Kinetic Resolution of Racemic Secondary Benzylic Alcohols by the Enantioselective Esterification Using Pyridine-3-carboxylic Anhydride (3-PCA) with Chiral Acyl-Transfer Catalysts

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The authors dedicate this paper to Professor *Dieter Seebach* on the celebration of his 75th birthday

Pyridine-3-carboxylic anhydride (3-PCA) was found to function as an efficient coupling reagent for the preparation of carboxylic esters from various carboxylic acids with alcohols under mild conditions by a simple experimental procedure. This novel condensation reagent 3-PCA was applicable not only for the synthesis of achiral carboxylic esters catalyzed by 4-(dimethylamino)pyridine (DMAP) but also for the production of chiral carboxylic esters by the combination of chiral nucleophilic catalyst, such as tetramisole (=2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*][1,3]thiazole) derivatives. An efficient kinetic resolution of racemic benzylic alcohols with achiral carboxylic acids was achieved by using 3-PCA in the presence of (*R*)-benzotetramisole ((*R*)-BTM), and a variety of optically active carboxylic esters were produced with high enantiomeric excesses by this new chiral induction system without using a tertiary amine.

Introduction. – Since the synthesis of carboxylic esters from carboxylic acids and alcohols, has been considered to be one of the most important reactions in the field of synthetic organic chemistry, medicinal chemistry, *etc.*, various condensation methods have been reported and are widely employed in the syntheses of natural and unnatural molecules that contain carboxylic ester moieties [1–12][1]). In 2007, we developed an effective method for the preparation of carboxylic esters from free carboxylic acids and alcohols by using pyridine-3-carboxylic anhydride (3-PCA), which is easily prepared from inexpensive pyridine-3-carboxylic acid (nicotinic acid), as condensation agent (*Scheme 1*) [13][14]. Fairly broad substrate scope had been accomplished in high yields through the 3-PCA-mediated coupling reactions between free carboxylic acids and alcohols.

We have recently reported the first asymmetric esterification of racemic secondary benzylic alcohols with free carboxylic acids using an aromatic anhydride [15] or bulky

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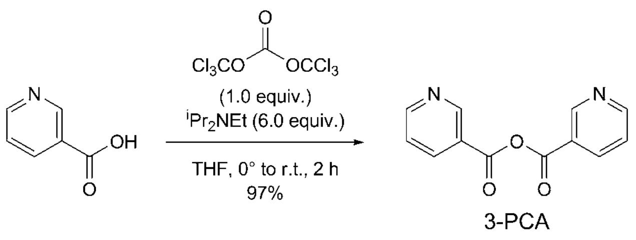
[1]) For reviews on dehydration reactions, see [1]. For DCC (=*N*,*N*′-dicyclohexylcarbodiimide), see [2]. For 2,4,6-trichlorobenzoyl chloride, see [3]. For 2,2′-dipyridyl disulfide/Ph_3P, see [4]. For *O*,*O*′-di(pyridin-2-yl)thiocarbonate (DPTC), see [5]. For di(pyridin-2-yl)carbonate (DPC), see [6]. For 2-methyl-6-nitrobenzoic anhydride (MNBA), see [7]. For 4-(trifluoromethyl)benzoic anhydride (TFBA), see [8]. For 4-nitrobenzoic anhydride/$Sc(OTf)_3$, see [9]. For dithiophen-2-yl carbonate (2-DTC), see [10]. For tetrakis(2-methyl-1*H*-imidazol-1-yl)silane, see [11]. For other condensation reagents, see [12].

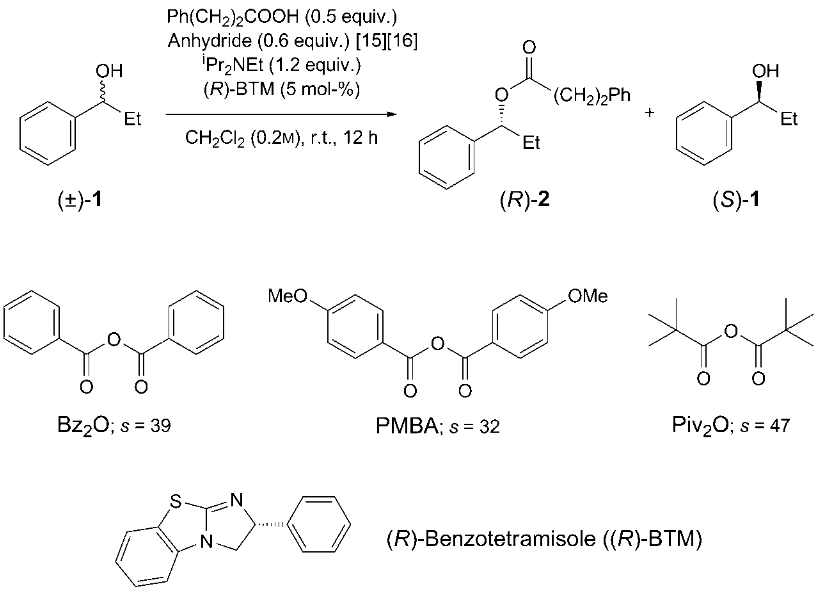
Scheme 1. *Preparation of Pyridine-3-carboxylic Anhydride* (3-PCA)



aliphatic carboxylic anhydride [16] as a coupling reagent by the novel mixed-anhydride formation technology (*Scheme 2*). The chiral induction was realized using the optically active acyl-transfer catalysts, such as (−)-tetramisole (=(−)-2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*][1,3]thiazole) and (*R*)-benzotetramisole (=(2*R*)-2,3-dihydro-2-phenylimidazo[2,1-*b*]benzothiazole; (*R*)-BTM), which were introduced by *Birman* and co-workers [17]. By only mixing racemic alcohols and achiral carboxylic acids with (*R*)-BTM in the presence of benzoic anhydride (Bz_2O), 4-methoxybenzoic anhydride (PMBA), or pivalic anhydride (=2,2-dimethylpropanoic anhydride; Piv_2O) at room temperature, the corresponding chiral carboxylic esters and the unreacted chiral alcohols were obtained in high enantiomeric excesses (ee).

In the present study, we attempted to apply 3-PCA as a new condensation reagent for the enantioselective coupling reaction to provide the chiral esters and alcohols from free carboxylic acids with alcohols *via* kinetic resolution of racemic alcohols[2]).

Scheme 2. *Kinetic Resolution of (±)-***1** *Using* Bz_2O*, PMBA, and* Piv_2O [15][16]



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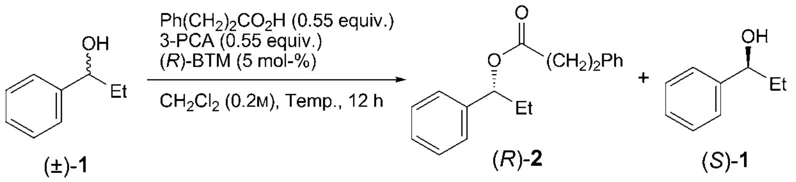
[2]) For a preliminarily communication for the asymmetric esterification using 3-PCA, see [18].

Results and Discussion. – First, we tried to optimize the temperature for the kinetic resolution of the racemic 1-phenylpropan-1-ol ((±)-**1**) with 3-phenylpropanoic acid in the presence of 3-PCA and (*R*)-BTM (*Table 1*). When the reaction was carried out at room temperature, the esterification smoothly proceeded, and the corresponding chiral ester (*R*)-**2** was obtained in good yield (44%) with a high selectivity (90% ee). Nearly half the amount of the unreacted alcohol (*S*)-**1** (46%) was also recovered in good optical purity (80% ee), indicating a very high selectivity factor (*s* value) [19] as shown in *Entry 1* ($s = 47$). It is worth remarking that the reaction could be carried out at 0° to afford the optically active carboxylic ester and alcohol in good yields with the highest selectivities ($s = 63$, *Entry 2*). On the other hand, even lower temperatures were not effective for this kinetic resolution, and both the reactivity and the ee values of the products diminished with the decreasing temperature (*Entries 3* and *4*). The use of a tertiary amine in this reaction is not necessary to obtain good chemical yields of the products, but it works as an inhibitor for providing the chiral carboxylic esters and alcohols with high ee values. For example, the addition of 1.1 equiv. of ethyl(diisopropyl)amine ($^{i}Pr_2NEt$) to the above model reaction under the optimized conditions afforded the lowest selectivity factor ($s = 2$, *Entry 5*).

Table 1. *Temperature Effect for the Kinetic Resolution of (±)-***1**

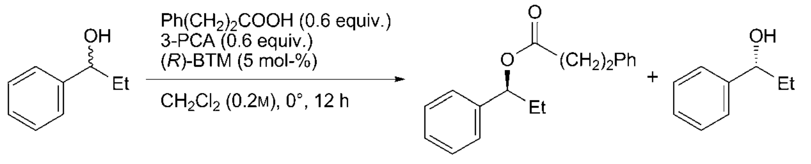


Entry	Temp. [°]	Yield (**2**; **1**) [%]	ee (**2**; **1**) [%]	*s*
1	r.t.	44; 46	90; 80	47
2	0	44; 45	93; 79	63
3	– 23	35; 53	90; 56	35
4	– 45	28; 61	80; 40	12
5[a])	0	38; 54	18; 11	2

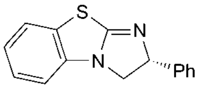
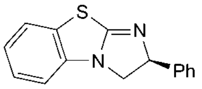
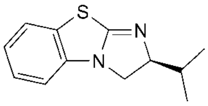
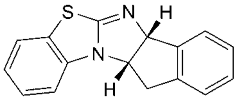
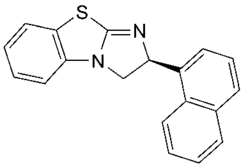
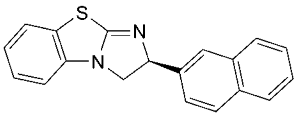
[a]) The reaction was carried out in the presence of 1.1 equiv. of $^{i}Pr_2NEt$ (*cf. Entry 2*).

We next screened a series of chiral acyl-transfer catalysts to examine their structural suitability for the kinetic resolution of racemic (±)-**1** under the above optimized reaction temperature with 0.6 equiv. of 3-phenylpropanoic acid and 3-PCA, respectively (*Table 2*). When the reaction was carried out in the presence of (*R*)- or (*S*)-BTM, we observed the high selectivity in both cases despite the difference of the absolute configuration at C(2) of the catalyst (*Entries 1* and *2*). Other BTM catalysts, such as (*S*)-^{i}Pr-BTM with branched alkyl chain instead of Ph ring at C(2), and fused-type compound, (*R*,*S*)-fused-BTM, afforded the moderate *s* values, respectively (*Entries 3* and *4*). We further applied (*S*)-*α*-Np-BTM (Np = naphthalenyl) and (*S*)-*β*-Np-BTM to the same reaction, and (*S*)-*α*-Np-BTM provided a moderate *s* value; on the contrary, (*S*)-*β*-Np-BTM as an alternative catalyst was found to function as the original BTM (*Entries 5* and *6*).

Table 2. *Catalyst Screening for the Kinetic Resolution of (±)-***1**



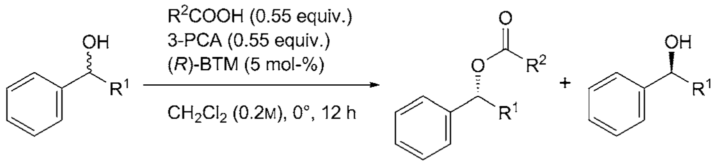
(±)-**1** (*S*)-**2** or (*R*)-**2** (*R*)-**1** or (*S*)-**1**

Entry	Catalyst		Yield		*s*
			Ester **2** [%] (% ee)	Alcohol **1** [%] (% ee)	
1		(*R*)-BTM	45 (– 91)	52 (– 81)	54
2		(*S*)-BTM	44 (91)	47 (85)	57
3		(*S*)-^{i}Pr-BTM	46 (90)	43 (79)	46
4		(*R*,*S*)-fused-BTM	38 (89)	44 (69)	36
5		(*S*)-*α*-Np-BTM	39 (89)	47 (63)	31
6		(*S*)-*β*-Np-BTM	44 (91)	41 (86)	56

We then applied a variety of carboxylic acids for the kinetic resolution of the racemic benzylic alcohols with aliphatic substituents at C(1), *i.e.*, (±)-**3** to extend the utility of this facile method for the asymmetric synthesis. As compiled in *Table 3*, all reactions effectively took place, and a variety of the corresponding (*R*)-carboxylic esters **4** and the unreacted (*S*)-alcohols **3** were obtained with high *s* values ($s = 22-94$) irrespective of the substituents (R^1 = Me, Et; ^{i}Pr, and ^{t}Bu) at C(1) of alcohols (±)-**3**. It was found that both propanoic and 3-phenylpropanoic acids were suitable for all the resolutions of the secondary benzylic alcohols (*Entries 1–4, 10–13*). Several other aliphatic carboxylic acids were further examined for the asymmetric esterification with

1-phenylpropan-1-ol ($R^1 = Et$) and excellent *s* values ($s = 22-50$) were observed (*Entries 5–9*), therefore, the generality of the present advanced kinetic resolution by using 3-PCA for a broad range of substrates was successfully demonstrated. It is also noteworthy that the asymmetric esterification of almost all the substrates listed in *Table 3* produced satisfactory *s* values that were superior to the preceding results which have been achieved by using an aromatic anhydride (Bz_2O or PMBA) [15] or an aliphatic anhydride (Piv_2O) [16] (see *Entries 1–6*, *10*, and *13*).

Table 3. *Kinetic Resolution of (±)-***3** *with Various Carboxylic Acids*



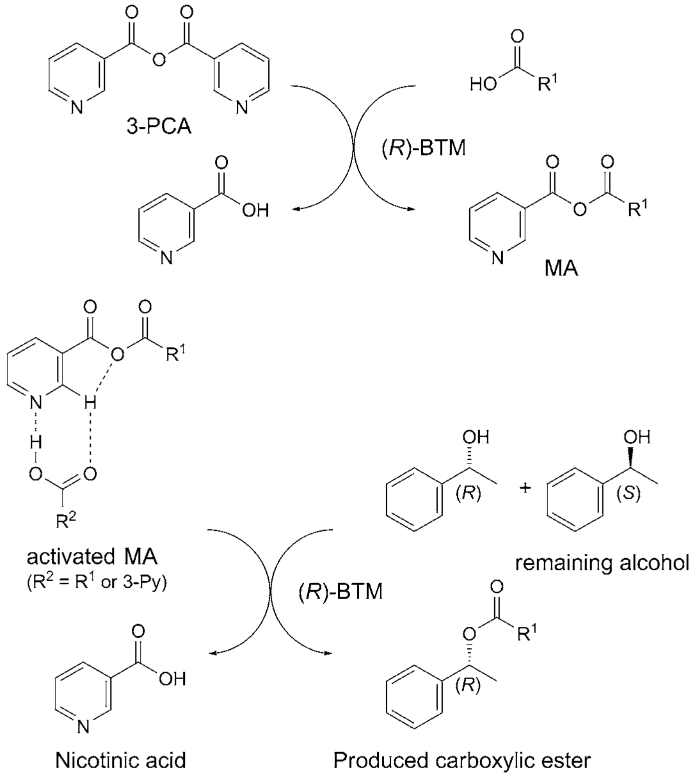
(±)-**3** (*R*)-**4** (*S*)-**3**

Entry	R^1	R^2	Yield (**4**; **3**) [%]	ee (**4**; **3**) [%]	*s*	*s*[a])	*s*[b])	*s*[c])
1	Me	Et	35; 41	91; 63	42	–	–	26
2	Me	$Ph(CH_2)_2$	41; 42	91; 71	45	–	–	33
3	Et	Et	40; 55	93; 64	56	38	39	43
4	Et	$Ph(CH_2)_2$	44; 45	93; 79	63	46	43	47
5	Et	$Ph(CH_2)_3$	44; 51	93; 57	49	31	39	41
6	Et	$Me_2CH(CH_2)_2$	43; 50	92; 70	50	22	23	40
7	Et	$CH_2{=}CHCH_2CH_2$	43; 54	91; 55	38	28	42	39
8	Et	$MeOCH_2$	45; 50	82; 70	22	14	15	26
9	Et	Cyclohexyl (c-C_6H_{11})	36; 59	93; 59	50	8	12	73
10	^iPr	Et	40; 53	95; 69	84	34	47	53
11	^iPr	$Ph(CH_2)_2$	45; 55	91; 73	49	33	46	1580
12	^tBu	Et	22; 78	93; 25	36	20	42	101
13	^tBu	$Ph(CH_2)_2$	37; 63	96; 55	94	22	88	81

[a]) The *s* value when using Bz_2O at room temperature [15]. [b]) The *s* value when using PMBA at room temperature [15]. [c]) The *s* value when using Piv_2O at room temperature [16].

Usually, it is necessary to employ tertiary amines, such as Et_3N and $^iPr_2NEt$, for the rapid formation of the mixed-anhydride (MA) derived from the carboxylic anhydrides and carboxylic acids, and for the completed production of the desired carboxylic esters from the intermediary MA with alcohols *via* transacylation in the effective ester synthesis. However, the kinetic resolution of the racemic alcohols with achiral carboxylic acids using 3-PCA and (*R*)-BTM does not require the presence of the tertiary amines. The proposed reaction pathway is depicted in *Scheme 3*. First, 3-PCA was activated by (*R*)-BTM to react with carboxylic acids (R^1CO_2H), and then the corresponding MA was gradually produced during the reaction. The formed MA has a (pyridin-3-yl)oxy moiety which has a strong negative electronic charge on the aromatic ring, so that N-atom in the pyridine ring coordinates with the protic parts of the starting aliphatic carboxylic acids or nicotinic acid generated from 3-PCA *in situ*. The successive nucleophilic substitution of the (pyridin-3-yl)oxy moiety with (*R*)-BTM, followed by

Scheme 3. *Proposed Reaction Pathway of the Kinetic Resolution*



the exchange with the chiral (*R*)-type alcohol in the racemic mixture, afforded the desired (*R*)-carboxylic esters and the recovery of the unreacted (*S*)-alcohol with high enantioselectivities. It is postulated that the higher activity of the MA in this new reaction system provided the favorable transacylation process for the synthesis of the desired chiral compounds without using tertiary amines.

The stable structures of MA (*i.e.*, **A**) generated from AcOH and nicotinic acid, and the activated MA (*i.e.*, **B** or **C**) with AcOH or nicotinic acid were determined by the theoretical calculation at the B3LYP/6-31G*//B3LYP/6-31G* level after searching all conformations of the molecules as depicted in *Fig. 1* [20]. It was found that the LUMO energy of **A** (– 1.95 eV) was significantly lowered by the coordination of the N-atom of the pyridine ring to the protic source of free carboxylic acids to give the strongly activated species **B** (LUMO energy –2.14 eV) and **C** (LUMO energy –2.24 eV). These results explain that the activation of **B** and **C** with (*R*)-BTM easily occurs in the absence of any base, such as tertiary amines, to afford the desired chiral carboxylic esters through the facile acyl-transfer reaction under the relatively lower temperature. We have already observed that tertiary amines can promote the reaction of carboxylic anhydrides with alcohols *via* another reaction pathway to produce the racemic materials; therefore, the present 3-PCA-mediated asymmetric esterification without

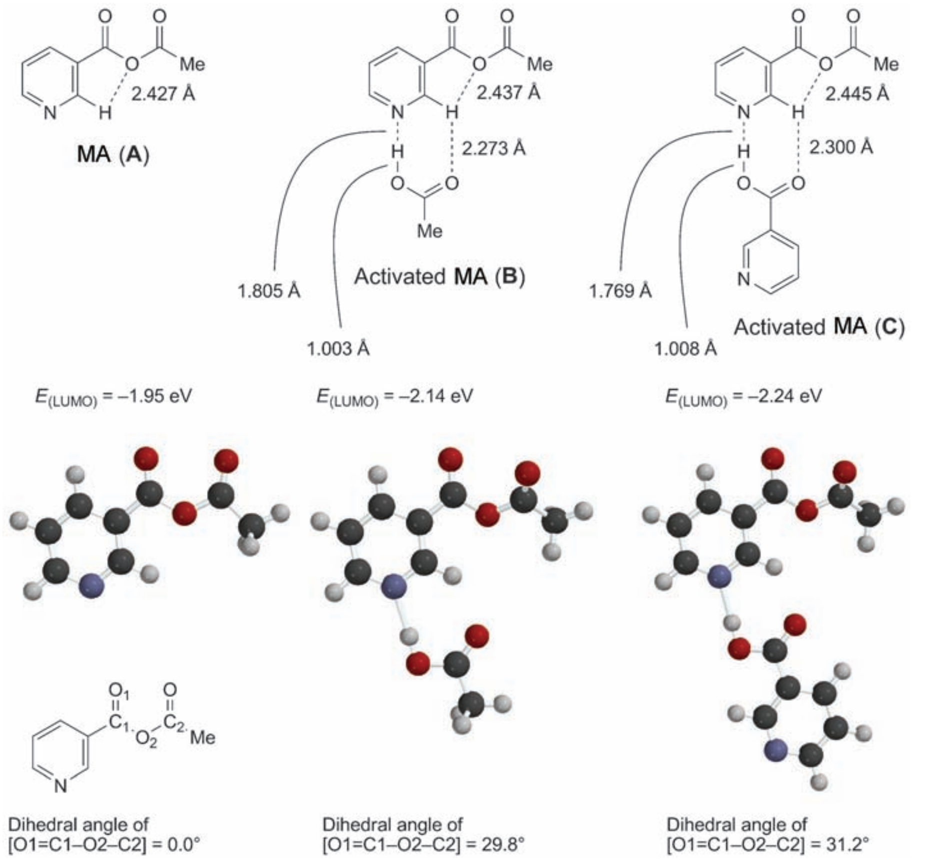


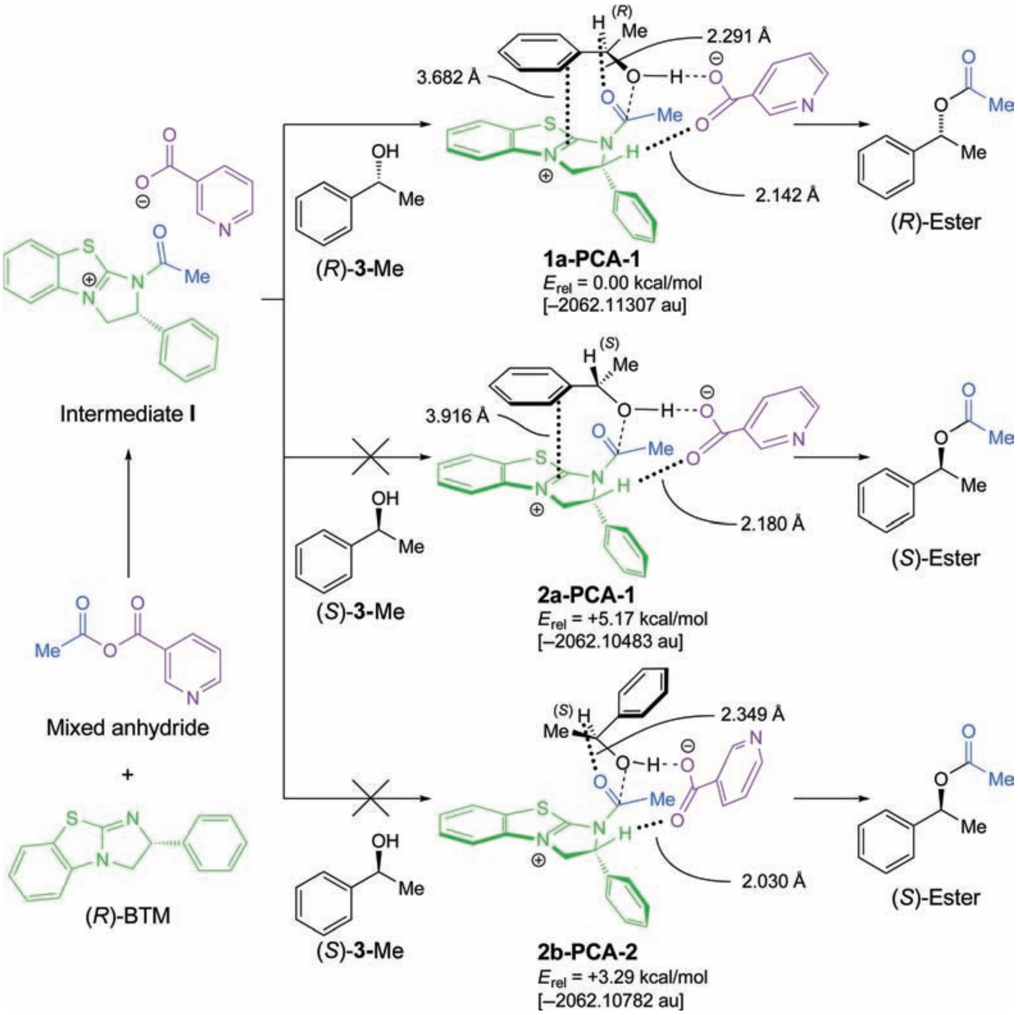
Fig. 1. *The Most Stable Structures and LUMO Energy Values of Mixed Anhydride* (**A**)*, and Activated Mixed Anhydrides* **B** *and* **C**. Calculated at B3LYP/6-31G*//B3LYP/6-31G* level after global conformational analysis

using any base is ultimately preferable to afford the desirable chiral carboxylic esters and secondary benzylic alcohols with high ee values.

Determination of the transition structures to form the optically active (*R*)-esters from racemic alcohol (±)-**3**-Me, (*R*)-BTM, and 3-PCA was carried out using DFT calculations at the B3LYP/6-31G*//B3LYP/6-31G* level of theory according to the previous studies of the kinetic resolution of the racemic alcohols [21]. Among the several calculated transition states forming the desired (*R*)-ester from (*R*)-alcohol, the most stable structure **1a-PCA-1** is depicted in *Scheme 4*. The *Cartesian* coordinates of the three-dimensional structures of these transition structures are given in the *Exper. Part*.

The high selectivity attained in the present kinetic resolution could be explained by the rapid transformation of (*R*)-alcohol into (*R*)-ester *via* this stabilized transition structures consisting of the nucleophile **3**-Me and intermediate **I** derived from the MA and (*R*)-BTM. A frequency analysis of **1a-PCA-1** revealed that the nucleophilic attack

Scheme 4. *Transition Structure* **1a-PCA-1** *Derived from (*R*)-***3***-Me with the Intermediary Zwitterionic Species* (Intermediate **I**)



of OH group of the alcohol to C=O moiety and deprotonation of alcohol with the pivalate anion proceeded *via* a concerted reaction mechanism, because the C–O bond-forming step and O–H bond-cleaving process occurred synchronously. The conformation of **1a-PCA-1** is stabilized by three attractive interactions: *i*) the H-bonding between the O-atom of the acyl donor moiety and H-atom at the benzylic position in (*R*)-alcohol (2.291 Å), *ii*) the H-bonding between O-atom of carboxylate anion in nicotinic acid and H-atom at the benzylic position in (*R*)-BTM (2.142 Å), *iii*) weak attractive interaction between aryl group of the alcohol and the positive electronic charge on the face of the dihydroimidazolium salt (3.682 Å). These interactions decrease the relative energy of **1a-PCA-1**, promoting the transformation of (*R*)-

alcohols to (R)-esters. On the other hand, several transition structures derived from (S)-alcohol and the intermediate **I** to produce (S)-ester were found, and representative transition structures are depicted in *Scheme 4*. In the structure **2a-PCA-1**, complexation of (S)-alcohol including (R)-BTM produced an unstable transition structure to afford the corresponding (S)-ester *via* a similar transacylation process. The interaction of O-atom in the acyl donor moiety with the H-atom at the benzylic position in (S)-alcohol is not observed in the structure **2a-PCA-1**; therefore, the relative energy of **2a-PCA-1** increases considerably ($E_{rel} = +5.17$ kcal/mol) compared with the value of the stable transition state **1a-PCA-1** ($E_{rel} = 0.00$ kcal/mol). Moreover, we found another transition structure, **2b-PCA-2**, that was stabilized by the attractive interaction between the O-atom in the acyl donor moiety and H-atom at the benzylic position in (S)-alcohol (2.349 Å); however, there is no π-cation attractive interaction between the aryl group of the alcohol and the positive electronic charge on the face of the dihydroimidazolium salt. The relative energy of the **2b-PCA-2** ($E_{rel} = +3.29$ kcal/mol) is lower than that of **2a-PCA-1** ($E_{rel} = +5.17$ kcal/mol) because the H-bondings efficiently decrease the energy of the former transition structure. As a result, the large energy gap between the two transition structures **1a-PCA-1** and **2b-PCA-2** ($E_{rel} = +3.29$ kcal/mol) causes the high enantioselectivity observed. All transition structures, including pyridine ring rotamer conformations, are collected in *Fig. 2*.

Conclusions. – We have developed a new chiral induction protocol for the asymmetric esterification of racemic secondary benzylic alcohols with achiral carboxylic acids by using 3-PCA in the presence of (R)-BTM under mild conditions. A variety of chiral carboxylic esters were prepared by the kinetic resolution of racemic alcohols with various achiral carboxylic acids under mild conditions through facile experimental procedure. It was found that 3-PCA could be utilized as an efficient coupling reagent to produce the chiral carboxylic esters and alcohols in the total absence of tertiary amines, such as Et_3N and $^iPr_2NEt$. The high reactivity of the mixed anhydride (MA) generated from 3-PCA with carboxylic acid promoted the appropriate transformation on the acylated compounds to give the desired chiral products. Further studies of the synthesis of newly designed condensation reagents to achieve the effective asymmetric MA method affording useful molecules are now in progress.

This study was partially supported by a Research Grant from the *Center for Chirality* and *Grants-in-Aid for Scientific Research* from the Ministry of Education, Science, Sports and Culture, Japan.

Experimental Part

General. All reactions were carried out under Ar in dried glassware. CH_2Cl_2 was distilled from P_2O_5 and then CaH_2, and dried over 4-Å molecular sieves (MS); benzene and toluene were distilled from P_2O_5, and dried over 4-Å MS, and THF and Et_2O were distilled from Na/benzophenone immediately prior to use. All reagents were purchased from *Tokyo Kasei Kogyo Co., Ltd.*, *Kanto Chemical Co., Inc.*, or *Aldrich Chemical Co., Inc.*, and used without further purification unless otherwise noted. TLC: *Wakogel B5F.* ^1H- and ^{13}C-NMR spectra: *JEOL AL-300* for ^1H and ^{13}C at 300 and 75 MHz, resp.; *JEOL LA-500* for ^1H and ^{13}C at 500 and 125 MHz, resp.; with tetramethylsilane (TMS) or $CDCl_3$ as internal standard.

General Procedure for the Asymmetric Esterification of Racemic 1-Phenylpropan-1-ol ((±)-**1**) *with 3-Phenylpropanoic Acid by Using 3-PCA in the Presence of (*R*)-BTM* (*Table 1*, *Entry 2; Table 3*, *Entry 4*):

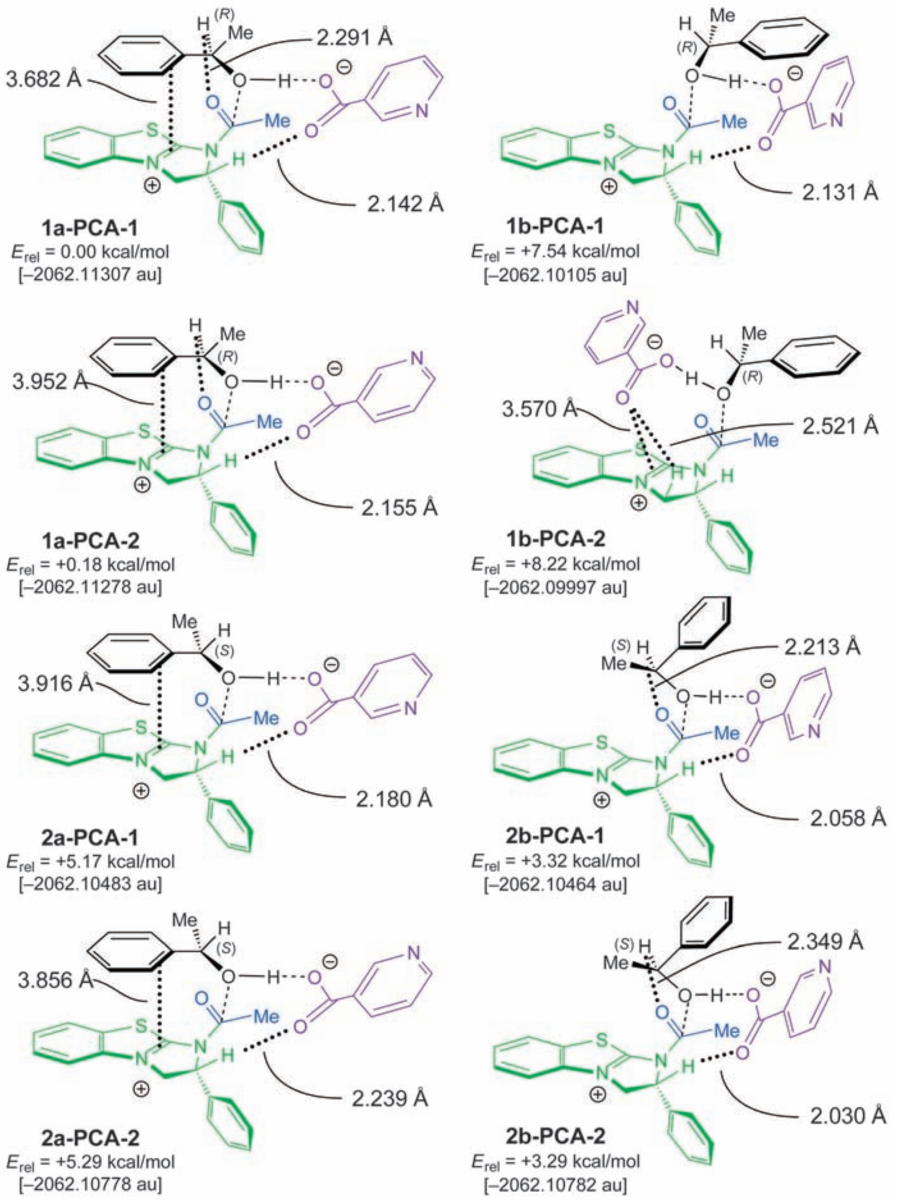


Fig. 2. *Transition Structures* **1a-PCA-1**, **1a-PCA-2**, **1b-PCA-1**, *and* **1b-PCA-2** *Derived from* (R)-**3**-*Me, and* **2a-PCA-1**, **2a-PCA-2**, **2b-PCA-1**, *and* **2b-PCA-2** *Derived from* (S)-**3**-*Me with the Intermediary Zwitterionic Species* (Intermediate **I**)

To a soln. of 3-phenylpropanoic acid (24.7 mg, 0.164 mmol), 3-PCA (37.8 mg, 0.166 mmol), and (*R*)-BTM (3.8 mg, 0.015 mmol) in CH_2Cl_2 (1.5 ml) at 0° was added racemic *1-phenylpropan-1-ol* ((±)-**1**; 40.8 μl, 0.300 mmol). After stirring the mixture for 12 h at 0°, sat. aq. $NaHCO_3$ was added at 0°. The org.

layer was separated, and the aq. layer was extracted with Et_2O. The combined org. layer was dried (Na_2SO_4). After filtration of the mixture and evaporation of the solvent, the crude product was purified by prep. TLC on silica to afford the corresponding optically active ester (*R*)-**2** (35.2 mg, 44%, 93% ee) and the unreacted optically active alcohol (*S*)-**1** (18.5 mg, 45%, 79% ee). $s = 63.1$.

Optically Active Alcohols. (S)*-1-Phenylethanol* (*Table 3*, *Entry 1*). HPLC (*CHIRALCEL OD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 28.1 (14.3%), 34.3 min (85.7%). ^{1}H-NMR ($CDCl_3$): 7.41 – 7.23 (*m*, 5 arom. H); 4.88 (*q*, *J* = 6.5, H–C(1)); 1.90 (br. *s*, OH); 1.48 (*d*, *J* = 6.5, Me(2)). ^{13}C-NMR ($CDCl_3$): 145.8; 128.5; 127.4; 125.3; 70.4; 25.1.

(S)*-1-Phenylpropan-1-ol* [22] (*Table 3*, *Entry 4*). HPLC (*CHIRALCEL OD-H*; iPrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 26.5 (10.4%), 30.4 min (89.6%). ^{1}H-NMR ($CDCl_3$): 7.12 – 6.96 (*m*, 5 arom. H); 4.31 (*dt*, *J* = 3.0, 6.6, H–C(1)); 1.79 (*d*, *J* = 3.0, OH); 1.64 – 1.38 (*m*, CH_2(2)); 0.65 (*t*, *J* = 7.5, Me(3)). ^{13}C-NMR ($CDCl_3$): 144.5; 128.3; 127.4; 125.9; 75.9; 31.8; 10.1.

*(1*S*)-2-Methyl-1-phenylpropan-1-ol* (*Table 3*, *Entry 10*). HPLC (*CHIRALCEL OD-Hx2*; ^{i}PrOH/hexane 1:9; flow rate, 0.5 ml/min): t_R 21.6 (84.7%), 24.5 min (15.3%). IR (neat): 3398, 3029, 1604, 1492, 760, 701. ^{1}H-NMR ($CDCl_3$): 7.31 – 7.15 (*m*, 5 arom. H); 4.27 (*dd*, *J* = 6.6, 3.0, H–C(1)); 1.95 – 1.79 (*m*, H–C(2), OH); 0.92 (*d*, *J* = 6.6, Me); 0.72 (*d*, *J* = 6.6, Me). ^{13}C-NMR ($CDCl_3$): 143.6; 128.1; 127.4; 126.5; 80.0; 35.2; 19.0; 18.2. HR-MS: 173.0930 ($[M + Na]^+$, $C_{10}H_{14}NaO^+$; calc. 173.0937).

*(1*S*)-2,2-Dimethyl-1-phenylpropan-1-ol* [23] (*Table 3*, *Entry 13*). HPLC (*CHIRALCEL OD-H*; iPrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 19.7 (77.3%), 24.1 min (22.7%). ^{1}H-NMR ($CDCl_3$): 7.26 – 7.13 (*m*, 5 arom. H); 4.30 (*d*, *J* = 2.7, H–C(1)); 1.78 (br. *s*, OH); 0.83 (*s*, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): 142.1; 127.6; 127.5; 127.2; 82.4; 35.6; 25.9.

*Optically Active Esters. (1*R*)-1-Phenylethyl Propanoate* (*Table 3*, *Entry 1*). HPLC (*CHIRALPAK AS-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.3 ml/min): t_R 15.1 (95.7%), 16.5 min (4.3%). IR (neat): 2985, 1736, 1450, 1188, 756, 702. ^{1}H-NMR ($CDCl_3$): 7.37 – 7.24 (*m*, 5 arom. H); 5.89 (*q*, *J* = 6.4, H–C(1′)); 2.35 (*qd*, *J* = 15.8, 7.6, 1 H, CH_2(2)); 2.33 (*qd*, *J* = 15.8, 7.6, 1 H, CH_2(2)); 1.53 (*d*, *J* = 6.4, Me(2′)); 1.13 (*t*, *J* = 7.6, Me(3)). ^{13}C-NMR ($CDCl_3$): 173.6; 141.9; 128.4; 127.7; 126.0; 72.0; 27.9; 22.2; 9.0. HR-MS: 201.0883 ($[M + Na]^+$, $C_{11}H_{14}NaO_2^+$; calc. 201.0886).

*(1*R*)-1-Phenylethyl 3-Phenylpropanoate* (*Table 3*, *Entry 2*). HPLC (*CHIRALCEL OD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.3 ml/min): t_R 24.1 (4.6%), 25.5 min (95.4%). IR (neat): 2978, 1736, 1597, 1442, 1157, 756, 702. ^{1}H-NMR ($CDCl_3$): 7.35 – 7.14 (*m*, 10 arom. H); 5.88 (*q*, *J* = 6.4, H–C(1′)); 2.94 (*t*, *J* = 8.0, CH_2(2)); 2.66 (*ddd*, *J* = 16.2, 7.6, 7.6, 1 H, CH_2(3)); 2.62 (*ddd*, *J* = 16.2, 7.6, 7.6, 1 H, CH_2(3)); 1.49 (*d*, *J* = 6.4, Me(2′)). ^{13}C-NMR ($CDCl_3$): 172.1; 141.6; 140.4; 128.4; 128.4; 128.3; 127.8; 126.2; 126.0; 72.3; 36.1; 30.9; 22.1. HR-MS: 277.1195 ($[M + Na]^+$, $C_{17}H_{18}NaO_2^+$; calc. 277.1199).

*(1*R*)-1-Phenylpropyl Propanoate* (*Table 3*, *Entry 3*). HPLC (*CHIRALCEL OJ-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 18.3 (96.6%), 23.1 min (3.4%). IR (neat): 3034, 1734, 1604, 1495, 756, 700. ^{1}H-NMR ($CDCl_3$): 7.30 – 7.16 (*m*, 5 arom. H); 5.60 (*dd*, *J* = 7.5, 6.6, H–C(1′)); 2.34 – 2.22 (*m*, 1 H, CH_2(2)); 1.93 – 1.65 (*m*, 1 H, CH_2(2)); 1.06 (*t*, *J* = 7.5, Me(3)); 0.81 (*t*, *J* = 7.5, Me(3′)). ^{13}C-NMR ($CDCl_3$): 173.8; 140.7; 128.3; 127.7; 126.5; 77.1; 29.4; 27.8; 9.9; 9.1. HR-MS: 215.1049 ($[M + Na]^+$, $C_{12}H_{16}NaO_2^+$; calc. 215.1043).

*(1*R*)-1-Phenylpropyl 3-Phenylpropanoate* (*Table 3*, *Entry 4*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 13.8 (96.3%), 19.3 min (3.7%). IR (neat): 3031, 1741, 1604, 1496, 752, 700. ^{1}H-NMR ($CDCl_3$): 7.27 – 7.14 (*m*, 7 arom. H); 7.13 – 7.07 (*m*, 3 arom. H); 5.59 (*t*, *J* = 7.0, H–C(1′)); 2.87 (*t*, *J* = 8.0, CH_2(2)); 2.61 (*ddd*, *J* = 16.0, 9.0, 9.0, 1 H, CH_2(3)); 2.57 (*ddd*, *J* = 16.0, 9.6, 9.0, 1 H, CH_2(3)); 1.86 – 1.66 (*m*, CH_2(2′)); 0.76 (*t*, *J* = 7.5, Me(3′)). ^{13}C-NMR ($CDCl_3$): 172.2; 140.48; 140.46; 128.4; 128.3; 128.2; 127.7; 126.5; 126.2; 77.4; 36.1; 30.9; 29.3; 9.8. HR-MS: 291.1344 ($[M + Na]^+$, $C_{18}H_{20}NaO_2^+$; calc. 291.1356).

*(1*R*)-1-Phenylpropyl 4-Phenylbutanoate* (*Table 3*, *Entry 5*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 11.8 (96.5%), 14.2 min (3.5%). IR (neat): 3030, 1734, 1603, 1496, 749, 700. ^{1}H-NMR ($CDCl_3$): 7.23 – 6.99 (*m*, 10 arom. H); 5.60 (*t*, *J* = 7.0, H–C(1′)); 2.53 (*t*, *J* = 7.5, 1 H, CH_2(2)); 2.29 (*dt*, *J* = 16.2, 7.5, 1 H, CH_2(4)); 2.24 (*dt*, *J* = 16.2, 6.6, 1 H, CH_2(4)); 1.93 – 1.65 (*m*, 1 H of CH_2(2), CH_2(3)); 0.80 (*t*, *J* = 7.5, Me(3′)). ^{13}C-NMR ($CDCl_3$): 172.7; 141.4; 140.6; 128.4; 128.3; 128.3; 127.7; 126.5; 125.9; 77.2; 35.0; 33.8; 29.3; 26.5; 9.9. HR-MS: 305.1507 ($[M + Na]^+$, $C_{19}H_{22}NaO_2^+$; calc. 305.1512).

*(1*R*)-1-Phenylpropyl 4-Methylpentanoate* (*Table 3*, *Entry 6*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 8.2 (95.9%), 9.9 min (4.1%). IR (neat): 3033, 1742, 1604, 1495, 757, 700. ^{1}H-NMR (CDCl$_3$): 7.31–7.13 (*m*, 5 arom. H); 5.59 (*t*, J = 7.5, H–C(1')); 2.33–2.17 (*m*, CH$_2$(2)); 1.93–1.63 (*m*, CH$_2$(2')); 1.52–1.36 (*m*, CH$_2$(3), H–C(4)); 0.88–0.73 (*m*, 3 Me). ^{13}C-NMR (CDCl$_3$): 173.3; 140.7; 128.3; 127.7; 126.5; 77.0; 33.7; 32.6; 29.3; 27.6; 22.19; 22.15; 9.9. HR-MS: 257.1509 ([M+Na]$^+$, $C_{15}H_{22}NaO_2^+$; calc. 257.1512).

*(1*R*)-1-Phenylpropyl Pent-4-enoate* (*Table 3*, *Entry 7*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 8.9 (95.7%), 10.7 min (4.3%). IR (neat): 3033, 1735, 1642, 1495, 755, 700. ^{1}H-NMR (CDCl$_3$): 7.27–7.15 (*m*, 5 arom. H); 5.76–5.67 (*m*, H–C(4)); 5.60 (*t*, J = 7.5, H–C(1')); 4.98–4.86 (*m*, CH$_2$(5)); 2.39–2.25 (*m*, CH$_2$(2), CH$_2$(3)); 1.89–1.68 (*m*, CH$_2$(2')); 0.80 (*t*, J = 7.5, Me(3')). ^{13}C-NMR (CDCl$_3$): 172.3; 140.5; 136.6; 128.3; 127.7; 126.5; 115.4; 77.2; 33.7; 29.3; 28.8; 9.9. HR-MS: 241.1207 ([M+Na]$^+$, $C_{14}H_{18}NaO_2^+$; calc. 241.1199).

*(1*R*)-1-Phenylpropyl 2-Methoxyacetate* (*Table 3*, *Entry 8*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:9; flow rate, 0.5 ml/min): t_R 9.3 (91.2%), 10.7 min (8.8%). IR (neat): 3033, 1756, 1496, 755, 701. ^{1}H-NMR (CDCl$_3$): 7.33–7.16 (*m*, 5 arom. H); 5.71 (*t*, J = 7.0, H–C(1')); 4.02 (*d*, J = 16.4, 1 H, CH$_2$(2)); 3.94 (*d*, J = 16.4, 1 H, CH$_2$(2)); 3.36 (*s*, MeO); 1.93–1.69 (*m*, CH$_2$(2')); 0.82 (*t*, J = 7.5, Me(3')). ^{13}C-NMR (CDCl$_3$): 169.7; 139.9; 128.4; 128.0; 126.6; 77.8; 69.9; 59.3; 29.2; 9.9. HR-MS: 231.0997 ([M+Na]$^+$, $C_{12}H_{16}NaO_3^+$; calc. 231.0992).

*(1*R*)-1-Phenylpropyl Cyclohexanecarboxylate* (*Table 3*, *Entry 9*). HPLC (*CHIRALCEL OJ-H*; ^{i}PrOH/hexane *1:50*; flow rate, 0.5 ml/min): t_R 10.1 (96.5%), 12.2 min (3.5%). IR (neat): 3032, 1736, 1450, 756, 702. ^{1}H-NMR (CDCl$_3$): 7.36–7.22 (*m*, 5 arom. H); 5.66 (*dd*, J = 7.2, 6.2, H–C(1')); 2.33 (*tt*, J = 11.3, 3.6, 1 H, CH$_2$(2)); 1.99–1.15 (*m*, CH$_2$(2'), c-Hex); 0.88 (*t*, J = 7.6, Me(3')). ^{13}C-NMR (CDCl$_3$): 175.3; 140.9; 128.3; 127.6; 126.3; 76.7; 43.3; 29.5; 29.0; 28.9; 25.7; 25.42; 25.39; 9.9. HR-MS: 269.1525 ([M+Na]$^+$, $C_{16}H_{22}NaO_2^+$; calc. 269.1512).

*(1*R*)-2-Methyl-1-phenylpropyl Propanoate* (*Table 3*, *Entry 10*). HPLC (*CHIRALCEL OJ-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 13.1 (97.6%), 16.2 min (2.4%). IR (neat): 3033, 1739, 1605, 1495, 739, 701. ^{1}H-NMR (CDCl$_3$): 7.39–7.13 (*m*, 5 arom. H); 5.40 (*d*, J = 7.5, H–C(1')); 2.37–2.18 (*m*, CH$_2$(2)); 2.09–1.93 (*m*, H–C(2')); 1.06 (*t*, J = 7.5, Me(3)); 0.89 (*d*, J = 6.6, Me); 0.72 (*d*, J = 6.6, Me). ^{13}C-NMR (CDCl$_3$): 173.6; 139.8; 128.1; 127.6; 126.9; 80.6; 33.5; 27.8; 18.7; 18.4; 9.1. HR-MS: 229.1200 ([M+Na]$^+$, $C_{13}H_{18}NaO_2^+$; calc. 229.1199).

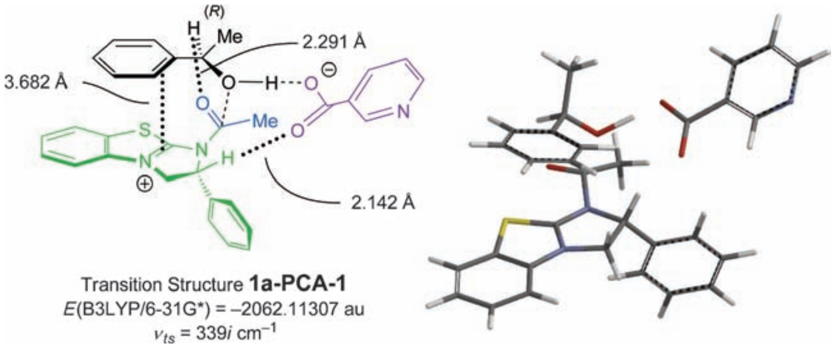
*(1*R*)-2-Methyl-1-phenylpropyl 3-Phenylpropanoate* (*Table 3*, *Entry 11*). HPLC (*CHIRALPAK AD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 11.1 (95.7%), 15.6 min (4.3%). IR (neat): 3030, 1734, 1604, 1496, 751, 699. ^{1}H-NMR (CDCl$_3$): 7.28–7.02 (*m*, 10 arom. H); 5.41 (*d*, J = 7.5, H–C(1')); 2.88 (*t*, J = 7.5, CH$_2$(2)); 2.65–2.53 (*m*, CH$_2$(3)); 2.07–1.83 (*m*, H–C(2')); 0.85 (*d*, J = 7.0, Me); 0.70 (*d*, J = 7.0, Me). ^{13}C-NMR (CDCl$_3$): 172.1; 140.4; 139.6; 128.4; 128.2; 128.1; 127.6; 127.0; 126.2; 81.0; 36.0; 33.4; 30.9; 18.6; 18.4. HR-MS: 305.1520 ([M+Na]$^+$, $C_{19}H_{22}NaO_2^+$; calc. 305.1512).

*(1*R*)-2,2-Dimethyl-1-phenylpropyl Propanoate* (*Table 3*, *Entry 12*). HPLC (*CHIRALCEL OD-H*; ^{i}PrOH/hexane 1:50; flow rate, 0.5 ml/min): t_R 15.3 (96.6%), 23.7 min (3.4%). IR (neat): 3033, 1740, 1495, 738, 702. ^{1}H-NMR (CDCl$_3$): 7.37–7.23 (*m*, 5 arom. H); 5.51 (*s*, H–C(1)); 2.56–2.30 (*m*, CH$_2$(2)); 1.17 (*t*, J = 7.5, Me(3)); 0.94 (*s*, ^{t}Bu). ^{13}C-NMR (CDCl$_3$): 173.4; 138.6; 127.7; 127.5; 127.4; 82.5; 35.0; 27.9; 26.0; 9.2. HR-MS: 234.1354 ([M+Na]$^+$, $C_{14}H_{20}NaO_2^+$; calc. 234.1356).

*(1*R*)-2,2-Dimethyl-1-phenylpropyl 3-phenylpropanoate* (*Table 3*, *Entry 13*). HPLC (*CHIRALPAK IC*; ^{i}PrOH/hexane 1:100; flow rate, 0.5 ml/min): t_R 13.1 (98.2%), 17.6 min (1.8%). IR (neat): 3030, 1737, 1604, 1496, 740, 702. ^{1}H-NMR (CDCl$_3$): 7.40–7.17 (*m*, 10 arom. H); 5.53 (*s*, H–C(1')); 3.00 (*t*, J = 7.5, CH$_2$(2)); 2.79–2.68 (*m*, CH$_2$(3)); 0.93 (*s*, ^{t}Bu). ^{13}C-NMR (CDCl$_3$): 172.0; 140.4; 138.4; 128.5; 128.2; 127.7; 127.6; 127.4; 126.2; 82.9; 36.0; 35.0; 30.9; 26.0. HR-MS: 319.1660 ([M+Na]$^+$, $C_{20}H_{24}NaO_2^+$; calc. 319.1669).

All calculations were performed with the program package Spartan '10 1.1.0 of *Wavefunction Inc.* (http://www.wavefun.com). All structures were optimized and subjected to frequency analysis with the B3LYP/6-31G* method, followed by single point B3LYP/6-31G* calculation to provide the thermodynamic properties. The structures and the cartesian coordinates are collected in *Tables 4–11* for the transition structures **1a-PCA-1**, **1b-PCA-1**, **1a-PCA-2**, **1b-PCA-2**, **2a-PCA-1**, **2b-PCA-1**, **2a-PCA-2**, and **2b-PCA-2**, resp.

Table 4. Cartesian *Coordinates* [Å] *for the Transtion Structure* **1a-PCA-1**[a])

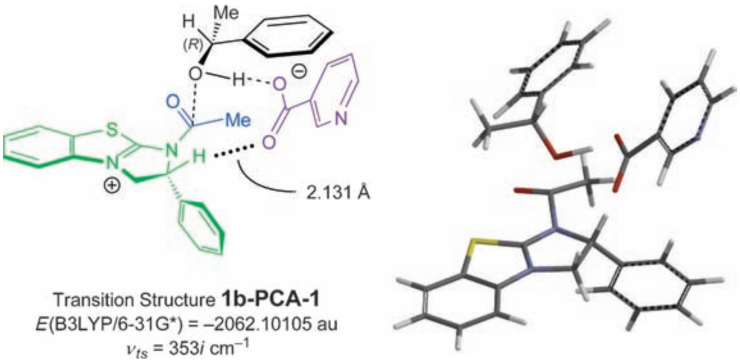


Transition Structure **1a-PCA-1**
E(B3LYP/6-31G*) = –2062.11307 au
ν_{ts} = 339i cm^{-1}

Cartesian coordinates [Å]			
Atom	*X*	*Y*	*Z*
6	– 0.306855969	0.567467087	2.300287838
6	0.992468813	1.189023783	2.752949714
1	1.342255822	0.623209481	3.617385387
1	1.764758029	1.181963142	1.983071968
1	0.802625416	2.225700615	3.056504004
8	– 1.195893441	0.216456461	3.076797741
7	– 0.815222973	1.066479151	0.995416071
6	– 2.076775047	0.848177577	0.668141184
7	– 2.333705881	1.036945210	– 0.636427758
6	– 1.093307918	1.295958045	– 1.378470173
6	– 0.026807673	1.413486959	– 0.229164976
6	0.613079698	2.786916313	– 0.155722310
6	1.907979912	2.954617712	– 0.661821290
6	2.502867785	4.217914147	– 0.660155265
6	1.814731839	5.318957162	– 0.149205668
6	0.524679931	5.155161478	0.361423516
6	– 0.074458725	3.895844773	0.354919647
1	– 1.075615702	3.774104839	0.762133543
1	– 0.013989182	6.007214483	0.767623003
1	2.282203149	6.299953148	– 0.142828301
1	3.509628254	4.337753922	– 1.051280855
1	2.443371801	2.090349659	– 1.046352879
1	0.741273695	0.647839230	– 0.361304291
1	– 0.885258308	0.454391825	– 2.045763427
1	– 1.175194685	2.220742693	– 1.954783792
8	0.532863788	– 1.031056403	1.506175756
6	– 0.223066050	– 2.198560668	1.695973952
6	– 0.966155310	– 2.614841677	0.423354273
6	– 2.182236971	– 3.306338712	0.505904593
6	– 2.861013311	– 3.710126107	– 0.645600131
6	– 2.331456437	– 3.425392578	– 1.905755603
6	– 1.119242588	– 2.737841115	– 2.000862055
6	– 0.442901430	– 2.332628562	– 0.846948068
1	0.498664414	– 1.796685623	– 0.927678350
1	– 0.691270492	– 2.523351917	– 2.977948912
1	– 2.857108121	– 3.739386807	– 2.804119015
1	– 3.804717283	– 4.243712238	– 0.558967640
1	– 2.603215205	– 3.527192509	1.485288468
1	– 0.979829133	– 1.981264596	2.468513237
6	0.657407561	– 3.347271148	2.223048588
1	1.151082210	– 3.035351637	3.149796649
1	0.056634334	– 4.240654261	2.429147908
1	1.429418478	– 3.613987366	1.493342332
1	1.806359991	– 1.157593784	1.240016576
8	2.913267131	– 1.267800313	1.040005523
6	3.274302101	– 0.875133810	– 0.149937315
8	2.531583220	– 0.346398742	– 0.990012055
16	– 3.453643879	0.365576608	1.598094456
6	– 3.656462749	0.815607326	– 1.011742745
6	– 4.435564926	0.453983717	0.102693779
6	– 5.792112939	0.184554012	– 0.044621447
1	– 6.398346013	– 0.099687547	0.810326773
6	– 6.355888156	0.283967947	– 1.318921993
1	– 7.413338519	0.076839189	– 1.451193783
6	– 5.574151081	0.643358796	– 2.423595081
1	– 6.030430347	0.711081857	– 3.406462884
6	– 4.212689244	0.915094655	– 2.285413233
1	– 3.603190811	1.189492978	– 3.140592811
6	4.723097645	– 1.111638267	– 0.461514447
6	5.597229979	– 1.698061300	0.458968684
1	5.225579163	– 1.990307125	1.435447090
6	6.925705741	– 1.891514172	0.090050598
1	7.638892281	– 2.343895748	0.773153925
6	7.327147578	– 1.491380227	– 1.186154410
1	8.359208037	– 1.629565805	– 1.506268886
7	6.506571111	– 0.927717691	– 2.083955174
6	5.233524578	– 0.749242148	– 1.714216105
1	4.566822567	– 0.296761089	– 2.444265385

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

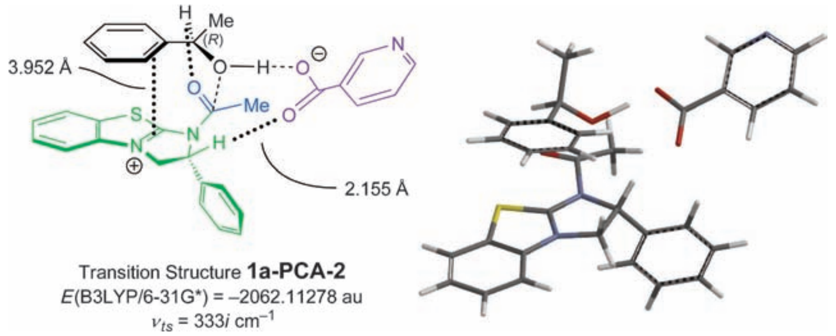
Table 5. Cartesian *Coordinates* [Å] *for the Transtion Structure* **1b-PCA-1**[a])



Cartesian coordinates [Å]				*Cartesian* coordinates [Å]			
Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
6	0.368096957	– 1.809025010	– 0.669783480	1	– 5.439301289	– 3.429577417	0.197862278
6	– 0.628975373	– 1.899254277	– 1.806016622	1	– 4.573516595	– 5.703842550	– 0.333615382
1	– 1.321518678	– 2.710193383	– 1.579675773	1	– 2.172791333	– 6.224749453	0.060357680
1	– 0.089065982	– 2.140666824	– 2.729240070	1	– 0.653924641	– 4.496231957	0.952449091
8	0.967966217	– 2.795905415	– 0.225104144	6	– 0.212771750	– 2.344644017	2.654512914
7	1.253981766	– 0.590568388	– 0.763253844	1	0.498823084	– 3.026947508	2.187951348
6	2.310865632	– 0.524776850	0.023374094	1	– 0.678717976	– 2.850007587	3.509434558
7	2.815179546	0.713719788	0.153295732	1	0.340817272	– 1.475819844	3.027089727
16	3.160640627	– 1.736335319	0.919612407	1	– 1.951275581	– 1.195833507	2.228373921
6	1.961059567	1.693943748	– 0.530624856	1	– 1.641011849	– 0.052081575	0.418150321
1	2.547270892	2.289848891	– 1.234393905	8	– 2.489556640	0.658618054	0.381571254
1	1.462456448	2.340251708	0.196494262	6	– 2.156205050	1.916957643	0.543726455
6	0.916520668	0.774021786	– 1.258136564	8	– 1.004428562	2.358694583	0.512696269
6	0.959617465	0.894760763	– 2.768638634	6	3.930356352	0.808551873	0.981169578
6	1.875502319	0.176495496	– 3.546795161	6	4.280148615	– 0.455833548	1.490988401
6	1.916707473	0.353326154	– 4.930052327	6	4.654221128	1.952663852	1.311760747
6	1.048370431	1.254874315	– 5.548771717	1	4.372280793	2.924532523	0.919056303
6	0.134179845	1.975454069	– 4.778233835	6	5.371870313	– 0.591551593	2.342893882
1	– 0.550222728	2.673354714	– 5.252861858	1	5.647912906	– 1.563215713	2.741718838
6	0.087284331	1.792870110	– 3.395585448	6	6.104504155	0.550863160	2.674683881
1	– 0.631152731	2.347294191	– 2.796091760	1	6.960253577	0.461707329	3.336895147
1	1.080006464	1.390241046	– 6.626390931	6	5.747145522	1.805741763	2.166597492
1	2.625644875	– 0.216706248	– 5.524676824	1	6.327061457	2.681836064	2.440826553
1	2.543671504	– 0.537970372	– 3.07325218	6	– 3.322703378	2.835838154	0.753578320
1	– 0.067831928	1.044201919	– 0.878084457	6	– 4.644880256	2.381588533	0.774328820
8	– 0.727210243	– 1.036886764	0.638299934	1	– 4.850857249	1.325926934	0.633335949
6	– 1.282846393	– 1.866691065	1.666809746	6	– 5.666062391	3.306702686	0.974667330
6	– 2.177255043	– 2.980004053	1.117207105	1	– 6.707248700	2.998050027	0.997754221
6	– 1.703345595	– 4.263254718	0.811245967	6	– 5.324210278	4.649275981	1.148215364
6	– 2.560718427	– 5.235614789	0.292092557	1	– 6.099707163	5.397206845	1.308260372
6	– 3.907784514	– 4.944267222	0.068709697	7	– 4.064183097	5.106565291	1.131895208
6	– 4.392054193	– 3.669478165	0.366675655	6	– 3.094932291	4.206223716	0.936982765
6	– 3.532279034	– 2.701461909	0.88652662	1	– 1.194513401	– 0.977536805	– 1.952878433
1	– 3.908900852	– 1.705463714	1.108435076	1	– 2.072902458	4.576261576	0.923552474

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

Table 6. Cartesian *Coordinates* [Å] *for the Transtion Structure* **1a-PCA-2**[a])

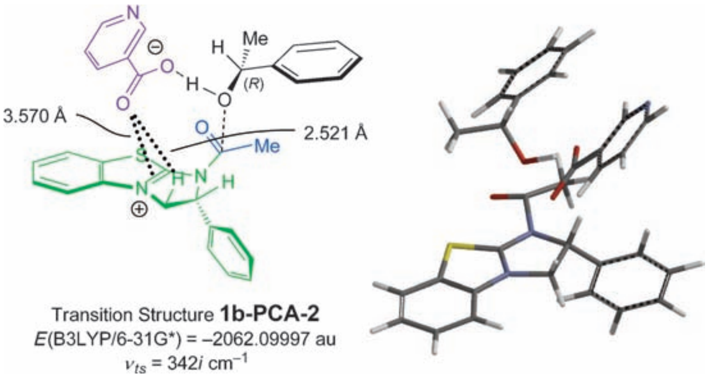


Transition Structure **1a-PCA-2**
E(B3LYP/6-31G*) = –2062.11278 au
ν_{ts} = 333i cm^{-1}

Cartesian coordinates [Å]			
Atom	*X*	*Y*	*Z*
6	–0.346167763	0.718049033	2.244974824
6	0.932195912	1.407034330	2.655433270
1	0.709130397	2.454956295	2.889642583
1	1.298262097	0.912449247	3.556136311
1	1.706827333	1.372049682	1.889025760
8	–1.232546060	0.405690888	3.039852165
7	–0.852827591	1.090349932	0.898256999
6	–2.106635568	0.821909480	0.579782728
7	–2.347485998	0.871257785	–0.740972012
6	–1.092969851	1.040737672	–1.487747952
6	–0.058866659	1.344885274	–0.345440427
6	0.498932021	2.754264715	–0.409493191
6	1.809586184	2.943138884	–0.864597178
6	2.332054329	4.232979400	–0.980912557
6	1.555054201	5.340520050	–0.639679621
6	0.248384082	5.156427635	–0.181083078
6	–0.277915288	3.869994760	–0.069825370
1	–1.293067638	3.734895673	0.296585869
1	–0.360313102	6.014170889	0.092480884
1	1.965967961	6.342917763	–0.724785725
1	3.352090676	4.369887053	–1.329830915
1	2.413545044	2.074963861	–1.115499600
1	0.752045594	0.613153346	–0.377145807
1	–0.857926498	0.112383406	–2.016366409
1	–1.175164087	1.867946960	–2.196644490
8	0.548691324	–0.918307836	1.580319817
6	–0.191034366	–2.083242242	1.838056624
6	–0.893730731	–2.602012504	0.580936500
6	–2.154996232	–3.204938346	0.670440398
6	–2.799255376	–3.702799482	–0.464546668
6	–2.187277890	–3.604170121	–1.714878258
6	–0.928249342	–3.005655596	–1.817241418
6	–0.287219369	–2.506781640	–0.680461497
1	0.686228010	–2.031975773	–0.768945507
1	–0.437721594	–2.934346450	–2.785802385
1	–2.684286689	–3.992462231	–2.600424827
1	–3.779507565	–4.164438660	–0.372140213
1	–2.638566137	–3.281347482	1.642690900
1	–0.971862669	–1.825354699	2.573465257
6	0.692468688	–3.175453351	2.468385621
1	1.159307615	–2.789574692	3.380949810
1	0.098594337	–4.060242000	2.725625317
1	1.486612470	–3.484031212	1.780011042
1	1.835605451	–1.032843363	1.378313298
8	2.953410956	–1.117901012	1.233394079
6	3.356789291	–0.763526303	0.046281726
8	2.633258902	–0.321150391	–0.858783418
16	–3.490593968	0.419271709	1.537205832
6	–3.661833457	0.591169974	–1.107387842
6	–4.453119798	0.341970221	0.029269446
6	–5.804519852	0.041190797	–0.104657570
1	–6.419167169	–0.155937627	0.768617538
6	–6.351055133	–0.005507000	–1.389266965
1	–7.404129747	–0.238402711	–1.512428482
6	–5.557352769	0.240850537	–2.516111903
1	–6.000758983	0.194663199	–3.506172747
6	–4.201271886	0.543786146	–2.391405700
1	–3.583794448	0.731543504	–3.264014189
6	4.832725153	–0.921732010	–0.179389115
6	5.692927548	–1.395404430	0.820262458
7	7.013290327	–1.545148433	0.657291577
6	7.522113868	–1.219345676	–0.538321914
1	8.598279914	–1.348947620	–0.648727593
6	6.757417846	–0.741124849	–1.604787110
1	7.228913622	–0.496437539	–2.552348625
6	5.386849113	–0.590345856	–1.418995670
1	4.733482980	–0.226367624	–2.205709578
1	5.286609308	–1.661987773	1.792017481

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

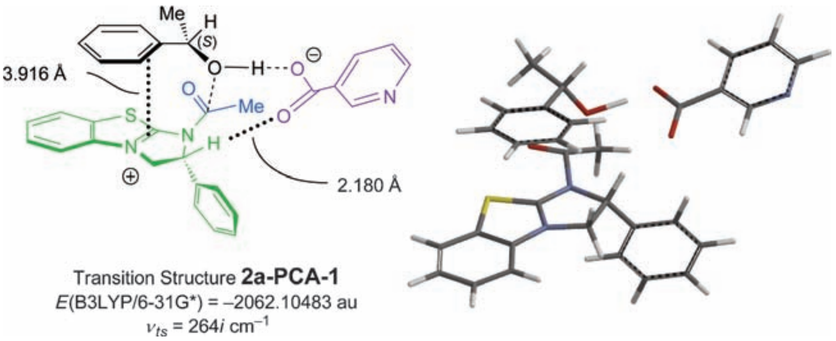
Table 7. Cartesian *Coordinates* [Å] *for Transtion Structure* **1b-PCA-2**[a])



Cartesian coordinates [Å]				*Cartesian* coordinates [Å]			
Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
6	0.143416256	2.009251882	0.374920475	1	–5.764903865	2.665129646	–0.188211551
6	–0.867433589	2.252462609	1.478075356	1	–5.287159413	5.108855478	–0.103633752
1	–1.584546010	2.991439966	1.121532784	1	–3.067912743	5.952265761	–0.847681445
1	–0.343325276	2.658599906	2.351028869	1	–1.343965506	4.379104569	–1.65125469
8	0.709517172	2.930040497	–0.228183378	6	–0.585334328	2.104703229	–2.964857433
7	1.090610422	0.870327331	0.706745776	1	0.037889426	2.925469972	–2.607024447
6	2.109113546	0.669932901	–0.107209060	1	–1.148016276	2.441986068	–3.844026125
7	2.689065616	–0.531885736	0.029530681	1	0.073680348	1.284453374	–3.268111152
16	2.830294453	1.678797652	–1.311574750	1	–2.122130081	0.775197023	–2.331135437
6	1.976862673	–1.344396521	1.022490496	1	–1.486099902	–0.168347240	–0.484994818
1	2.650376503	–1.619335077	1.839017389	8	–2.122752064	–1.060786432	–0.330465274
1	1.551942352	–2.229659952	0.546642614	6	–1.508675220	–2.190576837	–0.604032900
6	0.842542032	–0.366839947	1.505366713	8	–0.296175963	–2.311297477	–0.786561658
6	0.859872053	–0.123871820	3.001596580	6	3.758898152	–0.767431233	–0.829470959
6	1.849320311	0.667902972	3.599263798	6	3.990577338	0.352694340	–1.650258920
6	1.872797404	0.842312717	4.982110395	6	4.538091588	–1.918114903	–0.933627082
6	0.909978715	0.223519833	5.783636663	1	4.346269272	–2.780915249	–0.303543652
6	–0.078928372	–0.564951064	5.195020344	6	5.014946549	0.334668204	–2.590970326
1	–0.836501057	–1.041723861	5.810794148	1	5.198061255	1.194055347	–3.229274896
6	–0.104760173	–0.734794354	3.809513449	6	5.801475842	–0.814968677	–2.698380911
1	–0.883297636	–1.340512473	3.351401418	1	6.605226578	–0.845176151	–3.427723779
1	0.927622164	0.362214358	6.861139884	6	5.563163444	–1.925891670	–1.880295778
1	2.639454493	1.465756222	5.434145736	1	6.182322220	–2.811956981	–1.983135860
1	2.591013598	1.164082711	2.978438294	6	–2.417623050	–3.383019908	–0.654311678
1	–0.122461573	–0.772718463	1.202671039	6	–3.793792568	–3.291263247	–0.406121182
8	–0.840131861	0.980376233	–0.794806415	7	–4.627369486	–4.338330141	–0.436244654
6	–1.542837959	1.596929587	–1.882196563	6	–4.096901467	–5.533731813	–0.726815355
6	–2.572766815	2.622943086	–1.409996079	1	–4.793616323	–6.370795401	–0.747791735
6	–2.315519207	3.999034461	–1.352658854	6	–2.740984308	–5.738753519	–0.993088546
6	–3.286841071	4.887571428	–0.884889437	1	–2.371029116	–6.733479469	–1.224599386
6	–4.531816378	4.415410035	–0.465001003	6	–1.887193350	–4.641412091	–0.953424752
6	–4.799149682	3.045343862	–0.513172089	1	–1.405616357	1.348994393	1.770173416
6	–3.827034226	2.162385397	–0.982726299	1	–0.823169043	–4.729140975	–1.149863401
1	–4.033216142	1.094363501	–1.010979414	1	–4.233192021	–2.325533229	–0.171794385

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

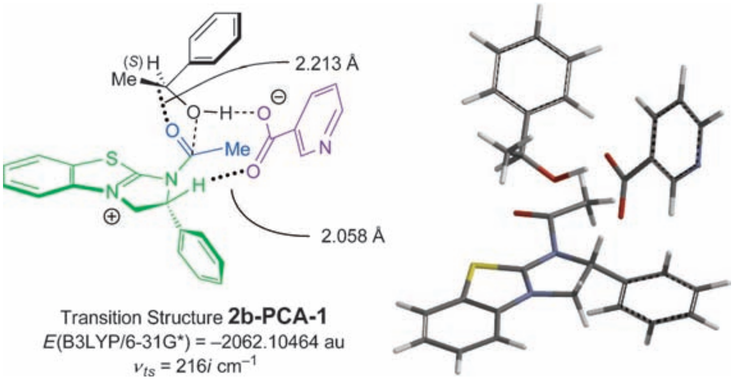
Table 8. Cartesian *Coordinates* [Å] *for Transtion Structure* **2a-PCA-1**[a])



Cartesian coordinates [Å]				*Cartesian* coordinates [Å]			
Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
6	0.509993616	– 0.497308660	2.063021282	1	0.432218715	3.056280355	– 2.827343834
7	0.953443106	– 0.788063013	0.656853834	1	2.728551391	3.965011504	– 2.475447722
6	2.183904184	– 0.482943150	0.294617964	1	3.652351364	4.092036256	– 0.169336407
7	2.382216747	– 0.533337286	– 1.034747653	1	2.308254251	3.336139252	1.754655401
16	3.588367685	– 0.041505004	1.204412023	6	0.197295340	2.652919553	3.128717809
6	1.109581351	– 0.750723082	– 1.735307311	1	– 0.549578599	2.328169686	3.859902824
6	0.130566693	– 1.094408481	– 0.554351663	1	0.324325216	3.737712752	3.229076724
1	– 0.721394783	– 0.410854374	– 0.560160508	1	1.137083674	2.154707548	3.371542153
6	– 0.353831481	– 2.532866921	– 0.601474412	1	– 1.249158247	2.841425943	1.579486213
6	0.480149610	– 3.606037415	– 0.259418776	1	– 2.001188059	0.793484992	1.408121974
6	0.022387861	– 4.918624656	– 0.371783234	8	– 3.091357838	0.764280259	1.302763929
6	– 1.271725765	– 5.172780379	– 0.833020571	6	– 3.480472606	0.550448026	0.070567459
6	– 2.106013268	– 4.108048577	– 1.174958449	8	– 2.730409048	0.366320642	– 0.895062070
6	– 1.651667835	– 2.792651391	– 1.058381301	6	4.498329826	0.048239733	– 0.336559004
1	– 2.301461080	– 1.959380557	– 1.312802464	6	3.676889224	– 0.226659333	– 1.445834652
1	– 3.116634278	– 4.297371189	– 1.526830271	6	4.174485734	– 0.179444897	– 2.746610036
1	0.675679505	– 5.742696171	– 0.097931535	1	3.534124301	– 0.389386192	– 3.597495687
1	1.486343440	– 3.417755911	0.108217591	6	5.519730280	0.149984927	– 2.917850504
1	0.819712021	0.166197355	– 2.256086146	1	5.930180345	0.195365229	– 3.921957495
1	1.195785892	– 1.575685651	– 2.446453478	6	6.343456051	0.422380188	– 1.819266664
6	– 0.599018945	– 1.405616416	2.552487165	1	7.387644760	0.674545141	– 1.977179560
1	– 1.435201065	– 1.483995181	1.857654639	6	5.837957344	0.375369987	– 0.517457529
1	– 0.957421280	– 1.004839903	3.501829159	1	6.476334941	0.591302110	0.334273343
1	– 0.180460998	– 2.404106991	2.722455272	1	– 1.627950758	– 6.195606366	– 0.920015516
8	1.445270204	– 0.151260159	2.791585043	6	– 4.969817194	0.530610013	– 0.101009763
8	– 0.653951848	0.920158773	1.600154402	6	– 5.850609475	0.762098461	0.960845532
6	– 0.302929927	2.291637836	1.724408454	1	– 5.455761603	0.964742960	1.950863783
6	0.602990935	2.745790234	0.574247292	6	– 7.220309659	0.725172016	0.712202497
6	1.891939031	3.259822558	0.754677286	1	– 7.940870521	0.901212933	1.505982389
6	2.655026664	3.692025383	– 0.336387216	6	– 7.654845191	0.453783062	– 0.586681395
6	2.139693340	3.619113199	– 1.629458373	1	– 8.719956624	0.414645299	– 0.812529425
6	0.853959465	3.103251389	– 1.825282268	7	– 6.828691329	0.228025380	– 1.618232060
6	0.098596788	2.669713377	– 0.735929419	6	– 5.516064430	0.272555983	– 1.365114533
1	– 0.900039224	2.268447309	– 0.894976505	1	– 4.845819691	0.096268895	– 2.203227273

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

Table 9. Cartesian *Coordinates* [Å] *for Transtion Structure* **2b-PCA-1**a)

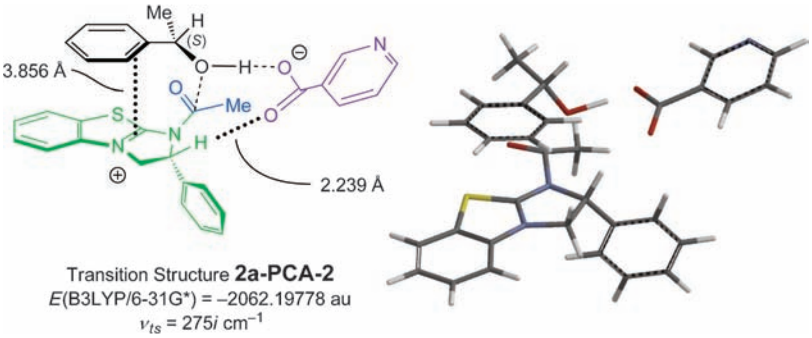


Transition Structure **2b-PCA-1**
E(B3LYP/6-31G*) = –2062.10464 au
ν_{ts} = 216i cm^{-1}

Cartesian coordinates [Å]				*Cartesian* coordinates [Å]			
Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
6	– 0.807427567	– 1.187271128	1.711292498	6	1.853803800	– 4.722450875	0.193176436
6	0.080019571	– 0.758828563	2.854387379	1	1.035475869	– 5.193075212	– 0.349627700
1	0.697098959	– 1.615908015	3.127395296	1	2.864268030	– 6.589190329	0.554154758
1	0.726686504	0.081358677	2.599435112	1	4.733410468	– 5.533071828	1.818938947
1	– 0.545935276	– 0.479579827	3.710954879	1	4.737946606	– 3.069660109	2.166396041
8	– 1.406497181	– 2.264921330	1.686948625	1	2.903375048	– 1.680132069	1.252724121
7	– 1.570282881	– 0.073317779	1.068679247	6	0.848573036	– 2.394683586	– 1.758821377
6	– 2.483037668	– 0.393171272	0.166506628	1	0.867158781	– 3.384811150	– 2.228283305
7	– 2.814611500	0.616922663	– 0.653153083	1	1.773184993	– 1.873892152	– 2.029228885
6	– 3.782183450	0.307316838	– 1.605654353	1	0.002341963	– 1.831165106	– 2.169124859
16	– 3.315768595	– 1.874520884	– 0.160826751	1	– 0.222058183	– 3.047931954	– 0.010600592
6	– 2.017160904	1.813729916	– 0.355774657	1	1.609443738	– 0.333326189	– 0.099351929
6	– 1.092923928	1.317322279	0.811253524	8	1.227554245	1.979762603	– 1.000684659
6	– 1.127887592	2.227750983	2.019866079	6	2.304983187	1.378913620	– 0.958303180
6	– 2.152465594	2.172101288	2.972999956	8	2.495008309	0.192796492	– 0.430751449
6	– 2.168288085	3.069688886	4.041111275	6	– 4.190560549	– 1.033770090	– 1.481277259
6	– 1.166644958	4.035903655	4.161803120	6	– 4.310417392	1.141531312	– 2.589180435
6	– 0.146188036	4.098480669	3.211804155	1	– 3.984006690	2.172696126	– 2.681596260
6	– 0.124734413	3.196464314	2.147333092	6	– 5.263869433	0.602973552	– 3.453548826
1	0.667766111	3.239979831	1.404501746	1	– 5.688514617	1.230861001	– 4.230816338
1	0.638692635	4.844639044	3.301073320	6	– 5.676675621	– 0.730092755	– 3.335806536
1	– 1.180724066	4.733460492	4.994959131	1	– 6.420323395	– 1.126152613	– 4.020448163
1	– 2.962622696	3.013029719	4.780748399	6	– 5.141486561	– 1.561657886	– 2.349141727
1	– 2.929265075	1.415858656	2.889834160	1	– 5.458582162	– 2.596746318	– 2.262939524
1	– 0.080314958	1.253497876	0.413098697	6	3.550467461	1.993115893	– 1.519658405
1	– 1.421025762	2.109316292	– 1.223195652	6	5.718645485	3.261249625	– 2.585518573
1	– 2.669554854	2.636788367	– 0.049650474	6	4.773584533	1.315619241	– 1.552068183
8	0.586336012	– 1.217487777	0.336774884	6	3.502612152	3.293354410	– 2.039765216
6	0.708639637	– 2.498934833	– 0.226356439	7	4.556158062	3.928666007	– 2.563376143
6	1.846659605	– 3.331875665	0.374107732	6	5.879260936	1.962965677	– 2.096951682
6	2.896727718	– 2.752841915	1.095258692	1	4.839030705	0.306419157	– 1.158926479
6	3.930242353	– 3.540080169	1.609668085	1	2.559081020	3.833268728	– 2.024588752
6	3.930093690	– 4.921422766	1.415709290	1	6.848161099	1.474543648	– 2.145140160
6	2.882888602	– 5.512211933	0.704126170	1	6.564604386	3.794282103	– 3.017647809

a) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

Table 10. Cartesian *Coordinates* [Å] *for Transtion Structure* **2a-PCA-2**[a])

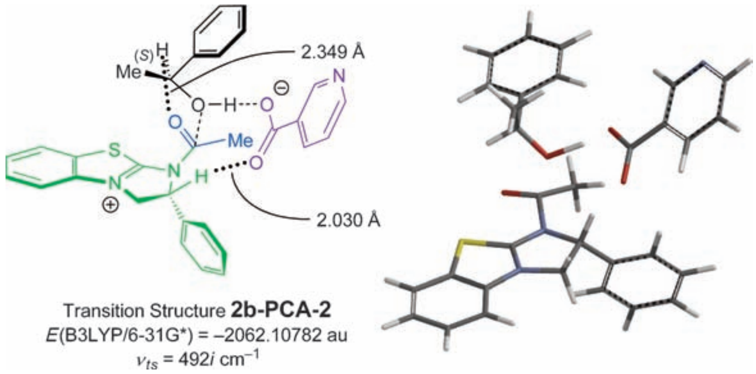


Transition Structure **2a-PCA-2**
E(B3LYP/6-31G*) = –2062.19778 au
ν_{ts} = 275i cm^{-1}

Cartesian coordinates [Å]				*Cartesian* coordinates [Å]			
Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
6	0.351970753	– 0.115919095	2.189971814	1	3.282305726	3.324490650	– 2.695589089
7	0.881408405	– 0.714897535	0.916881902	1	3.845239227	3.936075164	– 0.352174957
6	2.143786122	– 0.515360523	0.590594039	1	2.198415952	3.590232939	1.455113660
7	2.431577474	– 0.851286263	– 0.679605292	6	– 0.109805486	3.172395728	2.599807900
16	3.498981186	0.077868033	1.488501078	1	– 0.971326610	2.996860723	3.251904101
6	1.208300740	– 1.201002149	– 1.410562521	1	0.034231787	4.255621050	2.507190060
6	0.128984385	– 1.236928378	– 0.266735464	1	0.765658828	2.730219924	3.078500970
1	– 0.676229676	– 0.532387462	– 0.487357834	1	– 1.301605915	3.040400673	0.840128619
6	– 0.438407967	– 2.628577902	– 0.053167984	1	– 2.059348199	1.008495277	1.097771816
6	0.303608273	– 3.637969292	0.574549585	8	– 3.150387179	0.963534363	0.930488676
6	– 0.218294603	– 4.925594686	0.693175009	6	– 3.464617220	0.593000777	– 0.283535328
6	– 1.485162803	– 5.218189348	0.181580931	8	– 2.660996112	0.254306265	– 1.161841314
6	– 2.228709119	– 4.216073234	– 0.442498887	6	4.517467023	– 0.192189363	0.038576158
1	– 3.218370243	– 4.434857056	– 0.834365977	6	3.763817242	– 0.679939894	– 1.045201903
1	0.362366798	– 5.700276137	1.187134876	6	4.351761801	– 0.937486742	– 2.281833212
1	1.285787273	– 3.413991672	0.984027736	1	3.762274278	– 1.312425690	– 3.112636003
1	0.994235200	– 0.428839311	– 2.155203522	6	5.719676713	– 0.695686944	– 2.415588092
1	1.313640744	– 2.172650429	– 1.899040788	1	6.200751874	– 0.887738015	– 3.369851840
6	– 0.807658349	– 0.882510620	2.790350424	6	6.476214727	– 0.210498006	– 1.342268721
1	– 0.424114524	– 1.821360787	3.206997115	1	7.539285199	– 0.030438232	– 1.469424884
1	– 1.597260295	– 1.108633393	2.073427563	6	5.879736528	0.048174261	– 0.105372022
1	– 1.219672060	– 0.278003290	3.599586135	1	6.467231692	0.428699646	0.724963283
8	1.241515440	0.385128082	2.883694333	1	– 1.891456878	– 6.221622163	0.275855846
8	– 0.744250109	1.168115217	1.321420908	6	– 4.939576456	0.591817360	– 0.558341160
6	– 0.397370566	2.543427492	1.231881975	6	– 5.881126503	0.946839291	0.417444080
6	0.680005299	2.767821117	0.167346423	1	– 5.542507449	1.234223134	1.408981205
6	1.939542806	3.311621709	0.438367555	7	– 7.203155054	0.957108605	0.207611106
6	2.873256170	3.507903899	– 0.585549609	6	– 7.630876347	0.607136421	– 1.012633634
6	2.560011166	3.163311154	– 1.899238425	1	– 8.710018884	0.623176047	– 1.161084631
6	1.302876413	2.618590960	– 2.184200079	6	– 6.781418011	0.238730651	– 2.058543146
6	0.376305782	2.422515573	– 1.161134610	6	– 5.409941522	0.231846874	– 1.824514797
1	– 0.602132421	2.001683158	– 1.384445553	1	– 4.693672000	– 0.041070801	– 2.593237074
1	1.038859605	2.364838934	– 3.208824022	1	– 7.189837731	– 0.032806734	– 3.027696165

[a]) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

Table 11. Cartesian *Coordinates* [Å] *for Transtion Structure* **2b-PCA-2**a))



Cartesian coordinates [Å]			
Atom	*X*	*Y*	*Z*
6	– 0.755924489	– 1.036060133	1.370529967
6	0.291054223	– 0.734429519	2.417396742
1	0.828756794	– 1.662913112	2.615607803
1	1.003578564	0.029847875	2.103306347
1	– 0.206327860	– 0.403703548	3.336846701
8	– 1.508875795	– 2.013699278	1.435772788
7	– 1.439217988	0.180369804	0.809543029
6	– 2.553696051	0.005944388	0.126077037
7	– 2.916961380	1.074414215	– 0.604454364
6	– 4.111280712	0.928212990	– 1.307007400
16	– 3.634128611	– 1.341550691	– 0.003395312
6	– 1.921177714	2.146127374	– 0.489257551
6	– 0.857139644	1.518713859	0.483191722
6	– 0.597178043	2.382281592	1.700388341
6	– 1.483550756	2.415518912	2.784468138
6	– 1.240961370	3.261070654	3.866500842
6	– 0.113547951	4.086014248	3.871685569
6	0.771601475	4.058097377	2.792970064
6	0.534606444	3.207005054	1.711688986
1	1.224437249	3.172196249	0.872289050
1	1.654235629	4.691991416	2.795167515
1	0.076288814	4.742841926	4.716263987
1	– 1.929543074	3.273100924	4.707228182
1	– 2.354758274	1.765055369	2.790268923
1	0.069093197	1.364081745	– 0.076656450
1	– 1.486874896	2.373274766	– 1.467114664
1	– 2.380061528	3.047341394	– 0.072897436
8	0.414844475	– 1.244555502	– 0.113484136
6	0.395131577	– 2.575543778	– 0.606499712
6	1.230481488	– 3.552690026	0.221888685
6	2.543732059	– 3.252487960	0.612949241
6	3.299003361	– 4.174138469	1.339336015
6	2.758235852	– 5.414826245	1.684608166
6	1.451173383	– 5.722751286	1.304389913
6	0.695616525	– 4.795084514	0.584719697
1	– 0.329597149	– 5.033210375	0.309248885
1	1.015005847	– 6.681307480	1.576241169
1	3.348113092	– 6.132056470	2.249960378
1	4.314793304	– 3.921871371	1.635057043
1	2.974658688	– 2.290913311	0.352730880
6	0.826268446	– 2.571906770	– 2.081805284
1	0.751266965	– 3.577726870	– 2.510632047
1	1.862998279	– 2.234149016	– 2.183501036
1	0.185221586	– 1.893823971	– 2.656417299
1	– 0.645531330	– 2.921591680	– 0.550798782
1	1.537053135	– 0.606365424	– 0.309963061
8	1.657486316	1.747066960	– 1.281507912
6	2.623346510	0.999553462	– 1.079965968
8	2.571501279	– 0.166525625	– 0.497576622
6	– 4.660462265	– 0.349164419	– 1.091010472
6	– 4.736776823	1.859354280	– 2.134159862
1	– 4.304480504	2.841526477	– 2.297596943
6	– 5.933635843	1.484172447	– 2.746013211
1	– 6.440829578	2.191056257	– 3.395655304
6	– 6.486726374	0.215183868	– 2.536548075
1	– 7.419473683	– 0.052790263	– 3.023290823
6	– 5.852988119	– 0.714190193	– 1.707600747
1	– 6.281897277	– 1.698920866	– 1.547449459
6	4.001210002	1.418358700	– 1.506751818
6	6.519451783	2.138224845	– 2.279244011
6	5.126552457	0.606340449	– 1.311688407
6	4.186827623	2.655686197	– 2.130290332
6	5.468700758	3.024971860	– 2.524966635
7	6.365977815	0.947903419	– 1.684451098
1	5.013030981	– 0.362192020	– 0.832832833
1	3.325359052	3.295856652	– 2.293085151
1	5.656075578	3.976622104	– 3.014269511
1	7.535923733	2.394982958	– 2.575095993

a) Requested basis set is 6-31G(d). There are 215 shells and 647 basis functions.

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