Supplementary Material (ESI) for Chemical Communications

Supplementary information for:

Synthesis and microwave assisted polymerization of fluorinated 2-phenyl-2-oxazolines: The fastest 2-oxazoline monomer to date

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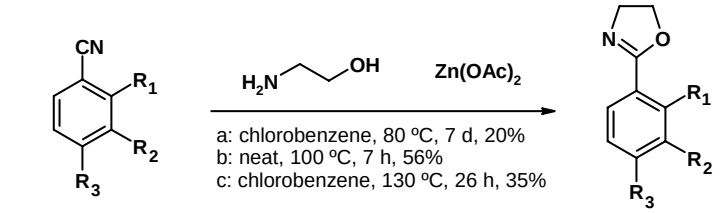
Synthesis Discussion

Although the synthesis of *o*-fluoro[1, 2] and *m*-fluoro[3] 2-phenyl-2-oxazoline were already reported starting from the corresponding aromatic acid or acid chlorides, we investigated the synthesis of the monofluorinated oxazolines **2a-c** from the corresponding benzonitriles according to a modified one step synthesis procedure (Scheme 2).[4]



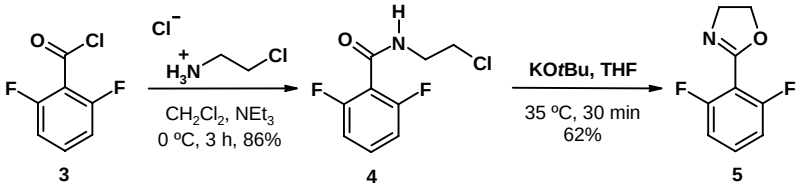
1a: R_1 = F; R_2 = R_3 = H
1b: R_2 = F; R_1 = R_3 = H
1c: R_3 = F; R_1 = R_2 = H

2a: R_1 = F; R_2 = R_3 = H
2b: R_2 = F; R_1 = R_3 = H
2c: R_3 = F; R_1 = R_2 = H

Scheme 1: Schematic representation of the one-step synthesis of the monofluoro-2-phenyl-2-oxazolines **2a-c**.

The monofluoro-benzonitriles **1a-c** were treated with 2-ethanolamine in the presence of a Lewis-acid catalyst, namely $Zn(OAc)_2$, to yield the desired oxazolines **2a-c** in moderate yields. The *meta*-fluorinated oxazoline *m*FOx **2b** could be isolated after a 7 h reaction at 100 °C in 56% yield. *m*FOx **2b** was obtained as liquid and could easily be purified by distillation. To achieve a homogenous reaction mixture, **1c** was dissolved in chlorobenzene which requires a significantly longer reaction time of 26 h at 130 °C yielding 35% of *p*FOx **2c**. The synthesis of *o*FOx **2a**, however, was accompanied by side reactions resulting in the formation of two additional products besides the desired oxazoline **2a**. The oxazoline ring formation to **2a** competes with a nucleophilic aromatic substitution reaction where the fluorine is substituted by ethanolamine. Once formed, this side product also undergoes an oxazoline ring formation with excess ethanolamine. The

formation of both side products was confirmed by GC-MS analysis. Reducing the reaction temperature to 80 °C to avoid the side product formation had only little success. The reaction becomes extremely slow while minor side product formation still takes place. Nonetheless, the reaction at 80 ºC was monitored by GC-MS and after seven days the constitution of the reaction mixture did not change significantly although additional 2-ethanolamine was added frequently. As a result, the reaction was stopped containing 31% **1a** and 45% **2a** together with 24% of side products. After filtration on SiO_2 and distillation, *o*FOx **2a** could finally be isolated in 20% yield. Due to the undesired side product formation during the synthesis of **2a** we changed our synthetic strategy to synthesize the *ortho*-difluoro analogue **5** *via* a two step procedure (Scheme 3), which is slightly different from the previously reported synthetic method for this compound using ethanol amine.[5]



Scheme 2: Schematic representation of the two-step synthesis of the *o*-difluoro-2-phenyl-2-oxazoline **5**.

Starting from the acid chloride **3** one can obtain amide **4** *via* a modified one step procedure in good yields of 86%.[6] Finally, the desired oxazoline **5** can be obtained by basic elimination of hydrogen chloride. As bases Na_2CO_3, KOH and potassium *tert*-butoxide were used. With sodium carbonate no conversion of **4** took place after stirring for 16 h at room temperature, while stirring for 16 h in the presence of KOH leads to the formation of **5** in 40% yield. The use of potassium *tert*-butoxide at a slightly higher

temperature of 35 °C and a short reaction time of only thirty minutes provided *o*DFOx **5** in 62% yield after distillation.

Experimental Section

Materials and Instrumentation. Analytical-grade solvents were purchased from Biosolve Ltd. All chemicals were obtained from Aldrich (Germany) except the fluorinated compounds which were purchased from Fluorochem (UK). Methyl tosylate and the 2-oxazolines were distilled prior to use (the latter over barium oxide) and stored under argon. Nitromethane, dried over molecular sieves (3 Å), was obtained from Fluka.

The polymerizations were performed in capped reaction vials (0.5 to 2 mL) in the single-mode microwave reactor Emrys Liberator (Biotage), equipped with a noninvasive IR sensor (accuracy: 2% for the measurement of the reaction temperatures). These vials were heated, allowed to cool to room temperature, and filled with argon prior to use. The specific polymerization reactions were terminated by quenching the reaction mixtures at predefined times by the addition of 50 μL water.

GC measurements were performed using an Interscience Trace GC with a Trace Column RTX-5 connected to a PAL autosampler. For the injection of polymerization mixtures, a special Interscience liner with additional glass wool was used.

Gel permeation chromatography was measured on a Shimadzu GPC, equipped with a system controller SCL-10Avp, a LC-10AD pump, a RID-10A refractive index detector, a UV/VIS detector DPD-10A, a degasser DGU-14A and a CTO-10A column oven and two PSS GRAM 10μ, 8 × 300 mm, 1000/30 Å columns utilizing DMA/LiCl as eluent. The RI-detector was calibrated using readycal PS standards.

GC-MS measurements were performed on a Shimadzu, GC-17A (Column: DB-SMS, 5% Phenyl-/95% Dimethylpolysiloxane, length = 30 m, inner diameter = 0.25 mm, film thickness = 0.1 μm) connected to an AOC-20i Autoinjector and a GCMS-QP5050A mass spectrometer. Ionization was managed by EI (electron impact).

Elemental analyses EA were carried out on a EuroVector EuroEA3000 elemental analyzer for CHNS-O.

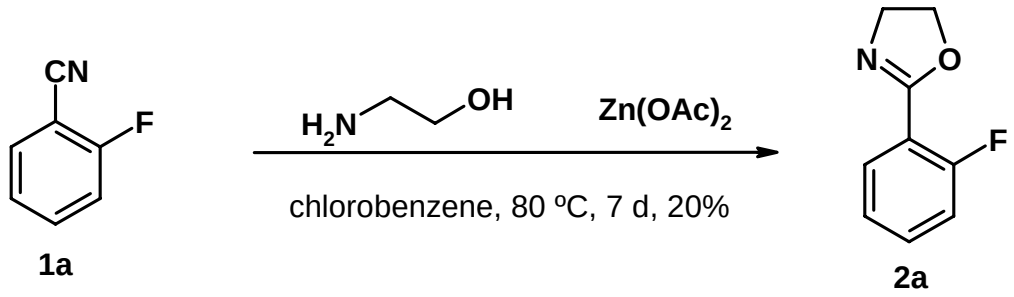
ESI-TOF measurements were performed utilizing a Bruker Daltonic Inc. BioTOF III spectrometer (m/z = 100 – 3000 Da at 2 GHz scan rate; resolution: 12000 – 30000 FWHM) coupled with an Agilent HPLC 1100 and a Gerstel MPS3 autosampler. (Eluent: methanol/water 80:20 isocratic. Sample concentration: 10 μmol/L in methanol. Sample volume: 4 μL).

All MALDI ToF MS experiments were performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer in linear mode. All spectra were obtained in the positive ion mode. Ionization was performed with a 337-nm pulsed nitrogen laser. Samples were prepared with a multiple-layer spotting technique utilizing DCTB as matrix and NaI as salt similar as described in literature [Meier, M. A. R.; Schubert, U. S. Rapid Commun. Mass Spectrom. 2003, 17, 713]. All data were processed using the Data Explorer software package (Applied Biosystems). All spectra are averaged over 500 laser shots over the complete sample area.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian AM-400 spectrometer in chloroform-d_3 or nitromethane-d_3 solutions and the chemical shifts are given relative to the residual solvent signal or hexafluoroisopropanol as internal standard.

Monomer synthesis:

Synthesis of 2-(*o*-Fluorophenyl)-2-oxazoline 2a.



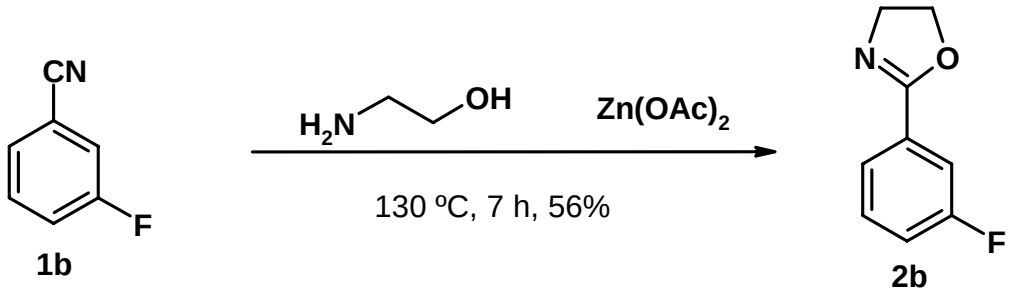
1a **2a**

A mixture of *o*-fluorobenzonitrile **1a** (10 mL, 11.38 g, 94 mmol) and zinc acetate-dihydrate (1.09 g, 5 mmol) was heated to 80 °C under argon. Subsequently, 2-aminoethanol (9 mL, 9.11 g, 149 mmol) was added dropwise within 15 minutes and the resulting mixture was stirred at 80 °C for 7 days. The reaction mixture was allowed to cool to ambient temperature and dichloromethane (150 mL) was added. The organic phase was washed with water (4×) and brine (2×). After drying over $MgSO_4$ and removing the solvent under reduced pressure, the crude product (12.3 g) was obtained as a red oily product. Further purification was performed by column chromatography (SiO_2, Eluent: cyclohexane/ethylacetate 3:1 + 2% NEt_3) yielding **2a** (3.34 g, 20.2 mmol) as a colorless liquid in 20% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.07 (t, 2H, ^3J (H, H) = 9.5 Hz, NCH_2), 4.37 (t, 2H, ^3J (H, H) = 9.5 Hz, OCH_2), 7.13 (m, 2H, *m*-H_{ar}), 7.41 (m, 1H, *p*-H_{ar}), 7.84 (t, *o*-H_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.21 (s, $N\underline{C}H_2$), 67.08 (s, OCH_2), 115.99 (d, ^2J (C, F) = 11 Hz, *i*-C_{ar}), 116.60 (d, ^2J (C, F) = 23 Hz, *m*-$C_{ar}F$), 123.90 (d, ^4J (C, F) = 3 Hz,

m-C_{ar}), 130.97 (s, *o*-C_{ar}), 132.78 (d, ^{3}J (C, F) = 9 Hz, *p*-C_{ar}), 161.13 (d, ^{1}J (C, F) = 258 Hz, *o*-C_{ar}F), 161.22 (d, ^{3}J (C, F) = 6 Hz, *N*=C*O*). ^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -109.66 (m). IR: $\tilde{\nu}$ [cm^{-1}] = 3073/2976 (CH), 2938/2906/2880 (CH_2), 1647 (C=N), 1613 (C=C), 1497 (CH), 1253/1111 (CF), 1222/1052 (CO), 765/742 (CH). MS: *m/z* (%) = 165 (47) [M^+], 135 (100) [M^+-CH_2O], 123 (10) [M^+-C_2H_4N], 95 (18) [M^+-C_3H_4NO]. EA: calculated: C 65.45; H 4.88; N 8.48. HR-MS (ESI+) calculated for $C_9H_8FNO + H^+$: 166.0663; found 166.0679; calculated for $C_9H_8FNO + Na^+$: 188.0482; found 188.0499.

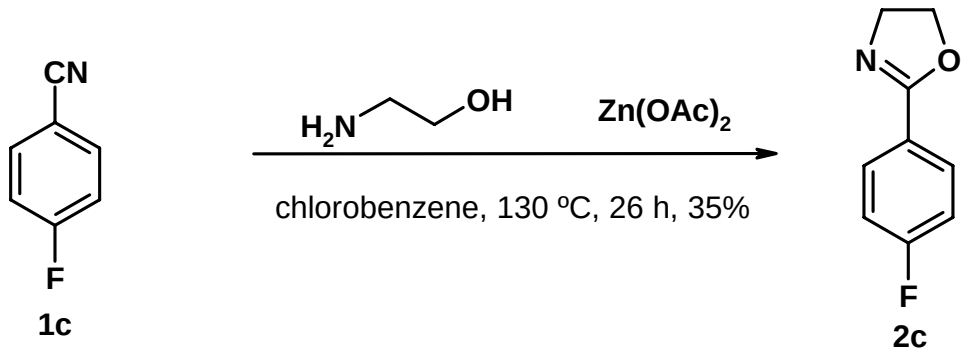
Synthesis of 2-(*m*-Fluorophenyl)-2-oxazoline 2b.



A mixture of *m*-fluorobenzonitrile **1b** (6.95 g, 57.4 mmol) and zinc acetate-dihydrate (642 mg, 2.9 mmol) was heated to 100 °C under argon and 2-aminoethanol (5.50 mL, 5.57 g, 91 mmol) was added drop wise within 15 minutes. The resulting mixture was stirred at 100 °C for 7 h. Subsequently, the reaction mixture was cooled to ambient temperature and dichloromethane (50 mL) was added. The organic phase was washed with water (4×), brine (2×) and dried over $MgSO_4$. After filtration and removing the solvent under reduced pressure, the slightly pinkish product was purified by distillation (64 °C at 0.03 Torr) to give **2b** (5.33 g, 32.3 mmol) as a colorless liquid in 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.99 (t, 2H, ^{3}J (H, H) = 9.5 Hz, NCH_2), 4.36 (t, 2H, ^{3}J (H, H) = 9.5 Hz, OCH_2), 7.10 (m, 1H, p-H_{ar}), 7.30 (m, 1H, o-H_{ar}), 7.58 (m, 1H, m-H_{ar}), 7.68 (m, 1H, m-$H_{ar}CF$). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.91 (s, $N\underline{C}H_2$), 67.71 (s, $O\underline{C}H_2$), 115.08 (d, ^{2}J (C, F) = 24 Hz, o-$C_{ar}F$), 118.12 (d, ^{2}J (C, F) = 21 Hz, p-C_{ar}), 123.81 (d, ^{4}J (C, F) = 3 Hz, o-C_{ar}), 129.80 (s, i-C_{ar}), 129.88 (d, ^{3}J (C, F) = 8 Hz, m-C_{ar}), 162.41 (d, ^{1}J (C, F) = 246 Hz, m-$C_{ar}F$), 163.46 (d, ^{4}J (C, F) = 3 Hz, N=$\underline{C}O$). ^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -112.77 (m). IR: $\tilde{\nu}$ [cm^{-1}] = 3076 (CH), 2977/2939/2907/2880 (CH_2), 1652 (C=N), 1612/1584 (C=C), 1453 (CH), 1359/1187 (CF), 1268/1054 (CO), 951/844 (CH), 711 (CH_2). MS: m/z (%) = 165 (60) [M^+], 135 (100) [M^+-CH_2O], 123 (11) [M^+-C_2H_4N], 108 (13) [M^+-C_2H_4NO], 95 (36) [M^+-C_3H_4NO]. HR-MS (ESI+) calculated for $C_9H_8FNO + H^+$: 166.0663; found 166.0658.

Synthesis of 2-(*p*-Fluorophenyl)-2-oxazoline 2c.

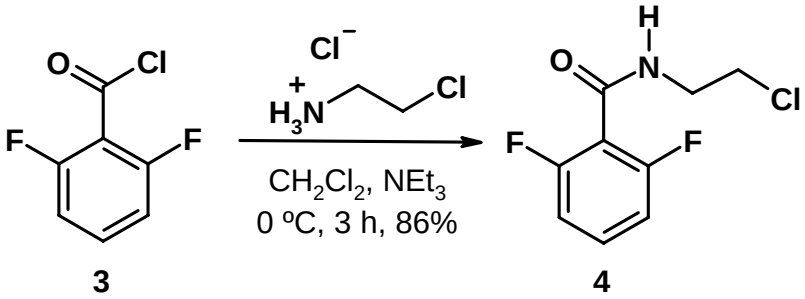


A mixture of *p*-fluorobenzonitrile **1c** (11.52 g, 95 mmol) and zincacetate-dihydrate (1.15 g, 5.2 mmol) in chlorobenzene (40 mL) was heated to 130 °C under argon. Subsequently, 2-aminoethanol (9 mL, 9.11 g, 150 mmol) was added within 15 minutes and stirring was continued at 130 °C for 26 h. The mixture was cooled to ambient temperature,

dichloromethane (50 mL) was added and the organic phase was washed with water (4×), brine (2×) and dried over $MgSO_4$. After removing the solvent under reduced pressure, a yellow oily crude product (7.20 g) was obtained. Further purification was achieved by column chromatography (SiO_2, Eluent: Cyclohexane/Ethylacetate 1:1 + 2% triethylamine) yielding **2c** (5.42 g, 32.8 mmol) as a colorless solid in 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.05 (t, 2H, ^3J (H, H) = 9.6 Hz, *N*CH_2), 4.43 (t, 2H, ^3J (H, H) = 9.6 Hz, *O*CH_2), 7.08 (m, 2H, *m*-H_{ar}), 7.95 (m, 2H, *o*-H_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.94 (s, *N*$\underline{C}H_2$), 67.73 (s, *O*$\underline{C}H_2$), 115.43 (d, ^2J (*m*-C_{ar}, F) = 23 Hz, *m*-C_{ar}), 124.00 (s, *i*-C_{ar}), 130.37 (d, ^3J (*o*-C_{ar}, F) = 9 Hz, *o*-C_{ar}), 163.74 (s, *N*=$\underline{C}O$), 164.64 (d, ^1J (*p*-C_{ar}, F) = 252 Hz, *p*-C_{ar}). ^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -108.27 (s). IR: $\tilde{\nu}$ [cm^{-1}] = 3060/2984 (CH), 2958/2941/2914/2887 (CH_2), 1651 (C=N), 1603/1508 (C=C), 1479 (CH), 1262/1065 (CO), 1199/1159 (CF), 846 (CH), 730 (CH_2). MS: *m/z* (%) = 165 (70) [M^+], 135 (100) [M^+-CH_2O], 123 (16) [M^+-C_2H_4N], 95 (36) [M^+-C_3H_4NO]. EA: calculated: C 65.45; H 4.88; N 8.48. found: C 65.32; H 4.91; N 8.22.

Synthesis of *N*-(2-Chloroethyl)-2-(2,6-Difluorophenyl)-acidamide 4.

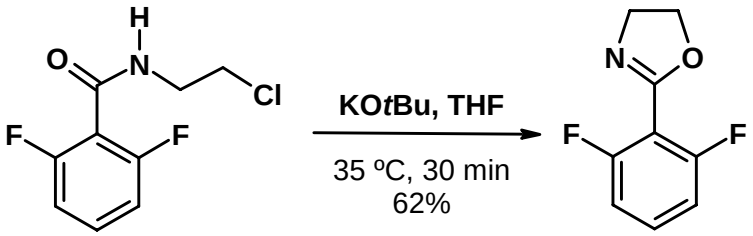


3 **4**

A suspension of 2,6-difluorobenzoic acid chloride **3** (14.07 g, 80 mmol) and 2-ethylammonium chloride (9.24 g, 80 mmol) in dry dichloromethane (150 mL) was cooled to 0 °C. Subsequently, triethylamine (25.8 mL, 18.75 g, 185 mmol) was added dropwise within one hour and the reaction mixture was stirred for two hours. The reaction was terminated by adding water (50 mL), the aqueous phase was twice extracted with dichloromethane (50 mL) and the combined organic phases were washed with water and brine. After drying over $MgSO_4$ the solvent was removed under vacuum and the crude product was purified by recrystallization from ethylacetate/cyclohexane yielding **4** (15.11 g, 69 mmol) as colorless crystals in 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.74 (t, 2H, ^3J (H, H) = 6 Hz, *N*CH_2), 3.81 (m, 2H, *O*CH_2), 6.41 (bs, 1H, *N*H), 6.96 (t, 2H, ^3J (H, H) = 8 Hz, *m*-H_{ar}), 7.38 (m, 1H, *p*-H_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 41.70/43.41 (2 × s, *N*$\underline{C}H_2$/*O*$\underline{C}H_2$), 111.93 (m, *m*-C_{ar}), 113.89 (t, ^2J (C, F) = 20 Hz, *i*-C_{ar}), 131.97 (t, ^3J (C, F) = 11 Hz, *p*-C_{ar}), 159.94 (dd, ^1J (C, F) = 246 Hz, ^3J (C, F') = 8 Hz, *o*-C_{ar}), 160.64 (s, $\underline{C}$=O). ^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -112.00 (t, 2F, ^4J (F, F) = 7 Hz, F-5). IR: $\tilde{\nu}$ [cm^{-1}] = 3353/3104 (NH), 3073 (CH), 2964/2939 (CH_2), 1643/1591 (C=C), 1625/1528 (C=O), 1365/1230/1195 (CF), 801 (CH), 768/655 (CCl). MS: *m/z* (%) = 219 (9) [M^+], 184 (7) [M^+-Cl], 170 (18) [M^+-CH_2Cl], 141 (100) [M^+-C_2H_5ClN], 113 (17) [M^+- C_3H_5ClNO]. EA: calculated: C 49.22; H 3.67; N 6.38. found: C 48.87; H 3.93; N 5.91.

Synthesis of 2-(2,6-Difluorophenyl)-2-oxazoline 5.



4 **5**

A solution of **4** (4.46 g, 20.3 mmol) in dry THF (45 mL) was heated to 35 °C and potassium *tert*-butoxide (3.46 g) was added portionwise within 30 minutes. After stirring another 30 minutes, the reaction was stopped by pouring the mixture into water (50 mL). The aqueous phase was extracted with dichloromethane (2 × 50 mL) and the combined organic phases were washed with water and brine. After drying over $MgSO_4$ and removing the solvent under reduced pressure, a colorless oily crude product (3.08 g) was obtained. Purification was performed by distillation (67 °C at 1 × 10^{-2} Torr) to give **5** (2.28 g, 12.5 mmol) in 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.07 (t, 2H, ^{3}J (H, H) = 10 Hz, *N*CH_2), 4.41 (t, 2H, ^{3}J (H, H) = 10 Hz, *O*CH_2), 6.92 (t, 2H, ^{3}J (H, F) = 8 Hz, *m*-H_{ar}), 7.35 (m, 1H, *p*-H_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.22 (s, *N*$\underline{C}H_2$), 67.58 (s, *O*$\underline{C}H_2$), 107.31 (t, ^{2}J (C, F) = 18 Hz, *i*-C_{ar}), 111.92 (dd, ^{2}J (C, F) = 18 Hz, ^{4}J (C, F') = 5 Hz, *m*-C_{ar}), 132.20 (t, ^{3}J (C, F) = 11 Hz, *p*-C_{ar}), 157.27 (s, *N*=$\underline{C}O$), 161.18 (dd, ^{1}J (C, F) = 256 Hz, ^{3}J (C, F') = 6 Hz, *o*-C_{ar}). ^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -109.20 (t, ^{4}J (F, F) = 8 Hz). IR: $\tilde{\nu}$ [cm^{-1}] = 3067 (CH), 2979/2908/2885 (CH_2), 1666 (C=N), 1622/1593 (C=C), 1467 (CH), 1253//1010 (CO), 1237/1195 (CF), 791 (CH), 738 (CH_2). MS: *m/z* (%) = 183 (37) [M^+], 153 (100) [M^+-CH_2O], 141 (9) [M^+-C_2H_4N], 126 (9) [M^+-C_2H_3NO], 113 (10) [M^+-C_3H_4NO]. EA: calculated: C 59.02; H 3.85; N 7.65. experimental: C 58.78; H 4.00; N 7.49.

Microwave-Assisted Polymerizations of 2-Oxazolines. The microwave vials were heated to 105 °C, allowed to cool to room temperature and filled with argon prior to use. For each polymerization, a stock solution was prepared in nitromethane ([Ox] = 1.4 M) with a monomer to initiator (MeOTs) ratio of [Ox]:[MeOTs] = 60. Subsequently, the stock solution was divided over different reaction vials (depending on the amount of solution the volume varied between 750 and 900 μL). After microwave-irradiation for predefined times, the polymerization mixtures were quenched by automated addition of 50 μL water (on the Emrys Liberator). Subsequently, the polymerization mixtures were one time diluted with chloroform to homogenize the solution and the resulting mixtures were analyzed by GC and GPC, respectively to investigate the polymerization kinetics.

MMFF94 calculations of 2a-c, 5 and methylated 2a-c$^+$, 5$^+$ [7]

MMFF94 calculations[7] were performed on **2a-c**, **5** and methylated **2a-c**$^+$, **5**$^+$ to obtain detailed information about the influence of the geometric structure onto their polymerization behavior. The results are summarized for the monomers **2a-c**, **5** in Table S1 and for the model compounds **2a-c**$^+$, **5**$^+$ in Table S2.

Table S1: Minimum structures of **2a-c** and **5**, which were calculated by a Monte Carlo simulation using the MMFF94 force field. Below the structures, the out-of-plane angles α [°] from the oxazoline unit and the attached aromatic ring are given. When more than one energetic minimum was found, the relative energies ΔE [kcal/mol] are given below the structures as well.[7]

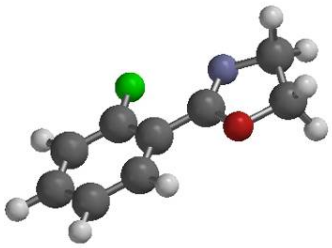
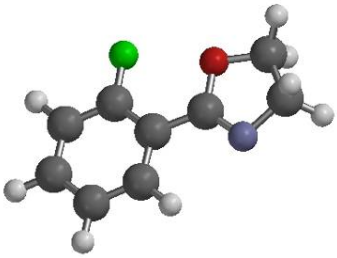
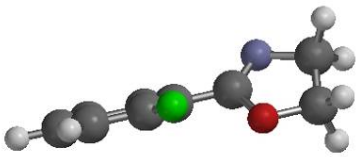
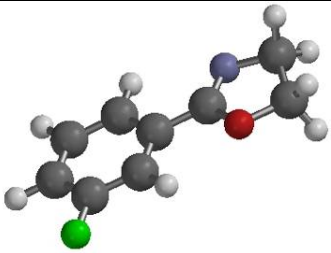
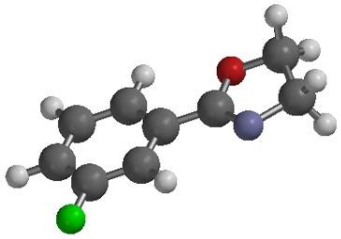
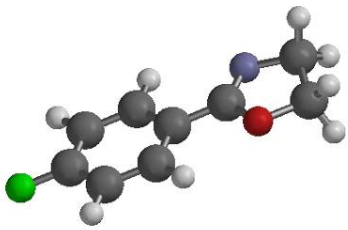
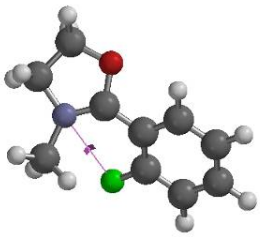
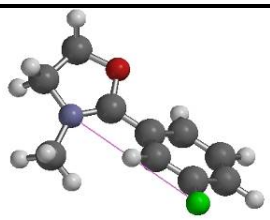
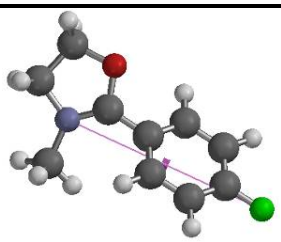
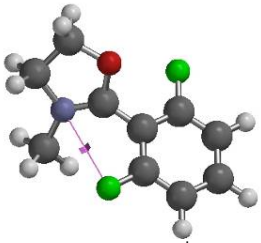
		
*o*FOx **2a** α (Ox-Ph) = 3.91° ΔE = 1.62	*o*FOx **2a** α (Ox-Ph) = 2.81° E = 0	*o*DFOx **5** α (Ox-Ph) = 38.73°
		
*m*FOx **2b** α (Ox-Ph) = 0.17° E = 0	*m*FOx **2b** α (Ox-Ph) = 0.27° ΔE = 0.12	*p*FOx **2c** α (Ox-Ph) = 0.11°

Table S2: Minimum structures of the methylated model compounds **2a-c**$^+$ and **5**$^+$ calculated by a Monte Carlo simulation using the MMFF94 force field. Below the structures, the distances d (N^+····F) [Å] are given.[7]

			
*o*FOx **2a**$^+$ d (N^+····F) = 2.99 Å	*m*FOx **2b**$^+$ d (N^+····F) = 5.40 Å	*p*FOx **2c**$^+$ d (N^+····F) = 6.52 Å	*o*DFOx **5**$^+$ d (N^+····F) = 3.04 Å

NMR spectra of 5 and methylated 5^+

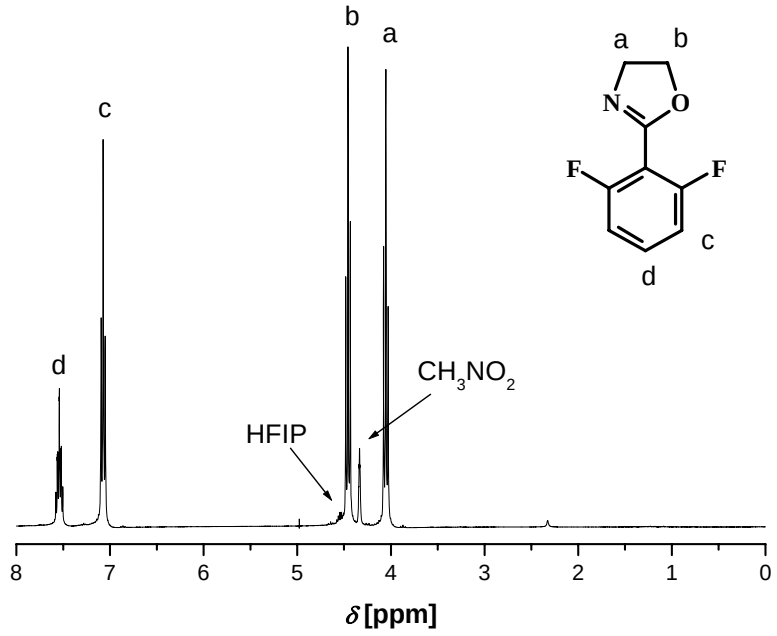


Figure S1: ^{1}H NMR of *o*DFOx **5** (400 MHz, nitromethane-d_3).

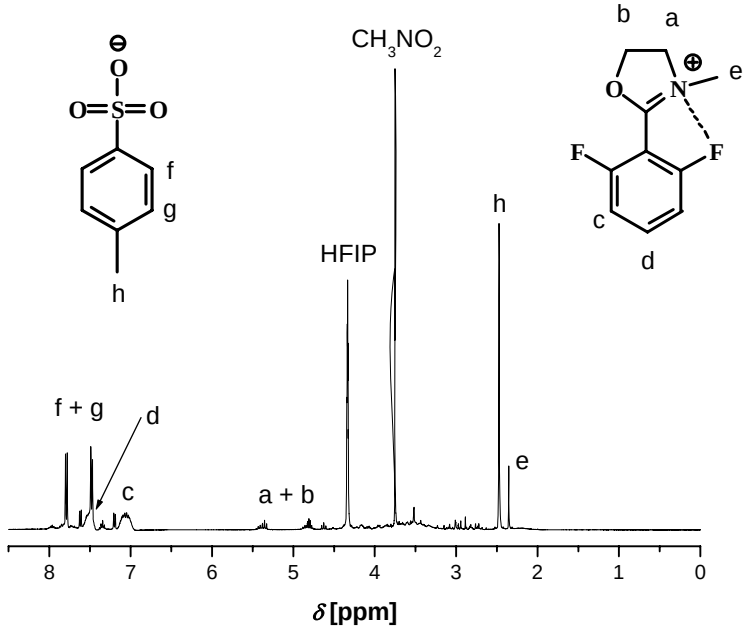


Figure S2: ^{1}H NMR of CH_3-*o*DFOx $\mathbf{5}^+$ (400 MHz, nitromethane-d_3).

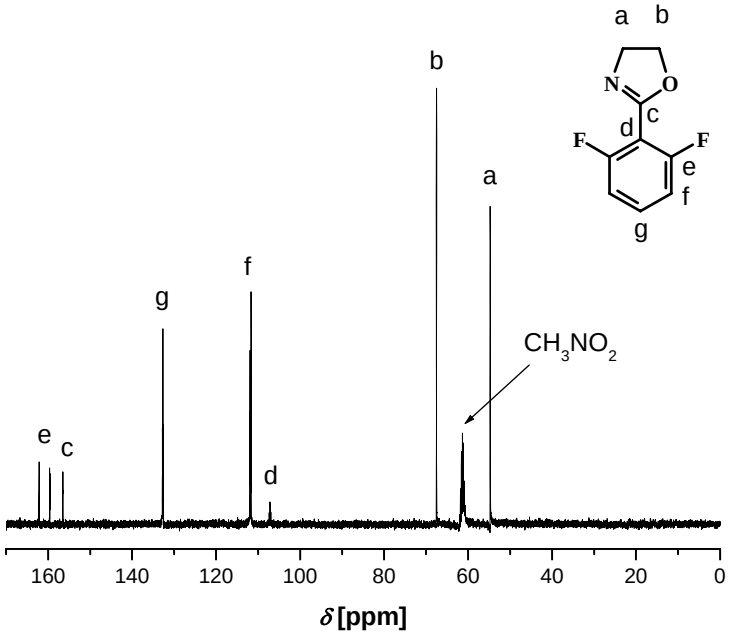


Figure S3: ^{13}C NMR of *o*DFOx **5** (101 MHz, nitromethane-d_3).

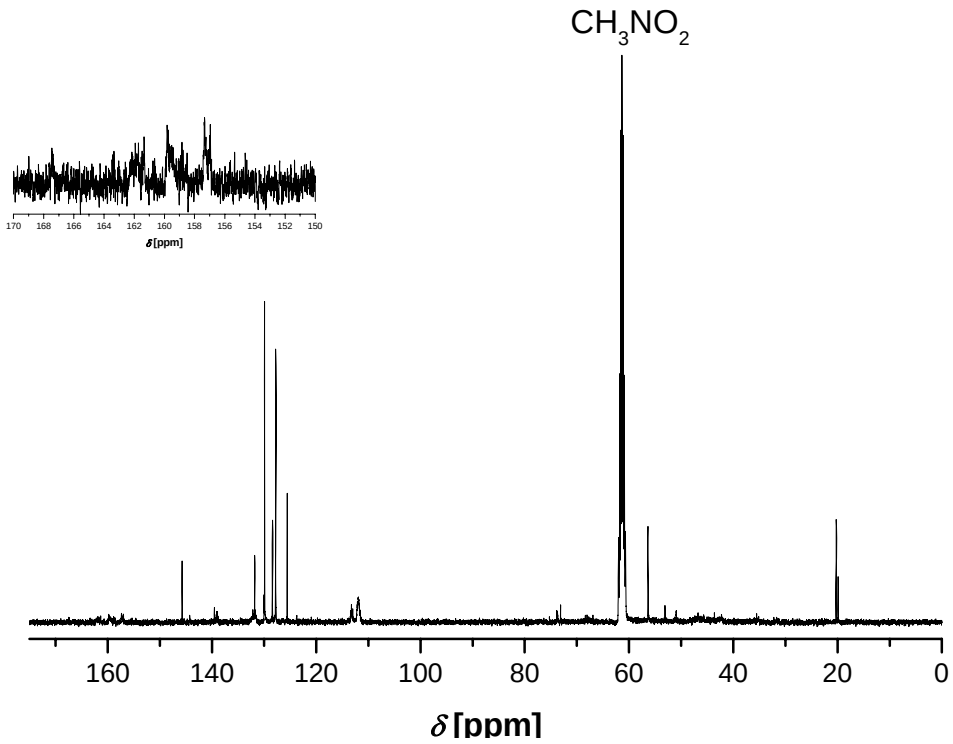


Figure S4: ^{13}C NMR of CH_3-*o*DFOx $\mathbf{5}^+$ (101 MHz, nitromethane-d_3).

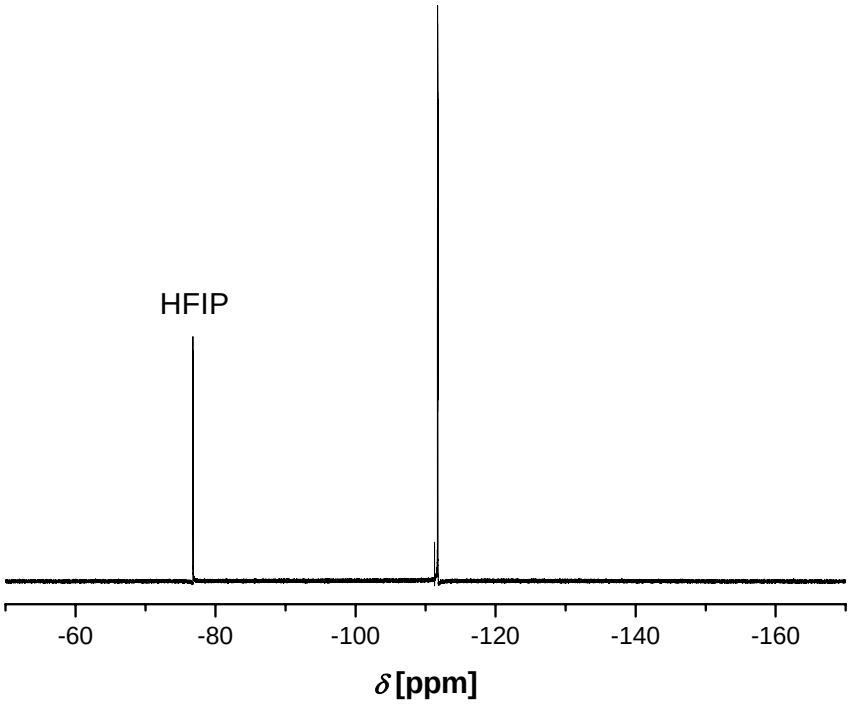


Figure S5: ^{19}F NMR of *o*DFOx **5** (374 MHz, nitromethane-d_3).

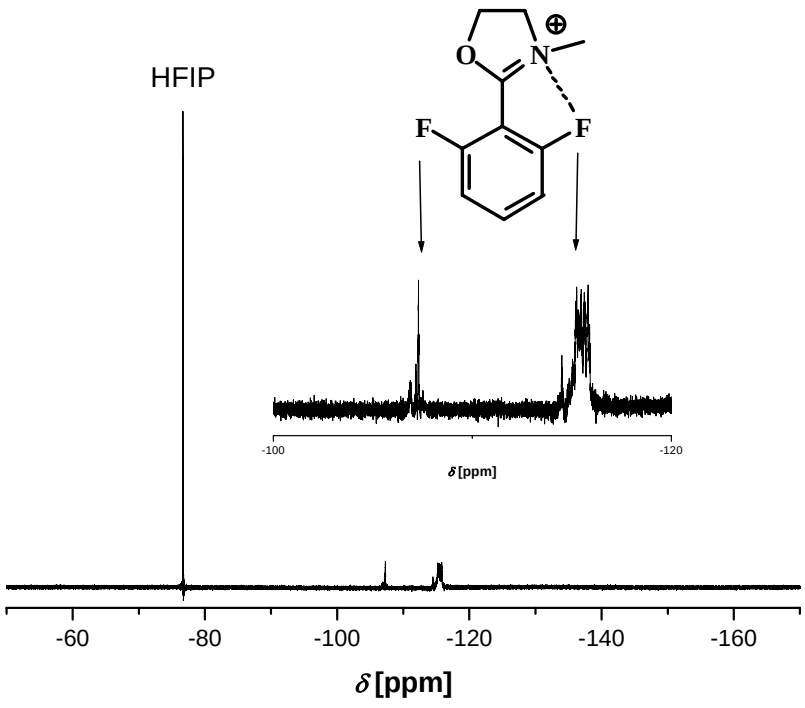


Figure S6: ^{19}F NMR of CH_3-*o*DFOx $\mathbf{5}^+$ (374 MHz, nitromethane-d_3).

MALDI-TOF-MS spectra of the polymers poly-2a-c and 5

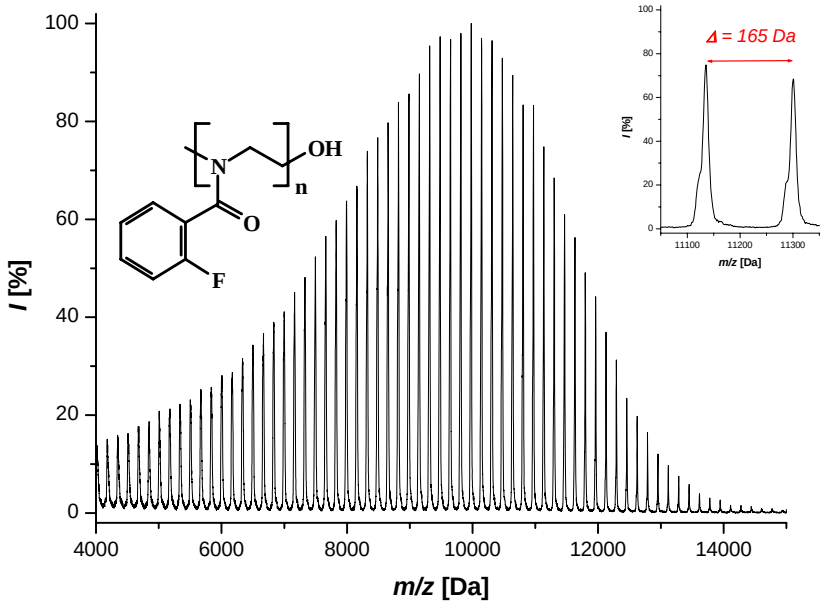


Figure S7: MALDI-TOF-MS spectrum of the polymer *poly*-**2a**.

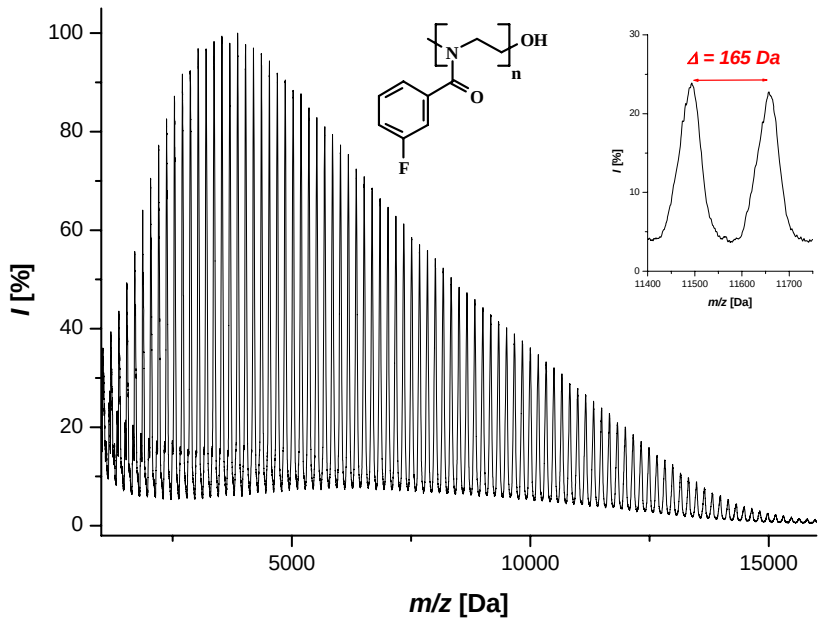


Figure S8: MALDI-TOF-MS spectrum of the polymer *poly*-**2b**.

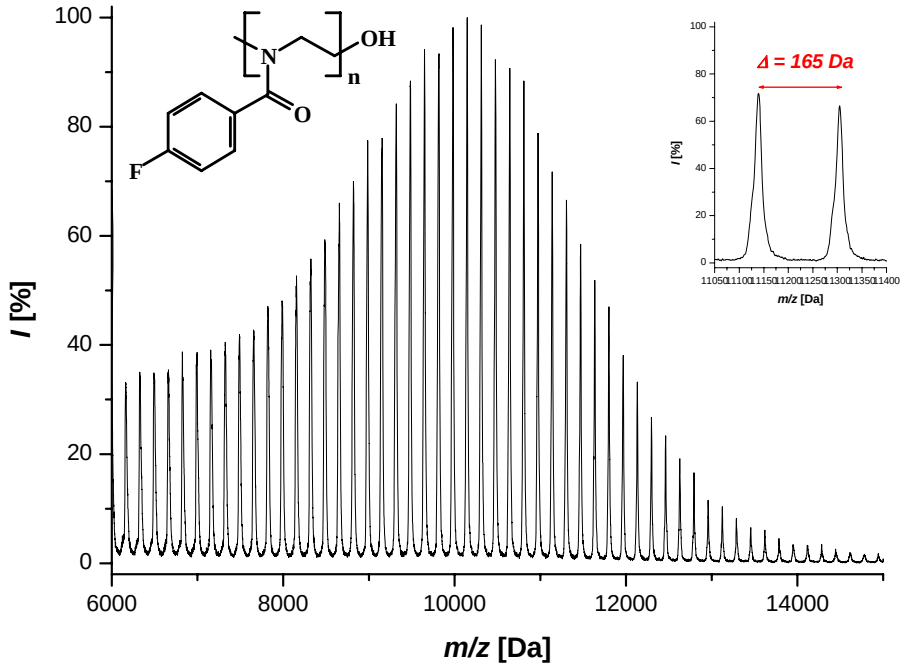


Figure S9: MALDI-TOF-MS spectrum of the polymer *poly*-**2c**.

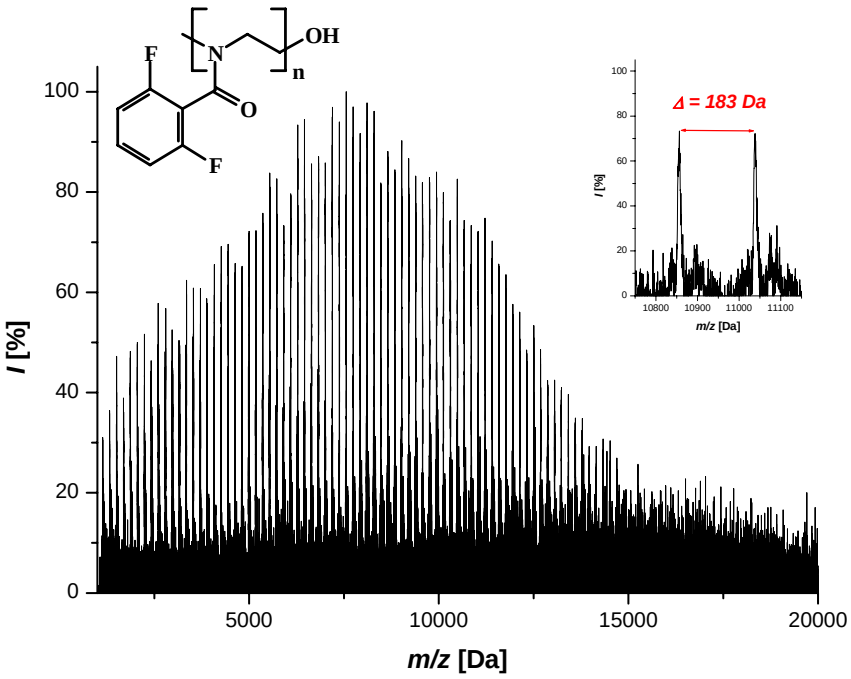


Figure S10: MALDI-TOF-MS spectrum of the polymer *poly*-**5**.

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