Rapid Microwave-Assisted Henry Reaction in Solvent-Free Processes

Changsheng Gan, Xing Chen, Guoyin Lai, Zhiyong Wang*

Hefei national laboratory for Physical Science at Microscale and Department of Chemistry, University of Science & Technology of China, Hefei 230026, P. R. of China
Fax +86(551)3603185; E-mail: zwang3@ustc.edu.cn

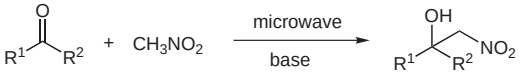
Received 20 October 2005

Abstract: The solvent-free Henry reactions of nitromethane with a series of carbonyl compounds were studied under microwave irradiation. By using different bases and Lewis acids, the solvent-free nitroaldol reaction of aldehydes were realized under microwave condition, affording the corresponding adducts with high yields. Particularly, aliphatic ketones, which were hardly carried out this reaction, could be the reaction substrates in the nitroaldol reactions by employment of 1,4-diazabicyclo[2.2.2]octane (DABCO) under a similar conditions, giving the corresponding adducts with moderate to good yields.

Key words: Henry reaction, microwave, Lewis acid, solvent-free, aliphatic ketones

Henry reaction (or nitroaldol reaction) is one of the fundamental synthetic tools for the construction of carbon–carbon bonds in organic chemistry.[1] The importance of the Henry reaction is typically further transformations involving the newly formed β-nitroalkanol functionality such as reduction to amines,[2] the Nef reaction to carbonyl compounds,[3] or dehydration to nitroalkenes.[4] In order to improve this reaction and extend the scope of the reaction substrates, many chemists are focusing in the investigation of the reaction conditions and the catalyst alteration. Henry reactions of aldehydes were studied in the presence of phase-transfer catalysts in aqueous media,[5] or solvent-free conditions.[6] Recently different reaction media, ionic liquid[7] and heterogeneous solid-phase catalysts,[8] were employed in this reaction to take advantage of easy product isolation and catalyst recycling. Several novel catalysts, such as proazaphosphatranes,[9] 1,1,3,3-tetramethylguanidine (TMG) and its cyclic analogues,[10] were utilized as effective catalysts for Henry reaction. However, to the best of our knowledge, ketones are not often used in the Henry reaction. Recently, we employed different organic bases and Lewis acids as the catalysts under microwave (MW) irradiation, promoting both the yields and the rates of Henry reactions greatly. Aliphatic ketones, especially, which are difficult substrates for the Henry reaction under traditional conditions, can be good reaction substrates under these new conditions, affording the corresponding products with moderate to good yields.

In a preliminary experiment, the Henry reaction of benzaldehyde and nitromethane was explored to determine the optimal conditions (Scheme 1). It was found that the amount of the triethylamine and the irradiation time had a great influence on the reaction yield (entries 1–4, Table 1). Prolonging the reaction time led to a reduction of product yield without significant improvement on the conversion efficiency, affording a large amount of the dehydration product. After careful examinations, the use of one equivalent of Et_3N under MW irradiation for 4 minutes at 80 °C were found to be the optimal condition for the nitroaldol addition (entry 4, Table 1). Subsequently, the scope of the reaction substrate was extended. Both aromatic and aliphatic aldehydes performed this Henry reaction rapidly and smoothly to give the desired β-nitroalkanols with good to excellent yields. It was found that electron-withdrawing substituted aromatic aldehydes favored this reaction, resulting in almost quantitative conversions (entries 5 and 6, Table 1), while the aromatic aldehydes bearing electron-rich group on the aromatic ring gave the corresponding products with lower yields and longer reaction time (entries 7 and 8, Table 1). On the other hand, the Henry reactions were not carried out under this condition when ketones were the reaction substrates (entries 11 and 12, Table 1). It was noted that the *para*-substitution of methoxy group in aromatic aldehydes disfavored the Henry reaction in comparison with the *ortho*-substitution (entries 7 and 8, Table 1) in spite of the steric hindrance of *ortho*-substitution. This implied that the electronic effect had an influence on this Henry reaction. Therefore the employment of a proper Lewis acid might be able to improve the reaction further.[9a]



Scheme 1

As a result, the influence of Lewis acids was scrutinized for different aldehydes. Initial experimental results confirmed that these Lewis acids could improve this reaction. For example, both the product yield and the rate of the reaction between benzaldehyde and nitromethane were improved in the presence of $MgSO_4$ (89%, 4 min) or LiBr (91%, 1.5 min; entry 1, Table 2). In particular, 50% mol of LiBr was the best catalyst among all Lewis acids tested. For 2- or 4-methoxy substituted benzaldehyde, the reaction yield was enhanced to 82% or 94%, respectively, in the presence of LiBr (entries 2 and 3, Table 2). As for 1-naphthylaldehyde, the reaction yield was enhanced from 85% to 97% while the reaction time was reduced from 4 minutes to 1 minute under the same condition (entry 4,

SYNLETT 2006, No. 3, pp 0387–0390
Advanced online publication: 06.02.2006
DOI: 10.1055/s-2006-932449; Art ID: W06805ST

Table 1 Microwave-Assisted Henry Reaction of Carbonyl Compounds[a]

Entry	R^1	R^2	Amount of Et_3N (equiv)	Time (min)	Yield (%)
1	C_6H_5	H	0	6	0
2	C_6H_5	H	0.2	6	62
3	C_6H_5	H	0.5	5	78
4	C_6H_5	H	1	4	83
5	*p*-ClC_6H_4	H	1	1	99
6	*p*-$(NO_2)C_6H_4$	H	1	1	99
7	*o*-$(MeO)C_6H_4$	H	1	6	85
8	*p*-$(MeO)C_6H_4$	H	1	7	68
9	1-Naphthyl	H	1	4	85
10	C_6H_{13}	H	1	5	89
11	C_6H_5	CH_3	1	10	0
12	$(CH_2)_5$		1	10	Trace

[a] Reactions were performed in a sealed tube with 1 equiv of aldehyde and 2.5 equiv nitromethane in the presence of Et_3N. The reaction procedure was described in ref.[11]

Table 2). The yields for aliphatic aldehydes were increased likewise (entry 5, Table 2). However, neither $MgSO_4$ nor LiBr activated ketones to carry out the corresponding reactions under the conditions, even when the reaction time was prologed to 10 minutes (entries 6 and 7, Table 2). Further experiments indicated that triethylamine hardly catalyzed the nitroaldol reaction for ketones either. In order to activate the ketones in this Henry reaction, we had to search for a new base to replace triethylamine. First of all, cyclohexanone was used as a model compound to detect the optimal conditions in the absence of Lewis acids (entries 1–5, Table 3). Inorganic bases, due to their strong basicity and insolubility in organic solvents, were hardly employed in this reaction. Intrigued by the effect of quaternary ammonium salts to this reaction,[5a,6] basic phase-transfer catalysts, such as tetra-*n*-butyl ammonium hydroxide (TBAH) and methenamine, were first employed in this reaction. Methenamine could catalyze the nitroaldol reaction of ketones, but gave the corresponding product with a low yield (entry 2, Table 3). The employment of TBAH (40% aqueous solution) on the other hand produced many by-products (entry 3, Table 3). The use of ethylenediamine gave rise to the corresponding addition product in a moderate yield (entry 4, Table 3). After many trials, DABCO was proved to be the most efficient catalyst among the bases tested (entries 5, Table 3). The influence of Lewis acid on this reaction was then investigated. It was found that addition of Lewis acids could improve the yields of Henry reactions of ketones further in the presence of DABCO (entries 6–8, Table 3). Of these, lithium bromide was the most effective Lewis acid, and prompted this nitroaldol reaction of aliphatic ketone, affording the corresponding product with a high yield of 91% for the reaction between cyclohexanone and nitromethane (entry 7, Table 3). Subsequently, a variety of ketones was employed to extend the scope of the reaction substrates (entries 9–20, Table 3). Among these different ketones, aliphatic ketones were activated to carry out this nitroaldol reaction smoothly, affording the corresponding adducts with good to moderate yields. For instance, cyclopentanone reacted with nitromethane in the presence of LiBr, giving the corresponding product with a yield of 90% (entry 10, Table 3). Steric hindrance also had an influence on the reactions. For example, the reaction of acetone afforded the adducts with a yield of 77% (entry 12, Table 3) while the reaction of 2-butanone afforded only 69% (entry 14, Table 3). However, 3-hydroxybutanone, with high steric hindrance, gave the corresponding adduct with a higher yield of 85% (entry 18, Table 3), which perhaps was attributed to the effect of the hydroxyl group. The neighboring hydroxyl group possibly improved the formation of the reaction transition state. Unfortunately, phenylacetone did not work for this nitroaldol reaction under the same conditions (entries 19 and 20).[12]

In conclusion, we developed a solvent-free Henry reaction under MW irradiation by using different organic base and Lewis acid. Both the reaction yield and the rate were enhanced largely. In particular, a variety of aliphatic ketones, which usually did not work in nitroaldol reactions, could be good substrates for this Henry reaction under this condition. Further extensions of the reaction substrates and the investigation of the reaction mechanism are in progress in our laboratory.

Table 2 Lewis Acid Promoted Henry Reaction of Nitromethane with Carbonyl Compounds[a]

Entry	R^1	R^2	Lewis acid	Time (min)	Yield (%)
1	C_6H_5	H	$MgSO_4$	4	89
			$MgSO_4$[b]	4	88
			LiBr	1.5	91
			$LiClO_4$	1.5	90
2	*o*-$(MeO)C_6H_4$	H	$MgSO_4$	5	91
			LiBr	1	94
3	*p*-$(MeO)C_6H_4$	H	$MgSO_4$	6	77
			LiBr	2	82
4	1-Naphthyl	H	$MgSO_4$	4	90
			LiBr	1	97
5	C_6H_{13}	H	$MgSO_4$	5	93
			LiBr	3	96
6	C_6H_5	CH_3	LiBr	10	0
7	$(CH_2)_5$		LiBr	10	Trace

[a] Reaction was conducted in a sealed tube with 1 equiv of aldehyde, 2.5 equiv of nitromethane and 1 equiv Et_3N in the presence of 50 mol% of the Lewis acid. The reaction procedure was listed in ref.[11]
[b] 100 mol% of Lewis acid were used.

Table 3 Microwave-Assisted Henry Reaction of Ketones[a]

Entry	R^1	R^2	Base	Lewis acid	Reaction time (min)	Yield (%)
1	$(CH_2)_5$		Et_3N	–	10	Trace
2	$(CH_2)_5$		Methenamine	–	10	23
3	$(CH_2)_5$		TBAH	–	2	36
4	$(CH_2)_5$		$(CH_2NH_2)_2$	–	10	52
5	$(CH_2)_5$		DABCO	–	10	80
6	$(CH_2)_5$		DABCO	$MgSO_4$	8	87
7	$(CH_2)_5$		DABCO	LiBr	3	91
8	$(CH_2)_5$		DABCO	$LiClO_4$	3	90
9	$(CH_2)_4$		DABCO	$MgSO_4$	8	88
10	$(CH_2)_4$		DABCO	LiBr	3	90
11	CH_3	CH_3	DABCO	$MgSO_4$	5	68
12	CH_3	CH_3	DABCO	LiBr	3	77
13	CH_3	C_2H_5	DABCO	$MgSO_4$	9	65
14	CH_3	C_2H_5	DABCO	LiBr	5	69
15	CH_3	$(CH_3)_2CHCH_2$	DABCO	$MgSO_4$	9	58
16	CH_3	$(CH_3)_2CHCH_2$	DABCO	LiBr	5	63
17	CH_3	$CH_3(OH)CH$	DABCO	$MgSO_4$	10	71
18	CH_3	$CH_3(OH)CH$	DABCO	LiBr	4	85
19	C_6H_5	CH_3	DABCO	$MgSO_4$	10	–[b]
20	C_6H_5	CH_3	DABCO	LiBr	10	–[b]

[a] Reaction was carried out in a sealed tube with 1 equiv of the ketone, 2.5 equiv of nitromethane and 1 equiv of base in the presence of 50 mol% of the Lewis acid. The reaction procedure was listed in ref.[11]
[b] No product found.

Acknowledgment

The authors are grateful to National Nature Science Foundation of China (No.20472078 and 30572234) for their support.

References and Notes

(1) For recent reviews dealing with the Henry reaction and its use, see: (a) Luzzio, F. A. *Tetrahedron* **2001**, *57*, 915. (b) Rosini, G. In *Comprehensive Organic Synthesis*, Vol. 1; Trost, B. M., Ed.; Pergamon: Oxford, **1999**. (c) Pinnick, H. W. In *Organic Reactions*, Vol. 38; Paquette, L. A., Ed.; Wiley: New York, **1990**, Chap. 3.
(2) Watanabe, M.; Murata, K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712.
(3) Chikasita, H.; Morita, Y.; Itoh, K. *Synth. Commun.* **1987**, *17*, 677.
(4) Anbazhagan, M.; Kumaran, G.; Sasidharan, M. *J. Chem. Res.* **1997**, *9*, 336.
(5) (a) Ballini, R.; Bosica, G. *J. Org. Chem.* **1997**, *62*, 425. (b) Zhou, C. L.; Zhou, Y. Q.; Wang, Z. Y. *Chin. Chem. Lett.* **2003**, *14*, 355.
(6) Ballini, R.; Fiorini, D.; Gil, M. V.; Palmieri, A. *Tetrahedron* **2004**, *60*, 2799.
(7) (a) Jiang, T.; Gao, H. X.; Han, B. X.; Zhao, G. Y.; Chang, Y. H.; Wu, W. Z.; Gao, L.; Yang, G. Y. *Tetrahedron Lett.* **2004**, *45*, 2699. (b) Qian, W. X.; Ju, F. Y.; Bao, W. L.; Zhang, Y. M. *J. Chem. Res., Synop.* **2004**, 154. (c) Khan, F. A.; Dash, J.; Satapathy, R.; Upadhyay, S. K. *Tetrahedron Lett.* **2004**, *45*, 3055.
(8) (a) Huh, S.; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *J. Am. Chem. Soc.* **2004**, *126*, 1010. (b) Akutu, K.; Kabashima, H.; Seki, T.; Hattori, H. *Appl. Catal., A* **2003**, *247*, 65. (c) Cwik, A.; Fuchs, A.; Hell, Z.; Clacens, J.-M. *Tetrahedron* **2005**, *61*, 4015. (d) Ballini, R.; Bosica, G.; Livi, D.; Palmieri, A.; Maggi, R.; Sartori, G. *Tetrahedron Lett.* **2003**, *44*, 2271.
(9) (a) Kisanga, P. B.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 4298. (b) Verkade, J. G.; Kisanga, P. B. *Tetrahedron* **2003**, *59*, 7819.
(10) (a) Simoni, D.; Invidiata, F. P.; Manfredini, S.; Ferroni, R.; Lampronti, I.; Pollini, G. P. *Tetrahedron Lett.* **1997**, *38*, 2749. (b) Simoni, D.; Rondanin, R.; Morini, M.; Baruchello, R.; Invidiata, F. P. *Tetrahedron Lett.* **2000**, *41*, 1607. (c) Ma, D. W.; Pan, Q. B.; Han, F. S. *Tetrahedron Lett.* **2002**, *43*, 9401.

(11) The Henry reactions were carried out in Emrys Creator microwave reactor from Personal Chemistry, Sweden. The mixture after reaction was cooled down with compressed air produced by SPB-3 Automatic Air Source from the Analytic Technique Institute of Agilent in Beijing.

Typical Experimental Procedure for the Microwave-Assisted Henry Reaction of Benaldehydes with Nitromethane.

To a 10 mL glass tube was added a mixture of benzaldehyde (0.212 g, 2 mmol), nitromethane (0.305 g, 5 mmol), Et_3N (0.202 g, 2 mmol), $MgSO_4$ (0.120 g, 1 mmol), and magnetic stir bar. The vessel was sealed with a pressure lock and placed into the cavity of microwave reactor. The reaction mixture was pre-stirred for 30 s. An initial microwave irradiation of 250 W was used, the temperature being ramped from r.t. to 80 °C. This step took about 50–60 s. At 80 °C the vessel was then held for a given time, as shown in Table 2. After cooling the reaction mixture to r.t. with compressed air, which took about 5 min, the vessel was opened and 5 mL of Et_2O was added to the mixture. Then it was filtered through a silica gel plug. The filtrate was washed with H_2O, and dried over anhyd $MgSO_4$. After the removal of solvent, the crude product was purified by short column chromatography with PE–EtOAc (5:1, v/v) as the eluent. For those substrates listed in entries 5 and 6 in Table 1 and entries 4 and 5 in Table 2, evaporation of Et_2O gave the pure products.

(12) **Spectral Data of Nitroalcohol Compounds.**

1-Phenyl-2-nitroethanol: IR (film): 3429, 1553 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.24 (br, 1 H), 4.50 (m, 1 H), 4.59 (m, 1 H), 5.43 (dd, *J* = 3.2, 9.5 Hz, 1 H), 7.38–7.42 (m, 5 H) ppm. ^{13}C NMR: 70.7, 80.9, 125.9, 128.6, 128.7, 138.2 ppm. HRMS: *m/z* calcd: 167.0582 $[M]^+$; found: 167.0579.

1-(4-Chlorophenyl)-2-nitroethanol: IR (film): 3431, 1597, 1556 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.19 (br, 1 H), 4.48 (dd, *J* = 3.4, 13.4 Hz, 1 H), 4.57 (dd, *J* = 9.2, 13.4 Hz, 1 H), 5.44 (dd, *J* = 3.4, 9.2 Hz, 1 H), 7.34 (d, *J* = 8.6 Hz, 2 H), 7.38 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: 70.3, 81.0, 127.4, 129.2, 134.8, 136.6 ppm. HRMS: *m/z* calcd: 201.0193 $[M]^+$; found: 201.0191.

1-(4-Nitrophenyl)-2-nitroethanol: IR (film): 3529, 1556, 1519 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.20 (br, 1 H), 4.55–4.66 (m, 2 H), 5.62 (m, 1 H), 7.64 (d, *J* = 8.6 Hz, 2 H), 8.27 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: 70.0, 80.7, 124.2, 127.0, 145.1, 148.1 ppm. HRMS: *m/z* calcd 212.0433 $[M]^+$; found: 212.0441.

1-(2-Methoxyphenyl)-2-nitroethanol: IR (film): 3537, 2922, 1552, 1493, 1378 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.13 (d, *J* = 5.7 Hz, 1 H), 3.89 (s, 3 H), 4.58 (dd, *J* = 8.9, 13.0 Hz, 1 H), 4.66 (dd, *J* = 3.3, 13.0 Hz, 1 H), 5.65 (m, 1 H), 6.92 (m, 1 H), 7.03 (m, 1 H), 7.34 (m, 1 H), 7.45 (m, 1 H) ppm. ^{13}C NMR: 55.6, 67.9, 80.0, 111.5, 121.3, 122.2, 126.1, 129.9, 157.2 ppm. HRMS: *m/z* calcd: 197.0688 $[M]^+$; found: 197.0693.

1-(4-Methoxyphenyl)-2-nitroethanol: IR (film): 3441, 1553 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.93 (br, 1 H), 3.80 (s, 3 H), 4.46 (dd, *J* = 3.2, 13.1 Hz, 1 H), 4.59 (dd, *J* = 9.5, 13.1 Hz, 1 H), 5.38 (dd, *J* = 3.2, 9.5 Hz, 1 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: 56.1, 73.1, 84.9, 114.4, 129.3, 135.2, 158.1 ppm. HRMS: *m/z* calcd 197.0688 $[M]^+$; found: 197.0694.

1-(1-Naphthyl)-2-nitroethanol: IR (film): 3448, 1553, 1378 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.92 (br, 1 H), 4.61–4.71 (m, 2 H), 6.26 (m, 1 H), 7.51–7.60 (m, 3 H), 7.75–7.77 (m, 1 H), 7.84–7.90 (m, 2 H), 8.02 (m, 1 H) ppm. ^{13}C NMR: 68.2, 80.8, 121.9, 123.8, 125.5, 126.0, 127.0, 129.2, 129.2, 129.6, 133.7, 133.8 ppm. HRMS: *m/z* calcd: 217.0739 $[M]^+$; found: 217.0735.

1-Nitrooctan-2-ol: IR (film): 3410, 1555 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3 H), 1.18–1.39 (m, 6 H), 1.40–1.54 (m, 4 H), 3.14 (br, 1 H), 4.22–4.30 (m, 1 H), 4.32–4.40 (m, 2 H) ppm. ^{13}C NMR: 14.0, 22.5, 25.0, 29.0, 31.6, 33.8, 68.8, 80.8 ppm. HRMS: *m/z* calcd 175.1208 $[M]^+$; found: 175.1215.

1-(Nitromethyl)cyclohexanol: IR (film): 3530, 3431, 2937, 2862, 1548, 1382 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.34 (m, 1 H), 1.48–1.59 (m, 4 H), 1.62–1.72 (m, 5 H), 2.32 (br, 1 H), 4.44 (s, 2 H) ppm. ^{13}C NMR: 21.5, 25.2, 34.9, 70.8, 84.8 ppm. HRMS: *m/z* calcd: 159.0895 $[M]^+$; found: 159.0889.

1-(Nitromethyl)cyclopentanol: IR (film): 3423, 2925, 1549, 1383 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.68–1.73 (m, 4 H), 1.81–1.91 (m, 4 H), 2.83 (br, 1 H), 4.54 (s, 2 H) ppm. ^{13}C NMR: 23.8, 38.2, 80.2, 83.7 ppm. HRMS: *m/z* calcd: 145.0739 $[M]^+$; found: 145.0745.

2-Methyl-1-nitropropan-2-ol: IR (film): 3385, 2924, 1548, 1461, 1260 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.26 (s, 6 H), 2.55 (br, 1 H), 4.33 (s, 2 H) ppm. ^{13}C NMR: 27.0, 69.8, 85.3 ppm. HRMS: *m/z* calcd 119.0582 $[M]^+$; found: 119.0587.

1-Nitro-2-methylbutan-2-ol: IR (film): 3441, 2924, 1553, 1381 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.99 (t, *J* = 7.5 Hz, 3 H), 1.30 (s, 3 H), 1.62 (q, *J* = 7.5 Hz, 2 H), 2.75 (br, 1 H), 4.44 (d, *J* = 11.8 Hz, 2 H) ppm. ^{13}C NMR: 8.0, 24.1, 32.7, 72.0, 84.1 ppm. HRMS: *m/z* calcd 133.0739 $[M]^+$; found: 133.0732.

2,4-Dimethyl-1-nitropentan-2-ol: IR (film): 3454, 2924, 1552, 1380 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.97–1.01 (m, 6 H), 1.33 (s, 3 H), 1.46–1.54 (m, 2 H), 1.76–1.91 (m, 1 H), 2.82 (br, 1 H), 4.42 (d, *J* = 11.8 Hz, 2 H) ppm. ^{13}C NMR: 22.5, 24.2, 29.9, 48.1, 72.3, 85.1 ppm. HRMS: *m/z* calcd 161.1052 $[M]^+$; found: 161.1058.

2-Methyl-1-nitrobutane-2,3-diol (mixture of the two diastereoisomers): IR (film): 3401, 2986, 1551, 1382 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.20–1.30 (m, 6 H), 2.88 (br, 2 H), 3.72–3.84 (m, 1 H), 4.43–4.71 (m, 2 H) ppm. ^{13}C NMR: 17.0, 20.3, 21.0, 70.9, 72.8, 74.2, 74.4, 80.9, 82.4 ppm. HRMS: *m/z* calcd: 149.0688 $[M]^+$; found: 149.0685.