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PAPER

Transimination reactions in [b-3C-im][NTf_2] ionic liquid†

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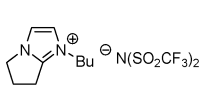
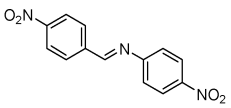
Compared to conventional molecular solvents, the ionic liquid [b-3C-im][NTf_2] was found to promote transimination reactions with up to ~100-fold rate enhancement. This rate effect observed at ambient temperature might be explained by the fact that the ionic liquid displays weak Lewis acidity with very low, if any, nucleophilicity and its imidazolium cation is expected to interact by associating with, and thus electrophilically activating, the C═N bond of the starting imine, leading to increased stabilization of the polar, charged intermediate species and ultimately, rapid product formation. Moreover, the presence of 1 mol% $Sc(OTf)_3$ in [b-3C-im][NTf_2] further facilitates the transimination reactions studied.

Introduction

As one of few reversible covalent bonds, imine formation and exchange are fundamental and ubiquitous reactions in organic chemistry,[1] and have found unique applications in the chemoselective conjugation of biomolecules and the folding study of supramolecular assemblies.[2] Although Schiff's base has been exhaustively investigated and studied for decades, its impact in chemical research has nevertheless been compromised, primarily due to its slow kinetics of imine bond exchange that limit the rapid response and sensitivity requirements for any new applications.[3] Herein we describe our development of a system that uses the ionic liquid [b-3C-im][NTf_2], previously developed by us,[4] to significantly accelerate the transimination reactions of imines **1** and **2** with various amines. This transimination reaction carried out in an ionic liquid, to our knowledge, has not been explored.[5]



[b-3C-im][NTf_2]



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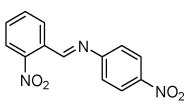

2

Ionic liquids are low-melting molten salts composed entirely of ions, and many of them are liquid at room temperature.[6] As neoteric solvents, ionic liquids carry numerous desirable properties, such as a wide liquid range, thermal stability, excellent solubility with many small molecules, attractive recyclability, and negligible vapor pressure that are well suited for a myriad of applications. Of them, ionic liquids with high polarity and negligible vapor pressure have been recognized and employed as environmentally benign media for a range of chemical processes and have been found to outperform molecular solvents in a number of synthetic reactions.[6] These include aziridination,[7] Michael reaction,[8] Diels–Alder cycloaddition,[9] acylative cleavage of ethers,[10] Heck reaction,[11] and Friedel–Crafts reaction.[12]

In our laboratory, we have a program to evaluate ionic liquids as novel and stable media for synthetic and biochemical applications.[4,5,13] We, and others, for example, have employed ionic liquids as reaction media to afford syntheses of complex heterocycles.[6b,13d,13e] With continuous development of novel ionic liquids for new applications, we exploited [b-3C-im][NTf_2] ionic liquid as the solvent to greatly facilitate the transimination reactions studied. This ionic liquid was selected primarily for its superior chemical stability over the common [bmim][PF_6] and [bdmim][PF_6].[4] In this work we report a more detailed study of the exchange in Schiff bases **1** and **1a**, and extend it to other imine systems.

Results and discussion

The major difference between molecular solvents and ionic liquids is the weak electrostatic association of organic cations with charge diffuse anions in ionic liquids. As known in the chemistry literature, many organic reactions performed in molecular solvents are catalyzed by Lewis acids and, recently, a number of these reactions have been reported to be significantly accelerated when carried out in pure ionic liquids.[14,15] Although other effects have been discussed and reported,[15] this rate increase observed in pure ionic liquids in some reactions was attributed to the inherent weak Lewis acidity of ionic liquids employed.[14] Realizing that metal triflates notably contributed to the transimination reactions in molecular solvents,[2c,3] we therefore envisaged that, without metal triflates, it should be possible to promote such reactions in ionic liquids. The transimination reaction studied is illustrated in Scheme 1.

We first studied the influence of the [b-3C-im][NTf_2] ionic liquid in the transimination reaction of isopropylamine with the imine **1**, *N*-(4-nitrobenzylidene)-4-nitroaniline, used as a model substrate (Scheme 2). Since transimination reactions can be sensitive to

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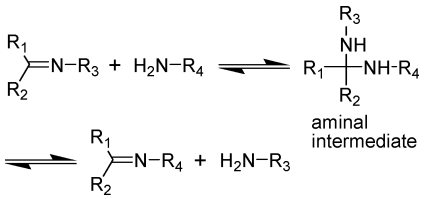
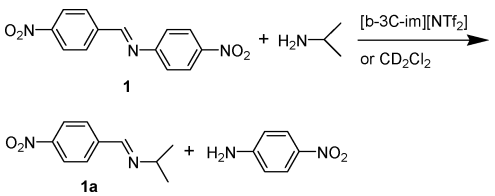
† Electronic supplementary information (ESI) available: Figures S1–S3, complete ^1H and ^{13}C NMR spectra of all compounds **1**, **1a–c**, **2**, and **2a–c**. See DOI: 10.1039/c0ob01094d



Scheme 1 A reversible transimination reaction.



Scheme 2 The transimination reaction of the imine **1** with isopropylamine, catalyzed by [b-3C-im][NTf_2] ionic liquid.

water, the hydrophobic [b-3C-im][NTf_2] ionic liquid was chosen for use in this study. The imine **1**, composed of an aromatic aldehyde and arylamine, was selected, rather than an aliphatic one, largely due to its known thermodynamic stability.[16] It is also known in the literature that electron-withdrawing substituents, such as nitro groups on aryl aldimines, retard hydrolysis.[17] The protocols developed by Chakraborti *et al.*[18] and Andrade *et al.*[19] were followed to prepare the imine substrates **1** and **2**, and the imine products **1a–c** and **2a–c**, respectively. All aldimine compounds prepared (**1**, **1a–c**, **2**, and **2a–c**) were readily purified with diethyl ether and isolated in high purity, and gave satisfactory spectroscopic data (for ^{1}H and ^{13}C NMR spectra, see ESI†). These results indicate that, irrespective of their nature or position, substituent groups present on aromatic rings react smoothly and the resulting corresponding imines are obtained with high isolated yields (80–89%, see Experimental section). Interestingly, sterically hindered *o*-nitrobenzaldehyde gave its corresponding imine in high yield, inferring that the nitro group around the reaction site does not affect its reactivity in imine formation. NMR spectra of the aldimines studied show that they all exist in a single form (likely the *trans* isomer) with no other stereoisomeric *cis* form being detected (ESI†).

When imine **1** (15 mM) was reacted with isopropylamine (15 mM) in deuterated dichloromethane (a common solvent used for transimination reactions) at ambient temperature, a time of 153 h (9190 min) was necessary to complete the reaction (Fig. 1). The time required at 50% conversion ($t_{1/2}$) for the transimination in CD_2Cl_2 was approximately 2070 min. The progress of the reaction could be readily monitored at the imine protons N=CH on both **1** and **1a** by ^{1}H NMR. It is also noted that the irreversible nature of the transimination reaction indicated the non-equilibrium formation of the Schiff base **1a** (Scheme 2). This could be understood by the fact that the use of *p*-nitroaniline, as an excellent leaving group, inhibits the reverse reaction of the imine adduct **1a** that was formed. To our delight, when carried out in [b-3C-im][NTf_2] ionic liquid, this transimination reaction was greatly accelerated and completed in 7.5 h (450 min) with a $t_{1/2}$ of approximately 150 min (Fig. 1). A kinetic study, shown in Fig. 1, clearly demonstrates the remarkable 14-fold difference in reaction rate ($t_{1/2}$) obtained in ionic liquid and in deuterated dichloromethane. This result suggested that the transimination reaction was greatly promoted if carried out in the [b-3C-im][NTf_2] ionic liquid.

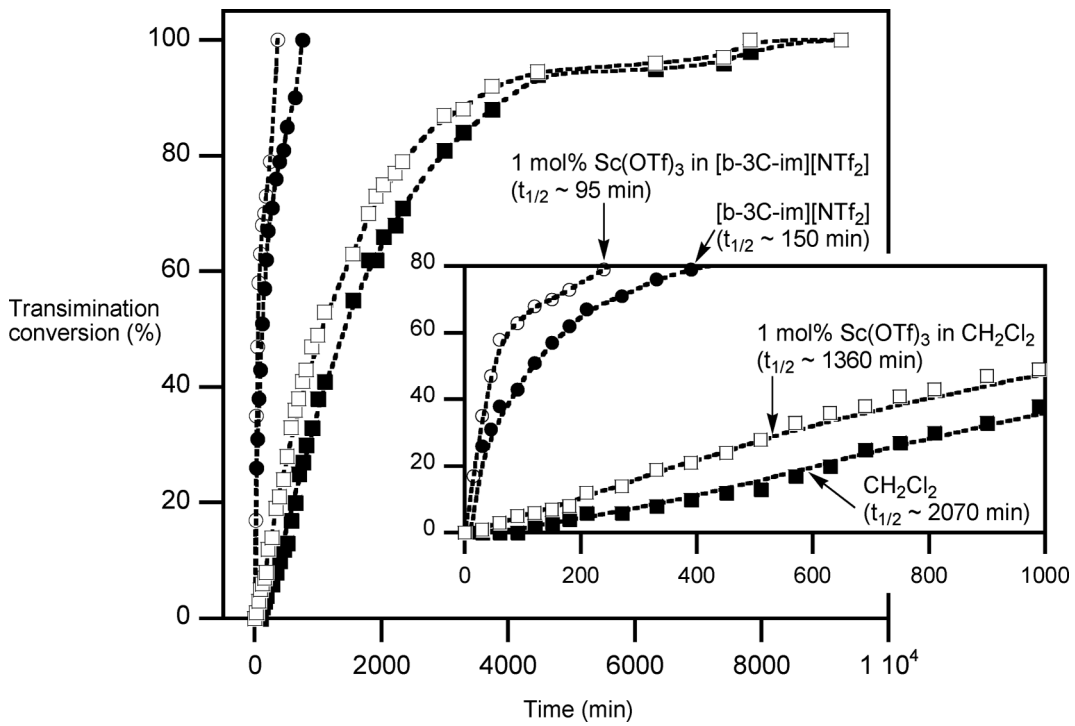
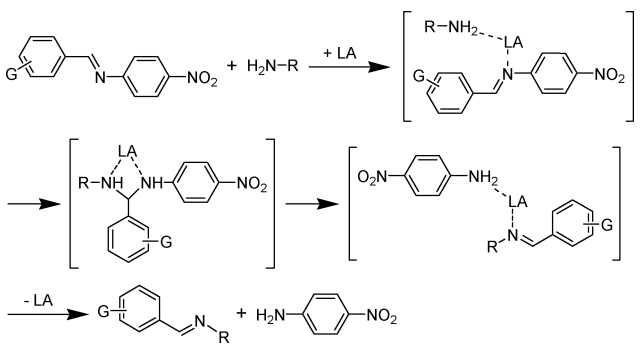


Fig. 1 Kinetic measurements of the transimination reactions of *N*-(4- nitrobenzylidene)-4-nitroaniline **1** (15 mM) with isopropylamine (15 mM) in [b-3C-im][NTf_2] ionic liquid and CD_2Cl_2 solvent at ambient temperature. Inset: details of early conversions of the transimination reactions. The progress of the transimination reactions could be readily monitored by ^{1}H NMR.

Solvent polarity can influence the outcome of chemical reactions. Imidazolium ionic liquids are polar; the polarity of these ionic liquids has previously been determined to be greater than common molecular solvents, such as CH_2Cl_2 and acetonitrile, similar to that of lower alcohols and dimethylsulfoxide (DMSO), but clearly less than that of water.[20,21] In order to correlate solvent polarity with the transimination reaction efficiency, we decided to investigate the solvent effect of the transimination reaction of **1** to **1a** in two polar molecular solvents: the aprotic DMSO and the protic methanol.[21] For reactions performed in DMSO-d_6 at ambient temperature, to our surprise, the ^{1}H NMR result showed that the imine adduct **1a** was not observed at all and only its polar aminal intermediate **S1** was fortuitously accumulated and obtained (Fig. S1, ESI†). This behavior was rather unexpected, since other transimination reactions could be studied in DMSO-d_6.[3] Under our experimental conditions (*i.e.*, 15 mM each for **1** and isopropylamine), the polar DMSO promoted the nucleophilic addition of isopropylamine to imine **1**, appeared to stabilize and "lock in" its polar aminal species **S1**, and essentially entrapped the amine reagent (Fig. S1, ESI†). As a result, this transimination reaction proceeded incompletely in this polar aprotic solvent. Attempts to perform the same transimination reaction in methanol-d_4 were also unsuccessful under our conditions (Fig. S2, ESI†).[3,22] The striking feature of this reaction conducted in deuterated methanol was that, in the presence of isopropylamine, methanol effectively acted as a nucleophile and readily reacted with the imine **1** to afford a polar hemiaminal ether intermediate **S2**, stabilized and trapped by the polar methanol solvent (Fig. S2, ESI†). This nucleophilicity of methanol for the polar reaction is not totally unexpected, and therefore it may be thought of as a reacting solvent for transimination reactions. In our hands, although DMSO, methanol and ionic liquids have similar solvent polarity properties, only [b-3C-im][NTf_2] ionic liquid greatly promotes and smoothly proceeds to completion of the transimination reactions studied.

When using [b-3C-im][Br] ionic liquid for the reaction of imine **1** with isopropylamine, transimination proceeded 2.7 times faster than when carried out with [b-3C-im][NTf_2] ionic liquid, suggesting that the imidazolium cation in [b-3C-im][Br] is more Lewis acidic than that of [b-3C-im][NTf_2].[23] This rate increase with [b-3C-im][Br] directly correlates with its significant downfield shift of imidazolium ring H-4 and H-5 protons in the ^{1}H NMR data: 7.51 and 7.61 ppm for [b-3C-im][Br] *vs.* 7.19 and 7.25 ppm for [b-3C-im][NTf_2], respectively, clearly indicating more electron deshielding and deficiency, and, accordingly, increasing the Lewis acidic nature of the imidazolium cation in [b-3C-im][Br] (Fig. S3, ESI†).[24] This result, along with the aforementioned results, is entirely consistent with the Lewis acidity and high polarity interpretations of [b-3C-im][NTf_2] ionic liquid for high reaction rates for polar transimination reactions.

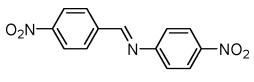
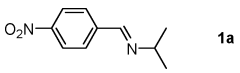
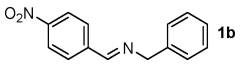
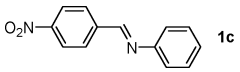
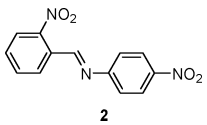
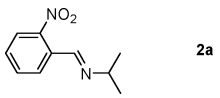
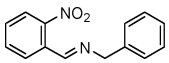
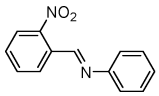
Lewis acidic metal ions are known to catalyze transimination reactions in molecular solvents.[2c,3] The Lewis acid catalyst $Sc(OTf)_3$ was selected in this study primarily because of its reported effectiveness in the catalysis of transimination reactions.[3] We employed infrared spectroscopy (FT-IR) to monitor the progress of the transimination reaction of **1** to **1a**. This IR assay, however, gave variable results, due mostly to the overlapped C═N bands centered around 1630 cm^{-1} in IR spectra. This transimination reaction was then followed by ^{1}H NMR, rates were quantitated by integration, and the data obtained were plotted in Fig. 1. Not surprisingly, as shown in Fig. 1, $Sc(OTf)_3$ promotes the transimination reaction in both ionic liquid and deuterated dichloromethane. With 1 mol% $Sc(OTf)_3$ in [b-3C-im][NTf_2] solvent, 50% conversion of **1** to **1a** was achieved shortly after 95 min, while a time of 150 min was required without the catalyst. A significant reduction in reaction time at 50% conversion in CD_2Cl_2 (1360 *vs.* 2070 min at $t_{1/2}$) was also obtained with 1 mol% $Sc(OTf)_3$ Lewis acid catalyst (Fig. 1). In our hands, no hydrolysis or decomposition of imines **1** and **1a** were observed when carried out in [b-3C-im][NTf_2] ionic liquid and CD_2Cl_2 during the entire experiment. Moreover, under identical experimental condition, the imine **1a** and *p*-nitroaniline did not show any detectable transimination reaction in both CD_2Cl_2 and [b-3C-im][NTf_2] within the experimental time (7 d and 820 min, respectively) at ambient temperature, evidently indicating the irreversibility of the transimination reaction of **1** to **1a**, and that the *p*-nitroaniline was an excellent leaving group. The reaction course of this Lewis acid-catalyzed transimination may be explained on the basis of Scheme 3. As shown in Scheme 3, the Lewis acid activates the starting imine and accordingly facilitates the reaction of imine exchange. In the mechanism, the Lewis acid may be the [b-3C-im] imidazolium cation in ionic liquid or the Sc(III) cation in $Sc(OTf)_3$.



Scheme 3 A mechanistic hypothesis for the transimination reaction catalyzed by a Lewis acid (LA). In this work, LA may be the [b-3C-im] cation, loosely associated with its anion [NTf_2], in ionic liquid, or $Sc(OTf)_3$.

Encouraged as we were by the results of the **1** → **1a** process, the substrate scope of this ionic liquid-promoted transimination reaction was examined. As shown in Table 1, in all cases the transiminations proceeded with complete reaction conversion and increased reaction rates in [b-3C-im][NTf_2] ionic liquid. The sterically hindered isopropylamine may account for the relatively slow conversion of imines **1** and **2** to imines **1a** and **2a**, respectively, as compared to other amines in both ionic and molecular solvents (entries 1 and 4, Table 1). In the cases of aliphatic benzylamine and aromatic aniline, transiminations in [b-3C-im][NTf_2] ionic liquid proceeded to completion in minutes, whereas hours of reaction time were required for both reactions carried out in CD_2Cl_2 (entries 2, 3, 5, and 6, Table 1). Table 1 also shows that, irrespective of the position of the nitro substituent group present on aromatic ring, both starting imines (**1** and **2**) reacted smoothly and gave the corresponding imines (**1a–c** and **2a–c**), inferring that the nitro group around the reaction site does not significantly affect its reactivity in imine formation. It is worth noting that, for the reaction of benzylamine with imine **1**, the largest rate increase

Table 1 Transimination reactions of imines **1** and **2** with isopropylamine, benzylamine, and aniline in the ionic liquid [b-3C-im][NTf_2] and the molecular solvent CD_2Cl_2 at ambient temperature.[a] Imines **1** and **2** were all 100% transiminated and converted to the corresponding imine adducts **1a–c** and **2a–c**, respectively

				Reaction time (min)[b]	
Entry	Starting imine	Amine	Product imine	[b-3C-im][NTf_2]	CD_2Cl_2
1	 **1**	Isopropylamine	 **1a**	450	9190
2		Benzylamine	 **1b**	20	1900
3		Aniline	 **1c**	20	1980
4	 **2**	Isopropylamine	 **2a**	750	9260
5		Benzylamine	 **2b**	50	1490
6		Aniline	 **2c**	60	1900

[a] Conditions: starting imine (15 mM), amine (15 mM), solvent (100 μL), rt. [b] Time required to achieve 100% conversion in the transimination reaction was monitored by ^{1}H NMR.

(~100-fold) in ionic liquid *vs.* CD_2Cl_2 was observed (entry 2, Table 1).

Conclusions

As noted at the very outset, a number of organic reactions carried out in ionic liquids proceed effectively when compared to those performed in conventional molecular solvents. In this work, we have developed an efficient platform for studying and facilitating transimination reactions in ionic liquid at ambient temperature. Our results suggested that the [b-3C-im][NTf_2] ionic liquid is acting as a polar, non-nucleophilic, but weakly Lewis acidic solvent, and would therefore promote the transimination reactions studied. This use of ionic liquid as reaction medium may potentially extend the scope of transimination reactions to new applications.

Experimental section

Gerneral

Flash chromatography was performed on silica gel (230–400 mesh). TLC was carried out on aluminium-backed silica plates precoated with silica (0.2 mm), which were developed using standard visualizing agents, such as UV fluorescence and iodine. Unless otherwise indicated, all reactions were carried out without the aid of dry nitrogen or argon. NMR spectra were recorded on a Varian Gemini 200 at 200 MHz (^{1}H) and 50 MHz (^{13}C), both in $CDCl_3$ unless otherwise stated. Chemical shifts were quoted in parts per million (ppm). The FT-IR spectra were recorded in Jasco FT-IR-460 Plus spectrometer. Melting points were determined on a Fargo MP-2D apparatus (Taiwan, ROC) and are uncorrected. Solvents and reagents were obtained from commercial sources and were used without further purification.

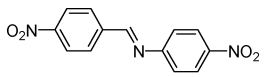
General procedure for transimination reactions in deuterated dichloromethane. To a NMR tube containing the imine **1** or **2** (2.0 mg, 0.007 mmol)[18,19] and CD_2Cl_2 (500 μL) was added the amine (0.007 mmol). The tube was then placed on a rotating shaker and the resulting solution was allowed to react at ambient temperature. The ^{1}H NMR spectrum was collected periodically.

General procedure for $Sc(OTf)_3$ catalyzed transimination reactions in deuterated dichloromethane. To a NMR tube containing the imine **1** or **2** (2.0 mg, 0.007 mmol)[18,19] and $Sc(OTf)_3$ (0.037 mg, 1 mol%) in CD_2Cl_2 (500 μL) was added the amine (0.007 mmol). The tube was then placed on a rotating shaker and the resulting solution was allowed to react at ambient temperature. The ^{1}H NMR spectrum was collected periodically.

General procedure for transimination reactions in [b-3C-im][NTf_2] ionic liquid. To an eppendorf tube containing the imine **1** or **2** (2.0 mg, 0.007 mmol) in [b-3C-im][NTf_2] (500 μL)[4] was added the amine (0.007 mmol). The tube was then placed on a rotating shaker and the resulting solution was allowed to react at ambient temperature. The reaction solution (40 μL) was pipetted at regular intervals, ranging from every 10 min for the faster reactions to every 30 min for the slower reaction, and then diluted with $CDCl_3$ (360 μL). The ^{1}H NMR was then recorded.

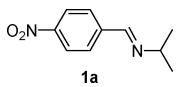
General procedure for $Sc(OTf)_3$ catalyzed transimination reactions in [b-3C-im][NTf_2] ionic liquid. To an eppendorf tube containing the imine **1** or **2** (2.0 mg, 0.007 mmol) and $Sc(OTf)_3$

(0.037 mg, 1 mol%) in [b-3C-im][NTf_2] (500 μL) was added the amine (0.007 mmol). The tube was then placed on a rotating shaker and the resulting solution was allowed to react at ambient temperature. The reaction solution (40 μL) was pipetted every 15 s and diluted with $CDCl_3$ (360 μL). The ^1H NMR spectrum was then collected.



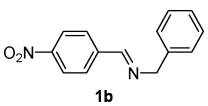
1

***N*-(4-nitrobenzylidene)-4-nitroaniline (1).** Yellow solid, mp 197–198 °C; IR (KBr, cm^{-1}) 1628; ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 9.2 Hz, ArH), 8.12 (2H, d, J = 9.0 Hz, ArH), 8.22 (2H, d, J = 9.2 Hz, ArH), 8.38 (2H, d, J = 9.0 Hz, ArH), 8.54 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 121.3, 124.1, 125.5, 129.9, 140.5, 146.1, 149.9, 156.6, 160.1; EI-HRMS m/z $[M]^+$ calcd for $C_{13}H_9N_3O_4$ 271.0593, found 271.0593.



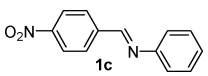
1a

***N*-(4-nitrobenzylidene)-isopropylamine (1a).** Brown solid, mp 52–53 °C; IR (KBr, cm^{-1}) 1644; ^1H NMR (200 MHz, $CDCl_3$) δ 1.29 (6H, d, J = 6.4 Hz, CH_3), 3.59–3.65 (1H, m, CH), 7.90 (2H, d, J = 11.0 Hz, ArH), 8.27 (2H, d, J = 11.0 Hz, ArH), 8.38 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.8, 61.7, 123.6, 128.6, 141.9, 148.7, 156.0; EI-HRMS m/z $[M]^+$ calcd for $C_{10}H_{12}N_2O_2$ 192.0899, found 192.0902.



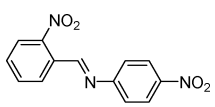
1b

***N*-(4-nitrobenzylidene)-benzylamine (1b).** Orange solid, mp 47–48 °C; IR (KBr, cm^{-1}) 1644; ^1H NMR (200 MHz, $CDCl_3$) δ 4.89 (2H, s, NCH_2), 7.26–7.38 (5H, m, ArH), 7.95 (2H, d, J = 8.6 Hz, ArH), 8.28 (2H, d, J = 8.6 Hz, ArH), 8.47 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 64.7, 123.4, 126.9, 127.6, 128.1, 128.5, 138.3, 141.3, 148.4, 159.1; EI-HRMS m/z $[M]^+$ calcd for $C_{14}H_{12}N_2O_2$ 240.0899, found 240.0897.



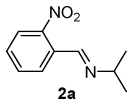
1c

***N*-(4-nitrobenzylidene)-aniline (1c).** Light yellow solid, mp 89–90 °C; IR (KBr, cm^{-1}) 1625; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24–7.38 (3H, m, ArH), 7.40–7.48 (2H, m, ArH), 8.08 (2H, d, J = 8.8 Hz, ArH), 8.33 (2H, d, J = 8.8 Hz, ArH), 8.56 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.9, 123.8, 127.3, 129.2, 129.2, 141.4, 149.8, 150.8, 157.2; EI-HRMS m/z $[M]^+$ calcd for $C_{13}H_{10}N_2O_2$ 226.0742, found 226.0741.



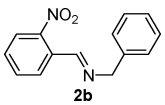
2

***N*-(2-nitrobenzylidene)-4-nitroaniline(2).** Brown solid, mp 144–145 °C; IR (KBr, cm^{-1}) 1617; ^1H NMR (200 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 9.2 Hz, ArH), 7.67–7.84 (2H, m, ArH), 8.12 (1H, m, ArH), 8.31 (3H, m, ArH), 8.94 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 121.5, 124.7, 125.0, 129.8, 130.2, 132.1, 133.8, 146.0, 149.4, 156.7, 158.8; EI-HRMS m/z $[M]^+$ calcd for $C_{13}H_9N_3O_4$ 271.0593, found 271.0591.



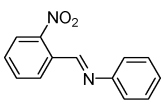
2a

***N*-(2-nitrobenzylidene)-isopropylamine (2a).** Brown liquid; IR (KBr, cm^{-1}) 1637; ^1H NMR (200 MHz, $CDCl_3$) δ 1.30 (6H, d, J = 6.2 Hz, CH_3), 3.63–3.70 (1H, m, CH), 7.27–7.71 (2H, m, ArH), 8.00–8.06 (2H, m, ArH), 8.72 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.8, 61.7, 123.6, 128.6, 130.0, 131.5, 133.5, 148.5, 154.0; FAB-HRMS m/z $[M+H]^+$ calcd for $C_{10}H_{13}N_2O_2$ 193.0977, found 193.0975.



2b

***N*-(2-nitrobenzylidene)-benzylamine (2b).** Brown liquid; IR (KBr, cm^{-1}) 1637; ^1H NMR (200 MHz, $CDCl_3$) δ 4.89 (2H, s, NCH_2), 7.25–7.31 (5H, m, ArH), 7.56–7.67 (2H, m, ArH), 8.01–8.12 (2H, m, ArH), 8.84 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 64.8, 124.0, 126.7, 127.7, 128.2, 129.6, 130.7, 130.9, 133.2, 138.4, 148.7, 157.5; FAB-HRMS m/z $[M+H]^+$ calcd for $C_{14}H_{13}N_2O_2$ 241.0977, found 241.0979.



2c

***N*-(2-nitrobenzylidene)-aniline (2c).** Red solid, mp 45–46 °C; IR (KBr, cm^{-1}) 1618; ^1H NMR (200 MHz, $CDCl_3$) δ 7.27–7.38 (3H, m, ArH), 7.40–7.50 (2H, m, ArH), 7.62–7.70 (1H, m, ArH), 7.71–7.80 (1H, m, ArH), 8.10 (1H, d, J = 6.2 Hz, ArH), 8.32 (1H, d, J = 6.2 Hz, ArH), 8.95 (1H, s, CH═N); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.9, 124.1, 124.2, 126.6, 130.6, 130.8, 132.2, 134.0, 148.9, 157.0, 159.2; EI-HRMS m/z $[M]^+$ calcd for $C_{13}H_{10}N_2O_2$ 226.0742, found 226.0748.

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