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Efficient and practical approach to esters from acids/ 2-oxoacids/ 2-oxoaldehydes &/ 2-oxoesters

Anil K. Padala [a,b], Varma Saikam [a,b], Asif Ali [c], Qazi Naveed Ahmed [a,b,*]

[a] Medicinal Chemistry Division, Indian Institute of Integrative Medicine (IIIM), Jammu, Jammu and Kashmir 180001, India
[b] Academy of Scientific and Innovative Research (AcSIR), 2-Rafi Marg, New Delhi, India
[c] Natural Product Division, Indian Institute of Integrative Medicine (IIIM), Jammu, Jammu and Kashmir 180001, India

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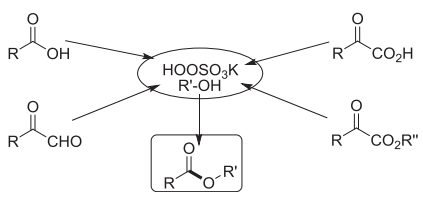
ABSTRACT

An efficient, mild, cost effective and practical method is presented for generation of esters (RCO_2R') from acids (RCO_2H)/ 2-oxoacids ($RCOCO_2H$)/ 2-oxoaldehydes (RCOCHO)/ 2-oxoesters ($RCOCO_2R''$) and alcohols by using oxone as catalyst. In addition to deciphering the scope of our process, we propose a mechanism for esterification through a common intermediate IV. Reaction with 2-oxoacids and 2-oxoaldehydes proceed with initial CO–C cleavage followed by oxone mediated esterification with alcohols. In addition, reaction with 2-oxoesters proceeds through CO–CO bond cleavage and *trans*-esterification.

1. Introduction

Esters are prevalent subunits in various natural products, pharmaceuticals, agrochemicals, and polymers. Besides, they also serve as important building blocks for organic synthesis and have been used as artificial fragrances/flavoring agents. Consequently, plethora of synthetic methods for construction of this important unit has been established.[1] However, in recent times the strategies adopted in the synthesis of molecules and materials have undergone considerable changes. Current strategies lay stress on the use of reagents that are mild, efficient, nontoxic, selective & cost effective and lack production of nonpolluting byproducts. In this direction, we developed an esterification method employing oxone as catalyst.

Oxone, a potassium triple salt containing potassium peroxymonosulfate, is a stable, white crystalline compound, non toxic, water soluble, easy to handle, and above all is economic. Oxone has been used efficiently in numerous transformations. In most of the reactions, anion peroxymonosulfate (HSO_5^-) has been subjected as an active oxidant within the mixture.[2] Even though oxidative potential of oxone has been demonstrated in diverse directions, no studies have been reported till date for its use as esterification catalyst employing acids/ 2-oxoacids/ 2-oxoadlehydes/ 2-oxoesters as reactants. In the course of our continued investigation of the aldehydes, acids, 2-oxoaldehydes, 2-oxoacids and 2-oxoesters,[3] we came across the unique ability of oxone to catalyze the reaction between acids/2-oxoacids/2-oxoaldehydes/2-oxoesters with alcohols. Herein, we present our preliminary results of this reaction, which proved to be tolerant to a wide range of functionalities and avoid the use of co-oxidants/additives. The earlier reports on this transformation utilized aldehydes as substrate of choice.[4] Our method employing acids as substrates belong to conventional esterification reaction, however, with 2-oxoaldehydes and 2-oxoacids, it is a decarbonylative &/decarboxylative esterification reaction, respectively. Surprisingly, the reaction of oxone with 2-oxoesters corresponds to *trans*-esterification reaction (see Scheme 1).



Scheme 1. Summary of this work.

* Corresponding author. E-mail address: naqazi@iiim.ac.in (Q.N. Ahmed).

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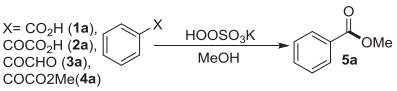
0040-4020/

2. Results and discussion

Our evaluation of the proposed esterifications reactions began with exposure of benzoicacid **1a** with different concentrations of oxone in methanol (Table 1, entry 1–8). To our best, we could isolate require product **5a** with 98% yield in 30 h when **1a** (1 mmol) was treated with 30 mol % of oxone (0.3 mmol) in 2 mL of methanol at 65 °C (entry 7). On the contrary, reaction of 2-oxoacid **2a** generated desired ester **5a** in low yields (20%) when stirred with 30 mol % of oxone in 2 mL of methanol for 36 h at 65 °C (entry 9). In order to improvise the yields of reaction, different test reactions were conducted at varying concentrations of oxone (entry 9–13). To our delight, we isolated **5a** in maximum yield (97%) when **2a** (1 mmol) was treated with 2.5 mmol of oxone in 2 mL of methanol for 30 h at 65 °C (entry 13). The same conditions when tested with phenylglyoxal **3a** and 2-oxoesters **4a** generated the desired product in maximum yields (entry 17 & 20, respectively).

Table 1
Optimization of reaction conditions[a]



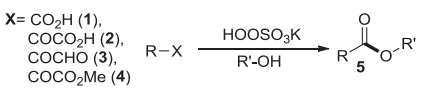
Entry	1a/2a/3a/4a	Oxone (mmol)	Temp (°C)	Time (h)	Yields (%)[f]
					5a
1	**1a**	1.5	rt	24	15
2	**1a**	1.5	65	24	98
3	″	1	″	″	98
4	″	0.5	″	″	96
5	″	0.3	″	″	90
6	″	0.2	″	″	75
7[b]	″	**0.3**	**65**	**30**	**98**
8	″	0.3	60	″	84
9	**2a**	″	65	36	20
10	″	1	″	″	48
11	″	1.5	″	″	69
12	″	2	″	36	89
13[c]	″	**2.5**	″	**30**	**97**
14	**3a**	1	″	36	50
15	″	1.5	″	″	72
16	″	2	″	″	90
17[d]	″	**2.5**	″	**30**	**99**
18	**4a**	1.5	″	″	60
19	″	2	″	″	84
20[e]	″	**2.5**	″	″	**96**

Reaction conditions: [a] 1a (1 mmol), oxone (0.3 mmol) and methanol (2 mL), 65 °C, 30 h; [b,c,d,e] 2a/3a/4a (1 mmol), oxone (2.5 mmol), and methanol (2 mL), 65 °C, 30 h; [f] Isolated yields.
Bold signifies the best suited conditions for different reactions mentioned in this Table.

Next, we investigated the scope of the esterification reaction against different substrates (Table 2). Primarily, it was observed that the reactions of benzoic acid/2-oxo-2-phenylacetic acid/2-oxo-2-phenylacetaldehyde and/methyl-2-oxo-2-phenylacetate with different alcohols under optimized conditions generated desired ester **5** in excellent yields despite the nature of carbon chain length (entries 1–6). In addition, we tested esterification reaction against different substrates with electronic/structural variation in methanol (entry 8–20). In general, we observed our protocol works well in all substrates tested. As an advantage, we observed that a wide range of functional groups were tolerant to our method. Furthermore, we investigated few more substrates against different alcohols (entry 21–30). Interestingly, we observed that our method has wide substrate scope. To highlight the importance of our reaction, alcohols like allyl alcohol, 2-methylprop-2-en-1-ol, benzyl alcohol and (*S*)-(+)-1,2- isopropylideneglycerol were being used against both aromatic and/aliphatic substrates successfully (entry 24, 25, 26, 28). In all the cases, we observed that time consumed for completion of the reaction with aliphatic acids is very less as compared to aromatic. A highlight in our studies toward the esterification of various substrates was the generation of same esters (RCO_2R') in excellent yields under mild conditions from corresponding acid (RCO_2H), 2-oxoacid ($RCOCO_2H$), 2-oxoaldehyde (RCOCHO) and/or 2-oxoester ($RCOCO_2R'$). In case of acids, it was observed to be a simple oxone mediated esterification reaction. However, in case of 2-oxoacid and 2-oxoaldehyde, it was possible through decarboxylative and decarbonylative esterification reaction, respectively. Surprisingly, the reactions with 2-oxoesters can be a good example of *trans*-esterification reaction involving CO—CO bond cleavage as well.

As proof of concept, we conducted few control experiments (Scheme 2). Along with, we also observed our reaction intermediates in each case. In experiment 1, 2 & 3, on reaction of **2r**, **3r** & **4r** with oxone under optimized concentrations, we isolated solely benzoic acid **1r**. This clearly indicates that oxone has potential to cleave CO—C bond in 2-oxoacids, 2-oxoaldehydes and/2-oxoesters through a common intermediate (**IV**). This intermediate is labile enough to get hydrolyzed by moisture in DMF. Along with, our reactions with **2**, **3** and **4** under optimized conditions generated different intermediates. However, in each case, we observed a minute quantity of acid throughout till completion of the reaction. This clearly indicates the presence of common intermediate (**IV**) in each case. Furthermore, in case of reaction with 2-oxo-2-(*m*-tolyl) acetaldehyde, we isolated an intermediate 2,2-dimethoxy-1-(*m*-tolyl)ethan-1-one (**IIr**). This intermediate on treatment with optimized concentration of oxone generated desired product in

Table 2
Substrate scope of esterification reactions[a]



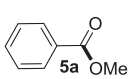
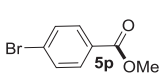
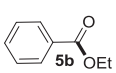
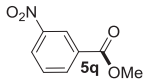
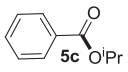
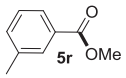
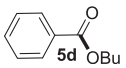
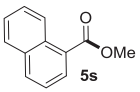
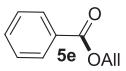
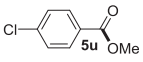
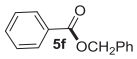
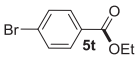
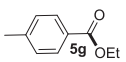
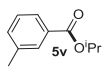
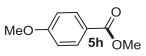
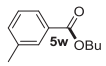
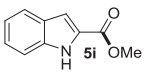
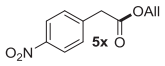
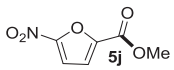
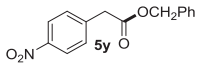
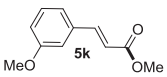
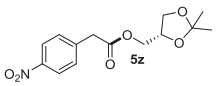
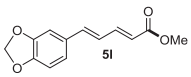
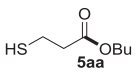
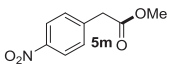
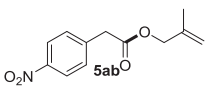
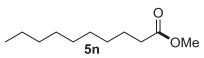
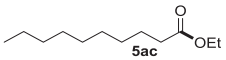
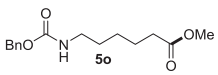
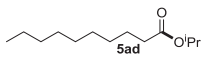
Entry	Product	(Yields %[b], time h)	Entry	Product	(Yields %[b], time h)
1		X=CO_2H–(98%, 30 h) $COCO_2H$–(97%, 30 h) COCHO–(99%, 30 h) $COCO_2Me$-(96%, 30 h)	16		X=CO_2H–(97%, 30 h) $COCO_2H$–(97%, 30 h) COCHO–(98%, 30 h) $COCO_2Me$–(94%, 30 h)
2		X=CO_2H-(97%, 30 h) $COCO_2H$–(96%, 30 h) COCHO–(98%, 30 h) $COCO_2Me$-(95%, 30 h)	17		X=CO_2H–(98%, 30 h) $COCO_2H$–(98%, 30 h) COCHO–(99%, 30 h) $COCO_2Me$–(95%, 30 h)

Table 2 (*continued*)

Entry	Product	(Yields %[b], time h)	Entry	Product	(Yields %[b], time h)
3		X=CO_2H-(74%, 40 h) $COCO_2H$–(72%, 40 h) COCHO-(75%, 40 h) $COCO_2Me$–(72%, 30 h)	18		X=CO_2H–(96%, 30 h) $COCO_2H$–(95%, 30 h) COCHO–(98%, 30 h)
4		X=CO_2H–(95%, 30 h) $COCO_2H$–(94%, 30 h) COCHO–(96%, 30 h) $COCO_2Me$–(95%, 30 h)	19		X=CO_2H–(92%, 30 h) $COCO_2H$–(90%, 30 h) COCHO–(94%, 30 h)
5		X=CO_2H–(82%, 40 h) $COCO_2H$–(80%, 40 h) COCHO–(84%, 40 h)	20		X=CO_2H–(97%, 40 h) $COCO_2H$–(95%, 40 h) COCHO–(99%, 40 h)
6		X=CO_2H–(81%, 40 h) $COCO_2H$–(80%, 40 h) COCHO–(85%, 40 h)	21		X=CO_2H–(95%, 30 h) $COCO_2H$–(96%, 30 h) COCHO–(98%, 30 h)
7		X=CO_2H–(96%, 30 h) $COCO_2H$–(95%, 30 h) COCHO–(99%, 30 h)	22		X=CO_2H–(75%, 40 h) $COCO_2H$-(74%, 40 h) COCHO–(76%, 40 h)
8		X=CO_2H–(96%, 30 h) $COCO_2H$-(95%, 30 h) COCHO–(97%, 30 h)	23		X=CO_2H–(94%, 30 h) $COCO_2H$–(94%, 30 h) COCHO–(96%, 30 h)
9		(90%, 36 h)	24		(96%, 4 h)
10		(95%, 12 h)	25		(97%, 4 h)
11		(92%, 15 h)	26		(75%, 24 h)
12		(94%, 15 h)	27		(98%, 4 h)
13		(98%, 4 h)	28		(80%, 4 h)
14		(98%, 4 h)	29		(98%, 4 h)
15		(96%, 4 h)	30		(80%, 4 h)

[a] Reaction condition: **1** (o.5 mmol), oxone (0.15 mmol), and alcohol (1.0 mL) at 65 °C, **2**/**3**/**4** (0.5 mmol), oxone (1.25 mmol), and alcohol (1.0 mL) at 65 °C.
[b] Isolated yields.

comparable yields (experiment 4). This perhaps indicated the esterification mechanism through this intermediate. Similarly, in case of 2-(4-bromophenyl)-2-oxoacetic acid reaction, we isolated methyl 2-(4-bromophenyl)-2-oxoacetate as intermediate. This intermediate, when treated under optimized conditions generated desired product in excellent yields and in fact was the idea behind the discovery of *trans*-esterification of 2-oxoesters. In addition, deuterium labeled experiments (5 and 6) confirm that the reaction

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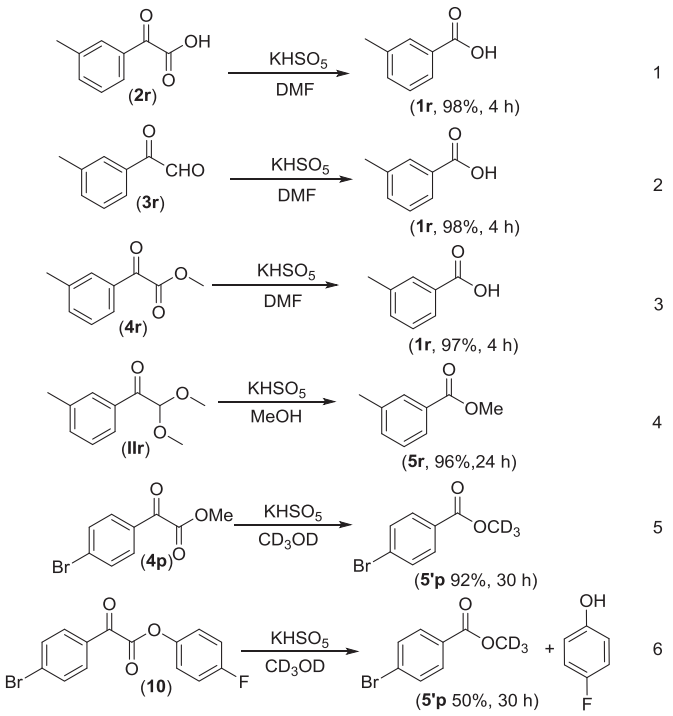
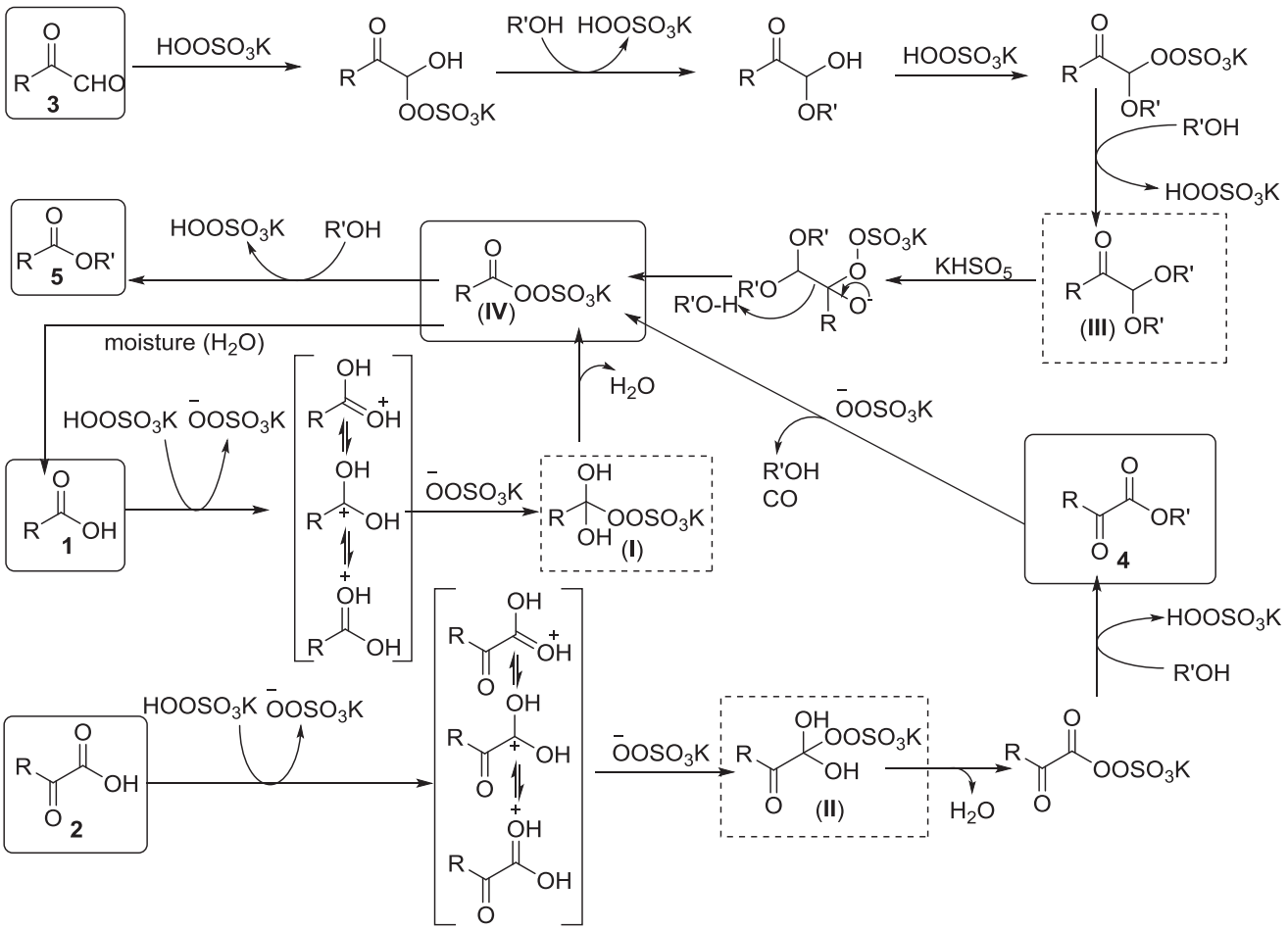


Scheme 2. Controlled experiments.

of 2-oxoester to ester occurs through CO–CO bond cleavage to respective ester and alcohol.

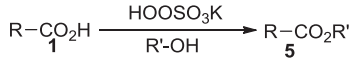
Based on previous literature reports[5] and the above mentioned results, a reaction mechanism in each case was proposed and outlined in Scheme 3. In case of acid, the oxone proton binds to carbonyl oxygen and generates resonance stabilized cationic transition state. The anion of potassium peroxymonosulfate ($^{-}OOSO_3K$) later attacks the carbocation based transition state to produce intermediate **I** that later undergoes dehydration reaction to **IV**. This intermediate predominantly undergoes esterification with alcohol to desired product **5**. However, small portion of **IV** can undergo hydrolysis with moisture to acid that ultimately can generate **5** through discussed pathway. The reaction of 2-oxoacids also follows similar path and generates 2- oxoesters **4** through intermediate **II**. The 2-oxoesters so generated are quite unstable in oxone environment and undergoes CO–CO cleavage to intermediate **IV** and respective alcohol. Intermediate **IV** later generates ester **5** through above discussed pathway. However, the reaction of 2-oxoaldehyde based mechanism is a little bit different. As depicted, the proposed intermediate in the oxidation of 2-oxoaldehydes is 2-oxoperoxyacetal **III**.[6] This intermediate through **IV** generates desired product **5**. Overall, we propose a pathway for each class through a common intermediate **IV**.

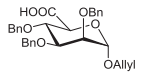
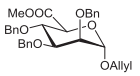
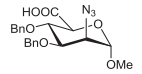
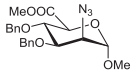
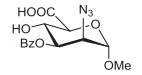
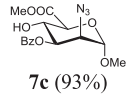
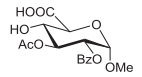
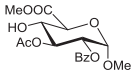
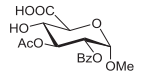
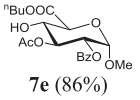
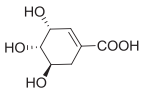
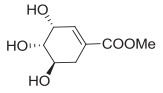
Since in our reactions alcohols are being used as solvents & nucleophilic reagent, we extended the application of our method on sugars and natural products. In each case, we isolated the desired product in excellent yields (Table 3). Imperative feature of our reaction was the capability of alcohols to functionalize acid



Scheme 3. Reaction mechanism.

Table 3
Substrate scope on sugars and natural product[a]



Entry	Substrate	Alcohol	Ester (yield)[b]
1	 **6a**	MeOH	 **7a** (94%)
2	 **6b**	MeOH	 **7b** (92%)
3	 **6c**	MeOH	 **7c** (93%)
4	 **6d**	MeOH	 **7d** (91%)
5	 **6e**	^{n}BuOH	 **7e** (86%)
6	 **8**	MeOH	 **9** (92%)

[a] Reaction condition: substrate (0.5 mmol), oxone (0.15 mmol), and alcohol (2 mL) at 60 °C.
[b] Isolated yields.

substrates with free hydroxyl groups. Our reactions avoided the possibility of self coupling products in each case (entry 3, 4, 5 & 6).

3. Conclusion

In summary, a common, mild, economical and metal-free method for the esterification of acids (RCO_2H)/ 2-oxoacids ($RCOCO_2H$)/ 2-oxoaldehydes (RCOCHO)/ 2-oxoesters ($RCOCO_2R''$) with alcohols has been developed. A broad range of esters (RCO_2R') were obtained in up to 99% yield. Our reaction revealed a good functional group tolerance and proceeded well with hydroxyl substituted substrates as well.

4. Experimental

4.1. General

All chemicals were obtained from Sigma–Aldrich Company and used as received. ^{1}H, and ^{13}C NMR spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines. All reactions were carried under aerobic condition.

4.2. General procedure for preparation of esters (RCO_2R') 5 from acids (RCO_2H) 1

A mixture of acid **1** (0.5 mmol), oxone (0.15 mmol) and alcohol (1.5 mL) in round bottomed flask was stirred at 65 °C. After completion of the reaction that was confirmed by thin layer chromatography the crude mixture was cooled to room temperature, filtered and purified by column chromatography using silica gel (100–200 #) with ethyl acetate and hexane as an eluent to afford the desired product **5** in 70–99 % yields.

4.3. General procedure for preparation of esters (RCO_2R') 5 from 2-oxoacids ($RCOCO_2H$) 3/2-oxoaldehydes (RCOCHO) 3 &/2-oxoesters ($RCOCO_2R''$) 4

A mixture of 2-oxoacids 2/2-oxoaldehydes 3/2-oxoesters 4 (0.5 mmol), oxone (1.25 mmol) and alcohol (1.5 mL) in round bottomed flask was stirred at 65 °C. After completion of the reaction that was confirmed by thin layer chromatography, the crude mixture was cooled to room temperature, filtered and purified by column chromatography using silica gel (100–200 #) with ethyl acetate and hexane as an eluent to afford the desired product 5 in 70–99 % yields.

4.4. Characterization data

*4.4.1. Methyl benzoate (**5a**).*[7a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08–8.00 (m, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.42 (t, J=7.7 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.09, 132.89, 130.18, 129.57, 128.35, 52.05.

*4.4.2. Ethyl benzoate (**5b**).*[7b] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08–8.01 (m, 2H), 7.53 (t, J=7.4 Hz, 1H), 7.41 (t, J=7.6 Hz, 2H), 4.37 (q, J=7.1 Hz, 2H), 1.38 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 132.76, 130.54, 129.52, 128.28, 60.90, 14.30.

*4.4.3. Isopropyl benzoate (**5c**).*[7m] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (dd, J=8.3, 1.3 Hz, 2H), 7.44 (ddd, J=7.0, 2.6, 1.3 Hz, 1H), 7.38–7.31 (m, 2H), 5.23–5.12 (m, 1H), 1.28 (d, J=6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.11, 132.71, 130.91, 129.51, 128.27, 68.33, 21.95.

*4.4.4. Butyl benzoate (**5d**).*[7n] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12–7.96 (m, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.42 (t, J=7.6 Hz, 2H), 4.32 (t, J=6.6 Hz, 2H), 1.75 (dt, J=14.5, 6.7 Hz, 2H), 1.48 (dq, J=14.7, 7.4 Hz, 2H), 0.98 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 166.72, 132.81, 130.53, 129.54, 128.33, 64.85, 30.79, 19.30, 13.79.

*4.4.5. Allyl benzoate (**5e**).*[5b] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01–7.96 (m, 2H), 7.50–7.45 (m, 1H), 7.35 (dd, J=10.8, 4.8 Hz, 2H), 6.02–5.89 (m, 1H), 5.33 (ddd, J=17.2, 3.0, 1.5 Hz, 1H), 5.23–5.19 (m, 1H), 4.74 (dt, J=5.6, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 166.30, 133.03, 132.24, 130.15, 129.66, 128.40, 118.25, 65.57.

*4.4.6. Benzyl benzoate (**5f**).*[5b] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.1 (dd, J=8.3, 1.3 Hz, 2H), 7.51–7.46 (m, 1H), 7.39–7.28 (m, 7H), 5.30 (s, 2H).

*4.4.7. Ethyl 4-methylbenzoate (**5g**).*[5b] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J=8.1 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H), 4.36 (q, J=7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 168.13, 144.81, 130.99, 130.44, 129.27, 62.15, 23.03.

*4.4.8. Methyl 4-methoxybenzoate (**5h**).*[5b] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J=8.8 Hz, 2H), 6.89 (d, J=8.8 Hz, 2H), 3.86 (s, 3H), 3.82 (s,

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3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 166.80, 163.32, 131.55, 122.56, 113.57, 55.33, 51.78.

*4.4.9. Methyl 1H-indole-2-carboxylate (**5i**).*[7e] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.20 (s, 1H), 7.69 (d, *J*=8.0 Hz, 1H), 7.42 (d, *J*=8.3 Hz, 1H), 7.32 (t, *J*=7.3 Hz, 1H), 7.25–7.21 (m, 1H), 7.15 (t, *J*=7.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 161.68, 135.97, 126.42, 126.05, 124.40, 121.62, 119.79, 110.96, 107.81, 51.07.

*4.4.10. Methyl 5-nitrofuran-2-carboxylate (**5j**).*[7o] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, *J*=3.8 Hz, 1H), 7.31 (d, *J*=3.8 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 157.42, 144.74, 118.95, 111.61, 52.98.

*4.4.11. Methyl (E)-3-(3-methoxyphenyl)acrylate (**5k**).*[7h] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (d, *J*=16.0 Hz, 1H), 7.26 (t, *J*=7.9 Hz, 1H), 7.08 (d, *J*=7.6 Hz, 1H), 7.01 (s, 1H), 6.91 (dd, *J*=8.2, 1.8 Hz, 1H), 6.41 (d, *J*=16.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.38, 159.87, 144.81, 135.69, 129.88, 120.74, 118.02, 116.10, 113.01, 55.20, 51.69.

*4.4.12. Methyl (2E,4E)-5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoate (**5l**).*[7p] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (dd, *J*=15.2, 10.8 Hz, 1H), 6.98 (d, *J*=1.1 Hz, 1H), 6.90 (d, *J*=8.0 Hz, 1H), 6.78 (dd, *J*=11.7, 6.7 Hz, 2H), 6.68 (dd, *J*=15.4, 10.8 Hz, 1H), 5.97 (s, 2H), 5.93 (d, *J*=15.3 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.59, 148.58, 148.29, 145.01, 140.30, 130.52, 124.46, 123.01, 119.91, 108.52, 105.85, 101.42, 51.53.

*4.4.13. Methyl 2-(4-nitrophenyl)acetate (**5m**).*[7l] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J*=8.6 Hz, 2H), 7.47 (d, *J*=8.6 Hz, 2H), 3.76 (s, 2H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.67, 147.10, 141.40, 130.36, 123.67, 52.36, 40.66.

*4.4.14. Methyl decanoate (**5n**).*[7g] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.66 (s, 3H), 2.30 (t, *J*=7.5 Hz, 2H), 1.61 (dd, *J*=14.4, 7.2 Hz, 2H), 1.28 (m, 12H), 0.88 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.27, 51.36, 34.06, 31.85, 29.40, 29.25, 29.13, 24.93, 22.64, 14.05.

*4.4.15. Methyl 6-(((benzyloxy)carbonyl)amino)hexanoate (**5o**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32–7.22 (m, 5H), 5.13 (s, 1H), 5.06 (s, 2H), 3.62 (s, 3H), 3.14 (dd, *J*=12.6, 6.3 Hz, 2H), 2.27 (t, *J*=7.3 Hz, 2H), 1.60 (dt, *J*=14.7, 7.3 Hz, 2H), 1.46 (dd, *J*=14.1, 7.0 Hz, 2H), 1.31 (dd, *J*=15.0, 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.13, 156.60, 136.71, 128.46, 128.36, 128.02, 127.28, 126.86, 66.46, 51.49, 40.78, 33.84, 29.54, 26.17, 24.49; HRMS (ESI) Calcd for $C_{15}H_{21}NaNO_4$: $[M+Na]^+$, 302.1363; Found: 302.1357.

*4.4.16. Methyl 4-bromobenzoate (**5p**).*[7c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, *J*=8.5 Hz, 2H), 7.57 (d, *J*=8.5 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 164.31, 129.68, 129.08, 127.00, 126.01, 50.26.

*4.4.17. Methyl 3-nitrobenzoate (**5q**).*[7f] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (s, 1H), 8.41 (ddd, *J*=18.7, 9.8, 4.4 Hz, 2H), 7.69 (t, *J*=8.0 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 164.86, 148.16, 135.23, 131.77, 129.68, 127.33, 124.45, 52.76.

*4.4.18. Methyl 3-methylbenzoate (**5r**).*[5b] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, *J*=5.1 Hz, 1H), 7.82 (s, 1H), 7.33 (dt, *J*=15.0, 7.5 Hz, 2H), 3.90 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.30, 138.14, 133.67, 130.13, 130.09, 128.26, 126.71, 52.04, 21.26.

*4.4.19. Methyl 2-naphthoate (**5s**).*[1h] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.99–8.93 (m, 1H), 8.20 (dd, *J*=7.3, 1.2 Hz, 1H), 8.01 (d, *J*=8.2 Hz, 1H), 7.88 (d, *J*=8.2 Hz, 1H), 7.63 (ddd, *J*=8.5, 6.8, 1.4 Hz, 1H), 7.56–7.52 (m, 1H), 7.49 (dd, *J*=8.1, 7.4 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 168.05, 133.88, 133.43, 131.39, 130.29, 128.59, 127.81, 127.08, 126.25, 125.87, 124.53, 52.17.

*4.4.20. Methyl 4-chlorobenzoate (**5t**).*[7c] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83 (d, *J*=8.3 Hz, 2H), 7.26 (d, *J*=8.3 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 166.13, 139.31, 130.94, 128.67, 128.55, 52.22.

*4.4.21. Ethyl 4-bromobenzoate (**5u**).*[7c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, *J*=8.5 Hz, 2H), 7.57 (d, *J*=8.5 Hz, 2H), 4.37 (q, *J*=7.1 Hz, 2H), 1.39 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.85, 131.64, 131.08, 129.39, 127.89, 61.23, 14.29.

*4.4.22. Isopropyl 3-methylbenzoate (**5v**).*[7d] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90–7.79 (m, 2H), 7.37–7.27 (m, 2H), 5.25 (hept, *J*=6.3 Hz, 1H), 2.39 (s, 3H), 1.36 (d, *J*=6.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.28, 138.00, 133.42, 130.88, 130.02, 128.15, 126.65, 68.21, 21.94, 21.24.

*4.4.23. Butyl 3-methylbenzoate (**5w**).*[7b] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (m, 2H), 7.33 (m, 2H), 4.31 (t, *J*=6.6 Hz, 2H), 2.40 (s, 3H), 1.75 (dt, *J*=14.5, 6.6 Hz, 2H), 1.53–1.44 (m, 2H), 0.98 (t, *J*=7.4 Hz, 3H).^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.83, 137.03, 132.49, 129.42, 129.01, 127.16, 125.62, 63.72, 29.76, 20.22, 18.23, 12.71.

*4.4.24. Allyl 2-(3-nitrophenyl)acetate (**5x**).*[7k] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J*=8.5 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H), 5.90 (dq, *J*=10.7, 5.8 Hz, 1H), 5.26 (dd, *J*=19.5, 13.8 Hz, 2H), 4.62 (d, *J*=5.7 Hz, 2H), 3.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.84, 147.18, 141.29, 131.64, 130.35, 123.72, 118.75, 65.91, 40.88.

*4.4.25. Benzyl 2-(4-nitrophenyl)acetate (**5y**).*[7k] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J*=8.6 Hz, 2H), 7.44 (d, *J*=8.4 Hz, 2H), 7.38–7.29 (m, 5H), 5.15 (s, 2H), 3.77 (s, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.04, 147.22, 141.23, 135.41, 130.37, 128.68, 128.54, 128.35, 123.76, 67.17, 40.96.

*4.4.26. (S)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 2-(3-nitrophenyl)acetate (**5z**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, *J*=8.6 Hz, 2H), 7.40 (d, *J*=8.6 Hz, 2H), 4.29–4.22 (m, 1H), 4.15 (dd, *J*=11.5, 4.3 Hz, 1H), 4.08 (dd, *J*=11.5, 6.0 Hz, 1H), 3.99 (dd, *J*=8.4, 6.6 Hz, 1H), 3.72 (s, 2H), 3.64 (dd, *J*=8.5, 6.1 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.05, 147.26, 140.97, 130.37, 123.81, 110.00, 73.41, 66.09, 65.55, 40.72, 26.67, 25.31; HRMS (ESI) Calcd for $C_{14}H_{17}NaNO_6$: $[M+Na]^+$, 318.0948; Found: 318.0953.

*4.4.27. Butyl 3-mercaptopropanoate (**5aa**).* ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.00 (dd, *J*=9.3, 4.0 Hz, 2H), 2.65 (m, 2H), 2.53 (t, *J*=6.8 Hz, 2H), 1.57–1.44 (m, 3H), 1.32–1.24 (m, 2H), 0.84–0.79 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.72, 64.60, 38.51, 30.61, 19.79, 19.12, 13.70; HRMS (ESI) Calcd for $C_7H_{14}O_2NaS$: $[M+Na]^+$, 185.0607; Found: 185.0602.

*4.4.28. 2-Methylallyl 2-(4-nitrophenyl)acetate (**5ab**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J*=8.7 Hz, 2H), 7.48 (d, *J*=8.7 Hz, 2H), 4.92 (s, 2H), 4.54 (s, 2H), 3.79 (s, 2H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.85, 147.13, 141.36, 139.44, 130.37, 123.70, 113.32, 68.47, 40.92, 19.42; HRMS (ESI) Calcd for $C_{12}H_{13}NaNO_4$: $[M+Na]^+$, 258.0737; Found: 258.0721.

*4.4.29. Ethyl decanoate (**5ac**).*[7i] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.10 (q, *J*=7.1 Hz, 2H), 2.26 (t, *J*=7.6 Hz, 2H), 1.64–1.56 (m, 2H), 1.30–1.21 (m, 15H), 0.86 (t, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 173.84, 60.08, 34.35, 31.84, 29.40, 29.25, 29.13, 24.97, 22.64, 14.21, 14.05.

*4.4.30. Isopropyl decanoate (**5ad**).*[7j] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.04–4.92 (m, 1H), 2.23 (t, *J*=7.5 Hz, 2H), 1.58 (dd, *J*=14.6, 7.3 Hz,

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2H), 1.29–1.22 (m, 12H), 1.21 (s, 3H), 1.19 (s, 3H), 0.86 (t, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 173.36, 67.23, 34.68, 31.84, 29.41, 29.25, 29.24, 29.10, 25.02, 22.64, 21.80, 14.05.

*4.4.31. 2,2-Dimethoxy-1-(m-tolyl)ethan-1-one (**IIr**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J*=6.8 Hz, 2H), 7.42–7.32 (m, 2H), 5.23 (s, 1H), 3.47 (s, 6H), 2.41 (s, 3H); HRMS (ESI) Calcd for $C_{11}H_{14}NaO_3$: $[M+Na]^+$, 217.0835; Found: 217.0833.

*4.4.32. Methyl 2-(4-bromophenyl)-2-oxoacetate (**4p**).*[7r] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.69–7.63 (m, 2H), 3.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.71, 163.39, 132.33, 131.52, 131.28, 130.67, 52.97; HRMS (ESI) Calcd for $C_9H_7NaBrO_3$: $[M+Na]^+$, 264.9471; Found: 264.9465.

*4.4.33. Methyl-d_3 2-(4-bromophenyl)-2-oxoacetate (**5'p**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J*=8.8, 2.0 Hz, 2H), 7.56 (dd, *J*=8.8, 2.0 Hz, 2H); MS (EI): *m*/*z*=219 $[M]^+$.

*4.4.34. 4-Fluorophenyl 2-(4-bromophenyl)-2-oxoacetate (**10**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J*=8.5 Hz, 1H), 7.66 (d, *J*=8.5 Hz, 1H), 7.21–7.06 (m, 2H).

*4.4.35. 3-Methylbenzoic acid (**1r**).*[7s] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.85 (br, 1H), 7.95–7.90 (m, 2H), 7.43–7.38 (m, 1H), 7.35 (dd, *J*=11.3, 4.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 172.89, 138.33, 134.66, 130.75, 129.30, 128.42, 127.43, 21.28.

*4.4.36. Methyl (1-O-allyl-2,3,4-tri-O-benzyl-D-glucopyranoside) urinate (**7a**).* Yield: 94%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.23 (m, 15H), 5.90–5.80 (m, 1H), 5.24 (dd, *J*=17.2, 1.4 Hz, 1H), 5.16 (dd, *J*=10.4, 1.4 Hz, 1H), 5.01 (d, *J*=3.0 Hz, 1H), 4.81–4.68 (m, 3H), 4.63 (d, *J*=11.1 Hz, 1H), 4.59 (s, 2H), 4.28–4.18 (m, 3H), 4.00 (dd, *J*=13.0, 6.1 Hz, 1H), 3.90 (dd, *J*=7.8, 3.0 Hz, 1H), 3.77 (t, *J*=3.1 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.94, 138.30, 138.27, 138.17, 133.58, 128.43, 128.05, 127.97, 127.80, 127.73, 127.71, 117.61, 97.83, 78.88, 76.06, 74.64, 74.60, 73.00, 72.48, 72.07, 68.67, 52.37; HRMS (ESI) Calcd for $C_{31}H_{33}NaO_7$: $[M+Na]^+$, 541.2197; Found: 541.2205.

*4.4.37. Methyl (1-O-methyl-2-azido-2-deoxy-3,4-di-O-benzyl-D-mannopyranoside) urinate (**7b**).* Yield: 92%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.24 (m, 10H), 4.90 (d, *J*=3.9 Hz, 1H), 4.74 (d, *J*=11.2 Hz, 1H), 4.70–4.63 (m, 3H), 4.29 (d, *J*=7.1 Hz, 1H), 4.13 (t, *J*=7.3 Hz, 1H), 3.98 (dd, *J*=7.4, 3.4 Hz, 1H), 3.84 (t, *J*=3.7 Hz, 1H), 3.66 (s, 3H), 3.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.48, 137.71, 137.41, 128.54, 128.49, 128.03, 128.00, 127.96, 127.86, 99.06, 78.18, 75.17, 74.28, 72.84, 71.84, 60.47, 55.89, 52.44; HRMS (ESI) Calcd for $C_{22}H_{25}NaN_3O_6$: $[M+Na]^+$, 450.1636; Found: 450.1641.

*4.4.38. Methyl (1-O-methyl-2-azido-2-deoxy-3-O-benzoyl-D-mannopyranoside) urinate (**7c**).* Yield: 93%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12–8.06 (m, 2H), 7.61–7.54 (m, 1H), 7.47–7.43 (m, 2H), 5.57 (dd, *J*=9.1, 3.7 Hz, 1H), 4.88 (d, *J*=2.3 Hz, 1H), 4.37 (t, *J*=8.9, 1H), 4.26 (d, *J*=8.9 Hz, 1H), 4.12 (dd, *J*=3.6, 2.5 Hz, 1H), 3.78 (s, 3H), 3.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.11, 164.89, 132.61, 129.00, 127.91, 127.51, 98.33, 71.56, 70.73, 65.88, 59.98, 54.80, 51.83; HRMS (ESI) Calcd for $C_{15}H_{17}NaN_3O_7$: $[M+Na]^+$, 374.0959; Found: 374.0935.

*4.4.39. Methyl (1-O-methyl-2-O-benzoyl-3-O-acetyl-D-glucopyranoside) urinate (**7d**).* Yield: 91%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, *J*=7.3 Hz, 2H), 7.58 (t, *J*=7.4 Hz, 1H), 7.45 (t, *J*=7.7 Hz, 2H), 5.62 (t, *J*=9.8 Hz, 1H), 5.18 (d, *J*=3.5 Hz, 1H), 5.02 (dd, *J*=10.2, 3.6 Hz, 1H), 4.29 (d, *J*=9.9 Hz, 1H), 4.00 (t, *J*=9.6 Hz, 1H), 3.88 (s, 3H), 3.45 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.91, 170.35, 165.84, 133.56, 129.92, 129.03, 128.59, 97.36, 71.38, 71.27, 70.40, 70.21, 55.92, 52.94; HRMS (ESI) Calcd for $C_{17}H_{20}NaO_9$: $[M+Na]^+$, 391.1000; Found: 391.1000.

4.4.40. Butyl (1-O-methyl-2-O-benzoyl-3-O-acetyl-D glucopyranoside) urinate. Yield: 86% ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (dd, *J*=8.2, 1.1 Hz, 2H), 7.51–7.47 (t, *J*=7.7 Hz, 1H), 7.36 (t, *J*=7.8 Hz, 2H), 5.55–5.49 (t, *J*=9.5 Hz, 1H), 5.08 (d, *J*=3.6 Hz, 1H), 4.93 (dd, *J*=10.2, 3.6 Hz, 1H), 4.22–4.12 (m, 3H), 3.90 (t, *J*=9.6 Hz, 1H), 3.35 (s, 3H), 1.95 (s, 3H), 1.64–1.58 (m, 2H), 1.34–1.29 (m, 2H), 0.86 (t, *J*=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.93, 169.96, 165.84, 133.56, 129.93, 129.05, 128.59, 97.27, 71.42, 71.26, 70.47, 70.18, 66.03, 55.86, 30.46, 19.05, 13.69; HRMS (ESI) Calcd for $C_{20}H_{26}NaO_9$: $[M+Na]^+$, 433.1469; Found: 433.1472.

*4.4.41. (−)-Methyl shikimate (**9**).*[7q] Yield: 92%; White solid, mp 112∼113 °C; $[\alpha]_D^{20}$=−142° (*c*=0.2, MeOH); ^{1}H NMR (CD_3COCD_3, 400 MHz) δ 6.72 (s, 1H), 4.37 (s, 1H), 4.15 (s, 1H), 4.00 (dd, *J*=11.3, 5.1 Hz, 1H), 3.68 (s, 4H), 3.08 (s, 2H), 2.67–2.57 (m, 1H), 2.16 (dd, *J*=18.0, 5.2 Hz, 1H); ^{13}C NMR (CD_3COCD_3, 101 MHz) δ 166.76, 138.00, 128.83, 71.34, 67.06, 65.83, 51.07, 30.40; MS (EI): *m*/*z*=188 $[M]^+$, 170 $[M-H_2O]^+$, 157$[M-OCH_3]^+$, 129 $[M-COOCH_3]^+$.

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Supplementary data

Supplementary data that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.067.

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