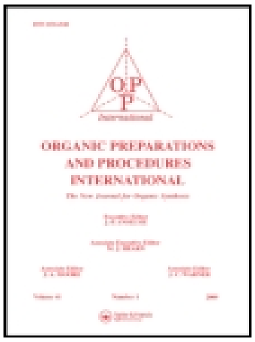


Taylor & Francis
Taylor & Francis Group

Organic Preparations and Procedures International
The New Journal for Organic Synthesis

ISSN: 0030-4948 (Print) 1945-5453 (Online) Journal homepage: http://www.tandfonline.com/loi/uopp20

Diphenylamine-Terephthalaldehyde Resin p-Toluenesulfonate (DTRT) as an Efficient Catalyst for Tetrahydropyranylation, Deprotection of Tetrahydropyranyl and Silyl Ethers, Esterification, and Transesterification

Kiyoshi Tanemura & Tsuneo Suzuki

To cite this article: Kiyoshi Tanemura & Tsuneo Suzuki (2016) Diphenylamine-Terephthalaldehyde Resin p-Toluenesulfonate (DTRT) as an Efficient Catalyst for Tetrahydropyranylation, Deprotection of Tetrahydropyranyl and Silyl Ethers, Esterification, and Transesterification, Organic Preparations and Procedures International, 48:1, 72-80, DOI: 10.1080/00304948.2016.1127103

To link to this article: http://dx.doi.org/10.1080/00304948.2016.1127103

Organic Preparations and Procedures International, 48:72–80, 2016
Copyright © Taylor & Francis Group, LLC
ISSN: 0030-4948 print / 1945-5453 online
DOI: 10.1080/00304948.2016.1127103

Taylor & Francis
Taylor & Francis Group

Diphenylamine-Terephthalaldehyde Resin *p*-Toluenesulfonate (DTRT) as an Efficient Catalyst for Tetrahydropyranylation, Deprotection of Tetrahydropyranyl and Silyl Ethers, Esterification, and Transesterification

Kiyoshi Tanemura and Tsuneo Suzuki

Chemical Laboratory, School of Life Dentistry at Niigata, Nippon Dental University, Hamaura-cho, Niigata 951-8580, Japan

Solid acid catalysts are frequently employed in organic synthesis because of simplified work-up procedure, use of the recycled catalysts, and minimized corrosion of metallic reaction vessels. Although several strongly acidic resin catalysts such as *Amberlyst 15*, *Dowex 50*, and *Nafion NR50* have been used as catalysts,[1] they are not suitable for use with acid-sensitive compounds. The few commercially available weakly acidic resins such as poly(4-vinylpyridinium *p*-toluenesulfonate) [polyPPTS][2] and poly(4-vinylpyridinium chloride) [polyPCl][3] are expensive. We recently reported that ***A***niline-***T***erephthalaldehyde ***R***esin *p*-***T***oluenesulfonate (***ATRT***) obtained by the condensation of aniline with terephthalaldehyde in the presence of *p*-toluenesulfonic acid acts as a mild polymeric acidic catalyst.[4] As a continuation of this study, the more hydrophobic ***D***iphenylamine-***T***erephthalaldehyde ***R***esin *p*-***T***oluenesulfonate (***DTRT***) was prepared and its effectiveness studied in various reactions. The present article describes the results for the tetrahydropyranylation of alcohols, the deprotection of tetrahydropyranyl and silyl ethers, the esterification of carboxylic acids, and the transesterification of carboxylic esters with alcohols catalyzed by ***DTRT*** and ***DTRT(H)*** [see below].

Treatment of diphenylamine with terephthaldehyde (*TPA*) in the presence of *p*-toluenesulfonic acid (*TsOH*) in methanol (*MeOH*) afforded ***DTRT.*** It is very insoluble in hot water and hot organic solvents such as chloroform, tetrahydrofuran, acetonitrile, dimethyl sulfoxide, and dimethyl formamide. The acid density of ***DTRT*** calculated from elemental analysis is 0.76 $\text{mmol}\cdot\text{g}^{-1}$. It lost its activity entirely after the fifth re-use in tetrahydropyranylation. Treatment of ***DTRT*** with TsOH in MeCN led to ***DTRT(H)*** with high sulfonate group content (acid density = 1.17 $\text{mmol}\cdot\text{g}^{-1}$) with the same solubility behavior as ***DTRT***. It could be recycled five times without significant loss of activity.

The reactions of nine alcohols including an allylic alcohol and alcohols incorporating acetal groups, double and triple bonds, and conjugated ketones with 1.5 equiv. of 3,4-

Received January 14, 2015; in final form September 15, 2015.

Address correspondence to Kiyoshi Tanemura, Chemical Laboratory, School of Life Dentistry at Niigata, Nippon Dental University, Hamaura-cho, Niigata 951-8580, Japan. E-mail: tanemura@ngt.ndu.ac.jp

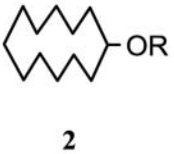
dihydro-2*H*-pyran in the presence of ***DTRT(H)*** at room temperature in MeCN or CH_2Cl_2 gave the corresponding tetrahydropyranyl (*THP*) ethers in good to excellent yields (Table 1).[5,6] Only 1.2–3.0 mol% of ***DTRT(H)*** is required to catalyze these reactions and in spite of its greater acidity, the acid-sensitive groups present in these alcohols survived the reaction conditions.

The results in the deprotection of THP ethers[7] and silyl ethers[8] are shown in Table 2. The cleavage of various THP ethers containing allylic carbons, double bonds, triple bonds, and enones catalyzed by 3–6 mol% of ***DTRT(H)*** at room temperature in MeOH afforded the corresponding alcohols in good yields (*Entries 1–8*). Similarly, treatment of triethylsilyl (*TES*) and *tert*-butyldimethylsilyl (*TBDMS*) ethers with only 0.6–1.2 mol% of ***DTRT(H)*** gave the corresponding alcohols in excellent yields at room temperature in MeOH. *TES* ethers **1c**, **2c**, **8c**, and **9c** were more easily cleaved than *TBDMS* ethers **1d**, **2d**, **8d**, and **9d** but the deprotection of *tert*-butyldiphenylsilyl (*TBDPS*) ethers **1e**, **2e**, **8e**, and **9e** did not occur under the conditions employed.

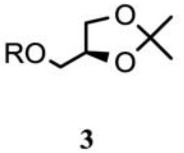
Table 3 indicates that in comparison with various weakly acidic solid acids, ***DTRT(H)*** showed the highest activity in the tetrahydropyranylation of 1-dodecanol (**1a**) (*Table 3, Reaction 1*), the deprotection of THP ether ***1b*** (*Reaction 2*), and the cleavage of TBDMS ether **1d** (*Reaction 3*). Two reasons may be considered for the higher activity of ***DTRT(H)*** compared to ***ATRT***: (1) Since ***DTRT(H)*** is more hydrophobic than ***ATRT***, the substrates may approach the catalyst more readily and (2) ***DTRT(H)*** is a stronger acid than ***ATRT*** because DPA is less basic than aniline.[9]

$CH_3(CH_2)_{11}OR$

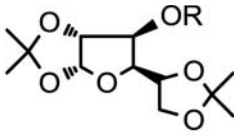
1



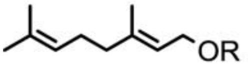
2



3



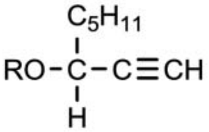
4



5

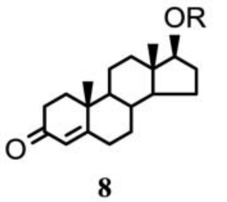
$PhCH_2OR$

6

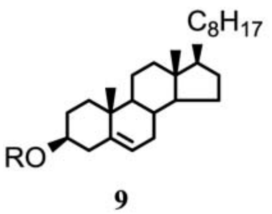


$RO-CH(C_5H_{11})-C\equiv CH$

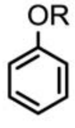
7



8



9



10

a, R = H; **b**, R = THP; **c**, R = TES; **d**, R = TBDMS; **e**, R = TBDPS

The esterification[10–12] of carboxylic acids using equimolar amounts of alcohols was carried out at reflux temperature in *n*-heptane[10,11] in the presence of 10 mol% of ***DTRT (H)*** (Table 4, *Entries 1, 4, 6*). The reactions without the solvent were considerably faster

Table 1

Tetrahydropyranylation of Alcohols Catalyzed by DTRT(H)[a]

Entry	Alcohol	Time (h)	Yield (%)	Bp (°C / mmHg)[b] or Mp (°C)
1	**1a**	2	91	107–110 / 1.5
2	**2a**	2	91	110–113 / 2.0
3	**3a**	5	99	90–93 / 1.5
4	**4a**	8	100	135–138 / 2.0
5[c]	**5a**	24	84	113–116 / 1.5
6	**6a**	1	100	91–92 / 2.0
7[c]	**7a**	8	88	118–121 / 17
8[d]	**8a**	3	100	99–100
9[e]	**9a**	2	99	146–147

a) Alcohol (1.0 mmol), DHP (1.5 mmol), DTRT(H) (10 mg, 1.2 mol%), MeCN (5 mL), RT. b) 1 mmHg = 133.322 Pa. c) DTRT(H) (25 mg) was used. d) MeCN (10 mL) was used. e) CH_2Cl_2 (5 mL) was used.

Table 2

Deprotection of THP Ethers[a] and Silyl Ethers[b] Catalyzed by DTRT(H)

Entry	Substrate	Time	Yield (%)
1	**1b**	3 h	94
2	**2b**	2 h	98
3[c]	**5b**	3 h	89
4	**6b**	3 h	81
5	**7b**	4 h	80
6	**8b**	3 h	90
7[d]	**9b**	6 h	90
8	**10b**	1 h	96
9	**1c**	10 min	91
10	**1d**	1 h	95
11	**1e**	1 h	0
12	**2c**	10 min	94
13	**2d**	5 h	100
14	**2e**	5 h	0
15[e]	**8c**	15 min	90
16[e]	**8d**	32 h	100
17[e]	**8e**	32 h	0
18[f]	**9c**	10 min	96
19[f]	**9d**	24 h	90
20[f]	**9e**	24 h	0

a) THP ether (1.0 mmol). DTRT(H) (25 mg, 3 mol%), MeOH (5 mL), RT. b) Silyl ether (1.0 mmol), DTRT(H) (5 mg, 0.6 mol%), MeOH (10 mL), RT. c) DTRT(H) (50 mg) was used. d) MeOH (5 mL) – CH_2Cl_2 (5 mL) was used. e) DTRT(H) (10 mg) was used. f) DTRT(H) (10 mg), MeOH (5 mL) - THF (5 mL) were used.

Table 3
Protection and Deprotection Reactions Catalyzed by Various Catalysts

Entry	Catalyst	Acid density (mmol·g^{-1})	Reaction 1[a] Time / Yield	Reaction 2[b] Time / Yield	Reaction 3[c] Time / Yield
1	ATRT	1.01	5 h / 96%	4 h / 97%	1.5 h / 100%
2	DTRT(H)	1.17	0.5 h / 100%[d]	0.5 h / 97%	1 h / 93%
3	PolyPPTS	3.5	4 h / 100%	8 h / 98%	2 h / 100%
4	PolyPCL	6.5	24 h / 92%	8 h / 98%	2 h / 99%
5	Montmorillonite K10	0.65	1.5 h / 81%[d]	15 h / 95%	15 h / 98%
6	Mordenite	0.512	1.5 h / 75%[d]	8 h / 98%	15 h / 0%

a) Compound **1a** (1.0 mmol), DHP (1.5 mmol), cat (0.10 mmol acidic units, 10 mol%), MeCN (5 mL), RT. b) Compound **1b** (1.0 mmol), cat (0.17 mmol acidic units, 17 mol%), MeOH (5 mL), RT. c) Compound **1d** (1.0 mmol), cat (0.017 mmol acidic units, 1.7 mol%), MeOH (10 mL), RT. d) Pyran oligomers were produced.

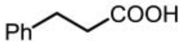
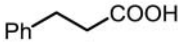
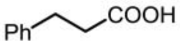
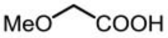
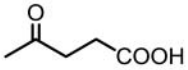
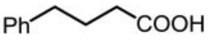
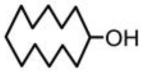
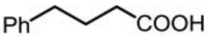
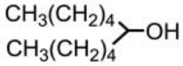
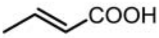
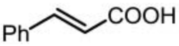
than those in *n*-heptane (*Entries 2, 5, 7*). Various substrates incorporating a double bond, a halogen, a methoxy group, a carbonyl group, and a triple bond reacted under neat conditions to give the corresponding esters in good yields (*Entries 5, 8–11*). It has been reported that cyclododecene (>25%) was produced as a by-product in the condensation of 4-phenylbutyric acid with an equimolar amount of cyclododecanol catalyzed by weakly acidic diphenylammonium triflate ($[Ph_2NH_2]^+[OTf]^-$).[11] In contrast, ***DTRT(H)*** catalyzed the esterification with secondary alcohols to the corresponding esters in good yields with less than 1% of the undesired alkenes being generated (*Entries 12, 13*).[11] Less reactive α,β-unsaturated carboxylic acids and benzoic acid were also converted to the corresponding esters in good yields (*Entries 14–16*).

The transesterification[10,12] of carboxylic esters with 1.5 equiv. of alcohols catalyzed by 10 mol% of ***DTRT(H)*** was performed in *n*-heptane as shown in Table 5; the transesterification of methyl 3-phenylpropionate proceeded much more rapidly without solvent than in *n*-heptane (*Entries 1, 2*). Similarly, various substrates reacted in neat conditions to give the corresponding esters in good to excellent yields. Ethyl and *n*-butyl 3-phenylpropionates were also converted into the *n*-octyl esters **11** in excellent yields (*Entries 4, 5*). Several functional groups such as a double bond, a methoxy group, and a carbonyl group survived these conditions unscathed (*Entries 7–9*). When secondary alcohols were employed, the corresponding esters were obtained in good yields and the yield of the alkenes was less than 1% (*Entries 12, 13*). The transesterification of methyl cinnamate and methyl benzoate also gave the esters in good yields (*Entries 14, 15*).

Although ***DTRT(H)*** could be recycled five times without loss of activity for the tetrahydropyranylation of alcohols, the esterification of carboxylic acids, and the transesterification of carboxylic esters, it gradually decomposed and was completely inactive upon the fifth re-cycling in the deprotection of THP ether **1b** at room temperature for 1 h in methanol. Its elemental analysis after the fifth use in the deprotection of **1b** showed that the proportion of the *p*-toluenesulfonate salt per diphenylamine unit had decreased from 33% to 18%. It partially decomposed when kept at room temperature for 1 h in methanol and in fact, a small amount of TsOH was detected from the filtrate after it was recovered. A longer reaction time (1.5 h) was required to complete the deprotection of **1b** when it was carried out using the filtrate obtained from the decomposition of ***DTRT(H)*** in MeOH mentioned above. This result suggests that both ***DTRT(H)*** and TsOH may catalyze the

Table 4

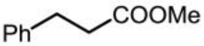
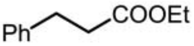
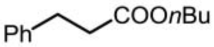
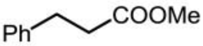
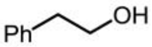
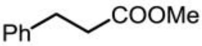
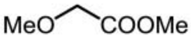
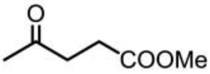
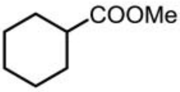
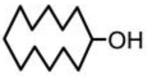
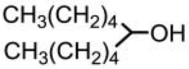
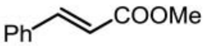
Esterification between Equimolar Amounts of Carboxylic Acids and Alcohols Catalyzed by DTRT (H)[a]

				R^1COOR^2 **11-22**		
Entry	R^1COOH	R^2OH	Time (h)		Yield (%)	Terephthalaldehyde p (℃ / mmHg)[b] or mp (℃)
1		$CH_3(CH_2)_7OH$	48	**11**	87	142 / 1.0
2[c]			8	**11**	92	
3[c,d]			8	**11**	40	
4			48	**12**	93	166 / 1.4
5[c]			6	**12**	87	
6	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_{11}OH$	48	**13**	92	27-28
7[c]			12	**13**	83	
8[c]			8	**14**	82	153 / 1.2
9[c]		$CH_3(CH_2)_7OH$	2	**15**	88	83 / 1.0
10[c]		$CH_3(CH_2)_7OH$	4	**16**	93	117 / 1.1
11[c]	Ph−C≡C−COOH	$CH_3(CH_2)_7OH$	16	**17**	83	151 / 1.0
12[c]			48	**18**	82[f]	179 / 0.9
13[c]			60	**19**	82[g]	150 / 1.0
14[c]		$CH_3(CH_2)_{11}OH$	48	**20**	83	129 / 1.6
15[c]		$CH_3(CH_2)_7OH$	48	**21**	83	147 / 1.0
16[c,e]	PhCOOH	$CH_3(CH_2)_7OH$	48	**22**	81	122 / 1.2

a) Carboxylic acid (2.0 mmol), alcohol (2.0 mmol), DTRT (H) (171 mg, 10 mol%), heptane (4 mL), reflux. b) 1 mmHg = 133.322 Pa. c) Without heptane, 110 ℃. d) ATRT (198 mg, 10 mol%) was used instead of DTRT (H). e) DTRT (H) (20 mol%) was used. f) Cyclododecene (0.3%) was obtained. g) 5-Undecene (0.6%) was obtained.

Table 5

Transesterification between Carboxylic Esters and 1.5 Equiv. of Alcohols Catalyzed by DTRT (H)[a]

Entry	R^1COOR^3	R^2OH	Time (h)	Yield of R^1COOR^2 **11-24** (%)	
1		$CH_3(CH_2)_7OH$	16	**11**	25
2[b]			16	**11**	94 (83)[e]
3[b,c]			16	**11**	42
4[b]		$CH_3(CH_2)_7OH$	24	**11**	94
5[b]		$CH_3(CH_2)_7OH$	62	**11**	97
6[b]			24	**23**[f]	94
7[b]			6	**12**	83
8[b]		$CH_3(CH_2)_7OH$	8	**15**	81
9[b]		$CH_3(CH_2)_7OH$	8	**16**	87
10[b]	$CH_3(CH_2)_{10}COOMe$	$CH_3(CH_2)_{11}OH$	24	**13**	98
11[b]		$CH_3(CH_2)_7OH$	24	**24**[g]	90
12[b]			48	**18**	82[h]
13[b]			72	**19**	80[i]
14[b]		$CH_3(CH_2)_7OH$	48	**21**	94
15[b,d]	PhCOOMe	$CH_3(CH_2)_7OH$	48	**22**	80

a) Carboxylic ester (2.0 mmol), alcohol (3.0 mmol), DTRT (H) (171 mg, 10 mol%), heptane (4 mL), reflux. b) Without heptane, 110 ℃. c) ATRT (198 mg, 10 mol%) was used instead of DTRT (H). d) DTRT (H) (20 mol%) was used. e) Parenthesis shows the yield in the experiment using 1.0 equiv. of 1-octanol. f) Bp 141℃/1.0 mmHg. g) Bp 108℃ / 0.9 mmHg. h) Cyclododecene (0.3%) was obtained. i) 5-Undecene (0.9%) was obtained.

deprotection of **1b**. Similarly, ***DTRT(H)*** lost 76% of its activity after the fifth re-cycling for the deprotection of TBDMS ether **1d** in MeOH.

In conclusion, ***DTRT(H)*** is an efficient catalyst for the tetrahydropyranylation of alcohols and the deprotection of THP and TBDMS ethers. In addition, ***DTRT(H)*** catalyzed the esterification of carboxylic acids with an equimolar amount of alcohols and the transesterification of carboxylic esters with 1.5 equiv. of alcohols. It is important to note that the dehydration of secondary alcohols to alkenes was largely suppressed in the synthesis of esters and that the corrosion of metallic vessels is minimized. The work-up procedure is remarkably simple, and ***DTRT(H)*** is easy to handle and quite stable in air for more than three years at room temperature.

Experimental Section

Melting points were determined on a Yamato melting point apparatus MP-21 and are uncorrected. IR spectra were recorded using a JEOL FT/IR-620 spectrophotometer. ^{1}H NMR spectra were measured on a Hitachi R-1200 spectrometer using tetramethylsilane as an internal standard. Grinding was carried out using an Absolute Mill ABS-W instrument (Osaka Chemical Co.). Column chromatography was performed on Wakogel C-200. PolyPPTS (2% cross-linked with divinylbenzene), PolyPCL (2% cross-linked with divinylbenzene), and Montmorillonite K10 (220–270 m^2/g) were purchased from Aldrich. Mordenite (synthetic zeolite HS-690, hydrogen mordenite, 420 m^2/g) was purchased from Wako Chemicals. Acid densities of the resin salts were calculated from elemental analyses (acid density = number of sulfur in nominal sample composition/nominal molecular weight × 1000). Silyl ethers were prepared using a reported method.[13] THP ethers[4,14] silyl ethers[15], and esters[10,16] were identified by comparison of their spectroscopic characteristics with those of authentic samples.

Synthesis of DTRT

Terephthalaldehyde (6.7 g, 50 mmol) was added to a solution of diphenylamine (16.9 g, 100 mmol) and TsOH.H_2O (19.0 g, 100 mmol) in MeOH (120 mL) in a 300 mL round bottom flask fitted with a reflux condenser with stirring using a spin bar. The solution was stirred at room temperature for 3 h and then at 60°C for 8 h. The dark green solid formed was collected, washed with MeOH (100 mL × 2), dried under reduced pressure (20 mmHg) for 1 h, and then ground to a powder (using a mill[17] at 15,000 rpm for 1 min). The resulting fine powder was suspended in MeOH (300 mL) and stirred for 0.5 h. The green solid was collected, washed with MeOH (100 mL × 3) and re-suspended and stirred in distilled water (300 mL) and then in acetone (300 mL), washed with ether (100 mL × 2) and finally dried under reduced pressure (1 mmHg) to give 27.7 g (71%) of a dark green powder, mp. > 280°C, whose nominal composition was approximately $C_{83.33}H_{69.75}N_{4.83}O_{8.75}S_{1.00}$. IR (KBr): 3398, 3020, 2969, 2921, 2854, 1699, 1599, 1556, 1508, 1306, 1242, 1218, 1167, 1113, 1031, 1009, 806, 788, 747, 681, 566 cm^{-1}.

Synthesis of DTRT(H)

A suspension of DTRT (5.0 g, 14.6 mmol free amine) and TsOH·H_2O (7.5 g, 39.5 mmol) in MeCN (50 mL) was stirred using a spin bar at 80°C for 8 h in a 100 mL round bottom flask fitted with a reflux condenser. The insoluble black powder was collected, washed with MeCN (100 mL × 3) and distilled water until the wash water reached a pH of 7.

The precipitate was washed with acetone (100 mL × 3), ether (100 mL × 2), and dried under reduced pressure (1 mmHg) at room temperature to give 5.4 g of a black powder, mp. > 280°C, whose nominal composition was approximately $C_{52.63}H_{46.74}N_{3.05}O_{6.11}S_{1.00}$. IR (KBr): 3422, 3020, 2921, 2860, 1699, 1602, 1576, 1507, 1307, 1242, 1218, 1164, 1118, 1032, 1009, 810, 747, 681 cm^{-1}.

General Procedure for Tetrahydropyranylation of Alcohols Catalyzed by DTRT(H)

DTRT(H) (10 mg, 1.2 mol%) was added to a solution of **1a** (186 mg, 1.0 mmol) and 3,4-dihydro-2H-pyran (126 mg, 1.5 mmol) in dry MeCN (5 mL). The mixture was stirred at room temperature for 2 h. The precipitated catalyst was collected and washed with MeCN (1.5 mL × 3). Evaporation of the filtrate gave a residue that was purified by column chromatography on silica gel using n-hexane–EtOAc (20:1) as eluent to afford **1b** (246 mg, 91%). THP ethers **3b**, **4b**, **7b**, **8b**, and **9b** were obtained as an inseparable mixture of diastereomers at C-2'.

General Procedure for Deprotection of THP Ethers Catalyzed by DTRT(H)

DTRT(H) (25 mg, 3 mol%) was added to a solution of **1b** (270 mg, 1.0 mmol) in dry CH_3OH (5 mL). The mixture was stirred at room temperature for 3 h and filtered. The solid collected was washed with CH_3OH (1.5 mL × 3) and the combined filtrate and washes were evaporated. The residue was purified by column chromatography on silica gel using hexane–acetone (5:1) as eluent to give **1a** (175 mg, 94%).

General Procedure for Deprotection of Silyl Ethers Catalyzed by DTRT(H).

DTRT(H) (5 mg, 0.6 mol%) was added to a solution of **1d** (300 mg, 1.0 mmol) in dry CH_3OH (10 mL). The mixture was stirred at room temperature for 1 h and treated in a manner similar to the procedure described above to give **1a** (186 mg, 100%).

General Procedure for Esterification Catalyzed by DTRT(H)

A mixture of 3-phenylpropionic acid (300 mg, 2.0 mmol), 1-octanol (260 mg, 2.0 mmol), and DTRT(H) (171 mg) was heated at 110°C for 8 h. Removal of DTRT(H) by filtration followed by evaporation of the filtrate at 40°C under reduced pressure gave a residue that was purified by column chromatography (hexane:EtOAc = 20:1) to give **11** (482 mg, 92%). The catalyst which was separated by filtration was used for the next experiment.

General Procedure for Transesterification Catalyzed by DTRT(H)

A mixture of methyl 3-phenylpropionate (328 mg, 2.0 mmol), 1-octanol (390 mg, 3.0 mmol), and DTRT(H) (171 mg) was stirred at 110°C for 4 h. The mixture was treated in a manner similar to the procedure described above to give **11** (493 mg, 94%).

Acknowledgments

We thank the Division of Chemical Analysis, Systems Engineering for the elemental analyses and Nippon Dental University for the award of a Research Promotion Grant

(NDUF-15-09). We deeply appreciate the help of Prof. Jean-Pierre Anselme, the Editor of the *Journal*, whose constructive comments helped us immensely to improve the manuscript.

References

1. G. Gelbard, *Ind. Eng. Chem. Res.*, **44**, 8468 (2005).
2. F. Menger and C. Chu, *J. Org. Chem.*, **46**, 5044 (1981).
3. R. D. Johnston, C. R. Marston, P. E. Krieger and G. L. Goe, *Synthesis*, 393 (1988).
4. K. Tanemura and T. Suzuki, *Tetrahedron Lett.*, **54**, 6740 (2013).
5. M. Miyashita, A. Yoshikoshi and P. A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977).
6. J. R. Stephens, P. L. Butler, C. H. Clow, M. C. Oswald, R. C. Smith and R. S. Mohan, *Eur. J. Org. Chem.*, 3827 (2003).
7. J. Liu and C.-H. Wong, *Tetrahedron Lett.*, **43**, 4037 (2002).
8. J. A. Marshall and K. C. Ellis, *Org. Lett.*, **5**, 1729 (2003).
9. F. G. Bordwell, *Acc. Chem. Res.*, **21**, 456 (1988).
10. K. Tanemura and T. Suzuki, *Tetrahedron Lett.*, **54**, 1972 (2013).
11. A. Sakakura, S. Nakagawa and K. Ishihara, *Tetrahedron*, **62**, 422 (2006).
12. T. Wakasugi, T. Misaki, K. Yamada and Y. Tanabe, *Tetrahedron Lett*., **41**, 5249 (2000).
13. E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).
14. K. Tanemura, T. Suzuki and T. Horaguchi, *Bull. Chem. Soc. Jpn*, **67**, 290 (1994).
15. K. Tanemura, T. Suzuki and T. Horaguchi, *J. Chem. Soc., Perkin Trans.*, **1**, 2997 (1992).
16. M. S. Rahimi, S. I. Mekhtiev, P. D. Shikhalizade, R. B. Tagiev, F. G. Gumbatova and I. A. Novruzov, *Azarbaycan Neft Tasarrufati*, 54 (1983).
17. Although it is possible to grind the product by hand, this process is very hard and may take a long time.