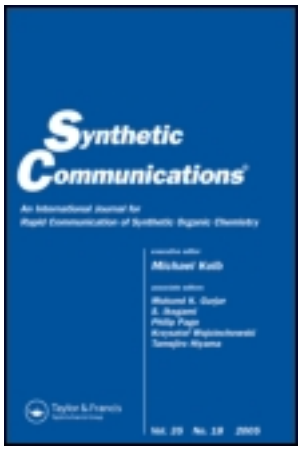

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Synthesis of Aryl-Substituted 1,3-Butadiones

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Synthesis of Aryl-Substituted 1,3-Butadiones

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ABSTRACT

The synthesis of several electron donor substituted 1-aryl-1,3-butadiones and their use as ligands in the formation of scandium(III) complexes is reported.

Key Words: Ketone; Scandium complexes; Acetylacetonate ligands.

Acetyl acetonates are well known ligands for the preparation of stable complexes with many metal ions. The reaction of lithiated imines of acetone with esters followed by imine hydrolysis is a general synthetic route for the preparation of 1-substituted 1,3-butadiones. We report here the synthesis of some electron rich 1-aryl-1,3-butadiones by this method.

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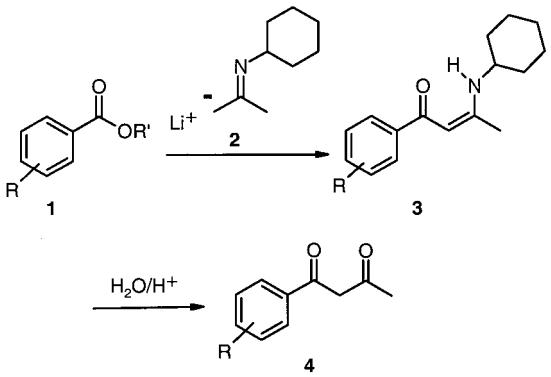
Alkyl aminobenzoates (**1**)[1] as readily available starting materials[2] were reacted with lithiated *N*-isopropylidene cyclohexylamine[3] (**2**) in THF at 0°C to the intermediate keto enamines **3**, which were hydrolyzed to give the target 1,3-butadiones **4**[4] (Sch. 1a). The hydrolysis of **3** is slow in acetic acid/THF at room temp., but much faster if refluxed in a mixture of aqueous 2 M HCl and acetone.

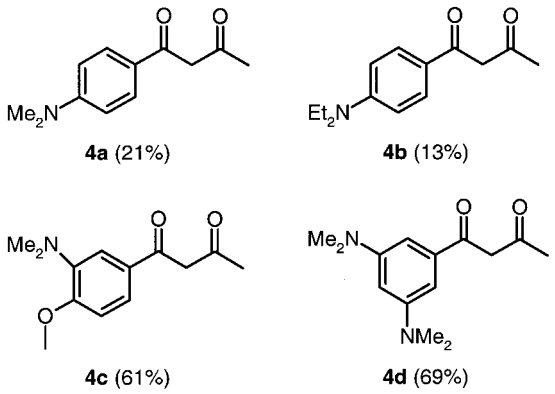
A 1,3-butadione in which the electron rich arene is separated from the dicarbonyl moiety was synthesized starting from **5**, which reacted with ethyl acetate and sodium to give ester **6**.[5] The double bond was hydrogenated and the reaction of the ester with **2** followed by acid catalyzed hydrolysis gave compound **8** (Sch. 2).

Proton and carbon NMR spectra of compounds **4a–d** (Sch. 1b) show signals for keto- and enol-tautomers with the enol form as the major isomer (80–90%). The fraction of the enol tautomere is smaller in **8** (65%) due to the lack of direct conjugation with the aromatic system. The absorption in UV/Vis spectra of compounds **4a–d** reaches longer wavelength and is more intensive as for the parent aromatic chromophore *N*,*N*-dimethylaniline.[6] Like *N*,*N*-dimethylaniline[7] compounds **4a–d** emit light upon excitation, but their emission maxima are shifted bathochromically. The photophysical properties of **8** are, as expected, similar to that of *N*,*N*-dimethyl-aniline. The redox potentials of compounds **4a–d** and **8** were examined by cyclic voltammetry and are summarized in Table 1. The oxidation of **4a–d** requires a more positive potential (+150 −200 mV) than the corresponding anilines due to the electron withdrawing character of the conjugated 1,3-butadione moiety.

Compounds **4a–d** were deprotonated with ammonia[10] and reacted with scandium(III) chloride to yield the corresponding complexes **9a–d**



Scheme 1a. Synthesis of amino-substituted 1-aryl-1,3-butadiones.



Scheme 1b. Synthesis of amino-substituted 1-aryl-1,3-butadiones.

Table 1. Electrochemical data of **4a–d** and **8**.

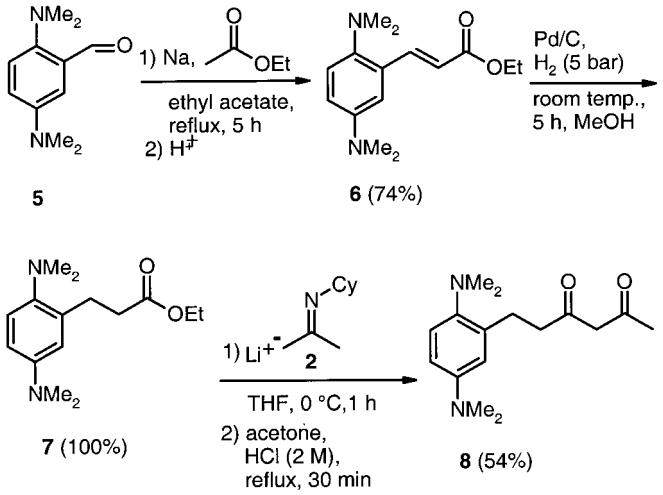
	4a	**4b**	**4c**	**4d**	**8**
$E_{p,a}^{a,b}$[V]	0.51 (0.37)[8]	0.52 (0.32)[8]	0.36 (0.16)[9]	0.23 (−0.04)[9]	−0.09[c]

[a]Potentials were determined by cyclic voltammetry in 0.1 M NBu_4PF_6 CH_3CN solution *vs* Fc/Fc^+ at 298 K with a scan rate of 0.1 V/s.
[b]$E_{p,a}$ = anodic peak potential; the oxidation is irreversible under the experimental conditions. Oxidation potential for the corresponding anilines are given in parenthesis. Reduction of the 1,3-butadione moiety requires potentials more negative than −2.24 V *vs* Fc/Fc^+.
[c]Formal reduction potential; redox process is reversible.

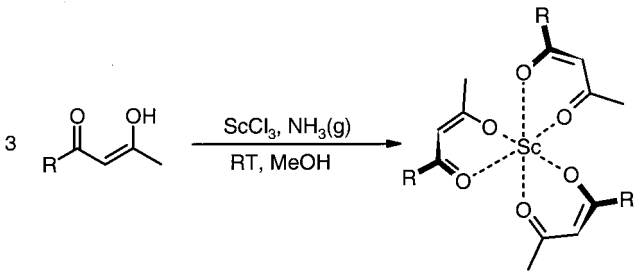
(Sch. 3). The UV/Vis absorption of the complexes is shifted bathochromic and their emission intensities are drastically reduced in comparison with the corresponding ligands. The oxidation potentials of **9a** (0.72 V)[11] and **9b** (0.70 V) are more positive as in the ligands, while **9c** (0.43) and **9d** (0.21) have similar oxidation potentials as the corresponding non-coordinated 1,3-butadiones.

EXPERIMENTAL

All ^1H NMR spectra were recorded at 400 MHz, all ^{13}C NMR spectra at 100 MHz in $CDCl_3$. The multiplicity of the ^{13}C signals



Scheme 2. Synthesis of 1,3-butadione 8.



4a: R = 4-Me_2N-C_6H_4-	9a: R = 4-Me_2N-C_6H_4-	(74%)
4b: R = 4-Et_2N-C_6H_4-	9b: R = 4-Et_2N-C_6H_4-	(62%)
4c: R = 3-Me_2N-4-MeO-C_6H_3-	9c: R = 3-Me_2N-4-MeO-C_6H_3-	(74%)
4d: R = 3,5-$(Me_2N)_2$-C_6H_3-	9d: R = 3,5-$(Me_2N)_2$-C_6H_3-	(67%)

Scheme 3. Synthesis of scandium(III) acetyl acetonate complexes.

was determined with the DEPT technique and quoted as: (+) for CH_3 or CH, (−) for CH_2 and (C_{quat}) for quaternary carbons. CC means column chromatography on silica gel. PE means petrol ether with a boiling range of 60–70°C. EA means ethyl acetate.

1-(4-*N*,*N*-Dimethylaminophenyl)-1,3-butadione (4a).[4] To a solution of *N*-isopropylidene cyclohexylamine (1.52 g, 11 mmol) in THF (100 mL) was added at 0°C LDA (12 mmol), the mixture was stirred

for 30 min, methyl 4-*N*,*N*-dimethylaminobenzoate (1.93 g, 10 mmol) was added and the reaction mixture was kept at room temp. overnight. The solvent was removed *in vacuo*, dichloromethane (100 mL) and diluted aqueous acetic acid (10 mL) were added and the mixture was stirred for 2 h. The organic phase was separated, washed with water, dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by CC (CH_2Cl_2/MeOH, 99:1) to give 280 mg (21%) of **4a** ($R_f = 0.44$); yellow solid, M.p. 113°C. IR (KBr): $\tilde{\nu} = 2916\,cm^{-1}$, 1611, 1377, 1189, 783, 505. UV/Vis (CH_3CN): λ_{max} (lg ε) = 200 nm (4.273), 244 (3.776), 362 (4.395). ^1H NMR: $\delta = 2.12$ (s, 3H, enol), 2.25 (s, 3H, keto), 3.04 (s, 6H, enol), 3.05 (s, 6H, keto), 3.98 (s, 2H, keto), 6.06 (s, 1H, enol), 6.64 (m, 4H, keto and enol), 7.81 (m, 4H, keto and enol), 16.52 (s, 1H, enol). ^{13}C NMR: $\delta = 24.9$ (+), 30.2 (+), 39.9 (+), 39.9 (+), 54.7 (−), 94.9 (+), 110.7 (+), 111.0 (+), 122.0 (C_{quat}), 129.0 (+), 131.0 (+), 153.1 (C_{quar}), 185.1 (C_{quat}), 189.4 (C_{quat}). MS (70 eV), *m*/*z* (%): 205 (100) [M^+], 190 (38) [$M^+ - CH_3$], 162 (4) [$M^+ - C(O)CH_3$]. $-C_{12}H_{15}NO_2$: calcd. C 70.22, H 7.37, N 6.82; found C 70.04, H 7.30, N 6.81.

1-(4-*N*,*N*-Diethylaminophenyl)-1,3-butadione (4b). *N*-Isopropylidene cyclohexylamine (1.95 g, 14 mmol), LDA (14 mmol) and ethyl 4-*N*,*N*-diethylaminobenzoate (2.21 g, 10 mmol) were allowed to react as described for **4a**. The solution was neutralized with 7.5 mL of HCl (2 M), evaporated to a volume of 30 mL, dichloromethane (200 mL) was added and the organic phase was separated, washed with sat. aqueous NH_4Cl (4 × 50 mL), water (1 × 50 mL), dried over Na_2SO_4 and evaporated *in vacuo*. CC (CH_2Cl_2/MeOH 99:1) yielded 300 mg (13%) of **4b** ($R_f = 0.44$); yellow solid, M.p. 53°C. IR (KBr): $\tilde{\nu} = 2971\,cm^{-1}$, 2931, 2900, 1603, 1522, 1196, 1009, 779. UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (4.279), 246 (3.749), 372 (4.530). ^1H NMR: $\delta = 1.22$ (m, 12H, keto and enol), 2.13 (s, 3H, enol), 2.28 (s, 3H, keto), 3.43 (m, 8H, keto and enol), 3.97 (s, 2H, keto), 6.05 (s, 1H, enol), 6.64 (m, 4H, keto and enol), 7.80 (m, 4H, keto and enol), 16.55 (s, 1H, OH, enol). ^{13}C NMR: $\delta = 12.4$ (+), 12.5 (+), 24.8 (+), 30.2 (+), 44.5 (−), 44.5 (−), 54.7 (−), 94.7 (+), 110.2 (+), 110.5 (+), 121.2 (C_{quat}), 129.3 (+), 131.3 (C_{quat}), 150.9 (C_{quat}), 185.0 (C_{quat}), 189.0 (C_{quar}). MS (70 eV), *m*/*z* (%): 233 (42) [M^+], 218 (100) [$M^+ - CH_3$], 190 (10) [$M^+ - C(O)CH_3$]. $-C_{14}H_{19}NO_2$: Calcd. C 72.07, H 8.21, N 6.00; found C 72.03, H 8.21, N 5.97.

1-(3-*N*,*N*-Dimethylamino-4-methoxyphenyl)-1,3-butadione (4c). *N*-Isopropylidene cyclohexylamine (1.64 g, 12 mmol), LDA (12 mmol) and methyl 3-*N*,*N*-dimethylamino-4-methoxybenzoate (1.68 g, 8 mmol) were reacted and worked up as described before. To the obtained yellow oil was added water (10 mL), aqueous HCl (10 mL, 2 M) and acetone (80 mL) and the mixture was refluxed for 2.5 h. Aqueous $NaHCO_3$ was

added to adjust the pH to neutral, the mixture was diluted with dichloromethane (100 mL), the organic phase was separated, washed with sat. aqueous NH_4Cl and water, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by CC (CH_2Cl_2/MeOH 99:1) to yield 1.14 g (61%) of **4c** ($R_f = 0.25$) as a yellow oil. IR (KBr): $\tilde{\nu} = 2944\,cm^{-1}$, 2834, 2783, 1592, 1510, 1252, 781. UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.166), 200 (4.155), 256 (4.194), 284 (4.059), 314 (4.075). ^1H NMR: $\delta = 2.17$ (s, 3H, enol), 2.28 (s, 3H, keto), 2.83 (s, 12H, keto and enol), 3.88 (s, 2H, keto), 3.95 (s, 3H, enol), 4.05 (s, 3H, keto), 6.11 (s, 1H, enol), 6.87 (m, 2H, keto and enol), 7.60 (m, 4H, keto and enol), 16.34 (s, 1H, enol). ^{13}C NMR: $\delta = 25.1$ (+), 43.1 (+), 43.2 (+), 54.8 (−), 55.6 (+), 55.7 (+), 95.8 (+), 110.1 (+), 110.4 (+), 116.9 (+), 122.5 (+), 124.9 (C_{quat}), 127.7 (C_{quat}), 155.9 (C_{quat}), 184.9 (C_{quat}), 190.9 (C_{quat}). MS (70 eV), *m*/*z* (%): 235 (100) [M^+], 220 (76) [$M^+ - CH_3$]. $-C_{13}H_{17}NO_3$: Calcd. C 66.35, H 7.29, N 5.96; found C 66.69, H 7.39, N 5.89.

1-[3,5-(*N*,*N*,*N*′,*N*′-Tetramethylamino)phenyl]-1,3-butadione (4d). *N*-Isopropylidene cyclohexylamine (735 mg, 5.3 mmol) dissolved in THF (50 mL) was treated with 5.3 mmol of LDA at 0°C as described before. Methyl 3,5-*N*,*N*,*N*′,*N*′-tetramethylaminobenzoate (790 mg, 3.6 mmol) was added at 0°C, the mixture was stirred at room temp. overnight, dichloromethane (100 mL) was added, the solution was washed with sat. aqueous NH_4Cl (3 × 100 mL) and water (1 × 100 mL), dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The yellow residue was heated in 50 mL of acetone and 3 mL of HCl (2 M) for 3 h to reflux, the reaction mixture was diluted with dichloromethane (200 mL) and adjusted to neutral pH with sat. aqueous $NaHCO_3$. The organic phase was separated, washed with sat. aqueous NH_4Cl and water, dried over $MgSO_4$ and the solvent was removed *in vacuo*. CC (CH_2Cl_2/MeOH 99:1) of the crude product gave 610 mg (69%) of **4d** ($R_f = 0.64$) as a yellow solid, M.p. 88°C. IR (KBr): $\tilde{\nu} = 2914\,cm^{-1}$, 2817, 1591, 1492, 1442, 1384, 1243, 771. UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.051), 240 (4.471), 296 (4.107), 340 (3.866). ^1H NMR: $\delta = 2.11$ (s, 3H, enol), 2.19 (s, 3H, keto), 2.91 (s, 24H, keto and enol), 3.98 (s, 2H, keto), 6.06 (s, 1H, enol), 6.13 (m, 2H, keto and enol), 6.57 (d, $^4J = 2.2$ Hz, 2H, enol), 6.62 (d, $^4J = 2.3$ Hz, 2H, keto), 16.20 (s, 1H, enol). ^{13}C NMR: $\delta = 25.6$ (+), 40.7 (+), 40.8 (+), 55.5 (−), 96.9 (+), 100.7 (+), 100.8 (+), 102.0 (+), 136.3 (C_{quat}), 151.6 (C_{quat}), 185.8 (C_{quat}), 192.7 (C_{quat}). MS (70 eV), *m*/*z* (%): 248 (100) [M^+], 233 (30) [$M^+ - CH_3$], 205 (76) [$M^+ - C(O)CH_3$]. $-C_{14}H_{20}N_2O_2$: Calcd. C 67.70, H 8.12, N 11.29; found C 67.68, H 8.23, N 11.11.

***Tris*[1-(4-*N*,*N*-dimethylaminophenyl)-1,3-butadionate]scandium(III) (9a).** 1-(4-*N*,*N*-Dimethylaminophenyl)-1,3-butadione (100 mg, 0.48 mmol) (**4a**) and scandium(III) chloride (27 mg, 0.11 mmol) were dissolved in 30 mL of methanol. Ammonia was bubbled through the solution and **9a** precipitates. The crystals were collected by filtration and washed with a small amount of methanol. Yield: 54 mg (74%) of **9a** as yellow crystals, M.p. 257°C. IR (KBr): $\tilde{\nu} = 2919\,cm^{-1}$, 2871, 2809, 1570, 1502, 778, 424. UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (4.817), 244 (4.278), 316 (4.244), 386 (5.046). ^1H NMR: $\delta = 2.10$ (s, 9H), 3.00 (s, 18H), 6.15 (s, 3H), 6.59 (d, $^3J = 9.0$ Hz, 6H), 7.86 (d, $^3J = 9.0$ Hz, 6H). ^{13}C NMR: $\delta = 27.5$ (+), 40.1 (+), 97.8 (+), 110.8 (+), 125.3 (C_{quat}), 129.8 (+), 152.6 (C_{quat}), 183.0 (C_{quat}), 190.4 (C_{quat}). MS (70 eV), *m*/*z* (%): 657 (32) [M^+], 453 (100) [$M^+ - C_{12}H_{14}NO_2$].

***Tris*[1-(4-*N*,*N*-diethylaminophenyl)-1,3-butandionate]scandium(III) (9b).** 1-(4-*N*,*N*-Diethylaminophenyl)-1,3-butadione (90 mg, 0.38 mmol) (**4b**) and scandium(III) chloride (22 mg, 0.09 mmol) were dissolved in 15 mL of methanol and ammonia was bubbled through the solution. The precipitated crystals were collected by filtration after 2 h, washed with water and dried to give 42 mg (62%) of **9a** as yellow crystals, M.p. 218°C. IR (KBr): $\tilde{\nu} = 2971\,cm^{-1}$, 2928, 1607, 1569, 1502, 1193, 777, 428. UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (4.803), 246 (4.222), 318 (4.244), 396 (5.050). ^1H NMR: $\delta = 1.17$ (t, $^3J = 7.0$ Hz, 18H), 2.08 (s, 9H), 3.36 (q, $^3J = 7.0$ Hz, 12H), 6.11 (s, 3H), 6.55 (d, $^3J = 9.0$ Hz, 6H), 7.83 (d, $^3J = 9.0$ Hz, 6H). ^{13}C NMR: $\delta = 12.5$ (+), 27.5 (+), 44.4 (−), 97.5 (+), 110.2 (+), 124.5 (C_{quat}), 130.1 (+), 150.1 (C_{quat}), 182.9 (C_{quat}), 190.0 (C_{quat}). MS (70 eV), *m*/*z* (%): 741 (78) [M^+], 509 (100) [$M^+ - C_{14}H_{19}NO_2$].

***Tris*[1-(3-*N*,*N*-dimethylamino-4-methoxyphenyl)-1,3-butandionate]scandium(III) (9c).** A solution of 1-(3-*N*,*N*-dimethylamino-4-methoxyphenyl)-1,3-butadione (200 mg, 0.85 mmol) (**4c**) and scandium(III) chloride (47 mg, 0.19 mmol) in 10 mL of methanol was treated with ammonia as described above and left overnight. Precipitated crystals were collected by filtration and washed with a small amount of methanol to yield 105 mg (74%) of **9c** as yellow crystals, M.p. 142°C. IR (KBr):$\tilde{\nu} = 2942\,cm^{-1}$, 2831, 2781, 1548, 1532, 1274, 779, 427. UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.727), 204 (4.721), 262 (4.680), 354 (4.712). ^1H NMR: $\delta = 2.14$ (s, 9H), 2.72 (s, 18H), 3.91 (s, 9H), 6.20 (s, 3H), 6.79 (d, $^3J = 8.5$ Hz, 3H), 7.54 (d, $^4J = 2.0$ Hz, 3H), 7.60 (dd, $^3J = 8.5$ Hz, $^4J = 2.0$ Hz, 3H). ^{13}C NMR: $\delta = 27.6$ (+), 43.1 (+), 55.5 (+), 98.8 (+), 110.1 (+), 117.9 (+), 123.1 (+), 130.6 (C_{quat}), 141.9 (C_{quat}), 155.3 (C_{quat}), 183.1 (C_{quat}), 192.3 (C_{quat}). MS (70 eV), *m*/*z* (%): 747 (86) [M^+], 513 (100) [$M^+ - C_{13}H_{16}NO_3$].

***Tris*[1-(3,5-*N*,*N*,*N*′,*N*′-tetramethylamino)phenyl-1,3-butandionate]scandium(III) (9d).** 1-[3,5-*N*,*N*,*N*′,*N*′-Tetramethylamino)phenyl]-1,3-butadione (100 mg, 0.4 mmol) (**4d**) and scandium(III) chloride (22 mg, 0.09 mmol) in 10 mL of methanol were treated with ammonia, overnight precipitated crystals were collected by filtration and washed with a small amount of methanol to yield 47 mg (67%) of **9d** as yellow crystals, M.p. 181°C. IR (KBr): $\tilde{\nu} = 2919\,cm^{-1}$, 2875, 2849, 2795, 1554, 1512, 1373, 1061, 778, 427. UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.584), 242 (4.932), 336 (4.618). ^1H NMR: $\delta = 2.12$ (s, 9H), 2.90 (s, 36H), 6.16 (t, $^4J = 2.2$ Hz, 3H), 6.19 (s, 3H), 6.72 (d, $^4J = 2.2$ Hz, 6H). ^{13}C NMR: $\delta = 27.6$ (+), 40.9 (+), 99.9 (+), 100.9 (+), 102.4 (+), 139.5 (C_{quat}), 151.4 (C_{quat}), 185.3 (C_{quat}), 192.6 (C_{quat}). MS (70 eV), *m*/*z* (%): 786 (100) [M^+], 539 (54) [$M^+ - C_{14}H_{19}N_2O_2$].

Ethyl *trans*-{3-[2,5-(*N*,*N*,*N*′,*N*′-tetramethylamino)phenyl]}acrylate (6). A solution of 2,5-(*N*,*N*,*N*′,*N*′-tetramethylamino)benzaldehyde (520 mg, 2.7 mmol) (**5**) in ethyl acetate (10 mL) was added at 0°C to sodium (75 mg, 3.3 mmol) in ethyl acetate (10 mL), the reaction mixture was refluxed for 5 h and then stirred overnight at room temp. Glacial acetic acid (0.25 mL) was added, the solution was washed with water, dried over Na_2SO_4 and the solvents were removed *in vacuo*. CC (PE/EA 7:3) of the crude product gave 530 mg (74%) of **6** ($R_f = 0.66$) as a yellow oil. IR (KBr): $\tilde{\nu} = 3037\,cm^{-1}$, 2979, 2826, 2786, 1711, 1505, 1168. UV/Vis (CH_3CN): λ_{max} (lg ε) = 204 nm (4.204), 268 (4.292), 398 (3.365). ^1H NMR: $\delta = 1.34$ (t, $^3J = 7.1$ Hz, 3H), 2.66 (s, 6H,), 2.90 (s, 6H), 4.26 (q, $^3J = 7.1$ Hz, 2H), 6.40 (d, $^3J = 16.1$ Hz, 1H) 6.80 (d, $^3J = 8.2$ Hz, 1H), 6.90 (s, 1H), 7.02 (d, $^3J = 8.2$ Hz, 1H), 8.13 (d, $^3J = 16.1$ Hz, 1H). ^{13}C NMR: $\delta = 14.3$ (+), 41.6 (+), 45.6 (+), 60.2 (−), 111.7 (C_{quat}), 116.1 (+), 117.5 (+), 119.7 (+), 129.3 (+), 129.4 (+),142.9 (C_{quat}), 143.0 (C_{quat}), 167.5 (C_{quat}). MS (70 eV), *m*/*z* (%): 262 (100) [M^+], 247 (12) [$M^+ - CH_3$]. $C_{15}H_{22}N_2O_2$: Calcd. C 68.67, H 8.45, N 10.68; found C 68.43, H 8.75, N 10.42.

Ethyl 3-[2,5-(*N*,*N*,*N*′,*N*′-tetramethylamino)phenyl]propionate (7). A mixture of ethyl *trans*-{3-[2,5-(*N*,*N*,*N*′,*N*′-tetramethylamino)phenyl]} acrylate (500 mg, 1.9 mmol) (**6**) and 30 mg of palladium on charcoal (10%) in 75 mL of methanol were pressurized with hydrogen (5 bar) for 5 h at room temp. The reaction mixture was filtered through celite, methanol was distilled off *in vacuo* and the crude product was purified by CC (PE/EA 8:2) to give 500 mg (quantitative yield) of **7** ($R_f = 0.34$) as a yellow oil. IR (KBr): $\tilde{\nu} = 3029\,cm^{-1}$, 2977, 2883, 2855, 1733, 1450, 1174, 944. UV/Vis (CH_3CN): λ_{max} (lg ε) = 208 nm (4.399), 262 (4.159), 312 (3.391). ^1H NMR: $\delta = 1.25$ (t, $^3J = 7.1$ Hz, 3H), 2.61 (s, 6H), 2.65 (m, 2H), 2.88 (s, 6H), 3.00 (m, 2H), 4.14 (q, $^3J = 7.1$ Hz, 2H), 6.61 (m, 2H),

7.07 (d, $^3J = 8.4$ Hz, 1H). ^{13}C NMR: $\delta = 14.2$ (+), 27.1 (−), 35.3 (−), 41.0 (+), 45.8 (+), 60.2 (−), 111.7 (+), 114.3 (+), 121.1 (+), 136.9 (C_{quat}), 143.2 (C_{quat}), 147.6 (C_{quat}), 173.6 (C_{quat}). MS (70 eV), *m/z* (%): 264 (100) [M^+]. $-C_{15}H_{24}N_2O_2$: calcd. C 68.15, H 9.15, N 10.60; found C 67.92, H 8.96, N 10.54.

6-[2,5-(*N*,*N*,*N*′,*N*′-Tetramethylamino)phenyl]-2,4-hexandione (**8**). To a solution of *N*-isopropylidene cyclohexylamine (420 mg, 3 mmol) and LDA (3 mmol) in THF (20 mL) at 0°C was added ethyl 3-[2,5-(*N*,*N*,*N*′,*N*′-tetramethylamino)phenyl]propionate (360 mg, 1.4 mmol, **7**) and the mixture was left overnight at room temp. Aqueous HCl (10 mL, 2 M) was added, the solution was refluxed for 30 min, the pH was then adjusted to neutral by addition of sat. aqueous $NaHCO_3$ and ethyl acetate was added for dilution. The organic phase was separated, washed with water, dried over Na_2SO_4 and the solvent was removed *in vacuo*. CC (PE/EA 1:1) yielded 210 mg (54%) of **8** ($R_f = 0.46$) as a yellow orange oil. IR (KBr): $\tilde{\nu} = 2934\ cm^{-1}$, 2856, 2820, 2761, 1609, 1510, 941. UV/Vis (CH_3CN): λ_{max} (lg ε) = 208 nm (4.391), 264 (4.295), 348 (2.705). ^{1}H NMR: $\delta = 2.04$ (s, 3H, enol), 2.21 (s, 3H, keto), 2.61 (m, 16H, keto and enol), 2.88 (m, 16H, keto and enol), 3.57 (s, 2H, keto), 5.53 (s, 1H, enol), 6.58 (m, 4H, keto and enol), 7.07 (m, 2H, keto and enol), 15.52 (s, 1H, enol). ^{13}C NMR: $\delta = 24.8$ (+), 26.1 (−), 27.5 (−), 39.4 (−), 41.0 (+), 44.9 (−), 45.9 (+), 57.8 (−), 99.8 (+), 111.7 (+), 114.2 (+), 121.0 (+), 136.9 (C_{quat}), 143.1 (C_{quat}), 147.6 (C_{quat}), 190.9 (C_{quat}), 194.2 (C_{quat}). MS (70 eV), *m/z* (%): 276 (100) [M^+]. $-C_{16}H_{24}N_2O_2$: calcd. C 69.53, H 8.75, N 10.14; found C 69.65, H 8.72, N 10.10.

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