Nucleophilic Reactivity of Ethers Against Terminal Epoxides in the Presence of BF_3: A Mechanistic Study

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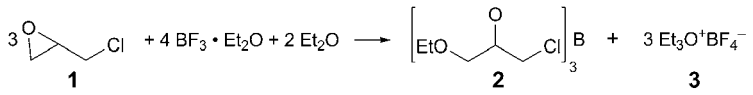
Dedicated to Professor *Metin Balci* on the occasion of his 65th birthday

In the presence of BF_3, a series of symmetrical and unsymmetrical ethers reacted with epichlorohydrin and 2-[(benzyloxy)methyl]oxirane, two terminal epoxides, to afford 1-alkoxy-3-chloropropan-2-ol and 1-alkoxy-3-(benzyloxy)propan-2-ol. The cleavage of unsymmetrical ethers occurred *via* an S_N2 or S_N1 mechanism. Secondary epoxides did not give similar ring-opening products.

Introduction. – The most common reaction of epoxides with oxygen nucleophiles is acid-catalyzed hydrolysis to give *trans*-diols [1]. $FeCl_3 \cdot 6\,H_2O$ supported on SiO_2 catalyzed ring openings of epoxides with alcohols, AcOH, and H_2O are also known [2].

To the best of our knowledge, reactions of epoxides with ethers in the presence of a catalyst or without catalyst are rare. The best known example is the reaction of Et_2O with epichlorohydrin (**1**) in the presence of BF_3 to give the boron derivative **2** and triethyloxonium tetrafluoroborate (**3**) [3] (*Scheme 1*).

Scheme 1. *Synthesis of Triethyl Tetrafluoroborate*

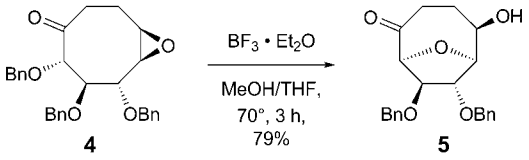


1 **2** **3**

Kolaczinski et al. [4] studied the conversion of 1,2-epoxyoctane in the presence of $BF_3 \cdot Et_2O$ and reported the formation of 1-ethoxyoctan-2-ol and 2-ethoxyoctan-1-ol. They proposed a mechanism based on a carbocation, which then cleaves the ether. The mechanism of the formation of 1-ethoxyoctan-2-ol was then studied by *Coxon* and *Lim* [5] in detail using deuterated epoxide. They showed that the reaction, when performed in Et_2O, occurs by inversion at C(1) by S_N2 attack. They reported no formation of 2-ethoxyoctan-1-ol.

In a recent example, reported by *Jürs* and *Thiem* [6], the O-atom of the BnO group in **4** behaves as a nucleophile to give cyclic ether **5** *via* an intramolecular ring opening in the presence of BF_3 as *Lewis* acid catalyst (*Scheme 2*).

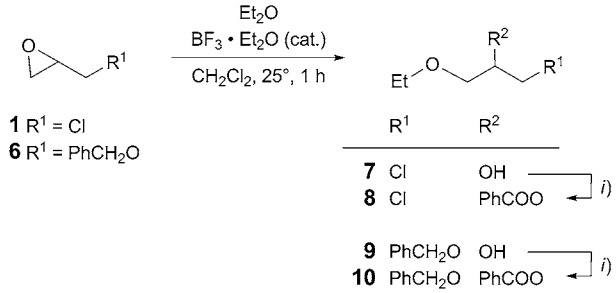
Scheme 2. *Intramolecular Ring Opening of Epoxide* **4**



However, there are a few examples for the reaction of ethers with terminal epoxides in the presence of $BF_3 \cdot Et_2O$. Although studies of *Coxon* and *Lim* [5] provided excellent information on the mechanistical aspects of the reaction, there are no reports on the behavior of different ethers. Interested in the mechanistic aspects of an intermolecular reaction of an epoxide with an ether, we decided to study this reaction using different epoxides and ethers in order to gain more insight into the reaction.

Results and Discussion. – All our experiments were performed in dry CH_2Cl_2 under N_2 atmosphere. The epoxides in CH_2Cl_2, and the ethers (1 – 1.5 mol-equiv.) and then the catalyst ($BF_3 \cdot Et_2O$; 0.1 mol-equiv.) were added to the mixture. After completion of the reactions, the formed alcohols were converted to their benzoates (or 4-nitrobenzoates) for further characterization (*Scheme 3*).

Scheme 3. *Ring Opening of Epoxides* **1** *and* **6** *with* Et_2O

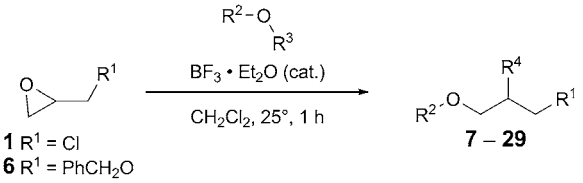


i) PhCOCl, DMAP (cat.), CH_2Cl_2, 24 h.

Terminal epoxides **1** and **6** underwent ring opening with different ethers in moderate yields. The products and yields *via* the corresponding ester derivatives are compiled in the *Table*. Based on the products listed in the *Table*, we propose a reaction mechanism as depicted in *Scheme 4*.

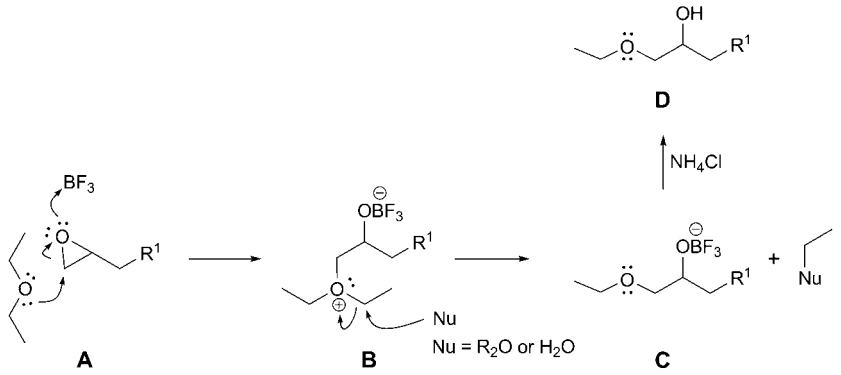
Recently, *Cresswell et al.* [7] have studied ring opening of benzylic epoxides with $BF_3 \cdot Et_2O$. They detected an attack of F^- on the benzylic C-atom by an S_N1 type ring opening. Since we did not obtain any fluoride derived from epoxide **1** and **6** in our experiments, we concluded that BF_3 behaves only as a *Lewis* acid, and the reaction proceeds *via* an S_N2 attack by the epoxide **A**. Thus, the reaction most probably starts with an S_N2 attack by the O-atom of the ether on the terminal position of the epoxide to give a trialkyl oxonium ion **B**. It is known that trialkyloxonium ions are strong alkylating reagents. Therefore, in the case of unsymmetrical trialkyl oxonium species

Table. *The Ring-Opening Reactions of Terminal Epoxides with Ethers in the Presence of $BF_3 \cdot Et_2O$*



Entry	Epoxide	R^2	R^3	Alcohol product (R^4; Yield)	Ester product (R^4; Yield)
1	**1**	Et	Et	**7** (R^4 = OH; 15%)	**8** (R^4 = PhCOO; 55%)
2	**6**	Et	Et	**9** (R^4 = OH; 25%)	**10** (R^4 = PhCOO; 69%)
3	**1**	Et	Allyl	**7** (R^4 = OH; 20%)	**8** (R^4 = PhCOO; 30%)
4	**6**	Et	Allyl	**9** (R^4 = OH; 51%)	**10** (R^4 = PhCOO; 47%)
5	**1**	Me	^{t}Bu	**14** (R^4 = OH; 35%)	**15** (R^4 = 4-O_2N–C_6H_4–COO; 40%)
6	**6**	Me	^{t}Bu	**16** (R^4 = OH; 46%)	**17** (R^4 = 4-O_2N–C_6H_4–COO; 66%)
7	**1**	Allyl	Ph	**18** (R^4 = OH; 33%)	**19** (R^4 = 4-O_2N–C_6H_4–COO; 28%)
8	**6**	Allyl	Ph	**20** (R^4 = OH; 21%)	**21** (R^4 = 4-O_2N–C_6H_4–COO; 32%)
9	**1**	Bu	Bu	**22** (R^4 = OH; 14%)	**23** (R^4 = 4-O_2N–C_6H_4–COO; 35%)
10	**6**	Bu	Bu	**24** (R^4 = OH; 55%)	**25** (R^4 = 4-O_2N–C_6H_4–COO; 40%)
11	**1**	$PhCH_2CH_2$	Me	**26** (R^4 = OH; 18%)	**27** (R^4 = 4-O_2N–C_6H_4–COO; 27%)
12	**6**	$PhCH_2CH_2$	Me	**28** (R^4 = OH; 10%)	**29** (R^4 = 4-O_2N–C_6H_4–COO; 30%)

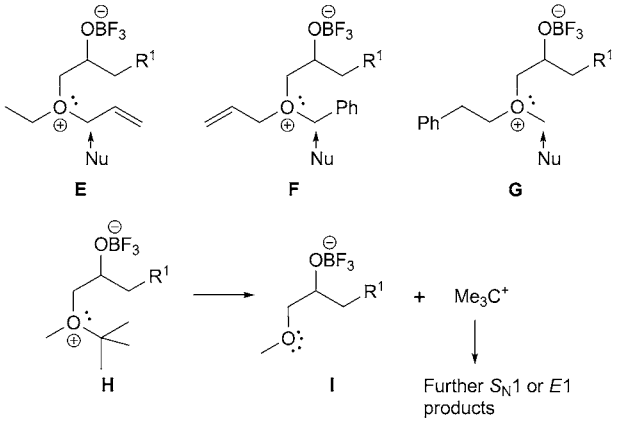
Scheme 4. *General Mechanism for Ring Opening of Epoxide*



(*Scheme 5*), the S_N2 attack of nucleophiles take place on the allylic *i.e.*, **E**, benzylic *i.e.*, **F**, or Me *i.e.*, **G** position to give the corresponding alcohols. Only ^{t}BuOMe behaves in contrast to this rule: **H** instead of undergoing an S_N2 reaction looses the ^{t}Bu group as a cation (*Scheme 5*).

We also wondered about the behavior of two secondary epoxides. For this purpose, we investigated the reaction of epoxides derived from cyclohexene and 1,4-dibromo-but-2-ene in Et_2O and in the presence of BF_3. Our study revealed that these epoxides did not undergo a ring-opening reaction. Therefore, it seems that in the presence of

Scheme 5. *Nucleophilic Attack at Trialkyloxonium Intermediates*



BF_3, a nucleophilic attack by the O-atom of ethers at epoxide is only possible in the case of terminal epoxides.

We also recognized that, when the reaction is performed using anisol as ether, no change was observed. This result can be attributed to the weaker nucleophilic character of the O-atom of anisol.

In conclusion, for the first time, we conducted the reaction of terminal epoxides **1** and **6** with a series of symmetrical or unsymmetrical ethers in the presence of BF_3. The results indicate that the reaction proceeds *via* two substitution reactions: *i*) nucleophilic attack of the O-atom of ethers at epoxides take place in the terminal position to give alkoxonium ions, *ii*) the cleavage of the formed alkoxonium ions takes place by a nucleophilic attack to give β-alkoxy alcohols. This study further presents examples for the nucleophilic behavior of ethers. These findings are also valuable for a comparison of the electrophilic character of alkyl groups on alkoxonium ions against nucleophilic attacks.

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Experimental Part

General. Column chromatography (CC): Silica gel *60* (SiO_2; 70–230 mesh). Benzyl glycidyl ether, epichlorohydrin, Et_2O, allyl ethyl ether, ^{t}BuOMe, allyl benzyl ether, and Bu_2O are commercially available compounds. Methyl 2-phenylethyl ether was synthesized as described in [8]. Solvents were purified and dried by standard procedures before use. IR Spectra (KBr): *Mattson-1000 FT-IR* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Varian* spectrometers. MS: *Varian-320*. Elemental analyses: *Leco CHNS-932* instrument.

Representative Procedure for Ring Opening of Epoxides with Ethers. To the soln. of epoxide **1** (1.45 mmol) in CH_2Cl_2 (3 ml) was added $BF_3 \cdot Et_2O$ (0.145 mmol; 10% mol-equiv.) at r.t. The mixture was stirred for 1–1.5 h. Sat. NH_4Cl soln. (7 ml) was added. The org. phase was extracted with CH_2Cl_2 (3×20 ml), and then dried (Na_2SO_4). Removal of the solvent gave crude alcohol **7**. Without further purification, the crude alcohol was submitted to esterification, whereby the soln. of **7** (79 mg, 0.37 mmol) was dissolved in CH_2Cl_2 (3 ml), followed by addition of *N*,*N*-dimethylpyridin-4-amine (3 mg, 5%) under

N_2. The soln. was cooled to 0°, and Et_3N (75 mg, 0.74 mmol) and PhCOCl (78 mg, 0.55 mmol) were added. The mixture was then stirred for 24 h. H_2O (7 ml) was added, and the org. phase was extracted with CH_2Cl_2 (3×10 ml). The combined CH_2Cl_2 solns. were dried (Na_2SO_4). Evaporation of the solvent and chromatography of the crude products on a SiO_2 *Chromatotron* eluting with AcOEt/hexane 3 : 7 gave pure benzoates **8**.

1-Chloro-3-ethoxypropan-2-yl Benzoate (**8**). Colorless oil. IR: 2976, 2873, 1723, 1602, 1451, 1316, 1271. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.07 (*dd*, $J = 8.8$, 1.6, H–C(2′), H–C(6′)); 7.57 (*tt*, $J = 7.6$, 1.2, H–(C(4′))); 7.45 (*t*, $J = 7.6$, H–C(3′), H–C(5′)); 5.38 (*quint.*, $J = 5.2$, H–C(2)); 3.88, 3.82 (*ABX*, $J_{AB} = 11.6$, $J_{AX} = 4.8$, $J_{BX} = 5.2$, CH_2(1)); 3.76, 3.73 (*ABX*, $J_{AB} = 10.4$, $J_{AX} = 5.2$, $J_{BX} = 5.2$, CH_2(3)); 3.61 – 3.53 (*m*, MeCH_2); 1.20 (*t*, $J = 7.0$, *Me*CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 165.9 (CO); 133.4 (C(4′)); 130.0 (C(2′), C(6′)); 129.8 (C(1′)); 128.6 (C(3′), C(5′)); 72.4; 68.8; 67.3; 43.3 (C(1)); 15.3 (*Me*CH_2). Anal. calc. for $C_{12}H_{15}ClO_3$ (242.70): C 59.39, H 6.23; found: C 59.09, H 5.92.

1-(Benzyloxy)-3-ethoxypropan-2-yl Benzoate (**10**). Colorless oil. IR: 3064, 3032, 2974, 2867, 1720, 1602, 1585, 1494, 1452, 1365. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.08 (*dd*, $J = 8.4$, 1.5, H–C(2″), H–C(6″)); 7.57 (*tt*, $J = 7.6$, 1.2, H–C(4″)); 7.44 (*t*, $J = 8.0$, H–C(3″), H–C(5″)); 7.33 – 7.26 (*m*, 5 arom. H); 5.42 (*quint.*, $J = 5.2$, H–C(2)); 4.62, 4.57 (*AB*, $J_{AB} = 12.2$, PhCH_2); 3.78 (*d*, $J = 5.2$, CH_2(1) or CH_2(3)); 3.74 (*d*, $J = 5.2$, CH_2(1) or CH_2(3)); 3.61 – 3.49 (*m*, MeCH_2); 1.18 (*t*, $J = 7.0$, *Me*CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 166.3 (CO); 138.3 (C(1′)); 133.2 (C(4″)); 130.5 (C(1″)); 130.0 (C(2″), C(6″)); 128.6 (C(3′), C(5′)); 128.5 (C(3″), C(5″)); 127.84 (C(4′)); 127.79 (C(2′), C(6′)); 73.5; 72.6; 69.3; 69.1; 67.1 (MeCH_2); 15.3 (*Me*CH_2). CI-MS: 317 (10), 315 (25), 166 (99). Anal. calc. for $C_{19}H_{22}O_4$ (314.38): C 72.59, H 7.05; found: C 70.65, H 6.99.

1-Chloro-3-methoxypropan-2-yl 4-Nitrobenzoate (**15**). Yellow oil. IR: 3115, 2920, 2843, 1729, 1607, 1529, 1409. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.30, 8.24 (*AA′BB′*, $J_{AB} = J_{A'B'} = 9.2$, H–C(3′), H–C(5′), H–C(2′), H–C(6′)); 5.42 (*quint.*, $J = 5.1$, H–C(2)); 3.87, 3.82 (*ABX*, $J_{AB} = 11.6$, $J_{AX} = 4.8$, $J_{BX} = 5.6$, CH_2(1)); 3.75, 3.71 (*ABX*, $J_{AB} = 10.4$, $J_{AX} = 5.2$; $J_{BX} = 4.8$, CH_2(3)); 3.42 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.2 (CO); 150.9 (C(4′)); 135.3 (C(1′)); 131.2 (C(3′), C(5′)); 123.8 (C(2′), C(6′)); 73.3 (C(2)); 71.0 (C(3)); 59.7 (Me); 42.9 (C(1)).

1-(Benzyloxy)-3-methoxypropane-2-yl 4-Nitrobenzoate (**17**). Yellow oil. IR: 3111, 3058, 3031, 2924, 1951, 1813, 1725, 1607, 1527, 1496. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.27, 8.21 (*AA′BB′*, $J_{AB} = J_{A'B'} = 9.0$, H–C(3″), H–C(5″), H–C(2″), H–C(6″)); 7.34 – 7.26 (*m*, 5 arom. H); 5.44 (*quint.*, $J = 5.2$, H–C(2)); 4.59, 4.55 (*AB*, $J_{AB} = 12.2$, PhCH_2); 3.77 (*d*, $J = 5.2$, CH_2(3)); 3.72, 3.69 (*ABX*, $J_{AB} = 11.0$, $J_{AX} = 5.6$, $J_{BX} = 4.6$ CH_2(1)); 3.38 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.4 (CO); 150.8 (C(4″)); 138.0 (C(1′)); 135.8 (C(1″)); 131.1 (C(3″), C(5″)); 128.6 (C(3′), C(5′)); 128.0 (C(4′)); 127.8 (C(2′), C(6′)); 123.7 (C(2″), C(6″)); 73.6; 73.4; 71.5; 68.8; 59.5 (Me). CI-MS: 346 (22), 345 (100). Anal. calc. for $C_{18}H_{19}NO_6$ (345.35): C 62.60, H 5.55, N 4.06; found: C 64.23, H 5.90, N 3.61.

1-Chloro-3-(prop-2-en-1-yloxy)propan-2-yl 4-Nitrobenzoate (**19**). Yellow oil. IR: 2918, 2863, 1729, 1608, 1528, 1348, 1271. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.29, 8.23 (*AA′BB′*, $J_{AB} = J_{A'B'} = 9.2$, H–C(3′), H–C(5′), H–C(2′), H–C(6′)); 5.88 (*ddt*, $J = 17.2$, 10.4, 5.6, H–C(2″)); 5.42 (*quint.*, $J = 5.2$, H–C(2)); 5.28 (*dq*, $J = 17.6$, 1.6, $H_{(E)}$–C(3″)); 5.20 (*dq*, $J = 10.4$, 1.6, $H_{(Z)}$–C(3″)); 4.06 – 4.03 (*m*, CH_2(1″)); 3.89, 3.84 (*ABX*, $J_{AB} = 12.0$, $J_{AX} = 4.8$, $J_{BX} = 5.6$, CH_2(3)); 3.77 (*d*, $J = 4.8$, CH_2(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.1 (CO); 150.9 (C(4′)); 135.3 (C(1′)); 134.2 C(2″); 131.2 (C(3′), C(5′)); 123.8 (C(2′), C(6′)); 117.9 (C(3″)); 73.4; 72.7; 68.2; 43.0 (C(1)). CI-MS: 301 (13), 299 (40), 167 (10), 166 (99).

1-(Benzyloxy)-3-(prop-2-en-1-yloxy)propan-2-yl 4-Nitrobenzoate (**21**). Yellow oil. IR: 2919, 2851, 1726, 1605, 1527, 1454, 1349, 1273. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.28, 8.21 (*AA′BB′*, $J_{AB} = J_{A'B'} = 8.8$, H–C(3″), H–C(5″), H–C(2″), H–C(6″)); 7.32 – 7.25 (*m*, 5 arom. H); 5.86 (*ddt*, $J = 16.6$, 10.4, 5.6, H–C(2‴)); 5.46 (*quint.*, $J = 5.2$, H–C(2)); 5.26 (*dq*, $J = 16.6$, 1.6, $H_{(E)}$–C(3‴)); 5.17 (*dq*, $J = 10.4$, 1.2, $H_{(Z)}$–C(3‴)); 4.59, 4.55 (*AB*, $J_{AB} = 12.0$, PhCH_2); 4.03 – 4.01 (*m*, CH_2(1‴)); 3.78 (*d*, $J = 5.2$, CH_2(3)); 3.75 (*d*, $J = 5.2$, CH_2(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.4 (CO); 150.8 (C(4″)); 138.0 (C(1′)); 135.9 (C(1″)); 134.5 C(2‴); 131.1 (C(3″), C(5″)); 128.6 (C(3′), C(5′)); 128.0 (C(4′)); 127.8 (C(2′), C(6′)); 123.7 (C(2″), C(6″)); 117.5 C(3‴); 73.5 (2 C); 72.5, 68.8 (2 C). CI-MS: 372 (21), 371 (100). Anal. calc. for $C_{20}H_{21}NO_6$ (371.38): C 64.68, H 5.70, N 3.77; found: C 65.54, H 6.07, N 3.83.

1-Butoxy-3-chloropropan-2-yl 4-Nitrobenzoate (**23**). Yellow oil. IR: 2959, 2933, 2872, 1730, 1608, 1529, 1348. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.29, 8.22 (*AA′BB′*, $J_{AB} = J_{A'B'} = 9.5$, H–C(3′), H–C(5′), H–C(2′), H–C(6′)); 5.40 (*quint.*, $J = 5.2$, H–C(2)); 3.88, 3.82 (*ABX*, $J_{AB} = 11.8$, $J_{AX} = 4.8$, $J_{BX} = 5.6$,

$CH_2(1)$); 3.76, 3.72 (*ABX*, $J_{AB}=10.6$, $J_{AX}=4.8$, $J_{BX}=5.6$, $CH_2(3)$); 3.54–3.45 (*m*, $MeCH_2CH_2CH_2$); 1.58–1.51 (*m*, $MeCH_2CH_2CH_2$); 1.34 (*sext.*, $J=7.4$, $MeCH_2CH_2CH_2$); 0.89 (*t*, $J=7.4$, Me). ^{13}C-NMR (100 MHz, $CDCl_3$); 164.1 (CO); 150.9 (C(4′)); 135.3 (C(1′)); 131.1 (C(3′), C(5′)); 123.8 (C(2′), C(6′)); 73.4; 71.8; 68.9; 43.1 (C(1)); 31.8 (C(2″)); 19.4 (C(3″)); 14.0 (C(4′)). CI-MS: 317 (60), 316 (28), 315 (98), 167 (35), 166 (83), 165 (99). Anal. calc. for $C_{14}H_{18}ClNO_5$ (315.75): C 53.25, H 5.75, N 4.44 found: C 52.69, H 5.76, N 4.47.

1-(Benzyloxy)-3-butoxypropan-2-yl 4-Nitrobenzoate (**25**). Yellow oil. IR: 3112, 3031, 2958, 2931, 2869, 1727, 1608, 1529, 1454. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.28, 8.22 (*AA′BB′*, $J_{AB}=J_{A'B'}=8.8$, H–C(3″), H–C(5′)′, H–C(2″), H–C(6″)); 7.31 (*m*, 5 arom. H); 5.45 (*quint.*, $J=5.2$, H–C(2)); 4.59, 4.55 (*AB*, $J_{AB}=12.2$, $PhCH_2$); 3.77 (*d*, $J=5.2$, $CH_2(1)$ or $CH_2(3)$); 3.72 (*d*, $J=5.2$, $CH_2(1)$ or $CH_2(3)$); 3.50, 3.44 (*ABX*, $J_{AB}=9.4$, $J_{AX}=6.4$, $J_{BX}=6.8$, $MeCH_2CH_2CH_2$); 1.56 (*m*, $MeCH_2CH_2CH_2$); 1.32 (*sext.*, $J=7.6$, $MeCH_2CH_2CH_2$); 0.88 (*t*, $J=7.4$, Me). ^{13}C-NMR (100 MHz, $CDCl_3$); 164.5 (CO); 150.8 (C(4″)); 138.1 (C(1′)); 135.9 (C(1″)); 131.1 (C(3″), C(5″)); 128.6 C(3′), C(5′)); 128.0 (C(4′)); 127.8 (C(2′), C(6′)); 123.7 (C(2″), C(6″)); 73.6; 73.5; 71.6; 69.4; 68.9; 31.8; 19.4; 14.0. CI-MS: 388 (23), 387 (100). Anal. calc. for $C_{21}H_{25}NO_6$ (387.43): C 65.10, H 6.50, N 3.62; found: C 65.05, H 6.64, N 3.57.

1-Chloro-3-(2-phenylethoxy)propan-2-yl 4-Nitrobenzoate (**27**). Yellow oil. IR: 2918, 2860, 1728, 1606, 1528, 1347, 1318, 1268. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.29, 8.19 (*AA′BB′*, $J_{AB}=J_{A'B'}=9.0$, H–C(3′), H–C(5′), H–C(2′), H–C(6′)); 7.27–7.17 (*m*, 5 arom. H); 5.39 (*quint.*, $J=5.2$, H–C(2)); 3.85–3.69 (*m*, $CH_2(3)$, $CH_2(1)$, $PhCH_2CH_2$); 2.89 (*t*, $J=6.8$, $PhOCH_2CH_2$). ^{13}C-NMR (100 MHz, $CDCl_3$); 164.1 (CO); 150.9 (C(4′)); 138.9 (C(1″)); 135.3 (C(1′)); 131.2 (C(3′), C(5′)); 129.1 (C(4″)); 128.6 (C(3″), C(5″)); 126.5 (C(2″), C(6″)); 123.8 (C(2′), C(6′)); 73.3; 72.7; 69.0; 43.0 (C(1)); 36.4 ($PhCH_2$). CI-MS: 365 (11), 363 (33), 166 (99). Anal. calc. for $C_{18}H_{18}ClNO_5$ (363.80): C 59.43, H 4.99, N 3.85 found: C 60.65, H 5.74, N 3.69.

1-(Benzyloxy)-3-(2-phenylethoxy)propan-2-yl 4-Nitrobenzoate (**29**). Yellow oil. IR: 2917, 2853, 1723, 1604,1525, 1493, 1449, 1347, 1316, 1270. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.28, 8.17 (*AA′BB′*, $J_{AB}=J_{A'B'}=9.2$, H–C(3″), H–C(5″), H–C(2″), H–C(6″)); 7.35–7.15 (*m*, 10 arom. H); 5.43 (*quint.*, $J=5.2$, H–C(2)); 4.56, 4.51 (*AB*, $J_{AB}=12.0$, $PhCH_2O$); 3.78–3.64 (*m*, $CH_2(1)$, $CH_2(3)$, $PhCH_2CH_2O$); 2.85 (*t*, $J=6.8$, $PhCH_2CH_2O$). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.4 (CO); 150.8 (C(4′)); 139.8 (C(1‴)); 138.0 (C(1′)); 135.9 (C(1″)); 131.1 (C(3″), C(5″)); 129.1 (C(2‴), C(6‴)); 128.6 (C(3′), C(5′)); 128.5 (C(3‴), C(5‴)); 128.0 (C(4′)); 127.8 (C(2′), C(6′)); 126.4 (C(4‴)); 123.7 (C(2″), C(6″)); 73.5; 73.4; 72.6; 69.5; 68.7; 36.4. CI-MS: 436 (25), 435 (100). Anal. calc. for $C_{25}H_{25}NO_6$ (435.47): C 68.95, H 5.79, N 3.22; found: C 68.85, H 5.95, N 3.25.

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