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Electronic Supplementary Information

Lanthanide Derivatives Comprising Arylhydrazones of β-Diketones: Cooperative *E/Z* Isomerization and Catalytic Activity in Nitroaldol Reaction

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1. Synthesis and analytical data for compounds $KH_2L^{1,2}$

Synthesis of $KH_2L^{1,2}$

$KH_2L^{1,2}$ were synthesized according to the Japp−Klingemann reaction[4] between the diazonium salt of substituted aniline and acetylacetone (or benzoylacetone in the case of KH_2L^2).

Diazotization: 0.0250 mol 2-amino-4-chloro-6-sulfophenol-1 (in the case of H_3L^2) was dissolved in 50.00 mL water upon addition of 1.500 g of crystalline KOH. The solution was cooled in an ice bath to 0 °C, and 0.025 mol $NaNO_2$ was added with subsequent addition of 5.00 mL HCl in portions of 0.20 mL for 1 h, under vigorous stirring. During the reaction the temperature of the mixture must not exceed +5 °C.

Azocoupling: For the preparation of compound KH_2L^2, 8.000 g CH_3COONa were added to a mixture of 0.0250 mol benzoylacetone with 100.0 mL ethanol. The mixture was cooled in an ice bath, and a suspension of 2-amino-4-chloro-6-sulfophenol-1 diazonium (prepared according to the procedure of section 2.2.1) was added in two equal portions under vigorous stirring for 1 h. On the next day, the formed precipitate of KH_2L^2 was filtered off and recrystallized from methanol. The syntheses of KH_2L^1 was performed analogously, but using 2-amino-4-nitro-6-sulfophenol-1 as a strarting material instead of 2-amino-4-chloro-6-sulfophenol-1, and acetylacetone instead of benzoylacetone.

KH_2L^1: Yield 81 % (based on pentane-2,4-dione), dark orange powder, soluble in water, DMSO, dimethylformamide, ethanol, acetone and insoluble in chloroform. Calcd for $C_{11}H_{10}KN_3O_8S$ (M = 383.38): C, 34.46; H, 2.63; N, 10.96. Found: C, 34.15; H, 2.37; N, 11.02 %. IR (KBr), cm^{-1}: 3450 (m br.) ν(OH), 3145 (m br.) ν(NH), 1656 (s) ν(C=O), 1640 (w) ν(C=O···H), 1594 (w) ν(C=N), 1561 (w), 1505 (s), 1445 (w), 1413 (w), 1367 (m), 1312 (m), 1276 (s), 1197 (s), 1073 (m), 1042 (s), 979 (w), 932 (w), 891 (w), 783 (w), 750 (w) cm^{-1}. ^1H NMR (DMSO-d_6): $\delta = 2.38$ (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 8.15−8.28 (2H, Ar−H), 9.87 (s, 1H, OH), 14.52 (s, 1H, NH). $^{13}C\{^1H\}$ (DMSO-d_6): δ = 26.43 (CH_3), 31.26 (CH_3), 124.71 (Ar−H), 127.45 (Ar−H), 128.98 (Ar−NO_2), 133.38 (Ar−NH−N), 134.45 (C=N), 140.75 (Ar−SO_3K), 146.34 (Ar−OH), 195.53 (C=O), 196.21 (C=O).

KH_2L^2: yield, 77 % (based on benzoylacetone), yellow powder, soluble in water, methanol, ethanol, and insoluble in chloroform. Anal. Calcd for $C_{16}H_{12}ClKN_2O_6S$ (M = 434.89): C, 44.19; H, 2.78; N, 6.44. Found: C, 44.05; H, 2.65; N, 6.28 %. IR (KBr), cm^{-1}: 3480 (m br.) ν(OH), 3267 (m br.) ν(NH), 1649 (s) ν(C=O), 1596 (w) ν(C=N), 1510 (s), 1448 (w), 1362 (w), 1327 (m), 1192 (b.m), 1128 (m), 1044 (s), 983 (w), 950 (w), 876 (m), 854 (m), 729 (m). ^1H NMR of a mixture of *E*-hydrazone and *Z*-hydrazone isomers, (300.13 MHz, DMSO-d_6). *E*-hydrazone, δ: 2.53 CH_3, 7.02−7.87 (5H, C_6H_5 and 2H, C_6H_4), 11.19 (s, 1H, HO–Ar), 14.23 (s, 1H, NH). *Z*-hydrazone, δ: 2.54 CH_3, 7.02−7.87 (5H, C_6H_5 and 2H, C_6H_4), 11.19 (s, 1H, HO–Ar), 11.95 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (100.61 MHz, DMSO-d_6). *E*-hydrazone, δ: 30.3 (CH_3), 114.8 (Ar−H), 121.7 (Ar−H), 123.2 (2Ar−H), 130.2 (Ar−Cl), 128.6 (2Ar−H), 131.3 (ArNH−N), 132.6 (Ar−SO_3K), 133.9 (Ar−H), 137.5 (Ar−CO), 138.1 (C=N), 140.9 (Ar−OH), 191.7 (ArC=O), 197.6 (CH_3C=O). *Z*-hydrazone, δ: 25.6 (CH_3), 114.8 (Ar−H), 121.0 (Ar−H), 123.2 (2Ar−H), 127.9 (Ar−Cl), 128.4 (2Ar−H), 131,2 (ArNH−N), 132.3 (Ar−SO_3K), 133.2 (Ar−H), 137.2 (Ar−CO), 138.1 (C=N), 141.2 (Ar−OH), 192.8 (ArC=O), 196.3 (CH_3C=O).

2. ^{1}H NMR spectra of compounds KH_2L^2, 1 and 2

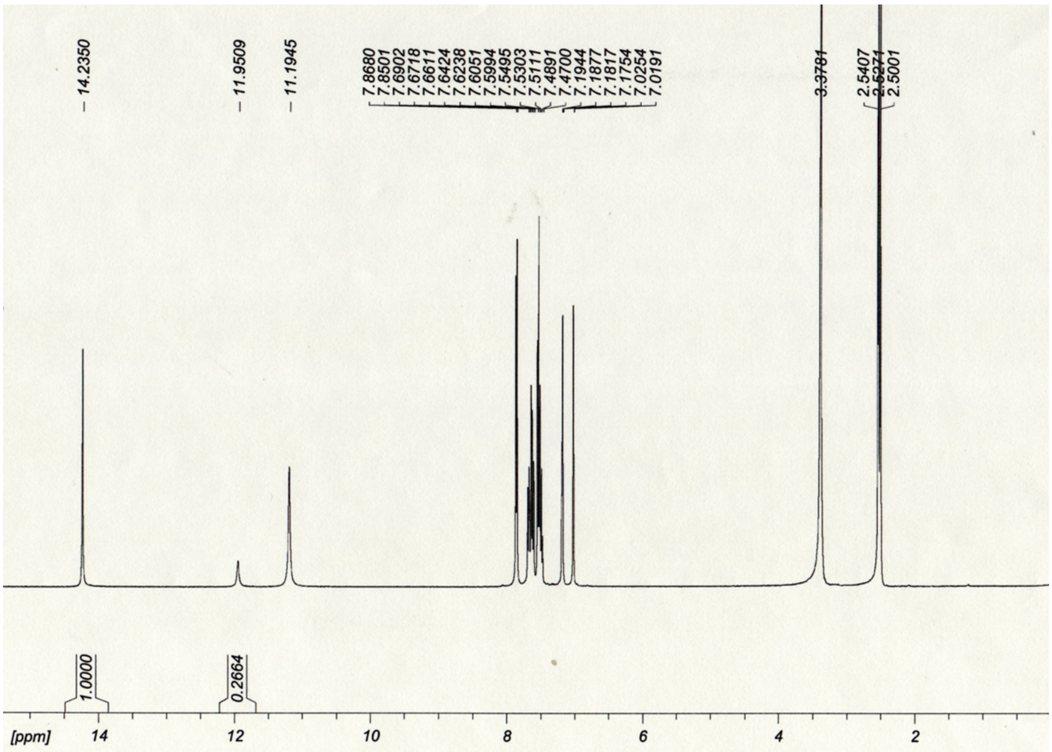

Fig. S1. ^{1}H NMR spectrum of KH_2L^2 in DMSO-d_6.

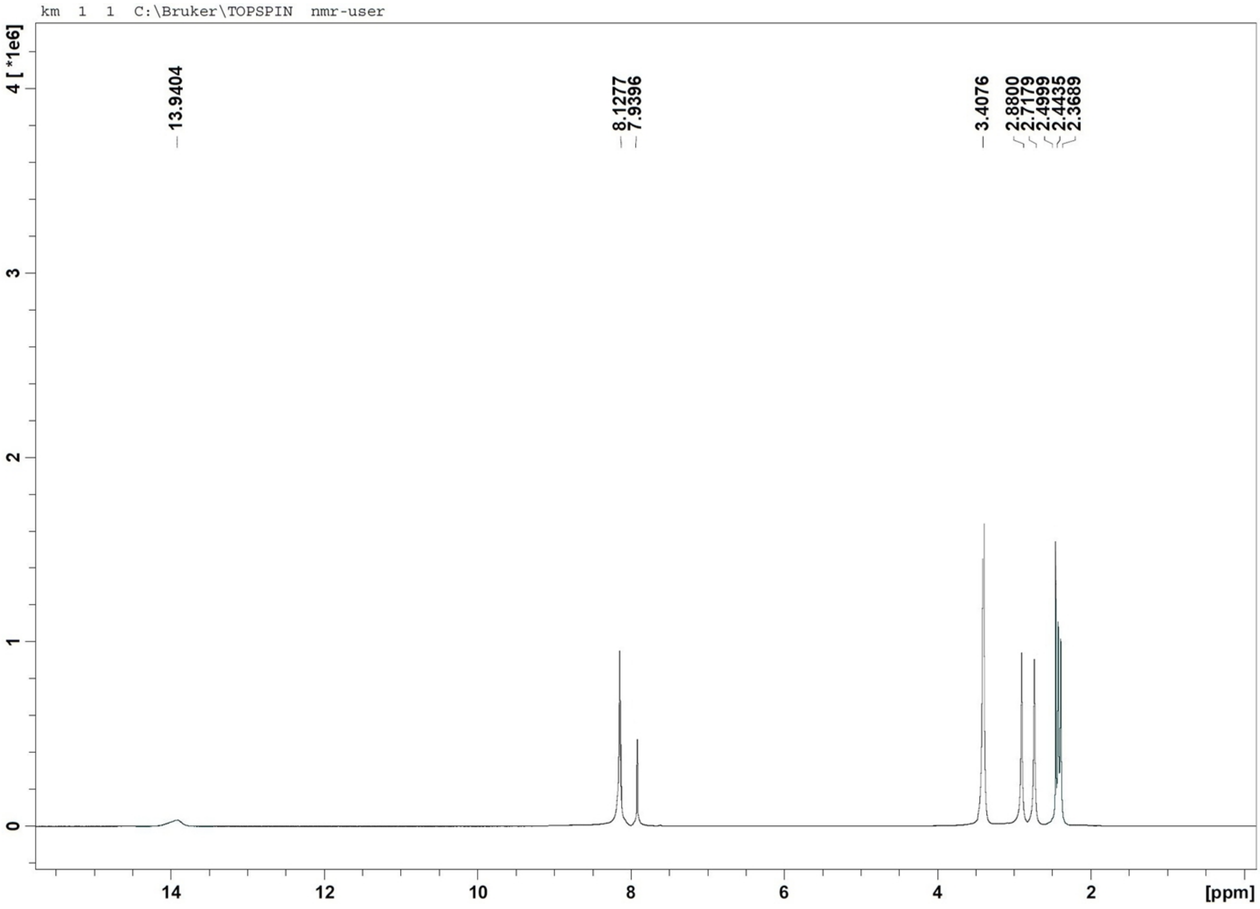

Fig. S2. ^{1}H NMR spectrum of $[KLa(HL^1)_2\{(CH_3)_2NCHO\}_2(H_2O)_3]$ (**1**) in DMSO-d_6.

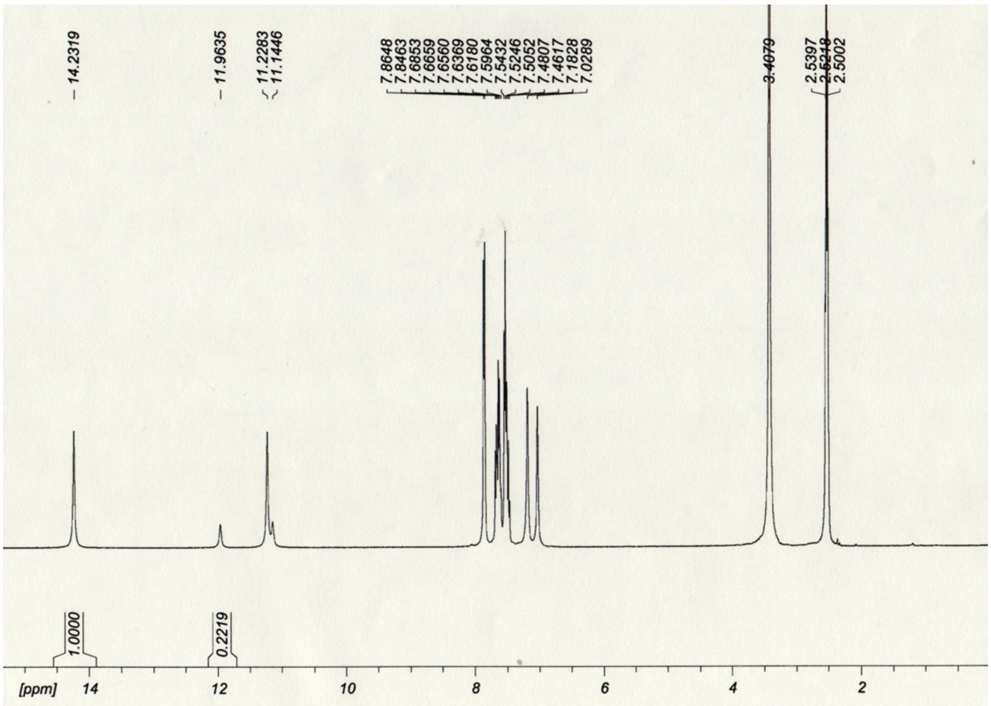

Fig. S3. ^{1}H NMR spectrum of $[Sm(H_2O)_9](H_2L^2)_3 \cdot 2H_2O$ (**2**) in DMSO-d_6.

3. X-ray data of compounds 1 and 2

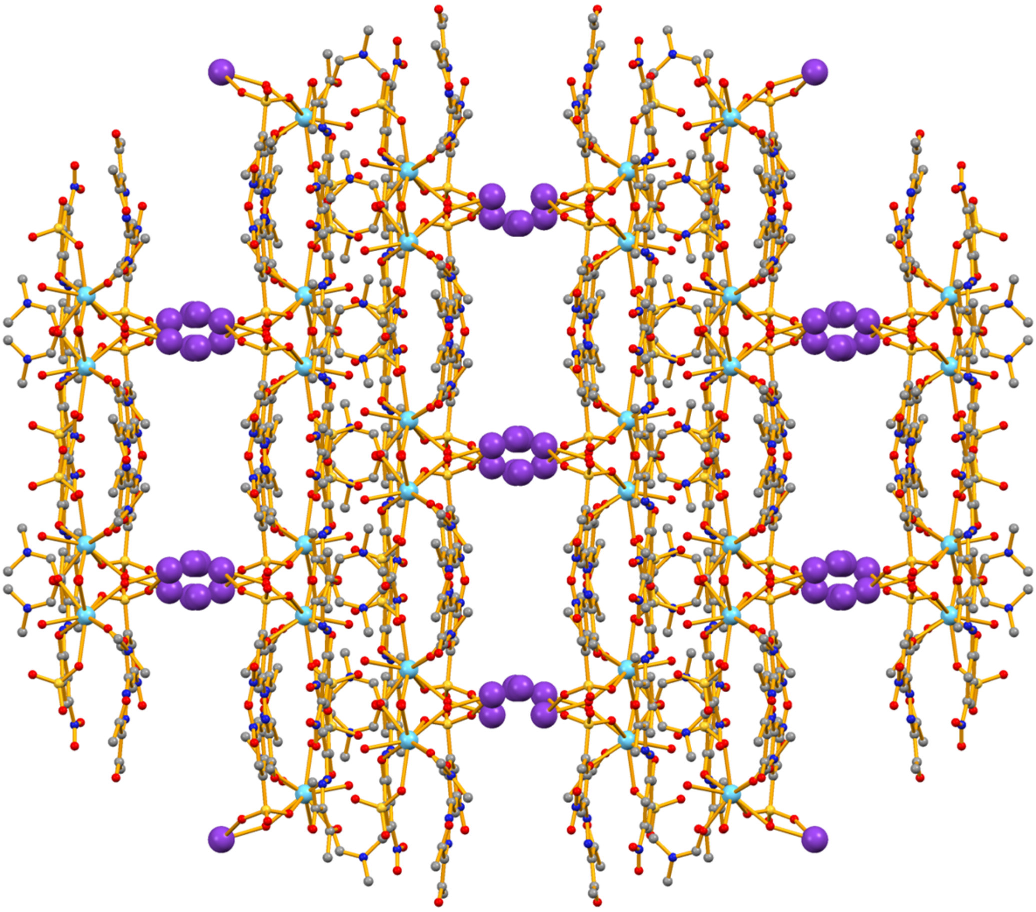

Fig. S4. Crystal packing diagram of **1**, viewed down the crystalographic *c* axis.

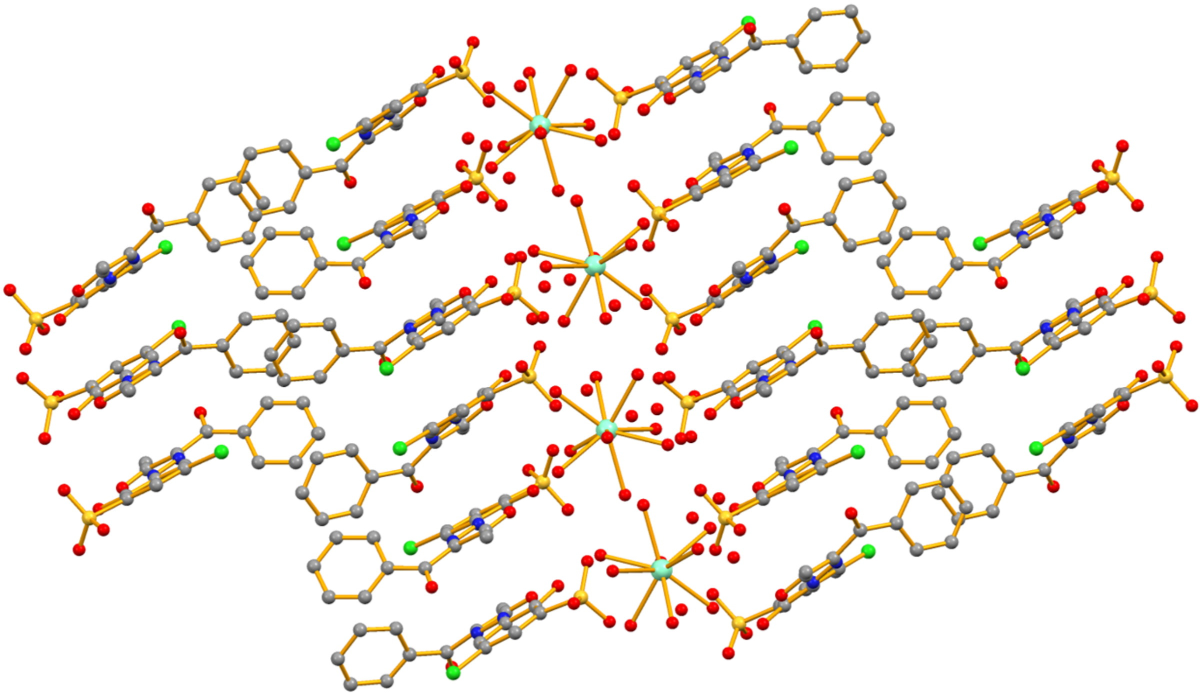

Fig. S5. Crystal packing diagram of **2**, viewed down the crystalographic *b* axis.

Table S1. Comparison of some selected bond distances (Å) and angles (°) in **1** and **2**

	1	**2**
In the organic L moieties		
N–N	1.297(11) 1.298(14)	1.277(9) 1.284(10) 1.292(9)
$C=O_{ketone}$	1.19(2), 1.21(2) 1.227(13), 1.254(13)	1.206(10), 1.216(10) 1.215(11), 1.219(13) 1.207(10), 1.250(11)
∠ between the aromatic ring and l.s. plane of OCCCO	11.79 12.08	23.57 28.58 29.30
OCCN torsion angle	175.23 179.71	145.46 146.85 150.54
Surrounding the lanthanide cations		
Metal-$O_{phenolate}$	2.442(8) 2.525(8)	-
Metal-$O_{sulphonate}$	2.610(8) 2.641(7)	-
Metal-O_{water}	2.579(8) 2.590(9) 2.600(7)	2.430(7) – 2.477(9)
Metal-O_{DMF}	2.458(9) 2.502(9)	-
M···M	8.538	6.810

Table S2. Hydrogen bond geometry [Å, °] in **1** and **2**.

D–H···A	*d*(H···A)	*d*(D···A)	∠(D–H···A)	Symmetry codes
1				
N1–H1···O1	2.40	2.698(13)	101	*intra*
N1–H1···O2	1.85	2.509(18)	133	*intra*
N4–H4···O6	2.31	2.661(12)	105	*intra*
N4–H4···O8	1.93	2.579(12)	132	*intra*
O60–H60A···O22	2.15	2.793(12)	123	*1/2-x,1/2+y,1/2-z*
O60–H60C···O23	1.88	2.796(10)	156	*intra*
O70–H70A···O23	1.84	2.742(13)	154	*1/2-x,1/2+y,1/2-z*
O70–H70C···O7	2.06	2.761(11)	127	*x,2-y,1/2+z*
O80–H80A···O3	2.03	2.841(15)	140	*x,1+y,z*
2				
N1–H1···O1	1.90	2.575(11)	134	*intra*
N1–H1···O3	2.27	2.620(10)	104	*Intra*
N3–H3···O4	1.93	2.590(9)	133	*Intra*
N3–H3···O6	2.30	2.644(9)	104	*intra*
N5–H5···O7	1.86	2.545(9)	136	*Intra*
N5–H5···O9	2.26	2.613(10)	105	*Intra*
O10–H110···O12B	2.36	3.11(2)	147	*1+x,y,z*
O30–H130···O6	2.59	3.197(11)	130	*1+x,y,z*
O30–H130···O31	2.50	2.859(12)	106	
O40–H140···O32	2.21	3.008(13)	155	
O50–H150···O7	2.36	2.726(13)	106	*x,-1+y,z*
O60–H160···O1W	2.28	2.710(12)	111	
O60–H160···O13B	2.53	2.82(2)	101	*1-x,-y,1-z*
O70–H170···O1W	1.85	2.673(15)	160	*1-x,-y,1-z*
O80–H180···O12B	2.15	2.94(3)	151	*1-x,-y,1-z*
O90–H190···O1	2.23	3.084(13)	178	*1-x,1-y,1-z*
O10–H210···O21B	2.08	2.797(17)	140	*1-x,1-y,1-z*
O10–H210···O22A	2.18	2.75(2)	123	*1-x,1-y,1-z*
O20–H220···O22B	2.41	2.960(17)	123	*1+x,-1+y,z*
O30–H230···O4	2.58	3.282(11)	140	*1+x,y,z*
O40–H240···O33	2.04	2.848(13)	159	*1-x,1-y,1-z*
O50–H250···O13B	2.30	2.82(2)	117	
O60–H260···O9	2.49	3.213(10)	143	*1-x,1-y,1-z*
O80–H280···O22A	1.82	2.53(3)	139	*1-x,1-y,1-z*
O80–H280···O22B	1.89	2.72(2)	164	*1-x,1-y,1-z*
O90–H290···O2W	2.11	2.94(2)	162	*1-x,1-y,1-z*

4. Calculation of the yield and selectivity for complex 1 in the Henry reaction

***Yield*:**

Total amount of compounds (see Fig. S6):

Bezaldehyde + *anti* + *syn* = 0.0989 + 0.2376 + 0.7624 = 1.0989

Percentage of the unreacted bezaldehyde: 0.0989/1.0989×100 = 9.0 %.

Conversion of benzaldehyde = yield of β-nitroalkanols = 100 – 9.0 = 91.0 %.

See Table 1, Entry 19.

***Selectivity*:**

Selectivity towards *anti*: 0.2376/(0.2376 + 0.7624) × 100 = 24 %.

Selectivity towards *syn*: 0.7624/(0.2376 + 0.7624) × 100 = 76 %.

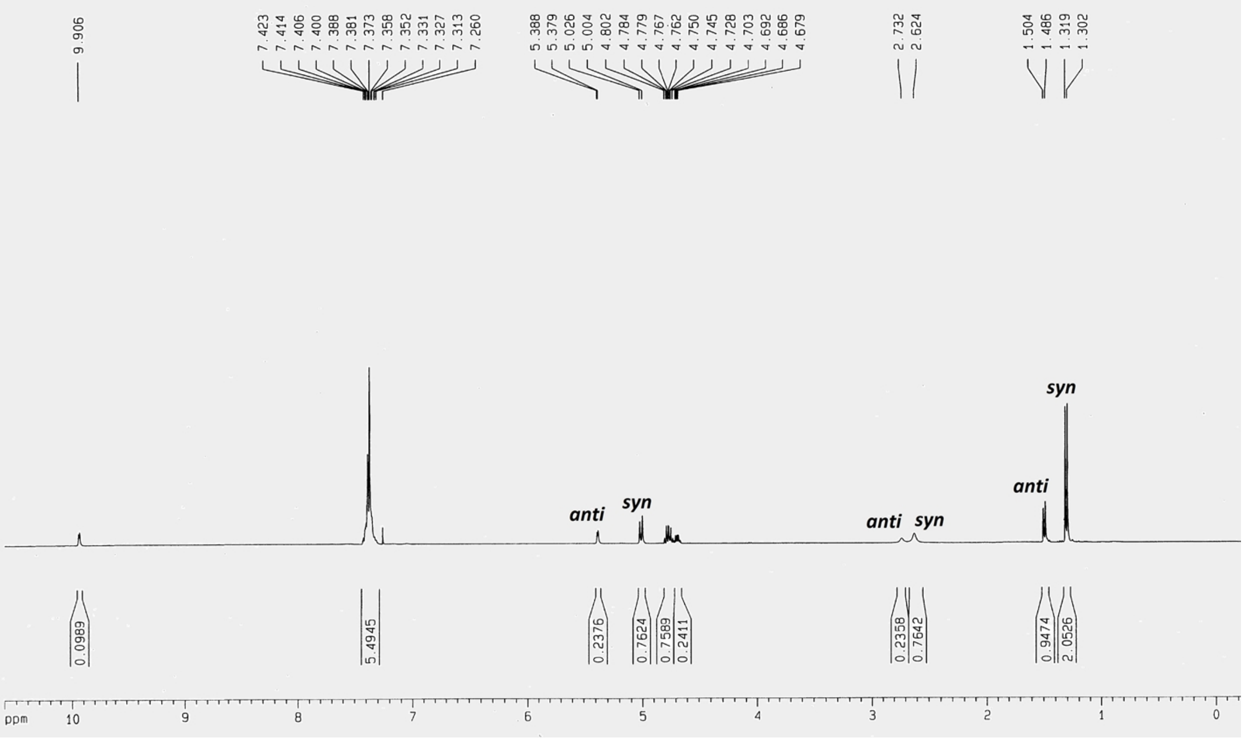

Fig. S6. Example of integration in the ^{1}H NMR spectrum for the determination of Henry reaction products (Table 1, Entry 19).

^{1}H NMR(400 MHz, $CDCl_3$) δ 9.91 (s, 0.1H), 7.42-7.31 (m, 5.00H + 0.49H Ar of benzaldehyde), 5.38 (d, J = 3.6 Hz, 0.24H) (*anti*), 5.02 (d, J = 8.8 Hz, 0.76H) (*syn*), 4.80-4.68 (m, 1H) (*syn* + *anti*), 2.73 (b, 0.24H) (*anti*), 2.62 (b, 0.76H) (*syn*), 1.50 (d, J = 7.2 Hz, 0.95H) (*anti*), 1.32 (d, J = 6.8 Hz, 2.05H) (*syn*).