Supporting Information

Investigation of the Dynamic Nature of 1,2-Oxazines Derived from Peralkyl Cyclopentadiene and Nitrosocarbonyl Species

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General Considerations. Dry THF, pyridine, DMSO, and CH₂Cl₂ were obtained from a Glass Contour solvent purification system. All other reagents and solvents were used as obtained from commercial sources. Grubbs 3rd generation catalyst, (iMesH₂)(C₅H₅N)₂(Cl)₂Ru=CHPH, was synthesized according to literature procedure.¹ H and ¹³C NMR spectra were recorded on a Bruker AVance 300 or 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard (CDCl₃, ¹H: 7.26 ppm and ¹³C: 77.16 ppm and DMSO-d₆, ¹H: 2.50 ppm). HRMS was performed on a Thermo LTQ Orbitrap with a resolution setting of 30,000. Gel permeation chromatography (GPC) was performed using a GPC setup consisting of: a Shimadzu pump, 3 in-line columns, and Wyatt light scattering and refractive index detectors THF as the mobile phase.

Synthesis of 3. Compounds 1 and 2 were synthesized according to the literature.²,³ Into a flame-dried, N₂-purged round bottom flask, N,N-carbonyldiimidazole (1.4 g, 8.7 mmol, 1.3 eq.), a stir bar, and 15 mL of CH₂Cl₂ were added. To this solution, 1 (1.9 g, 8.7 mmol, 1.3 eq.) was added portion-wise. The reaction mixture was then stirred at room temperature for 45 minutes. After this time, DMAP (81.8 mg, 0.7 mmol, 0.1 eq.) and 2 (1.1 g, 6.7 mmol, 1.0 eq.) in
15 mL of CH$_2$Cl$_2$ were added to the reaction mixture. The reaction mixture was then stirred at room temperature for 18 hours. The solution was then washed successively with 1 M HCl (2 × 30 mL), sat. NaHCO$_3$ (2 × 30 mL), and brine (2 × 30 mL). The organic layer was dried over Na$_2$SO$_4$ and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (10% EtOAc/Hex) on silica gel and the product was isolated as a white solid (70% yield). $^1$H NMR (300 MHz, CDCl$_3$) δ 6.20 (t, $J$ = 1.7 Hz, 2H), 4.03 (s, 2H), 3.91 (s, 2H), 3.19 (s, 2H), 2.62 (s, 2H), 1.65 (d, $J$ = 9.0 Hz, 12H), 1.56 (d, $J$ = 9.9 Hz, 1H), 1.41 (d, $J$ = 9.6 Hz, 1H), 0.84 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.7, 166.6, 138.0, 137.8, 135.1, 66.8, 55.2, 47.8, 45.2, 42.7, 39.1, 16.7, 10.9, 10.0. HRMS: [M+H]$^+$ calcd for C$_{22}$H$_{28}$NO$_4$, 370.2018; found, 370.20247.

**General Procedure for the Synthesis of Oxazines 8-10.** A N$_2$-purged round bottom flask was charged with 3 (0.586 g, 1.6 mmol, 1.0 eq.), tetrabutylammonium periodate (0.8371 g, 1.9 mmol, 1.2 eq.), a stir bar, and MeOH (50 mL). To this solution, hydroxyurea (1.9 mmol, 1.2 eq.) in 30 mL of MeOH was added dropwise. The reaction mixture was stirred vigorously and monitored by TLC. Upon consumption of 3, the organic layer was concentrated under reduced pressure and then taken up in EtOAc. The organic solution was then washed successively with sat. aq. Na$_2$SO$_3$ (2 × 30 mL) and sat. aq. NaHCO$_3$ (2 × 30 mL). The organic layer was dried over
Na₂SO₄ and then concentrated under reduced pressure. The crude material was purified by flash chromatography (50% EtOAc/Hex) on silica gel and the products were isolated as white solids.

8: Isolated yield = 64%. ¹H NMR (300 MHz, CDCl₃) δ 6.30 (t, J = 1.7 Hz, 2H), 4.30–4.12 (m, 2.5H), 3.90–3.81 (m, 1.5H), 3.31 (q, J = 1.6 Hz, 2H), 2.75 (s, 2H), 1.87–1.86 (m, 3H), 1.77–1.74 (m, 3H), 1.67–1.63 (m, 7H), 1.54–1.51 (m, 1H), 1.37 (s, .75H), 1.33 (s, 2.25H), 1.02 (s, 2.25H), 0.73 (s, 0.75H). ¹³C NMR (125 MHz, CDCl₃) δ 178.2, 177.1, 166.9, 139.8, 138.1, 132.5, 94.6, 79.7, 68.2, 66.8, 61.4, 48.1, 45.5, 42.9, 39.3, 24.0, 12.4, 12.1, 10.9, 9.4, 1.1. HRMS: [M+H]⁺ calcd for C₂₄H₃₂N₂O₆, 443.2182; found, 443.21971.

9: Isolated yield = 97%. ¹H NMR (300 MHz, CDCl₃) δ 6.30 (s, 2H), 4.31–4.20 (m, 2.5H), 4.13 (q, J = 7.08 Hz, 2H), 3.85 (s, 1.5H), 2.75 (s, 2H), 1.73 (m, 3H), 1.67–1.65 (m, 3H), 1.60–1.51 (m, 5H), 1.38–1.35 (m, 3H), 1.24 (q, J = 7.0 Hz, 3H), 1.04 (s, 2.25H), 0.73 (s, 0.75H). ¹³C NMR (125 MHz, CDCl₃) δ 177.09, 177.07, 166.9, 160.2, 138.0, 133.8, 94.2, 80.1, 77.3, 77.1, 76.8, 68.4, 66.6, 62.0, 61.5, 48.1, 45.4, 42.9, 39.3, 14.5, 13.0, 12.4, 12.0, 11.6, 10.8, 9.5, 1.0. HRMS: [M+H]⁺ calcd for C₂₅H₃₃N₂O₇, 473.2288; found, 473.23041.

10: Isolated yield = 88%. ¹H NMR (300 MHz, CDCl₃) δ 6.31 (t, J = 1.6 Hz, 2H), 4.36–4.14 (m, 2.5H), 3.89–3.81 (m, 1.5H), 3.31 (t, J = 1.6 Hz, 2H), 2.75 (s, 2H), 1.76–1.74 (m, 3H), 1.69–1.63 (m, 7H), 1.57–1.51 (m, 2H), 1.37 (s, .75H), 1.33 (s, 2.25H), 1.05 (s, 2.25H), 0.72 (s, 0.75H). ¹³C NMR (125 MHz, CDCl₃) δ 177.2, 177.07, 166.7, 164.7, 138.1, 132.2, 100.1, 95.0, 80.7, 68.6, 66.8, 61.7, 60.4, 48.2, 45.5, 43.0, 39.4, 12.7, 11.1, 9.3, 1.1. HRMS: [M+H]⁺ calcd for C₂₃H₃₀N₃O₆, 444.2135; found, 444.21479.

10a: ¹H NMR (300 MHz, CDCl₃) δ 6.31 (t, J = 1.7 Hz, 2H), 4.24 (d, J = 17.1 Hz, 1H), 4.17 (d, J=17.0 Hz, 1H), 3.87 (d, J= 10.9 Hz, 1H), 3.83 (d, J= 10.9 Hz, 1H), 3.32 (t, J = 1.7 Hz, 2H), 2.76 (s, 2H), 1.76 (d, J= 1.3 Hz, 3H), 1.69 (d, J= 1.3 Hz, 3H), 1.66–1.63 (m, 4H), 1.54 (d, J= 10.3 Hz, 1H) 1.33 (s, 3H), 1.05, (s, 3H).

10b: ¹H NMR (300 MHz, CDCl₃) δ 6.31 (t, J = 2.0 Hz, 2H), 4.35 (d, J = 11.8 Hz, 1H), 4.21 (d, J= 11.8 Hz, 1H), 3.32 (t, J= 1.6 Hz, 2H), 2.75 (s, 2H), 1.74 (d, J= 1.5 Hz, 3H), 1.66 (d, J= 1.1 Hz, 1H), 1.65–1.61 (m, 4H), 1.54 (d, 10.1 Hz, 1H), 1.37 (s, 3H), 0.73 (s, 3H).
**Synthesis of S1.** Preparation of S1 by an alternative method was previously reported. A round bottom flask was charged with 4-nitroaniline (0.7001 g, 5.0 mmol, 1.0 eq.), a stir bar, 2 mL of THF, 0.6 mL of sat. NaHCO₃, and 0.4 mL of H₂O. Phenyl chloroformate (0.64 mL, 5.1 mmol, 1.02 eq.) was then added drop-wise via an addition funnel. The resulting mixture was stirred at room temperature for 3 hours. The reaction mixture was then diluted with EtOAc and then washed with sat. NaHCO₃ (2 × 10 mL) followed by brine (1 × 10 mL). The organic layer was dried over Na₂SO₄ and then concentrated under reduced pressure. The resulting carbamate was used without further purification (97% crude yield). ¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.49 – 7.35 (m, 3H), 7.30 – 7.24 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 151.3, 150.2, 143.6, 143.5, 129.7, 126.4, 125.4, 121.6, 118.2.

**Synthesis of S2.** Preparation of S2 by an alternative method was previously reported.² Into a flame-dried, N₂-purged round bottom flask was added carbamate S1 (0.6 g, 2.32 mmol, 1.0 eq.), NEt₃ (0.32 mL, 2.32 mmol, 1.0 eq.), CH₂Cl₂ (2.32 mL) and a stir bar. Separately, hydroxylamine (0.559 g, 8 mmol) and potassium carbonate (2.222 g, 16 mmol) was free-based in dry DMSO (4 mL) for 12 hours. A solution of free-based hydroxylamine (2.32 mL in DMSO, 4.64 mmol, 2.0 eq.) was then added into the solution containing S1. The resulting mixture was then heated at 40 °C and stirred for 3 hours. After being removed from heat and returning to room temperature, the reaction mixture was added into 30 mL of H₂O and extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over Na₂SO₄ and then concentrated under reduced pressure. The desired product was obtained as a yellow solid (83% yield). ¹H NMR (500 MHz, DMSO) δ 9.49 (s, 1H), 9.27 (s, 1H), 9.15 (s, 1H), 8.14 (d, J = 9.0 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ 157.8, 146.4, 141.4, 124.8, 118.5.
Synthesis of 11. A round bottom flask was charged with 3 (0.336 g, 0.9 mmol, 1.0 eq.), 2 (0.359 g, 1.8 mmol, 1.2 eq.), a stir bar, and THF (10 mL). CuCl (0.037 g, 0.36 mmol, 0.4 eq.) and pyridine (7.3 µL, 0.09 mmol, 0.1 eq.) were then added. The reaction mixture was vigorously stirred under ambient conditions for 18 hours. EtOAc (10 mL) and sat. aq. EDTA (10 mL) were then added to the reaction mixture. The organic layer was separated and then washed successively with sat. EDTA (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over Na₂SO₄ and then concentrated under reduced pressure. The crude material was purified by flash chromatography (20% EtOAc/Hex) on silica gel and the product was isolated as a yellow solid (70% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, J= 8.9 Hz, 2H), 7.75 (s, 1H), 7.56 (d, J= 9.3 Hz, 2H), 6.27 (s, 2H), 4.39–4.16 (m, 2.5H), 3.92–3.84 (m, 1.5H), 3.32 (s, 2H), 2.77 (s, 2H), 1.77–1.75 (m, 3H), 1.71–1.65 (m, 6.5H), 1.56–1.53 (m, 1.5H), 1.46–1.43 (m, 3H), 1.10 (s, 2.25H), 0.78 (s, 0.75H). ¹³C NMR (126 MHz, CDCl₃) δ 177.11, 177.07, 166.8, 159.7, 143.7, 143.1, 139.2, 138.01, 137.98, 132.5, 125.1, 118.5, 100.0, 96.8, 96.3, 81.3, 68.1, 65.9, 62.1, 60.8, 48.1, 45.5, 42.9, 39.2, 15.3, 13.0, 12.7, 12.6, 12.5, 12.0, 11.1, 10.9, 9.3. HRMS (ESI): [M+H]⁺ calcd for C₂₉H₃₉N₄O₈, 565.2298; found, 565.23191.

Synthesis of poly(11).

Into a flame-dried, N₂-purged round bottom flask, monomer 11 (733 mg, 1.3 mmol, 35 eq.), a stir bar, and 2.6 mL of CH₂Cl₂ were added. Once homogeneous, the solution was cooled in an
ice bath at 0 °C and Grubbs 3\textsuperscript{rd} generation catalyst (26.6 mg, 0.04 mmol, 1.0 eq.) in 4.6 mL of CH\textsubscript{2}Cl\textsubscript{2} was quickly added. The reaction solution was stirred for 3 hours, during which time the ice bath expired. Ethyl vinyl ether (4.0 mL) was then added to the reaction mixture and the solution was stirred for an additional 10 minutes. The reaction mixture was then concentrated under reduced pressure and dissolved in a minimal amount of CH\textsubscript{2}Cl\textsubscript{2}. The polymer solution was then filtered through an alumina/Celite plug using CH\textsubscript{2}Cl\textsubscript{2} as eluent. The solution volume was reduced under reduced pressure and then added dropwise into an excess of methanol, causing the polymer to precipitate from solution. The polymer was then collected by vacuum filtration, washed with additional methanol, and then dried under vacuum to provide a light yellow powder (57\% yield). $M_\text{w} = 30.0$ kDa, $M_\text{n} = 25.7$ kDa, $D = 1.05$.

![Figure S1: RI trace of poly(11).](image)

**General method for monitoring the small-molecule isomerization**

Into a 20 mL flame-dried, N\textsubscript{2}-purged scintillation vial sealed with a rubber septum, oxazine (0.0298 g, 0.067 mmol, 1.0 eq.), 1,4-dicyanobenzene (0.0085 g, 0.066 mmol, 0.99 eq.), 4.5 mL DMSO-d\textsubscript{6}, and a stir bar were added. The vials were then submerged into a pre-heated oil bath maintained at the designated temperature. At designated time points, 0.3 mL aliquots were removed by syringe and transferred into NMR tubes and then frozen in an ice bath until the
NMR spectra were collected. Runs were done in triplicate. The amount of total oxazine was also assessed over the course of the experiment, and final values are shown in Table S1.

Table S1: Percent of initial total oxazine at the time point indicated.

<table>
<thead>
<tr>
<th>Oxazine</th>
<th>37 °C</th>
<th>60 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>91% (293 h)</td>
<td>85% (121 h)</td>
<td>93% (12 h)</td>
</tr>
<tr>
<td>9</td>
<td>99% (292 h)</td>
<td>94% (72 h)</td>
<td>91% (4 h)</td>
</tr>
<tr>
<td>10</td>
<td>95% (311 h)</td>
<td>87% (32 h)</td>
<td>95% (3 h)</td>
</tr>
<tr>
<td>11</td>
<td>96% (101 h)</td>
<td>86% (9 h)</td>
<td>93% (3 h)</td>
</tr>
</tbody>
</table>

Method for monitoring the isomerization of poly(11)

In an N₂-purged NMR tube, poly(11) (0.0051 g, 0.0002 mmol) was dissolved in anhydrous DMSO-d₆ (0.5 mL). The isomerization was monitored using a Bruker AVance 499 MHz spectrometer equipped with a variable temperature probe set to 60 °C, taking 8 scans every five minutes.

General Procedure for Nitrosocarbonyl Exchange between poly(11) and monomers 9 and 10

Into a 7 mL flame-dried, N₂-purged vial was charged with poly(11) (repeat unit = 1 eq.), DMSO (0.015 M repeat unit concentration), and a stir bar. To this solution was also added either 9 (to 0.030 M) or 10 (to 0.03 M). The vial was then sealed with a rubber septum and submerged into an oil bath preheated to 60 °C where it was maintained for 27 hours in the case of 9 or 7 hours in the case of 10. Each solution was added dropwise into an excess of cold methanol, causing precipitation of polymeric species [poly(9-co-11) and poly(10-co-11)]. The resulting mixtures were then centrifuged, decanted, and the resulting solids washed with methanol, and centrifuged twice more. The polymer residues were then collected and dried under vacuum.

General method for monitoring the small-molecule hydrolysis

Into a 20 mL scintillation vial sealed with a rubber septum, oxazine (0.0418 g, 0.074 mmol, 1.0 eq.), 1,4-dicyanobenzene (0.0101 g, 0.078 mmol, 1.05 eq.), 4.96 mL DMSO-d₆, 1.97 mL D₂O and a stir bar were added. The vials were then submerged into a pre-heated oil 60°C bath. At
designated time points, 0.3 mL aliquots were removed by syringe into NMR tubes and frozen in an ice bath until the NMR spectra were collected. Runs were done in duplicate.

Supporting Information References:
3. Peterson, G. I.; Church, D. C.; Boydston, A. J. *Polymer* 2014, 55, 5980-85.
Extended time plots for isomerization of 8. Black = 8a, red = 8b. Top = 37 °C, middle = 60 °C, bottom = 80 °C. Average of three runs, error bars = one standard deviation, lines are visual aid.
Representative NMR stacked plots of small molecule isomerization at 60 °C
\[ \begin{align*}
11a & \xrightarrow{\Delta} 3 \\
11b & \xrightarrow{\Delta} \end{align*} \]