Supporting Information

Light-controlled lyotropic liquid crystallinity of polyaspartates

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Table of Contents

Abbreviations and Symbols...........................................................................................................................2
Synthetic Procedures and Characterisation....................................................................................................3
    General Remarks........................................................................................................................................3
    3,5-Difluorotoluene (4).............................................................................................................................4
    2,6-Difluorophenyl diazonium salt (5).........................................................................................................9
    4-(2,6-Difluorophenyl)-azo-3,5-difluorotoluene (6).................................................................................14
    4-(2,6-Difluorophenyl)-azo-3,5-difluorobenzyl bromide (7).....................................................................20
    β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate (9).............................................................26
    β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate NCA (10).....................................................33
    Poly-β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate (PpFABLA, 1).....................................41
    Poly-β-[4-(2,6-difluorophenyl)azo(3,5-difluorobenzyl)]-L-aspartate-co-poly-β-benzyl-L-aspartate
      (PpFABLA-co-PBLA, 11).........................................................................................................................48
NMR Sample Preparation, Calculation of Alignment Properties, Illumination Experiments/History and
Enantiomer Differentiation..............................................................................................................................55
    NMR Sample Composition........................................................................................................................55
    Alignment Properties................................................................................................................................55
    NMR Sample: #1(+)...................................................................................................................................56
    NMR Sample: #1(–)..................................................................................................................................60
    NMR Sample: #11(+)................................................................................................................................67
    NMR Sample: #11(–)..................................................................................................................................70
References.......................................................................................................................................................76
<table>
<thead>
<tr>
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Synthetic Procedures and Characterisation

General Remarks

Chemicals were bought from commercial sources and used without further purification if not stated otherwise. Anhydrous THF and dichloromethane were bought from Acros (AcroSeal packaging). n-Hexane was distilled from sodium. Dimethylethanolamine was stored over molecular sieves (3 Å) for 7 d under Schlenk conditions, distilled under reduced pressure and stored inside the glovebox at –20 °C. Argon was used as inert gas. All glassware used under Schlenk conditions and inside the glovebox was flame-dried prior to use.

NMR spectra were recorded on Bruker Avance III HD (400 MHz proton frequency, equipped with a 5 mm BBFO probe with z-gradient), Bruker Avance III (600 MHz proton frequency, equipped with triple resonance broadband inverse probe) and Bruker Avance III HD (700 MHz proton frequency, equipped with QCI cryo probe, $^1$H/$^9$F/$^{31}$P/$^{13}$C/$^{15}$N/$^{2}$H) NMR spectrometers. The frequency, temperature and solvent is given individually for each NMR string. The spectra were referenced either to TMS added as internal standard (δ$_{1H}$ = 0.00 ppm and δ$_{13C}$ = 0.0 ppm) or to the (residual) solvent signal of acetone-$d_6$ (δ$_{1H}$ = 2.05 ppm and δ$_{13C}$ = 29.9 ppm), CDCl$_3$ (δ$_{1H}$ = 7.27 ppm and δ$_{13C}$ = 77.2 ppm), DMF-$d_7$ (δ$_{1H}$ = 2.75 ppm and δ$_{13C}$ = 29.8 ppm) and THF-$d_8$ (δ$_{1H}$ = 1.73 ppm and δ$_{13C}$ = 25.4 ppm). Signals were assigned by their chemical shift, scalar coupling and – whenever necessary – by acquisition of additional 2D NMR spectra (1H–1H COSY, 1H–13C HSQC, 1H–13C HMBC and 1H–19F HOESY) and labelled according to their fine structure with s (singlet), d (doublet), t (triplet), a combination of these (e.g. dt for doublet of triplets) and m (unresolved multiplet).

For TLC, silica TLC plates from Merck with green fluorescing indicator were used. Separation was performed in the presence of ambient light. In many cases two spots were observed. We believe this to be due to the formation of two isomers either by by ambient light alone or by ambient light in combination with the acidic surface of the TLC plate (acidochromism). IR spectra were recorded on a Bruker Alpha with Platinum-ATR probe resulting in lower observed signal intensities for vibrations at higher wavenumbers (e.g. C–H valence vibration). The samples were either measured as solids (neat) or in solution. Signals were labelled according to their intensity s (strong), m (medium), w (weak) and based on the type of vibration ν (valence), δ (deformation). For observation of the polymerisation progress by IR spectroscopy, 0.1 mL of the reaction mixture were taken as sample inside the glovebox using a syringe and were measured immediately at normal atmosphere. Mass spectra were recorded on Finnigan MAT 95 using EI, on Bruker Daltonik Impact II using ESI and on Bruker Daltonik Autoflex speed TOF/TOF using MALDI MS spectrometers. For MALDI-MS, the polymers were dissolved in chloroform (1 g/L) and DCTB (40 g/L in THF) and potassium trifluoroacetate (5 g/L in THF) were used as matrix. GPC was measured with a pre-column and three main columns (10$^5$, 10$^7$ and 10$^9$ Å, from PSS Mainz) in chloroform with 0.3 % (w/w) tetra-n-butylammonium bromide added as mobile phase at a flow rate of 0.25 mL/min and a temperature of 25 °C using a JASCO UV-2075 plus detector. 75 μL of the sample (1 g/L of polymer together with toluene as internal standard dissolved over night in the mobile phase) were injected and referenced to polystyrene standards (PSS Mainz) without further correction. As a consequence, the molecular weights obtained are not absolute and can only be interpreted qualitatively. UV-vis and CD spectra were recorded as reported in the main article.
3,5-Difluorobenzaldehyde (2, 50.0 g, 0.345 mol, 1.0 eq.), hydrazine monohydrate (138.0 g, 2.76 mol, 8.0 eq.) and potassium hydroxide (77.4 g, 1.38 mol, 4.0 eq.) were suspended in triethylene glycol (370 mL) in a 1 L flask with reflux condenser and slowly (over 2 h, reaction mixture otherwise tends to build a foam) heated to 150 °C.

After the orange suspension turned into a colourless solution, the reflux condenser was replaced by a Liebig condenser, the temperature was raised to 200 °C and the product was distilled from the reaction mixture. After completion of distillation, both the residual reaction mixture and the distillate were diluted separately with the same amount of water and the product was extracted from both phases with diethyl ether. The combined organic phases were washed with hydrochloric acid (1 M) and water and dried over magnesium sulfate. The product was isolated by fractional distillation under reduced pressure (80 °C bottom temperature, 65 °C top temperature, 0.2 bar) and obtained as colourless liquid (21.1 g, 0.16 mol, 97 % purity remainder is diethyl ether, 46 % yield).

**1H NMR:**
\[
\delta = 6.71 - 6.66 \text{ (m, } 2H, H_{2,2'}), \\
6.60 \text{ (tt, } ^3J_{HF} = 9.1 \text{ Hz, } ^4J_{HH} = 2.2 \text{ Hz, } 1H, H_4), \\
2.34 \text{ (s, } 3H, H_5) \text{ ppm.}
\]

**19F NMR:**
\[
\delta = -111.2 \text{ to } -111.3 \text{ (m, } 2F, F_{6,6'}) \text{ ppm.}
\]

**13C{1H} NMR:**
\[
\delta = 162.9 \text{ (dd, } ^1J_{CF} = 247.3 \text{ Hz, } ^3J_{CF} = 13.1 \text{ Hz, } 2C, C_{3,3'}), \\
141.7 \text{ (t, } ^3J_{CF} = 9.5 \text{ Hz, } 1C, C_1), \\
111.8 \text{ (dd, } ^2J_{CF} = 19.5 \text{ Hz, } ^4J_{CF} = 4.8 \text{ Hz, } 2C, C_{2,2'}) , \\
100.9 \text{ (t, } ^2J_{CF} = 25.4 \text{ Hz, } 1C, C_4), \\
21.4 \text{ (t, } ^4J_{CF} = 2.1 \text{ Hz, } 1C, C_5) \text{ ppm.}
\]

**ATR-IR:**
\[
\tilde{\nu} = 3100 - 2700 \text{ (w, } C-H, \tilde{\nu}), \\
1628 \text{ (s, } C=C, \tilde{\nu}), \\
1593 \text{ (s, } C=C, \tilde{\nu}), \\
1321 \text{ (s, } C-F, \tilde{\nu}), \\
1115 \text{ (s, fingerprint),} \\
841 \text{ (s, } C-H, \delta) \text{ cm}^{-1}.
\]
$^1$H NMR:
(CDCl$_3$, 600 MHz, 295 K)

$\delta = 6.71 - 6.66$ (m, 2H, H$_{2,2'}$),
6.60 (t, $^3J_{HF} = 9.1$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, H$_4$),
2.34 (s, 3H, H$_5$) ppm.
\(^{19}\text{F NMR:}\)

\((\text{CDCl}_{3}, 376 \text{ MHz}, 293 \text{ K})\)

\(\delta = -111.2\) to \(-111.3\) (m, 2F, F\(_{6,6}\) ppm.)
$^{13}$C{$^1$H} NMR:
(CDCl$_3$, 151 MHz, 295 K)

$\delta = 162.9$ (dd, $^{1}J_{CF} = 247.3$ Hz, $^{2}J_{CF} = 13.1$ Hz, 2C, C$_{3,3'}$),
141.7 (t, $^{3}J_{CF} = 9.5$ Hz, 1C, C$_1$),
111.8 (dd, $^{4}J_{CF} = 19.5$, $^{1}J_{CF} = 4.8$ Hz, 2C, C$_{2,2'}$),
100.9 (t, $^{5}J_{CF} = 25.4$ Hz, 1C, C$_4$),
21.4 (t, $^{6}J_{CF} = 2.1$ Hz, 1C, C$_5$) ppm.
ATR-IR:
(neat)

\[ \tilde{\nu} = 3100 - 2700 \text{ (w, C–H, \nu)}, \]
1628 (s, C=C, \nu),
1593 (s, C=C, \nu)
1321 (s, C–F, \nu)
1115 (s, fingerprint)
841 (s, C–H, \delta) \text{ cm}^{-1}. 
2,6-Difluorophenyl diazonium salt (5)

According to a literature-known procedure, 2,6-difluorophenyl diazonium salt (5) was prepared from 2,6-difluoroaniline (3, 59.9 g, 0.45 mol, 1.0 eq.), tetrafluoroboric acid solution (50 % (w/w) in water, 0.15 L, 1.22 mol, 2.7 eq.) and sodium nitrite (31.1 g, 0.45 mol, 1.0 eq.) in water. Product 5 (52.0 g, 0.23 mol, 51 % yield) was obtained as orange crystals and stored at –20 °C under argon in the dark.

**¹H NMR:**  
(acetone-\(d_6\), 600 MHz, 295 K)  
\[\delta = 8.65 \ (tt, \ ^{3}J_{HH} = 8.9 \text{ Hz}, \ ^{4}J_{HF} = 6.2 \text{ Hz}, \ 1H, \ H_4),\]
\[7.92 - 7.86 \ (m, \ 2H, \ H_3,3') \text{ ppm.}\]

(slightly different shifts observed as literature data \(^3\) is measured in DMSO-\(d_6\))

**¹⁹F NMR:**  
(acetone-\(d_6\), 376 MHz, 293 K)  
\[\delta = -100.0 \text{ to } -100.1 \ (m, \ 2F, \ F_5,5'),\]
\[-151.88 \ (s, \ 4F, \ ^{19}BF_4^-)\]
\[-151.91 \ (s, \ 4F, \ ^{11}BF_4^-) \text{ ppm.}\]

(data not given in literature\(^3\), BF\(_4^-\) signals were assigned according to their intensity and the natural abundance of boron isotopes)

**¹³C{¹H} NMR:**  
(acetone-\(d_6\), 151 MHz, 295 K)  
\[\delta = 162.1 \ (d, \ ^{1}J_{CF} = 278.7 \text{ Hz}, \ 2C, \ C_{2,2}),\]
\[148.7 \ (t, \ ^{2}J_{CF} = 11.3 \text{ Hz}, \ 1C, \ C_4),\]
\[116.0 \ (dd, \ ^{2}J_{CF} = 14.4 \text{ Hz}, \ ^{4}J_{CF} = 4.5 \text{ Hz}, \ 2C, \ C_{3,3}) \text{ ppm.}\]

(C\(_1\) is not observed, data not given in literature\(^3\))

**ATR-IR:**  
(neat)  
\[\tilde{\nu} = 3100 - 3000 \ (w, \ C–H, \ \nu),\]
\[2289 \ (w, \ R–N\equiv\text{N, } \nu)\]
\[1607 \ (m, \ C=C, \ \nu)\]
\[1495 \ (m, \ C=C, \ \nu)\]
\[1270 \ (m, \ C=F, \ \nu)\]
\[1018 \ (s, \ \text{fingerprint})\]
\[812 \ (m, \ C–H, \ \delta) \text{ cm}^{-1}.\]

(in accordance with data given in literature\(^3\))
\( ^1H\) NMR:

(acetone-\(d_6\), 600 MHz, 295 K)

\[ \delta = 8.65 \text{ (tt, } \ ^3J_{HH} = 8.9 \text{ Hz, } \ ^4J_{HF} = 6.2 \text{ Hz, 1H, } H_4) \]

7.92 – 7.86 (m, 2H, \( H_3,3' \)) ppm.

(slightly different shifts observed as literature data\(^2\) is measured in DMSO-\(d_6\))
$^{19}$F NMR:
(acetone-$d_6$, 376 MHz, 293 K)

$\delta = -100.0$ to $-100.1$ (m, 2F, $F_{5,5}$),
$-151.88$ (s, 4F, $^{10}$BF$_4^-$)
$-151.91$ (s, 4F, $^{11}$BF$_4^-$) ppm.
(data not given in literature, BF$_4^-$ signals were assigned according to their
intensity and the natural abundance of boron)
$^{13}$C($^1$H) NMR:
(acetone-$d_6$, 151 MHz, 295 K)

$\delta = 162.1$ (d, $^1J_{CF} = 278.7$ Hz, 2C, C$_{2,2'}$),
148.7 (t, $^3J_{CF} = 11.3$ Hz, 1C, C$_4$),
116.0 (dd, $^2J_{CF} = 14.4$ Hz, $^4J_{CF} = 4.5$ Hz, 2C, C$_{3,3'}$) ppm.
(C$_1$ is not observed, data not given in literature)
ATR-IR:
(neat)

$\tilde{\nu} = 3100 - 3000$ (w, C–H, v),
2289 (w, R–N=N, v)
1607 (m, C=C, v)
1495 (m, C=C, v)
1270 (m, C–F, v)
1018 (s, fingerprint)
812 (m, C–H, $\delta$) cm$^{-1}$.

(in accordance with data given in literature$^2$)
4-(2,6-Difluorophenyl)-azo-3,5-difluorotoluene (6)

According to a literature-known procedure, 4-(2,6-difluorophenyl)-azo-3,5-difluorotoluene (6) was prepared from 3,5-difluorotoluene (4, 19.2 g, 0.15 mol, 1.0 eq.), 2,6-difluorophenyl diazonium salt (5, 34.2 g, 0.15 mol, 1.0 eq.) and n-butyllithium (2.5 M in n-hexane, 60 mL, 0.15 mol, 1.0 eq.) in anhydrous THF. Purification was changed to filtration of the solution of the raw product in CHCl₃ through silica and evaporation of the solvent at reduced pressure. Product 6 (33.7 g, 0.13 mol, 84 % yield) was obtained as red crystals almost quantitatively as Z-isomer.

**TLC:**
\[ \frac{V_{ethylacetate}}{V_{cyclohexane}} = 1 / 4 \]
(E isomer is presumably formed on TLC and results in a second spot)

**¹H NMR:**
(CDCls, 600 MHz, 279 K)
\[ \delta = 7.25 - 7.18 \text{ (m, 1H, H}_2\text{)}, \]
\[ 6.87 \text{ (dd, } ^2J_{HF} = 8.2 \text{ Hz, } ^3J_{HH} = 8.2 \text{ Hz, 2H, H}2\text{,}7\text{,}2\text{,}7\text{,}2\text{),} \]
\[ 6.67 \text{ (d, } ^3J_{HF} = 9.3 \text{ Hz, 2H, H}23\text{,}23\text{),} \]
\[ 2.43 \text{ (s, 3H, H}E\text{, 3 }\% \text{n(n)}\text{),} \]
\[ 2.31 \text{ (s, 3H, H}E\text{, 97 }\% \text{n(n)}\text{)} \text{ ppm.} \]
(literature data measured in DMSO-\text{d}_6 and CDCls is unassigned)

**¹³C¹H NMR:**
(CDCls, 151 MHz, 279 K)
\[ \delta = 151.7 \text{ (dd, } ^1J_{CF} = 253.7 \text{ Hz, } ^2J_{CF} = 5.4 \text{ Hz, 2C, C}2\text{,}2\text{,}2\text{,}2\text{),} \]
\[ 151.4 \text{ (dd, } ^1J_{CF} = 253.1 \text{ Hz, } ^2J_{CF} = 6.1 \text{ Hz, 2C, C}2\text{,}2\text{,}2\text{,}2\text{),} \]
\[ 141.6 \text{ (t, } ^2J_{CF} = 9.2 \text{ Hz, 1C, C}2\text{,}4\text{),} \]
\[ 132.0 \text{ (t, } ^2J_{CF} = 17.1 \text{ Hz, 1C, C}2\text{,}5\text{),} \]
\[ 129.7 \text{ (t, } ^2J_{CF} = 9.4 \text{ Hz, 1C, C}2\text{,}8\text{),} \]
\[ 129.4 \text{ (t, } ^2J_{CF} = 17.2 \text{ Hz, 1C, C}2\text{,}1\text{),} \]
\[ 112.5 \text{ (dd, } ^2J_{CF} = 19.8 \text{ Hz, } ^1J_{CF} = 3.2 \text{ Hz, 2C, C}2\text{,}2\text{,}2\text{,}2\text{),} \]
\[ 112.0 \text{ (dd, } ^2J_{CF} = 19.9 \text{ Hz, } ^1J_{CF} = 3.7 \text{ Hz, 2C, C}2\text{,}7\text{,}2\text{,}7\text{,}2\text{),} \]
\[ 21.4 \text{ (t, } ^4J_{CF} = 1.7 \text{ Hz, 1C, C}2\text{,}9\text{)} \text{ ppm.} \]
(literature data measured in DMSO-\text{d}_6 is unassigned and assignment of individual lines was wrong for C2,2 and C6,6)

**ATR-IR:**
(neat)
\[ \nu = 3100 - 2900 \text{ (w, C–H, v),} \]
\[ 1613 \text{ (m, C=C, v)} \]
\[ 1507 \text{ (s, C=C, v)} \]
\[ 1240 \text{ (m, C–F, v)} \]
\[ 1016 \text{ (s, fingerprint)} \]
\[ 779 \text{ (m, C–H, } \delta \text{) cm}^{-1}. \]
(data not given in literature)

**EI-MS:**
calc. (for C13H8F4N2): 268
found:
\[ 268 [\text{M}^+] \text{ (product 6)} \]
\[ 155 [\text{M–C}_6\text{H}_3\text{F}_2]^+ \]
\[ 141 [\text{M–C}_6\text{H}_3\text{F}_2\text{N}]^+ \text{ and / or } [\text{M–C}_6\text{H}_3\text{F}_2]^+ \]
\[ 127 [\text{M–C}_6\text{H}_3\text{F}_2\text{N}_2]^+ \text{ and / or } [\text{M–C}_6\text{H}_3\text{F}_2\text{N}]^+ \]
\[ 113 [\text{M–C}_6\text{H}_3\text{F}_2\text{N}_2]^+ \]
$^1$H NMR:
(CDC$_3$, 600 MHz, 279 K)

$\delta$ = 7.25 – 7.18 (m, 1H, H$_{Z-8}$),
6.87 (dd, $^3$J$_{HF}$ = 8.2 Hz, $^3$J$_{HH}$ = 8.2 Hz, 2H, H$_{Z-7,Z-7'}$),
6.67 (d, $^3$J$_{HF}$ = 9.3 Hz, 2H, H$_{Z-3,Z-3'}$),
2.43 (s, 3H, H$_{E-9}$, 3 % (n/n)),
2.31 (s, 3H, H$_{Z-9}$, 97 % (n/n)) ppm.
(literature data$^{3,4}$ measured in DMSO-$d_6$ and CDCl$_3$ is unassigned)
$^{19}$F NMR:
(CDCl$_3$, 659 MHz, 279 K)

$\delta$ = –119.5 to –119.6 (m, 2F, F$_{11,11',Z}$),
–120.2 to –120.3 (m, 2F, F$_{10,10',Z}$) ppm.
(literature data$^3$ measured in DMSO-$d_6$ is unassigned)
$^{13}$C{'H} NMR:
(CDCl$_3$, 151 MHz; 279 K)

$\delta$ = 151.7 (dd, $^1J_{CF}$ = 253.7 Hz, $^2J_{CF}$ = 5.4 Hz, 2C, C$_{Z,6,6'}$),
151.4 (dd, $^1J_{CF}$ = 253.1 Hz, $^2J_{CF}$ = 6.1 Hz, 2C, C$_{Z,2,2'}$),
141.6 (t, $^3J_{CF}$ = 9.2 Hz, 1C, C$_{Z,4}$),
132.0 (t, $^2J_{CF}$ = 17.1 Hz, 1C, C$_{Z,5}$),
129.7 (t, $^3J_{CF}$ = 9.4 Hz, 1C, C$_{Z,8}$),
129.4 (t, $^2J_{CF}$ = 17.2 Hz, 1C, C$_{Z,1}$),
112.5 (dd, $^2J_{CF}$ = 19.8 Hz, $^4J_{CF}$ = 3.2 Hz, 2C, C$_{Z,3,3'}$),
112.0 (dd, $^2J_{CF}$ = 19.9 Hz, $^4J_{CF}$ = 3.7 Hz, 2C, C$_{Z,7,7'}$),
21.4 (t, $^4J_{CF}$ = 1.7 Hz, 1C, C$_{Z,9}$) ppm.

(literature data$^3$ measured in DMSO-$d_6$ is unassigned and assignment of individual lines was wrong for C$_{2,2'}$ and C$_{6,6'}$)
ATR-IR:
(neat)

\[ \tilde{\nu} = 3100 - 2900 \text{ (w, C–H, } \nu) \]

1613 (m, C=C, \( \nu \))

1507 (s, C=C, \( \nu \))

1240 (m, C–F, \( \nu \))

1016 (s, fingerprint)

779 (m, C–H, \( \delta \)) cm\(^{-1}\).

(data not given in literature)
EI-MS: calc. (for C\textsubscript{13}H\textsubscript{8}F\textsubscript{4}N\textsubscript{2}): 268
found: 268 [M]* (product 6)
155 [M–C\textsubscript{6}H\textsubscript{3}F\textsubscript{2}]*
141 [M–C\textsubscript{6}H\textsubscript{3}F\textsubscript{2}N]* and / or [M–C\textsubscript{6}H\textsubscript{3}F\textsubscript{2}]*
127 [M–C\textsubscript{6}H\textsubscript{3}F\textsubscript{2}N\textsubscript{2}]* and / or [M–C\textsubscript{6}H\textsubscript{3}F\textsubscript{2}N]*
113 [M–C\textsubscript{7}H\textsubscript{5}F\textsubscript{2}N\textsubscript{2}]*
4-(2,6-Difluorophenyl)-azo-3,5-difluorobenzyl bromide (7)

4-(2,6-Difluorophenyl)-azo-3,5-difluorobenzyl bromide (6, 32.2 g, 0.12 mol, 1.0 eq.) was dissolved in TCE (0.55 L) in a 1 L flask equipped with reflux condenser. N-Bromosuccinimide (25.9 g, 0.14 mol, 1.2 eq.) and one portion of dibenzoyl peroxide (75 % (w/w) remainder is water, total of 1.0 g, 0.003 mol, 0.025 eq.) are added and the reaction mixture heated to reflux over night. A second portion of dibenzoyl peroxide is added after 2 h. Reaction progress is followed by $^{19}$F NMR spectroscopy of the reaction solution, which reveals an 89 % (n/n) conversion of the starting material into 75 % (n/n) product 7 and 14 % (n/n) double brominated side product (cf. $^{19}$F NMR spectrum of reaction mixture). Further conversion of starting material is not attempted due to the over bromination observed. The reaction mixture is cooled to room temperature, quenched by addition of sodium bisulfite solution and the organic phase is separated. The organic phase is washed with water (5x), dried over magnesium sulfate and concentrated under reduced pressure to give a red oil that solidifies over night. The red solid is dissolved in CHCl$_3$, filtrated through silica and concentrated under reduced pressure. Product 7 (39.4 g, 0.077 mol, 68 % (w/w) purity, 64 % yield) is obtained as red solid almost quantitatively as E-isomer and is used directly without further purification / isolation. The remaining starting material 6 and the double brominated side product are still present after work up (cf. $^1$H and $^{19}$F NMR spectra in CDCl$_3$) but are not reactive and are removed effectively during the subsequent esterification).

**TLC:**
(CHCl$_3$)

$R_r =$ 0.48 and 0.56
(Z isomer is presumably formed on TLC and results in a second spot)

**$^{19}$F NMR:**
(TCE, 659 MHz, 300 K, taken directly from reaction mixture)

$\delta =$ –119.7 (d, $J = 8.4$ Hz, 2F, side product, double Br),
–120.7 (d, $J = 9.5$ Hz, 2F, product 7),
–121.1 to –121.3 (m, 2F, side product, double Br),
–121.6 to –121.7 (m, 2F, product 7),
–122.1 (d, $J = 10.6$ Hz, 2F, starting material 6),
–122.37 to –122.41 (m, 2F, starting material 6) ppm.
(data not given in literature$^3$)

**Composition:**
75 % (n/n) product 7
11 % (n/n) starting material 6
14 % (n/n) side product (double Br)

**$^1$H NMR:**
(CDCl$_3$, 700 MHz, 300 K, after work up)

$\delta =$ 6.56 (s, 1H, CHBr$_2$, side product, 16 % (n/n)),
5.95 (s, 4H, TCE, 4 % (n/n)),
4.43 (s, 2H, CH$_2$Br, product 7, 68 % (n/n)),
2.40 (s, 3H, CH$_3$, starting material 6, 13 % (n/n)) ppm.
(data not given in literature$^3$)
**$^{19}$F NMR:**  
(CDCl$_3$, 659 MHz, 300 K, after work up)  
$\delta = -118.9$ (d, $J = 9.1$ Hz, 2F, side product, double Br),  
$-119.9$ (d, $J = 9.1$ Hz, 2F, product 7),  
$-120.5$ to $-120.6$ (m, 2F, side product, double Br),  
$-120.9$ to $-121.0$ (m, 2F, product 7),  
$-121.3$ (d, $J = 10.4$ Hz, 2F, starting material 6),  
$-121.6$ to $-121.7$ (m, 2F, starting material 6) ppm.  
(data not given in literature$^3$)  
composition:  
71 % (n/n) product 7  
13 % (n/n) starting material 6  
16 % (n/n) side product (double Br)

**EI-MS:**

- calc. (for C$_{13}$H$_7^{79}$BrF$_4$N$_2$): 346  
  found: 346 [M]$^+$ (product 7)
- calc. (for C$_{13}$H$_7^{81}$BrF$_4$N$_2$): 348  
  found: 348 [M]$^+$ (product 7)
- calc. (for C$_{13}$H$_8^{79}$Br$_2$F$_4$N$_2$): 424  
  found: 424 [M]$^+$ (side product, double Br)
- calc. (for C$_{13}$H$_8^{81}$Br$_2$F$_4$N$_2$): 426  
  found: 426 [M]$^+$ (side product, double Br)
- calc. (for C$_{13}$H$_8^{81}$BrF$_4$N$_2$): 428  
  found: 428 [M]$^+$ (side product, double Br)
- calc. (for C$_{13}$H$_8$F$_4$N$_2$): 268  
  found: 268 [M]$^+$ (starting material 6)
\(^{19}\text{F NMR:}\)

(TCE, 659 MHz, 300 K, taken directly from reaction mixture)

\(\delta = -119.7\ (d, J = 8.4\text{ Hz}, 2\text{F, side product, double Br}),\)

\(-120.7\ (d, J = 9.5\text{ Hz}, 2\text{F, product 7}),\)

\(-121.1\text{ to }-121.3\ (m, 2\text{F, side product, double Br}),\)

\(-121.6\text{ to }-121.7\ (m, 2\text{F, product 7}),\)

\(-122.1\ (d, J = 10.6\text{ Hz}, 2\text{F, starting material 6}),\
-122.37\text{ to }-122.41\ (m, 2\text{F, starting material 6})\text{ ppm.}\)

(data not given in literature\(^4\))

composition:

75 \%(n/n) product 7
11 \%(n/n) starting material 6
14 \%(n/n) side product (double Br)
'H NMR:
(CDCl₃, 700 MHz, 300 K, after work up)

δ = 6.56 (s, 1H, CHBr₂, side product, 16 % (n/n)),
5.95 (s, 4H, TCE, 4 % (n/n)),
4.43 (s, 2H, CH₂Br, product 7, 68 % (n/n)),
2.40 (s, 3H, CH₃, starting material 6, 13 % (n/n)) ppm.
(data not given in literature⁴)
^19\text{F} \text{NMR:} \\
(CDCl_3, 659 \text{ MHz}, 300 \text{ K}, \text{after work up})

δ = −118.9 (d, J = 9.1 Hz, 2F, side product, double Br),  
−119.9 (d, J = 9.1 Hz, 2F, product 7),  
−120.5 to −120.6 (m, 2F, side product, double Br),  
−120.9 to −121.0 (m, 2F, product 7),  
−121.3 (d, J = 10.4 Hz, 2F, starting material 6),  
−121.6 to −121.7 (m, 2F, starting material 6) ppm. 

(data not given in literature)  

composition:  
71 \%(n/n) product 7  
13 \%(n/n) starting material 6  
16 \%(n/n) side product (double Br)
EI-MS:
calc. (for C_{13}H_{7}{^79}BrF_{4}N_{2}): 346
found: 346 [M]^+ (product 7)
calc. (for C_{13}H_{8}{^81}BrF_{4}N_{2}): 348
found: 348 [M]^+ (product 7)
calc. (for C_{13}H_{7}{^79}Br_{2}F_{4}N_{2}): 424
found: 424 [M]^+ (side product, double Br)
calc. (for C_{13}H_{8}{^81}Br_{2}F_{4}N_{2}): 426
found: 426 [M]^+ (side product, double Br)
calc. (for C_{13}H_{6}{^81}Br_{2}F_{4}N_{2}): 428
found: 428 [M]^+ (side product, double Br)
calc. (for C_{13}H_{6}F_{4}N_{2}): 268
found: 268 [M]^+ (starting material 6)
β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate (9)

Similar to a literature-known procedure for β-selective esterification of aspartic acid, L-aspartic acid copper (II) complex copper (II) salt octahydrate (8, 9.7 g, 0.018 mmol, 0.25 eq.) and L-aspartic acid (4.9 g, 0.036 mol, 0.5 eq.) are suspended in water (4.1 mL) and dimethylformamide (3.5 mL). N,N,N',N'-Tetramethylguanidine (9.3 mL, 0.072 mol, 1.0 eq.) is added and the mixture is stirred at room temperature for 2 h until a clear, blue solution is formed. Acetone (150 mL) is added to the suspension to enhance precipitation of the copper protected aspartate and the mixture is vigorously stirred until a fine suspension is formed. The solid is filtered off, washed with acetone (until the filtrate becomes almost colourless) and water and transferred into a flask. A solution of ethylenediaminetetraacetic acid (11.2 g, 0.038 mol, 0.5 eq.) and sodium bicarbonate (6.4 g, 0.076 mol, 1.0 eq.) in water (82 mL) is added and the suspension stirred overnight at room temperature. The solid is filtered off, washed with water (until the filtrate becomes almost colourless), methanol and diethyl ether and dried in vacuo overnight. Recrystallisation from acetone / water (2:1, 40 mL/g) yields product 9 (16.0 g, 0.040 mol, 56 % yield) as orange flakes. Acquisition of NMR spectra is only possible after addition of TFA (needed for dissolution of product 9).

**1H NMR:**  
(DMF-d$_7$ + TFA, 700 MHz, 300 K)  
\[ \delta = 8.92 \text{ (s, 3H, NH$_3^+$)}, \]  
\[ 7.74 - 7.68 \text{ (m, 1H, H$_a$)}, \]  
\[ 7.46 \text{ (d, } J_{HF} = 10.4 \text{ Hz, 2H, H$_{2,3}$)}, \]  
\[ 7.41 \text{ (dd, } J_{HF} = 9.2 \text{ Hz, } J_{HH} = 9.2 \text{ Hz, 2H, H$_{1,7}$)}, \]  
\[ 5.40 \text{ (d, } J_{HF} = 13.9 \text{ Hz, 1H, H$_b$)}, \]  
\[ 5.35 \text{ (d, } J_{HF} = 13.9 \text{ Hz, 1H, H$_a$)}, \]  
\[ 4.70 \text{ (pseudo-t, } J_{HF} = 5.6 \text{ Hz, 1H, H$_{11}$)}, \]  
\[ 3.38 \text{ (d, } J_{HF} = 5.7 \text{ Hz, 2H, H$_{15}$)} \text{ ppm.} \]

**19F NMR:**  
(DMF-d$_7$ + TFA, 659 MHz, 300 K)  
\[ \delta = -122.2 \text{ (d, } J_{HF} = 10.6 \text{ Hz, 2F, F$_{10.10'}$)}, \]  
\[ -122.9 \text{ (dd, } J_{HF} = 9.8 \text{ Hz, } J_{HF} = 6.1 \text{ Hz, 2F, F$_{11.11'}$)} \text{ ppm.} \]

**13C{1H} NMR:**  
(DMF-d$_7$ + TFA, 176 MHz, 300 K)  
\[ \delta = 170.2 \text{ (s, 1C, C$_{12-14}$)}, \]  
\[ 169.8 \text{ (s, 1C, C$_{12-14}$)}, \]  
\[ 155.5 \text{ (dd, } J_{CF} = 259.2 \text{ Hz, } J_{CF} = 4.0 \text{ Hz, 2C, C$_{6,6'}$)}, \]  
\[ 155.4 \text{ (dd, } J_{CF} = 259.7 \text{ Hz, } J_{CF} = 4.5 \text{ Hz, 2C, C$_{2,2'}$)}, \]  
\[ 142.76 \text{ (t, } J_{CF} = 10.1 \text{ Hz, 1C, C$_8$)}, \]  
\[ 133.11 \text{ (t, } J_{CF} = 10.6 \text{ Hz, 1C, C$_8$)}, \]  
\[ 131.51 \text{ (t, } J_{CF} = 10.1 \text{ Hz, 1C, C$_8$)}, \]  
\[ 130.65 \text{ (t, } J_{CF} = 10.2 \text{ Hz, 1C, C$_1$)}, \]  
\[ 113.50 \text{ (dd, } J_{CF} = 20.1 \text{ Hz, } J_{CF} = 3.6 \text{ Hz, 2C, C$_{7,7'}$)}, \]  
\[ 112.16 \text{ (dd, } J_{CF} = 21.5 \text{ Hz, } J_{CF} = 3.5 \text{ Hz, 2C, C$_{3,3'}$)}, \]  
\[ 65.08 \text{ (s, 1C, C$_9$)}, \]  
\[ 49.83 \text{ (s, 1C, C$_{14}$)}, \]  
\[ 34.85 \text{ (s, 1C, C$_{13}$)} \text{ ppm.} \]
ATR-IR:
(neat)
\[ \tilde{\nu} = 3566 \text{ (m, O–H, } \nu) , \\
2930 \text{ (m, C–H, } \nu) , \\
1718 \text{ (m, C=O, } \nu) , \\
1583 \text{ (m, C=C, } \nu) , \\
1516 \text{ (m, C=C, } \nu) , \\
1023 \text{ (s, fingerprint) ,} \\
785 \text{ (m, C–H, } \delta) \text{ cm}^{-1}. \]

HR-MS (ESI positive):
calc. (for C\textsubscript{17}H\textsubscript{14}F\textsubscript{4}N\textsubscript{3}O\textsubscript{4}):
400.09150
found: 400.09137 [M+H]\textsuperscript{+} (product 9)
calc. (for C\textsubscript{17}H\textsubscript{13}F\textsubscript{4}N\textsubscript{3}O\textsubscript{4}Na):
422.07344
found: 422.07319 [M+Na]\textsuperscript{+}
calc. (for C\textsubscript{34}H\textsubscript{27}F\textsubscript{8}N\textsubscript{6}O\textsubscript{8}):
799.17571
found: 799.17518 [2M+H]\textsuperscript{+}
calc. (for C\textsubscript{34}H\textsubscript{26}F\textsubscript{8}N\textsubscript{6}O\textsubscript{8}Na):
821.15766
found: 821.15683 [2M+Na]\textsuperscript{+}
**\(^1\)H NMR:**  
(DMF-\(d_7\) + TFA, 700 MHz, 300 K)  
\(\delta = 8.92\) (s, 3H, NH\(_3^+\)),  
7.74 – 7.68 (m, 1H, H\(_9\)),  
7.46 (d, \(^3J_{HF} = 10.4\) Hz, 2H, H\(_{3,3'}\)),  
7.41 (dd, \(^3J_{HF} = 9.2\) Hz, \(^3J_{HH} = 9.2\) Hz, 2H, H\(_{7,7'}\)),  
5.40 (d, \(^2J_{HF} = 13.9\) Hz, 1H, H\(_9\)),  
5.35 (d, \(^2J_{HF} = 13.9\) Hz, 1H, H\(_9'\)),  
4.70 (pseudo-t, \(^3J_{HH} = 5.6\) Hz, 1H, H\(_{14}\)),  
3.38 (d, \(^3J_{HH} = 5.7\) Hz, 2H, H\(_{13}\)) ppm.

[Chemical structure diagram]
$^{19}$F NMR: 
(DMF-$d_7$ + TFA, 659 MHz, 300 K)  
$\delta = -122.2$ (d, $^3J_{HF} = 10.6$ Hz, 2F, F$_{10,10'}$),  
$-122.9$ (dd, $^3J_{HF} = 9.8$ Hz, $^4J_{HF} = 6.1$ Hz, 2F, F$_{11,11'}$) ppm.
$^{13}$C{[^1]H} NMR: 
(DMF-$d_7$ + TFA, 176 MHz, 300 K)
\[\delta = 170.2 \text{ (s, 1C, C}_{12,15},)\]
\[169.8 \text{ (s, 1C, C}_{12,15},)\]
\[155.5 \text{ (dd, } J_{CC} = 259.2 \text{ Hz, } J_{CC} = 4.0 \text{ Hz, 2C, C}_{6,6} ,)\]
\[155.4 \text{ (dd, } J_{CC} = 259.7 \text{ Hz, } J_{CC} = 4.5 \text{ Hz, 2C, C}_{2,2} ,)\]
\[142.76 \text{ (t, } J_{CF} = 10.1 \text{ Hz, 1C, C}_2 ,)\]
\[133.51 \text{ (t, } J_{CF} = 10.6 \text{ Hz, 1C, C}_3 ,)\]
\[131.51 \text{ (t, } J_{CF} = 10.1 \text{ Hz, 1C, C}_3 ,)\]
\[130.65 \text{ (t, } J_{CF} = 10.2 \text{ Hz, 1C, C}_1 ,)\]
\[113.50 \text{ (dd, } J_{CF} = 20.1 \text{ Hz, } J_{CF} = 3.6 \text{ Hz, 2C, C}_{7,7} ,)\]
\[112.16 \text{ (dd, } J_{CF} = 21.5 \text{ Hz, } J_{CF} = 3.5 \text{ Hz, 2C, C}_{3,3} ,)\]
\[65.08 \text{ (s, 1C, C}_9 ,)\]
\[49.83 \text{ (s, 1C, C}_{14},)\]
\[34.85 \text{ (s, 1C, C}_{13} \text{ ppm.}\]
ATR-IR:
(neat)

\[ \tilde{\nu} = 3566 \text{ (m, O–H, } \nu) \],
2930 \text{ (m, C–H, } \nu) ,
1718 \text{ (m, C=O, } \nu) ,
1583 \text{ (m, C=C, } \nu) ,
1516 \text{ (m, C=C, } \nu) ,
1023 \text{ (s, fingerprint)} ,
785 \text{ (m, C–H, } \delta) \text{ cm}^{-1} .

HR-MS (ESI positive):

- **calc. (for C_{17}H_{14}F_{4}N_{3}O_{4}):**
  - found: 400.09150
  - 400.09137 [M+H]^+ (product 9)

- **calc. (for C_{17}H_{13}F_{4}N_{3}O_{4}Na):**
  - found: 422.07344
  - 422.07319 [M+Na]^+

- **calc. (for C_{34}H_{27}F_{8}N_{6}O_{8}):**
  - found: 799.17571
  - 799.17518 [2M+H]^+

- **calc. (for C_{34}H_{26}F_{8}N_{6}O_{8}Na):**
  - found: 821.15766
  - 821.15683 [2M+Na]^+
β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate NCA (10)

Similar to a literature-known procedure\(^7\) for formation of NCAs using phosgene solution, β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate (10, 7.3 g, 0.018 mol, 1.0 eq.) is suspended in THF (anhydrous, 75 mL) and (+)-α-pinene (15 mL) under inert conditions (Schlenk). Phosgene (20 % (w/w) in toluene, 13 mL, 0.023 mol, 1.3 eq.) is added and the mixture (suspension) is stirred at 40 °C for 1 h. The mixture becomes clear upon further addition of phosgene (20 % (w/w) in toluene, 20 mL, 0.036 mol, 2.0 eq.) added in two portions and further stirring at 40 °C for 1.5 h. The solution is cannulated into n-hexane (anhydrous, 500 mL) using a syringe filter (0.4 μm), the precipitate formed is filtered off, washed with n-hexane (anhydrous) and dried in vacuo. The crude NCA is dissolved in the minimal amount of THF (anhydrous, 20 mL), cannulated into another Schlenk flask using a syringe filter (0.4 μm) and overlayed with n-hexane (anhydrous, 60 mL) using a syringe pump. The NCA is crystallised over night, separated from the liquids and dried in vacuo. Purification of the NCA is repeated once after which product 10 (4.5 g, 0.011 mol, 57 % yield) is obtained as orange crystals and stored in the glovebox. All manipulations (including work-up and purification) are performed using Schlenk technique.

TLC: 
(V\textsubscript{ethyl acetate} / V\textsubscript{cyclohexane} = 1 / 1) 

\( R_f = 0.20 \)

\(^1\)H NMR: 
(THF-\textit{d}_6, 700 MHz, 300 K) 
\( \delta = \) 8.11 (s, 1H, H\textsubscript{17}), 7.54 – 7.47 (m, 1H, H\textsubscript{8}), 7.23 (d, \( \text{J}_{HF} = 9.8 \) Hz, 2H, H\textsubscript{3,3'}), 7.17 (dd, \( \text{J}_{HF} = 8.9 \) Hz, \( \text{J}_{HH} = 8.9 \) Hz, 2H, H\textsubscript{7,7'}), 5.25 (s, 2H, H\textsubscript{9}), 4.67 (dd, \( \text{J}_{HH} = 6.7 \) Hz, \( \text{J}_{HH} = 4.2 \) Hz, 1H, H\textsubscript{14}), 3.10 – 3.02 (m, 2H, H\textsubscript{13}) ppm.  
(protons at C\textsubscript{9} and C\textsubscript{13}, respectively, are diastereotopic. H\textsubscript{8} and H\textsubscript{9} collapse into a singlet. H\textsubscript{13} and H\textsubscript{13'} overlap resulting in a multiplet with strong coupling.)

\(^19\)F NMR: 
(THF-\textit{d}_6, 659 MHz, 300 K) 
\( \delta = \) –121.6 (d, \( \text{J}_{HF} = 9.9 \) Hz, 2F, F\textsubscript{10,10'}), –122.3 (dd, \( \text{J}_{HF} = 9.3 \) Hz, \( \text{J}_{HF} = 6.0 \) Hz, 2F, F\textsubscript{11,11'}) ppm.
\(^{13}\text{C}\{\text{H}\} \text{NMR:}\)  
\((\text{THF}-d_6, 176 \text{ MHz, 300 K})\)  
\(\delta = 171.0 \text{ (s, 1C, C}_{15}\),  
170.2 \text{ (s, 1C, C}_{12}\),  
156.5 \text{ (dd, } \text{ } J_{CF} = 260.7 \text{ Hz, } \text{ } J_{CF} = 4.0 \text{ Hz, 2C, C}_{6,6}\),  
156.4 \text{ (dd, } \text{ } J_{CF} = 260.9 \text{ Hz, } \text{ } J_{CF} = 4.6 \text{ Hz, 2C, C}_{22}\),  
152.9 \text{ (s, 1C, C}_{16}\),  
142.5 \text{ (t, } \text{ } J_{CF} = 9.8 \text{ Hz, 1C, C}_{4}\),  
133.1 \text{ (t, } \text{ } J_{CF} = 10.4 \text{ Hz, 1C, C}_{9}\),  
132.6 \text{ (t, } \text{ } J_{CF} = 10.0 \text{ Hz, 1C, C}_{5}\),  
131.9 \text{ (t, } \text{ } J_{CF} = 10.2 \text{ Hz, 1C, C}_{1}\),  
113.6 \text{ (dd, } \text{ } J_{CF} = 20.1 \text{ Hz, } \text{ } J_{CF} = 3.7 \text{ Hz, 2C, C}_{7,7}\),  
112.6 \text{ (dd, } \text{ } J_{CF} = 21.2 \text{ Hz, } \text{ } J_{CF} = 3.7 \text{ Hz, 2C, C}_{3,3}\),  
65.8 \text{ (s, 1C, C}_{14}\),  
54.9 \text{ (s, 1C, C}_{9}\),  
36.5 \text{ (s, 1C, C}_{15}\) ppm.  

\(\text{ATR-IR:}\)  
\((\text{from THF}-d_6 \text{ solution})\)  
\(\nu = 3400 \text{ – } 2800 \text{ (w, C–H and N–H, } \nu),\)  
1857 \text{ (m, C=O\text{NCA}, } \nu)\)  
1782 \text{ (s, C=O\text{NCA, } } \nu)\)  
1738 \text{ (s, C=O\text{ester, } } \nu)\)  
1171 \text{ (s, C–F, } \nu)\)  
1023 \text{ (s, fingerprint)\)  
787 \text{ (s, C–H, } \delta) \text{ cm}^{-1}.\)  

\(\text{HR-MS (ESI positive):}\)  
\((\text{after dissolution in methanol})\)  
\text{calc. (for C}_{18}\text{H}_{12}\text{F}_{4}\text{N}_{3}\text{O}_{5}:} \quad 426.07076  
\text{found:} \quad \text{not observed [M+H]}^+ \text{ (product 10)}  
\text{calc. (for C}_{18}\text{H}_{16}\text{F}_{4}\text{N}_{3}\text{O}_{5}:} \quad 414.10715  
\text{found:} \quad 414.10719 \text{ [M+H]}^+ \text{ (degradation product)}  
\text{calc. (for C}_{18}\text{H}_{15}\text{F}_{4}\text{N}_{3}\text{O}_{4}\text{Na}:} \quad 436.08909  
\text{found:} \quad 436.08908 \text{ [M+Na]}^+ \text{ (degradation product)}  
\text{calc. (for C}_{36}\text{H}_{31}\text{F}_{8}\text{N}_{6}\text{O}_{8}:} \quad 827.20701  
\text{found:} \quad 827.20721 \text{ [2M+H]}^+ \text{ (degradation product)}  
\text{calc. (for C}_{36}\text{H}_{30}\text{F}_{8}\text{N}_{6}\text{O}_{8}\text{Na}:} \quad 849.18895  
\text{found:} \quad 849.18905 \text{ [2M+Na]}^+ \text{ (degradation product)}\)
\[^1\text{H} \text{NMR:}\]
\(\text{(THF-}d_6, 700 \text{ MHz, 300 K)}\) 

\[\delta = 8.11 \text{ (s, 1H, } H_{17}),\]
\[7.54 - 7.47 \text{ (m, 1H, } H_6),\]
\[7.23 \text{ (d, } ^3J_{HF} = 9.8 \text{ Hz, 2H, } H_{3,3'},\]
\[7.17 \text{ (dd, } ^3J_{HF} = 8.9 \text{ Hz, } ^3J_{HH} = 8.9 \text{ Hz, 2H, } H_{7,7'},\]
\[5.25 \text{ (s, 2H, } H_9),\]
\[4.67 \text{ (dd, } ^3J_{HF} = 6.7 \text{ Hz, } ^3J_{HH} = 4.2 \text{ Hz, 1H, } H_{14}),\]
\[3.10 - 3.02 \text{ (m, 2H, } H_1),\]

(protons at C_9 and C_{13}, respectively, are diastereotopic. \(H_9\) and \(H_9'\) collapse into a singlet. \(H_{13}\) and \(H_{13'}\) overlap resulting in a multiplet with strong coupling.)
$^{19}$F NMR:
(THF-$d_6$, 659 MHz, 300 K)

$\delta = -121.6$ (d, $^3J_{HF} = 9.9$ Hz, 2F, F$_{10,10'}$),

$-122.3$ (dd, $^3J_{HF} = 9.3$ Hz, $^4J_{HF} = 6.0$ Hz, 2F, F$_{11,11'}$) ppm.
$^{13}$C{'H} NMR: 
(THF-$d_6$, 176 MHz, 300 K)

$\delta =$ 171.0 (s, 1C, C$_{15}$),
170.2 (s, 1C, C$_{13}$),
156.5 (dd, $^1J_{CF} = 260.7$ Hz, $^3J_{CF} = 4.0$ Hz, 2C, C$_{6,6'}$),
156.4 (dd, $^1J_{CF} = 260.9$ Hz, $^3J_{CF} = 4.6$ Hz, 2C, C$_{2,2'}$),
152.9 (s, 1C, C$_{16}$),
142.5 (t, $^3J_{CF} = 9.8$ Hz, 1C, C$_4$),
133.1 (t, $^3J_{CF} = 10.4$ Hz, 1C, C$_3$),
132.6 (t, $^2J_{CF} = 10.0$ Hz, 1C, C$_5$),
131.9 (t, $^2J_{CF} = 10.2$ Hz, 1C, C$_1$),
113.6 (dd, $^2J_{CF} = 20.1$ Hz, $^1J_{CF} = 3.7$ Hz, 2C, C$_{7,7'}$),
112.6 (dd, $^2J_{CF} = 21.2$ Hz, $^1J_{CF} = 3.7$ Hz, 2C, C$_{3,3'}$),
65.8 (s, 1C, C$_{14}$),
54.9 (s, 1C, C$_9$),
36.5 (s, 1C, C$_{13}$) ppm.
ATR-IR: (from THF-$d_6$ solution)

$\tilde{\nu} = 3400 – 2800$ (w, C–H and N–H, $\tilde{\nu}$),

$1857$ (m, C=O$_{\text{NCA}}$, $\tilde{\nu}$)

$1782$ (s, C=O$_{\text{NCA}}$, $\tilde{\nu}$)

$1738$ (s, C=O$_{\text{ester}}$, $\tilde{\nu}$)

$1171$ (s, C–F, $\tilde{\nu}$)

$1023$ (s, fingerprint)

$787$ (s, C–H, $\delta$) cm$^{-1}$.
HR-MS (ESI positive):
(after dissolution in methanol)
calc. (for C_{18}H_{12}F_{4}N_{3}O_{5}): 426.07076
found: not observed [M+H]^+ (product 10)
calc. (for C_{18}H_{12}F_{4}N_{3}O_{4}): 414.10715
found: 414.10719 [M+H]^+ (degradation product)
calc. (for C_{18}H_{12}F_{4}N_{3}O_{4}Na): 436.08909
found: 436.08908 [M+Na]^+ (degradation product)
calc. (for C_{36}H_{31}F_{8}N_{6}O_{8}): 827.20701
found: 827.20721 [2M+H]^+ (degradation product)
calc. (for C_{36}H_{30}F_{8}N_{6}O_{8}Na): 849.18895
found: 849.18905 [2M+Na]^+ (degradation product)

postulated degradation sequence resulting in $M = C_{18}H_{15}F_{4}N_{3}O_{4}$:
β-[4-(2,6-difluorophenyl)-azo-3,5-difluorobenzyl]-L-aspartate NCA (10, 1.07 g, 2.5 mmol) is suspended in dichloromethane (anhydrous, 40 mL) in the glovebox. Dimethylethanolamine solution (anhydrous, 10.0 mmol/L in dichloromethane, 0.5 mL, 5.0 μmol) is added to initiate the polymerisation (resulting in an initiator to monomer ratio of 500 to 1) and the mixture is stirred for 12 d at room temperature inside the glovebox. Polymerisation progress is followed visually (after 5 d the reaction mixture has cleared up) and by ATR-IR spectroscopy of the reaction mixture (disappearance of $\tilde{\nu} = 1782$ cm$^{-1}$ (s, C=O NCA), ν) and formation of $\tilde{\nu} = 1663$ cm$^{-1}$ (s, C=O amide, ν) after 12 d). The solution is added drop wise in $n$-hexane (300 mL), the precipitate is filtered off, washed with $n$-hexane and dried in vacuo over night. PpFABLA (1, 0.91 g, 96 % yield) is obtained as red fibrous solid. Acquisition of NMR spectra is only possible after addition of TFA. Signals in the NMR spectra show the typical broadening for polymers.

$^1$H NMR: (CDCl$_3$ + TFA, 400 MHz, 300 K)  
\[ \delta = 8.09 - 7.81 \text{ (m, 1H, H$_{16}$),} \]
\[ 7.41 - 7.29 \text{ (m, 1H, H$_{E-8}$),} \]
\[ 7.22 - 7.13 \text{ (m, 1H, H$_{Z-8}$),} \]
\[ 7.07 - 6.87 \text{ (m, 4H, H$_{E-3,3'}$ and E-7,7'),} \]
\[ 6.86 - 6.66 \text{ (m, 4H, H$_{Z-3,3'}$ and Z-7,7'),} \]
\[ 5.48 - 4.22 \text{ (m, 3H, H$_9$ and 14),} \]
\[ 3.64 - 2.69 \text{ (m, 2H, H$_{13}$)} \] ppm.

$^{19}$F NMR: (CDCl$_3$ + TFA, 376 MHz, 300 K)  
\[ \delta = -118.1 \text{ (s, 2F, F$_{Z-isomer}$),} \]
\[ -119.2 \text{ (s, 2F, F$_{Z-isomer}$),} \]
\[ -120.2 \text{ (s, 2F, F$_{E-isomer}$),} \]
\[ -121.1 \text{ (s, 2F, F$_{E-isomer}$)} \] ppm. (approx. 59 % E-isomer)

$^{13}\text{C}^{(1)}$H NMR: (CDCl$_3$ + TFA, 101 MHz, 300 K)  
broadened signals vanish in baseline

ATR-IR: (from CH$_2$Cl$_2$ solution)  
\[ \tilde{\nu} = 3297 \text{ (m, N–H, v)}, \]
\[ 3100 – 2900 \text{ (w, C–H, v),} \]
\[ 1754 \text{ (s, C=O$_{ester}$, v)}, \]
\[ 1663 \text{ (s, C=O$_{amide}$, v)}, \]
\[ 1160 \text{ (s, C–F, v)}, \]
\[ 1024 \text{ (s, fingerprint)}, \]
\[ 785 \text{ (s, C–H, $\delta$)} \] cm$^{-1}$.

GPC: (CHCl$_3$ + 0.3 % TBAB, 25 °C)  
\[ M_n = 160 \text{ kg/mol} \]
\[ M_w = 200 \text{ kg/mol} \]
\[ D_M = 1.30 \]

MALDI:  
\[ M_p = 130 \times 10^3 \text{ m/z} \]
\[ \delta = 8.09 - 7.81 \text{ (m, 1H, H}_{16},) \]
\[ 7.41 - 7.29 \text{ (m, 1H, H}_{E-8},) \]
\[ 7.22 - 7.13 \text{ (m, 1H, H}_{Z-8},) \]
\[ 7.07 - 6.87 \text{ (m, 4H, H}_{E-3,3'} \text{ and E-7,7'},) \]
\[ 6.86 - 6.66 \text{ (m, 4H, H}_{Z-3,3'} \text{ and Z-7,7'},) \]
\[ 5.48 - 4.22 \text{ (m, 3H, H}_{9} \text{ and } H_{14},) \]
\[ 3.64 - 2.69 \text{ (m, 2H, H}_{13},) \text{ ppm.} \]
$^{19}$F NMR:
(CDCl$_3$ + TFA, 376 MHz, 300 K)

$\delta = -118.1 \text{ (s, 2F, F}_{Z\text{-isomer}})$,
-119.2 \text{ (s, 2F, F}_{Z\text{-isomer}}),
-120.2 \text{ (s, 2F, F}_{E\text{-isomer})},
-121.1 \text{ (s, 2F, F}_{E\text{-isomer}}) \text{ ppm.}

(approx. 59 % E-isomer)
ATR-IR: (from CH$_2$Cl$_2$ solution)

$\tilde{\nu} =$ 3297 (m, N–H, $\nu$)
3100 – 2900 (w, C–H, $\nu$),
1754 (s, C=O$_{ester}$, $\nu$)
1663 (s, C=O$_{amide}$, $\nu$)
1160 (s, C–F, $\nu$)
1024 (s, fingerprint)
785 (s, C–H, $\delta$) cm$^{-1}$.
GPC:
(CHCl₃ + 0.3 % TBAB, 25 °C)  
\[ M_n = 160 \text{ kg/mol} \]
\[ M_w = 200 \text{ kg/mol} \]
\[ D_M = 1.30 \]
MALDI:

\[ M_p = 130 \times 10^3 \text{ m/z} \]
UV-vis and CD Spectra and Procedure for Determination of E/Z Ratio

Before acquisition of the first spectrum, the sample was irradiated with a violet (400 nm) LED for 5 min, which ensured the sample to be in the pss-E-1. The sample was measured in a series of 10 individual measurements and irradiation for a couple of seconds first with a green (525 nm) LED (measurements 1 to 6, resulting in pss-Z-1) and second with a violet (400 nm) LED again (measurements 6 to 10, restoring pss-E-1). The n-π* absorbance is intense enough to allow for an iterative calculation of isomeric ratio of polymer 1 for each individual measurement using:

\[
\text{absorbance} (\lambda) = x_{E-\text{isomer}} \cdot \text{absorbance}_{E-\text{isomer}} (\lambda) + (1 - x_{E-\text{isomer}}) \cdot \text{absorbance}_{Z-\text{isomer}} (\lambda)
\]

The absorbances obtained by this procedure for both isomers are given in the data repository.
Poly-β-[4-(2,6-difluorophenyl)azo(3,5-difluorobenzyl)]-L-aspartate-copoly-β-benzyl-L-aspartate (PpFABLA-co-PBLA, 11)

β-[4-(2,6-difluorophenyl)azo-3,5-difluorobenzyl]-L-aspartate NCA (10, 0.96 g, 2.25 mmol) and β-benzyl-L-aspartate NCA8 (0.19 g, 0.75 mmol) are suspended in dichloromethane (anhydrous, 50 mL) in the glovebox. Dimethylethanolamine solution (anhydrous, 10.0 mmol/L in dichloromethane, 0.6 mL, 6.0 μmol) is added to initiate the polymerisation (resulting in an initiator to monomer ratio of 500 to 1) and the mixture is stirred for 12 d at room temperature inside the glovebox. Polymerisation progress is followed visually (after 5 d the reaction mixture has cleared up) and by ATR-IR spectroscopy of the reaction mixture (disappearance of $\tilde{\nu} = 1782$ cm$^{-1}$ (s, C=O NCA, $\nu$) and formation of $\tilde{\nu} = 1663$ cm$^{-1}$ (s, C=O amide, $\nu$) after 12 d). The solution is added drop wise into $n$-hexane (400 mL), the precipitate is filtered off, washed with $n$-hexane and dried in vacuo over night. PpFABLA-co-PBLA (11, 0.98 g, 97 % yield) is obtained as red fibrous solid. Acquisition of NMR spectra is only possible after addition of TFA. Signals in the NMR spectra show the typical broadening for polymers.

$^1$H NMR:
(CDCl$_3$ + TFA, 400 MHz, 300 K)

$\delta = \begin{align*}
8.10 – 7.83 & \text{ (m, 1H + 1H, H$_{16}$ and 21),} \\
7.45 – 7.29 & \text{ (m, 1H, H$_{6,8}$),} \\
7.25 – 7.16 & \text{ (m, 1H + 5H, H$_{E,8}$ and 24,24',25,25',26),} \\
7.06 – 6.89 & \text{ (m, 4H, H$_{E,3,3'}$ and E-7,7'),} \\
6.86 – 6.69 & \text{ (m, 4H, H$_{Z,3,3'}$ and Z-7,7'),} \\
5.22 – 4.73 & \text{ (m, 3H + 3H, H$_{9,9',14}$ and 18,22,22'),} \\
3.27 – 2.83 & \text{ (m, 2H + 2H, H$_{13,13'}$ and 19,19') ppm.}
\end{align*}$

$^{19}$F NMR:
(CDCl$_3$ + TFA, 376 MHz, 300 K)

$\delta = \begin{align*}
-117.8 & \text{ (s, 2F, F$_{Z,isol}$),} \\
-119.0 & \text{ (s, 2F, F$_{Z,isol}$),} \\
-120.2 & \text{ (s, 2F, F$_{E,isol}$),} \\
-121.1 & \text{ (s, 2F, F$_{E,isol}$) ppm. (approx. 56 % E-isomer)}
\end{align*}$

$^{13}$C($^1$H) NMR:
(CDCl$_3$ + TFA, 101 MHz, 300 K)

Broadened signals vanish in baseline

ATR-IR:
(neat)

$\tilde{\nu} = \begin{align*}
3296 & \text{ (m, N–H, $\nu$)} \\
3100 – 2900 & \text{ (w, C–H, $\nu$),} \\
1734 & \text{ (s, C=O ester, $\nu$)} \\
1663 & \text{ (s, C=O amide, $\nu$)} \\
1161 & \text{ (s, C–F, $\nu$)} \\
1018 & \text{ (s, fingerprint)} \\
786 & \text{ (s, C–H, $\delta$) cm$^{-1}$.}
\end{align*}$

GPC:
(CHCl$_3$ + 0.3 % TBAB, 25 °C)

$M_n = 130$ kg/mol

$M_w = 150$ kg/mol

$D_M = 1.15$

MALDI:

$M_p = 180 \times 10^3$ m/z
$^1$H NMR:
(CDCl$_3$ + TFA, 400 MHz, 300 K)  

\[ \delta = 8.10 - 7.83 \text{ (m, 1H + 1H, H}_{16} \text{ and } 21) , \]
\[ 7.45 - 7.29 \text{ (m, 1H, H}_{6,8} ), \]
\[ 7.25 - 7.16 \text{ (m, 1H + 5H, H}_{Z-8} \text{ and } 24,24',25,25',26) , \]
\[ 7.06 - 6.89 \text{ (m, 4H, H}_{E,3,3'} \text{ and } E-7,7') , \]
\[ 6.86 - 6.69 \text{ (m, 4H, H}_{Z,3,3'} \text{ and } Z-7,7') , \]
\[ 5.22 - 4.73 \text{ (m, 3H + 3H, H}_{9,9',14} \text{ and } 18,22,22') , \]
\[ 3.27 - 2.83 \text{ (m, 2H + 2H, H}_{13,13'} \text{ and } 19,19') \text{ ppm.} \]
\( ^{19}\text{F NMR:} \)
(CDCl\(_3\) + TFA, 376 MHz, 300 K)

\[ \delta = -117.8 \text{ (s, 2F, } F_{Z\text{-isomer}}), \]
\[ -119.0 \text{ (s, 2F, } F_{Z\text{-isomer}}), \]
\[ -120.2 \text{ (s, 2F, } F_{E\text{-isomer}}), \]
\[ -121.1 \text{ (s, 2F, } F_{E\text{-isomer}}) \text{ ppm.} \]

(approx. 56% E-isomer)
ATR-IR: (neat)

\[ \tilde{\nu} = 3296 \text{ (m, N–H, } \tilde{\nu}) \]

3100 – 2900 (w, C–H, \( \tilde{\nu} \)),

1734 (s, C=Oester, \( \tilde{\nu} \))

1663 (s, C=Oamide, \( \tilde{\nu} \))

1161 (s, C–F, \( \tilde{\nu} \))

1018 (s, fingerprint)

786 (s, C–H, \( \delta \)) cm\(^{-1} \).
GPC:
(CHCl₃ + 0.3 % TBAB, 25 °C)

\[ M_n = 130 \text{ kg/mol} \]
\[ M_w = 150 \text{ kg/mol} \]
\[ \overline{D}_M = 1.15 \]
MALDI: 

\[ M_p = 180 \times 10^3 \text{ m/z} \]
UV-vis and CD Spectra

Before acquisition of the first spectrum, the sample was irradiated with a violet (400 nm) LED for 5 min that ensured the sample to be in the pss-E-11. The sample was measured in a series of 7 individual measurements and irradiation for a couple of seconds first with a green (525 nm) LED (measurements 1 to 5, resulting in pss-Z-11) and second with a violet (400 nm) LED again (measurements 5 to 7, restoring pss-E-11). Iterative calculation of isomeric ratios was not possible (inconsistent results depending on initial values) due to the weak absorbance of n-π* absorption bands and / or too little sampling of isomeric ratios.
NMR Sample Preparation, Calculation of Alignment Properties, Illumination Experiments/History and Enantiomer Differentiation

NMR Sample Composition

<table>
<thead>
<tr>
<th>#</th>
<th>polymer</th>
<th>analyte</th>
<th>m(polymer) in mg</th>
<th>m(solvent) in mg</th>
<th>m(analyte) in mg</th>
<th>w(polymer)a in % (w/w)</th>
<th>w(analyte)b in % (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(+)</td>
<td>PpFABLA (1)</td>
<td>(+)-IPC</td>
<td>46.1</td>
<td>185.5</td>
<td>6.0</td>
<td>19.9</td>
<td>13</td>
</tr>
<tr>
<td>I(−)</td>
<td>PpFABLA (1)</td>
<td>(−)-IPC</td>
<td>55.5</td>
<td>227.7</td>
<td>5.4</td>
<td>19.6</td>
<td>10</td>
</tr>
<tr>
<td>11(+)</td>
<td>PpFABLA-co-PBLA (11)</td>
<td>(+)-IPC</td>
<td>50.0</td>
<td>261.6</td>
<td>5.0</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>11(−)</td>
<td>PpFABLA-co-PBLA (11)</td>
<td>(−)-IPC</td>
<td>49.3</td>
<td>248.3</td>
<td>4.5</td>
<td>16.6</td>
<td>11</td>
</tr>
</tbody>
</table>

[a] \( \frac{m(\text{polymer})}{m(\text{polymer})+m(\text{solvent})} \)

[b] \( \frac{m(\text{analyte})}{m(\text{polymer})} \)

Alignment Properties

IPC (used as probe to investigate the alignment properties of the LLC phase) is additionally dissolved in a NMR sample consisting of the LLC phase (of PpFABLA (1) and PpFABLA-co-PBLA (11), respectively). In the magnetic field of the NMR spectrometer the LLC phase orients with respect to the magnetic field and induces a preferred orientation (with respect to the magnetic field) onto IPC. Thus, total couplings \( (T_{exp}) \) of IPC become measurable and are used together with their scalar couplings \( (J) \) to calculate the experimental dipolar coupling \( (D_{exp}) \) according to:\(^9\)

\[
D_{exp} = \frac{T_{exp} - J}{2}
\]

The alignment tensor is obtained from the experimental dipolar couplings \( (D_{exp}) \) and a structural model of IPC by singular value decomposition analysis\(^10\) using RDC@hotFCHT\(^11\). It describes the (mean) orientation of the analyte (used as probe) with respect to the magnetic field. Several alignment properties can be derived from the alignment tensor and can be used for comparison of different alignments induced\(^12\). The quality of RDC vector sampling is described by the condition number\(^11\). Dipolar couplings are back-calculated \( (D_{calc}) \) and should be in accordance with \( D_{exp} \) (due to the correct structural model of IPC). The deviation of modelled and experimental data is expressed as RMSD or as a quality factor\(^13\). The mean orientation of the alignment tensor is expressed by a set of three euler angles \((\alpha, \beta, \gamma)\) for which an uncertainty is derived by a Monte Carlo bootstrapping approach\(^10\). The axial and rhombic component of the Saupe tensor is described as \( D_a \) and \( D_r \), respectively and the strength of the alignment is described by the GDO\(^12\).
NMR Sample: #1(+)

Sample History:

1) sample preparation
2) irradiation with two violet (400 nm) LEDs for 5 d leading to E-isomeric state E’
   ➢ NMR data: $^2$H, $^{19}$F, $^1$H/$^{13}$C CLIP-HSQC$^{14}$ and $^1$H/$^{13}$C F1-coupled HSQC$^{15}$
3) irradiation with one green (525 nm) LED for 2 d leading to Z-isomeric state Z’
   ➢ NMR data: $^2$H, $^{19}$F and $^1$H/$^{13}$C CLIP-HSQC$^{14}$
4) irradiation with two violet (400 nm) LEDs for 4 d leading to E-isomeric state E’’
   ➢ NMR data: $^2$H and $^{19}$F

Comment on Isomer Ratio Obtained by Irradiation:

Due to the absence of thermal relaxation after switching of the LED, the isomer ratio remains the same as in the photostationary state (pss). It is referred to as pss-E-1 and pss-Z-1, respectively. We have no means yet to check for reproducibility of the isomer ratios. Once this is established this would allow for irradiating the sample until the same isomer ratio is reached again. This is the prerequisite to ensure reproducible alignment of the solute. Furthermore, tuning the polymer length is expected to result in lower critical concentrations$^{16}$ of the lyotropic liquid crystal and, consequently, a reduced optical density of the sample. This should simplify the photo-conversion of the sample by irradiation with LEDs. For now, after treating a sample with light, the states obtained (while being both e.g. anisotropic) are regarded as different and, therefore, denoted as E’ and E’’ in the particular case of sample #1(+). This difference also translates into slightly different quadrupolar splittings observed for the solvent TCE-$d_2$ in $^2$H NMR spectroscopy (e.g. 201 and 230 Hz for E’ and E’’ of sample #1(+), respectively).
### #1(+)-E':

![1H NMR spectrum](image1)

![19F NMR spectrum](image2)

| coupling  | experiment(a) | $T_{exp}$ in Hz | $D_{exp}$ in Hz(b) | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|-----------|---------------|-----------------|--------------------|------------------|---------------------------|
| C1-H1     | F1            | 110.8 ± 3.0     | -15.2 ± 1.7        | -14.0 ± 0.4      | 1.2                       |
| C2-H2     | F1            | 149.5 ± 5.0     | 11.4 ± 2.7         | 16.4 ± 2.9       | 5.0                       |
| C4-H4a    | F2            | 151.7 ± 15.0    | 12.4 ± 7.6         | 13.8 ± 0.2       | 1.4                       |
| C4-H4s    | F2            | 82.3 ± 2.0      | -22.3 ± 1.1        | 22.5 ± 1.7       | 0.2                       |
| C5-H5     | F1            | 110.0 ± 5.0     | -15.7 ± 2.8        | -14.7 ± 0.1      | 1.0                       |
| C7-H7s    | F2            | 127.6 ± 5.0     | -3.9 ± 2.6         | -0.4 ± 3.1       | 3.5                       |
| C8-H8     | F1            | 100.4 ± 2.5     | -12.2 ± 1.3        |                  |                           |
| C6-C8(a)  | avg(F1+F2)    | 3.48 ± 0.37     | 3.35 ± 0.10        | 0.13             |                           |
| C9-H9     | avg(F1+F2)    | 140.0 ± 2.3     | 8.2 ± 1.2          |                 |                           |
| C6-C9(a)  | avg(F1+F2)    | -2.33 ± 0.34    | -2.52 ± 0.14       | 0.19             |                           |
| C10-H10   | avg(F1+F2)    | 144.4 ± 0.8     | 9.8 ± 0.4          |                 |                           |
| C2-C10[a] | avg(F1+F2)    | -2.79 ± 0.12    | -2.75 ± 0.21       | 0.04             |                           |

[a] C-CH₃ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation
[b] Total couplings ($T_{exp}$) were extracted either from F1-coupled HSQC¹³ (F1) or CLIP-HSQC¹² (F2) NMR spectra. Avg(F1+F2) denotes the average of both couplings being displayed.
[c] calculated using scalar couplings taken from reference⁸

Temperature in K 293  Euler angle $\alpha$ in ° 15.4 ± 18.6

Quadrupolar splitting in Hz[a] 201  Euler angle $\beta$ in ° 90.2 ± 1.1

Number of D 9  Euler angle $\gamma$ in ° 150.9 ± 1.3

Condition number 3.0  $D_2 \cdot 10^3$ -1.28

RMSD in Hz 2.2  $D_4 \cdot 10^4$ -0.79

Quality factor 0.18  GDO $\cdot 10^3$ 2.57

[a] Quadrupolar splitting of TCE-$d_2$
### #1 (+)-Z’:

![Diagram](image)

#### ²H NMR spectrum

| Coupling | $T_{exp}$ in Hz | $D_{exp}$ in Hz | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|----------|-----------------|-----------------|-----------------|---------------------|
| C1-H1    | 141.3 ± 0.3     | 0.1 ± 0.3       | –               | –                   |
| C2-H2    | 127.1 ± 0.5     | 0.2 ± 0.4       | –               | –                   |
| C4-H4a   | 127.3 ± 0.5     | 0.2 ± 0.4       | –               | –                   |
| C4-H4s   | 126.7 ± 0.3     | 0.0 ± 0.3       | –               | –                   |
| C5-H5    | 141.8 ± 0.3     | 0.3 ± 0.4       | –               | –                   |
| C7-H7s   | 135.8 ± 0.3     | 0.3 ± 0.3       | –               | –                   |
| C8-H8    | 124.9 ± 0.2     | 0.1 ± 0.2       | –               | –                   |
| C6-C8    | –               | 0.03 ± 0.04     | –               | –                   |
| C9-H9    | 123.8 ± 0.2     | 0 ± 0.2         | –               | –                   |
| C6-C9    | –               | 0.01 ± 0.04     | –               | –                   |
| C10-H10  | 124.9 ± 0.2     | 0 ± 0.2         | –               | –                   |
| C2-C10   | –               | 0.00 ± 0.04     | –               | –                   |

[a] C-CH₃ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation

[b] calculated using scalar couplings taken from reference

[c] No fitting was performed, because $D_{exp}$ are zero within their estimated uncertainty ranges as expected in the absence of anisotropy.
#1(+)−E'':

$^2$H NMR spectrum

$^{19}$F NMR spectrum
NMR Sample: #1(–)

Sample History:

1) sample preparation

2) irradiation with two violet (400 nm) LEDs for 1 d leading to E-isomeric state E’
   ➢ NMR data: $^2\text{H}$, $^{19}\text{F}$, $^1\text{H}/^{13}\text{C}$ CLIP-HSQC$^{14}$ and $^1\text{H}/^{13}\text{C}$ F1-coupled HSQC$^{15}$

3) irradiation with one green (525 nm) LED for 2 d leading to Z-isomeric state Z’
   ➢ NMR data: $^2\text{H}$, $^{19}\text{F}$ and $^1\text{H}/^{13}\text{C}$ CLIP-HSQC$^{14}$

4) irradiation with two violet (400 nm) LEDs for 6 d leading to E-isomeric state E”
   ➢ NMR data: $^2\text{H}$ and $^{19}\text{F}$

5) irradiation of the sample’s lower part with one green (525 nm) LED for 2 d preserving the E-isomeric state E” of the sample’s upper part and leading to Z-isomeric state Z” of the sample’s lower part
   ➢ NMR data: $^2\text{H}$, $^2\text{H}$-image$^{18}$, $^{19}\text{F}$ and spatially selective $^1\text{H}/^{13}\text{C}$ CLIP-HSQC$^{19}$

6) irradiation with two violet (400 nm) LEDs for 4 d leading to E-isomeric state E”’
   ➢ NMR data: $^2\text{H}$ and $^{19}\text{F}$
#1(−)-E′:

| coupling     | experiment | $T_{exp}$ in Hz | $D_{exp}$ in Hz$^{[a]}$ | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|--------------|------------|----------------|-------------------------|-----------------|-----------------------------|
| C1-H1        | F1         | 116.3 ± 2.0    | −12.4 ± 1.2             | −12.6 ± 0.6     | 0.2                         |
| C2-H2        | F1         | 140.9 ± 1.0    | 7.1 ± 0.7               | 7.1 ± 2.6       | 0.0                         |
| C4-H4a       | F2         | 165.0 ± 20.0   | 19.1 ± 10.1             | 19.8 ± 0.0      | 0.7                         |
| C4-H4s       | F2         | 75.0 ± 5.0     | −25.9 ± 2.6             | −26.5 ± 2.0     | 0.6                         |
| C5-H5        | F1         | 113.8 ± 4.0    | −13.8 ± 2.3             | −14.3 ± 0.0     | 0.5                         |
| C7-H7s       | F2         | 137.5 ± 5.0    | 1.1 ± 2.6               | 2.3 ± 2.9       | 1.2                         |
| C8-H8        | F1         | 104.8 ± 1.5    | −10.0 ± 0.8             |                 |                             |
| C6-C8$^{[a]}$| F2         | 2.85 ± 0.23    | 2.65 ± 0.11             | 0.20            |                             |
| C9-H9        | avg(F1+F2) | 133.7 ± 2.3    | 5 ± 1.2                 |                 |                             |
| C6-C9$^{[a]}$| avg(F1+F2) | −1.42 ± 0.34   | −1.62 ± 0.12            | 0.20            |                             |
| C10-H10      | avg(F1+F2) | 133.4 ± 0.5    | 4.2 ± 0.3               |                 |                             |
| C2-C10$^{[a]}$|           | −1.22 ± 0.09   | −1.23 ± 0.21            | 0.01            |                             |

[a] C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation$^{17}$
[b] Total couplings ($T_{exp}$) were extracted either from F1-coupled HSQC$^{15}$ (F1) or CLIP-HSQC$^{14}$ (F2) NMR spectra. Avg(F1+F2) denotes the average of both couplings being displayed.
[c] calculated using scalar couplings taken from reference$^8$

temperature in K 293  euler angle $\alpha$ in ° 91.1 ± 6.6
quadrupolar splitting in Hz$^{[a]}$ 167  euler angle $\beta$ in ° 95.1 ± 0.9
number of $D$ 9  euler angle $\gamma$ in ° 155.0 ± 1.5
condition number 4.5  $D_s \cdot 10^3$ −1.00
RMSD in Hz 0.6  $D_t \cdot 10^4$ −2.19
quality factor 0.04  GDO $\cdot 10^3$ 2.01

[a] quadrupolar splitting of TCE-d$_2$
#1(−)-Z′:

$\Delta \gamma' \gamma$: 

$T_{\text{exp}}$ in Hz $D_{\text{exp}}$ in Hz $D_{\text{calc}}$ in Hz $|D_{\text{exp}} - D_{\text{calc}}|$ in Hz

| Coupling | $T_{\text{exp}}$ in Hz | $D_{\text{exp}}$ in Hz $^b$ | $D_{\text{calc}}$ in Hz $^b$ | $|D_{\text{exp}} - D_{\text{calc}}|$ in Hz $^b$ |
|----------|------------------------|-----------------------------|-----------------------------|---------------------------------|
| C1-H1    | 141.4 ± 0.3            | 0.2 ± 0.3                   | 0.2 ± 0.3                   | −                               |
| C2-H2    | 126.8 ± 0.3            | 0.0 ± 0.3                   | 0.0 ± 0.3                   | −                               |
| C4-H4a   | 126.5 ± 0.5            | −0.2 ± 0.4                  | −0.2 ± 0.4                  | −                               |
| C4-H4s   | 126.4 ± 0.5            | −0.2 ± 0.4                  | −0.2 ± 0.4                  | −                               |
| C5-H5    | 141.5 ± 0.2            | 0.1 ± 0.4                   | 0.1 ± 0.4                   | −                               |
| C7-H7s   | 135.8 ± 0.3            | 0.3 ± 0.3                   | 0.3 ± 0.3                   | −                               |
| C8-H8    | 124.9 ± 0.2            | 0.1 ± 0.2                   | 0.1 ± 0.2                   | −                               |
| C6-C8$^a$| 124.0 ± 0.2            | −0.03 ± 0.04                | −0.03 ± 0.04                | −                               |
| C9-H9    | 124.0 ± 0.2            | 0.1 ± 0.2                   | 0.1 ± 0.2                   | −                               |
| C6-C9$^a$| 124.0 ± 0.2            | −0.04 ± 0.04                | −0.04 ± 0.04                | −                               |
| C10-H10  | 124.9 ± 0.1            | 0.0 ± 0.1                   | 0.0 ± 0.1                   | −                               |
| C2-C10$^a$| 124.0 ± 0.2           | 0.00 ± 0.02                 | 0.00 ± 0.02                 | −                               |

[a] C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation$^{17}$

[b] calculated using scalar couplings taken from reference$^8$

[c] No fitting was performed, because $D_{\text{exp}}$ are zero within their estimated uncertainty ranges as expected in the absence of anisotropy.
#1(−)-E'':

$^1$H NMR spectrum

$^1$H NMR spectrum

$^1$F NMR spectrum

δ in ppm
#1(−) $E'$, $Z'$, : $E''$:

1 d
(2 x 400 nm)

2 d
(1 x 525 nm)

6 d
(2 x 400 nm)

2 d
(1 x 525 nm)

4 d
(2 x 400 nm)

$E'$

$Z'$

$E''$

$Z''$

$E'''$

$Z'''$

$E''''$

$Z''''$

$E''''$}

$^2$H NMR spectrum

$^2$H image NMR spectrum

$^1$H NMR spectra

samples's upper part

samples's lower part

$^1$F NMR spectra

$^1$F image NMR spectrum
Homogeneity:
The centrifugation procedure is routinely applied in preparation of LLC based alignment media to obtain a homogeneous sample and is used in this study for samples irradiated homogeneously. The sample was not centrifuged back and forth after irradiating the lower part with the green LED as this would destroy the phase boundary between the anisotropic, upper and the isotropic, lower part of the sample. Without centrifugation, diffusion and potentially also a non-homogeneous irradiation can lead to inhomogeneity (e.g. a concentration gradient). For the upper, anisotropic part, this becomes evident in the differences in quadrupolar splitting (of the solvent TCE-$d_2$), which were measured with spatial resolution.

<table>
<thead>
<tr>
<th>coupling</th>
<th>$T_{E'}$ in Hz</th>
<th>$T_{E''}$ in Hz$^b$</th>
<th>$T_{Z'}$ in Hz</th>
<th>$T_{Z''}$ in Hz$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-H1$^a$</td>
<td>116.3 ± 2.0</td>
<td></td>
<td>141.4 ± 0.3</td>
<td>141.5 ± 0.3</td>
</tr>
<tr>
<td>C2-H2$^a$</td>
<td>140.9 ± 1.0</td>
<td></td>
<td>126.8 ± 0.3</td>
<td>126.3 ± 0.3</td>
</tr>
<tr>
<td>C4-H4a</td>
<td>165.0 ± 20.0</td>
<td>158.0 ± 7.0</td>
<td>126.5 ± 0.5</td>
<td>127.1 ± 0.3</td>
</tr>
<tr>
<td>C4-H4s</td>
<td>75.0 ± 5.0</td>
<td>78.5 ± 5.0</td>
<td>126.4 ± 0.5</td>
<td>126.9 ± 0.3</td>
</tr>
<tr>
<td>C5-H5</td>
<td>113.8 ± 4.0$^c$</td>
<td>133.4 ± 7.0$^c$</td>
<td>141.5 ± 0.2</td>
<td>141.7 ± 0.3</td>
</tr>
<tr>
<td>C7-H7s</td>
<td>137.5 ± 5.0</td>
<td>136.4 ± 5.0</td>
<td>135.8 ± 0.3</td>
<td>136.0 ± 0.3</td>
</tr>
<tr>
<td>C8-H8</td>
<td>104.8 ± 1.5$^c$</td>
<td>119.3 ± 5.0$^c$</td>
<td>124.9 ± 0.2</td>
<td>124.6 ± 0.2</td>
</tr>
<tr>
<td>C9-H9</td>
<td>133.7 ± 2.3</td>
<td>128.3 ± 5.0</td>
<td>124.0 ± 0.2</td>
<td>123.8 ± 0.2</td>
</tr>
<tr>
<td>C10-H10</td>
<td>133.4 ± 0.5</td>
<td>127.8 ± 5.0</td>
<td>124.9 ± 0.1</td>
<td>124.6 ± 0.2</td>
</tr>
</tbody>
</table>

$^a$ could not be extracted from spatially resolved HSQC spectrum of sample’s upper part (state $E''$)
$^b$ extracted from spatially selective 1H/13C CLIP-HSQC$^{19}$
$^c$ If the states $E'$ and $E''$ of sample #1(–) are identical in isomer ratio of $Pp$FABLA (1), it is expected that the extracted total couplings of (–)-IPC are identical within experimental uncertainty. This is the case for most couplings. However, for two total couplings (C5-H5 and C8-H8) the requirement is not met. We believe this to be a consequence of the lack in reproducibility of isomer ratio and / or of the poor spectral quality.
NMR Sample: #11(+)

Sample History:

1) sample preparation

2) irradiation with two violet (400 nm) LEDs for 4 d leading to E-isomeric state E’
   ➢ NMR data: $^2$H, $^{19}$F and $^1$H/$^1$C CLIP-HSQC\textsuperscript{14}

3) irradiation with one green (525 nm) LED for 2 d leading to Z-isomeric state Z’
   ➢ NMR data: $^2$H, $^{19}$F and $^1$H/$^1$C CLIP-HSQC\textsuperscript{14}
#11(+)–E':

| coupling   | $T_{\text{exp}}$ in Hz | $D_{\text{exp}}$ in Hz | $D_{\text{calc}}$ in Hz$^b$ | $|D_{\text{exp}} - D_{\text{calc}}|$ in Hz |
|------------|-------------------------|-------------------------|-----------------------------|-------------------------------------------|
| C4-H4a     | 154.6 ± 2.0             | 13.9 ± 1.1              | 15.1 ± 0.2                  | 1.2                                       |
| C4-H4s     | 82.9 ± 0.5              | −22.0 ± 0.4             | −22.0 ± 1.5                 | 0.0                                       |
| C5-H5      | 124.2 ± 0.6             | −8.6 ± 0.6              | −8.4 ± 0.0                  | 0.2                                       |
| C7-H7a     | 228.0 ± 5.0             | 45.6 ± 2.6              | 43.4 ± 1.0                  | 2.2                                       |
| C7-H7s     | 121.0 ± 5.0             | −7.2 ± 2.6              | −4.5 ± 1.5                  | 2.7                                       |
| C9-H9      | 139.0 ± 0.2             | 7.7 ± 0.2               |                            |                                           |
| C6-C9$^a$  | −2.19 ± 0.04            | −2.19 ± 0.01            |                            | 0.0                                       |
| C10-H10    | 137.4 ± 0.2             | 6.3 ± 0.2               |                            |                                           |
| C2-C10$^a$ | −1.79 ± 0.04            | −1.80 ± 0.12            |                            | 0.01                                      |

$^a$ C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation$^{17}$

$^b$ calculated using scalar couplings taken from reference$^8$

temperature in K 293  
euler angle $\alpha$ in ° 54.8 ± 3.8
quadrupolar splitting in Hz$^a$ 281  
euler angle $\beta$ in ° 88.8 ± 1.0
number of $D$ 7  
euler angle $\gamma$ in ° 152.2 ± 0.6
condition number 6.1  
RMSD in Hz 1.4  
quality factor 0.07  

$^a$ quadrupolar splitting of TCE-$d_2$
#11(+)-Z':

| coupling     | $T_{exp}$ in Hz | $D_{exp}$ in Hz | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|--------------|-----------------|-----------------|-----------------|-------------------------------|
| C4-H4a       | 157.5 ± 5.0     | 15.3 ± 2.6      | 18.1 ± 0.6      | 2.8                           |
| C4-H4s       | 85.4 ± 2.0      | –20.7 ± 1.1     | –20.6 ± 2.5     | 0.1                           |
| C5-H5        | 114.2 ± 1.0     | –13.6 ± 0.8     | –13.4 ± 0.2     | 0.2                           |
| C7-H7a       | 230.0 ± 5.0     | 46.6 ± 2.6      | 45.6 ± 1.4      | 1.0                           |
| C7-H7s       | 116.0 ± 5.0     | –9.7 ± 2.6      | 8.7 ± 2.1       | 1.0                           |
| C9-H9        | 142.3 ± 0.5     | 9.3 ± 0.3       |                 |                               |
| C6-C9[a]     |                 | –2.66 ± 0.09    | –2.65 ± 0.02    | 0.01                          |
| C10-H10      | 140.2 ± 0.5     | 7.6 ± 0.3       |                 |                               |
| C2-C10[a]    |                 | –2.19 ± 0.09    | –2.22 ± 0.21    | 0.03                          |

[a] C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation

[b] calculated using scalar couplings taken from reference

| temperature in K | 293 | euler angle $\alpha$ in ° | 28.4 ± 2.5 |
| quadrupolar splitting in Hz[a] | 304 | euler angle $\beta$ in ° | 93.0 ± 1.6 |
| number of $D$ | 7 | euler angle $\gamma$ in ° | 155.8 ± 1.0 |
| condition number | 4.3 | $D_x \cdot 10^3$ | –1.12 |
| RMSD in Hz | 1.2 | $D_y \cdot 10^4$ | –2.65 |
| quality factor | 0.06 | GDO $\cdot 10^3$ | 2.28 |

[a] quadrupolar splitting of TCE-$d_2$
NMR Sample: #11 (−)

Sample History:

1) sample preparation

2) irradiation with two violet (400 nm) LEDs for 5 d leading to E-isomeric state E’
   ➢ NMR data: $^2$H, $^{19}$F and $^1$H/$^{13}$C CLIP-HSQC$^{14}$

3) irradiation with one green (525 nm) LED for 2 d leading to Z-isomeric state Z’
   ➢ NMR data: $^2$H, $^{19}$F and $^1$H/$^{13}$C CLIP-HSQC$^{14}$

4) irradiation with two violet (400 nm) LEDs for 4 d leading to E-isomeric state E”
   ➢ NMR data: $^2$H and $^{19}$F

5) irradiation of the sample’s upper part with one green (525 nm) LED for 2 d preserving the E-isomeric state E’’ of the samples’s lower part and leading to Z-isomeric state Z’’ of the samples’s upper part
   ➢ NMR data: $^2$H, $^3$H-image$^{18}$, $^{19}$F and spatially selective $^1$H/$^{13}$C CLIP-HSQC$^{16}$
### #11(−)-E′:

- **2^H NMR spectrum**
- **19^F NMR spectrum**

| coupling   | $T_{exp}$ in Hz | $D_{exp}$ in Hz$^b$ | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|------------|-----------------|---------------------|------------------|-----------------------------|
| C4-H4a     | 178.3 ± 3.0     | 25.7 ± 1.6          | 28.1 ± 0.6       | 2.4                         |
| C4-H4s     | 57.9 ± 1.0      | −34.5 ± 0.6         | −34.3 ± 1.7      | 0.2                         |
| C5-H5      | 107.9 ± 0.6     | −16.7 ± 0.6         | −16.5 ± 0.1      | 0.2                         |
| C7-H7a     | 233.5 ± 3.0     | 48.4 ± 1.6          | 48.2 ± 1.1       | 0.2                         |
| C7-H7s     | 132.4 ± 3.0     | −1.5 ± 1.6          | 0.1 ± 1.3        | 1.6                         |
| C9-H9      | 136.7 ± 0.4     | 6.5 ± 0.3           |                 |                             |
| C6-C9$^a$  | −1.86 ± 0.07    | −1.87 ± 0.02        | 0.01             |                             |
| C10-H10    | 132.3 ± 0.7     | 3.7 ± 0.4           |                 |                             |
| C2-C10$^a$ | −1.06 ± 0.11    | −1.09 ± 0.17        | 0.03             |                             |

[a] C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation$^{17}$
[b] calculated using scalar couplings taken from reference$^8$

d| temperature in K | 293 |
| quadrupolar splitting in Hz$^{a}$ | 300 |
| number of $D$ | 7 |
| condition number | 4.3 |
| RMSD in Hz | 1.1 |
| quality factor | 0.04 |

[a] quadrupolar splitting of TCE-$d$
#11(–)-Z':

| Coupling | $T_{exp}$ in Hz | $D_{exp}$ in Hz$^b$ | $D_{calc}$ in Hz | $|D_{exp} - D_{calc}|$ in Hz |
|----------|----------------|-------------------|----------------|------------------|
| C4-H4a   | 180.4 ± 4.0    | 26.8 ± 2.1        | 33.8 ± 0.6     | 6.0              |
| C4-H4s   | 55.8 ± 2.0     | -35.5 ± 1.1       | -35.4 ± 2.0    | 0.1              |
| C5-H5    | 92.2 ± 1.0     | -24.6 ± 0.8       | -24.0 ± 0.1    | 0.6              |
| C7-H7a   | 238.1 ± 3.0    | 50.7 ± 1.6        | 49.3 ± 1.4     | 1.4              |
| C7-H7s   | 128.2 ± 5.0    | -3.6 ± 2.6        | -0.6 ± 1.7     | 3.0              |
| C9-H9    | 138.6 ± 0.4    | 7.5 ± 0.3         |                |                  |
| C6-C9$^a$|                | -2.13 ± 0.07      | -2.12 ± 0.05   | 0.01             |
| C10-H10  | 132.6 ± 0.8    | 3.8 ± 0.5         |                |                  |
| C2-C10$^a$|               | -1.10 ± 0.13      | -1.30 ± 0.20   | 0.20             |

[a] C-CH$_3$ dipolar couplings calculated from corresponding C-H dipolar couplings according to a literature known relation$^{17}$
[b] calculated using scalar couplings taken from reference

temperature in K 293  
quadrupolar splitting in Hz$^a$ 324  
number of $D$ 7  
condition number 3.7  
RMSD in Hz 2.6  
quality factor 0.10

[a] quadrupolar splitting of TCE-$d_2$

euler angle $\alpha$ in ° 90.8 ± 2.6

euler angle $\beta$ in ° 99.6 ± 1.0

euler angle $\gamma$ in ° 160.9 ± 1.1

$D_x \cdot 10^3$ -1.29

$D_y \cdot 10^4$ -2.44

GDO $\cdot 10^3$ 2.61
### $\text{#11}(-)-\text{E''}$:

2H NMR spectrum

$\delta$ in ppm

$\text{Acetone}$

$\text{304 Hz}$

$\text{332 Hz}$

$\text{368 Hz}$

$\text{19}^\text{F}$ NMR spectrum

$\delta$ in ppm

$\text{-130}$

$\text{-120}$

$\text{-110}$
S-74
#11(−)  

\[ E''': Z'' : \]

(continued)

<table>
<thead>
<tr>
<th>Coupling</th>
<th>( T_E' ) in Hz</th>
<th>( T_E'' ) in Hz(^a)</th>
<th>( T_Z' ) in Hz</th>
<th>( T_Z'' ) in Hz(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-H4a</td>
<td>178.3 ± 3.0</td>
<td>181.8 ± 3.0</td>
<td>180.4 ± 4.0</td>
<td>180.2 ± 3.0</td>
</tr>
<tr>
<td>C4-H4s</td>
<td>57.9 ± 1.0</td>
<td>57.7 ± 2.0</td>
<td>55.8 ± 2.0</td>
<td>56.0 ± 3.0</td>
</tr>
<tr>
<td>C5-H5</td>
<td>107.9 ± 0.6</td>
<td>104.8 ± 3.0</td>
<td>92.2 ± 1.0</td>
<td>92.5 ± 2.0</td>
</tr>
<tr>
<td>C7-H7a</td>
<td>233.5 ± 3.0</td>
<td>238.0 ± 5.0</td>
<td>238.1 ± 3.0</td>
<td>240.7 ± 5.0</td>
</tr>
<tr>
<td>C7-H7s</td>
<td>132.4 ± 3.0</td>
<td>131.9 ± 3.0</td>
<td>128.2 ± 5.0</td>
<td>127.0 ± 5.0</td>
</tr>
<tr>
<td>C9-H9</td>
<td>136.7 ± 0.4</td>
<td>136.9 ± 0.6</td>
<td>138.6 ± 0.4</td>
<td>137.9 ± 1.5</td>
</tr>
<tr>
<td>C10-H10</td>
<td>132.3 ± 0.7</td>
<td>131.1 ± 1.0</td>
<td>132.6 ± 0.8</td>
<td>133.0 ± 0.7</td>
</tr>
</tbody>
</table>

\(^a\) extracted from spatially selective CLIP-HSQC acquired with a slice width of 0.5 cm and a spatial offset of 0.5 and −0.5 cm from the centre of the coil to excite the upper and lower part of the sample, respectively.
References


