Supporting information

In-silico rational design by molecular modeling of new ketones as photoinitiators in three-component photoinitiating systems: application on 3D printing

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Table S1. Summary of the FCs at 405 nm of monomers (TMPTA), under three-component photopolymerization systems between ketones (0.1%, w/w), Iod (Speedcure 938; 2%, w/w) and amine (Speedcure EDB; 2%, w/w).

Ketones:TMPTA=1:1000					
Ketone	1	2	3	4	5
FCs	50%	36%	44%	45%	67%
Ketone	6	7	8	9	10
FCs	57%	30%	41%	33%	43%

Table S2. Summary of the FCs at 405 nm of monomers (Ebecryl 40, under three-component photopolymerization systems between ketones (0.1%, w/w), Iod

(Speedcure 938; 2%, w/w) and amine (Speedcure EDB; 2%, w/w).

Ketones:Ebecryl 40=1:1000					
Ketone	1	2	3	4	5
FCs	56%	54%	63%	58%	54%
Ketone	6	7	8	9	10
FCs	69%	61%	67%	56%	51%

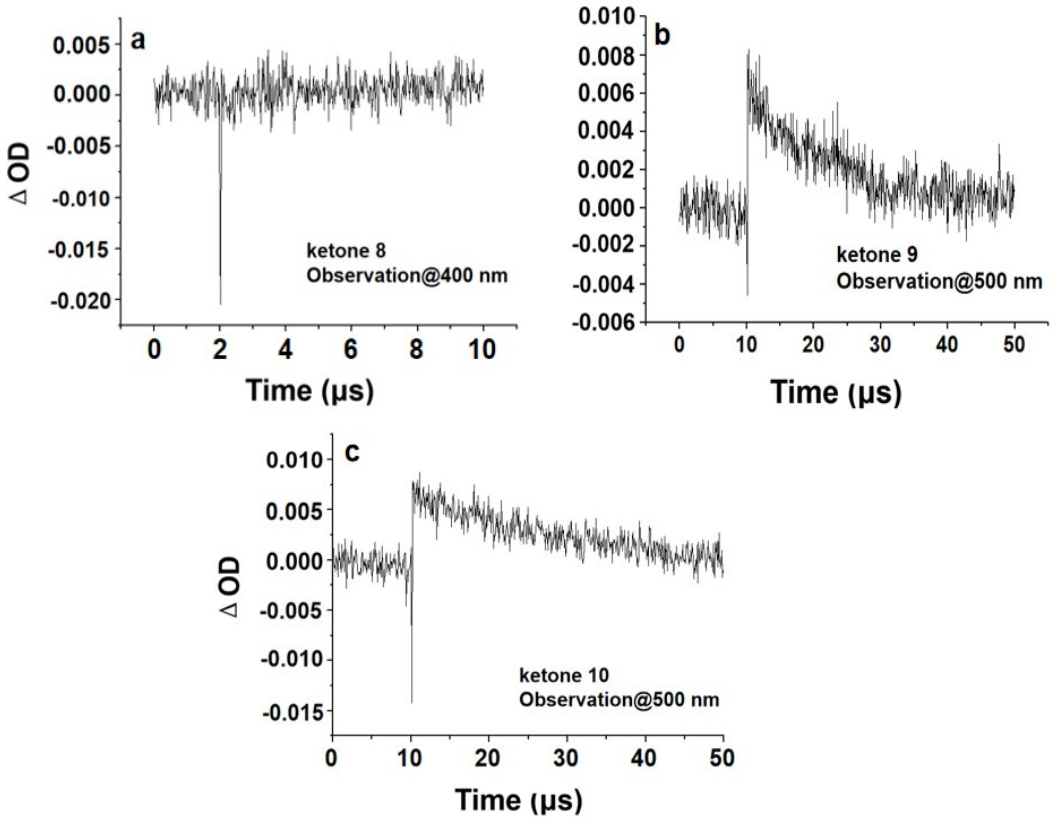


Figure S1. Laser flash photolysis for ketone 8, 9, 10: **(a)** ketone 8 (2.1×10^{-5}M in acetonitrile); **(b)** ketone 9 (2.7×10^{-6}M in acetonitrile); **(c)** ketone 10 (4.1×10^{-6} in acetonitrile). Laser excitation @ 355 nm.

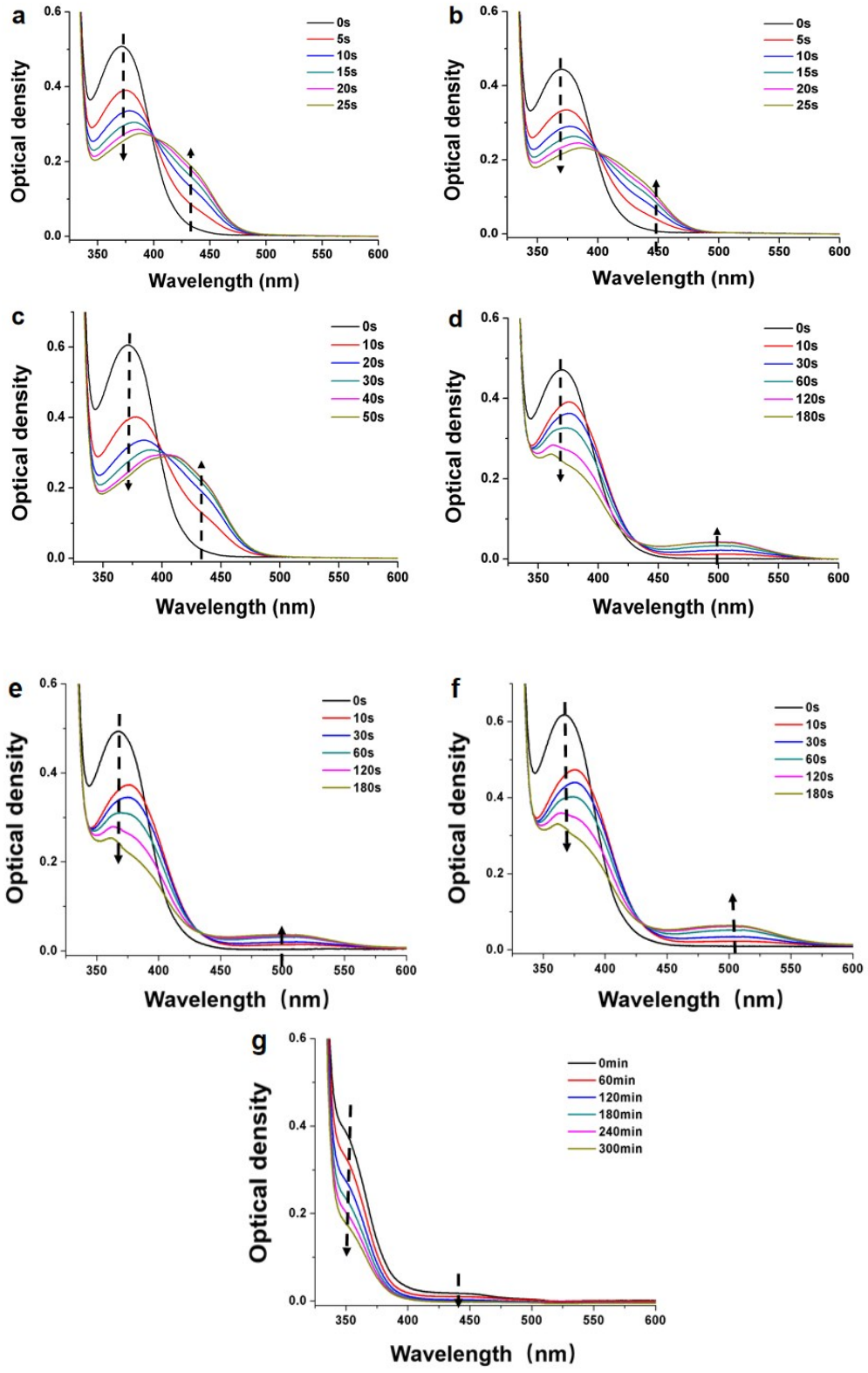
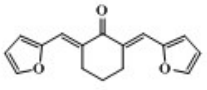
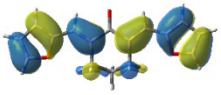
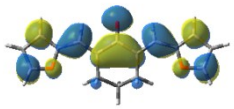
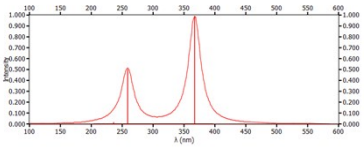
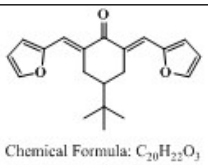
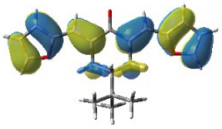
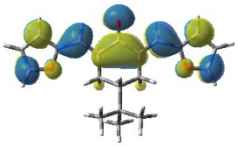
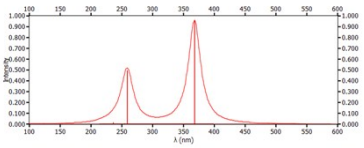
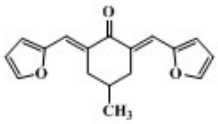
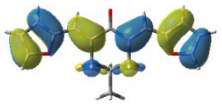
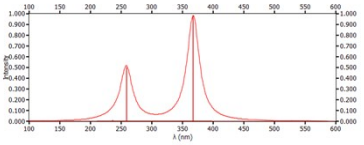
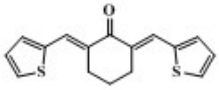
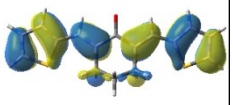
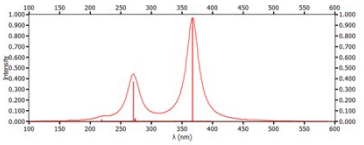
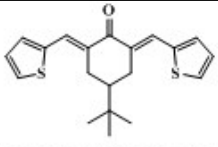
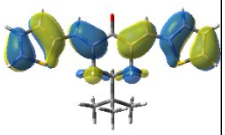
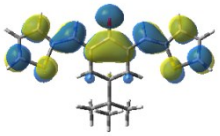
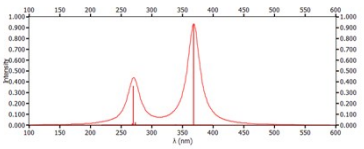


Figure S2. UV-vis absorption spectra of ketone 1-7 (5×10^{-6}g in 1g acetonitrile) co-initiated with iodonium salt (Speedcure 938, 1.46×10^{-4}M) and amine (Speedcure EDB,

4.07×10^{-4}M) upon exposure to LED@405nm under air in the solvent of acetonitrile: **(a)** ketone 1; **(b)** ketone 2; **(c)** ketone 3;**(d)** ketone 4; **(e)** ketone 5; **(f)** ketone 6; **(g)** ketone 7.

Ketone	HOMO	LUMO	Calculated UV spectra	E_T (kcal mol^{-1})
 Chemical Formula: $C_{16}H_{16}O_3$ Molecular Weight: 254,2850			 λmax=368nm F= 0.988	50.81
 Chemical Formula: $C_{20}H_{22}O_3$ Molecular Weight: 310,3930			 λmax=368nm F= 0.958	43.08
 Chemical Formula: $C_{17}H_{16}O_3$ Molecular Weight: 268,3120			 λmax=368nm F= 0.983	43.29
 Chemical Formula: $C_{16}H_{14}OS_2$ Molecular Weight: 286,4070			 λmax=368nm F= 0.965	51.32
 Chemical Formula: $C_{20}H_{22}OS_2$ Molecular Weight: 342,5150			 λmax=369nm F= 0.931	43.22

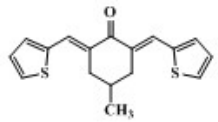
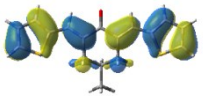
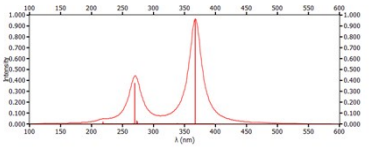
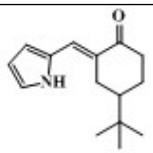
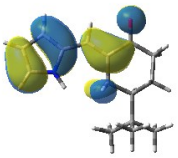
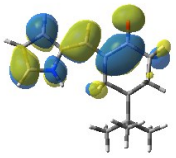
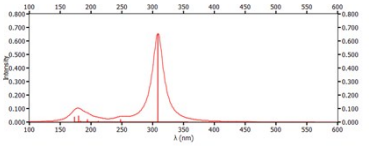
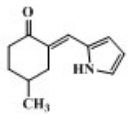
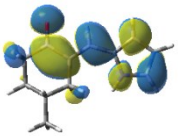
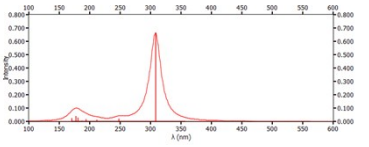
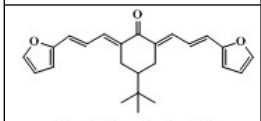
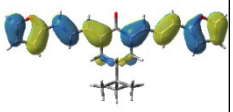
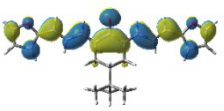
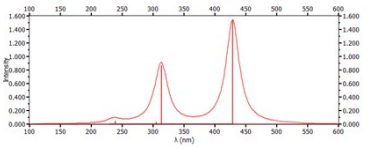
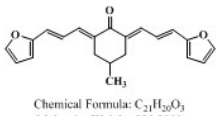
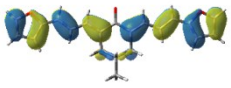
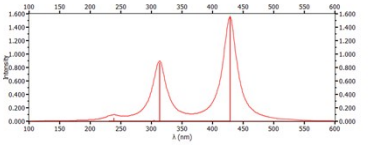
 Chemical Formula: $C_{17}H_{16}OS_2$ Molecular Weight: 300,4340			 λmax=368nm F= 0.960	43.42
 Chemical Formula: $C_{15}H_{21}NO$ Molecular Weight: 231,3390			 λmax=357nm F= 0.0001	46.67
 Chemical Formula: $C_{12}H_{15}NO$ Molecular Weight: 189,2580			 λmax=357nm F= 0.0007	46.72
 Chemical Formula: $C_{24}H_{26}O_3$ Molecular Weight: 362,4690			 λmax=429nm F= 1.538	41.67
 Chemical Formula: $C_{21}H_{20}O_3$ Molecular Weight: 320,3880			 λmax=429nm F= 1.552	41.85

Figure S3. Contour plots of HOMOs and LUMOs for ketone 1-10; structures optimized at the B3LYP/6-31G* level of theory; calculated UV spectra and triplet state energy of ketone 1-10.

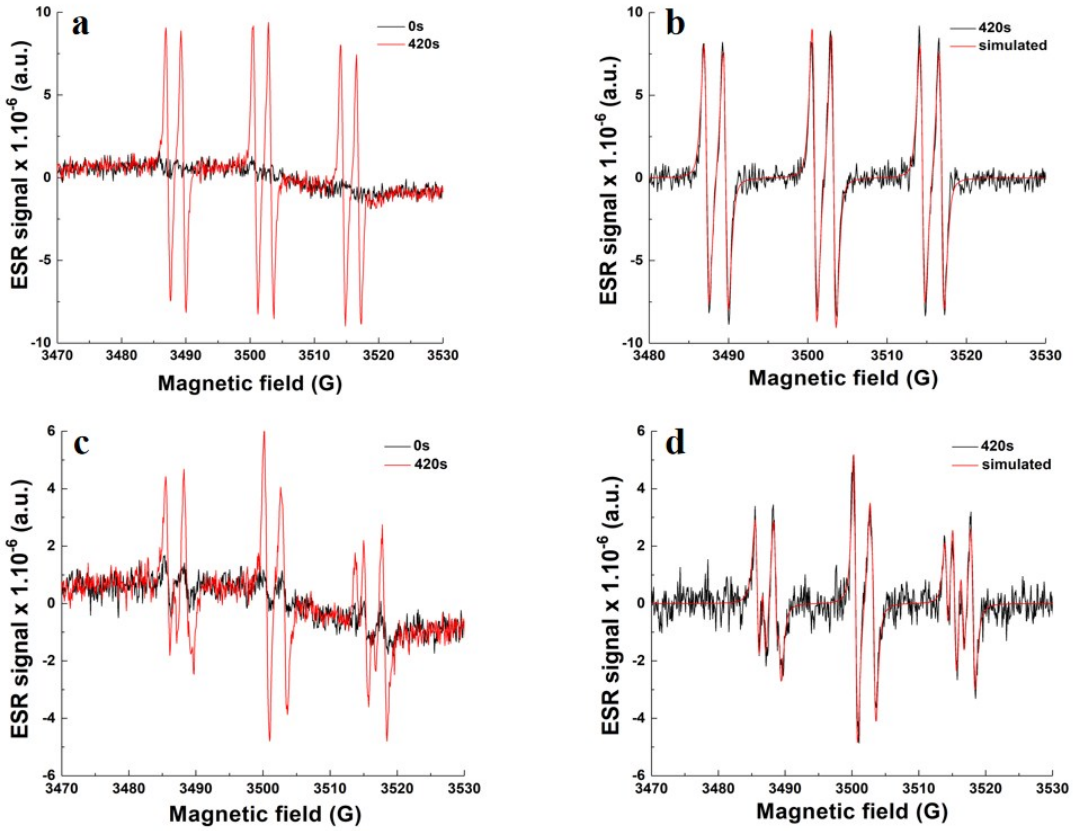


Figure S4. ESR spectra obtained from ESR-spin trapping experiment using PBN = 2 mg/mL (as spin trap agent); amine (Speedcure EDB) = 12.6 mg/mL and ketone 8, 9 = 0.8 mg/mL in acetonitrile under N_2. **left: (a), (c)** ketone 8, 9, Irradiation time =420s (red) and =0s (black) spectra; **right:(b), (d)** ketone 8, 9, irradiation time =420s (red) and simulated (black) spectra.

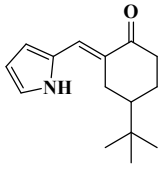
Synthetic procedures

2,6-*Bis*(furan-2-ylmethylene)cyclohexan-1-one ***ketone 1,*** [E. Aguilera, J. Varela, E. Birriel, E. Serna, S. Torres, G. Yaluff, N. Vera de Bilbao, B. Aguirre-Lûpez, N. Cabrera, S. Diaz Mazariegos, M. Tuena de Gûmez Puyou, A. Gûmez-Puyou, R. Pérez-Montfort, L. Minini, A. Merlino, H. Cerecetto, M. Gonzalez, G. Alvarez, ChemMedChem 2016, 11, 1328 – 1338]; 4-(*tert*-butyl)-2,6-bis(furan-2-ylmethylene) cyclohexan-1-one ***ketone 2,*** [N. Pinto, P. Retailleau, A. Voituriez, A. Marinetti, Chem.Commun.,2011,47, 1015–1017]; 2,6-*bis*(furan-2-ylmethylene)-4-methylcyclohexan-1-one ***ketone 3,*** [M. Ahmed Abdel-Rahman, M. Ali Hussein, Des.

Monomers Polym., 2013, 16, 377-388]; 2,6-*bis*(thiophen-2-ylmethylene) cyclohexan-1-one ***ketone 4,*** [N. Chakingala, A.B. Puthirath, M.V. Mahesh Kumar, A. Ayyappan, S. Jayalekshmi, P.A. Unnikrishnan, S. Prathapan, Dyes Pigm. 2018, 159, 367-377]; 4-(*tert*-butyl)-2,6-*bis*(thiophen-2-ylmethylene) cyclohexan-1-one ***ketone 5,*** [M. Ahmed Abdel-Rahman, M. Ali Hussein, Des. Monomers Polym., 2013, 16, 377-388]; 4-methyl-2,6-*bis*(thiophen-2-ylmethylene) cyclohexan-1-one ***ketone 6,*** [M. Ahmed Abdel-Rahman, M. Ali Hussein, Des. Monomers Polym., 2013, 16, 377-388] were synthesized as previously reported in the literature, without modifications and in similar yields.

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 peak $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm). All these carbazole photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

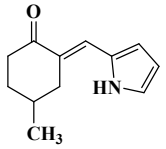
Synthesis of 2-((1H-pyrrol-2-yl) methylene)-4-(tert-butyl) cyclohexan-1-one ***ketone 7***,



Chemical Formula: $C_{15}H_{21}NO$
Exact Mass: 231.1623
Molecular Weight: 231.3390

4-*Tert*-butylcyclohexanone (1.55 g, 10 mmol, M = 154.25 g/mol) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Pyrrole-2-carbaldehyde (1.90 g, 20 mmol, M = 95.10 g/mol) and NaOH 1M (10 mL) were then added at 0°C. The mixture was stirred at room temperature overnight. The yellow precipitate was filtrated off, washed with ethanol and dried under vacuum (1.94 h, 84% yield). ^{1}H NMR ($CDCl_3$) δ : 1.00 (s, 9H), 1.48-1.55 (m, 2H), 1.98-2.04 (m, 1H), 2.30-2.39 (m, 2H), 2.62-2.69 (m, 1H), 2.90-2.96 (m, 1H), 6.38-6.39 (m, 1H), 6.59-6.60 (m, 1H), 7.02-7.03 (m, 1H), 7.65 (s, 1H), 9 31 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ : 23.9, 27.3, 30.0, 32.6, 39.7, 44.9, 111.5, 114.5, 122.2, 127.3, 129.0, 129.3, 200.8; HRMS (ESI MS) m/z: theor: 232.1696 found: 232.1698 ($[M+H]^+$ detected)

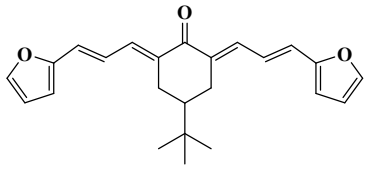
Synthesis of 2,6-bis((1H-pyrrol-2-yl)methylene)-4-methylcyclohexan-1-one ***ketone 8****,*



Chemical Formula: $C_{12}H_{15}NO$
Exact Mass: 189.1154
Molecular Weight: 189.2580

4-Methylcyclohexanone (1.12 g, 1.22 mL, 10 mmol, d = 0.914, M = 112.17 g/mol) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Pyrrole-2-carbaldehyde (1.90 g, 20 mmol, M = 95.10 g/mol) and NaOH 1M (10 mL) were then added at 0°C. The mixture was stirred at room temperature overnight. The yellow precipitate was filtrated off, washed with ethanol and dried under vacuum (1.48 g, 78% yield). ^{1}H NMR ($CDCl_3$) δ : 1.14 (d, 3H, J = Hz), 1.52-1.66 (m, 1H), 1.90-1.95 (m, 2H), 2.23-2.33 (m, 1H), 2.37-2.49 (m, 1H), 2.57-2.66 (m, 1H), 2.95-3.01 (m, 1H), 6.37 (s, 1H), 6.61 (s, 1H), 7.01 (s, 1H), 7.62 (s, 1H), 9.15 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ : 22.0, 29.6, 30.8, 37.1, 38.7, 111.4, 114.7, 121.9, 122.1? 126.9, 128.5, 129.3, 200.3; HRMS (ESI MS) m/z: theor: 190.1226 found: 190.1227 ($[M+H]^+$ detected)

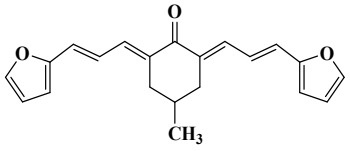
Synthesis of 4-(tert-butyl)-2,6-bis((E)-3-(furan-2-yl) allylidene)cyclohexan-1-one ***ketone 9****,*



Chemical Formula: $C_{24}H_{26}O_3$
Exact Mass: 362.1882
Molecular Weight: 362.4690

4-*Tert*-butylcyclohexanone (1.55 g, 10 mmol, M = 154.25 g/mol) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Trans-3-(2-furyl) acrolein (2.44 g, 20 mmol, M = 122.12 g/mol) and NaOH 1M (10 mL) were then added at 0°C. During stirring, a sticky solid formed so that THF (20-30 mL) was added to maintain the stirring of the solution. The solution was stirred at room temperature overnight. The yellow precipitate was filtrated off, washed with ethanol and dried under vacuum (2.24 g, 62% yield). ^{1}H NMR ($CDCl_3$) δ : 1.04 (s, 9H), 1.46-1.55 (m, 1H), 2.24 (t, 2H, J = 14.2 Hz), 3.03 (d, 2H, J = 15.8 Hz), 6.45 (m, 4H), 6.72 (d, 2H, J = 15.2 Hz), 6.95 (t, 2H, J = 14.9 Hz), 7.38 (d, 2H, J = 12.0 Hz), 7.45 (s, 2H); ^{13}C NMR ($CDCl_3$) δ : 27.3, 27.8, 32.6, 43.4, 111.7, 112.2, 122.0, 127.0, 135.6, 135.9, 143.5, 153.0, 188.9; HRMS (ESI MS) m/z: theor: 363.1955 found: 363.1952 ($[M+H]^+$ detected)

Synthesis of 2,6-bis((E)-3-(furan-2-yl) allylidene)-4-methylcyclohexan-1-one ***ketone 10****,*



Chemical Formula: $C_{21}H_{20}O_3$
Exact Mass: 320.1412
Molecular Weight: 320.3880

4-Methylcyclohexanone (1.12 g, 1.22 mL, 10 mmol, d = 0.914, M = 112.17 g/mol) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Trans-3-(2-furyl) acrolein (2.44 g, 20 mmol, M = 122.12 g/mol) and NaOH 1M (10 mL) were then added at 0°C. The mixture was stirred at room temperature overnight. The yellow precipitate was filtrated off, washed with ethanol and dried under vacuum (2.18 g, 68% yield). ^{1}H NMR ($CDCl_3$) δ : 1.14 (d, 3H, J = 6.5 Hz), 1.91-1.99 (m, 1H), 2.25-2.32 (m, 2H), 2.94 (dd, 2H, J = 16.1 Hz, J = 3.3 Hz), 6.44 (s, 4H), 6.72 (d, 2H, J = 15.2 Hz), 6.94 (t, 2H, J = 15.2 Hz), 7.39 (d, 2H, J = 12.1 Hz), 7.43 (s, 2H); ^{13}C NMR ($CDCl_3$) δ : 21.5, 28.4, 34.7, 111.6, 112.2, 122.2, 127.0, 134.8, 136.1, 143.4, 153.0, 188.5; HRMS (ESI MS) m/z: theor: 321.1485 found: 321.1489 ($[M+H]^+$ detected)