Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Materials:

Photoinitiators Derived From Natural Product Scaffolds: Mono-Chalcones in Three-Component Photoinitiating Systems and their Applications in 3D Printing

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Table S1. Summary of the FCs at 405 nm of monomers (PEG-diacrylate), under three-component photopolymerization systems between other chalcones (1.5%, w/w), iodonium salt (Speedcure 938, 1.5%, w/w) and amine (Speedcure EDB, 1.5%, w/w) between the thin films.

Chalcone initiating systems in PEG-diacrylate							
Chalcone	1	2	3	5	6	7	11
FCs	87.2%	81.4%	86.0%	71.4%	77.3%	80.5%	57.1%
Chalcone	12	13	14	15	16	17	18
FCs	58%	73.3%	73.5%	79.4%	64.6%	69%	79.5%
Chalcone	19	20	21	22	23	Blank	
FCs	73.5%	40.3%	74.7%	30.5%	79.5%	49%	

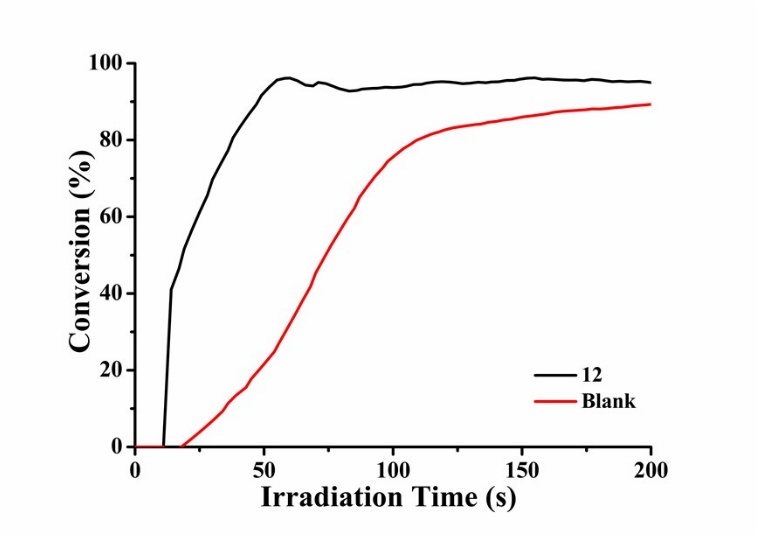


Figure S1. The photopolymerization profiles of PEG-diacrylate (conversion rate of C=C bonds vs irradiation time) initiated by iodonium salt (Speedcure 938) and amine (Speedcure EDB) upon exposure to LED@405nm in laminate, at the same weight ratio chalcones : Speedcure 938 : Speedcure EDB = 1.5%:1.5%:1.5% (w/w/w) in 1g PEG, in the presence of chalcone 12 in thick molds.

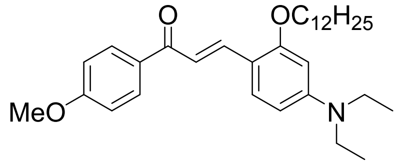
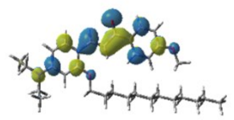
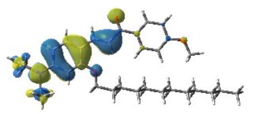
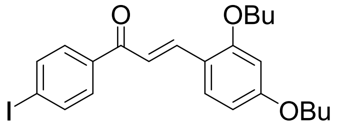
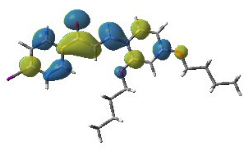
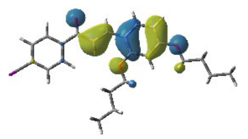
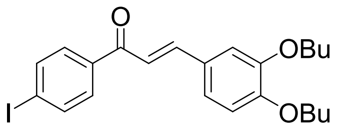
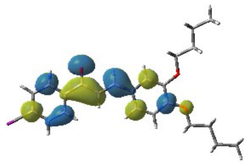
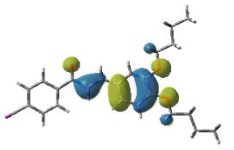
Chalcones	LUMO	HOMO
 chalcone 4		
 chalcone 9		
 chalcone 10		

Figure S2. Contour plots of HOMOs and LUMOs for chalcone 4, 9 and 10 structures optimized at the B3LYP/6-31G* level of theory of chalcones 4, 9 and 10.

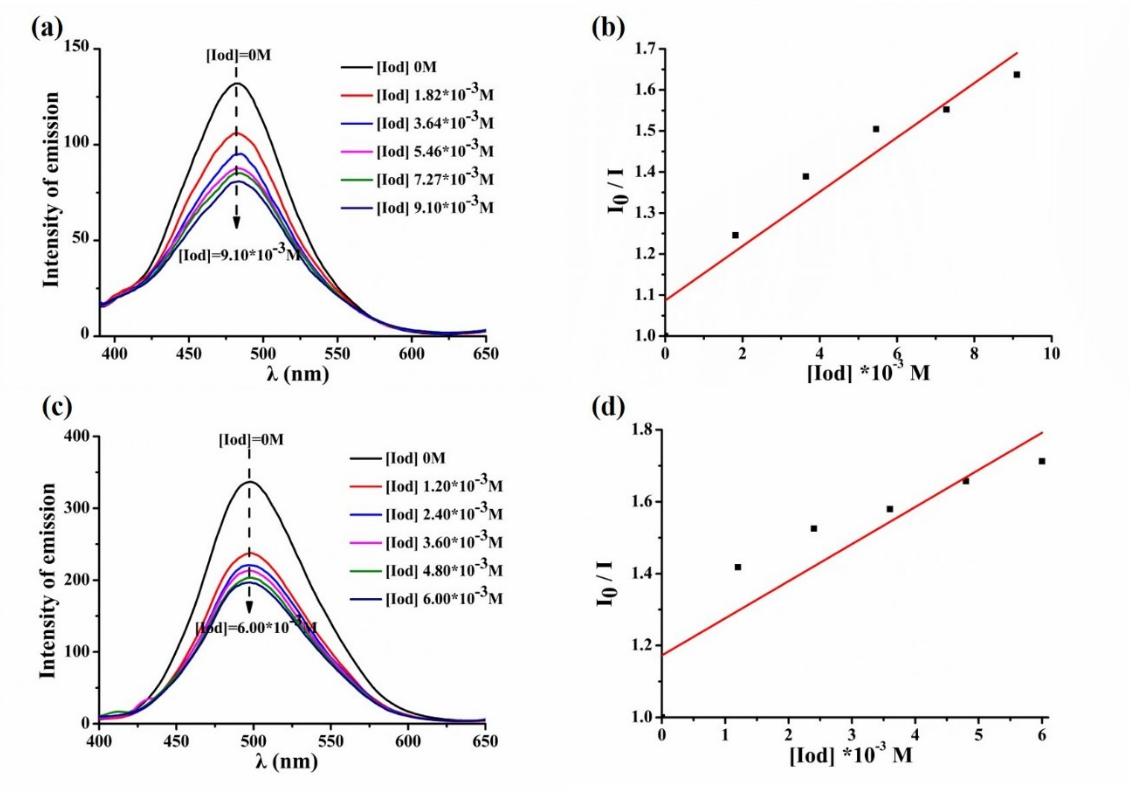
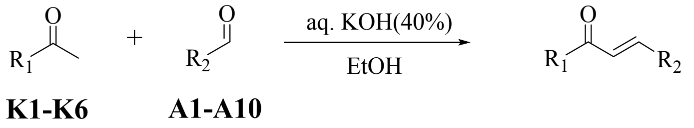


Figure S3. (a) Fluorescence quenching of chalcone 9 by iodonium salt (Speedcure 938); (b) Stern–Volmer treatment for the chalcone 9/iodonium salt fluorescence quenching; (c) Fluorescence quenching of chalcone 10 by iodonium salt (Speedcure 938); (d) Stern–Volmer treatment for the chalcone 10/Iod salt fluorescence quenching. [From the equation (2) : $\Phi^{et}{}_{Iod} = K^{sv}{}_{Iod}*[Iod]/(1+ K^{sv}{}_{Iod}*[Iod])$]

Synthesis of Chalcones 1-23

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 peak DMSO (49.5 ppm), $CDCl_3$ (77.0 ppm). All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.



1 (K3-A1): 91% yield; **2 (K2-A1):** 95% yield;
3 (K1-A1): 92% yield; **4 (K1-A2):** 81% yield;
5 (K1-A3): 80% yield; **6 (K1-A4):** 85% yield;
7 (K4-A3): 88% yield; **8 (K4-A2):** 75% yield;
9 (K4-A11): 84% yield; **10 (K4-A5):** 82% yield;
11 (K4-A4): 73% yield; **12 (K4-A6):** 89% yield;
13 (K2-A7): 88% yield; **14 (K1-A7):** 92% yield;
15 (K3-A8): 84% yield; **16 (K2-A8):** 90% yield;
17 (K1-A8): 88% yield; **18 (K5-A12):** 77% yield;
19 (K2-A8): 32% yield; **20 (K1-A8):** 85% yield;
21 (K4-A8): 88% yield; **22 (K5-A1):** 88% yield;
23 (K6-A8): 67% yield

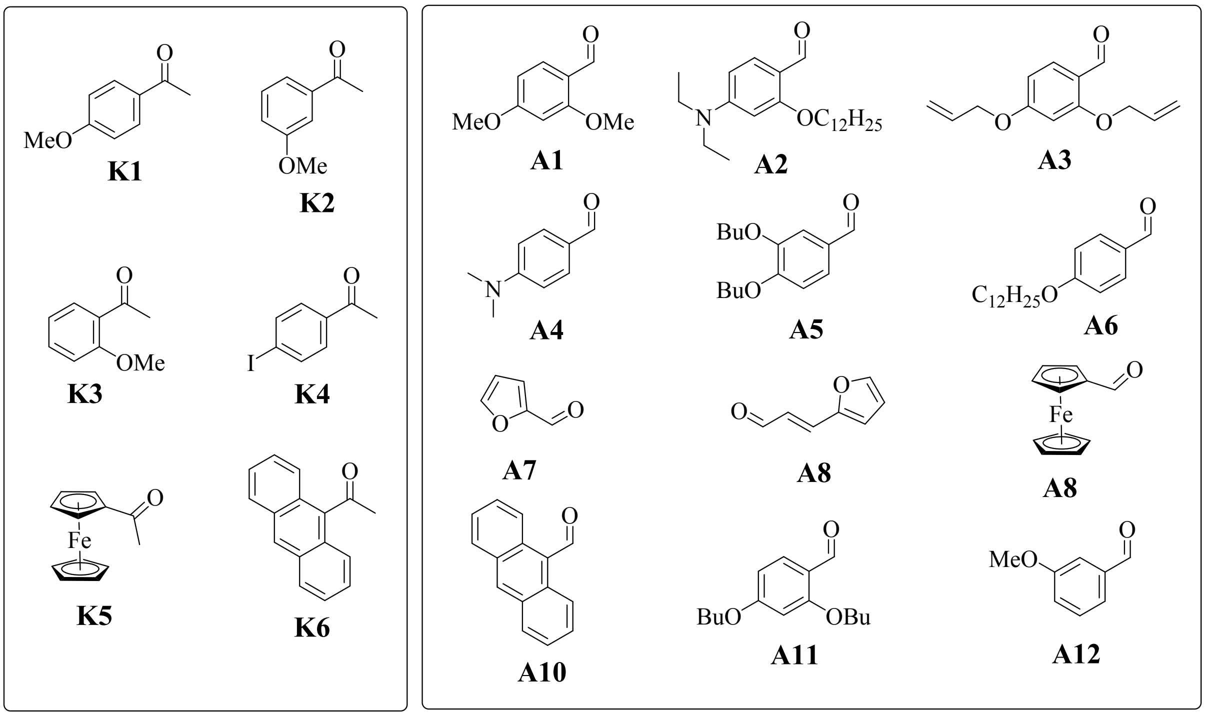
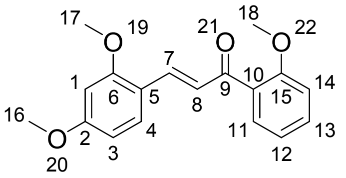


Figure S4. Synthetic route to chalcones 1-23.

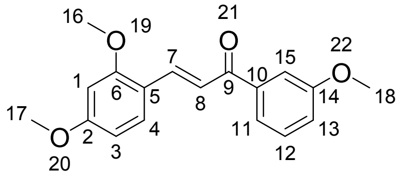
Synthesis of (E)-3-(2,4-dimethoxyphenyl)-1-(2-methoxyphenyl)prop-2-en-1-one (chalcone 1)



Chemical Formula: $C_{18}H_{18}O_4$
Molecular Weight: 298,34

2,4-Dimethoxybenzaldehyde (3.32 g, 20 mmol, M = 166.18 g/mol) and 2′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (5.43 g, 91% yield). ^{1}H NMR ($CDCl_3$) δ : 3.87 (s, H_{16}, 3H), 3.88 (s, H_{18}, 3H), 3.91 (s, H_{17}, 3H), 6.48 (d, H_1, 1H, J = 2.3 Hz), 6.53 (dd, H_3, 1H, J = 8.6 Hz, J= 2.5 Hz), 6.99-7.07 (m, $H_{12,13}$, 2H), 7.34 (d, H_8, 1H, J = 16.0 Hz), 7.43-7.47 (m, H_{14}, 1H), 7.55 (d, H_{11}, 1H, J = 8.6 Hz), 7.60 (dd, H_4, 1H, J = 7.5 Hz, J = 1.8 Hz), 7.89 (d, H_7, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$) δ : 55.5($C_{16,18}$), 55.7(C_{17}), 98.4(C_1), 105.4(C_3), 111.6(C_{14}), 117.6(C_5), 120.6(C8), 125.4(C_{12}), 129.9(C_{11}), 130.1(C_4), 130.4(C_{10}), 132.2(C_{13}), 139.3(C_7), 157.8(C_{15}), 160.2(C_6), 162.9(C_2), 193.8(C_9); HRMS (ESI MS) m/z: theor: 299.1278 found: 299.1279 ($[M+H]^+$ detected).

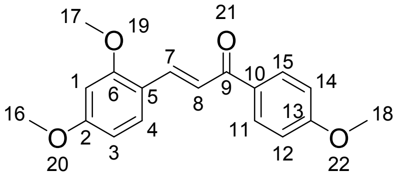
Synthesis of (E)-3-(2,4-dimethoxyphenyl)-1-(3-methoxyphenyl)prop-2-en-1-one (chalcone 2)



Chemical Formula: $C_{18}H_{18}O_4$
Molecular Weight: 298,34

2,4-Dimethoxybenzaldehyde (3.32 g, 20 mmol, M = 166.18 g/mol) and 3′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (5.67 g, 95% yield). ^{1}H NMR ($CDCl_3$) δ : 3.86 (s, H_{18}, 3H), 3.88 (s, H_{17}, 3H), 3.90 (s, H_{16}, 3H), 6.47 (d, H_1, 1H, J = 2.3 Hz), 6.54 (dd, H_3, 1H, J = 8.5 Hz, J = 2.3 Hz), 7.08-7.12 (m, H_{12}, 1H), 7.34-7.42 (m, H_{13}, 1H), 7.48-7.49 (m, H_4, 1H), 7.53-7.60 (m, $H_{11,15,8}$, 3H), 8.05 (d, H_7, 1H, J = 15.8 Hz); ^{13}C NMR ($CDCl_3$) δ : 55.4(C_{17}), 55.5(C_{18}), 55.6(C_{16}), 98.5(C_1), 105.4(C_3), 112.8(C_{15}), 117.2(C_{12}), 118.8(C_5), 120.5(C_{13}), 121.0(C_8), 129.4(C_4), 131.0(C_{11}), 140.3(C_{10}), 140.6(C_7), 159.8(C_6), 160.4(C_{14}), 163.1(C_2), 190.9(C_9); HRMS (ESI MS) m/z: theor: 299.1278 found: 299.1277 ($[M+H]^+$ detected).

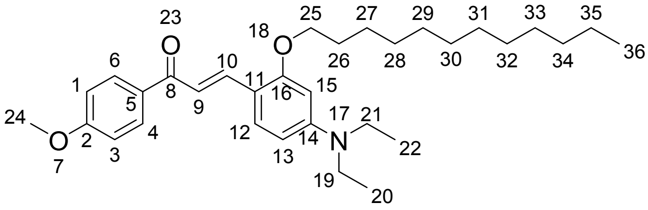
Synthesis of (E)-3-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (chalcone 3)



Chemical Formula: $C_{18}H_{18}O_4$
Molecular Weight: 298.3380

2,4-Dimethoxybenzaldehyde (3.32 g, 20 mmol, M = 166.18 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (5.49 g, 92% yield). ^1H NMR ($CDCl_3$) δ : 3.85 (s, H_{18}, 3H), 3.88 (s, H_{16}, 3H), 3.90 (s, H_{17}, 3H), 6.48 (d, H_1, 1H, J = 2.3 Hz), 6.53 (dd, H_3, 1H, J = 8.6 Hz, J= 2.5 Hz), 6.97 (d, $H_{12,14}$, 2H, J = 8.9 Hz), 7.43-7.47 (m, H_8, 1H), 7.53-7.58 (m, H_4, 1H), 8.01-8.03 (m, $H_{7,11,15}$, 3H); ^{13}C NMR ($CDCl_3$) δ : 55.4(C_{18}), 55.5(C_{16}), 55.6(C_{17}), 98.5(C_1), 105.4(C_3), 113.7($C_{12,14}$), 117.4(C_5), 120.4(C_8), 130.6(C_{10}), 130.7(C_{11}), 130.8(C_{15}), 131.8(C_4), 139.7(C_7), 160.3(C_6), 162.9(C_2), 163.1(C_{13}), 189.4(C_9); HRMS (ESI MS) m/z: theor: 299.1278 found: 299.1275 ($[M+H]^+$ detected).

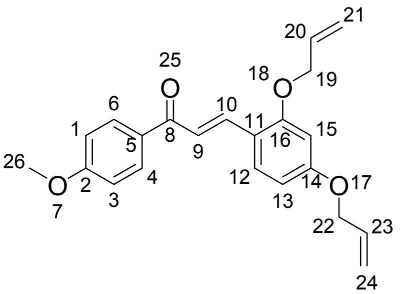
Synthesis of (E)-3-(4-(diethylamino)-2-(dodecyloxy)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (chalcone 4)



Chemical Formula: $C_{32}H_{47}NO_3$
Molecular Weight: 493.7320

4-(Diethylamino)-2-(dodecyloxy)benzaldehyde (7.23 g, 20 mmol, M = 361.57 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (8.00 g, 81% yield). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.05 – 7.97 (m, $H_{4,6,8}$, 3H), 7.56 (d, H_9, J = 15.5 Hz, 1H), 7.44 (d, H_{12}, J = 8.9 Hz, 1H), 6.98 – 6.91 (m, $H_{1,3}$, 2H), 6.28 (dd, H_{13}, J = 8.8, 2.4 Hz, 1H), 6.13 (d, H_{15}, J = 2.4 Hz, 1H), 4.04 (t, H_{25}, J = 6.4 Hz, 2H), 3.87 (s, H_{24}, 3H), 3.41 (q, $H_{19,21}$, J = 7.1 Hz, 4H), 1.97 – 1.83 (m, H_{26}, 2H), 1.61 – 1.49 (m, H_{27}, 2H), 1.41 – 1.24 (m, $H_{28\text{-}35}$, 16H), 1.21 (t, $H_{20,22}$, J = 7.1 Hz, 6H), 0.88 (t, H_{36}, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.7(C_8), 162.8(C_2), 160.8(C_{16}), 151.0(C_{14}), 141.5(C_{10}), 132.6($C_{5,12}$), 130.6($C_{4,6}$), 117.3(C_9), 113.7(C_{11}), 112.2($C_{1,3}$), 104.4(C_{13}), 94.9(C_{15}), 68.3(C_{25}), 55.5(C_{24}), 44.8($C_{19,21}$), 32.1(C_{26}), 29.8(C_{27}), 29.8($C_{28,29}$), 29.8(C_{30}), 29.7(C_{31}), 29.6(C_{32}), 29.5(C_{33}), 26.6(C_{34}), 22.8(C_{35}), 14.3(C_{36}), 12.9($C_{20,22}$); HRMS (ESI MS) m/z: theor: 494.3629 found: 494.3632 ($[M+H]^+$ detected).

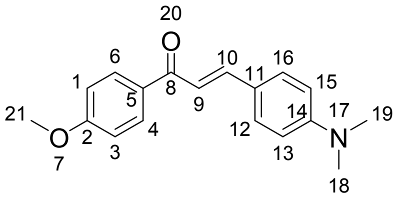
Synthesis of (E)-3-(2,4-bis(allyloxy)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (chalcone 5)



Chemical Formula: $C_{22}H_{22}O_4$
Molecular Weight: 350.4140

2,4-*Bis*(allyloxy)benzaldehyde (4.36 g, 20 mmol, M = 218.25 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (5.60 g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 – 7.99 (m, $H_{4,6,10}$, 3H), 7.59 (d, H_9, J = 15.5Hz, 1H), 7.55 (d, H_{12}, J = 8.5 Hz, 1H), 6.99 – 6.93 (m, $H_{1,3}$, 2H), 6.56 – 6.51 (m, H_{13}, 1H), 6.50 (d, H_{15}, J = 2.3 Hz, 1H), 6.18 – 5.97 (m, $H_{20,23}$, 2H), 5.50 – 5.37 (m, $H_{21,24}$, 2H), 5.36 – 5.27 (m, $H_{21,24}$, 2H), 4.61 (dt, H_{19}, J = 5.3, 1.5 Hz, 2H), 4.56 (dt, H_{22}, J = 5.3, 1.5 Hz, 2H), 3.87 (s, H_{26}, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 189.4(C_8), 163.2(C_2), 161.7(C_{16}), 159.4(C_{14}), 139.8(C_{10}), 132.9(C_{23}), 132.8(C_{20}), 131.8(C_6), 131.1(C_4), 130.8(C_{12}), 130.7(C_5), 120.6(C_9), 118.2(C_{21}), 118.2(C_{24}), 117.8(C_{11}), 113.8($C_{1,3}$), 106.6(C_{13}), 100.5(C_{15}), 69.4(C_{19}), 69.1(C_{22}), 55.6(C_{26}); HRMS (ESI MS) m/z: theor: 351.1591 found: 351.1590 ($[M+H]^+$ detected).

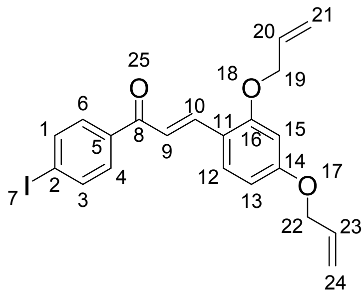
Synthesis of (E)-3-(4-(dimethylamino)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (chalcone 6)



Chemical Formula: $C_{18}H_{19}NO_2$
Molecular Weight: 281,36

4-(Dimethylamino)benzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (4.78 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 – 8.00 (m, $H_{4,6}$, 2H), 7.78 (d, H_{10}, J = 15.4 Hz, 1H), 7.58 – 7.53 (m, $H_{12,16}$, 2H), 7.35 (d, H_9, J = 15.4 Hz, 1H), 7.00 – 6.95 (m, $H_{1,3}$, 2H), 6.72 – 6.67 (m, $H_{13,15}$, 2H), 3.88 (s, H_{21}, 3H), 3.04 (s, $H_{18,19}$, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 189.1(C_8), 163.1(C_2), 152.1(C_{14}), 145.1(C_{10}), 132.1($C_{4,6}$), 130.7(C_5), 130.4($C_{12,16}$), 123.1(C_{11}), 117.0(C_9), 113.8($C_{1,3}$), 112.0($C_{13,15}$), 55.6(C_{21}), 40.3($C_{18,19}$); HRMS (ESI MS) m/z: theor: 282.1489 found: 282.1493 ($[M+H]^+$ detected).

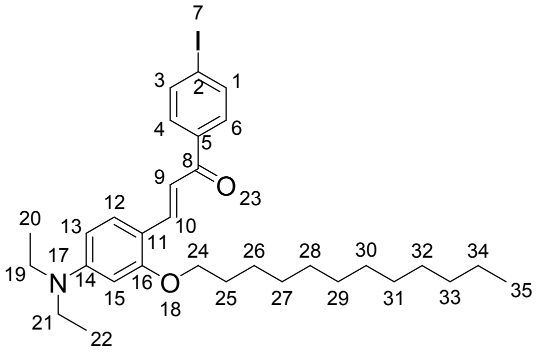
Synthesis of (E)-3-(2,4-bis(allyloxy)phenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 7)



Chemical Formula: $C_{21}H_{19}IO_3$
Molecular Weight: 446.2845

2,4-Bis(allyloxy)benzaldehyde (4.36 g, 20 mmol, M = 218.25 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (7.85 g, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, H_{10}, J = 15.8 Hz, 1H), 7.86 – 7.81 (m, $H_{1,3}$, 2H), 7.74 – 7.69 (m, $H_{9,12}$, 2H), 7.56 – 7.50 (m, $H_{4,6}$, 2H), 6.55 (dd, H_{13}, J = 8.6, 2.3 Hz, 1H), 6.50 (d, H_{15}, J = 2.3 Hz, 1H), 6.16 – 5.99 (m, $H_{20,23}$, 2H), 5.49 – 5.39 (m, $H_{21,24}$, 2H), 5.37 – 5.30 (m, $H_{21,24}$, 2H), 4.61 (dt, H_{19}, J = 5.2, 1.4 Hz, 2H), 4.58 (dt, H_{22}, J = 5.3, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.4(C_8), 162.2(C_{14}), 159.6(C_{16}), 141.3(C_{10}), 138.3($C_{1,3}$), 137.9(C_5), 132.8(C_{20}), 132.8(C_{23}), 131.5(C_{12}), 130.1($C_{4,6}$), 120.2(C_9), 118.4(C_{24}), 118.3(C_{21}), 117.5(C_{11}), 106.7(C_{13}), 100.5(C_{15}), 100.0(C_2), 69.4(C_{19}), 69.2(C_{22}); HRMS (ESI MS) m/z: theor: 447.0452 found: 447.0455 ($[M+H]^+$ detected).

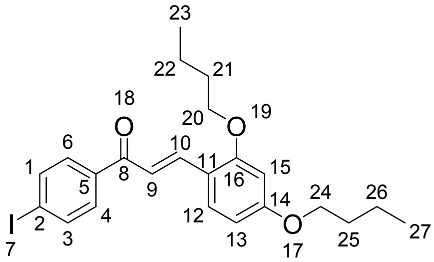
Synthesis of (E)-3-(4-(diethylamino)-2-(dodecyloxy)phenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 8)



Chemical Formula: $C_{31}H_{44}INO_2$
Molecular Weight: 589.6025

4-(Diethylamino)-2-(dodecyloxy)benzaldehyde (7.23 g, 20 mmol, M = 361.57 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (8.84 g, 75% yield). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.02 (d, H_{10}, J = 15.5 Hz, 1H), 7.84 – 7.78 (m, $H_{1;3}$, 2H), 7.72 – 7.68 (m, $H_{4,6}$, 2H), 7.47 (d, H_9, J = 14.8 Hz, 1H), 7.43 (d, H_{12}, J = 8.3 Hz, 1H), 6.28 (dd, H_{13}, J = 8.8, 2.4 Hz, 1H), 6.11 (d, H_{15}, J = 2.4 Hz, 1H), 4.04 (t, H_{24}, J = 6.3 Hz, 2H), 3.41 (q, $H_{19,21}$, J = 7.1 Hz, 4H), 1.94 – 1.83 (m, H_{25}, 2H), 1.57 – 1.46 (m, H_{26}, 2H), 1.43 – 1.25 (m, $H_{27\text{-}34}$, 16H), 1.21 (t, $H_{20,22}$, J = 7.1 Hz, 6H), 0.91 – 0.85 (t, H_{35}, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.4(C_8), 161.1(C_{16}), 151.4(C_{14}), 142.95(C_{10}), 139.2($C_{1,3}$), 137.7(C_5), 132.9($C_{4,6}$), 130.0(C_{12}), 116.7(C_9), 111.9(C_{11}), 104.5(C_{13}), 99.2(C_2), 94.7(C_{15}), 68.3(C_{24}), 44.8($C_{19,21}$), 34.3(C_{25}), 32.1(C_{26}), 29.8(C_{27}), 29.8(C_{28}), 29.7(C_{29}), 29.6(C_{30}), 29.5(C_{31}), 26.6(C_{32}), 22.8(C_{33}), 22.5(C_{34}), 14.3(C_{22}), 14.2(C_{20}), 12.8(C_{35}); HRMS (ESI MS) m/z: theor: 590.2489 found: 590.2491 ($[M+H]^+$ detected).

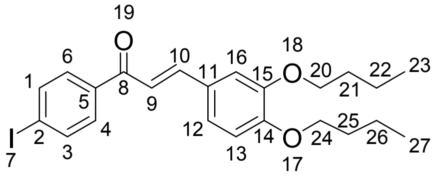
Synthesis of (E)-3-(2,4-dibutoxyphenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 9)



Chemical Formula: $C_{23}H_{27}IO_3$
Molecular Weight: 478.3705

2,4-Dibutoxybenzaldehyde (5.00 g, 20 mmol, M = 250.34 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (8.03 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, H_{10}, J = 15.7 Hz, 1H), 7.85 – 7.81 (m, $H_{1,3}$, 2H), 7.73 – 7.68 (m, $H_{4,6}$, 2H), 7.56 (d, H_9, J = 15.7 Hz, 1H), 7.51 (d, H_{12}, J = 8.6 Hz, 1H), 6.51 (dd, H_{13}, J = 8.6, 2.3 Hz, 1H), 6.46 (d, H_{15}, J = 2.3 Hz, 1H), 4.02 (dt, $H_{20,24}$, J = 16.2, 6.4 Hz, 4H), 1.92 – 1.81 (m, H_{21}, 2H), 1.82 – 1.74 (m, H_{25}, 2H), 1.62 – 1.45 (m, $H_{22,26}$, 4H), 1.00 (dt, $H_{23,27}$, J = 9.4, 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.6(C_8), 162.9(C_{14}), 160.4(C_{16}), 142.0(C_{10}), 138.4($C_{1,3}$), 137.9(C_5), 132.1($C_{4,6}$), 130.0(C_{12}), 119.9(C_9), 117.0(C_{11}), 106.1(C_{13}), 99.9(C_{15}), 99.8(C_2), 68.4(C_{24}), 68.1(C_{20}), 31.5(C_{25}), 31.4(C_{21}), 19.6(C_{26}), 19.4(C_{22}), 14.0(C_{27}), 14.0(C_{23}); HRMS (ESI MS) m/z: theor: 479.1078 found: 479.1082 ($[M+H]^+$ detected).

Synthesis of (E)-3-(3,4-dibutoxyphenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 10)

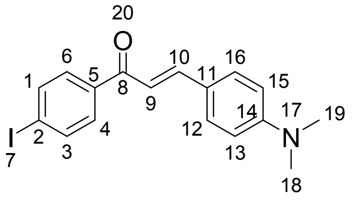


Chemical Formula: $C_{23}H_{27}IO_3$
Molecular Weight: 478,37

3,4-Dibutoxybenzaldehyde (5.00 g, 20 mmol, M = 250.34 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (7.84 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ:

7.88 – 7.84 (m, $H_{1,3}$, 2H), 7.74 (d, H_{10}, J = 13.5 Hz, 1H), 7.72 – 7.68 (m, $H_{4,6}$, 2H), 7.28 (d, H_{9}, J = 15.6 Hz, 1H), 7.20 (dd, H_{12}, J = 8.3, 2.0 Hz, 1H), 7.16 (d, H_{16}, J = 2.0 Hz, 1H), 6.89 (d, H_{13}, J = 8.3 Hz, 1H), 4.06 (t, $H_{20,24}$, J = 6.6 Hz, 4H), 1.88 – 1.78 (m, $H_{21,25}$, 4H), 1.58 – 1.48 (m, $H_{22,26}$, 4H), 1.00 (td, $H_{23,27}$, J = 7.4, 4.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.0(C_8), 152.2(C_{14}), 149.5(C_{15}), 146.0(C_{10}), 138.0($C_{1,3}$), 138.0(C_5), 130.0($C_{4,6}$), 127.7(C_{11}), 123.6(C_{12}), 119.4(C_9), 113.2(C_{13}), 113.2(C_{16}), 100.3(C_2), 69.4(C_{24}), 69.0(C_{20}), 31.5(C_{25}), 31.3(C_{21}), 19.4(C_{22}), 19.4(C_{26}), 14.0(C_{23}), 14.0(C_{27}); HRMS (ESI MS) m/z: theor: 479.1078 found: 479.1080 ($[M+H]^+$ detected).

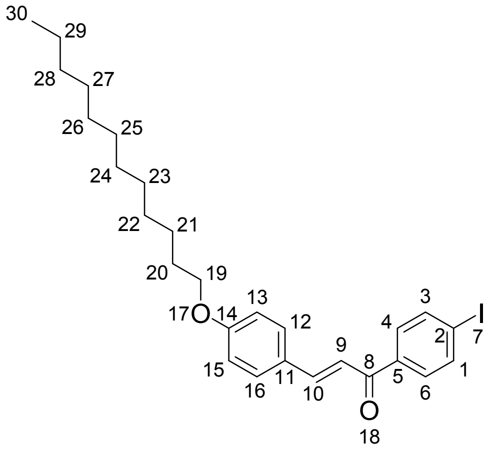
Synthesis of (E)-3-(4-(dimethylamino)phenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 11)



Chemical Formula: $C_{17}H_{16}INO$
Molecular Weight: 377,23

4-(Dimethylamino)benzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (5.51 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 – 7.82 (m, H_{16}, 2H), 7.79 (d, H_{10}, J = 15.5 Hz, 1H), 7.74 – 7.69 (m, H_{16}, 2H), 7.57 – 7.51 (m, H_{16}, 2H), 7.25 (d, H_9, J = 15.5 Hz, 1H), 6.73 – 6.65 (m, H_{16}, 2H), 3.05 (s, $H_{18,19}$, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.9(C_8), 152.4(C_{14}), 146.6(C_{10}), 138.6($C_{1,3}$), 137.9(C_5), 130.7($C_{4,6}$), 130.0($C_{12,16}$), 122.6(C_{11}), 116.4(C_9), 112.0($C_{13,15}$), 99.8(C_2), 40.3($C_{18,19}$); HRMS (ESI MS) m/z: theor: 378.0349 found: 378.0355 ($[M+H]^+$ detected).

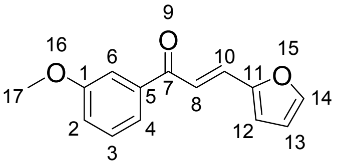
Synthesis of (E)-3-(4-(dodecyloxy)phenyl)-1-(4-iodophenyl)prop-2-en-1-one (chalcone 12)



Chemical Formula: $C_{27}H_{35}IO_2$
Molecular Weight: 518,48

4-Dodecyloxybenzaldehyde (5.81 g, 20 mmol, M = 290.44 g/mol) and 4′-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (9.23 g, 89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 – 7.83 (m, $H_{1,3}$, 2H), 7.77 (d, H_{10}, J = 15.5 Hz, 1H), 7.73 – 7.69 (m, $H_{12,16}$, 2H), 7.57 (t, $H_{4,6}$, J = 5.7 Hz, 2H), 7.32 (d, H_9, J = 15.6 Hz, 1H), 6.92 (q, $H_{13,15}$, J = 3.1 Hz, 2H), 4.00 (t, H_{19}, J = 6.6 Hz, 2H), 1.84 – 1.74 (m, H_{20}, 2H), 1.45 (m, H_{21}, 2H), 1.39 – 1.22 (m, $H_{22\text{-}29}$, 16H), 0.88 (t, H_{30}, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7 (C_8), 161.5(C_{14}), 145.4(C_{10}), 138.0($C_{1,3}$), 137.8(C_5), 130.3($C_{12,16}$), 129.9(C_4), 129.5(C_6), 127.2(C_{11}), 126.9(C_9), 119.0(C_2), 115.0(C_{13}), 114.6(C_{15}), 68.3(C_{19}), 31.9(C_{20}), 29.6(C_{21}), 29.6(C_{22}), 29.5(C_{23}), 29.4(C_{24}), 29.3(C_{25}), 29.1(C_{26}), 26.0(C_{27}), 26.0(C_{28}), 22.7(C_{29}), 14.1(C_{30}); HRMS (ESI MS) m/z: theor: 519.1754 found: 519.1752 ($[M+H]^+$ detected).

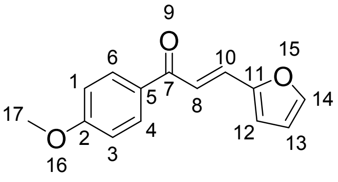
Synthesis of (E)-3-(furan-2-yl)-1-(3-methoxyphenyl)prop-2-en-1-one (chalcone 13)



Chemical Formula: $C_{14}H_{12}O_3$
Molecular Weight: 228.2470

Furfural (1.92 g, 20 mmol, M = 96.08 g/mol) and 3′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (4.02 g, 88% yield). ^1H NMR ($CDCl_3$) δ : 3.88 (s, 3H, H_{17}), 6.51-6.52 (m, 1H, H_{13}), 6.72 (d, 1H, J = 3.4 Hz, H_2), 7.11-7.14 (m, 1H, H_6), 7.38-7.45 (m, 2H, H_3 and H_8), 7.52-7.53 (m, 1H, H_{12}), 7.55-7.56 (m, 1H, H_{10}), 7.57-7.62 (m, 2H, H_{14} and H_4); ^{13}C NMR ($CDCl_3$) δ : 55.5 (C_{17}), 112.6 (C_{13}), 112.7 (C_3), 116.2(C_{12}), 119.4 (C_2), 119.5 (C_2), 121.0 (C_{10}), 129.6 (C_8), 130.7 (C_5), 139.4 (C_4, C_6), 144.9 (C_{14}), 151.7 (C_{11}), 159.9 (C_1, C_3), 189.6 (C_7); HRMS (ESI MS) m/z: theor: 229.0859 found: 229.0862 ($[M+H]^+$ detected).

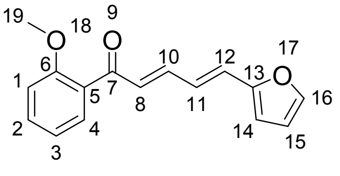
Synthesis of (E)-3-(furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (chalcone 14)



Chemical Formula: $C_{14}H_{12}O_3$
Molecular Weight: 228.2470

Furfural (1.92 g, 20 mmol, M = 96.08 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (4.20 g, 92% yield). ^1H NMR ($CDCl_3$) δ : 3.88 (s, 3H, H_{17}), 6.50-6.51 (m, 1H, H_{13}), 6.70 (d, 1H, J = 3.4 Hz, H_{12}), 6.97 (d, 2H, J = 9.0 Hz, H_1,H_3), 7.46 (d, 1H, J = 15.3 Hz, H_8), 7.51 (d, 1H, J = 1.4 Hz, H_{14}), 7.58 (d, 1H, J = 15.3 Hz, H_{10}), 8.04 (d, 2H, J = 9.0 Hz, H_4,H_6); ^{13}C NMR ($CDCl_3$) δ : 55.5 (C_{17}), 112.6 (C_{13}), 113.8 (C_{12}), 115.7 (C_1, C_3), 119.3 (C_{10}), 130.0 (C_9), 130.7 (C_5), 131.1 (C_4, C_6), 144.7 (C_{17}), 151.9 (C_{14}), 163.4 (C_2), 188.1 (C_7); HRMS (ESI MS) m/z: theor: 229.0859 found: 229.080 ($[M+H]^+$ detected).

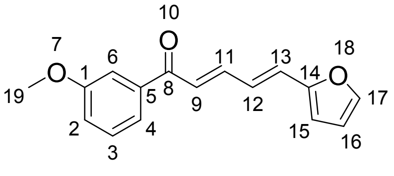
Synthesis of (2E,4E)-5-(furan-2-yl)-1-(2-methoxyphenyl)penta-2,4-dien-1-one (chalcone 15)



Chemical Formula: $C_{16}H_{14}O_3$
Molecular Weight: 254.2850

3-(Furan-2-yl)acrylaldehyde (2.44 g, 20 mmol, M = 122.12 g/mol) and 2′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (4.27 g, 84% yield). ^{1}H NMR ($CDCl_3$) δ : 3.81 (s, 3H, H_{19}), 6.36-6.39 (m, 2H, H_{15}, H_{12}), 6.63 (d, 1H, J = 15.3 Hz, H_{11}), 6.77-6.82 (m, 1H, H_{14}), 6.84 (d, 1H, J = 8.4 Hz, H_8), 6.89-6.96 (m, 2H, H_1, H_2), 7.24-7.31 (m, 1H, H_4), 7.35-7.39 (m, 2H, H_7, H_{16}), 7.50 (dd, 1H, J = 7.6 Hz, J = 1.8 Hz, H_3); ^{13}C NMR ($CDCl_3$) δ : 55.7 (C_{19}), 111.6 (C_1), 111.8 (C_{15}), 112.2 (C_{14}), 120.7 (C_{12}), 125.7 (C_3), 127.6 (C_4), 129.4 (C_8), 130.3 (C_5), 130.4 (C_2), 132.7 (C_{11}), 142.9 (C_{16}), 143.7 (C_{10}), 152.5 (C_{13}), 158.1 (C_6), 192.7 (C_7); HRMS (ESI MS) m/z: theor: 255.1016 found: 255.1019 ($[M+H]^+$ detected).

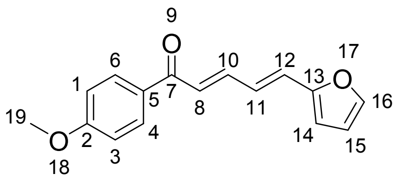
Synthesis of (2E,4E)-5-(furan-2-yl)-1-(3-methoxyphenyl)penta-2,4-dien-1-one (chalcone 16)



Chemical Formula: $C_{16}H_{14}O_3$
Molecular Weight: 254.2850

3-(Furan-2-yl)acrylaldehyde (2.44 g, 20 mmol, M = 122.12 g/mol) and 3′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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 (4.58 g, 90% yield). ^{1}H NMR ($CDCl_3$) δ : 3.87 (s, 3H, H_{19}), 6.45-6.46 (m, 1H, H_{16}), 6.49-6.50 (m, 1H, H_{12}), 6.78 (d, 1H, J = 15.4 Hz, H_{13}), 6.89-6.96 (m, 1H, H_{15}), 7.06 (d, 1H, J = 1.6 Hz),7.10-7.12 (m, 1H, H_2), 7.39 (t, 1H, J = 14.8 Hz, H_9), 7.46 (d, 1H, J = 1.6 Hz, H_6), 7.50-7.58 (m, 3H, H_4, H_{11}, H_{17}); ^{13}C NMR ($CDCl_3$) δ : 55.5 (C_{19}), 112.3 (C_{16}), 112.7 (C_{15}), 119.2 (C_6), 120.9 (C_3), 125.3 (C_{13}), 125.4 (C_2), 128.3 (C_9), 129.5 (C_5), 139.7 (C_4), 143.9 (C_{12}), 144.4 (C_{17}, C_{11}), 152.4 (C_{14}), 159.9 (C_1), 190.0 (C_8); HRMS (ESI MS) m/z: theor: 255.1016 found: 255.1014 ($[M+H]^+$ detected).

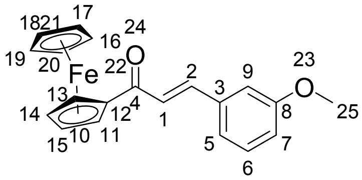
Synthesis of (2E,4E)-5-(furan-2-yl)-1-(4-methoxyphenyl)penta-2,4-dien-1-one (chalcone 17)



Chemical Formula: $C_{16}H_{14}O_3$
Molecular Weight: 254.2850

3-(Furan-2-yl)acrylaldehyde (2.44 g, 20 mmol, M = 122.12 g/mol) and 4′-methoxyacetophenone (3.00 g, 20 mmol, M = 150.18 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 SiO_2 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, 88% yield). ^{1}H NMR ($CDCl_3$) δ : 3.88 (s, 3H, H_{19}), 6.44-6.48 (m, 2H, H_{15}, H_{11}), 6.76 (d, 1H, J = 15.3 Hz, H_{12}), 6.89-6.95 (m, 1H, H_{14}), 6.96 (d, 2H, J = 8.9 Hz, H_1, H_3), 7.09 (d, 1H, J = 14.8 Hz, H_8), 7.45 (d, 1H, J = 1.6 Hz, H_{16}), 7.53 (dd, 1H, J = 14.6 Hz, J = 11.4 Hz, H_{10}), 7.99 (d, 2H, J = 8.9 Hz, H_4, H_6); ^{13}C NMR ($CDCl_3$) δ : 55.5 (C_{19}), 112.0 (C_{15}), 112.2 (C_{14}), 125.1 (C_1, C_3), 125.5 (C_{12}), 127.8 (C_8), 128.3 (C_5), 129.7 (C_4, C_6), 130.6 (C_{11}), 143.5 (C_{16}), 143.7 (C_{10}), 152.5 (C_{13}), 163.3 (C_2), 188.5 (C_7); HRMS (ESI MS) m/z: theor: 255.1016 found: 255.1012 ($[M+H]^+$ detected).

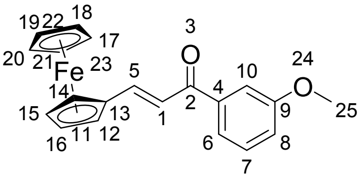
Synthesis of [3-(3-methoxyphenyl)-1-oxo-2-propen-1-yl]ferrocene (chalcone 18)



Chemical Formula: $C_{20}H_{18}FeO_2$
Molecular Weight: 346.2070

Acetylferrocene (2 g, 13.15 mmol, M = 228.07 g/mol) and KOH (0.74 g, 13.15 mmol, M = 56.11 g/mol) were dissolved in ethanol (20 mL) in a round bottomed flask. 2-Methoxybenzaldehyde (1.6 mL, 13.15 mmol, M = 136.15 g/mol) was added and the mixture was stirred at room temperature for 24 h. The reaction was stopped by neutralizing the stirred solution with 2M HCl. A dark red precipitate after neutralization appeared. It was then removed by filtration, washed with water, some cold ethanol, and pentane. A column chromatography with ether as eluent allowed to obtain 3.5 g, 77% yield of product as a powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.79 (d, J = 15.6 Hz, 1H, H_2), 7.37 (t, J = 7.9 Hz, 1H, H_5), 7.28 (d, J = 7.2 Hz, 1H, H_7), 7.22 – 7.09 (m, 2H, H_1, H_9), 6.99 (dd, J = 8.0, 1.8 Hz, 1H, H_6), 4.94 (s, 2H, H_{14}, H_{15}), 4.61 (s, 2H, H_{11}, H_{13}), 4.24 (s, 5H, H_{16}-H_{21}), 3.89 (s, 3H, H_{25}); HRMS (ESI MS) m/z: theor: 347.0729 found: 347.0728 ($[M+H]^+$ detected); Anal. Calc. for $C_{20}H_{18}FeO_2$: C, 69.4; H, 5.2; O, 9.2; Found: C, 69.6; H, 5.2; O, 9.1 %. Analyses were consistent with those previously reported in the literature. [E. Solcaniova, S. Toma, A. Fiedlerova, Investigation of substituent effects on the proton and carbon-13 NMR spectra of ferrocene analogs of chalcones, Organ. Magnet. Res. 1980, 14, 181-185].

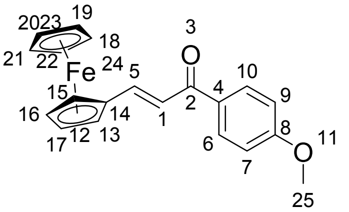
Synthesis of [3-(3-methoxyphenyl)-3-oxo-1-propenyl]ferrocene (chalcone 19)



Chemical Formula: $C_{20}H_{18}FeO_2$
Molecular Weight: 346.2070

3′-Methoxyacetophenone (2.81 g, 18.69 mmol, M = 150.18 g/mol) and KOH (1.05 g, 18.69 mmol, M = 56.11 g/mol) were dissolved in ethanol (20 mL) in a round bottomed flask and stirred at room temperature (r.t.) for 10 min. Ferrocenecarboxaldehyde (4 g, 18.69 mmol, M = 214.04 g/mol) was added and the mixture was stirred at room temperature for 24 h. The reaction was stopped by neutralizing the stirred solution with 2M HCl. A dark red precipitate after neutralization appeared. It was then removed by filtration, washed with water, some cold ethanol, and pentane. A column chromatography with ether as eluent allowed to obtain 2.11g, 32% yield of product as powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.75 (d, J = 15.4 Hz, 1H, H_1), 7.63 – 7.48 (m, 2H, H_7, H_{10}), 7.40 (t, J = 7.9 Hz, 1H, H_8), 7.17 – 7.05 (m, 2H, H_5, H_6), 4.64 – 4.56 (m, 2H, H_{15}, H_{16}), 4.53 – 4.45 (m, 2H, H_{12}, H_{14}), 4.18 (s, 5H, H_{17}-H_{21}), 3.88 (s, 3H, H_{25}); HRMS (ESI MS) m/z: theor: 347.0729 found: 347.0730 ($[M+H]^+$ detected); Anal. Calc. for $C_{20}H_{18}FeO_2$: C, 69.4; H, 5.2; O, 9.2; Found: C, 69.5; H, 5.1; O, 9.0 %. Analyses were consistent with those previously reported in the literature [E. Solcaniova, S. Toma, A. Fiedlerova, Investigation of substituent effects on the proton and carbon-13 NMR spectra of ferrocene analogs of chalcones, Organ. Magnet. Res. 1980, 14, 181-185].

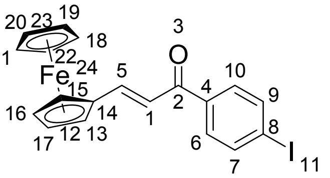
Synthesis of [3-(4-methoxyphenyl)-3-oxo-1-propen-1-yl]ferrocene (chalcone 20)



Chemical Formula: $C_{20}H_{18}FeO_2$
Molecular Weight: 346.2070

The substituted ketone (2.81 g, 18.69 mmol, M = 150.18 g/mol) and KOH (1.05 g, 18.69 mmol, M = 56.11 g/mol) were dissolved in ethanol (20 mL) in a round bottomed flask. The substituted aldehyde (4 g, 18.69 mmol, M = 214.04 g/mol) was added and the mixture was stirred at room temperature for 24 h. The reaction was stopped by neutralizing the stirred solution with 2M HCl. A dark red precipitate after neutralization appeared. It was then removed by filtration, washed with water, some cold ethanol, and pentane. A column chromatography with ether as eluent allowed to obtain 5.5 g, 85 % yield of product as a powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.00 (d, J = 8.8 Hz, 2H, H_7, H_9), 7.74 (d, J = 15.3 Hz, 1H, H_1), 7.15 (d, J = 15.3 Hz, 1H, H_5), 6.98 (d, J = 8.8 Hz, 2H, H_6, H_{10}), 4.59 (s, 2H, H_{13}, H_{15}), 4.47 (s, 2H, H_{16}, H_{17}), 4.18 (s, 5H, H_{18}-H_{22}), 3.88 (s, 3H, H_{25}); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 188.2 (C_2), 163.3 (C_8), 145.8 (C_1), 130.7 (C_6, C_{10}), 119.1 (C_4), 113.9 (C_5), 79.6 (C_{18}-C_{22}), 71.3 (C_7, C_9), 69.9 (C_{13}, C_{15}), 69.0 (C_{16}, C_{17}), 55.6 (C_{25}); HRMS (ESI MS) m/z: theor: 347.0729 found: 347.0731 ($[M+H]^+$ detected).

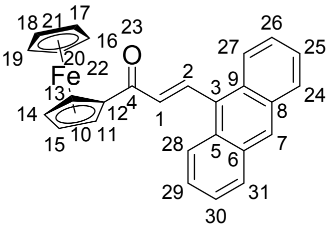
Synthesis of [3-(4-iodophenyl)-3-oxo-1-propen-1-yl]ferrocene (chalcone 21)



Chemical Formula: $C_{19}H_{15}FeIO$
Molecular Weight: 442.0775

Ferrocenecarboxaldehyde (4.28 g, 20 mmol, M = 214.04 g/mol) and 4'-iodoacetophenone (4.92 g, 20 mmol, M = 246.04 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 SiO_2 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 (7.78 g, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 – 7.83 (m, 2H, H_6, H_{10}), 7.76 (d, J = 15.3 Hz, 1H, H_5), 7.71 – 7.67 (m, 2H, H_7, H_9), 7.05 (d, J = 15.3 Hz, 1H, H_1), 4.60 (t, J = 1.8 Hz, 2H, H_{16}, H_{17}), 4.51 – 4.50 (m, 2H, H_{13}, H_{15}), 4.18 (s, 5H, H_{18}-H_{22}); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.0 (C_2), 147.7 (C_5), 138.1 (C_7, C_9), 137.9 (C_4), 129.9 (C_1), 118.6 (C_6, C_{10}), 100.1 (C_8), 79.1 (C_{18}-C_{22}), 71.7 (C_{13}, C_{15}), 70.0(C_{16}, C_{17}), 69.2 (C_{14}); HRMS (ESI MS) m/z: theor: 442.9590 found: 445.9588 ($[M+H]^+$ detected).

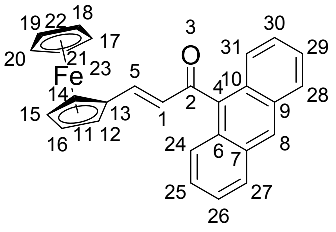
Synthesis of [3-(9-anthracenyl)-1-oxo-2-propen-1-yl]ferrocene (chalcone 22)



Chemical Formula: $C_{27}H_{20}FeO$
Molecular Weight: 416.3010

Anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) and acetylferrocene (4.56 g, 20 mmol, M = 228.07 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 SiO_2 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 (7.08 g, 88% yield). ^1H NMR ($CDCl_3$) δ : 4.32 (s, 5H, H_{16}-H_{21}), 4.64 (t, 2H, J = 1.9 Hz, H_{11}, H_{13}), 4.95 (t, 2H, J = 1.9 Hz H_{14}, H_{15}), 7.15 (d, 1H, J = 15.9 Hz, H_2), 7.52-7.59 (m, 4H, H_{25}, H_{26}, H_{29}, H_{30}), 8.07-8.09 (m, 2H, H_{24}, H_{31}), 8.37-8.39 (m, 2H, H_{27}, H_{28}), 8.51 (s, 1H, H_7), 875 (d, 1H, J = 15.9 Hz, H_1); HRMS (ESI MS) m/z: theor: 417.0936 found: 417.0938 ($[M+H]^+$ detected); HRMS (ESI MS) m/z: theor: 417.0936 found: 417.0938 ($[M+H]^+$ detected); Anal. Calc. for $C_{27}H_{20}FeO$: C, 77.9; H, 4.8; O, 3.8; Found: C, 77.8; H, 4.9; O, 3.9 %. Analyses were consistent with those previously reported in the literature. [P. Saravanan, S. Sundaramoorthy, R. Raghunathan, Regioselective synthesis of spiroxindolopyrrolidine:a one-step cycloaddition reaction twists inherent optical and fluorescence property of ferrocene–anthracene dyad, RSC Adv., 2016, 6, 100993-100996]

Synthesis of [(1E)-3-(9-anthracenyl)-3-oxo-1-propen-1-yl]ferrocene (chalcone 23)



Chemical Formula: $C_{27}H_{20}FeO$
Molecular Weight: 416.3010

9-Acetylanthracene (2.57 g, 11.68 mmol, M = 220.27 g/mol) and KOH (0.65 g, 11.68 mmol, M = 56.11 g/mol) were dissolved in ethanol (20 mL) in a round bottomed flask and stirred at room temperature (r.t.) for 10 min. Ferrocenecarboxaldehyde (2.5 g, 11.68 mmol, M = 214.04 g/mol) was added and the mixture was stirred at room temperature for 24 h. The reaction was stopped by neutralizing the stirred solution with 2M HCl. A dark red precipitate after neutralization appeared. It was then removed by filtration, washed with water, some cold ethanol, and pentane. A column chromatography with ether as eluent allowed to obtain 3.27 g, 67% yield of product as solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H, H_8), 8.10 – 8.00 (m, 2H, H_{24}, H_{31}), 7.94 (d, J = 9.1 Hz, 2H, H_{27}, H_{28}), 7.55 – 7.43 (m, 4H, H_{25}, H_{26}, H_{29}, H_{30}), 7.04 (d, J = 15.9 Hz, 1H, H_1), 6.90 (d, J = 15.9 Hz, 1H, H_5), 4.44 (s, 2H, H_{15}, H_{16}), 4.42 (s, 2H, H_{12}, H_{14}), 4.09 (s, 5H, H_{17}-H_{21}); HRMS (ESI MS) m/z: theor: 417.0936 found: 417.0938 ($[M+H]^+$ detected); Anal. Calc. for $C_{27}H_{20}FeO$: C, 77.9; H, 4.8; O, 3.8; Found: C, 77.8; H, 5.0; O, 4.0 %. Analyses were consistent with those reported in the literature [Y. Jung, K.-I. Son, Y.E. Oh, D.-Y. Noh, Ferrocenyl Chalcones Containing Anthracenyl Group: Synthesis, X-Ray Crystal Structures and Electrochemical Properties. Polyhedron 2008, 27, 861–867.]