Supporting Information

Chiral 1,2- and 1,3-Diol-functionalised Chromophores as Lego Building Blocks for Coupled Structures

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Characterization data of the diolfunctionalized nitroanilines:

rac.-N-Methyl-N-[1-(2,3-dihydroxypropyl)]-2-nitroaniline (**2**)

orange-red oil (63 %): ^{1}H NMR (DMSO) δ 2.80 (s, 3H), 3.07 (m, 1H), 3.28 (m, 3H), 3.70 ppm (m, 1H), 4.57 (t, J = 5.53 Hz, 1H), 4.70 (d, J = 5.21 Hz, 1H), 6.83 (ddd, J= 8.21 Hz, J = 6.95 Hz, ^{4}J = 1.26 Hz, 1H), 7.27 (dd, J = 8.69 Hz, ^{4}J = 1.26 Hz, 1H), 7.44 (ddd, J = 8.69 Hz, J= 6.95 Hz, ^{4}J = 1.74 Hz, 1H), 7.68 (dd, J = 8.21 Hz, ^{4}J = 1.74 Hz, 1H); ^{13}C NMR (DMSO) δ 41.6, 57.6 ppm, 64.7, 70.2, 118.6, 120.8, 126.8, 134.0, 140.1, 146.3; IR (NaCl) 3391 (s), 3084 (w), 2932 (w), 1605 (vs), 1564 (m), 1444 (s), 1344 (vs) cm^{-1}; Anal. Calcd for $C_{10}H_{14}N_2O_4$ (226.22): C, 53.09; H, 6.24; N, 12.38; Found: C, 52.77; H, 6.22; N, 12.54.

rac.-N-Methyl-N-[1-(2,3-dihydroxypropyl)]-2,4-dinitroaniline (**3**):

orange oil (63 %): ^{1}H NMR (DMSO) δ 2.94 (s, 3H), 3.34 (m, 4H), 3.58 (m, 1H), 3.79 (m, 1H), 4.73 (t, J = 5.84 Hz, 1H), 4.96 (d, J = 5.21 Hz, 1H), 7.40 (d, J = 9.64 Hz, 1H), 8.16 (dd, J = 9.64 Hz, ^{4}J = 2.84 Hz, 1H), 8.53 (d, ^{4}J = 2.84 Hz, 1H); ^{13}C NMR (DMSO) δ 41.5, 57.1, 63.9, 69.5, 119.0, 124.1, 127.5, 135.4 ppm, 135.5, 149.4; IR (NaCl) 3399 (s), 3085 (w), 2933 (w), 1604 (s), 1578 (s), 1463 (vs), 1327 (s) cm^{-1}; Anal. Calcd. for $C_{10}H_{13}N_3O_6$ (271.23): C, 44.28; H, 4.83; N, 15.49; Found: C, 43.68; H, 4.76; N, 15.30.

(R)-N-[1-(2,3-dihydroxypropyl)]-4-nitroaniline (**4**):

yellow solid (63 %): mp 138-141 °C; ε (MeOH, λ_{max} = 385 nm): ε = 2.00*10^{4} l*mol^{-1}*cm^{-1}; ^{1}H NMR (DMSO): δ 3.00 (m, 1H), 3.33 (m, 3H), 3.62 (m, 1H), 4.65 (t, J = 5.37 Hz, 1H), 4.88 (d, J = 5.06 Hz, 1H), 6.66 (d, J = 9.32 Hz, 2H), 7.25(t, J = 5.69 Hz, 1H), 7.96 (d, J = 9.32 Hz, 2H), ^{13}C NMR (DMSO): δ 46.1, 64.0, 70.3, 111.1, 126.5, 135.8, 155.3; IR (KBr), 3424 (s), 3314 (vs), 3105 (w), 2926 (m), 1603 (vs), 1548 (m), 1467 (s), 1335 (vs) cm^{-1}; Anal. Calcd for $C_9H_{12}N_2O_4$ (212.205): C, 50.94, H, 5.70; N, 13.20; Found: C, 50.09; H, 5.76; N, 12.62.

(R)-N-[1-(2,3-dihydroxypropyl)]-2-nitroaniline (**5**):

orange-red solid (61 %): mp 127-129 °C; ^{1}H NMR (DMSO): δ 3.23 (m, 1H), 3.42 (m, 3H), 3.72 (m, 1H), 4.77 (t, J = 5.37 Hz, 1H), 5.13 (d, J = 4.90 Hz, 1H), 6.65 (t, J = 8.53 Hz, 1H), 7.03 (d, J = 8.69 Hz, 1H), 7.51 (t, J = 8.53 Hz, 1H), 8.04 (d, J_{ab} = 8.69 Hz, 1H), 8.28 (t, J = 5.37 Hz, 1H), ^{13}C NMR (DMSO): δ 46.0, 64.1 ppm, 69.7, 115.0, 115.5, 126.5, 131.3 ppm, 136.9, 145.9; IR (KBr), 3366 (s), 3297 (vs), 3177 (vs), 2931 (w), 1629 (vs), 1518 (s), 1421 (s), 1271 (vs) cm^{-1}; Anal. Calcd for $C_9H_{12}N_2O_4$ (212.21): C, 50.94; H, 5.70, N, 13.20, Found: C, 50.43; H, 5.43; N, 13.23,.

(R)-N-[1-(2,3-dihydroxypropyl)]-2,4-dinitroaniline (**6**):

orange-yellow solid (51 %): mp 99-101 °C; ^{1}H NMR (DMSO): δ 3.39 (m, 3H), 3.59 (m, 1H), 3.75 (m, 1H), 4.82 (t, J = 5.53 Hz, 1H), 5.23 (d, J = 5.06 Hz, 1H), 7.23 (d, J = 9.63 Hz, 1 H), 8.24 (dd, J = 9.63 Hz, ^{4}J = 2.69 Hz, 1H), 8.84 (d, ^{4}J = 2.69 Hz, 1H), 8.91 (t, J = 5.21 Hz, 1H), ^{13}C NMR (DMSO):δ 46.5, 63.9, 69.6, 116.0, 123.9, 130.0, 130.3, 135.1, 148.9; IR (KBr) 3375 (s), 3274 (vs), 3091 (w), 2927 (w), 1624 (s), 1589 (s), 1419 (s), 1344 (vs); Anal. Calcd for $C_9H_{11}N_3O_6$ (257.202): C, 42.03; H, 4.31; N, 16.34; Found: C, 41.97; H, 4.05; N, 16.31.

(S)-N-[1-(2,3-dihydroxypropyl)]-4-nitroaniline (**7**):

yellow solid (81 %): mp 131-133 °C, ε (MeOH, λ_{max} = 386 nm): ε = 1.64*10^{4} l*mol^{-1}*cm^{-1}; ^{1}H NMR (DMSO): δ 3.07 (m, 1H), 3.32 (m, 3H), 3.62 (m, 1H), 4.65 (t, J = 5.53 Hz, 1H), 4.88 (d, J = 5.06 Hz, 1H), 6.67 (d, J = 9.32 Hz, 2H), 7.26 (t, J = 5.53 Hz, 1H), 7.96 (d, J = 9.32 Hz, 2H), ^{13}C NMR (DMSO):δ 45.7, 63.6, 69.9, 110.7, 126.1, 135.3, 154.8; IR (KBr): 3428 (s), 3317 (vs), 3108 (w), 2914 (w), 1600 (vs), 1553 (s), 1469 (s), 1309 (vs); Anal. Calcd for $C_9H_{12}N_2O_4$ (212.21): C, 50.95; H, 5.70; N, 13.20; Found: C, 50.83; H, 5.68; N, 13.16.

(S)-N-[1-(2,3-dihydroxypropyl)]-2-nitroaniline (**8**):

orange-red solid (84 %): mp 118-120 °C; ^{1}H NMR (DMSO): δ 3.25 (m, 1H), 3.44 (m, 3H), 3.74 (m, 1H), 4.78 (t, J = 5.37 Hz, 1H), 5.14 (d, J = 4.90 Hz, 1H), 6.68 (t, J_{bc} = 8.53 Hz, 1H), 7.06 (d, J = 8.85 Hz, 1H), 7.53 (t, J = 7,90 Hz, 1H), 8.06 (d, J = 8.53 Hz, 1H), 8.29 (t, J = 5.06 Hz, 1H), ^{13}C NMR (DMSO):δ 45.5, 63.6, 69.3, 114.9, 115.0, 126.1, 130.8, 136.5, 145.4; IR**:** (KBr) 3369 (vs), 3296, 3183 (vs), 3090 (w), 2959 (w), 1629 (s), 1522 (s), 1424 (s), 1355 (vs); Anal. Calcd for $C_9H_{12}N_2O_4$ (212.21): C, 50.95; H, 5.70; N, 13.20, Found: C, 50.10; H, 5.67; N, 12.69.

N-[2-(1,3-dihydroxypropyl)]-4-nitroaniline (**9**):

yellow solid (60 %): mp 116-118 °C; ^{1}H NMR (DMSO): δ 3.50 (m, 5H), 4.75 (t, J = 5.06 Hz, 2H), 6.69 (d, J = 9.48 Hz, 2H), 7.02 (bs, 2H), 7.95 (d, J = 9.48 Hz, 2H), ^{13}C- NMR (DMSO) 56.3, 60.1, 111.0, 126.1, 135.3, 154.6; IR (KBr) 3480 (s), 3396 (vs), 3296 (vs), 3089 (w), 2961 (m), 1606 (vs), 1545 (w), 1478 (s), 1310 (s); Anal. Calcd for $C_9H_{12}N_2O_4$ (212.21): C, 50.95; H, 5.70; N, 13.20; Found: C, 50.50; H, 5.65; N, 12.97.

N-[2-(1,3-dihydroxypropyl)]-2-nitroaniline (**10**):

orange-red solid (83 %): mp 97-99 °C; ^{1}H NMR (DMSO): δ 3.58 (m, 4H), 3.70 (m, 1H), 4.95 (t, J = 5.84 Hz, 1H), 6.65 (ddd, J = 8.69 Hz, J = 8.53 Hz, ^{4}J = 1.10 Hz, 1H), 7.13 (d, J = 8.06 Hz, 1H), 7.50 (ddd, J = 8.53 Hz, J = 8.06 Hz, ^{4}J = 1.58 Hz, 1H), 8.04 (dd, J_{ab} = 8.53 Hz, ^{4}J = 1.58 Hz, 1H), 8.31 (d, J = 7.74 Hz, 1H), ^{13}C NMR (DMSO):δ 55.1, 59.5, 114.9, 115.0, 126.2, 130.8 ppm, 136.4, 145.1; IR (KBr) 3433 (s), 3365 (vs), 3097 (w), 2934 (m), 1622 (vs), 1560 (w), 1420 (s), 1353 (s); Anal. Calcd for $C_9H_{12}N_2O_4$ (212.21): C, 50.95; H, 5.70; N, 13.20; Found: C, 49,74; H, 5.56; N, 12.66.

N-[2-(1,3-dihydroxypropyl)]-4-nitroaniline (**11**):

orange solid (89 %): mp 127-129 °C; ^{1}H NMR (DMSO): δ 3.62 (m, 4H), 3.92 (m, 1H), 5.10 (t, J = 5.06 Hz, 2H), 7.33 (d, J = 9.63Hz, 1H), 8.25 (dd, J = 9.63 Hz, ^{4}J = 2.69 H, 1H z), 8.85 (d, ^{4}J = 2.69 Hz, 1H), 8.90 (bs, 1H) ^{13}C NMR (DMSO): δ 55.9, 59.6, 116.0, 123.5, 129.5,

129.7, 134.7, 148.4; IR (KBr) 3501 (vs), 3438 (vs), 3334 (s), 3100 (w), 2958 (w), 1617 (s), 1575 (s), 1419 (s), 1341 (vs); Anal. Calcd for $C_9H_{11}N_3O_6$ (257.20): C, 42.03; H, 4.31; N, 16.34; Found: C, 41.76; H, 4.22; N, 16.20.

Characterization data of the boronate esters

rac.-N-Methyl-N-[1-propyl-(1`,3,2-dioxaborolan)- phenyl]-4-nitroaniline (**12**):

yellow solid (75 %): mp 134-136 °C; ^{1}H NMR ($CDCl_3$): δ 3.23 (s, 3H), 3.67 (m, 2H), 4.07 (dd, 1H), 4.50 (dd, 1H), 4.88 (m, 1H), 6.71 (d, J = 9.48 Hz, 2H), 7.39 (dd, J = 8.06 Hz, J = 7.24 Hz, 2H), 7.50 (dd, J = 7.24 Hz, ^{4}J = 1.42 Hz, 1H), 7.78 (dd, J = 8.06 Hz, J = 1.42 Hz, 2H), 8.13 (d, J = 9.48 Hz, 2H); ^{13}C CP MAS NMR (400 MHz): 36.3, 55.4, 69.5, 74.7, 110.2, 128.1, 131.9, 135.7, 155.1; IR (KBr) 3064 (w), 2901 (w), 1596 (vs), 1524 (s), 1474 (vs), 1367 (vs) cm^{-1}; Anal. Calcd for $C_{16}H_{17}BN_2O_4$ (312.13): C, 61.57; H, 5.49; N, 8.98; Found: C, 61.96; H, 5.53; N, 8.80.

rac.-N-Methyl-N-[1-propyl-(1`,3,2-dioxaborolan)-4`-bromphenyl]-4-nitroaniline (**14**):

yellow solid (75 %): mp 143-145 °C; ^{1}H NMR ($CDCl_3$): δ 3.23 (s, 3H), 3.67 (m, 2H), 4.07 (dd, 1H), 4.50 (dd, 1H), 4.88 (m, 1H), 6.71 (d, J = 9.49 Hz, 2H), 7.50 (d, J = 8.37 Hz, 2H), 7.62 (d, J_{gh} = 8.37 Hz, 2H), 8.13 (d, J_{ab} = 9.49 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 40.1, 56.6, 68.8, 75.8, 110.6, 120.4, 126.3, 128. 8, 131.2, 134.0, 136.3, 153.4 ppm; IR**:** (KBr) 3034 (w), 2917 (w), 1600 (vs), 1522 (s), 1483 (vs), 1333 (vs) cm^{-1}; Anal. Calcd for $C_{16}H_{16}BBrN_2O_4$ (391.03): C, 49.15; H, 4.12; N, 7.16; Found: C, 49.22; H, 4.19; N, 6.98.

rac.-N-Methyl-N-[1-propyl-(1`,3,2-dioxaborolan)-4`-formylphenyl]-4-nitroaniline (**15**):

yellow solid (71 %): mp 153 °C; ^{1}H NMR ($CDCl_3$): δ 3.24 (s, 3H), 3.72 (m, 2H), 4.11 (dd, 1H), 4.55 (dd, 1H), 4.92 (m, 1H), 6.71 (d, J = 9.48 Hz, 2H), 7.88 (d, J = 8.21 Hz, 2H), 7.94 (d, J = 8.21 Hz, 2H), 8.13 (d, J_{ab} = 9.49 Hz, 2H), 10.06 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 40.1, 56.5, 68.9, 76.0, 110.6, 126.3, 128.8, 135.3, 137.7, 153.4, 192.4; IR (KBr): 3039 (w), 2911 (w),

1695 (vs), 1595 (s), 1506 (vs), 1478 (s), 1372 (s), 1316 (vs) cm^{-1}; Anal. Calcd. for $C_{16}H_{16}BN_2O_4$ (311.13): C, 60.03; H, 5.04; N, 8.24, Found: C, 60.55; H, 5.11; N, 8.25.

rac.-N-Methyl-N-[1-propyl-(1`,3,2-dioxaborolan)-3`-nitrophenyl]-4-nitroaniline (**16**): yellow solid (75 %): mp 155 °C; ^1H NMR ($CDCl_3$): δ 3.24 (s, 3H), 3.73 (m, 2H), 4.13 (dd, 1H), 4.57 (dd, 1H), 4.94 (m, 1H), 6.71 (d, J = 9.48 Hz, 2H), 7.57 (dd, J = 8.21 Hz, J = 7.27 Hz, 1H) 8.08 (dd, J = 7.27 Hz, ^4J = 1.26 Hz, 1H), 8.13 (d, J = 9.48 Hz, 2H), 8.33 (ddd, J = 8.21 Hz, ^4J = 2.53 Hz, ^4J = 1.26 Hz, 1H), 8.60 (d, ^4J = 2.53 Hz, 1H); ^{13}C NMR ($CDCl_3$): 40.6, 56.9, 69.4, 76.7, 111.0, 126.6, 126.8, 129.5, 129.9, 134.6, 138.1, 141.1, 153.8; IR (KBr): 3083 (w), 2922 (w), 1597 (s), 1522 (vs), 1488 (s), 1350 (s), 1292 (vs) cm^{-1}; Anal. Calcd for $C_{16}H_{16}BN_3O_6$ (357.13): C, 53.81; H, 4.52; N, 11.77; Found: C, 53.95; H, 4.53; N, 11.69.

rac.1,4-Phenyl-[bis-1,3`,2`-dioxaborolan-(N-methyl-N-(1`-propyl)-4`-nitroaniline)] (**17**): yellow solid (82 %): mp 254-256 °C; ^1H NMR ($CDCl_3$): δ 3.23 (s, 6H), 3.67 (m, 4H), 4.09 (dd, 2H), 4.52 (dd, 2H), 4.90 (m, 2H), 6.71(d, J = 9.32 Hz, 4H), 7.78 (s, 4H), 8.13 (d, J = 9.32 Hz, 4H); ^{13}C CP MAS NMR (400 MHz): δ 42.2, 55.4, 66.4 ppm, 74.6 ppm, 108.1, 111.2, 125.3, 128.6, 136.0, 152.0; IR (KBr) 3095 (w), 2949 (w), 1600 (s), 1522 (m), 1487 (m), 1355 (s), 1326 (w) cm^{-1}; Anal. Calcd for $C_{26}H_{28}B_2N_4O_8$ (546.15): C, 57.18; H, 10.26; N, 5.17; Found: C, 56.67; H, 10.03; N, 5.12.

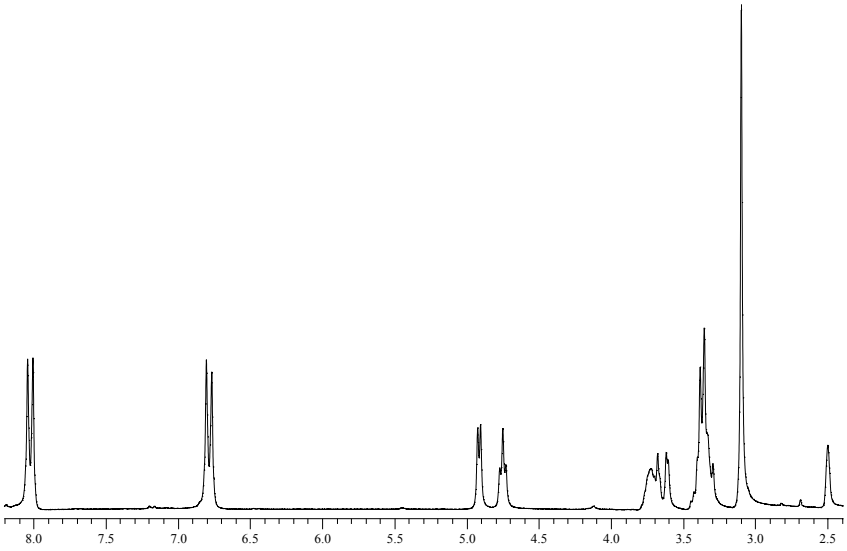

Figure S1: ^{1}H NMR of **1**.

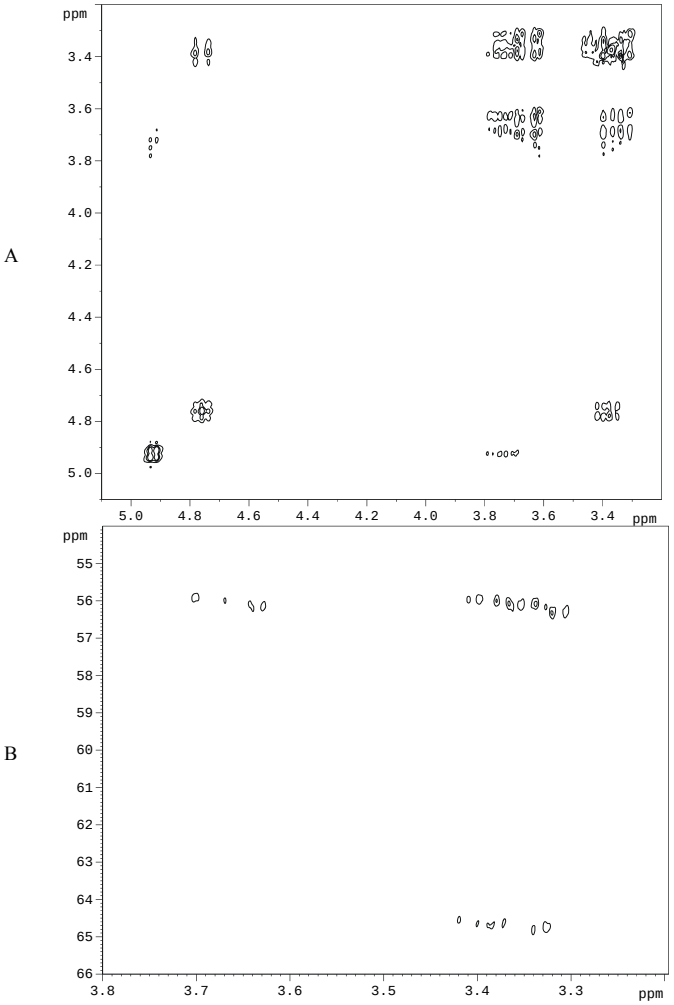

Figure S2: (A) H,H- and (B) C,H COSY NMR of **1**.

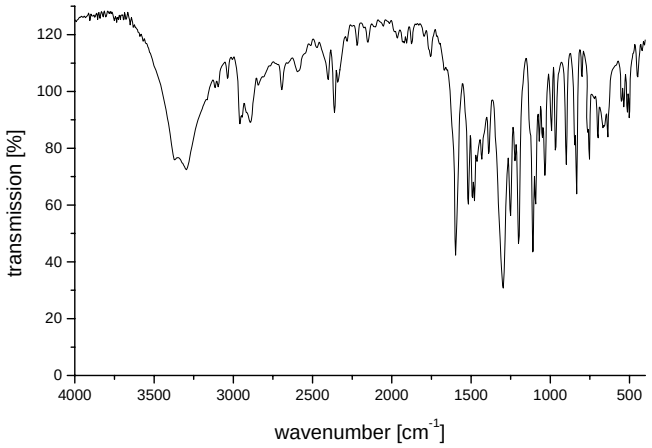

Figure S3: IR spectra of **1**.

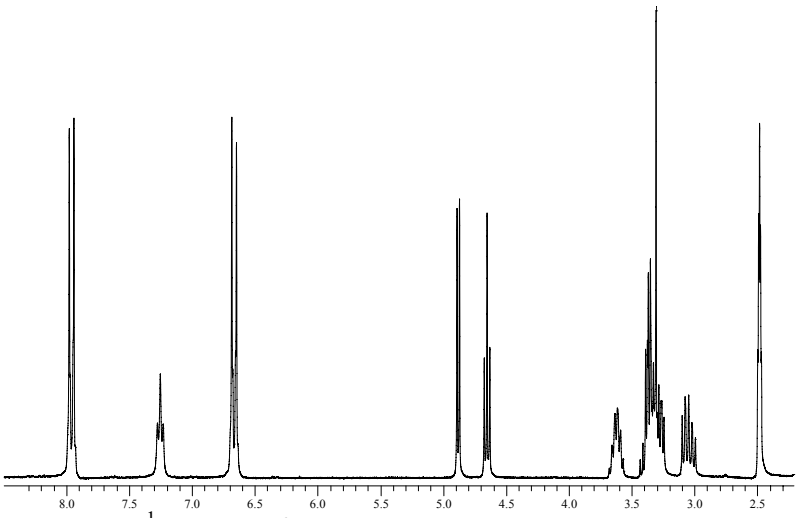

Figure S4: ^{1}H NMR of **4**.

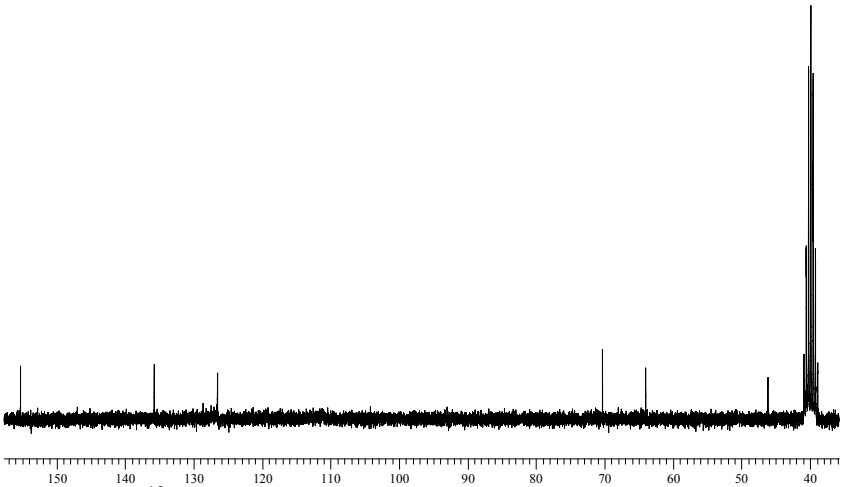

Figure S5: ^{13}C NMR of **4**.

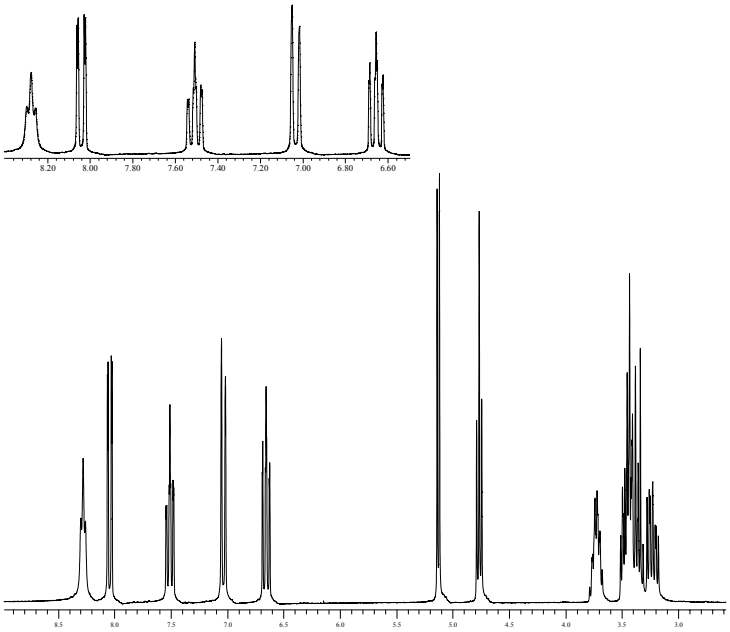

Figure S6: ^{1}H-NMR of compound **5**.

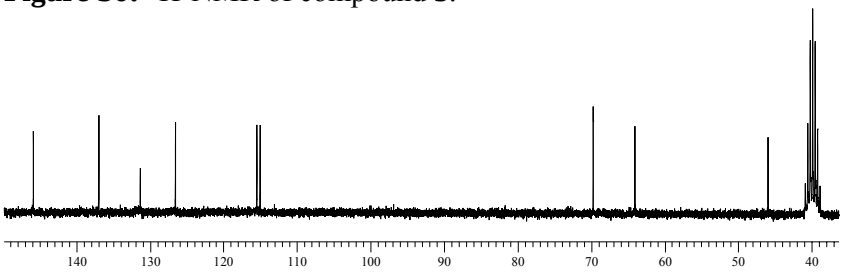

Figure S7: ^{13}C NMR of compound **5**.

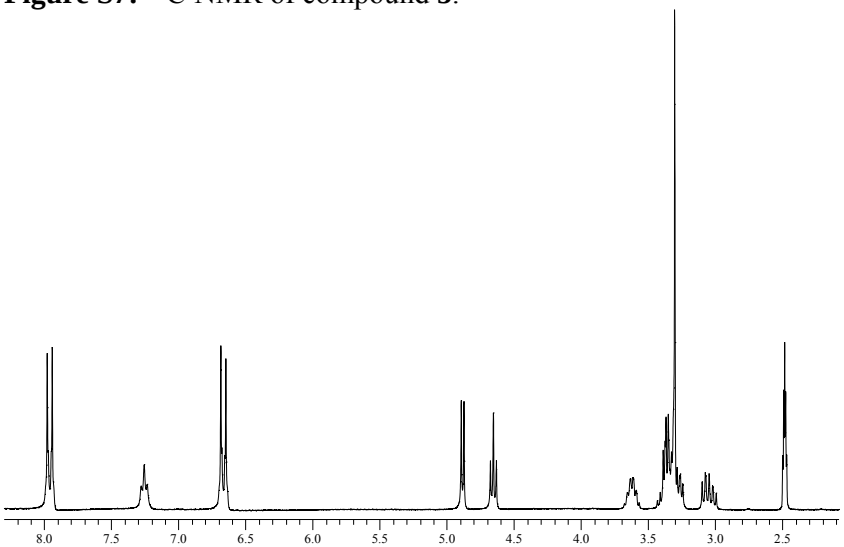

Figure S8: ^{1}H NMR of **7**.

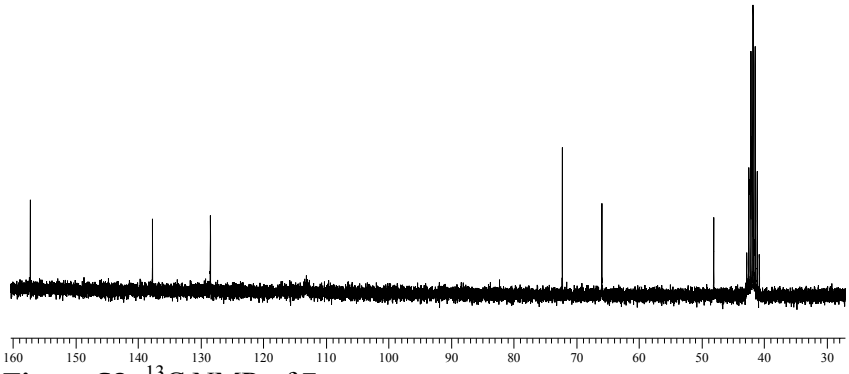

Figure S8: ^{13}C NMR of **7.**

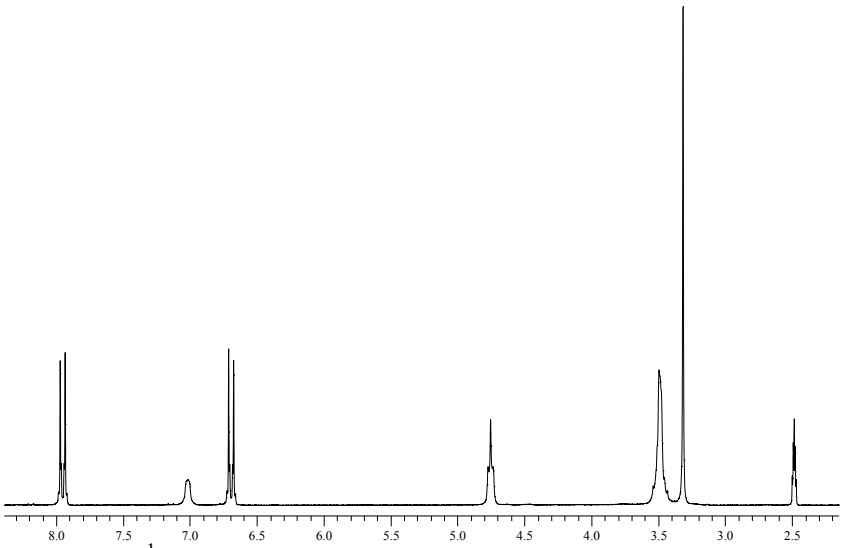

Figure S9: ^{1}H NMR of **9**.

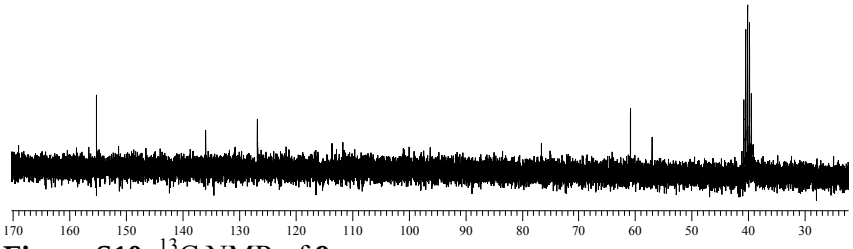

Figure S10: ^{13}C NMR of **9**.

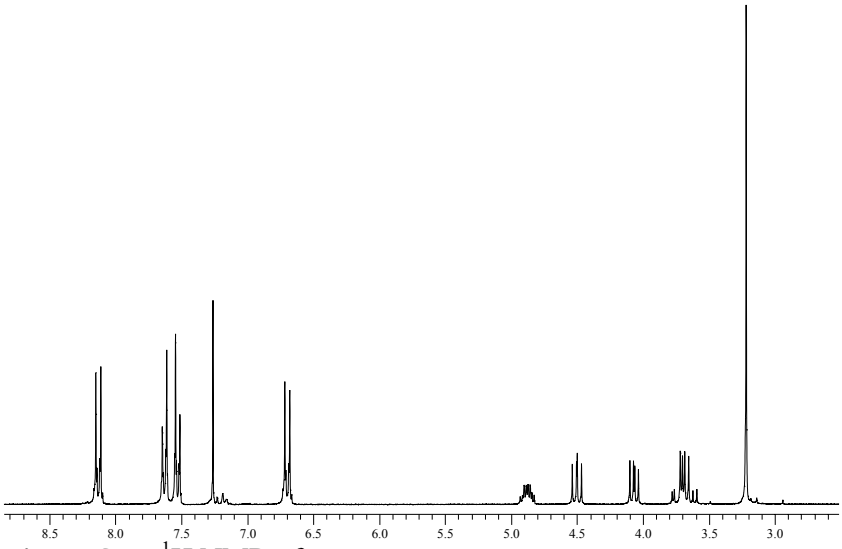

Figure S11: ^{1}H NMR of **15**.

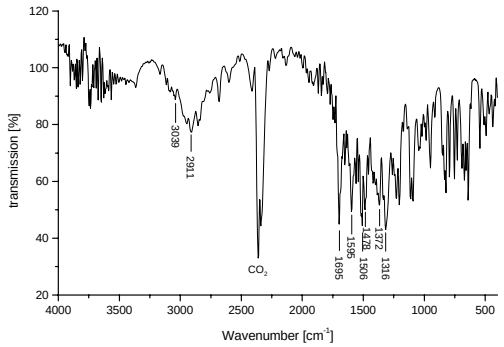

Figure S12: IR spectra of **15**.

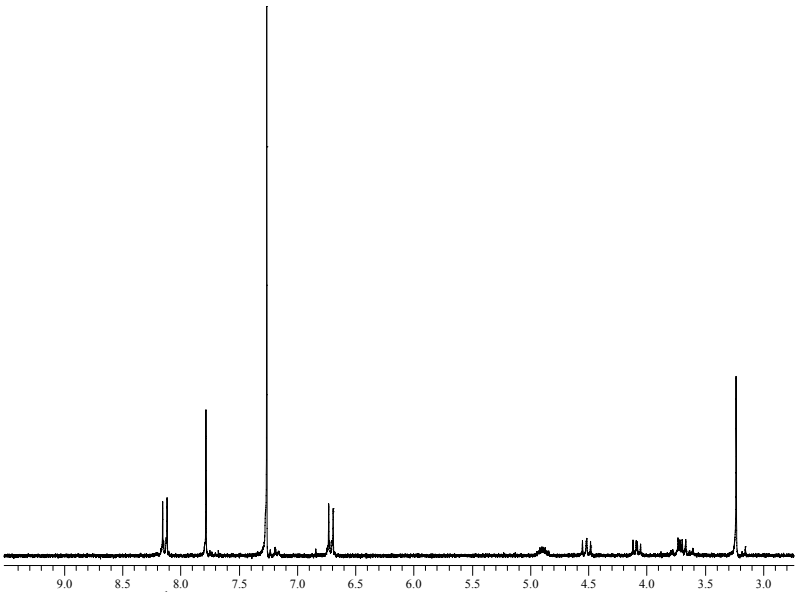

Figure S13: ^{1}H NMR of **17**.

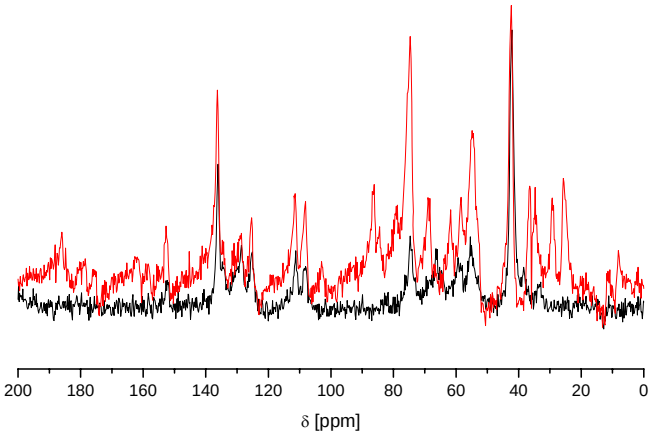

Figure S14: ^{13}C CP MAS NMR (5 kHz (–) and 7 kHz(–) of **17**.

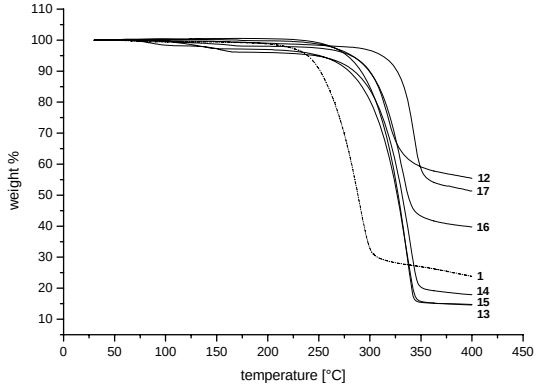

Figure S15: Thermogravimetric analysis of the esters **12-17** compared to compound **1.**

TABLE S3: UV/Vis absorption maxima ($\tilde{\nu}_{max}$) of solvatochromic compounds **1, 4, 7, 9** und **12-17**, measured in 27 solvents and the empirical *Kamlet-Taft* parameter[1] of the respective solvents.

solvents	α	β	π*	$\tilde{\nu}_{max}/10^{-3}$ cm^{-1}									
				1	**4**	**7**	**9**	**12**	**13**	**14**	**15**	**16**	**17**
diethyl ether	0	0.47	0.27	26.6	27.3	27.0	27.3	27.0	27.0	27.2	27.0	27.0	27.3
tetrahydrofuran	0	0.55	0.58	25.6	26.4	25.7	26.3	25.9	26.0	26.0	26.1	25.7	26.0
acetone	0.08	0.43	0.71	25.3	26.0	25.3	25.9	25.6	25.6	25.4	25.4	25.3	25.4
ethyl acetate	0	0.45	0.55	25.8	26.7	26.7	26.7	26.3	26.2	26.2	26.3	26.0	26.2
dimethylformamide	0	0.69	0.88	24.6	25.3	24.7	25.2	24.8	24.9	24.7	24.6	24.7	24.6
formamide	0.71	0.48	0.97	24.2	24.8	24.0	24.8	24.1	24.0	24.1	24.0	24.0	24.1
triethylamine	0	0.71	0.14	26.6	27.3	26.7	27.5	26.7	26.6	26.7	26.7	26.7	26.7
dimethyl sulfoxide	0	0.76	1.00	24.2	24.8	24.3	24.7	24.4	24.6	24.3	24.4	24.3	24.6
pyridine	0	0.64	0.87	24.8	25.3	24.8	25.4	24.8	25.0	24.8	24.8	24.8	24.9
acetonitrile	0.19	0.40	0.75	25.2	26.0	25.3	25.9	25.4	25.4	25.4	25.4	25.3	25.4
benzene	0	0.10	0.59	26.3	27.3	26.7	27.3	26.5	26.5	26.7	26.7	26.7	26.5
toluene	0	0.11	0.54	26.5	27.6	26.9	27.5	26.7	26.7	26.9	26.9	26.9	26.7
p-xylole	0	0.12	0.43	26.6	27.6	27.0	27.7	26.9	26.8	27.0	27.0	27.0	26.9
anisole	0	0.32	0.73	25.6	26.8	25.9	26.9	25.8	25.7	25.8	25.8	25.9	25.8
dichloromethane	0.13	0.10	0.82	25.6	26.9	25.8	26.9	25.7	25.6	25.8	25.8	25.8	25.7
1,2-dichloroethane	0	0.10	0.81	25.5	26.8	25.8	26.7	25.6	25.6	25.7	25.7	25.8	25.6
chloroform	0.20	0.10	0.58	25.7	27.0	26.0	27.0	25.8	25.8	25.9	26.0	25.8	25.8
tetra[1)]	0	0.05	0.28	-[5)]	-[5)]	-[5)]	-[5)]	27.5	27.4	27.4	27.6	27.7	-[5)]
TCE[2)]	0	0	0.95	25.4	26.6	25.5	26.5	25.4	26.0	25.5	25.5	25.5	25.4
TFE[3)]	1.51	0	0.73	24.6	25.7	24.7	25.9	24.7	24.7	24.7	24.7	24.7	24.7
HFI[4)]	1.96	0	0.65	24.4	25.5	24.3	25.8	24.3	24.1	24.2	24.3	24.3	24.8
methanol	0.98	0.66	0.60	25.4	26.0	25.5	25.8	25.4	25.4	25.4	25.4	25.5	25.5
ethanol	0.86	0.75	0.54	25.5	26.0	25.4	26.0	25.4	25.5	25.5	25.5	25.4	25.6
2-propanol	0.76	0.84	0.48	25.4	26.0	25.4	26.0	25.6	25.7	25.4	25.4	25.4	25.5
1-butanol	0.84	0.84	0.47	25.5	26.0	25.6	26.0	25.5	25.5	25.4	25.4	25.6	25.4
1,2-ethandiol	0.90	0.52	0.92	24.6	25.4	25.2	25.3	24.5	24.5	24.5	24.5	24.6	24.5
water	1.17	0.47	1.09	23.9	24.8	23.9	24.8	23.9	23.9	23.9	23.9	23.9	-[5)]

1) = tetrachloromethane, [2)] = 1,1,2,2,-tetrachloroethane, [3)] = 2,2,2-trifluoroethanol, [4)] = 1,1,1,3,3,3-hexafluoro-2-propanol, [5)] substance is unsoluble.

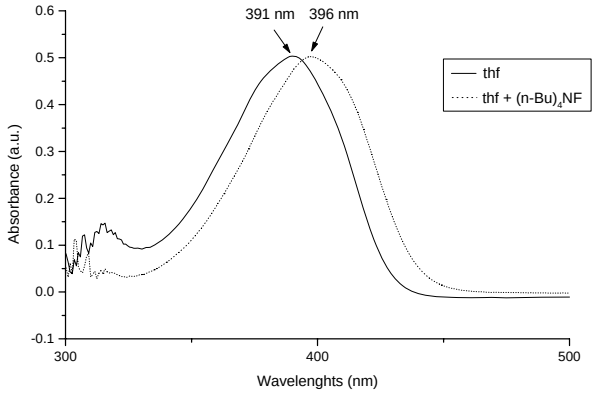

Figure S16: UV/Vis absorption s reference spectrum of compound **1** on addition of fluoride.

X-ray crystal structure analysis.

Crystal data was collected on a Bruker Smart CCD 1 k diffractometer (Mo-Kα-radiation λ = 71.073 pm) at low temperature (-70 °C) using oil-coated shock-cooled crystal [2]. The structure was solved by direct methods using SHELXS-97 [3]. The structure was refined by full-matrix least squares procedures on F^2, using SHELXL-97 [4]. All non hydrogen atoms were refined anisotropically. All hydrogen atom positions were taken from the difference Fourier map and refined freely.

Supplementary Material for the X-Ray-structure of 5:

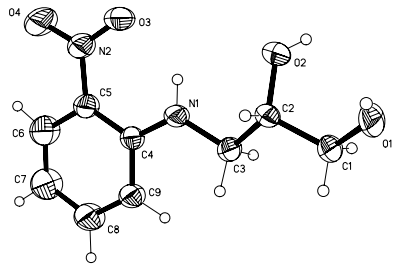

Figure S15: ORTEP drawing of compound **5**.

Table S2. Crystal data and structure refinement for 5.

Identification code 1

Empirical formula	C9 H12 N2 O4	
Formula weight	212.21	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	I222	
Unit cell dimensions	a = 6.8961(4) Å	α= 90°.
	b = 14.1021(8) Å	β= 90°.
	c = 20.3417(14) Å	γ = 90°.
Volume	1978.2(2) $Å^3$	
Z	8	
Density (calculated)	1.425 Mg/m^3	
Absorption coefficient	0.113 mm^{-1}	
F(000)	896	
Crystal size	0.4 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.89 to 26.48°.	
Index ranges	-8<=h<=8, 0<=k<=17, 0<=l<=25	
Reflections collected	15558	
Independent reflections	2055 [R(int) = 0.0356]	
Completeness to theta = 26.48°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00000 and 0.93263	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2049 / 2 / 185	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0934	
R indices (all data)	R1 = 0.0490, wR2 = 0.0989	
Absolute structure parameter	0.1(14)	
Largest diff. peak and hole	0.165 and -0.216 $e.Å^{-3}$	

Table S3. Bond lengths [Å] and angles [°] for **5.**

O(1)-H(1)	0.846(10)
O(1)-C(1)	1.424(2)
O(1)-H(1)	0.846(10)
C(1)-C(2)	1.507(2)
C(1)-H(2)	0.98(3)
C(1)-H(3)	0.91(2)
C(2)-O(2)	1.434(2)
C(2)-C(3)	1.517(2)
C(2)-H(4)	0.985(18)
O(2)-H(5)	0.850(10)

O(2)-H(5)	0.850(10)
C(3)-N(1)	1.449(2)
C(3)-H(6)	0.97(2)
C(3)-H(7)	1.02(2)
N(1)-C(4)	1.351(2)
N(1)-H(8)	0.83(2)
C(4)-C(5)	1.406(2)
C(4)-C(9)	1.414(2)
C(5)-C(6)	1.399(2)
C(5)-N(2)	1.436(3)
C(6)-C(7)	1.350(3)
C(6)-H(9)	0.98(3)
C(7)-C(8)	1.393(3)
C(7)-H(10)	1.00(3)
C(8)-C(9)	1.369(3)
C(8)-H(11)	1.01(3)
C(9)-H(12)	0.96(2)
N(2)-O(4)	1.224(2)
N(2)-O(3)	1.236(2)

H(1)-O(1)-C(1)	134(6)
H(1)-O(1)-H(1)	0(10)
C(1)-O(1)-H(1)	134(6)
O(1)-C(1)-C(2)	111.58(15)
O(1)-C(1)-H(2)	109.2(15)
C(2)-C(1)-H(2)	111.4(14)
O(1)-C(1)-H(3)	110.5(14)
C(2)-C(1)-H(3)	109.2(13)
H(2)-C(1)-H(3)	105(2)
O(2)-C(2)-C(1)	111.03(14)
O(2)-C(2)-C(3)	109.75(15)
C(1)-C(2)-C(3)	110.09(14)
O(2)-C(2)-H(4)	109.6(10)
C(1)-C(2)-H(4)	107.7(10)
C(3)-C(2)-H(4)	108.6(10)
H(5)-O(2)-C(2)	129(10)
H(5)-O(2)-H(5)	0(10)
C(2)-O(2)-H(5)	129(10)
N(1)-C(3)-C(2)	109.33(15)
N(1)-C(3)-H(6)	112.7(12)
C(2)-C(3)-H(6)	109.1(12)

N(1)-C(3)-H(7)	111.6(12)
C(2)-C(3)-H(7)	107.7(12)
H(6)-C(3)-H(7)	106.2(18)
C(4)-N(1)-C(3)	123.91(14)
C(4)-N(1)-H(8)	116.9(12)
C(3)-N(1)-H(8)	118.0(12)
N(1)-C(4)-C(5)	123.52(15)
N(1)-C(4)-C(9)	120.28(15)
C(5)-C(4)-C(9)	116.20(14)
C(6)-C(5)-C(4)	121.39(17)
C(6)-C(5)-N(2)	116.59(16)
C(4)-C(5)-N(2)	122.02(14)
C(7)-C(6)-C(5)	120.66(19)
C(7)-C(6)-H(9)	122.4(14)
C(5)-C(6)-H(9)	116.8(14)
C(6)-C(7)-C(8)	119.47(18)
C(6)-C(7)-H(10)	123.6(15)
C(8)-C(7)-H(10)	117.0(15)
C(9)-C(8)-C(7)	120.9(2)
C(9)-C(8)-H(11)	115.7(15)
C(7)-C(8)-H(11)	123.2(15)
C(8)-C(9)-C(4)	121.32(18)
C(8)-C(9)-H(12)	122.4(12)
C(4)-C(9)-H(12)	116.3(12)
O(4)-N(2)-O(3)	121.50(16)
O(4)-N(2)-C(5)	118.94(15)
O(3)-N(2)-C(5)	119.56(14)

Table S4. Torsion angles [°] for 5.

H(1)-O(1)-C(1)-C(2)	40(8)
O(1)-C(1)-C(2)-O(2)	63.6(2)
O(1)-C(1)-C(2)-C(3)	-174.67(18)
C(1)-C(2)-O(2)-H(5)	25(8)
C(3)-C(2)-O(2)-H(5)	-97(8)
O(2)-C(2)-C(3)-N(1)	-52.4(2)
C(1)-C(2)-C(3)-N(1)	-174.90(17)
C(2)-C(3)-N(1)-C(4)	-164.47(19)
C(3)-N(1)-C(4)-C(5)	-175.4(2)
C(3)-N(1)-C(4)-C(9)	4.8(3)
N(1)-C(4)-C(5)-C(6)	-178.1(2)

C(9)-C(4)-C(5)-C(6)	1.7(3)
N(1)-C(4)-C(5)-N(2)	1.6(3)
C(9)-C(4)-C(5)-N(2)	-178.6(2)
C(4)-C(5)-C(6)-C(7)	-0.5(4)
N(2)-C(5)-C(6)-C(7)	179.8(3)
C(5)-C(6)-C(7)-C(8)	-0.3(5)
C(6)-C(7)-C(8)-C(9)	-0.2(5)
C(7)-C(8)-C(9)-C(4)	1.5(4)
N(1)-C(4)-C(9)-C(8)	177.7(2)
C(5)-C(4)-C(9)-C(8)	-2.2(3)
C(6)-C(5)-N(2)-O(4)	1.0(3)
C(4)-C(5)-N(2)-O(4)	-178.8(2)
C(6)-C(5)-N(2)-O(3)	-178.6(2)
C(4)-C(5)-N(2)-O(3)	1.7(3)

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