Electronic Supplementary Material (ESI) for Chemical Science.

Highly Acidic *N*-Triflylphosphoramides as Chiral Brønsted Acid Catalysts: The Effect of Weak Hydrogen Bonds and Multiple Acceptors on Complex Structures and Aggregation

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Experimental data

NMR-Spectroscopy

All NMR spectroscopic investigations on model systems were performed on a Bruker Avance DRX 600 MHz spectrometer with TBI (Triple resonance broadband inverse) 5 mm CPPBBO 1H/19F-BB probe head with Z-gradient and BVT unit. Temperature was controlled in the VT-experiments by a BVT 3000 and BVT 3900 unit and liquid nitrogen. Further NMR experiments were performed on Bruker Avance III HD 400 MHz spectrometer equipped with 5 mm BBO BB-1H/D probe head with Z-Gradients. Spectrometer control and spectra processing was performed with Bruker Software TopSpin (Version 3.2 PL 1). Further data procession, data preparation and data presentation was performed with Microsoft Excel, Origin 2021, Corel Draw X7 and ChemDraw Professional. ^{1}H and ^{13}C chemical shifts were referenced to TMS or the respective solvent signals. The heteronuclei ^{15}N,^{19}F and ^{31}P were referenced, employing $\nu(X) = \nu(TMS) \cdot \Xi$reference / 100 % according to Harris et al.[1] The following frequency ratios and reference compounds were used: $\Xi(^{15}N) = 10.132912$ (lq. NH_3), $\Xi(^{19}F) = 94.094011$ (CCl_3F) and $\Xi(^{31}P) = 40.480742$ (H_3PO_4). To optimize the mixing times for the NOESY and HOESY experiments, we utilized the AU popt feature in Topspin to prevent spin diffusion. For all NMR measurements, 5 mm NMR tubes were used.

Pulse Sequences and Acquisition Parameters

Standard pulse sequences from the Bruker pulse sequence catalogue (zg, zg30, etc.) have been used. The respective pulse programs are not listed within the experimental part. Special pulse programs (qualitative detection of scalar coupling with modified ^{1}H ^{31}P HMBC measurements) are listed in Chapter "Qualitative Detection of ^{2hJPH} scalar coupling". The following acquisition parameter have been used:
^{1}H-NMR: Pulse program zg30, Relaxation delay = 2.00 s, Acquisition time = 2.54 s, SW = 22 - 24 ppm, TD = 66 K, ns = 1 - 256;
^{13}C NMR: Pulse program: zgpg30, Relaxation delay = 2.00 s, Acquisition time = 0.80 s, TD = 66 K; SW = 270.0 ppm, TD = 64k, NS = 1k - 4k;

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^{15}N NMR: Pulse program: zg30; Relaxation delay = 3.00 s, Acquisition time = 1.06 s; SW = 507.5 ppm, TD = 66 K; NS = 1K - 4K;

^{19}F-NMR: Pulse program: zg30; Relaxation delay = 2.00 s, Acquisition time = 5.79 s, SW = 20.0 ppm, TD = 131k, NS = 64;

^{31}P-NMR: Pulse program: zgpg30; Relaxation delay = 1.00 s, Acquisition time = 2.25 s, SW = 60.0 ppm, TD = 65k, NS = 256 - 512;

2D-^{1}H ^{1}H NOESY: Pulse program: noesygpph; Relaxation delay = 5.00 s, NS = 8 - 16, mixing time (D8) = 100.00 ms; TD F2 = 4096; increments (TD F1) = 512 - 1k;

2D-^{1}H ^{1}H COSY: Pulse program: cosygpqf; Relaxation delay = 5.00 s, NS = 4 - 16, TD F2 = 4096; increments (TD F1) = 512;

2D-^{1}H ^{13}C HSQC: Pulse program: hsqcedetgpsisp2.3; Relaxation delay = 4 - 8 s, NS = 8 - 32, $^1J_{XH}$ = 145 Hz; TD F2 = 4096; increments (TD F1) = 512 - 1k;

2D-^{1}H ^{13}C HMBC: Pulse program: hmbcgplpndqf; Relaxation delay = 4.00 s, NS = 8 - 16, $^1J_{XH}$ = 145 Hz, J_{XH}(long range) = 10 Hz; TD F2 = 4096; increments (TD F1) = 512 - 1k;

2D-^{1}H ^{31}P HMBC: Pulse program: inv4gplrndqf; Relaxation delay = 6.00 s, NS = 4 - 32, TD F2 = 4096; increments (TD F1) = 256 - 512;

2D-^{1}H ^{15}N HMBC: Pulse program: inv4gplrndqf; Relaxation delay = 4.00 s, NS = 4 - 16, delay for evolution of long range couplings (D6) = 20.00 ms; TD F2 = 4096; increments (TD F1) = 256;

2D-^{1}H ^{19}F HOESY: Pulse program: hoesyph; Relaxation delay = 5.00 s, NS = 8, mixing time (D8) = 350.00 ms; TD F2 = 4096; increments (TD F1) = 850 - 1250;

1D ^{1}H ^{31}P HMBC: Pulse program[2]: Relaxation delay = 4.00 s, Acquisition time = 1.23 s, SW = 22 ppm, TD F2 = 33 K NS = 256, CNST 3 = 22.

Mass Spectrometry

High resolution mass spectra were measured by the central analytics division in the Institute of Organic Chemistry. Gas chromatography coupled with a mass selective detector was performed on an Agilent 6890N Network GC-System.

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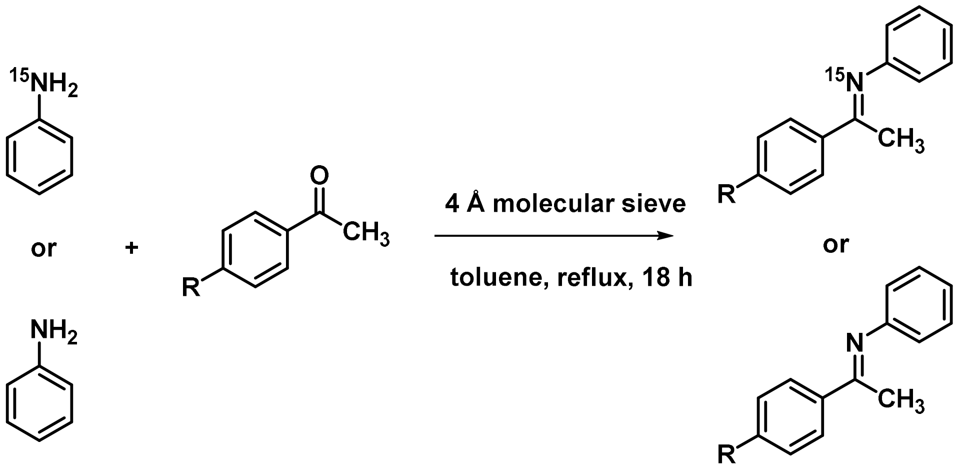
Chemistry

Deuterated solvents were purchased from Deutero or Sigma Aldrich. Where dry solvents were essential, CD_2Cl_2 was refluxed over CaH_2 for at least 5 h under Argon atmosphere and freshly distilled prior use. Toluene was refluxed over Na/Benzophenone under Argon atmosphere or purchased by Sigma Aldrich (dry, stored over molecular sieve). *(R)*-NTPA **1** was purchased by BLDpharm. All commercially available chemicals were purchased by Sigma Aldrich and used without further purification.

Synthesis of Imine Substrates

All imines were synthesized according to modified literature.[3–8] Characterization was performed on Bruker Avance III HD 400 MHz spectrometer equipped with 5 mm BBO BB-^{1}H/D probe head with Z-Gradients.

General procedure for the synthesis of imines (GP I):



Molecular sieves 4 Å (4 g) were weighed in to a 50 ml Schlenk flask equipped with a stopper. The setup was connected to a vacuum line and was evacuated and dried with a heat gun at 350 °C. Under Argon flow, Aniline or ^{15}N-Aniline (98 % ^{15}N) (10.5 mmol, 1.1 equiv.) and the respective ketone (10 mmol, 1.0 equiv.) were added to the Schlenk flask under argon atmosphere and were dissolved in 20 ml toluene. The stop cock was exchanged with a reflux

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condenser and a drying tube filled with CaCl2 and the solution was heated to reflux for 18 hours. The orange solution was filtered off from the molecular sieves and was concentrated under reduced pressure. The remaining solid was recrystallized from methanol. The product was obtained as yellow solid.

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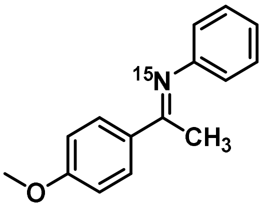
(*E*)-1-(4-methoxyphenyl)-*N*-phenylethane-1-imine (98% ^{15}N)



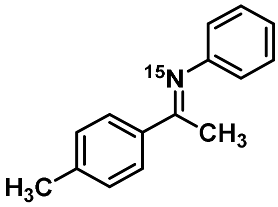
2

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (40 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[9]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.95 (m, 2H), 7.34 (m, 2H), 7.07 (m, 1H), 6.96 (m, 2H), 6.76 (m, 2H), 3.86 (s, 3H), 2.18 ppm (d, $^3J_{HN}$ =1.85 Hz, 3H).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 164.5, 161.9, 152.5, 132.5, 129.3, 129.2, 123.2, 119.9, 113.9, 55.8, 17.2 ppm.

(*E*)-1-(4-methylphenyl)-*N*-phenylethane-1-imine (98% ^{15}N)



3

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (25 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[9]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.86 (m, 2H), 7.34 (m, 2H), 7.25 (m, 2H), 7.06 (m, 1H), 6.76 (m, 2H), 2.40 (s, 3H) 2.18 ppm (d, $^3J_{HN}$ = 1.76 Hz, 3H).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 165.3, 152.4, 141.2, 137.3, 129.5, 129.3, 127.5, 123.3, 119.7, 21.5, 17.4 ppm.

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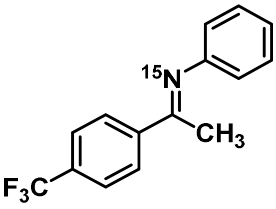
(*E*)-*N*-phenyl-1-(4-(trifluoromethyl)phenyl)ethane-1-imine (98% ^{15}N)



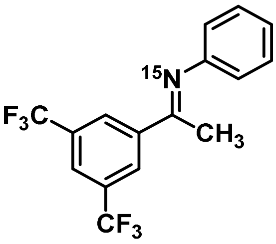
4

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (55 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[3]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 8.11 (m, 2H), 7.73 (m, 2H), 7.38 (m, 2H), 7.12 (m, 1H), 6.80 (m, 2H), 2.25 ppm (d, $^3J_{NH}$ = 1.8 Hz, 3H).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 164.5, 151.7, 143.2, 132.1, 129.4, 128.0, 125.6, 124.6, 123.9, 119.5, 17.5 ppm.

(*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-*N*-phenylethan-1-imine (98% ^{15}N)



5

^{15}N-labeled imine was synthesized following GP I and obtained as a yellow oil (18 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[3]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 8.47 (m, 2H), 8.01 (m, 1H), 7.39 (m, 2H), 7.14 (m, 1H), 6.81 (m, 2H), 2.29 ppm (d, 3H, $^3J_{NH}$ = 1.8 Hz).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 163.0, 151.1, 141.9, 131.9, 129.5, 127.8, 125.2, 124.3, 124.1, 123.8, 119. 4, 17.4 ppm.

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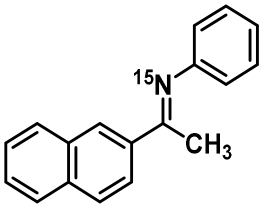
(*E*)-1-(naphthalen-2-yl)-*N*-phenylethan-1-imine (98% ^{15}N)



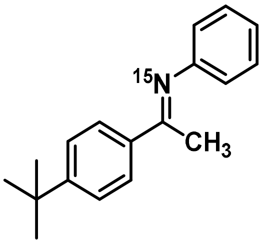
6

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (60 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[9]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 8.37 (s, 1H), 8.24 (m, 1H) 7.99 – 7.94 (m, 1H), 7.94 – 7.87 (m, 2H), 7.60 – 7.52 (m, 2H), 7.42 – 7.35 (m, 2H), 7.11 (m, 1H), 6.83 (m, 2H), 2.34 ppm (d, $^{3}J_{HN}$ = 1.76 Hz, 3H).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 165.3, 152.3, 137.3, 134.8, 133.3, 129.3, 129.2, 128.2, 128.1, 128.0, 127.6, 126.7, 124.6, 123.5, 119.7, 17.4 ppm.

(*E*)-*N*-phenyl-1-(4-(tert-butyl)phenyl)ethan-1-imine (98% ^{15}N)



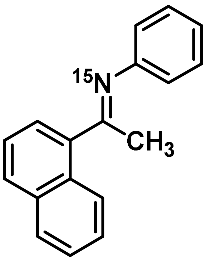
7

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (28 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[7]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.91 (m, 2H), 7.48 (m, 2H), 7.35 (m, 2H), 7.07 (m, 1H), 6.76 (m, 2H), 2.20 (d, $^{3}J_{HN}$ =1.83 Hz, 3H), 1.34 ppm (s, 9H).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 165.9, 154.9, 153.1, 137.9,129.6, 128.0, 126.3, 124.0, 120.4, 35.7, 32.0, 18.1 ppm.

(*E*)-1-(naphthalen-1-yl)-*N*-phenylethan-1-imine (98% ^{15}N)



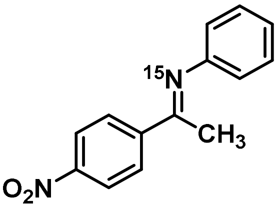
8

^{15}N-labeled imine was synthesized following GP I and obtained as yellow needles (42 %). The ratio between *E* and *Z* in solution was determined by ^{1}H-NMR to be 1.7 to 1. ^{1}H and ^{13}C NMR data were in accordance with literature.[3] Due to the presence of two isomers the ^{1}H and ^{13}C spectra are quite crowded in the aromatic region and therefore only representative signals are listed.

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 2.61 (*Z*, s, 3H), 2.33 ppm (*E*, s, 3H)

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 170.4 (*Z*), 169.2 (*E*), 29.9 (*Z*), 22.0 (*E*)

(*E*)-1-(4-nitrophenyl)-*N*-phenylethan-1-imine (98% ^{15}N)



9

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (28 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[10]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 8.29 (m, 2H), 8.15 (m, 2H), 7.39 (m, 2H), 7.13 (m, 1H), 6.80 (m, 2H), 2.27 ppm (d, $^{3}J_{HN}$ =1.73 Hz, 3H).

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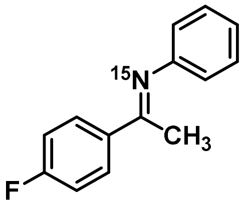
(*E*)-1-(4-fluorophenyl)-*N*-phenylethan-1-imine (98% ^{15}N)



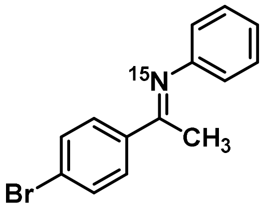
10

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (28 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[3]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 8.00 (m, 2H), 7.35 (m, 2H), 7.14 (m, 2H), 7.09 (m, 1H), 6.77 (m, 2H), 2.20 ppm (d, 3H, $^{3}J_{NH}$ = 1.8 Hz).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 164.6, 164.3, 152.1, 136.2, 129.7, 129.3, 123.5, 119.6, 115.5, 17.4 ppm.

(*E*)-1-(4-bromophenyl)-*N*-phenylethan-1-imine (98% ^{15}N)



11

^{15}N-labeled imine was synthesized following GP I and obtained as light-yellow needles (36 %) predominantly as *E* isomer (>99 % via ^{1}H-NMR). ^{1}H and ^{13}C NMR data were in accordance with literature.[3]

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.87 (m, 2H), 7.59 (m, 2H), 7.36 (m, 2H), 7.09 (m, 1H), 6.77 (m, 2H), 2.20 ppm (d, 3H, $^{3}J_{NH}$ = 1.8 Hz).

^{13}C-NMR (100.6 MHz, CD_2Cl_2): δC = 164.5, 151.9, 138.9, 131.8, 129.3, 129.2, 125.2, 123.6, 119.6, 17.3 ppm.

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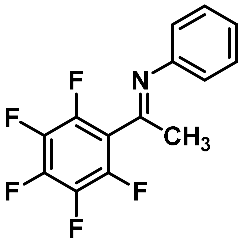
(*E*)-1-(perfluorophenyl)-*N*-phenylethan-1-imine



12

Imine was synthesized according to literature.[11] Molecular sieves 4 Å (4 g) were weighed in to a 50 ml Schlenk flask equipped with a reflux condenser and a stopper. The setup was connected to a vacuum line and was evacuated and dried with a heat gun at 350 °C. Under Argon flow, Aniline (10.5 mmol, 1.1 equiv.) and the respective ketone (10 mmol, 1.0 equiv.) were added to the Schlenk flask under argon atmosphere and were dissolved in 20 ml toluene. The stop cock was exchanged with a drying tube filled with $CaCl_2$ and the solution was stirred at room temperature for 18 hours. The orange solution was filtered through celite, concentrated under reduced pressure und purified by bulb-to-bulb distillation. The imine was obtained as an orange oil (25 %) as a mixture of *E* isomer and *Z* isomer (*E*/*Z* = 54/46 % via ^{1}H-NMR). ^{1}H and ^{19}F NMR data were in accordance with literature.[11]

<u>*E*-isomer</u>

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.22-7.13 (m, 3H), 6.67 (d, 2H, $^2J_{HH}$ = 7.48 Hz), 2.50 ppm (s, 3H).

^{19}F-NMR (376 MHz, CD_2Cl_2) δF = -139.4, -153.6, -161.5 ppm.

<u>*Z*-isomer</u>

^{1}H-NMR (400.1 MHz, CD_2Cl_2) δH = 7.40 (t, 2H, $^2J_{HH}$ = 7.89 Hz), 7.00 (t, 1H, $^2J_{HH}$ = 7.49 Hz), 6.34 (d, 2H, $^2J_{HH}$ = 8.29 Hz), 2.18 ppm (s, 3H).

^{19}F-NMR (376 MHz, CD_2Cl_2) δF = -143.6, - 154.7, -162.3 ppm.

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NMR Sample Preparation

General procedure for the preparation of binary NTPA•*E*/*Z*-imine complexes (GP II):

The NTPA catalyst was weighted into a 5 mm NMR tube and dried for 30 min at 130 °C under reduced pressure. After cooling the tube to room temperature, ^{15}N labelled imine was weighted directly into the NMR tube. The tube was evacuated and flushed with Argon three times. Deuterated and dry CD_2Cl_2 was added under Argon atmosphere, TMS was added, and the tube was closed and sealed with a parafilm. The sample was stored in a -80 °C freezer. For all samples a 1:1 ratio of catalyst/imine was used. Even after careful sample preparation, partial hydrolysis of the imine took place. Therefore, the catalyst/imine-ratios were slightly different from 1:1. The concentration of 25 mmol L^{-1} or 40 mmol L^{-1} was used for all samples.

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Steiner-Limbach correlation

Theory

All the investigations regarding the hydrogen bond analysis were done in accordance with our previous work on CPA/imine complexes and DSI/imine complexes.[3,12,13]

Experimental ^{1}H and ^{15}N chemical shifts

Table S1: Observed δ(^1H) and δ(^{15}N) chemical shifts and $^1J_{NH}$ coupling constants of NTPA/imine complexes at 180 K and 600 MHz in CD_2Cl_2. (- = not determined)

	δ(^{1}H) [ppm]	**δ(^{15}N) [ppm]**	**$^1J_{NH}$ [Hz]**
E-**2**	13.61	188.7	90.50
Z-**2**	13.92	197.7	89.62
E-**3**	14.01	196.9	-
Z-**3**	14.25	202.9	-
E-**4**	14.68	207.3	89.01
Z-**4**	14.85	211.1	
E-**5**	15.2	215.2	87.12
Z-**5**	15.28	-	86.90
E-**6**	14.18	197.1	90.55
Z-**6**	14.47	204.9	89.17
E-**7**	14.04	196.8	-
Z-**7**	14.24	202.5	-
E-**8**	-	-	-

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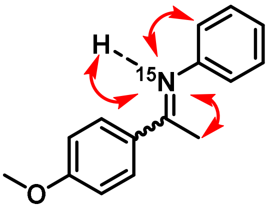
Z-**8**	14.92	215	89.91
E-**9**	14.85	-	-
Z-**9**	15.04	213.9	88.55
E-**10**	14.26	198.6	-
Z-**10**	14.46	205.6	89.18
E-**11**	14.38	201.6	-
Z-**11**	14.57	207.3	89.04
E-**12**	15.86	229.6	-
Z-**12**	16.04	228.45	

Referencing of the ^{15}N chemical shift

The ^{15}N chemical shifts are referenced by $\delta(\mathrm{OH\underline{N}})\mathrm{ref} = \delta(\mathrm{OH\underline{N}})_{\mathrm{obs}} - 340.8$ ppm. 340.8 ppm is the chemical shift of the free imine showing the strongest hydrogen bond in the previous work. Data points of phenols/carboxylic acids, tetrafluoroboric acid, TRIP, TiPSY and DSI were collected by K. Rothermel, N. Sorgenfrei, T. Hausler and M. Melikian, respectively.[3,12,13]

Chemical Shift Measurement

The ^{1}H and ^{15}N chemical shifts of all binary NTPA/imine complexes were determined using ^{1}H and ^{15}N NMR or ^{1}H,^{15}N-HMBC spectroscopy.



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The ^{1}H,^{15}N-HMBC spectra allowed for the detection of the ^{15}N chemical shift with respect to the hydrogen bond, the methyl group, or the aromatic proton.

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Complete Set of Spectra

*NTPA **1**/imine-**2** complex*

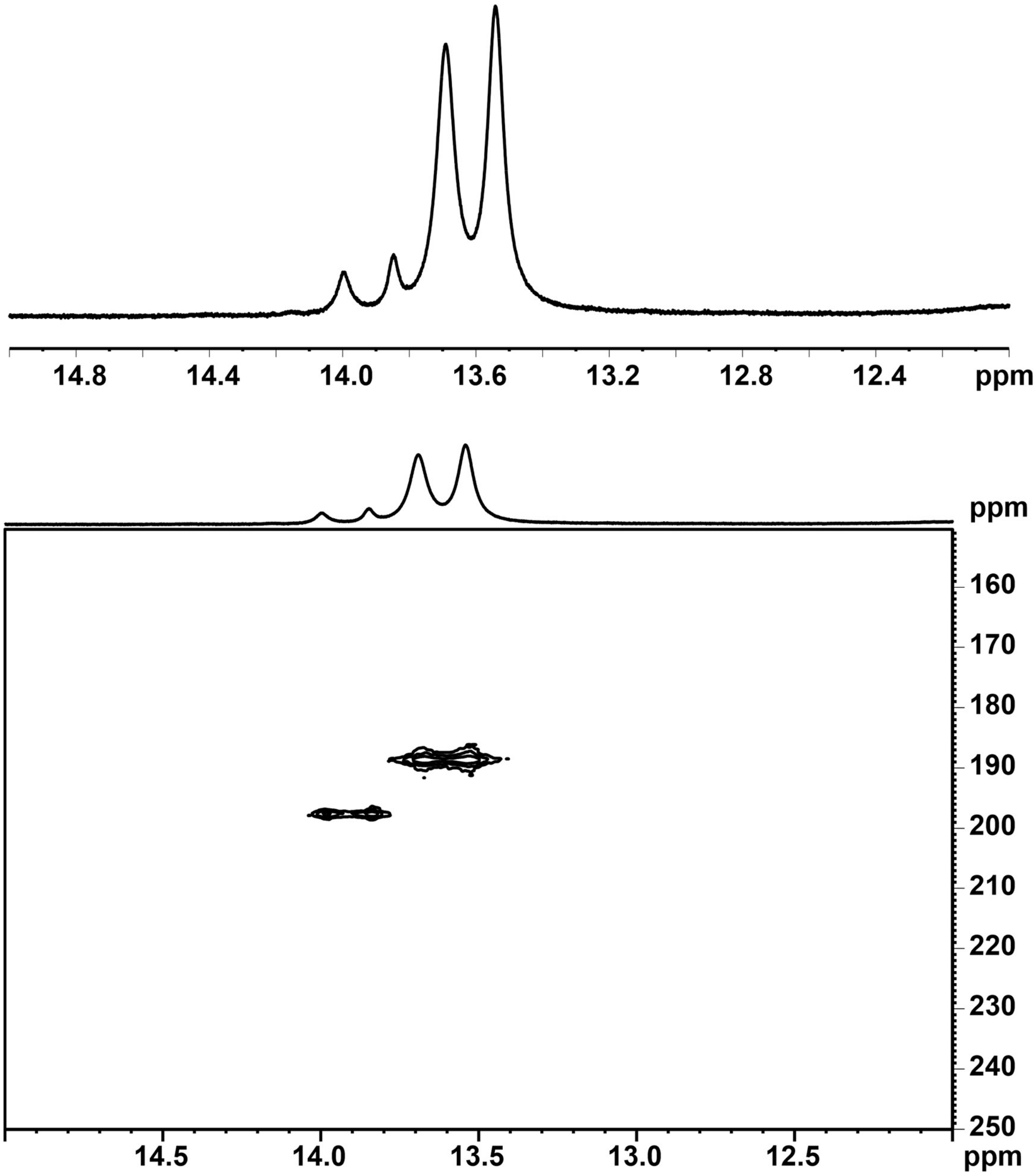

*Figure S1: Low field section of the ^1H spectrum of NTPA **1** and ^{15}N-labeled imine **2** at 180 K and 600 MHz in CD_2Cl_2. ^1H ^{15}N HMBC section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^1H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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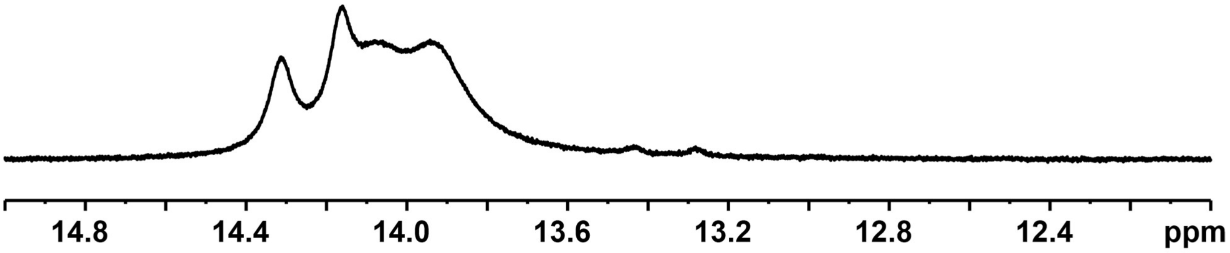
*NTPA **1**/imine-**3** complex*



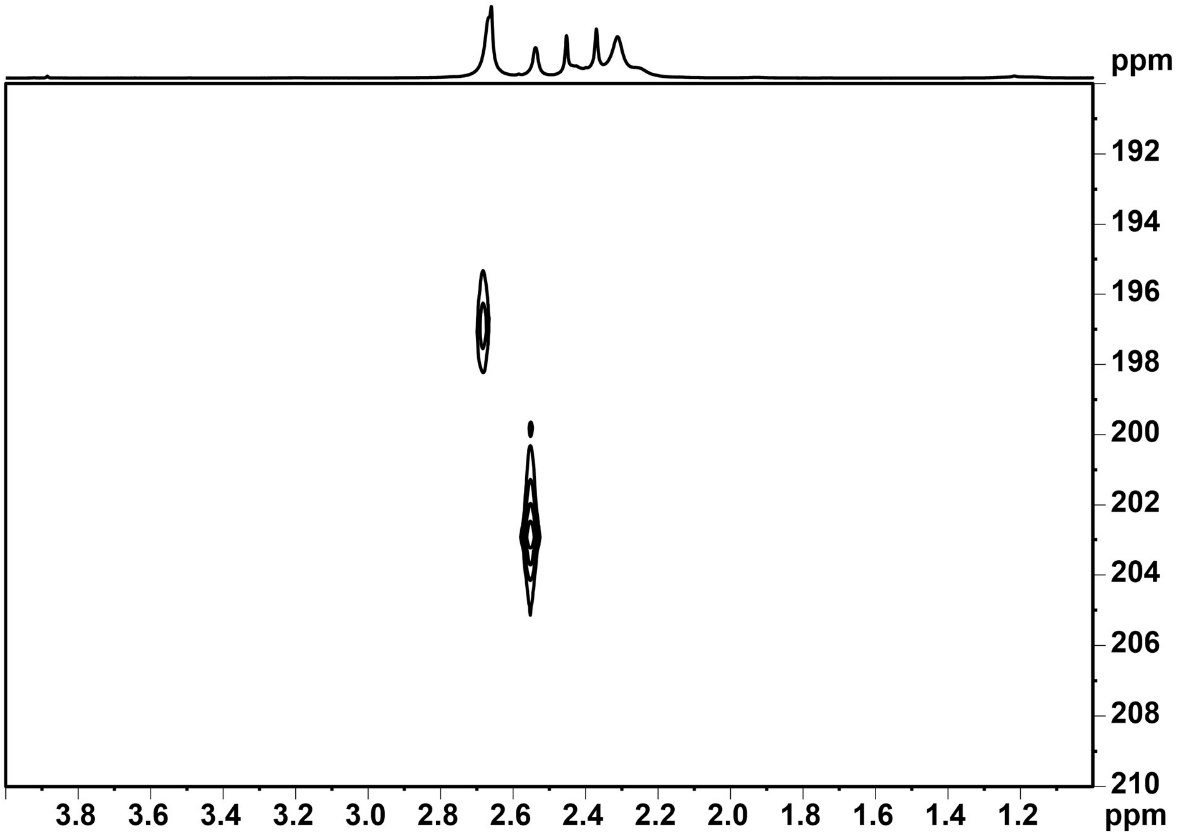


*Figure S2: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **3** at 180 K and 600 MHz in CD_2Cl_2. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **3** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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*NTPA **1**/imine-**4** complex*

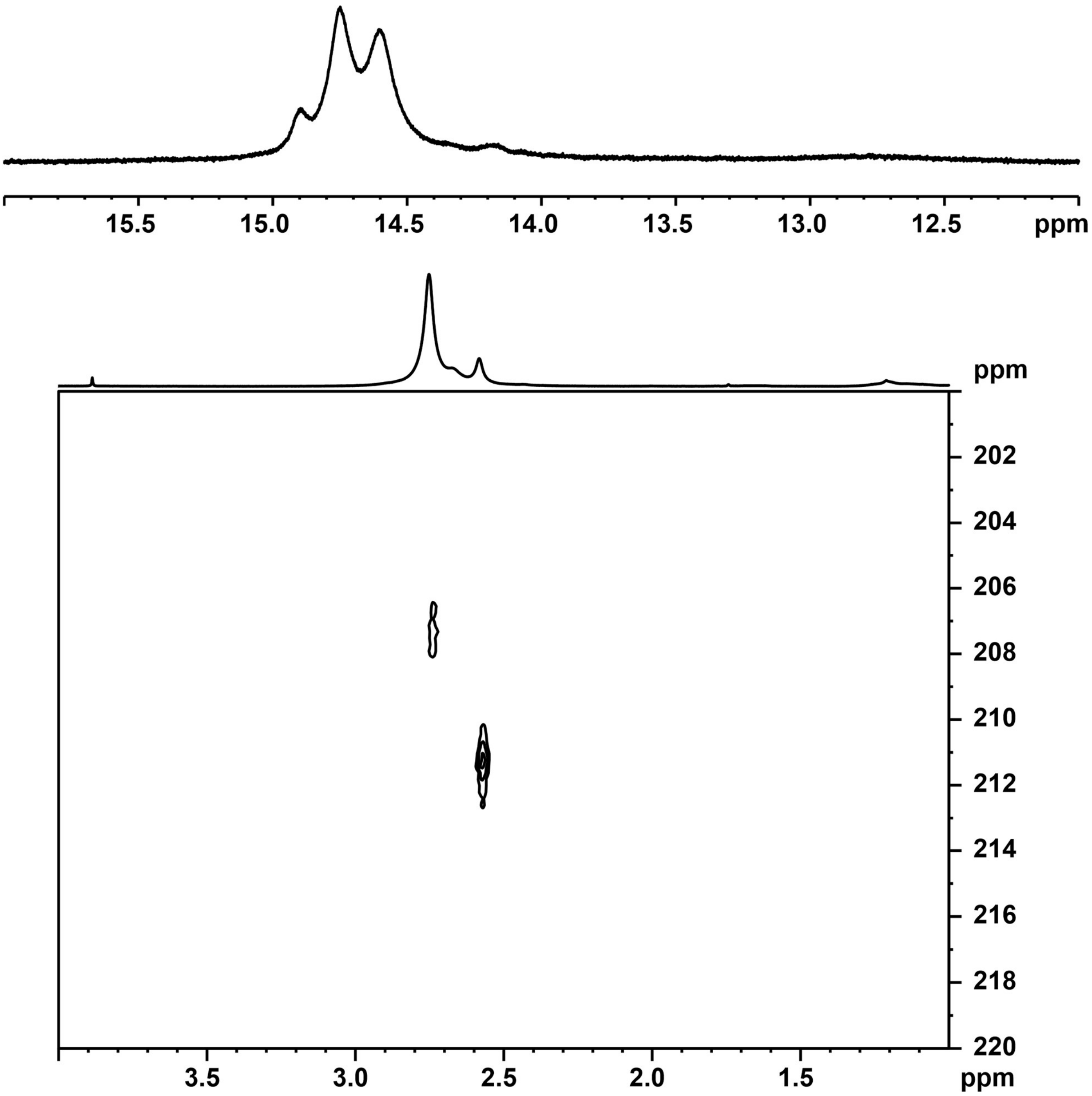

*Figure S3: Low field section of the ^1H spectrum of NTPA **1** and ^{15}N-labeled imine **4** at 180 K and 600 MHz in CD_2Cl_2. ^1H ^{15}N HMBC section for the of NTPA **1**/imine **4** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^1H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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*NTPA **1**/imine-**5** complex*

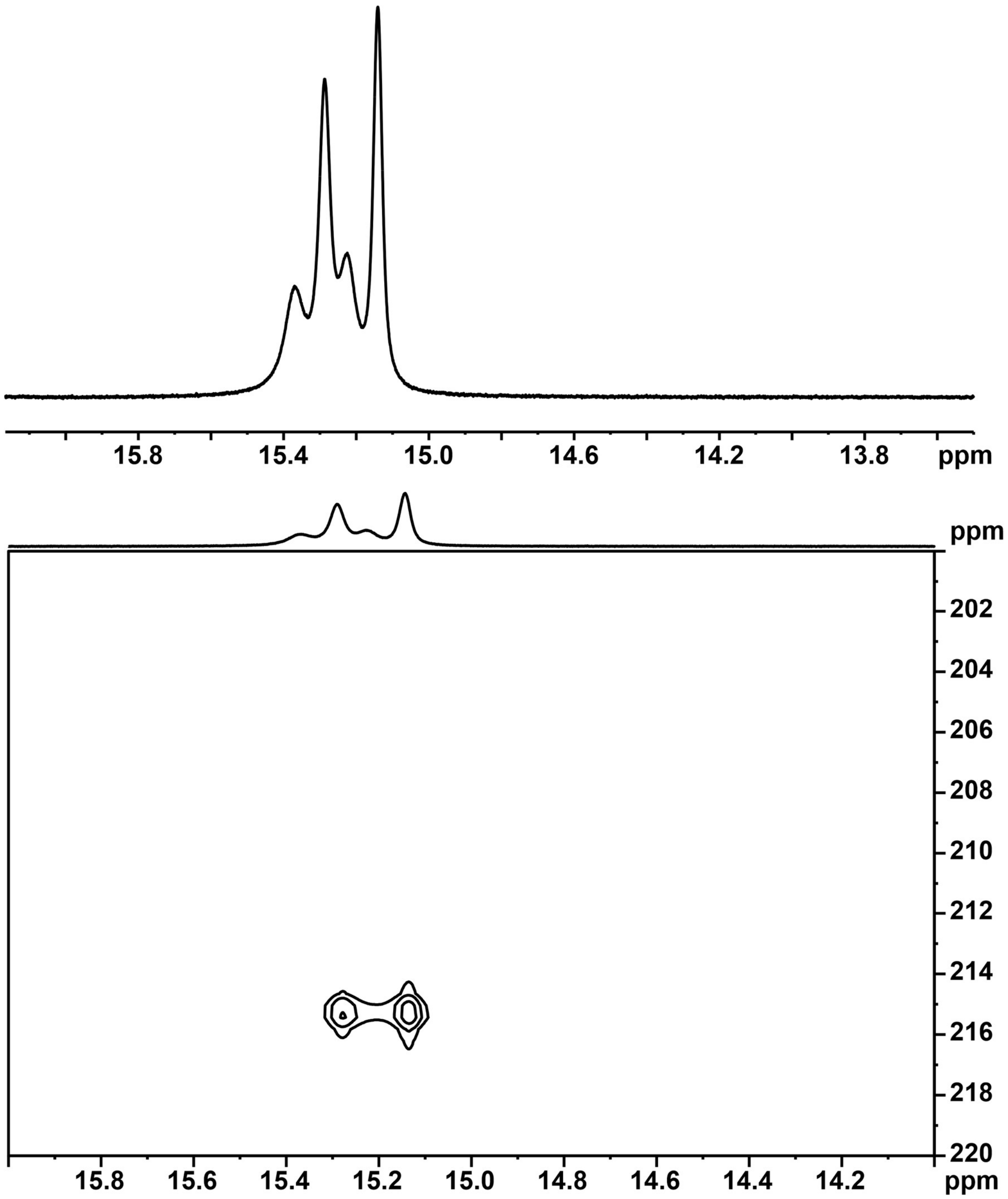

*Figure S4: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **5** at 180 K and 600 MHz in CD$_2$Cl$_2$. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **5** complex at 180 K and 600 MHz in CD$_2$Cl$_2$. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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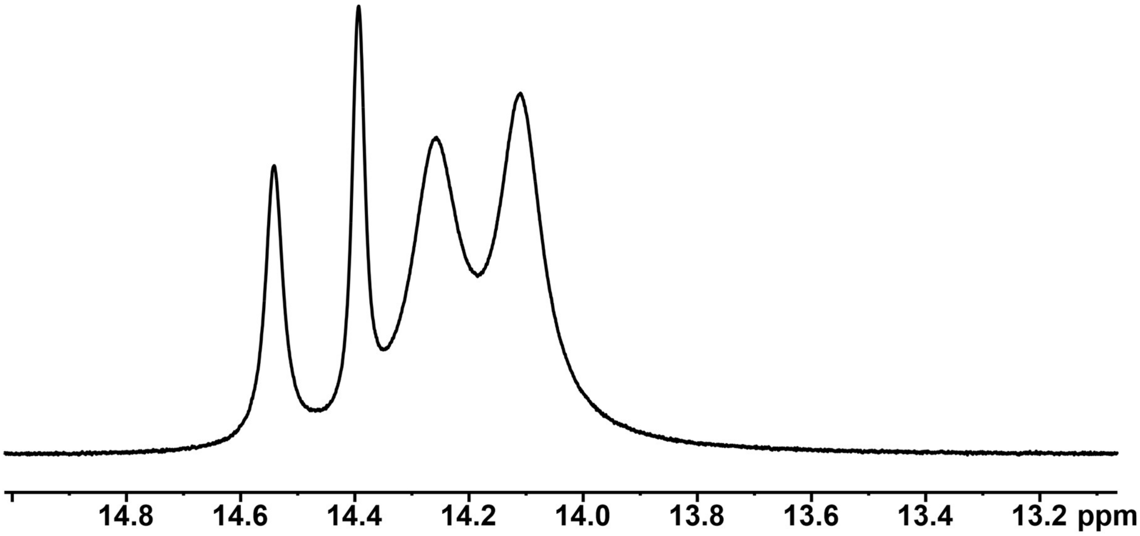
*NTPA **1**/imine-**6** complex*



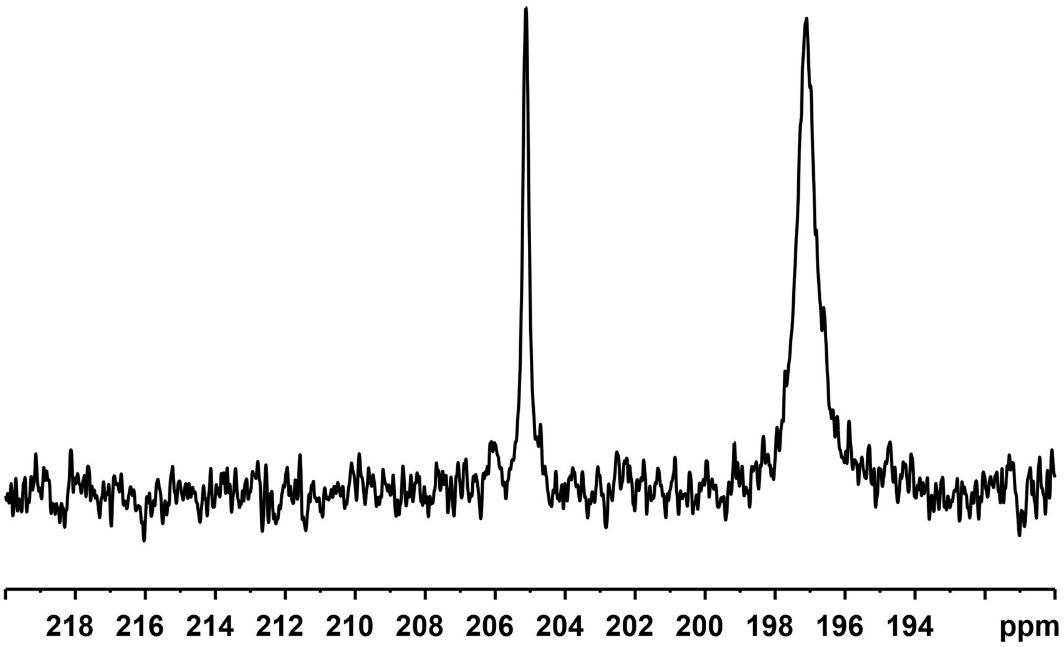


*Figure S5: Low field section of the ^1H spectrum of NTPA **1** and ^{15}N-labeled imine **6** at 180 K and 600 MHz in CD_2Cl_2. ^{15}N spectrum of NTPA **1**/imine **6** complex at 180 K and 600 MHz in CD_2Cl_2.*

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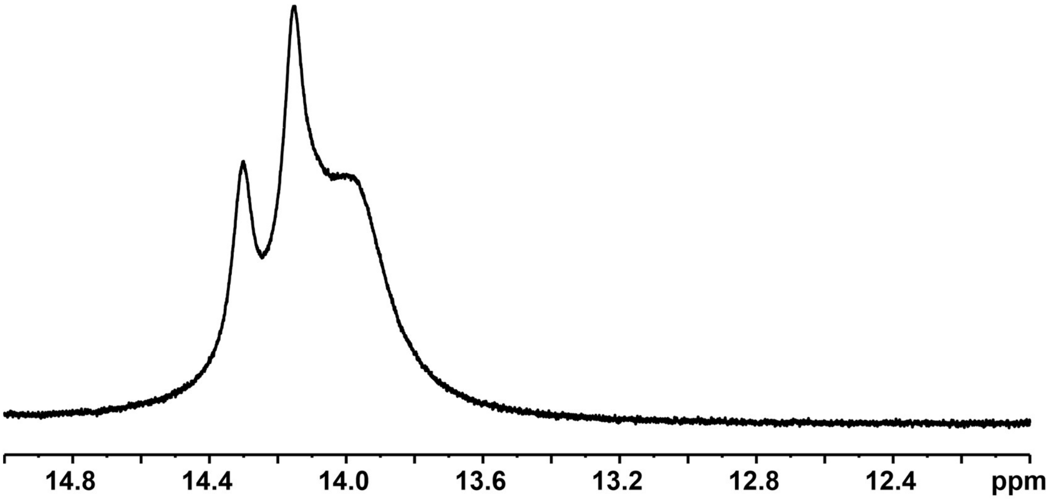
*NTPA **1**/imine-**7** complex*



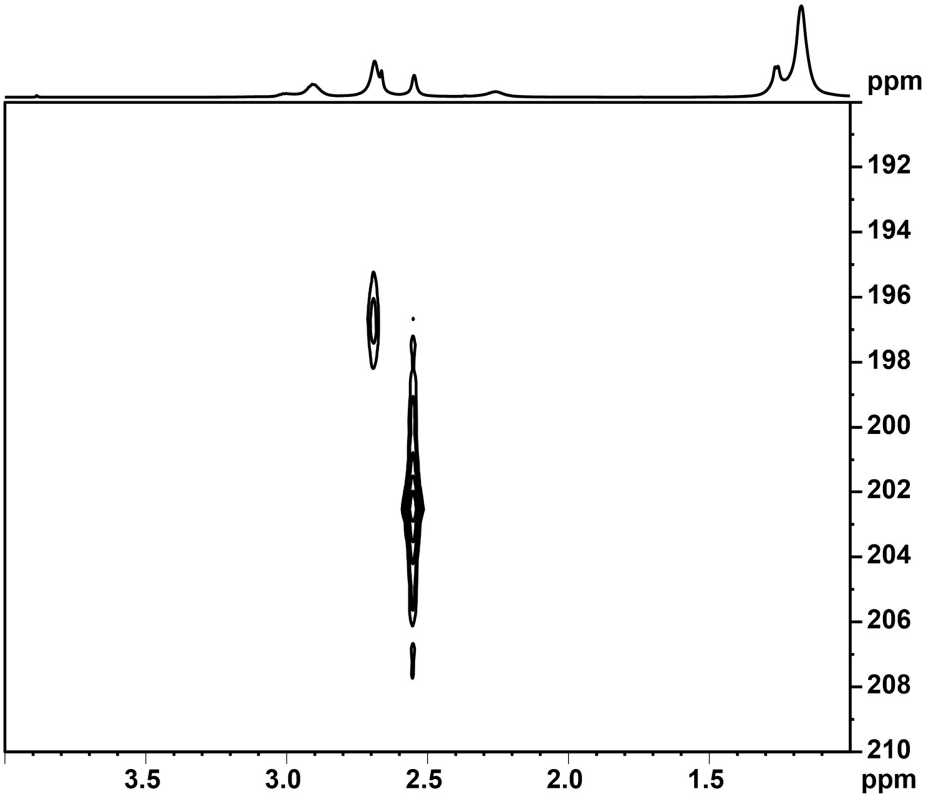


*Figure S6: Low field section of the ^1H spectrum of NTPA **1** and ^{15}N-labeled imine **7** at 180 K and 600 MHz in CD_2Cl_2. ^1H ^{15}N HMBC section for the of NTPA **1**/imine **7** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^1H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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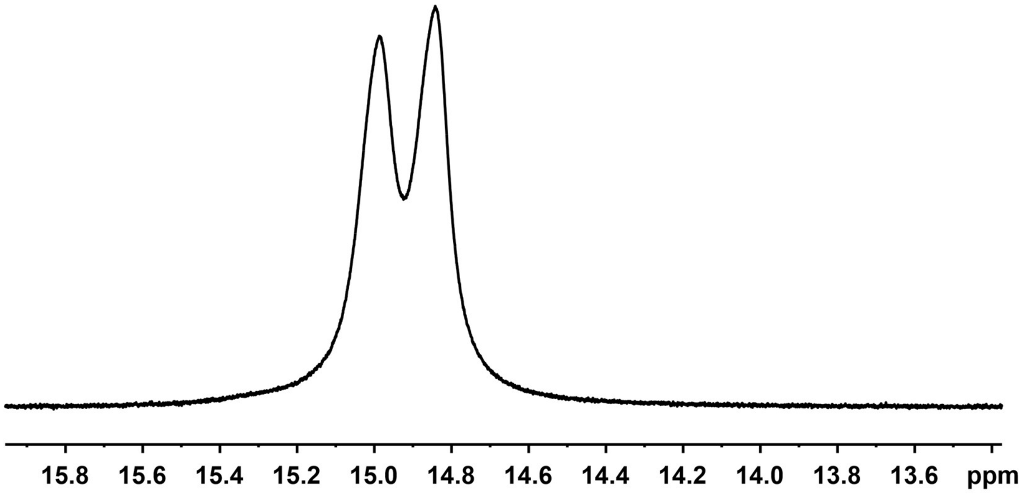
*NTPA **1**/imine-**8** complex*



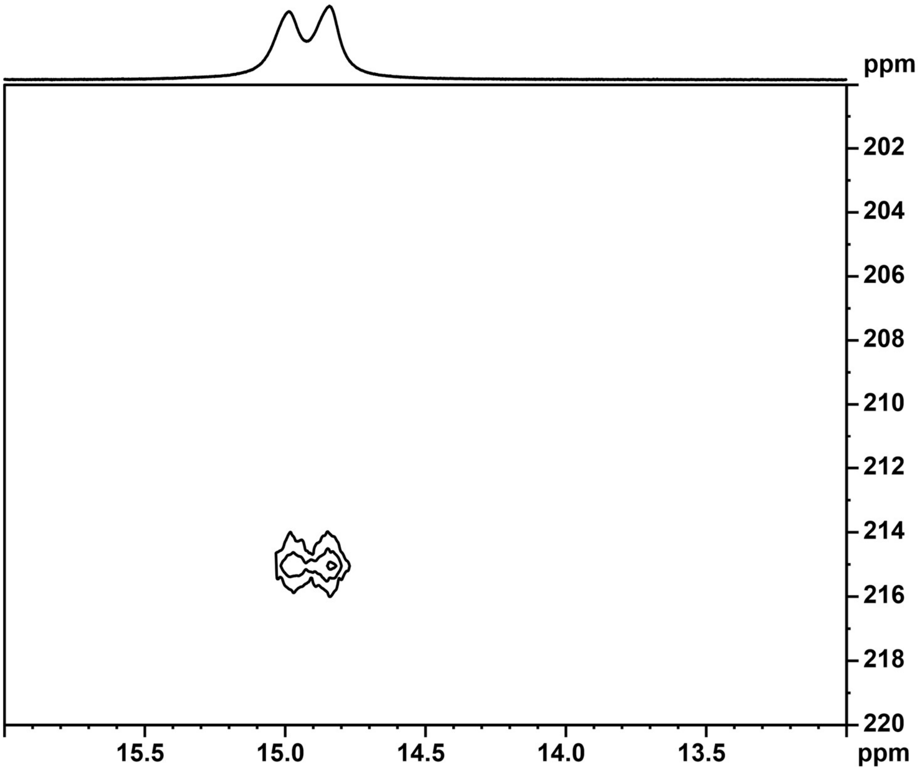


*Figure S7: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **8** at 180 K and 600 MHz in CD_2Cl_2. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **8** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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*NTPA **1**/imine-**9** complex*

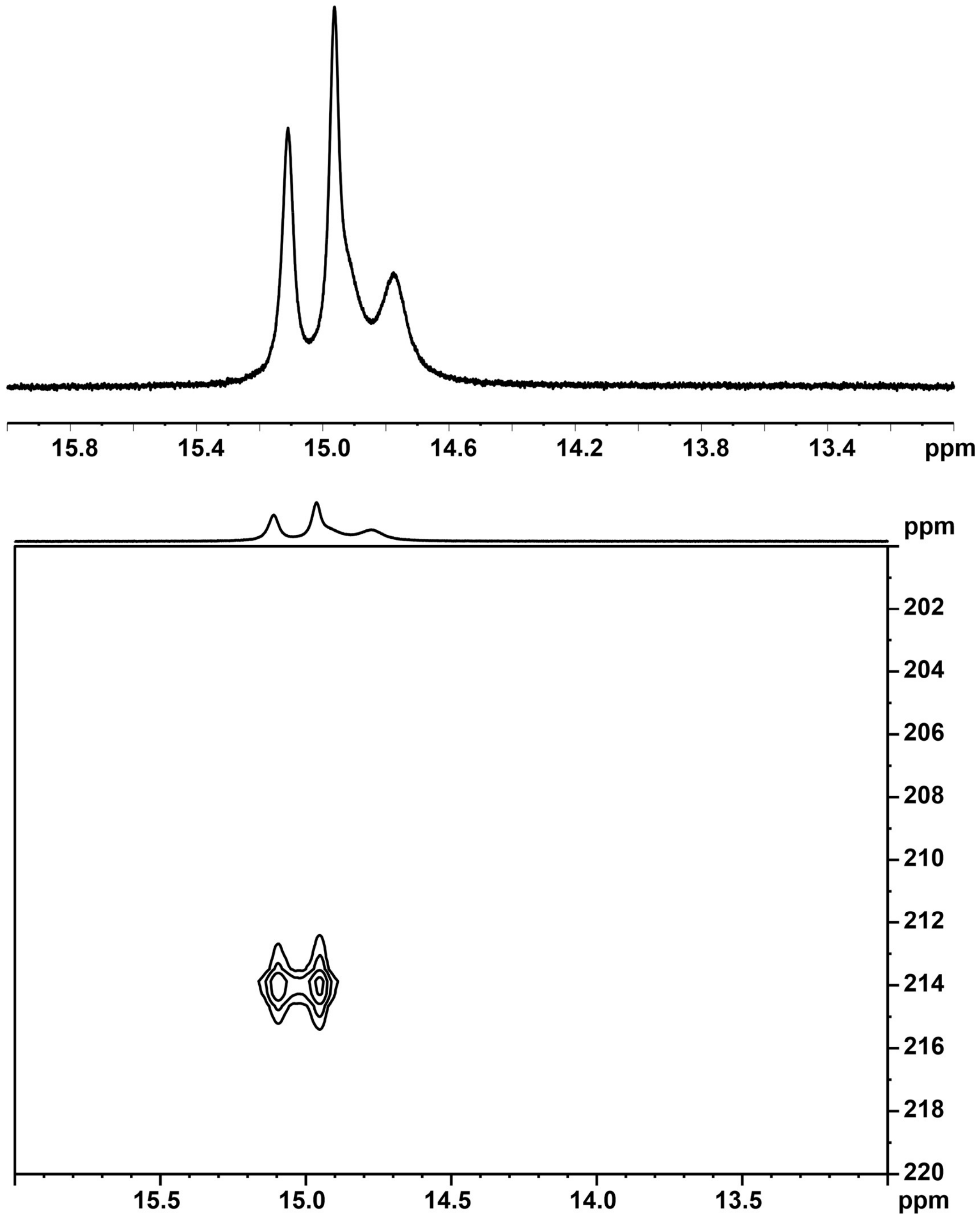

*Figure S8: Low field section of the ^1H spectrum of NTPA **1** and ^{15}N-labeled imine **9** at 180 K and 600 MHz in CD_2Cl_2. ^1H ^{15}N HMBC section for the of NTPA **1**/imine **9** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^1H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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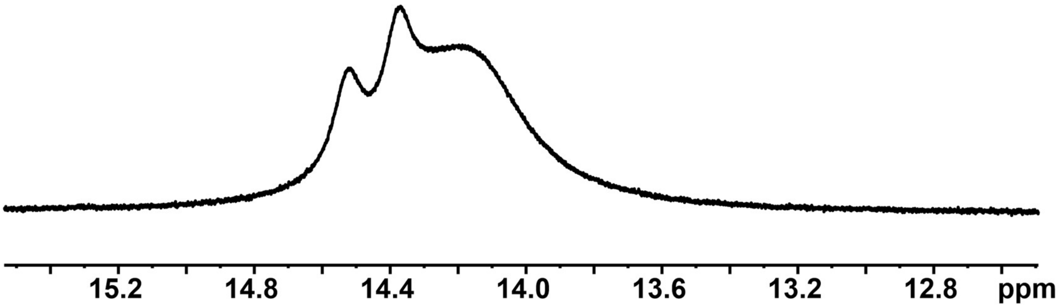
*NTPA **1**/imine-**10** complex*



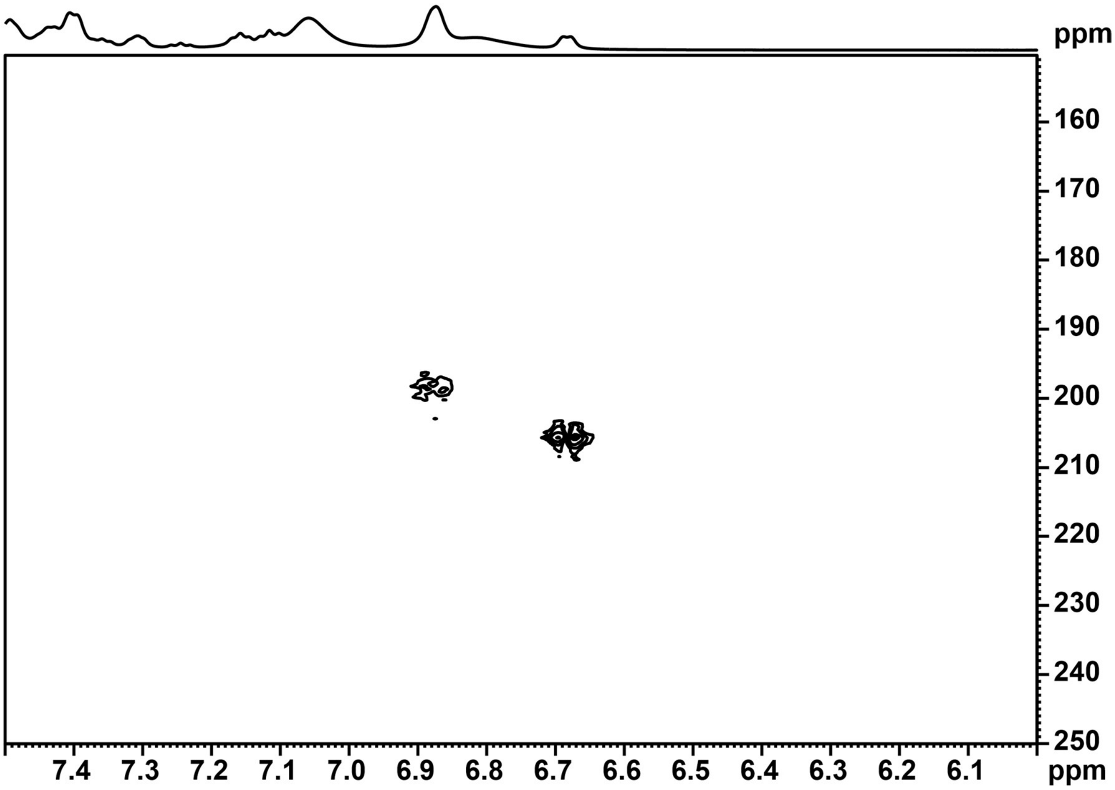


*Figure S9: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **10** at 180 K and 600 MHz in CD_2Cl_2. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **10** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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*NTPA **1**/imine-**11** complex*

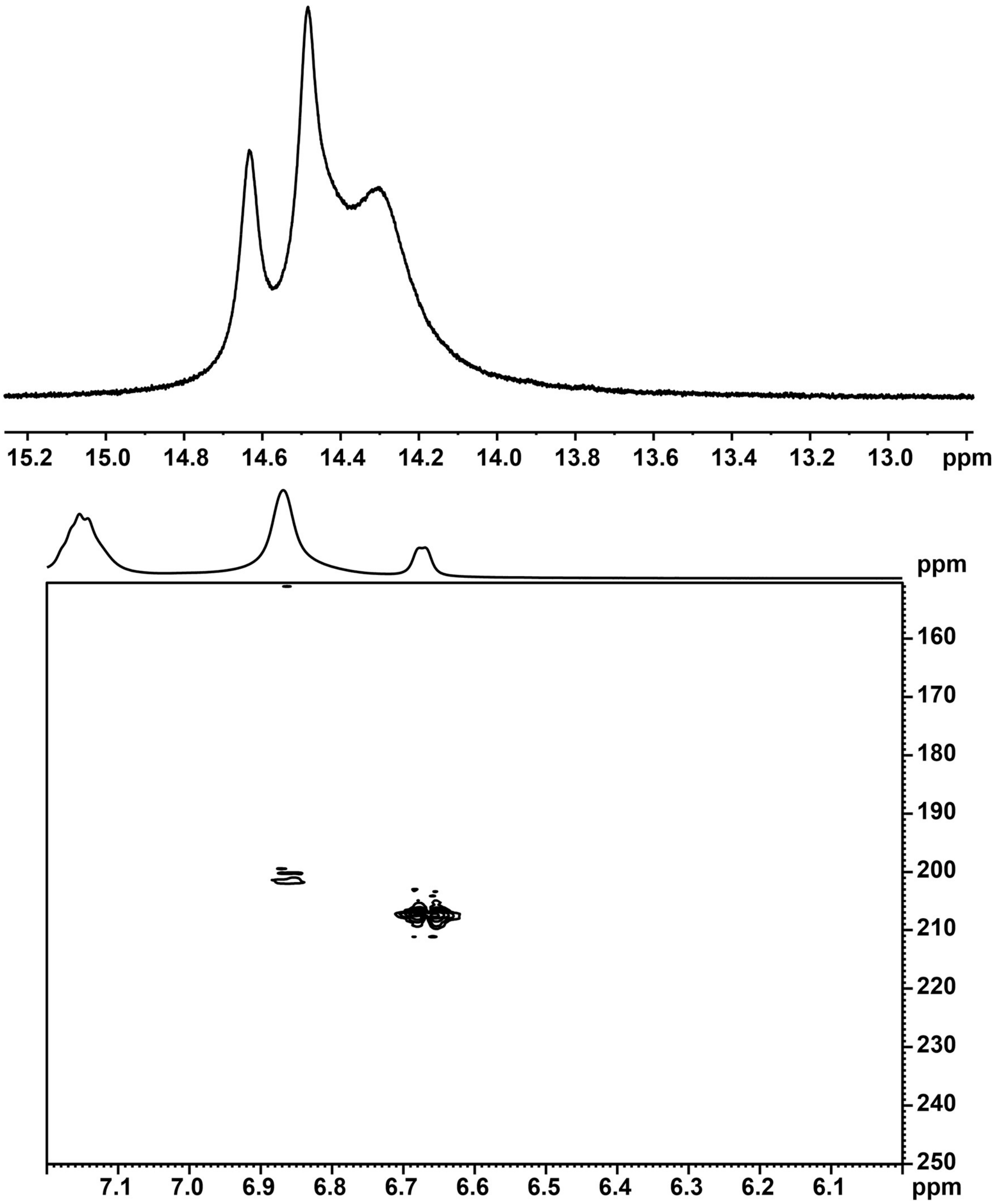

*Figure S10: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **11** at 180 K and 600 MHz in CD_2Cl_2. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **11** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-* complex.

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*NTPA **1**/imine-1**2** complex*

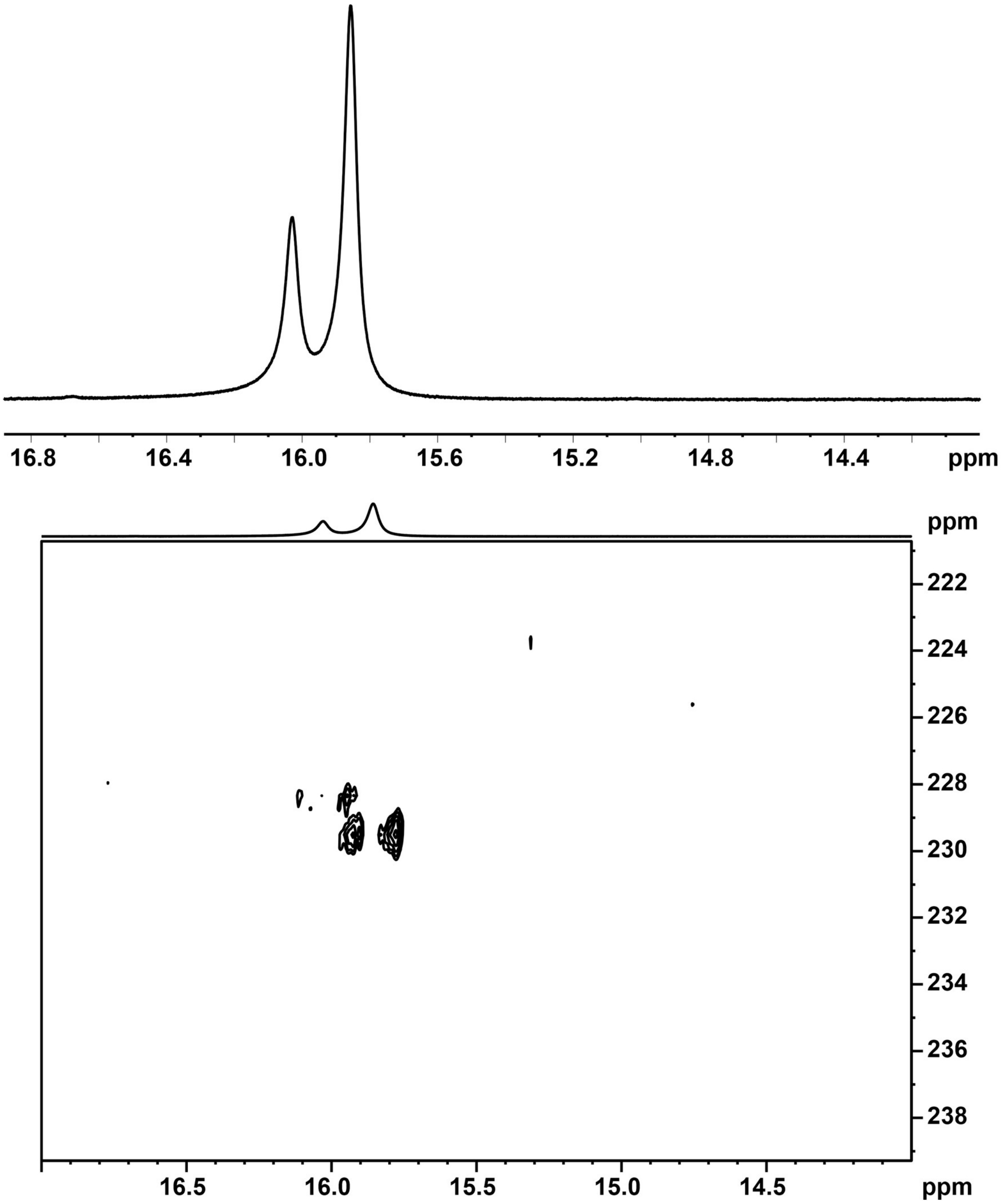

*Figure S11: Low field section of the ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **12** at 180 K and 600 MHz in CD_2Cl_2. ^{1}H ^{15}N HMBC section for the of NTPA **1**/imine **12** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H ^{15}N HMBC cross signals for E-* and *Z-complex.*

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NMR measurements at 273 K

All NMR spectra regarding the H-bond analysis were recorded at 180 K to reach the slow tumbling and slow exchange regime of the hydrogen-bonded protons. Since reactions using NTPA and CPA are carried out at higher temperatures as well, we also conducted NMR studies at 273 K whether temperature influences the binary complexes. At higher temperatures the H-bond appears as a single broad signal, preventing any further investigations on the H-bond situation (Figure S12, Figure S13). However, the H-bond is still present at this temperature indicating the formation of the binary complex at 273 K too (Figure S12), but the signal intensity of this signal is weak for intermolecular studies (NOESY/ROESY/HMBC). Furthermore, comparing the isomeric ratio of the binary *E*- and *Z*-complex at 180 K and 273 K (Figure S14), only slight changes are detected. Thus, the NMR spectra at 273 K show a complex formation and isomeric ratio like the one observed at 180 K. This is in accordance with the *ee*-values in Table 1 in the manuscript. In case no significant structure changes occur upon temperature reduction, the *ee* value is expected to increase at lower temperatures.

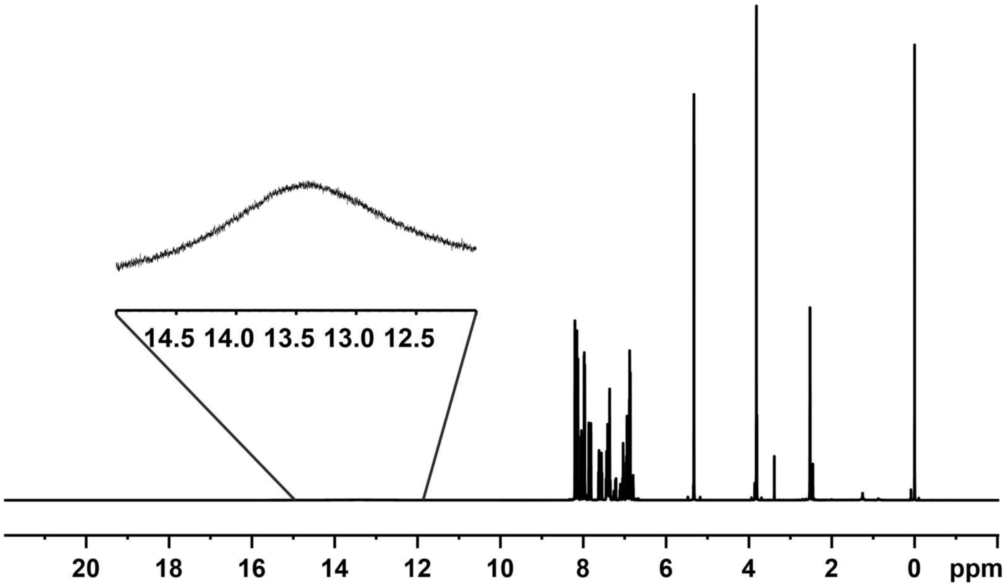

*Figure S12: ^{1}H spectrum of NTPA **1** and ^{15}N-labeled imine **2** at 273 K and 600 MHz in CD_2Cl_2. At 273 K, the H-bond peak for the E- and Z-complex appeared as a single broad signal, preventing any further investigations on the H-bond situation.*

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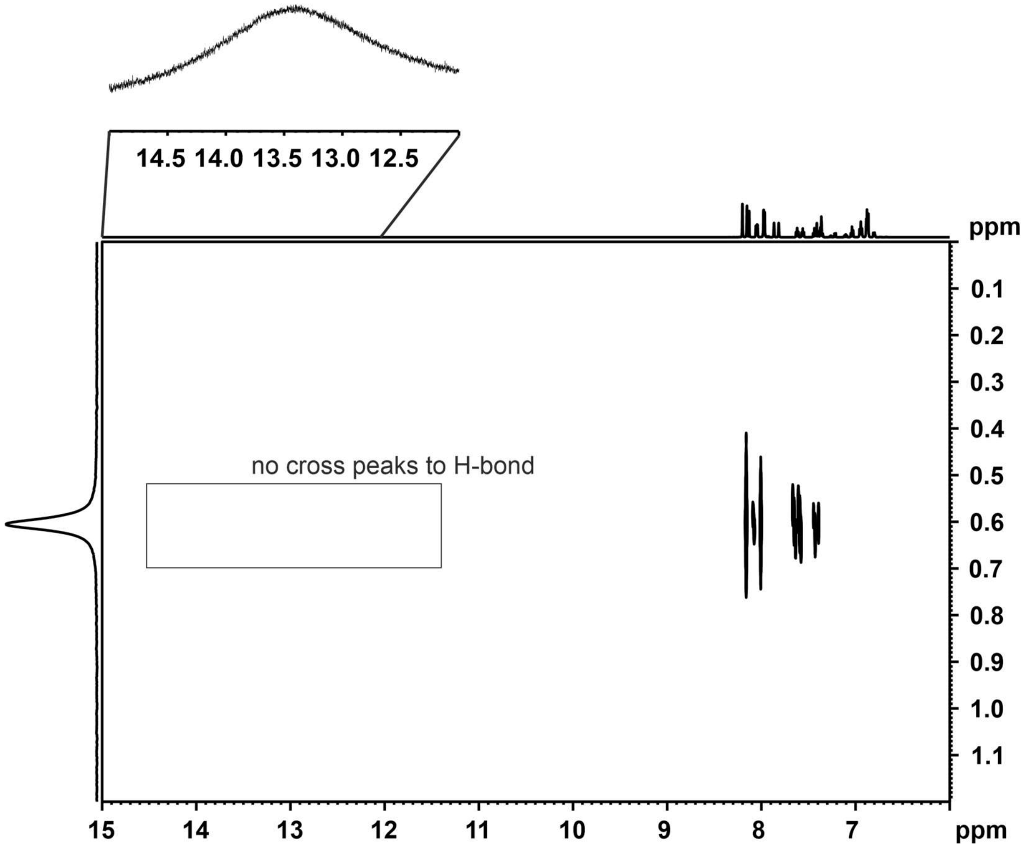

*Figure S13: ^{1}H ^{31}P HMBC spectrum of NTPA **1**/imine **2** complex at 273 K and 600 MHz in CD_2Cl_2. The section shows no ^{1}H ^{31}P HMBC cross signals for the H-bond due to significant line broadening at higher temperatures.*

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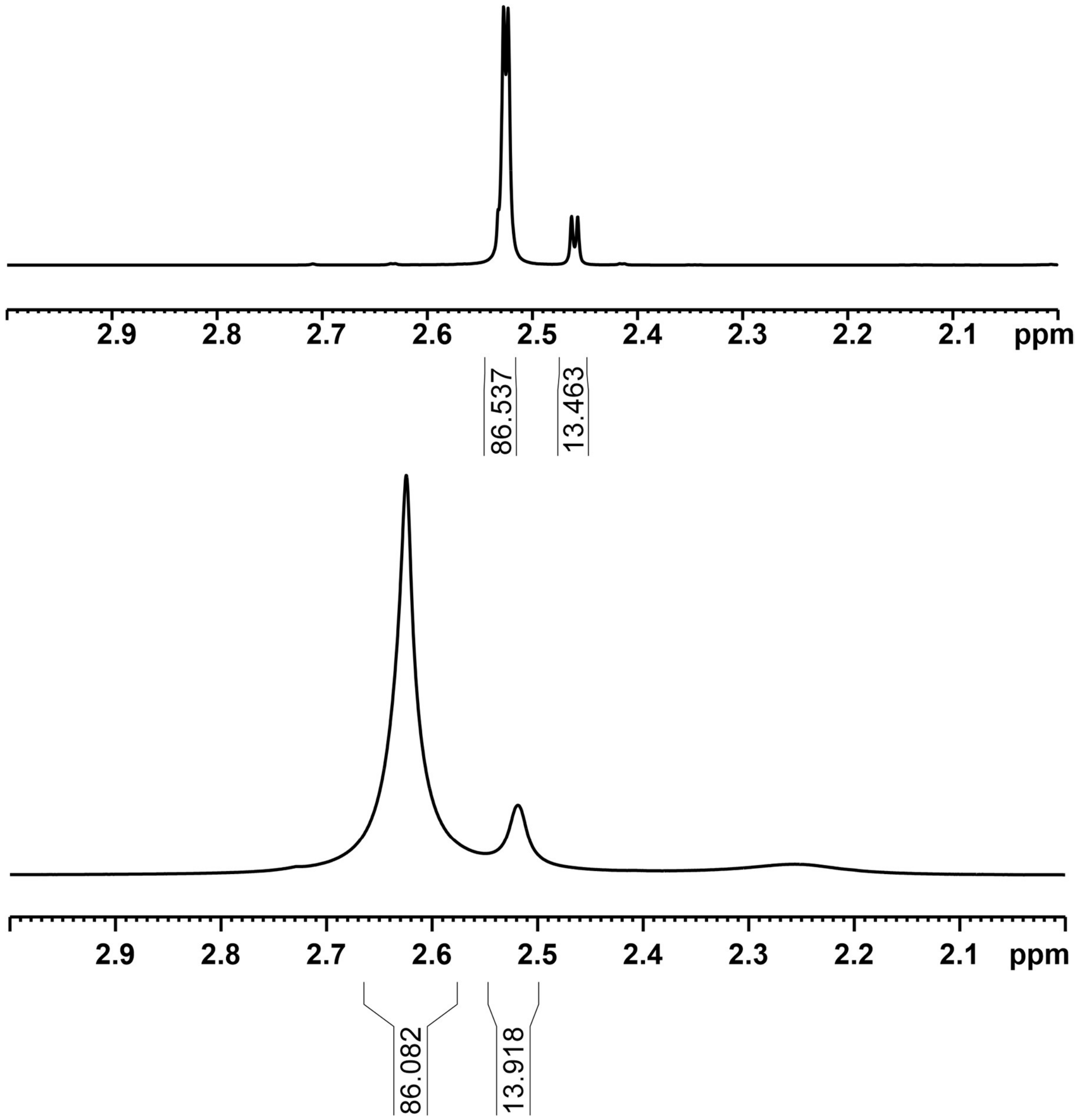

Figure S14: High field section of the ^1H spectrum of NTPA ***1*** *and ^{15}N-labeled imine* ***2*** *at 273 K (top) and 180 K (bottom), 600 MHz in CD_2Cl_2. At both temperatures the binary E- and Z-complex is visible in a similar isomeric ratio.*

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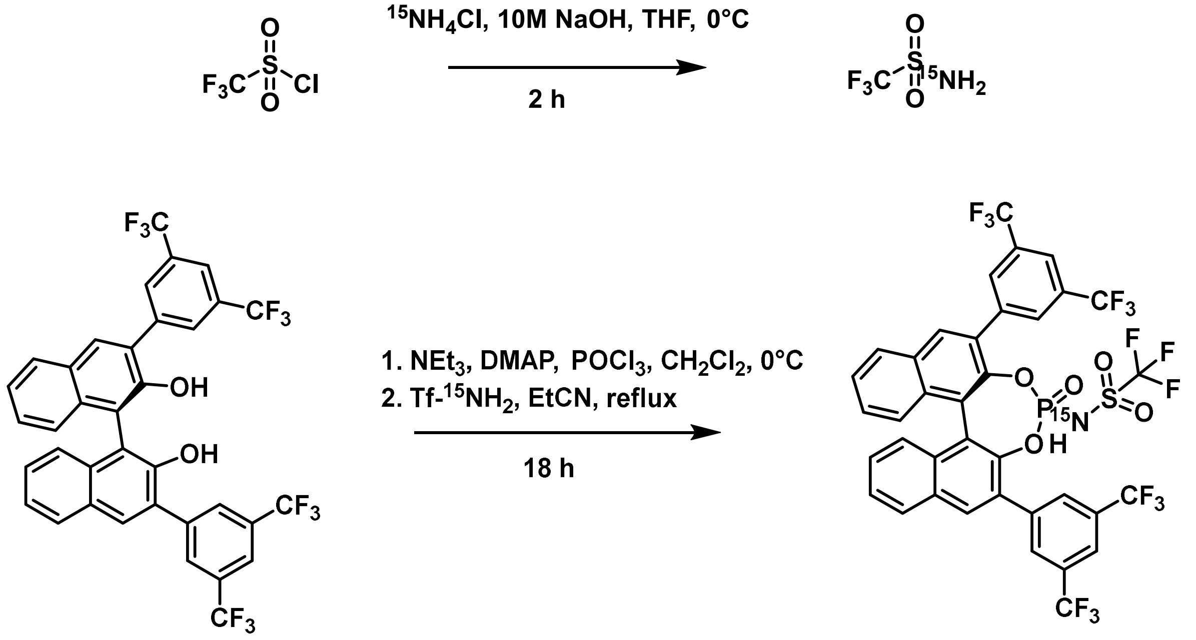
^{15}N-labeling of NTPA 1

Synthesis

The ^{15}N-labeled NTPA **1** was synthesized according to the procedure of Yamamoto et *al*.[14]



^{15}N-NTPA 1

^{15}N-labeled NTPA **1** was obtained as a beige solid (48 %). ^{1}H, ^{19}F and ^{31}P NMR data were in accordance with literature.[15]

^{1}H-NMR (400.1 MHz, CD_3CN) δH = 8.26 (s, 2H), 8.2 (m, 3H), 8.18 (s, 1H), 8.01 (d, 2H, $^{2}J_{HH}$ = 8.29 Hz), 7.92 (s, 2H), 7.48 (m, 2H), 7.33 – 7.18 ppm (m, 4H).

^{19}F-NMR (376 MHz, CD_3CN) δF = -62.0 (12F), -79.5 ppm (3F).

^{31}P-NMR (202 MHz, CD_3CN) δP = 1.25 ppm.

^{15}N-NMR (40.5 MHz, CD_3CN) δN = 101.87 ppm.

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Comparison of ^{15}N-labeled and not labeled NTPA 1

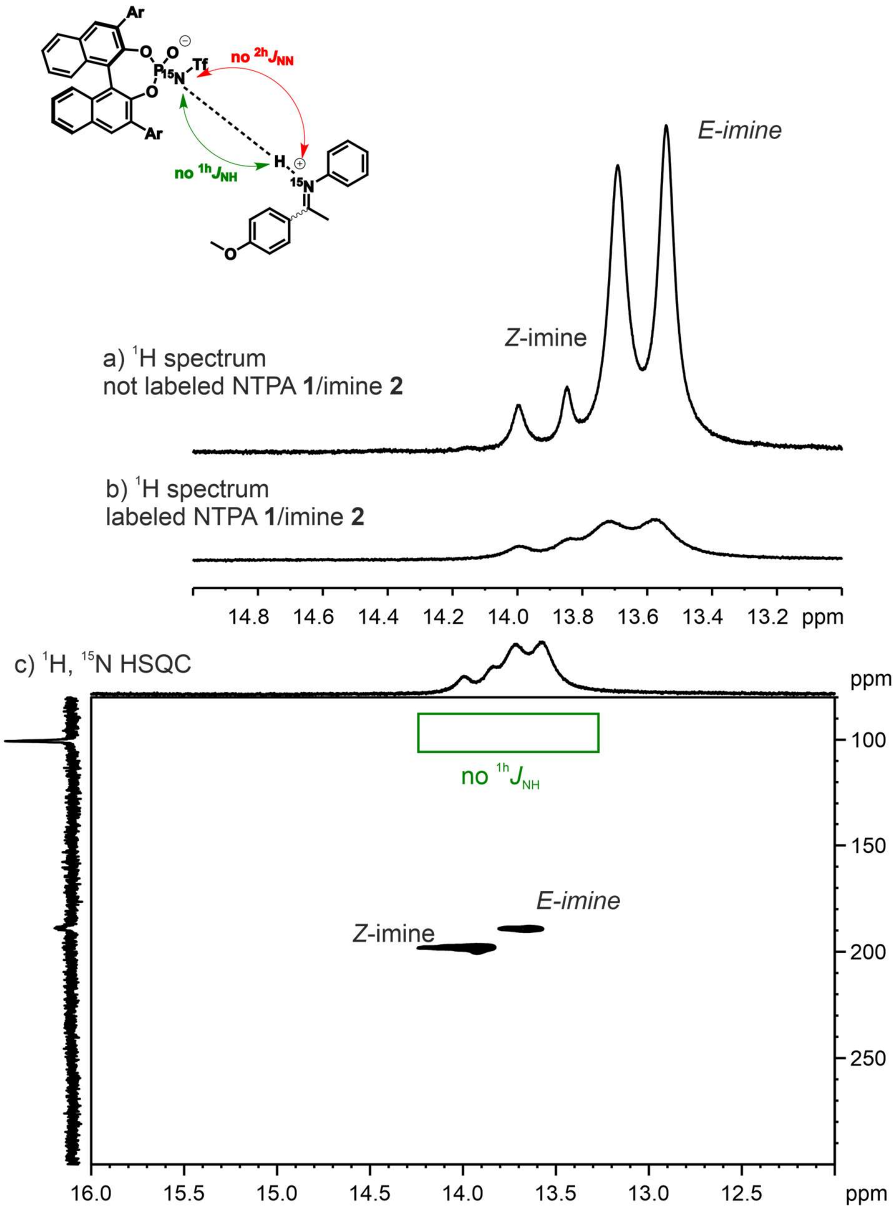

Figure S15: a) Low field section of the ^{1}H spectrum of NTPA ***1*** *and ^{15}N-labeled imine* ***2*** *at 180 K and 600 MHz in CD_2Cl_2. b) Low field section of the ^{1}H spectrum of ^{15}N-labeled NTPA* ***1*** *and ^{15}N-labeled imine* ***2*** *at 180 K and 600 MHz in CD_2Cl_2. C) ^{1}H,^{15}N-HSQC section of ^{15}N-labeled NTPA* ***1*** *and ^{15}N-labeled imine* ***2*** *at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic ^{1}H,^{15}N-HSQC cross signals between the nitrogen of the imine and the proton but not for the nitrogen of the NTPA catalyst.*

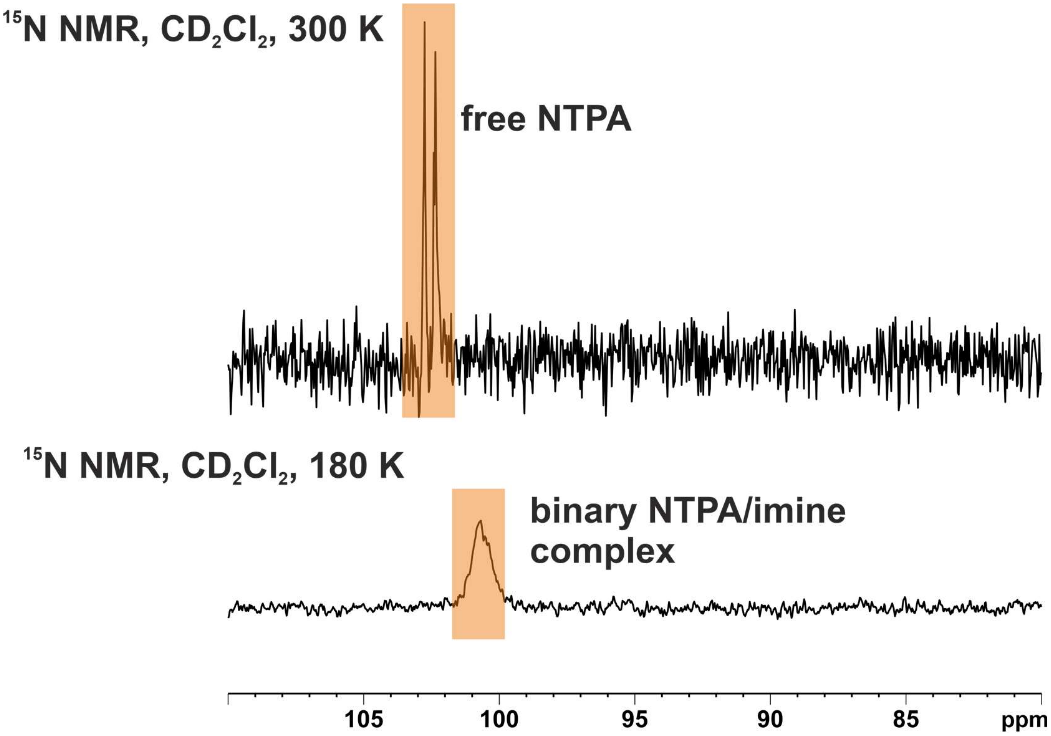

Figure S16: ^{15}*N spectrum of free NTPA* ***1*** *in* CD_2Cl_2 *at 300 K and* ^{15}*N spectrum of the binary complex NTPA* ***1****/imine* ***2*** *in* CD_2Cl_2 *at 180 K. The* ^{15}*N signal in the binary complex is slightly broadened.*

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Qualitative Detection of $^{2h}J_{PH}$ scalar coupling

The presence of a cross signal in the $^{1}H,^{31}P$-HMBC does not serve as a direct indication for a "covalent character". Theoretical studies suggest that for Fermi contact interaction - the spin polarization of nuclei mediated by electrons - covalent bonding between these nuclei is not an essential requirement.[16,17] The magnetization transfer between both involved nuclei can theoretically be mediated by relaxation interference of the ^{1}H chemical shift anisotropy (^{1}H-CSA) and ^{1}H-^{31}P dipolar interactions (DD) instead of a Fermi contact interaction (scalar coupling). Several NMR experimental studies on trans hydrogen bond scalar couplings in bio macromolecules suggest this phenomenon.[2,18–21] To ensure that the measured magnetization transfer between ^{1}H and ^{31}P is caused mainly by scalar coupling between ^{1}H and ^{31}P and is not mediated by a cross correlation between the ^{1}H-CSA and the $^{1}H,^{31}P$ dipole interaction, modified 1D $^{1}H,^{31}P$-HMBC experiments were carried out. For this purpose, if it is in fact a $^{2h}J_{PH}$ scalar coupling, Löhr et al. developed modified $^{1}H,^{31}P$-HMBC pulse sequences for the detection of scalar couplings.[2] Originally these pulse sequences were developed for the detection of scalar couplings across NH⋯OP and OH⋯OP hydrogen bonds in flavoproteins.[2] The modified 1D ^{1}H ^{31}P HMBC experiments were also used by our group for the detection of $^{2h}J_{PH}$ scalar coupling in CPA/imine complexes.[4]

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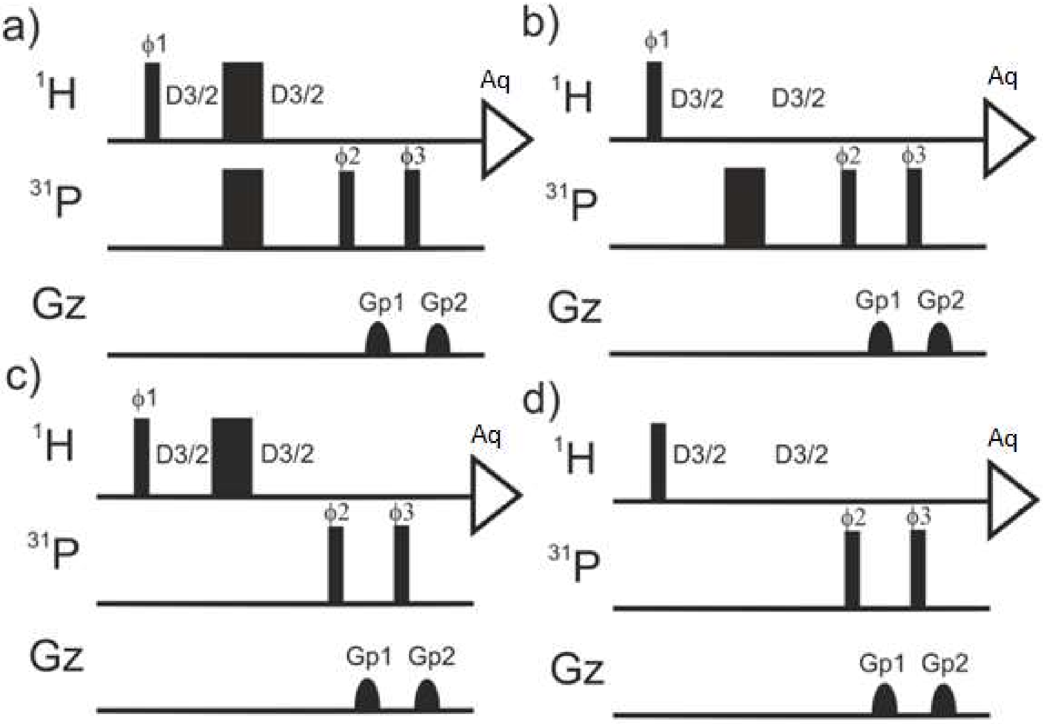

Figure S17: Modified 1D ^{1}H,^{31}P-HMBCs developed by Löhr et al.[2] a) Polarization transfer is mediated only by scalar coupling b) and c) Polarization transfer is mediated by ^{1}H-CSA and ^{1}H ^{31}P-DD cross relaxation. d) Polarization transfer is mediated by the sum of scalar coupling and the ^{1}H-CSA and ^{1}H ^{31}P-DD cross relaxation. Thin and wide bars indicate 90° and 180° pulses. All phases are x, unless otherwise specified. Pulse phases: ϕ1 = x, x, -x, -x; ϕ 2 = x, -x; ϕ 3 = 4 (x), 4 (-x).

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Chemical Exchange

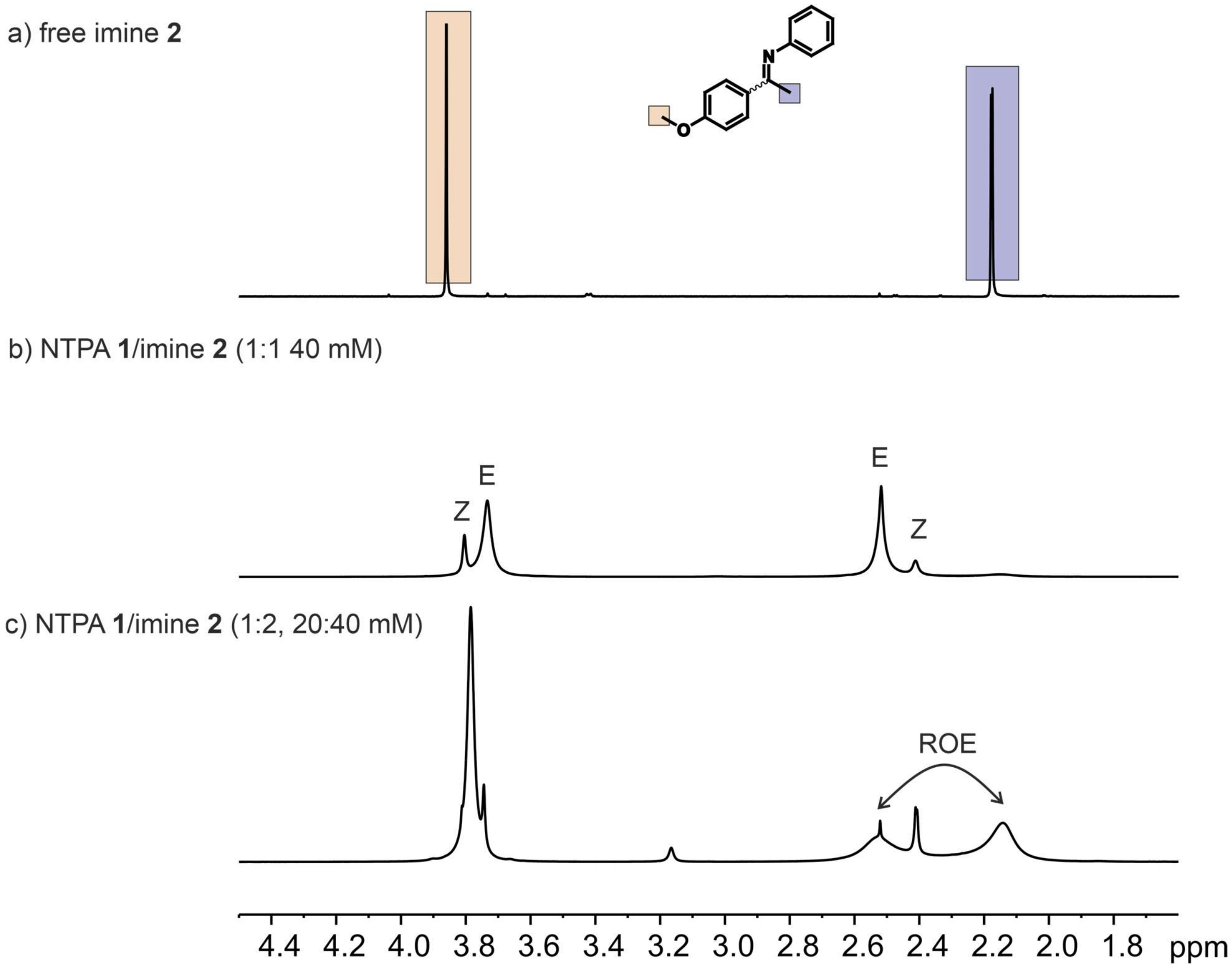

Figure S18: *a)* ^{1}*H spectrum of* ^{15}*N-labeled imine* ***2*** *at 293 K and 600 MHz in* CD$_2$Cl$_2$. *b)* ^{1}*H spectrum of NTPA* ***1*** *and* ^{15}*N-labeled imine* ***2*** *at 180 K and 600 MHz in* CD$_2$Cl$_2$. *No EXSY peaks between NTPA* ***1****/imine* ***2*** *complexes and free imine* ***2*** *were observed in a 1:1 sample. c) An excess of the imine* ***2*** *in the samples revealed EXSY peaks between the NTPA* ***1****/imine* ***2*** *complex and the free E-imine.*

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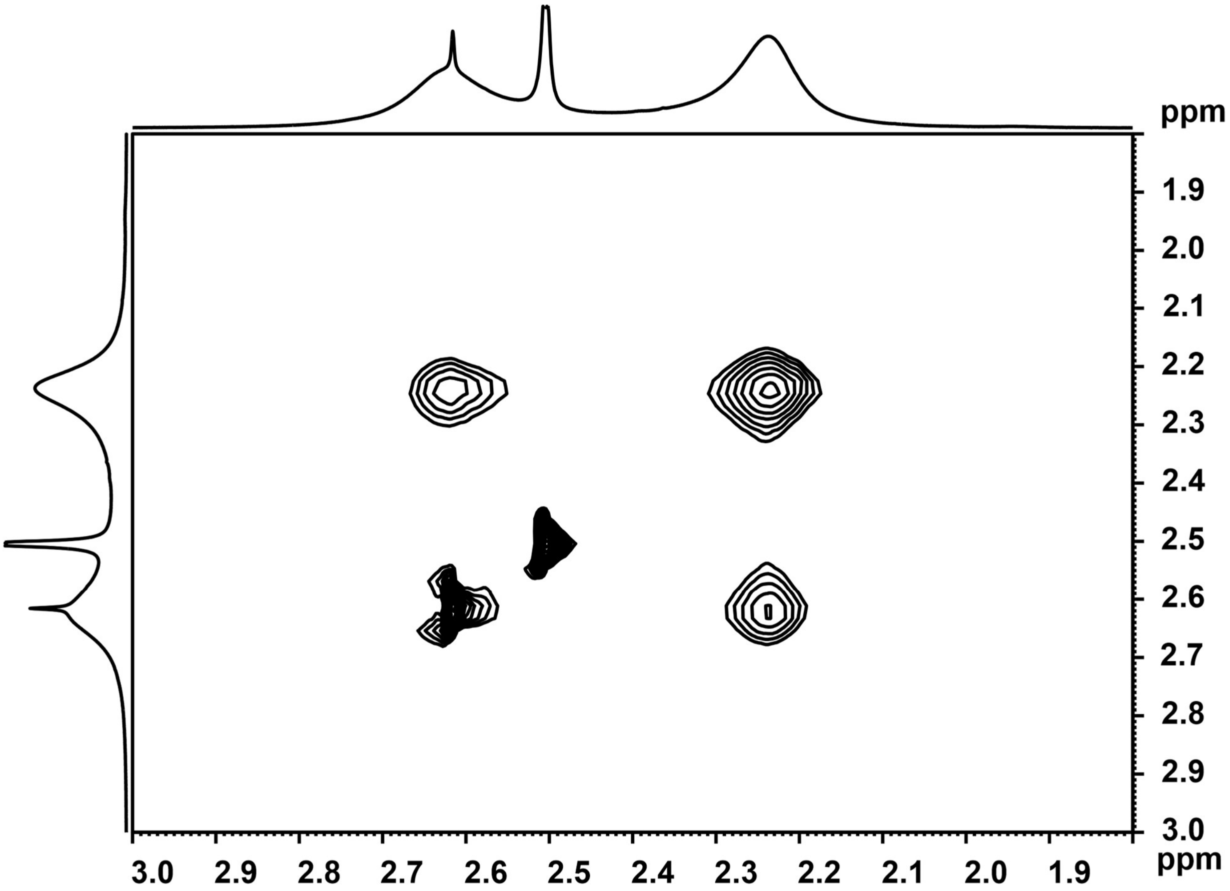

Figure S19: ^{1}H, ^{1}H-ROESY section for the of NTPA ***1****/imine* ***2*** *complex at 180 K and 600 MHz in* CD_2Cl_2*. The section shows exchange signals between the NTPA* ***1****/imine* ***2*** *complex and the free E-imine.*

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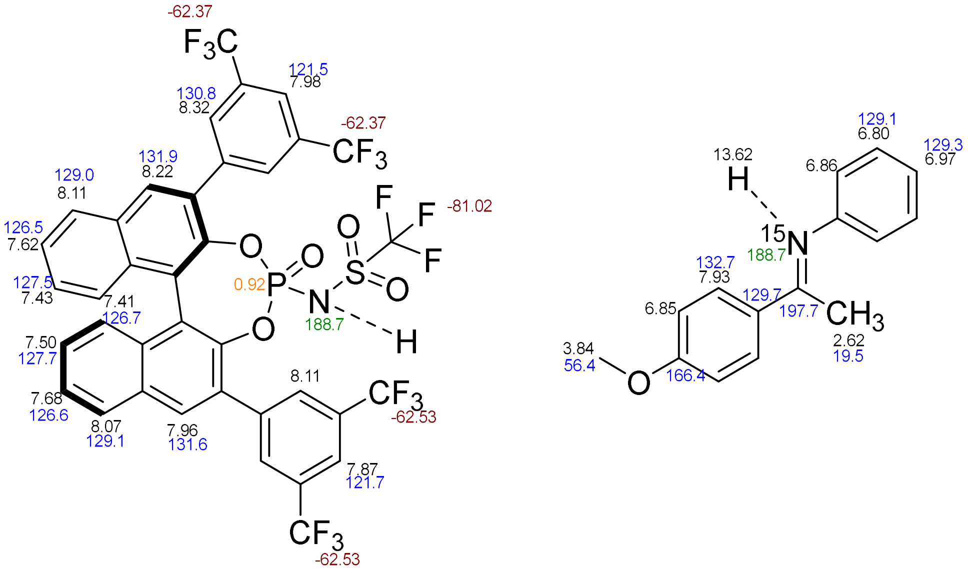
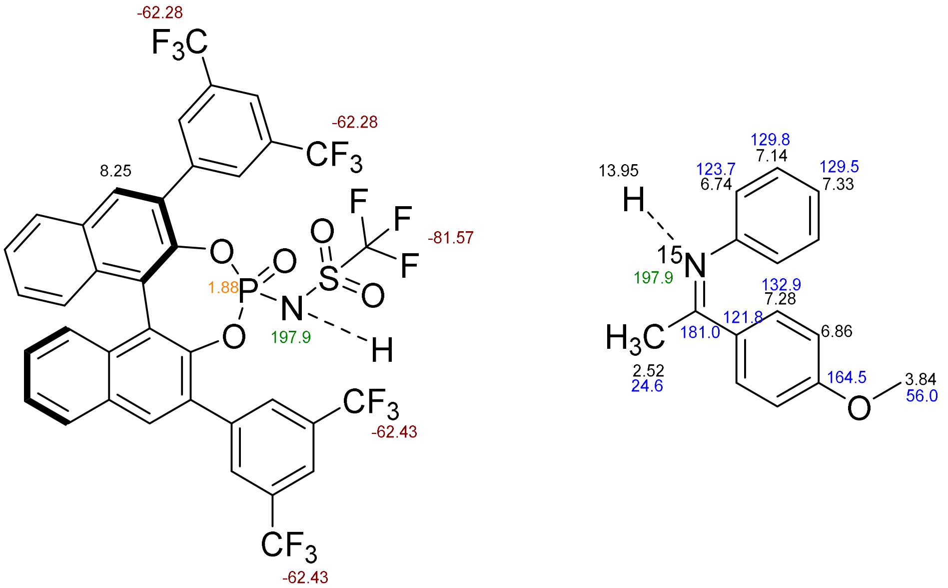
Assignments of the chemical shifts

^{1}H (black), ^{13}C (blue), ^{15}N (green), ^{19}F (red) and ^{31}P (yellow) chemical shifts of the binary complex with ^{15}N-labeled imine **2** and NTPA **1** were assigned with ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-TOCSY, ^{1}H,^{1}H-NOESY, ^{1}H,^{19}F-HOESY, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC, ^{1}H,^{15}N-HMBC and ^{1}H,^{31}P-HMBC at 180 K.

NTPA **1**/*E*-**2** complex



NTPA **1**/*Z*-**2** complex



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[b.] Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93053, Germany

Structure Identification of the Binary Complex

Binary NTPA 1/imine 2 complex

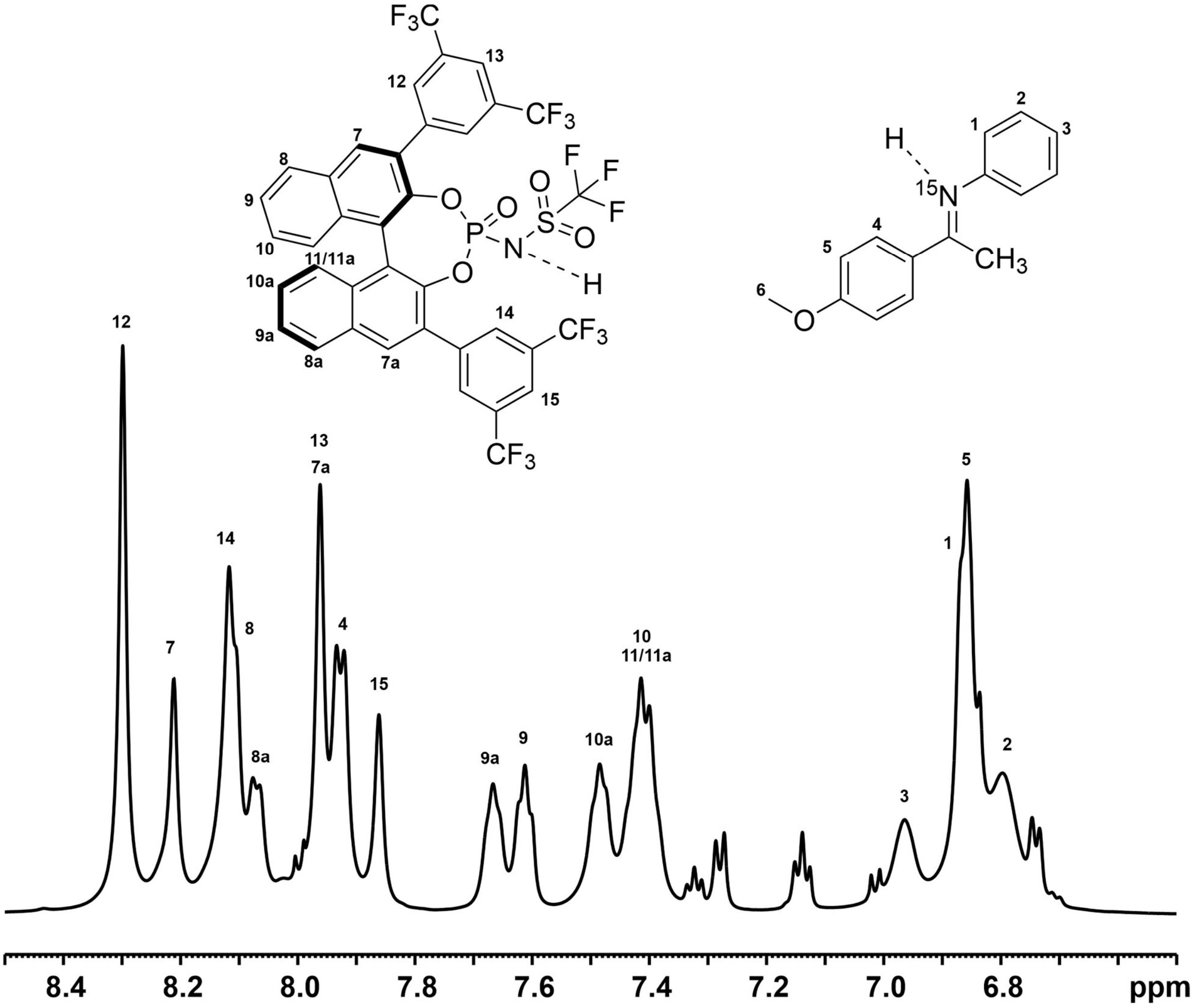

*Figure S20: ^{1}H-NMR section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD_2Cl_2.*

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Characteristic ^1H, ^1H-NOESY cross signals

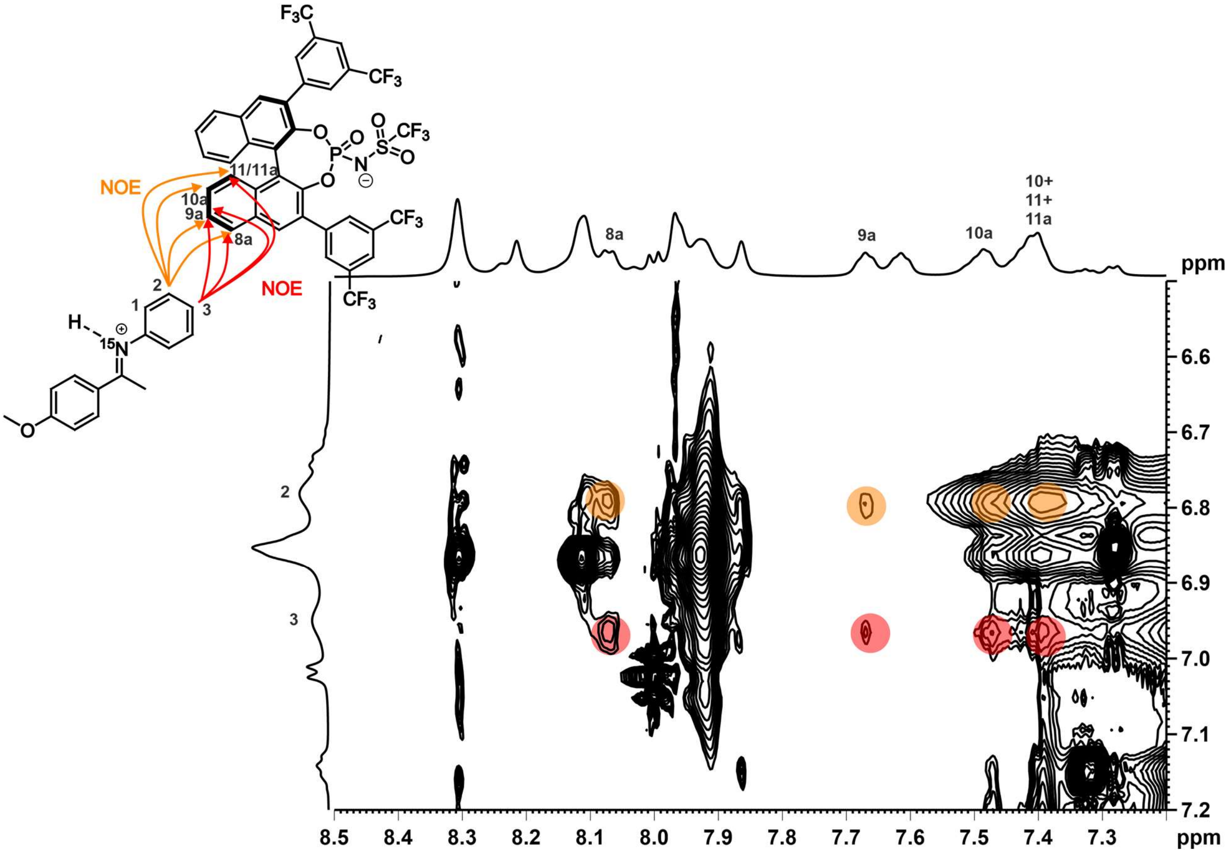

*Figure S21: ^1H, ^1H-NOESY section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic NOE cross signals between the NTPA backbone and the imine.*

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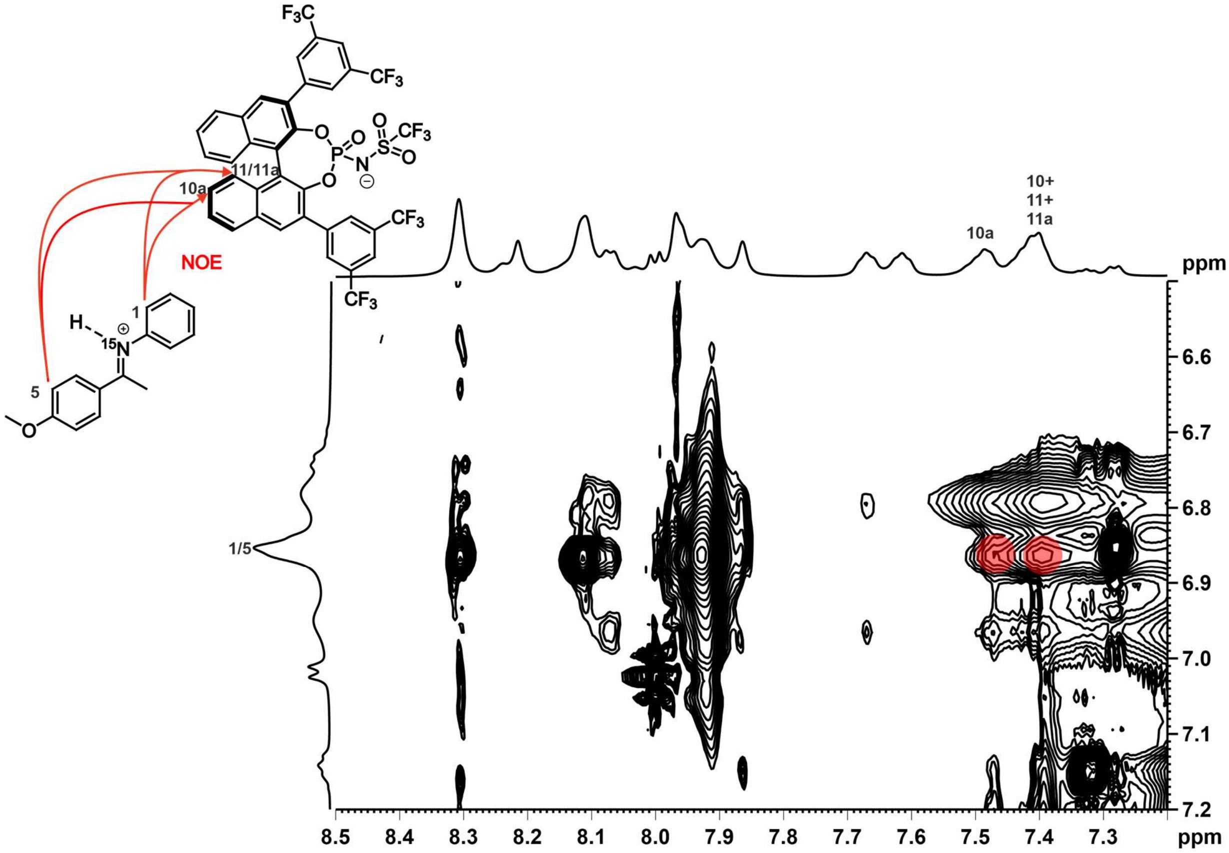

*Figure S22: ^{1}H, ^{1}H-NOESY section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD$_2$Cl$_2$. The section shows characteristic NOE cross signals between the NTPA backbone and the imine.*

Characteristic ^{1}H, ^{19}F-HOESY cross signals

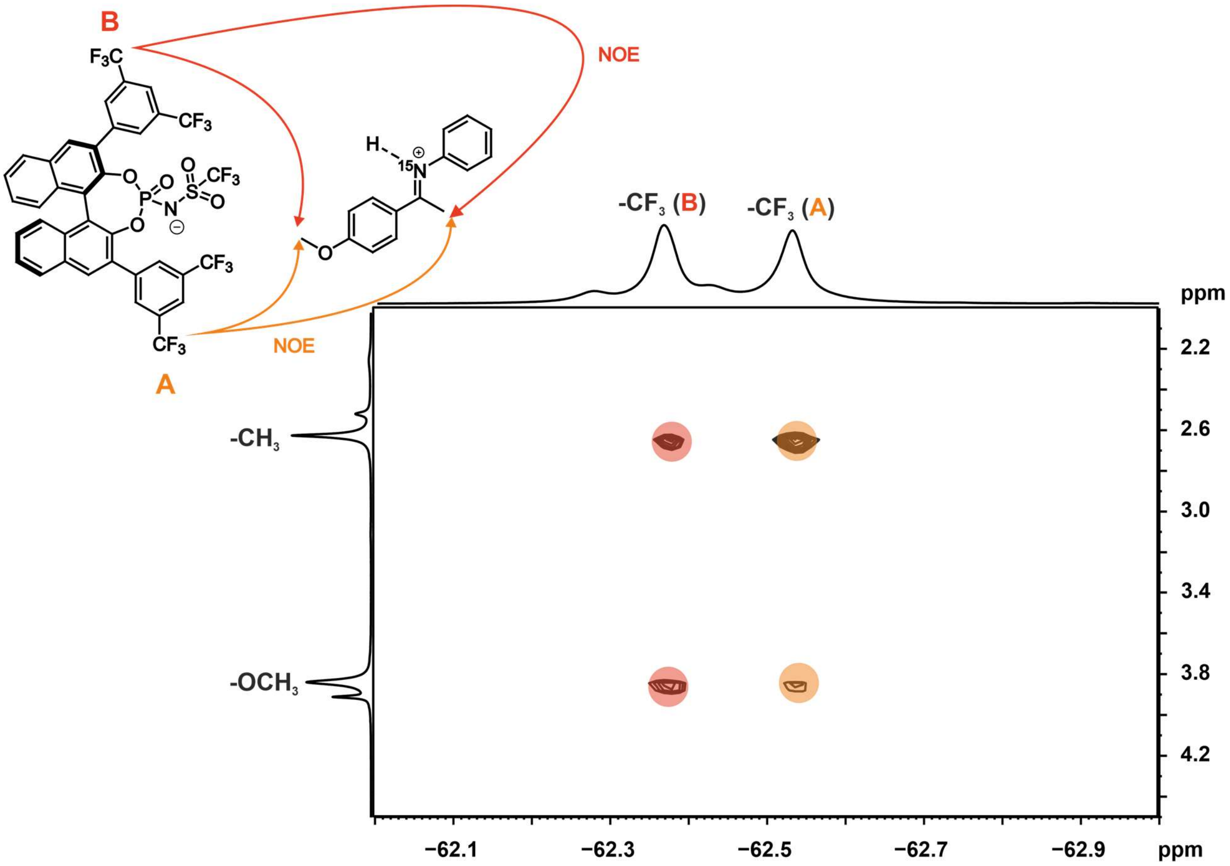

*Figure S23: ^{1}H, ^{19}F-HOESY section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic NOE cross signals between the NTPA backbone and the imine.*

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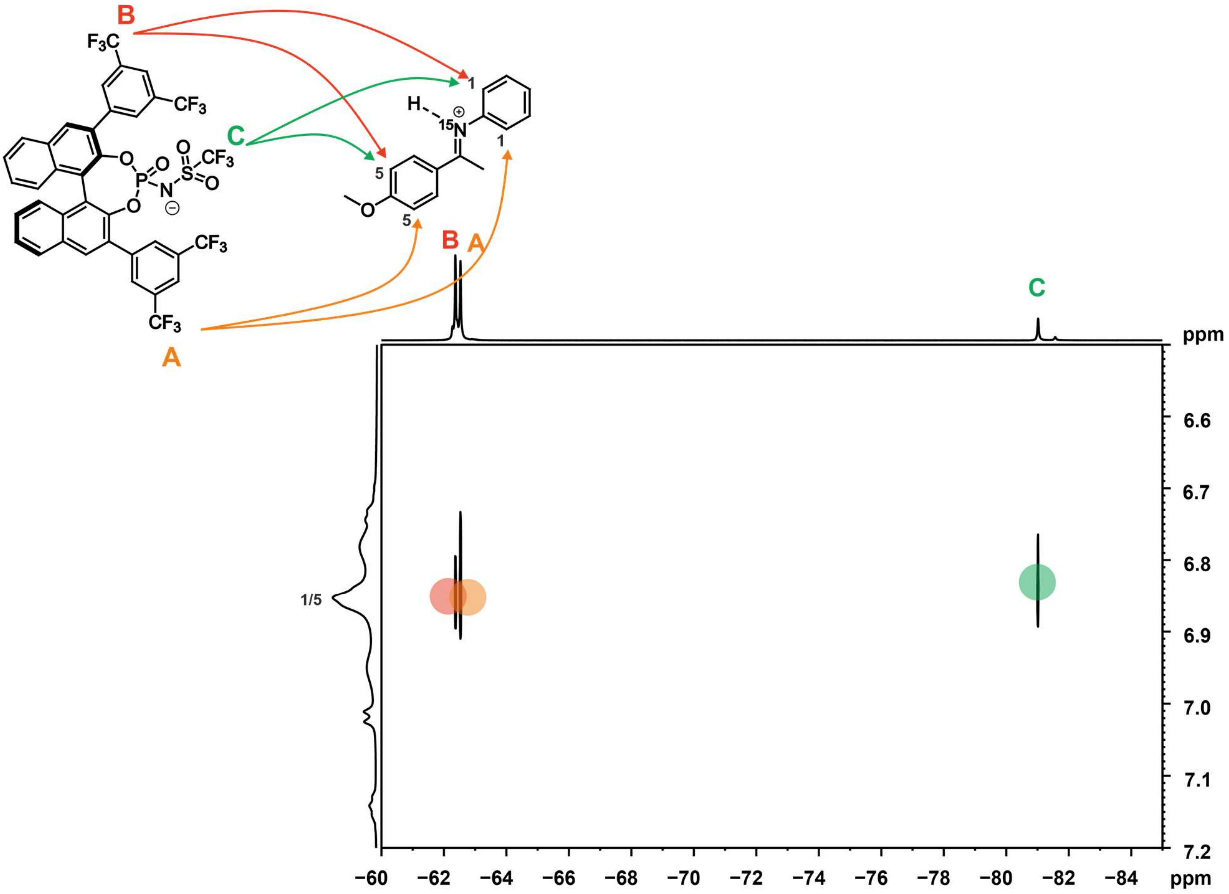

*Figure S24: ^{1}H, ^{19}F-HOESY section for the of NTPA **1**/imine **2** complex at 180 K and 600 MHz in CD_2Cl_2. The section shows characteristic NOE cross signals between the NTPA backbone and the imine.*

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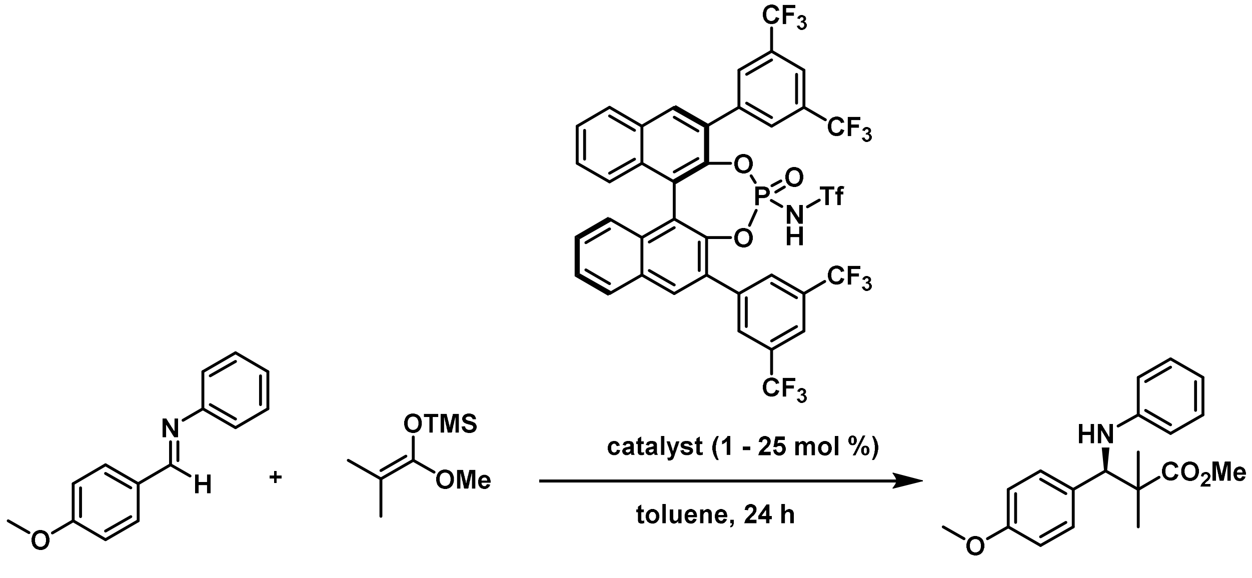
Asymmetric Mukaiyama-Mannich reaction

Reaction



13 **14** **15**

To a solution of aldimine **13** (42.2 mg, 0.2 mmol) and the NTPA catalyst **1** (0.002 – 0.05 mmol) in dry toluene at temperatures from -80 °C up to 80 °C was added dropwise a solution of ketene silyl acetal **14** (69.8 mg, 81.2 µL, 0.4 mmol) under argon atmosphere. After being stirred at the temperature for 24 hours, the mixture was quenched by addition of saturated $NaHCO_3$ (0.4 mL). THF (10 mL) and 1 M HCl (2 mL) was added at room temperature, the mixture was stirred for one hour and extracted with DCM (2x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethylacetate = 3:1). The product was obtained as a white solid and enantiomeric excess was determined by Daciel Chiralpak column. ^1H and ^{13}C NMR data was in accordance with literature.[22]

As our focus was directed towards the enantioselectivity of the reaction, given that chemical yields of up to 95% have already been reported[22], we isolated the product only once in a yield of 70%. Thus, in all reactions where we varied catalyst loading and temperature, the

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enantiomeric excess was directly determined after the work up, without undergoing purification via column chromatography or determination of the chemical yield.

^{1}H-NMR (400.1 MHz, $CDCl_3$) δH = δ = 7.18 (d, 2H, $^2J_{HH}$ = 8.73), 7.05 (t, 2H, $^2J_{HH}$ = 7.63), 6.81 (d, 2H, $^2J_{HH}$ = 8.62), 6.61 (t, 1H, $^2J_{HH}$ = 7.20), 6.49 (d, 2H, $^2J_{HH}$ = 7.72), 4.74 (brs, 1H), 4.44 (brs, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 1.26 (s, 3H), 1.15 ppm (s, 3H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δC = = 177.1, 158.8, 147.0, 131.1, 129.2, 129.0, 117.2, 113.7, 113.4, 63.8, 55.0, 52.1, 47.2, 24.4, 20.6 ppm.

HPLC Conditions

The conditions for separating major and minor enantiomer were previously established in the group of Yamamoto.[22] HPLC, Daciel Chiralpak YA-H, Hexane:*i*-PrOH = 99:1, Flow rate 0.5 mL/min, λ = 220 nm. t_R = 29.287 min (minor isomer), t_R = 41.787 min (major isomer).[22]
In this work, the product **15** consisting of major and minor isomer was isolated and detected by HPLC chromatography. Conditions were later optimized to Hexane:*i*-PrOH = 97:3, Flow rate 0.5 mL/min, Daciel Chiralpak IA. Major and minor isomer in all reactions were checked with a diode array detector. For all reactions the resulting UV-spectrum is shown below the HPLC chromatogram.

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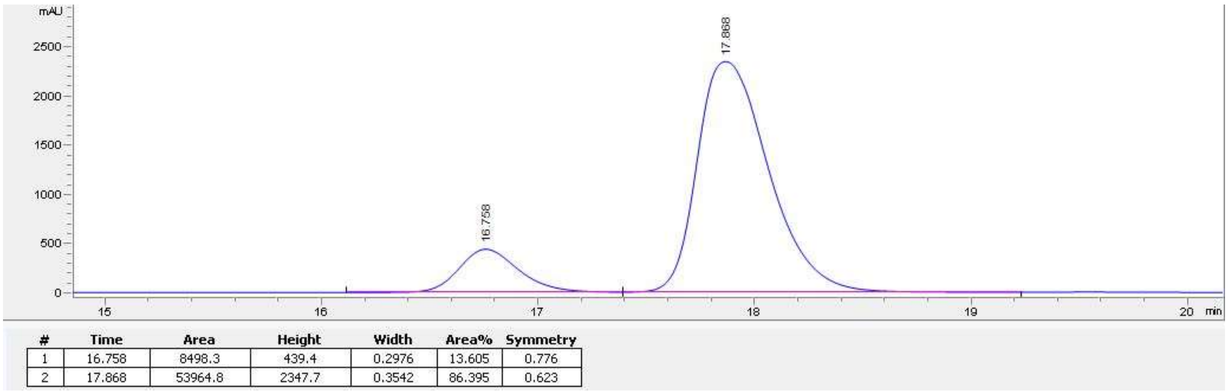
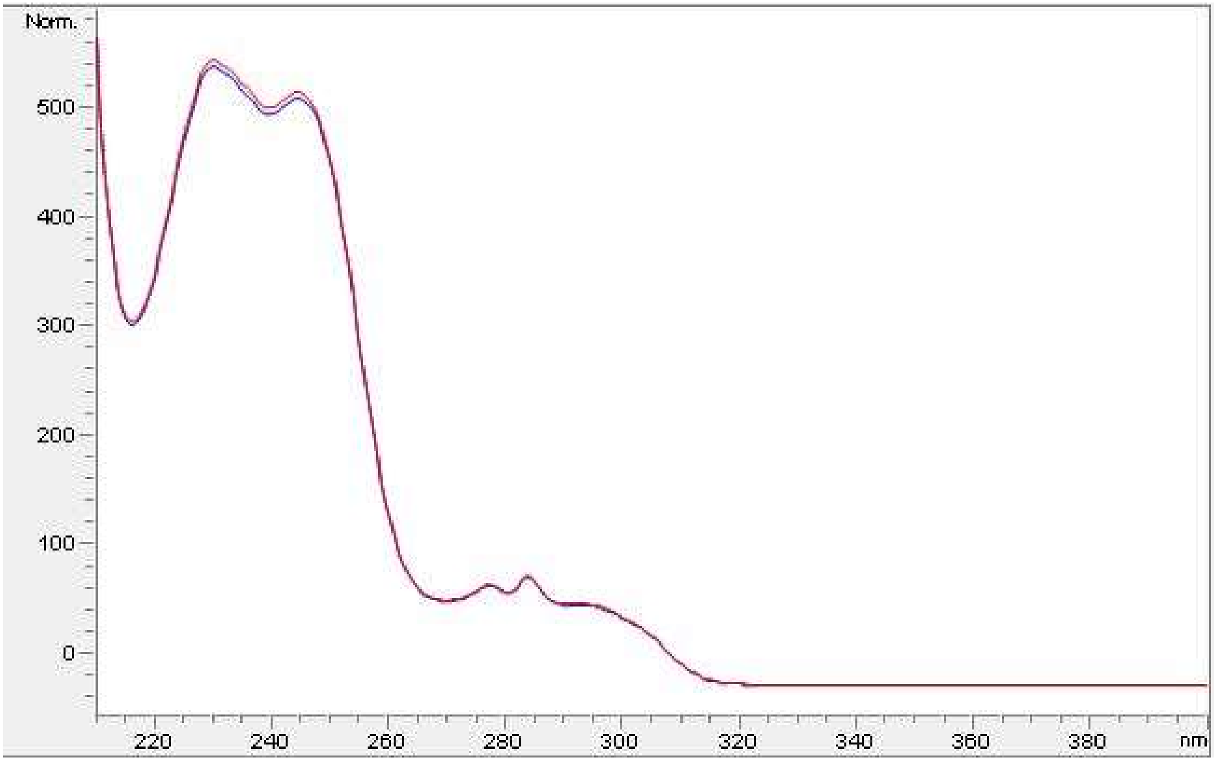
HPLC chromatograms

Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at r.t and 10% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.758	8498.3	439.4	0.2976	13.605	0.776
2	17.868	53964.8	2347.7	0.3542	86.395	0.623



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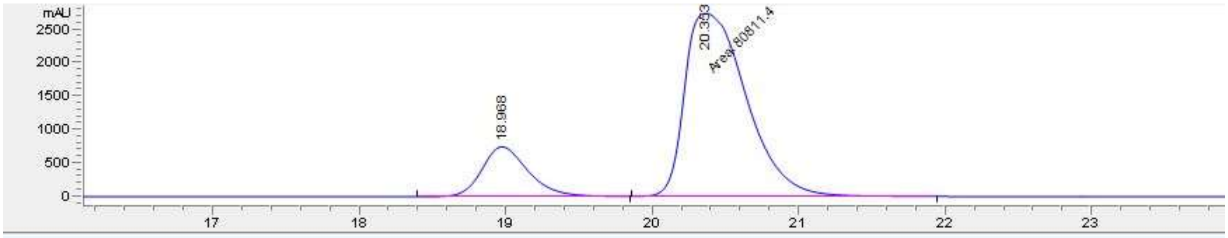
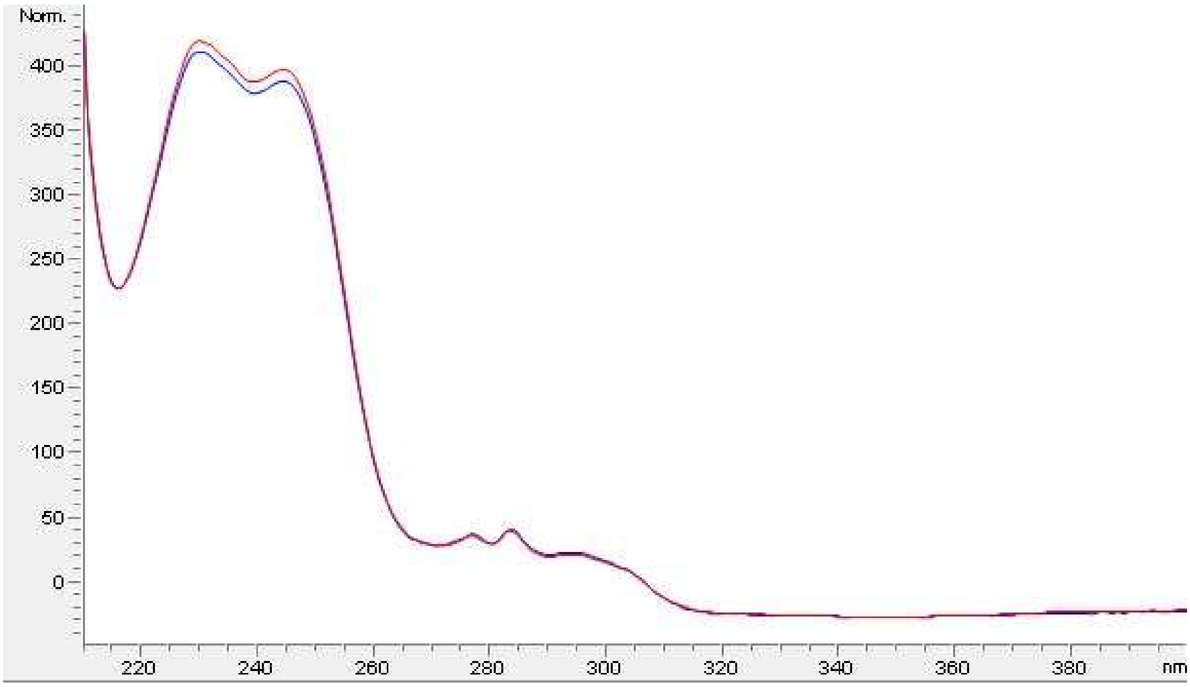
[b] *Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93053, Germany*

Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at r.t and 25% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	18.968	16384.8	741.9	0.3336	16.857	0.724
2	20.353	80811.4	2731.4	0.4931	83.143	0.482



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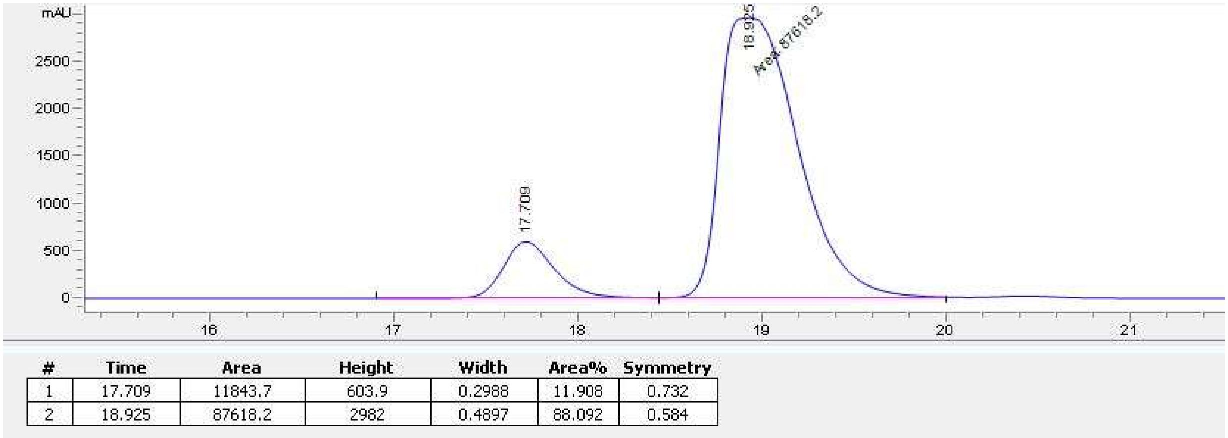
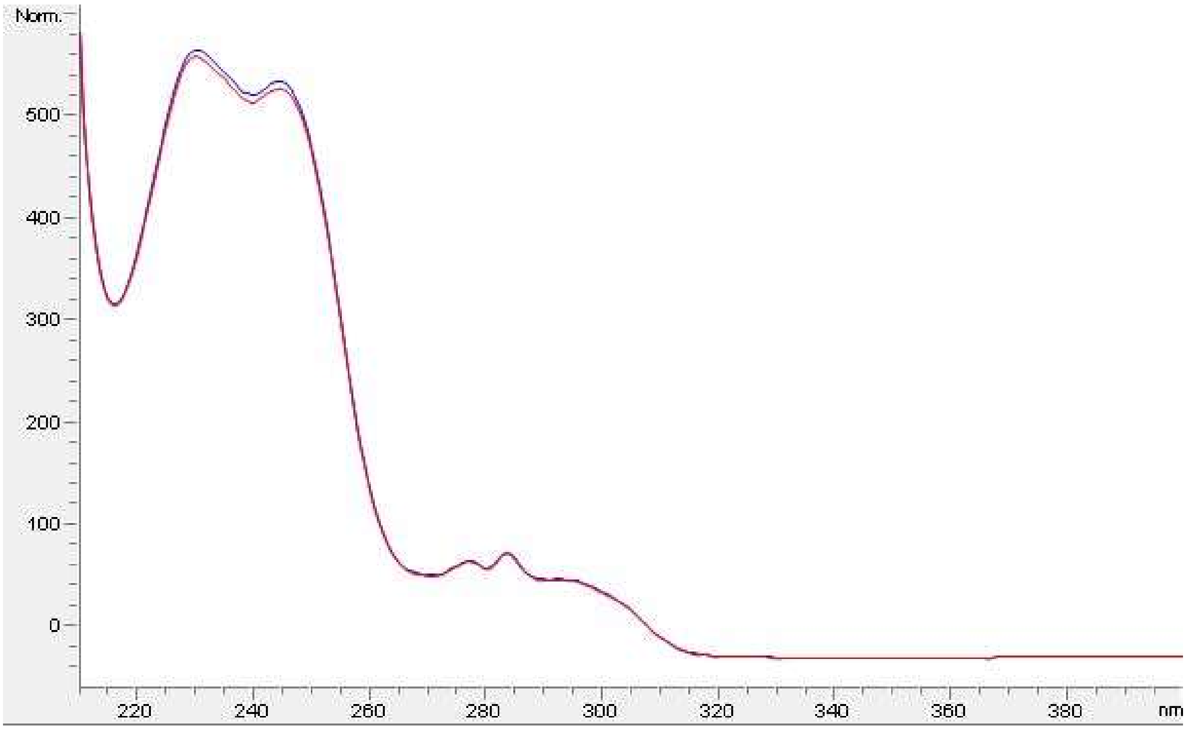
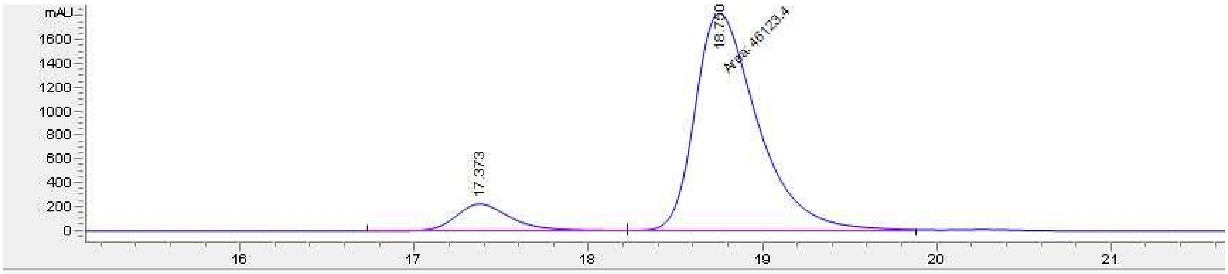
Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at -10 °C and 10% catalyst loading.



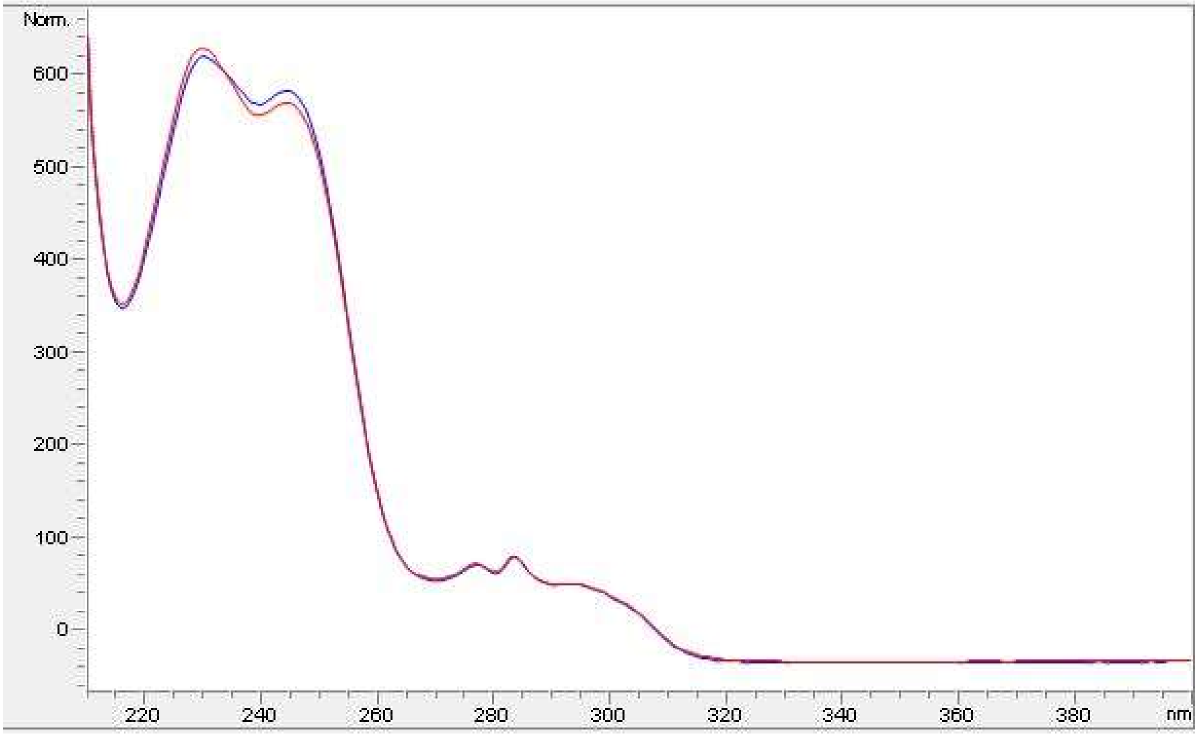
#	Time	Area	Height	Width	Area%	Symmetry
1	17.709	11843.7	603.9	0.2988	11.908	0.732
2	18.925	87618.2	2982	0.4897	88.092	0.584



Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at -10 °C and 25% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	17.373	5072.5	226.9	0.3369	9.908	0.709
2	18.75	46123.4	1826.8	0.4208	90.092	0.613



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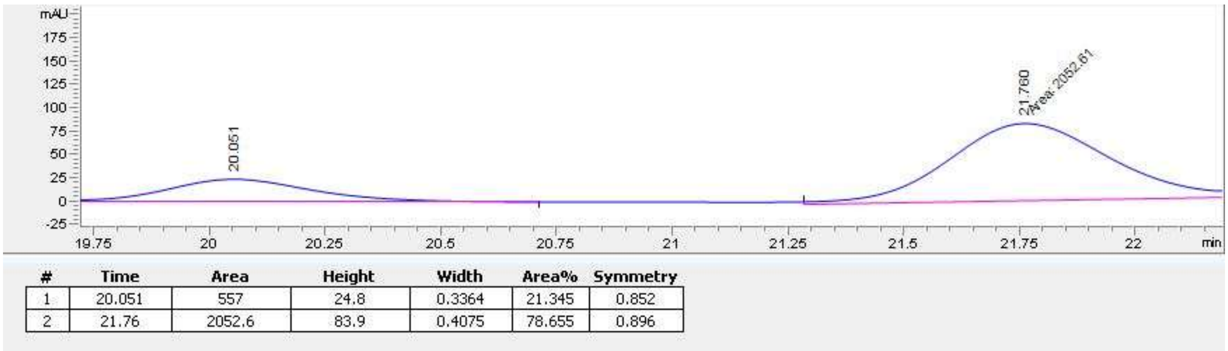
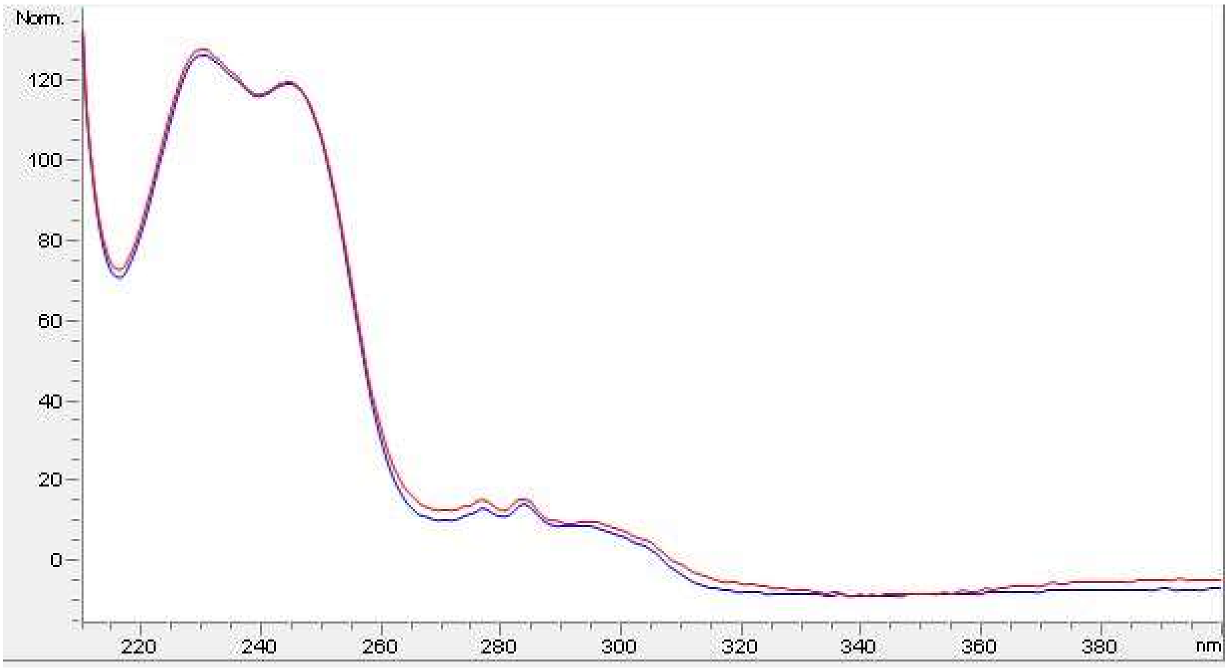
Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at 80 °C and 1% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	20.051	557	24.8	0.3364	21.345	0.852
2	21.76	2052.6	83.9	0.4075	78.655	0.896



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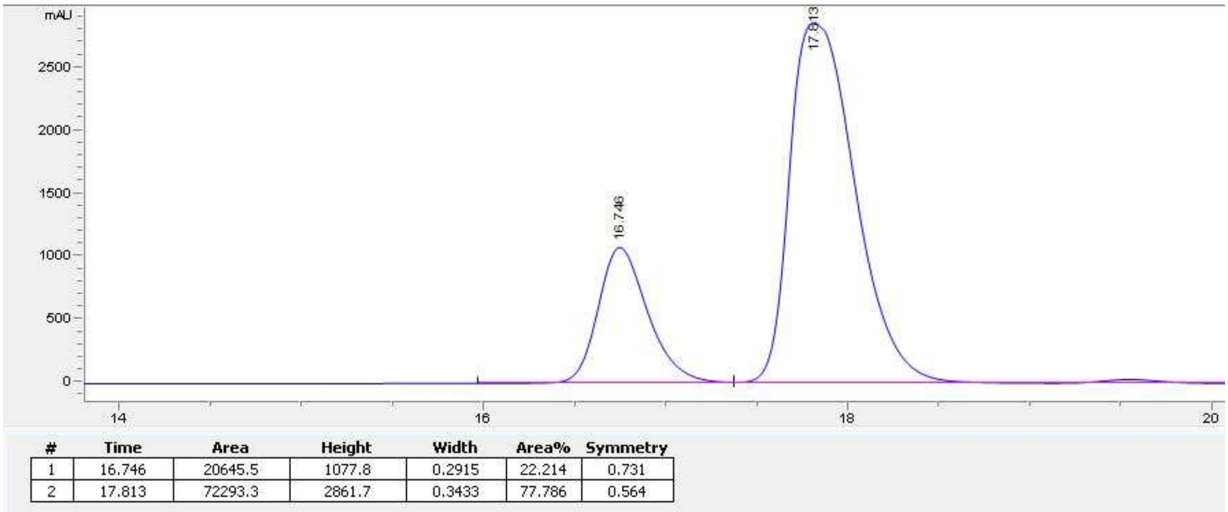
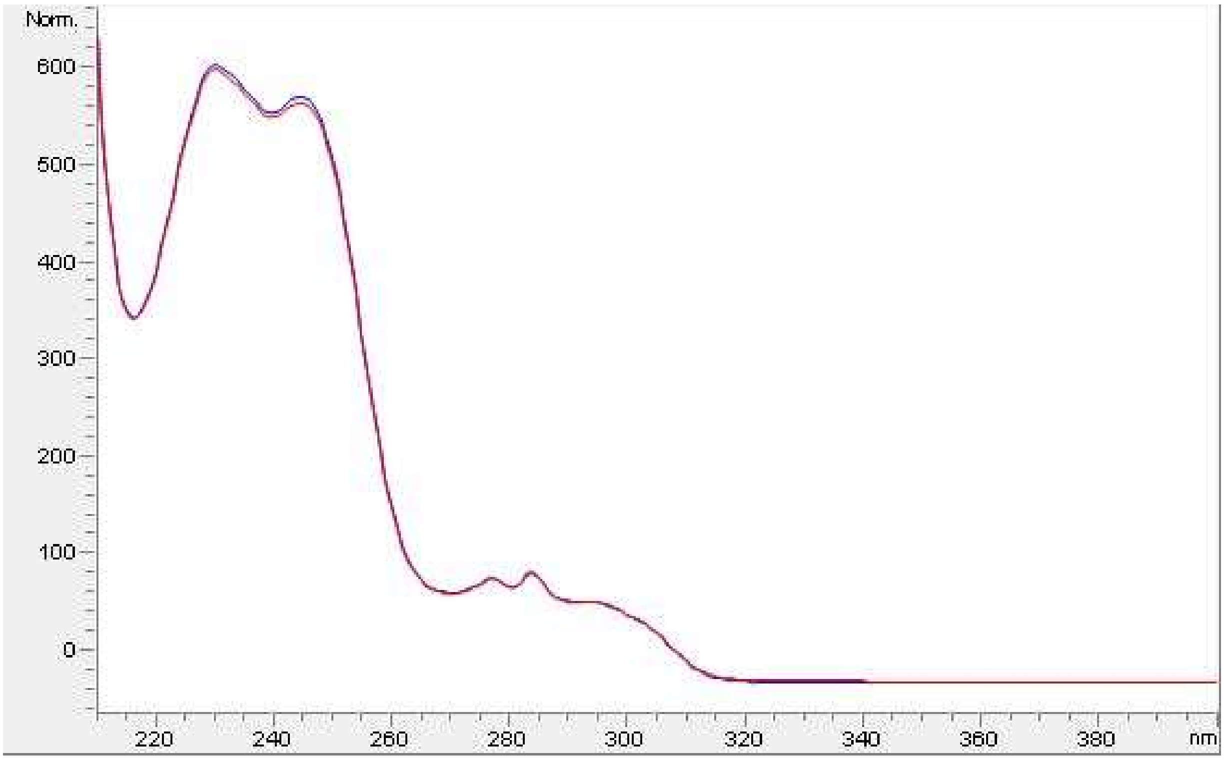
Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at 80 °C and 10% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.746	20645.5	1077.8	0.2915	22.214	0.731
2	17.813	72293.3	2861.7	0.3433	77.786	0.564



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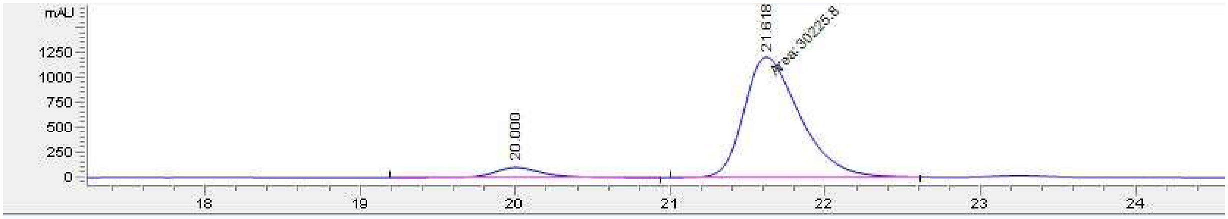
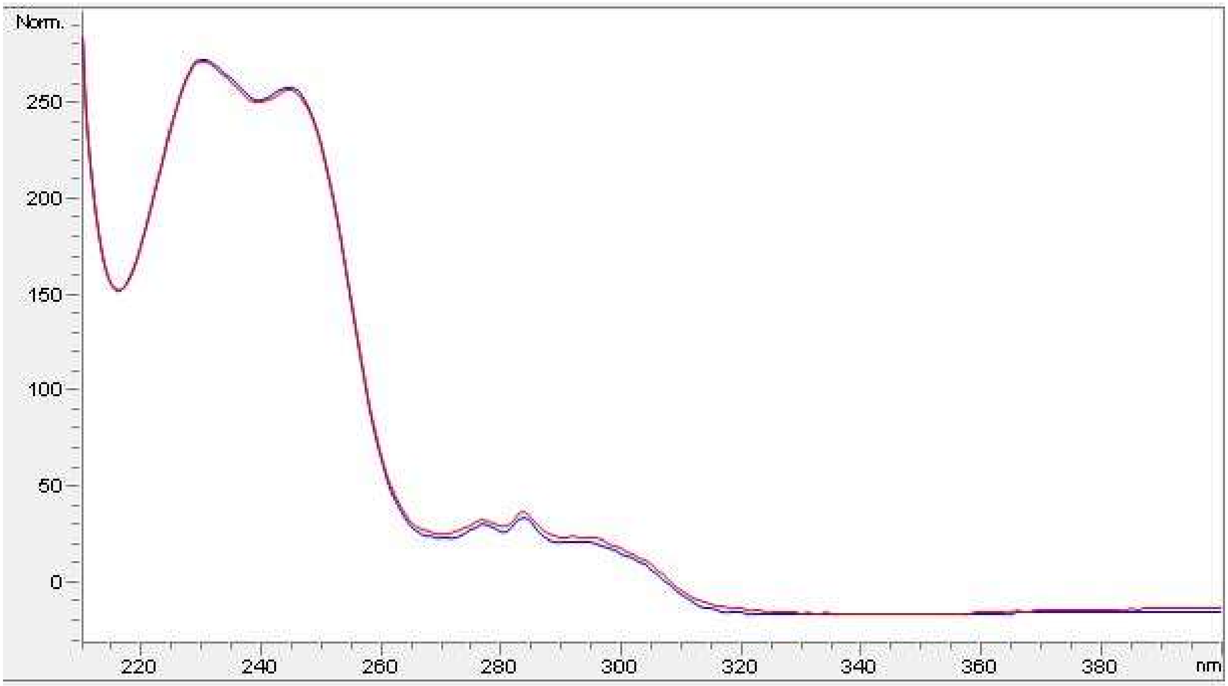
Asymmetric Mukaiyama-Mannich reaction with aldimine **13** and ketene silyl acetal **14** at -80 °C and 25% catalyst loading.



#	Time	Area	Height	Width	Area%	Symmetry
1	20	2229.7	100.6	0.3345	6.870	0.779
2	21.618	30225.8	1205.7	0.4178	93.130	0.648



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Molecular dynamics (MD) simulations

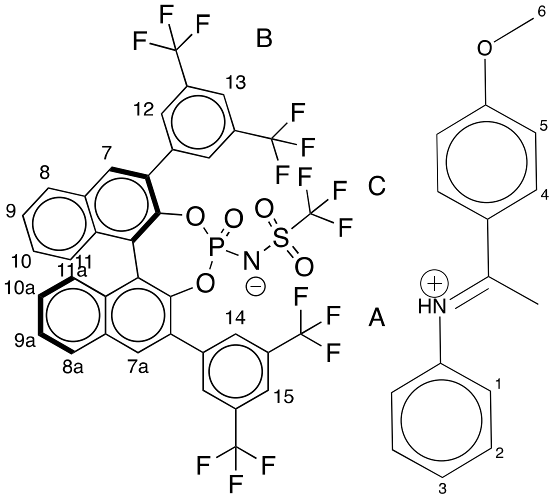

Figure S25: Model system, with numbered for comparison with the subsequent distance distributions

The model system consists of (2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4-oxidodinaphtho [2,1-d:1’,2’-f][1,3,2]dioxaphosphepin-4-yl) ((trifluoromethyl)sulfonyl)amide
and the molecule (E)-N-(1-(4-methoxyphenyl)-ethylidene)benzenaminium (see Figure S25).
The corresponding NMR-spectrum is given in Figure S26. Here it is not immediately clear how the underlying conformer species are constituted. MD-simulations were employed to suggest possible structures based on NOE-contacts. (see Figure S28)

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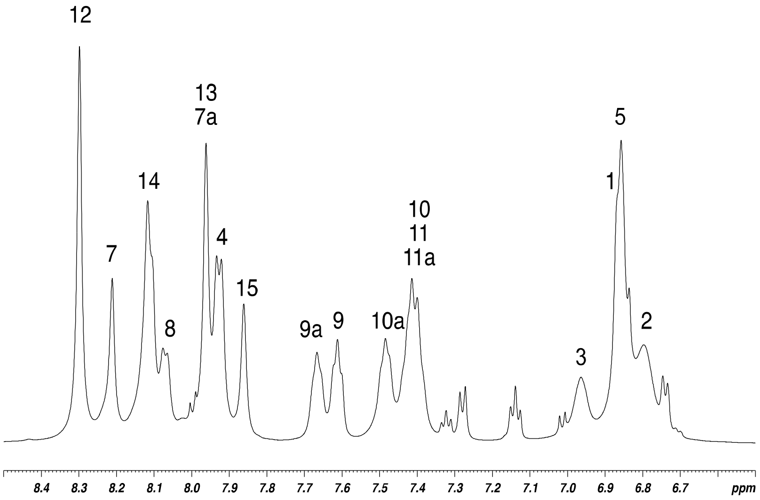

Figure S26: ^{1}*H NMR-spectrum of the model complex between and E-imine measured at* 180 *K and* 600 *MHz. Assignment by M. Hecht.*

For brevity's sake those molecules in Figure S25 will be referred to as "*NTPA*" and "*iminium*" respectively.

For the MD-investigation only the E-imine was simulated, because this one led to clear NOE-signals. Furthermore, the strong acidity of the NTPA led to the description as a purely ionic system, as a $NTPA^{-}$ and $iminium^{+}$ species.

Accordingly, only simulations of the ionic species were done.

Methods

Force Field parameters

Using ORCA[23] version 5.0.2 geometry optimizations of the individual ions were obtained at B3LYP def2-TZVP level using the conductor-like polarizable continuum Model[24] (CPCM) for CH_2Cl_2 and the D3BJ correction. The same parameters were used for optimization of the combined complex. Mayer bond orders were used as a check for validity.

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For the structure “tight” optimization was chosen, as well as a change in the grid to “defgrid3”. Frequencies were obtained numerically. RESP charges were obtained with Multiwfn 3.7[25]. Antechamber[26] was used for assigning GAFF[27] parameters. The imine the parameters “ce” and “na” were used as an approximation within the GAFF context for the iminium nitrogen and the neighboring carbon atom.

Similarly, the N^- of the NTPA-anion was approximated as an “ne” type, an inner sp^2 N in conjugated chain systems with 2 substituents.

Dichloromethane was described by a GAFF based force field, by Horinek[28], which was modified, so it used virtual sites.

Acpype[29] was used for conversion of the topology file formats. The force fields are given below.

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Simulation Details for comparison of distances with NOE data

The GROMACS[30] simulation package was used for all MD-simulations in versions of 2018 and newer.
Simulations of the E-imine were carried out within a box containing 1 iminium, 605 DCM and 1 NTPA molecule with a timestep of 2 fs for a total simulation time of 1.6 µs at 1 bar and 180 K.

For this the Parrinello-Rahman barostat (compressibility= $2.5e^{-5}$ bar^{-1}, τ_p=1 ps) and the v-rescale thermostat (τ_T=1 ps). For the data evaluation a relatively long equilibration period of 50 ns was excluded. This time corresponds to the initial formation of the complex.
At 180K no interconversion of I and II occurs. Complete ergodicity cannot be assumed. Simulations at higher temperatures (300K and more) were also tested, to see whether new preferential structures occur or exchange between motifs I and II occur on the simulation time scale. As there were no significant changes, the simulations at 180K will be evaluated in the discussion. The usual corrections for energy and pressure were employed during the simulations.

Simulation Details for the determination of free energy differences along the H-bond donor and acceptor H-coordinate

For the comparison between the H-bond possibilities towards the NTPA phosphate centered oxygen and nitrogen, umbrella sampling was performed with the parameters from above, starting from the oxygen bound situation (see Figure S65, Figure S66) at a umbrella distance of around 0.37 nm.
Umbrella windows were centered at distances of 0.42, 0.37, 0.32, 0.27, 0.22, 0.17, 0.12 and 0.08 nm between the E-iminium H and the NTPA's nitrogen atom with a force constant of k=1000 kJ mol^{-1} nm^{-2}. For every subsequent umbrella simulation the end point of the previous ones was taken. The data was written to the file every 500 steps. Two different

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PMFs were obtained with *gmx wham*.[31] Once for simulations that were run at 300K for 1000000000 steps (2μs), which also showed significant rotations of the iminium in the binding pocket along the umbrella steps. Subtrajectories yielded similar PMFs, which means quasi-ergodic sampling can be assumed (*Figure S68*).

Another short set (20 ns) of simulations at 180K, which do not show significant conformational changes (see *Figure S69*) along the umbrella coordinate, was also used to obtain PMFs as an estimate for moving the iminium molecule towards the nitrogen without rotations. Because of the qualitative similarity of the 180K and 300K PMFs the 300K simulations are assumed to be sufficiently sampled.

Mayer Bond Orders: An Initial Check for Validity

As the N^- atom is not a standardized atom in the GAFF context a quick check for validity of using the “ne” parameter was employed. This is by no means a comprehensive analysis. Instead serves as a plausibility argument: if the bond orders did not reflect the force field description, another model would be needed.

It is usually assumed that a negatively charged NTPA molecule has its charge centered fully on the nitrogen, which means that the bond towards its neighboring P and S atoms should be described as a single bond. The Mayer bond orders (from ORCA) obtained for the geometry optimization of the anion is shown in fig. Figure S27 (rounded to the second decimal point). The Mulliken gross atomic charge for the double bond oxygen atom is -0.5934 and for the formally negative nitrogen -0.4539.

The charges from the RESP fit are -0.6925900998/-0.7664559612 for O and N respectively using the default settings and -0.6978260556/-0.7417259377 after adding equivalencies for the fluoride atoms. The main charge seems nitrogen centered. Thus, an H-bond through oxygen is probably not caused simply by a higher charge on the oxygen compared to the nitrogen position.

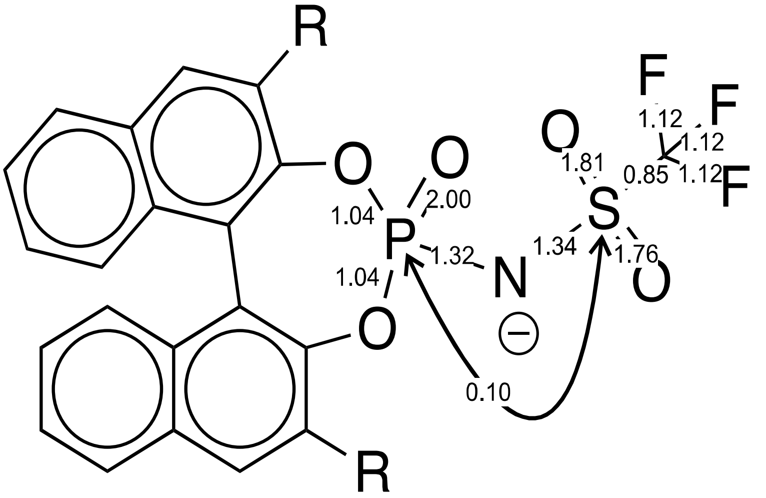

Figure S27: Mayer bond order between atoms of interest (rounded) for the NTPA anion (full data given in the DFT section)

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Comparison of Weighted Distances with NOE-Contacts

From the NMR-experiments the following NOE-contacts are known:

Table S2: NOE contacts between H positions on the iminium molecule and the molecule; "/" denotes a logical "or". For these the signals could not be assigned completely by due to overlap.

iminium	NTPA
2	8a
3	8a
2	9a
3	9a
1/5	10a/11/11a
2	10a/11/11a
3	10a/11/11a

Table S3: HOE contacts; "/" denotes a logical "or"

iminium	NTPA
1/5	C
A + B	6 and Me
A + B	1/5

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Evaluated Distances Related to the NOE-Contacts Allow for a Differentiation between Structure Motifs

Two distinct structure motifs have emerged from the simulations: they differ mainly by the rotation of the iminium by 180 ° (see Figure S28).

They will be referred to as motifs **I** and **II** in the following section.
It will be shown that **II** most probably does not correspond to the observed NOE-contacts in Table S2. Additionally, it will be shown that motif **I** contains contributions of two main conformers.

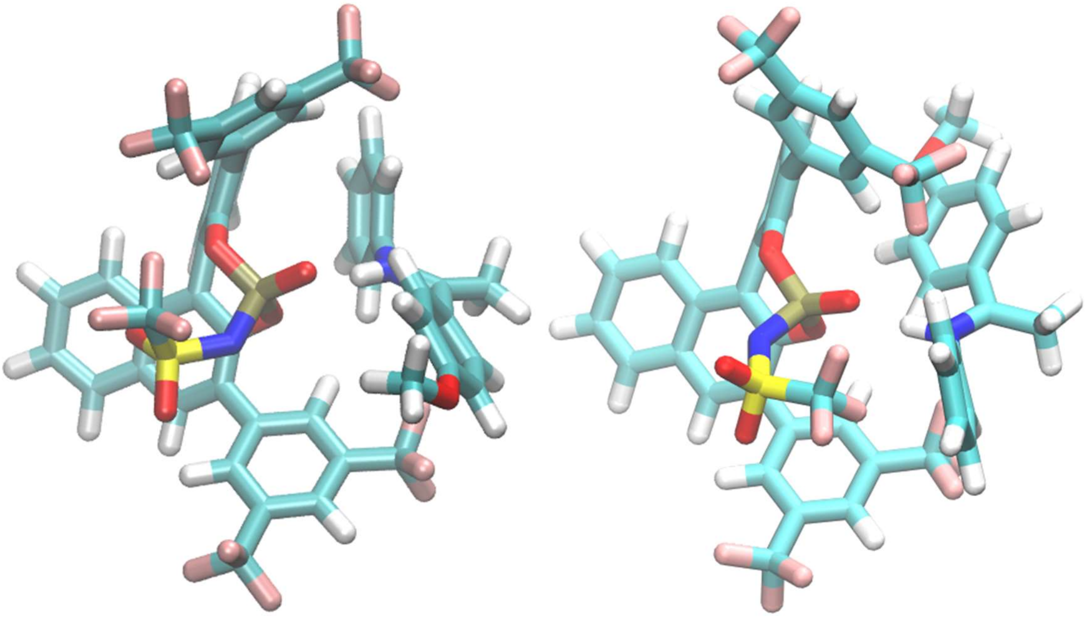

Figure S28: Structure motif I (left) and II (right) differ by the rotation of the iminium molecule in the binding pocket

As one can surmise from the NOE contacts (compare Figure S28 to Table S2) between the iminium positions **2** and **3** to the positions **8a**, **9a**, **10a** and possibly **11a**, the iminium-phenyl ring might be positioned on top of the NTPA-backbone.
We will discuss both sides of the NTPA-backbone separately. Due to the necessary number of distance distributions related to this discussion the results are presented first, and the distance distributions are shown afterwards. This is done for BINOL-sides separately.

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Distances Towards Atoms Situated on the “a” BINOL Side

First the BINOL-side denoted as “**a**” in Figure S25 will be discussed.

Due to the NOE-contacts small distances would have been expected between the iminium positions **2** and **3** towards positions **8a** and **9a** on the molecule. This is not the case for either motif **I** or **II** (in Figure S28) as the distances observed in the simulations are larger than 0.6 nm. NOE contacts can usually be found below this value (compare Figures S30, S31, S33, S34).

It is also not the case for the contacts assigned towards position **10a** from the imine positions **1**, **2** and **3** (compare Figures S35, S36, S37).

A possible contact from **11a** towards **1**, **2** and **3** seems possible only for structure motif **I**.

This lets us exclude the positioning of both motif **I** and **II** on the BINOL “a” side. In addition, it may be possible that just the nomenclature used for the BINOL “a” side and the “non-a” side needs to be reversed to be compatible with the NMR data.

Distances Towards Atoms Situated on the “non-a” BINOL Side

The difference between structure motif **I** and **II** regarding the distances from the other side of the BINOL-backbone not denoted as “a” becomes prominent.

I shows close distances between positions **2** or **3** on the iminium towards **8**, **9** or **10** of the of around and below 0.5 nm, whereas **II** does not. These distances likely correspond to possible NOE-contacts (see Figures S42, S43, S45, S46, S48, S49).

This allows for a similar exclusion of structure motif **II** for the other -side and promotes **I** to a strong candidate for the experimentally measured structure – provided the HOE contacts correspond to reasonable distances. *Figure S53* ff below confirm this. Still, it is not possible to differentiate whether **A** and **B** are in contact with atoms **1** or **5**. This means the initial arbitrary assignment of which side was denoted with “a” needs to be reversed. Motif **I** may well correspond to the NMR-results, whereas **II** can be excluded.

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Distance Distributions related to the NOE-Contacts of the “a” BINOL Side

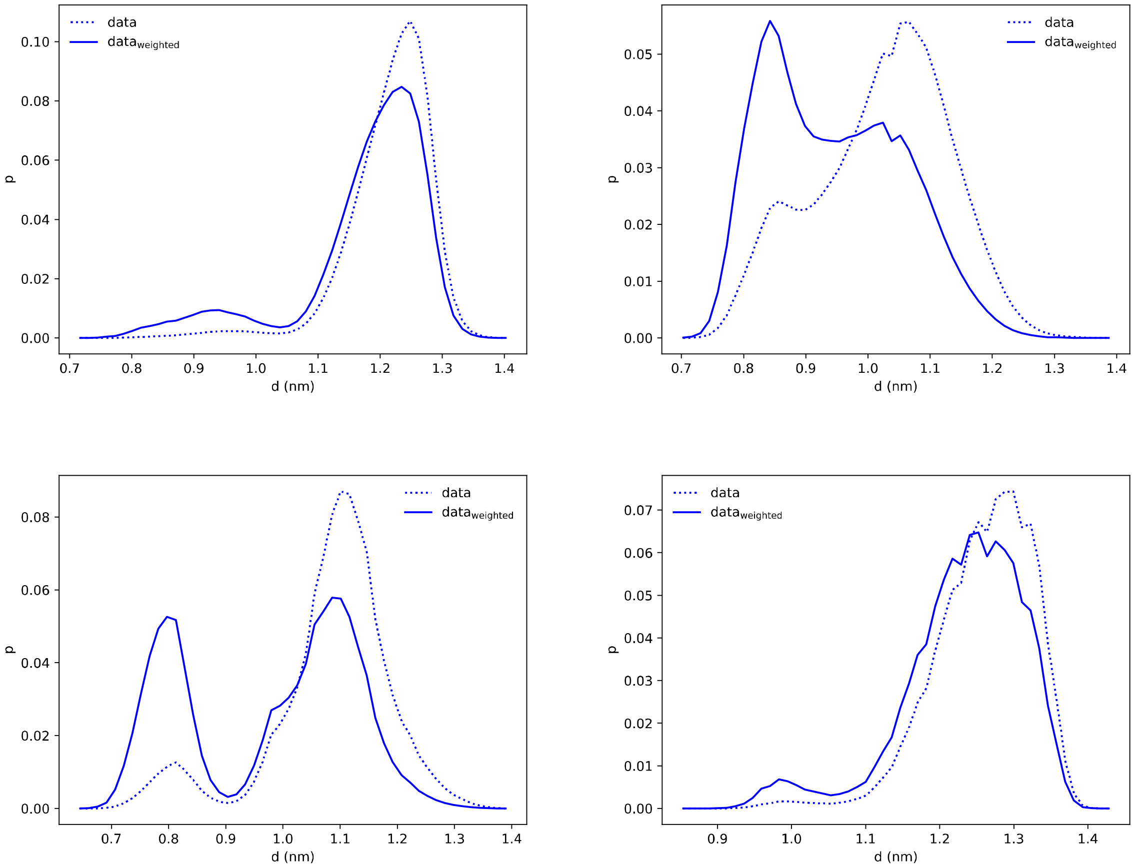

Figure S29: r^{-6} weighted and unweighted distance distributions between 1 and 8a. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

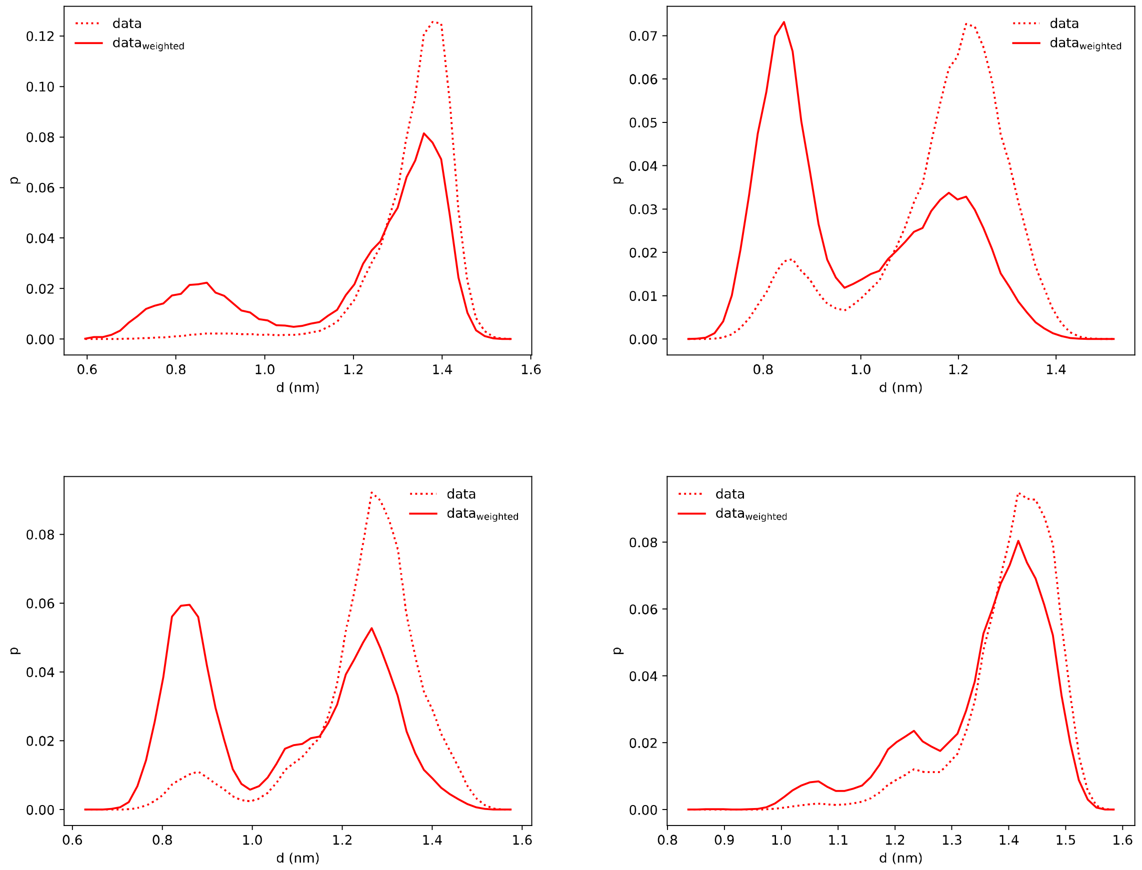

Figure S30: r^{-6} weighted and unweighted distance distributions between 2 and 8a. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

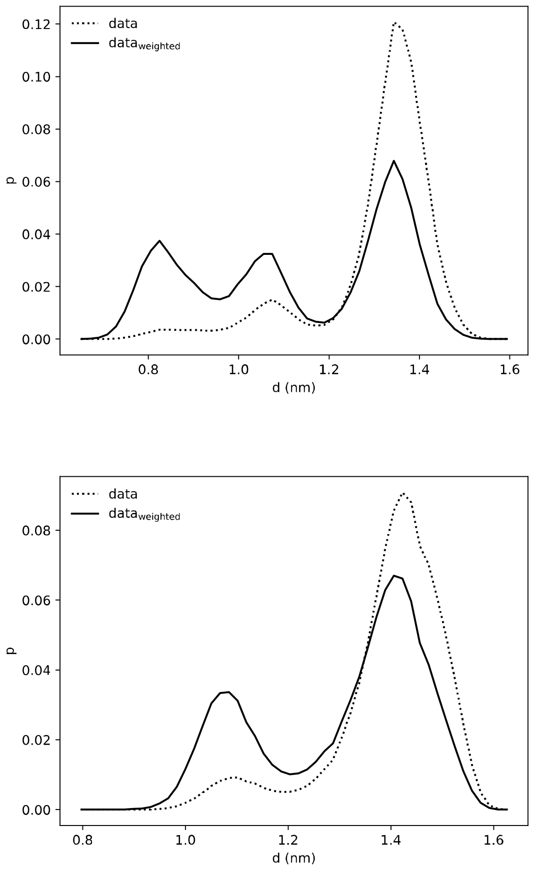

Figure S31: r^{-6} weighted and unweighted distance distributions between 3 and 8a. Distances for structure motif I are shown on the top and for II on the bottom.

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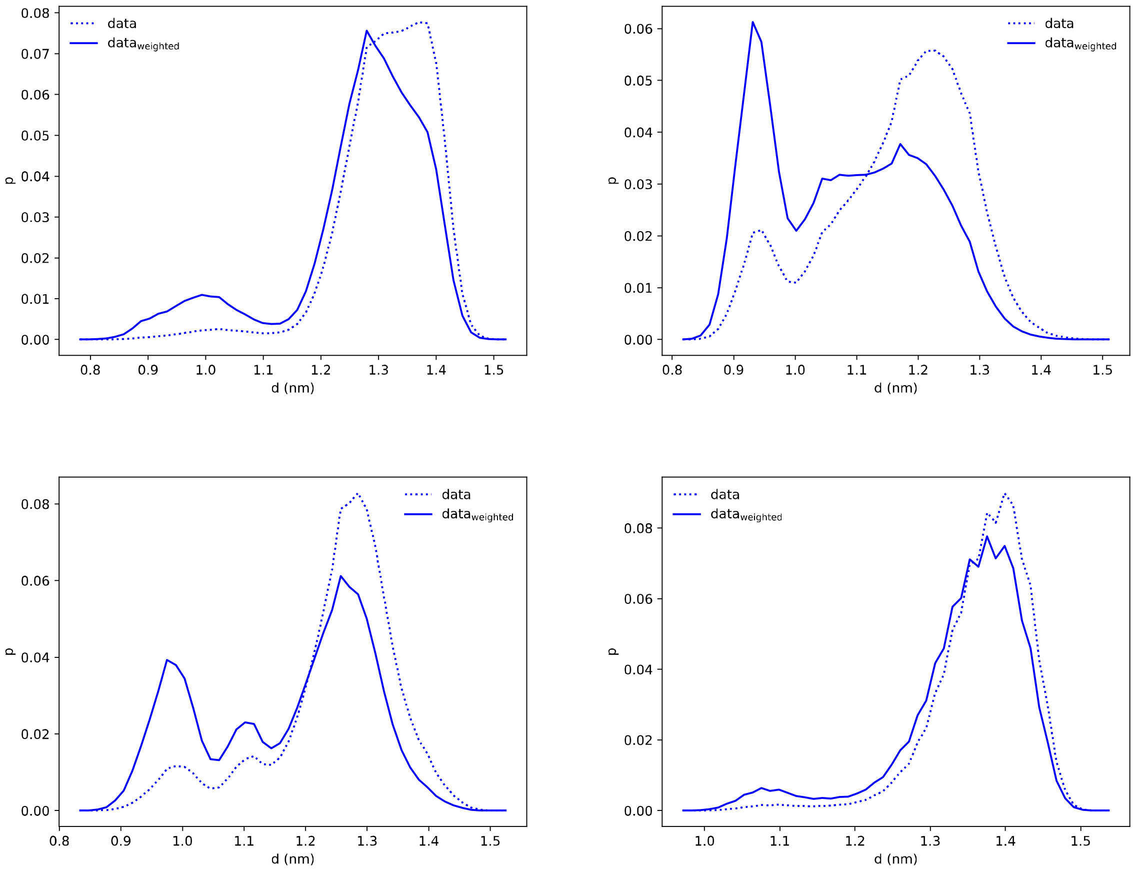

Figure S32: r^{-6} weighted and unweighted distance distributions between 1 and 9a. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

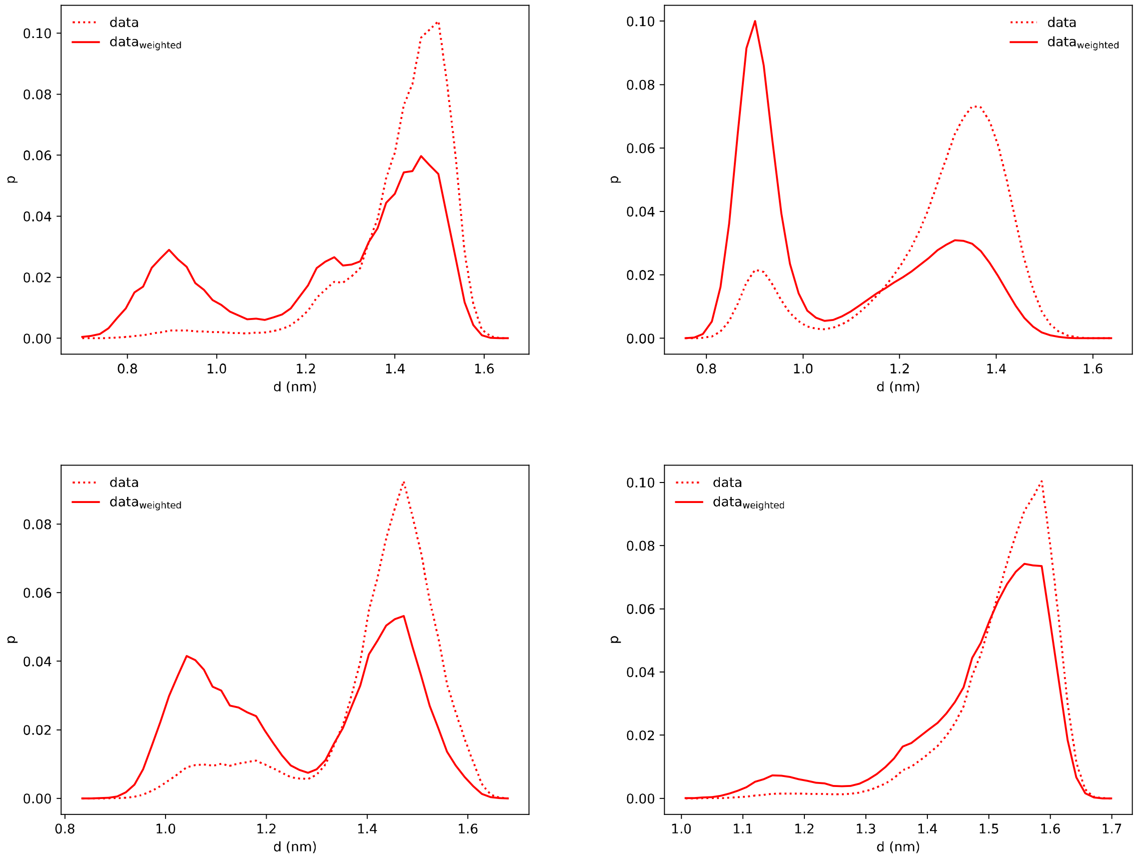

Figure S33: r^{-6} weighted and unweighted distance distributions between 2 and 9a. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

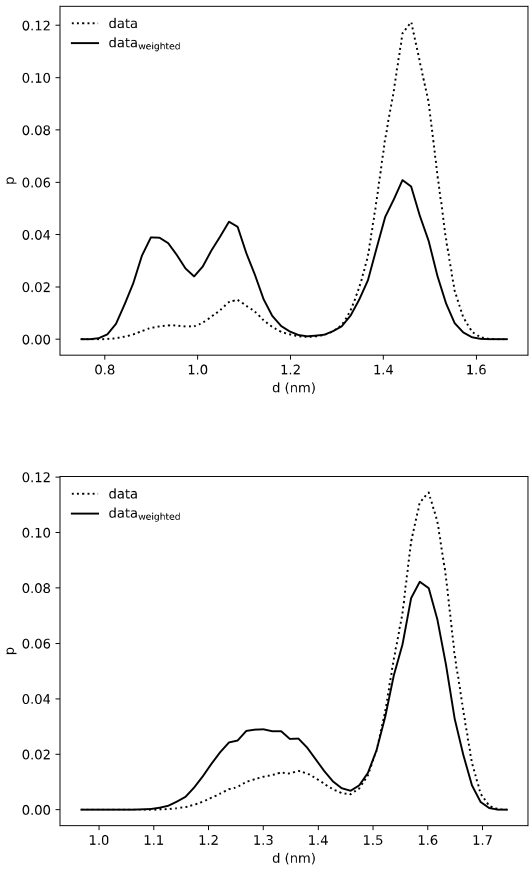

Figure S34: r^{-6} weighted and unweighted distance distributions between 3 and 9a. Distances for structure motif I are shown on the top and for II on the bottom.

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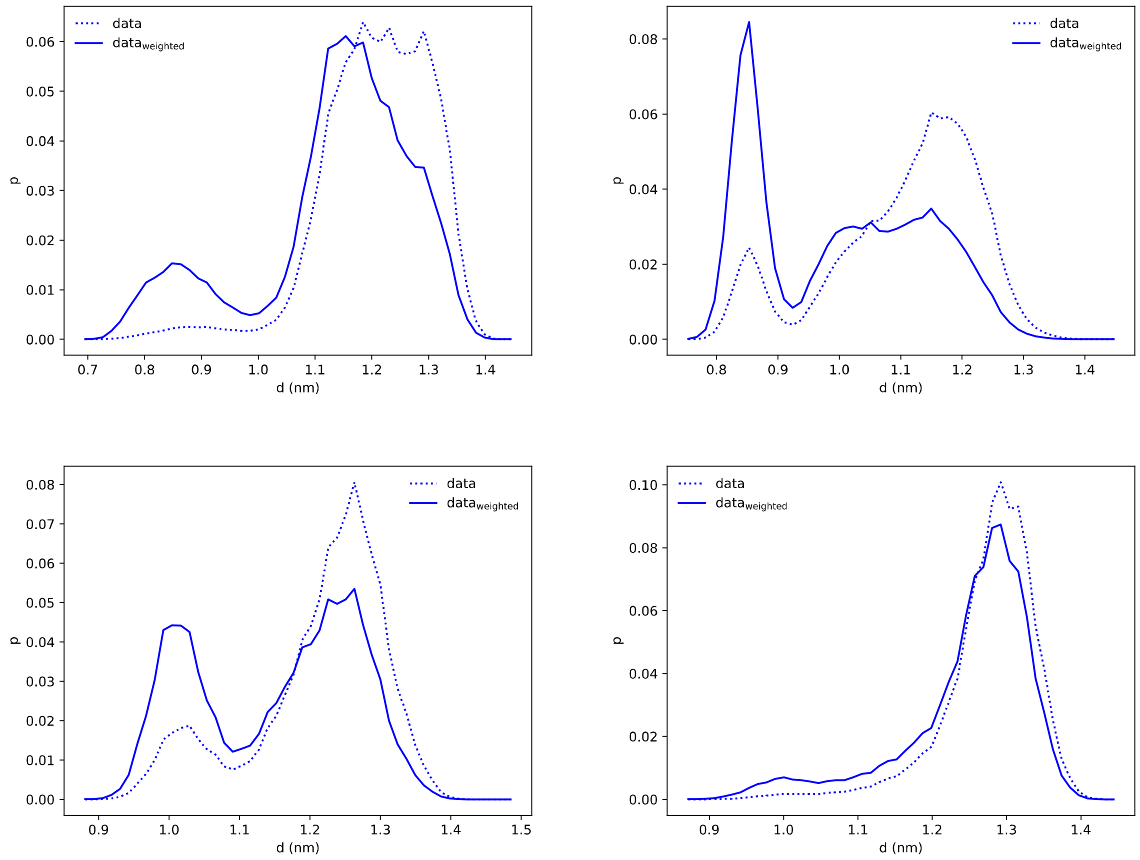

Figure S35: r^{-6} weighted and unweighted distance distributions between 1 and 10a. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

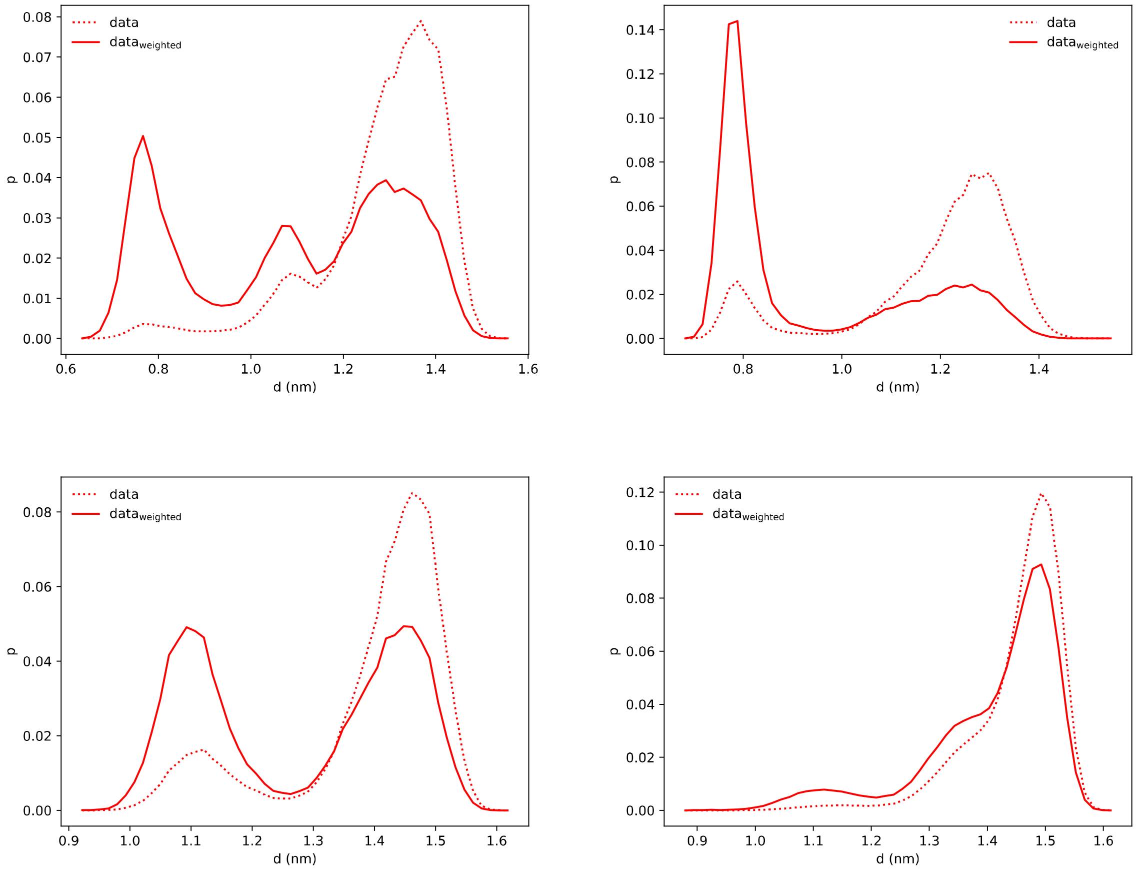

Figure S36: r^{-6} weighted and unweighted distance distributions between 2 and 10a. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

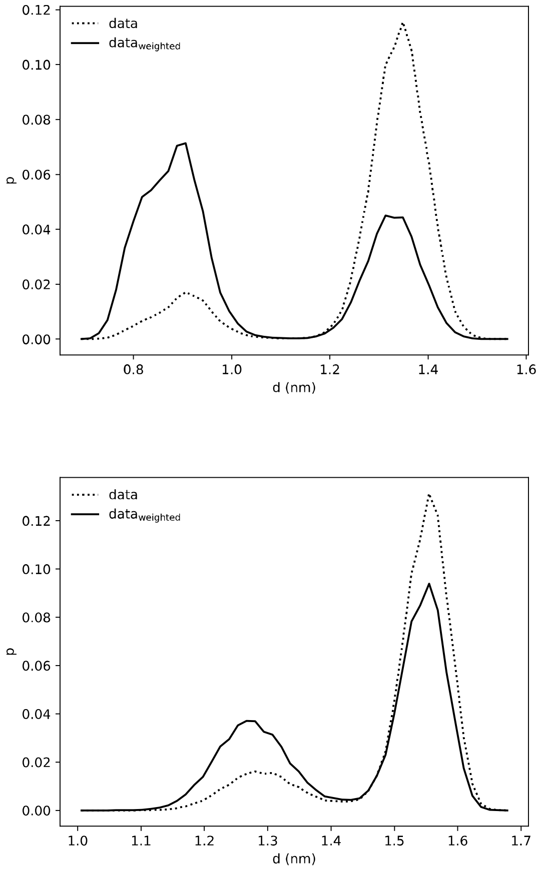

Figure S37: r^{-6} weighted and unweighted distance distributions between 3 and 10a. Distances for structure motif I are shown on the top and for II on the bottom.

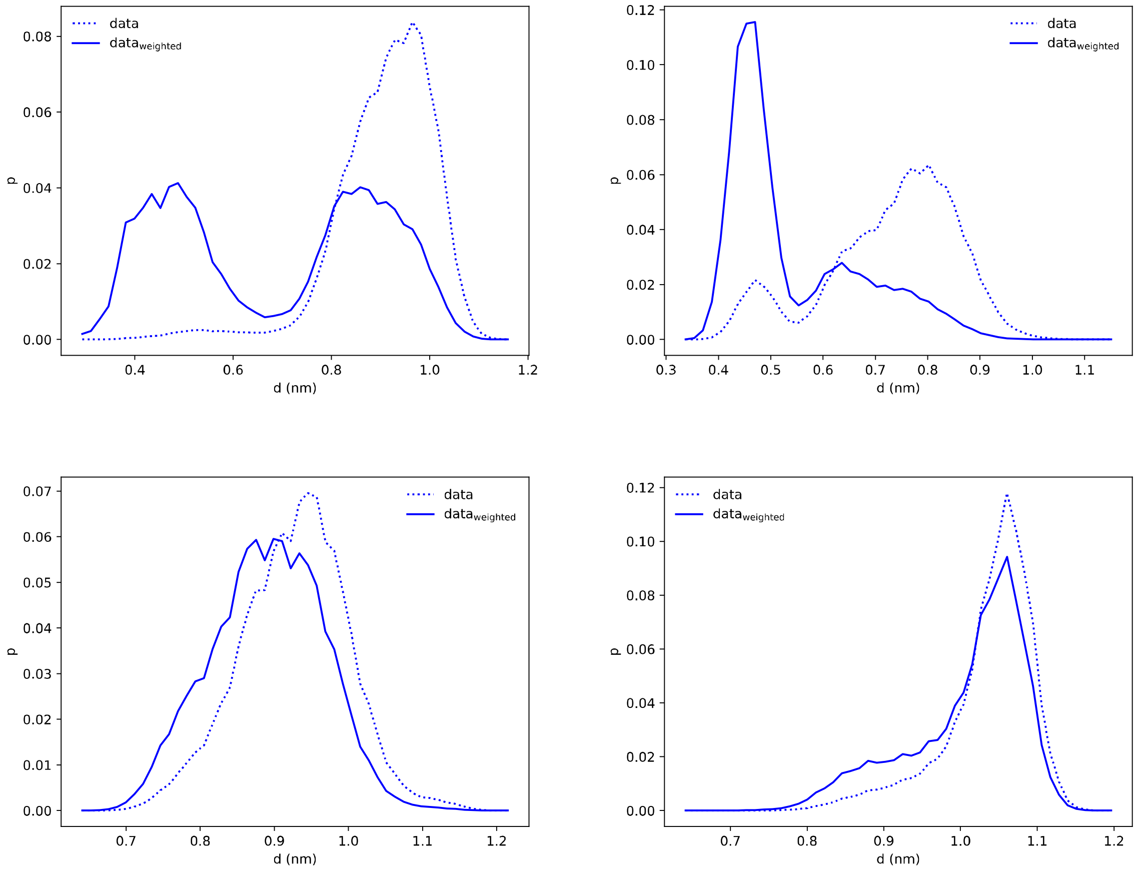

Figure S38: r^{-6} weighted and unweighted distance distributions between 1 and 11a. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

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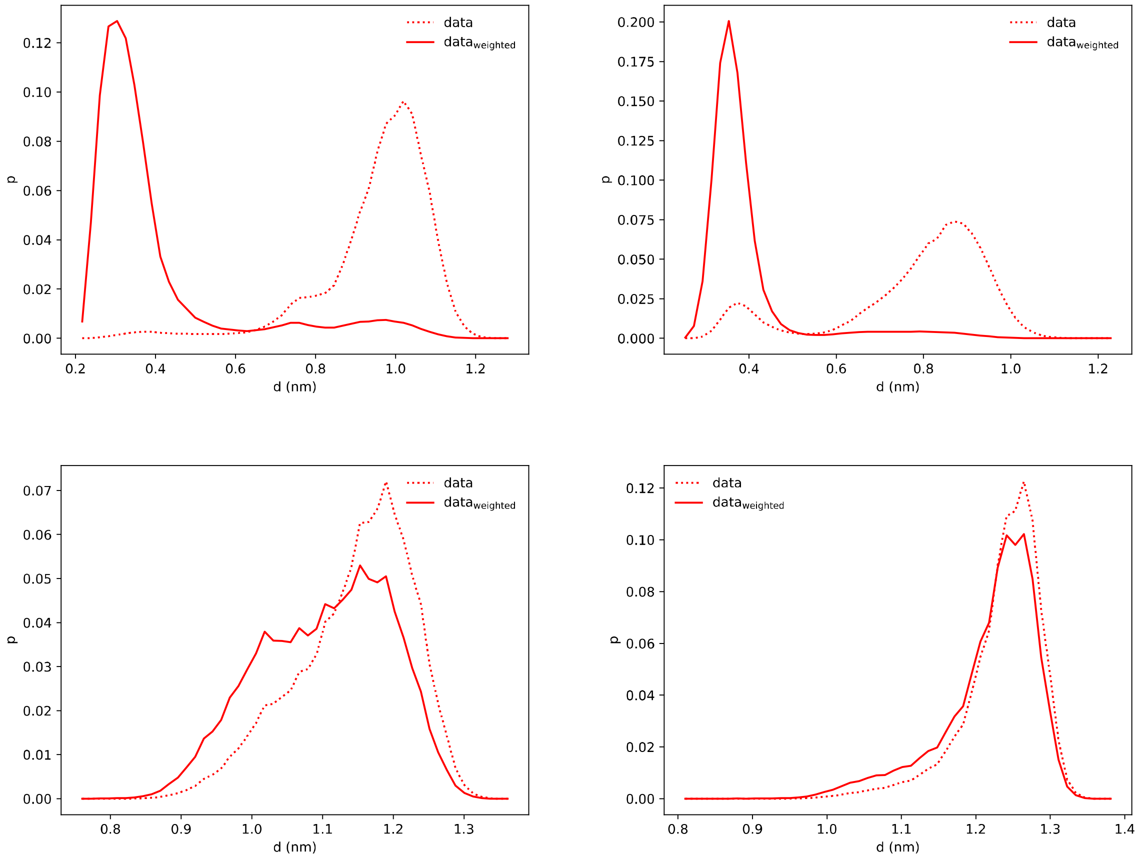

Figure S39: r^{-6} weighted and unweighted distance distributions between 2 and 11a. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

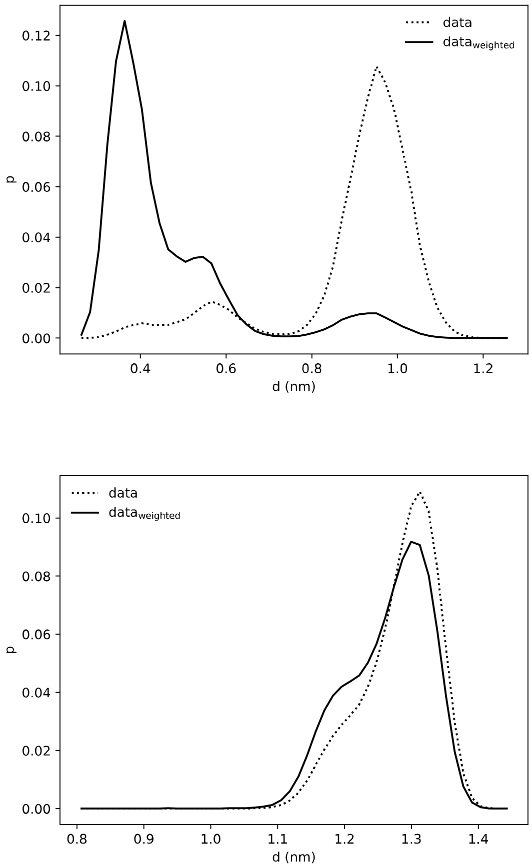

Figure S40: r^{-6} weighted and unweighted distance distributions between 3 and 11a. Distances for structure motif I are shown on the top and for II on the bottom.

Distance Distributions related to the NOE-Contacts of the “non-a” BINOL Side

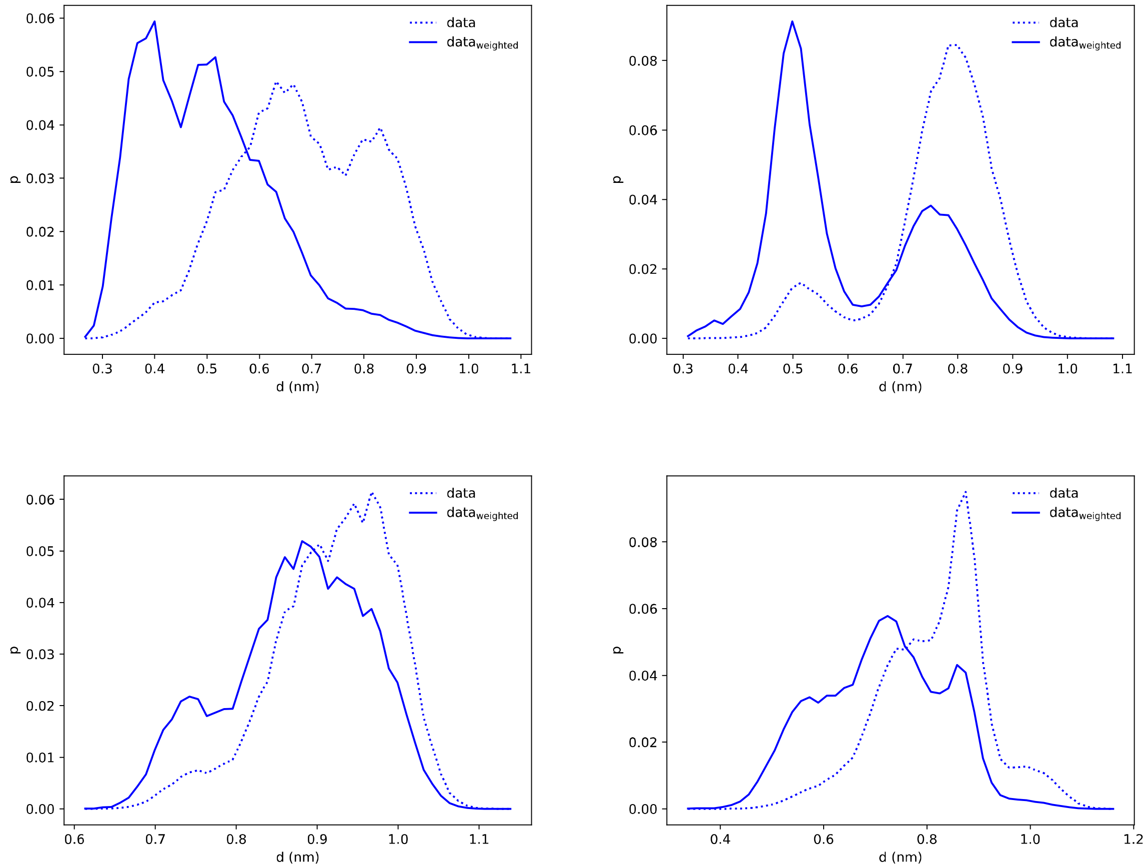

Figure S41: r^{-6} weighted and unweighted distance distributions between 1 and 8. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

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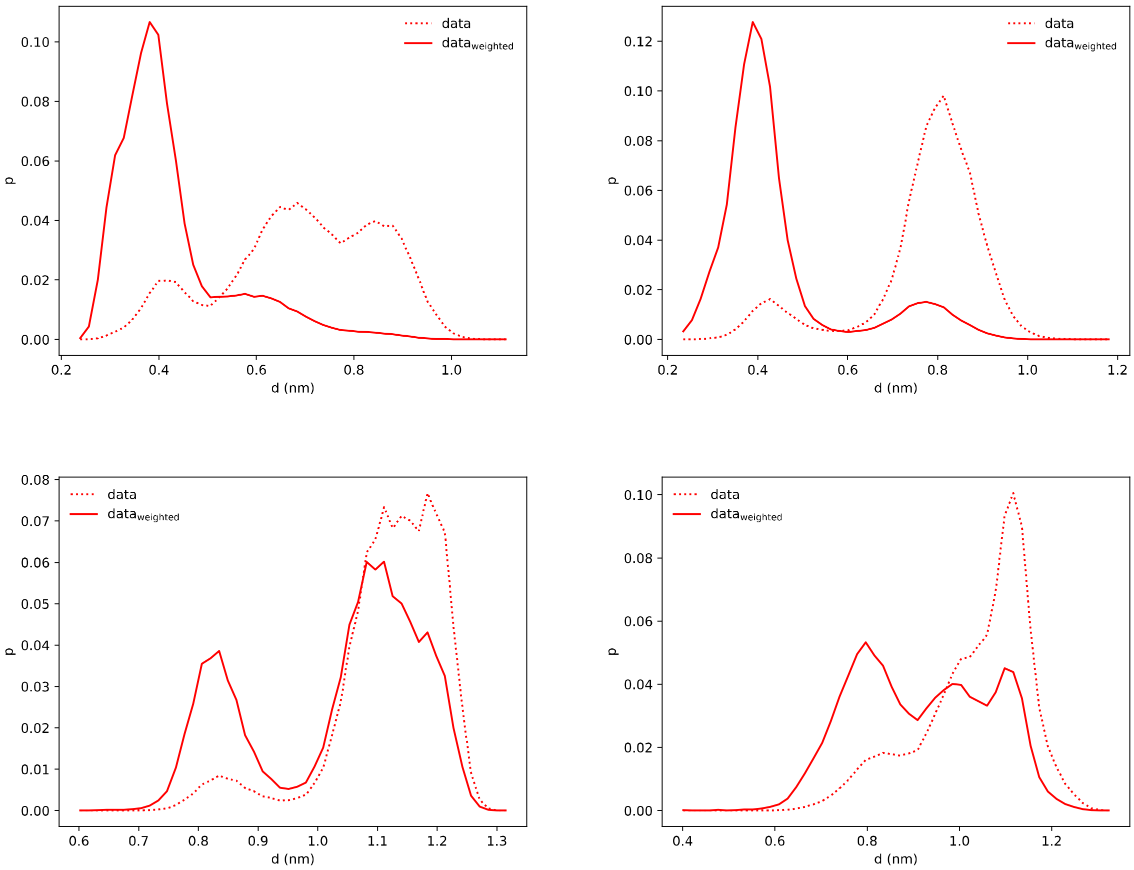

Figure S42: r^{-6} weighted and unweighted distance distributions between 2 and 8. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

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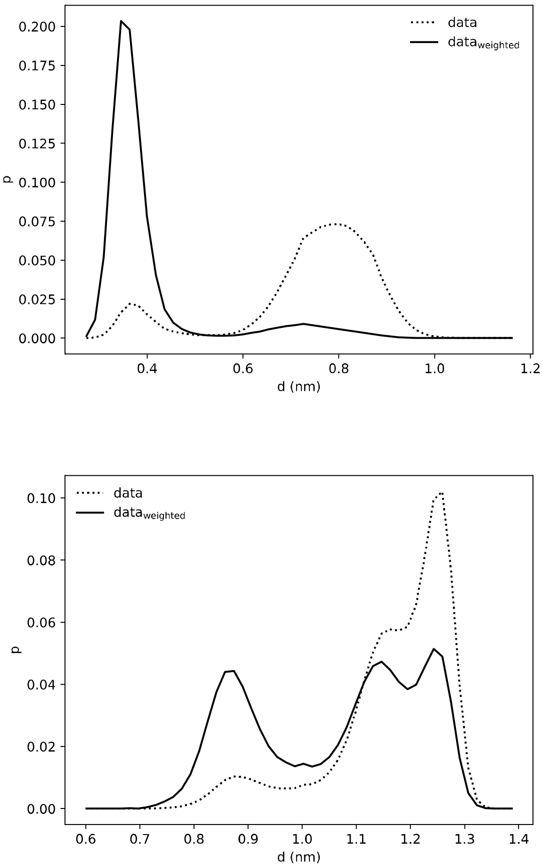


Figure S43: r^{-6} weighted and unweighted distance distributions between 3 and 8. Distances for structure motif I are shown on the top and for II on the bottom.

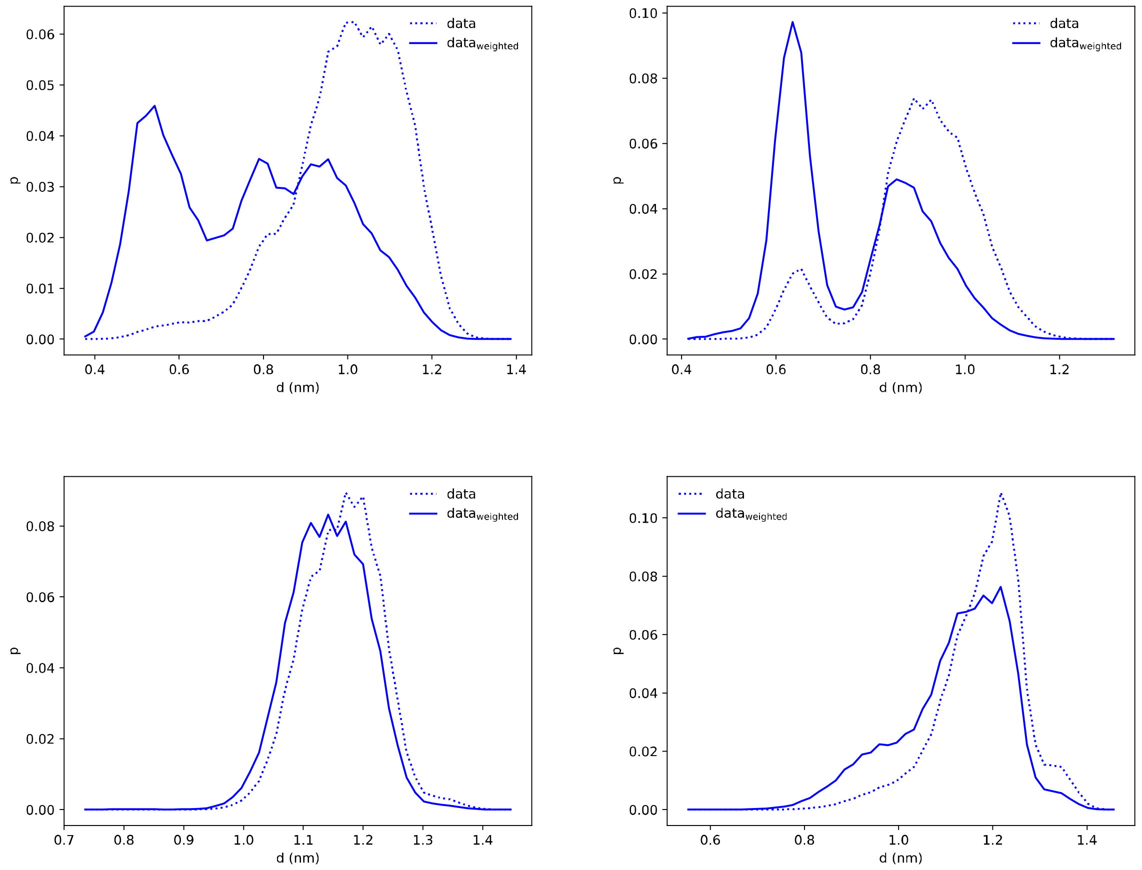


Figure S44: r^{-6} weighted and unweighted distance distributions between 1 and 9. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

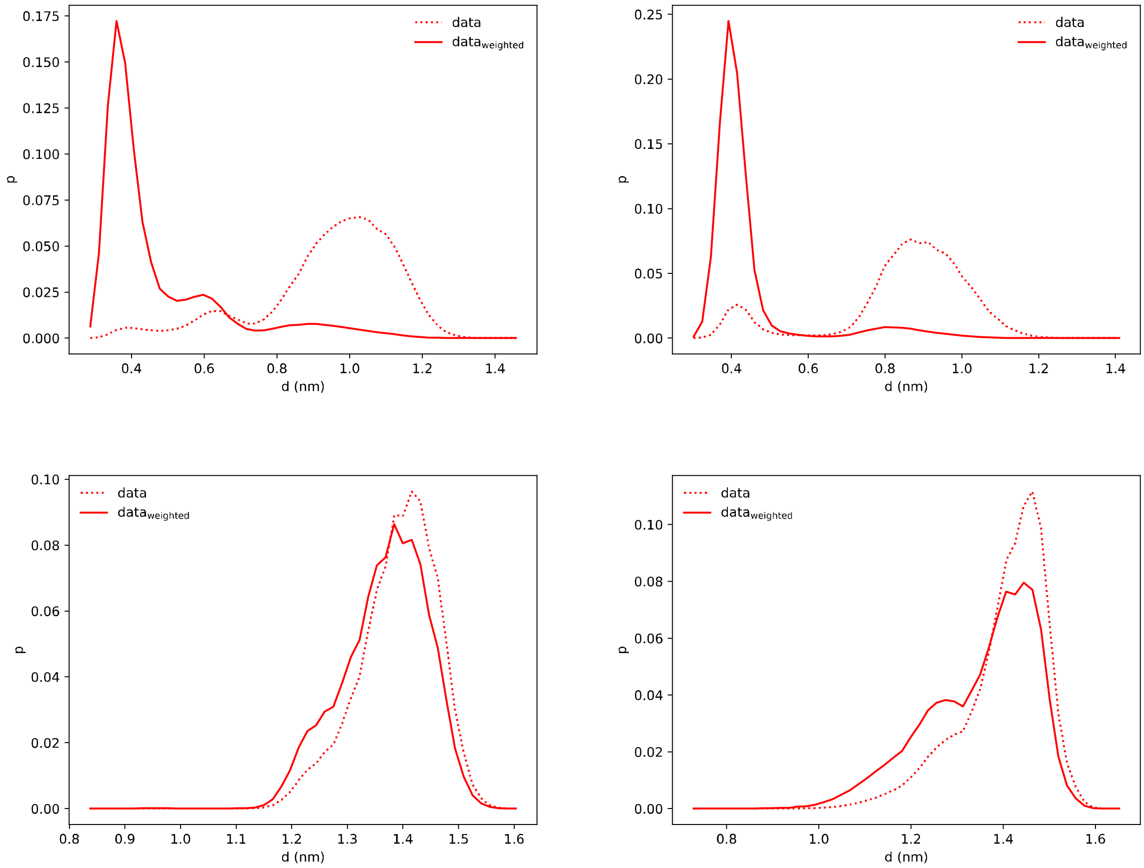
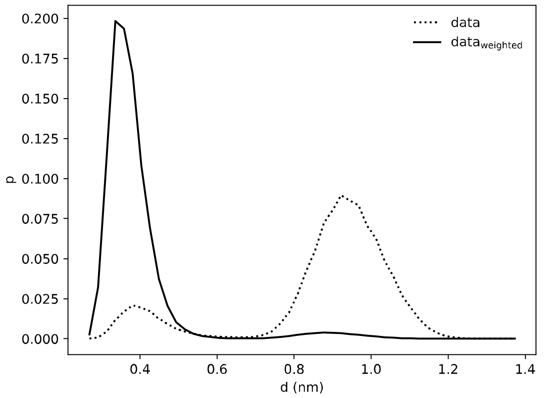


Figure S45: r^{-6} weighted and unweighted distance distributions between 2 and 9. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.



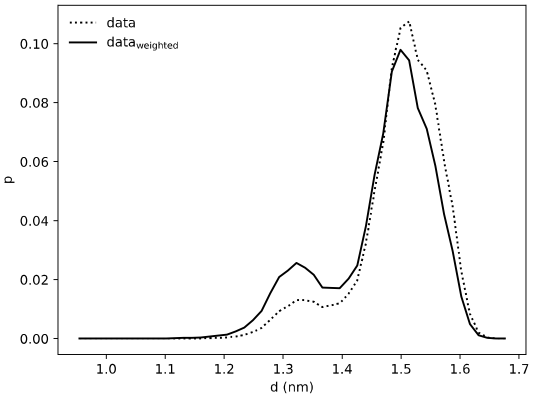


Figure S46: r^{-6} weighted and unweighted distance distributions between 3 and 9. Distances for structure motif I are shown on the top and for II on the bottom.

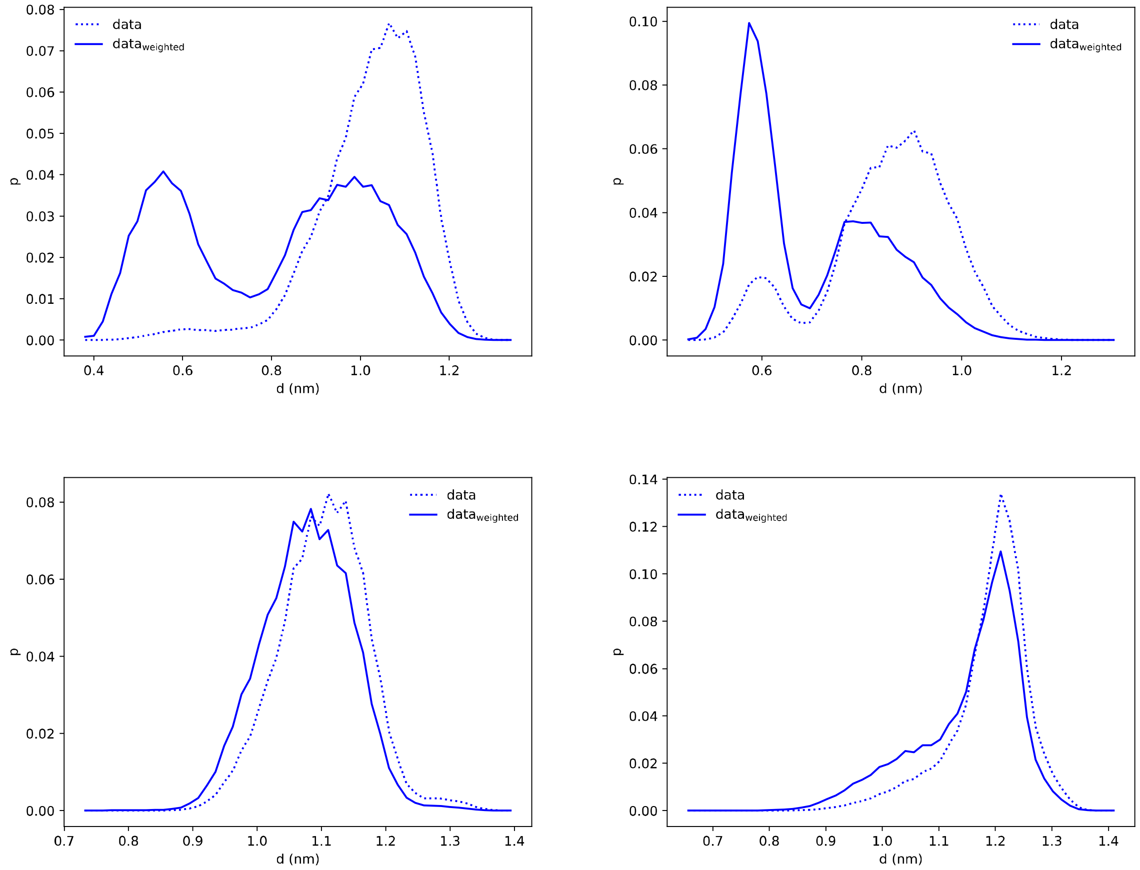


Figure S47: r^{-6} weighted and unweighted distance distributions between 1 and 10. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

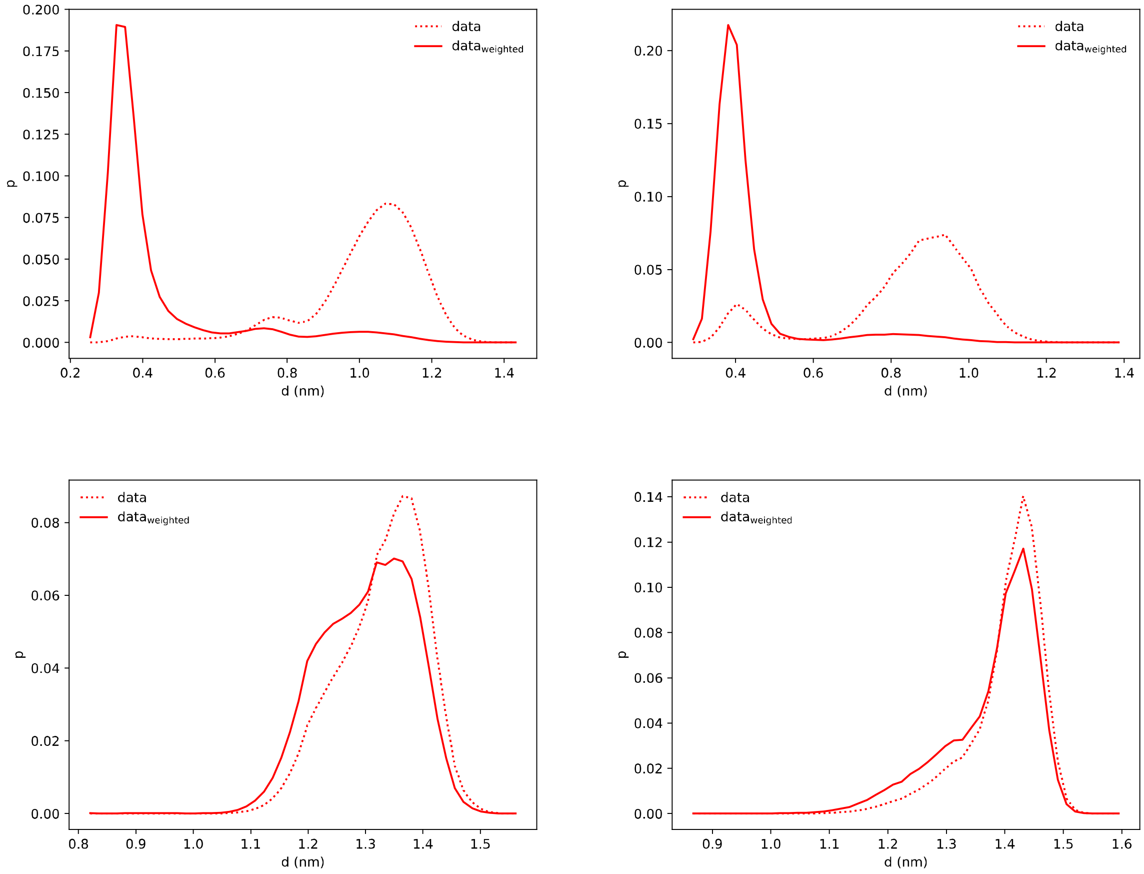
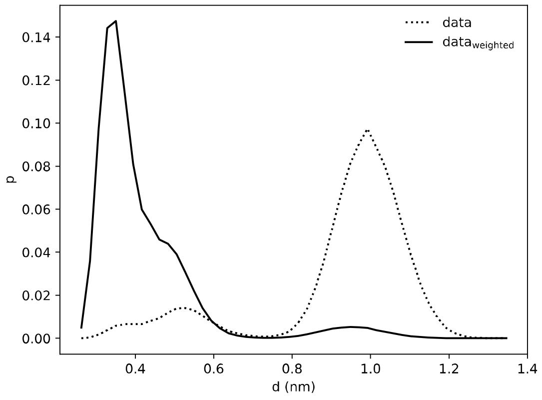


Figure S48: r^{-6} weighted and unweighted distance distributions between 2 and 10. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.



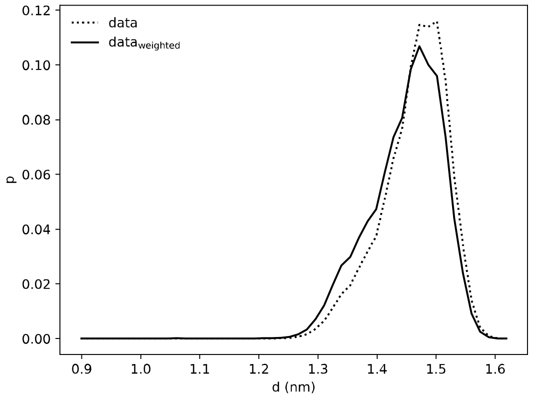


Figure S49: r^{-6} weighted and unweighted distance distributions between 3 and 10. Distances for structure motif I are shown on the top and for II on the bottom.

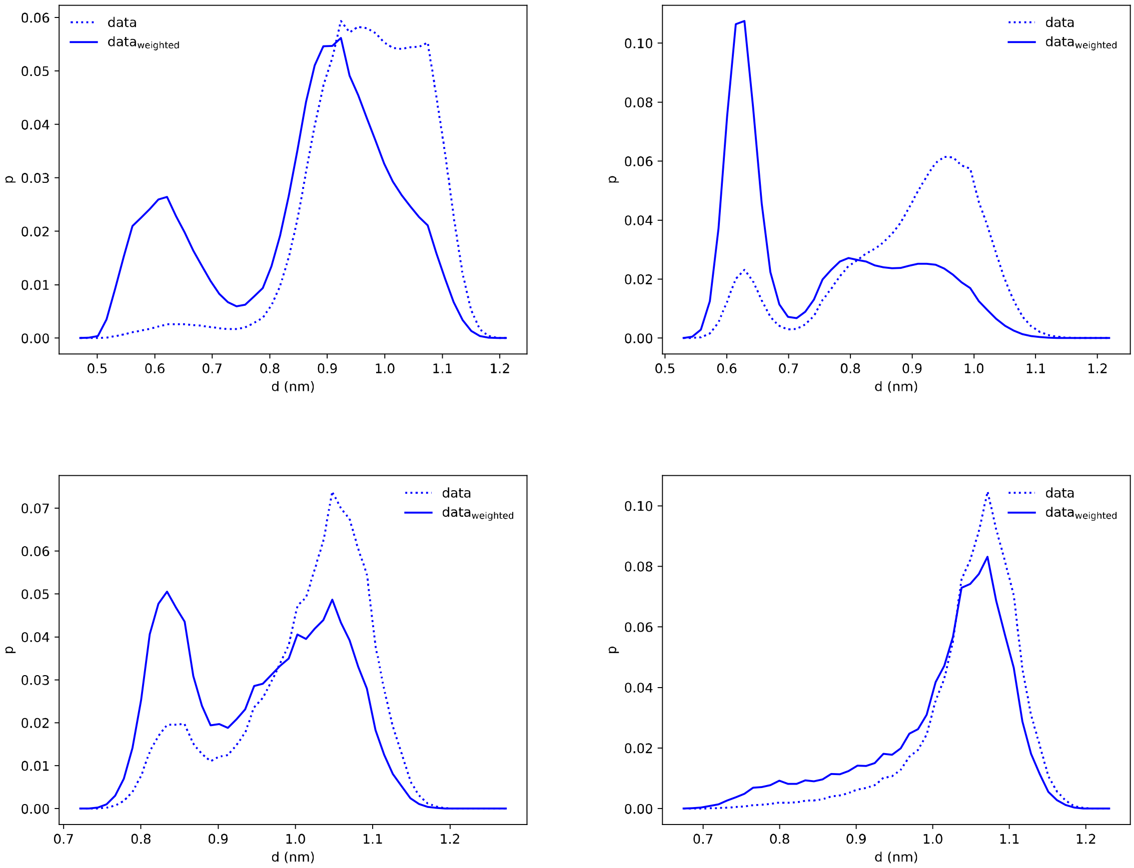


Figure S50: r^{-6} weighted and unweighted distance distributions between 1 and 11. As there are two possible hydrogen atoms corresponding to position 1, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.

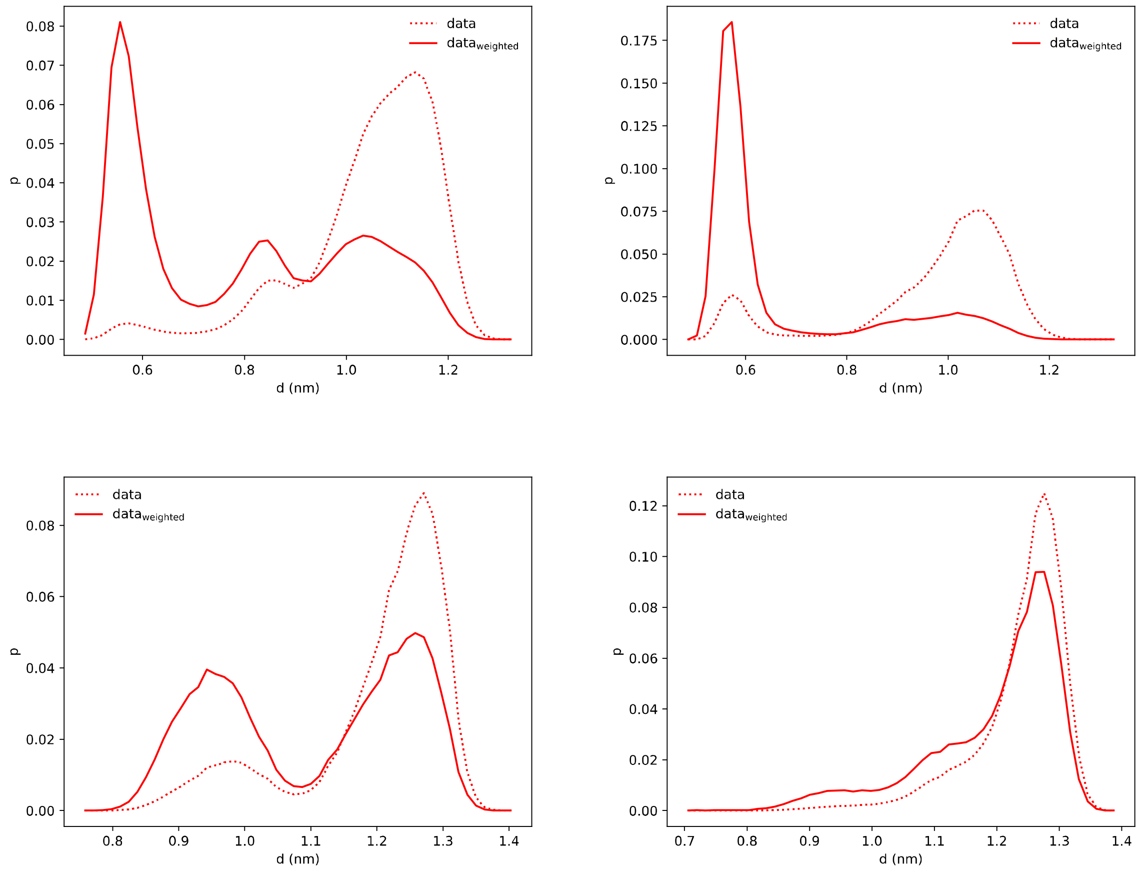
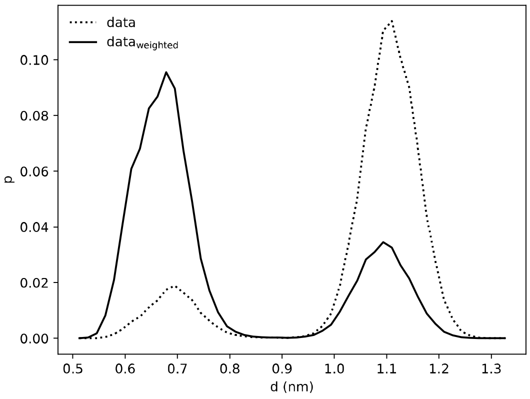


Figure S51: r^{-6} weighted and unweighted distance distributions between 2 and 11. As there are two possible hydrogen atoms corresponding to position 2, both are shown. Distances for structure motif I are shown on the top and for II on the bottom.



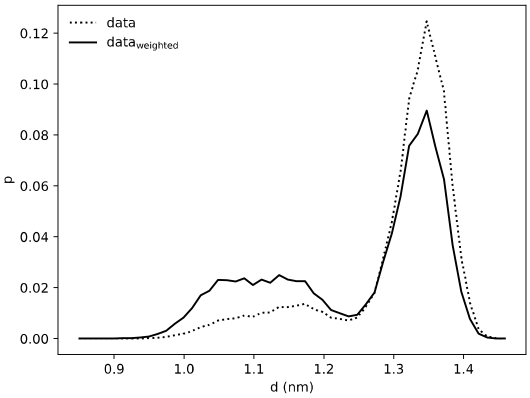


Figure S52: r^{-6} weighted and unweighted distance distributions between 3 and 11. Distances for structure motif I are shown on the top and for II on the bottom.

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HOE-Signals (involving CF_3 groups)

Differentiation between Iminium Positions 1 and 5

As it couldn't be decided based on the spectra whether the HOE-contacts to **A**, **B** and **C** on the NTPA-molecule were due to the iminium positions **1** or **5**, this is analyzed for the simulation results of structure **I**.

An analysis for structure motif **II** is not done because motif II was already excluded based on the previously shown NOE contacts.

No unambiguous assignment for the NOE-signal to **ANTPA** is possible: It either arises from position **1** or **5**. (see Figures S53, S54)

The same holds for the contact to **BNTPA.** (see Figures S55, S56)

However, it seems that the contact to **CNTPA** is more likely to stem from the **5** position on the imine. (see Figures S57, S58)

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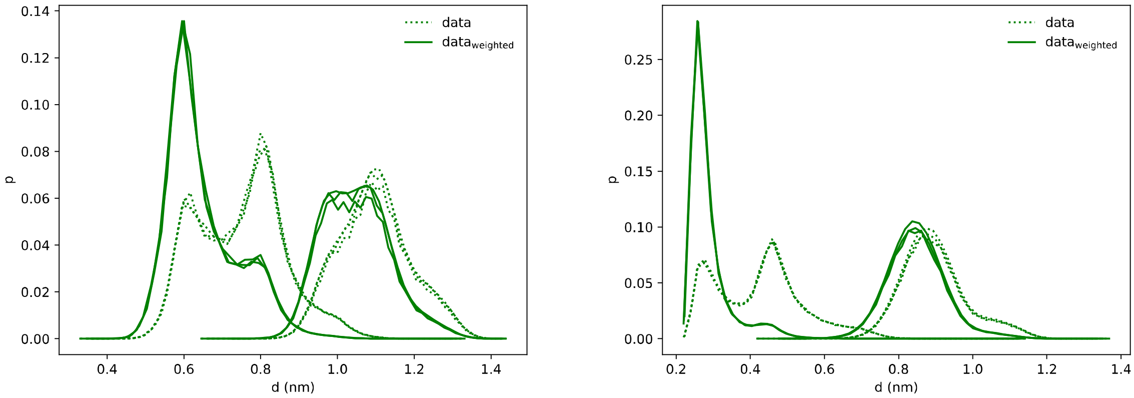

Figure S53: Distance distributions between iminium position 1 and the F atoms of the A (CF_3) group.

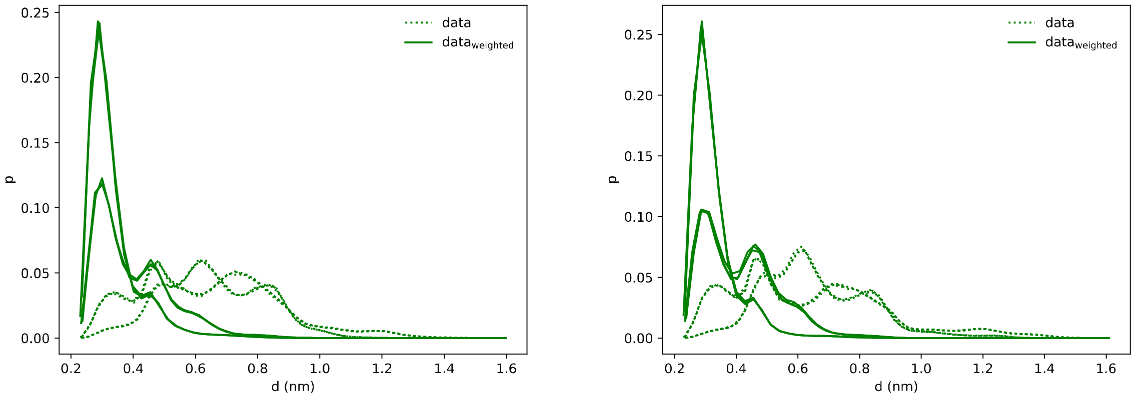

Figure S54: Distance distributions between iminium position 5 and the F atoms of the A (CF_3) group.

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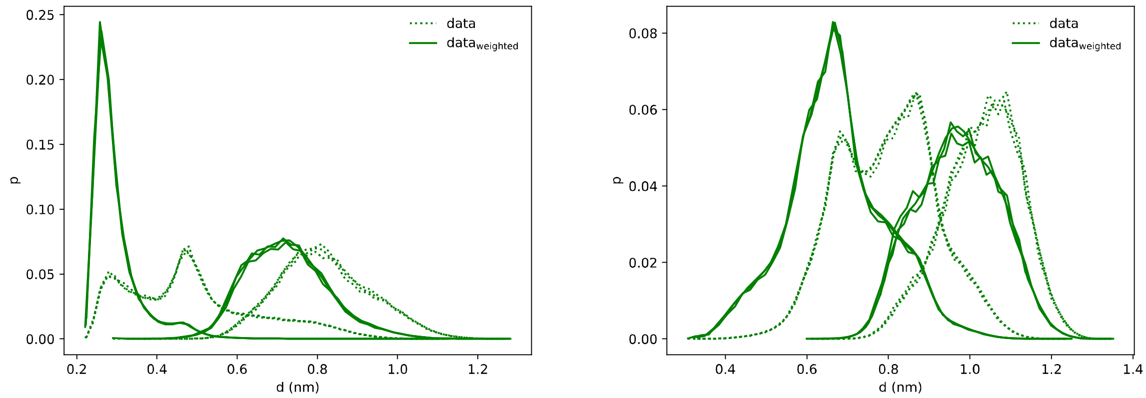

Figure S55: Distance distributions between iminium position 1 and the F atoms of the B (CF3) group.

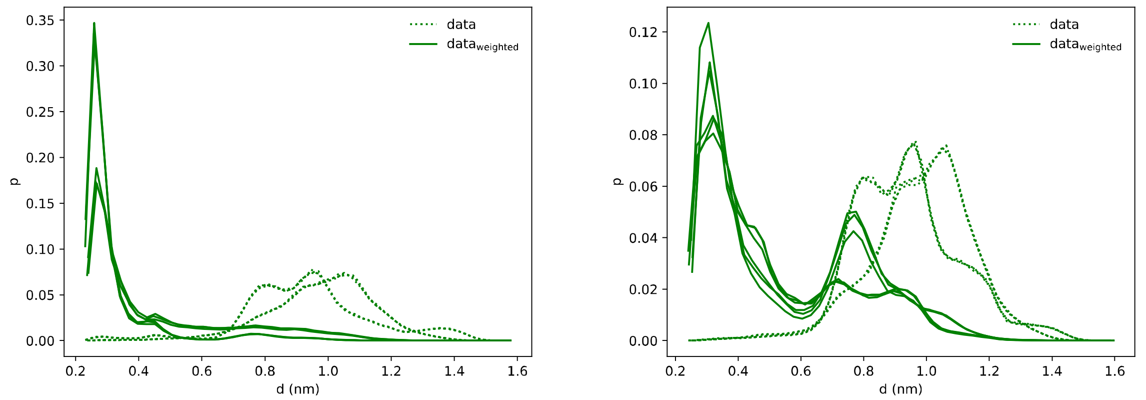

Figure S56: Distance distributions between iminium position 5 and the F atoms of the B (CF3) group.

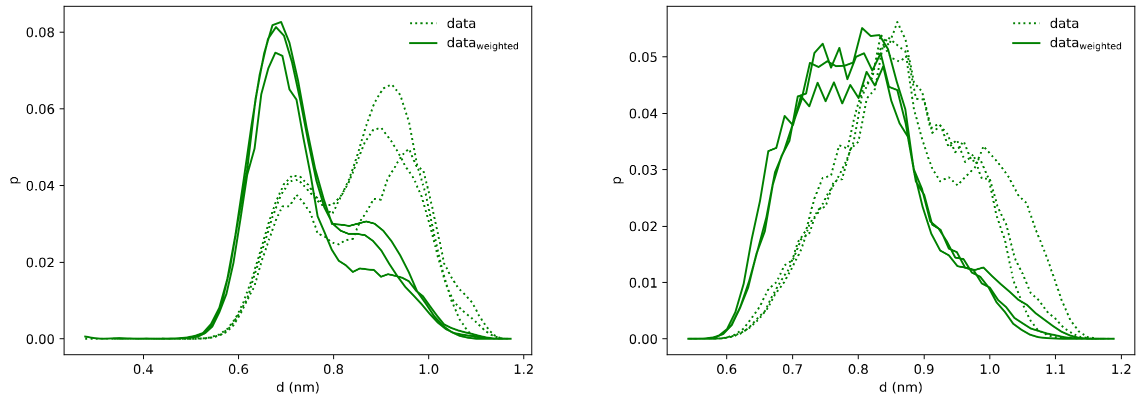

Figure S57: Distance distributions between iminium position 1 and the F atoms of the C (CF3) group.

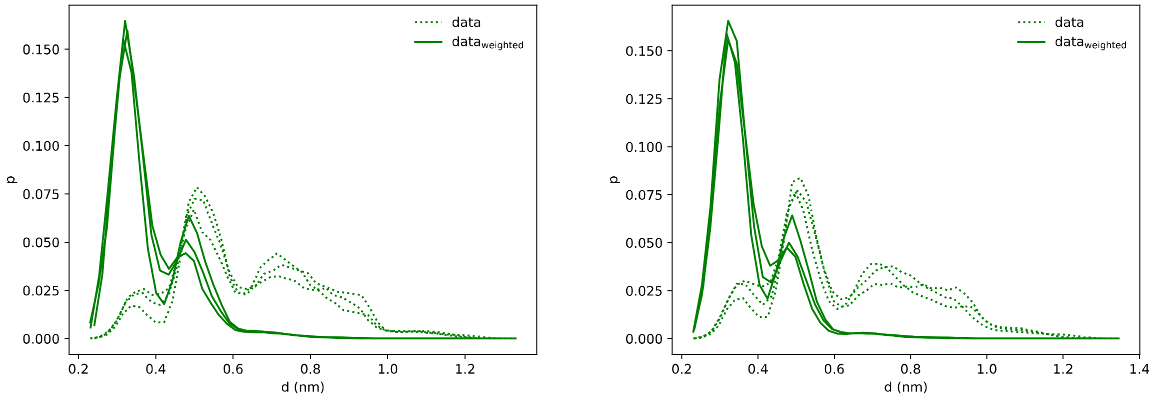

Figure S58: Distance distributions between iminium position 5 and the F atoms of the C (CF3) group.

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Distances to the Iminium Methoxy and Methyl Groups

The following figures only show the distance distributions for one of the equivalent H-atoms, because the distributions are representative. For all the distances can correspond to measurable contacts observable in the NMR spectra.

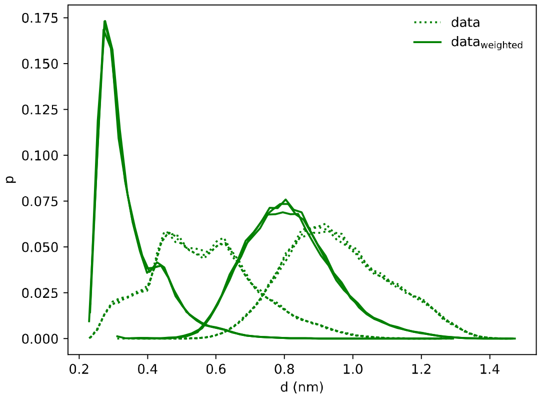

Figure S59: r^{-6} weighted and unweighted distance distributions between Me and the CF_3 group A. The individual lines shown are for each of the three F atoms of the A group.

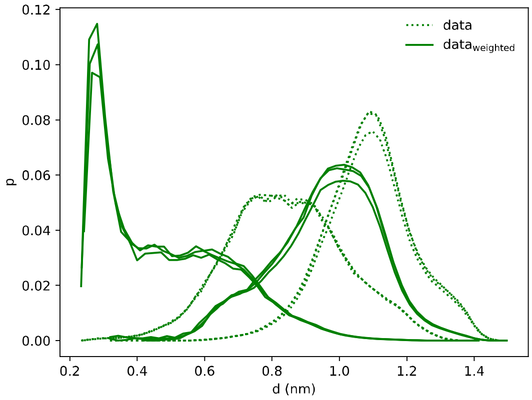

Figure S60: r^{-6} weighted and unweighted distance distributions between Me and the CF_3 group B. The individual lines shown are for each of the three F atoms of the B group.

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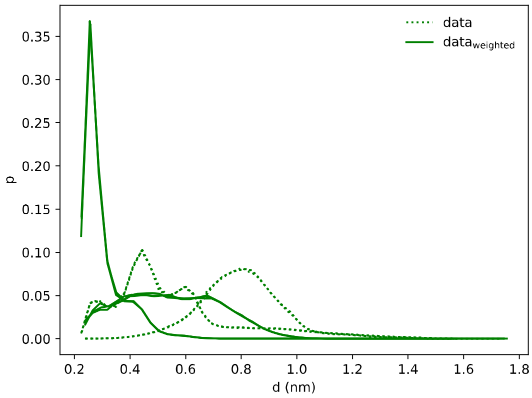

Figure S61: r^{-6} weighted and unweighted distance distributions between 6 and the CF_3 group A. The individual lines shown are for each of the three F atoms of the A group.

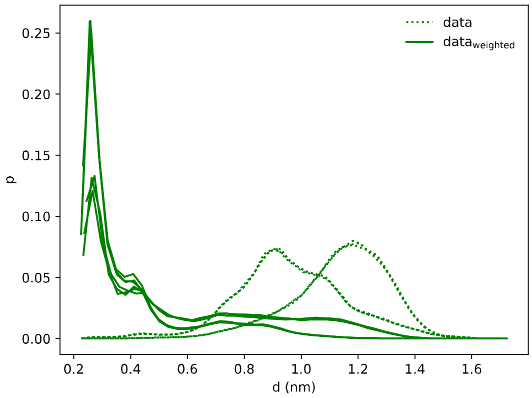

Figure S62: r^{-6} weighted and unweighted distance distributions between 6 and the CF_3 group B. The individual lines shown are for each of the three F atoms of the B group.

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Multiple Conformers of Interest correspond to structure motif I

The distance distributions frequently contained more than a single distribution for the system of interest **I**. Therefore, differences in the conformation of the cluster are shown below in Figure S63. For differentiation distances, which correspond to NOEs in one case but not in the second case can be used: e.g. Figure S65 depicts the time resolved distance between the iminium position **3** and the position **10**. The exchange on the 1.6 µs timescale is a rare event, so no quantitative population assignment is possible just from the simulation data. The times suggest a possible fast exchange on the NMR-timescale, so that a distinction between both species is probably unnecessary. Still, it seems that the right conformer of Figure S63 will be the one detected by its NOE-signals in the NMR and the left conformer (with a 3-10 distance of around 1 nm) should not show NOE signals. An additional DFT geometry optimization of the complex without explicit solvent (details see Methods above), starting from the solvated species (left side in Figure S63) obtained from the MD-simulation converged to the conformation, which corresponds to the NOE signals. This hints at the fact, that the second form (which should not correspond to NOE signals) may result from the solvation.

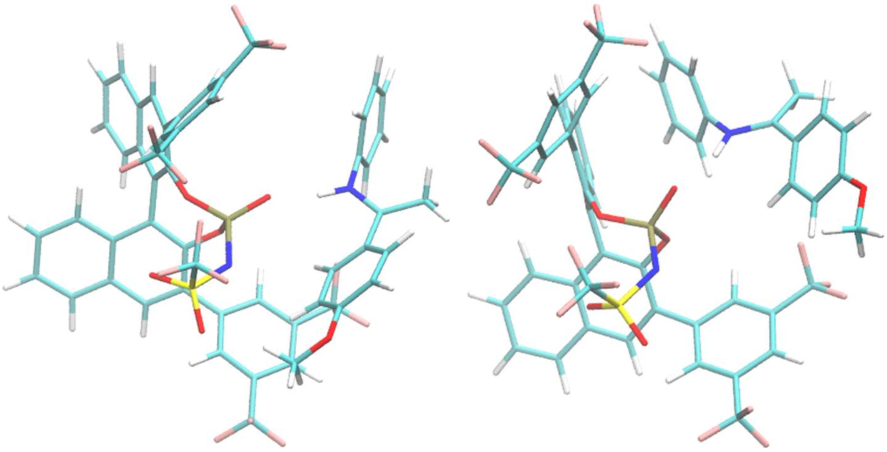

Figure S63: left: conformation with a 3-10 distance of around 1 *nm - should not show NOE-signals; right: conformation with a 3-10 distance of around* 0.5 *nm - NOE-signals can be expected*

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The H-bond orientation towards the NTPA oxygen atom

Complex **I** was identified as the most probable one. Considering the charge situation with a N^-, it seems unintuitive that a H-bond situation seems to occur on the phosphate oxygen. For such systems it is usually assumed that the H-bond occurs via the charged nitrogen atom. In the simulations of **I** closer contacts between the iminium hydrogen and the nitrogen anion had been expected - rather than the oxygen atom.

This stands in apparent opposition to the simulation results and is also surprising considering the charge distribution between oxygen and nitrogen. Figure S64 shows that in the simulations the distance distribution is inverted. The time resolved distances are given in Figure S66. A comparison with the time resolved distances of Figure S65 allows an assignment to the substructures of motif **I**. An additional (DFT) geometry optimization of the complex based on the structures obtained from MD did not deviate from the close oxygen distance compared to the nitrogen distance. In addition, the Mayer bond orders (given below with the optimized structure) resemble the ones of the geometry optimization of the isolated anion (given in Figure S27). While this is clearly no proof, these facts – together with the corresponding NMR evidence – strongly hints at a conformation, which looks like an oxygen-based hydrogen bond in the ground state. This casts doubt on possible transition states via an N-based hydrogen bond. Still, even if the TS occurs via N, it will mean that the TS occurs via a rare event, which is not favored by a pre-organization of the H-bond. This clearly shows that further investigations into the nature and catalytic mechanisms of NTPA systems are required.

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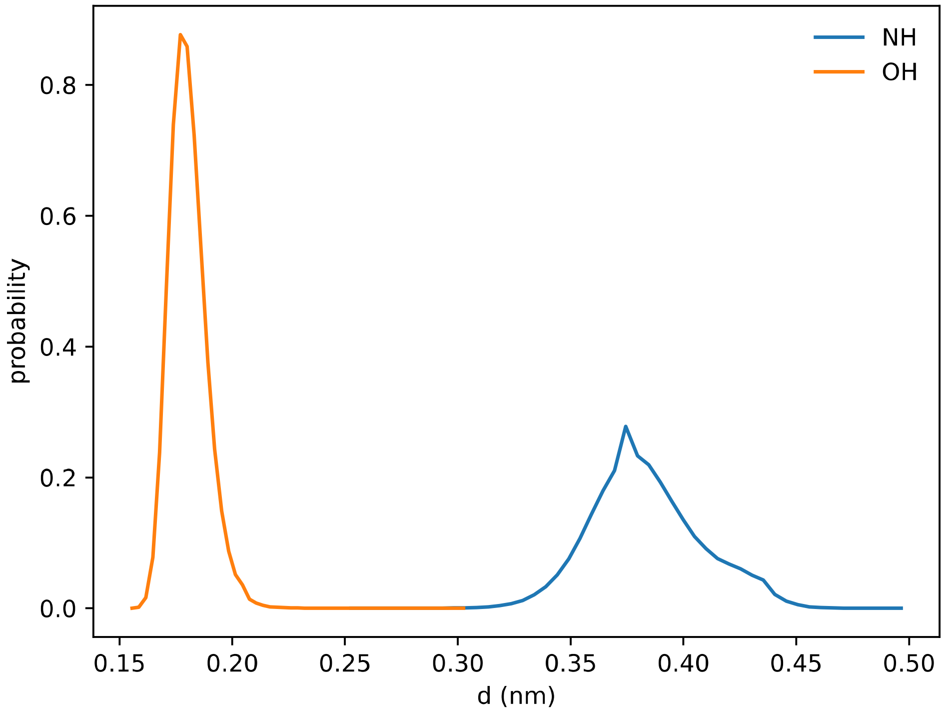

Figure S64: The distance distribution between groups and the iminium H-binding hydrogen atom suggests H-bonding via the oxygen atom rather than the N^-.

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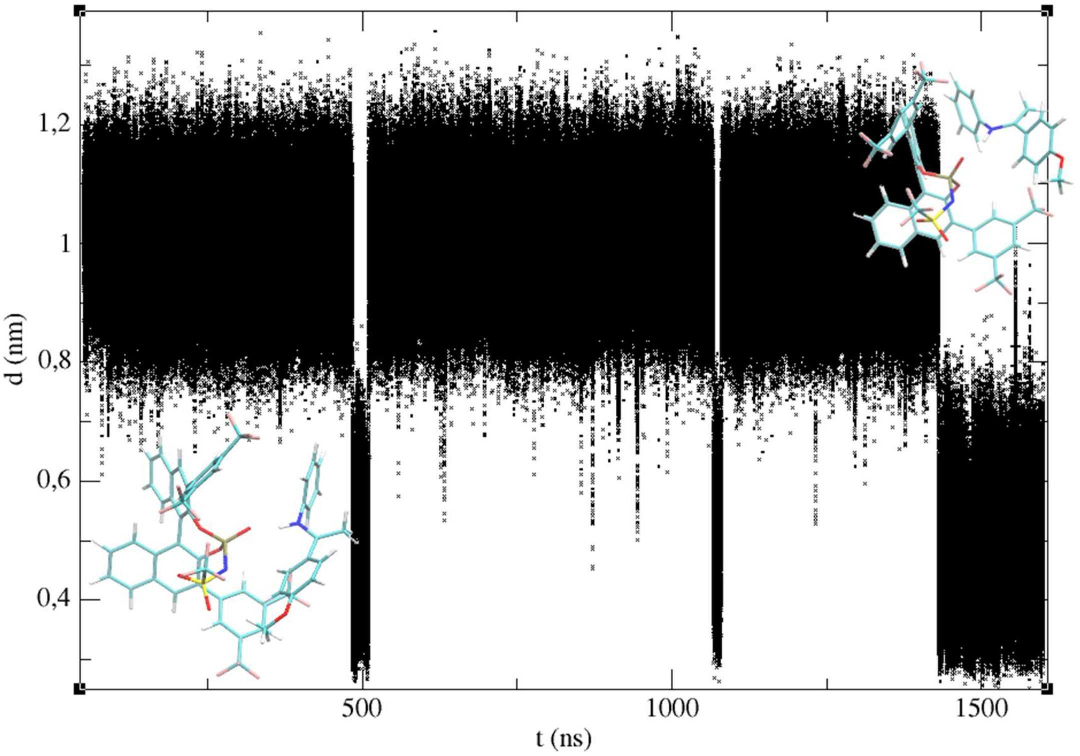

Figure S65: The distance between atoms, which correspond to an observed NOE contact can be used to differentiate species with and without a possible NOE signal provided the change in distances are sufficiently large. This is the case for example for the iminium position 3 and the position 10. It allows for a clear distinction between two different conformers. The exchange on the 1.6 *µs timescale is a rare event however (5 times for differently long periods), so no quantitative population assignment is possible. The times suggest a possible fast exchange on the NMR-timescale.*

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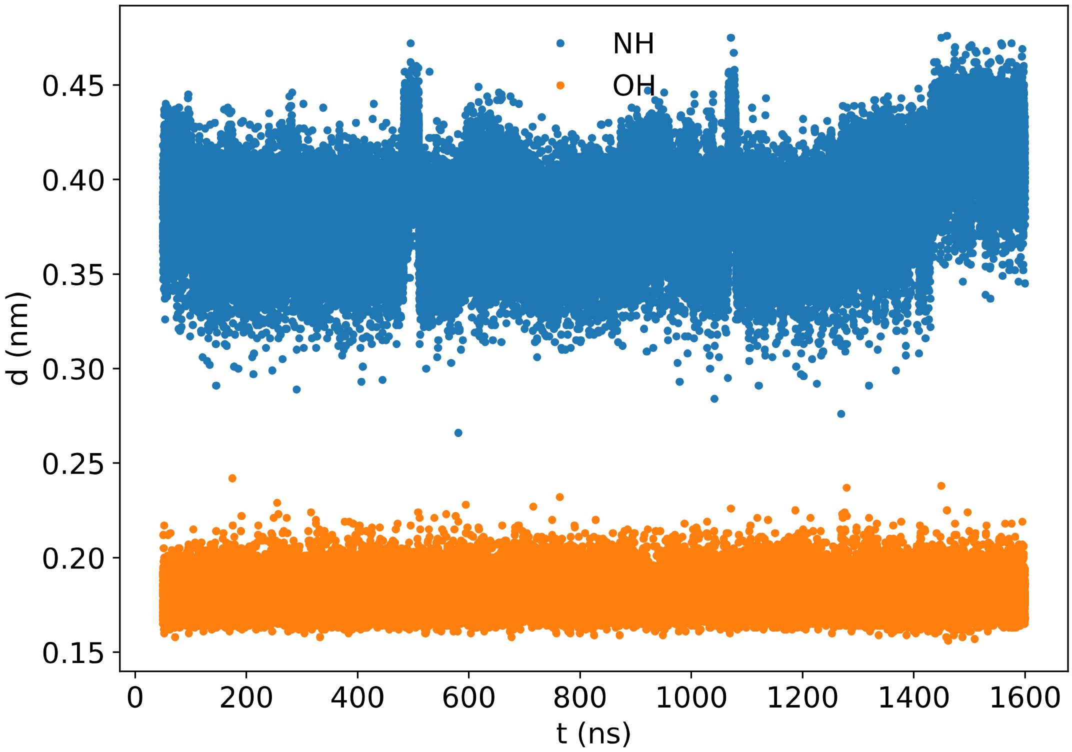

Figure S66: Time resolved distance between atoms on the NTPA (N/O) and the iminium H-binding hydrogen atom

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Potentials of mean force (PMFs) from umbrella sampling along the NTPA N$^-$ E-iminium H$^+$ distance suggests the “NTPA oxygen-based” H-bond as the preferred position

Figure S68 and *Figure S67* show the change in free energy for the process of umbrella pulling of the iminium H$^+$ towards the NTPA N$^-$ starting from the oxygen-based H-bond situation at around 0.38 nm.

It becomes clear that a second minimum exists closer towards the NTPA N$^-$. However, this is not well sampled in the short 180K simulation and long times (µs) are needed to assume convergence for the 300K simulations.

While the actual value of the difference between the most stable (O centered) and the second minimum (between O and N$^-$, closer to N$^-$) will not be exact due to the assumption for the NTPA group in the forcefield, a qualitative agreement can be expected: that means with the thermal energy at 180K in the NMR the global minimum should be mainly populated, which supports the experimental results.

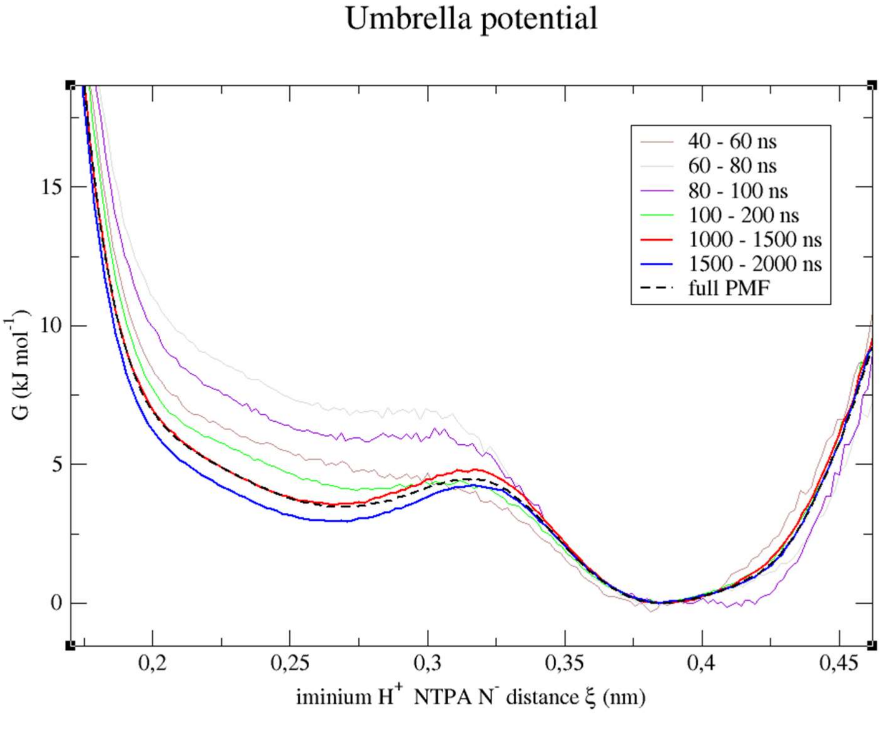

Figure S67: The 300K PMF shows a deeper minimum in the vicinity of the N$^-$ than the 180K simulation. PMFs of the corresponding sub-trajectories reveal that this is probably due to

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undersampling of the 180K PMF, and also occurs if only brief sub-trajectories are taken into account. If sufficiently long simulation times are taken into account the estimate of the PMF does (red, blue and dotted black curve) not change significantly.

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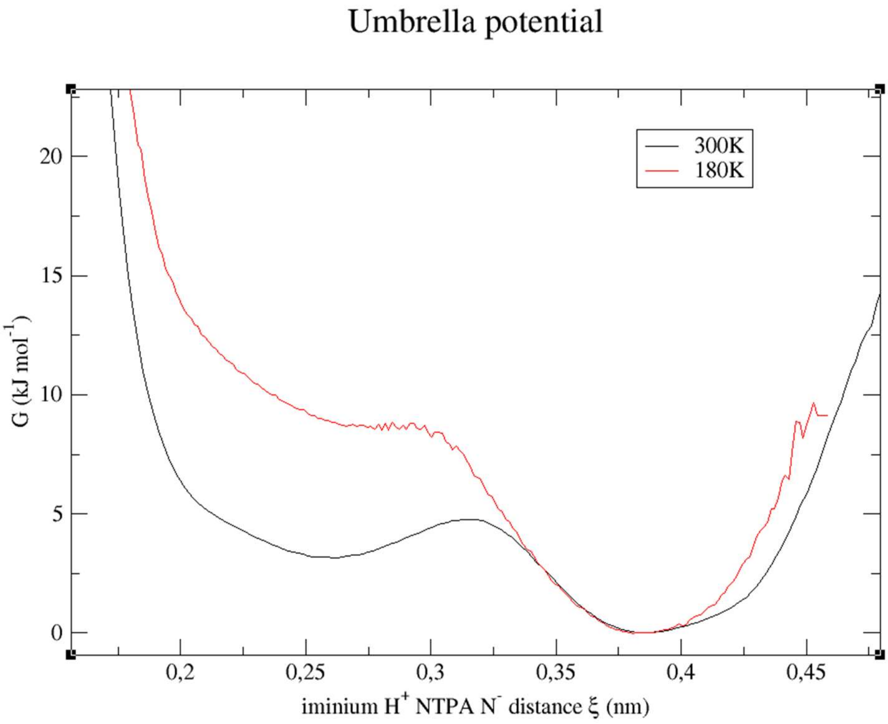

Figure S68: The PMFs for process of pulling the iminium H$^+$ towards the NTPA N$^-$ starting from the "oxygen-bound" H-bond situation (minimum around 0.38nm), reveals a second possible minimum for the simulation at 300K (or plateau in the 180K control simulation, which was not fully converged but does not include the many possible rotations of the 300K simulation). The minimum closer to N$^-$ (at around 0.2-0.3 nm) is less favored, suggesting the previously found structure with an oxygen based H-bond is prevalent in the system.

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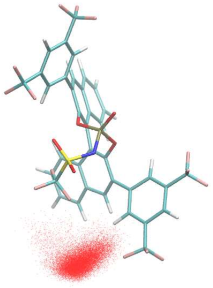	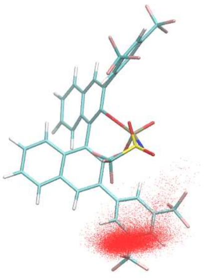	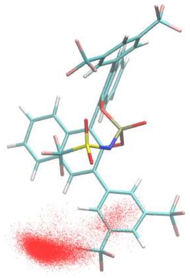	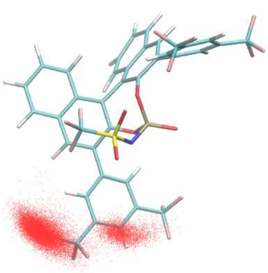
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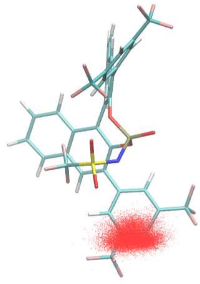	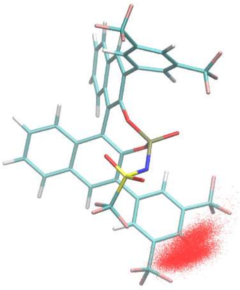	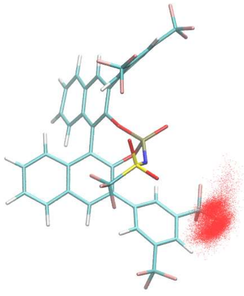	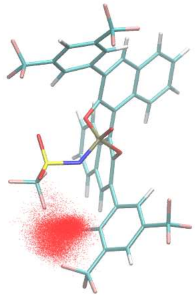
0.27	0.32	0.37	0.42

Figure S69: Overlay of 20000 subsequent MD-snapshots at 180K of the iminium methoxy oxygen (red points) relative to its position of the NTPA molecule (first frame shown: frames are rotated+translated to fit the NTPA molecule). The iminium's position is not changing much during the simulation windows.

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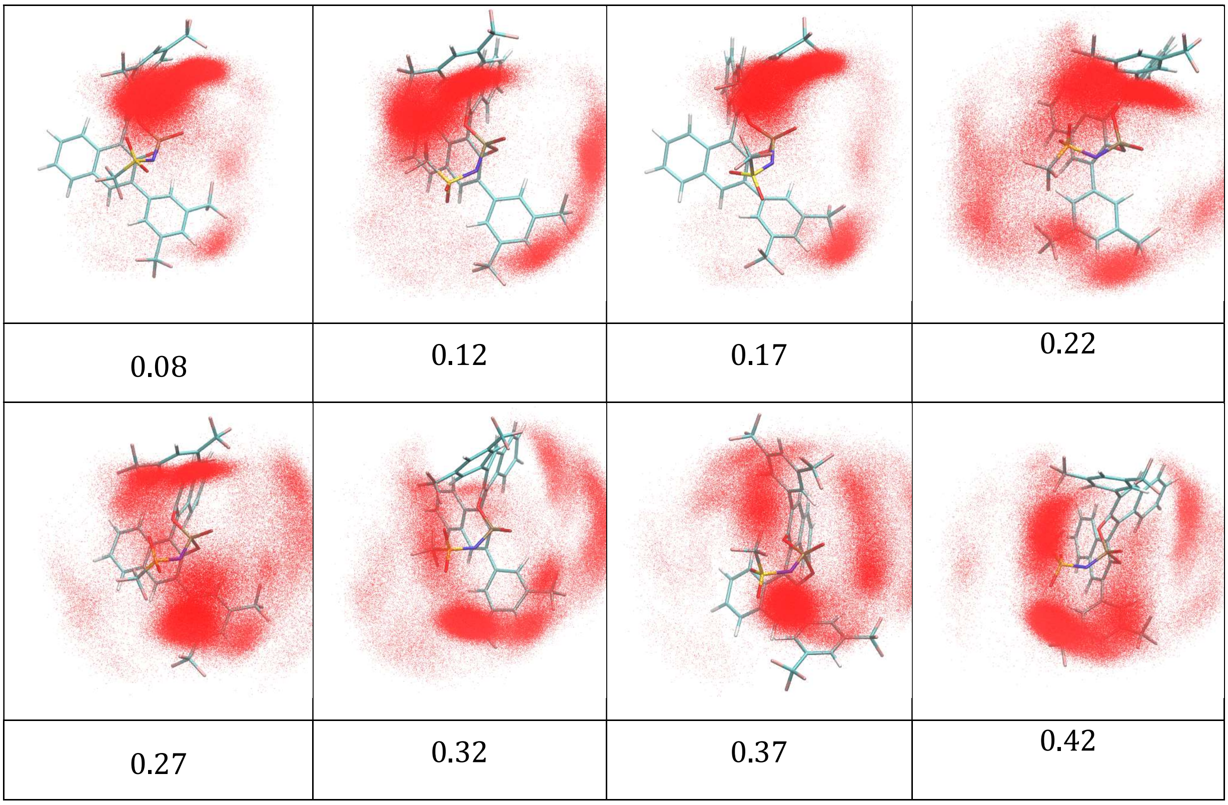

0.08 0.12 0.17 0.22

0.27 0.32 0.37 0.42

Figure S70: Overlay of the first 200000 subsequent MD-snapshots at 300K of the iminium methoxy oxygen (red points) relative to its position of the NTPA molecule (first frame shown: frames are rotated+translated to fit the NTPA molecule). The iminium's position is clearly changing during the simulation windows: The deepening of the second minimum in the PMFs at around 0.2-0.3 nm is clearly connected to this process.

Forcefield parameters used for the MD-simulations

NTPA-anion

```
[ moleculetype ]
;name          nrexcl
 NTP           3

[ atoms ]
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   3  ne    1  NTP    N   3   -0.7417259377    14.01000
   4  os    1  NTP   O1   4   -0.4652712854    16.00000
   5  os    1  NTP   O2   5   -0.3038336509    16.00000
   6  cp    1  NTP    C   6   -0.2713862117    12.01000
   7  ca    1  NTP   C1   7    0.3851728678    12.01000
   8  cp    1  NTP   C2   8   -0.1209486910    12.01000
   9  ca    1  NTP   C3   9   -0.2692929487    12.01000
  10   ca   1  NTP   C4  10    0.0844331351    12.01000
  11   ca   1  NTP   C5  11   -0.2256462747    12.01000
  12   ca   1  NTP   C6  12   -0.1345093487    12.01000
  13   ca   1  NTP   C7  13   -0.1264692488    12.01000
  14   ca   1  NTP   C8  14   -0.3047518097    12.01000
  15   ca   1  NTP   C9  15    0.3681113917    12.01000
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  17   ca   1  NTP  C11  17    0.1536764988    12.01000
  18   cp   1  NTP  C12  18   -0.0531660126    12.01000
  19   ca   1  NTP  C13  19   -0.3569141602    12.01000
  20   ca   1  NTP  C14  20    0.2948932857    12.01000
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25  ca   1  NTP  C19  25   -0.0530868561    12.01000
26  cp   1  NTP  C20  26    0.2842854286    12.01000
27  cp   1  NTP  C21  27    0.2988807348    12.01000
28  sy   1  NTP   S  28    0.9467154126    32.06000
29   o   1  NTP   O3  29   -0.5921943706    16.00000
30   o   1  NTP   O4  30   -0.5688279615    16.00000
31  c3   1  NTP  C22  31    0.4100038100    12.01000
32   f   1  NTP   F  32   -0.1610135216    19.00000
33   f   1  NTP   F1  33   -0.1610135216    19.00000
34   f   1  NTP   F2  34   -0.1610135216    19.00000
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   62  ha    1  NTP   H1   62    0.1558360623     1.00800
   63  ha    1  NTP   H2   63    0.1411753796     1.00800
   64  ha    1  NTP   H3   64    0.1432679458     1.00800
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   66  ha    1  NTP   H5   66    0.1847317680     1.00800
   67  ha    1  NTP   H6   67    0.1681273015     1.00800
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;   ai     aj funct   r           k
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     1      3   1   1.6050e-01   3.6685e+05 ;     P - N
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```
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1    5  1   1.6147e-01   2.7665e+05 ;    P - O2
3   28  1   1.6723e-01   2.6535e+05 ;    N - S
4    7  1   1.3696e-01   3.1514e+05 ;   O1 - C1
5   17  1   1.3696e-01   3.1514e+05 ;   O2 - C11
6    7  1   1.4058e-01   3.7673e+05 ;    C - C1
6   15  1   1.4058e-01   3.7673e+05 ;    C - C9
6   16  1   1.4854e-01   2.9405e+05 ;    C - C10
7    8  1   1.4058e-01   3.7673e+05 ;   C1 - C2
8    9  1   1.4058e-01   3.7673e+05 ;   C2 - C3
8   27  1   1.4854e-01   2.9405e+05 ;   C2 - C21
9   10  1   1.3984e-01   3.8585e+05 ;   C3 - C4
9   61  1   1.0860e-01   2.8937e+05 ;   C3 - H
10   11  1   1.3984e-01   3.8585e+05 ;   C4 - C5
10   15  1   1.3984e-01   3.8585e+05 ;   C4 - C9
11   12  1   1.3984e-01   3.8585e+05 ;   C5 - C6
11   62  1   1.0860e-01   2.8937e+05 ;   C5 - H1
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12   63  1   1.0860e-01   2.8937e+05 ;   C6 - H2
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13   64  1   1.0860e-01   2.8937e+05 ;   C7 - H3
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14   65  1   1.0860e-01   2.8937e+05 ;   C8 - H4
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18   19  1   1.4058e-01   3.7673e+05 ;  C12 - C13
18   26  1   1.4854e-01   2.9405e+05 ;  C12 - C20
19   20  1   1.3984e-01   3.8585e+05 ;  C13 - C14
19   66  1   1.0860e-01   2.8937e+05 ;  C13 - H5
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```
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21   67  1   1.0860e-01   2.8937e+05 ;   C15 - H6
22   23  1   1.3984e-01   3.8585e+05 ;   C16 - C17
22   68  1   1.0860e-01   2.8937e+05 ;   C16 - H7
23   24  1   1.3984e-01   3.8585e+05 ;   C17 - C18
23   69  1   1.0860e-01   2.8937e+05 ;   C17 - H8
24   25  1   1.3984e-01   3.8585e+05 ;   C18 - C19
24   70  1   1.0860e-01   2.8937e+05 ;   C18 - H9
26   40  1   1.4058e-01   3.7673e+05 ;   C20 - C28
26   44  1   1.4058e-01   3.7673e+05 ;   C20 - C32
27   35  1   1.4058e-01   3.7673e+05 ;   C21 - C23
27   39  1   1.4058e-01   3.7673e+05 ;   C21 - C27
28   29  1   1.4660e-01   4.1254e+05 ;    S - O3
28   30  1   1.4660e-01   4.1254e+05 ;    S - O4
28   31  1   1.8087e-01   1.9481e+05 ;    S - C22
31   32  1   1.3497e-01   2.9865e+05 ;   C22 - F
31   33  1   1.3497e-01   2.9865e+05 ;   C22 - F1
31   34  1   1.3497e-01   2.9865e+05 ;   C22 - F2
35   36  1   1.3984e-01   3.8585e+05 ;   C23 - C24
35   71  1   1.0860e-01   2.8937e+05 ;   C23 - H10
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36   49  1   1.5156e-01   2.6861e+05 ;   C24 - C34
37   38  1   1.3984e-01   3.8585e+05 ;   C25 - C26
37   72  1   1.0860e-01   2.8937e+05 ;   C25 - H11
38   39  1   1.3984e-01   3.8585e+05 ;   C26 - C27
38   45  1   1.5156e-01   2.6861e+05 ;   C26 - C33
39   73  1   1.0860e-01   2.8937e+05 ;   C27 - H12
40   41  1   1.3984e-01   3.8585e+05 ;   C28 - C29
```

```
  40    74  1   1.0860e-01    2.8937e+05 ;    C28 - H13
  41    42  1   1.3984e-01    3.8585e+05 ;    C29 - C30
  41    57  1   1.5156e-01    2.6861e+05 ;    C29 - C36
  42    43  1   1.3984e-01    3.8585e+05 ;    C30 - C31
  42    75  1   1.0860e-01    2.8937e+05 ;    C30 - H14
  43    44  1   1.3984e-01    3.8585e+05 ;    C31 - C32
  43    53  1   1.5156e-01    2.6861e+05 ;    C31 - C35
  44    76  1   1.0860e-01    2.8937e+05 ;    C32 - H15
  45    46  1   1.3497e-01    2.9865e+05 ;    C33 - F3
  45    47  1   1.3497e-01    2.9865e+05 ;    C33 - F4
  45    48  1   1.3497e-01    2.9865e+05 ;    C33 - F5
  49    50  1   1.3497e-01    2.9865e+05 ;    C34 - F6
  49    51  1   1.3497e-01    2.9865e+05 ;    C34 - F7
  49    52  1   1.3497e-01    2.9865e+05 ;    C34 - F8
  53    54  1   1.3497e-01    2.9865e+05 ;    C35 - F9
  53    55  1   1.3497e-01    2.9865e+05 ;    C35 - F10
  53    56  1   1.3497e-01    2.9865e+05 ;    C35 - F11
  57    58  1   1.3497e-01    2.9865e+05 ;    C36 - F12
  57    59  1   1.3497e-01    2.9865e+05 ;    C36 - F13
  57    60  1   1.3497e-01    2.9865e+05 ;    C36 - F14

[ pairs ]
;   ai     aj    funct
     1      6     1 ;     P - C
     1      8     1 ;     P - C2
     1     16      1 ;     P - C10
     1     18      1 ;     P - C12
     1     29      1 ;     P - O3
     1     30      1 ;     P - O4
     1     31      1 ;     P - C22
```

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```
2     7    1 ;    O - C1
2    17    1 ;    O - C11
2    28    1 ;    O - S
3     7    1 ;    N - C1
3    17    1 ;    N - C11
3    32    1 ;    N - F
3    33    1 ;    N - F1
3    34    1 ;    N - F2
4     9    1 ;   O1 - C3
4    15    1 ;   O1 - C9
4    16    1 ;   O1 - C10
4    17    1 ;   O1 - C11
4    27    1 ;   O1 - C21
4    28    1 ;   O1 - S
5     6    1 ;   O2 - C
5     7    1 ;   O2 - C1
5    19    1 ;   O2 - C13
5    25    1 ;   O2 - C19
5    26    1 ;   O2 - C20
5    28    1 ;   O2 - S
6     9    1 ;    C - C3
6    11    1 ;    C - C5
6    13    1 ;    C - C7
6    18    1 ;    C - C12
6    20    1 ;    C - C14
6    24    1 ;    C - C18
6    27    1 ;    C - C21
6    65    1 ;    C - H4
7    10    1 ;   C1 - C4
7    14    1 ;   C1 - C8
```

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```
7   17   1 ;   C1 - C11
7   25   1 ;   C1 - C19
7   35   1 ;   C1 - C23
7   39   1 ;   C1 - C27
7   61   1 ;   C1 - H
8   11   1 ;   C2 - C5
8   15   1 ;   C2 - C9
8   16   1 ;   C2 - C10
8   36   1 ;   C2 - C24
8   38   1 ;   C2 - C26
8   71   1 ;   C2 - H10
8   73   1 ;   C2 - H12
9   12   1 ;   C3 - C6
9   14   1 ;   C3 - C8
9   35   1 ;   C3 - C23
9   39   1 ;   C3 - C27
9   62   1 ;   C3 - H1
10   13   1 ;   C4 - C7
10   16   1 ;   C4 - C10
10   27   1 ;   C4 - C21
10   63   1 ;   C4 - H2
10   65   1 ;   C4 - H4
11   14   1 ;   C5 - C8
11   61   1 ;   C5 - H
11   64   1 ;   C5 - H3
12   15   1 ;   C6 - C9
12   65   1 ;   C6 - H4
13   62   1 ;   C7 - H1
14   16   1 ;   C8 - C10
14   63   1 ;   C8 - H2
```

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```
15    17    1 ;    C9 - C11
15    25    1 ;    C9 - C19
15    61    1 ;    C9 - H
15    62    1 ;    C9 - H1
15    64    1 ;    C9 - H3
16    19    1 ;   C10 - C13
16    21    1 ;   C10 - C15
16    23    1 ;   C10 - C17
16    26    1 ;   C10 - C20
16    70    1 ;   C10 - H9
17    20    1 ;   C11 - C14
17    24    1 ;   C11 - C18
17    40    1 ;   C11 - C28
17    44    1 ;   C11 - C32
17    66    1 ;   C11 - H5
18    21    1 ;   C12 - C15
18    25    1 ;   C12 - C19
18    41    1 ;   C12 - C29
18    43    1 ;   C12 - C31
18    74    1 ;   C12 - H13
18    76    1 ;   C12 - H15
19    22    1 ;   C13 - C16
19    24    1 ;   C13 - C18
19    40    1 ;   C13 - C28
19    44    1 ;   C13 - C32
19    67    1 ;   C13 - H6
20    23    1 ;   C14 - C17
20    26    1 ;   C14 - C20
20    68    1 ;   C14 - H7
20    70    1 ;   C14 - H9
```

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21	24	1 ;	C15 - C18
21	66	1 ;	C15 - H5
21	69	1 ;	C15 - H8
22	25	1 ;	C16 - C19
22	70	1 ;	C16 - H9
23	67	1 ;	C17 - H6
24	68	1 ;	C18 - H7
25	66	1 ;	C19 - H5
25	67	1 ;	C19 - H6
25	69	1 ;	C19 - H8
26	42	1 ;	C20 - C30
26	53	1 ;	C20 - C35
26	57	1 ;	C20 - C36
26	66	1 ;	C20 - H5
27	37	1 ;	C21 - C25
27	45	1 ;	C21 - C33
27	49	1 ;	C21 - C34
27	61	1 ;	C21 - H
29	32	1 ;	O3 - F
29	33	1 ;	O3 - F1
29	34	1 ;	O3 - F2
30	32	1 ;	O4 - F
30	33	1 ;	O4 - F1
30	34	1 ;	O4 - F2
35	38	1 ;	C23 - C26
35	50	1 ;	C23 - F6
35	51	1 ;	C23 - F7
35	52	1 ;	C23 - F8
35	72	1 ;	C23 - H11
35	73	1 ;	C23 - H12

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```
36   39   1 ;   C24 - C27
36   45   1 ;   C24 - C33
37   46   1 ;   C25 - F3
37   47   1 ;   C25 - F4
37   48   1 ;   C25 - F5
37   50   1 ;   C25 - F6
37   51   1 ;   C25 - F7
37   52   1 ;   C25 - F8
37   71   1 ;   C25 - H10
37   73   1 ;   C25 - H12
38   49   1 ;   C26 - C34
39   46   1 ;   C27 - F3
39   47   1 ;   C27 - F4
39   48   1 ;   C27 - F5
39   71   1 ;   C27 - H10
39   72   1 ;   C27 - H11
40   43   1 ;   C28 - C31
40   58   1 ;   C28 - F12
40   59   1 ;   C28 - F13
40   60   1 ;   C28 - F14
40   75   1 ;   C28 - H14
40   76   1 ;   C28 - H15
41   44   1 ;   C29 - C32
41   53   1 ;   C29 - C35
42   54   1 ;   C30 - F9
42   55   1 ;   C30 - F10
42   56   1 ;   C30 - F11
42   58   1 ;   C30 - F12
42   59   1 ;   C30 - F13
42   60   1 ;   C30 - F14
```

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[b] *Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93053, Germany*

```
    42    74     1 ;    C30 - H13
    42    76     1 ;    C30 - H15
    43    57     1 ;    C31 - C36
    44    54     1 ;    C32 - F9
    44    55     1 ;    C32 - F10
    44    56     1 ;    C32 - F11
    44    74     1 ;    C32 - H13
    44    75     1 ;    C32 - H14
    45    72     1 ;    C33 - H11
    45    73     1 ;    C33 - H12
    49    71     1 ;    C34 - H10
    49    72     1 ;    C34 - H11
    53    75     1 ;    C35 - H14
    53    76     1 ;    C35 - H15
    57    74     1 ;    C36 - H13
    57    75     1 ;    C36 - H14
    62    63     1 ;     H1 - H2
    63    64     1 ;     H2 - H3
    64    65     1 ;     H3 - H4
    67    68     1 ;     H6 - H7
    68    69     1 ;     H7 - H8
    69    70     1 ;     H8 - H9

[ angles ]
;  ai    aj    ak   funct   theta         cth
     1     3    28     1    1.3184e+02    6.5689e+02 ;     P - N      - S
     1     4     7     1    1.2318e+02    6.5019e+02 ;     P - O1     - C1
     1     5    17     1    1.2318e+02    6.5019e+02 ;     P - O2     - C11
     2     1     3     1    1.1353e+02    3.6987e+02 ;     O - P      - N
     2     1     4     1    1.1546e+02    3.6736e+02 ;     O - P      - O1
```

```
2   1   5   1   1.1546e+02   3.6736e+02 ;    O - P    - O2
3   1   4   1   1.0240e+02   3.7489e+02 ;    N - P    - O1
3   1   5   1   1.0240e+02   3.7489e+02 ;    N - P    - O2
3   28   29   1   1.0965e+02   5.8827e+02 ;    N - S    - O3
3   28   30   1   1.0965e+02   5.8827e+02 ;    N - S    - O4
3   28   31   1   1.0219e+02   5.3639e+02 ;    N - S    - C22
4   1   5   1   1.0184e+02   3.7656e+02 ;    O1 - P    - O2
4   7   6   1   1.1691e+02   5.8660e+02 ;    O1 - C1    - C
4   7   8   1   1.1691e+02   5.8660e+02 ;    O1 - C1    - C2
5   17   16   1   1.1691e+02   5.8660e+02 ;    O2 - C11    - C10
5   17   18   1   1.1691e+02   5.8660e+02 ;    O2 - C11    - C12
6   7   8   1   1.1152e+02   5.7572e+02 ;    C - C1    - C2
6   15   10   1   1.2069e+02   5.5480e+02 ;    C - C9    - C4
6   15   14   1   1.2069e+02   5.5480e+02 ;    C - C9    - C8
6   16   17   1   1.2111e+02   5.3555e+02 ;    C - C10    - C11
6   16   25   1   1.2111e+02   5.3555e+02 ;    C - C10    - C19
7   6   15   1   1.1838e+02   5.5815e+02 ;    C1 - C    - C9
7   6   16   1   1.2111e+02   5.3555e+02 ;    C1 - C    - C10
7   8   9   1   1.1838e+02   5.5815e+02 ;    C1 - C2    - C3
7   8   27   1   1.2111e+02   5.3555e+02 ;    C1 - C2    - C21
8   9   10   1   1.2069e+02   5.5480e+02 ;    C2 - C3    - C4
8   9   61   1   1.1986e+02   4.0166e+02 ;    C2 - C3    - H
8   27   35   1   1.2111e+02   5.3555e+02 ;    C2 - C21    - C23
8   27   39   1   1.2111e+02   5.3555e+02 ;    C2 - C21    - C27
9   8   27   1   1.2111e+02   5.3555e+02 ;    C3 - C2    - C21
9   10   11   1   1.2002e+02   5.5731e+02 ;    C3 - C4    - C5
9   10   15   1   1.2002e+02   5.5731e+02 ;    C3 - C4    - C9
10   9   61   1   1.1988e+02   4.0334e+02 ;    C4 - C3    - H
10   11   12   1   1.2002e+02   5.5731e+02 ;    C4 - C5    - C6
10   11   62   1   1.1988e+02   4.0334e+02 ;    C4 - C5    - H1
```

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```
10   15   14   1   1.2002e+02   5.5731e+02 ;   C4 - C9    - C8
11   10   15   1   1.2002e+02   5.5731e+02 ;   C5 - C4    - C9
11   12   13   1   1.2002e+02   5.5731e+02 ;   C5 - C6    - C7
11   12   63   1   1.1988e+02   4.0334e+02 ;   C5 - C6    - H2
12   11   62   1   1.1988e+02   4.0334e+02 ;   C6 - C5    - H1
12   13   14   1   1.2002e+02   5.5731e+02 ;   C6 - C7    - C8
12   13   64   1   1.1988e+02   4.0334e+02 ;   C6 - C7    - H3
13   12   63   1   1.1988e+02   4.0334e+02 ;   C7 - C6    - H2
13   14   15   1   1.2002e+02   5.5731e+02 ;   C7 - C8    - C9
13   14   65   1   1.1988e+02   4.0334e+02 ;   C7 - C8    - H4
14   13   64   1   1.1988e+02   4.0334e+02 ;   C8 - C7    - H3
15    6   16   1  1.2111e+02   5.3555e+02 ;   C9 - C    - C10
15   14   65   1   1.1988e+02   4.0334e+02 ;   C9 - C8    - H4
16   17   18   1   1.1152e+02   5.7572e+02 ;  C10 - C11   - C12
16   25   20   1   1.2069e+02   5.5480e+02 ;  C10 - C19   - C14
16   25   24   1   1.2069e+02   5.5480e+02 ;  C10 - C19   - C18
17   16   25   1   1.1838e+02   5.5815e+02 ;  C11 - C10   - C19
17   18   19   1   1.1838e+02   5.5815e+02 ;  C11 - C12   - C13
17   18   26   1   1.2111e+02   5.3555e+02 ;  C11 - C12   - C20
18   19   20   1   1.2069e+02   5.5480e+02 ;  C12 - C13   - C14
18   19   66   1   1.1986e+02   4.0166e+02 ;  C12 - C13   - H5
18   26   40   1   1.2111e+02   5.3555e+02 ;  C12 - C20   - C28
18   26   44   1   1.2111e+02   5.3555e+02 ;  C12 - C20   - C32
19   18   26   1   1.2111e+02   5.3555e+02 ;  C13 - C12   - C20
19   20   21   1   1.2002e+02   5.5731e+02 ;  C13 - C14   - C15
19   20   25   1   1.2002e+02   5.5731e+02 ;  C13 - C14   - C19
20   19   66   1   1.1988e+02   4.0334e+02 ;  C14 - C13   - H5
20   21   22   1   1.2002e+02   5.5731e+02 ;  C14 - C15   - C16
20   21   67   1   1.1988e+02   4.0334e+02 ;  C14 - C15   - H6
20   25   24   1   1.2002e+02   5.5731e+02 ;  C14 - C19   - C18
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```
21   20   25   1   1.2002e+02   5.5731e+02 ;   C15 - C14   - C19
21   22   23   1   1.2002e+02   5.5731e+02 ;   C15 - C16   - C17
21   22   68   1   1.1988e+02   4.0334e+02 ;   C15 - C16   - H7
22   21   67   1   1.1988e+02   4.0334e+02 ;   C16 - C15   - H6
22   23   24   1   1.2002e+02   5.5731e+02 ;   C16 - C17   - C18
22   23   69   1   1.1988e+02   4.0334e+02 ;   C16 - C17   - H8
23   22   68   1   1.1988e+02   4.0334e+02 ;   C17 - C16   - H7
23   24   25   1   1.2002e+02   5.5731e+02 ;   C17 - C18   - C19
23   24   70   1   1.1988e+02   4.0334e+02 ;   C17 - C18   - H9
24   23   69   1   1.1988e+02   4.0334e+02 ;   C18 - C17   - H8
25   24   70   1   1.1988e+02   4.0334e+02 ;   C19 - C18   - H9
26   40   41   1   1.2069e+02   5.5480e+02 ;   C20 - C28   - C29
26   40   74   1   1.1986e+02   4.0166e+02 ;   C20 - C28   - H13
26   44   43   1   1.2069e+02   5.5480e+02 ;   C20 - C32   - C31
26   44   76   1   1.1986e+02   4.0166e+02 ;   C20 - C32   - H15
27   35   36   1   1.2069e+02   5.5480e+02 ;   C21 - C23   - C24
27   35   71   1   1.1986e+02   4.0166e+02 ;   C21 - C23   - H10
27   39   38   1   1.2069e+02   5.5480e+02 ;   C21 - C27   - C26
27   39   73   1   1.1986e+02   4.0166e+02 ;   C21 - C27   - H12
28   31   32   1   1.0968e+02   5.2802e+02 ;     S - C22   - F
28   31   33   1   1.0968e+02   5.2802e+02 ;     S - C22   - F1
28   31   34   1   1.0968e+02   5.2802e+02 ;     S - C22   - F2
29   28   30   1   1.2141e+02   6.0668e+02 ;    O3 - S     - O4
29   28   31   1   1.0785e+02   5.4727e+02 ;    O3 - S     - C22
30   28   31   1   1.0785e+02   5.4727e+02 ;    O4 - S     - C22
32   31   33   1   1.0736e+02   5.9329e+02 ;     F - C22   - F1
32   31   34   1   1.0736e+02   5.9329e+02 ;     F - C22   - F2
33   31   34   1   1.0736e+02   5.9329e+02 ;    F1 - C22   - F2
35   27   39   1   1.1838e+02   5.5815e+02 ;   C23 - C21   - C27
35   36   37   1   1.2002e+02   5.5731e+02 ;   C23 - C24   - C25
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```
35   36   49   1   1.2077e+02   5.3137e+02 ;   C23 - C24   - C34
36   35   71   1   1.1988e+02   4.0334e+02 ;   C24 - C23   - H10
36   37   38   1   1.2002e+02   5.5731e+02 ;   C24 - C25   - C26
36   37   72   1   1.1988e+02   4.0334e+02 ;   C24 - C25   - H11
36   49   50   1   1.1177e+02   5.5229e+02 ;   C24 - C34   - F6
36   49   51   1   1.1177e+02   5.5229e+02 ;   C24 - C34   - F7
36   49   52   1   1.1177e+02   5.5229e+02 ;   C24 - C34   - F8
37   36   49   1   1.2077e+02   5.3137e+02 ;   C25 - C24   - C34
37   38   39   1   1.2002e+02   5.5731e+02 ;   C25 - C26   - C27
37   38   45   1   1.2077e+02   5.3137e+02 ;   C25 - C26   - C33
38   37   72   1   1.1988e+02   4.0334e+02 ;   C26 - C25   - H11
38   39   73   1   1.1988e+02   4.0334e+02 ;   C26 - C27   - H12
38   45   46   1   1.1177e+02   5.5229e+02 ;   C26 - C33   - F3
38   45   47   1   1.1177e+02   5.5229e+02 ;   C26 - C33   - F4
38   45   48   1   1.1177e+02   5.5229e+02 ;   C26 - C33   - F5
39   38   45   1   1.2077e+02   5.3137e+02 ;   C27 - C26   - C33
40   26   44   1   1.1838e+02   5.5815e+02 ;   C28 - C20   - C32
40   41   42   1   1.2002e+02   5.5731e+02 ;   C28 - C29   - C30
40   41   57   1   1.2077e+02   5.3137e+02 ;   C28 - C29   - C36
41   40   74   1   1.1988e+02   4.0334e+02 ;   C29 - C28   - H13
41   42   43   1   1.2002e+02   5.5731e+02 ;   C29 - C30   - C31
41   42   75   1   1.1988e+02   4.0334e+02 ;   C29 - C30   - H14
41   57   58   1   1.1177e+02   5.5229e+02 ;   C29 - C36   - F12
41   57   59   1   1.1177e+02   5.5229e+02 ;   C29 - C36   - F13
41   57   60   1   1.1177e+02   5.5229e+02 ;   C29 - C36   - F14
42   41   57   1   1.2077e+02   5.3137e+02 ;   C30 - C29   - C36
42   43   44   1   1.2002e+02   5.5731e+02 ;   C30 - C31   - C32
42   43   53   1   1.2077e+02   5.3137e+02 ;   C30 - C31   - C35
43   42   75   1   1.1988e+02   4.0334e+02 ;   C31 - C30   - H14
43   44   76   1   1.1988e+02   4.0334e+02 ;   C31 - C32   - H15
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  43   53   54   1   1.1177e+02   5.5229e+02 ;   C31 - C35   - F9
  43   53   55   1   1.1177e+02   5.5229e+02 ;   C31 - C35   - F10
  43   53   56   1   1.1177e+02   5.5229e+02 ;   C31 - C35   - F11
  44   43   53   1   1.2077e+02   5.3137e+02 ;   C32 - C31   - C35
  46   45   47   1   1.0736e+02   5.9329e+02 ;    F3 - C33   - F4
  46   45   48   1   1.0736e+02   5.9329e+02 ;    F3 - C33   - F5
  47   45   48   1   1.0736e+02   5.9329e+02 ;    F4 - C33   - F5
  50   49   51   1   1.0736e+02   5.9329e+02 ;    F6 - C34   - F7
  50   49   52   1   1.0736e+02   5.9329e+02 ;    F6 - C34   - F8
  51   49   52   1   1.0736e+02   5.9329e+02 ;    F7 - C34   - F8
  54   53   55   1   1.0736e+02   5.9329e+02 ;    F9 - C35   - F10
  54   53   56   1   1.0736e+02   5.9329e+02 ;    F9 - C35   - F11
  55   53   56   1   1.0736e+02   5.9329e+02 ;   F10 - C35   - F11
  58   57   59   1   1.0736e+02   5.9329e+02 ;   F12 - C36   - F13
  58   57   60   1   1.0736e+02   5.9329e+02 ;   F12 - C36   - F14
  59   57   60   1   1.0736e+02   5.9329e+02 ;   F13 - C36   - F14

[ dihedrals ] ; propers
; for gromacs 4.5 or higher, using funct 9
;   i    j    k    l   func   phase     kd      pn
    1    3   28   29    9   180.00   2.09200   3 ;    P-   N-   S-   O3
    1    3   28   29    9   180.00  28.45120   1 ;    P-   N-   S-   O3
    1    3   28   30    9   180.00   2.09200   3 ;    P-   N-   S-   O4
    1    3   28   30    9   180.00  28.45120   1 ;    P-   N-   S-   O4
    1    3   28   31    9   180.00   2.09200   3 ;    P-   N-   S-  C22
    1    3   28   31    9   180.00  28.45120   1 ;    P-   N-   S-  C22
    1    4    7    6    9   180.00   3.76560   2 ;    P-  O1-  C1-    C
    1    4    7    8    9   180.00   3.76560   2 ;    P-  O1-  C1-   C2
    1    5   17   16    9   180.00   3.76560   2 ;    P-  O2- C11-  C10
    1    5   17   18    9   180.00   3.76560   2 ;    P-  O2- C11-  C12
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2   1   3   28   9  180.00   4.18400  3 ;   O-   P-   N-   S
2   1   4   7    9    0.00   0.41840  3 ;   O-   P-  O1-  C1
2   1   4   7    9  180.00   3.34720  2 ;   O-   P-  O1-  C1
2   1   5   17   9    0.00   0.41840  3 ;   O-   P-  O2-  C11
2   1   5   17   9  180.00   3.34720  2 ;   O-   P-  O2-  C11
3   1   4   7    9    0.00   3.34720  2 ;   N-   P-  O1-  C1
3   1   5   17   9    0.00   3.34720  2 ;   N-   P-  O2-  C11
3  28  31   32   9    0.00   0.60436  3 ;   N-   S-  C22-  F
3  28  31   33   9    0.00   0.60436  3 ;   N-   S-  C22-  F1
3  28  31   34   9    0.00   0.60436  3 ;   N-   S-  C22-  F2
4   1   3   28   9  180.00   4.18400  3 ;  O1-   P-   N-   S
4   1   5   17   9    0.00   3.34720  2 ;  O1-   P-  O2-  C11
4   7   6   15   9  180.00  15.16700  2 ;  O1-  C1-   C-   C9
4   7   6   16   9  180.00  15.16700  2 ;  O1-  C1-   C-  C10
4   7   8   9    9  180.00  15.16700  2 ;  O1-  C1-  C2-   C3
4   7   8   27   9  180.00  15.16700  2 ;  O1-  C1-  C2-  C21
5   1   3   28   9  180.00   4.18400  3 ;  O2-   P-   N-   S
5   1   4   7    9    0.00   3.34720  2 ;  O2-   P-  O1-   C1
5  17  16   6    9  180.00  15.16700  2 ;  O2-  C11-  C10-   C
5  17  16   25   9  180.00  15.16700  2 ;  O2-  C11-  C10-  C19
5  17  18   19   9  180.00  15.16700  2 ;  O2-  C11-  C12-  C13
5  17  18   26   9  180.00  15.16700  2 ;  O2-  C11-  C12-  C20
6   7   8   9    9  180.00  15.16700  2 ;   C-  C1-  C2-   C3
6   7   8   27   9  180.00  15.16700  2 ;   C-  C1-  C2-  C21
6  15  10   9    9  180.00  15.16700  2 ;   C-  C9-  C4-   C3
6  15  10   11   9  180.00  15.16700  2 ;   C-  C9-  C4-   C5
6  15  14   13   9  180.00  15.16700  2 ;   C-  C9-  C8-   C7
6  15  14   65   9  180.00  15.16700  2 ;   C-  C9-  C8-   H4
6  16  17   18   9  180.00  15.16700  2 ;   C-  C10-  C11-  C12
6  16  25   20   9  180.00  15.16700  2 ;   C-  C10-  C19-  C14
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6   16   25   24    9  180.00  15.16700   2 ;    C-  C10-  C19-  C18
7    6   15   10    9  180.00  15.16700   2 ;   C1-    C-   C9-   C4
7    6   15   14    9  180.00  15.16700   2 ;   C1-    C-   C9-   C8
7    6   16   17    9  180.00   4.18400   2 ;   C1-    C-  C10-  C11
7    6   16   25    9  180.00   4.18400   2 ;   C1-    C-  C10-  C19
7    8    9   10    9  180.00  15.16700   2 ;   C1-   C2-   C3-   C4
7    8    9   61    9  180.00  15.16700   2 ;   C1-   C2-   C3-    H
7    8   27   35    9  180.00   4.18400   2 ;   C1-   C2-  C21-  C23
7    8   27   39    9  180.00   4.18400   2 ;   C1-   C2-  C21-  C27
8    7    6   15    9  180.00  15.16700   2 ;   C2-   C1-    C-   C9
8    7    6   16    9  180.00  15.16700   2 ;   C2-   C1-    C-  C10
8    9   10   11    9  180.00  15.16700   2 ;   C2-   C3-   C4-   C5
8    9   10   15    9  180.00  15.16700   2 ;   C2-   C3-   C4-   C9
8   27   35   36    9  180.00  15.16700   2 ;   C2-  C21-  C23-  C24
8   27   35   71    9  180.00  15.16700   2 ;   C2-  C21-  C23-  H10
8   27   39   38    9  180.00  15.16700   2 ;   C2-  C21-  C27-  C26
8   27   39   73    9  180.00  15.16700   2 ;   C2-  C21-  C27-  H12
9    8   27   35    9  180.00   4.18400   2 ;   C3-   C2-  C21-  C23
9    8   27   39    9  180.00   4.18400   2 ;   C3-   C2-  C21-  C27
9   10   11   12    9  180.00  15.16700   2 ;   C3-   C4-   C5-   C6
9   10   11   62    9  180.00  15.16700   2 ;   C3-   C4-   C5-   H1
9   10   15   14    9  180.00  15.16700   2 ;   C3-   C4-   C9-   C8
10   9    8   27    9  180.00  15.16700   2 ;   C4-   C3-   C2-  C21
10  11   12   13    9  180.00  15.16700   2 ;   C4-   C5-   C6-   C7
10  11   12   63    9  180.00  15.16700   2 ;   C4-   C5-   C6-   H2
10  15    6   16    9  180.00  15.16700   2 ;   C4-   C9-    C-  C10
10  15   14   13    9  180.00  15.16700   2 ;   C4-   C9-   C8-   C7
10  15   14   65    9  180.00  15.16700   2 ;   C4-   C9-   C8-   H4
11  10    9   61    9  180.00  15.16700   2 ;   C5-   C4-   C3-    H
11  10   15   14    9  180.00  15.16700   2 ;   C5-   C4-   C9-   C8
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11   12   13   14    9  180.00  15.16700   2 ;   C5-   C6-   C7-   C8
11   12   13   64    9  180.00  15.16700   2 ;   C5-   C6-   C7-   H3
12   11   10   15    9  180.00  15.16700   2 ;   C6-   C5-   C4-   C9
12   13   14   15    9  180.00  15.16700   2 ;   C6-   C7-   C8-   C9
12   13   14   65    9  180.00  15.16700   2 ;   C6-   C7-   C8-   H4
13   12   11   62    9  180.00  15.16700   2 ;   C7-   C6-   C5-   H1
14   13   12   63    9  180.00  15.16700   2 ;   C8-   C7-   C6-   H2
14   15    6   16    9  180.00  15.16700   2 ;   C8-   C9-   C-  C10
15    6   16   17    9  180.00   4.18400   2 ;   C9-   C-  C10-  C11
15    6   16   25    9  180.00   4.18400   2 ;   C9-   C-  C10-  C19
15   10    9   61    9  180.00  15.16700   2 ;   C9-   C4-   C3-   H
15   10   11   62    9  180.00  15.16700   2 ;   C9-   C4-   C5-   H1
15   14   13   64    9  180.00  15.16700   2 ;   C9-   C8-   C7-   H3
16   17   18   19    9  180.00  15.16700   2 ;  C10-  C11-  C12-  C13
16   17   18   26    9  180.00  15.16700   2 ;  C10-  C11-  C12-  C20
16   25   20   19    9  180.00  15.16700   2 ;  C10-  C19-  C14-  C13
16   25   20   21    9  180.00  15.16700   2 ;  C10-  C19-  C14-  C15
16   25   24   23    9  180.00  15.16700   2 ;  C10-  C19-  C18-  C17
16   25   24   70    9  180.00  15.16700   2 ;  C10-  C19-  C18-   H9
17   16   25   20    9  180.00  15.16700   2 ;  C11-  C10-  C19-  C14
17   16   25   24    9  180.00  15.16700   2 ;  C11-  C10-  C19-  C18
17   18   19   20    9  180.00  15.16700   2 ;  C11-  C12-  C13-  C14
17   18   19   66    9  180.00  15.16700   2 ;  C11-  C12-  C13-   H5
17   18   26   40    9  180.00   4.18400   2 ;  C11-  C12-  C20-  C28
17   18   26   44    9  180.00   4.18400   2 ;  C11-  C12-  C20-  C32
18   17   16   25    9  180.00  15.16700   2 ;  C12-  C11-  C10-  C19
18   19   20   21    9  180.00  15.16700   2 ;  C12-  C13-  C14-  C15
18   19   20   25    9  180.00  15.16700   2 ;  C12-  C13-  C14-  C19
18   26   40   41    9  180.00  15.16700   2 ;  C12-  C20-  C28-  C29
18   26   40   74    9  180.00  15.16700   2 ;  C12-  C20-  C28-  H13
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18   26   44   43    9  180.00  15.16700   2 ;   C12-  C20-  C32-  C31
18   26   44   76    9  180.00  15.16700   2 ;   C12-  C20-  C32-  H15
19   18   26   40    9  180.00   4.18400   2 ;   C13-  C12-  C20-  C28
19   18   26   44    9  180.00   4.18400   2 ;   C13-  C12-  C20-  C32
19   20   21   22    9  180.00  15.16700   2 ;   C13-  C14-  C15-  C16
19   20   21   67    9  180.00  15.16700   2 ;   C13-  C14-  C15-   H6
19   20   25   24    9  180.00  15.16700   2 ;   C13-  C14-  C19-  C18
20   19   18   26    9  180.00  15.16700   2 ;   C14-  C13-  C12-  C20
20   21   22   23    9  180.00  15.16700   2 ;   C14-  C15-  C16-  C17
20   21   22   68    9  180.00  15.16700   2 ;   C14-  C15-  C16-   H7
20   25   24   23    9  180.00  15.16700   2 ;   C14-  C19-  C18-  C17
20   25   24   70    9  180.00  15.16700   2 ;   C14-  C19-  C18-   H9
21   20   19   66    9  180.00  15.16700   2 ;   C15-  C14-  C13-   H5
21   20   25   24    9  180.00  15.16700   2 ;   C15-  C14-  C19-  C18
21   22   23   24    9  180.00  15.16700   2 ;   C15-  C16-  C17-  C18
21   22   23   69    9  180.00  15.16700   2 ;   C15-  C16-  C17-   H8
22   21   20   25    9  180.00  15.16700   2 ;   C16-  C15-  C14-  C19
22   23   24   25    9  180.00  15.16700   2 ;   C16-  C17-  C18-  C19
22   23   24   70    9  180.00  15.16700   2 ;   C16-  C17-  C18-   H9
23   22   21   67    9  180.00  15.16700   2 ;   C17-  C16-  C15-   H6
24   23   22   68    9  180.00  15.16700   2 ;   C18-  C17-  C16-   H7
25   20   19   66    9  180.00  15.16700   2 ;   C19-  C14-  C13-   H5
25   20   21   67    9  180.00  15.16700   2 ;   C19-  C14-  C15-   H6
25   24   23   69    9  180.00  15.16700   2 ;   C19-  C18-  C17-   H8
26   18   19   66    9  180.00  15.16700   2 ;   C20-  C12-  C13-   H5
26   40   41   42    9  180.00  15.16700   2 ;   C20-  C28-  C29-  C30
26   40   41   57    9  180.00  15.16700   2 ;   C20-  C28-  C29-  C36
26   44   43   42    9  180.00  15.16700   2 ;   C20-  C32-  C31-  C30
26   44   43   53    9  180.00  15.16700   2 ;   C20-  C32-  C31-  C35
27    8    9   61    9  180.00  15.16700   2 ;   C21-   C2-   C3-   H
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27   35   36   37    9  180.00  15.16700   2 ;   C21-  C23-  C24-  C25
27   35   36   49    9  180.00  15.16700   2 ;   C21-  C23-  C24-  C34
27   39   38   37    9  180.00  15.16700   2 ;   C21-  C27-  C26-  C25
27   39   38   45    9  180.00  15.16700   2 ;   C21-  C27-  C26-  C33
29   28   31   32    9    0.00   0.60436   3 ;    O3-    S-  C22-    F
29   28   31   33    9    0.00   0.60436   3 ;    O3-    S-  C22-   F1
29   28   31   34    9    0.00   0.60436   3 ;    O3-    S-  C22-   F2
30   28   31   32    9    0.00   0.60436   3 ;    O4-    S-  C22-    F
30   28   31   33    9    0.00   0.60436   3 ;    O4-    S-  C22-   F1
30   28   31   34    9    0.00   0.60436   3 ;    O4-    S-  C22-   F2
35   27   39   38    9  180.00  15.16700   2 ;   C23-  C21-  C27-  C26
35   27   39   73    9  180.00  15.16700   2 ;   C23-  C21-  C27-  H12
35   36   37   38    9  180.00  15.16700   2 ;   C23-  C24-  C25-  C26
35   36   37   72    9  180.00  15.16700   2 ;   C23-  C24-  C25-  H11
35   36   49   50    9    0.00   0.00000   0 ;  C23-  C24-  C34-   F6
35   36   49   51    9    0.00   0.00000   0 ;  C23-  C24-  C34-   F7
35   36   49   52    9    0.00   0.00000   0 ;  C23-  C24-  C34-   F8
36   35   27   39    9  180.00  15.16700   2 ;   C24-  C23-  C21-  C27
36   37   38   39    9  180.00  15.16700   2 ;   C24-  C25-  C26-  C27
36   37   38   45    9  180.00  15.16700   2 ;   C24-  C25-  C26-  C33
37   36   35   71    9  180.00  15.16700   2 ;   C25-  C24-  C23-  H10
37   36   49   50    9    0.00   0.00000   0 ;  C25-  C24-  C34-   F6
37   36   49   51    9    0.00   0.00000   0 ;  C25-  C24-  C34-   F7
37   36   49   52    9    0.00   0.00000   0 ;  C25-  C24-  C34-   F8
37   38   39   73    9  180.00  15.16700   2 ;   C25-  C26-  C27-  H12
37   38   45   46    9    0.00   0.00000   0 ;  C25-  C26-  C33-   F3
37   38   45   47    9    0.00   0.00000   0 ;  C25-  C26-  C33-   F4
37   38   45   48    9    0.00   0.00000   0 ;  C25-  C26-  C33-   F5
38   37   36   49    9  180.00  15.16700   2 ;   C26-  C25-  C24-  C34
39   27   35   71    9  180.00  15.16700   2 ;   C27-  C21-  C23-  H10
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39   38   37   72    9  180.00  15.16700   2 ;   C27-  C26-  C25-  H11
39   38   45   46    9    0.00   0.00000  0 ;   C27-  C26-  C33-   F3
39   38   45   47    9    0.00   0.00000  0 ;   C27-  C26-  C33-   F4
39   38   45   48    9    0.00   0.00000  0 ;   C27-  C26-  C33-   F5
40   26   44   43    9  180.00  15.16700   2 ;   C28-  C20-  C32-  C31
40   26   44   76    9  180.00  15.16700   2 ;   C28-  C20-  C32-  H15
40   41   42   43    9  180.00  15.16700   2 ;   C28-  C29-  C30-  C31
40   41   42   75    9  180.00  15.16700   2 ;   C28-  C29-  C30-  H14
40   41   57   58    9    0.00   0.00000  0 ;   C28-  C29-  C36-  F12
40   41   57   59    9    0.00   0.00000  0 ;   C28-  C29-  C36-  F13
40   41   57   60    9    0.00   0.00000  0 ;   C28-  C29-  C36-  F14
41   40   26   44    9  180.00  15.16700   2 ;   C29-  C28-  C20-  C32
41   42   43   44    9  180.00  15.16700   2 ;   C29-  C30-  C31-  C32
41   42   43   53    9  180.00  15.16700   2 ;   C29-  C30-  C31-  C35
42   41   40   74    9  180.00  15.16700   2 ;   C30-  C29-  C28-  H13
42   41   57   58    9    0.00   0.00000  0 ;   C30-  C29-  C36-  F12
42   41   57   59    9    0.00   0.00000  0 ;   C30-  C29-  C36-  F13
42   41   57   60    9    0.00   0.00000  0 ;   C30-  C29-  C36-  F14
42   43   44   76    9  180.00  15.16700   2 ;   C30-  C31-  C32-  H15
42   43   53   54    9    0.00   0.00000  0 ;   C30-  C31-  C35-   F9
42   43   53   55    9    0.00   0.00000  0 ;   C30-  C31-  C35-  F10
42   43   53   56    9    0.00   0.00000  0 ;   C30-  C31-  C35-  F11
43   42   41   57    9  180.00  15.16700   2 ;   C31-  C30-  C29-  C36
44   26   40   74    9  180.00  15.16700   2 ;   C32-  C20-  C28-  H13
44   43   42   75    9  180.00  15.16700   2 ;   C32-  C31-  C30-  H14
44   43   53   54    9    0.00   0.00000  0 ;   C32-  C31-  C35-   F9
44   43   53   55    9    0.00   0.00000  0 ;   C32-  C31-  C35-  F10
44   43   53   56    9    0.00   0.00000  0 ;   C32-  C31-  C35-  F11
45   38   37   72    9  180.00  15.16700   2 ;   C33-  C26-  C25-  H11
45   38   39   73    9  180.00  15.16700   2 ;   C33-  C26-  C27-  H12
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```
  49    36    35    71     9   180.00  15.16700   2 ;    C34-   C24-   C23-   H10
  49    36    37    72     9   180.00  15.16700   2 ;    C34-   C24-   C25-   H11
  53    43    42    75     9   180.00  15.16700   2 ;    C35-   C31-   C30-   H14
  53    43    44    76     9   180.00  15.16700   2 ;    C35-   C31-   C32-   H15
  57    41    40    74     9   180.00  15.16700   2 ;    C36-   C29-   C28-   H13
  57    41    42    75     9   180.00  15.16700   2 ;    C36-   C29-   C30-   H14
  62    11    12    63     9   180.00  15.16700   2 ;     H1-    C5-    C6-    H2
  63    12    13    64     9   180.00  15.16700   2 ;     H2-    C6-    C7-    H3
  64    13    14    65     9   180.00  15.16700   2 ;     H3-    C7-    C8-    H4
  67    21    22    68     9   180.00  15.16700   2 ;     H6-   C15-   C16-    H7
  68    22    23    69     9   180.00  15.16700   2 ;     H7-   C16-   C17-    H8
  69    23    24    70     9   180.00  15.16700   2 ;     H8-   C17-   C18-    H9

[ dihedrals ] ; impropers
; treated as propers in GROMACS to use correct AMBER analytical function
;   i     j     k     l  func  phase     kd      pn
     6     8     7     4     4  180.00   4.60240   2 ;      C-    C2-    C1-    O1
     7     9     8    27     4  180.00   4.60240   2 ;     C1-    C3-    C2-   C21
     7    15     6    16     4  180.00   4.60240   2 ;     C1-    C9-     C-   C10
     9    11    10    15     4  180.00   4.60240   2 ;     C3-    C5-    C4-    C9
    10     8     9    61     4  180.00   4.60240   2 ;     C4-    C2-    C3-     H
    10    12    11    62     4  180.00   4.60240   2 ;     C4-    C6-    C5-    H1
    10    14    15     6     4  180.00   4.60240   2 ;     C4-    C8-    C9-     C
    11    13    12    63     4  180.00   4.60240   2 ;     C5-    C7-    C6-    H2
    12    14    13    64     4  180.00   4.60240   2 ;     C6-    C8-    C7-    H3
    13    15    14    65     4  180.00   4.60240   2 ;     C7-    C9-    C8-    H4
    16    18    17     5     4  180.00   4.60240   2 ;    C10-   C12-   C11-    O2
    17    19    18    26     4  180.00   4.60240   2 ;    C11-   C13-   C12-   C20
    17    25    16     6     4  180.00   4.60240   2 ;    C11-   C19-   C10-     C
    19    21    20    25     4  180.00   4.60240   2 ;    C13-   C15-   C14-   C19
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```
20   18   19   66    4  180.00   4.60240   2 ;   C14-  C12-  C13-   H5
20   22   21   67    4  180.00   4.60240   2 ;   C14-  C16-  C15-   H6
20   24   25   16    4  180.00   4.60240   2 ;   C14-  C18-  C19-  C10
21   23   22   68    4  180.00   4.60240   2 ;   C15-  C17-  C16-   H7
22   24   23   69    4  180.00   4.60240   2 ;   C16-  C18-  C17-   H8
23   25   24   70    4  180.00   4.60240   2 ;   C17-  C19-  C18-   H9
35   37   36   49    4  180.00   4.60240   2 ;   C23-  C25-  C24-  C34
35   39   27    8    4  180.00   4.60240   2 ;   C23-  C27-  C21-   C2
36   27   35   71    4  180.00   4.60240   2 ;   C24-  C21-  C23-  H10
36   38   37   72    4  180.00   4.60240   2 ;   C24-  C26-  C25-  H11
38   27   39   73    4  180.00   4.60240   2 ;   C26-  C21-  C27-  H12
40   44   26   18    4  180.00   4.60240   2 ;   C28-  C32-  C20-  C12
41   26   40   74    4  180.00   4.60240   2 ;   C29-  C20-  C28-  H13
41   43   42   75    4  180.00   4.60240   2 ;   C29-  C31-  C30-  H14
43   26   44   76    4  180.00   4.60240   2 ;   C31-  C20-  C32-  H15
45   37   38   39    4  180.00   4.60240   2 ;   C33-  C25-  C26-  C27
53   42   43   44    4  180.00   4.60240   2 ;   C35-  C30-  C31-  C32
57   40   41   42    4  180.00   4.60240   2 ;   C36-  C28-  C29-  C30
```

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Iminium-cation

```
[ moleculetype ]
;name      nrexcl
 MAE        3

[ atoms ]
   1  na   1  MAE   N   1   -0.5019940291   14.01000
   2  ce   1  MAE   C   2   0.5055575319   12.01000
   3  ca   1  MAE  C1   3   0.4365084735   12.01000
   4  ca   1  MAE  C2   4   -0.3155317549   12.01000
   5  ca   1  MAE  C3   5   -0.0605277162   12.01000
   6  ca   1  MAE  C4   6   -0.1528215726   12.01000
   7  ca   1  MAE  C5   7   -0.0759100819   12.01000
   8  ca   1  MAE  C6   8   -0.2939740325   12.01000
   9  ca   1  MAE  C7   9   -0.1121681626   12.01000
  10  c3   1  MAE  C8  10   -0.4473984112   12.01000
  11  ca   1  MAE  C9  11   -0.0768536472   12.01000
  12  ca   1  MAE  C10  12   -0.3338791757   12.01000
  13  ca   1  MAE  C11  13   0.5264880982   12.01000
  14  ca   1  MAE  C12  14   -0.2640418041   12.01000
  15  ca   1  MAE  C13  15   -0.1237506703   12.01000
  16  os   1  MAE   O  16   -0.3668202686   16.00000
  17  c3   1  MAE  C14  17   0.0565960320   12.01000
  18  hn   1  MAE   H  18   0.3801451114    1.00800
  19  ha   1  MAE  H1  19   0.2004808690    1.00800
  20  ha   1  MAE  H2  20   0.1387034634    1.00800
  21  ha   1  MAE  H3  21   0.1473165056    1.00800
  22  ha   1  MAE  H4  22   0.1455940644    1.00800
  23  ha   1  MAE  H5  23   0.1877996713    1.00800
  24  hc   1  MAE  H6  24   0.1650739263    1.00800
```

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```
   25   hc    1   MAE    H7   25    0.1650739263     1.00800
   26   hc    1   MAE    H8   26    0.1650739263     1.00800
   27   ha    1   MAE    H9   27    0.1757174210     1.00800
   28   ha    1   MAE   H10   28    0.1784330807     1.00800
   29   ha    1   MAE   H11   29    0.1734240999     1.00800
   30   ha    1   MAE   H12   30    0.1666439014     1.00800
   31   h1    1   MAE   H13   31    0.0703470748     1.00800
   32   h1    1   MAE   H14   32    0.0703470748     1.00800
   33   h1    1   MAE   H15   33    0.0703470748     1.00800
[ bonds ]
;   ai     aj funct   r           k
    1      2   1   1.4209e-01   3.1263e+05 ;     N - C
    1      3   1   1.3840e-01   3.5187e+05 ;     N - C1
    1     18   1   1.0100e-01   3.4175e+05 ;     N - H
    2      9   1   1.4763e-01   3.0234e+05 ;     C - C7
    2     10   1   1.5159e-01   2.6836e+05 ;     C - C8
    3      4   1   1.3984e-01   3.8585e+05 ;    C1 - C2
    3      8   1   1.3984e-01   3.8585e+05 ;    C1 - C6
    4      5   1   1.3984e-01   3.8585e+05 ;    C2 - C3
    4     19   1   1.0860e-01   2.8937e+05 ;    C2 - H1
    5      6   1   1.3984e-01   3.8585e+05 ;    C3 - C4
    5     20   1   1.0860e-01   2.8937e+05 ;    C3 - H2
    6      7   1   1.3984e-01   3.8585e+05 ;    C4 - C5
    6     21   1   1.0860e-01   2.8937e+05 ;    C4 - H3
    7      8   1   1.3984e-01   3.8585e+05 ;    C5 - C6
    7     22   1   1.0860e-01   2.8937e+05 ;    C5 - H4
    8     23   1   1.0860e-01   2.8937e+05 ;    C6 - H5
    9     11   1   1.3984e-01   3.8585e+05 ;    C7 - C9
    9     15   1   1.3984e-01   3.8585e+05 ;    C7 - C13
   10     24   1   1.0969e-01   2.7665e+05 ;    C8 - H6
```

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```
   10    25  1   1.0969e-01   2.7665e+05 ;    C8 - H7
   10    26  1   1.0969e-01   2.7665e+05 ;    C8 - H8
   11    12  1   1.3984e-01   3.8585e+05 ;    C9 - C10
   11    27  1   1.0860e-01   2.8937e+05 ;    C9 - H9
   12    13  1   1.3984e-01   3.8585e+05 ;   C10 - C11
   12    28  1   1.0860e-01   2.8937e+05 ;   C10 - H10
   13    14  1   1.3984e-01   3.8585e+05 ;   C11 - C12
   13    16  1   1.3696e-01   3.1514e+05 ;   C11 - O
   14    15  1   1.3984e-01   3.8585e+05 ;   C12 - C13
   14    29  1   1.0860e-01   2.8937e+05 ;   C12 - H11
   15    30  1   1.0860e-01   2.8937e+05 ;   C13 - H12
   16    17  1   1.4316e-01   2.5824e+05 ;     O - C14
   17    31  1   1.0969e-01   2.7665e+05 ;   C14 - H13
   17    32  1   1.0969e-01   2.7665e+05 ;   C14 - H14
   17    33  1   1.0969e-01   2.7665e+05 ;   C14 - H15

[ pairs ]
;  ai    aj   funct
    1     5     1 ;     N - C3
    1     7     1 ;     N - C5
    1    11     1 ;     N - C9
    1    15     1 ;     N - C13
    1    19     1 ;     N - H1
    1    23     1 ;     N - H5
    1    24     1 ;     N - H6
    1    25     1 ;     N - H7
    1    26     1 ;     N - H8
    2     4     1 ;     C - C2
    2     8     1 ;     C - C6
    2    12     1 ;     C - C10
```

```
2   14   1 ;   C - C12
2   27   1 ;   C - H9
2   30   1 ;   C - H12
3   6    1 ;   C1 - C4
3   9    1 ;   C1 - C7
3   10   1 ;   C1 - C8
3   20   1 ;   C1 - H2
3   22   1 ;   C1 - H4
4   7    1 ;   C2 - C5
4   21   1 ;   C2 - H3
4   23   1 ;   C2 - H5
5   8    1 ;   C3 - C6
5   22   1 ;   C3 - H4
6   19   1 ;   C4 - H1
6   23   1 ;   C4 - H5
7   20   1 ;   C5 - H2
8   19   1 ;   C6 - H1
8   21   1 ;   C6 - H3
9   13   1 ;   C7 - C11
9   24   1 ;   C7 - H6
9   25   1 ;   C7 - H7
9   26   1 ;   C7 - H8
9   28   1 ;   C7 - H10
9   29   1 ;   C7 - H11
10   11   1 ;   C8 - C9
10   15   1 ;   C8 - C13
11   14   1 ;   C9 - C12
11   16   1 ;   C9 - O
11   30   1 ;   C9 - H12
12   15   1 ;   C10 - C13
```

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```
    12    17     1 ;    C10 - C14
    12    29     1 ;    C10 - H11
    13    27     1 ;    C11 - H9
    13    30     1 ;    C11 - H12
    13    31     1 ;    C11 - H13
    13    32     1 ;    C11 - H14
    13    33     1 ;    C11 - H15
    14    17     1 ;    C12 - C14
    14    28     1 ;    C12 - H10
    15    16     1 ;    C13 - O
    15    27     1 ;    C13 - H9
    16    28     1 ;      O - H10
    16    29     1 ;      O - H11
    18     4    1 ;      H - C2
    18     8    1 ;      H - C6
    18     9    1 ;      H - C7
    18    10     1 ;      H - C8
    19    20     1 ;     H1 - H2
    20    21     1 ;     H2 - H3
    21    22     1 ;     H3 - H4
    22    23     1 ;     H4 - H5
    27    28     1 ;     H9 - H10
    29    30     1 ;    H11 - H12

[ angles ]
;   ai    aj    ak    funct   theta        cth
     1     2     9     1   1.1919e+02    5.7823e+02 ;     N - C     - C7
     1     2    10     1   1.1956e+02    5.4894e+02 ;     N - C     - C8
     1     3     4     1   1.1834e+02    5.7823e+02 ;     N - C1    - C2
     1     3     8     1   1.1834e+02    5.7823e+02 ;     N - C1    - C6
```

```
2   1   3   1  1.2661e+02  5.2635e+02 ;   C - N   - C1
2   1   18  1  1.2554e+02  3.8995e+02 ;   C - N   - H
2   9   11  1  1.2082e+02  5.3974e+02 ;   C - C7  - C9
2   9   15  1  1.2082e+02  5.3974e+02 ;   C - C7  - C13
2   10  24  1  1.1059e+02  3.9162e+02 ;   C - C8  - H6
2   10  25  1  1.1059e+02  3.9162e+02 ;   C - C8  - H7
2   10  26  1  1.1059e+02  3.9162e+02 ;   C - C8  - H8
3   1   18  1  1.2554e+02  3.8995e+02 ;   C1 - N  - H
3   4   5   1  1.2002e+02  5.5731e+02 ;   C1 - C2  - C3
3   4   19  1  1.1988e+02  4.0334e+02 ;   C1 - C2  - H1
3   8   7   1  1.2002e+02  5.5731e+02 ;   C1 - C6  - C5
3   8   23  1  1.1988e+02  4.0334e+02 ;   C1 - C6  - H5
4   3   8   1  1.2002e+02  5.5731e+02 ;   C2 - C1  - C6
4   5   6   1  1.2002e+02  5.5731e+02 ;   C2 - C3  - C4
4   5   20  1  1.1988e+02  4.0334e+02 ;   C2 - C3  - H2
5   4   19  1  1.1988e+02  4.0334e+02 ;   C3 - C2  - H1
5   6   7   1  1.2002e+02  5.5731e+02 ;   C3 - C4  - C5
5   6   21  1  1.1988e+02  4.0334e+02 ;   C3 - C4  - H3
6   5   20  1  1.1988e+02  4.0334e+02 ;   C4 - C3  - H2
6   7   8   1  1.2002e+02  5.5731e+02 ;   C4 - C5  - C6
6   7   22  1  1.1988e+02  4.0334e+02 ;   C4 - C5  - H4
7   6   21  1  1.1988e+02  4.0334e+02 ;   C5 - C4  - H3
7   8   23  1  1.1988e+02  4.0334e+02 ;   C5 - C6  - H5
8   7   22  1  1.1988e+02  4.0334e+02 ;   C6 - C5  - H4
9   2   10  1  1.1924e+02  5.2300e+02 ;   C7 - C   - C8
9   11  12  1  1.2002e+02  5.5731e+02 ;   C7 - C9  - C10
9   11  27  1  1.1988e+02  4.0334e+02 ;   C7 - C9  - H9
9   15  14  1  1.2002e+02  5.5731e+02 ;   C7 - C13  - C12
9   15  30  1  1.1988e+02  4.0334e+02 ;   C7 - C13  - H12
11  9   15  1  1.2002e+02  5.5731e+02 ;   C9 - C7  - C13
```

```
    11    12    13     1    1.2002e+02    5.5731e+02 ;     C9 - C10    - C11
    11    12    28     1    1.1988e+02    4.0334e+02 ;     C9 - C10    - H10
    12    11    27     1    1.1988e+02    4.0334e+02 ;    C10 - C9     - H9
    12    13    14     1    1.2002e+02    5.5731e+02 ;    C10 - C11    - C12
    12    13    16     1    1.1920e+02    5.8241e+02 ;    C10 - C11    - O
    13    12    28     1    1.1988e+02    4.0334e+02 ;    C11 - C10    - H10
    13    14    15     1    1.2002e+02    5.5731e+02 ;    C11 - C12    - C13
    13    14    29     1    1.1988e+02    4.0334e+02 ;    C11 - C12    - H11
    13    16    17     1    1.1796e+02    5.2300e+02 ;    C11 - O     - C14
    14    13    16     1    1.1920e+02    5.8241e+02 ;    C12 - C11    - O
    14    15    30     1    1.1988e+02    4.0334e+02 ;    C12 - C13    - H12
    15    14    29     1    1.1988e+02    4.0334e+02 ;    C13 - C12    - H11
    16    17    31     1    1.0978e+02    4.2509e+02 ;      O - C14    - H13
    16    17    32     1    1.0978e+02    4.2509e+02 ;      O - C14    - H14
    16    17    33     1    1.0978e+02    4.2509e+02 ;      O - C14    - H15
    24    10    25     1    1.0758e+02    3.2970e+02 ;     H6 - C8     - H7
    24    10    26     1    1.0758e+02    3.2970e+02 ;     H6 - C8     - H8
    25    10    26     1    1.0758e+02    3.2970e+02 ;     H7 - C8     - H8
    31    17    32     1    1.0846e+02    3.2803e+02 ;    H13 - C14    - H14
    31    17    33     1    1.0846e+02    3.2803e+02 ;    H13 - C14    - H15
    32    17    33     1    1.0846e+02    3.2803e+02 ;    H14 - C14    - H15

[ dihedrals ] ; propers
; for gromacs 4.5 or higher, using funct 9
;    i     j     k     l  func   phase     kd      pn
     1     2     9    11     9  180.00   2.92880   2 ;     N-    C-    C7-    C9
     1     2     9    15     9  180.00   2.92880   2 ;     N-    C-    C7-   C13
     1     2    10    24     9    0.00   0.00000   0 ;     N-    C-    C8-    H6
     1     2    10    25     9    0.00   0.00000   0 ;     N-    C-    C8-    H7
     1     2    10    26     9    0.00   0.00000   0 ;     N-    C-    C8-    H8
```

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```
1    3    4    5    9  180.00  15.16700   2 ;    N-   C1-   C2-   C3
1    3    4    19    9  180.00  15.16700   2 ;    N-   C1-   C2-   H1
1    3    8    7    9  180.00  15.16700   2 ;    N-   C1-   C6-   C5
1    3    8    23    9  180.00  15.16700   2 ;    N-   C1-   C6-   H5
2    1    3    4    9  180.00   1.25520   2 ;    C-   N-   C1-   C2
2    1    3    8    9  180.00   1.25520   2 ;    C-   N-   C1-   C6
2    9    11    12    9  180.00  15.16700   2 ;    C-   C7-   C9-  C10
2    9    11    27    9  180.00  15.16700   2 ;    C-   C7-   C9-   H9
2    9    15    14    9  180.00  15.16700   2 ;    C-   C7-  C13-  C12
2    9    15    30    9  180.00  15.16700   2 ;    C-   C7-  C13-  H12
3    1    2    9    9  180.00   7.11280   2 ;   C1-    N-    C-   C7
3    1    2    10    9  180.00   7.11280   2 ;   C1-    N-    C-   C8
3    4    5    6    9  180.00  15.16700   2 ;   C1-   C2-   C3-   C4
3    4    5    20    9  180.00  15.16700   2 ;   C1-   C2-   C3-   H2
3    8    7    6    9  180.00  15.16700   2 ;   C1-   C6-   C5-   C4
3    8    7    22    9  180.00  15.16700   2 ;   C1-   C6-   C5-   H4
4    3    8    7    9  180.00  15.16700   2 ;   C2-   C1-   C6-   C5
4    3    8    23    9  180.00  15.16700   2 ;   C2-   C1-   C6-   H5
4    5    6    7    9  180.00  15.16700   2 ;   C2-   C3-   C4-   C5
4    5    6    21    9  180.00  15.16700   2 ;   C2-   C3-   C4-   H3
5    4    3    8    9  180.00  15.16700   2 ;   C3-   C2-   C1-   C6
5    6    7    8    9  180.00  15.16700   2 ;   C3-   C4-   C5-   C6
5    6    7    22    9  180.00  15.16700   2 ;   C3-   C4-   C5-   H4
6    5    4    19    9  180.00  15.16700   2 ;   C4-   C3-   C2-   H1
6    7    8    23    9  180.00  15.16700   2 ;   C4-   C5-   C6-   H5
7    6    5    20    9  180.00  15.16700   2 ;   C5-   C4-   C3-   H2
8    3    4    19    9  180.00  15.16700   2 ;   C6-   C1-   C2-   H1
8    7    6    21    9  180.00  15.16700   2 ;   C6-   C5-   C4-   H3
9    2    10    24    9    0.00   0.00000   0 ;   C7-    C-   C8-   H6
9    2    10    24    9    0.00   4.81160   1 ;   C7-    C-   C8-   H6
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 9    2   10   24    9  180.00   1.58992   3 ;    C7-    C-   C8-    H6
 9    2   10   25    9    0.00   0.00000   0 ;    C7-    C-   C8-    H7
 9    2   10   25    9    0.00   4.81160   1 ;    C7-    C-   C8-    H7
 9    2   10   25    9  180.00   1.58992   3 ;    C7-    C-   C8-    H7
 9    2   10   26    9    0.00   0.00000   0 ;    C7-    C-   C8-    H8
 9    2   10   26    9    0.00   4.81160   1 ;    C7-    C-   C8-    H8
 9    2   10   26    9  180.00   1.58992   3 ;    C7-    C-   C8-    H8
 9   11   12   13    9  180.00  15.16700   2 ;    C7-   C9-  C10-   C11
 9   11   12   28    9  180.00  15.16700   2 ;    C7-   C9-  C10-   H10
 9   15   14   13    9  180.00  15.16700   2 ;    C7-  C13-  C12-   C11
 9   15   14   29    9  180.00  15.16700   2 ;    C7-  C13-  C12-   H11
10    2    9   11    9  180.00   2.92880   2 ;    C8-    C-   C7-    C9
10    2    9   15    9  180.00   2.92880   2 ;    C8-    C-   C7-   C13
11    9   15   14    9  180.00  15.16700   2 ;    C9-   C7-  C13-   C12
11    9   15   30    9  180.00  15.16700   2 ;    C9-   C7-  C13-   H12
11   12   13   14    9  180.00  15.16700   2 ;    C9-  C10-  C11-   C12
11   12   13   16    9  180.00  15.16700   2 ;    C9-  C10-  C11-     O
12   11    9   15    9  180.00  15.16700   2 ;   C10-   C9-   C7-   C13
12   13   14   15    9  180.00  15.16700   2 ;   C10-  C11-  C12-   C13
12   13   14   29    9  180.00  15.16700   2 ;   C10-  C11-  C12-   H11
12   13   16   17    9  180.00   3.76560   2 ;   C10-  C11-    O-   C14
13   12   11   27    9  180.00  15.16700   2 ;   C11-  C10-   C9-    H9
13   14   15   30    9  180.00  15.16700   2 ;   C11-  C12-  C13-   H12
13   16   17   31    9    0.00   1.60387   3 ;   C11-    O-  C14-   H13
13   16   17   32    9    0.00   1.60387   3 ;   C11-    O-  C14-   H14
13   16   17   33    9    0.00   1.60387   3 ;   C11-    O-  C14-   H15
14   13   12   28    9  180.00  15.16700   2 ;   C12-  C11-  C10-   H10
14   13   16   17    9  180.00   3.76560   2 ;   C12-  C11-    O-   C14
15    9   11   27    9  180.00  15.16700   2 ;   C13-   C7-   C9-    H9
15   14   13   16    9  180.00  15.16700   2 ;   C13-  C12-  C11-     O
```

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  16    13    12    28     9  180.00  15.16700   2 ;     O-  C11-  C10-  H10
  16    13    14    29     9  180.00  15.16700   2 ;     O-  C11-  C12-  H11
  18     1     2     9     9  180.00   7.11280   2 ;     H-    N-    C-   C7
  18     1     2    10     9  180.00   7.11280   2 ;     H-    N-    C-   C8
  18     1     3     4     9  180.00   1.25520   2 ;     H-    N-   C1-   C2
  18     1     3     8     9  180.00   1.25520   2 ;     H-    N-   C1-   C6
  19     4     5    20     9  180.00  15.16700   2 ;    H1-   C2-   C3-   H2
  20     5     6    21     9  180.00  15.16700   2 ;    H2-   C3-   C4-   H3
  21     6     7    22     9  180.00  15.16700   2 ;    H3-   C4-   C5-   H4
  22     7     8    23     9  180.00  15.16700   2 ;    H4-   C5-   C6-   H5
  27    11    12    28     9  180.00  15.16700   2 ;    H9-   C9-  C10-  H10
  29    14    15    30     9  180.00  15.16700   2 ;   H11-  C12-  C13-  H12

[ dihedrals ] ; impropers
; treated as propers in GROMACS to use correct AMBER analytical function
;   i     j     k     l  func  phase     kd    pn
   1     2     9    10     4  180.00   4.60240   2 ;     N-    C-   C7-   C8
   1     3     8     4     4  180.00   4.60240   2 ;     N-   C1-   C6-   C2
   3     5     4    19     4  180.00   4.60240   2 ;    C1-   C3-   C2-   H1
   3     7     8    23     4  180.00   4.60240   2 ;    C1-   C5-   C6-   H5
   4     6     5    20     4  180.00   4.60240   2 ;    C2-   C4-   C3-   H2
   5     7     6    21     4  180.00   4.60240   2 ;    C3-   C5-   C4-   H3
   6     8     7    22     4  180.00   4.60240   2 ;    C4-   C6-   C5-   H4
   9    12    11    27     4  180.00   4.60240   2 ;    C7-  C10-   C9-   H9
   9    14    15    30     4  180.00   4.60240   2 ;    C7-  C12-  C13-  H12
  11    13    12    28     4  180.00   4.60240   2 ;    C9-  C11-  C10-  H10
  11    15     9     2     4  180.00   4.60240   2 ;    C9-  C13-   C7-    C
  12    14    13    16     4  180.00   4.60240   2 ;   C10-  C12-  C11-    O
  13    15    14    29     4  180.00   4.60240   2 ;   C11-  C13-  C12-  H11
  18     1     2     3     4  180.00   4.60240   2 ;     H-    N-    C-   C1
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```
DCM

[ atomtypes ]
 c3s      c3s         0.00000  0.00000   A     3.39967e-01   4.57730e-01
 cls      cls         0.00000  0.00000   A     3.30000e-01   1.20000e+00
 h2s      h2s         0.00000  0.00000   V     2.29317e-01   6.56888e-02
[ moleculetype ]
;name           nrexcl2
 DCM          3

[ atoms ]
;   nr  type  resi  res  atom  cgnr     charge      mass     ;
     1   c3s     1   DCM     Cs    1    -0.137416     14.01000 ;
     2   cls     1   DCM    Cls    2    -0.117537     35.45000 ;
     3   h2s     1   DCM     Hs    3     0.184786      0.00000 ;
     4   cls     1   DCM   Cls1    4    -0.115826     35.45000 ;
     5   h2s     1   DCM    Hs1    5     0.185993      0.00000 ;

[ bonds ]

        ;   ai     aj funct   r            k
            1      2   1    1.7860e-01    2.3347e+05 ;      C - cl2s
            1      4   1    1.7860e-01    2.3347e+05 ;      C - cl2s1



        [ angles ]
        ;   ai     aj     ak    funct   theta         cth
            2      1      4      1    1.1103e+02    4.5380e+02 ;     cl2s - C      - cl2s1

        [ virtual\_sites3 ]
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```
; Site  from              funct   a          b          c

3      1     2    4      4     -0.2831048825030728 -0.2831048825030728 -
3.154641146073173
5      1     2    4      4     -0.2831048825030728 -0.2831048825030728
3.154641146073173

[ exclusions ]

3 1 2  4 5
5 1 2 3 4
```

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DFT structure optimization results based on the MD-structure motif, which was identified with possible NOE-contacts

Final energy, structure and Mayer bond orders for the optimized neutral complex consisting of both NTPA and E-imin

The structure optimization based on a MD-snapshot was followed with a numerical frequency calculation (in ORCA 5.0.2 with B3LYP D3BJ def2-TZVP CPCM(CH2Cl2) NUMFREQ defgrid3). It yielded the following:

```
-------------------------   ----------------
Dispersion correction           -0.333128479
-------------------------   ----------------
-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -4798.906228846667
-------------------------   --------------------
```

All vibrational frequencies were shown to be positive, which let's us assume that the MD structure (corresponding to possible NOE-signals) found is actually a minimum structure. The fact that the H-bond H atom remains does not change its positioning is a good indication that the H-bond situation is as described (at least a local minimum exists that corresponds to the structure). While this is of course no proof, a more in-depth investigation (using e.g. relaxed scans) was not feasible. However, together with the experimental results this is a good indication. *Figure S71* shows the optimized structure, and the coordinates are given below:

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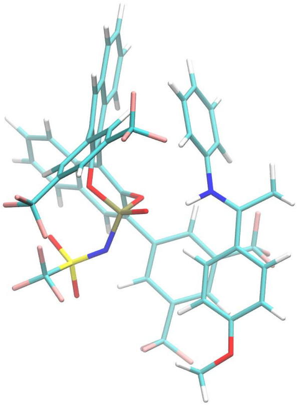

Figure S71: Optimized complex structure based on the MD-structure motif, related to the supposed NOE contacts.

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For comparison with the bond situation of the pure NTPA anion, the Mayer bond orders are given again for the obtained neutral iminium-NTPA complex: it is clear that the model used for the N- in the ff-MD should still hold true, because no fundamental changes occur in the vicinity.

```
Mayer bond orders larger than 0.100000
B(  0-N ,  1-C ) :   1.5470 B(  0-N ,  2-C ) :   0.8552 B(  0-N , 17-H ) :   0.8037
B(  1-C ,  8-C ) :   1.0361 B(  1-C ,  9-C ) :   1.0001 B(  2-C ,  3-C ) :   1.3750
B(  2-C ,  7-C ) :   1.3821 B(  3-C ,  4-C ) :   1.4143 B(  3-C , 18-H ) :   0.9644
B(  4-C ,  5-C ) :   1.3668 B(  4-C , 19-H ) :   0.9677 B(  5-C ,  6-C ) :   1.3778
B(  5-C , 20-H ) :   0.9672 B(  6-C ,  7-C ) :   1.3904 B(  6-C , 21-H ) :   0.9821
B(  7-C , 22-H ) :   0.9510 B(  8-C , 10-C ) :   1.2898 B(  8-C , 14-C ) :   1.2263
B(  9-C , 23-H ) :   0.9370 B(  9-C , 24-H ) :   0.9631 B(  9-C , 25-H ) :   0.9385
B( 10-C , 11-C ) :   1.5299 B( 10-C , 26-H ) :   0.8795 B( 11-C , 12-C ) :   1.2396
B( 11-C , 27-H ) :   0.9540 B( 12-C , 13-C ) :   1.2912 B( 12-C , 15-O ) :   1.1794
B( 13-C , 14-C ) :   1.5107 B( 13-C , 28-H ) :   0.9920 B( 14-C , 29-H ) :   0.9803
B( 15-O , 16-C ) :   0.8887 B( 16-C , 30-H ) :   0.9644 B( 16-C , 31-H ) :   0.9656
B( 16-C , 32-H ) :   0.9609 B( 17-H , 34-O ) :   0.1353 B( 33-P , 34-O ) :   1.7549
B( 33-P , 35-N ) :   1.3537 B( 33-P , 36-O ) :   0.9931 B( 33-P , 37-O ) :   1.0822
B( 35-N , 60-S ) :   1.3320 B( 36-O , 39-C ) :   0.7766 B( 37-O , 49-C ) :   0.8516
B( 38-C , 39-C ) :   1.4428 B( 38-C , 47-C ) :   1.0422 B( 38-C , 48-C ) :   0.7864
B( 39-C , 40-C ) :   1.2752 B( 40-C , 41-C ) :   1.4469 B( 40-C , 59-C ) :   0.8348
B( 41-C , 42-C ) :   1.2124 B( 41-C , 93-H ) :   0.9974 B( 42-C , 43-C ) :   1.2126
B( 42-C , 47-C ) :   1.2768 B( 43-C , 44-C ) :   1.5125 B( 43-C , 94-H ) :   0.9871
B( 44-C , 45-C ) :   1.2502 B( 44-C , 95-H ) :   0.9804 B( 45-C , 46-C ) :   1.5353
B( 45-C , 96-H ) :   0.9784 B( 46-C , 47-C ) :   1.2495 B( 46-C , 97-H ) :   0.9675
B( 48-C , 49-C ) :   1.4454 B( 48-C , 57-C ) :   1.0635 B( 49-C , 50-C ) :   1.2759
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B( 50-C , 51-C ) :   1.3974 B( 50-C , 58-C ) :   0.8896 B( 51-C , 52-C ) :   1.1910
B( 51-C , 98-H ) :   1.0111 B( 52-C , 53-C ) :   1.2041 B( 52-C , 57-C ) :   1.2298
B( 53-C , 54-C ) :   1.5091 B( 53-C , 99-H ) :   0.9919 B( 54-C , 55-C ) :   1.2411
B( 54-C ,100-H ) :   0.9848 B( 55-C , 56-C ) :   1.5257 B( 55-C ,101-H ) :   0.9806
B( 56-C , 57-C ) :   1.2478 B( 56-C ,102-H ) :   0.9776 B( 58-C , 72-C ) :   1.2915
B( 58-C , 76-C ) :   1.3964 B( 59-C , 67-C ) :   1.3874 B( 59-C , 71-C ) :   1.3105
B( 60-S , 61-O ) :   1.7859 B( 60-S , 62-O ) :   1.7941 B( 60-S , 63-C ) :   0.8518
B( 63-C , 64-F ) :   1.1262 B( 63-C , 65-F ) :   1.1191 B( 63-C , 66-F ) :   1.1101
B( 67-C , 68-C ) :   1.3374 B( 67-C ,103-H ) :   0.9451 B( 68-C , 69-C ) :   1.3418
B( 68-C , 81-C ) :   1.0033 B( 69-C , 70-C ) :   1.2812 B( 69-C ,104-H ) :   0.9742
B( 70-C , 71-C ) :   1.3550 B( 70-C , 77-C ) :   1.0110 B( 71-C ,105-H ) :   0.9708
B( 72-C , 73-C ) :   1.3855 B( 72-C ,106-H ) :   0.9674 B( 73-C , 74-C ) :   1.3213
B( 73-C , 89-C ) :   1.0075 B( 74-C , 75-C ) :   1.3472 B( 74-C ,107-H ) :   0.9593
B( 75-C , 76-C ) :   1.3686 B( 75-C , 85-C ) :   1.0035 B( 76-C ,108-H ) :   0.9307
B( 77-C , 78-F ) :   1.0804 B( 77-C , 79-F ) :   1.1509 B( 77-C , 80-F ) :   1.0947
B( 81-C , 82-F ) :   1.1010 B( 81-C , 83-F ) :   1.0990 B( 81-C , 84-F ) :   1.1341
B( 85-C , 86-F ) :   1.1350 B( 85-C , 87-F ) :   1.1293 B( 85-C , 88-F ) :   1.1307
B( 89-C , 90-F ) :   1.1182 B( 89-C , 91-F ) :   1.1151 B( 89-C , 92-F ) :   1.1287
```

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CARTESIAN COORDINATES (ANGSTROEM)
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  N    16.972588   19.993525   16.995068
  C    15.751628   19.706079   16.633159
  C    17.452732   21.211402   17.558156
  C    18.582937   21.795523   16.995924
  C    19.109955   22.943701   17.569733
  C    18.525455   23.490859   18.707039
  C    17.406030   22.888622   19.271234
  C    16.864586   21.743991   18.700285
  C    15.426904   18.327946   16.317053
  C    14.714254   20.770450   16.554805
  C    16.139491   17.274555   16.911274
  C    15.839231   15.954272   16.645012
  C    14.800471   15.650425   15.757433
  C    14.065608   16.690075   15.166551
  C    14.366710   18.001718   15.449986
  O    14.429975   14.403734   15.425565
  C    15.152619   13.296332   15.980159
  H    17.719715   19.284456   16.869863
  H    19.039746   21.348180   16.123808
  H    19.987936   23.401817   17.136475
  H    18.956389   24.370550   19.165305
  H    16.961076   23.299239   20.168111
  H    16.012741   21.253007   19.149522
  H    13.995852   20.646763   17.366715
  H    15.148102   21.764168   16.609596
  H    14.160551   20.670536   15.622305
  H    16.906575   17.482385   17.639200
  H    16.396998   15.176536   17.143134
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H	13.263549	16.439065	14.485506
H	13.790411	18.780034	14.971496
H	16.206755	13.345862	15.702138
H	14.697919	12.407511	15.552500
H	15.055417	13.278067	17.065789
P	19.726120	18.011149	18.114085
O	19.226384	18.449466	16.791644
N	19.704283	16.439168	18.351236
O	18.807004	18.764718	19.218562
O	21.200409	18.542447	18.473446
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C	19.174604	18.645698	20.554808
C	18.400522	17.791764	21.372985
C	18.833722	17.560228	22.654340
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C	20.489067	17.859237	24.452314
C	21.657400	18.405485	24.915535
C	22.410842	19.261996	24.085516
C	21.975580	19.573746	22.822459
C	20.762745	19.043355	22.319549
C	20.978096	20.274707	20.095576
C	21.419717	19.859536	18.859109
C	22.087788	20.711665	17.945140
C	22.314004	22.011527	18.329124
C	21.843262	22.514437	19.559843
C	22.009596	23.879080	19.900283
C	21.470770	24.384638	21.053930
C	20.735979	23.541698	21.913909
C	20.575706	22.211088	21.621569
C	21.137294	21.651361	20.448730

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C	22.480296	20.242568	16.598066
C	17.137264	17.198254	20.870769
S	20.535505	15.487106	19.250130
O	21.378367	16.107733	20.247030
O	19.746043	14.350096	19.666633
C	21.741404	14.755896	18.033671
F	22.531548	13.865891	18.648598
F	21.102119	14.131690	17.036678
F	22.516048	15.710946	17.503905
C	16.978468	15.820474	20.787611
C	15.766010	15.279513	20.363448
C	14.700353	16.098080	20.031755
C	14.860900	17.478458	20.120796
C	16.068135	18.028040	20.521533
C	23.173782	19.043815	16.406093
C	23.534536	18.642850	15.129235
C	23.205065	19.411455	14.015805
C	22.518773	20.599492	14.206833
C	22.159038	21.015355	15.485236
C	13.678644	18.354348	19.822142
F	14.006465	19.659613	19.730313
F	12.729939	18.262432	20.785337
F	13.072419	18.017262	18.662463
C	15.642886	13.784949	20.265480
F	16.501279	13.266224	19.356839
F	14.407359	13.386661	19.904872
F	15.924179	13.179088	21.441788
C	22.116532	21.452665	13.037324
F	22.646689	21.030841	11.875039
F	22.493996	22.742081	13.199850

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F	20.771196	21.471913	12.870487
C	24.259398	17.342080	14.921340
F	23.416167	16.354601	14.532889
F	24.876567	16.909156	16.036333
F	25.202400	17.436047	13.957774
H	18.259729	16.912351	23.305150
H	19.909258	17.186218	25.072190
H	22.011597	18.172967	25.911611
H	23.344971	19.672422	24.447528
H	22.569874	20.222659	22.195872
H	22.838017	22.682685	17.660263
H	22.554740	24.519146	19.217256
H	21.592961	25.431365	21.301176
H	20.289126	23.951140	22.810984
H	20.001569	21.582584	22.286220
H	17.808398	15.171354	21.029385
H	13.761438	15.675291	19.705734
H	16.184642	19.100383	20.584072
H	23.439042	18.435895	17.257174
H	23.483871	19.088610	13.023561
H	21.611256	21.938799	15.615934

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Final energy, structure and Mayer bond orders for the anion structure used for the force field creation

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Dispersion correction           -0.222525384
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FINAL SINGLE POINT ENERGY     -4087.914862335938
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CARTESIAN COORDINATES (ANGSTROEM)
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  P      1.561825    0.232380    0.403192
  O      2.702716   -0.633039    0.739012
  N      1.866703    1.800999    0.386125
  O      0.379086   -0.095533    1.469782
  O      0.865888   -0.093207   -1.019326
  C     -1.650776   -0.029601    0.235309
  C     -0.886040    0.439070    1.281428
  C     -1.359678    1.401076    2.212647
  C     -2.590439    1.967138    1.973612
  C     -3.354517    1.638699    0.834429
  C     -4.577872    2.298021    0.558599
  C     -5.302194    1.991318   -0.563281
  C     -4.823703    1.015224   -1.462908
  C     -3.650251    0.349159   -1.214774
  C     -2.887644    0.626398   -0.054210
  C     -1.195978   -1.191888   -0.570921
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C	0.028318	-1.177326	-1.202702
C	0.440715	-2.184982	-2.113685
C	-0.398970	-3.255242	-2.310870
C	-1.611325	-3.389300	-1.600905
C	-2.423553	-4.540129	-1.753123
C	-3.579988	-4.683314	-1.032228
C	-3.964736	-3.680550	-0.117444
C	-3.206792	-2.547772	0.040694
C	-2.018140	-2.356286	-0.705470
C	1.700253	-2.070712	-2.886253
C	-0.627623	1.731026	3.460206
S	1.238107	2.994469	-0.373960
O	-0.045237	2.768187	-1.002253
O	1.395655	4.220281	0.377138
C	2.401510	3.215996	-1.814481
F	2.426371	2.120059	-2.584876
F	2.003679	4.250145	-2.570623
F	3.649633	3.460573	-1.395361
C	-1.328630	1.713099	4.670104
C	-0.690185	2.018669	5.864239
C	0.661312	2.342578	5.886117
C	1.356233	2.363625	4.685973
C	0.725171	2.066361	3.483581
C	1.670748	-2.253742	-4.268784
C	2.837604	-2.162019	-5.019662
C	4.053378	-1.884127	-4.411632
C	4.082226	-1.706498	-3.033795
C	2.924420	-1.798156	-2.272905
C	2.829444	2.662122	4.668096
F	3.249171	3.270006	5.796549

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F	3.176140	3.458368	3.636056
F	3.566234	1.530363	4.542734
C	-1.470210	2.040862	7.147677
F	-2.561676	1.250680	7.104453
F	-1.911327	3.289574	7.445960
F	-0.731766	1.638078	8.203781
C	5.374637	-1.359669	-2.348990
F	6.455227	-1.709560	-3.077793
F	5.495670	-1.963812	-1.149084
F	5.479103	-0.027356	-2.120623
C	2.766973	-2.394425	-6.501784
F	1.722703	-1.750828	-7.069240
F	2.607245	-3.709215	-6.797920
F	3.877544	-1.987285	-7.145829
H	-2.978305	2.709009	2.660234
H	-4.922874	3.057770	1.249548
H	-6.233205	2.503586	-0.769745
H	-5.385802	0.794458	-2.361539
H	-3.293475	-0.387514	-1.919560
H	-0.112364	-4.038565	-3.001422
H	-2.103986	-5.309644	-2.445454
H	-4.192612	-5.567810	-1.151276
H	-4.865232	-3.808892	0.469832
H	-3.513202	-1.794799	0.751731
H	-2.374511	1.440818	4.675154
H	1.158795	2.570382	6.817288
H	1.287222	2.116951	2.564437
H	0.727782	-2.450613	-4.760767
H	4.956969	-1.806178	-4.996905
H	2.976617	-1.661428	-1.202022

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Mayer bond orders larger than 0.100000
B(  0-P ,  1-O ) :   1.9986 B(  0-P ,  2-N ) :   1.2713 B(  0-P ,  3-O ) :   1.0469
B(  0-P ,  4-O ) :   1.0315 B(  2-N , 27-S ) :   1.3392 B(  3-O ,  6-C ) :   0.9710
B(  4-O , 16-C ) :   0.9236 B(  5-C ,  6-C ) :   1.4642 B(  5-C , 14-C ) :   1.1051
B(  5-C , 15-C ) :   0.8586 B(  6-C ,  7-C ) :   1.2690 B(  7-C ,  8-C ) :   1.4547
B(  7-C , 26-C ) :   0.8981 B(  8-C ,  9-C ) :   1.1987 B(  8-C , 60-H ) :   0.9744
B(  9-C , 10-C ) :   1.2088 B(  9-C , 14-C ) :   1.2588 B( 10-C , 11-C ) :   1.5162
B( 10-C , 61-H ) :   0.9887 B( 11-C , 12-C ) :   1.2473 B( 11-C , 62-H ) :   0.9822
B( 12-C , 13-C ) :   1.5357 B( 12-C , 63-H ) :   0.9791 B( 13-C , 14-C ) :   1.2541
B( 13-C , 64-H ) :   0.9649 B( 15-C , 16-C ) :   1.4650 B( 15-C , 24-C ) :   1.0636
B( 16-C , 17-C ) :   1.2815 B( 17-C , 18-C ) :   1.4609 B( 17-C , 25-C ) :   0.9059
B( 18-C , 19-C ) :   1.2045 B( 18-C , 65-H ) :   0.9842 B( 19-C , 20-C ) :   1.2102
B( 19-C , 24-C ) :   1.2651 B( 20-C , 21-C ) :   1.5136 B( 20-C , 66-H ) :   0.9883
B( 21-C , 22-C ) :   1.2480 B( 21-C , 67-H ) :   0.9822 B( 22-C , 23-C ) :   1.5365
B( 22-C , 68-H ) :   0.9793 B( 23-C , 24-C ) :   1.2546 B( 23-C , 69-H ) :   0.9690
B( 25-C , 39-C ) :   1.3667 B( 25-C , 43-C ) :   1.3358 B( 26-C , 34-C ) :   1.3501
B( 26-C , 38-C ) :   1.3338 B( 27-S , 28-O ) :   1.7884 B( 27-S , 29-O ) :   1.8262
B( 27-S , 30-C ) :   0.8530 B( 30-C , 31-F ) :   1.1099 B( 30-C , 32-F ) :   1.1184
B( 30-C , 33-F ) :   1.1177 B( 34-C , 35-C ) :   1.3720 B( 34-C , 70-H ) :   0.9528
B( 35-C , 36-C ) :   1.3297 B( 35-C , 48-C ) :   1.0054 B( 36-C , 37-C ) :   1.3312
B( 36-C , 71-H ) :   0.9660 B( 37-C , 38-C ) :   1.3988 B( 37-C , 44-C ) :   1.0110
B( 38-C , 72-H ) :   0.9042 B( 39-C , 40-C ) :   1.3664 B( 39-C , 73-H ) :   0.9567
B( 40-C , 41-C ) :   1.3423 B( 40-C , 56-C ) :   1.0068 B( 41-C , 42-C ) :   1.3265
B( 41-C , 74-H ) :   0.9603 B( 42-C , 43-C ) :   1.4048 B( 42-C , 52-C ) :   1.0079
B( 43-C , 75-H ) :   0.9156 B( 44-C , 45-F ) :   1.1298 B( 44-C , 46-F ) :   1.1337
B( 44-C , 47-F ) :   1.1315 B( 48-C , 49-F ) :   1.1299 B( 48-C , 50-F ) :   1.1402
B( 48-C , 51-F ) :   1.1302 B( 52-C , 53-F ) :   1.1264 B( 52-C , 54-F ) :   1.1290
B( 52-C , 55-F ) :   1.1316 B( 56-C , 57-F ) :   1.1321 B( 56-C , 58-F ) :   1.1378
B( 56-C , 59-F ) :   1.1328
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