Lactonization of ω-Hydroxycarboxylic Acids Using (4,5-Dichloro-6-oxo-6*H*-pyridazin-1-yl)phosphoric Acid Diethyl Ester

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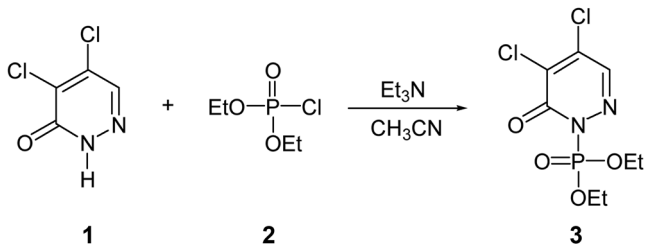
(4,5-Dichloro-6-oxo-6*H*-pyridazin-1-yl)phosphoric acid diethyl ester (**3**) is an efficient coupling agent for lactonization of aliphatic and aromatic ω-hydroxycarboxylic acids. Lactonization of ω-hydroxycarboxylic acids with **3** in the presence of equimolar amounts of a base gave the corresponding monoolides, diolides, triolides and/or tetraolides.

Key Words : Lactonization, ω-Hydroxycarboxylic acid, (6-Oxo-6*H*-pyridazin-1-yl)phosphoric acid diethyl ester, Lactone

Introduction

Lactonization is an important process in the synthesis of the natural product.[1] Accordingly, preparation of lactones from ω-hydroxycarboxylic acids is also major concern in synthetic organic chemistry. Although several useful methods have therefore been reported,[2-16] the research in this field still active even now.[17]

In connection with the research on the synthetic application of 2-substituted pyridazin-3(2*H*)-ones,[18] we found that 2-benzenesulfonyl-4,5-dichloropyridazin-3(2*H*)-ones serve as a coupling reagent.[19] However, this coupling regent requires two equivalents of carboxylic acids for the esterification and the amidation of carboxylic acids.[19] We therefore developed (4,5-disubstituted-6-oxo-6*H*-pyridazin-1-yl)phosphoric acid diethyl esters as novel and efficient coupling agent.[20] Herein we report a lactonization of ω-hydroxycarboxylic acids using (4,5-dichloro-6-oxo-6*H*-pyridazin-1-yl)phosphoric acid diethyl ester (**3**) as a coupling agent.



1 **2** **3**

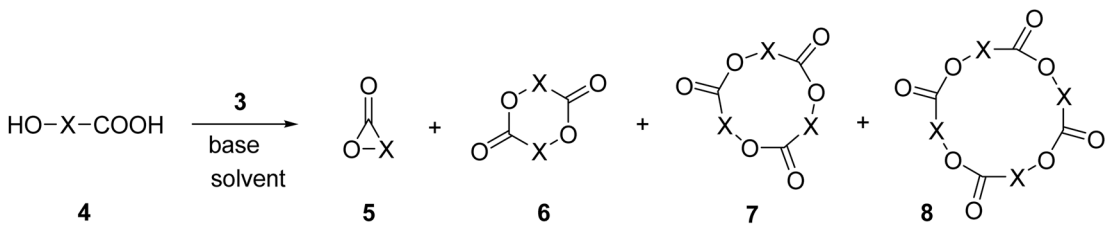
Scheme 1. Preparation of **3**.

Results and Discussion

(4,5-Dichloro-6-oxo-6*H*-pyridazin-1-yl)phosphoric acid diethyl ester (**3**) was easily prepared in 96% yields *via* the reaction of 4,5-dichloropyridazin-3(2*H*)-ones (**1**) with diethyl chlorophosphate (**2**) in the presence of triethylamine in acetonitrile at room temperature.[20]

Initially, direct lactonization of 2-hydroxyphenylacetic acid (**4a**) using **3** was studied in a variety of representative organic solvents and bases (Table 1). From the preliminary experiments, we selected potassium carbonate/ethyl acetate and *N,N*-dimethylaminopyridine/tetrahydrofuran system for the lactonization of ω-hydroxycarboxylic acids using **3**.

Results of the lactonization using various ω-hydroxycarboxylic acids listed in Table 2. The corresponding monoolides, diolides, triolides and/or tetraolides were obtained in moderate to high yields under the reaction conditions mentioned above. Lactonization of 2-hydroxybenzoic acid (**4b**) using **3** in the presence of DMAP in tetrahydrofuran at room temperature gave the corresponding triolide **7b** as the main (Table 2 entry 1). Whereas, treatment of 2-hydroxybenzoic acid (**4b**) using **3** in the presence of potassium carbonate in

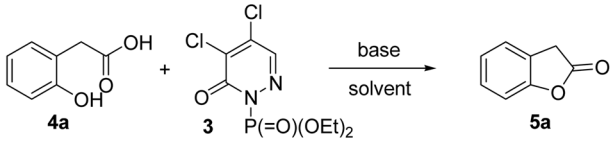


4 **5** **6** **7** **8**

X = Alkyl, ethenyl, aryl

Scheme 2. Lactonization of ω-hydroxycarboxylic acid using **3**.

Table 1. Lactonization of 2-hydroxyphenylacetic acid using **3** at room temperature



Entry	Base[a]	Solvent	Time	**5a** (%)[b]
1	Et_3N	THF	1.5 h	91
2	Et_3N	Toluene	1 h	92
3	Et_3N	Acetone	4 h	92
4	Et_3N	CH_3CN	7 h	82
5	Et_3N	CH_2Cl_2	31 h	89
6	Et_3N	$(Et)_2O$	40 min	93
7	Et_3N	EtOAc	3.5 h	93
8	Et_3N	H_2O	–	–
9	K_2CO_3	$(Et)_2O$	40 min	80
10	Cs_2CO_2	$(Et)_2O$	10 min	68
11	NaH	$(Et)_2O$	7 h	65
12	Na_2CO_3	$(Et)_2O$	3 h	91
13	DMAP	$(Et)_2O$	10 min	90
14	KO^{t}Bu	$(Et)_2O$	40 h	63
15	K_2CO_3	THF	4.5 h	95
16	DMAP	THF	20 min	96
17	K_2CO_3	Toluene	12 h	73
18	DMAP	Toluene	1 h	91
19	K_2CO_3	EtOAc	6.5 h	97
20	DMAP	EtOAc	20 min	88

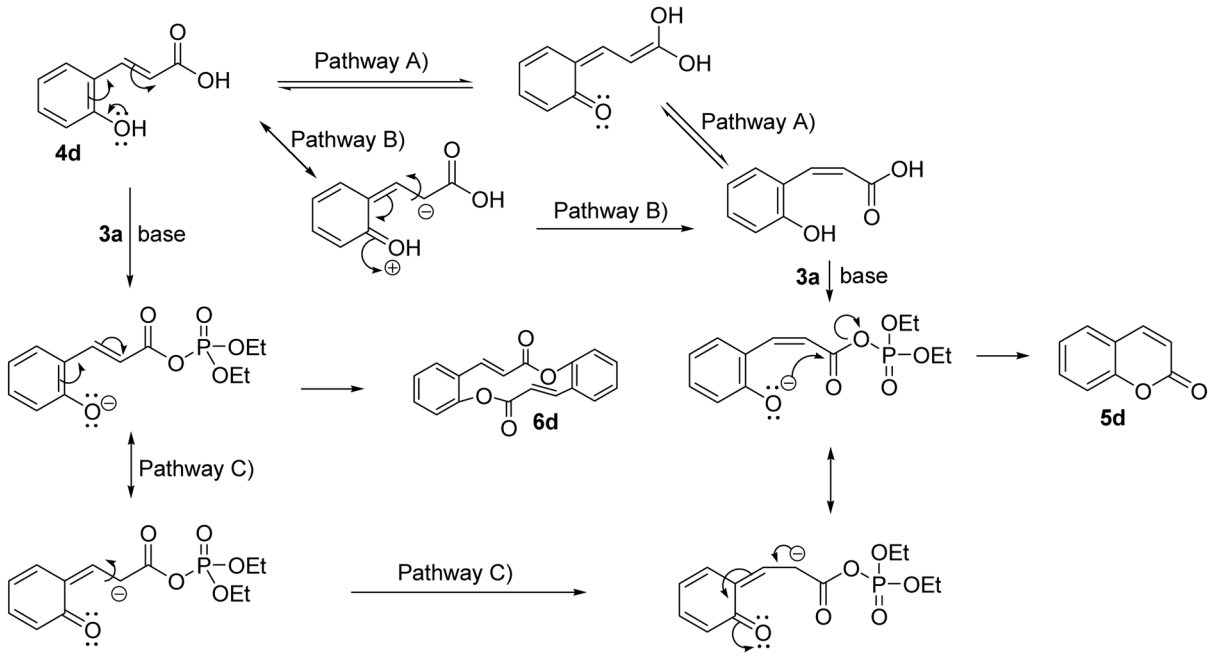
[a]DMAP = *N,N*-Dimethylaminopyridine. [b]Isolated yields.

ethyl acetate or tetrahydrofuran at room temperature gave trisalicylide (**7b**) and **8b** as main instead of the corresponding monoolide (Table 2 entries 2 and 3).

Lactonization of 3-(2-hydroxyphenyl)propanoic acid (**4c**) using **3** under three reaction conditions mentioned above afforded the corresponding lactone chroman-2-one (**5c**) in good and excellent yields (Table 2 entries 4-6). On the other hand, *trans*-3-(2-hydroxyphenyl)acrylic acid (**4d**) was reacted with **3** under three reaction conditions to give coumarin **5d** in 11-36% yields and the corresponding diolide **6d** in 44-59% yields, respectively (Table 2 entries 7-9). The synthesis of **5d** from **4d** was also reported.[21] Lactonization of 12-hydroxydodecanoic acid (**4e**) using **3** under *N,N*-dimethylaminopyridine/THF and potassium carbonate/EtOAc system gave the corresponding lactone **5e** (2-11%) and diolide **6e** (55%), respectively. However, the reaction of **4e** did not occur when potassium carbonate/THF system was used. Lactonization of 10-hydroxdecanoic acid (**4f**) using **3** in the presence of potassium carbonate in refluxing ethyl acetate gave the corresponding diolide **6f** in 81% yield (Table 2 entry 14), whereas the reaction of **4e** did not occur when potassium carbonate/THF system was used. Although reaction of **4f** with **3** under *N,N*-dimethylaminopyridine/THF system gave **6f**, the reaction did not occur completely. On the other hand, we could not detect the characteristic effect of the amounts of **3**, solvents and/or bases on the selectivity of the products under our conditions.

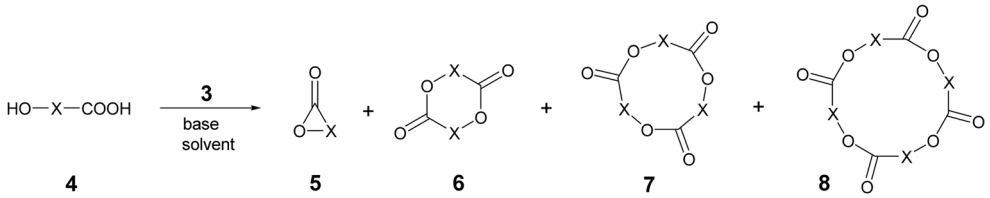
In order to cyclize *trans*-3-(2-hydroxyphenyl)acrylic acid (**4d**), *trans*-isomer must change to the corresponding *cis*-isomer. The lactonization of *trans*-3-(2-hydroxyphenyl)-acrylic acid (**4d**) to **5d** using compound **3** may proceed *via* the Pathway A, B and C. Among three pathways, the Pathway B and the Pathway C may be more favorable under the basic condition. On the other hand, the diolide **6d** may be yield by the cyclization between two *trans*-phenoxide intermediates.

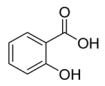
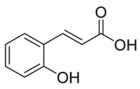
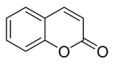
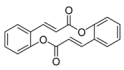
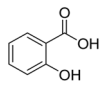
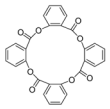
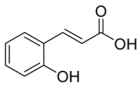
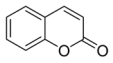
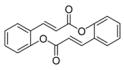
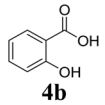
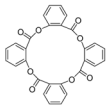
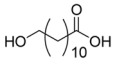
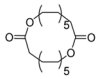
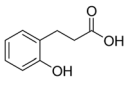
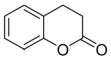
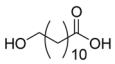
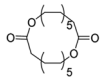
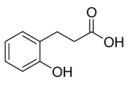
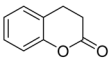
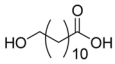
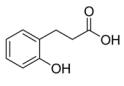
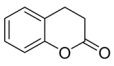
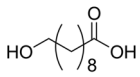
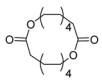
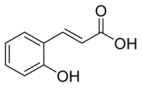
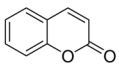
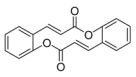
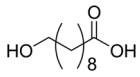
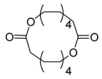
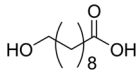
The structures of all synthesized compounds were esta-



Scheme 3

Table 2. Lactonization of ω-hydroxycarboxylic acid



Entry	ω-HO-XCOOH **4**	Conditions[a]	Product (%)[b]		Entry	ω-HO-XCOOH **4**	Conditions[a]	Product (%)[b]	
1	 **4b**	DMAP, THF, rt, 2 h	 **7b** (42)[c]	—	8	 **4d**	K_2CO_3, EtOAc, rt, 4 h	 **5d** (11)	 **6d** (44)
2	 **4b**	K_2CO_3, EtOAc, rt, 1 h	 **7b** (20)	 **8b** (39)	9	 **4d**	K_2CO_3, THF, rt, 12 h	 **5d** (36)	 **6d** (59)
3	 **4b**	K_2CO_3, THF, rt, 2 h	 **7b** (35)	 **8b** (50)	10	 **4e**	rf, 12 h	 **5e** (11)	 **6e** (55)
4	 **4c**	DMAP, THF, rt, 20min	 **5c** (99)	—	11	 **4e**	K_2CO_3, EtOAc, rf, 2 h	 **5e** (2)	 **6e** (55)
5	 **4c**	K_2CO_3, EtOAc, rt, 7 h	 **5c** (88)	—	12	 **4e**	K_2CO_3, THF, rf, 24 h	—	—
6	 **4c**	K_2CO_3, THF, rt, 15 min	 **5c** (100)	—	13	 **4f**	DMAP, THF, rf, 11 h	—	 **6f** (22)[c]
7	 **4d**	DMAP, THF, rt, 19 h	 **5d** (15)	 **6d** (57)	14	 **4f**	K_2CO_3, EtOAc, rf, 2 h	—	 **6f** (81)
					15	 **4f**	K_2CO_3, THF, rf, 24 h	—	—

[a]DMAP = *N,N*-Dimethylaminopyridine. rt = Room temperature. rf = Reflux. [b]Isolated yields. [c]We also detected two unknown products on TLC.

blished by ir, nmr, elemental analysis and/or mass spectrometry. In all the reactions described above, reusable 4,5-dichloropyridazin-3(2*H*)-one (**1**) was isolated quantitatively.

Conclusions

In conclusion, compound **3** is an efficient coupling agent for lactonization of aliphatic and aromatic ω-hydroxycarboxylic acids. It is noted that a simple method for the synthesis of various lactones was established by using equimolar amounts of ω-hydroxycarboxylic acids and **3** in the presence of equimolar amounts of a base. Compound **1** can be recovered quantitatively for reuse.

Experimental Section

General. Melting points were determined with a capillary apparatus and uncorrected. NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in δ units (ppm) relative to an internal standard (TMS). IR spectra were obtained on a Hitachi 270-50 or Mattson Genesis Series FT-IR spectrophotometer. Elemental analyses were performed with CHNS-932 (Leco). Mass spectra were obtained on a GC Mate 2, JEOL. The open-bed chromatography was carried out on silica gel (70-230 mesh, Merck) using gravity flow. The column was packed with slurries made from the elution solvent.

Typical procedure for lactonization. A solution of ω-

hydroxycarboxylic acids (3.0 mmol), compound **3** (1.36 g, 4.5 mmol) and a base (3.3 mmol) in solvent (30 mL) was stirred until ω-hydroxycarboxylic acids were disappeared at room temperature (or at reflux temperature). After filtering, the solvent was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (3.5 × 15 cm). The column was eluted with ethyl acetate/*n*-hexane (1:2, v/v). Fractions containing the product were combined and evaporated under reduced pressure to give the corresponding lactone, diolide, triolide and/or tetraolide, respectively.

Compound 5a: Liquid. R_f = 0.74 (EtOAc:*n*-hexane = 1:1, v/v). IR (KBr): 3070, 2950, 1810, 1620, 1600, 1480, 1460, 1400, 1330, 1300, 1230, 1120, 1060, 900, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.28 (d, 2H, J = 7.6 Hz), 7.05-7.14 (m, 2H), 3.70 ppm (s, 2H). ^{13}C NMR ($CDCl_3$): δ 174, 154.7, 132.9, 128.8, 124.7, 124.1, 123.1, 111.0 ppm. Elemental analysis calcd for $C_8H_6O_2$: C, 72.96; H, 5.44. Found: C, 73.05; H, 5.49. MS (EI): Exact mass calcd for $C_8H_6O_2$ 134.0368, Found: *m/z* 134 ($M^{+\cdot}$).

Compound 7b: mp 195-197 °C. R_f = 0.44 (CH_2Cl_2). IR (KBr) 3100, 2950, 1740, 1620, 1500, 1460, 1300, 1260, 1230, 1135, 1090, 1040, 760, 700, 540 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.97 (d, 3H, J = 7.6 Hz), 7.66 (t, 3H, J = 7.7 Hz), 7.52 (d, 3H, J = 7.6 Hz), 7.41 ppm (t, 3H, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$): δ 164.7, 148.6, 133.3, 126.2, 123.9, 123.8 ppm. Elemental analysis calcd for $C_{21}H_{12}O_6$: C, 70.00; H, 3.36. Found: C, 70.05; H, 3.39. MS (EI): Exact mass calcd for $C_{21}H_{12}O_6$ 360.0634, Found: *m/z* 360 ($M^{+\cdot}$).

Compound 8b: mp 240 °C decomposition. R_f = 0.22 (CH_2Cl_2). IR (KBr) 2923, 1723, 1602, 1486, 1450, 1286, 1286, 1248, 1218, 1202, 1115, 1073, 1031, 744, 687, 667 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.30 (d, 4H, J = 7.8 Hz), 7.64-7.59 (m, 4H, J = 7.5 Hz), 7.39 (t, 4H, J = 5.7 Hz), 7.20 ppm (d, 4H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ 163.1, 151.0, 134.8, 132.8, 126.5, 124.3, 122.3 ppm. Elemental analysis calcd for $C_{28}H_{16}O_8$: C, 70.00; H, 3.36. Found: C, 70.07; H, 3.40. MS (EI): Exact mass calcd for $C_{28}H_{16}O_8$ 480.0845, Found: *m/z* 480 ($M^{+\cdot}$).

Compound 5c: Liquid. R_f = 0.69 (EtOAc:*n*-hexane = 1:1, v/v). IR (KBr) 3100, 300, 2950, 2900, 1790, 1630, 1600, 1500, 1470, 1440, 1370, 1400, 1260, 1240, 1160, 1120, 1040, 1000, 920, 780 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.18-7.26 (m, 2H), 7.09 (d, 1H, J = 4.7 Hz), 7.01 (d, 1H, J = 8.1 Hz), 2.78 (t, 2H, J = 7.8 Hz), 2.72-2.77 ppm (m, 2H). ^{13}C NMR ($CDCl_3$): δ 168.6, 152.0, 128.2, 128.1, 124.4, 122.7, 116.8, 29.2, 23.6 ppm. Elemental analysis calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.01; H, 5.49. MS (EI): Exact mass calcd for $C_9H_8O_2$ 148.0524, Found: *m/z* 148 ($M^{+\cdot}$).

Compound 5d: mp 67-69 °C. R_f = 0.78 (EtOAc:CH_2Cl_2 = 1:4, v/v). IR (KBr) 3070, 2950, 1760, 1650, 1620, 1600, 1510, 1460, 1360, 1340, 1280, 1240, 1210, 1160, 1130, 1000 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.71 (d, 1H, J = 9.5 Hz), 7.48-7.57 (m, 2H), 7.26-7.35 (m, 2H), 6.43 ppm (d, 1H, J = 9.5 Hz). ^{13}C NMR ($CDCl_3$): δ 160.8, 154.1, 143.4, 131.8, 127.9, 124.4, 118.9, 116.9, 116.7 ppm. Elemental analysis calcd for $C_9H_6O_2$: C, 73.97; H, 4.14. Found: C, 74.05; H, 4.19. MS (EI): Exact mass calcd for $C_9H_6O_2$ 146.0368, Found: *m/z* 146 ($M^{+\cdot}$).

Compound 6d: mp 218-220 °C. R_f = 0.71 (EtOAc:CH_2Cl_2 = 1:4, v/v).

IR (KBr) 3070, 2940, 2860, 1730, 1710, 1620, 1600, 1560, 1460, 1400, 1260, 1180, 110, 930, 830 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.90 (d, 2H, J = 16.1 Hz), 7.41-7.52 (m, 6H), 7.30 (t, 2H, J = 7.4 Hz), 6.85 ppm (d, 2H, J = 16.1 Hz). ^{13}C NMR ($CDCl_3$): δ 164.2, 149.1, 143.1, 131.4, 130.9, 126.8, 126.1, 123.2, 121.5 ppm. Elemental analysis calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.14. Found: C, 74.06; H, 4.20. MS (EI): Exact mass calcd for $C_{18}H_{12}O_4$ 292.0736, Found: *m/z* 292 ($M^{+\cdot}$).

Compound 5e: Liquid (lit.[22] mp 2-3 °C). R_f = 0.62 (CH_2Cl_2). IR (KBr) 2950, 2880, 1740, 1270, 1240, 1220, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.16 (t, 2H, J = 5.16 Hz), 2.34-2.38 (m, 2H), 1.62-1.70 (m, 4H), 1.35-1.45 ppm (m, 14H). ^{13}C NMR ($CDCl_3$): δ 34.7, 29.7, 27.4, 22.7, 26.6, 26.4, 25.4, 25.3, 24.9, 24.5, 24.2 ppm. Elemental analysis calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. MS (EI): Exact mass calcd for $C_{12}H_{22}O_2$ 198.1620, Found: *m/z* 198 ($M^{+\cdot}$).

Compound 6e: mp 97-99 °C. R_f = 0.79 (EtOAc:*n*-hexane = 1:2, v/v). IR (KBr) 2950, 2880, 1740, 1270, 1240, 1220, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.10 (t, 4H, J = 5.9 Hz), 2.31 (t, 4H, J = 7.0 Hz), 1.57-1.66 (m, 8H), 1.28-1.41 ppm (m, 28H). ^{13}C NMR ($CDCl_3$): δ 173.9, 64.1, 53.4, 34.7, 29.5, 29.4, 28.9, 28.6, 26.1, 25.3 ppm. Elemental analysis calcd for $C_{24}H_{44}O_4$: C, 72.68; H, 11.18. Found; C, 72.71; H, 11.21. MS (EI): Exact mass calcd for $C_{24}H_{44}O_4$ 396.3240, Found: *m/z* 396 ($M^{+\cdot}$).

Compound 6f: mp 88-90 °C. R_f = 0.85 (EtOAc:*n*-hexane = 1:1, v/v). IR (KBr) 2923, 2853, 1734, 1274, 1237, 1186, 1109 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.05-4.13 (m, 4H), 2.28-2.34 (m, 4H), 1.61 (t, 8H, J = 7.0 Hz), 1.28 ppm (d, 20H, J = 12.2 Hz). ^{13}C NMR ($CDCl_3$): δ 64.0, 34.9, 29.4, 29.1, 29.0, 28.6, 26.1, 25.4 ppm. Elemental analysis calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.58; H, 10.70. MS (EI): Exact mass calcd for $C_{20}H_{36}O_4$ 340.2614, Found *m/z* 340 ($M^{+\cdot}$).

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