Supporting Information for:

Regiospecific normal Diels-Alder reaction of trans-1,2-biscoumarinylethenes

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General

Melting points were determined on an Analab melting point apparatus (Model- μThermocal 10) in open capillary tubes and are uncorrected. The IR spectra were recorded on a Jasco-4100 spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury plus 300 spectrometer (300 MHz) in CDCl$_3$/DMSO-d$_6$ with TMS as an internal standard and the chemical shifts are expressed in δ unit (ppm). The mass spectra were recorded on a Finnigan LCQ Advantage Max spectrometer. Elemental analysis was carried out with a Thermo finnigan, Flash EA 1112 instrument.

Experimental Procedures

Coumarin-4-acetic acids$^{14}$ and 7-diethylamino coumarin-3-carbaldehyde$^{13}$ were prepared by the reported methods.

General procedure for the synthesis of (E)-1-(7-diethylaminocoumarin-3-yl)-2-(7,8-substituted coumarin-4-yl)ethenes (3)

2 (1 mmol) and piperidine (1 mmol) were stirred in methanol (6 mL) for 15 min and 1 (0.245 g, 1 mmol) was added slowly at room temperature. After complete consumption of 1, the precipitated solid was collected by filtration and washed with small quantity of cold methanol followed by water to remove traces of piperidine. The solid (3) was washed with ethyl acetate. The second crop of 3 was obtained from filtrate; the filtrate was evaporated to obtain a sticky mass which was purified by column chromatography on silica gel using toluene - ethyl acetate
3-diethylaminocoumarin-3-carbaldehyde (1)

Brown solid; mp 155-157 °C; IR (neat) ν = 2978, 1737, 1714, 1671, 1608, 1505, 1259 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.30 (t, 6H, 2xCH₃, J = 7.0 Hz), 3.47 (q, 4H, 2xCH₂, J = 7.0 Hz), 6.48 (d, 1H, C8-H, J = 2.7 Hz), 6.63 (dd, 1H, C6-H, J = 2.7 & 9.0 Hz), 7.41 (d, 1H, C5-H, J = 9.0 Hz), 8.25 (s, 1H, C4-H); 10.12 (s, 1H, CHO).

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7-methylcoumarin-4-yl)ethane (3a)

(0.258 g, 64%); Orange solid; mp 231-233 °C; IR (neat) ν = 1698, 1609, 1575, 1513, 1352, 1252, 1192, 1132 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ = 1.25 (t, 6H, 2xCH₃, J = 7.5 Hz), 2.46 (s, 3H, CH₃), 3.47 (q, 4H, 2xCH₂, J = 7.5 Hz), 6.49 (s, 1H, C3-H), 6.51 (d, 1H, C8’-H, J = 2.0 Hz), 6.65 (dd, 1H, C6’-H, J = 2.0 & 9.0 Hz), 7.13-7.15 (m, 2H, C5’-H & C8-H), 7.20 (d, 1H, C10-H, J = 15.5 Hz), 7.37 (d, 1H, C6-H, J = 8.5 Hz), 7.77 (d, 1H, C5-H, J = 8.5 Hz), 7.79 (s, 1H, C4’-H), 7.99 (d, 1H, C9-H, J = 15.5 Hz); MS = 402.57 (M+1). Anal. Calcd. for C₂₅H₂₃NO₄ (401.45): C, 74.79; H, 5.77; N, 3.49%. Found: C, 74.58; H, 5.88; N, 3.52%.

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(coumarin-4-yl)ethene (3b)
(0.252 g, 65%); Dark red solid; mp 219-221 °C; IR (neat) ν = 1698, 1685, 1615, 1573, 1513, 1351, 1241, 1188, 1133 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.24 (t, 6H, 2xCH₃, J = 7.5 Hz), 3.45 (q, 4H, 2xCH₂, J = 7.5 Hz), 6.51 (d, 1H, C8'-H, J = 2.7 Hz), 6.56 (s, 1H, C3-H ), 6.62 (dd, 1H, C6'-H, J = 2.7 & 9.0 Hz), 7.14 (d, 1H, C10-H, J = 15.6 Hz), 7.29-7.36 (m, 3H, C5'-H, C6-H & C8-H), 7.54 (dt, 1H, C7-H, J = 1.5 & 8.0 Hz), 7.70 (s, 1H, C4'-H), 7.90 (dd, 1H, C5-H, J = 8.7 Hz), 8.07 (d, 1H, C9-H, J = 15.6 Hz); MS = 388.34 (M+1). Anal. Calcd. for C₂₄H₂₁NO₄ (387.43): C, 74.40; H, 5.46; N, 3.62%. Found: C, 74.60; H, 5.31; N, 3.49%.

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7-hydroxycoumarin-4-yl)ethene (3c)

(0.246 g, 61%); Red solid; mp 300 °C >; IR (neat) ν = 3165, 1705, 1682, 1608, 1578, 1508, 1409, 1353, 1319, 1192, 1130 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.13 (t, 6H, 2xCH₃, J = 7.5 Hz), 3.53 (q, 4H, 2xCH₂, J = 7.5 Hz), 6.41 (s, 1H, C3-H ), 6.57 (d, 1H, C8-H, J = 2.0 Hz), 6.72-6.76 (m, 2H, C6'-H & C8'-H, J = 2.0 & 9.0 Hz), 7.13 (dd, 1H, C6-H, J = 2.0 & 8.7 Hz), 7.43 (d, 1H, C10-H, J = 16.2 Hz), 7.47 (d, 1H, C5'-H, J = 8.7 Hz), 7.77 (d, 1H, C5-H, J = 8.7 Hz), 7.82 (d, 1H, C9-H, J = 16.2 Hz), 8.23 (s, 1H, C4'-H), 10.60 (bs, 1H, OH, exchangeable with D₂O); MS = 404.64 (M+1), Anal. Calcd. for C₂₄H₂₁NO₅ (403.43): C, 71.45; H, 5.25; N, 3.47%. Found: C, 71.32; H, 5.36; N, 3.53%.

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7-ethoxycarbonylamino coumarin-4-yl)ethene (3d)
(0.320 g, 67%); Red solid; mp 297-298 °C; IR (neat) v = 3267, 1733, 1681, 1614, 1581, 1516, 1394, 1217, 1127, 1064 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.14 (t, 6H, 2xCH₃, J = 7.2 Hz), 1.26 (t, 3H, CH₃, J = 6.9 Hz), 3.46 (q, 4H, 2xCH₂, J = 7.2 Hz), 4.17 (q, 2H, CH₂, J = 6.9 Hz), 6.53 (s, 1H, C3-H), 6.60 (d, 1H, C8'-H, J = 2.1 Hz), 6.78 (dd, 1H, C6'-H, J = 2.1 & 9.0 Hz), 7.45-7.58 (m, 4H, C5'-H, C6-H, C8-H & C10-H), 7.84 (d, 1H, C9-H, J = 16.0 Hz), 7.87 (d, 1H, C5-H, J = 8.7 Hz), 8.27 (s, 1H, C4-H), 10.18 (s, 1H, NH); MS = 475.58 (M+1). Anal. Calcd. for C₂₇H₂₆N₂O₆ (474.51): C, 68.34; H, 5.52; N, 5.90%. Found: C, 68.48; H, 5.47; N, 5.86%.

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7,8-dihydroxycoumarin-4-yl)ethene (3e)

(0.256 g, 61%); Dark red solid; mp 304-306 °C; IR (neat) v = 3291, 1674, 1609, 1581, 1557, 1508, 1305, 1242, 1180, 1128, 1027 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.30 (t, 6H, 2xCH₃, J = 6.9 Hz), 3.45 (q, 4H, 2xCH₂, J = 6.9 Hz), 6.40 (s, 1H, C3-H), 6.56 (d, 1H, C8'-H, J = 2.4 Hz), 6.74 (dd, 1H, C6'-H, J = 2.1 & 9.0 Hz), 6.86 (d, 1H, C6-H, J = 8.4 Hz), 7.27 (d, 1H, C5'-H, J = 8.7 Hz), 7.41 (d, 1H, C10-H, J = 15.3 Hz), 7.47 (d, 1H, C5-H, J = 9.0 Hz), 7.82 (d, 1H, C9-H, J = 15.3 Hz), 8.22 (s, 1H, C4'-H), 9.45 bs, 1H, OH, exchangeable with D₂O), 10.21 (bs, 1H, OH, exchangeable with D₂O); MS = 420.56 (M+1). Anal. Calcd. for C₂₄H₂₁NO₆ (419.43): C, 68.73; H, 5.05; N, 3.34%. Found: C, 68.63; H, 5.19; N, 3.29%.
(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7-chlorocoumarin-4-yl)ethene (3f)

(0.299 g, 71%); Orange solid; mp 270-271 °C; IR (neat) ν = 1698, 1609, 1572, 1511, 1411, 1254, 1192, 1133, 1081, 962 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.24 (t, 6H, 2xCH₃, J = 7.5Hz), 3.45 (q, 4H, 2xCH₂, J = 7.5 Hz), 6.51 (d, 1H, C8′-H, J = 2.4 Hz), 6.53 (s, 1H, C3-H), 6.62 (dd, 1H, C6′-H, J = 2.4 & 8.7 Hz), 7.12 (d, 1H, C10-H, J = 15.6 Hz), 7.27-7.35 (m, 3H, C5′-H, C6-H & C8-H), 7.69 (s, 1H, C4′-H), 7.81 (d, 1H, C5-H, J = 8.7 Hz), 8.02 (d, 1H, C9-H, J = 15.6 Hz); MS = 422.84 (M+1), 424.81 (M+3). Anal. Calcd. for C₂₄H₂₀ClNO₄ (421.87): C, 68.33; H, 4.78; N, 3.32%. Found: C, 68.48; H, 4.61; N, 3.34%.

(E)-1-(7-diethylaminocoumarin-3-yl)-2-(7-metoxycoumarin-4-yl)ethene (3g)

3c (0.403 g, 1 mmol) and K₂CO₃ (0.276 g, 2 mmol) were stirred in acetone (6 mL) at reflux temperature for 5 min. DMS (0.252 g, 2 mmol) was added slowly. After complete consumption of 3c, the precipitated solid was collected by filtration and washed with water. (0.394 g, 94%); Orange solid; mp 276-277 °C; IR (neat) ν = 1704, 1608, 1577, 1513, 1410, 1348, 1190, 1130, cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.24 (t, 6H, 2xCH₃, J = 7.5Hz), 3.45 (q, 4H, 2xCH₂, J = 7.5 Hz), 3.88 (s, 3H, OCH₃), 6.41 (s, 1H, 3-H), 6.52 (d, 1H, C8′-H, J = 2.4 Hz), 6.62 (dd, 1H, C6′-H, J = 2.4 & 9.0 Hz), 6.84 (d, 1H, C8-H, J = 2.1 Hz), 6.86 (dd, 1H, C6-H, J = 2.1 & 8.7 Hz) 7.12 (d, 1H, C10-H, J = 15.6 Hz), 7.33 (d, 1H, C5′-H, J = 8.7 Hz), 7.69 (s, 1H, C4′-
H), 7.95 (d, 1H, C5-H, $J = 8.7$ Hz), 8.03 (d, 1H, C9-H, $J = 15.6$ Hz); MS = 418.31 (M+1). Anal. Calcd. for C$_{25}$H$_{23}$NO$_5$ (417.45): C, 71.93; H, 5.55; N, 3.36%. Found: C, 71.81; H, 5.65; N, 3.39%.

$(E)$-1-(7-diethylaminocoumarin-3-yl)-2-(7,8-dimethoxycoumarin-4-yl)ethene (3h)

![Chemical structure of 3h](image)

3e (0.419 g, 1 mmol) and K$_2$CO$_3$ (0.552 g, 4 mmol) were stirred in acetone (6 mL) at reflux temperature, for 5 min. DMS (0.504 g, 4 mmol) was added slowly. After complete consumption of 3e, the precipitated solid was collected by filtration and washed with water. (0.414 g, 92%); Orange solid; mp 214-216 °C; IR (neat) $v$ = 1697, 1610, 1575, 1551, 1513, 1359, 1294, 1241, 1096 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 1.24 (t, 6H, $2x$CH$_3$, $J = 7.5$ Hz), 3.46 (q, 4H, $2x$CH$_2$, $J = 7.5$ Hz), 3.97 (s, 3H, OCH$_3$), 6.42 (s, 1H, C3-H), 6.54 (s, 1H, C8'-H), 6.64 (d, 1H, C6'-H, $J = 8.4$ Hz), 6.90 (d, 1H, C6-H, $J = 9.0$ Hz), 7.11 (d, 1H, C10-H, $J = 16.0$ Hz), 7.34 (d, 1H, C5'-H, $J = 8.7$ Hz), 7.60 (d, 1H, C5-H, $J = 9.0$ Hz), 7.69 (s, 1H, C4'-H), 8.04 (d, 1H, C9-H, $J = 16$ Hz); MS = 448.51 (M+1). Anal. Calcd. for C$_{26}$H$_{25}$NO$_6$ (447.48): C, 69.79; H, 5.63; N, 3.13%. Found: C, 69.58; H, 5.53; N, 3.19%.

General procedure for the synthesis of 7,7,8,8-tetracyano-3,4-substituted-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16)

3 (1 mmol) and 11 (0.256 g, 2 mmol) were refluxed in dioxane (6 mL) for appropriate time shown in Table 3. After complete consumption of 3, the solution was cooled to room temperature and was evaporated to obtain a sticky mass which was purified by column chromatography on silica gel using toluene - ethyl acetate.
7,7,8,8-tetracyano-3-methyl-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-
dibenzo[b,d]pyran-6-one (16a)

(0.451 g, 85%); buff solid; mp 269-270 °C; IR (neat) ν = 2975, 1702, 1594, 1519, 1251, 1128 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.23 (t, 6H, 2xCH₃, J = 6.9 Hz), 2.50 (s, 3H, CH₃), 3.50 (q, 4H, 2xCH₂, J = 6.9 Hz), 3.59 (d, 2H, C10-H, J = 7.2 Hz), 4.29 (t, 1H, C9-H, J = 7.2 Hz), 6.44 (d, 1H, C8'-H, J = 2.1 Hz), 6.64 (dd, 1H, C6'-H, J = 2.1 & 8.7 Hz), 7.22 (s, 1H, C8-H), 7.24 (d, 1H, C6-H, J = 7.8 Hz), 7.38 (d, 1H, C5'-H, J = 8.7 Hz), 7.58 (d, 1H, C5-H, J = 8.1 Hz), 7.93 (s, 1H, C4'-H); ¹³C NMR (CDCl₃, 300 MHz) δ = 12.4 (2xCH₃), 22.0 (Ar-CH₃), 28.3 (C10), 36.9 (C9), 42.3 (C8), 45.1 (2xCH₂), 46.5 (C7), 97.0 (C8'), 107.5 (C3'), 108.9 (CN), 109.2 (CN), 109.4 (C10b), 109.7(2xCN), 109.8 (C6'), 111.6 (C4a'), 114.6 (C6a), 117.7 (C4), 124.8 (C2), 127.2 (C1), 130.1 (C5'), 142.8 (C4'), 147.4 (C3), 152.0 (C7'), 152.3 (C10a), 152.9 (C4a'), 156.5 (C8a'), 157.1 (C2'), 161.5 (C6); MS = 530.46 (M+1); Anal. Calcd. for C₃₁H₂₃N₅O₄ (529.55): C, 70.31; H, 4.38; N, 13.23%. Found: C, 70.48; H, 4.47; N, 13.19%.

7,7,8,8-tetracyano-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-
dibenzo[b,d]pyran-6-one (16b)

(0.419 g, 81%); Pale yellow solid; mp 276-278 °C; IR (neat) ν = 2965, 1707, 1604, 1523, 1251, 1131 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.26 (t, 6H, 2xCH₃, J = 6.9 Hz), 3.48 (q, 4H, 2xCH₂,
J = 6.9 Hz), 3.64 (dd, 1H, C10a-H, J = 6.0 & 19.0 Hz), 3.73 (dd, 1H, C10b-H, J = 11.0 & 19.0 Hz), 4.35 (dd, 1H, C9-H, J = 6.0 & 11.0 Hz), 6.56 (d, 1H, C8'-H, J = 2.7 Hz), 6.68 (dd, 1H, C6'-H, J = 2.7 & 9.0 Hz), 7.41 (d, 1H, C5'-H, J = 9.0 Hz), 7.45-7.53 (m, 2H, C6-H, & C7-H), 7.77 (d, 1H, C5-H, & C8-H, J = 7.8 Hz), 7.99 (s, 1H, C4'-H); 13C NMR (CDCl3, 300 MHz) δ = 12.2 (2xCH3), 28.1 (C10), 36.8 (C9), 42.1 (C8), 44.9 (2xCH2), 46.3 (C7), 96.8 (C8'), 107.2 (C3'), 108.9 (CN), 109.1 (CN), 109.2 (2xCN), 109.4 (C10b), 109.5 (C6'), 111.3 (C4a'), 116.8 (C6a), 117.6 (C4), 124.9 (C2), 125.7 (C1), 129.9 (C5'), 135.0 (C3), 142.6 (C4'), 151.9 (C10a), 152.2 (C7), 152.6 (C4a), 156.4 (C8a'), 156.5 (C2'), 161.2 (C6); MS = 516.41 (M+1); Anal. Calcd. for C30H21N5O4 (515.52): C, 69.89; H, 4.11; N, 13.59%. Found: C, 69.71; H, 4.17; N, 13.64%.

7,7,8,8-tetracyano-3-hydroxy-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16c)

(0.432 g, 81%); Yellow solid; mp 282-284 °C; IR (neat) ν = 3502, 1698, 1592, 1518, 1251, 1132 cm⁻¹; 1H NMR (CDCl3, 300 MHz) δ = 1.14 (t, 6H, 2xCH3, J = 6.9 Hz), 3.50 (q, 4H, 2xCH2, J = 6.9 Hz), 3.68 (dd, 1H, C10a-H, J = 5.1 & 19.2 Hz), 3.85 (dd, 1H, C10b-H, J = 11.7 & 19.2 Hz), 4.35 (dd, 1H, C9-H, J = 5.1 & 11.7 Hz), 6.64 (d, 1H, C8'-H, J = 2.4 Hz), 6.71 (dd, 1H, C6'-H, J = 2.4 & 9.0 Hz), 6.88 (d, 1H, C8-H, J = 2.4), 6.95 (dd, 1H, C6-H, J = 2.4 & 8.7 Hz), 7.55 (d, 1H, C5'-H, J = 8.7 Hz), 7.84 (d, 1H, C5-H, J = 8.7 Hz), 8.44 (s, 1H, C4'-H), 11.3 (s, 1H, OH exchangeable with D2O); 13C NMR (CDCl3, 300 MHz) δ = 12.7 (2xCH3), 27.7 (C10), 36.2 (C9), 42.4 (C8), 44.7 (2xCH2), 47.4 (C7), 96.8 (C8'), 102.9 (C4), 103.9 (C10b), 107.6 (C3'), 109.9 (C4a'), 110.1 (C6'), 110.1 (CN), 110.2 (CN), 111.0 (CN), 111.2 (CN), 111.9 (C6a), 114.9 (C2), 128.4 (C5'), 130.8 (C1), 144.3 (C4'), 152.1 (C7), 154.5 (C10a), 155.0 (C8a'), 156.5 (C4a), 158.3 (C3), 161.6 (C2'), 164.3 (C6); MS = 532.61 (M+1); Anal. Calcd. for C30H21N5O5 (531.52): C, 67.79; H, 3.98; N, 13.18%. Found: C, 67.63; H, 3.84; N, 13.12%.
7,7,8,8-tetracyano-3-ethoxycarbonylamine-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16d)

(0.446 g, 74%); Buff solid; mp 202-203 °C; IR (neat) ν = 3200, 2978, 1703, 1595, 1518, 1422, 1213, 1132 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.25 (t, 6H, 2xCH₃, J = 7.2 Hz), 1.56 (t, 3H, CH₃, J = 7.6 Hz), 3.47 (q, 4H, 2x-CH₂, J = 7.2 Hz), 3.57 (d, 2H, C10-H, J = 7.0 Hz), 3.91 (q, 2H, OCH₂, J = 7.6 Hz), 4.27 (t, 1H, C9-H, J = 7.0 Hz), 6.39 (d, 1H, C8'-H, J = 2.2 Hz), 6.59 (dd, 1H, C6'-H, J = 2.2 & 8.2 Hz), 7.16-7.25 (m, 3H, C8-H, C6-H, C5'-H), 7.52 (d, 1H, C5-H, J = 8.0 Hz), 8.14 (s, 1H, C4'-H). 9.81 (bs, 1H, NH); MS = 603.61(M+1); Anal. Calcd. for C₃₃H₂₆N₆O₆ (602.60): C, 65.77; H, 4.35; N, 13.95%. Found: C, 65.63; H, 4.44, N, 13.99%.

7,7,8,8-tetracyano-3,4-dihydroxy-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16e)

(0.400 g, 73%); Orange solid; mp 226-228 °C; IR (neat) ν = 3348, 1716, 1674, 1577, 1518, 1314, 1252, 1131 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.14 (t, 6H, 2xCH₃, J = 6.9 Hz), 3.48 (q, 4H, 2xCH₂, J = 6.9 Hz), 3.68 (dd, 1H, C10a-H, J = 5.1 & 19.6 Hz), 3.84 (dd, 1H, C10b-H, J = 11.4 & 19.6 Hz), 4.36 (dd, 1H, C9-H, J = 5.1 & 11.4 Hz), 6.64 (s, 1H, C8'-H), 6.79 (d, 1H, C6'-H, J = 8.7 Hz), 6.96 (d, 1H, C6-H, J = 9.0 Hz), 7.36 (d, 1H, C5'-H, J = 8.7 Hz), 7.54 (d, 1H, C5-H, J = 9.0 Hz), 8.46 (s, 1H, C4'-H), 8.82 (bs, 1H, OH, exchangeable with D₂O), 10.84 (bs, 1H, OH,
exchangeable with D$_2$O; $^{13}$C NMR (CDCl$_3$, 300 MHz) $\delta = 12.3$ (2xCH$_3$), 27.3 (C10), 35.7 (C9), 42.0 (C8), 44.3 (2xCH2), 46.9 (C7), 96.4 (C8'), 103.4 (C3'), 107.2 (C4a'), 109.5 (CN), 109.7 (C6), 110.5 (CN), 110.6 (CN), 110.7 (CN), 111.5 (C10b), 113.5 (C2), 117.1 (C1), 128.2 (C6a), 130.3 (C5'), 132.5 (C4), 142.7 (C10a), 143.9 (C4'), 151.7 (C8a'), 152.3 (C4a), 154.7 (C7'), 156.1 (C3), 157.7 (C2'), 161.1 (C6); MS = 548.63 (M+1); Anal. Calcd. for C$_{30}$H$_{21}$N$_5$O$_6$ (547.52): C, 65.81; H, 3.87; N, 12.79%. Found: C, 65.75; H, 3.62; N, 12.66%.

7,7,8,8-tetracyano-3-chloro-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16f)

(0.419 g, 76%); Buff solid; mp 268-270 °C; IR (neat) $\nu =$ 2978, 1703, 1592, 1519, 1251, 1129 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta =$ 1.26 (t, 6H, 2xCH$_3$, $J =$ 7.2 Hz), 3.48 (q, 4H, 2xCH$_2$, $J =$ 7.2 Hz), 3.62 (dd, 1H, C10a-H, $J =$ 5.4 & 19.0 Hz), 3.74 (dd, 1H, C10b-H, $J =$ 11.0 & 19.0 Hz), 4.35 (dd, 1H, C9-H, $J =$ 5.4 & 11.0 Hz), 6.50 (d, 1H, C8'-H, $J =$ 1.8 Hz), 6.67 (dd, 1H, C6'-H, $J =$ 1.8 & 8.7 Hz), 7.41 (d, 1H, C5'-H, $J =$ 8.7 Hz), 7.45 (dd, 1H, C6-H, $J =$ 1.8 & 8.7 Hz), 7.51 (d, 1H, C8-H, $J =$ 1.8 Hz), 7.76 (d, 1H, C5-H, $J =$ 8.7 Hz), 8.00 (s, 1H, C4'-H); $^{13}$C NMR (CDCl$_3$, 300 MHz) $\delta =$ 12.1 (2xCH$_3$), 28.0 (C10), 36.8 (C9), 42.1 (C8), 44.8 (2xCH$_2$), 46.2 (C7), 96.7 (C8'), 107.1 (C3'), 108.7 (CN), 109.0 (CN), 109.0 (CN), 109.3 (CN), 109.5 (C6'), 109.8 (C6a), 110.9 (C4a), 115.5 (C10b), 117.6 (C2), 126.2 (C4), 129.8 (C1 &C5'), 141.0 (C3), 142.8 (C4'), 151.9 (C7'), 152.0 (C10a), 152.8 (C4a), 156.1 (C8a'), 156.3 (C2'), 161.2 (C6); MS = 550.86 (M+1); 552.81 (M+3); Anal. Calcd. for C$_{30}$H$_{20}$ClN$_5$O$_6$ (549.96): C, 65.52; H, 3.67; N, 12.73%. Found: C, 65.69; H, 3.54; N, 12.82%.
7,7,8,8-tetracyano-3-methoxy-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16g)

(0.443 g, 81%); Buff solid; mp 225-228 °C; IR (neat) ν = 2976, 1702, 1594, 1518, 1354, 1248, 1131 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.25 (t, 6H, 2xCH₃, J = 7.2 Hz), 3.46 (q, 4H, 2xCH₂, J = 7.2 Hz), 3.57 (d, 2H, C10-H, J = 8.7 Hz), 3.95 (s, 3H, OCH₃), 4.28 (t, 1H, C9-H, J = 8.7 Hz), 6.52 (d, 1H, C8'-H, J = 2.4 Hz), 6.67 (dd, 1H, C6'-H, J = 2.4 & 9.0 Hz), 6.92 (d, 1H, C8-H, J = 2.4), 6.98 (dd, 1H, C6-H, J = 2.4 & 9.0 Hz), 7.37 (d, 1H, C5'-H, J = 9.0 Hz), 7.57 (d, 1H, C5-H, J = 8.7 Hz), 7.91 (s, 1H, C4'-H); ¹³C NMR (CDCl₃, 300 MHz) δ = 12.4 (2xCH₃), 28.3 (C10), 36.9 (C9), 42.3 (C8), 45.0 (2xCH₂), 46.4 (C7), 56.3 (OCH₃), 97.0 (C8'), 101.3 (C4), 106.4 (C3'), 107.4 (C4a'), 109.3 (CN), 109.5 (C6), 109.7 (2xCN), 109.7 (CN), 110.4 (C10b), 111.6 (C6a), 114.2 (C2), 126.3 (C5'), 130.0 (C1), 142.6 (C4'), 152.0 (C7'), 152.1 (C10a), 155.0 (C8a'), 156.5 (C4a), 157.3 (C3), 161.5 (C2'), 165.3 (C6); MS = 546.43 (M+1); Anal. Calcd. for C₃₁H₂₃N₅O₅ (545.54): C, 68.25; H, 4.25; N, 12.84%. Found: C, 68.12; H, 4.32; N, 12.88%.

7,7,8,8-tetracyano-3,4-dimethoxy-9-(7-diethylaminocoumarin-3-yl)-7,8,9,10-tetrahydro-6H-dibenzo[b,d]pyran-6-one (16h)

(0.477 g, 83%); Yellowish orange solid; mp 218-220 °C; IR (neat) ν =2978, 1702, 1594, 1521, 1458, 1300, 1253, 1132, 1111 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.24 (t, 6H, 2xCH₃, J = 7.2 Hz, 2xCH₃, J = 7.2 Hz), 3.17 (q, 4H, 2xCH₂, J = 7.2 Hz), 3.57 (d, 2H, C10-H, J = 8.7 Hz), 3.95 (s, 3H, OCH₃), 4.28 (t, 1H, C9-H, J = 8.7 Hz), 6.52 (d, 1H, C8'-H, J = 2.4 Hz), 6.67 (dd, 1H, C6'-H, J = 2.4 & 9.0 Hz), 6.92 (d, 1H, C8-H, J = 2.4), 6.98 (dd, 1H, C6-H, J = 2.4 & 9.0 Hz), 7.37 (d, 1H, C5'-H, J = 9.0 Hz), 7.57 (d, 1H, C5-H, J = 8.7 Hz), 7.91 (s, 1H, C4'-H); ¹³C NMR (CDCl₃, 300 MHz) δ = 12.4 (2xCH₃), 28.3 (C10), 36.9 (C9), 42.3 (C8), 45.0 (2xCH₂), 46.4 (C7), 56.3 (OCH₃), 97.0 (C8'), 101.3 (C4), 106.4 (C3'), 107.4 (C4a'), 109.3 (CN), 109.5 (C6), 109.7 (2xCN), 109.7 (CN), 110.4 (C10b), 111.6 (C6a), 114.2 (C2), 126.3 (C5'), 130.0 (C1), 142.6 (C4'), 152.0 (C7'), 152.1 (C10a), 155.0 (C8a'), 156.5 (C4a), 157.3 (C3), 161.5 (C2'), 165.3 (C6); MS = 546.43 (M+1); Anal. Calcd. for C₃₁H₂₃N₅O₅ (545.54): C, 68.25; H, 4.25; N, 12.84%. Found: C, 68.12; H, 4.32; N, 12.88%.
Hz), 3.46 (q, 4H, 2xCH₂, J = 7.2 Hz), 3.56 (d, 2H, C10-H, J = 9.6 Hz), 4.01 (s, 6H, 2xOCH₃), 4.26 (t, 1H, C9-H, J = 9.6 Hz), 6.50 (d, 1H, C8'-H, J = 2.1 Hz), 6.65 (dd, 1H, C6'-H, J = 2.1 & 9.0 Hz), 6.99 (d, 1H, C6-H, J = 9.0 Hz), 7.36 (d, 1H, C5'-H, J = 9.0 Hz), 7.37 (d, 1H, C5-H, J = 9.0 Hz), 7.89 (s, 1H, C4'-H); MS = 576.56 (M+1); Anal. Calcd. for C₃₂H₂₅N₅O₆ (575.57): C, 66.78; H, 4.38; N, 12.17%. Found: C, 66.62; H, 4.51; N, 12.22%.

7-methyl-2-phenyl-11-(7-diethylaminocoumarin-3-yl)-3a,10,11,11a-tetrahydro[1]benzopyrano[3,4-e]isooindole-1,3,4-2H-trione (17)

(0.453 g, 79%); Yellowish orange solid; mp 290-291 °C; IR (neat) v = 2984, 1784, 1731, 1712, 1685, 1604, 1522, 1376, 1252, 1134 cm⁻¹, ¹H NMR (CDCl₃, 300 MHz) δ = 1.18 (t, 6H, 2xCH₃, J = 6.9 Hz), 2.43 (s, 3H, CH₃), 2.91 (t, 1H, C10a-H, J = 15 Hz), 3.26 (m, 2H, C10b-H & C11-H, J = 15 Hz), 3.38 (q, 4H, 2x CH₂, J = 6.9 Hz), 4.20 (t, 1H, C11a-H, J = 9 Hz), 4.86 (d, 1H, C3a-H, J = 9.0 Hz), 6.48 (d, 1H, C8'-H, J = 1.8 Hz), 6.56 (dd, 1H, C6'-H, J = 1.8 & 8.7 Hz), 7.10-7.36 (m, 8H, Ar-H), 7.54-7.56 (m, 2H, C4'-H & C9-H); ¹³C NMR (CDCl₃, 300 MHz) δ = 12.4 (2xCH₃), 21.6 (CH₃-Ar), 25.2 (C10), 36.2 (C11a), 40.8 (C3a), 41.3 (C11), 44.8 (2xCH₂), 97.2 (C8'), 108.3 (C3'), 109.0 (C6'), 116.3 (C4a'), 117.1 (C9a), 117.4 (C6), 119.2 (C3b), 125.7 (N-PhC), 126.3 (2C, N-PhC), 128.5 (C8), 128.8 (C5'), 129.0 (C9), 129.1 (2C, N-PhC), 131.7 (N-CPh), 140.0 (C4'), 143.5 (C7), 150.4 (C8a'), 150.5 (C5a), 152.9 (C9b), 155.8 (C7'), 160.2 (C2'), 162.3 (C4), 173.6 (C3), 175.1 (C1); MS = 575.68 (M+1); Anal. Calcd. for C₃₅H₃₀N₂O₆ (574.62): C, 73.16; H, 5.26; N, 4.88%. Found: C, 73.32; H, 5.18; N, 4.81%.

7-methyl-11-(7-diethylaminocoumarin-3-yl)-3a,10,11,11a-tetrahydro-1H-[1]benzopyrano[3,4-e]isobenzofuran-1,3,4-trione (18)
(0.386 g, 77%); Buff solid; mp 282-284 °C; IR (neat) ν = 2975, 1860, 1791, 1725, 1684, 1606, 1523, 1245, 1133 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.13 (t, 6H, 2xCH₃, J = 6.9 Hz), 2.43 (s, 3H, CH₃), 2.89 (t, 1H, C10a-H, J = 14 Hz), (C10b-H, C11-H, and 2xCH₂ merged in DMSO water) 4.34 (apparent t, 1H, C11a-H, J = 9 & 14 Hz), 4.89 (d, 1H, C3a-H, J = 9 Hz), 6.56 (d, 1H, C8’-H, J = 2.1 Hz), 6.74 (dd, 1H, C6’-H, J = 2.1 & 8.1 Hz), 7.25 (d, 1H, C5-H, J = 8.1 Hz), 7.29 (s, 1H, C6-H), 7.46 (d, 1H, C8-H, J = 8.7 Hz), 7.86-7.89 (m, 2H, C4’-H & C9-H); MS = 501.61 (M+1); Anal. Calcd. for C₂₉H₂₅NO₇ (499.51): C, 69.73; H, 5.04; N, 2.80%. Found: C, 69.64; H, 5.08; N, 2.71%

Diethyl-3-methyl-9-(7-diethylaminocoumarin-3-yl)-9,10-dihydro-6H-dibenzo[b,d]pyran-7,8-dicarboxylate (19)

(0.463 g, 81%); Yellowish orange solid; mp 271-272 °C; IR (neat) ν = 2976, 1713, 1606, 1522, 1414, 1231, 1132 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 1.15 (t, 6H, 2xCH₃, J = 7.5 Hz), 1.25 (t, 3H, CH₃, J = 6.9 Hz), 1.44 (t, 3H, CH₃, J = 7.2 Hz), 2.41 (s, 3H, CH₃), 3.14 (dd, 1H, C10a-H, J = 9.0 & 18.0 Hz), 3.37 (m, 5H, 2xCH₂, & C10b-H) 3.74 (dd, 1H, C9-H, J = 1.8 & 18 Hz), 4.25 (q, 2H, OCH₂), 4.5 (q, 2H, OCH₂), 6.41 (d, 1H, C8’-H, J = 2.1 Hz), 6.52 (dd, 1H, C6’-H, J = 2.1 & 9.0 Hz), 7.08-7.10 (m, 2H, C4-H & C5’-H), 7.22 (d, 1H, C2-H J = 8.7 Hz), 7.33 (s, 1H, C4’-
H), 7.53 (d, 1H, C1-H, J = 8.7 Hz); $^{13}$C NMR (CDCl$_3$, 300 MHz) δ = 12.4 (2xCH$_3$), 13.9 (CH$_3$), 14.0 (CH$_3$), 21.8 (CH$_3$-Ar), 28.3 (C10), 31.8 (C9), 44.8 (2xN-CH$_2$), 61.5 (O-CH$_2$), 61.9 (O-CH$_2$), 96.8 (C8’), 108.1 (C3’), 108.9 (C6’), 116.4 (C6a), 117.0 (2C, C4a, C10b), 117.2 (C4), 125.1 (C2), 126.1 (C1), 127.3 (C8), 129.2 (C5’), 138.6 (C7), 139.6 (C4’), 145.0 (C3), 150.4 (C10a), 151.0 (C8a’), 153.8 (C4a), 155.7 (C7’), 157.7 (C6), 162.2 (C2’), 165.0 (C8a), 167.3 (C7a); MS = 572.56 (M+1); Anal. Calcd. for C$_{33}$H$_{33}$NO$_8$ (571.62): C, 69.34; H, 5.82; N, 2.45%. Found: C, 69.48; H, 5.68; N, 2.54%. 
UV Spectra

UV-Vis absorption spectra of products (16a-16h and 17-19)
7-Methyl-3-alka

**SAMPLE**
- **Date:** Nov 2011
- **Method:** HPLC
- **Solvent:** ACN:0.05% HCL (80:20)
- **File:** main.sh
- **Data:** 154.6
- **Processing:**

**ACQUISITION**
- **Frequency:** 400.13 MHz
- **Number:** 1
- **Display:** 0.2

**Peaks**
- **Frequency:** 2.0
- **Area:** 2.0
- **Height:** 2.0
- **Intensity:** 2.0
- **Fit:** 2.0
- **Flags:** 2.0
- **In:** 2.0

**Additional Information**
- **ppm:** 0.98
- **Integration:** 1.0
19
7-Chloro-3-alkyhyde

**Acquisition**

**Sample**

- **Date:** Nov 8, 2011
- **DM:** H1
- **Solvent:** CDCl3, dm, 155.1
- **Temperature:** 298 K
- **Sample:** C
- **Instrument:** Bruker AV-400
- **Processing:** 2 pt
- **Acquisition:** 16
- **Scale:** 0.16
- **SNR:** C6.6
- **Acquisition:** 1 pt
- **SNR:** C6.6
- **Display:** 6.4
- **Larmor:** 5.05 GHz
- **Pulsed:** 55.83°
- **D sets:** 160
- **RTQ:** 4225.63 u
- **Gain:** 6 dB
- **Flags:** th
- **IP:** n
- **LP:** n
- **SP:** 1.409

**Chemical Shifts:**

- 7.34, 7.34, 6.40
- 5.71
- 2.88, 2.67, 5.0

**Diagram:**

[Chemical structure image]
7-Cl-BA
2 drops DMSO added

Sample
DEC. 5 VT
Date Oct 7, 2011
Solvent COCl3
File exp dpw 41

Acquisition
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ln 0.03 dm
at 1.11 dm
np 68942

sv 18667.9 lb
fb 10480 white
bs 5 0.10 ft
tpr 53 ft

pw 0.0
pt 0.0

d1 1.090 wav

d2 0.897 wps

d3 0.391 wer

tof 748.8

nt 1096

ntk 0.0

lock n

Gain 6

Flag 6

Display y

sp 49.5

vp 15184

ws 72

sc 0

wc 256

nzm 36.71

cl 122989

rf 1

rs 0

img 190.080

nm no ph

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**Diagram:**

- Structure of the molecule with labeled atoms.

**Notes:**

- Sample preparation details.
- Experimental conditions.
- Data acquisition settings.

**Display:**

- Spectral data with ppm values.