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PAPER

Effective Catalysis of Imine Metathesis by means of Fast Transiminations between Aromatic-Aromatic or Aromatic-Aliphatic Amines

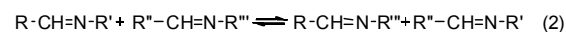
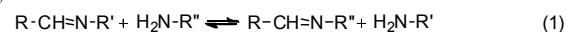
Maria Ciaccia, Silvia Pilati, Roberta Cacciapaglia, Luigi Mandolini and Stefano Di Stefano*

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This paper reports on a quantitative investigation of rates of amine-imine exchange reactions of primary amines with their benzylidene derivatives in organic solvents at room temperature. Exchange reactions involving aromatic-aromatic or aromatic-aliphatic amines were in all cases fast enough to allow their use in the effective catalysis of imine metathesis in the absence of acid and metal catalysis. Transiminations based on exchange between aromatic and aliphatic amines were retarded both by electron-donating and electron-withdrawing substituents in the *para*-position of the benzylidene moiety. This result was interpreted as arising from a change in the rate-determining step of the two-step transimination reaction.

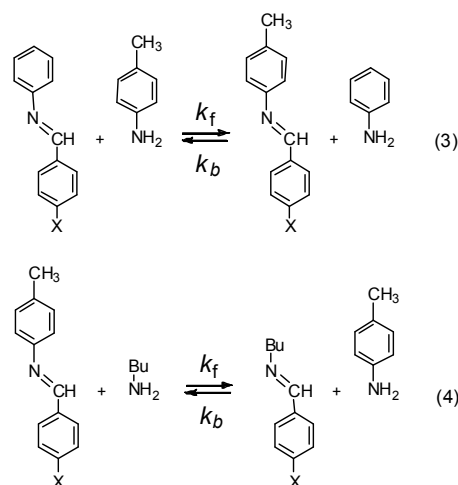
Introduction

The relevance of imines in chemistry and biology has been known for a long time,¹ but structure effects on rates and equilibria of important reactions involving the imine bond, such as transimination and imine metathesis, are still poorly understood. At variance with the common notion that the reactivity of imines toward nucleophiles is intrinsically low and becomes quite high only after protonation,^{1d,2} we recently reported amine-imine exchange reactions of sterically unhindered primary aliphatic amines with their benzylidene derivatives, eqn (1), to be surprisingly fast at ambient temperature in a variety of nonaqueous solvents in the absence of acid catalysis.³ These very fast transimination reactions involving aliphatic amines were utilized in the catalysis of imine metathesis, eqn (2), which occurs rapidly at ambient temperature under nonacidic conditions in the presence of catalytic amounts of primary aliphatic amines, as a result of coupled transimination reactions. These features are of great value for studies of dynamic covalent chemistry (DCC)⁴ based on exchange equilibria of imine bonds in organic solvents,⁵ but it is unknown whether similar features are displayed by imines derived from anilines.



With a view to filling this gap, we investigated rates and equilibria of transimination reactions based on aromatic amines, eqn (3), as well as of a mixed aromatic-aliphatic system, eqn (4). Here we show that in all cases transimination reactions are fast enough to allow their use in the effective catalysis of imine metathesis under mild conditions. We also show that attempts at

enhancing rates by replacing the *para*-hydrogen of the benzylidene moiety with electron-donating or electron-withdrawing substituents were unsuccessful, but afforded valuable mechanistic insights.



Results and discussion

Transimination

The progress of the exchange reactions of eqn (3) and eqn (4) was monitored by measuring variations with time of integrated intensities of suitable ¹H NMR signals of reactants or products or both. Experimental data were treated according to the standard kinetic equation for reversible reactions, second-order in both directions,⁶ that was found to fit to a good precision to a rate data for amine-imine exchange reactions in the aliphatic-aliphatic systems.³ A typical time-concentration profile is shown in Figure 1. A good adherence of data points to the kinetic equation was

obtained in all cases. Rate and equilibrium constants are summarized in Table 1 for the reaction of eqn (3) and in Table 2 for the reaction of eqn (4).

Table 1. Rates and equilibrium constants of imine-amine exchange between *N*-benzylideneanilines and *p*-toluidine, eqn (3), at 25 °C.^a

Entry	X	Solvent ^b	K^c	k_f (M ⁻¹ s ⁻¹) ^d	k_b (M ⁻¹ s ⁻¹) ^d	$t_{1/2}$ (s) ^e
1	H	CDCl ₃	2.6	1.0×10^{-1}	3.8×10^{-2}	85
2	H	CD ₂ Cl ₂	1.9	1.1×10^{-1}	5.9×10^{-2}	40
3	H	CD ₃ CN	3.7	1.3×10^{-1}	3.4×10^{-2}	70
4	OCH ₃	CDCl ₃	3.0	1.2×10^{-1}	4.0×10^{-2}	80
5	CN	CDCl ₃	4.5	1.1×10^{-1}	2.4×10^{-2}	140
6	NO ₂	CDCl ₃	7.2	0.94×10^{-1}	1.3×10^{-2}	240

^a Reactants at 60 mM in all cases. The reaction progress was monitored by ¹H NMR spectroscopy. ^b Water content below ¹H NMR detection limits. ^c The equilibrium constant was calculated from equilibrium concentrations of reactants and products. All values are the average of two to three independent runs. Error limits in the order of ± 20%. ^d The known values of K were introduced into eqn (S1) (see ESI) and the corresponding k_f values were obtained by a nonlinear fitting procedure to the data points. k_b values were calculated as $k_b = k_f / K$. ^e Calculated as $[Pd]_{t_{1/2}} = [Pd]_{\infty} / 2$, where Pdt is either aniline or *N*-benzylidene-*p*-toluidine.

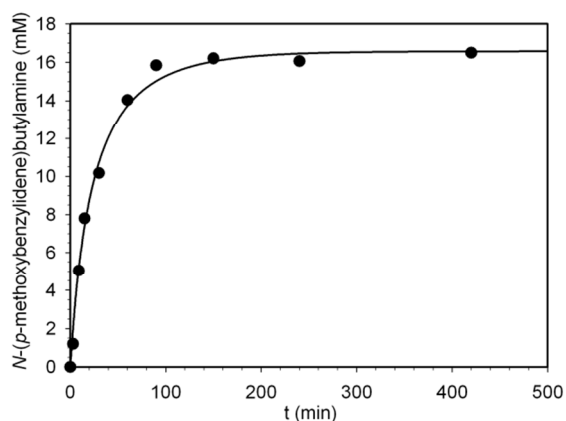


Fig. 1 Time-concentration profile of *N*-(*p*-methoxybenzylidene)butylamine production from reaction between 20 mM *N*-(*p*-methoxybenzylidene)aniline and 20 mM butylamine, CD₃Cl 25 °C. The curve is a plot of eqn (S1) (see ESI) with data from Table 2, entry 2.

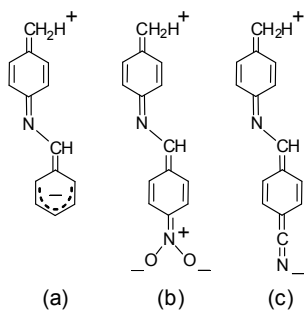


Fig. 2. Hyperconjugative interactions in *N*-benzylidene-*p*-toluidines. Participation in through-resonance with the electron withdrawing substituents is shown in structure (b) and (c).

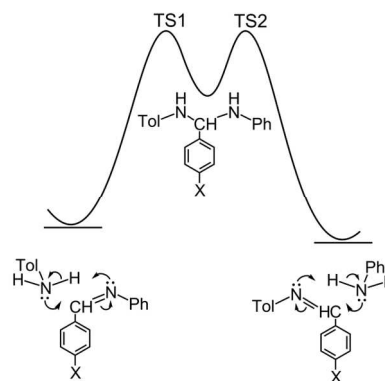


Fig. 3. Qualitative energy diagram for transimination reactions of Table 1.

As shown in Table 1, exchange equilibria involving aromatic amines are slightly biased towards products in all cases ($K > 1$), which is tantamount to saying that the methyl substituent stabilizes the imine product more than the amine reactant. We suggest that a hyperconjugative interaction, extended to the aromatic system of the benzylidene moiety (Figure 2, a), is responsible for imine stabilization. In line with this suggestion, the definite tendency of the equilibrium constants to moderately increase in the presence of electron withdrawing substituents (Table 1, entries 5 and 6), is a result of increased hyperconjugative interactions arising from through-resonance with the substituent (Figure 2, b,c).

As to rates of forward reactions, k_f values are not only remarkably independent of solvent (Table 1, entries 1-3),⁷ but also insensitive of the nature of *para* substituents. A virtually identical picture emerges from inspection of backward rate constants k_b , when the modest *thermodynamic handicap* suffered by *N*-benzylidene-*p*-toluidines bearing NO₂ and CN substituents is taken into account.

Amine-imine exchange is a two-step process, proceeding via a high energy aminal intermediate (Figure 3).³ There are two bond-making and two bond-breaking processes occurring simultaneously in the formation of TS1 from reactants, as well as of TS2 from products. While the C-N bond between the amine nitrogen is formed and the C=N double bond is transformed in a C-N single bond, a proton is transferred from the amine to the imine nitrogen.⁸ Thus, the lack of sensitivity to solvent and electronic effects of transiminations involving aromatic amines, eqn. (3), would suggest that the nature of the four-membered transition states TS1 and TS2 is substantially apolar, on account of a good balance between bond-making and bond-breaking processes.

At variance with the behavior of aromatic-aromatic transiminations, rates and equilibrium constants of the mixed aromatic-aliphatic transiminations listed in Table 2 and graphically displayed in the form of Hammett plots in Figures 4 and 5, are markedly dependent on electronic effects. Transimination equilibria are more shifted towards products and K values are strongly enhanced by electron-withdrawing substituents, most likely because hyperconjugation in *N*-benzylidenebutylamines, occurring with C-H and C-C bonds α to the imine nitrogen (Figure 6) is more important than in *N*-benzylidene-*p*-toluidines (Figure 2).

Table 2. Rates and equilibrium constants of imine-amine exchange between *N*-benzylidene-*p*-toluidines and butylamine, eqn (4), in CDCl₃ at 25 °C.^{a, b}

Entry	X	<i>K</i>	<i>k_f</i> (M ⁻¹ s ⁻¹)	<i>k_b</i> (M ⁻¹ s ⁻¹)	<i>t</i> _{1/2} (s) ^c
1	H	35	0.60	1.7 × 10 ⁻²	240
2	OCH ₃	23	3.3 × 10 ⁻²	1.4 × 10 ⁻³	1100
3	CN	120	3.4 × 10 ⁻³	2.8 × 10 ⁻⁵	11900
4	NO ₂	240	7.9 × 10 ⁻⁴	3.3 × 10 ⁻⁶	62000

^a Reactants at 20 mM in all cases. The reaction progress was monitored by ¹H NMR spectroscopy. ^b For analysis of rate and equilibrium data see footnotes c and d to Table 1. ^d Calculated as [Pdt]_{t_{1/2}} = [Pdt]_∞ / 2, where Pdt is either *p*-toluidine or *N*-benzylideneaniline.

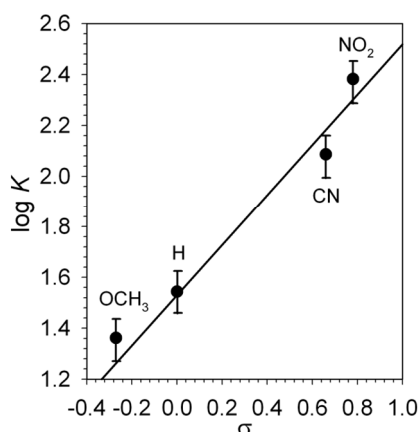


Fig. 4. Hammett plot for the equilibrium constants of transimination reactions between butylamine and *N*-benzylidene-*p*-toluidines (eqn (4)). Data from Table 2.

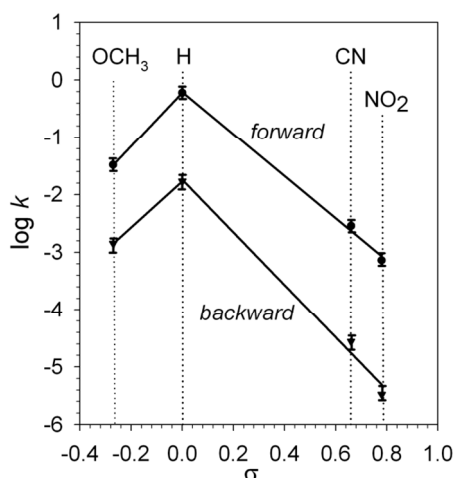


Fig. 5. Hammett plots for the second-order rate constants of the forward (*k_f*) and backward (*k_b*) transiminations between butylamine and *N*-benzylidene-*p*-toluidines of eqn (4). Data from Table 2.

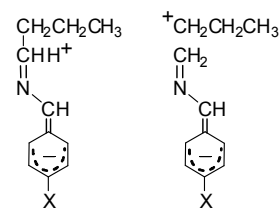
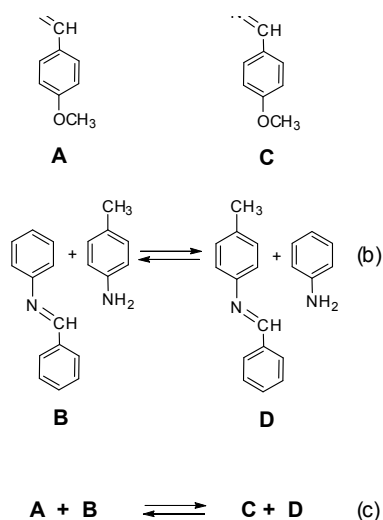


Fig. 6. Hyperconjugation with α C-H and α C-C bonds in *N*-benzylidenebutylamines.

Table 2 shows that forward (*k_f*) and backward (*k_b*) transimination rates are strongly retarded both by the electron-releasing OCH₃ and electron-withdrawing NO₂ and CN. Nonlinear Hammett plots are well documented,⁹ but those in which the plot is concave-down are less common. According to Leffler and Grunwald,¹⁰ a change in the rate-determining step with otherwise constant mechanism can cause a Hammett plot to be concave-down. Accordingly, we interpret the break in the Hammett plots in Figure 5, featuring concave-down shapes, as arising from a change in the rate-determining step of the two-step transimination reaction (Figure 3). It is likely that the large difference in basicity-nucleoficity between butylamine and *p*-toluidine causes an unbalance between bond-making and bond-breaking processes. Although a detailed description of TS1 and TS2 in terms of fractional charges on the four atoms undergoing bond changes is outside the scope of this work, there is no doubt that in terms of bond-making and bond-breaking processes the roles of the two nitrogen atoms in TS1 are reversed in TS2. If the uneven charge distribution is accompanied by a change of electron density on the benzylidene carbon of TS1, there will be by necessity a variation of electron density of opposite sign in TS2. As a consequence, substituents will have opposite effects on the chemical potential of the two transition states, and in any case the transition state destabilized by the substituent, independent of the electronic nature of the substituent itself, will become the rate-limiting transition state. Interestingly, an analogous concave-down Hammett plot, reported a long time ago for the reaction between butylamine and substituted benzaldehydes,¹¹ was rationalized using a similar argument.

Imine metathesis

As shown in a previous paper,³ fast transimination rates can be utilized in the generation of efficient dynamic systems based on imine metathesis catalyzed by primary amines under mild conditions. By way of illustration, let us consider the two transimination reactions (a) and (b) in Scheme 1, whose common feature is that the amine reactant in one reaction is a product in the other, and vice versa. Thus, if aniline is added to a mixture of **A** and **B**, it will react with **A** to give a mixture of **C** and *p*-toluidine. The latter, in turn, will react with **B** to give a mixture of **D** and aniline. In conclusion, aniline is consumed in step (a) and restored in step (b), while the opposite holds for *p*-toluidine. Thus, as the reactions proceed, **C** and **D** build up at the expenses of **A** and **B**, until the metathetic equilibrium (c) is established as a result of coupled transimination reactions. Imine metathesis is catalyzed by either amine or, more properly, by the mixture of



Scheme 1. Transimination reactions (a) and (b) and imine metathesis (c) catalyzed by primary amines.

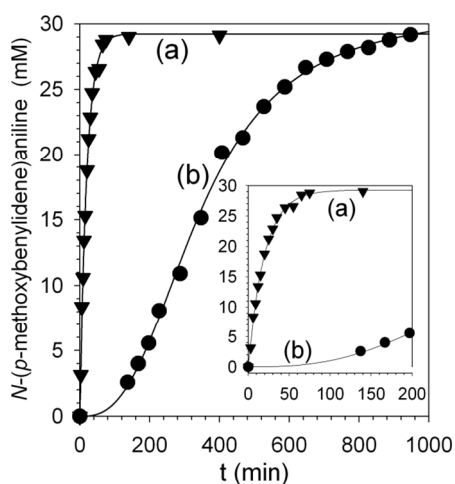


Fig. 7. Reaction progress as a function of time for amine-catalyzed (a) and background (b) metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and 60 mM *N*-benzylideneaniline in CD_2Cl_2 at 25 °C. Curve (a) is a plot of a first-order equation, curve (b) is a guide to the eye.

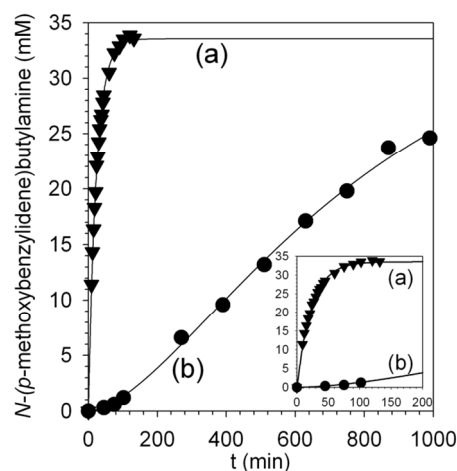
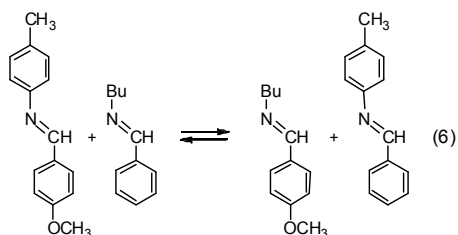


Fig. 8. Reaction progress as a function of time for amine-catalyzed (a) and background (b) metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and *N*-benzylidenebutylamine in CDCl_3 at 25 °C. The curves are guides to the eye.

two amines formed in the course of the reaction.

Experimental data fully consistent with expectations are shown in Figure 7. Starting from a mixture of imines **A** and **B** (60 mM each) in CD_2Cl_2 , the metathetic equilibrium (c) was reached in less than 100 min at 25 °C (curve a) in the presence of a 1:1 mixture of aniline and *p*-toluidine (9.0 mM each). Since the equilibrium constant turned out to be very close to 1, the reaction was predicted^{3,12} and found to obey first-order time dependence, as shown by the close adherence of data points to a first-order equation ($t_{1/2} = 14$ min). In the absence of added amines the reaction was much slower (curve b). The time-concentration profile has the sigmoid shape of the logistic curve of autocatalytic reactions. Similar results were obtained in CDCl_3 and CD_3OD (see ESI, Figure S1 and S2).

A clue to the mechanism of the seemingly spontaneous metathesis in the control experiment was found in the ^1H NMR spectra of the reaction mix. Tiny signals of the aldehydic hydrogens of benzaldehyde ($\delta = 10.04$) and *p*-anisaldehyde ($\delta = 9.90$), missing at the early stages but clearly visible in the course of the reaction, revealed the occurrence of slow hydrolytic processes, eqn (5), caused by reaction with trace amounts of adventitious water.¹³ These observations support the hypothesis that metathesis in the control reaction is actually catalyzed by the liberated amines. Since the amount of liberated amines increases on increasing reaction time, the concentration-time profile has the same shape of canonical autocatalytic processes, in which the catalyst is a product of the main reaction, rather than of an accidental side-reaction.



Analogous results were obtained for the metathesis reaction in the aromatic-aliphatic case (Figure 8). The reaction of *N-p*-(methoxybenzylidene)*p*-toluidine with *N*-benzylidenebutylamine (60 mM each) in CDCl_3 at 25 °C, eqn (6), was strongly accelerated by an equimolar mixture of *p*-toluidine and butylamine (9.0 mM each), the equilibrium being reached in less than 2 h (curve a). When a single amine (18 mM), either *p*-toluidine or butylamine, was used as a catalyst, similar equilibration rates were observed (see ESI Figure S3), because in either case the reaction was eventually catalyzed by the same mixture of amines. The sigmoid shape of the time-concentration profile of the control reaction (curve b) was again dictated by the liberation of minute amounts of amines produced by reaction of imines with adventitious water in the nominally anhydrous CDCl_3 . Consistently, trace amounts of benzaldehyde and *p*-anisaldehyde were detected in the course of reaction as tiny ^1H NMR signals in the aldehydic proton region.

Conclusions

In this work we have shown that amine-imine exchange reactions based on aromatic-aromatic and aromatic-aliphatic amines occur smoothly at ambient temperature in organic solvents under nonacidic conditions. When combined with our previous results based on amine-imine exchange reactions of the aliphatic-aliphatic type,³ the present work shows that imine metathesis catalyzed by substoichiometric amounts of primary amines of any kind has potential for the implementation of effective dynamic combinatorial libraries based on exchange of imine bonds in organic solvents in the absence of proton¹⁴ or metal catalysis.¹⁵

Experimental section

Instruments and general methods

^1H -NMR spectra were recorded on either a 200- or 300-MHz spectrometer. The spectra were internally referenced to the residual proton solvent signal. Kinetic experiments were carried out in the NMR tube in the thermostated probe of the spectrometer as previously reported.³

Materials

All reagents and solvents were purchased at the highest commercial quality and were used without further purification, unless otherwise stated. Deuterated halogen solvents were flashed through basic alumina immediately prior to use, while deuterated acetonitrile and methanol were first dried over activated molecular sieves (4Å) and then flashed through basic alumina immediately prior to use. Amines were freshly distilled before

use.

General Procedure for the Preparation of the Imines.

According to a literature procedure,¹⁶ an equimolar solution of amine and of aldehyde in benzene was refluxed for 4 h in a Dean-Stark apparatus. The solution was then concentrated under vacuum and the resulting imine was distilled twice under reduced pressure, in order to eliminate any trace of the corresponding amine. ^1H NMR data of isolated imines were in agreement with literature data.^{16,17}

Kinetics

All kinetic experiments were run in duplicate or triplicate. Kinetic runs were carried out on equimolar solutions of the substrates (20 mM in aliphatic amine - aromatic amine transiminations, 60 mM in all other experiments). The calculated amount of substrates was added to 600 μL of the deuterated solvent in the thermostated NMR tube ($T = 25^\circ\text{C}$). In imine metathesis experiments, the calculated volume of a 0.10 M solution of the amine catalyst was added to the reaction mixture. Spectra were recorded at time intervals. Time elapsed from reaction start and recording of the first ^1H NMR spectrum was typically 3-4 minutes. This time interval was necessary to allow thermal equilibration in the probe of the spectrometer after addition of the reactant, and shimming for field optimization. Product formation was monitored by measuring the area of the chosen ^1H NMR signal as a function of time. For transiminations experimental data were fitted to a standard kinetic equation for reversible reactions, second-order in both directions (eqn (S1), see ESI).⁶ Data of imine metathesis between aromatic imines experiments were fitted to a first-order kinetic equation.

Acknowledgements.

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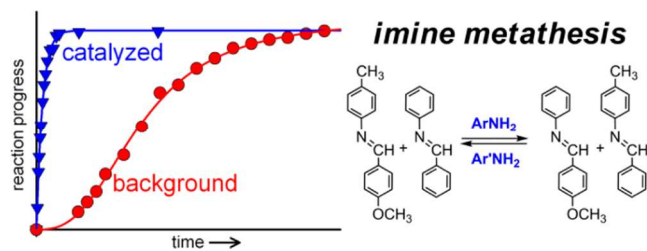
Notes and references

- Dipartimento di Chimica, Sapienza Università di Roma and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, I-00185 Rome, Italy; Fax: +39 06 49913629; Tel: +39 06 49913057; E-mail: stefano.distefano@uniroma1.it
- † Electronic Supplementary Information (ESI) available: Kinetic equations for reversible reaction second order in both directions, kinetic profiles for aromatic-aromatic imine metathesis in different solvents and for aromatic-aliphatic imine metathesis carried out in chloroform with varying initial mixtures of amine catalysts. See DOI: 10.1039/b000000x/
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Graphical Abstract

Transiminations involving aromatic or aliphatic amines were found to be fast enough to be effectively employed in the catalysis of imine metathesis



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