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Supporting Information

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Accompanying

"DNA-Based Asymmetric Catalysis"
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Table S1

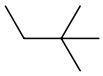
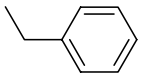
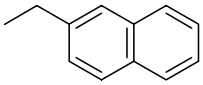
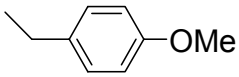
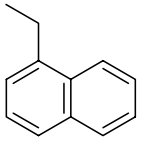
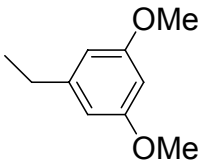
	Ligand 1 –R	T[b]	Diels-Alder product 4[a] endo:exo	e.e. endo (%)	e.e. exo (%)
1[c]	-Me	RT	94:6	8	19
2		RT	94:6	<5	<5
3		RT	94:6	19	13
4		RT	95:5	<5	-7
5		RT	96:4	17	15
6		RT	97:3	37	16
7		5 °C	98:2	49	18
8		5 °C	96:4	-21	<5

Table S1, Effect of the substituent [R] with a fixed spacer length [n] = 3 of ligand **1** on the copper catalyzed asymmetric Diels-Alder Reaction of cyclopentadiene (**2**) with aza-chalcone (**3**) in the presence of salmon testes DNA under standard reaction conditions (experimental section). a) Average of at least 2 experiments. Endo:exo ratio was determined by hplc, and confirmed by NMR analysis. E.e.'s were determined by hplc on an OD or ODH column. E.e values were reproducible within 1 % for the endo isomer and within 2-3 % for the exo product; b) RT = room temperature; c) conditions: 0.6 mM catalyst, 2.6 mg/ml DNA, 10 mM dienophile.

Table S2

	catalyst	ligand	T	Diels-Alder product 4		
				endo:exo	e.e. endo (%)	e.e. exo (%)
1[a]	$Cu(NO_3)_2$ / DNA	-	RT	95:5	10	13
2[b]	DNA	-	5 °C	n.d.[c]	<5 %	n.d.[c]
3[d]	DNA / $Cu(NO_3)_2$ / 9-aminoacridine	-	RT	94:6	7	18
4[e]	$Cu(NO_3)_2$ / ligand	**1a**	RT	95:5	-	-
5[e]	$Cu(NO_3)_2$ / ligand	**1f**	RT	93:7	-	-

Table S2, Control experiments. a) conversion 50-60 %. b) conversion < 5%. c) n.d. = not determined. d) quantitative conversion. e) conversion varies between 50-70 %, a slightly brown colored precipitate, most likely an insoluble form of the catalyst, is formed during the reaction.

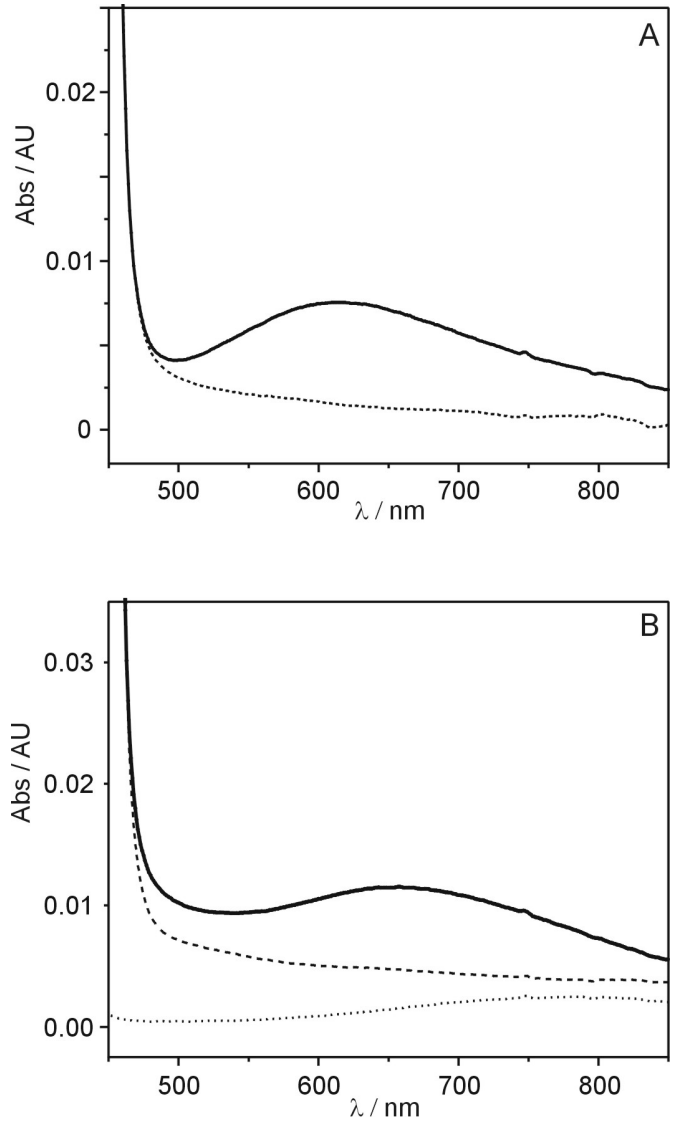


Figure S1, UV/Vis spectra. A) copper complex of **1a** (solid line) and free ligand **1a** (hashed line) without DNA; B) copper complex of **1a** (solid line), free ligand (hashed line) and $Cu(NO_3)_2$ (dotted line) in the presence of salmon testes DNA (0.8 mg/ml). All solutions were buffered (20 mM Mops, pH 6.5), ligand and copper concentrations were 150 μM.

Experimental and Synthetic Procedures

General remarks

Salmon testes and calt thymus DNA were obtained from Sigma. Dienophiles **3a-c** were prepared following published procedures.[1] Cyclopentadiene (**2**) was freshly prepared from its dimer prior to use. Mono-boc protected diamines (**5)** were obtained from Fluka, or prepared following literature procedures.[2]

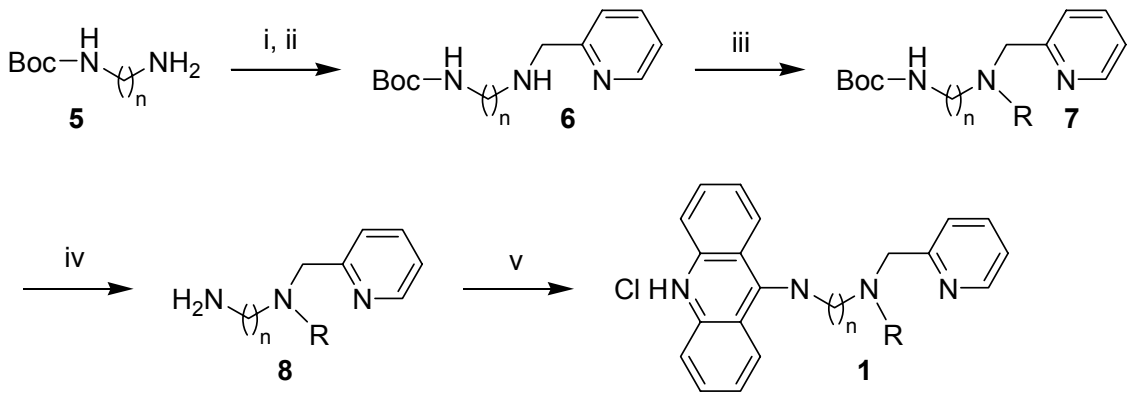
Dissolution of synthetic oligonucleotide.

The synthetic 16-mer $d(GACT)_2(AGTC)_2$ was obtained from Sigma-Genosys. The lyophilized powder was dissolved in buffer (20 mM Mops, 100 mM NaCl, pH 6.5), heated to 94 °C and slowly cooled to room temperature. After centrifugation the supernatant, containing the dissolved oligonucleotide, was decanted. Concentration was determined by UV/Vis, using ε_{260} = 31.3 OD/μg. CD spectroscopy showed the features typical for right-handed helical B-form DNA, *i.e.* a postive band at ~280 nm, a negative band near 240 nm and a crossover near 255 nm.[3]

Catalytic experiments, validation of workup procedure.

To a solution of salmon testes DNA and *in situ* prepared copper complex from ligand **1a**, at the typical concentrations described in the representative procedure for catalytic experiments, was added racemic Diels-Alder product **4a** to a final concentration of 0.6 mM. The mixture was incubated for 5 h at room temperature or 3 h at room temperature followed by 3 nights at 5 °C, after which **4a** was isolated by extraction following the standard work up procedure. In both cases no enantiomeric enrichment for both the endo and exo isomer was observed, as indicated by hplc analysis.

Synthesis of Ligands



Scheme S1. Synthesis of the ligands **1**. i. 2-pyridinecarboxaldehyde, MeOH; ii. $NaBH_4$; iii. R-Cl, K_2CO_3, CH_3CN, reflux; iv. TFA, thiophenol, CH_2Cl_2; v. 9-chloroacridine, phenol, 100 °C.

Reductive aminations (steps i & ii)

***tert*-butyl 3-[(2-pyridinylmethyl)amino]propylcarbamate (5a), general procedure.**
To a solution of mono-Boc protected propanediamine (1.51 g, 8.6 mmol) in methanol (30 ml) was added freshly distilled 2-pyridinecarboxaldehyde (923 mg, 1 eq). After stirring for 1 h at room temperature, NaBH4 (314 mg, 8.6 mmol) was added in small portions. Stirring was continued for 1 h at room temperature, after which time the reaction was quenched by addition of sat. NH4Cl solnd (10 ml). The pH was brought to >7 using a 2M $NaCO_3$ solution and the methanol was evaporated *in vacuo*. The aqueous phase was extracted with ethylacetate (3 × 20 ml) and the combined organic layers were washed with brine (10 ml), dried (Na_2SO_4) and the solvent evaporated to give pure **5a** (2.19 g, 8.3 mmol, 97 %) as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 9H), 1.71 (m, 2H), 2.73 (t, 2H, 6.6 Hz), 3.23 (m, 2H), 3.91 (s, 2H), 7.17 (dd,) 7.31 (d, 1H, J = 8.1 Hz), 7.65 (dd, 1H, J =), 8.57 (d, 1H, 4.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 28.14 (q), 29.43 (t), 38.57 (t), 46.73(t), 54.58 (t), 78.48 (s), 121.72 (d), 122.06 (d), 136.25 (d), 148.88 (d), 155.89 (s), 159.05 (s); HRMS calcd. for $C_{14}H_{23}N_3O_2$: 265,1790, found: 265.1781.

***tert*-butyl 4-[(2-pyridinylmethyl)amino]butylcarbamate (5b)**
Starting from mono-Boc protected 1,4-diaminobutane (1.06 g, 5.6) mmol, **5b** (1.53 g, 5.5 mmol, 98 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 136 (s, 9H), 1.48 (m, 4H), 2.60 (t, 2H, J = 6.6 Hz), 3.05 (m, 2H), 3.82 (s, 2H), 7.09 (m, 1H), 7.23 (d, 1H, J = 8.4 hz), 7.57 (m, 1H), 8.48 (d, 1H, J = 4.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 26.75 (t), 27.22 (t), 27.84 (q), 39.76 (t), 48.50 (t), 54.46 (t), 77.89 (s), 121.26 (d), 121.61 (d), 135.78 (d), 148.55 (d), 155.53 (s), 159.16 (s); MS (CI) 280 (M+1).

***tert*-butyl 4-[(2-pyridinylmethyl)amino]butylcarbamate (5c)**
Starting from mono-Boc protected 1,5-diaminopentane (1.1 g, 5.4) mmol, **5c** (1.58 g, 5.4 mmol, 98 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.35 (m, 2H), 1.41 (s, 9H), 1.48 (m, 2H), 1.56 (m, 2H), 2.66 (t, 2H, J = 7.0 Hz), 3.08 (m, 2H), 3.91 (s, 2H), 7.15 (m, 1H), 7.28 (d, 1H, J = 7.7 Hz), 7.63 (m, 1H), 8.54 (d, 1H, J = 4.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.87 (t), 27.78 (q), 29.04 (t), 29.30 (t), 48.71 (t), 54.43 (t), 77.80 (s), 121.19 (d), 121.56 (d), 135.71 (d), 148.48 (d), 155.47 (s), 159.12 (s); MS (CI) 294 (M+1).

***tert*-butyl 2-[(2-pyridinylmethyl)amino]ethylcarbamate (5d)**
Starting from mono-Boc protected ethylene diamine (1.02 g, 6.3) mmol, **5d** (1.38 g, 5.5 mmol, 87 %) was obtained as a slightly yellow oil. ^{1}H -NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 9H), 2.81 (m, 2H), 3.28 (m, 2H), 3.93 (s, 2H), 7.18 (m, 1H), 7.28 (d, 1H, J = 7.7 Hz), 7.64 (m, 1H), 8.56 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 28.19 (q), 40.01 (t), 48.49 (t), 54.26 (t), 78.80 (s), 121.94 (d), 122.20 (d), 136.52 (d), 148.97 (d), 156.03 (s), 159.05 (s); MS (CI) 252 (M+1).

Alkylations (step iii)

***tert*-butyl 3-[(1-naphthylmethyl)(2-pyridinylmethyl)amino]propylcarbamate (6a), general procedure**
A solution of **5a** (630 mg, 2.4 mmol), 1-chloromethylnaphtalene (548 mmol, 1.3 eq), K_2CO_3 (330 mg, 2.4 mmol) in CH_3CN was placed under nitrogen. After heating under reflux for 1 night the solvent was evaporated and the crude material redissolved in water (30 ml). Extraction with ethyl acetate (3×20 ml) was followed by washing the combined organic layers with brine. After drying

(Na_2SO_4) the ethyl acetate was evaporated and the crude material subjected to column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 20:10:1) which gave **6a** (701 mg, 1.73 mmol, 72 %) as a yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 9H), 1.71 (m, 2H), 2.59 (t, 2H, J = 6.6 Hz), 3.04 (m, 2H), 3.79 (s, 2H), 4.03 (s, 2H), 7.15 (m, 1H), 7.36 (d, 1H, J = 7.7 Hz), 7.41 (m, 1H), 7.48 (m, 2H), 7.53 (d, 1H, J = 6.6 Hz), 7.61 (m, 1H), 7.75 (d, 1H, J = 8.4 Hz), 7.82 (m, 1H), 8.14 (m, 1H), 8.57 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 26.48 (t), 28.27 (q), 38.79 (t), 51.89 (t), 57.15 (t), 60.10 (t), 78.22 (s), 121.71 (d), 123.05 (d), 124.17 (d), 124.96 (d), 125.34 (d), 125.48 (d), 127.18 (d), 127.70 (d), 128.22 (d), 132.00 (s), 133.54 (s), 134.40 (s), 136.05 (d), 148.69(d), 155.81 (s), 159.33 (s); MS (CI) 406 (M+1).

***tert*-butyl 4-[(1-naphthylmethyl)(2-pyridinylmethyl)amino]butylcarbamate (6b)**
Starting from **5b** (751 mg, 2.7 mmol) after purification by column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 10:1:1) resulted in **6b** (757 mg, 1.8 mmol, 67 %) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.37 (m, 2H), 1.40 (s, 9H), 1.56 (m, 2H), 2.53 (t, 2H, J = 7.3 Hz), 2.95 (m, 2H), 3.75 (s, 2H), 4.04 (s, 2H), 7.08 (m, 1H), 7.37 (m, 2H), 7.45 (m, 2H), 7.50 (d, 1H, 6.2 Hz), 7.54 (m, 1H), 7.72 (d, 1H, J = 8.4 Hz), 7.80 (m, 1H), 8.20 (m, 1H), 8.46 (d, 1H, J = 4.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.66 (t), 27.48 (t), 28.11 (q), 39.86 (t), 53.77 (t), 57.16 (t), 60.03 (t), 78.31 (s), 121.40 (d), 122.72 (d), 124.27 (d), 124.83 (d), 125.17 (d), 125.21 (d), 126.98 (d), 127.48 (d), 128.05 (d), 132.01 (s), 133.44 (s), 134.61 (s), 135. 81 (d), 148.28 (d), 15.68 (s), 159.82 (s); MS (CI) 420 (M+1).

***tert*-butyl 5-[(1-naphthylmethyl)(2-pyridinylmethyl)amino]pentylcarbamate (6c)**
Starting from **5c** (964 mg, 3.3 mmol) after column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 10:1:1) **6c** (997 mg, 2.3 mmol, 70 %) as a colorless oil^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.27 (m, 4H), 1.41 (s, 9H), 1.55 (m, 2H), 2.51 (t, 2H, J = 7.0 Hz), 2.98 (m, 2H), 3.75 (s, 2H), 4.03 (s, 2H), 7.07 (m, 1H), 7.37 (m, 2H), 7.37 (m, 2H), 7.51 (d, 1H, J = 7.0 Hz), 7.55 (m, 1H), 7.72 (d, 1H, J = 8.1 Hz), 7.81 (m, 1H), 8.22 (m, 1H), 8.46 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 24.10 (t), 26.11 (t), 28.09 (q), 29.32 (t), 40.05 (t), 53.92 (t), 57.18 (t), 60.10 (t), 78.28 (s), 121.33 (d), 122.68 (d), 124.31 (d), 124.80 (d), 125.13 (d), 125.14 (d), 132.02 (s), 133.43 (s), 134.69 (s), 135.75 (d), 148.20 (d), 155.63 (s), 159.95 (s); MS (CI) 434 (M+1).

***tert*-butyl 2-[(1-naphthylmethyl)(2-pyridinylmethyl)amino]ethylcarbamate (6d)**
Starting from **5d** (498 mg, 2.0 mmol) after column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 20:10:1) **6d** (573 mg, 1.46 mmol, 73 %) was obtained as a slightly yellow oil. (^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 9H), 2.68 (t, 2H, J = 5.9 Hz), 3.20 (m, 1H), 3.81 (s, 2H), 4.10 (s, 2H), 7.11 (m, 1H), 7.24 (d, 1H, J = 7.3 Hz), 7.37 (m, 1H), 7.46 (m, 2H), 7.56 (m, 1H), 7.73 (d, 1H, J = 8.1 Hz), 7.81 (m, 1H), 8.14 (m, 1H), 8.51 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 28.11 (q), 37.93 (t), 53.22 (t), 57.39 (t), 59.80 (t), 78.17 (s) 121.60 (d), 122.91 (d), 124.14 (d), 124.82 (d), 125.28 (d), 125.43 (d), 127.32 (d), 127.32 (d), 127.76 (d), 128.16 (d), 131.96 (s), 133.53 (s), 134.18 (s), 135.84 (d), 148.53 (d), 155.66 (s), 159.10 (s); MS (CI) 392 (M+1).

***tert*-butyl 3-[(3,5-dimethoxybenzyl)(2-pyridinylmethyl)amino]propylcarbamate (6e)**
Starting from **5a** (687 mg, 2.6 mmol) and 3,5-dimethoxybenzyl chloride (1.3 eq) after column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 20:10:1) **6e** (622 mg, 1.5 mmol, 58 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 9H), 1.68 (m, 2H), 2.53 (t, 2H, J = 6.6 Hz), 3.15 (m, 2H), 3.50 (s, 2H), 3.70 (s, 2H), 3.75 (s,

6H), 6.31 (s, 1H), 6.52 (s, 2H), 7.13 (m, 1H), 7.40 (d, 1H, J = 7.3 Hz) 7.62 (m, 1H), 8.54 (d, 1H, J = 4.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 26.44 (t), 28.28 (q), 38.95 (t), 51.68 (t), 55.01 (q), 58.67 (t), 59.73 (t), 78.35 (s), 98.73 (d), 106.32 (d), 121.78 (d), 136.26 (d) 141.49 (s), 148.83 (d), 155.94 (s), 159. 38 (s), 160.56 (s); MS (CI) 416 (M+1).

***tert*-butyl 2-[(3,5-dimethoxybenzyl)(2-pyridinylmethyl)amino]ethylcarbamate (6f)**
Starting from **5d** (248 mg, 1.0 mmol) and 3,5-dimethoxybenzyl chloride (1.3 eq) after column chromatography (Alox, akt III, neutral, heptane: ethyl acetate: triethyl amine 20:10:1) **6f** (335 mg, 0.84 mmol, 84 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 9H), 2.61 (t, 2H, J = 5.9 Hz), 3.20 (m, 2H), 3.59 (s, 2H), 3.78 (s, 2H), 3.78 (s, 6H), 6.32 (s, 1H), 6.51 (s, 2H), 7.13 (m, 1H), 7.37 (d, 1H, J = 7.7 Hz), 7.62 (m, 1H), 8.51 (d, 1H, J = 4.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 28.09 (q), 37.92 (t), 52.86 (t), 54.83 (q), 58.48 (t), 59.53 (t), 78.29 (s), 98.79 (d), 106.11 (d), 121.68 (d), 122.60 (d), 136.05 (d), 141.34 (s), 148.62 (d), 155.72 (s), 159.22 (s), 160.48 (s); MS (CI) 402 (M+1).

Deprotection (step iv).

N^1-(1-naphthylmethyl)-N^1-(2-pyridinylmethyl)-1,3-propanediamine (7a)
To a solution of **6a** (670 mg, 1.65 mmol) in CH_2Cl_2 (9 ml) was added thiophenol (1 ml) and trifluoroacetic acid (1 ml). After stirring for 6 h at room temperature a 1 M HCl solution (10 ml) was added. The CH_2Cl_2 was evaporated and the aqueous layer was extracted with diethyl ether (3×70 ml). The pH of the aqueous phase was brought to >10 by addition of 2 M NaOH. Extraction with CH_2Cl_2 (3×30 ml) was followed by washing of the combined organic layers with brine. After drying the solvent was removed *in vacuo* to give pure **7a** (291 mg, 0.95 mmol, 58 %) as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.73 (m, 2H), 2.61 (t, 2H, J = 7.0 Hz), 2.66 (t, 2H, J = 6.6 Hz), 3.79 (s, 2H), 4.06 (s, 2H), 7.12 (m, 1H), 7.37 (d, 1H. J = 7.3 Hz), 7.41 (m, 1H), 7.48 (m, 2H), 7.54 (d, 1H, J = 7.0 Hz), 7.58 (m, 1H), 7.75 (d, 1H, J = 8.1 Hz), 7.83 (m, 1H), 8.21 (m, 1H), 8.52 (d, 1H, J = 4.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 30.20 (t), 39.83 (t), 51.61 (t), 57.13 (t), 60.11 (t), 121.48 (d), 122.74 (d), 124.17 (d), 124.84 (d), 125.21 (d), 125.24 (d), 127.01 (d), 127.94 (d), 128.07 (d), 131.94 (s), 133.41 (s), 134.55 (s), 135.89 (d), 148.32 (d), 159.72 (s); HRMS calcd. for $C_{20}H_{23}N_3$: 305.1892, found: 305.1897.

N^1-(1-naphthylmethyl)-N^1-(2-pyridinylmethyl)-1,4-butanediamine (7b)
Starting from **6b** (750 mg, 1.79 mmol) after reacting overnight at room temperature, **7b** (514 mg, 1.61 mmol, 90 %) was obtained as a nearly colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.34 (m, 2H), 1.58 (m, 2H), 2.52 (m, 4H), 3.76 (s, 2H), 4.04 (2H), 7.07 (m, 1H), 7.37 (m, 2H), 7.45 (m, 2H), 7.53 (m, 2H), 7.72 (d, 1H, J = 8.4 Hz), 7.80 (m, 1H), 7.23 (m, 1H), 8.46 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.52 (t), 30.74 (t), 41.22 (t), 53.79 (t), 56.93 (t), 59.83 (t), 121.20 (d), 122.52 (d), 124.09 (d), 124.65 (d), 124.97 (d), 124.99 (d), 126.76 (d), 127.25 (d), 127.85 (d), 131.82 (s), 133.24 (s), 134.50 (s), 135.64 (d), 147.99 (d), 159.71 (s); MS (CI) 320 (M+1).

N^1-(1-naphthylmethyl)-N^1-(2-pyridinylmethyl)-1,5-pentanediamine (7c)
Starting from **6c** (978 mg, 2.25 mmol) after reacting overnight at room temperature, using 1.5 times as much TFA as in the general procedure, resulted in **7c** (724 mg, 2.17 mmol, 97 %) was obtained as a nearly colorless oil.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.24 (m, 4H), 1.57 (m, 2H), 2.54 (m, 4H), 3.76 (s, 2H), 4.04 (s, 2H), 7.06 (m, 1H), 7.37 (m, 2H), 7.45 (m, 2H), 7.53 (m, 2H), 7.72 (d, 1H, J = 8.4 Hz), 7.80 (m, 1H), 8.24 (m, 1H), 8.45 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ

23.91 (t), 26.05 (t), 32.93 (t), 41.50 (t), 53.82 (t), 56.94 (t), 59.94 (t), 121.03 (d), 122.38 (d), 124.09 (d), 124.56 (d), 124.87 (d, 2 overlapping signals), 126.73 (d), 127.14 (d), 127.75 (d), 131.80 (s), 133.18 (s), 134.53 (s), 135.42 (d), 147.99 (d), 159.79 (s); MS (CI) 334 (M+1).

N^1-(1-naphthylmethyl)-N^1-(2-pyridinylmethyl)-1,2-ethanediamine (7d)
Starting from **6d** (565 mg, 1.45 mmol) **7d** (345 mg, 1.19 mmol, 82 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.68 (t, 2H, J = 5.9 Hz), 2.78 (t, 2H, J = 5.9 Hz), 3.80 (s, 2H), 4.10 (s, 2H), 7.09 (m, 1H), 7.27 (d, 1H, J = 8.1 Hz), 7.37 (m, 1H), 7.45 (m, 2H), 7.50 (d, 1H, J = 7.0 Hz), 7.54 (m, 1H), 7.73 (d, 1H, J = 8.1 Hz), 7.80 (m, 1H), 8.17 (m, 1H), 8.48 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 39.21 (t), 57.21 (t), 57.57 (t), 60.34 (t), 121.43 (d), 122.73 (d), 124.06 (d), 124.76 (d), 125.16 (d), 125.25 (d), 127.21 (d), 127.56 (d), 128.05 (d), 131.92 (s), 133.40 (s), 134.39 (s), 135.74 (d), 148.36 (d), 159.47 (s).

N^1-(3,5-dimethoxybenzyl)-N^1-(2-pyridinylmethyl)-1,3-propanediamine (7e)
Starting from **6e** (557 mg, 1.34 mmol) **7e** (279 mg, 0.89 mmol, 66 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.66 (m, 2H), 2.53 (t, 2H, J = 7.0 Hz), 2.73 (t, 2H, J = 7 Hz), 3.56 (s, 2H), 3.73 (s, 2H), 3.78 (s, 6H), 6.33 4 (s, 1H), 6.56 (s, 2H), 7.14 (m, 1H), 7.52 (d, 1H, J = 8.1 Hz), 7.64 (m, 1H), 8.50 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 30.57 (t), 39.83 (t), 50.94 (t), 54.73 (q), 58.40 (t), 59.77 (t), 98.29 (d), 106.02 (d), 121.39 (d), 122.22 (d), 135.88 (d), 141.67 (s), 148.38 (d), 159.78 (s), 160.26 (s); HRMS calcd. for $C_{18}H_{25}N_3O_2$ 315.1947, found 315.2008.

N^1-(3,5-dimethoxybenzyl)-N^1-(2-pyridinylmethyl)-1,2-ethanediamine (7f)
Starting from **6f** (565 mg, 1.4 mmol) **7f** (345 mg, 1.15 mmol, 82 %) was obtained as a slightly yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.59 (t, 2H, J = 5.9 Hz), 2.77 (t, 2H, J = 5.9 Hz), 3.59 (s, 2H), 3.75 (s, 2H), 3.76 (s, 6H), 6.32 (s, 1H), 6.52 (s, 2H), 7.13 (m, 1H), 7.47 (d, 1H, J = 7.7 Hz), 7.63 (m, 1H), 8.50 (d, 1H, J = 4.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 39.26 (t), 54.84 (q), 56.82 (t), 58.79 (t), 60.06 (t), 98.41 (d), 106.28 (d), 121.56 (d), 122.45 (d), 135.98 (d), 141.51 (s), 148.52 (d), 159.59 (s), 160.37 (s); HRMS calcd. For $C_{17}H_{23}N_3O_2$: 301.1790, found 301.1784.

Coupling to acridine (step v).

N^1-(9-acridinyl)-N^3-(1-naphthylmethyl)-N^3-(2-pyridinylmethyl)-1,3-propanediamine (1a)
A mixture of **7a** (285 mg, 0.93 mmol), 9-chloroacridine (200 mg, 1 eq) and phenol (1 g) was placed under nitrogen and heated at 100 °C for 2h. After cooling to room temperature diethyl ether (50 ml) was added and the mixture was stirred for 1h. The diethyl ether was decanted from the dark oil, and fresh diethyl ether (50 ml) was added. After stirring for 2 days the hydrochloride salt of **1a** (437 mg, 0.84 mmol, 91 %) was isolated as a yellow solid. Dissolving a small amount in 1 M NaOH, followed by extraction with CH_2Cl_2 gave the free base as a dark yellow oil, which was used for analysis. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.88 (m, 2H), 2.71 (t, 2H, J = 6.2 Hz), 3.68 (t, 2H, J = 6.2 Hz), 3.80 (s, 2H), 4.04 (s, 2H), 7.02 (m, 1H), 7.16 (m, 3H), 7.32 (m, 3H), 7.41 (m, 1H), 7.46 (m, 1H), 7.57 (m, 2H), 7.68 (d, 1H, J = 8.1 Hz), 7.73 (d, 1H, J = 7.7 Hz), 7.82 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.8 Hz), 8.16 (d, 1H, J = 8.1 Hz), 8.43 (d, 1H, J = 4.8 Hz); HRMS calcd. for $C_{33}H_{30}N_4$: 482.2470, found: 482.2477

N^1-(9-acridinyl)-N^4-(1-naphthylmethyl)-N^4-(2-pyridinylmethyl)-1,4-butanediamine (1b)
Starting from **7b** (510 mg, 1.6 mmol) resulted in the hydrochloride salt of **1b** (690 mg, 1.29 mmol, 81 %) as a yellow solid. Treatment with base resulted in the free base that was used for

further characterisation. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.62 (m, 4H), 2.46 (t, 2H, J = 6.6 Hz), 3.54 (t, 2H, J = 6.6 Hz), 3.77 (s, 2H), 4.02 (s, 2H), 7.06 (m, 1H), 7.31 (m, 3H), 7.33 (d, 1H, J = 8.1 Hz), 7.38 (m, 2H), 7.48 (m, 2H), 7.64 (m, 2H), 7.67 (d, 1H, J = 8.1 Hz), 7.75 (m, 1H), 7.95 (dd, 2H, J = 8.8 Hz, J = 0.7 Hz), 8.05 (d, 2H, J = 8.4 Hz), 8.15 (m, 1H), 8.46 (m, 1H); HRMS calcd. For $C_{34}H_{32}N_4$: 496.2627, found: 496.2650.

***N*^{1}-(9-acridinyl)-*N*^{5}-(1-naphthylmethyl)-*N*^{5}-(2-pyridinylmethyl)-1,5-pentanediamine (1c)**
Starting from **7c** (720 mg, 2.16 mmol) resulted in the hydrochloride salt of **1c** (970 mg, 1,77 mmol, 82 %) as a yellow solid. Treatment with base resulted in the free base that was used for further characterisation. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.32 (m, 2H), 1.43 (m, 2H), 1.54 (m, 2H), 2.52 (t, 2H, J = 7.0 Hz), 3.54 (t, 2H, J= 7.3 Hz), 3.76 (s, 2H), 4.01 (s, 2H), 7.05 (m, 1H), 7.2-7.4 (m, 6H), 7.49 (m, 2H), 7.66 (m, 3H), 7.70 (d, 1H, J = 8.4 Hz), 7.97 (d, 2H, J = 8.8 Hz), 8.06 (d, 2H, J = 8.8 Hz), 8.17 (d, 1H, J = 8.4 Hz), 8.45 (m, 1H); HRMS calcd. For $C_{35}H_{34}N_4$: 510.2783, found: 510.2799.

***N*^{1}-(9-acridinyl)-*N*^{2}-(1-naphthylmethyl)-*N*^{2}-(2-pyridinylmethyl)-1,2-ethanediamine (1d)**
Starting from **7d** (340 mg, 1.16 mmol) resulted in the hydrochloride salt of **1d** (563 mg, 1.11 mmol, 96 %) as a yellow solid. Treatment with base resulted in the free base that was used for further characterisation. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.99 (t, 2H, J = 5.5 Hz), 3.90 (s, 2H), 3.92 (m, 2H), 4.15 (s, 2H), 7.08 (m, 2H), 7.15 (d, 1H, J = 7.7 Hz), 7.21 (m, 1H), 7.31 (m, 1H), 7.45 (m, 4H), 7.54 (m, 2H), 7.71 (d, 1H, J = 8.1 Hz), 7.78 (d, 1H, J = 8.1 Hz), 7.86 (d, 2H, J = 8.8 Hz), 7.96 (d, 2H, J = 8.4 Hz), 8.05 (d, 1H, J = 8.4 Hz), 8.48 (d, 1H, J = 4.7 Hz); HRMS calcd. For $C_{32}H_{28}N_4$: 468.2314, found: 468.2337.

***N*^{1}-(9-acridinyl)-*N*^{3}-(3,5-dimethoxybenzyl)-*N*^{3}-(2-pyridinylmethyl)-1,3-propanediamine (1e)**
Starting from **7e** (275 mg, 0.87 mmol) resulted in the hydrochloride salt of **1e** (361 mg, 0.68 mmol, 78 %) as a yellow solid. Treatment with base resulted in the free base that was used for further characterisation. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.95 (m, 2H), 2.73 (t, 2H, J = 6.2 Hz), 3.64 (s, 2H), 3.66 (2, 6H), 3.82 (s, 2H), 3.91 (t, 2H, J = 6.2 Hz), 6.33 (s, 1H), 6.56 (s, 2H), 7.09 (m, 1H), 7.26 (t, 2H, J = 6.6 Hz), 7.35 (d, 1H, J = 7.7 Hz), 7.52 (m, 1H), 7.64 (m, 2H), 8.04 (d, 4H, J = 9.5 Hz), 8.48 (m, 1H); MS (EI) 492 (M+).

***N*^{1}-(9-acridinyl)-*N*^{2}-(3,5-dimethoxybenzyl)-*N*^{2}-(2-pyridinylmethyl)-1,2-ethanediamine (1f)**
Starting from **7f** (540 mg, 1.8 mmol) resulted in the hydrochloride salt of **1f** (903 mg, 1.75 mmol, 97 % %) as a yellow solid. Treatment with base resulted in the free base that was used for further characterisation. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.96 (t, 2H, J = 5.5 Hz),3.64 (s, 6H), 3.68 (s, 2H), 3.86 (s, 2H), 3.97 (t, 2H, J = 5.5 Hz), 6.32 (s, 1H), 6.52 (s, 2H), 7.12 (m, 1H), 7.27 (m, 3H), 7.55 (m, 1H), 7.62 (m, 2H), 8.02 (d, 2H, J = 8.4 Hz), 8.24 (d, 2H, 8.4 Hz), 8.53 (d, 1H, J = 5.1 Hz); HRMS calcd. for $C_{30}H_{30}N_4O_2$: 478.2369, found: 478.2379.

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