Electronic Supplementary Information

From dioxime oxalates to dihydropyrroles and phenanthridines via iminyl radicals

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Acetone *O,O'*-oxalyldioxime (**1a**).[1] To a stirred solution of oxalyl chloride (1.27 g; 10 mmol) in ether (10 cm^3) at –40 ^oC was added a solution of acetone oxime (1.46 g; 20 mmol). The mixture was stirred at –40 ^oC for 20 min and then at rt for 1 hr. After this time the solvent was removed to give the dioxime oxalate as a colourless solid (1.62 g; 81 %).. The product was recrystallised from DCM/pentane at –20 ^oC to give the dioxime oxalate as colourless prisms, mp 58 – 62 ^oC (lit[1] = 66 -67 ^oC); ν_{max}(NaCl)/cm^{-1} 1716 (C=O); ^1H NMR, (300 MHz, $CDCl_3$) δ_H 2.10, 2.09 (2 x CH_3); δ_C 17.4, 21.3 (CH_3), 156.6, 166.5 (C=O, C=N).

Benzophenone dioxime oxalate (**1b**).[1] Benzophenone oxime (3.9 g, 20 mmol) was dissolved in dry ether (30 cm^3), and added dropwise to a stirred solution of oxalyl chloride (1.2 g, 10 mmol) in dry ether (20 cm^3) at -40°C. Once the addition was complete the reaction mixture was stirred at -40 °C for 20 min, and then warmed to room temperature. The reaction was then stirred at room temperature for 2 h. The solvent was removed at reduced pressure and the resultant white residue was recrystallised from dichloromethane and pentane at -20 °C to yield the title compound (2.8 g, 63 %). ^1H NMR ($CDCl_3$, 300 MHz): δ_H 7.2-7.4 (20 H, m, Ph<u>H</u>), ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 129.9 (ArCH), 129.6 (ArCH), 130.7 (ArCH), 131.9 (ArCH) [C=N and C=O not obs].

1-(2,4-dimethoxyphenyl)pent-4-en-1-one (**2b**) A solution of 1-(1-4-dimethoxyphenyl)ethanone (2 g, 11 mmol) in dry THF (5 cm^3) was added dropwise over 10 min to a suspension of potassium hydride (0.53 g, 13 mmol) in dry THF (25 cm^3) at 0°C under N_2. The yellow suspension was stirred at 23 °C for 30 min and BEt_3 (1M solution in THF, 13 cm^3, 13 mmol) was added dropwise at 15 °C over 15 min. After stirring the solution at 23 °C for 15 min, allyl bromide (1.99 g, 16.5 mmol) was added dropwise over 10 min and the resulting suspension

was stirred for 4 h at 23 °C and quenched with a 1:1 mixture of 30 % NaOH and 30 % H_2O_2 (15 cm^3) at 0 °C over 15 min. The reaction mixture was then diluted with H_2O (20 cm^3), the layers were separated and the organic layer diluted with Et_2O (75 cm^3) and washed with water (2×30 cm^3). The combined water layers were extracted with DCM (2×30 cm^3) and the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 5%) to afford **2b** as a colourless oil 77 %; ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 2.35 (2H, q, J = 7.2 Hz, CH_2), 2.97 (2H, t, J = 7.2 Hz, CH_2), 3.77 (3H, s, CH_3), 3.81 (3H, s, CH_3), 4.95 (2H, m, CH_2), 5.84 (1H, m , CH), 6.37 (1H, d, J = 2.3 Hz, CH), 6.44 (1H, dd, J = 8.7, 2.3 Hz, CH), 7.73 (1H, d, J = 8.7 Hz, CH); ^{13}C NMR δ_C 28.7, 43.0 (CH_2), 55.7 (CH_3)x2, 98.5, 105.2 (CH), 114.7 (CH_2), 121.4 (C), 133.0 (CH), 138.3 (CH), 160.8, 164.4, 199.6 (C); IR 2942, 1664, 1575 cm^{-1}.

1-(2,4-dimethoxyphenyl)pent-4-en-1-one oxime (**3b**). A suspension of 1-(2,4-dimethoxyphenyl)pent-4-en-1-one (1 g, 4.5 mmol), hydroxylamine hydrochloride (0.62g, 9 mmol) and sodium acetate (0.73, 9 mmol) in EtOH (25 cm^3) was heated under reflux conditions for 4 h, and the progress of the reaction was followed by TLC (EtOAc/hexane 1:2). Upon completion, the reaction mixture was poured into water (20 cm^3) and extracted with DCM (3 × 15 cm^3L). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane 10%) to afford the desired product in 71 % yield. Two isomers 7:3. ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 2.14 (2H, m, CH_2), 2.52/2.76 (2H, m, CH_2), 3.71 (3H, s, CH_3), 3.73 (3H, s, CH_3), 4.88 (2H, m, CH_2), 5.72 (1H, m, CH), 6.35-6.46 (2H, m, CH), 6.98/7.10 (1H, d, J = 8.8 Hz, CH); ^{13}C NMR δ_C 28.2/30.9, 30.3/34.9 (CH_2), 55.8/56.0 (CH_3)×2, 99.2/99.3, 104.6/104.8 (CH), 115.1/115.6 (CH_2), 118.9 (C), 130.2/131.2, 138.0/138.6 (CH), 157.5/158.9, 160.1, 161.7/161.9 (C); IR 3228, 1596, 925 cm^{-1}.

1-(2,4-dimethoxyphenyl)pent-4-en-1-one dioxime oxalate (**4b**). Mixture of 3 isomers; ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 2.06-2.70 (8H, m, CH_2), 3.71-3.81 (12H, m , CH_3), 4.97 (4H, m, CH_2), 5.77 (2H, m, CH), 6.43 (4H, m, CH), 7.51 (1H, m , CH), 8.16 (1H, m, CH); ^{13}C NMR δ_C 27.8/29.6/30.1 (CH_2)×2, 34.4/34.5/37.0 (CH_2)×2, 55.8 (CH_3)×4, 98.6/98.7/99.8 (CH)×2, 103.7/104.6/105.2 (CH×2), 115.7 (CH_2)×2, 120.7/129.6/130.5 (CH)×2, 121.4 (C)×2, 149.1 (C)×2, 156.3 (C)×2, 161.9 (C)×2, 169.9/174.6 (C)×2; IR**;** 2934, 1768, 1705, 1605, 1512 cm^{-1}.

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1 J. C. Jochims, S. Hehl and S. Herzberger, *Synthesis*, 1990, 1128-1132.

Photolysis of 2,2-dimethyl-1-phenylpent-4-en-1-one dioxime oxalate (**4c**). Compound **4c** (24.3 mg, 0.053 mmol) and MAP (1 eq) were dissolved in cyclohexane (2 cm^3) and the mixture was photolysed for 8 h at 85 °C. Chromatography yielded 3,4-dihydro-2,4,4-trimethyl-5-phenyl-2*H*-pyrrole **7c** (35 %), ^{1}H NMR, δ_H 7.64 – 7.7 (2H, m), 7.14 – 7.4 (3H, m), 4.10 (1H, dp, *J* 6.7, 8.4), 2.11 (2H, dd, *J* 6.7, 12.5), 1.39 (3H, d, *J* 6.9), 1.35 (6H, s); ^{13}C NMR, δ_C 129.8 (C), 128.5 (CH), 128.3 (CH), 63.7 (CH), 50.4 (C), 27.9 (CH_3), 27.1 (CH_2), 26.3 (CH_3), 22.6 (CH_3); *m/z* (%) 187 (100), 131 (60), 84 (80); HRMS; $C_{13}H_{18}N$ (MH^+) requires 188.1439; found 188.1432. Similar photolysis in toluene gave **7c** in 47 % yield.

5-(4-Methoxyphenyl)-2-methyl-3,4-dihydro-2*H*-pyrrole (**7a**). From photolysis of **4a** and MAP in toluene for 4 h at rt. Red oil; 61 %; ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 1.28 (3H, d, *J* = 6.8, CH_3), 1.46 (1H, m, CH_2), 2.15 (1H, m, CH_2), 2.78 (1H, m, CH_2), 2.96 (1H, m, CH_2), 3.78 (3H, s, CH_3), 4.20 (1H, m, CH), 6.83 (2H, d, *J* = 8.8 Hz, CH), 7.71 (2H, d, *J* = 8.8 Hz, CH); ^{13}C NMR δ_C 22.2 (CH_3), 30.7, 35.2 (CH_2), 55.6 (CH_3), 68.2 (CH), 113.8 (CH×2), 127.4 (C), 129.3 (CH×2), 161.2, 171.1 (C); IR 3268, 2923, 1684 cm^{-1} HRMS (CI); $C_{12}H_{16}NO$ requires 190.1232; found 190.1238.

5-(2,4-Dimethoxyphenyl)-2-methyl-3,4-dihydro-2*H*-pyrrole (**7b**)**.** A solution dioxime oxalate **4b** (400 mg, 0.57 mmol) and MAP (171 mg, 1.14 mmol) in toluene (25 cm^3) was photolysed for 4 h at rt by light from a 400 W UV lamp. After this time the toluene was evaporated to dryness to give a yellow oil. The oil was purified by column chromatography (10 % EtOAc/hexane) to give **7b** as a red oil 67 %; ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 1.28 (3H, d, *J* = 6.7 Hz, CH_3), 1.44 (1H, m, CH_2), 2.12 (1H, m, CH_2), 2.88 (1H, m, CH_2), 3.04 (1H, m, CH_2), 3.77 (3H, s, CH_3), 3.78 (3H, s, CH_3), 4.12 (1H, m, CH), 6.43 (2H, m , CH), 7.68 (1H, d, *J* = 8.5, CH); ^{13}C NMR δ_C 21.9 (CH_3), 30.1, 38.1 (CH_2), 55.5 (CH_3×2), 66.4 (CH), 98.6, 105.1 (CH), 116.6 (C), 131.7 (CH), 159.0, 165.8, 172.3 (C); IR 3018, 2964, 1609 cm^{-1} HRMS (CI); $C_{13}H_{18}NO_2$ requires 220.1338; found: 220.1337.

2,2-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole (**7d**)**.**[2] A solution dioxime oxalate **4d** (250 mg, 0.57 mmol) and MAP (1 equiv.) in toluene (15 cm^3) was photolysed for 4 h at rt by light from a 400 W UV lamp. After this time the toluene was evaporated to dryness to give a yellow oil.

2 J. Yamamoto, M. Akazome, T. Kondo and T. Mitsudo. *J. Org. Chem*. 1995, **60**, 8328.

Chromatography failed to give pure **7d** but it was clearly visible in the total product mixture (38% from NMR integral); ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 1.35 (6H, s, 2x CH_3), 1.9-3.0 (4H, m, 2 x CH_2), 7.3-7.6 (5H, m , ArH).

Benzylidene-3,4-dihydro(2H)pyrrole (**9**). From photolysis (5 h, rt) of **8** (500 mg; 3.6 mmol) and MAP (540 mg; 3.6 mmol) in toluene (400 cm^3); yellow oil (84 %). ^{1}H NMR and GC-MS showed this to be a mixture of two isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.45-2.75 (4 H, m, 2 x CH_2), 5.57 (1/2 H, dt, *J* 13.2, *J* 6.5, C=CHPh), 6.11 (1/2 H, dt, *J* 15.9, *J* 4.9, C=CHPh), 6.44 (1/2 H, d, *J* 15.9), 6.52 (1/2 H, d, *J* 13.2, HC=N), 7.25-7.40 (5 H, m, PhH); δ_C 18.0 (2xCH_2), 24.8 (CH_2), 29.2 (CH_2), 125.9, 126.7, 127.6, 127.9, 128.1, 128.8, 129.0 (ArCH), 132.6 (HC=N), 133.4 (HC=C) [note that several CHs overlapped]. The product was analyzed by GC/MS; *peak no. 471*, *E*- or *Z*-**9** (54 %), *m/z* (relative intensity); 157 (M^+, 22), 117 (100), 102 (6), 91 (27); *peak no. 502*, *E*- or *Z*-**9** (42 %), *m/z* (relative intensity) 157 (M^+,100), 129 (7), 117 (73); HRMS $C_{11}H_{12}N$ (MH^+) requires 158.0970; found; 158.0975.

Methyl 3-(2,4-dimethyl-3,4-dihydro-2H-pyrrol-5-yl)propanoate (**12c**). From benzophenone dioxime oxalate **11c**: yellow oil 61 %; ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 1.03/1.09 (3H, d, *J* = 7.2 Hz, CH_3), 1.10/1.19 (3H, d, *J* = 7.2 Hz, CH_3), 1.61 (1H, t, J = 6.7 Hz, CH_2), 2.22-2.84 (6H, m, CH, CH_2), 3.60 (3H, s, CH_3), 3.77/4.01 (1H, m, CH); ^{13}C NMR δ_C 16.4/17.1, 20.7/21.9 (CH_3), 24.9/25.1, 28.7/29.4, 38.5/39.2 (CH_2), 43.4/44.5 (CH), 50.6 (CH_3), 64.3/64.7 (CH), 172.8, 177.2 (C); IR 1764, 1646 cm^{-1}. Photolyses of dioxime oxalates **11a** and **11b** gave the product in yields of 41% and 58% (Note that **12a, 12b** and **12c** are the same dihydropyrrole).

Phenanthridine (**18a**). Yellow crystals; 67 %; mp 105-107 °C; ^{1}H NMR[3] (400 MHz, $CDCl_3$), δ_H 7.62-4.65 (2H, m, CH), 7.71-7.75 (2H, m, CH), 8.08 (1H, d, *J* = 8.1, CH), 8.22 (1H, d, *J* = 8.2 Hz, CH), 8.61 (1H, dd, *J* = 8.1, 1.2 Hz, CH), 8.65 (1H, d, *J* = 8.3, CH), 9.32 (1H, s, CH); ^{13}C NMR δ_C 121.7, 122.1 (CH), 123.9, 126.9 (C), 127.3, 128.4, 128.6, 130.0, 130.8 (CH), 132.3, 144.3 (C), 153.4 (CH).

6-Methylphenanthridine (**18b**). Yellow crystals; 73 %; mp 81-83 °C; ^{1}H NMR[2] (400 MHz, $CDCl_3$), δ_H 3.02 (3H, s, CH_3), 7.57-7.76 (3H, m, CH), 7.79-7.85 (1H, m, CH), 8.11 (1H, dd, *J* = 8.1, 1.1 Hz, CH), 8.19 (1H, d, *J* = 8.2 Hz, CH), 8.51 (1H, d, *J* = 8.1 Hz, CH), 8.59 (1H, d, *J* = 8.1

3 M. Lysen, J. L. Kristensen, P. Vedsø and M. Begtrup, *Org. Lett.* 2002, **4**, 257-259.

Hz, CH); ^{13}C NMR δ_C 23.3 (CH_3), 122.0, 122.3 (CH), 123.8, 125.9 (C), 126.3, 126.5, 127.3, 128.6, 129.4, 130.5 (CH), 132.5, 143.7, 158.9 (C).

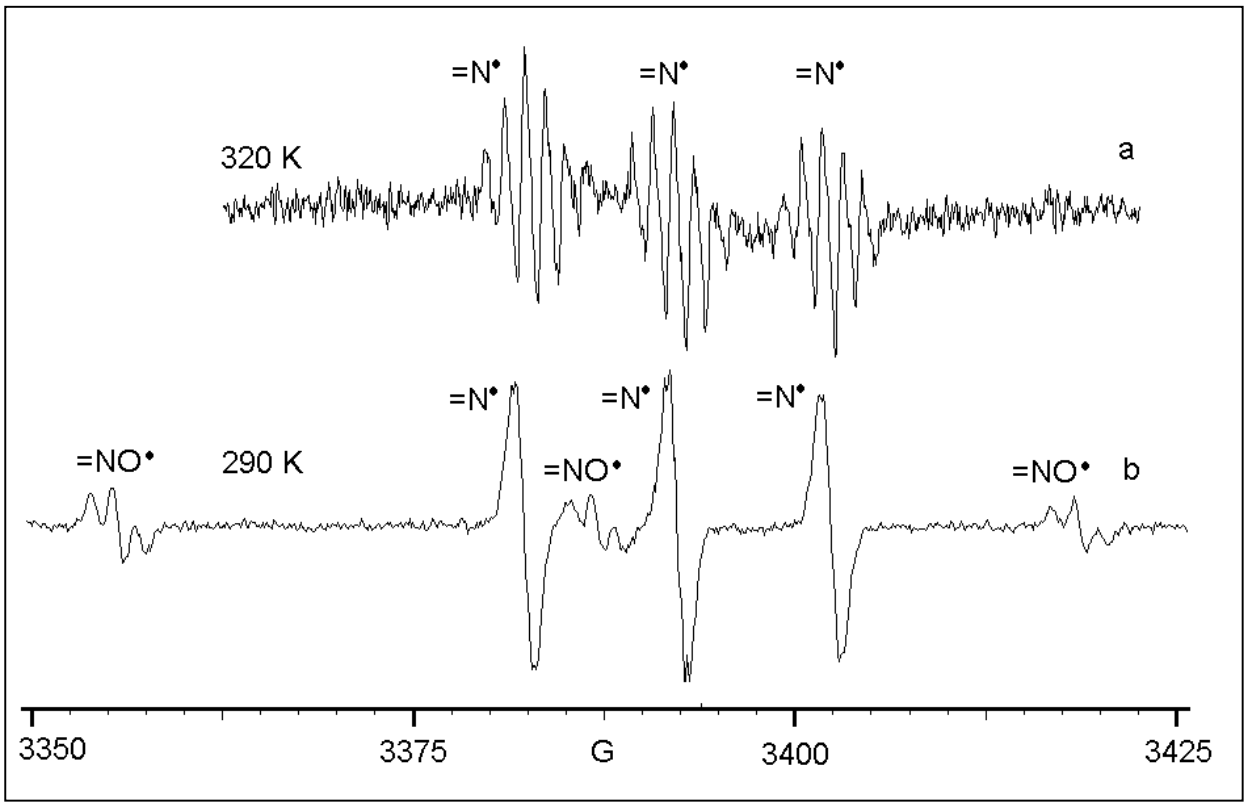
6-Phenylphenanthridine (**18c**). Yellow crystals; 59 %; mp 104-106 °C; ^{1}H NMR[2] (400 MHz, $CDCl_3$), δ_H 7.50-7.80 (8H, m, CH), 7.88 (1H, ddd, J = 8.3, 7.0, 1.3 Hz, CH), 8.11 (1H, dd, J = 8.3, 1.3 Hz, CH), 8.26 (1H, dd, J = 8.0, 1.6 Hz, CH), 8.64 (1H, d, J = 8.0 Hz, CH), 8.72 (1H, d, J = 8.3 Hz, CH); ^{13}C NMR δ_C 121.9, 122.2 (CH), 123.7, 125.2 (C), 126.9, 127.1. 128.4, 128.7, 128.8, 128.9 (CH), 129.7 (CH)×2, 130.2 (CH), 130.5 (CH)×2, 133.4, 139.8, 143.8, 161.4 (C).

[1,3]Dioxolo[4,5-*j*]phenanthridine (trisphaeridine, 18d). Yellow solid; 59 %; mp 144-146 °C; ^{1}H NMR[4] (400 MHz, $CDCl_3$), δ_H 6.00 (2H, s, CH_2), 7.33 (1H, s, CH), 7.62 (1H, td, J = 7.5, 1.5, CH), 7.62 (1H, td, J = 7.5, 1.2 Hz, CH), 7.91 (1H, s, CH), 8.13 (1H, dd, J = 7.4, 1.2 Hz, CH), 8.37 (1H, dd, J = 8.4, 1.2 Hz, CH), 9.08 (1H, s, CH); ^{13}C NMR δ_C 99.9 (CH), 101.9 (CH_2), 105.5, 122.0 (CH), 123.0, 124.3 (C), 126.7, 128.0, 130.0 (CH), 130.3, 144.0, 148.2, 151.5 (C), 151.7 (CH); IR**;** 1620, 1580, 1498, 1464 cm^{-1}; HRMS (CI^+) $C_{14}H_{10}NO_2$ requires 224.0712; found: 224.0712.

4 R. Sanz, Y. Fernandez, M. P. Castroviejo, A. Perez and F. J. Fananas, *Eur. J. Org. Chem.* 2007, 62-69.

EPR Spectra. EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Solutions of freshly prepared dioxime oxalate (ca. 0.1-0.2 M) and 4-methoxyacetophenone (MAP, usually 2 mol equiv.) in *t*-butylbenzene were placed in 0.4 mm o.d. quartz tubes and deaerated by bubbling nitrogen gas for 20 min. Samples were irradiated in the resonant cavity by unfiltered light from a 500 W super pressure Hg arc. In all cases where spectra were obtained, hfs were checked with the aid of computer simulations using the Bruker SimFonia software package. Microwave power 1.0 mW; modulation amplitude 1.0 G_{pp},

Spectra of dimethyl- and diphenyl-iminyls from 1a,b

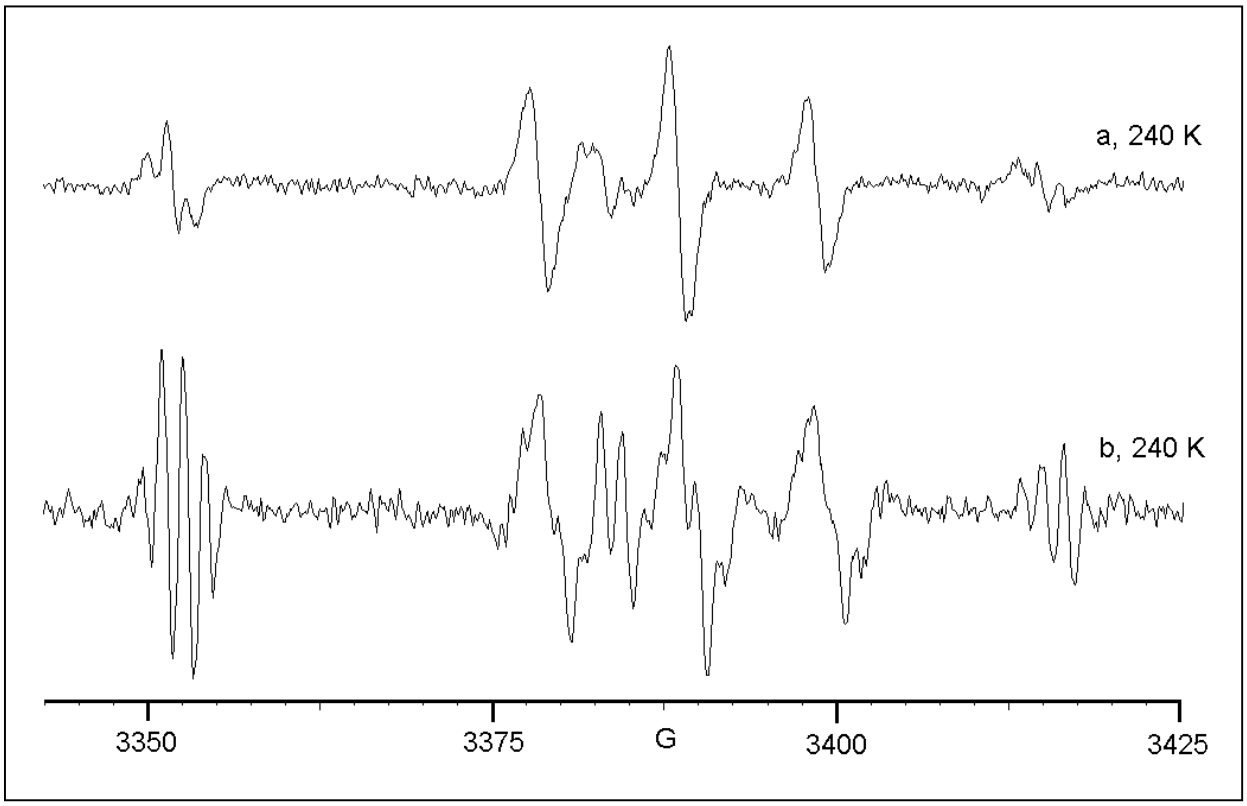


Upper spectrum (a): Dimethyliminyl radical ($Me_2C{=}N•$) obtained from photolysis of dioxime oxalate **1a** with MAP in PhBu-*t* at 320 K. g = 2.0034, a(N) = 9.8, a(6H) = 1.4 G. Gain 1.4 x 10^6

Lower spectrum (b): Photolysis of **1b** at 290 K gave spectrum b containing diphenyliminyl $Ph_2C{=}N•$ [g = 2.003, a(N) = 10.0 G, denoted by: =N•] together with diphenyliminoxyl

Ph_2C=NO• [g = 2.006, a(N) = 31.3, a(2H) = 1.4 G, denoted by: =NO•]. Gain 5.0 x 10^5. Note the much higher signal/noise ratio of (**b**) as compared to (**a**).

Spectra of biphenyliminyls from 15b and 15c



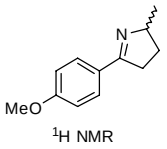
Upper Spectrum (a): Photolysis of **15c** at 240 K gave BiPhC(Ph)=N• [g = 2.003, a(N) = 10.1 G] and BiPhC(Ph)=NO• [g = 2.006, a(N) = 31.6, a(2H) = 1.5 G]

Lower Spectrum (b): Photolysis of **15b** at 240 K gave BiPhC(Me)=N• [g = 2.003, a(N) = 10.0, a(3H) ~ 1.3 G] and BiPhC(Me)=NO• [g = 2.006, a(N) = 31.8, a(3H) = 1.5 G].

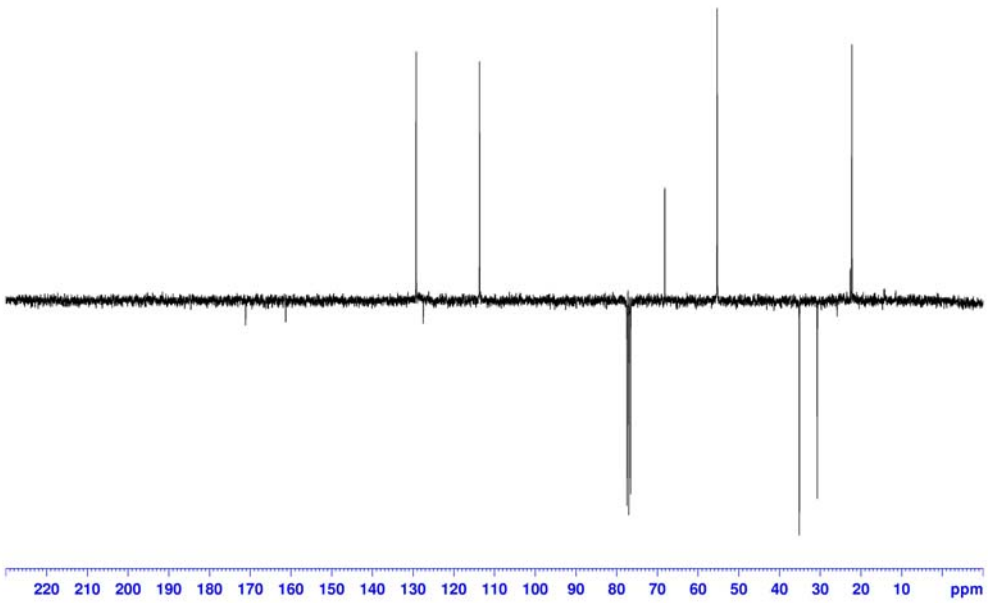
For literature data on these and related iminyl and iminoxyl radicals see: A. R. Forrester and F. A. Neugebauer, in *Landolt-Bornstein, Magnetic Properties of Free Radicals, Vol. II9c1*, eds. H. Fischer and K.-H. Hellwege, Springer-Verlag, Berlin, 1979, p. 115.

NMR Spectra of Dihydropyrroles

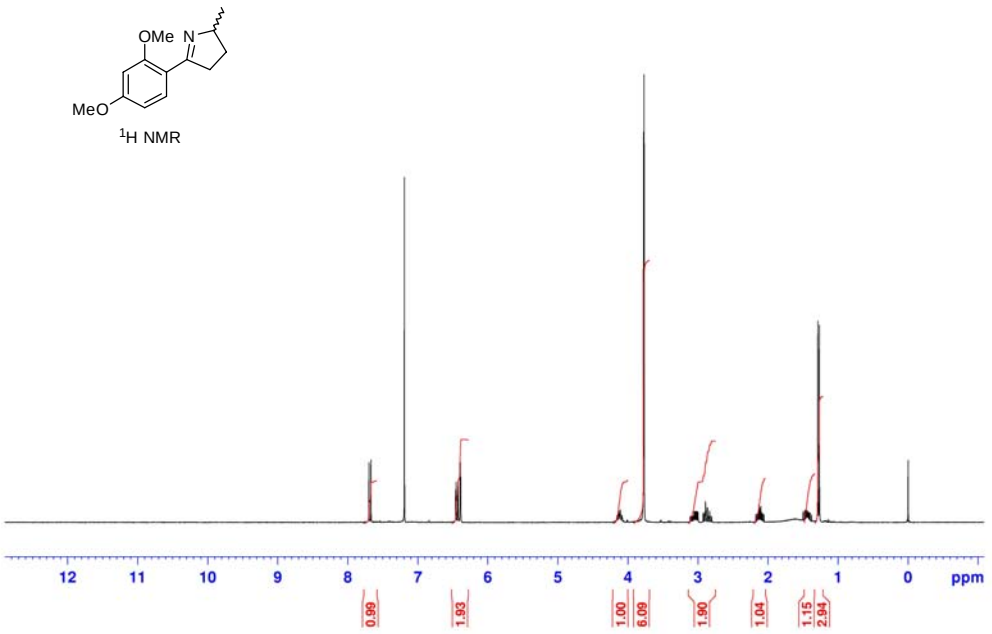
NMR spectra of 7a

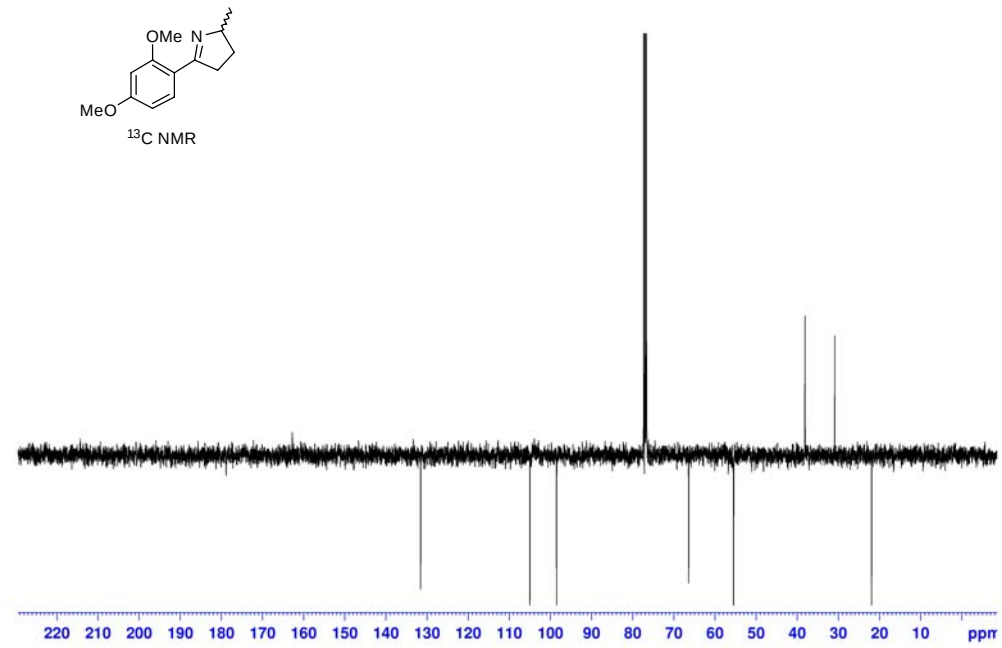


^{1}H NMR



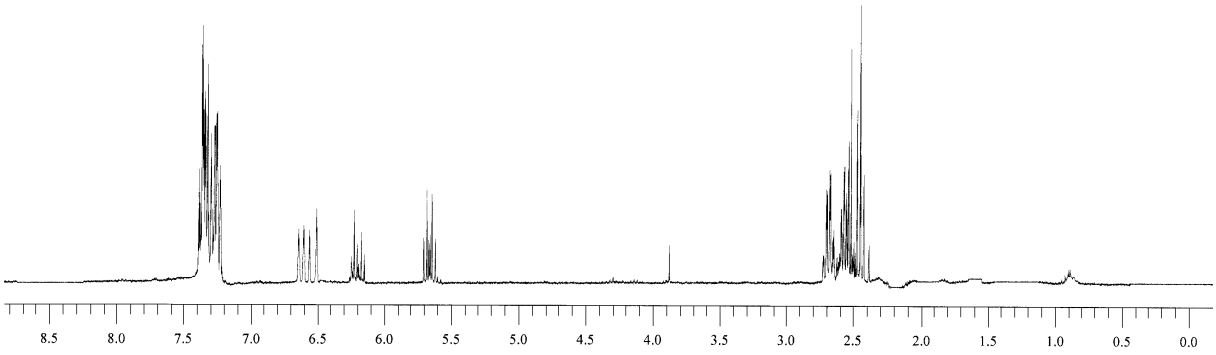
NMR Spectra of 7b



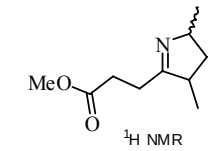


^{1}H NMR spectrum of 9

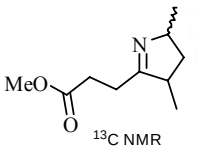
2-Benzylidiene-3,4-Dihydro-2H-Pyrole



NMR Spectra of 12a (=12b = 12c)



^{1}H NMR



^{13}C NMR