Supplementary information for "Experimental evidence of Chalcogen bonding at oxygen."

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February 12, 2020

Contents

1 Experimental information

1.1 Synthetic procedures

1.1.1 Typical procedure for preparation of oximes 2 and 3

Cyclohexanone oxime (556.8 mg, 4.920 mmol) and sodium hydride (60% suspension in mineral oil, 249.5 mg, 6.238 mmol) were dissolved in anhydrous THF (10 mL) and stirred at room temperature for 5 minutes. This was then added slowly to a cooled solution of 2,4-dinitrofluorobenzene (950.6 mg, 5.108 mmol) in a further 5 mL anhydrous THF, then stirred for 1h at room temperature. The mixture was then diluted with water (100 mL) and extracted into ethyl acetate (2×30 mL). The combined organic layers were washed with brine (3×50 mL)

and dried ($MgSO_4$), then evaporated to afford the O-aryl oxime as a pale yellow solid (895.1 mg, 65%, m.p. 100.2—-100.9°C).

Acetone oxime: yield 72%, m.p. 88.5–88.9°C.

1.2 Crystallisation procedures

Crystals suitable for x-ray diffraction analysis were grown by slow evaporation from acetone at −20°C.

2 Crystallographic information

Data was collected on a Rigaku Synergy diffractometer and processed using the CrysalisPro suite. Structures were solved using the intrinsic phasing method of SHELXT integrated in Olex2.[1,2] IAM refinement was performed using SHELXL in Olex2, and multipole refinement was carried out in MoPro.[3]

XYZ parameters and ADPs were refined against the high angle data (<0.8 Å), then charge density parameters were refined against the full data set using the CGLS method. This was followed by a least squares refinement of XYZ parameters and ADPs against the full data set in the case of **3**. Attempts to refine **2** using least squares gave a singular matrix, so only the atoms directly involved in the Ch-bond were refined.

All manipulation of experimental electron density was performed using the VMoPro set of programs.

2.1 Electrostatic potential map of 2

The σ-hole is less visible in **2** as it is partially neutralised by the lone pair of the oxygen of the nitro group. We include it here for comparison with **3** (figure 1).

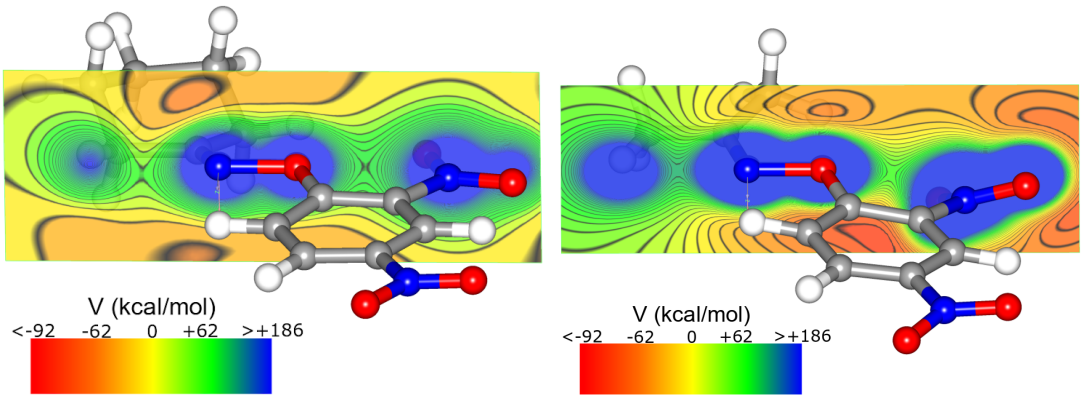

Figure 1: ESP map for **2** (left) and **3** (right).

3 Characterisation data

3.1 Cyclohexanone *O*-aryl oxime 2

3.1.1 ^{1}H NMR spectrum

20/12/2019 9:16:09 AM

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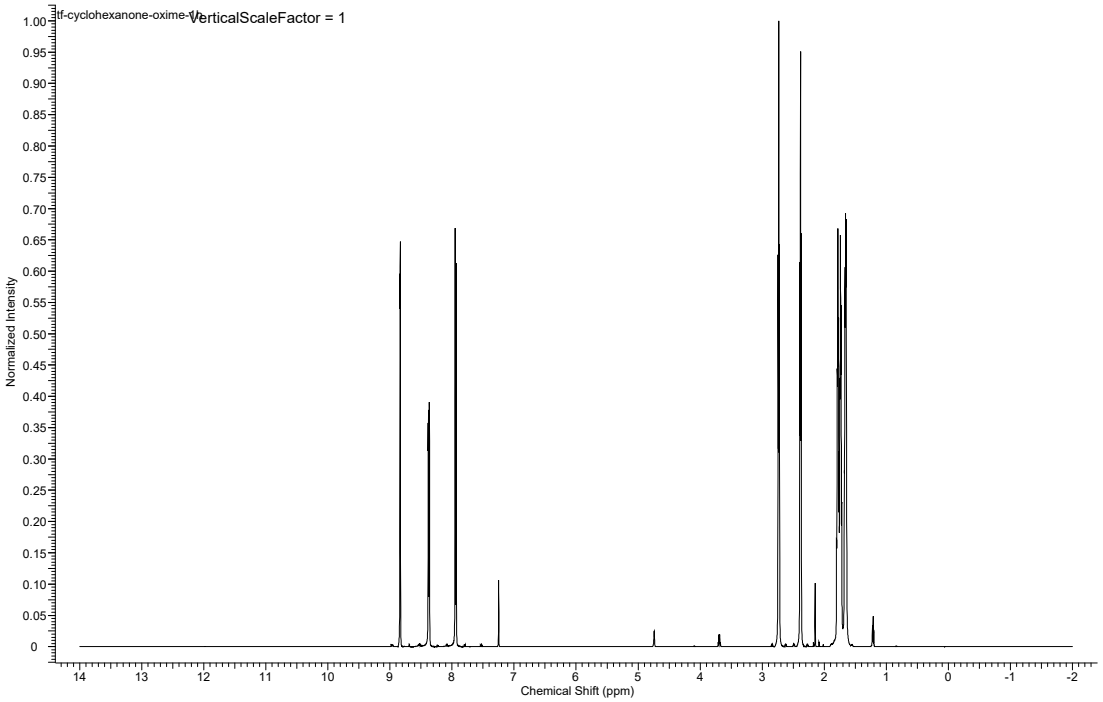

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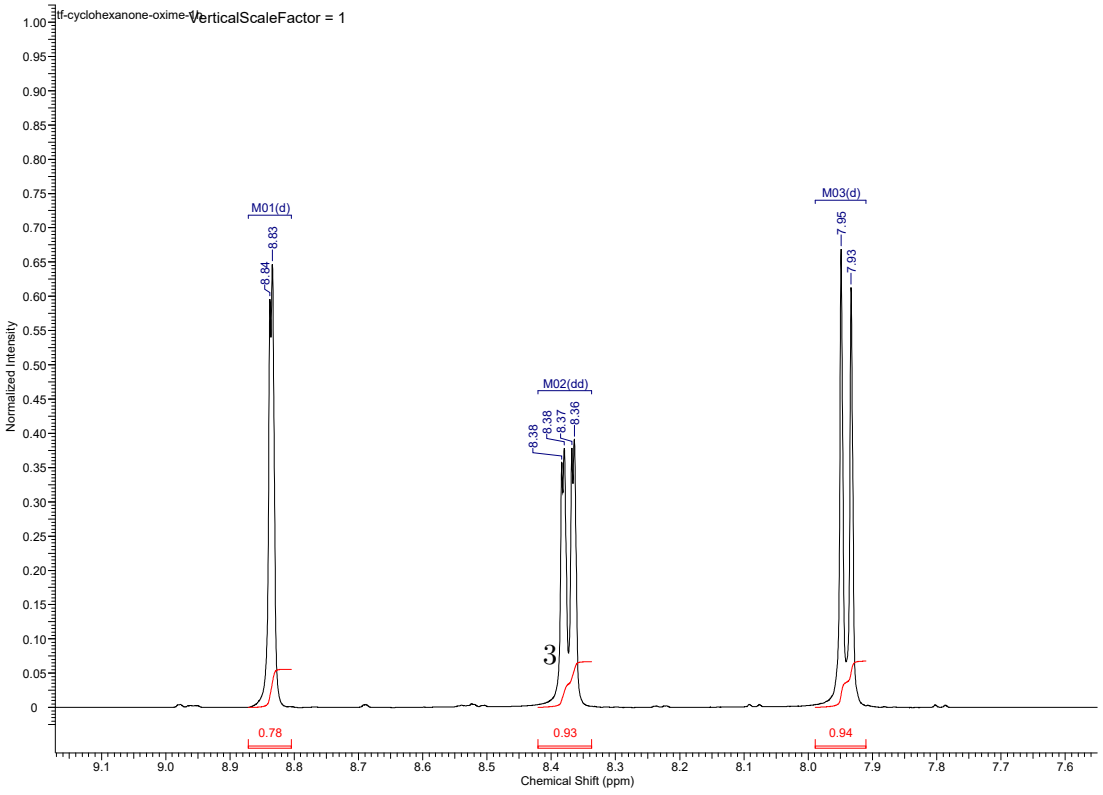

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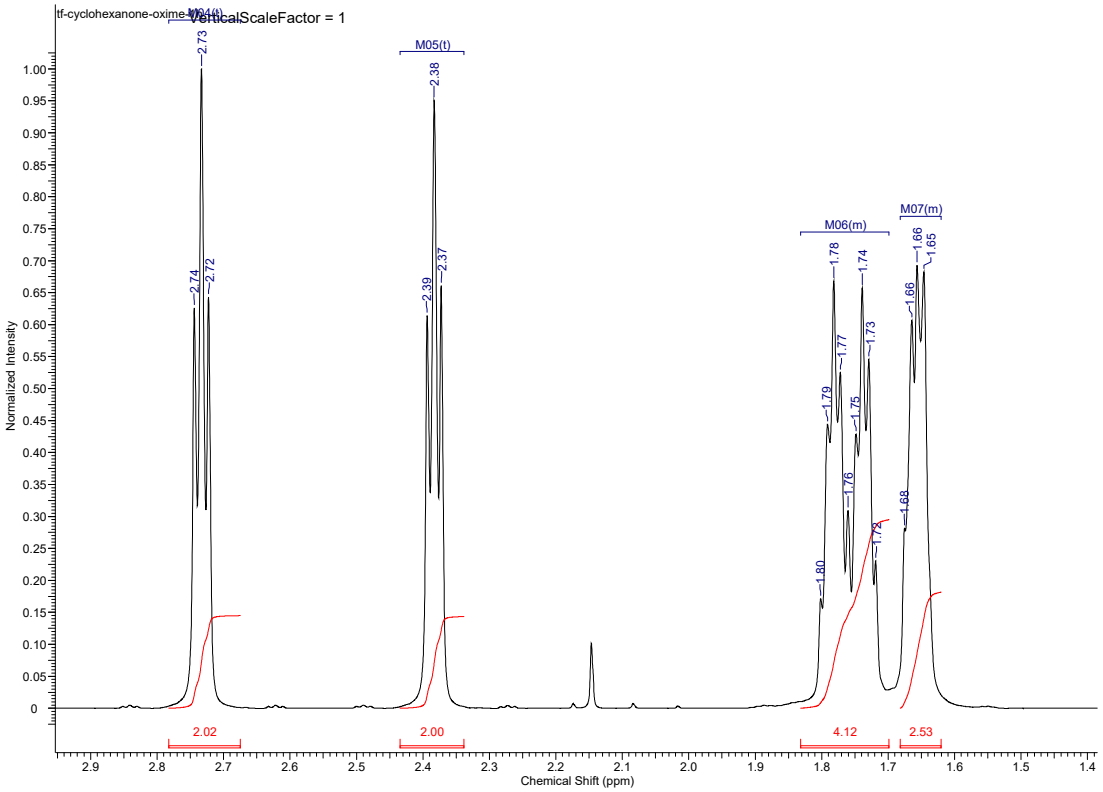

3.1.2 ^{13}C NMR spectrum

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Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	60.00
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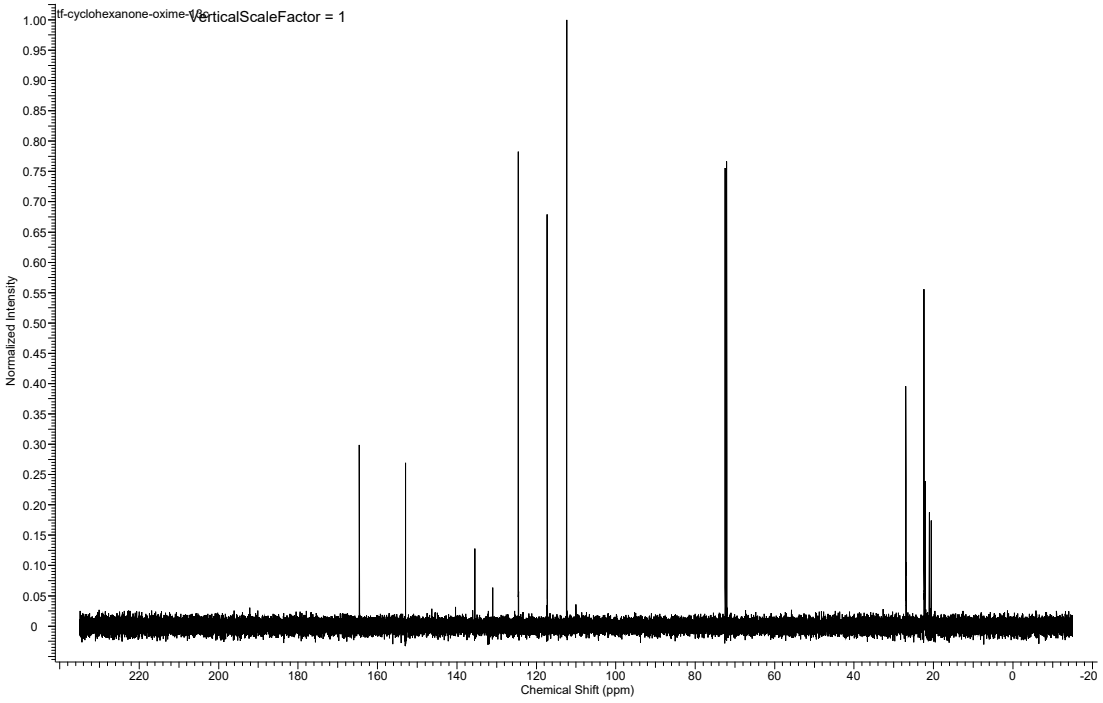
Sweep Width (Hz)	37718.06	***Temperature (degree C)***	25.000		



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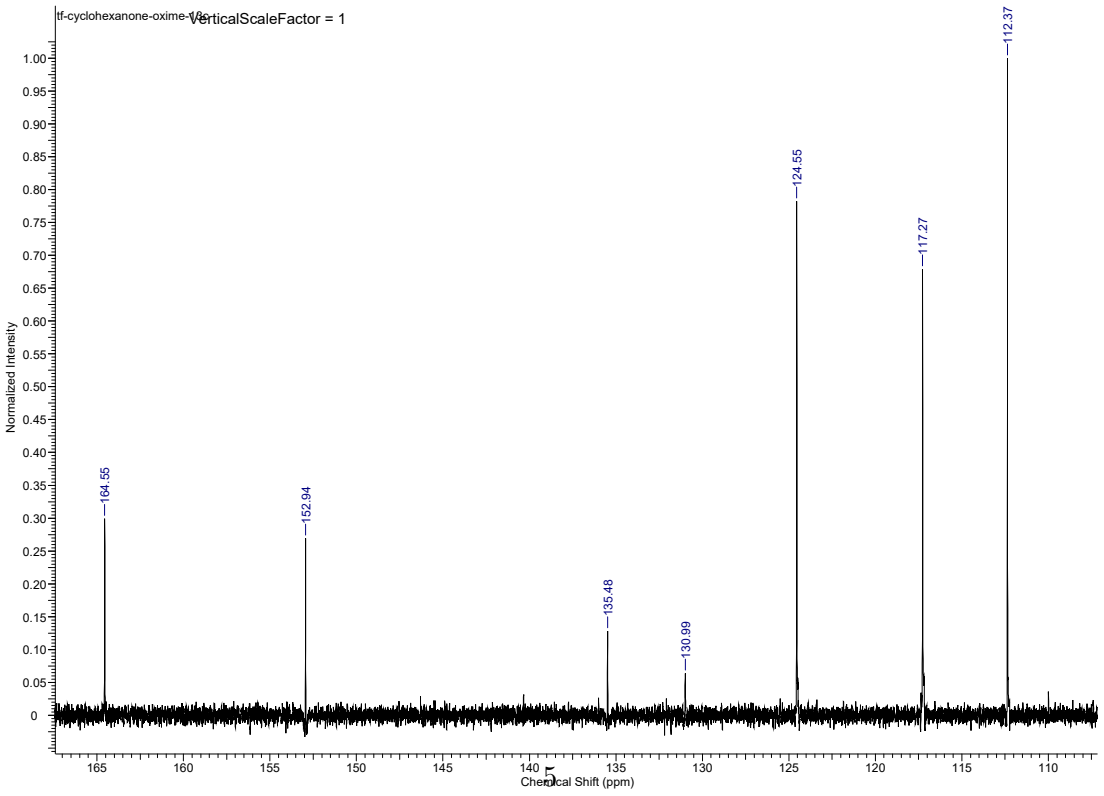
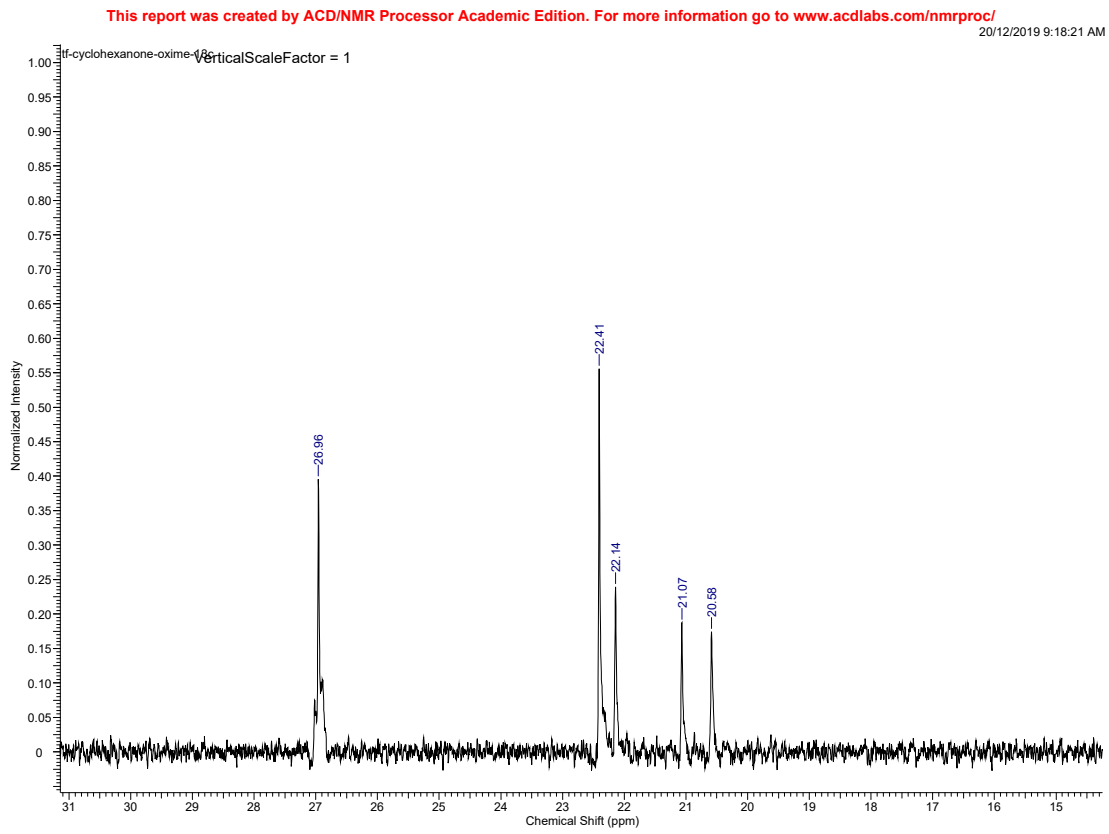
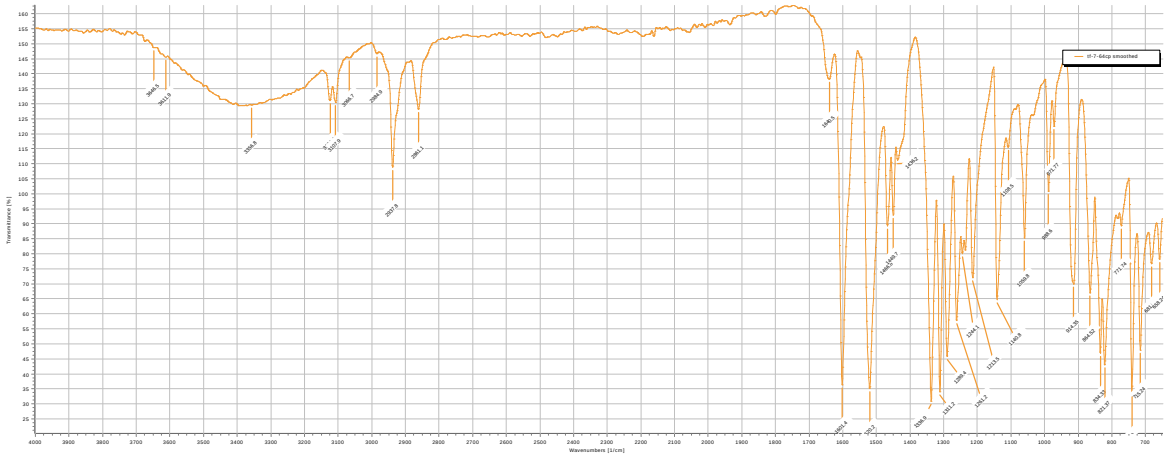




3.1.3 ATR-IR spectrum



3.2 Acetone *O*-aryl oxime 3

3.2.1 ^{1}H NMR spectrum

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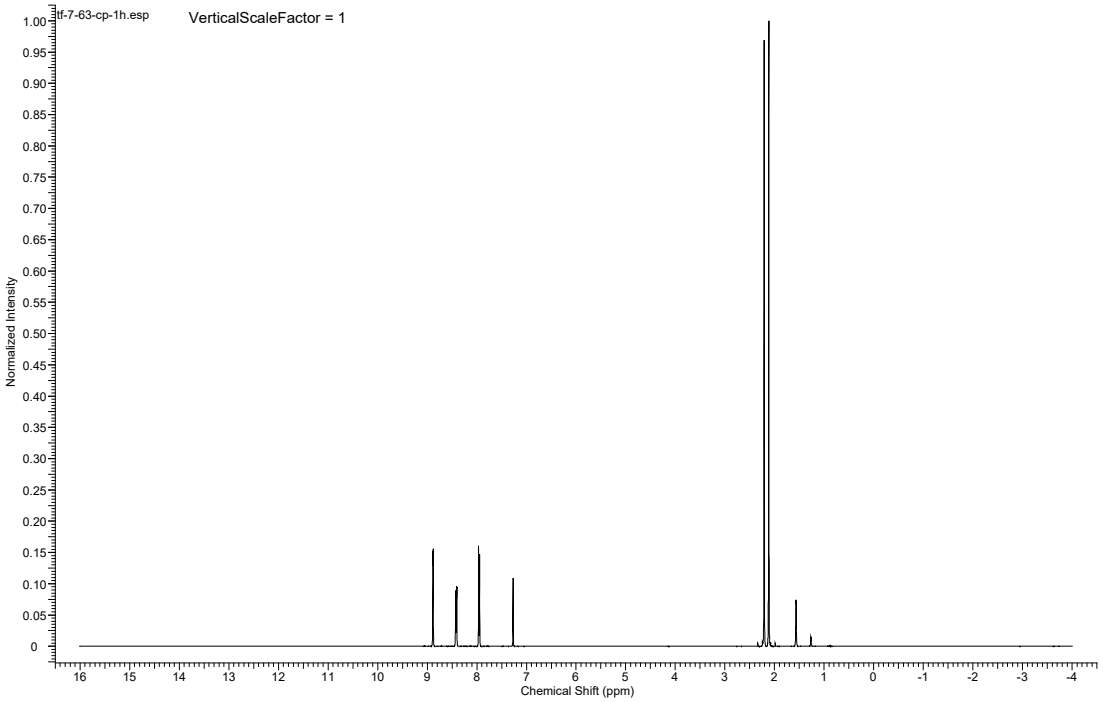

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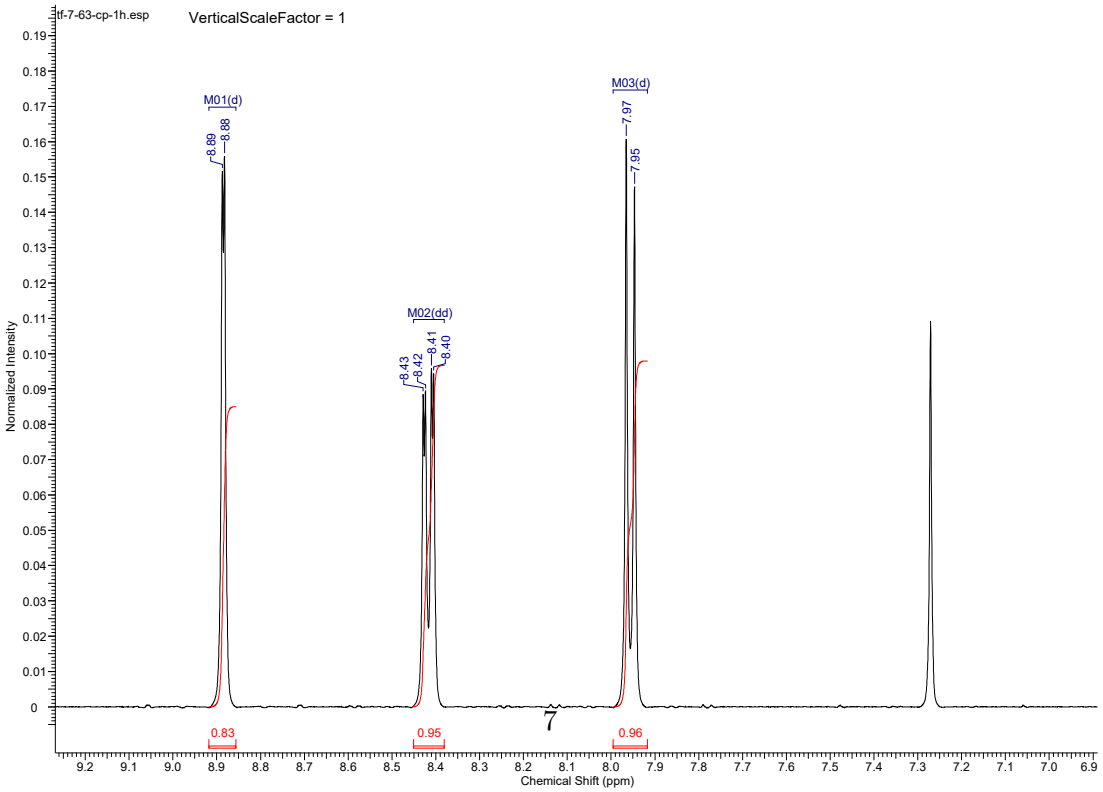

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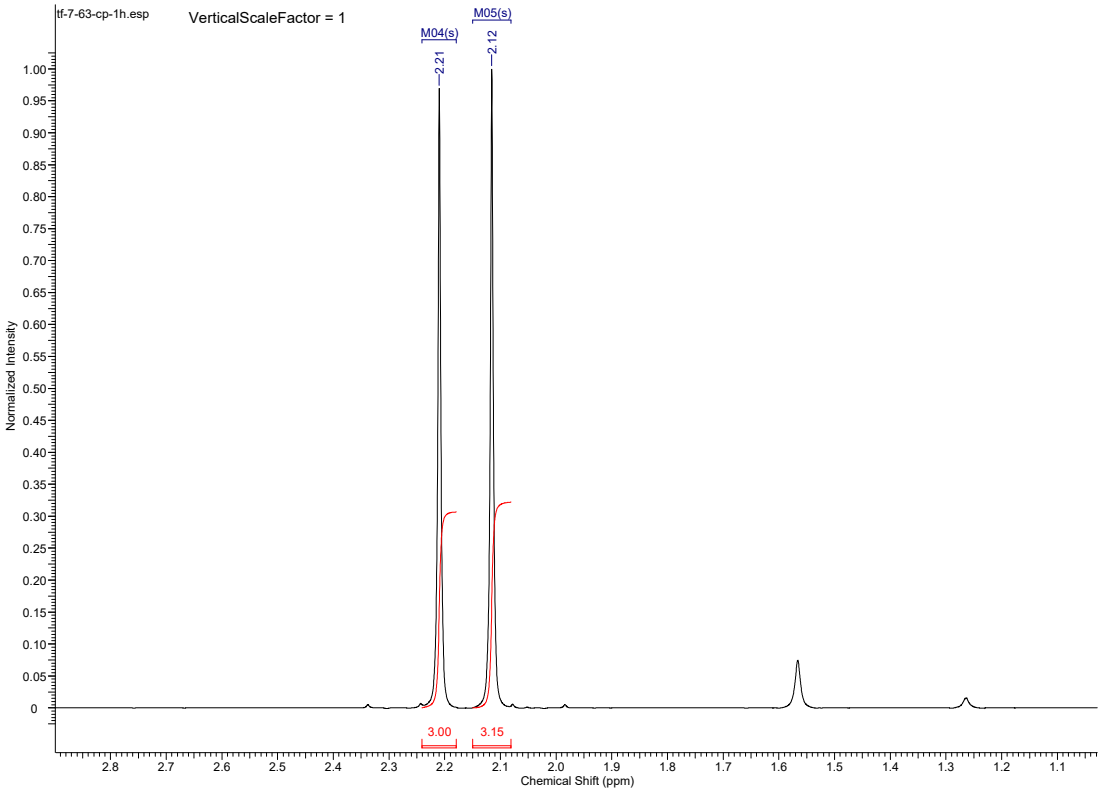
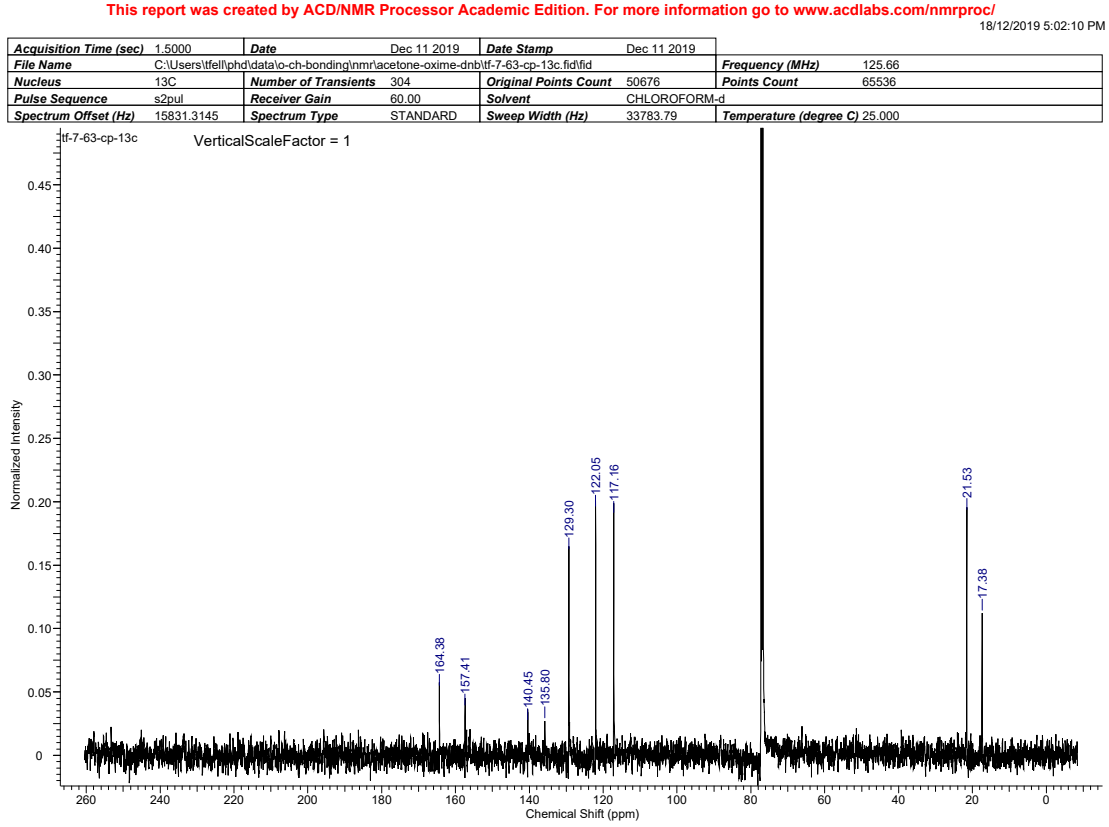
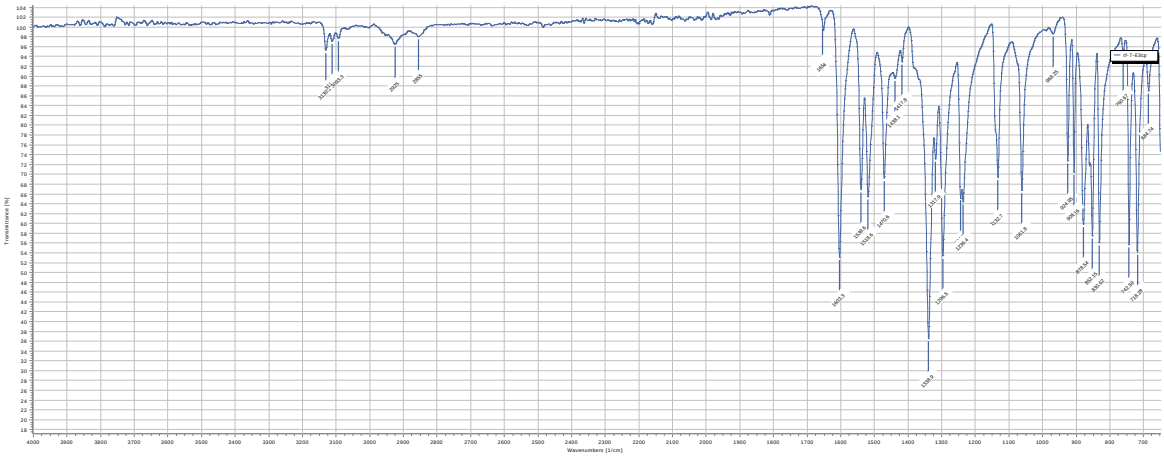


3.2.2 ^{13}C NMR spectrum



3.2.3 ATR-IR spectrum



4 Computational details

Single point energy calculations were performed on the solid phase geometries using M06-2X/aug-cc-pVQZ level as implemented in the Gaussian16 suite.[4–6] NBO7.0 was used for the

NBO calculations.[7] QTAIM analysis of the DFT electron density was performed using Multiwfn.[8]

Optimisation caused a torsion of the nitro group as discussed in the main text. The equilibrium dihedral angles were 29.7° in both cases. Structures are shown in figure 2.

4.1 Z-matrices

4.1.1 2,2-dimethylcyclohexanone *O*-aryl oxime 1

```
Tag Symbol NA NB NC Bond Angle Dihedral
1 O
2 C 1 2.3891491
3 C 2 1 2.3933261 119.1508483
4 C 3 2 1 2.3970127 62.2556619 -0.9384816
5 H 4 3 2 0.9300007 150.9299591 -179.4670767
6 C 1 2 3 1.3473627 32.2250296 0.7943859
7 O 3 2 1 2.3210947 177.1401203 -172.4650763
8 O 2 1 6 2.3413624 67.2370811 -179.3915452
9 N 7 3 2 1.2476374 33.9116318 -11.7982929
10 N 1 6 4 1.4890211 110.2698900 1.8672842
11 N 8 2 1 1.2081882 34.0355934 177.3832167
12 O 9 7 3 1.2394334 124.8098573 -179.7415876
13 C 2 1 6 1.3848625 150.2923257 1.5189326
14 H 13 2 1 0.9299901 120.8994111 178.7666578
15 C 10 1 6 1.2716397 109.3423789 177.1771474
16 C 4 3 2 1.3724194 31.2176804 -179.4603442
17 H 16 4 3 0.9300790 120.6818371 -179.9548341
18 O 11 8 2 1.2431845 121.7057285 -177.3504035
19 C 15 10 1 1.5325661 126.7863645 1.7299947
20 H 19 15 10 0.9697545 109.8982265 -102.2768189
21 H 19 15 10 0.9699371 109.8706090 16.8158744
22 C 19 15 10 1.5233072 108.9758556 137.2754197
23 H 22 19 15 0.9701134 108.8637653 -69.6628605
24 H 22 19 15 0.9708067 108.8103886 173.2902505
25 C 22 19 15 1.5295797 113.5148222 51.8475136
26 H 25 22 19 0.9700332 109.3564494 -179.6858003
27 H 25 22 19 0.9701021 109.3524519 62.2657607
28 C 25 22 19 1.5517360 111.2915881 -58.7044446
29 H 28 25 22 0.9702275 109.0563154 176.2451104
30 H 28 25 22 0.9699963 109.0746755 -66.2543940
31 C 28 25 22 1.5311817 112.6477372 55.0006038
32 C 31 28 25 1.5399996 98.6476196 -173.0229507
33 H 32 31 28 1.0699997 109.4712002 -173.6129525
34 H 32 31 28 1.0699995 109.4712478 -53.6128790
35 H 32 31 28 1.0700002 109.4712235 66.3871180
36 C 31 28 25 1.5400003 119.5867207 68.6781468
37 H 36 31 28 1.0699993 109.4712188 54.2472399
38 H 36 31 28 1.0699999 109.4711703 174.2472474
39 H 36 31 28 1.0700001 109.4712045 -65.7527818
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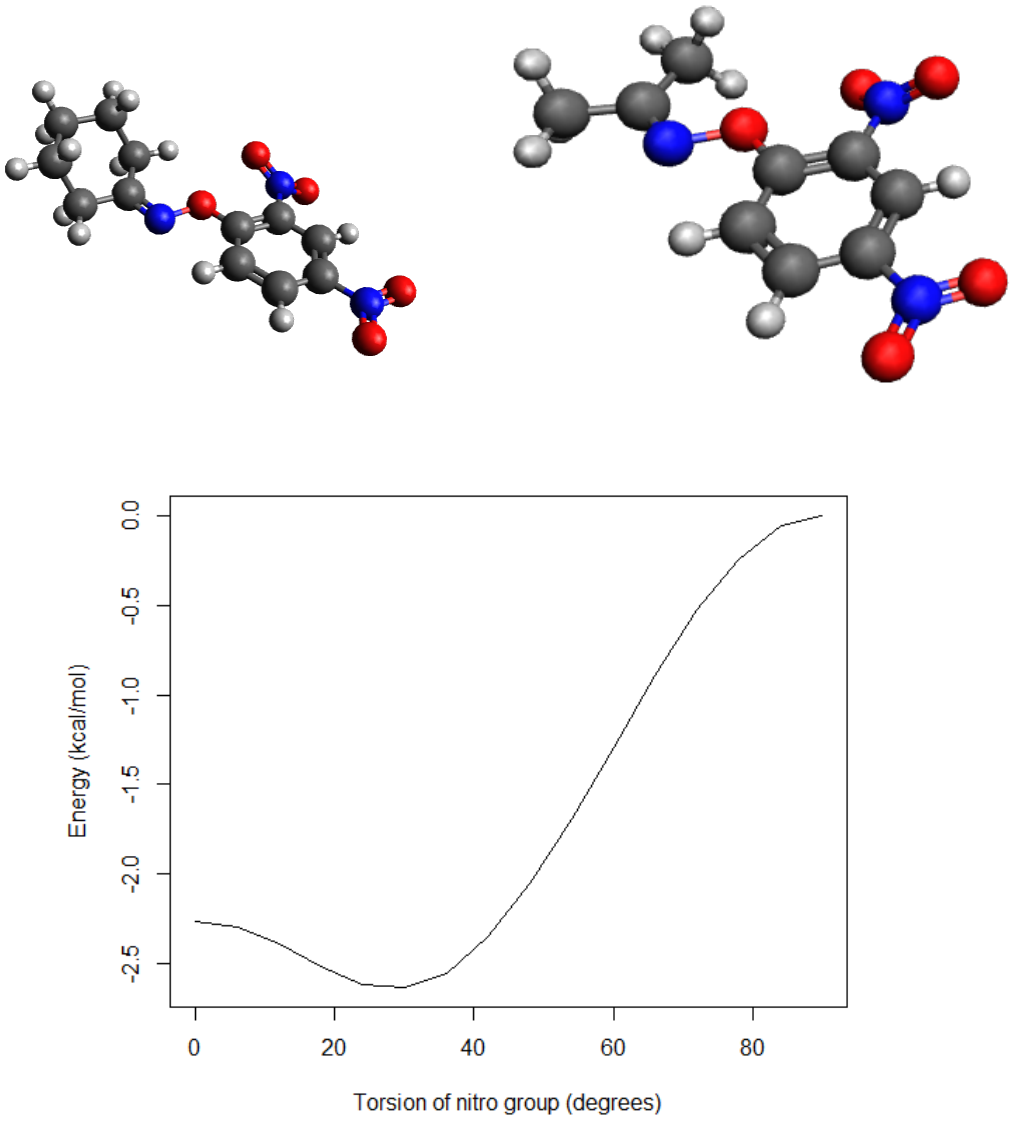

Figure 2: Gas phase geometries of **2** and **3**. Potential energy surface for the torsion of the nitro group is also shown.

4.1.2 Cyclohexanone *O*-aryl oxime 2

```
Tag Symbol NA NB NC Bond Angle Dihedral
1 O
2 O 1 6.2717057
3 O 1 2 2.5421805 95.9158279
4 O 2 1 3 2.1666833 79.6214327 -2.3961519
5 O 3 1 4 2.1643834 120.0174945 0.2228801
6 N 3 1 5 1.2263926 91.8412415 -0.4676020
7 N 4 2 1 1.2228920 28.1779292 1.9865922
8 N 1 3 6 1.4557011 160.5531202 -175.9271607
9 C 6 3 1 2.4254553 149.9784548 -1.0603416
10 H 9 6 3 0.9300494 87.7983036 179.7770169
11 C 1 8 3 2.4172733 82.7388124 -178.9900153
12 H 11 1 8 0.9300408 91.7460476 -4.0464029
13 C 9 6 3 1.3904996 32.9338067 1.1200831
14 C 9 6 3 1.3827773 151.4822365 -1.7481502
15 C 11 1 8 1.3813027 148.6539316 175.5480988
16 H 15 11 1 0.9299170 120.2034722 -179.9080419
17 C 1 8 11 1.3454737 111.9277497 1.9073304
18 C 8 1 17 1.2790133 109.7589976 164.4873130
19 C 18 8 1 1.5001231 115.3419556 179.9243116
20 H 19 18 8 0.9700589 109.4178504 108.1887707
21 H 19 18 8 0.9699638 109.4370145 -9.9916337
22 C 19 18 8 1.5339397 111.0454249 -130.9135674
23 H 22 19 18 0.9699995 109.5241064 67.4650889
24 H 22 19 18 0.9700638 109.5269861 -174.1628208
25 C 22 19 18 1.5261967 110.6143729 -53.3525389
26 H 25 22 19 0.9700081 109.6281244 179.3321039
27 H 25 22 19 0.9699220 109.6264441 -62.0925840
28 C 18 8 1 1.4970045 127.5965182 -0.6727179
29 H 28 18 8 0.9700147 109.5415060 11.7919457
30 H 28 18 8 0.9699894 109.5350817 -106.6083035
31 C 25 22 19 1.5222329 110.1589911 58.6213234
32 H 31 25 22 0.9700961 109.1929123 -179.1293670
33 H 31 25 22 0.9700363 109.2027391 63.1205705
```

4.1.3 Acetone *O*-aryl oxime 3

```
Tag Symbol NA NB NC Bond Angle Dihedral
1 O
2 O 1 6.2367776
3 O 1 2 3.9349822 50.8799347
4 O 2 1 3 2.1685664 80.6490501 -171.1323237
5 O 3 1 2 2.1699508 39.2339025 132.9221633
6 N 5 3 1 1.2265730 27.9156260 -30.0639230
7 N 4 2 1 1.2279884 28.1048352 2.0043742
8 N 1 5 3 1.4479932 148.5974589 -169.9773513
9 C 7 4 2 2.4556922 88.6574503 -174.1914962
10 H 9 7 4 0.9299756 89.1162462 7.2664793
```

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11 C 9 7 4 1.3822892 150.5270257 -175.3962748
12 H 11 9 7 0.9300258 119.7834487 -174.4525092
13 C 9 7 4 1.3925438 31.2315591 -170.2174229
14 C 1 8 11 1.3494700 111.9311234 5.4342777
15 C 13 9 7 1.3817843 122.0750099 179.7497649
16 H 15 13 9 0.9299322 121.0580975 -179.8690074
17 C 15 13 9 1.3852548 117.8859948 0.1408872
18 C 8 1 14 1.2814057 109.5149592 -178.9352009
19 C 18 8 1 1.4909004 126.3996995 -2.6488853
20 H 19 18 8 0.9598970 109.4807717 -87.9894998
21 H 19 18 8 0.9601233 109.4593564 152.0059644
22 H 19 18 8 0.9600109 109.4695536 32.0269783
23 C 18 8 1 1.4942080 115.3216591 176.4193872
24 H 23 18 8 0.9599133 109.4694116 -115.0630803
25 H 23 18 8 0.9599258 109.4704479 124.9299720
26 H 23 18 8 0.9600255 109.4672122 4.9300993
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References

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