Bidentate Substrate Binding in Brønsted Acid Catalysis: Structural Space, Hydrogen Bonding and Dimerization

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1. General information

1.1 Chemicals

Deuterated solvents were purchased from Deutero or Sigma Aldrich. Where dry solvents were essential, CD_2Cl_2 was freshly distilled over CaH_2 and Toluene-d_8 was refluxed over Na/Benzophenone under argon atmosphere. Non-deuterated toluene was refluxed over Na/Benzophenone under Argon atmosphere or purchased by Sigma Aldrich (dry, stored over molecular sieve). All commercially available chemicals were purchased by Sigma Aldrich or abcr and used without further purification.

1.2 Sample preparation

The chiral phosphoric acid was weighed into a 5 mm NMR tube and dried at 150 °C for at least 20 min under reduced pressure. After the tube came to room temperature, the respective imine was weighed directly into the NMR tube. The tube was evacuated and flushed with Argon three times. Dry CD_2Cl_2 (0.6 mL) was added under Argon flow and TMS atmosphere (0.5 mL) was added. The tube was closed and sealed with parafilm. The samples were stored in the fridge at -80 °C.

For the preparation of the "*E*-only sample", prior to adding the solvent the tube was cooled to -80 °C in an acetone/liquid nitrogen bath. Under Argon flow, cooled CD_2Cl_2 (0.6 mL) was added to the CPA and imine. TMS atmosphere (0.5 mL) was added and the tube was closed and sealed with parafilm. The samples were stored in the fridge at -80 °C. *E*-only samples were transported at -80 °C in an acetone/liquid nitrogen cooling bath and only inserted in a pre-cooled spectrometer at 180 K.

For the *in situ* UV VIS illumination experiments, a glass fiber based illumination setup developed by our group was employed.[1,2] The sample preparation was analogous, except only 0.35 mL of solvent were used. After solvation, the glass fiber was inserted into the ambered tube and fixated with parafilm.

1.3 NMR spectrometer, data procession and referencing

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 $^{1}H/^{19}F$-BB probe head with Z-gradient and BVT unit. Temperature was controlled in the VT-

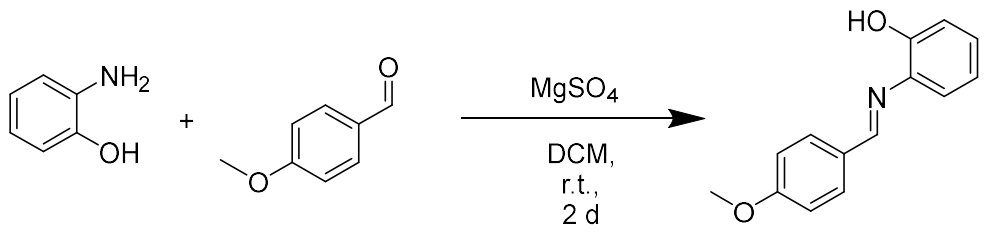
experiments by a BVT 3000 and BVT 3900 unit and liquid nitrogen. Further NMR experiments were performed on Bruker Avance III HD 400 MHz spectrometer equipped with 5 mm BBO BB-1H/D probe head with Z-Gradients. Spectrometer control and spectra processing was performed with Bruker Software TopSpin (Version 3.2 PL 1). Further plotting of the spectra was performed with Corel Draw 2020 software. ^{1}H,^{13}C chemical shifts were referenced to TMS or the respective solvent signals. The heteronucleus ^{31}P was referenced, employing $\nu(X) = \nu(TMS) \cdot \Xi_{reference} / 100\ \%$ according to Harris et al.[3] The following frequency ratios and reference compounds was used: $\Xi(^{31}P) = 40.480742$ (H_3PO_4). For all NMR measurements, 5 mm NMR tubes were used.

1.4 Pulse sequences and acquisition parameters

^{1}H-NMR: Pulse program zg30, Relaxation delay = 2.00 s, Acquisition time = 2.54 s, SW = 22 – 24 ppm, TD = 66 K, ns = 16 – 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; ^{31}P-NMR: Pulse program: zgpg30; Relaxation delay = 1.00 s, Acquisition time = 2.25 s, SW =20 - 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) = 300.00 ms; TD = 4096; increments = 512 - 1k; 2D-^{1}H,^{1}H ROESY: Pulse program: roesyphpr.2; Relaxation delay = 5.00 s, NS = 8, mixing time (D8) = 100.00 ms; TD = 4096; increments = 1k; 2D-^{1}H,^{1}H COSY: Pulse program: cosygpqf; Relaxation delay = 5.00 s, NS = 4-16, TD = 4096; increments = 512; 2D-^{1}H,^{13}C HSQC: Pulse program: hsqcedetgpsisp2.3; Relaxation delay = 4 - 8 s, NS = 8-32, $^{1}J_{XH}$ = 145 Hz; TD = 4096; increments = 512 - 1k; 2D-^{1}H,^{13}C HMBC: Pulse program: hmbcgplpndqf; Relaxation delay = 4.00 s, NS = 8-16, $^{1}J_{XH}$ = 145 Hz, J_{XH}(long range) = 10 Hz; TD = 4096; increments = 512 - 1k; 2D-^{1}H,^{31}P HMBC: Pulse program: inv4gplrndqf; Relaxation delay = 6.00 s, NS = 4-32, TD = 4096; increments = 256 – 512

2. Imine synthesis

(E)-2-((4-methoxybenzylidene)amino)phenol (2a)

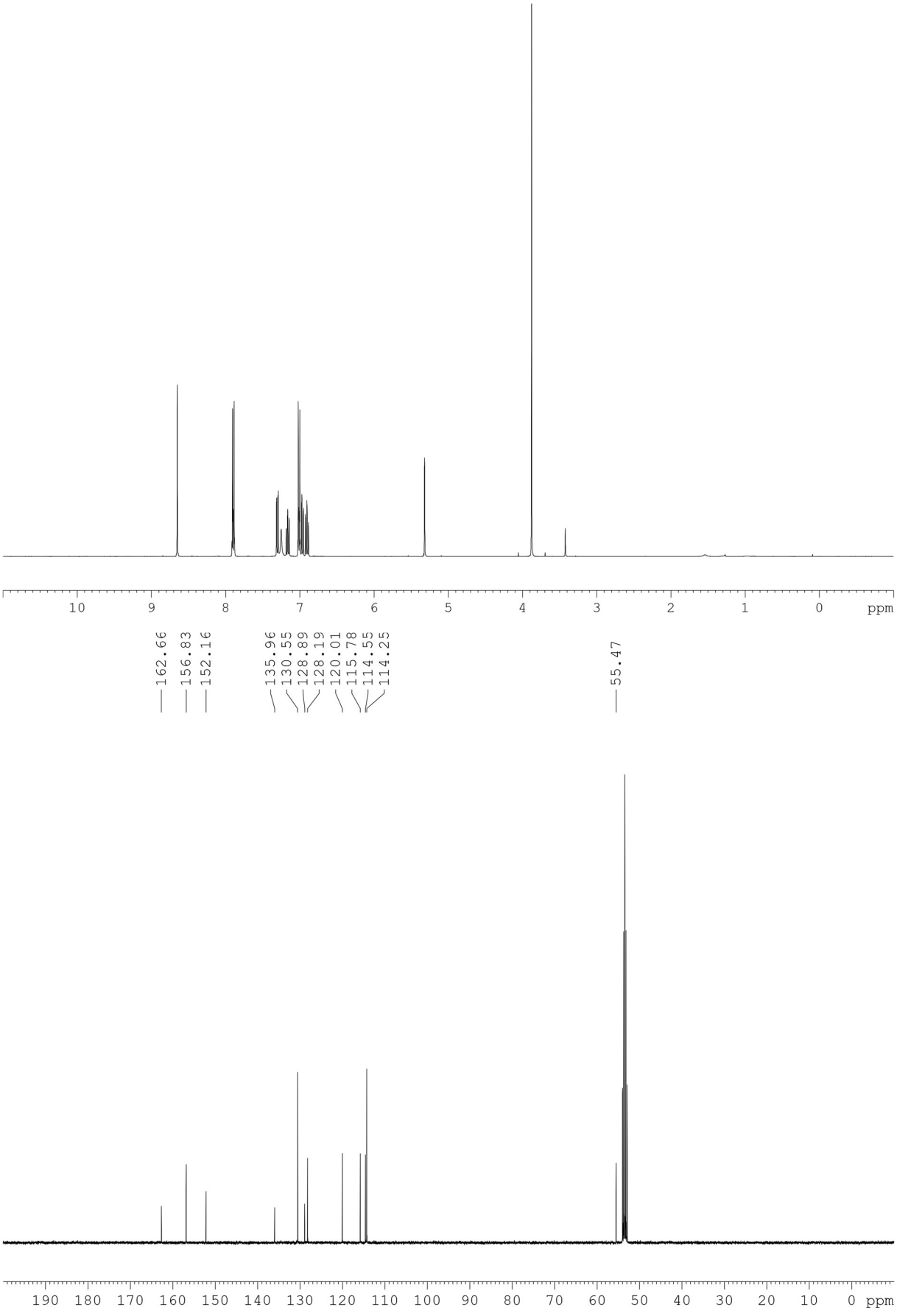


2-Aminophenol (7.00 mmol, 0.65 g, 0.55 mL, 1.7 eq), 4-Methoxybenzaldehyde (4.05 mmol, 0.55 g, 1.0 eq) and $MgSO_4$ (4.70 g) were weighed into a 50 mL Schlenk flask and dissolved in 20 mL DCM. The solution was stirred for two days at room temperature. Afterwards, the solvent was removed under reduced pressure to give a yellow solid. The crude product was recrystallized in methanol two times to give the product as yellow crystals. (0.55 g, 2.60 mmol, 37%).

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 8.65 (s, 1H), 7.90 (m, 2H), 7.30 (dd, 1H, ^{3}J = 8.0 Hz, ^{4}J = 1.5 Hz), 7.25 (s, 1H), 7.16 (m, 1H), 7.01 (m, 2H), 6.97 (dd, 1H, ^{3}J = 8.1 Hz, ^{4}J = 1.4 Hz), 6.90 (m, 1H), 3.88 (s, 1H).

^{13}C-NMR: (100.6 MHz, CD_2Cl_2): δ_C = 162.7, 156.8, 152.2, 135.9, 130.5, 128.9, 128.2, 120.0, 115.8, 114.6, 114.3, 55.5.

HR-MS (EI, *m/z*): found 226.08607 (M-H)+ (calculated 226.08626 for $C_{14}H_{12}NO_2$); Diff(ppm) = -0.81.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2
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ppm
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114.25
55.47
190
180
170
160
150
140
130
120
110
100
90
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40
30
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10
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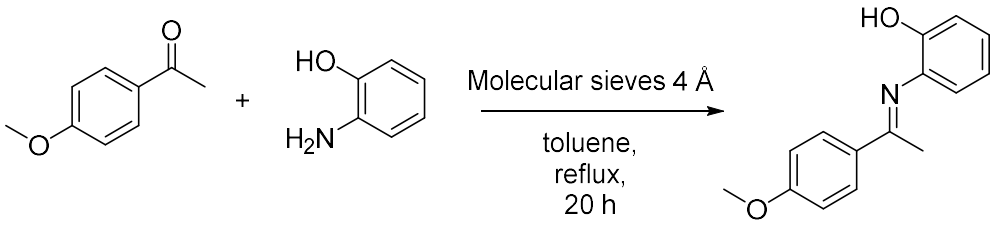
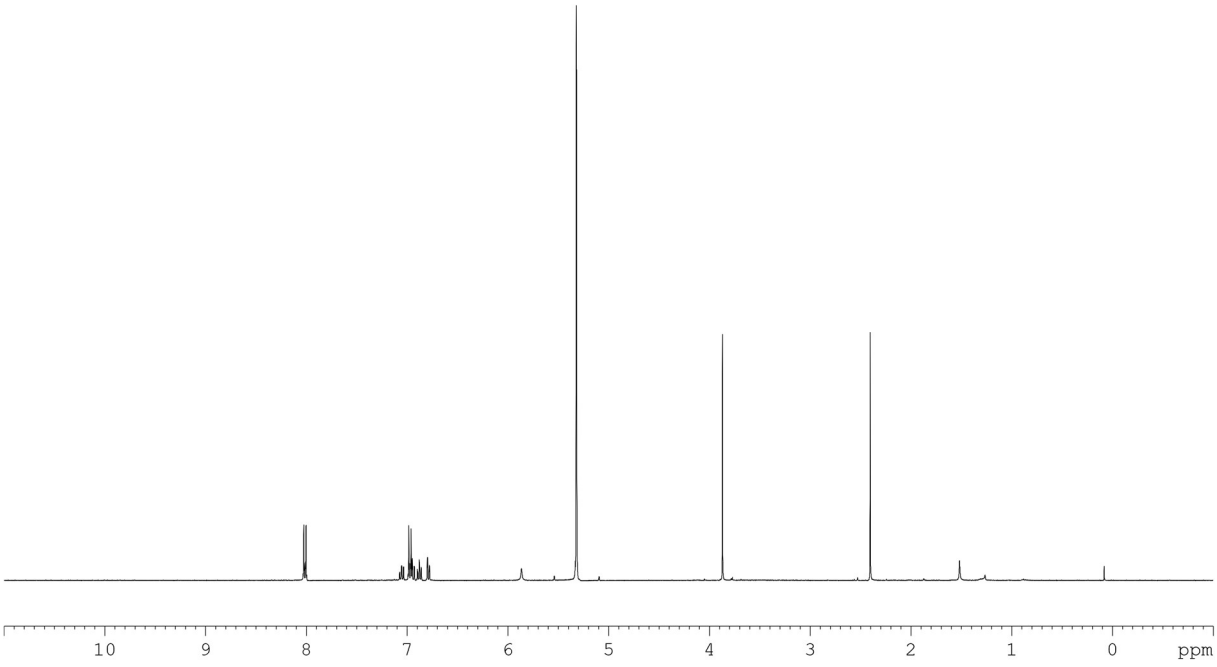
(E)-2-((1-(4-methoxyphenyl)ethylidene)amino)phenol (2b)



The molecular sieves 4 Å (approx. 4 g) were weighed into a 50 mL Schlenk flask and dried with a heat gun at 350 °C for 30 min under reduced pressure. 2-Aminophenol (30.0 mmol, 3.27 g, 3.0 eq) and 1-(4-methoxyphenyl)ethan-1-one (10 mmol, 1.50 g, 1.0 eq.) were added under argon flow and dissolved in 20 mL anhydrous toluene. Under argon flow, a reflux condenser was added to the setup. After flushing it for 3 min with argon, a drying tube containing $CaCl_2$ was added to the setup and the solution was refluxed for 20 h. The reaction mixture was allowed to cool down and the solvent was removed under reduced pressure. The crude product was obtained as an orange solid and was purified two times using a bulb-to-bulb distillation (0.01 mbar, 170 °C) to give the imine **2b** as an orange solid (0.313 g, 1.30 mmol, 13 %).

^{1}H-NMR: (400.1 MHz, CD2Cl2): δ_H = 8.02 (m, 2H), 7.06 (m, 1H), 6.97 (m, 2H), 6.94 (m, 1H, ^3J = 8.1 Hz, ^4J = 1.3 Hz), 6.88 (td, 1H, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 6.79 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.5 Hz), 5.86 (s, 1H), 3.87 (s, 3H), 2.40 (s, 3H).

HR-MS (EI, *m/z*): found 240.10166 (M-H)+ (calculated 240.10191 for $C_{15}H_{14}NO_2$); Diff(ppm) = -1.04.


10
9
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5
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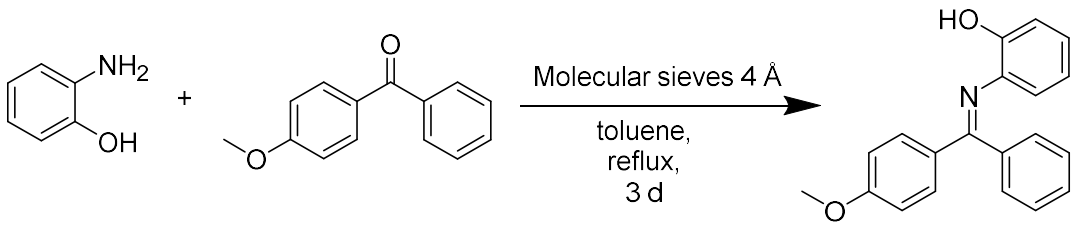
ppm

(E)-2-(((4-methoxyphenyl)(phenyl)methylene)amino)phenol (2c)

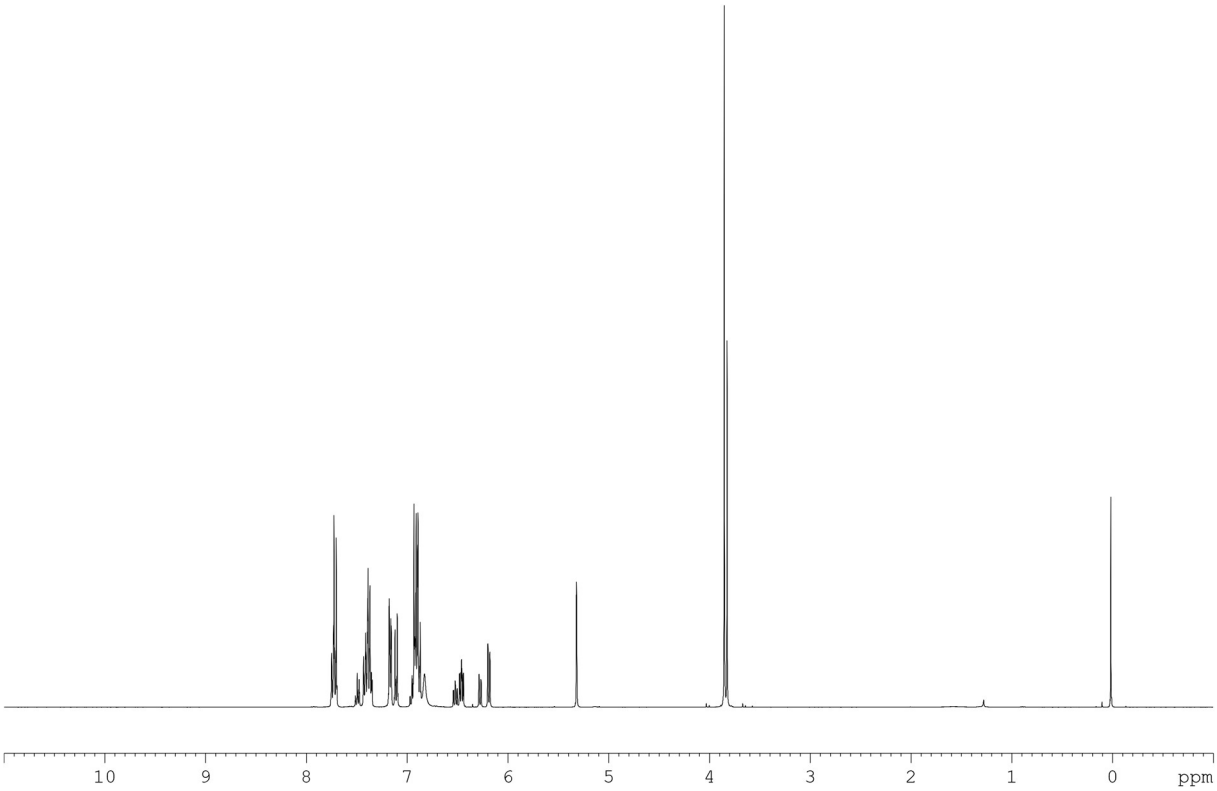


The molecular sieves 4 Å (approx. 4 g) were weighed into a 50 mL Schlenk flask and dried at 350 °C under reduced pressure for 30 min. 2-Aminophenol (30.0 mmol, 3.27 g, 3.0 eq) and (4-methoxy-phenyl)(phenyl)methanone (10 mmol, 2.12 g, 1.0 eq.) were added under argon flow and dissolved in 20 mL anhydrous toluene. Under argon flow, a reflux condenser was added to the setup and flushed with argon for 3 min. A drying tube filled with $CaCl_2$ was added to the setup and the solution was refluxed for 3 d. After cooling down, the mixture was filtrated, and the solvent was removed under reduced pressure to give an orange solid. The crude product was purified two times using a bulb-to-bulb distillation (0.01 mbar, 190 °C) to give the imine **2c** as an orange solid (0.516 g, 1.7 mmol, 17 %) as a mixture of *E* and *Z*-isomer (ratio major/minor = 1.9 : 1).

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 7.74 (m, 2H, minor), 7.72 (m, 2H, major), 7.49 (m, 1H, minor), 7.44 – 7.33 (m, both), 7.17 (m, 2H, major), 7.11 (m, 2H, minor), 6.99 - 6.86 (m, both), 6.83 (s, 1H, broad, both, OH group), 6.52 (m, 1H, minor), 6.45 (m, 1H, major), 6.26 (dd, 1H, ^{3}J = 8.0 Hz, ^{4}J = 1.4 Hz minor), 6.17 (dd, 1H, ^{3}J = 8.0 Hz, ^{4}J = 1.4 Hz, major), 3.84 (s, 3H, major), 3.81 (s, 3H, minor).

^{13}C-NMR: (100.6 MHz, CD_2Cl_2): δ_C = 169.4 (minor), 169.0 (major), 162.6 (major), 160.8 (minor), 151.9 (minor), 151.7 (major), 140.6, 140.0, 136.9, 136.8, 132.6, 131.6, 131.3, 131.3, 130.0, 129.4 (minor), 129.4 (major), 128.8 (major), 128.6, 128.5 (minor), 126.6 (minor), 126.4 (major), 120.9 (major), 120.7 (minor), 119.6 (minor), 119.5 (major), 114.8 (minor), 114.6 (major), 114.1 (minor), 113.9 (major), 55.8 (major), 55.7 (minor).

HR-MS (EI, *m/z*): found 302.11714 (M-H)+ (calculated 302.11756 for $C_{20}H_{16}NO_2$); Diff(ppm) = -1.36.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0
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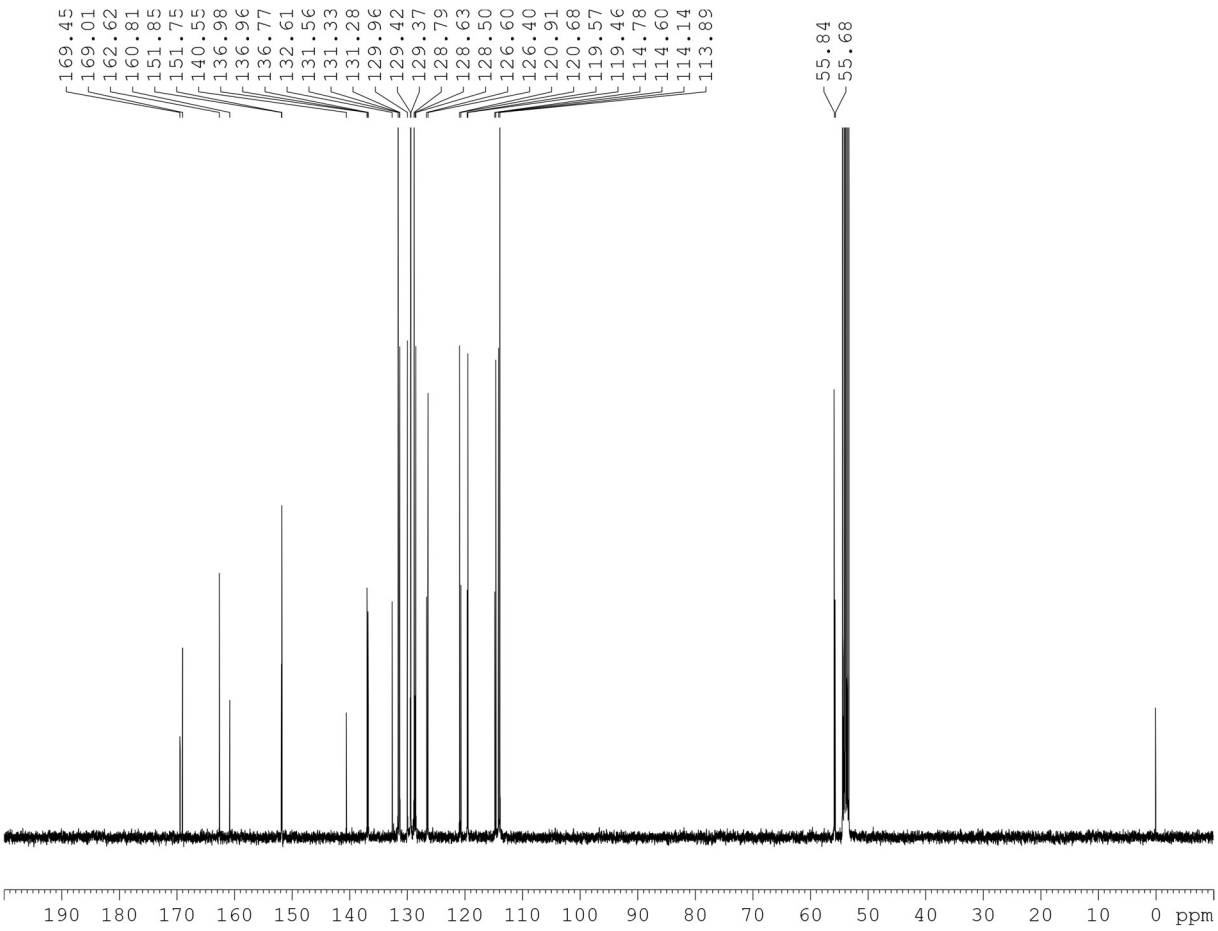
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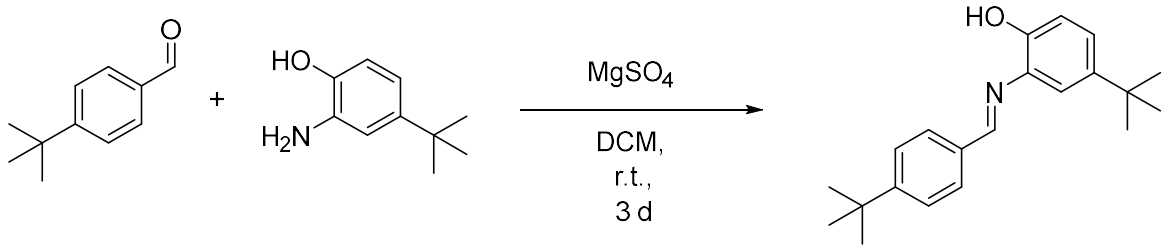
128.50
126.60
126.40
120.91
120.68
119.57
119.46
114.78
114.60
114.14
113.89
55.84
55.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(E)-4-(tert-butyl)-2-((4-(tert-butyl)benzylidene)amino)phenol (3a)

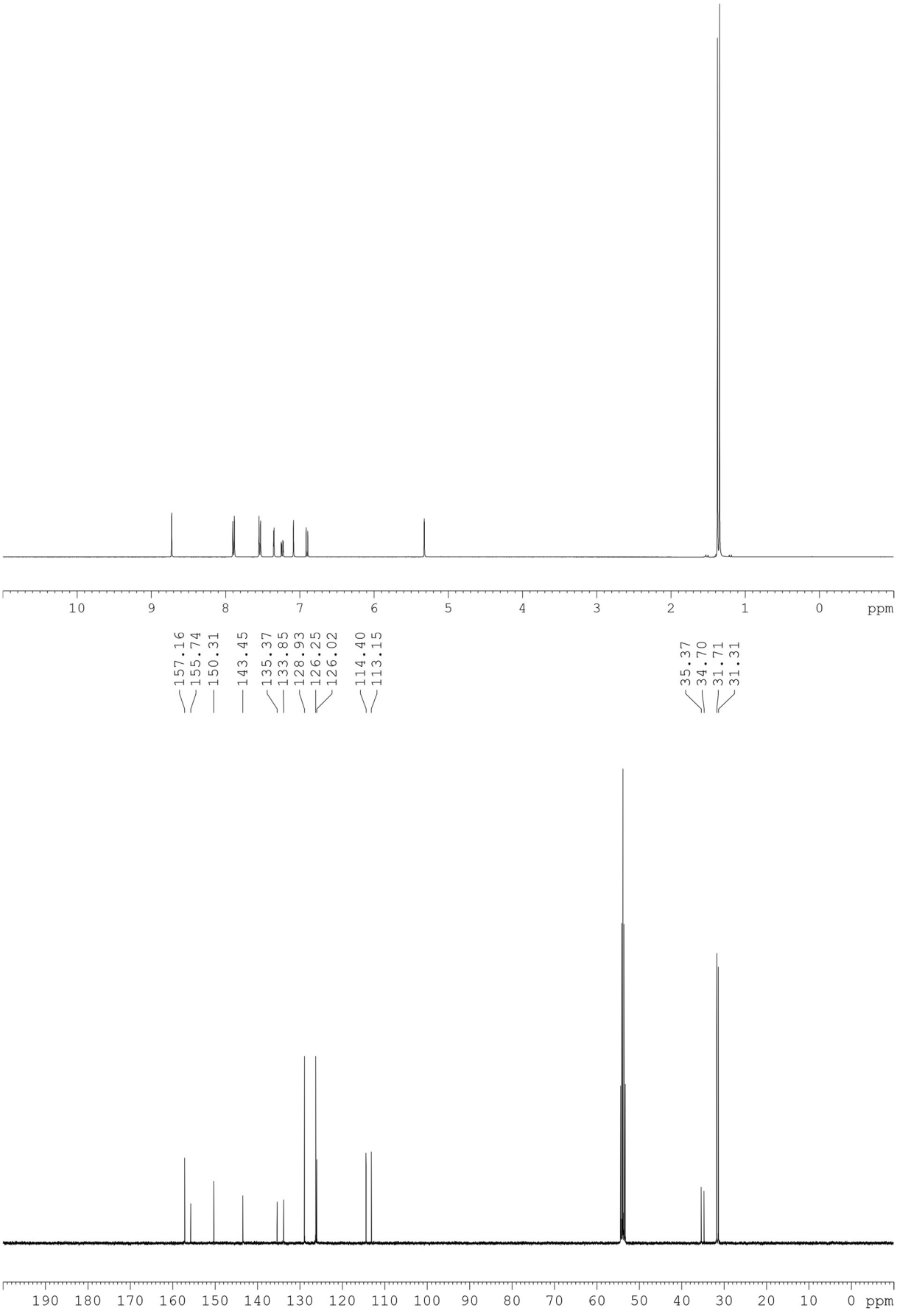


The aldehyde (0.811 g, 0.836 mL, 5.0 mmol, 1.0 eq.) and the hydroxy aniline (0.826 g, 5.0 mmol, 1.0 eq.) and $MgSO_4$ (5 g) were dissolved in 20 mL DCM and stirred for 3 days at room temperature. Afterwards, $MgSO_4$ was filtrated off and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation (160 °C, 0.1 mbar) to give imine **3a** (0.883 mg, 2.85 mmol, 57%) as yellow oil which solidified as yellow to white solid after several days/weeks.

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 8.72 (s, 1H), 7.89 (m, 2H), 7.54 (m, 2H), 7.35 (d, 1H, ^{4}J = 2.3 Hz), 7.23 (dd, 1H, ^{3}J = 8.5 Hz, ^{4}J = 2.3 Hz), 7.08 (s, 1H), 6.9 (d, 1H, ^{3}J = 8.5 Hz), 1.37 (s, 9H), 1.34 (s, 9H).

^{13}C-NMR: (100.6 MHz, CD_2Cl_2): δ_C = 157.2, 155.7, 150.3, 143.5, 135.4, 133.8, 128.9, 126.3, 126.0, 114.4, 113.1, 35.4, 34.7, 31.7, 31.3.

HR-MS (EI, *m/z*): found 308.20058 (M-H)+ (calculated 308.20089 for $C_{21}H_{16}NO$); Diff(ppm) = - 1.02.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133.85
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126.25
126.02
114.40
113.15
35.37
34.70
31.71
31.31
190
180
170
160
150
140
130
120
110
100
90
80
70
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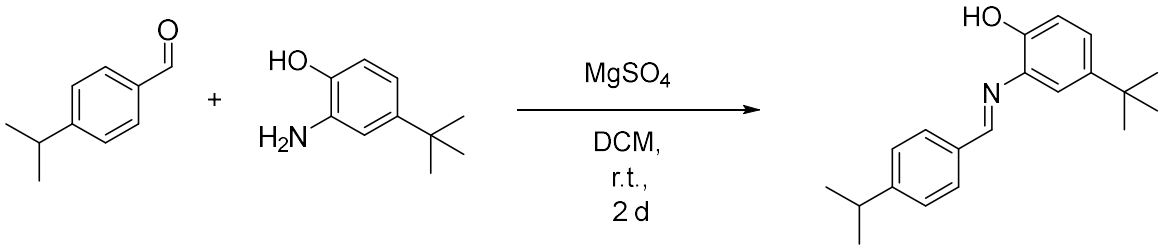
50
40
30
20
10
0 ppm

(E)-4-(tert-butyl)-2-((4-isopropylbenzylidene)amino)phenol (3b)

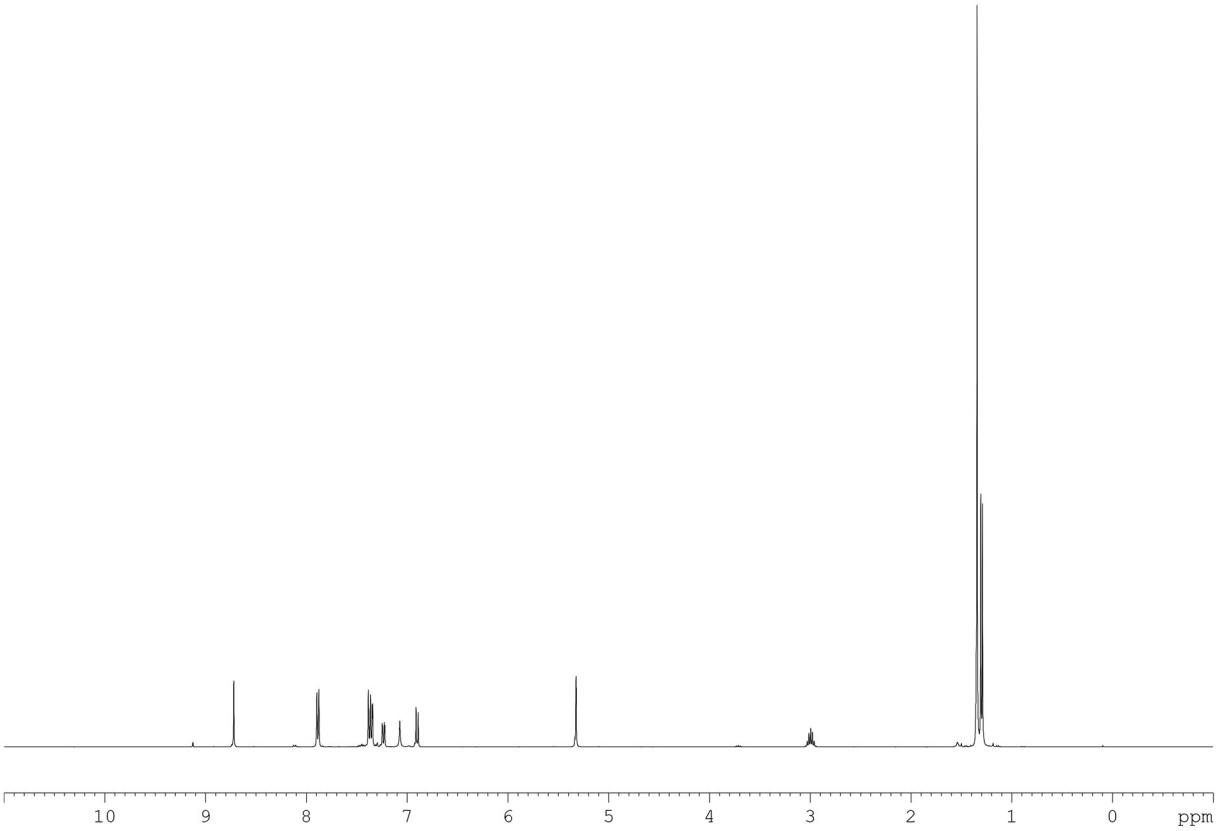


The aldehyde (1.48 g, 1.52 mL, 10.0 mmol, 1.0 eq.) and the hydroxy aniline (1.65 g, 10.0 mmol, 1.0 eq.) and $MgSO_4$ (6 g) were dissolved in 20 mL dry DCM and stirred for 2 days at room temperature. Afterwards, $MgSO_4$ was filtrated off and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation (180 °C, 0.1 mbar) to give imine **3b** (0.93 g, 3.2 mmol, 32 %) as a yellow oil.

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 8.72 (s, 1H), 7.89 (m, 2H), 7.37 (m, 2H), 7.35 (d, ^4J = 2.3 Hz), 7.23 (dd, 1H, ^3J = 8.4 Hz, ^4J = 2.3 Hz), 7.07 (s, 1H), 6.90 (d, 1H, ^3J = 8.4 Hz), 3.00 (sept, 1H, ^3J = 6.9 Hz), 1.34 (s, 9H), 1.30 (d, 6H, ^3J = 6.9 Hz).

^{13}C-NMR: (100.6 MHz, CD_2Cl_2): δ_C = 156.8, 153.1, 149.9, 143.0, 135.0, 133.9, 128.8, 127.0, 125.6, 114.0, 112.7, 34.3, 34.2, 31.3, 23.5.

HR-MS (EI, *m/z*): found 295.19322 (M)+ (calculated 295.19307 for $C_{20}H_{25}NO$); Diff(ppm) = + 0.53.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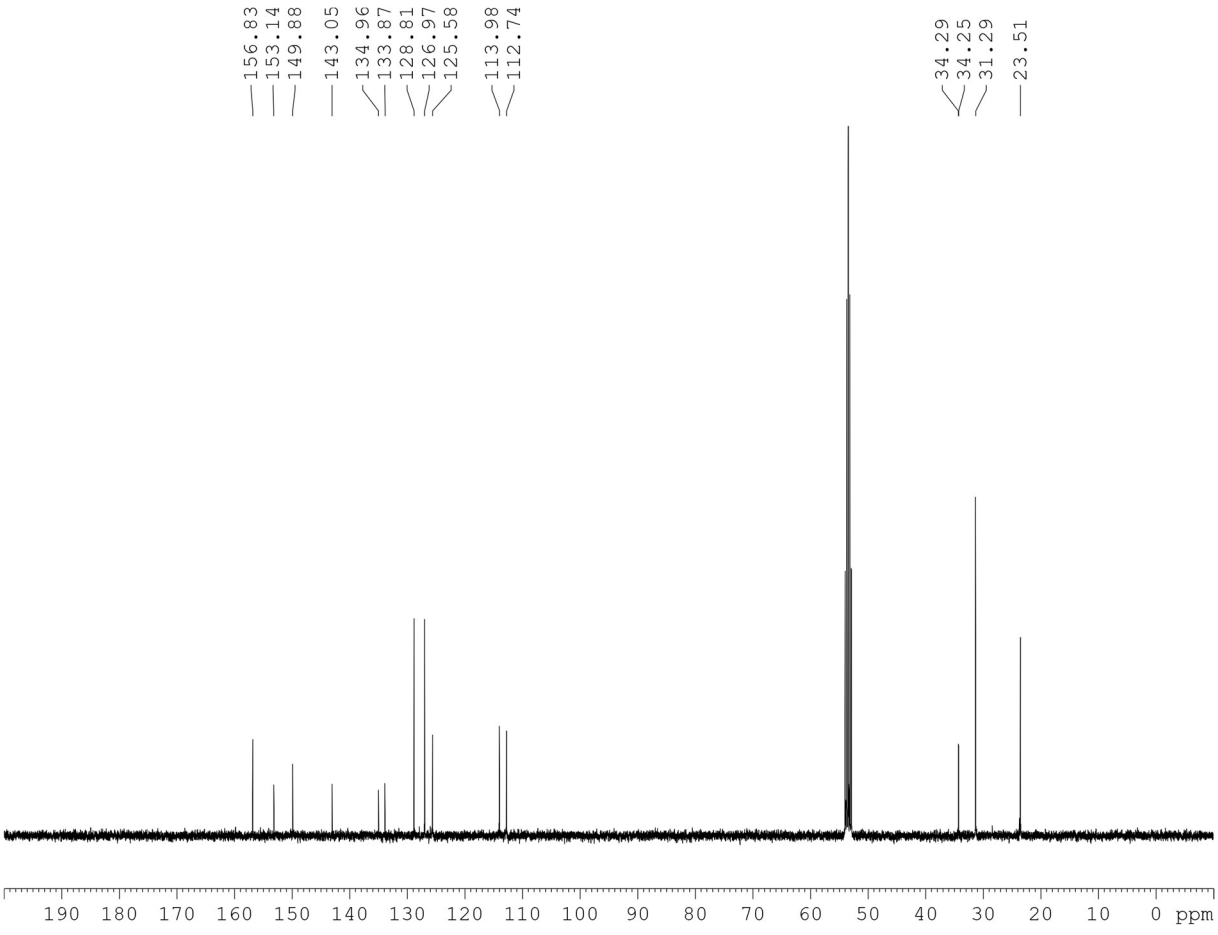
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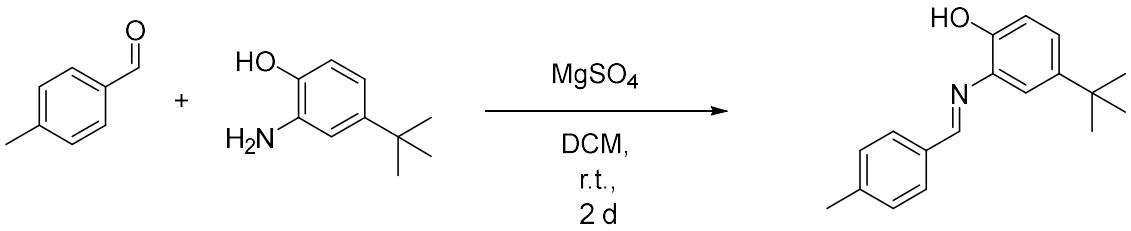
126.97
125.58
113.98
112.74
34.29
34.25
31.29
23.51
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(E)-4-(tert-butyl)-2-((4-methylbenzylidene)amino)phenol (3c)

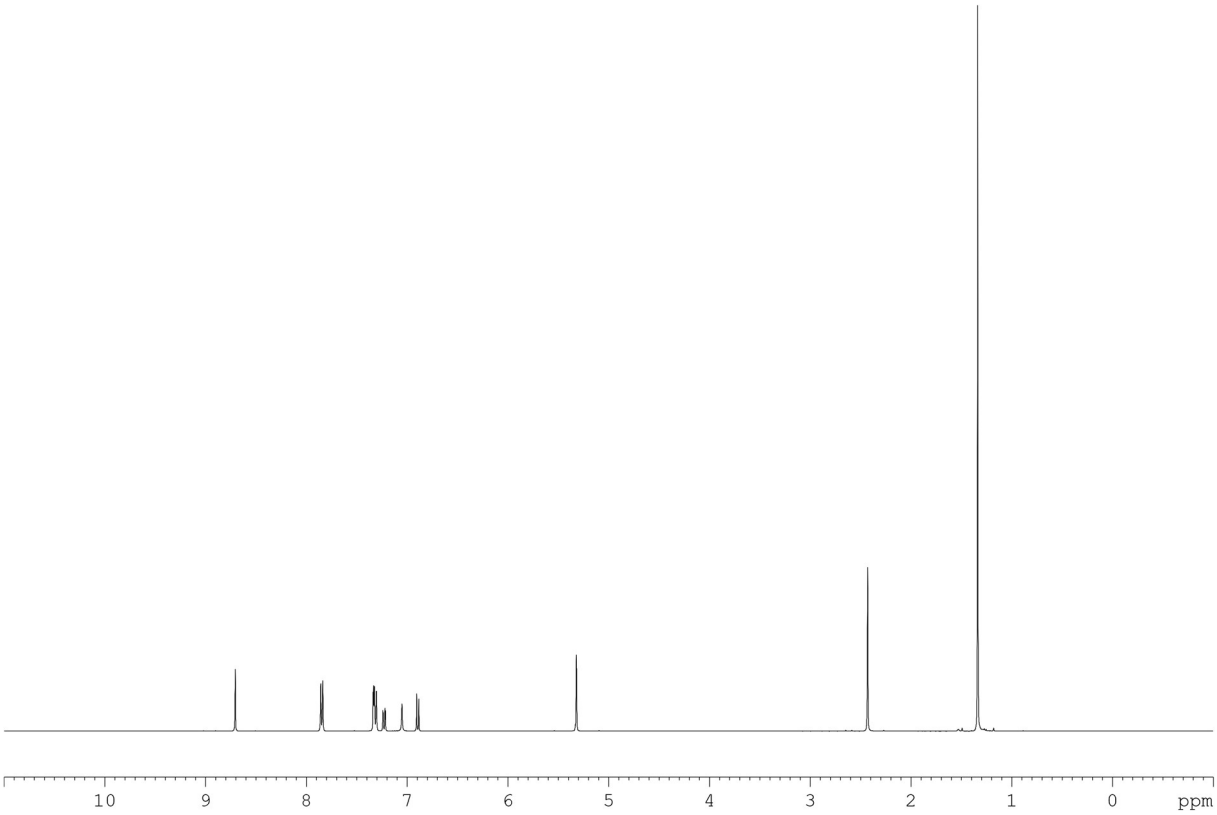


The aldehyde (1.20 g, 1.02 mL, 10.0 mmol, 1.0 eq.) and the hydroxy aniline (1.65 g, 10.0 mmol, 1.0 eq.) and $MgSO_4$ (7 g) were dissolved in 20 mL dry DCM and stirred for 2 days at room temperature. Afterwards, $MgSO_4$ was filtrated off and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation (175 °C, 0.1 mbar) to give imine **3c** (1.76 g, 6.0 mmol, 60 %) as a yellow oil.

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 8.71 (s, 1H), 7.85 (m, 2H), 7.34 (d, 1H, ^{4}J = 2.3 Hz), 7.32 (d, 2H, ^{3}J = 7.9 Hz), 7.23 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.3 Hz), 7.05 (s, 1H), 6.90 (d, 1H, ^{3}J = 8.4 Hz), 2.43 (s, 3H), 1.34 (s, 9H).

^{13}C-NMR: (100.6 MHz, CD_2Cl_2): δ_C = 156.8, 149.9, 143.1, 142.3, 134.9, 133.5, 129.5, 128.7, 125.6, 114.0, 112.8, 34.3, 31.3, 21.4.

HR-MS (EI, *m/z*): found 266.15369 (M-H)+ (calculated 266.15394 for $C_{18}H_{20}NO$); Diff(ppm) = -0.95.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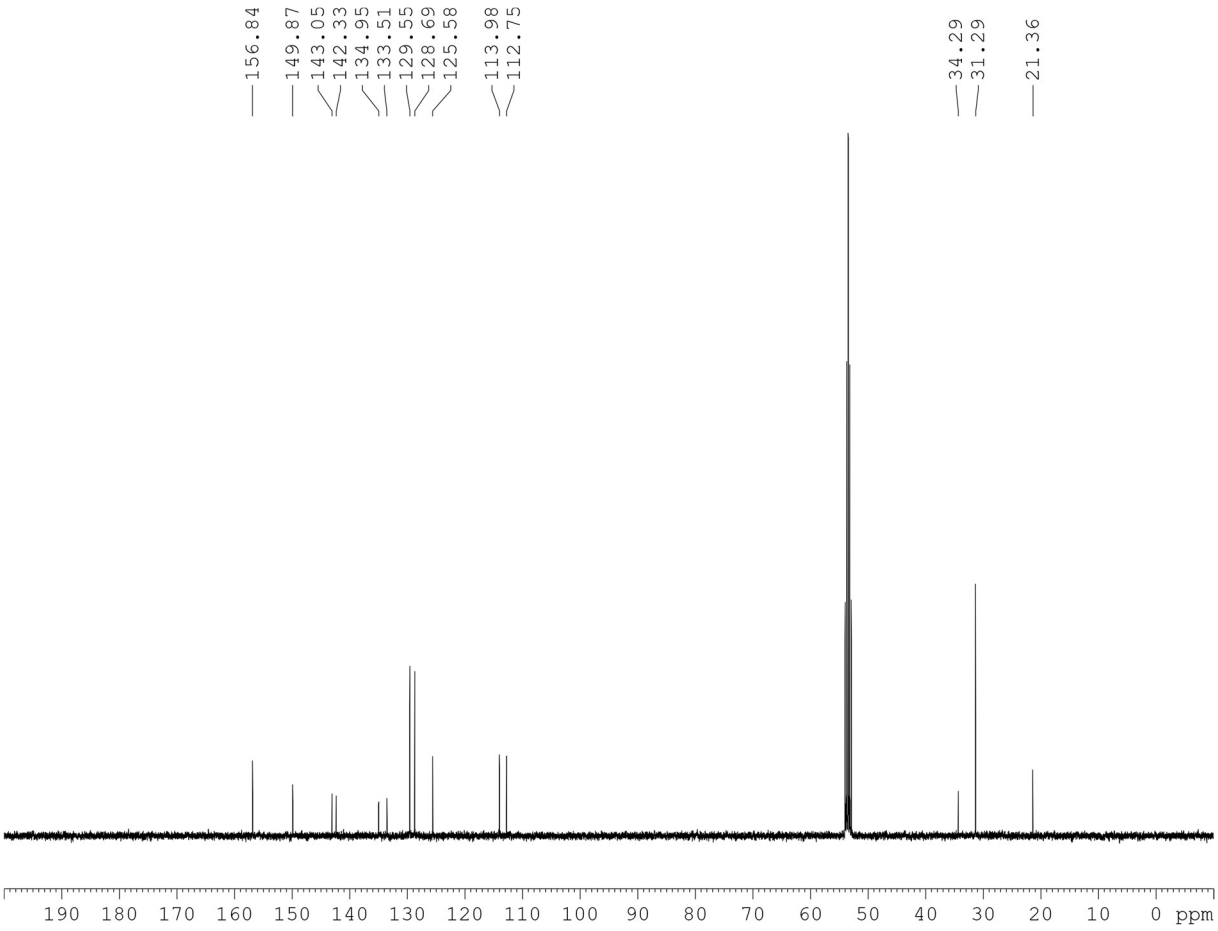
ppm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134.95
133.51
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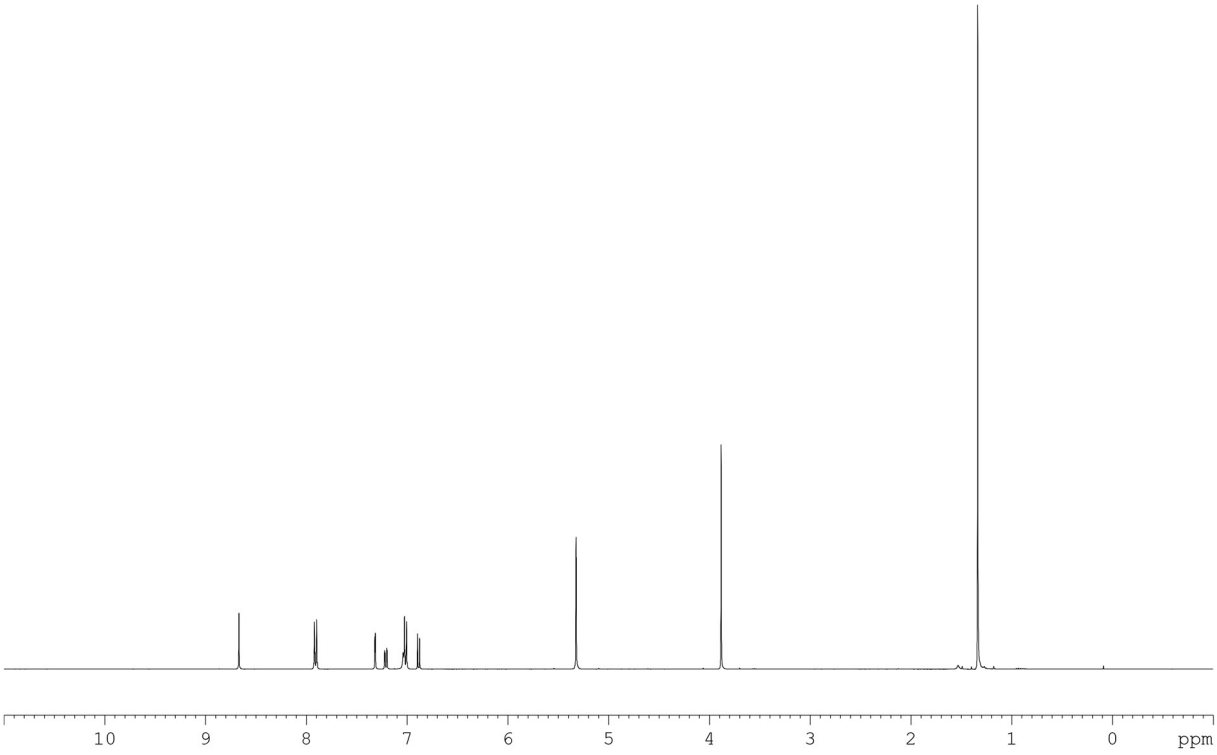
125.58
113.98
112.75
34.29
31.29
21.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

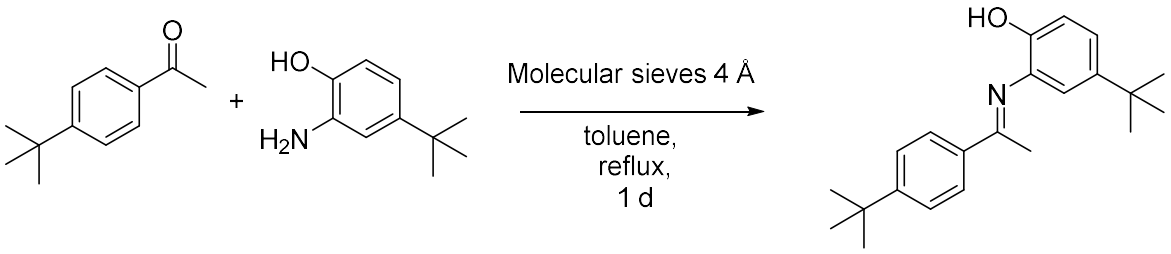
(E)-4-(tert-butyl)-2-((4-methoxybenzylidene)amino)phenol (3d)

The aldehyde (0.68 g, 0.55 mL, 5.0 mmol, 1.0 eq.) and the hydroxy aniline (0.83 g, 5.0 mmol, 1.0 eq.) and $MgSO_4$ (7 g) were dissolved in 20 mL dry DCM and stirred for 2 days at room temperature. Afterwards, $MgSO_4$ was filtrated off and the solvent was removed under reduced pressure. The crude product was recrystallized in methanol to give imine **3d** (0.55 g, 2.4 mmol, 48 %) as a pale orange solid.

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 8.71 (s, 1H), 7.85 (m, 2H), 7.34 (d, 1H, ^4J = 2.3 Hz), 7.32 (d, 2H, ^4J = 7.9 Hz), 7.23 (dd, 1H, ^3J = 8.6 Hz, ^4J = 2.3 Hz), 7.05 (s, 1H), 6.90 (d, 1H, ^3J = 8.6 Hz), 2.43 (s, 3H), 1.34 (s, 9H).



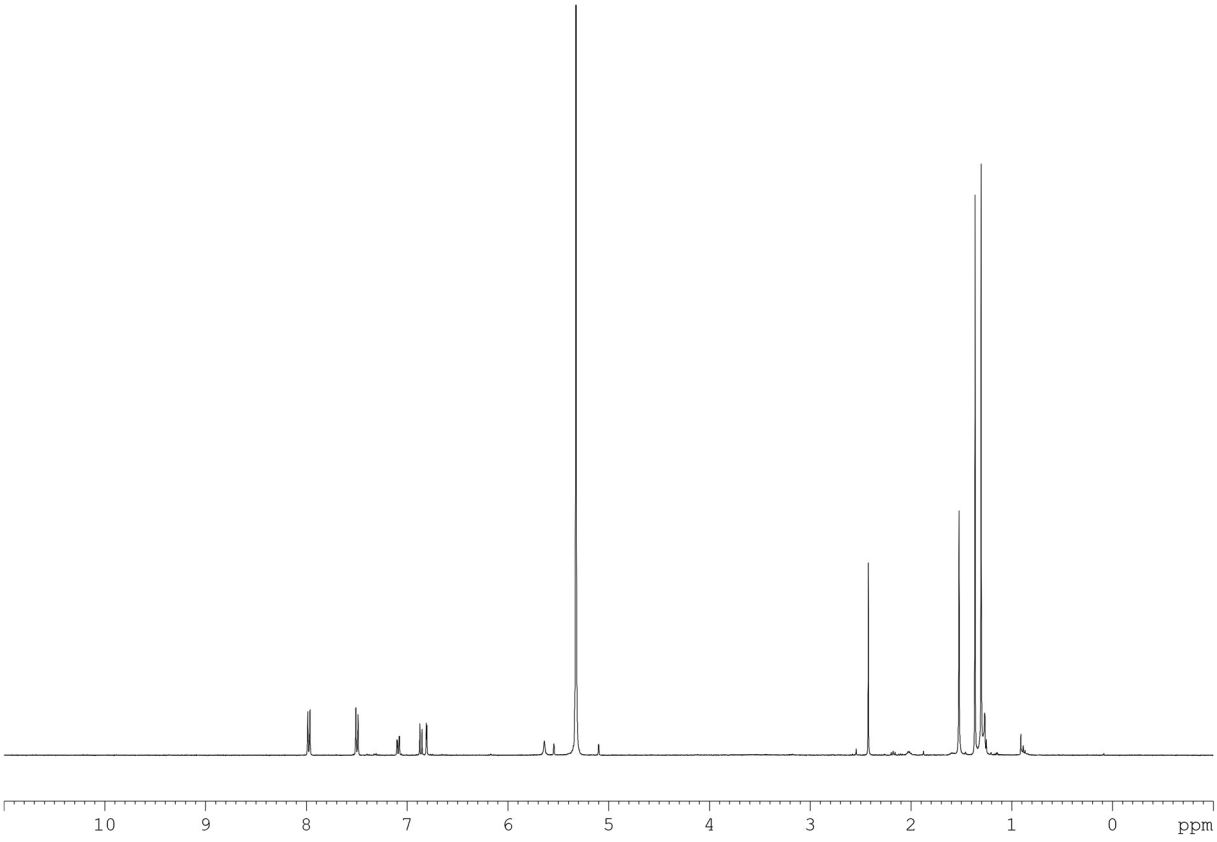
(E)-4-(tert-butyl)-2-((1-(4-(tert-butyl)phenyl)ethylidene)amino)phenol (3e)



The molecular sieves 4 Å (approx. 4 g) were weighed into a 50 mL Schlenk flask and dried with a heat gun at 350 °C for 30 min under reduced pressure. The aminophenol (1.65 g, 10.0 mmol, 3.0 eq.) and the ketone (0.881 g, 5 mmol, 1.0 eq.) were added under argon flow and dissolved in 20 mL anhydrous toluene. Under argon flow, a reflux condenser was added to the setup. After flushing it for 3 min with argon, a drying tube containing $CaCl_2$ was added to the setup and the solution was refluxed for 1 d. The reaction mixture was allowed to cool down and the solvent was removed under reduced pressure. The crude product was obtained as an dark brown solution and purified by recrystallization in Et_2O/MeOH (4:1) to give the imine **3e** (0.108 g, 0.33 mmol, 6.5%) as a colorless powder.

^{1}H-NMR: (400.1 MHz, CD_2Cl_2): δ_H = 7.98 (m, 2H), 7.50 (m, 2H), 7.09 (dd, 1H, ^3J = 8.4 Hz, ^4J = 2.3 Hz), 6.86 (d, 1H, ^3J = 8.4 Hz), 6.87 (d, 1H, ^4J = 2.3 Hz), 5.64 (s, 1H), 2.43 (s, 3H), 1.36 (s, 9H), 1.30 (s, 9H).

HR-MS (EI, *m/z*): found 322.21654 (M-H)+ (calculated 322.21654 for $C_{18}H_{20}NO$); Diff(ppm) = - 0.01.


10
9
8
7
6
5
4
3
2
1
0
ppm

3. Diffusion ordered spectroscopy (DOSY)

DOSY measurements were performed with the convection suppressing DSTE (double stimulated echo) pulse sequence developed by Jerschow and Müller in a pseudo 2D mode.[4] Smoothed square (SMSQ10.100) gradient shapes and a linear gradient ramp with 20 increments between 5% and 95% of the maximum gradient strength (5.35 G/mm) were used. The diffusion time delay was set to 45 ms. For the homospoil gradient strengths, values of 100, -13.17, 20 and -17.13 % were used. Gradient pulse lengths (p16) were first optimized to obtain a sigmoidal signal decay for increasing gradient strength (3.0 ms for TMS, 6.0 – 6.5 ms for CPA/imine complexes). NMR spectra were processed with Bruker TopSpin 3.2 (T1/T2 relaxation package) and diffusion coefficients were derived according to Jerschow and Müller[4] Tetramethylsilan was added to the samples to reference chemical shifts and the viscosity of each sample.

The molecular radii were derived by the Stokes-Einstein equation[5] using Chens correction.[6]

$$D_i = \frac{k_B T}{6\pi\eta r_H} * (1 + 0.695 * \left(\frac{r_{solv}}{r_H}\right)^{2.234}$$

D_i is the self-diffusion coefficient derived by the measurement, η is the viscosity of the solvent, r_H is the hydrodynamic radius of the observed molecule and r_{solv} the radius of the solvent. No form factor correction was applied. The viscosity was determined by measuring the diffusion coefficient of the reference tetramethylsilane (TMS) and solving the equation for η with the literature value[7] of the radius of 2.96 Å.

To estimate the error, diffusion coefficients for different signals of the same complex were averaged and the standard deviation was determined. The molecular radii were calculated based on the averaged diffusion coefficient, the averaged diffusion coefficient plus the standard deviation and the averaged diffusion coefficient minus the standard deviation. The resulting radii are given as the radius derived from the averaged diffusion coefficient and the error range is given by:

$$Error\ range = \frac{1}{2} * [\left(r_i^{aver} - r_i^{aver+StDev}\right) + (r_i^{aver-StDev} - r_i^{aver})]$$

Where r_i^{aver} is the radius derived from the averaged diffusion coefficient, $r_i^{aver+StDev}$ is the minimum radius derived from the averaged diffusion coefficient plus the standard deviation

and $r_i^{aver-StDe}$ is the maximum radius derived from the averaged diffusion coefficient minus the standard deviation.

Table S1: Measured self diffusion coefficients of **1a**/**2a** at a concentration of 50 mM at 180 K in CD_2Cl_2 for signals 1-5 which were unambiguously assigned to one of the three different species A, B or C (see chemical shift assignment Figure S1). The determined coefficients are similar for all three species within the precision of the measurement (signal intensities were low).

Entry	Chem. Shift [ppm]	Assignment	Self diffusion coefficient [m^2/s]
1	9.58	Species C	3.21E-11
2	8.63	Species A	3.72E-11
3	8.57	Species B	3.55E-11
4	6.69	Species B	3.10E-11
5	3.55	Species C	3.09E-11
6	0.00	TMS	1.90E-10

The self diffusion coefficients determined for signals 1-5 are similar within the error of the experiment, considering the low signal intensities. This clearly shows, that all three species are similar in size, i.e. $[CPA/imine]_2$ dimers. An average hydrodynamic radius of 11.8 ± 0.87 Å was derived based on the averaged self diffusion coefficient of entries 1-5.

As a reference for monomeric CPA/imine systems, the system depicted below was used. The chemical shift assignment and structural investigations on this system were done in our previous research.[8] As probe signals, one signal of the CPA for the CPA/*E* and CPA/*Z* complex, as well as one signal of the imine for the CPA/*E* and CPA/*Z* complex was selected. All signals were similar and based on the averaged self diffusion coefficient, the average hydrodynamic radius of 8.8 ± 0.15 Å was determined.

Table S2: Measured self diffusion coefficients of the monomeric reference system (see below) at a concentration of 50 mM at 180 K in CD_2Cl_2.

Entry	Chem. Shift [ppm]	Assignment	Self diffusion coefficient [m^2/s]
1	7.88	CPA/E (CPA)	4.76E-11
2	7.75	CPA/Z (CPA)	4.93E-11
3	3.80	CPA/Z (Imin)	4.98E-11
4	2.54	CPA/E (Imin)	4.81E-11
5	0.00	TMS	2.02E-10

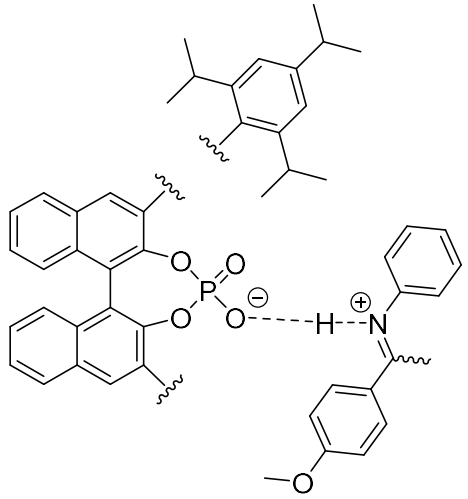


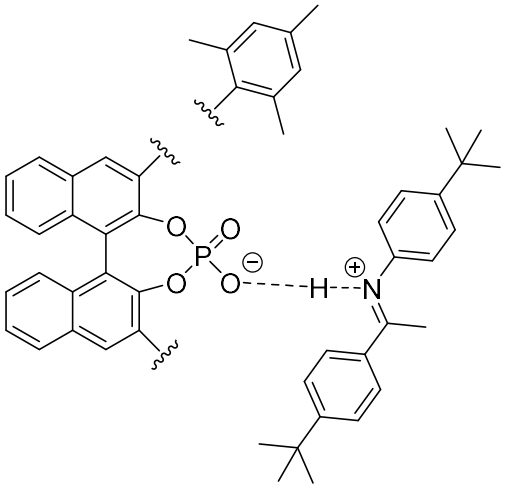
Table S3: Measured self diffusion coefficients of **1b**/**3a** at a concentration of 25 mM at 180 K in CD_2Cl_2.

Entry	Chem. Shift [ppm]	Assignment	Self diffusion coefficient [m^2/s]
1	8.81	Imine	4.08E-11
2	8.03	CPA	3.90E-11
3	7.92	CPA	3.96E-11
4	6.29	CPA	3.86E-11
5	5.90	CPA	3.87E-11
6	1.44	Imine	3.88E-11
7	0.98	Imine	3.90E-11
8	0.00	TMS	2.06E-10

The self diffusion coefficients of entries 1, 6 and 7 (imine) are identical to the ones of the CPA (2-5), showing that both molecules are part of the same complex. Hence, the self diffusion coefficients were averaged and a hydrodynamic radius of 10.93 ± 0.15 Å was determined.

Table S4: Measured self diffusion coefficients of the monomeric reference system depicted below at a concentration of 100 mM and a 1:1 ratio at 180 K in CD_2Cl_2.

Entry	Chem. Shift [ppm]	Assignment	Self diffusion coefficient [m^2/s]
1	7.77	CPA/E (CPA)	4.00E-11
2	2.64	CPA/E (Imin)	4.16E-11
3	1.16	CPA/E (Imin)	4.12E-11
4	0.00	TMS	1.99E-10



To put the found hydrodynamic radius of **1b**/**3a** (see Table S3) into relation, the reference system depicted above was selected to mimic the steric properties and hydrodynamic radius of a monomeric CPA/imine complex. The chemical shift analysis for this system was done previously[9] and it was also clarified that the CPA/imine complex is monomeric. Based on the averaged self-diffusion coefficients, a hydrodynamic radius of 10.2 ± 0.16 Å was derived. The obtained radius of the monomeric reference system is close to the one of **1b**/**3a**, validating that **1b**/**3a** is indeed a monomeric CPA/imine complex.

Table S5: Measured self diffusion coefficients of **1c**/**2a** at a 1:1 ratio and a concentration of 10 mM at 180 K in CD_2Cl_2.

Entry	Chem. Shift [ppm]	Assignment	Self diffusion coefficient [m^2/s]
1	4.02	Imine	3.56E-11
2	0.00	TMS	2.13E-10

As a probe signal for the **1c**/**2a** complex, the methoxy group of **2a** was selected. Based on the self diffusion coefficient, a hydrodynamic radius of ~ 12.36 Å was determined.

4. Chemical Shift assignments

Chemical shifts of CPA/imine complexes were assigned using ^{1}H-, ^{13}C-, ^{31}P-NMR, ^{1}H ^{13}C HSQC, ^{1}H ^{13}C HMBC, ^{1}H ^{31}P HMBC, ^{1}H COSY, ^{1}H TOCSY and ^{1}H NOESY spectra. ^{1}H chemical shifts are given in black, ^{13}C chemical shifts are given in green, ^{31}P chemical shifts are given in red, multiplicities and coupling constants are given in blue.

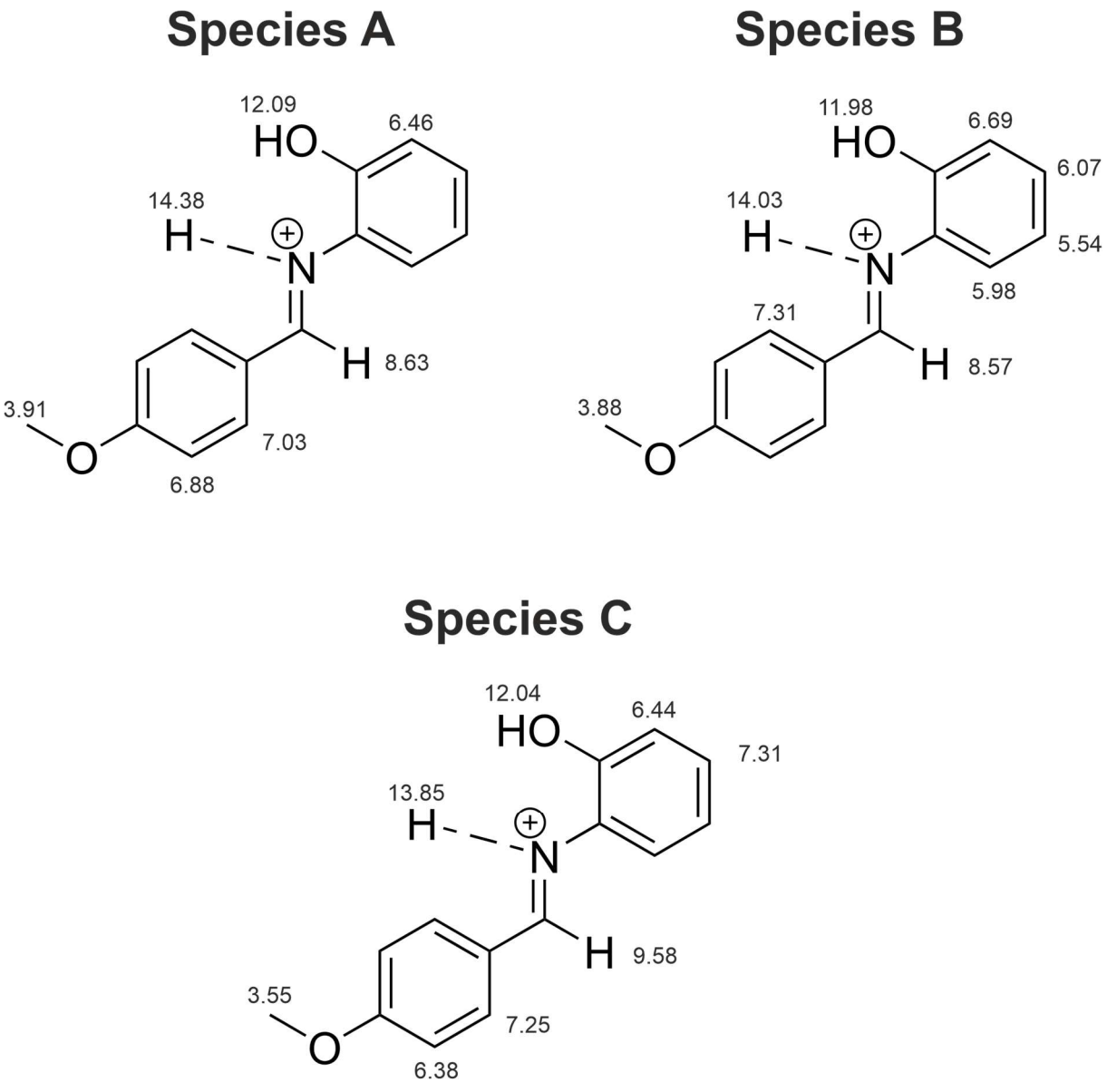


Figure S1: Proton chemical shift assignment of **1a**/**2a** at a concentration of 50 mM in CD_2Cl_2 at 180 K and 600 MHz.

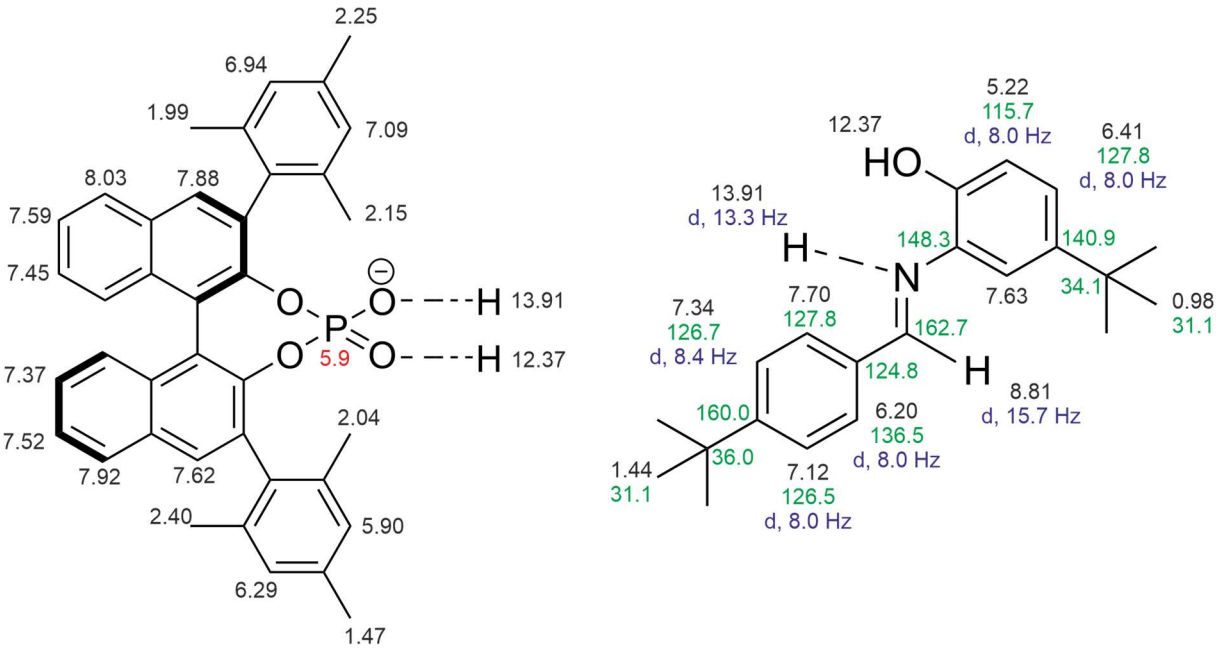


Figure S2: Proton chemical shift assignment of **1b**/**3a** at a concentration of 25 mM in CD_2Cl_2 at 180 K and 600 MHz.

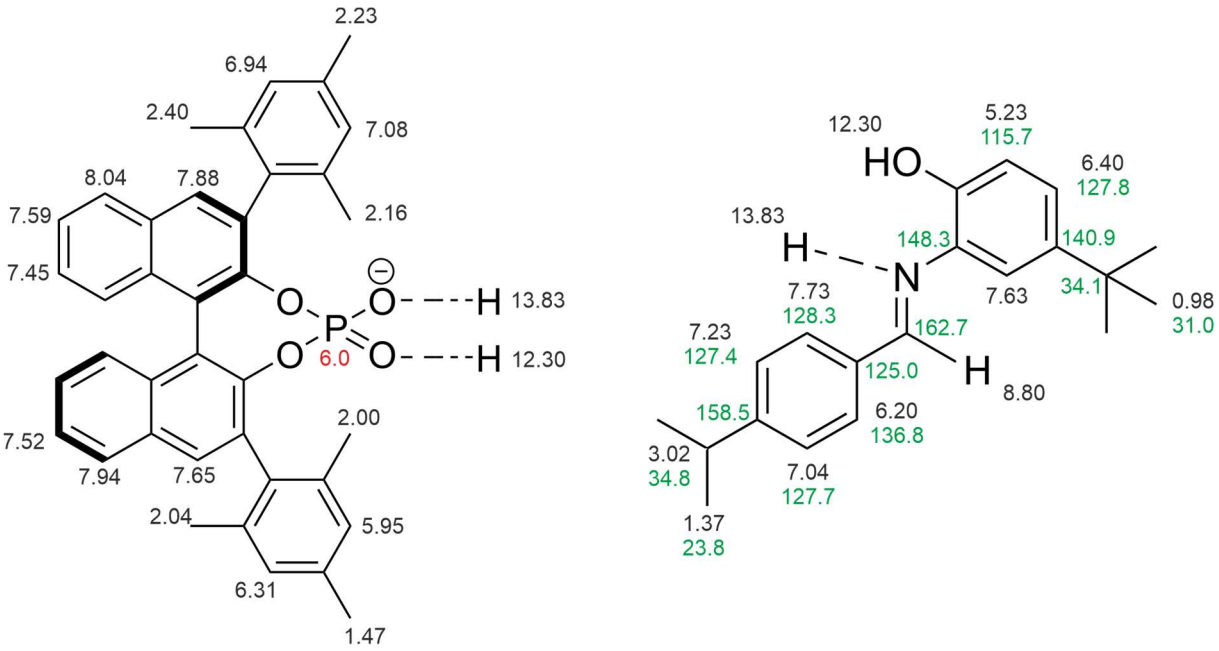


Figure S3: Proton chemical shift assignment of **1b**/**3b** at a concentration of 25 mM in CD_2Cl_2 at 180 K and 600 MHz.

5. Initial system screening

5.1 Solvent screening

Initially, toluene-d_8 was tried as solvent to investigate the CPA/imine complexes, because in this solvent the best stereoselectivities were obtained in the optimization screening by Akiyama.[10] However, the measured spectra showed severe line broadening and signal overlap. This is similar to our previous NMR investigations, where toluene was not suitable as a solvent.[11] We assume, that changing the solvent from toluene to dichloromethane does not drastically change the structural space of the investigated CPA/imine systems. However, it should be noted that during the reaction optimization by Akiyama on the example of one N-(*ortho*-hydroxyphenyl) imine and one CPA, the enantioselectivity in toluene (87% *ee*) was significantly higher than in dichloromethane (13% *ee*).

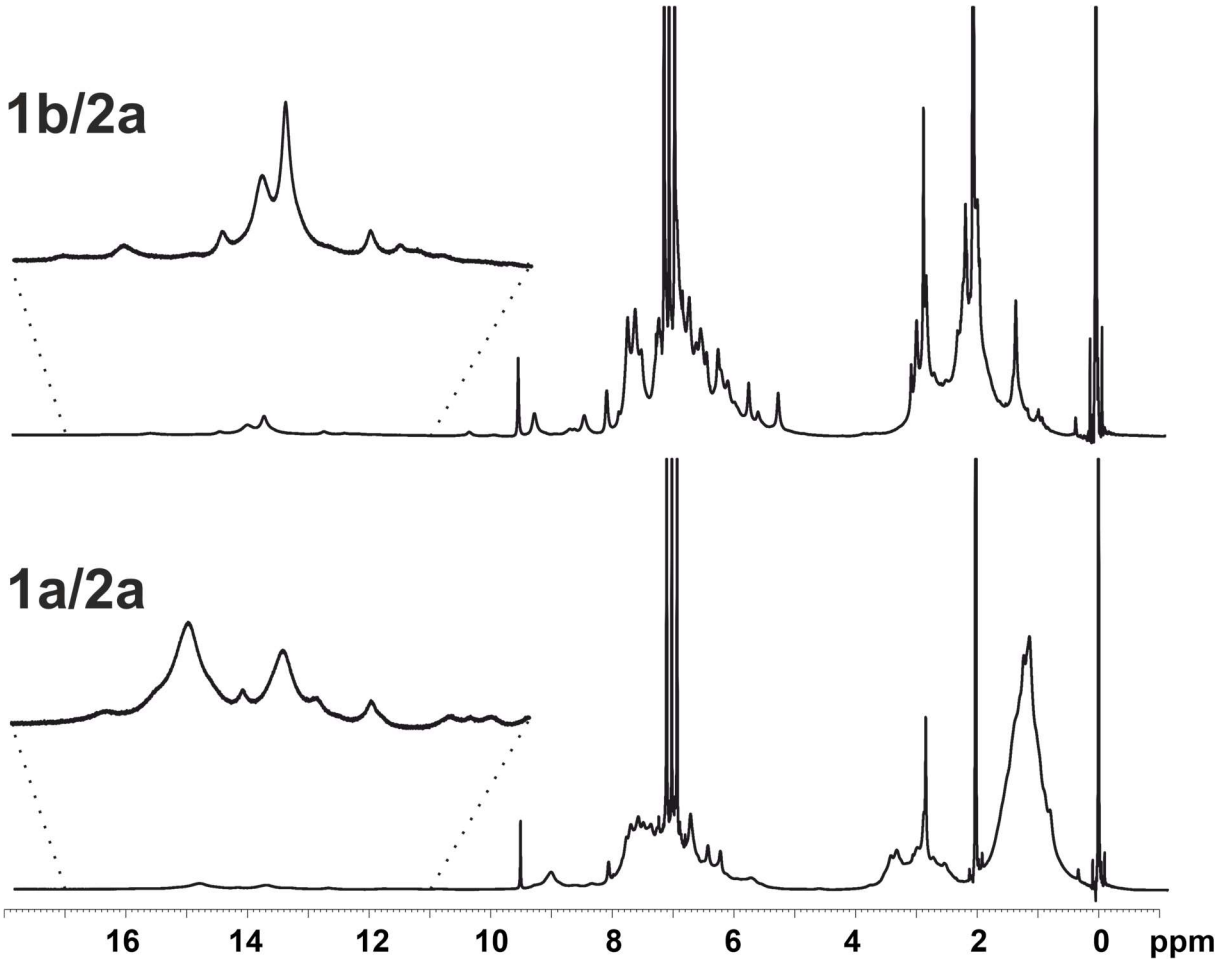


Figure S4: ^{1}H NMR spectra of **1a**/**2a** and **1b**/**2a** in toluene-d_8 at a temperature of 180 K and 600 MHz.

5.2 Intramolecular hydrogen bonding

As imines **2a**-**c** have both a hydrogen bond donor (-OH) and acceptor (C=N), the formation of intra- and intermolecular hydrogen bonds is possible. To confirm, that all observed hydrogen bonded proton signals (see Figure 2 and Figure S6) stem from CPA/imine hydrogen bonds, the proton spectra of imines **2a**-**c** (see Figure S5) were recorded under analogous conditions (temperature, concentration, sample, sample preparation) as the CPA/imine samples. The resulting spectra clearly show, that none of the monitored hydrogen bonded proton signals for systems **1a**-**b**/**2a**-**c** originate from the imines alone.

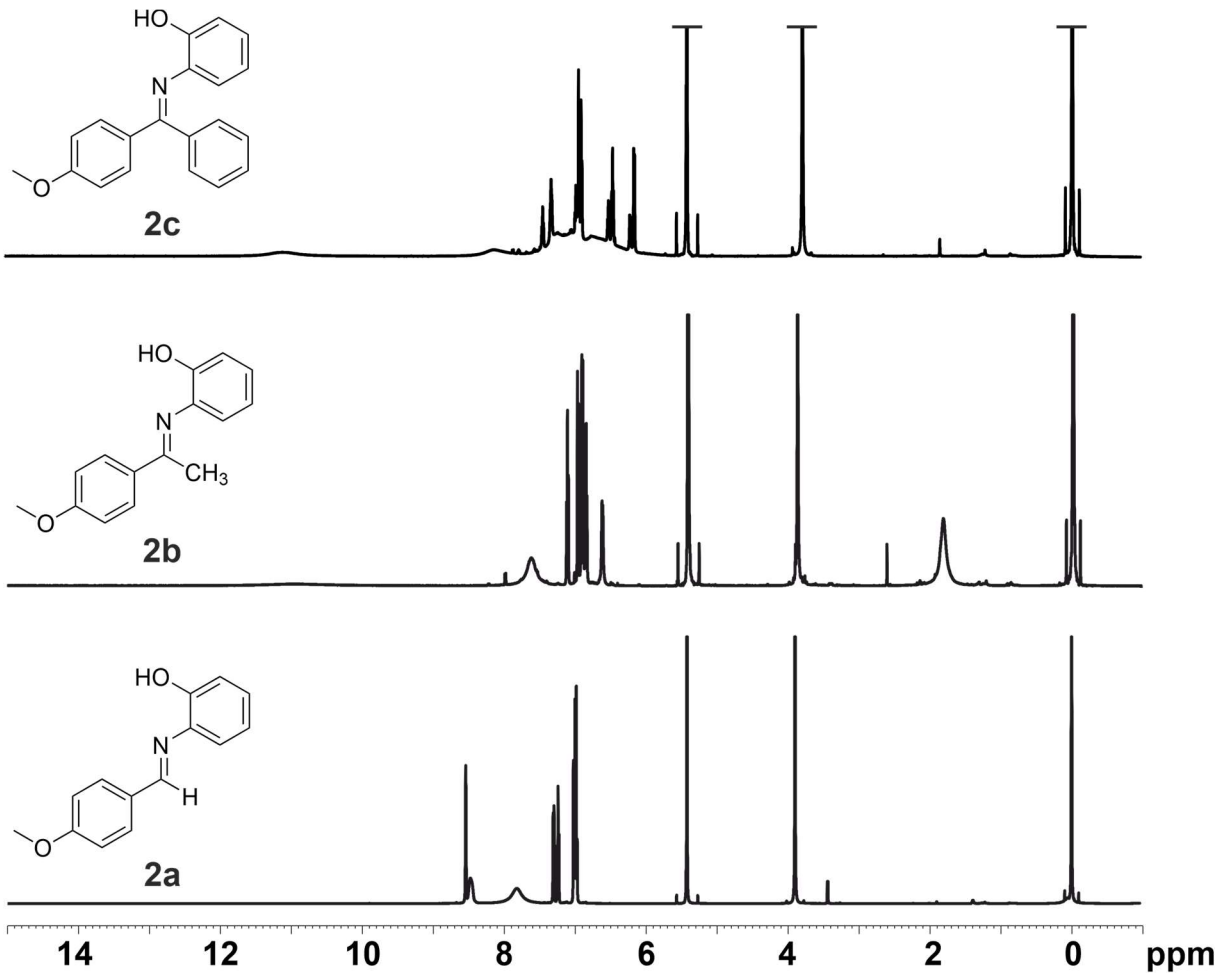


Figure S5: ^{1}H NMR spectra of imines **2a** (25 mM), **2b** (10 mM) and **2c** (10 mM) in CD_2Cl_2 at 180 K and 600 MHz (concentrations are analogous to the samples of **1a**-**b**/**2a**-**c**). For **2b** and **2c**, broad peaks at 11 ppm are observed which indicate the presence of inter- and/or intramolecular hydrogen bonds. However, these signals were not observed in the samples with the catalysts.

*5.3. ^{1}H NMR spectra for systems **1b/2a-c***

For samples containing catalyst **1b** and imines **2a**-**c**, the recorded ^{1}H NMR spectra (see Figure S6) were similar to the ones with catalyst **1a** (see Figure 2). For imines **2b** and **2c** many hydrogen bonded proton signals were monitored, reflecting a broad structural space of the complexes. For imine **2a** however, 8 hydrogen bonded proton signal, reflecting 4 different complexes were observed. In contrast to **1a**/**2a** (see Figure 2), the set of PO^{-}---H-N^{+} hydrogen bonds as well as the set of PO---H-O hydrogen bonds have different chemical shifts within the set (2 H-bonds at 14-14.5 ppm, 2 H-bonds at 13 ppm for PO^{-}---H-N^{+}; 2 H-bonds at 12.4 ppm, 2 H-bonds at 11.5 ppm for PO---H-O), which indicates a structural difference.

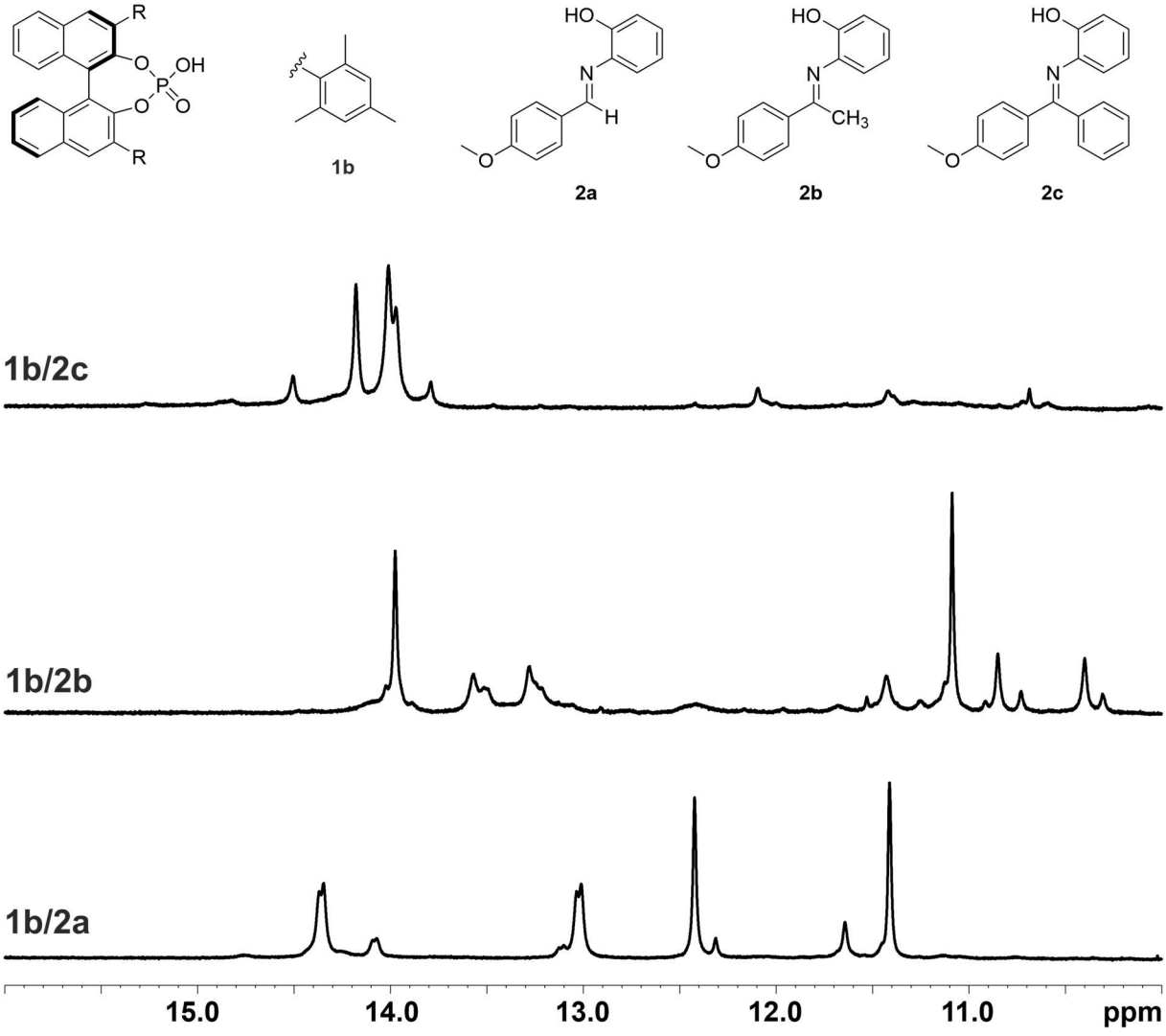


Figure S6: Section of the ^{1}H NMR spectra of **1b**/**2a** (bottom), **1b**/**2b** (middle) and **1b**/**2c** (top) at a 1:1 ratio and a concentration of 10 mM in CD_2Cl_2 at 600 MHz and 180 K. For **1b**/**2a**, 8 hydrogen bonds reflecting 4 different CPA/imine species were observed, while for **2b** and **2c** a multitude of different species was found.

5.4. E/Z isomerization experiments

For the system **1a**/**2a** (see Figure 2), a second sample was prepared at low temperature (see Sample Preparation). In our previous work,[9] this method was applied to exclusively populate CPA/*E*-imine species. In our previous work,[8,12] the employed imines were predominantly present as the *E*-isomer, but in presence of a chiral phosphoric acid, CPA/*Z*-imine complexes were significantly populated (*E*:*Z* ratios up to approx. 50:50) due to a reduced steric repulsion within the binding pocket of the catalyst. However, at temperatures < -80 °C, the *E*-imine cannot isomerize. Hence, if the sample is prepared at low temperatures, it becomes possible to suppress CPA/*Z*-imine complexes. For **1a**/**2a**, the population of hydrogen bonded proton signals A, B and C (see Figure S7) are similar for the low-temperature ("*E*-only") and room-temperature sample ("*E*/*Z*"). This indicates, that all 3 species feature an *E*-imine. The slight offset most likely originates in an insufficient equilibration of the "*E*-only" sample prior to the measurement.

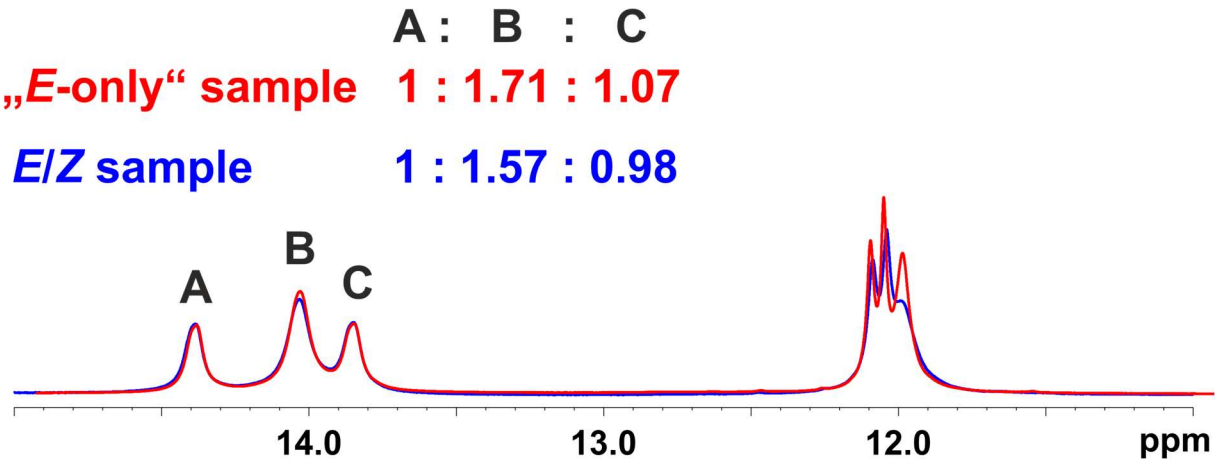


Figure S7: Comparison of the ^{1}H NMR spectra of 2 samples of **1a**/**2a** which were prepared at low temperature (red) and at room temperature (blue) in CD_2Cl_2 at 180 K and 600 MHz. No significant differences were observed, indicating that all 3 species feature an *E*-imine.

To further corroborate the assignment of all species as *E*-imine, photoisomerization experiments were carried out. In our previous work it was shown, that it is possible to increase the population of the CPA/*Z*-imine *via* illuminating the sample with an appropriate wavelength to induce a photoisomerization process.[13] Hence, **1a**/**2a** (1 : 1 ratio, 50 mM) was illuminated at 180 K first at a wavelength of 13.5 h and afterwards additionally for 3 h at 280 nm (see Figure S8). However, only minor changes in the integral ratios of the hydrogen bonded proton signals A, B and C were monitored, which could also originate in a change in relaxation times under

illumination. This indicates, that all three species feature the same imine configuration, which is most likely the more stable *E*.

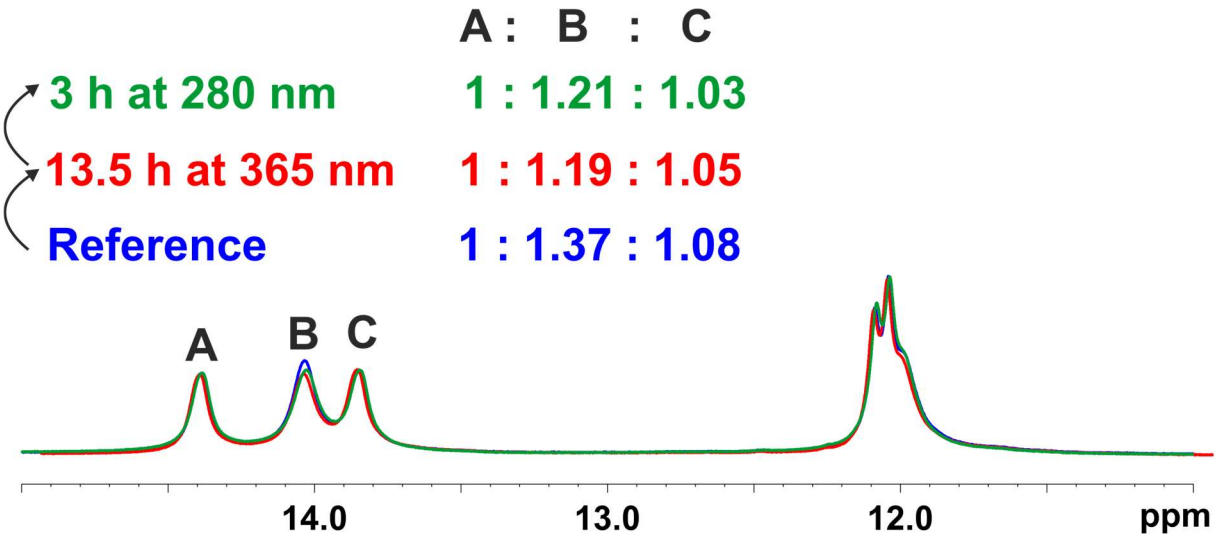


Figure S8: Comparison of the hydrogen bonding section of the ^{1}H-NMR spectra of **1a**/**2a** at 180 K and 600 MHz in CD_2Cl_2. The blue spectrum is the reference spectrum prior to illumination, the red spectra was recorded after 13.5 h of continuous illumination at 365 nm and the green spectrum was recorded after following illumination at 280 nm for 3 h. Minor changes in the populations of species A, B and C were detected but unlikely originate in a change of the imine configuration.

6. Accessing CPA/imine monomers

In our previous research,[12] we identified the structure of [CPA/imine]$_2$ complexes featuring CPA **1b** and imines without additional hydrogen bond donor. In these structures, two stacked imines are nested within the binding pocket created by the 3,3'-substituents of the two catalyst molecules in a shifted phase to phase arrangement. Thereby, the 3,3'-substituents of the two catalyst molecules are close to each other. Initially we tried to modify the catalyst to hinder dimerization.

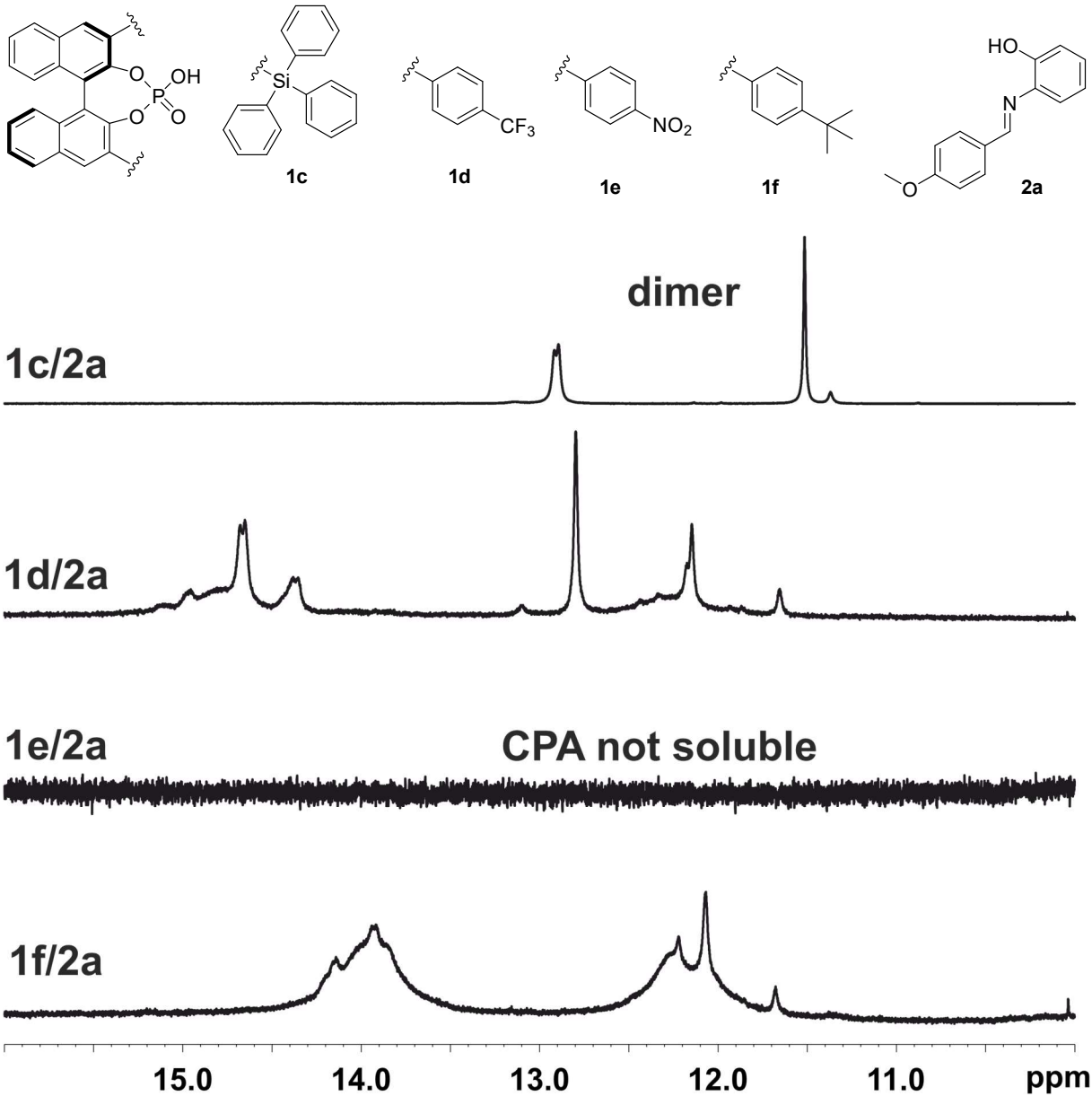


Figure S9: Section of the ^{1}H NMR spectra of **1c-f/2a** in CD_2Cl_2 at a ratio of 1:1 and a concentration of 10 mM at a temperature of 180 K.

For the combination of **1c**/**2a** (see Figure S9, top), the steric bulk of the catalyst was increased to minimize the available space inside the binding pocket, so that two stacked imines would not fit in. The measured ^{1}H NMR spectrum showed only two hydrogen bonds, reflecting one distinct species. However, DOSY measurements (see Table S5) showed that the monitored complex is still a dimer, giving a hydrodynamic radius of ~ 12.36 Å, which is close to the previously reported hydrodynamic radius of monodentate CPA/imine dimers.[12] For catalysts **1d-f**, the idea was to introduce electronic (**1d** and **1e**) or steric (**1f**) repulsion to the 3,3'-substituents. Catalyst **1e** was not soluble in CD_2Cl_2 at low temperature and hence no hydrogen bonded proton signals are observed. For **1d**/**2a** and **1f**/**2a**, no clear and well defined hydrogen bonded proton NMR signals were observed or the spectra could not be analyzed in more detail due to signal overlap and line broadening.

In our previous research, we observed that installing sterically bulky groups such as *tert*-butyl groups on both sides of the imine can efficiently prevent dimerization of CPA/imine complexes.[9] Hence, imine **3a** was selected and screened with different catalysts. **1b**/**3a** gave a well defined spectrum with only one monomeric species (see Figure 3), thus showing that this approach can give the intended result. For **1a**/**3a**, a similar spectrum was recorded but with significantly broadened lines. Additionally, for **1a**/**3a** spontaneous gel formation – most likely by CPA catalyzed polymerization of **3a** – occurred after some time (the shown spectrum in Figure S10 was measured immediately after sample preparation). For **1c**/**3a**, **1g**/**3a** and **1h**/**3a**, only severely line broadened hydrogen bonded proton signals were found, highlighting the broad possible structural space of bidentate CPA/imine complexes.

After receiving a well resolved spectrum of monomeric **1b**/**3a**, we slightly changed the *para*-substituent or alpha-substituent to explore if the determined structure for **1b**/**3a** is retained if the imines are modulated. When changing the *tert*-butyl group to an *iso*-propyl group for **1b**/**3b** (see Figure S11), again a well resolved spectrum with one defined species was obtained (see Figure S3 for chemical shift assignment). However, when going to a methyl-substituent (**1b**/**3c**) or methoxy-substituent (**1b**/**3d**) or if the alpha-substituent is changed from hydrogen to methyl (**1b**/**3e**), again various broad hydrogen bonded proton signals are detected. This again highlights, that for N-(*ortho*-hydroxyarl) substituted imines, a broad structural space is possible and that only for certain CPA/imine combinations, well defined complexes are obtained.

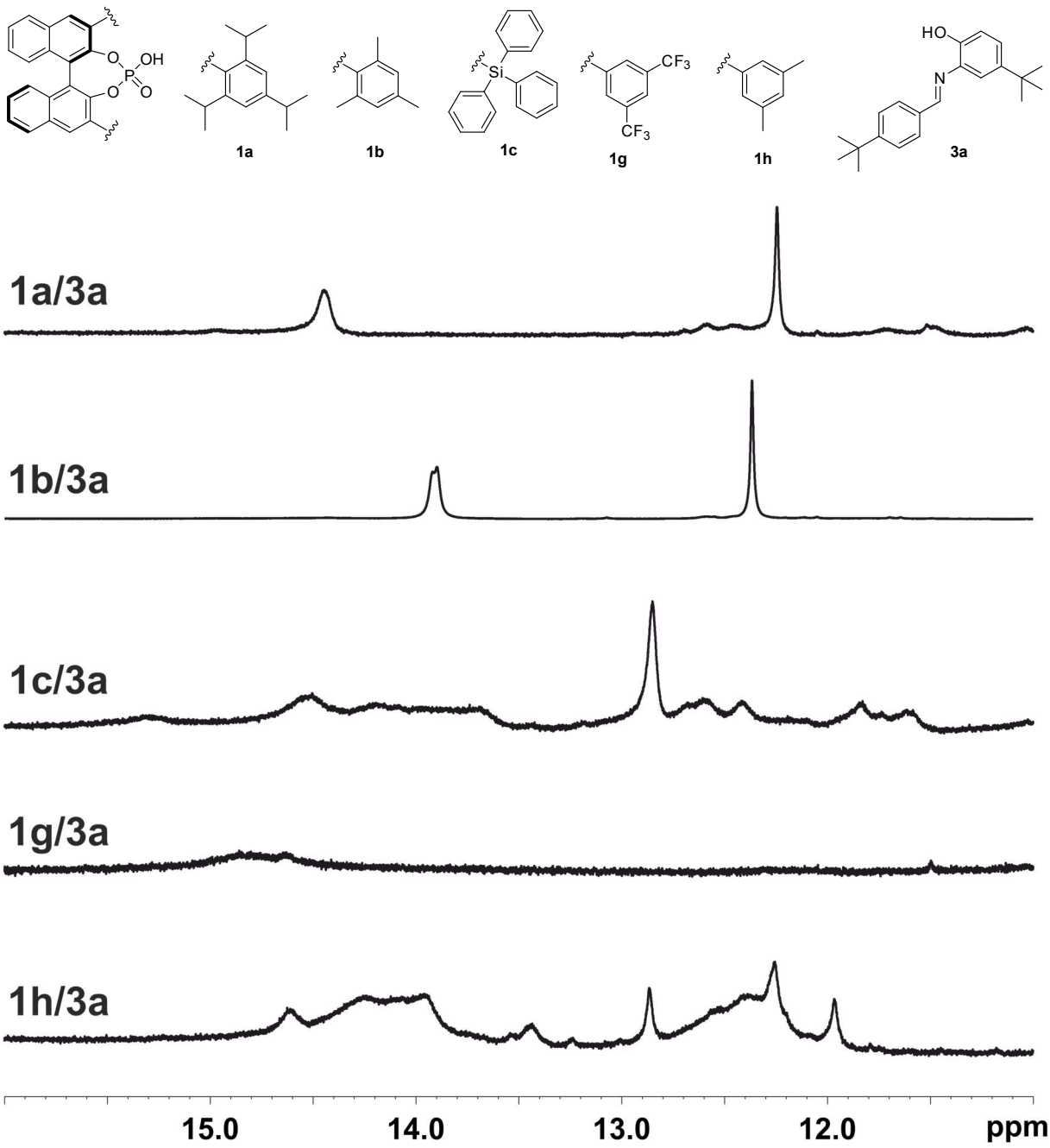


Figure S10: Section of the ^{1}H NMR spectra of **1a-c,g,h/3a** in CD_2Cl_2 at a ratio of 1:1 and a concentration of 10 mM at a temperature of 180 K.

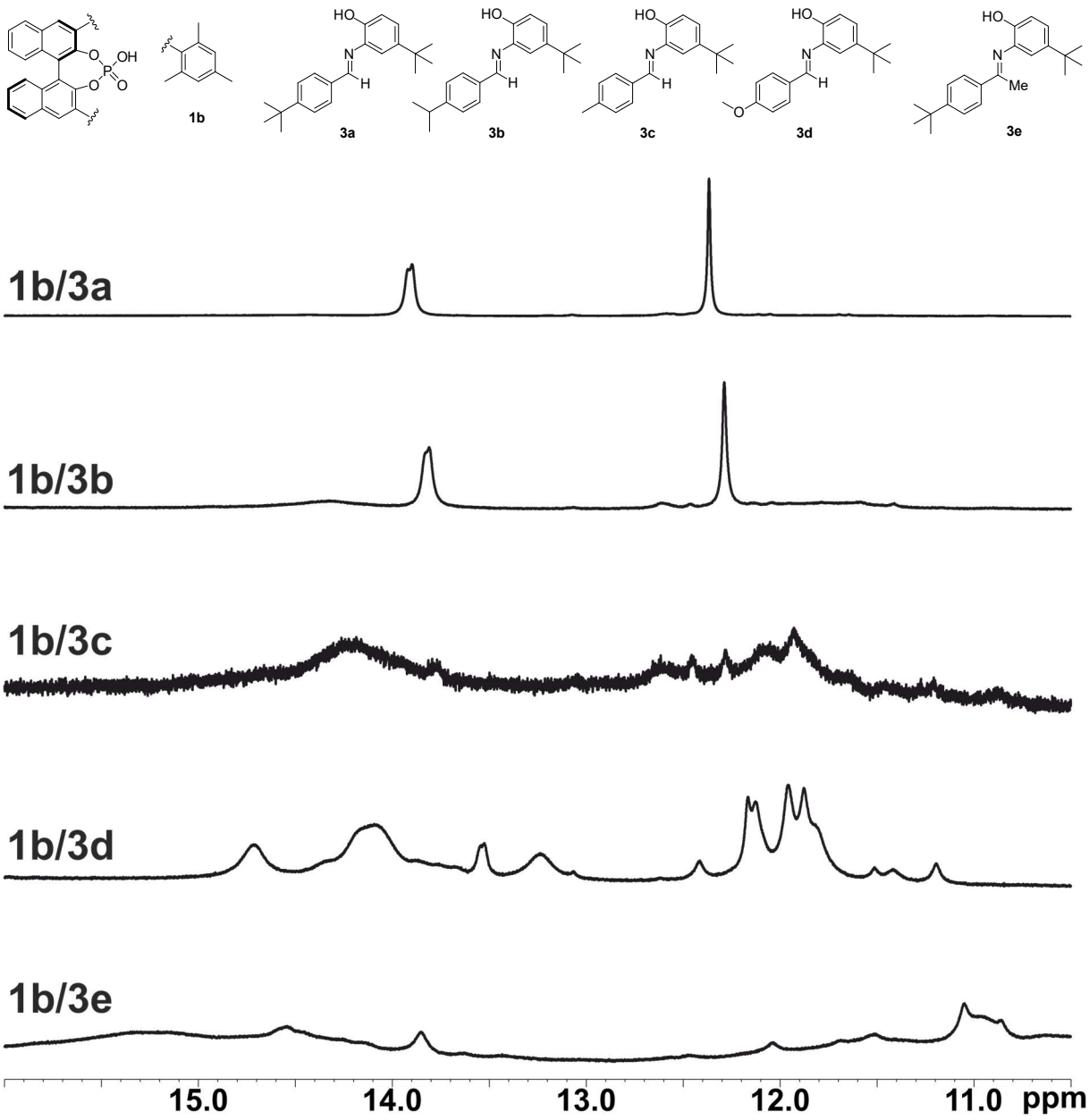


Figure S11: Section of the ^{1}H NMR spectra of **1b**/**3a-e** in CD_2Cl_2 at a ratio of 1:1 and a concentration of 25 mM at a temperature of 180 K.

7. Hydrogen bond analysis

Due to their partial covalent character, hydrogen bonds can be characterized via the detection of scalar coupling between the involved nuclei.[13,14] For the system **1b**/**3a**, the full scalar coupling matrix between the two hydrogen bonded protons (PO^----H-N^+ in red and PO---H-O blue; see Figure S12) and the CPA as well as imine was detected *via* ^{1}H ^{1}H COSY and ^{1}H ^{31}P HMBC spectra. This clearly validates the assignment as hydrogen bonds and confirms the postulated binding motif featuring two hydrogen bonds as a rigid anchor.

In our previous research with imines featuring no additional hydrogen bond donor, the CPA/imine complexes could be characterized as hydrogen bond assisted ion pairs by analysis of the ^{1}H and ^{15}N chemical shifts as well as J_{NH} coupling constants and comparison to reference systems with weak and very strong acids.[13,14] For CPA/imine complexes with imines **2** and **3**, we assume that the complexes are also present mainly as ion pairs, especially as the cooperativity effect of the second PO---H-O hydrogen bond is expected to better stabilize the resulting phosphate, which suggests an even stronger proton transfer on the imine substrate, resulting in a stronger ion pair character. This would be reflected by the $^{1h}J_{NH}$ coupling constant, which could not be accessed as imines **2** and **3** could not be ^{15}N labelled. However, the $^{3h}J_{HH}$ coupling between the hydrogen bonded proton and the α-H of the imine (see e.g. Figure 12; doublet splitting was observed for all systems with α-H imines) can only be present if the NH binding order is relatively close to 1, clearly indicating that the proton is strongly transferred on the imine, which results in an ion pair character. However, as there is still detectable magnetization transfer by scalar coupling to the CPA (see Figure 12 signal C), the proton transfer is not complete and the complex is best described as hydrogen bond assisted ion pair.

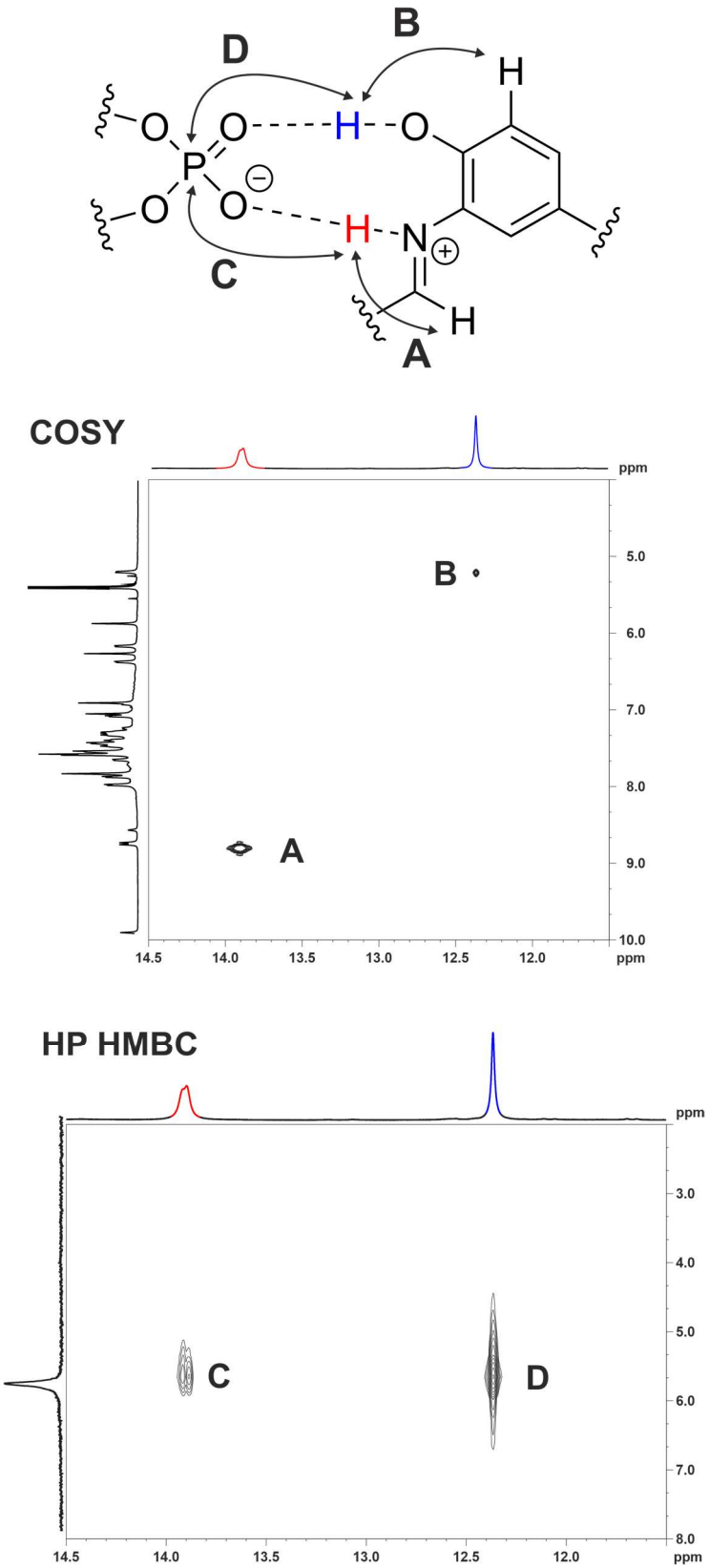


Figure S12: Excerpts of the ^{1}H ^{1}H COSY and ^{1}H ^{31}P HMBC spectra of **1b**/**3a** at a 1:1 ratio and a concentration of 25 mM at 180 K in CD_2Cl_2. The cross peaks A-D clearly show the full scalar coupling matrix of the hydrogen bonded protons.

8. NOE studies

In the computed structure model for the bidentate complex **1b**/**3a** (see Figure 4) the imine is located in between the two 3,3'-substituents of the catalyst. The performed NOESY study (see Figure S13) validated this structure model, as only NOE contacts between the imine and the two 3,3'-substituents were found and none to the BINOL backbone, which would be typical for monodentate CPA/imine complexes.[8,12] One site of the imine has only contact to one 3,3'-substituent (NOE cross peaks A and B or C-E), which could be resolved due to the signal splitting of the C_2-symmetric catalyst in the CPA/imine complex.

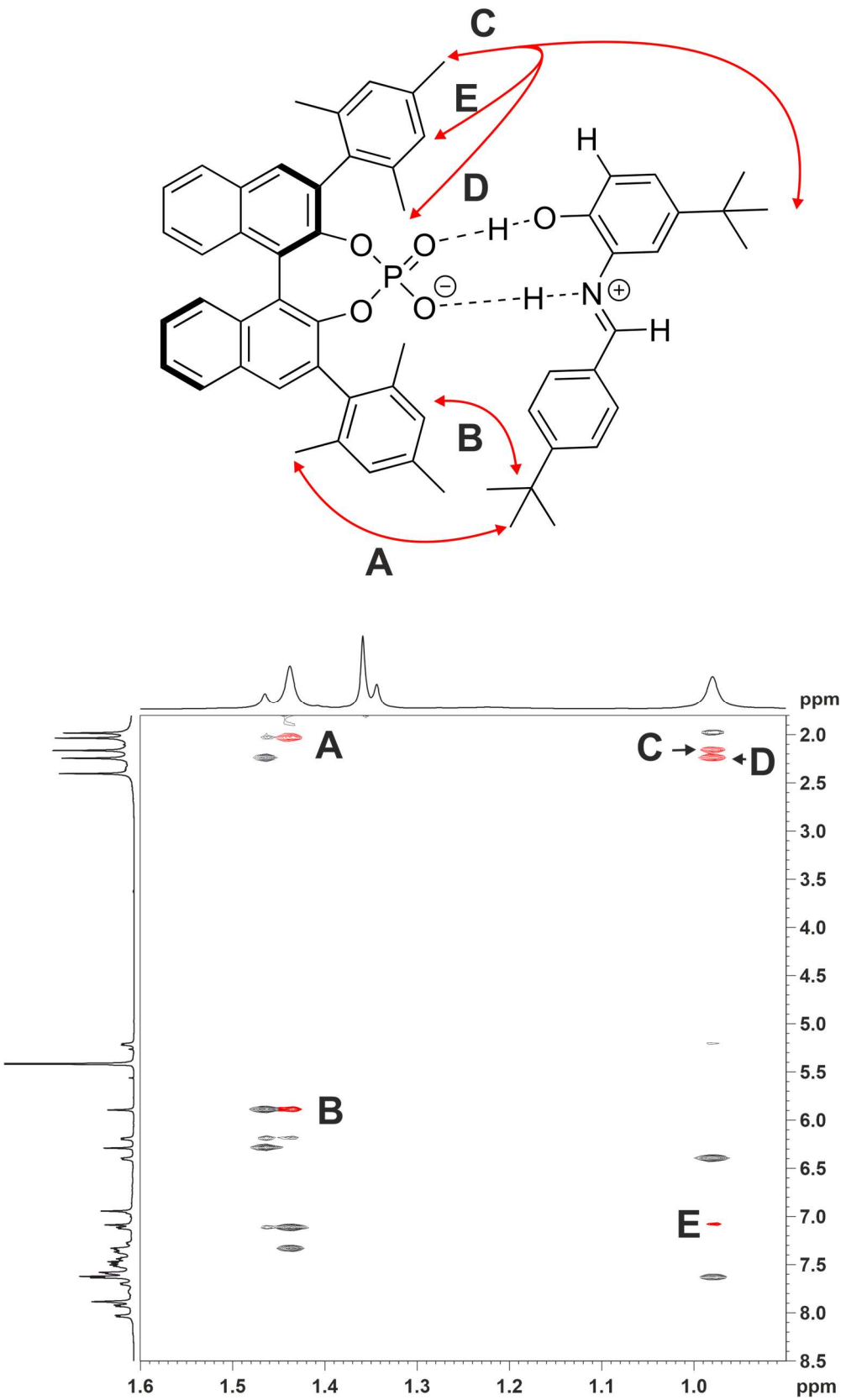


Figure S13: Excerpt of the NOESY spectrum of **1b**/**3a** at a 1:1 ratio and a concentration of 25 mM at 180 K in CD_2Cl_2. The cross peaks A-E shown in red validate the theoretically computed structure model.

9. Computational Details

9.1 Molecular dynamics (MD) simulations

9.1.1 Simulation details (**1a**/**2a**)

For the generation of the phosphate and iminium forcefields GAFF[15] parameters were used. For the iminium-ions the problem appears that the double bond atoms are not well described with the standard GAFF parameters. Due to prior investigations in our group, the parameters of “ce” and “na” were chosen as an approximation.

The parameters were assigned with antechamber[16]. For the point charges geometry optimizations with orca (versions 4.1.2/ 4.2.1)[17] at (B3LYP 6-311G**) level were done and RESP-fits using Multiwfn[18] 3.6 with a Merz Kollman grid of 6 points/Å^2 or finer with at least 4 layers per atom were used. Constraints were set for equivalent charges on CH_2 and CH_3. The conversion to a GROMACS topology was done with the tool acpype[19].

The DCM force-field is derived of a density-corrected DCM (GAFF based) force field by Horinek[20] with additional virtual sites. (see appended force fields section 9.1.3)

The MD-runs were performed with a timestep of 2 fs at 200K (v-rescale thermostat, tau = 1.0 ps) at a concentration of 50mM in DCM, 1 bar (Parrinello-Rahman barostat with isotropic scaling, compressibility = 2.5e^{-5} bar^{-}1) with a cutoff of 1 nm with the GROMACS package [RMG-Q7] in versions ranging from 2018-2020 employing the verlet scheme.

PME was used for the coulomb interactions. A potential shift coulomb modifier was employed.

Dispersion corrections were added for energy and pressure.

Constraints for all bonds were used (LINCS, lincs-order = 4, number of iterations 2, verlet-buffer-tolerance = 0.0001 kJ/mol/ps).

For the first simulation all molecules were placed into the simulation box at random.

The obtained cluster-size distributions however do not correspond to the experimental distribution. This is due to the nature of the forcefields used. (Once associated to either a CPA-iminium monomer or dimer the ions do not diffuse away from one another on the simulation time scale. Whereas in the experiments dissociation happens as phosphoric acid and imine respectively even though nearly everything is incorporated in CPA-iminium dimers.)

While this leads to the "wrong" representation of aggregates in the system during normal simulation times, this does not mean that they cannot be studied:

For this we make a distinction between dimers where the iminium group and the alcohol group of one single imine form hydrogen bond with the same phosphate (non-bridging) and those where they form hydrogen bonds with two different phosphates (bridging dimers). That means the bridging dimers consist of two phosphoric acid residues interconnected via two iminium residues, whereas for non-bridging dimers one would assume stacking of the imines of two "monomer units" (each with their individual phosphate).

We expect that non-bridging dimers would have been readily seen in the initial simulation (compare to cluster size distributions tab S6). There only around 20% of "dimer" was detected. This corresponds to the identified bridging dimer and therefore we anticipate that bridging-dimers will correspond to the experimentally found dimers.

For the determination of free energy differences between the bridging dimers with four H-bonds each Thermodynamic Integration (TI)[21] is used (employing the lambda vector implementation of GROMACS with "vdw", "coul" and "restraint"-lambdas, use of soft core potentials with sc_alpha = 0.5, sc_power = 1).

We achieve this by uncoupling one single iminium molecule and keeping the rest of the aggregate constant, which converges the dH/dlambda values faster than if the four molecules were to be coupled simultaneously. For this, simulations of at least 60 ns were employed. The derivative dH/dlambda was written out every 500 steps.

To fix the positions even in the uncoupled state distance constraints (umbrella-type, force constant of 1000 kJ/mol/nm^2) set to the mean value of the unconstrained simulation are used along the HBs and coupled during the simulations.

Because the constraints are chosen differently (namely to the average from the unconstrained simulation) for all dimers they do not cancel one another and need to be removed at the end.

Therefore the TI procedure is given by:

- First one completely coupled system without constraints,
- then a constraining step for the completely interacting system,

- followed by coulomb decoupling in steps of delta lambda = 0.1,
- subsequent VdW decoupling in steps of delta lambda = 0.1,
- and finally the removal of the constraints.

For the last part of the integration Mclaurin integration (of Newton Cotes formula - used points 0.83 0.5 0.167) was employed.

9.1.2 Results (**1a**/**2a**)

9.1.2.1 Simulation of randomly placed ions in DCM

Because the question regarding the **1a**/**2a** system was 'What might be hidden behind the three different H-bond situations?' those were investigated. As a starting point the phosphate oxygen and iminium H(N) H(O) distances were therefore obviously of interest:

An initial evaluation of the radial distribution functions (RDFs) between phosphate oxygen (named O1 and O2) and the iminium hydrogen bonding atoms (both the alcohol and iminium group) of the box showed that while there is one main distance both for the iminium H(N) and for the alcohol H(O) towards the phosphorus atoms- the situation is a bit more complicated. (Additionally: Obviously the situation is not even completely converged, because O1 and O2 are not yet equivalent, which means additional species have been sampled, which did not interconvert on our timescale.)

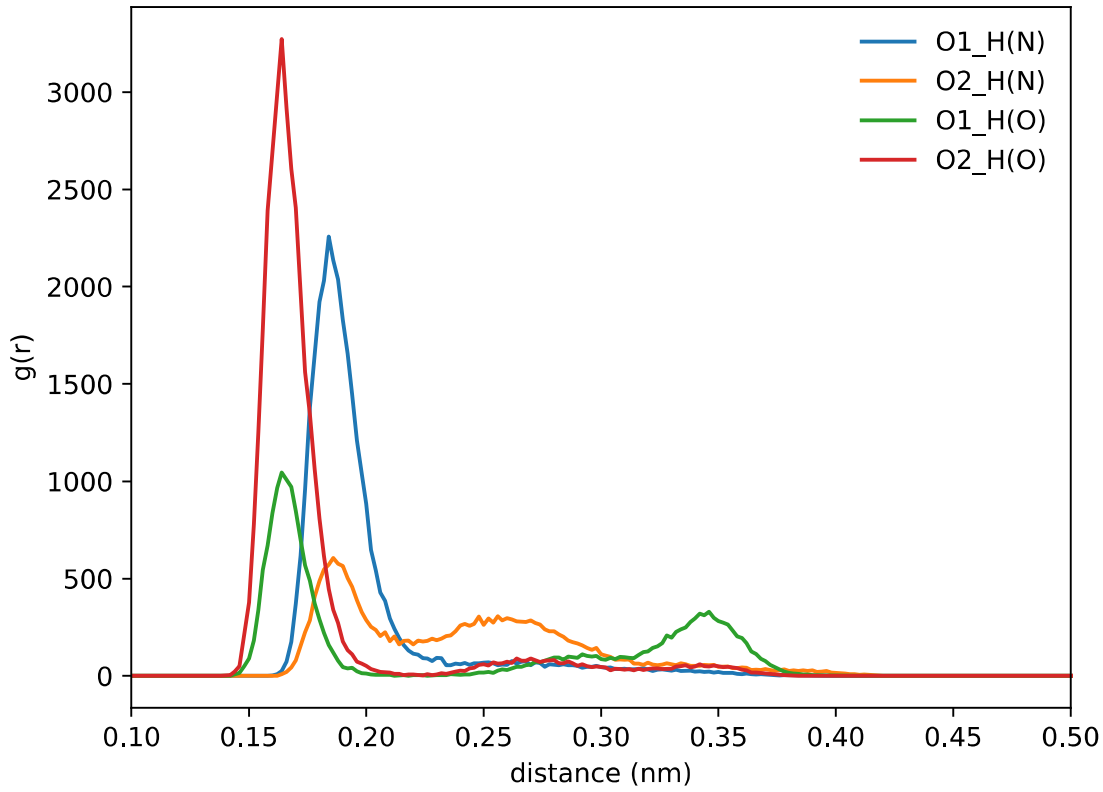


Figure S14: Distance RDF between phosphate oxygens and iminium H bonding atoms.

Therefore, the situations needed to be analyzed in more detail:

A simple cluster-size search (based of cutoff – excluding the solvent) showed that just inserting molecules into our simulation box did not reproduce the experimental dimers since our classical force fields cannot describe bond-breaking and formation which is necessary for the correct description of the dissociation process of both monomers and dimers.

The hydrogen-bonding situation differ between the observed monomers and dimers.

To elucidate this, first the monomer situation will be discussed: In case of the monomers two hydrogen bonds are formed between the CPA and imine. This can lead to the two different situations regarding the phosphate oxygen – namely one “bifurcated” bond towards one single oxygen or a single bond towards each of the CPA oxygens. (see fig. S15) Interestingly those interconvert quite slowly (rare events on the 100 ns timescale). This is not an equilibration issue because it happens in both directions (see figures S16/S17).

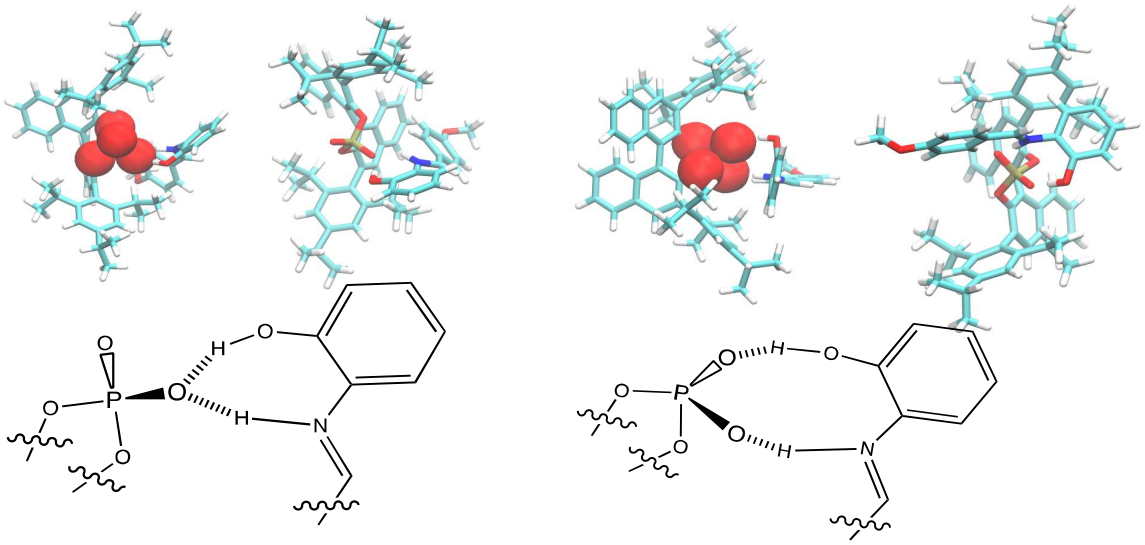


Figure S15: Different possible H-bond situations occurring for the monomers

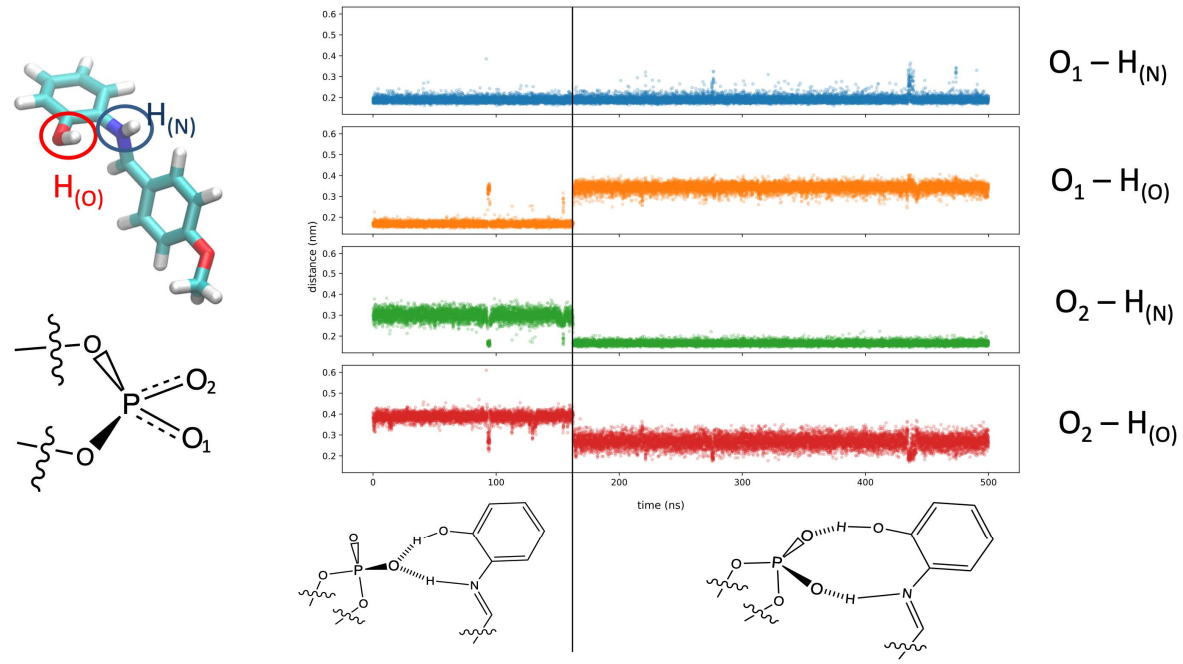


Figure S16: Example of bond switching by the OH group

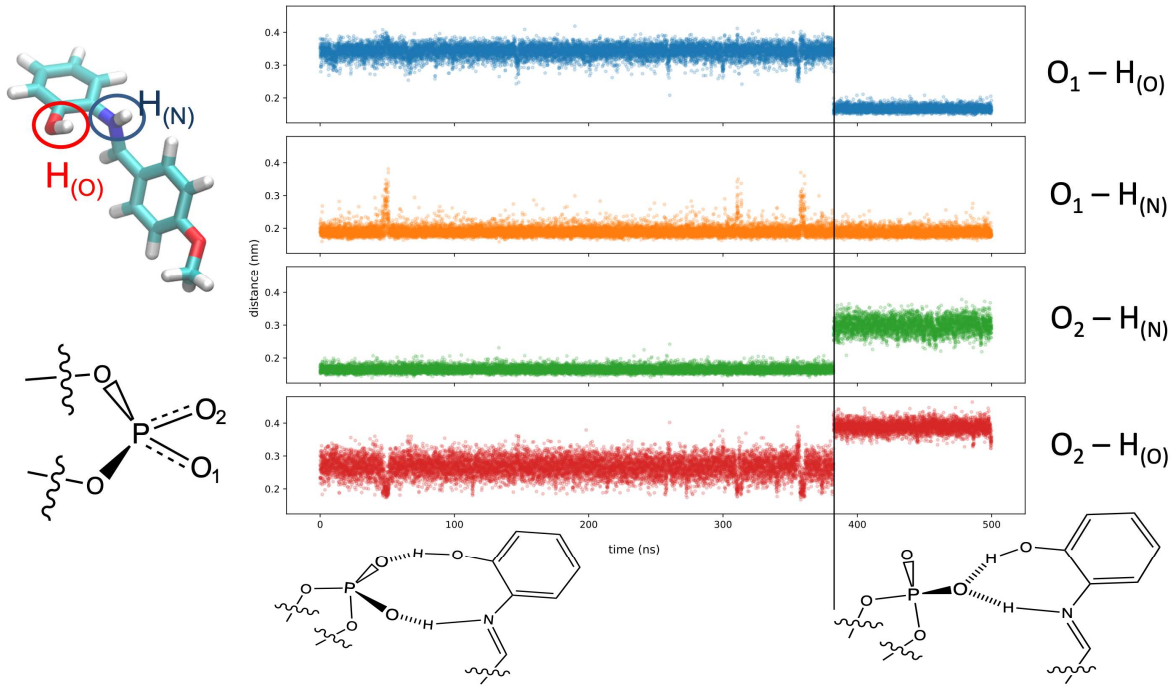


Figure S17: Example of bond switching by the OH group

Opposed to the monomers the observed dimer is different. (see fig. S18) Not only is every individual iminium molecule forming an H-bond with two different CPA moieties; both imines are stacked on top of one another, leading to an asymmetry with regard to the positioning of alcohol and iminium groups. That in turn has another interesting consequence, which once more shows that a bidentate binding motif does not exclude orientational flexibility: We could observe two conformers (see fig. 19), which differ in the positioning of the CPA on the OH-side. The corresponding BINOL backbone can therefore be positioned either parallel or orthogonal to a plane given by the imines. This leads to different accessibilities of the substrate moiety.

Table S6: Clustersizes (in atoms - solvent for cluster search ignored) and their probabilities for the initial (randomly positioned ions) simulation broken down in the combination of cations and anions

cutoff	**0.35**				**0.4**			
	clustsize	probability (%)	cation	anion	clustsize	probability (%)	cation	anion
	142	75.22	1	1	142	74.09	1	1
	284	18.25	2	2	284	18.63	2	2
	426	4.54	3	3	426	4.96	3	3
	568	1.29	4	4	568	1.45	4	4
	710	0.55	5	5	710	0.67	5	5
	852	0.12	6	6	852	0.15	6	6
	994	0.04	7	7	994	0.05	7	7
cutoff	**0.45**				**0.5**			
	clustsize	probability (%)	cation	anion	clustsize	probability (%)	cation	anion
	142	72.57	1	1	142	70.29	1	1
	284	19.11	2	2	284	19.7	2	2
	426	5.52	3	3	426	6.37	3	3
	568	1.68	4	4	568	2.05	4	4
	710	0.83	5	5	710	1.09	5	5
	852	0.22	6	6	852	0.36	6	6
	994	0.07	7	7	994	0.13	7	7

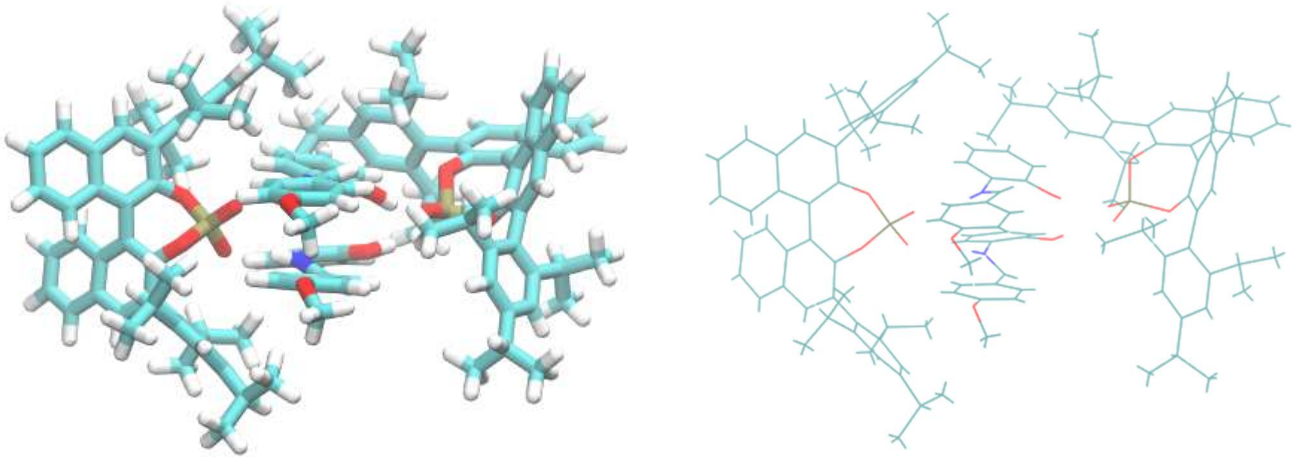


Figure S18: Snapshot of the observed bridging dimer (both OH groups toward one single CPA, NH groups towards the second CPA residue)

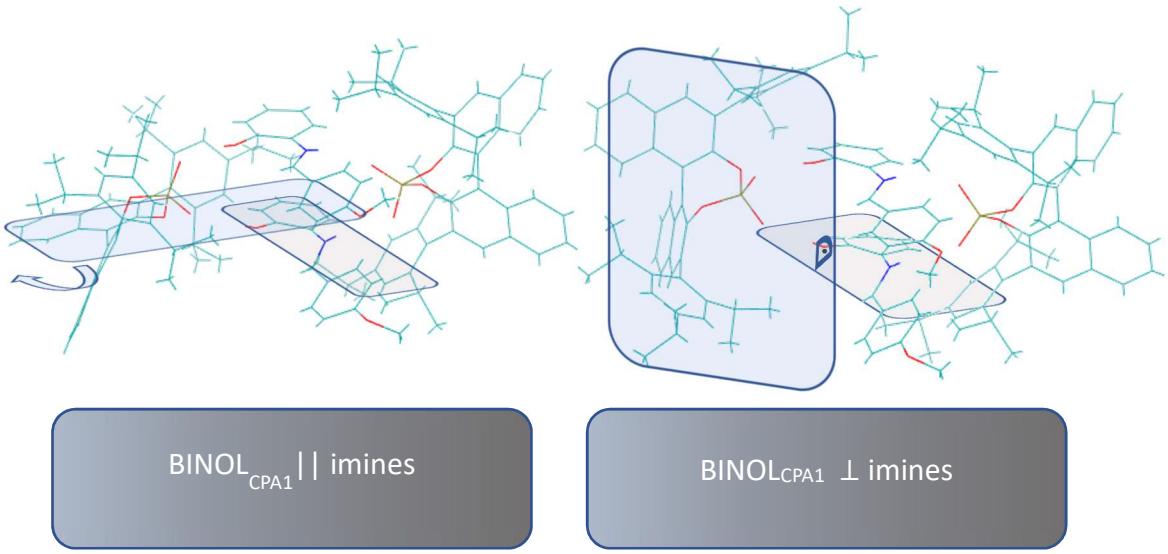


Figure S19: Snapshots showing the conformational flexibility of the observed bridging dimer (flip of the CPA residue connected via OH bonds)

9.1.2.2 Simulation of bridging dimeric species – Thermodynamic integration (TI)

Due to the aforementioned equilibration issues TI[21] was chosen in order to obtain insight into the possible other bridging dimers. Those are characterized with respect to their respective functional groups' positions (in tab. S7).

Table S7: Summary of the possible bridging dimers

		iminium MeO groups	**NH groups**
dimer 0		same direction for both imines	towards one single CPA group (asymmetric)
dimer 1		same direction for both imines	towards two different CPA groups (symmetric)
dimer 2		different direction for both imines	towards two different CPA groups (symmetric)
dimer 3		different direction for both imines	towards one single CPA group (asymmetric)

Table S8: Summary of the Thermodynamic Integration (**1a** case)

	$-\Delta G_c$ [kJ/mol]	$-\Delta G_{coul}$ [kJ/mol]	$-\Delta G_{vdw}$ [kJ/mol]	$-\Delta G_{c2}$ [kJ/mol]	$\Delta\Delta G_{(i-0)}$ [kJ/mol]
0	-0.02	220.1	44.4	-21.3	0.0
1	-0.55	211.5	50.0	-18.9	1.0
2	-0.08	217.1	45.3	-19.8	0.6
3	-0.02	198.2	48.0	-17.0	14.1

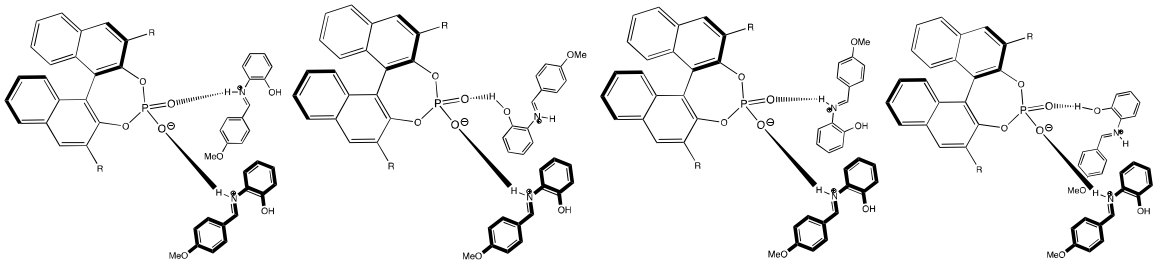


Figure S20: Schematic sketch of bond situations in the dimers as described in table S7 (only one CPA shown) - left to right: I) "same direction for both MeOH" – "NH (OH) groups oriented towards one single CPA"; II) "different directions for MeOH groups" – "NH groups oriented towards different CPAs"; III) "different directions for MeOH groups" – "NH (OH) groups oriented towards one single CPA", IV) "same direction for both MeOH" – "NH groups oriented towards different CPAs"

Table S8 gives an overview over the results from the TI. Here ΔG_c denotes the difference in free Energy due to the constrained H-bonds (and ΔG_{c2} to the released constraints). $\Delta G_{coul/vdw}$ are due to the switching of coulomb or VdW interactions. *(ΔG_{tot} would correspond to the solvation free energy ΔG_{solv} if not only one of the 2a molecules were coupled but the whole dimer.)* The decisive term is **$\Delta\Delta G_{(i-0)}$** – even if is not completely converged due to the influence of rare

events (and corresponding changes in the relative values). While the absolute value of ΔΔ**G** might is not completely converged no large qualitative differences can be expected. It clearly shows that “dimer 3” is definitively not accessible.

An investigation of the short range interactions sheds some light on the differences between the iminium dimers: The short range LJ interaction shows that while the symmetric dimers “1” and “2” show comparable LJ(iminium-iminium) stabilization, the asymmetric ones “0” and “3” show a major difference. – This is unsurprising because “0” shows an iminium stacking motif whereas the imines barely overlap in case of “3”. (see fig. S21) The apparent “loss” of LJ(iminium-iminium) of “0” is related to the aforementioned (see fig. S19) orientational change of the CPA residue on the alcohol side and is compensated by the LJ(CPA-iminium) interaction. (see fig. S22)

Summarily: ***There is no indication of non-bridging dimers from the cluster size distributions and we identified three similarly stable bridging dimers (“0”,”1”,”2”). Those might correspond to the three experimentally different H-bond signals from H-NMR.***

In addition, dimer “0” shows orientational flexibility on the OH side, which is possible due to LJ energy compensation switching between imines and CPA.

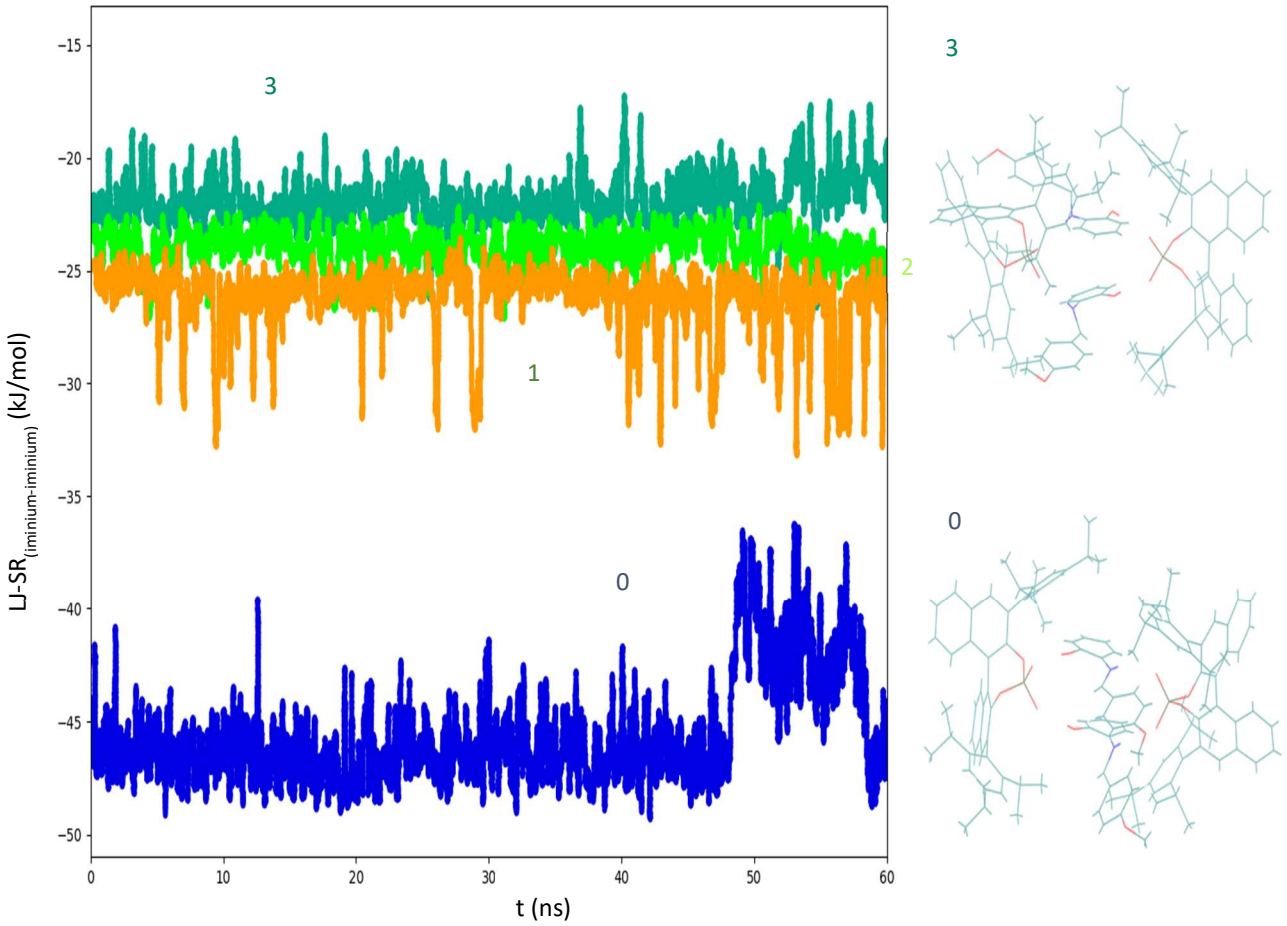


Figure S21: Short range LJ(iminium-iminium) energies for the bridging imines (for the unconstrained TI run)

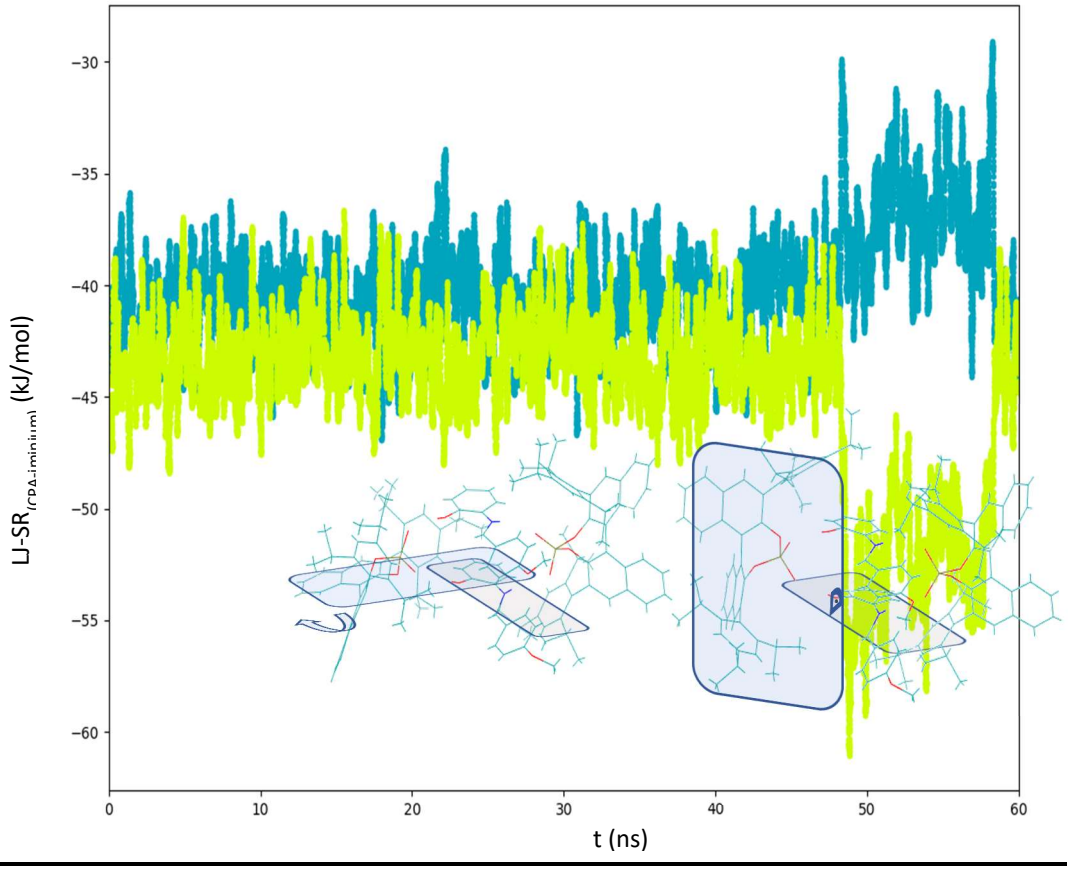


Figure S22: Short range LJ(CPA-iminium) energies between CPA and each of the two imines individually for dimer "0" (for the unconstrained TI run)

9.1.3 Comparison with system (**1e**/**2a**)

The catalyst **1e** is poorly soluble in CH_2Cl_2 (DCM), which prevented an extensive NMR study.

Still the question appeared, whether our model system with catalyst **1a** is comparable for small amounts dissolved in DCM (beneath the NMR detection limit) or whether different H-bond situations are dominating.

Keeping the iminium molecule **2a** identical and changing **1a** to the (R,R'=Ph-NO_2)-CPA **1e** we investigated the differences.

Two different approaches were employed when investigating the **1e** system:

- An unconstrained simulation to check the behavior of **1e**/**2a** in solution (as a check for non-bridged dimers created by stacking of iminium ions)
- Simulations constrained to the 4 bridging dimers analogous to the **1a**/**2a** system

<u>Unconstrained simulation</u>

Starting with a NVT simulation of **1e**/**2a** (10 molecules each) ions an initial box was generated by solvating it in DCM (3300 molecules) for the NpT simulation, which was then run for >120 ns. We observed that the phase separation from DCM persists for the mayor part of the ions and we ended up in the situation where only few **1e**/**2a** species with the CPA bound via two H-bonds to a single iminium molecule in solution. For those no stacking of the iminium molecules was observed.

Still there appear persistent non-bridging species on the route towards the 1:1 species, where either the CPA backbone stacks with the iminium molecule or the NO_2 groups are part of the H-bonds. (examples see fig. S24)

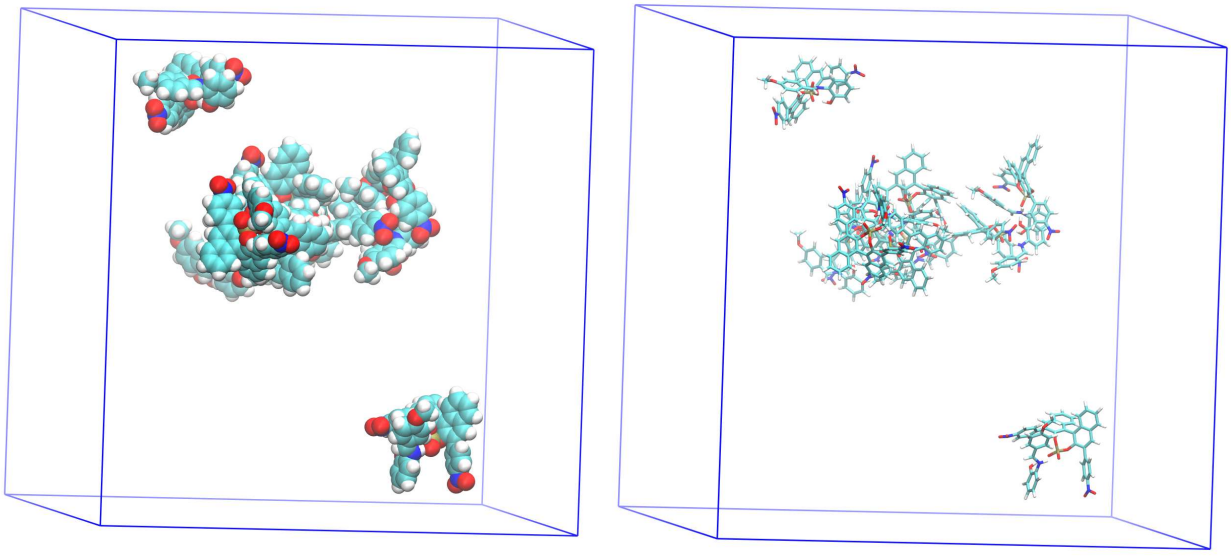


Figure S23: **1e**/**2a** in DCM (solvent not shown) showing phase separation and single 1:1 **1e**/**2a** species in solution (left: VdW representation, right: stick representation)

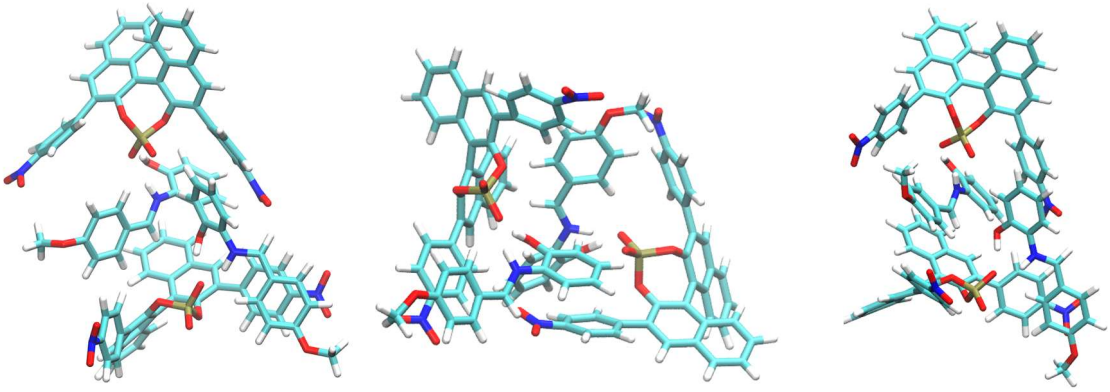


Figure S24: Snapshots of **1e**/**2a** in DCM showing different non-bridging 2:2 species

These are not stable over the whole simulation time, so the question remains whether they are equilibrium species or only intermediary appearances during the equilibration towards the single 1:1 **1e**/**2a** species observed in the end.

Constrained simulations

Similar conformations as above in the **1a**/**2a** case were enforced by a single set of umbrella constraints where the distances were taken from one of the constrained simulations above (in contrast to the previous system, where all distances had been taken from individual equilibrium runs. - Otherwise identical conditions as before were employed to the **1a**/**2a** case) assuming identical H-bond lengths for all conformers and avoiding (see fig. S24) the various other possible conformations.

The results of the thermodynamic integration (dH/dλ averaged over at least 30 ns) are given as follows (see table S9):

Table S9: Summary of the Thermodynamic Integration for the **1e** case

	$-\Delta G_c$ [kJ/mol]	$-\Delta G_{coul}$ [kJ/mol]	$-\Delta G_{vdw}$ [kJ/mol]	$-\Delta G_{c2}$ [kJ/mol]	$\Delta\Delta G_{(i-0)}$ [kJ/mol]
0	23	218	47	-29	0
1	13	210	47	-22	-10
2	16	205	41	-21	-17
3	34	207	43	-28	-2

The differences between the conformations are clearly larger than in our previous **1a** case.

Of exceptional note is that there is a large term associated with constraining the geometry to the desired conformers in the first place, which was negligible in the case of **1a** as they naturally occurred. That already means our system does not prefer the suggested conformations of **1a**. Therefore, this part of the coupling was not done in a single step (as in **1a**) but employed the same McLaurin steps as the uncoupling process.

Furthermore different 2:2 bridging complexes can be observed, in the fully coupled but unconstrained case. Here at least one of the NO_2 groups is involved in the H-bonds. This does not resemble the **1a** cases at all but rather show structures reminiscent of π-stacked structures.

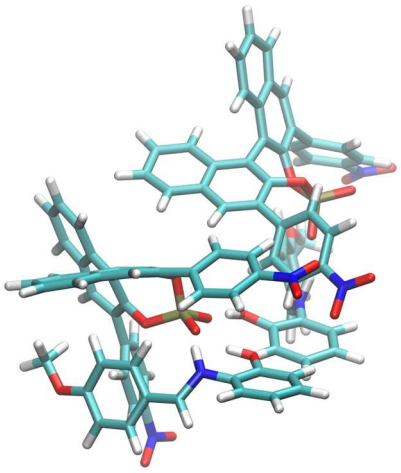


Figure S25: Snapshot taken for a fully interacting (**1e** case) but non constrained 2:2 system reveals different H-bond situations opposed to **1a** case

A comparison of the constrained (bridging-dimers) systems **1a** to **1e** shows the fact that the two systems differ in their H-bonding situations. (**1a** yields 3 practically equally stable cases whereas **1e** shows strong differences).

It hints at the fact that for the **1e** case the 'mono'-cluster (1:1 CPA/iminium) is decisive.

9.1.4 Force Field parameters

9.1.4.1 Combination rules

Combination rules '2' is used.

This corresponds to the use of LJ parameters σ (nm) and ϵ (kJ/mol) with the combination rules of: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \left(\epsilon_i * \epsilon_j\right)^{(1/2)}$. Pair generation is used both for coulomb and LJ with the respective multiplicative factors:

fudgeLJ=0.5, fudgeQQ= 0.833

9.1.4.2 Atomtypes

[atomtypes]

;name bond_type mass charge ptype sigma epsilon Amb

c3s c3s 0.00000 0.00000 A 3.39967e-01 4.57730e-01 ; 1.91 0.1094

cls cls 0.00000 0.00000 A 3.30000e-01 1.20000e+00 ; DH scaled or correct density

h2s h2s 0.00000 0.00000 V 2.29317e-01 6.56888e-02 ; 1.29 0.0157

ca ca 0.00000 0.00000 A 3.39967e-01 3.59824e-01 ; 1.91 0.0860

cp cp 0.00000 0.00000 A 3.39967e-01 3.59824e-01 ; 1.91 0.0860

os os 0.00000 0.00000 A 3.00001e-01 7.11280e-01 ; 1.68 0.1700

p5 p5 0.00000 0.00000 A 3.74177e-01 8.36800e-01 ; 2.10 0.2000

o o 0.00000 0.00000 A 2.95992e-01 8.78640e-01 ; 1.66 0.2100

c3 c3 0.00000 0.00000 A 3.39967e-01 4.57730e-01 ; 1.91 0.1094

ha ha 0.00000 0.00000 A 2.59964e-01 6.27600e-02 ; 1.46 0.0150

hc hc 0.00000 0.00000 A 2.64953e-01 6.56888e-02 ; 1.49 0.0157

ce ce 0.00000 0.00000 A 3.39967e-01 3.59824e-01 ; 1.91 0.0860

na na 0.00000 0.00000 A 3.25000e-01 7.11280e-01 ; 1.82 0.1700

oh oh 0.00000 0.00000 A 3.06647e-01 8.80314e-01 ; 1.72 0.2104

ho ho 0.00000 0.00000 A 0.00000e+00 0.00000e+00 ; 0.00 0.0000

hn hn 0.00000 0.00000 A 1.06908e-01 6.56888e-02 ; 0.60 0.0157

```
h4      h4        0.00000  0.00000   A    2.51055e-01   6.27600e-02 ; 1.41  0.0150
h1      h1        0.00000  0.00000   A    2.47135e-01   6.56888e-02 ; 1.39  0.0157
```

9.1.4.3 Molecule definitions

9.1.4.3.1 DCM

dcm.itp

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;name          nrexcl2
 DCM          3

[ atoms ]
;   nr  type  resi  res  atom  cgnr     charge      mass     ;
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    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 ]
    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

9.1.4.3.1 2a

[moleculetype]

;name nrexcl

COU 3

[atoms]

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2 ca 1 COU C1 2 0.526755 12.01000 ; qtot 0.000

3 ca 1 COU C2 3 -0.315126 12.01000 ; qtot 0.000

4 ca 1 COU C3 4 -0.054992 12.01000 ; qtot 0.000

5 ca 1 COU C4 5 -0.060231 12.01000 ; qtot 0.000

6 ca 1 COU C5 6 -0.132069 12.01000 ; qtot 0.000

7 ce 1 COU C6 7 0.114329 12.01000 ; qtot 0.000

8 na 1 COU N 8 -0.146003 14.01000 ; qtot 0.000

9 ca 1 COU C7 9 0.086116 12.01000 ; qtot 0.000

10 ca 1 COU C8 10 0.319648 12.01000 ; qtot 0.000

11 ca 1 COU C9 11 -0.317838 12.01000 ; qtot 0.000

12 ca 1 COU C10 12 -0.033055 12.01000 ; qtot 0.000

13 ca 1 COU C11 13 -0.115345 12.01000 ; qtot 0.000

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   16   ho    1   COU    H   16    0.429366     1.00800 ; qtot 0.000
   17   hn    1   COU   H1   17    0.262125     1.00800 ; qtot 0.000
   18   ha    1   COU   H2   18    0.158792     1.00800 ; qtot 0.000
   19   ha    1   COU   H3   19    0.187615     1.00800 ; qtot 0.000
   20   ha    1   COU   H4   20    0.158076     1.00800 ; qtot 0.000
   21   ha    1   COU   H5   21    0.170400     1.00800 ; qtot 0.000
   22   ha    1   COU   H6   22    0.188612     1.00800 ; qtot 0.000
   23   ha    1   COU   H7   23    0.149913     1.00800 ; qtot 0.000
   24   ha    1   COU   H8   24    0.189841     1.00800 ; qtot 0.000
   25   h4    1   COU   H9   25    0.143911     1.00800 ; qtot 0.000
   26   ha    1   COU   H10   26    0.154738     1.00800 ; qtot 0.000
   27   os    1   COU   O1   27    -0.322577    16.00000 ; qtot 0.000
   28   c3    1   COU   C13   28    0.034780    12.01000 ; qtot 0.000
   29   h1    1   COU   H11   29    0.080600     1.00800 ; qtot 0.000
   30   h1    1   COU   H12   30    0.080600     1.00800 ; qtot 0.000
   31   h1    1   COU   H13   31    0.080600     1.00800 ; qtot 0.000
[ bonds ]
;   ai    aj funct   r           k
    1     2   1    1.3984e-01    3.8585e+05 ;     C - C1
    1     6   1    1.3984e-01    3.8585e+05 ;     C - C5
    1    18   1    1.0860e-01    2.8937e+05 ;     C - H2
    2     3   1    1.3984e-01    3.8585e+05 ;    C1 - C2
    2    27   1    1.3696e-01    3.1514e+05 ;    C1 - O1
    3     4   1    1.3984e-01    3.8585e+05 ;    C2 - C3
    3    19   1    1.0860e-01    2.8937e+05 ;    C2 - H3
    4     5   1    1.3984e-01    3.8585e+05 ;    C3 - C4
    4    20   1    1.0860e-01    2.8937e+05 ;    C3 - H4
```

```
   5     6   1    1.3984e-01    3.8585e+05 ;    C4 - C5
   5     7   1    1.4763e-01    3.0234e+05 ;    C4 - C6
   6    21   1    1.0860e-01    2.8937e+05 ;    C5 - H5
   7     8   1    1.4209e-01    3.1263e+05 ;    C6 - N
   7    25   1    1.0916e-01    2.8267e+05 ;    C6 - H9
   8     9   1    1.3840e-01    3.5187e+05 ;     N - C7
   8    17   1    1.0100e-01    3.4175e+05 ;     N - H1
   9    10   1    1.3984e-01    3.8585e+05 ;    C7 - C8
   9    14   1    1.3984e-01    3.8585e+05 ;    C7 - C12
  10    11   1    1.3984e-01    3.8585e+05 ;    C8 - C9
  10    15   1    1.3637e-01    3.2133e+05 ;    C8 - O
  11    12   1    1.3984e-01    3.8585e+05 ;    C9 - C10
  11    22   1    1.0860e-01    2.8937e+05 ;    C9 - H6
  12    13   1    1.3984e-01    3.8585e+05 ;   C10 - C11
  12    23   1    1.0860e-01    2.8937e+05 ;   C10 - H7
  13    14   1    1.3984e-01    3.8585e+05 ;   C11 - C12
  13    26   1    1.0860e-01    2.8937e+05 ;   C11 - H10
  14    24   1    1.0860e-01    2.8937e+05 ;   C12 - H8
  15    16   1    9.7300e-02    3.1079e+05 ;     O - H
  27    28   1    1.4316e-01    2.5824e+05 ;    O1 - C13
  28    29   1    1.0969e-01    2.7665e+05 ;   C13 - H11
  28    30   1    1.0969e-01    2.7665e+05 ;   C13 - H12
  28    31   1    1.0969e-01    2.7665e+05 ;   C13 - H13

[ pairs ]
;  ai    aj   funct
   1     4     1 ;     C - C3
   1     7     1 ;     C - C6
   1    19     1 ;     C - H3
```

1 28 1 ; C - C13

2 5 1 ; C1 - C4

2 20 1 ; C1 - H4

2 21 1 ; C1 - H5

2 29 1 ; C1 - H11

2 30 1 ; C1 - H12

2 31 1 ; C1 - H13

3 6 1 ; C2 - C5

3 7 1 ; C2 - C6

3 28 1 ; C2 - C13

4 8 1 ; C3 - N

4 21 1 ; C3 - H5

4 25 1 ; C3 - H9

4 27 1 ; C3 - O1

5 9 1 ; C4 - C7

5 17 1 ; C4 - H1

5 19 1 ; C4 - H3

6 8 1 ; C5 - N

6 20 1 ; C5 - H4

6 25 1 ; C5 - H9

6 27 1 ; C5 - O1

7 10 1 ; C6 - C8

7 14 1 ; C6 - C12

7 20 1 ; C6 - H4

7 21 1 ; C6 - H5

8 11 1 ; N - C9

8 13 1 ; N - C11

8 15 1 ; N - O

8 24 1 ; N - H8

9 12 1 ; C7 - C10

9 16 1 ; C7 - H

9 22 1 ; C7 - H6

9 25 1 ; C7 - H9

9 26 1 ; C7 - H10

10 13 1 ; C8 - C11

10 17 1 ; C8 - H1

10 23 1 ; C8 - H7

10 24 1 ; C8 - H8

11 14 1 ; C9 - C12

11 16 1 ; C9 - H

11 26 1 ; C9 - H10

12 15 1 ; C10 - O

12 24 1 ; C10 - H8

13 22 1 ; C11 - H6

14 15 1 ; C12 - O

14 17 1 ; C12 - H1

14 23 1 ; C12 - H7

15 22 1 ; O - H6

17 25 1 ; H1 - H9

18 3 1 ; H2 - C2

18 5 1 ; H2 - C4

18 21 1 ; H2 - H5

18 27 1 ; H2 - O1

19 20 1 ; H3 - H4

19 27 1 ; H3 - O1

22 23 1 ; H6 - H7

23 26 1 ; H7 - H10

24 26 1 ; H8 - H10

[angles]

; ai aj ak funct theta cth

1 2 3 1 1.2002e+02 5.5731e+02 ; C - C1 - C2

1 2 27 1 1.1920e+02 5.8241e+02 ; C - C1 - O1

1 6 5 1 1.2002e+02 5.5731e+02 ; C - C5 - C4

1 6 21 1 1.1988e+02 4.0334e+02 ; C - C5 - H5

2 1 6 1 1.2002e+02 5.5731e+02 ; C1 - C - C5

2 1 18 1 1.1988e+02 4.0334e+02 ; C1 - C - H2

2 3 4 1 1.2002e+02 5.5731e+02 ; C1 - C2 - C3

2 3 19 1 1.1988e+02 4.0334e+02 ; C1 - C2 - H3

2 27 28 1 1.1796e+02 5.2300e+02 ; C1 - O1 - C13

3 2 27 1 1.1920e+02 5.8241e+02 ; C2 - C1 - O1

3 4 5 1 1.2002e+02 5.5731e+02 ; C2 - C3 - C4

3 4 20 1 1.1988e+02 4.0334e+02 ; C2 - C3 - H4

4 3 19 1 1.1988e+02 4.0334e+02 ; C3 - C2 - H3

4 5 6 1 1.2002e+02 5.5731e+02 ; C3 - C4 - C5

4 5 7 1 1.2082e+02 5.3974e+02 ; C3 - C4 - C6

5 4 20 1 1.1988e+02 4.0334e+02 ; C4 - C3 - H4

5 6 21 1 1.1988e+02 4.0334e+02 ; C4 - C5 - H5

5 7 8 1 1.1919e+02 5.7823e+02 ; C4 - C6 - N

5 7 25 1 1.1699e+02 3.8995e+02 ; C4 - C6 - H9

6 1 18 1 1.1988e+02 4.0334e+02 ; C5 - C - H2

6 5 7 1 1.2082e+02 5.3974e+02 ; C5 - C4 - C6

7 8 9 1 1.2661e+02 5.2635e+02 ; C6 - N - C7

7 8 17 1 1.2554e+02 3.8995e+02 ; C6 - N - H1

8 7 25 1 1.1558e+02 4.2258e+02 ; N - C6 - H9

8 9 10 1 1.1834e+02 5.7823e+02 ; N - C7 - C8

8 9 14 1 1.1834e+02 5.7823e+02 ; N - C7 - C12

```
   9     8    17     1   1.2554e+02   3.8995e+02 ;    C7 - N     - H1
   9    10    11     1   1.2002e+02   5.5731e+02 ;    C7 - C8    - C9
   9    10    15     1   1.1990e+02   5.8158e+02 ;    C7 - C8    - O
   9    14    13     1   1.2002e+02   5.5731e+02 ;    C7 - C12   - C11
   9    14    24     1   1.1988e+02   4.0334e+02 ;    C7 - C12   - H8
  10     9    14     1   1.2002e+02   5.5731e+02 ;    C8 - C7    - C12
  10    11    12     1   1.2002e+02   5.5731e+02 ;    C8 - C9    - C10
  10    11    22     1   1.1988e+02   4.0334e+02 ;    C8 - C9    - H6
  10    15    16     1   1.0858e+02   4.1003e+02 ;    C8 - O     - H
  11    10    15     1   1.1990e+02   5.8158e+02 ;    C9 - C8    - O
  11    12    13     1   1.2002e+02   5.5731e+02 ;    C9 - C10   - C11
  11    12    23     1   1.1988e+02   4.0334e+02 ;    C9 - C10   - H7
  12    11    22     1   1.1988e+02   4.0334e+02 ;   C10 - C9    - H6
  12    13    14     1   1.2002e+02   5.5731e+02 ;   C10 - C11   - C12
  12    13    26     1   1.1988e+02   4.0334e+02 ;   C10 - C11   - H10
  13    12    23     1   1.1988e+02   4.0334e+02 ;   C11 - C10   - H7
  13    14    24     1   1.1988e+02   4.0334e+02 ;   C11 - C12   - H8
  14    13    26     1   1.1988e+02   4.0334e+02 ;   C12 - C11   - H10
  27    28    29     1   1.0978e+02   4.2509e+02 ;    O1 - C13   - H11
  27    28    30     1   1.0978e+02   4.2509e+02 ;    O1 - C13   - H12
  27    28    31     1   1.0978e+02   4.2509e+02 ;    O1 - C13   - H13
  29    28    30     1   1.0846e+02   3.2803e+02 ;   H11 - C13   - H12
  29    28    31     1   1.0846e+02   3.2803e+02 ;   H11 - C13   - H13
  30    28    31     1   1.0846e+02   3.2803e+02 ;   H12 - C13   - H13

[ dihedrals ] ; propers
; for gromacs 4.5 or higher, using funct 9
;   i     j     k     l  func   phase     kd      pn
    1     2     3     4     9   180.00  15.16700   2 ;     C-   C1-   C2-   C3
```

1 2 3 19 9 180.00 15.16700 2 ; C- C1- C2- H3

1 2 27 28 9 180.00 3.76560 2 ; C- C1- O1- C13

1 6 5 4 9 180.00 15.16700 2 ; C- C5- C4- C3

1 6 5 7 9 180.00 15.16700 2 ; C- C5- C4- C6

2 1 6 5 9 180.00 15.16700 2 ; C1- C- C5- C4

2 1 6 21 9 180.00 15.16700 2 ; C1- C- C5- H5

2 3 4 5 9 180.00 15.16700 2 ; C1- C2- C3- C4

2 3 4 20 9 180.00 15.16700 2 ; C1- C2- C3- H4

2 27 28 29 9 0.00 1.60387 3 ; C1- O1- C13- H11

2 27 28 30 9 0.00 1.60387 3 ; C1- O1- C13- H12

2 27 28 31 9 0.00 1.60387 3 ; C1- O1- C13- H13

3 2 27 28 9 180.00 3.76560 2 ; C2- C1- O1- C13

3 4 5 6 9 180.00 15.16700 2 ; C2- C3- C4- C5

3 4 5 7 9 180.00 15.16700 2 ; C2- C3- C4- C6

4 3 2 27 9 180.00 15.16700 2 ; C3- C2- C1- O1

4 5 6 21 9 180.00 15.16700 2 ; C3- C4- C5- H5

4 5 7 8 9 180.00 2.92880 2 ; C3- C4- C6- N

4 5 7 25 9 180.00 2.92880 2 ; C3- C4- C6- H9

5 4 3 19 9 180.00 15.16700 2 ; C4- C3- C2- H3

5 7 8 9 9 180.00 7.11280 2 ; C4- C6- N- C7

5 7 8 17 9 180.00 7.11280 2 ; C4- C6- N- H1

6 1 2 3 9 180.00 15.16700 2 ; C5- C- C1- C2

6 1 2 27 9 180.00 15.16700 2 ; C5- C- C1- O1

6 5 4 20 9 180.00 15.16700 2 ; C5- C4- C3- H4

6 5 7 8 9 180.00 2.92880 2 ; C5- C4- C6- N

6 5 7 25 9 180.00 2.92880 2 ; C5- C4- C6- H9

7 5 4 20 9 180.00 15.16700 2 ; C6- C4- C3- H4

7 5 6 21 9 180.00 15.16700 2 ; C6- C4- C5- H5

7 8 9 10 9 180.00 1.25520 2 ; C6- N- C7- C8

7 8 9 14 9 180.00 1.25520 2 ; C6- N- C7- C12

8 9 10 11 9 180.00 15.16700 2 ; N- C7- C8- C9

8 9 10 15 9 180.00 15.16700 2 ; N- C7- C8- O

8 9 14 13 9 180.00 15.16700 2 ; N- C7- C12- C11

8 9 14 24 9 180.00 15.16700 2 ; N- C7- C12- H8

9 8 7 25 9 180.00 7.11280 2 ; C7- N- C6- H9

9 10 11 12 9 180.00 15.16700 2 ; C7- C8- C9- C10

9 10 11 22 9 180.00 15.16700 2 ; C7- C8- C9- H6

9 10 15 16 9 180.00 3.76560 2 ; C7- C8- O- H

9 14 13 12 9 180.00 15.16700 2 ; C7- C12- C11- C10

9 14 13 26 9 180.00 15.16700 2 ; C7- C12- C11- H10

10 9 8 17 9 180.00 1.25520 2 ; C8- C7- N- H1

10 9 14 13 9 180.00 15.16700 2 ; C8- C7- C12- C11

10 9 14 24 9 180.00 15.16700 2 ; C8- C7- C12- H8

10 11 12 13 9 180.00 15.16700 2 ; C8- C9- C10- C11

10 11 12 23 9 180.00 15.16700 2 ; C8- C9- C10- H7

11 10 9 14 9 180.00 15.16700 2 ; C9- C8- C7- C12

11 10 15 16 9 180.00 3.76560 2 ; C9- C8- O- H

11 12 13 14 9 180.00 15.16700 2 ; C9- C10- C11- C12

11 12 13 26 9 180.00 15.16700 2 ; C9- C10- C11- H10

12 11 10 15 9 180.00 15.16700 2 ; C10- C9- C8- O

12 13 14 24 9 180.00 15.16700 2 ; C10- C11- C12- H8

13 12 11 22 9 180.00 15.16700 2 ; C11- C10- C9- H6

14 9 8 17 9 180.00 1.25520 2 ; C12- C7- N- H1

14 9 10 15 9 180.00 15.16700 2 ; C12- C7- C8- O

14 13 12 23 9 180.00 15.16700 2 ; C12- C11- C10- H7

15 10 11 22 9 180.00 15.16700 2 ; O- C8- C9- H6

17 8 7 25 9 180.00 7.11280 2 ; H1- N- C6- H9

18 1 2 3 9 180.00 15.16700 2 ; H2- C- C1- C2

```
  18    1    2   27    9  180.00  15.16700  2 ;   H2-   C-   C1-   O1
  18    1    6    5    9  180.00  15.16700  2 ;   H2-   C-   C5-   C4
  18    1    6   21    9  180.00  15.16700  2 ;   H2-   C-   C5-   H5
  19    3    2   27    9  180.00  15.16700  2 ;   H3-   C2-   C1-   O1
  19    3    4   20    9  180.00  15.16700  2 ;   H3-   C2-   C3-   H4
  22   11   12   23    9  180.00  15.16700  2 ;   H6-   C9-   C10-   H7
  23   12   13   26    9  180.00  15.16700  2 ;   H7-   C10-   C11-   H10
  24   14   13   26    9  180.00  15.16700  2 ;   H8-   C12-   C11-   H10

[ dihedrals ] ; impropers
; treated as propers in GROMACS to use correct AMBER analytical function
;   i    j    k    l  func   phase    kd     pn
    1    3    2   27    4  180.00   4.60240  2 ;    C-   C2-   C1-   O1
    1    5    6   21    4  180.00   4.60240  2 ;    C-   C4-   C5-   H5
    2    4    3   19    4  180.00   4.60240  2 ;   C1-   C3-   C2-   H3
    3    5    4   20    4  180.00   4.60240  2 ;   C2-   C4-   C3-   H4
    4    6    5    7    4  180.00   4.60240  2 ;   C3-   C5-   C4-   C6
    5   25    7    8    4  180.00   4.60240  2 ;   C4-   H9-   C6-    N
    9    7    8   17    4  180.00   4.60240  2 ;   C7-   C6-    N-   H1
    9   11   10   15    4  180.00   4.60240  2 ;   C7-   C9-   C8-    O
    9   13   14   24    4  180.00   4.60240  2 ;   C7-  C11-  C12-   H8
   10   12   11   22    4  180.00   4.60240  2 ;   C8-  C10-   C9-   H6
   10   14    9    8    4  180.00   4.60240  2 ;   C8-  C12-   C7-    N
   11   13   12   23    4  180.00   4.60240  2 ;   C9-  C11-  C10-   H7
   12   14   13   26    4  180.00   4.60240  2 ;  C10-  C12-  C11-  H10
   18    1    6    2    4  180.00   4.60240  2 ;   H2-   C-   C5-   C1
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9.1.4.3.3 1a

```
[ moleculetype ]
;name            nrexcl
 PIA             3


[ atoms ]
    1   ca    1   PIA    C   1    -0.087898    12.01000 ;
    2   ca    1   PIA   C1   2    -0.201812    12.01000 ;
    3   ca    1   PIA   C2   3    -0.119114    12.01000 ;
    4   ca    1   PIA   C3   4     0.051137    12.01000 ;
    5   ca    1   PIA   C4   5     0.230956    12.01000 ;
    6   ca    1   PIA   C5   6    -0.289697    12.01000 ;
    7   cp    1   PIA   C6   7    -0.108763    12.01000 ;
    8   ca    1   PIA   C7   8     0.294717    12.01000 ;
    9   cp    1   PIA   C8   9    -0.078915    12.01000 ;
   10   ca    1   PIA   C9  10    -0.330488    12.01000 ;
   11   cp    1   PIA  C10  11    -0.112668    12.01000 ;
   12   ca    1   PIA  C11  12     0.054017    12.01000 ;
   13   ca    1   PIA  C12  13     0.230184    12.01000 ;
   14   ca    1   PIA  C13  14    -0.330135    12.01000 ;
   15   cp    1   PIA  C14  15    -0.078833    12.01000 ;
   16   ca    1   PIA  C15  16     0.295949    12.01000 ;
   17   ca    1   PIA  C16  17    -0.120041    12.01000 ;
   18   ca    1   PIA  C17  18    -0.201878    12.01000 ;
   19   ca    1   PIA  C18  19    -0.088877    12.01000 ;
   20   ca    1   PIA  C19  20    -0.289958    12.01000 ;
   21   os    1   PIA    O  21    -0.446130    16.00000 ;
   22   p5    1   PIA    P  22     1.316091    30.97000 ;
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23 o 1 PIA O1 23 -0.751621 16.00000 ;

24 o 1 PIA O2 24 -0.751814 16.00000 ;

25 os 1 PIA O3 25 -0.448087 16.00000 ;

26 cp 1 PIA C20 26 -0.102737 12.01000 ;

27 cp 1 PIA C21 27 -0.103767 12.01000 ;

28 ca 1 PIA C22 28 0.124283 12.01000 ;

29 ca 1 PIA C23 29 -0.422979 12.01000 ;

30 ca 1 PIA C24 30 0.198337 12.01000 ;

31 ca 1 PIA C25 31 -0.472431 12.01000 ;

32 ca 1 PIA C26 32 0.127149 12.01000 ;

33 ca 1 PIA C27 33 0.124660 12.01000 ;

34 ca 1 PIA C28 34 -0.467962 12.01000 ;

35 ca 1 PIA C29 35 0.194577 12.01000 ;

36 ca 1 PIA C30 36 -0.420254 12.01000 ;

37 ca 1 PIA C31 37 0.121976 12.01000 ;

38 c3 1 PIA C32 38 0.464838 12.01000 ;

39 c3 1 PIA C33 39 0.614021 12.01000 ;

40 c3 1 PIA C34 40 0.367455 12.01000 ;

41 c3 1 PIA C35 41 0.615426 12.01000 ;

42 c3 1 PIA C36 42 0.464726 12.01000 ;

43 c3 1 PIA C37 43 0.365226 12.01000 ;

44 ha 1 PIA H 44 0.103024 1.00800 ;

45 ha 1 PIA H1 45 0.126351 1.00800 ;

46 ha 1 PIA H2 46 0.114013 1.00800 ;

47 ha 1 PIA H3 47 0.143870 1.00800 ;

48 ha 1 PIA H4 48 0.152776 1.00800 ;

49 ha 1 PIA H5 49 0.152378 1.00800 ;

50 ha 1 PIA H6 50 0.113906 1.00800 ;

51 ha 1 PIA H7 51 0.126714 1.00800 ;

52 ha 1 PIA H8 52 0.103501 1.00800 ;

53 ha 1 PIA H9 53 0.144375 1.00800 ;

54 ha 1 PIA H10 54 0.175565 1.00800 ;

55 ha 1 PIA H11 55 0.161889 1.00800 ;

56 ha 1 PIA H12 56 0.160612 1.00800 ;

57 ha 1 PIA H13 57 0.175227 1.00800 ;

58 c3 1 PIA C38 58 -0.311950 12.01000 ;

59 hc 1 PIA H14 59 -0.010235 1.00800 ;

60 c3 1 PIA C39 60 -0.673244 12.01000 ;

61 c3 1 PIA C40 61 -0.315322 12.01000 ;

62 c3 1 PIA C41 62 -0.828149 12.01000 ;

63 hc 1 PIA H15 63 -0.023730 1.00800 ;

64 c3 1 PIA C42 64 -0.430976 12.01000 ;

65 hc 1 PIA H16 65 -0.058729 1.00800 ;

66 c3 1 PIA C43 66 -0.241386 12.01000 ;

67 c3 1 PIA C44 67 -0.827532 12.01000 ;

68 hc 1 PIA H17 68 -0.024567 1.00800 ;

69 c3 1 PIA C45 69 -0.317438 12.01000 ;

70 c3 1 PIA C46 70 -0.674627 12.01000 ;

71 c3 1 PIA C47 71 -0.311715 12.01000 ;

72 hc 1 PIA H18 72 -0.009849 1.00800 ;

73 c3 1 PIA C48 73 -0.239919 12.01000 ;

74 c3 1 PIA C49 74 -0.429416 12.01000 ;

75 hc 1 PIA H19 75 -0.058438 1.00800 ;

76 hc 1 PIA H20 76 0.065650 1.00800 ;

77 hc 1 PIA H21 77 0.065650 1.00800 ;

78 hc 1 PIA H22 78 0.065650 1.00800 ;

79 hc 1 PIA H23 79 0.138721 1.00800 ;

80 hc 1 PIA H24 80 0.138721 1.00800 ;

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 81  hc   1  PIA  H25  81   0.138721    1.00800 ;
 82  hc   1  PIA  H26  82   0.046179    1.00800 ;
 83  hc   1  PIA  H27  83   0.046179    1.00800 ;
 84  hc   1  PIA  H28  84   0.046179    1.00800 ;
 85  hc   1  PIA  H29  85   0.085577    1.00800 ;
 86  hc   1  PIA  H30  86   0.085577    1.00800 ;
 87  hc   1  PIA  H31  87   0.085577    1.00800 ;
 88  hc   1  PIA  H32  88   0.166897    1.00800 ;
 89  hc   1  PIA  H33  89   0.166897    1.00800 ;
 90  hc   1  PIA  H34  90   0.166897    1.00800 ;
 91  hc   1  PIA  H35  91   0.064411    1.00800 ;
 92  hc   1  PIA  H36  92   0.064411    1.00800 ;
 93  hc   1  PIA  H37  93   0.064411    1.00800 ;
 94  hc   1  PIA  H38  94   0.065673    1.00800 ;
 95  hc   1  PIA  H39  95   0.065673    1.00800 ;
 96  hc   1  PIA  H40  96   0.065673    1.00800 ;
 97  hc   1  PIA  H41  97   0.139000    1.00800 ;
 98  hc   1  PIA  H42  98   0.139000    1.00800 ;
 99  hc   1  PIA  H43  99   0.139000    1.00800 ;
100  hc   1  PIA  H44 100   0.045808    1.00800 ;
101  hc   1  PIA  H45 101   0.045808    1.00800 ;
102  hc   1  PIA  H46 102   0.045808    1.00800 ;
103  hc   1  PIA  H47 103   0.085269    1.00800 ;
104  hc   1  PIA  H48 104   0.085269    1.00800 ;
105  hc   1  PIA  H49 105   0.085269    1.00800 ;
106  hc   1  PIA  H50 106   0.064991    1.00800 ;
107  hc   1  PIA  H51 107   0.064991    1.00800 ;
108  hc   1  PIA  H52 108   0.064991    1.00800 ;
109  hc   1  PIA  H53 109   0.166545    1.00800 ;
```

```
  110   hc    1   PIA   H54  110    0.166545     1.00800 ;
  111   hc    1   PIA   H55  111    0.166545     1.00800 ;
[ bonds ]
;  ai    aj funct   r           k
    1     2   1    1.3984e-01    3.8585e+05 ;     C - C1
    1     6   1    1.3984e-01    3.8585e+05 ;     C - C5
    1    44   1    1.0860e-01    2.8937e+05 ;     C - H
    2     3   1    1.3984e-01    3.8585e+05 ;    C1 - C2
    2    45   1    1.0860e-01    2.8937e+05 ;    C1 - H1
    3     4   1    1.3984e-01    3.8585e+05 ;    C2 - C3
    3    46   1    1.0860e-01    2.8937e+05 ;    C2 - H2
    4     5   1    1.3984e-01    3.8585e+05 ;    C3 - C4
    4     7   1    1.4058e-01    3.7673e+05 ;    C3 - C6
    5     6   1    1.3984e-01    3.8585e+05 ;    C4 - C5
    5    10   1    1.3984e-01    3.8585e+05 ;    C4 - C9
    6    47   1    1.0860e-01    2.8937e+05 ;    C5 - H3
    7     8   1    1.4058e-01    3.7673e+05 ;    C6 - C7
    7    11   1    1.4854e-01    2.9405e+05 ;    C6 - C10
    8     9   1    1.4058e-01    3.7673e+05 ;    C7 - C8
    8    21   1    1.3696e-01    3.1514e+05 ;    C7 - O
    9    10   1    1.4058e-01    3.7673e+05 ;    C8 - C9
    9    26   1    1.4854e-01    2.9405e+05 ;    C8 - C20
   10    48   1    1.0860e-01    2.8937e+05 ;    C9 - H4
   11    12   1    1.4058e-01    3.7673e+05 ;   C10 - C11
   11    16   1    1.4058e-01    3.7673e+05 ;   C10 - C15
   12    13   1    1.3984e-01    3.8585e+05 ;   C11 - C12
   12    17   1    1.3984e-01    3.8585e+05 ;   C11 - C16
   13    14   1    1.3984e-01    3.8585e+05 ;   C12 - C13
   13    20   1    1.3984e-01    3.8585e+05 ;   C12 - C19
```

14 15 1 1.4058e-01 3.7673e+05 ; C13 - C14

14 49 1 1.0860e-01 2.8937e+05 ; C13 - H5

15 16 1 1.4058e-01 3.7673e+05 ; C14 - C15

15 27 1 1.4854e-01 2.9405e+05 ; C14 - C21

16 25 1 1.3696e-01 3.1514e+05 ; C15 - O3

17 18 1 1.3984e-01 3.8585e+05 ; C16 - C17

17 50 1 1.0860e-01 2.8937e+05 ; C16 - H6

18 19 1 1.3984e-01 3.8585e+05 ; C17 - C18

18 51 1 1.0860e-01 2.8937e+05 ; C17 - H7

19 20 1 1.3984e-01 3.8585e+05 ; C18 - C19

19 52 1 1.0860e-01 2.8937e+05 ; C18 - H8

20 53 1 1.0860e-01 2.8937e+05 ; C19 - H9

21 22 1 1.6147e-01 2.7665e+05 ; O - P

22 23 1 1.4866e-01 4.0125e+05 ; P - O1

22 24 1 1.4866e-01 4.0125e+05 ; P - O2

22 25 1 1.6147e-01 2.7665e+05 ; P - O3

26 33 1 1.4058e-01 3.7673e+05 ; C20 - C27

26 37 1 1.4058e-01 3.7673e+05 ; C20 - C31

27 28 1 1.4058e-01 3.7673e+05 ; C21 - C22

27 32 1 1.4058e-01 3.7673e+05 ; C21 - C26

28 29 1 1.3984e-01 3.8585e+05 ; C22 - C23

28 42 1 1.5156e-01 2.6861e+05 ; C22 - C36

29 30 1 1.3984e-01 3.8585e+05 ; C23 - C24

29 54 1 1.0860e-01 2.8937e+05 ; C23 - H10

30 31 1 1.3984e-01 3.8585e+05 ; C24 - C25

30 43 1 1.5156e-01 2.6861e+05 ; C24 - C37

31 32 1 1.3984e-01 3.8585e+05 ; C25 - C26

31 55 1 1.0860e-01 2.8937e+05 ; C25 - H11

32 41 1 1.5156e-01 2.6861e+05 ; C26 - C35

33 34 1 1.3984e-01 3.8585e+05 ; C27 - C28

33 39 1 1.5156e-01 2.6861e+05 ; C27 - C33

34 35 1 1.3984e-01 3.8585e+05 ; C28 - C29

34 56 1 1.0860e-01 2.8937e+05 ; C28 - H12

35 36 1 1.3984e-01 3.8585e+05 ; C29 - C30

35 40 1 1.5156e-01 2.6861e+05 ; C29 - C34

36 37 1 1.3984e-01 3.8585e+05 ; C30 - C31

36 57 1 1.0860e-01 2.8937e+05 ; C30 - H13

37 38 1 1.5156e-01 2.6861e+05 ; C31 - C32

38 58 1 1.5375e-01 2.5179e+05 ; C32 - C38

38 59 1 1.0969e-01 2.7665e+05 ; C32 - H14

38 60 1 1.5375e-01 2.5179e+05 ; C32 - C39

39 61 1 1.5375e-01 2.5179e+05 ; C33 - C40

39 62 1 1.5375e-01 2.5179e+05 ; C33 - C41

39 63 1 1.0969e-01 2.7665e+05 ; C33 - H15

40 64 1 1.5375e-01 2.5179e+05 ; C34 - C42

40 65 1 1.0969e-01 2.7665e+05 ; C34 - H16

40 66 1 1.5375e-01 2.5179e+05 ; C34 - C43

41 67 1 1.5375e-01 2.5179e+05 ; C35 - C44

41 68 1 1.0969e-01 2.7665e+05 ; C35 - H17

41 69 1 1.5375e-01 2.5179e+05 ; C35 - C45

42 70 1 1.5375e-01 2.5179e+05 ; C36 - C46

42 71 1 1.5375e-01 2.5179e+05 ; C36 - C47

42 72 1 1.0969e-01 2.7665e+05 ; C36 - H18

43 73 1 1.5375e-01 2.5179e+05 ; C37 - C48

43 74 1 1.5375e-01 2.5179e+05 ; C37 - C49

43 75 1 1.0969e-01 2.7665e+05 ; C37 - H19

58 76 1 1.0969e-01 2.7665e+05 ; C38 - H20

58 77 1 1.0969e-01 2.7665e+05 ; C38 - H21

58 78 1 1.0969e-01 2.7665e+05 ; C38 - H22

60 79 1 1.0969e-01 2.7665e+05 ; C39 - H23

60 80 1 1.0969e-01 2.7665e+05 ; C39 - H24

60 81 1 1.0969e-01 2.7665e+05 ; C39 - H25

61 91 1 1.0969e-01 2.7665e+05 ; C40 - H35

61 92 1 1.0969e-01 2.7665e+05 ; C40 - H36

61 93 1 1.0969e-01 2.7665e+05 ; C40 - H37

62 88 1 1.0969e-01 2.7665e+05 ; C41 - H32

62 89 1 1.0969e-01 2.7665e+05 ; C41 - H33

62 90 1 1.0969e-01 2.7665e+05 ; C41 - H34

64 85 1 1.0969e-01 2.7665e+05 ; C42 - H29

64 86 1 1.0969e-01 2.7665e+05 ; C42 - H30

64 87 1 1.0969e-01 2.7665e+05 ; C42 - H31

66 82 1 1.0969e-01 2.7665e+05 ; C43 - H26

66 83 1 1.0969e-01 2.7665e+05 ; C43 - H27

66 84 1 1.0969e-01 2.7665e+05 ; C43 - H28

67 109 1 1.0969e-01 2.7665e+05 ; C44 - H53

67 110 1 1.0969e-01 2.7665e+05 ; C44 - H54

67 111 1 1.0969e-01 2.7665e+05 ; C44 - H55

69 106 1 1.0969e-01 2.7665e+05 ; C45 - H50

69 107 1 1.0969e-01 2.7665e+05 ; C45 - H51

69 108 1 1.0969e-01 2.7665e+05 ; C45 - H52

70 97 1 1.0969e-01 2.7665e+05 ; C46 - H41

70 98 1 1.0969e-01 2.7665e+05 ; C46 - H42

70 99 1 1.0969e-01 2.7665e+05 ; C46 - H43

71 94 1 1.0969e-01 2.7665e+05 ; C47 - H38

71 95 1 1.0969e-01 2.7665e+05 ; C47 - H39

71 96 1 1.0969e-01 2.7665e+05 ; C47 - H40

73 100 1 1.0969e-01 2.7665e+05 ; C48 - H44

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   73   101  1   1.0969e-01   2.7665e+05 ;   C48 - H45
   73   102  1   1.0969e-01   2.7665e+05 ;   C48 - H46
   74   103  1   1.0969e-01   2.7665e+05 ;   C49 - H47
   74   104  1   1.0969e-01   2.7665e+05 ;   C49 - H48
   74   105  1   1.0969e-01   2.7665e+05 ;   C49 - H49

[ pairs ]
;  ai    aj    funct
    1     4     1 ;     C - C3
    1    10     1 ;     C - C9
    1    46     1 ;     C - H2
    2     5     1 ;    C1 - C4
    2     7     1 ;    C1 - C6
    2    47     1 ;    C1 - H3
    3     8     1 ;    C2 - C7
    3    10     1 ;    C2 - C9
    3    11     1 ;    C2 - C10
    4     9     1 ;    C3 - C8
    4    12     1 ;    C3 - C11
    4    16     1 ;    C3 - C15
    4    21     1 ;    C3 - O
    4    45     1 ;    C3 - H1
    4    47     1 ;    C3 - H3
    4    48     1 ;    C3 - H4
    5     8     1 ;    C4 - C7
    5    11     1 ;    C4 - C10
    5    26     1 ;    C4 - C20
    5    46     1 ;    C4 - H2
    6     3     1 ;    C5 - C2
```

6 7 1 ; C5 - C6

6 9 1 ; C5 - C8

6 45 1 ; C5 - H1

6 48 1 ; C5 - H4

7 10 1 ; C6 - C9

7 13 1 ; C6 - C12

7 15 1 ; C6 - C14

7 17 1 ; C6 - C16

7 22 1 ; C6 - P

7 25 1 ; C6 - O3

7 26 1 ; C6 - C20

7 46 1 ; C6 - H2

8 12 1 ; C7 - C11

8 16 1 ; C7 - C15

8 23 1 ; C7 - O1

8 24 1 ; C7 - O2

8 25 1 ; C7 - O3

8 33 1 ; C7 - C27

8 37 1 ; C7 - C31

8 48 1 ; C7 - H4

9 11 1 ; C8 - C10

9 22 1 ; C8 - P

9 34 1 ; C8 - C28

9 36 1 ; C8 - C30

9 38 1 ; C8 - C32

9 39 1 ; C8 - C33

10 21 1 ; C9 - O

10 33 1 ; C9 - C27

10 37 1 ; C9 - C31

10 47 1 ; C9 - H3

11 14 1 ; C10 - C13

11 18 1 ; C10 - C17

11 20 1 ; C10 - C19

11 21 1 ; C10 - O

11 22 1 ; C10 - P

11 27 1 ; C10 - C21

11 50 1 ; C10 - H6

12 15 1 ; C11 - C14

12 19 1 ; C11 - C18

12 25 1 ; C11 - O3

12 49 1 ; C11 - H5

12 51 1 ; C11 - H7

12 53 1 ; C11 - H9

13 16 1 ; C12 - C15

13 18 1 ; C12 - C17

13 27 1 ; C12 - C21

13 50 1 ; C12 - H6

13 52 1 ; C12 - H8

14 17 1 ; C13 - C16

14 19 1 ; C13 - C18

14 25 1 ; C13 - O3

14 28 1 ; C13 - C22

14 32 1 ; C13 - C26

14 53 1 ; C13 - H9

15 20 1 ; C14 - C19

15 22 1 ; C14 - P

15 29 1 ; C14 - C23

15 31 1 ; C14 - C25

15 41 1 ; C14 - C35

15 42 1 ; C14 - C36

16 17 1 ; C15 - C16

16 21 1 ; C15 - O

16 23 1 ; C15 - O1

16 24 1 ; C15 - O2

16 28 1 ; C15 - C22

16 32 1 ; C15 - C26

16 49 1 ; C15 - H5

17 20 1 ; C16 - C19

17 52 1 ; C16 - H8

18 53 1 ; C17 - H9

19 50 1 ; C18 - H6

20 49 1 ; C19 - H5

20 51 1 ; C19 - H7

21 26 1 ; O - C20

25 27 1 ; O3 - C21

26 35 1 ; C20 - C29

26 48 1 ; C20 - H4

26 56 1 ; C20 - H12

26 57 1 ; C20 - H13

26 58 1 ; C20 - C38

26 59 1 ; C20 - H14

26 60 1 ; C20 - C39

26 61 1 ; C20 - C40

26 62 1 ; C20 - C41

26 63 1 ; C20 - H15

27 30 1 ; C21 - C24

27 49 1 ; C21 - H5

27 54 1 ; C21 - H10

27 55 1 ; C21 - H11

27 67 1 ; C21 - C44

27 68 1 ; C21 - H17

27 69 1 ; C21 - C45

27 70 1 ; C21 - C46

27 71 1 ; C21 - C47

27 72 1 ; C21 - H18

28 31 1 ; C22 - C25

28 41 1 ; C22 - C35

28 43 1 ; C22 - C37

28 94 1 ; C22 - H38

28 95 1 ; C22 - H39

28 96 1 ; C22 - H40

28 97 1 ; C22 - H41

28 98 1 ; C22 - H42

28 99 1 ; C22 - H43

29 32 1 ; C23 - C26

29 55 1 ; C23 - H11

29 70 1 ; C23 - C46

29 71 1 ; C23 - C47

29 72 1 ; C23 - H18

29 73 1 ; C23 - C48

29 74 1 ; C23 - C49

29 75 1 ; C23 - H19

30 41 1 ; C24 - C35

30 42 1 ; C24 - C36

30 100 1 ; C24 - H44

30 101 1 ; C24 - H45

30 102 1 ; C24 - H46

30 103 1 ; C24 - H47

30 104 1 ; C24 - H48

30 105 1 ; C24 - H49

31 54 1 ; C25 - H10

31 67 1 ; C25 - C44

31 68 1 ; C25 - H17

31 69 1 ; C25 - C45

31 73 1 ; C25 - C48

31 74 1 ; C25 - C49

31 75 1 ; C25 - H19

32 42 1 ; C26 - C36

32 43 1 ; C26 - C37

32 106 1 ; C26 - H50

32 107 1 ; C26 - H51

32 108 1 ; C26 - H52

32 109 1 ; C26 - H53

32 110 1 ; C26 - H54

32 111 1 ; C26 - H55

33 36 1 ; C27 - C30

33 38 1 ; C27 - C32

33 40 1 ; C27 - C34

33 88 1 ; C27 - H32

33 89 1 ; C27 - H33

33 90 1 ; C27 - H34

33 91 1 ; C27 - H35

33 92 1 ; C27 - H36

33 93 1 ; C27 - H37

34 37 1 ; C28 - C31

34 57 1 ; C28 - H13

34 61 1 ; C28 - C40

34 62 1 ; C28 - C41

34 63 1 ; C28 - H15

34 64 1 ; C28 - C42

34 65 1 ; C28 - H16

34 66 1 ; C28 - C43

35 38 1 ; C29 - C32

35 39 1 ; C29 - C33

35 82 1 ; C29 - H26

35 83 1 ; C29 - H27

35 84 1 ; C29 - H28

35 85 1 ; C29 - H29

35 86 1 ; C29 - H30

35 87 1 ; C29 - H31

36 56 1 ; C30 - H12

36 58 1 ; C30 - C38

36 59 1 ; C30 - H14

36 60 1 ; C30 - C39

36 64 1 ; C30 - C42

36 65 1 ; C30 - H16

36 66 1 ; C30 - C43

37 39 1 ; C31 - C33

37 40 1 ; C31 - C34

37 76 1 ; C31 - H20

37 77 1 ; C31 - H21

37 78 1 ; C31 - H22

37 79 1 ; C31 - H23

37 80 1 ; C31 - H24

37 81 1 ; C31 - H25

38 57 1 ; C32 - H13

39 56 1 ; C33 - H12

40 56 1 ; C34 - H12

40 57 1 ; C34 - H13

41 55 1 ; C35 - H11

42 54 1 ; C36 - H10

43 54 1 ; C37 - H10

43 55 1 ; C37 - H11

44 3 1 ; H - C2

44 5 1 ; H - C4

44 45 1 ; H - H1

44 47 1 ; H - H3

45 46 1 ; H1 - H2

50 51 1 ; H6 - H7

51 52 1 ; H7 - H8

52 53 1 ; H8 - H9

58 79 1 ; C38 - H23

58 80 1 ; C38 - H24

58 81 1 ; C38 - H25

59 76 1 ; H14 - H20

59 77 1 ; H14 - H21

59 78 1 ; H14 - H22

59 79 1 ; H14 - H23

59 80 1 ; H14 - H24

59 81 1 ; H14 - H25

60 76 1 ; C39 - H20

60 77 1 ; C39 - H21

60 78 1 ; C39 - H22

61 88 1 ; C40 - H32

61 89 1 ; C40 - H33

61 90 1 ; C40 - H34

62 91 1 ; C41 - H35

62 92 1 ; C41 - H36

62 93 1 ; C41 - H37

63 88 1 ; H15 - H32

63 89 1 ; H15 - H33

63 90 1 ; H15 - H34

63 91 1 ; H15 - H35

63 92 1 ; H15 - H36

63 93 1 ; H15 - H37

64 82 1 ; C42 - H26

64 83 1 ; C42 - H27

64 84 1 ; C42 - H28

65 82 1 ; H16 - H26

65 83 1 ; H16 - H27

65 84 1 ; H16 - H28

65 85 1 ; H16 - H29

65 86 1 ; H16 - H30

65 87 1 ; H16 - H31

66 85 1 ; C43 - H29

66 86 1 ; C43 - H30

66 87 1 ; C43 - H31

67 106 1 ; C44 - H50

67 107 1 ; C44 - H51

67 108 1 ; C44 - H52

68 106 1 ; H17 - H50

68 107 1 ; H17 - H51

68 108 1 ; H17 - H52

68 109 1 ; H17 - H53

68 110 1 ; H17 - H54

68 111 1 ; H17 - H55

69 109 1 ; C45 - H53

69 110 1 ; C45 - H54

69 111 1 ; C45 - H55

70 94 1 ; C46 - H38

70 95 1 ; C46 - H39

70 96 1 ; C46 - H40

71 97 1 ; C47 - H41

71 98 1 ; C47 - H42

71 99 1 ; C47 - H43

72 94 1 ; H18 - H38

72 95 1 ; H18 - H39

72 96 1 ; H18 - H40

72 97 1 ; H18 - H41

72 98 1 ; H18 - H42

72 99 1 ; H18 - H43

73 103 1 ; C48 - H47

73 104 1 ; C48 - H48

73 105 1 ; C48 - H49

74 100 1 ; C49 - H44

74 101 1 ; C49 - H45

74 102 1 ; C49 - H46

75 100 1 ; H19 - H44

75 101 1 ; H19 - H45

75 102 1 ; H19 - H46

75 103 1 ; H19 - H47

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   75   104     1 ;   H19 - H48
   75   105     1 ;   H19 - H49

[ angles ]
;  ai    aj    ak    funct   theta       cth
    1     2     3     1    1.2002e+02    5.5731e+02 ;     C - C1    - C2
    1     2    45     1    1.1988e+02    4.0334e+02 ;     C - C1    - H1
    1     6     5     1    1.2002e+02    5.5731e+02 ;     C - C5    - C4
    1     6    47     1    1.1988e+02    4.0334e+02 ;     C - C5    - H3
    2     1     6     1    1.2002e+02    5.5731e+02 ;    C1 - C     - C5
    2     1    44     1    1.1988e+02    4.0334e+02 ;    C1 - C     - H
    2     3     4     1    1.2002e+02    5.5731e+02 ;    C1 - C2    - C3
    2     3    46     1    1.1988e+02    4.0334e+02 ;    C1 - C2    - H2
    3     2    45     1    1.1988e+02    4.0334e+02 ;    C2 - C1    - H1
    3     4     5     1    1.2002e+02    5.5731e+02 ;    C2 - C3    - C4
    3     4     7     1    1.2069e+02    5.5480e+02 ;    C2 - C3    - C6
    4     3    46     1    1.1988e+02    4.0334e+02 ;    C3 - C2    - H2
    4     5     6     1    1.2002e+02    5.5731e+02 ;    C3 - C4    - C5
    4     5    10     1    1.2002e+02    5.5731e+02 ;    C3 - C4    - C9
    4     7     8     1    1.1838e+02    5.5815e+02 ;    C3 - C6    - C7
    4     7    11     1    1.2111e+02    5.3555e+02 ;    C3 - C6    - C10
    5     4     7     1    1.2069e+02    5.5480e+02 ;    C4 - C3    - C6
    5     6    47     1    1.1988e+02    4.0334e+02 ;    C4 - C5    - H3
    5    10     9     1    1.2069e+02    5.5480e+02 ;    C4 - C9    - C8
    5    10    48     1    1.1988e+02    4.0334e+02 ;    C4 - C9    - H4
    6     1    44     1    1.1988e+02    4.0334e+02 ;    C5 - C     - H
    6     5    10     1    1.2002e+02    5.5731e+02 ;    C5 - C4    - C9
    7     8     9     1    1.1152e+02    5.7572e+02 ;    C6 - C7    - C8
    7     8    21     1    1.1691e+02    5.8660e+02 ;    C6 - C7    - O
```

7 11 12 1 1.2111e+02 5.3555e+02 ; C6 - C10 - C11

7 11 16 1 1.2111e+02 5.3555e+02 ; C6 - C10 - C15

8 7 11 1 1.2111e+02 5.3555e+02 ; C7 - C6 - C10

8 9 10 1 1.1838e+02 5.5815e+02 ; C7 - C8 - C9

8 9 26 1 1.2111e+02 5.3555e+02 ; C7 - C8 - C20

8 21 22 1 1.2318e+02 6.5019e+02 ; C7 - O - P

9 8 21 1 1.1691e+02 5.8660e+02 ; C8 - C7 - O

9 10 48 1 1.1986e+02 4.0166e+02 ; C8 - C9 - H4

9 26 33 1 1.2111e+02 5.3555e+02 ; C8 - C20 - C27

9 26 37 1 1.2111e+02 5.3555e+02 ; C8 - C20 - C31

10 9 26 1 1.2111e+02 5.3555e+02 ; C9 - C8 - C20

11 12 13 1 1.2069e+02 5.5480e+02 ; C10 - C11 - C12

11 12 17 1 1.2069e+02 5.5480e+02 ; C10 - C11 - C16

11 16 15 1 1.1152e+02 5.7572e+02 ; C10 - C15 - C14

11 16 25 1 1.1691e+02 5.8660e+02 ; C10 - C15 - O3

12 11 16 1 1.1838e+02 5.5815e+02 ; C11 - C10 - C15

12 13 14 1 1.2002e+02 5.5731e+02 ; C11 - C12 - C13

12 13 20 1 1.2002e+02 5.5731e+02 ; C11 - C12 - C19

12 17 18 1 1.2002e+02 5.5731e+02 ; C11 - C16 - C17

12 17 50 1 1.1988e+02 4.0334e+02 ; C11 - C16 - H6

13 12 17 1 1.2002e+02 5.5731e+02 ; C12 - C11 - C16

13 14 15 1 1.2069e+02 5.5480e+02 ; C12 - C13 - C14

13 14 49 1 1.1988e+02 4.0334e+02 ; C12 - C13 - H5

13 20 19 1 1.2002e+02 5.5731e+02 ; C12 - C19 - C18

13 20 53 1 1.1988e+02 4.0334e+02 ; C12 - C19 - H9

14 13 20 1 1.2002e+02 5.5731e+02 ; C13 - C12 - C19

14 15 16 1 1.1838e+02 5.5815e+02 ; C13 - C14 - C15

14 15 27 1 1.2111e+02 5.3555e+02 ; C13 - C14 - C21

15 14 49 1 1.1986e+02 4.0166e+02 ; C14 - C13 - H5

15 16 25 1 1.1691e+02 5.8660e+02 ; C14 - C15 - O3

15 27 28 1 1.2111e+02 5.3555e+02 ; C14 - C21 - C22

15 27 32 1 1.2111e+02 5.3555e+02 ; C14 - C21 - C26

16 15 27 1 1.2111e+02 5.3555e+02 ; C15 - C14 - C21

16 25 22 1 1.2318e+02 6.5019e+02 ; C15 - O3 - P

17 18 19 1 1.2002e+02 5.5731e+02 ; C16 - C17 - C18

17 18 51 1 1.1988e+02 4.0334e+02 ; C16 - C17 - H7

18 17 50 1 1.1988e+02 4.0334e+02 ; C17 - C16 - H6

18 19 20 1 1.2002e+02 5.5731e+02 ; C17 - C18 - C19

18 19 52 1 1.1988e+02 4.0334e+02 ; C17 - C18 - H8

19 18 51 1 1.1988e+02 4.0334e+02 ; C18 - C17 - H7

19 20 53 1 1.1988e+02 4.0334e+02 ; C18 - C19 - H9

20 19 52 1 1.1988e+02 4.0334e+02 ; C19 - C18 - H8

21 22 23 1 1.1546e+02 3.6736e+02 ; O - P - O1

21 22 24 1 1.1546e+02 3.6736e+02 ; O - P - O2

21 22 25 1 1.0184e+02 3.7656e+02 ; O - P - O3

23 22 24 1 1.1580e+02 3.8325e+02 ; O1 - P - O2

23 22 25 1 1.1546e+02 3.6736e+02 ; O1 - P - O3

24 22 25 1 1.1546e+02 3.6736e+02 ; O2 - P - O3

26 33 34 1 1.2069e+02 5.5480e+02 ; C20 - C27 - C28

26 33 39 1 1.2063e+02 5.3053e+02 ; C20 - C27 - C33

26 37 36 1 1.2069e+02 5.5480e+02 ; C20 - C31 - C30

26 37 38 1 1.2063e+02 5.3053e+02 ; C20 - C31 - C32

27 28 29 1 1.2069e+02 5.5480e+02 ; C21 - C22 - C23

27 28 42 1 1.2063e+02 5.3053e+02 ; C21 - C22 - C36

27 32 31 1 1.2069e+02 5.5480e+02 ; C21 - C26 - C25

27 32 41 1 1.2063e+02 5.3053e+02 ; C21 - C26 - C35

28 27 32 1 1.1838e+02 5.5815e+02 ; C22 - C21 - C26

28 29 30 1 1.2002e+02 5.5731e+02 ; C22 - C23 - C24

28 29 54 1 1.1988e+02 4.0334e+02 ; C22 - C23 - H10

28 42 70 1 1.1207e+02 5.2802e+02 ; C22 - C36 - C46

28 42 71 1 1.1207e+02 5.2802e+02 ; C22 - C36 - C47

28 42 72 1 1.1047e+02 3.9162e+02 ; C22 - C36 - H18

29 28 42 1 1.2077e+02 5.3137e+02 ; C23 - C22 - C36

29 30 31 1 1.2002e+02 5.5731e+02 ; C23 - C24 - C25

29 30 43 1 1.2077e+02 5.3137e+02 ; C23 - C24 - C37

30 29 54 1 1.1988e+02 4.0334e+02 ; C24 - C23 - H10

30 31 32 1 1.2002e+02 5.5731e+02 ; C24 - C25 - C26

30 31 55 1 1.1988e+02 4.0334e+02 ; C24 - C25 - H11

30 43 73 1 1.1207e+02 5.2802e+02 ; C24 - C37 - C48

30 43 74 1 1.1207e+02 5.2802e+02 ; C24 - C37 - C49

30 43 75 1 1.1047e+02 3.9162e+02 ; C24 - C37 - H19

31 30 43 1 1.2077e+02 5.3137e+02 ; C25 - C24 - C37

31 32 41 1 1.2077e+02 5.3137e+02 ; C25 - C26 - C35

32 31 55 1 1.1988e+02 4.0334e+02 ; C26 - C25 - H11

32 41 67 1 1.1207e+02 5.2802e+02 ; C26 - C35 - C44

32 41 68 1 1.1047e+02 3.9162e+02 ; C26 - C35 - H17

32 41 69 1 1.1207e+02 5.2802e+02 ; C26 - C35 - C45

33 26 37 1 1.1838e+02 5.5815e+02 ; C27 - C20 - C31

33 34 35 1 1.2002e+02 5.5731e+02 ; C27 - C28 - C29

33 34 56 1 1.1988e+02 4.0334e+02 ; C27 - C28 - H12

33 39 61 1 1.1207e+02 5.2802e+02 ; C27 - C33 - C40

33 39 62 1 1.1207e+02 5.2802e+02 ; C27 - C33 - C41

33 39 63 1 1.1047e+02 3.9162e+02 ; C27 - C33 - H15

34 33 39 1 1.2077e+02 5.3137e+02 ; C28 - C27 - C33

34 35 36 1 1.2002e+02 5.5731e+02 ; C28 - C29 - C30

34 35 40 1 1.2077e+02 5.3137e+02 ; C28 - C29 - C34

35 34 56 1 1.1988e+02 4.0334e+02 ; C29 - C28 - H12

35 36 37 1 1.2002e+02 5.5731e+02 ; C29 - C30 - C31

35 36 57 1 1.1988e+02 4.0334e+02 ; C29 - C30 - H13

35 40 64 1 1.1207e+02 5.2802e+02 ; C29 - C34 - C42

35 40 65 1 1.1047e+02 3.9162e+02 ; C29 - C34 - H16

35 40 66 1 1.1207e+02 5.2802e+02 ; C29 - C34 - C43

36 35 40 1 1.2077e+02 5.3137e+02 ; C30 - C29 - C34

36 37 38 1 1.2077e+02 5.3137e+02 ; C30 - C31 - C32

37 36 57 1 1.1988e+02 4.0334e+02 ; C31 - C30 - H13

37 38 58 1 1.1207e+02 5.2802e+02 ; C31 - C32 - C38

37 38 59 1 1.1047e+02 3.9162e+02 ; C31 - C32 - H14

37 38 60 1 1.1207e+02 5.2802e+02 ; C31 - C32 - C39

38 58 76 1 1.0980e+02 3.8744e+02 ; C32 - C38 - H20

38 58 77 1 1.0980e+02 3.8744e+02 ; C32 - C38 - H21

38 58 78 1 1.0980e+02 3.8744e+02 ; C32 - C38 - H22

38 60 79 1 1.0980e+02 3.8744e+02 ; C32 - C39 - H23

38 60 80 1 1.0980e+02 3.8744e+02 ; C32 - C39 - H24

38 60 81 1 1.0980e+02 3.8744e+02 ; C32 - C39 - H25

39 61 91 1 1.0980e+02 3.8744e+02 ; C33 - C40 - H35

39 61 92 1 1.0980e+02 3.8744e+02 ; C33 - C40 - H36

39 61 93 1 1.0980e+02 3.8744e+02 ; C33 - C40 - H37

39 62 88 1 1.0980e+02 3.8744e+02 ; C33 - C41 - H32

39 62 89 1 1.0980e+02 3.8744e+02 ; C33 - C41 - H33

39 62 90 1 1.0980e+02 3.8744e+02 ; C33 - C41 - H34

40 64 85 1 1.0980e+02 3.8744e+02 ; C34 - C42 - H29

40 64 86 1 1.0980e+02 3.8744e+02 ; C34 - C42 - H30

40 64 87 1 1.0980e+02 3.8744e+02 ; C34 - C42 - H31

40 66 82 1 1.0980e+02 3.8744e+02 ; C34 - C43 - H26

40 66 83 1 1.0980e+02 3.8744e+02 ; C34 - C43 - H27

40 66 84 1 1.0980e+02 3.8744e+02 ; C34 - C43 - H28

41 67 109 1 1.0980e+02 3.8744e+02 ; C35 - C44 - H53

41 67 110 1 1.0980e+02 3.8744e+02 ; C35 - C44 - H54

41 67 111 1 1.0980e+02 3.8744e+02 ; C35 - C44 - H55

41 69 106 1 1.0980e+02 3.8744e+02 ; C35 - C45 - H50

41 69 107 1 1.0980e+02 3.8744e+02 ; C35 - C45 - H51

41 69 108 1 1.0980e+02 3.8744e+02 ; C35 - C45 - H52

42 70 97 1 1.0980e+02 3.8744e+02 ; C36 - C46 - H41

42 70 98 1 1.0980e+02 3.8744e+02 ; C36 - C46 - H42

42 70 99 1 1.0980e+02 3.8744e+02 ; C36 - C46 - H43

42 71 94 1 1.0980e+02 3.8744e+02 ; C36 - C47 - H38

42 71 95 1 1.0980e+02 3.8744e+02 ; C36 - C47 - H39

42 71 96 1 1.0980e+02 3.8744e+02 ; C36 - C47 - H40

43 73 100 1 1.0980e+02 3.8744e+02 ; C37 - C48 - H44

43 73 101 1 1.0980e+02 3.8744e+02 ; C37 - C48 - H45

43 73 102 1 1.0980e+02 3.8744e+02 ; C37 - C48 - H46

43 74 103 1 1.0980e+02 3.8744e+02 ; C37 - C49 - H47

43 74 104 1 1.0980e+02 3.8744e+02 ; C37 - C49 - H48

43 74 105 1 1.0980e+02 3.8744e+02 ; C37 - C49 - H49

58 38 59 1 1.0980e+02 3.8744e+02 ; C38 - C32 - H14

58 38 60 1 1.1151e+02 5.2635e+02 ; C38 - C32 - C39

59 38 60 1 1.0980e+02 3.8744e+02 ; H14 - C32 - C39

61 39 62 1 1.1151e+02 5.2635e+02 ; C40 - C33 - C41

61 39 63 1 1.0980e+02 3.8744e+02 ; C40 - C33 - H15

62 39 63 1 1.0980e+02 3.8744e+02 ; C41 - C33 - H15

64 40 65 1 1.0980e+02 3.8744e+02 ; C42 - C34 - H16

64 40 66 1 1.1151e+02 5.2635e+02 ; C42 - C34 - C43

65 40 66 1 1.0980e+02 3.8744e+02 ; H16 - C34 - C43

67 41 68 1 1.0980e+02 3.8744e+02 ; C44 - C35 - H17

67 41 69 1 1.1151e+02 5.2635e+02 ; C44 - C35 - C45

68 41 69 1 1.0980e+02 3.8744e+02 ; H17 - C35 - C45

70 42 71 1 1.1151e+02 5.2635e+02 ; C46 - C36 - C47

70 42 72 1 1.0980e+02 3.8744e+02 ; C46 - C36 - H18

71 42 72 1 1.0980e+02 3.8744e+02 ; C47 - C36 - H18

73 43 74 1 1.1151e+02 5.2635e+02 ; C48 - C37 - C49

73 43 75 1 1.0980e+02 3.8744e+02 ; C48 - C37 - H19

74 43 75 1 1.0980e+02 3.8744e+02 ; C49 - C37 - H19

76 58 77 1 1.0758e+02 3.2970e+02 ; H20 - C38 - H21

76 58 78 1 1.0758e+02 3.2970e+02 ; H20 - C38 - H22

77 58 78 1 1.0758e+02 3.2970e+02 ; H21 - C38 - H22

79 60 80 1 1.0758e+02 3.2970e+02 ; H23 - C39 - H24

79 60 81 1 1.0758e+02 3.2970e+02 ; H23 - C39 - H25

80 60 81 1 1.0758e+02 3.2970e+02 ; H24 - C39 - H25

82 66 83 1 1.0758e+02 3.2970e+02 ; H26 - C43 - H27

82 66 84 1 1.0758e+02 3.2970e+02 ; H26 - C43 - H28

83 66 84 1 1.0758e+02 3.2970e+02 ; H27 - C43 - H28

85 64 86 1 1.0758e+02 3.2970e+02 ; H29 - C42 - H30

85 64 87 1 1.0758e+02 3.2970e+02 ; H29 - C42 - H31

86 64 87 1 1.0758e+02 3.2970e+02 ; H30 - C42 - H31

88 62 89 1 1.0758e+02 3.2970e+02 ; H32 - C41 - H33

88 62 90 1 1.0758e+02 3.2970e+02 ; H32 - C41 - H34

89 62 90 1 1.0758e+02 3.2970e+02 ; H33 - C41 - H34

91 61 92 1 1.0758e+02 3.2970e+02 ; H35 - C40 - H36

91 61 93 1 1.0758e+02 3.2970e+02 ; H35 - C40 - H37

92 61 93 1 1.0758e+02 3.2970e+02 ; H36 - C40 - H37

94 71 95 1 1.0758e+02 3.2970e+02 ; H38 - C47 - H39

94 71 96 1 1.0758e+02 3.2970e+02 ; H38 - C47 - H40

95 71 96 1 1.0758e+02 3.2970e+02 ; H39 - C47 - H40

97 70 98 1 1.0758e+02 3.2970e+02 ; H41 - C46 - H42

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  97    70    99     1   1.0758e+02   3.2970e+02 ;   H41 - C46   - H43
  98    70    99     1   1.0758e+02   3.2970e+02 ;   H42 - C46   - H43
 100    73   101     1   1.0758e+02   3.2970e+02 ;   H44 - C48   - H45
 100    73   102     1   1.0758e+02   3.2970e+02 ;   H44 - C48   - H46
 101    73   102     1   1.0758e+02   3.2970e+02 ;   H45 - C48   - H46
 103    74   104     1   1.0758e+02   3.2970e+02 ;   H47 - C49   - H48
 103    74   105     1   1.0758e+02   3.2970e+02 ;   H47 - C49   - H49
 104    74   105     1   1.0758e+02   3.2970e+02 ;   H48 - C49   - H49
 106    69   107     1   1.0758e+02   3.2970e+02 ;   H50 - C45   - H51
 106    69   108     1   1.0758e+02   3.2970e+02 ;   H50 - C45   - H52
 107    69   108     1   1.0758e+02   3.2970e+02 ;   H51 - C45   - H52
 109    67   110     1   1.0758e+02   3.2970e+02 ;   H53 - C44   - H54
 109    67   111     1   1.0758e+02   3.2970e+02 ;   H53 - C44   - H55
 110    67   111     1   1.0758e+02   3.2970e+02 ;   H54 - C44   - H55

[ dihedrals ] ; propers
; for gromacs 4.5 or higher, using funct 9
;   i     j     k     l  func   phase     kd      pn
    1     2     3     4     9   180.00  15.16700   2 ;    C-   C1-   C2-   C3
    1     2     3    46     9   180.00  15.16700   2 ;    C-   C1-   C2-   H2
    1     6     5     4     9   180.00  15.16700   2 ;    C-   C5-   C4-   C3
    1     6     5    10     9   180.00  15.16700   2 ;    C-   C5-   C4-   C9
    2     1     6     5     9   180.00  15.16700   2 ;   C1-    C-   C5-   C4
    2     1     6    47     9   180.00  15.16700   2 ;   C1-    C-   C5-   H3
    2     3     4     5     9   180.00  15.16700   2 ;   C1-   C2-   C3-   C4
    2     3     4     7     9   180.00  15.16700   2 ;   C1-   C2-   C3-   C6
    3     4     5     6     9   180.00  15.16700   2 ;   C2-   C3-   C4-   C5
    3     4     5    10     9   180.00  15.16700   2 ;   C2-   C3-   C4-   C9
    3     4     7     8     9   180.00  15.16700   2 ;   C2-   C3-   C6-   C7
```

3 4 7 11 9 180.00 15.16700 2 ; C2- C3- C6- C10

4 3 2 45 9 180.00 15.16700 2 ; C3- C2- C1- H1

4 5 6 47 9 180.00 15.16700 2 ; C3- C4- C5- H3

4 5 10 9 9 180.00 15.16700 2 ; C3- C4- C9- C8

4 5 10 48 9 180.00 15.16700 2 ; C3- C4- C9- H4

4 7 8 9 9 180.00 15.16700 2 ; C3- C6- C7- C8

4 7 8 21 9 180.00 15.16700 2 ; C3- C6- C7- O

4 7 11 12 9 180.00 4.18400 2 ; C3- C6- C10- C11

4 7 11 16 9 180.00 4.18400 2 ; C3- C6- C10- C15

5 4 3 46 9 180.00 15.16700 2 ; C4- C3- C2- H2

5 4 7 8 9 180.00 15.16700 2 ; C4- C3- C6- C7

5 4 7 11 9 180.00 15.16700 2 ; C4- C3- C6- C10

5 10 9 8 9 180.00 15.16700 2 ; C4- C9- C8- C7

5 10 9 26 9 180.00 15.16700 2 ; C4- C9- C8- C20

6 1 2 3 9 180.00 15.16700 2 ; C5- C- C1- C2

6 1 2 45 9 180.00 15.16700 2 ; C5- C- C1- H1

6 5 4 7 9 180.00 15.16700 2 ; C5- C4- C3- C6

6 5 10 9 9 180.00 15.16700 2 ; C5- C4- C9- C8

6 5 10 48 9 180.00 15.16700 2 ; C5- C4- C9- H4

7 4 3 46 9 180.00 15.16700 2 ; C6- C3- C2- H2

7 4 5 10 9 180.00 15.16700 2 ; C6- C3- C4- C9

7 8 9 10 9 180.00 15.16700 2 ; C6- C7- C8- C9

7 8 9 26 9 180.00 15.16700 2 ; C6- C7- C8- C20

7 8 21 22 9 180.00 3.76560 2 ; C6- C7- O- P

7 11 12 13 9 180.00 15.16700 2 ; C6- C10- C11- C12

7 11 12 17 9 180.00 15.16700 2 ; C6- C10- C11- C16

7 11 16 15 9 180.00 15.16700 2 ; C6- C10- C15- C14

7 11 16 25 9 180.00 15.16700 2 ; C6- C10- C15- O3

8 7 11 12 9 180.00 4.18400 2 ; C7- C6- C10- C11

8 7 11 16 9 180.00 4.18400 2 ; C7- C6- C10- C15

8 9 10 48 9 180.00 15.16700 2 ; C7- C8- C9- H4

8 9 26 33 9 180.00 4.18400 2 ; C7- C8- C20- C27

8 9 26 37 9 180.00 4.18400 2 ; C7- C8- C20- C31

8 21 22 23 9 0.00 0.41840 3 ; C7- O- P- O1

8 21 22 23 9 180.00 3.34720 2 ; C7- O- P- O1

8 21 22 24 9 0.00 0.41840 3 ; C7- O- P- O2

8 21 22 24 9 180.00 3.34720 2 ; C7- O- P- O2

8 21 22 25 9 0.00 3.34720 2 ; C7- O- P- O3

9 8 7 11 9 180.00 15.16700 2 ; C8- C7- C6- C10

9 8 21 22 9 180.00 3.76560 2 ; C8- C7- O- P

9 26 33 34 9 180.00 15.16700 2 ; C8- C20- C27- C28

9 26 33 39 9 180.00 15.16700 2 ; C8- C20- C27- C33

9 26 37 36 9 180.00 15.16700 2 ; C8- C20- C31- C30

9 26 37 38 9 180.00 15.16700 2 ; C8- C20- C31- C32

10 5 6 47 9 180.00 15.16700 2 ; C9- C4- C5- H3

10 9 8 21 9 180.00 15.16700 2 ; C9- C8- C7- O

10 9 26 33 9 180.00 4.18400 2 ; C9- C8- C20- C27

10 9 26 37 9 180.00 4.18400 2 ; C9- C8- C20- C31

11 7 8 21 9 180.00 15.16700 2 ; C10- C6- C7- O

11 12 13 14 9 180.00 15.16700 2 ; C10- C11- C12- C13

11 12 13 20 9 180.00 15.16700 2 ; C10- C11- C12- C19

11 12 17 18 9 180.00 15.16700 2 ; C10- C11- C16- C17

11 12 17 50 9 180.00 15.16700 2 ; C10- C11- C16- H6

11 16 15 14 9 180.00 15.16700 2 ; C10- C15- C14- C13

11 16 15 27 9 180.00 15.16700 2 ; C10- C15- C14- C21

11 16 25 22 9 180.00 3.76560 2 ; C10- C15- O3- P

12 11 16 15 9 180.00 15.16700 2 ; C11- C10- C15- C14

12 11 16 25 9 180.00 15.16700 2 ; C11- C10- C15- O3

12 13 14 15 9 180.00 15.16700 2 ; C11- C12- C13- C14

12 13 14 49 9 180.00 15.16700 2 ; C11- C12- C13- H5

12 13 20 19 9 180.00 15.16700 2 ; C11- C12- C19- C18

12 13 20 53 9 180.00 15.16700 2 ; C11- C12- C19- H9

12 17 18 19 9 180.00 15.16700 2 ; C11- C16- C17- C18

12 17 18 51 9 180.00 15.16700 2 ; C11- C16- C17- H7

13 12 11 16 9 180.00 15.16700 2 ; C12- C11- C10- C15

13 12 17 18 9 180.00 15.16700 2 ; C12- C11- C16- C17

13 12 17 50 9 180.00 15.16700 2 ; C12- C11- C16- H6

13 14 15 16 9 180.00 15.16700 2 ; C12- C13- C14- C15

13 14 15 27 9 180.00 15.16700 2 ; C12- C13- C14- C21

13 20 19 18 9 180.00 15.16700 2 ; C12- C19- C18- C17

13 20 19 52 9 180.00 15.16700 2 ; C12- C19- C18- H8

14 13 12 17 9 180.00 15.16700 2 ; C13- C12- C11- C16

14 13 20 19 9 180.00 15.16700 2 ; C13- C12- C19- C18

14 13 20 53 9 180.00 15.16700 2 ; C13- C12- C19- H9

14 15 16 25 9 180.00 15.16700 2 ; C13- C14- C15- O3

14 15 27 28 9 180.00 4.18400 2 ; C13- C14- C21- C22

14 15 27 32 9 180.00 4.18400 2 ; C13- C14- C21- C26

15 14 13 20 9 180.00 15.16700 2 ; C14- C13- C12- C19

15 16 25 22 9 180.00 3.76560 2 ; C14- C15- O3- P

15 27 28 29 9 180.00 15.16700 2 ; C14- C21- C22- C23

15 27 28 42 9 180.00 15.16700 2 ; C14- C21- C22- C36

15 27 32 31 9 180.00 15.16700 2 ; C14- C21- C26- C25

15 27 32 41 9 180.00 15.16700 2 ; C14- C21- C26- C35

16 11 12 17 9 180.00 15.16700 2 ; C15- C10- C11- C16

16 15 14 49 9 180.00 15.16700 2 ; C15- C14- C13- H5

16 15 27 28 9 180.00 4.18400 2 ; C15- C14- C21- C22

16 15 27 32 9 180.00 4.18400 2 ; C15- C14- C21- C26

16 25 22 21 9 0.00 3.34720 2 ; C15- O3- P- O

16 25 22 23 9 0.00 0.41840 3 ; C15- O3- P- O1

16 25 22 23 9 180.00 3.34720 2 ; C15- O3- P- O1

16 25 22 24 9 0.00 0.41840 3 ; C15- O3- P- O2

16 25 22 24 9 180.00 3.34720 2 ; C15- O3- P- O2

17 12 13 20 9 180.00 15.16700 2 ; C16- C11- C12- C19

17 18 19 20 9 180.00 15.16700 2 ; C16- C17- C18- C19

17 18 19 52 9 180.00 15.16700 2 ; C16- C17- C18- H8

18 19 20 53 9 180.00 15.16700 2 ; C17- C18- C19- H9

19 18 17 50 9 180.00 15.16700 2 ; C18- C17- C16- H6

20 13 14 49 9 180.00 15.16700 2 ; C19- C12- C13- H5

20 19 18 51 9 180.00 15.16700 2 ; C19- C18- C17- H7

21 8 9 26 9 180.00 15.16700 2 ; O- C7- C8- C20

25 16 15 27 9 180.00 15.16700 2 ; O3- C15- C14- C21

26 9 10 48 9 180.00 15.16700 2 ; C20- C8- C9- H4

26 33 34 35 9 180.00 15.16700 2 ; C20- C27- C28- C29

26 33 34 56 9 180.00 15.16700 2 ; C20- C27- C28- H12

26 33 39 61 9 0.00 0.00000 0 ; C20- C27- C33- C40

26 33 39 62 9 0.00 0.00000 0 ; C20- C27- C33- C41

26 33 39 63 9 0.00 0.00000 0 ; C20- C27- C33- H15

26 37 36 35 9 180.00 15.16700 2 ; C20- C31- C30- C29

26 37 36 57 9 180.00 15.16700 2 ; C20- C31- C30- H13

26 37 38 58 9 0.00 0.00000 0 ; C20- C31- C32- C38

26 37 38 59 9 0.00 0.00000 0 ; C20- C31- C32- H14

26 37 38 60 9 0.00 0.00000 0 ; C20- C31- C32- C39

27 15 14 49 9 180.00 15.16700 2 ; C21- C14- C13- H5

27 28 29 30 9 180.00 15.16700 2 ; C21- C22- C23- C24

27 28 29 54 9 180.00 15.16700 2 ; C21- C22- C23- H10

27 28 42 70 9 0.00 0.00000 0 ; C21- C22- C36- C46

27 28 42 71 9 0.00 0.00000 0 ; C21- C22- C36- C47

27 28 42 72 9 0.00 0.00000 0 ; C21- C22- C36- H18

27 32 31 30 9 180.00 15.16700 2 ; C21- C26- C25- C24

27 32 31 55 9 180.00 15.16700 2 ; C21- C26- C25- H11

27 32 41 67 9 0.00 0.00000 0 ; C21- C26- C35- C44

27 32 41 68 9 0.00 0.00000 0 ; C21- C26- C35- H17

27 32 41 69 9 0.00 0.00000 0 ; C21- C26- C35- C45

28 27 32 31 9 180.00 15.16700 2 ; C22- C21- C26- C25

28 27 32 41 9 180.00 15.16700 2 ; C22- C21- C26- C35

28 29 30 31 9 180.00 15.16700 2 ; C22- C23- C24- C25

28 29 30 43 9 180.00 15.16700 2 ; C22- C23- C24- C37

28 42 70 97 9 0.00 0.65084 3 ; C22- C36- C46- H41

28 42 70 98 9 0.00 0.65084 3 ; C22- C36- C46- H42

28 42 70 99 9 0.00 0.65084 3 ; C22- C36- C46- H43

28 42 71 94 9 0.00 0.65084 3 ; C22- C36- C47- H38

28 42 71 95 9 0.00 0.65084 3 ; C22- C36- C47- H39

28 42 71 96 9 0.00 0.65084 3 ; C22- C36- C47- H40

29 28 27 32 9 180.00 15.16700 2 ; C23- C22- C21- C26

29 28 42 70 9 0.00 0.00000 0 ; C23- C22- C36- C46

29 28 42 71 9 0.00 0.00000 0 ; C23- C22- C36- C47

29 28 42 72 9 0.00 0.00000 0 ; C23- C22- C36- H18

29 30 31 32 9 180.00 15.16700 2 ; C23- C24- C25- C26

29 30 31 55 9 180.00 15.16700 2 ; C23- C24- C25- H11

29 30 43 73 9 0.00 0.00000 0 ; C23- C24- C37- C48

29 30 43 74 9 0.00 0.00000 0 ; C23- C24- C37- C49

29 30 43 75 9 0.00 0.00000 0 ; C23- C24- C37- H19

30 29 28 42 9 180.00 15.16700 2 ; C24- C23- C22- C36

30 31 32 41 9 180.00 15.16700 2 ; C24- C25- C26- C35

30 43 73 100 9 0.00 0.65084 3 ; C24- C37- C48- H44

30 43 73 101 9 0.00 0.65084 3 ; C24- C37- C48- H45

30 43 73 102 9 0.00 0.65084 3 ; C24- C37- C48- H46

30 43 74 103 9 0.00 0.65084 3 ; C24- C37- C49- H47

30 43 74 104 9 0.00 0.65084 3 ; C24- C37- C49- H48

30 43 74 105 9 0.00 0.65084 3 ; C24- C37- C49- H49

31 30 29 54 9 180.00 15.16700 2 ; C25- C24- C23- H10

31 30 43 73 9 0.00 0.00000 0 ; C25- C24- C37- C48

31 30 43 74 9 0.00 0.00000 0 ; C25- C24- C37- C49

31 30 43 75 9 0.00 0.00000 0 ; C25- C24- C37- H19

31 32 41 67 9 0.00 0.00000 0 ; C25- C26- C35- C44

31 32 41 68 9 0.00 0.00000 0 ; C25- C26- C35- H17

31 32 41 69 9 0.00 0.00000 0 ; C25- C26- C35- C45

32 27 28 42 9 180.00 15.16700 2 ; C26- C21- C22- C36

32 31 30 43 9 180.00 15.16700 2 ; C26- C25- C24- C37

32 41 67 109 9 0.00 0.65084 3 ; C26- C35- C44- H53

32 41 67 110 9 0.00 0.65084 3 ; C26- C35- C44- H54

32 41 67 111 9 0.00 0.65084 3 ; C26- C35- C44- H55

32 41 69 106 9 0.00 0.65084 3 ; C26- C35- C45- H50

32 41 69 107 9 0.00 0.65084 3 ; C26- C35- C45- H51

32 41 69 108 9 0.00 0.65084 3 ; C26- C35- C45- H52

33 26 37 36 9 180.00 15.16700 2 ; C27- C20- C31- C30

33 26 37 38 9 180.00 15.16700 2 ; C27- C20- C31- C32

33 34 35 36 9 180.00 15.16700 2 ; C27- C28- C29- C30

33 34 35 40 9 180.00 15.16700 2 ; C27- C28- C29- C34

33 39 61 91 9 0.00 0.65084 3 ; C27- C33- C40- H35

33 39 61 92 9 0.00 0.65084 3 ; C27- C33- C40- H36

33 39 61 93 9 0.00 0.65084 3 ; C27- C33- C40- H37

33 39 62 88 9 0.00 0.65084 3 ; C27- C33- C41- H32

33 39 62 89 9 0.00 0.65084 3 ; C27- C33- C41- H33

33 39 62 90 9 0.00 0.65084 3 ; C27- C33- C41- H34

34 33 26 37 9 180.00 15.16700 2 ; C28- C27- C20- C31

34 33 39 61 9 0.00 0.00000 0 ; C28- C27- C33- C40

34 33 39 62 9 0.00 0.00000 0 ; C28- C27- C33- C41

34 33 39 63 9 0.00 0.00000 0 ; C28- C27- C33- H15

34 35 36 37 9 180.00 15.16700 2 ; C28- C29- C30- C31

34 35 36 57 9 180.00 15.16700 2 ; C28- C29- C30- H13

34 35 40 64 9 0.00 0.00000 0 ; C28- C29- C34- C42

34 35 40 65 9 0.00 0.00000 0 ; C28- C29- C34- H16

34 35 40 66 9 0.00 0.00000 0 ; C28- C29- C34- C43

35 34 33 39 9 180.00 15.16700 2 ; C29- C28- C27- C33

35 36 37 38 9 180.00 15.16700 2 ; C29- C30- C31- C32

35 40 64 85 9 0.00 0.65084 3 ; C29- C34- C42- H29

35 40 64 86 9 0.00 0.65084 3 ; C29- C34- C42- H30

35 40 64 87 9 0.00 0.65084 3 ; C29- C34- C42- H31

35 40 66 82 9 0.00 0.65084 3 ; C29- C34- C43- H26

35 40 66 83 9 0.00 0.65084 3 ; C29- C34- C43- H27

35 40 66 84 9 0.00 0.65084 3 ; C29- C34- C43- H28

36 35 34 56 9 180.00 15.16700 2 ; C30- C29- C28- H12

36 35 40 64 9 0.00 0.00000 0 ; C30- C29- C34- C42

36 35 40 65 9 0.00 0.00000 0 ; C30- C29- C34- H16

36 35 40 66 9 0.00 0.00000 0 ; C30- C29- C34- C43

36 37 38 58 9 0.00 0.00000 0 ; C30- C31- C32- C38

36 37 38 59 9 0.00 0.00000 0 ; C30- C31- C32- H14

36 37 38 60 9 0.00 0.00000 0 ; C30- C31- C32- C39

37 26 33 39 9 180.00 15.16700 2 ; C31- C20- C27- C33

37 36 35 40 9 180.00 15.16700 2 ; C31- C30- C29- C34

37 38 58 76 9 0.00 0.65084 3 ; C31- C32- C38- H20

37 38 58 77 9 0.00 0.65084 3 ; C31- C32- C38- H21

37 38 58 78 9 0.00 0.65084 3 ; C31- C32- C38- H22

37 38 60 79 9 0.00 0.65084 3 ; C31- C32- C39- H23

37 38 60 80 9 0.00 0.65084 3 ; C31- C32- C39- H24

37 38 60 81 9 0.00 0.65084 3 ; C31- C32- C39- H25

38 37 36 57 9 180.00 15.16700 2 ; C32- C31- C30- H13

39 33 34 56 9 180.00 15.16700 2 ; C33- C27- C28- H12

40 35 34 56 9 180.00 15.16700 2 ; C34- C29- C28- H12

40 35 36 57 9 180.00 15.16700 2 ; C34- C29- C30- H13

41 32 31 55 9 180.00 15.16700 2 ; C35- C26- C25- H11

42 28 29 54 9 180.00 15.16700 2 ; C36- C22- C23- H10

43 30 29 54 9 180.00 15.16700 2 ; C37- C24- C23- H10

43 30 31 55 9 180.00 15.16700 2 ; C37- C24- C25- H11

44 1 2 3 9 180.00 15.16700 2 ; H- C- C1- C2

44 1 2 45 9 180.00 15.16700 2 ; H- C- C1- H1

44 1 6 5 9 180.00 15.16700 2 ; H- C- C5- C4

44 1 6 47 9 180.00 15.16700 2 ; H- C- C5- H3

45 2 3 46 9 180.00 15.16700 2 ; H1- C1- C2- H2

50 17 18 51 9 180.00 15.16700 2 ; H6- C16- C17- H7

51 18 19 52 9 180.00 15.16700 2 ; H7- C17- C18- H8

52 19 20 53 9 180.00 15.16700 2 ; H8- C18- C19- H9

58 38 60 79 9 0.00 0.66944 3 ; C38- C32- C39- H23

58 38 60 80 9 0.00 0.66944 3 ; C38- C32- C39- H24

58 38 60 81 9 0.00 0.66944 3 ; C38- C32- C39- H25

59 38 58 76 9 0.00 0.62760 3 ; H14- C32- C38- H20

59 38 58 77 9 0.00 0.62760 3 ; H14- C32- C38- H21

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59 38 60 79 9 0.00 0.62760 3 ; H14- C32- C39- H23

59 38 60 80 9 0.00 0.62760 3 ; H14- C32- C39- H24

59 38 60 81 9 0.00 0.62760 3 ; H14- C32- C39- H25

60 38 58 76 9 0.00 0.66944 3 ; C39- C32- C38- H20

60 38 58 77 9 0.00 0.66944 3 ; C39- C32- C38- H21

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61 39 62 88 9 0.00 0.66944 3 ; C40- C33- C41- H32

61 39 62 89 9 0.00 0.66944 3 ; C40- C33- C41- H33

61 39 62 90 9 0.00 0.66944 3 ; C40- C33- C41- H34

62 39 61 91 9 0.00 0.66944 3 ; C41- C33- C40- H35

62 39 61 92 9 0.00 0.66944 3 ; C41- C33- C40- H36

62 39 61 93 9 0.00 0.66944 3 ; C41- C33- C40- H37

63 39 61 91 9 0.00 0.62760 3 ; H15- C33- C40- H35

63 39 61 92 9 0.00 0.62760 3 ; H15- C33- C40- H36

63 39 61 93 9 0.00 0.62760 3 ; H15- C33- C40- H37

63 39 62 88 9 0.00 0.62760 3 ; H15- C33- C41- H32

63 39 62 89 9 0.00 0.62760 3 ; H15- C33- C41- H33

63 39 62 90 9 0.00 0.62760 3 ; H15- C33- C41- H34

64 40 66 82 9 0.00 0.66944 3 ; C42- C34- C43- H26

64 40 66 83 9 0.00 0.66944 3 ; C42- C34- C43- H27

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65 40 64 85 9 0.00 0.62760 3 ; H16- C34- C42- H29

65 40 64 86 9 0.00 0.62760 3 ; H16- C34- C42- H30

65 40 64 87 9 0.00 0.62760 3 ; H16- C34- C42- H31

65 40 66 82 9 0.00 0.62760 3 ; H16- C34- C43- H26

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66 40 64 87 9 0.00 0.66944 3 ; C43- C34- C42- H31

67 41 69 106 9 0.00 0.66944 3 ; C44- C35- C45- H50

67 41 69 107 9 0.00 0.66944 3 ; C44- C35- C45- H51

67 41 69 108 9 0.00 0.66944 3 ; C44- C35- C45- H52

68 41 67 109 9 0.00 0.62760 3 ; H17- C35- C44- H53

68 41 67 110 9 0.00 0.62760 3 ; H17- C35- C44- H54

68 41 67 111 9 0.00 0.62760 3 ; H17- C35- C44- H55

68 41 69 106 9 0.00 0.62760 3 ; H17- C35- C45- H50

68 41 69 107 9 0.00 0.62760 3 ; H17- C35- C45- H51

68 41 69 108 9 0.00 0.62760 3 ; H17- C35- C45- H52

69 41 67 109 9 0.00 0.66944 3 ; C45- C35- C44- H53

69 41 67 110 9 0.00 0.66944 3 ; C45- C35- C44- H54

69 41 67 111 9 0.00 0.66944 3 ; C45- C35- C44- H55

70 42 71 94 9 0.00 0.66944 3 ; C46- C36- C47- H38

70 42 71 95 9 0.00 0.66944 3 ; C46- C36- C47- H39

70 42 71 96 9 0.00 0.66944 3 ; C46- C36- C47- H40

71 42 70 97 9 0.00 0.66944 3 ; C47- C36- C46- H41

71 42 70 98 9 0.00 0.66944 3 ; C47- C36- C46- H42

71 42 70 99 9 0.00 0.66944 3 ; C47- C36- C46- H43

72 42 70 97 9 0.00 0.62760 3 ; H18- C36- C46- H41

72 42 70 98 9 0.00 0.62760 3 ; H18- C36- C46- H42

72 42 70 99 9 0.00 0.62760 3 ; H18- C36- C46- H43

72 42 71 94 9 0.00 0.62760 3 ; H18- C36- C47- H38

72 42 71 95 9 0.00 0.62760 3 ; H18- C36- C47- H39

72 42 71 96 9 0.00 0.62760 3 ; H18- C36- C47- H40

73 43 74 103 9 0.00 0.66944 3 ; C48- C37- C49- H47

73 43 74 104 9 0.00 0.66944 3 ; C48- C37- C49- H48

73 43 74 105 9 0.00 0.66944 3 ; C48- C37- C49- H49

74 43 73 100 9 0.00 0.66944 3 ; C49- C37- C48- H44

74 43 73 101 9 0.00 0.66944 3 ; C49- C37- C48- H45

74 43 73 102 9 0.00 0.66944 3 ; C49- C37- C48- H46

75 43 73 100 9 0.00 0.62760 3 ; H19- C37- C48- H44

75 43 73 101 9 0.00 0.62760 3 ; H19- C37- C48- H45

75 43 73 102 9 0.00 0.62760 3 ; H19- C37- C48- H46

75 43 74 103 9 0.00 0.62760 3 ; H19- C37- C49- H47

75 43 74 104 9 0.00 0.62760 3 ; H19- C37- C49- H48

75 43 74 105 9 0.00 0.62760 3 ; H19- C37- C49- H49

[dihedrals] ; impropers

; treated as propers in GROMACS to use correct AMBER analytical function

; i j k l func phase kd pn

1 3 2 45 4 180.00 4.60240 2 ; C- C2- C1- H1

1 5 6 47 4 180.00 4.60240 2 ; C- C4- C5- H3

2 4 3 46 4 180.00 4.60240 2 ; C1- C3- C2- H2

3 5 4 7 4 180.00 4.60240 2 ; C2- C4- C3- C6

4 6 5 10 4 180.00 4.60240 2 ; C3- C5- C4- C9

4 8 7 11 4 180.00 4.60240 2 ; C3- C7- C6- C10

5 9 10 48 4 180.00 4.60240 2 ; C4- C8- C9- H4

7 9 8 21 4 180.00 4.60240 2 ; C6- C8- C7- O

8 10 9 26 4 180.00 4.60240 2 ; C7- C9- C8- C20

11 15 16 25 4 180.00 4.60240 2 ; C10- C14- C15- O3

12 14 13 20 4 180.00 4.60240 2 ; C11- C13- C12- C19

12 16 11 7 4 180.00 4.60240 2 ; C11- C15- C10- C6

12 18 17 50 4 180.00 4.60240 2 ; C11- C17- C16- H6

13 15 14 49 4 180.00 4.60240 2 ; C12- C14- C13- H5

13 17 12 11 4 180.00 4.60240 2 ; C12- C16- C11- C10

13 19 20 53 4 180.00 4.60240 2 ; C12- C18- C19- H9

14 16 15 27 4 180.00 4.60240 2 ; C13- C15- C14- C21

17 19 18 51 4 180.00 4.60240 2 ; C16- C18- C17- H7

18 20 19 52 4 180.00 4.60240 2 ; C17- C19- C18- H8

28 30 29 54 4 180.00 4.60240 2 ; C22- C24- C23- H10

28 32 27 15 4 180.00 4.60240 2 ; C22- C26- C21- C14

29 31 30 43 4 180.00 4.60240 2 ; C23- C25- C24- C37

30 32 31 55 4 180.00 4.60240 2 ; C24- C26- C25- H11

33 35 34 56 4 180.00 4.60240 2 ; C27- C29- C28- H12

33 37 26 9 4 180.00 4.60240 2 ; C27- C31- C20- C8

35 37 36 57 4 180.00 4.60240 2 ; C29- C31- C30- H13

38 36 37 26 4 180.00 4.60240 2 ; C32- C30- C31- C20

39 34 33 26 4 180.00 4.60240 2 ; C33- C28- C27- C20

40 34 35 36 4 180.00 4.60240 2 ; C34- C28- C29- C30

41 31 32 27 4 180.00 4.60240 2 ; C35- C25- C26- C21

42 29 28 27 4 180.00 4.60240 2 ; C36- C23- C22- C21

44 1 6 2 4 180.00 4.60240 2 ; H- C- C5- C1

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;name            nrexcl
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    2   ca    1   PIE    C1   2    -0.1987372338    12.01000 ; qtot 0.000
    3   ca    1   PIE    C2   3    -0.1103289115    12.01000 ; qtot 0.000
    4   ca    1   PIE    C3   4     0.0972749636    12.01000 ; qtot 0.000
    5   ca    1   PIE    C4   5     0.2190309538    12.01000 ; qtot 0.000
    6   ca    1   PIE    C5   6    -0.2947057622    12.01000 ; qtot 0.000
    7   cp    1   PIE    C6   7    -0.2119597284    12.01000 ; qtot 0.000
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    9   cp    1   PIE    C8   9    -0.2680034767    12.01000 ; qtot 0.000
   10   ca    1   PIE    C9   10   -0.2455738072    12.01000 ; qtot 0.000
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   21   os    1   PIE    O    21   -0.4823558839    16.00000 ; qtot 0.000
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24 o 1 PIE O2 24 -0.7174534898 16.00000 ; qtot 0.000

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27 cp 1 PIE C21 27 0.3531595930 12.01000 ; qtot 0.000

28 ca 1 PIE C22 28 -0.2196471945 12.01000 ; qtot 0.000

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37 ca 1 PIE C31 37 -0.2183995477 12.01000 ; qtot 0.000

38 ha 1 PIE H 38 0.1080241742 1.00800 ; qtot 0.000

39 ha 1 PIE H1 39 0.1306428676 1.00800 ; qtot 0.000

40 ha 1 PIE H2 40 0.1084957706 1.00800 ; qtot 0.000

41 ha 1 PIE H3 41 0.1574196784 1.00800 ; qtot 0.000

42 ha 1 PIE H4 42 0.1007662540 1.00800 ; qtot 0.000

43 ha 1 PIE H5 43 0.0994134081 1.00800 ; qtot 0.000

44 ha 1 PIE H6 44 0.1083808311 1.00800 ; qtot 0.000

45 ha 1 PIE H7 45 0.1302744844 1.00800 ; qtot 0.000

46 ha 1 PIE H8 46 0.1079520057 1.00800 ; qtot 0.000

47 ha 1 PIE H9 47 0.1570010539 1.00800 ; qtot 0.000

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51 ha 1 PIE H13 51 0.1546300859 1.00800 ; qtot 0.000

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   52   ha    1   PIE   H14   52    0.1671842564     1.00800 ; qtot 0.000
   53   ha    1   PIE   H15   53    0.1618629331     1.00800 ; qtot 0.000
   54   no    1   PIE    N    54    0.7752070158    14.01000 ; qtot 0.000
   55   no    1   PIE   N1    55    0.7798518044    14.01000 ; qtot 0.000
   56   ha    1   PIE   H16   56    0.1608407620     1.00800 ; qtot 0.000
   57   ha    1   PIE   H17   57    0.1659472384     1.00800 ; qtot 0.000
   58   o     1   PIE   O4    58   -0.4613937353    16.00000 ; qtot 0.000
   59   o     1   PIE   O5    59   -0.4548860852    16.00000 ; qtot 0.000
   60   o     1   PIE   O6    60   -0.4561546789    16.00000 ; qtot 0.000
   61   o     1   PIE   O7    61   -0.4625768413    16.00000 ; qtot 0.000
[ bonds ]
;  ai    aj funct   r           k
    1     2   1    1.3984e-01    3.8585e+05 ;     C - C1
    1     6   1    1.3984e-01    3.8585e+05 ;     C - C5
    1    38   1    1.0860e-01    2.8937e+05 ;     C - H
    2     3   1    1.3984e-01    3.8585e+05 ;    C1 - C2
    2    39   1    1.0860e-01    2.8937e+05 ;    C1 - H1
    3     4   1    1.3984e-01    3.8585e+05 ;    C2 - C3
    3    40   1    1.0860e-01    2.8937e+05 ;    C2 - H2
    4     5   1    1.3984e-01    3.8585e+05 ;    C3 - C4
    4     7   1    1.4058e-01    3.7673e+05 ;    C3 - C6
    5     6   1    1.3984e-01    3.8585e+05 ;    C4 - C5
    5    10   1    1.3984e-01    3.8585e+05 ;    C4 - C9
    6    41   1    1.0860e-01    2.8937e+05 ;    C5 - H3
    7     8   1    1.4058e-01    3.7673e+05 ;    C6 - C7
    7    11   1    1.4854e-01    2.9405e+05 ;    C6 - C10
    8     9   1    1.4058e-01    3.7673e+05 ;    C7 - C8
    8    21   1    1.3696e-01    3.1514e+05 ;    C7 - O
    9    10   1    1.4058e-01    3.7673e+05 ;    C8 - C9
```

9	26	1	1.4854e-01	2.9405e+05 ;	C8 - C20
10	42	1	1.0860e-01	2.8937e+05 ;	C9 - H4
11	12	1	1.4058e-01	3.7673e+05 ;	C10 - C11
11	16	1	1.4058e-01	3.7673e+05 ;	C10 - C15
12	13	1	1.3984e-01	3.8585e+05 ;	C11 - C12
12	17	1	1.3984e-01	3.8585e+05 ;	C11 - C16
13	14	1	1.3984e-01	3.8585e+05 ;	C12 - C13
13	20	1	1.3984e-01	3.8585e+05 ;	C12 - C19
14	15	1	1.4058e-01	3.7673e+05 ;	C13 - C14
14	43	1	1.0860e-01	2.8937e+05 ;	C13 - H5
15	16	1	1.4058e-01	3.7673e+05 ;	C14 - C15
15	27	1	1.4854e-01	2.9405e+05 ;	C14 - C21
16	25	1	1.3696e-01	3.1514e+05 ;	C15 - O3
17	18	1	1.3984e-01	3.8585e+05 ;	C16 - C17
17	44	1	1.0860e-01	2.8937e+05 ;	C16 - H6
18	19	1	1.3984e-01	3.8585e+05 ;	C17 - C18
18	45	1	1.0860e-01	2.8937e+05 ;	C17 - H7
19	20	1	1.3984e-01	3.8585e+05 ;	C18 - C19
19	46	1	1.0860e-01	2.8937e+05 ;	C18 - H8
20	47	1	1.0860e-01	2.8937e+05 ;	C19 - H9
21	22	1	1.6147e-01	2.7665e+05 ;	O - P
22	23	1	1.4866e-01	4.0125e+05 ;	P - O1
22	24	1	1.4866e-01	4.0125e+05 ;	P - O2
22	25	1	1.6147e-01	2.7665e+05 ;	P - O3
26	33	1	1.4058e-01	3.7673e+05 ;	C20 - C27
26	37	1	1.4058e-01	3.7673e+05 ;	C20 - C31
27	28	1	1.4058e-01	3.7673e+05 ;	C21 - C22
27	32	1	1.4058e-01	3.7673e+05 ;	C21 - C26
28	29	1	1.3984e-01	3.8585e+05 ;	C22 - C23

```
   28    53   1    1.0860e-01    2.8937e+05 ;    C22 - H15
   29    30   1    1.3984e-01    3.8585e+05 ;    C23 - C24
   29    48   1    1.0860e-01    2.8937e+05 ;    C23 - H10
   30    31   1    1.3984e-01    3.8585e+05 ;    C24 - C25
   30    54   1    1.4689e-01    2.6920e+05 ;    C24 - N
   31    32   1    1.3984e-01    3.8585e+05 ;    C25 - C26
   31    49   1    1.0860e-01    2.8937e+05 ;    C25 - H11
   32    52   1    1.0860e-01    2.8937e+05 ;    C26 - H14
   33    34   1    1.3984e-01    3.8585e+05 ;    C27 - C28
   33    57   1    1.0860e-01    2.8937e+05 ;    C27 - H17
   34    35   1    1.3984e-01    3.8585e+05 ;    C28 - C29
   34    50   1    1.0860e-01    2.8937e+05 ;    C28 - H12
   35    36   1    1.3984e-01    3.8585e+05 ;    C29 - C30
   35    55   1    1.4689e-01    2.6920e+05 ;    C29 - N1
   36    37   1    1.3984e-01    3.8585e+05 ;    C30 - C31
   36    51   1    1.0860e-01    2.8937e+05 ;    C30 - H13
   37    56   1    1.0860e-01    2.8937e+05 ;    C31 - H16
   54    58   1    1.2260e-01    6.2074e+05 ;     N - O4
   54    59   1    1.2260e-01    6.2074e+05 ;     N - O5
   55    60   1    1.2260e-01    6.2074e+05 ;    N1 - O6
   55    61   1    1.2260e-01    6.2074e+05 ;    N1 - O7

[ pairs ]
;  ai    aj   funct
    1     4     1 ;     C - C3
    1    10     1 ;     C - C9
    1    40     1 ;     C - H2
    2     5     1 ;    C1 - C4
    2     7     1 ;    C1 - C6
```

2 41 1 ; C1 - H3

3 8 1 ; C2 - C7

3 10 1 ; C2 - C9

3 11 1 ; C2 - C10

4 9 1 ; C3 - C8

4 12 1 ; C3 - C11

4 16 1 ; C3 - C15

4 21 1 ; C3 - O

4 39 1 ; C3 - H1

4 41 1 ; C3 - H3

4 42 1 ; C3 - H4

5 8 1 ; C4 - C7

5 11 1 ; C4 - C10

5 26 1 ; C4 - C20

5 40 1 ; C4 - H2

6 3 1 ; C5 - C2

6 7 1 ; C5 - C6

6 9 1 ; C5 - C8

6 39 1 ; C5 - H1

6 42 1 ; C5 - H4

7 10 1 ; C6 - C9

7 13 1 ; C6 - C12

7 15 1 ; C6 - C14

7 17 1 ; C6 - C16

7 22 1 ; C6 - P

7 25 1 ; C6 - O3

7 26 1 ; C6 - C20

7 40 1 ; C6 - H2

8 12 1 ; C7 - C11

8 16 1 ; C7 - C15

8 23 1 ; C7 - O1

8 24 1 ; C7 - O2

8 25 1 ; C7 - O3

8 33 1 ; C7 - C27

8 37 1 ; C7 - C31

8 42 1 ; C7 - H4

9 11 1 ; C8 - C10

9 22 1 ; C8 - P

9 34 1 ; C8 - C28

9 36 1 ; C8 - C30

9 56 1 ; C8 - H16

9 57 1 ; C8 - H17

10 21 1 ; C9 - O

10 33 1 ; C9 - C27

10 37 1 ; C9 - C31

10 41 1 ; C9 - H3

11 14 1 ; C10 - C13

11 18 1 ; C10 - C17

11 20 1 ; C10 - C19

11 21 1 ; C10 - O

11 22 1 ; C10 - P

11 27 1 ; C10 - C21

11 44 1 ; C10 - H6

12 15 1 ; C11 - C14

12 19 1 ; C11 - C18

12 25 1 ; C11 - O3

12 43 1 ; C11 - H5

12 45 1 ; C11 - H7

12 47 1 ; C11 - H9

13 16 1 ; C12 - C15

13 18 1 ; C12 - C17

13 27 1 ; C12 - C21

13 44 1 ; C12 - H6

13 46 1 ; C12 - H8

14 17 1 ; C13 - C16

14 19 1 ; C13 - C18

14 25 1 ; C13 - O3

14 28 1 ; C13 - C22

14 32 1 ; C13 - C26

14 47 1 ; C13 - H9

15 20 1 ; C14 - C19

15 22 1 ; C14 - P

15 29 1 ; C14 - C23

15 31 1 ; C14 - C25

15 52 1 ; C14 - H14

15 53 1 ; C14 - H15

16 17 1 ; C15 - C16

16 21 1 ; C15 - O

16 23 1 ; C15 - O1

16 24 1 ; C15 - O2

16 28 1 ; C15 - C22

16 32 1 ; C15 - C26

16 43 1 ; C15 - H5

17 20 1 ; C16 - C19

17 46 1 ; C16 - H8

18 47 1 ; C17 - H9

19 44 1 ; C18 - H6

20 43 1 ; C19 - H5

20 45 1 ; C19 - H7

21 26 1 ; O - C20

25 27 1 ; O3 - C21

26 35 1 ; C20 - C29

26 42 1 ; C20 - H4

26 50 1 ; C20 - H12

26 51 1 ; C20 - H13

27 30 1 ; C21 - C24

27 43 1 ; C21 - H5

27 48 1 ; C21 - H10

27 49 1 ; C21 - H11

28 31 1 ; C22 - C25

28 52 1 ; C22 - H14

28 54 1 ; C22 - N

29 32 1 ; C23 - C26

29 49 1 ; C23 - H11

29 58 1 ; C23 - O4

29 59 1 ; C23 - O5

30 52 1 ; C24 - H14

30 53 1 ; C24 - H15

31 48 1 ; C25 - H10

31 58 1 ; C25 - O4

31 59 1 ; C25 - O5

32 53 1 ; C26 - H15

32 54 1 ; C26 - N

33 36 1 ; C27 - C30

33 55 1 ; C27 - N1

33 56 1 ; C27 - H16

34 37 1 ; C28 - C31

34 51 1 ; C28 - H13

34 60 1 ; C28 - O6

34 61 1 ; C28 - O7

35 56 1 ; C29 - H16

35 57 1 ; C29 - H17

36 50 1 ; C30 - H12

36 60 1 ; C30 - O6

36 61 1 ; C30 - O7

37 55 1 ; C31 - N1

37 57 1 ; C31 - H17

38 3 1 ; H - C2

38 5 1 ; H - C4

38 39 1 ; H - H1

38 41 1 ; H - H3

39 40 1 ; H1 - H2

44 45 1 ; H6 - H7

45 46 1 ; H7 - H8

46 47 1 ; H8 - H9

48 53 1 ; H10 - H15

48 54 1 ; H10 - N

49 52 1 ; H11 - H14

49 54 1 ; H11 - N

50 55 1 ; H12 - N1

50 57 1 ; H12 - H17

51 55 1 ; H13 - N1

51 56 1 ; H13 - H16

[angles]

```
;  ai    aj    ak   funct   theta       cth
    1     2     3     1   1.2002e+02   5.5731e+02 ;    C - C1    - C2
    1     2    39     1   1.1988e+02   4.0334e+02 ;    C - C1    - H1
    1     6     5     1   1.2002e+02   5.5731e+02 ;    C - C5    - C4
    1     6    41     1   1.1988e+02   4.0334e+02 ;    C - C5    - H3
    2     1     6     1   1.2002e+02   5.5731e+02 ;   C1 - C     - C5
    2     1    38     1   1.1988e+02   4.0334e+02 ;   C1 - C     - H
    2     3     4     1   1.2002e+02   5.5731e+02 ;   C1 - C2    - C3
    2     3    40     1   1.1988e+02   4.0334e+02 ;   C1 - C2    - H2
    3     2    39     1   1.1988e+02   4.0334e+02 ;   C2 - C1    - H1
    3     4     5     1   1.2002e+02   5.5731e+02 ;   C2 - C3    - C4
    3     4     7     1   1.2069e+02   5.5480e+02 ;   C2 - C3    - C6
    4     3    40     1   1.1988e+02   4.0334e+02 ;   C3 - C2    - H2
    4     5     6     1   1.2002e+02   5.5731e+02 ;   C3 - C4    - C5
    4     5    10     1   1.2002e+02   5.5731e+02 ;   C3 - C4    - C9
    4     7     8     1   1.1838e+02   5.5815e+02 ;   C3 - C6    - C7
    4     7    11     1   1.2111e+02   5.3555e+02 ;   C3 - C6    - C10
    5     4     7     1   1.2069e+02   5.5480e+02 ;   C4 - C3    - C6
    5     6    41     1   1.1988e+02   4.0334e+02 ;   C4 - C5    - H3
    5    10     9     1   1.2069e+02   5.5480e+02 ;   C4 - C9    - C8
    5    10    42     1   1.1988e+02   4.0334e+02 ;   C4 - C9    - H4
    6     1    38     1   1.1988e+02   4.0334e+02 ;   C5 - C     - H
    6     5    10     1   1.2002e+02   5.5731e+02 ;   C5 - C4    - C9
    7     8     9     1   1.1152e+02   5.7572e+02 ;   C6 - C7    - C8
    7     8    21     1   1.1691e+02   5.8660e+02 ;   C6 - C7    - O
    7    11    12     1   1.2111e+02   5.3555e+02 ;   C6 - C10   - C11
    7    11    16     1   1.2111e+02   5.3555e+02 ;   C6 - C10   - C15
    8     7    11     1   1.2111e+02   5.3555e+02 ;   C7 - C6    - C10
    8     9    10     1   1.1838e+02   5.5815e+02 ;   C7 - C8    - C9
```

8 9 26 1 1.2111e+02 5.3555e+02 ; C7 - C8 - C20

8 21 22 1 1.2318e+02 6.5019e+02 ; C7 - O - P

9 8 21 1 1.1691e+02 5.8660e+02 ; C8 - C7 - O

9 10 42 1 1.1986e+02 4.0166e+02 ; C8 - C9 - H4

9 26 33 1 1.2111e+02 5.3555e+02 ; C8 - C20 - C27

9 26 37 1 1.2111e+02 5.3555e+02 ; C8 - C20 - C31

10 9 26 1 1.2111e+02 5.3555e+02 ; C9 - C8 - C20

11 12 13 1 1.2069e+02 5.5480e+02 ; C10 - C11 - C12

11 12 17 1 1.2069e+02 5.5480e+02 ; C10 - C11 - C16

11 16 15 1 1.1152e+02 5.7572e+02 ; C10 - C15 - C14

11 16 25 1 1.1691e+02 5.8660e+02 ; C10 - C15 - O3

12 11 16 1 1.1838e+02 5.5815e+02 ; C11 - C10 - C15

12 13 14 1 1.2002e+02 5.5731e+02 ; C11 - C12 - C13

12 13 20 1 1.2002e+02 5.5731e+02 ; C11 - C12 - C19

12 17 18 1 1.2002e+02 5.5731e+02 ; C11 - C16 - C17

12 17 44 1 1.1988e+02 4.0334e+02 ; C11 - C16 - H6

13 12 17 1 1.2002e+02 5.5731e+02 ; C12 - C11 - C16

13 14 15 1 1.2069e+02 5.5480e+02 ; C12 - C13 - C14

13 14 43 1 1.1988e+02 4.0334e+02 ; C12 - C13 - H5

13 20 19 1 1.2002e+02 5.5731e+02 ; C12 - C19 - C18

13 20 47 1 1.1988e+02 4.0334e+02 ; C12 - C19 - H9

14 13 20 1 1.2002e+02 5.5731e+02 ; C13 - C12 - C19

14 15 16 1 1.1838e+02 5.5815e+02 ; C13 - C14 - C15

14 15 27 1 1.2111e+02 5.3555e+02 ; C13 - C14 - C21

15 14 43 1 1.1986e+02 4.0166e+02 ; C14 - C13 - H5

15 16 25 1 1.1691e+02 5.8660e+02 ; C14 - C15 - O3

15 27 28 1 1.2111e+02 5.3555e+02 ; C14 - C21 - C22

15 27 32 1 1.2111e+02 5.3555e+02 ; C14 - C21 - C26

16 15 27 1 1.2111e+02 5.3555e+02 ; C15 - C14 - C21

16 25 22 1 1.2318e+02 6.5019e+02 ; C15 - O3 - P

17 18 19 1 1.2002e+02 5.5731e+02 ; C16 - C17 - C18

17 18 45 1 1.1988e+02 4.0334e+02 ; C16 - C17 - H7

18 17 44 1 1.1988e+02 4.0334e+02 ; C17 - C16 - H6

18 19 20 1 1.2002e+02 5.5731e+02 ; C17 - C18 - C19

18 19 46 1 1.1988e+02 4.0334e+02 ; C17 - C18 - H8

19 18 45 1 1.1988e+02 4.0334e+02 ; C18 - C17 - H7

19 20 47 1 1.1988e+02 4.0334e+02 ; C18 - C19 - H9

20 19 46 1 1.1988e+02 4.0334e+02 ; C19 - C18 - H8

21 22 23 1 1.1546e+02 3.6736e+02 ; O - P - O1

21 22 24 1 1.1546e+02 3.6736e+02 ; O - P - O2

21 22 25 1 1.0184e+02 3.7656e+02 ; O - P - O3

23 22 24 1 1.1580e+02 3.8325e+02 ; O1 - P - O2

23 22 25 1 1.1546e+02 3.6736e+02 ; O1 - P - O3

24 22 25 1 1.1546e+02 3.6736e+02 ; O2 - P - O3

26 33 34 1 1.2069e+02 5.5480e+02 ; C20 - C27 - C28

26 33 57 1 1.1986e+02 4.0166e+02 ; C20 - C27 - H17

26 37 36 1 1.2069e+02 5.5480e+02 ; C20 - C31 - C30

26 37 56 1 1.1986e+02 4.0166e+02 ; C20 - C31 - H16

27 28 29 1 1.2069e+02 5.5480e+02 ; C21 - C22 - C23

27 28 53 1 1.1986e+02 4.0166e+02 ; C21 - C22 - H15

27 32 31 1 1.2069e+02 5.5480e+02 ; C21 - C26 - C25

27 32 52 1 1.1986e+02 4.0166e+02 ; C21 - C26 - H14

28 27 32 1 1.1838e+02 5.5815e+02 ; C22 - C21 - C26

28 29 30 1 1.2002e+02 5.5731e+02 ; C22 - C23 - C24

28 29 48 1 1.1988e+02 4.0334e+02 ; C22 - C23 - H10

29 28 53 1 1.1988e+02 4.0334e+02 ; C23 - C22 - H15

29 30 31 1 1.2002e+02 5.5731e+02 ; C23 - C24 - C25

29 30 54 1 1.1901e+02 5.5898e+02 ; C23 - C24 - N

```
   30    29    48    1   1.1988e+02   4.0334e+02 ;   C24 - C23   - H10
   30    31    32    1   1.2002e+02   5.5731e+02 ;   C24 - C25   - C26
   30    31    49    1   1.1988e+02   4.0334e+02 ;   C24 - C25   - H11
   30    54    58    1   1.1776e+02   5.7488e+02 ;   C24 - N     - O4
   30    54    59    1   1.1776e+02   5.7488e+02 ;   C24 - N     - O5
   31    30    54    1   1.1901e+02   5.5898e+02 ;   C25 - C24   - N
   31    32    52    1   1.1988e+02   4.0334e+02 ;   C25 - C26   - H14
   32    31    49    1   1.1988e+02   4.0334e+02 ;   C26 - C25   - H11
   33    26    37    1   1.1838e+02   5.5815e+02 ;   C27 - C20   - C31
   33    34    35    1   1.2002e+02   5.5731e+02 ;   C27 - C28   - C29
   33    34    50    1   1.1988e+02   4.0334e+02 ;   C27 - C28   - H12
   34    33    57    1   1.1988e+02   4.0334e+02 ;   C28 - C27   - H17
   34    35    36    1   1.2002e+02   5.5731e+02 ;   C28 - C29   - C30
   34    35    55    1   1.1901e+02   5.5898e+02 ;   C28 - C29   - N1
   35    34    50    1   1.1988e+02   4.0334e+02 ;   C29 - C28   - H12
   35    36    37    1   1.2002e+02   5.5731e+02 ;   C29 - C30   - C31
   35    36    51    1   1.1988e+02   4.0334e+02 ;   C29 - C30   - H13
   35    55    60    1   1.1776e+02   5.7488e+02 ;   C29 - N1    - O6
   35    55    61    1   1.1776e+02   5.7488e+02 ;   C29 - N1    - O7
   36    35    55    1   1.1901e+02   5.5898e+02 ;   C30 - C29   - N1
   36    37    56    1   1.1988e+02   4.0334e+02 ;   C30 - C31   - H16
   37    36    51    1   1.1988e+02   4.0334e+02 ;   C31 - C30   - H13
   58    54    59    1   1.2508e+02   6.4183e+02 ;    O4 - N     - O5
   60    55    61    1   1.2508e+02   6.4183e+02 ;    O6 - N1    - O7

[ dihedrals ] ; propers
; for gromacs 4.5 or higher, using funct 9
;   i     j     k     l  func   phase     kd      pn
    1     2     3     4     9   180.00  15.16700   2 ;     C-    C1-    C2-    C3
```

1 2 3 40 9 180.00 15.16700 2 ; C- C1- C2- H2

1 6 5 4 9 180.00 15.16700 2 ; C- C5- C4- C3

1 6 5 10 9 180.00 15.16700 2 ; C- C5- C4- C9

2 1 6 5 9 180.00 15.16700 2 ; C1- C- C5- C4

2 1 6 41 9 180.00 15.16700 2 ; C1- C- C5- H3

2 3 4 5 9 180.00 15.16700 2 ; C1- C2- C3- C4

2 3 4 7 9 180.00 15.16700 2 ; C1- C2- C3- C6

3 4 5 6 9 180.00 15.16700 2 ; C2- C3- C4- C5

3 4 5 10 9 180.00 15.16700 2 ; C2- C3- C4- C9

3 4 7 8 9 180.00 15.16700 2 ; C2- C3- C6- C7

3 4 7 11 9 180.00 15.16700 2 ; C2- C3- C6- C10

4 3 2 39 9 180.00 15.16700 2 ; C3- C2- C1- H1

4 5 6 41 9 180.00 15.16700 2 ; C3- C4- C5- H3

4 5 10 9 9 180.00 15.16700 2 ; C3- C4- C9- C8

4 5 10 42 9 180.00 15.16700 2 ; C3- C4- C9- H4

4 7 8 9 9 180.00 15.16700 2 ; C3- C6- C7- C8

4 7 8 21 9 180.00 15.16700 2 ; C3- C6- C7- O

4 7 11 12 9 180.00 4.18400 2 ; C3- C6- C10- C11

4 7 11 16 9 180.00 4.18400 2 ; C3- C6- C10- C15

5 4 3 40 9 180.00 15.16700 2 ; C4- C3- C2- H2

5 4 7 8 9 180.00 15.16700 2 ; C4- C3- C6- C7

5 4 7 11 9 180.00 15.16700 2 ; C4- C3- C6- C10

5 10 9 8 9 180.00 15.16700 2 ; C4- C9- C8- C7

5 10 9 26 9 180.00 15.16700 2 ; C4- C9- C8- C20

6 1 2 3 9 180.00 15.16700 2 ; C5- C- C1- C2

6 1 2 39 9 180.00 15.16700 2 ; C5- C- C1- H1

6 5 4 7 9 180.00 15.16700 2 ; C5- C4- C3- C6

6 5 10 9 9 180.00 15.16700 2 ; C5- C4- C9- C8

6 5 10 42 9 180.00 15.16700 2 ; C5- C4- C9- H4

7 4 3 40 9 180.00 15.16700 2 ; C6- C3- C2- H2

7 4 5 10 9 180.00 15.16700 2 ; C6- C3- C4- C9

7 8 9 10 9 180.00 15.16700 2 ; C6- C7- C8- C9

7 8 9 26 9 180.00 15.16700 2 ; C6- C7- C8- C20

7 8 21 22 9 180.00 3.76560 2 ; C6- C7- O- P

7 11 12 13 9 180.00 15.16700 2 ; C6- C10- C11- C12

7 11 12 17 9 180.00 15.16700 2 ; C6- C10- C11- C16

7 11 16 15 9 180.00 15.16700 2 ; C6- C10- C15- C14

7 11 16 25 9 180.00 15.16700 2 ; C6- C10- C15- O3

8 7 11 12 9 180.00 4.18400 2 ; C7- C6- C10- C11

8 7 11 16 9 180.00 4.18400 2 ; C7- C6- C10- C15

8 9 10 42 9 180.00 15.16700 2 ; C7- C8- C9- H4

8 9 26 33 9 180.00 4.18400 2 ; C7- C8- C20- C27

8 9 26 37 9 180.00 4.18400 2 ; C7- C8- C20- C31

8 21 22 23 9 0.00 0.41840 3 ; C7- O- P- O1

8 21 22 23 9 180.00 3.34720 2 ; C7- O- P- O1

8 21 22 24 9 0.00 0.41840 3 ; C7- O- P- O2

8 21 22 24 9 180.00 3.34720 2 ; C7- O- P- O2

8 21 22 25 9 0.00 3.34720 2 ; C7- O- P- O3

9 8 7 11 9 180.00 15.16700 2 ; C8- C7- C6- C10

9 8 21 22 9 180.00 3.76560 2 ; C8- C7- O- P

9 26 33 34 9 180.00 15.16700 2 ; C8- C20- C27- C28

9 26 33 57 9 180.00 15.16700 2 ; C8- C20- C27- H17

9 26 37 36 9 180.00 15.16700 2 ; C8- C20- C31- C30

9 26 37 56 9 180.00 15.16700 2 ; C8- C20- C31- H16

10 5 6 41 9 180.00 15.16700 2 ; C9- C4- C5- H3

10 9 8 21 9 180.00 15.16700 2 ; C9- C8- C7- O

10 9 26 33 9 180.00 4.18400 2 ; C9- C8- C20- C27

10 9 26 37 9 180.00 4.18400 2 ; C9- C8- C20- C31

11 7 8 21 9 180.00 15.16700 2 ; C10- C6- C7- O

11 12 13 14 9 180.00 15.16700 2 ; C10- C11- C12- C13

11 12 13 20 9 180.00 15.16700 2 ; C10- C11- C12- C19

11 12 17 18 9 180.00 15.16700 2 ; C10- C11- C16- C17

11 12 17 44 9 180.00 15.16700 2 ; C10- C11- C16- H6

11 16 15 14 9 180.00 15.16700 2 ; C10- C15- C14- C13

11 16 15 27 9 180.00 15.16700 2 ; C10- C15- C14- C21

11 16 25 22 9 180.00 3.76560 2 ; C10- C15- O3- P

12 11 16 15 9 180.00 15.16700 2 ; C11- C10- C15- C14

12 11 16 25 9 180.00 15.16700 2 ; C11- C10- C15- O3

12 13 14 15 9 180.00 15.16700 2 ; C11- C12- C13- C14

12 13 14 43 9 180.00 15.16700 2 ; C11- C12- C13- H5

12 13 20 19 9 180.00 15.16700 2 ; C11- C12- C19- C18

12 13 20 47 9 180.00 15.16700 2 ; C11- C12- C19- H9

12 17 18 19 9 180.00 15.16700 2 ; C11- C16- C17- C18

12 17 18 45 9 180.00 15.16700 2 ; C11- C16- C17- H7

13 12 11 16 9 180.00 15.16700 2 ; C12- C11- C10- C15

13 12 17 18 9 180.00 15.16700 2 ; C12- C11- C16- C17

13 12 17 44 9 180.00 15.16700 2 ; C12- C11- C16- H6

13 14 15 16 9 180.00 15.16700 2 ; C12- C13- C14- C15

13 14 15 27 9 180.00 15.16700 2 ; C12- C13- C14- C21

13 20 19 18 9 180.00 15.16700 2 ; C12- C19- C18- C17

13 20 19 46 9 180.00 15.16700 2 ; C12- C19- C18- H8

14 13 12 17 9 180.00 15.16700 2 ; C13- C12- C11- C16

14 13 20 19 9 180.00 15.16700 2 ; C13- C12- C19- C18

14 13 20 47 9 180.00 15.16700 2 ; C13- C12- C19- H9

14 15 16 25 9 180.00 15.16700 2 ; C13- C14- C15- O3

14 15 27 28 9 180.00 4.18400 2 ; C13- C14- C21- C22

14 15 27 32 9 180.00 4.18400 2 ; C13- C14- C21- C26

15 14 13 20 9 180.00 15.16700 2 ; C14- C13- C12- C19

15 16 25 22 9 180.00 3.76560 2 ; C14- C15- O3- P

15 27 28 29 9 180.00 15.16700 2 ; C14- C21- C22- C23

15 27 28 53 9 180.00 15.16700 2 ; C14- C21- C22- H15

15 27 32 31 9 180.00 15.16700 2 ; C14- C21- C26- C25

15 27 32 52 9 180.00 15.16700 2 ; C14- C21- C26- H14

16 11 12 17 9 180.00 15.16700 2 ; C15- C10- C11- C16

16 15 14 43 9 180.00 15.16700 2 ; C15- C14- C13- H5

16 15 27 28 9 180.00 4.18400 2 ; C15- C14- C21- C22

16 15 27 32 9 180.00 4.18400 2 ; C15- C14- C21- C26

16 25 22 21 9 0.00 3.34720 2 ; C15- O3- P- O

16 25 22 23 9 0.00 0.41840 3 ; C15- O3- P- O1

16 25 22 23 9 180.00 3.34720 2 ; C15- O3- P- O1

16 25 22 24 9 0.00 0.41840 3 ; C15- O3- P- O2

16 25 22 24 9 180.00 3.34720 2 ; C15- O3- P- O2

17 12 13 20 9 180.00 15.16700 2 ; C16- C11- C12- C19

17 18 19 20 9 180.00 15.16700 2 ; C16- C17- C18- C19

17 18 19 46 9 180.00 15.16700 2 ; C16- C17- C18- H8

18 19 20 47 9 180.00 15.16700 2 ; C17- C18- C19- H9

19 18 17 44 9 180.00 15.16700 2 ; C18- C17- C16- H6

20 13 14 43 9 180.00 15.16700 2 ; C19- C12- C13- H5

20 19 18 45 9 180.00 15.16700 2 ; C19- C18- C17- H7

21 8 9 26 9 180.00 15.16700 2 ; O- C7- C8- C20

25 16 15 27 9 180.00 15.16700 2 ; O3- C15- C14- C21

26 9 10 42 9 180.00 15.16700 2 ; C20- C8- C9- H4

26 33 34 35 9 180.00 15.16700 2 ; C20- C27- C28- C29

26 33 34 50 9 180.00 15.16700 2 ; C20- C27- C28- H12

26 37 36 35 9 180.00 15.16700 2 ; C20- C31- C30- C29

26 37 36 51 9 180.00 15.16700 2 ; C20- C31- C30- H13

27 15 14 43 9 180.00 15.16700 2 ; C21- C14- C13- H5

27 28 29 30 9 180.00 15.16700 2 ; C21- C22- C23- C24

27 28 29 48 9 180.00 15.16700 2 ; C21- C22- C23- H10

27 32 31 30 9 180.00 15.16700 2 ; C21- C26- C25- C24

27 32 31 49 9 180.00 15.16700 2 ; C21- C26- C25- H11

28 27 32 31 9 180.00 15.16700 2 ; C22- C21- C26- C25

28 27 32 52 9 180.00 15.16700 2 ; C22- C21- C26- H14

28 29 30 31 9 180.00 15.16700 2 ; C22- C23- C24- C25

28 29 30 54 9 180.00 15.16700 2 ; C22- C23- C24- N

29 28 27 32 9 180.00 15.16700 2 ; C23- C22- C21- C26

29 30 31 32 9 180.00 15.16700 2 ; C23- C24- C25- C26

29 30 31 49 9 180.00 15.16700 2 ; C23- C24- C25- H11

29 30 54 58 9 180.00 2.51040 2 ; C23- C24- N- O4

29 30 54 59 9 180.00 2.51040 2 ; C23- C24- N- O5

30 29 28 53 9 180.00 15.16700 2 ; C24- C23- C22- H15

30 31 32 52 9 180.00 15.16700 2 ; C24- C25- C26- H14

31 30 29 48 9 180.00 15.16700 2 ; C25- C24- C23- H10

31 30 54 58 9 180.00 2.51040 2 ; C25- C24- N- O4

31 30 54 59 9 180.00 2.51040 2 ; C25- C24- N- O5

32 27 28 53 9 180.00 15.16700 2 ; C26- C21- C22- H15

32 31 30 54 9 180.00 15.16700 2 ; C26- C25- C24- N

33 26 37 36 9 180.00 15.16700 2 ; C27- C20- C31- C30

33 26 37 56 9 180.00 15.16700 2 ; C27- C20- C31- H16

33 34 35 36 9 180.00 15.16700 2 ; C27- C28- C29- C30

33 34 35 55 9 180.00 15.16700 2 ; C27- C28- C29- N1

34 33 26 37 9 180.00 15.16700 2 ; C28- C27- C20- C31

34 35 36 37 9 180.00 15.16700 2 ; C28- C29- C30- C31

34 35 36 51 9 180.00 15.16700 2 ; C28- C29- C30- H13

34 35 55 60 9 180.00 2.51040 2 ; C28- C29- N1- O6

34 35 55 61 9 180.00 2.51040 2 ; C28- C29- N1- O7

35 34 33 57 9 180.00 15.16700 2 ; C29- C28- C27- H17

35 36 37 56 9 180.00 15.16700 2 ; C29- C30- C31- H16

36 35 34 50 9 180.00 15.16700 2 ; C30- C29- C28- H12

36 35 55 60 9 180.00 2.51040 2 ; C30- C29- N1- O6

36 35 55 61 9 180.00 2.51040 2 ; C30- C29- N1- O7

37 26 33 57 9 180.00 15.16700 2 ; C31- C20- C27- H17

37 36 35 55 9 180.00 15.16700 2 ; C31- C30- C29- N1

38 1 2 3 9 180.00 15.16700 2 ; H- C- C1- C2

38 1 2 39 9 180.00 15.16700 2 ; H- C- C1- H1

38 1 6 5 9 180.00 15.16700 2 ; H- C- C5- C4

38 1 6 41 9 180.00 15.16700 2 ; H- C- C5- H3

39 2 3 40 9 180.00 15.16700 2 ; H1- C1- C2- H2

44 17 18 45 9 180.00 15.16700 2 ; H6- C16- C17- H7

45 18 19 46 9 180.00 15.16700 2 ; H7- C17- C18- H8

46 19 20 47 9 180.00 15.16700 2 ; H8- C18- C19- H9

48 29 28 53 9 180.00 15.16700 2 ; H10- C23- C22- H15

48 29 30 54 9 180.00 15.16700 2 ; H10- C23- C24- N

49 31 30 54 9 180.00 15.16700 2 ; H11- C25- C24- N

49 31 32 52 9 180.00 15.16700 2 ; H11- C25- C26- H14

50 34 33 57 9 180.00 15.16700 2 ; H12- C28- C27- H17

50 34 35 55 9 180.00 15.16700 2 ; H12- C28- C29- N1

51 36 35 55 9 180.00 15.16700 2 ; H13- C30- C29- N1

51 36 37 56 9 180.00 15.16700 2 ; H13- C30- C31- H16

[dihedrals] ; impropers

; treated as propers in GROMACS to use correct AMBER analytical function

; i j k l func phase kd pn

1 3 2 39 4 180.00 4.60240 2 ; C- C2- C1- H1

1 5 6 41 4 180.00 4.60240 2 ; C- C4- C5- H3

2 4 3 40 4 180.00 4.60240 2 ; C1- C3- C2- H2

3 5 4 7 4 180.00 4.60240 2 ; C2- C4- C3- C6

4 6 5 10 4 180.00 4.60240 2 ; C3- C5- C4- C9

4 8 7 11 4 180.00 4.60240 2 ; C3- C7- C6- C10

5 9 10 42 4 180.00 4.60240 2 ; C4- C8- C9- H4

7 9 8 21 4 180.00 4.60240 2 ; C6- C8- C7- O

8 10 9 26 4 180.00 4.60240 2 ; C7- C9- C8- C20

11 15 16 25 4 180.00 4.60240 2 ; C10- C14- C15- O3

12 14 13 20 4 180.00 4.60240 2 ; C11- C13- C12- C19

12 16 11 7 4 180.00 4.60240 2 ; C11- C15- C10- C6

12 18 17 44 4 180.00 4.60240 2 ; C11- C17- C16- H6

13 15 14 43 4 180.00 4.60240 2 ; C12- C14- C13- H5

13 17 12 11 4 180.00 4.60240 2 ; C12- C16- C11- C10

13 19 20 47 4 180.00 4.60240 2 ; C12- C18- C19- H9

14 16 15 27 4 180.00 4.60240 2 ; C13- C15- C14- C21

17 19 18 45 4 180.00 4.60240 2 ; C16- C18- C17- H7

18 20 19 46 4 180.00 4.60240 2 ; C17- C19- C18- H8

28 30 29 48 4 180.00 4.60240 2 ; C22- C24- C23- H10

28 32 27 15 4 180.00 4.60240 2 ; C22- C26- C21- C14

29 27 28 53 4 180.00 4.60240 2 ; C23- C21- C22- H15

29 31 30 54 4 180.00 4.60240 2 ; C23- C25- C24- N

30 32 31 49 4 180.00 4.60240 2 ; C24- C26- C25- H11

30 58 54 59 4 180.00 4.60240 2 ; C24- O4- N- O5

31 27 32 52 4 180.00 4.60240 2 ; C25- C21- C26- H14

33 35 34 50 4 180.00 4.60240 2 ; C27- C29- C28- H12

33 37 26 9 4 180.00 4.60240 2 ; C27- C31- C20- C8

34 26 33 57 4 180.00 4.60240 2 ; C28- C20- C27- H17

34 36 35 55 4 180.00 4.60240 2 ; C28- C30- C29- N1

35 37 36 51 4 180.00 4.60240 2 ; C29- C31- C30- H13

35 60 55 61 4 180.00 4.60240 2 ; C29- O6- N1- O7

36 26 37 56 4 180.00 4.60240 2 ; C30- C20- C31- H16

38 1 6 2 4 180.00 4.60240 2 ; H- C- C5- C1

9.2 Geometry optimization of 1b/3a

The structure of the complex **1b**/**3a** (see Figure 4) was optimized with GAUSSIAN[22] using TPSS,[23] the def2-SVP basis set[24,25] along with the D3 version of Grimme's dispersion with the D3 damping function[26] an „ultrafine" integration grid, and the SMD[27] implicit solvent for CH_2Cl_2 with an epsilon value of eps=16.2 to mimic the solvent properties at 180 K.[8] Considering this structure is similar to known structures,[28] no frequency analysis was performed.

The optimized structure is given below:

1\1\GINC-NODE0599\FOpt\RTPSSTPSS\def2SVP\C59H60N1O5P1\MAG24964\16-Apr-
2020\0\\#p tpsstpss/def2svp empiricaldispersion=gd3 int=ultrafine opt
scrf=(smd, solvent=ch2cl2, read)\\e1kombi\\0,1\C,6.1909568563,-1.78881
77742,-3.9331692683\C,5.8049083302,-2.8903039276,-3.1229283401\C,4.818
7376043,-2.7460262924,-2.1584308845\C,4.168264312,-1.4915503117,-1.952
1631679\C,4.5311424406,-0.3858467278,-2.8057439312\C,5.5599735257,-0.5
648323881,-3.7796771752\C,3.1430016725,-1.2956646087,-0.9583936278\C,2
.4721253206,-0.0704355878,-0.9292931916\C,2.7986523906,1.0271788558,-1
.7826144402\C,3.839876094,0.854299916,-2.6851727676\C,2.7384201326,-2.
3621176803,0.0023471007\C,3.6720009752,-2.9779563729,0.9111457956\C,3.
2168866205,-4.0547774622,1.7566607786\C,1.8521089617,-4.4586376561,1.7
06184883\C,0.9272897935,-3.8168565278,0.8920336916\C,1.3981338083,-2.7
592903387,0.056594759\C,5.0264933945,-2.5438912433,1.0408780459\C,5.89
51874027,-3.1653357346,1.9254884224\C,5.4555542803,-4.2529799699,2.727
347597\C,4.1407924284,-4.6823985808,2.6464571995\O,1.4457027832,0.1003
051973,-0.0092194836\P,-0.0291849237,-0.5925085014,-0.3837511933\O,-0.
6100939504,-0.0125743295,-1.6550632913\O,-0.8252652583,-0.5765040185,0
.9170908325\O,0.4752577034,-2.133131884,-0.7714015132\C,2.0194794579,2
.3019246585,-1.7011100398\C,-0.5124453467,-4.2266819319,0.8762370592\C

,-1.0273739618,-4.9513968533,-0.2297617786\C,-2.3687116852,-5.37317244
35,-0.2039549884\C,-3.2157550308,-5.0933118515,0.884944246\C,-2.689191
9318,-4.3506413812,1.9570122896\C,-1.3509644799,-3.9126181139,1.975544
2565\C,1.0982784853,2.6334422229,-2.7292143842\C,0.3595752352,3.824644
4198,-2.6191378413\C,0.5185065133,4.7031150517,-1.530981921\C,1.444906
5747,4.3579021051,-0.5319973723\C,2.1949073712,3.1681465967,-0.5937251
186\C,3.1680438618,2.8235397537,0.512006901\C,0.8882331124,1.719189999
7,-3.9168796578\C,-0.2942992569,5.9761814109,-1.4454570418\C,-0.833148
7832,-3.0944919351,3.1386544029\C,-0.1507051858,-5.2678123576,-1.42149
37119\C,-4.6364675205,-5.6128703381,0.9136941006\C,0.4509156474,3.0696
56308,2.8985083664\C,0.4009142665,4.469854027,3.0932073738\C,-0.617590
7172,5.1901697275,2.4237853326\C,-1.537663444,4.5460961171,1.600521211
7\C,-1.4826345614,3.1400508761,1.4174110007\C,-0.4660558789,2.40952218
73,2.0811556522\C,1.4062168503,5.2182207912,3.9828193619\C,2.428451148
6,4.2691320915,4.6405268897\C,2.1773322036,6.2472960979,3.1150884253\C
,0.6328268585,5.9640943484,5.1014000194\C,-2.4808929881,2.5467354906,0
.5595985436\N,-2.6633912502,1.2703983068,0.3424066904\C,-3.6583791923,
0.7949611249,-0.5818555959\C,-3.5029201948,1.0702326098,-1.9652566911\
C,-4.5472523972,0.672560802,-2.8168990284\C,-5.6669360827,-0.010174462
4,-2.3200765409\C,-5.7907377186,-0.3461607137,-0.9553910356\C,-4.75761
62046,0.079539994,-0.0953764974\C,-6.9723046097,-1.1550831139,-0.38441
22316\C,-8.0202647717,-1.4913201834,-1.4648741247\C,-6.4251771789,-2.4
822510214,0.2003401968\C,-7.6688437884,-0.3444605497,0.7371648396\O,-2
.4008146344,1.6889550427,-2.454113795\H,6.9759303815,-1.9147728351,-4.
6868065708\H,6.2861085916,-3.8641739609,-3.2652728125\H,4.524247264,-3
.6062194009,-1.5505613748\H,5.8328105991,0.2865826313,-4.413534288\H,4
.1265066664,1.6823237406,-3.3426038816\H,1.5239638162,-5.2865369611,2.
344175515\H,5.3767114165,-1.7007335741,0.4387172121\H,6.9282547549,-2.
8106848447,2.010735144\H,6.1538919772,-4.7393244591,3.4171756053\H,3.7

834213089,-5.5064848252,3.2743777529\H,-1.5985027842,1.1905938982,-2.0
868288539\H,-1.9917819678,0.5336694073,0.7377256799\H,-2.7601935516,-5
.9420730703,-1.0566961439\H,-3.3372050035,-4.1034167252,2.8073470839\H
,-0.3697203282,4.0662553701,-3.4020119012\H,1.5835140902,5.0260090337,
0.3254492765\H,3.2770402122,3.6621894017,1.2189899603\H,2.8210984423,1
.9412048772,1.0793280306\H,4.1668740442,2.5769237502,0.1085191414\H,0.
7458868953,0.6778877971,-3.5837970119\H,-0.0043014725,2.022224979,-4.4
892683784\H,1.7559316061,1.7387058788,-4.6022095231\H,-0.0893524655,6.
6380506662,-2.3078560383\H,-1.3776535114,5.7555155416,-1.4614405273\H,
-0.0718965506,6.5375222515,-0.5227181417\H,-1.645116534,-2.8651932212,
3.8494775033\H,-0.0363926513,-3.6247487706,3.690900759\H,-0.409710406,
-2.1427635634,2.7729010417\H,0.7982805428,-5.7415946577,-1.1111988546\
H,-0.6636488895,-5.9453655935,-2.1243099354\H,0.1138667111,-4.34361557
35,-1.9674040738\H,-5.110353992,-5.5518632735,-0.081322172\H,-4.654195
0921,-6.678058297,1.2163720859\H,-5.2590693865,-5.0541106524,1.6323017
111\H,1.2256006211,2.4747221746,3.3868776517\H,-0.6866619295,6.2759372
205,2.5420040303\H,-2.3116003496,5.1253142286,1.0863315678\H,-0.385140
1742,1.3269339895,1.9450412327\H,3.1248563128,4.8565596379,5.264343022
6\H,1.9369117441,3.5266522427,5.293897468\H,3.0283276261,3.7274592107,
3.8880910569\H,2.884508083,6.8139542304,3.7473417626\H,1.4970069859,6.
9708951984,2.6336310163\H,2.7555460631,5.7383175668,2.3243159071\H,0.0
619781269,5.2540895906,5.7261660168\H,1.3450742076,6.5020593385,5.7527
225172\H,-0.0731646152,6.7048833206,4.6877107005\H,-4.4494097753,0.885
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