Chem. Commun.

Supporting Information:

A Novel Protecting Group Methodology for Syntheses using Nitroxides

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Electronic Supplementary Material (ESI) for Chemical Communications

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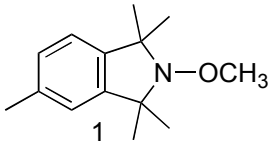
Experimental Section

General Methods: All air-sensitive reactions were carried out under ultra-high pure argon. Protection and deprotection were performed under standard laboratory conditions in air. All other reagents were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 400 MHz or Varian 400 MHz spectrometers and referenced to the relevant solvent peak. HPLC was performed with a HP Agilent 1100 HPLC instrument equiped with a Diode Array Detector (254nm) and an Agilent ZORBAX Eclipse Plus C18 (4.6x250mm, 5µm) analytical column (isocratic gradient 90% MeOH in water over 15 minutes with a flow rate of 1 mL min^{-1}). High Resolution Mass Spectrometry (HRMS) was performed with an Agilent accurate mass QTOF LC-MS spectrometer. Compounds **2**[1], **4**[2], **6**[3], **8**[4], **9-12**[5] and **14**[6] were synthesised as previously described and were consistent with reported literature data.[1-6]

Protection: Nitroxide (1 mmol.) was dissolved in dimethylsulfoxide (5 ml/mmol.), stirred and subsequently cooled to ca. 10 °C. To the stirred solution was added $FeSO_4.7H_2O$ (2.5 mol eq.). Hydrogen peroxide (30% in water, 5 mol. eq.) was added dropwise to the stirring solution over a prolonged period of time (30 minutes/ mmol. nitroxide). The reaction was monitored by thin layer chromatography and upon completion deionised water (25 mL) was added. The aqueous solution was extracted with diethyl ether (3 x 20 mL). The organic phase was dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The crude mixture was purified via column chromatography.

Deprotection: Methoxyamine (0.5 mmol.) was stirred in dichloromethane (10 ml/mmol.) at room temperature. Solid mCPBA (≤77%, 2.5 mol eq.) was added portionwise over a period of 5 minutes. The reaction was monitored via thin layer chromatography and upon disappearance of starting material, dichloromethane (10 ml) was added. The organic layer was washed with saturated sodium bicarbonate solution (1 x 10 ml) and water (2 x 10 ml). The organic phase was then dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The crude mixture was purified via column chromatography.

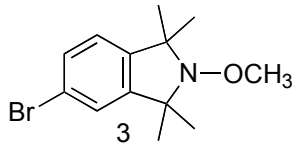
2-Methoxy-1,1,3,3,5-pentamethylisoindoline (1):



1

Protection was achieved via the general method described above. Purification via column chromatography (10 % diethyl ether: hexane) yielded the desired methoxyamine **1** (0.152 g, 74%) as a low melting solid. Care must be taken as the product is volatile. . ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.01 (dd, *J* = 7.8, 23.5 Hz, 2 H), 6.90 (s, 1 H), 3.77 (s, 3 H), 2.34 (s, 3 H), 1.41 (br. s., 12 H); ^{13}C NMR (101MHz, $CDCl_3$) δ= 145.2 (Ar-q-C), 142.3 (Ar-q-C), 136.8(Ar-CH), 128.0(Ar-CH), 122.0(Ar-CH), 121.2(Ar-CH), 67.0 (2 x q-C), 66.8 (N-O-CH_3), 65.4 (4 x CH_3), 21.4 (Ar-CH_3).

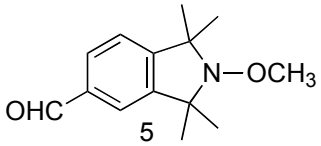
5-Bromo-2-methoxy-1,1,3,3-tetramethylisoindoline (3):



3

Protection was achieved via the general method described above. Purification via column chromatography (10 % ethyl acetate: hexane) yielded the desired methoxyamine **3** (0.284 g, 96%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.34 (dd, *J* = 1.8, 8.2 Hz, 1 H), 7.21 (d, *J* = 1.8 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 1 H), 3.77 (s, 3 H), 1.41 (br. s., 12 H); ^{13}C NMR (101MHz, $CDCl_3$) δ = 147.5 (2 x Ar-q-C), 144.2 (Ar-q-C), 130.2 (Ar-CH), 124.8 (Ar-CH), 123.3 (Ar-CH), 120.7 (Ar-C-Br), 67.0 (2 x q-C), 66.9 (N-O-CH_3), 65.5 (4 x CH_3).

5-Formyl-2-methoxy-1,1,3,3-tetramethylisoindoline (5):

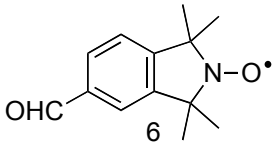


5

To a stirred solution of **3** (1.041 g, 3.66 mmol) in anhydrous tetrahydrofuran (25 mL) at -78 °C was added n-BuLi (1.6 M, 2.75 mL, 4.4 mmol) in a dropwise fasion. The solution was stirred at -78 °C for 10 minutes. Anhydrous *N, N*-dimethylformamide (0.85 mL, 1.10 mmol) was subsequently added dropwise and the solution was stirred for 1 hour while being allowed to warm slowly to room temperature. Upon completion of the reaction ice water (50 mL) was added and the aqueous solution was extracted with diethyl ether (3 x 50 mL). The organic

phase was washed with water (2 x 20 mL) and then dried with Na_2SO_4, filtered and the solvent removed *in vacuo*. The resultant yellow oil was purified via column chromatography (10 % diethyl ether: hexane) to yield **5** (0.740, 87%) as a colourless solid. M.p. 66-67 °C. . ^{1}H NMR ($CDCl_3$, 400MHz) δ = 9.98 (s, 1 H), 7.75 (dd, *J*=7.8, 1.6 Hz, 1 H), 7.64 (d, *J*=1.2 Hz, 1 H), 7.25-7.27 (d, *J*=7.8 Hz, 2 H), 3.78 (s, 3 H), 1.46 (br, s, 12 H); ^{13}C NMR ($CDCl_3$, 101MHz): δ = 192.0 (Ar-CHO), 152.5 (Ar-q-C), 136.1 (Ar-q-C), 130.1 (Ar-q-C), 122.4 (2 x Ar-CH), 122.2 (Ar-CH), 67.3 (2 x q-C), 66.9 (N-O-CH_3), 65.6 (4 x CH_3); HRMS (*m/z*): $[M+Na]^+$ calculated for $C_{14}H_{19}NO_2Na$, 256.1313; found, 256.1311.

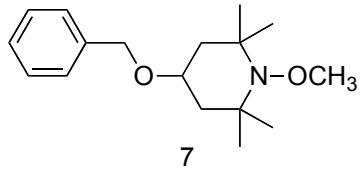
5-Formyl-1,1,3,3-tetramethylisoindoline-2-yloxyl (6):



6

Deprotection of **5** was achieved via the general method described previously. Purification via column chromatography (15 % diethyl ether: hexane) yielded the desired nitroxide **6** (0.191 g, 88%) as a yellow solid. M.p. 139-140 °C. (Lit. 139-141 °C)[3]; HRMS (*m/z*): $[M+Na]^+$ calculated for $C_{13}H_{16}NO_2Na$•, 256.1313; found, 256.1311.

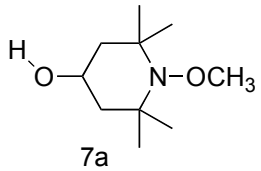
4-(Benzyloxy)-1-methoxy-2,2,6,6-tetramethylpiperidine (7):



7

Protection was achieved via the general method described previously. Purification via column chromatography (10 % ethyl acetate: hexane) yielded the desired methoxyamine (0.1864 g, 68%) as a pale orange oil. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.23 - 7.40 (m, 5 H), 4.52 (s, 2 H), 3.62 - 3.72 (m, 1 H), 3.61 (s, 3 H), 1.90 (dt, *J*=12.9, 1.6 Hz, 2 H), 1.50 (t, *J*=11.7 Hz, 2 H), 1.22 (s, 6 H), 1.10 ppm (s, 6 H); ^{13}C NMR ($CDCl_3$, 101MHz) δ = 138.8 (Ar-q-C), 128.3 (2 x Ar-CH), 127.5 (Ar-CH), 127.4 (2 x Ar-CH), 70.1(Ar-CH_2-), 65.4 (Ar-O-CH-), 59.9 (N-O-CH_3), 45.0 (2 x q-C), 33.2 (2 x CH_2), 20.9 (4 x CH_3); HRMS (*m/z*): $[M+H]^+$ calculated for $C_{17}H_{28}NO_2^+$, 278.2115; found, 278.1018.

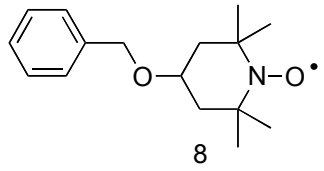
1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol (7a):



7a

Protection was achieved via the general method described previously. Following extraction the solvent was removed *in vacuo* to give a white solid (0.138, 74%). Purification was not performed due to the volatile nature of the compound and the lack of chromaphore for TLC identification. M.p. 77-79 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ = 3.94 (t, *J* = 11.2 Hz, 1 H), 3.61 (s, 3 H), 2.99 (s, 1 H), 1.80 (d, *J* = 10.6 Hz, 2 H), 1.45 (t, *J* = 11.7 Hz, 2 H), 1.21 (s, 6 H), 1.13 (s, 6 H); ^{13}C NMR (101MHz, $CDCl_3$) δ = 65.4 (N-O-CH_3), 63.3 (CH-OH), 60.0 (2 x q-C), 48.3 (2 x CH_2), 33.0 (2 x CH_3), 20.8 (2 x CH_3). HRMS (*m/z*): $[M+H]^+$ calculated for $C_{10}H_{22}NO_2^+$, 188.1645; found, 188.1644.

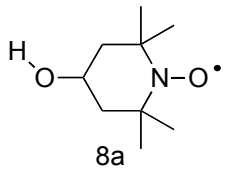
4-Benzyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (8):



8

4-Hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (0.310 g, 1.8 mmol) in anhydrous *N,N*-dimethylformamide (2 mL) was stirred at 0 °C. NaH (60% in mineral oil, 0.110 g, 1.5 eq.) was added and the solution stirred for 10 minutes at 0 °C before warming to room temperature for a further 30 minutes. Benzyl bromide (0.23 mL, 0.341 g, 2.0 mmol) was added dropwise and the solution stirred for a further 1 hour. The reaction was subsequently poured onto ice and water (15 mL) was added slowly. The aqueous solution was extracted with diethyl ether (3 x 10 mL) and the combined organic phases were dried with Na_2SO_4, filtered and the solvent removed *in vacuo*. The resultant red oil was purified via column chromatography (20% ethyl acetate: hexanes) to yield the desired product (**8**, 0.463 g, 97 %) as a red/orange solid. M.p. 61-63 °C. (Lit. 63-64 °C)[4]; HRMS (*m/z*): $[M+Na]^+$ calculated for $C_{16}H_{24}NO_2Na•$, 285.1705; found, 285.0603. $[M+K]^+$ calculated for $C_{16}H_{24}NO_2K•$, 301.1444; found, 301.1445.

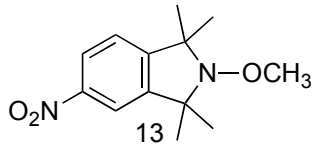
4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (8a):



8a

Deprotection was achieved via the general method described previously. The reaction mixture was analysed via a GC-MS study demonstrated in a later section of this supporting information.

2-Methoxy-1,1,3,3-tetramethyl-5-nitroisoindoline (13)



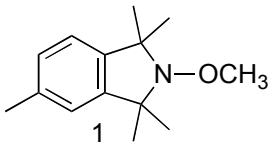
13

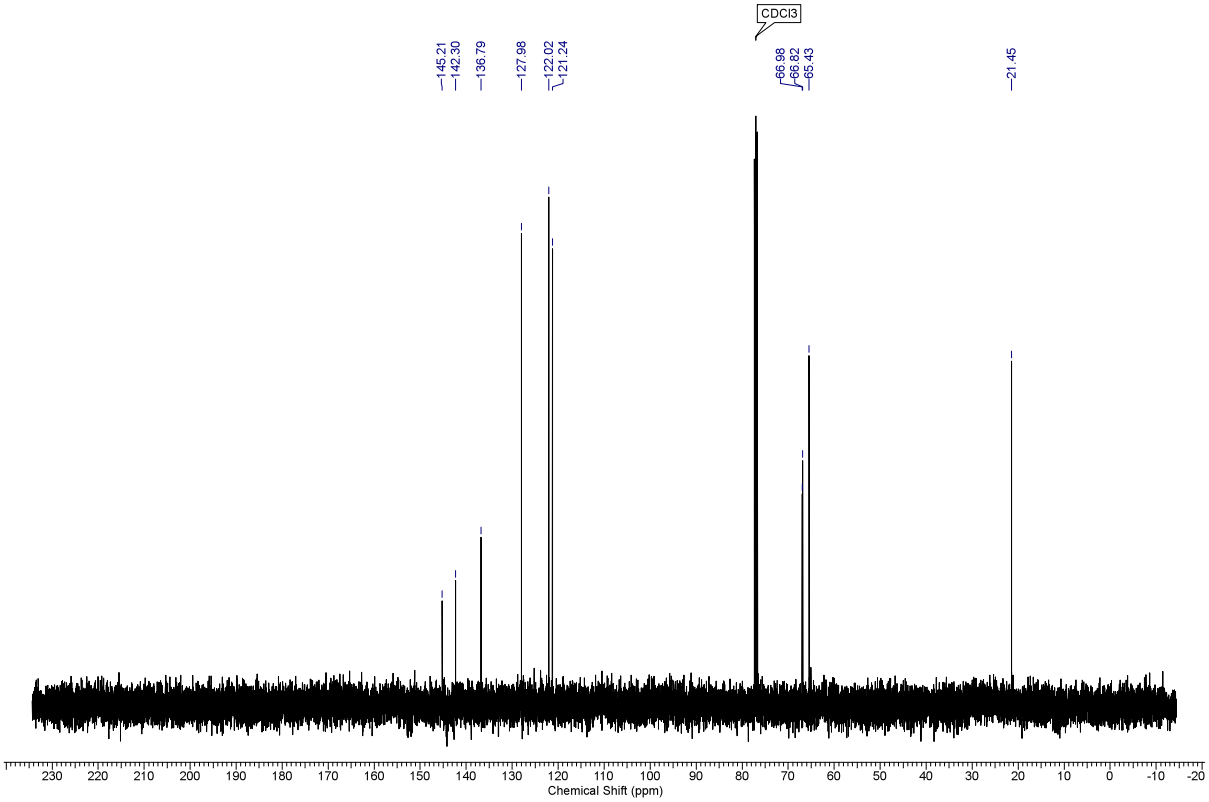
Protection was achieved via the general method described previously. Purification via column chromatography (10 % ethyl acetate: hexane) yielded the desired methoxyamine (0.218 g, 87%) as a pale yellow solid. M.p. 64-66°C. ^{1}H NMR (400MHz, $CDCl_3$) δ = 8.12 (dd, *J* = 2.3, 8.2 Hz, 1 H), 7.96 (d, *J* = 1.8 Hz, 1 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 3.78 (s, 3 H), 1.47 (br. s., 12 H); 13C NMR (101MHz ,$CDCl_3$) δ = 152.7, 147.8, 147.1, 123.1, 122.4, 117.3, 67.3, 67.1, 65.6; HRMS (m/z): $[M+Na]^+$ calculated for $C_{13}H_{18}N_2O_3Na$, 273.1215; found, 273.1224.

Electronic Supplementary Material (ESI) for Chemical Communications

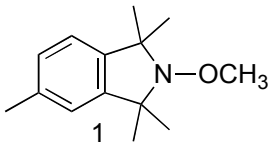
^{1}H and ^{13}C NMR Spectra and HPLC traces

2-Methoxy-1,1,3,3,5-pentamethylisoindoline (1)





2-Methoxy-1,1,3,3,5-pentamethylisoindoline (1)



Dr B. A. Chalmers - HPLC Analysis Report

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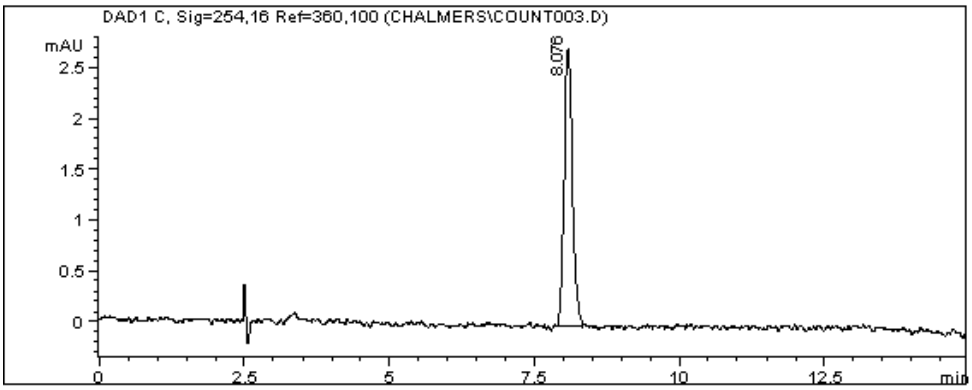

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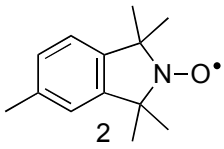
Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

5-Methyl-1,1,3,3-tetramethylisoindoline-2-yloxyl (2)



2

Dr B. A. Chalmers - HPLC Analysis Report

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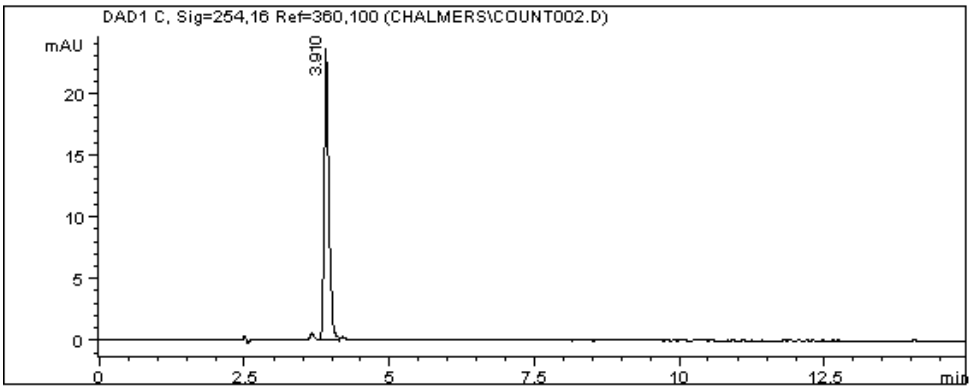

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Conditions and other information
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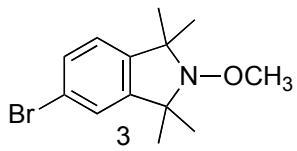
5-Bromo-2-methoxy-1,1,3,3-tetramethylisoindoline (3)



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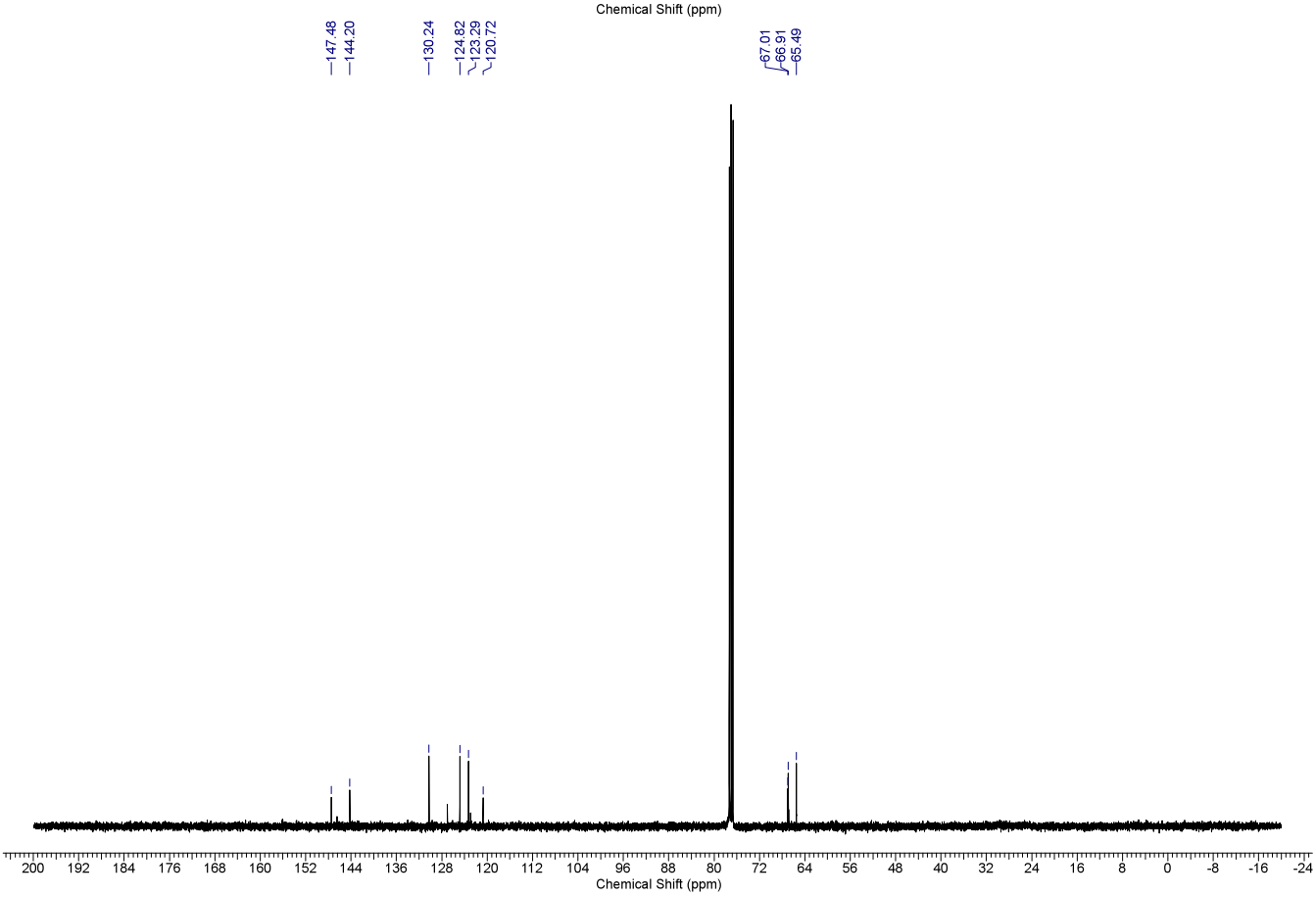
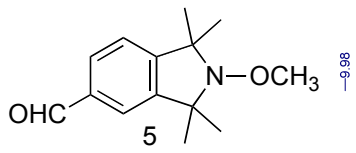
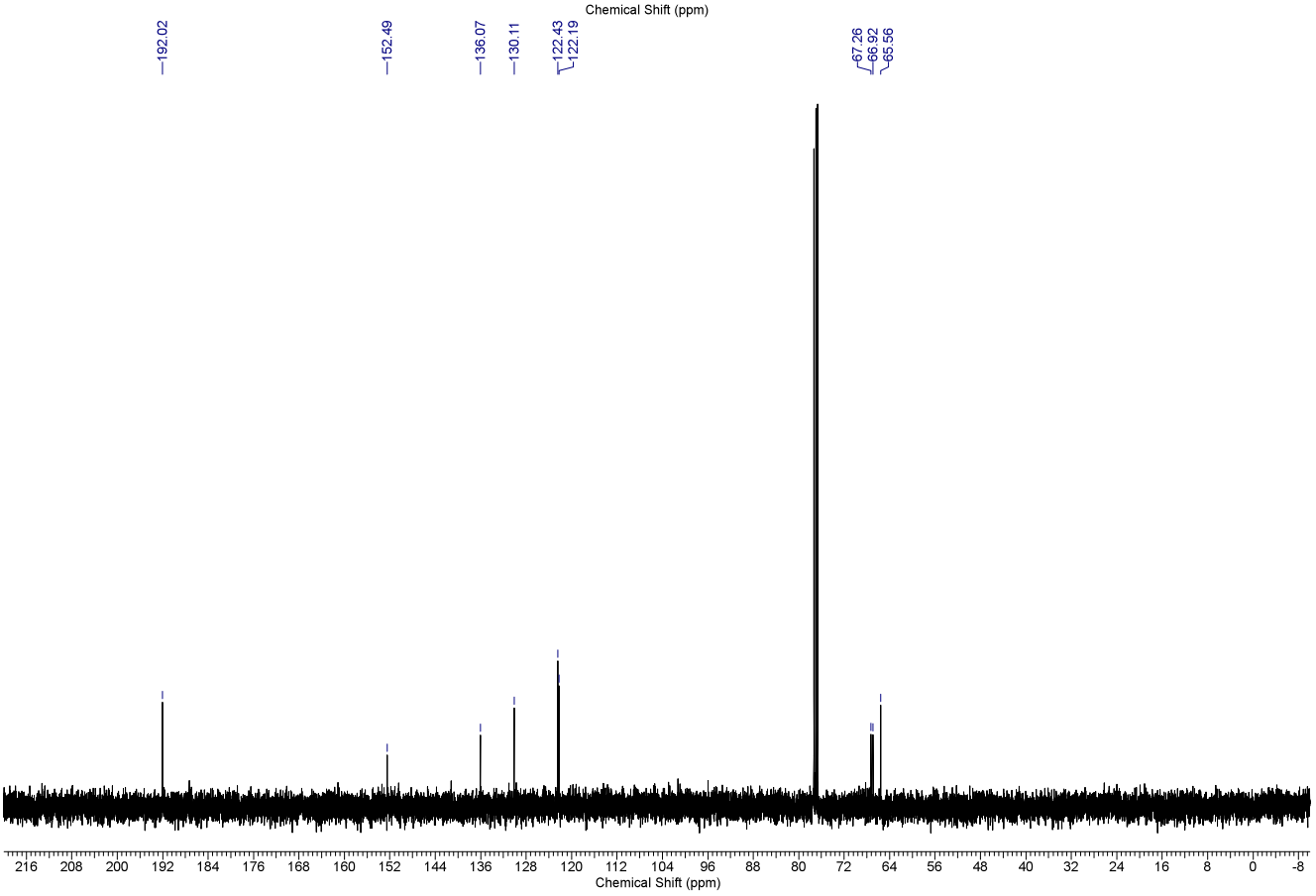
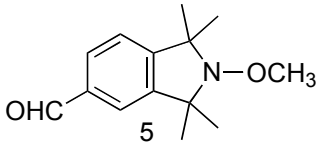


5-Formyl-2-methoxy-1,1,3,3-tetramethylisoindoline (5)





5-Formyl-2-methoxy-1,1,3,3-tetramethylisoindoline (5)



Dr B. A. Chalmers - HPLC Analysis Report

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Vial:            5
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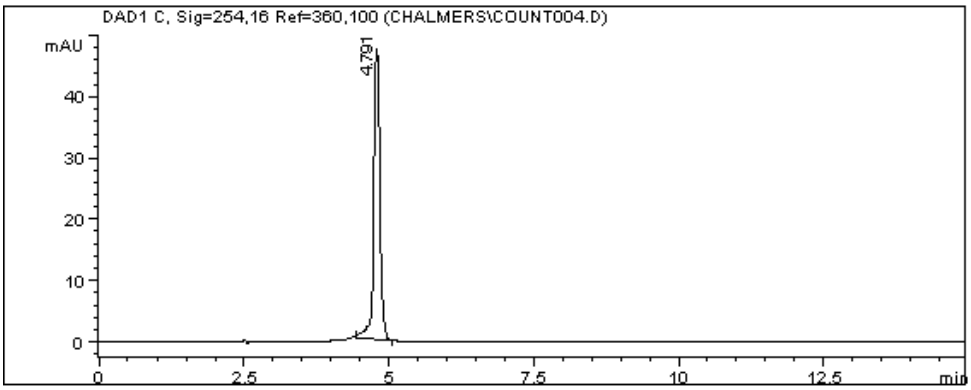

Peak No.	Time (Min)	Area	Area (%)
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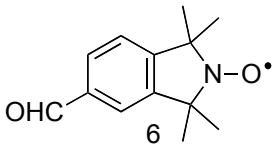
Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

5-Formyl-1,1,3,3-tetramethylisoindoline-2-yloxyl (6)



Dr B. A. Chalmers - HPLC Analysis Report

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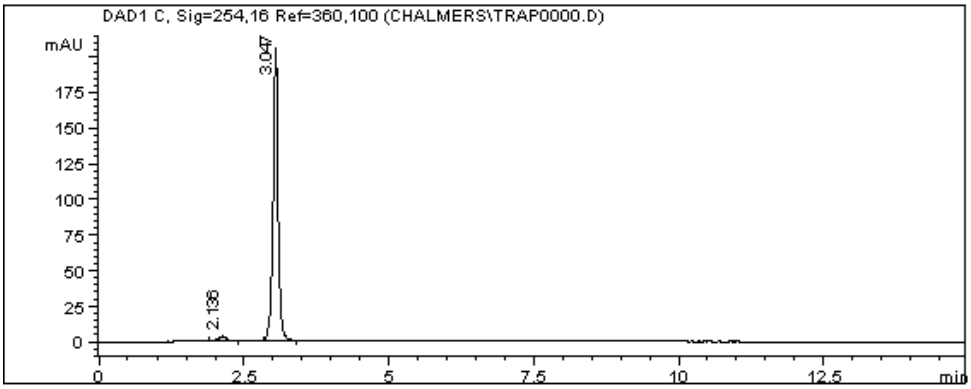

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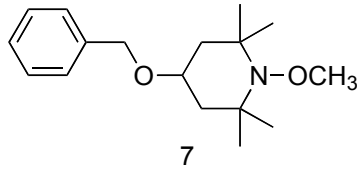
2	3.047	1267.880	97.154

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

4-(Benzyloxy)-1-methoxy-2,2,6,6-tetramethylpiperidine (7)



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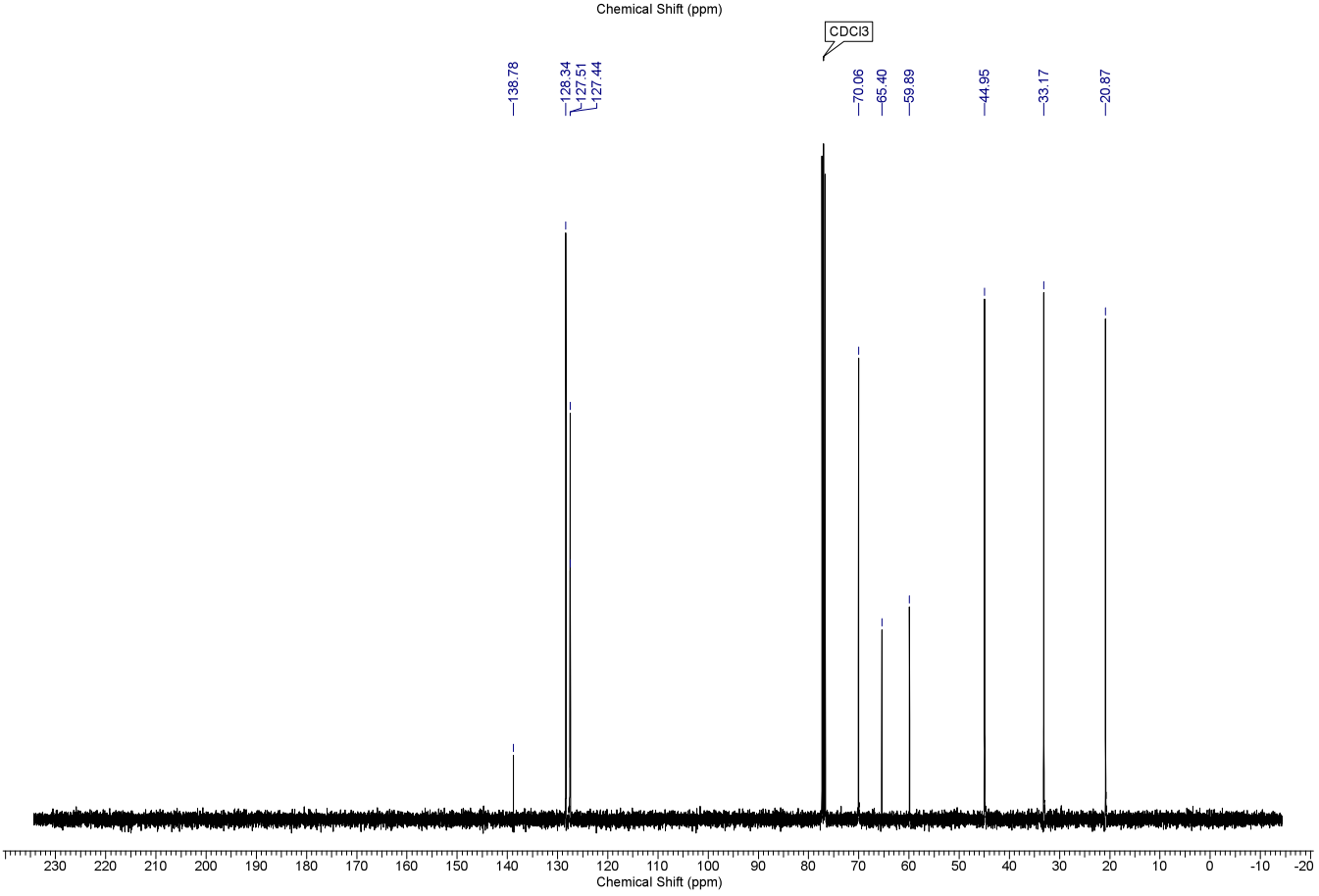
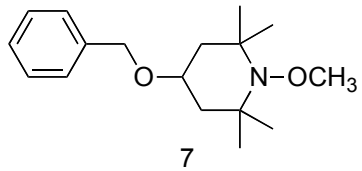


4-(Benzyloxy)-1-methoxy-2,2,6,6-tetramethylpiperidine (7)



7

Dr B. A. Chalmers - HPLC Analysis Report

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================================================================================
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Time:            11:32:49 AM    Monday, 15 July 2013
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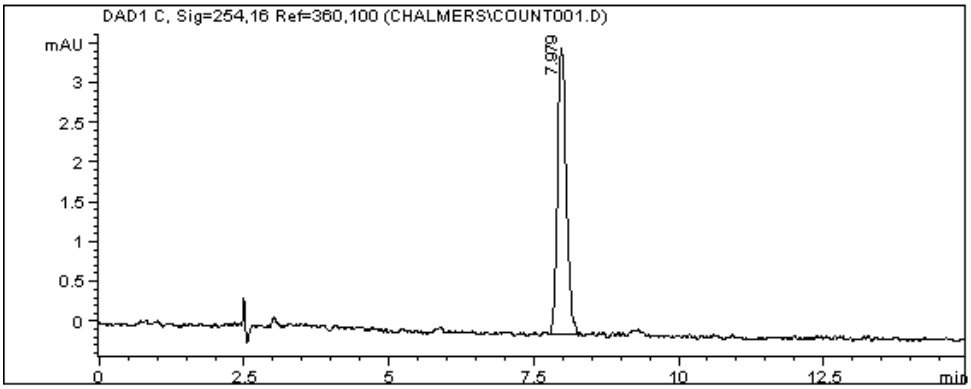
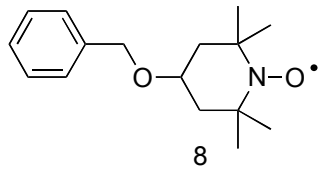


Peak No.	Time (Min)	Area	Area (%)
1	7.979	37.449	100.000

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

4-benzyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (8)



8

Dr B. A. Chalmers - HPLC Analysis Report

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================================================================================
Sample Name:   BnOTEMP02
File:          C:\HPCHEM\1\DATA\CHALMERS\COUNT005.D
Method:        C:\HPCHEM\1\METHODS\CHALMERS.M
Operator(s):    Chalmers
Vial:           1
Time:           12:40:27 PM    Monday, 15 July 2013
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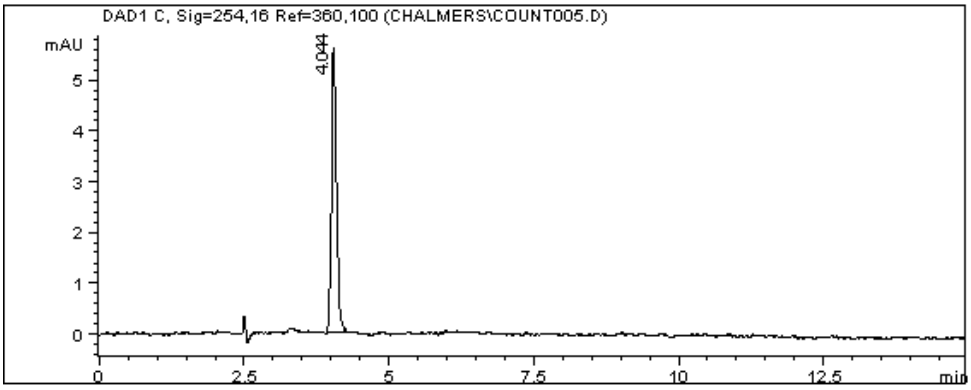
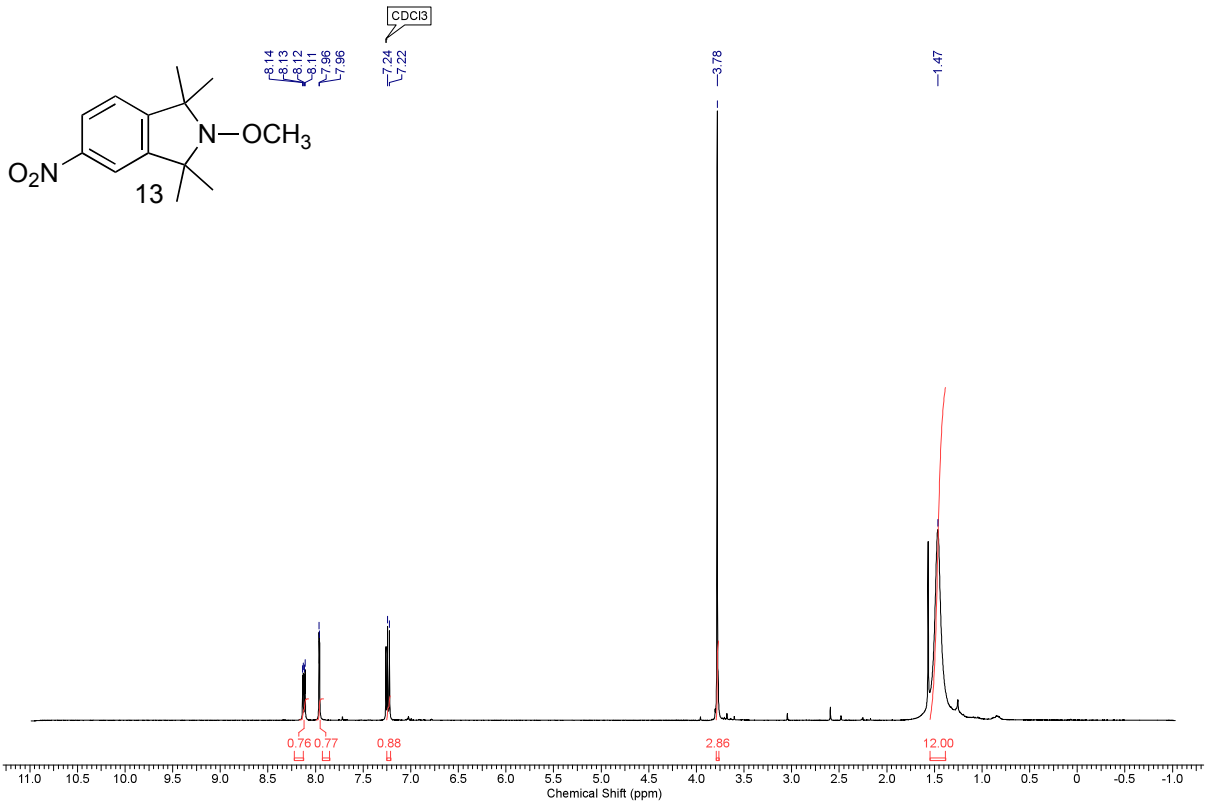


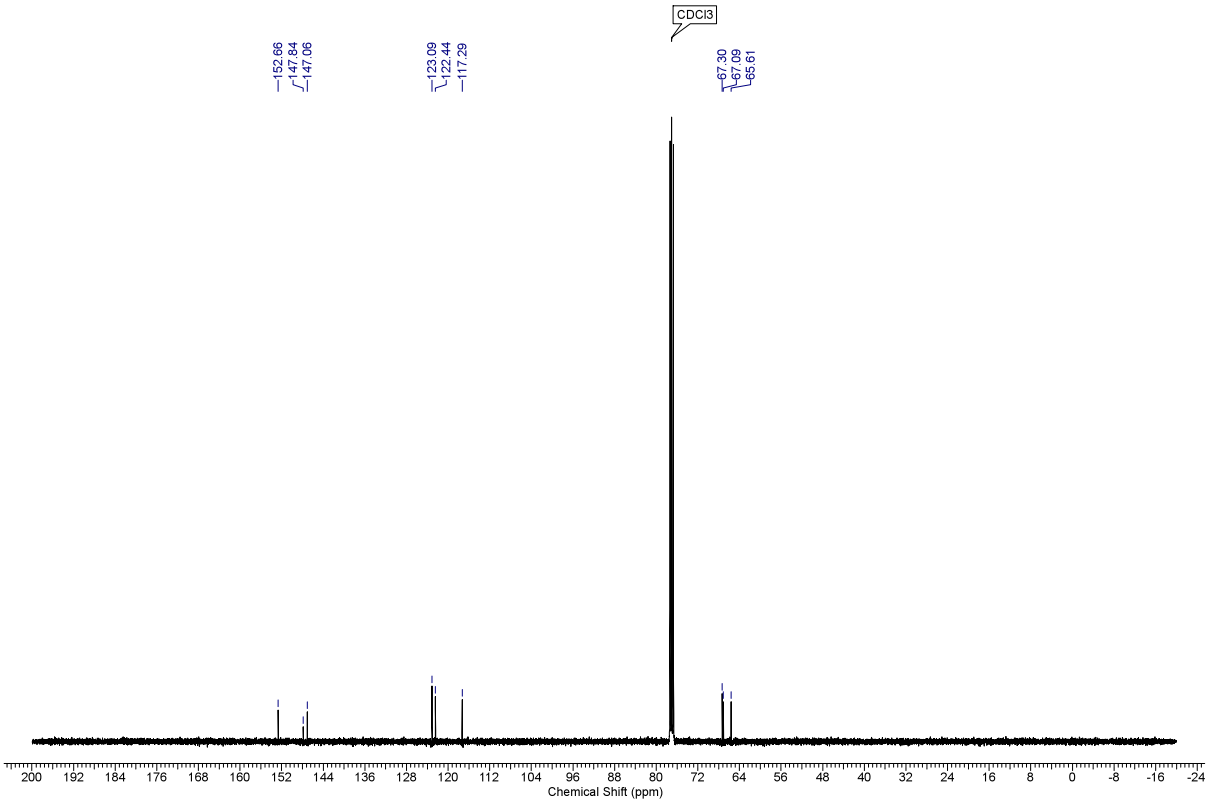
Peak No.	Time (Min)	Area	Area (%)
1	4.044	33.689	100.000

Conditions and other information

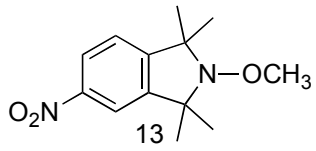
Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

2-Methoxy-1,1,3,3-tetramethyl-5-nitroisoindoline (13)





2-Methoxy-1,1,3,3-tetramethyl-5-nitroisoindoline (13)



Dr B. A. Chalmers - HPLC Analysis Report

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================================================================================
Sample Name:    NITRO-TMIOMT
File:           C:\HPCHEM\1\DATA\CHALMERS\TRAP0001.D
Method:         C:\HPCHEM\1\METHODS\CHALMERS.M
Operator(s):     Chalmers
Vial:            2
Time:            2:41:06 PM     Wednesday, 17 July 2013
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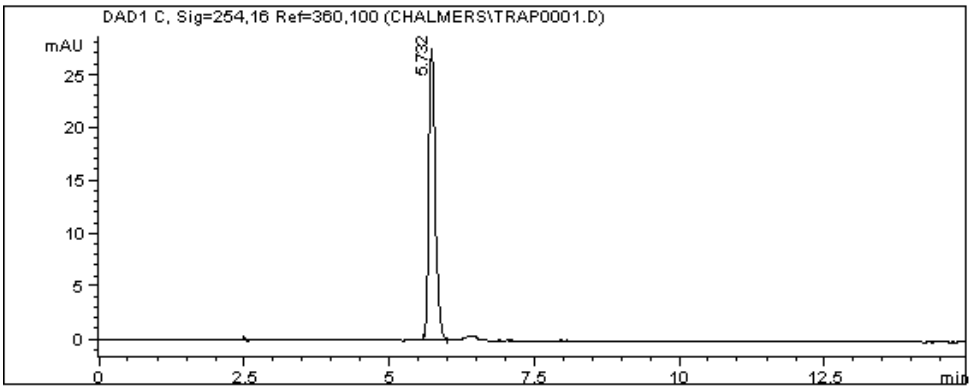
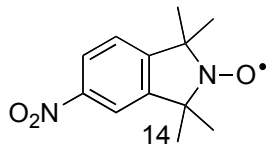


Peak No.	Time (Min)	Area	Area (%)
1	5.732	215.614	100.000

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

1,1,3,3-Tetramethyl-5-nitroisoindoline-2-yloxyl (14)



Dr B. A. Chalmers - HPLC Analysis Report

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================================================================================
Sample Name:    NITRO-TMIO
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Method:         C:\HPCHEM\1\METHODS\CHALMERS.M
Operator(s):     Chalmers
Vial:            3
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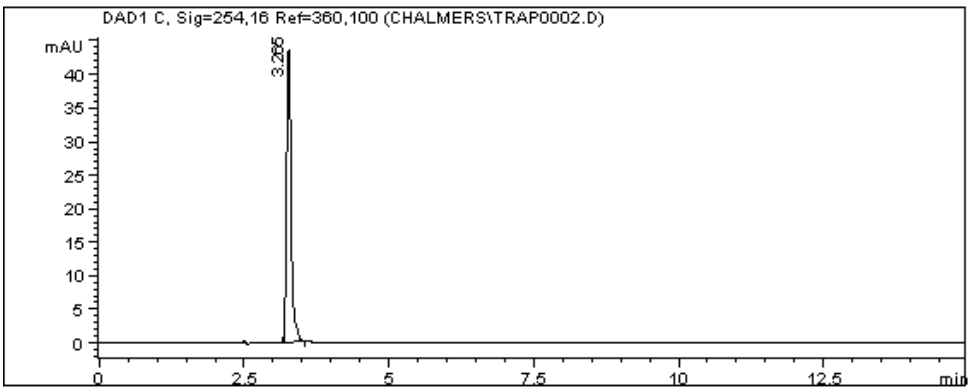


Peak No.	Time (Min)	Area	Area (%)
1	3.265	237.067	100.000

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
Injection size: 1uL
Solvent System: 90% Methanol / 10% Water

Electronic Supplementary Material (ESI) for Chemical Communications

GC-MS Studies

Detection of Formaldehyde:

GC-MS Conditions:

Column	Agilent 19091S-413 HP5-MS Max temperature: 325 ºC Nominal length: 30.0 m Nominal diameter: 320.00 µm Nominal film thickness: 0.25 µm Mode: Constant flow Initial flow: 1.0 mL/min. Nominal init pressure: 0.68 psi Average velocity: 37 cm/sec. Inlet: Front Inlet Outlet: MSD Outlet pressure: Vacuum
Front Inlet	Mode: Split Initial temp: 260 ºC (On) Pressure: 0.68 psi (On) Split ratio: 20:1 Split flow: 20.0 ml/min. Total flow: 24.2 ml/min. Gas saver: Off Gas type: Helium
Oven	Initial temp: 100 ºC (On) Maximum temp: 325 ºC Initial time: 1.00 min. Equilibration time: 0.00 min. Ramp Rate: 20 ºC/min. Final Temp.: 300 ºC Final Time: 15 min. Post temp: 100 ºC Post time: 0.00 min. Run time: 15.00 min.
Injector	Sample Washes: 3 Sample Pumps: 3 Injection Volume: 1.00 µl Syringe Size: 10.0 µl Pre Inj. Solvent Washes: 3 Post Inj. Solvent Washes: 6 Viscosity Delay: 0 sec. Plunger Speed: Fast Pre-Injection Dwell: 0.00 min. Post-Injection Dwell: 0.00 min.

2,4-Dinitrophenylhydrazine solution

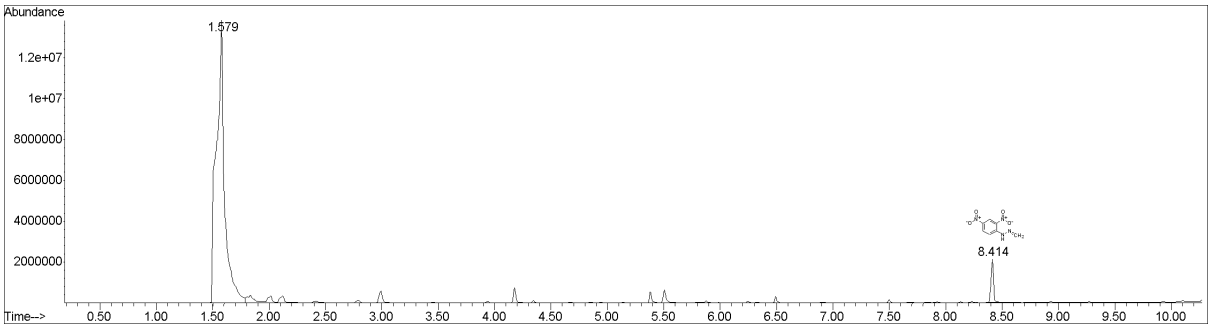
2,4-Dinitrophenylhydrazine (0.150g, 0.76 mmol) was dissolved in concentrated H_2SO_4 (0.75 ml). To the solution was then added water (1 ml) dropwise followed by ethanol (3.75 ml). The resultant 0.14 M solution was used undiluted.

Reaction Conditions:

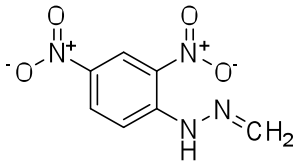
Formaldehyde (0.2 ml, ~35% in H_2O) was added to a solution of 2,4-dinitrophenylhydrazine (0.2 ml). A yellow precipitate was formed. To the resultant suspension was added methylene chloride (0.5 ml). The organic phase was then immediately separated and analysed via GCMS.

GC-MS Results

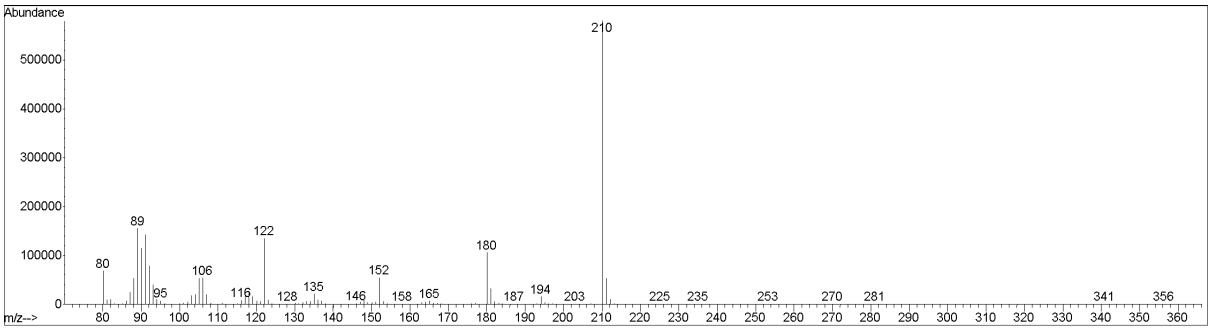
GC-MS Trace 1 – Reaction of formaldehyde with 2,4-dinitrophenylhydrazine



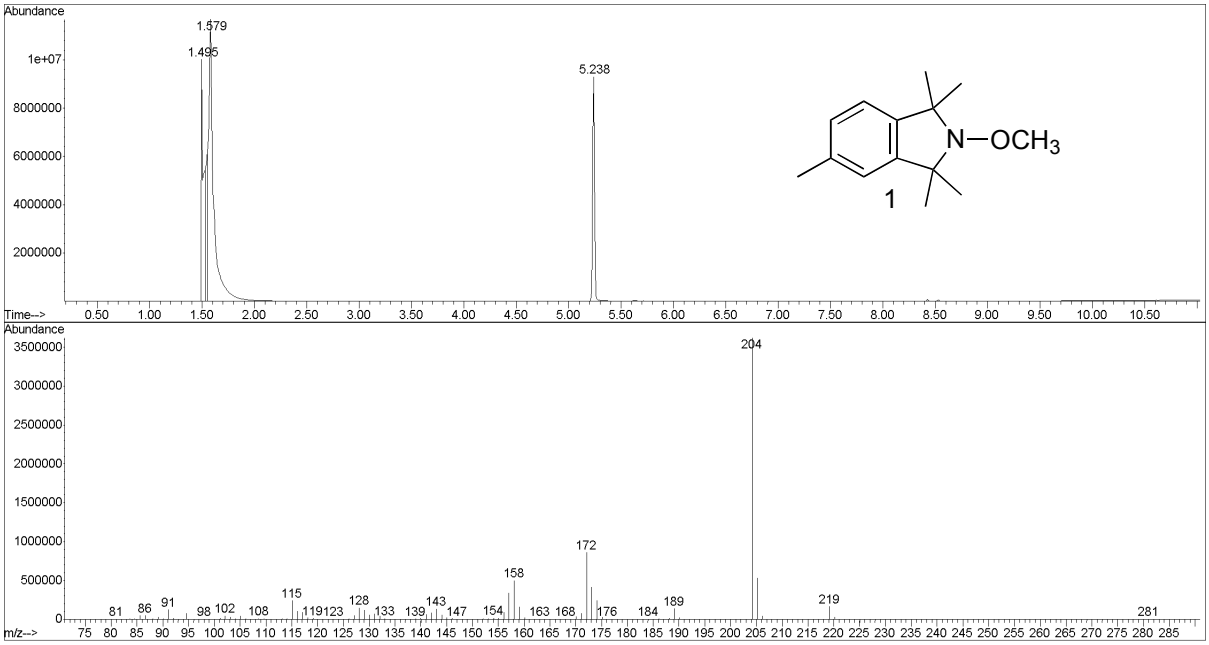
1-(2,4-Dinitrophenyl)-2-methylenehydrazine (8.414min.)



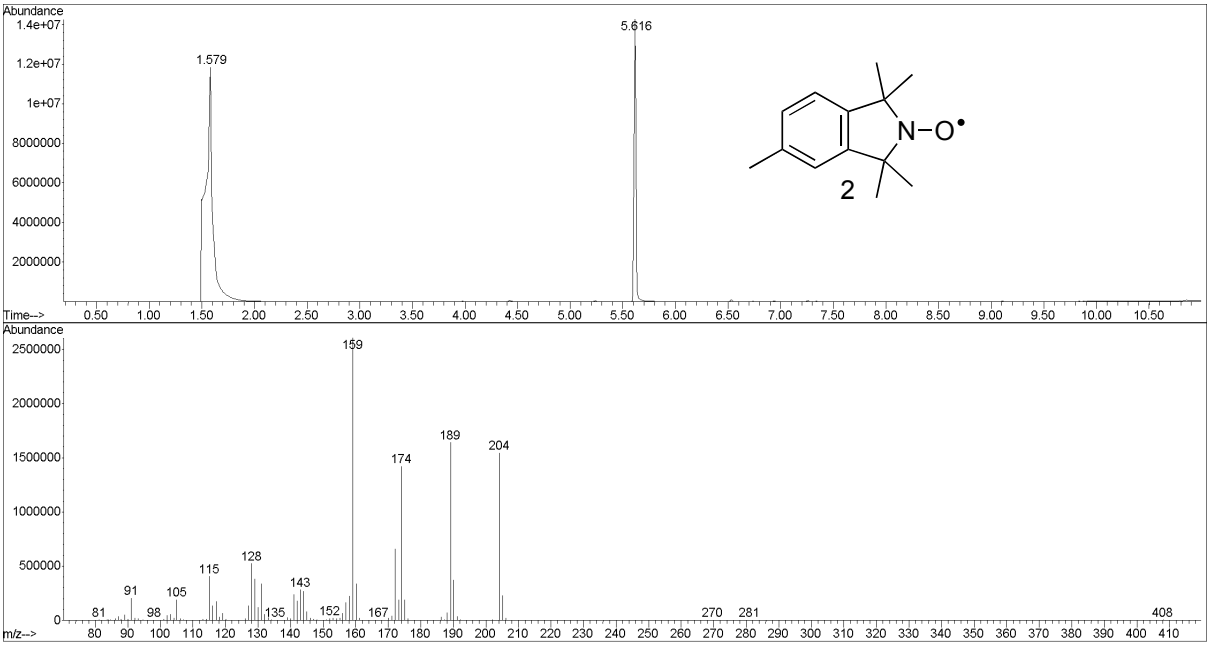
Chemical Formula: $C_7H_6N_4O_4$
Exact Mass: 210.0389
Molecular Weight: 210.1490
m/z: 210.0389 (100.0%)



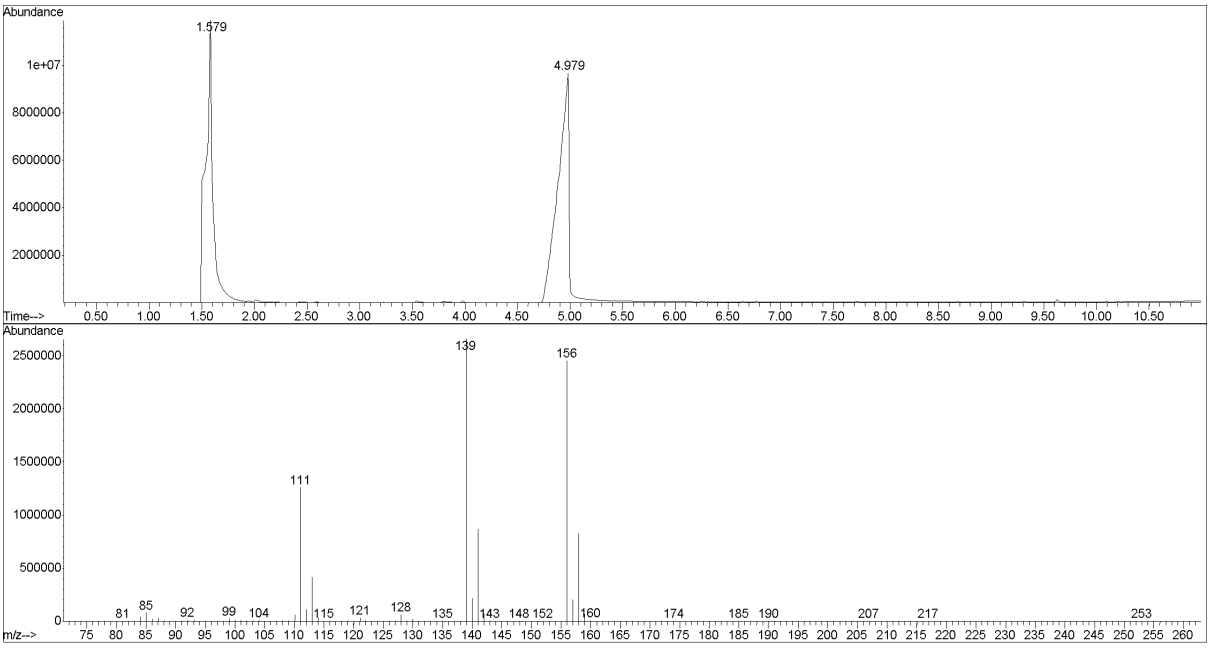
GC-MS Trace 2 – 2-Methoxy-1,1,3,3,5-pentamethylisoindoline (**1**) (5.238 min.) in methylene chloride.



GC-MS Trace 3 – 1,1,3,3,5-Pentamethylisoindolin-2-yloxyl (**2**) (5.616 min.) in methylene chloride.



GC-MS Trace 4 – 3-Chloroperbenzoic acid (4.979 min.) in methylene chloride.

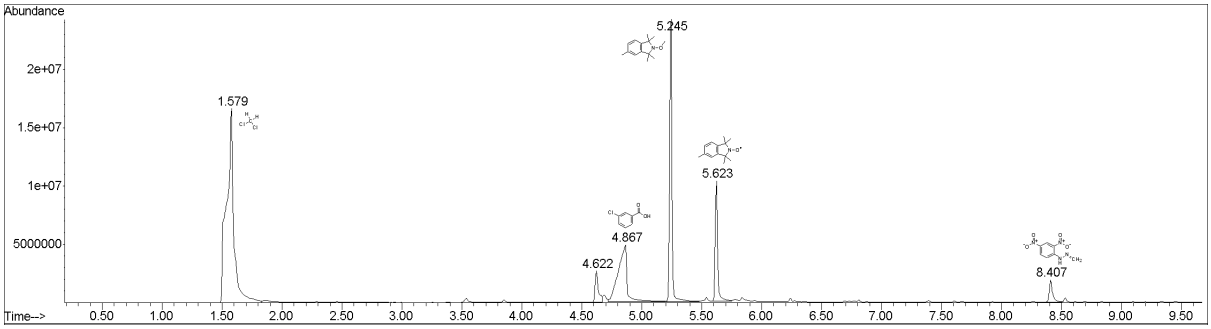


Reaction conditions:

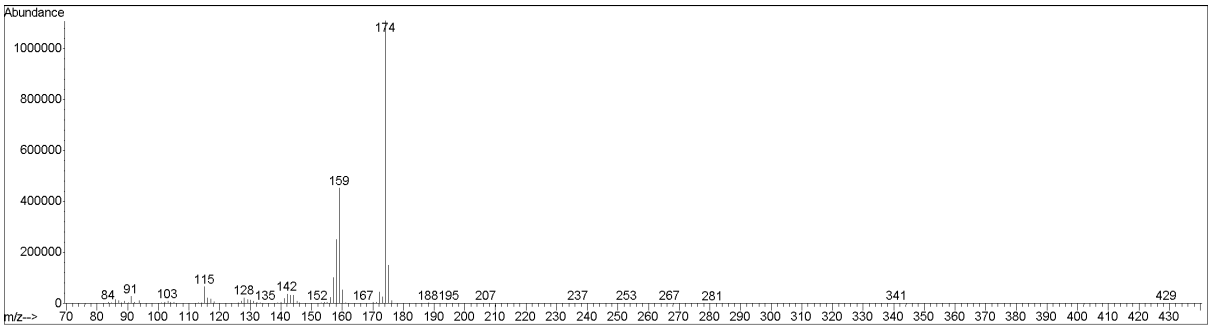
1,1,3,3,5-Pentamethylisoindolin-2-yloxyl (0.008 g, 0.04 mmol) was dissolved in methylene chloride (5 ml). The solution was then added to a solid sample of 3-chloroperbenzoic acid (0.004 g, 0.02 mmol). The result solution was sealed and shaken intermittently for 20 minutes at room temperature to ensure complete reaction. To the solution was then added 2,4-dinitrophenylhydrazine (0.14 M, 0.3 ml, 0.04 mmol) and the mixed solution was analysed via GC-MS.

GC-MS Results

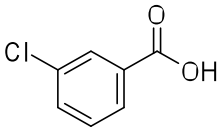
GC-MS Trace 5 – 3-Chloroperbenzoic acid (0.5 eq.) reaction with 2-methoxy-1,1,3,3,5-pentamethylisoindoline followed by addition of 2,4-dinitrophenylhydrazine.



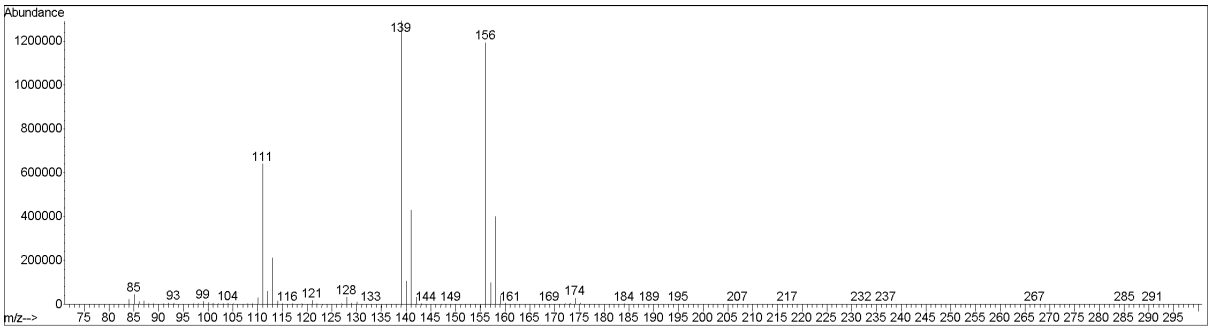
Unidentified compound (4.622min.)



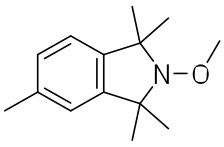
3-Chlorobenzoic Acid (4.867min.)



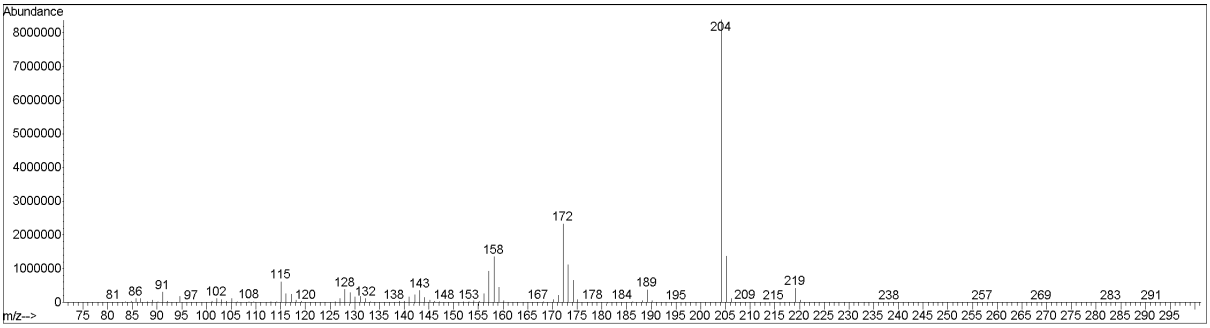
Chemical Formula: $C_7H_5ClO_2$
Exact Mass: 155.9978
Molecular Weight: 156.5650
m/z: 155.9978 (100.0%), 157.9949 (32.0%)



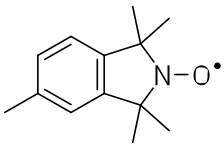
2-Methoxy-1,1,3,3,5-pentamethylisoindoline (**1**) (5.245min.)



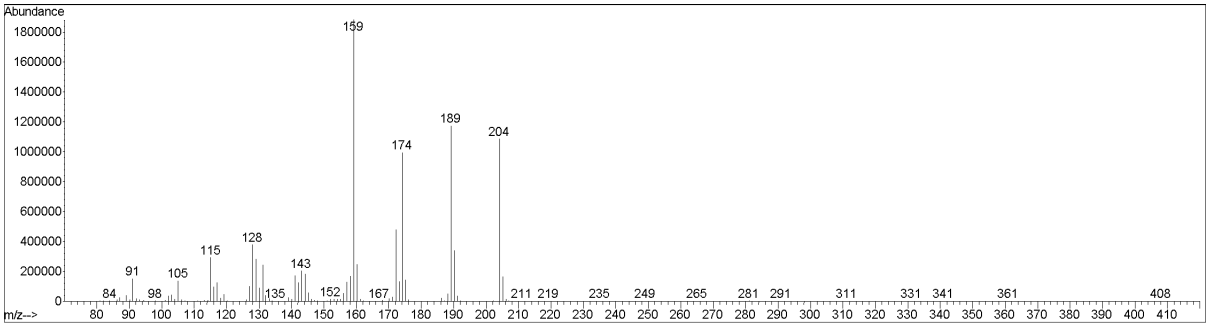
Chemical Formula: $C_{14}H_{21}NO$
Exact Mass: 219.1623
Molecular Weight: 219.3280
m/z: 219.1623 (100.0%)



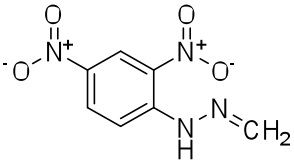
1,1,3,3,5-Pentamethylisoindolin-2-yloxyl (**2**), (5.623 min.)



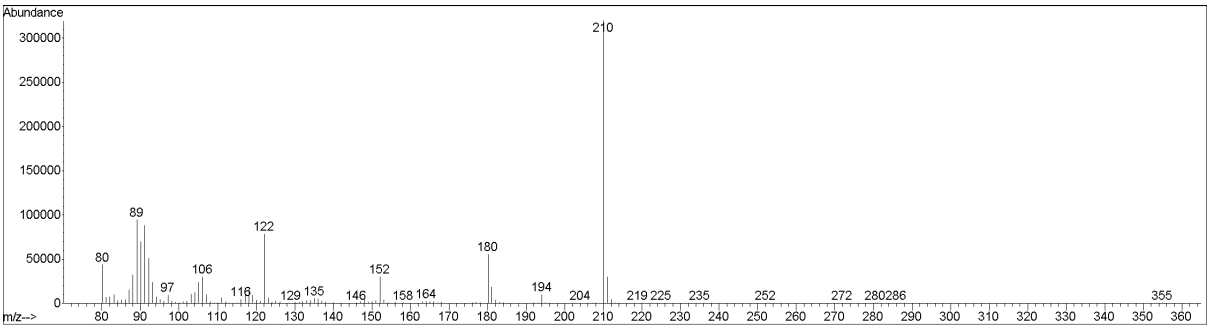
Chemical Formula: $C_{13}H_{18}NO^{\bullet}$
Exact Mass: 204.1388
Molecular Weight: 204.2930
m/z: 204.1388 (100.0%)



1-(2,4-Dinitrophenyl)-2-methylenehydrazine (8.407min.)



Chemical Formula: $C_7H_6N_4O_4$
Exact Mass: 210.0389
Molecular Weight: 210.1490
m/z: 210.0389 (100.0%)

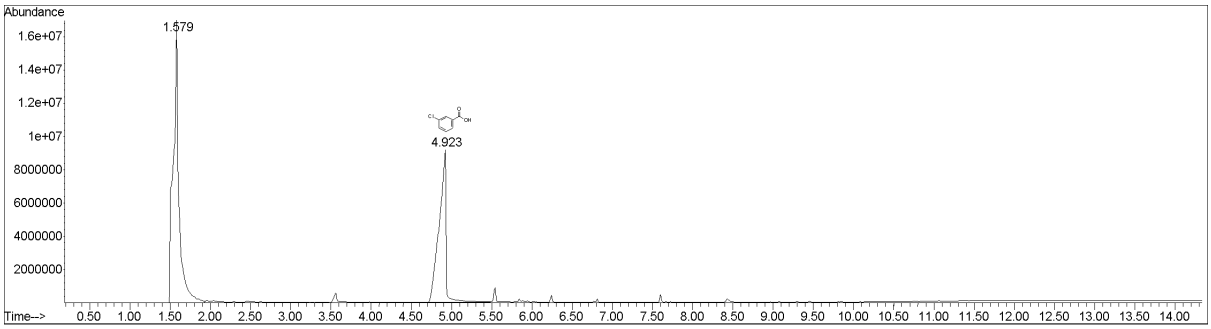


In order to ensure that mCPBA acid and 2,4-DNPH did not produce the observed 1-(2,4-dinitrophenyl)-2-methylenehydrazine, a control experiment was performed.

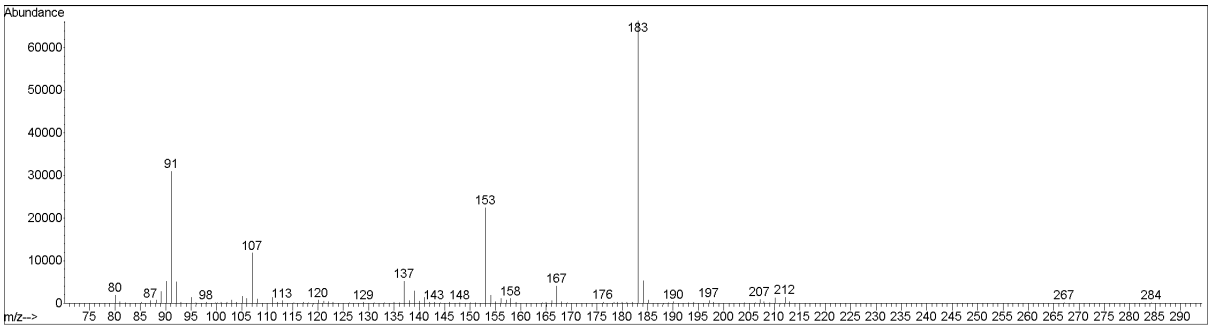
Reaction conditions:

To a solution of mCPBA (0.004 g, 0.02 mmol) in methylene chloride (0.5 ml) was added 2,4-DNPH (0.14 M, 0.2 ml, 0.03 mmol). The resultant solution was shaken and analysed by GC-MS.

GC-MS Trace 6 – 2,4-DNPH and mCPBA in methylene chloride



Minor peak observed (8.428min.) does not correspond to 1-(2,4-dinitrophenyl)-2-methylenehydrazine.



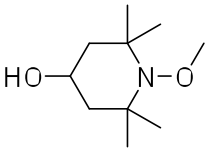
TEMPOL GC-MS Study

GC-MS Conditions:

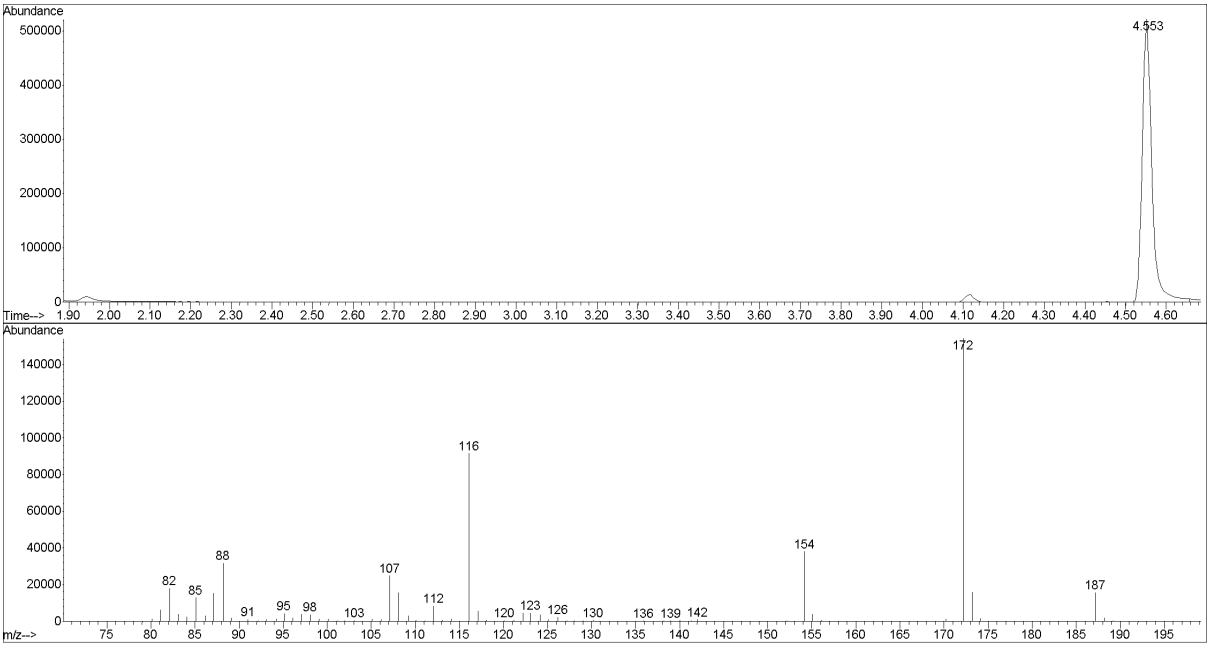
Column	Agilent 19091S-413 HP5-MS Max temperature: 325 ºC Nominal length: 30.0 m Nominal diameter: 320.00 µm Nominal film thickness: 0.25 µm Mode: Constant flow Initial flow: 1.2 mL/min Nominal init pressure: 2.15 psi Average velocity: 41 cm/sec. Inlet: Front Inlet Outlet: MSD Outlet pressure: Vacuum
Front Inlet	Mode: Split Initial temp: 200 ºC (On) Pressure: 2.15 psi (On) Split ratio: 20:1 Split flow: 24.0 ml/min. Total flow: 28.3 ml/min. Gas saver: Off Gas type: Helium
Oven	Initial temp: 100 ºC (On) Maximum temp: 325 ºC Initial time: 0.00 min. Equilibration time: 0.00 min. Ramp Rate: 10 ºC/min. Final Temp.: 300 ºC Final Time: 15 min. Post temp: 100 ºC Post time: 0.00 min. Run time: 30.00 min.
Injector	Sample Washes: 3 Sample Pumps: 3 Injection Volume: 0.20 µl Syringe Size: 10.0 µl Pre Inj. Solvent Washes: 3 Post Inj. Solvent Washes: 6 Viscosity Delay: 0 sec. Plunger Speed: Fast Pre-Injection Dwell: 0.00 min. Post-Injection Dwell: 0.00 min.

GC-MS Trace 7 – 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol in methylene chloride.

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol (**7a**), (4.553 min.)

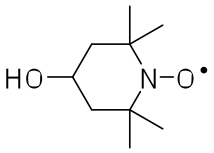


Chemical Formula: $C_{10}H_{21}NO_2$
Exact Mass: 187.1572
Molecular Weight: 187.2830
m/z: 187.1572 (100.0%)

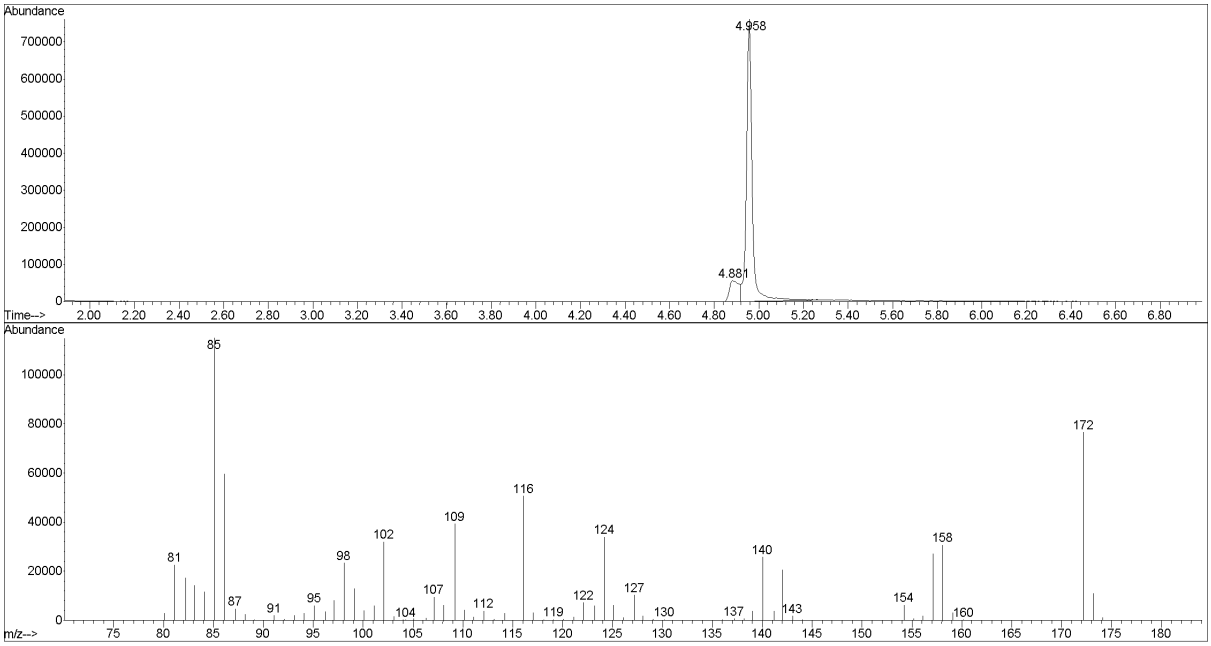


GC-MS Trace 8 – 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl in methylene chloride.

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (8a), (4.958 min.)



Chemical Formula: $C_9H_{18}NO_2^{\bullet}$
Exact Mass: 172.1338
Molecular Weight: 172.2480
m/z: 172.1338 (100.0%)

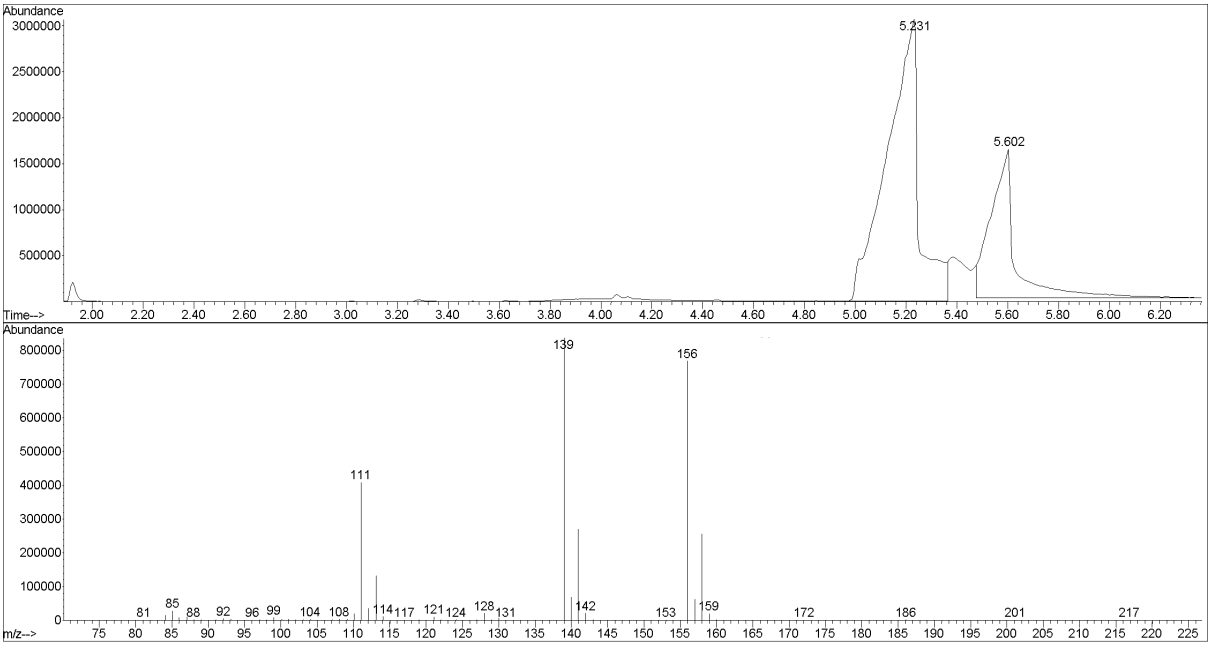


Deprotection Reaction

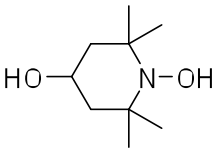
Reaction Conditions:

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol (**7a**), (0.010 g, 0.05 mmol) was dissolved in methylene chloride (1 ml). The solution was then added to a solid sample of 3-chloroperbenzoic acid (0.026 g, 0.10 mmol). The result solution was sealed and shaken intermittently for 20 minutes at room temperature to ensure complete reaction. The solution was analysed via GC-MS.

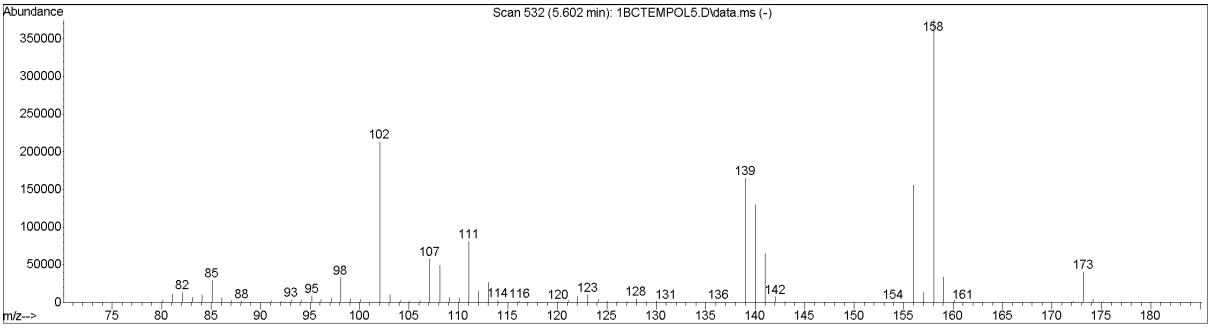
GC-MS Trace 9 – Reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl with mCPBA (5.231 min.) in methylene chloride.



2,2,6,6-Tetramethylpiperidine-1,4-diol (5.602 min.)



Chemical Formula: $C_9H_{19}NO_2$
Exact Mass: 173.1416
Molecular Weight: 173.2560
m/z: 173.1416 (100.0%)



References

1. K. Thomas, B. A. Chalmers, K. E. Fairfull-Smith and S. E. Bottle, *Eur. J. Org. Chem.*, 2013, **5**, 853-857.
2. A. S. Micallef, R. C. Bott, S. E. Bottle, G. Smith, J. M. White, K. Matsuda and H. Iwamura, *Journal of the Chemical Society, Perkin Transactions 2*, 1999, 65-72.
3. S. E. Bottle, D. G. Gillies, D. L. Hughes, A. S. Micallef, A. I. Smirnov and L. H. Sutcliffe, *Journal of the Chemical Society, Perkin Transactions 2*, 2000, 1285-1291.
4. H. Zhang, Z. Guo and J. Huang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2002, **40**, 4398-4403.
5. K. E. Fairfull-Smith and S. E. Bottle, *Eur. J. Org. Chem.*, 2008, **32**, 5391-5400.
6. R. Bolton, D. G. Gillies, L. H. Sutcliffe and X. Wu, *Journal of the Chemical Society, Perkin Transactions 2*, 1993, 2049-2052.