

Highly Regioselective α -Alkylation of $\alpha,\beta,\gamma,\delta$ -Unsaturated Aldehydes Through Morita–Baylis–Hillman-Type Reaction

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1. General information

All the reagents and catalysts were purchased from Aldrich, TCI, and used without further purification unless otherwise mentioned. All the solvents were purchased from Merck or SD Fine and used for the purification of products. Thin-layer chromatography (SiO₂, TLC) was performed on Merck TLC silica gel 60 F₂₅₄ visualized by ultraviolet irradiation, KMnO₄ solution or iodine staining. Column chromatography was performed on Merck silica gel 60-120 using standard flash chromatographic methods. The NMR spectra were recorded on Bruker Advance III (500 MHz) spectrometer and were referenced against the residual solvent peaks [CDCl₃: δ 7.26 ppm (¹H NMR) and 77.00 ppm (¹³C NMR)]. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Infrared spectra were recorded on Perkin Elmer Spectrum Two FT-IR spectrometer. Selected absorption bands are reported in wavenumbers (cm⁻¹). The HRMS data for all the compounds was recorded (in positive ion mode) with Waters Synapt-G2S ESI-Q-TOF Mass instrument. Aldehyde **1g**,¹ Michler's hydrol **2a**,² (4-(diethylamino)phenyl)(4-(dipropylamino)phenyl)methanol **2b**³ and 9H-thioxanthen-9-ol **2d**⁴ were prepared according to the reported procedure.

2. General procedure for the Reaction optimization for the regioselective α -alkylation of $\alpha,\beta,\gamma,\delta$ -unsaturated aldehyde **1d**

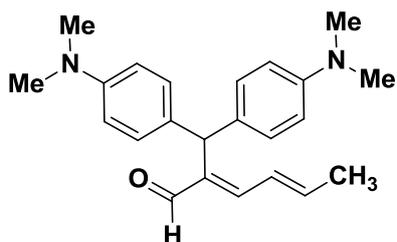
To a solution of alcohol **2a** (65 mg, 0.24 mmol) in solvent, catalyst and aldehyde **1d** (30 mg, 0.20 mmol) and acid additive (as mentioned in Table 1) were added and stirred for the stated time. Then, the reaction mixture was diluted with Et₂O (2 mL) and quenched with saturated aq. NaHCO₃. The reaction mixture was then extracted with Et₂O (10 mL) and the separated Organic layer was filtered through a short pad of silica using Et₂O (30 ml) and dried over anhydrous sodium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, hexane/EtOAc) in case of isolated yield.

3. Experimental procedure and characterization data for products **5aa–5fc**

Alcohol **2a** or **2d** (0.24 mmol) was dissolved in DCE (200 μ L) into a glass vial. To the above solution pyrrolidine (5.0 μ L, 0.06 mmol), aldehyde **1** (0.20 mmol) and benzoic acid (as mentioned in Table 2) were added and stirred vigorously at room temperature. After stated time reaction was diluted with Et₂O (2 mL) and quenched with saturated aq.

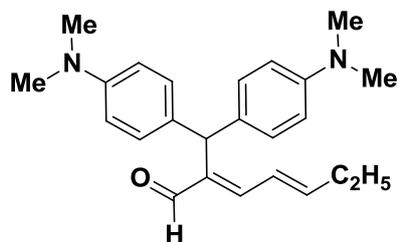
NaHCO₃. The reaction mixture was then extracted with Et₂O (10 mL) and the separated Organic layer was filtered through a short pad of silica using Et₂O (30 ml) and dried over anhydrous sodium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, hexane/EtOAc).

(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)hexa-2,4-dienal (5aa)



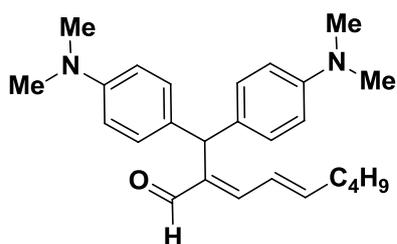
The reaction was performed by following the experimental procedure and the product **5aa** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (60 mg, 86% yield). ¹H NMR: δ 9.44 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.97-6.90 (m, 1H), 6.67 (d, *J* = 7.0 Hz, 4H), 6.27-6.14 (m, 2H), 5.49 (s, 1H), 2.91 (s, 12H), 1.76 (d, *J* = 5.5 Hz, 3H). ¹³C NMR: δ 194.6, 150.3, 149.2, 149.1, 141.9, 141.3, 130.4, 129.7, 129.5, 128.1, 112.7, 45.1, 40.8, 19.1. FTIR (film) ν_{max}: 2926, 2855, 2805, 1681, 1635, 1613, 1519, 1447, 1351, 1165, 1126, 1070, 948, 814, 713 cm⁻¹. ESI-HRMS calculated for C₂₃H₂₈N₂O (M+H)⁺: 349.2274 and found: 349.2275.

(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)hepta-2,4-dienal (5ba)



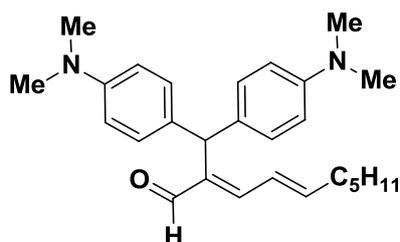
The reaction was performed by following the experimental procedure and the product **5ba** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (60 mg, 83% yield). ¹H NMR: δ 9.45 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.93-6.92 (m, 1H), 6.67 (d, *J* = 7.5 Hz, 4H), 6.20-6.19 (m, 2H), 5.51 (s, 1H), 2.91 (s, 12H), 2.08 (bs, 2H), 0.90-0.88 (m, 3H). ¹³C NMR: δ 194.7, 150.7, 149.2, 147.8, 142.2, 130.5, 129.6, 125.7, 112.8, 45.1, 40.8, 26.2, 12.5. FTIR (film) ν_{max}: 2926, 2849, 2805, 1680, 1633, 1614, 1519, 1349, 1227, 1124, 948, 814, 714 cm⁻¹. ESI-HRMS calculated for C₂₄H₃₀N₂O (M+H)⁺: 363.2431 and found: 363.2407.

(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)nona-2,4-dienal (5ca)



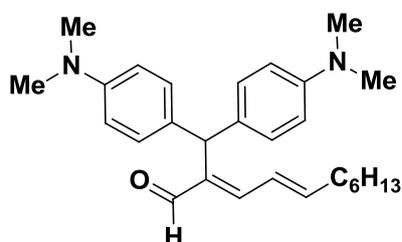
The reaction was performed by following the experimental procedure and the product **5ca** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (66 mg, 85% yield). $^1\text{H NMR}$: δ 9.45 (s, 1H), 7.00 (d, $J = 9.0$ Hz, 4H), 6.93-6.91 (m, 1H), 6.67 (d, $J = 8.5$ Hz, 4H), 6.22-6.11 (m, 2H), 5.51 (s, 1H), 2.91 (s, 12H), 2.07-2.03 (m, 2H), 1.31-1.20 (m, 4H), 0.85 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$: δ 194.6, 150.7, 149.2, 146.5, 142.2, 130.4, 129.6, 126.7, 112.7, 45.0, 40.8, 32.8, 30.4, 22.1, 13.8. **FTIR** (film) ν_{max} : 2926, 2856, 2799, 1681, 1633, 1614, 1519, 1455, 1350, 1165, 948, 814 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 391.2744 and found: 391.2723.

(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)deca-2,4-dienal (5da)



The reaction was performed by following the experimental procedure and the product **5da** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (69 mg, 85% yield). $^1\text{H NMR}$: δ 9.44 (s, 1H), 7.00 (d, $J = 7.0$ Hz, 4H), 6.93-6.91 (m, 1H), 6.68 (bs, 4H), 6.22-6.12 (m, 2H), 5.50 (s, 1H), 2.91 (s, 12H), 2.05-2.04 (m, 2H), 1.30-1.20 (m, 6H), 0.87 (bs, 3H). $^{13}\text{C NMR}$: δ 194.6, 150.7, 149.2, 146.6, 142.1, 129.6, 126.7, 112.7, 45.1, 40.8, 33.1, 29.7, 27.9, 22.4, 14.0. **FTIR** (film) ν_{max} : 2923, 2859, 2793, 1685, 1609, 1513, 1446, 1345, 1188, 954, 809 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{27}\text{H}_{36}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 405.2900 and found: 405.2916.

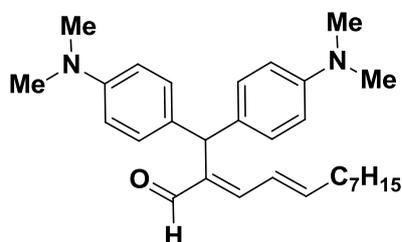
(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)undeca-2,4-dienal (5ea)



The reaction was performed by following the experimental procedure and the product **5ea** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (70 mg, 84% yield). $^1\text{H NMR}$: δ 9.45 (s, 1H), 7.00 (d, $J = 7.5$ Hz, 4H), 6.93-6.91 (m, 1H), 6.67 (d, $J = 7.5$ Hz, 4H), 6.22-6.12 (m, 2H), 5.51 (s, 1H), 2.91 (s, 12H), 2.05-2.04 (m, 2H), 1.29-1.22 (m, 8H), 0.88-0.87 (m, 3H). $^{13}\text{C NMR}$: δ 194.6, 150.7, 149.2, 146.6, 142.1, 130.4, 129.6, 126.7, 112.7, 45.1, 40.8, 33.2, 31.8, 29.7, 28.3, 22.7, 14.1. **FTIR** (film) ν_{max} : 2925, 2880, 2855, 1680, 1632, 1614, 1518, 1348, 1165,

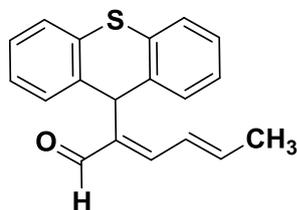
1126, 948, 813, 800 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{28}\text{H}_{38}\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺: 419.3057 and found: 419.3070.

(2E,4E)-2-(bis(4-(dimethylamino)phenyl)methyl)dodeca-2,4-dienal (5fa)



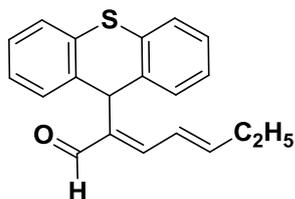
The reaction was performed by following the experimental procedure and the product **5fa** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (74 mg, 86% yield). **¹H NMR**: δ 9.48 (s, 1H), 7.01 (d, J = 8.0 Hz, 4H), 6.93-6.91 (m, 1H), 6.67 (d, J = 7.5 Hz, 4H), 6.23-6.13 (m, 2H), 5.51 (s, 1H), 2.92 (s, 12H), 2.05-2.04 (m, 2H), 1.30-1.24 (m, 10H), 0.89-0.88 (m, 3H). **¹³C NMR**: δ 194.7, 150.7, 149.2, 146.6, 142.1, 130.4, 129.7, 129.6, 126.7, 123.5, 112.7, 45.1, 40.8, 40.7, 33.2, 31.9, 31.6, 29.7, 28.7, 28.2, 22.7, 22.6, 14.1. **FTIR** (film) ν_{max} : 2923, 2885, 2859, 1685, 1609, 1513, 1445, 1345, 1189, 954, 809 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺: 433.3213 and found: 433.3242.

(2E,4E)-2-(9H-thioxanthen-9-yl)hexa-2,4-dienal (5ad)



The reaction was performed by following the experimental procedure and the product **5ad** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.7:0.3) as a pale yellow sticky liquid (55 mg, 94% yield). **¹H NMR**: δ 9.70 (s, 1H), 7.41 (d, J = 7.5 Hz, 2H), 7.36-7.34 (m, 1H), 7.19-7.16 (m, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.05-7.04 (m, 2H), 6.38-6.31 (m, 1H), 6.26-6.21 (m, 1H), 5.30 (s, 1H), 1.77 (d, J = 7.0 Hz, 3H). **¹³C NMR**: δ 193.8, 153.3, 143.6, 137.8, 135.1, 132.7, 128.7, 127.5, 126.7, 126.5, 126.3, 41.1, 19.1. **FTIR** (film) ν_{max} : 3059, 2922, 2853, 1680, 1634, 1457, 1378, 1189, 1114, 969, 748 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{19}\text{H}_{16}\text{OS}$ ($\text{M}+\text{H}$)⁺: 293.0995 and found: 293.1001.

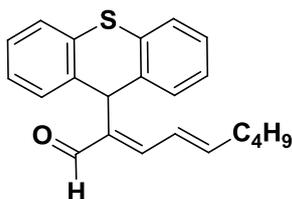
(2E,4E)-2-(9H-thioxanthen-9-yl)hepta-2,4-dienal (5bd)



The reaction was performed by following the experimental procedure and the product **5bd** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.7:0.3) as a pale yellow sticky liquid (57 mg, 93% yield). **¹H NMR**: δ 9.68 (s,

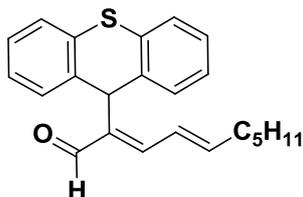
1H), 7.40 (d, $J = 7.5$ Hz, 2H), 7.33-7.31 (m, 1H), 7.17 (t, $J = 7.0$ Hz, 2H), 7.12 (t, $J = 7.5$ Hz, 2H), 7.07-7.05 (m, 2H), 6.39-6.33 (m, 1H), 6.26-6.20 (m, 1H), 5.34 (s, 1H), 2.13-2.07 (m, 2H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR: δ 193.8, 153.4, 150.2, 138.4, 135.1, 132.6, 127.8, 126.7, 126.4, 126.3, 41.1, 26.4, 12.7. **FTIR** (film) ν_{max} : 3053, 2922, 2853, 2716, 1680, 1632, 1458, 1378, 1191, 1122, 971, 748 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{20}\text{H}_{18}\text{OS}$ ($\text{M}+\text{H}^+$): 307.1151 and found: 307.1163.

(2E,4E)-2-(9H-thioxanthen-9-yl)nona-2,4-dienal (5cd)



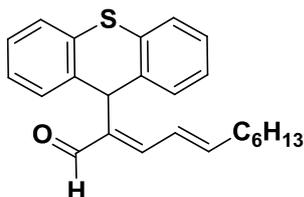
The reaction was performed by following the experimental procedure and the product **5cd** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.3) as a pale yellow sticky liquid (61 mg, 91% yield). ^1H NMR: δ 9.70 (s, 1H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.35-7.33 (m, 1H), 7.19-7.11 (m, 4H), 7.07-7.06 (m, 2H), 6.33-6.29 (m, 1H), 6.23-6.18 (m, 1H), 5.33 (s, 1H), 2.07-2.06 (m, 2H), 1.32-1.29 (m, 2H), 1.22-1.18 (m, 2H), 0.82 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 193.8, 153.5, 148.9, 138.1, 135.1, 132.7, 127.7, 127.4, 126.7, 126.4, 126.3, 41.1, 32.9, 30.5, 22.0, 13.7. **FTIR** (film) ν_{max} : 3060, 2956, 2928, 2858, 2716, 2716, 1678, 1630, 1457, 1441, 1184, 1122, 974, 747 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{22}\text{H}_{22}\text{OS}$ ($\text{M}+\text{H}^+$): 335.1464 and found: 335.1459.

(2E,4E)-2-(9H-thioxanthen-9-yl)deca-2,4-dienal (5dd)



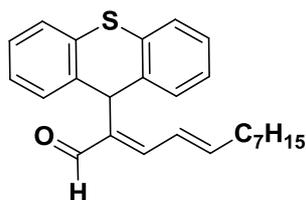
The reaction was performed by following the experimental procedure and the product **5dd** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.3) as a pale yellow sticky liquid (65 mg, 93% yield). ^1H NMR: δ 9.69 (s, 1H), 7.42-7.40 (m, 2H), 7.35-7.33 (m, 1H), 7.17 (t, $J = 7.0$ Hz, 2H), 7.16-7.11 (m, 2H), 7.07-7.05 (m, 2H), 6.34-6.23 (m, 1H), 6.21-6.18 (m, 1H), 5.33 (s, 1H), 2.08-2.04 (m, 2H), 1.35-1.29 (m, 2H), 1.26-1.19 (m, 2H), 1.18-1.13 (m, 2H), 0.85-0.82 (m, 3H). ^{13}C NMR: δ 193.8, 153.6, 149.0, 135.1, 132.7, 127.6, 127.4, 126.7, 126.5, 126.3, 41.1, 33.2, 31.1, 28.1, 22.4, 14.0. **FTIR** (film) ν_{max} : 3061, 2955, 2923, 2853, 2728, 1680, 1632, 1457, 1376, 1200, 1120, 947, 747 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{23}\text{H}_{24}\text{OS}$ ($\text{M}+\text{H}^+$): 349.1621 and found: 349.1622.

(2E,4E)-2-(9H-thioxanthen-9-yl)undeca-2,4-dienal (**5ed**)



The reaction was performed by following the experimental procedure and the product **5ed** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.3) as a yellow sticky liquid (67 mg, 92% yield). $^1\text{H NMR}$: δ 9.69 (s, 1H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.35-7.33 (m, 1H), 7.19-7.16 (m, 2H), 7.14-7.11 (m, 2H), 7.07-7.05 (m, 2H), 6.34-6.29 (m, 1H), 6.23-6.18 (m, 1H), 5.33 (s, 1H), 2.08-2.05 (m, 2H), 1.31-1.30 (m, 2H), 1.26-1.23 (m, 2H), 1.18 (s, 4H), 0.87-0.84 (m, 3H). $^{13}\text{C NMR}$: δ 193.8, 153.6, 149.0, 138.0, 135.1, 132.7, 127.6, 127.4, 126.7, 126.5, 126.3, 41.1, 33.2, 31.5, 28.6, 28.4, 22.5, 14.0. **FTIR** (film) ν_{max} : 3066, 2926, 2856, 2716, 1680, 1631, 1457, 1378, 1198, 1119, 971, 747 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{24}\text{H}_{26}\text{OS}$ ($\text{M}+\text{H}$) $^+$: 363.1777 and found: 363.1759.

(2E,4E)-2-(9H-thioxanthen-9-yl)dodeca-2,4-dienal (**5fd**)



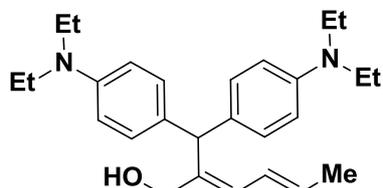
The reaction was performed by following the experimental procedure and the product **5fd** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (71 mg, 94% yield). $^1\text{H NMR}$: δ 9.70 (s, 1H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.35-7.33 (m, 1H), 7.19-7.11 (m, 4H), 7.07-7.05 (m, 2H), 6.34-6.29 (m, 1H), 6.23-6.18 (m, 1H), 5.33 (s, 1H), 2.08-2.04 (m, 2H), 1.33-1.25 (m, 4H), 1.19 (bs, 6H), 0.88-0.86 (m, 3H). $^{13}\text{C NMR}$: δ 193.8, 153.6, 149.0, 138.0, 135.1, 132.7, 127.6, 126.7, 126.5, 126.3, 41.1, 33.2, 31.7, 29.0, 28.9, 28.4, 22.6, 14.1. **FTIR** (film) ν_{max} : 3066, 2923, 2853, 1684, 1634, 1459, 1278, 1197, 1116, 974, 747 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{25}\text{H}_{28}\text{OS}$ ($\text{M}+\text{H}$) $^+$: 377.1934 and found: 377.1947.

4. Experimental procedure and characterization data for products **6ab–6cc**

Alcohol **2b** or **2c** (0.24 mmol) was dissolved in DCE (200 μL) into a glass vial. To the above solution pyrrolidine (5.0 μL , 0.06 mmol), aldehyde (0.20 mmol) and benzoic acid (as mentioned in Table 2) were added and stirred vigorously at room temperature. After stated time, reaction was diluted with MeOH (2 mL) and cooled to 0 $^{\circ}\text{C}$. NaBH_4 (76 mg, 2.0 mmol) was then slowly added and reaction mixture was stirred for 3 h at the same temperature before quenched with H_2O and extracted with DCM (10 x 3 mL). Organic

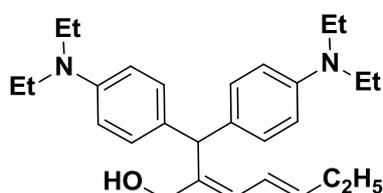
layer was dried over anhydrous sodium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (SiO₂, hexane/EtOAc).

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)hexa-2,4-dienal (6ab)



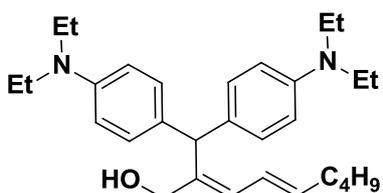
The reaction was performed by following the experimental procedure and the product **6ab** was purified by flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a yellow sticky liquid (76 mg, 94% yield). ¹H NMR: δ 7.04 (d, *J* = 8.0 Hz, 4H), 6.63 (d, *J* = 8.5, 4H), 6.36-6.30 (m, 2H), 5.80-5.73 (m, 1H), 5.27 (s, 1H), 4.04 (s, 2H), 3.33 (q, *J* = 7.0 Hz, 8H), 1.74 (d, *J* = 6.5 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 12H), 1.11 (s, 1H). ¹³C NMR: δ 146.4, 139.9, 130.7, 129.9, 129.5, 127.7, 127.3, 111.9, 65.8, 48.7, 44.4, 18.5, 12.7. FTIR (film) *v*_{max}: 3374, 2969, 2930, 2870, 1610, 1515, 1450, 1395, 1375, 1355, 1265, 1196, 965, 810 cm⁻¹. ESI-HRMS calculated for C₂₇H₃₈N₂O (M+H)⁺: 407.3057 and found: 407.3065.

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)hepta-2,4-dien-1-ol (6bb)



The reaction was performed by following the experimental procedure and the product **6bb** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a yellow sticky liquid (78 mg, 93% yield). ¹H NMR: δ 7.05 (d, *J* = 8.5 Hz, 4H), 6.63 (d, *J* = 8.5, 4H), 6.33-6.26 (m, 2H), 5.81-5.76 (m, 1H), 5.26 (s, 1H), 4.06 (s, 2H), 3.34 (q, *J* = 7.0 Hz, 8H), 2.11-2.06 (m, 2H), 1.16 (t, *J* = 7.0 Hz, 12H), 1.12-1.09 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H). ¹³C NMR: δ 146.4, 140.3, 137.8, 129.9, 129.5, 127.9, 125.1, 112.0, 66.0, 48.9, 44.4, 26.0, 13.5, 12.7. FTIR (film) *v*_{max}: 3373, 2966, 2930, 2870, 1610, 1515, 1462, 1395, 1375, 1355, 1265, 1196, 965, 810 cm⁻¹. ESI-HRMS calculated for C₂₈H₄₀N₂O (M+H)⁺: 421.3213 and found: 421.3237.

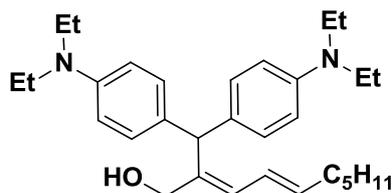
(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)nona-2,4-dienal (6cb)



The reaction was performed by following the experimental procedure and the product **6cb** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a pale yellow sticky liquid (82 mg, 91% yield). ¹H NMR: δ 7.03 (d, *J* = 8.5 Hz, 4H), 6.62 (d, *J* = 8.5, 4H), 6.31-6.25 (m,

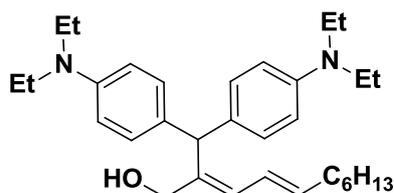
2H), 5.76-5.71 (m, 1H), 5.24 (s, 1H), 4.05 (s, 2H), 3.35-3.30 (m, 8H), 2.06-2.02 (m, 2H), 1.32-1.26 (m, 4H), 1.16-1.13 (m, 12H), 1.09 (s, 1H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 146.4, 140.2, 136.3, 129.9, 129.5, 128.0, 126.0, 111.9, 66.0, 48.8, 44.3, 32.6, 31.4, 22.2, 13.9, 12.6. **FTIR** (film) ν_{max} : 3380, 2966, 2929, 2868, 1615, 1515, 1465, 1399, 1375, 1355, 1265, 1198, 965, 810 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 449.3526 and found: 449.3532.

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)deca-2,4-dien-1-ol (6db)



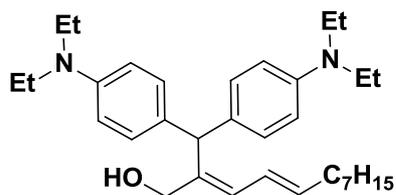
The reaction was performed by following the experimental procedure and the product **6db** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a pale yellow sticky liquid (86 mg, 93% yield). ^1H NMR: δ 7.03 (d, $J = 8.5$ Hz, 4H), 6.61 (d, $J = 8.5$, 4H), 6.31-6.25 (m, 2H), 5.77-5.71 (m, 1H), 5.24 (s, 1H), 4.05 (s, 2H), 3.32 (q, $J = 7.0$ Hz, 8H), 2.06-2.01 (m, 2H), 1.37-1.23 (m, 6H), 1.14 (t, $J = 7.0$ Hz, 12H), 1.10-1.09 (m, 1H), 0.88-0.86 (m, 3H). ^{13}C NMR: δ 146.4, 140.1, 136.4, 129.9, 129.5, 128.0, 125.9, 111.9, 66.0, 48.8, 44.3, 32.9, 31.4, 28.9, 22.5, 14.0, 12.6. **FTIR** (film) ν_{max} : 3386, 2966, 2926, 2868, 1610, 1515, 1465, 1395, 1375, 1355, 1265, 1199, 965, 811 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{31}\text{H}_{46}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 463.3683 and found: 463.3672.

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)undeca-2,4-dien-1-ol (6eb)



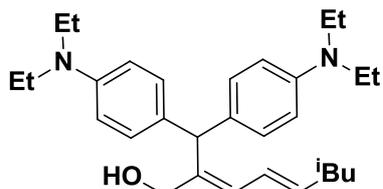
The reaction was performed by following the experimental procedure and the product **6eb** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a yellow sticky liquid (90 mg, 94% yield). ^1H NMR: δ 7.03 (d, $J = 8.0$ Hz, 4H), 6.61 (d, $J = 8.5$, 4H), 6.31-6.25 (m, 2H), 5.76-5.71 (m, 1H), 5.24 (s, 1H), 4.05 (s, 2H), 3.32 (q, $J = 7.0$ Hz, 8H), 2.06-2.01 (m, 2H), 1.33-1.25 (m, 8H), 1.14 (t, $J = 7.0$ Hz, 12H), 1.09-1.08 (m, 1H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 146.4, 140.1, 136.4, 129.9, 129.5, 128.0, 125.9, 111.9, 66.0, 48.8, 44.3, 32.9, 31.7, 29.2, 28.9, 22.6, 14.1, 12.6. **FTIR** (film) ν_{max} : 3369, 2968, 2925, 2855, 1610, 1515, 1465, 1395, 1375, 1355, 1261, 1196, 965, 810 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 477.3839 and found: 477.3834.

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)dodeca-2,4-dien-1-ol (6fb)



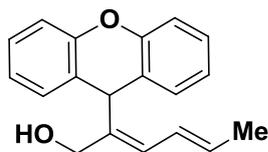
The reaction was performed by following the experimental procedure and the product **6fb** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a yellow sticky liquid (92 mg, 94% yield). $^1\text{H NMR}$: δ 7.03 (d, $J = 8.0$ Hz, 4H), 6.61 (d, $J = 8.5$, 4H), 6.31-6.25 (m, 2H), 5.76-5.71 (m, 1H), 5.24 (s, 1H), 4.04 (d, $J = 3.5$ Hz, 2H), 3.32 (q, $J = 7.0$ Hz, 8H), 2.03 (q, $J = 7.0$ Hz, 2H), 1.34-1.25 (m, 10H), 1.14 (t, $J = 7.0$ Hz, 12H), 1.09-1.08 (m, 1H), 0.88 (t, $J = 3.5$ Hz, 3H). $^{13}\text{C NMR}$: δ 146.4, 140.1, 136.4, 129.9, 129.5, 128.0, 125.9, 111.9, 66.0, 48.8, 44.3, 32.9, 31.9, 29.3, 29.2, 22.7, 14.1, 12.6. **FTIR** (film) ν_{max} : 3373, 2966, 2924, 2855, 1610, 1515, 1465, 1395, 1375, 1355, 1261, 1195, 965, 810 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{33}\text{H}_{50}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 491.3996 and found: 491.3968.

(2E,4E)-2-(bis(4-(diethylamino)phenyl)methyl)-7-methylocta-2,4-dien-1-ol (6gb)



The reaction was performed by following the experimental procedure and the product **6gb** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.0:1.0) as a yellow sticky liquid (82 mg, 91% yield). $^1\text{H NMR}$: δ 7.04 (d, $J = 8.5$ Hz, 4H), 6.63-6.60 (m, 4H), 6.32-6.23 (m, 2H), 5.75-5.69 (m, 1H), 5.24 (s, 1H), 4.06 (d, $J = 3.5$ Hz, 2H), 3.33 (q, $J = 7.0$ Hz, 8H), 1.94-1.91 (m, 2H), 1.63-1.57 (m, 1H), 1.16-1.13 (m, 12H), 1.11-1.09 (m, 1H), 0.85 (d, $J = 7.0$ Hz, 6H). $^{13}\text{C NMR}$: δ 146.4, 140.3, 134.9, 129.9, 129.5, 127.9, 127.1, 112.0, 66.1, 48.9, 44.4, 42.3, 28.5, 22.3, 12.6. **FTIR** (film) ν_{max} : 3396, 2967, 2926, 2871, 1612, 1517, 1469, 1374, 1351, 1265, 1198, 965, 810 cm^{-1} . **ESI-HRMS** calculated for $\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$: 449.3526 and found: 449.3551.

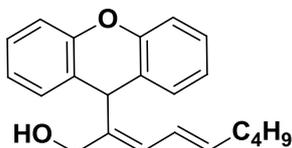
(2E,4E)-2-(9H-xanthen-9-yl)hexa-2,4-dien-1-ol (6ac)



The reaction was performed by following the experimental procedure and the product **6ac** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (33 mg, 59% yield). $^1\text{H NMR}$: δ 7.22-7.19 (m, 2H), 7.14-7.13 (m, 2H), 7.05-6.99 (m, 4H), 6.74-6.69 (m, 1H), 6.38 (d, $J = 11.0$ Hz, 1H), 6.02-5.95 (m, 1H), 5.49 (s, 1H), 3.87 (s, 2H), 1.90 (d, $J = 6.5$ Hz, 3H), 0.96 (m, 1H). $^{13}\text{C NMR}$:

δ 151.2, 140.3, 132.6, 129.0, 128.2, 126.7, 126.2, 123.2, 121.6, 116.6, 96.1, 63.7, 37.0, 18.6. **FTIR** (film) ν_{\max} : 3340, 2912, 1600, 1575, 1480, 1449, 1319, 1253, 962, 751 cm^{-1} . ESI-HRMS calculated for $\text{C}_{19}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{H}$)⁺: 279.1380 and found: 279.1382.

(2E,4E)-2-(9H-xanthen-9-yl)nona-2,4-dien-1-ol (**6cc**)

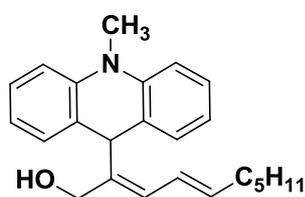


The reaction was performed by following the experimental procedure and the product **6cc** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (35 mg, 55% yield). ¹H NMR: δ 7.24-7.19 (m, 2H), 7.15-7.13 (m, 2H), 7.06-6.99 (m, 4H), 6.71-6.66 (m, 1H), 6.39 (d, J = 10.5 Hz, 1H), 6.01-5.95 (m, 1H), 5.50 (s, 1H), 3.87 (d, J = 6.0 Hz, 2H), 2.24-2.20 (m, 2H), 1.49-1.43 (m, 2H), 1.42-1.35 (m, 2H), 1.00 (t, J = 6.0 Hz, 1), 0.96-0.93 (m, 3H). ¹³C NMR: δ 151.2, 140.5, 138.3, 129.3, 129.0, 128.2, 126.9, 124.7, 123.2, 121.7, 116.6, 63.8, 37.0, 32.8, 31.5, 22.3, 14.0. **FTIR** (film) ν_{\max} : 3333, 2925, 1601, 1575, 1480, 1449, 1318, 1253, 965, 751 cm^{-1} . ESI-HRMS calculated for $\text{C}_{22}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{H}$)⁺: 321.1849 and found: 321.1846.

5. Experimental procedure and characterization data for the MBH-type reaction of aldehyde **1d** with N-methylacridinium iodide

Acridinium salt **7** (0.24 mmol) was dissolved in DCE (200 μL) into a mass vial. To the above solution pyrrolidine (5.0 μL , 0.06 mmol), aldehyde **1d** (0.20 mmol) and DMAP (24.4 mg, 0.20 mmol) were added and stirred vigorously at room temperature. After stated time reaction was diluted with MeOH (2 mL) and cooled to 0 $^{\circ}\text{C}$. NaBH_4 (75.7 mg, 2.0 mmol) was then slowly added and reaction mixture was stirred for 4hr. The reaction mixture was then quenched with H_2O and extracted with DCM (10 x 3 mL). Organic layer was dried over anhydrous sodium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2 , hexane/EtOAc).

(2E,4E)-2-(10-methyl-9,10-dihydroacridin-9-yl)deca-2,4-dien-1-ol (**8d**)



The reaction was performed by following the general experimental procedure and the product **8d** was obtained after flash column chromatography (silica gel, Hexane/EtOAc 9.5:0.5) as a yellow sticky liquid (54 mg, 78% yield). ¹H NMR:

δ 7.22-7.18 (m, 2H), 7.13 (d, $J = 7.5$ Hz, 2H), 6.98-6.87 (m, 4H), 6.72-6.67 (m, 1H), 6.23 (d, $J = 11.0$ Hz, 1H), 5.93-5.87 (m, 1H), 5.46 (s, 1H), 3.96 (s, 2H), 3.39 (s, 3H), 2.21-2.17 (m, 2H), 1.47-1.44 (m, 2H), 1.34-1.26 (m, 4H), 1.11-1.10 (m, 1 H), 0.92 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR: δ 142.3, 141.5, 137.5, 128.6, 127.6, 125.4, 125.3, 124.7, 120.6, 112.4, 112.1, 64.1, 41.5, 33.2, 33.0, 31.4, 29.0, 22.6, 14.1. FTIR (film) ν_{max} : 3365, 2957, 2925, 2858, 1601, 1595, 1475, 1449, 1349, 1270, 965, 748 cm^{-1} . ESI-HRMS calculated for $\text{C}_{24}\text{H}_{29}\text{NO}$ (M+H) $^{+}$: 348.2322 and found: 348.2310.

6. Reference

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7. ^1H NMR and ^{13}C NMR spectra

