Supplementary Information for

Enhanced photodecarboxylation of an aryl ester in polyethylene films

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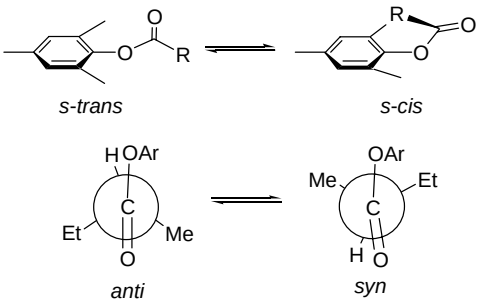
Table S-1. Some Physical Properties of Polyethylene Films Employed [a]

film	T_m, °C	cryst., %	*sg*, g cm^{-3}	V_{PE}, Å^3
PE0(u)	116	0	0.856	177
PE46(u)	~116, 121	46	0.918	139
PE46(s)	118	47		121
PE50(u)	123	50	0.917	144
PE50(s)	123	58		141
PE68(u)	129	68	0.945	124
PE68(s)	125, 132	84		113
PE74(u)	130	74	0.952	129
PE74(s)		70		120

[a] Melting temperatures from DSC (T_m), crystallinities (%), densities (*sg*), and calculated mean hole free volumes from positron annihilation studies (V_{PE}). Gu, W.; Hill, A. J.; Wang, X.; Cui, C.; Weiss, R. G. *Macromolecules* **2000**, *33*, 7801-7811. Luo, C.; Meakin, P.; Hill, A. J.; Weiss, R. G. To be submitted for publication.

Scheme S-1. 2D representations of possible conformers from DFT calculations. *s-Trans* or *s-cis* refers to the relative conformation of the ester group with respect to the aromatic ring. *Anti* or *syn* refers to the rotamers at the chiral carbon center.



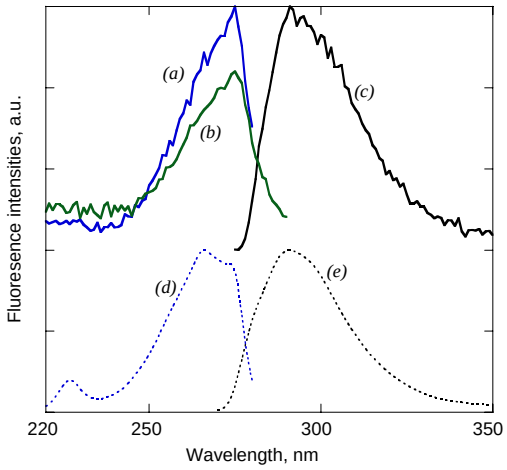


Figure S-1. Steady state fluorescence spectra of aryl ester **1** in **PE0** and in methylcyclohexane. Excitation spectra of **1** in **PE0** monitored at (*a*) 290 nm and at (*b*) 310 nm. (*c*) Emission spectrum in **PE0** excited at 266 nm. (*d*) Excitation spectrum at 290 nm in methylcyclohexane. (*e*) Emission spectrum in methylcyclohexane excited at 266 nm. Note that the emission and excitation spectra in **PE0** are somewhat distorted by self-absorption phenomena.

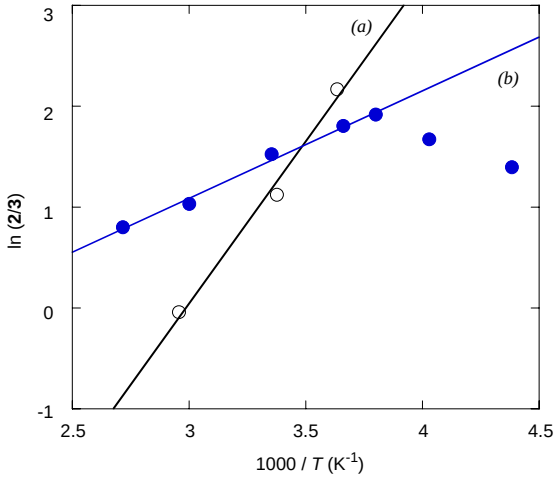
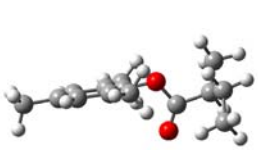
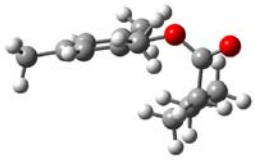


Figure S-2. Temperature dependence of photodecarboxylation and cage-escape products from irradiation of **1** (*a*) in **PE46**(u) and (*b*) in methylcyclohexane solutions. Lines are Arrenius type linear fits. Only data below -10 °C were used for fits in methylcyclohexane.

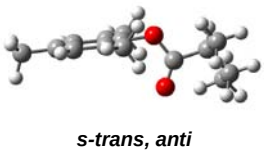
Table S-2. DFT Calculations of the Four Conformers Corresponding to Energy Minima of Aryl Ester **1**. [a]



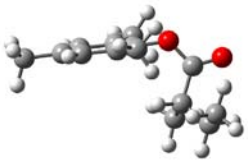
s-trans, syn



s-cis, syn



s-trans, anti



s-cis, anti

Conformation		Energy, Hartree	ΔE, Kcal mol^{-1}	Population, %	μ, debye	Quadrupole Moment, debye Å^{-1} Xx	Yy	zz	xy	xz	yz	V, Å^3 [b]
A	*s-trans, anti*	-696.2287749	≡ 0	78.85	1.52	-87.8	-92.9	-104.5	+0.8	-4.0	+0.7	269
B	*s-trans, syn*	-696.2270676	+1.32	21.04	1.77	-86.8	-92.5	-106.5	-0.3	+2.9	+0.0	333
C	*s-cis, anti*	-696.2184705	+6.58	0.11	4.02	-100.1	-94.1	-103.0	+4.0	-5.4	+3.2	236
D	*s-cis, syn*	-696.2092039	+12.6	<0.01	4.12	-101.1	-94.1	-102.9	-4.7	-6.9	-3.7	330

[a] At B3LYP/6-311G+(2d,p)//B3LYP/6-31G(d) level. Zero point energies were scaled by 0.9804 and corrected. See also Scheme S-1 for conformation nomenclature. [b] Van der Waals volumes are calculated by the PM3 method for the optimized conformations.

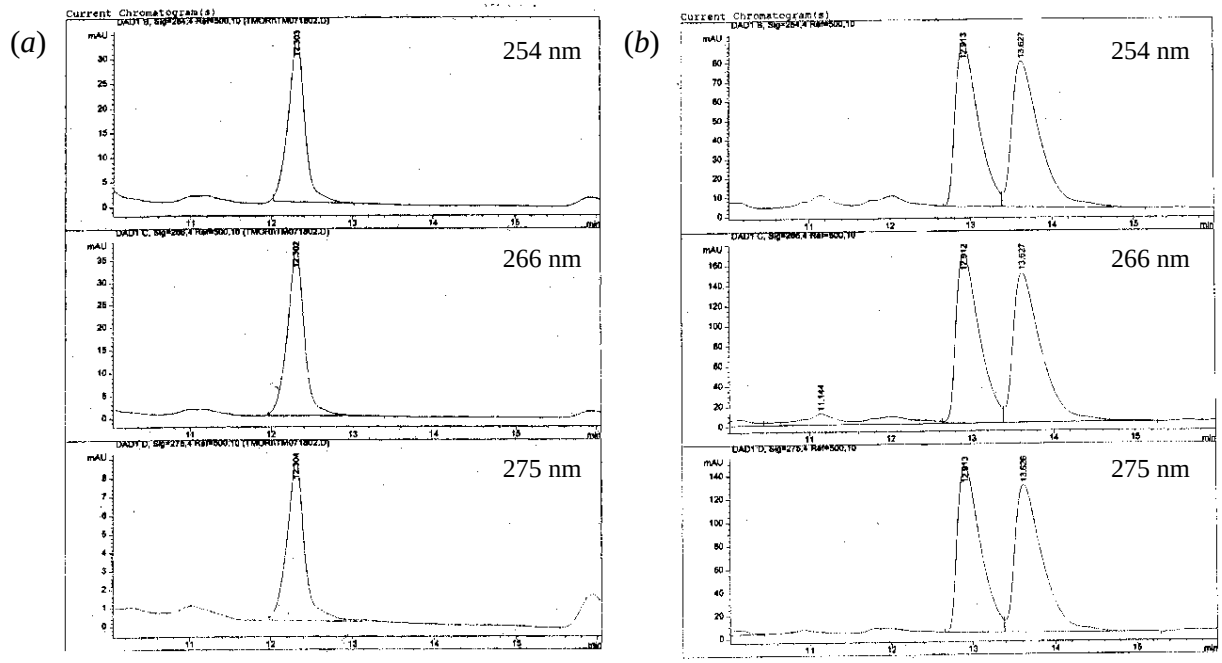


Figure S-3. Typical HPLC chromatograms of **2** from irradiations of *(S)*-**1** (*a*) and of racemic **1** *(b)* using a DAICEL OJ-H column (5 µm, 4.6 × 250 mm) and 99.5 : 0.5 hexane : *iso*-propanol as eluent. The reported %ees are the averaged ratios of peak areas of the two enantiomers from simultaneous measurements at 254, 266, and 275 nm. The x- and y-axes are optical density and time in minutes, respectively.