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Full Paper

tert-Butylating Reagent

Development of a Triazine-Based *tert*-Butylating Reagent, TriAT-*t*Bu

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Abstract: A new *tert*-butylating reagent, 2,4,6-tris(*tert*-butoxy)-1,3,5-triazine (TriAT-*t*Bu) has been developed for the acid-catalyzed *tert*-butylation of alcohols and carboxylic acids. The reaction of various alcohols and carboxylic acids with TriAT-*t*Bu in the presence of a catalytic amount of an acid provided the corresponding *tert*-butyl ethers and esters in good to high yields. TriAT-*t*Bu is an air-stable solid synthesized in good yield from inexpensive starting materials, namely, cyanuric chloride, *t*BuOH, and sodium hydride.

Introduction

We have recently reported the development of a triazine-based *O*-benzylating reagent, 2,4,6-tris(benzyloxy)-1,3,5-triazine (TriBOT)[1] and a *para*-methoxybenzylating reagent (TriBOT-PM),[2] which can be considered as the formal trimer of the smallest unit of benzyl imidate (Figure 1). These reagents have several characteristic features: (1) they can be easily synthesized from the corresponding inexpensive alcohols and cyanuric chloride in one step; (2) they are non-hygroscopic solids, non-irritants, and non-allergens and can be stored and handled in air at room temperature; (3) the co-product isocyanuric acid can be easily removed by filtration under standard workup conditions. Our next goal is to demonstrate the possibility of using this concept for designing an alkylating reagent, 2,4,6-tris(alkyloxy)-1,3,5-triazine (TriAT).

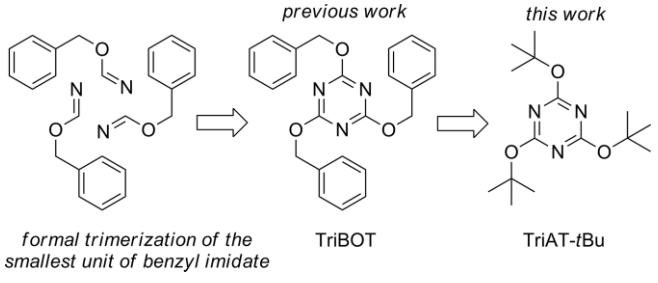


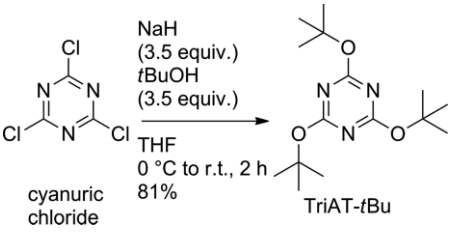
Figure 1. Concept for the design of TriAT-*t*Bu.

The *tert*-butyl group has been widely employed as a protecting group for hydroxy and carboxy functional groups, because deprotection can be readily achieved under acidic conditions with the liberation of isobutene, while *tert*-butyl ethers are tolerated under various reaction conditions.[3] The traditional methods for preparing *tert*-butyl ethers and esters involve the reaction of a large excess of isobutene or *tert*-butyl 2,2,2-trichloroacetimidate (*tert*-BTCAI) in the presence of an acid catalyst.[3,4] However, handling and storage of the flammable gaseous isobutene is inconvenient and potentially hazardous, and *tert*-BTCAI is sensitive to moisture and heat.[5] By analogy with TriBOT and TriBOT-PM, a triazine-based *tert*-butylating reagent is expected to solve these problems.

Herein, we report the development of a *tert*-butylating reagent, 2,4,6-tris(*tert*-butoxy)-1,3,5-triazine (TriAT-*t*Bu).[6]

Results and Discussion

According to the procedure for the synthesis of TriBOT-PM,[2] TriAT-*t*Bu was synthesized from cyanuric chloride and 3.5 equiv. of *t*BuONa prepared from *t*BuOH and sodium hydride, in 81 % yield (Scheme 1). As expected, TriAT-*t*Bu is a non-hygroscopic crystalline solid and stable in air at room temperature for over one year. Irritating or allergenic properties were not observed in our laboratory.[7]



Scheme 1. Synthesis of TriAT-*t*Bu.

Our investigations began with the *tert*-butylation of hexadecanol (**1a**) with TriAT-*t*Bu using TfOH as an acid catalyst (Table 1). The reaction of **1a** proceeded to give *tert*-butyl ether

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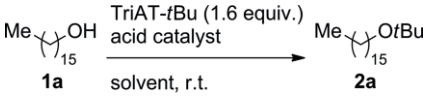
2a in 95 % yield (Entry 1). The reaction using $Bi(OTf)_3$ as a strong Lewis acid afforded the product in an excellent yield (Entry 2), while the use of $Sc(OTf)_3$ as a mild Lewis acid[8] necessitated a longer reaction time of 12 h (Entry 3). On the other hand, dropwise addition of TriAT-*t*Bu solution (CH_2Cl_2) in the presence of $Sc(OTf)_3$ considerably shortened the reaction time (initial concentration of **1a**: 0.14 M; final concentration: 0.1 M; dropwise addition time: 4 h; total reaction time: 5.5 h, vide infra; Entry 4). Reduction of the amount of TriAT-*t*Bu to 1.0 equiv. decreased the yield to 85 % (Entry 5). Compared with the reaction using isobutene (approximately 10 equiv.),[4a,4b] it can be said that the reaction using 1.6 equiv. of TriAT-*t*Bu is efficient. Unlike benzylation using TriBOT and TriBOT-PM, ethereal solvents (1,4-dioxane, DME, Et_2O) were not effective for the reaction (Entries 6–8). Since the *tert*-butyl cation was reported to be more stable than the benzyl cation,[9] we expected that the reaction could be conducted under milder conditions. However, even 20 mol-% of other acids such as H_2SO_4, 10-camphorsulfonic acid (CSA), and $LiClO_4$ afforded poor to moderate yields (Entries 9–11). We used $Sc(OTf)_3$ as a standard catalyst for further investigations, because it is a milder[8] and easy-to-handle reagent.

Table 1. Screening of solvents and acid catalysts for the *tert*-butylation of alcohol **1a**.



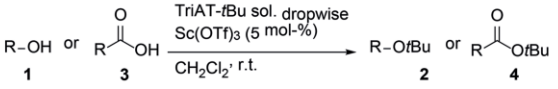
Entry	Solvent	Acid catalyst (mol-%)	Time [h]	Yield [%][a]
1	CH_2Cl_2	TfOH (5)	3	95
2	CH_2Cl_2	$Bi(OTf)_3$ (5)	3	93[b]
3	CH_2Cl_2	$Sc(OTf)_3$ (5)	12	92
4	CH_2Cl_2	$Sc(OTf)_3$ (5)[c]	5.5	93
5	CH_2Cl_2	$Sc(OTf)_3$ (5)[d]	4	85
6	1,4-dioxane	$Sc(OTf)_3$ (5)	24	32
7	DME	$Sc(OTf)_3$ (5)	24	26
8	Et_2O	$Sc(OTf)_3$ (5)	24	51
9	CH_2Cl_2	H_2SO_4 (20)	36	51
10	CH_2Cl_2	CSA (20)[e]	36	12[b]
11	CH_2Cl_2	$LiClO_4$ (20)	63	59[b]

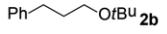
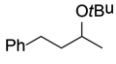
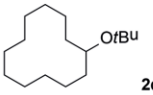
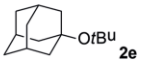
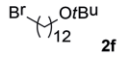
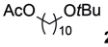
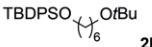
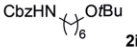
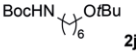
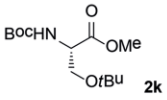
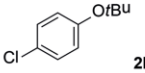
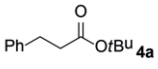
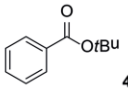
[a] Isolated yields. [b] NMR yields using an internal standard. [c] Solution of TriAT-*t*Bu was added dropwise over 4 h (additional reaction time: 1.5 h). [d] Solution of TriAT-*t*Bu (1.0 equiv.) was added dropwise over 3 h (additional reaction time: 1 h). [e] TriAT-*t*Bu (1.0 equiv.) was used.

We explored the scope of this newly designed protocol for a variety of alcohols and carboxylic acids to establish the general synthetic applicability of this method (Table 2). The reaction of 3-phenylpropanol (**1b**) gave the corresponding ether **2b** in an excellent yield (Entry 1). Secondary alcohols **1c** and **1d** afforded the *tert*-butyl ethers **2c** and **2d** in 74 % and 67 % yields, respectively (Entries 2, 3), although an excess amount of TriAT-*t*Bu (4 equiv.) was required. A tertiary alcohol was found to be inert to *tert*-butylation (Entry 4). High yields were maintained when base-labile functionalities such as bromoalkyl and acetoxy groups are present in the alcohols (Entries 5, 6). The *tert*-butyldiphenylsilyl group (TBDPS) as a hydroxy protecting group was tolerated in the reaction, affording the expected product in 95 % yield (Entry 7). Amino protecting groups such as benzyloxycarbonyl (Cbz) and *tert*-butoxycarbonyl (Boc) groups are compatible with the reaction conditions (Entries 8, 10). When the reaction of an alcohol bearing a Cbz group (**1i**) was conducted by adding TriAT-*t*Bu in one portion in the presence of TfOH as a catalyst, the reaction was complete in only 2.5 h (Entry 9). However, the reaction of an alcohol having a Boc group (**1j**) under the same conditions resulted in 61 % yield of *tert*-butyl ether, perhaps due to the deprotection of the Boc group and the inevitable neutralization of TfOH by the resulting amine (Entry 11). Addition of TriAT-*t*Bu in one portion in the presence of a strong acid catalyst such as TfOH is effective for the *tert*-butylation of acid-stable alcohols. No racemization occurred during the reaction of **1k** (Entry 12). The reaction of *para*-chlorophenol gave the corresponding *tert*-butyl ether in 59 % yield (Entry 13). Aliphatic and aromatic carboxylic acids **3a** and **3b** were also converted into the corresponding *tert*-butyl esters **4a** and **4b** in moderate yields (Entries 14, 17) by TriAT-*t*Bu under the same conditions. In the case of carboxylic acids, the yields of the esters were increased when TriAT-*t*Bu was added in one portion rather than dropwise, in the presence of 40 mol-% of sulfuric acid (Entries 15, 18) or 5 mol-% of $Bi(OTf)_3$ (Entry 16).

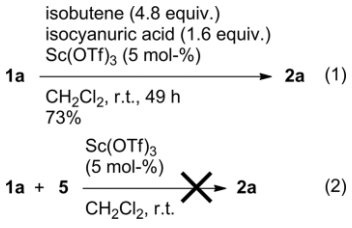
Time-course analysis was performed to clarify the reaction profile of the *tert*-butylation of **1a**. The reaction was initiated by the addition of $Sc(OTf)_3$ to a CH_2Cl_2 solution of **1a** (0.1 M) and TriAT-*t*Bu (0.16 M) in an air-tight tube. Aliquots of the reaction mixture were withdrawn at appropriate intervals and analyzed by ^1H NMR spectroscopy using *p*-nitrotoluene as an internal standard (Figure 2).[10] After the initiation of the reaction, the amount of TriAT-*t*Bu (triangles) decreased rapidly and completely disappeared within 30 min (Figure 2b, Table 3).[11,12] At this time, the yield of **2a** (squares) was 47 % based on **1a**, and 9.8 % based on the total number (4.8 equiv.) of *tert*-butyl groups. Other products formed were isobutene (dots) (54 %), *N*-*tert*-butylisocyanuric acid (**5**) (29 %), which was probably generated by *N*-*tert*-butylation of TriAT-*t*Bu (the yields in parentheses were calculated based on the number of *tert*-butyl groups).[2] Almost all of the *tert*-butyl groups generated from TriAT-*t*Bu (93 % based on 4.8 equiv. of *tert*-butyl groups) were successfully monitored, despite the formation of the volatile isobutene. After complete decomposition of TriAT-*t*Bu, the rate of formation of **2a** decreased sharply, and it took 10 h to reach 90 % yield of **2a** (based on **1a**) (Figure 2c). During this time, the isobutene concentration also gradually decreased. Other experiments revealed that the *tert*-butylation of **1a** using isobutene under similar conditions requires a longer time [Equation (1)], while the reaction using **5** does not proceed at all [Equation (2)]. Thus, these results may indicate the reaction mechanism changed after TriAT-*t*Bu had disappeared; during the first 30 min, the highly reactive *tert*-butyl cation species, which is rapidly liberated from TriAT-*t*Bu, reacts with alcohol **1a** to give **2a** in competition with elimination to form the stable isobutene; however, once has TriAT-*t*Bu disappeared, the cationic species needs to be regenerated from isobutene. Thus, it is reasonable to assume that suppression of the competing genera-

Table 2. Scope and limitations of alcohols and carboxylic acids for *tert*-butylation.



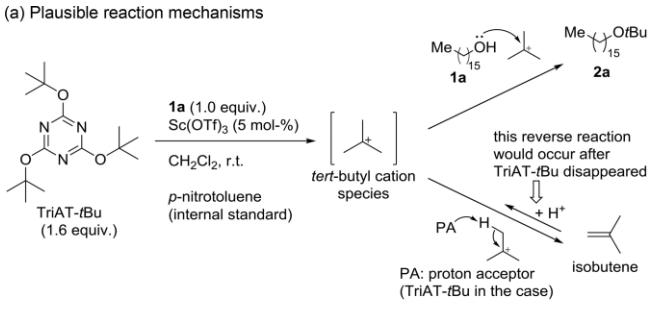
Entry	2 or 4	TriAT-*t*Bu [equiv.]	Dropwise addition time [h]	Additional reaction time [h]	Yield [%][a]
1	 **2b**	1.6	4	1	93
2	 **2c**	4	8	1	74
3	 **2d**	4	8	1	67
4	 **2e**	4	8	1	0
5	 **2f**	2.4	6	1	95
6	 **2g**	2.4	6	1	95
7	 **2h**	3.2	8	2	95
8[b]	 **2i**	3.2	16	4	85
9[c,d]	**2i**	3.2	–	2.5	90
10[b]	 **2j**	3.2	16	3	90
11[c,d]	**2j**	3.2	–	2.5	61
12	 **2k**	3.2	8	4	72 99% *ee*
13	 **2l**	1.6	4	5	59
14	 **4a**	4	8	1	76
15[d,e]	**4a**	4	–	16	88
16[d,f]	**4a**	4	–	45 min	81
17	 **4b**	3.2	8	1	65
18[d,e]	**4b**	4	–	16	79

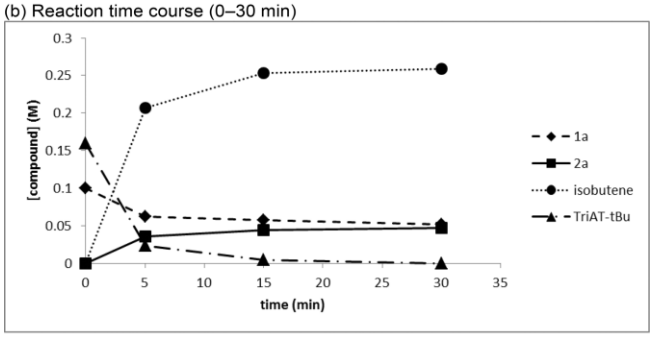
[a] Isolated yield. [b] $Sc(OTf)_3$ (10 mol-%) was used. [c] TfOH (5 mol-%) was used. [d] TriAT-*t*Bu was added in one portion. [e] H_2SO_4 (40 mol-%) was used as an acid catalyst. [f] $Bi(OTf)_3$ (5 mol-%) was used.



tion of isobutene from TriAT-*t*Bu would be effective for reducing the reaction time. Recently, we showed that the nitrogen atom of TriBOT exhibits basic character under strongly acidic conditions.[13] Thus, in the present system, TriAT-*t*Bu can act as a proton acceptor to promote the generation of isobutene from the *tert*-butyl cation species (Figure 2a). Therefore, maintaining a low concentration of TriAT-*t*Bu using the dilution method would be effective for shortening the reaction time. This consideration

agrees with the fact (Table 1, Entries 3 and 4) that dropwise addition of TriAT-*t*Bu solution shortened the reaction time as compared with a one-portion addition.





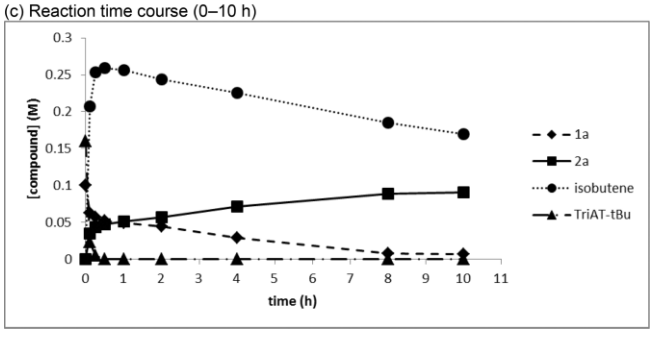
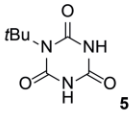


Figure 2. Reaction profile of the *tert*-butylation using TriAT-*t*Bu.

Table 3. Amount of *tert*-butyl derivatives at 30 min after initiation of the reaction.

	tert-Butyl groups [equiv.]	Yield [%] based on total number (4.8 equiv.) of *tert*-butyl groups
2a	0.47	9.8 (47)[a]
 isobutene	2.59	54
 **5**	1.41	29
Total	4.47	93

[a] Yield based on **1a**.

Conclusions

We have developed a new *tert*-butylating reagent based on triazine chemistry. The reactions of several alcohols and carboxylic acids with TriAT-*t*Bu in the presence of an acid catalyst proceeded to give the corresponding *tert*-butyl ethers and esters in good yields. Time-course analysis of the reaction revealed that the *tert*-butyl cation generated in situ from activated TriAT-*t*Bu is responsible for the rapid formation of the product.

Experimental Section

General: ^{1}H NMR spectra were recorded with 400 MHz spectrometers. Chemical shifts for ^{1}H NMR are reported in parts per million (δ) relative to tetramethylsilane as the internal standard. Coupling constant (J) are reported in Hertz [Hz]. The following abbreviations are used for spin multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br. = broad. ^{13}C NMR spectra were recorded with 100 MHz spectrometers. Chemical shifts for ^{13}C NMR are reported in parts per million (δ) relative to the solvent ($CDCl_3$: δ = 77.16; [D_6]DMSO: δ = 39.52 ppm). Analytical thin layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm silica gel impregnated with a fluorescent indicator (254 nm). Flash chromatography was performed using silica gel (spherical, neutral, 40–100 mesh). Chiral HPLC was performed using Daicel CHIRALPAK IA-3. Reagents were of commercial grade and used without any purification unless otherwise noted. High-purity, solvent-grade dichloromethane, THF and diethyl ether were purchased from commercial sources. 1,4-Dioxane and 1,2-dimethoxyethane were purchased from commercial sources and distilled from calcium hydride before use.

General Procedure for the *tert*-Butylation of Alcohol 1 by Using TriAT-*t*Bu: To a solution of alcohol **1** (0.500 mmol) and $Sc(OTf)_3$ (0.025 mmol) in CH_2Cl_2 (3.5 mL), a solution of TriAT-*t*Bu (237.9 mg, 0.800 mmol) in CH_2Cl_2 (1.36 mL) was added dropwise at room temperature over 4 h. After the dropwise addition was complete, the residual TriAT-*t*Bu in the test tube was rinsed with CH_2Cl_2 (0.14 mL) into the mixture over 1 min. The mixture was stirred for a total of 5.5 h and washed with satd. aqueous $NaHCO_3$ (60 mL), H_2O (100 mL), and brine (40 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc) to afford **2**.

2,4,6-Tris(*tert*-butoxy)-1,3,5-triazine (TriAT-*t*Bu): To a suspension of NaH (60 %, 11.20 g, 280 mmol) in THF (100 mL), *tert*-butyl alcohol (26.6 mL, 280 mmol) in THF (50 mL) was added dropwise at 0 °C over 30 min. Cyanuric chloride (14.75 g, 80.0 mmol) in THF (50 mL) was added dropwise over 15 min. After stirring at 0 °C for an additional 10 min and at room temperature for 2 h, the mixture was poured into H_2O and ice. The precipitate was filtered, and washed with hexane (100 mL). The precipitate was recrystallized from CH_2Cl_2 to give 2,4,6-tris(*tert*-butoxy)-1,3,5-triazine (TriAT-*t*Bu, 16.2 g, 68 %) as colorless crystals. The residue and hexane filtrate were combined and recrystallized to give TriAT-*t*Bu (3.1 g, 13 %). M.p. 170 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 172.0, 82.0, 28.5 ppm. $C_{15}H_{27}N_3O_3$ (297.40): calcd. C 60.58, H 9.15, N 14.13; found C 60.42, H 9.34, N 14.03. HRMS (DART$^+$): calcd. for $C_{15}H_{28}N_3O_3$ [M + H]$^+$ 298.2131; found 298.2129. IR (KBr): $\tilde{\nu}$ = 3006, 2985, 2933, 1562, 1392, 1163, 1132, 850, 820, 499, 471 cm^{-1}.

***tert*-Butyl Hexadecyl Ether (2a):** ^{1}H NMR ($CDCl_3$): δ = 3.32 (t, J = 6.8 Hz, 2 H), 1.51 (m, 2 H), 1.37–1.25 (m, 26 H), 1.18 (s, 9 H), 0.88 (t,

J = 7.3 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 72.5, 61.8, 32.1, 30.9, 29.84, 29.83, 29.81, 29.80, 29.7, 29.5, 27.7, 26.4, 22.8, 14.3 ppm. $C_{20}H_{42}O$ (298.55): calcd. C 80.46, H 14.18; found C 80.06, H 14.54. HRMS (DART$^+$): calcd. for $C_{20}H_{43}O$ [M + H]$^+$ 299.3314; found 299.3299. IR ($CHCl_3$): $\tilde{\nu}$ = 2927, 2854, 1466, 1363, 1182, 1072 cm^{-1}.

***tert*-Butyl 3-Phenylpropyl Ether (2b):**[14] ^{1}H NMR ($CDCl_3$): δ = 7.30–7.24 (m, 2 H), 7.23–7.14 (m, 3 H), 3.36 (t, J = 6.4 Hz, 2 H), 2.68 (t, J = 7.9 Hz, 2 H), 1.90–1.80 (m, 2 H), 1.19 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 142.4, 128.6, 128.4, 125.8, 72.7, 60.9, 32.6, 32.3, 27.8 ppm. HRMS (DART$^+$): calcd. for $C_{13}H_{21}O$ [M + H]$^+$ 193.1592; found 193.1573. IR ($CHCl_3$): $\tilde{\nu}$ = 3041, 2981, 2935, 2871, 1603, 1363, 1074 cm^{-1}.

***tert*-Butyl 1-Methyl-3-phenylpropyl Ether (2c):**[15] ^{1}H NMR ($CDCl_3$): δ = 7.31–7.14 (m, 5 H), 3.68–3.58 (m, 1 H), 2.74–2.54 (m, 2 H), 1.85–1.64 (m, 2 H), 1.19 (s, 9 H), 1.16 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 142.7, 128.45, 128.43, 125.8, 73.4, 67.1, 40.7, 32.6, 28.8, 23.2 ppm. $C_{14}H_{22}O$ (206.33): calcd. C 81.50, H 10.75; found C 81.14, H 11.03. HRMS (DART$^+$): calcd. for $C_{14}H_{23}O$ [M + H]$^+$ 207.1749; found 207.1745. IR ($CHCl_3$): $\tilde{\nu}$ = 3037, 2987, 2966, 2933, 2866, 1603, 1496, 1456, 1365, 1254, 1182, 1126, 815, 467 cm^{-1}.

***tert*-Butyl Cyclododecyl Ether (2d):**[5j] ^{1}H NMR ($CDCl_3$): δ = 3.66–3.55 (m, 1 H), 1.65–1.51 (m, 2 H), 1.47–1.24 (m, 20 H), 1.19 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 73.2, 68.7, 32.1, 28.9, 24.7, 24.2, 23.41, 23.39, 21.2 ppm. HRMS (DART$^+$): calcd. for $C_{16}H_{33}O$ [M + H]$^+$ 241.2531; found 241.2539. IR ($CHCl_3$): $\tilde{\nu}$ = 3035, 2939, 2864, 1471, 1363, 1255, 1184, 1012, 737, 702, 455 cm^{-1}.

12-Bromododecyl *tert*-Butyl Ether (2f): ^{1}H NMR ($CDCl_3$): δ = 3.41 (t, J = 6.9 Hz, 2 H), 3.32 (t, J = 6.9 Hz, 2 H), 1.90–1.80 (m, 2 H), 1.58–1.37 (m, 4 H), 1.37–1.22 (m, 14 H), 1.18 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 72.5, 61.8, 34.2, 33.0, 30.9, 29.74, 29.70, 29.67, 29.6, 28.9, 28.3, 27.7, 26.4 ppm. $C_{16}H_{33}BrO$ (321.34): calcd. C 59.80, H 10.35; found C 59.71, H 10.63. HRMS (DART$^+$): calcd. for $C_{16}H_{34}BrO$ [M + H]$^+$ 321.1793; found 321.1778. IR ($CHCl_3$): $\tilde{\nu}$ = 2985, 2929, 2856, 1466, 1392, 1363, 1234, 1186, 1074, 1018, 908, 870, 746, 561, 453 cm^{-1}.

10-Acetoxy-1-*tert*-butoxydecane (2g): ^{1}H NMR ($CDCl_3$): δ = 4.05 (t, J = 6.9 Hz, 2 H), 3.32 (t, J = 6.9 Hz, 2 H), 2.05 (s, 3 H), 1.67–1.45 (m, 4 H), 1.38–1.24 (m, 12 H), 1.18 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 171.4, 72.5, 64.8, 61.8, 30.8, 29.64, 29.58, 29.4, 28.7, 27.7, 26.4, 26.0, 21.2 ppm. $C_{16}H_{32}O_3$ (272.43): calcd. C 70.54, H 11.84; found C 70.33, H 11.94. HRMS (DART$^+$): calcd. for $C_{16}H_{33}O_3$ [M + H]$^+$ 273.2430; found 273.2447. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 2856, 1728, 1465, 1392, 1365, 1072, 800, 742, 679, 430 cm^{-1}.

***tert*-Butyl 6-(*tert*-Butyldiphenylsilyloxy)hexyl Ether (2h):** ^{1}H NMR ($CDCl_3$): δ = 7.70–7.64 (m, 4 H), 7.45–7.33 (m, 6 H), 3.65 (t, J = 6.4 Hz, 2 H), 3.31 (t, J = 6.9 Hz, 2 H), 1.62–1.45 (m, 4 H), 1.42–1.24 (m, 4 H), 1.18 (s, 9 H), 1.04 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 135.7, 134.3, 129.6, 127.7, 72.5, 64.1, 61.7, 32.7, 30.8, 27.7, 27.0, 26.2, 25.9, 19.4 ppm. $C_{26}H_{40}O_2Si$ (412.69): calcd. C 75.67, H 9.77; found C 75.39, H 9.99. HRMS (DART$^+$): calcd. for $C_{26}H_{41}O_2Si$ [M + H]$^+$ 413.2876; found 413.2899. IR ($CHCl_3$): $\tilde{\nu}$ = 3072, 2989, 2935, 2810, 1473, 1427, 1363, 1109, 1005, 823, 615, 505 cm^{-1}.

Benzyl *N*-(6-*tert*-Butoxyhexyl)carbamate (2i): ^{1}H NMR ($CDCl_3$): δ = 7.38–7.28 (m, 5 H), 5.09 (s, 2 H), 4.73 (br. s, 1 H), 3.31 (t, J = 6.6 Hz, 2 H), 3.24–3.11 (m, 2 H), 1.58–1.43 (m, 4 H), 1.40–1.28 (m, 4 H), 1.18 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.5, 136.8, 128.6, 128.3, 128.2, 72.6, 66.7, 61.6, 41.2, 30.7, 30.1, 27.7, 26.8, 26.1 ppm. $C_{18}H_{29}NO_3$ (307.43): calcd. C 70.32, H 9.51, N 4.56; found C 70.27, H 9.80, N 4.52. HRMS (DART$^+$): calcd. for $C_{18}H_{30}NO_3$ [M + H]$^+$ 308.2226; found 308.2248. IR ($CHCl_3$): $\tilde{\nu}$ = 3452, 3006, 2937, 2862, 1716, 1516, 1363, 1257, 1186, 1136, 1076, 924, 800, 661, 445 cm^{-1}.

***tert*-Butyl *N*-(6-*tert*-Butoxyhexyl)carbamate (2j):** ^{1}H NMR ($CDCl_3$): δ = 4.53 (br. s, 1 H), 3.32 (t, J = 6.4 Hz, 2 H), 3.16–3.01 (m, 2 H), 1.57–1.44 (m, 4 H), 1.44 (s, 9 H), 1.38–1.29 (m, 4 H), 1.18 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.1, 79.1, 72.5, 61.6, 40.7, 30.7, 30.1, 28.5, 27.7, 26.8, 26.1 ppm. $C_{15}H_{31}NO_3$ (273.41): calcd. C 65.89, H 11.43, N 5.12; found C 65.55, H 11.58, N 5.10. HRMS (DART$^+$): calcd. for $C_{15}H_{32}NO_3$ [M + H]$^+$ 274.2382; found 274.2396. IR ($CHCl_3$): $\tilde{\nu}$ = 3456, 2981, 2937, 2860, 1707, 1508, 1365, 1255, 1171, 1074, 908, 791, 725, 669, 436 cm^{-1}.

Boc-L-Ser(*Ot*Bu)OMe (2k): M.p. 41.0–41.6 °C. ^{1}H NMR ($CDCl_3$): δ = 5.36 (br. d, 1 H), 4.39 (ddd, J = 3.0, 3.0, 9.2 Hz, 1 H), 3.80 (dd, J = 3.0, 9.2 Hz, 1 H), 3.74 (s, 3 H), 3.56 (dd, J = 3.0, 9.2 Hz, 1 H), 1.46 (s, 9 H), 1.13 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 171.6, 155.8, 79.9, 73.4, 62.2, 54.4, 52.3, 28.4, 27.4 ppm. $C_{13}H_{25}NO_5$ (275.34): calcd. C 56.71, H 9.15, N 5.09; found C 56.73, H 9.32, N 5.05, HRMS (DART$^+$): calcd. for $C_{13}H_{26}NO_5$ [M + H]$^+$ 276.1811; found 276.1808. IR ($CHCl_3$): $\tilde{\nu}$ = 3444, 3041, 2981, 1749, 1709, 1506, 1367, 1350, 1298, 1165, 1101, 1070, 1045, 804, 727, 665, 457 cm^{-1}.

***tert*-Butyl *p*-Chlorophenyl Ether (2l):**[16] ^{1}H NMR ($CDCl_3$): δ = 7.25–7.19 (m, 2 H), 6.95–6.88 (m, 2 H), 1.33 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.1, 129.0, 128.7, 125.6, 79.0, 28.9 ppm. HRMS (DART$^+$): calcd. for $C_{10}H_{17}ClNO$ [M + NH_4]$^+$ 202.0999,; found 202.0990. IR ($CHCl_3$): $\tilde{\nu}$ = 2985, 1487, 1367, 1157, 1093, 1011, 926, 893, 850, 810, 787, 733, 681, 538 cm^{-1}.

***tert*-Butyl 3-Phenylpropionate (4a):**[14] ^{1}H NMR ($CDCl_3$): δ = 7.31–7.23 (m, 2 H), 7.23–7.15 (m, 3 H), 2.91 (t, J = 7.8 Hz, 2 H), 2.54 (t, J = 7.8 Hz, 2 H), 1.42 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 172.4, 140.9, 128.51, 128.46, 126.2, 80.4, 37.2, 31.3, 28.2 ppm. HRMS (DART$^+$): calcd. for $C_{13}H_{22}NO_2$ [M + NH_4]$^+$ 224.1651; found 224.1632. IR ($CHCl_3$): $\tilde{\nu}$ = 3066, 2987, 2933, 2868, 1722, 1496, 1454, 1369, 1300, 1147, 953, 847, 739, 478 cm^{-1}.

***tert*-Butyl Benzoate (4b):**[17] ^{1}H NMR ($CDCl_3$): δ = 8.02–7.97 (m, 2 H), 7.54–7.49 (m, 1 H), 7.44–7.39 (m, 2 H), 1.60 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.9, 132.5, 132.1, 129.5, 128.3, 81.1, 28.3 ppm. HRMS (DART$^+$): calcd. for $C_{11}H_{15}O_2$ [M + H]$^+$ 179.1072; found 179.1069. IR ($CHCl_3$): $\tilde{\nu}$ = 2983, 1707, 1450, 1369, 1315, 1296, 1254, 1167, 1120, 908, 849, 741, 463 cm^{-1}.

***N*-(*tert*-Butyl)isocyanuric Acid (5):** M.p. 188 °C (decomp.). ^{1}H NMR (DMSO): δ = 11.10 (br. s, 2 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (DMSO): δ = 150.2, 148.4, 60.6, 29.5 ppm. $C_7H_{11}N_3O_3$ (185.18): calcd. C 45.40, H 5.99, N 22.69; found C 45.36, H 5.85, N 22.55. HRMS (DART$^+$): calcd. for $C_7H_{12}N_3O_3$ [M + H]$^+$ 186.0879; found 186.0855. IR ($CHCl_3$): $\tilde{\nu}$ = 3219, 3093, 2987, 2945, 2854, 1755, 1714, 1684, 1460, 1396, 1236, 1022, 812, 764, 719, 450 cm^{-1}.

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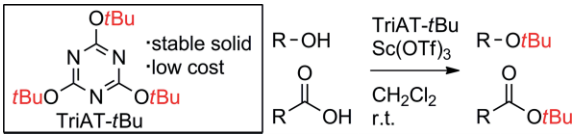

A new *tert*-butylating reagent, 2,4,6-tris(*tert*-butoxy)-1,3,5-triazine (TriAT-*t*Bu) has been developed for the acid-catalyzed *tert*-butylation of alcohols and carboxylic acids. The reaction of various alcohols and carboxylic acid with TriAT-*t*Bu in the presence of a catalytic amount of an acid provided the corresponding *tert*-butyl ethers and esters in good yields.

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