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FULL PAPER

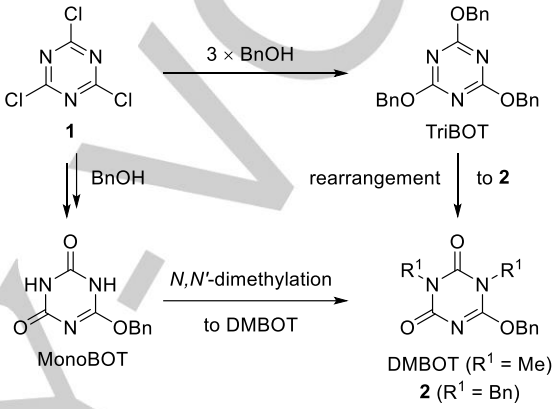
Preparation of Alkyl Ethers with Diallyltriazinedione-Type Acid-Catalyzed Alkylating Agents (ATTACKs-R)

Hikaru Fujita,[a] Rina Yamashita,[a] Takanori Fujii,[a] Kohei Yamada,[a] Masanori Kitamura,[a] and Munetaka Kunishima*[a]

Abstract: Diallyltriazinedione-type acid-catalyzed alkylating agents (ATTACKs-R) with 10 different alkyl groups (R), including benzyl, substituted benzyl, allyl, and methyl groups were synthesized. The palladium-catalyzed intramolecular *O*-to-*N* allylic rearrangement of 2,4-bis(allyloxy)-6-chloro-1,3,5-triazine was developed to introduce various alkoxy groups into the *N*,*N*′-dialkylated triazinedione skeleton. *O*-Alkylation of alcohols with ATTACKs-R was carried out in 1,4-dioxane in the presence of 2,6-di-*tert*-butylpyridinium trifluoromethanesulfonate or trifluoromethanesulfonic acid as a catalyst. Six selected ATTACKs-R bearing benzylic R groups were employed to prepare alkyl ethers from primary, secondary, and tertiary alcohols. The reactions of ATTACKs-R bearing an *o*-nitro-substituted benzyl group tended to afford low yields. Comparison of four different triazinedione-based benzylating reagents suggested that the *N*,*N*′-substituents affected the reactivity.

Introduction

2,4,6-Tris(benzyloxy)-1,3,5-triazine (TriBOT, Scheme 1) has been previously reported as a triazine-based acid-catalyzed *O*-benzylating reagent.[1,2] TriBOT was designed as an atom-economic reagent and was readily prepared from cyanuric chloride (**1**) and benzyl alcohol. This reagent was then employed to convert alcohols and carboxylic acids into the corresponding benzyl ethers and esters, respectively, under non-basic conditions. A series of triazine-based acid-catalyzed reagents were developed for *p*-methoxybenzylation,[3] *tert*-butylation,[4] and allylation.[5] During the mechanistic studies on TriBOT, one of the intermediates, 6-(benzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (MonoBOT), was synthesized in two steps from **1**.[6] Kinetic studies indicated the high reactivity of MonoBOT compared to that of TriBOT. Subsequently, further exploration of the core structure led to *N*,*N*′-dimethylated benzyloxytriazinedione (DMBOT, R^1 = Me) as a next-generation reagent for acid-catalyzed *O*-benzylation.[7] *N*,*N*′-Dibenzylated analog **2** (R^1 = Bn), which can also be employed for acid-catalyzed *O*-benzylation,[8,9] is accessible through rearrangement of the benzyl groups in TriBOT.[10]



Scheme 1. Previous synthetic routes toward *N*,*N*′-dialkylated benzyloxytriazinediones.

DMBOT exhibits superior reactivity to that of MonoBOT owing to the fixed triazinedione skeleton comprising alkyl groups on the nitrogen atoms. The *O*-benzylation reaction with DMBOT is typically catalyzed by trifluoromethanesulfonic acid (TfOH) or 2,6-di-*tert*-butylpyridinium trifluoromethanesulfonate (**3**). The latter is suitable for the *O*-benzylation of acid-labile alcohols. Benzyl cation species (possibly benzyl trifluoromethanesulfonate) are formed during the reaction and react with alcohols. DMBOT is practical to use due to its favorable physical properties (a non-hygroscopic stable solid sufficiently soluble in organic solvents) and easy removal of its coproduct. To date, notwithstanding the practicability of DMBOT, the *N*,*N*′-dialkylated triazinedione skeleton has been solely applied to *O*-benzylation.

This paper describes the development of a series of triazinedione-based reagents for acid-catalyzed *O*-alkylation. A new synthetic approach toward the acid-catalyzed reagents extends the scope of the alkyl groups transferred onto alcohols.

Results and Discussion

The synthetic routes toward DMBOT and **2** from **1** require benzyl alcohol, the alkyl source for the reagent, in the first step of the synthesis. Thus, it is inconvenient to introduce various alkyl groups into the reagent via these routes. Therefore, this paper reports a new synthetic strategy—catalytic intramolecular *O*-to-*N* allylic rearrangement[11,12] of a bis(allyloxy)triazine—to construct an *N*,*N*′-diallylated triazinedione skeleton bearing a chloro group,

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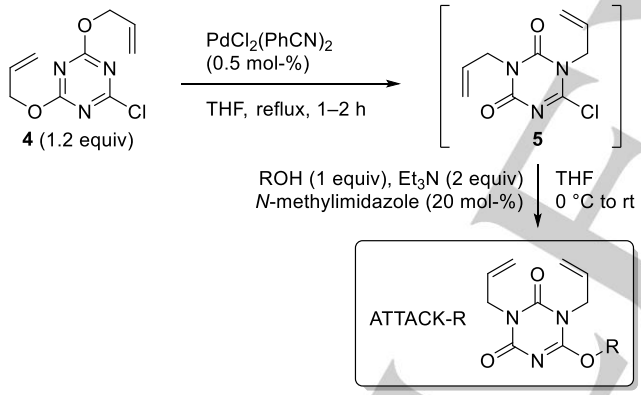
which can be replaced in the last step of the synthesis. As illustrated in Table 1, 2,4-bis(allyloxy)-6-chloro-1,3,5-triazine (**4**, 1.2 equiv) was heated in THF with $PdCl_2(PhCN)_2$ (0.5 mol-%) to form 1,3-diallyl-6-chloro-1,3,5-triazine-2,4(1*H*,3*H*)-dione (**5**). This was subsequently treated with an alcohol (ROH, 1 equiv), Et_3N (2 equiv), and *N*-methylimidazole (20 mol-%) to afford the corresponding diallyltriazinedione-type acid-catalyzed alkylating agents (ATTACKs-R). ATTACKs-R with various benzylic alkyl groups [benzyl (Bn), *p*-methoxybenzyl (PMB), *p*-methylbenzyl (MBn), F_{13}-fluorous benzyl (*F*$_{13}$Bn), *p*-bromobenzyl (PBB), *p*-nitrobenzyl (PNB), *o*-nitrobenzyl (ONB), and 4,5-dimethoxy-2-nitrobenzyl (DMNB); entries 1–8; synthetically useful protecting groups for alcohols[13]] as well as allyl and methyl groups (entries 9 and 10, respectively) were obtained in 85–100% yield. The addition of a catalytic amount of *N*-methylimidazole facilitated the substitution with alcohols to afford ATTACKs-R. Notably, ATTACK-*F*$_{13}$Bn was prepared from the expensive F_{13}-fluorous benzyl alcohol in high yield (95%, entry 4). These results are comparable to the results of the previous synthesis of a triazinedione-based acid-catalyzed reagent for the introduction of the *F*$_{13}$Bn group (48% yield based on the alcohol in two steps).[14] This reagent lacked *N*,*N*′-dialkyl groups and thus resembled MonoBOT. While ATTACK-PMB, ATTACK-allyl, and ATTACK-Me were liquid at room temperature, all the other ATTACKs-R were obtained as non-hygroscopic solids similar to DMBOT.

Table 1. Synthesis of ATTACKs-R from various alcohols.



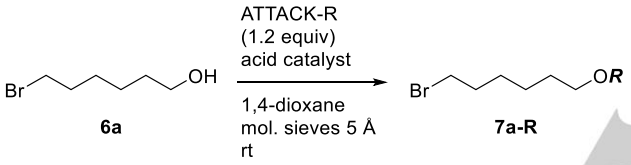
Entry	R	Structure	Time [h][a]	Yield [%][b]
1	Bn		2.5	97
2	PMB	OMe	6	93
3	MBn	Me	1.5	86
4	*F*$_{13}$Bn	C_6F_{13}	2.5	95
5	PBB	Br	1.5	quant.
6	PNB	NO_2	1.5	99
7	ONB	O_2N	4	94
8	DMNB	O_2N, OMe, OMe	3	85
9	allyl		19	quant.
10	Me	CH_3	6	86

[a] Reaction time for the second step. [b] Isolated yield.

Following the procedure for DMBOT,[7] acid-catalyzed *O*-alkylation with ATTACKs-R (1.2 equiv) was conducted in 1,4-dioxane, at room temperature, in the presence of molecular sieves 5 Å (Table 2). Initially, catalyst **3** and primary alcohol **6a** bearing a base-labile bromoalkyl group were employed for the reaction. Several entries in this Table display yields determined by ^{1}H NMR spectroscopic analysis with an internal standard; these are referred to as the NMR yields hereafter. The *O*-benzylation with ATTACK-Bn and **3** (10 mol-%) afforded the corresponding benzyl ether **7a-Bn** in 3.5 h with 88% isolated yield (entry 1). The reaction of ATTACK-PMB was completed in 20 min, with a smaller amount of **3** (2 mol-%), to afford **7a-PMB** in 80% isolated yield (entry 2). The acid catalysts **3** (10 mol-%, entry 3) and $Sc(OTf)_3$ (10 mol-%, entry 4) were used for the *O*-*p*-methylbenzylation with ATTACK-MBn, providing **7a-MBn** in 87% isolated yield and 92% NMR yield, respectively, within one hour. The reactions with ATTACK-*F*$_{13}$Bn (entry 5) and ATTACK-PBB (entry 6) in the presence of **3** (10 mol-%) afforded **7a-*F*$_{13}$Bn** and **7a-PBB** with 91% isolated yield and 93% NMR yield in 2 and 24 h, respectively. The syntheses of the nitrobenzyl ethers **7a-PNB** and **7a-ONB** with the same catalyst were unfruitful (14 and 0% NMR yield, 68 and 72 h, entries 7 and 8, respectively), while **7a-DMNB** was obtained with 26% NMR yield in seven hours (entry 9). As the *O*-allylation of **6a** with ATTACK-allyl and **3** (10 mol-%) was sluggish at room temperature (29% NMR yield in 29 h, entry 10), the reaction was carried out at 50 °C to improve the yield (84% isolated yield in 6.5 h, entry 11). Next, the *O*-alkylation of **6a** was carried out with TfOH as the acid catalyst to strongly activate the ATTACKs-R. Entries 12 and 13 reveal that the introduction of the *F*$_{13}$Bn and PBB groups with TfOH (10 mol-%) resulted in shorter reaction times (30 min and five hours, respectively) than those observed with **3** in entries 5 and 6 to afford the products in 99% NMR yield (entry 12) and 86% isolated yield (entry 13), respectively. In contrast to the reaction of the low-yielding *O*-*p*-nitrobenzylation with **3** (entry 7), the reaction with TfOH (20 mol-%) afforded **7a-PNB** with 82% isolated yield in 23 h (entry 14). The *O*-*o*-nitrobenzylation proceeded with TfOH (20 mol-%), albeit a low isolated yield (16%, entry 15). The isolated yield of **7a-DMNB** in the reaction with 10 mol-% TfOH (20%, entry 16) was comparable to the NMR yield with **3** (26%, entry 9). The low yields

observed in the syntheses of **7a-ONB** (0–12 %) and **7a-DMNB** (26–29%) were attributed to the competing side reactions caused by the *o*-nitro groups. *o*-Nitrosobenzaldehyde formation via neighboring group participation was reported during the hydrolysis of *o*-nitrobenzyl *p*-toluenesulfonate in aqueous MeCN.[15] This suggested that similar side reactions affording nitroso compounds could occur during the reactions of ATTACK-ONB and ATTACK-DMNB. To the best of our knowledge, the reaction of *O*-*o*-nitrobenzylation with ONB 2,2,2-trichloroacetimidate[16] has not been reported although 2,2,2-trichloroacetimidates are widely used for acid-catalyzed *O*-alkylation. DMNB 2,2,2-trichloroacetimidate was used to prepare a DMNB ether using TfOH as an acid catalyst.[17,18] The low yields (29–30%) together with the afforded results (entries 9 and 16) suggest limitation of the DMNB ether synthesis under acid-catalyzed conditions. *O*-Allylation with TfOH (10 mol-%) at room temperature produced **7a-allyl** with 35% NMR yield in 24 h (entry 17). *O*-Methylation of **6a** was carried out with TfOH (10 mol-%) at reflux temperature to afford **7a-Me** with 56% isolated yield in seven hours (entry 18).

Table 2. Acid-catalyzed *O*-alkylation of **6a** with ATTACKs-R.



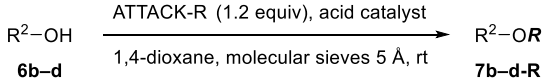
Entry	R	Acid catalyst [mol-%]	Time	Yield [%][a,b]
1	Bn	**3** (10)	3.5 h	88 (96)
2	PMB	**3** (2)	20 min	80 (89)
3	MBn	**3** (10)	45 min	87 (93)
4	MBn	$Sc(OTf)_3$ (10)	1 h	(92)
5	F_{13}Bn	**3** (10)	2 h	91 (98)
6	PBB	**3** (10)	24 h	(93)
7	PNB	**3** (10)	68 h	(14)
8	ONB	**3** (10)	72 h	nd[c]
9	DMNB	**3** (10)	2 h	(26)
10	allyl	**3** (10)	29 h	(29)
11[d]	allyl	**3** (10)	6.5 h	84 (89)
12	F_{13}Bn	TfOH (10)	30 min	(99)
13	PBB	TfOH (10)	5 h	86 (94)
14	PNB	TfOH (20)	23 h	82 (91)
15	ONB	TfOH (20)	69 h	16
16	DMNB	TfOH (10)	2.5 h	20 (29)
17	allyl	TfOH (10)	24 h	(35)
18[e]	Me	TfOH (10)	7 h	56 (66)

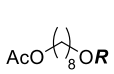
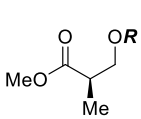
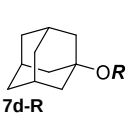
[a] Isolated yield. [b] Yields in parentheses were calculated from ^{1}H NMR spectroscopic analysis using an internal standard. [c] Not detected. [d] The reaction was carried out at 50 °C. [e] The reaction was carried out at room temperature to reflux temperature.

The reactivity of the ATTACKs-R (except for R = ONB, DMNB, and Me) observed in Table 2 was in the order: ATTACKs with R = PMB >MBn >F_{13}Bn >Bn >PBB >allyl >PNB. This is consistent with the order of carbocation stability (PMB cation >benzyl cation >allyl cation)[19] as well as that of the electron-donating ability based on σ_p^+ constants [OMe (–0.78) >Me (–0.31) >H (0) >Br (0.15) >NO_2 (0.79)], where a lower σ_p^+ value indicates stronger conjugative stabilization toward a cationic reaction center by a *p*-substituent.[20] Thus, development of a positive charge at the reaction center is suggested during the *O*-alkylation with these ATTACKs-R.

Table 3 summarizes the results of the acid-catalyzed *O*-alkylation reactions with selected ATTACKs-R (R = Bn, PMB, MBn, F_{13}Bn, PBB, and PNB) for 10-acetoxydecanol (**6b**), chiral β-hydroxy ester **6c**, and 1-adamantanol (**6d**). The syntheses of **7b–d-Bn** with **3** (10 mol-%) resulted in high yields (89–97%, entry 1). The *O*-*p*-methoxybenzylation reactions were conducted with **3** (2 mol-%) to afford **7b-PMB**, **7c-PMB**, and **7d-PMB** in 89, 87, and 62% yield, respectively (entry 2). The use of **3** (10 mol-%) and the corresponding ATTACKs-R produced **7b–d-MBn** and **7b–d-*F*$_{13}$Bn** in high yields (87–99%, entries 3 and 4, respectively). The introduction of the PBB group into **6b** and **6c** with ATTACK-PBB in the presence of **3** (10 mol-%) proceeded smoothly to afford **7b-PBB** and **7c-PBB** in 89 and 85%, respectively (entry 5). Entry 6 illustrates that the use of TfOH (10 mol-%) improved the yields of **7b-PBB** and **7c-PBB** (90 and 95%, respectively). The use of the same acid catalyst afforded **7d-PBB** in 63% yield (entry 6). The syntheses of **7b–d-PNB** were carried out with TfOH (20 mol-%). On the other hand, **7b-PNB** was afforded in 84% yield at room temperature, while heating at 50 °C was required to produce **7c-PNB** and **7d-PNB** in high yields (95 and 92%, respectively, entry 7). HPLC analyses indicated that no racemization occurred during the acid-catalyzed *O*-alkylation reactions of **6c**.

Table 3. Acid-catalyzed *O*-alkylation of **6b-d** with selected ATTACKs-R.



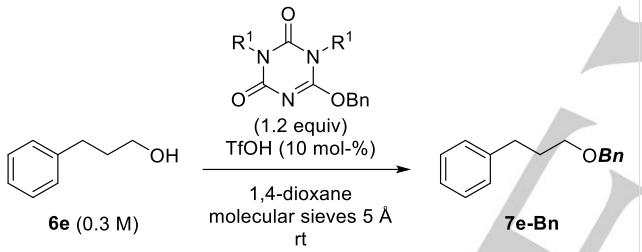
Entry	R	Acid catalyst [mol-%]	Reaction time, yield[a]		
			 **7b-R**	 **7c-R**	 **7d-R**
1	Bn	**3** (10)	4.5 h, 97%	5 h, 93%[b]	9.5 h, 89%
2	PMB	**3** (2)	10 min, 89%	10 min, 87%[b]	10 min, 62%
3	MBn	**3** (10)	1 h, 98%	1 h, 96%[b]	2 h, 87%
4	F_{13}Bn	**3** (10)	2 h, 98%	4 h, 99%[b]	3 h, 92%

5	PBB	**3** (10)	24 h, 89%	24 h, 85%[b]	–[c]
6	PBB	TfOH (10)	5 h, 90%	7 h, 93%[b]	6 h, 63%
7	PNB	TfOH (20)	24 h, 84%	4 h, 95%[b,d]	5 h, 92%[d]

[a] Isolated yield. [b] No racemization was observed. [c] Not conducted. [d] The reaction was carried out at 50 °C.

Table 4 compares the acid-catalyzed *O*-benzylation of 3-phenylpropanol (**6e**) with that of MonoBOT, DMBOT, ATTACK-Bn, and **2** in the presence of TfOH (10 mol-%). Similar to DMBOT (entry 2), ATTACK-Bn and **2** afforded the corresponding benzyl ether **7e-Bn** in excellent yields (97–100% NMR yield, entries 3 and 4, respectively). The difference in the reaction times (5, 4, and 1.5 h and 50 min for MonoBOT, DMBOT, ATTACK-Bn, and **2**, respectively) suggested that the reactivity of the triazinedione-based reagents is affected by the *N*,*N*′-dialkyl groups. These results indicated higher reactivity of ATTACK-Bn over that of DMBOT.

Table 4. Comparison of acid-catalyzed *O*-benzylation with triazinedione-based reagents.



Entry	Triazinedione	R^1	Time	Yield [%][a]
1[b,c]	MonoBOT	H	5 h	82
2[b]	DMBOT	Me	4 h	97
3	ATTACK-Bn	allyl	1.5 h	quant.
4	**2**	Bn	50 min	97

[a] Calculated from ^{1}H NMR spectroscopic analysis using an internal standard. [b] Data from ref.[7] [c] The reaction concentration of **6e** was 115 mM.

Conclusions

The scope of the alkyl groups in the acid-catalyzed *O*-alkylating reagents based on the *N*,*N*′-dialkyl triazinedione skeleton has been extended to prepare ethers bearing Bn, PMB, MBn, F_{13}Bn, PBB, PNB, ONB, DMNB, allyl, and methyl groups. This was achieved by a new synthetic strategy to construct the skeleton. After the palladium-catalyzed *O*-*N* allylic rearrangement of **4** to a common intermediate **5**, a variety of alkylating reagents ATTACKs-R can be efficiently prepared by nucleophilic substitution with an alcohol. The use of the corresponding ATTACKs-R with the acid catalyst (**3** or TfOH) successfully afforded Bn, PMB, MBn, F_{13}Bn, PBB, PNB, allyl, and methyl ethers. Since the syntheses of ONB and DMNB ethers under acid-catalyzed conditions are challenging, the reactions of ATTACKs-ONB and DMNB proceeded, but in low yields. Comparison of DMBOT and ATTACK-Bn indicated that the reactivity was improved by replacing the *N*,*N*′-dimethyl groups with *N*,*N*′-diallyl groups.

Experimental Section

Nuclear magnetic resonance [^{1}H NMR (400 or 600 MHz), ^{13}C NMR (100 or 150 MHz)] spectra were determined on a JEOL JNM-ECS400 spectrometer. Chemical shifts for ^{1}H NMR are reported as δ values relative to tetramethylsilane as the internal standard and coupling constants are in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Chemical shifts for ^{13}C NMR were reported in ppm relative to the center line of a triplet at 77.16 ppm for $CDCl_3$. Mass spectra were measured on a Micromass Zq2000 spectrometer (ESI-MS), JMS-SX102A (FAB). Chiral HPLC was performed on a JASCO LC-2000 series using Daicel CHIRALPAK AS. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F_{254}. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 6 N (spherical, neutral, 40–100 mesh) or diol-functionalized silica gel (spherical, DIOL, 100 Å, 40–75 mesh). Reagents were commercial grades and were used without any purification unless otherwise noted. Dehydrated CH_2Cl_2, THF, and 1,4-dioxane were purchased from commercial sources. All reactions sensitive to oxygen or moisture were conducted under a N_2 atmosphere. Known compounds (**2**[8,9], **3**[21]) were prepared as described in the literature.

2,4-Diallyloxy-6-chloro-1,3,5-triazine (4):[22] Allyl alcohol (4.10 mL, 60.3 mmol) and ethyldiisopropylamine (10.5 mL, 60.3 mmol) were added to a solution of cyanuric chloride (3.69 g, 20.0 mmol) in CH_2Cl_2 (40 mL) at –10 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (100 mL) and then extracted with CH_2Cl_2 (3× 20 mL). The combined organic layer was washed with brine (100 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a colorless oil (4.33 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.09–5.98 (m, 2H), 5.49–5.41 (m, 2H), 5.37–5.31 (m, 2H), 4.99–4.91 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.9, 172.0, 131.0, 119.7, 69.7; IR ($CHCl_3$): 3047, 3032, 3005, 1556, 1537, 1329 cm^{-1}; HRMS (DART-TOF) Calcd for $C_9H_{11}ClN_3O_2$ ([M + H]$^+$) 228.0540, found 228.0546; Anal. Calcd for $C_9H_{10}ClN_3O_2$: C, 47.49; H, 4.43; N, 18.46. Found: C, 47.59; H, 4.46; N, 18.42.

General procedure for preparation of ATTACK-R (GP-1). Bis(benzonitrile)palladium(II) chloride (0.5 mol-%) was added to a solution of **4** (1.2 equiv) in THF (0.24 M) at room temperature. The solution was heated at reflux for 1–2 h and then cooled to 0 °C. An alcohol (ROH, 1 equiv), *N*-methylimidazole (20 mol-%), and Et_3N (2 equiv) were added. The reaction mixture was stirred at 0 °C to room temperature until TLC monitoring indicated complete conversion. The reaction mixture was poured into aqueous citric acid (10%) and then extracted with CH_2Cl_2. The organic layer was washed with brine, dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford ATTACK-R.

1,3-Diallyl-6-(benzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-Bn): Following GP-1, bis(benzonitrile)palladium(II) chloride (9.6 mg, 25 µmol) was added to a solution of **4** (1.366 g, 6.00 mmol) in THF (25 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. Benzyl alcohol (519.9 µL, 5.00 mmol), *N*-methylimidazole (79.0 µL, 1.00 mmol), and Et_3N (1.39 mL, 10.0 mmol) were added. The reaction mixture was stirred for 30 min at 0 °C and for 2 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and then extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was washed with brine (30 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 7:3) afforded a white solid (1.46 g, 97%). Mp 67.0–67.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.43–7.37 (m, 5H), 5.90 (ddt, *J* = 17.2, 10.3, 5.9 Hz, 1H), 5.81 (ddt, *J* = 16.4, 10.3, 5.9 Hz, 1H), 5.48 (s, 2H), 5.30 (dd, *J* = 17.2, 1.0 Hz, 1H), 5.24–5.16 (m, 3H), 4.51 (d, *J* = 5.9 Hz, 2H), 4.47 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.6, 154.0, 150.4, 133.9, 131.2, 130.6, 129.2, 128.9, 128.8, 119.3, 118.6, 71.9, 45.0, 44.7; HRMS (DART-TOF) Calcd for $C_{16}H_{18}N_3O_3$ ([M + H]$^+$) 300.1348, found 300.1355; Anal. Calcd for $C_{16}H_{17}N_3O_3$: C, 64.20; H, 5.72; N, 14.04. Found: C, 64.16; H, 5.87; N, 14.01.

1,3-Diallyl-6-(4-methoxybenzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-PMB): Bis(benzonitrile)palladium(II) chloride (19.2 mg, 50.1 µmol) in THF (5.0 mL) was added to a solution of **4** (2.73 g, 12.0 mmol) in THF (45 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. 4-Methoxybenzyl alcohol (1.24 mL, 9.96 mmol), Et_3N (2.79 mL, 20.0 mmol), and *N*-methylimidazole (158 µL, 2.00 mmol) were added. The reaction mixture was stirred for 6 h at 0 °C and then allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure. Column chromatography (diol-functionalized silica gel, hexane/$CHCl_3$ = 7:3) afforded a clear colorless oil (3.05 g, 93%): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.39–7.32 (m, 2H), 6.95–6.88 (m, 2H), 5.97–5.72 (m, 2H), 5.42 (s, 2H), 5.34–5.12 (m, 4H), 4.51 (d, *J* = 6.0 Hz, 2H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 160.3, 158.5, 154.0, 131.2, 130.8, 130.6, 125.9, 119.2, 118.5, 114.2, 55.4, 45.0, 44.7; IR ($CHCl_3$): 2997, 1678, 1606, 1516, 1473, 1259, 1036 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{19}N_3NaO_4$ ([M + Na]$^+$) 352.1273, found 352.1256.

1,3-Diallyl-6-[(4-methylbenzyl)oxy]-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-MBn): Following GP-1, bis(benzonitrile)palladium(II) chloride (7.7 mg, 20.0 µmol) was added to a solution of **4** (1.093 g, 4.80 mmol) in THF (5.0 mL) at room temperature. The solution was heated at reflux for 1.5 h and then cooled to 0 °C. 4-Methylbenzyl alcohol (488.6 mg, 4.00 mmol) in THF (3.0 mL), *N*-methylimidazole (63.3 µL, 0.80 mmol), and Et_3N (1.1 mL, 7.89 mmol) were added. The reaction mixture was stirred for 30 min at 0 °C and for 1 h at room temperature. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (20 mL) and then extracted with CH_2Cl_2 (5 × 10 mL). The combined organic layer was washed with brine (20 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (CH_2Cl_2/EtOAc = 19:1) afforded a white solid (1.084 g, 86%). Mp 56.7–58.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.30 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 5.90 (ddt, *J* = 17.2, 10.3, 5.8 Hz, 1H), 5.80 (ddt, *J* = 17.0, 10.4, 5.8 Hz, 1H), 5.44 (s, 2H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.25–5.14 (m, 3H), 4.51 (d, *J* = 5.8 Hz, 2H), 4.45 (d, *J* = 5.8 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.6, 154.0, 150.4, 139.2, 131.2, 130.9, 130.6, 129.5, 129.1, 129.0, 119.3, 118.6, 72.0, 45.0, 44.7, 21.4; HRMS (DART-TOF) Calcd for $C_{17}H_{19}N_3O_3$ ([M + H]$^+$): 314.1505, found 314.1500; Anal. Calcd for $C_{17}H_{20}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.11; H, 6.29; N, 13.39.

1,3-Diallyl-6-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyloxy]-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-*F*$_{13}$Bn): Following GP-1, bis(benzonitrile)palladium(II) chloride (2.3 mg, 6.0 µmol) was added to a solution of **4** (273.2 mg, 1.20 mmol) in THF (2.0 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)benzyl alcohol (454.2 mg, 1.00 mmol) in THF (3.0 mL), *N*-methylimidazole (15.8 µL, 0.20 mmol), and Et_3N (278.8 µL, 2.00 mmol) were added. The reaction mixture was stirred for 1 h at 0 °C and for 1.5 h at room temperature. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (20 mL) and then extracted with CH_2Cl_2 (5 × 10 mL). The combined organic layer was washed with brine (20 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/acetone = 4:1) afforded a white solid (614.1 mg, 95%). Mp 44.4–45.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.37 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 5.90 (ddt, *J* = 17.2, 10.3, 6.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.1, 6.0 Hz, 1H), 5.46 (s, 2H), 5.30 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.24–5.15 (m, 3H), 4.51 (d, *J* = 6.0 Hz, 2H), 4.47 (d, *J* = 6.0 Hz, 2H), 3.00–2.89 (m, 2H), 2.43–2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.6, 154.0, 150.4, 140.4, 132.5, 131.3, 130.7, 129.4, 128.9, 128.5, 119.8, 119.3, 118.7–109.2 (m), 71.6, 45.1, 44.8, 33.0, 32.9, 32.8, 26.4, 26.3; HRMS (DART-TOF) Calcd for $C_{24}H_{21}F_{13}N_3O_3$ ([M + H]$^+$) 646.1375, found 646.1383; Anal. Calcd for $C_{24}H_{20}F_{13}N_3O_3$: C, 44.60; H, 3.12; N, 6.51. Found: C, 44.64; H, 3.16; N, 6.46.

1,3-Diallyl-6-(4-bromobenzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-PBB): Following GP-1, bis(benzonitrile)palladium(II) chloride (9.6 mg, 25 µmol) in THF (5.0 mL) was added to a solution of **4** (1.366 g, 6.00 mmol) in THF (7.0 mL) at room temperature. The solution was heated at reflux for 1.5 h and then cooled to 0 °C. 4-Bromobenzyl alcohol (935.2 mg, 5.00 mmol) in THF (8.0 mL), Et_3N (1.4 mL, 10.0 mmol), and *N*-methylimidazole (79.2 µL, 1.00 mmol) were added. The reaction mixture was stirred for 10 min at 0 °C and for 1.5 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (50 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 7:3) afforded a white solid (1.91 g, quant.). Mp 62.2–63.3 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55–7.52 (m, 2H), 7.30–7.27 (m, 2H), 5.95–5.75 (m, 2H), 5.43 (s, 2H), 5.33–5.16 (m, 4H), 4.56 (ddd, *J* = 6.0, 1.5, 1.5 Hz, 2H), 4.47 (ddd, *J* = 5.5, 1.6, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.4, 153.8, 150.3, 132.9, 132.1, 131.1, 130.6, 130.5, 123.4, 119.3, 118.7, 71.0, 45.0, 44.8; IR (KBr): 3087, 1739, 1684, 1610, 1479, 1446, 1286 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{16}H_{17}BrN_3O_3$ ([M + H]$^+$) 378.0453, found 378.0443; Anal. Calcd for $C_{16}H_{16}BrN_3O_3$: C, 50.81; H, 4.26; N, 11.11: C, 64.20; H, 5.72; N, 14.04. Found: C, 50.77 ; H, 4.21; N, 11.51.

1,3-Diallyl-6-(4-nitrobenzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-PNB): Following GP-1, bis(benzonitrile)palladium(II) chloride (9.6 mg, 25 µmol) in THF (5.0 mL) was added to a solution of **4** (1.366 g, 6.00 mmol) in THF (25 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. 4-Nitrobenzyl alcohol (765.7 mg, 5.00 mmol) in THF (8.0 mL), Et_3N (1.4 mL, 10.0 mmol), and *N*-methylimidazole (79.2 µL, 1.00 mmol) were added. The reaction mixture was stirred for 15 min at 0 °C and for 1.5 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (50 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 1:1 to 1:3) afforded a white solid (1.70 g, 99%). Mp 122.6–123.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.31–8.24 (m, 2H), 7.62–7.54 (m, 2H), 5.97–5.77 (m, 2H), 5.59 (s, 2H), 5.36–5.17 (m, 4H), 4.55–4.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 158.3, 153.6, 150.1, 148.2, 140.9, 131.0, 130.6, 129.0, 124.1, 119.2, 118.8, 69.9, 45.1, 44.8; IR (KBr): 1685, 1612, 1595, 1477, 1441, 1344, 1284 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{16}H_{17}N_4O_5$ ([M + H]$^+$) 345.1199, found 345.1191; Anal. Calcd for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.54 ;H, 4.68; N, 16.19.

1,3-Diallyl-6-(2-nitrobenzyloxy)-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-ONB): Following GP-1, bis(benzonitrile)palladium(II) chloride

(9.6 mg, 25 µmol) was added to a solution of **4** (1.366 mg, 6.00 mmol) in THF (12 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. 2-Nitrobenzyl alcohol (765.7 mg, 10.0 mmol) in THF (13 mL), Et_3N (1.4 mL, 10.0 mmol), and *N*-methylimidazole (79.2 µL, 1.00 mmol) were added. The reaction mixture was stirred for 30 min at 0 °C and for 3.5 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (50 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (twice, CH_2Cl_2/EtOAc = 19:1 to 7:3 for the first chromatography, and hexane/EtOAc = 6:4 to 5:5 for the second chromatography) afforded a white solid (1.611 g, 94%). Mp 131.1–132.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18–8.12 (m, 1H), 7.73–7.65 (m, 1H), 7.62–7.54 (m, 2H), 5.97–5.75 (m, 4H), 5.35–5.16 (m, 4H), 4.53–4.45 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 158.3, 153.7, 150.2, 148.0, 134.0, 131.1, 130.6, 130.5, 130.1, 129.6, 125.6, 119.2, 118.8, 68.4, 45.2, 44.8; IR (KBr): 3076, 2952, 1739, 1682, 1606, 1469, 1342 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{16}H_{17}N_4O_5$ ([M + H]$^+$) 345.1199, Found 345.1214; Anal. Calcd for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.58; H, 4.75; N, 16.17.

1,3-Diallyl-6-(4,5-dimethoxy-2-nitrobenzyloxy)-1,3,5-triazine-2,4(*1H,3H*)-dione (ATTACK-DMNB): Following GP-1, bis(benzonitrile)palladium(II) chloride (3.9 mg, 10 µmol) in THF (3.0 mL) was added to a solution of **4** (546.4 mg, 2.40 mmol) in THF (2.0 mL) at room temperature. The solution was heated at reflux for 1.5 h and then cooled to 0 °C. 4,5-Dimethoxy-2-nitrobenzyl alcohol (426.4 mg, 2.00 mmol) in THF (5.0 mL), Et_3N (554.5 µL, 4.00 mmol), and *N*-methylimidazole (31.6 µL, 0.400 mmol) were added. The reaction mixture was stirred for 10 min at 0 °C and for 3 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (twice, hexane/EtOAc = 1:1 for the first chromatography, and $CHCl_3$/acetone =19:1 for the second chromatography) afforded a yellow solid (687.4 mg, 85%). Mp 143.7–144.9 °C ; ^{1}H NMR ($CDCl_3$): *δ* 7.75 (s, 1H), 7.06 (s, 1H), 5.95–5.76 (m, 2H), 5.84 (s, 2H), 5.34–5.16 (m, 4H), 4.50 (ddd, *J* = 5.9, 1.7, 1.7 Hz, 2H), 4.46 (ddd, *J* = 5.9, 1.6, 1.6 Hz, 2H), 3.99 (s, 3H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$): *δ* 158.4, 153.7, 153.3, 150.2, 149.3, 140.8, 131.1, 130.5, 123.8, 119.1, 118.7, 113.0, 108.6, 68.7, 56.8, 56.6, 45.1, 44.8; IR (KBr): 2972, 1734, 1678, 1601, 1437, 1294, 1217 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{20}N_4NaO_7$ ([M + Na]$^+$) 427.1230, found 427.1209.

1,3-Diallyl-6-allyloxy-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-allyl): Following GP-1, bis(benzonitrile)palladium(II) chloride (9.6 mg, 25 µmol) was added to a solution of **4** (1.366 g, 6.00 mmol) in THF (6 mL) at room temperature. The solution was heated at reflux for 1 h and then cooled to 0 °C. Allyl alcohol (340 µL, 5.00 mmol), Et_3N (1.4 mL, 10.0 mmol), and *N*-methylimidazole (79.2 µL, 1.00 mmol) were added. The reaction mixture was stirred for 15 min at 0 °C and for 1.5 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layer was washed with brine (50 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 7:3) afforded a white solid (1.23 g, quant.). ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 6.05–5.95 (m, 1H), 5.95–5.79 (m, 2H), 5.46–5.19 (m, 6H), 4.99–4.94 (m, 2H), 4.53–4.47 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 158.4, 154.0, 150.4, 131.2, 130.6, 130.4, 120.5, 119.3, 118.6, 70.7, 45.0, 44.7; IR (KBr): 3076, 2952, 1739, 1682, 1606, 1469, 1342 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{12}H_{16}N_3O_3$ ([M + H]$^+$) 250.1192, Found 345.1214; Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.58; H, 4.75; N, 16.17. Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.78; H, 6.12; N, 16.76.

1,3-Diallyl-6-methoxy-1,3,5-triazine-2,4(1*H*,3*H*)-dione (ATTACK-Me): Following GP-1, bis(benzonitrile)palladium(II) chloride (9.6 mg, 25 µmol) in THF (5.0 mL) was added to a solution of **4** (1.366 g, 6.00 mmol) in THF (20 mL) at room temperature. The solution was heated at reflux for 2 h and then cooled to 0 °C. Methanol (197.8 µL, 5.00 mmol), Et_3N (1.4 mL, 10.1 mmol), and *N*-methylimidazole (79.0 µL, 1.00 mmol) were added. The reaction mixture was stirred for 10 min at 0 °C and for 6 h at room temperature. The reaction mixture was poured into aqueous citric acid (10%, 30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (60 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 3:2) afforded a clear yellow oil (963.3 mg, 86%). ^{1}H NMR ($CDCl_3$): *δ* 5.97–5.77 (m, 2H), 5.33–5.18 (m, 4H), 4.51 (ddd, *J* = 6.0, 1.4, 1.4 Hz, 2H), 4.48 (ddd, *J* = 6.0, 1.4, 1.4 Hz, 2H), 4.07 (s, 3H); ^{13}C NMR ($CDCl_3$): *δ* 159.2, 153.9, 150.2, 131.2, 130.6, 119.0, 118.5, 57.0, 44.9, 44.6; IR ($CHCl_3$): 3051, 2997, 1680, 1612, 1483, 1434 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{10}H_{13}N_3NaO_3$ ([M + Na]$^+$) 246.0855, found 246.0861; Anal. Calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82. Found: C, 53.69 ;H, 6.02; N, 18.69.

General procedure for acid-catalyzed *O*-alkylation with ATTACK-R and 3 (GP-2). Pyridinium salt **3** (10 mol-%) was added to a mixture of an alcohol (1 equiv), ATTACK-R (1.2 equiv), and molecular sieves 5A (25 mg/mL) in 1,4-dioxane (0.2 M) at room temperature. The reaction mixture was stirred until TLC monitoring indicated complete conversion. The reaction mixture was diluted with Et_2O or EtOAc and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ and brine, dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product.

General procedure for acid-catalyzed *O*-alkylation with ATTACK-R and trifluoromethanesulfonic acid (GP-3). Trifluoromethanesulfonic acid (10 mol-%) was added to a mixture of an alcohol (1 equiv), ATTACK-R (1.2 equiv), and molecular sieves 5A (25 mg/mL) in 1,4-dioxane (0.2 M) at room temperature. The reaction mixture was stirred until TLC monitoring indicated complete conversion. The reaction mixture was diluted with Et_2O or EtOAc and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ and brine, dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product.

Benzyl 6-bromohexyl ether (7a-Bn):[23] Following GP-2, **3** (10.2 mg, 30 µmol) was added to a mixture of **6a** (40.8 µL, 0.300 mmol), ATTACK-Bn (107.8 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.2 mL). After 3.5 h, the reaction mixture was diluted with EtOAc (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/acetone = 97:3) followed by recycling preparative HPLC afforded a clear colorless oil (71.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.40–7.23 (m, 5H), 4.50 (s, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.86 (quint, *J* = 7.0 Hz, 2H), 1.63 (quint, *J* = 7.1 Hz, 2H), 1.52–1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 138.7, 128.5, 127.8, 127.6, 73.0, 70.3, 34.0, 32.9, 29.7, 28.1, 25.5; HRMS (DART-TOF) Calcd for $C_{13}H_{20}BrO$ ([M + H]$^+$) 271.0698, found 271.0689.

6-Bromohexyl 4-methoxybenzyl ether (7a-PMB):[24] Following GP-2 with slight modification, **3** (2.0 mg, 5.9 µmol) in 1,4-dioxane (0.4 mL) was added to a mixture of **6a** (40.8 µL, 0.300 mmol), ATTACK-PMB (122.1 mg, 0.37 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.1 mL) at room temperature. After 20 min, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/CH_2Cl_2 = 1:1) afforded a clear colorless oil (72.4

mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29–7.23 (m, 2H), 6.91–6.85 (m, 2H), 4.43 (s, 2H), 3.81 (s, 3H), 3.44 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.86 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.61 (tt, *J* = 6.8, 6.8 Hz, 2H) 1.49–1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 130.8, 129.3, 113.8, 72.7, 70.0, 55.4, 34.0, 32.8, 29.7, 28.1, 25.5; HRMS (DART-TOF) Calcd for $C_{14}H_{25}BrNO_2$ ($[M + NH_4]^+$) 318.1069, found 318.1069.

6-Bromohexyl 4-methylbenzyl ether (7a-MBn): Following GP-2, **3** (13.7 mg, 40 µmol) was added to a mixture of **6a** (54.5 µL, 0.400 mmol), ATTACK-MBn (150.4 mg, 0.480 mmol), and molecular sieves 5A (50.0 mg) in 1,4-dioxane (2.0 mL) at room temperature. After 45 min, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/$CHCl_3$ = 6:4) followed by recycling preparative HPLC afforded a clear colorless oil (99.6 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.46 (s, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.86 (quint, *J* = 7.2 Hz, 2H), 1.61 (quint, *J* = 7.0 Hz, 2H), 1.51–1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 135.6, 129.1, 127.9, 72.9, 70.1, 34.0, 32.9, 29.7, 28.1, 25.5, 21.3; HRMS (DART-TOF) Calcd for $C_{14}H_{25}BrNO$ ($[M + NH_4]^+$) 304.1099, found: 304.1112 Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42. Found: C, 59.05; H, 7.50.

6-Bromohexyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyl ether (7a-*F*$_{13}$Bn): Following GP-2, **3** (4.8 mg, 14 µmol) was added to a mixture of **6a** (19.0 µL, 0.140 mmol), ATTACK-*F*$_{13}$Bn (108.2 mg, 0.168 mmol), and molecular sieves 5A (25 mg) in 1,4-dioxane (1.0 mL) at room temperature. After 2 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/acetone = 97:3) followed by recycling preparative HPLC afforded a clear colorless oil (78.8 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.48 (s, 2H), 3.47 (t, *J* = 6.7 Hz, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.96–2.86 (m, 2H), 2.46–2.25 (m, 2H), 1.86 (quint, *J* = 7.3 Hz, 2H), 1.63 (quint, *J* = 7.1 Hz, 2H), 1.51–1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 137.3, 128.5, 128.3, 118.4–111.2 (m), 72.7, 70.4, 34.0, 33.3, 33.1, 32.91, 32.87, 29.7, 28.1, 26.33, 26.2, 25.6; HRMS (DART-TOF) Calcd for $C_{21}H_{26}BrF_{13}NO$ ($[M + NH_4]^+$) 634.0990, found: 634.0960 Anal. Calcd for $C_{21}H_{22}BrF_{13}O$: C, 40.86; H, 3.59. Found: C, 40.96; H, 3.68.

4-Bromobenzyl 6-bromohexyl ether (7a-PBB):[25] Following GP-3, trifluoromethanesulfonic acid (2.6 µL, 30 µmol) was added to a mixture of **6a** (40.8 µL, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 5 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/CH_2Cl_2 = 7:3) afforded a clear colorless oil (89.8 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.43 (m, 2H), 7.24–7.17 (m, 2H), 4.44 (s, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.41 (t, *J* = 6.4 Hz, 2H), 1.86 (tt, *J* = 6.6, 6.6 Hz, 2H), 1.62 (tt, *J* = 7.3, 6.4 Hz, 2H), 1.52–1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 131.6, 129.4, 121.5, 72.3, 70.5, 34.0, 32.8, 29.7, 28.1, 25.5; HRMS (DART-TOF) Calcd for $C_{13}H_{19}Br_2O$ ($[M + H]^+$) 348.9803, found 348.9797.

6-Bromohexyl 4-nitrobenzyl ether (7a-PNB): Following GP-3 with slight modification, trifluoromethanesulfonic acid (5.2 µL, 60 µmol) was added to a mixture of **6a** (40.8 µL, 0.300 mmol), ATTACK-PNB (124.0 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 23 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/CH_2Cl_2 = 1:1) afforded a pale yellow solid (77.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.17 (m, 2H), 7.54–7.46 (m, 2H), 4.60 (s, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 6.9 Hz, 2H), 1.88 (tt, *J* = 6.4, 6.4 Hz, 2H), 1.67 (tt, *J* = 6.9, 6.9 Hz, 2H), 1.55–1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 146.5, 127.8, 123.8, 71.8, 71.0, 34.0, 32.8, 29.6, 28.1, 25.5; IR (KBr): 2943, 2868, 1510, 1342, 1128, 1105, 841, 739 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{13}H_{19}BrNO_3$ ($[M + H]^+$) 316.0548, found 316.0562; Anal. Calcd for $C_{13}H_{18}BrNO_3$: C, 49.38; H, 5.74; N, 4.43. Found: C, 49.44 ;H, 5.71; N, 4.39.

6-Bromohexyl 2-nitrobenzyl ether (7a-ONB): Following GP-3 with slight modification, trifluoromethanesulfonic acid (26.2 µL, 300 µmol) was added to a mixture of **6a** (204.2 µL, 1.50 mmol), ATTACK-ONB (619.8 mg, 1.80 mmol), and molecular sieves 5A (187.5 mg) in 1,4-dioxane (7.5 mL) at room temperature. After 69 h, the reaction mixture was diluted with Et_2O (30 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (twice, hexane/CH_2Cl_2 = 7:3 to 0:1 for the first chromatography, and hexane/EtOAc = 9:1 for the second chromatography) afforded a white solid (76.4 mg, 16%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–8.03 (m, 1H), 7.82–7.76 (m, 1H), 7.68–7.62 (m, 1H), 7.47–7.40 (m, 1H), 4.87 (s, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 1.89 (tt, *J* = 7.1, 7.1 Hz, 2H), 1.68 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.54–1.41 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.4, 135.5, 133.7, 128.7, 127.9, 124.7, 71.2, 69.5, 34.0, 32.8, 29.6, 28.1, 25.5; IR ($CHCl_3$): 3039, 3014, 2941, 2864, 1531, 1344, 11110, 707 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{13}H_{22}BrN_2O_3$ ($[M + NH_4]^+$) 333.0814, Found 333.0811; Anal. Calcd for $C_{13}H_{18}BrNO_3$: C, 49.38; H, 5.74; N, 4.43. Found: C, 49.44; H, 5.71; N, 4.39.

6-Bromohexyl 4,5-dimethoxy-2-nitrobenzyl ether (7a-DMNB): Following GP-3, trifluoromethanesulfonic acid (2.6 µL, 30 µmol) was added to a mixture of **6a** (40.8 µL, 0.300 mmol), ATTACK-DMNB (145.6 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 2.5 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/AcOEt = 9:1) afforded a yellow solid (22.4 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.30 (s, 1H), 4.89 (s, 2H), 4.00 (s, 3H), 3.96 (s, 3H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 1.89 (tt, *J* = 6.6, 6.6 Hz, 2H), 1.71 (tt, *J* = 6.9, 6.9 Hz, 2H) 1.56–1.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 147.6, 139.3, 131.4, 109.5, 107.9, 71.2, 69.6, 56.5, 33.9, 32.8, 29.7, 28.1, 25.6; IR (KBr): 2937, 1518, 1462, 1319, 1273, 1223, 1115 cm^{-1}; HRMS (DART-TOF) Calcd for Calcd for $C_{15}H_{23}BrNO_5$ ($[M + H]^+$) 376.0760, found 376.0759; Anal. Calcd for $C_{15}H_{22}BrNO_5$: C, 47.88; H, 5.89; N, 3.72. Found: C, 47.74; H, 5.91; N, 3.68.

Allyl 6-bromohexyl ether (7a-allyl):[5] Following GP-2 with slight modification, **3** (13.7 mg, 40 µmol) was added to a mixture of **6a** (54.5 µL, 0.400 mmol), ATTACK-allyl (118.5 mg, 0.48 mmol), and molecular sieves 5A (50 mg) in 1,4-dioxane (2.0 mL) at 50 °C. After 6.5 h, the reaction mixture was diluted with Et_2O (10 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/CH_2Cl_2 = 6:4) afforded a clear colorless oil (74.1 mg, 84%).^{1}H NMR (600 MHz, $CDCl_3$): δ 5.96–5.82 (m, 1H), 5.33–5.22 (m, 1H), 5.22–5.12 (m, 1H), 4.01–3.92 (m, 2H), 3.43 (t, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 7.5 Hz, 2H), 1.87 (tt, *J* = 7.1, 7.1 Hz, 2H), 1.61 (tt, *J* = 7.1, 7.1 Hz, 2H), 1.50–1.35 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.1, 116.9, 72.0, 71.3, 34.0, 32.9, 29.7, 28.1, 25.5; IR ($CHCl_3$): 3053, 2939, 2864, 1188, 928, 818, 700 cm^{-1}; HRMS (DART-TOF) Calcd for $C_9H_{21}BrNO$ ($[M + NH_4]^+$) 238.0807, Found 238.0809.

6-Bromohexyl methyl ether (7a-Me):[26] Following GP-3 with slight modification, trifluoromethanesulfonic acid (2.7 µL, 31 µmol) was added to

a mixture of **6a** (42.2 µL, 0.310 mmol), ATTACK-Me (83.3 mg, 0.373 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (0.2 M) at room temperature. The reaction mixture was stirred for 1 h at room temperature, for 30 min at 40 °C, for 30 min at 60 °C, for 30 min at 80 °C, for 4.5 h at reflux, and then cooled to room temperature. The reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/AcOEt = 19:1) afforded a clear colorless oil (33.8 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.41 (t, J = 7.0 Hz, 2H), 3.37 (t, J = 6.2 Hz, 2H), 3.33 (s, 3H), 1.87 (tt, J = 7.0, 7.0 Hz, 2H), 1.63–1.55 (m, 2H), 1.51–1.42 (m, 2H), 1.42–1.33 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 72.8, 58.7, 34.0, 32.9, 29.6, 28.1, 25.5; IR ($CHCl_3$): 2937, 2862, 1720, 1111, 754, 700 cm^{-1}; HRMS (DART-TOF) Calcd for $C_7H_{16}BrO$ ([M + H]$^+$) 195.0385, found 195.0390.

1-Acetoxydecyl 10-benzyl ether (7b-Bn):[7] Following GP-2, **3** (10.2 mg, 30 µmol) was added to a mixture of **6b** (64.9 mg, 0.300 mmol), ATTACK-Bn (107.8 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 4.5 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (88.7 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.20 (m, 5H), 4.50 (s, 2H), 4.05 (t, J = 6.9 Hz, 2H), 3.46 (t, J = 6.7 Hz, 2H), 2.04 (s, 3H), 1.74–1.48 (m, 4H), 1.50–1.15 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 138.8, 128.5, 127.7, 127.6, 73.0, 70.6, 64.8, 29.9, 29.61, 29.56, 29.4, 28.7, 26.3, 26.0, 21.2; HRMS (DART-TOF) Calcd for $C_{19}H_{34}NO_3$ ([M + NH_4]$^+$): 324.2539, found: 324.2529.

Methyl (2*R*)-3-(benzyloxy)-2-methylpropionate (7c-Bn):[7] Following GP-2, **3** (17.1 mg, 50 µmol) was added to a mixture of **6c** (55.2 µL, 0.500 mmol), ATTACK-Bn (179.6 mg, 0.600 mmol), and molecular sieves 5A (62.5 mg) in 1,4-dioxane (2.5 mL) at room temperature. After 5 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (96.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.21 (m, 5H), 4.52 (s, 2H), 3.69 (s, 3H), 3.66 (dd, J = 9.2, 7.4 Hz, 1H), 3.49 (dd, J = 8.7, 6.0 Hz, 1H), 2.87–2.71 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 138.2, 128.4, 127.69, 127.66, 73.2, 72.0, 51.8, 40.3, 14.1; HRMS (DART-TOF): Calcd for $C_{12}H_{17}O_3$ ([M + H]$^+$) 209.11789, found: 209.1182.

1-Adamantyl benzyl ether (7d-Bn):[7] Following GP-2, **3** (13.7 mg, 40 µmol) was added to a mixture of **6d** (60.9 mg, 0.400 mmol), ATTACK-Bn (143.7 mg, 0.480 mmol), and molecular sieves 5A (50.0 mg) in 1,4-dioxane (2.0 mL) at room temperature. After 9.5 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/acetone = 97:3) afforded a clear colorless oil (85.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.18 (m, 5H), 4.51 (s, 2H), 2.17 (br s, 3H), 1.94–1.79 (m, 6H), 1.72–1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 128.4, 127.6, 127.1, 72.8, 62.4, 41.9, 36.6, 30.7; HRMS (DART-TOF) Calcd for $C_{17}H_{23}O$ ([M + H]$^+$) 243.1749, found: 243.1760.

10-Acetoxydecyl 4-methoxybenzyl ether (7b-PMB):[27] Following GP-2 with slight modification, **3** (2.0 mg, 5.9 µmol) in 1,4-dioxane (0.4 mL) was added to a mixture of **6b** (64.9 mg, 0.300 mmol), ATTACK-PMB (122.1 mg, 0.37 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.1 mL) at room temperature. After 10 min, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/AcOEt = 9:1) afforded a clear colorless oil (89.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 2H), 6.91–6.84 (m, 2H), 4.43 (s, 2H), 4.05 (t, J = 6.7 Hz, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.7 Hz, 2H), 2.05 (s, 3H), 1.67–1.55 (m, 4H), 1.36–1.25 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 159.2, 130.9, 129.3, 113.8, 72.6, 70.3, 64.8, 55.3, 29.9, 29.6, 29.5, 29.3, 28.7, 26.3, 26.0, 21.1; HRMS (DART-TOF) Calcd for $C_{20}H_{33}O_4$ ([M + H]$^+$) 337.2379, found 337.2363.

Methyl (2*R*)-3-[(4-methoxybenzyl)oxy]-2-methylpropionate (7c-PMB):[28,29] Following GP-2 with slight modification, **3** (2.0 mg, 5.9 µmol) in 1,4-dioxane (0.4 mL) was added to a mixture of **6c** (33.1 µL, 0.300 mmol), ATTACK-PMB (122.1 mg, 0.37 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.1 mL) at room temperature. After 10 min, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (57.7 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.20 (m, 2H), 6.91–6.84 (m, 2H), 4.48–4.43 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.63 (dd, J = 9.2, 7.3 Hz, 1H), 3.46 (dd, J = 9.2, 6.0 Hz, 1H), 2.81–3.71 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.3, 159.1, 130.2, 129.2, 113.7, 72.7, 71.6, 55.2, 51.7, 40.1, 14.0; HRMS (DART-TOF) Calcd for $C_{13}H_{19}O_4$ ([M + H]$^+$) 239.1283, found 239.1285.

1-Adamantyl 4-methoxybenzyl ether (7d-PMB): Following GP-2 with slight modification, **3** (2.0 mg, 5.9 µmol) in 1,4-dioxane (0.4 mL) was added to a mixture of **6d** (45.7 mg, 0.300 mmol), ATTACK-PMB (122.1 mg, 0.37 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.1 mL) at room temperature. After 10 min, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/Et_2O = 19:1) afforded a clear colorless oil (50.6 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.24 (m, 2H), 6.90–6.82 (m, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 2.17 (br s, 3H), 1.84 (d, J = 2.3 Hz, 6H), 1.70–1.59 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 132.3, 129.1, 113.8, 72.7, 62.1, 55.4, 41.9, 36.6, 30.7; IR (KBr): 2912, 2850, 1612, 1512, 1244, 1084, 1024, 822 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{18}H_{25}O_2$ ([M + H]$^+$) 273.1855, found 273.1842.

10-Acetoxydecyl 4-methylbenzyl ether (7b-MBn): Following GP-2, **3** (13.7 mg, 40 µmol) was added to a mixture of **6b** (86.5 mg, 0.400 mmol), ATTACK-MBn (150.4 mg, 0.480 mmol), and molecular sieves 5A (50.0 mg) in 1,4-dioxane (2.0 mL) at room temperature. After 45 min, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 19:1) afforded a clear colorless oil (125.5 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 4.46 (s, 2H), 4.05 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 2.34 (s, 3H), 2.04 (s, 2H), 1.67–1.54 (m, 4H), 1.40–1.18 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 137.2, 135.7, 129.1, 127.8, 72.8, 70.4, 64.7, 29.9, 29.6, 29.5, 29.3, 28.7, 26.3, 26.0, 21.3, 21.1; HRMS (DART-TOF) Calcd for $C_{20}H_{33}O_3$ ([M + H]$^+$) 321.2430, found 321.2441. Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.07. Found: C, 74.95; H, 10.22.

Methyl (2*R*)-3-[(4-methylbenzyl)oxy]-2-methylpropionate (7c-MBn): Following GP-2, **3** (34.1 mg, 0.100 mmol) was added to a mixture of **6c** (110.4 µL, 1.00 mmol), ATTACK-MBn (376.0 mg, 1.20 mmol), and molecular sieves 5A (125 mg) in 1,4-dioxane (5.0 mL) at room temperature. After 1 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography

(hexane/EtOAc = 19:1) followed by recycling preparative HPLC afforded a clear colorless oil (206.6 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 4.50 (d, J = 13.4 Hz, 1H), 4.46 (d, J = 13.4 Hz, 1H), 3.69 (s, 3H), 3.63 (dd, J = 8.7, 7.2 Hz, 1H), 3.47 (dd, J = 9.2, 6.0 Hz, 1H), 2.85–2.70 (m, 1H), 2.34 (s, 3H), 1.17 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 137.4, 135.2, 129.1, 127.8, 73.1, 71.9, 51.8, 40.3, 21.3, 14.1; HRMS (DART-TOF): Calcd for $C_{13}H_{22}NO_3$ ([M + NH_4]$^+$) 240.1600, found: 240.1588. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.03; H, 8.37.

1-Adamantyl 4-methylbenzyl ether (7d-MBn): Following GP-2, **3** (17.1 mg, 50 µmol) was added to a mixture of **6d** (76.1 mg, 0.400 mmol), ATTACK-MBn (188.0 mg, 0.600 mmol), and molecular sieves 5A (62.5 mg) in 1,4-dioxane (2.0 mL) at room temperature. After 2 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/Et_2O = 19:1) followed by recycling preparative HPLC afforded a white solid (110.5 mg, 86%). Mp 47.9–48.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.46 (s, 2H), 2.32 (s, 3H), 2.17 (br s, 3H), 1.92–1.78 (m, 6H), 1.72–1.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.7, 129.0, 128.9, 127.6, 72.7, 62.3, 46.0, 41.9, 41.7, 36.7, 36.6, 36.5, 31.2, 30.8, 30.7, 21.3; HRMS (DART-TOF): Calcd for $C_{18}H_{25}O$ ([M + H]$^+$): 257.1905, found: 257.1903. Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.14; H, 9.41.

10-Acetoxydecyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyloxy ether (7b-*F*$_{13}$Bn): Following GP-2, **3** (5.0 mg, 15 µmol) was added to a mixture of **6b** (31.6 mg, 0.15 mmol), ATTACK-*F*$_{13}$Bn (113.1 mg, 0.175 mmol), and molecular sieves 5A (25 mg) in 1,4-dioxane (1 mL) at room temperature. After 2 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 19:1) afforded a clear colorless oil (91.3 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.48 (s, 2H), 4.05 (t, J = 6.9 Hz, 2H), 3.46 (t, J = 6.9 Hz, 2H), 3.00–2.83 (m, 2H), 2.44–2.24 (m, 2H), 2.04 (s, 3H), 1.70–1.57 (m, 4H), 1.42–1.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 138.5, 137.4, 128.4, 128.3, 119.8–108.9 (m), 72.7, 70.7, 64.8, 33.3, 33.1, 33.0, 29.9, 29.63, 29.59, 29.4, 28.7, 26.32, 26.27, 26.25, 26.0, 21.1; HRMS (DART-TOF) Calcd for $C_{27}H_{34}F_{13}O_3$ ([M + H]$^+$): 653.2300, Found: 653.2272 Anal. Calcd for $C_{27}H_{33}F_{13}O_3$: C, 49.70; H, 5.10, found: C, 49.78; H, 5.28.

Methyl (2*R*)-3-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyloxy]-2-methylpropionate (7c-*F*$_{13}$Bn): Following GP-2, **3** (3.0 mg, 8.8 µmol) was added to a mixture of **6c** (9.8 µL, 88.8 µmol), ATTACK-*F*$_{13}$Bn (68.9 mg, 0.11 mmol), and molecular sieves 5A (12.5 mg) in 1,4-dioxane (0.6 mL) at room temperature. After 4 h, the reaction mixture was diluted with Et_2O (40 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 19:1) afforded a clear colorless oil (48.9 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 4.50 (s, 2H), 3.70 (s, 3H), 3.66 (dd, J = 9.2, 7.3 Hz, 1H), 3.49 (dd, J = 9.2, 6.0 Hz, 1H), 2.97–2.85 (m, 2H), 2.87–2.70 (m, 1H), 2.46–2.25 (m, 2H), 1.18 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 138.6, 136.8, 128.4, 128.2, 119.8–109.4 (m), 72.9, 72.1, 51.9, 40.3, 33.1 (t, J = 21.5 Hz), 26.27, 26.25, 14.1; HRMS (DART-TOF): Calcd for $C_{20}H_{23}F_{13}NO_3$ ([M + NH_4]$^+$): 572.1470, found: 572.1461; Anal. Calcd for $C_{20}H_{19}F_{13}O_3$: C, 43.33; H, 3.45. Found: C, 43.71; H, 3.65.

1-Adamantyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyl ether (7d-*F*$_{13}$Bn):[14] Following GP-2, **3** (5.7 mg, 17 µmol) was added to a mixture of **6d** (25.6 mg, 0.17 mmol), ATTACK-*F*$_{13}$Bn (130.1 mg, 0.20 mmol), and molecular sieves 5A (25.0 mg) in 1,4-dioxane (1.0 mL) at room temperature. After 3 h, the reaction mixture was diluted with Et_2O (50 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 97:3) afforded a clear colorless oil (90.5 mg, 92%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.31 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 4.48 (s, 2H), 2.95–2.82 (m, 2H), 2.47–2.22 (m, 2H), 2.18 (br s, 3H), 1.93–1.79 (m, 6H), 1.75–1.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.0, 128.3, 128.2, 118.8–108.4 (m), 72.9, 62.2, 46.0, 41.9, 36.9, 36.8, 36.6, 36.5, 33.4, 33.2, 33.0, 31.2, 30.9, 30.7, 26.32, 26.27, 26.2; HRMS (DART-TOF): Calcd for $C_{25}H_{29}F_{13}NO$ ([M + NH_4]$^+$): 606.2042, found: 606.2014.

10-Acetoxydecyl 4-bromobenzyl ether (7b-PBB): *Synthesis following GP-2.* Pyridinium salt **3** (10.2 mg, 30 µmol) in 1,4-dioxane (0.6 mL) was added to a mixture of **6b** (64.9 mg, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (0.9 mL) at room temperature. After 24 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 19:1) afforded a clear colorless oil (103.0 mg, 89%).

Synthesis following GP-3. Trifluoromethanesulfonic acid (2.6 µL, 30 µmol) was added to a mixture of **6b** (64.9 mg, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (0.6 mL) at room temperature. After 5 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (104.1 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$):δ 7.49–7.43 (m, 2H), 7.24–7.18 (m, 2H), 4.44 (s, 2H), 4.05 (t, J = 6.9 Hz, 2H), 3.45 (t, J = 6.5 Hz, 2H), 2.05 (s, 3H), 1.66–1.56 (m, 4H), 1.38–1.26 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 137.9, 131.6, 129.4, 121.4, 72.2, 70.8, 64.8, 29.9, 29.61, 29.57, 29.55, 29.4, 28.7, 26.3, 26.0, 21.2; IR ($CHCl_3$): 3051, 2931, 2858, 2401, 1728, 1261 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{19}H_{30}BrO_3$ ([M + H]$^+$) 385.1378, found 385.1366; Anal. Calcd for $C_{19}H_{29}BrO_3$: C, 59.22; H, 7.59; N, 0. Found: C, 58.84 ;H, 7.63; N, 0.10.

Methyl (2*R*)-3-[(4-bromobenzyl)oxy]-2-methylpropionate (7c-PBB):[30] *Synthesis following GP-2.* Pyridinium salt **3** (10.2 mg, 30 µmol) in 1,4-dioxane (0.6 mL) was added to a mixture of **6c** (33.1 µL, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (0.9 mL) at room temperature. After 24 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (73.5 mg, 85%).

Synthesis following GP-3. Trifluoromethanesulfonic acid (2.6 µL, 30 µmol) was added to a mixture of **6c** (33.1 µL, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 7 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a clear colorless oil (79.7 mg, 93%), which was used for HPLC analysis.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49–7.43 (m, 2H), 7.21–7.15 (m, 2H), 4.47 (s, 2H), 3.70 (s, 3H), 3.64 (dd, *J* = 9.1, 7.3 Hz, 1H), 3.48 (dd, *J* = 9.1, 5.8 Hz, 1H), 2.83–2.73 (m, 1H), 1.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.3, 137.3, 131.6, 129.3, 121.6, 72.5, 72.2, 51.9, 40.3, 14.1; IR ($CHCl_3$): 2956, 2868, 1734, 1489, 1092, 1012 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{12}H_{16}BrO_3$ ([M + H]$^+$) 287.0283, found 287.0279.

1-Adamantyl 4-bromobenzyl ether (7d-PBB):[30] Following GP-3 with slight modification, trifluoromethanesulfonic acid (2.6 µL, 30 µmol) was added to a mixture of **6d** (45.7 mg, 0.300 mmol), ATTACK-PBB (136.2 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 6 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 49:1) followed by recycling preparative HPLC afforded a white solid (60.6 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.46–7.40 (m, 2H), 7.25–7.19 (m, 2H), 4.45 (s, 2H), 2.17 (br s, 3H), 1.86–1.78 (m, 6H), 1.70–1.58 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.4, 131.4, 129.2, 120.9, 73.1, 61.8, 41.8, 36.6, 30.7; IR ($CHCl_3$): 2910, 1848, 1485, 1350, 1120, 1088 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{17}H_{25}BrNO$ ([M + NH_4]$^+$) 338.1120, found 338.1106.

10-Acetoxydecyl 4-nitrobenzyl ether (7b-PNB): Following GP-3 with slight modification, trifluoromethanesulfonic acid (5.2 µL, 60 µmol) was added to a mixture of **6b** (64.9 mg, 0.300 mmol), ATTACK-PNB (124.0 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. After 24 h, the reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1) afforded a yellow oil (88.5 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.17 (m, 2H), 7.53–7.47 (m, 2H), 4.60 (s, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.05 (s, 3H), 1.70–1.56 (m, 4H), 1.42–1.28 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 147.4, 146.6, 127.8, 123.7, 71.7, 71.3, 64.8, 29.8, 29.60, 29.57, 29.5, 29.3, 28.7, 26.3, 26.0, 21.2; IR ($CHCl_3$): 3051, 2931, 1728, 1523, 1348, 1259, 1192 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{19}H_{30}NO_5$ ([M + H]$^+$) 352.2124, found 352.2132; Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.93; H, 8.32; N, 3.99. Found: C, 64.60;H, 8.48; N, 3.95.

Methyl (2*R*)-3-[(4-nitrobenzyl)oxy]-2-methylpropionate (7c-PNB): Following GP-3 with slight modification, trifluoromethanesulfonic acid (5.2 µL, 60 µmol) was added to a mixture of **6c** (33.1 µL, 0.300 mmol), ATTACK-PNB (124.0 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. The reaction mixture was heated at 50 °C for 4 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 9:1 to 17:3) afforded a pale yellow solid (72.5 mg, 95%). Mp 37.0–37.6 °C; ^{1}H NMR (40 MHz, $CDCl_3$): δ 8.24–8.17 (m, 2H), 7.47–7.44 (m, 2H), 4.62 (s, 2H), 3.71 (s, 3H), 3.71 (dd, *J* = 8.7, 7.8 Hz, 1H), 3.56 (dd, *J* = 8.7, 6.0 Hz, 1H), 2.89–2.76 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.2, 147.5, 146.0, 127.7, 123.7, 72.7, 72.0, 52.0, 40.2, 14.1; IR (KBr): 2371, 1728, 1517, 1344, 1107, 1012 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{12}H_{16}NO_5$ ([M + H]$^+$) 254.1029, found 254.1028; Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.84 ;H, 6.10; N, 5.51.

1-Adamantyl 4-nitrobenzyl ether (7d-PNB): Following GP-3 with slight modification, trifluoromethanesulfonic acid (5.2 µL, 60 µmol) was added to a mixture of **6d** (45.6 mg, 0.300 mmol), ATTACK-PNB (124.0 mg, 0.360 mmol), and molecular sieves 5A (37.5 mg) in 1,4-dioxane (1.5 mL) at room temperature. The reaction mixture was heated at 50 °C for 5 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O (6 mL) and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried with Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Silica gel column chromatography (hexane/EtOAc = 19:1) afforded a white solid (79.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.15 (m, 2H), 7.55–7.49 (m, 2H), 4.62 (s, 2H), 2.20 (s, 3H), 1.84 (m, 6), 1.72–1.59 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.2, 147.2, 127.7, 123.6, 73.5, 61.5, 41.8, 36.5, 30.7; IR (KBr): 2927, 2887, 2854, 1521, 1344, 1124, 1101 cm^{-1}; HRMS (DART-TOF) Calcd for $C_{17}H_{22}NO_3$ ([M + H]$^+$) 288.1600, found 288.1593; Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.69 ;H, 7.46; N, 4.79.

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Keywords: Nitrogen heterocycles • Alcohols • Ethers • Protecting groups • Synthetic methods

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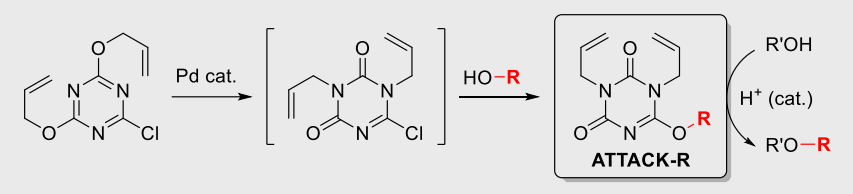

Diallyltriazinedione-type acid-catalyzed alkylating agents (ATTACKs-R) have been developed in combination with various alkyl groups (R). ATTACKs-R were prepared via the palladium-catalyzed *O-N* allylic rearrangement of 2,4-bis(allyloxy)-6-chloro-1,3,5-triazine followed by substitution of the chloro group with an alcohol.

O-Alkylating agents*

*Hikaru Fujita, Rina Yamashita, Takanori Fujii, Kohei Yamada, Masanori Kitamura, and Munetaka Kunishima**

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Preparation of Alkyl Ethers with Diallyltriazinedione-Type Acid-Catalyzed Alkylating Agents (ATTACKs-R)

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