Dissociation or Cyclization: Options for a Triad of Radicals Released from Oxime Carbamates.

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General Experimental Section

All reagents and solvents were purchased from either Sigma Aldrich or Alfa Aesar and used without further purification. Toluene and tetrahydrofuran were distilled over sodium and dichloromethane was distilled over calcium hydride. Benzaldehyde oxime and acetophenone oxime were prepared according to the literature procedure,\textsuperscript{1} as was N-benzylpent-4-en-1-amine.\textsuperscript{2} Column chromatography was carried out using Silica 60A (particle size 40-63 µm, Silicycle, Canada) as the stationary phase, and TLC was performed on precoated silica gel plates (0.20 mm thick, Sil G UV\textsubscript{254}, Macherey-Nagel, Germany) and observed under UV light. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on Bruker AV III 500, Bruker AV II 400 and Bruker AV 300 instruments. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (\textit{J}) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: \textit{s} = singlet, \textit{d} = doublet, \textit{t} = triplet, \textit{dd} = double doublet, \textit{q} = quartet, \textit{m} = multiplet, \textit{b} = broad.

Melting points (M.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. Mass spectrometry was carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea, UK.

CDI Oxime Carbamate General Procedure

To a 0 °C solution of amine (1.0 equiv.) in THF (30 mL) was added sodium hydride (1.2 equiv.). After 5 min. 1,1-carbonyldiimidazole (CDI) (3.0 equiv) was added and the suspension was allowed to warm to rt for 18 h. The solvent was removed under reduced pressure and the crude residue was re-dissolved in EtOAc (100 mL) and washed with NH\textsubscript{4}Cl (3 × 100 mL), dried over MgSO\textsubscript{4}, filtered and concentrated under reduced pressure. To a solution of oxime (1.2 equiv.) in THF (20 mL) at 0 °C, pre-treated with sodium hydride (0.3 equiv.), was added a THF solution (10 mL) of the imidazole intermediate. The reaction
mixture was stirred at 0 °C for 30 min and allowed to warm to rt and stirred for 18 h. The solvent was removed under reduced pressure and the crude residue was re-dissolved in EtOAc (100 mL) and washed with NH4Cl (3 × 100 mL), dried over MgSO4, filtered and purified by column chromatography (CH2Cl2/EtOAc (98:2) as eluent). *(For the cases where the imidazole carboxylate intermediate was characterized, its spectral data immediately follows the characterization data for the resultant oxime carbamate.)*

**Scheme S2.** General procedure for the synthesis of oxime carbamates. Reagents and conditions: i) R1R2NH, CDI, NaH, THF, O °C to rt, 18 h; ii) oxime, NaH, THF, O °C to rt, 18 h.

**Benzaldehyde N,N-diethylcarbamoyl oxime (2a)**

To a solution of benzaldehyde oxime (0.510 g, 4.21 mmol, 1.0 equiv.) and pyridine (0.41 mL, 5.06 mmol, 1.2 equiv.) in CH2Cl2 (30 mL) at 0 °C was added dropwise diethylcarbamoyl chloride (0.64 mL, 5.06 mmol, 1.2 equiv.) the solution was stirred for 18 h. The reaction mixture was diluted with CH2Cl2 (100 mL), washed with 1M HCl (100 mL), sat. aqueous NaHCO3 (100 mL), brine (100 mL), dried (MgSO4), concentrated under reduced pressure and purified by column chromatography (10% EtOAc/CH2Cl2) to yield the title compound as a yellow oil, yield = 31%. 1H NMR (400 MHz, CDCl3, 294 K): δ = 1.24 (t, J = 7.0 Hz, 6H, Hd), 3.40 (q, J = 7.0 Hz, 4H, Hc), 7.39–7.49 (m, 3H, HAr), 7.76 (m, 2H, HAr), 8.35 (s, 1H, Hb); 13C NMR (75 MHz, CDCl3, 298 K): δ = 14.3, 41.6, 128.2, 128.8, 130.6, 131.3, 147.9, 154.2; LRESI-MS: m/z = 221 [MH]+; HRESI-MS: m/z = 221.1284, [MH]+ (calcd. for C12H17N2O2, 221.1290).
Acetophenone *N*-ethylcarbamoyl oxime (2b)

**CDI Oxime Carbamate Route:** Prepared from ethylamine (2 M in THF) (1.54 mL, 3.09 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.022 g, 0.927 mmol) and acetophenone oxime (0.626 g, 4.63 mmol) to give a colorless oil (0.087 g, 14%). $^1$H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 1.22$ (t, $J = 7.3$ Hz, 3H, $H_d$), 2.43 (s, 3H, $H_b$), 3.38 (m, 2H, $H_c$), 6.44 (br, 1H, $H_{NH}$), 7.41-7.47 (m, 3H, $H_Ar$), 7.67 (d, $J = 6.96$ Hz, 2H, $H_a$). $^{13}$C NMR (125 MHz, CDCl$_3$, 297 K): $\delta = 13.9$, 14.3, 42.6, 127.0, 128.2, 130.4, 135.6, 154.6, 160.3; LR-ESIMS: $m/z = 207$ [MH]$^+${; HRESI-MS: $m/z = 207.1137$, [MH]$^+$ (calcd. for C$_{11}$H$_{15}$N$_2$O$_2$, 207.1134).

Acetophenone *N,N*-diethylcarbamoyl oxime (2c)

**CDI Oxime Carbamate Route:** Prepared from diethylamine (0.22 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.447 g, 93%). $^1$H NMR (300 MHz, CDCl$_3$, 294 K): $\delta = 1.22$ (t, $J = 7.1$ Hz, 6H, $H_d$), 2.36 (s, 3H, $H_b$), 3.38 (q, $J = 7.1$ Hz, 4H, $H_c$), 7.37–7.42 (m, 3H, $H_Ar$), 7.76 (d, $J = 7.6$ Hz, 2H, $H_a$); $^{13}$C NMR (75 MHz, CDCl$_3$, 295 K): $\delta = 13.9$, 14.3, 42.2, 127.0, 128.4, 130.2, 135.3, 154.2, 160.5; LR-ESIMS: $m/z = 257$ [MNa]$^+$; HR-ESIMS: $m/z = 257.1265$ (calcd. for C$_{13}$H$_{18}$N$_2$O$_2$Na, 257.1260).

*N,N*-Diethyl-1H-imidazole-1-carboxamide
$^1$H NMR (400 MHz, CDCl$_3$, 294 K): $\delta = 1.27$ (t, $J = 7.1$ Hz, 6H, $H_e$), 3.45 (q, $J = 7.1$ Hz, 4H, $H_d$), 7.10 (s, 1H, $H_b$), 7.23 (s, 1H, $H_c$), 7.88 (s, 1H, $H_a$); $^{13}$C NMR (100 MHz, CDCl$_3$, 296 K): $\delta = 13.2, 42.6, 117.8, 129.5, 136.6, 151.2$.

**Acetophenone $N,N$-dibenzylcarbamoyl oxime (2d)**

CDI Oxime Carbamate Route: Prepared from dibenzylamine (0.42 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part 2 NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless crystalline solid (0.348 g, 47%). M.p. = 79 °C; $^1$H NMR (500 MHz, CDCl$_3$, 294 K): $\delta = 2.24$ (s, 3H, $H_b$), 4.54 (br, 2H, $H_c$), 4.61 (br, 2H, $H_c'$), 7.28–7.45 (m, 13H, $H_{Ar}$), 7.79 (d, $J = 6.8$ Hz, 2H, $H_a$); $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): (both isomers) $\delta = 14.8, 31.4, 49.7, 50.6, 53.9, 127.3, 127.4, 128.0, 128.7, 128.9, 129.0, 129.1, 130.8, 135.4, 137.4, 155.7, 161.8; LR-ESIMS: $m/z = 359$ [MH]$^+$; HR-ESIMS: $m/z = 359.1761$ (calcd. for C$_{23}$H$_{23}$O$_2$N$_2$, 359.1754).

$N,N$-Dibenzyl-$1H$-imidazole-$1$-carboxamide

$^1$H NMR (500 MHz, CDCl$_3$, 295 K): $\delta = 4.49$ (s, 4H, $H_d$), 6.94 (s, 1H, $H_b$), 7.13–7.17 (m, 4H, $H_{benzylA}$), 7.27–7.32 (m, 7H, $H_{c,benzylA}$), 7.86 (s, 1H, $H_a$); $^{13}$C NMR (126 MHz, CDCl$_3$, 295 K): $\delta = 50.8, 117.9, 127.6, 128.2, 129.2, 130.0, 135.2, 137.1, 152.5; LR-ESIMS: $m/z = 292$ [MH]$^+$; HR-ESIMS: $m/z = 292.1449$ (calcd. for C$_{18}$H$_{13}$N$_3$O, 292.1444).
Acetophenone N-allylcarbamoyl oxime (2e)

![Chemical Structure]

**CDI Oxime Carbamate Route:** Prepared from allylamine (0.08 mL, 2.06 mmol), CDI (1.0 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.156 g, 35%). $^1$H NMR (300 MHz, CDCl$_3$, 294 K): $\delta = 2.44$ (s, 3H, H$_b$), 4.00 (m, 2H, H$_d$), 5.16–5.29 (m, 2H, H$_f$), 5.86–5.96 (m, 1H, H$_e$), 6.57 (br, 1H, H$_c$), 7.40–7.47 (m, 3H, H$_{Ar}$), 7.67 (d, $J = 7.6$ Hz, 2H, H$_a$); $^{13}$C NMR (75 MHz, CDCl$_3$, 295 K): $\delta = 14.6, 43.5, 116.4, 126.8, 127.0, 128.7, 130.6, 134.0, 155.5, 160.3$. LRESI-MS: $m/z = 219$ [MH]$^+$; HRESI-MS: $m/z = 219.1136$, [MH]$^+$ (calcd. for C$_{12}$H$_{15}$N$_2$O$_2$, 219.1134).

**N- Allyl-1H-imidazole-1-carboxamide**

![Chemical Structure]

$^1$H NMR (300 MHz, CDCl$_3$, 295 K): $\delta = 4.00–4.04$ (m, 2H, H$_c$), 5.18–5.29 (m, 2H, H$_g$), 5.84–5.96 (m, 1H, H$_e$), 7.02 (s, 1H, H$_b$), 7.48 (s, 1H, H$_c$), 7.55–7.60 (br, 1H, H$_d$), 8.25 (s, 1H, H$_a$); $^{13}$C NMR (100 MHz, CDCl$_3$, 295 K): $\delta = 43.3, 116.5, 117.4, 129.8, 133.2, 135.9, 148.9$.

Acetophenone N,N-diallylcarbamoyl oxime (2f)

![Chemical Structure]

**CDI Oxime Carbamate Route:** Prepared from diallylamine (0.26 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part 2 NaH (0.090 g, 3.71 mmol) and acetophenone oxime (0.417 g, 3.09 mmol) to give a colorless oil (0.260 g, 49%). $^1$H NMR (500 MHz, CDCl$_3$, 295 K): $\delta = 2.34$ (s, 3H, H$_b$), 3.97 (br, 4H, H$_c$), 5.19–5.23 (m, 4H,
H, 5.80–5.88 (m, 2H, Hd), 7.36–7.41 (m, 3H, HAr), 7.75 (d, J = 7.6 Hz, 2H, Ha); $^{13}$C NMR (75 MHz, CDCl$_3$, 295 K): $\delta$ = 14.4, 48.7, 49.7, 116.8, 117.8, 127.0, 128.2, 128.5, 130.3, 133.2, 135.1, 154.5, 161.1; LR-ESIMS: $m/z$ = 281 [MH]$^+$; HR-ESIMS: $m/z$ = 218.1265 (calcd. for C$_{12}$H$_{18}$N$_2$O$_2$Na, 281.1260).

$\text{N,N-Diallyl-1H-imidazole-1-carboxamide}$

$^{1}$H NMR (500 MHz, CDCl$_3$, 294 K): $\delta$ = 4.00 (d, J = 5.3 Hz, 4H, H$_d$); 5.26–5.39 (m,4H, H$_f$), 5.83–5.96 (m, 2H, H$_e$), 7.08 (s, 1H, H$_b$), 7.31 (s, 1H, H$_c$), 7.99 (s, 1H, H$_a$); $^{13}$C NMR (125 MHz, CDCl$_3$, 295 K): $\delta$ = 50.2, 117.9, 118.8, 129.6, 131.7, 136.9, 151.8.

$\text{Acetophenone N,N-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (2g)}$

$\text{CDI Oxime Carbamate Route:}$ Prepared from $\text{N-benzylpent-4-en-1-amine}$ (0.579 g, 3.30 mmol), CDI (1.605 g, 9.91 mmol), NaH (0.095 g, 3.96 mmol) then for part (ii) NaH (0.024 g, 1.00 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.237 g, 21%). $^1$H NMR (300 MHz, CDCl$_3$, 294 K): $\delta$ = 1.68–1.79 (m, 2H, H$_j$), 2.07–2.14 (m, 2H, H$_e$), 2.19 (s, 3H, H$_b$), 3.27–3.43 (br, 2H, H$_d$), 4.62 (s, 2H, H$_c$), 4.97–5.08 (m, 2H, H$_f$), 5.74–5.88 (m, 1H, H$_g$), 7.29–7.43 (m, 8H, HAr), 7.78 (br, 2H, H$_a$); $^{13}$C NMR (75 MHz, CDCl$_3$, 295 K): $\delta$ = 14.8, 27.1, 27.7, 31.4, 46.4, 51.2, 115.5, 127.4, 127.9, 128.7, 128.9, 129.0, 129.1, 130.7, 133.5, 135.5, 138.0; LR-ESIMS: $m/z$ = 337 [MH]$^+$; HR-ESIMS: $m/z$ = 337.1909 (calcd. for C$_{21}$H$_{25}$N$_2$O$_2$, 337.1911).
**N-Benzyl-N-(pent-4-en-1-yl)-1H-imidazole-1-carboxamide**

\[
\begin{align*}
&\text{N-Benzyl-N-(pent-4-en-1-yl)-1H-imidazole-1-carboxamide} \\
&\text{1H NMR (300 MHz, CDCl}_3\text{, 294 K): } \delta = 1.73–1.88 \text{ (m, 2H, } H_j), 2.02–2.09 \text{ (m, 2H, } H_e), \\
&3.36–3.42 \text{ (m, 2H, } H_g), 4.66 \text{ (s, 2H, } H_d), 4.97–5.05 \text{ (m, 2H, } H_i), 5.67–5.80 \text{ (m, 1H, } H_h), 7.12 \\
&\text{ (s, 1H, } H_b), 7.24–7.27 \text{ (m, 3H, } H_{c,Ar}), 7.32–7.44 \text{ (m, 3H, } H_{Ar}), 8.11 \text{ (s, 1H, } H_a); \\
&\text{13C NMR (75 MHz, CDCl}_3\text{, 295 K): } \delta = 26.7, 31.1, 48.4, 52.1, 116.3, 118.5, 127.5, 128.6, 128.8, 129.6, \\
&135.7, 137.0, 137.2, 151.8.
\end{align*}
\]

**1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethanone N,N-diethylcarbamoyl oxime (8a)**

\[
\begin{align*}
&\text{CDI Oxime Carbamate Route: Prepared from diethylamine (0.21 mL, 2.06 mmol), CDI} \\
&(1.000 g, 6.17 mmol), \text{NaH (0.057 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol)} \\
&\text{and 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethanone oxime (0.596 g, 2.47 mmol) to give a} \\
&\text{colorless oil (0.355 g, 50%).} \text{1H NMR (400 MHz, CDCl}_3\text{, 294 K): } \delta = (\text{trans isomer}) 1.91 \text{ (t,} \\
&J = 6.9 \text{ Hz, 6H, } H_j), 2.72 \text{ (s, 3H, } H_b), 3.37 \text{ (br, 4H, } H_i), 3.84 \text{ (s, 3H, } H_a), 6.94 \text{ (d, } J = 8.8 \text{ Hz,} \\
&2H, H_b), 7.30–7.38 \text{ (m, 4H, } H_{c,Ar}), 7.43 \text{ (dt, } J = 1.4 \text{ Hz, 7.6 Hz, 1H, } H_e), 7.54 \text{ (dd, } J = 1.1 \text{ Hz,} \\
&7.4 \text{ Hz, 1H, } H_g); \text{13C NMR (100 MHz, CDCl}_3\text{, 295 K): } \delta = (\text{all isomers}) 17.7, 17.9, 41.7, \\
&42.4, 55.3, 114.0, 126.9, 129.6, 130.0 (\times 2), 130.2, 133.1, 135.5, 140.1, 154.3, 159.2, 164.7; \text{LR-ESIMS: } m/z = 363 \text{ [M} Na^+\text{]; HR-ESIMS: } m/z = 363.1680 \text{ (calcd. for C}_{20}\text{H}_{24}\text{N}_{2}\text{O}_{3}\text{Na,} \\
&363.1679).}
\end{align*}
\]
Attempted Synthesis of Oxime Carbamate 13.

Prepared from $N$-benzylpent-4-en-1-amine (0.089 g, 0.51 mmol), CDI (0.247 g, 1.52 mmol), NaH (0.145 g, 0.61 mmol) then for part (ii) NaH (0.037 g, 0.15 mmol) and 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethanone oxime (0.147 g, 0.61 mmol) to give, after column chromatography (20% EtOAc/Pet Ether), 3-methoxy-6-methylphenanthridine 10 (0.050 g, yield = 44%) whose $^1$H NMR spectrum matched that reported in the literature.\(^1\)

UV Photolyses of Oxime Carbamates

Photolysis of acetophenone $N,N$-diethylcarbamoyl oxime (2c) with alkenes

The oxime carbamate 2c (ca. 50 mg, ~0.15 mmol), MAP (50 mg, 1 equiv. wt/wt) and the alkene (2 equiv.) in PhCF$_3$ (2.0 mL) in a quartz tube were deaerated with argon for 15 min. The tube was placed ca. 15 cm from a 400 W medium pressure Hg arc lamp and then photolyzed at ambient temperature for 8 h. The solvent was evaporated and the total product mixture examined by $^1$H NMR and GC-MS.

1. With acrylamide: The NMR spectrum showed the extent of reaction was small. GC-MS: $t_R$/min; 4.1 (M$^+$ 120, PhC(=O)Me), 4.8 (M$^+$ 119, PhC(=NH)Me), 8.8 (M$^+$ 190, ImNEt$_2$), 15.8 (M$^+$ 236, Im$_2$). Probably Et$_2$NH was formed but due to its volatility it evaporated with the solvent.

2. With norbornene: The NMR spectrum and GC-MS showed a complex set of compounds including Et$_2$NH, PhC(=O)O, ImNEt$_2$, Im-Im and many other unidentified...
components. The adducts of Im and Et$_2$N with norbornene could not be observed with certainty.

**Photolysis of acetophenone N$_2$N-diallylcarbamoyl oxime (2f)**

The oxime carbamate 2f (53 mg, 0.15 mmol) and MAP (1 equiv. wt/wt) in PhCF$_3$ (2.0 mL) in a quartz tube were deaerated with argon for 15 min. The tube was placed ca. 15 cm from a 400 W medium pressure Hg arc lamp and then photolyzed at ambient temperature for 3 h. $^1$H NMR and GC-MS of the whole reaction mixture showed a complex array of products. GC-MS: t$_R$/min; 4.8 (M$^+$ 119, PhC(=NH)Me), 10.7 (M$^+$ 214, Im-N(allyl)$_2$), 14.5 & 16.1 (M$^+$ 258, unreacted oxime carbamate), 15.8 (M$^+$ 236, C$_{16}$H$_{16}$N$_2$, Im$_2$), together with several minor unidentified peaks.

**Photolysis of acetophenone N-benzyl-N-pent-4-en-1-yl-carbamoyl oxime (2g)**

The oxime carbamate 2g (52 mg, 0.15 mmol) and MAP (1 equiv. wt/wt) in PhCF$_3$ (2.0 mL) in a quartz tube were deaerated with argon for 15 min. The tube was placed ca. 15 cm from a 400 W medium pressure Hg arc lamp and then photolyzed at ambient temperature for 3 h. $^1$H NMR and GC-MS of the whole reaction mixture showed a complex array of products. GC-MS: t$_R$/min; 4.1 (M$^+$ 120, PhC(=O)Me), 4.8 (M$^+$ 119, PhC(=NH)Me), 8.7 (M$^+$ 173, C$_{12}$H$_{15}$N, N-(pent-4-en-1-ylidene)-1-phenylmethanamine), 8.9 (M$^+$ 175, C$_{12}$H$_{17}$N, 1-benzyl-2-methylpyrrolidine), 9.8 (M$^+$ 173, C$_{12}$H$_{15}$N, 1-benzyl-2-methyleneypyrrrolidine), 13.6 (M$^+$ 209, C$_{15}$H$_{15}$N, Im-Bn), 15.8 (M$^+$ 236, C$_{16}$H$_{16}$N$_2$, Im$_2$), 16.7 (M$^+$ 292, C$_{20}$H$_{24}$N$_2$, Im-N(Bn)(CH$_2$)$_3$CH=CH$_2$) together with several minor unidentified peaks. The photolysis was repeated in PhMe solvent but gave a very similar set of products.
Photolysis of 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethanone N,N-diethylcarbamoyl oxime (8a)

The oxime carbamate 8a (20 mg) and MAP (1 equiv. wt/wt) in PhCF$_3$ (2.0 mL) in a quartz tube were deaerated with argon for 15 min. The tube was placed ca. 10 cm from a 400 W medium pressure Hg arc lamp and then photolyzed at ambient temperature for 3 h. The $^1$H and $^{13}$C NMR spectra showed the presence of 3-methoxy-6-methylphenanthridine 10 $^1$H NMR (400 MHz, CDCl$_3$, 295 K) $\delta$ = 2.94 (s, 3H), 3.89 (s, 3H), 7.11-7.26 (m, 3H), 7.35 -7.48 (m, 6H), 7.49-7.57 (m, 4H), 7.65-7.78 (t, 1H), 7.96-8.47 (m, 3H) essentially identical to those in the literature.$^1$ The yield (60%) was determined by reference to added CH$_2$Br$_2$ standard. The photolysis was repeated without the MAP and gave 3-methoxy-6-methylphenanthridine 10 (61%). In both cases the spectra showed the presence of some unidentified by-products.

EPR Spectroscopy

EPR spectra were obtained at 9.5 GHz with 100 kHz modulation employing a Bruker EMX 10/12 spectrometer fitted with a rectangular ER4122 SP resonant cavity and with a Bruker ER4122-SHQE X band cavity on EMX and EMX Micro consoles at Manchester. Stock solutions of each oxime carbamate (2 to 15 mg) and MAP (1 equiv. wt/wt) in tert-butylbenzene (0.5 mL) were prepared and sonicated if necessary. An aliquot (0.2 mL), to which any additional reactant had been added, was placed in a 4 mm o.d. quartz tube, de-aerated by bubbling nitrogen for 15 min. Photolysis in the resonant cavity was by unfiltered light from a 500 W super pressure mercury arc lamp or, in the Manchester experiments, the light source was a Luxtel CL300BUV lamp. Solutions in cyclopropane were prepared on a vacuum line by distilling in the cyclopropane, degassing with three freeze-pump-thaw cycles and finally flame sealing the tubes. In all cases where spectra were obtained, hfs were
assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages. EPR signals were digitally filtered and double integrated using the Bruker WinEPR software and radical concentrations were calculated by reference to the double integral of the signal from a known concentration of the stable radical DPPH [1 $\times$ $10^{-3}$ M in PhMe], run under identical conditions, as described previously. The majority of EPR spectra were recorded with 2.0 mW power, 0.8 G$_{pp}$ modulation intensity and gain of ca. 10$^6$.

**Sample EPR Spectra**

**Figure S1.** EPR Spectrum recorded during photolysis of acetophenone $N$-ethylcarbamoyl oxime (2b) with MAP in $t$-BuPh at 205 K.

Note that the larger 1:1:1 triplet ($a(N) = 31$ G) is a persistent iminoxyl radical PhC(Me)=N-$O^*$ generated from traces of oxime PhC(Me)=N-OH present in the starting material.
Figure S2. EPR Spectrum recorded during photolysis of acetophenone \( N,N \)-diethylcarbamoyl oxime (2c) with MAP in \( t \)-BuPh at 210 K.

Central 1:1:1 triplet is \( \text{PhC(Me)=N}^\bullet \) and the \( \text{Et}_2\text{N}^\bullet \) radical appears as a pentet of 1:1:1 triplets.
The iminoxyl \( \text{PhC(Me)=N-O}^\bullet \) is present in only a trace.

Figure S3. EPR Spectrum recorded during photolysis of acetophenone \( N,N \)-dibenzylcarbamoyl oxime (2d) with MAP in \( t \)-BuPh at 210 K.

\( \text{PhC(Me)=N}^\bullet \) (central 1:1:1 triplet), the \( \text{Bn}_2\text{N}^\bullet \) radical (pentet of 1:1:1 triplets) and the iminoxyl \( \text{PhC(Me)=N-O}^\bullet \).
**Figure S4.** EPR Spectrum recorded during photolysis of acetophenone $N$-benzyl-$N$-pent-4-enylcarbamoyl oxime (2g) with MAP in $t$-BuPh at 210 K.

**Table S1.** Summary of Isotropic EPR Parameters of Dialkylaminyl Radicals in $t$-BuPh Solution.

| Radical          | T/K  | $g$-factor | $a$(N) | $a$(H$^\beta$) | $a$(H$^\beta$) |
|------------------|------|------------|--------|----------------|----------------|
| Et$_2$N*         | 210  | 2.0047     | 14.4   | 35.7 (2H)      | 35.7 (2H)      |
| allyl$_2$N*      | 210  | 2.0048     | 14.6   | 36.0 (2H)      | 36.0 (2H)      |
| Bn$_2$N*         | 220  | 2.0046     | 14.3   | 37.1 (2H)      | 37.1 (2H)      |
| BnN(*)Pentenyl   | 230  | 2.0048     | 14.2   | 36.9 (2H)      | 35.4 (2H)      |
Derivation of Kinetic Equations (1 & 2) for Cyclization of Aminyl Radicals.

For a general Aminyl radical, let RN(•)Pe be N, the iminyl radical, Im, and the cyclized radical C. In the temperature region where decarboxylation is fast the mechanism may be represented by:

\[ \text{NC(O)O–Im} / \text{UV} \rightarrow \text{N} + \text{Im} + \text{CO}_2 \]
\[ \text{N} \rightarrow \text{C} \quad k_c \text{ (forwards)} \]
\[ \text{C} \rightarrow \text{N} \quad k_c \text{ (backwards)} \]
\[ \text{Im} + \text{Im} \rightarrow \text{non-radical products} \]
\[ \text{Im} + \text{N} \rightarrow \text{non-radical products} \]
\[ \text{Im} + \text{C} \rightarrow \text{non-radical products} \]
\[ \text{N} + \text{N} \rightarrow \text{non-radical products} \]
\[ \text{N} + \text{C} \rightarrow \text{non-radical products} \]
\[ \text{C} + \text{C} \rightarrow \text{non-radical products} \]

Assuming all the terminations are fast and diffusion controlled with the same rate constant 2k_t then, making the steady-state approximation:

\[ \frac{d[C]}{dt} = 0 = k_c[N] – k_c[C] – 2k_t[N][C] – 2k_t[C]^2 – 2k_t[C][Im] \]

Rearranging: \[ \frac{k_c}{2k_t} = \frac{[C]}{[N]} \times \{ \frac{k_c}{2k_t} + [N] + [C] + [Im] \} \]

Since equi-molar amounts of N and Im are formed in the initial photochemical bond fission then:

\[ [Im] = [N] + [C] \]

On substituting: \[ \frac{k_c}{2k_t} = \frac{[C]}{[N]} \times \{ \frac{k_c}{2k_t} + 2[Im] \} \]

If reverse cyclization is negligible \( k_c/2k_t \ll 2[Im] \) this simplifies to:

\[ \frac{k_c}{2k_t} = 2[C][Im]/[N] \quad \text{or} \]
\[ \frac{k_c}{2k_t} = 2[C][Im]/([Im] - [C]) \quad \text{or} \]
\[ \frac{k_c}{2k_t} = 2[Im]^2/[N] – 2[Im] \quad \text{[i.e. equation (1) in main text].} \]
**Table S2.** SSEPR Kinetics of cyclization of pentenylBnN* (6g) from oxime carbamate 2g in t-BuPh + MAP \( \{ k_c/2k_t = 2[\text{Im-N}][\text{Im}]/[\text{N}]\} \).

| Dial Temp | Actual T/K | scans | Gain | \([R_2N]/[\text{Im}]\) d. i. | \([R_2N]/[\text{Im}]\) M | \([\text{Im}]/[R_2N]\) M | \(k_c/2k_t\) | log\(k_c/2k_t\) | log\(2k_t\) | 10^7/T | log \(\eta\) n-C7 | log \(\eta\) t-BuPh | log\(2k_t\) t-BuPh | log \(k_t\) t-BuPh |
|-----------|------------|-------|------|-----------------------------|--------------------------|-----------------------------|----------------|----------------|----------------|------------|----------------|----------------|--------------------|--------------------|
| 210       | 210.55     | 20.00 | 2.0E+06 | 0.76  | 132  | 2.15E-07 | 2.83E-07 | 6.79E-08 | 1.79E-07 | -6.748  | 9.292  | 4.750  | 0.17  | 1.06  | 8.402 | 1.65E+00 |
| 230       | 230.93     | 20.00 | 2.0E+06 | 0.876 | 87.8 | 1.81E-07 | 2.06E-07 | 2.56E-08 | 5.84E-08 | -7.233  | 9.498  | 4.330  | 0.00  | 0.66  | 8.834 | 1.60E+00 |
| 250       | 251.31     | 20.00 | 2.0E+06 | 0.647 | 45.6 | 7.55E-08 | 1.17E-07 | 4.12E-08 | 1.27E-07 | -6.895  | 9.671  | 3.979  | -0.15 | 0.37  | 9.150 | 2.26E+00 |
| 270       | 271.69     | 20.00 | 2.0E+06 | 0.563 | 53.1 | 8.27E-08 | 1.47E-07 | 6.42E-08 | 2.28E-07 | -6.642  | 9.818  | 3.681  | -0.27 | 0.16  | 9.388 | 2.75E+00 |
| 290       | 292.07     | 16.00 | 2.0E+06 | 0.37  | 32   | 4.40E-08 | 1.19E-07 | 7.49E-08 | 4.05E-07 | -6.393  | 9.944  | 3.424  | -0.38 | -0.01 | 9.569 | 3.18E+00 |
| 300       | 302.26     | 5.00  | 2.0E+06 | 0.33  | 20.4 | 3.90E-08 | 1.18E-07 | 7.92E-08 | 4.80E-07 | -6.319  | 10.001 | 3.308  | -0.43 | -0.07 | 9.643 | 3.32E+00 |

**NB:** d.i. = double integral

S16
Computational Methods

Radical ground-state calculations were carried out using the Gaussian 09 program package.\(^3\) Becke’s three-parameter hybrid exchange potential (B3)\(^4\) was used with the LYP correlation functional, B3LYP. This method has previously described the chemistry of iminyl radicals accurately. The correlation consistent polarized triple zeta cc-pvtz basis set was employed. Geometries were fully optimized for all model compounds. Optimized structures were characterized as minima or saddle points by frequency calculations. The experimental kinetic and spectroscopic data was all obtained in the non-polar hydrocarbon solvents tert-butylbenzene or cyclopropane. Solvent effects, particularly differences in solvation between the neutral reactants and neutral transition states, are therefore expected to be minimal. In view of this, no attempt was made to computationally model the effect of the solvent.
DFT Computed Structures and Energies UB3LYP/cc-pvtz

\( \text{Et}_2\text{NC}(=\text{O})\text{O}^* \)

\( E = -401.86984733 \) \( \text{AU} \).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 0.000675 1.224248 -0.000057 |
| 2             | 8             | 0           | -0.941377 1.937184 0.455037 |
| 3             | 8             | 0           | 0.945427 1.936052 -0.455066 |
| 4             | 6             | 0           | 1.128339 -0.843176 -0.581491 |
| 5             | 1             | 0           | 0.730028 -1.709333 -1.112508 |
| 6             | 1             | 0           | 1.588475 -0.194424 -1.326221 |
| 7             | 7             | 0           | -0.000120 -0.116922 -0.000064 |
| 8             | 6             | 0           | 2.167960 -1.275228 0.449639 |
| 9             | 1             | 0           | 1.730873 -1.916892 1.215659 |
| 10            | 1             | 0           | 2.968869 -1.834086 -0.036401 |
| 11            | 1             | 0           | 2.606643 -0.406584 0.939502 |
| 12            | 6             | 0           | -1.129342 -0.841866 0.581509 |
| 13            | 1             | 0           | -1.588840 -0.192432 1.326037 |
| 14            | 1             | 0           | -0.731351 -1.708293 1.112777 |
| 15            | 6             | 0           | -2.169364 -1.273112 -0.449552 |
| 16            | 1             | 0           | -2.970862 -1.831031 0.036595 |
| 17            | 1             | 0           | -2.607138 -0.404142 -0.939651 |
| 18            | 1             | 0           | -1.732904 -1.915412 -1.215396 |

TS for decarboxylation of \( \text{Et}_2\text{NC}(=\text{O})\text{O}^* \)

\( E = -401.86545744 \) \( \text{AU} \)

Virtual freq. = -233.5 \( \text{cm}^{-1} \)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -0.000312 1.445611 -0.000073 |
| 2             | 8             | 0           | -1.141617 1.869317 -0.017927 |
| 3             | 8             | 0           | 1.141034 1.869391 0.018030 |
| 4             | 6             | 0           | 1.054573 -0.862476 -0.676309 |
| 5             | 1             | 0           | 0.633267 -1.752998 -1.148323 |
| 6             | 1             | 0           | 1.461671 -0.199028 -1.436750 |
| 7             | 7             | 0           | -0.000029 -0.145559 -0.000242 |
| 8             | 6             | 0           | 2.182708 -1.261704 0.292584 |
| 9             | 1             | 0           | 1.818244 -1.913858 1.085865 |
| 10            | 1             | 0           | 2.950423 -1.798530 -0.264311 |
| 11            | 1             | 0           | 2.618364 -0.368067 0.732081 |
| 12            | 6             | 0           | -1.054162 -0.862765 0.676244 |
| 13            | 1             | 0           | -1.461353 -0.199284 1.436608 |
| 14            | 1             | 0           | -0.632485 -1.753049 1.148365 |
| 15            | 6             | 0           | -2.182346 -1.262471 -0.292408 |
| 16            | 1             | 0           | -2.949909 -1.799231 0.264761 |
| 17            | 1             | 0           | -2.618239 -0.369056 -0.732131 |
| 18            | 1             | 0           | -1.817881 -1.914821 -1.085523 |

\( \text{Et}_2\text{N}^* \)

\( E = -213.22037859 \) \( \text{AU} \)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -1.021795 -0.646940 -0.054149 |
| 2             | 1             | 0           | -0.676793 -0.915413 -1.062901 |
| 3             | 1             | 0           | -1.320289 -1.565501 0.458196 |
| 4             | 7             | 0           | 0.000030 -0.000444 0.729940 |
| 5             | 6             | 0           | -2.254577 0.267164 -0.170909 |
| 6             | 1             | 0           | -2.011953 1.184475 -0.708158 |
EtNHC(=O)O*

E = -323.21827632 AU.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.062681 -0.018785 0.004062 |
| 2             | 8             | 0           | 2.135113 -0.619075 -0.298843 |
| 3             | 8             | 0           | 1.206706 1.236627 0.000671 |
| 4             | 6             | 0           | -1.331376 0.049867 0.601284 |
| 5             | 1             | 0           | -1.776010 -0.411666 1.484663 |
| 6             | 1             | 0           | -1.067944 1.070572 0.872832 |
| 7             | 7             | 0           | -0.083871 -0.647211 0.302272 |
| 8             | 1             | 0           | -0.078305 -1.650801 0.219273 |
| 9             | 6             | 0           | -2.317126 0.043840 -0.562473 |
| 10            | 1             | 0           | -2.582897 -0.974713 -0.849846 |
| 11            | 1             | 0           | -3.234744 0.562677 -0.282040 |
| 12            | 1             | 0           | -1.892671 0.544452 -1.432358 |

TS for decarboxylation of EtNHC(=O)O*

E = -323.20532264AU

Virtual freq. = -425.3 cm⁻¹

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -1.291938 0.094475 -0.025020 |
| 2             | 8             | 0           | -1.178147 1.301012 0.065118 |
| 3             | 8             | 0           | -1.912142 -0.816643 -0.467149 |
| 4             | 6             | 0           | 1.316108 -0.734378 0.041564 |
| 5             | 1             | 0           | 1.923768 -1.392942 0.675348 |
| 6             | 1             | 0           | 0.970079 -1.325638 -0.805402 |
| 7             | 7             | 0           | 0.160559 -0.363896 0.818440 |
| 8             | 1             | 0           | 0.375479 0.266531 1.590210 |
| 9             | 6             | 0           | 2.171068 0.453685 -0.418731 |
| 10            | 1             | 0           | 2.549114 1.018697 0.434155 |
| 11            | 1             | 0           | 3.023010 0.091650 -0.994004 |
| 12            | 1             | 0           | 1.585527 1.125926 -1.043338 |

EtNH*

E = -134.56263278 AU

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 0.138952 0.544005 0.047587 |
| 2             | 1             | 0           | 0.199543 1.048423 1.026418 |
| 3             | 1             | 0           | 0.157910 1.336045 -0.704811 |
| 4             | 7             | 0           | 1.321718 -0.263261 -0.103614 |
| 5             | 1             | 0           | 1.194610 -1.089578 0.492656 |
| 6             | 6             | 0           | -1.181056 -0.231858 -0.024395 |
$\text{H}_2\text{NC}(=\text{O})\text{O}^*$

$E = -244.56609719$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 6             | 0           |                         | 0.060593 | -0.000144 | -0.000638 |
| 2             | 8             | 0           |                         | 0.761036  | 1.049325  | 0.001129  |
| 3             | 8             | 0           |                         | 0.761235  | -1.049161  | 0.001127  |
| 4             | 7             | 0           |                         | -1.282250 | -0.000060 | -0.011086 |
| 5             | 1             | 0           |                         | -1.782308 | 0.869594  | 0.031675  |
| 6             | 1             | 0           |                         | -1.783070 | -0.869619 | 0.031706  |

$\text{H}_2\text{N}$

$E = -55.90310608$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 7             | 0           |                         | 0.000000  | 0.000000  | 0.142650  |
| 2             | 1             | 0           |                         | 0.000000  | 0.802801  | -0.499276 |
| 3             | 1             | 0           |                         | 0.000000  | -0.802801 | -0.499276 |

TS for decarboxylation of $\text{H}_2\text{NC}(=\text{O})\text{O}^*$

$E = -244.54516576$ AU

Virtual freq. = -478.1 cm$^{-1}$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 6             | 0           |                         | -0.380591 | 0.096370 | -0.000072 |
| 2             | 8             | 0           |                         | 0.045063 | 1.233787 | 0.000190  |
| 3             | 8             | 0           |                         | -1.290154 | -0.649057 | -0.000071 |
| 4             | 7             | 0           |                         | 1.241128  | -0.644377 | -0.000289 |
| 5             | 1             | 0           |                         | 1.777494  | -0.374502 | 0.823988  |
| 6             | 1             | 0           |                         | 1.778875  | -0.370923 | -0.822479 |

EtOC(O)O$^*$

$E = -343.08597348$ AU

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 8             | 0           |                         | 0.144653 | -0.508821 | -0.000025 |
| 2             | 6             | 0           |                         | -1.091305 | -0.057818 | -0.000027 |
| 3             | 8             | 0           |                         | -2.053243 | -0.871916 | -0.000043 |
| 4             | 8             | 0           |                         | -1.421653 | 1.142774  | -0.000020 |
| 5             | 6             | 0           |                         | 1.213020  | 0.487937  | 0.000007  |
| 6             | 1             | 0           |                         | 1.098808 | 1.112851  | -0.884686 |
| 7             | 1             | 0           |                         | 1.098722 | 1.112891  | 0.884661  |
| 8             | 6             | 0           |                         | 2.523453  | -0.261925 | 0.000087  |
| 9             | 1             | 0           |                         | 3.348396 | 0.451001  | 0.000110  |
| 10            | 1             | 0           |                         | 2.612461 | -0.891079 | 0.884804  |
| 11            | 1             | 0           |                         | 2.612545 | -0.891120 | -0.884592 |
**EtO**

$E = -154.43337450$ AU

| Center Number | Atomic Number | Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|------|---------------|---------------|---------------|
| 1             | 6             | 0    | 1.041496      | -0.602709     | 0.000000      |
| 2             | 1             | 0    | 0.927594      | -1.231346     | 0.883110      |
| 3             | 1             | 0    | 0.927594      | -1.231346     | -0.883110     |
| 4             | 1             | 0    | 2.051475      | -0.188353     | 0.000000      |
| 5             | 6             | 0    | 0.000000      | 0.508439      | 0.000000      |
| 6             | 1             | 0    | 0.130254      | 1.189168      | 0.862933      |
| 7             | 1             | 0    | 0.130254      | 1.189168      | -0.862933     |
| 8             | 8             | 0    | -1.302018     | 0.104791      | 0.000000      |

TS for CO$_2$ loss from EtOC(O)O

$E = -343.06522549$ AU

Virtual freq. = $-573.3$ cm$^{-1}$

| Center Number | Atomic Number | Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|------|---------------|---------------|---------------|
| 1             | 8             | 0    | -0.126432     | -0.405971     | 0.664925      |
| 2             | 6             | 0    | 1.277231      | 0.142487      | 0.003741      |
| 3             | 8             | 0    | 0.954339      | 1.317232      | -0.041268     |
| 4             | 8             | 0    | 2.104445      | -0.670552     | -0.204075     |
| 5             | 6             | 0    | -1.176972     | -0.666495     | -0.246767     |
| 6             | 1             | 0    | -0.800460     | -0.703324     | -1.271212     |
| 7             | 1             | 0    | -1.506720     | -1.678506     | 0.026693      |
| 8             | 6             | 0    | -2.322785     | 0.319055      | -0.084597     |
| 9             | 1             | 0    | -3.145483     | 0.036947      | -0.742491     |
| 10            | 1             | 0    | -2.682385     | 0.327146      | 0.943218      |
| 11            | 1             | 0    | -1.988600     | 1.321786      | -0.347117     |

**EtC(O)O**

$E = -267.82942164$ AU

| Center Number | Atomic Number | Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|------|---------------|---------------|---------------|
| 1             | 8             | 0    | 1.126267      | 1.120387      | -0.015323     |
| 2             | 6             | 0    | -0.769009     | -0.261393     | 0.634152      |
| 3             | 1             | 0    | -0.836666     | -1.310241     | 0.926372      |
| 4             | 1             | 0    | -0.898128     | 0.352886      | 1.527474      |
| 5             | 6             | 0    | -1.840748     | 0.087261      | -0.410416     |
| 6             | 1             | 0    | -2.833303     | -0.084652     | 0.003230      |
| 7             | 1             | 0    | -1.770418     | 1.132734      | -0.706791     |
| 8             | 1             | 0    | -1.732437     | -0.530042     | -1.301686     |
| 9             | 6             | 0    | 0.607995      | -0.017438     | 0.109567      |
| 10            | 8             | 0    | 1.383923      | -0.921795     | -0.290729     |

**Et**

$E = -79.19223009$ AU

| Center Number | Atomic Number | Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|------|---------------|---------------|---------------|
| 1             | 6             | 0    | -0.691914     | 0.000263      | -0.001704     |
| 2             | 1             | 0    | -1.102842     | 0.892680      | -0.477544     |
| 3             | 1             | 0    | -1.103344     | -0.876310     | -0.506679     |
**CO₂**

\[ E = -188.66056821 \text{ AU} \]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y   | Z       |
| 1             | 6             | 0           | 0.000000    | 0.000000 | 0.000000 |
| 2             | 8             | 0           | 0.000000    | 0.000000 | 1.160367 |
| 3             | 8             | 0           | 0.000000    | 0.000000 | -1.160367|

**DFT Computed Structures CBS-QB3**

**Et₂NCO₂**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y   | Z       |
| 1             | 6             | 0           | 0.000037    | 1.218991 | 0.000009 |
| 2             | 8             | 0           | -0.948805   | 1.927844 | 0.451240 |
| 3             | 8             | 0           | 0.948906    | 1.927790 | -0.451248|
| 4             | 6             | 0           | 1.131832    | -0.851525| -0.583528|
| 5             | 1             | 0           | 0.735398    | -1.732274| -1.096477|
| 6             | 1             | 0           | 1.576806    | -0.209107| -1.346478|
| 7             | 7             | 0           | -0.000007   | -0.126607| -0.000004|
| 8             | 6             | 0           | 2.190149    | -1.253361| 0.445877 |
| 9             | 1             | 0           | 1.767061    | -1.886232| 1.230405 |
| 10            | 1             | 0           | 2.995165    | -1.812607| -0.038623|
| 11            | 1             | 0           | 2.623102    | -0.367544| 0.914884 |
| 12            | 6             | 0           | -1.131879   | -0.851465| 0.583528 |
| 13            | 1             | 0           | -1.576824   | -0.209016| 1.346469 |
| 14            | 1             | 0           | -0.735486   | -1.732226| 1.096490 |
| 15            | 6             | 0           | 2.190213    | -1.253266| -0.445873|
| 16            | 1             | 0           | -2.995257   | -1.812467| 0.038633 |
| 17            | 1             | 0           | -2.623124   | -0.367435| -0.914893|
| 18            | 1             | 0           | -1.767154   | -1.886166| -1.230392|

**TS for decarboxylation of Et₂NC(=O)O⁺**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y   | Z       |
| 1             | 6             | 0           | 0.000014    | 1.433870 | 0.000000|
| 2             | 8             | 0           | 1.142089    | 1.858171 | -0.002359|
| 3             | 8             | 0           | -1.142060   | 1.858181 | 0.002355 |
| 4             | 6             | 0           | -1.060082   | -0.874046| 0.673272 |
| 5             | 1             | 0           | -0.645404   | -1.779739| 1.127799 |
| 6             | 1             | 0           | -1.454401   | -0.217202| 1.450044 |
| 7             | 7             | 0           | 0.000000    | -0.154494| 0.000008 |
| 8             | 6             | 0           | -2.201244   | -1.235724| -0.299357|
| 9             | 1             | 0           | -1.849401   | -1.876031| -1.111354|
| 10            | 1             | 0           | -2.978209   | -1.773427| 0.248808 |
| 11            | 1             | 0           | -2.621389   | -0.321055| -0.715470|
| 12            | 6             | 0           | 1.060062    | -0.874063| -0.673233|
| 13            | 1             | 0           | 1.454384    | -0.217227| -1.450045|
| 14            | 1             | 0           | 0.645367    | -1.779752| -1.127789|
| 15            | 6             | 0           | 2.201228    | -1.235755| 0.299351 |
| 16            | 1             | 0           | 2.978181    | -1.773469| -0.248820|
| 17            | 1             | 0           | 2.621390    | -0.321090| 0.715458 |
| 18            | 1             | 0           | 1.849384    | -1.876055| 1.111353 |
### Et₂N

**Center**  | **Atomic Number** | **Type** | **Coordinates (Ångstroms)** | X     | Y     | Z     |
|-----------|------------------|---------|----------------------------|-------|-------|-------|
| 1         | 6                | 0       | -1.024150                  | -0.646745 | -0.062593 |
| 2         | 1                | 0       | -0.683690                  | -0.904260 | -1.078780 |
| 3         | 1                | 0       | -1.316007                  | -1.573197 | 0.446060  |
| 4         | 7                | 0       | 0.000023                   | -0.000393 | 0.725594  |
| 5         | 6                | 0       | -2.263292                  | 0.266312  | -0.161969 |
| 6         | 1                | 0       | -2.028068                  | 1.187778  | -0.700496 |
| 7         | 1                | 0       | -3.068527                  | -0.246521 | -0.694593 |
| 8         | 1                | 0       | -2.615962                  | 0.533755  | 0.835998  |
| 9         | 6                | 0       | 1.024044                   | 0.646698  | -0.062188 |
| 10        | 1                | 0       | 1.315703                   | 1.572882  | 0.445621  |
| 11        | 1                | 0       | 0.683538                   | 0.904809  | -1.078207 |
| 12        | 6                | 0       | 2.263380                   | -0.266028 | -0.162134 |
| 13        | 1                | 0       | 3.068521                   | 0.247326  | -0.694401 |
| 14        | 1                | 0       | 2.616079                   | -0.534057 | 0.835665  |
| 15        | 1                | 0       | 2.028360                   | -1.187187 | -0.701274 |

### EtNHCO₂

**Center**  | **Atomic Number** | **Type** | **Coordinates (Ångstroms)** | X     | Y     | Z     |
|-----------|------------------|---------|----------------------------|-------|-------|-------|
| 1         | 6                | 0       | 1.058015                   | -0.015535 | 0.005440  |
| 2         | 8                | 0       | 2.140172                   | -0.579501 | -0.329877 |
| 3         | 8                | 0       | 1.167856                   | 1.242969  | 0.054562  |
| 4         | 6                | 0       | -1.335692                  | -0.015220 | 0.612666  |
| 5         | 1                | 0       | -1.804231                  | -0.560473 | 1.436637  |
| 6         | 1                | 0       | -1.082630                  | 0.977070  | 0.984664  |
| 7         | 7                | 0       | -0.075313                  | -0.683100 | 0.288434  |
| 8         | 1                | 0       | -0.056989                  | -1.682143 | 0.147491  |
| 9         | 6                | 0       | -2.288424                  | 0.092838  | -0.578039 |
| 10        | 1                | 0       | -2.545107                  | -0.894967 | -0.970790 |
| 11        | 1                | 0       | -3.216235                  | 0.587138  | -0.277511 |
| 12        | 1                | 0       | -1.835228                  | 0.674832  | -1.383410 |

### EtNHCO₂ TS for CO₂ loss

**Center**  | **Atomic Number** | **Type** | **Coordinates (Ångstroms)** | X     | Y     | Z     |
|-----------|------------------|---------|----------------------------|-------|-------|-------|
| 1         | 6                | 0       | -1.285858                  | 0.101668  | -0.022563 |
| 2         | 8                | 0       | -1.137029                  | 1.302475  | 0.093324  |
| 3         | 8                | 0       | -1.925914                  | -0.784936 | -0.478873 |
| 4         | 6                | 0       | 1.315878                   | -0.745634 | 0.025373  |
| 5         | 1                | 0       | 1.938724                   | -1.410922 | 0.641139  |
| 6         | 1                | 0       | 0.970506                   | -1.323874 | -0.834392 |
| 7         | 7                | 0       | 0.155132                   | -0.409007 | 0.817968  |
| 8         | 1                | 0       | 0.377217                   | 0.193597  | 1.612810  |
| 9         | 6                | 0       | 2.147382                   | 0.469793  | -0.416332 |
| 10        | 1                | 0       | 2.526457                   | 1.020642  | 0.448463  |
| 11        | 1                | 0       | 3.000268                   | 0.137785  | -1.012668 |
| 12        | 1                | 0       | 1.540036                   | 1.149344  | -1.015612 |

### EtNH

**Center**  | **Atomic Number** | **Type** | **Coordinates (Ångstroms)** | X     | Y     | Z     |
|-----------|------------------|---------|----------------------------|-------|-------|-------|
| 1         | 6                | 0       | 0.140924                   | 0.543124  | 0.044163  |
| 2         | 1                | 0       | 0.204078                   | 1.046616  | 1.026350  |
| 3         | 1                | 0       | 0.160226                   | 1.338471  | -0.708208 |
| 4         | 7                | 0       | 1.324329                   | -0.268915 | -0.111277 |
| 5         | 1                | 0       | 1.186019                   | -1.095998 | 0.485820  |
| 6         | 6                | 0       | -1.184505                  | -0.230864 | -0.026008 |
| 7         | 1                | 0       | -1.249483                  | -0.970033 | 0.778535  |
| 8         | 1                | 0       | -2.037114                  | 0.447364  | 0.066966  |
| 9         | 1                | 0       | -1.272539                  | -0.757577 | -0.979460 |
### H2NCO₂

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|---------|---------|---------|
|                                             | 1      | 6      | 0    | 0.062572| -0.000098| 0.000411|
|                                             | 2      | 8      | 0    | 0.761217| 1.051279 | 0.001046|
|                                             | 3      | 8      | 0    | 0.761351| -1.051168| 0.001045|
|                                             | 4      | 7      | 0    | -1.283493| -0.000041| -0.010827|
|                                             | 5      | 1      | 0    | -1.785708| 0.871252 | 0.030753|
|                                             | 6      | 1      | 0    | -1.785819| -0.871269| 0.030765|

### H2NCO₂ TS for CO₂ loss

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|---------|---------|---------|
|                                             | 1      | 6      | 0    | -0.378919| 0.095330| -0.000006|
|                                             | 2      | 8      | 0    | 0.043975 | 1.234715| 0.000007|
|                                             | 3      | 8      | 0    | -1.289322| -0.649480| -0.000001|
|                                             | 4      | 7      | 0    | 1.239526 | -0.643613| -0.000008|
|                                             | 5      | 1      | 0    | 1.779790 | -0.374341| 0.824725|
|                                             | 6      | 1      | 0    | 1.779824 | -0.374237| -0.824683|

### H2N

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | Coordinates (Angstroms) | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|-------------------------|---------|---------|---------|
|                                             | 1      | 7      | 0    | 0.000000                | 0.000000| 0.143963|
|                                             | 2      | 1      | 0    | 0.000000                | 0.801947| -0.503869|
|                                             | 3      | 1      | 0    | 0.000000                | -0.801947| -0.503869|

### CO₂

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | Coordinates (Angstroms) | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|-------------------------|---------|---------|---------|
|                                             | 1      | 6      | 0    | 0.000000                | 0.000000| 0.000000|
|                                             | 2      | 8      | 0    | 0.000000                | 0.000000| 1.160367|
|                                             | 3      | 8      | 0    | 0.000000                | 0.000000| -1.160367|

### EtO₃CO₂

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | Coordinates (Angstroms) | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|-------------------------|---------|---------|---------|
|                                             | 1      | 8      | 0    | 0.144662                | -0.509564| 0.000015|
|                                             | 2      | 6      | 0    | -1.093391               | -0.057343| 0.000018|
|                                             | 3      | 8      | 0    | -2.053830               | -0.873356| -0.000083|
|                                             | 4      | 8      | 0    | -1.419578               | 1.144531 | -0.000066|
|                                             | 5      | 6      | 0    | 1.212172                | 0.489735 | 0.000025|
|                                             | 6      | 1      | 0    | 1.098979                | 1.116667 | -0.886625|
|                                             | 7      | 1      | 0    | 1.098924                | 1.116711 | 0.886636|
|                                             | 8      | 6      | 0    | 2.524163                | -0.263373| 0.000084|
|                                             | 9      | 1      | 0    | 3.353574                | 0.448388 | 0.000091|
|                                             | 10     | 1      | 0    | 2.610383                | -0.894360| 0.886716|
|                                             | 11     | 1      | 0    | 2.610437                | -0.894404| -0.886511|

### EtO₃CO₂ TS for CO₂ loss

| Center Atomic Atomic Coordinates (Angstroms) | Number | Atomic | Type | Coordinates (Angstroms) | X       | Y       | Z       |
|---------------------------------------------|--------|--------|------|-------------------------|---------|---------|---------|
|                                             | 1      | 8      | 0    | -0.116960               | -0.436008| 0.666844|

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| Center | Atomic Number | Atomic Type | X                | Y                | Z                |
|--------|----------------|-------------|------------------|------------------|------------------|
| EtO    |                |             |                  |                  |                  |
|        | 1              | 6           | 0.994572         | -0.604756        | 0.000000         |
|        | 2              | 1           | 0.848571         | -1.218685        | 0.888548         |
|        | 3              | 1           | 0.848571         | -1.218685        | -0.888548        |
|        | 4              | 1           | 2.012778         | -0.209669        | 0.000000         |
|        | 5              | 6           | 0.000000         | 0.588952         | 0.000000         |
|        | 6              | 1           | 0.187938         | 1.191429         | 0.902496         |
|        | 7              | 1           | 0.187938         | 1.191429         | -0.902496        |
|        | 8              | 8           | -1.255879        | 0.044876         | 0.000000         |
| EtCO₂  |                |             |                  |                  |                  |
|        | 1              | 8           | 0.742035         | 1.231486         | 0.000029         |
|        | 2              | 6           | -0.688749        | -0.748462        | 0.000053         |
|        | 3              | 1           | -0.684284        | -1.408679        | -0.873894        |
|        | 4              | 1           | -0.684284        | -1.408495        | 0.874143         |
|        | 5              | 6           | -1.907243        | 0.177562         | -0.000043        |
|        | 6              | 1           | -2.825579        | -0.412557        | -0.00007         |
|        | 7              | 1           | -1.915500        | 0.820808         | 0.881705         |
|        | 8              | 1           | -1.915478        | 0.820662         | -0.881899        |
|        | 9              | 6           | 0.626069         | -0.016370        | 0.000004         |
|        | 10             | 8           | 1.742584         | -0.592500        | -0.000046        |
| Et     |                |             |                  |                  |                  |
|        | 1              | 6           | -0.693527        | 0.000262         | -0.001737        |
|        | 2              | 1           | -1.107133        | 0.894093         | -0.478482        |
|        | 3              | 1           | -1.107621        | -0.877967        | -0.506838        |
|        | 4              | 1           | -1.093628        | -0.016901        | 1.025742         |
|        | 5              | 6           | 0.794217         | 0.000002         | -0.019115        |
|        | 6              | 1           | 1.352723         | 0.925821         | 0.042451         |
|        | 7              | 1           | 1.351517         | -0.926631        | 0.042241         |
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2a benzaldehyde O-diethylcarbamoyl oxime
400 MHz, CDCl3,

2a, 100 MHz, CDCl3
Acetophenone N-ethylcarbamoyl oxime (zO)
(500 MHz, CDCl₃, 298 K)
Acetophenone N,N-diethylcarbamoyl oxime (2c)
(300 MHz, CDCl₃, 294 K)

Acetophenone N,N-diethylcarbamoyl oxime (2c)
(75 MHz, CDCl₃, 295 K)
$N,N$-Diethyl-$1H$-imidazole-$1$-carboxamide
(400 MHz, CDCl$_3$, 294 K)

$N,N$-Diethyl-$1H$-imidazole-$1$-carboxamide
(100 MHz, CDCl$_3$, 296 K)
Acetophenone N,N-dibenzylcarbamoyl oxime (2d)
(500 MHz, CDCl₃, 294 K)

Acetophenone N,N-dibenzylcarbamoyl oxime (2d)
(75 MHz, CDCl₃, 208 K)
N,N-Dibenzyl-1H-imidazole-1-carboxamide
(500 MHz, CDCl₃, 295 K)
Acetophenone N-allylcarbamoyl oxime (2e)
(300 MHz, CDCl₃, 294 K)

Acetophenone N-allylcarbamoyl oxime (2e)
(75 MHz, CDCl₃, 295 K)
Acetophenone N,N-diallylcarbamoyl oxime (2f)
(500 MHz, CDCl₃, 295 K)

Acetophenone N,N-diallylcarbamoyl oxime (2f)
(75 MHz, CDCl₃, 295 K)
$N,N$-Diallyl-$1H$-imidazole-1-carboxamide
(500 MHz, CDCl$_3$, 294 K)

$N,N'$-Diallyl-$1H$-imidazole-1-carboxamide
(125 MHz, CDCl$_3$, 295 K)
Acetophenone $N,N$-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (2a)
(300 MHz, CDCl$_3$, 294 K)

Acetophenone $N,N$-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (2g)
(75 MHz, CDCl$_3$, 295 K)
1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethanone
N,N-diethylcarbamoyl oxime (8a)
(400 MHz, CDCl₃, 294 K)

1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethanone
N,N-diethylcarbamoyl oxime (8a)
(100 MHz, CDCl₃, 295 K)