Supplementary Material

Efficient formylation of alcohols and thiols by means of formamides and benzoyl chloride

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Author Contributions

Do T. T. and P. Huy acquired funding for, conceived and designed the project. Do T. T. has performed all experiments and analysis under supervision and guidance of P. Huy. Do T. T. has processed, evaluated and interpreted the analytical data with the support of P. Huy. Do T. T. has written the supporting information, which have been proof-read by P. Huy. P. Huy has written the manuscript, which has been proof-read and approved by Do T. T.

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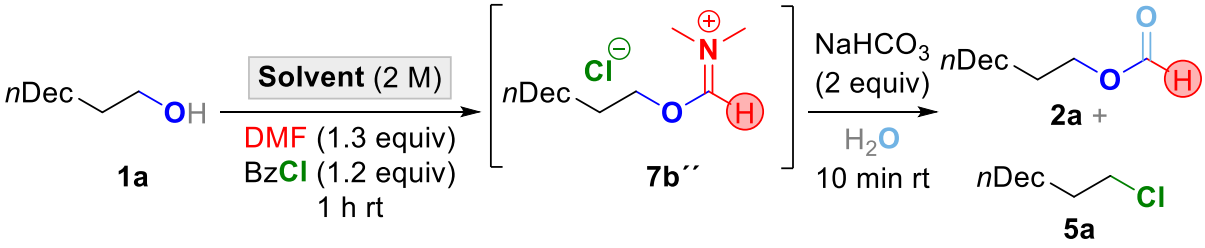
1. Method Development

1.1. Solvent Screening

The current protocol for the synthesis of formic acid esters of type **2** is based on a previously published procedure for the formation imidate salts chlorides of type **7**.[1,2] At the outset, a solvent screening was performed using 1-dodecanol (**1a**) as model substrate and dimethylformamide (DMF) and benzoyl chloride (BzCl) as the reagents (Table S1). In most of the tested solvents, full conversion of starting material **1a** was accomplished. However, a pronounced difference in terms of selectivity between the chlorination and the formylation, which affect to the yield of formate products, could be observed. When MeCN was applied, the two products **2a** and **5a** were formed in the best ratio of 92:8 and **2a** was obtained in 77% yield (entry 1).

Table S1. Solvent screening utilizing alcohol **1a**.



entry	solvent	conv. [%][1]	ratio 2a:5a[2]	yield 2a [%][3]	lab journal No.
1	MeCN	≥98	92:8	77	DTT-258
2	MTBE	95	83:17	64	DTT-259
3	THF	≥98	75:25	63	DTT-260
4	2-MeTHF	88	81:19	70	DTT-261c
5	acetone	73	93:7	64	DTT-261a
6	toluene	≥98	85:15	74	DTT-261

According to general protocol A (chapter 2.2.1, page 8), 1-dodecanol (500 μmol, 1.0 equiv) was allowed to react with the BzCl and FPyr in the indicated **solvent** (2 M, instead of MeCN) at room temperature for 1 h. After aqueous work up, yields were determined by means of ^{1}H NMR with mesitylene as internal standard.

In the case of the moderately polar aprotic solvents MTBE, THF, 2-MeTHF, and acetone, **2a** was generated in lower yields between 64 and 70% and ratio of **2a** with regard to **5a** of 75:25 to 83:17 (entries 2-5). In the case of acetone, no full consumption of **1a** was reached, which

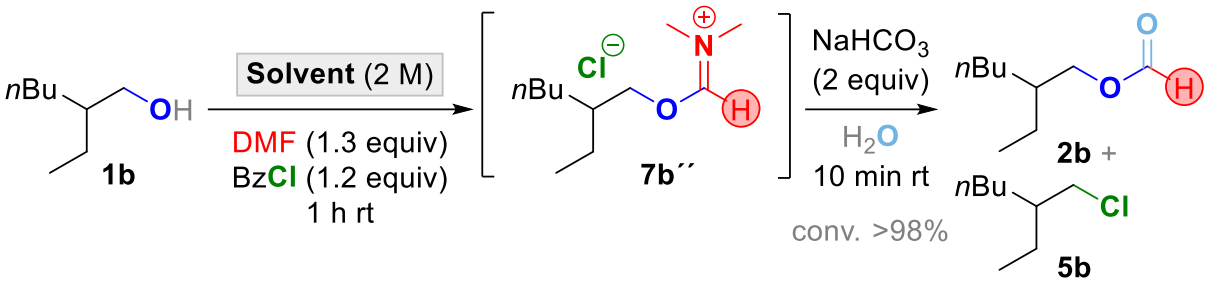
[1] The conversion of alcohol **1a** was determined from the triplet at 3.64 ppm in ^{1}H NMR of the crude material, using mesitylene as NMR standard.

[2] The ratio of **2a**/**5a** was calculated from the integration ratio of the triplets at 4.16 ppm and 3.53 ppm in the ^{1}H NMR spectrum of the crude product.

[3] The yield of **2a** was determined from the ratio of triplet at 4.16 ppm and singlet at 2.27 ppm (mesitylene) in the ^{1}H NMR spectrum of the crude product.

may be rationalized by hydrolysis of BzCl by means of water. Interestingly, the non-polar solvent toluene gave rise of **2a** in 74% yield (entry 6), which is comparable to MeCN. Because of the toxicity of toluene, MeCN was selected as the optimum solvent for the further evaluation of the reaction conditions**.** In fact, a second solvent evaluation harnessing 2-ethyl-1-ethanol, which is sterically more shielded alcohol in comparison to dodecanol, confirmed that MeCN allows for the best chemical yield of the wanted formic acid ester (**Table S2**)

Table S2. Solvent screening with β-ethyl-α-hexanol.



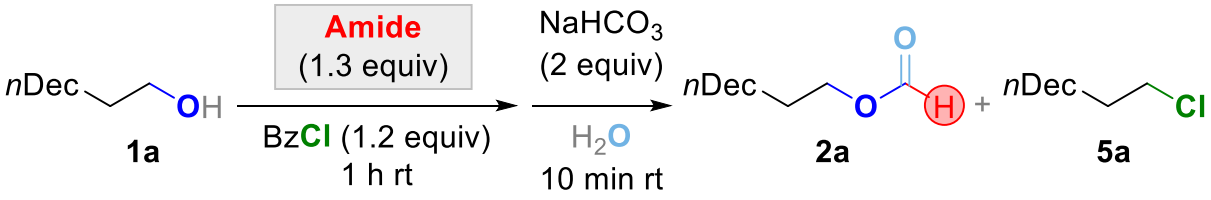
Entry	Solvent	ratio 2b:5b	Yield 2b [%]	Lab Journal No.
1	MeCN	97:3	84	DTT-253
2	MTBE	90:10	75	DTT-252
3	toluene	90:10	71	DTT-257
4	THF	88:12	70	DTT-254
5	2-MeTHF	83:17	69	DTT-255
6	acetone	78:22	69	DTT-256

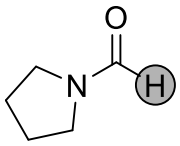
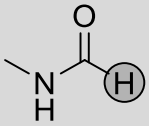
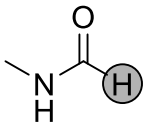
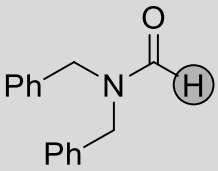
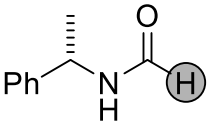
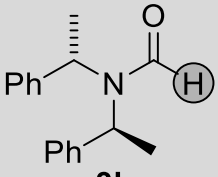
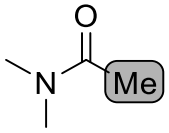
According to general protocol A (chapter 2.2.1, page 8), 2-ethylhexan-1-ol (500 μmol, 1.0 equiv) was allowed to react with the BzCl and FPyr in the indicated **solvent** (2 M, instead of MeCN) at room temperature for 1 h. After aqueous work up, yields were determined by means of ^{1}H NMR with mesitylene as internal standard. The conversion of the starting material was calculated based on the ratios of **1b**, **2b** and **5b** as given by the ^{1}H NMR spectra of the crude product.

1.2. Reagent Screening

Next, a representative range of Lewis bases was screened as formylation reagents in the transformation of alcohol **1a** to the formate product **2a** (Table S3)**.** After a reaction duration of 60 min, the application of FPyr, DMF, and methyl formamide delivered ester **2** in comparable yields 77-79% (entries 1,4 and 5). However, the use of DMF also resulted in the generation of the chloride **5a** and dodecyl benzoate in 6 and 8% yield, respectively, as side-products. After 60 min with DMF complete conversion had been accomplished, while in the case of FPyr and methyl formamide incomplete conversion of alcohol **1a** was observed (89%). Nevertheless, similar yields of **2a** were attained, because less side-products ≤2% arise with these formamides.

Table S3. Probing of various amide reagents in the synthesis of formic acid ester **2a**.



Entry	Amide	Conv. [%]	2a / 5a	Yield 2a [%]	Lab Journal No.
1	 **3i** (FPyr)	89	97:3	77	DTT-267
2[a]		≥98	≥98:2	86	DTT-269
3[b]		93	96:4	80	DTT-267-3
4	 **3j**	89	≥98:2	79	DTT-263
5	 **3h** (DMF)	≥98	92:8	77	DTT-258
6	 **3k**	79	70:30	45	DTT-265
7	 **3l**	62	≥98:2	48	DTT-266
8[c]	 **3l**	85	85:15	42	DTT-268
9[c]	 **3m** (DMA)	66	≤2:98	≤2	DTT-264

According to general protocol A (chapter 2.2.1, page 8), 1-dodecanol (0.50 mmol, 1.0 equiv) was allowed to react with the amide of type **3** (0.65 mmol, 1.30 equiv, instead of FPyr) and BzCl (0.6 mmol, 1.20 equiv) in MeCN (2.0 M) for 1 h at room temperature. After aqueous work up, yields determined by means of ^{1}H NMR with mesitylene as internal standard. The conversion of the starting material was calculated based on the ratios of **1a**, **2a** and **5a** as given by the ^{1}H NMR spectra of the crude product. a. t = 3 h b. with 1.5 equiv FPyr and 1.3 equiv BzCl, t = 2 h. c. dodecyl benzoate were observed in 64% yield.

In the instance of FPyr the conversion could be enhanced to 93% by changing the reaction duration from 1 to 3 h (entry 2), and finally to complete consumption by raising the amount of BzCl and FPyr to 1.3 and 1.5 equiv, respectively (entry 3). Application of other formamides with bulkier alkyl groups delivered the desired yields lower than 50% (entries 4–8). Interestingly, DMA did not allow the analogous synthesis of *N*-dodecyl acetamide **2**, in this case dodecyl benzoate was obtained as the main product in 64% yield (entry 9). Therefore, formamides are exclusively capably to transfer their acyl group onto alcohols, which may be rationalized by the lack of catalytic activity for form C-Cl bonds according to all of our previous studies. Other amides are likely too sterically to shielded to form imidate salts with benzoyl chloride.

2. Experiment Part

2.1. General Conditions

Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra, the latter recorded with broadband proton decoupling were measured at room temperature in $CDCl_3$ using Bruker instruments (Avance II 400 or Avance I 500). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS), using the residual solvent signal (^{13}C NMR) or TMS (^{1}H NMR) as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Low- and high-resolution mass spectra (MS/HRMS) were measured on a *Thermo Electron* (MAT95-XP) spectrometer, which is paired with a preceding gas chromatograph (GC) or liquid chromatograph (LC). The samples have been ionized through electron impact ionization (EI) on an *Agilent* (7890/5977A or 8890/5977B) GC-MS equipped with a HP-5 capillary column using helium carrier gas or by applying electron spray ionization (ESI) on an *Agilent* (1260/6130) Quadrupole LC-MS or *Waters Acquity* (UPLC H-Class/Xevo G2-XS) Time-of-Flight (TOF) LC-MS. Optical rotations were determined on a *Dr. Kernchen Gyromat-HP* using a 2 cm long cuvette. Melting points (uncorrected) were determined on a Hot Stage *METTLER* (FP82HT) coupled with a central processor (FP90) and a microscope from *Leitz* (LABORLUX 12 POL S).

Analytical TLC was carried out using precoated silica gel plates (Fluka TLC plates silica gel 60 F_{254} on PET-foils). TLC plates were visualized under UV irradiation (254 nm) or with $KMnO_4$-(3 g $KMnO_4$ and 20 g K_2CO_3 in 300 mL water) and $Ce(SO_4)_2$/PMA (= phosphomolybdic acid, 10 g $Ce(SO_4)_2$-4 H_2O, 25 g PMA, 80 mL 95% H_2SO_4, 920 mL water) stain solutions.

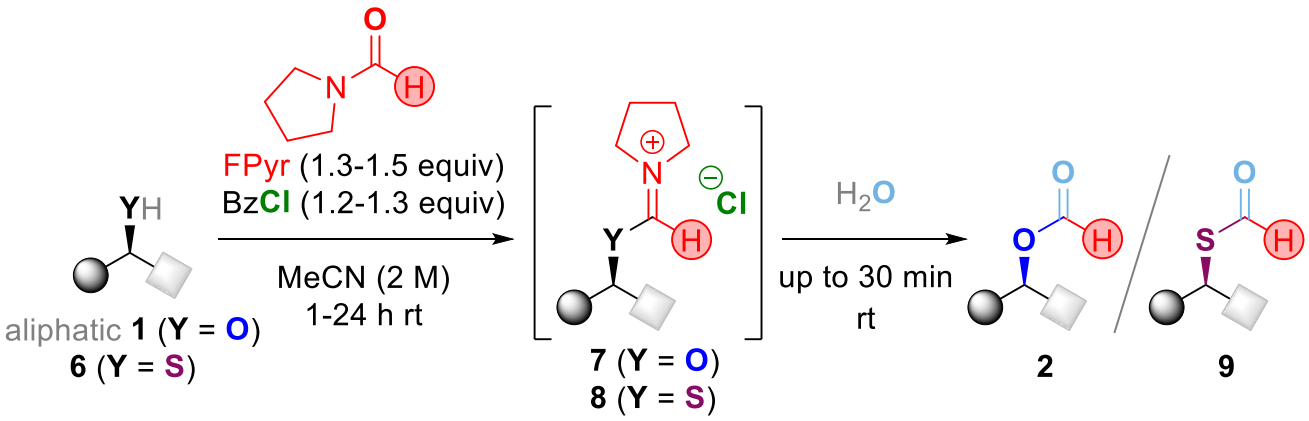
Chemicals were purchased from *Sigma-Aldrich, Acros*, *TCI chemicals*, *Carbolution* and *Alfa Aesar* and used without further purification. *n*-Heptane, *n*-Pentane, and EtOAc were distilled prior usage; all other solvents were utilized without further purification. Dry solvents were purchased from *Acros*.

2.2. General Procedures

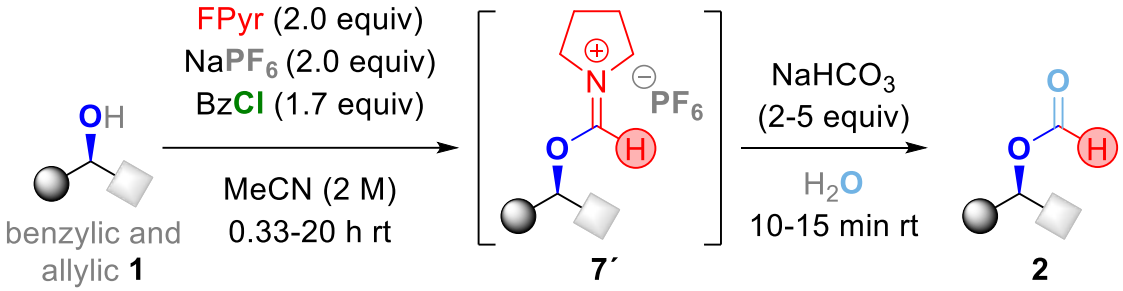
For a representative gram scale procedure for the preparation of formats see chapter 2.3.1.11 (page 31).

2.2.1. General Procedure A: Synthesis of Formates 2 and Thioformates 9

Reaction Scale: For optimization studies, in which yields are determined by internal NMR standard, 0.5 mmol of starting material have been used. For the isolation after chromatographic purification, reactions have been carried out typically on a 1.0 to 2.0 mmol scale.



Procedure for Aliphatic Alcohols and Thiols: A 4 mL glass vial is charged with the alcohol **1** and thiol **6**, respectively, (0.50-2.00 mmol, 1.00 equiv), the FPyr (or DMF, 0.65-3.00 mmol, 1.30-1.50 equiv) and the dry MeCN (0.25-1.0 mL, 2.0 M). In the following, benzoyl chloride (0.60-2.6 mmol, 1.20-1.30 equiv) is added by means of an Eppendorf pipette[4] at room temperature, the glass vial is closed with a screw cap and the reaction mixture is stirred at 400 rpm at room temperature for 1 to 24 h.



Procedure for Benzylic and Allylic Alcohols: A 4 mL glass vial is charged with the alcohol **1** (0.50-1.0 mol, 1.00 equiv), FPyr (1.0-2.0 mmol, 2.00 equiv) and dry MeCN (0.25-0.50 mL, 2.0 M). Next, $NaPF_6$ (1.0-2.0 mmol, 2.00 equiv) is added to the reaction mixture,[5] benzoyl chloride (0.75-1.7 mmol, 1.70 equiv) is then added by means of an Eppendorf pipette and the

[4] Due to the high viscosity of some liquid reaction components the amount of starting materials **1** and reagents is additionally checked by weighing.

[5] $NaPF_6$ should be handled quickly and stored under an atmosphere of protective gas, since this salt is hygroscopic.

glass vial is immediately closed with a screw cap to avoid absorption of water due to the hygroscopic nature of $NaPF_6$. In some cases, the addition of BzCl by means of a syringe pump within 15 min allows for improved yields (see individual procedures). Finally, the reaction suspension is stirred at 400 rpm at room temperature for 20 min to 20 h.[6]

Aqueous Work Up Alcohols: Saturated aqueous $NaHCO_3$ solution is added dropwise to the reaction mixture until the reaction vial is almost filled completely (2-3 mL, 2-5 equiv, 1.1 M)[7] and stirring is continued for further 10-15 min. Next, the reaction mixture is taken up with a 20 mL syringe. The reaction vessel is then rinsed with MTBE/H_2O (2 x 2 mL/2 mL) and additional MTBE (4 mL), whereby all phases are collected in the 20 mL syringe. In the following, the organic phase is washed with brine (1 x 4 mL), dried over $MgSO_4$, concentrated under reduced pressure and the residue is dried for 5 min on a rotary evaporator either at 20 mbar or 50 mbar depending on the volatility of the product.

Aqueous Work Up Thiols: The reaction mixture is diluted EtOAc (2 mL) and taken up with a 20 mL syringe. Subsequently, the reaction vial is rinsed with EtOAc (3x4 mL) and finally with 1 M NaOAc solution in water (4 mL),[(8)] whereby all phases are collected in the 20 mL syringe. Finally, the organic phase is washed with brine (4 mL), dried over $MgSO_4$, concentrated under reduced pressure and the residue is dried for 5 min on a rotary evaporator at 20 mbar.

Determination of Yield by Internal Standard: An accurately weighed amount of mesitylene (10-30 mg) is added to the crude material and the mixture is dissolved in $CDCl_3$ (approximately 500 µL). Finally, a 50-100 µL aliquot of the resulting clear solution is transferred to an NMR tube and diluted with further $CDCl_3$ (ca. 500 µL).

Purification: The crude product was purified by column chromatography on silica gel (ultrapure) using a silica/crude product weight ratio of 10:1 to 40:1, depending on the complexity of the separation. Elution was performed with MTBE/*n*-heptane and in the case of volatile formats MTBE/*n*-pentane mixtures, respectively. Fractions of 4–10 mL were collected, with product **2** typically eluting between the fifth and tenth fraction. In most case, alkyl chloride and alkyl benzoate side-products are eluted before the desired formats. Thin-layer chromatography (TLC) visualization was generally performed using PMA staining and UV irradiation for π-system-containing compounds. After concentration of the product containing fractions under reduced pressure and drying at 20 mbar for 5 – 10 minutes, the formats **2** were

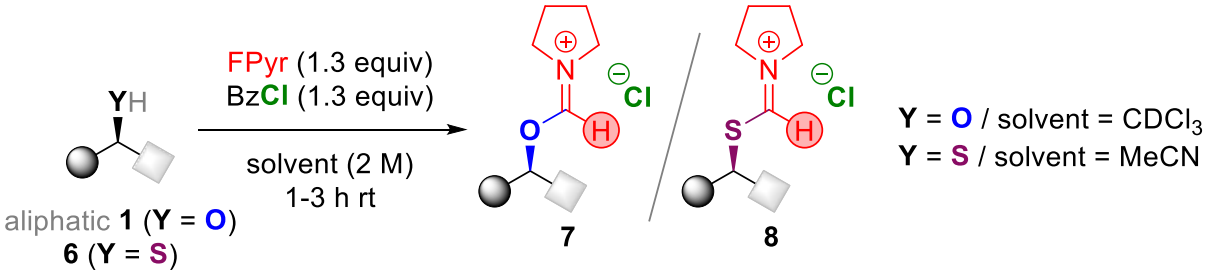
[6] Especially with electron rich benzylic alcohols short reaction durations ≤1 h allowed for enhanced yields, because of the lability of type **7´** intermediates.

[7] According to a safety data sheet of Sigma-Aldrich, the solubility of $NaHCO_3$ in water is 93.4 g/L at 20°C (see https://www.sigmaaldrich.com/DE/en/sds/sigald/s6014?userType=anonymous). This corresponds to a concentration of approximately 1.1 mol/L.

[8] A swift separation of the organic from the aqueous phase is important to avoid hydrolysis of the thioformate products. Addition of saturated $NaHCO_3$, 1 M NaOH and NaOAc solution and water, respectively, to the reaction mixture resulted in severely diminished yields and the crude material contained large portions of the starting material.

obtained as colourless thin oils or in some cases as solids in typically >95% purity according to ^{1}H NMR and GC MS. Some volatile formats were dried at 50 instead of 20 mbar, after removal of *n*-heptane concentration with MTBE at the rotary evaporator for two to three times.

2.2.2. General Procedure B: Synthesis of Imidate Chloride Salts of Type 7 and 8



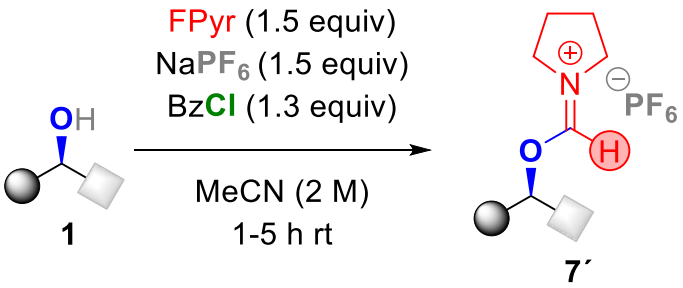
Reaction: A 4 mL glass vial is charged with alcohol **1** and thiol **6**, respectively, (1.00 mmol, 1.00 equiv), FPyr (123.9 µL, 128.9 mg, 1.30 mmol, 1.30 equiv) and $CDCl_3$ in case of alcohols and dry MeCN in the instance of thiols. (0.50 ml, 2 M). Next, BzCl (151.0 µL, 182.7 mg, 1.30 mmol, 1.30 equiv) is added at room temperature under stirring at 400 rpm and the resulting solution is stirred for the indicated time period (1-3 h).

Sample Preparation Alcohols: Next, a small aliquot of the reaction solution (50 µL) is withdrawn using an Eppendorf pipette, diluted with $CDCl_3$ (500 µL) and immediately subjected to NMR spectroscopy.

Sample Preparation Thiols: Afterwards, a small aliquot of the reaction solution (50 µL) is withdrawn using an Eppendorf pipette, transferred to 10 mL pointed-shaped flask and dried at the rotary evaporator at 20 mbar for 5 min. The residue is suspended in $CDCl_3$ (circa 600 µL), filtered through a glass pipette with a 5 mm layer of $MgSO_4$ and a plug of wool into an NMR tube and immediately subjected to NMR spectroscopy.

Characterization: The product ratios and conversion are determined with the aid of the ^{1}H NMR spectrum under consideration of the alkanol starting material **1**, alkyl formate **2**, alkyl benzoate, alkyl chloride **5** and the desired iminium salt **7** and **8**, respectively. After complete NMR characterization (^{13}C, HHCOSY, HSQC, HMBC and NOESY) another ^{1}H NMR spectrum is recorded to check the rate of decomposition of imidate **7** and **8**.

2.2.3. General Procedure C: Synthesis of Imidate Hexafluorophosphate Salts 7´



Reaction: A 4 mL glass vial is loaded with alcohol **1** (1.00 mmol, 1.00 equiv), FPyr (142.9 μL, 148.7 mg, 1.50 mmol, 1.50 equiv), $NaPF_6$ (251.9 mg, 1.50 mmol, 1.50 equiv) in dry MeCN (0.50 mL, 2.0 M). Next, BzCl (151.0 μL, 182.7 mg, 1.30 mmol, 1.30 equiv, 1.30 mmol, 1.30 equiv) is added at room temperature under stirring 400 rpm.

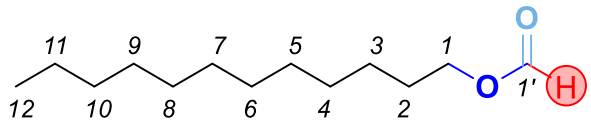
Sample Preparation: After 1-5 h of stirring, a 50 μL sample of the reaction mixture is withdrawn with an Eppendorf pipette and transferred to 10 mL pointed-shaped flask. The sample is subsequently concentrated at the rotary evaporator at 20 mbar for 5 min and the remaining solid is mixed with $CDCl_3$ (ca. 600 μL). In the following, the resulting suspension is filtered through a glass pipette containing a plug of wool and a 5 mm layer of $MgSO_4$ into a NMR tube.

Characterization: See general Procedure B above.

2.3. Experimental Procedures and Analytical Data

2.3.1. Synthesis of Aliphatic Formates of Type 2

2.3.1.1. Synthesis of 1-Dodecyl Formate (2a)



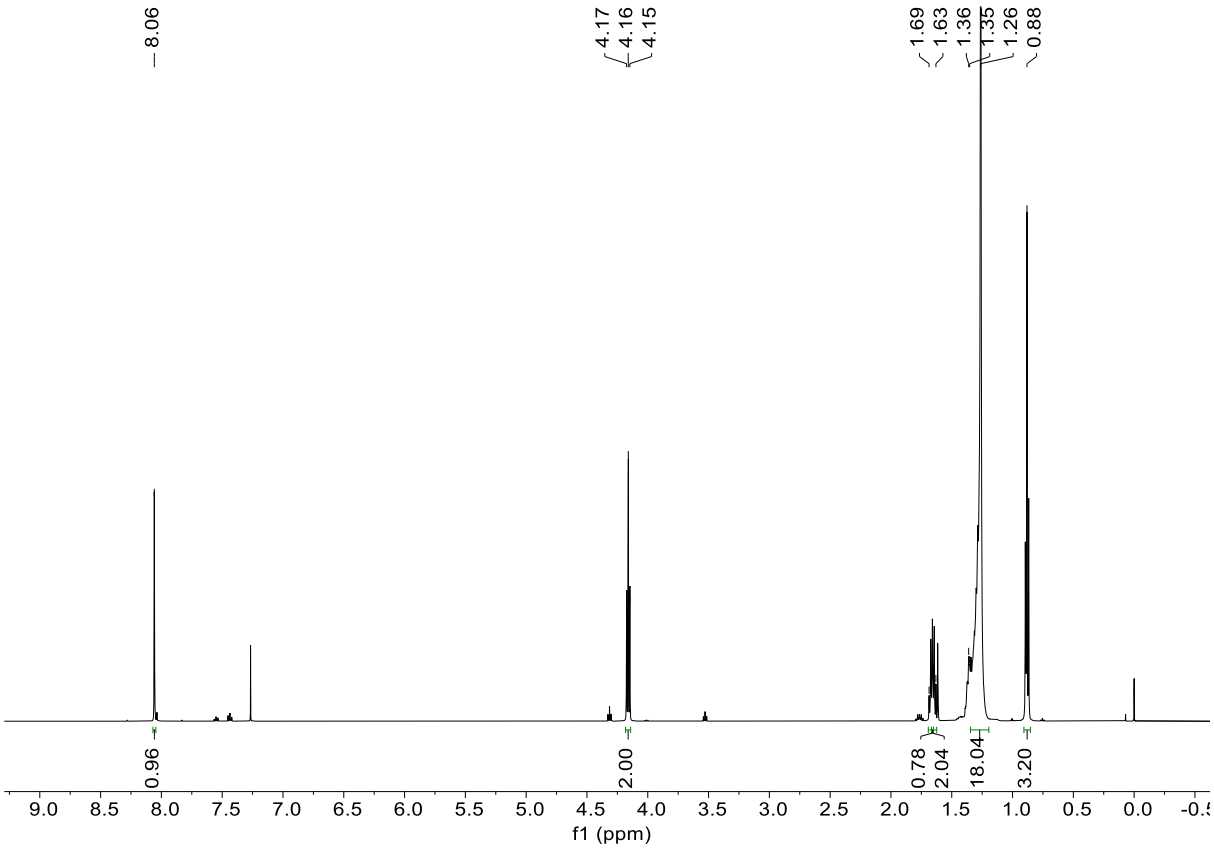
2a

DTT-269: In accordance with general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from dodecanol **1a** (95.3 µL, 93.1 mg, 0.50 mmol, 1.00 equiv) using FPyr (71.5 µL, 74.3 mg, 0.75 mmol, 1.50 equiv) and BzCl (75.5 µL, 91.4 mg, 0.65 mmol, 1.30 equiv) in dry MeCN (0.25 mL, 2.0 M). After stirring for 3 h, saturated $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M) was added. The ^{1}H NMR of the crude material (102.9 mg, 90%) with mesitylene (11.4 mg) as internal standard verified full conversion of alcohol **1a** and product **2a** in 86% yield.

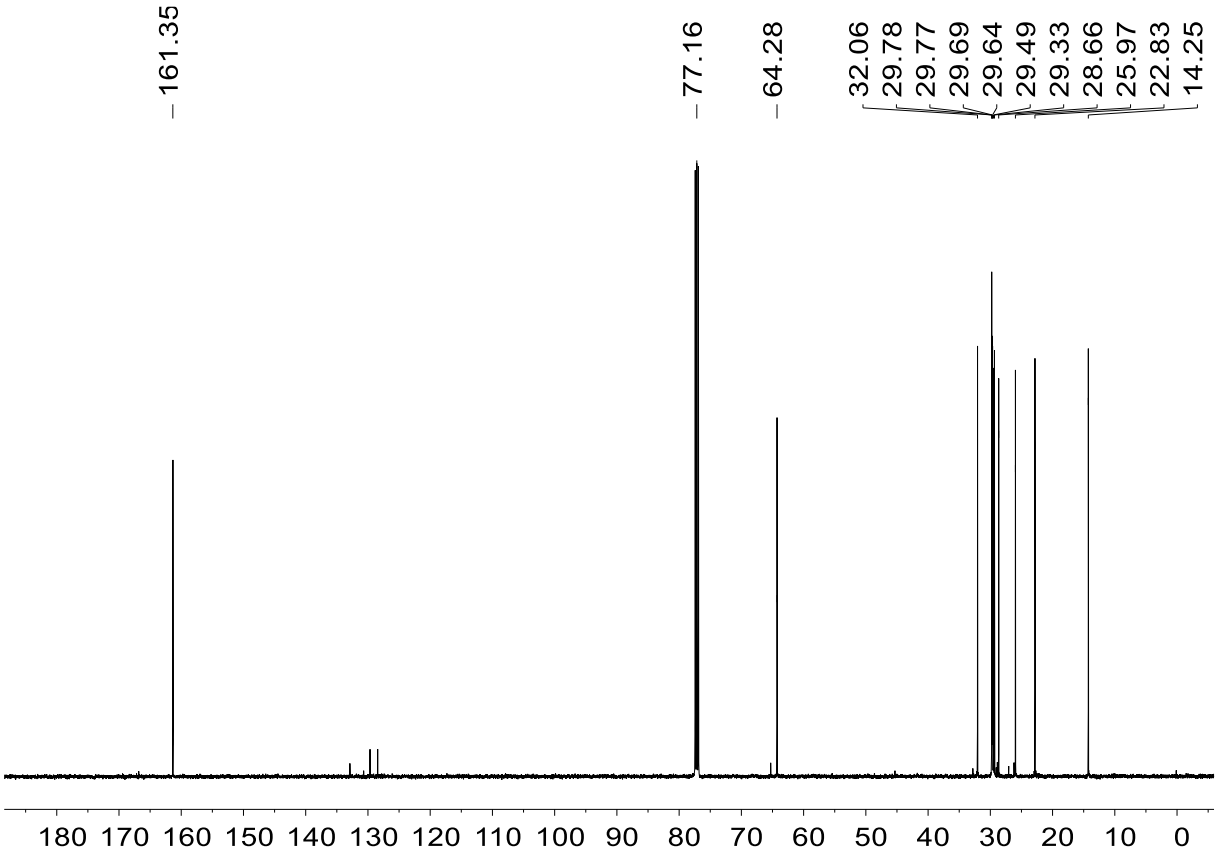
DTT-271: According to general procedure A (chapter 2.2.1, page 8) 1-dodecanol (**1a**, 449.0 µL, 372.7 mg, 2.00 mmol, 1.00 equiv) was allowed to react with FPyr (286 µL, 297.4 mg, 3.00 mmol, 1.50 equiv) and BzCl (302 µL, 365.5 mg, 2.60 mmol, 1.30 equiv) in MeCN (1 mL, 2 M) for 2 h. Then, $NaHCO_3$ solution (3.0 mL, 1.70 equiv, 1.1 M) was added. After aqueous work up, the ^{1}H NMR spectrum of the crude material (436.9 mg, 96%) verified full conversion of alcohol **1a**. Finally, purification with the aid of column chromatography on silica gel (8.6 g, ratio weight crude product/SiO_2 1:20) using MTBE/*n*-heptane 4:96 as solvent mixture and drying in high vacuum for several hours furnished dodecyl formate **2a** as a colourless oil (389.1 mg, 1.82 mmol) in 91% yield.

M ($C_{13}H_{26}O_2$) = 214.19 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 4:96) = 0.52; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.06 (s, 1H, 1'-H), 4.16 (t, $^3J_{1,2}$ = 5.0 Hz, 2H, 1-H), 1.69-1.63 (m, 2H, 2-H), 1.34-1.26 (m, 18H, 3-H to 11-H), 0.88 (t, $^3J_{12,11}$ = 5.0 Hz, 3H, 12-H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ [ppm] = 161.35 (C-1'), 64.28 (C-1), 32.06 (C-10 or C-11), 29.78, 29.77, 29.69, 29.64, 29.49, 29.33 (C-3 to C-9), 28.66 (C-2), 25.97 (C-10), 22.83 (C-10 or C-11), 14.25 (C-12); **GC MS** (EI, 70 eV) m/z [u] (%) = 169 (9, [dodecanyl]$^+$), 140 (24, [decene]$^+$), 125 (16, [nonenyl]$^+$), 112 (20, [octene]$^+$), 111 (45, [octenyl]$^+$), 110 (7, [octyne]$^+$). 98 (33, [heptene]$^+$), 97 (76, [heptenyl]$^+$), 96 (19, [heptyne]$^+$), 85 (14, [hexanyl]$^+$), 84 (54, [hexene]$^+$), 83 (97, [hexenyl]$^+$), 71 (23, [pentyl]$^+$), 70 (77, [pentene]$^+$), 69 (100, [pentenyl]$^+$), 57 (58, [butanyl]$^+$), 56 (58, [butene]$^+$), 55 (99, [pentenyl]$^+$); **HR MS** (EI, $[C_{13}H_{25}O_2]^+$) calc. 213.18491 u, found 213.1853 u.

The NMR data is in agreement with literature data.[1]

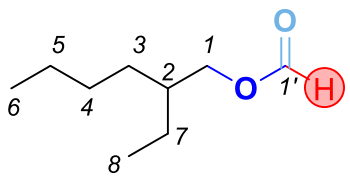


^{1}H NMR spectrum of 1-dodecyl formate (**2a**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 1-dodecyl formate (**2a**, 126 MHz, $CDCl_3$).

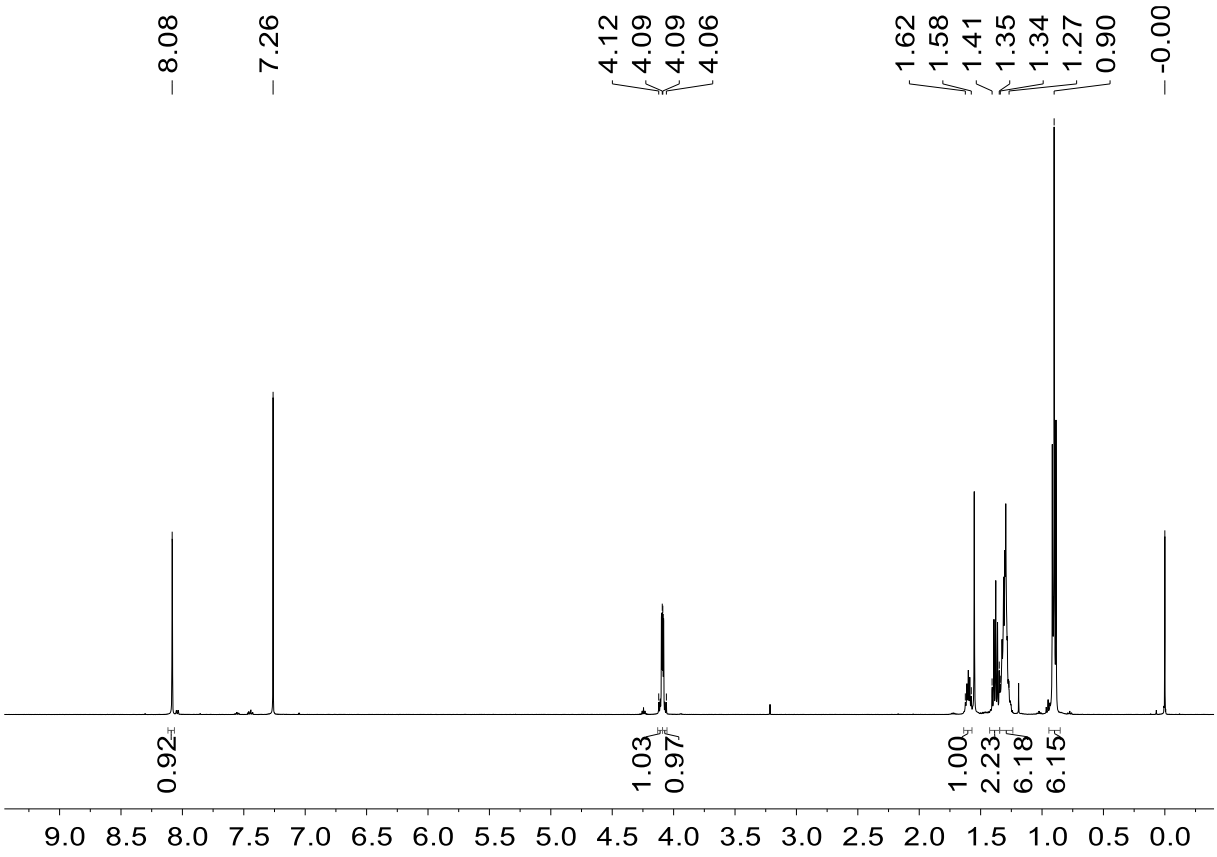
2.3.1.2. Synthesis of 2-Ethylhex-1-yl formate (2b)



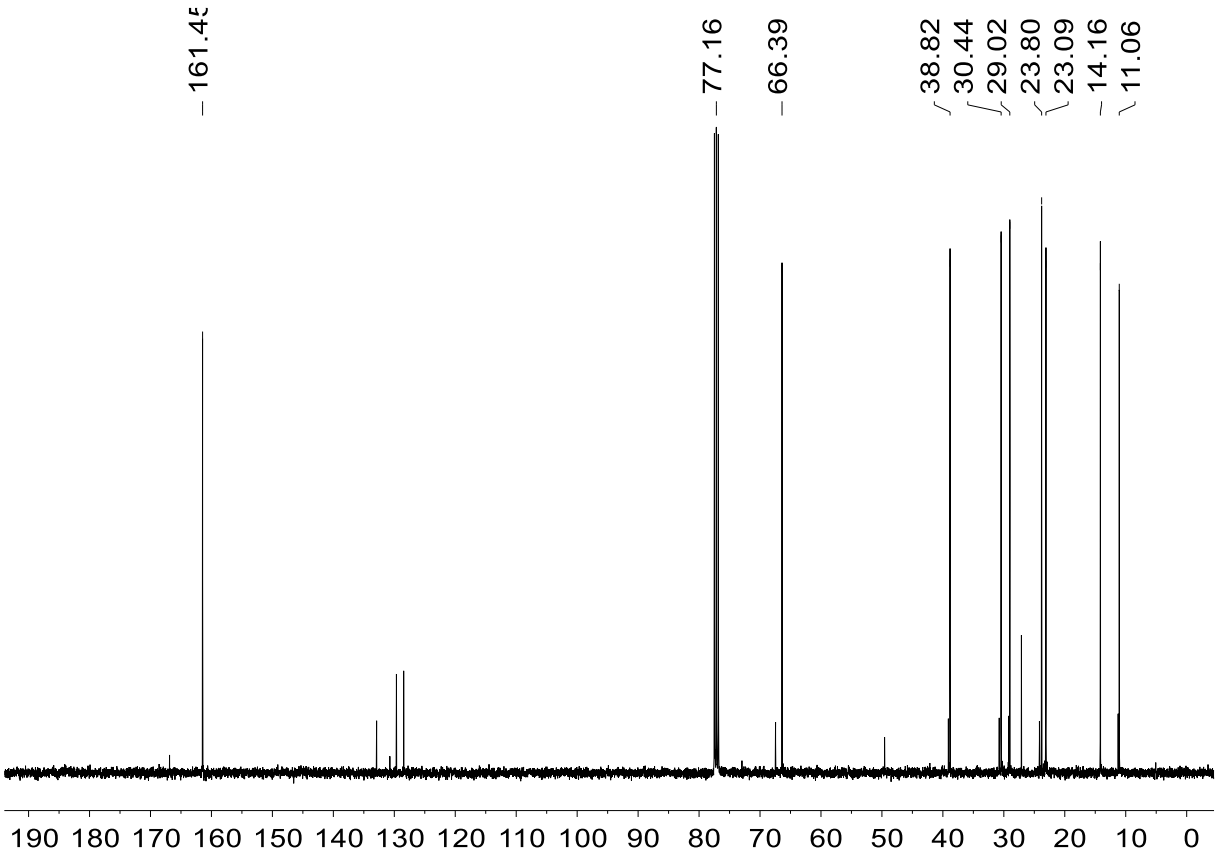
2b

DTT-270: In agreement with general protocol A (chapter 2.2.1, page 8), title compound was produced from 2-ethylhexan-1-ol (**1b**, 313.8 µL, 260.5 mg, 2.00 mmol, 1.00 equiv), FPyr (286.0 µL, 297.4 mg, 3.00 mmol, 1.50 equiv) and BzCl (302.1 µL, 365.5 mg, 2.60 mmol, 1.30 equiv) in MeCN (1.0 mL, 2.0 M) under stirring for 3 h. After quenching with saturated $NaHCO_3$ solution (2.0 mL, 1.2 equiv, 1.1 M), the ^{1}H NMR of the crude material (346.2 mg, 109%) verified full conversion of alcohol **1b**. Finally, purification with the aid of column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:14) using MTBE/*n*-heptane 4:96 as solvent mixture afforded formate **2b** as a colourless oil (265.1 mg, 1.68 mmol, 84%) after drying in high vacuum.

M ($C_9H_{18}O_2$) = 158.24 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 4:96) = 0.51; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.08 (s, 1H, 1'-H), 4.11 (ddd, $^2J_{1a,1b}$ = 11.0 Hz, $^3J_{1a,2}$ = 5.7 Hz, $^4J_{1a.1'}$ = 0.7 Hz, 1H, 1-H_a), 4.08 (ddd, $^2J_{1b,1a}$ = 11.0 Hz, $^3J_{1b,2}$ = 5.8 Hz, $^4J_{1b.1'}$ = 0.7 Hz, 1H, 1-H_b), 1.62-1.58 (m, 1H, 2-H), 1.41-1.35 (m, 2H, 7-H), 1.34 - 1.27 (m, 6H, 3-H, 4-H, 5-H), 0.90 (t, $^3J_{6,5}$ = $^3J_{8,7}$ = 7.5 Hz, 6H, 6-H, 8-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 161.45 (C-1'), 66.39 (C-1), 38.82 (C-2), 30.44 (C-3), 29.02 (C-7), 23.80 (C-4), 23.09 (C-8), 14.16 (C-5), 11.06 (C-6); **GC MS** (EI, 70 eV) m/z [u] (%) = 112 (7, $Bu(Et)CHCH_2]^+$), 99 (2, [heptyl]$^+$), 98 (3, [heptene]$^+$), 97 (3, [heptenyl]$^+$), 83 (34, [hexenyl]$^+$), 70 (79, [pentyl]$^+$), 57 (100, [Bu]$^+$), 55 (47, [butenyl]$^+$).
The NMR data is in approximate agreeing with literature data.[3]

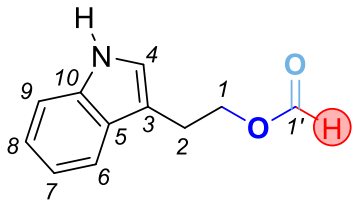


^{1}H NMR spectrum of 2-ethyl-1-hexyl formate (**2b**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-ethyl-1-hexyl formate (**2b**, 101 MHz, $CDCl_3$).

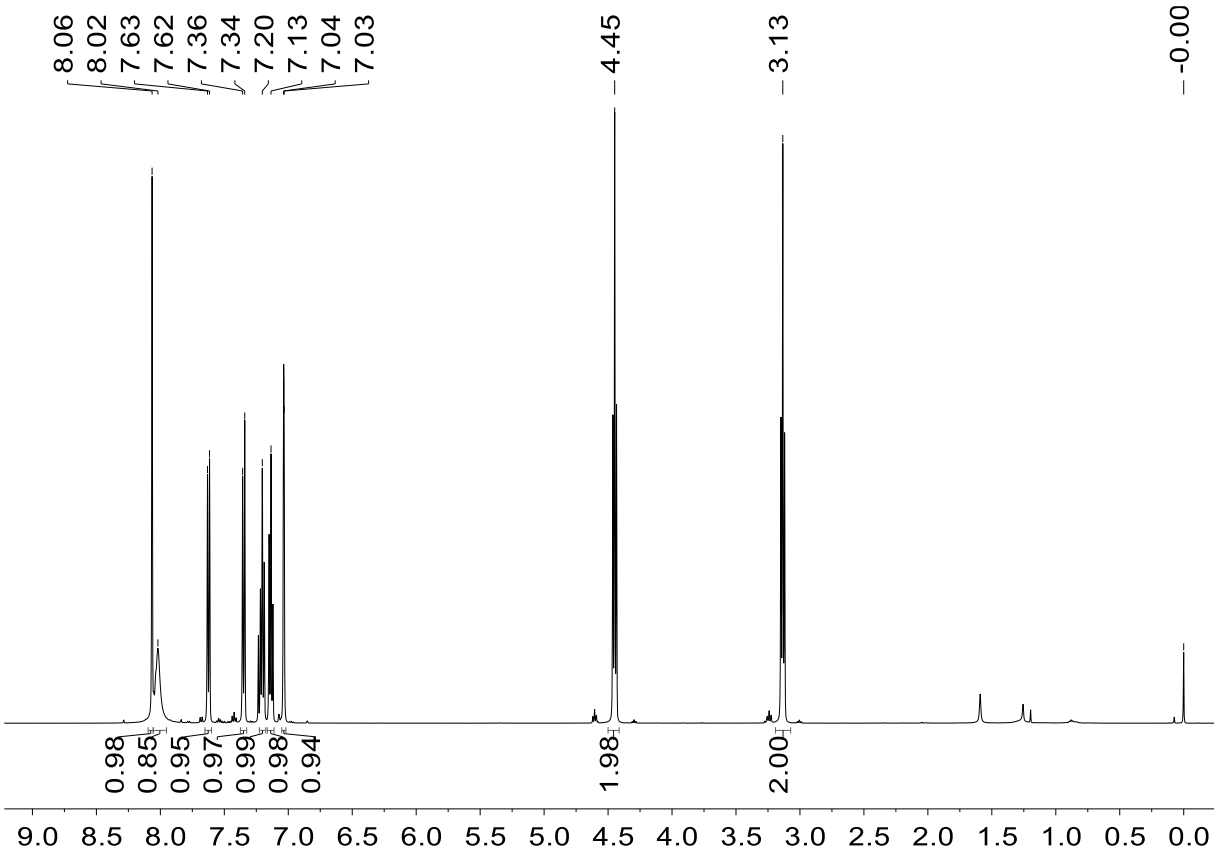
2.3.1.3. Synthesis of 2-(1H-indol-3-yl)-1-ethyl Formate (2c)



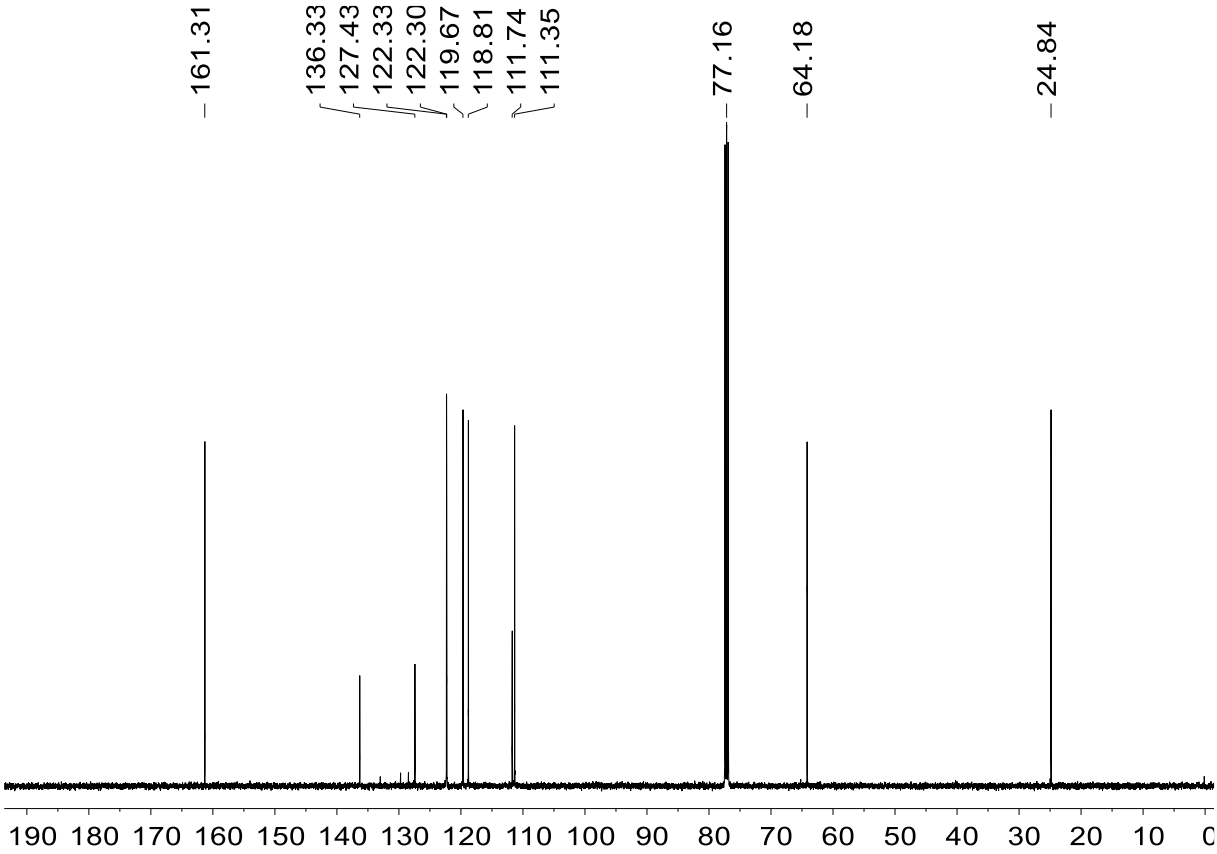
2c

DTT-281: In accordance with general protocol A (chapter 2.2.1, page 8), 2-(1H-indol-3-yl)-1-ethanol (**1c**, 161.0 mg, 1.00 mmol, 1.00 equiv) was reacted with FPyr (143.0 µL, 148.7 mg, 1.50 mmol, 1.50 equiv) and BzCl (151.0 µL, 182.7 mg, 1.30 mmol, 1.30 equiv) in MeCN (0.5 mL, 2.0 M). After 2 h of stirring and addition of $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M), the ^{1}H NMR of the crude material (200.9 mg, 106%) verified full conversion of alcohol **1c**. Finally, purification with the aid of column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:35) using MTBE/*n*-heptane 20:80 as solvent mixture yielded the title compound **2c** (173.5 mg, 0.92 mmol, 92%) as a colourless liquid.

M ($C_{11}H_{11}NO_2$) = 189.08 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 20:80) = 0.38; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.06 (s, 1H, 1'-H), 8.02 (br. s, 1H, NH), 7.62 (d, $^3J_{9,8}$ = 7.9 Hz, 1H, 9-H), 7.35 (d, $^3J_{6,7}$ = 8.1 Hz, 1H, 6-H), 7.20 (ψ-t, ^3J = 7.7 Hz, 1H, 7-H), 7.13 (ψ-t, ^3J = 7.5 Hz, 1H, 8-H), 7.03 (d, $^3J_{4,NH}$ = 2.4 Hz, 1H, 4-H), 4.45 (t, $^3J_{1,2}$ = 7.3 Hz, 2H, 1-H), 3.13 (t, $^3J_{2,1}$ = 7.1 Hz, 2H, 2-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 161.31 (C-1'), 136.33 (C-10), 127.43 (C-3), 122.33 (C-7), 122.30 (C-4), 119.67 (C-8), 118.81 (C-9), 111.74 (C-5), 111.35 (C-6), 64.18 (C-1), 24.84 (C-2); **GC MS** (EI, 70 eV) m/z [u] (%) = 189 (33, $[M]^+$), 144 (13, $[M\text{-}OCHO]^+$), 143 (68, $[M\text{-}OCHO\text{-}H]^+$), 142 (7, [2-indol-ethene]$^+$), 131 (11), 130 (100, 7, [3-methylenindole]$^+$, 129 (5), 128 (5), 116 (3, [indole]$^+$), 115 (10, [indole-H]$^+$), 103 (11, [styrene]$^+$), 77 (12, [Ph]$^+$); **HR MS** (EI, $[C_{11}H_{12}N]^+$) calc. 189.07843 u, found 189.07865 u.

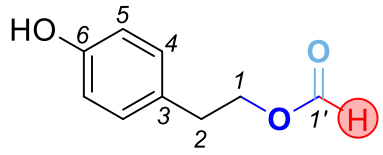


^{1}H NMR spectrum of 2-(1H-indol-3-yl)ethyl formate **2c** (500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-(1H-indol-3-yl)ethyl formate **2c** (126 MHz, $CDCl_3$).

2.3.1.4. Synthesis of 2-(4-Hydroxyphenyl)-1-ethyl Formate (2d)

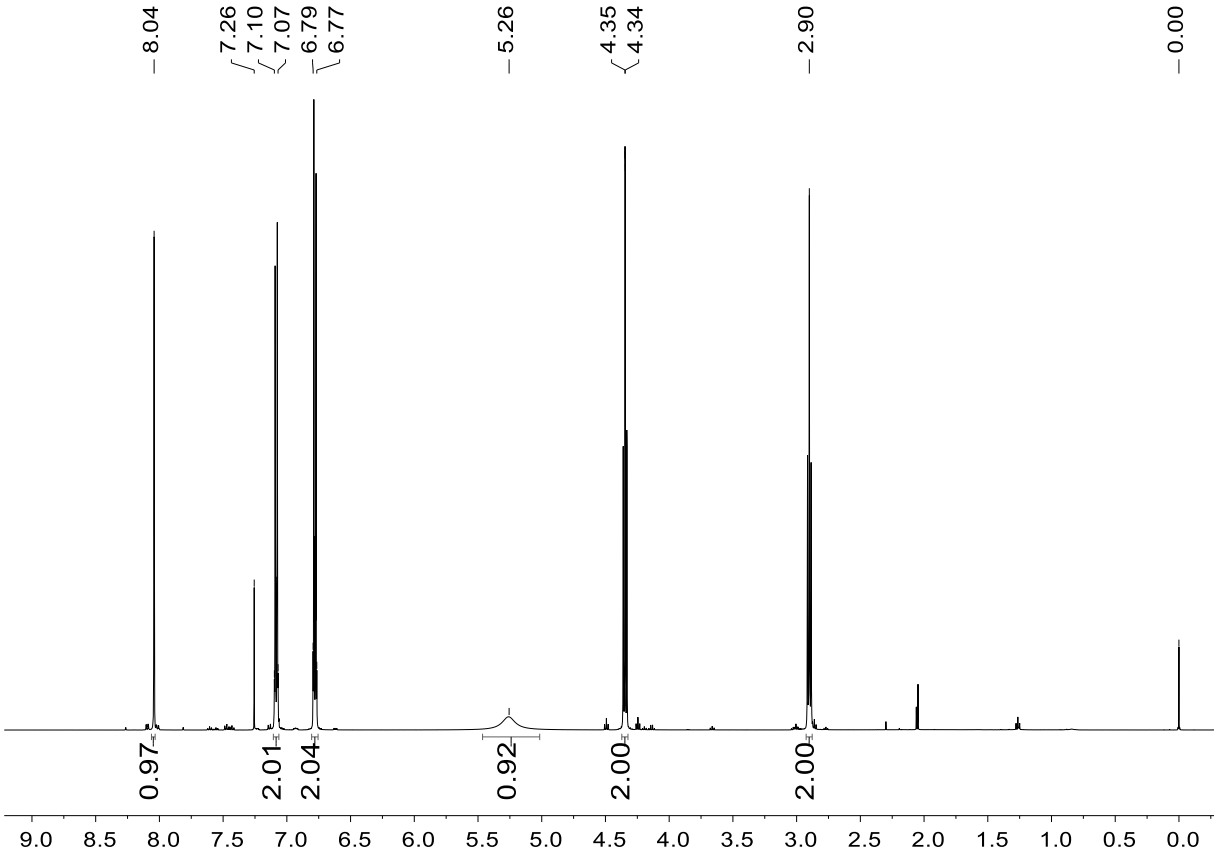


2d

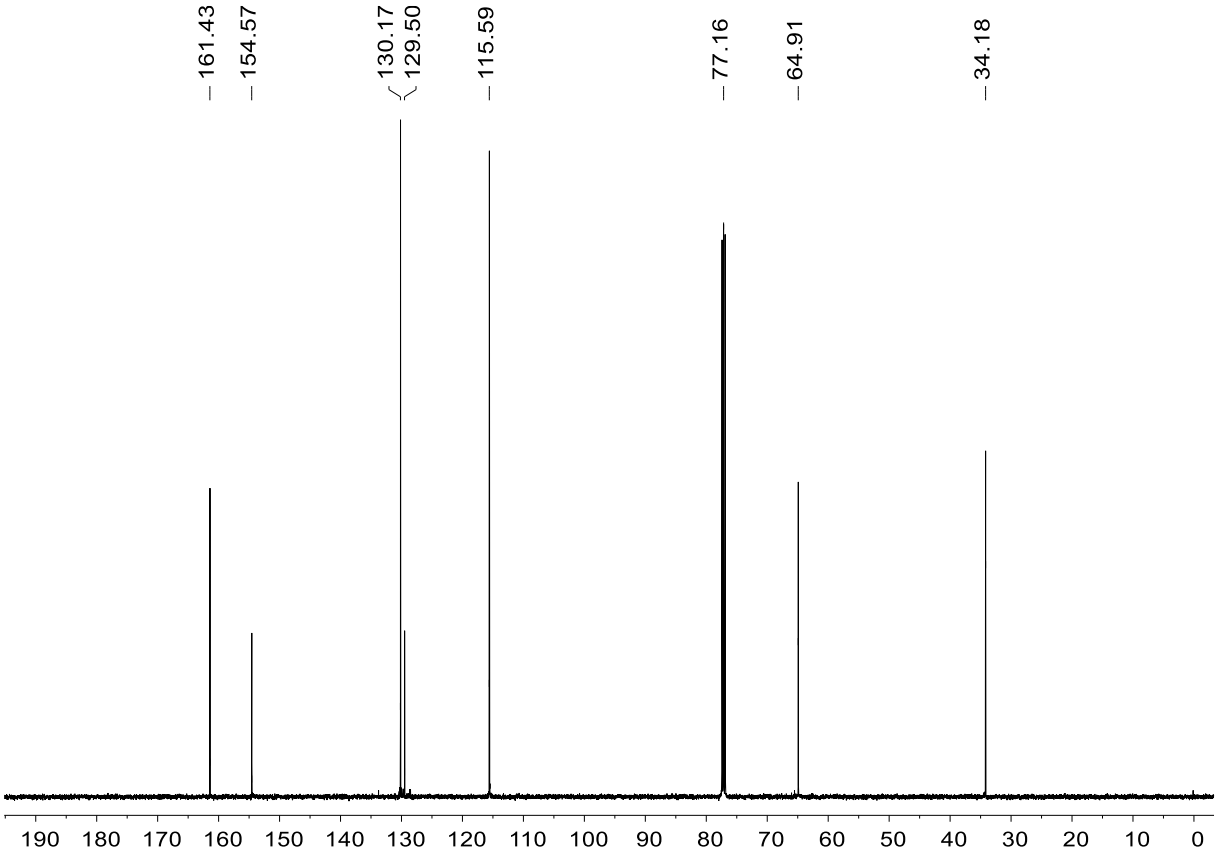
DTT-289: Following general protocol A (chapter 2.2.1, page 8), the title compound was synthesized using 2-(4-hydroxyphenyl)-1-ethanol (**1d**, 138.2 mg, 1.00 mmol, 1.00 equiv), FPyr (162.0 µL, 168.5 mg, 1.70 mmol, 1.70 equiv), MeCN (0.5 mL, 2.0 M) and BzCl (174.3 µL, 210.9 mg, 1.50 mmol, 1.50 equiv). After 4 h stirring, and quenching with a saturated solution of $NaHCO_3$(2.0 mL, 2.2 equiv, 1.1 M) ^{1}H NMR of the crude material (193.7 mg, 117%) verified full conversion of alcohol **1d**. Eventually, purification by means of column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:25) using MTBE/*n*-heptane 30:70 as solvent mixture afforded formate **2d** as a pink pastel liquid (149.1 mg, 0.90 mmol, 90%) after drying in high vacuum.

M ($C_9H_{10}O_3$) = 166.06 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 50:50) = 0.41; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.04 (s, 1H, 1'-H), 7.10 - 7.07 (m, 2H, 4-H), 6.79-6.77 (m, 2H, 5-H), 5.26 (s, 1H, OH), 4.35 (td, $^3J_{1,2}$ = 7.0 Hz, $^2J_{1,1'}$ = 0.8 Hz, 2H, 1-H), 2.90 (t, $^3J_{1,2}$ = 7.0 Hz, 2H, 2-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 161.43 (C-1'), 154.57 (C-6), 130.17 (C-4), 129.50 (C-3), 115.59 (C-5), 64.91 (C-1), 34.18 (C-2); **GC MS** (EI, 70 eV) m/z [u] (%) = 166 (4, $[M]^+$), 121 (12, $[M\text{-}OCHO]^+$), 120 (100, $[M\text{-}OCHO\text{-}H]^+$), 119 (7, [4-HO-styrene]$^+$), 108 (6), 107 (73, [(4-hydroxylphenyl) methyl]$^+$, 91 (9, $[Bn]^+$), 77 (19, $[Ph]^+$); **HR MS** (EI, $[C_9H_{10}O_3]^+$) calc. 166.06245 u, found 166.06286 u.

The NMR data is in match with the literature.[4]

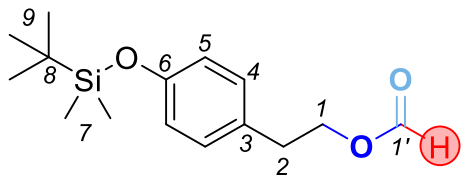


^{1}H NMR spectrum of 2-(4-hydroxyphenyl)-1-ethyl formate (**2d**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-(4-hydroxyphenyl)-1-ethyl formate (**2d**, 126 MHz, $CDCl_3$).

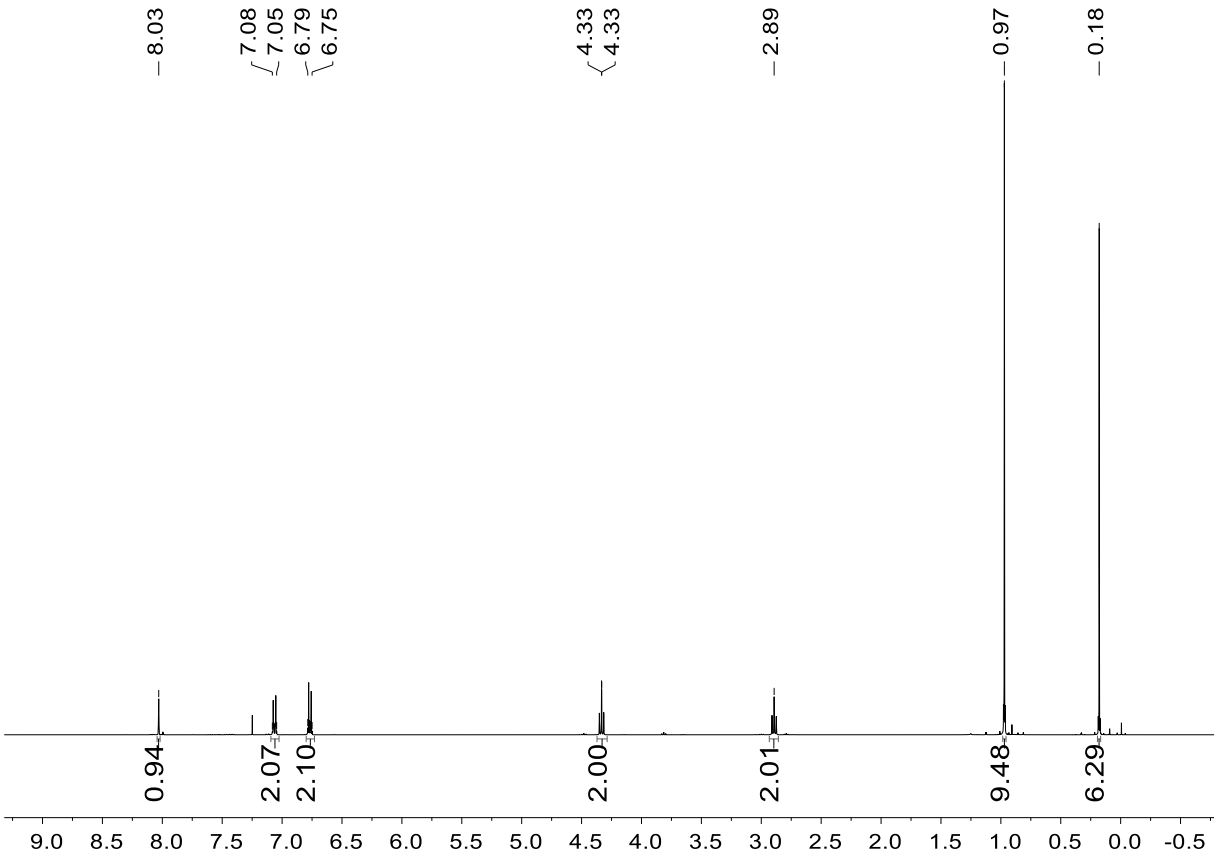
2.3.1.5. Synthesis of 2-(4-(*tert*-Butyldimethylsilyloxy)phenyl-1-ethyl Formate (2e)



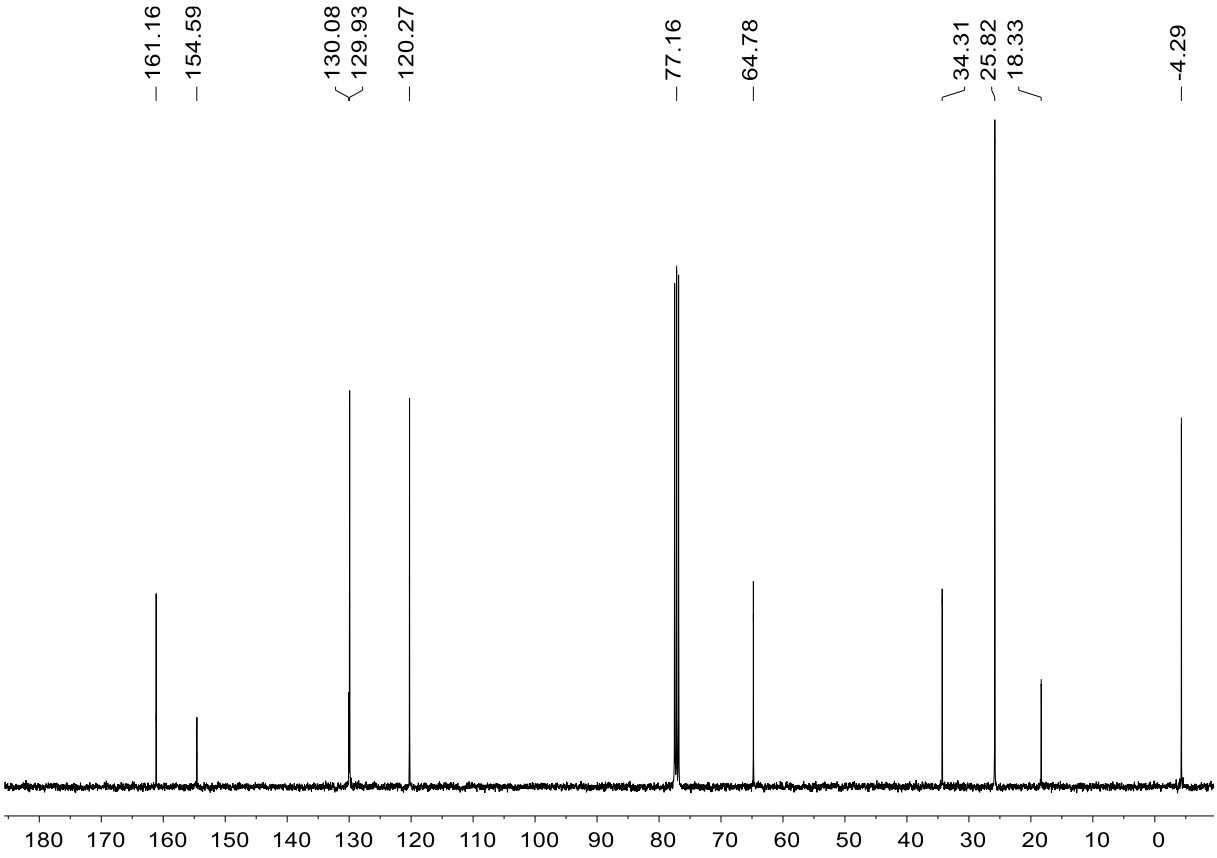
2e

DTT-290: In accordance with general protocol A (chapter 2.2.1, page 8), the title compound was produced with 2-(4-(*tert*-butyldimethylsilyloxy)-1-phenyl ethanol (**1e**, 126 mg, 0.50 mmol, 1.00 equiv), FPyr (62.0 µL, 64.4 mg, 0.65 mmol, 1.30 equiv), MeCN (0.25 mL, 2.0 M) and BzCl (69.7 µL, 84.3 mg, 0.60 mmol, 1.20 equiv). After 2 h of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M) the ^{1}H NMR of the crude material (134.6 mg, 170%) proved full conversion of alcohol **1e**. In the end, the purification with the aid of column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:37) using MTBE/*n*-heptane 20:80 as solvent mixture furnished product **2e** in 77% yield (108.2 mg, 0.39 mmol) as a colourless liquid. The production of the starting material is described in chapter [2.3.4.1.] (page 87).

M ($C_{15}H_{24}O_3Si$) = 280.15 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 10:90) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.03 (s, 1H, 1'-H), 7.08-7.05 (m, 2H, 4-H), 6.79-6.75 (m, 2H, 5-H), 4.33 (td, $^3J_{1,2}$ = 7.1 Hz, $^4J_{1,1'}$ = 0.9 Hz, 2H, 1-H), 2.89 (t, $^3J_{3,2}$=7.1, 2H, 3-H), 0.97 (s, 9H, 9-H), 0.18 (s, 6H, 7-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 161.16 (C-1'), 154.59 (C-6), 130.08 (C-3), 129.93 (C-5), 120.27 (C-4), 64.78 (C-1), 34.31 (C-2), 25.82 (C-9), 18.33 (C-8), -4.29 (C-7); **GC MS** (EI, 70 eV) m/z [u] (%) = 280 (20, $[M]^+$), 236 (3), 235 (12, $[M\text{-}OCHO]^+$), 234 (41, $[M\text{-}OCHO\text{-}H]^+$), 224 (9), 223 (5), 221 (4, $[M\text{-}OCHO\text{-}CH_2]^+$), 219 (10), 195 (16), 178 (37), 177 (100, $[4\text{-}(Me_2SiO)styrene]^+$), 163 (10), 151 (11), 149 (15) ,103 (82), 75 (40); **HR MS** (EI, $[C_{15}H_{24}O_3Si]^+$) calc. 280.14892 u, found 280.14885 u.

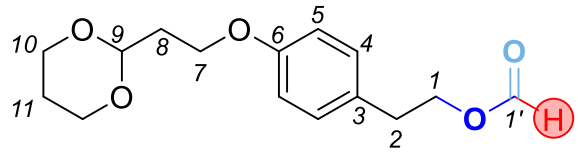


^{1}H NMR spectrum of 2-(4-(*tert*-butyldimethylsilyloxy)phenyl-1-ethyl formate (**2e**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 4-((*tert*-butyldimethylsilyl)oxy)phenethyl formate **2e** (101 MHz, $CDCl_3$).

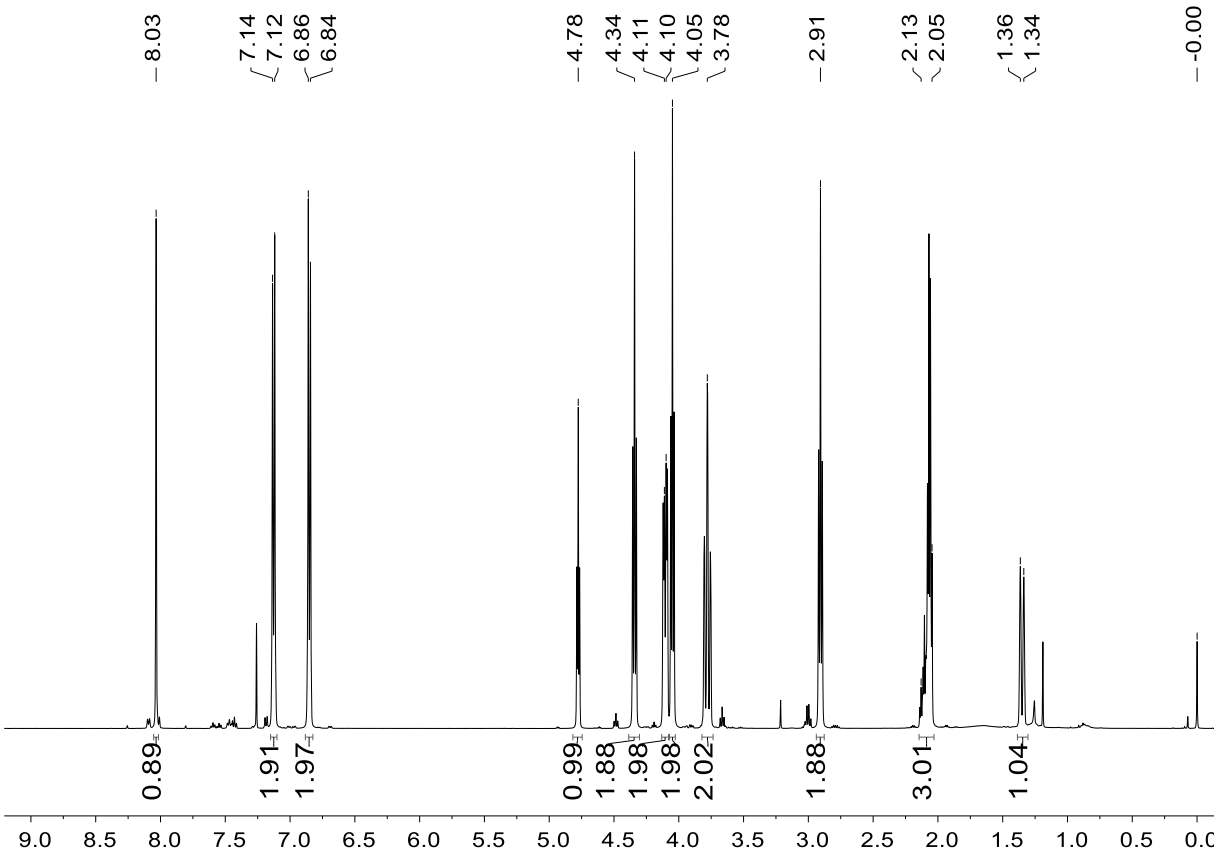
2.3.1.6. Synthesis of 2-(4-(2-(1,3-Dioxan-2-yl)ethoxy)phenyl)-1-ethyl Formate (2f)



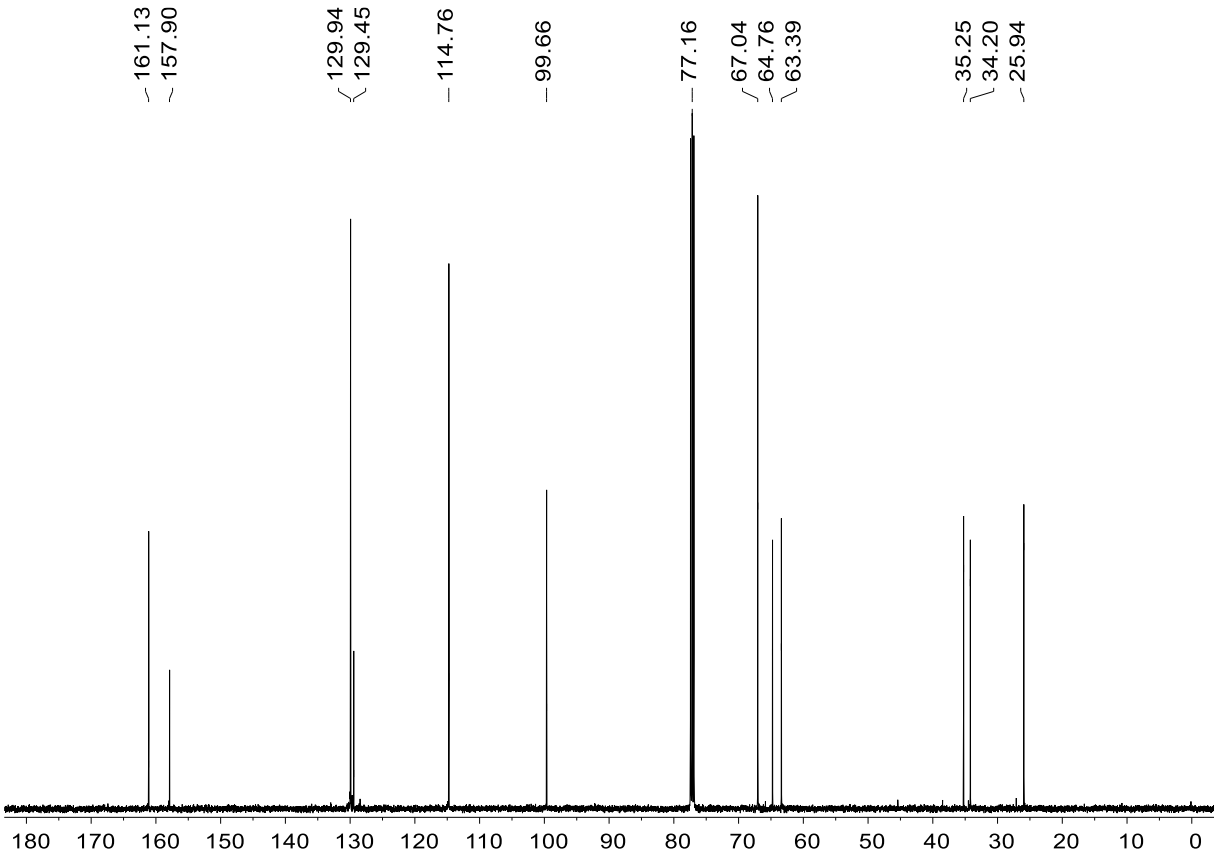
2f

DTT-282: As described in general protocol A (chapter 2.2.1, page 8), 2-(4-(2-(1,3-dioxan-2-yl)ethoxy)phenyl)-1-ethanol (**1f**, 252.1 mg, 1.0 mmol, 1.0 equiv) was transformed with FPyr (43.0 µL, 148.7 mg, 1.50 mmol, 1.50 equiv) and BzCl (151,0 µL, 182.7 mg, 1.30 mmol, 1.30 equiv) in MeCN (0.5 mL, 2.0 M) into the title compound After 2 h of stirring and addition of $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M), the ^{1}H NMR of the crude material (307.1 mg, 107%) verified full conversion of alcohol **1f**. Afterwards, the purification with the aid of column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:16) using MTBE/*n*-heptane 30:70 as solvent mixture allowed the isolation of product **2f** in 96% yield (268.0 mg, 0.96 mmol) as a colorless solid. The preparation of the starting material is delineated in chapter 2.3.4.2 (page 83).

M ($C_{15}H_{20}O_5$) = 280.13 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 30:70) = 0.38; **mp.** = 75-76 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.03 (s, 1H,1'-H), 7.13 (ψ-d, $^3J_{4,5}$ = 8.2 Hz, 2H, 4-H), 6.85 (d, $^3J_{5,4}$ = 8.2 Hz, 2H, 5-H), 4.78 (t, $^3J_{9,8}$ = 5.3 Hz, 1H, 9-H), 4.34 (t, $^3J_{1,2}$ = 7.0 Hz, 2H, 1-H), 4.11 (ψ-dd, $^2J_{10a,10b}$ = 11.6 Hz, $^3J_{10a,11a}$ = 4.9 Hz, 2H, 10-H_a), 4.05 (t, $^3J_{7,8}$ = 6.3 Hz, 2H, 7-H), 3.78 (ψ-t, *J* = 12.3 Hz, 2H, 10-H_b), 2.91 (t, $^3J_{2,1}$ = 7.0 Hz, 2H, 2-H,), 2.15-2.03 (m, 3H, 8-H, 11-H_b), 1.35 (ψ-d, 1H, 11-H_a); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 161.01 (C-1'), 157.78 (C-6), 129.83 (C-5), 129.34 (C-3), 114.65 (C-4), 99.54 (C-9), 66.93 (C-10), 64.65 (C-1), 63.28 (C-7), 35.13 (C-8), 34.09 (C-2), 25.83 (C-11); **GC MS** (EI, 70 eV) m/z [u] (%) = 280 (22, $[M]^+$), 235 (10, $[M\text{-}OCHO]^+$), 234 (49, $[M\text{-}OCHO\text{-}H]^+$), 176 (10), 121 (7, $[phenoxyethyl]^+$), 120 (33), 115 (38), 114 (20, $[vinyldioxane]^+$), 107 (31, $[hydroxyphenylmethylene]^+$), 100 (47, $[methylenedioxane]^+$), 91(16, $[Bn]^+$), 87 (100, $[1,3\text{-}dioxanyl]^+$), 77 (16, $[Ph]^+$); **HR-MS** (EI, $[C_{15}H_{20}O_5]^+$) calc. 280.13053 u, found 280.13099 u.

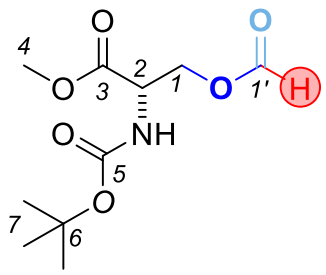


^{1}H NMR spectrum of 2-(4-(2-(1,3-dioxan-2-yl)ethoxy)phenyl)-1-ethyl formate (**2f**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-(4-(2-(1,3-dioxan-2-yl)ethoxy)phenyl)-1-ethyl formate (**2f**, 126 MHz, $CDCl_3$).

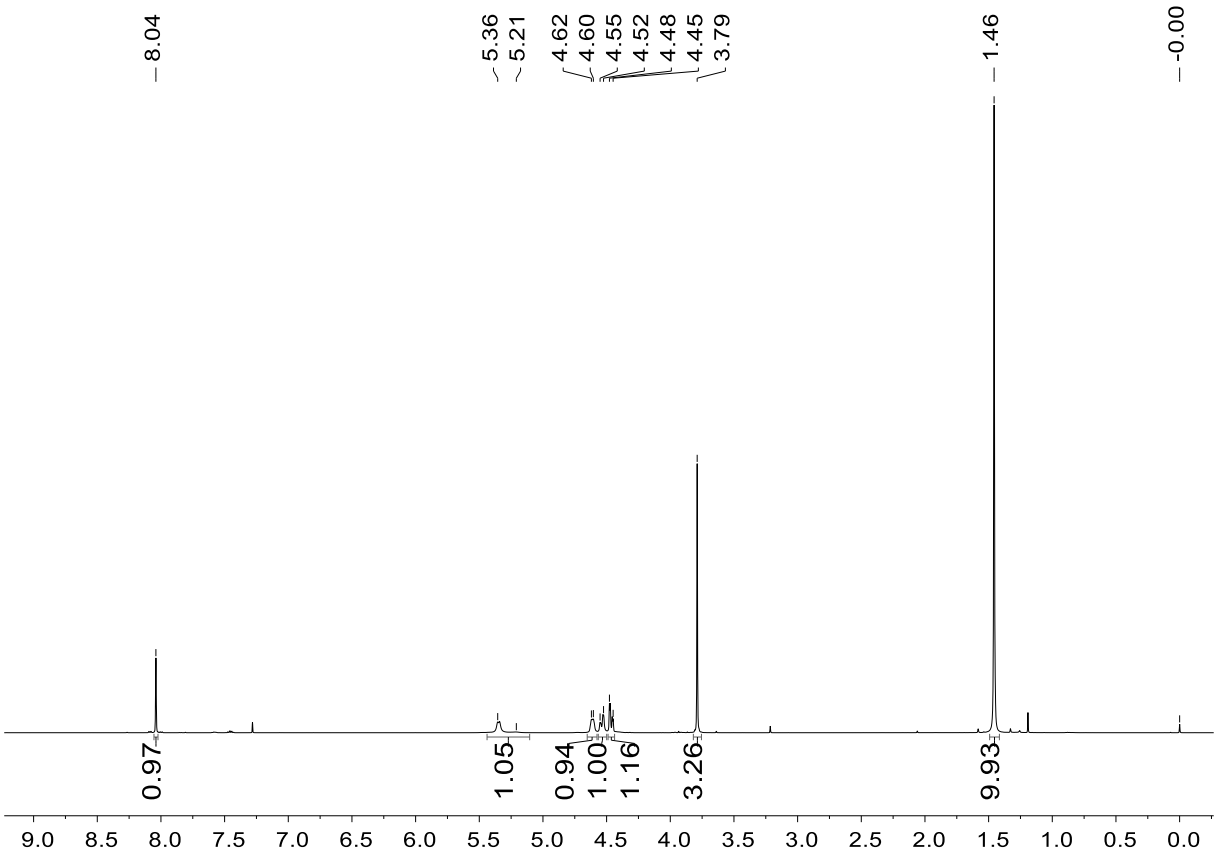
2.3.1.7. Synthesis of (2*S*)-Methyl *N*-(*tert*-butoxycarbonyl)-O-formyl-L-serinate (2g)



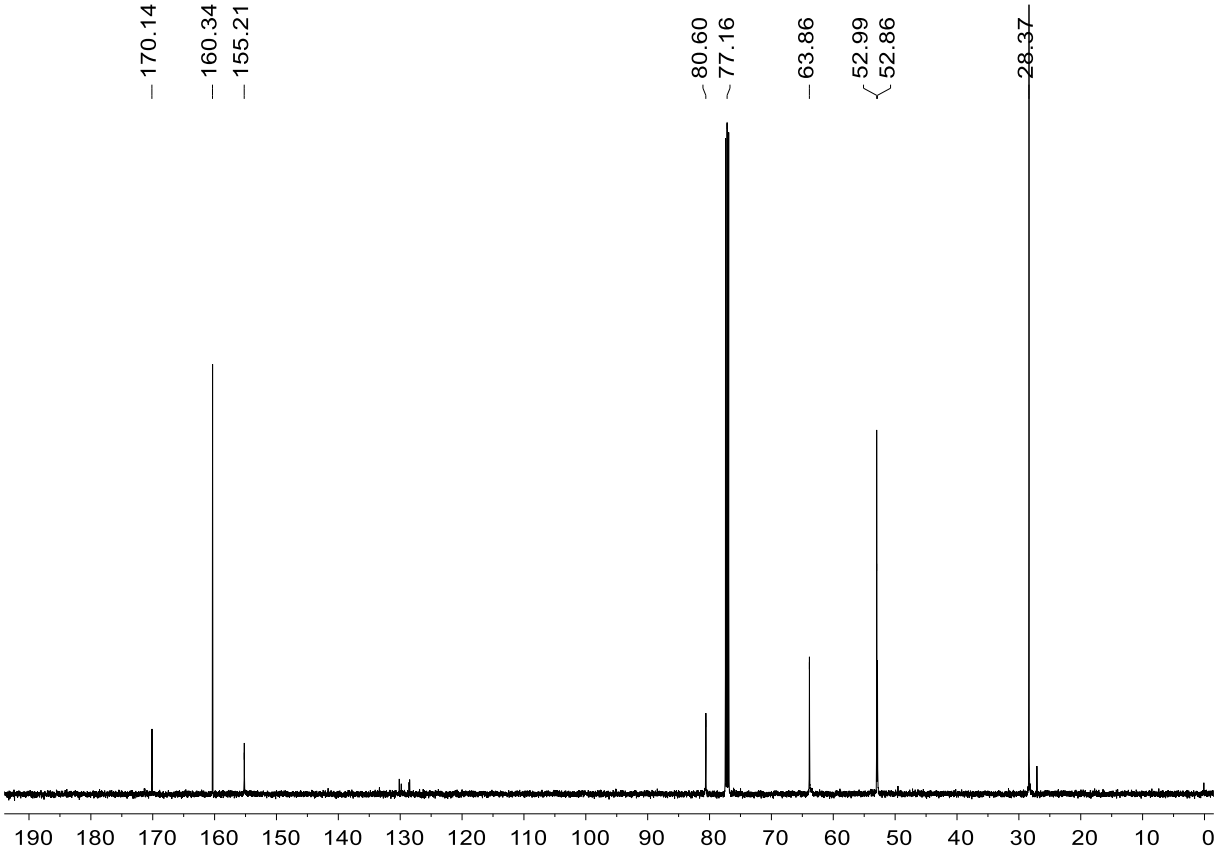
2g

DTT-284: As delineated in general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from methyl (*tert*-butoxycarbonyl)-L-serinate (**1g** 219.2 mg, 1.00 mmol, 1.00 equiv) with FPyr (143.0 µL, 148.7 mg, 1.50 mmol, 1.50 equiv) and BzCl (151.0 µL, 182.7 mg, 1.30 mmol, 1.30 equiv) in MeCN (0.5 mL, 2.0 M). past 2 h of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M) ^{1}H NMR of the crude material (256.9 mg, 104%) confirmed 61% conversion of alcohol **1g**. Finally, purification with column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:27) using MTBE/*n*-heptane 20:80 as solvent mixture gave ester **2g** in 46% yield (114.0 mg, 0.46 mmol) as a colourless oil.

M ($C_{10}H_{17}NO_6$) = 247.11 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 50:50) = 0.20; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.04 (s, 1H, 1'-H), 5.36-5.21 (m, 1H, NH), 4.62-4.60 (m, 1H, 2-H), 4.53 (dd, $^3J_{1a,1b}$ = 11.5 Hz, $^2J_{1a,2}$ = 3.6 Hz, 1H, 1-H_a), 4.47 (dd, $^3J_{1b,1a}$ = 11.3 Hz, $^2J_{1b,2a}$ = 3.6 Hz, 1H, 1-H_b), 3.79 (s, 3H, 4-H), 1.46 (s, 9H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 170.14 (C-3), 160.34 (C-1´), 155.21 (C-5), 80.60 (C-6), 63.86 (C-1), 52.99 (C-4), 52.86 (C-2), 28.37 (C--7);); **GC MS** (EI, 70 eV) m/z [u] (%) = 188 (17, $[M\text{-}CO_2Me]^+$), 146 (10), 88 (55), 86 (7), 59 (31, $[CO_2Me]^+$), 57 (100, $[butyl]^+$); **HR-MS** (ESI, $[C_{10}H_{17}NO_6Na]^+$) calc. 270.0948 u, found 27.0950 u; **$[\alpha]^D_{20}$** ($CHCl_3$, c = 1.06 g/100 mL, T = 27.2 °C) = +32.1.

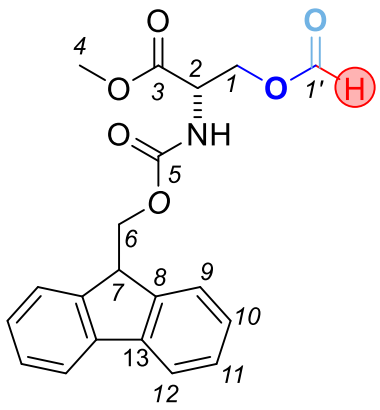


^{1}H NMR spectrum of methyl *N*-(*tert*-butoxycarbonyl)-O-formyl-L-serinate (**2g**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of methyl *N*-(*tert*-butoxycarbonyl)-O-formyl-L-serinate (**2g**, 126 MHz, $CDCl_3$).

2.3.1.8. Synthesis of Methyl (2*S*)-*N*-((9H-Fluoren-9-yl)methoxycarbonyl)-*O*-formyl-L-serinate (2h)

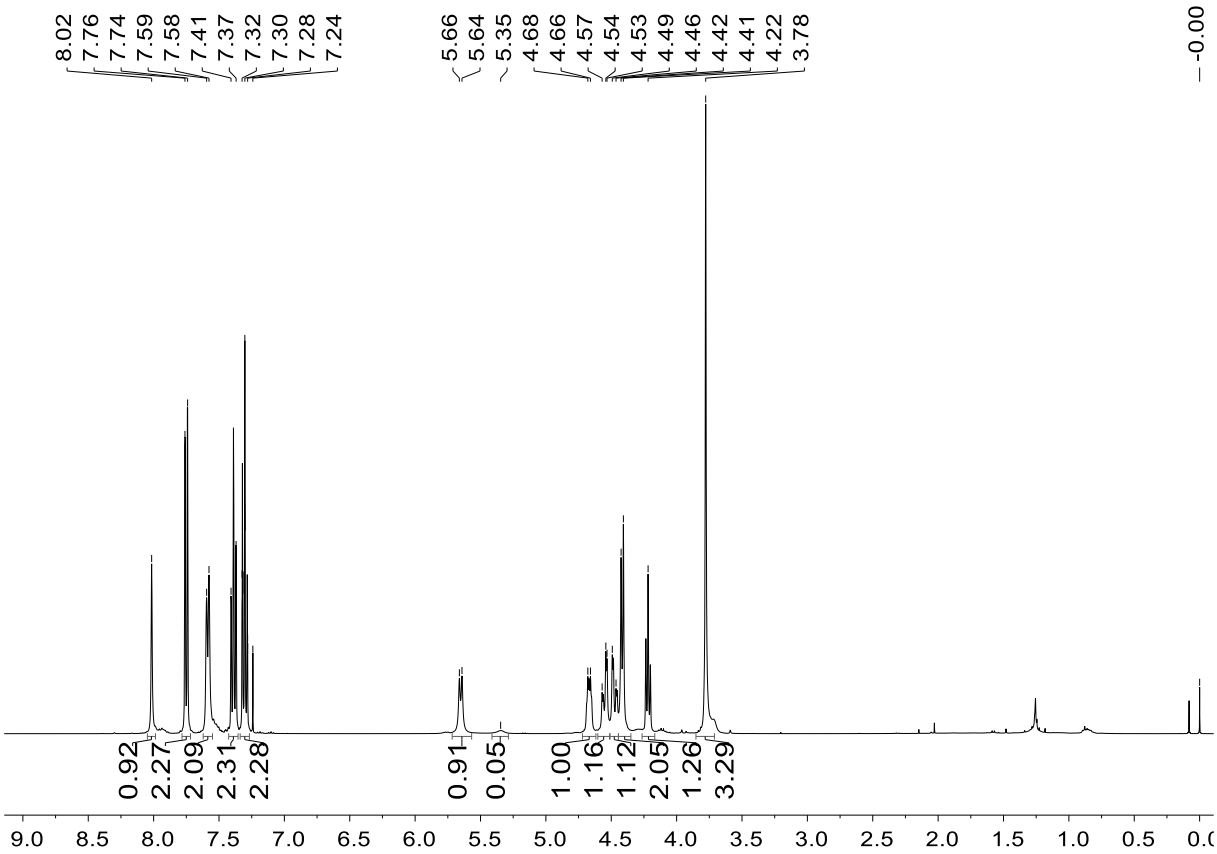


2h

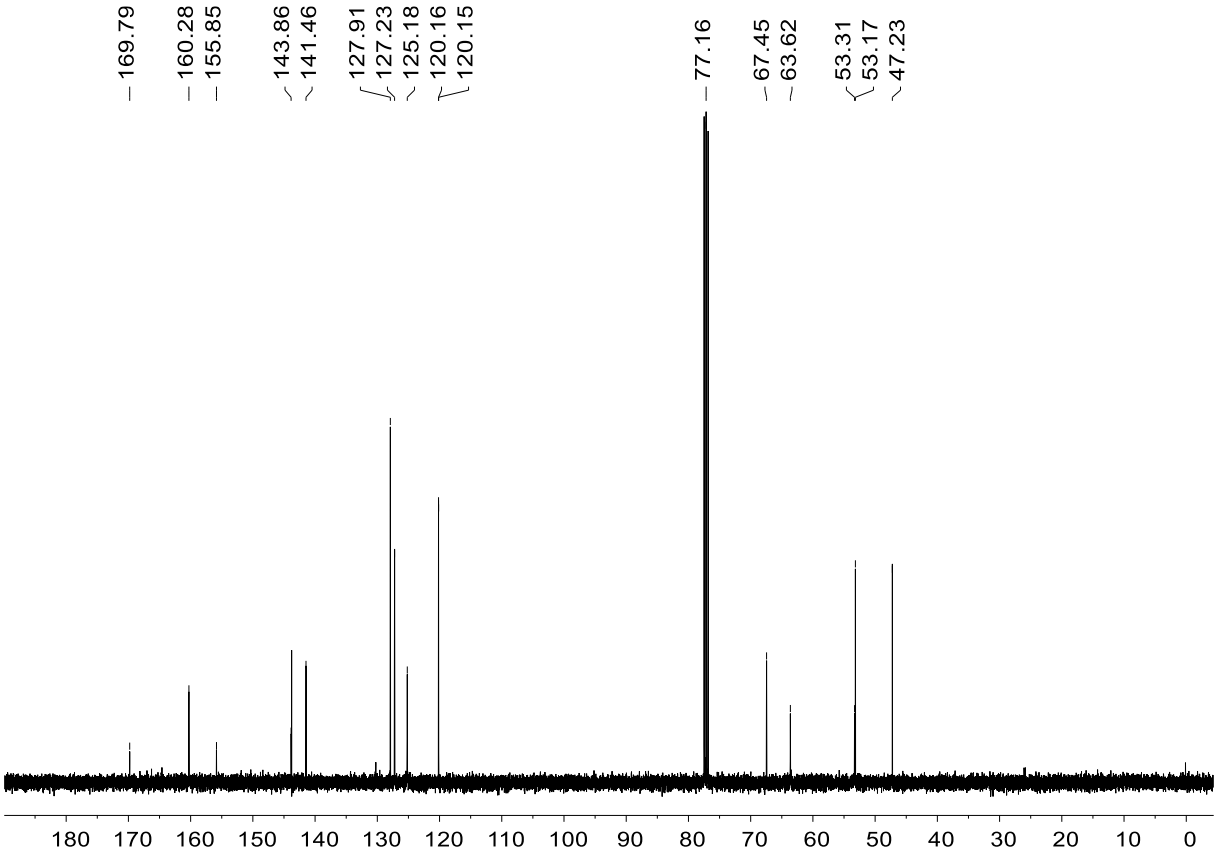
DTT-288: As stated in general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from methyl *N*-((9H-fluoren-9-yl)methoxycarbonyl)-L-serinate (**1h**, 148.5 mg, 0.50 mmol, 1.00 equiv) using FPyr (62.0 µL, 64.4 mg, 0.65 mmol, 1.30 equiv) and BzCl (69.7 µL, 84.3 mg, 0.60 mmol, 1.20 equiv) in MeCN (0.25 mL, 2.0 M). After 2 h of stirring and addition of saturated $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), purification of the crude title compound (236.8 mg, 128%) with the aid of column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:30) using MTBE/*n*-heptane 50:50 as solvent mixture gave product **2h** in 40% yield (73.8 mg, 0.20 mmol) as a colourless oil.

DTT-320: In accordance with general protocol A (chapter 2.2.1, page 8) methyl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-serinate (130.0 mg, 0.44 mmol, 1.00 equiv) was allowed to react with FPyr (95.3 µL, 99.2 mg, 1.00 mmol, 2.30 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.90 equiv) **in the presence of $NaPF_6$** (134.0 mg, 0.80 mmol, 1.80 equiv) in MeCN (0.25 mL, 2.0 M) for 4 h. After work up with saturated $NaHCO_3$ solution (2.0 mL, 5.0 equiv, 1.1 M) ^{1}H NMR of the crude material (137 mg, 84%) confirmed the full conversion of alcohol **1h**. Finally, purification by means of column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:50) using EtOAc/toluene 20:80 as solvent mixture afforded diester **2h** in 80% yield (129.3 mg, 0.35 mmol) as a colourless solid.

M ($C_{20}H_{19}NO_6$) = 369.37 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 50:50) = 0.24; **mp.** = 97-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.03 (s, 1H, 1'-H), 7.76-7.74 (m, 2H, 12-H), 7.59 (d, $^3J_{8,9}$ = 7.2 Hz, 2H, 9-H), 7.41-7.37 (m, 2H, 11-H), 7.32-7.28 (m, 2H, 10-H), 5.65 (d, $^3J_{NH,2}$ = 8.0 Hz, 1H, NH, rotamer 1), 5.35 (br. s, 1H, NH, rotamer 1), 4.68-4.66 (m, 1H, 2-H), 4.54 (dd, $^2J_{1a,1b}$ = 11.3 Hz, $^3J_{1a,2}$ = 3.8 Hz, 1H, 1-H_a), 4.48 (dd, $^2J_{1b,1a}$ = 11.4 Hz, $^3J_{1b,2}$ = 3.2 Hz, 1H, 1-H_b), 4.42 (d, $^3J_{6,7}$ = 7.1 Hz, 2H, 6-H), 4.22 (t, $^3J_{7,6}$ = 6.9 Hz, 1H, 7-H), 3.78 (s, 3H, 4-H); **^{13}C NMR** (101 MHz, $CDCl_3$)w δ [ppm] = 169.79 (C-3), 160.28 (C-1'), 155.85 (C-5), 143.86, 141.46 (C-8, C-13), 127.91 (C-11), 127.23 (C-10), 125.18 (C-9), 120.16 (C-12), 67.45 (C-6), 63.62 (C-1), 53.31 (C-2), 53.17 (C-4), 47.23 (C-7); **LC MS** (ESI, 30.0 V) m/z [u] 392 ([M+Na]$^+$); **$[\alpha]^D_{20}$** ($CHCl_3$, c = 0.69 g/100 mL, T = 26.4 °C) = +24.4; **HR MS** (ESI, [$C_{20}H_{19}NO_6$+Na]$^+$) calc. 392.1104 u, found 392.1094 u.

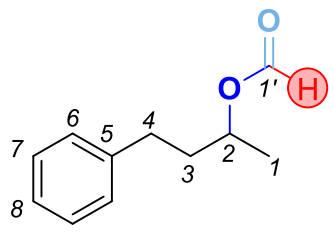


^{1}H NMR spectrum of methyl (2*S*)-*N*-((9H-Fluoren-9-yl)methoxycarbonyl)-*O*-formyl-L-serinate (**2h**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of methyl (2*S*)-*N*-((9H-Fluoren-9-yl)methoxycarbonyl)-*O*-formyl-L-serinate (**2h**, 101 MHz, $CDCl_3$).

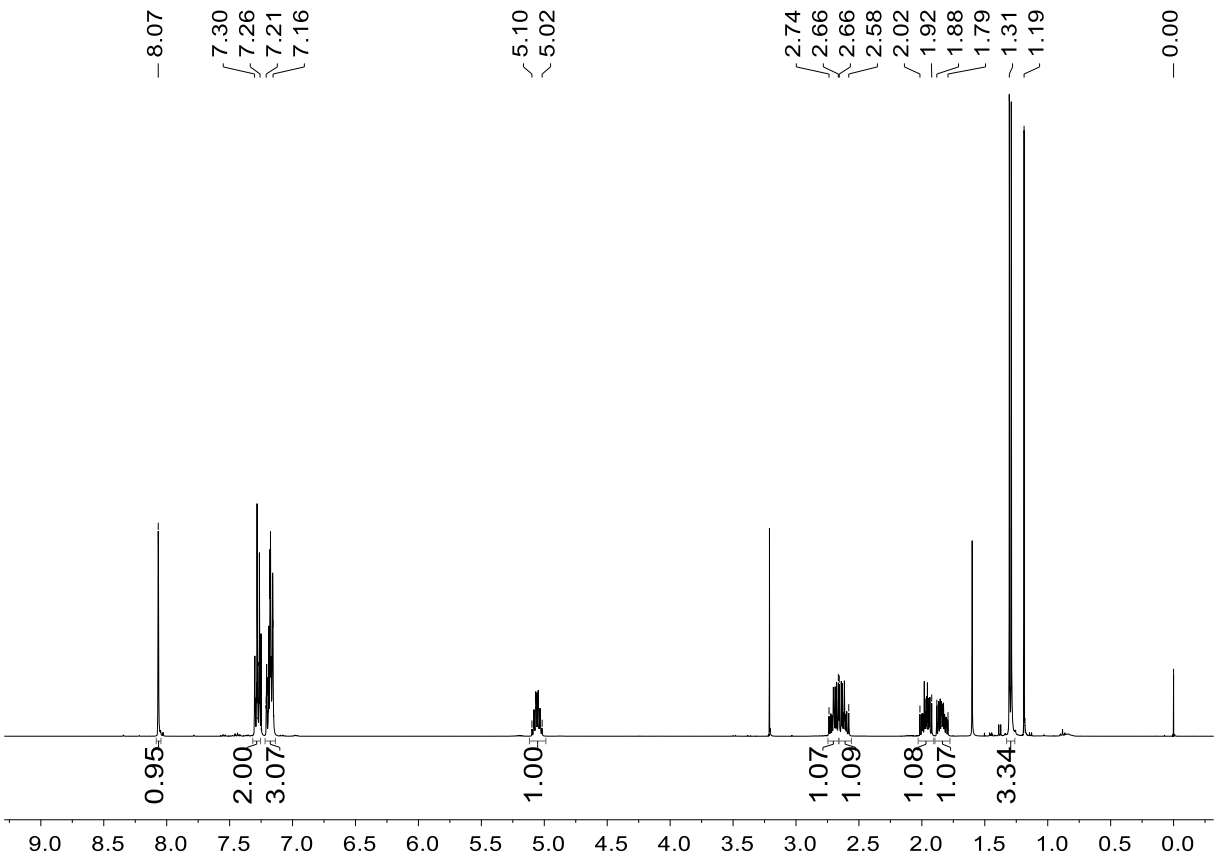
2.3.1.9. Synthesis of *rac*-4-Phenylbutan-2-yl Formate (2i)



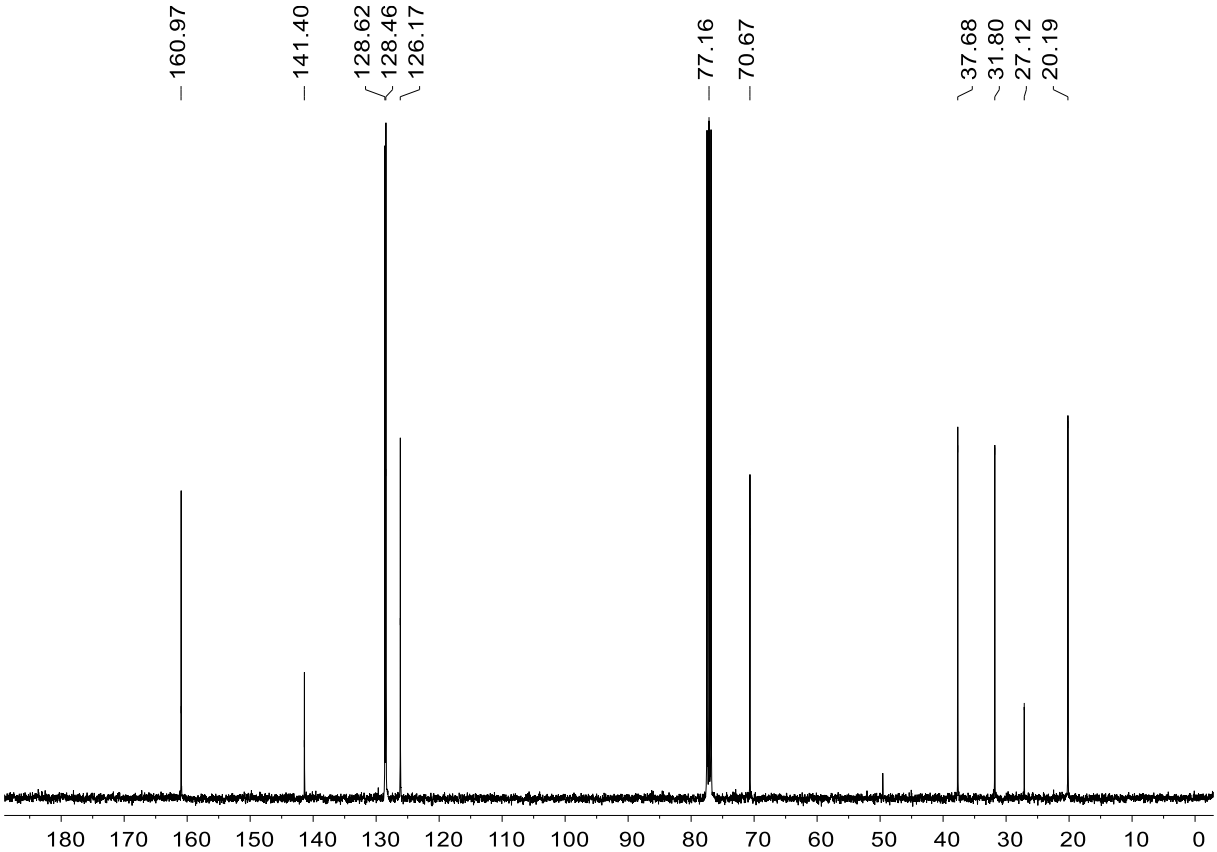
2l

DTT-276: In accordance with general protocol A (chapter 2.2.1, page 8), the tile compound was prepared from 4-phenyl-2-butanol (**1l**, 300.4 mg, 2.00 mmol, 1.00 equiv), FPyr (286.0 µL, 297.4 mg, 3.00 mmol, 1.50 equiv) and BzCl (302.1 µL, 365.5 mg, 2.60 mmol, 1.30 equiv) in MeCN (1.0 mL, 2.0 M). After 3 h of stirring and work up with $NaHCO_3$ solution (2 mL, 1.2 equiv, 1.1 M) ^{1}H NMR of the crude material (388.5 mg, 109%) verified full conversion of alcohol **1l**. Finally, purification applying column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:13) using MTBE/*n*-heptane 4:96 as solvent mixture gave the title compound as a colourless oil (338.4 mg, 1.90 mmol, 95%) after drying in high vacuum.

M ($C_{11}H_{14}O_2$) = 178.10 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 4:96) = 0.39; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.07 (s, 1H, 1'-H), 7.30-7.26 (m, 2H, 7-H), 7.21-7.16 (m, 3H, 6-H, 8-H), 5.10-5.02 (m, 1H, 2-H), 2.70 (ddd, $^2J_{4a,4b}$ = 13.8 Hz, $^3J_{4a,3a}$ = 10.0 Hz, $^3J_{4a,3b}$ = 5.6 Hz, 1H, 4-H_a), 2.62 (ddd, $^2J_{4b,4a}$ = 13.9 Hz, $^3J_{4b,3a}$ = 9.7 Hz, $^3J_{4b,3b}$ = 6.4 Hz, 1H, 4-H_b), 2.02-1.92 (m, 1H, 3-H_a), 1.88-1.79 (m, 1H, 3-H_b), 1.30 (d, $^3J_{1,2}$ = 6.3 Hz, 3H, 1-H); **^{13}C NMR** (101 MHz $CDCl_3$) δ [ppm] = 160.97 (C-1'), 141.40 (C-5), 128.62, 128.46 (C-6, C-7), 126.17 (C-8), 70.67 (C-2), 37.68 (C-4), 31.80 (C-3), 20.19 (C-1); **GC MS** (EI, 70 eV) m/z [u] (%) = 132 (45, $[M\text{-}COCHO]^+$), 118 (10, $PhCHCHCH_3]^+$), 117 (100, $[PhCHCHCH_2]^+$), 115 (9), 105 (5, $[PhCHCH_3]^+$), 104 (4, $[PhCHCH_2]^+$), 91 (50, $[C_6H_5CH_2+H]^+$), 77 (7, $[Ph]^+$), 65 (9, $[Cp]^+$); **HR MS** (EI, $[PhCH_2CH_2CHCH_3]^+$,) calc. 133.10118 u found 133.1016 u.

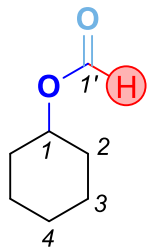


^{1}H NMR spectrum of 4-phenylbutan-2-yl formate (**2l**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 4-phenylbutan-2-yl formate (**2l**, 101 MHz, $CDCl_3$).

2.3.1.10. Synthesis of Cyclohexyl Formate (2j)

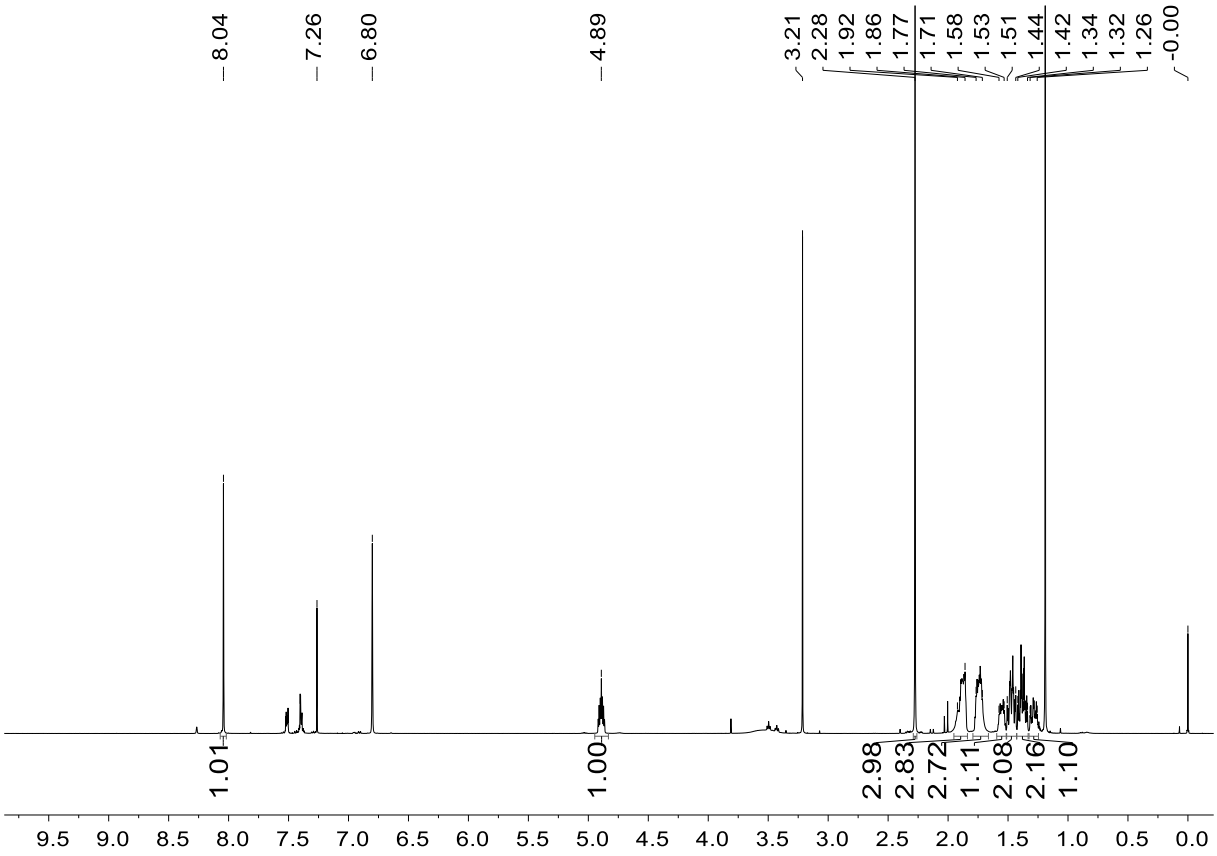


2j

DTT-311: In accordance with general protocol A (chapter 2.2.1, page 8), cyclohexanol (50.1 mg, 0.50 mmol, 1.00 equiv), FPyr (74.4 mg, 0.75 mmol, 1.50 equiv), MeCN (0.25 mL, 2.0 M) and BzCl (91.4 mg, 0.65 mmol, 1.30 equiv) were combined and stirred for 16 h. Past work up with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), the ^1H NMR spectrum of the crude material (88.5 mg, 138%) with mesitylene (13.7 mg, 0.11 mmol) as internal standard verified full conversion of alcohol **1j** and the yield of volatile **2j** of 67%.

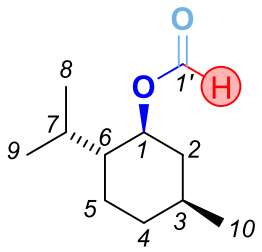
M ($C_7H_{12}O_2$) = 128.17 g/mol; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.04 (s, 1H, 1'-H), 4.89 (ψ-sept, *J* = 4.3 Hz, 1H, 1-H), 1.92-1.86 (m, 2H), 1.77-1.71 (m, 2H), 1.58-1.53 (m, 1H), 1.51-1.44 (m, 2H), 1.42-1.34 (m, 2H), 1.32-1.26 (m, 1H).

NMR data is consistent with literature. [5]



^1H NMR spectrum of crude cyclohexyl formate (**2j**) with mesitylene as internal standard (500 MHz, $CDCl_3$)

2.3.1.11. Synthesis of (1*S*,2*R*,5*S*)-(+)-Menthyl Formate (2k)



2k

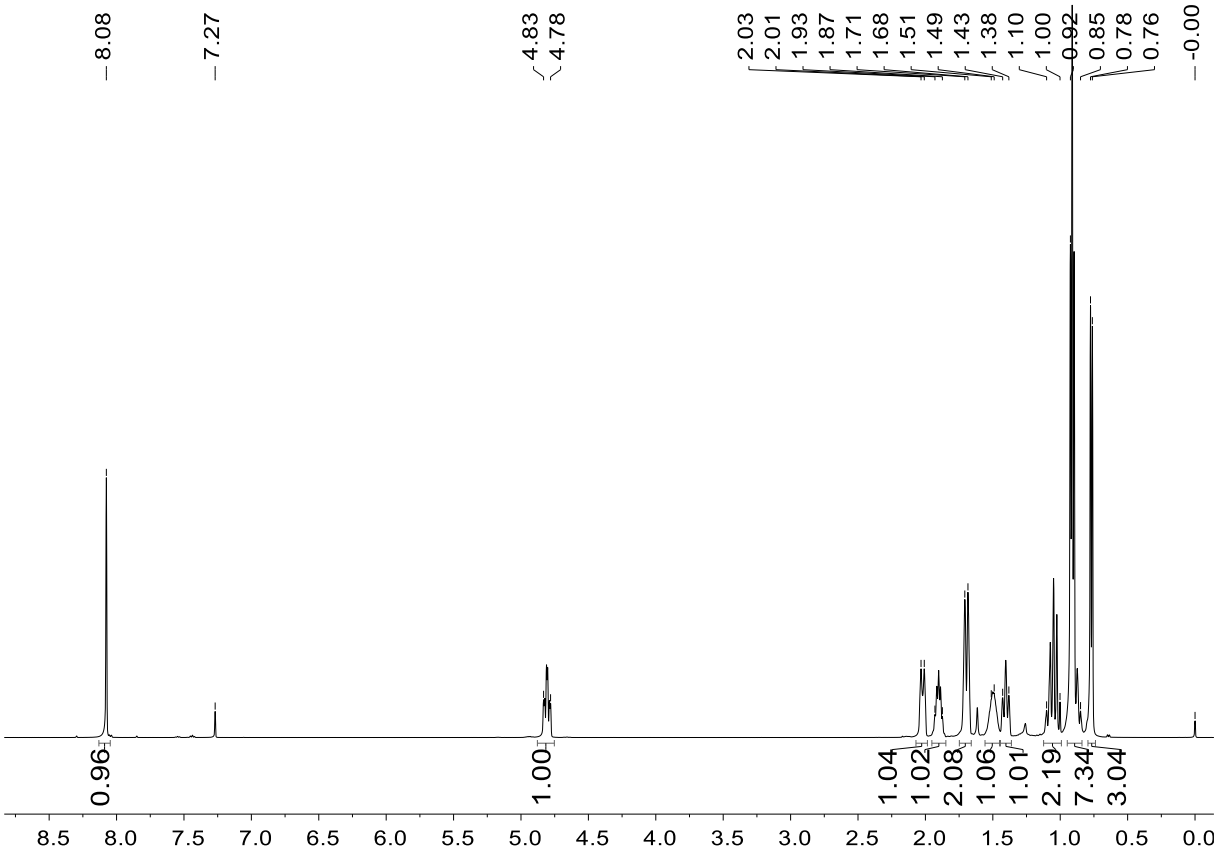
DTT-344: In accordance with general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from (*1S,2R,5S*)-(+)-menthol (**1k**, 156.3 mg, 1.00 mmol, 1.00 equiv), FPyr (190.6 µL, 198.2 mg, 2.00 mmol, 2.00 equiv) and BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) in MeCN (1.0 mL, 2.0 M). After 3 h of stirring and quenching with saturated solution of $NaHCO_3$ (2.0 mL, 2.2 equiv, 1.1 M), ^{1}H NMR of the crude material (218.8 mg, 119%) verified full conversion of alcohol **1k**. Finally, purification engaging column chromatography on silica gel (6 g, ratio weight crude product/SiO_2 1:27) with MTBE/*n*-heptane 3:97 as solvent mixture allowed for the isolation of formate **2k** in 90% (165.0 mg, 0.90 mmol) as a colourless oil.

Gramscale Protocol, DTT-345: In alignment to general protocol A (chapter 2.2.1, page 8), menthol (1.563 g, 10.0 mmol, 1.00 equiv), FPyr (1.62 mL, 1.685 g, 17.0 mmol, 1.70 equiv) and dry MeCN (5.0 mL, 2.0 M) were added to 50 mL flask containing a stir bar. Next, BzCl (1.74 mL, 2.108. mg, 15.0 mmol, 1.5 equiv) was added dropwise to the reaction mixture under stirring (400 rpm) at room temperature with the help of a syringe, and the resulting solution was stirred for 3 h. Thereafter. $NaHCO_3$ solution (20.0 mL, 2.2 equiv, 1.1 M) was added and the quenched reaction mixture was stirred for a further 10 min. Then, the mixture was diluted with MTBE (20 mL) and poured into a 100 mL extraction funnel. The reaction flask was subsequently washed with MTBE/H_2O (2 x 10 mL/10 mL) and additional MTBE (10 mL). The organic phase was washed with brine (1 x 20 mL), dried over $MgSO_4$, concentrated under reduced pressure and the residue is dried for 5 min on a rotary evaporator at 20 mbar. The ^{1}H NMR of the crude material (1.95 g, 106%) showed full conversion of alcohol **1k**.

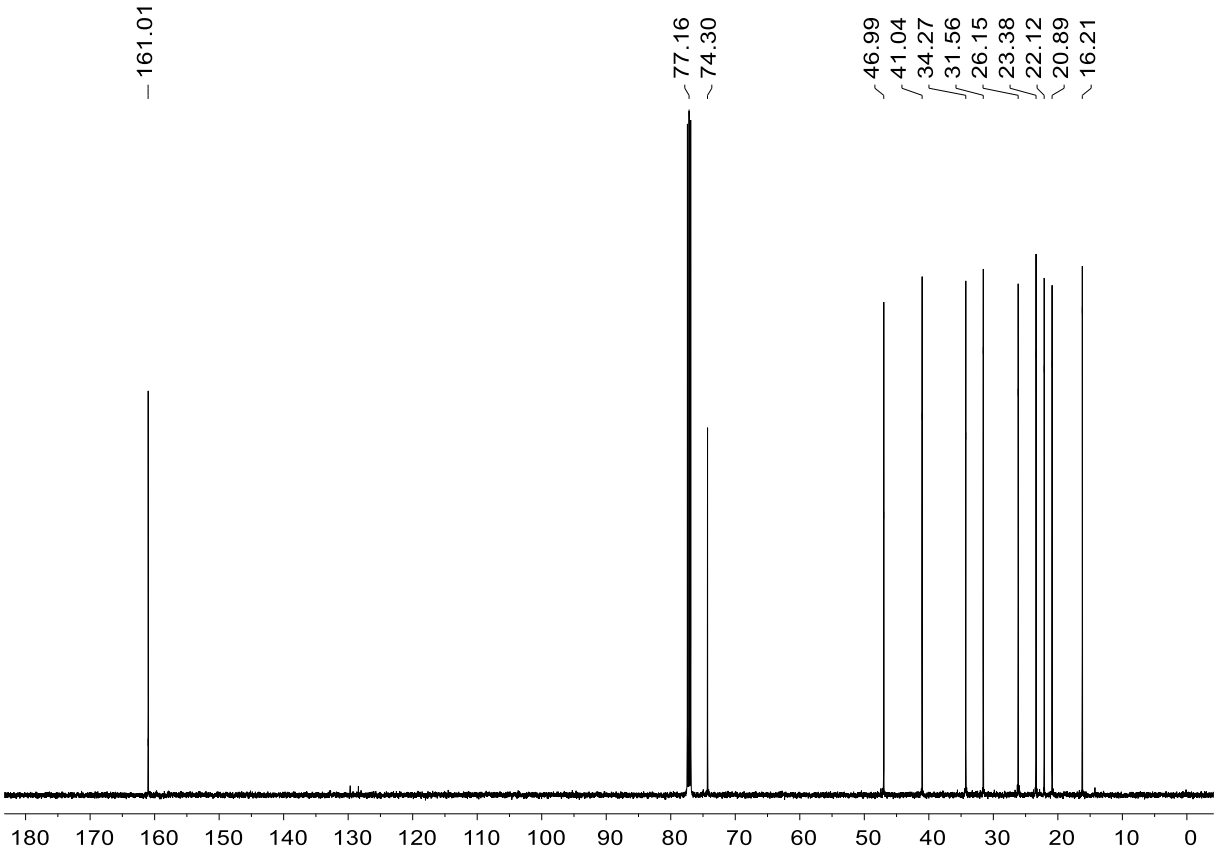
In the end, the crude product was purified by column chromatography on silica gel (25 g, ratio weight crude product/SiO_2 1:13) using MTBE/*n*-heptane 3:97 as eluent mixture. After concentration of the product containing fractions under reduced pressure and drying at 20 mbar for 5 minutes at the rotary evaporator, the formate **2k** was obtained in 94% yield (1.732 g, 9.40 mmol) as colourless oil.

M ($C_{11}H_{20}O_2$) = 184.28 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 3:97) = 0.47; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.08 (s, 1H, 1'-H), 4.81 (ψ-td, ^3J = 11.0, 4.3 Hz, 1H, 1-H), 2.02 (ψ-d, J = 11.8 Hz, 1H, 2-H_a), 1.93-1.87 (m, 1H, 3-H), 1.71-1.68 (m, 2H, 5-H_a, 4-H_a), 1.51-1.49 (m, 1H, 7-H), 1.41 (ψ-t, J = 11.5 Hz, 1H, 6-H), 1.10-1.00 (m, 2H, 2-H_b, 5-H_b), 0.92-0.85 (m, 7H, 4-H_b, 8-H, 9-H; amongst at 0.91 ψ-t, J = 6.6 Hz), 0.77 (d, $^3J_{9,3}$ = 7.0 Hz, 3H, 10-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 161.01 (C.1'), 74.30 (C-1), 46.99 (C-6), 41.04 (C-2), 34.27 (C-5), 31.56 (C-7), 26.15 (**C-3**), 23.38 (C-4), 22.12, 20.89 (C-8, C-9), 16.21 (C-10); **GC MS** (EI, 70 eV) m/z [u] (%) = 138 (34, [M-CO_2H-H]$^+$), 123 (44), 109 (9), 95 (100, [methylcyclohexenyl]$^+$), 81 (69), 67 (22), 55 (23, [butenyl]$^+$); $\mathbf{[\alpha]^D_{20}}$ ($CHCl_3$, c = 1.23 g/100 mL, T = 25.9 °C) = +82.5.

The NMR data is in good match with literature data of the enantiomer of **2k**.[6]

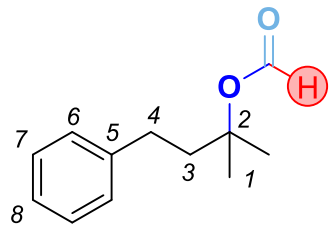


^{1}H NMR spectrum of menthyl formate (**2k**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of menthyl formate (**2k**, 126 MHz, $CDCl_3$).

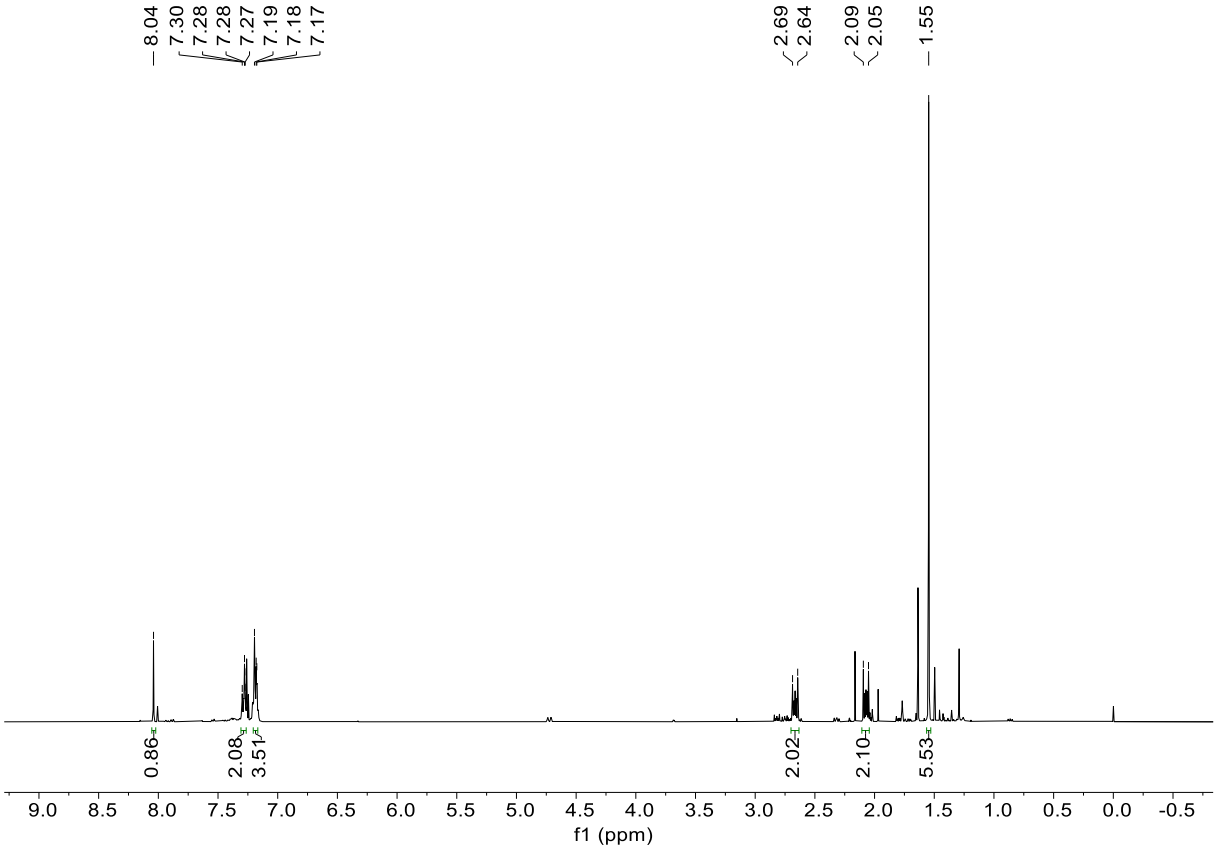
2.3.1.12. Synthesis of 2-Methyl-4-phenylbutan-2-yl formate (2l)



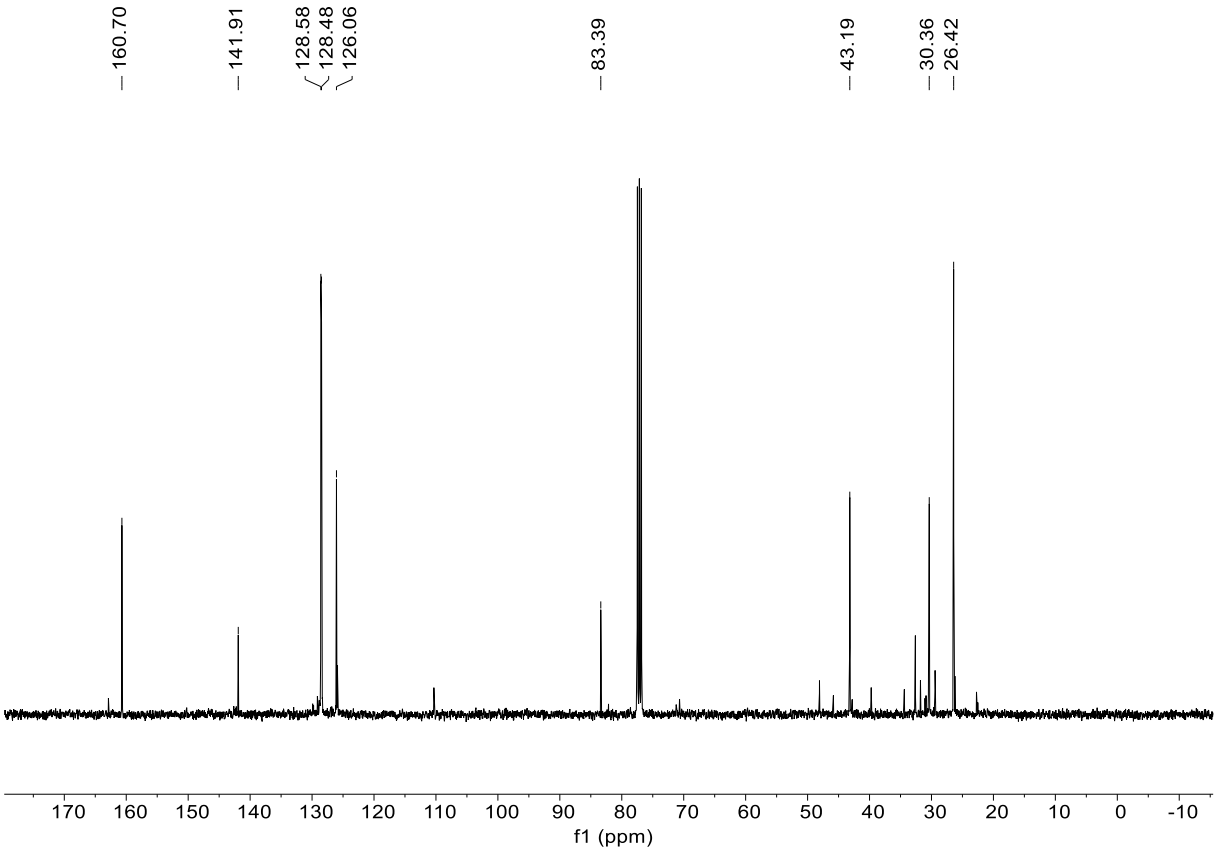
2l

DTT-333: In accordance with general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from 2-methyl-4-phenyl-2-butanol (328.4 mg, 2.00 mmol, 1.00 equiv), FPyr (381.3 µL, 396.5 mg, 4.00 mmol, 2.00 equiv) and BzCl (395.0 µL, 477.9 mg, 3.40 mmol, 1.70 equiv) in dry MeCN (1.0 mL, 2.0 M). After 2 h of stirring and work up with $NaHCO_3$ solution (3.0 mL, 1.7 equiv, 1.1 M) ^{1}H NMR of the crude material (582 mg, 151%) confirmed full conversion of alcohol **1l**. Finally, the purification with the aid of column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:12) using MTBE/*n*-heptane 5:95 as solvent mixture allowed to isolate the ester **2l** in 44% yield (169.5, 0.88 mmol) as a colourless oil.

M ($C_{12}H_{16}O_2$) = 192.26 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 8:92) = 0.46; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.04 (s, 1H, 1'-H), 7.30-7.28 (m, 2H, 7-H), 7.20-7.18 (m, 32H, 6-H, 8-H), 2.69-2.64 (m, 2H, 4-H), 2.10- 2.05 (m, 2H, 3-H), 1.55 (s, 6H, 1-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 160.71 (C-1'), 141.92 (C-5), 128.59, 128.48 (C-6, C-7), 126.07 (C-8), 83.40 (C-2), 43.20 (C-4), 30.37 (C-3), 26.43 (C-1).

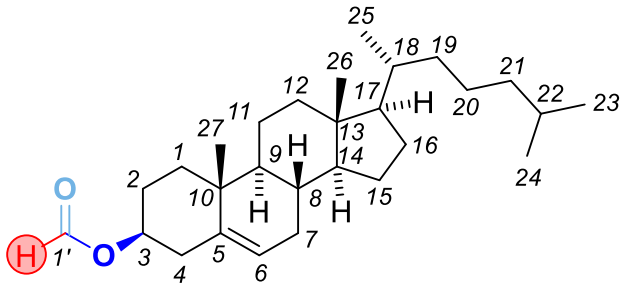


^{1}H NMR spectrum of 2-methyl-4-phenylbutan-2-yl formate (**2l**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-methyl-4-phenylbutan-2-yl formate (**2l**, 126 MHz, $CDCl_3$).

2.3.1.13. Synthesis of Cholesteryl Formate (2m)



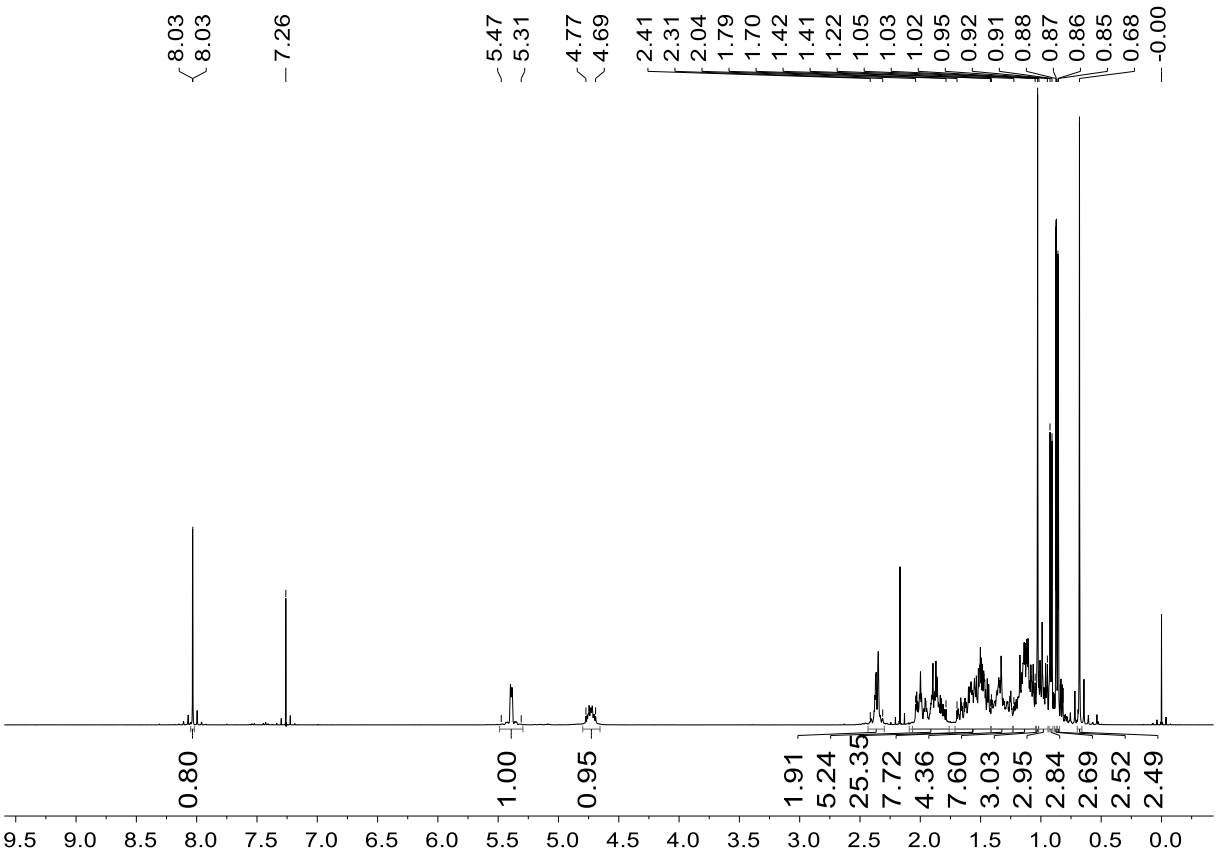
2m

DTT-291: In accordance with general protocol A (chapter 2.2.1, page 8) cholesterol (193.3 mg, 0.50 mmol, 1.00 equiv) was permitted to react with FPyr (71.5 µL, 74.4 mg, 0.75 mmol, 1.50 equiv) and BzCl (76.5 µL, 91.4 mg, 0.65 mmol, 1.30 equiv) in MeCN (0.25 mL, 2.0 M) for 2 h. After quenching with saturated $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), the ^{1}H NMR of the crude material (285.6 mg, 138%) verified full conversion of alcohol **1m**. Finally, purification with the help of column chromatography on silica gel (7 g, ratio weight crude product/SiO_2 1:24) using MTBE/*n*-heptane 10:90 as solvent mixture gave product **2m** in 83% yield (172.3 mg, 0.42 mmol) as a colorless solid.

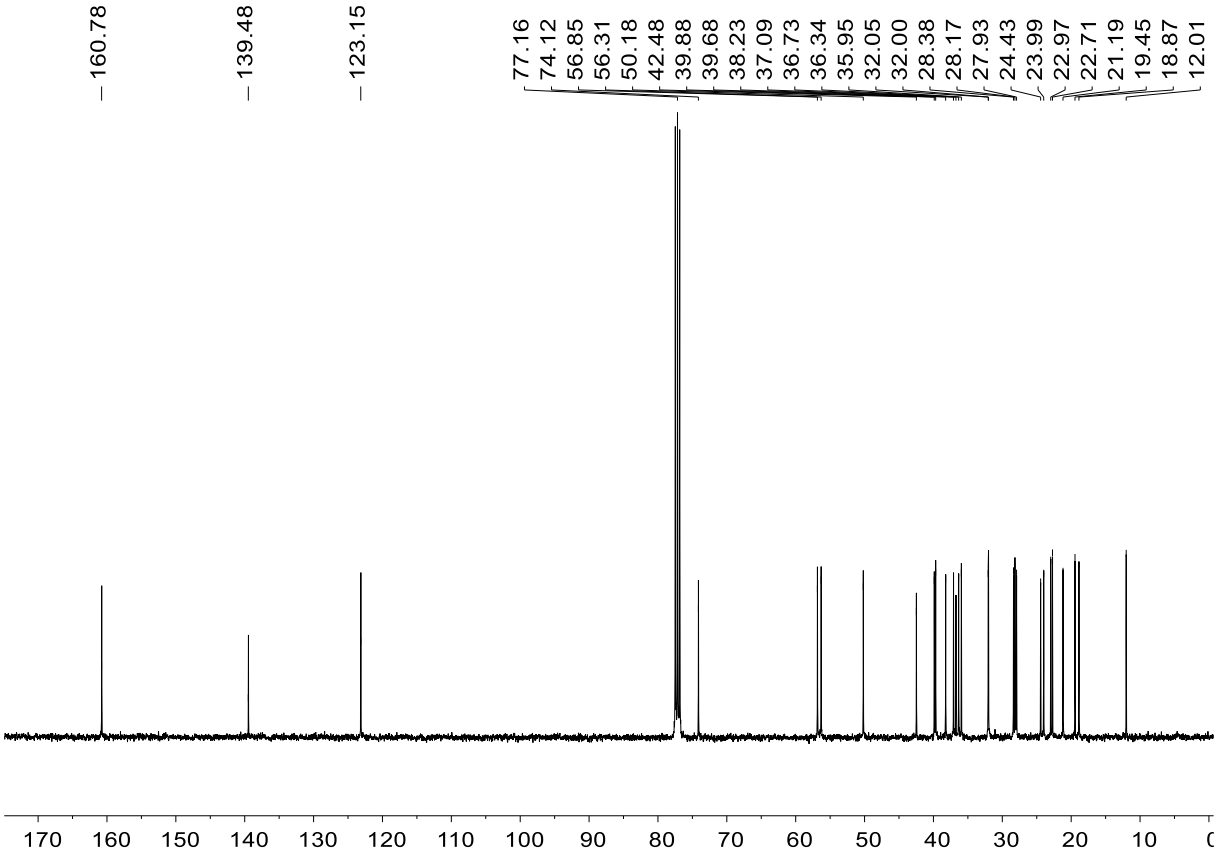
M ($C_{28}H_{46}O_2$) = 414.35 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 4:96) = 0.51; **mp.** = 93-95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.03 (d, $^4J_{1',3}$ = 0.9 Hz, 1H, 1'-H), 5.47-5.31 (m, 1H, 6-H), 4.77-4.69 (m, 1H, 3-H), 2.42-2.31 (m, 2H, 4-H), 2.04-1.78 (m, 5H), 1.70-1.41 (m, 8H), 1.40-1.24 (m, 4H), 1.22- 1.05 (m, 7H), 1.03 (s, 3H, 27-H), 1.00-0.95 (m, 2H), 0.91 (d, $^3J_{25,18}$ = 6.5 Hz, 3H, 25-H), 0.88 (d, $^3J_{23,22}$ = 1.8 Hz, 3H, 23-H), 0.86 (d, $^3J_{24,23}$ = 1.8 Hz, 3H, 24-H), 0.68 (s, 3H, 26-H);

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 160.78 (C-1'), 139.48 (C-5), 123.15 (C-6), 74.12 (C-3), 56.85, 56.31, 50.18, 42.48, 39.88, 39.68, 38.23, 37.09, 36.73, 36.34, 35.95, 32.05, 32.00, 28.38, 28.17, 27.93, 24.43, 23.99, 22.97 (C-23), 22.71 (C-24), 21.i19, 19.45 (C-27), 18.87 (C-25), 12.01 (C-26); **LC MS** (ESI, 30.0 V) m/z [u] = 437 ($[M+Na]^+$), 369 ($[M-OCHO]^+$), 270 ($[C_{20}H_{30}]^+$); **$[\alpha]^D_{20}$** ($CHCl_3$, c = 1.995 g/100 mL, T = 25.5 °C) = -51.0.

The NMR data is in agreement with published data.[7]

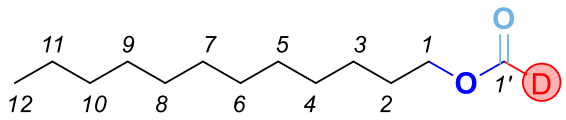


^{1}H NMR spectrum of cholesteryl formate (**2m**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of cholesteryl formate (**2m**, 101 MHz, $CDCl_3$).

2.3.1.14. Synthesis of deuterated 1-Dodecyl Formate (2n)

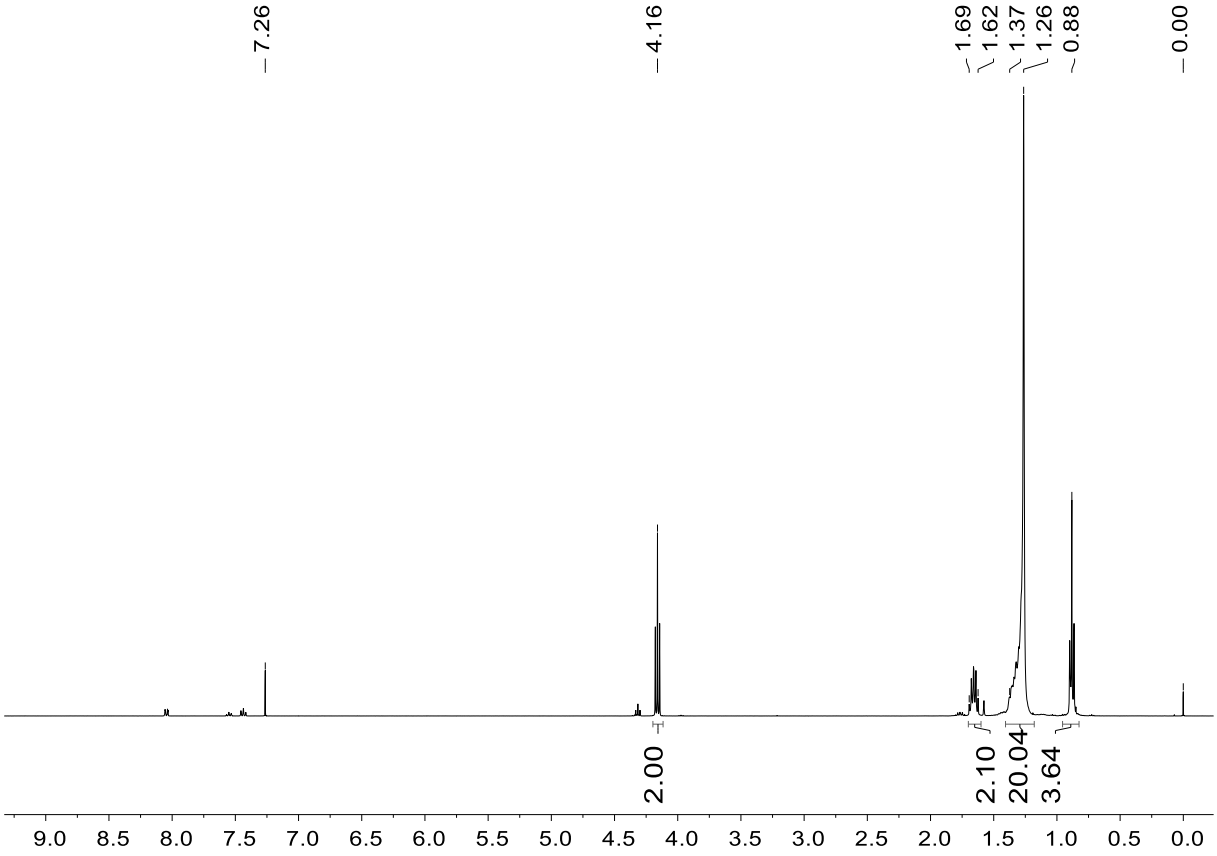


2n

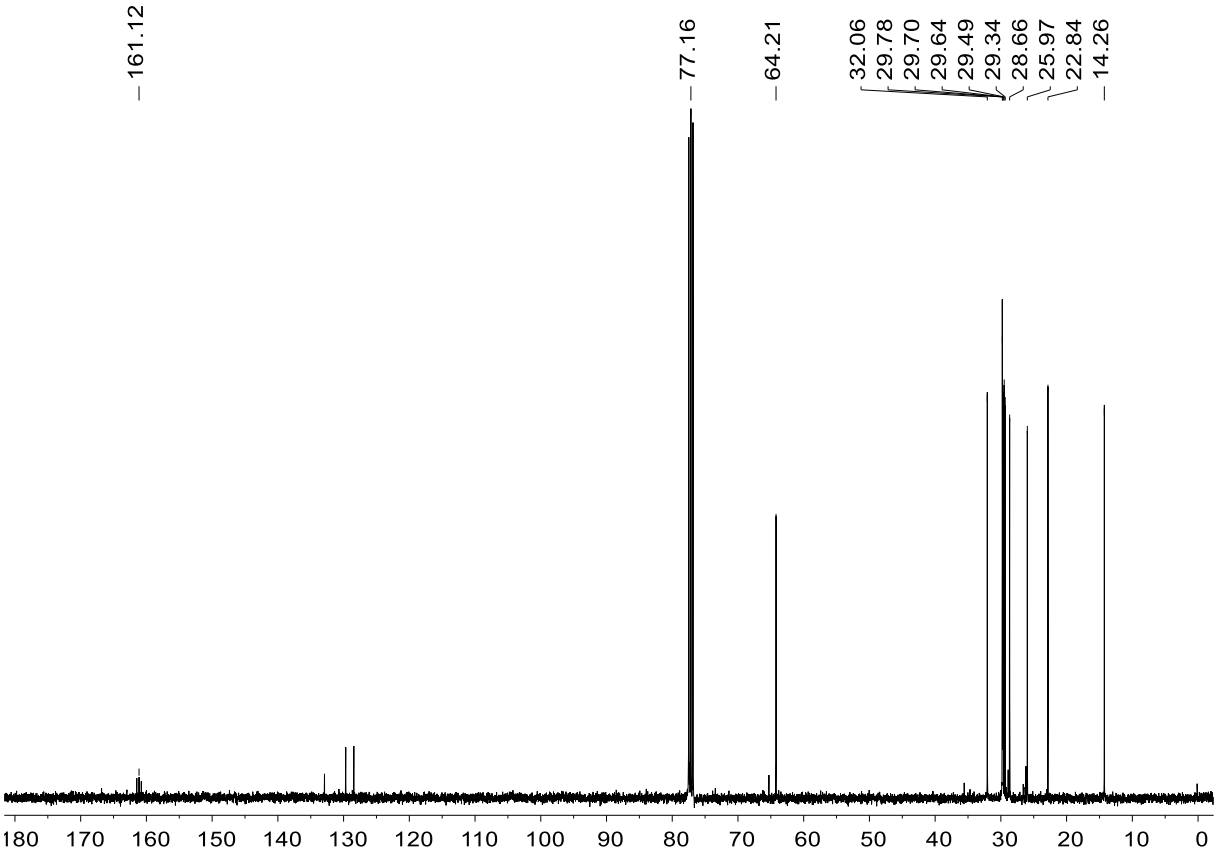
DTT-347: Following general procedure A (chapter 2.2.1, page 8), the title compound was manufactured from 1-dodecanol (**1a**, 224.5 µL, 186.3 mg, 1.00 mmol, 1.00 equiv), DMF-D_7 (132.2 µL, 136.2 mg, 1.70 mmol, 1.70 equiv) and BzCl (174.3 µL, 210.8 mg, 1.50 mmol, 1.50 equiv) in dry MeCN (0.5 mL, 2.0 M). After 3 h of and quenching with saturated $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M), ^{1}H NMR of the crude material (239.1 mg, 104%) verified full conversion of alcohol **1a**. Finally, purification relying on column chromatography on silica gel (5 g, ratio weight crude product/SiO_2 1:21) using MTBE/*n*-heptane 1:99 as solvent mixture enabled the isolation of product **2n** in 79% yield (170.4 mg, 0.79 mmol) as a colourless oil.

M ($C_{13}H_{25}DO_2$) = 215.36 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 4:96) = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 4.16 (t, $^3J_{1,2}$ = 6.9 Hz, 2H, 1-H), 1.69-1.62 (m, 2H, 2-H),1.34-1.26 (m, 18H, 3-H to 11-H), 0.88 (t, $^3J_{11,12}$ = 6.9 Hz, 3H, 12-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 161.12 (t, $^1J_{C,D}$ = 34 Hz, C-1´), 64.21 (C-1), 32.06, 29.78, 29.69, 29.70, 29.64, 29.49, 29.34, 28.66, 25.97, 22.84, 14.26 (C-2 to C-12); **GC MS** (EI, 70 eV) m/z [u] (%): 168 ([M-OCDO-H]$^+$, 8), 140 ([M-$(CH_2)_2$OCDO]$^{+\cdot}$, 2), 123 (100, [nonadienyl]$^+$), 97 (8, [pentenyl]$^+$); **HR MS** (EI, 30 eV)

$[C_{13}H_{25}O_2]^+$ = $[M\text{-}D]^+$calc. 213.18491 u found 213.1850 u, $[C_{12}H_{24}]^+$calc. 168.18725 u found 168.1874 u, $[C_{10}H_{20}]^+$calc. 140.15595 u found 140.1561 u.



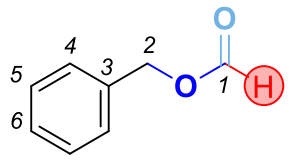
^{1}H NMR spectrum of 1-dodecyl formate - d (**2n**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 1-dodecyl formate – d (**2n**, 101 MHz, $CDCl_3$).

2.3.2. Synthesis of Benzylic and Allylic Formates of Type 2

2.3.2.1. Synthesis of Benzyl Formate (2o)



2o

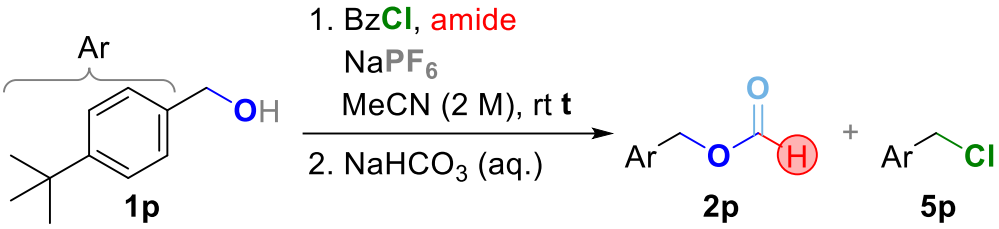
DTT-324: In accordance to the general protocol A (chapter 2.2.1, page 8), the title compound was synthesized using benzyl alcohol (51.8 µL, 54.4 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv). After 2.5 h stirring and work up with a saturated solution of $NaHCO_3$ (2.0 mL, 1.1 M, 4.4 equiv), the ^{1}H NMR of the crude material (75.9 mg, 111%) with mesitylene as internal standard verified 96% conversion of alcohol **1o** and target compound **2o** in 80% yield.

DTT-324b: In alignment to general protocol B (chapter 2.2.1, page 8), a mixture of benzyl alcohol (104.6 µL, 110.0 mg, 1.00 mmol, 1.00 equiv), FPyr (196 µL, 198.6 mg, 2.00 mmol, 2.00 equiv), $NaPF_6$ (268.4 mg, 1.70 mmol, 1.70 equiv), dry MeCN (0.50 mL, 2.0 M) and BzCl (197 µL, 238 mg, 1.70 mmol, 1.70 equiv) was stirred for 2.5 h at ambient temperature. Past quenching with $NaHCO_3$ solution (2.0 mL, 1.1 M, 2.2 equiv) and aqueous work up, the ^{1}H NMR of the crude material confirmed full conversion. Finally, purification with the aid of column chromatography on silica gel harnessing MTBE/*n*-heptane 1:99 as eluent mixture afforded the volatile benzylic formate **2o** as a colourless oil (95.3 mg, 0.70 mmol, 70%) after drying for 5 min at 50 mbar at the rotary evaporator.

M ($C_8H_8O_2$) = 136.15 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/ *n*-heptane 1:99) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.14 (t, $^4J_{1,2}$ = 0.9 Hz, 1H, 1-H), 7.38 - 7.32 (m, 5H, 4-H, 5-H, 6-H), 5.20 (s, 2H, 2-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 160.91 (C-1), 135.34 (C-3), 128.79 (C-4), 128.65 (C-5), 128.50 (C-6), 65.83 (C-2); **GC MS** (EI, 70 eV) m/z [u] (%) = 136 (74, $[M]^+$), 108 (35, $[PhCH_2OH]^+$), 107 (37, $[PhCHOH)]^+$), 91 (100, $[benzyl]^+$), 90 (79), 79 (35, $[PhH_2]^+$), 77 (33, $[Ph]^+$), 65 (22, $[C_5H_5]^+$).

The NMR data is in match with the literature. [8]

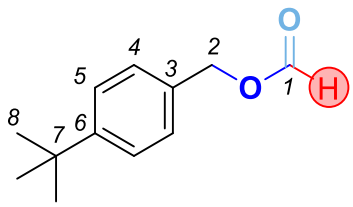
2.3.2.2. Synthesis of 4-*tert*-Butylbenzyl Formate (2p)



1p **2p** **5p**

entry	BzCl (equiv)	amide (equiv)	$NaPF_6$	t [h]	conv. [%]	yield 2p [%]	yield 5p [%]
1[a]	1.7	FPyr (2.0)	/	2	>98	<2	89
2[a]	1.3	FPyr (1.5)	1.7	1.3	37	63	/
3[a]	1.3	FPyr (1.5)	1.7	24	30	67	/
4[b]	1.7	FPyr (2.0)	1.7	2	97	86	/
5	1.7	MF (2.0)	1.7	3	85	77[a] (60[b])	5
6[a,c]	1.1	DMF (1.2)	/	3	73	13	66
7[a,c,d]	1.1	DMF (1.2)	/	3	93	36	50
8[e]	/	FPyr (2.0)	2.0	1	69	30	59

The title compound was prepared according to procedure A (chapter 2.2.1, page 8). a. Yield determined with the aid of mesitylene as internal standard or the ratios of CH_2 signals in the ^1H NMR. b. Isolated yield after chromatography purification. c. Reactions carried out at -10 °C in MTBE under Argon atmosphere, quenching with 1 M NaOAc solution (aq.) at rt. d. Quenching with NaOAc solution (1.0 M) at -10 °C instead of rt. e. with 0.5 equiv TCT instead of BzCl.



2p

Under standard conditions according to general protocol A, the reaction of substrate **1p** afforded mainly *tert*-benzyl chloride in 89% yield without formation of the desired product **2p** (entry 1). The addition of $NaPF_6$ to the reaction mixture to stabilize the intermediate iminium ion enabled generation of formate **2p** as major product in 63% yield after 1.3 h reaction duration (entry 2). An increase of the reaction time to 24 h resulted in a slightly improved yield of 67% (entry 3). Conversely, when the amount of the reagents BzCl and FPyr was increased to 1.70 and 2.00 equiv, respectively, a 86% yield of **2p** was accomplished after 2 h of reaction time (entry 4). Finally, methylformamide instead of FPyr enabled the production of format **2p** in a 77% yield as determined by internal NMR standard (entry 5). In an attempt to reproduce the formylation conditions of Asensio,[3] benzylic alcohol **1p** was allowed to reaction with BzCl and DMF in the absence of $NaPF_6$ (entries 6+7). However, the best yield we were able to achieve was 36%. Finally, formylation with 0.5 equiv of TCT (cyanuric chloride) instead of BzCl furnished the title compound in a depleted yield of 59% (entry 8). TCT has been applied by our group as chlorination reagent for alcohols previously, but the current results verify that it is less suitable for formyl group transfer. [3]

Entry 1, DTT-330: In accordance with general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from 4-*tert*-butylbenzyl alcohol (82.0 mg, 0.50 mmol, 1.00 equiv) using BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) and FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv) in dry MeCN (0.25 mL. 2.0 M). After 2 h of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^{1}H NMR of the crude material (102.0 mg,123%) uncovered full consumption of the starting alcohol and chloride **5p** as main product in 89% yield, as determined with mesitylene as internal standard.

Entry 2, DTT-294: Following general protocol A (chapter 2.2.1, page 8), a mixture of 4-*tert*-butylbenzyl alcohol (82.1mg, 0.50 mmol, 1.00 equiv), FPyr (71.5 µL, 74.3 mg, 0.75 mmol, 1.5 equiv), $NaPF_6$ (154.0 mg 0.80 mmol, 1.6 equiv), BzCl (75.5 µL, 91.4 mg, 0.65 mmol, 1.3 equiv) and dry MeCN (0.25 mL, 2 M) were stirred at room temperature for 5 h. Past quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M) was ^{1}H NMR of the crude material (95.6 mg, 99%) verified 70% consumption of the starting alcohol and formate **2p** is main product in 63% yield according to mesitylene as internal standard.

Entry 3, DTT-299: As stated in general procedure A (chapter 2.2.1, page 8), 4-*tert*-butylbenzyl alcohol (82.1mg, 0.50 mmol, 1.00 equiv), FPyr (71.5 µL, 74.3 mg, 0.75 mmol, 1.50 equiv), $NaPF_6$ (154.0 mg 0.80 mmol, 1.60 equiv) and MeCN (0.25 mL, 2.0 M) were added into a 4 mL vial. Then, BzCl (0.25 mL, 2.6 M, 1.30 equiv) was added dropwise by syringe pump within 5 min. After 24 h of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^{1}H NMR of the crude material (91.7 mg, 96%) revealed 63% conversion of the starting alcohol and formate **2p** in 63% yield, as determined from the relation of the respective singlets in the ^{1}H NMR spectrum.

Entry 4, DTT-327: As described in general protocol A (chapter 2.2.1, page 8), 4-*tert*-butylbenzyl alcohol (164.2 mg, 1.00 mmol, 1.00 equiv), FPyr (190.6 µL, 198.2 mg, 2.00 mmol, 2.00 equiv), $NaPF_6$ (284.0 mg, 1.70 mmol, 1.70 equiv), dry MeCN (0.5 mL, 2.0 M) and BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) were stirred for 2 h. After addition of $NaHCO_3$ (2.0 mL, 2.2 equiv, 1.1 M), ^{1}H NMR of the crude material (234.9 mg, 122%) confirmed full consumption of the starting alcohol. Finally, chromatographic purification on silica gel (3 g, mass crude material/SiO_2 1:13) with MTBE/*n*-heptane 1:99 provided the title compound **2p** in 86% yield as a colourless liquid (165.2 mg, 0.86 mmol).

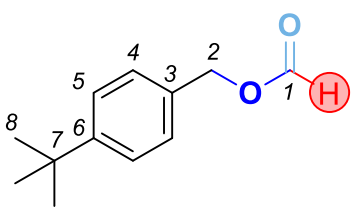
Entry 5, DTT-585: According to general protocol A (chapter 2.2.1, page 8), 4-*tert*-butylbenzyl alcohol (164.2 mg, 1.00 mmol, 1.00 equiv) was permitted to react with *N*-methylformamide (MF, 117.8 µL, 118.2 mg, 2.00 mmol, 2.00 equiv) and BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) in the presence of $NaPF_6$ (284.0 mg, 1.70 mmol, 1.70 equiv) in dry MeCN (0.5 mL, 2.0 M) for 2 h. Subsequently $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M) was added and ^{1}H NMR of the crude material (399.9 mg, 208%) revealed 85% consumption of the starting alcohol and formate **2p** in 77% yield, as determined with the aid of mesitylene as internal standard.

Finally, chromatographic purification on silica gel (6 g, mass crude material/SiO_2 1:15) with MTBE/*n*-heptane 1:99 provided the ester **2p** in 60% yield as a colourless liquid (115.3 mg, 0.60 mmol).

Entry 6, DTT-588: According to the protocol of Asensio and co-workers, 2.3.4.1. a 4 mL vial was charged with 4-*tert*-butylbenzyl alcohol (82.1 mg, 0.50 mmol, 1.00 equiv), DMF (42.4 µL, 40.2 mg, 0.75 mmol, 1.50 equiv) and MTBE (0.25 mL, 2.0 M) under an atmosphere of argon. The reaction was placed in an ice bath with NaCl salt to reduce the temperature to -10 °C. Next, BzCl (0.25 mL, 2.6 M, 1.30 equiv) was added dropwise. After 1 h of stirring at -10 °C the ice bath was removed and a 1.0 M solution of NaOAc in water (3.0 mL, 6.0 equiv, 1.0 M) was added at rt and the mixture stirred for further 30 min. Next, the mixture was diluted with MTBE (7 mL) and water (3 mL), the organic phase was washed with brine (3 mL) and the organic phase was dried over $MgSO_4$. Finally, ^{1}H NMR of the crude material (75.0 mg, 78%) revealed 78% conversion of the starting alcohol, formate **2p** and chloride **5p** in 13% and 66%, respectively.

Entry 7, DTT-588-2: Following the method of Asensio and co-workers, 2.3.4.1 a 4 mL vial was loaded with 4-*tert*-butylbenzyl alcohol (82.1mg, 0.50 mmol, 1.00 equiv), DMF (42.4 µL, 40.2 mg, 0.75 mmol, 1.50 equiv), and MeCN (0.25 mL, 2.0 M) under an atmosphere of argon. Subsequently, the reaction vessel was placed in an ice bath with NaCl salt to reduce the temperature to -10 °C and BzCl (0.25 mL, 2.6 M, 1.30 equiv) was added dropwise. After 1 h of stirring a 1.0 M solution of NaOAc in water (3.0 mL) was added at -10 °C and the resulting mixture was stirred for a further 30 min (at -10 °C). After aqueous work up as stated in entry 6, ^{1}H NMR of the crude material (180.6 mg, 187%) revealed 93% conversion of the starting alcohol, 36% yield of formate **2p** and 50% of chloride **5p** as a main product.

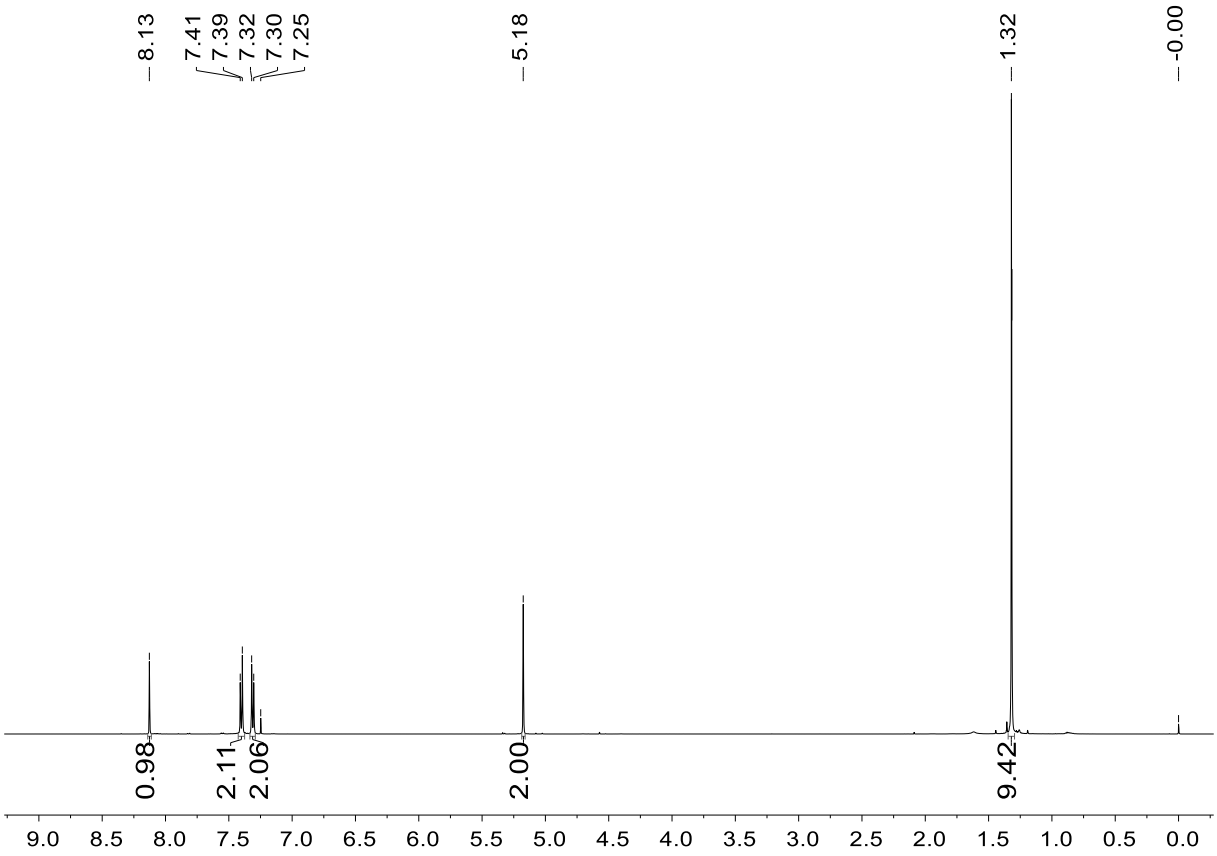
Entry 8, DTT622: In aligment to general protocol A (chapter 2.2.1, page 8), a 4 mL glass vial was charged with 4-*tert*-butyl benzylalcohol (**1p**, 83.0 mg, 0.50 mmol, 1.00 equiv), FPyr (97 µL, 100.8 mg, 1.0 mmol, 2.0 equiv) and dry MeCN (0.25 mL, 2.0 M). Next, $NaPF_6$ (168.0 mg, 1.0 mmol, 2.00 equiv) and TCT (2,4,6-trichloro-1,3,5-triazine, 46.7 mg, 0.25 mmol, 0.5 equiv) were added to the reaction mixture at room temperature. After stirring for 1 h with 400 rpm, saturated aqueous $NaHCO_3$ solution (2 mL, 4.40 equiv, 1.1 M) was added. Past aqueous work up, ^{1}H NMR of the crude material (133.8 mg, 139%) verified 69% conversion and formate **2p** in 59% yield.



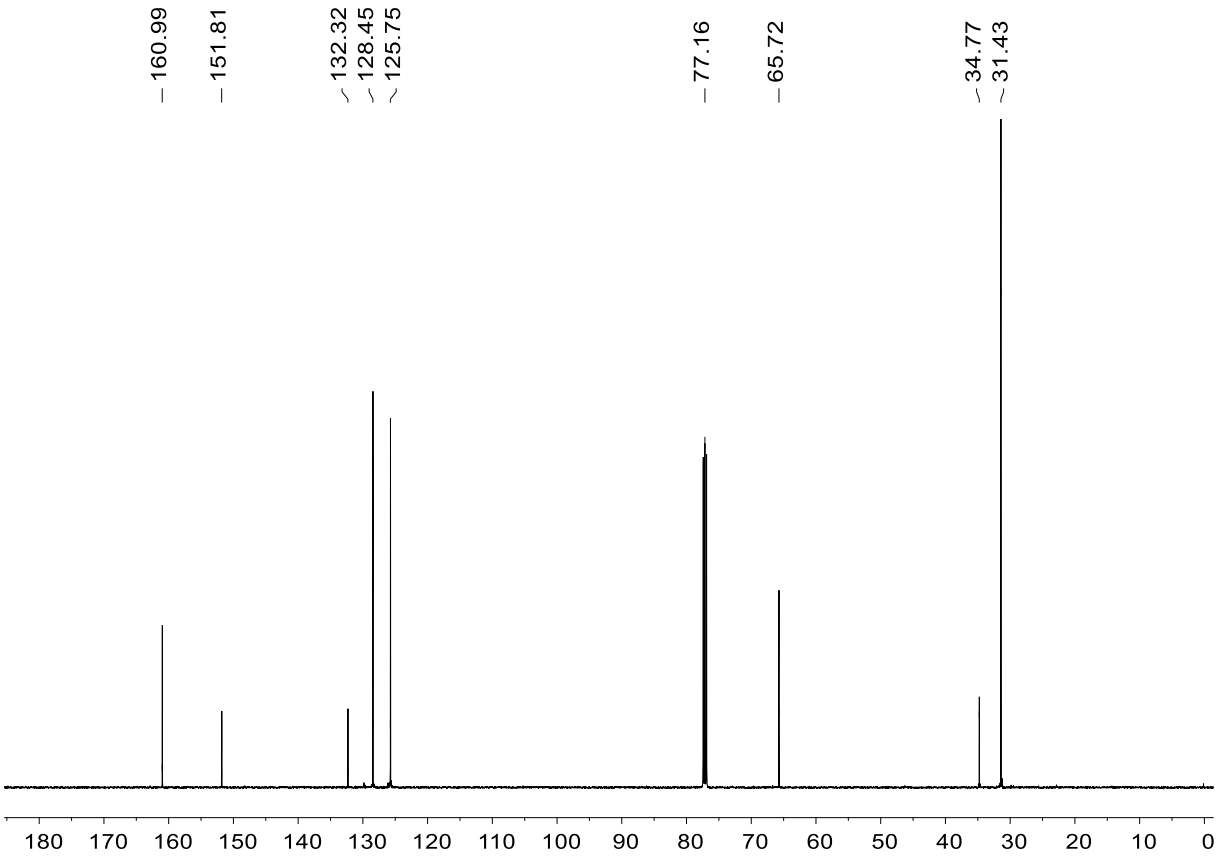
M ($C_{12}H_{16}O_2$) = 192.26 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 1:99) = 0.23; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.13 (s, 1H, 1-H), 7.41-7.39 (m, 2H, 5-H), 7.32-7.30 (m, 2H, 4-H), 5.18 (s, 2H, 2-H), 1.32 (s, 9H, 8-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 160.99 (C-1), 151.81 (C-6), 132.32 (C-3), 128.45 (C-4), 125.75 (C-5), 65.72 (C-2), 34.77 (C-7), 31.53 (C-8); **GC MS** (EI, 70 eV) m/z [u] (5) = 192 (20, $[M]^+$),

177 (100, $[M\text{-}CH_3]^+$), 149 (7), 147 (6, $[M\text{-}OCHO]^+$), 131 (28), 117 (9, [Phenyl-iso-propenyl]$^+$), 115 (9), 105 (4), 91 (16, $[Bn]^+$), 79 (3, $[PhH_2]^+$), 77 (5, $[Ph]^+$); **HR MS** (EI, $[C_{12}H_{16}O_2]^+$) calc. 192.1145 u found 192.11444 u.

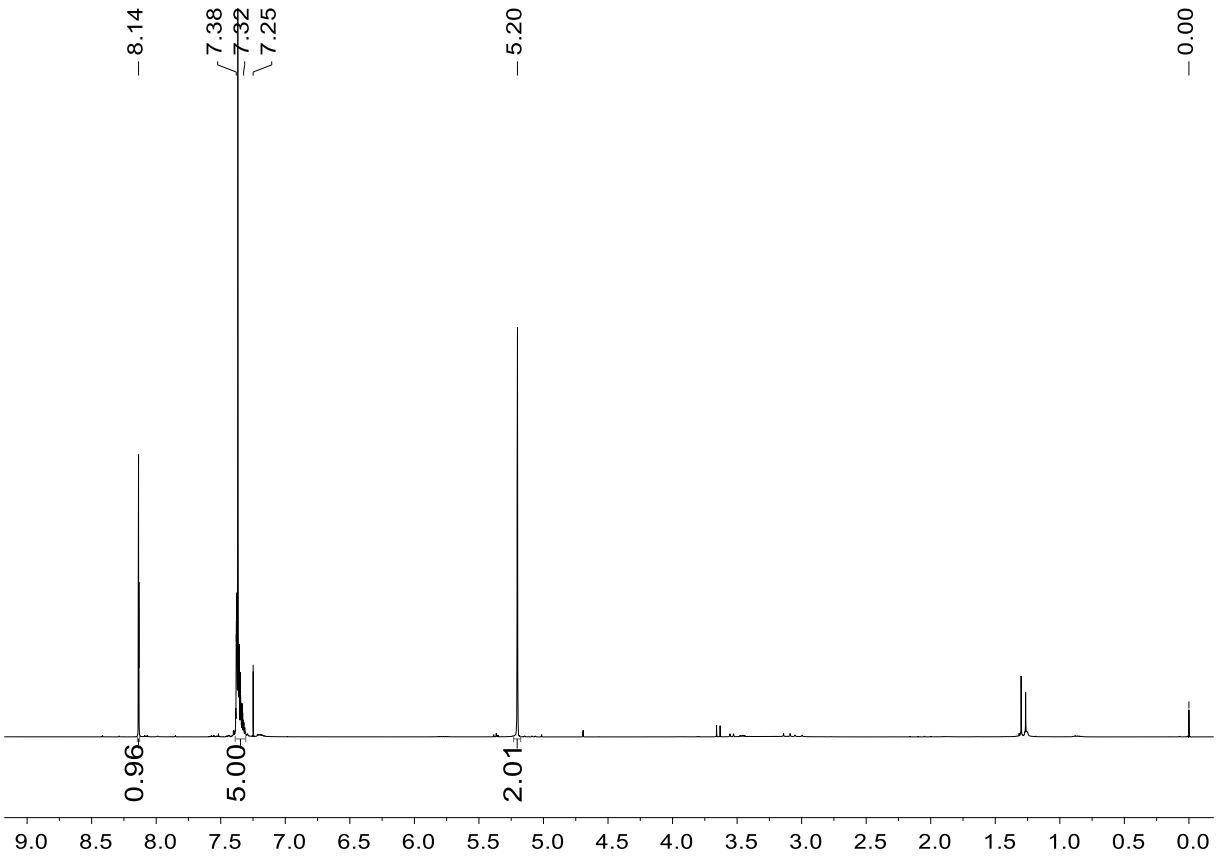
The NMR data is in agreement with the literature.[1]



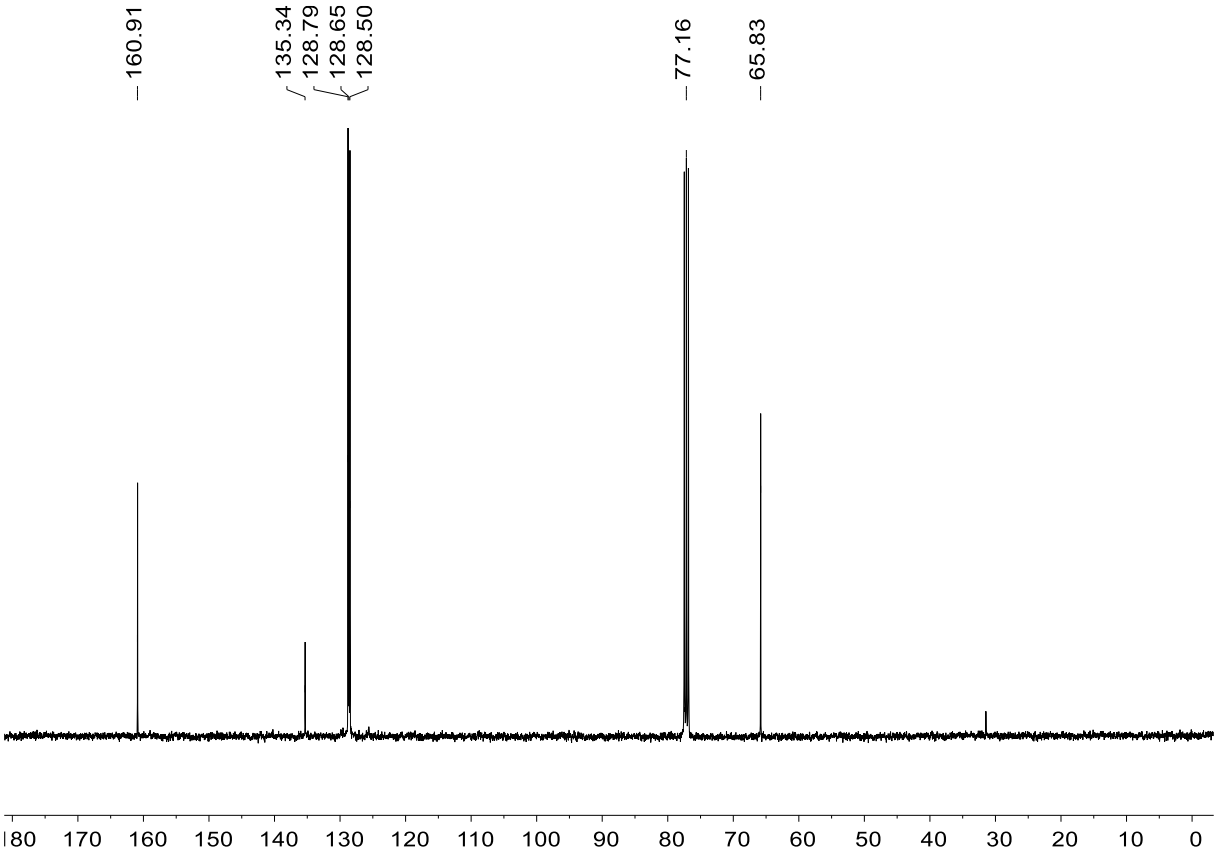
^{1}H NMR spectrum of 4-*tert*-butylbenzyl formate (**2p**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 4-*tert*-butylbenzyl formate (**2p**, 126 MHz, $CDCl_3$).

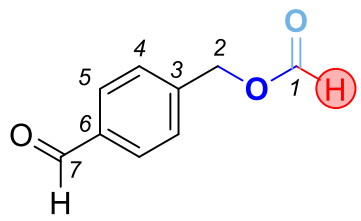


^{1}H NMR spectrum of benzyl formate (**2o**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of benzyl formate (**2o**, 101 MHz, $CDCl_3$).

2.3.2.3. Synthesis of (4-Formylbenzyl) Formate (2q)



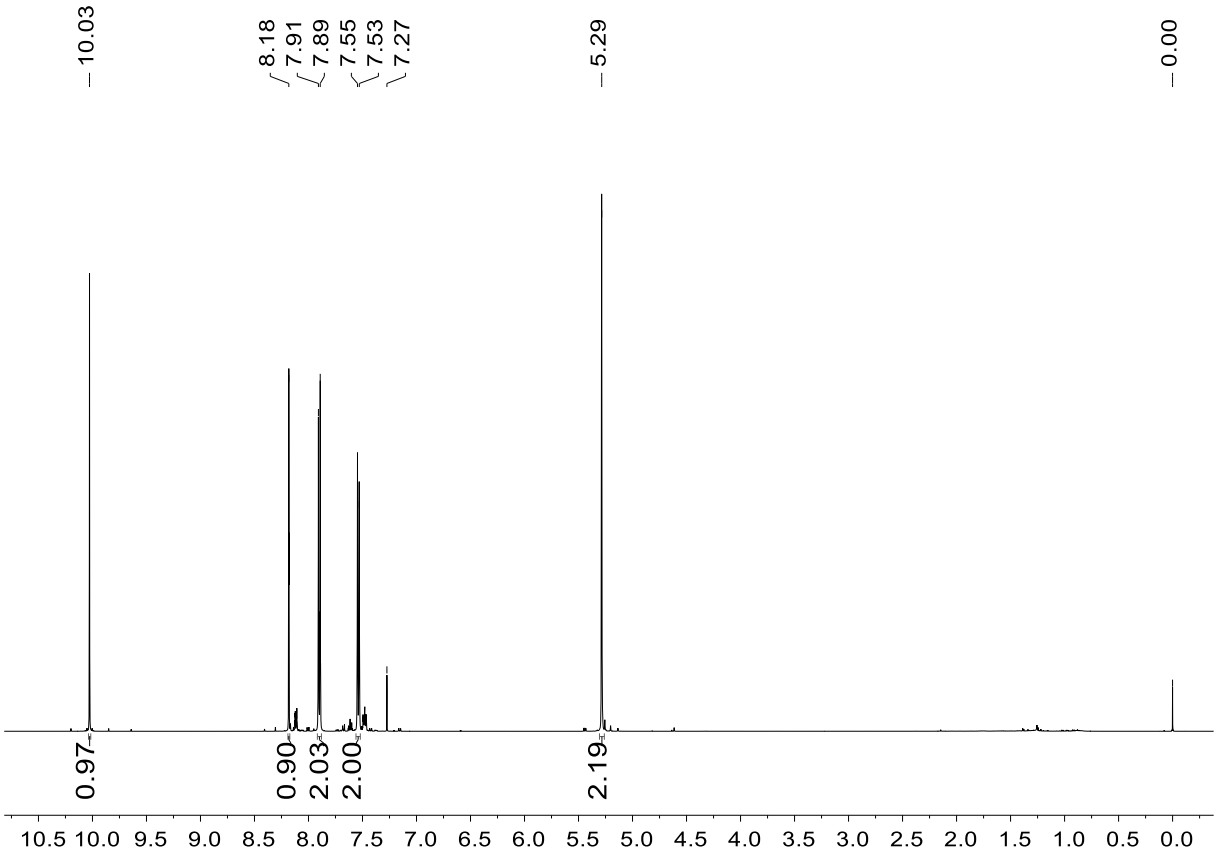
2q

DTT-321: In accordance to the general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from 4-(hydroxymethyl) benzaldehyde (68.3 mg, 0.50 mmol, 1.00 equiv) and FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv) with $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 2.5 h stirring and work up with $NaHCO_3$ solution (2.0 mL, 4.40 equiv, 1.1 M), ^{1}H NMR of the crude material (75.9 mg, 111%) using mesitylene as internal standard verified 93% conversion of alcohol **1q** and target molecule **2q** in 73% yield.

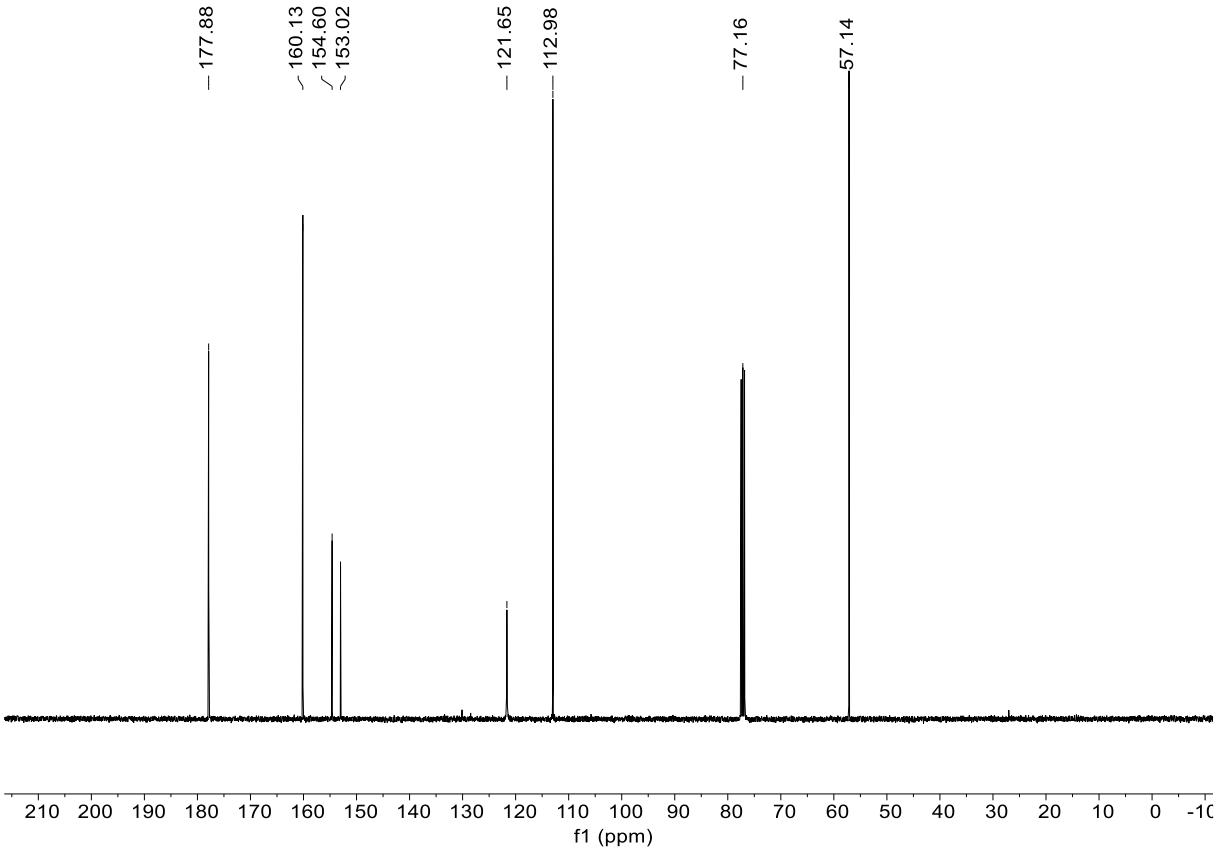
DTT-335: In agreement with general protocol A (chapter 2.2.1, page 8), the title compound was produced from of 4-(hydroxymethyl) benzaldehyde (136.5 mg, 1.00 mmol, 1.00 equiv) with FPyr (190.6 µL, 198.3 mg, 2.00 mmol, 2.00 equiv), $NaPF_6$ (284.8 mg, 1.70 mmol, 1.70 equiv) and BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) in dry MeCN (0.5 mL, 2.0 M). After 4 h of stirring and quenching with $NaHCO_3$ solution (3.0 mL, 3.30 equiv, 1.1 M), the ^{1}H NMR of the crude material (182.6 mg, 111%) showed 94% conversion of alcohol **1q**. Eventually, purification with the aid of column chromatography on silica gel (2 g, ratio weight crude product/SiO_2 1:20) using MTBE/*n*-heptane 1:99 as solvent mixture. Afterwards, 4-formylbenzyl formate **2q** was collected as a colourless oil (131.4 mg, 0.80 mmol, 80%) after drying at 20 mbar for 5 min at the rotary evaporator.

M ($C_9H_8O_3$) = 164.16 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 20:80) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 10.03 (s, 1H, 7-H), 8.18 (t, $^4J_{1,2}$ = 1.0 Hz, 1H, 1-H), 7.91-7.89 (m, 2H, 5-H), 7.55-7.53 (m, 2H, 4-H), 5.29 (s, 2H, 2-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 177.88 (C-7), 160.13 (C-1), 154.60 (C-5), 153.02 (C-4), 121.65 (C-6), 112.98 (C-5), 57.14 (C-2).

The NMR data is in match with the literature.[8]

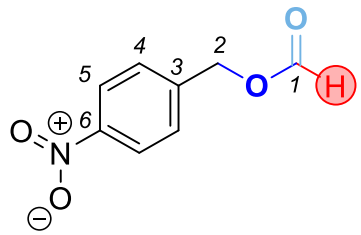


^{1}H NMR spectrum of 4-formylbenzyl formate (**2q**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 4-formylbenzyl formate (**2q**, 126 MHz, $CDCl_3$).

2.3.2.4. Synthesis of 4-Nitrobenzyl Formate (2r)



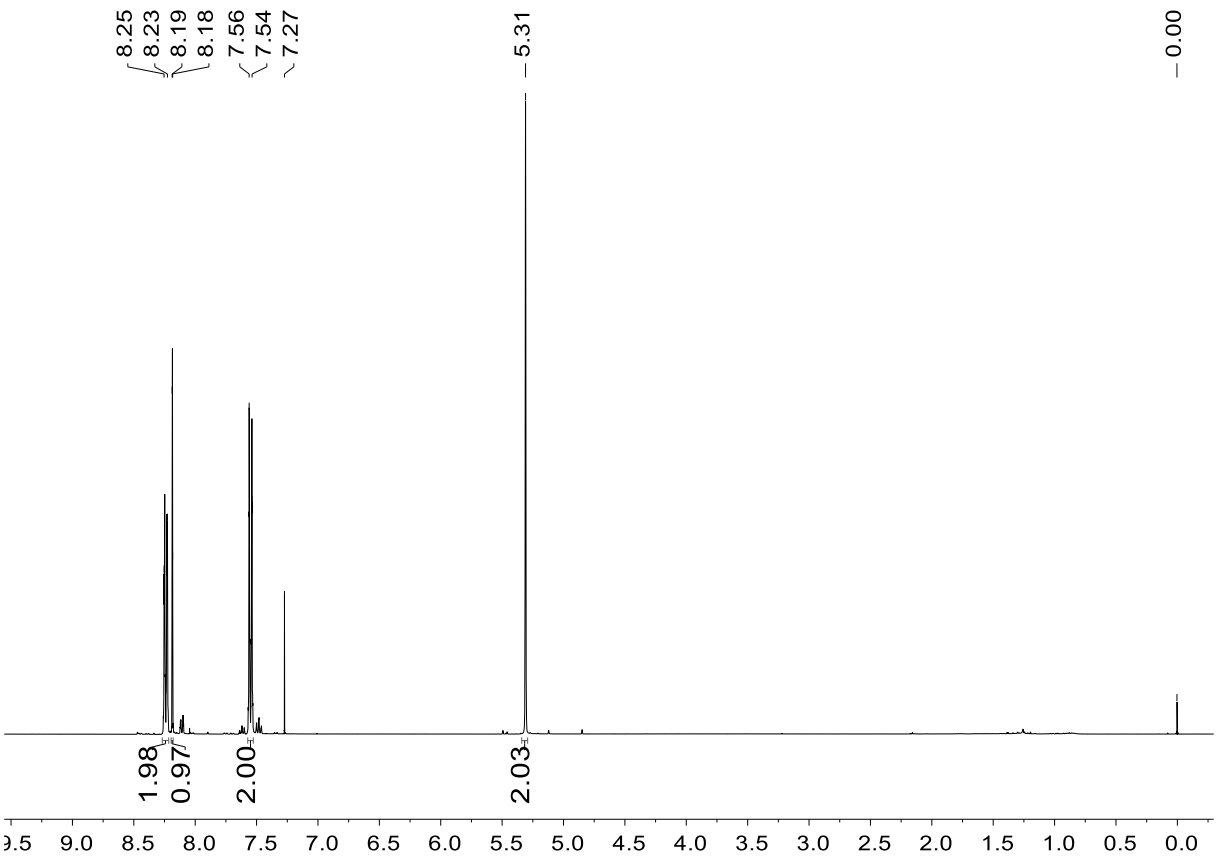
2r

DTT-322: According to general protocol A (chapter 2.2.1, page 8), a mixture of 4-nitrobenzyl alcohol (76.6 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) was allowed to stir for 2.5 h. Subsequent aqueous work up with $NaHCO_3$ solution (2.0 mL, 4.40 equiv, 1.1 M), ^{1}H NMR of the crude material (91.0 mg, 100%) with mesitylene as internal standard indicated 90% conversion of alcohol **1r** and formic acid ester **2r** in 75%.

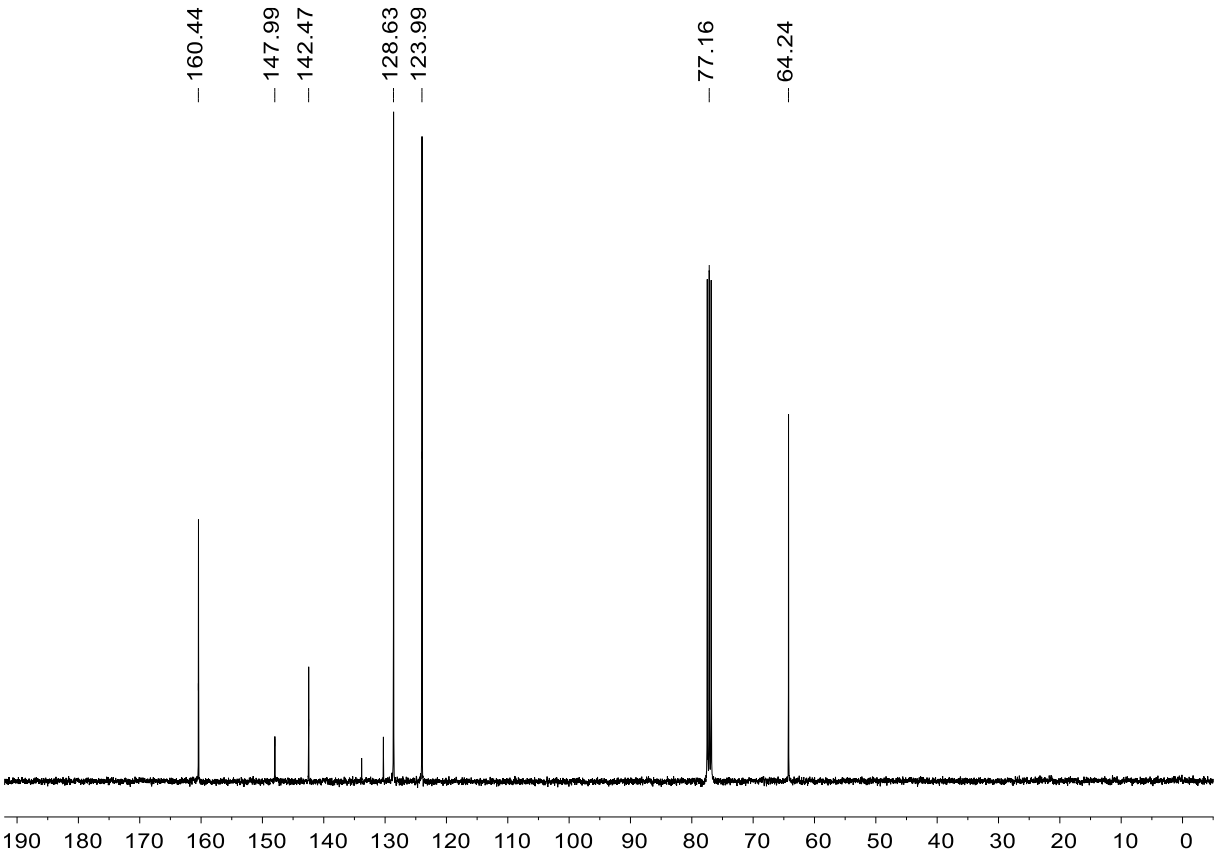
DTT-322b: Based on general protocol A (chapter 2.2.1, page 8), 4-(hydroxymethyl) benzaldehyde (152.2 mg, 1.00 mmol, 1.00 equiv) was reacted with FPyr (190.6 µL, 198.3 mg, 2.00 mmol, 2.00 equiv), BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) and $NaPF_6$ (284.8 mg, 1.70 mmol, 1.70 equiv) in dry MeCN (0.5 mL, 2.0 M) for 3 h. Past work up with $NaHCO_3$ solution (3.0 mL, 3.30 equiv, 1.1 M), the ^{1}H NMR of the crude material showed full conversion of alcohol **1r**. Finally, purification with the aid of column chromatography on silica gel using MTBE/*n*-heptane 20:80 as solvent mixture. After drying at the rotary evaporator for 20 mbar for 5 minutes, 4-nitrobenzyl formate (**2r**) was isolated as a colourless oil (164.2 mg, 0.91 mmol, 91%).

M ($C_8H_7NO_4$) = 181.15 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 1:99) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.25-8.23 (m, 2H, 5-H), 8.19-8.18 (m, 1H, 1-H), 7.55-7.52 (m, 2H, 4-H), 5.30 (s, 2H, 2-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 160.44 (C-1), 147.99 (C-6), 142.47 (C-3), 128.63 (C-4), 123.99 (C-5), 64.24 (C-2); **GC MS** (EI, 70 eV) m/z [u] (%) = 181 (45, $[M]^+$), 153 (17), 152 (9), 136 (42, $[M\text{-}OCHO]^+$), 135 (6, $[M\text{-}NO_2]^+$), 107 (30, $[PhNO]^+$), 106 (16), 90 (17, $[Bn\text{-}H]^+$), 89 (100), 79 (12, $[PhH_2]^+$), 78 (34, $[PhH]^+$), 77 (31, $[Ph]^+$), 76 (6), 63 (16), 51 (14); **HR MS** (EI, $[C_8H_7O_4N]^+$) calc 181.03696 u, found 131.03687 u.

The NMR data is in match with the literature.[8]

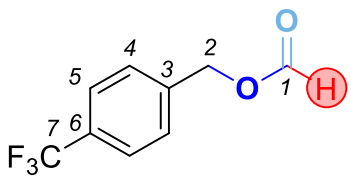


^{1}H NMR spectrum of 4-nitrobenzyl formate (**2r**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 4-nitrobenzyl formate (**2r**, 101 MHz, $CDCl_3$).

2.3.2.5. Synthesis of 4-(Trifluoromethyl)benzyl Formate (2s)



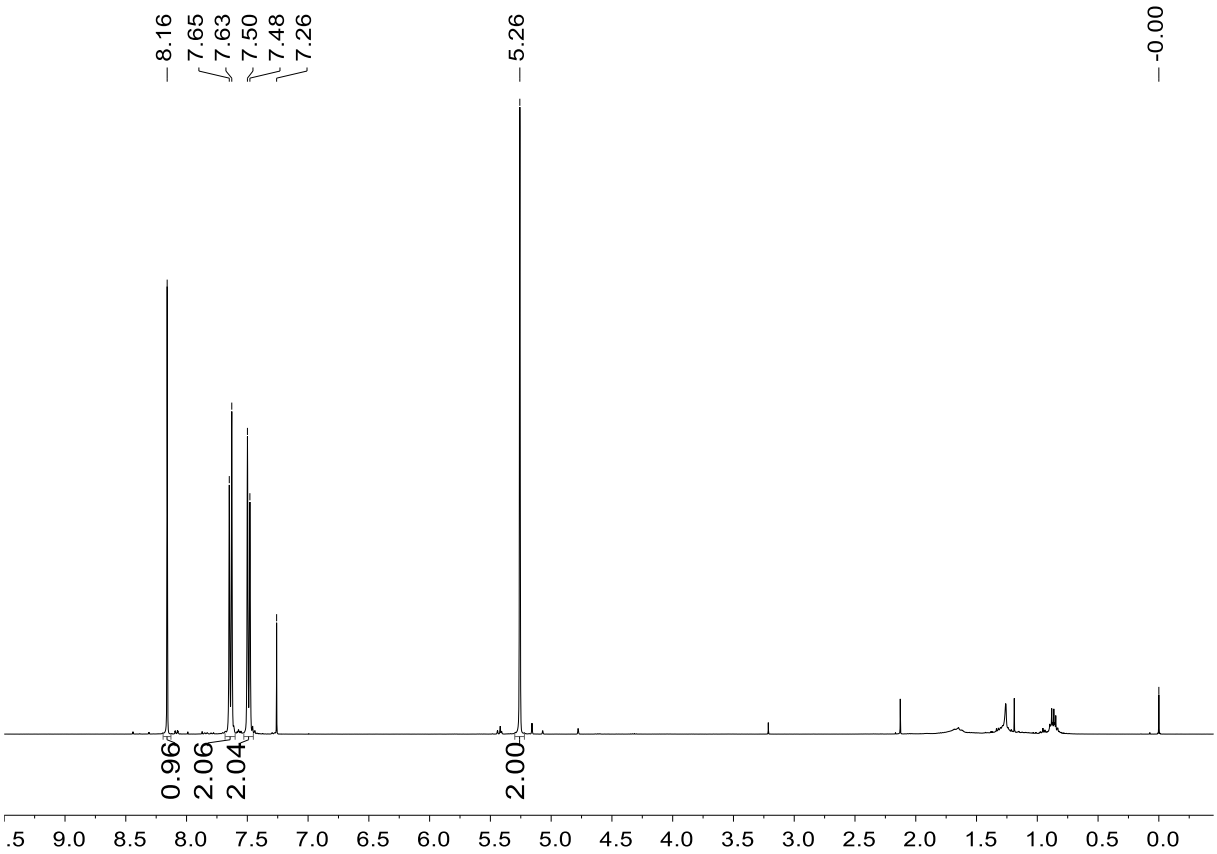
2s

DTT-323: In accordance to the general protocol A (chapter 2.2.1, page 8), the title compound was produced from a mixture of 4-(trifluoromethyl)benzyl alcohol (88.1 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv). After 2.5 h of stirring and work up with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), the ^{1}H NMR of the crude material (105.9 mg, 105%) using mesitylene as internal standard verified 87% conversion of alcohol **1s** and the target compound **2s** in 74% yield.

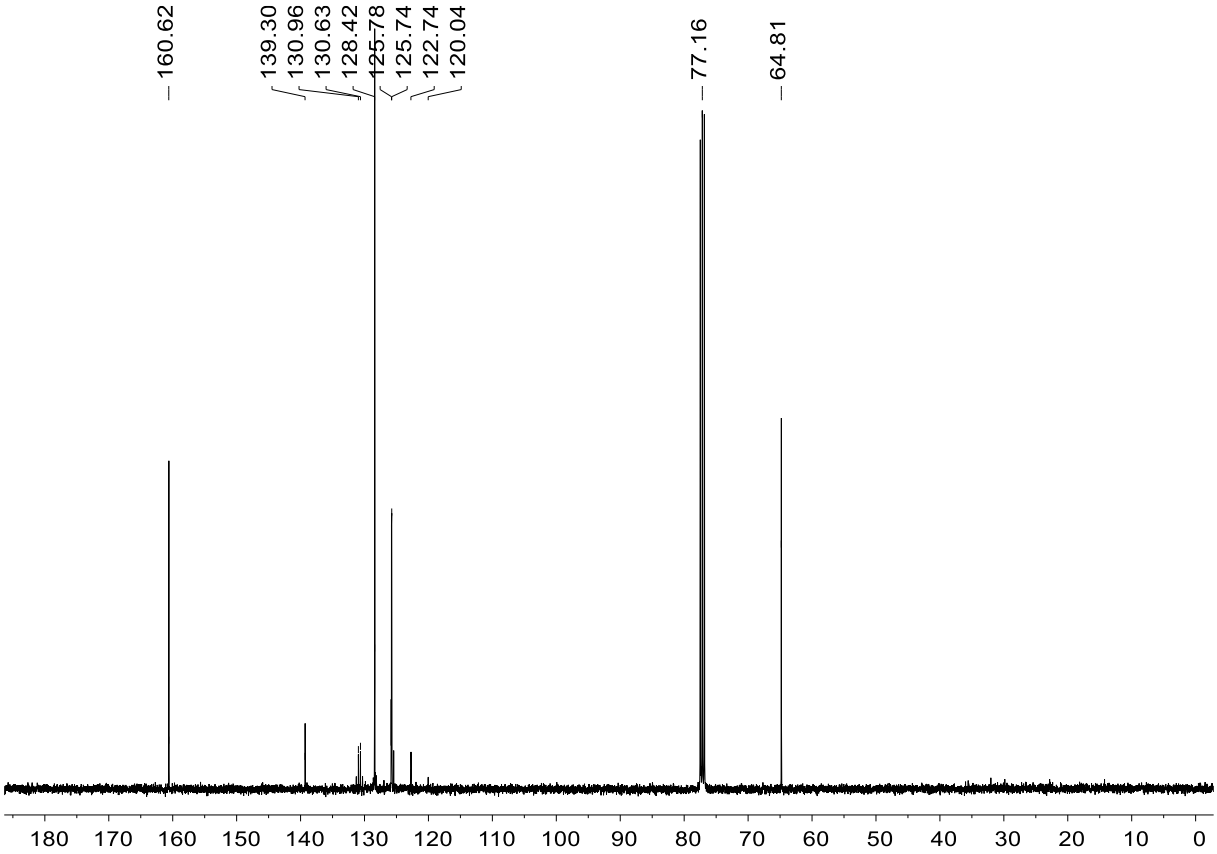
DTT-323: In alignment to general protocol A (chapter 2.2.1, page 8), the title compound was prepared from 4-(trifluoromethyl)benzyl alcohol (193.4 mg, 1.00 mmol, 1.00 equiv) with FPyr (190.6 µL, 200.0 mg, 2.00 mmol, 2.00 equiv), $NaPF_6$ (168.4 mg, 1.70 mmol, 1.70 equiv) and BzCl (197.5 µL, 240.0 mg, 1.7 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 2.5 h stirring, the saturated solution of $NaHCO_3$ (2.0 mL, 2.00 equiv, 1.1 M) was added. After aqueous work up with $NaHCO_3$ solution (3.0 mL, 3.3 equiv, 1.1 M), the ^{1}H NMR of the crude material indicated 87% conversion of alcohol **1s** and the title compound in 74% based on the ratio of the singlets of the respective compounds. In the end, purification with the aid of column chromatography on silica gel using MTBE/*n*-heptane 1:99 as solvent mixture, which afforded 4-(trifluoromethyl)benzyl formate (**2s**) as a colourless oil (140.8 mg, 0.69 mmol, 70%) after drying at the rotary evaporator at 20 mbar for 5 min.

M ($C_9H_7F_3O_2$) = 204.15 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 1:99) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.15 (s, 1H, 1-H), 7.65-7.63 (m, 2H, 5-H), 7.50-7.48 (m, 2H, 4-H), 5.26 (s, 2H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ [ppm] = 160.62 (C-1), 139.80 (C-3), 130.72 (q, $^2J_{6,F}$ = 32 Hz, C-6), 128.42 (C-4), 125.76 (q, $^3J_{5,F}$ = 3.8 Hz, C-5), 124.09 (q, $^1J_{7,F}$ = 272 Hz, C-7), 64.73 (C-2); **GC MS** (EI, 70 eV) m/z [u] (%) = 204 (67, $[M]^+$), 185 (26, $[M\text{-}F]^+$), 176 (25), 175 (15), 160 (8), 159 (89, $[M\text{-}OCHO]^+$), 157 (88, $[M\text{-}OCHO\text{-}H]^+$), 132 (6), 127 (48), 119 (15), 109 (43, $[PhCH_2OH_2]^+$), 108 (14, $[PhCH_2OH]^+$), 107 (100, $[PhCHOH]^+$), 89 (17), 79 (16, $[PhH_2]^+$), 77 (13, $[Ph]^+$); **HR MS** (EI, $[C_9H_7F_3O_2]^+$) calc 204.03927 u, found 204.03944 u.

The NMR data is in match with the literature.[8]

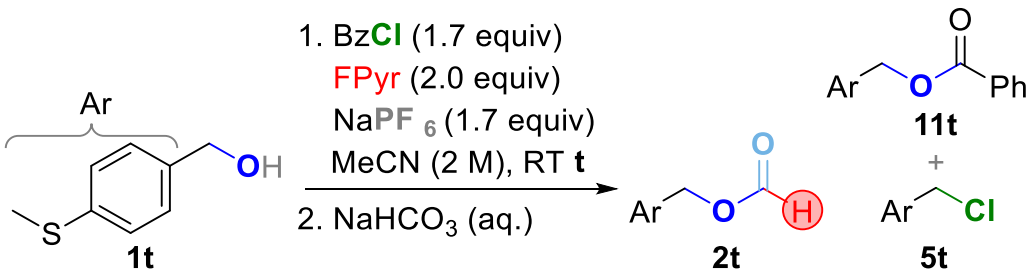


^{1}H-NMR spectrum of 4-(trifluoromethyl)benzyl formate (**2s**, 400 MHz, $CDCl_3$).



^{13}C-NMR spectrum of 4-(trifluoromethyl)benzyl formate (**2s**, 100 MHz, $CDCl_3$).

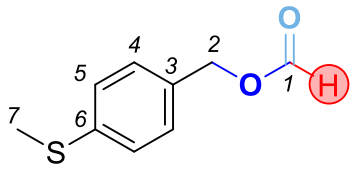
2.3.2.6. Synthesis of 4-Methythioxybenzyl Formate (2t)



Entry	Condition (reaction duration)	Conv.	Yield 2t (%)	Yield 5t (%)	Yield 11t (%)	Lab Journal
1	general protocol A (2.5 h)	76	8	43	15	DTT-328
2	general protocol A (70 min)	85	16	17	7	DTT-584-3
3	general protocol A (30 min)	71	31	2	5	DTT-584-2
4	HCOOH (2.6 equiv), Ac_2O (1.3 equiv)	62	60[(a)]	/	/	DTT-610

The title compound was prepared according to procedure A (chapter 2.2.1, page 8). Yields and conversion were determined based on the ratio of singlets of the CH_2 groups of each compound in the ^1H NMR spectra. (a) isolated yield.

For the formation of the benzylic formate **2t** short reaction times were crucial and allowed the synthesis in a moderate yield of 31% (entries 1-3). In order to isolate analytical pure ester **2t**, the 4-methylthio benzyl alcohol (**1t**) was formylated with the aid of the mixed anhydride of formic and acetic acid according to a known procedure (for exemplary protocol see [1]).



2t

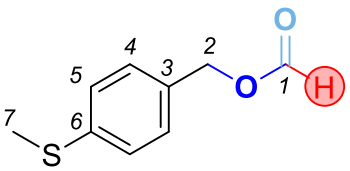
Entry 1, DTT-328: In accordance to the general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from 4-methylthioenzyl alcohol (69.1 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 2.5 h stirring and work up with a solution of $NaHCO_3$ (2.0 mL, 4.4 equiv, 1.1 M), the ^1H NMR of the crude material (66.7 mg, 72%) using the integration ratio of the singlets of the CH_2 groups verified 76% conversion of alcohol **1t** and the formate in 7% yield alongside 43% of chloride **5t** as main product.

Entry 2, DTT-584-3: In agreement with the general protocol A (chapter 2.2.1, page 8), the title compound was accessed from 4-methylthiobenzyl alcohol (69.1 mg, 0.50 mmol, 1.00 equiv) with FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol,

1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 70 min of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), the ^{1}H NMR of the crude product (203.4 mg, 220%) confirmed 85% conversion of alcohol **1t** and the formate ester **2t** in 16% yield.

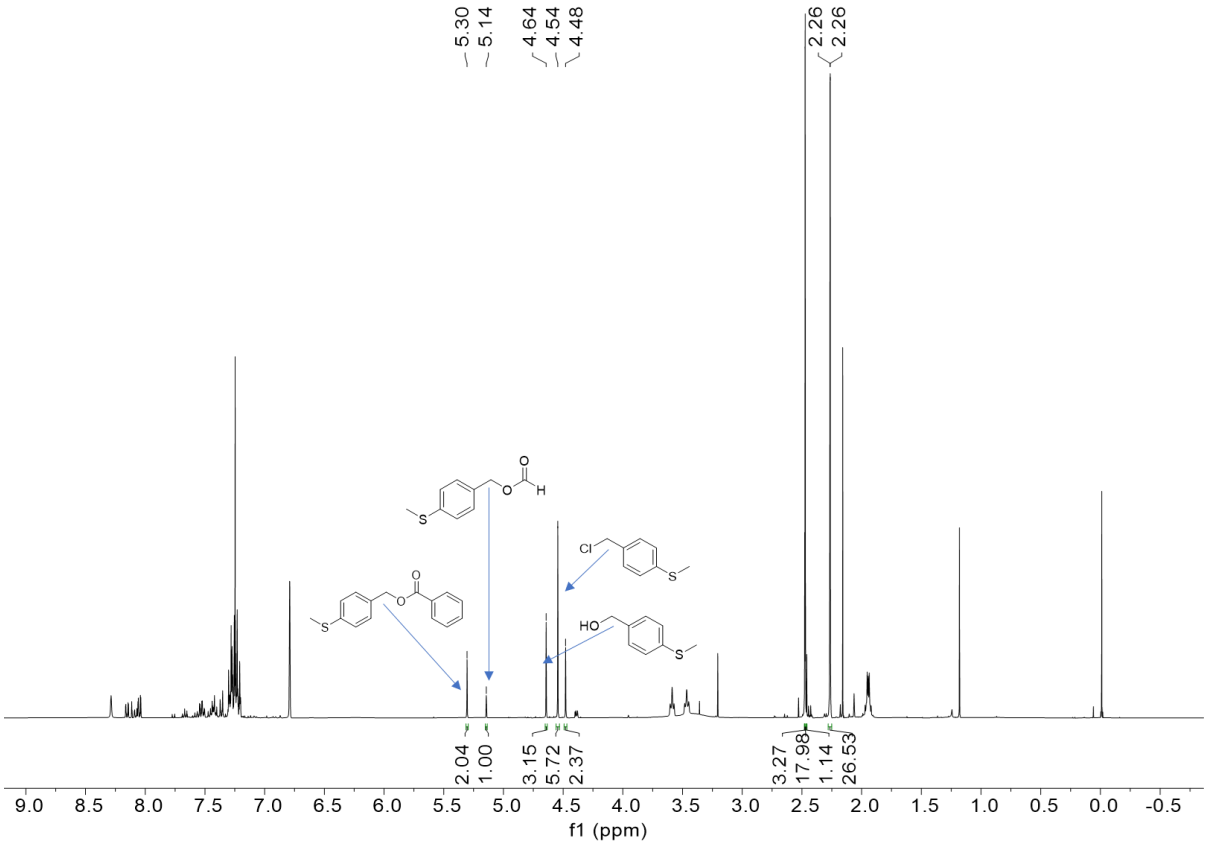
Entry 3, DTT-584-2: In accordance to the general protocol A (chapter 2.2.1, page 8), the title compound was prepared from 4-methylthiobenzyl alcohol (69.1 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 0.5 h stirring and addition of a solution of $NaHCO_3$ (2.0 mL, 4.4 equiv, 1.1 M), the ^{1}H NMR of the crude material (203.4 mg, 220%) indicated 71% conversion of alcohol **1t** and 31% yield of formate **2t**.

Entry 4, DTT- 610: A 4 mL vial was charged with formic acid (98.3 µL, 2.60 mmol, 2.60 equiv) and Ac_2O (123.6 µL, 1.30 mmol, 1.30 equiv) and the resulting mixture was stirred at 40 °C for 2 h. Then, the reaction was cooled in an ice bath, 4-methylthiobenzyl alcohol (138.2 mg, 1.00 mmol, 1.00 equiv) was added and the mixture was stirred at 0 °C for 15 min and subsequently at rt for 20 h. Next, a saturated solution of $NaHCO_3$ in water (3 mL, 1.1 M) was added dropwise under cooling to 0 °C. After stirring for 10 min the mixture was taken up with a 20 mL syringe under dilution with EtOAc (5 mL). The organic phase was washed further with $NaHCO_3$ solution (2 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The ^{1}H NMR spectrum of the crude material (180.0 mg, 99%) indicated 62% conversion of alcohol **1t**. Finally, purification by means of column chromatography on silica gel (11.9 g, ratio weight crude product/SiO_2 1:66) with MTBE/*n*-heptane 10:90 as solvent mixture and drying at the rotary evaporator at 20 mbar for 5 min delivered formate **2t** as a colourless oil (109.1 mg, 0.60 mmol, 60%).

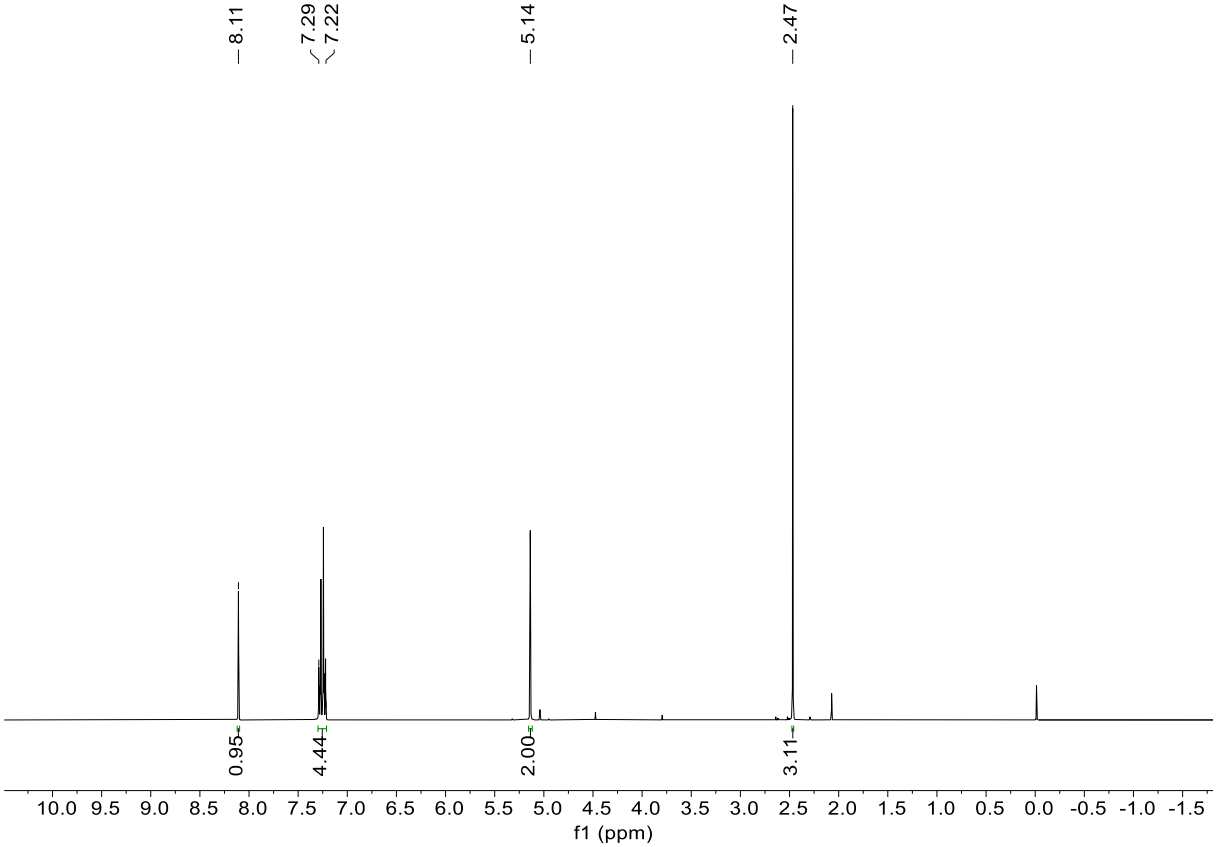


M ($C_9H_{10}O_2S$) = 182.24 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.11 (s, 1H, 1-H), 7.29 – 7-22 (m, 4H, 5-H, 4-H), 5.14 (s, 2H, 2-H), 2.47 (s, 3H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 160.87 (C-1), 139.36 (C-6), 131.98 (C-3), 129.17 (C-4), 126.65 (C-5), 65.46 (C-2), 15.79 (C-7);); **GC MS** (EI, 70 eV) m/z [u] (%) = 182 (43, $[M]^+$), 139 (5), 138 (10), 137 (100, $[M\text{-}OCHO]^+$), 123 (4, [4-methylthiophenyl]$^+$) 122 (22), 121 (17), 91 (8, $[Bn]^+$), 89 (8), 78 (11), 77 (13, $[Ph]^+$); **HR MS** (EI, $[C_9H_{10}O_2S]^+$), calc 182.0396 u, found 182.0398 u.

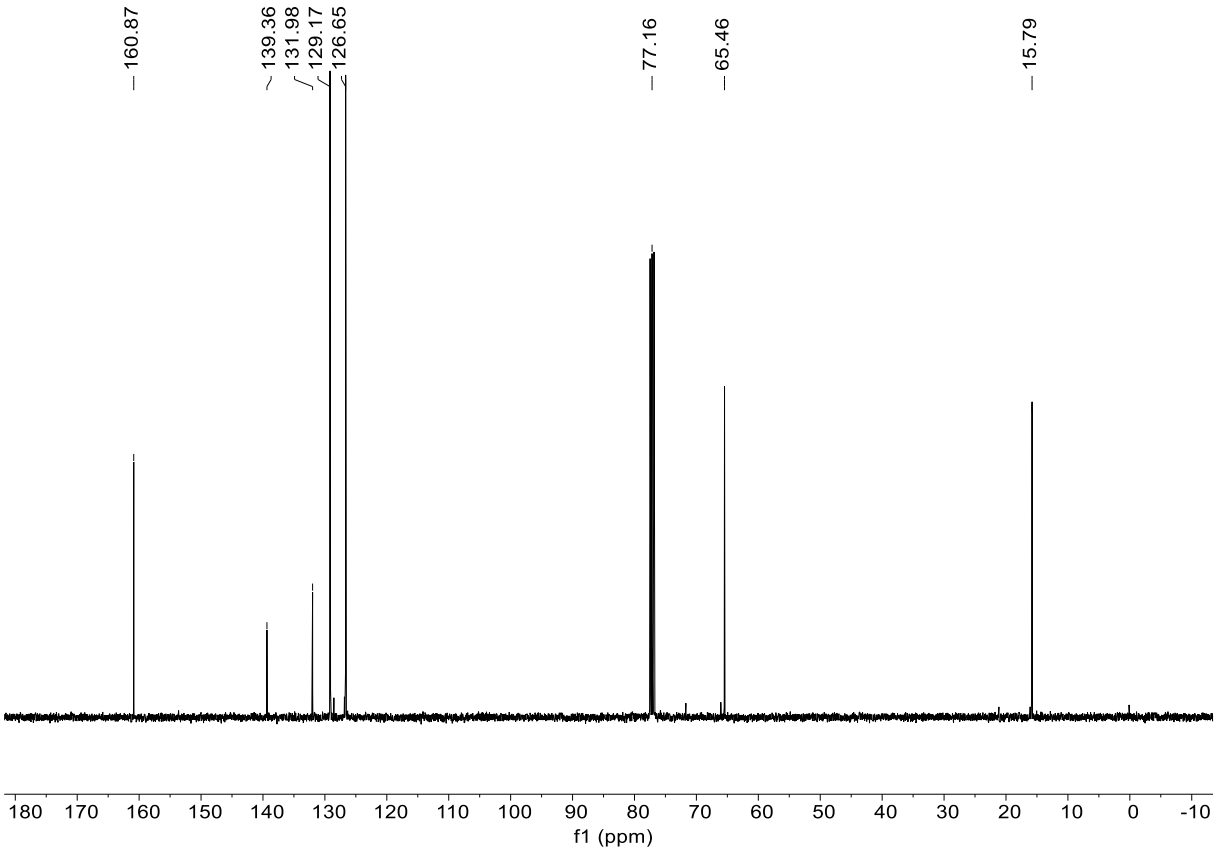
The NMR data is in agreement with reported data.[8]



Exemplary ^{1}H NMR spectrum of crude 4-(methylthio)benzyl formate (**2t,** 400 MHz, $CDCl_3$).

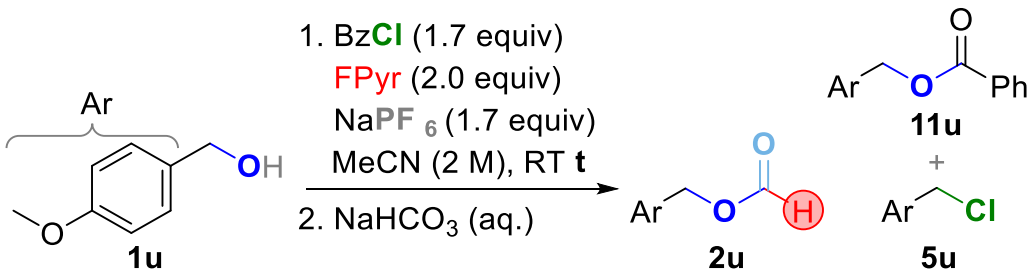


^{1}H NMR spectrum of 4-Methythioxybenzyl Formate (**2t**, 500 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4-Methythioxybenzyl Formate (**2t**, 127 MHz, $CDCl_3$)

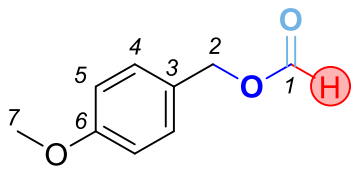
2.3.2.7. Synthesis of 4-Methoxybenzyl Formate (2u)



Entry	Condition (deviation from GP)	Conv.	Yield 2u	Yield 5u (%)	Yield 11u	Lab Journal
1	General protocol A	45	/	≤2	35	DTT-583a
2	General protocol A (0.5 h duration)	79	≤2	21	22	DTT-583-2
3	General protocol A, work up with NaOAc (aq.)	67	/	/	33	DTT-583b
4	HCOOH (2.6 equiv), Ac_2O (1.3 equiv)	66	46[(a)]	/	/	DTT-609

The title compound was prepared according to procedure A (chapter 2.2.1, page 8). Yields and conversion were determined based on the ratio of singlets of the CH_2 groups of each compound in the ^1H NMR spectra. (a) isolated yield. GP = general procedure

The previous approach did not allow for the production of 4-methoxybenzyl formate (**2u**, entries 1 to 3). In order to obtain analytical comparison data, the ester **2u** was synthesis by a known method utilizing the mixed anhydride of formic and acetic acid (for exemplary protocol see [1]).



2t

Entry 1, DTT-583b: In accordance to the general protocol A (chapter 2.2.1, page 8), 4-methoxybenzyl alcohol (77.2 mg, 0.50 mmol, 1.00 equiv) was reacted with FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M) for 2.5 h. Past quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^1H NMR of the crude material (73.8 mg, 89%) proved 45% conversion and benzoate **11u** in 35% yield based on the ratio of the singlets of the -CH_2- moiety of all compounds, Thereby, the desired formate **2u** was not observed.

Entry 2, DTT-583-2: According to the general protocol A (chapter 2.2.1, page 8), 4-methylthoxybenzyl alcohol (77.2 mg, 0.50 mmol, 1.00 equiv) was allowed to react with FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.0 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M) for 0.5 h. Subsequent to a work up with $NaHCO_3$ (2.0 mL, 4.4 equiv, 1.1 M), the ^1H NMR of the crude

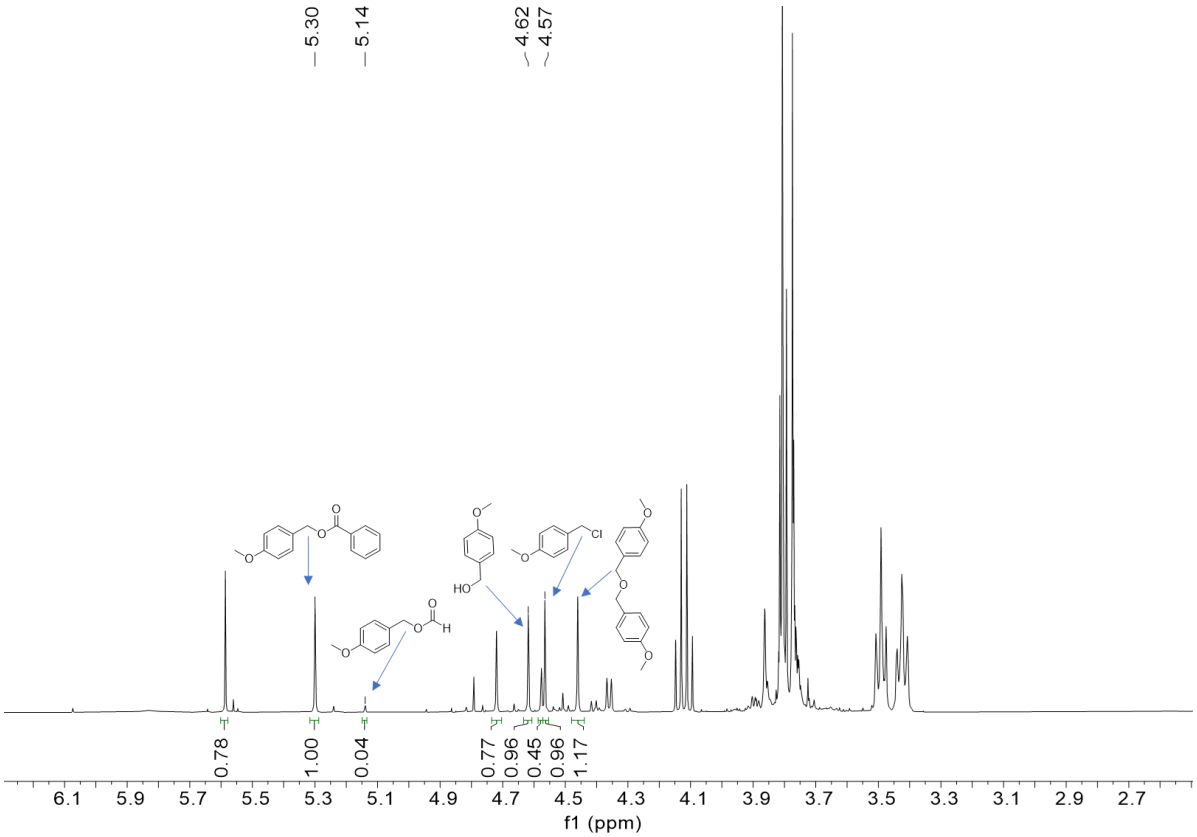
material (371.6 mg, 223%) showed 79% conversion of alcohol **1u** and benzoate **11u** in 22% and chloride **5u** 21% yield of. Formate product **2u** was only observed in small traces.

Entry 3, DTT-583b: Following general procedure A (chapter 2.2.1, page 8), a mixture of 4-methoxybenzyl alcohol (77.2 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M) was stirred 2.5 h at ambient temperature. Past quenching with a solution of NaOAc in water (2.0 mL, 4.00 equiv, 1.0 M) instead of $NaHCO_3$, the ^{1}H NMR of the crude material (371.6 mg, 223%) indicated 67% conversion of alcohol **1u** and benzoate **10u** in 33% yield as main product.

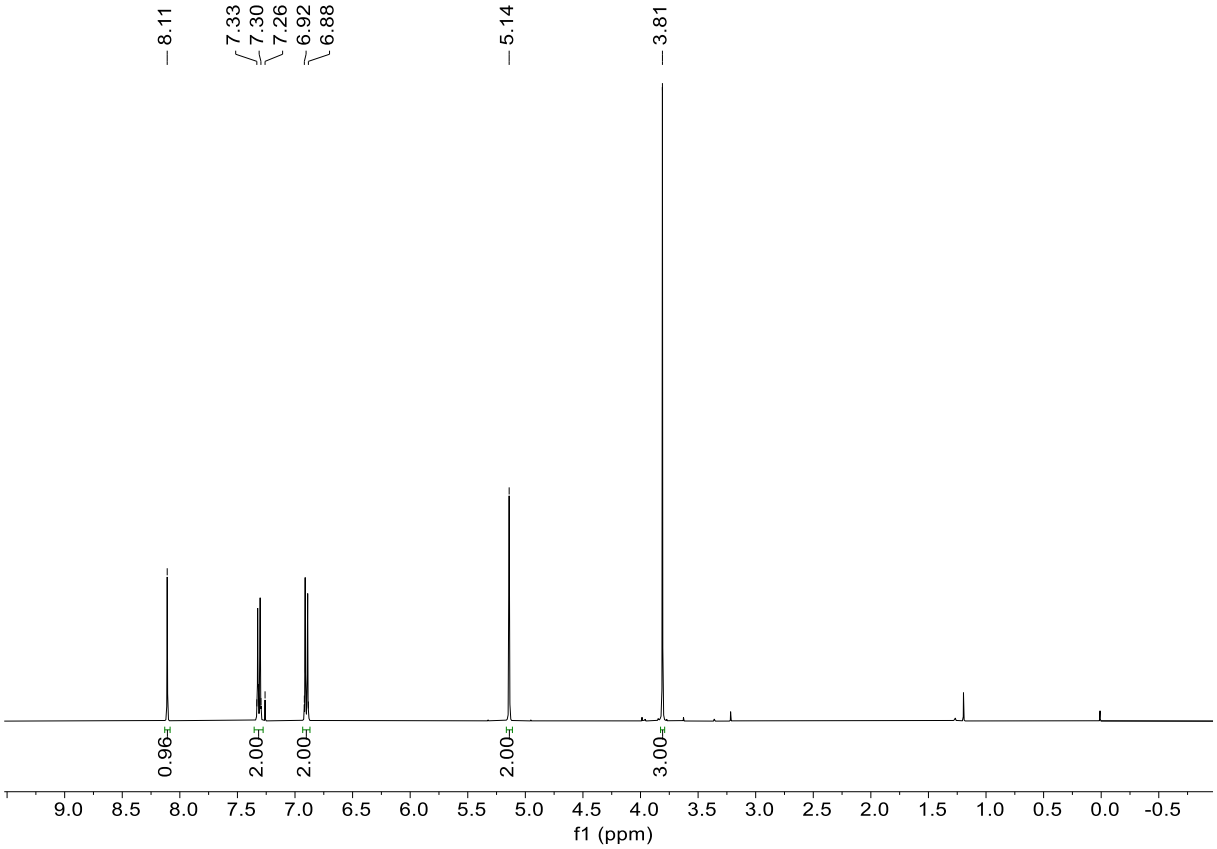
Entry 4, DTT- 609: A 4 mL vial was charged with formic acid (98.3 µL, 2.60 mmol, 2.60 equiv) and Ac_2O (123.6 µL, 1.30 mmol, 1.30 equiv) and the resulting solution was stirred at 40 °C for 2 h. Next, the reaction mixture was placed in an ice bath, 4-methoxybenzyl alcohol (154.4 mg, 1.00 mmol, 1.00 equiv) was added and the reaction solution stirred at 0 °C for 15 min and afterwards for 20 h at rt. Next, a saturated solution of $NaHCO_3$ in water (3 mL, 1.1 M) was added dropwise under cooling at 0 °C. After 10 min of further stirring, the mixture was taken up with the aid of a 20 mL syringe and diluted with EtOAc (5 mL). The organic phase was washed further with $NaHCO_3$ solution (2 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The ^{1}H NMR spectrum of the crude material (171.2 mg, 103%) indicated 66% conversion of alcohol **1u**. Finally, purification by means of column chromatography on silica gel (14.6 g, ratio weight crude product/SiO_2 1:85) with MTBE/*n*-heptane 10:90 as solvent mixture and drying at the rotary evaporator at 20 mbar for 5 min afforded formate **2u** as a colourless oil (73.9 mg, 0.46 mmol, 46%).

M ($C_9H_{10}O_3$) = 166.06; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.11 (s, 1H, 1-H), 7.33 – 7-30 (m, 2H, 5-H), 6.92 – 6.88 (m, 2H, 4-H), 5.14 (s, 2H, 2-H), 3.81 (s, 3H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 160.97 (C-1), 159.93 (C-6), 130.35 (C-5), 127.45 (C-3), 114.12 (C-4), 65.61 (C-2), 55.37 (C-7); **GC MS** (EI, 70 eV) m/z [u] (%) = 166 (30, $[M]^+$), 122 (10), 121 (100, $[M-OCHO]^+$), 120 (15), 91 (16, $[Bn]^+$), 89 (7), 78 (16), 77 (23, $[Ph]^+$); **HR MS** (EI, $[C_9H_{10}O_3]^+$), calc 166.0625 u, found 166.0626 u.

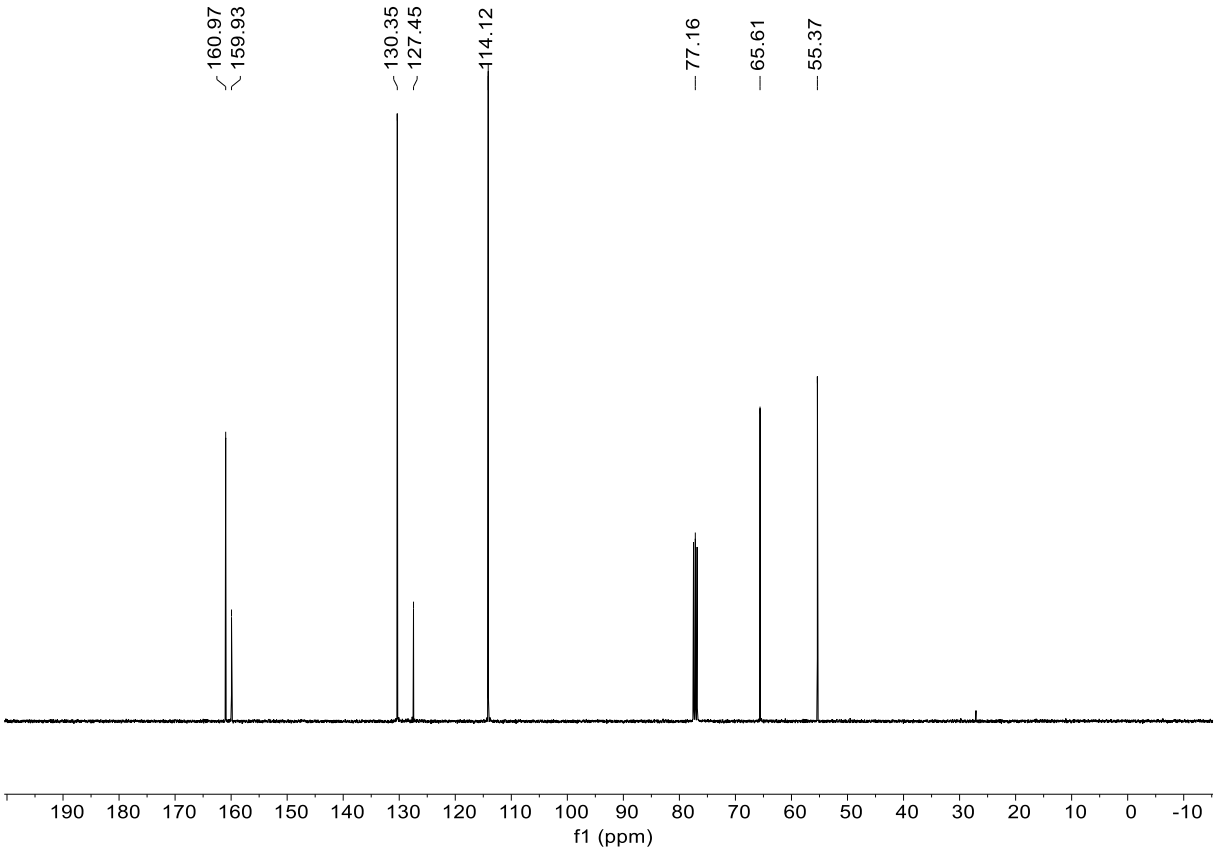
The NMR data is in agreement with comparison data.[9]



Exemplary ^{1}H NMR spectrum of crude product from DTT-583-2 (400 MHz, $CDCl_3$).

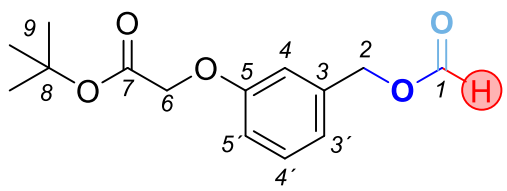


^{1}H NMR spectrum of 4-methoxybenzyl formate (**2u**, 500 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4-methoxybenzyl formate (**2u**, 126 MHz, $CDCl_3$)

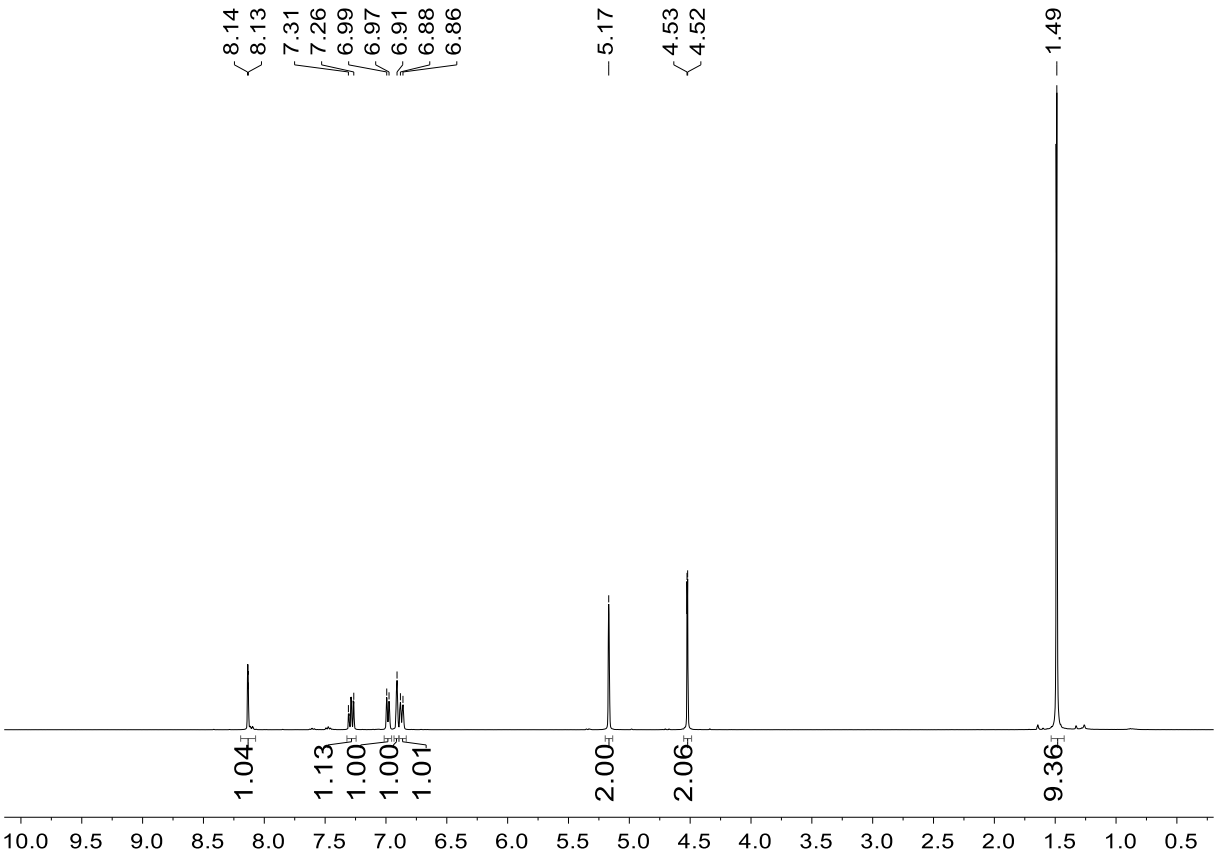
2.3.2.8. Synthesis of *tert*-Butyl 2-(3-(formyloxymethyl)phenoxy) Acetate (2v)



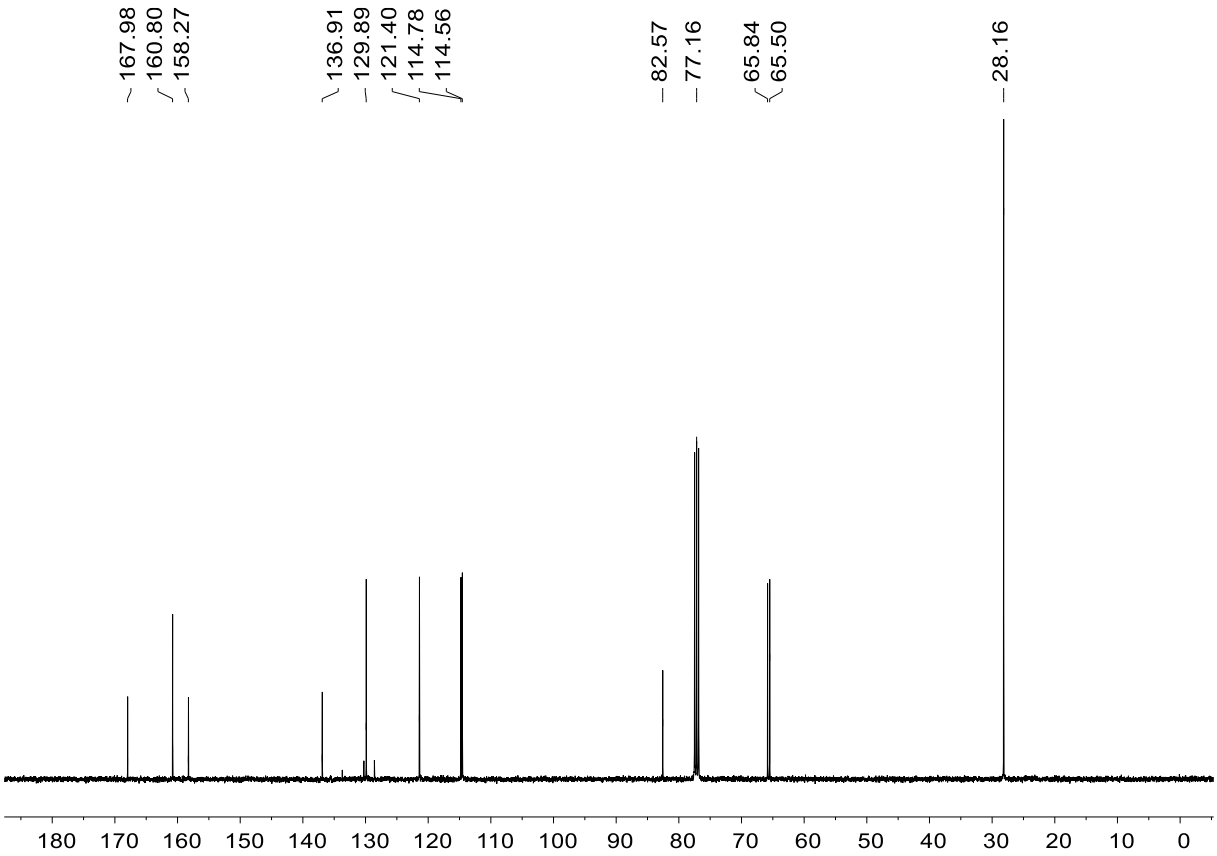
2v

DTT-346: As given in general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from *tert*-butyl 2-(3-(hydroxymethyl)phenoxy) acetate (119.1 mg, 0.50 mmol, 1.00 equiv) using FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 4 h of stirring and quenching with $NaHCO_3$ solution (2.0 mL, 2.20 equiv, 1.1 M), ^{1}H NMR of the crude material (138.2 mg, 104%) indicated complete consumption of alcohol **1v.** Finally, purification by means of column chromatography on silica gel (4.1 g, ratio weight crude product/SiO_2 1:30) with MTBE/*n*-heptane 15:85 as eluent mixture. After drying at the rotary evaporator at 20 mbar for 5 minutes, formate **2v** was obtained as a colourless oil (114.0 mg, 0.43 mmol, 86%).
The starting alcohol was prepared as stated in chapter 2.3.4.4 (page 88).

M ($C_{14}H_{18}O_5$) = 266.29 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 15:85) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.14- 8.13 (m, 1H, 1-H), 7.29 (ψ-td, *J* = 8.0, 1.7 Hz ,1H, 5'-H), 6.98 (d, $^3J_{3',4'}$= 5.0 Hz, 1H, 3'-H), 6.91 (s, 1H, 4-H), 6.88-6.86 (m, 1H, 4'-H); 5.15 (s, 2H, 2-H), 4.53-4.52 (m, 2H, 6-H), 1.49 (s, 9H, H-9); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 167.98 (C-7), 160.80 (C-1), 158.27 (C-5), 136.91 (C-3), 129.89 (C-4), 121.40 (C-4'), 114.78 (C-3'), 114.56 (C-5'), 82.57 (C-8), 65.84 (C-6), 65.44 (C-2), 28.16 (C-9); **GC MS** (EI, 70 eV) m/z [u] (%) = 266 (17, $[M]^+$), 210 (9, [M-iso-butenyl]$^+$), 166 (15), 165 (23, [M-COO*t*Bu]$^+$), 120 (8), 119 (19), 90 (11), 89 (26), 77 (11, $[Ph]^+$), 57 (100, $[butyl]^+$); **HR MS** (EI, $[C_{14}H_{18}O_5]^+$), calc 266.11488 u, found 266.11488 u.

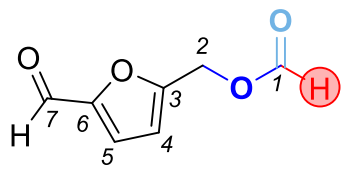


^{1}H NMR spectrum of *tert*-butyl 2-(3-(formyloxymethyl)phenoxy)acetate (**5w** , 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of *tert*-butyl 2-(3-(formyloxymethyl)phenoxy)acetate (**5w**, 101 MHz, $CDCl_3$).

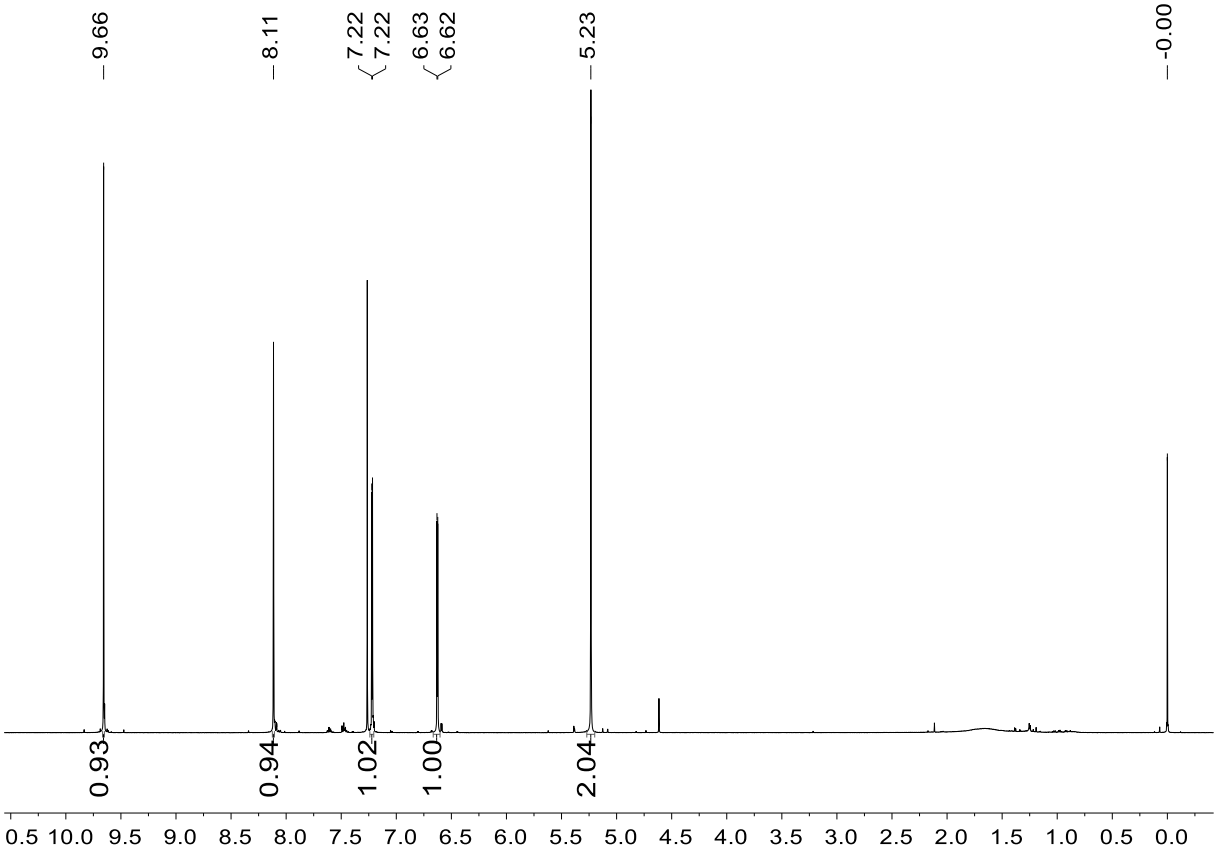
2.3.2.9. Synthesis of (5-Formylfuran-2-yl)methyl Formate (2w)



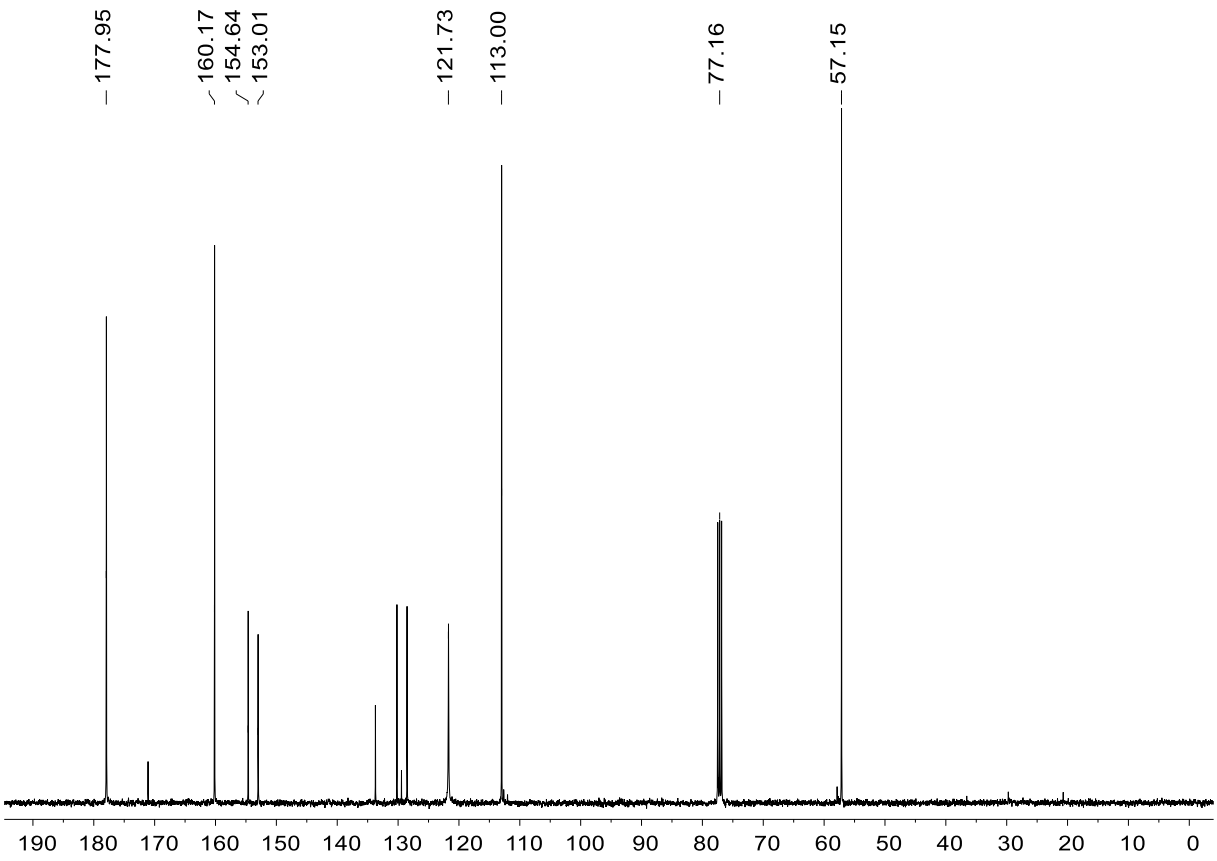
2w

DTT-316: According to the general protocol A (chapter 2.2.1, page 8), to a mixture of (5-formylfuran-2-yl) methanol (126.1 mg, 1.00 mmol, 1.00 equiv), FPyr (190.6 µL, 198.3 mg, 2.00 mmol, 2.00 equiv) and $NaPF_6$ (284.8 mg, 1.70 mmol, 1.70 equiv) in dry MeCN (0.5 mL, 2.0 M) BzCl (197.5 µL, 239.0 mg, 1.70 mmol, 1.70 equiv) was added dropwise by syringe pump within 15 min, and the resulting mixture was stirred at ambient temperature for 3 h. After work up with $NaHCO_3$ solution (2.0 mL, 2.2 equiv, 1.1 M), ^{1}H NMR of the crude material (598.2 mg, 415%) verified full conversion of alcohol **1w**. Finally, purification by means of column chromatography on silica gel (4.2 g, ratio weight crude product/SiO_2 1:7) with MTBE/*n*-heptane 30:70 as solvent mixture and drying at the rotary evaporator at 50 mbar for 5 min delivered formate **2w** as a colourless oil (128.8 mg, 0.84 mmol, 84%).

M ($C_7H_6O_4$) = 154.12 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 30:70) = 0.30; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 9.66 (s, 1H, 7-H), 8.11 (t, $^4J_{7,6}$ = 0.9 Hz, 1H, 1-H), 7.22 (d, $^3J_{3,4}$ = 3.5 Hz, 1H, 5-H), 6.63 (d, $^3J_{4,3}$ = 3.5 Hz, 1H, 4-H), 5.23 (s, 2H, 2-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 177.94 (C-7), 160.16 (C-1), 154.64 (C-5), 153.01 (C-4), 121.72 (C-6), 112.99 (C-5), 57.14 (C-2) The NMR data is in agreement with the literature. [10]

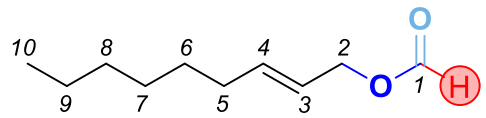


^{1}H NMR spectrum of (5-formylfuran-2-yl)methyl formate (**2w**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of (5-formylfuran-2-yl)methyl formate (**2w**, 126 MHz, $CDCl_3$).

2.3.2.10. Synthesis of *trans*-2-Nonen-1-yl Formate (2x)

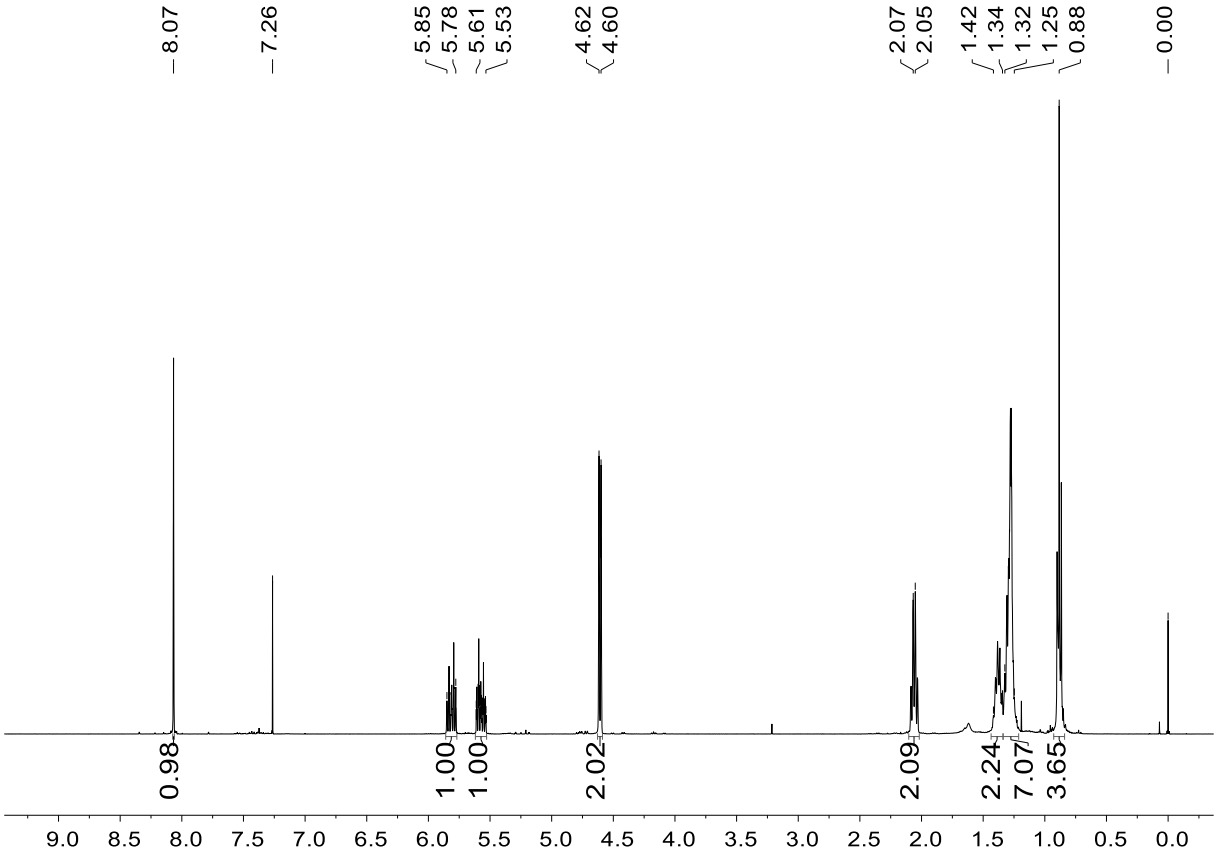


2x

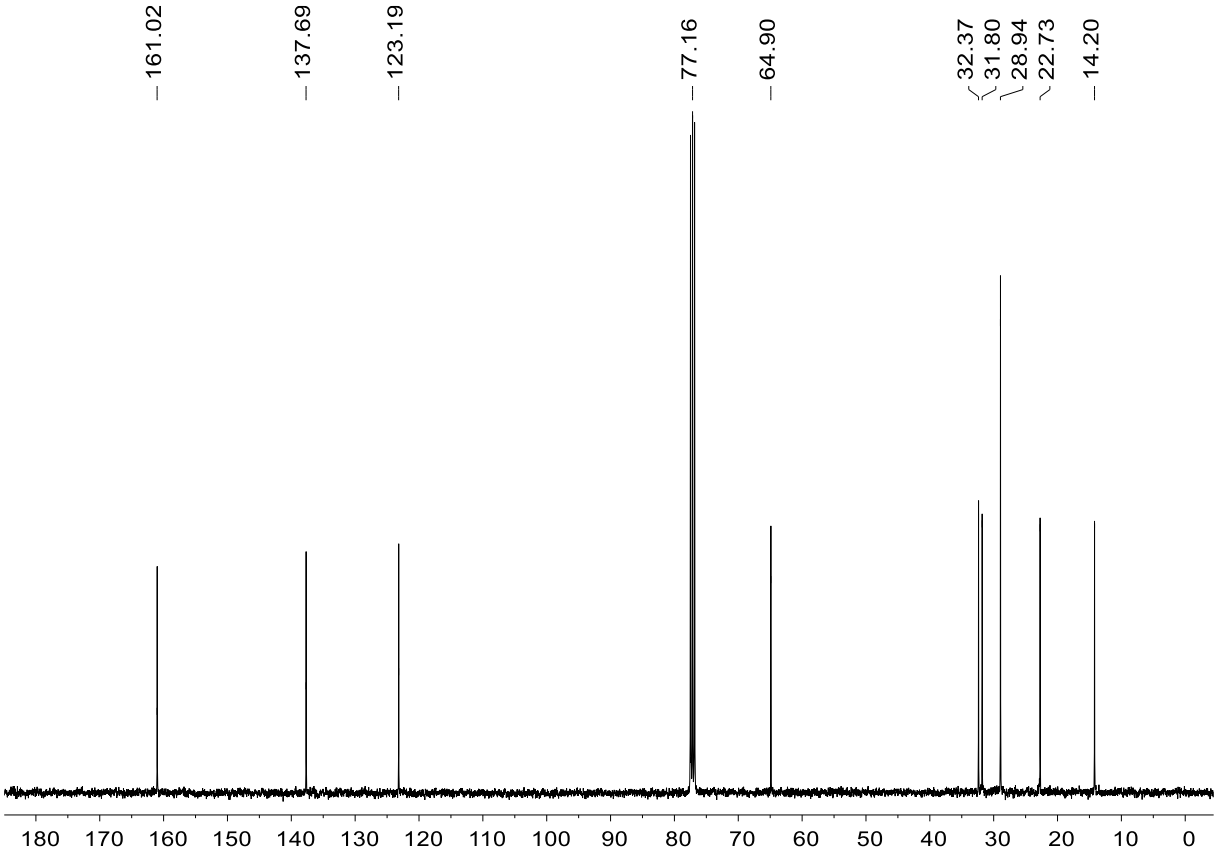
DTT-326: As described in general protocol A (chapter 2.2.1, page 8), *trans*-2-nonen-1-ol (71.0 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) were combined and stirred for 3 h. Subsequent quenching with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^{1}H NMR of the crude material (100.0 mg, 109%) proved full conversion of alcohol **1x**. After all, purification with the aid of column chromatography on silica gel (3.0 g, ratio weight crude product/SiO_2 1:30) using MTBE/*n*-heptane 1:99 as solvent mixture and drying at the rotary evaporator at 50 mbar for 5 min enabled the isolation of formate **2x** as a colourless oil (65.8 mg, 0.39 mmol, 77%).

M ($C_{10}H_{18}O_2$) = 170.25 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 1:99) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.07 (s, 1H, 1-H), 5.82 (dtt, $^3J_{3,4}$ = 14.8 Hz, $^3J_{3,2}$ = 6.7 Hz, $^4J_{3,5}$ = 1.2, 1H, 4-H), 5.57 (ddt, $^3J_{4,3}$ = 15.0 Hz, $^3J_{4,5}$ = 6.6 Hz, $^4J_{4,2}$ = 1.5 Hz, 1H, 3-H), 4.62-4.60 (m, 2H, 2-H), 2.09-2.03 (m, 2H, 5-H), 1.42-1.34 (m, 2H, 6-H), 1.32-1.25 (m, 6H, 7-H, 8-H, 9-H), 0.90-0.87 (m, 3H, 10-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 160.88 (C-1), 137.55 (C-4), 123.04 (C-3), 64.76 (C-2), 32.24 (C-5), 31.67 (C-6), 28.80 (C-7), 28.79 (C-8), 22.59 (C-9), 14.07 (C-10); **GC MS** (EI, 70 eV) m/z [u] (%) = 124 (45, $[M\text{-}OCHO\text{-}H]^+$), 109 (8, $[octyl]^+$, 95 (50, $[heptyl]^+$), 83 (26, $[hexenyl]^+$), 82 (50, $[hexadiene]^+$), 81 (50, $[hexadienyl]^+$), 69 (43, $[pentenyl]^+$), 68 (50, $[pentadiene]^+$), 67 (73, $[pentadienyl]^+$), 57 (47, $[butyl]^+$), 56 (29, $[butene]^+$), 55 (79, $[butenyl]^+$), 54 (100, $[butadiene]^+$).

The NMR data is in match with the literature. [11]

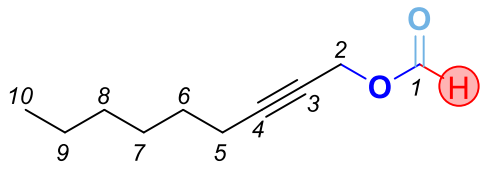


^{1}H NMR spectrum of *E*-2-nonen-1-yl formate (**2x**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of *E*-2-nonen-1-yl formate (**2x**, 101 MHz, $CDCl_3$).

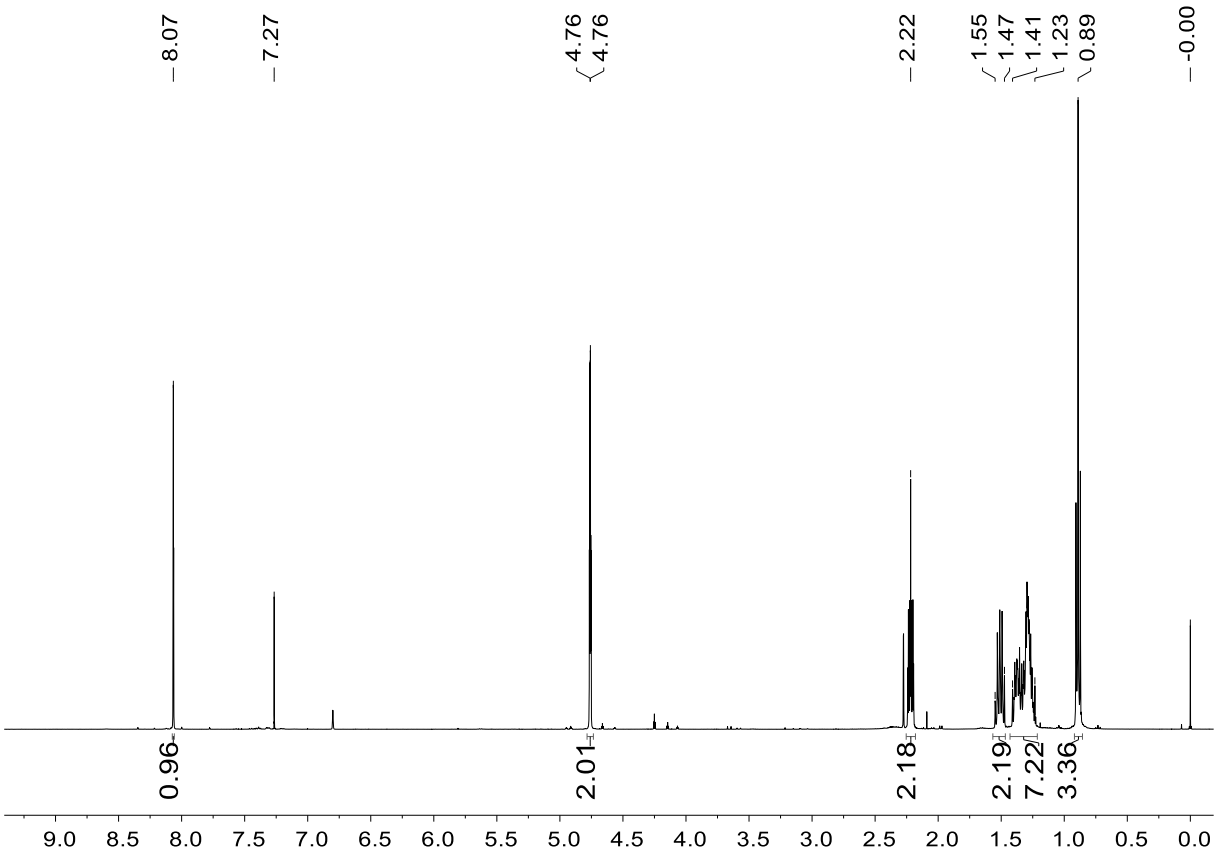
2.3.2.11. Synthesis of 2-Nonyn-1-yl Formate (2y)



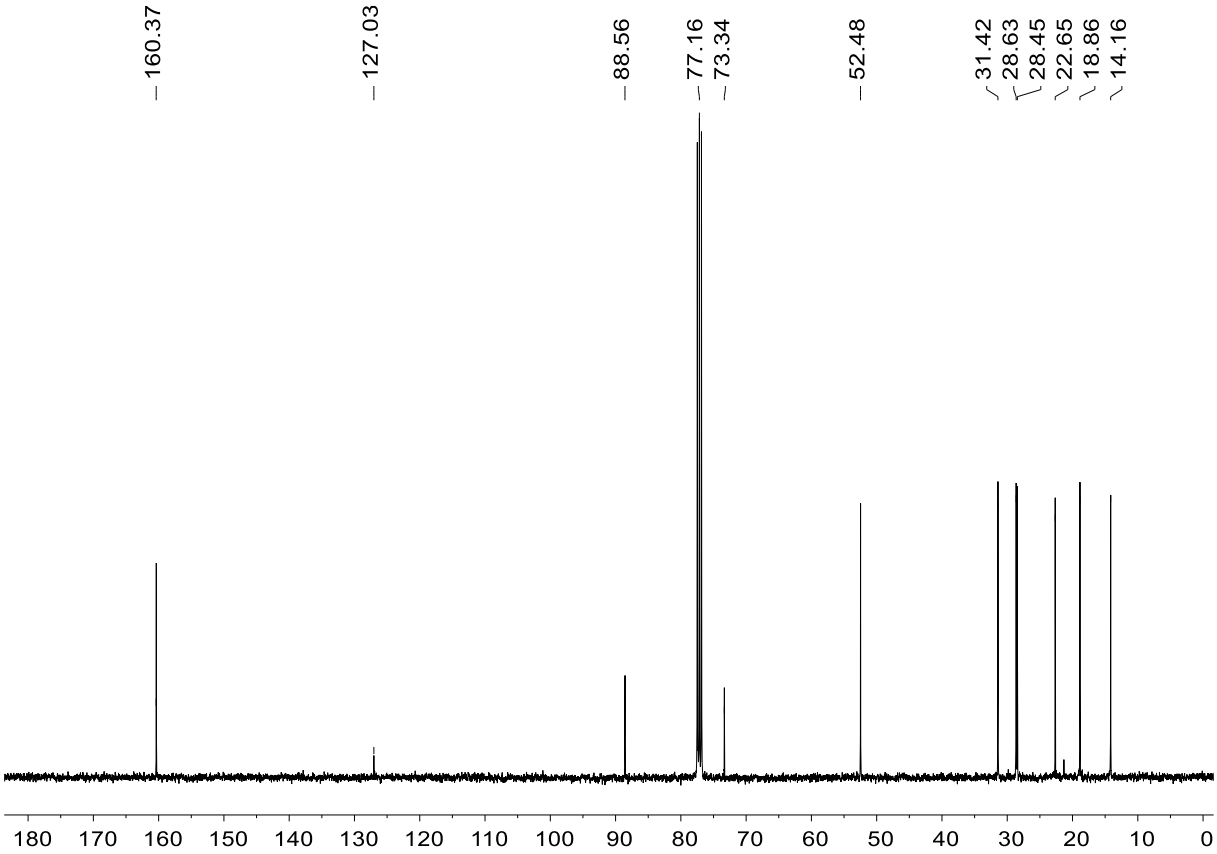
2y

DTT-325: In accordance to the general protocol 2.2.1.2 (chapter 2.2.1, page 8), the title compound was synthesized from 2-nonyn-1-ol (70.0 mg, 0.50 mmol, 1.00 equiv), FPyr (95.3 µL, 99.1 mg, 1.00 mmol, 2.00 equiv), $NaPF_6$ (142.0 mg, 0.85 mmol, 1.70 equiv) and BzCl (98.7 µL, 119.5 mg, 0.85 mmol, 1.70 equiv) in dry MeCN (0.25 mL, 2.0 M). After 3 h of stirring and work up with $NaHCO_3$ solution (2.0 mL, 4.40 equiv, 1.1 M), ^{1}H NMR of the crude material (93.0 mg, 102%) verified 93% conversion of alcohol **1y**. Finally, purification with the aid of column chromatography on silica gel (2.7 g, ratio weight crude product/SiO_2 1:30) using MTBE/*n*-heptane 1:99 as eluent system and drying at 20 mbar for 5 minutes at the rotary evaporator allowed for the isolation of formate **2y** as a colourless oil (79.0 mg, 0.47 mmol, 94%).

M ($C_{10}H_{16}O_2$) = 168.24 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 1:99) = 0.23; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.06 (t, $^4J_{1,2}$ = 1.0 Hz, 1H, 1-H), 4.75 (td, $^5J_{2,5}$ = 2.3 Hz, $^4J_{1,2}$ = 1.0 Hz, 2H, 2-H), 2.21 (tt, $^3J_{5,6}$ = 7.1 Hz, $^5J_{5,2}$ = 2.2 Hz, 2H, 5-H), 1.55-1.47 (m, 2H, 6-H), 1.41-1.23 (m, 6H, 7-H, 8-H, 9-H), 0.88 (t, $^3J_{10,9}$ = 7.0 Hz, 3H, 10-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 160.37 (C-1), 88.43 (C-3), 73.20 (C-4), 52.34 (C-2), 31.29 (C-5), 28.50 (C-6), 28.31 (C-7), 22.52 (C-8), 18.72 (C-9), 14.03 (C-10); **GC MS** (EI, 70 eV) m/z [u] (%) = 109 (36, [octynyl]$^+$, 95 (20, [heptadienyl]$^+$), 93 (64, [heptatrienyl]$^+$), 83 (52, [hexenyl]$^+$), 81 (48, [hexadienyl]$^+$), 79 (56), 70 (68, [pentene]$^+$), 69 (54, [pentenyl]$^+$), 68 (32, [pentadiene]$^+$), 67 (100, [pentadienyl]$^+$), 55 (96, [butenyl]$^+$).

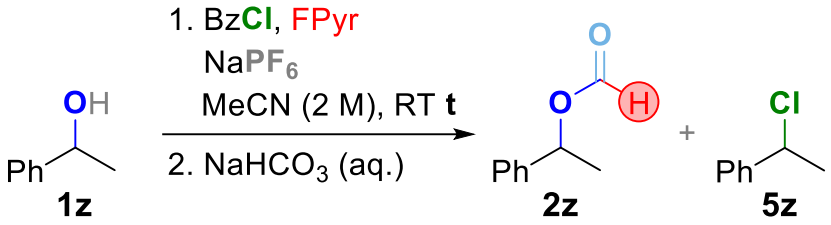


^{1}H NMR spectrum of 2-nonyn-1-yl formate (**2y**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-nonyn-1-yl formate (**2y**, 100 MHz, $CDCl_3$).

2.3.2.12. Synthesis of *rac*-1-Phenylethyl Formate (2z)



Entry	BzCl	FPyr (equiv)	$NaPF_6$	t (h)	Conv.	Yield 2z (%)	Yield 5z
1[a]	1.2	1.3	/	2	85	20	66
2[a]	1.2	1.3	1.3	2	82	48	37
3[a]	1.3	1.5	1.7	5.5	≥98	34	46
4	1.7	2.0	1.7	1	≥98	84[a] (72)[b]	8[a]

The title compound was prepared according to procedure A (chapter 2.2.1, page 8). a. The yield was determined by mesitylene as internal standard, b. Isolated yield.

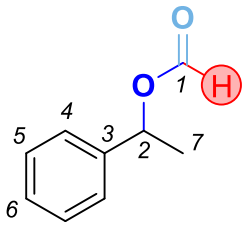
The reaction of substrate 1-phenylethanol in the absence of $NaPF_6$ delivered chloride **5z** as the predominant product with a yield of 66%, while formate **5r** was observed only as side-product in 20% yield (entry 1). The yield of **2z** could be increased to 48% by addition of $NaPF_6$ to the reaction mixture (entry 2). An elongation of the reaction time to 5.5 h effected pronounced formation of the unwanted chloride product **5z** in 46% yield. When the amount of the reagents BzCl and FPyr was increased to 1.70 and 2.00 equiv, respectively, and the reaction time was reduced to 1 h, full conversion was achieved and **2z** was generated in 84% yield (entry 4).

Entry 1, DTT-274: Following general protocol A (chapter 2.2.1, page 8), a mixture of 1-phenylethanol (60.5 µL, 61.1 mg, 0.50 mmol, 1.00 equiv), FPyr (62.0 µL, 64.4 mg, 0.65 mmol, 1.30 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (69.7 µL, 84.3 mg, 0.60 mmol, 1.3 equiv) were stirred with 400 rpm at rt for 2 h. After work up with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^{1}H NMR of the crude material (75 mg, 100%) with mesitylene as internal standard uncovered 85% consumption of the starting alcohol, and chloride **5z** as main product in 66% alongside formate **2z** in 20% yield.

Entry 2, DTT-273: As described in general protocol A (chapter 2.2.1, page 8), a mixture of 1-phenylethanol (60.5 µL, 61.1 mg, 0.50 mmol, 1.00 equiv), FPyr (62.0 µL, 64.4 mg, 0.65 mmol, 1.30 equiv), $NaPF_6$ (108.9 mg, 0.65 mmol, 1.30 equiv), dry MeCN (0.25 mL, 2.0 M) and BzCl (69.7 µL, 84.3 mg, 0.60 mmol, 1.30 equiv) was stirred for 2 h. Past work up with $NaHCO_3$ solution (2.0 mL, 4.4 equiv, 1.1 M), ^{1}H NMR of the crude material (69.6 mg, 94%) with mesitylene as internal standard proved 82% conversion and formate **2z** in 48% and chloride **5z** in 37% yield.

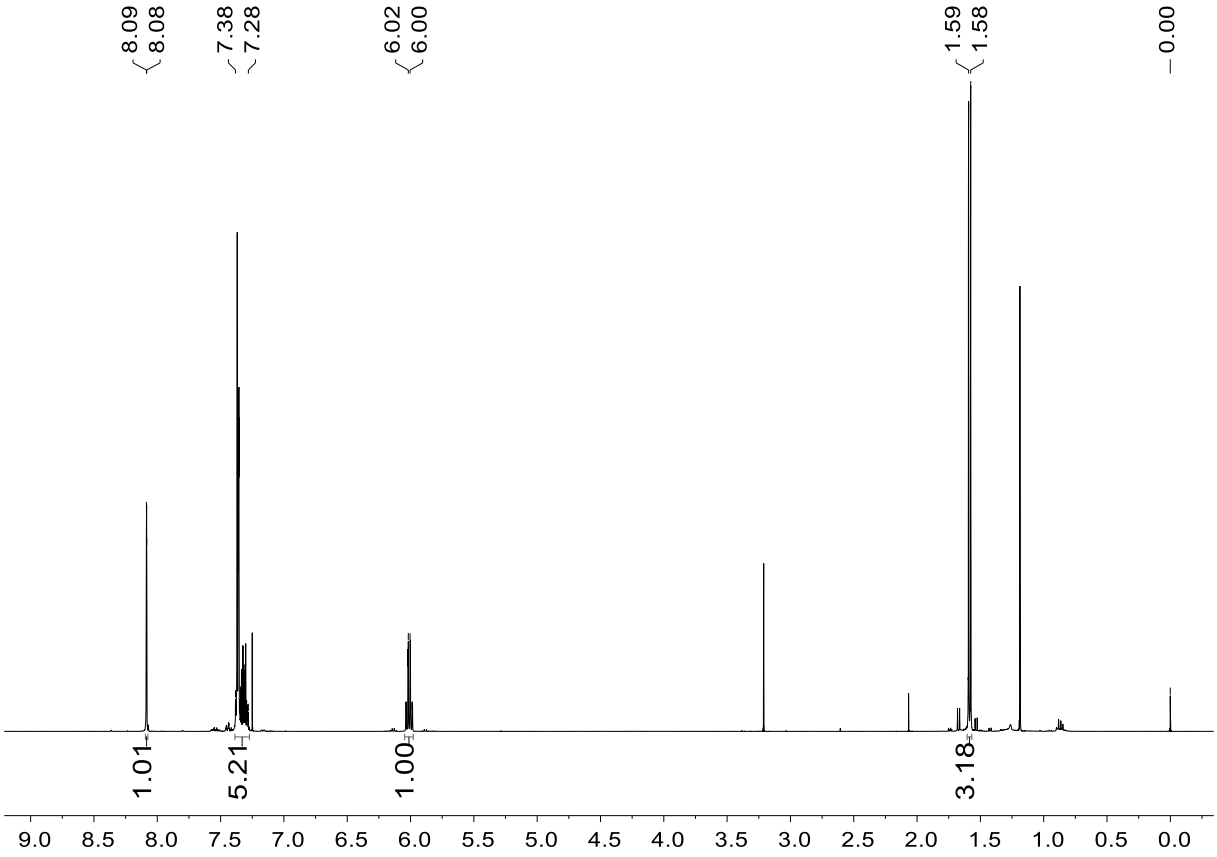
Entry 3, DTT-293: As delineated in general protocol A (chapter 2.2.1, page 8), the title compound was obtained from 1-phenylethanol (121.0 µL, 122.2 mg, 1.00 mmol, 1.00 equiv), FPyr (143.0 µL, 148.7 mg,1.50 mmol, 1.50 equiv) and BzCl (151.0 µL, 182.7 mg, 1.30 mmol, 1.30 equiv) in the presence of $NaPF_6$ (268.1 mg, 1.60 mmol, 1.60 equiv) in dry MeCN (0.5 mL, 2.0 M). After a reaction duration of 5.5 h and aqueous work up using $NaHCO_3$ solution (2.0 mL, 1.1 M, 2.2 equiv), ^{1}H NMR of the crude material (205.0 mg, 137%) using mesitylene as internal standard reveled full conversion of alcohol **1z** and formate **2z** in 34% yield besides chloride **5z** in 46% yield**.**

Entry 4, DTT-352: Based on the general protocol A (chapter 2.2.1, page 8), the title compound was synthesized from 1-phenylethanol (246.9 µL, 244.4 mg, 2.00 mmol, 1.00 equiv), FPyr (424.1 µL, 337.0 mg, 3.40 mmol, 1.70 equiv) and BzCl (348.5 µL, 421.7 mg, 3.00 mmol, 1.50 equiv) using $NaPF_6$ (502.7 mg, 3.00 mmol, 1.50 equiv) in dry MeCN (1.0 mL, 2.0 M). After 1 h stirring at rt and work up with $NaHCO_3$ solution (2.0 mL, 1.1 M, 1.1 equiv), ^{1}H NMR of the crude material (410.0 mg, 137%) with mesitylene as internal standard confirmed full conversion of alcohol **1z** and ester **2z** in 84% and chloride **5z** in 6% yield. Finally, column chromatographic purification with SiO_2 (4.2 g, ratio mass crude/SiO_2 1:10) with MTBE/*n*-pentane 1:99 provided the product **2z** in 72% yield as colourless oil (216.0 mg, 1.44 mmol) after drying at the rotary evaporator for 5 min at 20 mbar.

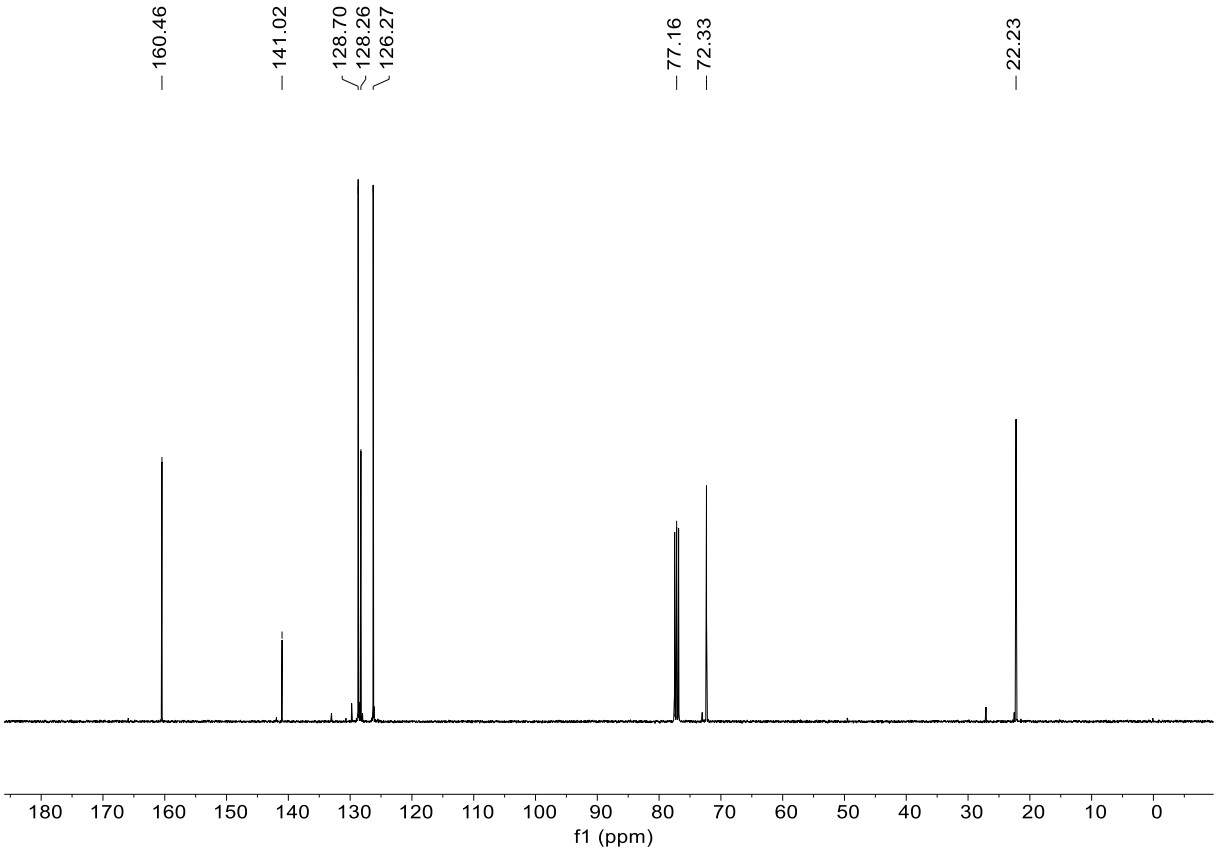


M ($C_9H_{10}O_2$) = 150.18 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-pentane 1:99) = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.09-8.08 (m, 1H, 1-H), 7.38-7.28 (m, 5H, 4-H, 5-H, 6-H), 6.01 (qd, $^3J_{2,7}$ = 6.6 Hz, $^4J_{2,1}$ = 1.0 Hz, 1H, 2-H), 1.58 (d, $^3J_{7,2}$ = 6.6 Hz, 3H, 7-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 160.46 (C-1), 141.02 (C-3), 128.70 (C-4), 128.26 (C-6), 126.27 (C-5), 72.33 (C-1), 22.23 (C-7); **GC MS** (EI, 70 eV) m/z [u] (%) = 150 (38, $[M]^+$), 121 (11, $[PhC(OH)CH_3]^+$) 105 (72, $PhCHCH_3]^+$), 104 (100, [styrene]$^+$), 91 (4, $[Bn]^+$), 79 (39, $[PhH_2]^+$), 78 (25, $[PhH]^+$), 77 (41, $[Ph]^+$).

The NMR data is in agreement with the literature.[1]



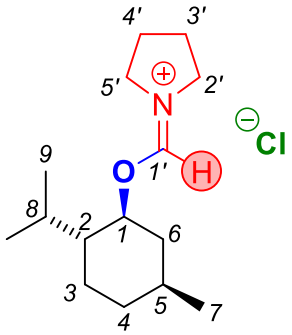
^{1}H NMR spectrum of 1-phenylethyl formate (**2z**, 400 MHz, $CDCl_3$).



^{13}C NMR spectrum of 1-phenylethyl formate (**2z**, 101 MHz, $CDCl_3$).

2.3.3. Synthesis of Imidate Salts of Type 7

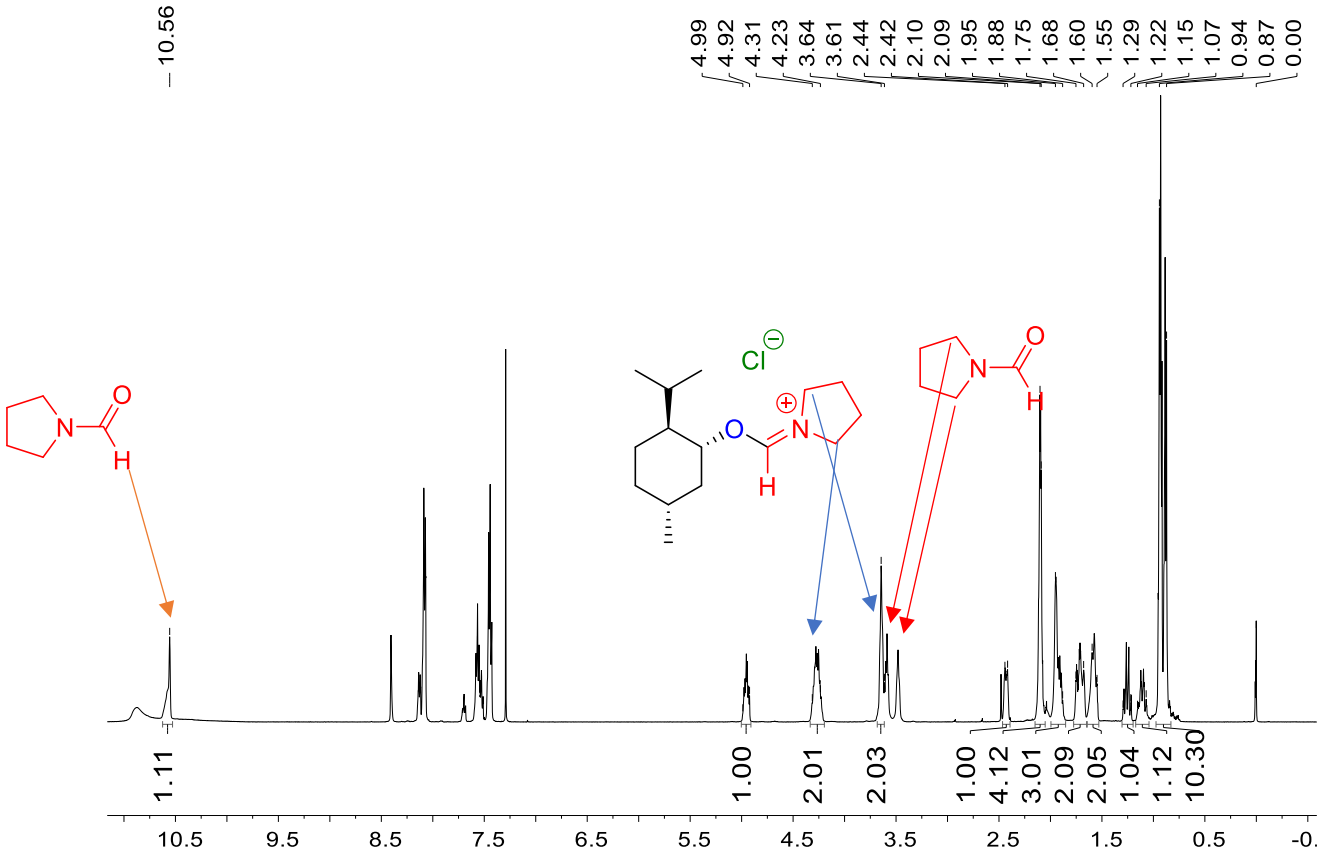
2.3.3.1. Synthesis of (1*S*,2*R*,5*S*)-((Menthyloxy)methylidene) Pyrrolidinium Chloride (7k)



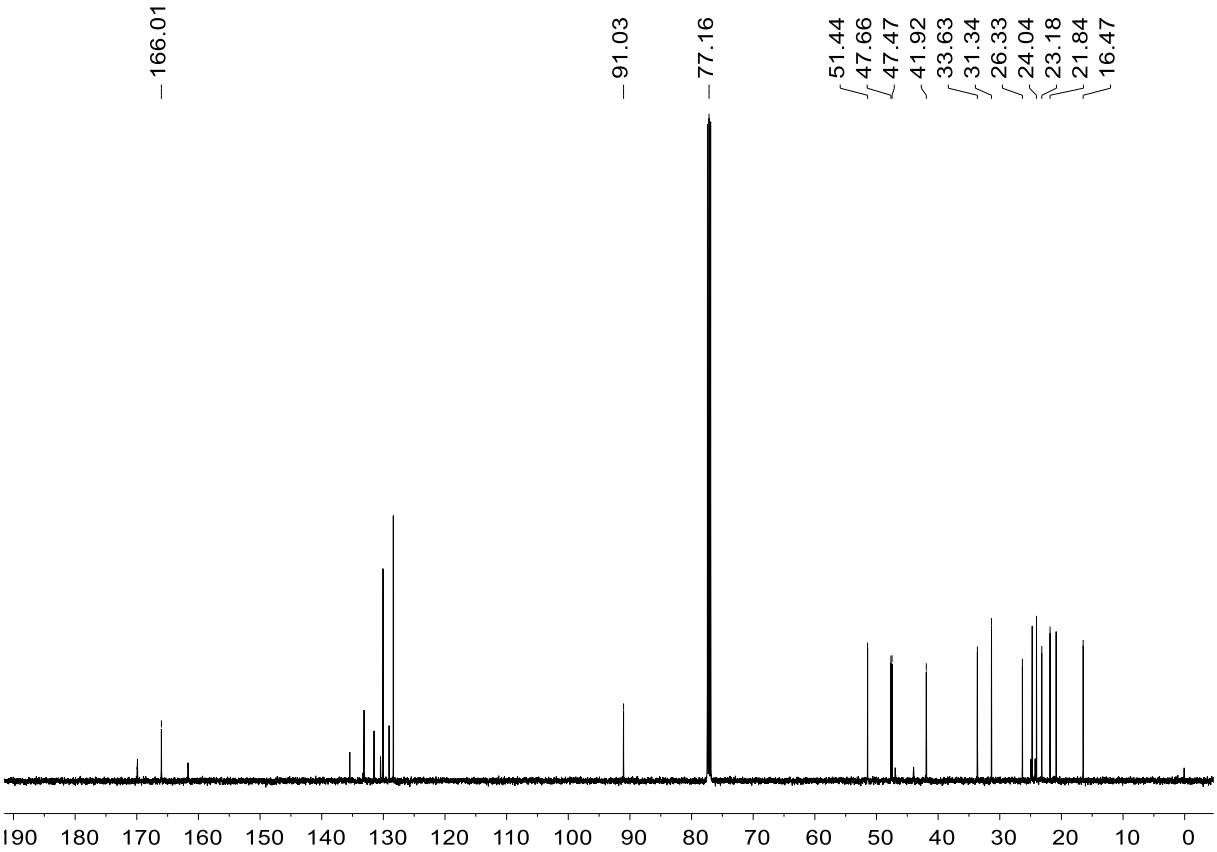
7k

DTT-431: In accordance with general protocol B (chapter 2.2.2, page 10), the title compound was prepared form (1S,2R,5S)-(+)-menthol (156.3 mg, 1.00 mmol, 1.0 equiv), FPyr (143.0 µL, 148.7 mg, 1.50 mmol, 1.5 equiv) and BzCl (151.0 µL, 182,7 mg, 1.3 mmol, 1.3 equiv) in $CDCl_3$ (0.5 mL, 2.0 M). A sample, which had been withdrawn after 80 min of reaction duration, showed full conversion of alcohol **1k** and the salt **7k** in ≥98% yield according to the ^{1}H NMR spectrum as determined by the relation of the multiplets of 1-H. After 7 days, only 10% decomposition of **7k** was observed in the ^{1}H NMR.

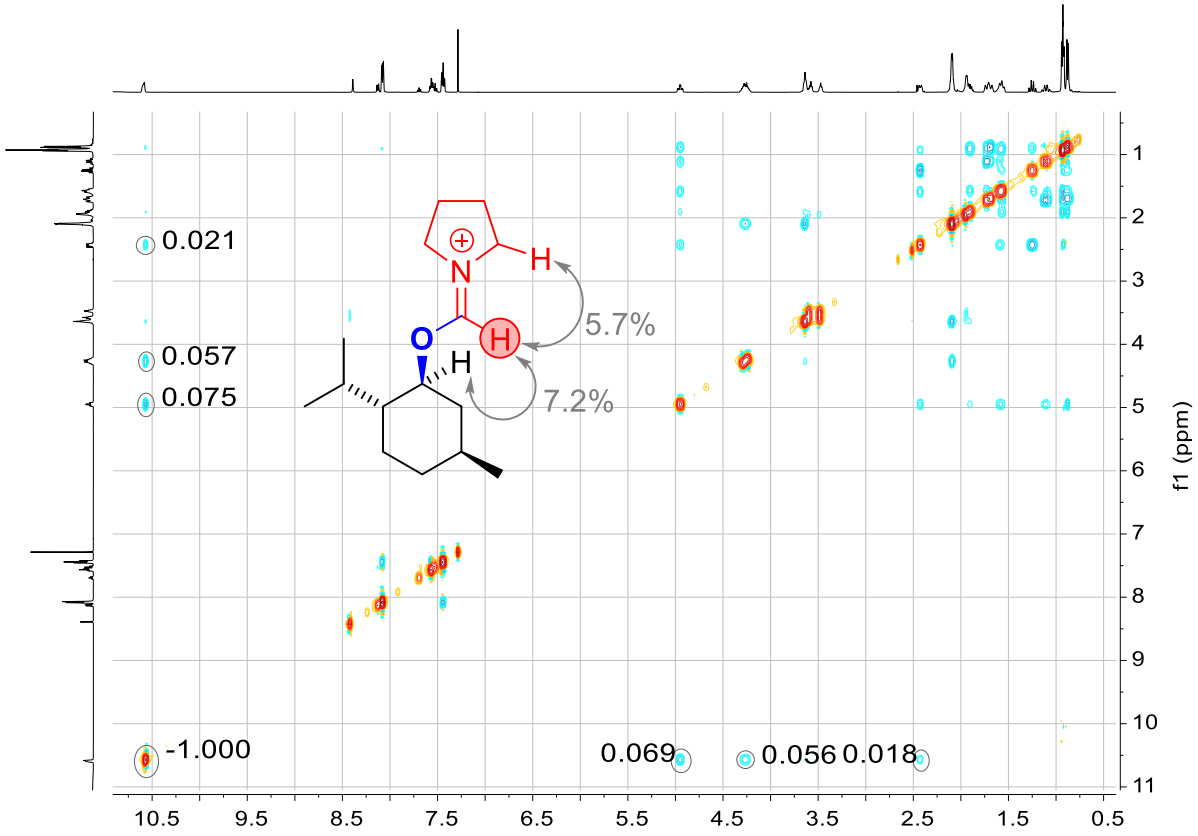
M ($C_{15}H_{28}ClNO$) = 273.85 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 10.56 (s, 1H, 1´-H), 4.99-4.92 (m, 1H, 1-H), 4.31-4.23 (m, 2H, 2'-H), 3.64-3.61 (m, 2H, 5'-H), 2.44-2.42 (m, 1H, 6-H_a), 2.10-2.09 (m, 4H, 3'-H, 4'-H), 1.95-1.88 (m, 1H, 5-H), 1.75-1.68 (m, 2H, 3-H_a, 4-H_a),1.60-1.55 (m, 2H, 2-H, 8-H), 1.29-1.22 (m 1H, 6-H_b), 1.15-1.07 (m, 1H, 3-H_b), 0.94-0.87 (m, 10H, 4-H_b, 7-H, 9-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 166.01 (C-1'), 91.03 (C-1), 51.44 (C-2'), 47.66 (C-5'), 47.47 (C-8), 41.92 (C-6), 33.63 (C-3), 31.34 (C-2), 26.33 (C-5), 24.04 (C-3'), 23.18 (C-4'), 21.84 (C-9), 16.45 (C-7).



^{1}H NMR spectrum of (1*S*,2*R*,5*S*)-((menthyloxy)methylidene) dimethyliminium chloride (**7k**, 500 MHz, $CDCl_3$)

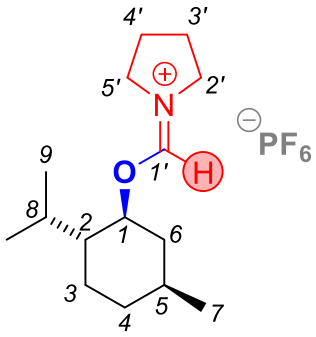


^{13}C NMR spectrum of (1*S*,2*R*,5*S*)-((menthyloxy)methylidene) pyrrolidinium chloride (**7k**, 126 MHz, $CDCl_3$).



NOESY spectrum of (1*S*,2*R*,5*S*)-((menthyloxy)methylidene) pyrrolidinium chloride (**7k**, 500 MHz, $CDCl_3$).

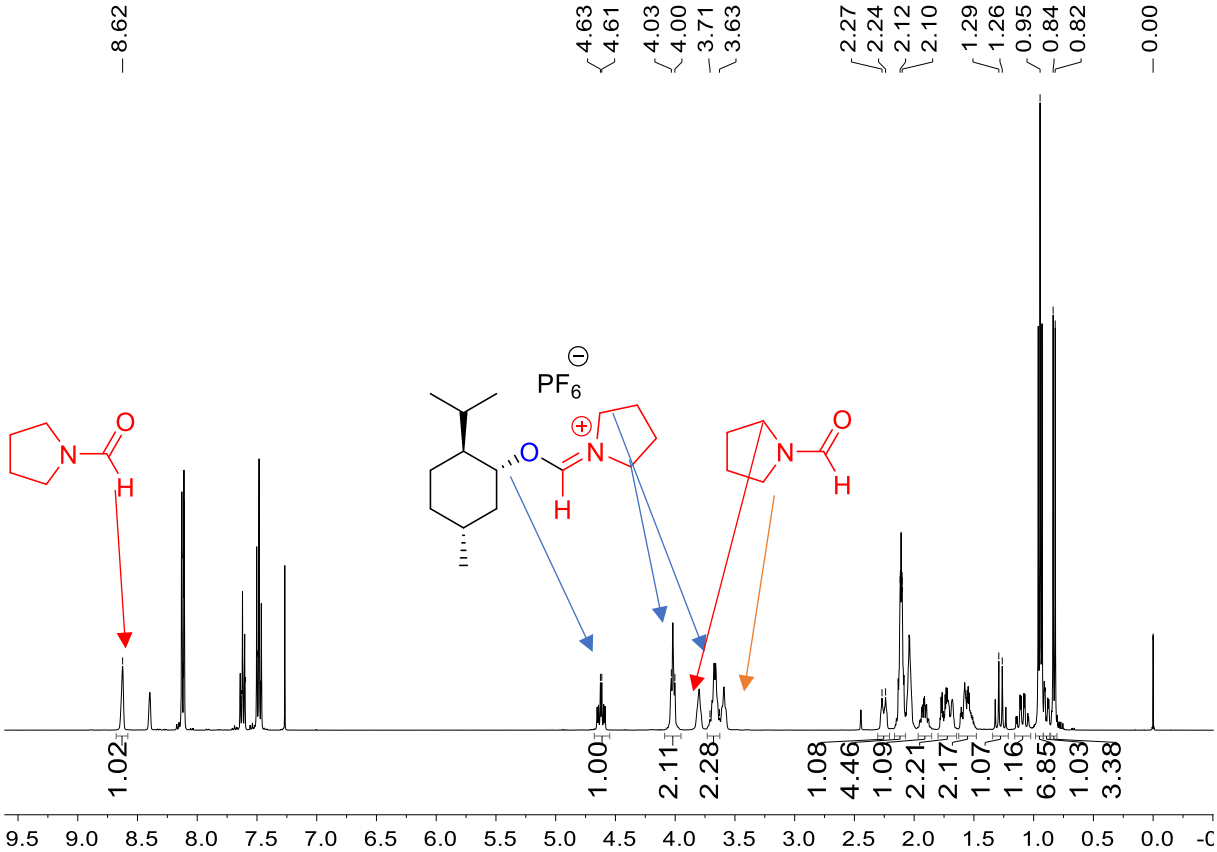
2.3.3.2. Synthesis of (1*S*,2*R*,5*S*)-((Menthyloxy)methylidene) Pyrrolidinium Hexafluorophosphate (7k')



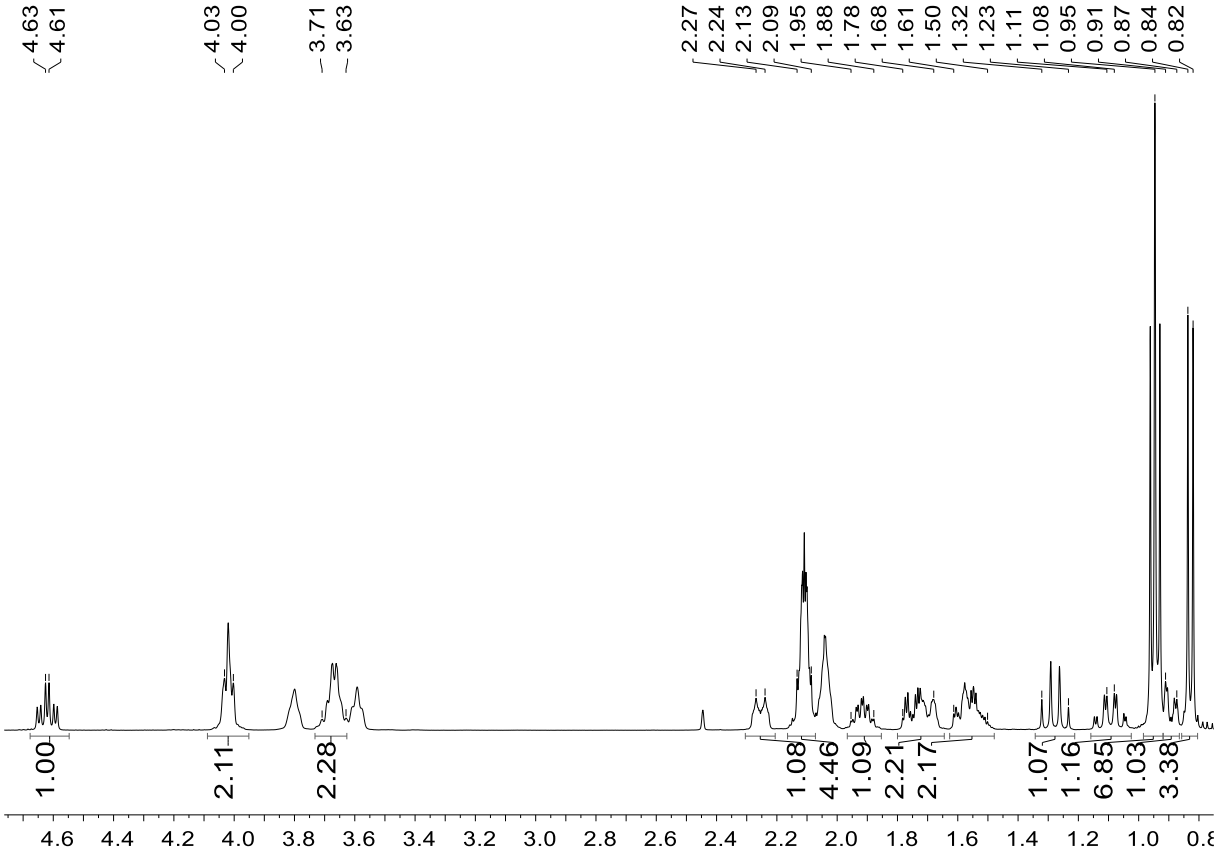
7k´7k'

DTT-431b: In accordance with general protocol C (chapter 2.2.3, page 10), the title compound was prepared from menthol (156.3 mg, 1.00 mmol, 1.00 equiv), FPyr (143.0 µL, 148.7 mg, 1.50 mmol, 1.50 equiv), $NaPF_6$ (284.8 mg, 1.70 mmol, 1.70 equiv) and BzCl (151.0 µL, 182,7 mg, 1.30 mmol, 1.30 equiv) in MeCN (0.5 mL, 2.0 M). The ^{1}H NMR spectrum of a sample withdrawn after 60 min of reaction duration showed full conversion of alcohol **1k** and iminium cation **7k'** as exclusive product.

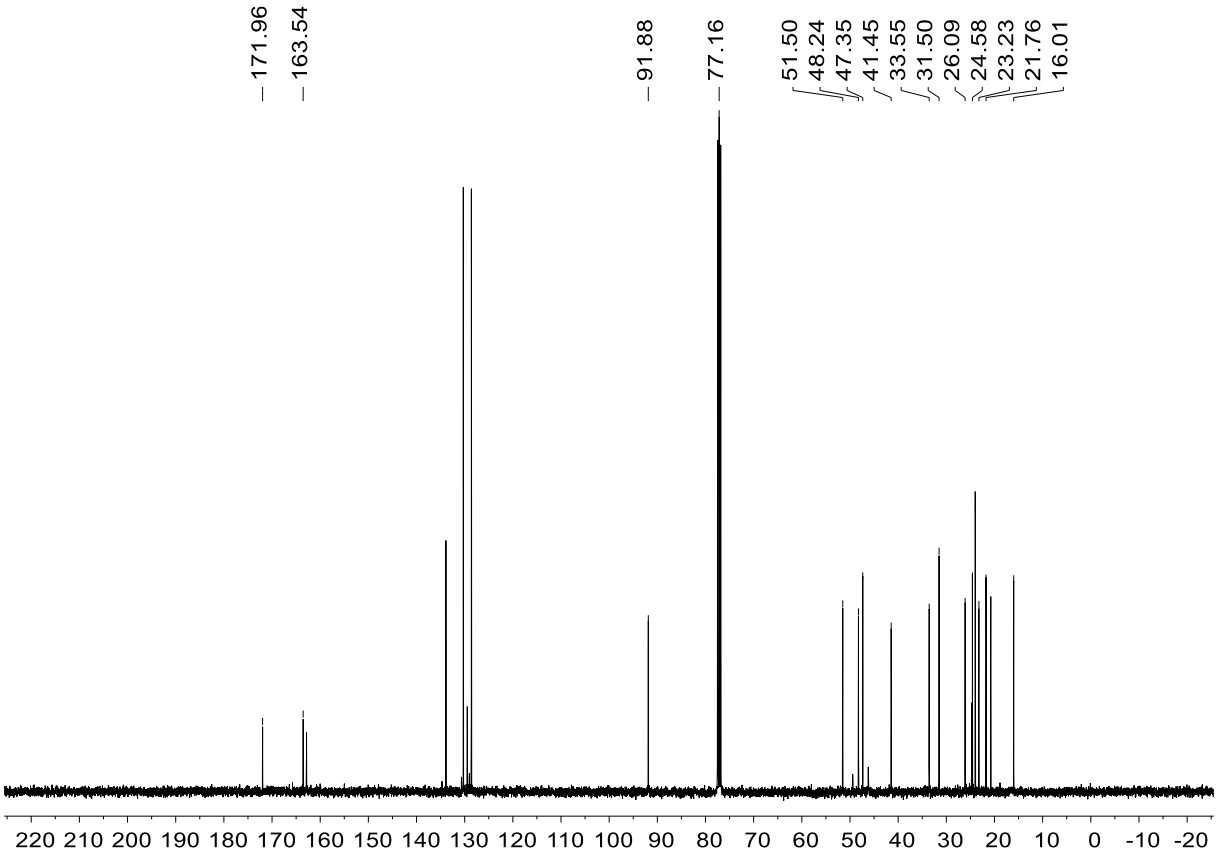
M ($C_{15}H_{28}F_6NOP$) = 383.36 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 8.62 (s, 1H, 1'-H), 4.62 (ψ-td, ^3J = 11.0 Hz, 4.7 Hz, 1H, 1-H), 4.03-4.00 (m, 2H, 2'-H), 3.71-3.63 (m, 2H, 5'-H), 2.27-2.24 (m, 1H, 6-H_a), 2.13–2.09 (m, 4H, 3'-H, 4'-H), 1.95-1.88 (m, 1H, 5-H), 1.78-1.68 (m, 2H, 4-H_a, 3-H_a), 1.61-1.50 (m, 2H, 2-H, 8-H), 1.28 (ψ-q, J = 11.9 Hz, 1H, 6-H_b), 1.10 (ψ-qd, J = 12.8 Hz, 3.4 Hz, 1H, 3-H_b), 0.95 (t, $^3J_{9,8}$ = 6.7 Hz, 6H, 9-H), 0.91-0.87 (m, 1H, 4-H_b), 0.83 (d, $^3J_{7,5}$ = 6.9 Hz, 3H, 7-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 163.54 (C-1'), 91.88 (C-1), 51.50 (C-2'), 48.24 (C-5'), 47.35 (C-8), 41.45 (C-6), 33.55 (C-3), 31.50 (C-2), 26.09 (C-5), 24.58 (C-3', C-4'), 23.23 (C-4), 21.76 (C-9), 16.01 (C-7); **^{31}P NMR** (162 MHz, $CDCl_3$) δ [ppm] = -143.71 (hept, $^1J_{P-F}$ = 711 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = 72.41 (d, $^1J_{P-F}$ = 712 Hz).



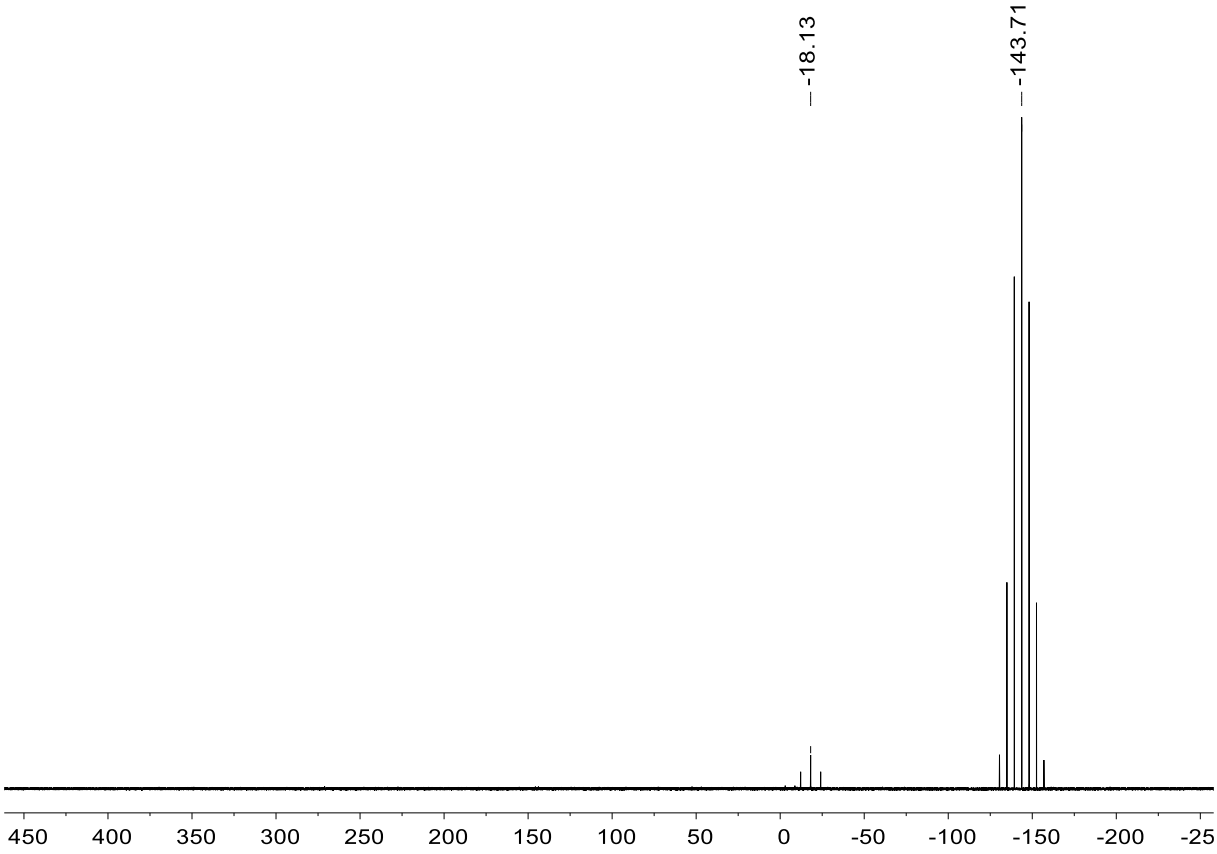
^{1}H NMR spectrum of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluoro-phosphate (**7k'**, 500 MHz, $CDCl_3$).



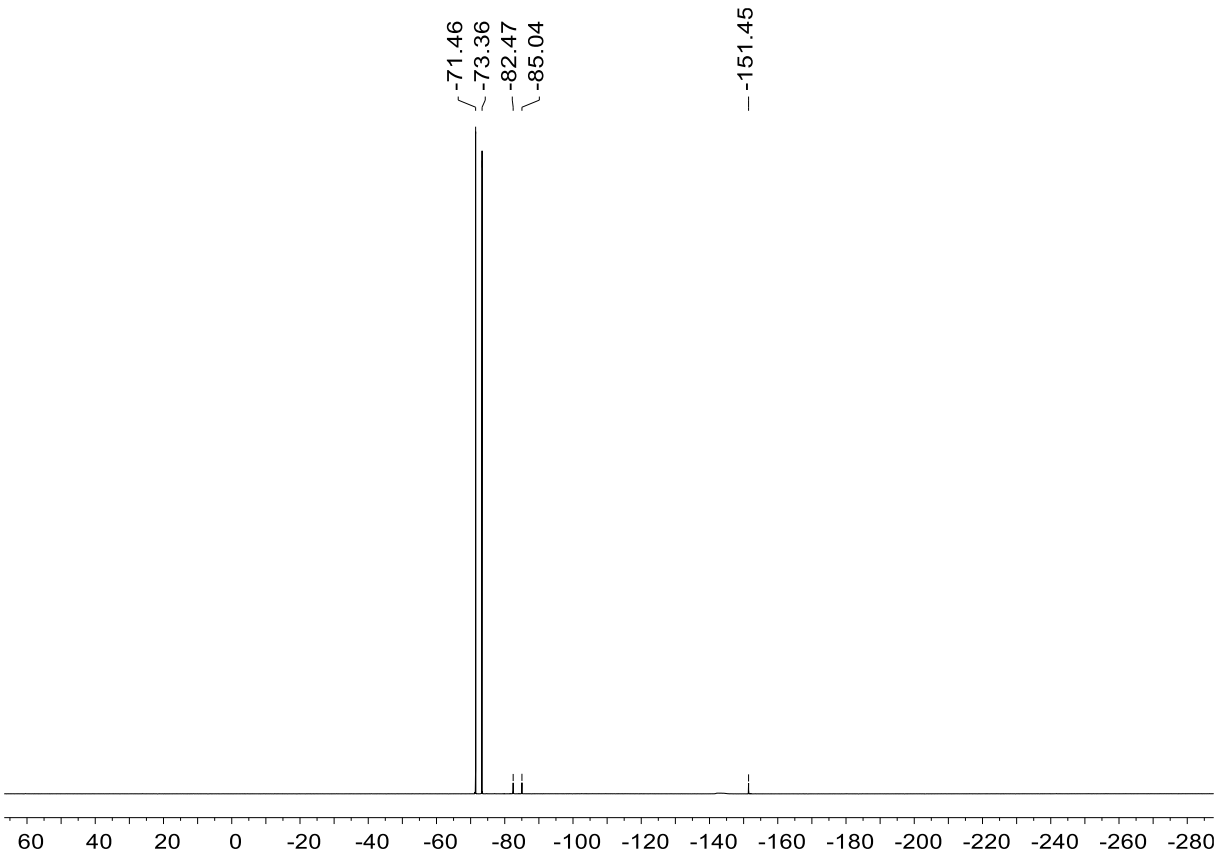
Excerpt of the ^{1}H NMR spectrum of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluoro-phosphate (**7k'**, 500 MHz, $CDCl_3$).



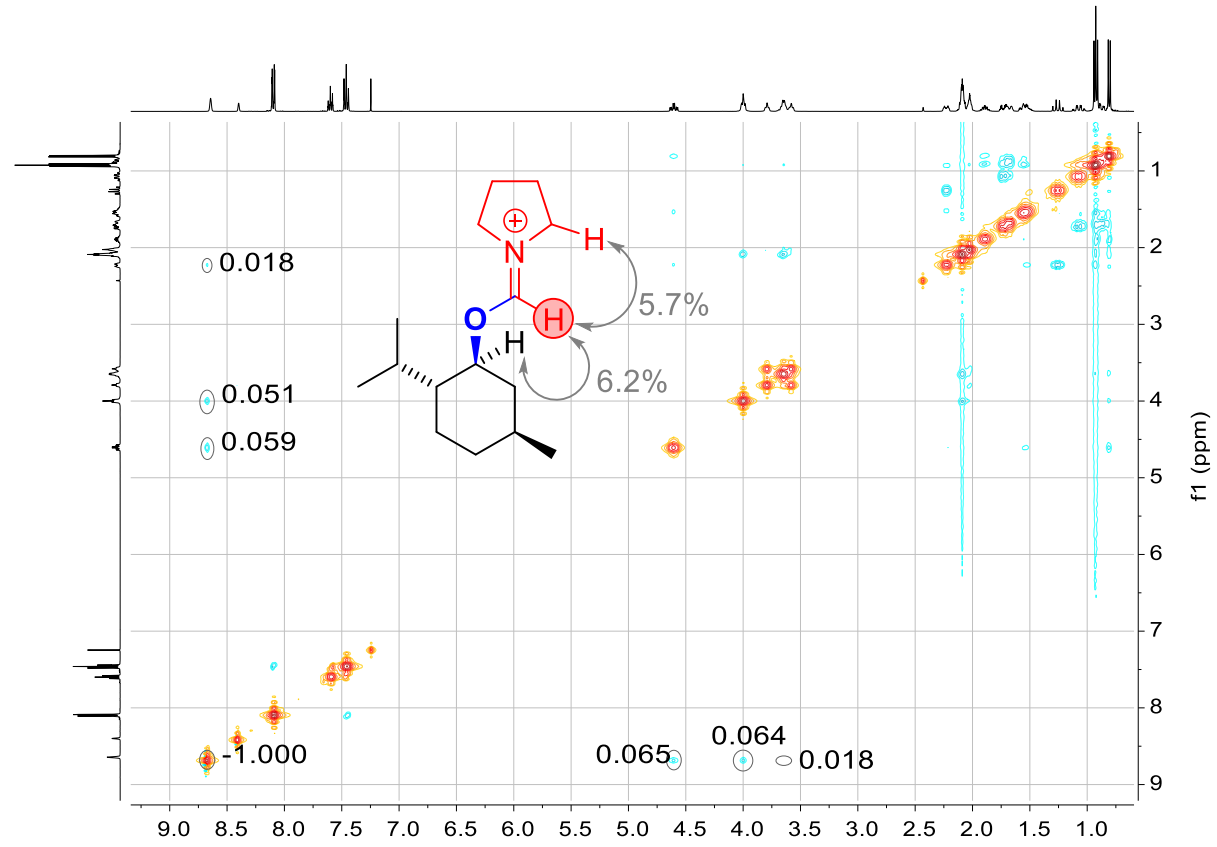
^{13}C NMR spectrum of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7k'**, 101 MHz, $CDCl_3$).



^{31}P NMR spectrum of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7k'**, 162 MHz, $CDCl_3$).

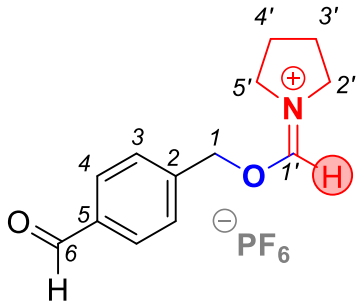


^{19}F NMR of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7k'**, 377 MHz, $CDCl_3$).



NOESY spectrum of (1S,2R,5S)-((menthyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7k'**, 500 MHz, $CDCl_3$).

2.3.3.3. Synthesis of ((4-Formylbenzyloxy)methylidene) Pyrrolidinium Hexafluorophosphate (7q´)

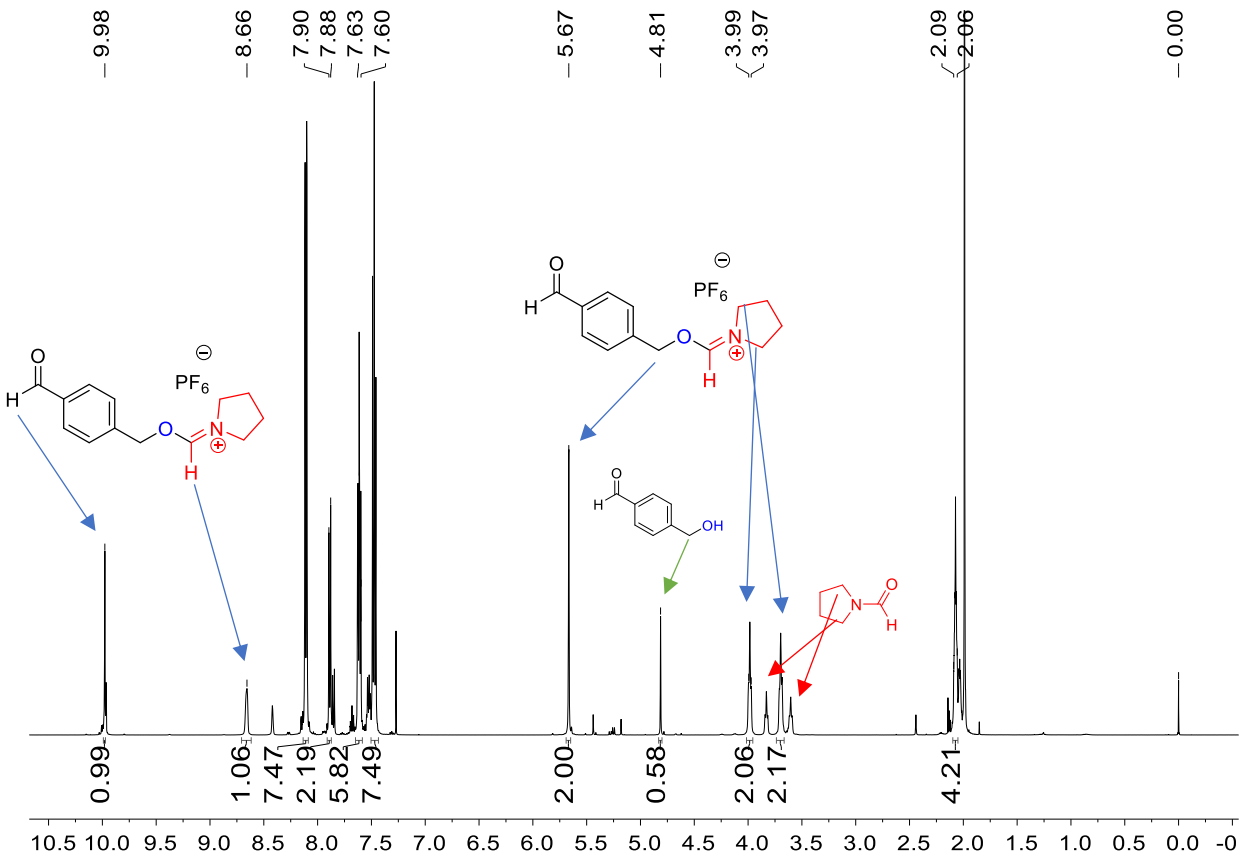


7q´q

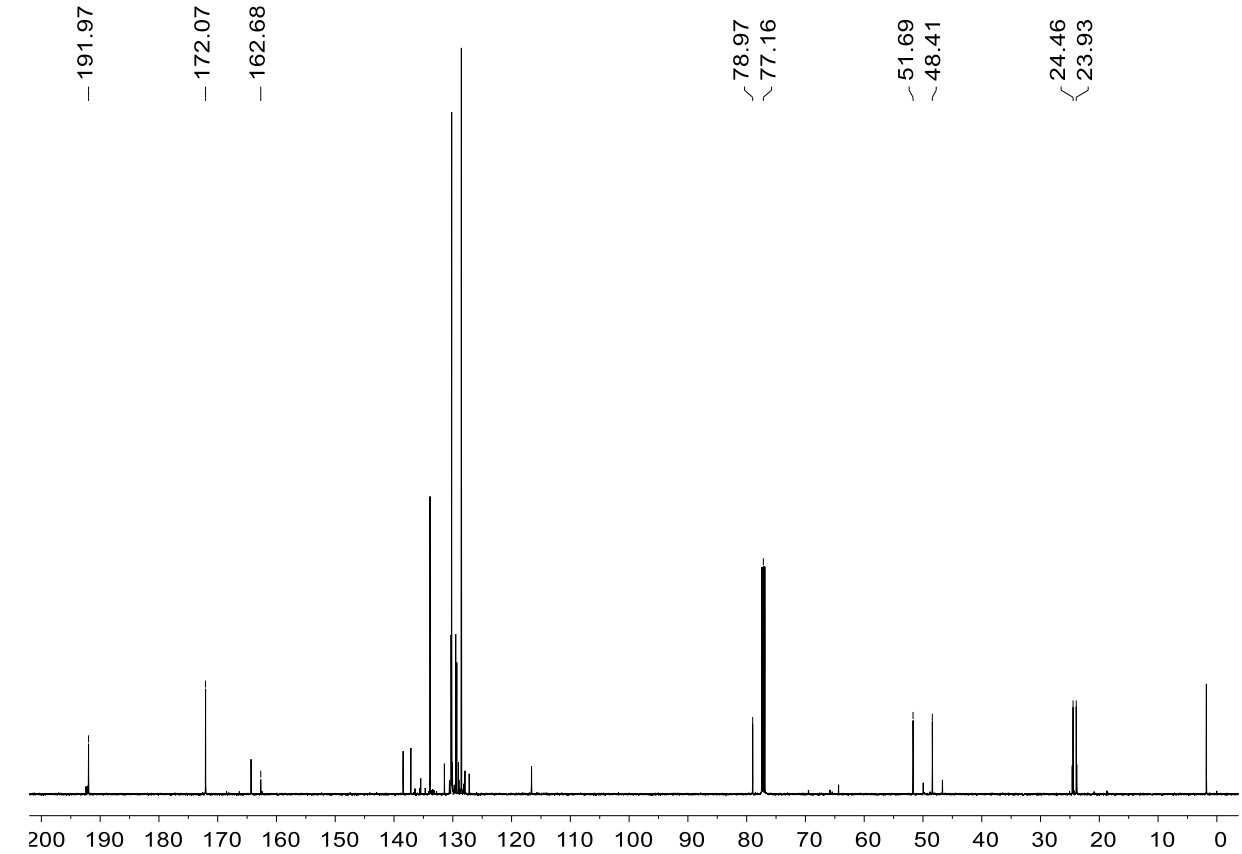
DTT-432: According to general protocol C (chapter 2.2.3, page 10), the title compound was synthesized from 4-(hydroxymethyl) benzaldehyde (136.2 mg, 1.00 mmol, 1.0 equiv), FPyr (104.8 µL, 109.1 mg, 1.10 mmol, 1.1 equiv), $NaPF_6$ (284.8 mg, 1.70 mmol, 1.70 equiv) and BzCl (139.4 µL, 168,7 mg, 1.20 mmol, 1.2 equiv) in MeCN (0.5 mL, 2.0 M). The ^{1}H NMR spectrum of a sample withdrawn after 80 min reaction time indicated 88% conversion of alcohol **1q** and salt **7q´** in 88% yields. After 7 days, 10% decomposition of **7q´** could be observed as determined by ^{1}H NMR spectroscopy.

M ($C_{13}H_{16}F_6NO_2P$) = 263.24 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 9.98 (s, 1H, 6-H), 8.66 (br. s, 1H, 1'-H), 7.90-7.88 (m, 2H, 3-H), 7.63-7.60 (m, 2H, 4-H), 5.67 (s, 2H, 1-H), 3.99-3.97 (m, 2H, 2'-H), 3.71-3.69 (m, 2H, 5'-H), 2.09-2.06 (m, 4H, 3'-H,4'-H); **^{13}C NMR** (126 MHz, $CDCl_3$)[9] δ [ppm] = 191.97 (C-6), 172.07 (C-1'), 162.7 (C-5), 78.97 (C-1), 51.69 (C-2´), 48.41 (C-5´), 24.46, 23.93 (C-3´, C-4´); **^{31}P NMR** (202 MHz, $CDCl_3$) δ [ppm] = -144.27 (sept, $^1J_{P-F}$ = 703 Hz); **^{19}F NMR** (470 MHz, $CDCl_3$) δ [ppm] = -72.22 (d,$^1J_{P-F}$ = 726 Hz).

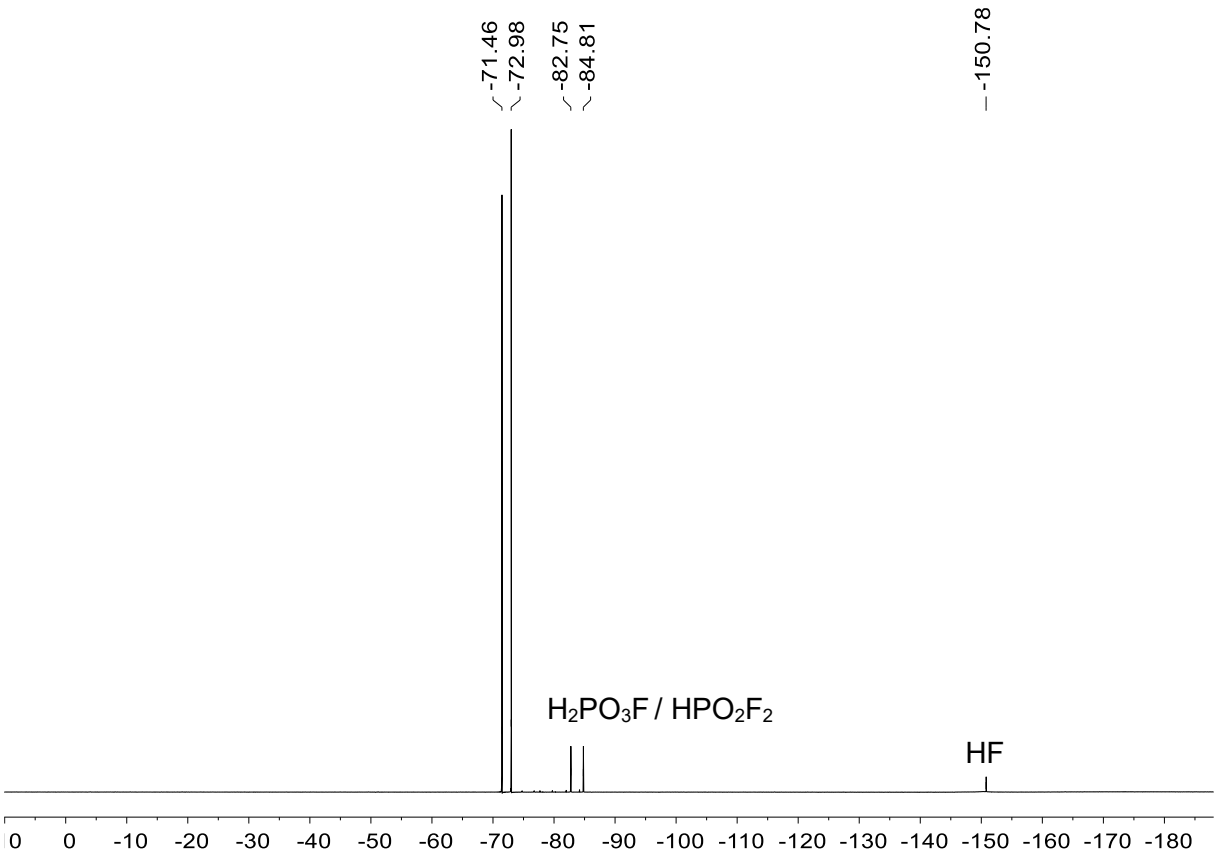
[9] Only signals that could be unambiguously assigned to amidate salt **7q´** are stated.



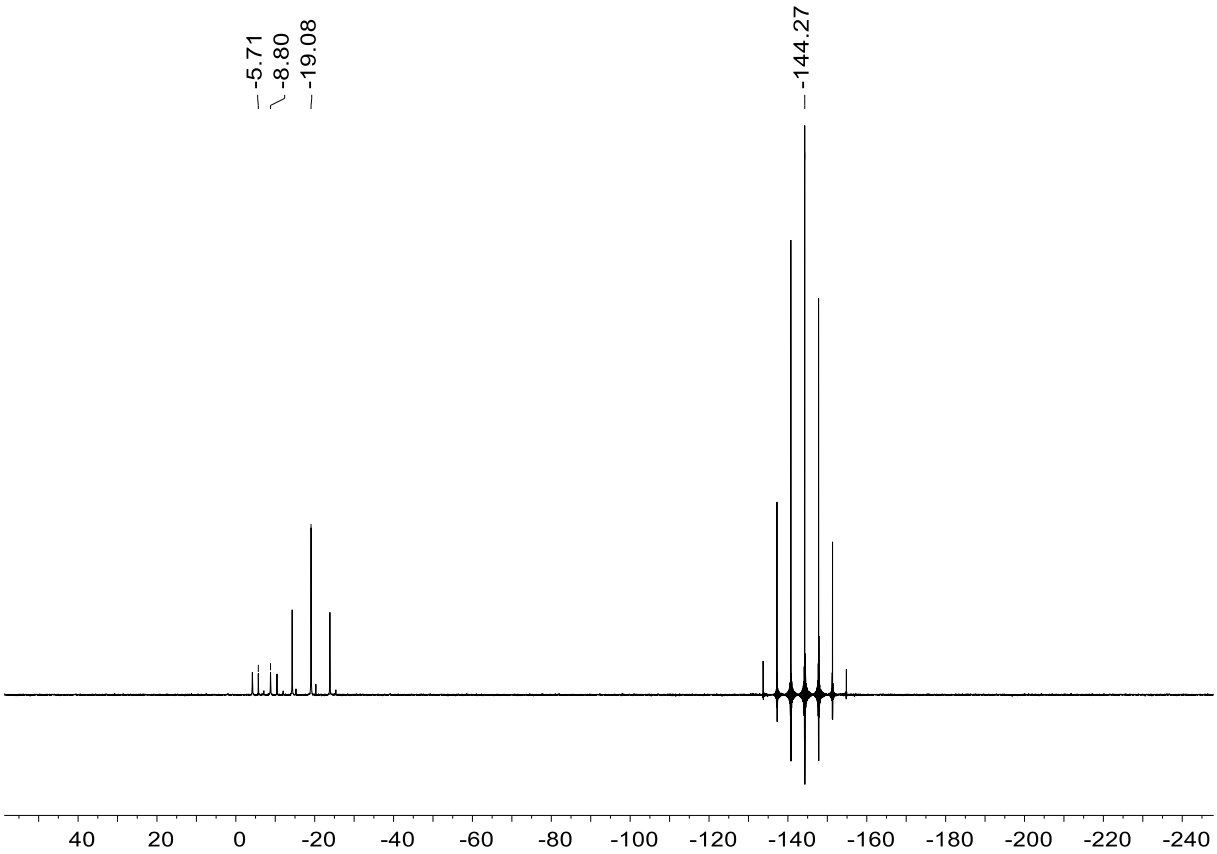
^{1}H NMR spectrum of ((4-formylbenzyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7q´**, 500 MHz, $CDCl_3$).



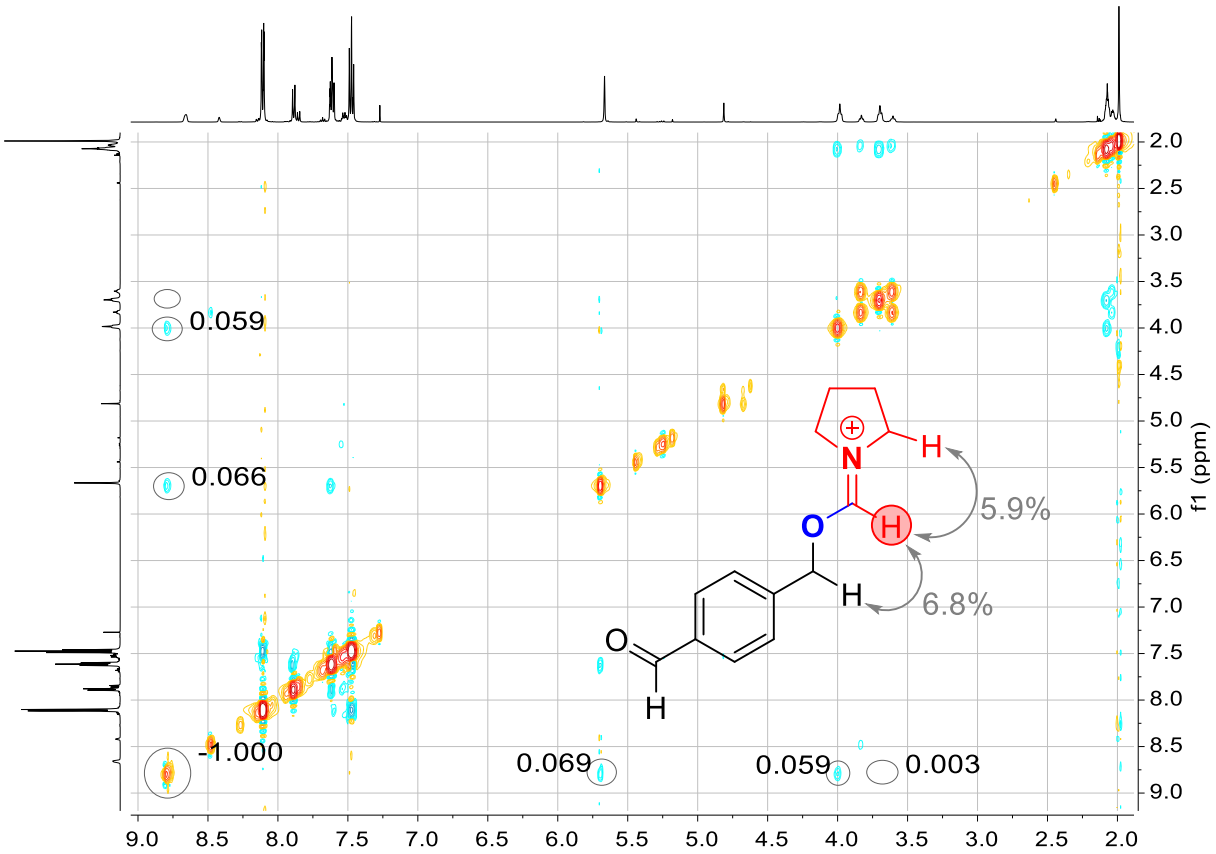
^{13}C NMR spectrum of ((4-formylbenzyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7q´**, 126 MHz, $CDCl_3$).



^{19}F NMR spectrum of ((4-formylbenzyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7q´**, 470 MHz, $CDCl_3$).



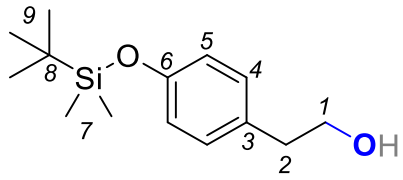
^{31}P NMR spectrum of ((4-formylbenzyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7q´**, 202 MHz, $CDCl_3$).



NOESY spectrum of ((4-formylbenzyloxy)methylidene) pyrrolidinium hexafluorophosphate (**7q´**, 500 MHz, $CDCl_3$).

2.3.4. Synthesis of Alcohols of Type 1

2.3.4.1. Synthesis of 2-(4-(*tert*-Butyldimethylsilyl)oxyphenyl)ethan-1-ol (1e)



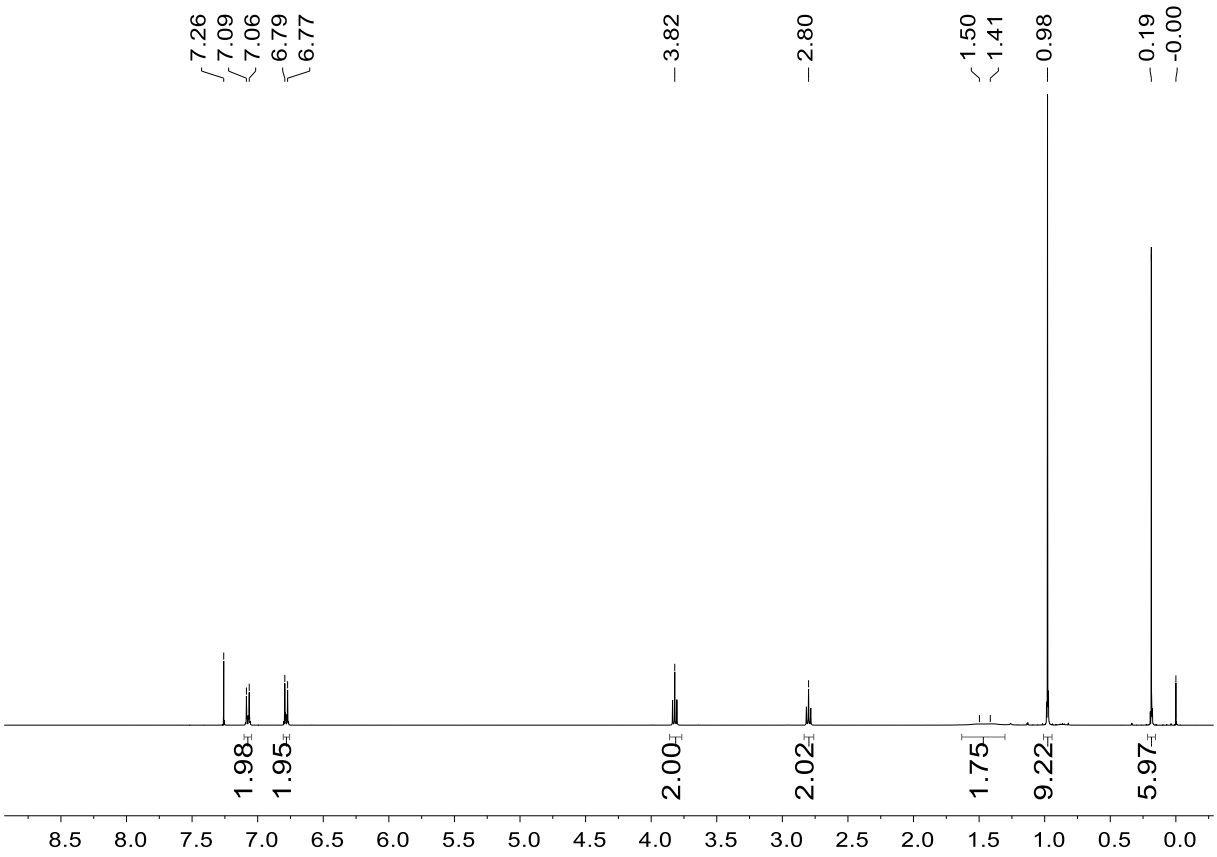
1e

DTT-180: A 25 mL round bottom flask was loaded with 2-(4-hydroxylphenyl)ethanol (694.4 mg, 5.0 mmol, 1.0 equiv), *tert*-butyl dimethylsilylchloride (TBDMSCl, 1.810 g, 12.0 mmol, 2.40 equiv) and EtOAc (10.0 mL, 0.5 M). Next, the reaction solution was cooled down to 0 °C in an ice bath and triethylamine (1.76 mL, 12.5 mmol, 2.50 equiv) was added under vigorous stirring within 20 min with the aid of a syringe pump. After 15 min of stirring, the ice bath was removed and the reaction mixture was allowed to stir overnight (16 h) at room temperature.

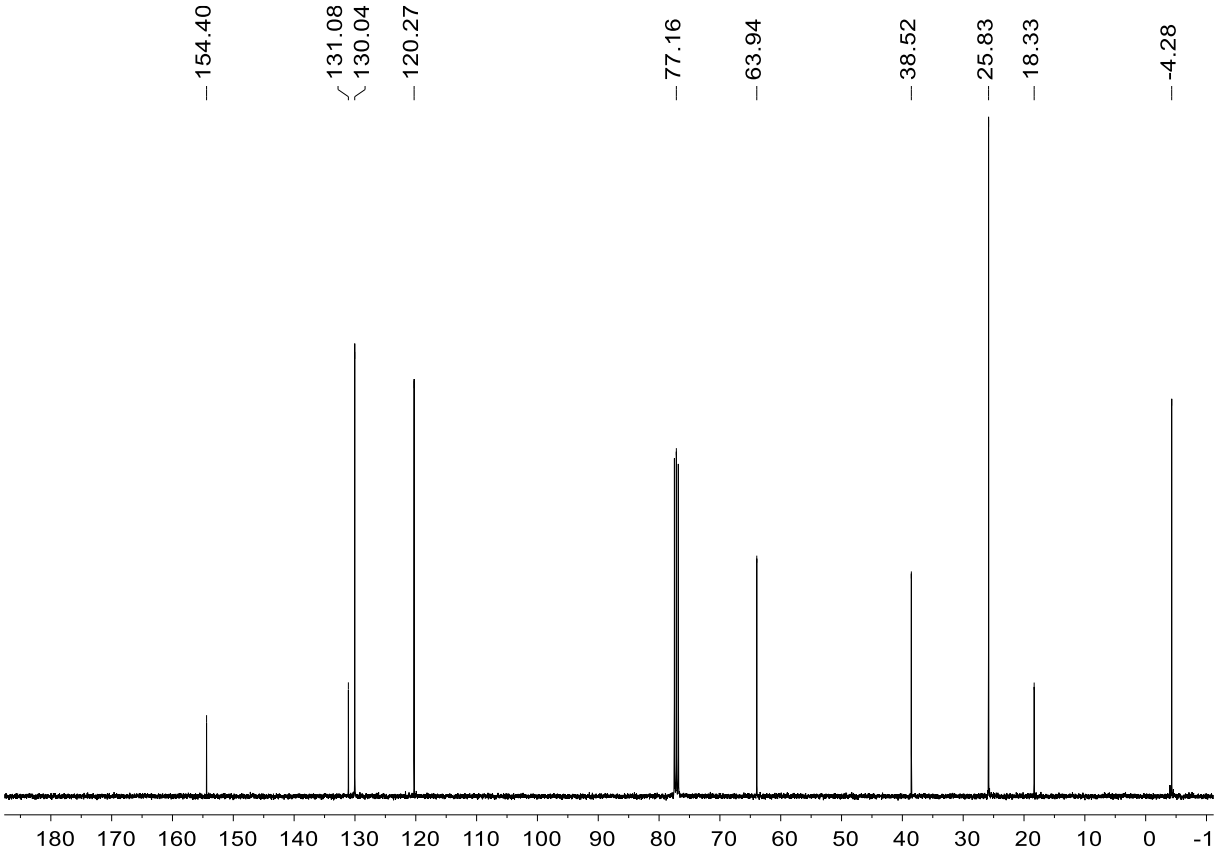
Subsequently, the reaction mixture was diluted with EtOAc (20 mL) and 1 N solution of HCl in water (10 mL), the organic phase was washed with brine (10 mL), dried over $MgSO_4$, concentrated under reduced pressure and dried at 20 mbar for 10 min at the rotary evaporator. ^{1}H NMR of the crude material (1.794 g, 142%) indicated 51:49 mixture of the title compound and the twofold silylated ether ((*tert*-butyldimethylsilyl)(2-(4-(*tert*-Butyldimethylsilyl) oxyphenyl)ethyl) ether). Column chromatographic purification on silica gel (17.0 g SiO_2, mass crude product/SiO_2 1:10) with EtOAc/*n*-heptane 50:50 and drying at 5 mbar for 10 min at the rotary evaporator enabled the isolation of the alcohol **1e** as a colourless liquid (554.3 mg, 2.19 mmol, 44%).

M ($C_{14}H_{24}O_2Si$) = 252.43 g/mol, $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 50:50) = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 7.09-7.06 (m, 2H, 4-H), 6.80-6.77 (m, 2H, 5-H), 3.82 (t, $^3J_{1,2}$ = 6.6 Hz, 2H, 1-H), 2.80 (t, $^3J_{2,1}$ = 6.6 Hz, 2H, 2-H), 1.50-1.41 (m, 1H, OH), 0.98 (s, 9H, 9-H), 0.19 (s, 6H, 7-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 154.40 (C-6), 131.08 (C-4), 130.04 (C-5), 120.27 (C-3), 63.94 (C-1), 38.52 (C-2), 25.83 (C-9), 18.33 (C-8), -4.28 (C-7); **GC MS** (EI, 70 eV) m/z [u] (%) = 252 (37, $[M]^+$), 221 (12, $[M\text{-}CH_2OH]^+$), 196 (23), 195 (100, [M-*iso*-butane]$^+$), 178 (15), 177 (94, [4-(Me_2SiO)styrene]$^+$), 163 (9), 161 (8), 151 (12), 149 (17) , 91 (7, $[Bn]^+$), 75 (9), 73 (18); **HR MS** (EI, $[C_{14}H_{24}O_2Si]^+$) calc. 252.15401 u, found 252.15396 u.

The NMR data is in agreement with the literature.[12]

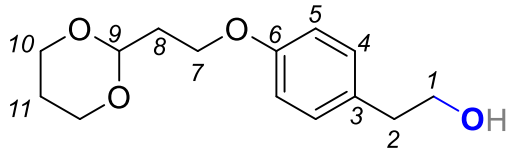


^{1}H NMR spectrum of 2-(4-(*tert*-butyldimethylsilyloxy)phenyl)ethan-1-ol (**1e**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-(4-(*tert*-butyldimethylsilyloxy)phenyl)ethan-1-ol (**1e**, 125 MHz, $CDCl_3$).

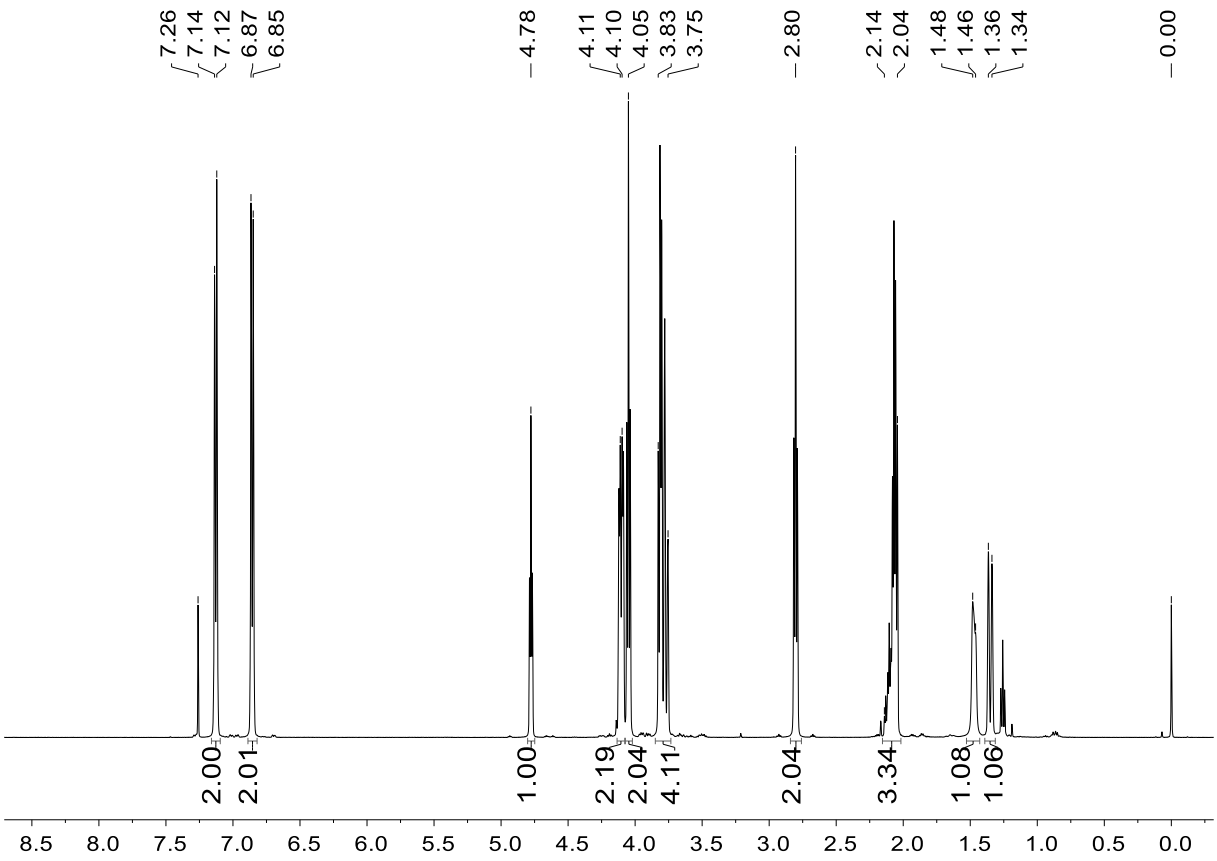
2.3.4.2. Synthesis of 2-(4-(2-(1,3-Dioxan-2-yl)ethoxy)phenyl)ethan-1-ol (1f)



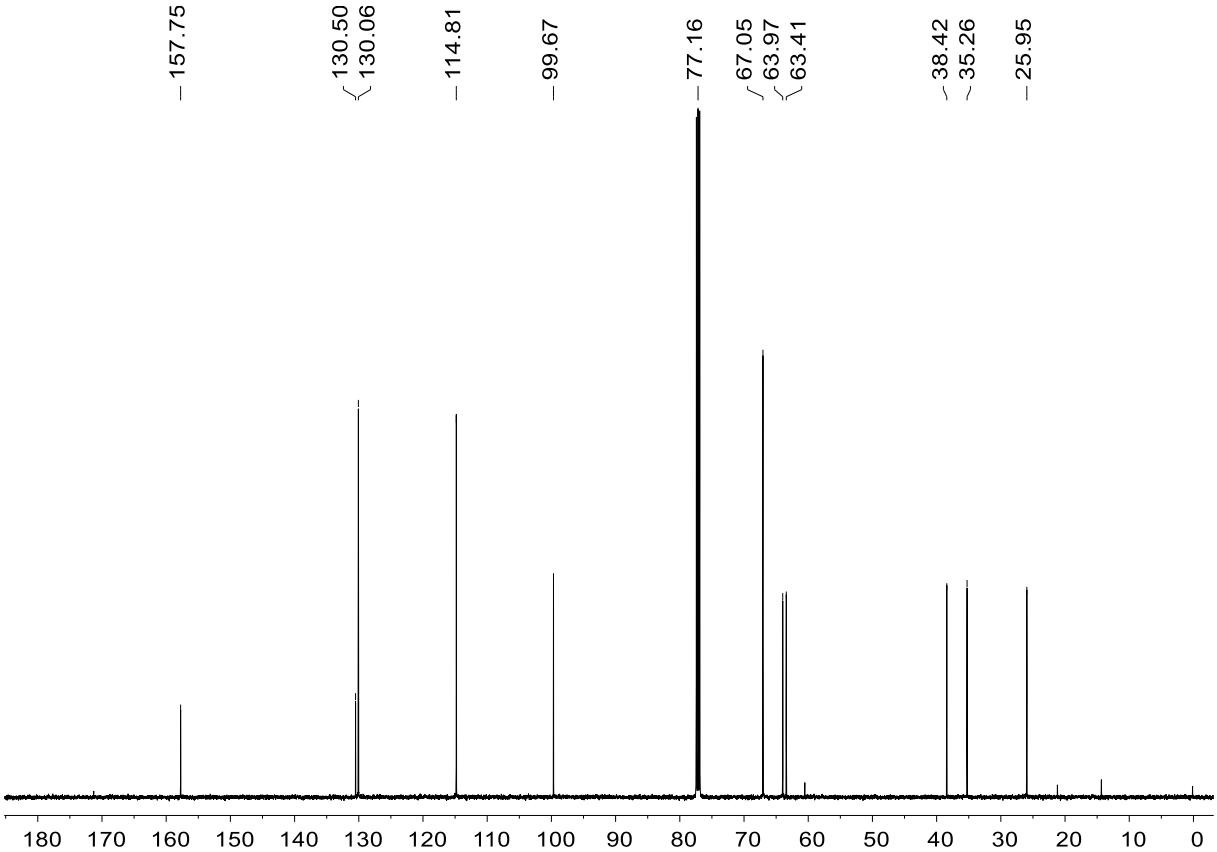
1f

DTT-114: In alignment to reference [1], 2-(4-hydroxyphenyl) ethanol (2.763 g, 20.0 mmol, 1.00 equiv) was dissolved in dry MeCN (10.0 mL, 1.0 M) in a 50 mL round bottom flask. Then, fine-powdered K_2CO_3 (4.422 g, 32.00 mmol, 1.60 equiv) and 2-(2-bromoethyl)-1,3-dioxane (4.10 mL, 5.851 g, 30.00 mmol, 1.50 equiv) were added to the reaction solution, the reaction flask was equipped with a reflux condenser and placed in aluminum heating block, which had been preheated to100°C. After stirring at 400 rpm for 16 h at 100 °C, the reaction was allowed to cool down to ambient temperature and diluted with MTBE (30 mL) and H_2O (20 mL). Next, the organic phase was washed with brine (20 mL), dried over $MgSO_4$, concentrated under reduced pressure and dried on a rotary evaporator for 5 min at 5 mbar. ^{1}H NMR of the crude material (6.54 g, 129%) confirmed full conversion of 2-(4-hydroxyphenyl) ethanol. Finally, purification with the aid of column chromatography on silica gel (40 g, ratio weight crude product/SiO_2 1:8) using a gradient of MTBE/*n*-heptane from 33:67 to 67:33 as eluent system delivered the title compound **1f** in quantitative yield (5.105 g, 20.2 mmol) as a colourless solid.

M ($C_{14}H_{20}O_4$) = 252.31 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 33:67) = 0.47, **mp**. = 80-81 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 7.13 (d, $^3J_{4,5}$ = 8.6 Hz, 2H, 4-H), 6.87-6.85 (m, 2H, 5-H), 4.78 (t, $^3J_{9,8}$ = 5.5 Hz, 1H, 9-H), 4.10 (dd, $^3J_{10a,11b}$ = 11.8 Hz, $^3J_{10a,11a}$ = 5.0 Hz, 2H, 10-H_a), 4.05 (t, $^3J_{7,8}$ = 6.3 Hz, 2H, 7-H), 3.83-3.75 (m, 4H, 1-H, 10-H_b), 2.80 (t, $^3J_{2,1}$ = 6.6, 2H, 2-H), 2.14-2.04 (m, 3H, 8-H, 11-H_a), 1.48-1.46 (m, 1H, OH), 1.36-1.34 (d, $^3J_{11a,10b}$ = 13.5 Hz, 1H, 11-H_b); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 157.75 (C-6), 130.50 (C-3), 130.06 (C-4), 114.81 (C-5), 99.67 (C-9), 67.05 (C-10), 63.87 (C-1), 63.41 (C-7), 38.42 (C-2), 35.26 (C-8), 25.95 (C-11); **GC MS** (EI, 70 eV) m/z [u] (%) = 252 (46, $[M]^+$), 221 (35, $[M\text{-}CH_2OH]^+$), 175 (9), 163 (17, [M-dioxan-H_2]$^+$), 138 (7, [2-(4-hydroxyphenyl) ethanol]$^+$), 121 (5, [phenylethanol]$^+$), 115 (45, [1-(1,3-dioxan)ethyl]$^+$), 114 (23, [1-(1,3-dioxan)ethenyl]$^+$), 107 (77, [phenoxymethyl]$^+$), 100 (61), 91(16, [phenylmethyl]$^+$), 87 (100, [1,3-dioxanyl]$^+$), 78 (12, [PhH]$^+$), 77 (22, [Ph]$^+$), 59 (28), 57 (29); **HR MS** (EI, $[C_{14}H_{20}O_4]^+$) calc. 252.13561 u, found 252.13627 u.

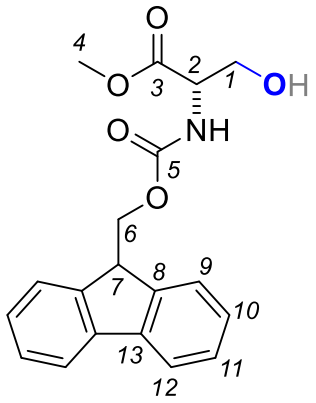


^{1}H NMR spectrum of 2-(4-(2-(1,3-dioxan-2-yl)ethoxy)phenyl)ethan-1-ol (**1f**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of 2-(4-(2-(1,3-dioxan-2-yl)ethoxy)phenyl)ethan-1-ol **1f** (126 MHz, $CDCl_3$).

2.3.4.3. Synthesis of Methyl L-*N*-((9*H*-Fluoren-9-yl)methoxycarbonyl)-serinate (1h)

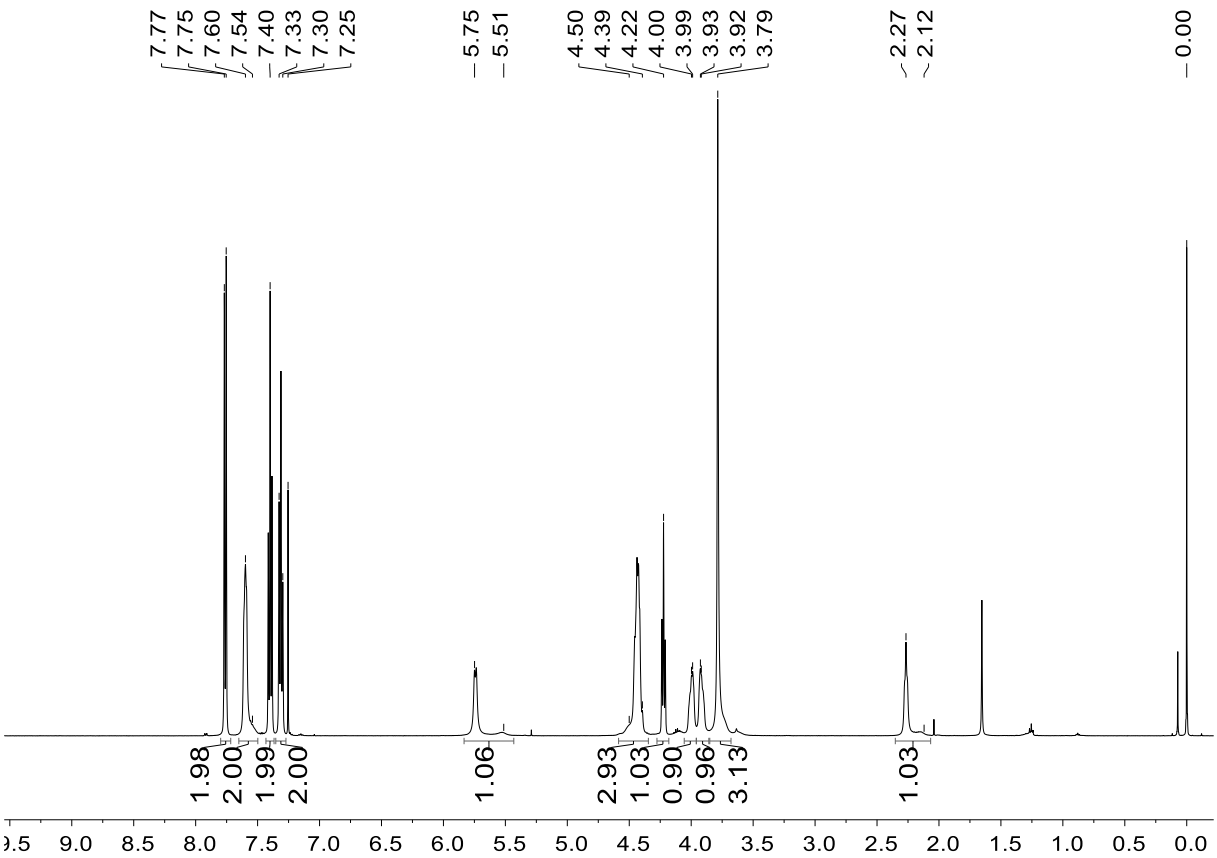


1h

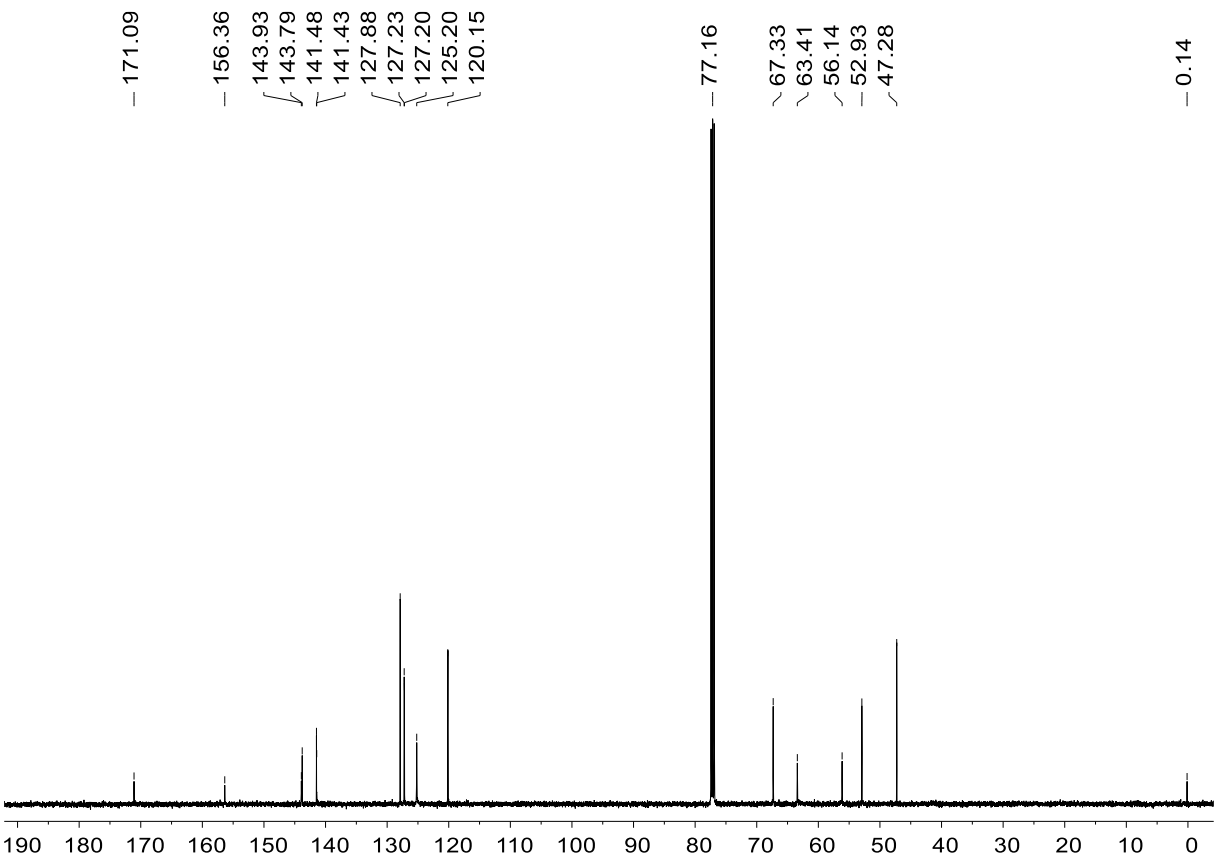
DTT-84:[3] A 50 mL round bottom flask was charged with fine-powdered K_2CO_3 (3.455 g, 25.0 mmol, 2.50 equiv), L-serine methyl ester hydrochloride (1.556 g, 10.0 mmol, 1.00 equiv) and H_2O (10.0 mL, 1.0 M) and the mixture was cooled in an ice bath. Next, FmocCl (3.363 g, 13.00 mmol, 1.30 equiv) was dissolved in THF (10.0 mL, 1.0 M) and the resulting solution was added under vigorous stirring within 20 min with the aid of a syringe pump to the reaction mixture. After 15 min of stirring, the ice bath was removed and the reaction mixture was stirred overnight (19 h) at rt.

In the following, the reaction mixture was diluted with H_2O (10 mL) and MTBE (15 mL) and the aqueous phase was extracted with further MTBE (2x10 mL). Subsequently, the collected organic phases were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Finally, the crude material (4.080 g, 137%, yellow solid) was purified by column chromatography on silica gel (40.1 g SiO_2, mass crude product/SiO_2 1:10) with MTBE/*n*-heptane 50:50. Thereby, the crude material was dissolved in the minimal amount of CH_2Cl_2 (2.0 mL) under heating to apply it to the silica gel column. After drying at the rotary evaporator at 5 mbar for 10 min the alcohol **1h** was isolated as a colourless solid (2.624 g, 8.80 mmol, 88%).

M ($C_{19}H_{19}NO_5$) = 341.36 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-heptane 50:50) = 0.24; **mp**. = 127-128 °C (lit. mp. 114.3-115.8 °C);[14,15] **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 7.77 (d, $^3J_{9,10}$ = 7.5 Hz, 2H, 12-H), 7.60 (ψ-t, *J* = 7.9 Hz, 2H, 9-H), 7.40 (ψ-t, *J* = 7.5 Hz, 2H, 11-H), 7.33-7.30 (m, 2H, 10-H), 5.75-5.51 (m, 1H, NH), 4.50-4.39 (m, 3H, 2-H, 6-H), 4.22 (t, $^3J_{5,6}$ = 6.9 Hz, 1H, 7-H), 4.00-4.39 (m, 1H, 1-H_a), 3.93-3.92 (m, 1H, 1-H_b), 3.79 (s, 3H, 4-H), 2.27-2.12 (m, 1H, OH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 171.09 (C-3), 156.36 (C-5), 143.93/143.79 (C-8), 141.48/141.43 (C-13), 127.88 (C11-), 127.23/127.20 (C-10), 125.20 (C-9), 120.15 (C-12), 67.33 (C-6), 63.41 (C-1), 56.14 (C-2), 52.93 (C-4), 47.28 (C-7); **GC MS** (EI, 70 eV) m/z [u] (%) = 272 (9), 271 (7), 270 (27), 163 (11), 115 (27), 114 (31), 107 (44), 100 (71), 9 (16), 87 (100), 77 (14, $[Ph]^+$).
In the ^{13}C NMR spectrum in some instances are two signals visible for one C atom because of rotational isomers. Analytical data is in agreement with literature.[14]

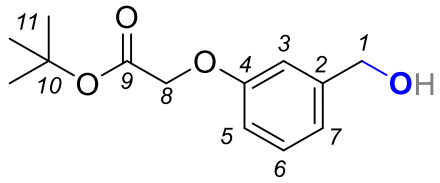


^{1}H NMR spectrum of methyl L-*N*-((9*H*-fluoren-9-yl)methoxycarbonyl)-serinate (**1h**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum of methyl L-*N*-((9*H*-fluoren-9-yl)methoxycarbonyl)-serinate (**1h**, 126 MHz, $CDCl_3$).

2.3.4.4. Synthesis of *tert*-Butyl 2-(3-(Hydroxymethyl)phenoxy)acetate (1v)



1v1v

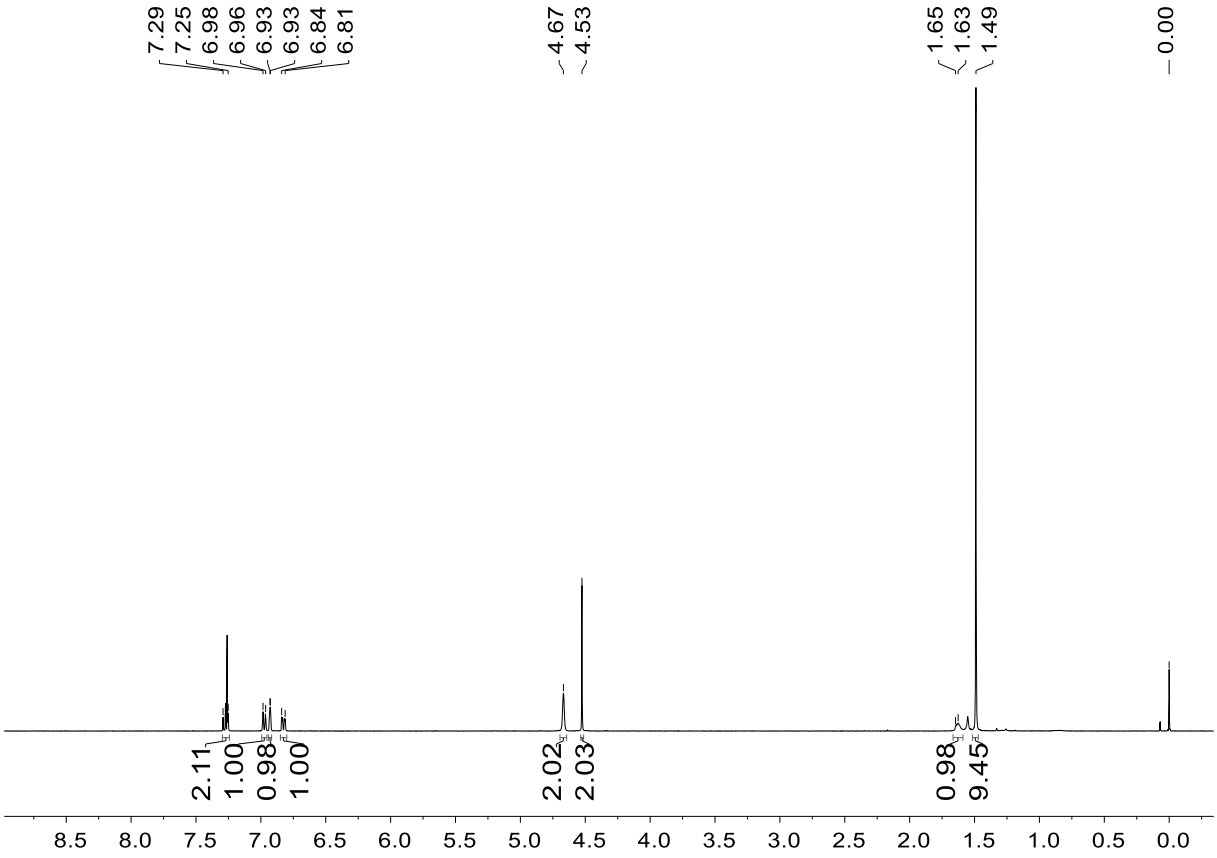
DTT-334: According to reference [1], 3-hydroxy benzaldehyde (1.264 g, 10.0 mmol, 1.00 equiv) was dissolved in MeCN (10.0 mL, 1.0 M) in 50 mL flask. Then, *tert*-butyl 2-bromoacetate (1.92 mL, 2.535 g, 13.0 mmol, 1.30 equiv) and fine-powdered K_2CO_3 (2.10 g, 15.0 mmol, 1.50 equiv) were added and the reaction mixture was stirred at 80°C overnight for 16 h.

In the following, the mixture was cooled in an ice bath, diluted with MeOH (10 mL, MeOH/MeCN 1:1, 0.5 M) and $NaBH_4$ (580.0 mg, 15.00 mmol, 1.50 equiv) was added in three portions within 10 min, whereby a hydrogen gas evolution occurred. After 15 min of stirring the ice bath was removed and the reaction suspension was allowed to stir for additional 2 h at room temperature. In the following, the reaction suspension was diluted with MTBE (20 mL), the mixture was cooled in an ice bath and 2 N HCl solution in water (20 mL) was added dropwise . After the H_2 gas evolution had ceased, the aqueous phase (pH ≤ 0) was extracted with further MTBE (2x10 mL), the collected organic phases were washed with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*.

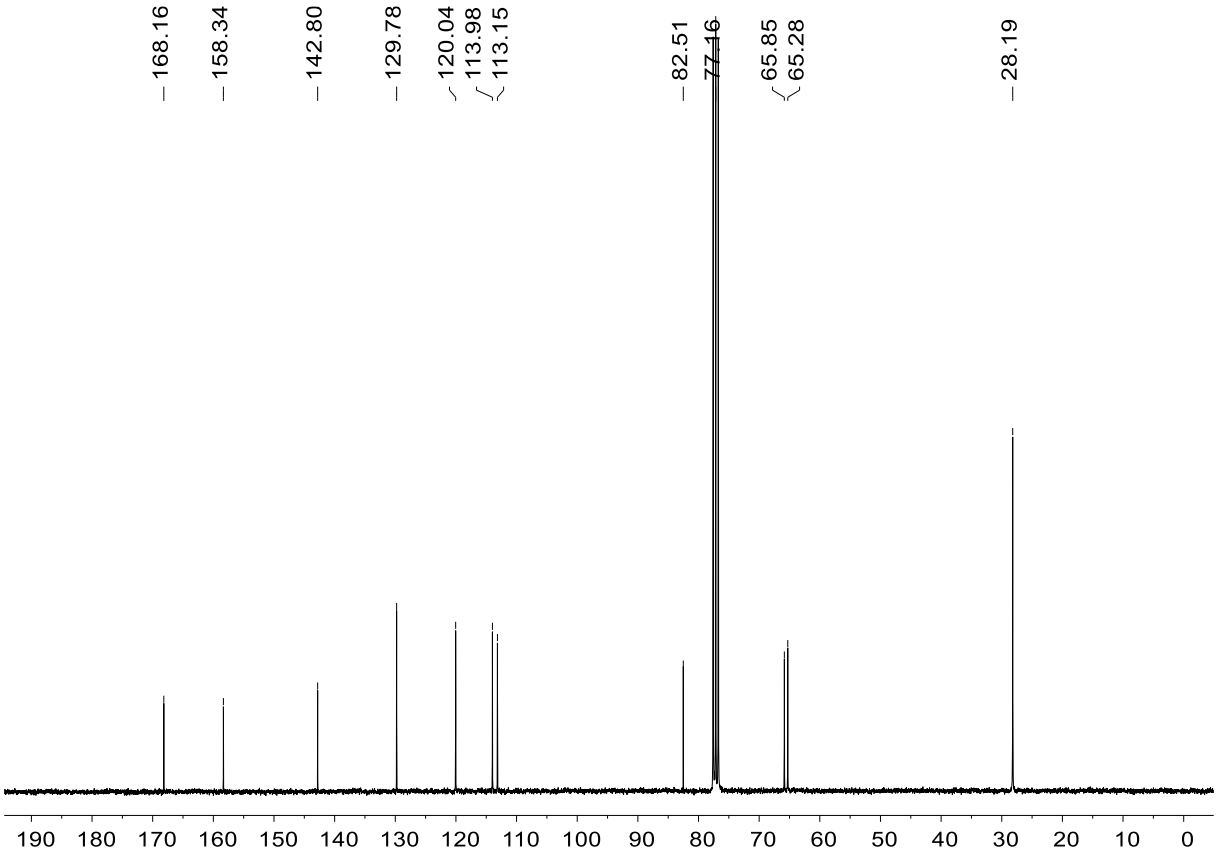
Eventually, the crude alcohol **1v** (2.959 g, 111%) was purified by column chromatography on silica gel using an eluent gradient MTBE/*n*-heptane 20:80 to 50:50. Drying at 20 mbar for 15 min at the rotary evaporator afforded the title compound **1v** as a colorless oil in 71% yield (1.697 g, 7.12 mmol).

M ($C_{13}H_{18}O_4$) = 238.28 g/mol; $\mathbf{r_f}$ (SiO_2, MTBE/*n*-Heptane 60:40) = 0.38; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 7.29-7.25 (m, 1H, 6-H), 6.98-6.96 (m, $^3J_{7,6}$ = 7.5 Hz, 1H, 7-H), 6.93 (br. s, 1H, 3-H), 6.84-6.81 (m, 1H, 5-H), 4.67 (s, 2H, 1-H), 4.53 (s, 2H, 8-H), 1.65-1.63 (m, 1H, OH) 1.49 (s, 9H, 11-H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ [ppm] = 168.16 (C-9), 158.34 (C-4), 142.80 (C-2), 129.78 (C-6), 120.04 (C-7), 113.98 (C-5), 113.15 (C-3), 82.51 (C-10), 65.85 (C-8), 65.28 (C-1), 28.19 (C-11).

The NMR data is in agreement with the literature.[1]



^{1}H NMR spectrum of *tert*-butyl 2-(3-(hydroxymethyl)phenoxy)acetate (**1v**, 500 MHz, $CDCl_3$)

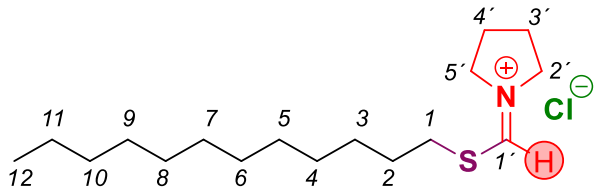


^{13}C NMR spectrum of *tert*-butyl 2-(3-(hydroxymethyl)phenoxy)acetate (**1v**, 500 MHz, $CDCl_3$).

2.4. Synthesis of Thioformates 9

2.4.1. Synthesis of Thioimidate Salts of Type 8

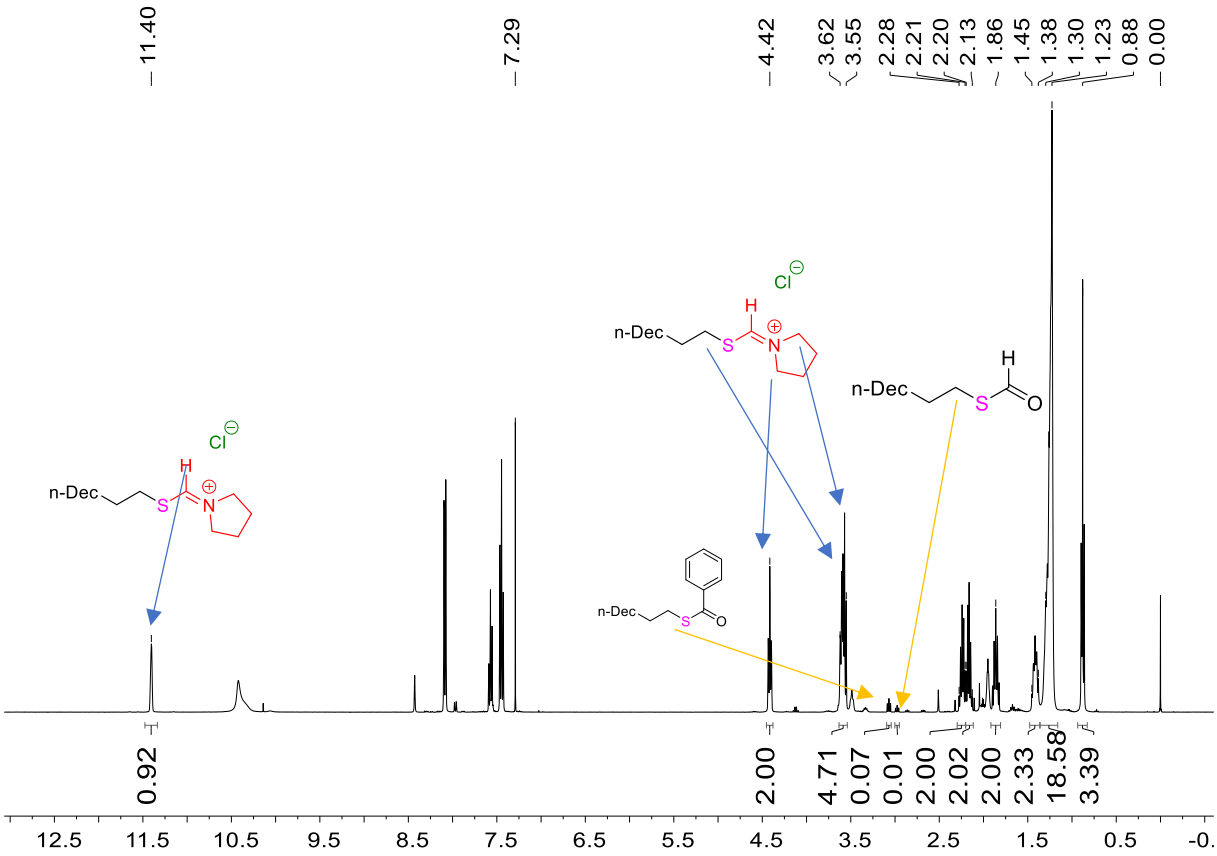
2.4.1.1. Synthesis of *N*-((1-Dodecylthio)methylidene) Pyrrolidinium Chloride (8a)



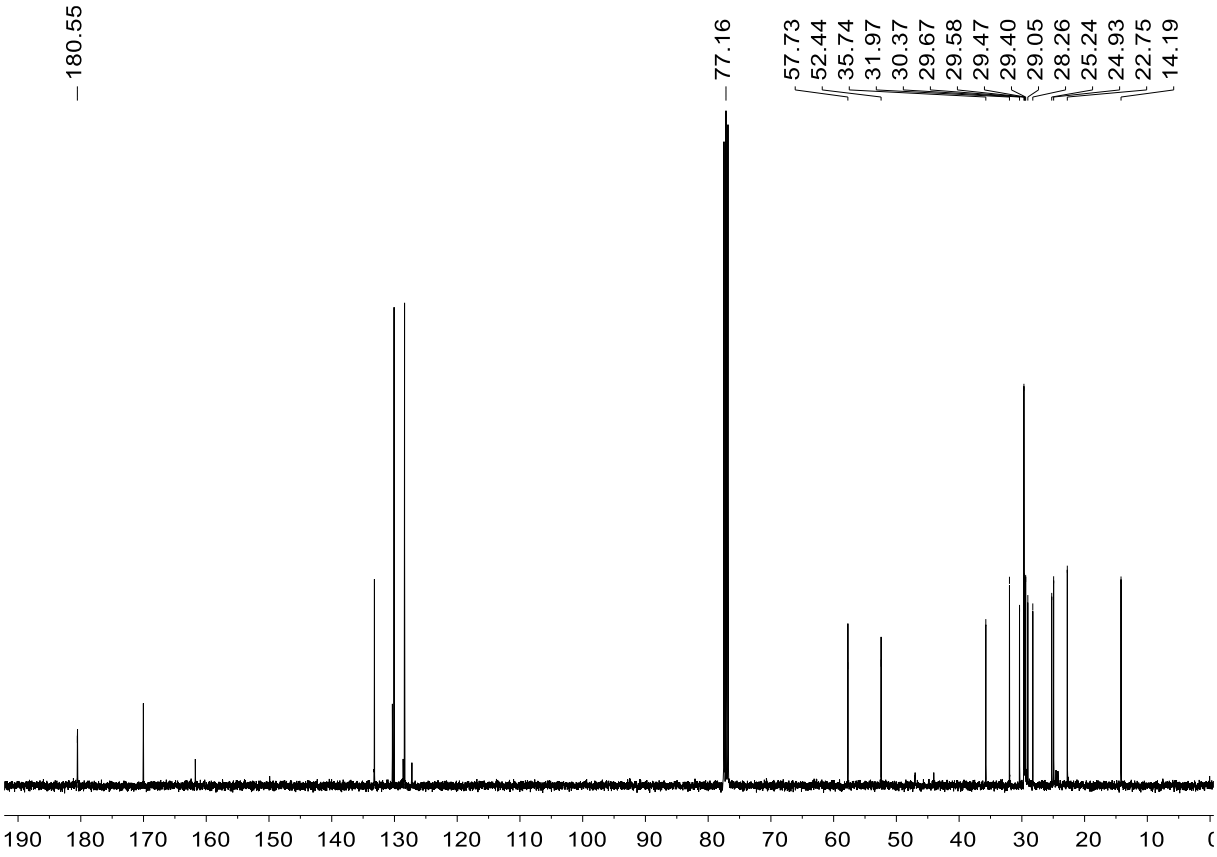
8a

DTT-451: According to general protocol B (chapter 2.2.2, page 10) the title compound was prepared from 1-dodecane thiol (186.6 µL, 180.3 mg, 1.00 mmol, 1.00 equiv), FPyr (1.30 equiv) and BzCl (1.20 equiv) in and dry MeCN (2.0 M). After 1 h of stirring at room temperature, the ^{1}H NMR spectrum of a sample showed full conversion of thiol **5a**. The ratio of salt **8a** / dodecylthiobenzoate / dodecylthioformate / dodecanethiol was found to be 95:3:0:1:2. A ^{1}H NMR after one week of storage indicated no decomposition.

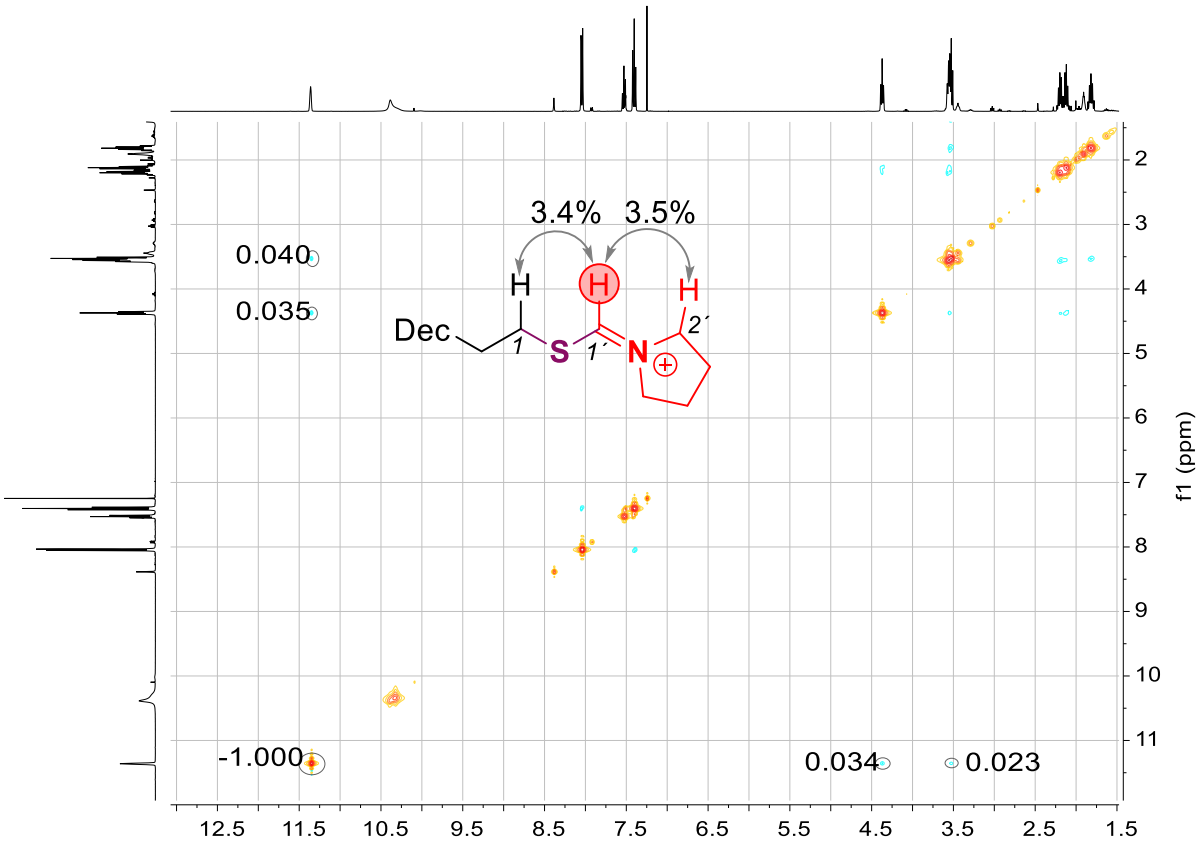
M ($C_{17}H_{34}ClNS$) = 319.98 g/mol; l**^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 11.40 (s, 1H, 1'-H), 4.42 (t, $^{3}J_{2',3'}$ = 6.7 Hz, 2H, 2'-H), 3.60 (t, $^{3}J_{5',4'}$ = 6.9 Hz, 2H, 5´-H), 3.62-3.55 (m, 4H, 1-H, 2´-H), 2.24 (p, $^{3}J_{4'-5'}$ = 6.5 Hz, $^{3}J_{4'-3'}$ = 7.6 Hz, 2H, 4'-H), 2.28-2.21 (m, 2H, 3´-H), 2.20-2.13 (m, 2H, 4´-H), 1.86 (ψ-p, ^{3}J = 7.4 Hz, 2H, 2-H), 1.45-1.38 (m, 2H, 3-H), 1.30-1.23 (m, 16H, 4-H to 11-H), 0.88 (t, $^{3}J_{12,11}$ = 6.9 Hz, 3H, 12-H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 180.55 (C-1'), 57.73 (C-5'), 52.44 (C-2'), 35.74 (C-1), 31.97 (C-4 to C-11), 30.37 (C-2), 29.67, 29.58, 29.47, 29.40 (C-4 to C-11), 29.05 (C-3), 25.22 (C-4'), 24.92 (C-3'), 25.24 (C-4´), 24.93 (C-3´), 22.75 (C-12).



^{1}H NMR spectrum of *N*-((1-dodecylthio)methylidene) pyrrolidinium chloride (**8a**, 400 MHz, $CDCl_3$).

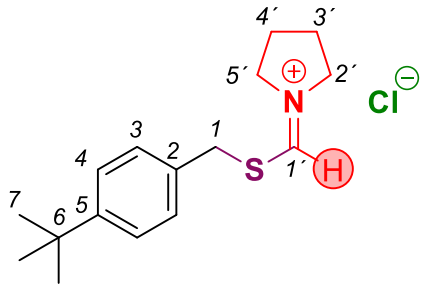


^{13}C NMR spectrum of *N*-((1-dodecylthio)methylidene) pyrrolidinium chloride (**8a**, 101 MHz, $CDCl_3$).



NOESY spectrum of *N*-((1-dodecylthio)methylidene) pyrrolidinium chloride (**8a**, 400 MHz, $CDCl_3$).

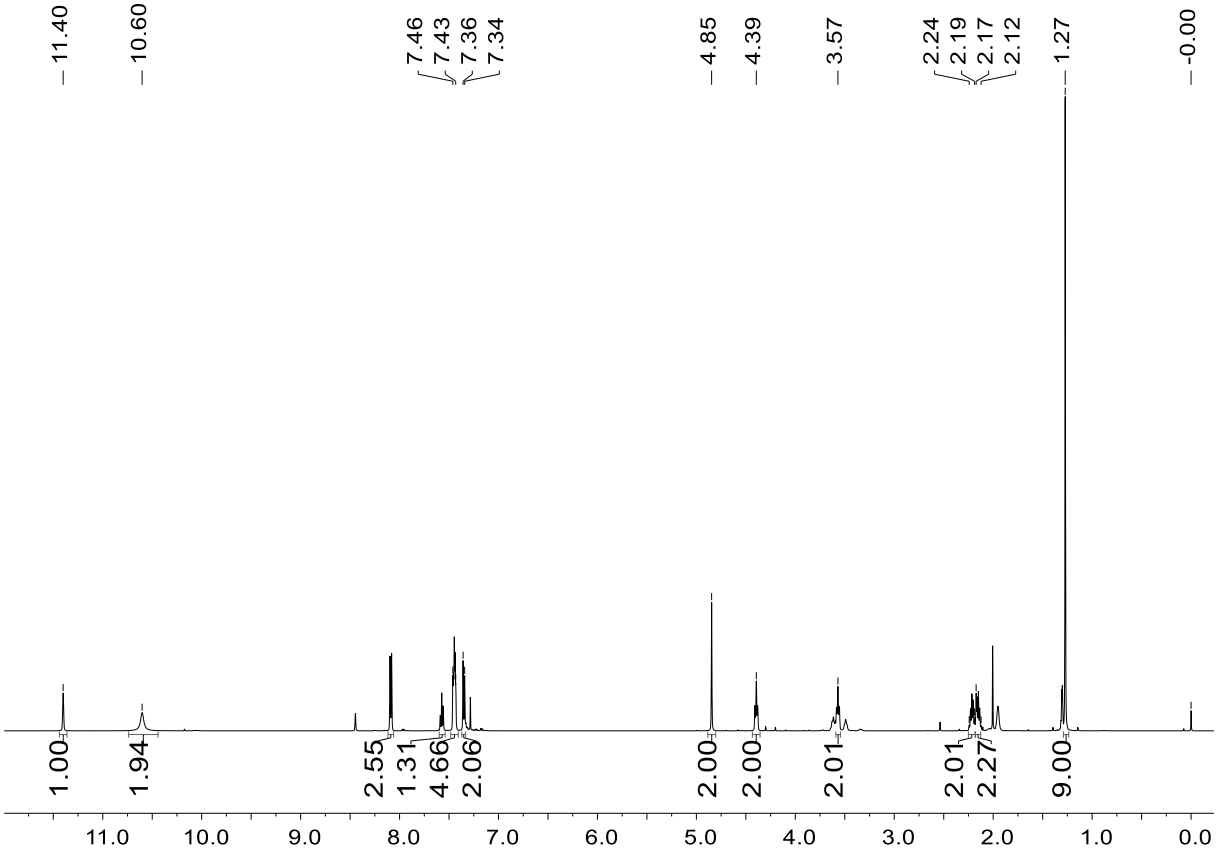
2.4.1.2. Synthesis of *N*-((4-*tert*-Butylphenyl)methylidene) Pyrrolidinium Chloride (8p)



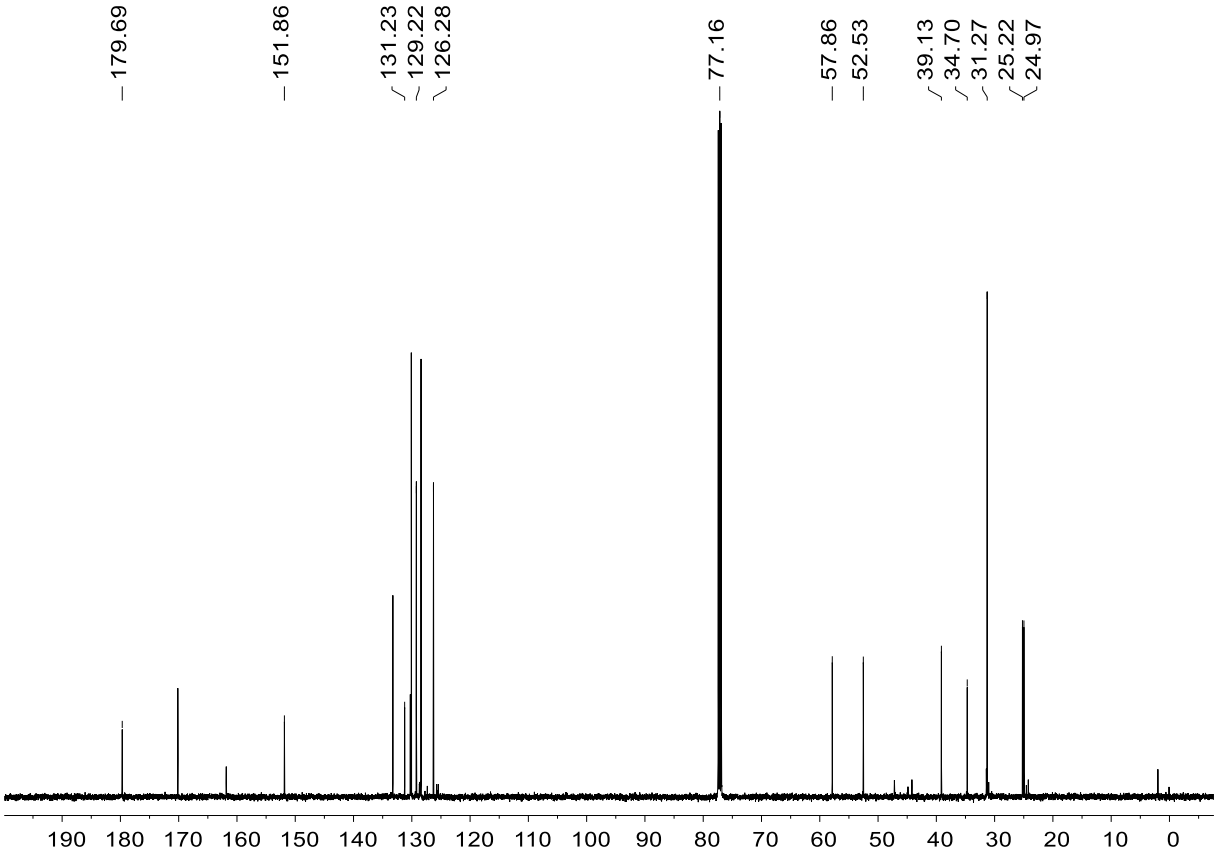
8p

DTT-450a: As described in general protocol B (chapter 2.2.2, page 10) the imidate salt **8p** was accessed from 1-dodecane thiol 4-*tert*-butylbenzylthiol (**6p**, 238.1 µL, 202.4 mg, 1.00 mmol, 1.00 equiv), FPyr (1.30 equiv) and BzCl (1.20 equiv) in and dry MeCN (2.0 M). After 1 h of stirring at room temperature, the ^{1}H NMR spectrum of a sample verified full consumption of thiol **6p** and cation **8p** in ≥98% yield. ^{1}H NMR after 1 week of storage showed no decomposition of the title compound.

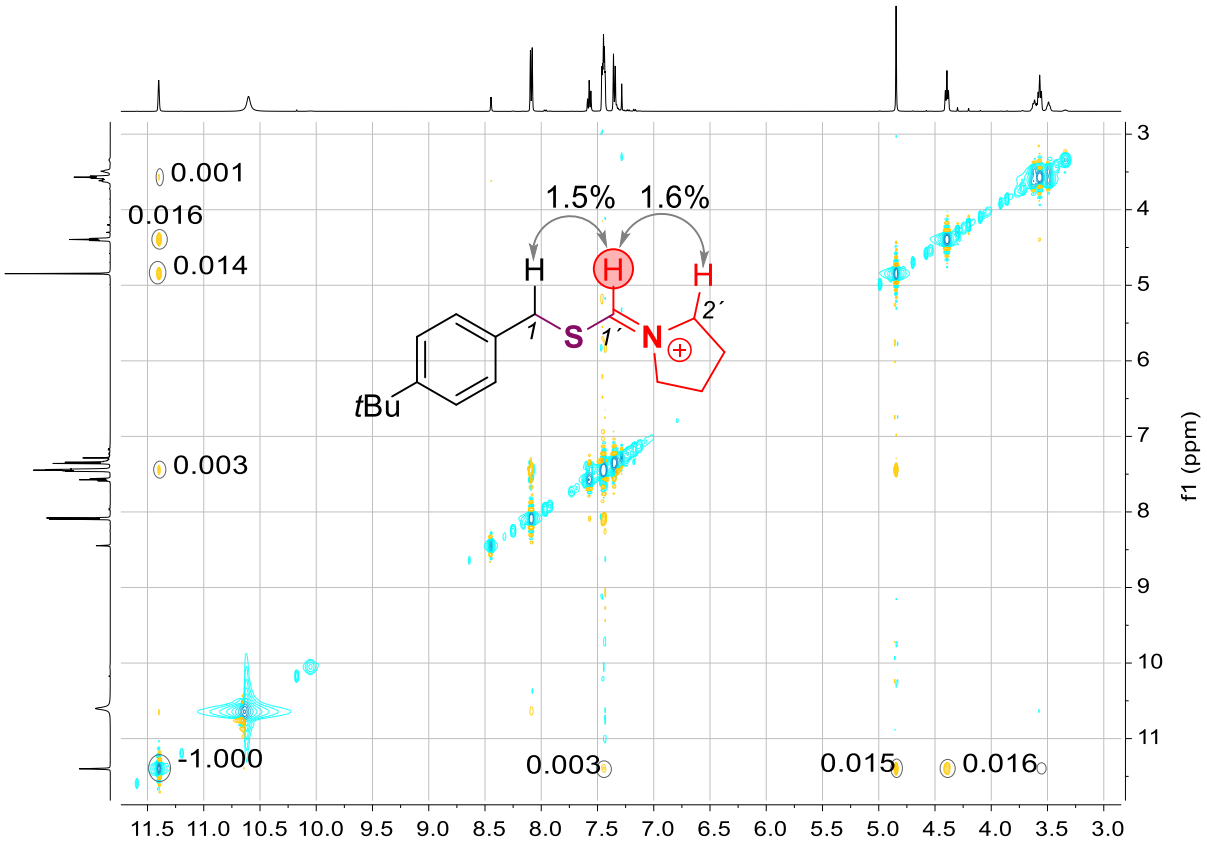
M ($C_{16}H_{24}NSCl$) = 297.89 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 11.40 (s, 1H, 1'-H), 7.46-7.43 (m, 2H, 3-H), 7.36-7.34 (m, 2H, 4-H), 4.85 (s, 2H, 1-H), 4.39 (t, $^{3}J_{2',3'}$ = 6.9 Hz, 2H, 2'-H), 3.57 (t, $^{3}J_{5',4'}$ = 6.9 Hz, 2H, 5'-H) 2.24-2.19 (m, 2H, 4'-H), 2.17-2.12 (m, 2H, 3'-H), 1.27 (s, 9H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 179.69 (C-1'), 151.86 (C-5), 131.23 (C-2), 129.22 (C-3), 126.28 (C-4), 57.86 (C-2'), 52.53 (C-5'), 39.13 (C-1), 34.70 (C-6), 31.27 (C-7), 25.22 (C-3'), 24.97 (C-4').



^{1}H NMR spectrum *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium chloride (**8p**, 500 MHz, $CDCl_3$).

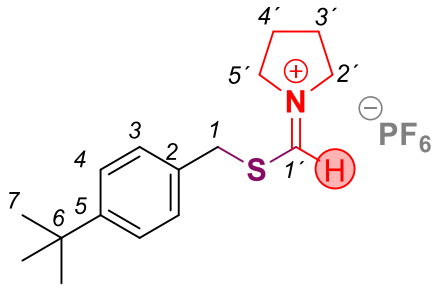


^{13}C NMR spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium chloride (**8p**, 126 MHz, $CDCl_3$).



NOESY spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium chloride (**8p**, 500 MHz, $CDCl_3$).

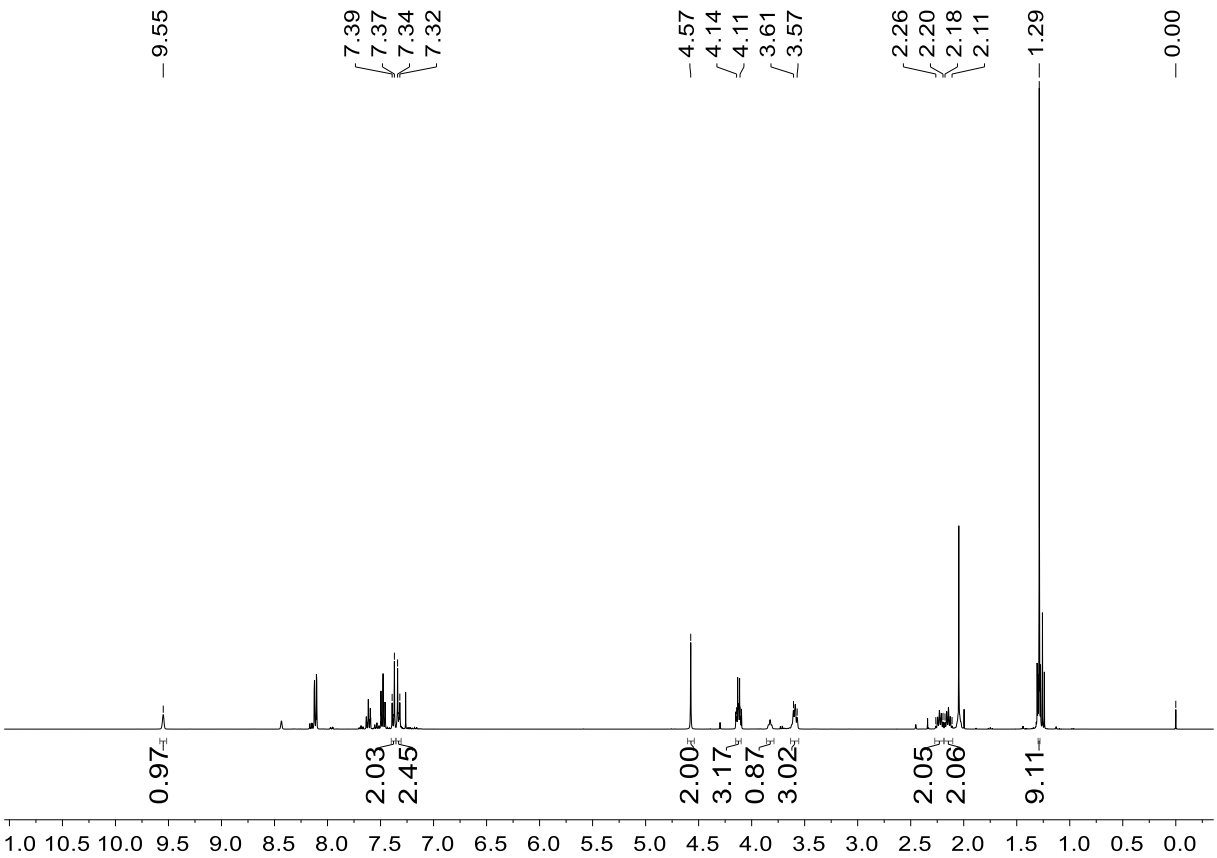
2.4.1.3. Synthesis of *N*-((4-*tert*-Butylphenyl)methylidene) Pyrrolidinium Hexafluorophosphate (8p')



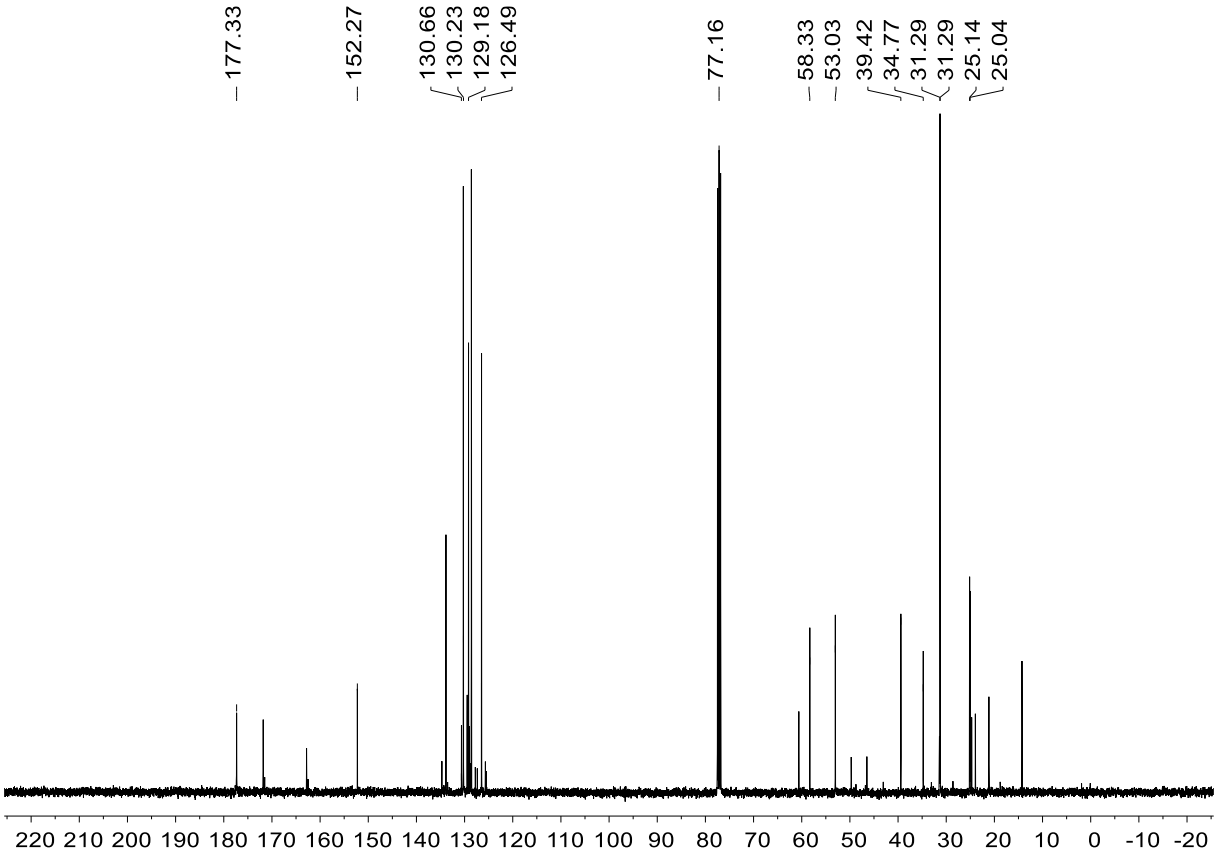
8p´8p'

DTT-450b: In alignment to general protocol B (chapter 2.2.2, page 10) a 4 mL vial was charged with 4-tert-butylbenzylthiol **6p** (238.1 µL, 202.4 mg, 1.00 mmol, 1.00 equiv), FPyr (123.9 µL, 128.9 mg, 1.30 mmol, 1.30 equiv), $NaPF_6$ (217.8 mg, 1.30 mmol, 1.30 equiv) and dry MeCN (0.50 mL, 2.0 M). Subsequently, BzCl (139.4 µL, 168.7 mg, 1.20 mmol, 1.20 equiv) was added and the reaction mixture was stirred at room temperature. After 5 h, a 50 µL of reaction mixture was withdrawn using an Eppendorf pipette, transferred to 10 mL pointed-shaped flask and dried at 20 mbar for 5 min at the rotary evaporator. The remaining solid was dissolved in $CDCl_3$ (600 µL) and the resulting suspension was filtered through a glass pipette containing a wool plug and a 5 mm layer of $MgSO_4$ into a NMR tube. The ^{1}H NMR proved full conversion of thiol **7p** and since no other product could be observed the yield of **8p´** was quantitative (≥98%). After 7 d of storage no decomposition had occurred, since the ^{1}H NMR remained unaltered.

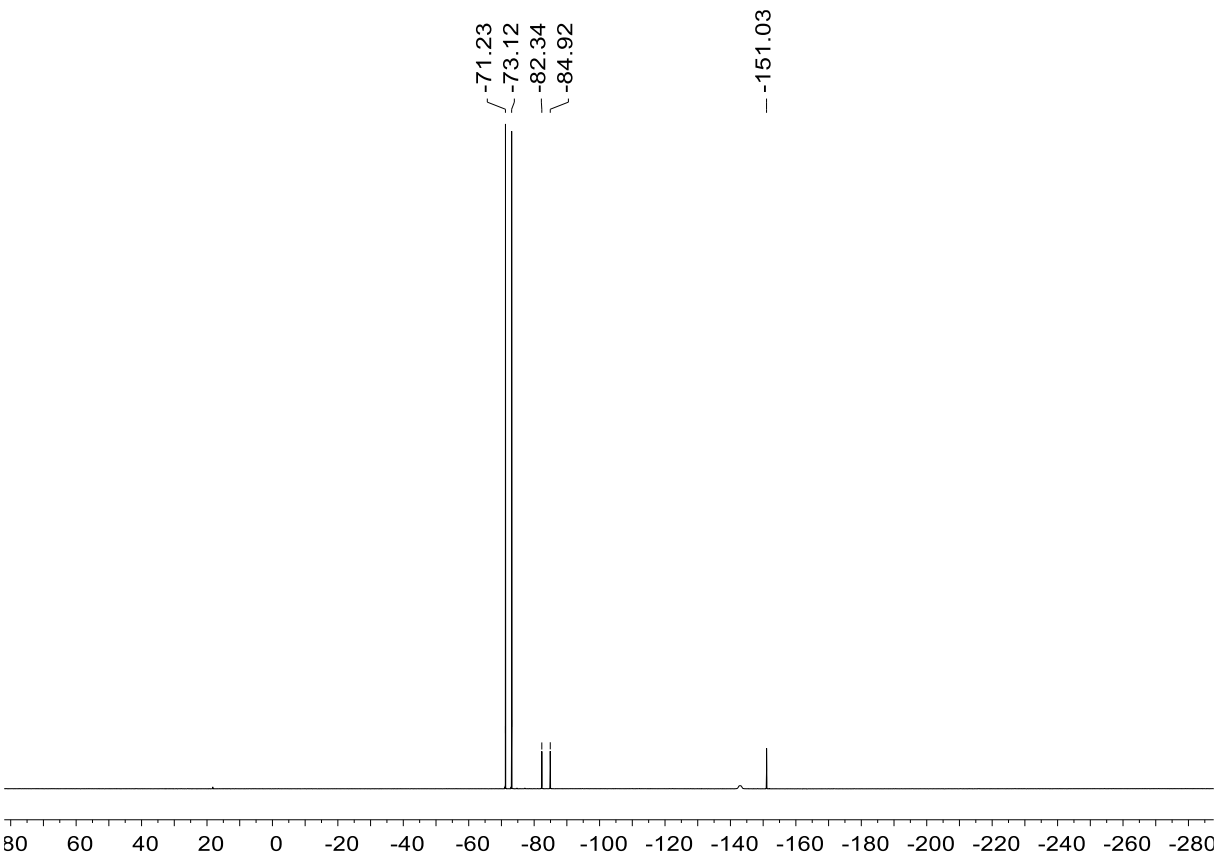
M ($C_{16}H_{24}F_6NPS$) = 407.40 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 9.47 (s, 1H, 1'-H), 7.39-7.37 (m, 2H, 3-H), 7.34-7.32 (m, 2H, 4-H), 4.57 (s, 2H, 1-H), 4.14-4.11 (m, 2H, 2'-H), 3.61-3.57 (m, 2H, 5'-H), 2.26-2.20 (m, 2H, 4'-H), 2.18-2.11 (m, 2H, 3'-H), 1.29 (s, 9H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 177.33 (C-1'), 152.27 (C-5), 130.23 (C-2), 129.18 (C-4), 126.49 (C-3), 58.33 (C-2'), 53.03 (C-5'), 39.42 (C-1), 34.77 (C-6), 31.29 (C-7), 25.14 (C-4'), 25.04 (C-3'); **^{31}P NMR** (162 MHz, $CDCl_3$) δ [ppm] = -143.64 (sept, $^1J_{P-F}$ = 705 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] = -72.18 (d, $^1J_{P-F}$ = 709 Hz).



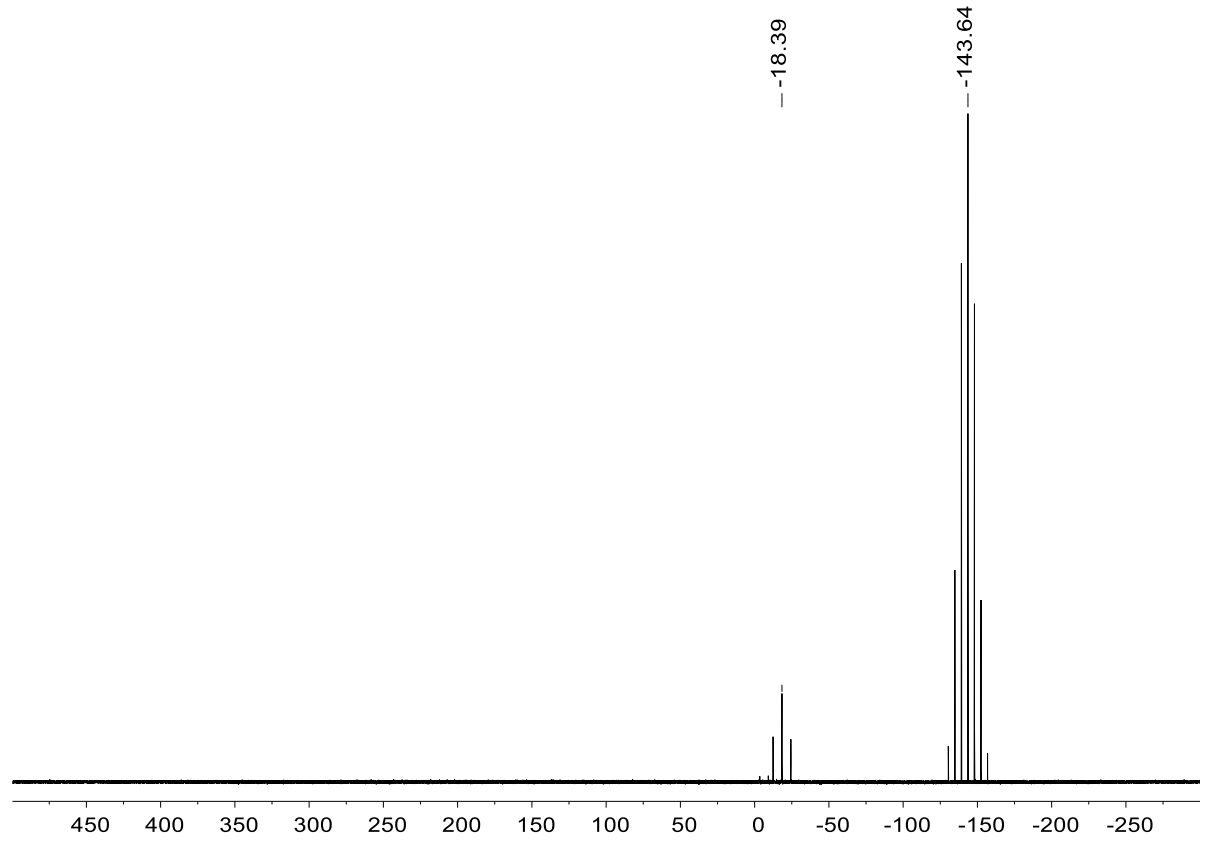
^{1}H NMR spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium hexafluorophosphate after 1 h of reaction duration (**8p'**, 400 MHz, $CDCl_3$).



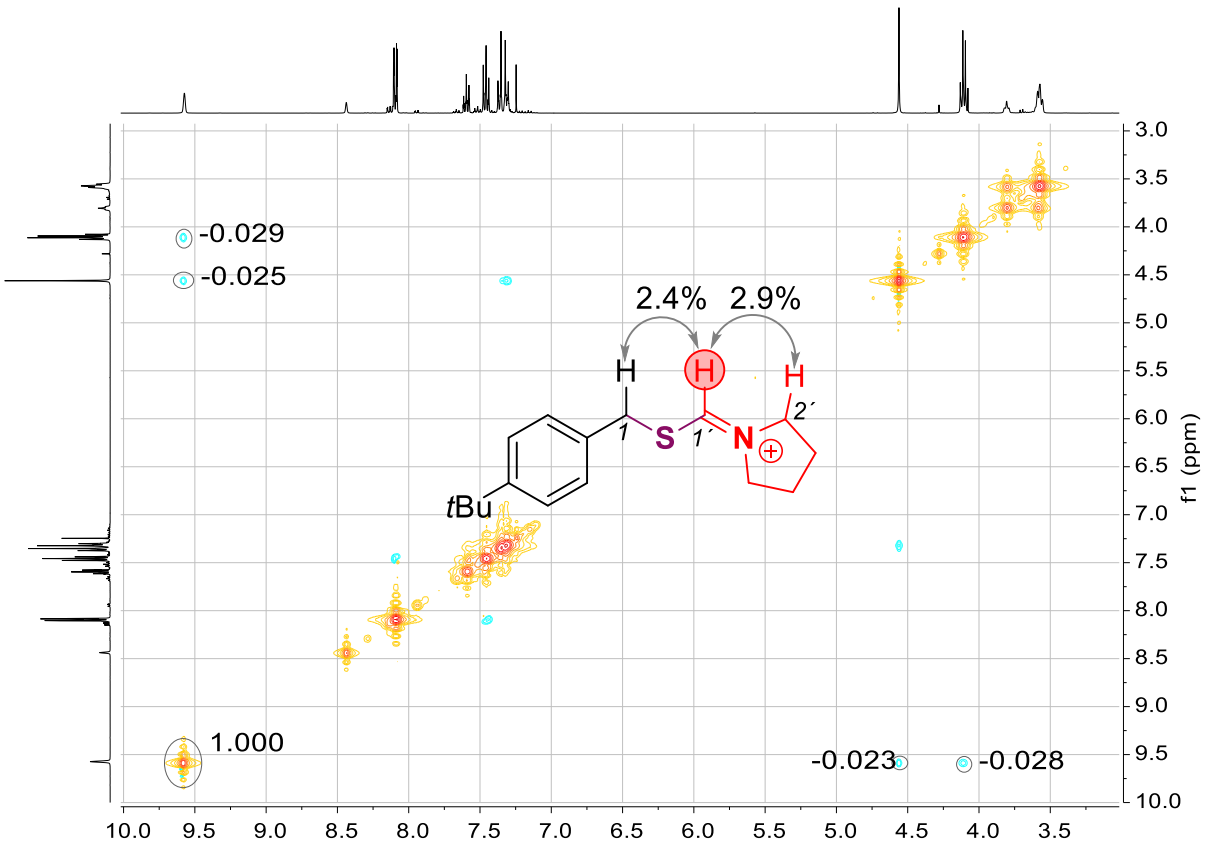
^{13}C NMR spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium hexafluorophosphate (**8p'**, 101 MHz, $CDCl_3$).



^{19}F NMR spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium hexafluorophosphate (**8p'**, 376 MHz, $CDCl_3$).



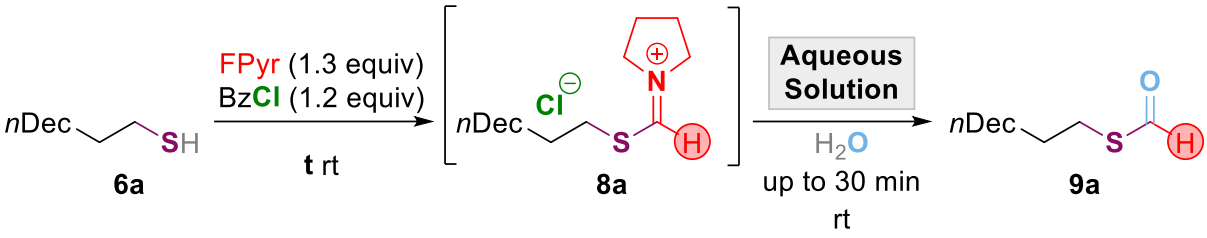
^{31}P NMR spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium hexafluorophosphate (**8p'**, 162 MHz, $CDCl_3$).



NOESY spectrum of *N*-((4-*tert*-butylphenyl)methylidene) pyrrolidinium hexafluorophosphate (**8p'**, 400 MHz, $CDCl_3$).

2.4.2. Synthesis of Thiofomates of Type 9

2.4.2.1. Synthesis of *S*-1-Dodecyl Thioformate (9a)



Entry	Aqueous Solution (M)	Yield 9a (%)	Yield 8a (%)	Yield 6a (%)
1[a]	$NaHCO_3$ (1.1 M)	37	4	40
2[a]	NaOH (1.0 M)	/	/	29
3[a]	H_2O	37	/	42
4[b]	NaOAc (1.0 M)	67	/	n.d.
5[b]	Washing with NaOAc (1.0 M)	81	/	n.d.

a. yield determined with mesitylene as internal NMR standard. B. Yield based on isolated material after chromatography.

Formylation of dodecylthiol **6a** under standard conditions provided thioformate **9a** in moderate yield of 37% (entry 1). Since the crude material contained large portions of starting material (40%), the low yield is reasoned most likely by hydrolysis of the title compound during the work up. Indeed, when the reaction was quenched with 1 M NaOH solution, no thioester was observed (entry 2). Water instead of saturated $NaHCO_3$ did not allow for an enhanced yield (entry 3). However, mildly basic NaOAc enabled the production of thioester **9a** in 67% yield (entry 4). Dilution of the reaction mixture with EtOAc and washing of the collected organic phases with 1 M NaOAc solution minimized the contact of the thioformate with water and consequently resulted in an improved yield of 81%.

Entry 1, DTT-370: As delineated in general procedure A (chapter 2.2.1, page 8) 1-dodecanethiol (**6a**, 101.2 mg, 0.50 mmol, 1.00 equiv) was allowed to react with FPyr (71.5 µL, 74.3 mg, 0.75 mmol, 1.50 equiv) and BzCl (75.5 µL, 91.37 mg, 0.65 mmol, 1.30 equiv) in MeCN (0.25 mL, 2.0 M) for 18 h. In deviation from the general protocol saturated **$NaHCO_3$** solution (2.0 mL, 4.40 equiv, 1.1 M) was added to the reaction mixture and the resulting mixture was stirred at rt for a further 30 min. Then, the mixture was taken up with a 20 mL syringe and the reaction vial was successively rinsed with EtOAc (4 mL) and water (3 mL), the collected organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. the ^{1}H NMR spectrum of the crude material (184.5 mg, 160%) with mesitylene as internal standard showed dodecyl formate **9a** in 37% and thiol **6a** in 40% yield, which corresponds to 60% conversion based on re-obtained starting material.

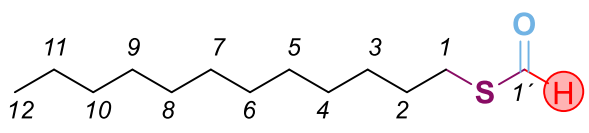
Entry 2, DTT-377: The title compound was prepared according general procedure A (chapter 2.2.1, page 8) using 1-dodecanethiol **7a** (101.2 mg, 0.50 mmol, 1.00 equiv), FPyr (1.50 equiv),

and BzCl (1.30 equiv) in MeCN (0.25 mL, 2.0 M) under stirring for 18 h. The work up was carried out as described in entry 1 with the deviation that 1.0 N aqueous **NaOH** solution (2.0 mL, 4.00 equiv) was used instead of $NaHCO_3$. ^1H NMR spectroscopy of the crude material (134.3 mg, 116%) with mesitylene as internal standard revealed 71% conversion based on re-isolated thiol **6a**, dodecyl formate **9a** could not be observed at all.

Entry 3, DTT-387_2: Following general procedure A (chapter 2.2.1, page 8) 1-dodecanethiol **7a** (101.2 mg, 0.50 mmol, 1.00 equiv) was permitted to react with FPyr (1.50 equiv) and BzCl (1.2 equiv) in MeCN (0.25 mL, 2.0 M) for 18 h. The work up was performed as delineated in entry 1 with the deviation that H_2O (2.0 mL, 2.00 equiv) was applied for quenching instead of $NaHCO_3$. Eventually, the crude material (137.0 mg, 119%) was subjected to ^1H NMR spectroscopy with mesitylene as internal standard, which proved dodecyl formate **9a** in 37% and thiol **6a** in 42% yield, respectively.

Entry 4, DTT-395: Based on general protocol A (chapter 2.2.1, page 8) the title compound was produced from 1-dodecanethiol (**6a**, 404.0 mg, 2.00 mmol, 1.00 equiv), FPyr (247.8 µL, 257.7 mg, 2.60 mmol, 1.30 equiv) and BzCl (267.2 µL, 323.3 mg, 2.40 mmol, 1.20 equiv) in MeCN (1.0 mL, 2.0 M) under stirring for 18 h. The work up conducted out as stated in entry 2 with the deviation that 1.0 M NaOAc solution (2.0 mL, 1.0 equiv) was used instead of $NaHCO_3$. After work up, ^1H NMR of the crude product (614.1 mg, 133%) verified 71% conversion of thiol **6a** (ratio of dodecyl thiobenzoate / dodecyl formate / dodecyl thiol 4:67:29). Finally, purification with the aid of column chromatography on silica gel (10 g, ratio weight crude product/SiO_2 1:16) using MTBE/*n*-heptane 1:99 as solvent mixture and drying at the rotary evaporator at 20 mbar for 5 min yielded formate **9a** as a colourless oil (312.1 mg, 1.36 mmol, 68%).

Entry 5, DTT-453: Following general protocol A (chapter 2.2.1, page 8) dodecyl thioformate **9a** was synthesized from 1-dodecanethiol (**6a**, 404.0 mg, 2.00 mmol, 1.00 equiv) using FPyr (247.8 µL, 257.7 mg, 2.60 mmol, 1.30 equiv) and BzCl (267.2 µL, 323.3 mg, 2.40 mmol, 1.20 equiv) in MeCN (1.0 mL, 2.0 M). After 5 h of stirring at rt, and aqueous work up, ^1H NMR of the crude product (1018 mg, 221%) verified 77% conversion of thiol **6a** (relation of dodecyl thiobenzoate / dodecyl formate / dodecyl thiol 2:75:23). Finally, purification by means of column chromatography on silica gel (14.5 g, ratio weight crude product/SiO_2 1:13) with EtOAc/*n*-heptane 1:99 as solvent mixture and drying at the rotary evaporator at 20 mbar for 5 min furnished thioester **9a** as a colourless oil (374.0 mg, 1.62 mmol, 81%).

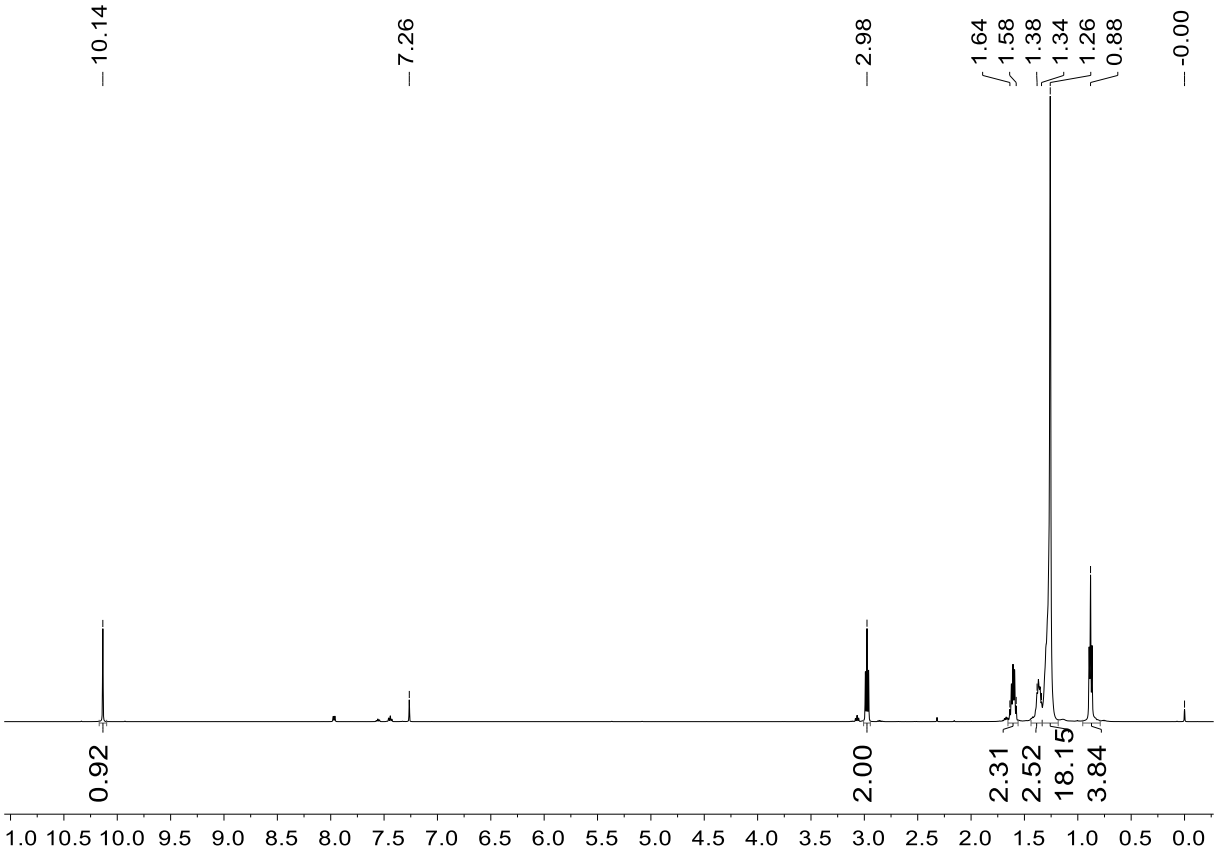


9a

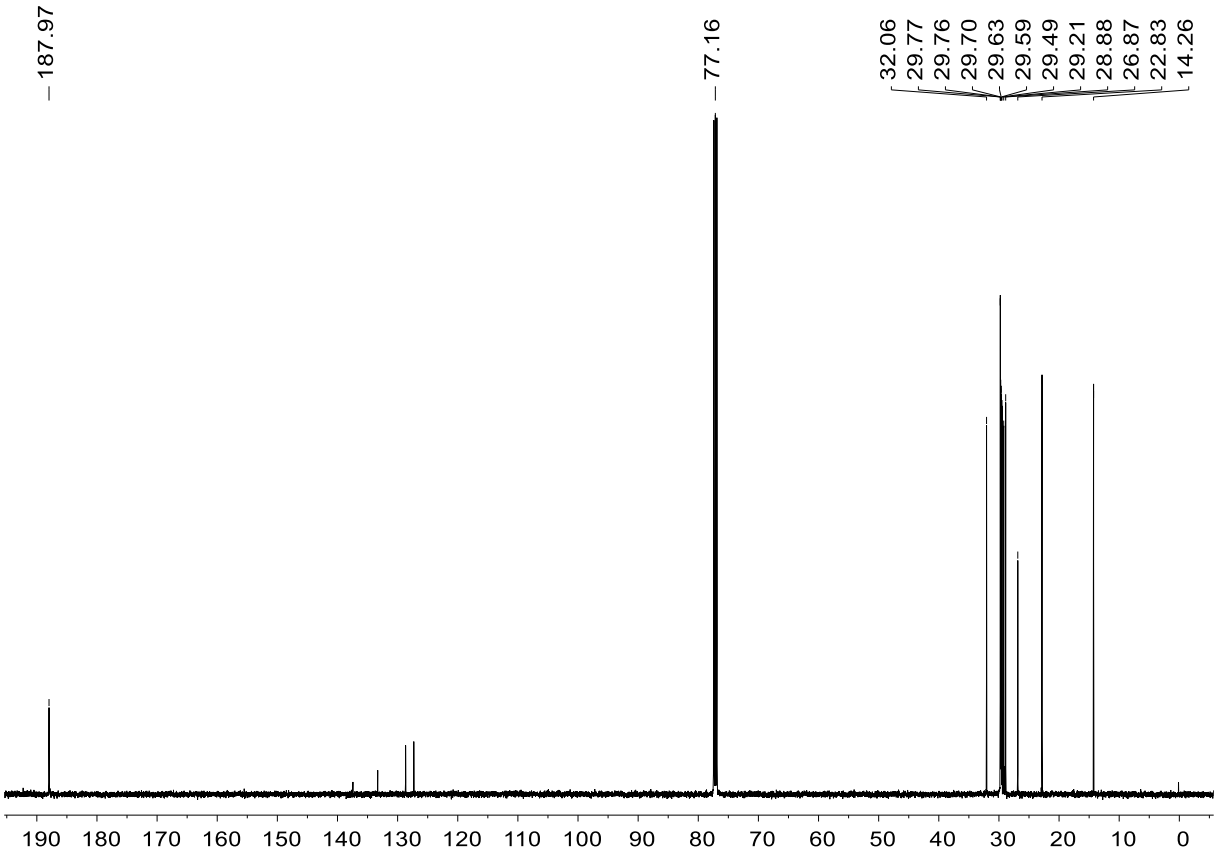
M ($C_{13}H_{26}OS$) = 230.41 g/mol; $\mathbf{r_f}$ (EtOAc/*n*-heptane 1:99) = 0.27; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 10.14 (s, 1H, 1'-H), 2.98 (s, 2H, 1-H), 1.60 (ψ-pent, ^3J = 7.7 Hz, 2H, 2-H), 1.38-1.34 (m, 2H, 3-H) 1.34-1.26 (m, 16H, 4-H to 11-H), 0.88 (t, $^3J_{12,11}$ = 7.7 Hz, 3H, 12-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 187.97 (C-1'), 32.06 (C-10 or C-11), 29.77, 29.79,

29.70, 29.63, 29.59, 29.49 (C-4 to C-9), 29.21 (C-2), 28.88 (C-3), 26.87 (C-1), 22.83 (C-10 or C-11), 14.26 (C-12); **GC MS** (EI, 70 eV) m/z [u] = 201 (100, $[M\text{-}CHO]^+$), 193 (22, $[M\text{-}SCHO]^+$), 97 (14, $[heptenyl]^+$), 97 (22, $[hexenyl]^+$), 69 (19, $[pentenyl]^+$), 55 (28, $[butenyl]^+$).

The NMR data is in agreement with literature.[16]

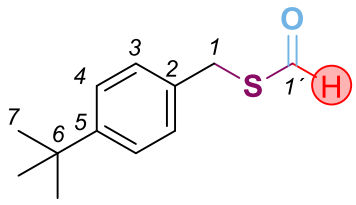


^{1}H NMR spectrum of S-1-dodecyl thioformate (**9a**, 500 MHz, $CDCl_3$)



^{13}C NMR spectrum of S-1-dodecyl thioformate (**9a**, 126 MHz,$CDCl_3$).

2.4.3. Synthesis of S-(4-*tert*-Butylbenzyl) Thioformate (9p)

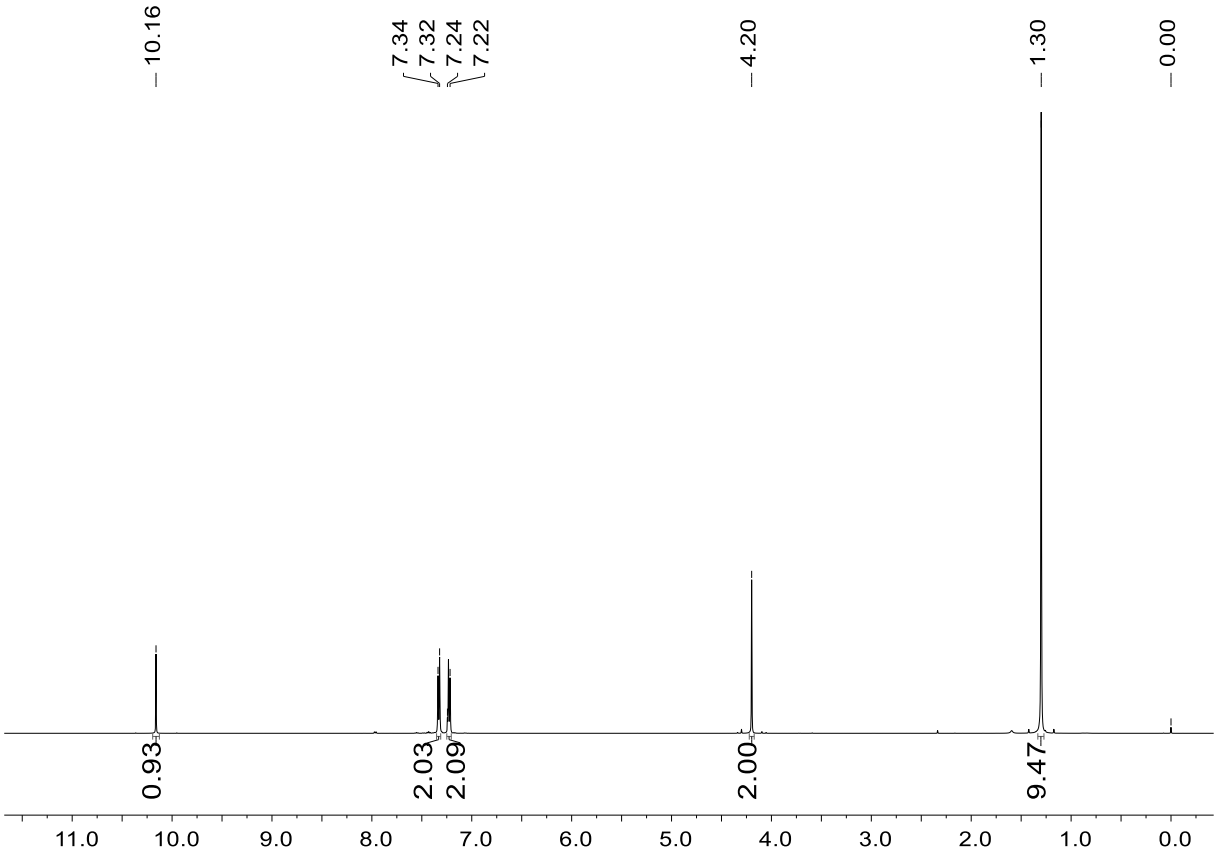


9p

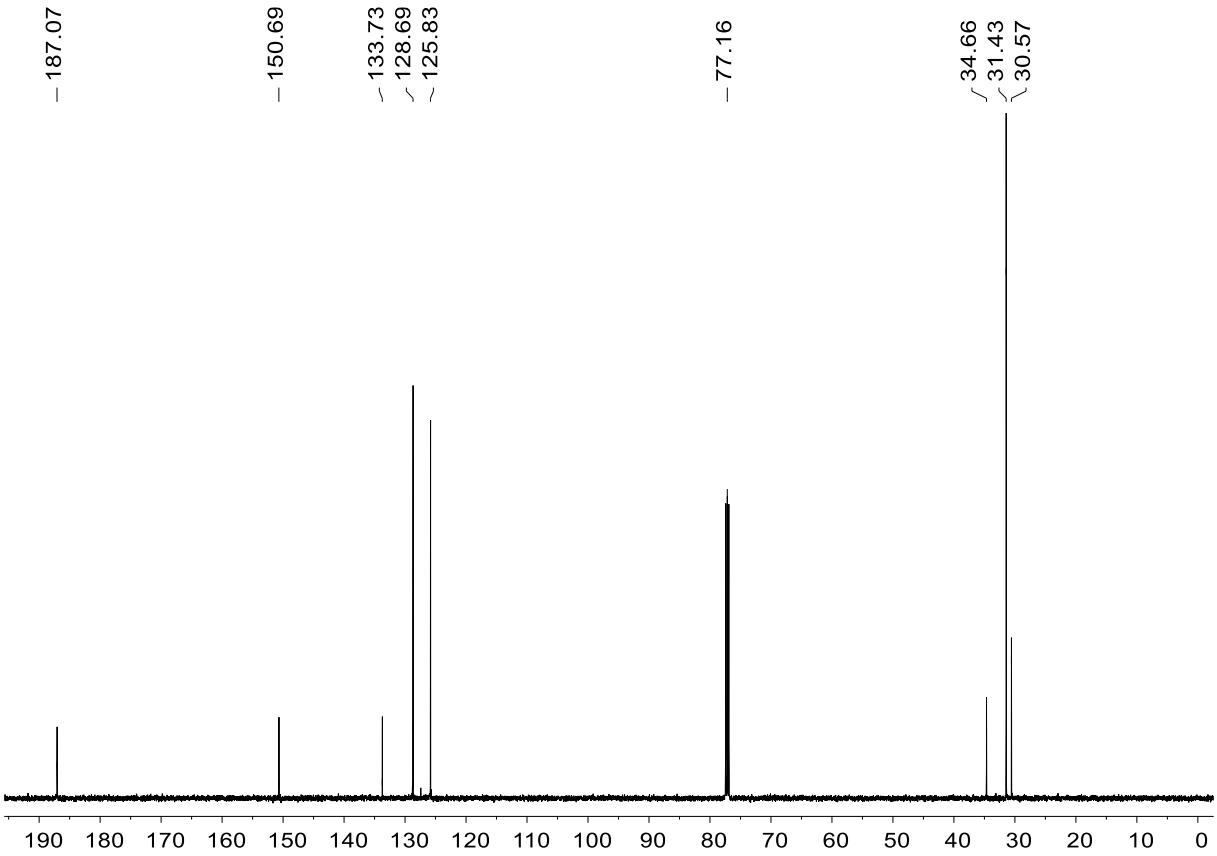
DTT-452: Based on general protocol A (chapter 2.2.1, page 8) 4-*tert*-butylbenzyl thiol (**6p**, 373.2 µL, 360.6 mg, 2.00 mmol, 1.00 equiv) was reacted with FPyr (247.8 µL, 257.7 mg, 2.60 mmol, 1.30 equiv) and BzCl (267.2 µL, 323.3 mg, 2.40 mmol, 1.20 equiv) in MeCN (1.0 mL, 2.0 M) for 5 h. After aqueous work up, ^{1}H NMR of the crude material (1.000 g, 240%) verified ≥98% conversion of thiol **6p**. Finally, purification with the aid of column chromatography on silica gel (14.2 g, ratio weight crude product/SiO_2 1:14) using EtOAc/*n*-heptane 1:99 as solvent mixture and drying at the rotary evaporator for 5 min at 20 mbar provided the title compound as a colourless oil (353.0 mg, 1.69 mmol, 85%).

M ($C_{12}H_{16}OS$) = 208.32 g/mol; $\mathbf{r_f}$ (EtOAc/*n*-heptane 1:99) = 0.39; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 10.16 (s, 1H, 1'-H), 7.34-7.32 (m, 2H, 4-H), 7.24-7.22 (m, 2H, 3-H), 4.20 (s, 2H, 1-H), 1.30 (s, 9H, 7-H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 187.07 (C-1), 150.69 (C-6), 133.73 (C-2), 128.69 (C-3), 125.83 (C-4), 34.66 (C-6), 31.43 (C-7), 30.57 (C-1); **GC MS** (EI, 70 eV) m/z [u] = 208 (21, $[M]^+$), 193 (42, $[M\text{-}CH_3]^+$), 165 (9), 148 (14), 147 (100, $[M\text{-}SCHO]^+$), 132 (32),131 (15), 117 (22), 115 (13), 105 (10), 91 (17, $[Bn]^+$), 77 (4, $[Ph]^+$); **HR MS** (EI, $[C_{12}H_{16}OS]^+$) calc. 208.09164 u, found 208.0921 u.

The NMR data is in agreement with literature.[16]



^{1}H NMR spectrum *S*-(4-*tert*-butylbenzyl) thioformate (**9p**, 500 MHz, $CDCl_3$).



^{13}C NMR spectrum *S*-(4-*tert*-butylbenzyl) thioformate (**9p**, 126 MHz, $CDCl_3$).

3. Appendix

3.1. List of Abbreviations

$(1\text{-PE})_2$F = N,N-bis((S)-1-phenylethyl)formamide

1-PEF = (S)-N-(1-phenylethyl)formamide

2-MeTHF = 2-methyl tetrahydrofurane

aq. = aqueous

BZ = Ben Zoller

BzCl = benzoyl chloride

conv. = conversion

DBF = N,N-dibenzylformamide

DMA = dimethylacetamide

DMF = dimethylformamide

equiv = equivalents

FPyr = 1-formylpyrrolidine

MeCN = acetonitrile

MF = methylformamide

mp. = melting point

MTBE = methyl-*tert*-butylether

*n*Hep = *n*-heptane

NMR = nuclear magnetic resonance

*n*Pen = *n*-peptane

THF = tetrahydrofurane

TMS = tetramethylsilane

References

1. Huy, P. H.; Motsch, S.; Kappler, S. M. *Angew. Chem. Int. Ed*. **2016**, *55*, 10145–10149.
2. Kohlmeyer, C.; Schäfer, A.; Huy, P. H.; Hilt, G. *ACS Catal*. **2020**, *10*, 11567–11577.
3. Barluenga, J.; Campos, P. J., Gonzalez-Nuñez, E.; Asensio, G. *Synthesis* **1985**, 426.
4. Ram, R. N.; Meher, N. K. *Tetrahedron* **2002**, *58*, 2997–3001.
5. Álvarez-Calero, J. M.; Jorge, Z. D.; Massanet, G. M. *Org. Lett*. **2016**, *18*, 6344–6347.
6. Yoshida, K.; Matsumoto, Y.; Masuda, J.; Kitagaki, S. *Synlett* **2022**, *33*, 1570.
7. Ramírez-Vázquez, D. G.; Viñas-Bravo, O.; Martínez-Pascual, R.; Pérez-Picaso, L.; Castro-Cerritos, K. V.; *Synth. Commun*. **2021**, *51*, 585-592.
8. Fang, W.-Y.; Zha, G.-F.; Qin, H.-L. *Org. Lett*. **2019**, *21*, 8657–8661.
9. Johnson, T. C.; Clarkson, G. J.; Wills, M. *Organometallics* **2011**, *30*, 1859-1868.
10. Dutta, S. *Carbohydr. Res*. **2020**, *497*, 108140.
11. Fernández-Mateos, A.; Madrazo, S. E.; Teijón, P. H.; González, R. R. *Eur. J. Org. Chem*. **2010**, *2010*, 856–861.
12. Toop, H. D.; Don, A. S.; Morris, J. C. *Org. Biomol. Chem*. **2015***, 13*, 11593–11596.
13. Huy, P. H.; Filbrich, I. *Chem. Eur. J*. **2018**, *24*, 7410-7416.
14. Craig, A. J.; Ermolovich, Y.; Cameron, A.; Rodler, A.; Wang, H.; Hubert, M.; Björkling, F.; Molchanova, N.; Brimble, M. A.; Moodie, W. K.; Svenson, J. *ACS Med. Chem. Lett*. **2023**, *14*, 802–809.
15. Murakami, S.; Brudy, C.; Bachmann, M.; Takemoto, Y.; Pieber; B. *Synthesis* **2023**, *55*, 1367-1374.
16. Tanaka, K.; Ajiki, K. *Org. Lett*. **2005**, *7*, 1537–1539.