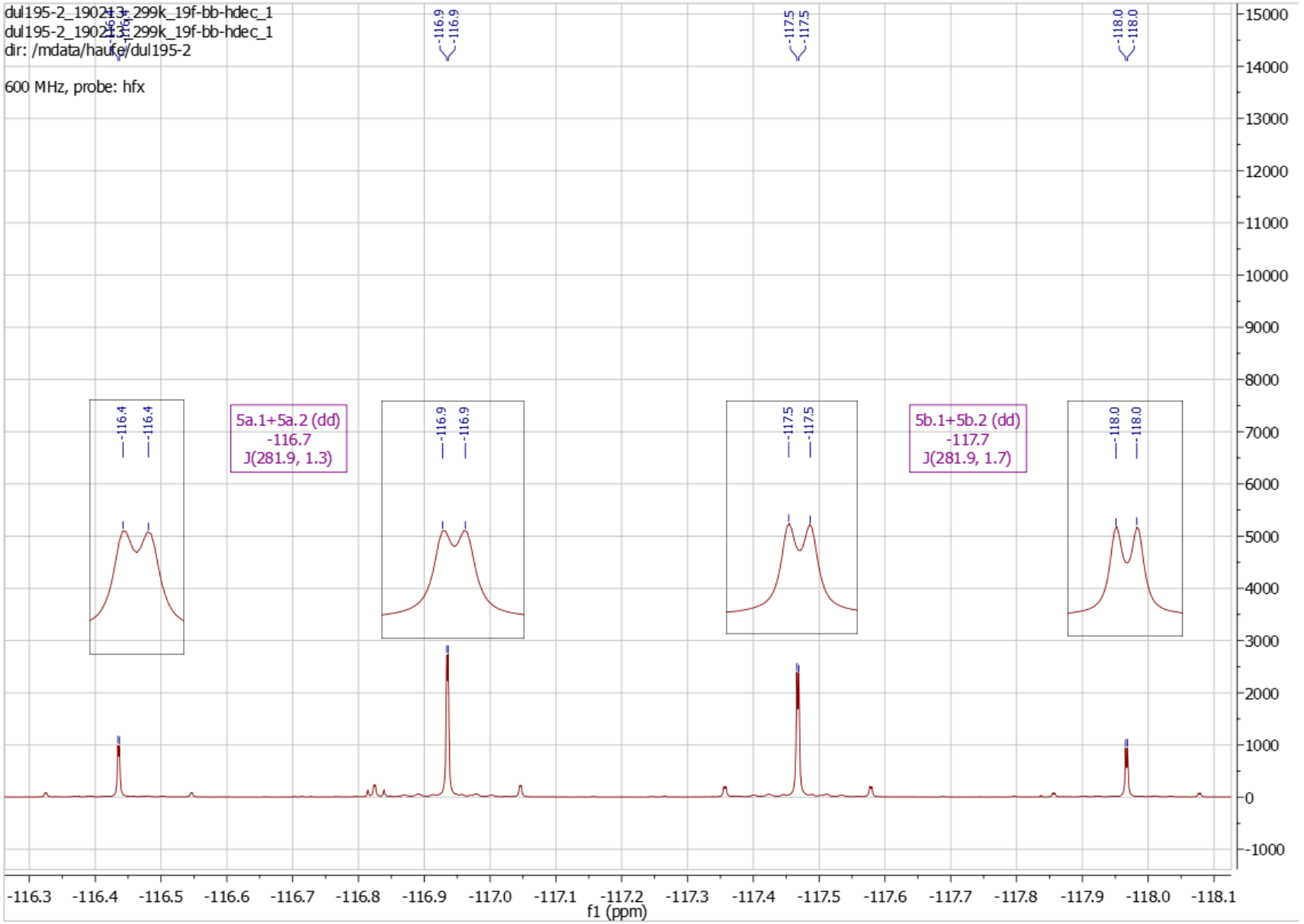
11. Oxidative desulfurization-fluorination of 9a

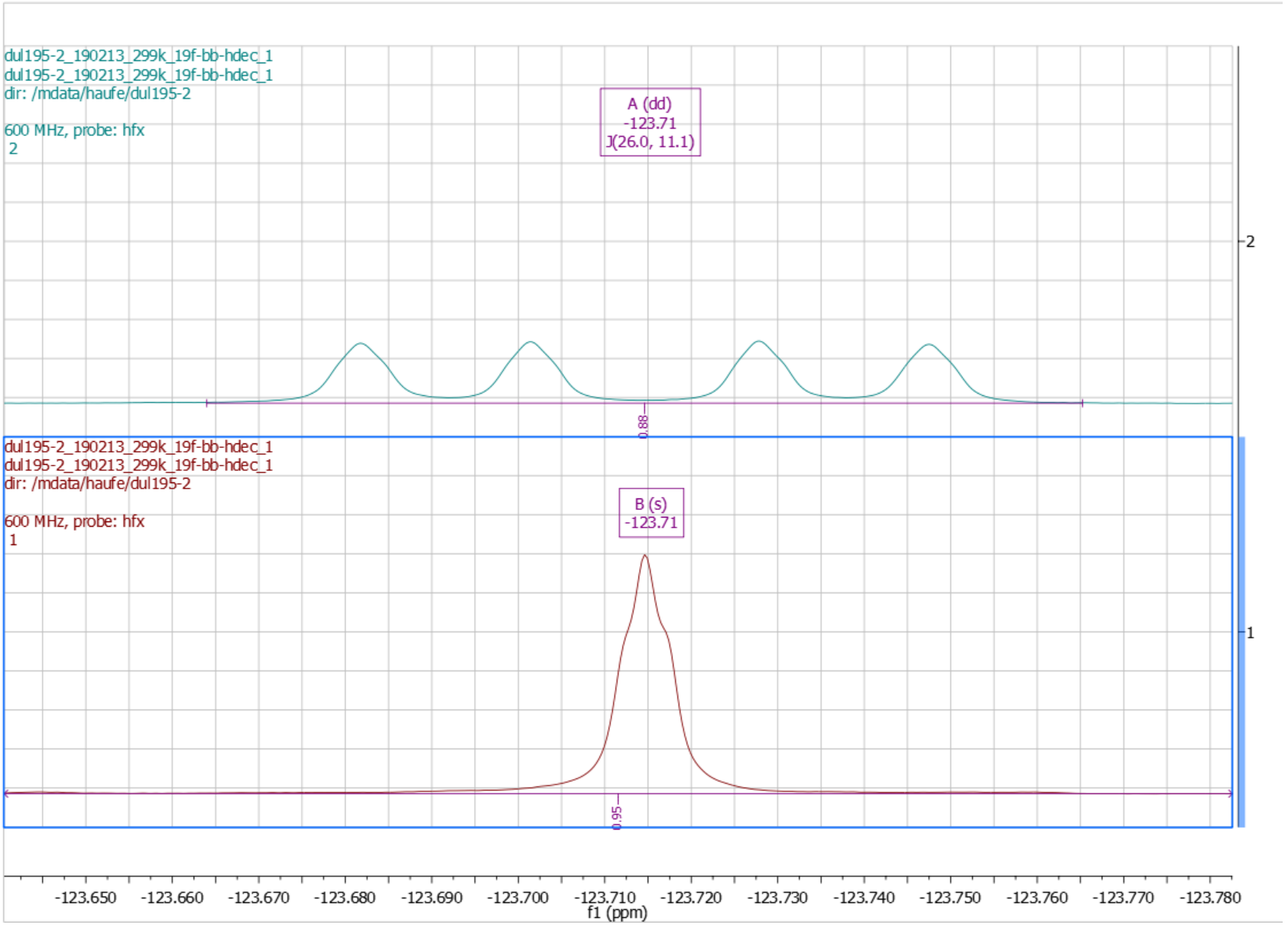



dul195_230512_299K_13C_1 — dul195_230512_299K_13C_1 — dir: /mdata/haufe/dul195 — 600 MHz, probe: autoX_DB
f1 (ppm)
1 (d) 165.96 J(32.2)
8,15 (d) 166.57 J(1.8)
1 (d) 165.72 J(32.0)
8,15 (d) 166.66 J(1.7)
2 (d) 96.94 J(219.0)
2 (d) 96.36 J(219.8)
5 (d) 82.99 J(166.4)
6 (s) 62.85
6 (s) 63.08
4 (dd) 30.09 J(24.8, 5.8)
3 (dt) 26.87 J(25.4, 6.2)
4 (td) 28.60 J(22.3, 3.7)
3 (dd) 24.74 J(20.6, 3.2)
7 (s) 13.98
7 (s) 13.95
9,14 (s) 131.16
9,14 (s) 131.09
11,12 (s) 135.03
11,12 (s) 134.92
10,13 (s) 124.06
10,13 (s) 123.98
5 (t) 116.06 J(239.6)


dul95_240512_299K_19f_1 — dul95_240512_299K_19f_1 — dir: /mdata/haufe/dul95 — — 600 MHz, probe: autoX_DB —
f1 (ppm)
A (m)
-117.3
B (dd)
-123.7
J(26.1, 11.2)
5.1 (dt)
-116.4
J(56.6, 16.4)
5.2 (dt)
-116.9
J(56.2, 16.3)
5.3 (dddd)
-117.4
J(56.4, 18.4, 16.6, 1.4)
5.4 (dddd)
-117.9
J(56.5, 18.6, 16.6, 1.5)
C (dd)
-123.9
J(27.7, 11.2)
2 (dd)
-123.7
J(26.1, 11.2)
A (tddd)
-219.9
J(47.0, 26.9, 23.1, 1.0)
B (dd)
-123.9
J(27.7, 11.2)
D (tddd)
-219.9
J(47.0, 26.9, 23.1, 1.0)


dul195-2_190213_299k_19f-bb-hdec_1
dul195-2_190213_299k_19f-bb-hdec_1
dir: /mdata/haufe/dul195-2
600 MHz, probe: hfx
dul195-2_190213_299k_19f-bb-hdec_1
dul195-2_190213_299k_19f-bb-hdec_1
dir: /mdata/haufe/dul195-2
600 MHz, probe: hfx
A (dd)
-116.69
J(281.9, 1.3)
B (dd)
-117.72
J(281.9, 1.6)
1.00
1.01
-116.0
-116.2
-116.4
-116.6
-116.8
-117.0
-117.2
-117.4
-117.6
-117.8
-118.0
-118.2
-118.4
-118.6
f1 (ppm)


dul195-2_190213_299k_19f-bb-hdec_1
dul195-2_190213_299k_19f-bb-hdec_1
dir: /mdata/haufe/dul195-2
600 MHz, probe: hfx
-116.4
-116.4
-116.9
-116.9
-117.5
-117.5
-118.0
-118.0
5a.1+5a.2 (dd)
-116.7
J(281.9, 1.3)
5b.1+5b.2 (dd)
-117.7
J(281.9, 1.7)
f1 (ppm)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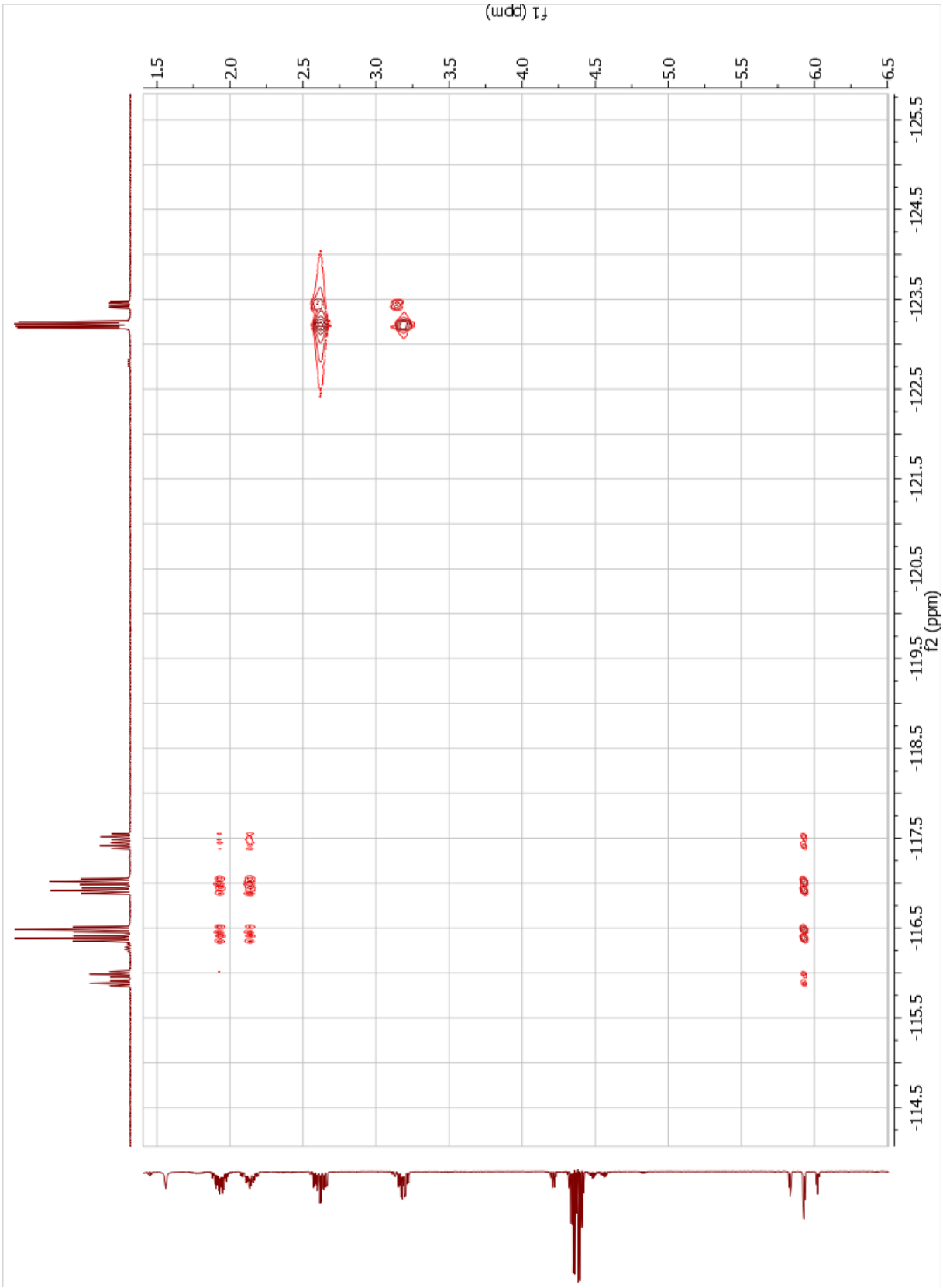
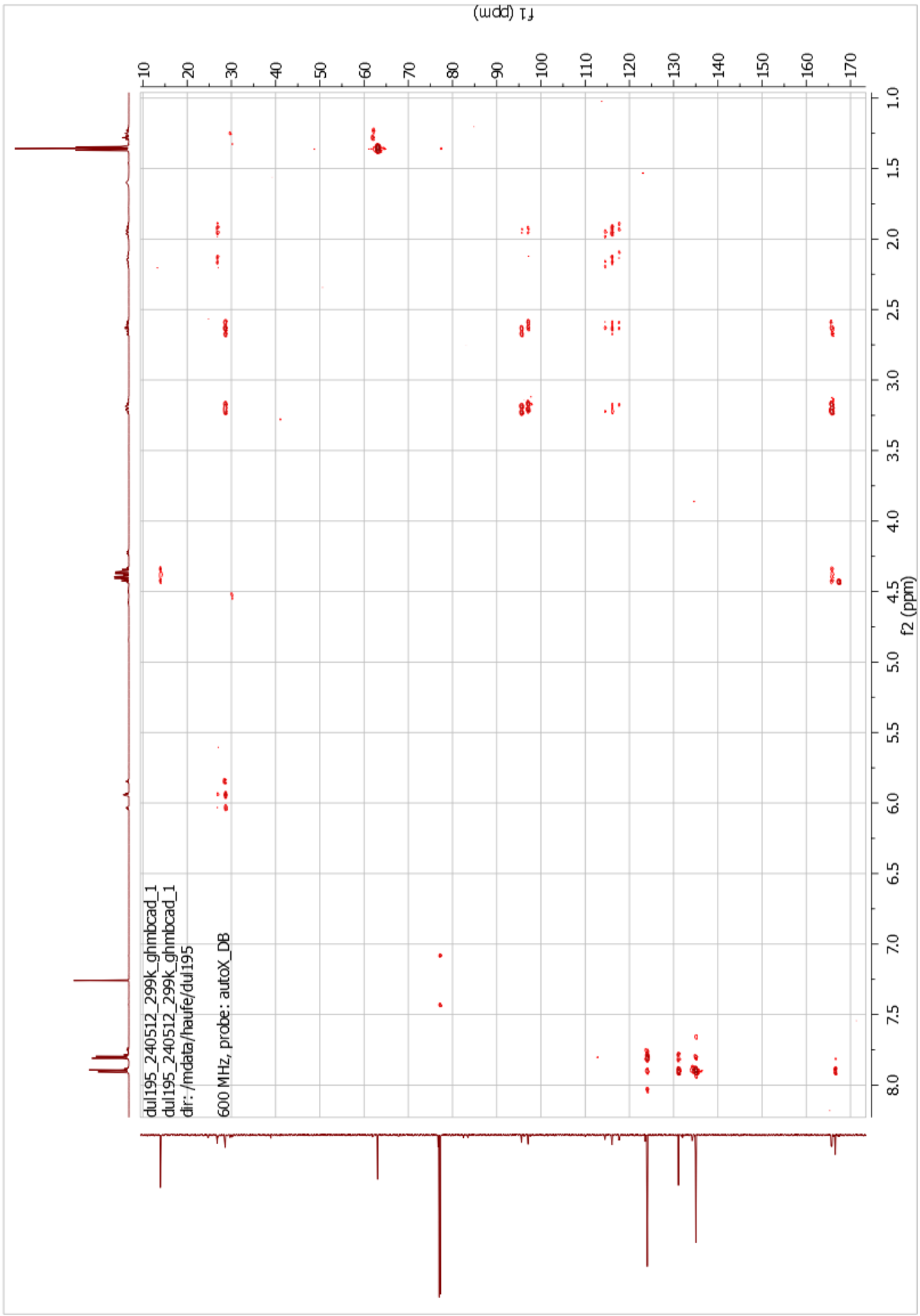
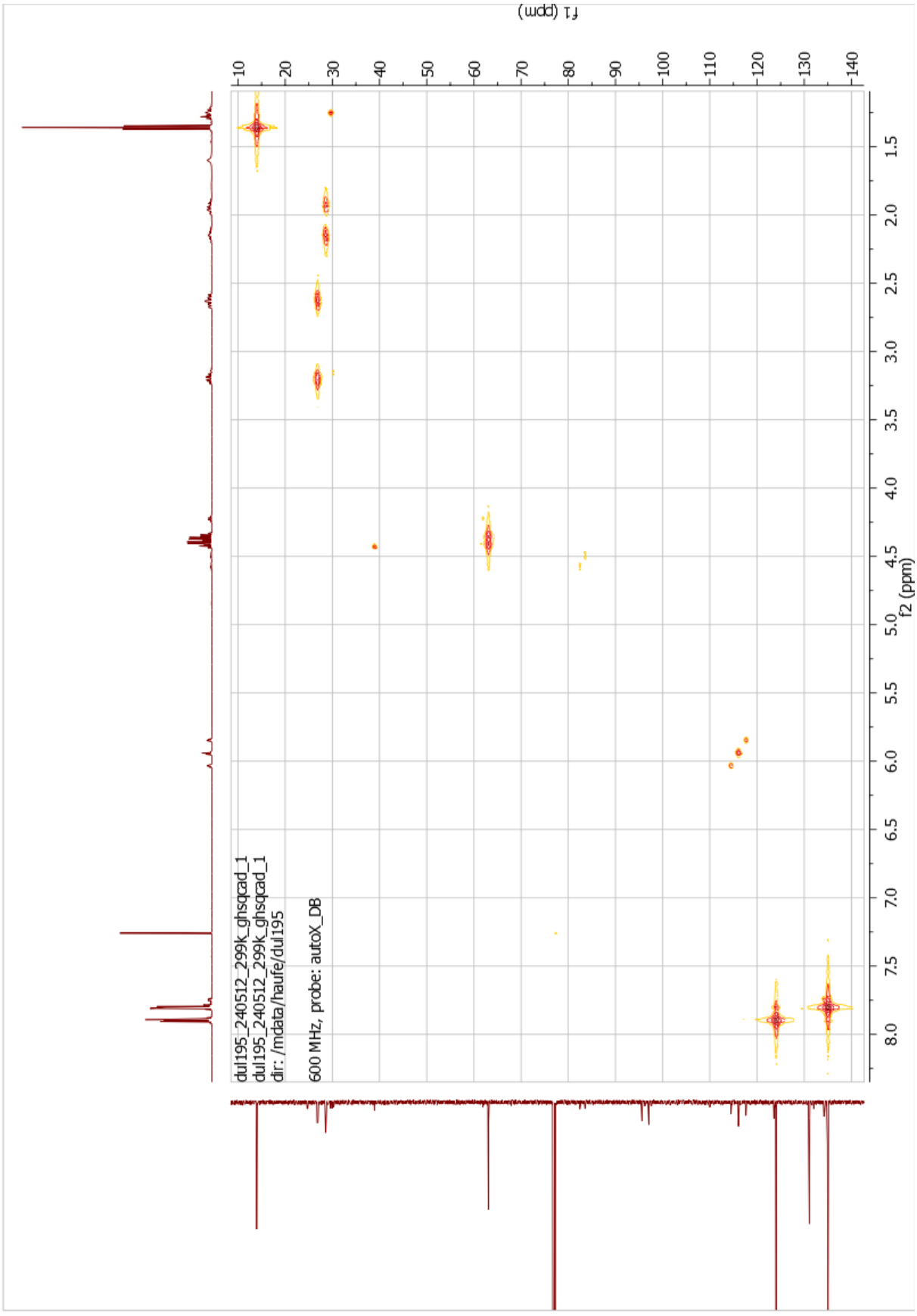
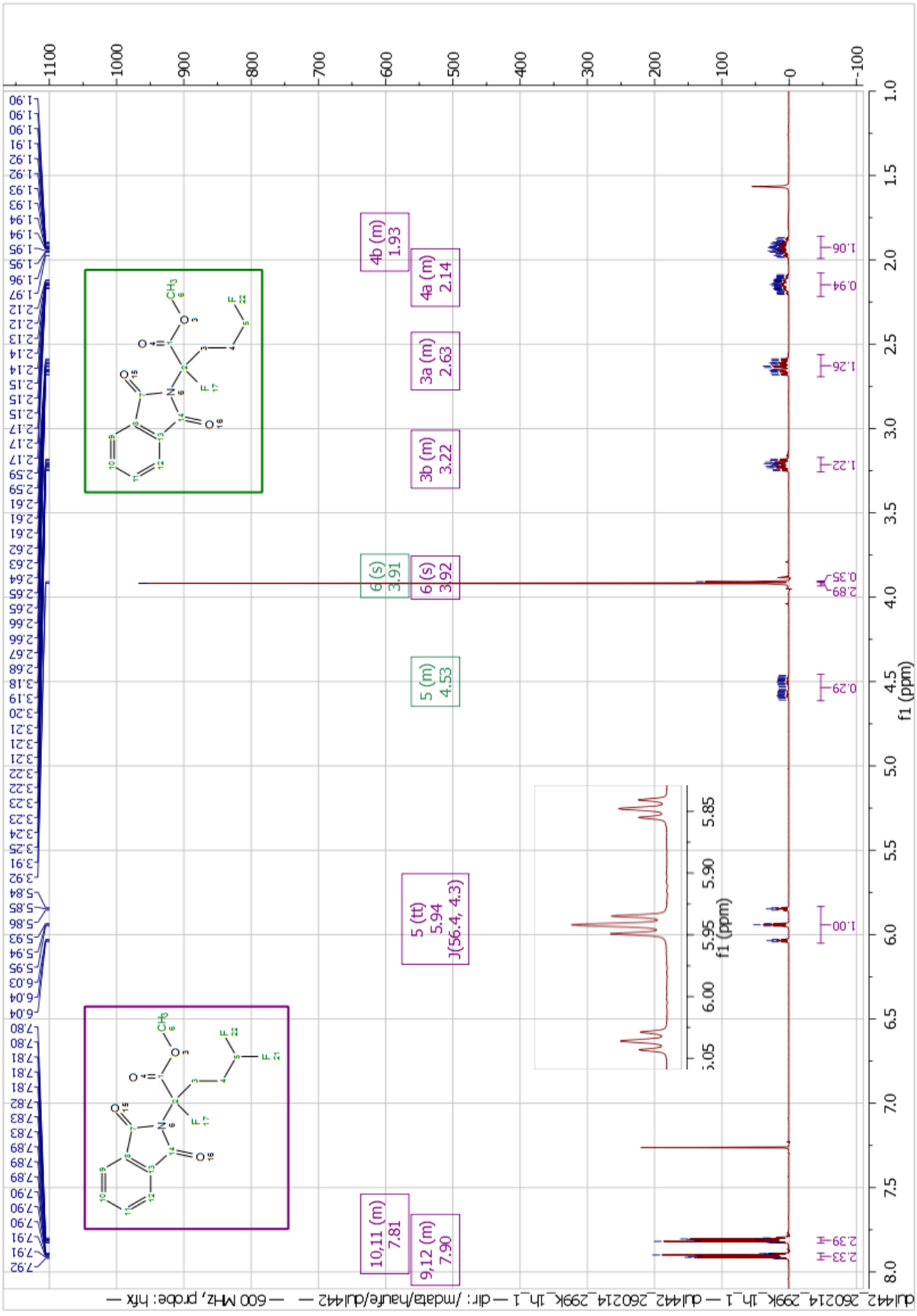
dul195-2_190213_299k_19f-bb-hdec_1
dir: /mdata/haufe/dul195-2
600 MHz, probe: hfx
2
A (dd)
-123.71
J(26.0, 11.1)
0.88
2
dul195-2_190213_299k_19f-bb-hdec_1
dul195-2_190213_299k_19f-bb-hdec_1
dir: /mdata/haufe/dul195-2
600 MHz, probe: hfx
1
B (s)
-123.71
0.95
1
-123.650
-123.660
-123.670
-123.680
-123.690
-123.700
-123.710
-123.720
-123.730
-123.740
-123.750
-123.760
-123.770
-123.780
f1 (ppm)

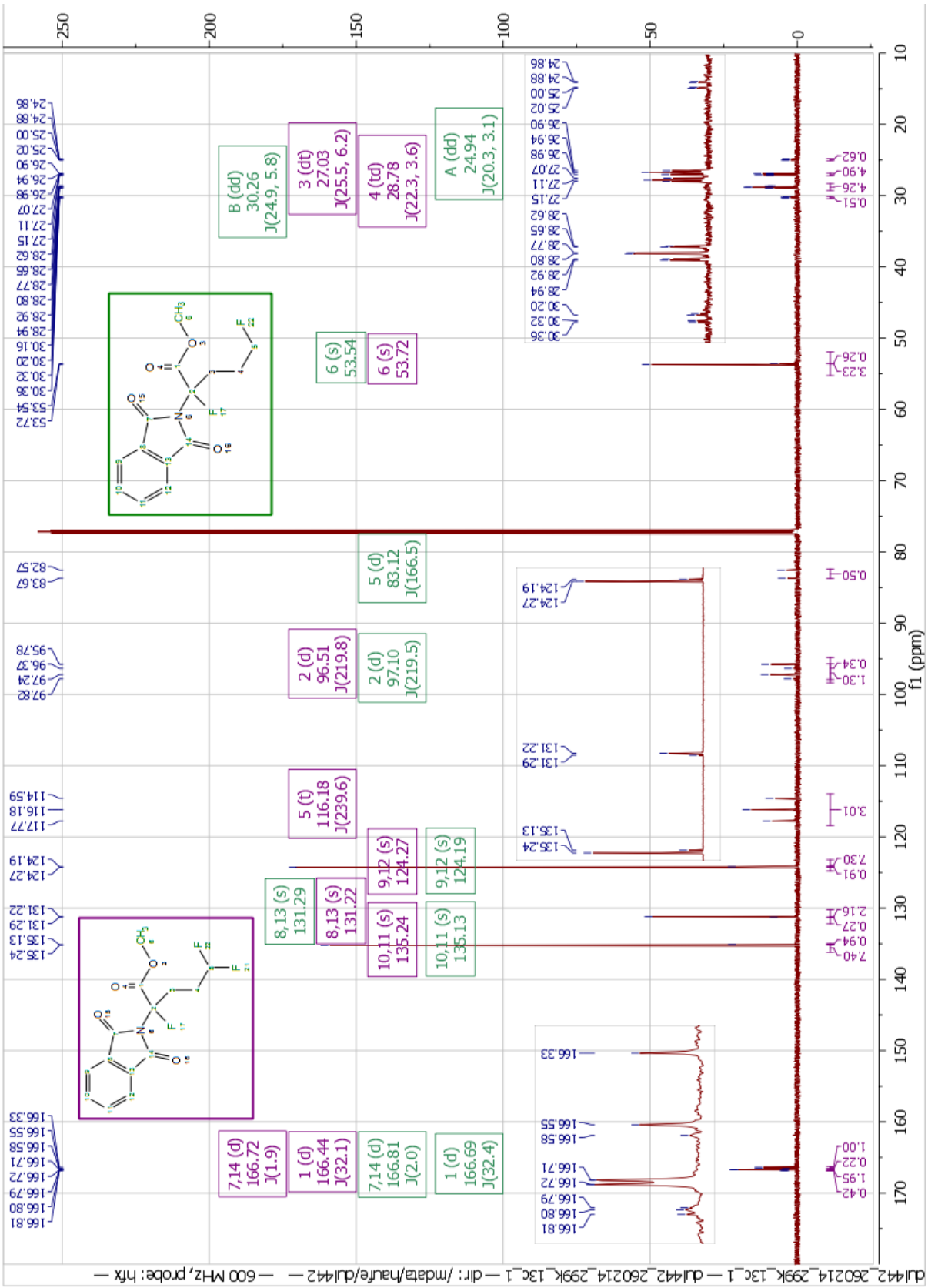

f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f2 (ppm)
-114.5
-115.5
-116.5
-117.5
-118.5
-119.5
-120.5
-121.5
-122.5
-123.5
-124.5
-125.5

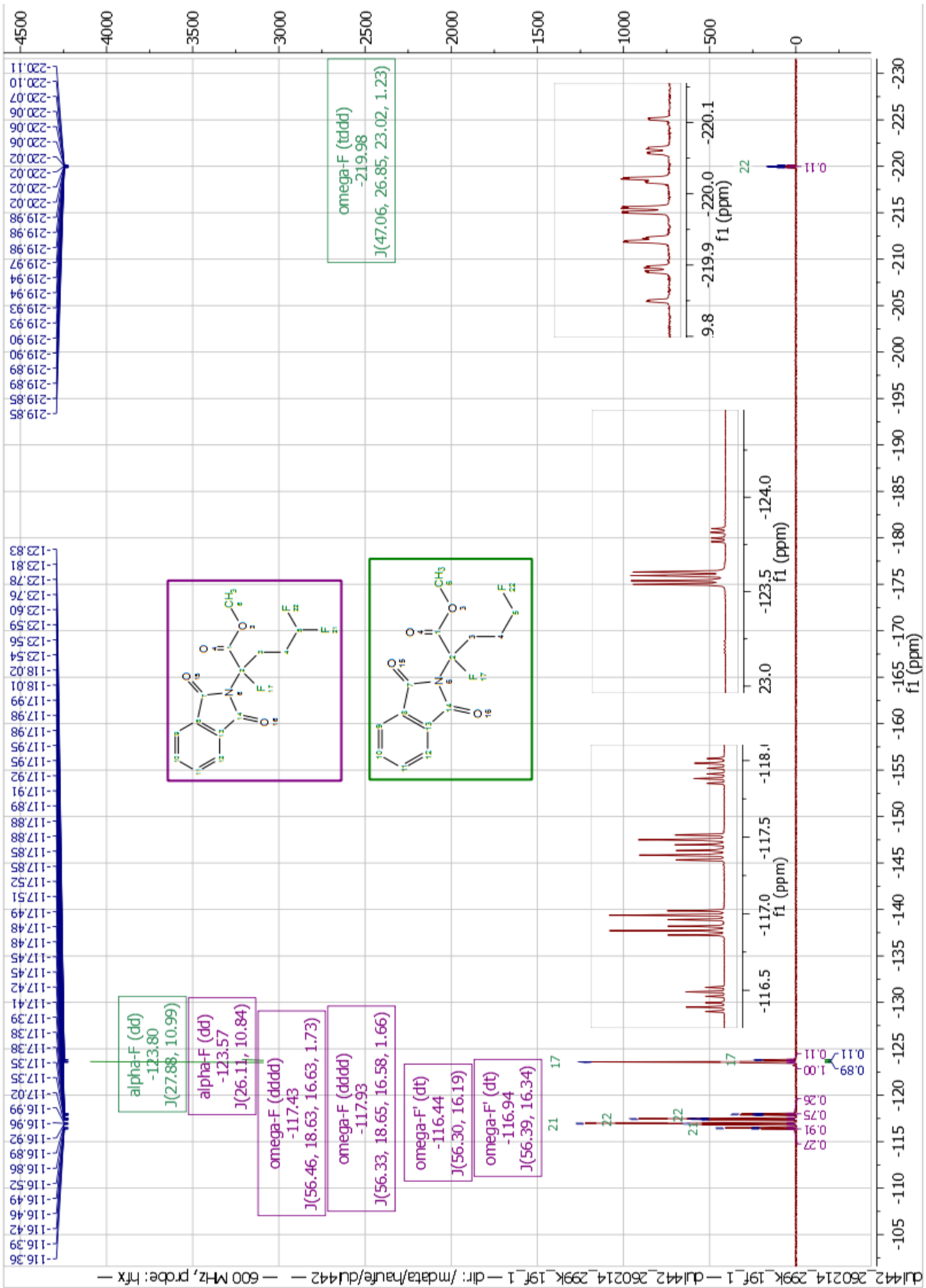

f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
dul195_240512_299k_ghmbcad_1
dul195_240512_299k_ghmbcad_1
dir: /mdata/haufe/dul195
600 MHz, probe: autoX_DB


f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
dul195_240512_299k_ghsqcad_1
dul195_240512_299k_ghsqcad_1
dir: /mdata/haufe/dul195
600 MHz, probe: autoX_DB

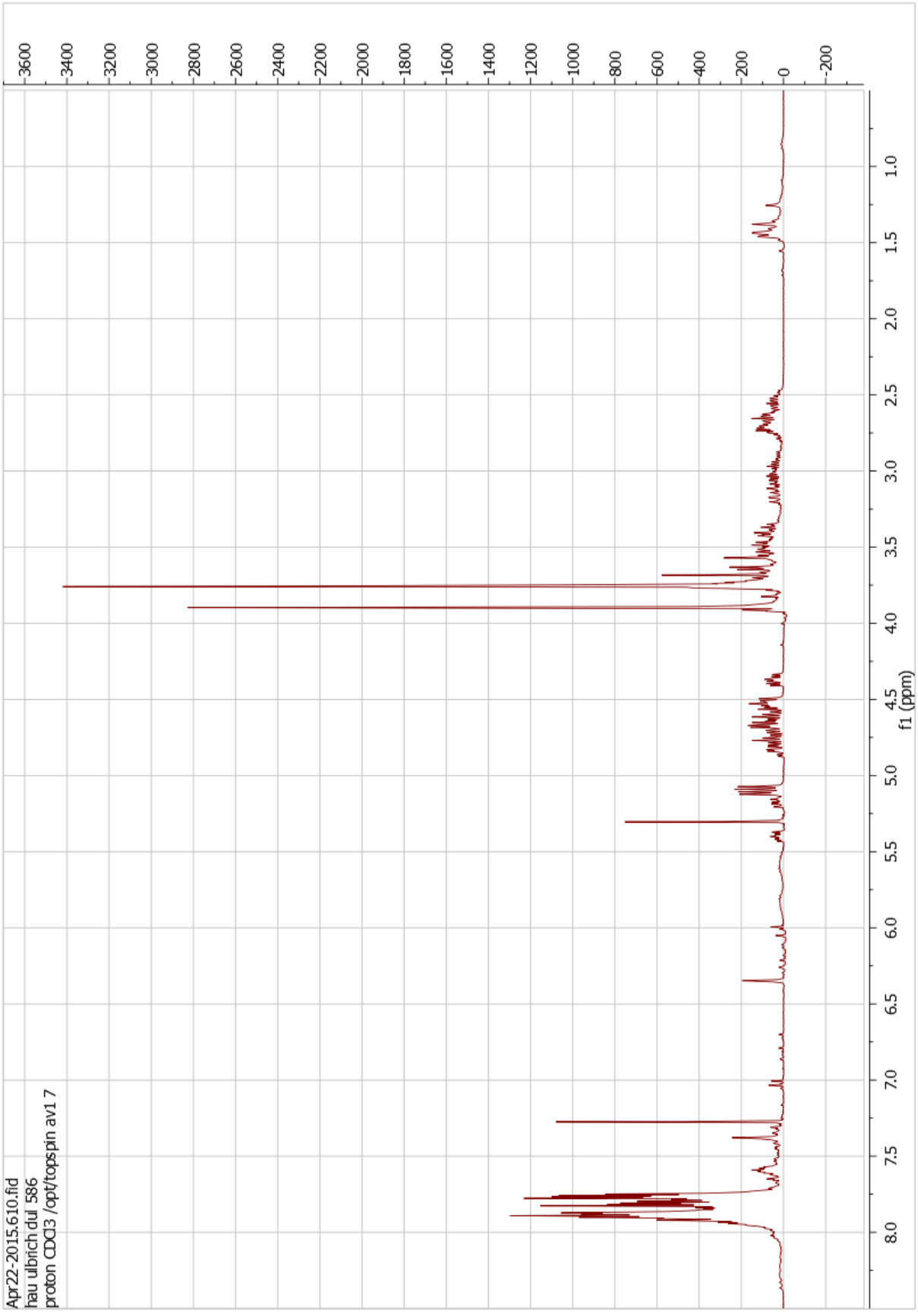
12. Oxidative desulfurization-fluorination of 10b

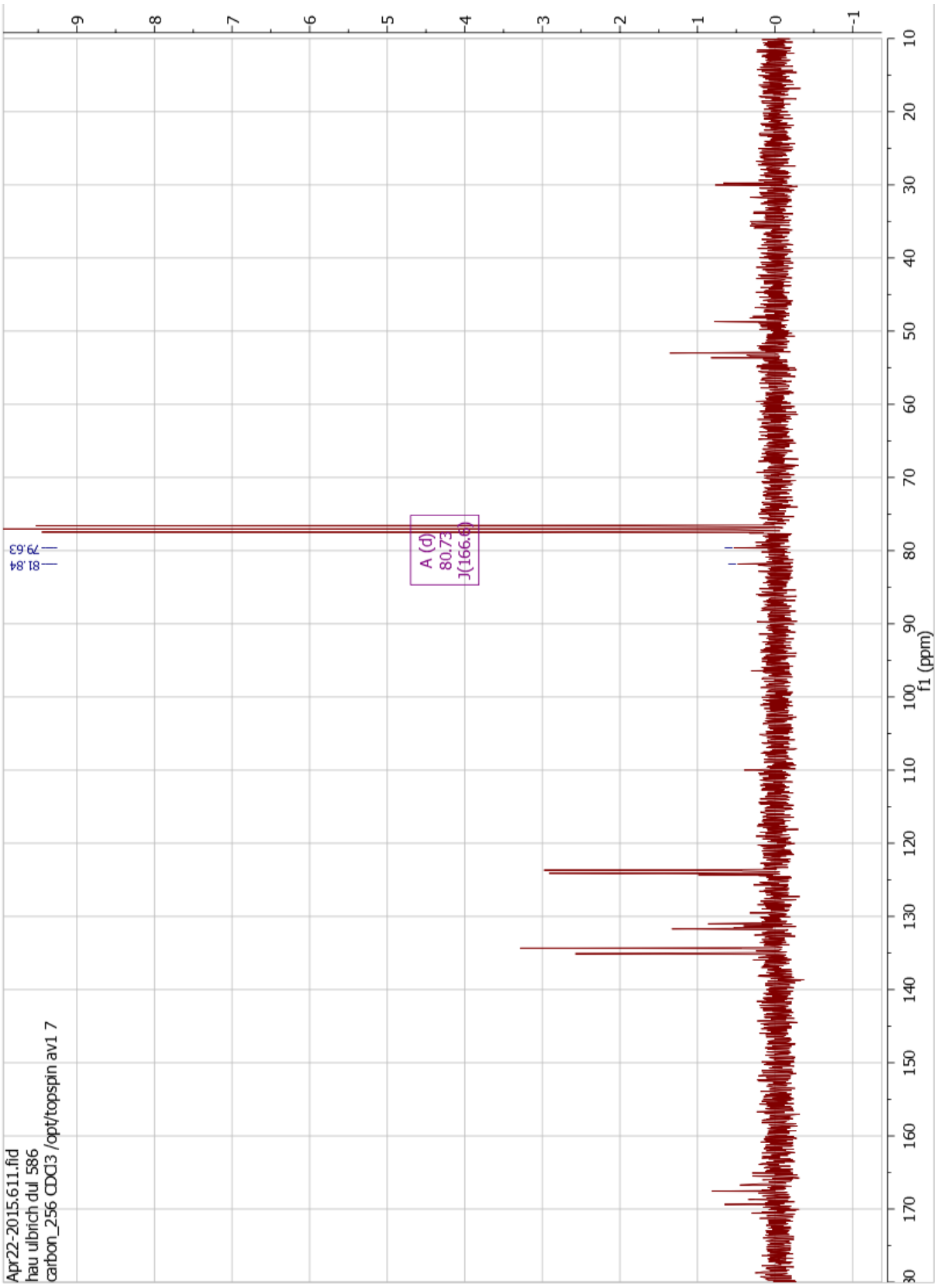


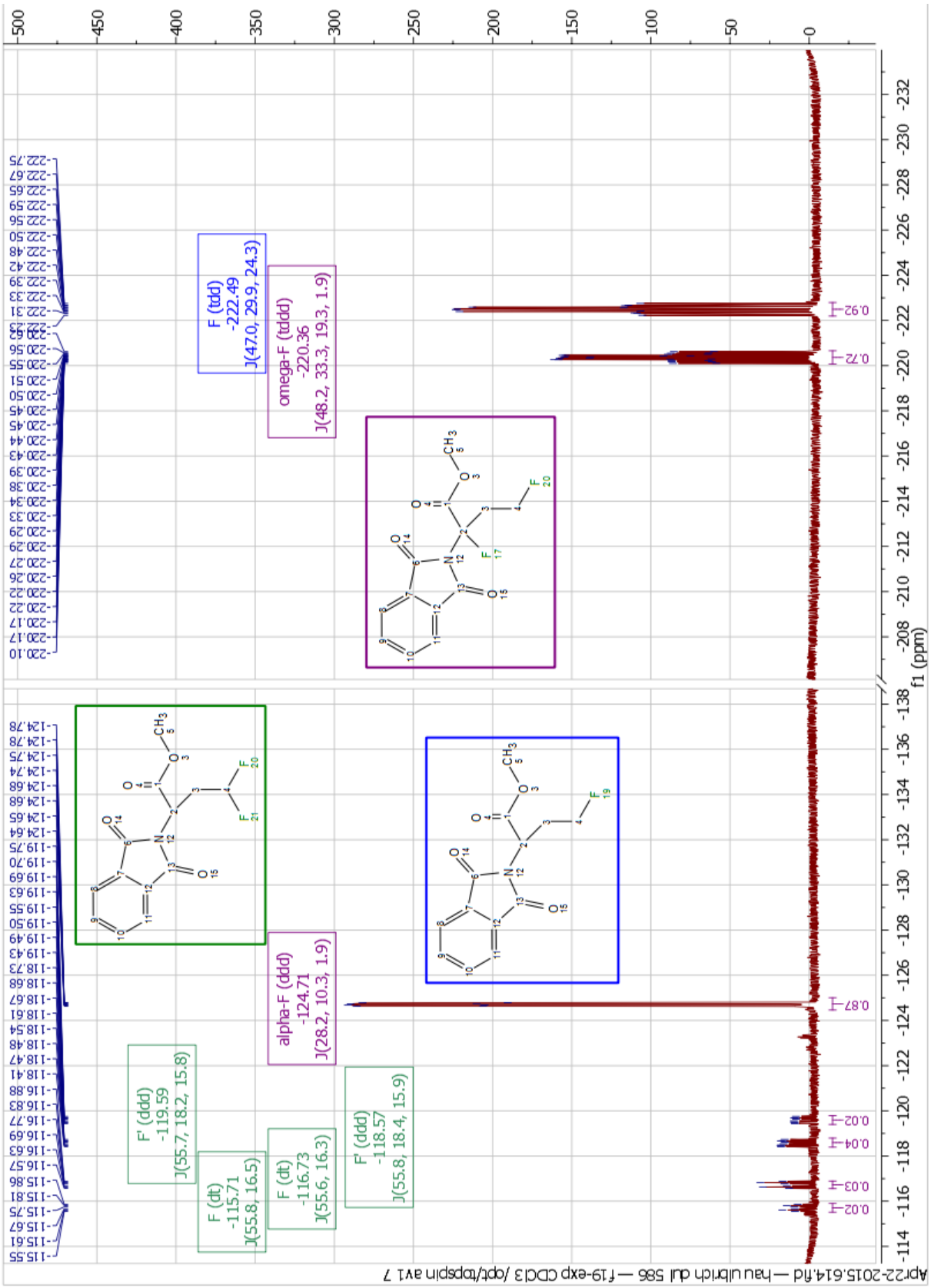

dul442_260214_299k_13c_1 — dul442_260214_299k_13c_1 — dir: /mdata/haufe/dul442 — 600 MHz, probe: hfx
f1 (ppm)
B (dd) 30.26 J(24.9, 5.8)
3 (dt) 27.03 J(25.5, 6.2)
4 (td) 28.78 J(22.3, 3.6)
A (dd) 24.94 J(20.3, 3.1)
6 (s) 53.54
6 (s) 53.72
5 (d) 83.12 J(166.5)
2 (d) 96.51 J(219.8)
2 (d) 97.10 J(219.5)
5 (t) 116.18 J(239.6)
8,13 (s) 131.29
8,13 (s) 131.22
9,12 (s) 124.27
9,12 (s) 124.19
10,11 (s) 135.24
10,11 (s) 135.13
7,14 (d) 166.72 J(1.9)
1 (d) 166.44 J(32.1)
7,14 (d) 166.81 J(2.0)
1 (d) 166.69 J(32.4)


alpha-F (dd)
-123.80
J(27.88, 10.99)
alpha-F (dd)
-123.57
J(26.11, 10.84)
omega-F (dddd)
-117.43
J(56.46, 18.63, 16.63, 1.73)
omega-F (dddd)
-117.93
J(56.33, 18.65, 16.58, 1.66)
omega-F' (dt)
-116.44
J(56.30, 16.19)
omega-F' (dt)
-116.94
J(56.39, 16.34)
omega-F (tdddd)
-219.98
J(47.06, 26.85, 23.02, 1.23)
f1 (ppm)

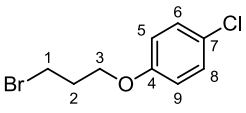
13. Oxidative desulfurization-fluorination of 12




Apr22-2015.611.fid
hau ulbrich dul 586
carbon_256 CDCl3 /opt/topspin av1 7
81.84
79.63
A (d)
80.73
J(166.6)
f1 (ppm)


F (tdd)
-222.49
J(47.0, 29.9, 24.3)
omega-F (tdddd)
-220.36
J(48.2, 33.3, 19.3, 1.9)
alpha-F (ddd)
-124.71
J(28.2, 10.3, 1.9)
F' (ddd)
-119.59
J(55.7, 18.2, 15.8)
F (dt)
-115.71
J(55.8, 16.5)
F (dt)
-116.73
J(55.6, 16.3)
F' (ddd)
-118.57
J(55.8, 18.4, 15.9)
0.92
0.72
0.87
0.02
0.04
0.03
0.02
f1 (ppm)

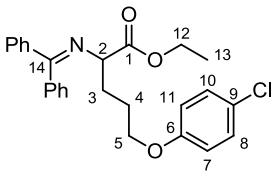
14. Synthesis of 1-bromo-3-(4-chlorophenyl)oxypropane (SI 1)



SI 1

To a suspension of NaH (60& in mineral oil, 4.038 g, 101 mg) in DMF (100 mL) was added 4-chlorophenol (13.001 g, 101 mmol) at 0 °C. After stirring 1 h at this temperature, the solution was over 30 min added to a solution of 1,3-dibromopropane (31 mL, 303 mmol, 3.0 eq.) in DMF (100 mL) and the solution stirred at r.t. for 25.5 h. Afterwards the reaction was quenched with half conc. aqueous $NaHCO_3$ (400 mL) and the mixture extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with sat. aqueous NaCl (2 × 150 mL) and dried over $MgSO_4$. The product was purified by vacuum distillation using a 27 cm Vigreux column. Yield: 6.929 g (28 mmol, 28%); bp.: 103-104 °C (0.03 mbar). ^{1}H NMR (400 MHz, $CDCl_3$)*:* δ 2.31 (p, $^3J_{H,H}$ = 6.1 Hz, 2 H, 2-CH_2), 3.59 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, 1-CH_2), 4.07 (t, $^3J_{H,H}$ = 5.8 Hz, 2 H, 3-CH_2), 6.82-6.85 (m, 2 H, 5/9-CH), 7.22-7.26 (m, 2 H, 6/8-CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 29.9 (t, C-1), 32.2 (t, C-2), 65.6 (t, C-3), 115.8 (d, C-5/9), 125.8 (s, C-7), 129.3 (d, C-6/8), 157.3 (s, C-4). MS (EI-GC-inlet): *m*/*z* 250/248 (15/13) $[M]^+$, 130/128 (35/100) $[C_6H_5ClO]^+$, 99 (15), 75 (37), 63 (13), 41 (38).

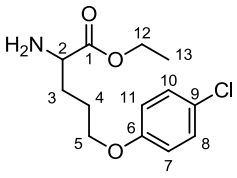
15. Synthesis of ethyl 5-(4-chlorophenyl)oxy-2-(diphenylmethylene)amino-pentanoate (SI 2)



SI 2

To a solution of ethyl *N*-(diphenylmethylene)glycinate (**3 a**) (2.734 g, 10.2 mmol) in DMSO (30 mL) was added KO*t*Bu (1.145 g, 10.2 mmol) at 0 °C. After stirring for 30 min, 1-bromo-3-(4-chlorophenyl)oxypropane (**SI 1**) (2.545 g, 10.2 mmol) was added and the solution stirred over night. The conducted workup is described in the article for compound **5 a**. The crude product was used in the following step without purification. Yield: 4.026 g (crude product). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.26 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, 13-CH_3), 1.65-1.88 (m, 2 H, 3-CH_2), 1.98-2.20 (m, 2 H, 4-CH_2), 3.81-3.88 (m, 2 H, 5-CH_2), 6.72-6.78 (m, 2 H, 7/11-CH), 7.14-7.21 (m, 2 H, 8/10-CH), 7.27-7.68 (m, 8 H, 8 × Ph-CH), 7.78-7.85 (m, 2 H, 2 × Ph-CH). The signals of C-2 und C-12 were covered by signals of the starting material and could not be identified. **MS-ES(+)-EM**: *m*/*z* calcd for $C_{26}H_{26}ClNO_3H^+$: 436.1674/438.1647, found: 436.1672/438.1653 $[M+H]^+$.

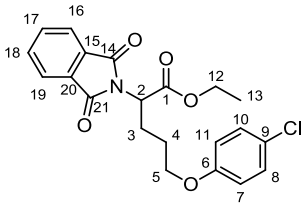
16. Synthesis of ethyl 5-(4-chlorophenyl)oxy-2-aminopentanoate (SI 3)



SI 3

The product mixture from above (4.001 g) was dissolved in ethanol (40 mL) and treated with 15% aqueous citric acid (20 mL). After stirring for 1 h at r.t. the workup as described for **7 a** followed. The crude product was slightly contaminated with benzophenone but had a satisfactory purity to be used in the next step. Yield: 488 mg (crude product). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.27 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, 13-CH_3), 1.75-2.01 (m, 4 H, 3-CH_2 und 4-CH_2), 3.60 (dd, $^3J_{H,H}$ = 7.3, 5.2 Hz, 1 H, 2-CH), 3.95 (t, $^3J_{H,H}$ = 5.9 Hz, 2 H, 5-CH_2), 4.18 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, 12-CH_2), 6.76-6.86 (m, 2 H, 7/11-CH), 7.17-7.25 (m, 2 H, 8/10-CH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 14.2 (q, C-13), 25.4 (t, C-4), 30.7 (t, C-3), 53.9 (d, C-2), 61.3 (t, C-12), 67.6 (t, C-5), 115.7 (d, C-7/11), 125.5 (s, C-9), 129.3 (d, C-8/10), 157.5 (s, C-6), 174.7 (s, C-1). **MS-ES(+)-EM**: *m*/*z* calcd for $C_{13}H_{18}ClNO_3H^+$: 272.1048/274.1019, found: 272.1044/274.1018 $[M+H]^+$; calcd for $C_{13}H_{18}ClNO_3Na^+$: 294.0867/296.0838, found: 294.0866/296.0840 $[M+Na]^+$.

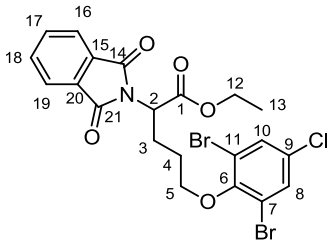
17. Synthesis of ethyl 5-(4-chlorophenyl)oxy-2-phthalimidopentanoate (19)



19

In a pre-heated oil bath ethyl 2-amino-5-(4-chlorphenyl)oxypentanoate (**SI 3**) (300 mg, 1.10 mmol) and finely mortared phthalic anhydride (164 mg, 1.11 mmol) were mixed and heated to 145 °C for 1 h in an open vessel. The product was purified by column chromatography (CyH/EtOAc, 5:1) and isolated as a white solid. Yield: 242 mg (0.60 mmol, 55%): mp.: 93-94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, 13-CH_3), 1.76-1.86 (m, 2 H, 4-CH_2), 2.40-2.47 (m, 2 H, 3-CH_2), 3.94 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, 5-CH_2), 4.21 (m, 2 H, 12-CH_2), 4.91 (dd, $^3J_{H,H}$ = 10.1, 5.6 Hz, 1 H, 2-CH), 6.76-6.80 (m, 2 H, 7/11-CH), 7.16-7.20 (m, 2 H, 8/10-CH), 7.72-7.78 (m, 2 H, 17/18-CH), 7.83-7.90 (m, 2 H, 16/19-CH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 14.1 (q, C-13), 25.5 (t, C-3), 26.1 (t, C-4), 52.0 (d, C-2), 61.9 (t, C-12), 67.2 (t, C-5), 115.7 (d, C-7/11), 123.6 (d, C-16/19), 125.5 (s, C-9), 129.2 (d, C-8/10), 131.8 (s, C-15/20), 134.2 (d, C-17/18), 157.4 (s, C-6), 167.7 (s, C-17/21), 169.1 (s, C-1). **MS-ES(+)-EM:** *m*/*z* calcd for $C_{21}H_{20}{}^{35}ClNO_5H^+$: 402.1103, found: 402.1095 $[M+H]^+$; calcd for $C_{21}H_{20}ClNO_5Na^+$: 424.0922/426.0895, found: 424.0916/426.0892 $[M+Na]^+$.

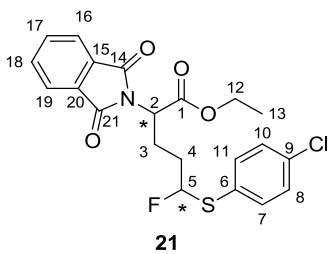
18. Reaction of ethyl 5-(4-chlorophenyl)oxy-2-phthalimidopentanoate (19) with DBH and Olah's reagent



20

Ethyl 5-(4-chlorophenyl)oxy-2-phthalimidopentanoate (**19**) (100 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (3 mL) and treated with Olah's reagent (0.35 mL, 1.50 mmol, 6.0 eq.) and DBH (286 mg, 1.00 mmol, 4.0 eq.). After stirring over night and quenching with sat. aqueous $NaHCO_3$ and sat. aqueous $NaSO_3$ the mixture was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic phases washed with 1 M aqueous HCl and sat. aqueous NaCl. The organic solution was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Ethyl 5-(2,6-dibromo-4-chlorphenyl)oxy-2-phthalimidopentanoate was identified as the sole product. Yield: 141 mg (0.25 mmol, 100%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, 13-CH_3), 1.83-1.95 (m, 2 H, 4-CH_2), 2.42-2.67 (m, 2 H, 3-CH_2), 4.00 (m, 2 H, 5-CH_2), 4.23 (m, 2 H, 12-CH_2), 4.97 (dd, $^3J_{H,H}$ = 10.7, 4.9 Hz, 1 H, 2-CH), 7.48 (s, 2 H, 8/10-CH), 7.72-7.80 (m, 2 H, 17/18-CH), 7.84-7.91 (m, 2 H, 16/19-CH). **MS-ES(+)-EM**: *m*/*z* calcd for $C_{21}H_{18}{}^{79}Br^{81}Br^{35}ClNO_5H^+$ 559.9284 $[M+H]^+$, found: 559.9293, calcd for $C_{21}H_{18}{}^{79}Br^{81}Br^{35}ClNO_5Na^+$: 581.9112, found: 581.9110 $[M+Na]^+$.

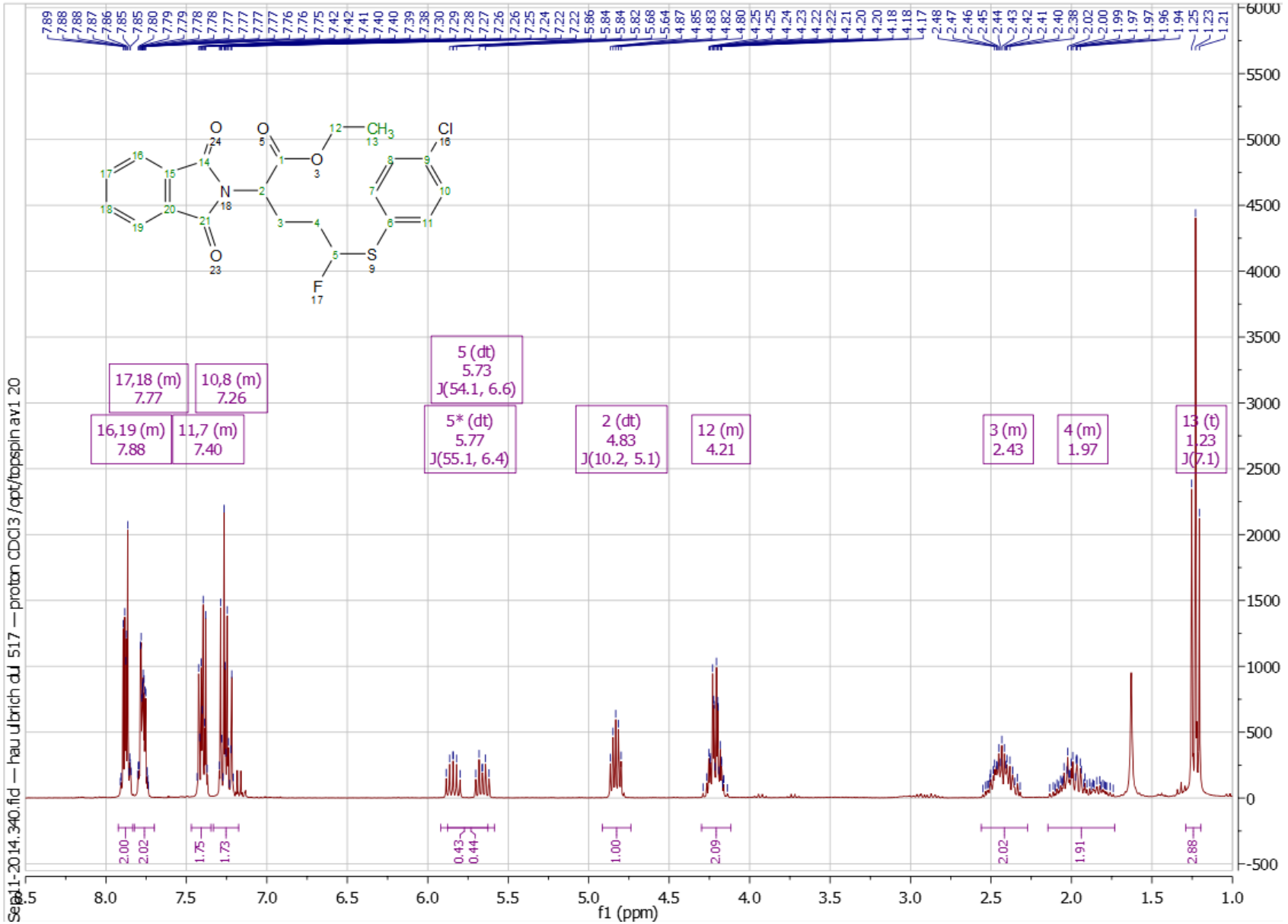
19. Synthesis of ethyl 5-(4-chlorophenyl)thio-5-fluoro-2-phthalimido-pentanoate (21)



21

Making use of a method described by ROBINS und WNUK,[1] ethyl 5-(4-chlorophenyl)thio-2-phthalimidopentanoate (**5 b**) (448 mg, 1.07 mmol) was dissolved in abs. CH_2Cl_2 (4 mL) in an argon atmosphere and treated with $SbCl_3$ (36 mg, 0.16 mmol, 0.15 eq.) and DAST (0.39 mL, 3.21 mmol, 3.0 eq.). The yellow solution was stirred for 21 h at r.t. and the now red solution neutralized with ice/sat. aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3 × 10 mL), the organic phases dried over $MgSO_4$ and the product purified by column chromatography (CyH/EtOAc, 5:1), which led to a brown oil. The diastereomers were formed in an expected 1:1 ratio and could not be separated. Yield: 426 mg (0.98 mmol, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, 13-CH_3), 1.94-2.05 (m, 2 H, 4-CH_2), 2.38-2.48 (m, 2 H, 3-CH_2), 4.14-4.25 (m, 2 H, 12-CH_2), 5.73 (dt, $^2J_{H,F}$ = 54.1 Hz, $^3J_{H,H}$ = 6.6 Hz, 1 H, 5-CHF), 5.77 (dt, $^2J_{H,F}$ = 55.1 Hz, $^3J_{H,H}$ = 6.4 Hz, 1 H, 5*-CHF), 7.22-7.31 (m, 2 H, 8/10-CH), 7.37-7.43 (m, 2 H,

7/11-CH), 7.74-7.81 (m, 2 H, 17/18-CH), 7.84-7.89 (m, 2 H, 16/19-CH). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 14.1 (s, C-13), 24.9 (dt, $^3J_{C,F}$ = 3.3 Hz, C-3), 25.2 (dt, $^3J_{C,F}$ = 3.5 Hz, C-3*), 31.9 (dt, $^2J_{C,F}$ = 23.4 Hz, C-4), 32.1 (dt, $^2J_{C,F}$ = 23.0 Hz, C-4*), 51.4 (d, C-2), 51.5 (d, C-2*), 62.1 (t, C-12), 100.57 (dd, $^1J_{C,F}$ = 219.5 Hz, C-5), 100.60 (dd, $^1J_{C,F}$ = 219.3 Hz, C-5*), 123.6 (d, C-16/19), 129.18 (d, C-8/10), 129.23 (d, C-8*/10*), 130.2 (s, C-6), 130.8 (s, C-6*), 131.61 (s, C-15/20), 131.64 (s, C-15*/20*), 133.7 (dd, $^4J_{C,F}$ = 1.9 Hz, C-7/11), 134.1 (dd, $^4J_{C,F}$ = 1.9 Hz, C-7*/11*), 134.4 (d, C-17/18), 134.51 (s, C-9), 134.54 (s, C-9*), 167.5 (s, C-14/21), 167.6 (s, C-14*/21*), 168.58 (s, C-1), 168.60 (s, C-1*). **^{19}F NMR** (564 MHz, $CDCl_3$): δ −145.6 (ddd, $^2J_{F,H}$ = 54.1 Hz, $^3J_{F,H}$ = 18.4, 12.8 Hz, 1 F, 5-CHF), −147.0 (dt, $^2J_{F,H}$ = 55.2 Hz, $^3J_{F,H}$ = 16.8 Hz, 1 F, 5*-CHF). **MS-ES(+)-EM**: *m*/*z* calcd for $C_{21}H_{19}ClFNO_4SNa^+$: 458.0600/460.0571, found: 458.0594/460.0571 $[M+Na]^+$.


17,18 (m)
7.77
10,8 (m)
7.26
16,19 (m)
7.88
11,7 (m)
7.40
5 (dt)
5.73
J(54.1, 6.6)
5* (dt)
5.77
J(55.1, 6.4)
2 (dt)
4.83
J(10.2, 5.1)
12 (m)
4.21
3 (m)
2.43
4 (m)
1.97
13 (t)
1.23
J(7.1)
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1.73
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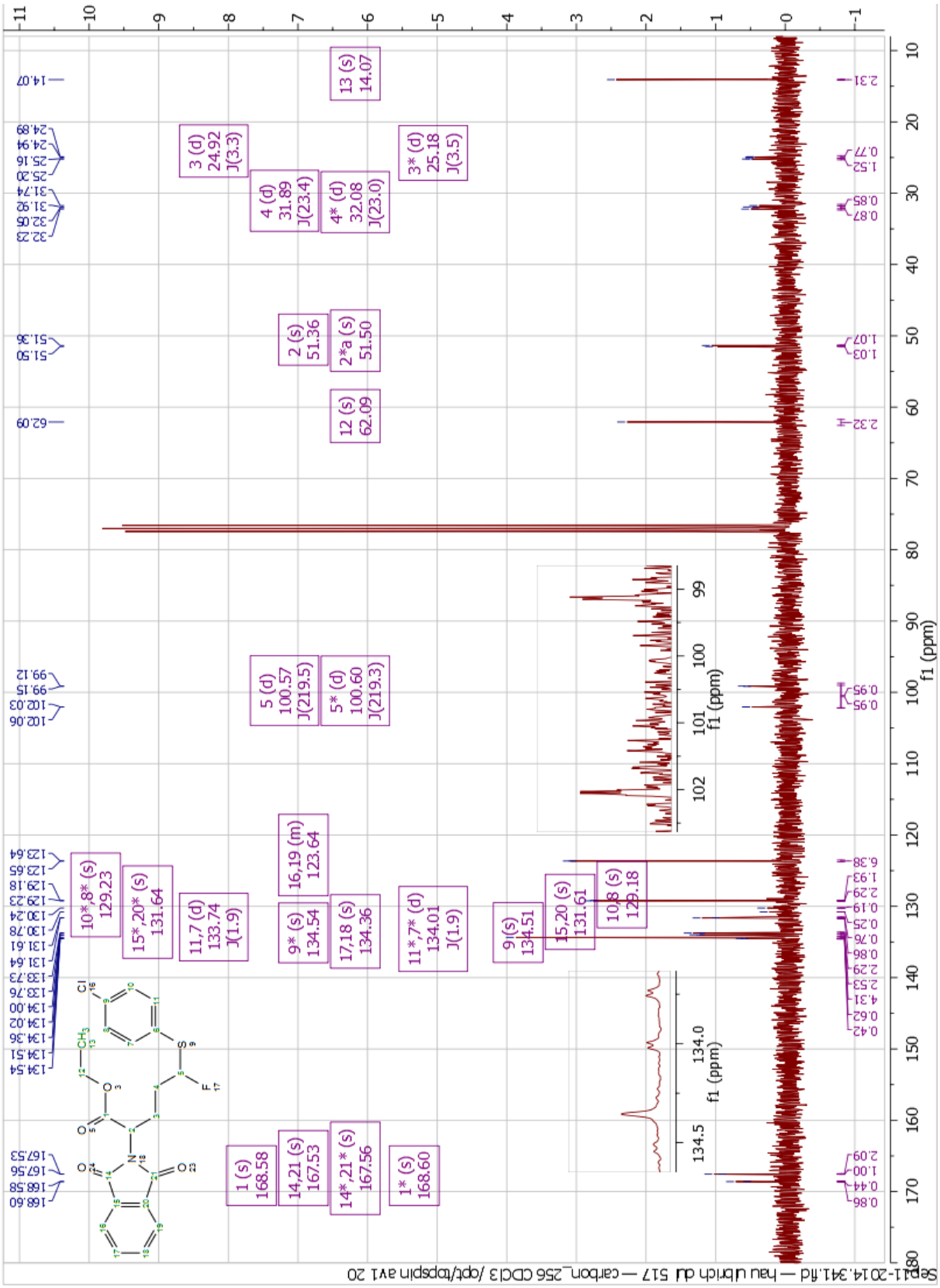
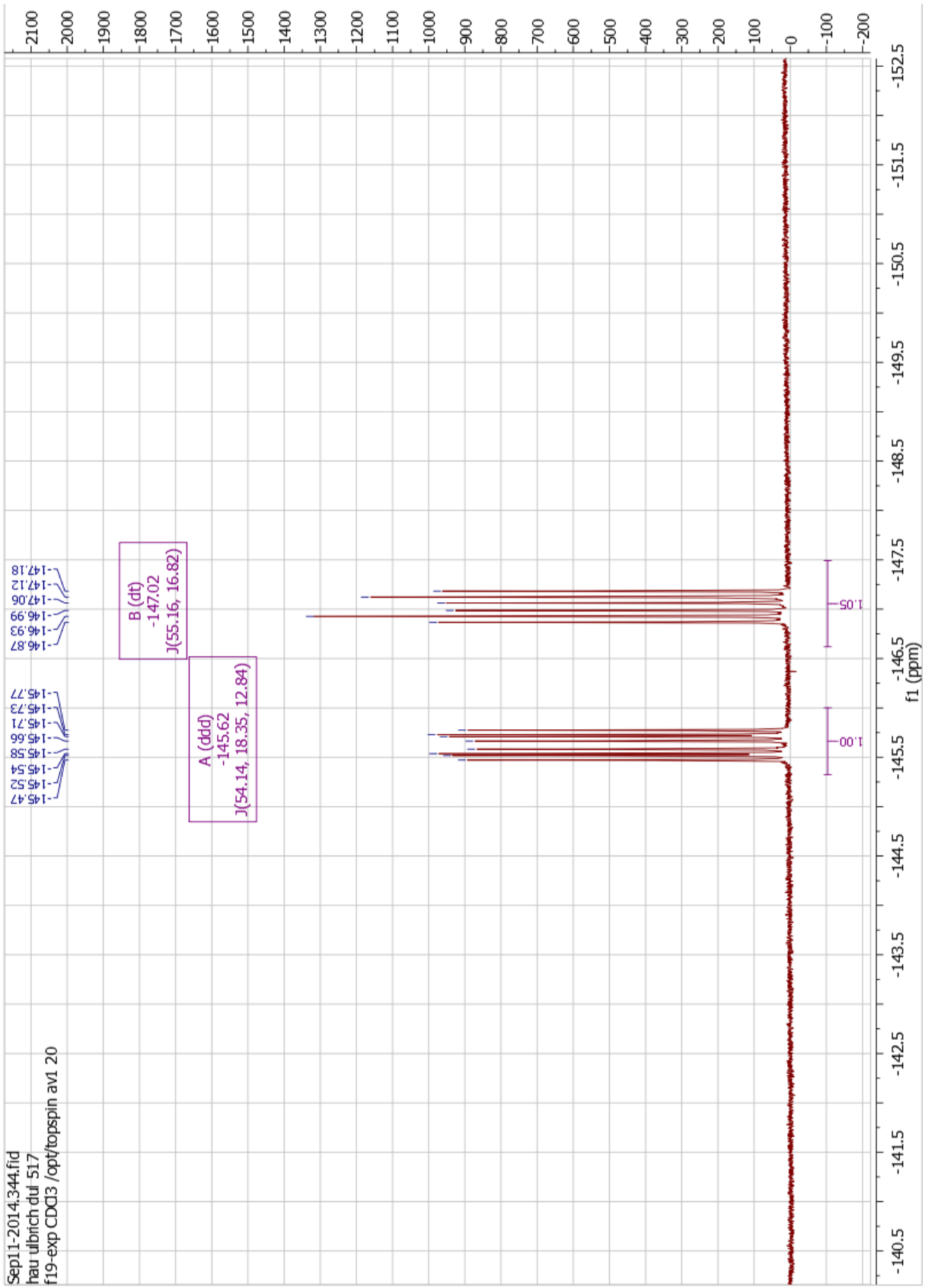
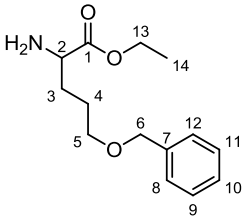
0.44
1.00
2.09
2.02
1.91
2.88
f1 (ppm)


Sept-2014.341.fid — hau Ulrich du 517 — carbon_256 CDCl3 /opt/topspin av1 20
f1 (ppm)
1 (s) 168.58
14,21 (s) 167.53
14*,21* (s) 167.56
1* (s) 168.60
10*,8* (s) 129.23
15*,20* (s) 131.64
11,7 (d) 133.74 J(1.9)
9* (s) 134.54
16,19 (m) 123.64
17,18 (s) 134.36
11*,7* (d) 134.01 J(1.9)
9 (s) 134.51
15,20 (s) 131.61
10,8 (s) 129.18
5 (d) 100.57 J(219.5)
5* (d) 100.60 J(219.3)
2 (s) 51.36
2*a (s) 51.50
12 (s) 62.09
3 (d) 24.92 J(3.3)
4 (d) 31.89 J(23.4)
4* (d) 32.08 J(23.0)
3* (d) 25.18 J(3.5)
13 (s) 14.07


Sep11-2014.344.fid
hau ulbrich dul 517
f19-exp CDCl3 /opt/topspin av1 20
B (dt)
-147.02
J(55.16, 16.82)
A (ddd)
-145.62
J(54.14, 18.35, 12.84)
-147.18
-147.12
-147.06
-146.99
-146.93
-146.87
-145.77
-145.73
-145.71
-145.66
-145.58
-145.54
-145.52
-145.47
1.05
1.00
f1 (ppm)

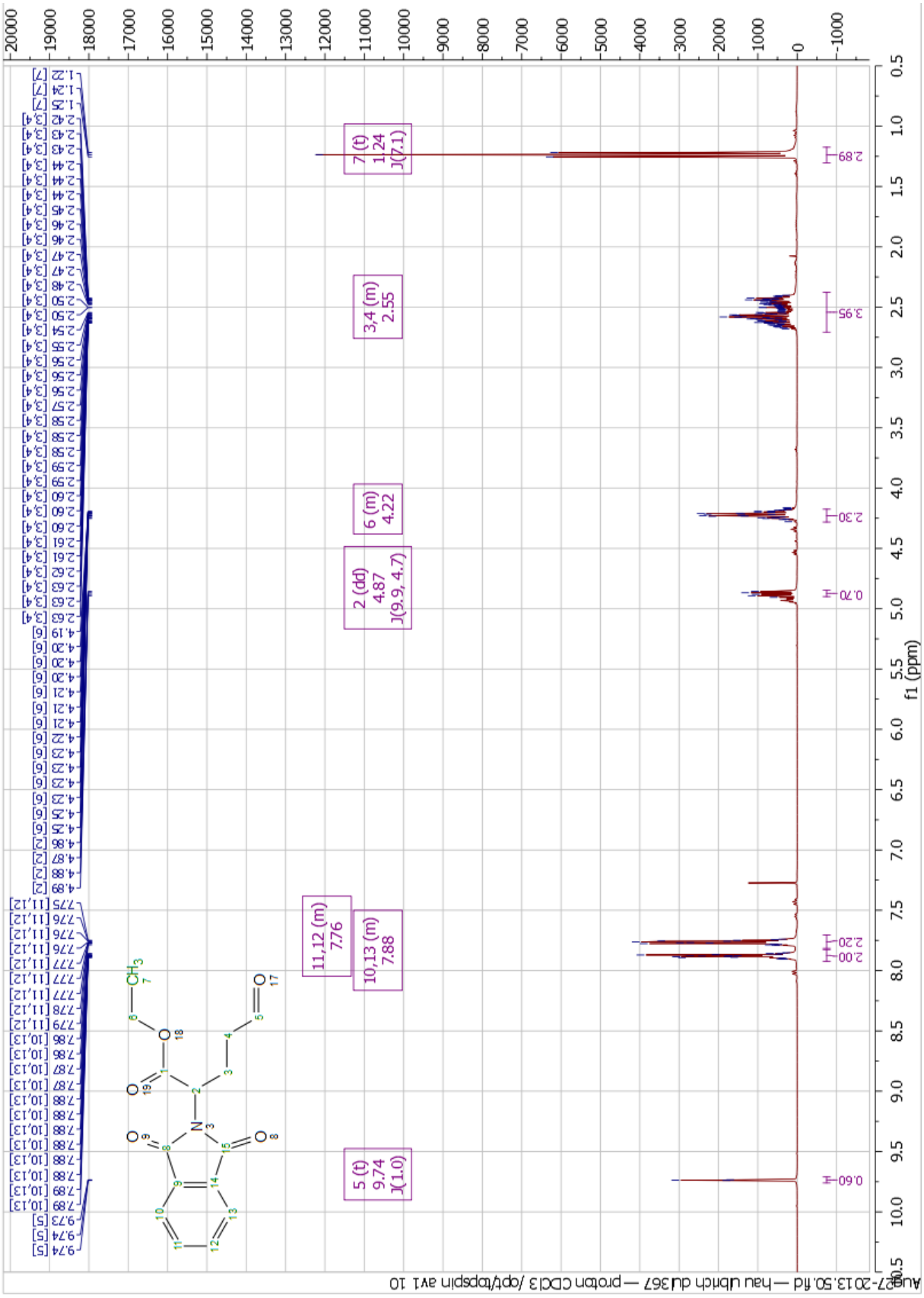
20. Ethyl 2-amino-5-benzyloxypentanoate (SI 4)

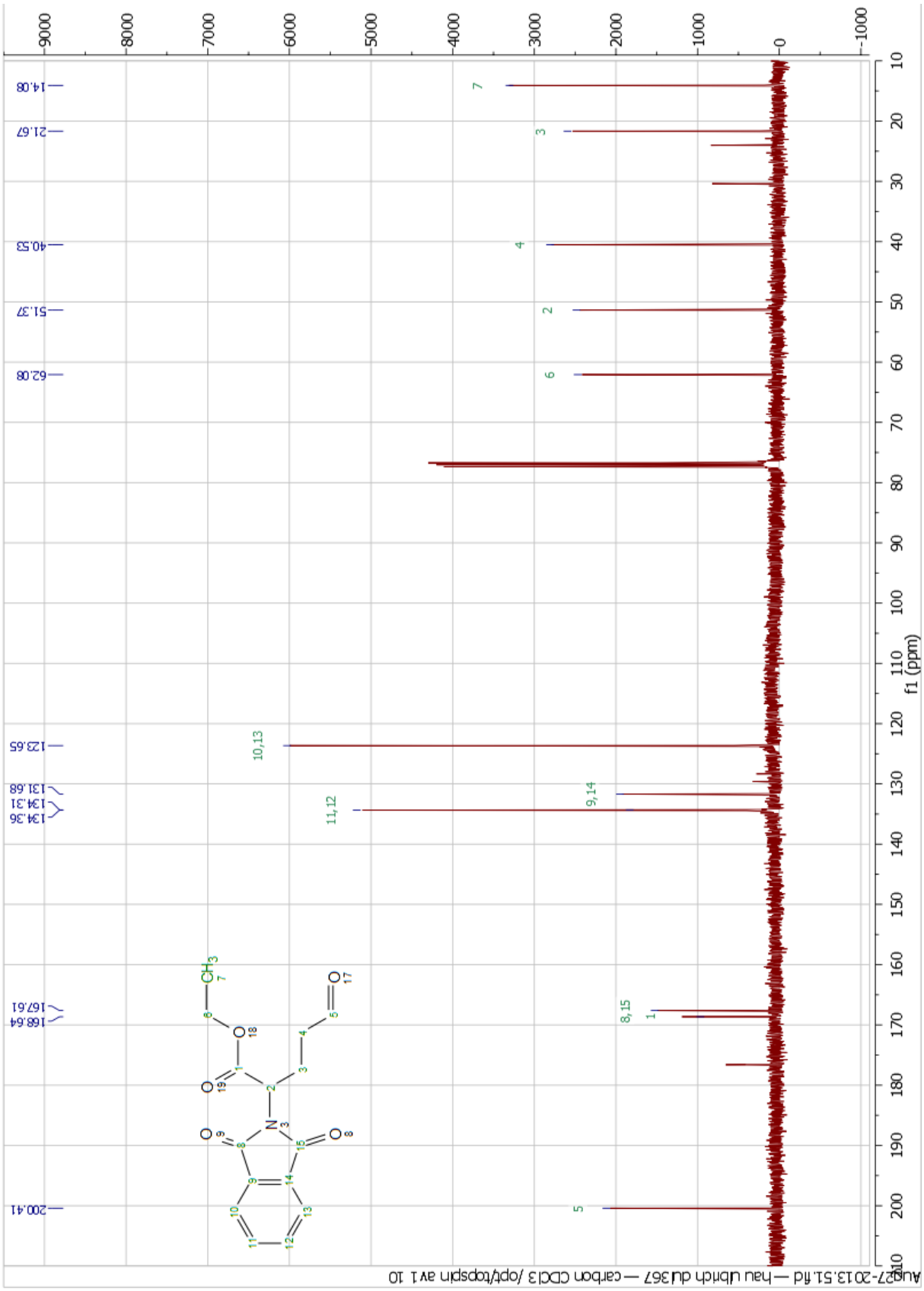


SI 4

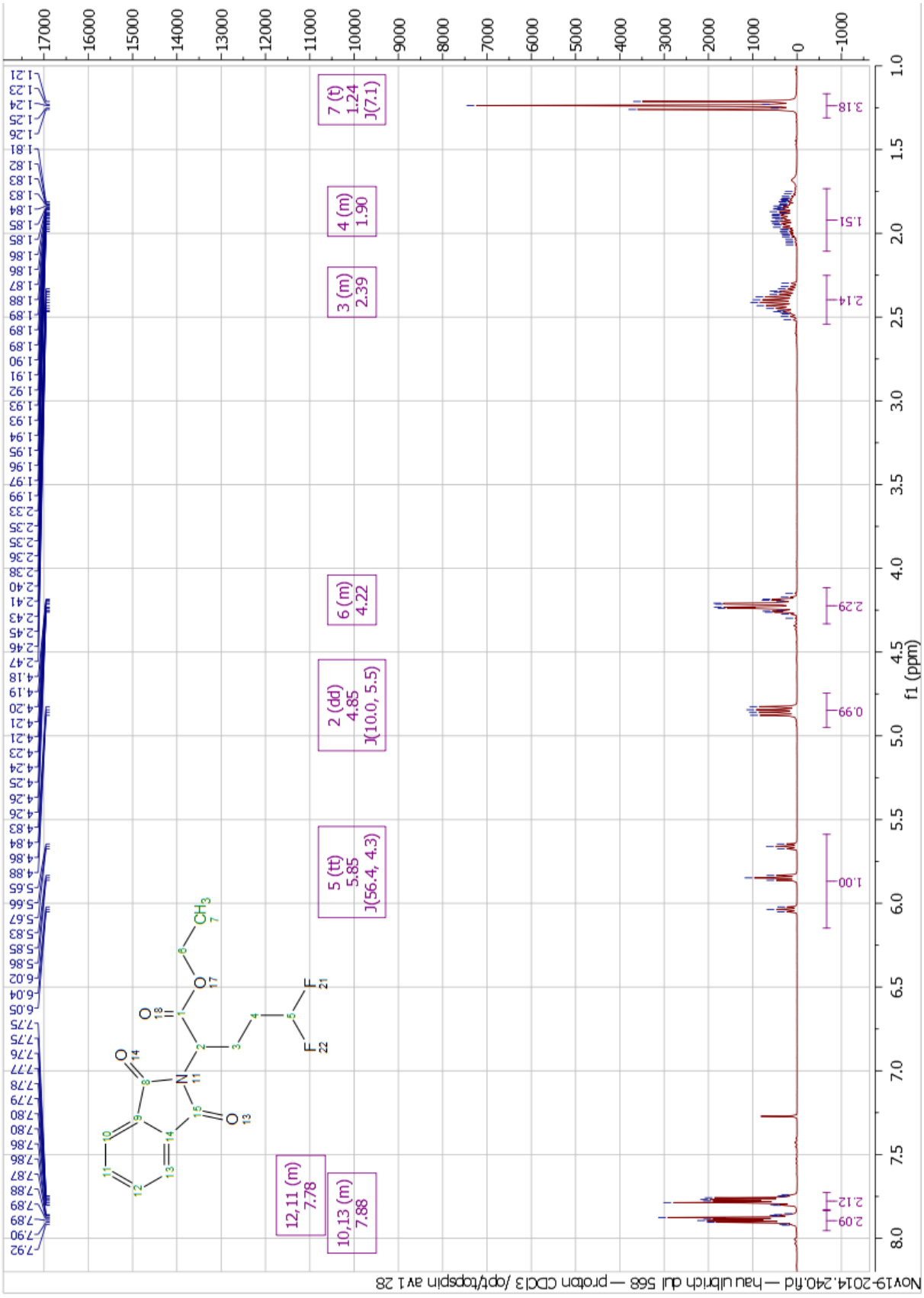
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, 14-CH_3), 1.58-1.92 (m, 4 H, 3-CH_2 und 4-CH_2), 3.45 (dd, $^{3}J_{H,H}$ = 7.1, 5.5 Hz, 1 H, 2-CH), 3.50 (t, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, 5-CH_2), 4.17 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2 H, 13-CH_2), 4.50 (s, 2 H, 6-CH_2), 7.23-7.40 (m, 5 H, 8/12-CH, 9/11-CH und 10-CH). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 14.2 (q, C-14), 25.9 (t, C-4), 31.7 (t, C-3), 54.3 (d, C-2), 60.8 (t, C-13), 59.9 (t, C-5), 72.9 (t, C-6), 127.5 (d, C-10), 127.6 (t, C-8/12), 128.3 (t, C-9/11), 138.4 (s, C-7), 176.0 (s, C-1). **MS-ES(+)-EM**: *m/z* calcd for $C_{14}H_{21}NO_3Na^+$: 274.1414, found: 252.1599 $[M+H]^+$; calcd for $C_{14}H_{21}NO_3H^+$: 252.1594, found: 74.1418 $[M+Na]^+$.

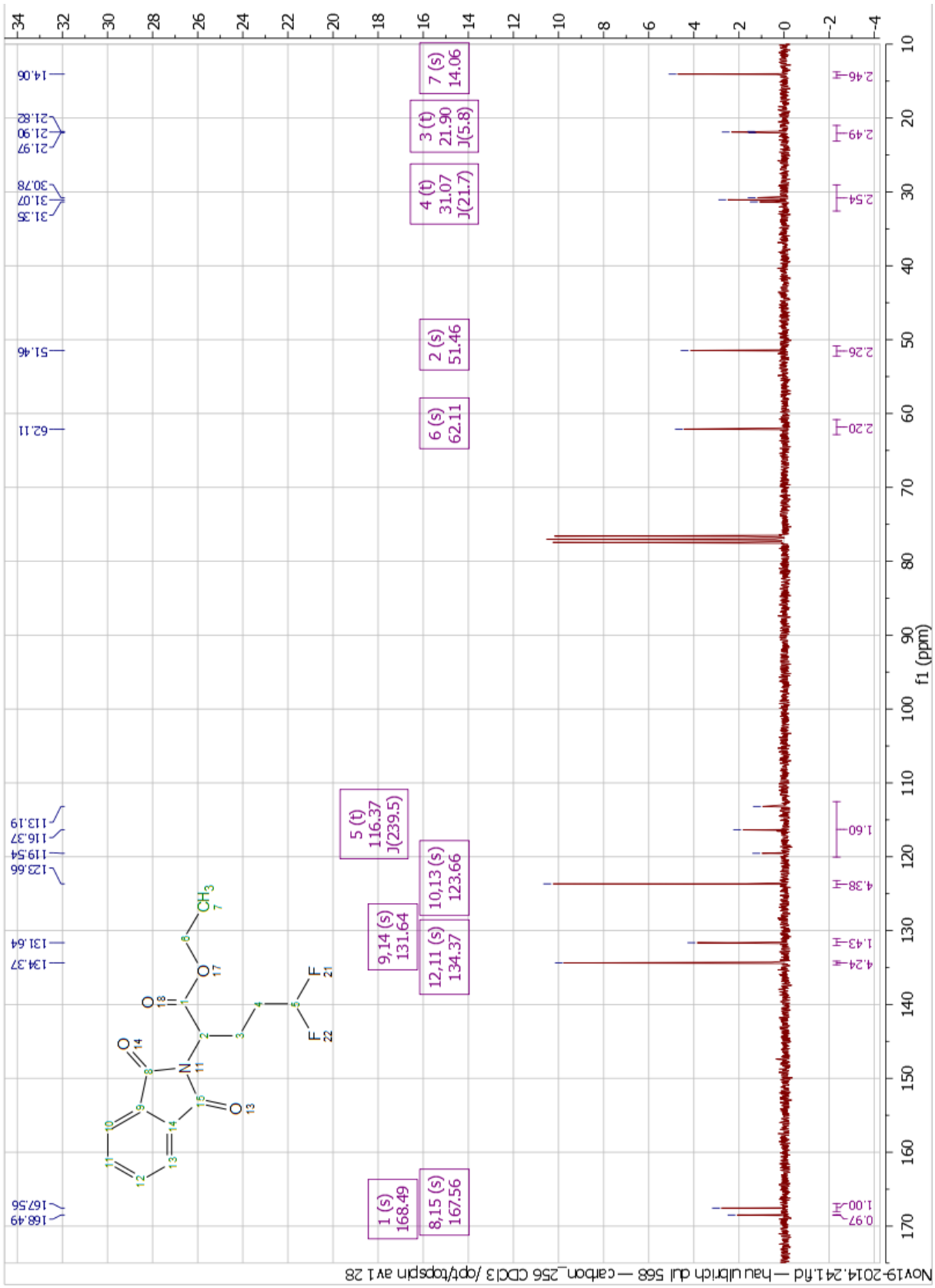
21. Ethyl 5-oxo-2-phthalimidopentanoate (26)

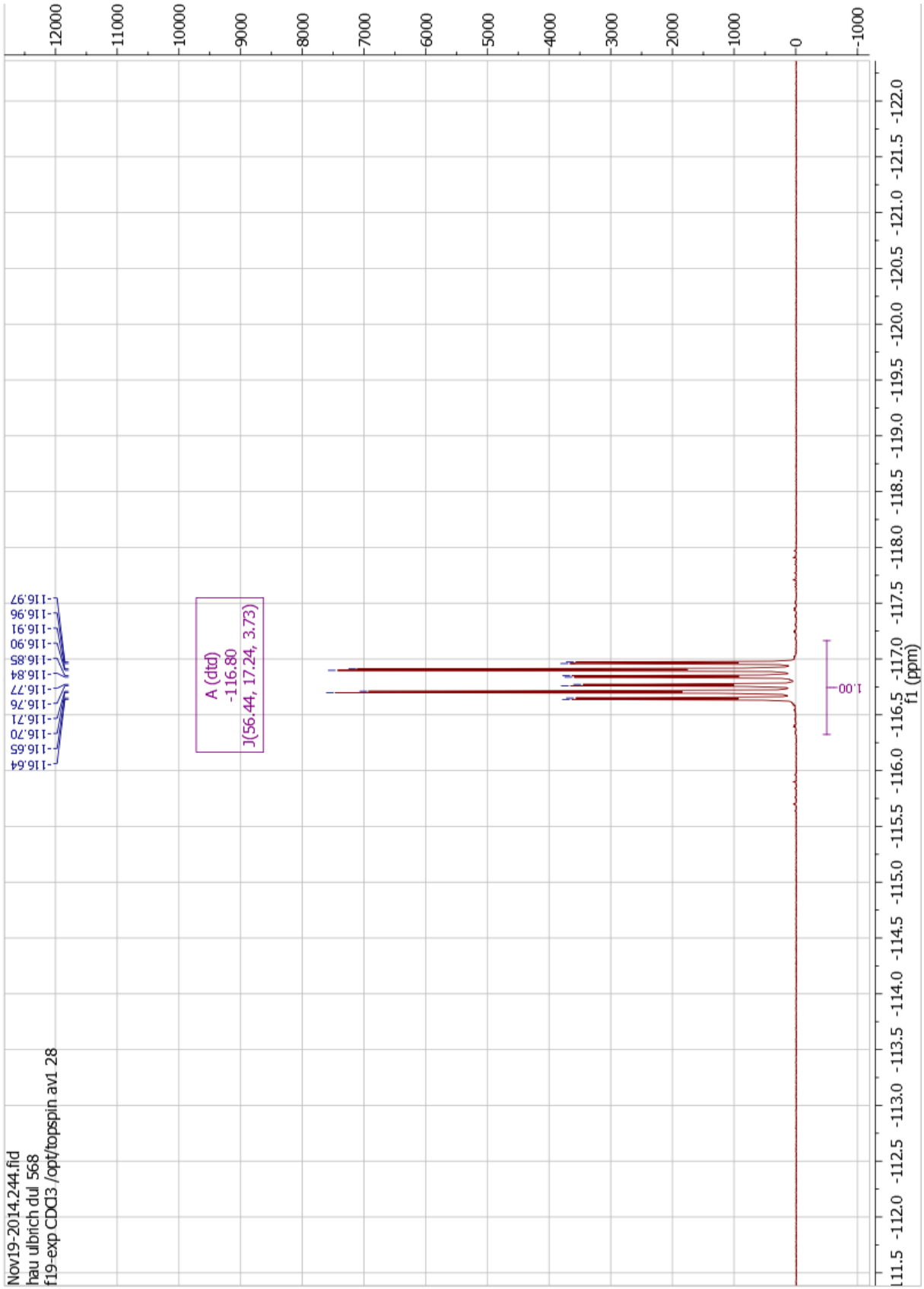



14.08
21.67
40.53
51.37
62.08
123.65
131.68
134.31
134.36
167.61
168.64
200.41
f1 (ppm)

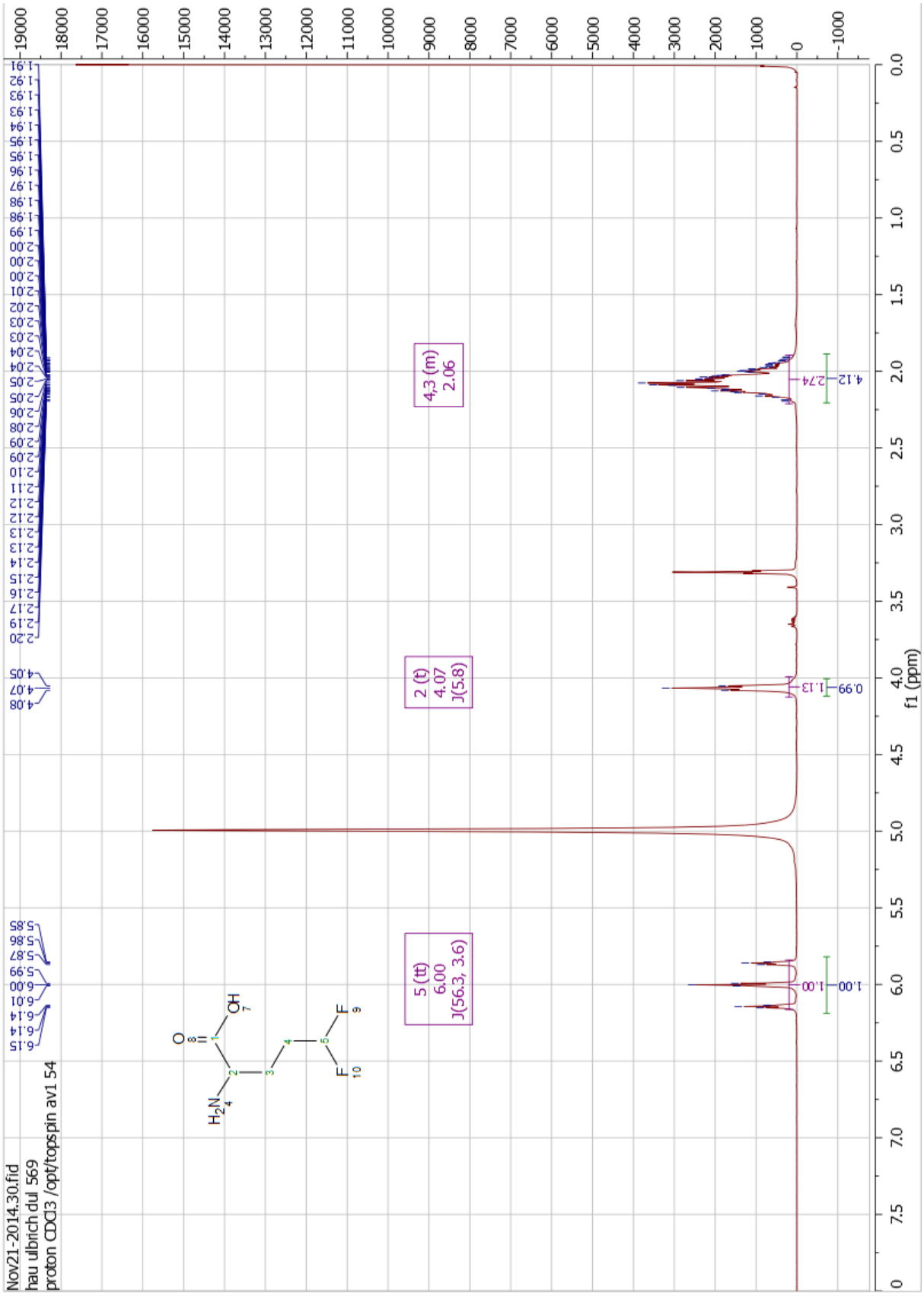
22. Ethyl 5,5-difluoro-2-phthalimidopentanoate (27)

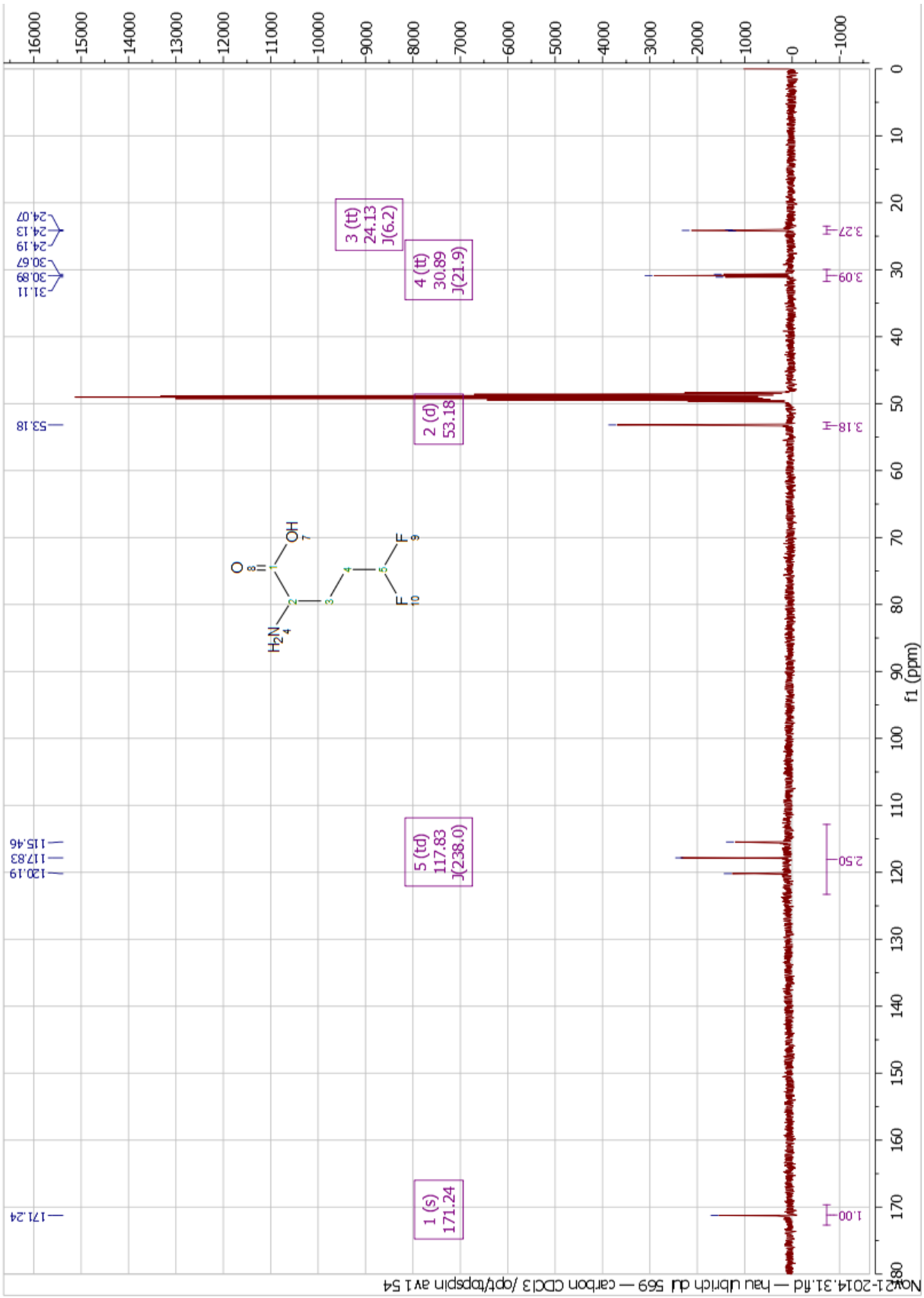


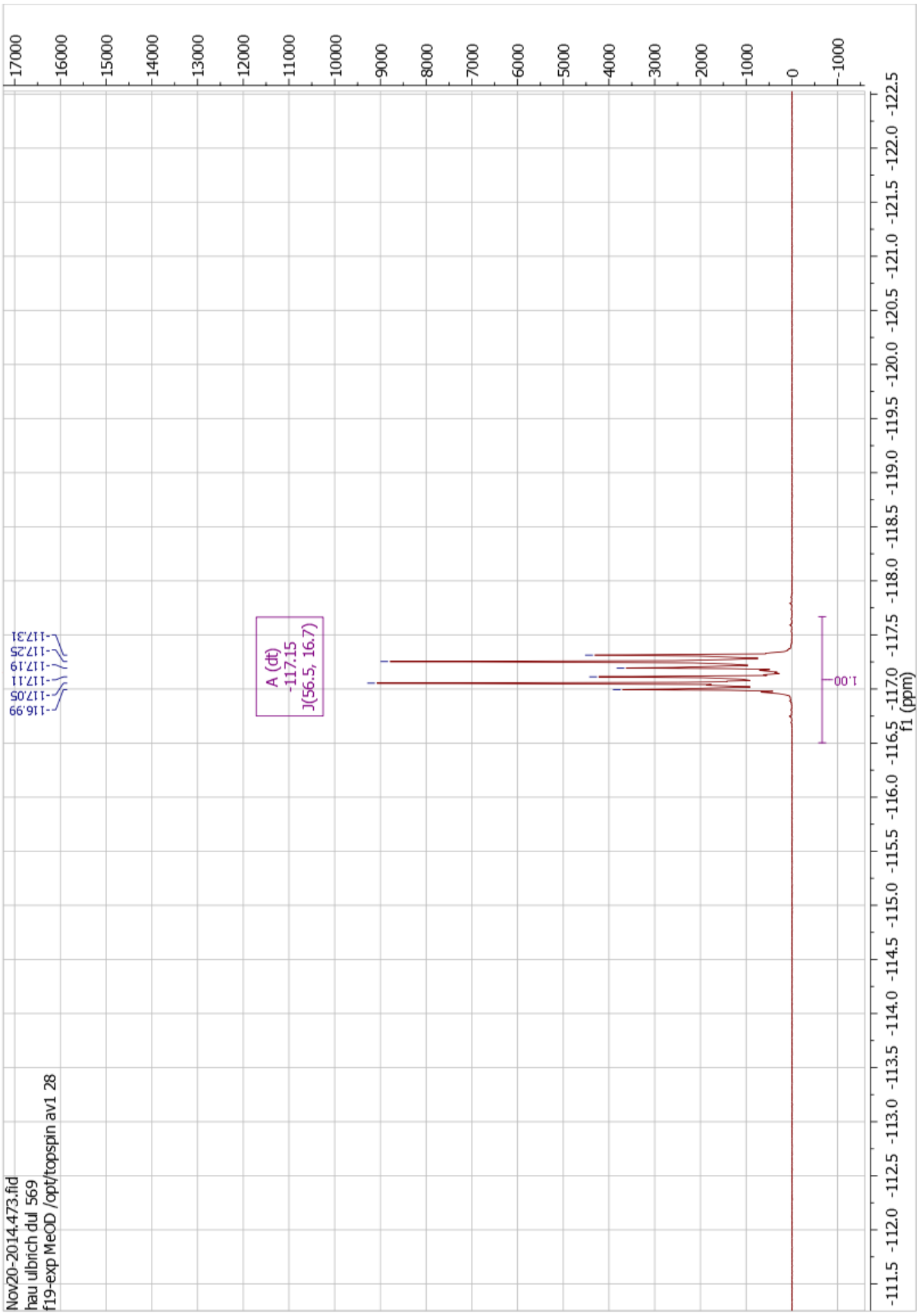

Nov19-2014.241.fid — hau ulbrich dul 568 — carbon_256 CDCl3 /opt/topspin av1 28
f1 (ppm)
1 (s) 168.49
8,15 (s) 167.56
9,14 (s) 131.64
12,11 (s) 134.37
10,13 (s) 123.66
5 (t) 116.37 J(239.5)
6 (s) 62.11
2 (s) 51.46
4 (t) 31.07 J(21.7)
3 (t) 21.90 J(5.8)
7 (s) 14.06
168.49
167.56
134.37
131.64
123.66
119.54
116.37
113.19
62.11
51.46
31.35
31.07
30.78
21.97
21.90
21.82
14.06
0.97
1.00
1.43
4.24
4.38
1.60
2.46
2.49
2.54
2.26
2.20

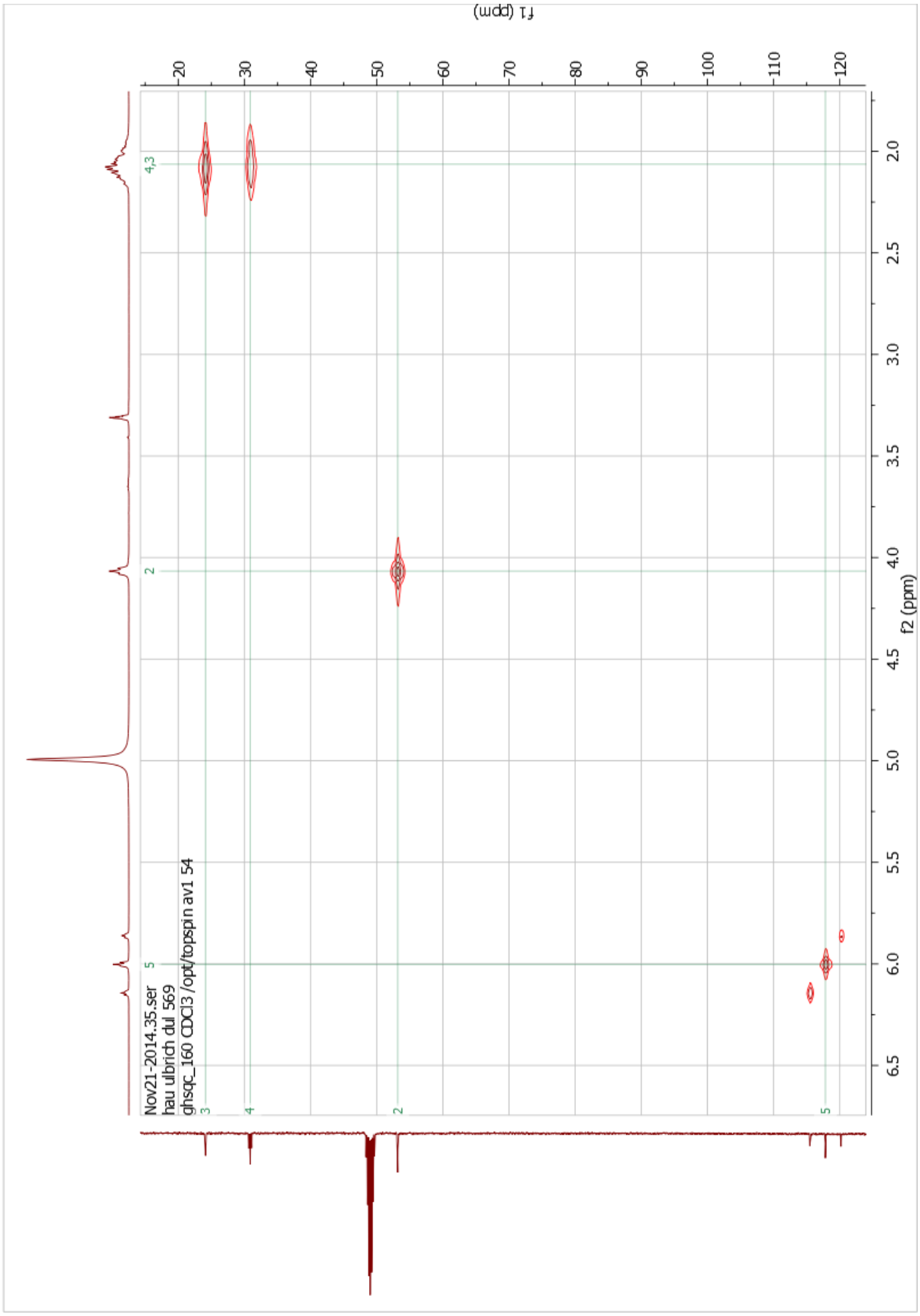

Nov19-2014.244.fid
hau ulbrich dul 568
f19-exp CDCl3 /opt/topspin av1 28
A (dtd)
-116.80
J(56.44, 17.24, 3.73)
1.00
f1 (ppm)

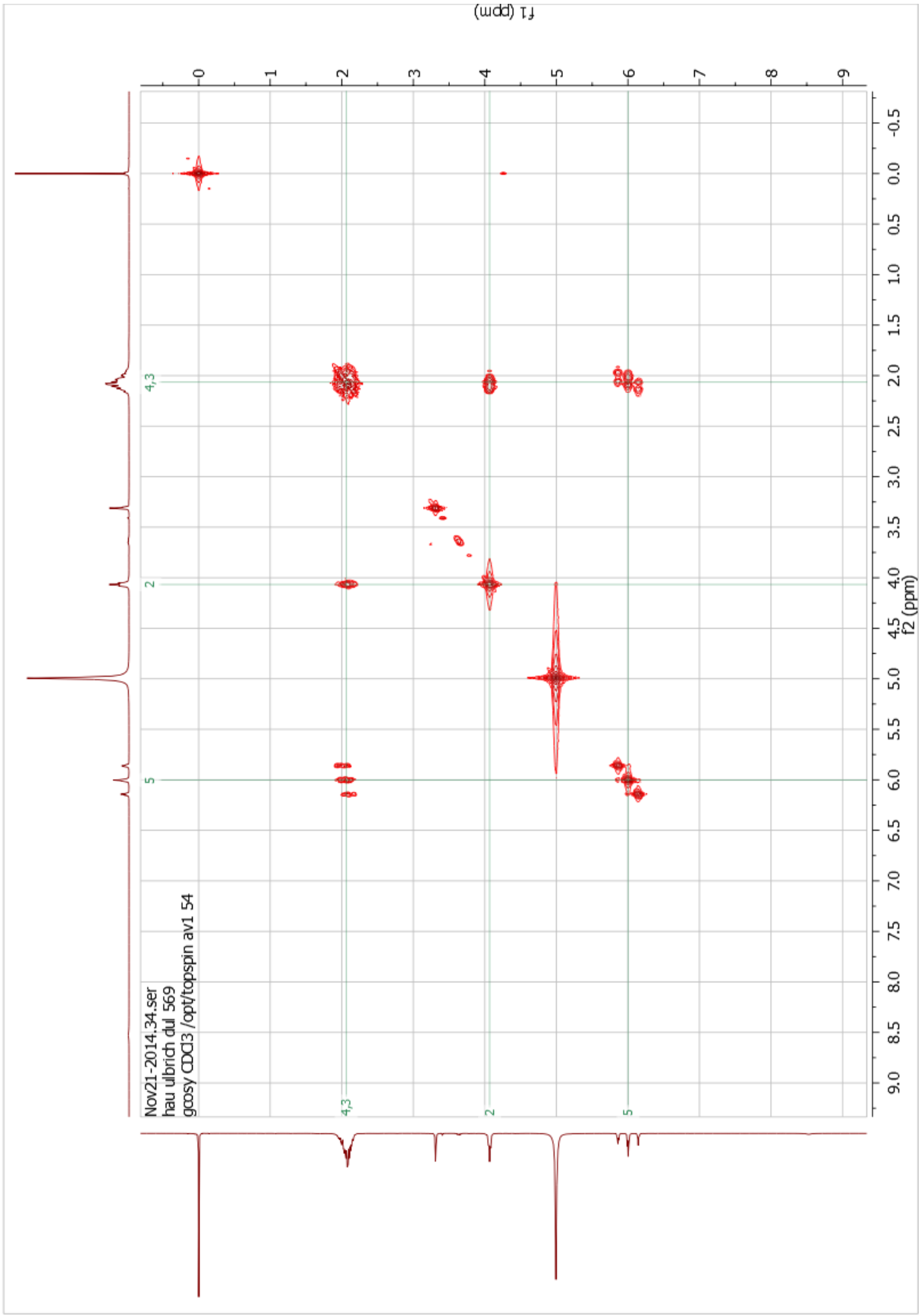
23. 2-Amino-5,5-difluoropentanoic acid hydrochloride (28)

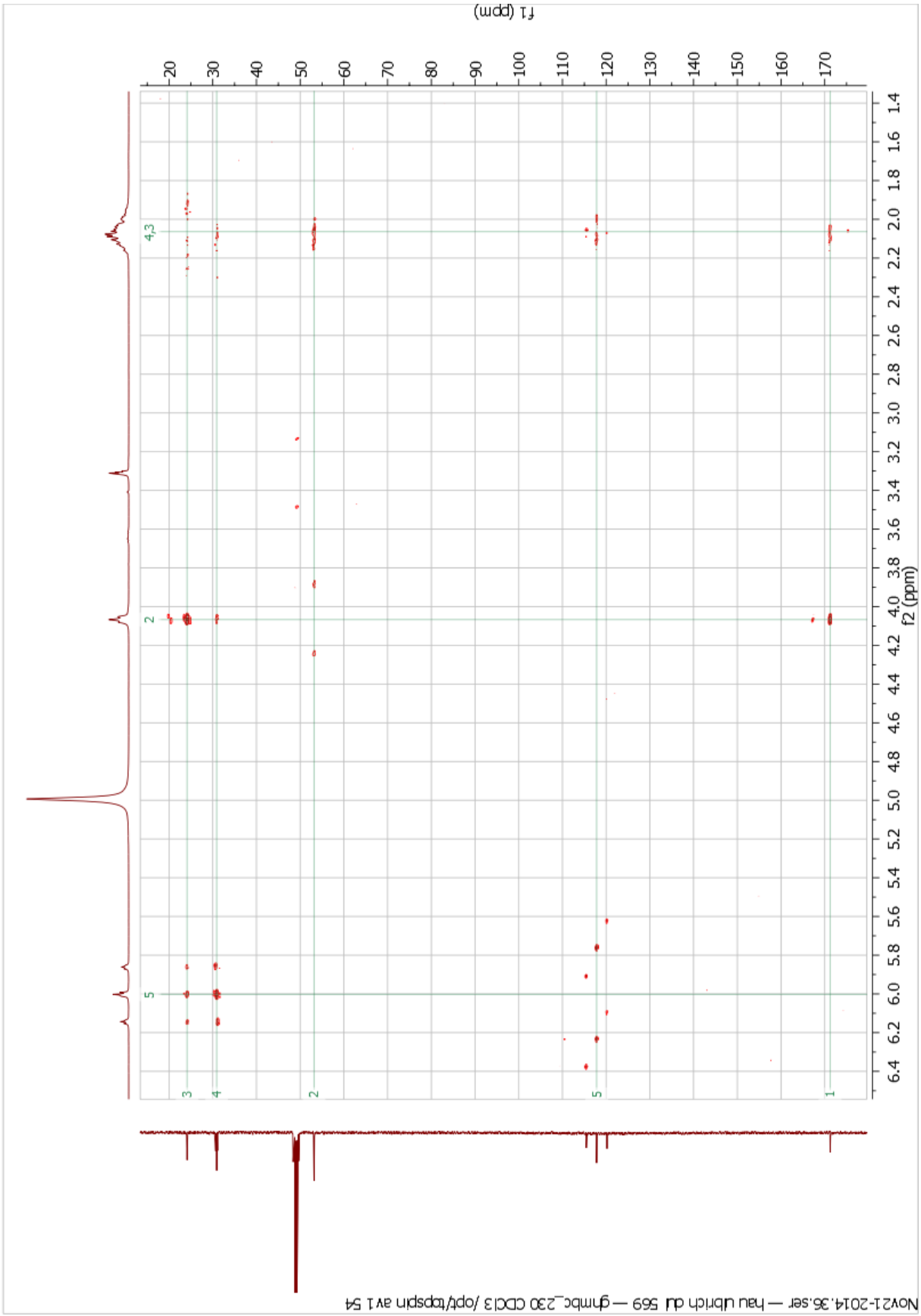



Nov21-2014.31.fid — hau ubrich dul 569 — carbon CDCl3 /opt/topspin av1 54
1 (s)
171.24
2 (d)
53.18
3 (tt)
24.13
J(6.2)
4 (tt)
30.89
J(21.9)
5 (td)
117.83
J(238.0)
171.24
53.18
31.11
30.89
30.67
24.19
24.13
24.07
130.19
117.83
115.46
1.00
3.18
2.50
3.09
3.27
f1 (ppm)

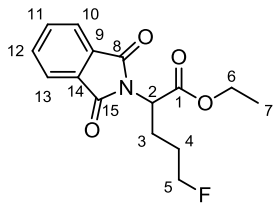

Nov20-2014.473.fid
hau ulbrich dul 569
f19-exp MeOD /opt/topspin av1 28
-116.99
-117.05
-117.11
-117.19
-117.25
-117.31
A (dt)
-117.15
J(56.5, 16.7)
1.00
f1 (ppm)


f1 (ppm)
20
30
40
50
60
70
80
90
100
110
120
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
4,3
2
5
3
4
2
5
Nov21-2014.35.ser
hau ulbrich dul 569
ghsqc_160 CDCl3 /opt/topspin av1 54


f1 (ppm)
f2 (ppm)
Nov21-2014.34.ser
hau ulbrich dul 569
gcosy CDCl3 /opt/topspin av1 54
4,3
2
5


Nov21-2014.36.ser — hau Ubrich dJ 569 — gHmbc_230 CDCl3 /opt/topspin av1 54
f1 (ppm)
f2 (ppm)
4,3
2
5
3
4
2
5
1

24. Synthesis of ethyl 5-fluoro-2-phthalimidopentanoate (29)

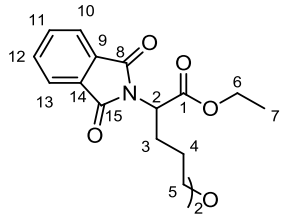


29

A solution of ethyl 5-oxo-2-phthalimidopentanoate (**25**) (291 mg, 1.0 mmol) in abs. CH_2Cl_2 (3 mL) was treated with Deoxo-Fluor® (2.7 M in toluene) (0.41 mL, 1.1 mmol) and the solution stirred at r.t. for 18.5 Stunden. After quenching with ice/sat. aqueous $NaHCO_3$ the mixture was extracted with CH_2Cl_2 (2 × 10 mL), the combined organic phases dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The product was isolated by column chromatography (CyH/EtOAc, 2:1) as a yellowish oil. Yield: 62 mg (0.21 mmol, 21%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, 7-CH_3), 1.55-1.90 (m, 2 H, 4-CH_2), 2.25-2.51 (m, 2 H, 3-CH_2), 4.22 (m, 2 H, 6-CH_2), 4.46 (dm, $^2J_{H,F}$ = 47.1 Hz, 2 H, 5-CH_2F), 4.87 (dd, $^3J_{H,H}$ = 10.2, 5.4 Hz, 1 H, 2-CH), 7.71-7.81 (m, 2 H, 11/12-CH), 7.83-7.92 (m, 2 H, 10/13-CH). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 14.1 (q, C-7), 24.9 (dt, $^3J_{C,F}$ = 5.1 Hz, C-3), 27.4 (dt, $^2J_{C,F}$ = 20.2 Hz, C-4), 51.8 (d, C-2), 62.0 (t, C-6), 83.0 (dt, $^1J_{C,F}$ = 239.5 Hz, C-5), 123.6 (d, C-10/13), 131.7 (s, C-9/14), 134.3 (d, C-11/12), 167.7 (s, C-8/15), 168.9 (s, C-1). **^{19}F NMR** (282 MHz, $CDCl_3$): δ −219.7 (tt, $^2J_{F,H}$ = 47.1 Hz, $^3J_{F,H}$ = 25.3 Hz, 1 F, 5-CH_2F). **MS-ES(+)-EM**: *m*/*z* calcd for $C_{15}H_{16}FNO_4H^+$ 294.1136, found: 294.1137 $[M+H]^+$, calcd for $C_{15}H_{16}FNO_4Na^+$: 316.0956, found: 316.0954 $[M+Na]^+$; calcd for $C_{15}H_{16}FNO_4CH_3OHNa^+$: 348.1218, found: 348.1213 $[M+MeOH+Na]^+$.

5,5'-Oxy-bis(ethyl 2-phthalimidopentanoate) (**SI 5**) was identified as a byproduct.

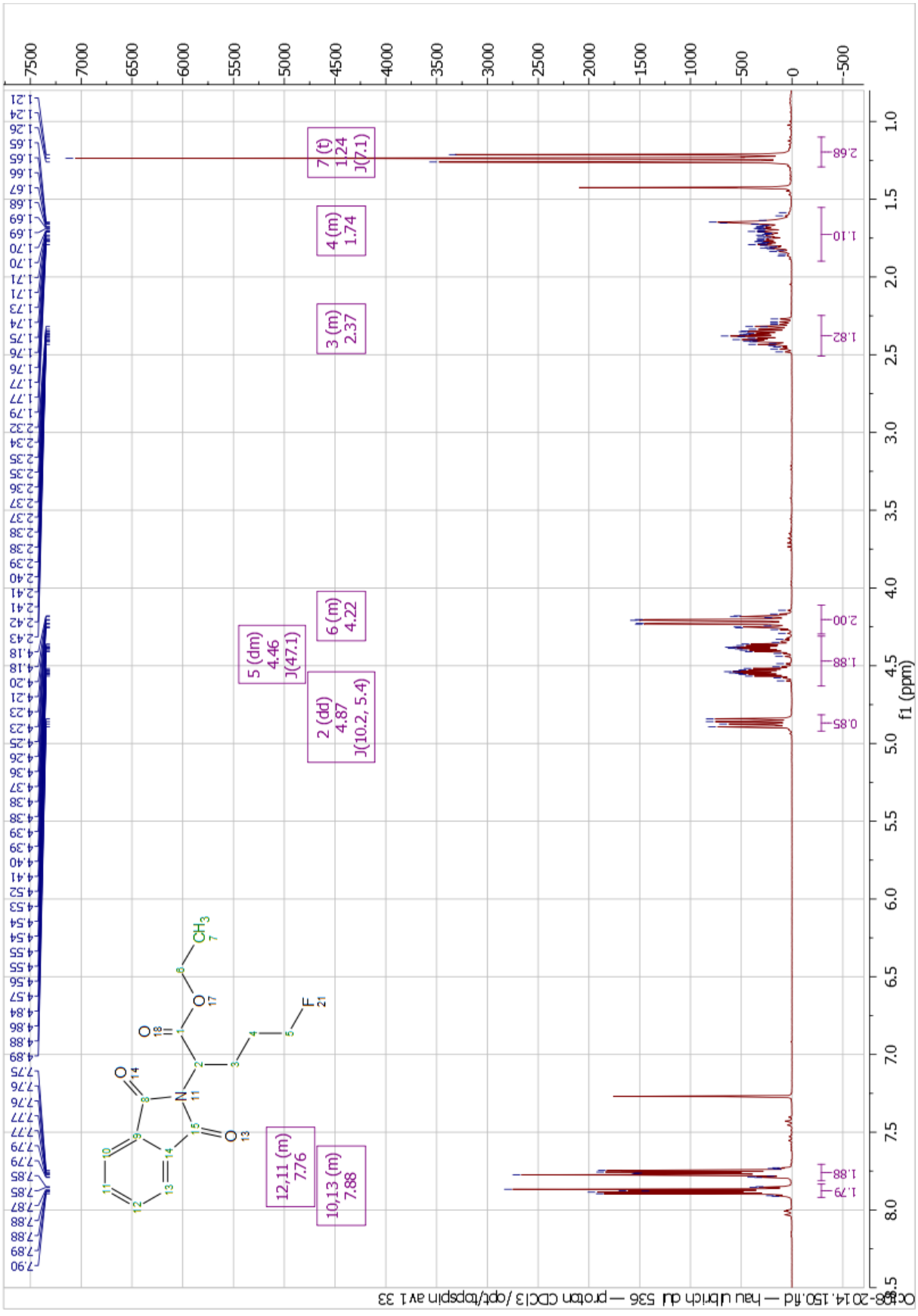
Ethyl 5,5'-oxy-bis(ethyl 2-phthalimidopentanoate) (SI 5)

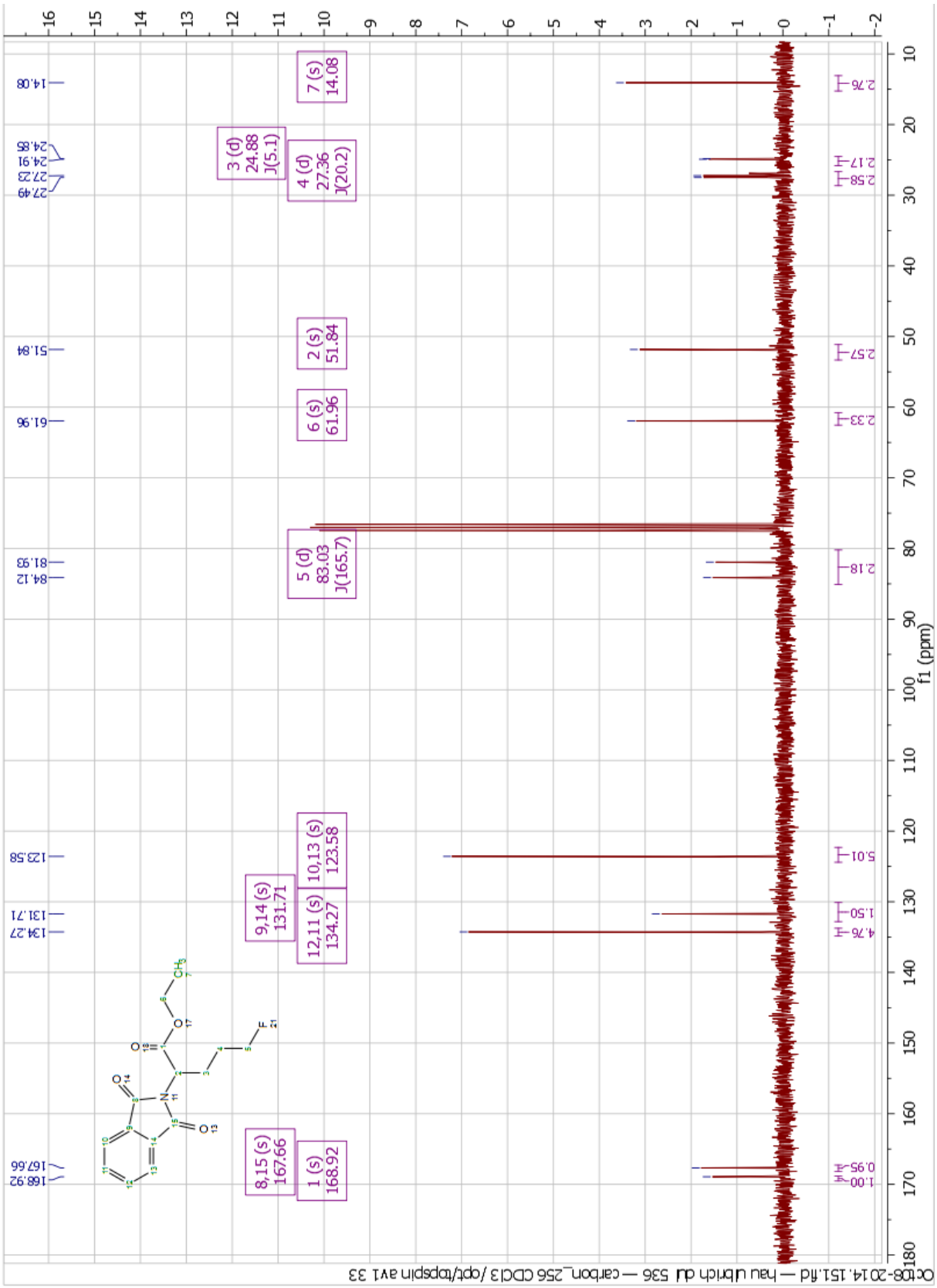


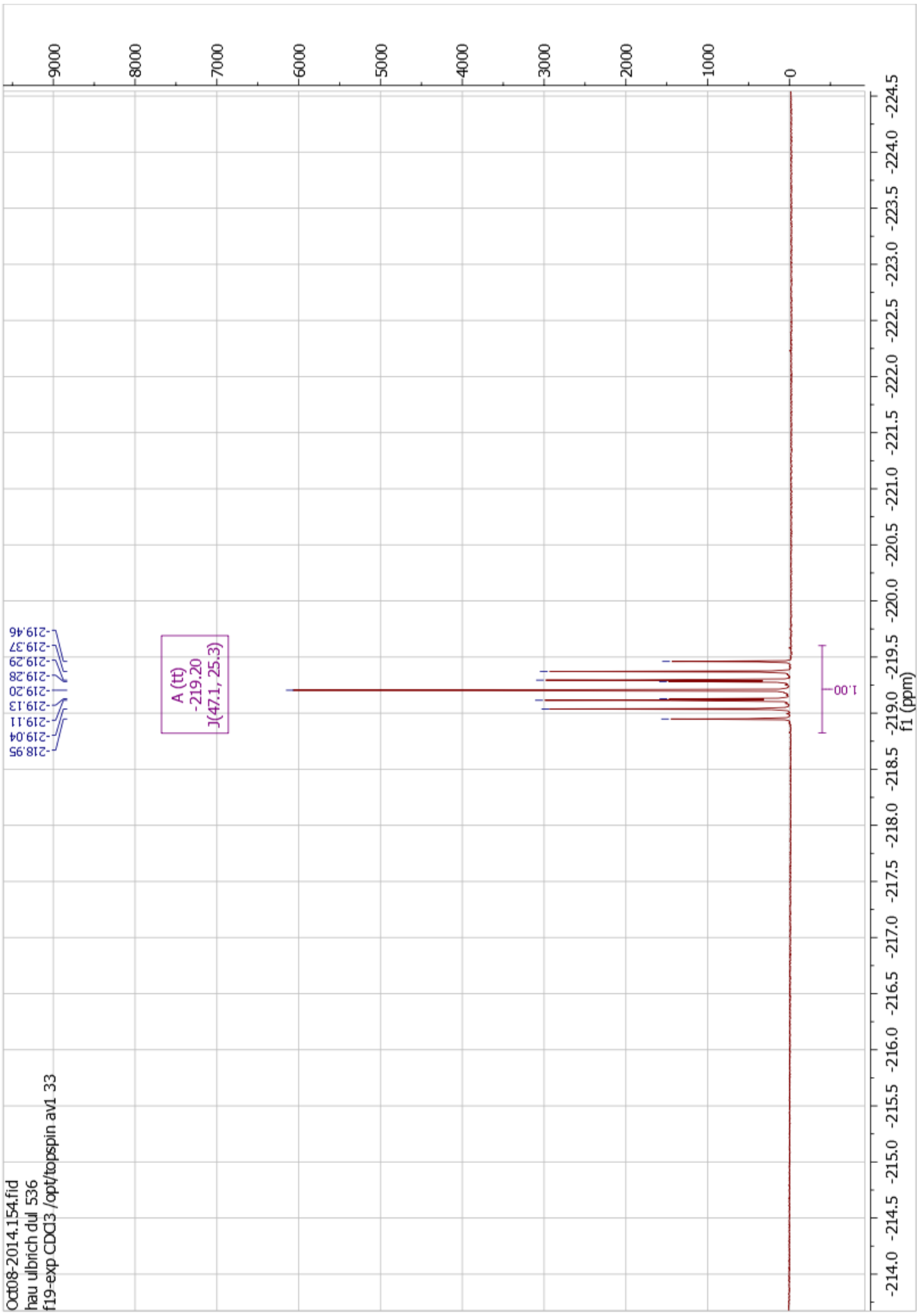
SI 5

Yield: 18 mg (0.03 mmol, 6%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 7/7'-CH_3), 1.53-1.75 (m, 4 H, 4/4'-CH_2), 2.25-2.41 (m, 4 H, 3/3'-CH_2), 3.68 (t, $^3J_{H,H}$ = 6.4 Hz, 4 H, 5/5'-CH_2), 4.21 (m, 4 H, 6/6'-CH_2), 4.88 (dd, $^3J_{H,H}$ = 10.1, 5.6 Hz, 2 H, 2/2'-CH), 7.71-7.80 (m, 4 H, 11/11'/12/12'-CH), 7.83-7.91 (m, 4 H, 10/10'/13/13'-CH). **MS-ES(+)-EM**: *m*/*z* calcd for $C_{30}H_{32}N_2O_9Na^+$: 587.2000, found 587.2004 $[M+Na]^+$; calcd for $C_{30}H_{32}N_2O_9CH_3OHNa^+$: 619.2262, found: 619.2241 $[M+MeOH+Na]^+$.

5-Fluoro-2-phthalimidopentanoate (29)




Oct08-2014.151.fid — hau Ubrich dJ 536 — carbon_256 CDCl3 /opt/topspin av1 33
f1 (ppm)
168.92
167.66
134.27
131.71
123.58
84.12
81.93
61.96
51.84
27.49
27.23
24.91
24.85
14.08
1 (s) 168.92
8,15 (s) 167.66
12,11 (s) 134.27
9,14 (s) 131.71
10,13 (s) 123.58
5 (d) 83.03 J(165.7)
6 (s) 61.96
2 (s) 51.84
3 (d) 24.88 J(5.1)
4 (d) 27.36 J(20.2)
7 (s) 14.08
1.00
0.95
4.76
1.50
5.01
2.18
2.33
2.57
2.58
2.17
2.76

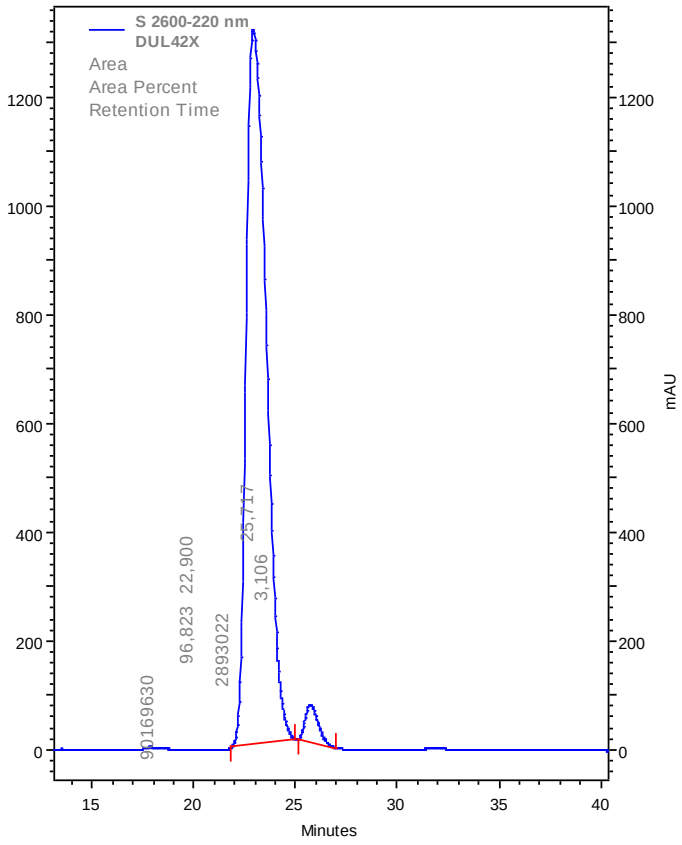

Oct08-2014.154.fid
hau ulbrich dul 536
f19-exp CDCl3 /opt/topspin av1 33
A (tt)
-219.20
J(47.1, 25.3)
-218.95
-219.04
-219.11
-219.13
-219.20
-219.28
-219.29
-219.37
-219.46
1.00
f1 (ppm)

25. (*R*)-*tert*-Butyl 5-benzyloxy-2-phthalimidopentanoate (35)

HPLC

Column: Daicel Chiralpak-IA

Eluent: ACN/H_2O 50:50



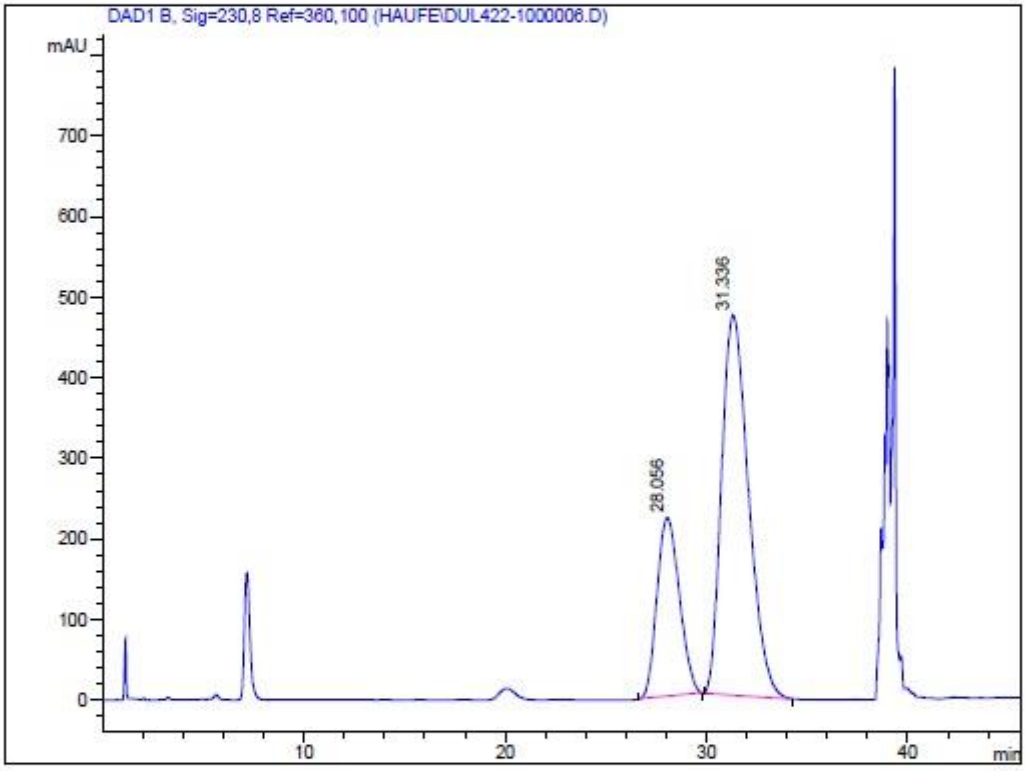
26. (*R*)-*tert*-Butyl 5-hydroxy-2-phthalimidopentanoate (43)

```
Sample Name      : DUL422-1                        Seq Line    :          0
                                                   Location    :     Vial 1
Injection Date   : Wed, 16. Sep. 2015              Inj. No.    :          0
                                                   Inj. Vol.   :       2 µl

Data file:   C:\CHEM32\1\DATA\HAUFE\DUL422-1000006.D

Acq. Method->C:\CHEM32\1\METHODS\RP CHIRAL\RP CHIRAL_20-80.M

sample info: Chiralcel OJ-RH, 4,6x150mm, 5µm,
             A= H2O, B=ACN/H2O=90/10
             sample in ACN
                                                                        ->
```




```
Signal  1: DAD1 B, Sig=230,8 Ref=360,100

|Peak|   RT    | Type  | Width |   Area    | Area % |     Name      |
| #  | [min]   |       | [min] |           |        |               |
|----|---------|-------|-------|-----------|--------|---------------|
|   1|   28.056|MM     |  1.283| 17022.973|  28.003|               |
|   2|   31.336|MM     |  1.548| 43767.410|  71.997|               |
-------------------------------------------------------------------------

=========================================================================
                        *** End of Report ***

 Mon, 19. Oct. 2015    11:02:26 am          Page   1 of 1
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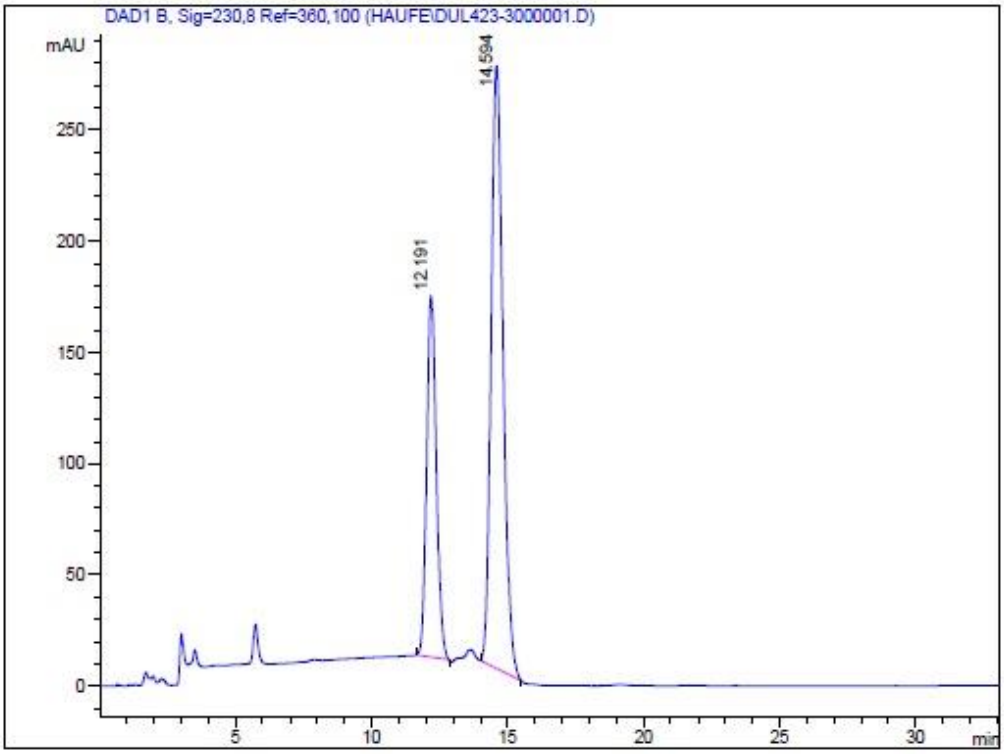
27. (*R*)-*tert*-Butyl 5-oxo-2-phthalimidopentanoate (36)

```
Sample Name      : DUL423-3                      Seq Line    :          0
                                                 Location    :      Vial 3
Injection Date   : Mon, 10. Aug. 2015            Inj. No.    :          0
                                                 Inj. Vol.   :        3 µl

Data file:   C:\CHEM32\1\DATA\HAUFE\DUL423-3000001.D

Acq. Method->C:\CHEM32\1\METHODS\RP CHIRAL\RP CHIRAL_35-65.M

sample info: Chiralcel OJ-RH, 4,6x150mm, 5µm,
             A=H2O, B=ACN/H2O=90/10
             unbekannte menge Probe in 0,5mL ACN gelöst.
                                                                          ->
```




```
Signal  1: DAD1 B, Sig=230,8 Ref=360,100

|Peak|   RT    | Type  | Width |   Area    | Area % |     Name      |
| #  | [min]   |       | [min] |           |        |               |
|----|---------|-------|-------|-----------|--------|---------------|
|   1|  12.191|MM     |  0.411|  4005.491|  32.734|               |
|   2|  14.594|MM     |  0.507|  8231.046|  67.266|               |
-------------------------------------------------------------------

===================================================================
                        *** End of Report ***


 Mon, 7. Sep. 2015     01:55:41 pm          Page   1 of 1
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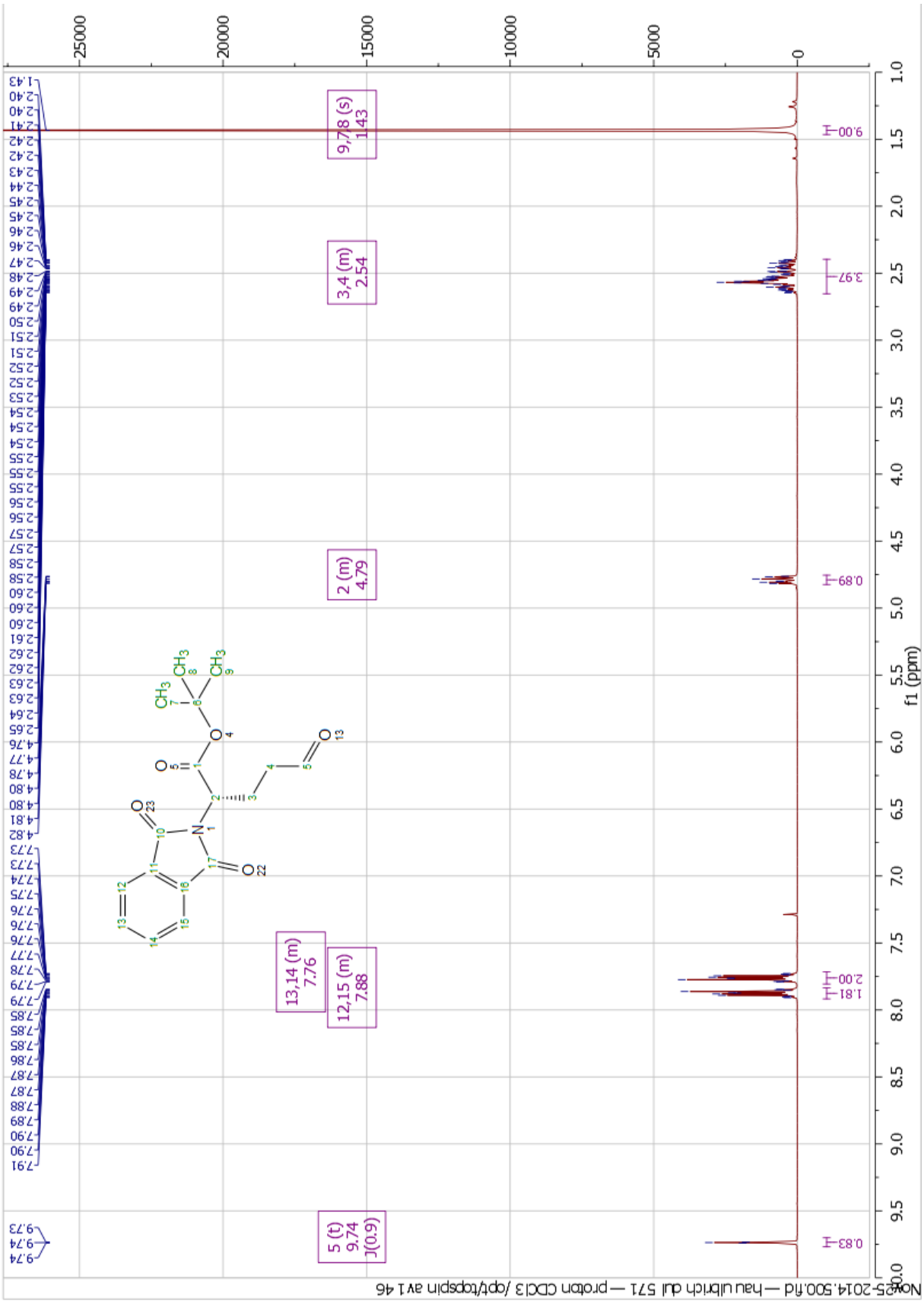
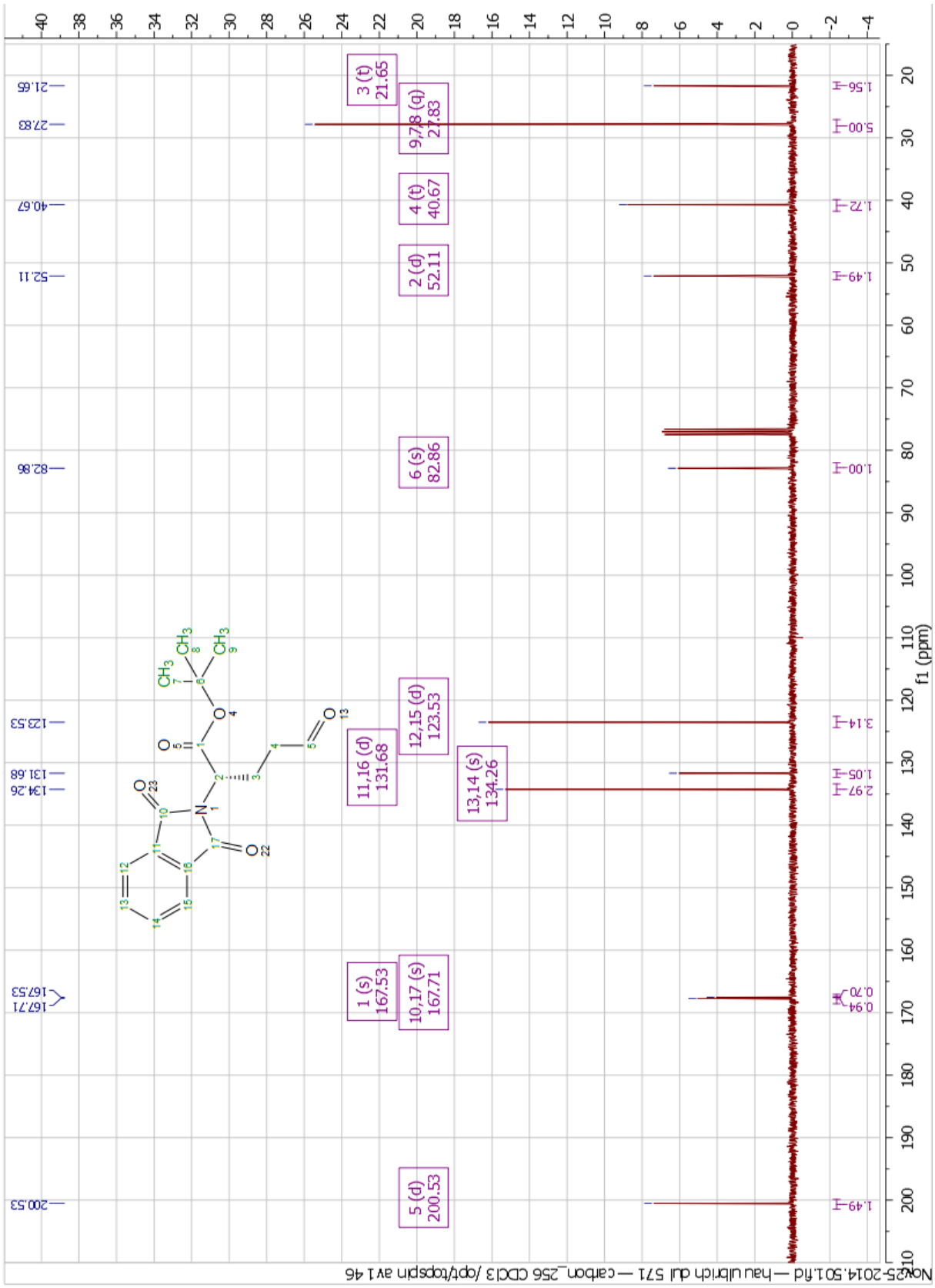
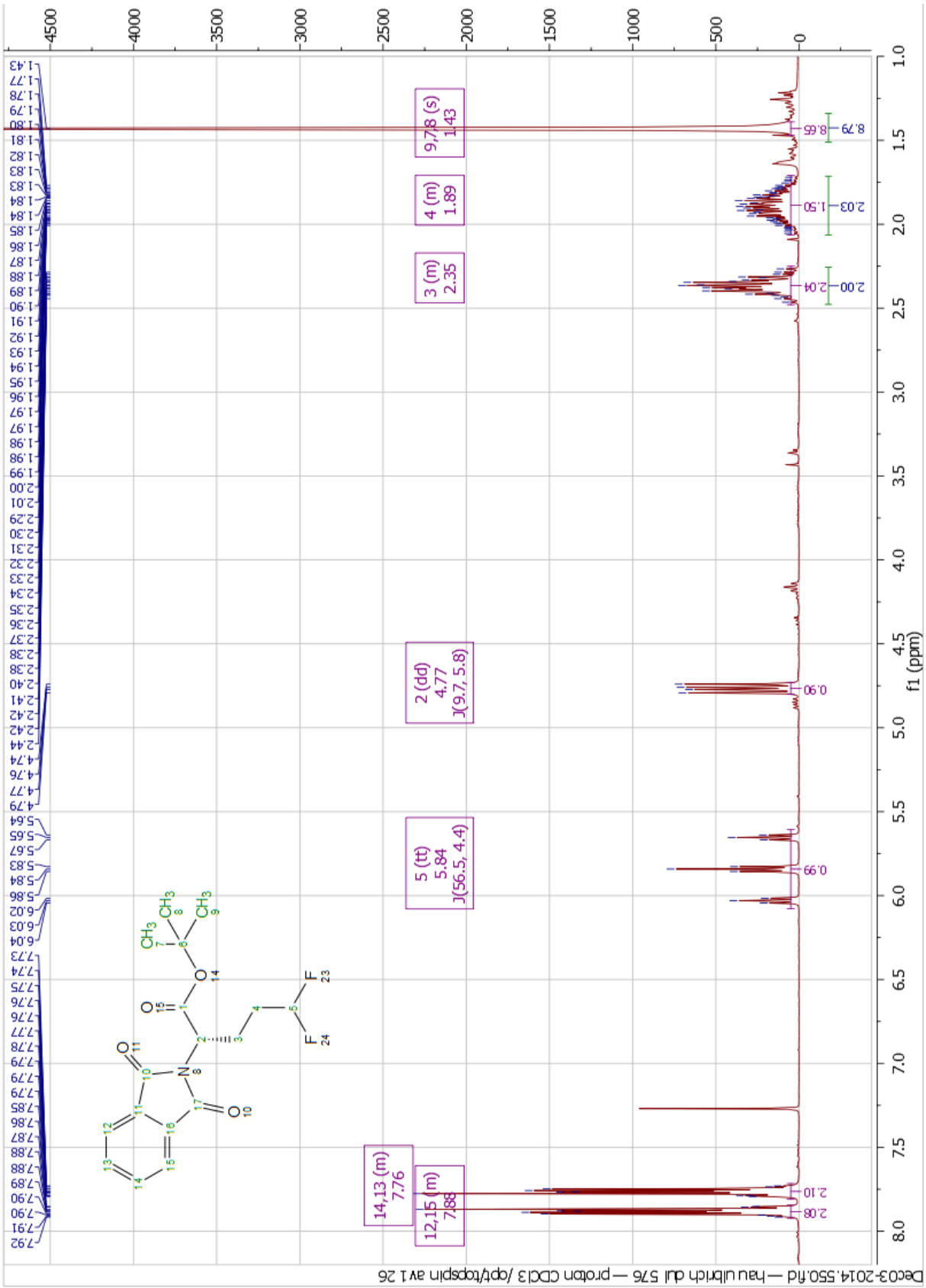
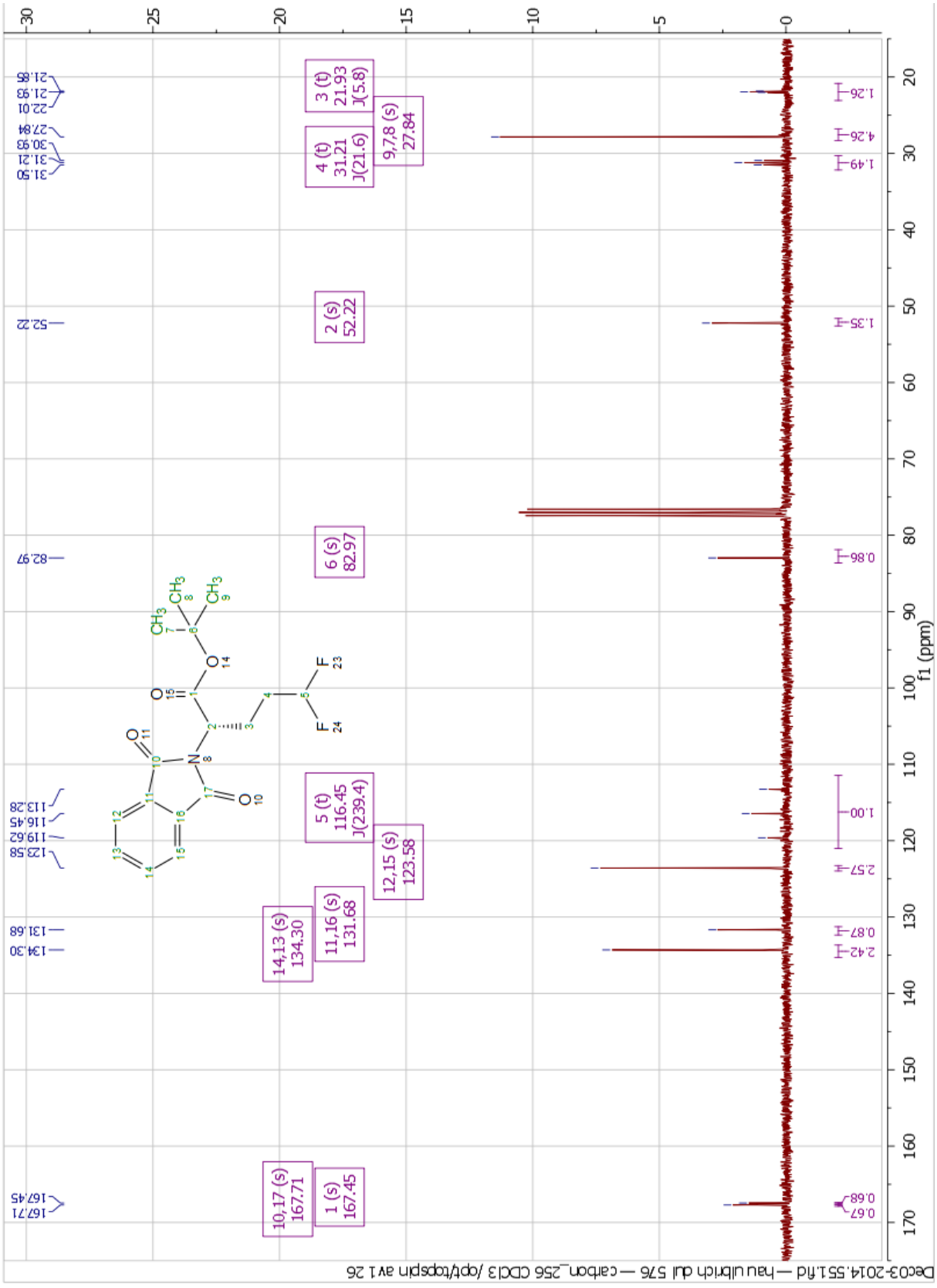

9,78 (s)
1,43
3,4 (m)
2,54
2 (m)
4,79
13,14 (m)
7,76
12,15 (m)
7,88
5 (t)
9,74
J(0,9)
9,00
3,97
0,89
1,81
2,00
0,83
f1 (ppm)

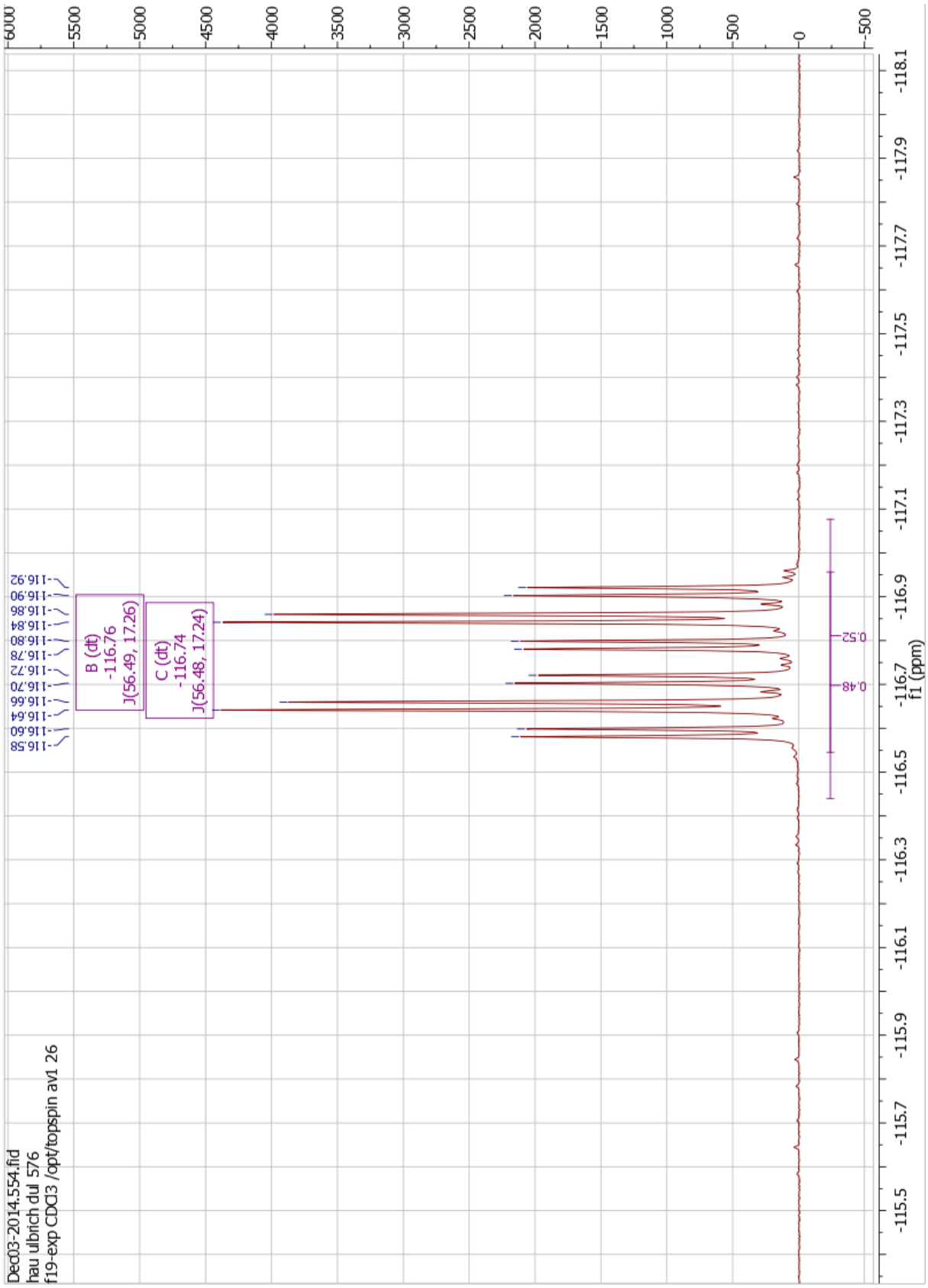

Nov25-2014.501.fid — hau ulbrich dul 571 — carbon_256 CDCl3 /opt/topspin av 1 46
f1 (ppm)
200.53
167.71
167.53
134.26
131.68
123.53
82.86
52.11
40.67
27.83
21.65
5 (d) 200.53
1 (s) 167.53
10,17 (s) 167.71
11,16 (d) 131.68
12,15 (d) 123.53
13,14 (s) 134.26
6 (s) 82.86
2 (d) 52.11
4 (t) 40.67
9,78 (q) 27.83
3 (t) 21.65
1.49
0.94
0.70
3.14
1.05
2.97
1.00
1.49
1.72
5.00
1.56

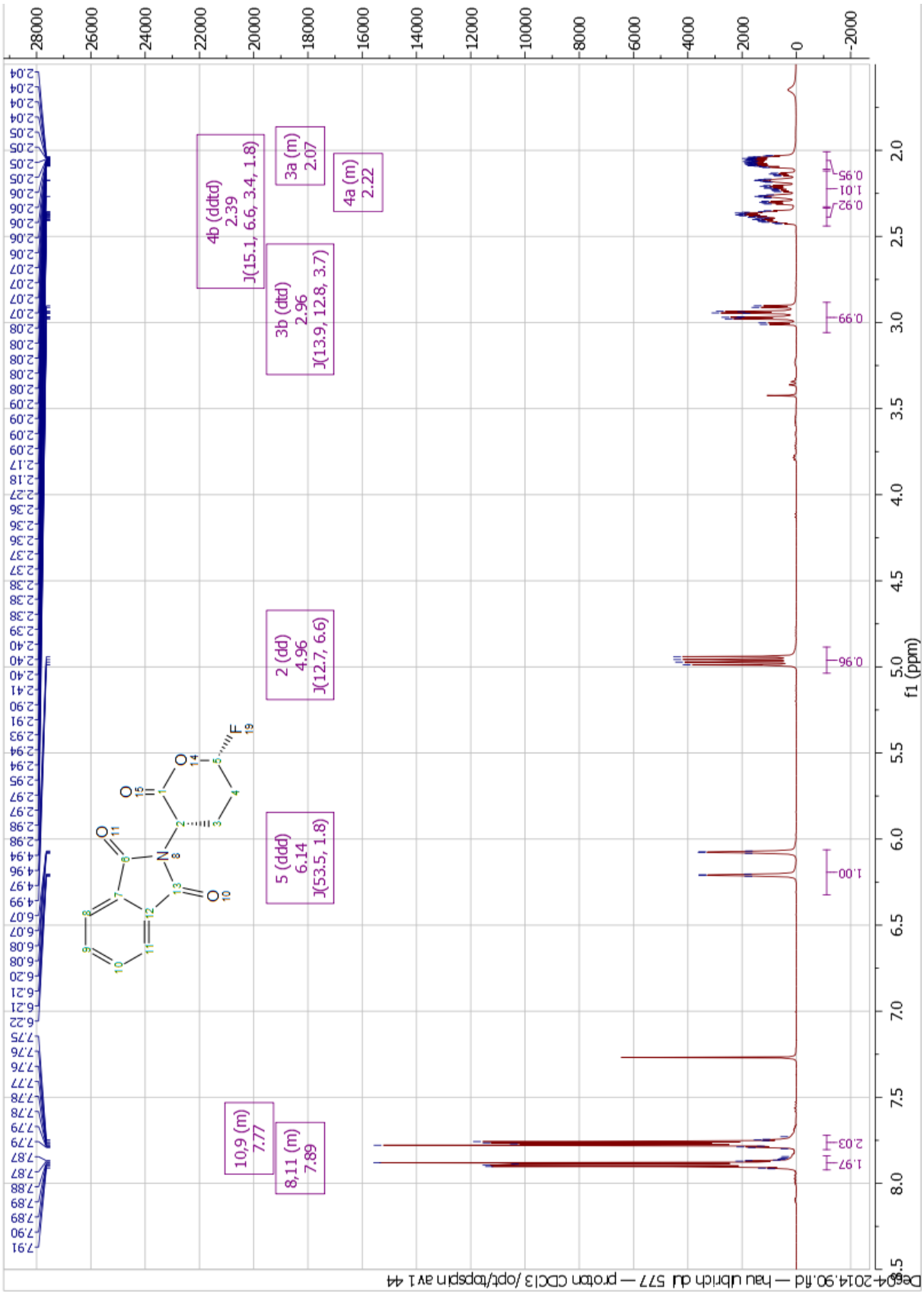
28. Reaction of 36 with Deoxo-Fluor

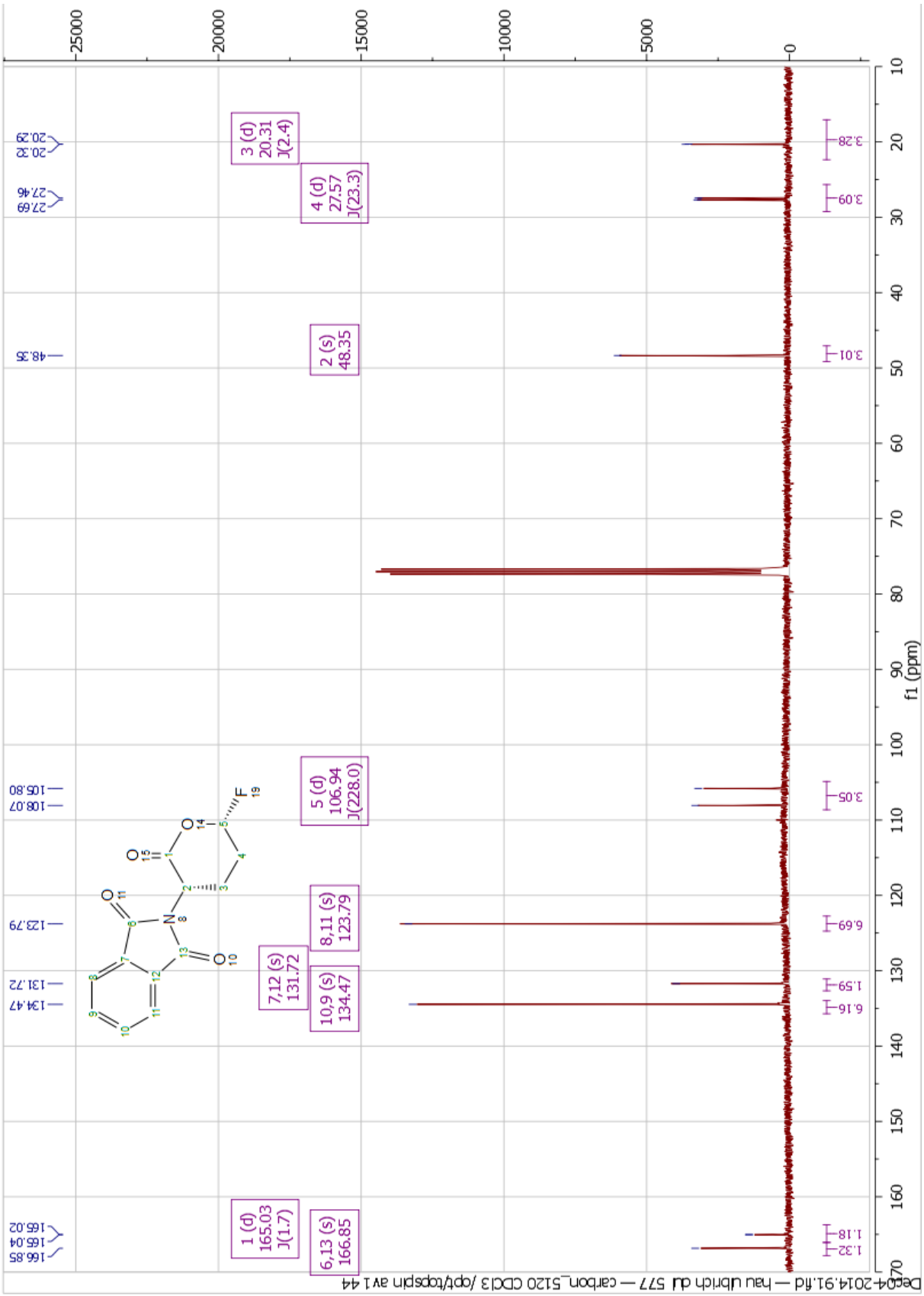


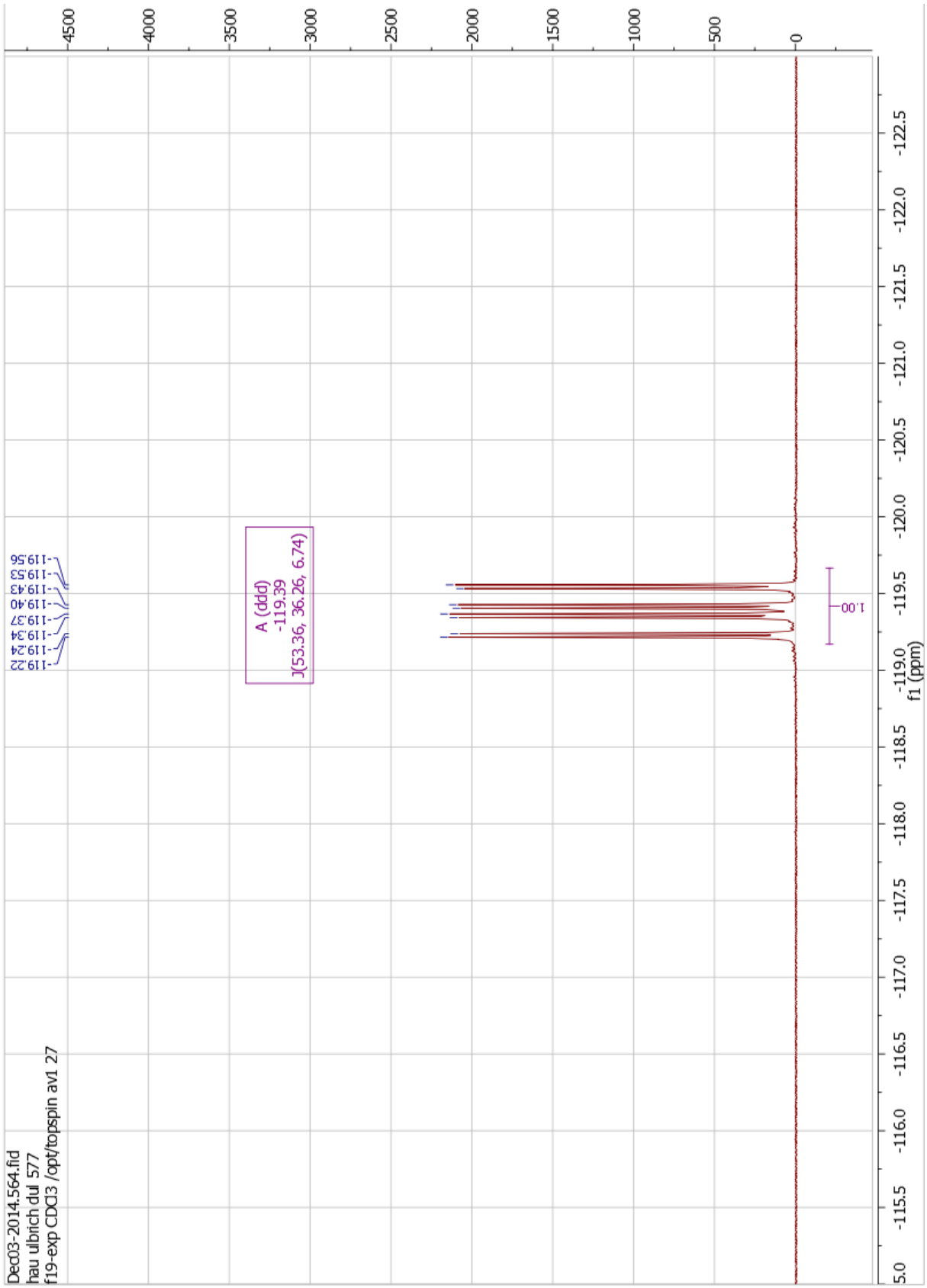
5-Fluoro-2-phthalimido-δ-butyrolactone (38)



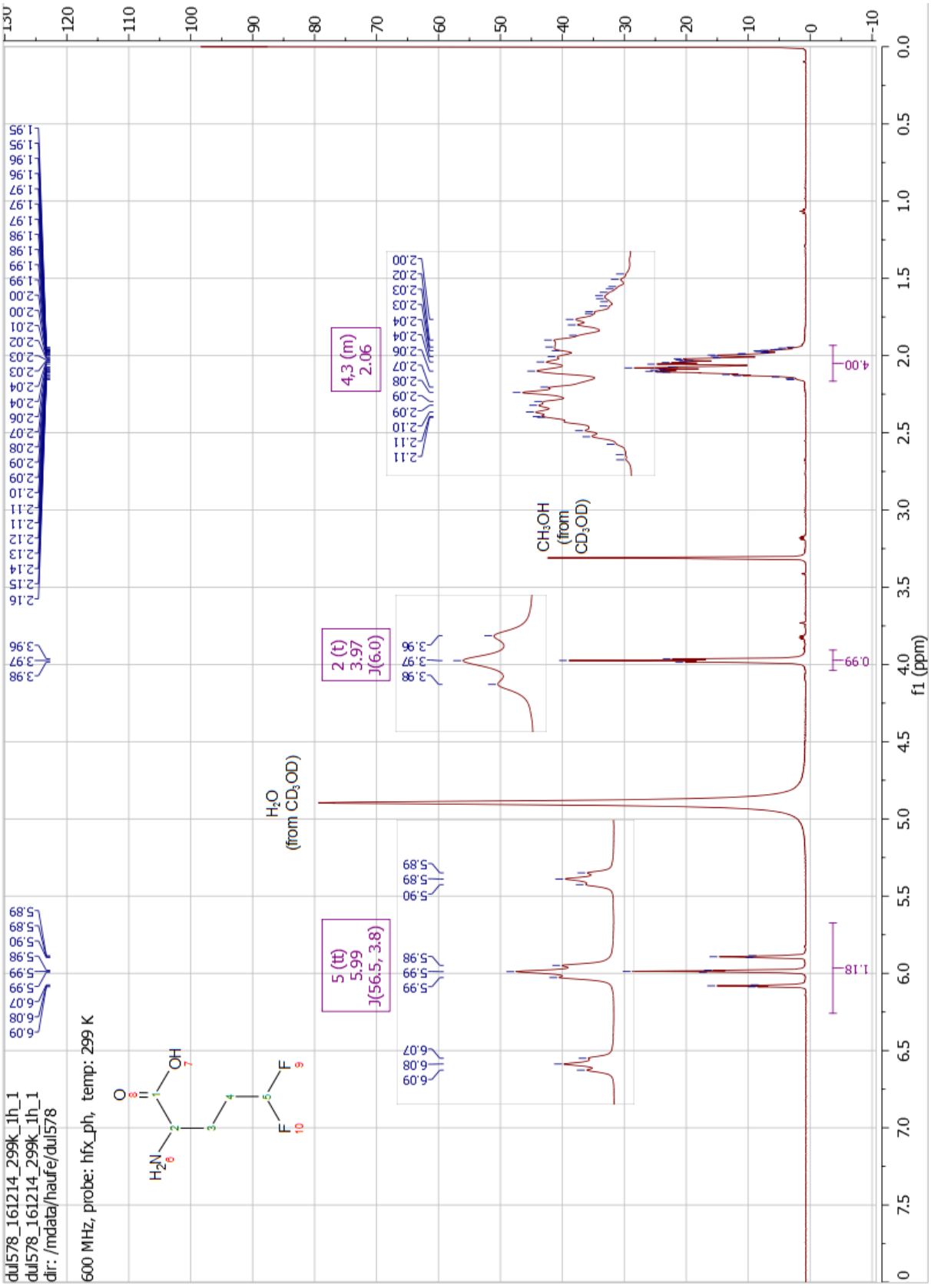

Dec03-2014.554.fid
hau ulbrich dul 576
f19-exp CDCl3 /opt/topspin av1 26
B (dt)
-116.76
J(56.49, 17.26)
C (dt)
-116.74
J(56.48, 17.24)
0.52
0.48
f1 (ppm)

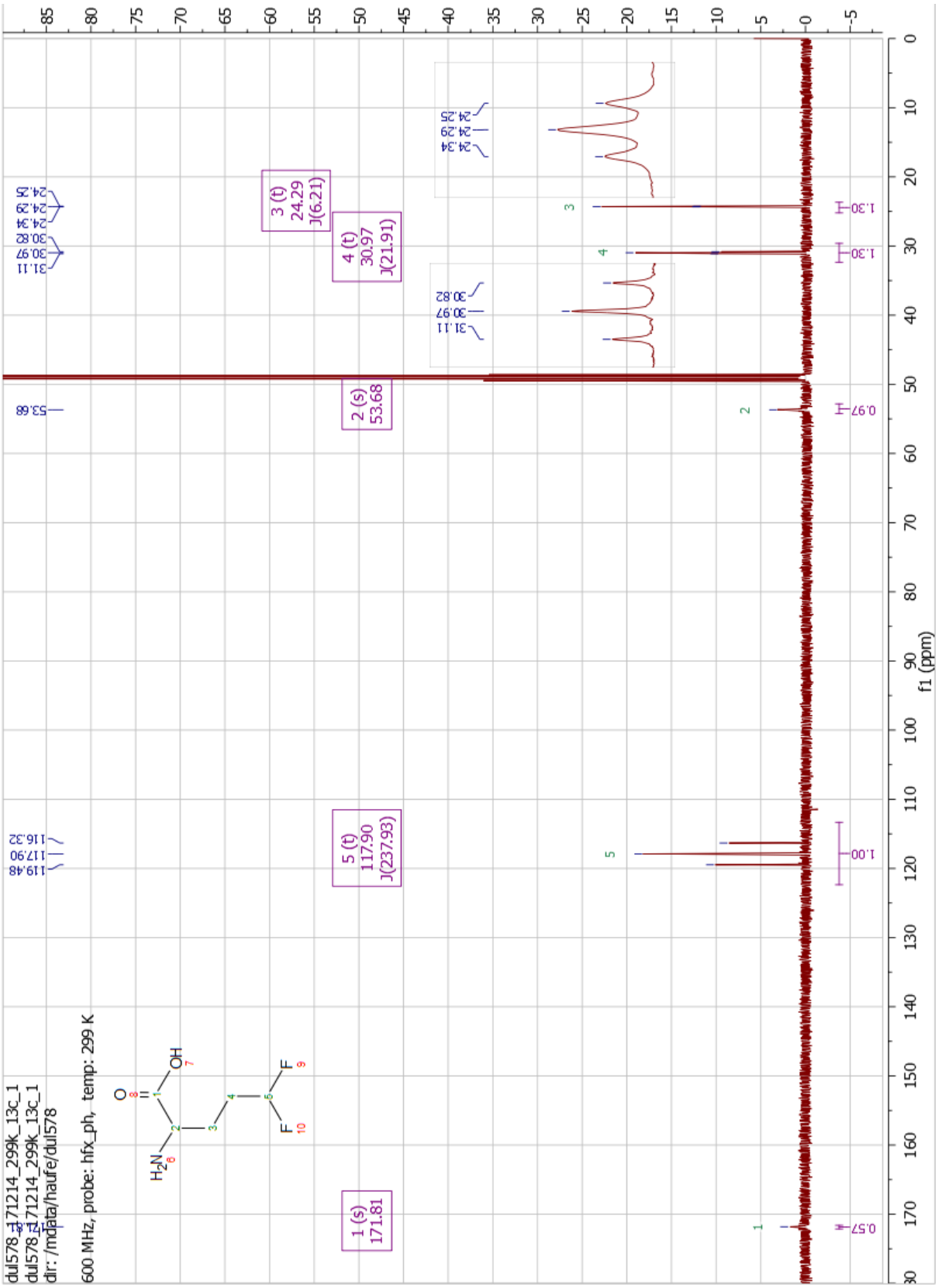

10,9 (m)
7.77
8,11 (m)
7.89
5 (ddd)
6.14
J(53.5, 1.8)
2 (dd)
4.96
J(12.7, 6.6)
3b (dtd)
2.96
J(13.9, 12.8, 3.7)
4b (ddtd)
2.39
J(15.1, 6.6, 3.4, 1.8)
4a (m)
2.22
3a (m)
2.07
1.00
0.96
0.99
0.92
1.01
0.95
2.03
1.97
f1 (ppm)

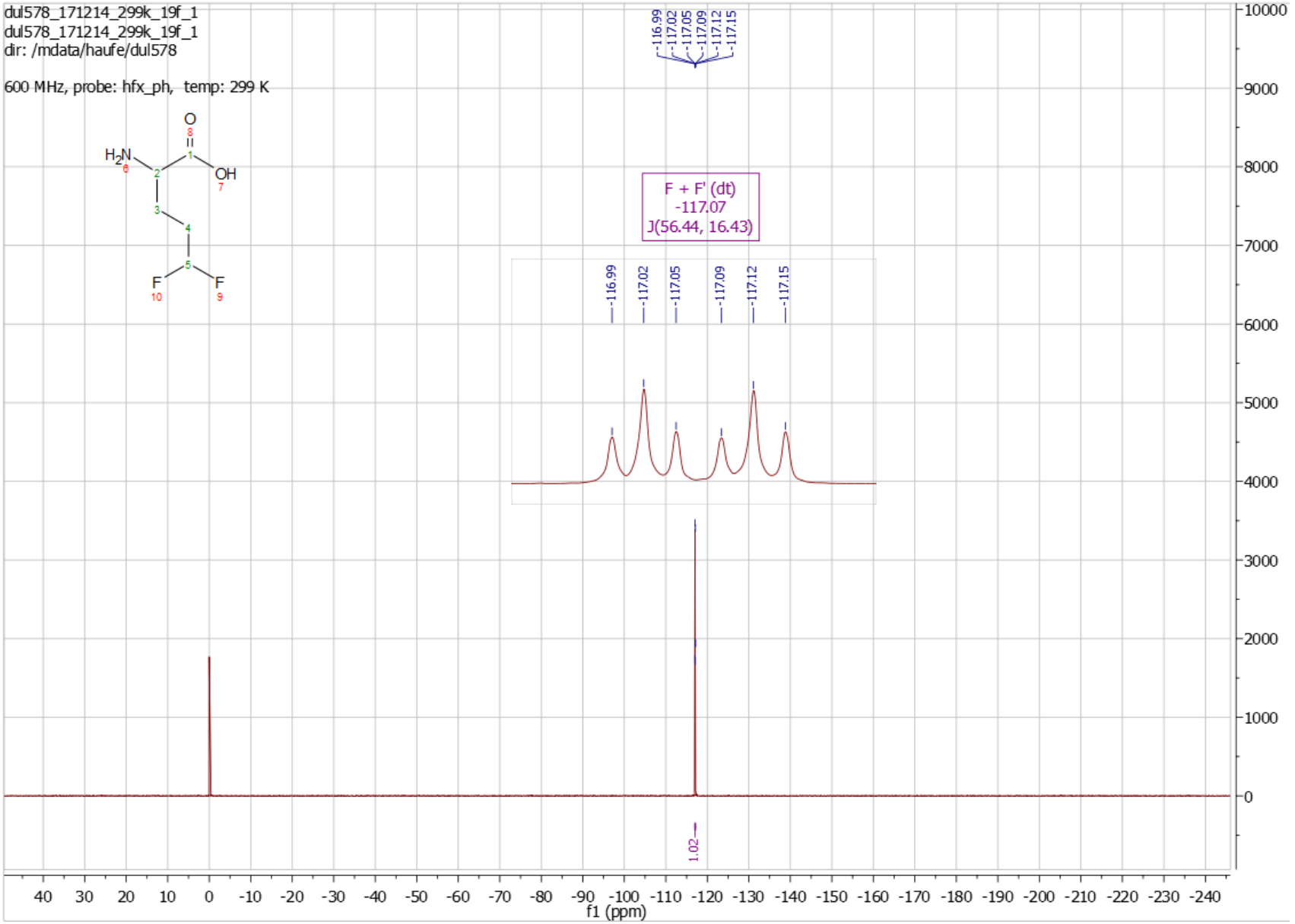

Dec04-2014.91.fid — hau ubrich dul 577 — carbon_5120 CDCl3 /opt/topspin av 1 44
f1 (ppm)
1 (d)
165.03
J(1.7)
6,13 (s)
166.85
7,12 (s)
131.72
10,9 (s)
134.47
8,11 (s)
123.79
5 (d)
106.94
J(228.0)
2 (s)
48.35
3 (d)
20.31
J(2.4)
4 (d)
27.57
J(23.3)
166.85
166.04
166.02
134.47
131.72
123.79
108.07
105.80
48.36
27.69
27.46
20.30
20.29
1.32
1.18
6.16
1.59
6.69
3.05
3.01
3.09
3.28


Dec03-2014.564.fid
hau ulbrich dul 577
f19-exp CDCl3 /opt/topspin av1 27
A (ddd)
-119.39
J(53.36, 36.26, 6.74)
-119.22
-119.24
-119.34
-119.37
-119.40
-119.43
-119.53
-119.56
1.00
f1 (ppm)

29. (*R*)-2-Amino-5,5-difluoropentanoic acid hydrochloride (39)



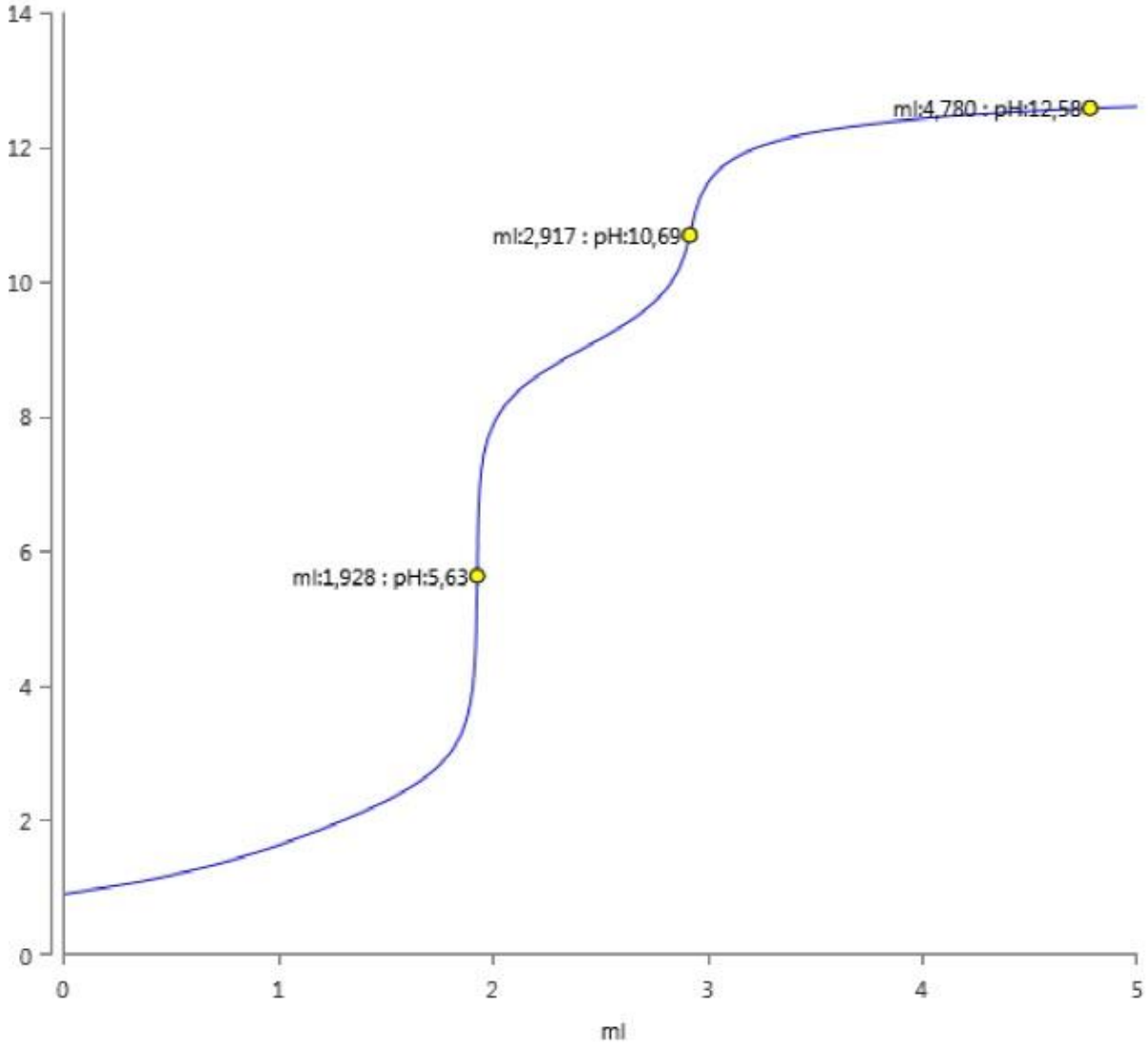

dul578_171214_299k_13c_1
dul578_171214_299k_13c_1
dir: /mdata/haufe/dul578
600 MHz, probe: hfx_ph, temp: 299 K
1 (s)
171.81
2 (s)
53.68
3 (t)
24.29
J(6.21)
4 (t)
30.97
J(21.91)
5 (t)
117.90
J(237.93)
f1 (ppm)


dul578_171214_299k_19f_1
dul578_171214_299k_19f_1
dir: /mdata/haufe/dul578
600 MHz, probe: hfx_ph, temp: 299 K
F + F' (dt)
-117.07
J(56.44, 16.43)
-116.99
-117.02
-117.05
-117.09
-117.12
-117.15
1.02
f1 (ppm)

Determination of the pK_a value

Datenbank Proben

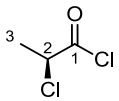
Methode	pKa-Messung Cyclopropylamine Kathi
Datum	16.10.2015 11:00
Anwender	admin
Bezeichnung	DUL 451-I
Status	Ready
Probenmenge	189,65
Kommentar	0,1M Lsg. Probe in 10 mL 0,1M HCl titriert mit 1 M NaOH
EQ 1	1,93
EQ2	2,92
HP2 [ml]	3,35
HP2 [pH]	12,11



TitriSoft Freitag, 16. Oktober 2015 1/1

30. Derivatization of 39 with (*S*)-2-Chloropropionic acid chloride (40)

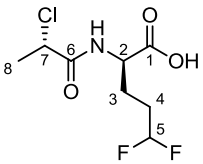
(*S*)-2-Chloropropionic acid chloride (40)



40

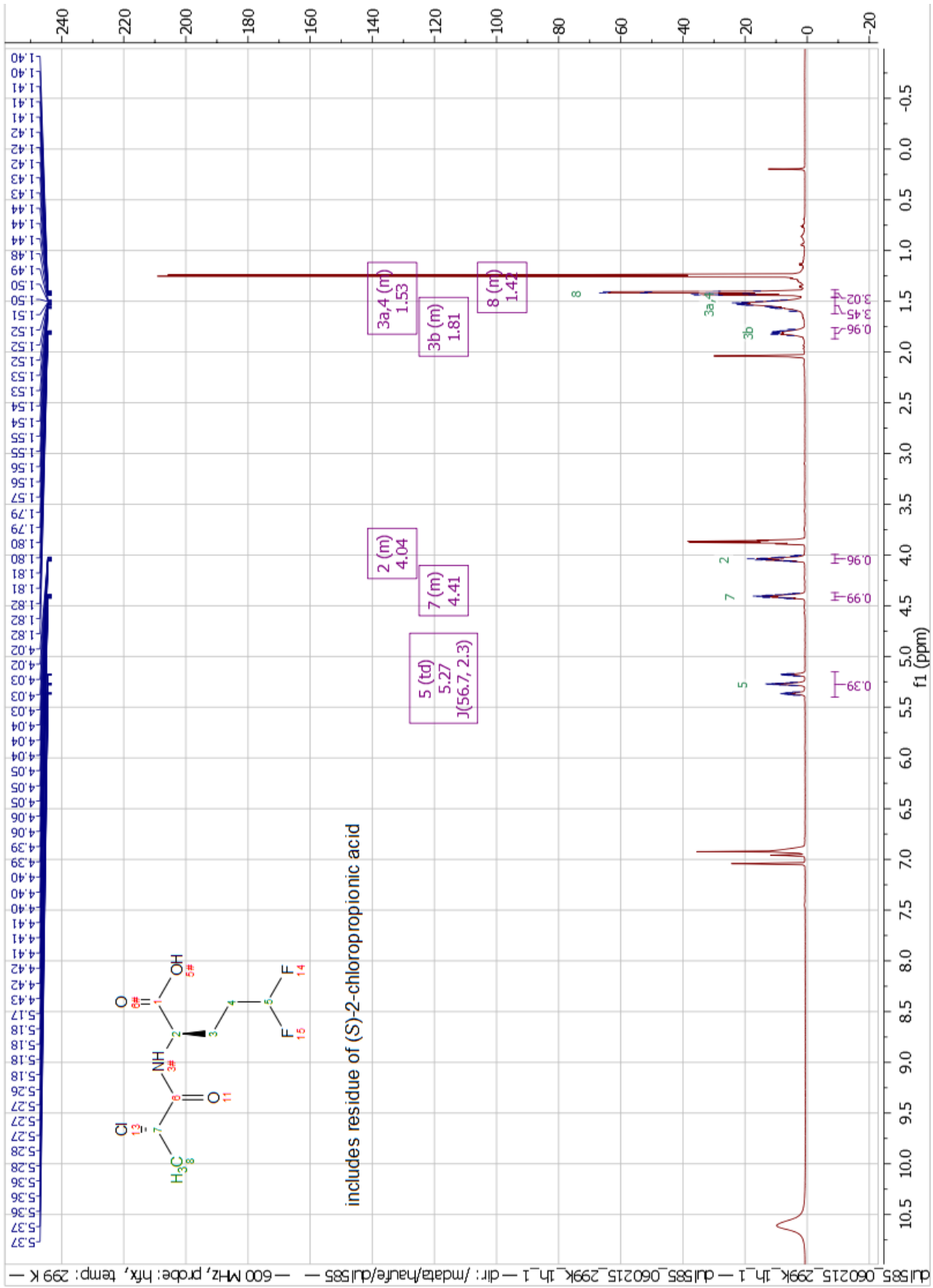
^{1}H NMR (300 MHz, toluene-d_8): δ 1.05 (d, $^{3}J_{H,H}$ = 6.9 Hz, 3 H, 3-CH_3), 3.69 (q, $^{3}J_{H,H}$ = 6.9 Hz, 1 H, 2-CH). **^{13}C NMR** (75 MHz, toluene-d_8): δ 20.8 (q, C-3), 60.4 (d, C-2), 170.7 (s, C-1). The spectroscopic data are approximately consistent with the ones reported by Laue who used $CDCl_3$ as NMR solvent.[2]

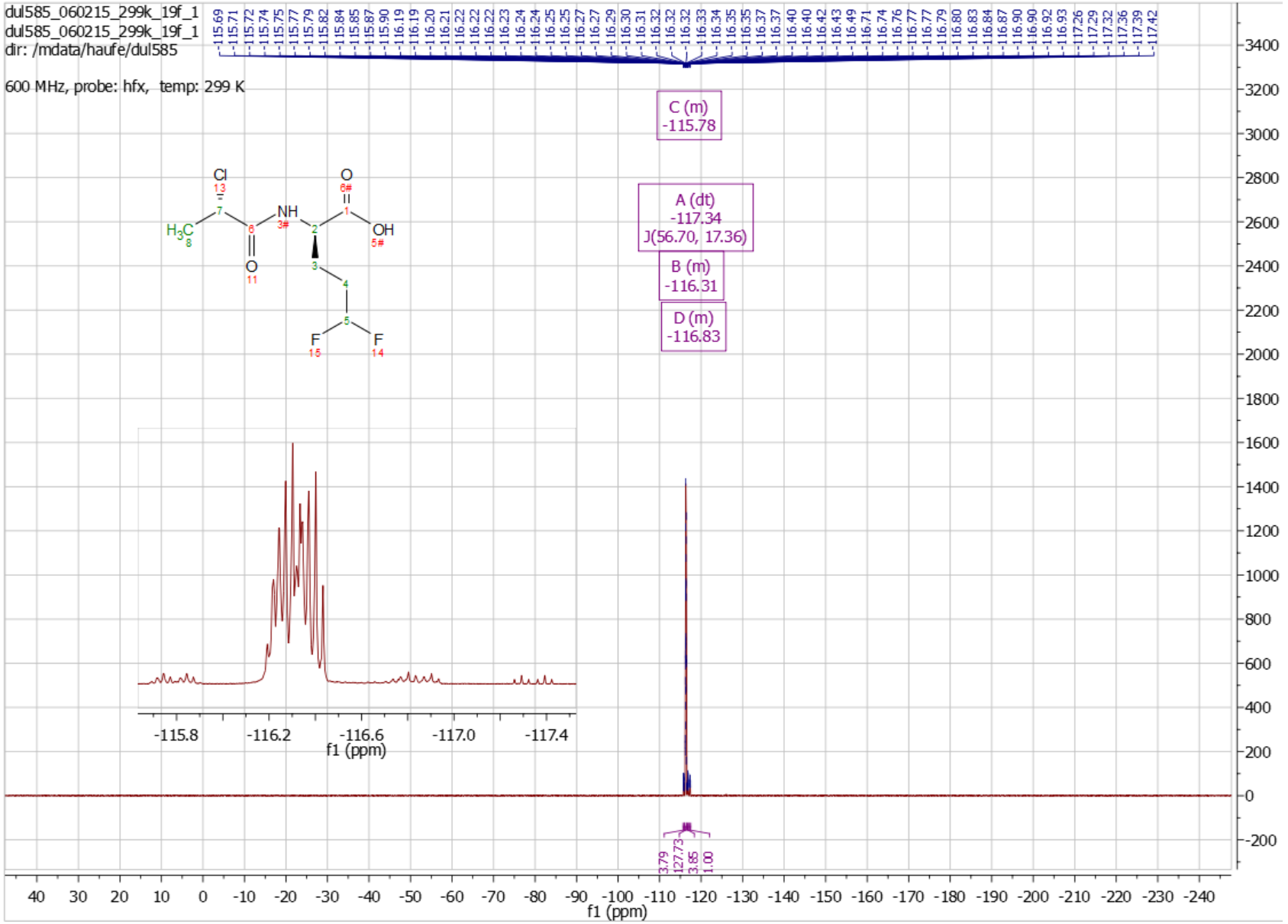
(*R*)-N-[(S)-2-Chloropropionyl]-2-amino-5,5-difluoropentanoic acid (41)



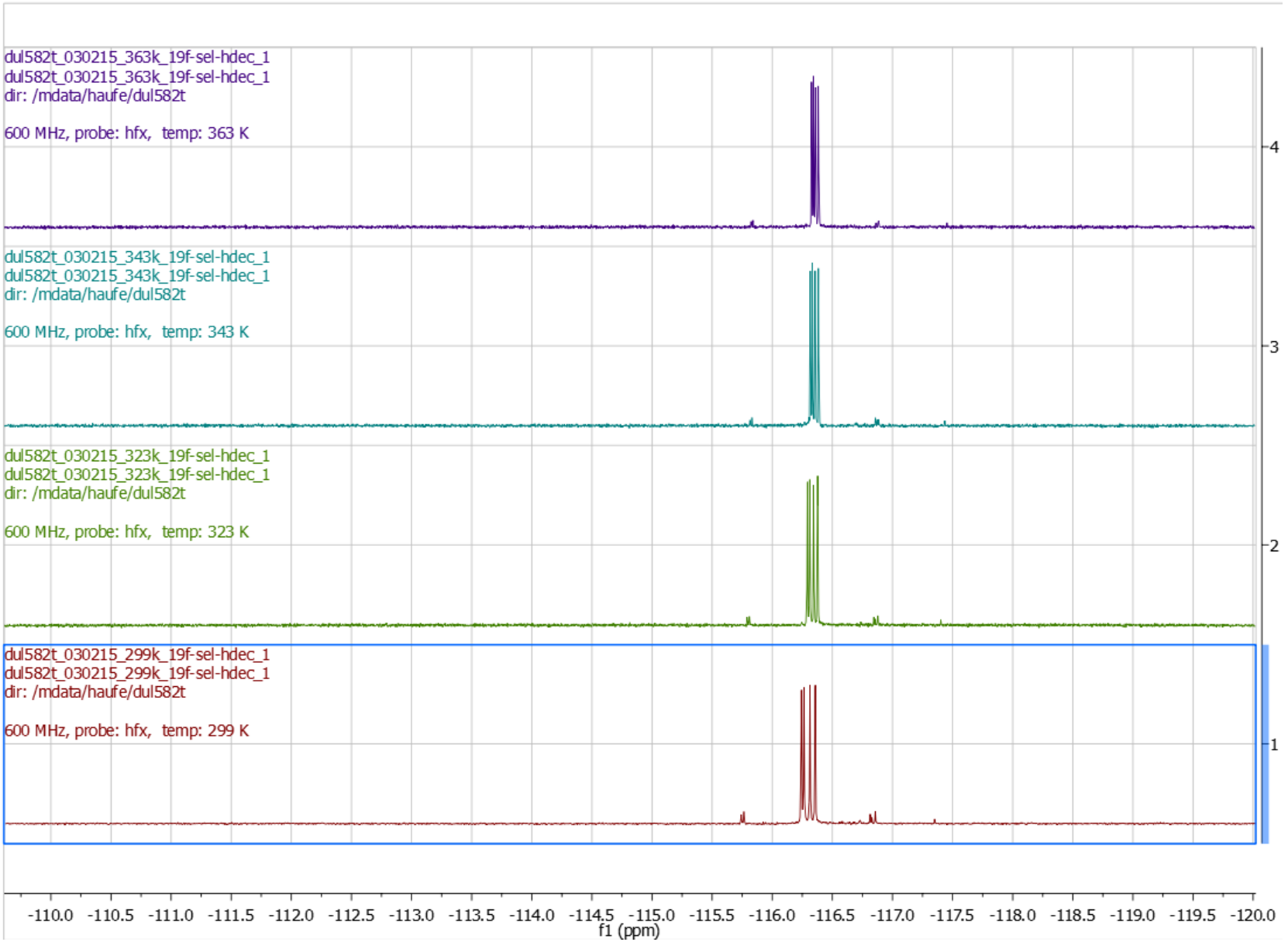
41

Yield: 50 mg (0.26 mmol, 96%). **^{1}H NMR** (600 MHz, toluene-d_8): δ 1.39-1.46 (m, 6 H, 8-CH_3 und 8*-CH_3),1.46-1.62 (m, 6 H, 3-CH^a, 4-CH_2, 3*-CH^a, 4*-CH_2), 1.76-1.87 (m, 2 H, 3-CH^b und 3*^{b}-CH), 3.99-4.08 (m, 2 H, 2-CH und 2*-CH), 4.37-4.45 (m, 2 H, 7-CH und 7*-CH), 5.27 (tm, $^{2}J_{H,F}$ = 56.7 Hz, 2 H, 5-CH und 5*-CH). **^{19}F NMR** (564 MHz, toluene-d_8): δ −116.2/−116.3 (AB-Signal, $^{2}J_{F,F}$ = 282.0 Hz, $^{2}J_{H,F}$ = 56.5 Hz, $^{3}J_{F,H}$ = 17.4 Hz, 2 F, 5-CF_2H, 32%), −116.3/−116.4 (AB-signal, $^{2}J_{F,F}$ = 282.0 Hz, $^{2}J_{H,F}$ = 56.7 Hz, $^{3}J_{F,H}$ = 17.4 Hz, 2 F, 5*-CF_2H, 68%). **MS-ES(+)-EM**: *m*/*z* calcd for $C_8H_{12}{}^{35}ClF_2NO_3H^+$: 244.0547, found: 244.0553 $[M+H]^+$; calcd for $C_8H_{12}{}^{35}ClF_2NO_3Na^+$: 266.0366, found: 266.0372 $[M+Na]^+$; calcd for $C_8H_{12}{}^{35}ClF_2NO_3{}^+$: 288.0185, 288.0191 $[M-H+2Na]^+$. **MS-ES(−)-EM**: *m*/*z* calculated for $C_8H_{11}{}^{35}ClF_2NO_3Na^-$, 242.0385 $[M-H]^-$, 242.0390.


dul585_060215_299K_1h_1 — dul585_060215_299K_1h_1 — dir: /mdata/haufe/dul585 — 600 MHz, probe: hfx, temp: 299 K
includes residue of (S)-2-chloropropionic acid
3a,4 (m) 1.53
3b (m) 1.81
8 (m) 1.42
2 (m) 4.04
7 (m) 4.41
5 (td) 5.27 J(56.7, 2.3)
0.39
0.99
0.96
3.02
3.45
0.96
f1 (ppm)


dul585_060215_299k_19f_1
dul585_060215_299k_19f_1
dir: /mdata/haufe/dul585
600 MHz, probe: hfx, temp: 299 K
C (m)
-115.78
A (dt)
-117.34
J(56.70, 17.36)
B (m)
-116.31
D (m)
-116.83
Cl
O
NH
OH
F
F
f1 (ppm)
f1 (ppm)

dul585_090215_299k_19f-bb-hdec_1 — dul585_090215_299k_19f-bb-hdec_1 — dir: /mdata/hauke/dul585 — — 600 MHz, probe: hf
(R)-F + (R)-F' (m)
-116.32
(S)-F + (S)-F' (m)
-116.29
1: (2R)-diastereomer
2: (2S)-diastereomer
1.00
0.42
f1 (ppm)


dul582t_030215_363k_19f-sel-hdec_1
dul582t_030215_363k_19f-sel-hdec_1
dir: /mdata/haufe/dul582t
600 MHz, probe: hfx, temp: 363 K
dul582t_030215_343k_19f-sel-hdec_1
dul582t_030215_343k_19f-sel-hdec_1
dir: /mdata/haufe/dul582t
600 MHz, probe: hfx, temp: 343 K
dul582t_030215_323k_19f-sel-hdec_1
dul582t_030215_323k_19f-sel-hdec_1
dir: /mdata/haufe/dul582t
600 MHz, probe: hfx, temp: 323 K
dul582t_030215_299k_19f-sel-hdec_1
dul582t_030215_299k_19f-sel-hdec_1
dir: /mdata/haufe/dul582t
600 MHz, probe: hfx, temp: 299 K
4
3
2
1
-110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0
f1 (ppm)

31. References

[1] M. J. Robins, S. F. Wnuk, *J. Org. Chem.* **1993**, *58*, 3800-3801.
[2] K. W. Laue, *PhD Thesis*, University of Münster, 1998.