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Enantioselective Michael addition of aldehydes to nitroolefins catalyzed by pyrrolidine-HOBt

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ABSTRACT

The oxytriazole catalyst "pyrrolidine-HOBt" developed for asymmetric Michael addition of cyclohexanone to nitroolefins is now evaluated for the asymmetric Michael addition of aldehydes to nitroolefins under similar reaction conditions. The results of this study indicate that, the oxytriazole catalyst "pyrrolidine-HOBt" is equally effective in promoting the Michael addition of aldehydes to nitroolefins on employing benzoic acid as an additive. The desired products, γ-nitrocarbonyl compounds were obtained in good yields and high enantioselectivities.

1. Introduction

Organocatalytic asymmetric synthesis is regarded as a standard for effective organic synthesis these days. Over the past few years, remarkable efforts and impartial advancements have been witnessed in the development of catalytic asymmetric synthesis. As a result, asymmetric organocatalysis[1] has gained significant attention from the scientific community and has become a powerful alternate and/or complementary protocol to enzymatic and organometallic catalysis. In particular, asymmetric aminocatalysis has emerged as a handy tool for the construction of chiral building blocks by means of enamine or iminium mechanisms.[2] Undoubtedly, the Michael addition reaction is one of the favorite choices to explore effectiveness of new catalyst designs. As the Michael addition reaction results in the formation of functionalized products with multiple stereogenic centers in a single step, it has been the focus of many research groups. In this endeavour, a large number of designed organocatalysts bearing pyrrolidine moiety were developed and investigated on a wide variety of donor and acceptor substrates and found to be efficient with varied levels of success.[3–5] Among the Michael products, γ-nitrocarbonyls were more prominent as they serve as versatile templates for the construction of various bioactive compounds.[5,6] The generation of all-carbon quaternary stereogenic centers is considered to be a challenging task in asymmetric synthesis.[7] Although, a large number of organocatalysts were known to be highly efficient for Michael addition of unmodified carbonyls to nitroolefins, only a few of them were found to be effective for the Michael reaction aldehydes and nitroolefins.[8] Therefore, an investigation into new catalytic methods for this transformation is desirable.

In continuation of our research on organocatalysis,[9] we recently developed a proline-oxytriazole compound, "pyrrolidine-HOBt" **1** (Fig. 1) as an efficient catalyst for the asymmetric Michael addition reaction of ketones to nitroolefins in water under additive-free conditions. Having been encouraged by this study and considering the consistency of the catalytic mechanism *via* an enamine pathway,[10] we therefore started our investigations to evaluate catalyst **1** for the asymmetric Michael reaction of aldehydes to nitroolefins. Herein we report on the use of pyrrolidine-HOBt **1** as an effective organocatalyst for the asymmetric Michael reaction of aldehydes to nitroolefins providing Michael adducts with high yields and selectivities.

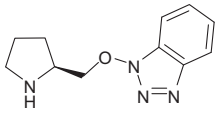

Figure 1. Pyrrolidine-HOBt.

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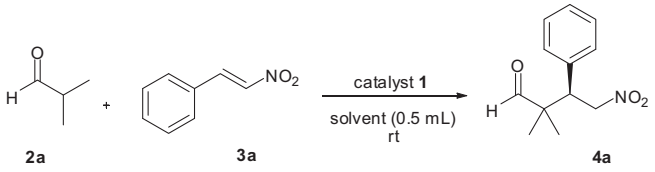
0957-4166/

2. Results and discussion

Herein we have studied two types of aldehydes (α,α-disubstituted and α-substituted) to establish the scope of this catalyst for this transformation. In this effort, we started our investigations using two different model reactions and then extended our studies with screening experiments. The two sets of experimental results are presented. The first set was conducted on a model reaction using isobutyraldehyde **2a** as the donor and nitrostyrene **3a** as the acceptor (Scheme 1) to evaluate the efficacy of "pyrrolidine-HOBt" catalyst **1** for asymmetric Michael additions of α,α-disubstituted aldehydes to nitroolefins. The reaction optimization involved experimental screening involving variation of solvent, additive, temperature and substrates. Initially, the reactions were simultaneously carried out in various solvents using 10–20 mol% of the catalyst at room temperature and the results are summarized in Table 1. As evident from the survey, the Michael reaction worked well in all solvents irrespective of the polar/non-polar nature to afford the product γ-nitrocarbonyl compound **4a** in good yield and enantioselectivity (Table 1, entries 1–20). However, the reaction performed in water was found to be more effective in terms of yield (64–78%) and enantioselectivity (67–76% ee) among the conditions tested and formed a basis for further screening (Table 1, entries 7–9).



2a 3a 4a

Scheme 1. Michael addition of isobutyraldehyde to nitrostyrene.

Table 1
Screening of solvents and catalyst loading[a]

Entry	Solvent	**1** (mol%)	Time (d)	Yield[b] (%)	ee[c](%)
1	Neat	10	3	51	46
2	Neat	20	2	56	53
3	THF	10	3	62	55
4	THF	20	2	64	63
5	Toluene	10	3	55	49
6	Toluene	20	2	59	51
7	$CHCl_3$	10	3	61	54
8	$CHCl_3$	20	2	65	62
9	MeOH	10	3	57	52
10	MeOH	20	2	60	61
11	H_2O	10	3	65	65
12	H_2O	20	2	71	69
13	Dioxane	10	3	58	61
14	Dioxane	20	2	63	64
15	DMSO	10	2	65	43
16	DMSO	20	2	69	52
17	DMF	10	2	67	51
18	DMF	20	2	73	58

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol).
[b] Isolated yields.
[c] Determined by chiral stationary phase HPLC.

Encouraged by these results, we then tested the effect of acid additives in the above transformation. The role of an acid additive in promoting the proline organocatalysis is well studied and widely accepted. In anticipation, we examined the effect of various acid additives using 20 mol% of catalyst at room temperature and benzoic acid played effective role in promoting the reaction in combination with catalyst **1** (Table 2, entries 7–10) and the subsequent experiments were carried out with 20:10 mol% catalyst-additive combination (Table 2, entry 8).

Table 2
Screening of additives[a]

Entry	additive	(mol%)	Time (h)	Yield[b] (%)	ee[c](%)
1	TFA	5	36	61	64
2	TFA	10	36	70	66
3	PhOH	5	48	63	61
4	PhOH	10	48	65	69
5	HCOOH	5	36	62	73
6	HCOOH	10	36	76	74
7	PhCOOH	5	36	73	71
8	PhCOOH	10	36	81	76

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol) catalyst **1** (20 mol%), water, rt.
[b] Isolated yields.
[c] Determined by chiral stationary phase HPLC.

After establishing the optimal solvent and additive factors, we then conducted temperature screening experiments to find out the optimal temperature conditions required to catalyze maximum output for the reaction. As shown in Table 3, the highest catalytic performance was observed at 0 °C (Table 3, entry 2), while the reactions conducted at other temperatures suffered either from long reaction times or loss of yield with no substantial improvement in enantioselectivities (Table 3, entries 1, 3 and 4).

Table 3
Effect of temperature[a]

Entry	Temp.(°C)	Time (h)	Yield[b] (%)	ee[c](%)
1	25	36	83	84
2	0	36	87	89
3	-10	60	75	87
4	-20	72	68	89

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol) catalyst **1** (20 mol%), PhCOOH (10 mol%), water, rt.
[b] Isolated yields.
[c] Determined by chiral stationary phase HPLC.

Having set the optimal reaction conditions for the Michael addition of isobutyraldehyde **2a** to nitrostyrene **3a**, we then conducted substrate screening experiments to determine the generality of the catalyst for this transformation. As shown in Tables 4 and 5, all substrate combinations involving variations in nitroolefins **3b–k** reacted smoothly with isobutyraldehyde **2a** (Table 4, entries 1–9) and cyclopentanecarboxaldehyde **2b** (Table 5, entries 1–8) under the optimized reaction conditions and the corresponding Michael products **4b–j** and **5a–h** were obtained in good yields with high levels of enantioselectivities regardless of the nature of substitution pattern on the nitroolefins. However, reactions of nitroolefins with electron donating substitutions were found to be slightly inferior in overall productivity over that of electron withdrawing substituents (Tables 4 and 5, entries 4 and 5, respectively). However, this complete study indicates a good scope for "pyrrolidine-HOBt" in promoting the conjugate addition of α,α-disubstituted aldehydes to nitroolefins using and providing access to a variety of γ-nitrocarbonyl compounds with an all-carbon quaternary center in high enantioselectivities.

The second set of experimental studies were conducted on a model reaction designed with propaldehyde **6a** as the donor sub-

Table 4
Screening of solvents using **1**[a]

Entry	Solvent	Time (h)	Yield[b] (%)	(*syn/anti*)[c]	ee[d](%)
1	Neat	36	55	7:3	63
2	DMF	24	79	8:2	53
3	THF	24	64	9:1	71
4	CH_3CN	24	61	85:15	58
5	CH_2Cl_2	36	59	6:4	66
6	$CHCl_3$	24	68	7:3	70
7	Dioxane	24	65	85:15	59
8	Toluene	24	69	8:2	69
9	Hexane	36	63	7:3	62
10	MeOH	24	66	8:2	71
11	DMSO	24	81	85:15	55
12	H_2O	24	73	9:1	77

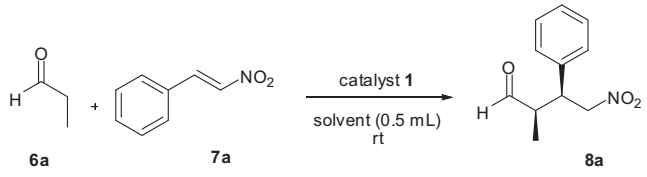
[a] Reaction conditions: propaldehyde (4 mmol), nitrostyrene (1 mmol), solvent (0.5 mL), catalyst (20 mol%); [b] Isolated yields of *syn*-product; [c] Determined by ^{1}H NMR of crude produt; [d] Ee of *syn*-product determined by chiral stationary phase HPLC.

Table 5
Screening of additives[a]

Entry	additive	(mol%)	Time (h)	Yield[b](%)	(*syn/anti*)[c]	ee[d](%)
1	TFA	5	24	73	9:1	65
2	TFA	10	24	78	93:7	73
3	pTSA	5	36	65	8:2	57
4	pTSA	10	24	69	8:2	59
5	HCOOH	5	24	71	91:9	67
6	HCOOH	10	24	79	94:6	75
7	PhCOOH	5	24	81	93:7	74
8	PhCOOH	10	24	93	95:5	87
9	CSA	5	36	68	8:2	60
10	CSA	10	24	74	8:2	69
11	PhOH	5	36	63	9:1	61
12	PhOH	10	36	77	9:1	75

[a] Reaction conditions: propaldehyde (4 mmol), nitrostyrene (1 mmol) catalyst **1** (20 mol%), water, rt; [b] Isolated yields of *syn*-product; [c] Determined by ^{1}HNMR of crude product; [d] Ee of *syn*-product determined by chiral stationary phase HPLC.

strate and nitrostyrene **7a** as the acceptor (Scheme 2) and then extended to other substrates. This study includes screening of solvents, additives, concentrations and temperature to establish optimal parameters required for the productive outcome of the catalytic cycle. To start with, solvent screening experiments were conducted using 20 mol% of the catalyst **1** at room temperature and the results are summarized in Table 4. The Michael reaction progressed well in all solvents irrespective of the polar/non-polar nature to afford the product γ-nitroaldehyde **8a** with moderate to good yields and stereoselectivities (Table 4, entries 1–12). However, water mediated reaction was found to be more effective (Table 4, entry 12) among the conditions screened and was adopted for further screening studies.



Scheme 2. Michael addition of propaldehyde to nitrostyrene.

In order to improve the reaction outcome, we then conducted additive screening experiments to ascertain the effect of acid additives on the catalytic performance of **1**. It has been well documented that the presence of an acid additive accelerates enamine formation and thereby enhances the catalytic efficiency as the reaction progress. As shown in Table 5, screening experiments were conducted using 5 mol% or 10 mol% of various acid additives and 20 mol% of catalyst **1** in water at room temperature. Again the use of 10 mol% of benzoic acid turned out to be the most efficient additive in combination with catalyst **1** (Table 5, entry 8).

Having improved the reaction outcome with additive screening, we then turned our attention to evaluate the effect of catalyst loading and temperature on the overall reaction performance. As shown in Table 6, screening experiments were designed in a manner to define both the parameters at each attempt. The results indicate the supremacy of the pre-established conditions (Table 5, entry 8), over these modifications (Table 6, entries 1–5). In comparison, this study suffered either with long reaction times or loss of yield with no considerable improvement in stereoselectivities (Table 6 *Vs* Table 5, entry 8).

Table 6
Effect of temperature and catalyst loading[a]

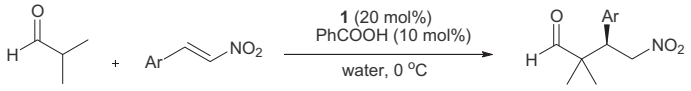
Entry	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield[b] (%)	(*syn/anti*)[c]	ee[d] (%)
1	20	0	48	84	96:6	88
2	15	RT	36	81	94:6	83
3	15	0	48	72	92:8	86
4	10	RT	36	75	92:8	81
5	5	RT	60	65	92:8	63

[a] Reaction conditions: propaldehyde (4 mmol), nitrostyrene (1 mmol), PhCOOH (10 mol%), neat; [b] Isolated yields of *syn-product;* [c] Determined by ^{1}H NMR of crude produt; [d] Ee of *syn*-product determined by chiral stationary phase HPLC.

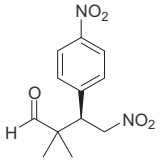
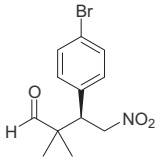
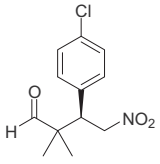
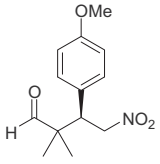
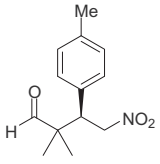
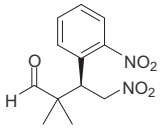
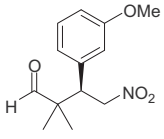
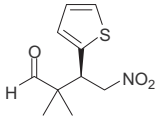
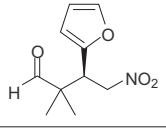
With the optimal assessment on model substrate, we then extended the study to evaluate the substrate generality of this transformation. In order to achieve this, experiments are designed using a series of aldehydes and nitroolefins in different combinations as shown in Tables 9 and 10. All substrate designs involving variations in nitroolefins **7b–j** reacted smoothly with propionaldehyde **6a** (Table 9, entries 1–9) and other aldehydes **6b–f** (Table 10, entries 1–9) under the optimized reaction conditions and the corresponding Michael products **8b–j** and **8k–s** were obtained in good yields and high stereoselectivities irrespective of the nature of substitution pattern in nitroolefins. However, reactions involving branched aldehydes (Table 10, entries 5 and 9) were found to be slightly inferior in overall productivity over that of others. Significantly, the catalytic effect of "pyrrolidine-HOBt" could be extended to Michael reaction of aldehydes and nitroolefins meeting to the objectives and in good agreement to those reported in the literature.[3]

The absolute stereochemical outcome of the above two set of experimental results for asymmetric Michael reaction of aldehydes and nitroolefins could be rationized by considering the possible transition state[10,11] model as shown in Figure 2. The pyrrolidine ring of the catalyst activates aldehyde towards enamine formation and the bulky oxytriazole template serves as an efficient stereocontrol element, providing effective steric coverage and also participates in H-bonding interactions in the pool of nitroolefin, benzoic acid with the aid of water molecule as depicted in Figure 2. The complete arrangement results in a compact transition state, wherein the nucleophilic enamine attacks the nitroolefin from *Si*

Table 7
Enantioselective Michael addition of isobutyraldehyde to nitroolefins[a]

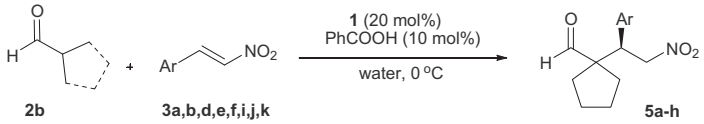


2a **3b-j** **4b-j**

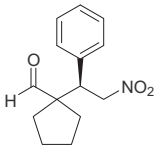
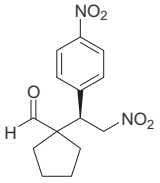
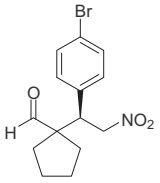
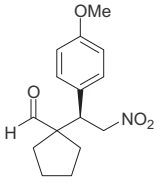
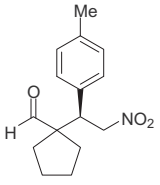
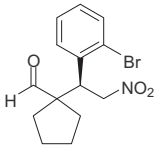
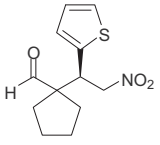
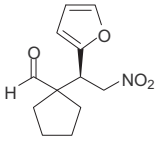
Entry	Product		Time (h)	Yield[b] (%)	ee[c] (%)
1		**4b**	36	91	93
2		**4c**	36	89	91
3		**4d**	36	86	88
4		**4e**	48	78	84
5		**4f**	48	73	81
6		**4g**	36	85	84
7		**4h**	48	82	77
8		**4i**	48	81	83
9		**4j**	48	84	79

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitroolefin (1 mmol).
[b] Isolated yields.
[c] Determined by chiral stationary phase HPLC.

Table 8
Enantioselective Michael addition of cyclopentanecarboxyaldehyde to nitroolefins[a]

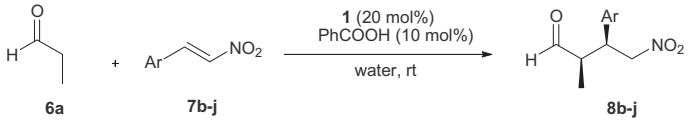


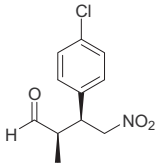
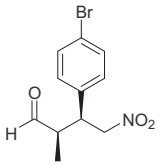
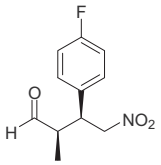
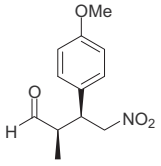
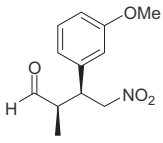
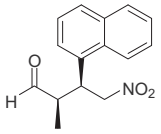
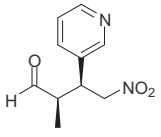
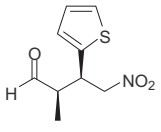
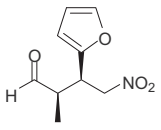
2b **3a,b,d,e,f,i,j,k** **5a-h**

Entry	Product		Time (h)	Yield[b] (%)	ee[c] (%)
1		**5a**	36	85	79
2		**5b**	36	91	92
3		**5c**	36	89	90
4		**5d**	48	69	74
5		**5e**	48	71	76
6		**5f**	36	87	83
7		**5g**	48	82	81
8		**5h**	48	84	80

[a] Reaction conditions: cyclopentanecarboxaldehyde (4 mmol), nitroolefin (1 mmol).
[b] Isolated yields.
[c] Determined by chiral stationary phase HPLC.

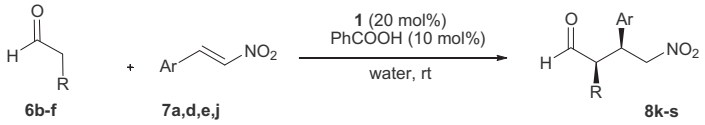
Table 9
Enantioselective Michael addition of propaldehyde to nitroolefins[a]

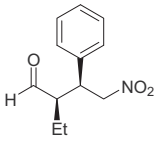
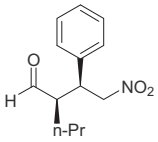
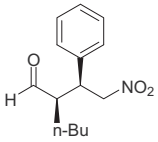
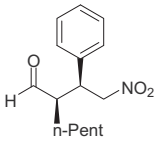
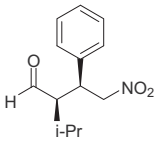
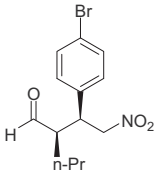
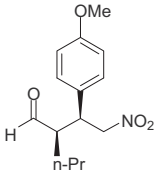
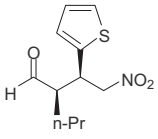
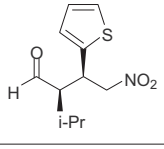


Entry	Product		Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d](%)
1		**8b**	24	91	92:8	89
2		**8c**	24	93	95:5	91
3		**8d**	24	91	93:7	87
4		**8e**	36	79	91:9	82
5		**8f**	36	82	90:10	85
6		**8g**	36	89	91:9	84
7		**8h**	36	85	92:8	79
8		**8i**	36	84	92:8	86
9		**8j**	36	86	93:7	83

[a] Reaction conditions: propaldehyde (4 mmol), nitroolefin (1 mmol); [b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product; [d] Ee of *syn*-product determined by chiral stationary phase HPLC.

Table 10
Enantioselective Michael addition of different aldehyde to nitroolefins[a]



Entry	Product		Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d](%)
1		**8k**	24	91	94:6	86
2		**8l**	24	95	96:4	91
3		**8m**	24	92	92:8	88
4		**8n**	24	91	93:7	85
5		**8o**	36	77	85:15	73
6		**8p**	24	95	95:5	92
7		**8q**	24	86	90:10	78
8		**8r**	24	89	92:8	83
9		**8s**	36	79	80:20	71

[a] Reaction conditions: aldehyde (4 mmol), nitroolefin (1 mmol); [b] Isolated yields.
[c] Determined by ^{1}HNMR of crude product; [d] Determined by chiral stationary phase HPLC.

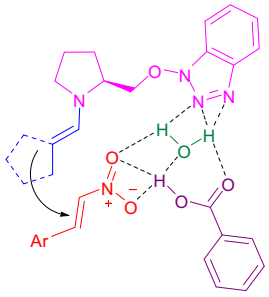


Figure 2. Proposed transition state.

face and leads to the formation of desired products with high stereooselectivities.

3. Conclusions

In conclusion, we have demonstrated the application of "pyrrolidine-HOBt" **1** as an effective organocatalyst for the enantioselective Michael addition of aldehydes to nitroolefins. This catalytic method was found to be effective in terms of yield and enantioselectivities, when performed in water using 20 mol% of catalyst and 10 mol% of benzoic acid as an additive at 0 °C/rt for 24–48 h. Further investigations to extend the scope of this catalyst for other transformations are underway in our laboratory.

4. Experimental

4.1. General

All solvents and reagents were purified by standard techniques. Crude products were purified by column chromatography on silica gel of 100–200 mesh. IR spectra were recorded on Perkin–Elmer 683 spectrometer. Optical rotations were obtained on Jasco Dip 360 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Brucker Avance 300. Chemical shifts were reported in parts per million with respect to internal TMS. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL. Chiral HPLC analysis was carried out on chiral pak OD-H, IA or columns using a mixture of isopropanol and hexanes as the eluent.

4.1.1. General procedure for the Michael addition of α,α-disubstituted aldehydes to nitroolefins

To a mixture of catalyst **1** (20 mol%), and aldehyde (4 mmol) in water (0.5 mL)was added PhCOOH (10 mol%) and stirred for 20 min. at 0 °C or at rt. Then, nitroolefin (1 mmol) was added to the resulting mixture and stirred for appropriate time (Tables 7–10) at 0 °C or at rt. After completion of the reaction (monitored by TLC), the mixture was purified by silica-gel column chromatography to afford the desired product. Relative and absolute configurations of the products were determined by comparison of ^{1}H NMR, ^{13}C NMR and specific rotation values with those reported in the literature.[8]

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