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Supplementary Information

Bis-Chalcone Derivatives Derived from Natural Products as Near-UV/Visible Light Sensitive Photoinitiators for 3D/4D Printing

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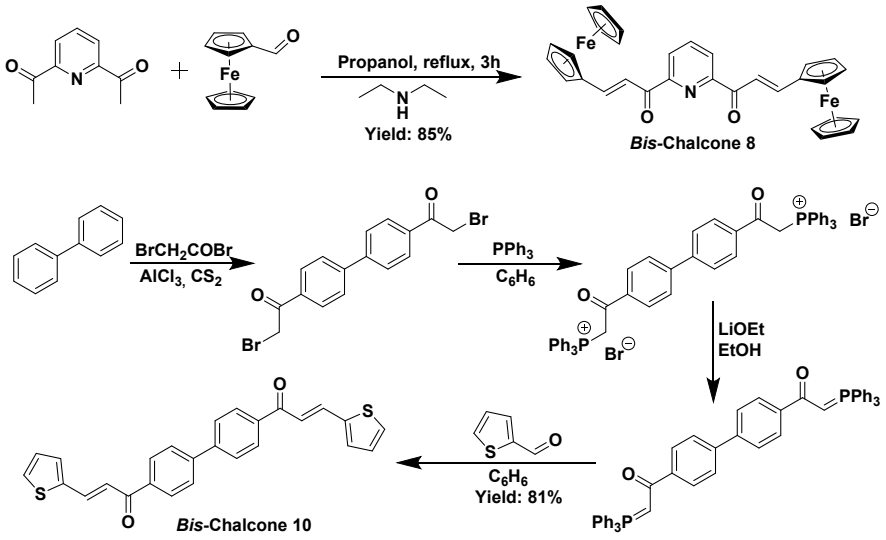


Fig. S1 Previously reported synthetic routes to *bis*-chalcones 8 and 10.

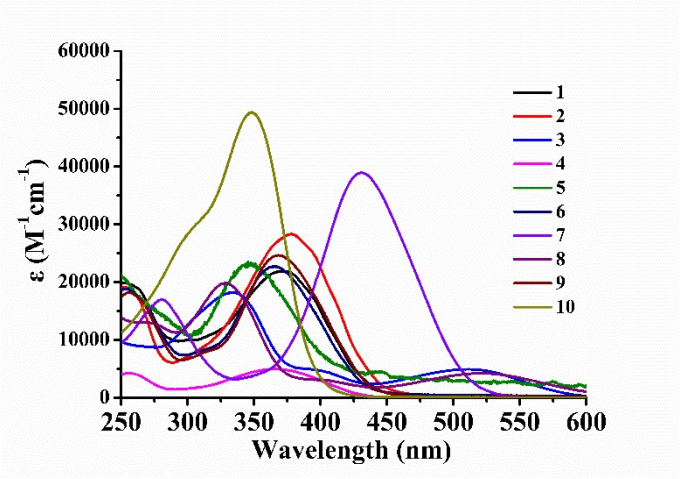


Fig.S2 The UV-visible absorption spectra of *bis*-chalcones 1-10 in acetonitrile.

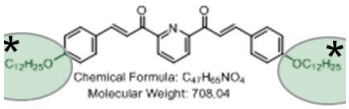
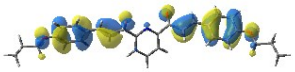
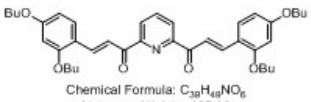
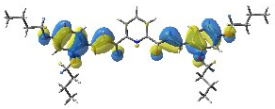
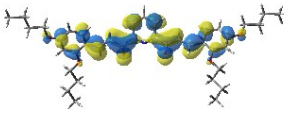
	HOMO	LUMO
(*Bis*-chalcones 5)  *Replaced by OC_3H_7		
(*Bis*-chalcones 9) 		

Fig. S3 Contour plots of HOMOs and LUMOs for *bis*-chalcones 5 and 9 optimized at the B3LYP/6-31G* level of theory.

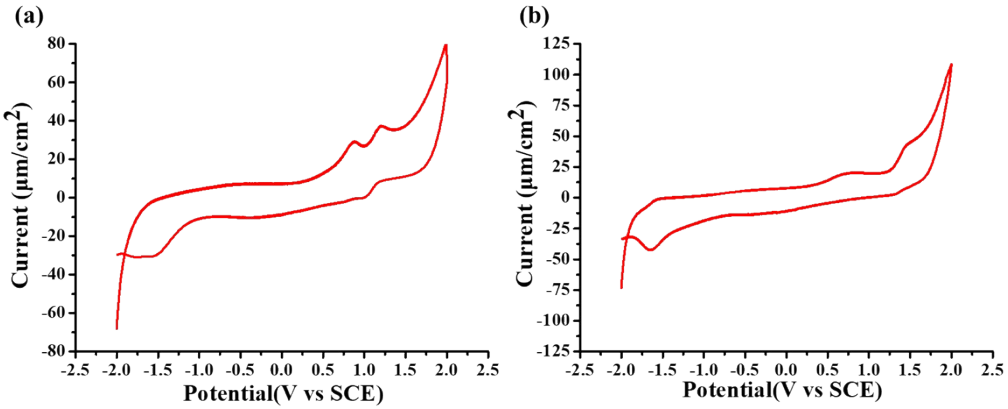
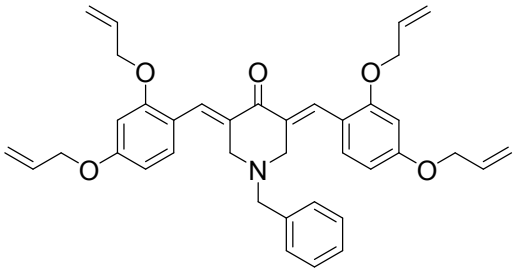


Fig. S4 Cyclic voltammetry of electrochemical reactions of *bis*-chalcones 5 and 9 in acetonitrile solvent against saturated calomel electrode (SCE) under nitrogen saturated solution: (a) *bis*-chalcone 5; (b) *bis*-chalcone 9.

Synthesis of the different *bis*-chalcones

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peaks: DMSO (2.49 ppm), $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peaks: DMSO (49.5 ppm), $CDCl_3$ (77.0 ppm), respectively. All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%), which were checked by high field NMR analysis.

Synthesis of 1-benzyl-3,5-*bis*((E)-2,4-*bis*(allyloxy)benzylidene)piperidin-4-one (*bis*-chalcone 1)

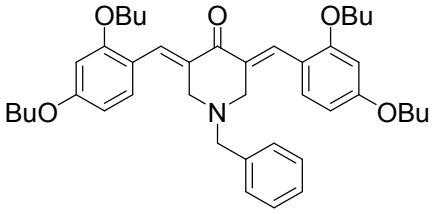


Chemical Formula: $C_{38}H_{39}NO_5$
Molecular Weight: 589.7320

2,4-*Bis*(allyloxy)benzaldehyde (4.36 g, 20 mmol, M = 218.25 g/mol) and 1-benzylpiperidin-4-one (1.89 g, 10 mmol, M = 189.26 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure.

Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.48 g, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.24-7.15 (m, 5H), 7.04 (d, J = 8.4 Hz, 2H), 6.45 (dt, J = 8.4, 2.3 Hz, 4H), 6.13-5.96 (m, 4H), 5.48-5.42 (m, 2H), 5.42-5.36 (m, 2H), 5.33-5.30 (m, 2H), 5.29-5.26 (m, 2H), 4.55 (m, 8H), 3.80 (s, 4H), 3.66 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.76, 159.02, 133.03, 132.99, 131.34, 129.21, 128.30, 127.25, 118.11, 117.85, 105.58, 100.37, 69.34, 69.05, 31.03; HRMS (ESI MS) m/z: theor: 590.2901 found: 590.2904 ($[M+H]^+$ detected).

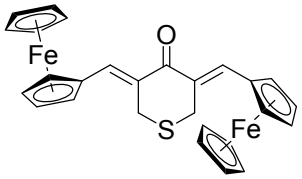
Synthesis of 1-benzyl-3,5-*bis*((E)-2,4-dibutoxybenzylidene)piperidin-4-one (*bis*-chalcone 2)



Chemical Formula: $C_{42}H_{55}NO_5$
Molecular Weight: 653.9040

2,4-Butoxybenzaldehyde (5.00 g, 20 mmol, M = 250.34 g/mol) and 1-benzylpiperidin-4-one (1.89 g, 10 mmol, M = 189.26 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (5.75 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.25-7.15 (m, 5H), 7.04 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 2.3 Hz, 2H), 6.41 (dd, J = 8.5, 2.3 Hz, 2H), 3.98 (td, J = 6.5, 3.0 Hz, 8H), 3.80 (s, 4H), 3.66 (s, 2H), 1.87-1.73 (m, 8H), 1.57-1.44 (m, 8H), 0.99 (t, J = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.61, 161.42, 159.69, 137.92, 132.32, 131.32, 131.29, 129.18, 128.26, 127.16, 117.72, 104.92, 99.71, 68.37, 67.89, 60.97, 54.86, 31.38, 31.28, 19.40, 19.34, 13.95, 13.93; HRMS (ESI MS) m/z: theor: 654.4153 found: 654.4150 ($[M+H]^+$ detected).

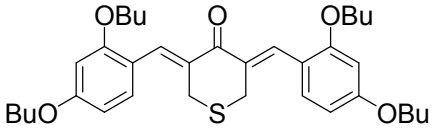
Synthesis of 3,5-*bis*(ferrocenyle)tetrahydro-4H-thiopyran-4-one (*bis*-chalcone 3)



Chemical Formula: $C_{27}H_{24}Fe_2OS$
Molecular Weight: 508.2380

Ferrocenecarboxyaldehyde (3.68 g, 17.21 mmol, M = 214.04 g/mol)) and tetrahydro-4H-thiopyran-4-one (1.0 g, 8.61 mmol, M = 116.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 4.44 (s, 4H), 4.38 (s, 4H), 4.13 (s, 10H), 3.84 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 78.7, 71.2, 71.0, 67.0, 53.5, 30.0; HRMS (ESI MS) m/z: theor: 509.0319 found: 509.0322 ($[M+H]^+$ detected).

Synthesis of 3,5-*bis*((Z)-2,4-dibutoxybenzylidene)tetrahydro-4H-thiopyran-4-one (*bis*-chalcone 4)

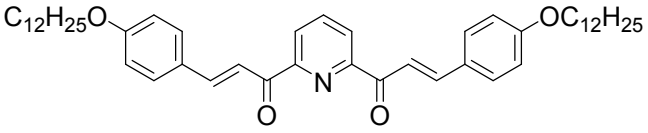


Chemical Formula: $C_{35}H_{48}O_5S$
Molecular Weight: 580.8240

2,4-Butoxybenzaldehyde (5.00 g, 20 mmol, M = 250.34 g/mol) and tetrahydro-4H-thiopyran-4-one (1.16 g, 10 mmol, M = 116.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.82 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.18 (d, J = 9.1 Hz, 2H), 6.51-6.45 (m, 4H), 3.98 (td, J = 6.5, 3.2 Hz, 8H), 3.84 (s, 4H), 1.86-1.74 (m, 8H), 1.56-1.44 (m, 8H), 0.98 (td, J = 7.4, 4.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.23, 161.51, 159.54, 132.88, 132.58, 131.47, 117.56, 105.01, 99.96, 68.45,

68.01, 31.43, 31.32, 30.66, 19.43, 19.39, 13.99, 13.97; HRMS (ESI MS) m/z: theor: 654.4153 found: 654.4150 ($[M+H]^+$ detected).

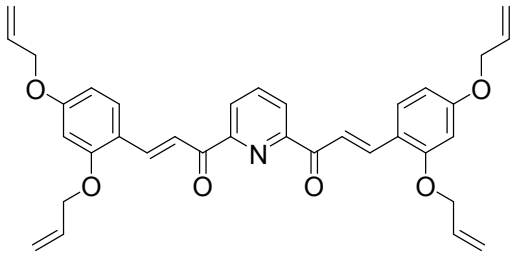
Synthesis of (2E,2'E)-1,1'-(pyridine-2,6-diyl)*bis*(3-(4-(dodecyloxy)phenyl)prop-2-en-1-one) (*bis*-chalcone 5)



Chemical Formula: $C_{47}H_{65}NO_4$
Molecular Weight: 708.0400

4-(Dodecyloxy)benzaldehyde (5.81 g, 20 mmol, M = 290.45 g/mol) and 2,6-diacetylpyridine (1.63 g, 10 mmol, M = 163.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (5.73 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.30 (m, 4H), 8.08-8.03 (m, 1H), 8.00 (dd, J = 14.6, 4.9 Hz, 2H), 7.71 (d, J = 8.7 Hz, 4H), 6.97 (d, J = 8.8 Hz, 4H), 4.04 (t, J = 6.6 Hz, 4H), 1.88-1.78 (m, 4H), 1.56-1.45 (m, 4H), 1.44-1.26 (m, 32H), 0.90 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.63, 161.57, 153.37, 144.97, 138.18, 130.51, 127.75, 125.56, 118.36, 115.00, 68.27, 58.31, 31.91, 29.67, 29.64, 29.62, 29.59, 29.41, 29.35, 29.21, 26.03, 22.68, 18.38, 14.09; HRMS (ESI MS) m/z: theor: 708.4986 found: 708.0982 ($[M+H]^+$ detected).

Synthesis of (2E,2'E)-1,1'-(pyridine-2,6-diyl)*bis*(3-(2,4-bis(allyloxy)phenyl)prop-2-en-1-one) (*bis*-chalcone 6)

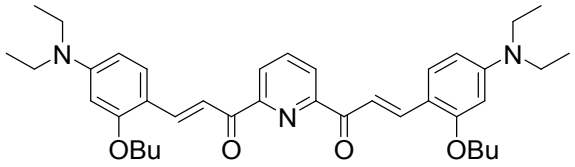


Chemical Formula: $C_{35}H_{33}NO_6$
Molecular Weight: 563.6500

2,4-*Bis*(allyloxy)benzaldehyde (4.36 g, 20 mmol, M = 218.25 g/mol) and 2,6-diacetylpyridine (1.63 g, 10 mmol, M = 163.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed

several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.27 g, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.31 (m, 6H), 8.02 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 6.54 (dd, J = 8.6, 2.3 Hz, 2H), 6.50 (d, J = 2.3 Hz, 2H), 6.04 (ddq, J = 15.8, 11.5, 5.2 Hz, 4H), 5.47-5.35 (m, 4H), 5.33 (dd, J = 10.5, 1.3 Hz, 2H), 5.23 (dd, J = 10.6, 1.3 Hz, 2H), 4.57 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.30, 162.10, 159.56, 153.79, 140.39, 137.99, 132.72, 132.53, 130.52, 125.41, 119.25, 118.16, 117.99, 117.92, 106.74, 100.22, 69.37, 69.02; HRMS (ESI MS) m/z: theor: 564.2381 found: 564.2380 ([M+H]$^+$ detected).

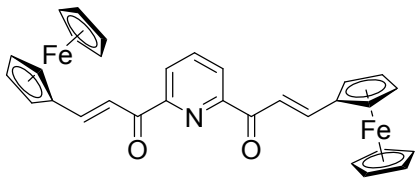
Synthesis of (2E,2'E)-1,1'-(pyridine-2,6-diyl)*bis*(3-(4-(diethylamino)-2-(dodecyloxy)phenyl)prop-2-en-1-one) (*bis*-chalcone 7)



Chemical Formula: $C_{39}H_{51}N_3O_4$
Molecular Weight: 625.8540

4-(Diethylamino)-2-(butoxy)benzaldehyde (4.99 g, 20 mmol, M = 249.35 g/mol) and 2,6-diacetylpyridine (1.63 g, 10 mmol, M = 163.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (5.19 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.25 (m, 6H), 7.98 (t, J = 7.7 Hz, 1H), 7.65 (d, J = 8.9 Hz, 2H), 6.29 (dd, J = 8.8, 2.3 Hz, 2H), 6.12 (d, J = 2.3 Hz, 2H), 3.99 (t, J = 6.5 Hz, 4H), 3.41 (q, J = 7.1 Hz, 8H), 1.82 (dt, J = 14.3, 6.5 Hz, 4H), 1.45 (dq, J = 14.7, 7.4 Hz, 4H), 1.21 (td, J = 7.0, 3.0 Hz, 12H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.34, 160.98, 154.47, 151.29, 141.50, 137.61, 131.32, 124.77, 115.77, 112.63, 104.44, 94.71, 68.10, 44.66, 31.18, 19.34, 13.78, 12.75; HRMS (ESI MS) m/z: theor: 626.3952 found: 626.3958 ([M+H]$^+$ detected).

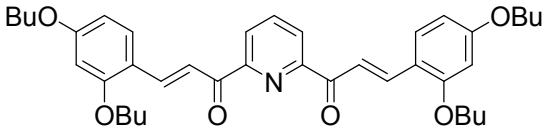
Synthesis of 2,6-*bis*(3- ferrocenyl- 1 -oxoprop-2-enyl)pyridine (*bis*-chalcone 8)



Chemical Formula: $C_{31}H_{25}Fe_2NO_2$
Molecular Weight: 555.2360

Ferrocenecarboxyaldehyde (3.94 g, 18.39 mmol, M = 214.04 g/mol)) and tetrahydro-4H-thiopyran-4-one (1.5 g, 9.19 mmol, M = 163.17 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.2 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, J = 7.7 Hz, 2H), 8.04 (s, J = 7.5 Hz, 5H), 4.75-4.70 (m, 4H), 4.59-4.53 (m, 4H), 4.22 (s, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 153.8, 147.4, 138.3, 125.6, 118.1, 79.7, 71.8, 70.1, 69.4; HRMS (ESI MS) m/z: theor: 556.0657 found: 556.0558 ($[M+H]^+$ detected).

Synthesis of (2E,2'E)-1,1'-(pyridine-2,6-diyl)*bis*(3-(2,4-dibutoxyphenyl)prop-2-en-1-one) (*bis*-chalcone 9)

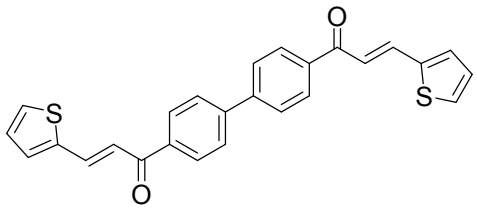


Chemical Formula: $C_{39}H_{49}NO_6$
Molecular Weight: 627.8220

2,4-Butoxybenzaldehyde (5.00 g, 20 mmol, M = 250.34 g/mol) and 2,6-diacetylpyridine (1.63 g, 10 mmol, M = 163.18 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (5.40 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 16.1 Hz, 2H), 8.32 (d, J = 8.9 Hz, 2H), 8.29 (d, J = 17.4 Hz, 2H), 8.04-7.99 (m, 1H), 7.67 (d, J = 8.6 Hz, 2H), 6.51 (dd, J = 8.6, 2.3 Hz, 2H), 6.46 (d, J = 2.3 Hz, 2H), 3.99 (dt, J = 18.6,

6.6 Hz, 8H), 1.85-1.73 (m, 8H), 1.58-1.46 (m, 4H), 1.46 -1.35 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.61, 162.95, 160.48, 154.04, 141.04, 138.06, 131.23, 125.43, 119.20, 117.54, 106.16, 99.60, 68.55, 68.07, 31.39, 31.14, 19.37, 13.97, 13.84; HRMS (ESI MS) m/z: theor: 628.3633 found: 628.3633 ($[M+H]^+$ detected).

Synthesis of (2E,2'E)-1,1'-([1,1'-biphenyl]-4,4'-diyl)*bis*(3-(thiophen-2-yl)prop-2-en-1-one) (*bis*-chalcone 10)



Chemical Formula: $C_{26}H_{18}O_2S_2$
Molecular Weight: 426,55

4,4'-Diacetylbiphenyl (2,38 g, 10 mmol, M = 238.28 g/mol) and 2-thiophenecarboxaldehyde (2.24 g, 20 mmol, M = 112.15 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO2 using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (2.85 g, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02-7.95 (m, 4H), 7.95-7.90 (m, 2H), 7.89 – 7.81 (m, 2H), 7.67-7.58 (m, 4H), 7.31 (d, J = 5.1 Hz, 2H), 7.23 (dt, J = 16.7, 3.7 Hz, 2H), 6.97 (dt, J = 7.2, 3.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.18, 144.13, 140.39, 137.43, 132.23, 129.13, 129.03, 128.43, 127.50, 120.63, 120.60; HRMS (ESI MS) m/z: theor: 427.0821 found: 427.0825 ($[M+H]^+$ detected).