Supporting Information

Formation of Breslow Intermediates from N-Heterocyclic Carbenes and Aldehydes Involves Autocatalysis by the Breslow Intermediate, and a Hemiacetal

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S1. General Experimental and Analytical Procedures

Tetrahydrofuran-d₈ was passed through neutral aluminum oxide (Brockmann activity 1) and degassed by several freeze-pump-thaw cycles prior to use. The solvent tetrahydrofuran-d₈ was stored over 4 Å molecular sieves in a glovebox over several weeks before usage. All samples for NMR experiments were prepared in a glovebox (UNILAB GLOVEBOX, 1200/780) from M.Braun Inertgassysteme GmbH. For this glovebox, Argon BIP® from AIR Products was used and the O₂ and H₂O levels were <1 ppm. The following NMR spectrometers were used: Bruker Avance II 600: 1H (600.20 MHz), 13C (150.92 MHz); Bruker DRX 500: 1H (500.13 MHz), 13C (125.76 MHz); Bruker Avance 400: 1H (400.13 MHz), 13C (100.61 MHz). Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS) or solvent residual signals. The following abbreviations are used for chemical shift multiplicities in 1H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, ps = pseudo. NMR signals were assigned by evaluation of 1D and 2D NMR data (1H, 1H COSY, 1H, 1H NOESY, 1H, 13C HMQC, 1H, 13C HMBC). Melting points were determined on a Büchi apparatus and are uncorrected.

For kinetic measurements, sublimed 1,3-bis(2,6-disopropylphenyl)imidazolidin-2-yliden (SIPr, 1a) was used (see below). 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihyrimidazol-2-ylidine (IMes, 1b) was purchased from Sigma Aldrich, and THF-d₈ from DEUTEROGmbH. All aldehydes were distilled prior to use and stored in a glovebox under argon atmosphere.

S2. Synthetic Procedures and Characterizations

S2.1. Synthesis of 1,3-Bis(2,6-disopropylphenyl)imidazolidin-2-ylidene (SIPr, 1a)

S2.1.1. 1,3-Bis(2,6-diisopropylphenyl)imidazoliunium-2-carboxylate (S2)

| Compound     | m or V   | n [mmol] | eq |
|--------------|----------|----------|----|
| azolium salt | 10.00 g  | 23.4     | 1.00 |
| KHMDS        | 4.57 g   | 22.9     | 0.98 |
| THF          | 100 mL   |          |    |

Based on a procedure by Louie[2] the azolium salt S1 was suspended in 100 mL anhydrous and degassed THF, and treated with KHMDS. The suspension was stirred for 2 h at r.t.. n-Pentane (50 mL) was added, and the mixture was filtered over cellite and washed several times with degassed and distilled n-pentane and THF. The filtrate was then treated with CO₂ (balloon with cannula) for 2 h and a colorless precipitate was formed. The precipitate was filtered off and washed with little anhydrous and degassed THF and n-pentane. After removal of the solvent, the product was obtained as a colorless solid in 52 % (5.31 g, 12.2 mmol) yield over two steps.

S2:

C₉₃H₁₀₂N₂O₂, $M = 434.62$ g mol⁻¹

Yield: 52 % (5.13 g, 12.2 mmol)

Appearance: Colorless solid.

m.p.: 172.3 °C, [lit. (decomposition): 188 °C][3]
S2.1.2. 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SiPr, 1a)

The CO\textsubscript{2} adduct of SiPr (SiPr\textperiodcentered CO\textsubscript{2}, S2) was thermally decomposed according to the procedures by Delaude et al.\textsuperscript{[3]} and Louie et al.\textsuperscript{[2]} In a glovebox, a sublimation apparatus was charged with SiPr\textperiodcentered CO\textsubscript{2} S2 (2.32 g, 5.34 mmol) and sealed with PTFE tape. Under reduced pressure (0.2 mbar) the SiPr\textperiodcentered CO\textsubscript{2} was kept for 1 h at 130 °C to regenerate SiPr (1a). The temperature was then raised to 145°C to sublime the free SiPr (1a) formed. After sublimation, the SiPr (1a) product was obtained as a colorless solid in 82% yield (1.71 g, 4.39 mmol) and was stored in a glovebox. The \textsuperscript{1}H NMR spectra of SiPr (1a) thus prepared were identical to literature data.\textsuperscript{[2]}

\begin{itemize}
    \item 1a: C\textsubscript{27}H\textsubscript{38}N\textsubscript{2}, M = 390.60 g mol\textsuperscript{-1}
    \item Yield: 82% (1.71 g, 4.39 mmol)
    \item Appearance: Colorless solid.
\end{itemize}

S2.2. Synthesis of Anisaldehyde-\textsubscript{d\textsubscript{1}} (2b-\textsubscript{d\textsubscript{1}})

Based on a literature procedure by Polavarapu et al.\textsuperscript{[4]}, \textsubscript{p}-anisil (S3, 2.40 g, 8.90 mmol) was dissolved in 30 mL 1,4-dioxane. Upon addition of D\textsubscript{2}O (1.94 g, 96.8 mmol) to the yellow solution, a yellow precipitate formed. KCN (4.68 g, 71.9 mmol) was added in portions, and the suspension was stirred for 16 h. Water (120 mL) was then added, and the mixture was extracted with diethyl ether (3 x 50 mL). The organic phase was washed with sat. NaHCO\textsubscript{3} (aq.) (2 x 50 mL) and dried over MgSO\textsubscript{4}. The solvent was removed under reduced pressure. Purification of the remaining crude product by distillation (87 °C, 3.2 mbar) afforded 480 mg of the aldehyde 2b-\textsubscript{d\textsubscript{1}} as a colorless liquid (3.50 mmol, 39%). The deuteration degree of 2b-\textsubscript{d\textsubscript{1}} was found to be >98% (\textsuperscript{1}H NMR).

\begin{itemize}
    \item 2b-\textsubscript{d\textsubscript{1}}: C\textsubscript{8}H\textsubscript{7}DO\textsubscript{2}, M = 137.16 g mol\textsuperscript{-1}
    \item Yield: 39% (480 mg, 3.50 mmol)
    \item Appearance: Colorless liquid.
\end{itemize}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 298 K) δ [ppm] = 7.84 (d, \textsubscript{3}J\textsubscript{H-H} = 8.8 Hz, 2H, H-3), 7.01 (d, \textsubscript{3}J\textsubscript{H-H} = 8.8 Hz, 2H, H-4), 3.89 (s, 3H, OMe).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, 298 K) δ [ppm] = 190.5 (1C, C-1, t, \textsubscript{1}J\textsubscript{CD} = 26.8 Hz), 164.6 (1C, C-5), 132.0 (2C, C-3), 129.8 (1C, C-2), 114.3 (2C, C-4), 55.6 (1C, OMe).
Figure S1. $^1$H NMR spectrum (top, 300 MHz, CDCl$_3$, 298 K) and multiplicity-edited $^{13}$C DEPTQ NMR spectrum (bottom, 75 MHz) of $2b$-$d_1$. 
S3. Kinetic Measurements

S3.1. General Procedure for Kinetic Measurements

For a typical series of kinetic measurements, stock solutions of sublimed SIPr (1a), freshly distilled anisaldehyde (2b) and anisaldehyd-d$_1$ (2b-d$_1$) in THF-d$_8$ were prepared in a glovebox. In a glovebox, the SIPr stock solution and additional THF-d$_8$ were transferred into the NMR tube, which was then sealed with a septum and PTFE tape. The NMR tube was taken from the glovebox, thermostated to 298 K in the NMR spectrometer, and the first $^1$H NMR was recorded. For starting the reaction, the aldehyde stock solution was added by means of a syringe. The NMR tube was briefly shaken vigorously and reinserted into the spectrometer. $^1$H NMR spectra were acquired using DS = 0, NS = 6, D1 = 20 s (400 MHz); DS = 0, NS = 6, D1 = 21 s (600 MHz). The use of these parameters was necessary to account for the long relaxation time of the aldehydic proton. The spectra obtained were processed using TopSpin 4.0.6 with multi-integration. The following $^1$H NMR resonances were used for integration: 1a, 3.23 (sep., 4H); 2b, 7.76 (d, 2H); BI$_{1a,2b}$, 6.37 (d, 2H). The ratios of the integrated signals were normalized by the number of protons measured and converted to concentrations over the course of the reaction. According to a procedure by Burès et al., calculations for VTNA analysis followed.$^5$ In the last step, the data were plotted in OriginPro 2016 and when necessary, a linear regression was fitted to the data.

S3.2. 1:1 Reactions for Breslow Intermediate Formation

S3.2.1. Time course of the Breslow Intermediate BI$_{1a,2b}$ Formation

In a glovebox SIPr (1a) was dissolved in 500 µL THF-d$_8$ in a NMR tube. The aldehyde 2b was added via a Hamilton syringe and the course of the reaction was monitored by $^1$H NMR.

Table S1. Concentration used in the 1:1 reaction of SIPr (1a) with anisaldehyde (2b).

| Compound          | m or V | $c[a]$ | n [mmol] |
|-------------------|--------|--------|----------|
| SIPr (1a)         | 19.5 mg| 0.10   | 0.050    |
| Anisaldehyde (2b) | 6.7 µL | 0.11   | 0.055    |
| THF-d$_8$         |        |        | 500      |

[a] Concentration [mol L$^{-1}$] in the NMR, total volume 500 µL in THF-d$_8$. 

S5
**Figure S2.** Concentration/time profile of the reaction of SIPr (1a) with anisaldehyde (2b) to the Breslow intermediate BI$_{1a,2b}$, ca. 1:1.1 ratio of SIPr (1a) to aldehyde 2b (${ }^{1}$H NMR, 400 MHz, THF-$d_8$, 298 K, DS = 72).

**S3.2.2. Observation of Kinetic Isotope Effect**

In a glovebox, 300 µL of a SIPr (1a) stock solution (78.1 mg; 0.2 mmol in 1 mL THF-$d_8$) were diluted with 300 µL THF-$d_8$. Either anisaldehyde (2b) or anisaldehyde-$d_1$ (2b-$d_1$) were added by means of a Hamilton syringe to start the reaction. The course of the reaction was monitored by $^{1}$H NMR.

**Table S2.** Concentration used for identification of a KIE, ca. 1:1 reaction of SIPr (1a) and anisaldehyde (2b).

| Entry | Anisaldehyde (2b/2b-$d_1$) | \([\text{L}^{-1}]\) | \(n\) [mmol] |
|-------|-------------------------|----------------|-------------|
| 118    | 7.3                     | 0.1$^*$        | 0.06        |
| 120    | 7.3                     | 0.1$^*$        | 0.06        |

[a] Concentration [mol L$^{-1}$] in the NMR, total volume 600 µL in THF-$d_8$. 
S3.3. Isolation Method

S3.3.1. Determination of the Reaction Order in Anisaldehyde (2b)

In a glovebox, stock solutions of SIPr (1a) (292.9 mg; 0.75 mmol in 2 mL THF-d₈) and anisaldehyde (2b) (60.8 µL, 0.50 mmol in 1 mL THF-d₈) were prepared. All kinetic measurements were performed like described in the general procedure for kinetic measurements.
Table S3. Concentration used for isolation method, 7.5-fold excess of SiPr (1a) at t₀.

| Compound               | Stock solution | In NMR tube |
|------------------------|----------------|-------------|
|                        | V [µL] | c [mol L⁻¹] | n [mmol] | V [µL] | c[^a] |
| SiPr (1a)              | 400    | 0.375       | 0.15     | 0.30  |
| Anisaldehyde (2b)      | 40     | 0.500       | 0.02     | 0.04  |
| (additional) THF-d₈    | 60     |             |          | 500   |

[^a] Concentration [mol L⁻¹] in the NMR solution, total volume 500 µL in THF-d₈.

Table S4. Concentration used for isolation method, 5-fold excess of SiPr (1a) at t₀.

| Compound               | Stock solution | In NMR tube |
|------------------------|----------------|-------------|
|                        | V [µL] | c [mol L⁻¹] | n [mmol] | V [µL] | c[^a] |
| SiPr (1a)              | 400    | 0.375       | 0.15     | 0.30  |
| Anisaldehyde (2b)      | 60     | 0.500       | 0.03     | 0.06  |
| (additional) THF-d₈    | 40     |             |          | 500   |

[^a] Concentration [mol L⁻¹] in the NMR solution, total volume 500 µL in THF-d₈.

Figure S5. Top: Concentration/time profiles of the reaction of SiPr (1a) with anisaldehyde (2b) to the Breslow intermediate Bl₁a,₂b, 7.5-fold excess of the NHC component at t₀, (¹H NMR, 400 MHz, THF-d₈, 298 K). Bottom: kinetic data analysis; left: first order (ln[2b]/[2b]₀ vs. t), right: second order (1/[2b] vs t).
**S3.3.2. Attempt to Determine the Reaction Order in SIPr (1a)**

In a glovebox, a NMR tube was charged with SIPr (1a), and the latter was dissolved in 500 µL THF-\(d_8\). Anisaldehyde (2b) was added to the NMR tube with a syringe, and the course of the reaction was monitored by \(^1\)H NMR. The kinetic experiment was performed as described in the general procedure for kinetic measurements.

### Table S5. Concentration used for isolation method, 10-fold excess of SIPr (1a) at \(t_0\)

| Compound          | m or V | \(c^{[a]}\) | n [mmol] |
|-------------------|--------|-------------|----------|
| SIPr (1a)         | 5.9 mg | 0.03        | 0.015    |
| Anisaldehyde (2b) | 18.2 µL| 0.30        | 0.150    |
| THF-\(d_8\)       | 500    |             |          |

[a] Concentration [mol L\(^{-1}\)] in the NMR, total volume 500 µL in THF-\(d_8\).
S3.3.3. Proton Inventory

The proton inventory study was carried out at 7-fold excess of SIPr (1a) relative to aldehyde (2b, 2b-d1), as described in the literature. In a glovebox, stock solutions of SIPr (1a) (410.1 mg, 1.0 mmol in 5 mL THF-d8), anisaldehyde-d1 2b-d1 (14.6 µL, 0.12 mmol in 1 mL THF-d8) and anisaldehyde 2b (14.6 µL, 0.12 mmol in 1 mL THF-d8) were prepared. For the proton inventory, two sets of measurements (11 kinetic runs each) with different molar fractions n of anisaldehyde-d1 were monitored for 2 h by 1H NMR. The molar fraction n of anisaldehyde-d1 was increased in a stepwise manner. The kinetic experiments were performed as described in the general procedure for kinetic measurements. The concentration of SIPr was 0.14 mol·L⁻¹ (400 µL stock solution + 100 µL THF-d8) and for the aldehyde mixtures 0.02 mol·L⁻¹ in every tube. The rate constant k was determined via the integrated rate equation from the slope by plotting ln[2b]/[2b]₀ against t.

Table S6. Concentration used for proton inventory, 7-fold excess of SIPr (1a) at t₀.

| Entry [I-ALW] | Anisaldehyde (2b) | Anisaldehyde-d1 (2b-d1) |
|---------------|-------------------|-------------------------|
| Set 1 | Set 2 | n [%] | c [mol L⁻¹] | n [mmol] | n [%] | c [mol L⁻¹] | n [mmol] |
| 091, 102      | 100              | 0.02          | 0.0120       | 0        | 0        | 0        |
| 092, 103      | 90               | 0.018         | 0.0108       | 10       | 0.002   | 0.0012   |
| 093, 104      | 80               | 0.016         | 0.0096       | 20       | 0.004   | 0.0024   |
| 094, 105      | 70               | 0.014         | 0.0084       | 30       | 0.006   | 0.0036   |
| 095, 106      | 60               | 0.012         | 0.0072       | 40       | 0.008   | 0.0048   |
| 096, 107      | 50               | 0.010         | 0.0060       | 50       | 0.010   | 0.0060   |
| 097, 108      | 40               | 0.008         | 0.0048       | 60       | 0.012   | 0.0072   |
| 098, 109      | 30               | 0.006         | 0.0036       | 70       | 0.014   | 0.0084   |
| 099, 110      | 20               | 0.004         | 0.0024       | 80       | 0.016   | 0.0096   |
| 100, 111      | 10               | 0.002         | 0.0012       | 90       | 0.018   | 0.0108   |
| 101, 112      | 0                | 0             | 0            | 100      | 0.020   | 0.0120   |
A linear correlation with the fractional factor $\Phi$ indicates the transfer of one proton, and a quadratic one the transfer of two protons in the rate-limiting step:

Equation for transfer of one proton:

$$ \frac{k_D}{k_H} = (1 - n + n\Phi) $$  \hspace{1cm} (1)

Equation for the transfer of two protons:

$$ \frac{k_D}{k_H} = (1 - n + n\Phi)^2 $$  \hspace{1cm} (2)

For the proton inventory the inverse kinetic isotope effect $k_n/k_H$ was calculated for every measurement and plotted against the molar fraction $n$ (anisaldehyde-$d_1$).

### Table S7. Calculated values of the inverse kinetic isotope effect $k_n/k_H$ for a proton inventory.

| $n$ ($2b-d_1$) | Set 1 $k_n/k_H$ | Set 2 $k_n/k_H$ | Averaged $k_n/k_H$ | Calculated (1H*) | Calculated (2H*) |
|----------------|-----------------|-----------------|--------------------|------------------|------------------|
| 0.0            | 1.0000          | 1.0000          | 1.0000             | 1.0000           | 1.0000           |
| 0.1            | 0.9744          | 0.9794          | 0.9769             | 0.9367           | 0.8774           |
| 0.2            | 0.8619          | 0.9324          | 0.8971             | 0.8734           | 0.7628           |
| 0.3            | 0.6818          | 0.8278          | 0.7548             | 0.8100           | 0.6562           |
| 0.4            | 0.7108          | 0.6938          | 0.7023             | 0.7467           | 0.5576           |
| 0.5            | 0.6991          | 0.7467          | 0.7179             | 0.6834           | 0.4670           |
| 0.6            | 0.6583          | 0.5560          | 0.6072             | 0.6201           | 0.3845           |
| 0.7            | 0.5932          | 0.6682          | 0.6307             | 0.5568           | 0.3100           |
| 0.8            | 0.5591          | 0.4253          | 0.4922             | 0.4934           | 0.2435           |
| 0.9            | 0.3040          | 0.4691          | 0.3866             | 0.4301           | 0.1850           |
| 1.0            | 0.4216          | 0.3120          | 0.3668             | 0.3668           | 0.1345           |

Figure S8. Proton Inventory, set 1: $k_n/k_H$ plotted vs. molar fraction $n$ ($2b-d_1$), rate constants were determined by first-order analysis of aldehyde concentrations vs. $t$. Every measurement was monitored by $^1$H NMR (400 MHz, and 600 MHz, THF-$d_8$, 298 K).
Figure S9. Proton Inventory, set 2: \( k_n/k_H \) plotted vs. molar fraction \( n (2b-d_1) \), rate constants were determined by first-order analysis of aldehyde concentrations vs. \( t \). Every measurement was monitored by \( ^1H \) NMR (400 MHz, and 600 MHz, THF-\( d_8 \), 298 K).

Figure S10. Proton Inventory, \( k_n/k_H \) plotted vs. molar fraction \( n (2b-d_1) \), black full squares represent averaged values of the rate constants determined in the two individual sets of measurements (sets 1 and 2 above), together with the error margins. A linear regression (for the transfer of one proton) and a quadratic regression (transfer of two protons) were calculated. The inverse kinetic isotope effect \( k_D/k_H \) (fractionation factor \( \Phi \)) was determined by using the data of the pure aldehydes, so the last and the first measurement of the proton inventory.
S3.4. Variable Time Normalization Analysis

For this method, the starting concentration of one reactant is constant. To determine the order in the other reactant, the concentration of this reactant is varied. By manipulation of the time scale and testing of different reaction orders, it is possible to achieve overlapping of the measurements. When the measurements overlap well, the right orders in the reactants are found.

S3.4.1. Set 1: Variable Time Normalization Analysis with Moderate Excess in SIPr (1a)

In a glovebox, stock solutions of SIPr (1a) (468.7 mg SIPr; 1.2 mmol in 5 mL THF-d8), anisaldehyde (2b) (146 µL, 1.2 mmol in 1 mL THF-d8) and anisaldehyde-d1 (2b-d1) (146 µL, 1.2 mmol in 1 mL THF-d8) were prepared. For referencing, a standard sample consisting of 450 µL of the SIPr (1a) stock solution and 150 µL THF-d8 was prepared. All kinetic measurements were performed as described in the general procedure for kinetic measurements.

Table S8. Concentrations used for reaction monitoring by 1H NMR, reaction of SIPr (1a) with anisaldehyde 2b/2b-d1, moderate (up to 1.5-fold) excess of SIPr (1a).

| Entry | SIPr (1a) V [µL] | Anisaldehyde (2b) c[a] [mol L⁻¹] | n [mmol] | (Additional) THF-d8 V [µL] |
|-------|-----------------|---------------------------------|----------|--------------------------|
| [I-ALW-] | 450 | 0.18 | 0.108 | 0 | 0 | 150 |
| 215 | 400 | 0.16 | 0.096 | 70 | 0.14 | 0.084 | 130 |
| 216 | 450 | 0.18 | 0.108 | 60 | 0.12 | 0.072 | 90 |
| 217 | 400 | 0.16 | 0.096 | 60 | 0.12 | 0.072 | 140 |
| 218 | 450 | 0.18 | 0.108 | 70 | 0.14 | 0.084 | 80 |
| 219[b] | 400 | 0.16 | 0.096 | 60 | 0.12 | 0.072 | 140 |
| 220[b] | 450 | 0.18 | 0.108 | 70 | 0.14 | 0.084 | 80 |

[a] Concentration [mol L⁻¹] in the NMR, total volume 600 µL in THF-d8. [b] For this measurement, anisaldehyde-d1 (2b-d1) was used.

Table S9. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d1, moderate (up to 1.5-fold) excess of SIPr (1a).

| I-ALW | 215 | 216 | 217 | 218 | 219[b] | 220[b] |
|-------|-----|-----|-----|-----|--------|--------|
| c[a] (1a) | 0.16 | 0.18 | 0.16 | 0.18 | 0.16 | 0.18 |
| c[a] (2b/2b-d1) | 0.14 | 0.12 | 0.12 | 0.14 | 0.12 | 0.14 |

[a] Concentration [mol L⁻¹] in the NMR, total volume 600 µL in THF-d8. [b] For this measurement, anisaldehyde-d1 (2b-d1) was used.

Comparison of “Different Excess” Experiments

Here, ALW216, 217 and ALW215, 218 have the same initial concentration in 2b and are different excess experiments in 1a. They need to be compared to determine the order in 1a. The best overlap of the data was found for an order of 0.9 in 1a.

Table S10. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d1, moderate (up to 1.5-fold) excess of SIPr (1a), runs for comparison of “Different Excess” experiments are highlighted in the same color.

| I-ALW | 215 | 216 | 217 | 218 | 219[b] | 220[b] |
|-------|-----|-----|-----|-----|--------|--------|
| c[a] (1a) | 0.16 | 0.18 | 0.16 | 0.18 | 0.16 | 0.18 |
| c[a] (2b/2b-d1) | 0.14 | 0.12 | 0.12 | 0.14 | 0.12 | 0.14 |

[a] Concentration [mol L⁻¹] in the NMR, total volume 600 µL in THF-d8. [b] For this measurement, anisaldehyde-d1 (2b-d1) was used.
Figure S11. Variable time normalization analysis (VTNA): Reaction order of 0.9 in SIPr (1a). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by 1H NMR (400 MHz, THF-d8, 298 K).

Here, ALW215, 217 and ALW216, 218 have the same initial concentration in 1a and are different excess experiments in 2b. They need to be compared to determine the order in 2b. The best overlap was found for an order of 1.2 in 2b.

Table S11. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d1, moderate (up to 1.5-fold) excess of SIPr (1a), runs for comparison of “Different Excess” experiments are highlighted in the same color.

| I-ALW | 215 | 216 | 217 | 218 | 219[b] | 220[b] |
|-------|-----|-----|-----|-----|--------|--------|
| c(1a) | 0.16| 0.18| 0.16| 0.18| 0.16   | 0.18   |
| c(2b-d1) | 0.14| 0.12| 0.12| 0.14| 0.12   | 0.14   |

[a] Concentration [mol L⁻¹] in the NMR, total volume 600 μL in THF-d8. [b] For this measurement, anisaldehyde-d1 (2b-d1) was used.
Figure S12. Variable time normalization analysis (VTNA): Reaction order of 1.2 in aldehyde 2b/2b-d. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d) were obtained by 1H NMR (400 MHz, THF-d8, 298 K).

Figure S13. Variable time normalization analysis (VTNA): Reaction order of 0.9 in SIPr (1a), 1.2 in aldehyde 2b/2b-d gave best overlap (R² = 0.99 with 2b, R² = 0.99 with 2b-d1). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by 1H NMR (400 MHz, THF-d8, 298 K).
Comparison of “Same Excess” Experiments

Here, ALW217, 218 and ALW219, 220 are same excess experiments with a difference in concentration of 0.02 mol L\(^{-1}\) in 1a and 2b. These reaction profiles need to be compared to analyze for product acceleration or inhibition. The reactions became faster in the presence of BI\(_{1a,2b-2b-d1}\), indicating product acceleration.

Table S12. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-\(d1\), moderate (up to 1.5-fold) excess of SIPr (1a), runs for comparison of “Same Excess” experiments are highlighted in the same color.

| I-ALW | 215 | 216 | 217 | 218 | 219\(\text{[b]}\) | 220\(\text{[b]}\) |
|-------|-----|-----|-----|-----|-------------|-------------|
| \(c\)\(\text{[a]}\) (1a) | 0.16 | 0.18 | 0.16 | 0.18 | 0.16 | 0.18 |
| \(c\)\(\text{[a]}\) (2b/2b-\(d1\)) | 0.14 | 0.12 | 0.12 | 0.14 | 0.12 | 0.14 |

[a] Concentration [mol L\(^{-1}\)] in the NMR, total volume 600 μL in THF-\(d8\). [b] For this measurement, anisaldehyde-\(d1\) (2b-\(d1\)) was used.

Figure S14. Time shift for same excess experiments: Concentration of SIPr (1a) vs. t, t-shift = 5 min for ALW217 and 11 min for ALW219. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-\(d1\) (2b-\(d1\)) were obtained by \(^1\)H NMR (400 MHz, THF-\(d8\), 298 K).

Table S13. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-\(d1\), moderate (up to 1.5-fold) excess of SIPr (1a), runs for comparison of “Same Excess” experiments are highlighted in the same color.

| I-ALW | 215 | 216 | 217 | 218 | 219\(\text{[b]}\) | 220\(\text{[b]}\) |
|-------|-----|-----|-----|-----|-------------|-------------|
| \(c\)\(\text{[a]}\) (1a) | 0.16 | 0.18 | 0.16 | 0.18 | 0.16 | 0.18 |
| \(c\)\(\text{[a]}\) (2b/2b-\(d1\)) | 0.14 | 0.12 | 0.12 | 0.14 | 0.12 | 0.14 |

[a] Concentration [mol L\(^{-1}\)] in the NMR, total volume 600 μL in THF-\(d8\). [b] For this measurement, anisaldehyde-\(d1\) (2b-\(d1\)) was used.
Figure S15. Time shift for same excess experiments: Concentration of aldehyde (2b/2b-d1) vs. t, t-shift = 5 min for ALW217 and 11 min for ALW219. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by 1H NMR (400 MHz, THF-d8, 298 K).

Subsequently, an order of 0.4 in BI1a,2b was determined from the best linearity for all measurements.

Simultaneous Consideration of all Contributions to the Kinetic Order

Figure S16. Variable time normalization analysis (VTNA): reaction order of 0.9 in SIPr (1a), 1.2 in aldehyde 2b/2b-d1, 0.4 in Breslow intermediate BI1a,2b-d1 gave best overlap (R² = 0.99). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by 1H NMR (400 MHz, THF-d8, 298 K).
Determination of KIE by a KIE Normalization Factor $f_{\text{KIE}}$

Introduction of a KIE normalization factor $f_{\text{KIE}} = 1.8$ gave best overlap and best linearity for all measurements.

![Graph](image)

**Figure S17.** Variable time normalization analysis (VTNA): reaction order of 0.9 in SIPr (1a), 1.2 in aldehyde 2b/2b-$d_1$, 0.4 in Breslow intermediate BI$_{1a,2b}$ and a normalization factor for KIE $f_{\text{KIE}}$ of 1.8 gave best overlap ($R^2 = 0.99$). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-$d_1$ (2b-$d_1$) were obtained by $^1$H NMR (400 MHz, THF-$d_8$, 298 K).

### S3.4.2. Set 2: Variable Time Normalization Analysis with Moderate Excess in Aldehyde (2b)

**Table S14.** Concentrations used for reaction monitoring by $^1$H NMR, reaction of SIPr (1a) with anisaldehyde 2b/2b-$d_1$, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-$d_1$.

| Entry  | SIPr (1a) | Anisaldehyde (2b) | THF-$d_8$ |
|--------|-----------|--------------------|-----------|
| [Laboratory] | V [µL][a] | c [b] | n [mmol] | V [µL][a] | c [b] | n [mmol] | V [µL] |
| Standard | 450 | 0.18 | 0.108 | 0 | 0 | 0 | 150 |
| 221 | 250 | 0.10 | 0.060 | 80 | 0.16 | 0.096 | 270 |
| 222 | 250 | 0.10 | 0.060 | 90 | 0.18 | 0.108 | 260 |
| 223 | 300 | 0.12 | 0.072 | 90 | 0.18 | 0.108 | 210 |
| 224 | 300 | 0.12 | 0.072 | 100 | 0.20 | 0.120 | 200 |
| 225[b] | 250 | 0.10 | 0.060 | 90 | 0.18 | 0.108 | 260 |
| 226[b] | 300 | 0.12 | 0.072 | 100 | 0.20 | 0.120 | 200 |

[a] The stock solutions described for set 1 were also used for this set of experiments, performed as stated under S3.5.1. [b] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 µL in THF-$d_8$. [c] For this measurement, anisaldehyde-$d_1$ (2b-$d_1$) was used.
Table S15. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-d.

| I-ALW | 221 | 222 | 223 | 224 | 225[b] | 226[b] |
|-------|-----|-----|-----|-----|--------|--------|
| $c^{[a]} (1a)$ | 0.10 | 0.10 | 0.12 | 0.12 | 0.10 | 0.12 |
| $c^{[b]} (2b/2b-d)$ | 0.16 | 0.18 | 0.18 | 0.20 | 0.18 | 0.20 |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 μL in THF-$d_6$. [b] For this measurement, anisaldehyde-$d_1$ (2b-d) was used.

Comparison of “Different Excess” Experiments

Table S16. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-d, runs for comparison of “Different Excess” experiments are highlighted in the same color.

| I-ALW | 221 | 222 | 223 | 224 | 225[b] | 226[b] |
|-------|-----|-----|-----|-----|--------|--------|
| $c^{[a]} (1a)$ | 0.10 | 0.10 | 0.12 | 0.12 | 0.10 | 0.12 |
| $c^{[b]} (2b/2b-d)$ | 0.16 | 0.18 | 0.18 | 0.20 | 0.18 | 0.20 |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 μL in THF-$d_6$. [b] For this measurement, anisaldehyde-$d_1$ (2b-d) was used.

Figure S18. Variable time normalization analysis (VTNA); Reaction order of 0.4 in SIPr (1a). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-$d_1$ (2b-d) were obtained by $^1$H NMR (600 MHz, THF-$d_6$, 298 K).

Table S17. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-d, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-d, runs for comparison of “Different Excess” experiments are highlighted in the same color.

| I-ALW | 221 | 222 | 223 | 224 | 225[b] | 226[b] |
|-------|-----|-----|-----|-----|--------|--------|
| $c^{[a]} (1a)$ | 0.10 | 0.10 | 0.12 | 0.12 | 0.10 | 0.12 |
| $c^{[b]} (2b/2b-d)$ | 0.16 | 0.18 | 0.18 | 0.20 | 0.18 | 0.20 |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 μL in THF-$d_6$. [b] For this measurement, anisaldehyde-$d_1$ (2b-d) was used.
Figure S19. Variable time normalization analysis (VTNA): Reaction order of 1.7 in aldehyde 2b/2b-d. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by ¹H NMR (600 MHz, THF-d₈, 298 K).

Figure S20. Variable time normalization analysis (VTNA): Reaction order of 0.4 in SIPr (1a), 1.7 in aldehyde 2b/2b-d1 gave best overlap (R² = 0.97 with 2b, R² = 0.99 with 2b-d1). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d1 (2b-d1) were obtained by ¹H NMR (600 MHz, THF-d₈, 298 K).
Comparison of “Same Excess” Experiments

Here, ALW221, 223 and ALW222, 224 are same excess experiments with a difference in concentration of 0.02 mol L$^{-1}$ in 1a and 2b. These reaction profiles need to be compared to analyze for product acceleration or inhibition. The reactions became faster in the presence of BI$_{1a,2b}$-$d_1$, indicating product acceleration.

Table S18. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-$d_1$, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-$d_1$, runs for comparison of “Same Excess” experiments are highlighted in the same color.

| I-ALW | 221 | 222 | 223 | 224 | 225$^b$ | 226$^b$ |
|-------|-----|-----|-----|-----|-----|-----|
| c$^{(1)}$ (1a) | 0.10 | 0.10 | 0.12 | 0.12 | 0.10 | 0.12 |
| c$^{(1)}$ (2b/2b-$d_1$) | 0.16 | 0.18 | 0.18 | 0.20 | 0.18 | 0.20 |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 μL in THF-$d_8$. [b] For this measurement, anisaldehyde-$d_1$ (2b-$d_1$) was used.

Figure S21. Time shift for same excess experiments: Concentration of SIPr (1a) vs. t, t-shift = 4 min for ALW221 and 2.5 min for ALW222. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-$d_1$ (2b-$d_1$) were obtained by $^1$H NMR (600 MHz, THF-$d_8$, 298 K).

Table S19. Concentrations used in VTNA of the reaction of SIPr (1a) with anisaldehyde 2b/2b-$d_1$, moderate (up to 1.8-fold) excess of anisaldehyde 2b/2b-$d_1$, runs for comparison of “Same Excess” experiments are highlighted in the same color.

| I-ALW | 221 | 222 | 223 | 224 | 225$^b$ | 226$^b$ |
|-------|-----|-----|-----|-----|-----|-----|
| c$^{(1)}$ (1a) | 0.10 | 0.10 | 0.12 | 0.12 | 0.10 | 0.12 |
| c$^{(1)}$ (2b/2b-$d_1$) | 0.16 | 0.18 | 0.18 | 0.20 | 0.18 | 0.20 |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 600 μL in THF-$d_8$. [b] For this measurement, anisaldehyde-$d_1$ (2b-$d_1$) was used.
Figure S22. Time shift for same excess experiments: Concentration of aldehyde (2b/2b-d$_1$) vs. $t$, $t$-shift = 4 min for ALW221 and 2.5 min for ALW222. Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d$_1$ (2b-d$_1$) were obtained by $^1$H NMR (600 MHz, THF-$d_8$, 298 K).

Simultaneous Consideration of all Contributions to the Kinetic Order

Figure S23. Variable time normalization analysis (VTNA): Reaction order of 0.4 in SIPr (1a), 1.7 in aldehyde 2b/2b-d$_1$, 0.4 in Breslow intermediate BI$_{1a,2b}$ gave best overlap ($R^2 = 0.99$). Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d$_1$ (2b-d$_1$) were obtained by $^1$H NMR (600 MHz, THF-$d_8$, 298 K).
Determination of KIE by a KIE Normalization Factor $f_{\text{KIE}}$

Introduction of a KIE normalization factor $f_{\text{KIE}} = 1.8$ gave best overlap and best linearity for all measurements.

Figure S24. Variable time normalization analysis (VTNA): Reaction order of 0.4 in SIPr (1a), 1.7 in aldehyde 2b/2b-d, 0.4 in Breslow intermediate $\text{BI}_{1a,2b}-d_1$ and a normalization factor for KIE $f_{\text{KIE}}$ of 1.8 gave best overlap ($R^2 = 0.99$), Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-$d_1$ (2b-$d_1$) were obtained by $^1$H NMR (600 MHz, THF-$d_8$, 298 K).

S3.4.3. “Same Excess” Experiments with Reaction Product $\text{BI}_{1a,2b}$ added at $t_0$

In a glovebox, stock solutions of SIPr (1a) (93.7 mg SIPr; 0.24 mmol in 1 mL THF-$d_8$) and anisaldehyde (2b) (146 µL, 1.2 mmol in 1 mL THF-$d_8$) were prepared. For sample ALW240, first 20 µL of the anisaldehyde stock solution were added to the SIPr solution and left for 6 h until the aldehyde was consumed completely. Then, additional 70 µL of the aldehyde stock solution were added, and the reaction was monitored by $^1$H NMR spectroscopy.

Table S20. Concentrations used for comparison of same excess experiments of the reaction of SIPr (1a) with anisaldehyde (2b), moderate (up to 1.8-fold) excess of anisaldehyde 2b.

| Entry | [I-ALW-] | V [µL] | SIPr (1a) | V [µL] | Anisaldehyde (2b) | V [µL] |
|-------|----------|--------|-----------|--------|--------------------|--------|
|       |          |        | c [mol L$^{-1}$] | n [mmol] | c [mol L$^{-1}$] | n [mmol] | THF-$d_8$ |
| 238   | 200      | 0.08   | 0.048     | 70     | 0.14               | 0.084  | 330       |
| 239   | 300      | 0.12   | 0.072     | 90     | 0.18               | 0.108  | 210       |
| 240   | 300      | 0.12   | 0.072     | 20     | 0.04               | 0.024  | 210       |
| 240   | +70      |        | +0.14     |        | +0.084             |        |           |

Here, ALW238, 223 and ALW239 are same excess experiments with a difference in concentration of 0.04 mol L$^{-1}$ in 1a and 2b. An additional experiment with reaction product at $t_0$ (0.04 mol L$^{-1}$) was performed for additional probing of autocatalysis by $\text{BI}_{1a,2b}$. After time shift the course of the reaction of ALW238 and 239 should give an overlay if the product has no effect on the reaction rate. The reaction rate increases in the presents of $\text{BI}_{1a,2b}$ and an overlay of the reaction courses of ALW239 and 240 indicate product acceleration.
Table S21. Concentrations used in VTNA probing for autocatalysis by BI_{1a,2b} in the reaction of SIPr (1a) with anisaldehyde 2b, moderate (up to 1.8-fold) excess of anisaldehyde 2b.

|     | I-ALW | 238 | 239 | 240 |
|-----|-------|-----|-----|-----|
| c_{a} (1a) | 0.08 | 0.12 | 0.08 |
| c_{a} (2b) | 0.14 | 0.18 | 0.14 |
| c_{a} (BI_{1a,2b}) | 0.00 | 0.00 | 0.04 |

[a] Concentration [mol L⁻¹] in the NMR solution, total volume 600 μL in THF-d₈.

Figure S25. Time shift for same excess experiments: Concentration of SIPr (1a) vs. t, t-shift = 6 min for ALW238 and ALW240, Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) were obtained by ¹H NMR (600 MHz, THF-d₈, 298 K).

Figure S26. Time shift for same excess experiments: Concentration of aldehyde 2b vs. t, t-shift = 6 min for ALW238 and ALW240, Concentration/time profiles of the reaction of SIPr (1a) with anisaldehyde (2b) or anisaldehyde-d₁ (2b-d₁) were obtained by ¹H NMR (600 MHz, THF-d₈, 298 K).
S3.5. NMR Characterization of the Complex 1a-BI_{1a,2b}

S3.5.1. NMR Comparison of the Complex 1a-BI_{1a,2b} with Pure SiPr (1a)

Two NMR tubes, equipped with J Young valves, were charged under inert conditions with SiPr (1a, see Tables below for amounts). The solid was dissolved in 500 µL THF-\text{d}_8 (each). To NMR tube B, anisaldehyde (2b) was added by means of a Hamilton syringe. The NMR sample B was monitored by $^1$H NMR until all aldehyde was consumed. $^1$H, $^{13}$C, and HMBC NMR spectra were then recorded of both the pure SiPr (1a) solution (sample A) and of sample B, containing the SiPr-Breslow intermediate complex 1a-BI_{1a,2b}. The $^1$H NMR spectra of sample B did not indicate any shift differences between the Breslow intermediate BI_{1a,2b} alone\cite{7} and the BI_{1a,2b} portion in the complex 1a-BI_{1a,2b}. For the recording of the $^{13}$C NMR spectrum of SiPr-Breslow intermediate complex 1a-BI_{1a,2b}, the D1 time was increased in a stepwise manner to 6 s, 10 s, 15 s and 20 s. Nevertheless, no resonance of the C2 carbene C-atom at 244.7 ppm could be detected in the $^{13}$C NMR spectrum. In the $^1$H,$^{13}$C HMBC of the complex 1a-BI_{1a,2b}, a cross peak of the carbene carbon C2 at 244.7 ppm and H4 and H5 at 3.84 ppm was detected.

| compound          | NMR tube A | c\textsuperscript{(a)} | n [mmol] |
|-------------------|------------|------------------------|----------|
| SiPr (1a)         | 19.5 mg    | 0.10                   | 0.05     |
| THF-\text{d}_8    | 500 µL     |                        |          |

| compound          | NMR tube B | c\textsuperscript{(a)} | n [mmol] |
|-------------------|------------|------------------------|----------|
| SiPr (1a)         | 39 mg      | 0.20                   | 0.10     |
| anisaldehyde (2b) | 6.1 µL     | 0.10                   | 0.05     |
| THF-\text{d}_8    | 500 µL     |                        |          |

[a] Concentration [mol L$^{-1}$] in the NMR solution, total volume 500 µL in THF-\text{d}_8.

Figure S27. Multiplicity-edited $^{13}$C DEPTQ NMR spectra (151 MHz, 289 K, THF-\text{d}_8). Top: SiPr (1a); bottom: SiPr-Breslow intermediate complex 1a-BI_{1a,2b}. Inset: enlarged view of the spectral region 240-250 ppm of both traces (tubes A and B).
Figure S28. $^1$H,$^{13}$C HMBC spectrum (600 MHz/151 MHz, THF-$d_8$, 298 K) of SIPr-Breslow intermediate complex 1a·Bl$_{1a,2b}$. 
S4. Computational Details

The conformational space for each structure was explored using the OPLS3 force field\(^\text{[1]}\) and a modified Monte Carlo search algorithm implemented in MacroModel.\(^\text{[1,2]}\) An energy cut-off of 84 kJ mol\(^{-1}\) was employed for the conformational analysis, and structures with heavy-atom root-mean-square deviations (RMSD) less than 1.0–1.5 Å after the initial force field optimizations were considered to be the same conformer. The remaining structures were subsequently optimized with the meta-GGA functional TPSS,\(^\text{[13]}\) Grimme’s dispersion correction D3 with Becke-Johnson damping,\(^\text{[14]}\) the double-\(\zeta\) basis set 6-31+G(d,p), and the IEPCM continuum model for tetrahydrofuran.\(^\text{[15]}\) Density fitting was used to accelerate the calculations. An integration grid corresponding to 99 radial shells and 974 angular points was used throughout this investigation for the numerical integration of the density. Vibrational analysis verified that each structure was a minimum or a transition state. Following the intrinsic reaction coordinates (IRC) confirmed that all transition states connected the corresponding reactants and products on the potential energy surface. Thermal corrections were obtained from unscaled harmonic vibrational frequencies at the same level of theory for a standard state of 1 mol\(\cdot\)L\(^{-1}\) and 298.15 K. Entropic contributions to free energies were obtained from partition functions evaluated with Grimme’s quasi-harmonic approximation.\(^\text{[16]}\) Electronic energies were subsequently obtained from single-point calculations of the TPSS-D3BJ geometries employing Neese’s domain-based local pair-natural orbital (DLPNO) approach to the CCSD(T) method [DLPNO-CCSD(T)] with the default normalPNO settings.\(^\text{[13]}\) The triple-\(\zeta\) cc-pVTZ basis set,\(^\text{[17]}\) and the SMD continuum model for THF.\(^\text{[18]}\) All density functional theory calculations were performed with Gaussian 16\(^\text{[17]}\) while the DLPNO-CCSD(T) calculations were performed with ORCA.\(^\text{[19]}\)

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