

Supplementary Material (ESI) for Chemical Communications

Solar Light-driven Photocatalyzed Alkylations. Chemistry on the Window Ledge

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1) Experimental details

2) Table of parameters of the synthesis of TBADT and 17 by the EATOS method

1) Experimental details

General: ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer with appropriate DEPT experiments. Chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in Pyrex glass reactors, in Pavia (Italy, latitude $45^{\circ}11'$ N, $9^{\circ}09'$ E, 77 m above sea level) in July-September 2008 period. The light flux measured ranged from 20 to 45 Wm^{-2} (in the 295-400 nm region) and $400\text{-}520\text{ Wm}^{-2}$ (450-950 nm) as shown in Figure S1.

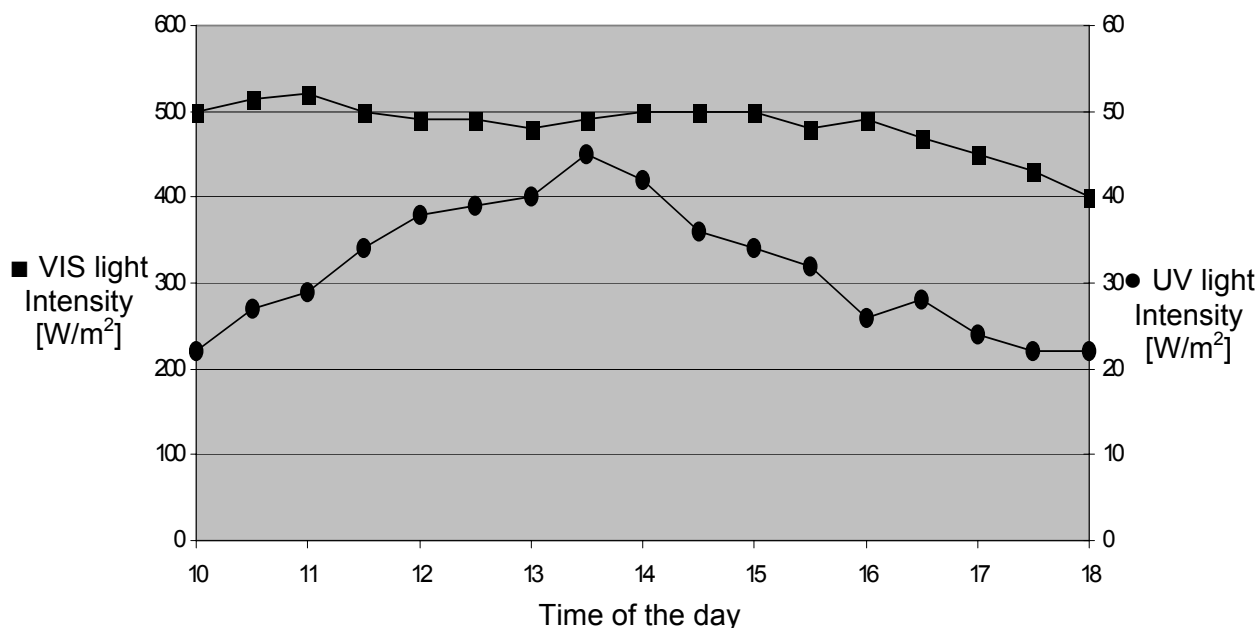


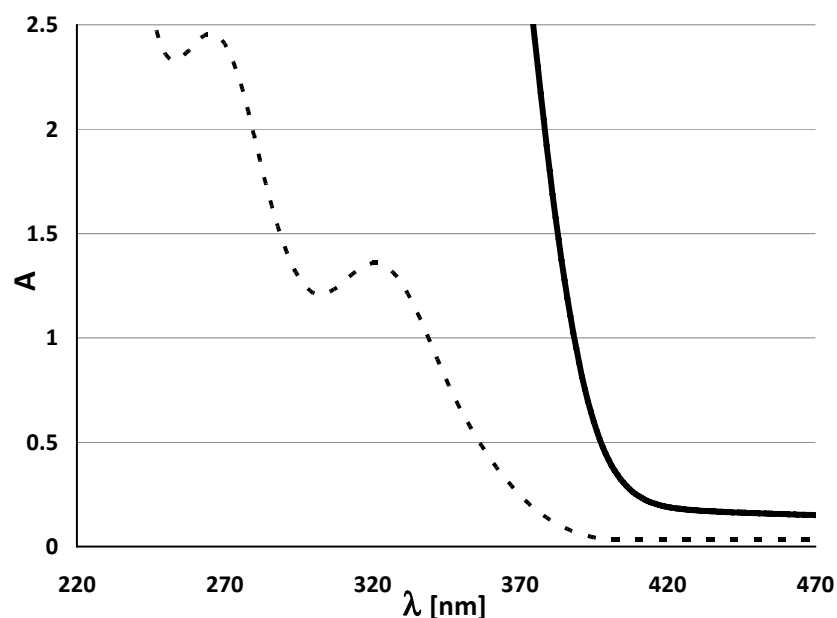
Figure S1. Typical pattern of the visible and UV light intensity during a day of irradiation.

Compounds **1-10** were commercial available, and were freshly distilled before use. Acetonitrile (HPLC purity grade), acetone (purum for synthesis) and water (HPLC purity grade) were purchased from Carlo Erba and used as received.

Preparation of the photocatalyst. The literature preparation of TBADT,^{S1} a white powder, was made more eco-friendly by introducing a more straightforward purification procedure that allowed reducing the amount of solvent used in this step.

Tetrabutylammonium bromide (2.4 g) and sodium tungstate dihydrate (5.0 g) were dissolved each in 150 mL of deionized water in two Erlenmeyer flasks and kept at 90°C under vigorous stirring. Concentrated hydrochloric acid was added dropwise to both solutions in order to adjust the pH at 2 (the tungstate solution assumed a slightly green color). The two solutions were then mixed and maintained at 90°C for 30 min under stirring. A white suspension of TBADT was formed, cooled to r.T. and filtered on a Buchner funnel. The solid phase was washed with water and then dried in oven at 120°C for 3 hours. After cooling to room temperature, the resulting white solid was suspended in dichlorometane (20 mL of solvent per gram of solid) and kept under stirring for 2 hours. Pure TBADT was separated from the yellow supernatant solution by filtration on a Buchner funnel. Using this modified procedure, the yields of the photocatalyst varied in the range 85-95% (based on the content of tungsten) and the purity was >90% as evaluated by UV analysis ($\epsilon_{323} = 1.35 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in acetonitrile).^{S2}

Figure S2 UV spectra of TBADT solutions 10^{-4} M (dotted line) and 2×10^{-3} M (solid line) in acetonitrile. In the experiments below, TBADT was used at a 2×10^{-3} M concentration, thus ensuring that >99% of the UV-A radiation (corresponding to 5% of the overall solar emission) was absorbed.



Solar light induced photocatalyzed functionalization of olefins. General procedure. A solution (100 mL) of the hydrogen donor (**1-6**, 0.1-0.45 M), and an electron-poor olefin (**7-10**, 0.1-0.5 M) in the presence of 660 mg of TBADT (2×10^{-3} M) in the chosen solvent (MeCN or acetone-water 4:1) was poured in a glass Pyrex vessel and purged for 10 minutes with nitrogen, capped and exposed to sunlight on a window ledge. The course of the reaction was monitored by gas chromatography (GC). During these experiments the light flux measured ranged from 20 to 45 Wm^{-2} (in the 295-400 nm region) and from 400 to 520 Wm^{-2} (between 450 and 950 nm) and the temperature of the solution remained below 50 °C. After the completion of the reaction (detected by GC analysis) the solvent was removed in vacuo from the photolyzed solution and the end products isolated by bulb-to bulb distillation. Blank experiments where the vessel was covered with an aluminum foil ruled out any thermal process; furthermore, no reaction occurred when TBADT was omitted.

Synthesis of 3-cyclohexylpropanenitrile (11) 5.40 mL of cyclohexane (**1**, 50 mmol, 0.5 M), 650 μL of acrylonitrile (**7**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 5 days. After purification of the crude mixture by vacuum distillation, 727 mg of 3-cyclohexylpropanenitrile (**11**, 53% yield) were

obtained as a colorless oil. The spectroscopic data of compound **11** were in accordance with literature.^{S3}

Synthesis of 3-cyclohexylcyclohexanone (12) 5.40 mL of cyclohexane (**1**, 50 mmol, 0.5 M), 970 μL of 2-cyclohexen-1-one (**8**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 8 days. After purification of the crude mixture by vacuum distillation, 721 mg of 3-cyclohexylcyclohexanone (**12**, 40% yield) were obtained as a colorless oil. Spectroscopic data of compound **12** were in accordance with literature.^{S4}

Synthesis of dimethyl 2-cyclohexylsuccinate (13) 5.40 mL of cyclohexane (**1**, 50 mmol, 0.5 M), 1.25 mL of dimethyl maleate (**9**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 5 days. After purification of the crude mixture by vacuum distillation, 1.55 g of dimethyl 2-cyclohexylsuccinate (**13**, 68% yield) were obtained as a colorless oil.

13: $^1\text{H-NMR}$ (CDCl_3)^{S5} δ 0.95-1.20 (m, 5 H), 1.55-1.70 (m, 6 H), 2.35-2.40 (m, 1 H), 2.65-2.75 (m, 2 H), 3.60 (s, 3 H), 3.65 (s, 3 H); $^{13}\text{C-NMR}$ (CDCl_3)^{S5} δ 25.9 (CH_2), 26.1 (2 CH_2), 29.9 (CH_2), 30.4 (CH_2), 33.0 (CH), 39.8 (CH_2), 46.8 (CH), 51.3 (CH_3), 51.5 (CH_3), 172.7, 174.7.; IR (neat) ν/cm^{-1} 2929, 2854, 1738, 1436, 1261, 1163, 1009; Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_4$: C 63.14, H 8.83. Found: C 63.1, H 8.8.

Synthesis of methyl 3-cyclopentylpropanoate (14) 4.65 mL of cyclopentane (**2**, 50 mmol, 0.5 M), 900 μL of methyl acrylate (**10**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 7 days. After purification of the crude mixture by vacuum distillation, 672 mg of methyl 3-cyclopentylpropanoate (**14**, 43% yield) were obtained as a colorless oil.

14: $^1\text{H-NMR}$ (CDCl_3) δ 0.90-1.00 (m, 2 H), 1.25-1.65 (m, 9 H), 2.05-2.15 (t, 2 H, $J = 8$ Hz), 3.45 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3) δ 24.8 (2 CH_2), 30.9 (CH_2), 32.1 (2 CH_2), 33.0 (CH), 39.4 (CH_2), 50.9 (CH_3), 173.8; IR (neat) ν/cm^{-1} 2952, 2867, 1742, 1437, 1225, 1196, 1174, 1020, 917; Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_2$: C 69.19, H 10.32. Found: C 69.2, H 10.3.

Synthesis of dimethyl 2-((N-methylformamido)methyl)succinate (15) 3.10 mL of *N,N*-dimethylformamide (**3**, 40 mmol, 0.4 M), 1.25 mL of dimethyl maleate (**9**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 11 days. After purification of the crude mixture by vacuum distillation, 1.39 g of dimethyl 2-

((*N*-methylformamido)methyl)succinate (**15**, 64% yield) were obtained as a colorless oil. Spectroscopic data of compound **15** were in accordance with literature data.^{S6} The same reaction was performed by using a lower concentration of **3** (1.55 mL, 20 mmol, 0.2 M) while maintaining the same concentration of **9** (1.25 mL, 10 mmol, 0.1 M) in acetonitrile (100 mL, 5 days irradiation), giving 1.32 g of **15** (61% yield).

Synthesis of dimethyl 2-(1,4-dioxan-2-yl)succinate (16) 4.25 mL of 1,4-dioxane (**4**, 50 mmol, 0.5 M), 1.25 mL of dimethyl maleate (**9**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 5 days. After purification of the crude mixture by vacuum distillation, 1.37 g of dimethyl 2-(1,4-dioxan-2-yl)succinate (**16**, two diastereomers, 59% yield) were obtained as a colorless oil. The same reaction was performed by using a lower concentration of **4** (1.70 mL, 20 mmol, 0.2 M) while maintaining the same concentration of **9** (1.25 mL, 10 mmol, 0.1 M) in acetonitrile (100 mL, 6 days irradiation), giving 1.21 g of **16** (52% yield).

16: ¹H-NMR (CDCl₃, mixture of two diastereoisomers) δ 2.55 (dd, 1 H, *J* = 5 and 18 Hz), 2.70-2.85 (m, 2 H), 2.95-3.05 (m, 1 H), 3.30-3.40 (m, 1 H), 3.55 (dd, 1 H, *J* = 3 and 15 Hz), 3.70-3.80 (m, 4 H), 3.70 (s, 3 H), 3.76 (s, 3 H); ¹³C-NMR (CDCl₃, mixture of two diastereoisomers) major diastereoisomer: δ 32.1 (CH₂), 43.4 (CH), 51.8 (CH₃), 52.0 (CH₃), 66.2 (CH₂), 67.1 (CH₂), 68.6 (CH₂), 75.2 (CH), 171.9, 172.1; minor diastereoisomer: δ 31.8 (CH₂), 43.4 (CH), 51.7 (CH₃), 52.1 (CH₃), 66.2 (CH₂), 66.9 (CH₂), 69.4 (CH₂), 74.4 (CH), 172.3, 172.4; IR (neat, mixture of two diastereoisomers) ν/cm^{-1} 2956, 2857, 1736, 1438, 1258, 1167, 1118, 1006; Anal. Calcd. for C₁₀H₁₆O₆ C 51.72, H 6.94. Found: C 51.7, H 6.9.

Synthesis of dimethyl 2-heptanoylsuccinate (17) 2.40 mL of 1-heptanal (**5**, 10 mmol, 0.1 M), 1.25 mL of dimethyl maleate (**9**, 10 mmol, 0.1 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 3 days. After purification of the crude mixture by vacuum distillation, 2.32 g of dimethyl 2-heptanoylsuccinate (**17**, 90%) were obtained as a colorless oil. The reaction proceeded also under cloudy sky (a 20% conversion of both reagents per day). The same reaction was performed using higher concentrations of **5** (2.80 mL, 20 mmol, 0.2 M) and **9** (3.10 mL, 25 mmol, 0.25 M) in acetonitrile (100 mL, 5 days irradiation), giving 4.65 g of **17** (90% yield). Finally, the reaction was further optimized using even higher concentrations of **5** (6.30 mL, 45 mmol, 0.45 M) and **9** (6.25 mL, 50 mmol, 0.50 M) both in acetonitrile (100 mL, 5 days irradiation) and acetone-water 4:1 mixture (100 mL, 7 days irradiation), giving 10.5 g (90%

yield) and 9.2 g (79% yield) of **17**, respectively. The spectroscopic data of compound **17** were in accordance with literature.^{S7}

Synthesis of 4-oxodecanitrile (18) 2.80 mL of 1-heptanal (**5**, 20 mmol, 0.2 M), 1.60 mL of acrylonitrile (**7**, 25 mmol, 0.25 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 8 days. After purification of the crude mixture by vacuum distillation, 2.34 g of 4-oxodecanitrile (**18**, 70%) were obtained as a colorless oil. The spectroscopic data of compound **18** were in accordance with literature.^{S7}

Synthesis of 3-heptanoylcyclohexanone (19) 2.80 mL of 1-heptanal (**5**, 20 mmol, 0.2 M), 2.40 mL of cyclohex-2-enone (**8**, 25 mmol, 0.25 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 8 days. After purification of the crude mixture by vacuum distillation, 3.70 g of 3-heptanoylcyclohexanone (**19**, 88%) were obtained as a colorless oil. The spectroscopic data of compound **19** were in accordance with literature.^{S7}

Synthesis of methyl 4-oxodecanoate (20) 2.80 mL of 1-heptanal (**5**, 20 mmol, 0.2 M), 2.25 mL of methyl acrylate (**10**, 25 mmol, 0.25 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 8 days. After purification of the crude mixture by vacuum distillation, 2.80 g of methyl 4-oxodecanoate (**20**, 70%) were obtained as a colorless oil. The same reaction was performed using higher concentrations of **5** (6.30 mL, 45 mmol, 0.45 M) and **10** (4.50 mL, 50 mmol, 0.50 M) in acetonitrile (100 mL, 12 days irradiation) giving 4.69 g (52% yield) of **20**. The spectroscopic data of compound **20** were in accordance with literature.^{S7}

Synthesis of dimethyl 2-(4-methoxybenzoyl)succinate (21) 1.20 mL of *p*-anisaldehyde (**6**, 10 mmol, 0.1 M), 1.50 mL of dimethyl maleate (**9**, 12 mmol, 0.12 M) and 664 mg of TBADT (0.2 mmol, 2×10^{-3} M) were dissolved in 100 mL of acetonitrile and illuminated for 11 days. A consumption of 70% of the aldehyde **6** was measured; after purification of the crude mixture by vacuum distillation, 1.82 g of dimethyl 2-(4-methoxybenzoyl)succinate (**21**, 65% yield, 93 % yield based on the consumption of **6**) were obtained as a colorless oil.

21: ¹H-NMR (CDCl₃) δ 3.00-3.05 (d, 2 H, *J* = 7 Hz), 3.65 (s, 6 H), 3.80 (s, 3 H), 4.80-4.85 (t, 1 H, *J* = 7 Hz), 6.95-8.05 (AA'BB' system, 4 H); ¹³C-NMR (CDCl₃) δ 33.0 (CH₂), 48.8 (CH), 51.9 (CH₃), 52.6 (CH₃), 55.4 (CH₃), 113.8 (2 CH), 128.5, 131.2 (2 CH), 164.0, 169.2, 171.7, 192.2; IR (neat)

ν/cm^{-1} 2955, 1736, 1676, 1602, 1263, 1171, 1026, 845; Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_6$: C 59.99, H 5.75.
Found: C 60.0, H 5.8.

2) Table of parameters of the synthesis of TBADT and 17 by the EATOS method

EATOS (Environmental Assessment Tool for Organic Synthesis) software was downloaded from Professor J. O. Metzger web site (<http://www.chemie.uni-oldenburg.de/oc/metzger/eatos/>). Physical and environmental information (including risk and safety phrases, toxicity and ecological parameters) of the compounds considered were obtained from the safety data sheets available on Sigma Aldrich web site (www.sigma-aldrich.com). The price of the compounds and materials used (of reasonable purity) were obtained from Sigma Aldrich web site too, by choosing the largest quantity marketed. Below are reported the data as obtained by applying the software.

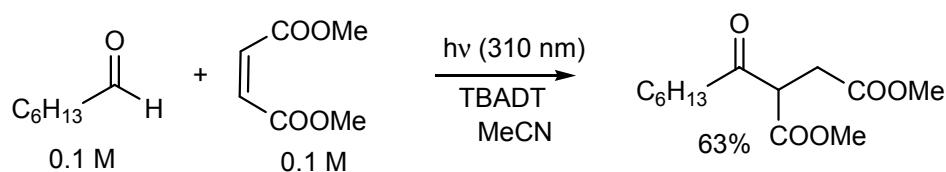
Table of parameters for the synthesis of TBADT as described in the literature^{S1}

	S⁻¹	E	E_{in}	E_{out}	€/kg
Sodium Tungstate	1.10	0.00	2.21	0.00	157.8
Tetrabutyl ammonium bromide	0.52	0.10	1.32	0.10	321.1
HCl 37% aq	1.44	1.25	2.90	6.27	13.2
Reactants	3.06	1.35	6.43	6.37	492.1
NaCl	0.00	0.28	0.00	0.28	0.0
NaBr	0.00	0.12	0.00	0.12	0.0
Water	0.00	0.15	0.00	0.15	0.0
Coupled Products	0.00	0.55	0.00	0.55	0.0
Water	441.53	441.53	441.53	441.53	9.2
Solvents	441.53	441.53	441.53	441.53	9.2
Acetonitrile	121.47	121.47	364.39	303.66	13580
Dichloromethane	29.25	29.25	58.50	195.00	703.7
Auxiliaries (purification)	150.72	150.72	422.89	498.66	14284
Total	595.31	594.15	870.85	947.11	14785

Table of parameters for the optimized synthesis of TBADT.

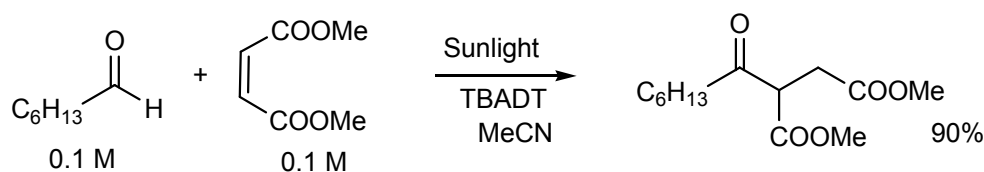
	S^{-1}	E	E_{in}	E_{out}	€/kg
Sodium Tungstate	1.10	0.00	2.21	0.00	157.8
Tetrabutyl ammonium bromide	0.53	0.10	1.32	0.10	321.1
HCl 37% aq	0.24	0.05	0.48	0.05	2.2
Reactants	1.87	0.15	4.01	0.15	481.1
NaCl	0.00	0.28	0.00	0.28	0.0
NaBr	0.00	0.12	0.00	0.12	0.0
Water	0.00	0.15	0.00	0.15	0.0
Coupled Products	0.00	0.55	0.00	0.55	0.0
Water	66.23	66.23	66.23	66.23	1.4
Solvents	66.23	66.23	66.23	66.23	1.4
Dichloromethane	29.25	29.25	58.50	195.00	703.7
Auxiliaries (purification)	29.25	29.25	58.50	195.00	703.7
Total	97.35	96.18	132.74	261.93	1186.2

Table of parameters for the synthesis of ketoester 17 under irradiation by lamps (phosphor coated, centre of emission 310 nm).



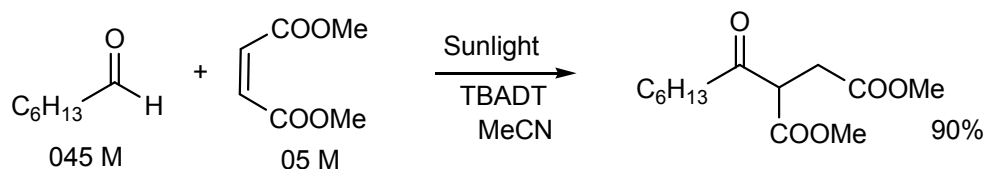
	S^{-1}	E	E_{in}	E_{out}	€/kg
1-Heptanal	0.70	0.00	1.05	0.00	33.6
Dimethylmaleate	0.89	0.58	3.54	1.96	75.5
Reactants	1.59	0.58	4.59	1.96	109.1
Acetonitrile	47.92	47.92	167.65	95.86	5400
Solvents	47.92	47.92	167.65	95.86	5400
TBADT	0.16	0.00	0.64	0.16	65.8
Catalyst	0.16	0.00	0.64	0.16	192.6
Total	49.67	48.50	172.88	97.98	5702

Table of parameters of the synthesis of ketoester 17 under sunlight exposure (heptanal 0.1 M; dimethylmaleate 0.1 M) in acetonitrile.



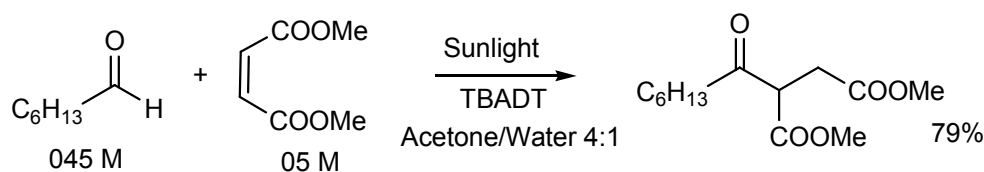
	S^{-1}	E	E_{in}	E_{out}	€/kg
1-Heptanal	0.49	0.00	0.74	0.00	23.5
Dimethylmaleate	0.62	0.11	2.48	0.37	53.6
Reactants	1.11	0.11	3.22	0.37	77.1
Acetonitrile	33.55	33.55	117.42	67.1	3780
Solvents	33.55	33.55	117.42	67.1	3780
TBADT	0.12	0.00	0.45	0.11	134.8
Catalyst	0.12	0.00	0.45	0.11	134.8
Total	34.78	33.66	121.09	67.58	3992

Table of parameters of the synthesis of ketoester 17 under sunlight exposure (heptanal 0.45 M; dimethylmaleate 0.5 M) in acetonitrile.



	S^{-1}	E	E_{in}	E_{out}	€/kg
1-heptanal	0.49	0.00	0.74	0.00	23.5
Dimethylmaleate	0.69	0.19	2.75	0.58	59.5
Reactants	1.18	0.19	3.49	0.58	83.0
Acetonitrile	7.46	7.46	26.10	14.91	840
Solvents	7.46	7.46	26.10	14.91	840
TBADT	0.02	0.00	0.10	0.00	30.0
Catalyst	0.02	0.00	0.10	0.00	30.0
Total	8.66	7.65	26.79	15.49	953.0

Table of parameters of the synthesis of ketoester 17 under sunlight exposure (heptanal 0.45 M; dimethylmaleate 0.5 M) in acetone-water 4:1.



	S^{-1}	E	E_{in}	E_{out}	€/kg
1-heptanal	0.56	0.00	0.84	0.00	26.8
Dimethylmaleate	0.78	0.34	3.14	1.11	67.8
Reactants	1.34	0.34	3.98	1.11	94.6
Acetone	6.88	6.88	13.76	20.65	126.1
Water	2.18	2.18	2.18	2.18	11.1
Solvents	9.06	9.06	15.94	22.83	137.2
TBADT	0.03	0.00	0.03	0.00	34.2
Catalyst	0.03	0.00	0.03	0.00	34.2
Total	10.43	9.40	19.95	23.94	266.0

References

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