Simple and Convenient Method for the Synthesis of 2-Substituted Glutaconaldehyde Salts and 2-Substituted Glutaconaldehyde Derivatives

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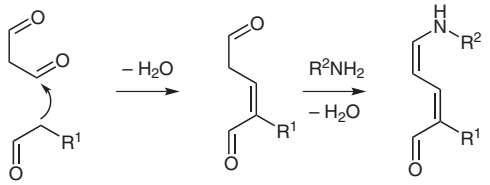
In memory of the late Dr. Christian Marazano who passed away on 12th November 2008

Abstract: Convenient and scalable syntheses of 2-substituted glutaconaldehyde salts were accomplished from the corresponding pyridinium salts. Glutaconaldehyde salts were additionally converted into aminopentadienal derivatives.

Key words: Zincke aldehydes, aminopentadienal derivatives, pyridinium salts, glutaconaldehyde

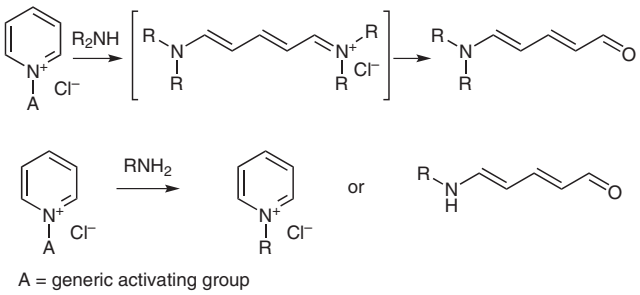
We have proposed[1] recently that the biosynthetic pathway of manzamine alkaloids could involve substituted 5-aminopenta-2,4-dienals, which could be formed by condensation of malonaldehyde with an aldehyde and subsequently with an amine (Scheme 1).



Scheme 1 Biogenetic scenario for the formation of aminopentadienals

In order to test the chemical feasibility of this modification of the Baldwin and Whitehead hypothesis,[2] the synthesis of aminopentadienals and one of their plausible precursors, the glutaconaldehydes, was necessary.

The ability of aminopentandienals to function both as nucleophiles[1] and electrophiles could allow for their use as tailored reagents towards creating synthetic diversity. The easiest way to obtain aminopentadienals (Zincke aldehydes) is to open appropriately activated pyridinium salts as described over a century ago by Zincke and König.[3] Although examples appeared recently in the literature notably by Vanderwal and Marazano,[4] the potential of these compounds as versatile intermediates for natural product synthesis remains largely unexploited. One limitation for a more widespread use of Zincke aldehydes may be their accessibility. Indeed, the use of two equivalents of amine required to form the intermediate iminium is clearly not adapted for convergent synthesis involving a highly functionalized secondary amine. Another issue is also the availability and the stability of the more reactive Zincke aldehydes derived from primary amines due to their propensity to form a pyridinium salt (Scheme 2).[5]



Scheme 2

To overcome the above drawbacks, we investigated the possibility to form aminopentadienals directly from amine salts and glutaconaldehyde salts. Moreover, one advantage of this strategy is that the starting materials are water soluble whereas the final compound is soluble in the organic phase. This should allow some unstable aldehydes to be easily obtained with sufficient purity for the next step through simple extraction.

The salts of glutaconaldehydes, first described by Baumgarten[6] in 1924, have been mostly used in the literature for intramolecular Diels–Alder[7] reactions (after O-acetylation) and for the synthesis of polyenic compounds.[8] Sodium or potassium salts of unsubstituted glutaconaldehydes could be easily obtained by simple filtration.[9] However substituted glutaconaldehydes salts were rarely made and the preparation involved a tedious removal of a large quantity of water along with repeated precipitation and filtration steps.[10] Moreover, the reactivity was highly dependant of the method of preparation and purification.

The new approach begins with the ring opening of 2,4-dinitropyridinium salts **1**[1b,11] using dimethylamine to afford a mixture of (dimethylamino)pentadienals **2** and **3** (Table 1). 2,4-Dinitroaniline released during the reaction is insoluble in water and is removed easily by simple filtration before hydrolysis of the iminium salt. The relatively modest yield of **2c** can be explained by the solubility of

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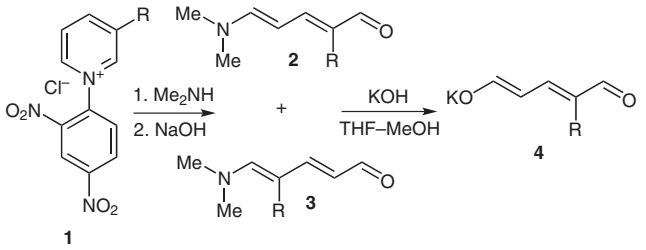
this compound in water. In this particular case, the minimum amount of water should be used to remove the dinitroaniline. The mixture of **2e** and **3e** appears unstable, therefore it should be used directly in the next step. According to the literature, the reaction of **1e** with dimethylamine affords only one compound **2e** in 53% yield.[12] We observed that the experimental conditions used for hydrolysis of the intermediate iminium salt could change the proportion of **2e/3e** from 2:1 to 9:1. However, when the ratio **2e/3e** increases the overall yield of the reaction simultaneously decreases. This result could be due to the greater instability of **3e** compared to **2e** under the hydrolysis conditions.

Table 1 Synthesis of 2-Subtituted Glutaconaldehyde Salts



Zincke salt	R	Ratio **2/3**	Yield (%)	Product	Yield (%)
1a	H	1:0	83	**4a**	93
1b	Me	1:0	84	**4b**	80
1c	$(CH_2)_2OH$	1:0	51	**4c**	83
1d[a]	$(CH_2)_{10}OH$	5:1	–	**4d**	71[b]
1e	OMe	2:1	91	**4e**	65
–[c]	Br	–[b]	82	**4f**	69

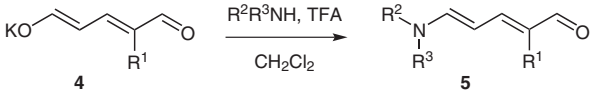
[a] The precursor of Zincke salt **1d** was obtained in 3 steps from 3-methylpicoline.
[b] Yield over two steps.
[c] **2f** was obtained directly by bromination of **2a**.[13]

To simplify the purification of **4** it was necessary to find a suitable solvent or a mixture of solvents where potassium hydroxide and the (dimethylamino)pentadienal are soluble whilst the glutaconaldehyde salt formed precipitates out of solution. Initial attempts with a mixture of tetrahydrofuran–water resulted in a biphasic system without any precipitation. Finally a solvent system of tetrahydrofuran–methanol or diethyl ether–methanol did indeed dissolve potassium hydroxide and allowed for precipitation of the glutaconaldehyde salt **4**. Although the crude product obtained directly by filtration of the reaction seems clean by NMR, it is crucial to dissolve the solid in cold methanol or ethanol and then filter the solution through Celite. Although few insoluble materials were removed during the process, it is not yet clearly understood why the reactivity could be so different.[14] Moreover, absence of water during the reaction allows the formation of an anhydrous salt **4**.

This procedure, thus, provides a convenient and reliable access to 2-substituted glutaconaldehyde salts where the substituent could be an alkyl group, a functionalized chain, or a heteroatom. Moreover, the purification involves simple extraction or filtration allowing for the process to be scalable.

Zincke aldehydes **5** derived from primary amines or secondary amines could be obtained easily by coupling glutaconaldehyde **4** with the corresponding amines (Table 2). The reaction of one equivalent of alkylammonium trifluoroacetate salt (or 1 equivalent of the amine and 1 equivalent trifluoroacetate) and a slight excess of **4** in dichloromethane afforded, after simple extraction, only one isomer **5**, which could be used without further purification. Indeed, unreacted starting materials or possible byproducts like pyridinium salts will remain in the aqueous phase, whilst the product **5** will stay in the organic phase. It was observed that the addition of one drop of water to the solution accelerated the reaction.

Table 2 Synthesis of 2-Substituted Aminopentadienal

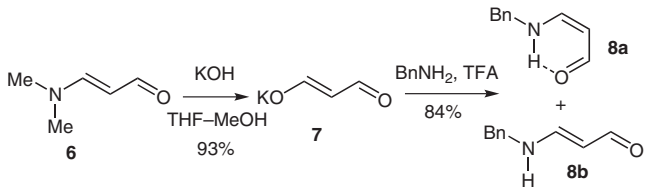


Entry	Substrate	R^1	R^2R^3NH[a]	Product	Yield (%)
1	**4a**	H	$BnNH_2$	**5a**	98
2	**4a**	H	Bn_2NH	**5b**	97
3	**4b**	Me	$BnNH_2$	**5c**	79
4	**4b**	Me	$BuNH_2$	**5d**	82
5	**4b**	Me	$PMBNH_2$	**5e**	82
6	**4c**	$(CH_2)_2OH$	$BnNH_2$	**5f**	70[b]
7	**4d**	$(CH_2)_{10}OH$	$PMBNH_2$	**5g**	88
8	**4e**	OMe	$PMBNH_2$	**5h**	92
9	**4f**	Br	$BnNH_2$	**5i**	63[b]
10	**4f**	Br	$PMBNH_2$	**5j**	53[b]

[a] PMB = 4-methoxybenzyl.
[b] Yield after column chromatography.

Some aminopentadienals **5** could be further purified by column chromatography (Table 2, entry 6, 9, and 10), but it is not really required and can increase the possible risk of cyclization or decomposition of the compound. Secondary amines (Table 2, entry 2) could also react with **4**. Thus, this method, which uses only one equivalent of amine, is a good alternative for the preparation of Zincke aldehydes.

The same strategy could also be applied to obtain malonaldehyde salts (Scheme 3). Commercially available 3-(dimethylamino)prop-2-enal (**6**) could be hydrolyzed to the salt **7** under the same conditions described above for the glutaconaldehyde salts. However, the reaction of **7**



Scheme 3

with benzylamine afforded a mixture of *cis*/*trans*-enamine **8** in a 1:1 ratio.[15]

In summary, we have described a convenient method for the preparation of 2-substituted glutaconaldehyde salts and 2-substituted aminopentadienals. These useful intermediates should find application in a range of synthetic programs. Further work is in progress in our laboratory to investigate the enamine-like reactivity of these species.

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. CH_2Cl_2 was distilled from P_2O_5. THF was distilled from Na/benzophenone ketyl immediately before use. All other solvents were used as obtained from commercial sources. Analytical TLC was performed on Merck silica gel plates (60 F_{254}) and visualized by UV fluorescence or $KMnO_4$. Flash column chromatography was carried out using Merck silica gel (Geduran SI 60, 0.040–0.063 mm). Melting points were measured on a Büchi melting point B-540 apparatus. IR spectra were recorded on a Perkin-Elmer Spectrum-BX spectrophotometer equipped with an ATR sampling accessory. ^{1}H NMR spectra were recorded at 300 MHz or 500 MHz on a Bruker Avance DPX-300 instrument or Bruker AMX-500 instrument. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker Avance DPX-300 instrument referenced to the appropriate $CHCl_3$ [δ = 7.26 (^{1}H), δ = 77.16 (^{13}C)], MeOH [δ = 3.31 (^{1}H), δ = 49.0 (^{13}C)], or DMSO peak [δ = 2.50 (^{1}H), δ = 39.5 (^{13}C)].

(2*E*,4*E*)-5-(Dimethylamino)penta-2,4-dienal (2a)

Me_2NH (50 mL, 40 wt% in H_2O, 394.8 mmol) was added to a stirred soln of Zincke salt **1a** (50 g, 177.6 mmol) in EtOH (300 mL) at r.t. The mixture was stirred at reflux for 90 min, concentrated in vacuo, and treated with cold H_2O (250 mL). The yellow 2,4-dinitroaniline was removed by filtration through Celite. The filtrate was basified with 5 M NaOH soln (100 mL) and extracted with CH_2Cl_2 (4 × 100 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give **2a** as an orange-brown solid; yield: 18.5 g (83%); mp 56 °C.

IR: 2913, 1556, 1012, 973, 836 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.88 (s, 6 H, CH_3), 5.18 (dd, *J* = 12.3, 11.5 Hz, 1 H, CH), 5.73 (dd, *J* = 14.3, 8.4 Hz, 1 H, CH), 6.73 (d, *J* = 12.3 Hz, 1 H, CH), 7.03 (dd, *J* = 14.3, 11.5 Hz, 1 H, CH), 9.2 (d, *J* = 8.4 Hz, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.7, 97.1, 119.5, 152.7, 156.8, 192.2.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_7H_{11}NNaO$: 148.0738; found: 148.0738.

(2*E*,4*E*)-5-Hydroxypenta-2,4-dienal Potassium Salt (4a)[9b]

KOH (1.58 g, 85%, 24.0 mmol) was dissolved in MeOH (5 mL) under argon. THF (45 mL) was added, followed by the addition of **2a** (3 g, 24.0 mmol). The mixture was stirred at reflux for 5 h, the slurry was cooled in an ice bath, and Et_2O (100 mL) was added. The brown solid was filtered and rinsed with CH_2Cl_2 (200 mL). The crude solid was dissolved in MeOH–EtOH (9:1, 300 mL) and filtered through Celite. The filtrate was concentrated in vacuo to give **4a** as a brown solid; yield: 3.05 g (93%); mp >400 °C.

IR: 2786, 1595, 1516, 1370, 1186, 1021, 847, 649 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.11 (dd, *J* = 13.1, 9.2 Hz, 2 H, 2 CH), 7.05 (t, *J* = 13.1 Hz, 1 H, CH), 8.67 (d, *J* = 9.2 Hz, 2 H, 2 CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 106.7, 160.3, 184.9.

MS (ESI$^-$): *m*/*z* (%) = 97 ([M – K]$^-$, 100).

(2*E*,4*E*)-5-(Dimethylamino)-2-methylpenta-2,4-dienal (2b)

Me_2NH (95 mL, 40 wt% in H_2O, 357.1 mmol) was added to a stirred soln of Zincke salt **1b** (105.6 g, 357.1 mmol) in EtOH (300 mL) at r.t. The mixture was stirred at reflux for 1 h, concentrated in vacuo, and treated with cold H_2O (200 mL). The yellow 2,4-dinitroaniline was removed by filtration through Celite. The filtrate was washed with Et_2O (5 × 300 mL), basified with 5 M NaOH soln (200 mL), and extracted with CH_2Cl_2 (5 × 400 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give **2b** as a red solid; yield: 42 g (84%); mp 73 °C.

IR: 2909, 1555, 1380, 1187, 957, 800 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3), 2.96 (s, 6 H, 2 CH_3), 5.22 (t, *J* = 12.5 Hz, 1 H, CH), 6.76 (d, *J* = 12.5 Hz, 1 H, CH), 6.85 (d, *J* = 12.5 Hz, 1 H, CH), 9.18 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.19, 41.2 (br s), 95.0, 126.1, 151.5, 153.7, 192.8.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_8H_{14}NO$: 140.1075; found: 140.1078.

(2*E*,4*E*)-5-Hydroxy-2-methylpenta-2,4-dienal Potassium Salt (4b)

KOH (7.57 g, 85%, 114.9 mmol) was dissolved in MeOH (23 mL) under argon. THF (160 mL) was added, followed by the addition of **2b** (16 g, 115.0 mmol). The mixture was stirred at reflux for 6 h, the slurry was cooled in an ice bath, and Et_2O (500 mL) was added. The brown solid was filtered and rinsed with CH_2Cl_2 (1 L). The crude solid was dissolved EtOH (800 mL). The soln was cooled to –20 °C and filtered through Celite. The filtrate was concentrated in vacuo to give **4b** as a yellow solid; yield: 14.02 g (80%); mp >400 °C.

IR: 3164, 2974, 1502, 1342, 1712, 1604, 1502, 1342, 1263, 1203, 1190, 1000, 824 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.50 (s, 3 H, CH_3), 5.10 (dd, *J* = 12.7, 9.3 Hz, 1 H, CH), 6.92 (d, *J* = 12.7 Hz, 1 H, CH), 8.57 (s, 1 H, CH), 8.68 (d, *J* = 9.3 Hz, 1 H, CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 9.7, 103.9, 111.1, 158.9, 183.5, 183.6.

HRMS (ESI$^-$): *m*/*z* [M – K]$^-$ calcd for $C_6H_7O_2$: 111.0446; found: 111.0437.

1-(2,4-Dinitrophenyl)-3-(2-hydroxyethyl)pyridinium Chloride (1c)

A soln of 1-chloro-2,4-dinitrobenzene (2.02 g, 10 mmol) and 3-(2-hydroxyethyl)pyridine (1.2 g, 9.76 mmol) in acetone (20 mL) was stirred at reflux for 16 h. The mixture was cooled to 0 °C and the white slurry was filtered and rinsed with acetone to afford **1c** as a light brown solid; yield: 2.55 g (78%); mp 158 °C.

IR: 3216, 2947, 1609, 1538, 1340, 1053, 819, 735, 683 cm^{-1}.

^{1}H NMR (500 MHz, CD_3OD): δ = 3.21 (t, *J* = 5.5 Hz, 2 H, CH_2), 3.97 (br t, *J* = 5.5 Hz, 2 H, CH_2), 8.36 (dd, *J* = 9.0, 6.0 Hz, 1 H, CH), 8.38 (d, *J* = 9.0 Hz, 1 H, CH), 8.91 (dt, *J* = 9.0, 1.5 Hz, 1 H, CH), 8.95 (dd, *J* = 9.0, 3.0 Hz, 1 H, CH), 9.23 (dt, *J* = 6.0, 1.5 Hz, 1 H, CH), 9.29 (d, *J* = 3.0 Hz, 1 H, CH), 9.30 (br s, 1 H, CH).

^{13}C NMR (75 MHz, CD_3OD): δ = 36.7, 61.7, 123.2, 128.8, 131.1, 132.7, 140.2, 143.3, 144.6, 144.8, 146.9, 150.7, 151.1.

HRMS (ESI$^+$): *m*/*z* [M – Cl]$^+$ calcd for $C_{13}H_{12}N_3O_5$: 290.0777; found: 290.0776.

(2*E*,4*E*)-5-(Dimethylamino)-2-(2-hydroxyethyl)penta-2,4-dienal (2c)

A 5.6 M soln of Me_2NH in EtOH (14 mL, 78.4 mmol) was added to a stirred soln of Zincke salt **1c** (12 g, 36.9 mmol) in EtOH (300 mL) at r.t. under argon. The mixture was stirred at reflux for 1 h, concentrated in vacuo, and treated with cold H_2O (100 mL). The yellow 2,4-dinitroaniline was removed by filtration through Celite. The filtrate was washed with Et_2O (3 × 50 mL), basified with 2.5 M NaOH soln (25 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give **2c** as a red solid; yield: 3.18 g (51%); mp 74 °C.

IR: 3225, 2953, 2901, 2833, 1631, 1537, 1342, 678 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.91 (s, 6 H, 2 CH_3), 3.25 (br s, 1 H, OH), 3.58 (t, *J* = 6.4 Hz, 2 H, CH_2), 5.29 (t, *J* = 12.3 Hz, 1 H, CH), 6.79 (d, *J* = 12.3 Hz, 1 H, CH), 6.88 (d, *J* = 12.3 Hz, 1 H, CH), 9.05 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1, 40.9 (br s), 61.8, 94.6, 126.5, 153.0, 156.1, 193.1.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_9H_{16}NO_2$: 170.1181; found: 170.1181.

(2*E*,4*E*)-5-Hydroxy-2-(2-hydroxyethyl)penta-2,4-dienal Potassium Salt (4c)

KOH (545 mg, 85%, 8.27 mmol) was dissolved in MeOH (4 mL) under argon. THF (25 mL) was added, followed by the addition of **2c** (1.4 g, 8.28 mmol). The mixture was stirred at reflux for 5 h then the slurry was cooled in an ice bath and Et_2O (50 mL) was added. The brown solid was filtered and rinsed with CH_2Cl_2 (100 mL). The crude solid was dissolved EtOH (50 mL). The soln was cooled to –30 °C and filtered through Celite. The filtrate was concentrated in vacuo to give **4c** as a light brown solid; yield: 1.25 g (83%); mp 250 °C (dec).

IR: 3251, 2904, 2799, 1503, 1327, 1196, 1164, 1031, 687 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.29 (t, *J* = 7.5 Hz, 2 H, CH_2), 3.28 (t, *J* = 7.5 Hz, 2 H, CH_2), 5.25 (dd, *J* = 13.0, 9.0 Hz, 1 H, CH), 6.94 (d, *J* = 13.0 Hz, 1 H, CH), 8.54 (s, 1 H, CH), 8.73 (d, *J* = 9.0 Hz, 1 H, CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 28.9, 60.2, 104.0, 113.2, 159.6, 184.0, 184.3.

HRMS (ESI$^-$): *m*/*z* [M – K]$^-$ calcd for $C_7H_9O_3$: 141.0552; found: 141.0550.

1-(2,4-Dinitrophenyl)-3-(10-hydroxydecyl)pyridinium Chloride (1d)

A soln of 1-chloro-2,4-dinitrobenzene (12.5 g, 61.7 mmol) and 3-(10-hydroxydecyl)pyridine[16] (13.2 g, 56.1 mmol) in MeOH (20 mL) was stirred at reflux for 48 h under argon. H_2O (60 mL) was added. The aqueous phase was washed with CH_2Cl_2 (3 × 50 mL) and concentrated in vacuo to give **1d** as a sticky red foam; yield: 21.4 g (87%).

IR: 3340, 3013, 2923, 2852, 1611, 1538, 1341 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 1.27–1.42 (m, 14 H, 7 CH_2), 1.70–1.76 (m, 2 H, CH_2), 2.92 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.40 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.42 (br s, 1 H, OH), 8.22 (dd, *J* = 8.1, 6.0 Hz, 1 H, CH), 8.31 (d, *J* = 8.7 Hz, 1 H, CH), 8.68 (d, *J* = 8.1 Hz, 1 H, CH), 8.83 (dd, *J* = 8.7, 2.5 Hz, 1 H, CH), 9.1 (d, *J* = 2.5 Hz, 1 H, CH), 9.14 (d, *J* = 6.0 Hz, 1 H, CH), 9.24 (s, 1 H, CH).

^{13}C NMR (75 MHz, CD_3CN): δ = 26.7, 29.4, 29.9, 30.0, 30.1, 30.2, 30.8, 33.1, 33.7, 62.4, 123.0, 128.9, 131.3, 132.9, 139.7, 144.4, 144.5, 145.4, 146.1, 149.7, 150.7.

HRMS (ESI$^+$): *m*/*z* [M – Cl]$^+$ calcd for $C_{21}H_{28}N_3O_5$: 402.2029; found: 402.2039.

(2*E*,4*E*)-5-Hydroxy-2-(10-hydroxydecyl)penta-2,4-dienal Potassium Salt (4d)

A 5.6 M Me_2NH soln in EtOH (10 mL, 56 mmol) was added to a stirred soln of Zincke salt **1d** (14 g, 26.5 mmol) in EtOH (200 mL) at r.t. under argon. The mixture was stirred at reflux for 1 h, concentrated in vacuo, and treated with cold H_2O (600 mL). The yellow 2,4-dinitroaniline was removed by filtration through Celite. The filtrate was washed with Et_2O (5 × 300 mL), basified with 2.5 M NaOH soln (60 mL), and extracted with CH_2Cl_2 (3 × 300 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a mixture of **2d** and **3d** (7.4 g). The crude residue was used without further purification.

KOH (1.5 g, 85%, 22.7 mmol) was dissolved in MeOH (4.5 mL) under argon. A soln of crude **2d** and **3d** in THF (41 mL) was added. The mixture was stirred at reflux for 5 h then the slurry was cooled in an ice bath and Et_2O (200 mL) was added. The green solid was filtered and rinsed with CH_2Cl_2 (100 mL). The crude solid was dissolved MeOH (20 mL). The soln was cooled to –30 °C, filtered through Celite. The filtrate was concentrated in vacuo to give **4c** as a green solid; yield: 4.7 g (71%); mp 166–167 °C.

IR: 3261, 2915, 2847, 1606, 1503, 1366, 1332, 1271, 1191, 1092 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.22–1.48 (m, 16 H, 8 CH_2), 2.02 (br s, 2 H, CH_2), 3.35 (t, *J* = 6.3 Hz, 2 H, CH_2), 5.11 (dd, *J* = 12.8, 9.3 Hz, 1 H, CH), 6.81 (d, *J* = 12.8 Hz, 1 H, CH), 8.52 (s, 1 H, CH), 8.63 (d, *J* = 9.3 Hz, 1 H, CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 24.2, 25.5, 27.9, 28.9, 29.1, 29.4, 32.5, 60.6, 103.1, 116.9, 158.6, 183.3, 183.7.

HRMS (ESI$^+$): *m*/*z* calcd for $C_{15}H_{26}O_3Na$ [M – K + H + Na]$^+$: 277.1780; found: 277.1776.

(2*E*,4*E*)-5-Hydroxy-2-methoxypenta-2,4-dienal Potassium Salt (4e)

A 5.6 M soln of Me_2NH in EtOH (7 mL, 39.2 mmol) was added to a stirred soln of Zincke salt **1e** (4.90 g, 15.71 mmol) in EtOH (80 mL) at r.t. under argon. The mixture was stirred at reflux for 30 min, concentrated in vacuo, and treated with cold H_2O (80 mL). The yellow 2,4-dinitroaniline was removed by filtration through Celite. The filtrate was basified with 1 M NaOH soln (80 mL) and extracted with CH_2Cl_2 (4 × 100 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a mixture of **2e** and **3e** (2.22 g, 91%). The crude residue was used without further purification.

KOH (943 mg, 85%, 14.29 mmol) was dissolved in MeOH (3 mL) under argon. A soln of crude **2e** and **3e** in THF (20 mL) was added. The mixture was stirred at reflux for 3 h then the slurry was cooled in an ice bath and Et_2O (30 mL) was added. The brown solid was filtered and rinsed with CH_2Cl_2 (50 mL). The crude solid was dissolved in EtOH (50 mL). The soln was cooled to –20 °C and filtered through Celite. The filtrate was concentrated in vacuo to give **4e** as a beige solid; yield: 1.54 g (65%); mp 166 °C (dec).

IR: 2989–2755, 1491, 1256, 1126, 1029, 1000, 745 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 3.59 (s, 3 H, OCH_3), 5.69 (dd, *J* = 11.9, 11.9 Hz, 1 H, CH), 6.94 (d, *J* = 11.9 Hz, 1 H, CH), 8.20 (s, 1 H, CHO), 8.58 (d, *J* = 11.9 Hz, 1 H, CH).

^{13}C NMR (75 MHz, CD_3OD): δ = 59.3, 105.9, 143.0, 154.1, 178.8, 186.3.

HRMS (ESI⁻): *m/z* [M – K]⁻ calcd for $C_6H_7O_3$: 127.0395; found: 127.0393.

(2*E*,4*E*)-2-Bromo-5-(dimethylamino)penta-2,4-dienal (2f)[13]
Br_2 (1.68 mL, 32.9 mmol) in CH_2Cl_2 (10 mL) was added to a stirred soln of **2a** (3.43 g, 27.4 mmol) in CH_2Cl_2 (60 mL) at –10 °C and under argon. After 30 min at r.t., Et_2O was added and the slurry was filtered and rinsed with Et_2O. The solid was dissolved in CH_2Cl_2 (100 mL) and the organic layer was washed with sat. aq $NaHCO_3$ (100 mL) and brine (100 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (CH_2Cl_2–MeOH, 9:1) to give **2f** as a brown solid; yield: 4.61 (82%); mp 96 °C.

IR: 2907, 2802, 1607, 1538, 1385, 1216, 1128, 992, 806, 681 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 2.69 (br s, 3 H, CH_3), 2.83 (br s, 3 H, CH_3), 5.24 (dd, *J* = 12.5, 11.4 Hz, 1 H, CH), 6.74 (d, *J* = 12.5 Hz, 1 H, CH), 7.05 (d, *J* = 11.4 Hz, 1 H, CH), 8.69 (s, 1 H, CHO).

¹³C NMR (75 MHz, $CDCl_3$): δ = 37.2, 45.1, 97.1, 111.0, 153.3, 155.1, 183.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for $C_7H_{11}{}^{79}BrNO$: 204.0024; found: 204.0018; calcd for $C_7H_{11}{}^{81}BrNO$: 206.0004; found: 205.9998.

(2*E*,4*E*)-2-Bromo-5-hydroxypenta-2,4-dienal Potassium Salt (4f)
KOH (2.84 g, 85%, 50.8 mmol) was dissolved in MeOH (10 mL) under argon. THF (60 mL) was added, followed by the addition of **2f** (10.38 g, 50.8 mmol). The mixture was stirred at reflux for 5 h then cooled in an ice bath. The brown slurry was filtered and rinsed with CH_2Cl_2 (100 mL). The crude solid was dissolved EtOH (1 L). The soln was cooled to –20 °C and filtered through Celite. The filtrate was concentrated in vacuo to give **4f** as a light brown solid; yield: 7.53 g (69%); mp >400 °C.

IR: 2797, 1618, 1503, 1353, 1129, 820 cm⁻¹.

¹H NMR (300 MHz, CD_3OD): δ = 5.83 (dd, *J* = 12.6, 9.3 Hz, 1 H, CH), 7.60 (d, *J* = 12.6 Hz, 1 H, CH), 8.48 (s, 1 H, CHO), 8.86 (d, *J* = 9.3 Hz, 1 H, CH).

¹³C NMR (75 MHz, CD_3OD): δ = 102.4, 112.0, 159.9, 179.5, 189.7.

HRMS (ESI⁻): *m/z* [M – K]⁻ calcd for $C_5H_4{}^{79}BrO_2$: 174.9395; found: 174.9387; calcd for $C_5H_4{}^{81}BrO_2$: 176.9374; found: 176.9369.

2-Substituted Aminopentadienals 5; General Procedure
Glutaconaldehyde **4** (2.1 mmol) was added to a stirred soln of alkylammonium trifluoroacetate salt (2 mmol) in CH_2Cl_2 (10 mL); H_2O (1 drop) was added. After 30 min, the mixture was quenched with sat. aq $NaHCO_3$ (25 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a 2-substituted aminopentadienal.

(2*E*,4*E*)-5-(Benzylamino)penta-2,4-dienal (5a)
Red oil; yield: 186 mg (98%).

IR: 3253, 3026, 1556, 1139, 748, 698 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 4.31 (br s, 2 H, CH_2), 5.39 (br s, 1 H, NH), 5.49 (dd, *J* = 12.8, 11.6 Hz, 1 H, CH), 5.82 (dd, *J* = 14.4, 8.4 Hz, 1 H, CH), 6.95 (dd, *J* = 12.8, 8.4 Hz, 1 H, CH), 7.10 (dd, *J* = 14.4, 11.6 Hz, 1 H, CH), 7.20–7.49 (m, 5 H, 5 H_{Ar}), 9.29 (d, *J* = 8.4 Hz, 1 H, CHO).

¹³C NMR (75 MHz, $CDCl_3$): δ = 48.7, 98.6, 120.7, 127.1, 127.2, 128.8, 137.1, 149.3, 157.2, 192.7.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for $C_{12}H_{14}NO$: 188.1075; found: 188.1082.

(2*E*,4*E*)-5-(Dibenzylamino)penta-2,4-dienal (5b)
Brown oil; yield: 86 mg (97%).

IR: 3027, 1657, 1565, 1130, 696 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 4.26 (s, 4 H, 2 CH_2), 5.41 (dd, *J* = 12.8, 11.6 Hz, 1 H, CH), 5.74 (dd, *J* = 14.6, 8.4 Hz, 1 H, CH), 7.00 (d, *J* = 12.8 Hz, 1 H, CH), 7.04–7.33 (m, 11 H, 10 H_{Ar}, CH), 9.23 (d, *J* = 8.4 Hz, 1 H, CHO).

¹³C NMR (75 MHz, $CDCl_3$): δ = 53.2, 98.3, 121.1, 127.0, 127.5, 128.1, 128.2, 128.5, 129.0, 135.7, 140.4, 151.8, 156.5, 192.5.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for $C_{19}H_{20}NO$: 278.1545; found: 278.1547.

(2*E*,4*E*)-5-(Benzylamino)-2-methylpenta-2,4-dienal (5c)[1a]
Orange solid; yield: 2.4 g (79%).

(2*E*,4*E*)-5-(Butylamino)-2-methylpenta-2,4-dienal (5d)[4a]
Red solid; yield: 2.5 g (82%).

(2*E*,4*E*)-5-(4-Methoxybenzylamino)-2-methylpenta-2,4-dienal (5e)
Red solid; yield: 4.0 g (82%); mp 83–84 °C.

IR: 3220, 2958, 2831, 1548, 1511, 1173, 808 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, CH_3), 3.81 (s, 3 H, CH_3), 4.25 (d, *J* = 5.3 Hz, 2 H, CH_2), 5.26 (br s, 1 H, NH), 5.54 (t, *J* = 12.1 Hz, 1 H, CH), 6.85 (d, *J* = 12.1 Hz, 1 H, CH), 6.90 (d, *J* = 8.4 Hz, 2 H, CH_2), 6.93 (dd, *J* = 12.1, 8.4 Hz, 1 H, CH), 7.23 (d, *J* = 8.4 Hz, 2 H, CH_2), 9.17 (s, 1 H, CH).

¹³C NMR (75 MHz, $CDCl_3$): δ = 9.17, 55.4, 96.3, 114.3, 127.2, 129.1, 129.3, 147.5, 153.7, 159.4, 193.1.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for $C_{14}H_{17}NNaO_2$: 254.1157; found: 254.1169.

(2*E*,4*E*)-5-(Benzylamino)-2-(2-hydroxyethyl)penta-2,4-dienal (5f)
The residue was purified by flash chromatography (CH_2Cl_2–MeOH, 98:2) to give **5f** as an orange solid; yield: 150 mg (70% from **4c**); mp 107 °C.

IR: 3452, 3257, 3022, 2925, 2556, 2356, 1537, 1454, 1385, 1315, 1193, 1006, 819, 749, 701 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 2.54 (t, *J* = 6.5 Hz, 2 H, CH_2), 2.79 (br s, 1 H, OH), 3.63 (t, *J* = 6.5 Hz, 2 H, CH_2OH), 4.34 (d, *J* = 6 Hz, 2 H, CH_2), 5.52 (br s, 1 H, NH), 5.62 (dd, *J* = 12.0, 12.0 Hz, 1 H, CH), 6.96 (d, *J* = 12.0 Hz, 1 H, CH), 6.99 (dd, *J* = 12.0, 9.0 Hz, 1 H, CH), 7.25–7.42 (m, 5 H, 5 H_{Ar}), 9.18 (s, 1 H, CHO).

¹³C NMR (75 MHz, $CDCl_3$): δ = 28.2, 49.0, 62.0, 96.2, 127.7, 127.9, 128.0, 129.0, 137.0, 149.3, 156.0, 193.9.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for $C_{14}H_{17}NNaO_2$: 254.1157; found: 254.1156.

(*E*)-12-Hydroxy-2-[(*E*)-3-(4-methoxybenzylamino)prop-2-enylidene]dodecanal (5g)
Red oil; yield: 4.62 g (88%).

IR: 3294, 2921, 2850, 1607, 1564, 1555, 1509, 1440, 1244, 1170, 1084, 1170, 1083, 1032, 811 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): δ = 1.25 (m, 14 H, 7 CH_2), 1.53 (m, 2 H, CH_2), 2.22 (t, *J* = 7.5 Hz, 2 H, CH_2), 3.59 (t, *J* = 6.4 Hz, 2 H, CH_2), 3.77 (br s, 1 H, OH), 3.78 (s, 3 H, OCH_3), 4.24 (br s, 2 H, CH_2N), 5.53 (t, *J* = 12.2 Hz, 1 H, CH), 5.57 (br s, 1 H, NH), 6.78 (d, *J* = 12.2 Hz, 1 H, CH), 6.86–6.70 (m, 3 H, 3 CH), 7.21 (d, *J* = 8.5 Hz, 2 H, 2 CH), 9.10 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 25.8, 28.6, 29.4, 29.5, 29.6, 29.7, 32.8, 55.3, 62.8, 96.2, 113.9, 114.2, 128.3, 128.9, 129.3, 131.9, 147.8, 154.0, 159.2, 192.9.

HRMS (ESI$^+$): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{35}NNaO_3$: 396.2515; found: 396.2516.

(2*Z*,4*E*)-2-Methoxy-5-(4-methoxybenzylamino)penta-2,4-dienal (5h)

Dark red oil; yield: 339 mg (92%).

IR: 3285, 2932, 2834, 1555, 1509, 1440, 1243, 1142, 1029, 813, 748 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.21 (s, 2 H, CH_2), 5.64 (dd, *J* = 12.4, 12.4 Hz, 1 H, CH), 5.80 (s, 1 H, NH), 6.44 (d, *J* = 12.4 Hz, 1 H, CH), 6.86 (d, *J* = 7.7 Hz, 2 H, H_{Ar}), 6.92 (d, *J* = 12.4 Hz, 1 H, CH), 7.12 (d, *J* = 7.7 Hz, 2 H, H_{Ar}), 8.86 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.9, 55.3, 59.3, 93.4, 113.9, 114.1, 128.9, 142.9, 147.4, 147.6, 159.1, 185.4.

HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{14}H_{18}NO_3$: 248.1287; found: 248.1278.

(2*Z*,4*E*)-5-(Benzylamino)-2-bromopenta-2,4-dienal (5i)[17]

The residue was purified by flash chromatography (CH_2Cl_2–MeOH, 100:0 then 97.5:2.5) to give **5i** as an orange solid; yield: 261 mg (63%, from **4f**); mp 155 °C.

IR: 3184, 3001, 1590, 1504, 1450, 1111, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35–4.44 (m, 2 H, CH_2), 5.16 (br s, 1 H, NH), 5.85 (dd, *J* = 12.5, 11.5 Hz, 1 H, CH), 7.06–7.16 (m, 1 H, CH), 7.22–7.45 (m, 6 H, 5 H_{Ar}, CH), 9.06 (s, 1 H, CHO).

HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{12}H_{13}{}^{79}BrNO$: 266.0181; found: 266.0178; calcd for $C_{12}H_{13}{}^{81}BrNO$: 268.0156; found: 268.0160.

(2*Z*,4*E*)-2-Bromo-5-(4-methoxybenzylamino)penta-2,4-dienal (5j)

The residue was purified by flash chromatography (CH_2Cl_2–MeOH, 100:0 then 97.5:2.5) to give **5j** as an orange oil; yield: 315 mg (53%, from **4f**).

IR: 3223, 3026, 1592, 1501, 1115, 810, 685 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 4.34 (d, *J* = 6.9 Hz, 2 H, CH_2), 5.71–5.91 (m, 1 H, CH), 6.83–6.98 (m, 3 H, 2 H_{Ar}, CH), 7.15–7.40 (m, 4 H, 2 H_{Ar}, CH, NH), 8.85 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.3, 55.3, 97.5, 111.7, 114.2, 128.2, 129.1, 152.1, 154.5, 159.1, 184.0.

HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{13}H_{15}{}^{79}BrNO$: 296.0286; found: 296.0281; calcd for $C_{13}H_{15}{}^{81}BrNO$: 298.0266; found: 298.0262.

(*E*)-3-Hydroxypent-2-enal Potassium Salt (7)

KOH (8.46 g, 85%, 128.4 mmol) was dissolved in MeOH (30 mL) under argon. THF (180 mL) was added, followed by the addition of 3-(dimethylamino)pent-2-enal (**6**, 15 g, 151.3 mmol). The mixture was stirred at reflux for 5 h then the slurry was cooled in an ice bath and Et_2O (100 mL) was added. The brown solid was filtered and rinsed with CH_2Cl_2 (200 mL). The crude solid was dissolved in MeOH (300 mL) and filtered through Celite. The filtrate was concentrated in vacuo to give **7** as an orange solid; yield: 13.24 g (93%); mp 280 °C (dec).

IR: 3366, 2768, 1712, 1555, 1348, 1262, 1167, 1020, 818 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 5.25 (t, *J* = 10.0 Hz, 1 H, CH), 8.63 (d, *J* = 10.0 Hz, 2 H, 2 CH).

^{13}C NMR (75 MHz, CD_3OD): δ = 110.2, 192.2.

(*E*)-3-(Benzylamino)pent-2-enal (8)

Malonaldehyde salt **7** (104 mg, 0.94 mmol) was added to a stirred soln of TFA (72 μL, 0.93 mmol) and $BnNH_2$ (100 μL, 0.92 mmol) in CH_2Cl_2 (5 mL); H_2O (1 drop) was added. After 30 min, the mixture was quenched with sat. aq $NaHCO_3$ (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to give **8** as an orange oil; yield: 125 mg (84%).

IR: 3212, 3022, 2769, 1583, 1168 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.94–4.04 (br s, 2 H_A, CH_2), 4.11 (d, *J* = 6.0 Hz, 2 H_B, CH_2), 4.75 (dd, *J* = 7.0, 2.1 Hz, 1 H_A, CH), 5.07 (dd, *J* = 13.1, 8.1 Hz, 1 H_B, CH), 5.43–5.72 (br s, 1 H_B, NH), 6.54 (ddd, *J* = 12.9, 7.0, 3.0 Hz, 1 H_A, CH), 6.92–7.12 (m, 5 H_A, 6 H_B, 10 H_{Ar}, CH), 8.81–8.84 (m, 1 H_B, CH), 8.85 (dd, *J* = 3.0, 2.1 Hz, 1 H_A, CH), 9.74–10.07 (m, 1 H_A, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.4, 95.2, 127.2, 127.9, 128.2, 128.9, 129.0, 137.3, 154.4, 188.5.

MS (EI, 70 eV): *m/z* (%) = 161 ([M]$^+$, 47), 91 (100).

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