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

Roy T. McBurney* and John C. Walton*

University of St. Andrews, EaStCHEM School of Chemistry, St. Andrews, Fife, KY16 9ST, UK

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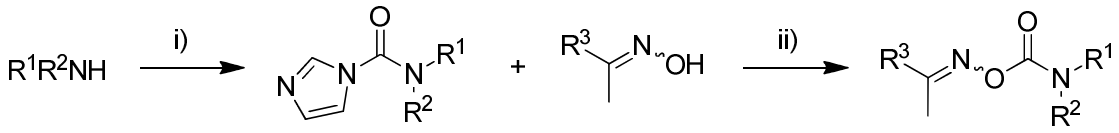
General Experimental Section

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,[1] as was *N*-benzylpent-4-en-1-amine.[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_{254}, Macherey-Nagel, Germany) and observed under UV light. ^{1}H and ^{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 (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, 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

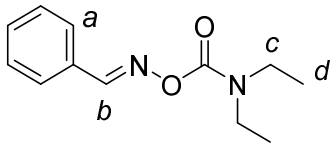
To a 0 °C solution of amine (1.0 equiv.) in THF (30 mL) was added sodium hydride (1.2 equiv.). After 5 min. 1,1-carbonyldiimidazole (CDI) (3.0 equiv) was added and the suspension was allowed to warm to rt for 18 h. The solvent was removed under reduced pressure and the crude residue was re-dissolved in EtOAc (100 mL) and washed with NH_4Cl (3 × 100 mL), dried over $MgSO_4$, 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 imidiazole 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 NH_4Cl (3 × 100 mL), dried over $MgSO_4$, filtered and purified by column chromatography (CH_2Cl_2/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.)*



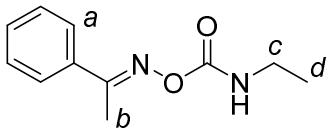
Scheme S2. General procedure for the synthesis of oxime carbamates. Reagents and conditions: i) R^1R^2NH, CDI, NaH, THF, O °C to rt, 18 h; ii) oxime, NaH, THF, O °C to rt, 18 h.

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



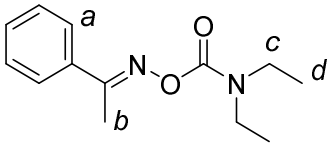
To a solution of benzaldehyde oxime (0.510 g, 4.21 mmol, 1.0 equiv.) and pyridine (0.41 mL, 5.06 mmol, 1.2 equiv.) in CH_2Cl_2 (30 mL) at 0 °C was added dropwise diethylcarbamoyl chloride (0.64 mL, 5.06 mmol, 1.2 equiv.) the solution was stirred for 18 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 1M HCl (100 mL), sat. aqueous $NaHCO_3$ (100 mL), brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography (10% EtOAC/CH_2Cl_2) to yield the title compound as a yellow oil, yield = 31%. ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ = 1.24 (t, J = 7.0 Hz, 6H, H_d), 3.40 (q, J = 7.0 Hz, 4H, H_c), 7.39–7.49 (m, 3H, H_{Ar}), 7.76 (m, 2H, H_{Ar}), 8.35 (s, 1H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$, 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 $C_{12}H_{17}N_2O_2$, 221.1290).

Acetophenone *N*-ethylcarbamoyl oxime (2b)



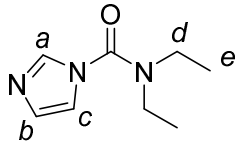
CDI Oxime Carbamate Route: Prepared from ethylamine (2 M in THF) (1.54 mL, 3.09 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.022 g, 0.927 mmol) and acetophenone oxime (0.626 g, 4.63 mmol) to give a colorless oil (0.087 g, 14%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.22 (t, J = 7.3 Hz, 3H, H_d), 2.43 (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): δ = 13.9, 14.3, 42.6, 127.0, 128.2, 130.4, 135.6, 154.6, 160.3; LRESI-MS: *m/z* = 207 $[MH]^+$; HRESI-MS: *m/z* = 207.1137, $[MH]^+$ (calcd. for $C_{11}H_{15}N_2O_2$, 207.1134).

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



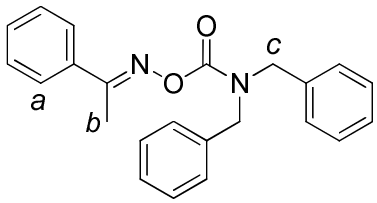
CDI Oxime Carbamate Route: Prepared from diethylamine (0.22 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.447 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 1.22 (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): δ = 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 $C_{13}H_{18}N_2O_2Na$, 257.1260).

***N,N*-Diethyl-1*H*-imidazole-1-carboxamide**



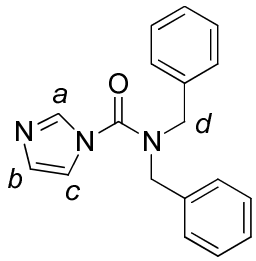
^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ = 1.27 (t, J = 7.1 Hz, 6H, H_e), 3.45 (q, J = 7.1 Hz, 4H, H_d), 7.10 (s, 1H, H_b), 7.23 (s, 1H, H_c), 7.88 (s, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 13.2, 42.6, 117.8, 129.5, 136.6, 151.2.

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



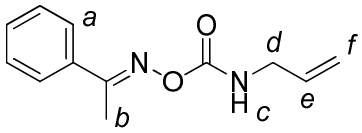
CDI Oxime Carbamate Route: Prepared from dibenzylamine (0.42 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part 2 NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless crystalline solid (0.348 g, 47%). M.p. = 79 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 294 K): δ = 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) δ = 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 [M*H*]$^+$; HR-ESIMS: *m/z* = 359.1761 (calcd. for $C_{23}H_{23}O_2N_2$, 359.1754).

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



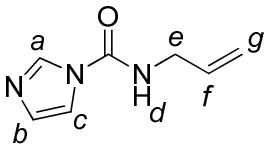
^{1}H NMR (500 MHz, $CDCl_3$, 295 K): δ = 4.49 (s, 4H, H_d), 6.94 (s, 1H, H_b), 7.13–7.17 (m, 4H, $H_{benzylAr}$), 7.27–7.32 (m, 7H, $H_{c,benzylAr}$), 7.86 (s, 1H, H_a); ^{13}C NMR (126 MHz, $CDCl_3$, 295 K): δ = 50.8, 117.9, 127.6, 128.2, 129.2, 130.0, 135.2, 137.1, 152.5; LR-ESIMS: *m/z* = 292 [M*H*]$^+$; HR-ESIMS: *m/z* = 292.1449 (calcd. for $C_{18}HN_3O$, 292.1444).

Acetophenone *N*-allylcarbamoyl oxime (2e)



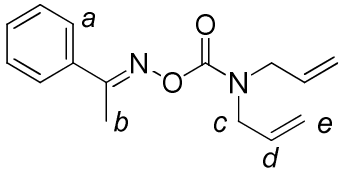
CDI Oxime Carbamate Route: Prepared from allylamine (0.08 mL, 2.06 mmol), CDI (1.0 g, 6.17 mmol), NaH (0.060 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.156 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 2.44 (s, 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): δ = 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 $C_{12}H_{15}N_2O_2$, 219.1134).

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



^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ = 4.00–4.04 (m, 2H, H_e), 5.18–5.29 (m, 2H, H_g), 5.84–5.96 (m, 1H, H_f), 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): δ = 43.3, 116.5, 117.4, 129.8, 133.2, 135.9, 148.9.

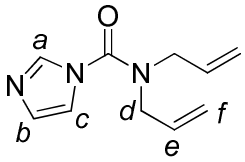
Acetophenone *N*,*N*-diallylcarbamoyl oxime (2f)



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): δ = 2.34 (s, 3H, H_b), 3.97 (br, 4H, H_c), 5.19–5.23 (m, 4H,

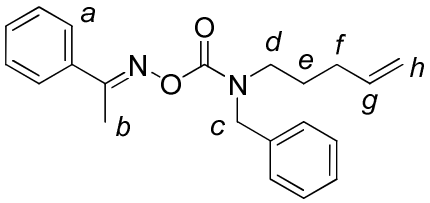
H_e), 5.80–5.88 (m, 2H, H_d), 7.36–7.41 (m, 3H, H_{Ar}), 7.75 (d, J = 7.6 Hz, 2H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 14.4, 48.7, 49.7, 116.8, 117.8, 127.0, 128.2, 128.5, 130.3, 133.2, 135.1, 154.5, 161.1; LR-ESIMS: *m/z* = 281 $[MH]^+$; HR-ESIMS: *m/z* = 218.1265 (calcd. for $C_{15}H_{18}N_2O_2Na$, 281.1260).

_N,N_-Diallyl-1_H_-imidazole-1-carboxamide



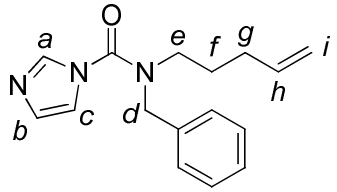
^{1}H NMR (500 MHz, $CDCl_3$, 294 K): δ = 4.00 (d, J = 5.3 Hz, 4H, H_d); 5.26–5.39 (m,4H, H_f), 5.83–5.96 (m, 2H, H_e), 7.08 (s, 1H, H_b), 7.31 (s, 1H, H_c), 7.99 (s, 1H, H_a); ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 50.2, 117.9, 118.8, 129.6, 131.7, 136.9, 151.8.

Acetophenone _N,N_-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (2g)



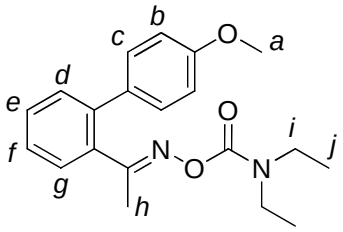
CDI Oxime Carbamate Route: Prepared from *N*-benzylpent-4-en-1-amine (0.579 g, 3.30 mmol), CDI (1.605 g, 9.91 mmol), NaH (0.095 g, 3.96 mmol) then for part (ii) NaH (0.024 g, 1.00 mmol) and acetophenone oxime (0.334 g, 2.47 mmol) to give a colorless oil (0.237 g, 21%). ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 1.68–1.79 (m, 2H, H_f), 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_h), 5.74–5.88 (m, 1H, H_g), 7.29–7.43 (m, 8H, H_{Ar}), 7.78 (br, 2H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 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 $C_{21}H_{25}N_2O_2$, 337.1911).

***N*-Benzyl-*N*-(pent-4-en-1-yl)-1*H*-imidazole-1-carboxamide**



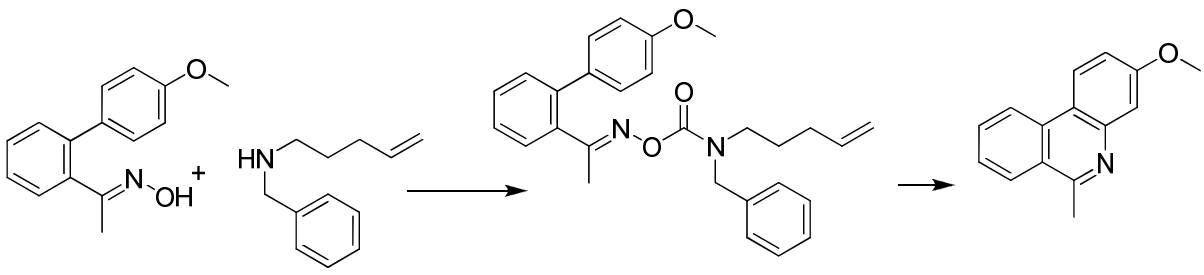
^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ = 1.73–1.88 (m, 2H, H_f), 2.02–2.09 (m, 2H, H_e), 3.36–3.42 (m, 2H, H_g), 4.66 (s, 2H, H_d), 4.97–5.05 (m, 2H, H_i), 5.67–5.80 (m, 1H, H_h), 7.12 (s, 1H, H_b), 7.24–7.27 (m, 3H, $H_{c,Ar}$), 7.32–7.44 (m, 3H, H_{Ar}), 8.11 (s, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 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.

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



CDI Oxime Carbamate Route: Prepared from diethylamine (0.21 mL, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.057 g, 2.47 mmol) then for part (ii) NaH (0.015 g, 0.62 mmol) and 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethanone oxime (0.596 g, 2.47 mmol) to give a colorless oil (0.355 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ = (*trans* isomer) 1.91 (t, J = 6.9 Hz, 6H, H_j), 2.72 (s, 3H, H_h), 3.37 (br, 4H, H_i), 3.84 (s, 3H, H_a), 6.94 (d, J = 8.8 Hz, 2H, H_b),7.30–7.38 (m, 4H, $H_{c,d,f}$), 7.43 (dt, J = 1.4 Hz, 7.6 Hz, 1H, H_e), 7.54 (dd, J = 1.1 Hz, 7.4 Hz, 1H, H_g); ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = (all isomers) 17.7, 17.9, 41.7, 42.4, 55.3, 114.0, 126.9, 129.6, 130.0 (×2), 130.2, 133.1, 135.5, 140.1, 154.3, 159.2, 164.7; LR-ESIMS: *m/z* = 363 $[MNa]^+$; HR-ESIMS: *m/z* = 363.1680 (calcd. for $C_{20}H_{24}N_2O_3Na$, 363.1679).

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_2NH 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_2NH, PhC(=O)O), $ImNEt_2$, Im-Im and many other unidentified

components. The adducts of Im and Et_2N with norbornene could not be observed with certainty.

Photolysis of acetophenone *N,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. ^1H 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 photolysed at ambient temperature for 3 h. ^1H 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-methylenepyrrolidine), 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)$(CH_2)_3CH=CH_2$) 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 ^1H and ^{13}C NMR spectra showed the presence of 3-methoxy-6-methylphenanthridine **10** ^1H NMR (400 MHz, $CDCl_3$, 295 K) δ = 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_2Br_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.

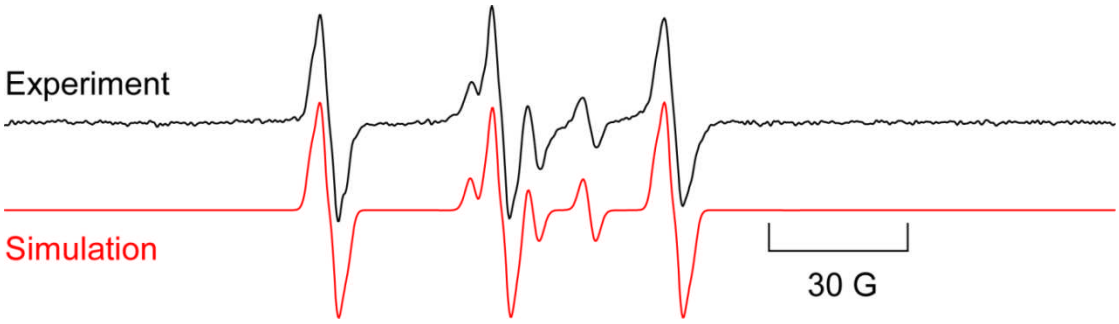
EPR Spectroscopy

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 × 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}.

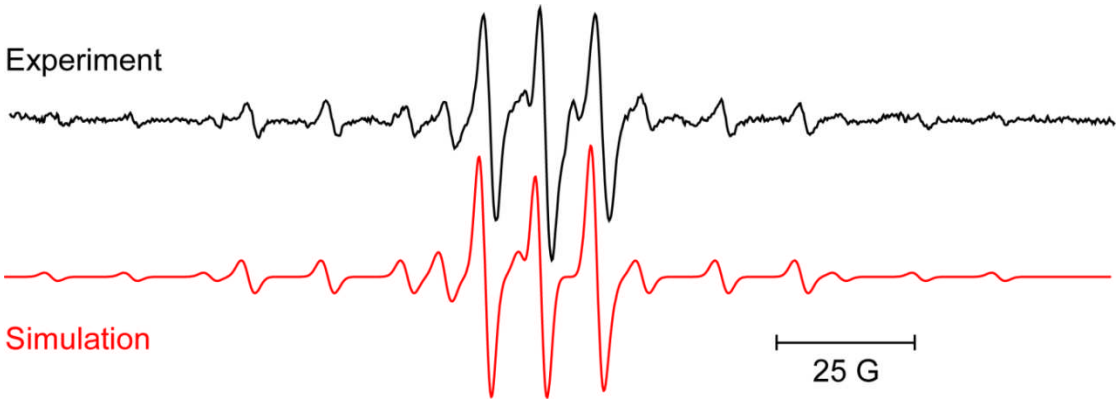
Sample EPR Spectra

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



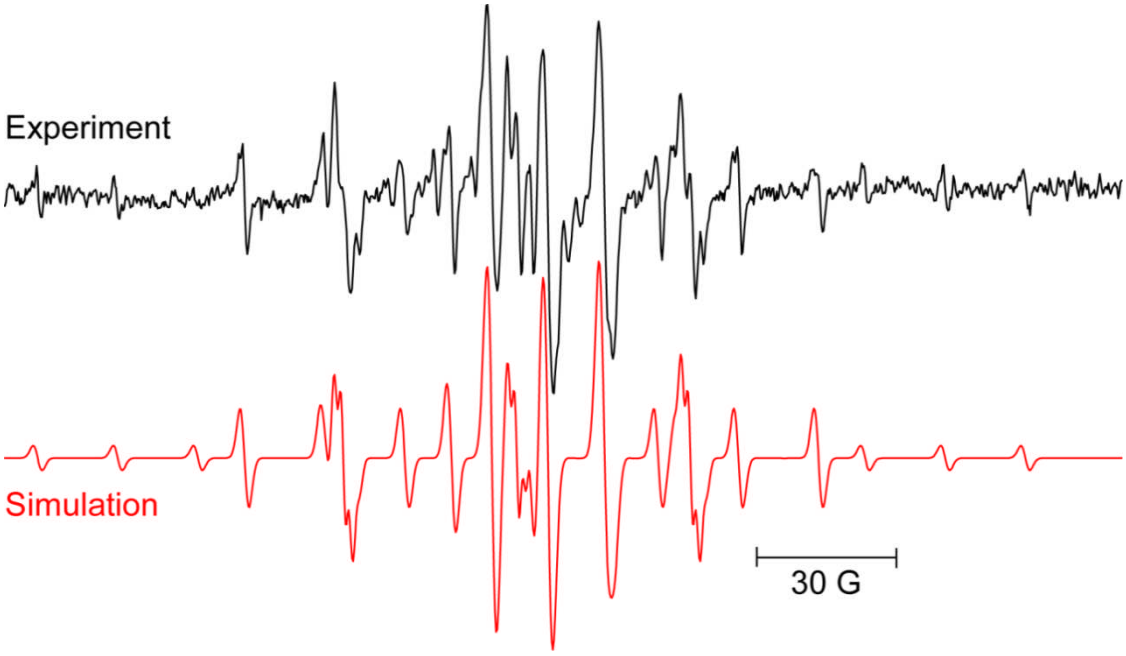
Note that the larger 1:1:1 triplet (a(N) = 31 G) is a persistent iminoxyl radical PhC(Me)=N-O• generated from traces of oxime PhC(Me)=N-OH present in the starting material.

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 PhC(Me)=N$^{\bullet}$ and the $Et_2N^{\bullet}$ radical appears as a pentet of 1:1:1 triplets. The iminoxyl 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.



Note the presence of PhC(Me)=N$^{\bullet}$ (central 1:1:1 triplet), the $Bn_2N^{\bullet}$ radical (pentet of 1:1:1 triplets) and the iminoxyl 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.

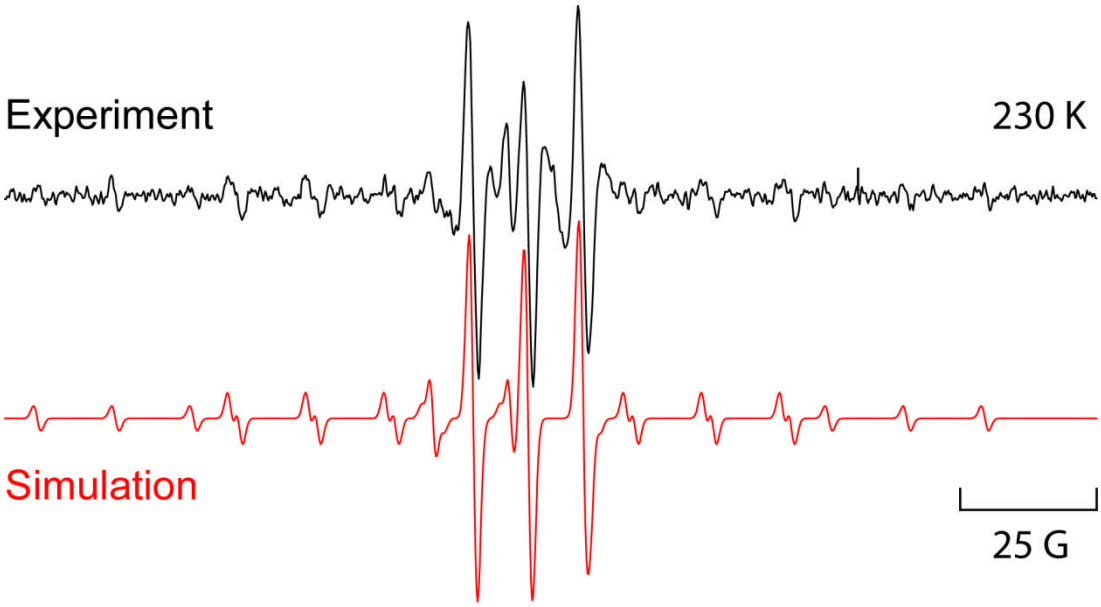


Table S1. Summary of Isotropic EPR Parameters of Dialkylaminyl Radicals in *t*-BuPh Solution.

Radical	**T/K**	***g*-factor**	***a*(N)**	***a*(H^{β})**	***a*(H^{β})**
$Et_2N^{\bullet}$	210	2.0047	14.4	35.7 (2H)	35.7 (2H)
$allyl_2N^{\bullet}$	210	2.0048	14.6	36.0 (2H)	36.0 (2H)
$Bn_2N^{\bullet}$	220	2.0046	14.3	37.1 (2H)	37.1 (2H)
BnN($^{\bullet}$)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($^{\bullet}$)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:

$NC(O)O–Im / UV \rightarrow N + Im + CO_2$
$N \rightarrow C$ k_c (forwards)
$C \rightarrow N$ k_{-c} (backwards)
$Im + Im \rightarrow$ non-radical products
$Im + N \rightarrow$ non-radical products
$Im + C \rightarrow$ non-radical products
$N + N \rightarrow$ non-radical products
$N + C \rightarrow$ non-radical products
$C + C \rightarrow$ 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:

$$d[C]/dt = 0 = k_c[N] - k_{-c}[C] - 2k_t[N][C] - 2k_t[C]^2 - 2k_t[C][Im]$$

Rearranging: $k_c/2k_t = [C]/[N] \times \{k_{-c}/2k_t + [N] + [C] + [Im]\}$

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

$$[Im] = [N] + [C]$$

On substituting: $k_c/2k_t = [C]/[N] \times \{k_{-c}/2k_t + 2[Im]\}$

If reverse cyclization is negligible $\{k_{-c}/2k_t << 2[Im]\}$ this simplifies to:

$k_c/2k_t = 2[C][Im]/[N]$ or

$k_c/2k_t = 2[C][Im]/\{[Im] - [C]\}$ or

$k_c/2k_t = 2[Im]^2/[N] - 2[Im]$ [i.e. equation (1) in main text].

Table S2. SSEPR Kinetics of cyclization of pentenylBnN$^{\bullet}$ (**6g**) from oxime carbamate **2g** in *t*-BuPh + MAP {$k_c/2k_t$ = 2[Im-N][Im]/[N]}.

Dial Temp	Actual T/K	scans	Gain	$[R_2N]$/ [Im]	d. i. Im	$[R_2N]$ M	[Im] M	[Im]-$[R_2N]$ M	$k_c/2kt$	log$k_c/2k_t$	log$2k_t$ n-C7	$10^3/T$	log η n-C7	log η t-BuPh	log$2k_t$ t-BuPh	log k_c 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

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

$Et_2NC(=O)O^{\bullet}$

E = -401.86984733 AU.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000675	1.224248	-0.000057
2	8	0	-0.943173	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	-0.731951	-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 $Et_2NC(=O)O^{\bullet}$

E = -401.86545744 AU

Virtual freq. = -233.5 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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

$Et_2N^{\bullet}$

E = -213.22037859 AU

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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

7	1	0	-3.050956	-0.245700	-0.711593
8	1	0	-2.620299	0.537322	0.818957
9	6	0	1.021655	0.646860	-0.053745
10	1	0	1.319891	1.565169	0.459209
11	1	0	0.676592	0.915907	-1.062321
12	6	0	2.254693	-0.266818	-0.171074
13	1	0	3.050946	0.246623	-0.711399
14	1	0	2.620460	-0.537532	0.818623
15	1	0	2.012333	-1.183840	-0.708935

EtNHC(=O)O$^{\bullet}$

E = -323.21827632 AU.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	1.484463
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	-2.582857	-0.974713	-0.849946
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$^{\bullet}$

E = -323.20532264AU

Virtual freq. = -425.3 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	-0.461749
4	6	0	1.316108	-0.733478	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	-0.418711
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$^{\bullet}$

E = -134.56263278 AU

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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

7	1	0	-1.243774	-0.972428	0.775406
8	1	0	-2.031693	0.444319	0.072273
9	1	0	-1.269745	-0.752722	-0.978099

$H_2NC(=O)O^{\bullet}$

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	-1.782908	0.869594	0.031675
6	1	0	-1.783070	-0.869619	0.031706

H_2N

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 $H_2NC(=O)O^{\bullet}$

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

$EtOC(O)O^{\bullet}$

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	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.691914	0.000263	-0.001704
2	1	0	-1.102842	0.892680	-0.477544
3	1	0	-1.103344	-0.876103	-0.506679

4	1	0	-1.090249	-0.017351	1.023509
5	6	0	0.791894	0.000000	-0.018660
6	1	0	1.348875	0.923714	0.041550
7	1	0	1.347682	-0.924521	0.041348

CO_2

E = -188.66056821 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

Et_2NCO_2

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 $Et_2NC(=O)O^{\bullet}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000014	1.433870	0.000001
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	0.673727
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	-0.673723
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

Et_2N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	0.444606
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

$EtNHCO_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	0.612866
5	1	0	-1.804231	-0.560473	1.436637
6	1	0	-1.082630	0.977070	0.989464
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

$EtNHCO_2$ TS for CO_2 loss

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	-0.745434	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 Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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

$H2NCO_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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

$H2NCO_2$ TS for CO_2 loss

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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 Number	Atomic 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 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

$EtOCO_2$

Center Number	Atomic 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

$EtOCO_2$ TS for CO_2 loss

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

2	6	0	1.263568	0.145565	0.004942
3	8	0	0.921190	1.317624	-0.025501
4	8	0	2.109009	-0.644020	-0.221121
5	6	0	-1.180132	-0.690894	-0.238355
6	1	0	-0.806740	-0.762316	-1.264710
7	1	0	-1.541345	-1.684969	0.063557
8	6	0	-2.293358	0.339606	-0.095270
9	1	0	-3.133813	0.069378	-0.739633
10	1	0	-2.641545	0.387618	0.937816
11	1	0	-1.922932	1.323859	-0.386701

EtO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.994572	-0.604756	0.000000
2	1	0	0.845471	-1.218685	0.888548
3	1	0	0.845471	-1.218685	-0.888548
4	1	0	2.012778	-0.209669	0.000000
5	6	0	0.000000	0.588952	0.000000
6	1	0	0.187938	1.191429	0.902496
7	1	0	0.187938	1.191429	-0.902496
8	8	0	-1.255879	0.044876	0.000000

$EtCO_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.742035	1.231486	0.000029
2	6	0	-0.688749	-0.748462	0.000053
3	1	0	-0.684284	-1.408679	-0.873894
4	1	0	-0.684303	-1.408495	0.874143
5	6	0	-1.907243	0.177562	-0.000043
6	1	0	-2.825579	-0.412557	-0.000007
7	1	0	-1.915500	0.820808	0.881705
8	1	0	-1.915478	0.820662	-0.881899
9	6	0	0.620690	-0.016370	0.000004
10	8	0	1.742584	-0.592500	-0.000046

Et

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.693527	0.000262	-0.001737
2	1	0	-1.107133	0.894093	-0.478482
3	1	0	-1.107621	-0.877967	-0.506838
4	1	0	-1.093628	-0.016901	1.025742
5	6	0	0.794217	0.000002	-0.019115
6	1	0	1.352723	0.925821	0.042451
7	1	0	1.351517	-0.926631	0.042241

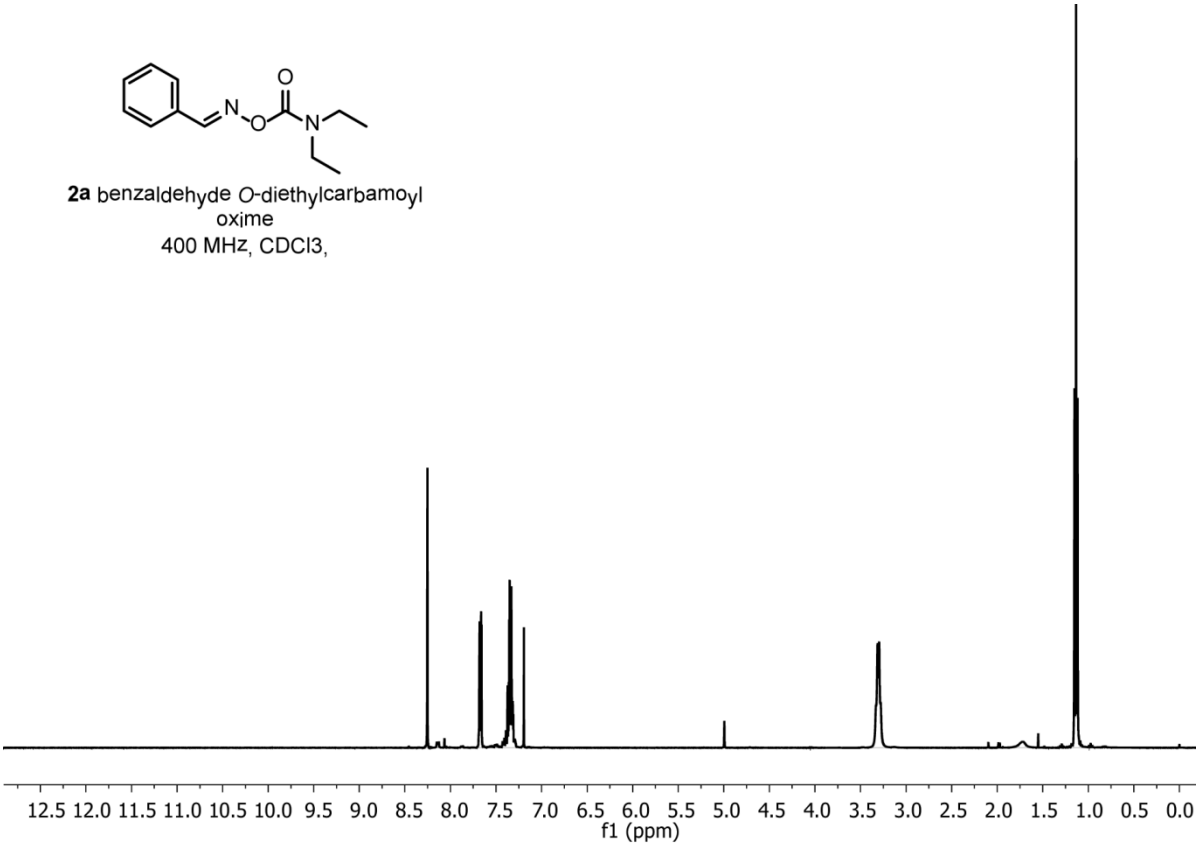
References:

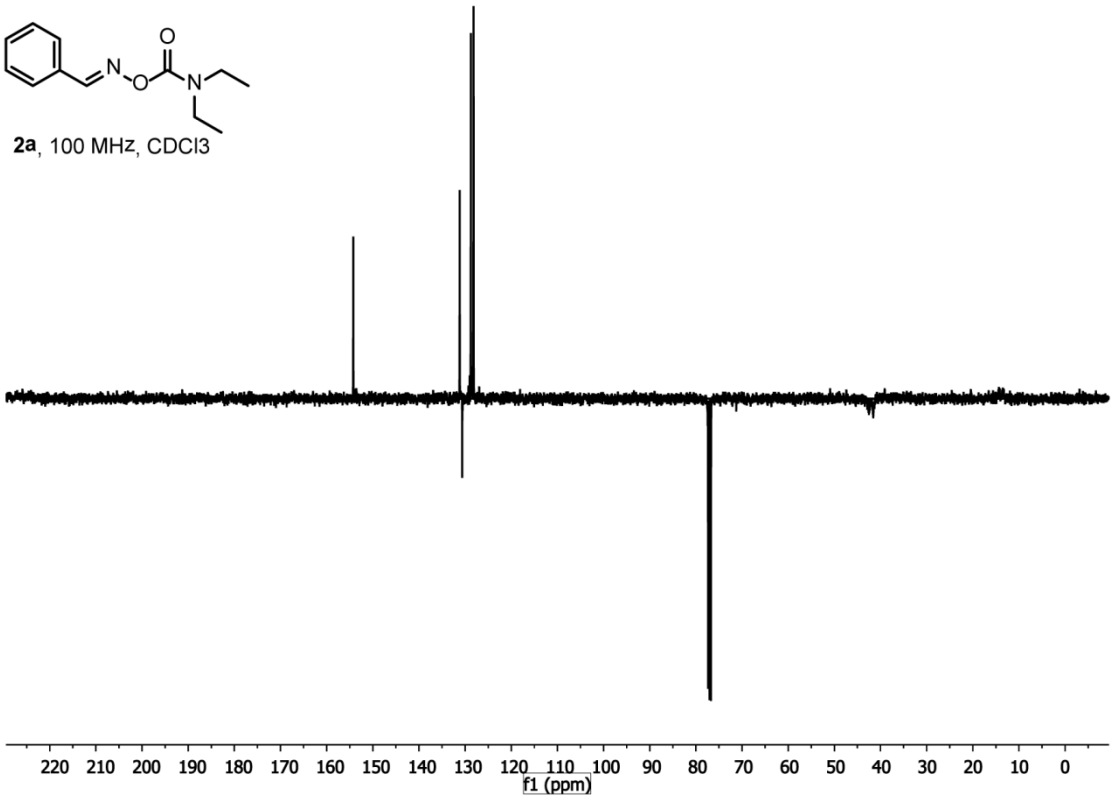
(1) McBurney, R. T.; Slawin, A. M. Z.; Smart, L. A.; Yu, Y.; Walton, J. C. *Chem. Commun.* **2011**, *47*, 7974–7976.

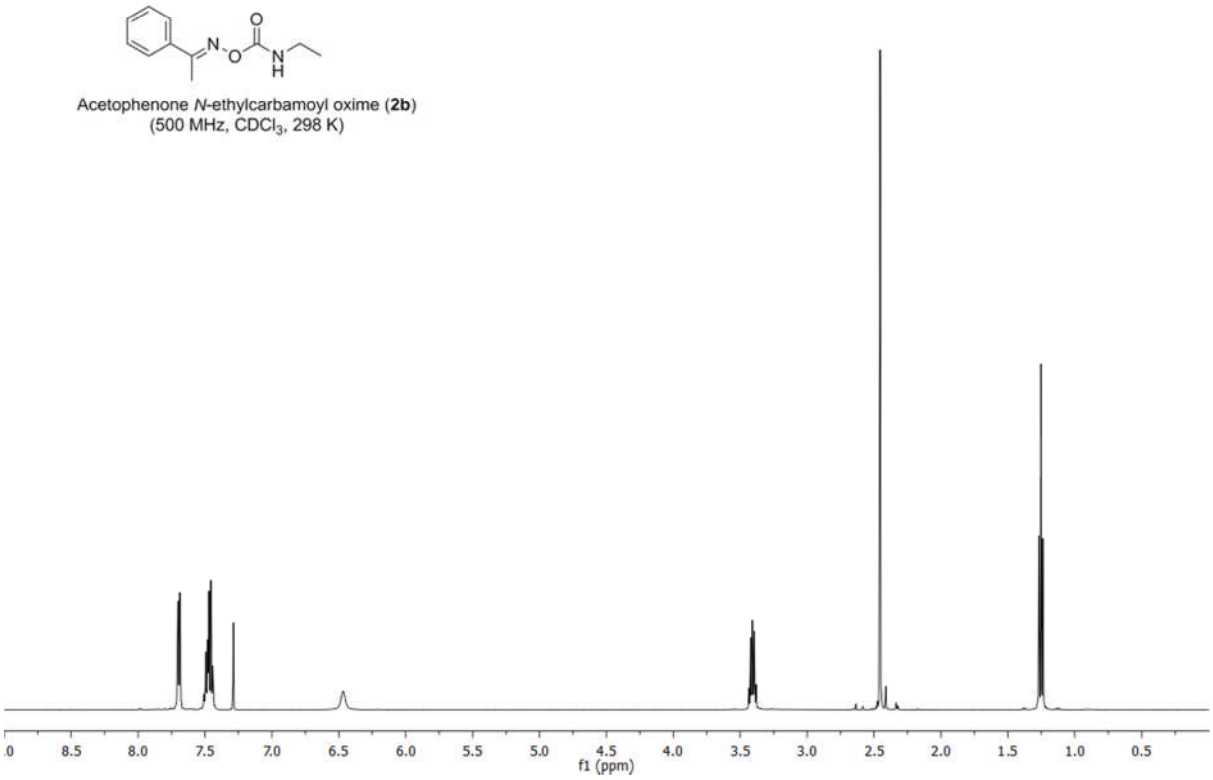
(2) Gribkov, D. V.;Hultzsch, K. C. *Angew. Chem. Int. Ed.*, **2004**, *43*, 5542.

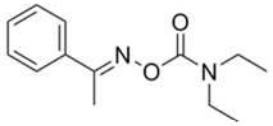
(3) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

(4) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648.

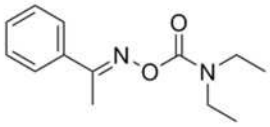

2a benzaldehyde O-diethylcarbamoyl oxime
400 MHz, CDCl3,
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2a, 100 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

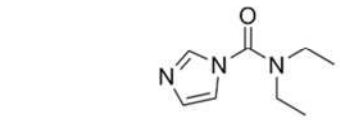

Acetophenone N-ethylcarbamoyl oxime (2b)
(500 MHz, CDCl3, 298 K)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



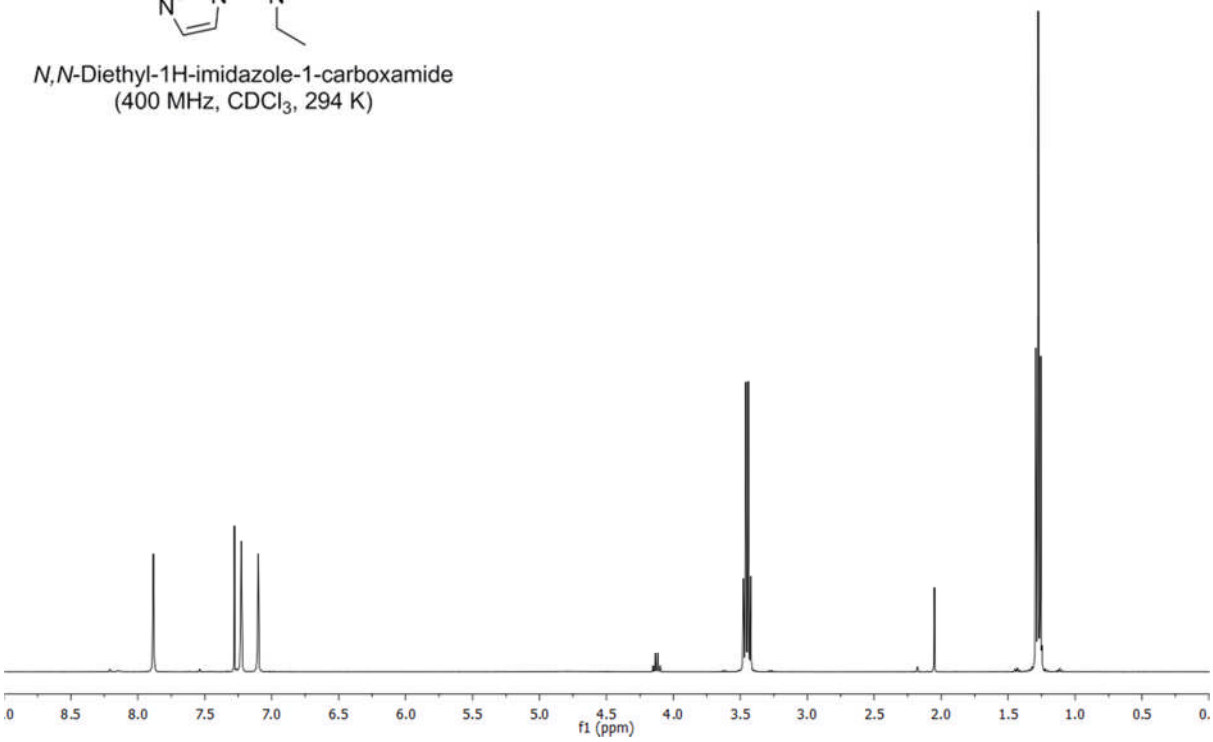
Acetophenone *N,N*-diethylcarbamoyl oxime (**2c**)
(300 MHz, $CDCl_3$, 294 K)

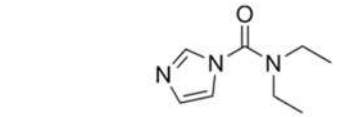


Acetophenone *N,N*-diethylcarbamoyl oxime (**2c**)
(75 MHz, $CDCl_3$, 295 K)

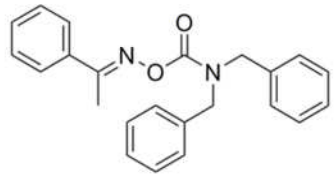


N,N-Diethyl-1H-imidazole-1-carboxamide
(400 MHz, $CDCl_3$, 294 K)

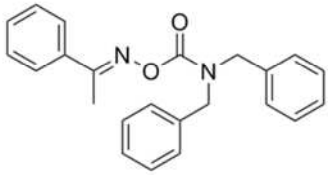




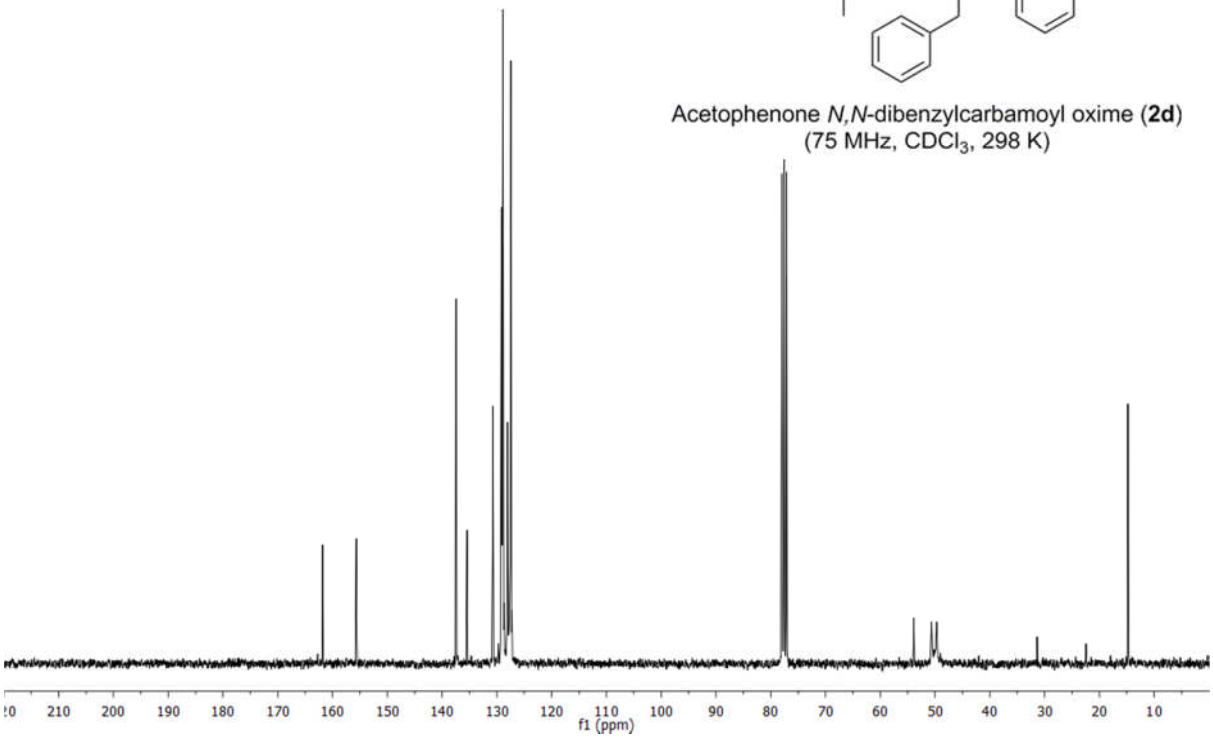
N,N-Diethyl-1H-imidazole-1-carboxamide
(100 MHz, $CDCl_3$, 296 K)

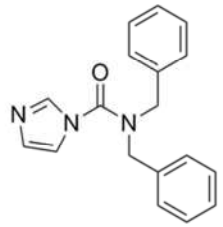


Acetophenone *N,N*-dibenzylcarbamoyl oxime (**2d**)
(500 MHz, CDCl3, 294 K)

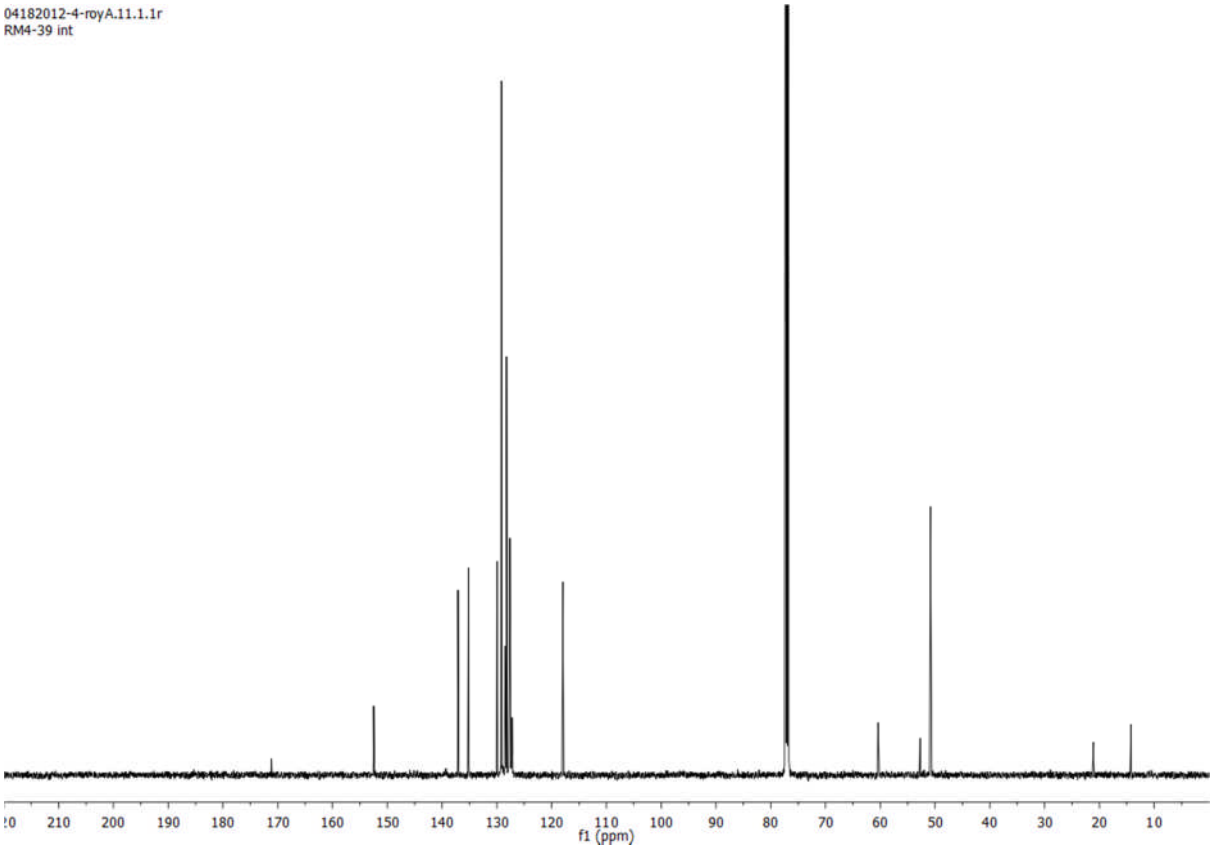


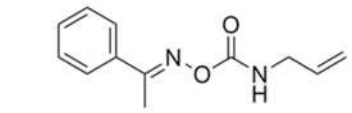
Acetophenone *N,N*-dibenzylcarbamoyl oxime (**2d**)
(75 MHz, $CDCl_3$, 298 K)



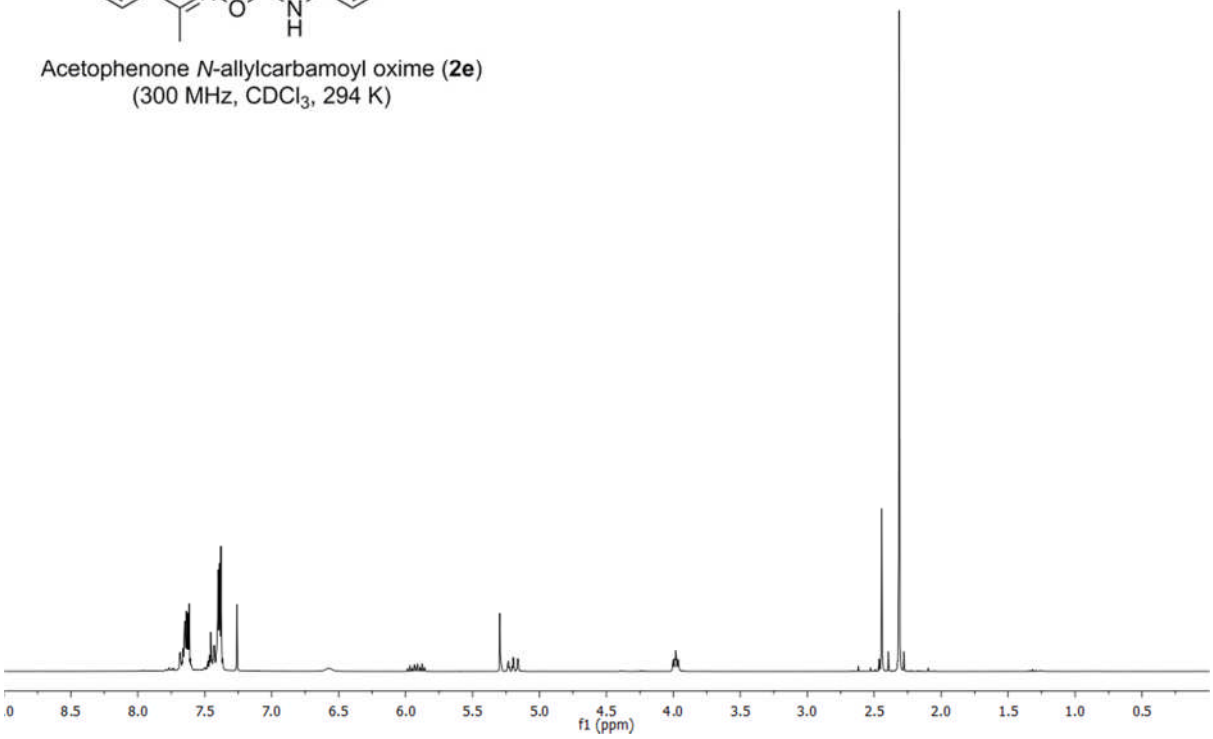


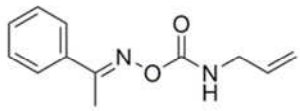
N,N-Dibenzyl-1H-imidazole-1-carboxamide
(500 MHz, $CDCl_3$, 295 K)



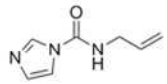


Acetophenone *N*-allylcarbamoyl oxime (**2e**)
(300 MHz, $CDCl_3$, 294 K)

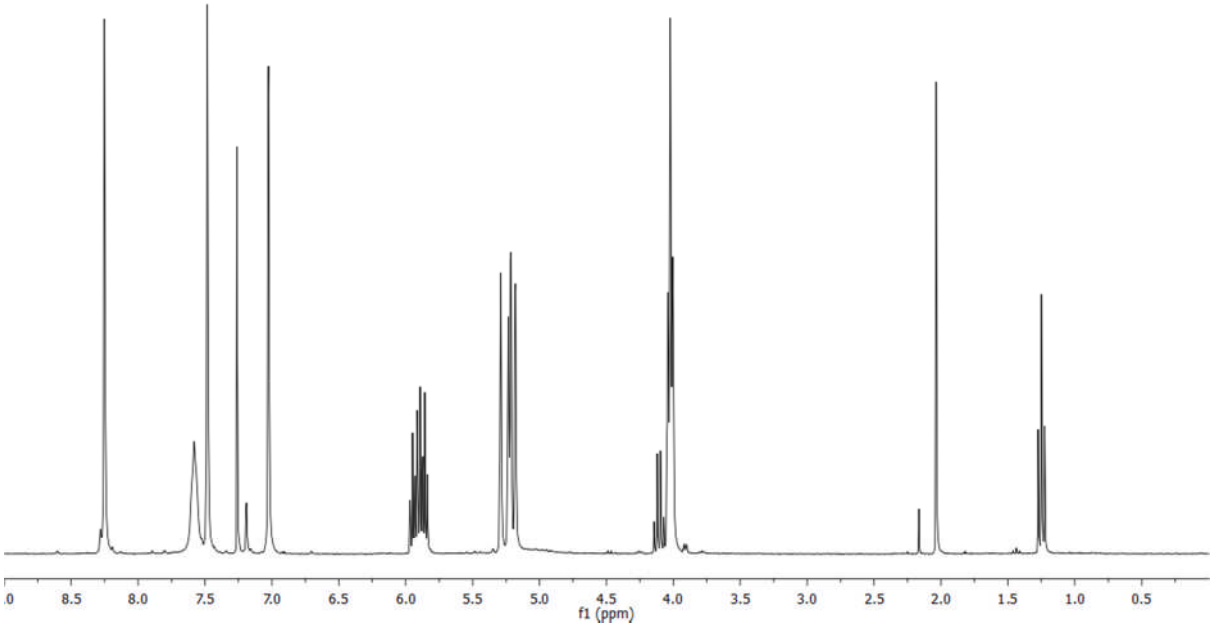


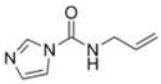


Acetophenone *N*-allylcarbamoyl oxime (**2e**)
(75 MHz, $CDCl_3$, 295 K)

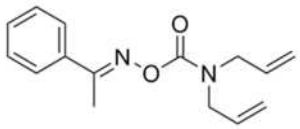


N-Allyl-1H-imidazole-1-carboxamide
(300 MHz, $CDCl_3$, 295 K)

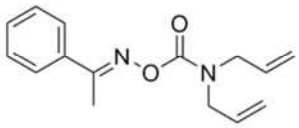




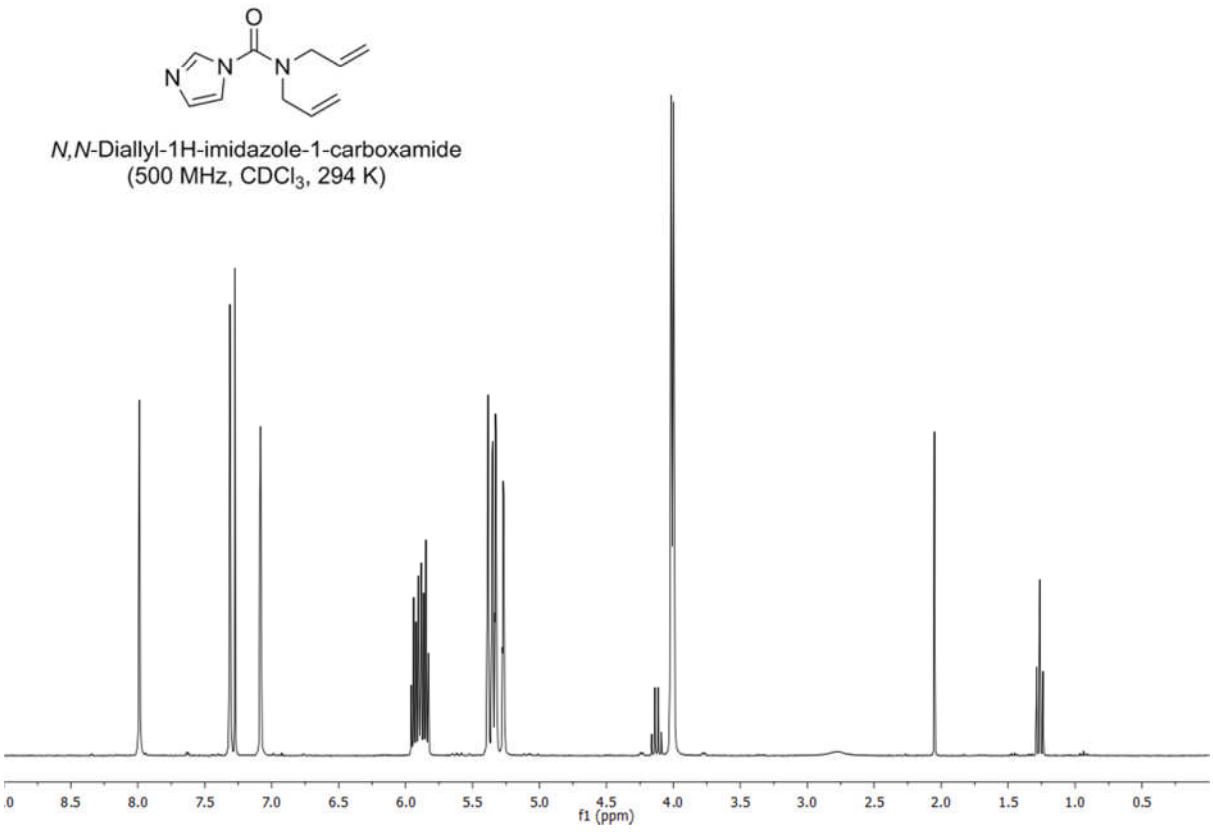
N-Allyl-1H-imidazole-1-carboxamide
(100 MHz, $CDCl_3$, 295 K)

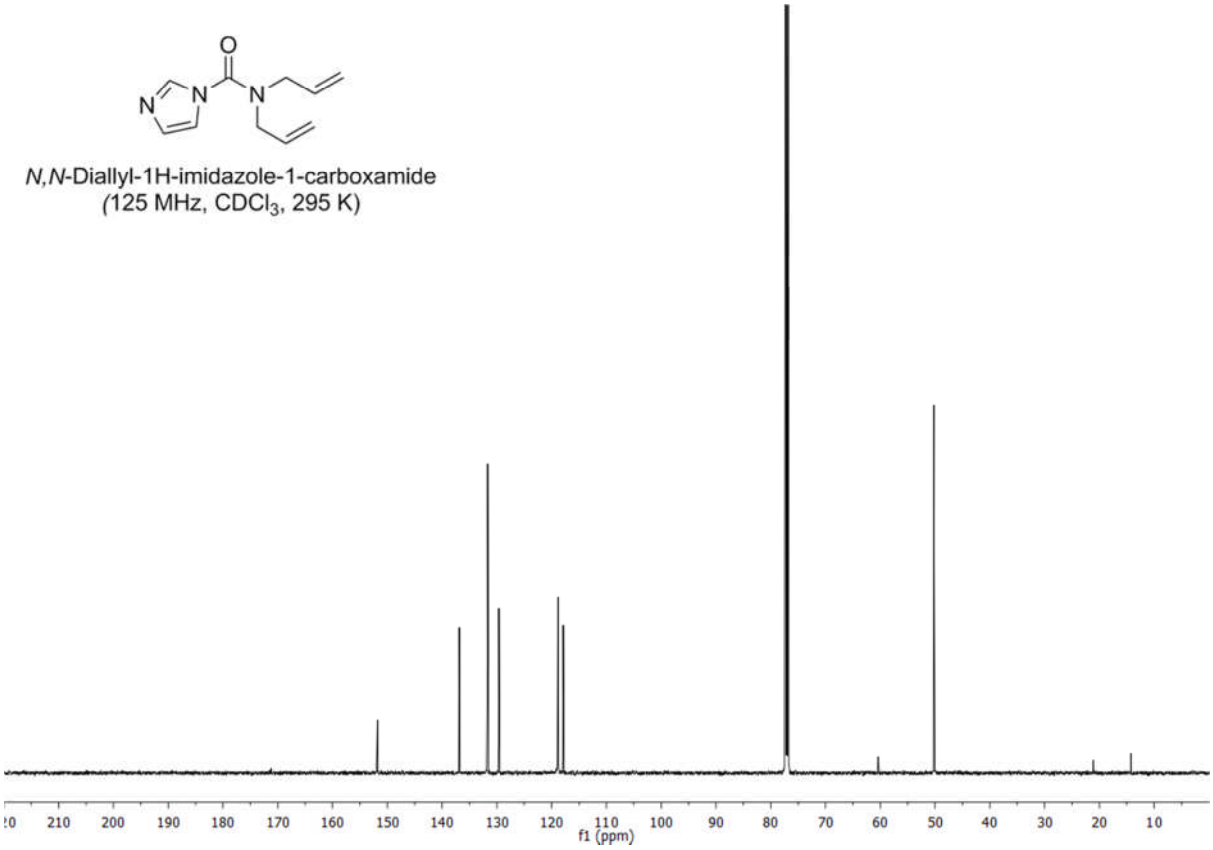


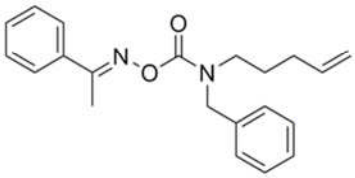
Acetophenone *N,N*-diallylcarbamoyl oxime (**2f**)
(500 MHz, $CDCl_3$, 295 K)



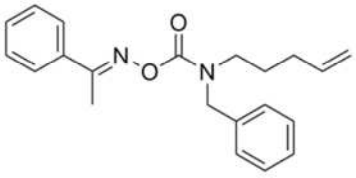
Acetophenone *N,N*-diallylcarbamoyl oxime (**2f**)
(75 MHz, $CDCl_3$, 295 K)


N,N-Diallyl-1H-imidazole-1-carboxamide
(500 MHz, CDCl3, 294 K)
f1 (ppm)

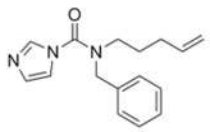

N,N-Diallyl-1H-imidazole-1-carboxamide
(125 MHz, CDCl3, 295 K)
f1 (ppm)



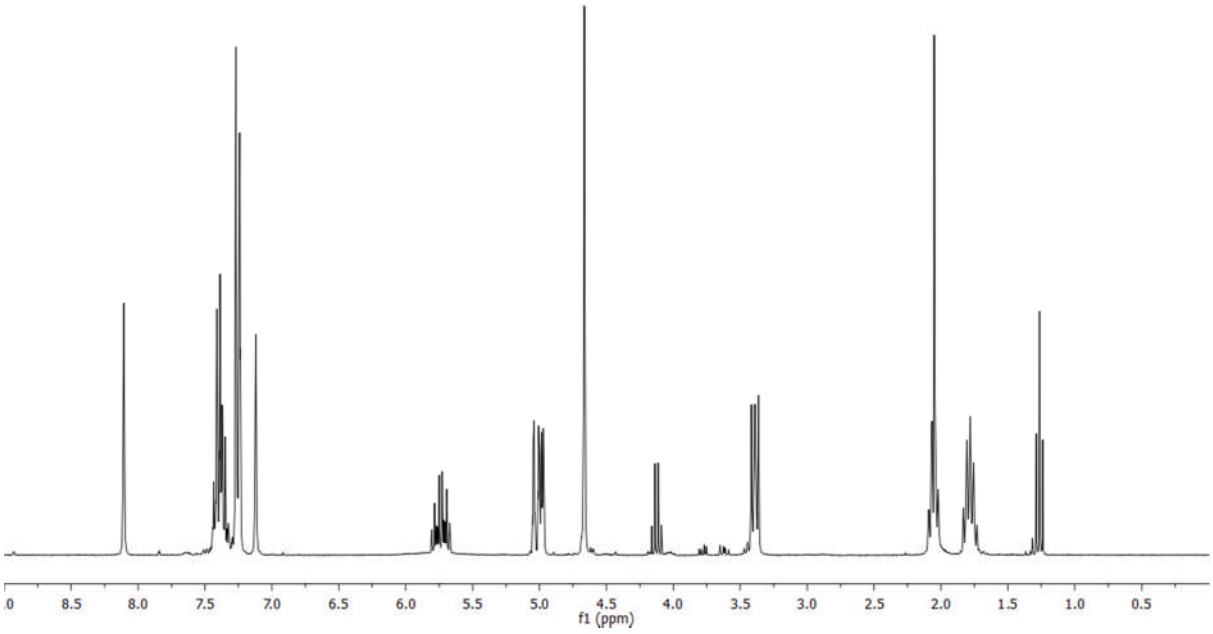
Acetophenone *N,N*-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (**2g**)
(300 MHz, $CDCl_3$, 294 K)

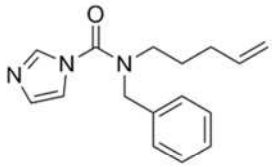


Acetophenone *N,N*-(benzyl(pent-4-en-1-yl)carbamoyl) oxime (**2g**)
(75 MHz, $CDCl_3$, 295 K)

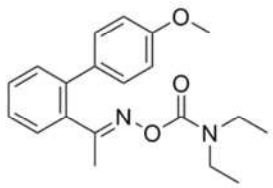


N-Benzyl-*N*-(pent-4-en-1-yl)-1H-imidazole-1-carboxamide
(300 MHz, $CDCl_3$, 294 K)

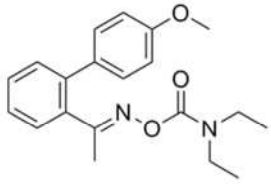




N-Benzyl-*N*-(pent-4-en-1-yl)-1H-imidazole-1-carboxamide
(75 MHz, $CDCl_3$, 295 K)



1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethanone
N,N-diethylcarbamoyl oxime (**8a**)
(400 MHz, $CDCl_3$, 294 K)



1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethanone
N,N-diethylcarbamoyl oxime (**8a**)
(100 MHz, $CDCl_3$, 295 K)