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Anhydrides from aldehydes or alcohols *via* an oxidative cross coupling

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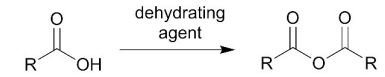
A novel metal-free oxidative cross coupling for the synthesis of symmetrical and mixed anhydrides from aldehydes or benzylic alcohols has been developed. The aldehydes or alcohols were converted *in situ* into their corresponding acyl chlorides, which were then reacted with an array of carboxylic acids. The methodology has a general applicability, and was successfully employed to prepare either aromatic or aliphatic symmetrical anhydrides and mixed anhydrides, which are very unstable compounds.

Introduction

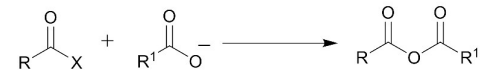
Carboxylic anhydrides are an important class of organic compounds with many applications such as acylating agents or intermediates in organic synthesis, especially in the preparation of peptides and drugs. Traditional syntheses of carboxylic anhydrides consist in the treatment of carboxylic acids with dehydrative coupling agents, including phosgene[1], thionyl chloride,[2] sulfonyl chloride[3], phosphoranes[4], isocyanates,[5] 1,3,5-triazines[6] and carbodiimides[7] (Scheme 1, path 1). These procedures are affected from many drawbacks, such as the use of unstable or difficult to handle reagents, complex workup and substrate scope limited only to symmetrical anhydrides. Alternatively the anhydrides are prepared by reacting acylating agents (such as acyl halides, activated esters or reactant anhydrides)[8] with carboxylates (Scheme 1, path 2). Recently many efforts[9] have been directed towards the substitution of carboxylic acids and their derivatives with the aldehydes and alcohols, both as acyl source, especially for the preparation of esters and amides. There are very few examples on the use of aldehydes for the synthesis of symmetric anhydrides (Scheme 1, path 3). Very recently Patel,[10] Niknam,[11] and Ray[12] have reported pioneering examples of oxidative self-coupling of aromatic aldehydes to symmetric aromatic carboxylic anhydrides. These methodologies make use of an excess of TBHP, in decane or in toluene, as an oxidant and cuprous-based catalysts. Electron-rich aromatic aldehydes gave good results, but either aromatic aldehydes with electron withdrawing substituents and aliphatic aldehydes failed in these reactions.

1) Synthesis of symmetric anhydrides from carboxylic acids



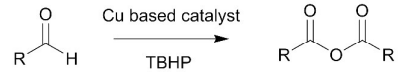
R = Alkyl and Aryl

2) Synthesis of symmetric and mixed anhydrides from acylating agents and carboxylates



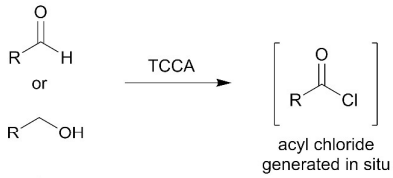
R, R^1 = Alkyl and Aryl

3) Synthesis of symmetric anhydrides from aldehydes via oxidative self couplings

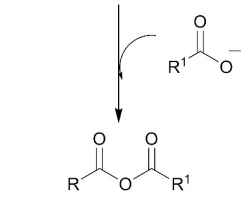


R = Aryl without electron-withdrawing substituents

4) This work: synthesis of symmetric or mixed anhydrides from either aldehydes or alcohols



R, R^1 = Alkyl and Aryl



Symmetric or mixed anhydrides

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra and spectral data of the synthesized compounds. See DOI: 10.1039/x0xx00000x

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Scheme 1. Strategies to form carboxylic anhydrides

Due to our interest in using aldehydes[13] for the preparations of amides and esters, we checked the viability of these reagents in the preparation of anhydrides (Scheme 1, path 4).

Results and Discussion

In particular, in relation to our recently reported metal-free oxidative esterifications of aldehydes[13a] we have tested the possibility to transform directly aldehydes into carboxy anhydrides by the use of trichloroisocyanuric acid (TCCA). We began our investigation by treating benzaldehyde (Table 1, **1a**, 1.1 mmol) with TCCA (Table 1, **2**, 1.1 mmol) in dichloromethane (3.25 mL) at room temperature. The reaction was monitored by TLC until the disappearance of the aldehyde and the quantitatively formation of benzoyl chloride. This reaction mixture, containing the acyl chloride **3** generated *in situ*, was treated with benzoic acid (Table 1, **4a**, 1.0 mmol) and NEt_3 in the presence of a catalytic amount of DMAP (Table 1, entry 1, 2.0 mmol/10 mol %) at 0°C, and, after 1 h at room temperature, the desired anhydride was formed in 37 % yield (Table 1, **5a**, entry 1). Different bases were screened, including DBU (Table 1, entry 2, 2.0 mmol), DABCO (Table 1, entry 3, 2.0 mmol), pyridine (Table 1, entry 4, 2.0 mmol) and NEt_3 (Table 1, entry 5, 2.0 mmol), furnishing the product **5a** in, respectively trace, 74 %, 84 % and 98 % yield. Then MgO (Table 1, entry 6, 2.0 mmol), ZnO (Table 1, entry 7, 2.0 mmol) and $CsCO_3$ (Table 1, entry 8, 2.0 mmol) were tested and the desired anhydride was obtained in, respectively 45 %, 40 % and 22 % yield. Using Fe_2O_3 as a base the anhydride **5a** was obtained in trace. Triethylamine gave the best result.

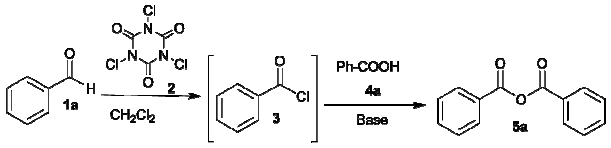
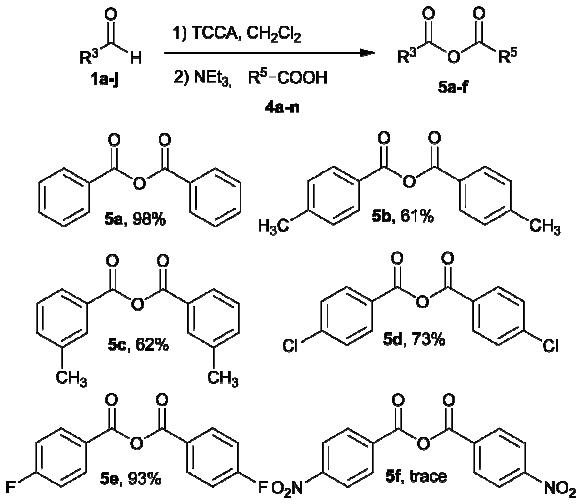


Table 1. Screening of reaction conditions

entry	base	yield[a] (%)
1[b]	NEt_3/DMAP	37
2[b]	DBU	trace
3[b]	DABCO	74
4[b]	pyridine	84
5[b]	NEt_3	98
6[b]	MgO	45
7[b]	ZnO	40
8[b]	$CsCO_3$	22
9[b]	Fe_2O_3	trace

[a] Yield refers to isolated product. [b] Reaction conditions: benzaldehyde **1a** (1.1 mmol), TCCA **2** (1.1 mmol) in CH_2Cl_2 (3.25 mL) at room temperature, until quantitatively formation of benzoyl chloride **3**. Benzoic acid **4a** and a base were added to the reaction mixture at 0 °C, and after 1h at room temperature the desired benzoic anhydride **5a** was obtained.

After the reaction conditions were optimized, the scope of the reaction was tested (Scheme 2). Firstly the reactivity of aryl aldehydes with aryl benzoic acids, to furnish symmetrical anhydrides, was investigated. Generally, electron-rich aromatic aldehydes (**5b** and **5c**, Scheme 2) reacted with the corresponding acids furnished the anhydrides in 61 % and 62 % yield respectively. Then aromatic aldehydes with electron-withdrawing substituents such as fluorine and chlorine were reacted, and were converted to the corresponding anhydrides in very good yields (**5d** and **5e**, Table 2). *p*-Nitro benzaldehyde was subjected to the optimized reaction conditions but the corresponding *p*-nitrobenzoic anhydride **5f** was obtained only in trace.



Scheme 2. Evaluation of aromatic aldehyde substrate scope.

Then aliphatic aldehydes, which typically cannot survive under strong oxidative conditions, were tested, with the corresponding acids and gave the corresponding symmetrical anhydrides in good yields (**5g**-**5l** , Scheme 3). The synthesis of aliphatic anhydrides from aldehydes is, to the best of our knowledge, unprecedented. Notably, even sterically hindered pivalaldehyde reacted well, giving the pivalic anhydride in good yield (**5i**, Scheme 3).

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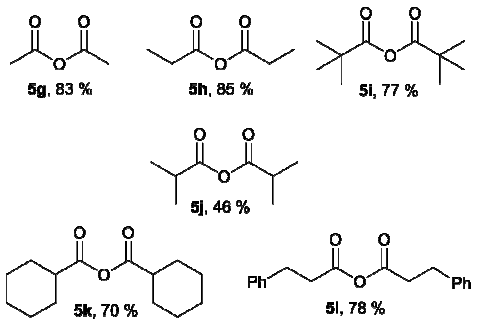
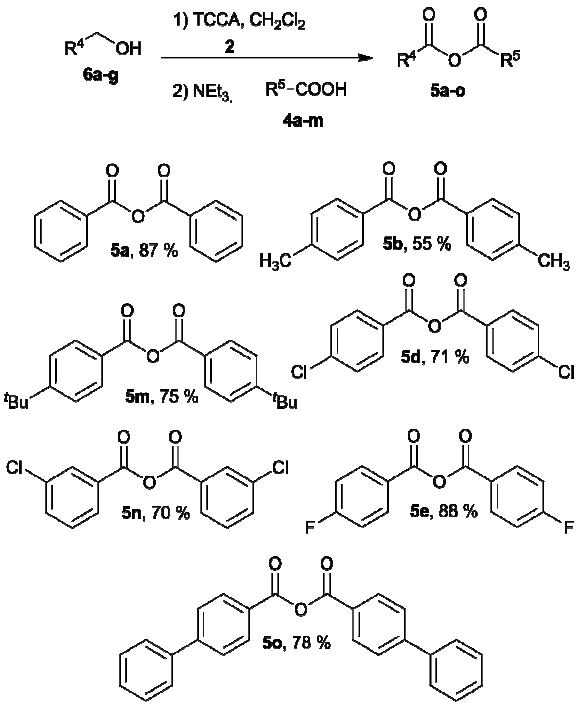


Scheme 3. Evaluation of aliphatic aldehyde substrate scope.

Alcohols are easily available and stable compounds. Their direct conversion into acid anhydrides would be an interesting and effective synthetic route.[14] In view of our interest in the use of alcohols[15a] in metal-free oxidative esterification we treated benzyl alcohol (Scheme 4, **6a**, 1.1 mmol) with TCCA (Scheme 4, **2**, 1.1 mmol) in dichloromethane (3.25 mL) at room temperature. The reaction was monitored by TLC until the disappearance of the alcohol and the quantitatively formation of benzoyl chloride. This reaction mixture, containing the acyl chloride **3** generated *in situ*, was treated with benzoic acid (Scheme 4, **4a**, 1.0 mmol) and NEt_3 (Scheme 4, 2.0 mmol) at 0°C, and, after 1 h at room temperature, the desired anhydride was formed in 87 % yield (Scheme 4, **5a**). The methodology was applied to variously substituted benzylic alcohols with the analogous carboxylic acids, affording the corresponding symmetrical anhydrides (Scheme 4). Neither the electronic properties nor steric effects of substituents on the aromatic ring of the benzyl alcohols were found to have any influence on the reaction. Benzylic alcohols with aliphatic groups (Scheme 4, **5b** and **5m**) and phenylic residues (Scheme 4, **5o**) were well tolerated providing the desired anhydrides in good yields. The reaction carried out on alcohols with halide substituents on the aromatic ring furnished the desired anhydrides too (Scheme 4, **5d**, **5e** and **5l**). To the best of our knowledge, this approach to anhydrides from aldehydes and alcohols with carboxylic acids, *via* acyl chloride formation, is unprecedented.[16]



Scheme 4. Evaluation of benzylic alcohol substrate scope.

Then the procedure was tested for the synthesis of mixed anhydrides. Mixed anhydrides are useful intermediates for the synthesis of carboxylic esters and amides,[17] but their tendency to disproportionate into the two symmetrical anhydrides often makes the synthesis and isolation of these products difficult or impossible.[18] The procedure was effectively employed to prepare mixed anhydrides from aldehydes and alcohols (Table 2, entries 1-8). Notably this procedure is an alternative but effective route to prepare the mixed anhydrides employed in the Yamaguchi esterification[17a] (Table 2, entry 6), a mild synthesis for highly functionalized esters.

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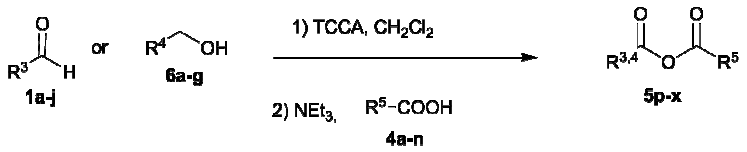
Table 2. Preparation of mixed anhydrides from aldehydes and alcohols.



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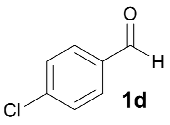
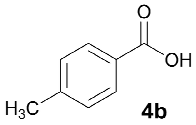
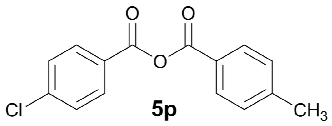
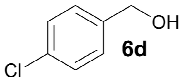
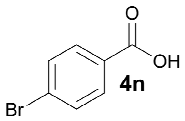
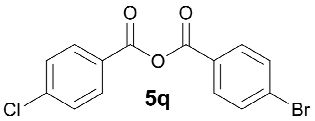
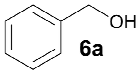
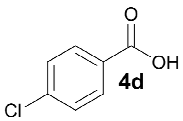
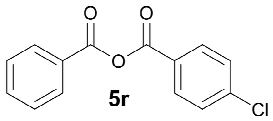
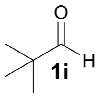
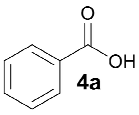
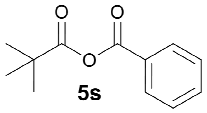
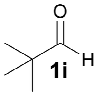
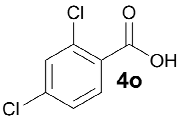
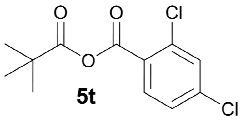
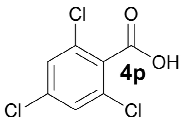
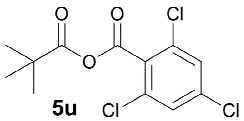
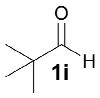
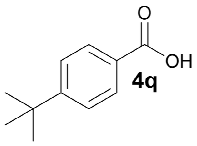
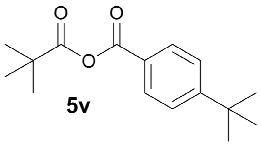
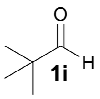
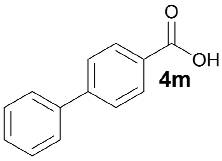
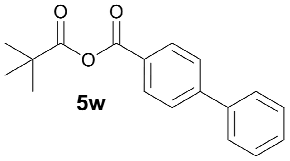
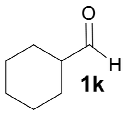
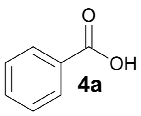
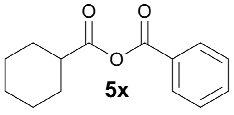
1	 1d		 4b	 5p
2		 6d	 4n	 5q
3		 6a	 4d	 5r
4	 1i		 4a	 5s
5	 1i		 4o	 5t
6	 1i		 4p	 5u
7	 1i		 4q	 5v
8	 1i		 4m	 5w
9	 1k		 4a	 5x

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The scrambling of benzoic pivalic anhydride **5s** was studied. The ^{13}C NMR investigations showed that mixed anhydride is stable in the reaction mixture, and the scrambling takes place during the workup procedures. At the end of the reaction, the crude reaction mixture was portioned into four parts. One was directly submitted NMR spectroscopy,[19] and (Figure 1, plot 1) showed only the presence of pure mixed anhydride **5s**. It is to underline that, by this methodology, it is possible to obtain pure mixed anhydrides in the crude reaction mixture, which would be directly used as useful intermediate reactants for other transformations. Another portion was dried in vacuo (25°C, 5.4 mbar), and analysed by NMR spectroscopy. ^{13}C NMR spectrum (Figure 1, plot 2) indicated that the vacuum drying facilitates the scrambling process and involves the formation of both benzoic anhydride **5a** and pivalic anhydride **5i**. Similarly flash chromatography, promotes the disproportionation into the two symmetrical anhydrides **5a** and **5i** (Figure 1, plot 3). By contrast the aqueous workup furthers the formation of only one symmetrical anhydride, the pivalic anhydride **5i**, and the desired mixed anhydride, the benzoic pivalic anhydride **5s** (Figure 1, plot 4).

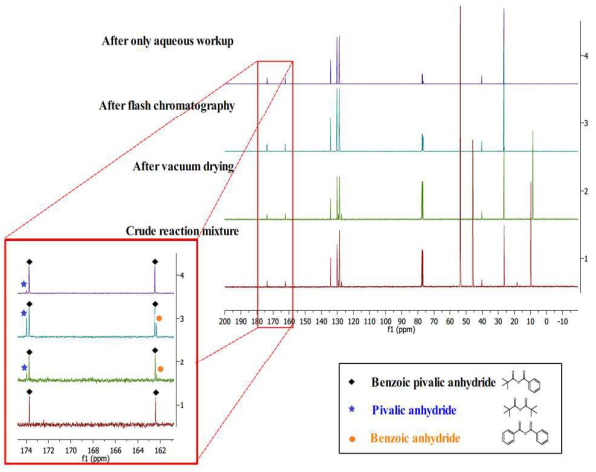
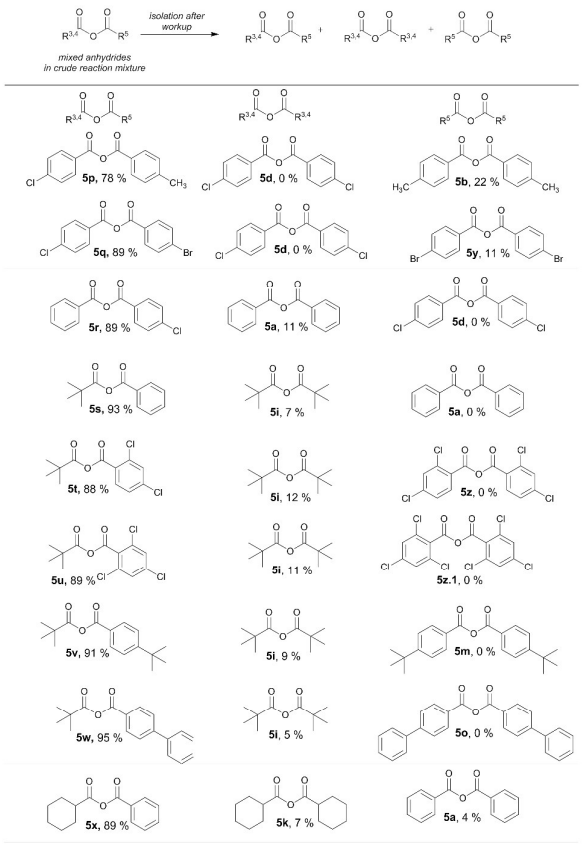


Figure 1. ^{13}C NMR investigations of benzoic pivalic anhydride **5t** scrambling process.

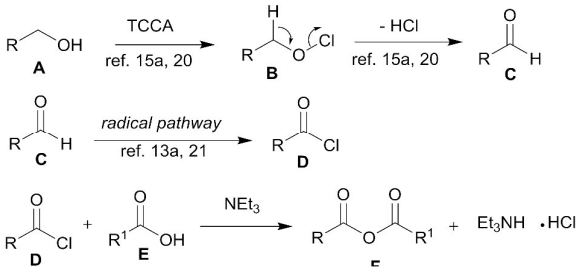
The mixed anhydrides were isolated after standard workup, and their purity was examined by ^{1}H NMR. It was possible to determine the ratio of mixed and symmetrical anhydrides as reported in Table 3.

Table 3. Ratio of mixed and symmetrical anhydrides after standard work up and purification.



The ratio of mixed and symmetrical anhydrides derived from the establishment of an equilibrium and depends on steric effects, electronic effects and reactivity.[20]

A plausible reaction mechanism is reported in Scheme 5. On the basis of previously published papers[15a, 21] alcohol **A** reacts with TCCA, generating the hypochlorite compound **B**, which readily loses hydrogen chloride to form the aldehyde **C**. Then aldehyde **C** is converted into the acyl chloride **D**, following a radical pathway.[13a, 22] In the final step, the acyl chloride **D** reacts, in the presence of triethylamine, with carboxylic acid **E** to give the corresponding anhydride **F** .



Scheme 5. Proposed reaction mechanism.

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Conclusion

In conclusion, a new metal free methodology for the synthesis of carboxylic anhydrides from aromatic and aliphatic aldehydes, and primary benzylic alcohols with carboxylic acids has been developed. By this procedure it was possible to obtain both aromatic and aliphatic symmetrical anhydrides. This one-pot procedure was successfully applied to prepare mixed anhydrides, and a study on their disproportionation was carried out. The mixed anhydrides are unstable products, and in the literature are not present timely and accurate characterization studies, however here it has been possible to prepare, isolate and characterize them appropriately. The procedure appears to have general applicability, has an optimal stoichiometric ratio of reactants and makes use of green reagents and mild reaction conditions.

Experimental section

General Information

All reagents and solvents were as obtained by commercial source. All the reactions were run under Argon atmosphere using standard techniques. All solvents were dried by usual methods and distilled under Argon. Aldehydes were fresh distilled before use. Column chromatography was generally performed on silica gel (pore size 60 ~~A°~~ Å, 32-63 ~~mm~~ nm particle size) and reactions were monitored by thin-layer chromatography (TLC) analysis was performed with Merck Kieselgel 60 F254 plates and visualized using UV light at 254 nm, $KMnO_4$ and 2,4-DNP staining. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance III 400 spectrometer (400 MHz or 100 MHz, respectively) using $CDCl_3$ solutions and TMS as an internal standard. Chemical shifts are reported in parts per million (ppm, d) relative to internal tetramethylsilane standard (TMS, d 0.00). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet; dd, doublet of doublets; br, broad. The coupling constants, J, are reported in Hertz (Hz). The IR spectra were recorded on a Jasco FTIR-480 Plus Fourier Transform spectrometer. High resolution mass spectra HRMS (HESI-FT-ORBITRAP) were recorded on a Q-Exactive Thermo Scientific mass spectrometer. Melting points were determined in open capillary tubes and are uncorrected.

General Procedure from aldehydes

TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of an aldehyde (1.1 mmol) in 3.25 mL dichloromethane, under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the aldehyde. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5a**-**5f**, the solvent was evaporated under reduced pressure and the residue purified by flash chromatography.

For the products **5g-5l** the reaction mixture was washed three times with a solution of 5 % HCl and then three times with a solution of 5 % $NaHCO_3$; the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure providing the desired anhydride.

Compound characterizations

Benzoic anhydride 5a: Colorless oil; (221 mg, 0.98 mmol, 98 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 7.6 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H).[23] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 134.4, 130.4, 128.8, 128.7.[23] IR (neat, cm^{-1}): ν = 2923, 2852, 1786, 1725, 1599, 1452, 1280, 1040, 997, 701.[6]

4-methylbenzoic anhydride 5b: White solid; (155 mg, 0.61 mmol, 61 % yield); mp 97 °C;[23] R_f = 0.45 (Hexane/EtOAc, 4.5:05). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 7.7 Hz, 4H), 7.31 (d, *J* = 7.8 Hz, 4H), 2.45 (s, 6H).[23] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 145.5, 130.6, 129.5, 126.2, 21.8.[23] IR (neat, cm^{-1}): ν = 3050, 2952, 2924, 1775, 1712, 1610, 1411, 1301, 1226, 1211, 1172, 1052, 1016, 824, 751.[11]

3-methylbenzoic anhydride 5c: White solid; (157 mg, 0.62 mmol, 62 % yield); mp 65-67 °C;[26] R_f = 0.44 (Hexane/EtOAc, 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.95 (m, 4H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 6H).[23] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 138.8, 135.3, 131.0, 128.8, 128.7, 127.7, 21.3.[23] IR (neat, cm^{-1}): ν = 3031, 2922, 2865, 1785, 1723, 1607, 1589, 1487, 1381, 1285, 1250, 1153, 1031, 998, 743.[26]

4-chlorobenzoic anhydride 5d:[23] White solid; (215 mg, 0.73 mmol, 73 % yield); mp 180-182 °C; R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.2 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 141.4, 131.9, 129.4, 127.1. IR (neat, cm^{-1}): ν = 2924, 1785, 1721, 1592, 1487, 1401, 1291, 1175, 1092, 1011, 743.[11]

4-fluorobenzoic anhydride 5e:[24] White solid; (243 mg, 0.93 mmol, 93 % yield); mp 113-115 °C; R_f = 0.62 (Hexane/EtOAc, 4.5:0.5).[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 – 8.16 (m, 4H), 7.23 - 7.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 (d, J_{C-F} = 255 Hz), 161.2, 133.3 (d, J_{C-F} = 9 Hz), 125.0 (d, J_{C-F} = 3 Hz), 116.5 (d, J_{C-F} = 11 Hz). IR (neat, cm^{-1}): ν = 3114, 3086, 2925, 1786, 1721, 1606, 1507, 1306, 1239, 1223, 1157, 844, 759.

Acetic anhydride 5g: Colorless oil, (85 mg, 0.83 mmol, 83 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18 (s, 1H).[31] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 22.0.[32] IR (neat, cm^{-1}): ν = 3031, 2948, 1839, 1755, 1438, 1379.

Propionic anhydride 5h:[33] Colorless oil, (111 mg, 0.85 mmol, 85 % yield); R_f = 0.61 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (q, *J* = 7.4 Hz, 4H), 1.17 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 28.6, 8.3. IR (neat, cm^{-1}): ν = 2986, 2948, 2660, 1716, 1467, 1240, 1080.

Pivalic anhydride 5i: Yellow oil; (143 mg, 0.77 mmol, 77 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (s, 18H).[25] ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 39.9, 26.3.[26] IR (neat, cm^{-1}): ν = 2977, 1701, 1484, 1415, 1305, 1201, 937, 869.

Isobutyric anhydride 5j: Yellow oil; (73 mg, 0.46 mmol, 46 % yield); R_f = 0.63 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (dt, *J* = 14.0, 7.0 Hz, 2H), 1.20 (d, *J* = 7.0 Hz, 12H).

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^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 35.0, 18.1. IR (neat, cm^{-1}): ν = 2979, 2939, 2880, 1812, 1746, 1471, 1388, 1020, 964, 738. HRMS (HESI-FT-ORBITRAP) calcd for $C_8H_{14}NaO_3$ $[M+Na]^+$: 181,0835, found 181,0834.

Cyclohexanecarboxylic anhydride 5k:[27] Colorless oil; (166 mg, 0.70 mmol, 70 % yield); R_f = 0.55 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (tt, *J* = 11.1, 3.7 Hz, 2H), 1.96 - 1.93 (m, 4H), 1.82 – 1.72 (m, 4H), 1.68 – 1.59 (m, 2H), 1.51 - 1.43 (m, 4H), 1.34 – 1.21 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 43.9, 28.4, 25.5, 25.1. IR (neat, cm^{-1}): ν = 2934, 2857, 1810, 1742, 1451, 1308, 1239, 1140, 1084, 1066, 992, 922.

3-phenylpropanoic anhydride 5l:[28] Colorless oil; (220 mg, 0.78 mmol50 % yield); R_f = 0.57 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 - 7.25 (m,4H), 7.20 - 7.15 (m, 6H), 2.92 (t, *J* = 7.7 Hz, 4H), 2.70 (t, *J* = 7.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 139.4, 128.5, 128.2, 126.4, 36.6, 30.0. IR (neat, cm^{-1}): ν = 3087, 3029, 2927, 1817, 1747, 1604, 1497, 1455, 1046, 749.

General Procedure from benzylic alcohols

TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of a benzylic alcohol (1.1 mmol) in 3.25 mL dichloromethane under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the alcohol. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5a**, **5b**, **5m**, **5d**, **5n**, **5e** and **5o** the solvent was evaporated under reduced pressure and the residue purified by flash chromatography.

Compound characterizations

Benzoic anhydride 5a: (197 mg, 0.87 mmol, 87 % yield).

4-methylbenzoic anhydride 5b: (139 mg, 0.55 mmol, 55 % yield).

4-(*tert*-butyl)benzoic anhydride 5m:[29] Colorless oil; (253 mg, 0.75 mmol, 75 % yield); R_f = 0.43 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.1 Hz, 4H), 7.53 (d, *J* = 8.1 Hz, 4H), 1.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5, 158.5, 130.5, 126.2, 125.9, 35.3, 31.0. IR (neat, cm^{-1}): ν = 2964, 2906, 2869, 1785, 1723, 1607, 1410, 1226, 1179, 1043, 765.

4-chlorobenzoic anhydride 5d:(209 mg, 0.71 mmol, 71 % yield)

3-chlorobenzoic anhydride 5n: White solid; (206 mg, 0.70 mmol, 64 % yield); mp 94-96 °C;[23] R_f = 0.4 (Hexane/EtOAc, 4.2:0.8). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.49 (t, *J* = 7.9 Hz, 2H).[23] ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 135.2, 134.7, 130.4, 130.3, 128.6.[23] IR (neat, cm^{-1}): ν = 3073, 2926, 1792, 1575, 1471, 1424, 1277, 1202, 1039, 998, 736.[6]

4-fluorobenzoic anhydride 5e: (230 mg, 0.88 mmol, 88% yield).

[1,1'-biphenyl]-4-carboxylic anhydride 5o:[24] White solid; (295 mg, 0.78 mmol, 78 % yield); mp 138-140 °C; R_f = 0.158 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.4 Hz, 4H), 7.68 (d, *J* = 7.2 Hz, 4H), 7.53 (t, *J* = 7.4 Hz, 4H), 7.46 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 147.3, 139.6, 131.2, 129.1, 128.6, 127.6, 127.5, 127.4 IR (neat, cm^{-1}): ν = 3032, 2943, 1779, 1717, 1605, 1486, 1450, 1406, 1227, 1175, 1001, 744.

General Procedure for mixed anhydrides 5p-5x:

TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of an aldehyde or a benzylic alcohol (1.1 mmol) in 3.25 mL dichloromethane under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the aldehyde or the alcohol. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5p**, **5q** and **5r**, the solvent was evaporated under reduced pressure and the residue purified by flash chromatography. For the products **5s-5x** the reaction mixture was washed three times with a solution of 5 % HCl and then three times with a solution of 5 % $NaHCO_3$; the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure providing the desired anhydride.

Compound characterizations

4-chlorobenzoic 4-methylbenzoic anhydride 5p: White solid; (209 mg, 78 % 4-chlorobenzoic 4-methylbenzoic anhydride and 22% of 4-methylbenzoic anhydride); mp 100-104 °C; R_f = 0.46 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 8.04 - 8.01 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.33 - 7.30 (m, 2H), 2.45 (s, 3H). The ^{1}H NMR spectrum indicates about 78 % of 4-chlorobenzoic 4-methylbenzoic anhydride and about 22 % of 4-methylbenzoic anhydride ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1, 161.6, 145.8, 141.1, 131.8, 130.6, 129.6, 129.2, 127.4, 125.8, 21.8. ^{13}C NMR signals display the presence of 4-chlorobenzoic 4-methylbenzoic anhydride and 4-methylbenzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 2917, 1789, 1717, 1609, 1592, 1400, 1222, 1171, 1063, 1007, 843, 1063, 1007, 843, 739. HRMS (HESI-FT-ORBITRAP) calcd for $C_{15}H_{11}ClNaO_3$ $[M+Na]^+$: 297,0289, found 297,0286.

4-bromobenzoic 4-chlorobenzoic anhydride 5q: White solid; (247 mg, 89 % 4-bromobenzoic 4-chlorobenzoic anhydride and 11 % 4-bromobenzoic anhydride); mp 212-216 °C; R_f = 0.51 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H). The ^{1}H NMR spectrum indicates about 89 % of 4-bromobenzoic 4-chlorobenzoic anhydride and about 11 % of 4-bromobenzoic anhydride[30]. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.3, 141.4, 132.4, 131.9, 131.9, 130.2, 129.4, 127.5, 127.1. ^{13}C NMR signals display the presence of 4-bromobenzoic 4-chlorobenzoic anhydride and 4-bromobenzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3078, 3101, 1785, 1719, 1590, 1482, 1340, 1251, 1090, 844. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_8BrClNaO_3$ $[M+Na]^+$: 360,9238, found 360,9234.

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Benzoic 4-chlorobenzoic anhydride 5r: White solid; (218 mg, 89 % benzoic 4-chlorobenzoic anhydride and 11 % benzoic anhydride); mp 105-111 °C; R_f = 0.48 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.48 (m, 4H). The ^{1}H NMR spectrum indicates about 89% of benzoic 4-chlorobenzoic anhydride and about 11% of benzoic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0, 161.5, 141.1, 134.6, 131.8, 130.5, 129.2, 128.9, 128.5, 127.2. ^{13}C NMR signals display the presence of benzoic 4-chlorobenzoic anhydride and benzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3071, 1784, 1722, 1598, 1451, 1401, 1212, 1173, 1039, 997, 701. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_9ClNaO_3$ $[M+Na]^+$: 283,0132, found 283,0128.

Benzoic pivalic anhydride 5s: Colorless oil; (156 mg, 93 % benzoic pivalic anhydride and 7 % pivalic anhydride); R_f = 0.41 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 1.35 (s, 9H). The ^{1}H NMR spectrum indicates about 93 % of benzoic pivalic anhydride and about 7 % of pivalic anhydride ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 162.2, 134.1, 130.1, 128.8, 128.5, 40.1, 26.3. ^{13}C NMR signals display the presence of benzoic pivalic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3065, 2978, 2937, 1802, 1733, 1601, 1480, 1542, 1240, 1067, 1011, 912, 700. HRMS (HESI-FT-ORBITRAP) calcd for $C_{12}H_{14}NaO_3$ $[M+Na]^+$: 229,0835, found 229,0834.

2,4-dichlorobenzoic pivalic anhydride 5t: Colorless oil; (228 mg, 88 % 2,4-dichlorobenzoic pivalic anhydride and 12 % pivalic anhydride); R_f = 0.66 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 1.32 (s, 9H). The ^{1}H NMR spectrum indicates about 88 % of 2,4-dichlorobenzoic pivalic anhydride and about 12% of pivalic anhydride.^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.0, 160.2, 139.6, 135.5, 133.1, 131.2, 127.1, 126.7, 39.9, 26.3. ^{13}C NMR signals display the presence of benzoic 2,4-dichlorobenzoic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3096, 2978, 2937, 1806, 1738, 1585, 1479, 1376, 1231, 1054, 1001, 734. HRMS (HESI-FT-ORBITRAP) calcd for $C_{12}H_{12}Cl_2NaO_3$ $[M+Na]^+$: 297,0056, found 297,0054.

2,4,6-trichlorobenzoic pivalic anhydride 5u: Colorless oil; (262 mg, 89 % 2,4,6-trichlorobenzoic pivalic anhydride and 11 % pivalic anhydride); R_f = 0.44 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 1.28 (s, 9H). The ^{1}H NMR spectrum indicates about 89 % of 2,4,6-trichlorobenzoic pivalic anhydride and about 11 % of pivalic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 159.2, 136.7, 132.6, 130.6, 128.1, 40.0, 26.3. ^{13}C NMR signals display the presence of 2,4,6-trichlorobenzoic pivalic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3083, 2978, 2937, 1818, 1751, 1579, 1550, 1480, 1371, 1237, 1098, 998, 961. HRMS (HESI-FT-ORBITRAP) calcd for $C_{12}H_{11}Cl_3NaO_3$ $[M+Na]^+$: 330,9666, found 330,9667.

4-(*tert*-butyl)benzoic pivalic anhydride 5v: Colorless oil; (197 mg, 91 % of 4-(*tert*-butyl)benzoic pivalic anhydride and 9 % of pivalic anhydride); R_f = 0.44 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 1.35 (s, 9H), 1.33 (s, 9H). he ^{1}H NMR spectrum indicates about 91 % of 4-(*tert*-butyl)benzoic pivalic anhydride and about 9 % of pivalic anhydride.^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 162.2, 158.1, 130.1, 126.1, 125.6, 40.0, 35.0, 30.8, 26.4. ^{13}C NMR signals display the presence of benzoic 4-(*tert*-butyl)benzoic pivalic anhydride and of pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3061, 2968, 2908, 1802, 1731, 1608, 1461, 1409, 1365, 1252, 1070, 1000, 849. HRMS (HESI-FT-ORBITRAP) calcd for $C_{16}H_{22}NaO_3$ $[M+Na]^+$: 285,1461, found 285,1457.

[1,1'-biphenyl]-4-carboxylic pivalic anhydride 5w: Yellow solid; (240 mg, 95 % [1,1'-biphenyl]-4-carboxylic pivalic anhydride and 5 % pivalic anhydride.); mp 86 - 91°C; R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.48 - 7.37 (m, 3H), 1.37 (s, 9H). The ^{1}H NMR spectrum indicates about 95 % of [1,1'-biphenyl]-4-carboxylic pivalic anhydride and about 5 % of pivalic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 162.1, 146.8, 139.3, 130.6, 128.8, 128.3, 127.4, 127.1, 127.0, 40.1, 26.34. ^{13}C NMR signals display the presence of [1,1'-biphenyl]-4-carboxylic pivalic anhydride and pivalic anhydride.in the carbonyl region. IR (neat, cm^{-1}): ν = 3060, 3032, 2977, 2936, 1780, 1728, 1607, 1480, 1406, 1279, 1250, 1071, 1000, 748. HRMS (HESI-FT-ORBITRAP) calcd for $C_{18}H_{18}NaO_3$ $[M+Na]^+$: 305,1148, found 305,1148.

Benzoic cyclohexanecarboxylic anhydride 5x: Colorless oil; (198 mg, 89 % benzoic cyclohexanecarboxylic anhydride 7 % cyclohexanecarboxylic anhydride and 4 % benzoic anhydride.); R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.57 (dd, *J* = 10.9, 8.8 Hz, 1H), 2.05 (d, *J* = 13.0 Hz, 2H), 1.81 - 1.78 (m, 2H), 1.67 – 1.53 (m, 3H), 1.38 - 1.24 (m, 3H). The ^{1}H NMR spectrum indicates about 89 % of benzoic cyclohexanecarboxylic anhydride, about 7 % of cyclohexanecarboxylic anhydride and about 4 % of benzoic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 162.5, 134.3, 130.3, 128.7, 44.1, 28.4, 25.5, 25.1. ^{13}C NMR signals display the presence of benzoic cyclohexanecarboxylic anhydride, of cyclohexanecarboxylic anhydride and of benzoic anhydride.in the carbonyl region. IR (neat, cm^{-1}): ν = 3064, 2935, 2857, 1806, 1731, 1600, 1452, 1263, 1235, 994, 701. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$: 255,0992, found 255,0990.

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Notes and references

1 (a) H. Rinderknecht and V. Ma, *Helv. Chim. Acta*, 1964, **47**, 162. (b) R. Kocz, J. Roestamadji and S. Mobashery, *J. Org. Chem.*, 1994, **59**, 2913.

2 F. Kazemi, H. Sharghi and M. A. Nasseri, *Synthesis*, 2004, **2**, 205.

3 (a) W. K. Fife and Z. D. Zhang, *Tetrahedron Lett.*, 1986, **27**, 4937. (b) F. Kazemi and A. R. Kiasat, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2003, **178**, 2287. (c) F. Kazemi, A. R. Kiasat and B. Mombaini, *Synth. Commun.*, 2007, **37**, 3219.

4 (a) R. Mestres and C. Palomo, *Synthesis*, 1981, **3**, 218. (b) Y. Kawamura, Y. Sato, T. Horie and M. Tsukayama, *Tetrahedron Lett.*, 1997, **38**, 7893.

5 K. S. Keshavamurthy, Y. D. Vankar and D. N. Dhar, *Synthesis*, 1982, **6**, 506.

6 Z. J. Kamiński, B. Kolesińska and M. Małgorzata, *Synth. Commun.*, 2004, **34**, 3349.

7 (a) T. Hata, K. Tajima and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2746. (b) A. Stadler and C. O. Kappe, *Tetrahedron*, 2001, **57**, 3915. (c) P. A. Clarke, N. E. Kayaleh, M. A. Smith, J. R. Baker, S. J. Bird and C. Chan, *J. Org. Chem.*, 2002, **67**, 5226.

8 (a) S. Fukuoka, S. Takimoto, T. Katsuki and M. Yamaguchi, *Tetrahedron Lett.*, 1987, **28,** 4711. (b) A. R. Hajipour and G. Mazloumi, *Synth. Commun*., 2002, **32**, 23. (c) R. R. Srivastava and G. W. Kabalka, *Tetrahedron Lett.*, 1992, **33**, 593. (d) W. Nakanishi, Y. Ikeda and H. Iwamura, *J. Org. Chem.*, 1982, **47**, 2275.

9 (a) K. Ekoue-Kovi and C. Wolf, *Chem. Eur. J.*, 2008, **14**, 6302. (b) S. Tang, J. Yuan, C. Liu and A. Lei, *Dalton Trans.*, 2014, **43**, 13460. (c) C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li, A. Lei, , *Angew. Chem. Int. Ed.*, 2011, **50**, 5144. (d) S. Gowrisankar, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.*, 2011, **50**, 5139. (e) J. Xia, A. Shao, A. Tang, X. Gao, M. Gao, A. Lei, *Org. Biomol. Chem.*, 2015, **13**, 6154.

10 N. Khatun, S. K. Santra, A. Banerjee and B. S. Patel, *Eur. J. Org. Chem.*, 2015, 1309.

11 D. Saberi, F. Shojaeyan and K. Niknam, *Tetrahedron Lett.*, 2016, **57**, 566.

12 Y. Nuree, R. Singha, M. Ghosh, P. Roy and K. Ray, *Tetrahedron Lett.*, 2016, **57**, 1479.

13 (a) S. Gaspa, A. Porcheddu and L. De Luca, *Org. Lett.*, 2015, **17**, 3666. (b) G. Dettori, S. Gaspa, A. Porcheddu and L. De Luca, *Adv. Synth. Catal.*, 2012, **354**, 2949. (c) M. Pilo, A. Porcheddu and L. De Luca, *Org. Biomol. Chem.*, 2013, **11**, 8241. (d) R. Cadoni, A. Porcheddu and L. De Luca, *Org. Lett.*, 2012, **14**, 5014. (e) A. Porcheddu and L. De Luca, *Adv. Synth. Catal.*, 2014, **356,** 2709.

14 The only example of synthesis of anhydrides from alcohols was reported by C. Hofmann, J. M. Schumann and P. R. Schreiner, *J. Org. Chem.*, 2015, **80**, 1972. In this paper mixed anhydrides prepared from alcohols and carboxylic acids were not isolated and characterized, but directly used as intermediates to perform a kinetic resolution of diols.

15 (a) S. Gaspa, A. Porcheddu, and L. De Luca, *Adv. Synth. Catal.*, 2016, **358**, 154. (b) G. Dettori, S. Gaspa, A. Porcheddu and L. De Luca, *Org. Biomol. Chem.*, 2014, **12**, 4582. (c) S. Gaspa, A. Porcheddu and L. De Luca, *Org. Biomol. Chem.*, 2013, **11**, 3803.

16 Schreiner and Szpilman reported a direct formation of anhydrides from aldehydes (ref. 14 and ref.17c,e), which appear to proceed *via* different mechanism.

17 (a) J. Inanaga, K. Hirata, H. Saeki, T. Katsuki and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1989. (b) M. M. Hikota, H. Tone, K. Horita and O. Yonemitsu, *Tetrahedron*, 1990, **46**, 4613. (c) H. Toledo, E. Pisarevsky, A. Abramovich, and A. M. Szpilman, *Chem. Commun.*, 2013, **49**, 4367. (d) C. Hofmann, M. M. Schuler, R. C. Wende and P. R. Schreiner, *Chem. Commun.*, 2014, **50**, 1221. (e) C. Hofmann, S. M. M. Schuler, R. Wende, P.R. Szpilman, *Chem. Commun.*, 2014, **50**, 1221.

18 C. D. Hurd and M. F. Dull, *J. Am. Chem. Soc.*, 1932, **54**, 3427.

19 ^{1}H NMR spectra were recordered, see supporting information.

20 I. Dhimitruka and J. SantaLucia, *Org. Lett.*, 2006, **8**, 47.

21 (a) H. Veisi, *Synthesis*, 2010, 2631. (b) N. Srilakshmi-Krishnaveni, K. Suredra and K. Rama Rao, *Adv. Synth. Catal.*, 2004, **346**, 346; (c) U. Tilstam and H. Weinmann, *Org. Process Res. Dev.*, 2002, **6**, 384. d) R. Filler, *Chem. Rev.* 1963, **63**, 21.

22 (a) S. R. Wilson, S. Tofigh and R. N. Misra, *J. Org. Chem.*, 1982, **47**, 1360. (b) D. Ginsburg, *J. Am. Chem. Soc.*, 1951, **73**, 702.

23 W. Phakhodee, C. Duangkamol, S. Wangngae and M. Pattarawarapan, *Tetrahedron Letters*, 2016, **57**, 325.

24 Y. Li, D. Xue, C. Wang, Z.-T. Liu and J. Xiao, *Chem. Comm.*, 2012, **48**, 1320.

25 K. Griesbaum, H.-J. G., W. Volpp and I.-C. Jung *Chem. Ber.*, 1991, **124**, 947.

26 M. Al-Talib, I. Jibril, J. C. Jochims and G. Huttner, *Chem. Ber.*, 1984, **117**, 3211.

27 Y. Hamada, K. Makino, J. Ohtaka and Y. Hamada, *Heterocycles*, 2009, **77**, 629.

28 M. C. Sheikh, S. Takagi, T. Yoshimura and H. Morita, *Tetrahedron*, 2010, **66**, 7272.

29 M. D. Konieczynska, C. Dai and C. R. J. Stephenson, *Org. Biomol. Chem.*, 2012, **10**, 4509.

30 V. Cirriez, C. Rasson and O. Riant, *Adv. Synth. Cat.*, 2013, **355**, 3137.

31 K. Sakai, Y. Nakahara and T. Ogawa, *Tetrahedron Lett.*, 1990, **31**, 3035.

32 R. Köster, A. Sporzyński, W. Schüßler, D. Bläser and R. Boese, *Chem. Ber.*, 1994, **127**, 1191.

33 C. Hofmann, J. M. Schümann and P. R. Schreiner, *J. Org. Chem.*, 2015, **80**, 1972.

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