Electronic Supplementary Information

for

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

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Kinetic equation for reversible reactions, second order in both directions

$$\mathbf{A} + \mathbf{B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{C} + \mathbf{D}$$

From ref S1, the standard kinetic equation is given in eqn (S1).

$$[Pdt] = \frac{\{-b \cdot [1 - g \cdot exp(p \cdot t)] + r \cdot [1 + g \cdot exp(p \cdot t)]\}}{\{2a \cdot [1 - g \cdot exp(p \cdot t)]\}} \qquad \text{(S1)}$$

where

$$p = \frac{k_f \cdot r}{[\mathrm{C}]_e \cdot [\mathrm{D}]_e}$$

$$g = \frac{b - r}{b + r}$$

$$r = \sqrt{b^2 - 4a \cdot c}$$

$$a = [\mathrm{C}]_e \cdot [\mathrm{D}]_e - [\mathrm{A}]_e \cdot [\mathrm{B}]_e$$

$$b = -\left\{\left([\mathrm{A}]_0 + [\mathrm{B}]_0\right) \cdot [\mathrm{C}]_e \cdot [\mathrm{D}]_e + \left([\mathrm{C}]_0 + [\mathrm{D}]_0\right) \cdot [\mathrm{A}]_e \cdot [\mathrm{B}]_e\right\}$$

$$c = [\mathrm{A}]_0 \cdot [\mathrm{B}]_0 \cdot [\mathrm{C}]_e \cdot [\mathrm{D}]_e - [\mathrm{A}]_e \cdot [\mathrm{B}]_e \cdot [\mathrm{C}]_0 \cdot [\mathrm{D}]_0$$

In our experiments $[\mathrm{A}]_0 = [\mathrm{B}]_0$ and $[\mathrm{C}]_0 = [\mathrm{D}]_0 = 0$ in all cases.

The equilibrium constant $K = k_f / k_b$ is defined in terms of equilibrium concentration of reactants and products.

$$K = \frac{[C]_e \cdot [D]_e}{[A]_e \cdot [B]_e}.$$

[S1] N. E., Meagher, D. B. Rorabacher *J. Phys. Chem.* **1994**, *98,* 12590-12593.

Aromatic-aromatic and aromatic-aliphatic imine metathesis (typical experiments)

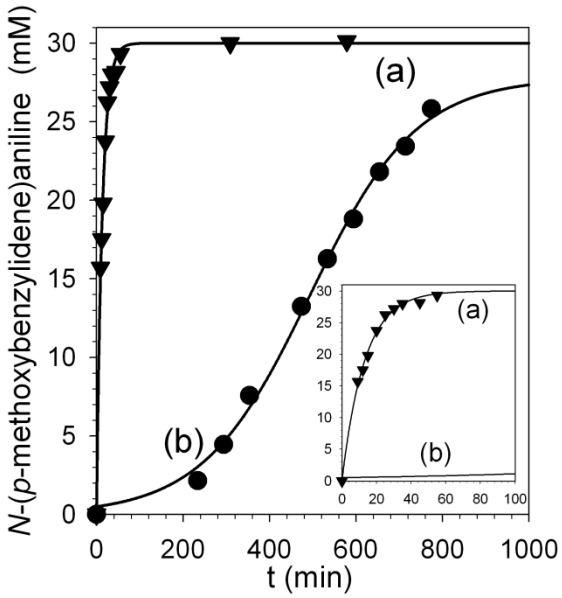

Figure S1. Reaction progress as a function of time for 18 mM amine-catalyzed (a) and background (b) metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and 60 mM *N*-benzylideneaniline in $CDCl_3$ at 25 °C. Curve (a) is a plot of a first-order equation, curve (b) is a guide to the eye.

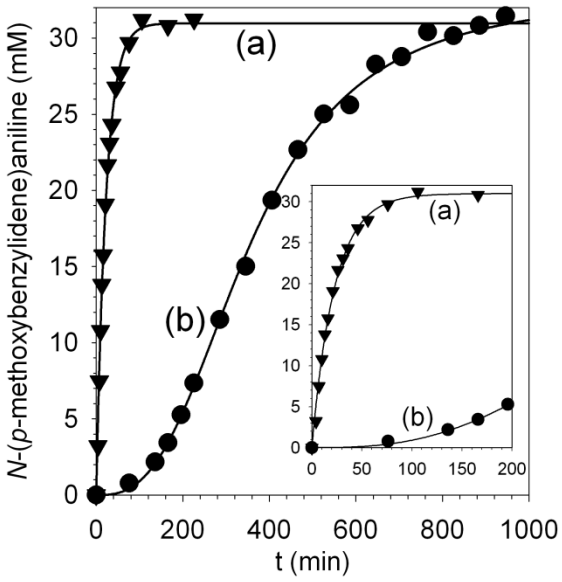

Figure S2. Reaction progress as a function of time for 18 mM amine-catalyzed (a) and background (b) metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and 60 mM *N*-benzylideneaniline in CD_3OD at 25 °C. Curve (a) is a plot of a first-order equation, curve (b) is a guide to the eye.

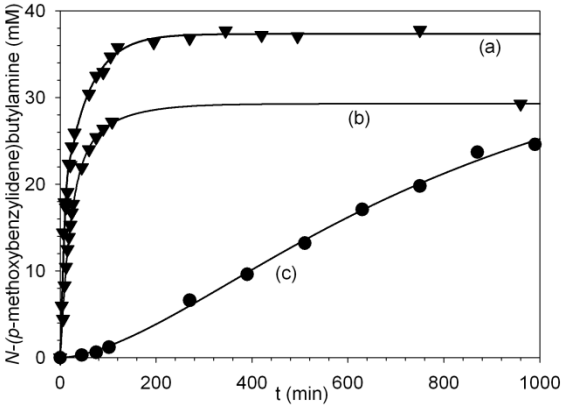

Figure S3. Reaction progress as a function of time for 18 mM butylamine catalyzed (a), 18 mM toludine catalyzed (b), and background (c) metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and *N*-benzylidenebutylamine in $CDCl_3$ at 25 °C. The curves are guides to the eye.

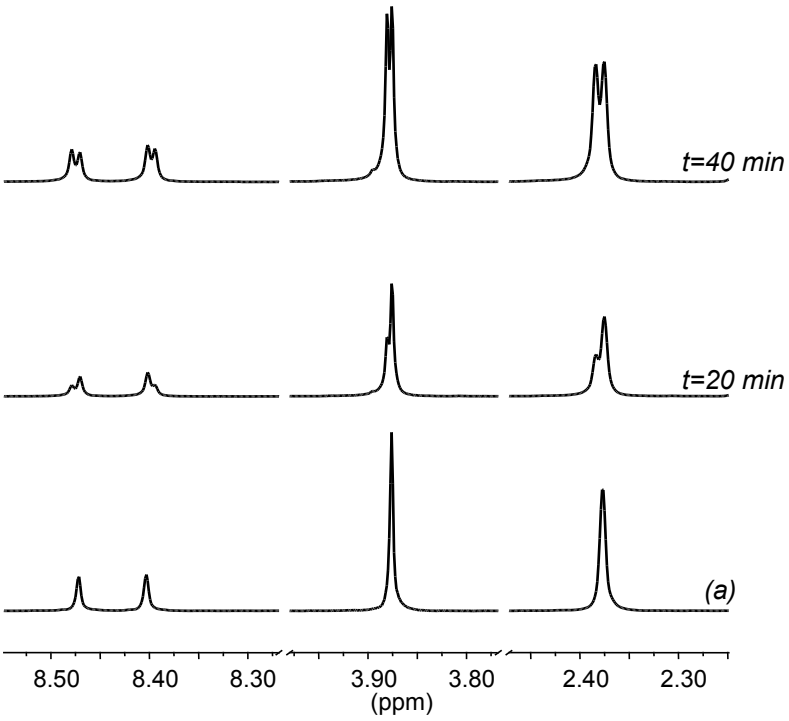

Figure S4. Metathesis between 60 mM *N*-(*p*-methoxybenzylidene)*p*-toluidine and 60 mM *N*-benzylideneaniline in $CDCl_3$ at 25 °C. Monitoring of imine (δ = 8.35 – 8.40 ppm), -OCH_3 (δ = 3.85-3.90 ppm), or –CH_3 (δ = 2.35 – 2.40 ppm) signals gave coincident results, within experimental errors.

Kinetic measurements (data reported in the main text, Table 1)

Notes

***i*)** One typical kinetic run has been here reported for each entry of Table 1 (main text). Average data of two to three independent runs have been given, on the other hand, in Table 1 (see footnote *c* to the same table in the main text).

***ii*)** Data of the transimination between *N*-(*p*-X-benzylidene)anilines and *p*-toluidine (eqn (1), X = OCH_3, CN, NO_2, and Table 1 of the main text, entries 4-6) have been obtained by monitoring of the equilibration process starting from products of eqn (1), *i. e.* from *N*-(*p*-X-benzylidene)toluidines and aniline.

iii) Monitoring of imine or methyl signals gave coincident results, within experimental errors. A deconvolution procedure was adopted for integration of imine signals.

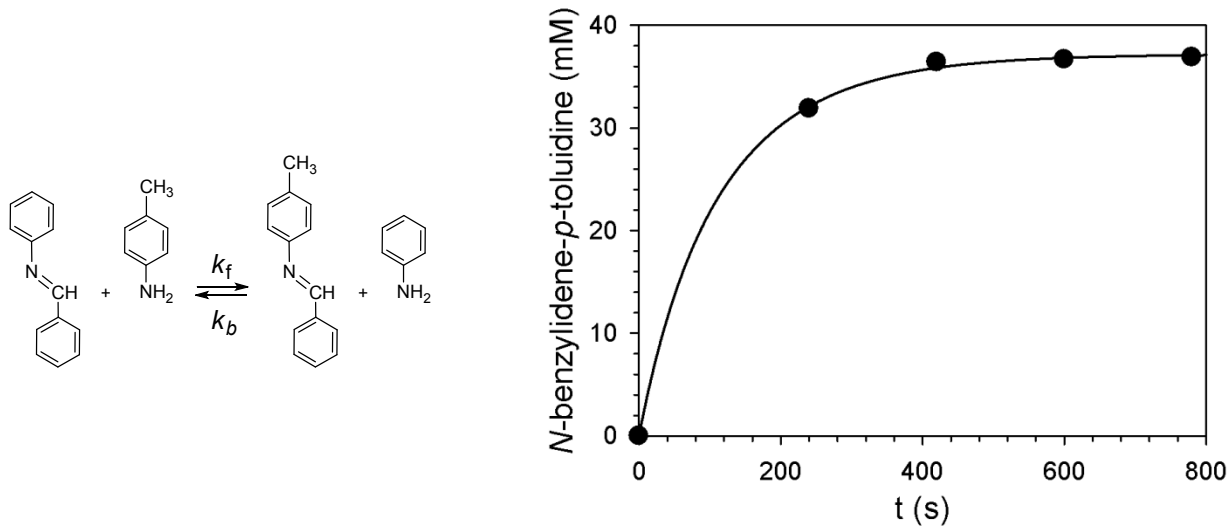

Figure S5. ^{1}H NMR monitoring of the transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in $CDCl_3$, 25 °C.

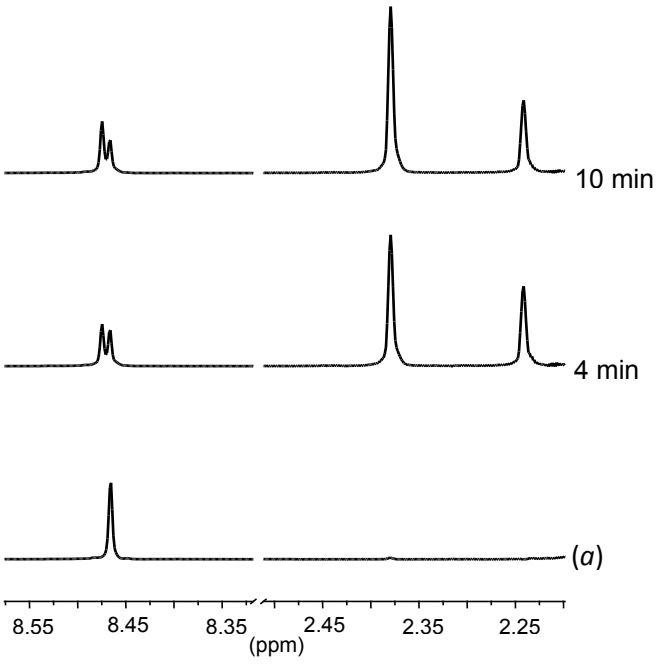

Figure S6. Transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of *p*-toluidine (*a*), and at the given reaction times.

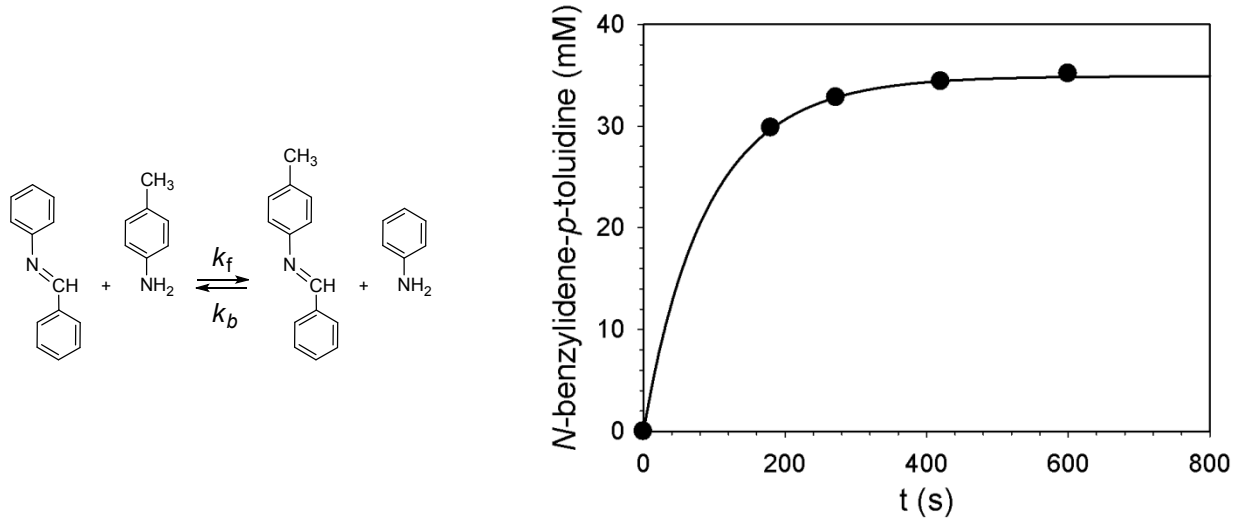

Figure S7. ^{1}H NMR monitoring of the transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in CD_2Cl_2, 25 °C.

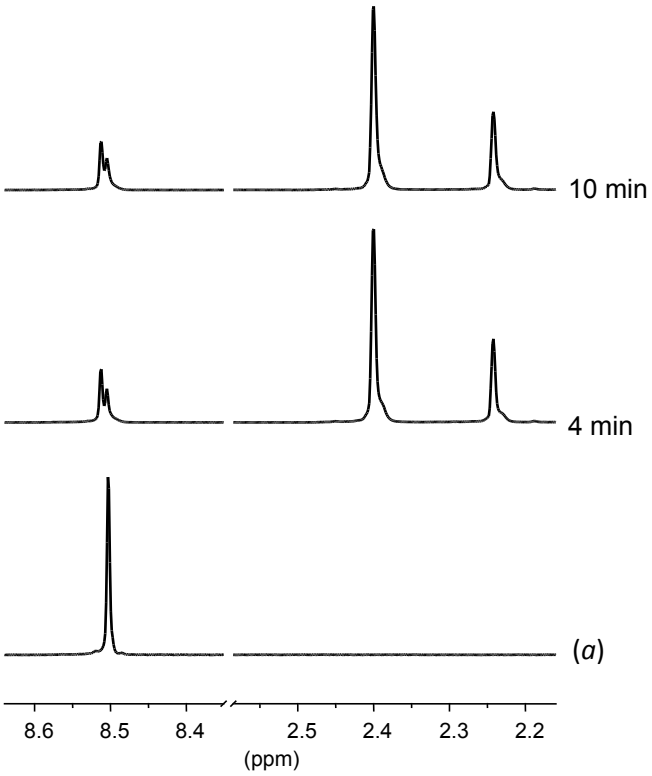

Figure S8. Transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in CD_2Cl_2, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of *p*-toluidine (*a*), and at the given reaction times.

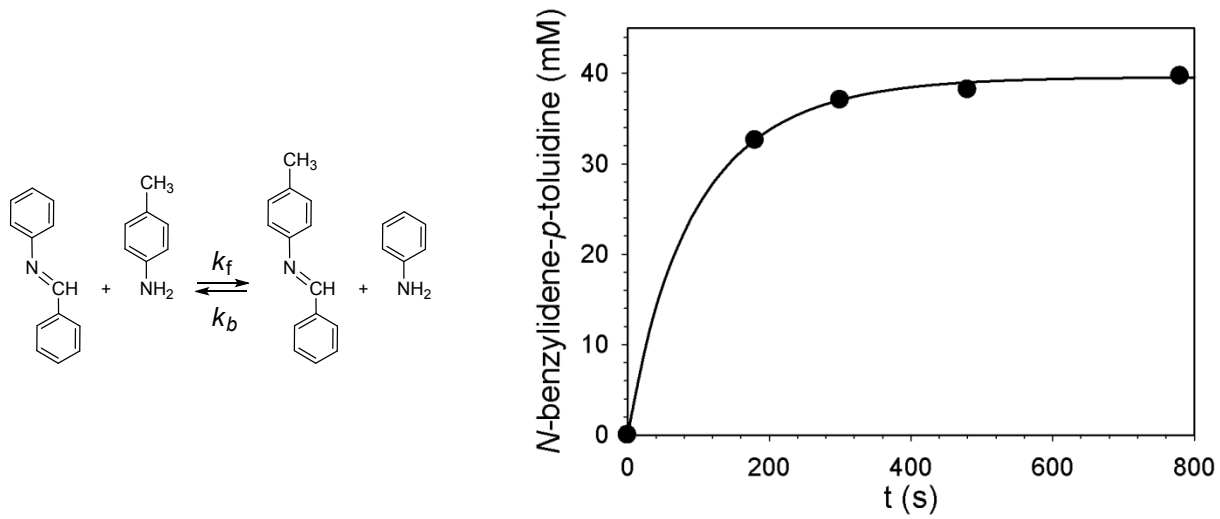

Figure S9. ^{1}H NMR monitoring of the transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in CD_3CN, 25 °C.

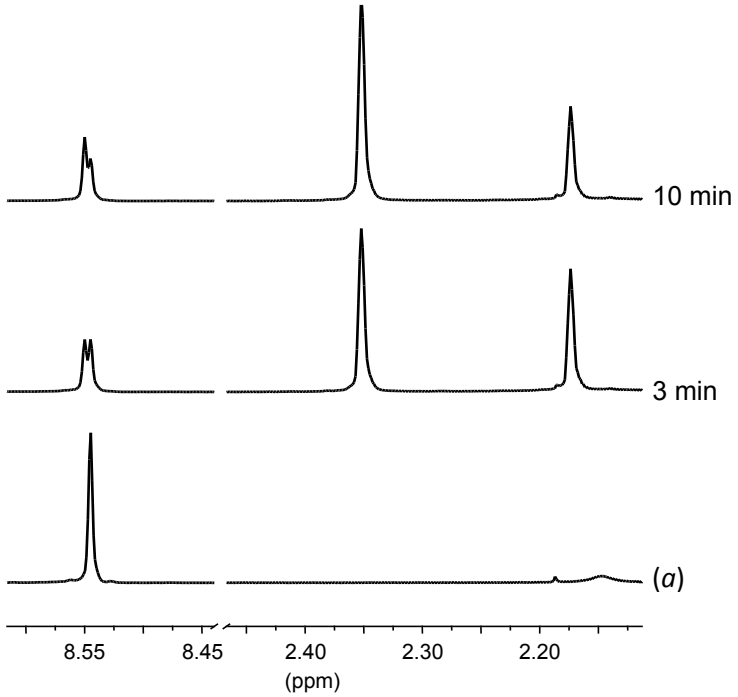

Figure S10. Transimination between 60 mM *N*-benzylideneaniline and 60 mM *p*-toluidine in CD_3CN, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of *p*-toluidine (*a*), and at the given reaction times.

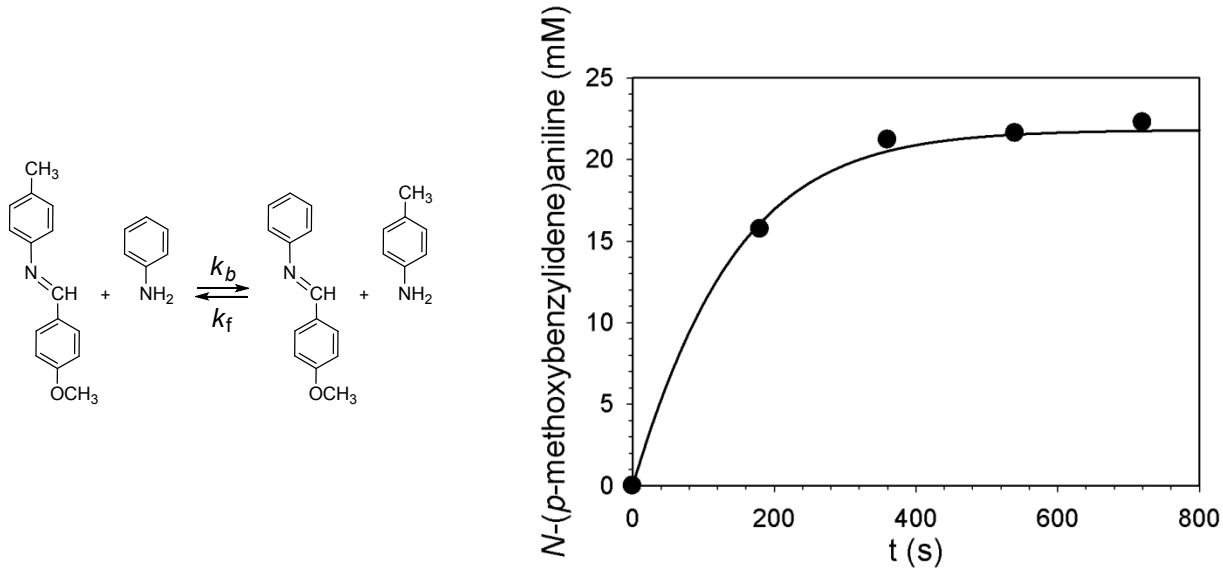

Figure S11. ^{1}H NMR monitoring of the transimination between 60 mM *N*-(*p*-methoxybenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C.

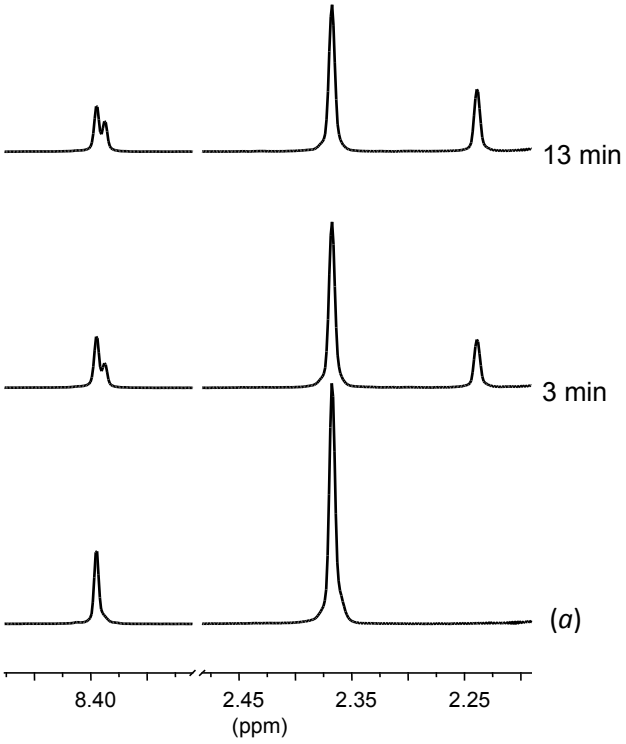

Figure S12. Transimination between 60 mM *N*-(*p*-methoxybenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of aniline (*a*), and at the given reaction times.

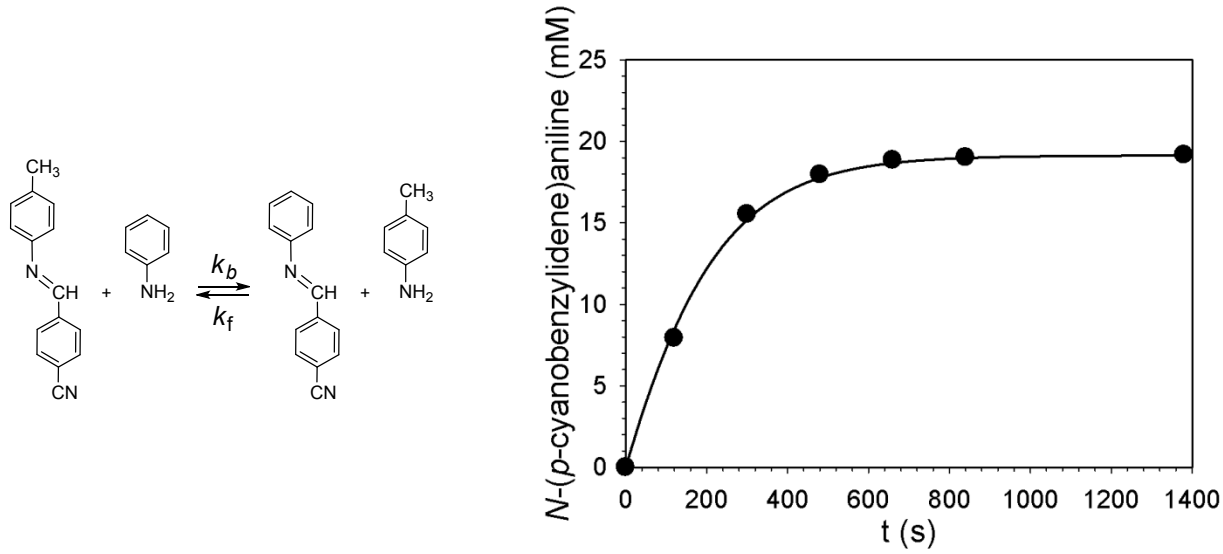

Figure S13. ^{1}H NMR monitoring of the transimination between 60 mM *N*-(*p*-cyanobenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C.

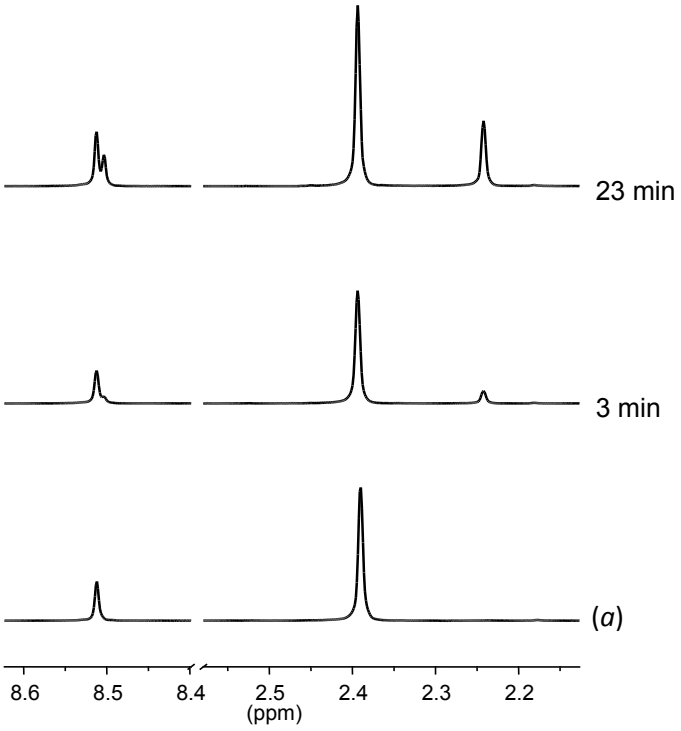

Figure S14. Transimination between 60 mM *N*-(*p*-cyanobenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of aniline (*a*), and at the given reaction times.

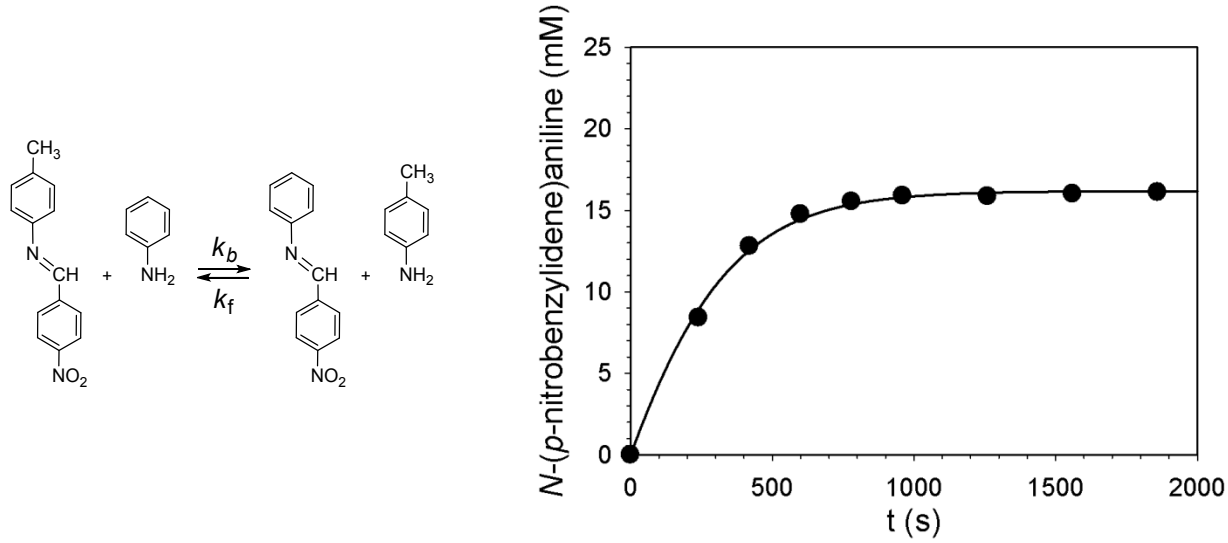

Figure S15. ^{1}H NMR monitoring of the transimination between 60 mM *N*-(*p*-nitrobenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C.

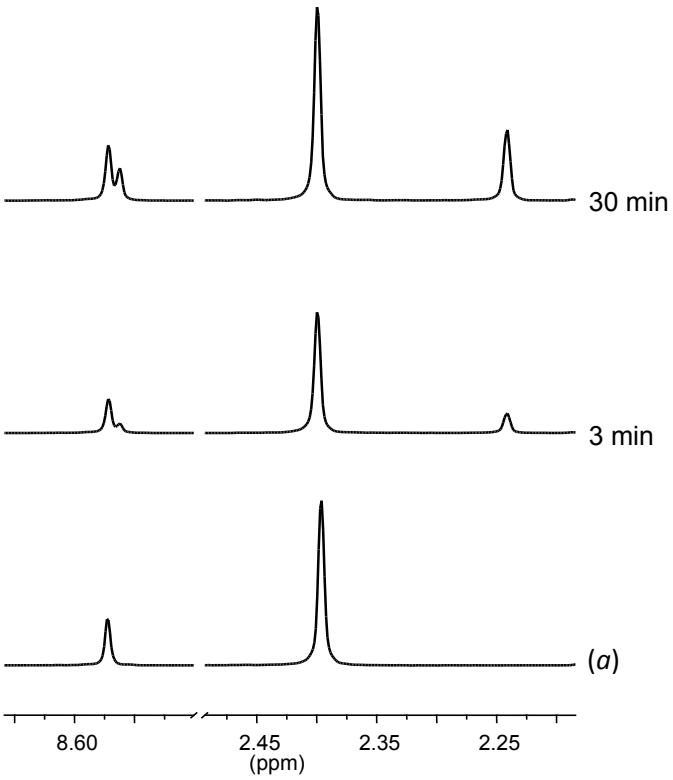

Figure S16. Transimination between 60 mM *N*-(*p*-nitrobenzylidene)-*p*-toluidine and 60 mM aniline in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of aniline (*a*), and at the given reaction times.

Kinetic measurements (data reported in the main text, Table 2)

Notes

***i*)** One typical kinetic run has been here reported for each entry of Table 2 (main text). Average data of two to three independent runs have been given, on the other hand, in Table 2 (see footnote *c* to the same table in the main text).

***ii*)** Data of the transimination between *N*-benzylidene-*p*-toluidine and butylamine (eqn (4), X = H and Table 2 of the main text, entry 1) have been obtained by monitoring of the equilibration process starting from products of eqn (4), *i. e.* from *N*-benzylidenebutylamine and *p*-toluidine.

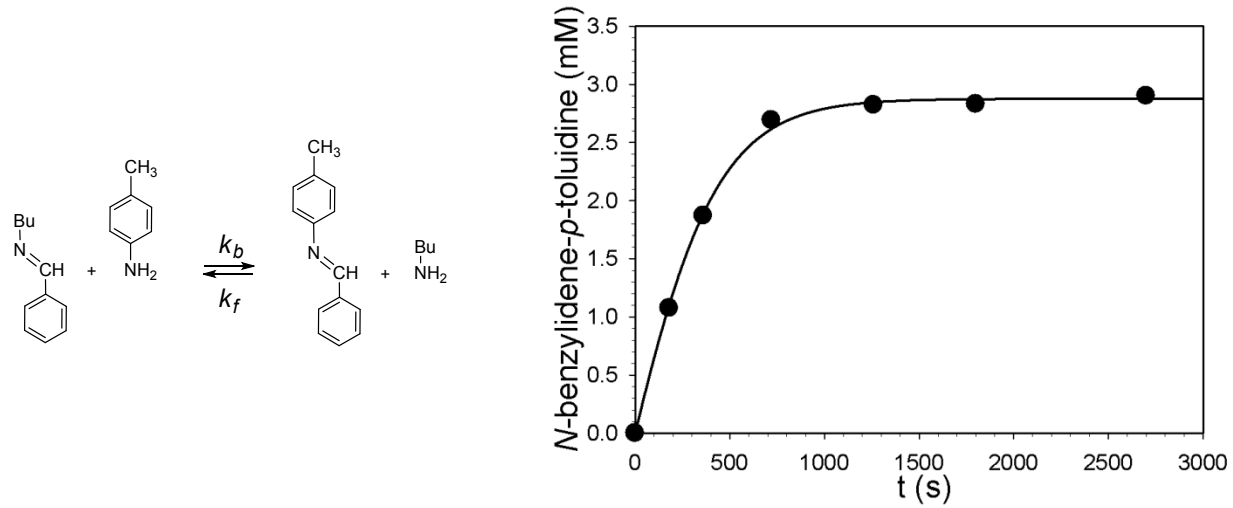

Figure S17. ^{1}H NMR monitoring of the transimination between 20 mM *N*-benzylidenebutylamine and 20 mM *p*-toluidine in $CDCl_3$, 25 °C.

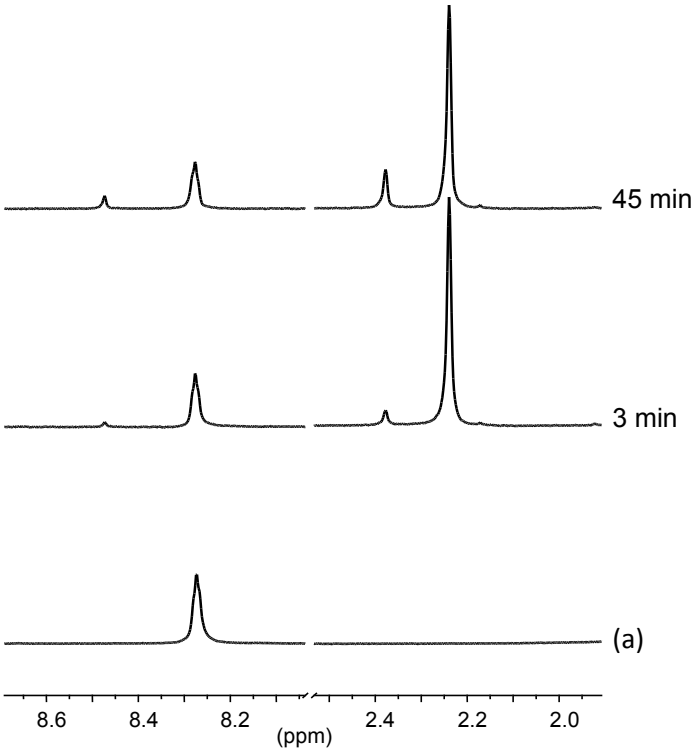

Figure S18. Transimination between 20 mM *N*-benzylidenebutylamine and 20 mM *p*-toluidine in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of *p*-toluidine (*a*), and at the given reaction times.

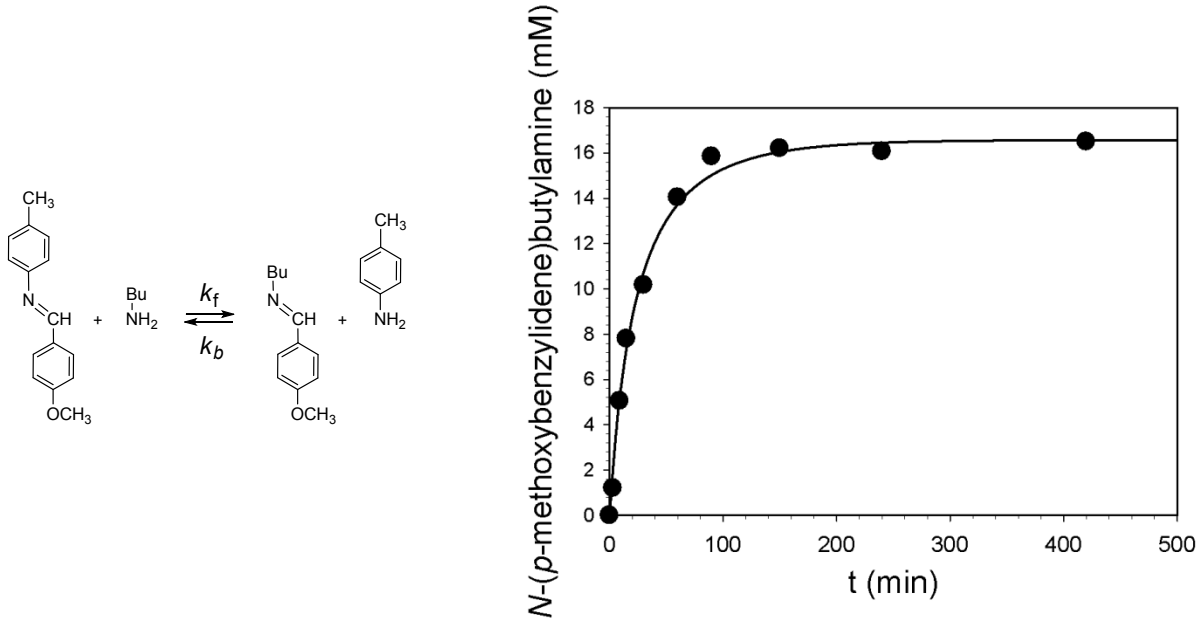

Figure S19. ^{1}H NMR monitoring of the transimination between 20 mM *N*-(*p*-methoxybenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C.

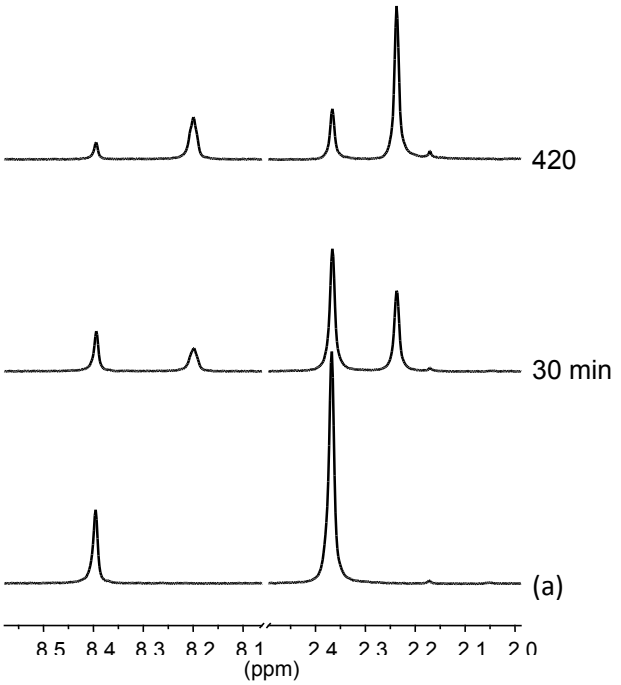

Figure S20. Transimination between 20 mM *N*-(*p*-methoxybenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of butylamine (*a*), and at the given reaction times.

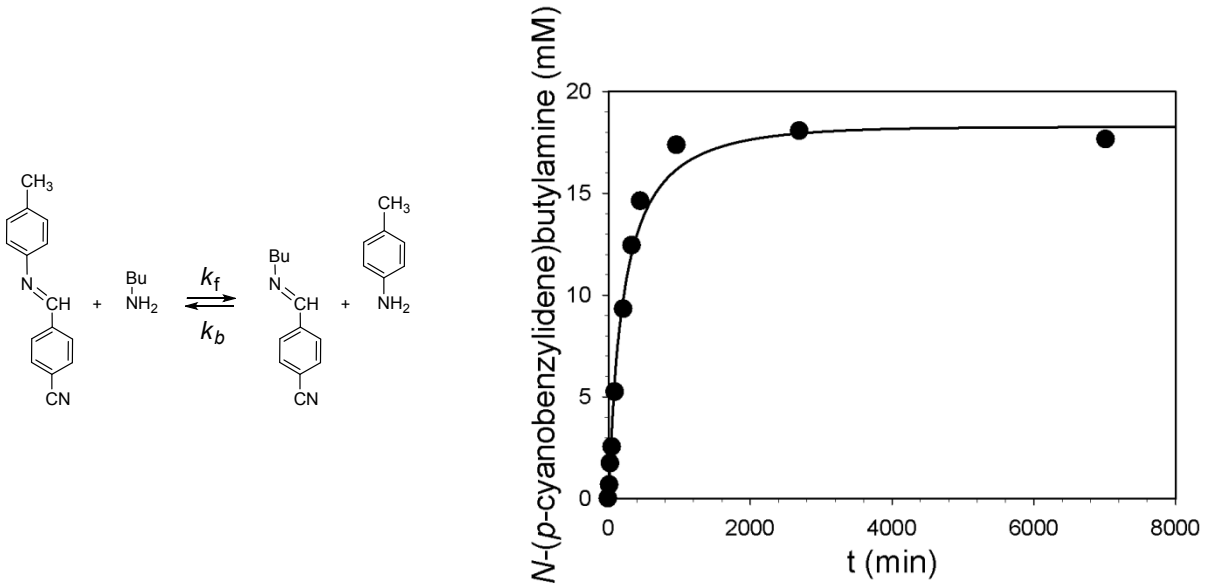

Figure S21. ^{1}H NMR monitoring of the transimination between 20 mM *N*-(*p*-cyanobenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C.

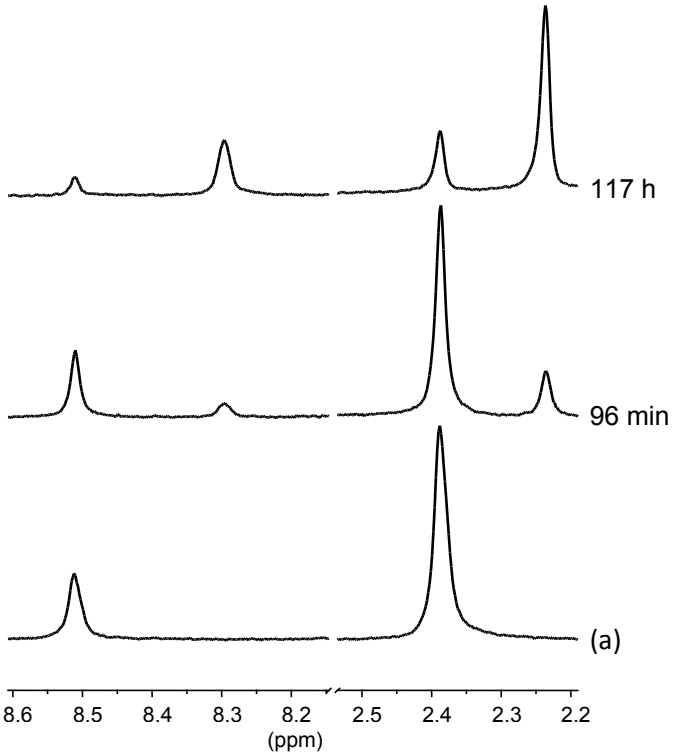

Figure S22. Transimination between 20 mM *N*-(*p*-cyanobenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C. Imine (left) and methyl region (right) of the ^{1}H-NMR spectra before addition of aniline (*a*), and at the given reaction times.

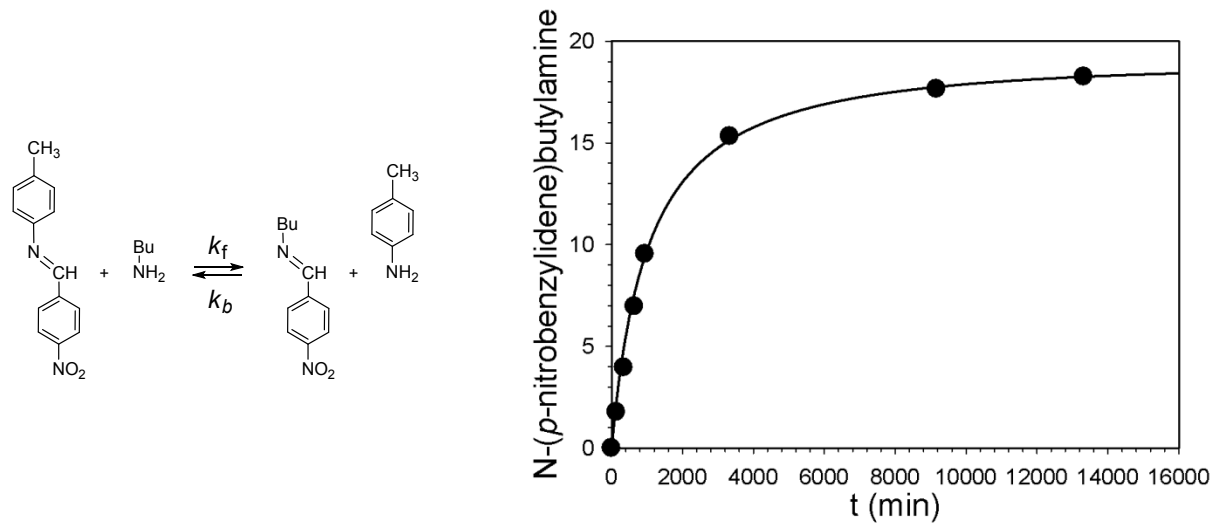

Figure S23. ^{1}H NMR monitoring of the transimination between 20 mM *N*-(*p*-nitrobenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C.

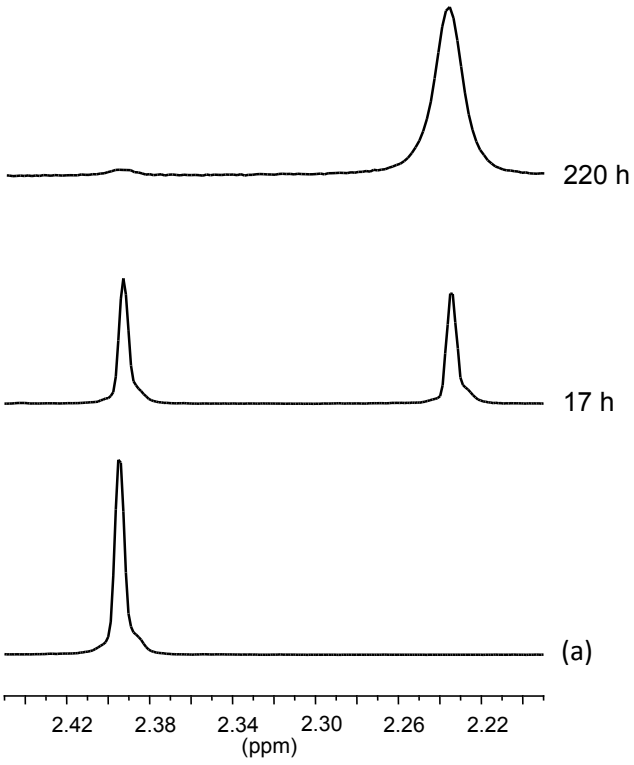

Figure S24. Transimination between 20 mM *N*-(*p*-nitrobenzylidene)-*p*-toluidine and 20 mM butylamine in $CDCl_3$, 25 °C. Methyl region of the ^{1}H-NMR spectra before addition of butylamine (*a*), and at the given reaction times.