The *Baylis–Hillman* Adducts as Valuable Source for One-Pot Multi-Step Synthesis: A Facile Synthesis of Substituted Piperidin-2-ones

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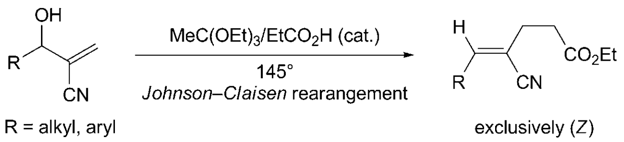
A facile, convenient, and one-pot multi-step synthesis of substituted piperidin-2-ones from the *Baylis–Hillman* alcohols derived from various aldehydes and acrylonitrile, involving *Johnson–Claisen* rearrangement, reduction of an α,β-unsaturated nitrile moiety into the saturated amine-skeleton, followed by cyclization, in an operationally simple procedure, is described.

Introduction. – In continuation of our interest in the synthesis of heterocyclic molecules [1], we herein report a simple, facile, and one-pot multi-step synthesis of piperidin-2-one derivatives, that is, 5-substituted and 3,5-disubstituted piperidin-2-ones from *Baylis–Hillman* adducts. The piperidin-2-one moiety occupies a special place in nitrogen heterocyclic chemistry because of the presence of this moiety in a variety of biologically important compounds and therefore, the development of simple procedures for the synthesis of such frameworks is an attractive endeavor in heterocyclic chemistry [2][1]).

Results and Discussion. – Applications of the *Baylis–Hillman* adducts in various organic transformation methodologies have been well documented in the literature [1][4][5]. We have, some time ago, developed a stereo-defined synthesis of functionalized trisubstituted alkenes, *i.e.*, ethyl (4*Z*)-4-cyanoalk-4-enoates *via* the *Johnson–Claisen* (*Claisen* orthoester) rearrangement[2]) of the *Baylis–Hillman* alcohols, which represent CN-substituted allylic alcohols, with triethyl orthoacetate (*Scheme 1*) [7a][3]).

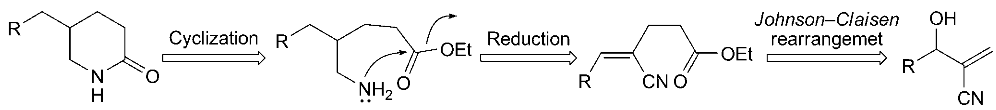
Scheme 1. Johnson–Claisen *Rearrangement of 3-Hydroxy-2-methylidenealkanenitriles* [6]



[1]) For a leading review on synthesis of piperidones and piperidines, see [3].
[2]) For leading references on the *Johnson–Claisen* rearrangement, see [6].
[3]) For other *Johnson–Claisen* rearrangement of *Baylis–Hillman* adducts, see [7b][7c].

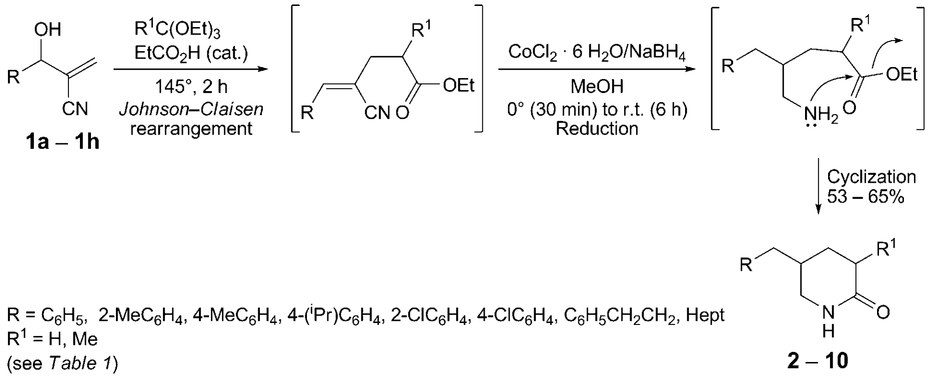
It occurred to us that (4*Z*)-4-cyanoalk-4-enoates would be excellent starting materials for the synthesis of piperidin-2-one derivatives by complete reduction of the ene-nitrile functionality into an amino group, which would be in the proximity of the ester group for a possible cyclization to a six-membered heterocyclic framework with a provision for having a different substitution profile at the 3- and 5-positions. It also occurred to us that the entire operation can be performed in one-pot, starting from the *Baylis–Hillman* adducts involving a *Johnson–Claisen* rearrangement and reduction, followed by cyclization, to provide the piperidin-2-one framework (*Scheme 2*).

Scheme 2. *Retro-Synthetic Aspect for the Synthesis of the Piperidin-2-one Framework*



Accordingly, we have first selected 2-[hydroxy(phenyl)methyl]prop-2-enenitrile (**1a**), a *Baylis–Hillman* alcohol (*B–H* alcohol) derived from benzaldehyde and acrylonitrile (= prop-2-enenitrile), as a substrate for this multi-step probing. The best result was obtained when **1a** (1 mmol) was treated with triethyl orthoacetate (1 ml) at 145° in the presence of a catalytic amount of propanoic acid (3 drops) for 2 h, followed (after removing the excess of orthoester under reduced pressure) by treatment with $CoCl_2 \cdot 6\,H_2O$ (2 mmol)/$NaBH_4$ (10 mmol)[4]) in MeOH at 0° for 30 min and then for 6 h at room temperature, thus providing 5-benzylpiperidin-2-one (**2**) as a colorless solid in 60% yield, after workup and purification by column chromatography (*Scheme 3* and *Table 1*, *Entry 1*). This was indeed an encouraging result in the sense that three steps were performed in one-pot to produce the desired **2** in an acceptable yield.

Scheme 3. *One-Pot Three-Step Synthesis of 5-Substituted Piperidin-2-ones*



R = C_6H_5, 2-MeC_6H_4, 4-MeC_6H_4, 4-(^{i}Pr)C_6H_4, 2-ClC_6H_4, 4-ClC_6H_4, $C_6H_5CH_2CH_2$, Hept
R^1 = H, Me
(see *Table 1*)

To understand the general character of this reaction, we have, according to *Scheme 3*, successfully transformed representative *B–H* alcohols **1b**–**1f**, obtained from various aromatic aldehydes and acrylonitrile, into the corresponding 5-arylmethylpi-

[4]) For literature reports on reduction of CN group using $CoCl_2 \cdot 6\,H_2O/NaBH_4$, see [8].

Table 1. *One-Pot Three-Step Synthesis of Substituted piperidin-2-ones*[a])

Entry	*B–H* alcohol	R	R^1	Product[b])	Yield[c]) [%]
1	**1a**	C_6H_5	H	**2**	60
2	**1b**	$2\text{-}MeC_6H_4$	H	**3**	58
3[d])	**1c**	$4\text{-}MeC_6H_4$	H	**4**	64
4	**1d**	$4\text{-}({}^iPr)C_6H_4$	H	**5**	56
5	**1e**	$2\text{-}ClC_6H_4$	H	**6**	53
6	**1f**	$4\text{-}ClC_6H_4$	H	**7**	55
7[d])	**1g**	$C_6H_5CH_2CH_2$	H	**8**	59
8	**1h**	Heptyl	H	**9**	65
9[e])	**1a**	C_6H_5	Me	**10**	61

[a]) All reactions were carried out on a 1 mmol scale of *B–H* alcohols **1a**–**1h**, which were prepared according to a literature procedure [9]. [b]) Compounds **2**–**10** were obtained as colorless solids and were fully characterized (see *Exper. Part*). [c]) Yields are of the pure products, based on *B–H* alcohols. [d]) The structures of these molecules were also established by X-ray diffraction analysis (*Figs. 1* and *2*, *Table* 2). [e]) Isolated as a 1 : 1 mixture of diastereoisomers.

peridin-2-ones **3**–**7** in 53–64% yield of isolated products (*Table 1*, *Entries 2*–*6*). With the same procedure, we also have successfully transformed *B–H* alcohols **1g** and **1h**, obtained from the corresponding aliphatic aldehydes (hydrocinnamaldehyde and octanal) and acrylonitrile, into 5-alkylpiperidin-2-ones **8** and **9** in 59 and 65% yield, respectively (*Table 1*, *Entries* 7 and *8*). Piperidin-2-ones **4** and **8** delivered suitable single crystals for an X-ray crystal-structure analysis, which further confirmed the structures of these compounds (*Figs. 1* and *2*, *Table* 2).

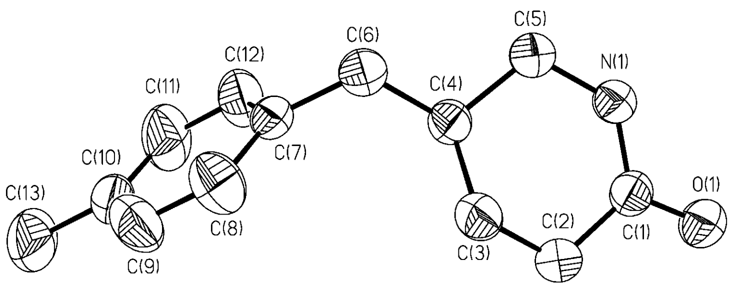


Fig. 1. *ORTEP Diagram of compound* **4** (H-atoms are omitted for clarity)

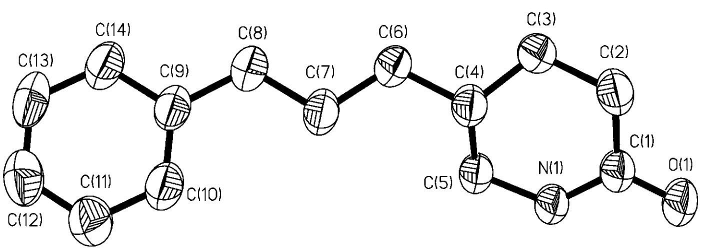


Fig. 2. *ORTEP Diagram of compound* **8** (H-atoms are omitted for clarity)

Table 2. *Crystallographic Data for Compounds* **4** *and* **8**[a])

		4	**8**
Crystallized from		MeOH	MeOH
Empirical formula		$C_{13}H_{17}NO$	$C_{14}H_{19}NO$
Formula weight [g mol^{-1}]		203.28	217.30
Crystal color, habit		colorless, plate	colorless, block
Crystal dimensions [mm]		$0.42 \times 0.21 \times 0.07$	$0.46 \times 0.38 \times 0.23$
Temperature [K]		298	298
Crystal system		Monoclinic	Triclinic
Space group		$P2_1/c$	$P\bar{1}$
Z		4	2
Reflections for cell determination		2316	2438
2θ Range for cell determination [°]		1.43 – 26.27	1.49 – 26.07
Unit cell parameters	a [Å]	14.335(5)	5.8744(15)
	b [Å]	5.812(2)	8.040(2)
	c [Å]	14.026(5)	14.260(4)
	α [°]	90.00	74.375(4)
	β [°]	96.357(6)	89.430(4)
	γ [°]	90.00	73.780(4)
V [Å^3]		1161.4(7)	621.2(3)
$F(000)$		440	236
D_x [g cm^{-3}]		1.163	1.162
μ (MoK_α) [mm^{-1}]		0.073	0.072
Transmission factors [min; max]		0.9700; 0.9949	0.9674; 0.9835
Scan type		Φ and ω	Φ and ω
$2\theta_{max}$ [°]		26.27	26.07
Reflections measured		11271	6507
Symmetry-independent reflections		2316	2438
R_{int}		0.0270	0.0244
R_1, wR_2 [$I \geq 2\sigma(I)$]		0.0464, 0.1246	0.0571, 0.1589
R_1, wR_2 (all data)		0.0684, 0.1386	0.0716, 0.1714
Goodness-of-fit on F^2		1.045	1.023

[a]) Detailed X-ray crystallographic data of **4** and **8** are available from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK under CCDC-635054 and -635055, respectively.

With the intention to extend this new synthesis to the preparation of 3,5-disubstituted piperidin-2-ones, we have used triethyl orthopropanoate for the *Johnson – Claisen* rearrangement. Thus, *B – H* alcohol **1a**, on successive treatment with triethyl orthopropanoate and $CoCl_2 \cdot 6\,H_2O/NaBH_4$ according to the same procedure (as in the case of triethyl orthoacetate) provided 5-benzyl-3-methylpiperidin-2-one (**10**) in 61% yield (*Scheme 3* and *Table 1*, *Entry 9*). However, the ^{1}H- and ^{13}C-NMR spectra clearly indicate that this molecule is *ca.* 1:1 mixture of diastereoisomers. In the ^{1}H-NMR spectrum, *Me*–C(3) appeared as two *doublet*s of equal intensities at 1.19 and 1.23 ppm, thus indicating for **10** a 1:1 mixture of diastereoisomers. Two *singlet*s at 6.46 and 6.50 ppm are attributed to the NH groups of the diastereoisomers. In the ^{13}C-NMR spectrum, two signals at 175.7 and 176.2 ppm for one C=O, two signals at 139.2 and

139.4 ppm for one quaternary C-atom of the Ph group, and twelve signals for six aliphatic C-atoms clearly indicate that this compound is a mixture of diastereoisomers.

In conclusion, we have successfully developed a convenient and operationally simple one-pot three-step procedure for the synthesis of 5-substituted and 3,5-disubstituted piperidin-2-ones from *Baylis–Hillman* alcohols, by *Johnson–Claisen* rearrangement, reduction, and cyclization, thus demonstrating the application of *Baylis–Hillman* adducts as a versatile source for one-pot multi-step syntheses.

Experimental Part

General. M.p.: *Superfit* (India) capillary melting point apparatus; uncorrected. IR Spectra: *JASCO-FT-IR* model *5300* spectrometer using solid samples as KBr plates, in cm^{-1}. ^1H- (400 MHz) and ^{13}C-NMR (50 MHz) spectra: in $CDCl_3$ on a *BRUKER-AVANCE-400* and *BRUKER-AC-200* spectrometer; δ in ppm, J in Hz; tetramethylsilane (TMS, 0 ppm) as internal standard. MS: *Shimadzu-LCMS-2010A* mass spectrometer. Elemental analyses: *Thermo-Finnigan Flash EA 1112* analyzer. X-Ray diffraction measurements: at 298 K on a *Bruker SMART APEX CCD* area detector system, using graphite monochromated MoK_α radiation and fine-focus sealed tube ($\lambda = 0.71073$ Å).

5-Benzylpiperidin-2-one (**2**). To a stirred soln. of propanenitrile **1a** (1 mmol, 0.159 g) in triethyl orthoacetate (=1,1,1-triethoxyethane; 1 ml) was heated at 145° in the presence of a cat. amount of propanoic acid (3 drops) for 2 h. Excess orthoester (along with propanoic acid) was distilled off under reduced pressure. The residue was diluted with MeOH (8 ml), and $CoCl_2 \cdot 6\,H_2O$ (2 mmol, 0.476 g) was added. The resulting soln. was cooled to 0°, and $NaBH_4$ (10 mmol, 0.38 g) was added in three portions within 15 min (H_2 gas evolution was observed). The mixture (black formed precipitate) was stirred for 30 min at 0°, and then allowed to warm to r.t. and stirred for further 6 h. MeOH was removed under reduced pressure. Then, the residue was diluted with 4N HCl (15 ml) and extracted with AcOEt (3 × 20 ml). The combined org. layers were washed with H_2O (20 ml) and dried over anh. Na_2SO_4. After evaporation of the solvent, the residue was purified by CC (SiO_2; AcOEt) to furnish 5-benzylpiperidin-2-one (**2**) as a colorless solid in 60% (0.114 g) yield. M.p. 107–109°. IR: 3300–2800 (multiple bands), 1662. ^1H-NMR: 1.46–1.60 (*m*, 1 H); 1.85–1.96 (*m*, 1 H); 2.00–2.15 (*m*, 1 H); 2.25–2.49 (*m*, 2 H); 2.55–2.70 (*m*, 2 H); 2.95–3.04 (*m*, 1 H); 3.20–3.29 (*m*, 1 H); 6.27 (br. *s*, 1 H, D_2O exchangeable); 7.14 (*d*, $J = 6.8$, 2 H); 7.19–7.34 (*m*, 3 H). ^{13}C-NMR: 26.9; 30.7; 35.1; 39.6; 47.3; 126.5; 128.6; 128.9; 139.2; 172.6. LC-MS: 190 ($[M+H]^+$). Anal. calc. for $C_{12}H_{15}NO$: C 76.16, H 7.99, N 7.40; found: C 76.18, H 8.04, N 7.45.

5-(2-Methylbenzyl)piperidin-2-one (**3**). Yield: 58%. M.p. 103–105°. IR: 3300–2800 (multiple bands), 1666. ^1H-NMR: 1.49–1.64 (*m*, 1 H); 1.83–1.97 (*m*, 1 H); 2.00–2.12 (*m*, 1 H); 2.25–2.50 (*m*, 5 H); 2.63 (*d*, $J = 7.2$, 2 H); 2.97–3.07 (*m*, 1 H); 3.21–3.30 (*m*, 1 H); 6.35 (br. *s*, 1 H, D_2O exchangeable); 7.05–7.20 (*m*, 4 H). ^{13}C-NMR: 19.4; 27.0; 30.6; 33.9; 36.7; 47.2; 125.9; 126.5; 129.7; 130.5; 135.9; 137.5; 172.7. LC-MS: 204 ($[M+H]^+$). Anal. calc. for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.89; found: C 76.67, H 8.49, N 6.93.

5-(4-Methylbenzyl)piperidin-2-one (**4**). Yield: 64%. M.p. 111–113°. IR: 3200–2850 (multiple bands), 1662. ^1H-NMR: 1.45–1.58 (*m*, 1 H); 1.85–1.94 (*m*, 1 H); 1.99–2.10 (*m*, 1 H); 2.25–2.49 (*m*, 5 H); 2.51–2.65 (*m*, 2 H); 2.94–3.03 (*m*, 1 H); 3.20–3.28 (*m*, 1 H); 6.19 (br. *s*, 1 H); 7.03 (*d*, $J = 7.6$, 2 H); 7.10 (*d*, $J = 7.6$, 2 H). ^{13}C-NMR: 21.0; 26.8; 30.6; 35.2; 39.2; 47.2; 128.7; 129.2; 135.9; 136.1; 172.6. LC-MS: 204 ($[M+H]^+$). Anal. calc. for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.89; found: C 76.70, H 8.41, N 7.00.

5-[4-(1-Methylethyl)benzyl]piperidin-2-one (**5**). Yield: 56%. M.p. 95–96°. IR: 3320–2850 (multiple bands), 1664. ^1H-NMR: 1.23 (*d*, $J = 6.8$, 6 H); 1.45–1.59 (*m*, 1 H); 1.86–1.95 (*m*, 1 H); 1.99–2.12 (*m*, 1 H); 2.25–2.67 (*m*, 4 H); 2.83–3.04 (*m*, 2 H); 3.21–3.28 (*m*, 1 H); 6.11 (br. *s*, 1 H, D_2O exchangeable); 7.06 (*d*, $J = 7.8$, 2 H); 7.15 (*d*, $J = 7.8$, 2 H). ^{13}C-NMR: 24.0; 26.9; 30.6; 33.7; 35.1; 39.2; 47.2; 126.5; 128.8; 136.5; 146.9; 172.7. LC-MS: 232 ($[M+H]^+$). Anal. calc. for $C_{15}H_{21}NO$: C 77.88, H 9.15, N 6.05; found: C 77.96, H 9.17, N 6.03.

5-(2-Chlorobenzyl)piperidin-2-one (**6**). Yield: 53%. M.p: 106–108°. IR: 3200–2950 (multiple bands), 1672. ^1H-NMR: 1.48–1.60 (*m*, 1 H); 1.85–1.96 (*m*, 1 H); 2.01–2.14 (*m*, 1 H); 2.27–2.50 (*m*, 2 H); 2.54 – 2.70 (*m*, 2 H); 2.94 – 3.05 (*m*, 1 H); 3.21 – 3.30 (*m*, 1 H); 6.05 (br. *s*, 1 H); 7.08 (*d*, $J = 7.6$, 1 H); 7.11 – 7.33 (*m*, 2 H); 7.36 (*d*, $J = 8.0$, 1 H). ^{13}C-NMR: 26.9; 30.6; 33.7; 37.0; 47.2; 126.8; 128.0; 129.8; 131.1; 134.2; 137.1; 172.5. LC-MS: 224 ($[M + H]^+$), 226 ($[M + 2 + H]^+$). Anal. calc. for $C_{12}H_{14}ClNO$: C 64.43, H 6.31, N 6.26; found: C 64.57, H 6.39, N 6.25.

5-(4-Chlorobenzyl)piperidin-2-one (**7**). Yield: 55%. M.p: 109 – 111°. IR: 3300 – 2950 (multiple bands), 1657. ^{1}H-NMR: 1.45 – 1.59 (*m*, 1 H); 1.83 – 1.93 (*m*, 1 H); 1.98 – 2.12 (*m*, 1 H); 2.24 – 2.49 (*m*, 2 H); 2.52 – 2.68 (*m*, 2 H); 2.92 – 3.03 (*m*, 1 H); 3.18 – 3.29 (*m*, 1 H); 6.15 (br. *s*, 1 H); 7.06 (*d*, $J = 8.0$, 2 H); 7.27 (*d*, $J = 8.0$, 2 H). ^{13}C-NMR: 26.7; 30.5; 35.0; 38.8; 47.1; 128.6; 130.2; 132.2; 137.7; 172.5. LC-MS: 224 ($[M + H]^+$), 226 ($[M + 2 + H]^+$). Anal. calc. for $C_{12}H_{14}ClNO$: C 64.43, H 6.31, N 6.26; found: C 64.28, H 6.30, N 6.21.

5-(3-Phenylpropyl)piperidin-2-one (**8**). Yield: 59%. M.p. 88 – 90°. IR: 3300 – 2840 (multiple bands), 1664. ^{1}H-NMR: 1.29 – 1.50 (*m*, 3 H); 1.56 – 1.95 (*m*, 4 H); 2.26 – 2.47 (*m*, 2 H); 2.56 – 2.66 (*m*, 2 H); 2.88 – 2.97 (*m*, 1 H); 3.28 – 3.38 (*m*, 1 H); 6.06 (br. *s*, 1 H); 7.13 – 7.31 (*m*, 5 H). ^{13}C-NMR: 26.9; 28.6; 30.6; 32.6; 33.0; 35.8; 47.4; 125.7; 128.2; 141.9; 172.6. LC-MS: 218 ($[M + H]^+$). Anal. calc. for $C_{14}H_{19}NO$: C 77.38, H 8.81, N 6.45; found: C 77.55, H 8.81, N 6.48.

5-Octylpiperidin-2-one (**9**). Yield: 65%. M.p. 59 – 61°. IR: 3300 – 2800 (multiple bands), 1674. ^{1}H-NMR: 0.88 (*t*, $J = 6.8$, 3 H); 1.20 – 1.51 (*m*, 15 H); 1.71 – 1.80 (*m*, 1 H); 1.84 – 1.95 (*m*, 1 H); 2.24 – 2.48 (*m*, 2 H); 2.89 – 2.98 (*m*, 1 H); 3.29 – 3.38 (*m*, 1 H); 6.19 (br. *s*, 1 H, D_2O exchangeable). ^{13}C-NMR: 14.1; 22.7; 27.0; 27.1; 29.3; 29.5; 29.7; 30.8; 31.9; 33.1; 47.7; 172.8. LC-MS: 212 ($[M + H]^+$). Anal. calc. for $C_{13}H_{25}NO$: C 73.88, H 11.92, N 6.63; found: C 73.69, H 11.99, N 6.60.

5-Benzyl-3-methylpiperidin-2-one (**10**). Yield: 61%. M.p. 84 – 86°. IR: 3300 – 2900 (multiple bands), 1658. ^{1}H-NMR: 1.19, 1.23 (2*d*, $J = 6.8$, 3 H); 1.60 – 2.78 (*m*, 6 H); 2.92 – 3.05 (*m*, 1 H); 3.15 – 3.30 (*m*, 1 H); 6.46, 6.50 (2 br. *s*, NH of diastereoisomers, 1 H); 7.05 – 7.38 (*m*, 5 H). ^{13}C-NMR: 17.1; 18.5; 31.7; 33.8; 34.3; 35.7; 35.9; 36.3; 39.2; 40.3; 46.9; 47.9; 126.3; 128.5; 128.8; 139.2; 139.4; 175.7; 176.2. ^{1}H- and ^{13}C-NMR data clearly indicate that this product is a mixture of 1 : 1 diastereoisomers.

We thank *DST* (New Delhi) for funding this project. *R. J. R.* thanks *CSIR* (New Delhi) for his research fellowship. *D. V. L.* thanks *UGC* (New Delhi) for his research fellowship. We thank *UGC* (New Delhi) for support and providing some instrumental facilities. We thank the *National Single Crystal X-Ray Facility* funded by DST. We also thank Professor *S. Pal*, School of Chemistry, University of Hyderabad for helpful discussions regarding X-ray data analysis.

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Received October 5, 2009