Electronic Supporting Information

Part II: Kinetic Measurements

"Size-driven inversion of selectivity in esterification reactions: secondary beat primary alcohols"

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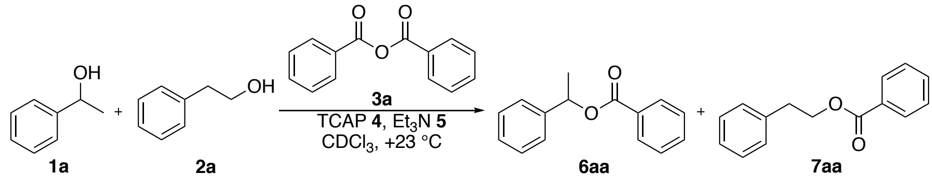
1. Competition Experiments

1.1 Set up

Technical details: NMR tubes were dried in the oven for at least 12 h. $CDCl_3$ and Et_3N were freshly distilled under N_2 from CaH_2 before use. Hamilton syringes were cleaned with acetone, dried under vacuum, and flushed with nitrogen prior to use. A GC vial holder (Shimadzu 221-44998-91) was connected to the coolant circuit of a cryostat maintaining +23 °C constantly and placed on a magnetic stirrer. The speed of stirring was fixed at 750 rpm for all the experiments described here.

Preparation of stock solutions: A guideline for the preparation of stock solutions for competition experiments is described in the following:



Temperature control: +23 °C

Three $CDCl_3$ stock solutions are prepared under nitrogen (Table S22). Stock solution A contains the secondary alcohol **1a** and primary alcohol **2a** each at a concentration of 0.05 M. Stock solution B contains benzoic anhydride **3a** (0.1 M), while stock solution C consists of a 0.15 M Et_3N (**5**) and catalyst TCAP (**4**) at a concentration of 0.005 M.

Table S22. Preparation of initial $CDCl_3$ stock solutions.

Stock solution	Compound	Concentration (mol L^{-1})	Volume (mL)	n (mol)	M.W. (g mol^{-1})	Mass (mg)
Stock A	**1a**	0.05	2	$100 \cdot 10^{-6}$	122.16	12.2
	2a	0.05	2	$100 \cdot 10^{-6}$	122.16	12.2
Stock B	**3a**	0.1	2	$200 \cdot 10^{-6}$	226.23	45.2
Stock C	**TCAP**	0.005	5	$25 \cdot 10^{-6}$	174.24	4.4
	Et_3N	0.15	5	$750 \cdot 10^{-3}$	101.19	75.9

Following these initial preparations, stock solution B was diluted in four discrete steps as shown in Table S23. The concentrations of the new solutions have been fixed at 20, 35, 50, and 70% of the initial stock solution B.

Table S23. Dilution of stock solution B.

Stock solution	Concentration (mol L^{-1})	Vol. B[b] (mL)	Volume (mL)
Stock B1 (20%)[a]	0.020	0.20	1
Stock B2 (35%)[a]	0.035	0.35	1
Stock B3 (50%)[a]	0.050	0.50	1
Stock B4 (70%)[a]	0.070	0.70	1

[a]Concentration relative to stock solution B; [b]Initial volume of stock solution B.

Methodology: Under nitrogen 0.4 mL of stock solution A, 0.4 mL of stock solution C, and 0.4 mL of stock solution B1 are transferred to a GC vial by use of a Hamilton syringe. The GC vial is then capped under nitrogen and placed in the GC vial holder with stirring.

Composition of each prepared GC vial for one competition experiment (**method A**):

In order to run competition experiments to defined turnover points, reaction solutions with identical concentrations for catalyst, substrate alcohols, and auxiliary base, but different initial anhydride concentrations were prepared in four different GC vials:

GC vial 1: 0.4 mL Stock A; 0.4 mL Stock C; 0.4 mL Stock B1
GC vial 2: 0.4 mL Stock A; 0.4 mL Stock C; 0.4 mL Stock B2
GC vial 3: 0.4 mL Stock A; 0.4 mL Stock C; 0.4 mL Stock B3
GC vial 4: 0.4 mL Stock A; 0.4 mL Stock C; 0.4 mL Stock B4

In terms of the actual starting concentrations (mol/L) for all components this yields:
GC vial 1: **1a** and **2a**: 0.017, **3a**: 0.007, **Et_3N**: 0.050, **TCAP**: 0.002
GC vial 2: **1a** and **2a**: 0.017, **3a**: 0.012, **Et_3N**: 0.050, **TCAP**: 0.002
GC vial 3: **1a** and **2a**: 0.017, **3a**: 0.017, **Et_3N**: 0.050, **TCAP**: 0.002
GC vial 4: 1a and **2a**: 0.017, **3a**: 0.023, **Et_3N**: 0.050, **TCAP**: 0.002

Composition of each prepared GC vial for one competition experiment (**method B**):
For anhydride **3m**, **3n**, **3v**, and **3w** a higher TCAP concentration is used (Table S24).

Table S24. Preparation of initial $CDCl_3$ stock solutions for anhydrides 3m, 3n, 3v, and 3w.

Stock	Compound	Molaritiy (mol L^{-1})	Volume (mL)	n (mol)	M.W. (g mol^{-1})	Mass (mg)
Stock A	**1a**	0.05	2	$100{\cdot}10^{-6}$	122.16	12.2
	2a	0.05	2	$100{\cdot}10^{-6}$	122.16	12.2
Stock B	**3m**	0.1	2	$200{\cdot}10^{-6}$	282.13	56.4
Stock C	**TCAP**	0.02	5	$100{\cdot}10^{-6}$	174.24	17.4
	Et_3N	0.15	5	$750{\cdot}10^{-3}$	101.19	75.9

In terms of the actual starting concentrations (mol/L) for all components this yields:

GC-vial 1: **1a** and **2a**: 0.017, **3a**: 0.007, **Et_3N**: 0.050, **TCAP**: 0.007
GC-vial 2: **1a** and **2a**: 0.017, **3a**: 0.012, **Et_3N**: 0.050, **TCAP**: 0.007
GC-vial 3: **1a** and **2a**: 0.017, **3a**: 0.017, **Et_3N**: 0.050, **TCAP**: 0.007
GC-vial 4: 1a and **2a**: 0.017, **3a**: 0.023, **Et_3N**: 0.050, **TCAP**: 0.007

Preparation of NMR samples: The competition experiment is considered finished when the reaction with the highest anhydride concentration (GC vial 4) is over. The reaction is monitored by ^{1}H NMR. NMR tubes are dried under vacuum using a special home-made apparatus and flushed with nitrogen three times to eliminate moisture. The GC vials are placed in a Schlenk flask and flushed with nitrogen three times as well. Then, 0.6 mL of the solution contained in the GC vial is transferred to the NMR tube under nitrogen. The NMR tube is then capped and the relative concentrations of all reactants/products determined by ^{1}H NMR spectroscopy.

1.2 ^{1}H NMR measurement

The ^{1}H NMR spectra of the competition experiments were edited by *MestReNova* 10.0. The spectra were corrected by using automatic phase correction and Bernstein polynomial fit with polynomial order 3 and referenced by the solvent signal of $CDCl_3$ (δ = 7.26 ppm). For the secondary alcohol **1** and ester **6** the hydrogen signal of the methyl group was integrated as a measure of the evolution of the reaction. If there was an overlap with other signals, the corresponding CH signal was used instead. For the primary alcohol **2** and ester **7** the hydrogen signal of one of the two CH_2 groups was integrated as a measure of turnover.

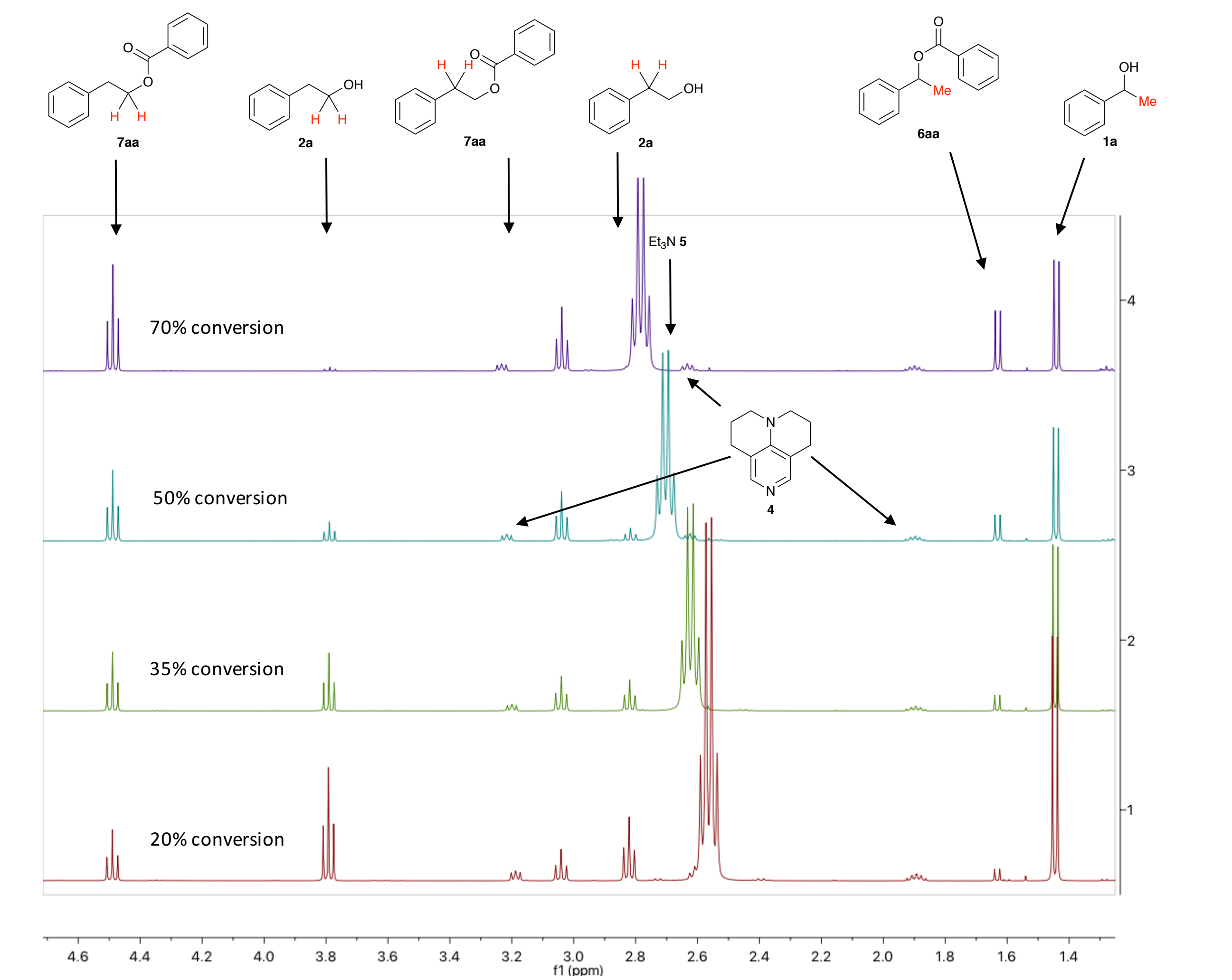
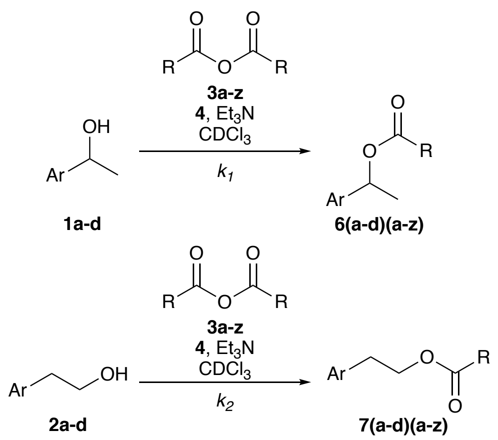


Figure S395. Example of the stacked ^{1}H NMR spectra for the competition experiment between **1a** and **2a** with **3a**.

Scheme S1. **General equation for the competition experiment.**



We determined that after full conversion the reactions were in equilibrium. Because of this, we can calculate the relative natural logarithm of rate constants from the product ratios as defined in Eq. 1.

$$ln(k_{\mathrm{rel}}) = ln\left(\frac{k_2}{k_1}\right) = ln\left(\frac{k_{(2a-d+3a-z)}}{k_{(1a-d+3a-z)}}\right) \qquad \text{Eq. 1}$$

The relative rate constant is directly related to the chemoselectivity and the degree of conversion (Eq. 2).[1]

$$k_{\mathrm{rel}} = \frac{ln(1-conv(1+C)}{ln(1-conv(1-C)} \qquad \text{Eq. 2}$$

The conversion is defined by Eq. 3, whereby the integrals of the [1]H NMR correspond to the concentrations.

$$Conversion(\%) = \left(\frac{[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]+[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]}{[\mathbf{1}\boldsymbol{a-d}]+[\mathbf{2}\boldsymbol{a-d}]+[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]+[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]}\right)\cdot 100 \qquad \text{Eq. 3}$$

The chemoselctivity is defined by Eq. 4:

$$Chemoselectivity_{exp}\ (C_{exp}) = \frac{[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]-[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]}{[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]+[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]} \qquad \text{Eq. 4}$$

A correction factor *f* was introduced, which defines the exact ratio of both reactants present in the reaction medium (this should be close to the ideal 1:1), to avoid the human error in the preparation of the samples (Eq. 5):

$$f = \frac{[\mathbf{1}\boldsymbol{a-d}]+[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]}{[\mathbf{2}\boldsymbol{a-d}]+[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]} \qquad \text{Eq. 5}$$

This correction factor *f* was now allowed in the equation for chemoselectivity and Eq. 6 was defined.

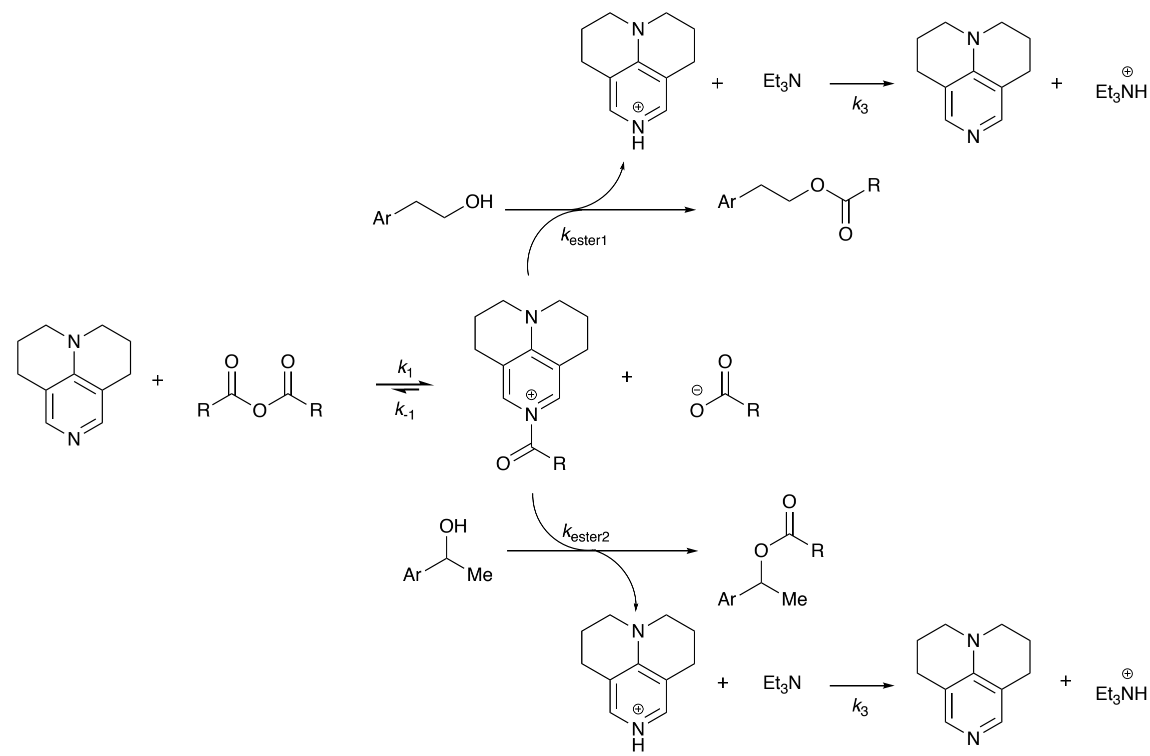
$$Chemoselectivity\ (C) = \frac{[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]\cdot f-[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]}{[\mathbf{7}(\boldsymbol{a-d})(\boldsymbol{a-z})]\cdot f+[\mathbf{6}(\boldsymbol{a-d})(\boldsymbol{a-z})]} \qquad \text{Eq. 6}$$

1.3 Simulation of competition experiments

With the help of the CoPaSi[2] and pro Fit7 programs the k_{rel}-values for the competition experiments have been simulated. Scheme S2 shows the reactions used in Copasi, in which the *k* values have been modified in order to achieve the k_{rel}-values. The values k_1, k_{-1} and k_3 have been used as constants:
k_1 = 0.1 l·mol^{-1}·s^{-1}; k_{-1} = 0.001 l·mol^{-1} · s^{-1}; k_3 = 0.1 l·mol^{-1} ·s^{-1}, while k_{ester1} and k_{ester2} have been allowed to vary.

Scheme S2. **Model reaction used in CoPaSi for the simulation of the rate constants.**

a)



b)

$$[TCAP] + [AcX] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [TCAP\text{-}Ac]^+ + [X]^-$$

$$[R_1\text{-}OH] + [TCAP\text{-}Ac]^+ \xrightarrow{k_{ester1}} [R_1\text{-}Ester] + [TCAP\text{-}H]^+$$

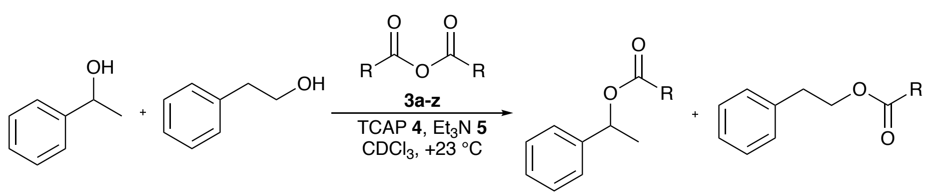
$$[R_2\text{-}OH] + [TCAP\text{-}Ac]^+ \xrightarrow{k_{ester2}} [R_2\text{-}Ester] + [TCAP\text{-}H]^+$$

$$[TCAP\text{-}H]^+ + [Et_3N] \xrightarrow[k_3]{} [TCAP] + [Et_3N\text{-}H]^+$$

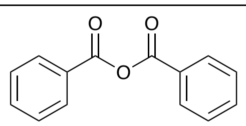
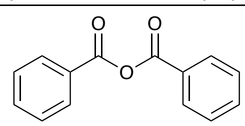
The rate constants of the different competition experiments were simulated by CoPaSi by using the starting concentrations of the experiments. The simulated concentrations over the time were used to calculate the conversion by Eq. 3 and chemolselectivity by Eq. 4. In Figures S397 to S414 the simulated rate constants were plotted over the rate constants optimized in the competition experiments.

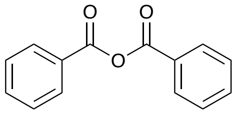
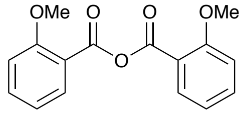
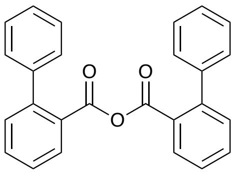
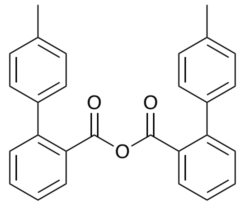
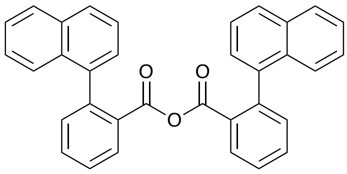
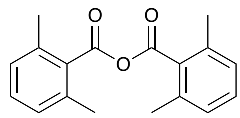
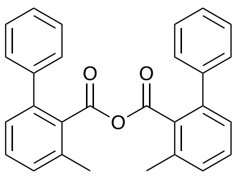
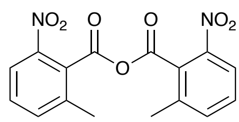
1.4 Results of competition experiments

Table S25. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between 1a and 2a with the benzoic anhydride derivates 3a-z.**

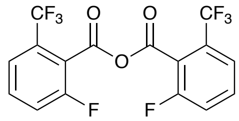


1a **2a** **6a(a-z)** **7a(a-z)**

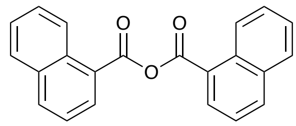
 **3a** [a]				 **3a** [a]			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
17.327	0.747	8.030	2.083	18.800	0.739	7.883	2.065

32.458	0.682	7.237	1.979	30.782	0.692	7.390	2.000
44.865	0.630	7.235	1.979	49.786	0.600	7.184	1.972
65.024	0.466	7.197	1.974	67.421	0.434	7.109	1.961
		7.425 ± 0.404	2.004 ± 0.053			7.392 ± 0.349	2.000 ± 0.046
 **3a** [a]				 **3b** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.064	0.738	7.787	2.052	21.398	0.770	9.447	2.246
34.050	0.678	7.291	1.987	32.000	0.704	7.936	2.071
48.181	0.613	7.260	1.982	43.279	0.638	7.253	1.981
68.460	0.422	7.217	1.976	64.039	0.528	10.629	2.364
		7.389 ± 0.267	2.000 ± 0.036			8.816 ± 1.517	2.166 ± 0.172
 **3f** [a]				 **3g** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
20.941	0.561	4.099	1.411	17.566	0.649	5.369	1.681
35.654	0.514	4.082	1.407	31.215	0.608	5.342	1.676
49.668	0.474	4.343	1.469	45.859	0.542	5.217	1.652
70.432	0.334	4.433	1.489	64.013	0.423	5.234	1.655
		4.239 ± 0.176	1.444 ± 0.041			5.291 ± 0.076	1.666 ± 0.014
 **3h** [a]				 **3m** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
28.594	0.546	4.202	1.436	14.772	0.235	1.658	0.505
31.968	0.522	4.014	1.390	27.764	0.216	1.678	0.518
43.895	0.490	4.190	1.433	41.483	0.189	1.680	0.519
64.131	0.392	4.515	1.507	50.951	0.179	1.693	0.527
		4.230 ± 0.208	1.441 ±0.049			1.677 ± 0.015	0.517 ± 0.009
 **3n** [b]				 **3o** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
15.100	0.409	2.556	0.938	17.862	0.251	1.759	0.565
25.211	0.391	2.592	0.952	29.042	0.234	1.763	0.567

37.344	0.361	2.606	0.958	45.374	0.204	1.762	0.566
51.015	0.309	2.533	0.929	59.984	0.171	1.765	0.568
		2.572 ± 0.033	0.944 ± 0.013			1.762 ± 0.002	0.566 ± 0.001

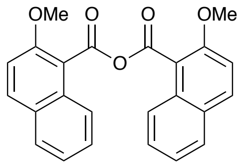


3p [a]

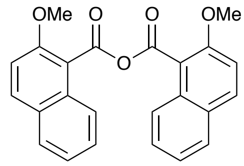


3q [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
17.788	0.494	3.271	1.185	19.518	0.727	7.506	2.016
30.707	0.465	3.331	1.203	33.004	0.668	6.878	1.928
45.640	0.414	3.333	1.204	48.070	0.591	6.601	1.887
63.113	0.330	3.323	1.201	67.513	0.427	6.752	1.910
		3.315 ± 0.029	1.198 ± 0.009			6.934 ± 0.397	1.935 ± 0.056

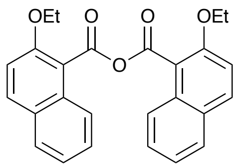


3r [a]

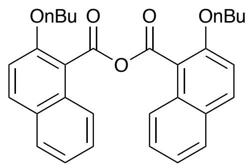


3r [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
16.011	0.278	1.866	0.624	15.990	0.241	1.709	0.536
29.034	0.227	1.734	0.550	29.613	0.215	1.685	0.522
42.598	0.196	1.697	0.529	44.272	0.191	1.688	0.524
60.549	0.148	1.636	0.492	59.847	0.152	1.649	0.500
		1.733 ± 0.097	0.549 ± 0.055			1.683 ± 0.025	0.520 ± 0.015

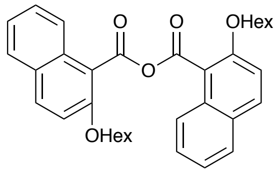


3s [a]

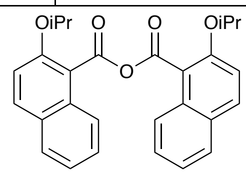


3t [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
17.294	0.192	1.534	0.428	18.603	0.156	1.417	0.349
28.528	0.189	1.576	0.455	30.733	0.139	1.403	0.338
42.451	0.161	1.542	0.433	44.669	0.106	1.336	0.290
60.189	0.174	1.782	0.578	56.151	0.091	1.328	0.283
		1.609 ± 0.117	0.473 ± 0.071			1.371 ± 0.046	0.315 ± 0.033

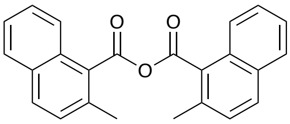
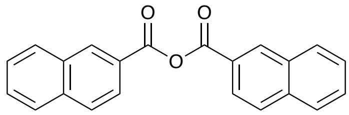


3u [a]



3v [b]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
11.958	0.168	1.436	0.362	18.228	0.287	1.920	0.652
22.578	0.146	1.396	0.334	32.025	0.190	1.597	0.468
31.121	0.120	1.339	0.292	45.787	0.185	1.673	0.514

40.183	0.118	1.363	0.310	60.648	0.150	1.648	0.499
		1.384 ± 0.042	0.324 ± 0.031			1.709 ± 0.144	0.534 ± 0.081
 **3w** [b]				 **3z** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
16.326	0.150	1.393	0.332	18.236	0.771	9.148	2.213
26.380	0.149	1.422	0.352	35.773	0.699	8.218	2.106
39.869	0.138	1.437	0.362	48.018	0.641	8.200	2.104
64.087	0.097	1.405	0.340	70.144	0.420	10.706	2.371
		1.414 ± 0.019	0.346 ± 0.013			9.068 ± 1.178	2.199 ± 0.126

[a]Competition experiments were carrying out by method A. [b]Competition experiments were carrying out by method B.

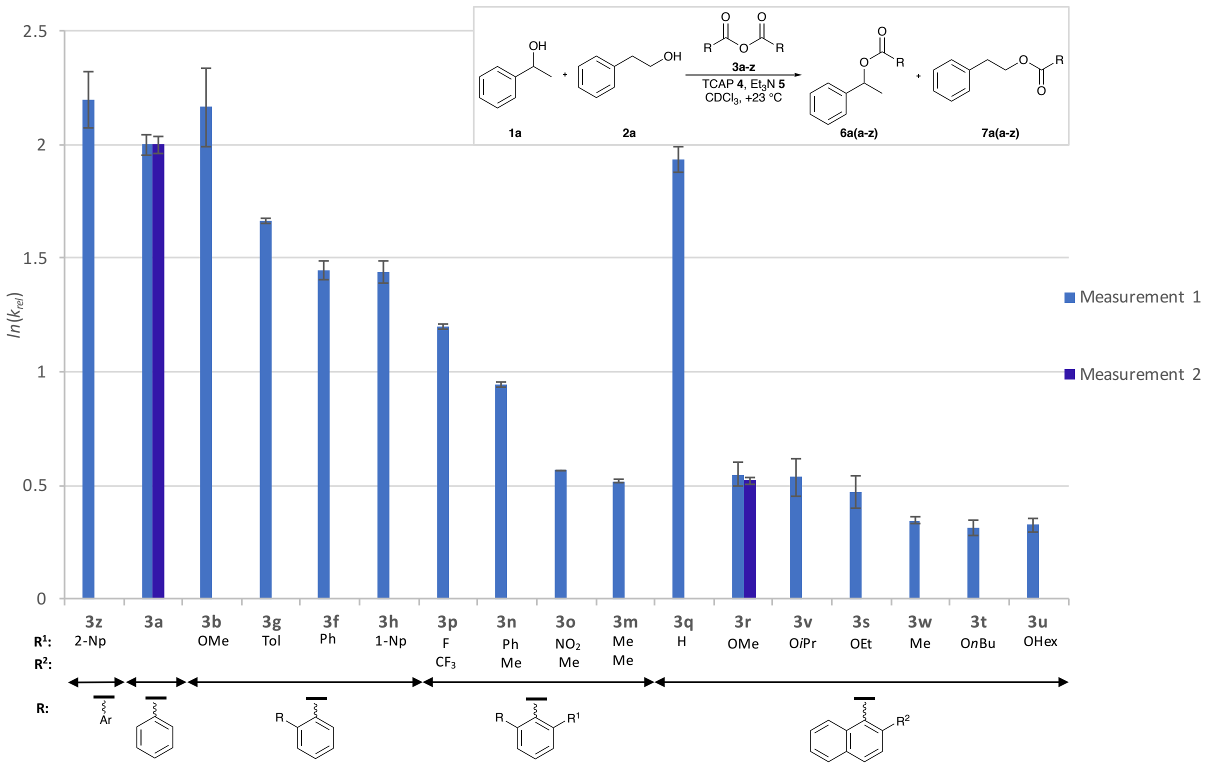


Figure S396. $ln(k_{rel})$ of competition experiment between **1a** and **2a** with the benzoic anhydride derivates **3a-z**.

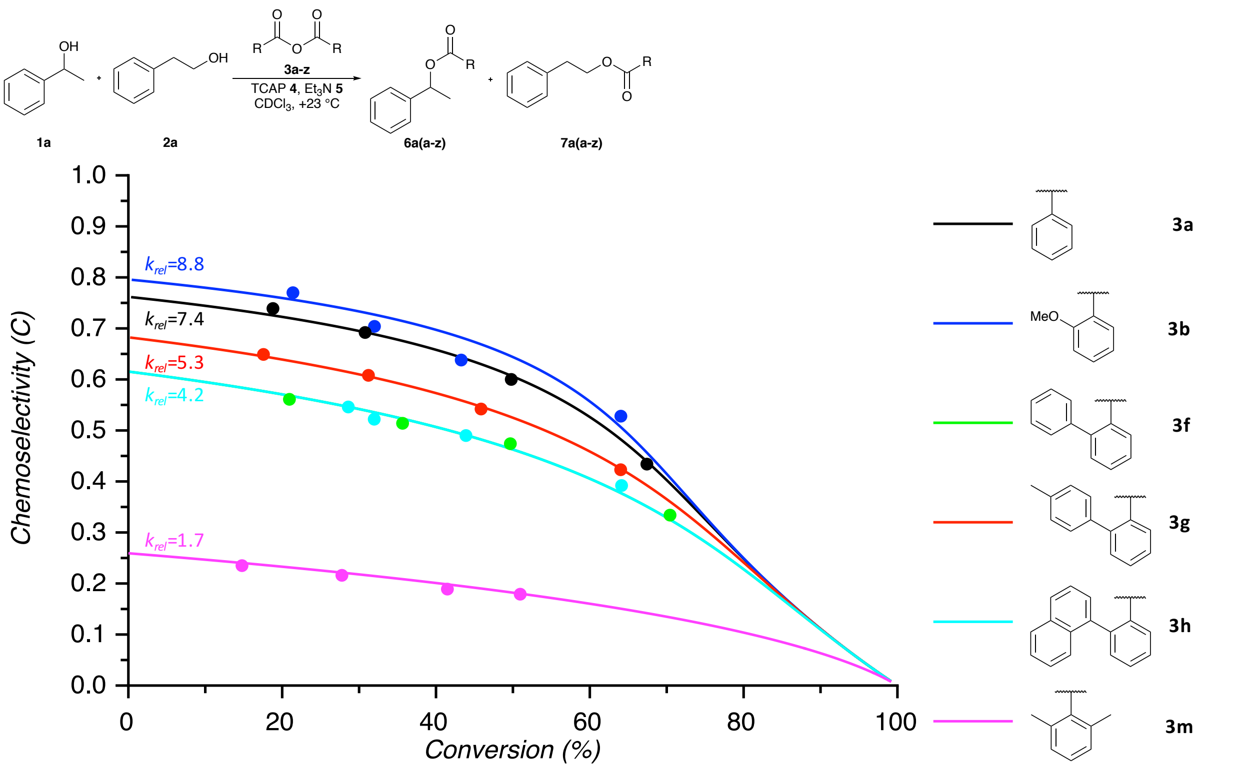


Figure S397. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1a** vs. **2a** with the benzoic anhydride derivates **3a-m**.

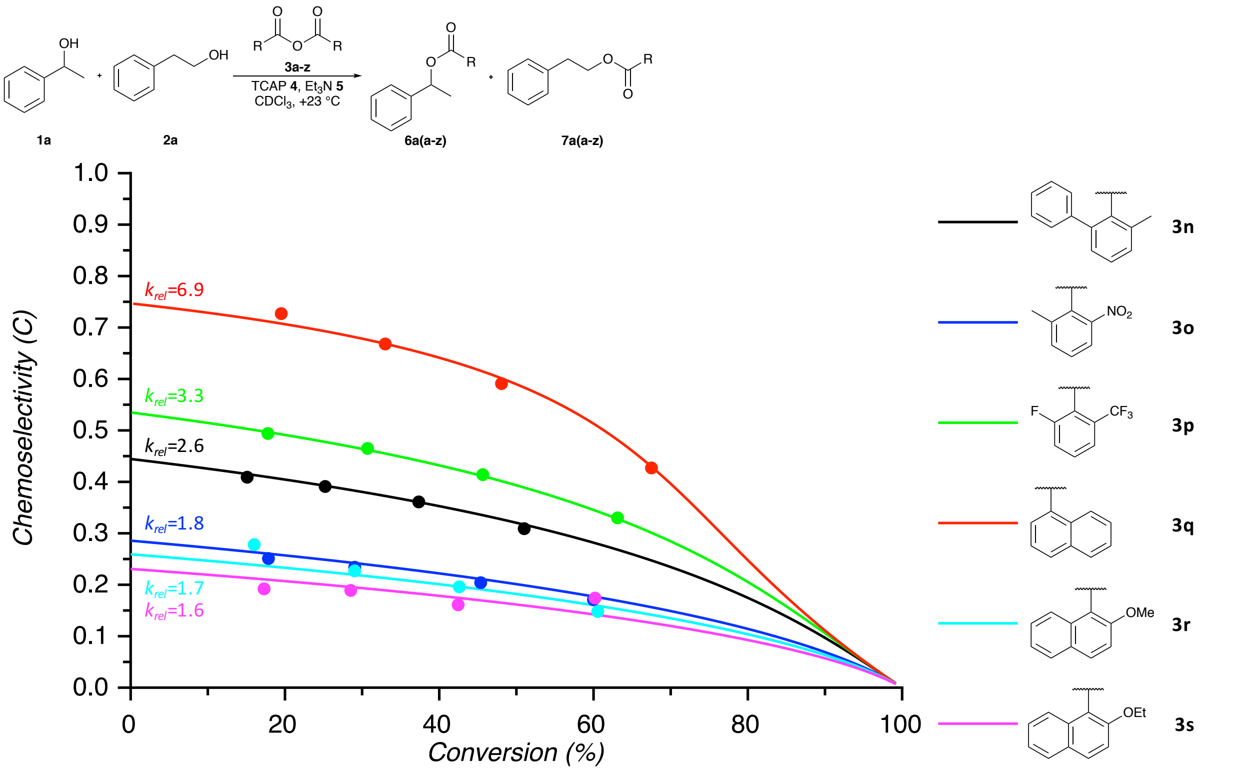


Figure S398. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1a** vs. **2a** with the benzoic anhydride derivates **3n-s**.

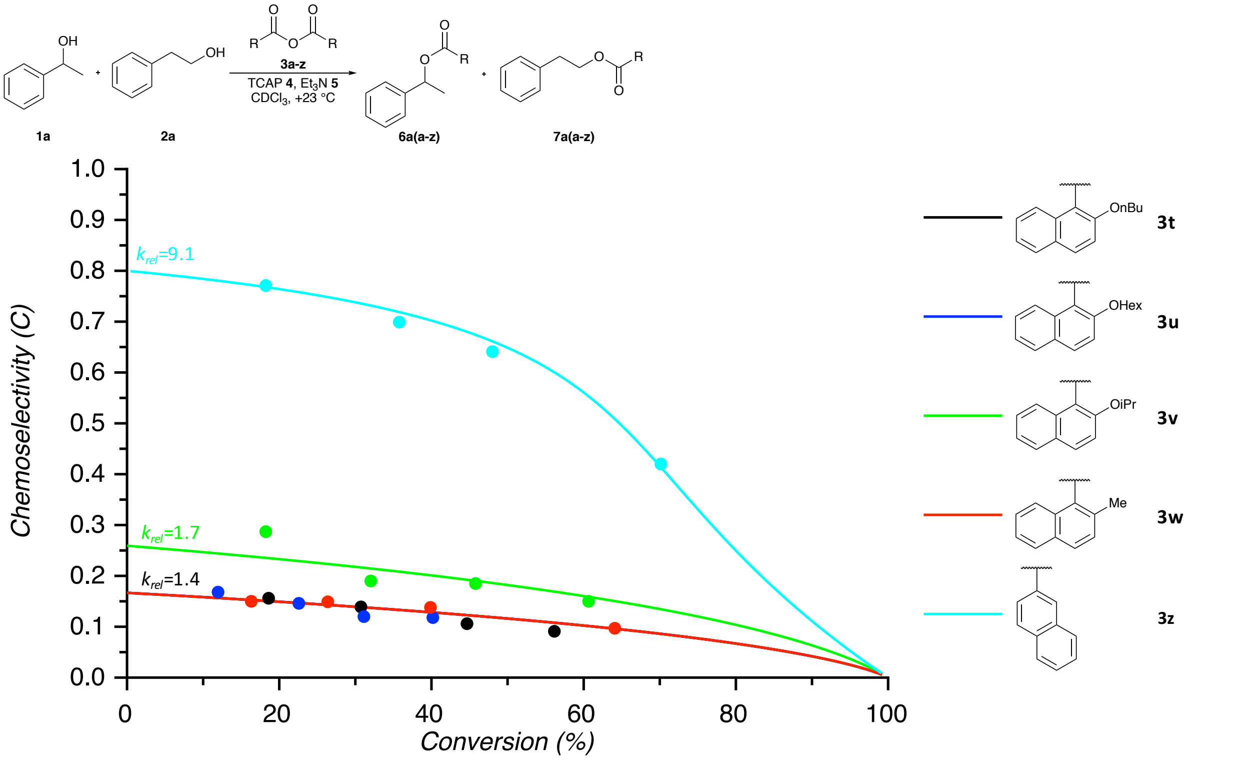


Figure S399. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1a** vs. **2a** with the benzoic anhydride derivates **3t-z**.

Table S26. **Integral limits (ppm), and relative and absolut integral values for competition experiments of alcohol 1a vs. 2a using benzoic anhydride derivates 3a-z.**

Conv		integral limits (ppm)		integral	absolut	Conv		integral limits (ppm)		integral	absolut
20%	**1a**	1.48	1.52	2.05	176288.03	**20%**	**1a**	1.45	1.50	2.17	158754.08
	2a	3.82	3.88	1.00	85461.20		**2a**	3.79	3.85	1.00	73179.15
	6aa	1.67	1.71	0.09	8101.74		**6aa**	1.65	1.68	0.11	8242.71
	7aa	4.52	4.57	0.43	37140.88		**7aa**	4.49	4.55	0.49	35952.05
35%	**1a**	1.48	1.52	3.06	165770.44	**35%**	**1a**	1.45	1.50	2.95	97651.85
	2a	3.82	3.88	1.00	54194.91		**2a**	3.79	3.85	1.00	33088.37
	6aa	1.67	1.71	0.36	19275.40		**6aa**	1.64	1.69	0.31	10342.66
	7aa	4.51	4.57	1.22	66301.26		**7aa**	4.49	4.55	1.11	36771.14
50%	**1a**	1.47	1.52	4.81	135879.56	**50%**	**1a**	1.44	1.50	6.26	84552.22
	2a	3.82	3.88	1.00	28249.78		**2a**	3.79	3.86	1.00	13513.93
	6aa	1.67	1.70	0.96	27246.40		**6aa**	1.64	1.68	1.57	21209.06
	7aa	4.52	4.57	2.78	78538.02		**7aa**	4.48	4.56	4.08	55148.35
70%	**1a**	1.47	1.52	20.16	110309.40	**70%**	**1a**	1.45	1.50	1.00	65566.79
	2a	3.81	3.88	1.00	5471.71		**2a**	3.79	3.85	0.03	1857.00
	6aa	1.66	1.71	10.68	58464.21		**6aa**	1.64	1.68	0.62	40818.91
	7aa	4.51	4.58	19.72	107916.45		**7aa**	4.49	4.55	1.02	67088.75
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.46	1.50	2.11	153572.34	**20%**	**1a**	1.47	1.51	1.00	149053.20

	2a	3.79	3.86	1.00	72288.82		**2a**	2.83	2.88	0.43	63758.16
	6aa	1.65	1.68	0.11	7666.71		**6ab**	1.62	1.66	0.05	8130.75
	7aa	4.49	4.55	0.46	33397.82		**7ab**	4.46	4.54	0.26	38991.21
35%	**1a**	1.45	1.50	3.26	93143.49	**35%**	**1a**	1.45	1.51	1.00	143835.19
	2a	3.79	3.86	1.00	28573.14		**2a**	2.83	2.88	0.32	46127.51
	6aa	1.64	1.69	0.41	11615.91		**6ab**	1.61	1.66	0.11	15295.93
	7aa	4.49	4.55	1.37	39068.17		**7ab**	4.46	4.54	0.39	56629.29
50%	**1a**	1.45	1.50	5.68	85846.33	**50%**	**1a**	1.45	1.50	1.00	118833.09
	2a	3.79	3.85	1.00	15114.08		**2a**	2.81	2.89	0.24	28113.51
	6aa	1.64	1.68	1.31	19845.39		**6ab**	1.61	1.67	0.18	21863.54
	7aa	4.48	4.56	3.58	54034.80		**7ab**	4.46	4.55	0.57	67321.77
70%	**1a**	1.45	1.49	1.00	63389.19	**70%**	**1a**	1.44	1.51	1.00	97581.15
	2a	3.78	3.85	0.02	1465.57		**2a**	X	X	X	X
	6aa	1.64	1.69	0.66	41846.74		**6ab**	1.61	1.67	0.44	43320.01
	7aa	4.49	4.55	1.06	67013.79		**7ab**	4.46	4.54	0.89	86972.31
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.47	1.53	2.10	153980.43	**20%**	**1a**	1.51	1.57	1.00	100829.77
	2a	3.80	3.88	1.00	73632.49		**2a**	3.84	3.92	0.50	50492.69
	6af	1.31	1.36	0.21	15750.78		**6ag**	1.40	1.44	0.07	6746.96
	7af	4.24	4.31	0.49	36192.96		**7ag**	4.30	4.37	0.20	20584.71
35%	**1a**	1.47	1.53	2.75	143465.91	**35%**	**1a**	1.50	1.57	1.00	96002.14
	2a	3.80	3.88	0.95	49480.99		**2a**	3.83	3.90	0.37	35661.31
	6af	1.30	1.36	0.59	30601.61		**6ag**	1.40	1.44	0.15	13927.14
	7af	4.24	4.32	1.15	60014.41		**7ag**	4.30	4.38	0.37	35942.86
50%	**1a**	1.46	1.52	3.68	114347.12	**50%**	**1a**	1.49	1.55	1.00	83714.24
	2a	3.78	3.86	0.82	25449.09		**2a**	3.82	3.89	0.24	20229.54
	6af	1.31	1.37	1.33	41183.08		**6ag**	1.39	1.45	0.28	23270.37
	7af	4.24	4.31	2.34	72885.05		**7ag**	4.31	4.38	0.58	48894.04
70%	**1a**	1.44	1.52	1.00	73405.44	**70%**	**1a**	1.48	1.55	1.00	68256.48
	2a	X	X	X	X		**2a**	3.80	3.88	0.09	6371.73
	6af	1.30	1.37	0.90	66286.60		**6ag**	1.39	1.45	0.60	41008.78
	7af	4.23	4.32	1.13	82614.41		**7ag**	4.30	4.39	0.95	64936.52
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.45	1.51	1.00	111445.92	**20%**	**1a**	1.46	1.52	1.00	10934.95
	2a	2.83	2.90	0.43	48047.89		**2a**	3.83	3.88	0.58	6374.34
	6ah	0.55	0.61	0.07	8283.99		**6am**	1.65	1.69	0.13	1402.54

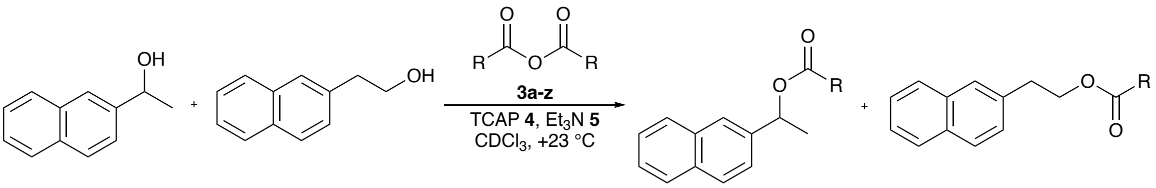
	7ah	2.01	2.24	0.34	37948.04		**7am**	4.54	4.58	0.13	1433.33
35%	**1a**	1.44	1.52	1.00	100721.14	**35%**	**1a**	1.47	1.52	1.00	9517.59
	2a	2.83	2.90	0.38	38517.08		**2a**	3.82	3.88	0.54	5118.82
	6ah	0.54	0.62	0.09	9224.11		**6am**	1.66	1.69	0.28	2665.52
	7ah	2.02	2.23	0.37	37352.61		**7am**	4.54	4.58	0.28	2629.13
50%	**1a**	1.46	1.51	1.00	91109.49	**50%**	**1a**	1.47	1.51	1.00	8084.78
	2a	2.82	2.89	0.29	26133.05		**2a**	3.82	3.86	0.48	3906.38
	6ah	0.54	0.62	0.15	13240.53		**6am**	1.65	1.70	0.51	4127.90
	7ah	2.01	2.24	0.55	50313.71		**7am**	4.54	4.59	0.47	3838.27
70%	**1a**	1.43	1.50	1.00	69415.43	**70%**	**1a**	1.45	1.50	1.00	6810.63
	2a	2.82	2.89	0.10	7248.14		**2a**	3.80	3.85	0.43	2904.16
	6ah	0.55	0.63	0.32	22513.66		**6am**	1.65	1.69	0.73	4950.92
	7ah	2.00	2.24	0.95	65678.65		**7am**	4.53	4.58	0.65	4432.60
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	4.85	4.93	1.00	5178.23	**20%**	**1a**	1.45	1.50	1.00	13795.12
	2a	3.83	3.90	1.97	10205.15		**2a**	3.80	3.86	0.58	7952.86
	6an	5.83	5.90	0.10	493.83		**6ao**	1.67	1.75	0.16	2143.09
	7an	4.16	4.24	0.52	2669.40		**7ao**	4.58	4.64	0.17	2300.69
35%	**1a**	4.86	4.93	1.00	3699.06	**35%**	**1a**	1.44	1.49	1.00	12396.25
	2a	3.81	3.89	1.80	6644.69		**2a**	3.79	3.86	0.53	6572.25
	6an	5.82	5.91	0.18	648.67		**6ao**	1.68	1.72	0.29	3566.99
	7an	4.15	4.22	0.93	3436.35		**7ao**	4.58	4.64	0.30	3694.35
50%	**1a**	4.85	4.91	1.00	3279.49	**50%**	**1a**	1.44	1.49	1.00	9734.43
	2a	3.83	3.87	1.51	4967.35		**2a**	3.78	3.85	0.46	4469.33
	6an	5.83	5.89	0.30	993.76		**6ao**	1.66	1.72	0.57	5534.27
	7an	4.17	4.22	1.49	4882.22		**7ao**	4.57	4.64	0.56	5413.37
70%	**1a**	4.84	4.91	1.00	2969.74	**70%**	**1a**	1.42	1.48	1.00	7822.17
	2a	3.80	3.86	1.19	3520.71		**2a**	3.77	3.86	0.38	2944.99
	6an	5.84	5.89	0.53	1573.46		**6ao**	1.68	1.72	1.00	7784.74
	7an	4.17	4.23	2.26	6705.29		**7ao**	4.56	4.63	0.90	7041.93
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	4.85	4.94	1.00	4410.30	**20%**	**1a**	1.48	1.52	2.24	158872.25
	2a	3.81	3.90	1.68	7408.01		**2a**	3.80	3.88	1.00	71084.39
	6ap	6.14	6.23	0.10	432.21		**6aq**	1.73	1.78	0.13	9070.66
	7ap	4.55	4.61	0.60	2646.86		**7aq**	4.63	4.68	0.52	36877.91
35%	**1a**	4.84	4.93	1.00	3522.29	**35%**	**1a**	1.47	1.52	2.74	150388.06

	2a	3.81	3.89	1.03	3620.60		**2a**	3.78	3.86	0.86	47150.35
	6ap	6.15	6.22	0.36	1268.60		**6aq**	1.73	1.78	0.34	18899.92
	7ap	4.55	4.62	1.82	6417.08		**7aq**	4.62	4.69	1.10	60017.94
50%	**1a**	4.86	4.94	1.00	4070.65	**50%**	**1a**	1.45	1.50	5.65	122860.05
	2a	3.82	3.88	1.38	5618.69		**2a**	3.77	3.85	1.00	21747.27
	6ap	6.13	6.22	0.19	790.87		**6aq**	1.72	1.79	1.41	30678.77
	7ap	4.55	4.62	1.11	4515.90		**7aq**	4.63	4.69	3.47	75495.91
70%	**1a**	4.84	4.93	1.00	2894.30	**70%**	**1a**	1.45	1.50	1.00	92557.24
	2a	3.81	3.88	0.61	1778.20		**2a**	3.76	3.85	0.02	2285.34
	6ap	6.14	6.22	0.72	2088.46		**6aq**	1.73	1.80	0.65	59703.91
	7ap	4.55	4.63	3.03	8769.86		**7aq**	4.63	4.68	1.01	93177.71
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.45	1.51	1.00	11382.60	**20%**	**1a**	1.46	1.52	1.00	11228.03
	2a	3.80	3.84	0.59	6701.88		**2a**	3.80	3.86	0.60	6789.54
	6ar	1.72	1.76	0.13	1490.77		**6ar**	1.71	1.75	0.14	1552.58
	7ar	4.67	4.72	0.15	1730.27		**7ar**	4.66	4.73	0.15	1682.03
35%	**1a**	1.43	1.49	1.00	10198.68	**35%**	**1a**	1.45	1.48	1.00	9729.35
	2a	3.78	3.83	0.55	5609.02		**2a**	3.79	3.85	0.57	5519.10
	6ar	1.70	1.75	0.29	2953.02		**6ar**	1.71	1.75	0.30	2939.83
	7ar	4.66	4.72	0.30	3107.75		**7ar**	4.66	4.72	0.32	3090.84
50%	**1a**	1.43	1.49	1.00	8504.15	**50%**	**1a**	1.44	1.49	1.00	8308.79
	2a	3.78	3.83	0.50	4256.75		**2a**	3.77	3.83	0.49	4078.58
	6ar	1.70	1.75	0.52	4429.71		**6ar**	1.71	1.76	0.56	4640.21
	7ar	4.66	4.73	0.52	4413.06		**7ar**	4.66	4.73	0.55	4547.12
70%	**1a**	1.44	1.48	1.00	6261.48	**70%**	**1a**	1.43	1.48	1.00	6319.60
	2a	3.76	3.82	0.43	2700.32		**2a**	3.77	3.82	0.43	2687.13
	6ar	1.70	1.75	1.06	6652.01		**6ar**	1.69	1.78	1.03	6507.26
	7ar	4.66	4.73	0.98	6116.35		**7ar**	4.66	4.73	0.94	5946.50
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.45	1.50	1.00	114161.73	**20%**	**1a**	4.85	4.94	1.00	3101.61
	2a	3.80	3.86	0.58	66350.65		**2a**	3.81	3.89	1.98	6138.66
	6as	1.71	1.75	0.16	18655.85		**6at**	6.28	6.36	0.19	574.53
	7as	4.64	4.71	0.15	17350.68		**7at**	4.63	4.71	0.54	1671.57
35%	**1a**	1.45	1.49	1.00	102424.25	**35%**	**1a**	4.85	4.92	1.00	2800.84
	2a	3.78	3.84	0.55	56730.60		**2a**	3.81	3.86	1.87	5226.78
	6as	1.70	1.76	0.31	31770.09		**6at**	6.28	6.38	0.36	1002.36
	7as	4.64	4.71	0.28	28719.51		**7at**	4.63	4.70	1.00	2799.85

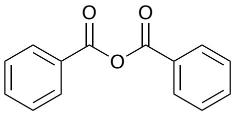
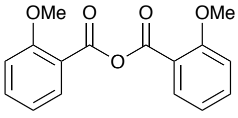
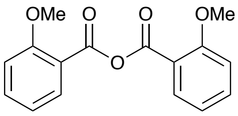
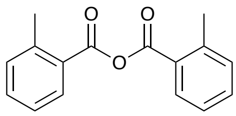
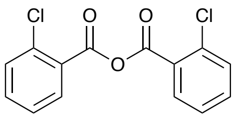
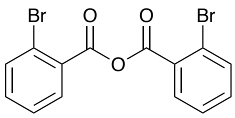
50%	**1a**	1.44	1.49	1.00	84540.10	**50%**	**1a**	4.84	4.92	1.00	1907.36
	2a	3.76	3.84	0.50	42283.53		**2a**	3.80	3.86	1.77	3376.44
	6as	1.70	1.76	0.56	47715.90		**6at**	6.27	6.37	0.66	1262.79
	7as	4.65	4.72	0.48	40953.72		**7at**	4.64	4.69	1.72	3279.84
70%	**1a**	1.44	1.48	1.00	55439.14	**70%**	**1a**	4.84	4.92	1.00	1564.10
	2a	3.75	3.82	0.44	24249.76		**2a**	3.80	3.85	1.67	2613.85
	6as	1.69	1.76	1.13	62702.13		**6at**	6.28	6.36	1.04	1622.69
	7as	4.65	4.72	0.92	50737.92		**7at**	4.64	4.70	2.63	4107.55
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	4.86	4.93	1.00	4191.87	**20%**	**1a**	4.85	4.94	1.00	3533.51
	2a	3.82	3.87	2.28	9547.47		**2a**	3.82	3.89	1.85	6520.24
	6au	6.27	6.37	0.11	455.58		**6av**	6.28	6.37	0.15	523.86
	7au	4.64	4.70	0.36	1524.34		**7av**	3.10	3.17	0.56	1981.07
35%	**1a**	4.84	4.90	1.00	3257.45	**35%**	**1a**	4.84	4.92	1.00	3098.84
	2a	3.79	3.85	2.21	7195.10		**2a**	3.81	3.88	1.70	5267.01
	6au	6.28	6.35	0.24	765.94		**6av**	6.29	6.37	0.35	1083.34
	7au	4.64	4.69	0.76	2466.14		**7av**	3.10	3.16	1.04	3234.79
50%	**1a**	4.85	4.93	1.00	2622.02	**50%**	**1a**	4.85	4.91	1.00	2620.37
	2a	3.81	3.85	2.13	5588.86		**2a**	3.81	3.86	1.50	3920.74
	6au	6.29	6.36	0.37	975.48		**6av**	6.29	6.37	0.59	1555.82
	7au	4.64	4.70	1.12	2943.44		**7av**	3.10	3.17	1.77	4625.93
70%	**1a**	4.84	4.92	1.00	1941.96	**70%**	**1a**	4.83	4.92	1.00	1664.57
	2a	3.79	3.85	2.04	3955.53		**2a**	3.80	3.87	1.27	2111.46
	6au	6.29	6.36	0.54	1049.35		**6av**	6.30	6.37	1.06	1769.28
	7au	4.65	4.69	1.63	3167.53		**7av**	3.11	3.16	2.91	4846.20
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.47	1.52	1.00	11172.34	**20%**	**1a**	1.46	1.50	1.00	178823.71
	2a	3.82	3.89	0.59	6544.01		**2a**	3.80	3.86	0.47	83172.16
	6aw	1.72	1.78	0.16	1810.19		**6az**	1.70	1.74	0.04	7824.08
	7aw	4.67	4.74	0.14	1523.30		**7az**	4.55	4.62	0.22	39924.06
35%	**1a**	1.47	1.52	1.00	9634.80	**35%**	**1a**	1.45	1.50	1.00	132382.53
	2a	3.80	3.88	0.57	5514.49		**2a**	3.80	3.86	0.28	37681.03
	6aw	1.72	1.77	0.29	2799.60		**6az**	1.70	1.74	0.12	16090.96
	7aw	4.68	4.75	0.25	2411.14		**7az**	4.56	4.62	0.45	59417.12
50%	**1a**	1.46	1.50	1.00	8240.37	**50%**	**1a**	1.46	1.51	1.00	80271.37
	2a	3.80	3.87	0.53	4353.50		**2a**	3.80	3.86	0.16	12870.24

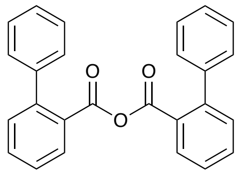
	6aw	1.73	1.78	0.53	4334.84		**6az**	1.70	1.74	0.21	16906.37
	7aw	4.67	4.74	0.44	3639.04		**7az**	4.55	4.61	0.62	50050.14
70%	**1a**	1.45	1.51	1.00	4664.11	**70%**	**1a**	1.46	1.50	1.00	58510.61
	2a	3.79	3.86	0.45	2100.55		**2a**				
	6aw	1.70	1.77	1.38	6435.48		**6az**	1.70	1.74	0.69	40349.64
	7aw	4.68	4.75	1.07	5006.78		**7az**	4.56	4.62	1.11	64742.91

Table S27. **Conversion, corrected chemoselectivity, relative rate, and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between 1b and 2b with the benzoic anhydride derivates 3a-z.**

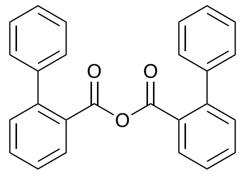


1b **2b** **6b(a-z)** **7b(a-z)**

 **3a** [a]				 **3b** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.239	0.533	3.717	1.313	20.723	0.568	4.187	1.432
34.266	0.485	3.664	1.298	32.491	0.505	3.830	1.343
48.215	0.430	3.639	1.292	45.970	0.441	3.659	1.297
62.151	0.356	3.623	1.287	65.137	0.350	3.841	1.346
		3.661 ± 0.041	1.298 ± 0.011			3.879 ± 0.221	1.354 ± 0.056
 **3b** [a]				 **3c** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
21.169	0.558	4.070	1.404	18.492	0.369	2.352	0.855
32.628	0.500	3.778	1.329	31.427	0.315	2.197	0.787
46.360	0.447	3.753	1.323	44.290	0.283	2.198	0.787
66.561	0.344	3.916	1.365	65.192	0.230	2.320	0.841
		3.879 ± 0.146	1.355 ± 0.037			2.267 ± 0.081	0.818 ± 0.036
 **3d** [a]				 **3e** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.949	0.487	3.233	1.173	13.654	0.516	3.393	1.222
29.913	0.460	3.259	1.181	23.631	0.473	3.217	1.168
47.512	0.398	3.243	1.176	35.691	0.439	3.228	1.172
58.269	0.350	3.243	1.177	46.499	0.404	3.257	1.181
		3.244 ± 0.011	1.177 ± 0.003			3.274 ± 0.081	1.186 ± 0.025

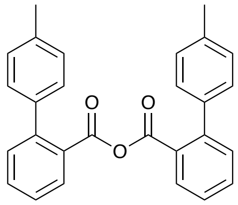


3f [a]

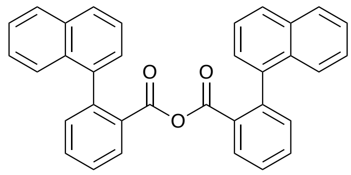


3f [a]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.843	0.328	2.127	0.755	23.536	0.316	2.110	0.747
34.398	0.290	2.094	0.739	33.180	0.308	2.183	0.780
47.819	0.264	2.135	0.758	46.687	0.278	2.211	0.793
66.389	0.211	2.197	0.787	66.382	0.216	2.240	0.807
		2.138 ± 0.043	0.760 ± 0.020			2.186 ± 0.056	0.782 ± 0.026

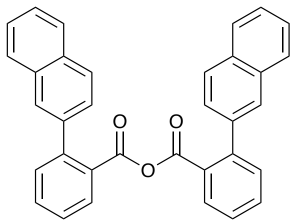


3g [a]

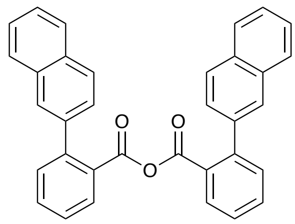


3h [a]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.399	0.354	2.273	0.821	19.368	0.253	1.777	0.575
34.474	0.320	2.275	0.822	28.270	0.260	1.875	0.629
49.636	0.281	2.289	0.828	41.916	0.270	2.083	0.734
69.299	0.213	2.331	0.846	62.767	0.226	2.206	0.791
		2.292 ± 0.027	0.829 ± 0.012			1.985 ± 0.195	0.682 ± 0.098

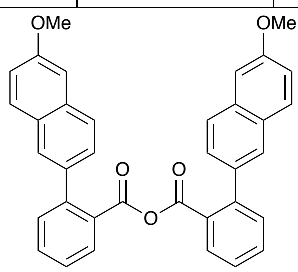


3i [a]

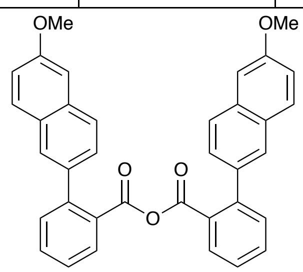


3i [a]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.483	0.409	2.593	0.953	23.250	0.384	2.511	0.921
30.816	0.376	2.584	0.949	31.630	0.375	2.592	0.952
42.731	0.345	2.602	0.956	46.187	0.334	2.605	0.958
58.687	0.298	2.701	0.994	58.494	0.298	2.691	0.990
		2.620 ± 0.054	0.963 ± 0.021			2.600 ± 0.074	0.955 ± 0.028

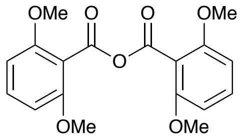
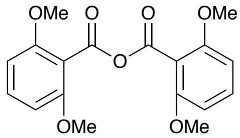
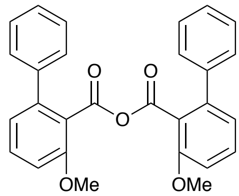
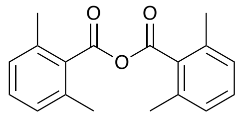
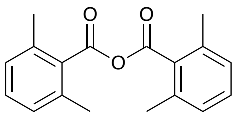
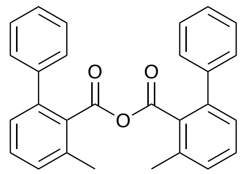
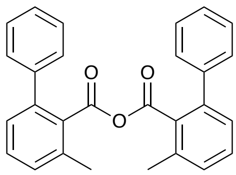
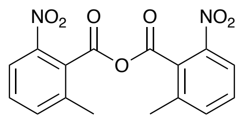


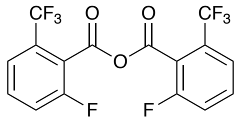
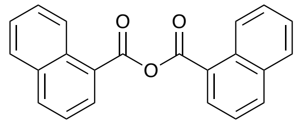
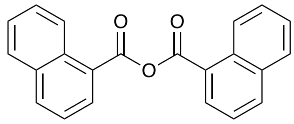
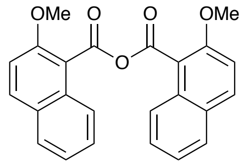
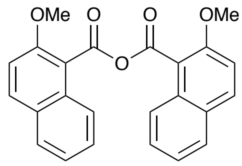
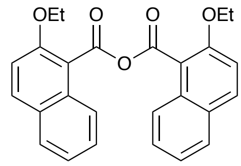
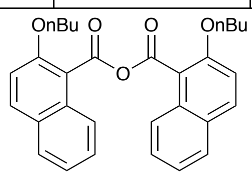
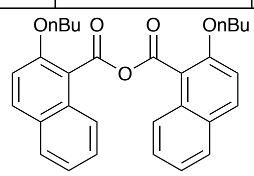
3j [a]

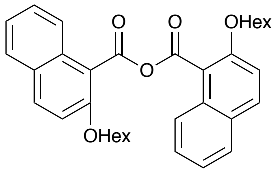
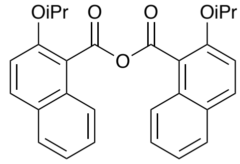
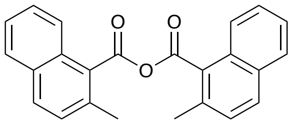
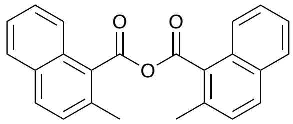
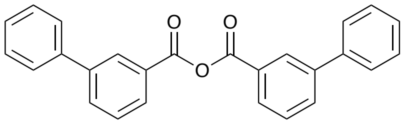
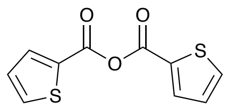
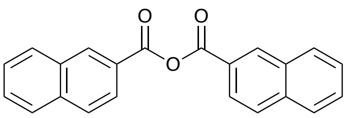


3j [a]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
22.952	0.412	2.703	0.994	26.185	0.361	2.410	0.879
38.811	0.382	2.799	1.029	31.560	0.393	2.723	1.002

44.061	0.362	2.779	1.022	42.462	0.364	2.748	1.011
61.048	0.302	2.856	1.049	62.318	0.302	2.919	1.071
		2.784 ± 0.063	1.024 ± 0.023			2.700 ± 0.212	0.991 ± 0.080
 **3k** [a]				 **3k** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
16.231	0.516	3.457	1.240	16.069	0.550	3.821	1.340
29.872	0.508	3.762	1.325	30.568	0.516	3.887	1.358
42.676	0.466	3.798	1.334	42.732	0.470	3.856	1.350
56.251	0.402	3.790	1.332	55.942	0.406	3.821	1.341
		3.702 ± 0.164	1.308 ± 0.045			3.846 ± 0.032	1.347 ± 0.008
 **3l** a				 **3m** [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.625	0.541	3.780	1.330	18.603	-0.196	0.643	-0.441
31.082	0.511	3.842	1.346	30.400	-0.174	0.656	-0.422
46.478	0.451	3.806	1.337	44.337	-0.160	0.644	-0.439
61.580	0.375	3.867	1.352	61.599	-0.127	0.652	-0.428
		3.824 ± 0.038	1.341 ± 0.010			0.649 ± 0.006	-0.432 ± 0.009
 **3m** [b]				 **3n** [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.076	-0.202	0.637	-0.451	16.893	-0.041	0.913	-0.091
30.772	-0.182	0.642	-0.443	28.427	-0.015	0.965	-0.036
43.008	-0.160	0.648	-0.434	38.912	-0.021	0.948	-0.053
60.680	-0.123	0.663	-0.411	60.625	-0.012	0.960	-0.041
		0.648 ± 0.011	-0.435 ± 0.017			0.946 ± 0.023	-0.055 ± 0.025
 **3n** [b]				 **3o** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
16.011	-0.034	0.928	-0.075	17.773	-0.172	0.682	-0.383
28.114	-0.014	0.968	-0.033	32.992	-0.145	0.698	-0.359
42.178	-0.009	0.977	-0.024	47.610	-0.133	0.687	-0.376

58.384	-0.014	0.957	-0.044	68.379	-0.093	0.702	-0.353
		0.957 ± 0.021	-0.044 ± 0.022			0.692 ± 0.010	-0.368 ± 0.014
 **3p** [a]				 **3q** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.641	0.183	1.507	0.410	19.275	0.481	3.187	1.159
35.592	0.161	1.504	0.408	29.512	0.447	3.122	1.138
49.588	0.140	1.501	0.406	43.631	0.400	3.105	1.133
69.022	0.105	1.498	0.404	64.929	0.302	3.092	1.129
		1.502 ± 0.004	0.407 ± 0.003			3.127 ± 0.042	1.140 ± 0.013
 **3q** [a]				 **3r** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.488	0.478	3.170	1.154	22.681	-0.130	0.741	-0.299
31.878	0.442	3.141	1.145	29.273	-0.113	0.763	-0.271
44.590	0.397	3.117	1.137	42.486	-0.105	0.755	-0.281
65.116	0.314	3.277	1.187	56.599	-0.095	0.741	-0.299
		3.176 ± 0.071	1.156 ± 0.022			0.750 ± 0.011	-0.287 ± 0.014
 **3r** [a]				 **3s** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
16.922	-0.144	0.728	-0.318	23.857	-0.205	0.620	-0.478
28.651	-0.105	0.779	-0.250	29.637	-0.189	0.633	-0.457
42.269	-0.105	0.755	-0.280	41.733	-0.169	0.636	-0.452
56.040	-0.097	0.740	-0.301	58.905	-0.134	0.647	-0.436
		0.750 ± 0.022	-0.287 ± 0.029			0.634 ± 0.011	-0.456 ± 0.017
 **3t** [a]				 **3t** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.563	-0.267	0.548	-0.602	16.163	-0.284	0.528	-0.638
31.600	-0.241	0.550	-0.597	28.314	-0.256	0.539	-0.618
45.793	-0.219	0.542	-0.612	41.220	-0.230	0.540	-0.616
62.014	-0.182	0.535	-0.625	54.527	-0.201	0.538	-0.620
		0.544 ± 0.007	-0.609 ± 0.012			0.536 ± 0.005	-0.623 ± 0.010

 3u [a]				 3v [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.083	-0.299	0.505	-0.684	19.475	-0.206	0.628	-0.466
30.529	-0.274	0.509	-0.675	34.864	-0.165	0.661	-0.414
41.613	-0.240	0.524	-0.646	48.620	-0.141	0.668	-0.404
59.167	-0.195	0.527	-0.640	68.114	-0.114	0.651	-0.429
		0.516 ± 0.011	-0.661 ± 0.022			0.652 ± 0.018	-0.428 ± 0.027
 3w [b]				 3w [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.016	-0.250	0.571	-0.561	16.766	-0.218	0.615	-0.487
25.050	-0.241	0.566	-0.569	25.953	-0.221	0.593	-0.522
35.847	-0.209	0.587	-0.533	34.853	-0.181	0.634	-0.456
50.242	-0.183	0.587	-0.534	51.164	-0.172	0.601	-0.509
		0.578 ± 0.011	-0.549 ± 0.019			0.611 ± 0.018	-0.493 ± 0.029
 3x [a]				 3y [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.473	0.528	3.636	1.291	16.035	0.669	5.720	1.744
26.315	0.512	3.688	1.305	26.757	0.640	5.711	1.742
39.035	0.460	3.570	1.272	36.368	0.603	5.612	1.725
50.393	0.422	3.662	1.298	49.745	0.548	5.770	1.753
		3.639 ± 0.051	1.292 ± 0.014			5.703 ± 0.066	1.741 ± 0.012
 3z [a]							
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$				
20.198	0.590	4.482	1.500				
34.311	0.533	4.269	1.451				
50.038	0.465	4.243	1.445				
68.626	0.345	4.287	1.456				
		4.320 ± 0.109	1.463 ± 0.025				

[a]Competition experiments were carrying out by method A. [b]Competition experiments were carrying out by method B.

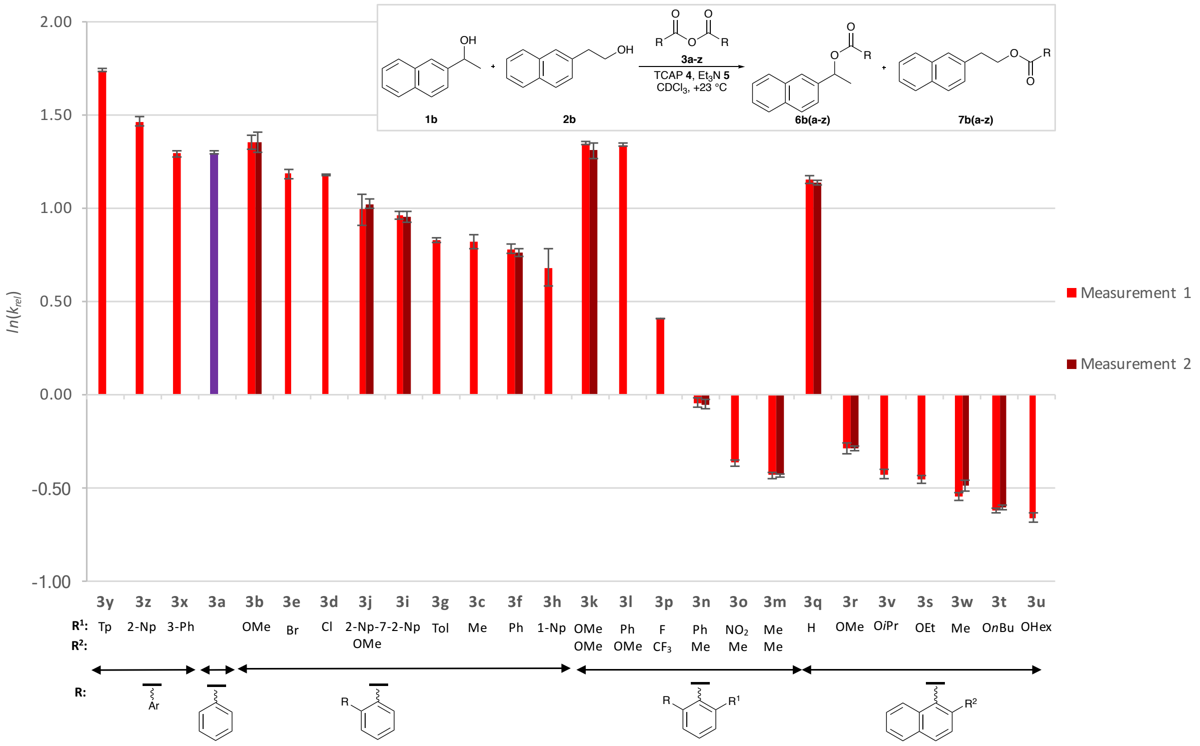


Figure S400. *ln*(k_{rel}) of competition experiment between **1b** and **2b** with the benzoic anhydride derivates **3a-z**.

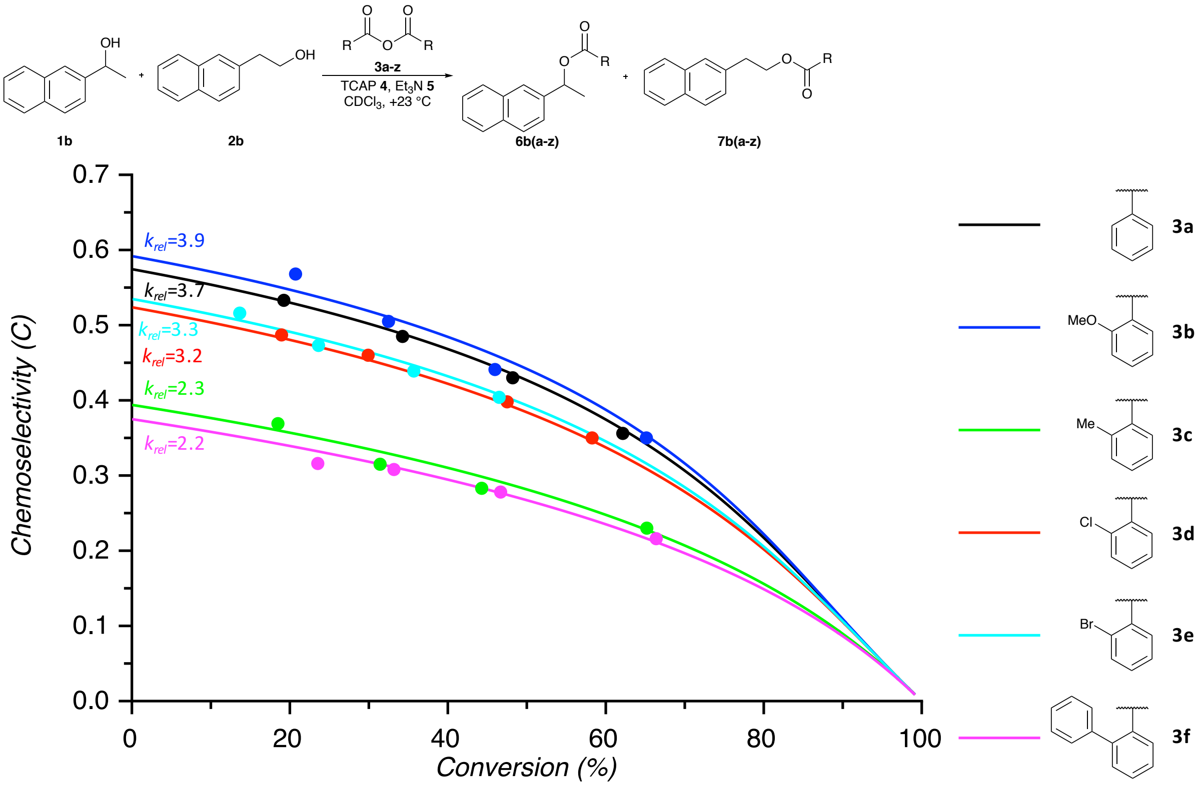


Figure S401. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1b** vs. **2b** with the benzoic anhydride derivates **3a-f**.

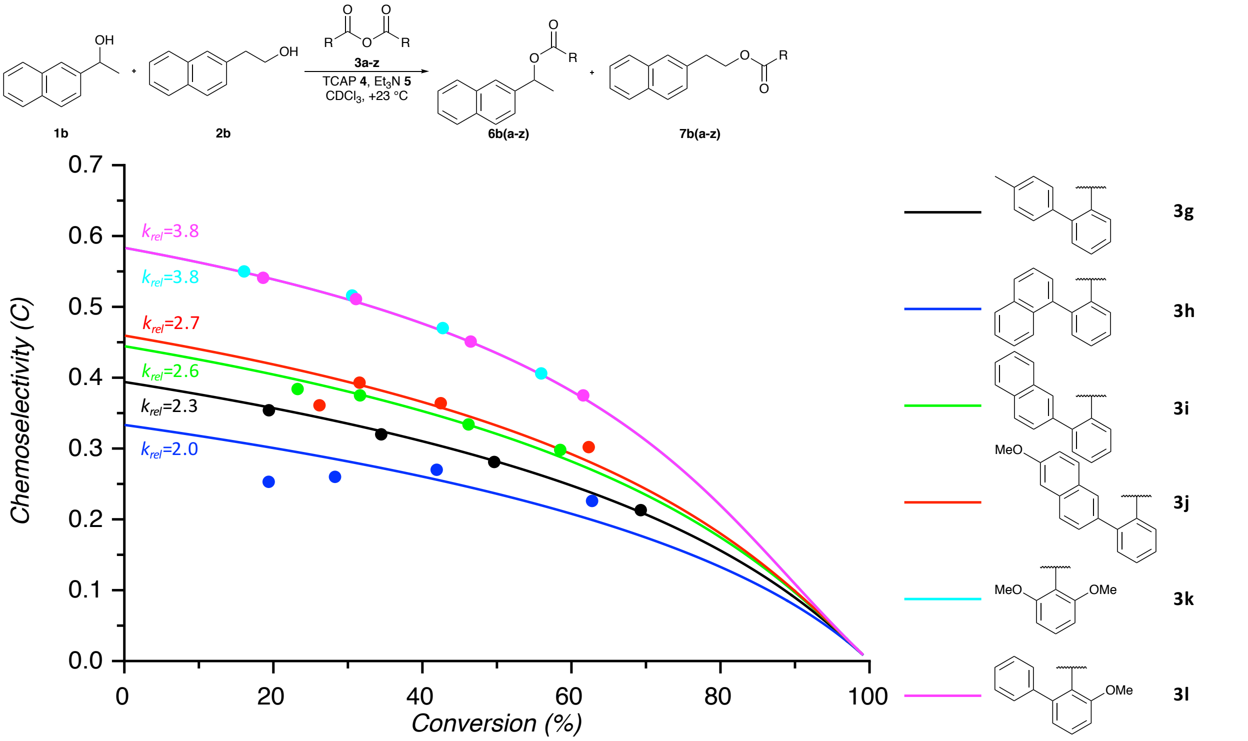


Figure S402. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1b** vs. **2b** with the benzoic anhydride derivates **3g-l**.

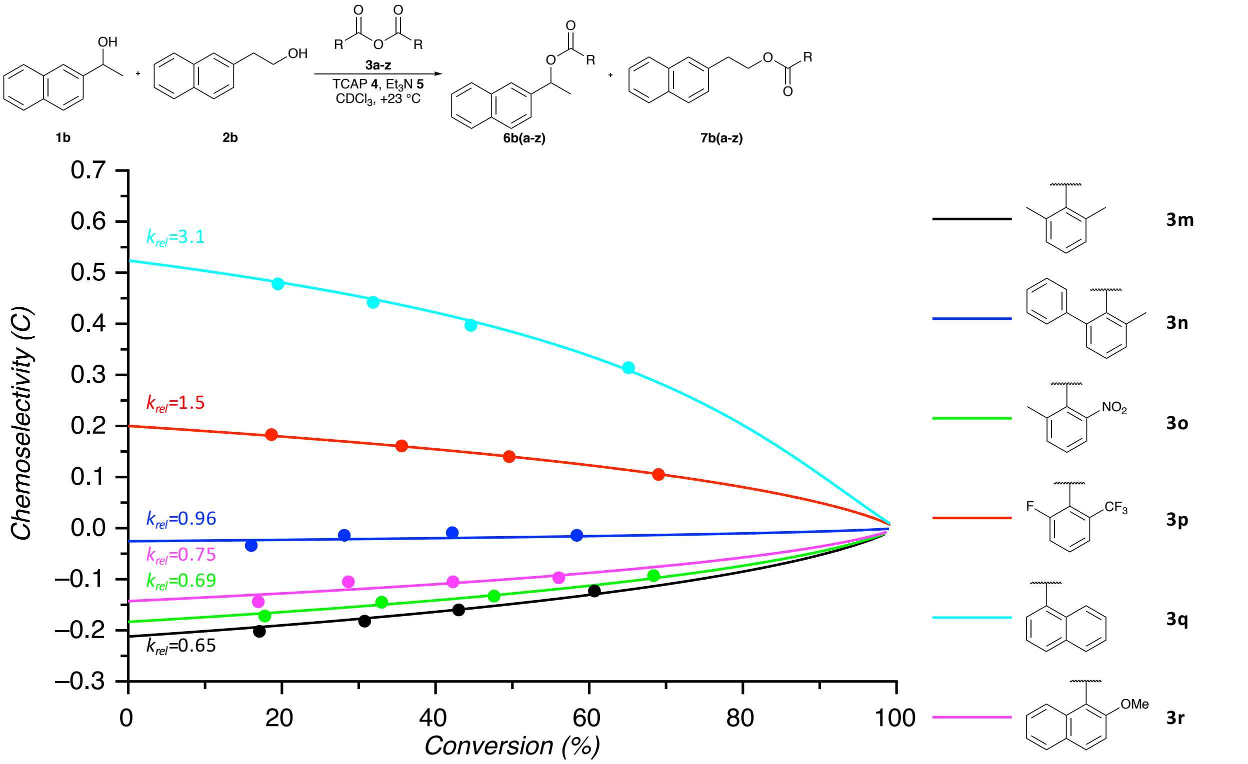


Figure S403. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1b** vs. **2b** with the benzoic anhydride derivates **3m-r**.

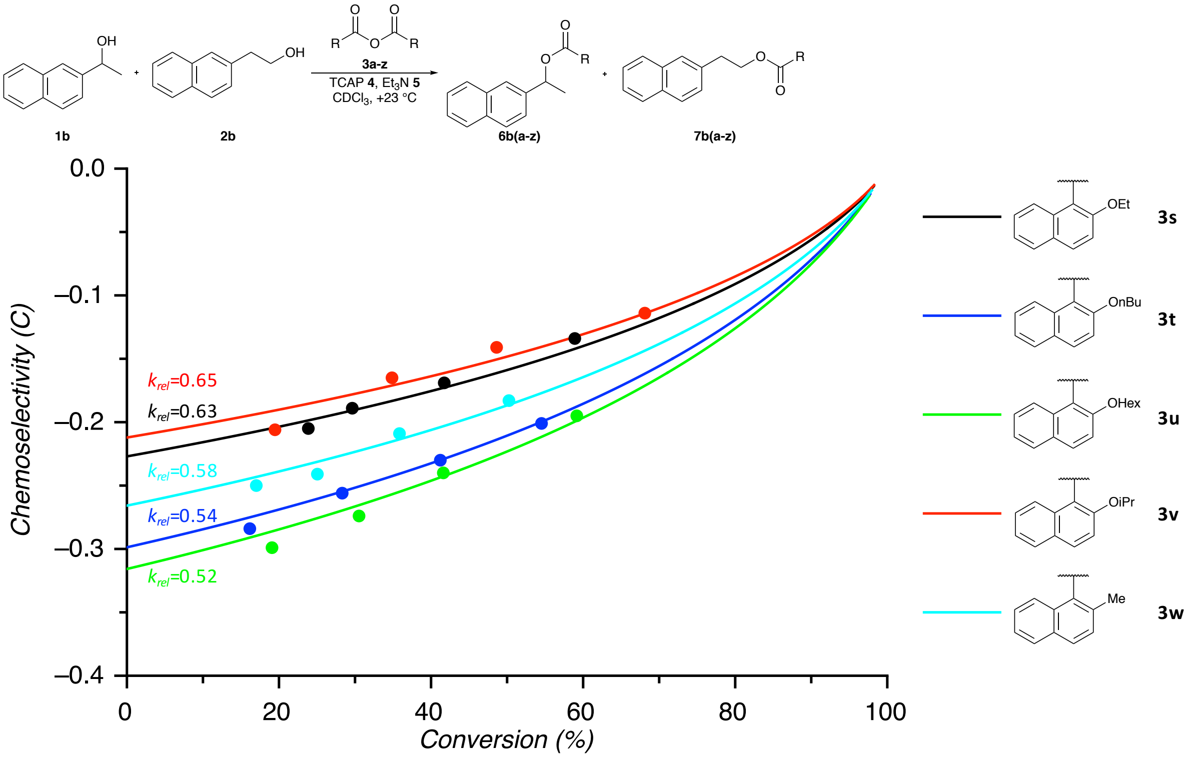


Figure S404. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1b** vs. **2b** with the benzoic anhydride derivates **3s-w**.

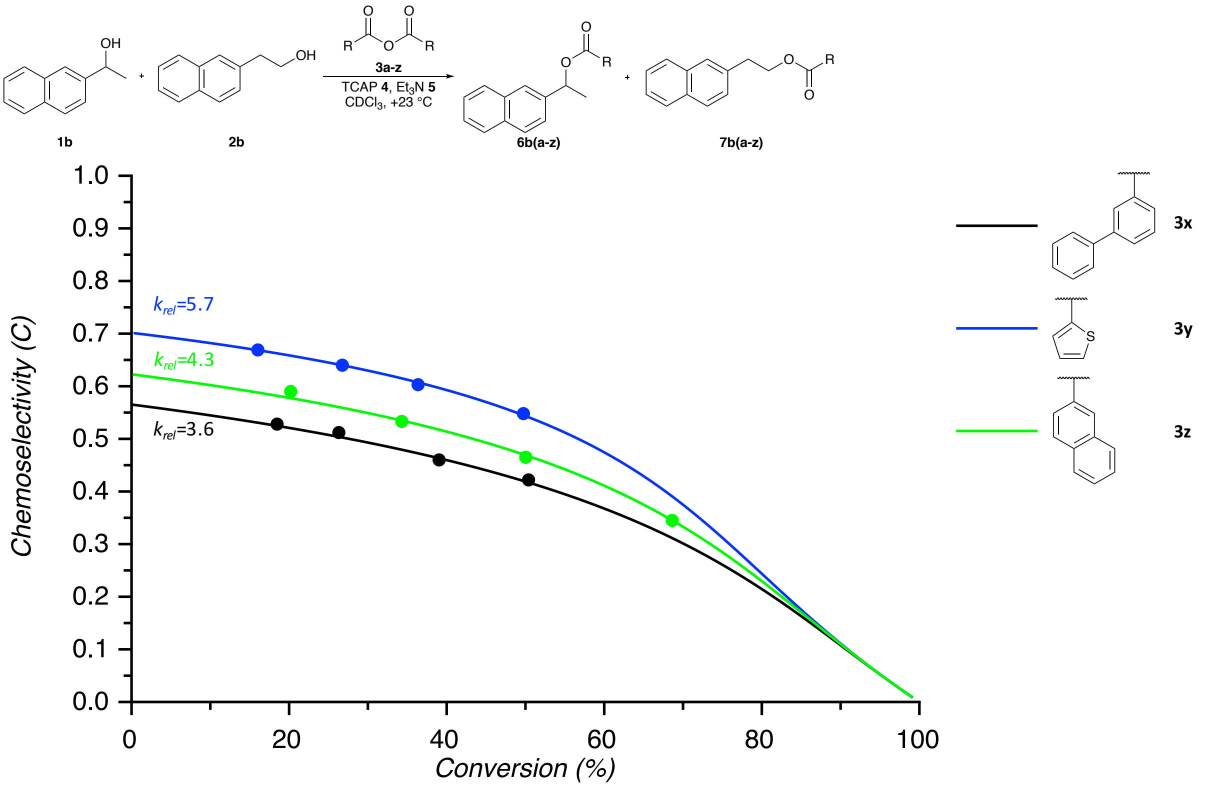


Figure S405. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1b** vs. **2b** with the benzoic anhydride derivates **3x-z**.

Table S28. **Integral limits (ppm), relative and absolut integral values for competition experiments of alcohol 1b vs. 2b using benzoic anhydride derivates 3a-z.**

Conv		integral limits (ppm)		integral	absolut	Conv		integral limits (ppm)		integral	absolut
20%	**1b**	1.53	1.57	1.00	138189.16			1.57	1.61	1.00	138057.38
	2b	3.87	3.93	0.52	71373.74			3.02	3.08	0.49	67813.68
	6ba	1.74	1.78	0.10	13625.01			1.74	1.78	0.10	14275.32
	7ba	4.58	4.64	0.22	29864.60			4.58	4.66	0.24	33408.62
35%	**1b**	1.53	1.57	1.00	122625.65	**35%**		1.57	1.62	1.00	133629.12
	2b	3.87	3.93	0.39	48237.29			3.00	3.08	0.39	51870.68
	6ba	1.74	1.78	0.21	26335.68			1.74	1.78	0.20	26338.90
	7ba	4.58	4.64	0.41	50202.27			4.58	4.66	0.38	50704.58
50%	**1b**	1.53	1.57	1.00	109698.16	**50%**		1.56	1.61	1.00	106406.78
	2b	3.87	3.93	0.28	31031.81			3.01	3.07	0.29	30404.93
	6ba	1.74	1.78	0.38	41658.63			1.74	1.78	0.35	36924.96
	7ba	4.58	4.64	0.63	69211.78			4.59	4.66	0.59	62971.53
70%	**1b**	1.53	1.57	1.00	89338.98	**70%**		1.54	1.61	1.00	70375.69
	2b	3.87	3.93	0.17	15446.45			2.99	3.06	0.11	8087.34
	6ba	1.74	1.78	0.67	59667.04			1.72	1.79	0.78	55175.71
	7ba	4.58	4.64	0.93	83388.89			4.58	4.67	1.03	72702.06
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.56	1.62	1.00	144350.16	**20%**	**1b**	1.53	1.59	1.00	110844.21
	2b	3.00	3.09	0.49	70180.69		**2b**	3.88	3.95	0.57	63146.58
	6bb	1.74	1.78	0.10	14268.86		**6bc**	1.73	1.78	0.13	14614.77
	7bb	4.59	4.65	0.24	33989.00		**7bc**	4.56	4.65	0.19	21349.20
35%	**1b**	1.54	1.61	1.00	121135.50	**35%**	**1b**	1.53	1.59	1.00	98246.31
	2b	3.01	3.08	0.38	46448.10		**2b**	3.86	3.98	0.49	47716.08
	6bb	1.74	1.79	0.19	23547.56		**6bc**	1.71	1.79	0.28	27105.56
	7bb	4.57	4.66	0.38	45523.18		**7bc**	4.56	4.65	0.34	33814.25
50%	**1b**	1.54	1.61	1.00	111136.01	**50%**	**1b**	1.53	1.58	1.00	85446.77
	2b	3.00	3.08	0.29	31970.70		**2b**	3.86	3.95	0.42	35636.82
	6bb	1.73	1.79	0.35	38843.17		**6bc**	1.72	1.77	0.47	39850.66
	7bb	4.59	4.65	0.58	64343.65		**7bc**	4.56	4.65	0.55	47051.06
70%	**1b**	1.54	1.61	1.00	75038.82	**70%**	**1b**	1.51	1.59	1.00	52667.98
	2b	2.98	3.05	0.13	9681.17		**2b**	3.86	3.95	0.26	13617.33
	6bb	1.71	1.79	0.74	55704.75		**6bc**	1.72	1.78	1.01	53368.72
	7bb	4.57	4.66	0.99	74420.54		**7bc**	4.56	4.64	1.06	55687.82
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**

20%	**1b**	1.49	1.58	1.00	98024.90	**20%**	**1b**	1.48	1.58	1.00	104210.49
	2b	3.85	3.92	0.51	50118.57		**2b**	3.85	3.97	0.55	56811.63
	6bd	1.73	1.79	0.11	10663.00		**6be**	1.74	1.80	0.07	7446.37
	7bd	4.58	4.67	0.20	19887.09		**7be**	4.58	4.67	0.14	15004.82
35%	**1b**	1.48	1.57	1.00	93111.17	**35%**	**1b**	1.51	1.56	1.00	94834.35
	2b	3.84	3.92	0.43	40437.42		**2b**	3.84	3.92	0.49	46277.31
	6bd	1.73	1.79	0.19	18068.37		**6be**	1.74	1.80	0.14	13549.13
	7bd	4.59	4.67	0.34	31705.89		**7be**	4.58	4.69	0.26	24851.03
50%	**1b**	1.48	1.57	1.00	78236.32	**50%**	**1b**	1.50	1.58	1.00	122944.74
	2b	3.84	3.91	0.31	23902.54		**2b**	3.83	3.92	0.40	49039.36
	6bd	1.72	1.79	0.40	31484.69		**6be**	1.73	1.81	0.25	30880.63
	7bd	4.58	4.66	0.61	47858.38		**7be**	4.58	4.68	0.42	52118.21
70%	**1b**	1.49	1.55	1.00	105148.77	**70%**	**1b**	1.49	1.56	1.00	80269.37
	2b	3.82	3.91	0.23	23800.09		**2b**	3.82	3.91	0.31	25028.98
	6bd	1.72	1.79	0.61	64268.56		**6be**	1.73	1.80	0.39	30975.72
	7bd	4.58	4.69	0.84	88263.79		**7be**	4.59	4.68	0.59	47612.57
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.54	1.59	1.82	125306.90	**20%**	**1b**	1.54	1.60	1.00	117846.77
	2b	3.87	3.97	1.00	68531.53		**2b**	3.88	3.96	0.60	70512.60
	6bf	1.39	1.45	0.35	24071.30		**6bf**	1.38	1.41	0.14	16951.64
	7bf	4.33	4.40	0.45	30761.28		**7bf**	4.30	4.38	0.20	23312.49
35%	**1b**	1.54	1.61	2.08	119861.42	**35%**	**1b**	1.53	1.59	1.00	87391.79
	2b	3.87	3.95	0.99	57220.64		**2b**	3.88	3.95	0.47	40755.58
	6bf	1.40	1.44	0.62	35886.83		**6bf**	1.36	1.43	0.33	28509.76
	7bf	4.33	4.41	0.77	44168.45		**7bf**	4.30	4.39	0.38	32912.35
50%	**1b**	1.53	1.59	2.49	94794.18	**50%**	**1b**	1.53	1.58	1.00	84217.83
	2b	3.86	3.94	0.98	37434.16		**2b**	3.86	3.94	0.42	35219.69
	6bf	1.40	1.44	1.27	48402.26		**6bf**	1.36	1.42	0.54	45566.55
	7bf	4.33	4.42	1.47	55855.40		**7bf**	4.30	4.39	0.63	53351.12
70%	**1b**	1.52	1.60	0.85	60441.72	**70%**	**1b**	1.52	1.58	1.00	42708.68
	2b	3.85	3.93	0.22	16038.66		**2b**	3.86	3.93	0.28	12154.66
	6bf	1.40	1.45	0.92	65691.52		**6bf**	1.37	1.43	1.09	46685.37
	7bf	4.33	4.41	0.94	67439.13		**7bf**	4.29	4.38	1.15	49124.61
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.52	1.59	1.00	97814.96	**20%**	**1b**	1.55	1.60	1.00	107415.94
	2b	3.86	3.93	0.56	55121.62		**2b**	3.00	3.07	0.54	57760.06
	6bg	1.42	1.47	0.14	14018.35		**6bh**	0.65	0.71	0.09	9213.50

	7bg	4.34	4.42	0.20	19213.95		**7bh**	3.96	4.10	0.17	18790.70
35%	**1b**	1.51	1.57	1.00	84782.38	**35%**	**1b**	1.52	1.59	1.00	95727.23
	2b	3.84	3.92	0.47	39767.84		**2b**	3.00	3.06	0.49	47218.87
	6bg	1.42	1.49	0.31	25996.72		**6bh**	0.66	0.70	0.13	12861.68
	7bg	4.33	4.42	0.38	32599.85		**7bh**	3.96	4.10	0.28	26611.78
50%	**1b**	1.50	1.56	1.00	73559.48	**50%**	**1b**	1.51	1.59	1.00	79105.74
	2b	3.84	3.89	0.38	27726.69		**2b**	3.00	3.05	0.41	32203.41
	6bg	1.41	1.47	0.55	40825.01		**6bh**	0.65	0.70	0.22	17732.96
	7bg	4.33	4.41	0.64	46762.17		**7bh**	3.94	4.10	0.48	37654.19
70%	**1b**	1.49	1.55	1.00	53117.89	**70%**	**1b**	1.53	1.58	1.00	57011.87
	2b	3.81	3.88	0.24	12648.00		**2b**	2.99	3.04	0.28	15734.27
	6bg	1.42	1.48	1.20	63483.90		**6bh**	0.65	0.70	0.48	27312.75
	7bg	4.34	4.41	1.18	62849.94		**7bh**	3.94	4.11	0.95	54182.15
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.51	1.60	1.00	112159.70	**20%**	**1b**	1.53	1.60	1.00	112744.23
	2b	3.88	3.95	0.55	61351.01		**2b**	3.87	3.97	0.51	57332.86
	6bi	1.32	1.37	0.11	12800.56		**6bi**	1.30	1.36	0.17	18777.73
	7bi	4.27	4.36	0.18	20307.86		**7bi**	4.26	4.36	0.24	27617.59
35%	**1b**	1.53	1.59	1.00	116984.97	**35%**	**1b**	1.52	1.59	1.00	101111.40
	2b	3.87	3.95	0.47	55432.36		**2b**	3.87	3.96	0.45	45925.11
	6bi	1.31	1.36	0.24	27918.50		**6bi**	1.32	1.35	0.24	23957.97
	7bi	4.27	4.36	0.35	40816.87		**7bi**	4.27	4.35	0.35	35867.60
50%	**1b**	1.53	1.59	1.00	93487.61	**50%**	**1b**	1.54	1.60	1.00	75816.25
	2b	3.86	3.94	0.39	36907.94		**2b**	3.86	3.94	0.37	28182.15
	6bi	1.31	1.37	0.39	36328.08		**6bi**	1.32	1.36	0.44	33723.94
	7bi	4.26	4.35	0.53	49823.62		**7bi**	4.28	4.35	0.59	45088.23
70%	**1b**	1.50	1.59	1.00	64237.79	**70%**	**1b**	1.51	1.58	1.00	66000.46
	2b	3.87	3.94	0.27	17203.14		**2b**	3.86	3.93	0.27	17917.86
	6bi	1.31	1.37	0.71	45369.83		**6bi**	1.30	1.35	0.70	46241.10
	7bi	4.27	4.36	0.86	55025.81		**7bi**	4.27	4.34	0.86	56432.91
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.55	1.61	1.00	106688.00	**20%**	**1b**	1.51	1.60	0.99	96088.92
	2b	3.00	3.08	0.48	51617.49		**2b**	2.97	3.06	0.55	52687.55
	6bj	1.34	1.38	0.18	19382.66		**6bj**	1.32	1.38	0.15	14816.99
	7bj	4.30	4.38	0.27	29078.34		**7bj**	4.27	4.35	0.26	24899.37
35%	**1b**	1.52	1.60	1.00	102875.55	**35%**	**1b**	1.51	1.58	1.00	59820.68

	2b	2.97	3.06	0.45	46065.27		**2b**	2.97	3.06	0.43	25820.90
	6bj	1.31	1.39	0.24	24551.89		**6bj**	1.32	1.38	0.31	18654.23
	7bj	4.28	4.36	0.35	36500.84		**7bj**	4.27	4.34	0.49	29236.28
50%	**1b**	1.52	1.58	1.00	74167.99	**50%**	**1b**	1.50	1.58	1.00	79897.65
	2b	2.97	3.05	0.37	27366.50		**2b**	2.94	3.05	0.36	28427.99
	6bj	1.33	1.39	0.37	27692.07		**6bj**	1.31	1.38	0.39	31501.77
	7bj	4.28	4.36	0.52	38223.87		**7bj**	4.26	4.35	0.54	43346.37
70%	**1b**	1.50	1.58	1.00	56728.93	**70%**	**1b**	1.49	1.58	1.02	60012.97
	2b	2.96	3.04	0.21	11985.57		**2b**	2.95	3.04	0.23	13371.13
	6bj	1.33	1.38	0.78	44099.18		**6bj**	1.29	1.39	0.76	45047.33
	7bj	4.26	4.36	0.93	52965.70		**7bj**	4.24	4.36	0.91	53626.95
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.55	1.62	1.00	135326.38	**20%**	**1b**	1.55	1.63	1.00	138250.59
	2b	3.00	3.08	0.53	71105.84		**2b**	3.00	3.08	0.55	75635.56
	6bk	1.72	1.77	0.08	10616.50		**6bk**	1.74	1.76	0.09	11763.88
	7bk	4.62	4.71	0.18	23807.61		**7bk**	4.61	4.71	0.18	24670.95
35%	**1b**	1.55	1.61	1.00	120089.36	**35%**	**1b**	1.55	1.60	1.00	138415.16
	2b	2.99	3.07	0.41	48892.30		**2b**	3.01	3.08	0.42	58627.11
	6bk	1.73	1.77	0.18	21024.36		**6bk**	1.72	1.77	0.17	23953.37
	7bk	4.62	4.70	0.36	42755.32		**7bk**	4.63	4.70	0.35	48312.11
50%	**1b**	1.54	1.61	1.00	97636.68	**50%**	**1b**	1.55	1.61	1.00	99124.50
	2b	2.99	3.06	0.31	30360.92		**2b**	3.00	3.07	0.32	31426.24
	6bk	1.71	1.77	0.29	28761.81		**6bk**	1.72	1.77	0.30	29395.68
	7bk	4.62	4.70	0.53	52049.83		**7bk**	4.62	4.69	0.53	52995.97
70%	**1b**	1.54	1.61	1.00	83256.56	**70%**	**1b**	1.53	1.60	1.00	81993.18
	2b	2.99	3.06	0.21	17459.92		**2b**	3.00	3.06	0.21	16959.44
	6bk	1.71	1.78	0.50	41580.76		**6bk**	1.71	1.79	0.51	41760.42
	7bk	4.62	4.70	0.78	64925.91		**7bk**	4.62	4.70	0.78	64249.08
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.54	1.60	1.00	117931.02	**20%**	**1b**	1.54	1.60	1.00	10740.89
	2b	2.99	3.06	0.52	61534.98		**2b**	3.00	3.06	0.70	7529.05
	6bl	1.39	1.43	0.09	11025.03		**6bm**	1.71	1.78	0.26	2759.70
	7bl	4.30	4.41	0.21	24728.91		**7bm**	4.63	4.68	0.11	1168.97
35%	**1b**	1.53	1.61	1.00	94669.69	**35%**	**1b**	1.55	1.60	1.00	8473.94
	2b	2.99	3.06	0.41	38557.40		**2b**	2.98	3.06	0.76	6451.62
	6bl	1.38	1.43	0.18	17087.21		**6bm**	1.73	1.78	0.57	4816.00
	7bl	4.31	4.38	0.36	34462.34		**7bm**	4.61	4.68	0.25	2140.27

50%	**1b**	1.53	1.59	1.00	82452.99	**50%**	**1b**	1.55	1.60	1.00	6726.54
	2b	2.98	3.07	0.30	24549.27		**2b**	2.98	3.05	0.82	5537.92
	6bl	1.38	1.44	0.34	28134.27		**6bm**	1.73	1.79	0.99	6660.64
	7bl	4.29	4.39	0.61	50296.89		**7bm**	4.62	4.70	0.46	3089.74
70%	**1b**	1.53	1.58	1.00	59550.09	**70%**	**1b**	1.54	1.60	1.00	4226.81
	2b	2.98	3.07	0.17	10069.63		**2b**	2.99	3.06	0.93	3931.87
	6bl	1.38	1.46	0.62	37097.64		**6bm**	1.72	1.78	2.12	8950.62
	7bl	4.29	4.41	0.92	55040.47		**7bm**	4.62	4.72	1.04	4395.45
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.55	1.60	1.00	10188.66	**20%**	**1b**	1.54	1.59	1.00	11281.04
	2b	3.00	3.06	0.69	7016.37		**2b**	3.90	3.96	0.63	7124.81
	6bm	1.73	1.78	0.28	2895.51		**6bn**	1.32	1.38	0.20	2236.04
	7bm	4.63	4.69	0.12	1225.56		**7bn**	4.26	4.32	0.12	1301.20
35%	**1b**	1.55	1.60	1.00	8607.62	**35%**	**1b**	1.55	1.59	1.00	9116.64
	2b	3.00	3.05	0.72	6168.21		**2b**	3.91	3.96	0.64	5843.03
	6bm	1.72	1.79	0.55	4724.82		**6bn**	1.33	1.36	0.40	3633.07
	7bm	4.62	4.69	0.24	2050.79		**7bn**	4.26	4.33	0.25	2240.13
50%	**1b**	1.55	1.59	1.00	6610.57	**50%**	**1b**	1.54	1.58	1.00	7494.57
	2b	3.00	3.06	0.82	5447.23		**2b**	3.89	3.95	0.64	4811.24
	6bm	1.73	1.78	1.05	6954.83		**6bn**	1.33	1.38	0.74	5548.69
	7bm	4.62	4.69	0.49	3212.75		**7bn**	4.25	4.33	0.46	3454.86
70%	**1b**	1.54	1.60	1.00	4040.98	**70%**	**1b**	1.54	1.59	1.00	5491.52
	2b	3.00	3.04	0.95	3857.11		**2b**	3.90	3.98	0.64	3489.67
	6bm	1.74	1.79	2.24	9071.17		**6bn**	1.31	1.36	1.45	7949.66
	7bm	4.63	4.69	1.10	4461.24		**7bn**	4.26	4.32	0.86	4731.88
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.56	1.61	1.00	11492.55	**20%**	**1b**	1.53	1.58	1.00	11258.82
	2b	3.91	3.97	0.64	7313.85		**2b**	3.88	3.94	0.72	8155.52
	6bn	1.32	1.37	0.21	2449.56		**6bo**	1.77	1.82	0.26	2964.07
	7bn	4.27	4.32	0.12	1411.06		**7bo**	4.66	4.74	0.13	1409.21
35%	**1b**	1.54	1.59	1.00	9791.71	**35%**	**1b**	1.51	1.58	1.00	8754.75
	2b	3.90	3.96	0.64	6286.31		**2b**	3.88	3.93	0.76	6678.45
	6bn	1.32	1.37	0.41	3968.92		**6bo**	1.76	1.81	0.61	5310.67
	7bn	4.26	4.32	0.25	2443.56		**7bo**	4.67	4.73	0.30	2621.48
50%	**1b**	1.54	1.59	1.00	8626.84	**50%**	**1b**	1.51	1.57	1.00	6521.28
	2b	3.89	3.96	0.64	5556.59		**2b**	3.87	3.93	0.84	5497.40

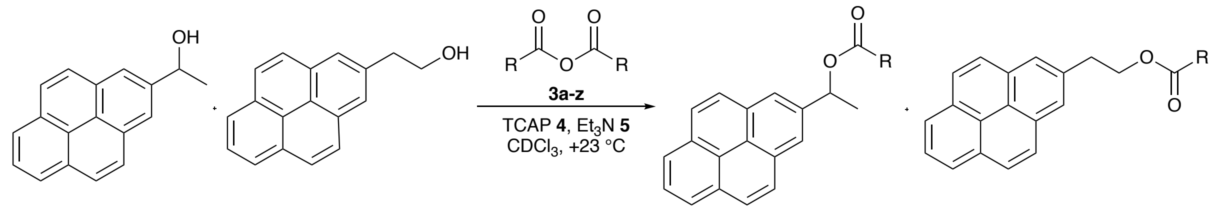
	6bn	1.32	1.39	0.66	5677.34		**6bo**	1.75	1.82	1.17	7629.25
	7bn	4.27	4.32	0.40	3417.92		**7bo**	4.68	4.72	0.59	3860.64
70%	**1b**	1.55	1.59	1.00	5276.23	**70%**	**1b**	1.50	1.56	1.00	3523.82
	2b	3.88	3.94	0.66	3476.25		**2b**	3.85	3.92	1.01	3542.65
	6bn	1.32	1.39	1.59	8379.45		**6bo**	1.75	1.81	2.96	10443.85
	7bn	4.26	4.32	0.98	5181.89		**7bo**	4.66	4.73	1.64	5778.50
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	5.02	5.12	1.00	4403.10	**20%**	**1b**	1.56	1.63	1.00	142359.24
	2b	3.91	3.98	1.81	7969.64		**2b**	3.89	3.98	0.46	66163.39
	6bp	6.31	6.41	0.18	792.70		**6bq**	1.82	1.87	0.12	16901.82
	7bp	4.64	4.71	0.51	2258.35		**7bq**	4.73	4.79	0.19	27190.84
35%	**1b**	5.02	5.10	1.00	3515.27	**35%**	**1b**	1.56	1.61	1.00	121949.29
	2b	3.91	3.97	1.62	5700.52		**2b**	3.90	3.97	0.44	53947.23
	6bp	6.31	6.39	0.43	1501.09		**6bq**	1.82	1.88	0.20	24210.60
	7bp	4.65	4.72	1.15	4033.07		**7bq**	4.73	4.79	0.33	40484.47
50%	**1b**	5.02	5.10	1.00	2816.48	**50%**	**1b**	1.54	1.61	1.01	105817.90
	2b	3.89	3.97	1.50	4227.68		**2b**	3.90	3.96	0.34	35865.01
	6bp	6.30	6.40	0.74	2094.44		**6bq**	1.82	1.87	0.37	38645.67
	7bp	4.65	4.72	1.96	5510.57		**7bq**	4.73	4.78	0.54	56599.30
70%	**1b**	5.02	5.11	1.00	1552.31	**70%**	**1b**	1.55	1.61	1.00	68452.98
	2b	3.89	3.98	1.24	1920.77		**2b**	3.89	3.95	0.18	12076.77
	6bp	6.30	6.40	1.61	2505.99		**6bq**	1.82	1.88	0.84	57478.64
	7bp	4.65	4.71	3.98	6184.98		**7bq**	4.73	4.79	1.00	68528.25
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.56	1.62	1.00	140510.08	**20%**	**1b**	1.51	1.59	1.00	97827.21
	2b	3.90	3.99	0.47	66384.13		**2b**	2.97	3.05	0.75	73484.28
	6bq	1.83	1.87	0.12	16544.75		**6br**	1.77	1.83	0.24	23607.28
	7bq	4.72	4.78	0.20	27712.91		**7br**	4.76	4.83	0.13	12514.69
35%	**1b**	1.56	1.62	1.00	140464.66	**35%**	**1b**	1.50	1.58	1.00	83503.29
	2b	3.90	3.98	0.42	59575.53		**2b**	2.97	3.03	0.75	62859.58
	6bq	1.81	1.88	0.22	31194.83		**6br**	1.78	1.84	0.46	38779.28
	7bq	4.73	4.79	0.36	50902.58		**7br**	4.75	4.83	0.26	21742.96
50%	**1b**	1.56	1.61	1.00	105099.12	**50%**	**1b**	1.50	1.55	1.00	72927.69
	2b	3.90	3.97	0.33	34960.37		**2b**	2.95	3.01	0.82	59850.04
	6bq	1.82	1.87	0.37	39409.88		**6br**	1.76	1.83	0.88	64238.94
	7bq	4.72	4.78	0.55	58245.18		**7br**	4.76	4.82	0.50	36590.78

70%	**1b**	1.55	1.61	1.00	68151.95	**70%**	**1b**	1.49	1.54	1.00	44861.13
	2b	3.88	3.96	0.17	11566.60		**2b**	2.94	3.00	0.92	41178.02
	6bq	1.84	1.87	0.81	55485.47		**6br**	1.77	1.84	1.61	72181.21
	7bq	4.73	4.79	1.02	69408.92		**7br**	4.75	4.83	0.95	42497.52
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.52	1.57	1.00	96297.39	**20%**	**1b**	1.56	1.60	1.00	101976.48
	2b	2.96	3.04	0.77	74453.49		**2b**	3.90	3.96	0.74	75709.53
	6br	1.79	1.83	0.35	33414.40		**6bs**	1.80	1.86	0.40	41027.48
	7br	4.76	4.83	0.19	18396.38		**7bs**	4.77	4.84	0.17	17669.44
35%	**1b**	1.51	1.58	1.00	85024.95	**35%**	**1b**	1.55	1.59	1.00	63618.75
	2b	2.97	3.03	0.77	65280.61		**2b**	3.87	3.94	0.83	52863.98
	6br	1.79	1.83	0.49	41246.29		**6bs**	1.82	1.86	0.95	60391.52
	7br	4.76	4.84	0.27	22980.97		**7bs**	4.76	4.84	0.44	27978.97
50%	**1b**	1.51	1.56	1.00	63585.37	**50%**	**1b**	1.54	1.61	1.00	80968.57
	2b	2.94	3.01	0.83	52572.62		**2b**	3.89	3.96	0.77	62252.03
	6br	1.78	1.83	0.89	56573.25		**6bs**	1.81	1.85	0.54	43933.65
	7br	4.74	4.82	0.51	32435.82		**7bs**	4.77	4.84	0.24	19667.10
70%	**1b**	1.49	1.55	1.00	39173.87	**70%**	**1b**	1.53	1.58	1.00	40572.92
	2b	2.93	3.00	0.95	37025.69		**2b**	3.85	3.93	0.95	38736.71
	6br	1.78	1.82	1.65	64694.79		**6bs**	1.80	1.86	2.00	81202.17
	7br	4.74	4.83	1.00	39212.18		**7bs**	4.77	4.83	0.99	40161.23
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	5.03	5.08	0.41	3351.68	**20%**	**1b**	5.03	5.09	1.00	3450.05
	2b	2.99	3.05	0.97	7963.33		**2b**	3.00	3.07	2.26	7803.34
	6bt	6.45	6.53	0.12	968.47		**6bt**	6.45	6.52	0.26	906.06
	7bt	4.74	4.80	0.15	1187.68		**7bt**	4.74	4.80	0.30	1022.59
35%	**1b**	5.02	5.08	0.38	2198.39	**35%**	**1b**	5.01	5.09	1.00	2804.83
	2b	2.99	3.03	0.96	5467.55		**2b**	2.99	3.05	2.49	6974.80
	6bt	6.43	6.55	0.25	1417.46		**6bt**	6.45	6.53	0.55	1551.63
	7bt	4.74	4.79	0.30	1722.35		**7bt**	4.73	4.80	0.67	1867.30
50%	**1b**	5.00	5.09	1.00	1600.70	**50%**	**1b**	5.01	5.08	1.00	1659.81
	2b	2.97	3.04	2.98	4769.93		**2b**	2.98	3.06	2.79	4633.02
	6bt	6.46	6.53	1.27	2033.03		**6bt**	6.45	6.55	1.03	1710.00
	7bt	4.74	4.82	1.67	2667.85		**7bt**	4.74	4.80	1.30	2156.78
70%	**1b**	5.00	5.07	1.00	958.32	**70%**	**1b**	5.00	5.08	1.00	1233.71
	2b	2.98	3.04	3.75	3597.51		**2b**	2.99	3.04	3.30	4076.38
	6bt	6.46	6.54	2.76	2646.80		**6bt**	6.46	6.53	1.90	2346.71

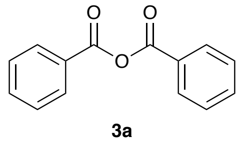
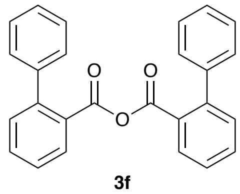
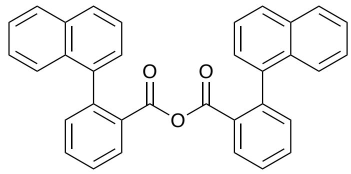
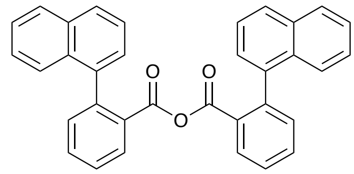
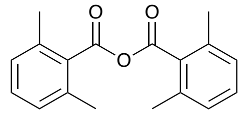
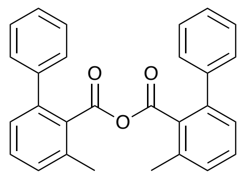
	7bt	4.74	4.79	3.87	3708.37		**7bt**	4.74	4.80	2.56	3153.19
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	5.02	5.10	1.00	2909.71	**20%**	**1b**	1.55	1.58	1.00	10313.89
	2b	3.90	3.95	2.48	7223.07		**2b**	3.90	3.96	0.72	7385.09
	6bu	6.45	6.53	0.33	972.77		**6bv**	1.78	1.85	0.31	3153.96
	7bu	4.74	4.80	0.39	1130.26		**7bv**	4.75	4.79	0.13	1346.30
35%	**1b**	5.01	5.08	1.00	1972.28	**35%**	**1b**	1.53	1.60	1.00	7881.14
	2b	3.89	3.94	2.60	5121.93		**2b**	3.90	3.96	0.77	6094.68
	6bu	6.46	6.54	0.64	1259.85		**6bv**	1.79	1.83	0.68	5367.42
	7bu	4.75	4.79	0.74	1464.61		**7bv**	4.74	4.80	0.32	2496.15
50%	**1b**	5.00	5.08	1.00	1510.27	**50%**	**1b**	1.53	1.59	1.00	6125.16
	2b	3.88	3.93	3.00	4534.07		**2b**	3.89	3.95	0.84	5135.38
	6bu	6.45	6.53	1.08	1632.44		**6bv**	1.78	1.85	1.24	7590.07
	7bu	4.75	4.79	1.40	2119.35		**7bv**	4.73	4.80	0.60	3663.53
70%	**1b**	4.99	5.06	1.00	732.62	**70%**	**1b**	1.53	1.58	1.00	2770.63
	2b	3.87	3.92	3.81	2794.22		**2b**	3.86	3.94	1.08	2997.57
	6bu	6.46	6.53	2.46	1801.00		**6bv**	1.77	1.84	3.13	8684.96
	7bu	4.74	4.79	3.51	2569.91		**7bv**	4.74	4.80	1.65	4558.90
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	1.54	1.61	1.00	11939.03	**20%**	**1b**	1.53	1.61	1.00	12197.78
	2b	3.90	3.97	0.75	8957.90		**2b**	3.90	3.96	0.74	9012.68
	6bw	6.46	6.56	0.09	1081.94		**6bw**	6.48	6.54	0.09	1055.25
	7bw	4.78	4.83	0.11	1304.99		**7bw**	4.77	4.86	0.11	1343.00
35%	**1b**	1.54	1.59	1.00	8713.27	**35%**	**1b**	1.54	1.61	1.00	10512.30
	2b	3.89	3.95	0.78	6761.84		**2b**	3.89	3.96	0.78	8196.71
	6bw	6.46	6.55	0.15	1310.06		**6bw**	6.46	6.55	0.16	1638.96
	7bw	4.78	4.85	0.18	1581.27		**7bw**	4.77	4.84	0.20	2051.34
50%	**1b**	1.54	1.60	1.00	7495.43	**50%**	**1b**	1.53	1.61	1.00	7624.65
	2b	3.89	3.95	0.81	6037.10		**2b**	3.90	3.95	0.78	5928.27
	6bw	1.79	6.56	0.25	1909.16		**6bw**	6.47	6.55	0.24	1797.16
	7bw	4.78	4.84	0.31	2347.32		**7bw**	4.77	4.85	0.30	2296.69
70%	**1b**	1.54	1.58	1.00	5544.48	**70%**	**1b**	1.54	1.59	1.00	5357.79
	2b	3.88	3.94	0.93	5144.55		**2b**	3.89	3.97	0.93	5009.27
	6bw	6.47	6.55	0.49	2703.46		**6bw**	6.47	6.58	0.50	2700.86
	7bw	4.78	4.84	0.63	3519.85		**7bw**	4.78	4.84	0.67	3588.44
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**

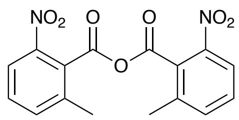
20%	**1b**	1.52	1.59	1.00	118219.38	**20%**	**1b**	1.52	1.59	1.00	134723.06
	2b	3.88	3.96	0.55	65023.42		**2b**	3.87	3.94	0.48	64055.90
	6bx	1.75	1.80	0.09	11146.02		**6by**	1.71	1.76	0.06	7741.89
	7bx	4.60	4.69	0.21	25160.32		**7by**	4.53	4.60	0.18	24224.05
35%	**1b**	1.52	1.61	1.00	110540.10	**35%**	**1b**	1.52	1.59	1.00	131337.12
	2b	3.88	3.96	0.48	53206.82		**2b**	3.87	3.94	0.38	50138.53
	6bx	1.75	1.81	0.15	16114.34		**6by**	1.70	1.77	0.11	14319.10
	7bx	4.61	4.68	0.31	34576.58		**7by**	4.53	4.60	0.31	40755.30
50%	**1b**	1.54	1.59	1.00	93846.41	**50%**	**1b**	1.53	1.60	1.00	116677.84
	2b	3.88	3.96	0.38	35694.47		**2b**	3.86	3.95	0.30	35151.24
	6bx	1.75	1.81	0.26	24767.51		**6by**	1.70	1.77	0.17	20065.01
	7bx	4.61	4.68	0.49	46403.08		**7by**	4.53	4.61	0.44	51168.65
70%	**1b**	1.52	1.60	1.00	77106.88	**70%**	**1b**	1.52	1.59	1.00	110704.53
	2b	3.88	3.96	0.27	20548.30		**2b**	3.87	3.96	0.18	19584.98
	6bx	1.75	1.80	0.41	31697.03		**6by**	1.71	1.77	0.30	32803.16
	7bx	4.60	4.68	0.67	51962.27		**7by**	4.53	4.61	0.64	70570.90
Conv		**integral limits (ppm)**		**integral**	**absolut**						
20%	**1b**	1.52	1.57	2.01	13124.35						
	2b	2.97	3.03	1.00	6525.30						
	6bz	1.77	1.82	0.18	1183.26						
	7bz	4.63	4.69	0.47	3072.24						
35%	**1b**	1.52	1.57	2.67	12141.23						
	2b	3.87	3.93	0.99	4484.97						
	6bz	1.77	1.83	0.51	2330.48						
	7bz	4.63	4.69	1.10	5016.74						
50%	**1b**	1.53	1.57	4.09	10480.92						
	2b	3.87	3.93	1.00	2561.39						
	6bz	1.77	1.83	1.49	3823.99						
	7bz	4.63	4.69	2.73	7014.06						
70%	**1b**	1.52	1.57	10.70	7876.14						
	2b	3.87	3.93	1.00	735.76						
	6bz	1.78	1.83	8.75	6438.67						
	7bz	4.63	4.70	11.96	8802.32						

Table S29. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between 1c and 2c with the benzoic anhydride derivates 3a-z.**

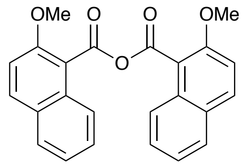


1c **2c** **6c(a-z)** **7c(a-z)**

 **3a** [a]				 **3f** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.714	0.483	3.174	1.155	21.350	0.203	1.590	0.464
31.491	0.419	2.931	1.075	34.215	0.197	1.639	0.494
45.678	0.386	3.049	1.115	48.643	0.174	1.646	0.498
61.985	0.312	3.019	1.105	62.690	0.152	1.688	0.524
		3.043 ± 0.100	1.113 ± 0.033			1.641 ± 0.040	0.495 ± 0.024
 **3h** [a]				 **3h** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
20.753	0.298	1.995	0.691	27.961	0.294	2.041	0.714
33.008	0.267	1.957	0.671	36.446	0.258	1.948	0.667
49.300	0.224	1.920	0.652	51.136	0.222	1.936	0.660
72.569	0.157	1.937	0.661	71.888	0.162	1.955	0.670
		1.952 ± 0.032	0.669 ± 0.016			1.970 ± 0.048	0.678 ± 0.024
 **3m** [b]				 **3n** [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
20.998	-0.305	0.493	-0.708	17.933	-0.208	0.627	-0.467
39.156	-0.277	0.480	-0.733	29.165	-0.188	0.636	-0.453
50.350	-0.243	0.488	-0.718	44.854	-0.168	0.629	-0.463
62.223	-0.200	0.501	-0.691	59.468	-0.140	0.632	-0.459
		0.491 ± 0.009	-0.712 ± 0.018			0.631 ± 0.004	-0.460 ± 0.006

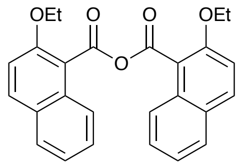


3o [a]

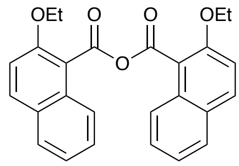


3r [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
18.877	-0.282	0.526	-0.642	17.336	-0.110	0.785	-0.242
30.094	-0.265	0.521	-0.651	28.334	-0.106	0.777	-0.252
49.260	-0.233	0.508	-0.678	41.481	-0.101	0.764	-0.269
65.218	-0.178	0.524	-0.646	57.474	-0.092	0.747	-0.292
		0.520 ± 0.008	-0.654 ± 0.016			0.768 ± 0.017	-0.264 ± 0.022

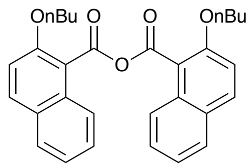


3s [a]

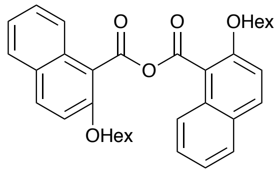


3s [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
16.889	-0.204	0.635	-0.453	15.789	-0.242	0.584	-0.537
28.245	-0.217	0.593	-0.522	27.534	-0.226	0.582	-0.542
41.994	-0.223	0.548	-0.602	37.978	-0.197	0.601	-0.510
56.535	-0.146	0.631	-0.461	54.467	-0.202	0.536	-0.624
		0.602 ± 0.041	-0.509 ± 0.069			0.576 ± 0.028	-0.553 ± 0.049

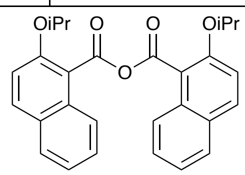


3t [a]

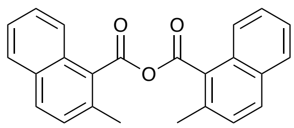


3u [a]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
15.078	-0.290	0.524	-0.647	15.933	-0.286	0.527	-0.640
30.097	-0.283	0.498	-0.698	28.877	-0.283	0.502	-0.690
40.906	-0.266	0.490	-0.714	39.925	-0.270	0.487	-0.719
56.014	-0.219	0.502	-0.690	64.994	-0.176	0.531	-0.634
		0.503 ± 0.018	-0.687 ± 0.035			0.512 ± 0.021	-0.671 ± 0.041



3v [b]



3w [b]

Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
17.945	-0.215	0.617	-0.483	18.698	-0.355	0.440	-0.820
30.058	-0.193	0.625	-0.470	31.586	-0.333	0.433	-0.836
48.717	-0.167	0.619	-0.479	47.193	-0.291	0.434	-0.834
69.207	-0.131	0.603	-0.506	66.237	-0.222	0.436	-0.829
		0.616 ± 0.009	-0.485 ± 0.015			0.436 ± 0.003	-0.830 ± 0.007

[a]Competition experiments were carrying out by method A. [b]Competition experiments were carrying out by method B.

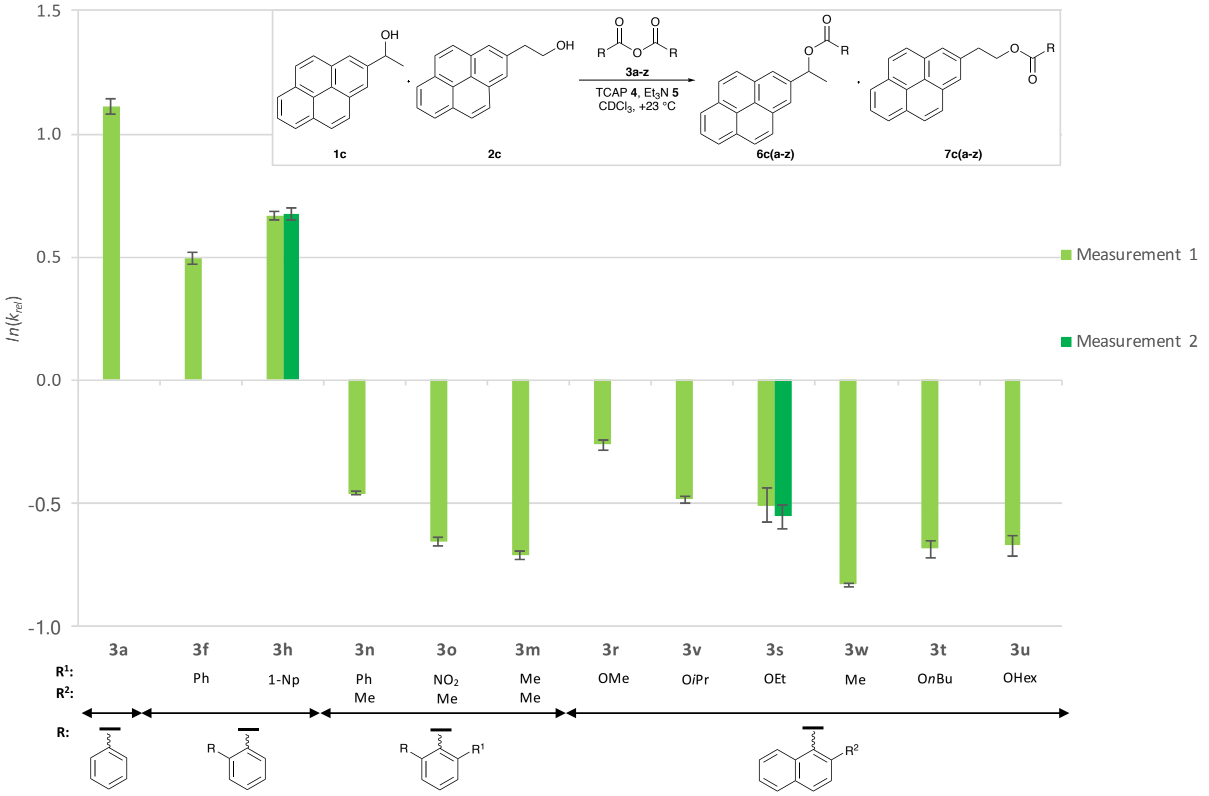


Figure S406. *ln*(k_{rel}) of competition experiment between **1c** and **2c** with the benzoic anhydride derivates **3a-z**.

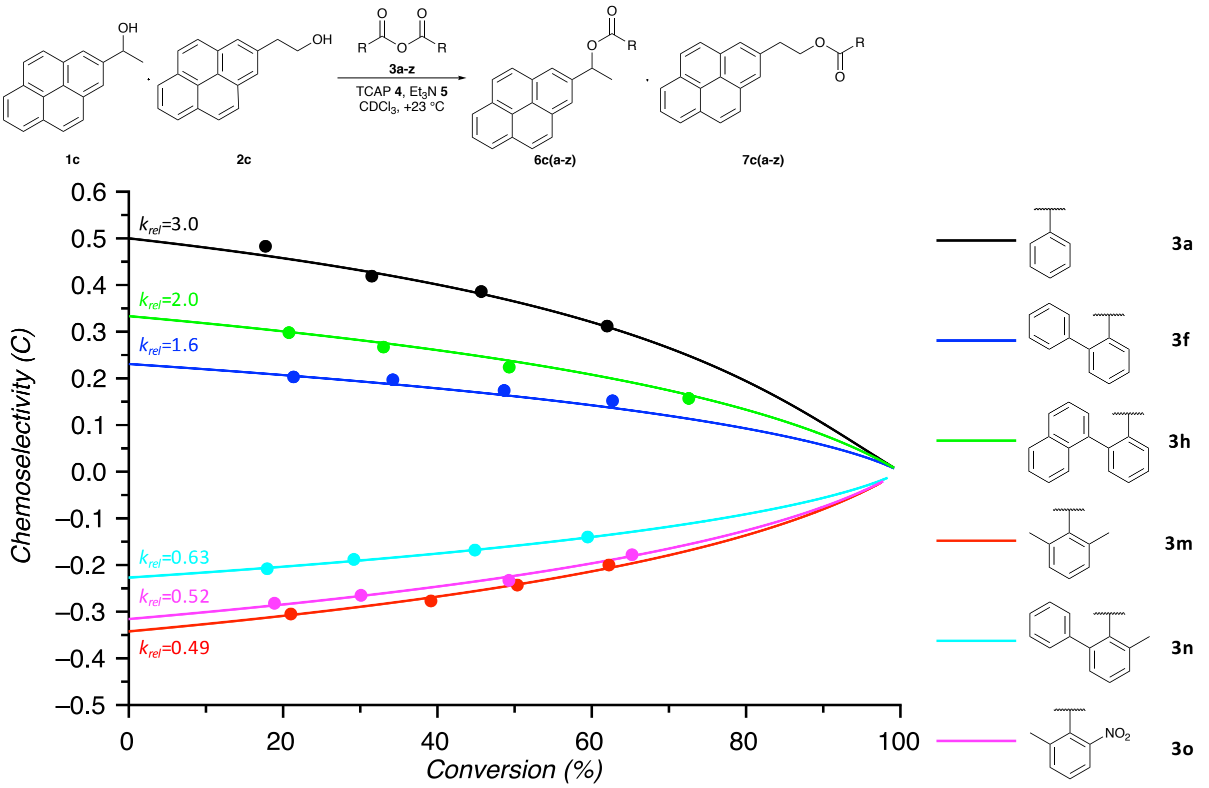


Figure S407. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1c** vs. **2c** with the benzoic anhydride derivates **3a-o**.

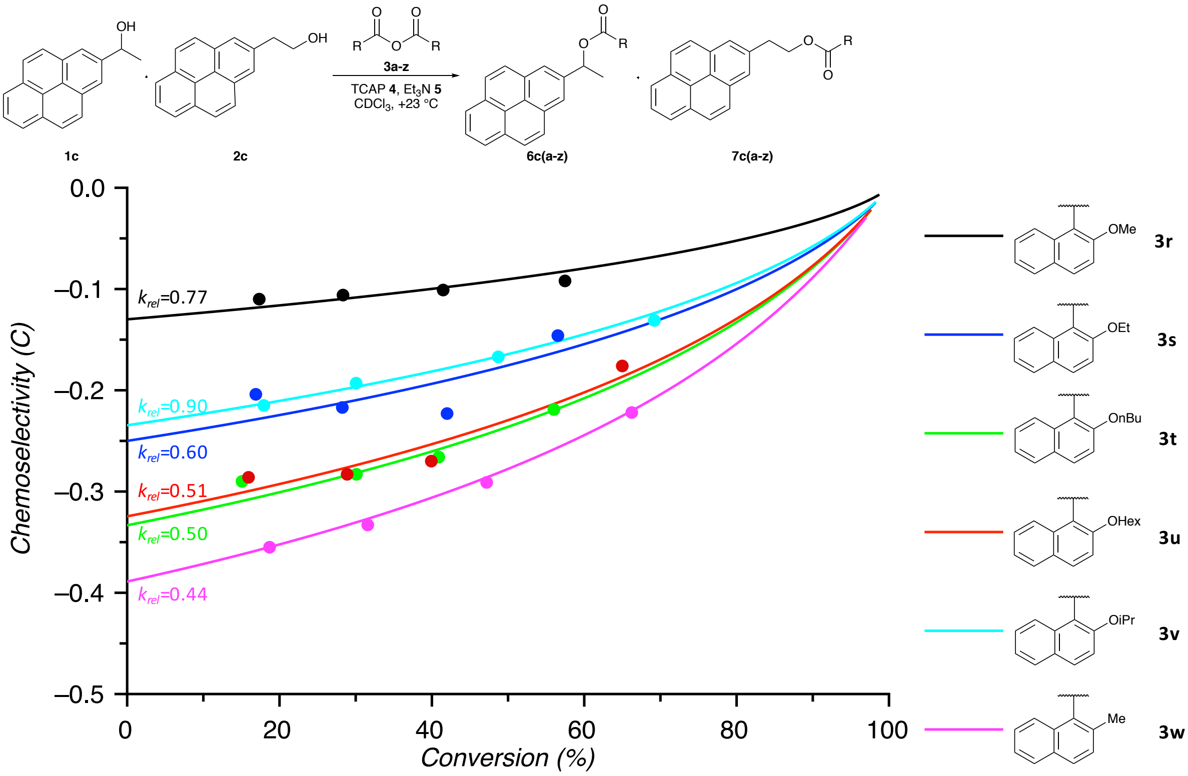


Figure S408. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1c** vs. **2c** with the benzoic anhydride derivates **3r-w**.

Table S30. Integral limits (ppm), relative and absolut integral values for competition experiments of alcohol 1c and 2c using benzoic anhydride derivates 3a-z.

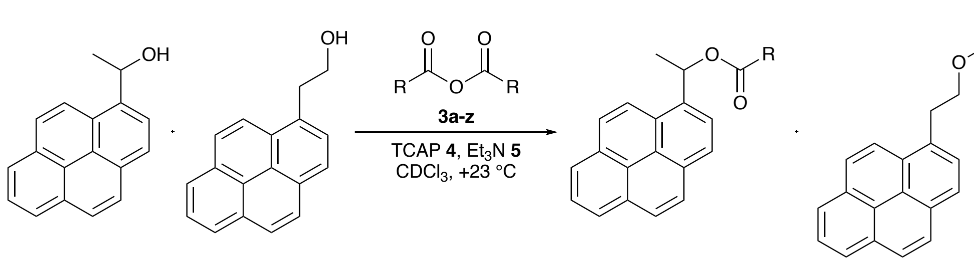
Conv		integral limits (ppm)		integral	absolut	Conv		integral limits (ppm)		integral	absolut
20%	**1c**	1.67	1.72	1.00	11756.87	**20%**	**1c**	1.57	1.64	1.00	102864.46
	2c	4.04	4.08	0.53	6266.52		**2c**	3.16	3.25	0.57	58568.60
	6ca	6.51	6.59	0.03	396.46		**6cf**	1.42	1.49	0.21	21391.45
	7ca	4.72	4.77	0.19	2243.30		**7cf**	4.36	4.43	0.20	20253.81
35%	**1c**	1.68	1.72	1.00	10815.92	**35%**	**1c**	1.57	1.66	1.00	88243.89
	2c	4.02	4.09	0.45	4830.85		**2c**	3.17	3.24	0.52	45515.28
	6ca	6.51	6.62	0.07	809.07		**6cf**	1.43	1.50	0.38	33786.67
	7ca	4.71	4.78	0.36	3916.76		**7cf**	4.37	4.43	0.36	31744.42
50%	**1c**	1.68	1.72	1.00	7594.73	**50%**	**1c**	1.57	1.63	1.00	70474.44
	2c	4.03	4.09	0.34	2605.59		**2c**	3.16	3.22	0.46	32143.66
	6ca	6.52	6.60	0.13	983.98		**6cf**	1.43	1.50	0.68	48088.79
	7ca	4.72	4.79	0.59	4480.37		**7cf**	4.37	4.43	0.61	42885.28
70%	**1c**	1.68	1.73	1.00	6192.53	**70%**	**1c**	1.57	1.63	1.00	48233.93
	2c	4.03	4.10	0.21	1316.81		**2c**	3.14	3.22	0.39	19013.28
	6ca	6.53	6.59	0.25	1540.16		**6cf**	1.43	1.49	1.16	55916.68
	7ca	4.72	4.78	0.94	5798.11		**7cf**	4.36	4.43	1.01	48697.97
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**

20%	**1c**	5.30	5.38	0.33	3356.52	**20%**	**1c**	5.30	5.36	0.33	3162.42
	2c	3.27	3.32	0.59	6059.96		**2c**	3.27	3.31	0.54	5140.35
	6ch	5.96	6.08	0.06	566.86		**6ch**	5.96	6.07	0.08	775.19
	7ch	4.16	4.21	0.11	1105.65		**7ch**	4.14	4.23	0.15	1449.83
35%	**1c**	5.31	5.37	0.33	2934.90	**35%**	**1c**	5.29	5.38	0.33	2420.58
	2c	3.26	3.33	0.55	4853.46		**2c**	3.26	3.33	0.51	3661.06
	6ch	5.97	6.08	0.10	924.72		**6ch**	5.96	6.07	0.12	893.66
	7ch	4.15	4.22	0.19	1717.04		**7ch**	4.15	4.23	0.21	1544.23
50%	**1c**	5.29	5.36	0.33	1942.42	**50%**	**1c**	5.29	5.38	0.34	1960.09
	2c	3.27	3.32	0.44	2611.34		**2c**	3.26	3.33	0.42	2425.81
	6ch	5.98	6.09	0.20	1193.78		**6ch**	5.97	6.09	0.22	1295.08
	7ch	4.14	4.23	0.33	1964.60		**7ch**	4.14	4.23	0.35	2025.47
70%	**1c**	5.27	5.36	0.34	1205.12	**70%**	**1c**	5.28	5.37	0.35	1263.13
	2c	3.26	3.31	0.29	1045.72		**2c**	3.25	3.33	0.29	1044.87
	6ch	5.98	6.07	0.53	1881.84		**6ch**	5.98	6.08	0.53	1915.11
	7ch	4.14	4.23	0.75	2689.61		**7ch**	4.15	4.22	0.73	2650.94
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1c**	5.30	5.39	1.00	1433.00	**20%**	**1c**	5.31	5.38	1.00	1532.88
	2c	4.04	4.10	2.29	3277.67		**2c**	4.04	4.10	2.15	3290.06
	6cm	6.59	6.67	0.38	537.84		**6cn**	6.27	6.36	0.28	422.95
	7cm	4.76	4.83	0.39	557.29		**7cn**	4.40	4.47	0.35	542.98
35%	**1c**	5.30	5.37	1.00	1000.67	**35%**	**1c**	5.30	5.38	1.00	1328.15
	2c	4.04	4.08	2.73	2732.98		**2c**	4.04	4.10	2.27	3011.53
	6cm	6.60	6.67	0.99	988.19		**6cn**	6.27	6.37	0.53	700.88
	7cm	4.78	4.82	1.07	1070.34		**7cn**	4.40	4.46	0.70	931.81
50%	**1c**	5.27	5.36	1.00	756.62	**50%**	**1c**	5.29	5.36	1.00	881.37
	2c	4.03	4.09	3.17	2401.30		**2c**	4.03	4.09	2.67	2355.36
	6cm	6.59	6.67	1.65	1250.91		**6cn**	6.29	6.36	1.10	972.43
	7cm	4.77	4.82	1.94	1467.89		**7cn**	4.41	4.46	1.59	1404.65
70%	**1c**	5.28	5.35	1.00	478.82	**70%**	**1c**	5.28	5.35	1.00	633.02
	2c	4.01	4.07	3.66	1754.25		**2c**	4.02	4.08	2.96	1873.40
	6cm	6.60	6.68	2.87	1375.97		**6cn**	6.29	6.36	2.09	1325.95
	7cm	4.76	4.82	3.58	1714.86		**7cn**	4.41	4.46	3.09	1954.32
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1c**	5.30	5.38	1.00	432.54	**20%**	**1c**	1.68	1.74	1.00	10104.16
	2c	4.04	4.09	3.72	1609.93		**2c**	4.04	4.10	0.68	6850.35
	6co	6.61	6.66	2.92	1263.63		**6cr**	6.73	6.81	0.08	800.64

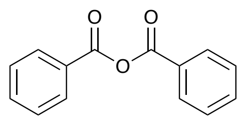
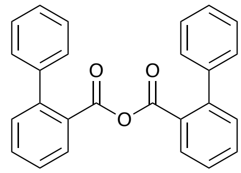
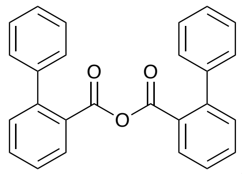
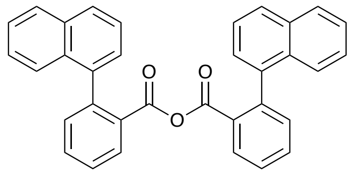
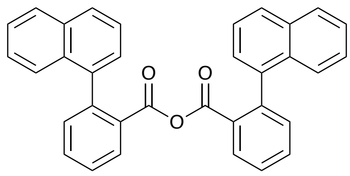
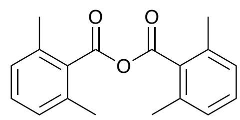
	7co	4.77	4.82	3.75	1621.37		**7cr**	4.90	4.97	0.12	1248.11
35%	**1c**	1.60	1.67	1.00	55877.83	**35%**	**1c**	1.68	1.74	1.00	8343.90
	2c	3.95	4.03	0.86	48056.27		**2c**	4.03	4.08	0.71	5898.19
	6co	6.56	6.67	0.21	11513.34		**6cr**	6.72	6.81	0.15	1266.71
	7co	4.73	4.82	0.25	13697.74		**7cr**	4.90	4.98	0.24	1997.70
50%	**1c**	1.60	1.67	1.00	35736.66	**50%**	**1c**	1.68	1.74	1.00	6706.82
	2c	3.95	4.03	1.06	37923.83		**2c**	4.03	4.07	0.76	5097.69
	6co	6.56	6.67	0.52	18448.06		**6cr**	6.73	6.80	0.28	1878.47
	7co	4.74	4.81	0.65	23050.18		**7cr**	4.90	4.96	0.45	3026.05
70%	**1c**	1.60	1.68	1.00	20021.54	**70%**	**1c**	1.67	1.72	1.00	3698.63
	2c	3.94	4.03	1.34	26899.65		**2c**	4.00	4.07	0.86	3191.14
	6co	6.56	6.66	1.11	22199.68		**6cr**	6.73	6.82	0.56	2080.45
	7co	4.74	4.82	1.55	31067.85		**7cr**	4.90	4.96	0.94	3484.53
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1c**	5.30	5.38	0.33	3253.81	**20%**	**1c**	5.30	5.36	0.33	3218.21
	2c	3.27	3.33	0.70	6989.40		**2c**	4.02	4.07	0.74	7294.10
	6cs	6.75	6.82	0.08	829.13		**6cs**	1.92	1.97	0.26	2562.97
	7cs	4.88	4.95	0.11	1084.50		**7cs**	4.87	4.92	0.10	996.87
35%	**1c**	5.29	5.37	0.32	2661.81	**35%**	**1c**	5.28	5.35	0.33	2705.16
	2c	3.26	3.32	0.77	6312.34		**2c**	3.25	3.30	0.80	6556.84
	6cs	6.75	6.80	0.17	1359.95		**6cs**	1.93	1.96	0.49	4023.84
	7cs	4.88	4.96	0.23	1860.46		**7cs**	4.87	4.94	0.22	1780.50
50%	**1c**	5.27	5.38	0.31	1866.88	**50%**	**1c**	5.28	5.34	0.33	1705.18
	2c	3.26	3.31	0.90	5344.38		**2c**	4.00	4.05	0.95	4957.51
	6cs	6.74	6.82	0.32	1881.79		**6cs**	6.73	6.81	0.28	1453.93
	7cs	4.88	4.94	0.47	2808.69		**7cs**	4.87	4.94	0.43	2216.09
70%	**1c**	5.26	5.36	0.34	1178.26	**70%**	**1c**	5.25	5.32	0.33	1149.71
	2c	3.24	3.30	0.97	3412.42		**2c**	3.99	4.04	1.22	4176.73
	6cs	6.75	6.83	0.62	2176.82		**6cs**	6.71	6.81	0.65	2242.62
	7cs	4.88	4.95	0.90	3149.96		**7cs**	4.88	4.93	0.95	3261.61
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1c**	5.31	5.38	1.00	4071.49	**20%**	**1c**	5.31	5.37	1.00	3253.00
	2c	3.27	3.33	2.26	9206.27		**2c**	3.26	3.33	2.22	7221.62
	6ct	6.75	6.81	0.24	986.27		**6cu**	6.73	6.82	0.26	837.47
	7ct	4.87	4.95	0.27	1107.72		**7cu**	4.86	4.94	0.28	926.77
35%	**1c**	5.30	5.37	1.00	2494.91	**35%**	**1c**	5.30	5.36	0.33	2115.72

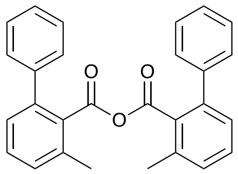
	2c	3.26	3.33	2.53	6316.33		**2c**	3.26	3.32	0.81	5195.02
	6ct	6.74	6.81	0.63	1567.06		**6cu**	6.74	6.81	0.19	1237.84
	7ct	4.88	4.93	0.69	1733.90		**7cu**	4.88	4.93	0.21	1351.61
50%	**1c**	5.29	5.36	1.00	1999.42	**50%**	**1c**	5.27	5.35	0.32	1575.97
	2c	3.25	3.32	2.89	5781.44		**2c**	3.26	3.31	0.99	4851.01
	6ct	6.74	6.81	1.07	2145.30		**6cu**	6.74	6.82	0.34	1648.97
	7ct	4.87	4.93	1.24	2479.57		**7cu**	4.88	4.93	0.41	2020.80
70%	**1c**	5.29	5.34	1.00	1023.40	**70%**	**1c**	5.26	5.35	1.00	580.51
	2c	3.25	3.30	3.55	3635.14		**2c**	3.26	3.29	3.72	2160.24
	6ct	6.74	6.81	2.15	2202.46		**6cu**	6.73	6.81	3.19	1849.25
	7ct	4.87	4.94	2.77	2830.73		**7cu**	4.87	4.93	4.25	2467.91
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1c**	5.31	5.39	0.68	3826.23	**20%**	**1c**	5.30	5.38	1.00	1497.90
	2c	4.04	4.10	1.42	7937.58		**2c**	4.03	4.10	2.31	3460.40
	6cv	6.74	6.81	0.19	1058.96		**6cw**	6.72	6.83	0.34	505.88
	7cv	4.87	4.94	0.23	1291.51		**7cw**	4.91	4.97	0.32	473.08
35%	**1c**	5.29	5.38	0.55	2250.12	**35%**	**1c**	5.29	5.36	1.00	1177.91
	2c	4.03	4.09	1.31	5336.60		**2c**	4.02	4.08	2.61	3068.49
	6cv	6.75	6.82	0.31	1259.11		**6cw**	6.74	6.83	0.72	846.04
	7cv	4.87	4.94	0.42	1709.13		**7cw**	4.91	4.99	0.69	812.28
50%	**1c**	5.29	5.37	0.50	1618.55	**50%**	**1c**	5.26	5.35	1.00	834.64
	2c	4.03	4.07	1.29	4211.87		**2c**	4.02	4.09	3.18	2657.29
	6cv	6.74	6.81	0.65	2110.86		**6cw**	6.74	6.82	1.53	1272.86
	7cv	4.88	4.93	0.87	2854.46		**7cw**	4.89	4.99	1.58	1320.88
70%	**1c**	5.29	5.34	0.31	807.10	**70%**	**1c**	5.27	5.33	1.00	387.29
	2c	4.03	4.06	1.05	2764.76		**2c**	4.01	4.06	4.76	1845.09
	6cv	6.75	6.81	1.08	2854.54		**6cw**	6.75	6.82	4.13	1600.66
	7cv	4.89	4.93	1.57	4132.46		**7cw**	4.92	4.97	5.00	1937.95

Table S31. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between 1d and 2d with the benzoic anhydride derivates 3a-z.**



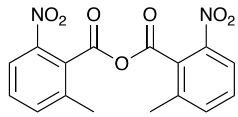
1d **2d** **6d(a-z)** **7d(a-z)**

 **3a** [a]				 **3f** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.064	0.468	3.069	1.121	19.818	0.416	2.679	0.986
34.010	0.399	2.826	1.039	31.226	0.417	2.908	1.067
46.989	0.365	2.897	1.064	47.469	0.363	2.895	1.063
67.907	0.264	2.821	1.037	65.222	0.286	2.909	1.068
		2.903 ± 0.116	1.065 ± 0.039			2.848 ± 0.112	1.046 ± 0.040
 **3f** [a]				 **3h** [a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
7.242	0.343	2.100	0.742	24.366	0.549	4.065	1.402
32.996	0.388	2.716	0.999	34.690	0.428	3.097	1.130
56.133	0.332	2.930	1.075	49.087	0.363	2.949	1.081
78.670	0.211	3.140	1.144	70.556	0.253	2.882	1.059
		2.721 ± 0.449	0.990 ± 0.176			3.248 ± 0.552	1.168 ± 0.159
 **3h** [a]				 **3m** [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
28.496	0.470	3.318	1.199	20.908	-0.324	0.471	-0.754
34.266	0.418	2.993	1.096	34.746	-0.275	0.496	-0.701
47.848	0.362	2.891	1.062	48.333	-0.232	0.512	-0.670
69.707	0.258	2.878	1.057	64.942	-0.195	0.495	-0.704
		3.020 ± 0.205	1.104 ± 0.066			0.493 ± 0.017	-0.707 ± 0.043



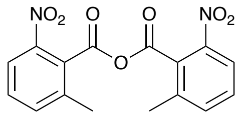
3n [b]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
16.904	-0.025	0.947	-0.055
25.895	0.009	1.021	0.021
42.796	-0.001	0.997	-0.003
58.368	-0.028	0.914	-0.090
		0.970 ± 0.048	-0.032 ± 0.050



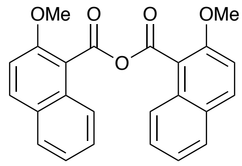
3o [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
21.167	-0.231	0.589	-0.530
38.493	-0.185	0.617	-0.482
50.943	-0.159	0.627	-0.467
73.652	-0.108	0.631	-0.461
		0.616 ± 0.019	-0.485 ± 0.031



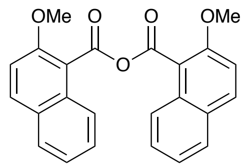
3o [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
19.744	-0.213	0.617	-0.483
33.775	-0.181	0.637	-0.451
50.721	-0.153	0.639	-0.447
66.828	-0.117	0.650	-0.431
		0.636 ± 0.014	-0.453 ± 0.021



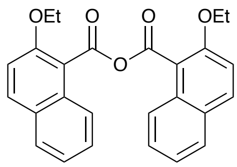
3r [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
18.527	-0.185	0.660	-0.416
30.336	-0.159	0.680	-0.386
46.938	-0.135	0.685	-0.378
/	/	/	/
		0.675 ± 0.013	-0.393 ± 0.020



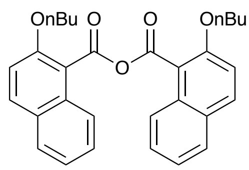
3r [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
25.608	-0.155	0.695	-0.364
32.899	-0.151	0.688	-0.374
48.263	-0.128	0.695	-0.365
61.162	-0.108	0.696	-0.363
		0.693 ± 0.003	-0.366 ± 0.005



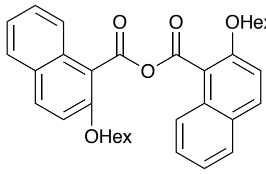
3s [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
17.449	-0.373	0.423	-0.860
24.990	-0.306	0.482	-0.729
45.871	-0.256	0.486	-0.721
65.663	-0.193	0.493	-0.707
		0.471 ± 0.032	-0.754 ± 0.071



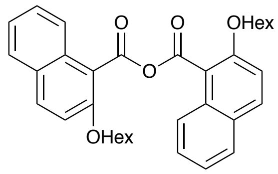
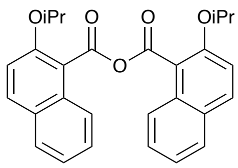
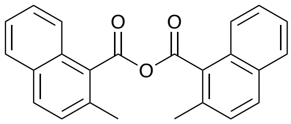
3t [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
16.534	-0.402	0.395	-0.929
28.117	-0.352	0.420	-0.868
45.059	-0.307	0.421	-0.866
54.431	-0.280	0.417	-0.874
		0.413 ± 0.012	-0.884 ± 0.030



3u [a]

Conv.	Chem.	k_{rel}	$ln(k_{rel})$
18.834	-0.385	0.408	-0.897
30.891	-0.347	0.418	-0.872
42.056	-0.318	0.418	-0.871
56.572	-0.262	0.432	-0.838
		0.419 ± 0.010	-0.870 ± 0.015

 **3u** [a]				 **3v** [b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
25.902	-0.359	0.419	-0.871	19.218	-0.306	0.495	-0.702
32.081	-0.344	0.419	-0.869	31.273	-0.279	0.500	-0.694
45.851	-0.305	0.421	-0.865	43.831	-0.241	0.515	-0.663
62.440	-0.255	0.409	-0.895	67.123	-0.175	0.519	-0.657
		0.417 ± 0.006	-0.875 ± 0.013			0.507 ± 0.011	-0.679 ± 0.022
 **3w** [b]							
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$				
18.189	-0.380	0.414	-0.881				
28.084	-0.342	0.432	-0.840				
42.387	-0.296	0.445	-0.810				
58.476	-0.239	0.456	-0.785				
		0.437 ± 0.018	-0.829 ± 0.036				

[a]Competition experiments were carrying out by method A. [b]Competition experiments were carrying out by method B.

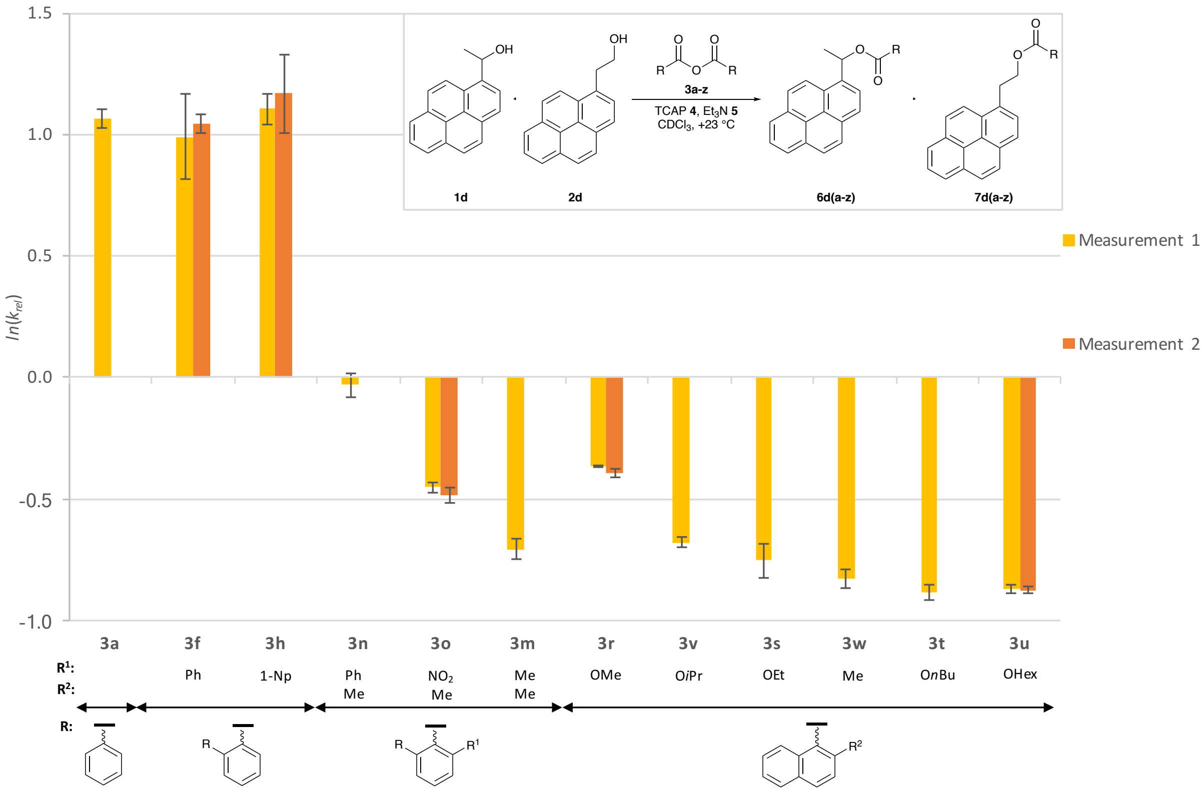


Figure S409. $ln(k_{rel})$ of competition experiment between **1d** and **2d** with the benzoic anhydride derivates **3a-z**.

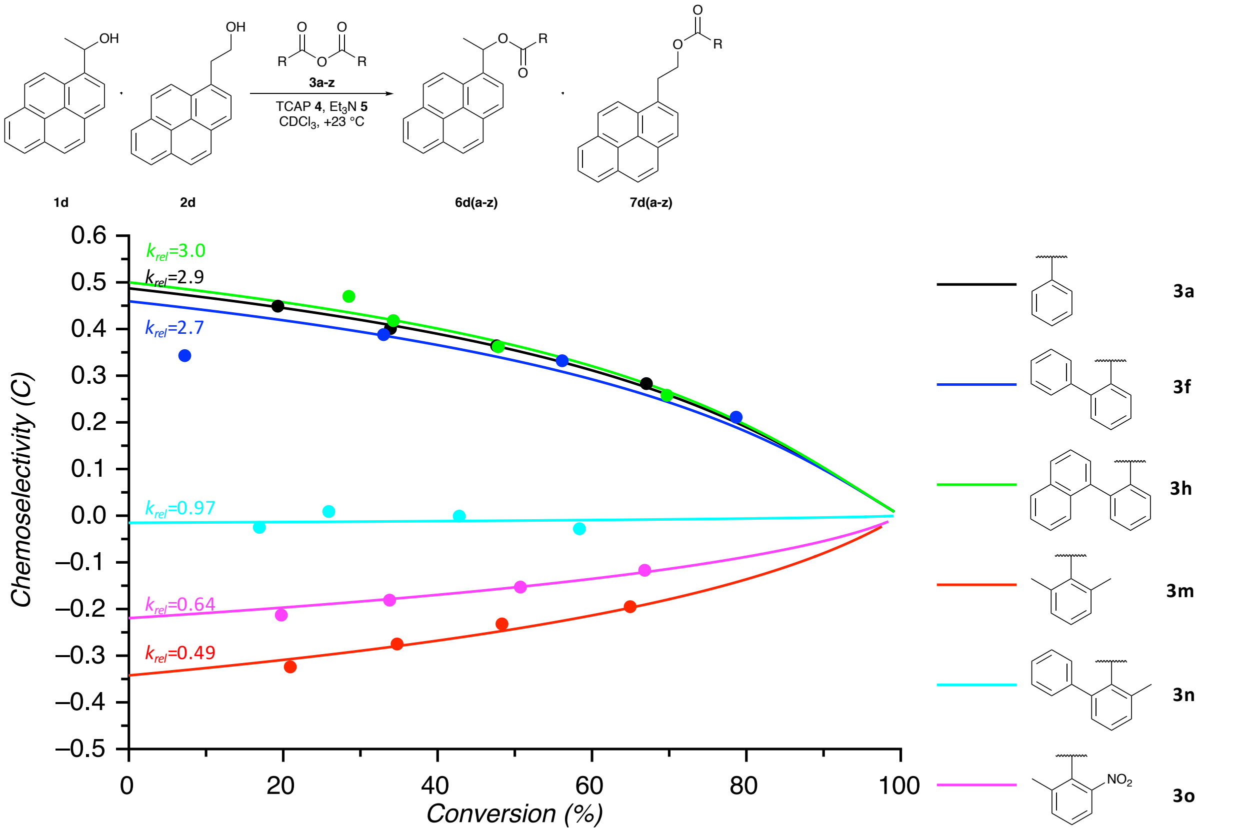


Figure S410. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1d** vs. **2d** with the benzoic anhydride derivates **3a-o**.

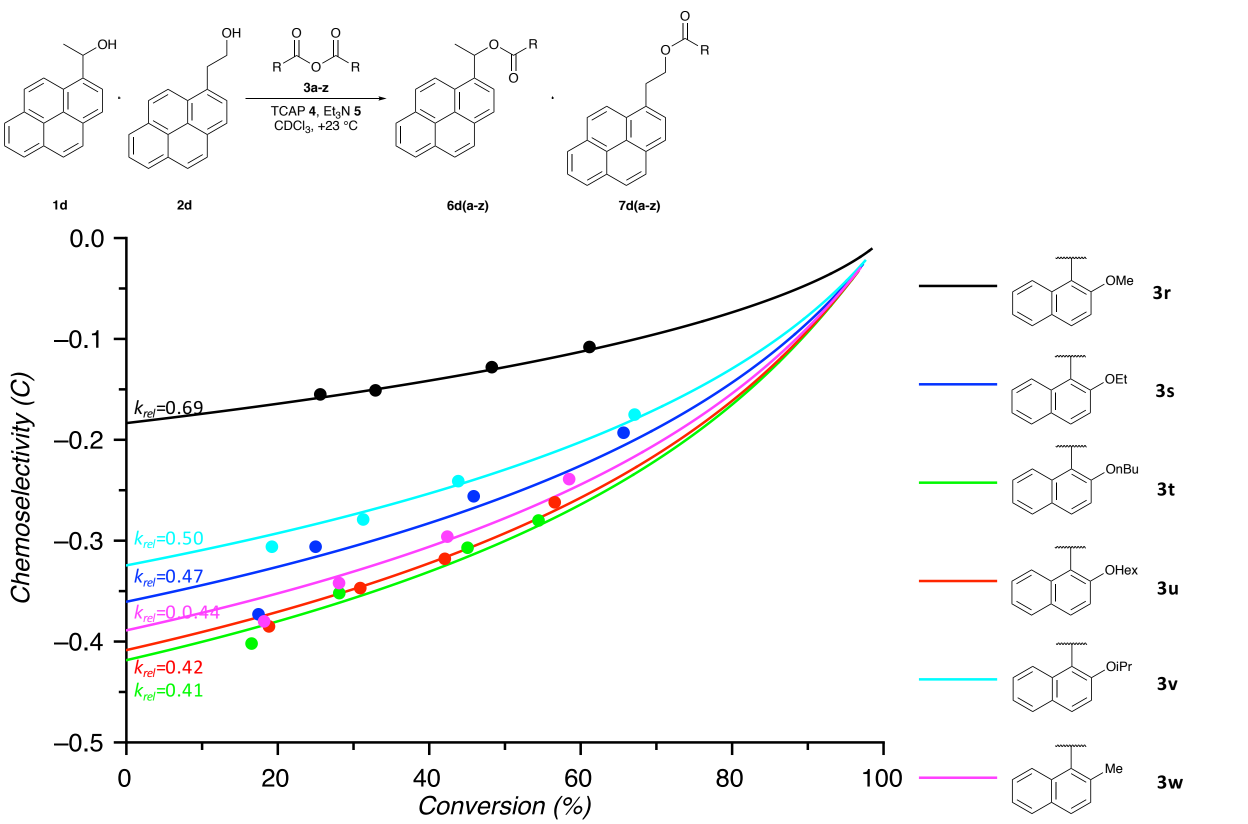


Figure S411. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1d** vs. **2d** with the benzoic anhydride derivates **3r-w**.

Table S32. **Integral limits (ppm), relative and absolut integral values for competition experiments of alcohol 1d and 2d using benzoic anhydride derivates 3a-z.**

Conv		integral limits (ppm)		integral	absolut	Conv		integral limits (ppm)		integral	absolut
20%	**1d**	5.87	5.93	0.62	816.12	**20%**	**1d**	1.67	1.73	1.00	106684.96
	2d	3.53	3.59	1.00	1309.26		**2d**	3.96	4.05	0.57	60877.83
	6da	1.93	1.96	0.21	276.12		**6df**	1.49	1.54	0.05	5426.21
	7da	4.70	4.75	0.39	508.77		**7df**	4.35	4.42	0.06	6687.69
35%	**1d**	5.88	5.93	0.76	2519.63	**35%**	**1d**	1.66	1.72	1.00	83780.09
	2d	3.54	3.60	1.00	3304.52		**2d**	3.97	4.05	0.40	33369.15
	6da	1.93	1.97	0.59	1941.05		**6df**	1.49	1.56	0.26	21803.13
	7da	4.71	4.76	0.91	3006.30		**7df**	4.34	4.43	0.35	29402.04
50%	**1d**	5.87	5.94	1.00	3052.18	**50%**	**1d**	1.64	1.70	1.00	56768.93
	2d	3.53	3.60	1.00	3046.87		**2d**	3.96	4.04	0.23	13145.62
	6da	1.93	1.97	1.28	3891.08		**6df**	1.50	1.57	0.62	35048.23
	7da	4.71	4.77	1.81	5517.48		**7df**	4.34	4.42	0.74	41884.34
70%	**1d**	5.89	5.94	1.77	965.62	**70%**	**1d**	1.63	1.72	1.00	34167.09
	2d	3.54	3.59	1.00	544.06		**2d**	3.94	4.04	0.06	1947.18
	6da	1.93	1.97	5.32	2892.18		**6df**	1.50	1.57	1.70	57927.69
	7da	4.70	4.76	6.08	3309.46		**7df**	4.32	4.46	1.56	53371.91
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	1.73	1.77	1.00	11859.14	**20%**	**1d**	1.72	1.78	1.00	10741.69
	2d	4.03	4.09	0.53	6281.97		**2d**	3.57	3.64	0.45	4867.45
	6df	1.55	1.61	0.13	1559.77		**6dh**	6.63	6.78	0.06	637.72
	7df	4.42	4.47	0.21	2466.94		**7dh**	2.71	2.85	0.33	3518.27
35%	**1d**	1.70	1.78	1.00	11384.22	**35%**	**1d**	1.72	1.78	1.00	10226.45
	2d	4.04	4.09	0.44	4999.95		**2d**	3.57	3.64	0.41	4160.29
	6df	1.56	1.60	0.22	2553.27		**6dh**	6.64	6.77	0.08	858.61
	7df	4.42	4.48	0.35	4013.90		**7dh**	2.70	2.85	0.39	4005.44
50%	**1d**	1.72	1.77	1.00	9326.87	**50%**	**1d**	1.71	1.78	1.00	8689.41
	2d	4.04	4.08	0.33	3078.65		**2d**	3.57	3.65	0.31	2680.72
	6df	1.55	1.61	0.44	4057.53		**6dh**	6.65	6.77	0.15	1295.74
	7df	4.41	4.47	0.61	5695.73		**7dh**	2.69	2.85	0.60	5182.70
70%	**1d**	1.71	1.76	1.00	5864.49	**70%**	**1d**	1.72	1.77	1.00	4787.60
	2d	4.02	4.08	0.20	1162.08		**2d**	3.57	3.64	0.15	729.99
	6df	1.56	1.61	0.87	5128.27		**6dh**	6.65	6.77	0.36	1736.74
	7df	4.41	4.48	1.04	6092.68		**7dh**	2.70	2.84	1.16	5550.70
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**

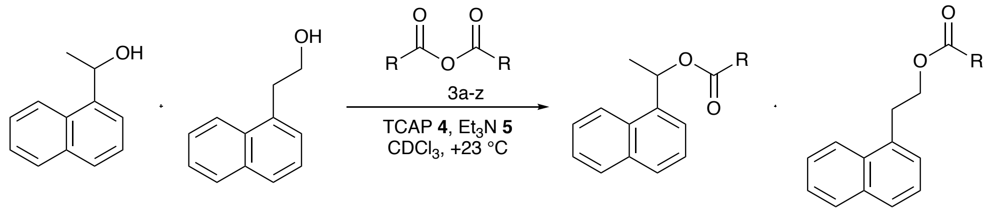
20%	**1d**	1.72	1.77	1.00	11592.42	**20%**	**1d**	5.94	6.02	1.00	3410.60
	2d	3.57	3.64	0.51	5962.85		**2d**	4.05	4.10	2.23	7610.04
	6dh	6.63	6.77	0.04	455.71		**6dm**	7.27	7.32	0.38	1287.86
	7dh	2.69	2.85	0.30	3459.25		**7dm**	4.74	4.80	0.36	1239.26
35%	**1d**	1.72	1.78	1.00	10420.03	**35%**	**1d**	5.93	6.02	1.00	2729.15
	2d	3.57	3.63	0.42	4347.86		**2d**	4.05	4.10	2.51	6855.66
	6dh	6.64	6.78	0.08	844.50		**6dm**	7.27	7.34	0.78	2137.51
	7dh	2.71	2.83	0.41	4256.29		**7dm**	4.74	4.80	0.84	2281.70
50%	**1d**	1.72	1.77	1.00	7281.39	**50%**	**1d**	5.93	6.00	1.00	1534.80
	2d	3.57	3.63	0.32	2312.57		**2d**	4.04	4.11	2.91	4459.66
	6dh	6.64	6.78	0.15	1101.37		**6dm**	7.27	7.32	1.45	2221.63
	7dh	2.70	2.84	0.64	4688.29		**7dm**	4.75	4.80	1.69	2600.09
70%	**1d**	1.72	1.77	1.00	5006.19	**70%**	**1d**	5.91	5.98	1.00	937.25
	2d	3.57	3.63	0.15	756.37		**2d**	4.03	4.10	3.71	3473.81
	6dh	6.67	6.77	0.37	1838.63		**6dm**	7.26	7.33	3.30	3093.35
	7dh	2.70	2.86	1.20	5984.19		**7dm**	4.74	4.80	3.97	3720.54
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	5.94	6.01	1.00	1812.83	**20%**	**1d**	1.74	1.79	1.00	13060.86
	2d	4.05	4.11	1.99	3608.92		**2d**	4.06	4.13	0.71	9327.78
	6dn	6.89	6.97	0.21	379.75		**6do**	7.29	7.35	0.10	1363.91
	7dn	4.36	4.43	0.39	712.18		**7do**	4.77	4.84	0.13	1709.01
35%	**1d**	5.94	6.01	1.00	1551.87	**35%**	**1d**	1.73	1.78	1.00	10331.23
	2d	4.05	4.12	2.04	3163.03		**2d**	4.05	4.12	0.78	8048.83
	6dn	6.89	6.99	0.35	535.76		**6do**	7.29	7.35	0.22	2274.30
	7dn	4.37	4.43	0.72	1118.34		**7do**	4.79	4.86	0.30	3069.03
50%	**1d**	5.91	5.99	1.00	1184.64	**20%**	**1d**	1.74	1.78	1.00	6858.67
	2d	4.04	4.10	2.04	2411.08		**2d**	4.04	4.11	0.90	6173.11
	6dn	6.90	6.99	0.75	888.15		**6do**	7.29	7.35	0.47	3208.55
	7dn	4.36	4.42	1.52	1799.97		**7do**	4.77	4.86	0.68	4642.84
70%	**1d**	5.92	5.99	1.00	726.44	**20%**	**1d**	1.73	1.78	1.00	3509.21
	2d	4.02	4.09	2.04	1479.62		**2d**	4.04	4.12	1.04	3648.32
	6dn	6.90	6.99	1.50	1087.51		**6do**	7.29	7.36	0.97	3418.85
	7dn	4.35	4.44	2.67	1936.28		**7do**	4.78	4.84	1.49	5225.08
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	1.73	1.79	1.00	9777.91	**20%**	**1d**	1.74	1.78	1.00	8741.61
	2d	4.04	4.10	0.58	5719.32		**2d**	3.58	3.64	0.73	6419.57
	6do	7.29	7.36	0.11	1106.48		**6dr**	2.00	2.04	0.43	3721.99

	7do	4.79	4.84	0.11	1084.57		**7dr**	4.88	4.94	0.20	1734.57
35%	**1d**	1.73	1.77	1.00	7173.09	**35%**	**1d**	1.73	1.77	1.00	6257.78
	2d	4.04	4.10	0.66	4713.31		**2d**	3.57	3.64	0.79	4925.14
	6do	7.29	7.35	0.27	1931.75		**6dr**	2.00	2.04	0.62	3851.15
	7do	4.78	4.84	0.29	2112.65		**7dr**	4.87	4.94	0.30	1892.74
50%	**1d**	1.72	1.77	1.00	5330.08	**50%**	**1d**	1.73	1.76	1.00	4595.78
	2d	4.04	4.09	0.71	3764.40		**2d**	3.58	3.62	0.82	3786.65
	6do	7.30	7.35	0.46	2450.45		**6dr**	2.01	2.04	1.19	5478.61
	7do	4.79	4.85	0.53	2814.77		**7dr**	4.88	4.93	0.60	2738.12
70%	**1d**	1.72	1.78	1.00	2509.42	**70%**	**1d**	1.72	1.76	1.00	3347.10
	2d	4.02	4.10	0.90	2268.99		**2d**	3.56	3.62	0.94	3144.84
	6do	7.28	7.35	1.38	3474.35		**6dr**	2.00	2.04	2.14	7171.01
	7do	4.78	4.86	1.75	4399.53		**7dr**	4.88	4.94	1.10	3685.85
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	1.75	1.81	1.00	48612.03	**20%**	**1d**	1.76	1.81	1.00	79110.15
	2d	3.59	3.66	0.85	41187.16		**2d**	3.59	3.68	0.72	56813.98
	6dr	2.02	2.08	1.15	55864.12		**6ds**	2.00	2.07	0.30	23971.38
	7dr	4.89	4.97	0.57	27859.06		**7ds**	3.89	3.96	0.09	7176.53
35%	**1d**	1.76	1.82	1.00	83923.66	**35%**	**1d**	1.74	1.82	1.00	70901.54
	2d	3.60	3.67	0.71	59819.42		**2d**	3.60	3.67	0.77	54276.03
	6dr	2.02	2.06	0.28	23623.38		**6ds**	2.02	2.06	0.48	33739.55
	7dr	4.89	4.96	0.13	10577.60		**7ds**	3.88	3.96	0.16	11336.41
50%	**1d**	1.74	1.82	1.00	69177.61	**50%**	**1d**	1.75	1.79	1.00	44515.94
	2d	3.57	3.67	0.76	52454.35		**2d**	3.58	3.65	0.95	42183.05
	6dr	2.02	2.07	0.54	37527.81		**6ds**	2.01	2.05	1.31	58205.52
	7dr	4.88	4.98	0.26	17905.64		**7ds**	3.89	3.97	0.50	22092.53
70%	**1d**	/	/	/	/	**70%**	**1d**	1.73	1.79	1.00	23609.82
	2d	/	/	/	/		**2d**	3.57	3.65	1.28	30257.75
	6dr	/	/	/	/		**6ds**	2.01	2.06	3.42	80746.86
	7dr	/	/	/	/		**7ds**	3.87	3.97	1.45	34129.28
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	5.94	6.03	1.00	4167.17	**20%**	**1d**	5.94	6.02	1.00	3781.82
	2d	3.57	3.65	2.33	9713.83		**2d**	3.58	3.65	2.37	8955.69
	6dt	1.99	2.04	0.90	3766.05		**6du**	1.99	2.04	1.06	3992.14
	7dt	4.83	4.92	0.26	1064.63		**7du**	4.85	4.92	0.31	1171.83
35%	**1d**	5.93	6.01	1.00	2685.97	**35%**	**1d**	5.93	6.02	1.00	2929.49

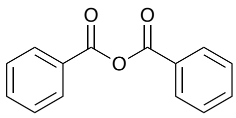
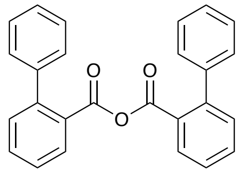
	2d	3.58	3.63	2.63	7071.44		**2d**	3.57	3.65	2.72	7982.67
	6dt	1.99	2.03	1.84	4941.19		**6du**	1.99	2.05	2.14	6259.81
	7dt	4.84	4.91	0.59	1573.14		**7du**	4.86	4.92	0.69	2013.89
50%	**1d**	5.91	6.01	1.00	1634.00	**50%**	**1d**	5.93	6.00	1.00	1833.11
	2d	3.57	3.63	3.32	5432.28		**2d**	3.56	3.63	3.18	5833.51
	6dt	1.99	2.04	4.29	7012.16		**6du**	1.98	2.06	3.72	6826.93
	7dt	4.84	4.92	1.51	2460.66		**7du**	4.86	4.92	1.28	2343.72
70%	**1d**	5.91	5.98	1.00	1054.11	**70%**	**1d**	5.92	5.98	1.00	1160.59
	2d	3.56	3.62	4.02	4241.79		**2d**	3.56	3.62	4.13	4796.11
	6dt	1.99	2.04	6.90	7269.95		**6du**	2.00	2.06	7.52	8730.37
	7dt	4.85	4.91	2.60	2738.26		**7du**	4.85	4.91	2.97	3451.21
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1d**	5.94	6.01	1.00	2646.84	**20%**	**1d**	1.72	1.80	1.00	11608.84
	2d	3.58	3.63	2.07	5484.31		**2d**	3.58	3.65	0.75	8666.11
	6du	1.99	2.03	1.54	4082.17		**6dv**	1.99	2.03	0.33	3864.51
	7du	4.85	4.92	0.40	1046.12		**7dv**	4.83	4.91	0.11	1326.40
35%	**1d**	5.94	6.00	1.00	2345.48	**35%**	**1d**	1.73	1.78	1.00	7437.10
	2d	3.58	3.63	2.24	5253.07		**2d**	3.57	3.63	0.83	6148.35
	6du	1.99	2.02	2.14	5029.80		**6dv**	1.97	2.04	0.66	4916.35
	7du	4.85	4.91	0.57	1343.68		**7dv**	4.85	4.91	0.24	1776.17
50%	**1d**	5.92	5.99	1.00	1333.95	**50%**	**1d**	1.72	1.78	1.00	5628.06
	2d	3.57	3.63	2.78	3706.65		**2d**	3.55	3.63	0.95	5368.68
	6du	1.99	2.02	4.19	5592.10		**6dv**	1.97	2.02	1.19	6676.41
	7du	4.85	4.91	1.25	1669.56		**7dv**	4.83	4.92	0.47	2666.30
70%	**1d**	5.91	5.99	1.00	797.55	**70%**	**1d**	1.70	1.77	1.00	2572.21
	2d	3.56	3.61	3.80	3029.24		**2d**	3.55	3.62	1.36	3494.32
	6du	1.98	2.03	9.73	7759.03		**6dv**	1.98	2.03	3.69	9491.11
	7du	4.85	4.92	3.15	2514.77		**7dv**	4.85	4.92	1.67	4307.80
Conv		**integral limits (ppm)**		**integral**	**absolut**						
20%	**1d**	1.74	1.78	1.00	10432.60						
	2d	4.05	4.11	0.76	7914.57						
	6dw	2.00	2.05	0.33	3461.74						
	7dw	4.89	4.94	0.10	998.19						
35%	**1d**	1.73	1.79	1.00	8864.61						
	2d	4.04	4.11	0.83	7366.85						
	6dw	1.99	2.05	0.60	5297.49						
	7dw	4.88	4.96	0.19	1652.98						

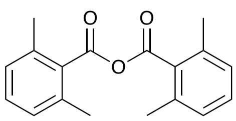
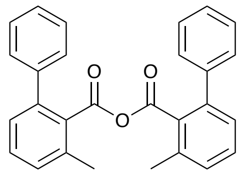
50%	**1d**	1.71	1.77	1.00	5021.82						
	2d	4.02	4.09	0.98	4944.37						
	6dw	2.00	2.07	1.20	6025.89						
	7dw	4.89	4.95	0.41	2083.48						
70%	**1d**	1.70	1.76	1.00	3079.79						
	2d	4.02	4.07	1.26	3889.10						
	6dw	2.01	2.06	2.57	7929.13						
	7dw	4.88	4.97	1.00	3081.98						

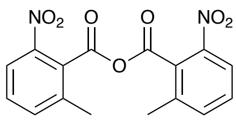
Table S33. Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding [1]H NMR measurements for competition experiments between 1e and 2e with the benzoic anhydride derivates 3a-z.



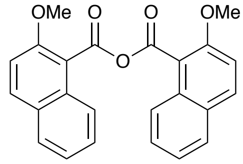
1e **2e** **6e(a-z)** **7e(a-z)**

 **3a** [a]				 **3f** [a]			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
19.042	0.688	6.329	1.845	20.815	0.545	3.894	1.360
34.538	0.636	6.194	1.824	33.349	0.494	3.736	1.318
44.548	0.601	6.377	1.853	44.413	0.474	3.994	1.385
61.044	0.486	6.298	1.840	65.286	0.365	4.139	1.420
		6.299 ± 0.077	1.840 ± 0.012			3.941 ± 0.170	1.371 ± 0.043

 **3m** [b]				 **3n** [b]			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
24.829	0.117	1.311	0.271	20.074	0.368	2.364	0.860
32.182	0.104	1.291	0.256	33.108	0.372	2.597	0.954
43.399	0.081	1.245	0.219	43.460	0.348	2.645	0.973
58.687	0.073	1.267	0.237	61.522	0.285	2.701	0.994
		1.279 ± 0.029	0.246 ± 0.022			2.577 ± 0.148	0.945 ± 0.059

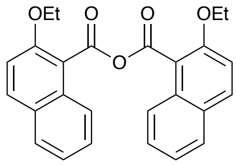


3o [a]

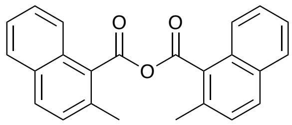


3r [a]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.994	0.277	1.872	0.627	15.328	0.258	1.774	0.573
31.244	0.253	1.868	0.625	27.452	0.188	1.567	0.449
44.754	0.136	1.453	0.374	39.457	0.187	1.631	0.489
58.697	0.146	1.606	0.474	54.583	0.080	1.277	0.245
		1.700 ± 0.206	0.525 ± 0.124			1.562 ± 0.209	0.439 ± 0.139



3s [a]



3w [b]

Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.458	0.186	1.515	0.415	17.812	-0.053	0.890	-0.116
29.492	0.120	1.335	0.289	26.456	0.003	1.008	0.008
41.841	0.135	1.433	0.359	39.266	0.022	1.059	0.057
57.750	0.089	1.328	0.283	54.764	0.019	1.061	0.059
		1.402 ± 0.089	0.337 ± 0.063			1.004 ± 0.080	0.002 ± 0.082

[a]Competition experiments were carrying out by method A. [b]Competition experiments were carrying out by method B.

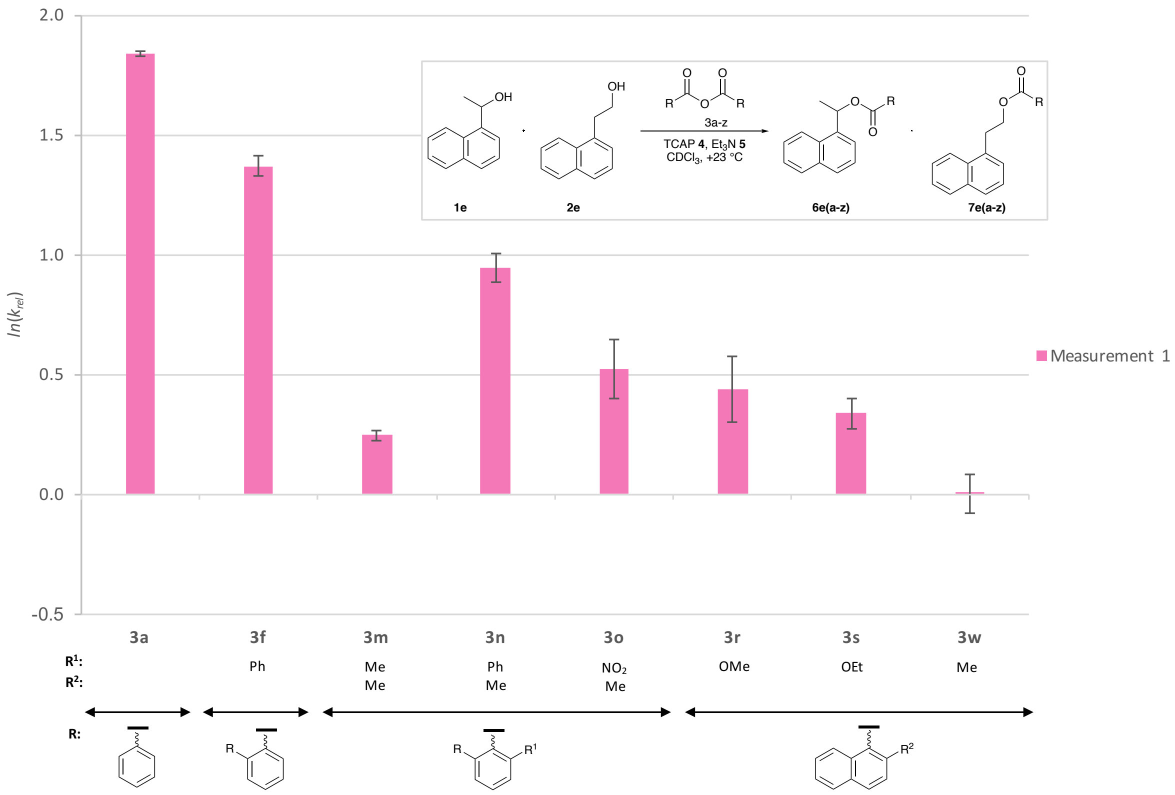


Figure S412. *ln*(k_{rel}) of competition experiment between **1e** and **2e** with the benzoic anhydride derivates **3a-z**.

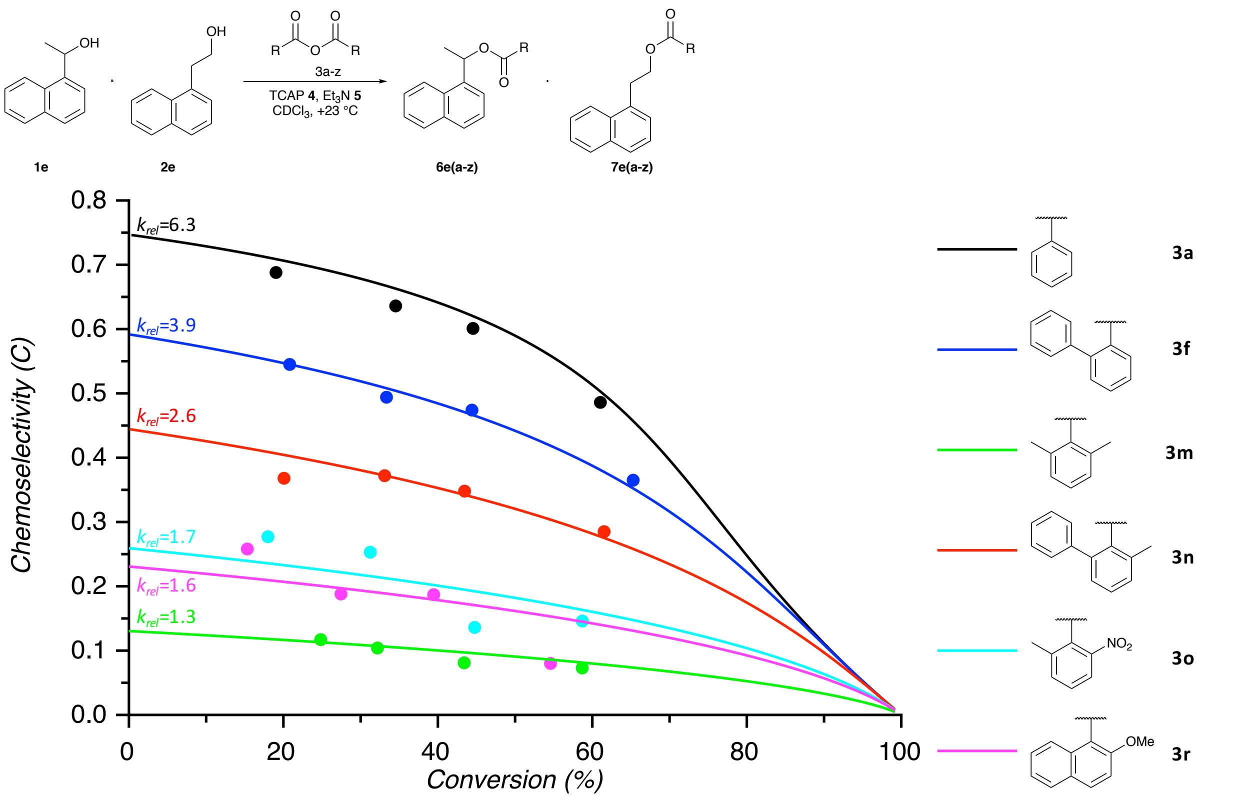


Figure S413. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1e** vs. **2e** with the benzoic anhydride derivates **3a-r**.

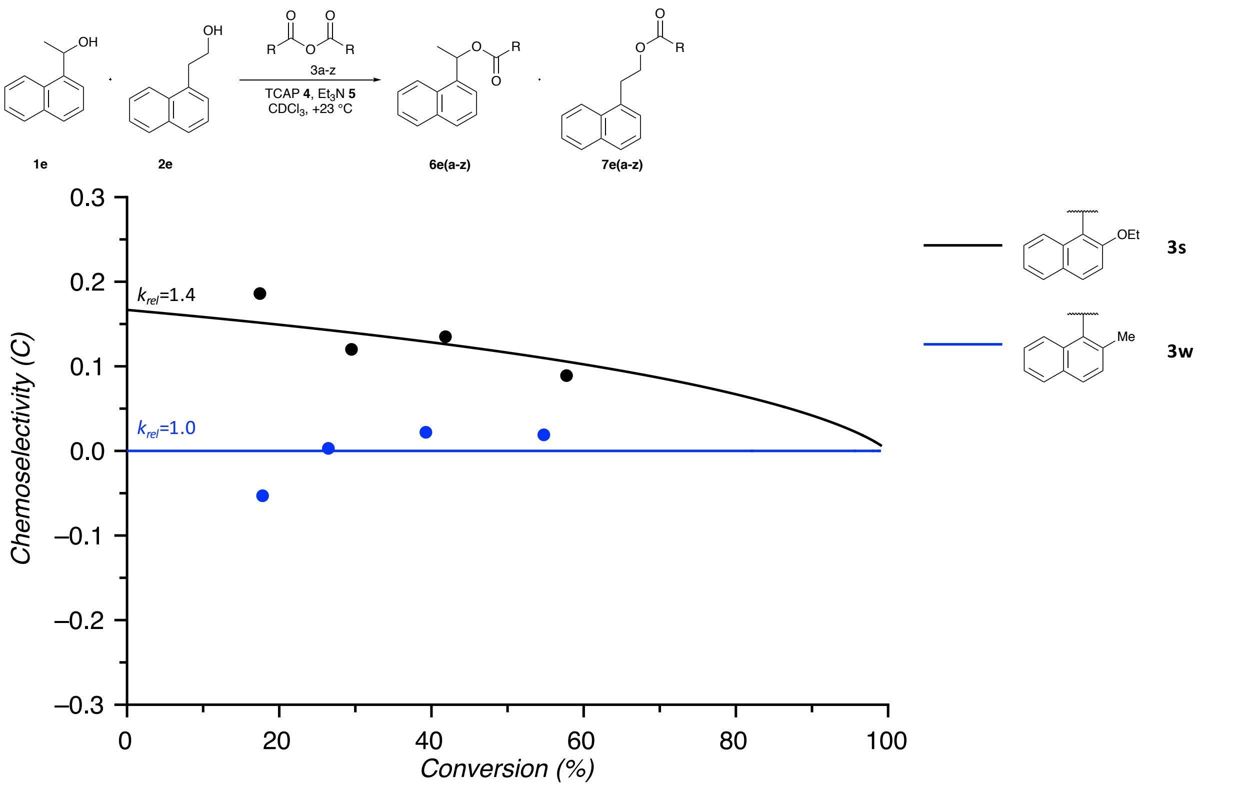


Figure S414. Plot of conversion vs. corrected chemoselectivity for competiton experiment **1e** vs. **2e** with the benzoic anhydride derivates **3s,w**.

Table S34. **Integral limits (ppm), relative and absolut integral values for competition experiments of alcohol 1e and 2e using benzoic anhydride derivates 3a-z.**

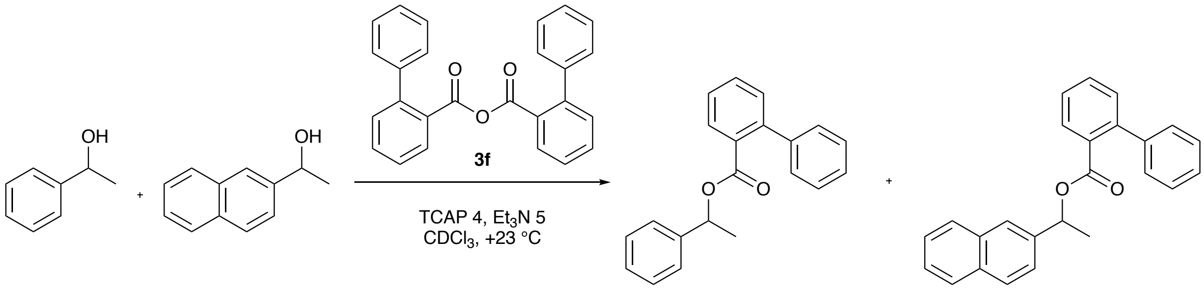
Conv		integral limits (ppm)		integral	absolut	Conv		integral limits (ppm)		integral	absolut
20%	**1e**	1.61	1.70	1.00	123311.00	**20%**	**1e**	1.62	1.70	1.00	114561.25
	2e	3.94	4.01	0.39	48622.50		**2e**	3.92	4.00	0.48	54493.23
	6ea	1.80	1.86	0.07	8508.33		**6ef**	1.45	1.53	0.11	12307.13
	7ea	4.62	4.69	0.20	25101.02		**7ef**	4.32	4.41	0.23	26195.97
35%	**1e**	1.64	1.68	1.00	112699.69	**35%**	**1e**	1.63	1.67	1.00	101042.94
	2e	4.62	4.69	0.39	43723.42		**2e**	3.92	3.99	0.40	40072.15
	6ea	1.81	1.85	0.15	17194.10		**6ef**	1.44	1.53	0.20	20405.99
	7ea	3.94	4.00	0.26	29462.56		**7ef**	4.31	4.42	0.40	40151.84
50%	**1e**	1.62	1.67	1.00	98978.59	**50%**	**1e**	1.61	1.68	1.00	93447.22
	2e	4.61	4.69	0.57	56447.77		**2e**	3.91	3.99	0.29	26720.81
	6ea	1.81	1.86	0.22	21507.25		**6ef**	1.46	1.51	0.30	27590.64
	7ea	3.93	4.02	0.22	22124.89		**7ef**	4.32	4.39	0.56	52732.37
70%	**1e**	1.62	1.69	1.00	82538.46	**70%**	**1e**	1.62	1.66	1.00	60343.16
	2e	3.92	4.00	0.08	6550.16		**2e**	3.91	3.98	0.12	7235.27
	6ea	1.79	1.87	0.46	38273.34		**6ef**	1.46	1.51	0.70	42028.41
	7ea	4.61	4.71	0.86	70975.80		**7ef**	4.32	4.40	1.01	61244.14
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1e**	1.64	1.69	1.00	11933.29	**20%**	**1e**	1.65	1.70	1.00	14592.11
	2e	3.95	4.03	0.62	7443.64		**2e**	3.95	4.03	0.51	7471.91
	6em	1.82	1.88	0.28	3349.99		**6en**	1.32	1.38	0.15	2155.87
	7em	4.64	4.71	0.24	2853.00		**7en**	4.28	4.33	0.20	2882.54
35%	**1e**	1.64	1.68	1.00	10395.69	**35%**	**1e**	1.65	1.69	1.00	10116.96
	2e	3.95	4.01	0.66	6853.36		**2e**	3.95	4.01	0.43	4357.98
	6em	1.83	1.86	0.40	4183.93		**6en**	1.33	1.37	0.27	2692.97
	7em	4.65	4.70	0.36	3751.58		**7en**	4.29	4.36	0.37	3699.84
50%	**1e**	1.63	1.68	1.00	9192.98	**50%**	**1e**	1.64	1.69	1.00	9387.45
	2e	3.94	4.01	0.67	6161.04		**2e**	3.95	4.00	0.36	3414.45
	6em	1.82	1.87	0.66	6043.48		**6en**	1.34	1.39	0.40	3757.34
	7em	4.65	4.71	0.59	5394.14		**7en**	4.27	4.35	0.53	4930.05
70%	**1e**	1.65	1.69	1.00	6591.75	**70%**	**1e**	1.63	1.68	1.00	7186.85
	2e	3.96	4.01	0.62	4098.21		**2e**	3.95	4.00	0.24	1691.44
	6em	1.83	1.87	1.18	7770.92		**6en**	1.33	1.37	0.79	5695.22
	7em	4.65	4.71	1.04	6883.56		**7en**	4.29	4.35	0.91	6568.44
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**

20%	**1e**	1.64	1.70	1.00	100026.50	**20%**	**1e**	1.64	1.68	1.00	12022.55
	2e	3.94	4.02	0.52	52091.29		**2e**	3.30	3.37	0.64	7728.17
	6eo	6.95	7.09	0.05	5087.10		**6er**	7.03	7.15	0.04	518.58
	7eo	4.68	4.77	0.16	15886.22		**7er**	4.77	4.84	0.15	1812.77
35%	**1e**	1.62	1.69	1.00	86472.68	**35%**	**1e**	1.61	1.67	1.00	10665.32
	2e	3.93	4.03	0.49	41957.46		**2e**	3.29	3.34	0.59	6245.99
	6eo	6.96	7.07	0.10	8901.36		**6er**	7.05	7.14	0.10	1017.54
	7eo	4.68	4.77	0.32	27462.70		**7er**	4.77	4.83	0.28	3018.99
50%	**1e**	1.62	1.69	1.00	68459.99	**50%**	**1e**	1.59	1.67	1.00	8940.38
	2e	3.92	4.03	0.47	32023.12		**2e**	3.28	3.34	0.54	4843.90
	6eo	6.96	7.06	0.19	13179.73		**6er**	7.05	7.12	0.16	1401.69
	7eo	4.67	4.77	0.53	36555.94		**7er**	4.78	4.84	0.47	4238.00
70%	**1e**	1.62	1.70	1.00	54866.42	**70%**	**1e**	1.59	1.63	1.00	7070.03
	2e	3.93	4.02	0.40	22044.73		**2e**	3.28	3.33	0.57	4021.90
	6eo	6.97	7.08	0.32	17827.75		**6er**	7.03	7.15	0.34	2369.46
	7eo	4.67	4.78	0.87	47652.22		**7er**	4.78	4.85	0.81	5759.33
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1e**	1.62	1.68	1.00	12061.04	**20%**	**1e**	5.62	5.70	1.00	3655.65
	2e	3.92	3.99	0.61	7385.67		**2e**	3.95	4.02	2.01	7332.33
	6es	7.05	7.16	0.06	666.05		**6ew**	7.10	7.17	0.23	843.00
	7es	4.76	4.83	0.16	1930.64		**7ew**	4.79	4.85	0.41	1487.67
35%	**1e**	1.61	1.67	1.00	10484.27	**35%**	**1e**	5.63	5.70	1.00	3149.30
	2e	3.92	3.97	0.59	6154.51		**2e**	3.95	4.00	1.98	6248.90
	6es	7.06	7.13	0.12	1227.29		**6ew**	7.10	7.17	0.36	1127.55
	7es	4.76	4.82	0.29	3043.31		**7ew**	4.79	4.85	0.72	2258.57
50%	**1e**	1.58	1.64	1.00	5290.69	**50%**	**1e**	5.61	5.69	1.00	2680.12
	2e	3.89	3.94	0.52	2766.75		**2e**	3.94	3.99	1.96	5250.00
	6es	7.06	7.14	0.37	1957.41		**6ew**	7.11	7.16	0.62	1670.82
	7es	4.75	4.85	0.89	4688.08		**7ew**	4.79	4.85	1.31	3518.14
70%	**1e**	1.58	1.66	1.00	8709.11	**70%**	**1e**	5.61	5.67	1.00	1955.31
	2e	3.91	3.96	0.56	4855.99		**2e**	3.92	3.99	1.95	3814.08
	6es	7.06	7.15	0.19	1644.83		**6ew**	7.11	7.17	1.16	2267.09
	7es	4.75	4.84	0.50	4381.02		**7ew**	4.79	4.84	2.46	4817.47

1.5 Investigation of size effects of the alcohol starting materials

To explore the influence of the aromatic surface of the alcohol substrates in the selectivity, two secondary alcohols **1** bearing different-size aromatic surfaces were tested with acid anhydrides **3f** and **3s**. These were repeated for the primary alcohols **2** bearing different-size aromatic surfaces.

The preparation of the competition experiments is shown for the following example:



For these three $CDCl_3$ stock solutions are prepared under nitrogen (Table S35). Stock A contains the secondary alcohols **1a** and **1b** and having a concentration of 0.05 M each. Stock B gathers anhydride **3f** (0.1 M) while Stock C consists of a 0.15 M Et_3N and catalyst TCAP in a concentration of 0.005 M (method C).

Table S35. Preparation of initial $CDCl_3$ Stocks

Stock	Compound	Molaritiy (mol L^{-1})	Volume (mL)	n (mol)	M.W. (g mol^{-1})	Mass (mg)
Stock A	**1a**	0.05	2	$100 \cdot 10^{-6}$	122.16	12.2
	1b	0.05	2	$100 \cdot 10^{-6}$	172.08	17.2
Stock B	**3f**	0.1	2	$200 \cdot 10^{-6}$	378.13	75.6
Stock C	**TCAP**	0.005	5	$25 \cdot 10^{-6}$	174.24	4.4
	Et_3N	0.15	5	$750 \cdot 10^{-3}$	101.19	75.9

Because the anthracene alcohols **1f/2f** are not soluable with this concentration, stock solutions with lower concentration are prepared. Stock A contains the secondary alcohols **1a** and **1b** and having a concentration of 0.02 M each. Stock B gathers anhydride **3f** (0.04 M) while Stock C consists of a 0.06 M Et_3N and catalyst TCAP in a concentration of 0.002 M (method D).

The following procedure is equivalent to the procedure explained in **1.1.**

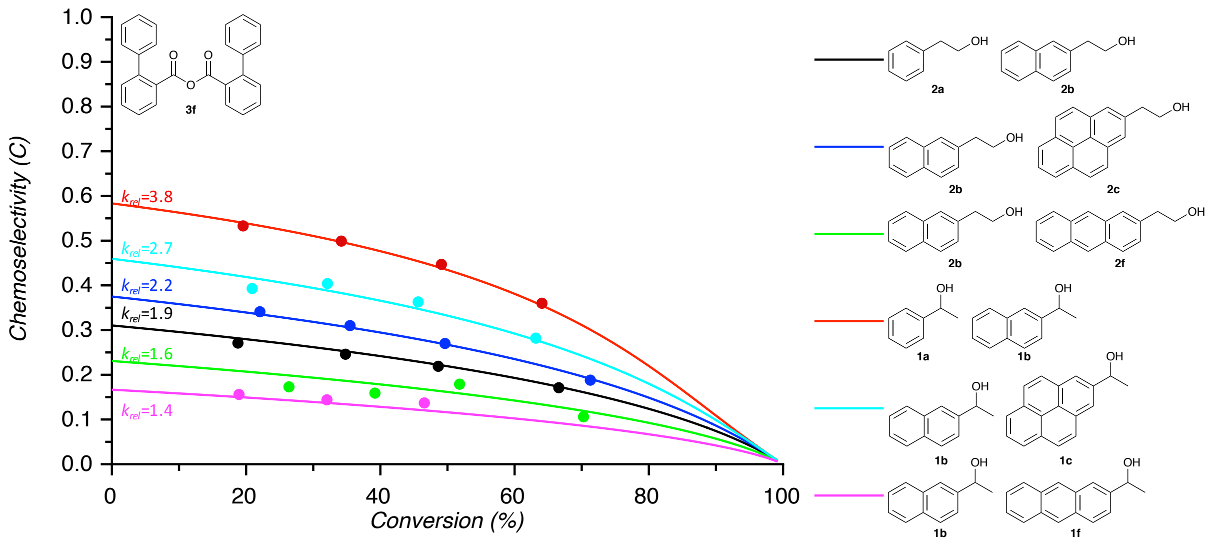


Figure S415. Plot of conversion vs. corrected chemoselectivity for competition experiment between primary alcohols **2** and between secondary alcohols **1** with the **3f**.

Table S36. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between primary alcohols 2 and between secondary alcohols 1 with the 3f.**

Primary Alcohol 2				**Secondary Alcohol 1**			
2a vs. **2b**[a]				**1a** vs. **1b**[a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
18.777	0.271	1.850	0.615	19.550	0.533	3.727	1.316
34.802	0.246	1.870	0.626	34.182	0.499	3.822	1.341
48.628	0.219	1.881	0.632	49.097	0.447	3.911	1.364
66.587	0.171	1.886	0.635	64.076	0.360	3.878	1.355
		1.872 ± 0.016	0.627 ± 0.008			3.835 ± 0.081	1.344 ± 0.021
2a vs. **2b**[a]				**1a** vs. **1b**[a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.667	0.287	1.918	0.651	19.317	0.560	4.033	1.395
33.648	0.258	1.917	0.651	32.417	0.509	3.871	1.354
49.330	0.222	1.909	0.647	48.055	0.439	3.745	1.320
65.984	0.175	1.901	0.642	63.610	0.375	4.106	1.413
		1.911 ± 0.008	0.648 ± 0.004			3.939 ± 0.163	1.370 ± 0.041
2b vs. **2c**[a]				**1b** vs. **1c**[a]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
22.051	0.341	2.230	0.802	20.901	0.393	2.538	0.931
35.480	0.310	2.223	0.799	32.116	0.404	2.821	1.037
49.631	0.270	2.211	0.793	45.634	0.363	2.831	1.041
71.284	0.188	2.169	0.774	63.152	0.282	2.744	1.009
		2.208 ± 0.027	0.792 ± 0.012			2.733 ± 0.136	1.005 ± 0.051
2b vs. **2f**[b]				**1b** vs. **1f**[b]			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
26.382	0.173	1.504	0.408	18.936	0.156	1.419	0.350
39.193	0.159	1.516	0.416	32.038	0.144	1.423	0.353
51.806	0.179	1.701	0.531	46.550	0.137	1.465	0.382
70.269	0.106	1.515	0.415				
		1.559 ± 0.107	0.443 ± 0.067			1.436 ± 0.030	0.362 ± 0.021

[a]Competition experiments were carrying out by method C. [b]Competition experiments were carrying out by method D.

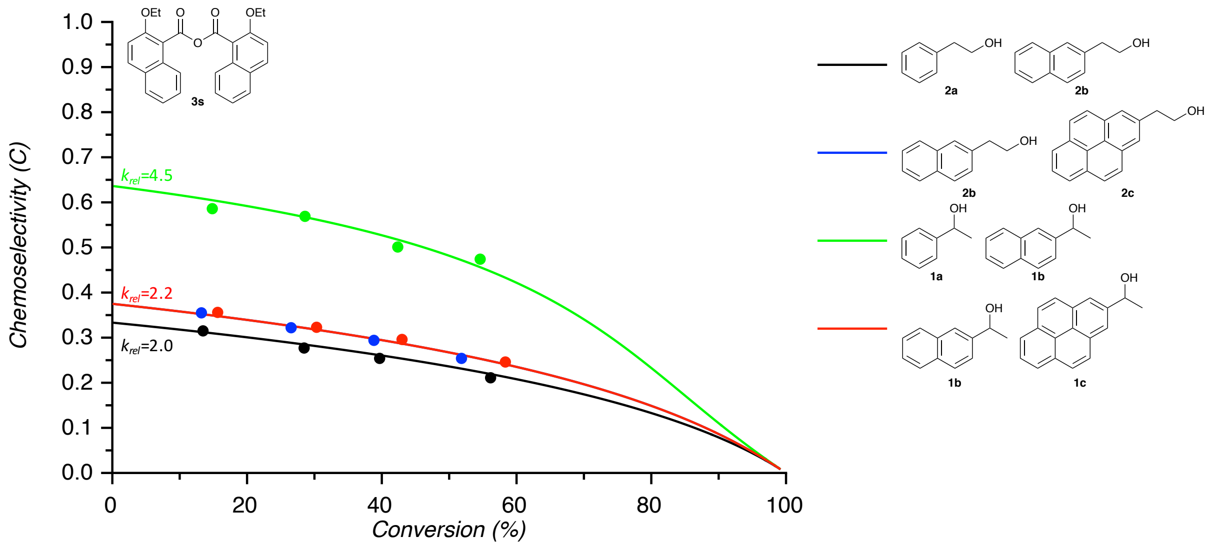


Figure S416. Plot of conversion vs. corrected chemoselectivity for competition experiment between primary alcohols **2** and between secondary alcohols **1** with the **3s**.

Table S37. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments between primary alcohols 2 and between secondary alcohols 1 with the 3s.**

Primary Alcohol 2				Secondary Alcohol 1			
2a vs. **2b**[a]				**1a** vs. **1b**[a]			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
13.462	0.315	2.012	0.699	14.839	0.586	4.233	1.443
28.467	0.277	1.963	0.674	28.598	0.569	4.530	1.511
39.676	0.254	1.960	0.673	42.367	0.501	4.258	1.449
56.147	0.211	1.945	0.665	54.601	0.474	4.826	1.574
		1.970 ± 0.029	0.678 ± 0.015			4.462 ± 0.278	1.494 ± 0.062
2b vs. **2c**[a]				**1b** vs. **1c**[a]			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
13.224	0.355	2.217	0.796	15.636	0.356	2.244	0.808
26.538	0.322	2.179	0.779	30.318	0.323	2.232	0.803
38.829	0.294	2.181	0.780	43.002	0.296	2.260	0.816
51.825	0.254	2.147	0.764	58.341	0.246	2.240	0.807
		2.181 ± 0.019	0.780 ± 0.009			2.244 ± 0.014	0.808 ± 0.006

[a]Competition experiments were carrying out by method C.

Table S38. **Integral limits (ppm), relative and absolut integral values for competition experiments exploring the influence of the aromatic surface of the alcohol substrates.**

Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**2a**	3.82	3.86	1.01	7417.52	**20%**	**2a**	3.84	3.89	1.00	84722.34
	2b	3.90	3.94	0.95	6989.27		**2b**	3.92	3.98	0.94	79748.30
	7af	4.22	4.27	0.16	1165.37		**7af**	4.25	4.31	0.14	12078.47
	7bf	4.32	4.37	0.29	2165.09		**7bf**	4.34	4.39	0.27	23214.67
35%	**2a**	3.82	3.86	1.00	6266.53	**35%**	**2a**	3.83	3.88	1.00	64812.26
	2b	3.89	3.94	0.82	5154.13		**2b**	3.91	3.97	0.82	53236.34
	7af	4.23	4.27	0.35	2206.52		**7af**	4.24	4.30	0.33	21325.16

	7bf	4.33	4.37	0.62	3889.67		**7bf**	4.33	4.40	0.59	38539.49
50%	**2a**	3.81	3.86	0.97	5346.70	**50%**	**2a**	3.82	3.88	1.00	53023.27
	2b	3.89	3.93	0.68	3742.00		**2b**	3.91	3.96	0.69	36480.80
	7af	4.23	4.27	0.59	3240.05		**7af**	4.25	4.30	0.62	32648.38
	7bf	4.33	4.37	0.98	5363.14		**7bf**	4.34	4.40	1.03	54490.05
70%	**2a**	3.80	3.84	1.00	3846.85	**70%**	**2a**	3.82	3.87	1.00	35490.42
	2b	3.89	3.92	0.53	2028.54		**2b**	3.90	3.96	0.52	18629.20
	7af	4.23	4.28	1.22	4683.30		**7af**	4.25	4.31	1.18	41953.10
	7bf	4.32	4.37	1.83	7025.71		**7bf**	4.34	4.39	1.78	63025.90
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**2b**	3.92	3.95	1.00	7244.42	**20%**	**2b**	3.94	3.97	1.00	6761.49
	2c	4.06	4.09	0.61	4425.00		**2f**	3.98	4.01	0.83	5627.88
	7bf	4.32	4.37	0.33	2418.50		**7bf**	4.32	4.36	0.28	1899.61
	7cf	4.46	4.51	0.55	3998.54		**7ff**	4.37	4.41	0.38	2540.32
35%	**2b**	3.92	3.96	5.72	8435.69	**35%**	**2b**	3.93	3.97	1.00	5911.60
	2c	4.05	4.10	4.12	6086.62		**2f**	3.97	4.01	0.77	4544.42
	7bf	4.32	4.37	1.00	1472.68		**7bf**	4.32	4.37	0.49	2923.63
	7cf	4.46	4.51	1.79	2635.51		**7ff**	4.37	4.41	0.65	3815.82
50%	**2b**	3.91	3.95	1.00	5029.62	**50%**	**2b**	3.93	3.97	1.00	3972.85
	2c	4.05	4.09	0.50	2505.89		**2f**	3.97	4.01	0.66	2613.15
	7bf	4.32	4.37	0.58	2939.61		**7bf**	4.33	4.36	0.74	2955.92
	7cf	4.46	4.52	0.89	4485.54		**7ff**	4.37	4.42	1.04	4123.62
70%	**2b**	3.90	3.95	1.00	3278.96	**70%**	**2b**	3.93	3.96	1.00	2563.26
	2c	4.03	4.08	0.30	978.15		**2f**	3.97	4.01	0.58	1479.66
	7bf	4.32	4.38	1.42	4653.01		**7bf**	4.32	4.36	1.70	4359.43
	7cf	4.46	4.51	1.80	5914.78		**7ff**	4.37	4.41	2.03	5195.81
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1a**	1.48	1.50	1.00	11876.37	**20%**	**1a**	1.50	1.52	1.00	132320.89
	1b	1.56	1.58	0.80	9461.83		**1b**	1.58	1.60	0.79	104578.66
	6af	1.30	1.32	0.10	1181.14		**6af**	1.32	1.34	0.09	12183.66
	6bf	1.39	1.41	0.34	4004.13		**6bf**	1.41	1.43	0.34	44532.99
35%	**1a**	1.47	1.50	1.00	10603.89	**35%**	**1a**	1.50	1.52	1.00	108757.59
	1b	1.55	1.57	0.61	6491.10		**1b**	1.57	1.60	0.63	69012.89
	6af	1.30	1.32	0.20	2170.54		**6af**	1.32	1.34	0.19	20378.45
	6bf	1.39	1.41	0.63	6707.65		**6bf**	1.40	1.44	0.60	64890.51
50%	**1a**	1.47	1.49	1.00	9536.12	**50%**	**1a**	1.49	1.52	1.00	96544.29

	1b	1.55	1.57	0.42	4004.33		**1b**	1.57	1.60	0.44	42593.51
	6af	1.30	1.32	0.37	3514.59		**6af**	1.31	1.34	0.37	35297.52
	6bf	1.39	1.41	1.00	9545.66		**6bf**	1.41	1.44	0.97	93419.94
70%	**1a**	1.47	1.49	1.00	7636.27	**70%**	**1a**	1.49	1.52	1.00	70248.63
	1b	1.54	1.57	0.23	1765.08		**1b**	1.57	1.59	0.21	15081.89
	6af	1.30	1.32	0.69	5271.57		**6af**	1.32	1.35	0.66	46075.36
	6bf	1.39	1.41	1.51	11496.92		**6bf**	1.41	1.44	1.47	103084.63
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**1b**	5.03	5.08	1.00	4743.43	**20%**	**1b**	1.56	1.58	1.00	10701.18
	1c	5.32	5.38	0.69	3283.78		**1f**	1.60	1.61	0.78	8359.98
	6bf	6.01	6.06	0.15	713.14		**6bf**	1.38	1.40	0.19	2068.55
	6cf	6.29	6.35	0.30	1407.95		**6ff**	1.42	1.44	0.22	2384.12
35%	**1b**	5.03	5.09	1.00	4020.26	**35%**	**1b**	1.56	1.58	1.00	9229.97
	1c	5.32	5.37	0.55	2225.98		**1f**	1.59	1.62	0.76	7041.82
	6bf	6.01	6.06	0.25	997.03		**6bf**	1.38	1.40	0.38	3535.54
	6cf	6.29	6.34	0.49	1958.03		**6ff**	1.42	1.44	0.45	4135.30
50%	**1b**	5.03	5.08	1.00	2851.22	**50%**	**1b**	1.55	1.58	1.00	7721.54
	1c	5.32	5.37	0.43	1240.09		**1f**	1.59	1.61	0.68	5280.74
	6bf	6.01	6.06	0.43	1220.19		**6bf**	1.38	1.40	0.68	5270.25
	6cf	6.29	6.34	0.78	2213.95		**6ff**	1.42	1.44	0.78	6053.39
70%	**1b**	5.02	5.08	1.00	2227.40	**70%**	**/**	**/**	**/**	**/**	**/**
	1c	5.31	5.36	0.27	611.82		**/**	**/**	**/**	**/**	**/**
	6bf	6.01	6.07	0.86	1926.25		**/**	**/**	**/**	**/**	**/**
	6cf	6.29	6.36	1.32	2939.81		**/**	**/**	**/**	**/**	**/**
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
20%	**2a**	3.80	3.86	1.00	72898.02	**20%**	**2b**	3.91	3.96	1.00	7905.81
	2b	3.88	3.94	1.00	72617.05		**2c**	4.05	4.10	0.76	6044.42
	7as	4.66	4.72	0.10	7124.25		**7bs**	4.76	4.81	0.10	759.79
	7bs	4.73	4.81	0.21	15238.04		**7cs**	4.89	4.94	0.17	1366.21
35%	**2a**	3.79	3.85	1.00	63124.19	**35%**	**2b**	3.91	3.95	1.00	9588.53
	2b	3.86	3.92	0.87	54859.71		**2c**	4.04	4.08	0.68	6497.65
	7as	4.65	4.71	0.26	16126.04		**7bs**	4.76	4.81	0.23	2165.81
	7bs	4.74	4.81	0.49	30825.69		**7cs**	4.90	4.95	0.38	3645.15
50%	**2a**	3.77	3.84	1.00	53164.48	**50%**	**2b**	3.90	3.94	1.00	6643.24
	2b	3.85	3.91	0.79	41746.55		**2c**	4.04	4.07	0.58	3843.46
	7as	4.65	4.71	0.41	22008.50		**7bs**	4.76	4.81	0.39	2587.48
	7bs	4.75	4.81	0.76	40418.24		**7cs**	4.89	4.94	0.61	4069.00

70%	**2a**	3.75	3.81	1.00	35326.58	**70%**	**2b**	3.88	3.94	1.00	5599.18
	2b	3.83	3.90	0.64	22571.00		**2c**	4.02	4.07	0.48	2662.11
	7as	4.64	4.71	0.78	27632.20		**7bs**	4.76	4.81	0.65	3648.46
	7bs	4.74	4.81	1.32	46496.56		**7cs**	4.90	4.94	0.94	5238.61
20%	**1a**	4.83	4.91	1.00	37709.74	**20%**	**1b**	5.03	5.08	1.00	4727.36
	1b	4.99	5.08	0.83	31218.60		**1c**	6.48	6.53	0.11	532.70
	6as	6.29	6.36	0.03	1292.18		**6bs**	5.32	5.37	0.85	4015.55
	6bs	6.46	6.54	0.24	9082.13		**6cs**	6.75	6.81	0.23	1087.70
Conv		**integral limits (ppm)**		**integral**	**absolut**	**Conv**		**integral limits (ppm)**		**integral**	**absolut**
35%	**1a**	4.81	4.92	1.00	30586.08	**35%**	**1b**	5.02	5.08	1.00	4184.38
	1b	4.98	5.07	0.62	18998.60		**1c**	6.48	6.53	0.26	1085.77
	6as	6.29	6.37	0.12	3525.34		**6bs**	5.31	5.36	0.73	3071.94
	6bs	6.45	6.54	0.52	15892.23		**6cs**	6.75	6.82	0.50	2071.32
50%	**1a**	4.80	4.89	1.00	30112.24	**50%**	**1b**	5.02	5.07	1.00	2901.50
	1b	4.96	5.05	0.46	13916.38		**1c**	6.48	6.53	0.44	1269.05
	6as	6.28	6.37	0.23	6971.02		**6bs**	5.30	5.36	0.61	1770.53
	6bs	6.44	6.54	0.83	24904.35		**6cs**	6.76	6.82	0.78	2255.81
70%	**1a**	4.80	4.88	1.00	23680.11	**70%**	**1b**	5.01	5.06	1.00	2296.37
	1b	4.95	5.04	0.29	6889.20		**1c**	6.48	6.54	0.79	1819.22
	6as	6.27	6.38	0.39	9134.58		**6bs**	5.30	5.34	0.46	1064.78
	6bs	6.45	6.54	1.16	27454.11		**6cs**	6.75	6.82	1.26	2887.95

2.0 Effects of reaction conditions

2.1 Investigation of temperature effects

Giese *et al.*[3] documented that a decrease in the reaction temperature often implies an increase in selectivity. We thus tested the effects of reaction temperature on selectivities for the anhydrides **3f** and **3t**, and the alcohol system **1b/2b**. By varying the temperature from +40 °C to -10 °C we observed only moderate changes in the rate constants for anhydride **3f**. By using the well-known Eyring equation Eq. 14 an activation entropy difference of -7.4 J K^{-1}·mol was found for anhydride **3f** and a slightly larger value of -10.3 J K^{-1}·mol for anhydride **3t**. Because of the rather similar rate constants at different temperatures, these small differecens hardly merit any further discussion.

$$k_1 = \frac{k_B T}{h} \cdot e^{-\frac{\Delta G_1^{\neq}}{RT}} \qquad \text{Eq. 7}$$

$$\frac{k_2}{k_1} = \frac{e^{-\frac{\Delta G_2^{\neq}}{RT}}}{e^{-\frac{\Delta G_1^{\neq}}{RT}}} \qquad \text{Eq. 8}$$

$$\frac{k_2}{k_1} = e^{-\frac{\Delta G_2^{\neq}}{RT}+\frac{\Delta G_1^{\neq}}{RT}} \qquad \text{Eq. 9}$$

$$ln\frac{k_2}{k_1} = -\frac{\Delta G_2^{\neq}}{RT} + \frac{\Delta G_1^{\neq}}{RT} \qquad \text{Eq. 10}$$

$$ln\frac{k_2}{k_1} = -\frac{\Delta H_2^{\neq} - T\Delta S_2^{\neq}}{RT} + \frac{\Delta H_1^{\neq} - T\Delta S_1^{\neq}}{RT} \qquad \text{Eq. 11}$$

$$ln\frac{k_2}{k_1} = -\frac{\Delta H_2^{\neq}}{RT} + \frac{\Delta S_2^{\neq}}{R} + \frac{\Delta H_1^{\neq}}{RT} - \frac{\Delta S_1^{\neq}}{R} \qquad \text{Eq. 12}$$

$$ln\frac{k_2}{k_1} = \frac{\Delta H_1{}^{\neq} - \Delta H_2{}^{\neq}}{RT} - \frac{\Delta S_1{}^{\neq} - \Delta S_2{}^{\neq}}{R} \quad \text{Eq. 13}$$

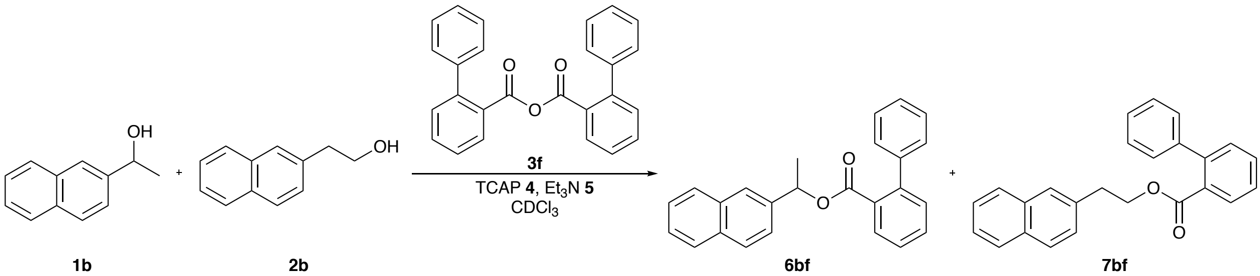
$$\Delta\Delta H^{\neq} = \Delta H_1^{\neq} - \Delta H_2^{\neq}$$
$$\Delta\Delta S^{\neq} = \Delta S_1^{\neq} - \Delta S_2^{\neq}$$
$$R = 8.31451\ J\ K^{-1} \cdot mol$$

$$\ln(k_{rel}) = ln\frac{k_2(\mathbf{2a\text{-}d})}{k_1(\mathbf{1a\text{-}d})} = \frac{\Delta\Delta H^{\neq}}{R \cdot T} - \frac{\Delta\Delta S^{\neq}}{R} \quad \text{Eq. 14}$$

<u>Anhydride **3f**</u>

$$ln\frac{k_2}{k_1} = \frac{-32.544}{T} + 0.887 \quad \text{Eq. 15}$$

$$\Delta\Delta H^{\neq} = \Delta H_1^{\neq} - \Delta H_2^{\neq} = -270.587\ J\ mol^{-1} \quad \text{Eq. 16}$$
$$\Delta\Delta S^{\neq} = \Delta S_1^{\neq} - \Delta S_2^{\neq} = -7.37\ J\ K^{-1} \cdot mol \quad \text{Eq. 17}$$



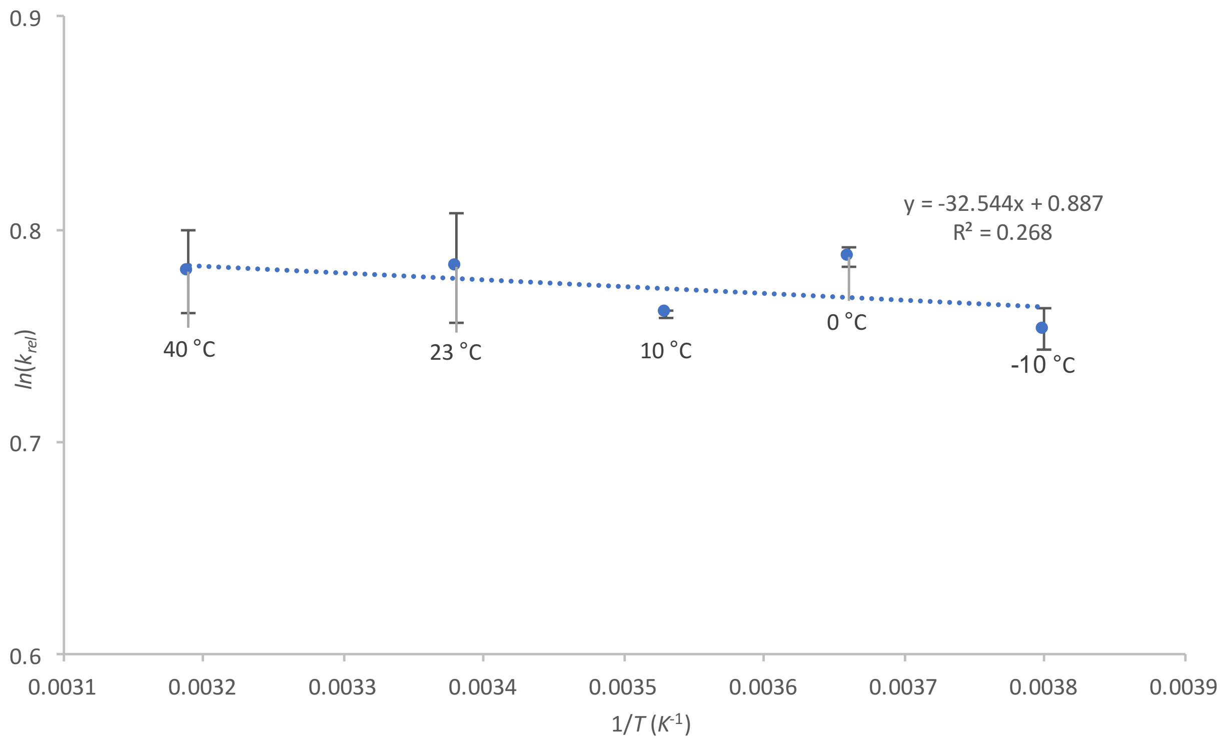
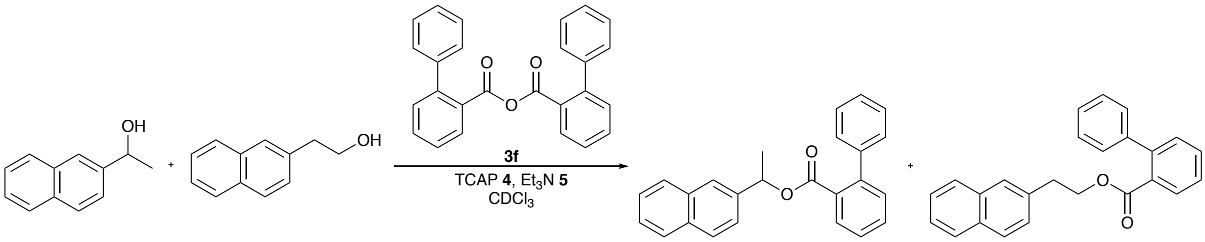


Figure S417. Eyring plot of $ln(k_{rel})$ at different temperatures.

Table S39. **Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for temperature depending competition experiments.**



-10 °C				0 °C			
263.15				273.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
28.549	0.307	2.118	0.751	21.380	0.333	2.180	0.780
35.849	0.288	2.101	0.742	35.652	0.306	2.205	0.791
49.554	0.261	2.153	0.767	51.628	0.263	2.204	0.790
68.366	0.194	2.119	0.751	67.267	0.208	2.198	0.788
		2.123 ± 0.022	0.753 ± 0.010			2.197 ± 0.011	0.787 ± 0.005
10 °C				23 °C			
283.15				296.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
21.311	0.325	2.137	0.760	23.536	0.316	2.11	0.747
33.809	0.299	2.136	0.759	33.18	0.308	2.183	0.78
49.121	0.261	2.145	0.763	46.687	0.278	2.211	0.793
66.701	0.203	2.137	0.759	66.382	0.216	2.24	0.807
		2.139 ± 0.004	0.760 ± 0.002			2.186 ± 0.056	0.782 ± 0.026
40 °C							
313.15							
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$				
19.077	0.329	2.137	0.759				
33.251	0.303	2.154	0.767				
49.391	0.273	2.225	0.800				
66.915	0.211	2.212	0.794				
		2.182 ± 0.043	0.780 ± 0.020				

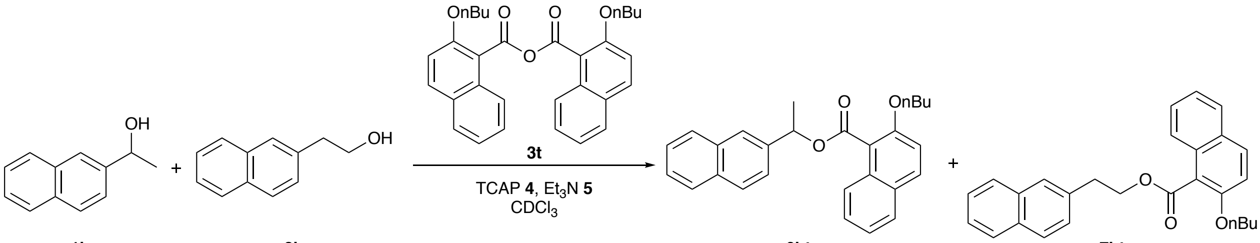
Anhydride **3t**

$$ln\frac{k_2}{k_1} = \frac{-545.281}{T} + 1.235 \quad \text{Eq. 18}$$

$$\Delta\Delta H^{\neq} = \Delta H_1^{\neq} - \Delta H_2^{\neq} = -4533.744\frac{J}{mol} = -4.534\ kJ\ mol^{-1} \quad \text{Eq. 19}$$

$$\Delta\Delta S^{\neq} = \Delta S_1^{\neq} - \Delta S_2^{\neq} = -10.268\ J\ K^{-1} \cdot mol \quad \text{Eq. 20}$$

These reults show that primary alcohol **2b** has a higher activation enthalpy than secondary alcohol **1b**. The activation entropy for alcohol **1b** is less negative as the activation entropy for alcohol **2b**. This means that the transititon state for reraction of secondary alcohol **1b** is more highly organized as compared to primary alcohol **2b** (see SI III).



1b 2b 6bt 7bt

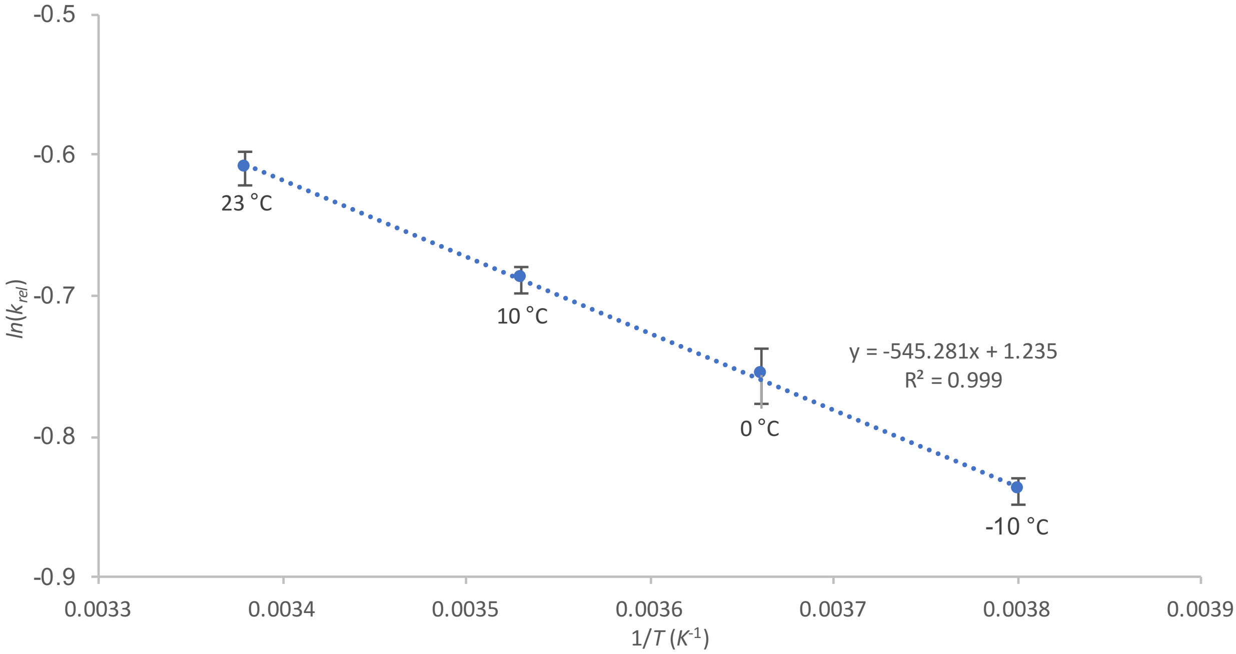
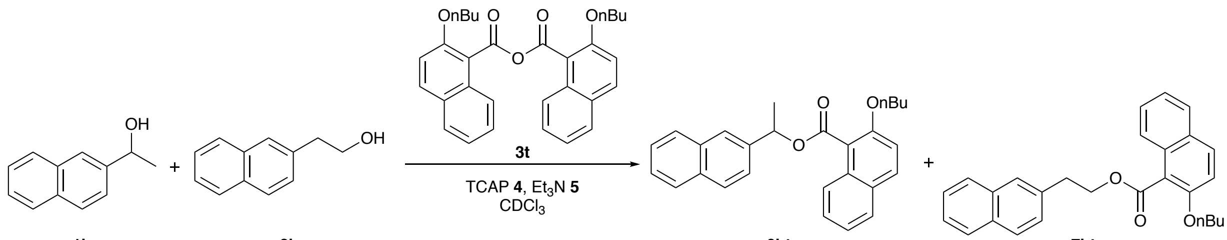


Figure S418. Eyring plot of $ln(k_{rel})$ at different temperatures.

Table S40. Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for temperature depending competition experiments.



1b 2b 6bt 7bt

-10 °C				-10 °C			
263.15				263.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
19.611	-0.363	0.429	-0.847	17.231	-0.354	0.445	-0.811
29.796	-0.336	0.435	-0.833	30.063	-0.330	0.441	-0.820
39.880	-0.309	0.437	-0.828	40.531	-0.310	0.434	-0.835
56.167	-0.265	0.429	-0.846	55.966	-0.258	0.440	-0.820
		0.432 ± 0.004	-0.839 ± 0.009			0.440 ± 0.004	-0.821 ± 0.010
0 °C				0 °C			
273.15				273.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
13.716	-0.346	0.460	-0.776	11.669	-0.318	0.497	-0.700
28.087	-0.304	0.477	-0.740	21.103	-0.324	0.469	-0.757

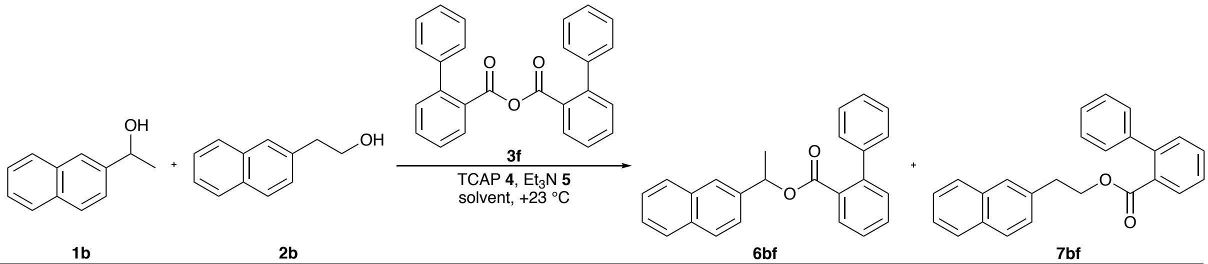
34.965	-0.300	0.463	-0.771	31.796	-0.297	0.475	-0.744
47.670	-0.257	0.478	-0.739	45.346	-0.270	0.469	-0.758
		0.469 ± 0.009	-0.757 ± 0.020			0.477 ± 0.013	-0.740 ± 0.027
10 °C				10 °C			
283.15				283.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
13.443	-0.308	0.505	-0.684	13.636	-0.316	0.495	-0.704
22.639	-0.299	0.497	-0.700	24.994	-0.296	0.494	-0.705
33.320	-0.275	0.500	-0.693	34.766	-0.270	0.503	-0.687
47.716	-0.237	0.507	-0.680	52.725	-0.227	0.504	-0.686
		0.502 ± 0.005	-0.689 ± 0.009			0.499 ± 0.005	-0.695 ± 0.010
23 °C				23 °c			
296.15				296.15			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.563	-0.267	0.548	-0.602	16.163	-0.284	0.528	-0.638
31.600	-0.241	0.550	-0.597	28.314	-0.256	0.539	-0.618
45.793	-0.219	0.542	-0.612	41.220	-0.230	0.540	-0.616
62.014	-0.182	0.535	-0.625	54.527	-0.201	0.538	-0.620
		0.544 ± 0.007	-0.609 ± 0.012			0.536 ± 0.005	-0.623 ± 0.010

2.2 Investigation of solvent effects

As shown in earlier studies,[4] the solvent can in principle change the relative rate constants determined here. Competition experiments with the alcohol system **1b/2b** were thus carried out with anhydride **3f** in CH_2Cl_2, MeCN, THF, hexafluoroisopropanol, and trifluorotoluene. Instead of the common four different conversion points, only the 50% conversion point of the competition experiments was used for this type of solvent testing in triplicate form. For the solvent $CDCl_3$ the computed rate constant from the results in section **1.4** was used [k_{rel}=2.4, $ln(k_{rel})$=0.76, α=2.2, β=0.8]. No significant differences in the rate constants were found for these solvents. When plotting the $ln(k_{rel})$ values against Hunter's parameter for solvent hydrogen bond donor and acceptor ability (α and β, Eq. 21), no systematic solvent dependence can be identified.

$$ln(k_{rel}) = 0.60 + 0.07 \cdot \alpha + 0.05 \cdot \beta \qquad \text{Eq. 21}$$

Table S41. **Conversion, corrected chemoselectivity, relative rate, and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments carrying out in different solvents.**



TFT α=1.3; β=1.7				MeCN α=1.7; β=5.1			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
48.266	0.259	2.117	0.750	45.912	0.342	2.665	0.980
49.435	0.259	2.132	0.757	46.518	0.324	2.534	0.930
49.729	0.247	2.061	0.723	46.850	0.329	2.584	0.949

		2.103 ± 0.037	0.743 ± 0.018			2.594 ± 0.066	0.953 ± 0.025
THF α=0.8; β=5.9				DCM α=1.9; β=2.0			
Conv.	*Chem.*	k_{rel}	*ln(*k_{rel}*)*	*Conv.*	*Chem.*	k_{rel}	*ln(*k_{rel}*)*
48.721	0.356	2.868	1.053	51.120	0.309	2.539	0.932
48.942	0.334	2.686	0.988	51.345	0.299	2.463	0.901
49.896	0.325	2.636	0.969	52.132	0.305	2.538	0.931
		2.730 ± 0.122	1.004 ± 0.044			2.513 ± 0.044	0.921 ± 0.018

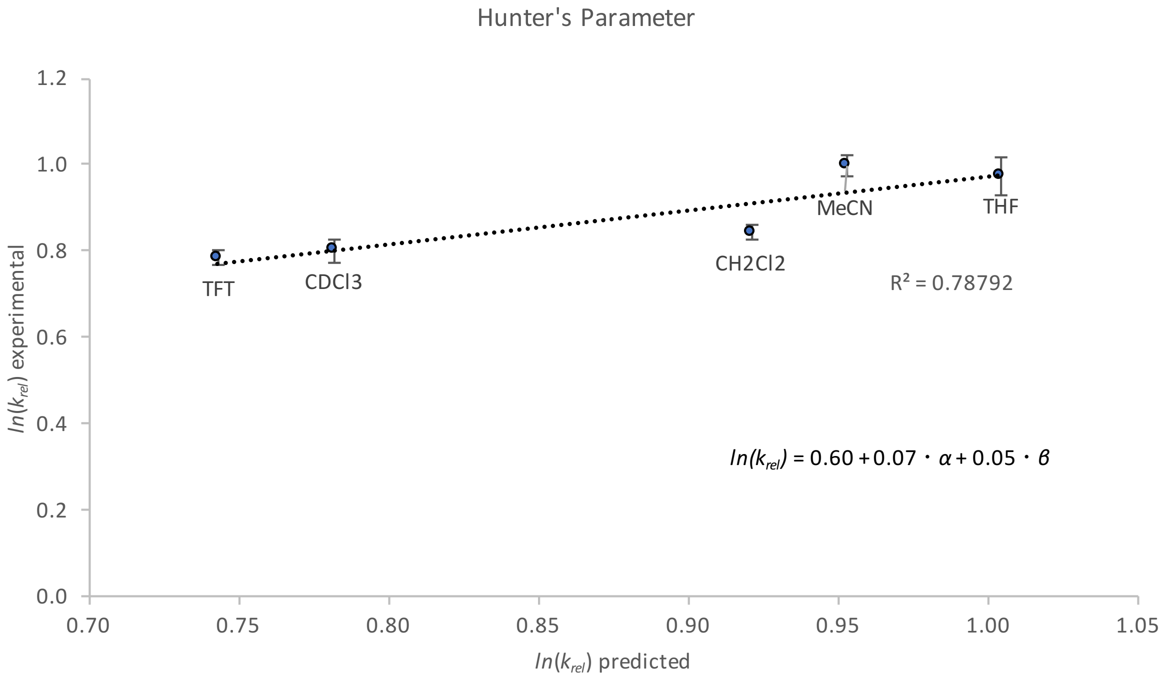
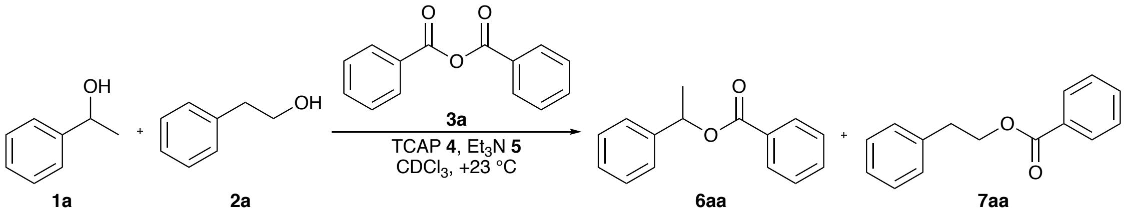


Figure S419. Plot of predicted ln(k_{rel}) valus against experimental ln(k_{rel}) valus. The predicted ln(k_{rel}) valus are using the Hunter's parameter and Eq. 14.

2.4 Investigation of catalyst concentration

To quantify the role the catalyst concentration on the selectivity values, two types of competition experiments were carried out. First the alcohol system **1a/2a** was tested with anhydride **3a** and TCAP (**4**) concentrations of 2, 5, 10 and 20 mol%. No differences in the relative rate constants were found in these experiments. Additionally, the alcohol system **1b/2b** with anhydride **3f** was explored with TCAP concentrations of 1, 2,5,10 and 20 mol%, and again no significant changes of the relative rate constant was observed. In the case of alcohol system **1a/2a** also the uncatalyzed background reaction with anhydride **3a** was studied. Et_3N (**5**) was still used as the auxiliary base in excess. After a reaction time of appox. 4 weeks the turnover of anhydride **3a** was not yet fully complete by ^1H NMR spectroscopy. However, for the background reaction a selectivity value of around ln(k_{rel}) = 3.28 was obtained, which indicated a significant increase in selectivity in comparison to the catalysed reaction of **1a/2a** with **3a** (ln(k_{rel}) = 2.00). No background reaction was found for the reaction of the alcohol system **1b/2b** with anhydride **3o** (one of the selectivity inverting anhydrides). Even after 4 weeks no significant formation of product esters **1bo/2bo** could be observed.



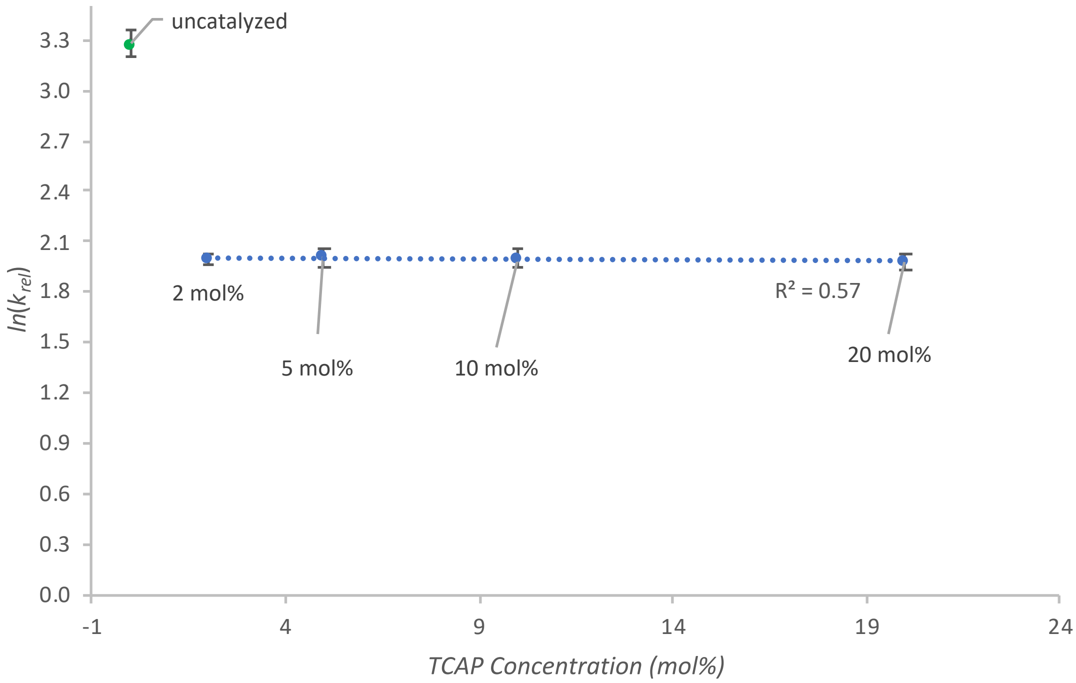
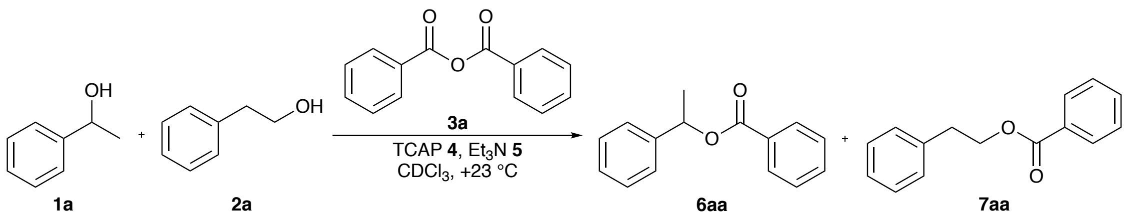


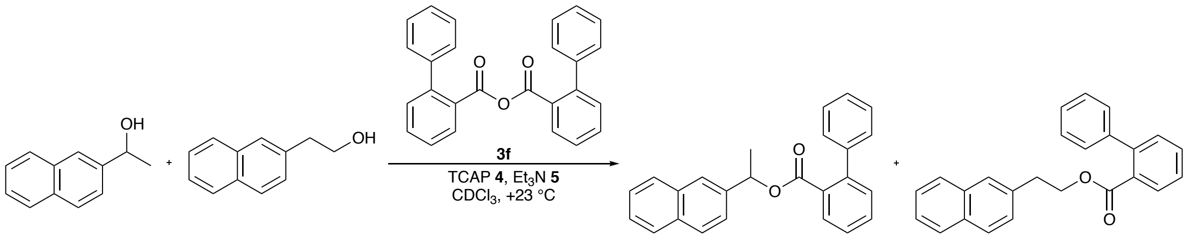
Figure S420. Plot of TCAP concentration vs. ln(k_{rel}) for the competiton experiment of alcohol **1b** and **2b** with anhydride **3a.**

Table S42. Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for catalyst concentration depending competition experiments.



uncatalysed				*2 mol%*			
Conv.	*Chem.*	k_{rel}	*ln(k_{rel})*	*Conv.*	*Chem.*	k_{rel}	*ln(k_{rel})*
9.777	0.918	25.794	3.250	19.286	0.732	7.675	2.038
18.354	0.922	30.120	3.405	33.515	0.683	7.378	1.998
27.557	0.897	25.593	3.242	50.440	0.595	7.153	1.967
38.102	0.872	24.991	3.219	67.167	0.439	7.201	1.974
		26.624 ± 2.040	3.279 ± 0.074			7.352 ± 0.236	1.995 ± 0.032
5 *mol%*				10 *mol%*			
Conv.	*Chem.*	k_{rel}	*ln(k_{rel})*	*Conv.*	*Chem.*	k_{rel}	*ln(k_{rel})*
17.327	0.747	8.030	2.083	18.163	0.742	7.939	2.072
32.458	0.682	7.237	1.979	33.282	0.676	7.146	1.967
44.865	0.630	7.235	1.979	50.866	0.593	7.151	1.967
65.024	0.466	7.197	1.974	70.882	0.390	7.415	2.004
		7.425 ± 0.404	2.004 ± 0.053			7.413 ± 0.373	2.002 ± 0.049

20 *mol%*							
Conv.	*Chem.*	*k*rel	*ln(k*rel*)*				
18.645	0.735	7.700	2.041				
31.963	0.679	7.105	1.961				
49.558	0.595	6.983	1.944				
70.055	0.399	7.140	1.966				
		7.232 ± 0.319	1.978 ± 0.043				



1b 2b 6bf 7bf

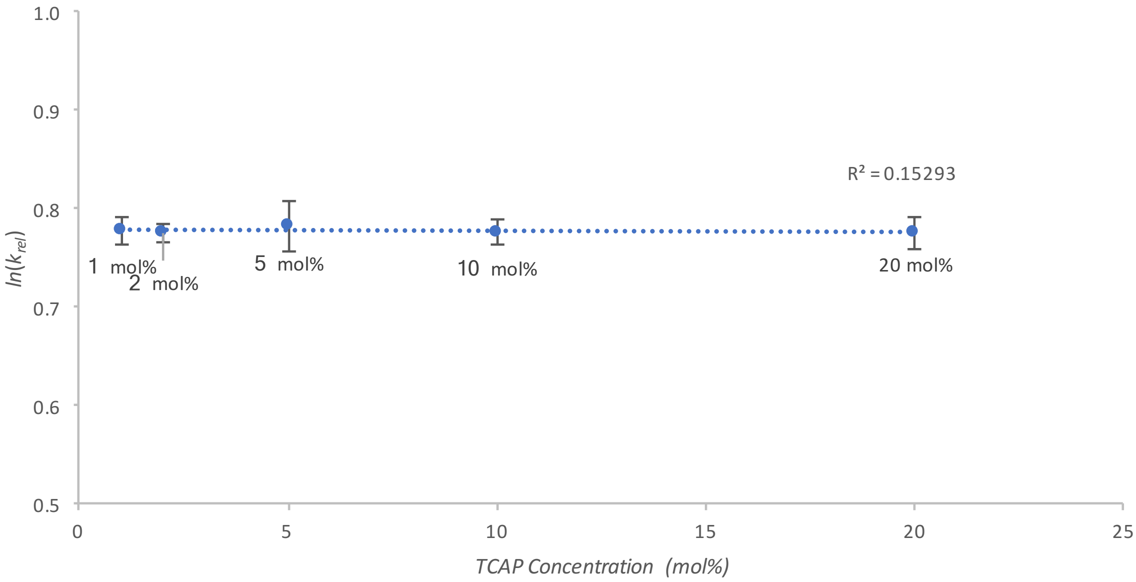
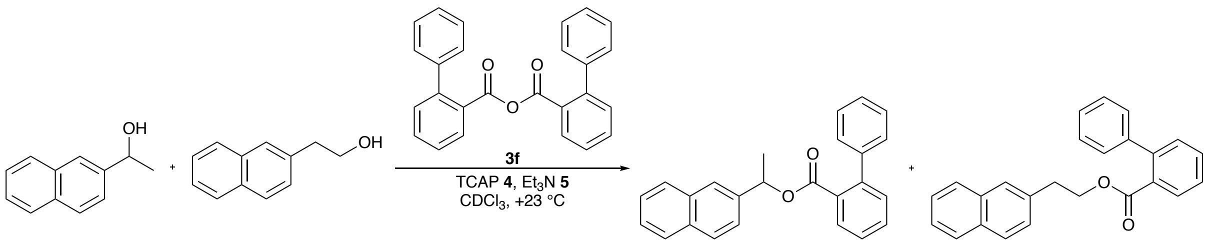


Figure S421. Plot of TCAP concentration vs. ln(k_{rel}) for competiton experiment of alcohol **1b** and **2b** with **3f**.

Table S43. Conversion, corrected chemoselectivity, relative rate, and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for catalyst concentration depending competition experiments.



1b 2b 6bf 7bf

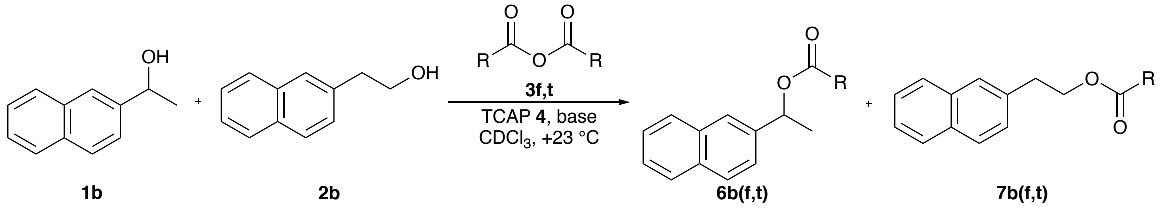
1 *mol%*				1 *mol%*			
Conv.	*Chem.*	*k*rel	*ln(k*rel*)*	*Conv.*	*Chem.*	*k*rel	*ln(k*rel*)*
27.324	0.315	2.146	0.764	20.870	0.327	2.143	0.762
34.258	0.302	2.162	0.771	32.600	0.310	2.184	0.781
49.193	0.269	2.194	0.786	47.006	0.281	2.232	0.803
69.128	0.202	2.211	0.794	66.423	0.210	2.191	0.785

		2.178 ± 0.030	0.779 ± 0.014			2.188 ± 0.036	0.783 ± 0.020
2 *mol%*				2 *mol%*			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
20.995	0.328	2.151	0.766	27.483	0.320	2.179	0.779
32.915	0.307	2.174	0.776	34.042	0.303	2.162	0.771
46.458	0.272	2.167	0.773	49.806	0.266	2.191	0.784
65.069	0.216	2.198	0.787	68.877	0.203	2.216	0.796
		2.172 ± 0.019	0.776 ± 0.009			2.187 ± 0.023	0.782 ± 0.010
5 *mol%*				5 *mol%*			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
23.536	0.316	2.110	0.747	18.843	0.328	2.127	0.755
33.180	0.308	2.183	0.780	34.398	0.290	2.094	0.739
46.687	0.278	2.211	0.793	47.819	0.264	2.135	0.758
66.382	0.216	2.240	0.807	66.389	0.211	2.197	0.787
		2.186 ± 0.056	0.782 ± 0.026			2.138 ± 0.043	0.760 ± 0.020
10 *mol%*				10 *mol%*			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
21.143	0.331	2.167	0.773	28.456	0.308	2.123	0.753
34.967	0.297	2.141	0.761	33.425	0.301	2.144	0.763
50.527	0.263	2.181	0.780	49.678	0.262	2.159	0.770
69.336	0.200	2.208	0.792	66.691	0.208	2.183	0.781
		2.174 ± 0.028	0.777 ± 0.013			2.152 ± 0.025	0.767 ± 0.012
20 *mol%*				20 *mol%*			
Conv.	*Chem.*	k_{rel}	*ln*(k_{rel})	*Conv.*	*Chem.*	k_{rel}	*ln*(k_{rel})
28.479	0.316	2.170	0.775	21.600	0.321	2.120	0.751
34.753	0.296	2.131	0.757	33.006	0.302	2.143	0.762
47.043	0.272	2.173	0.776	43.784	0.268	2.099	0.741
68.129	0.206	2.216	0.796	65.116	0.211	2.151	0.766
		2.173 ± 0.035	0.776 ± 0.016			2.128 ± 0.024	0.755 ± 0.011

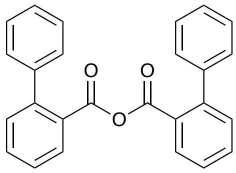
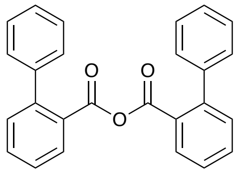
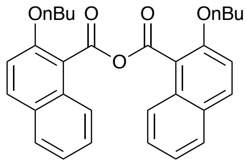
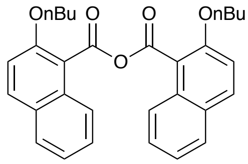
2.4 Investigation of auxiliary base effects

The auxiliary base can, in principle, also influence the rate constant.[5] The alcohol system **1b/2b** with anhydrides **3f** and **3t** was tested with Et_3N and the larger Hünig base. For both anhydrides, no differences in rate constants were found.

Table S44. Conversion, corrected chemoselectivity, relative rate and natural logarithm of relative rate with standard derivations calculated from corresponding ^{1}H NMR measurements for competition experiments using different auxiliary bases.



1b **2b** **6b(f,t)** **7b(f,t)**

 3f				 3f			
Et_3N				**Hünig base**			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
23.536	0.316	2.110	0.747	20.706	0.312	2.064	0.725
33.180	0.308	2.183	0.780	34.832	0.292	2.111	0.747
46.687	0.278	2.211	0.793	50.053	0.260	2.156	0.768
66.382	0.216	2.240	0.807	70.545	0.188	2.139	0.760
		2.186 ± 0.056	0.782 ± 0.026			2.117 ± 0.040	0.750 ± 0.019
 3t				 3t			
Et_3N				**Hünig base**			
Conv.	*Chem.*	k_{rel}	$ln(k_{rel})$	*Conv.*	*Chem.*	k_{rel}	$ln(k_{rel})$
17.563	-0.267	0.548	-0.602	15.860	-0.275	0.540	-0.616
31.600	-0.241	0.550	-0.597	27.068	-0.249	0.551	-0.596
45.793	-0.219	0.542	-0.612	38.198	-0.248	0.523	-0.648
62.014	-0.182	0.535	-0.625	52.567	-0.204	0.541	-0.615
		0.544 ± 0.007	-0.609 ± 0.012			0.539 ± 0.012	-0.619 ± 0.022

3.0 References

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