Electronic Supplementary Material (ESI) for Chemical Science

Electronic Supplementary Information

Rapid and Selective Spiro-Cyclizations of *O*-Centred Radicals onto Aromatic Acceptors.

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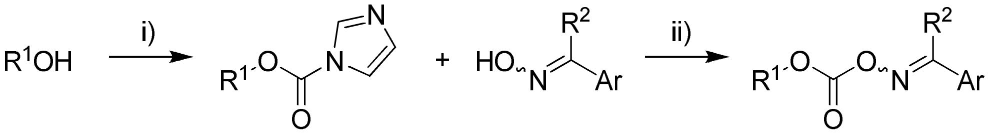
General Experimental Section

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, acetophenone oxime, and oxime carbonates **6a,b** were prepared according to the literature procedure.[1] 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. ^1H 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 Carbonate General Procedure

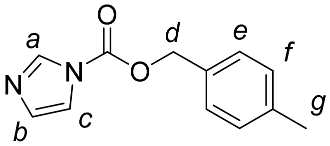
To a 0 °C solution of 1,1-carbonyldiimidazole (3 equiv.) in THF (30 cm^3) was added alcohol (1 equiv.). The reaction was stirred and allowed to warm to rt over 2 h. The solvent was removed under reduced pressure and the crude residue was re-dissolved in EtOAc (100 cm^3) and washed with NH_4Cl (3 × 100 cm^3), dried over $MgSO_4$, filtered and concentrated under reduced pressure. To a solution of oxime (1.5 equiv.) in THF (20 cm^3) at 0 °C, pre-treated with sodium hydride (0.3 equiv.), was added a THF solution (10 cm^3) 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 cm^3) and washed with NH_4Cl (3 × 100 cm3), dried over $MgSO_4$, filtered and purified by column chromatography (CH_2Cl_2/Pet Ether 40:60 (1:1) as eluent).



Scheme S1. General procedure for the synthesis of oxime carbonates. Reagents and conditions: i) R^{1}OH, CDI, THF, O °C to rt, 2 h; ii) oxime, NaH, THF, O °C to rt, 18 h.

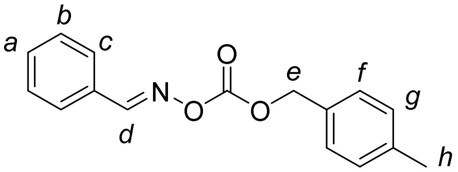
Synthesis and Experimental Section

4-Methylbenzyl 1*H*-imidazole-1-carboxylate (5c)



Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 2.29 (s, 3H, H_g), 5.29 (s, 2H, H_d), 6.96 (m, 1H, H_b), 7.13 (d, J = 8.0 Hz, 2H, H_f), 7.25 (d, J = 8.0 Hz, 2H, H_e) 7.34 (t, J=1.4 Hz, 1H, H_c), 8.05 (*m*, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 21.3, 69.9, 117.2, 128.9, 129.5, 130.6, 131.0, 137.1, 139.2, 148.6.

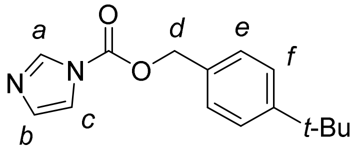
Benzaldehyde *O*-(4-methylbenzyloxy)carbonyl oxime (6c)



Oxime Carbonate CDI Route: Prepared from 4-methylbenzyl alcohol (0.25 g, 2.06 mmol), CDI (1.00 g, 6.17 mmol), benzaldehyde oxime (0.374 g, 3.09 mmol) and sodium hydride (0.015 g, 0.62 mmol) to give a colourless solid, 0.54 g, yield = 84%. M. p. = 68 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 2.39 (s, 3H, H_h), 5.29 (s, 2H, H_e), 7.22 (d, J = 7.8 Hz, 2H, H_g), 7.37 (d, J = 7.8 Hz, 2H, H_f) 7.41-7.51 (m, 3H, $H_{a,b}$), 7.79-7.70 (m, 2H, H_c), 8.35 (*s*, 1H, H_d); ^{13}C NMR (100 MHz,

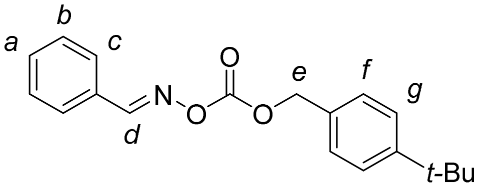
$CDCl_3$, 295 K): δ = 21.3, 70.3, 128.4, 128.5, 128.9, 129.3, 129.4, 129.8, 131.7, 138.7, 153.8; 155.9; LRESI-MS: m/z = 270 [M*H*]$^+$; HRESI-MS: m/z = 270.1120 [M*H*]$^+$ (calcd. for $C_{16}H_{16}NO_3$, 270.1130).

4-*t*-Butylbenzyl 1*H*-imidazole-1-carboxylate (5d)



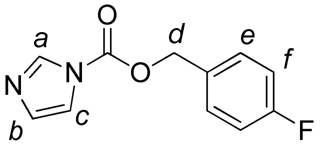
Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ = 1.35 (s, 9H, H_{tBu}), 5.41 (s, 2H, H_d), 7.07 (s, 1H, H_b), 7.35-7.55 (m, 5H, $H_{c,e,f}$), 8.17 (s, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 296 K): δ = 31.3, 34.7, 69.8, 117.2, 125.8, 128.7, 130.6, 131.0, 137.2, 148.7, 152.4.

(*E*)-Benzaldehyde *O*-(((4-(*t*-butyl)benzyl)oxy)carbonyl) oxime (6d)



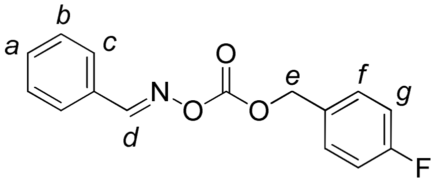
Oxime Carbonate CDI Route: Prepared from 4-*t*-butylbenzyl alcohol (0.41 g, 2.46 mmol), CDI (1.00 g, 6.17 mmol), benzaldehyde oxime (0.355 g, 2.94 mmol) and sodium hydride (0.017 g, 0.62 mmol) to give a colourless solid, 0.25 g, yield = 33%. M.p. 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 1.22 (s, 9H, H_{tBu}), 5.18 (s, 2H, H_e), 7.26-7.39 (m, 7H, $H_{a,b,f,g}$), 7.66-7.58 (m, 2H, H_c) 8.22 (s, 1H, H_d); ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 31.3, 34.7, 70.3, 125.7, 128.4, 128.7, 128.9, 129.8, 131.8, 132.2, 151.9, 153.8, 155.9; LRESI-MS: m/z = 312 [M*H*]$^+$; HRESI-MS: m/z = 312.1598 [M*H*]$^+$ (calcd. for $C_{19}H_{22}NO_3$, 312.1600).

4-Fluorobenzyl 1*H*-imidazole-1-carboxylate (5f)



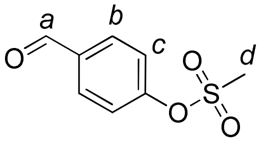
^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ = 5.38 (s, 2H, H_d), 7.06–7.12 (m, 3H, $H_{b,f}$), 7.41–7.45 (m, 3H, $H_{c,e}$), 8.16 (s, 1H, H_a); ^{19}F NMR (376 MHz, $CDCl_3$, 294 K): δ = -122.2; ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 69.2, 115.9 (d, $^{2}J_{CF}$ = 21.7 Hz), 117.2, 129.8 (d, $^{4}J_{CF}$ = 3.3 Hz), 130.6, 131.0 (d, $^{3}J_{CF}$ = 8.4 Hz), 137.1, 148.5, 163.2 (d, $^{1}J_{CF}$ = 248.7 Hz).

Benzaldehyde *O*-(((4-fluorobenzyl)oxy)carbonyl) oxime (6f)



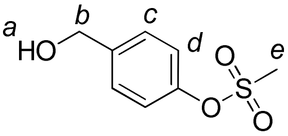
Oxime Carbonate CDI Route: Prepared from 4-(fluoro)benzyl alcohol (0.23 cm^3, 2.06 mmol), CDI (1.00 g, 6.17 mmol), benzaldehyde oxime (0.374 g, 3.09 mmol) and sodium hydride (0.015 g, 0.062 mmol) to give a colourless crystals, 0.499 g, yield = 87%. M.p. = 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 295 K): δ = 5.29 (s, 2H, H_e), 7.10 (t, J = 8.7 Hz, 2H), 7.37–7.49 (m, 5H), 7.74 (d, J = 7.1 Hz, 2H), 8.36 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, 294 K): δ = -113.1; ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 69.6, 115.7 (d, $^{2}J_{CF}$ = 22.4 Hz), 128.4, 128.9, 129.7, 130.6 (d, $^{4}J_{CF}$ = 3.3 Hz), 130.8 (d, $^{3}J_{CF}$ = 8.6 Hz), 131.9, 153.7, 156.0, 163.0 (d, $^{1}J_{CF}$ = 247.6 Hz); LR-ESIMS: m/z = 274 $[MH]^+$; HR-ESIMS: m/z = 274.0877 $[MH]^+$ (calcd. for $C_{15}H_{13}NO_3F$, 274.0879).

4-(Mesyloxy)benzaldehyde



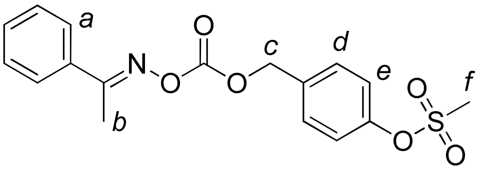
A suspension of methane sulfonyl chloride (4.5 cm^3, 57.7 mmol), 4-hydroxybenzaldehyde (4.70 g, 38.5 mmol) and potassium carbonate (26.56 g, 192.5 mmol) in THF (200 cm^3) was heated at reflux for 18 h. The solvent was removed under reduced pressure, the crude residue was redissolved in CH_2Cl_2 (100 cm^3), washed with H_2O (2 × 100 cm^3), dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography (10% $EtOAc/CH_2Cl_2$) to yield the title compound as a colourless solid (5.81 g, yield = 75%). M.p = 68 °C: ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 3.21$ (s, 3H, H_d), 7.45 (d, $J = 8.6$ Hz, 2H, H_c), 7.95 (d, $J = 8.6$ Hz, 2H, H_b), 10.01 (s, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 38.1$, 122.7, 131.6, 135.1, 153.3, 190.6; LR-ESIMS: $m/z = 201$ $[MH]^+$; HR-ESIMS: $m/z = 201.0214$ (calcd. for $C_8H_9O_4S$, 201.0216).

4-(Hydroxymethyl)phenyl methanesulfonate



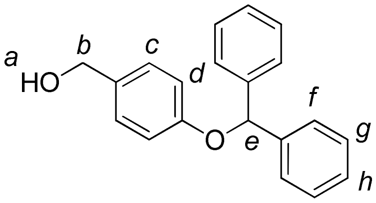
A solution of 4-(mesyloxy)benzaldehyde (3.715 g, 18.6 mmol) and sodium borohydride (2.821 g, 74.2 mmol) in THF (150 cm^3) and methanol (1 cm^3) was stirred for 18 h. The reaction was neutralised with 1M HCl and the mixture concentrated under reduced pressure. The crude residue was redissolved in CH_2Cl_2 (100 cm^3), washed with 1M HCl (100 cm^3), sat. aqueous $NaHCO_3$ (100 cm^3), brine (100 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure and purified by column chromatography (10% $EtOAc/CH_2Cl_2$) to yield the title compound as a colourless oil (2.521 g, yield = 68%). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 2.03$ (s, 1H, H_a), 3.11 (s, 3H, H_e), 4.68 (s, 2H, H_b), 7.25 (d, $J = 8.7$ Hz, 2H, H_c), 7.39 (d, $J = 8.7$ Hz, 2H, H_d); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): $\delta = 37.4$, 64.3, 122.1, 128.5, 140.3, 148.5; LR-ESIMS: $m/z = 220$ $[MNH_4]^+$; HR-ESIMS: $m/z = 220.0640$ (calcd. for $C_8H_{14}NO_4S$, 220.0638).

(*E*)-4-(((((1-Phenylethylidene)amino)oxy)carbonyl)oxy)methyl)phenyl methanesulfonate (6g)



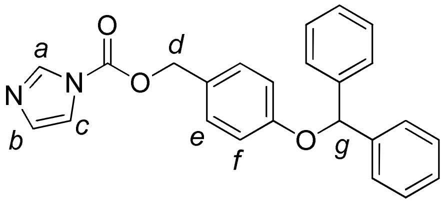
Oxime Carbonate CDI Route: Prepared from 4-(hydroxymethyl)phenyl methanesulfonate (0.412 g, 2.06 mmol), CDI (1.000 g, 6.17 mmol), NaH (0.015 g, 0.62 mmol) and acetophenone oxime (0.417 g, 3.09 mmol) to give a crystalline powder (0.297 g, 40%). M.p. = 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 2.39$ (s, 3H, H$_b$), 3.15 (s, 3H, H$_f$), 5.30 (s, 2H, H$_c$), 7.31 (d, J = 8.7 Hz, 2H, H$_d$), 7.38–7.45 (m, 3H, H$_{Ar}$), 7.52 (d, J = 8.7 Hz, 2H, H$_e$), 7.73 (d, J = 8.1 Hz, 2H, H$_a$); ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): $\delta = 14.5$, 37.5, 69.0, 122.3, 127.0, 128.6, 130.5, 130.7, 134.4, 134.4, 149.4, 153.8, 163.0; LR-ESIMS: m/z = 381 [MNH_4]$^+$; HR-ESIMS: m/z = 381.1114 (calcd. for $C_{17}H_{21}N_2O_6S$, 381.1115).

4-(Benzhydryloxy)phenylmethanol



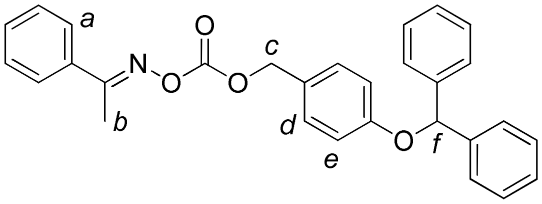
A suspension of bromodiphenylmethane (2.030 g, 8.21 mmol, 1.5 equiv.), 4-hydroxybenzaldehyde (0.669 g, 5.48 mmol, 1.0 equiv.) and potassium carbonate (3.781 g, 27.40 mmol, 5.0 equiv.) in THF (60 cm^3) was heated at reflux for 18 h. The solvent was removed under reduced pressure and the crude residue was redissolved in H_2O (100 cm^3) and extracted into CH_2Cl_2 (2 × 100 cm^3) to give 4-(benzhydryloxy)benzaldehyde which was used without further purification. A solution of 4-(benzhydryloxy)benzaldehyde (1.512 g) and sodium borohydride (0.797 g, 20.96 mmol, 4 equiv.) in THF (50 cm^3) and methanol (1 cm^3) was stirred for 18 h. The solution was neutralised with 1M HCl before the solvent was removed under reduced pressure. The crude residue was redissolved in EtOAc and the organic layer was washed with 1M HCl (100 cm^3), sat. aqueous $NaHCO_3$ (100 cm^3), brine (100 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Further purification by column chromatography (5% EtOAc/CH_2Cl_2) yielded the title compound as a colourless solid (0.507 g, yield = 32%). M.p. = 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 1.53$ (br, 1H, H_a), 4.57 (s, 2H, H_b), 6.22 (s, 1H, H_e), 6.94 (d, $J = 8.6$ Hz, 2H, H_d), 7.22 (d, $J = 8.6$ Hz, 2H, H_c), 7.27 (t, $J = 7.4$ Hz, 2H, H_h), 7.34 (t, $J = 7.3$ Hz, 4H, H_g), 7.42 (d, $J = 7.2$ Hz, 4H, H_f); ^{13}C NMR (125 MHz, $CDCl_3$, 299 K): $\delta = 65.0$, 81.8, 116.2, 126.9, 127.8, 128.6, 128.6, 133.4, 141.2, 157.7; LR-ESIMS: $m/z = 308$ $[MNH_4]^+$; HR-ESIMS: $m/z = 308.1649$ (calcd. for $C_{20}H_{22}NO_2$, 308.1645).

4-(Benzhydryloxy)benzyl 1*H*-imidazole-1-carboxylate (5i)



^{1}H NMR (500 MHz, $CDCl_3$, 295 K): $\delta = 5.19$ (s, 2H, H_d), 6.10 (s, 1H, H_f), 6.85 (d, $J = 8.7$ Hz, 2H, H_f), 6.93 (s, 1H, H_b), 7.14–7.30 (m, 13H, $H_{c,Ar}$), 8.01 (s, 1H, H_a); ^{13}C NMR (125 MHz, $CDCl_3$, 299 K): $\delta = 69.7$, 81.8, 116.3, 117.2, 126.3, 126.9, 127.9, 128.7, 130.6, 130.6, 137.2, 140.9, 148.7, 158.8.

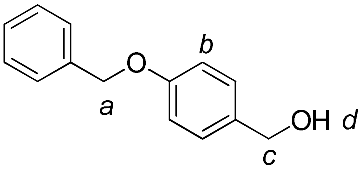
Acetophenone *O*-(((4-(benzhydryloxy)benzyl)oxy)carbonyl) oxime (6i)



Oxime Carbonate CDI Route: Prepared from (4-(benzhydryloxy)phenyl)methanol (0.363 g, 1.25 mmol), CDI (0.607 g, 3.75 mmol), acetophenone oxime (0.253 g, 1.87 mmol) and sodium hydride (0.009 g, 0.037 mmol) to give a colourless solid (0.240 g, yield = 42%). M.p. = 93 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 2.40$ (s, 3H, H_b), 5.26 (s, 2H, H_c), 6.30 (s, 1H, H_f), 7.04 (d, $J = 8.7$ Hz, 2H, H_e), 7.29–7.51 (m, 15H, $H_{d,Ar}$), 7.79 (d, $J = 7.9$ Hz, 2H, H_a); ^{13}C NMR (125

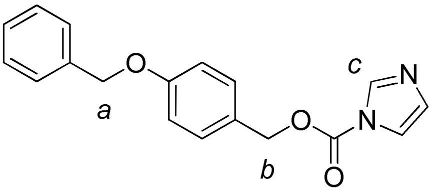
MHz, $CDCl_3$, 299 K): δ = 14.4, 70.1, 81.8, 116.2, 126.9, 127.1, 127.4, 127.9, 128.7, 128.7, 130.7 (× 2), 134.6, 141.1, 154.0, 158.6, 162.6; LR-ESIMS: *m/z* = 469 $[MNH_4]^+$; HR-ESIMS: *m/z* = 469.2112 (calcd. for $C_{29}H_{29}N_2O_4$, 469.2122).

4-(Benzyloxy)benzyl alcohol



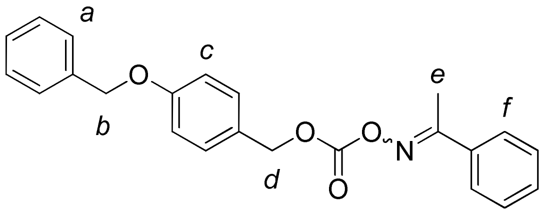
A suspension of 4-(hydroxymethyl)phenol (1.020 g, 8.22 mmol, 1.0 equiv.), benzyl bromide (1.46 cm^3, 12.3 mmol, 1.5 equiv.) and K_2CO_3 (5.50 g, 40 mmol, 5.0 equiv.) in THF (60 cm^3) was heated at reflux for 18 h. The solvent was removed under reduced pressure and the crude residue was redissolved in H_2O (200 cm^3) and extracted into CH_2Cl_2 (3 × 100 cm^3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by column chromatography (gradient elution, Pet Ether 40:60 to CH_2Cl_2) to yield the title compound as a colourless solid, 0.947 g, yield = 54%. ^1H NMR and ^{13}C NMR spectra were consistent with literature values.[2] ^1H NMR (300 MHz, $CDCl_3$, 294 K): δ = 1.60 (t, *J* = 5.5 Hz, 1H, H_d), 4.65 (d, *J* = 5.5 Hz, 2H, H_c), 5.10 (s, 2H, H_a), 6.99 (d, *J* = 7.8 Hz, 2H, H_b), 7.27–7.47 (m, 7H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 65.5, 70.5, 115.4, 127.9, 128.4, 129.0, 129.1, 133.8, 137.4, 158.8.

4-(Benzyloxy)benzyl 1*H*-imidazole-1-carboxylate (5h)



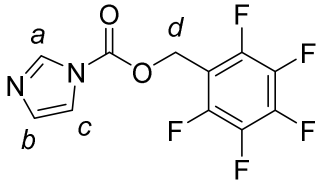
^1H NMR (300 MHz, $CDCl_3$, 294 K): δ = 5.09 (s, 2H, H_a), 5.35 (s, 2H, H_b), 6.99–7.05 (m, 3H, H_{Ar}), 7.33–7.45 (m, 8H, H_{Ar}), 8.13 (s, 1H, H_c); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 70.2, 70.5, 115.5, 117.6, 126.7, 127.9, 128.5, 129.1, 131.1, 131.2, 131.3, 137.0, 137.6, 159.9; LR-ESIMS: *m/z* = 331 [M*Na*]$^+$; HR-ESIMS: *m/z* = 331.1056 (calcd. for $C_{18}H_{16}N_2O_3Na$, 331.1053).

Acetophenone *O*-((4-(benzyloxy)benzyl)oxy)carbonyl oxime (6h)



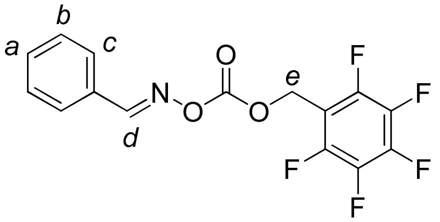
Oxime Carbonate CDI Route: Prepared from 4-(benzyloxy)benzyl alcohol (0.447 g, 2.087 mmol), CDI (1.014 g, 6.26 mmol), acetophenone oxime (0.418 g, 3.086 mmol) and sodium hydride (0.015 g, 0.061 mmol) to give a colourless solid, 0.630 g, yield = 81%. M.p = 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): $\delta = 2.37$ (s, 3H, H$_e$), 5.08 (s, 2H, H$_b$), 5.24 (s, 2H, H$_d$), 6.98 (d, *J* = 8.7 Hz, 2H, H$_c$), 7.30–7.44 (m, 10H, H$_{Ar}$), 7.74 (d, *J* = 1.4 Hz, 2H, H$_f$); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 14.4, 70.0, 70.1, 114.9, 127.0, 127.3, 127.5, 128.1, 128.6, 128.6, 130.6, 130.7, 134.6, 136.8, 154.0, 159.3, 162.6; LR-ESIMS: *m/z* = 393 [M*NH₄*]$^+$; HR-ESIMS: *m/z* = 393.1804 (calcd. for $C_{23}H_{25}N_2O_4$, 393.1804).

(Perfluorophenyl)methyl *1H*-imidazole-1-carboxylate



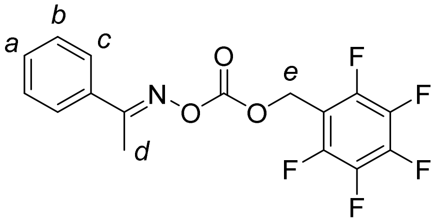
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 5.55 (s, 2H, H$_d$), 7.08 (s, 1H, H$_b$), 7.41 (s, 1H, H$_c$), 8.11 (s, 1H, H$_a$); ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 56.4, 117.1, 130.9 (× 2), 137.0, 137.7 (d, J_F = 255.8 Hz), 142.4 (d, J_F = 262.1 Hz)), 145.8 (d, J_F = 252.7 Hz*)*, 148.0.

(*E*)-Benzaldehyde *O*-(((perfluorophenyl)methoxy)carbonyl) oxime (7a)



Oxime Carbonate CDI Route: Prepared from pentafluorobenzyl alcohol (0.41 g, 2.06 mmol), CDI (1.00 g, 6.17 mmol), benzaldehyde oxime (0.355 g, 2.94 mmol) and sodium hydride (0.017 g, 0.62 mmol) to give a colourless solid, 0.16 g, yield = 22%. M.p. = 84°C; ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 5.33 (s, 2H, H_e), 7.36-7.38 (m, 3H, $H_{a,b}$), 7.64-7.66 (m, 2H, H_a), 8.36 (s, 1H, H_d); ^{19}F NMR (376 MHz, $CDCl_3$, 294 K): δ = -141.6 (m, 2F), -151.9 (m, 1F), -161.7 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 69.6, 115.7 (d, *J* = 22 Hz), 128.4, 128.9, 129.7, 130.6 (d, *J* = 3 Hz), 130.8 (d, *J* = 9 Hz), 131.8, 153.7, 156.0, 163.1 (d, *J* = 245 Hz); LRESI-MS: 274 $[MH]^+$; HRESI-MS: 274.0877 $[MH]^+$ (calcd. for $C_{15}H_{13}FNO_3$, 274.0874).

(*E*)-Acetophenone O-(((perfluorophenyl)methoxy)carbonyl) oxime (7b)



Oxime Carbonate CDI Route: Prepared from pentafluorobenzyl alcohol (0.41 g, 2.06 mmol), CDI (1.00 g, 6.17 mmol), acetophenone oxime (0.334 g, 2.47 mmol) and sodium hydride (0.015 g, 0.62 mmol) to give a colourless solid, 0.20 g, yield = 27%. M.p. 89 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 2.41(s, 3H, H_d), 5.42 (s, 2H, H_e), 7.31-7.67 (m, 3H, $H_{a,b}$), 7.71-7.85 (m, 2H, H_c); ^{19}F NMR (376 MHz, $CDCl_3$, 295 K): δ = -161.77 (m, 2F), -152.07 (m, 1F), -141.60 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 14.3, 57.0, 127.0, 128.7, 130.9, 134.2, 153.4, 163.4; LRESI-MS: *m/z* = 360 $[MH]^+$; HRESI-MS: *m/z* = 360.0650 $[MH]^+$ (calcd. for $C_{16}H_{10}F_5NO_3$, 360.0659).

UV Photolyses of Oxime Carbonates

A solution of oxime carbonate **6h** (0.050 g, 0.133 mmol) and 4-methoxyacetophenone (0.050 g, 0.333 mmol) in $PhCF_3$ (2 cm^3) was irradiated for 5 h at rt. ^1H NMR product analysis (w.r.t. MAP) revealed no identifiable products or by-products.

A solution of oxime carbonate **6h** (0.057 g, 0.152 mmol) and 4-methoxyacetophenone (0.057 g, 0.379 mmol) in $PhCH_3$ (2 cm^3) was irradiated for 5 h at rt. ^1H NMR product analysis (w.r.t. MAP) revealed no identifiable products or by-products.

A solution of oxime carbonate **6g** (0.057 g, 0.157 mmol) and 4-methoxyacetophenone (0.057 g, 0.379 mmol) in $PhCF_3$ (2 cm^3) was irradiated for 3 h at rt. ^1H NMR product analysis (w.r.t. MAP) revealed no identifiable products or by-products.

A solution of oxime carbonate **6i** (0.054 g, 0.120 mmol) and 4-methoxyacetophenone (0.054 g, 0.360 mmol) in $PhCF_3$ (2 cm^3) was irradiated for 3 h at rt. ^1H NMR product analysis (w.r.t. MAP) revealed no identifiable products or by-products.

X-Ray Crystallographic Data

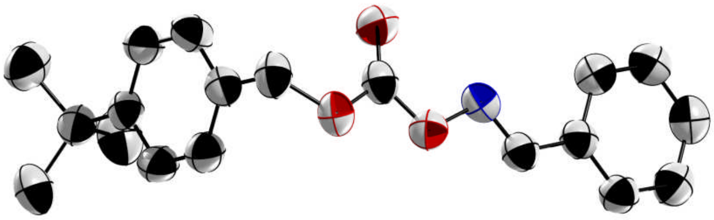


Figure S1. The crystal structure of **6d**.

Table S1. Crystal data and structural refinement for **6d**.

Identification Code	**6d**
CCDC Code	923531
Empirical Formula	$C_{19}H_{21}NO_3$
Formula Weight	311.38
Crystal Colour, Habit	colourless, prism
Crystal Dimensions	0.120 × 0.030 × 0.030 mm
Crystal System	triclinic
Lattice Type	Primitive

Lattice Parameters	a = 6.229(3) Å	α = 88.61(4)°
	b = 11.758(7) Å	β = 77.64(6)°
	c = 12.009(7) Å	γ = 83.80(4)°
Volume	854.1(8) $Å^3$	
Space Group	P-1 (#2)	
Z Value	2	
Density (calculated)	1.211 g/cm^3	
F(000)	332.00	
μ(CuKα)	6.585 cm^{-1}	
Diffractometer	Saturn70	
Radiation	CuKα (λ = 1.54187 Å)	
Take-off Angle	2.8°	
Detector Aperture	2.0 - 2.5 mm horizontal 2.0 mm vertical	
Crystal to Detector Distance	21 mm	
Voltage, Current	40 kV, 20 mA	
Temperature	-100.0 °C	
Scan Type	ω-2θ	
$2\theta_{max}$	135.9°	
No. of Reflections Measured	Total: 8939, Unique: 3049 (R_{int} = 0.1235)	
Corrections	Lorentz-polarization Secondary Extinction (coefficient: 2.77200e-002)	
Structure Solution	Direct Methods	
Refinement	Full-matrix least-squares on F^2	
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$	
Least Squares Weights	w = 1/ [σ^2 (Fo^2) + $(0.1263 \cdot P)^2$ + 0.0000 · P] where P = (Max(Fo^2,0) + $2Fc^2$)/3	
$2\theta_{max}$ cutoff	135.9°	
Anomalous Dispersion	All non-hydrogen atoms	
No. Observations (All reflections)	3049	
No. Variables	209	
Reflection/Parameter Ratio	14.59	
Residuals: R1 (I>2.00σ(I))	0.0752	
Residuals: R (All reflections)	0.0964	
Residuals: wR^2 (All reflections)	0.2094	
Goodness of Fit Indicator	0.899	
Max Shift/Error in Final Cycle	0.000	
Maximum peak in Final Diff. Map	0.28 e/$Å^3$	
Minimum peak in Final Diff. Map	-0.31 e/$Å^3$	

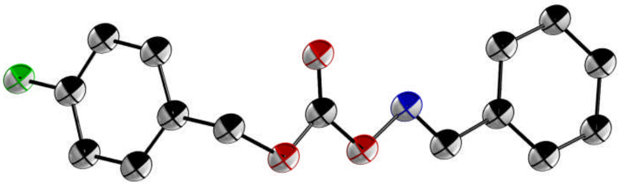


Figure S2. The crystal structure of **6f**.

Table S2. Crystal data and structural refinement for **6f**.

Identification Code	**6f**	
CCDC Code	923532	
Empirical Formula	$C_{15}H_{12}FNO_3$	
Formula Weight	273.26	
Crystal Colour, Habit	colourless, prism	
Crystal Dimensions	0.240 × 0.100 × 0.020 mm	
Crystal System	monoclinic	
Lattice Type	Primitive	
Lattice Parameters	a = 14.698(2) Å	β = 97.309(4)°
	b = 4.5311(5) Å	
	c = 19.448(3) Å	
Volume	1284.7(3) $Å^3$	
Space Group	P21/n (#14)	
Z Value	4	
Density (calculated)	1.413 g/cm^3	
F(000)	568.00	
μ(CuKα)	9.169 cm^{-1}	
Diffractometer	Saturn70	
Radiation	CuKα (λ = 1.54187 Å)	
Voltage, Current	40 kV, 20 mA	
Temperature	-100.0 °C	
Detector Aperture	70 × 70 mm	
ω oscillation Range	1.0 - 0.0°	
Pixel Size	0.034 mm	
$2\theta_{max}$	136.3°	
No. of Reflections Measured	Total: 15766, Unique: 2261 (R_{int} = 0.0465)	
Corrections	Lorentz-polarization	
Structure Solution	Direct Methods	
Refinement	Full-matrix least-squares on F^2	
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$	
Least Squares Weights	w = 1/ [$\sigma2(Fo^2) + (0.1764 . P)^2$ + 10.2369 . P] where P = $(Max(Fo^2,0) + 2Fc^2)/3$	
$2\theta_{max}$ cutoff	136.3°	
Anomalous Dispersion	All non-hydrogen atoms	
No. Observations (All reflections)	2261	
No. Variables	181	
Reflection/Parameter Ratio	12.49	
Residuals: R1 (I>2.00σ(I))	0.1206	
Residuals: R (All reflections)	0.1361	
Residuals: wR^2 (All reflections)	0.3223	
Goodness of Fit Indicator	0.924	
Max Shift/Error in Final Cycle	0.000	
Maximum peak in Final Diff. Map	0.78 $e/Å^3$	
Minimum peak in Final Diff. Map	-1.18 $e/Å^3$	

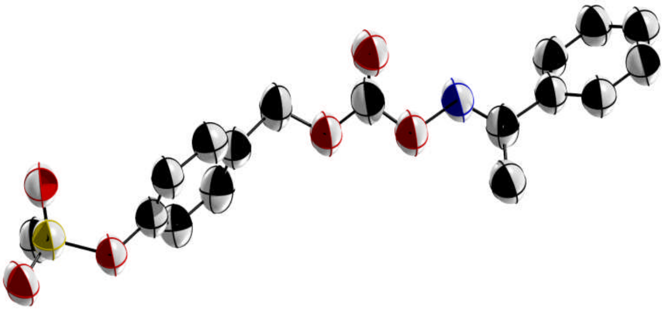


Figure S3. The crystal structure of **6g**.

Table S3. Crystal data and structural refinement for **6g**.

Identification Code	**6g**
CCDC Code	923533
Empirical Formula	$C_{17}H_{17}NO_6S$
Formula Weight	363.38
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions	0.100 × 0.100 × 0.010 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 5.707(7) Å α = 98.61(6)° b = 7.877(11) Å β = 91.40(8)° c = 18.99(3) Å γ = 91.03(3)°
Volume	843(2) $Å^3$
Space Group	P-1 (#2)
Z Value	2
Density (calculated)	1.431 g/cm^3
F(000)	380.00
μ(CuKα)	20.189 cm^{-1}
Diffractometer	Saturn70
Radiation	CuKα (λ = 1.54187 Å)
Voltage, Current	40 kV, 20 mA
Temperature	-100.0 °C
Detector Aperture	70 × 70 mm
Pixel Size	0.034 mm
$2\theta_{max}$	136.5°
No. of Reflections Measured	Total: 11643, Unique: 2905 (R_{int} = 0.1733)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.371 - 0.980) Secondary Extinction (coefficient: 4.59600e-002)
Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2) + (0.2000 \cdot P)^2$

	+ 0.0000 · P]
	where P = (Max(Fo^2,0) + $2Fc^2$)/3
$2\theta_{max}$ cutoff	136.5°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2905
No. Variables	227
Reflection/Parameter Ratio	12.80
Residuals: R1 (I>2.00σ(I))	0.1261
Residuals: R (All reflections)	0.1731
Residuals: wR^2 (All reflections)	0.4028
Goodness of Fit Indicator	1.233
Max Shift/Error in Final Cycle	0.034
Maximum peak in Final Diff. Map	0.56 e/$Å^3$
Minimum peak in Final Diff. Map	-0.41 e/$Å^3$

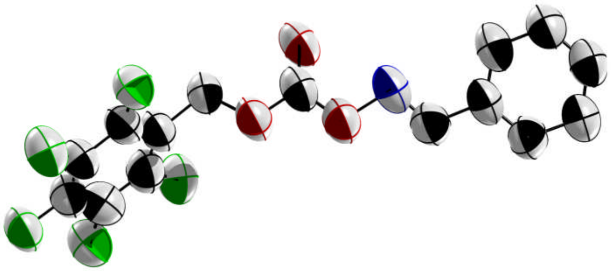


Figure S4. The crystal structure of **7a**.

Table S4. Crystal data and structural refinement for **7a**.

Identification Code	**7a**	
CCDC Code	923534	
Empirical Formula	$C_{15}H_8F_5NO_3$	
Formula Weight	345.23	
Crystal Colour, Habit	colourless, platelet	
Crystal Dimensions	0.120 × 0.030 × 0.010 mm	
Crystal System	monoclinic	
Lattice Type	Primitive	
Lattice Parameters	a = 7.89(3) Å	β = 102.65(7)°
	b = 5.60(2) Å	
	c = 16.51(6) Å	
Volume	712(5) $Å^3$	
Space Group	$P2_1$ (#4)	
Z Value	2	
Density (calculation)	1.611 g/cm^3	
F(000)	348.00	
μ(CuKα)	13.875 cm^{-1}	
Diffractometer	Saturn70	
Radiation	CuKα (λ = 1.54187 Å)	
Take-off Angle	2.8°	
Detector Aperture	2.0 - 2.5 mm horizontal	

	2.0 mm vertical
Crystal to Detector Distance	21 mm
Voltage, Current	40 kV, 20 mA
Temperature	-100.0 °C
Scan Type	ω-2θ
2θ_{max}	137.0°
No. of Reflections Measured	Total: 7300, Unique: 2479 (R_{int} = 0.1756) Friedel pairs: 1029
Corrections	Lorentz-polarization Secondary Extinction (coefficient: 1.24810e-001)
Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 – Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + $(0.2000 \cdot P)^2$ + 0.0000 · P] where P = (Max(Fo^2,0) + $2Fc^2$)/3
2θ_{max} cutoff	137.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2479
No. Variables	218
Reflection/Parameter Ratio	11.37
Residuals: R1 (I>2.00σ(I))	0.1561
Residuals: R (All reflections)	0.1971
Residuals: wR^2 (All reflections)	0.4300
Goodness of Fit Indicator	1.078
Flack Parameter	-0.2(9)
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map	0.57 e/Å^3
Minimum peak in Final Diff. Map	-0.42 e/Å^3

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 carbonate (2 to 15 mg) and MAP (1 equiv. wt/wt) in *tert*-butylbenzene or benzene (0.5 cm^3) were prepared and sonicated if necessary. An aliquot (0.2 cm^3), 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.

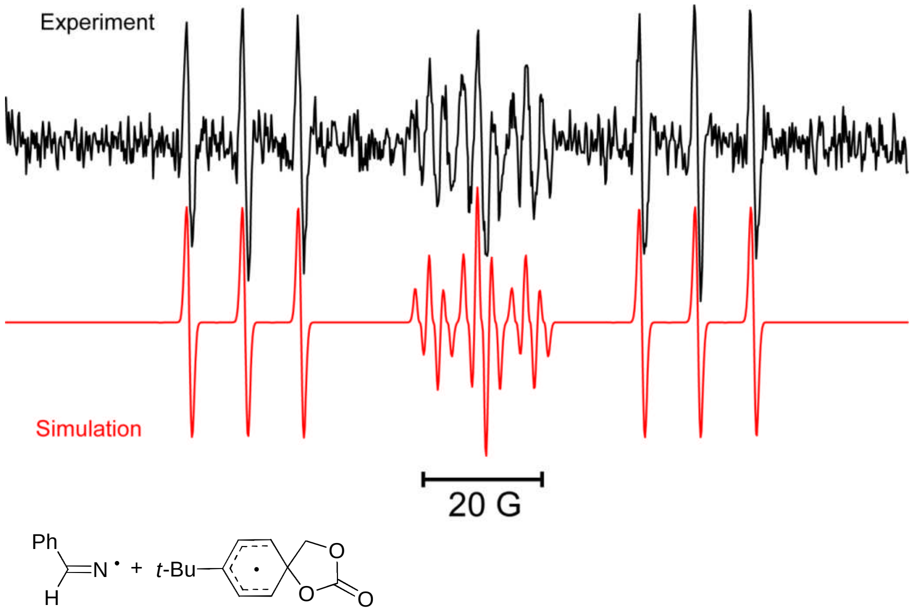


Figure S5. EPR spectrum obtained during UV photolysis of 4-*t*-butylbenzyloxy oxime carbonate **6d** in *t*-BuPh at 215 K.

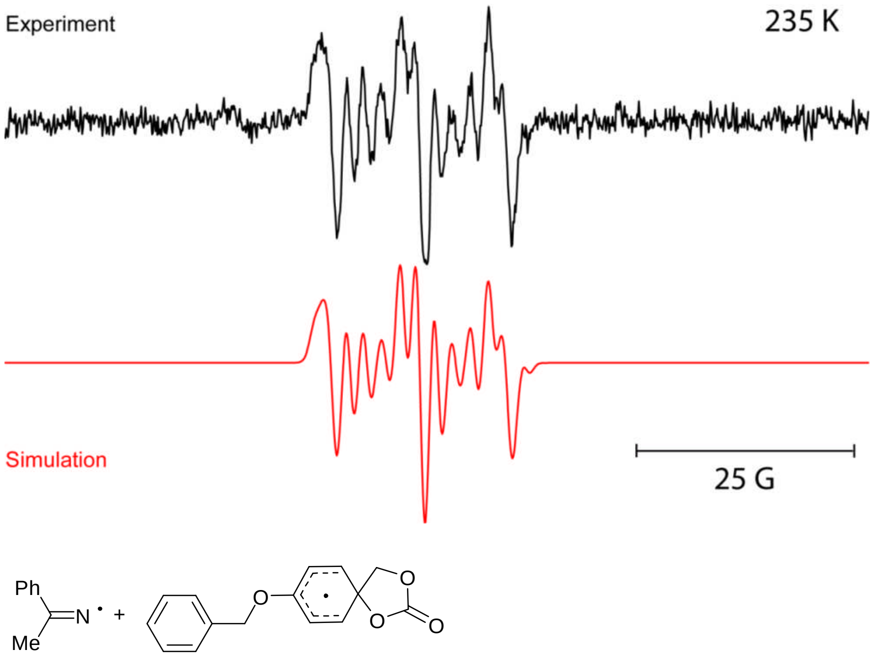


Figure S6. EPR spectrum obtained during UV photolysis of acetophenone *O*-((4-(benzyloxy)benzyl)oxy)carbonyl oxime **6h** in *t*-BuPh at 235 K.

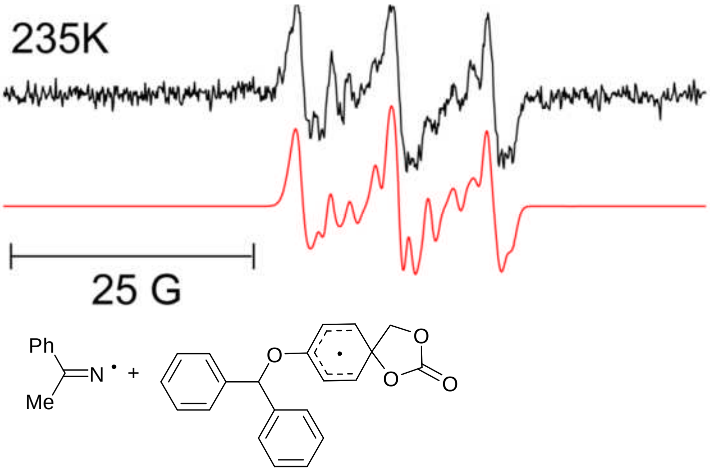


Figure S7. EPR spectrum obtained during UV photolysis of acetophenone *O*-(((4-(benzhydryloxy)benzyl)oxy)carbonyl) oxime **6i** in *t*-BuPh at 235 K.

Derivation of Kinetic Equations (1 & 2) for Cyclization of Benzyloxycarbonyloxyl radicals.

For a general benzyloxycarbonyloxyl radical, let BnOC(O)O$^{\bullet}$ be BO, the iminyl radical, Im, and the spirocyclized radical SP.

In the temperature region before the onset of decarboxylation the mechanism may be represented by:

BO–IM / UV → BO + Im	
BO → SP	k_c (forwards)
SP → BO	k_{-c} (backwards)
Im + Im → non-radical products	
Im + BO → non-radical products	
Im + SP → non-radical products	
BO + BO → non-radical products	
BO + SP → non-radical products	
SP + SP → 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:

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

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

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

$$[Im] = [BO] + [SP]$$

On substituting: $k_c/2k_t = [SP]/[BO] \times \{k_{-c}/2k_t + 2[Im]\}$ (1)

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

$k_c/2k_t = 2[SP][Im]/[BO]$ (2) or

$k_c/2k_t = 2[SP][Im]/\{[Im] - [SP]\}$ (3)

Table S5. Kinetic EPR of 4-FBnOC(O)ON=CHPh **6f** + MAP on hv in cyclopropane

T/ K	Gain	d.i. Im	[Sp]/ [Im]	d.i. Spiro	[Im]/ M	[Spiro]	Im-Spiro	$k_{sp}/2kt$	log2kt (nC7)	$10^3/T$	log η n-C7	log η c-C3H6	log2kt c-C3H6	log k_{sp}	k_{sp}
180	1.00	0.39	0.75	–	4.940E-11	3.705E-11	1.235E-11	2.964E-10	8.895	5.556	0.51	-0.63	10.042	0.514	3.264
190	1.00	0.42	0.84	–	5.616E-11	4.717E-11	8.985E-12	5.897E-10	9.039	5.263	0.39	-0.67	10.099	0.870	7.405
200	1.00	0.38	0.96	–	5.348E-11	5.134E-11	2.139E-12	2.567E-09	9.168	5.000	0.28	-0.70	10.150	1.560	36.292
215	1.00	0.38	1	–	5.749E-11	5.749E-11	0.000E+00	#DIV/0!	9.340	4.651	0.13	-0.74	10.218	#DIV/0!	#DIV/0!

kc/2kt = 2[Sp][Im]/{[Im] -[Sp]}

[DPPH]	1.00E-03
Gain DPPH	1.00E+00
Doub. Int DPPH	4.90E+06
temp DPPH	290
F[c]	1
F[a]	1

-1.871	1.084E+01
4.044E-01	2.134E+00

Table S6. Estimate of Kinetic EPR of 2,3,4,5,6-pentaF-BnOC(O)ON=CHPh (7a): hv in t-BuPh + MAP

Dial Temp	**Actual T K**	**scans**		**Gain**	**[Sp]/[Im]**	**D Int Im**	**[Spiro] M**	**[Im] M**	**Im-Spiro M**	**ksp/2kt**	**logksp/2kt**	**log2kt n-C7**	**10^3/T**	**log η n-C7**	**log η t-BuPh**	**log2kt BuPh**	**log ksp t-BuPh**	**ksp s-1**
235	236.02	20.00		2.0E+06	0.2	4.7	5.65E-10	2.82E-09	2.26E-09	1.41E-09	-8.850	9.54	4.24	-0.04	0.58	8.92	7.15E-02	1.18E+00
													0.000				1.05E+01	

Table S7. Kinetic EPR of BnOC(O)ON=CHPh **6a** on photolysis with + MAP in cyclopropane

Temp K	**Gain**	**d.i.** Im	**No** scans	**[Sp]/[Im]**	**d.i./scans** Im	**[Im]**	**[Spiro]**	**[Box]** Im-Spiro	**k_{sc}/2kt**	**log2kt** (nC7)	**10^3/T**	**log η** n-C7	**log η** c-C3H6	**log2kt** c-C3H6	**log ksc**	**ksc**	logksc visc uncorr
160	2.00E+06	20.8	11	0.54	1.89	7.903E-09	4.268E-09	3.636E-09	1.856E-08	8.553	6.250	0.81	-0.55	9.906	2.175	149.509	0.82
170	2.00E+06	17.3	10	0.67	1.73	7.683E-09	5.148E-09	2.535E-09	3.120E-08	8.734	5.882	0.65	-0.59	9.978	2.472	296.559	1.23
180	2.00E+06	13.5	10	0.81	1.35	6.348E-09	5.142E-09	1.206E-09	5.412E-08	8.895	5.556	0.51	-0.63	10.042	2.775	595.972	1.63
190	2.00E+06	16.4	10	0.93	1.64	8.140E-09	7.570E-09	5.698E-10	2.163E-07	9.039	5.263	0.39	-0.67	10.099	3.434	2716.344	2.37
													-1.52	10.25			
													0.23	1.32			

BnOCOO [Sp]/[Im] data from EPRs in cyclopropane

160	0.54
170	0.67
180	0.81
190	0.93
200	0.92
210	0.91
220	0.89
230	0.8

DFT Optimised Structures [3]

Optimised coordinates for 1,3-dioxaspiro[4.5]decadien-2-onyl 9a

UB3LYP/6-311+G(2d,p)
E = -534.85114998 AU

```
Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -2.285294    1.225399   -0.156791
      2          6           0       -0.939883    1.245963    0.039998
      3          6           0       -0.946564   -1.248056    0.027609
      4          6           0       -2.291849   -1.218212   -0.169011
      5          6           0       -2.991255    0.005961   -0.260088
      6          1           0       -2.826064    2.160798   -0.241240
      7          1           0       -0.397744    2.182699    0.102251
      8          1           0       -0.409456   -2.188247    0.080335
      9          1           0       -2.837626   -2.149795   -0.262875
     10          1           0       -4.061248    0.009631   -0.421204
     11          6           0       -0.130103   -0.003935    0.164766
     12          6           0        0.767767   -0.012426    1.445267
     13          1           0        0.610346   -0.909114    2.044324
     14          1           0        0.602546    0.871053    2.061447
     15          8           0        2.115351   -0.001831    0.974152
     16          6           0        2.150319    0.002310   -0.383509
     17          8           0        3.149879    0.008258   -1.028769
     18          8           0        0.899822   -0.001308   -0.896944
```

Optimised coordinates for 1,3-dioxaspiro[4.5]decadien-2-onyl 9a

UB3LYP/cc-pvtz
E = -534.88203281AU

```
Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0       -2.135140    1.337436    0.058358
      2          6           0       -0.797341    1.180241    0.237230
      3          6           0       -1.074449   -1.263099   -0.175018
      4          6           0       -2.407401   -1.055548   -0.342205
      5          6           0       -2.968800    0.234628   -0.228154
      6          1           0       -2.570273    2.325422    0.132942
      7          1           0       -0.159119    2.028674    0.448833
      8          1           0       -0.643507   -2.249460   -0.284513
      9          1           0       -3.050769   -1.893965   -0.574749
     10          1           0       -4.029740    0.379085   -0.371796
     11          6           0       -0.130681   -0.155235    0.144791
     12          6           0        0.771561   -0.458075    1.372669
     13          1           0        0.799969   -1.526916    1.590489
     14          1           0        0.465911    0.089352    2.260226
     15          8           0        2.072814   -0.021026    0.982397
     16          6           0        2.133044    0.079858   -0.373310
     17          8           0        3.127424    0.293355   -0.988377
     18          8           0        0.905108   -0.091508   -0.914970
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Optimised coordinates for 4-F-1,3-dioxaspiro[4.5]decadien-2-onyl 9f

UB3LYP/6-311+G(2d,p)
E = -634.12236852 AU

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Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0        1.777072   -1.229985    0.273249
      2          6           0        0.433567   -1.090524    0.424615
      3          6           0        0.644115    1.318983   -0.202567
```

4	6	0	1.985910	1.144062	-0.342136
5	6	0	2.548918	-0.119659	-0.106166
6	1	0	2.268842	-2.180242	0.440132
7	1	0	-0.179535	-1.936699	0.711717
8	1	0	0.189695	2.282713	-0.396597
9	1	0	2.632988	1.961561	-0.634672
10	6	0	-0.272851	0.206991	0.182285
11	6	0	-1.247273	0.584992	1.329124
12	1	0	-1.327272	1.668220	1.444197
13	1	0	-0.970523	0.133124	2.279397
14	8	0	-2.512623	0.061518	0.920598
15	6	0	-2.499246	-0.169251	-0.420914
16	8	0	-3.452263	-0.482717	-1.058931
17	8	0	-1.251782	0.002116	-0.919736
18	9	0	3.877543	-0.272184	-0.244951

Optimised coordinates for 4-F1,3-dioxaspiro[4.5]decadien-2-onyl 9f

UB3LYP/cc-pvtz

E = -634.156720611 AU

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.778046	-1.230192	0.264381
2	6	0	0.435181	-1.093389	0.416144
3	6	0	0.643164	1.318211	-0.194040
4	6	0	1.984282	1.145629	-0.334114
5	6	0	2.550719	-0.118031	-0.107258
6	1	0	2.269772	-2.179595	0.425338
7	1	0	-0.176389	-1.939998	0.698858
8	1	0	0.187737	2.280759	-0.382016
9	1	0	2.629217	1.964692	-0.620761
10	6	0	-0.273020	0.203928	0.182861
11	6	0	-1.247099	0.571973	1.333231
12	1	0	-1.323480	1.653419	1.457473
13	1	0	-0.968073	0.114164	2.278593
14	8	0	-2.510716	0.052790	0.921398
15	6	0	-2.499752	-0.165371	-0.421863
16	8	0	-3.453442	-0.469931	-1.061783
17	8	0	-1.252146	0.007336	-0.918292
18	9	0	3.875836	-0.267950	-0.247126

Optimised coordinates for 4-BnO-1,3-dioxaspiro[4.5]decadien-2-onyl 9h

UB3LYP/6-311+G(2d,p)

E = -880.529939407 AU

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.250448	1.014080	-0.566347
2	6	0	-0.899009	0.991572	-0.541758
3	6	0	-0.997506	-0.821228	1.150854
4	6	0	-2.361491	-0.773821	1.099864
5	6	0	-3.019286	0.131287	0.241599
6	1	0	-2.784251	1.711729	-1.200427
7	1	0	-0.327014	1.670737	-1.163681
8	1	0	-0.501851	-1.526000	1.807522
9	1	0	-2.929724	-1.439789	1.734843
10	6	0	-0.126843	0.027053	0.296260
11	6	0	1.049216	0.681465	1.061484
12	1	0	1.236259	0.176542	2.012050
13	1	0	0.892881	1.744370	1.234647
14	8	0	2.187725	0.517005	0.212129
15	6	0	1.939678	-0.468444	-0.695314
16	8	0	2.755235	-0.905785	-1.444840
17	8	0	0.652439	-0.867774	-0.625955
18	8	0	-4.360272	0.256287	0.118531
19	6	0	-5.218295	-0.617393	0.880343

```
     20          1           0       -5.027219   -0.465352    1.946456
     21          1           0       -4.983055   -1.654660    0.625096
     22          6           0       -6.645004   -0.292498    0.543544
     23          6           0       -7.363110    0.621644    1.313804
     24          6           0       -7.265337   -0.890851   -0.553426
     25          6           0       -8.678783    0.936702    0.992585
     26          1           0       -6.889050    1.090412    2.169255
     27          6           0       -8.579879   -0.577191   -0.878039
     28          1           0       -6.715088   -1.604032   -1.157303
     29          6           0       -9.288483    0.337616   -0.104896
     30          1           0       -9.227822    1.647013    1.599039
     31          1           0       -9.052505   -1.048128   -1.731626
     32          1           0      -10.314394    0.579964   -0.355333
```

Optimised coordinates for 4-Ph2CHO-1,3-dioxaspiro[4.5]decadien-2-onyl 9i

UB3LYP/6-311+G(2d,p)

E = -1111.64089538   AU

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Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      2          6           0        2.512212    0.525985   -0.593458
      3          6           0        2.763744   -0.845333    1.458655
      4          6           0        1.416161   -0.968043    1.511382
      5          6           0        0.579699   -0.379863    0.526443
      6          1           0        0.535029    0.884063   -1.238062
      7          1           0        2.947381    1.120330   -1.388662
      8          1           0        3.388384   -1.312443    2.210731
      9          1           0        0.941263   -1.525505    2.309838
     10          6           0        3.458080   -0.126456    0.356121
     11          6           0        4.588985    0.817625    0.841022
     12          1           0        4.854739    0.621953    1.882074
     13          1           0        4.329560    1.868044    0.721844
     14          8           0        5.715387    0.527308    0.009679
     15          6           0        5.520000   -0.653789   -0.638673
     16          8           0        6.343205   -1.186227   -1.315255
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     19          6           0       -1.684606   -0.200060   -0.333710
     20          1           0       -1.225551   -0.399472   -1.305734
     21          6           0       -2.882744   -1.121500   -0.196525
     22          6           0       -3.008002   -2.210528   -1.057957
     23          6           0       -3.847747   -0.925008    0.791626
     24          6           0       -4.077864   -3.091395   -0.937671
     25          1           0       -2.261067   -2.374686   -1.827145
     26          6           0       -4.912744   -1.808414    0.919087
     27          1           0       -3.770905   -0.076067    1.459723
     28          6           0       -5.031782   -2.892332    0.053681
     29          1           0       -4.163928   -3.931621   -1.616178
     30          1           0       -5.655507   -1.647204    1.691319
     31          1           0       -5.866635   -3.576084    0.150625
     32          6           0       -2.025534    1.278113   -0.246851
     33          6           0       -2.547966    1.918645   -1.371923
     34          6           0       -1.854770    2.007486    0.927919
     35          6           0       -2.899543    3.261774   -1.322484
     36          1           0       -2.684421    1.361756   -2.293104
     37          6           0       -2.206139    3.353876    0.977808
     38          1           0       -1.437985    1.524045    1.802239
     39          6           0       -2.730302    3.984169   -0.144635
     40          1           0       -3.302429    3.745691   -2.204219
     41          1           0       -2.066083    3.910511    1.896895
     42          1           0       -3.001033    5.032377   -0.105130
```

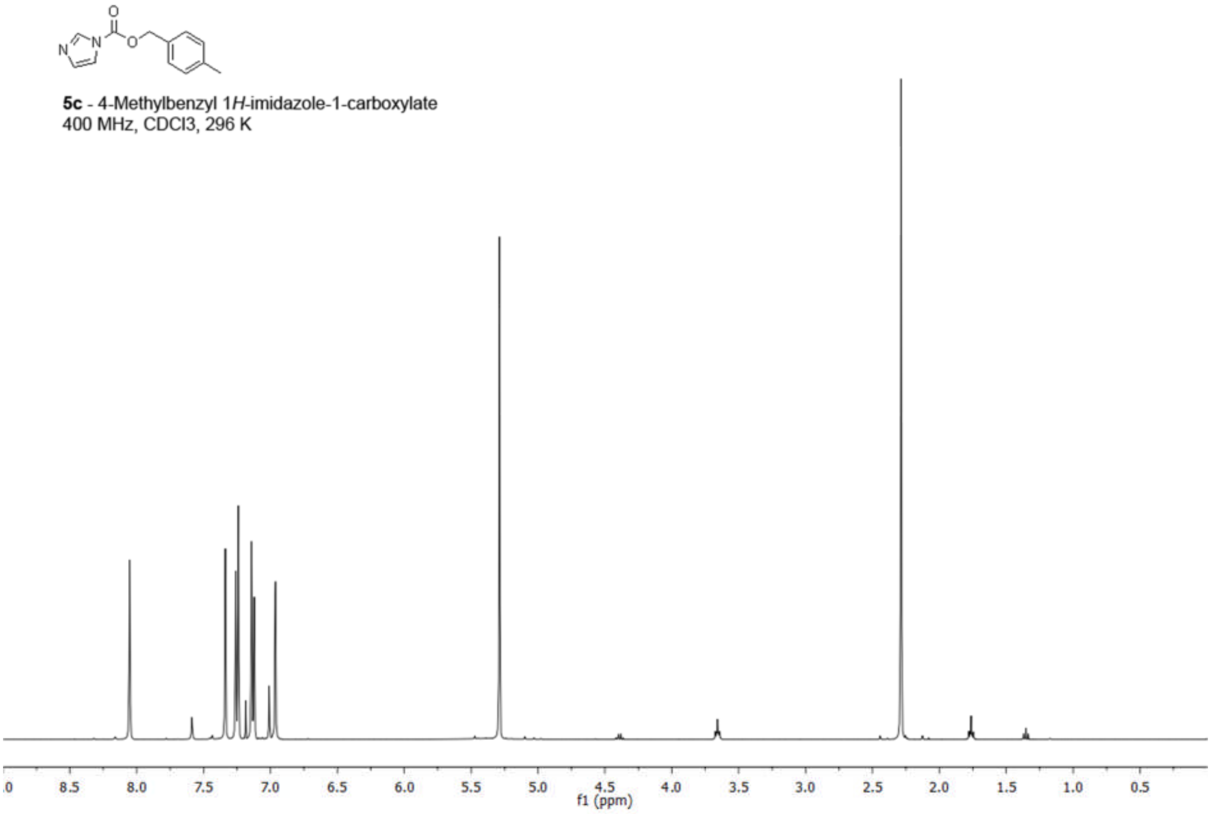
Computational results for cyclization of benzyloxycarbonyloxyl and substituted analogs ArCH$_2$OC(O)O$^\bullet$ in *spiro*- (5-*exo*) and *ortho*- (6-*endo*) modes.

	$PhCH_2OC(O)O$				$4\text{-}FC_6H_4CH_2OC(O)O$				$C_6F_5CH_2OC(O)O$			
Method//opt. geom.	*Spiro*		*Ortho*		*Spiro*		*Ortho*		*Spiro*		*Ortho*	
	$\Delta E^{\ddagger}_{298}$	ΔH_{298}	$\Delta E^{\ddagger}_{298}$	ΔH_{298}	$\Delta E^{\ddagger}_{29}$	ΔH_{29}	$\Delta E^{\ddagger}_{29}$	ΔH_{29}	$\Delta E^{\ddagger}_{298}$	ΔH_{298}	$\Delta E^{\ddagger}_{298}$	ΔH_{298}
UB3PW91/6-311+G(2d,p)// UB3PW91/6-311+G(2d,p)	9.13	-7.38	15.10	6.95	3.91	-3.58	11.07	2.99	6.21	-2.74	12.51	-4.97
UB3LYP/6-31+G(d)// UB3LYP/6-31+G(d)	5.50	-0.82	11.82	5.08								
UB3LYP/6-311+G(2d,p)// UB3LYP/6-311+G(2d,p)	5.89	-0.45	12.01	5.74	5.38	0.38	12.65	6.35	7.70	0.59	13.72	-2.13
UB3LYP/cc-pVTZ// UB3LYP/cc-pVTZ//	6.35	-0.03	12.35	5.74	5.83	0.16	13.02	6.45	7.74	0.72	13.58	-2.25
M062X/6-311+G(2d,p)// UB3LYP/6-311+G(2d,p)	2.93	-8.85	8.93	-3.60	2.20	-8.70	9.74	-2.19	5.01	-8.95	12.0	-11.46
MP2/6-311+G(2d,p)// UB3LYP/6-311+G(2d,p)	18.16	0.10	23.08	7.30	17.45	0.42	24.44	7.99	24.96	1.64	33.10	-1.17

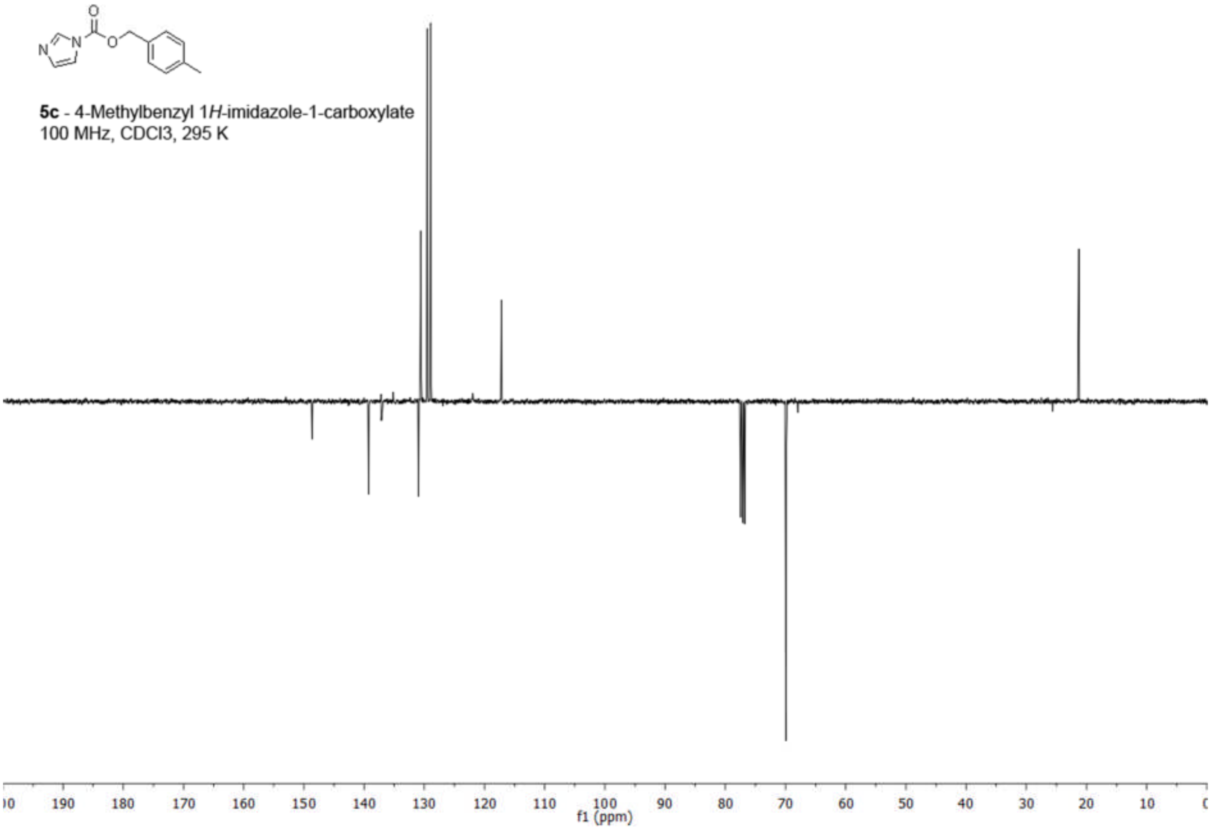
References

1. (*a*) R. T. McBurney, A. M. Z. Slawin, L. A. Smart, Y. Yu and J. C. Walton, *Chem. Commun.*, 2011, **47**, 7974; (*b*) R. T. McBurney, A. D. Harper, A. M. Z. Slawin and J. C. Walton, *Chem. Sci.*, 2012, **3**, 3436.
2. W. Kurosawa, T. Kan and T. Fukuyama, *J. Am. Chem. Soc.*, 2003, **125**, 8112.
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.

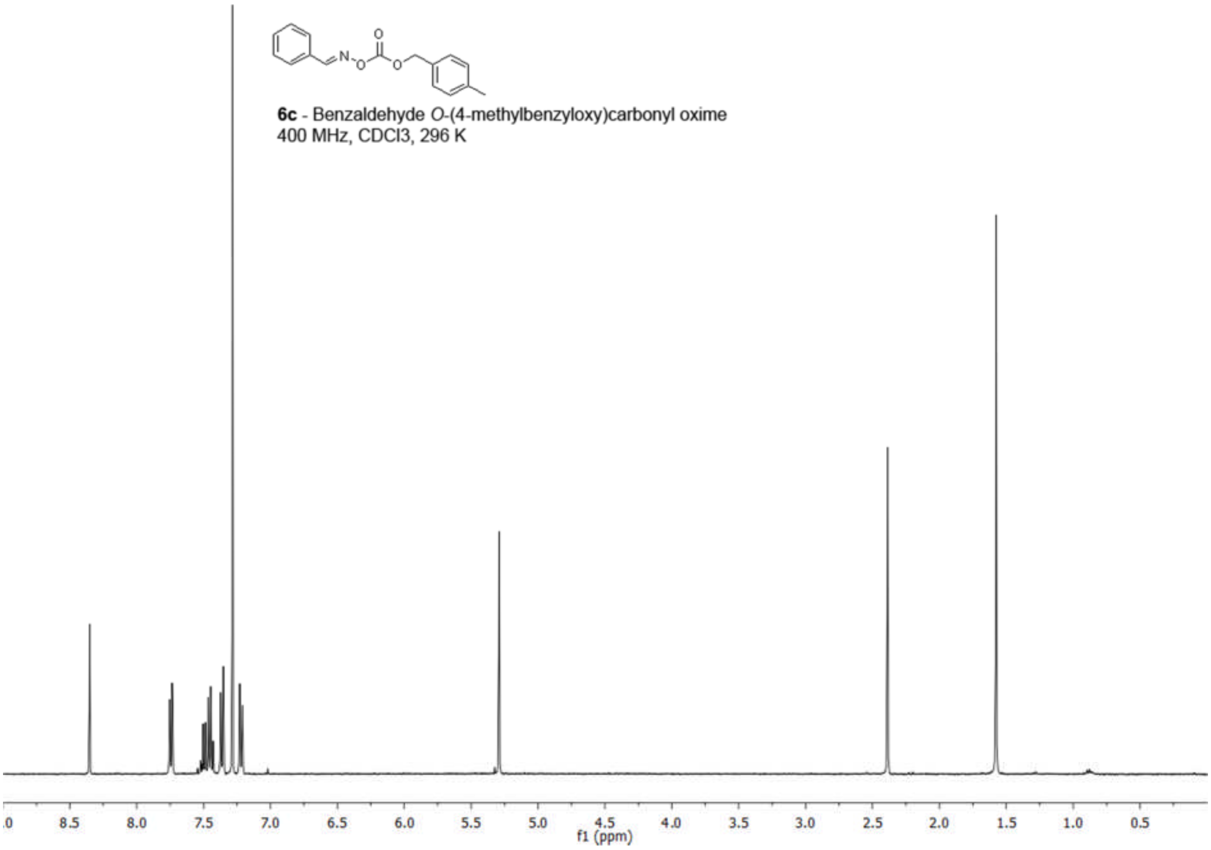
^{1}H and ^{13}C NMR Spectra of Novel Compounds



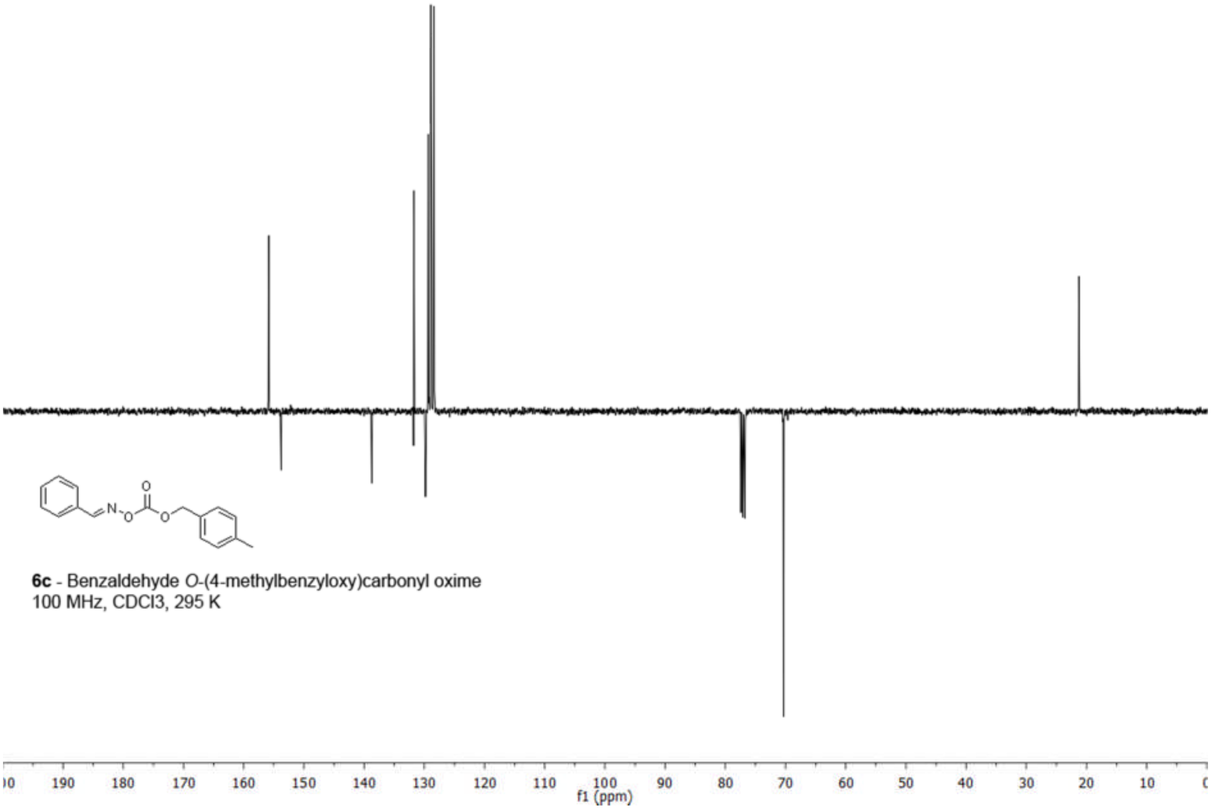
5c - 4-Methylbenzyl 1*H*-imidazole-1-carboxylate
400 MHz, CDCl3, 296 K



5c - 4-Methylbenzyl 1*H*-imidazole-1-carboxylate
100 MHz, CDCl3, 295 K



6c - Benzaldehyde *O*-(4-methylbenzyloxy)carbonyl oxime
400 MHz, CDCl3, 296 K



6c - Benzaldehyde *O*-(4-methylbenzyloxy)carbonyl oxime
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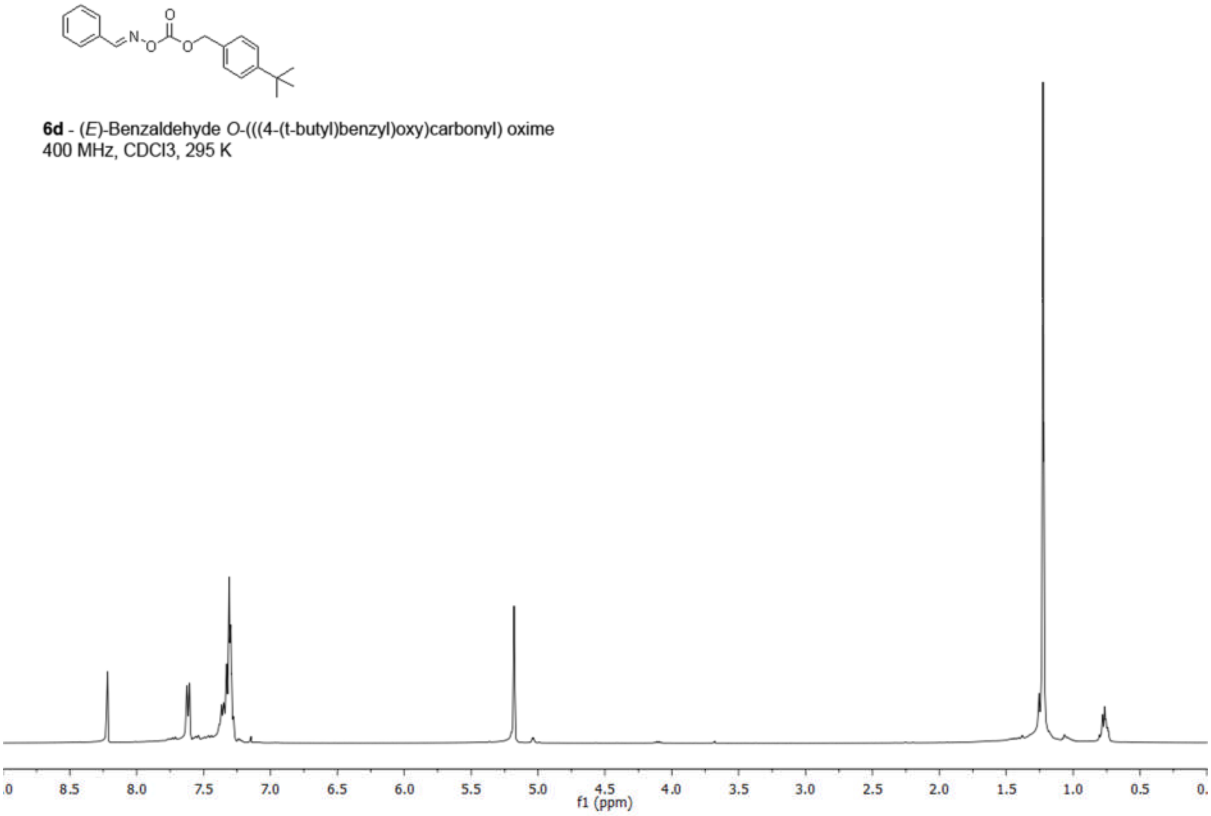
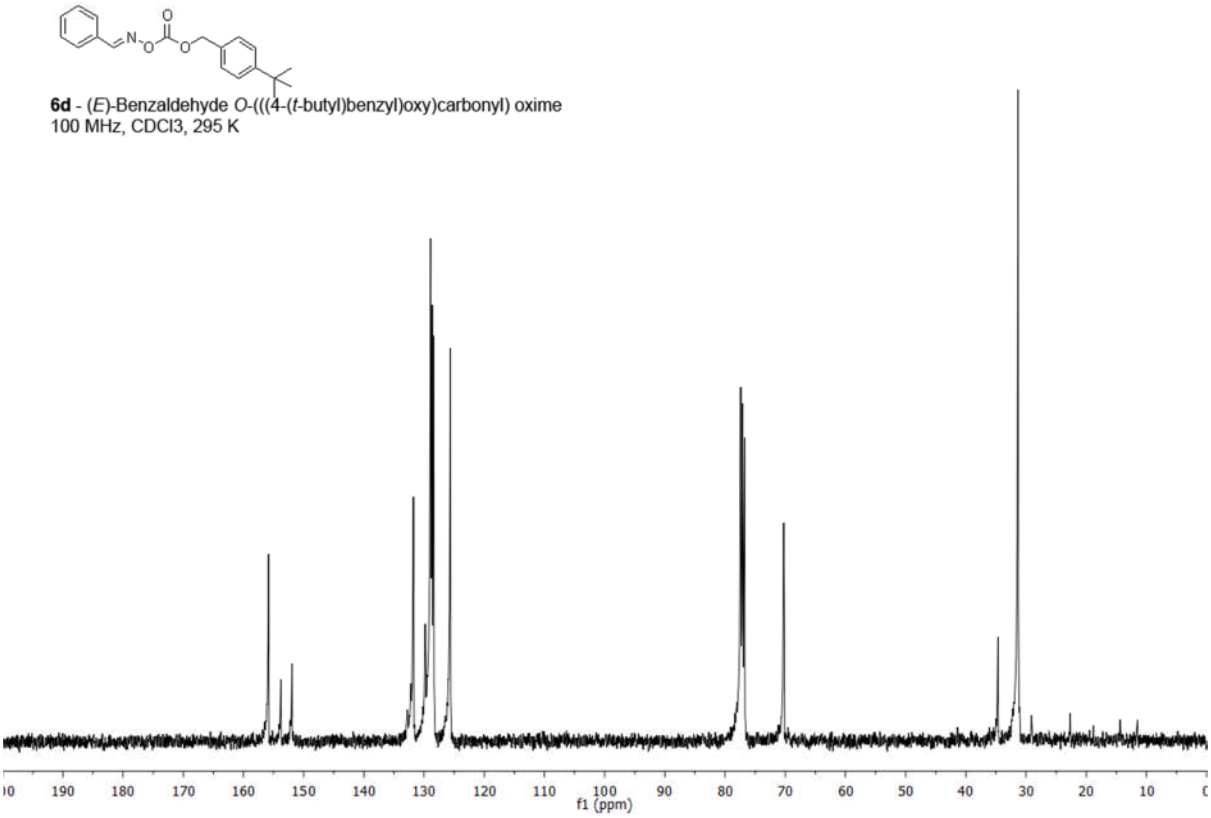
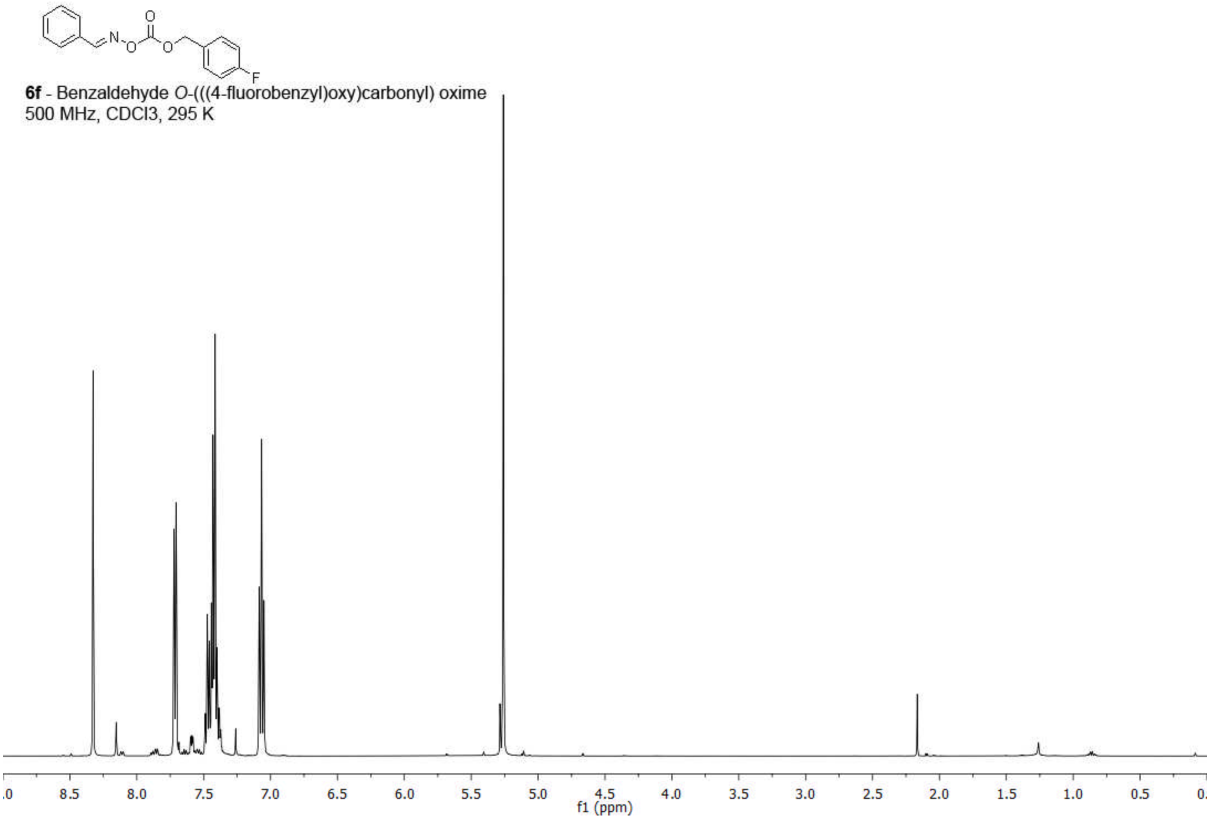


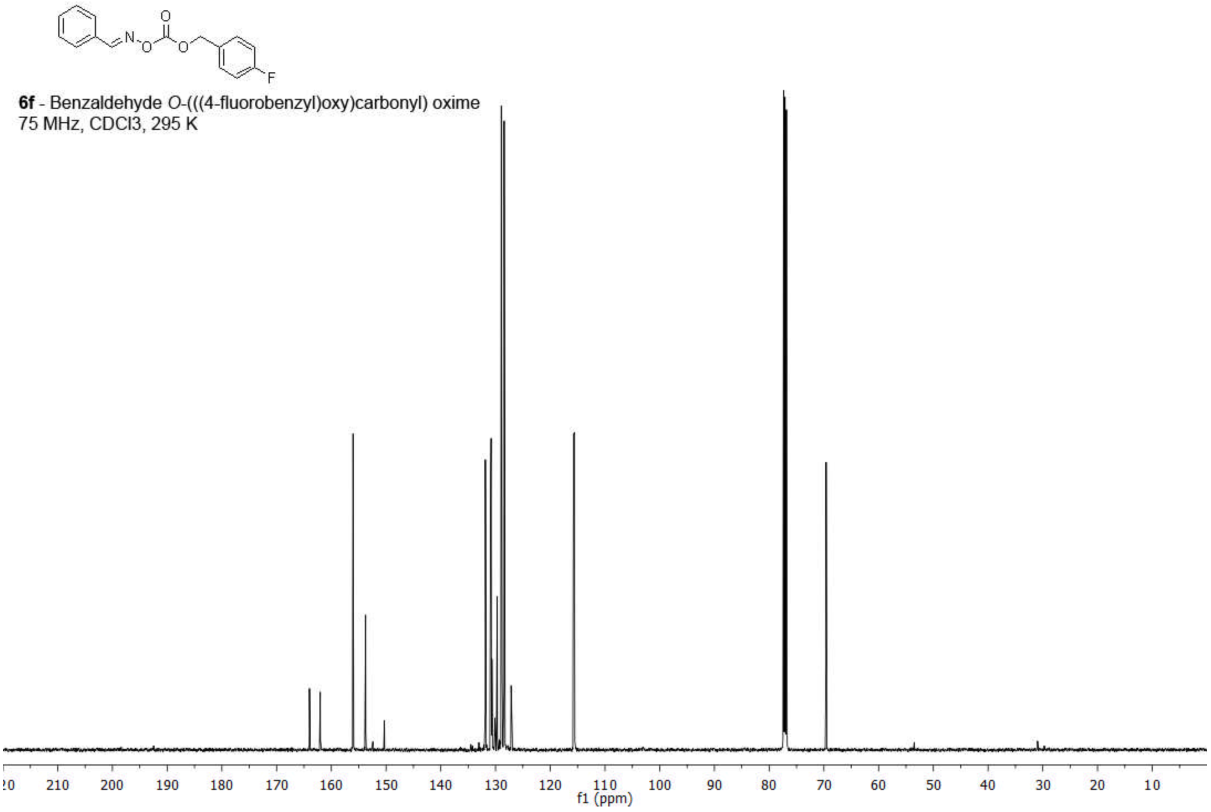
6d - (*E*)-Benzaldehyde *O*-(((4-(t-butyl)benzyl)oxy)carbonyl) oxime
400 MHz, CDCl3, 295 K



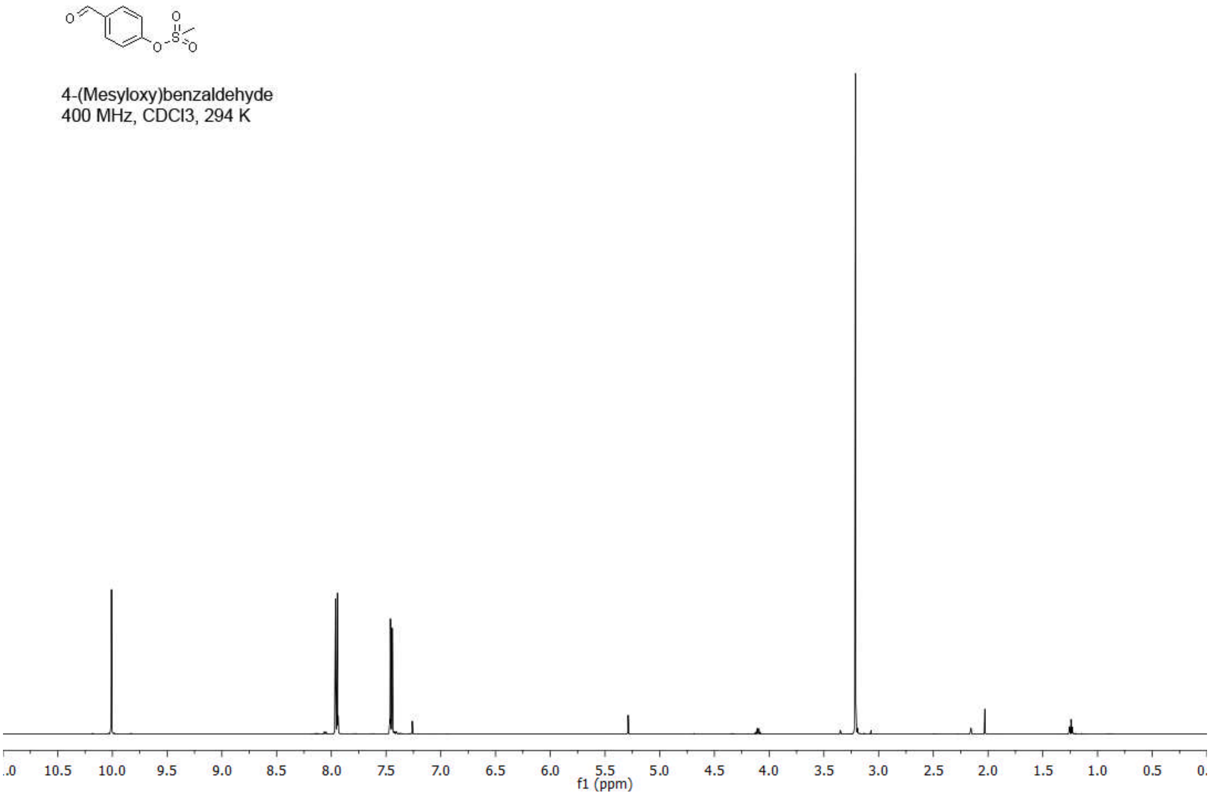
6d - (*E*)-Benzaldehyde *O*-(((4-(*t*-butyl)benzyl)oxy)carbonyl) oxime
100 MHz, CDCl3, 295 K

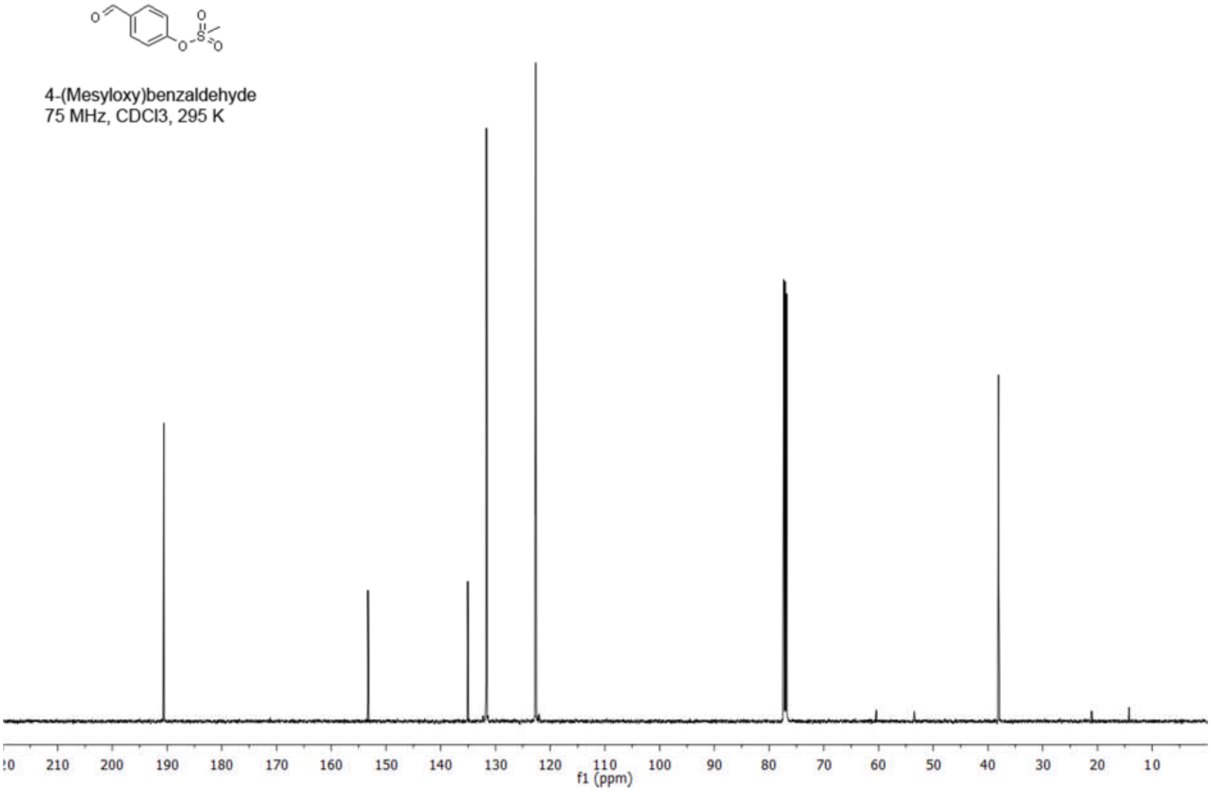


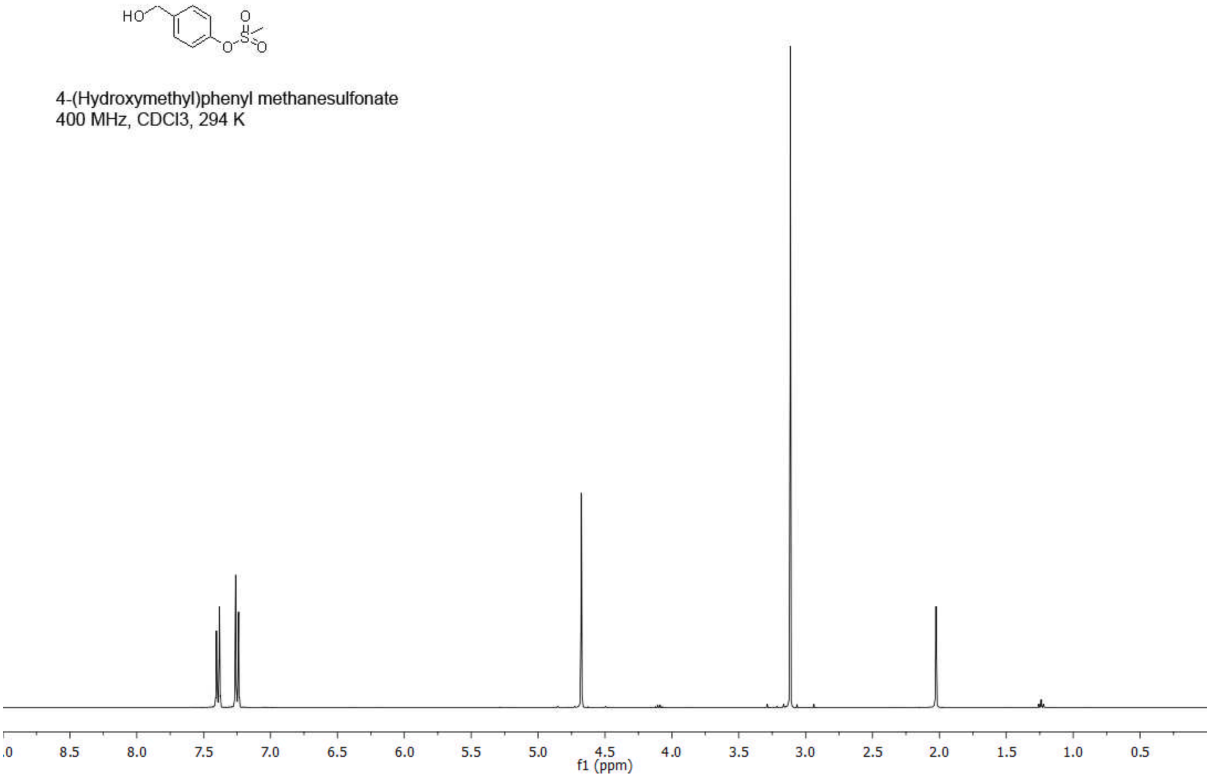
6f - Benzaldehyde *O*-(((4-fluorobenzyl)oxy)carbonyl) oxime
500 MHz, CDCl3, 295 K



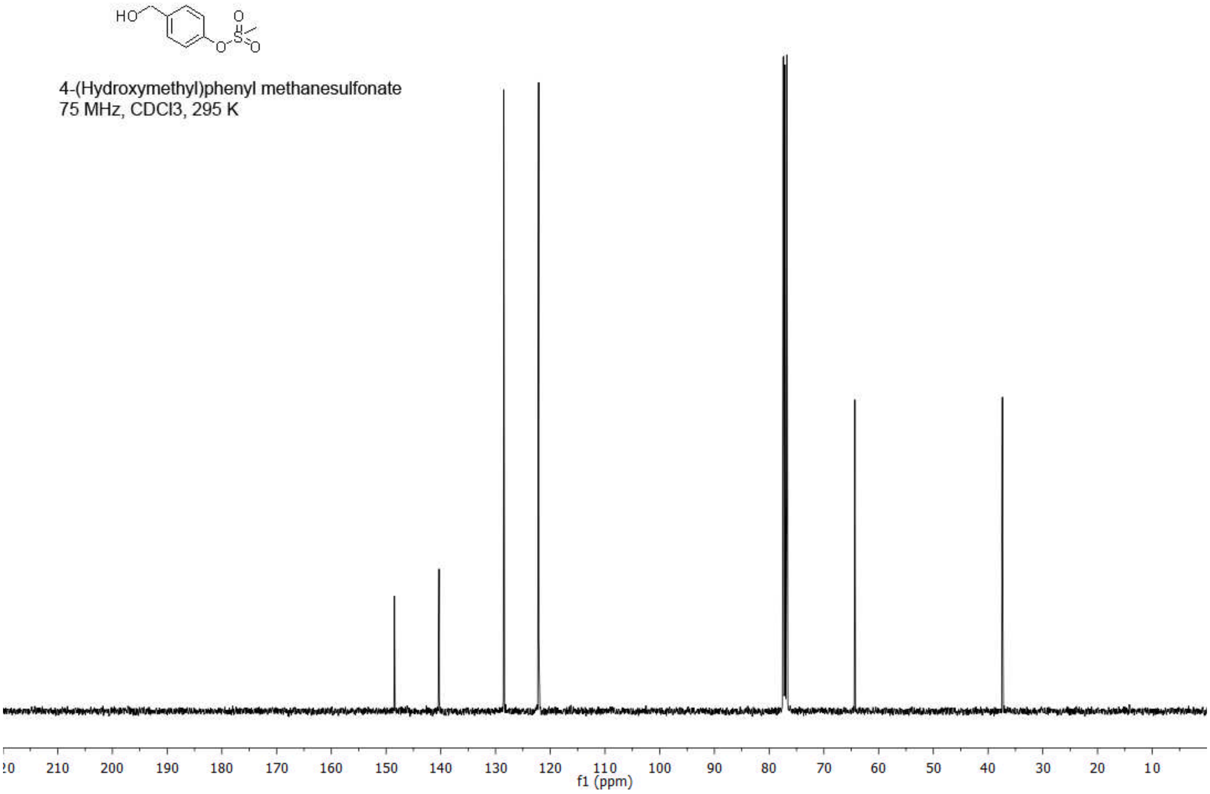
6f - Benzaldehyde *O*-(((4-fluorobenzyl)oxy)carbonyl) oxime
75 MHz, CDCl3, 295 K


4-(Mesyloxy)benzaldehyde
400 MHz, CDCl3, 294 K
.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.
f1 (ppm)

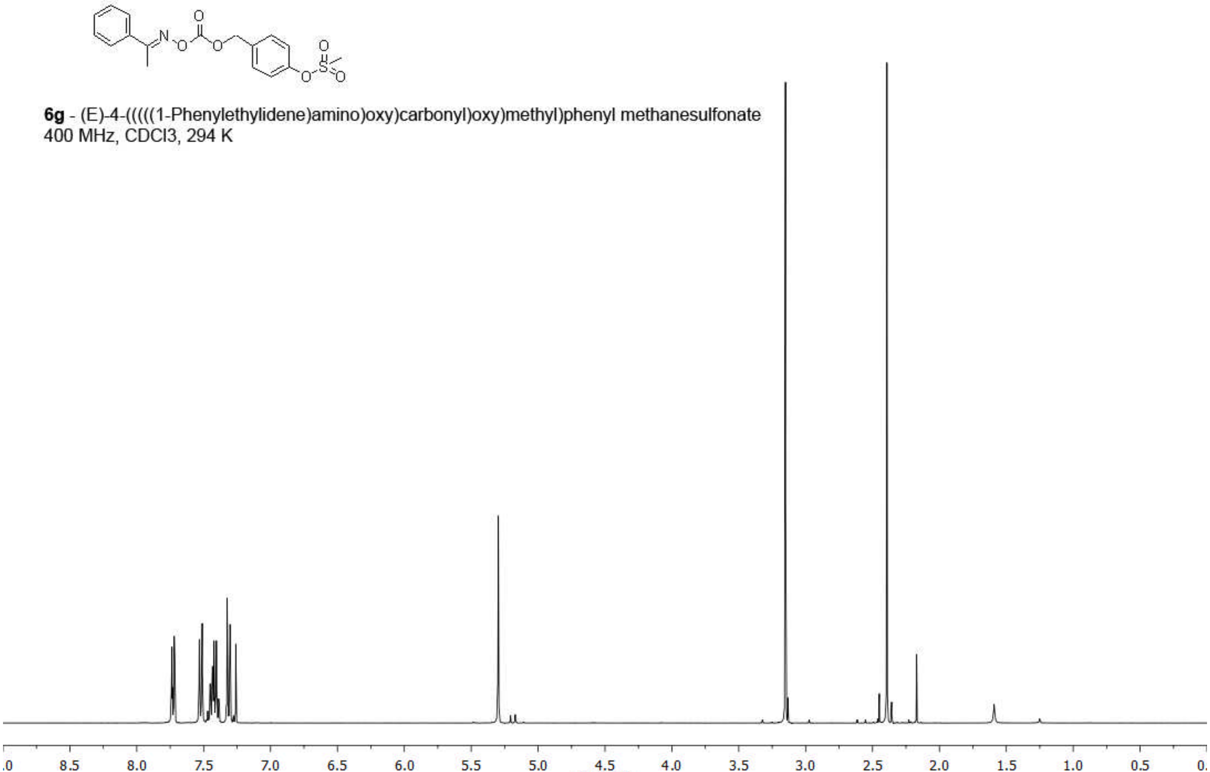

4-(Mesyloxy)benzaldehyde
75 MHz, CDCl3, 295 K
!0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



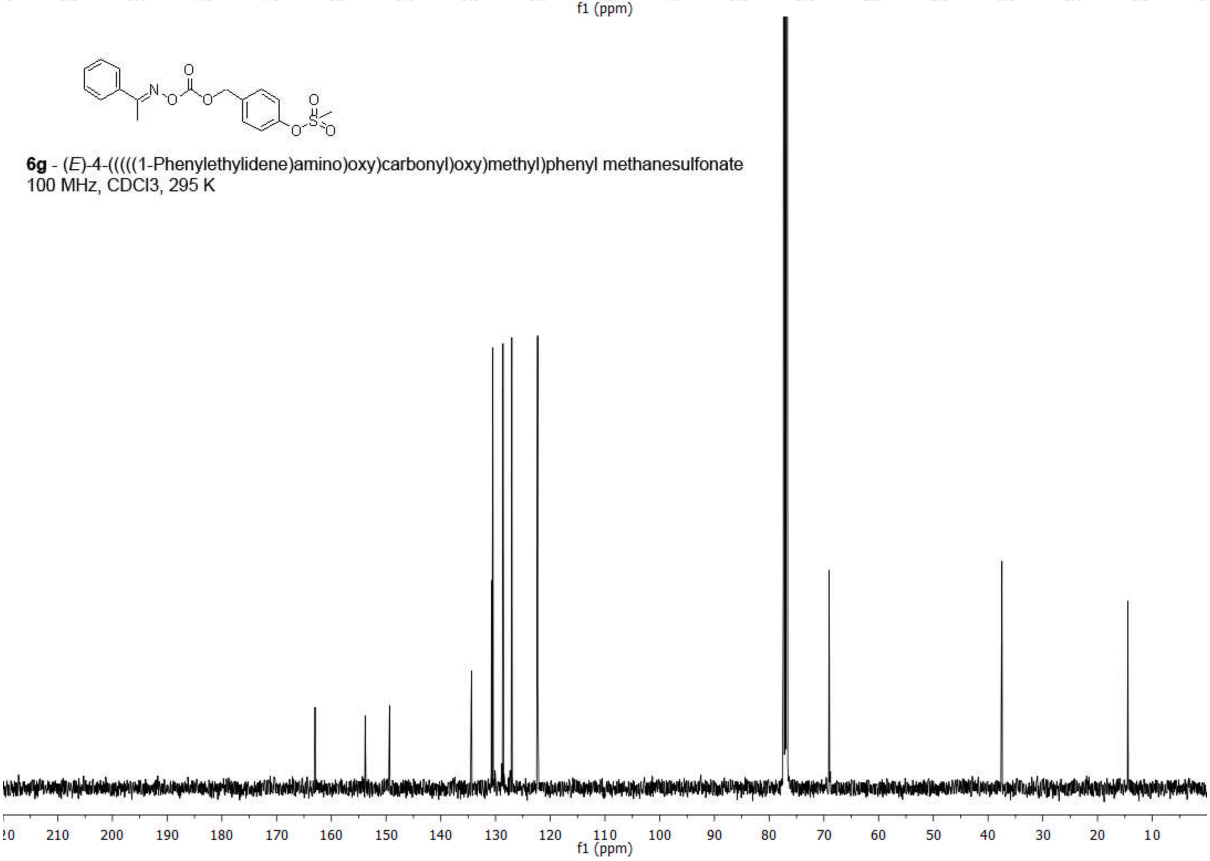
4-(Hydroxymethyl)phenyl methanesulfonate
400 MHz, CDCl3, 294 K



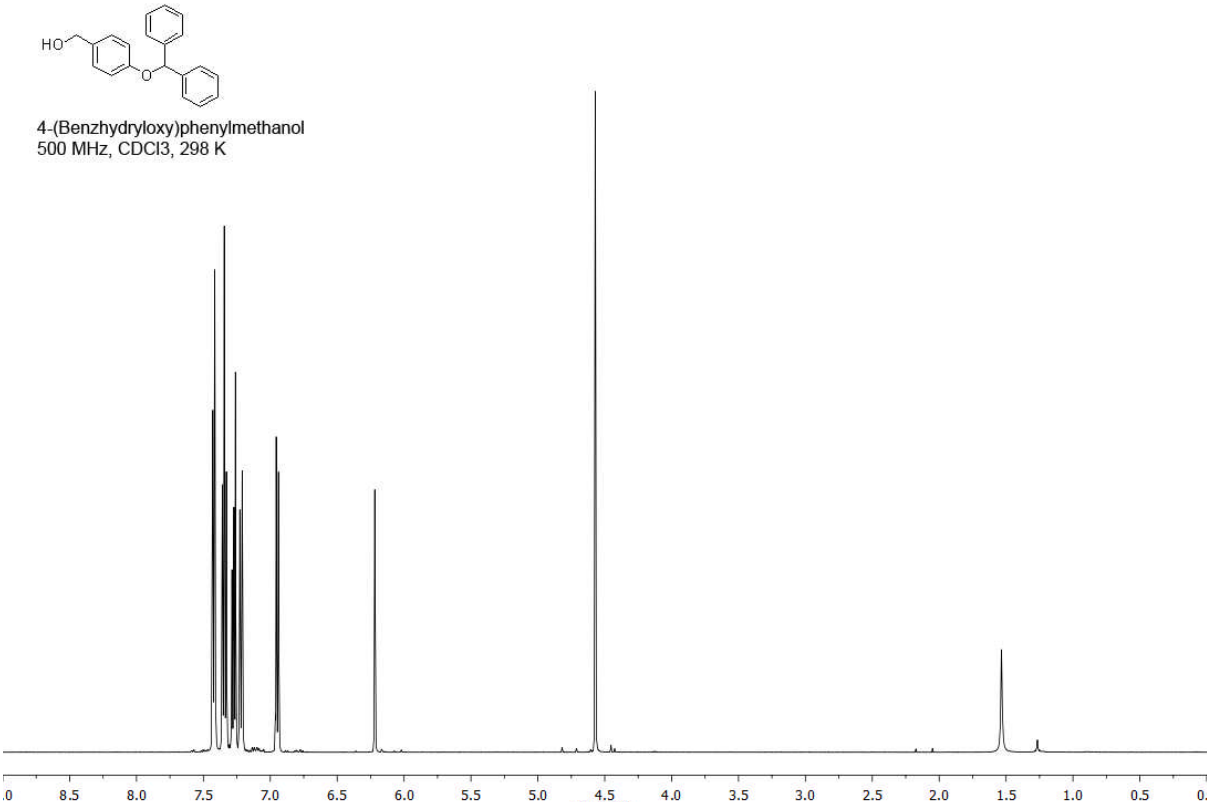
4-(Hydroxymethyl)phenyl methanesulfonate
75 MHz, CDCl3, 295 K



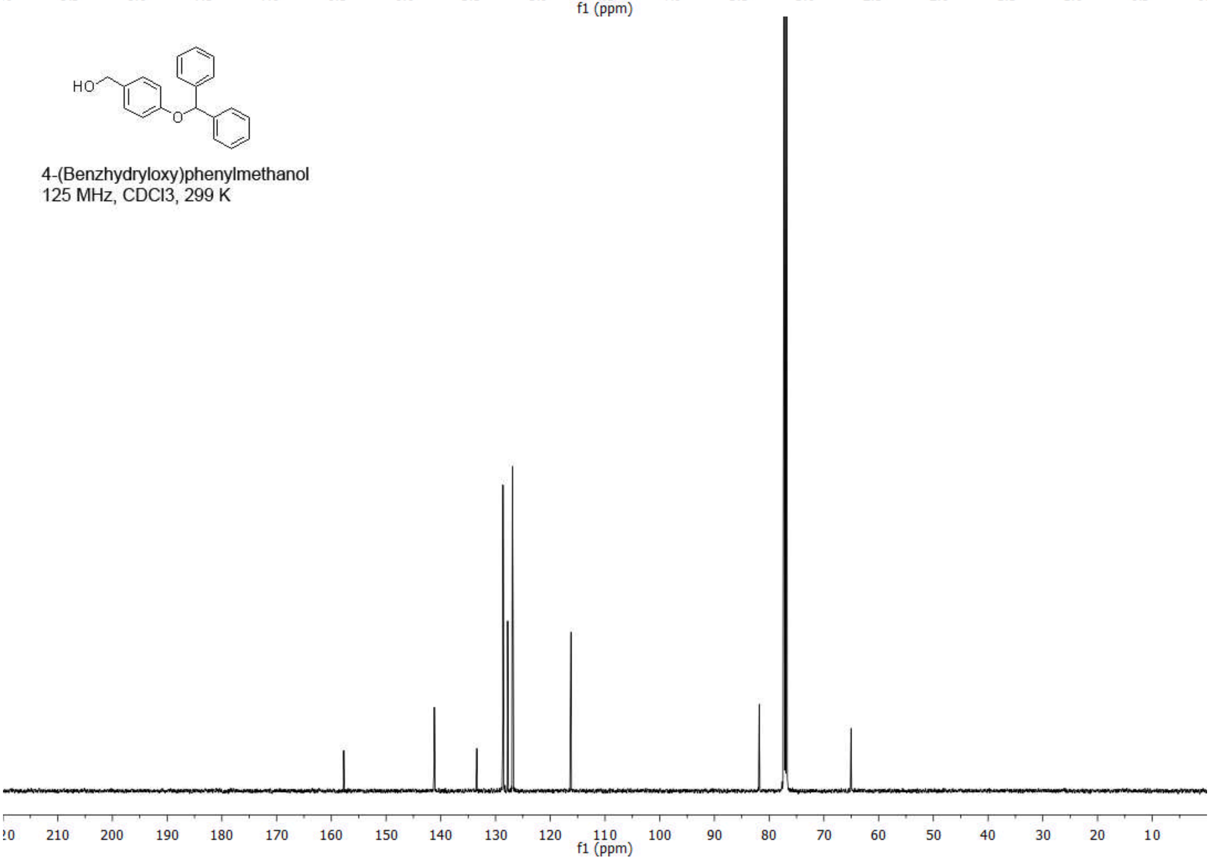
6g - (E)-4-(((((1-Phenylethylidene)amino)oxy)carbonyl)oxy)methyl)phenyl methanesulfonate
400 MHz, CDCl3, 294 K



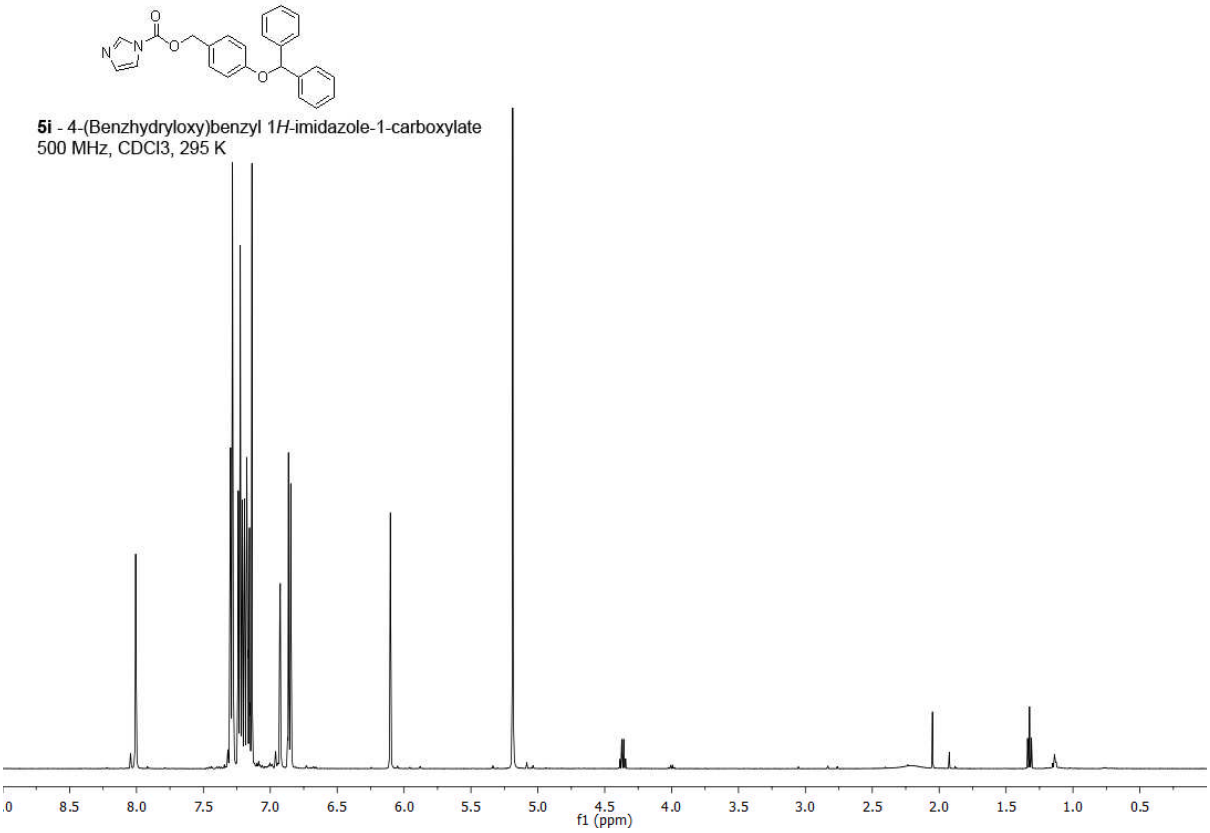
6g - (*E*)-4-(((((1-Phenylethylidene)amino)oxy)carbonyl)oxy)methyl)phenyl methanesulfonate
100 MHz, CDCl3, 295 K



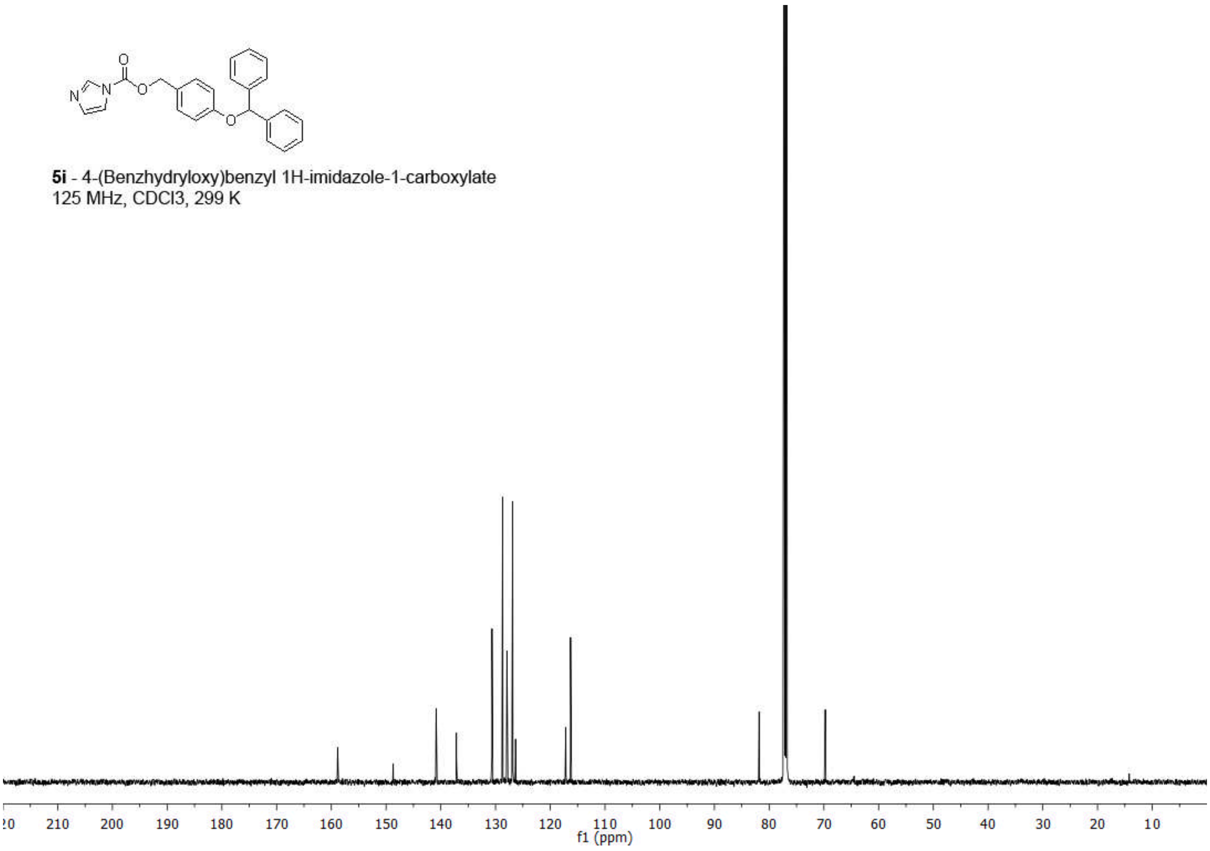
4-(Benzhydryloxy)phenylmethanol
500 MHz, CDCl3, 298 K



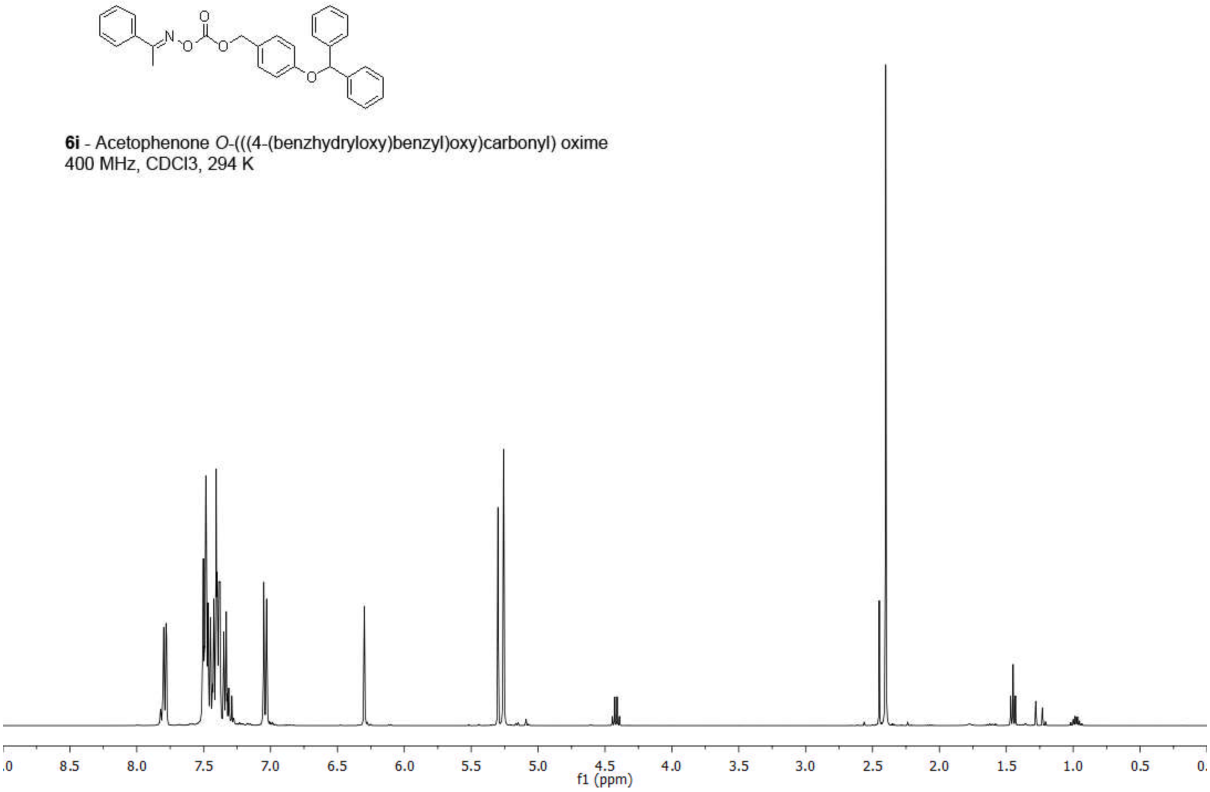
4-(Benzhydryloxy)phenylmethanol
125 MHz, CDCl3, 299 K



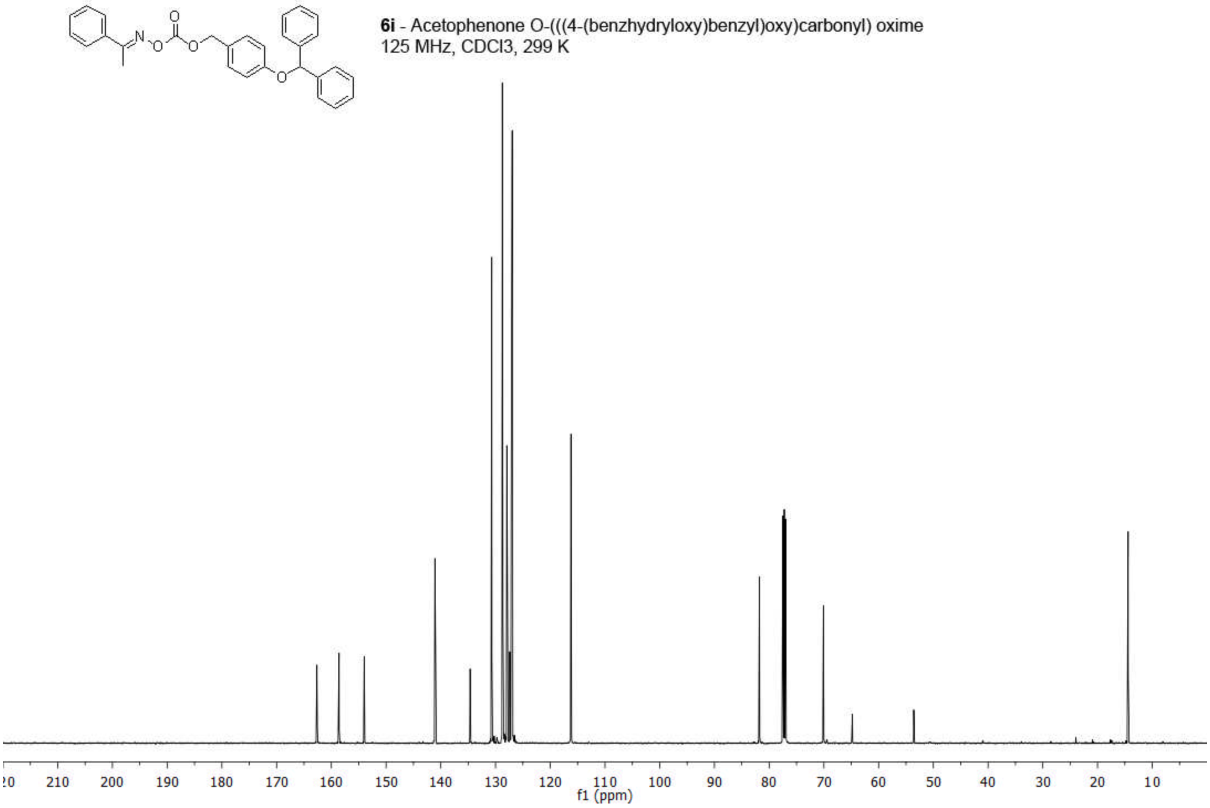
5i - 4-(Benzhydryloxy)benzyl 1*H*-imidazole-1-carboxylate
500 MHz, CDCl3, 295 K



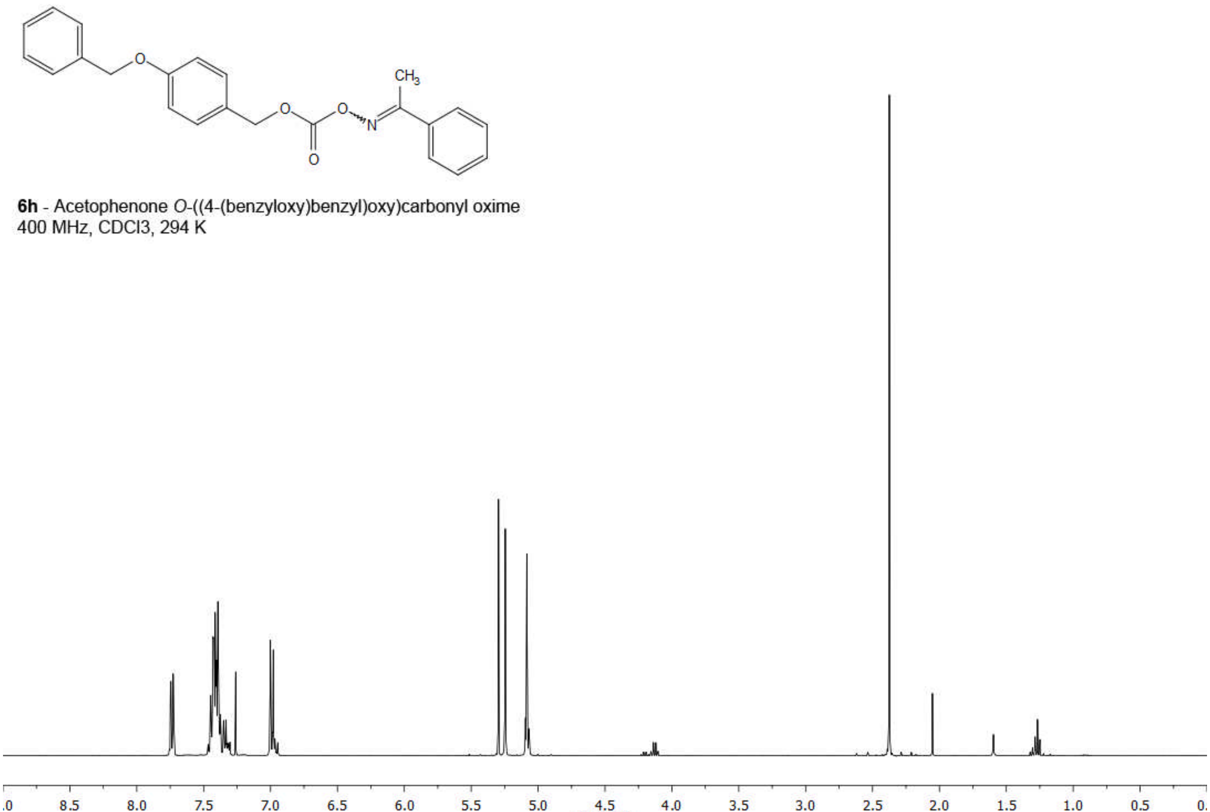
5i - 4-(Benzhydryloxy)benzyl 1H-imidazole-1-carboxylate
125 MHz, CDCl3, 299 K



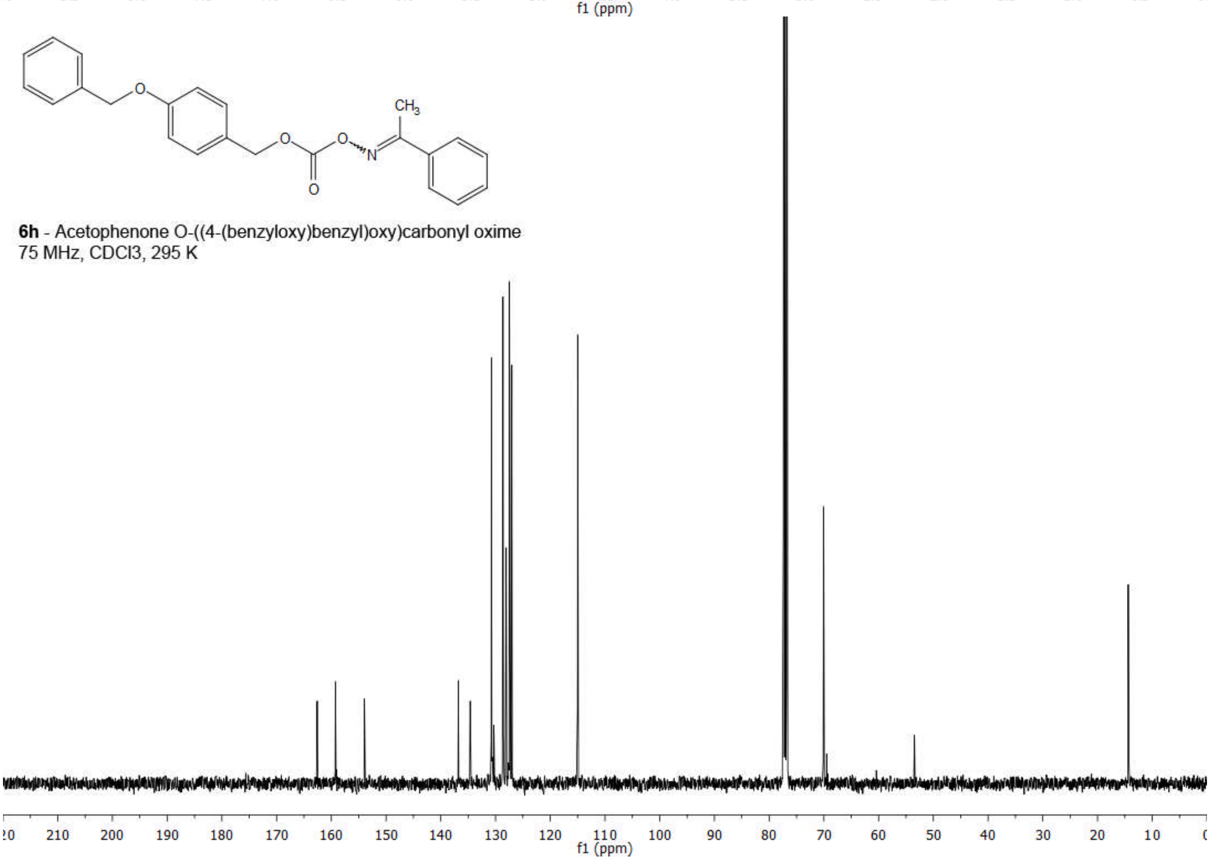
6i - Acetophenone *O*-(((4-(benzhydryloxy)benzyl)oxy)carbonyl) oxime
400 MHz, CDCl3, 294 K



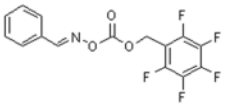
6i - Acetophenone O-(((4-(benzhydryloxy)benzyl)oxy)carbonyl) oxime
125 MHz, CDCl3, 299 K



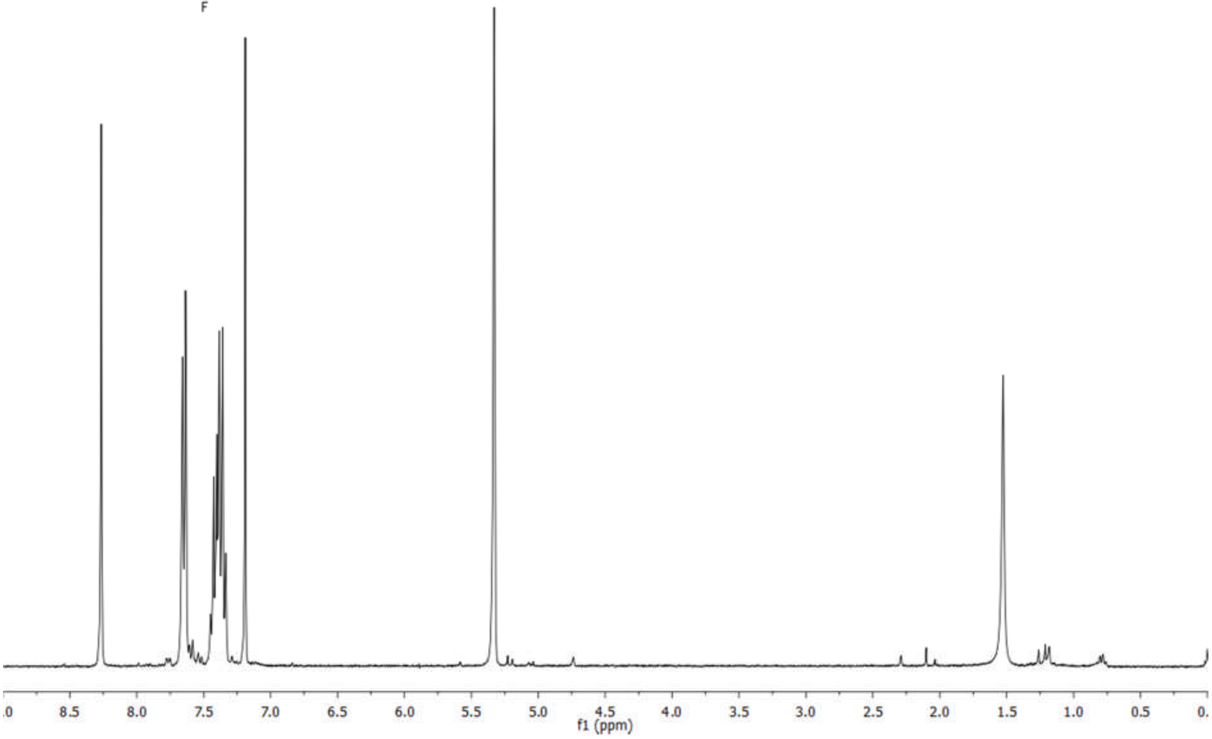
6h - Acetophenone *O*-((4-(benzyloxy)benzyl)oxy)carbonyl oxime
400 MHz, CDCl3, 294 K

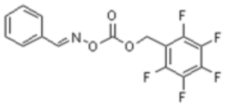


6h - Acetophenone O-((4-(benzyloxy)benzyl)oxy)carbonyl oxime
75 MHz, CDCl3, 295 K

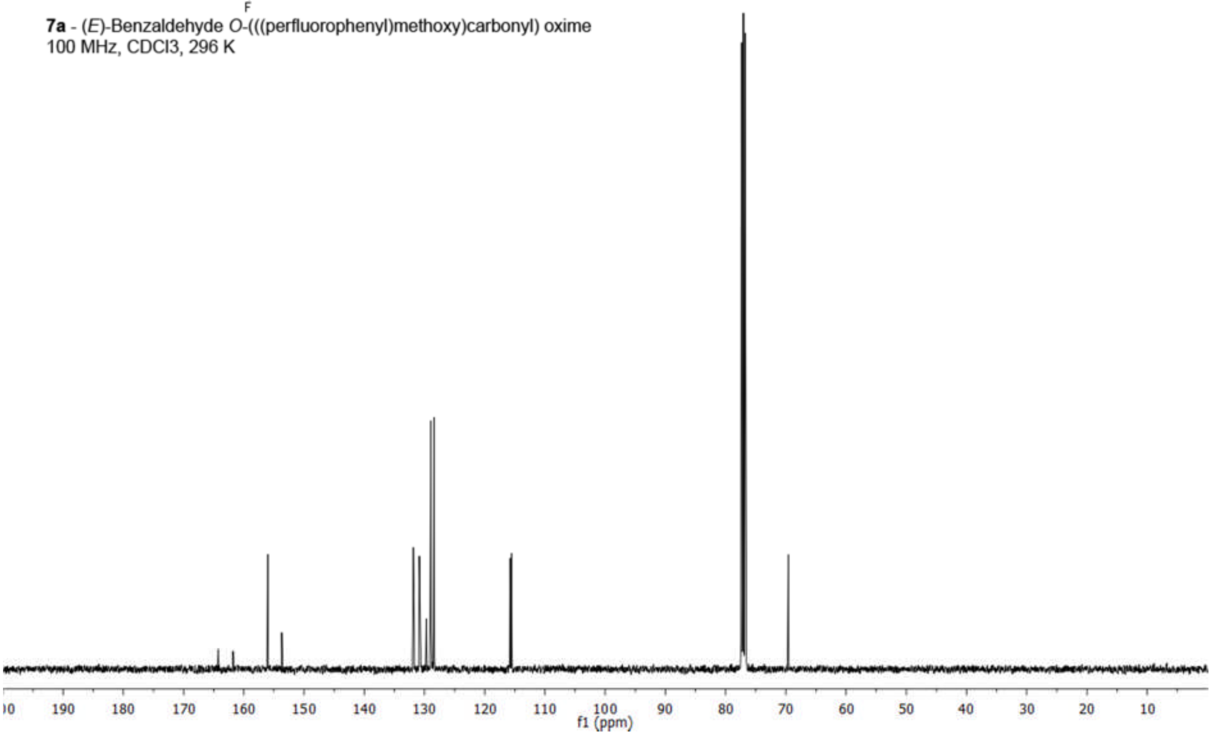


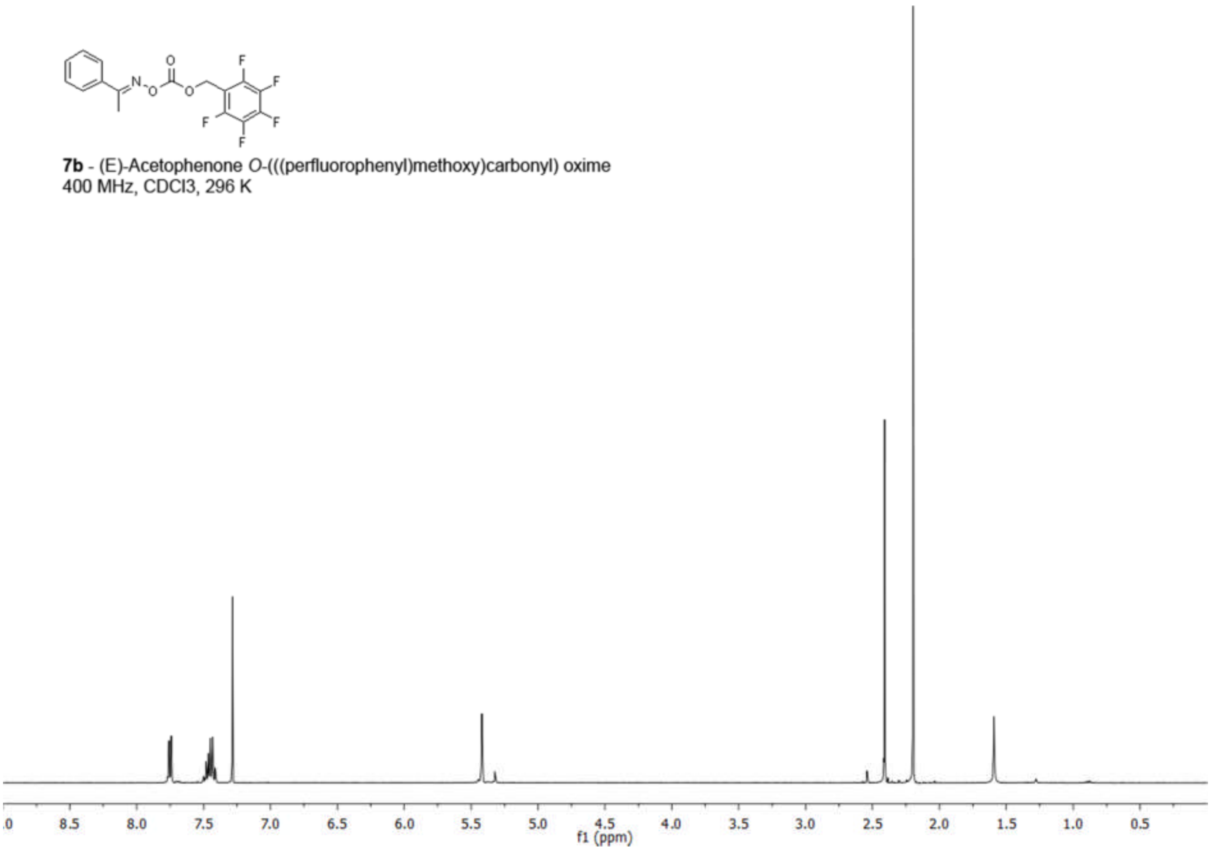
7a - (E)-Benzaldehyde *O*-(((perfluorophenyl)methoxy)carbonyl) oxime
400 MHz, CDCl3, 295 K



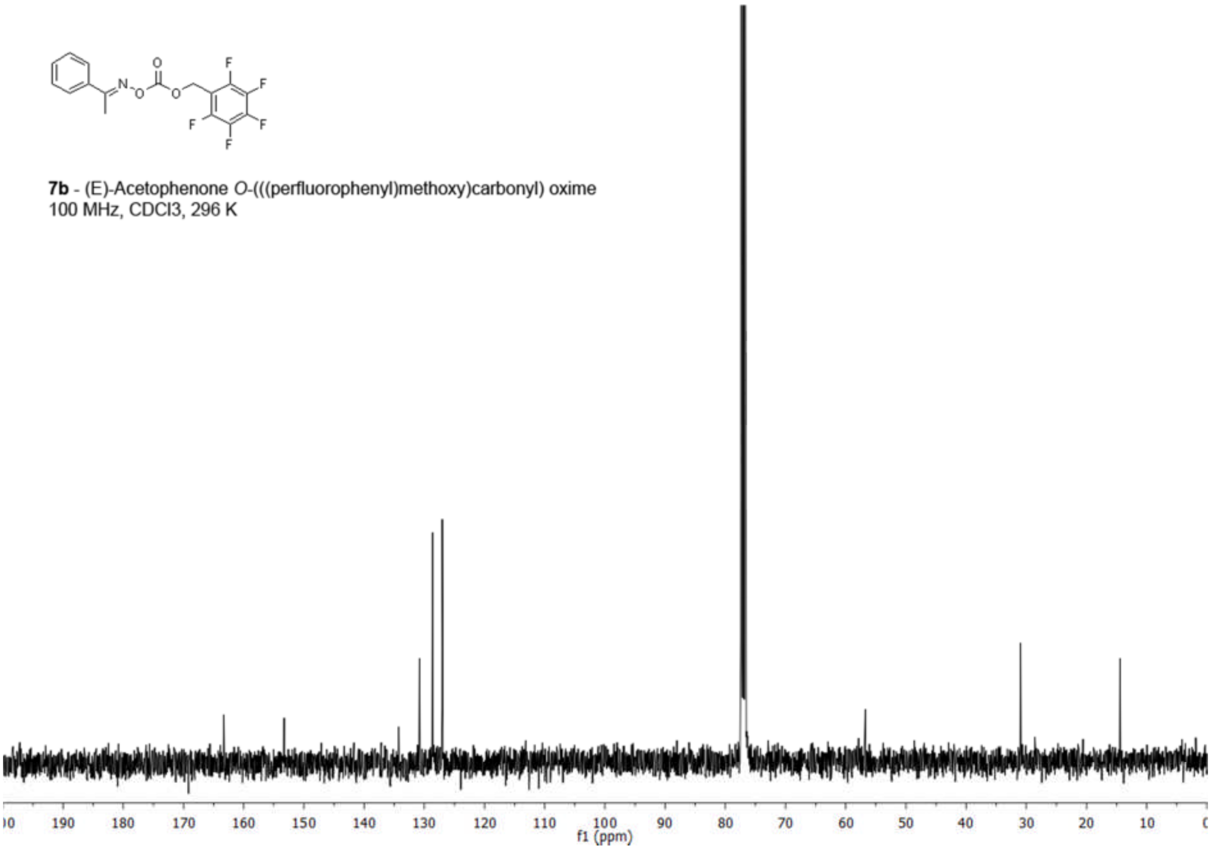


7a - (*E*)-Benzaldehyde *O*-(((perfluorophenyl)methoxy)carbonyl) oxime
100 MHz, CDCl3, 296 K





7b - (E)-Acetophenone *O*-(((perfluorophenyl)methoxy)carbonyl) oxime
400 MHz, CDCl3, 296 K



7b - (E)-Acetophenone *O*-(((perfluorophenyl)methoxy)carbonyl) oxime
100 MHz, CDCl3, 296 K