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PIFA-mediated oxidative cycloisomerization of 2-propargyl-1,3-dicarbonyl compounds: divergent synthesis of furfuryl alcohols and furfurals

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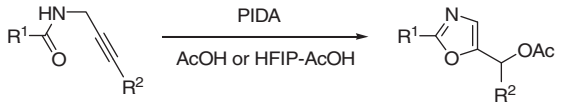
ABSTRACT

$PhI(OCOCF_3)_2$ (PIFA) in the presence of trifluoroacetic acid (TFA) in CH_2Cl_2 efficiently promotes the oxidative cycloisomerization of 2-propargyl 1,3-dicarbonyl compounds to give 4,5-disubstituted furfuryl alcohols. PIFA in hexafluoroisopropanol (HFIP) or PIFA-BF_3·OEt\$_2$ in CH_2Cl_2 bring about the direct formation of furfurals from 2-propargyl 1,3-dicarbonyl compounds. In a few cases, PhI=O is suitable for the direct formation of furfurals.

The synthesis of furan compounds has attracted a great deal of attention due to their widespread application not only to biologically active compounds[1] but also to versatile building block in organic synthesis.[2] In particular, the metal-catalyzed cascade reaction based on the cyclization of alkyl ketone derivatives with electrophiles[3] or nucleophiles[4] has been developed as one of the straightforward procedure for the synthesis of highly functionalized furans. Furthermore, the metal-catalyzed oxidative cycloisomerization of alkyl ketones with various oxidants provides us a facile synthetic method to synthesize furan compounds concomitantly with the incorporation of oxygen functional groups.[5,6]

There has been considerable growth in the application of hypervalent iodine reagents for carrying out synthetic organic transformation.[7] For the synthesis of heterocyclic compounds, iodine(III) oxidants, such as phenyliodine(III) diacetate (PIDA), and phenyliodine(III) bis(trifluoroacetate) (PIFA) are frequently used in the metal-catalyzed oxidative addition of carbon or hetero atom nucleophiles to alkyne compounds.[8,9] Under the metal-free conditions, PIFA also showed its efficiency in the intramolecular oxidative amidation and carboxylation of 4-alkynylcarboxylic acid derivatives[10] or in the oxidative cycloisomerization of enynols.[11,12] These cyclizations are suggested to proceed through the activation of the triple bond by iodonium ions.[10–12] Recently, we found that PIDA efficiently promotes the formation of 2,5-disubstituted oxazolylmethyl acetates via the oxidative cycloisomerization of propargylamides (Scheme 1).[13,14] As our further studies on the iodine(III) oxidants-mediated oxidative cycloisomerization of alkyne compounds, we describe herein the PIFA-mediated oxidative cycloisomerization of 2-propargyl 1,3-dicarbonyl compounds for the divergent synthesis of 4,5-disubstituted furfuryl alcohols and furfurals.

Based on our previous works of the metal-free oxidative cycloisomerization of propargylamides,[13] our preliminary examinations focused on the reaction of 4,4-dibenzoyl-butyne (**1a**) with PIDA (1.5 equiv) in AcOH or in hexafluoroisopropanol (HFIP)-AcOH (Table 1, entries 1 and 2). It turned out that the expected furfuryl acetate **2a** was obtained in 59% or 65% yield at 60 °C. To our delight, when PIFA (1.5 equiv) was employed as an oxidant in CH_2Cl_2, the corresponding trifluoroacetate **3a** was formed in 73% yield (by ^{1}H NMR analysis) at rt for 5 h (entry 3). Since a part of **3a** was hydrolyzed into furfuryl alcohol **4a** during the work-up and/or column chromatography on silica gel, the crude reaction mixture was treated with K_2CO_3 in EtOH for 30 min. Thus, after the alcoholysis, **4a** was isolated in 69% yield (entry 3). By the addition of trifluoroacetic acid (TFA, 1.2 equiv), the use of 1.2 equiv PIFA brought about the similar result to entry 3 (entry 4). It should be mentioned that



Scheme 1. Oxidative cycloisomerization of *N*-propargylamides by PIDA.

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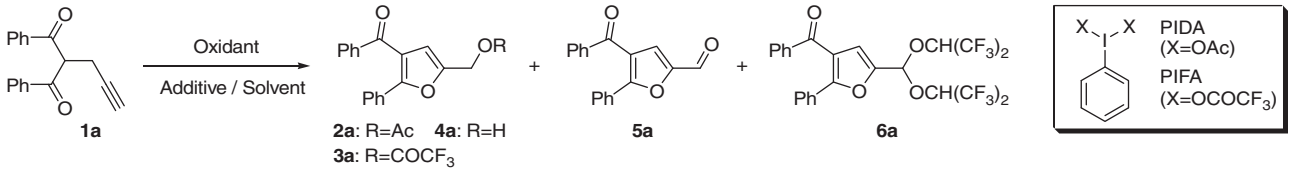
Table 1
Screening of oxidants for the oxidative cycloisomerization of **1a**



Entry	Oxidant (equiv)	Additive (equiv)	Solvent	(°C)	(h)	**2a** or **3a**[a] (%)	**5a**[a] (%)	**Other**[a] (%)
1	PIDA (1.5)		AcOH	60	20	59	1	
2	PIDA (1.5)		HFIP-AcOH (1:1)	60	4	65	1	
3	PIFA (1.5)		CH_2Cl_2	rt	5	73 (**4a**: 69)[b]	9	
4	PIFA (1.2)	TFA (1.2)	CH_2Cl_2	rt	5	72 (**4a**: 70)[b]	4	
5	PIFA (3)		DCE	90	18	33	27	
6	PIFA (3)		HFIP	60	4	0	47	**6a** 28
7	PIFA (3)		HFIP	rt	19	0	51	
8	PIFA (3)	TFA (3)	HFIP	rt	22	0	56	
9	PIFA (2)	$BF_3{\cdot}OEt_2$ (1)	CH_2Cl_2	rt	2	0	78 (77)	
10	PhI=O (3)		DCE–HFIP (3:1)	60	23	0	33	
11	PhI=O (3)	Silica gel[c]	DCE	60	21	0	18	
12	IBX (3)		DMSO	60	4	0	7	**1a** 57

[a] Yields were determined by ^{1}H NMR analysis. Yields in parentheses were isolated yields.
[b] After the reaction of **1a** with PIFA was completed, the crude reaction mixture was treated with K_2CO_3 in EtOH for 30 min.
[c] Silica gel 60N (spherical form, neutral pH, particle size: 100–210 μm) was used.

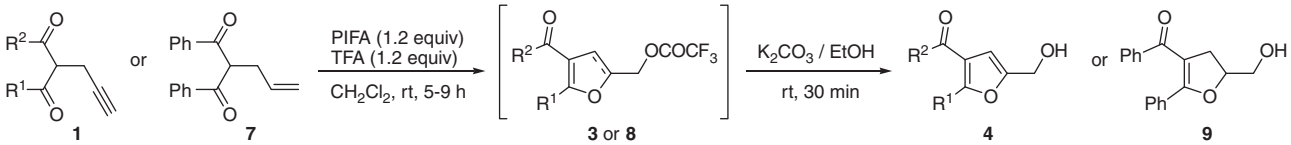
furfural **5a** was observed as a by-product (1–9%) in all cases (entries 1–4).

Our further efforts were focused on the direct formation of **5a** from **1a** (Table 1, entries 5–12). Although the reaction of **1a** with 3 equiv PIFA in DCE under the reflux conditions gave **5a** in only 27% yield (entry 5), the use of HFIP as a solvent improved the yield of **5a** (47–56%, entries 6–9). In the refluxing HFIP, however, acetal **6a** was yielded along with **5a** (entry 6).[15] An addition of $BF_3{\cdot}OEt_2$ exerted a remarkable effect even on the 2 equiv PIFA-mediated formation of **5a** in CH_2Cl_2 to afford **5a** in 77% yield (entry 10).[16] Other oxidants, such as PhI=O[17] and 2-iodoxybenzoic acid (IBX)[11b] were inferior to PIFA (entries 10–12).

Under the optimized conditions, we next turned our attention to the scope of substrates in the formation of furfuryl alcohols **4** (Table 2)[18] and furfurals **5** (Table 3).[19] Thus, in the presence of TFA (1.2 equiv), not only diketones **1a, d–g** but ketoester **1b**, **c** also successfully reacted with PIFA (1.2 equiv) in CH_2Cl_2. After the alcoholysis of **3**, furfuryl alcohols **4** were obtained in 41–78% yields (Table 2, entries 1–7). The present procedure could be applied to the oxidative cyclization of allyl compound **7** to give dihydrofuran **9** in 65% yield (entry 8). As shown in Table 3, by the PFIA-$BF_3{\cdot}OEt_2$-mediated systems (Method A), benzoylester **1b** as well as **1a** was efficiently converted into the corresponding furfural **5b** in 61% yield (entry 2). In the reaction of aliphatic ketones **1c–g**, however, Method A did not bring about good results (24–48%, entries 3–7). On the other hand, the use of PhI=O (3 equiv) as an oxidant in DCE–HFIP (Method C) or PhI=O-silica gel in DCE (Method D) works well for the formation of furfurals **5c–e** (46–71%, entries 3–5). In the cases of the bulky aliphatic ketones **1f**, **g**, PIFA in HFIP (Method B) yielded superior results to the Methods A and C (entries 6 and 7).

In summary, we have demonstrated the divergent synthesis of 4,5-disubstituted furfuryl alcohols and furfurals through the PIFA-mediated oxidative cycloisomerization of 2-propargyl 1,3-dicarbonyl compounds. For the divergent procedure, it is critical to appropriately select additives (TFA and $BF_3{\cdot}OEt_2$) and solvents (CH_2Cl_2 and HFIP). In a few examples for the formation of furfurals, PhI=O is an effective oxidant. Ongoing work is directed toward a better understanding of the effects of additives and solvents for the present reactions.

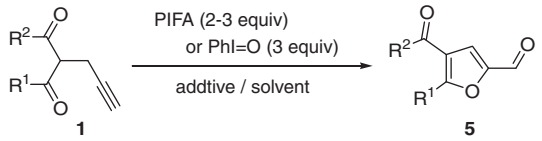
Table 2
The oxidative cycloisomerization of various 2-propargyl-1,3-diketones **1** for the formation of furfuryl alcohols **4**



Entry	Substrate	R^1	R^2	Product	Yield[a] (%)
1	**1a**	Ph	Ph	**4a**	70
2	**1b**	Ph	OEt	**4b**	60
3	**1c**	Me	OEt	**4c**	68
4	**1d**	Me	Me	**4d**	41
5	**1e**	Et	Et	**4e**	64
6	**1f**	*i*Pr	*i*Pr	**4f**	71
7	**1g**	*t*Bu	*t*Bu	**4g**	78
8	**7**	-	-	**9**	65

[a] Isolated yields.

Table 3
The oxidative cycloisomerization of various 2-propargyl-1,3-diketones **1** for the formation of furfurals **5**



1 **5**

Entry	Substrate	Method A[a]			Method B[a]			Method C or D[a]		
		(°C)	(h)	**5**[b] (%)	(°C)	(h)	**5**[b] (%)	(°C)	(h)	**5**[b] (%)
1	**1a**	rt	2	78 (77)	rt	19	51	60	23	33
2	**1b**	rt	3	60 (61)	60	4	53	60	19	31
3	**1c**	rt	17	48	60	19	53	60	19	59 (57)
4	**1d**	rt	5	30	rt	19	26[c]	60	22	68 (71)
5	**1e**	rt	9	38	rt	19	41	60	22	45 (46)
6	**1f**	rt	21	24[d]	rt	22	41 (41)	60	22	15
7	**1g**	rt	17	35	rt	21	72 (68)	60	20	0

[a] Method A: PIFA (entries 1, 2, and 7: 2 equiv, entries 3–6: 3 equiv), $BF_3{\cdot}OEt_2$ (1 equiv)/CH_2Cl_2. Method B: PIFA (entries 1–6: 3 equiv, entry 7: 2 equiv)/HFIP. Method C (entries 1–3): PhI=O (3 equiv)/DCE–HFIP (3:1). Method D (entries 4–7): PhI=O (3 equiv), silica gel/DCE.
[b] Yields were determined by ^1H NMR analysis. Yields in parentheses were isolated yields.
[c] Furfuryl alcohol **4d**: 22%.
[d] Furfuryl trifluoroacetate **3f**: 17%.

Acknowledgments

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References and notes

1. (a) Landquist, J. K. In *Comprehensive Heterocyclic Chemistry*; Katrizky, A. R., Ed.; Pergamon Press: New York, 1984; Vol. 1, pp 144–184; (b) Francesconi, I.; Wilson, W. D.; Tanious, F. A.; Hall, J. E.; Bender, B. C.; Tidwell, R. R.; McCurdy, D.; Boykin, D. W. *J. Med. Chem.* **1999**, *42*, 2260; (c) Mortensen, D. S.; Rodriguez, A. L.; Carlson, K. E.; Sun, J.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. *J. Med. Chem.* **2001**, *44*, 3838; (d) Hosoya, T.; Aoyama, H.; Ikemoto, T.; Kihara, Y.; Hiramatsu, T.; Endo, M.; Suzuki, M. *Bioorg. Med. Chem.* **2003**, *11*, 663; (e) Wiesner, J.; Mitsch, A.; Jomaa, H.; Schlitzer, M. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 2159; (f) Pomel, V.; Klicic, J.; Covini, D.; Church, D. D.; Shaw, J. P.; Roulin, K.; Burgat-Charvillon, F.; Valognes, D.; Camps, M.; Chabert, C.; Gillieron, C.; Françon, B.; Perrin, D.; Leroy, D.; Gretener, D.; Nichols, A.; Vitte, P. A.; Carboni, S.; Rommel, C.; Schwarz, M. K.; Rückle, T. *J. Med. Chem.* **2006**, *49*, 3857; (g) Mugnaini, C.; Rajamaki, S.; Tintori, S.; Corelli, F.; Massa, S.; Witvrouw, M.; Debyser, Z.; Veljkovic, V.; Botta, M. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5370.
2. (a) Reid, S. T. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1983; Vol. 33, pp 1–95; (b) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795–815; (c) Keay, B. A. *Chem. Soc. Rev.* **1999**, *28*, 209–215; (d) Schröter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005**, *61*, 2245–2267; (e) Wright, D. L. *Prog. Heterocycl. Chem.* **2005**, *17*, 1–32.
3. (a) Arcadi, A.; Rossi, E. *Tetrahedron Lett.* **1996**, *37*, 6811; (b) Cacchi, S.; Fabrizi, G.; Moro, L. *J. Org. Chem.* **1997**, *62*, 5327; (c) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Parisi, L. M. *Tetrahedron* **2003**, *59*, 4661; (d) Li, Y.; Yu, Z. *J. Org. Chem.* **2009**, *74*, 8904; (e) Fukuda, Y.; Shiragami, H.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5816; (f) Sniady, A.; Wheeler, K. A.; Dembinski, R. *Org. Lett.* **2005**, *7*, 1769; See also: (g) Crone, B.; Kirsch, S. F. *J. Org. Chem.* **2007**, *72*, 5435.
4. (a) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164; (b) Patil, N. T.; Wu, H.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 4531; (c) Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679; (d) Xiao, Y.; Zhang, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1903; (e) Xiao, Y.; Zhang, J. *Adv. Synth. Catal.* **2009**, *351*, 617–629; (f) Liu, R.; Zhang, J. *Chem. Eur. J.* **2009**, *15*, 9303; (g) Li, W.; Zhang, J. *Chem. Commun.* **2010**, 8839; (h) Zhang, J.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 6704; (i) Zhang, G.; Huang, X.; Li, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 6944.
5. (a) Cheng, G.; Hu, Y. *Chem. Commun.* **2007**, 3285–3287; (b) Jana, R.; Paul, S.; Biswas, A.; Ray, J. K. *Tetrahedron Lett.* **2010**, *51*, 273. Oxidative cyclization of propargyl enol ethers, see; (c) Jiang, H.; Yao, W.; Cao, H.; Huang, H.; Cao, D. *J. Org. Chem.* **2010**, *75*, 5347; (d) Cao, H.; Jiang, H.; Yuan, G.; Chen, Z.; Qi, C.; Huang, H. *Chem. Eur. J.* **2010**, *16*, 10553.
6. Synthesis of furan by the oxidative coupling of alkyne and 1,3-dicarbonyl compounds: (a) Yan, R.; Huang, J.; Luo, J.; Wen, P.; Huang, G.; Liang, Y. *Synlett* **2010**, 1071–1074; (b) Fries, P.; Halter, D.; Kleinschek, A.; Hartung, J. *J. Am. Chem. Soc.* **2011**, *133*, 3906; (c) Lee, Y. R.; Byun, M. W.; Kim, B. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 1080; (d) Karade, N. N.; Shirodkar, S. G.; Patil, M. N.; Potrekar, R. A.; Karade, H. N. *Tetrahedron Lett.* **2003**, *44*, 6729.
7. Recent reviews: (a) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073; (b) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 202086; (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299; (d) Ciufolini, M. A.; Braun, N. A.; Canesi, S.; Ousmer, M.; Chang, J.; Chai, D. *Synthesis* **2007**, *24*, 3759; (e) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656; (f) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523; (g) Miyamoto, K.; Ochiai, M. *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 228; (h) Satam, V.; Harad, A.; Rajule, R.; Pati, H. *Tetrahedron* **2010**, *66*, 7659; (i) Zhdankin, V. V. *J. Org. Chem.* **2010**, *76*, 1185.
8. Recent examples, Ag-catalyzed synthesis of pyrroles: (a) Liu, W.; Jiang, H.; Huang, L. *Org. Lett.* **2010**, *12*, 312; Pd-catalyzed synthesis of oxinoles: (b) Tang, S.; Peng, P.; Pi, S.-F.; Liang, Y.; Wang, N.-X.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1179; Pd-catalyzed synthesis of lactones: (c) Tong, X.; Beller, M.; Tse, M. K. *J. Am. Chem. Soc.* **2007**, *129*, 4906; (d) Welbes, L. L.; Lyons, T. W.; Cychosz, K. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 5836; (e) Tsujihara, T.; Takenaka, K.; Onitsuka, K.; Hatanaka, M.; Sasai, H. *J. Am. Chem. Soc.* **2009**, *131*, 3452; Rh-catalyzed metallonitrene/alkyne metathesis: (f) Thornton, A. R.; Blakey, S. B. *J. Am. Chem. Soc.* **2008**, *130*, 5020; (g) Thornton, A. R.; Martin, V. I.; Blakey, S. B. *J. Am. Chem. Soc.* **2009**, *131*, 2434.
9. For reviews on the oxidative additions of carbon or hetero atom nucleophiles to alkynliodonium compounds: (a) Ochiai, M. Chemistry of Hypervalent Compound In Akiba, K., Ed.; Wiley: New York, 1999; pp 359–387; (b) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.
10. (a) Serna, S.; Tellitu, I.; Dominguez, E.; Moreno, I.; SanMartin, R. *Org. Lett.* **2005**, *7*, 3073; (b) Tellitu, I.; Serna, S.; Herrero, M. T.; Moreno, I.; Dominguez, E.; SanMartin, R. *J. Org. Chem.* **2007**, *72*, 1526.
11. (a) Du, X.; Chen, H.; Chen, Y.; Chen, J.; Liu, Y. *Synlett* **2011**, 1010; See also: (b) Du, X.; Chen, H.; Liu, Y. *Chem. Eur. J.* **2008**, *14*, 9495.
12. Recently, the metal-free oxidative carbocyclization of δ-alkynyl-β-ketoesters was reported,see: Rodríguez, A.; Moran, W. J. *Org. Lett.* **2011**, *13*, 2220.
13. Saito, A.; Matsumoto, A.; Hanzawa, Y. *Tetrahedron Lett.* **2010**, *51*, 2247.
14. Our recent study on the synthesis of heterocyclic compounds from alkyne compounds: (a) Saito, A.; Kanno, A.; Hanzawa, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3931; (b) Saito, A.; Hironaga, M.; Oda, S.; Hanzawa, Y. *Tetrahedron Lett.* **2007**, *48*, 6852; (c) Saito, A.; Oda, S.; Fukaya, H.; Hanzawa, Y. *J. Org. Chem.* **2009**, *74*, 1517; (d) Saito, A.; Kasai, J.; Odaira, Y.; Fukaya, H.; Hanzawa, Y. *J. Org. Chem.* **2009**, *74*, 5644; (e) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372; (f) Saito, A.; Iimura, K.; Hanzawa, Y. *Tetrahedron Lett.* **2010**, *51*, 1471; (g) Saito, A.; Kasai, J.; Konishi, T.; Hanzawa, Y. *J. Org. Chem.* **2010**, *75*, 6980.
15. Since **5a** was not converted into **6a** in the refluxing HFIP in the presence of TFA, **5a** would not be involved in the formation of **6a**.
16. Furfuryl trifluoroacetate **3a** might be assumed as an intermediate for the formation of furfural **5a**. Under the PIFA (1 equiv)-$BF_3{\cdot}OEt_2$ (1 equiv)-mediated conditions, however, the reaction of **3a** gave furfural **5a** in only 21% yield along with **4a** (11%), and thus **3a** would not take part in the predominant route to **5a** from **1a**.
17. Oxidation with PhI=O and silica gel was reported, see: Sohmiya, H.; Kimura, T.; Fujita, M.; Ando, T. *Tetrahedron* **1998**, *54*, 13737.
18. Representative procedure for the preparation of furfuryl alcohol derivatives: TFA (36 μL, 0.48 mmol) and PIFA (206 mg, 0.48 mmol) were added to a solution of **1a** (63.6 mg, 0.4 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C, and the reaction mixture was stirred at rt for 5 h. The mixture was diluted with ether and sat. $NaHCO_3$ aq. was added. After the aqueous solution was extracted with ether, the combined organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was treated with K_2CO_3 (120 mg) in EtOH (2.0 mL) for 30 min. And then, the mixture was diluted with ether, filtered, and concentrated in vacuo. The residue was purified by silica gel column

chromatography (hexane/AcOEt = 75/25) gave **4a** (77.4 mg, 70%) as a colorless oil. IR (neat) ν cm^{-1}; 3429, 1651. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.70 (s, 2H), 6.59 (s, 1H), 7.26–7.32 (m, 3H), 7.33–7.41 (m, 2H), 7.46–7.54 (m, 1H), 7.64–7.71 (m, 2H), 7.80–7.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 57.3, 111.5, 121.4, 127.5, 128.2, 128.3, 129.1, 129.5, 129.7, 132.9, 137.8, 152.9, 155.9, 191.8. FAB-LM *m/z*: 279 (M^++H). FAB-HM Calcd for $C_{18}H_{15}O_3$: 279.1021. Found: 279.1021.

19. Representative procedure for the preparation of furfurals: *Method A*; A solution of **1a** (63.6 mg, 0.4 mmol) in CH_2Cl_2 (2.0 mL) was added to a mixture of PIFA (344 mg, 0.8 mmol) and $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C, and the reaction mixture was stirred at rt for 2 h. The mixture was diluted with ether and sat. $NaHCO_3$ aq. was added. After the aqueous solution was extracted with ether, the combined organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/AcOEt = 80/20) gave **5a** (84.7 mg, 77%) as a colorless oil. IR (neat) ν cm^{-1}; 1680, 1664. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.31–7.48 (m, 5H), 7.47 (s, 1H), 7.53–7.62 (m, 1H), 7.78–7.87 (m, 4H), 9.73 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 122.6, 123.8, 127.9, 128.0, 128.4, 128.5, 129.5, 130.6, 133.4, 136.9, 150.2, 159.6, 177.4, 190.2. FAB-LM *m/z*: 277 (M^++H). FAB-HM Calcd for $C_{18}H_{13}O_3$: 277.0865. Found: 277.0854. *Method B*; PIFA (344 mg, 0.8 mmol) was added to a solution of **1g** (88.9 mg, 0.4 mmol) in HFIP (4.0 mL) at 0 °C, and the reaction mixture was stirred at rt for 21 h. The mixture was diluted with ether and sat. $NaHCO_3$ aq. was added. After the aqueous solution was extracted with ether, the combined organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/AcOEt = 80/20) gave **5g** (68.0 mg, 72%) as a colorless solid. Mp 52 °C. IR (KBr) ν cm^{-1}; 1685. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.27 (s, 9H), 1.36 (s, 9H), 7.28 (s, 1H), 9.60 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 27.4, 28.7, 35.1, 44.8, 120.6, 121.6, 148.8, 169.2, 177.4, 206.3. FAB-LM *m/z*: 237 (M^++H). FAB-HM Calcd for $C_{14}H_{21}O_3$: 237.1491. Found: 237.1497. *Method D*; A solution of **1d** (55.2 mg, 0.4 mmol) in DCE (2.0 mL) was added to a mixture of PhI=O (264 mg, 1.2 mmol) and silica gel (240 mg) in DCE (2.0 mL) at rt, and the reaction mixture was stirred at 60 °C for 22 h. The mixture was diluted with ether and filtered. After concentration of the filtrate to dryness, purification of the residue by silica gel column chromatography (hexane/AcOEt = 80/20) gave oxazolylmethyl acetate **5d** (42.9 mg, 71%) as a white solid. Mp 98 °C. IR (KBr) ν cm^{-1}; 1672. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.44 (s, 3H), 2.67 (s, 3H), 7.44 (s, 1H), 9.55 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.8, 28.9, 121.2, 123.4, 150.2, 164.0, 177.2, 192.9. FAB-LM *m/z*: 153 (M^++H). FAB-HM Calcd for $C_8H_9O_3$: 153.0552. Found: 153.0556.