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The formation of peroxide degradation products of photochromic triphenylimidazolyl radical-dimers

Electronic Supporting Information

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General methods

All reagents were purchased from Sigma Aldrich, Alfa Aesar or Fischer and were used as received. The compound 2,4,5-triphenylimidazole is available commercially. The known compounds 2-(2′-chlorophenyl)-4,5-diphenylimidazole,[1] 2-(4′-chlorophenyl)-4,5-diphenylimidazole,[1] 2-(2′-methylphenyl)-4,5-diphenylimidazole,[1] 2-(2′,4′,6′-trimethylphenyl)-4,5-diphenylimidazole[2] were synthesised as reported previously, utilising microwave heating (180 °C, 5 min, 2 mmol scale in 4 ml acetic acid).[3] The respective 2C-1′N dimers of the imidazoles were synthesised as reported previously.[2] Solvent purification system (Innovative Technologies Inc.) dried solvents and de-ionised water were used where appropriate.

NMR spectra were recorded either on a Varian Mercury-400, a Varian VNMRS-600 or a Varian VNMRS-700 spectrometer. *J* coupling (^1H–^1H) values are given in Hz and chemical shifts, δ, in ppm, are internally referenced to the residual protiated solvent or the solvent ^{13}C resonance. NMR spectra of the parent imidazoles are reported in DMSO-d_6. In this solvent the NH proton is non-labile, both allowing this proton to be observed in the ^1H spectrum and additionally making the phenyl rings in the 4- and 5-positions of the imidazole inequivalent. In $CDCl_3$ the spectrum was complicated by partial exchange.

Mass spectra (MS) were recorded on a LCT Premier XE ESI mass spectrometer (Waters Ltd., UK). MS data were processed using Waters MassLynx (*ver.* 4.1) software. Accurate mass spectrometry (Acc-MS) utilised a lock-mass correction to provide < 3 mDa precision and used Elemental Composition (ver. 4.0) embedded within Waters MassLynx (*ver.* 4.1) software for analysis. The deviation between calculated and experimental mass is provided in units of parts per million (ppm) for each accurate mass presented.

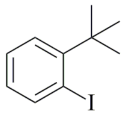
Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer Spectrum 100 ATR spectrometer (Perkin-Elmer, Norwalk, CT) with Spectrum Express 1.01 software. 16 scans were performed between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. Typically, only the most intense peaks with energies greater than 1450 cm^{-1} are listed, except where they provide a characteristic peak outside of this range. Bands are designated strong (s), weak (w), broad (br.) or as a shoulder (sh.), relative to other peaks.

Melting points were recorded on a TA Instruments Q1000 differential scanning calorimeter (DSC) and are taken as the onset of the melting event. The temperature was programmed to rise from room temperature (25 °C) to 300 °C at a heating rate of 10 °C min^{-1}. The same DSC instrument was used to study the decomposition of **6**. Thermogravimetric analysis was performed on a Perkin Elmer Pyris 1 TGA purged with nitrogen at a rate of 50 ml min^{-1} and using a similar temperature programme to that used for DSC.

Microwave reactions were carried out in septum-containing, crimp-capped, sealed vials in an Emrys Optimizer (Personal Chemistry) reactor. The wattage was automatically adjusted to maintain the desired temperature for the desired period of time.

Synthesis

2-*tert*-butyliodobenzene

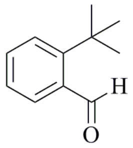


$C_{10}H_{13}I$
MW: 260.11

The compound 2-*tert*-butylaniline (5 ml, 4.79 g, 32.1 mmol) was added to a solution of concentrated H_2SO_4 (6 ml) diluted with water (24 ml), forming a pale pink suspension, and cooled to -40 °C. Sodium nitrite (2.29 g, 33.1 mmol) dissolved in water (20 ml) was added and the solution stirred for 10 min. The temperature was adjusted to -15 °C and a pre-cooled solution of KI (17.1 g, 103 mmol) in water (40 ml) was added at which point the solution turned red. The solution was stirred for a further hour whilst warming to 0 °C. The solution was cautiously neutralised with dilute aqueous NaOH solution (1 M, 100 ml) before being extracted with hexanes (3 x 30 ml). The hexanes layers were combined and dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude material was eluted through a silica plug (hexanes) to give the title compound as a red oil (3.37 g, 40%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.00 (1 H, dd, J = 7.9 and 1.4), 7.44 (1 H, dd, J = 7.9 and 1.7), 7.28 (1 H, td, J = 7.3 and 1.4), 6.83 (1 H, td, J = 7.3 and 1.7), 1.53 (9 H, s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 143.7, 128.0, 127.7, 127.6, 95.3, 36.9, 30.0. Analyses matched those previously reported.[4]

2-*tert*-butylbenzaldehyde

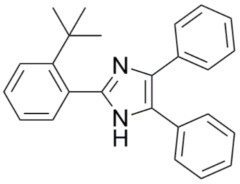


$C_{11}H_{14}O$
MW: 162.2

To a nitrogen filled flask was added a solution of 2-*tert*-butyliodobenzene (1.02 g, 3.9 mmol) in dry tetrahydrofuran (10 ml). The solution was cooled to -78 °C before *n*-butyllithium (1.6 M in hexanes, 3.2 ml, 5.1 mmol) was added, causing the solution to turn orange. The solution was stirred for 30 min at -78 °C. Dry *N*,*N*-dimethylformamide (DMF) (1 ml, 0.94 g, 12.3 mmol) was added dropwise and the mixture was stirred for a further 2 h. After allowing the solution to warm to r.t., water (15 ml) was added cautiously and the flask was opened to air, causing the now red solution to turn green. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 10 ml). The combined organic layers were dried over $MgSO_4$ and eluted through a silica plug (diethyl ether) to remove a yellow impurity and excess DMF. The crude material was purified by Kugelrohr distillation (0.2 mbar) giving the product as the lowest boiling point fraction (454 mg, 72%). It was observed that the product degraded (yellow colouration developed) within the course of a couple of days if exposed to light or kept at r.t. and therefore should be used immediately.

^{1}H NMR (400 MHz; $CDCl_3$): δ 10.85 (1 H, s, H_9), 7.93 (1 H, d, J = 7.8), 7.44-7.54 (2 H, m), 7.28-7.36 (1 H, m), 1.52 (9 H, s, H_8). Analysis matched that previously reported.[5]

2-(2′-*tert*-butylphenyl)-4,5-diphenylimidazole, 1

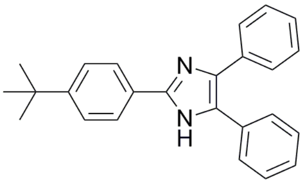


$C_{25}H_{24}N_2$
MW: 352.47

The compounds 2-*tert*-butylbenzaldehyde (356 mg, 2.2 mmol), benzil (463 mg, 2.2 mmol) and ammonium acetate (385 mg, 5.0 mmol) were suspended in acetic acid (4 ml) and sealed in a microwave vial. The solution was heated to 180 °C under microwave irradiation for 5 min. The solution was allowed to cool to r.t before being poured into ice-water (30 ml), neutralised with K_2CO_3 and extracted with CH_2Cl_2 (3 x 20 ml). The CH_2Cl_2 layers were separated, combined, dried over $MgSO_4$, filtered and reduced to a beige solid *in vacuo*. The crude solid was recrystallised from hot acetonitrile to afford the title compound as white needles (445 mg, 58%). Single crystals suitable for X-ray diffraction were produced by recrystallisation from nitromethane.

M.p. 266 °C (from acetonitrile). FT-IR (solid): $\tilde{\nu}_{max}$/cm^{-1} 3072 (CH), 3033 (CH), 2972 (CH), 2912 (CH), 1604 (Ar), 1546 (Ar), 1505 (w, Ar), 1483(s), 1445 (s), 758 (s), 739 (s), 694 (s). ^{1}H NMR (500 MHz; DMSO-d_6): δ 12.40 (1 H, s, NH), 7.52-7.59 (3 H, m), 7.45-7.49 (2 H, m), 7.42 (1 H, td, J = 7.6 and 1.7), 7.38 (2 h, t, J = 8.1), 7.4 (1 H, dd, J = 7.6 and 1.7), 7.26-7.33 (4 H, m), 7.19 (1 H, tt, J = 7.4 and 1.3), 1.29 (9 H, s). ^{13}C{^{1}H} NMR (126 MHz; DMSO-d_6): δ 149.8, 147.7, 135.5, 135.4, 132.4, 131.2, 131.2, 128.9, 128.6, 128.2, 127.9, 127.4, 127.0, 126.5, 126.5, 126.3, 125.2, 36.0, 31.5. Acc-MS (ES$^+$): m/z 353.2022 [M+H]$^+$, calcd. for $C_{25}H_{25}N_2$ 353.2018 ($|\Delta m/z|$ = 1.1 ppm).

2-(4′-*tert*-butylphenyl)-4, 5-diphenylimidazole, 3

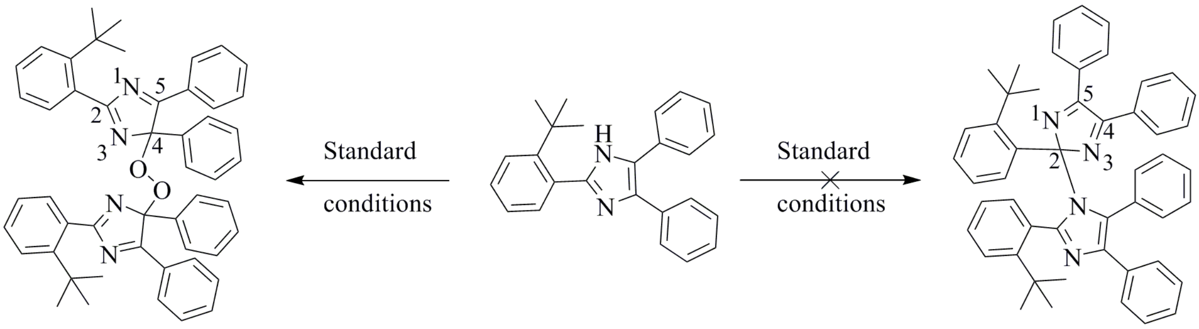


$C_{25}H_{24}N_2$
MW: 352.47

The compounds 4-*tert*-butylbenzaldehyde (0.2 ml, 194 mg, 1.2 mmol), benzil (253 mg, 1.2 mmol) and ammonium acetate (360 mg, 4.7 mmol) were suspended in acetic acid (4 ml) and sealed in a microwave vial. The solution was heated to 180 °C under microwave irradiation for 5 min. The solution was allowed to cool to r.t before being poured into ice-water (30 ml), neutralised with K_2CO_3 and extracted with CH_2Cl_2 (3 x 20 ml). The CH_2Cl_2 layers were separated, combined, dried over $MgSO_4$, filtered and reduced to a pale yellow solid *in vacuo*. The crude solid was recrystallised from hot acetonitrile to afford the title compound as white needles (261 mg, 62%). Alternatively, the crude material could be recrystallised from hot ethyl acetate, followed by cooling (-10 °C). Single crystals suitable for X-ray diffraction were produced by recrystallisation from acetonitrile.

M.p. 286 °C (from acetonitrile). FT-IR (solid): $\tilde{\nu}_{max}/cm^{-1}$ 3064 (CH), 3026 (CH)), 2969 (CH), 2910, 2873, 1605 (Ar), 1585 (ar), 1491 (s)), 1451 (s), 837 (s), 764 (s), 694 (s) cm^{-1}. ^{1}H NMR (600 MHz; DMSO-d_6): δ 12.61 (1 H, s, NH), 8.02 (2 H, dt, J = 8.7 and 2.0), 7.56 (2 H, dd, J = 7.0 and 1.3), 7.50 (4 H, tt, J = 7.3 and 2.0), 7.44 (2 H, t, J = 7.9), 7.37 (1 H, tt, J = 7.3 and 1.3), 7.30 (2 H, t, J = 7.9), 7.22 (1 H, tt, J = 7.3 and 1.3), 1.32 (9 H, s). ^{13}C{^{1}H} (151 MHz; DMSO-d_6): δ 150.8, 145.6, 137.0, 135.3, 131.2, 128.6, 128.4, 128.1, 127.9, 127.7, 127.7, 127.1, 126.4, 125.4, 125.0, 34.4, 31.1. Acc-MS (ES$^+$): m/z 353.20145 $[M+H]^+$, calcd. for $C_{25}H_{25}N_2$ 353.20176 ($|\Delta m/z|$ = 0.6 ppm).

Attempted oxidation of 2-(2′-*tert*-butylphenyl)-4,5-diphenylimidazole, 1, to 2-(2'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical, 2



$C_{50}H_{46}N_4O_2$
MW: 734.9

Complicated mixture
of isomers

$C_{50}H_{46}N_4$
MW: 702.9

The compound 2-(2′-*tert*-butylphenyl)-4,5-diphenylimidazole, **1**, (75 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (25 ml). KOH (1.35 g, 24 mmol) and $K_3[Fe(CN)_6]$ (3.7 g, 11 mmol) dissolved in water (25 ml) was added and the biphasic system was rapidly stirred for 2 h. The CH_2Cl_2 layer was separated and washed with water (3 x 20 ml) until the aqueous layer was colourless. The CH_2Cl_2 layer was dried over $MgSO_4$, filtered and reduced *in vacuo* to an off-white solid. NMR showed a complicated mixture of products which could not be separated. The mixture is believed to contain various peroxides of 2-(2'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical as evidenced by accurate mass spectrometry and X-ray crystallography. The mixture is also believed to contain traces of a dimer species based on accurate mass spectrometry, although the nature of its dimerisation has not been established.

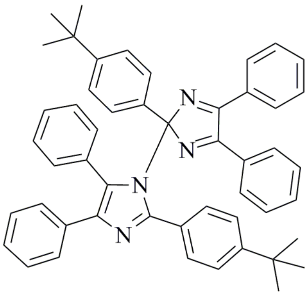
Acc-MS (ESI^+): m/z 702.3739 $[M]^+$, calcd. for $C_{50}H_{46}N_4$ 702.3722 ($|\Delta|$ = 2.4 ppm) and 351.1852 $[M/2]^+$, calcd. for $C_{25}H_{23}N_2$ 351.1861 ($|\Delta m/z|$ = 2.6 ppm).

Peroxide of 2-(2'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical 2: Compound 5

Single crystals suitable for X-ray diffraction were produced by recrystallisation from 1,2-dichloroethane.

Acc-MS (ESI^+): m/z 735.3677 $[M+H]^+$, calcd. for $C_{50}H_{47}N_4O_2$, 735.3699 ($|\Delta m/z|$ = 3.0 ppm).

2C-1'N dimer of 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical 4: Compound 4-CN

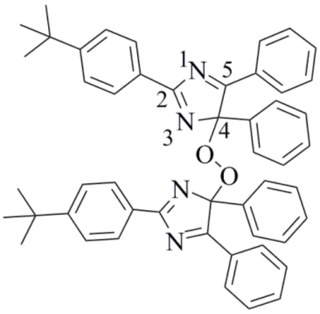


$C_{50}H_{46}N_4$
MW: 702.93

The compound 2-(4′-*tert*-butylphenyl)-4,5-diphenylimidazole, **3** (76 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (25 ml). KOH (1.35 g, 24 mmol) and $K_3[Fe(CN)_6]$ (3.7 g, 11 mmol) dissolved in water (25 ml) was added and the biphasic system was rapidly stirred for 2 h. The CH_2Cl_2 layer was separated and washed with water (3 x 20 ml) until the aqueous layer was colourless. The CH_2Cl_2 layer was dried over $MgSO_4$, filtered and reduced *in vacuo* to a light and temperature sensitive yellow solid. Flash chromatography (SiO_2; 3:1 hexanes:CH_2Cl_2) afforded the 2C-1′N dimer of radical **4**, **4-CN**, as a yellow-green solid (64 mg, 83%). Single crystals suitable for X-ray diffraction were produced by recrystallisation from hexanes.

M.p. 177 °C (from CH_2Cl_2). ^1H NMR (400 MHz; $CDCl_3$): δ 7.38-7.49 (6 H, m), 7.24-7.32 (12 H, m), 7.11-7.16 (4 H, m), 7.06-7.11 (4 H, m), 6.93 (2 H, dt, $J = 8.6$ and 1.8), 1.27 (9 H, s), 1.20 (9 H, s). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): δ 166.4, 151.2, 150.9, 149.2, 137.9, 135.4, 134.7, 133.0, 132.2, 131.8, 131.6, 131.0, 130.5, 129.9, 129.4, 128.1, 127.8, 127.7, 127.5, 127.2, 126.2, 124.6, 124.4, 112.5, 34.7, 34.5, 31.4, 31.3. Acc-MS (ES$^+$): *m/z* 703.37958 $[M+H]^+$ (100%), calcd. for $C_{50}H_{47}N_4$ 703.37952 ($|\Delta m/z| = 0.1$ ppm) and 351.18631 $[M/2]^+$ (5%), calcd. for $C_{25}H_{23}N_2$ 351.18558 ($|\Delta m/z| = 2.1$ ppm).

Peroxide of 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical 4: Compound 6



$C_{50}H_{46}N_4O_2$
MW: 734.9

Mixture of
diastereomers

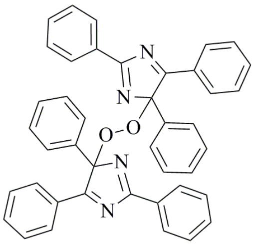
Single crystals suitable for X-ray diffraction were produced by recrystallisation from ethyl acetate.

Acc-MS (ESI$^+$): *m/z* 735.3702 $[M+H]^+$, calcd. for $C_{50}H_{47}N_4O_2$, 735.3699 ($|\Delta m/z| = 0.4$ ppm).

General formation of peroxides of TPIRs

For a series of known TPIRs, peroxide formation was observed by mass-spectrometry following irradiation under an oxygen atmosphere in acetonitrile (see main text). The existence of the peroxides was confirmed by the following accurate mass spectral data.

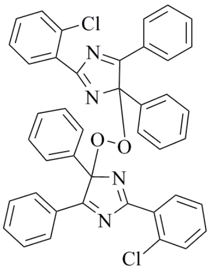
Proposed peroxide of 2,4,5-diphenylimidazolyl radical



$C_{42}H_{30}N_4O_2$
MW: 622.71

Acc-MS (ESI$^+$): *m/z* 623.2455 $[M+H]^+$, calcd. for $C_{42}H_{31}N_4O_2$ 623.2447 ($|\Delta m/z|$ = 1.3 ppm).

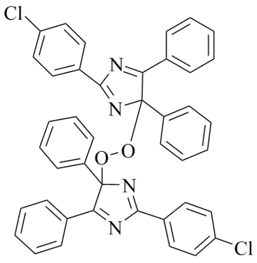
Proposed peroxide of 2-(2′-chlorophenyl)-4,5-diphenylimidazolyl radical



$C_{42}H_{28}Cl_2N_4O_2$
MW: 691.60

Acc-MS (ESI$^+$): *m/z* 691.1693 $[M+H]^+$, calcd. for $C_{42}H_{29}N_4O_2Cl_2$ 691.1668 ($|\Delta m/z|$ = 3.6 ppm).

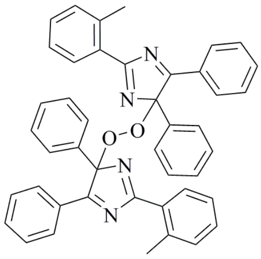
Proposed peroxide of 2-(4′-chlorophenyl)-4,5-diphenylimidazolyl radical



$C_{42}H_{28}Cl_2N_4O_2$
MW: 691.60

Acc-MS (ESI$^+$): *m/z* 691.1681 $[M+H]^+$, calcd. for $C_{42}H_{29}N_4O_2Cl_2$ 691.1668 ($|\Delta m/z|$ = 1.9 ppm).

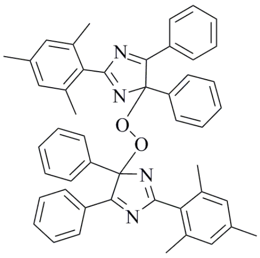
Proposed peroxide of 2-(2′-methylphenyl)-4,5-diphenylimidazolyl radical



$C_{44}H_{34}N_4O_2$
MW: 650.77

Acc-MS (ESI$^+$): *m/z* 651.2746 [M+H]$^+$, calcd. for $C_{44}H_{35}N_4O_2$ 651.2760 (|Δ*m/z*| = 2.1 ppm).

Proposed peroxide of 2-(2′,4′,6′-trimethylphenyl)-4,5-diphenylimidazolyl radical



$C_{48}H_{42}N_4O_2$
MW: 706.87

Acc-MS (ESI$^+$): *m/z* 707.3378 [M+H]$^+$, calcd. for $C_{48}H_{43}N_4O_2$ 707.3386 (|Δ*m/z*| = 1.1 ppm).

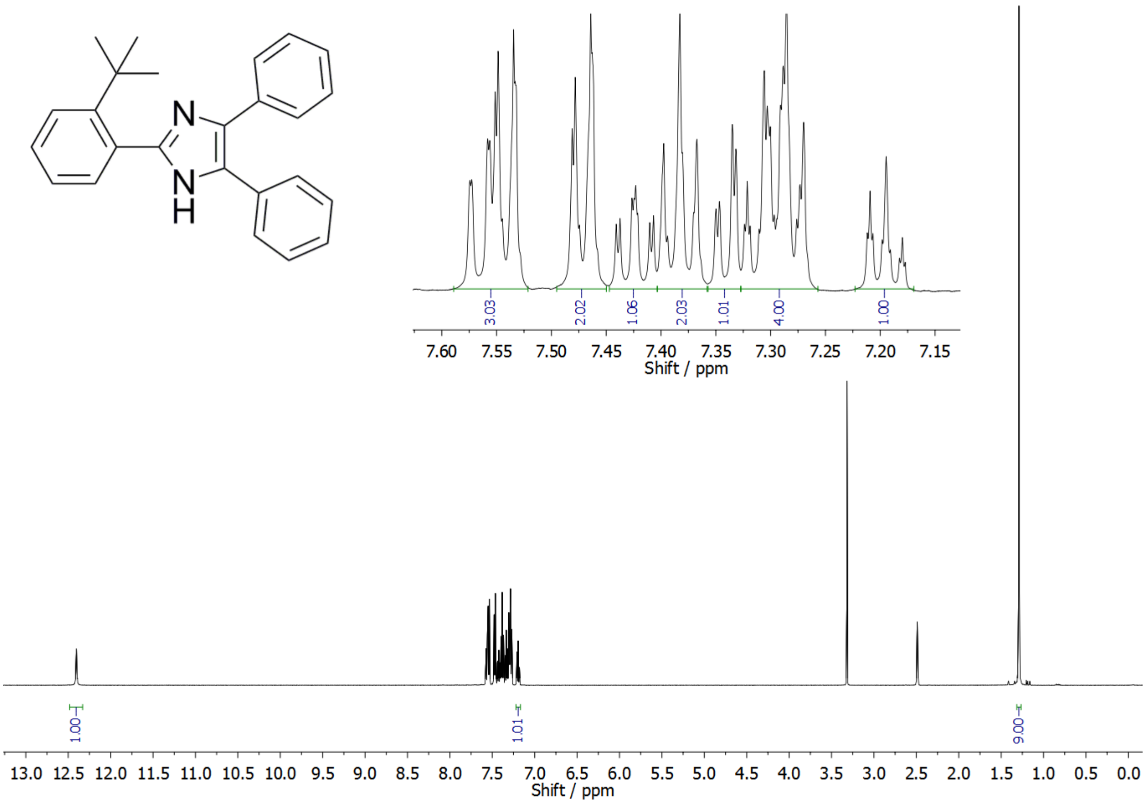


Fig. S1 500 MHz ^{1}H NMR spectrum of 2-(2′-*tert*-butylphenyl)-4,5-diphenylimidazole, **1**, in DMSO-d_6.

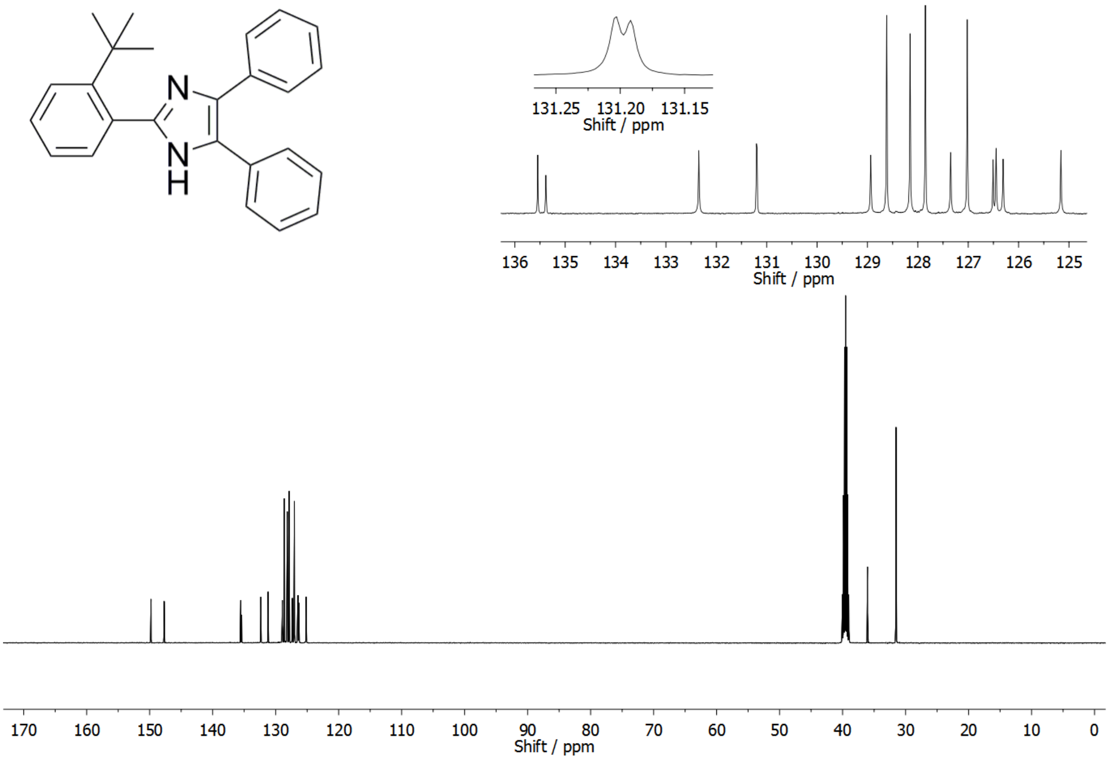


Fig. S2 126 MHz ^{13}C{^{1}H} NMR spectrum of 2-(2′-*tert*-butylphenyl)-4,5-diphenylimidazole, **1**, in DMSO-d_6.

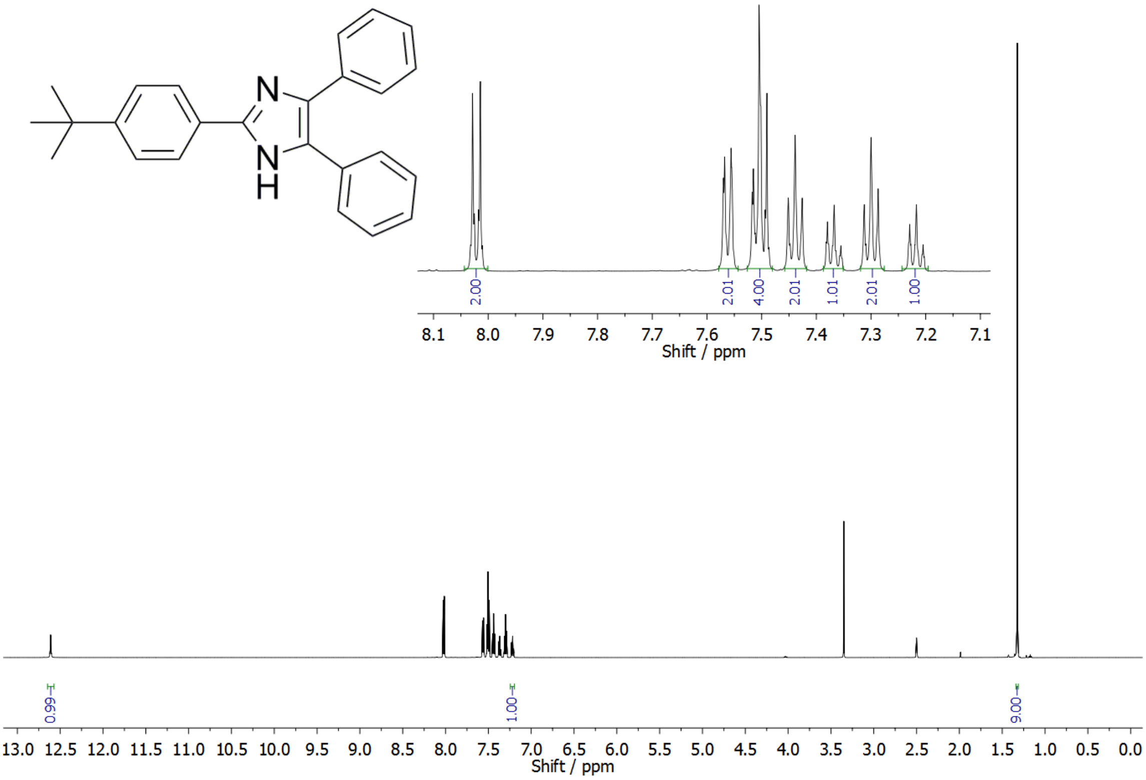


Fig. S3 600 MHz ^{1}H NMR spectrum of 2-(4′-*tert*-butylphenyl)-4,5-diphenylimidazole, **3**, in DMSO-d_6.

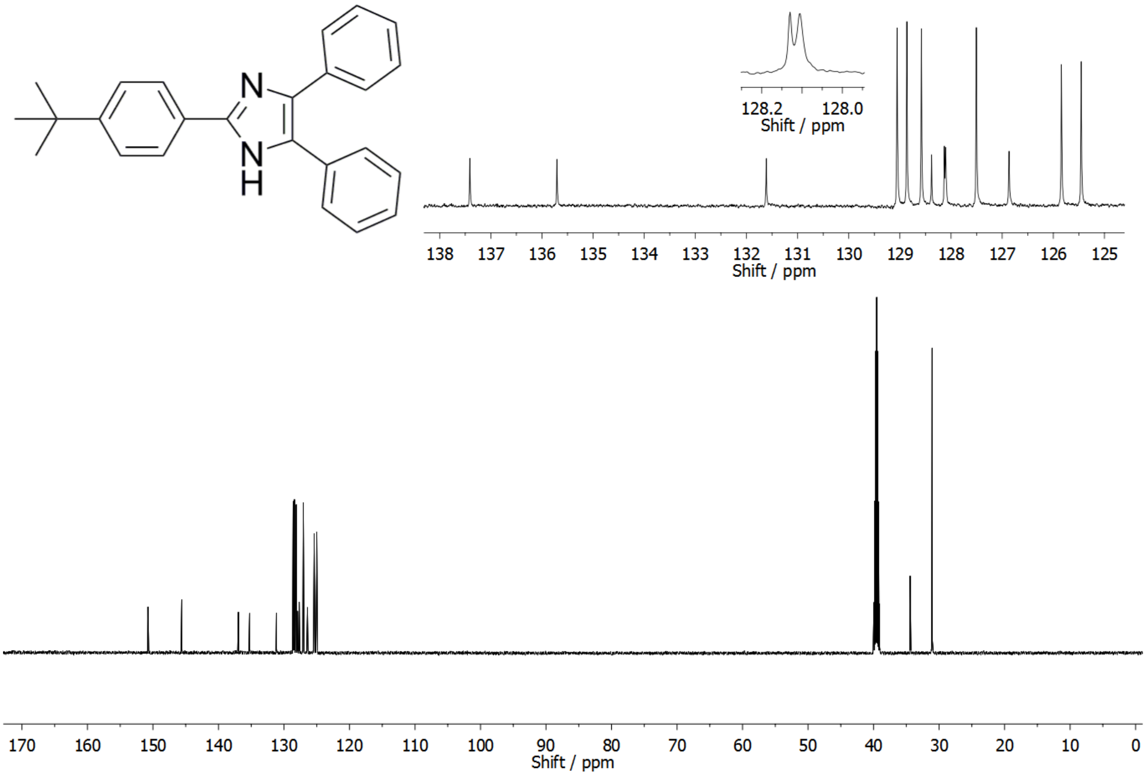


Fig. S4 151 MHz ^{13}C{^{1}H} NMR spectrum of 2-(4′-*tert*-butylphenyl)-4,5-diphenylimidazole, **3**, in DMSO-d_6.

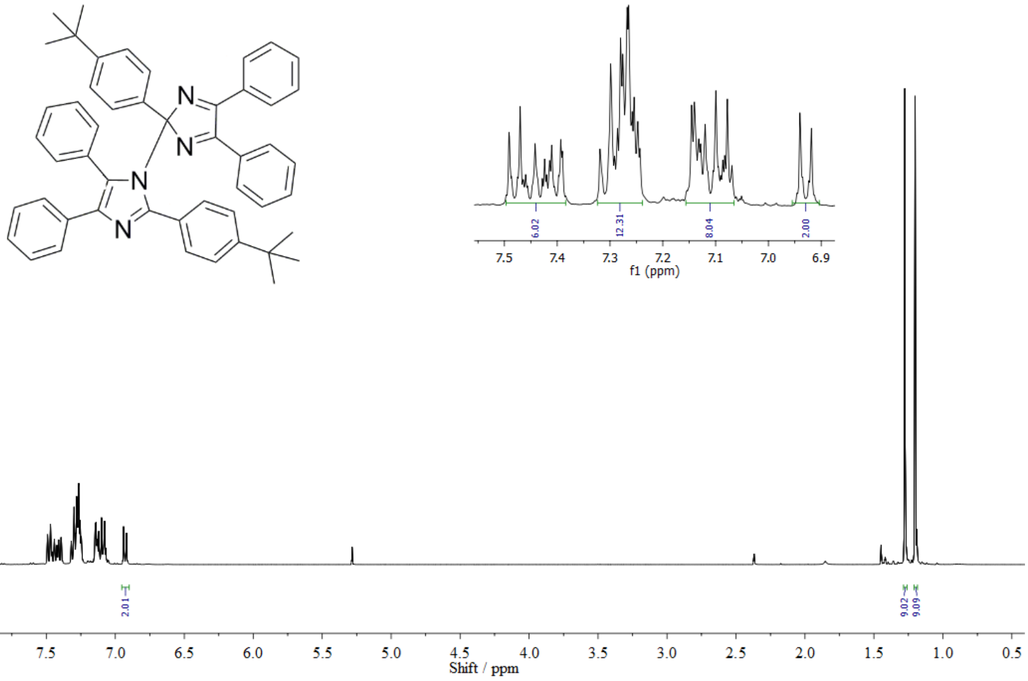


Fig. S5 400 MHz ^{1}H NMR spectrum of **4-CN,** the 2C-1'N dimer of the 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical **4** in $CDCl_3$.

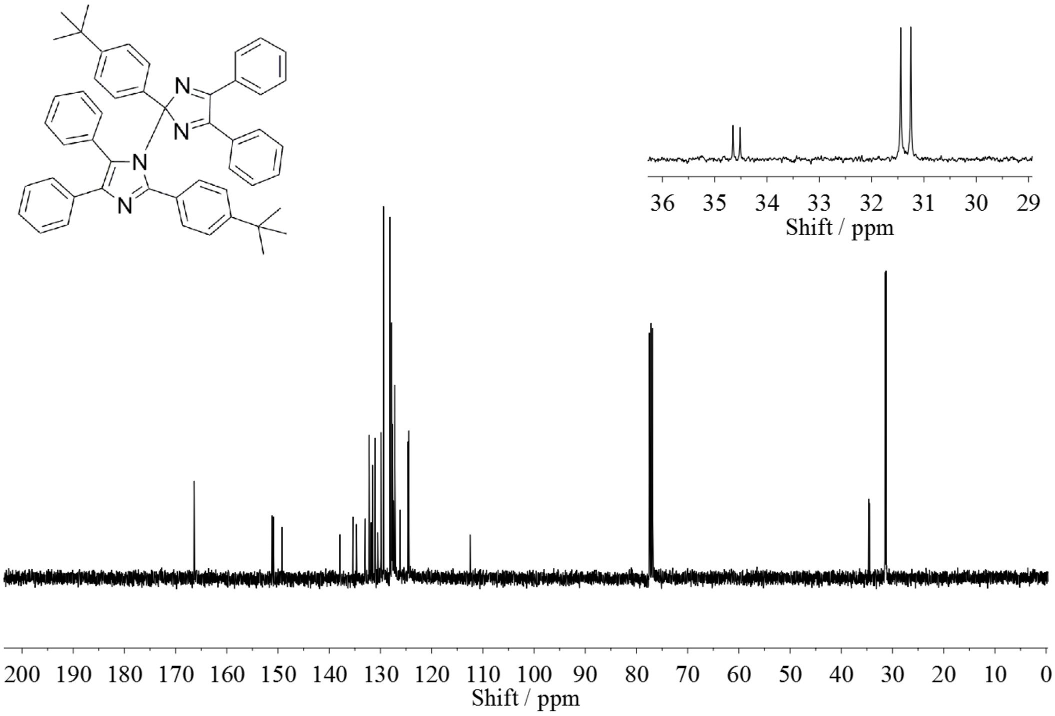


Fig. S6 101 MHz ^{13}C{^{1}H} NMR spectrum of **4-CN,** the 2C-1'N dimer of the 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical **4** in $CDCl_3$.

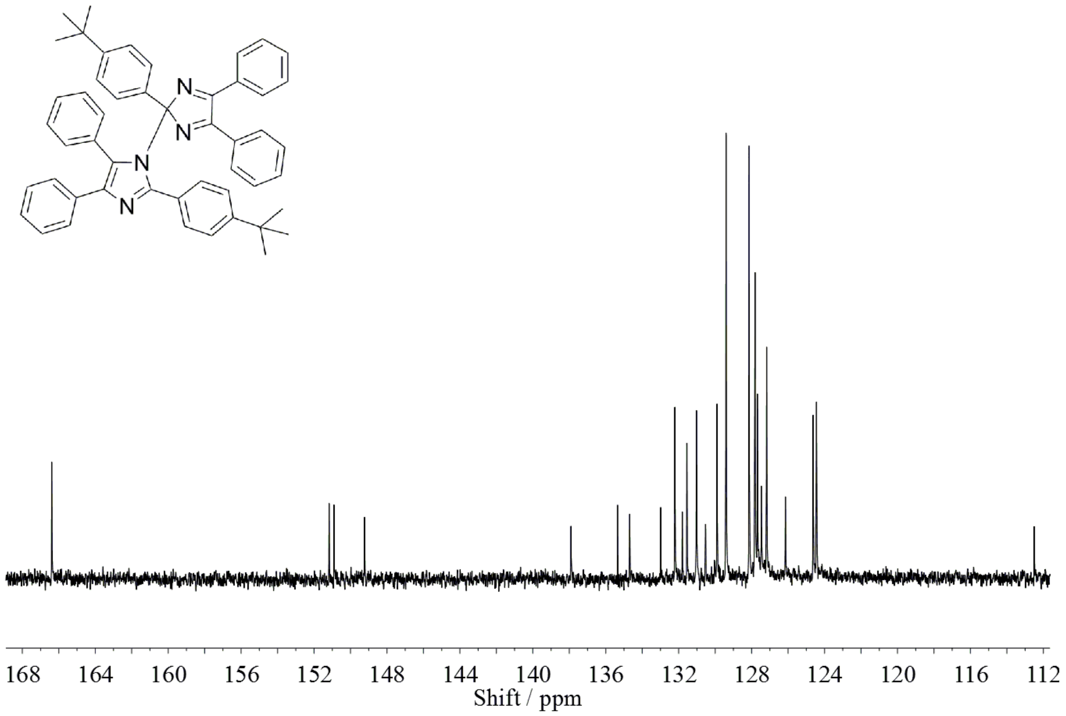


Fig. S7 Aromatic region of the 101 MHz ^{13}C{^{1}H} NMR spectrum of **4-CN,** the 2C-1'N dimer of the 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl radical **4** in $CDCl_3$.

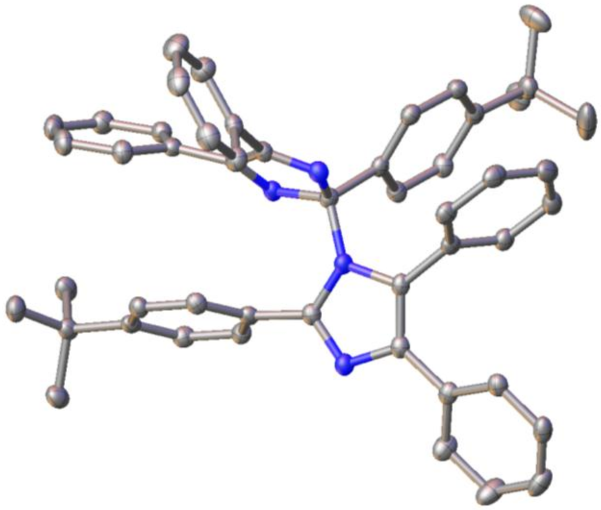


Fig. S8 SC-XRD molecular structure of Form II of **4-CN**, the 2C-1′N dimer of the 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazole radical, **4**. Hydrogen atoms are omitted for clarity.

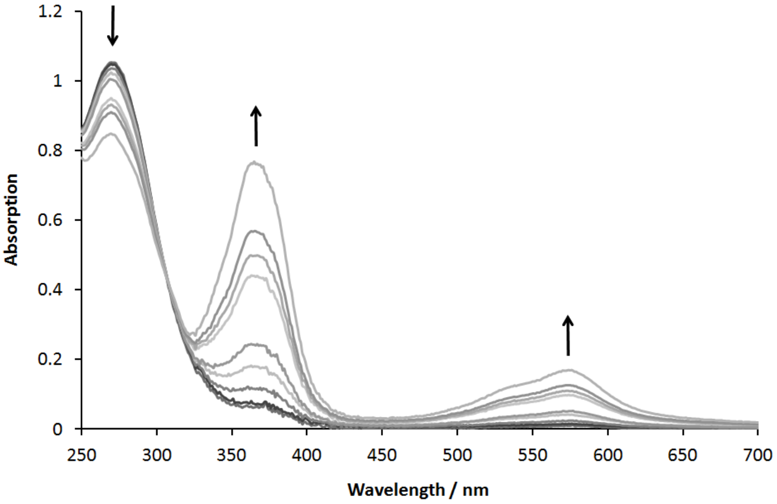


Fig. S9 UV-visible absorption spectroscopic monitoring of the photochromism of **4-CN** in dilute dichloromethane solution. Spectra were recorded with a *ca*. 2-5 s interval of irradiation at 365 nm from a 100 mW LED. The arrows indicate the direction of spectral change upon irradiation.

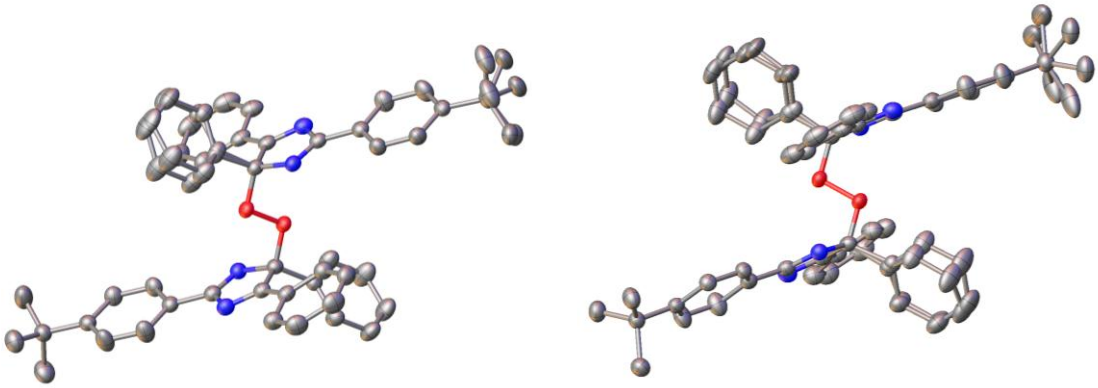


Fig. S10 SC-XRD molecular structure of 2-(4'-*tert*-butylphenyl)-4,5-diphenylimidazolyl peroxide, **6** (Form II), at 100 K. The asymmetric unit contains two independent molecules, *i.e.* *Z′* = 2, both of which are shown here. One *tert*-butyl group and one (left) or two (right) of the phenyl groups of each molecule is disordered, modelled over two sites with 50:50 occupancy. Hydrogen atoms are omitted for clarity.

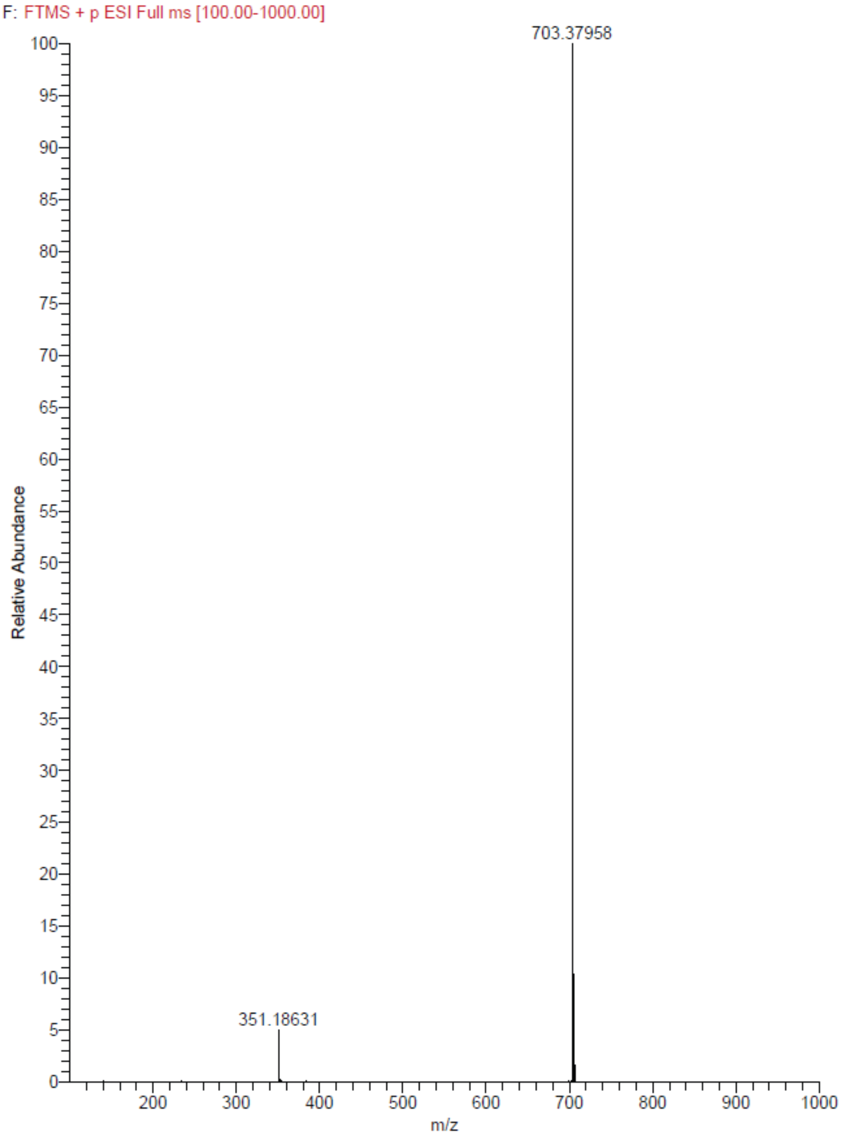
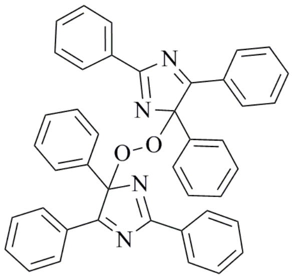
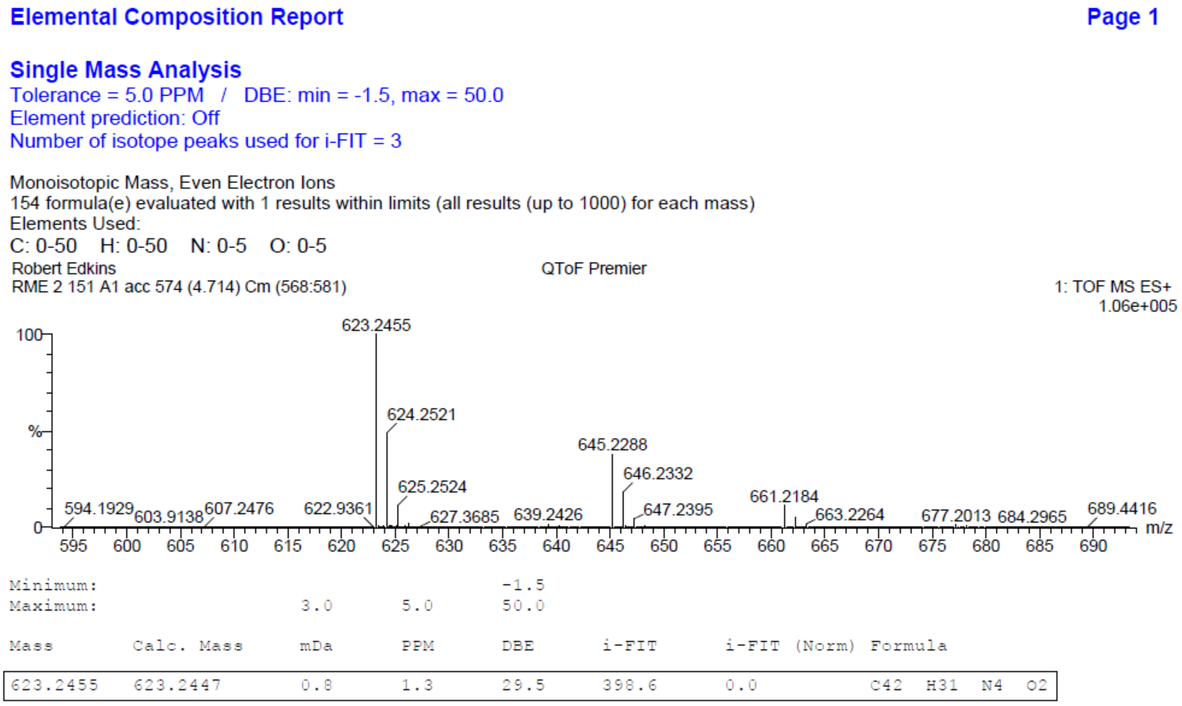


Fig. S11 Electrospray mass spectrum of **4-CN** before irradiation under oxygen atmosphere. *m/z* = 703.37958 corresponds to [**4-CN**+H]$^+$ (calculated for $C_{50}H_{47}N_4$ 703.37952). *m/z* 351.18631 corresponds to [**4-CN**/2]$^+$ (calculated for $C_{25}H_{23}N_2$ 351.18558).





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
154 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5
Robert Edkins QToF Premier
RME 2 151 A1 acc 574 (4.714) Cm (568:581) 1: TOF MS ES+
1.06e+005

```
Minimum:                                        -1.5
Maximum:                       3.0       5.0    50.0

Mass       Calc. Mass         mDa       PPM    DBE      i-FIT      i-FIT (Norm) Formula

623.2455   623.2447           0.8       1.3    29.5     398.6      0.0          C42  H31  N4  O2
```

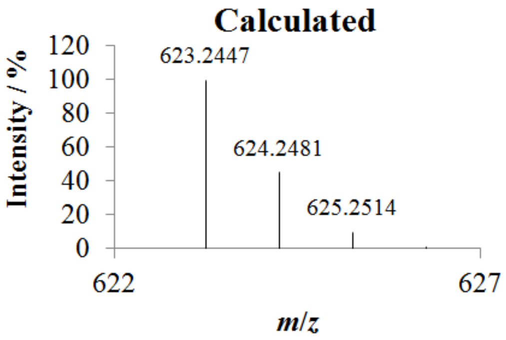
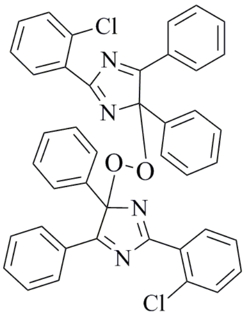
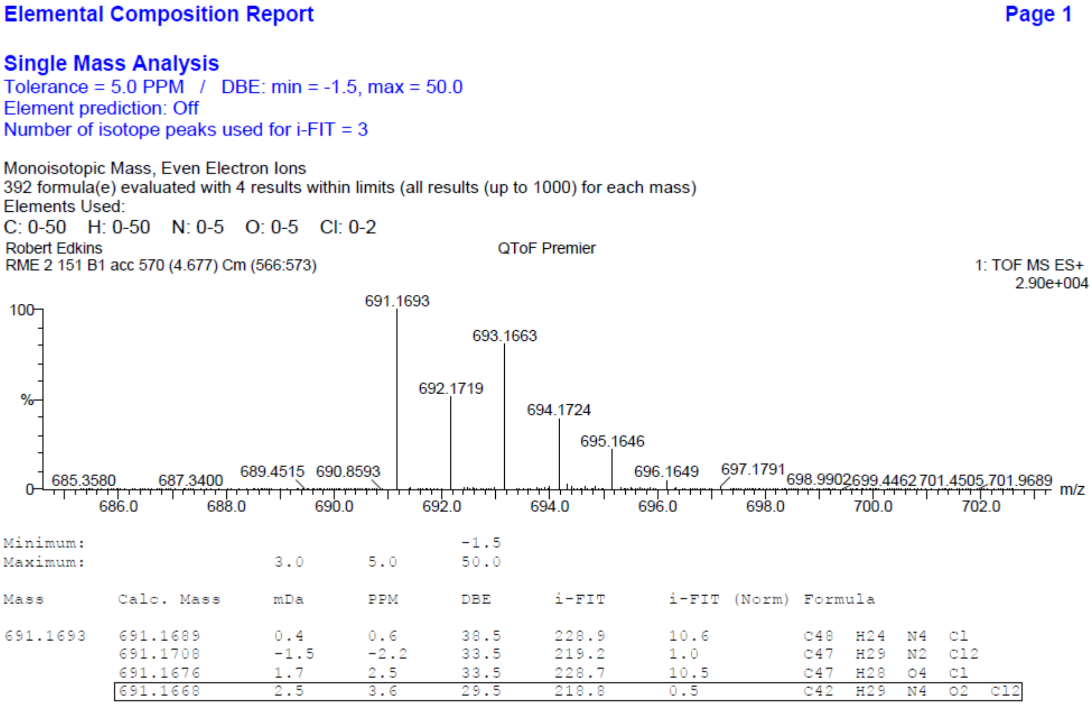


Fig. S12 Proposed peroxide of the 2,4,5-triphenylimidazolyl radical (top). Accurate mass spectrum (ESI$^+$ MS) of the [peroxide+H]$^+$ (m/z = 623.2455) and [peroxide+Na]$^+$ (m/z = 645.2288) formed following irradiation of the radical's 2C-1′N dimer under an oxygen atmosphere. The best fit between calculated and observed mass of [peroxide+H]$^+$ is highlighted in the list of possible formulae (middle). Calculated isotope pattern of [peroxide+H]$^+$ for comparison (bottom).





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
392 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5 Cl: 0-2

Robert Edkins QToF Premier
RME 2 151 B1 acc 570 (4.677) Cm (566:573) 1: TOF MS ES+
2.90e+004

```
Minimum:                                       -1.5
Maximum:                       3.0      5.0    50.0

Mass      Calc. Mass           mDa      PPM    DBE     i-FIT     i-FIT (Norm) Formula

691.1693  691.1689             0.4      0.6    38.5    228.9     10.6         C48  H24  N4  Cl
          691.1708             -1.5     -2.2   33.5    219.2     1.0          C47  H29  N2  Cl2
          691.1676             1.7      2.5    33.5    228.7     10.5         C47  H28  O4  Cl
          691.1668             2.5      3.6    29.5    218.8     0.5          C42  H29  N4  O2  Cl2
```

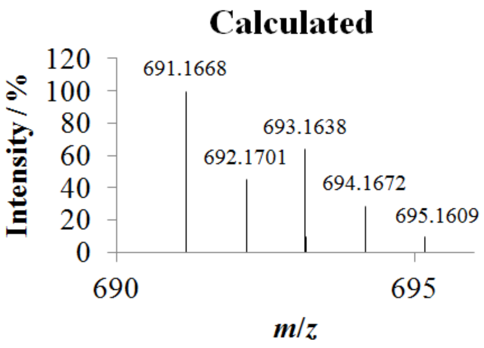
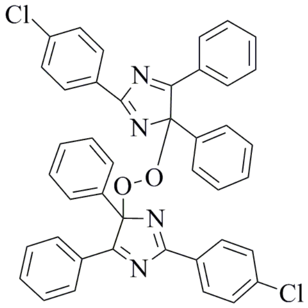
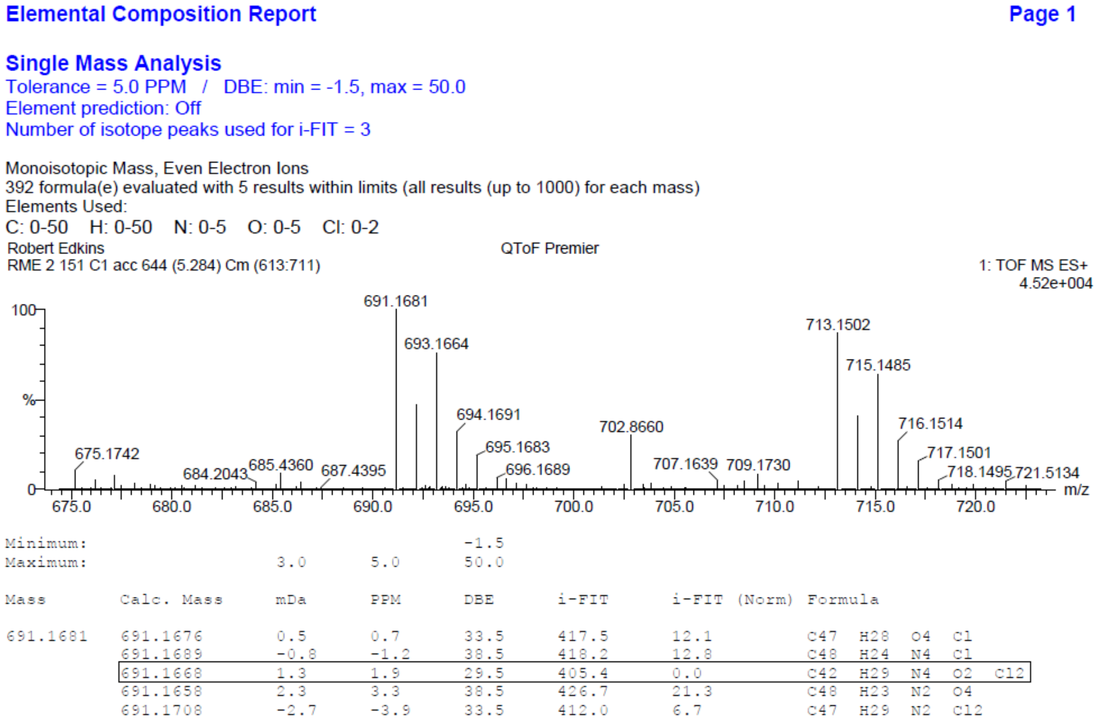


Fig. S13 Proposed peroxide of the 2-(2′-chlorophenyl)-4,5-diphenylimidazolyl radical (top). Accurate mass spectrum (ESI$^+$ MS) of the [peroxide+H]$^+$ (*m/z* = 691.1693) formed following irradiation of the radical's 2C-1′N dimer under an oxygen atmosphere. The best fit between calculated and observed mass of [peroxide+H]$^+$ is highlighted in the list of possible formulae (middle). Calculated isotope pattern of [peroxide+H]$^+$ for comparison (bottom).





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
392 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5 Cl: 0-2

Robert Edkins QToF Premier
RME 2 151 C1 acc 644 (5.284) Cm (613:711) 1: TOF MS ES+
4.52e+004

```
Minimum:                                   -1.5
Maximum:                  3.0      5.0     50.0

Mass       Calc. Mass     mDa      PPM     DBE      i-FIT     i-FIT (Norm) Formula

691.1681   691.1676       0.5      0.7     33.5     417.5     12.1         C47  H28  O4   Cl
           691.1689       -0.8     -1.2    38.5     418.2     12.8         C48  H24  N4   Cl
           691.1668       1.3      1.9     29.5     405.4     0.0          C42  H29  N4   O2   Cl2
           691.1658       2.3      3.3     38.5     426.7     21.3         C48  H23  N2   O4
           691.1708       -2.7     -3.9    33.5     412.0     6.7          C47  H29  N2   Cl2
```

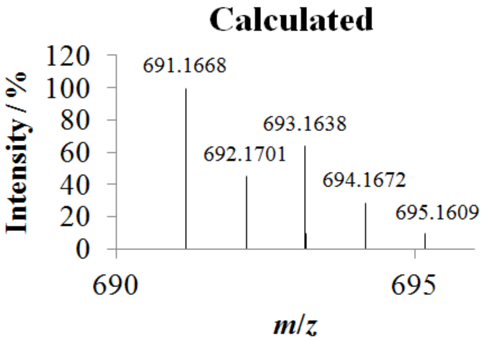
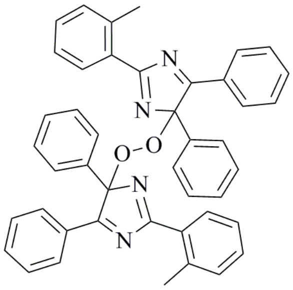
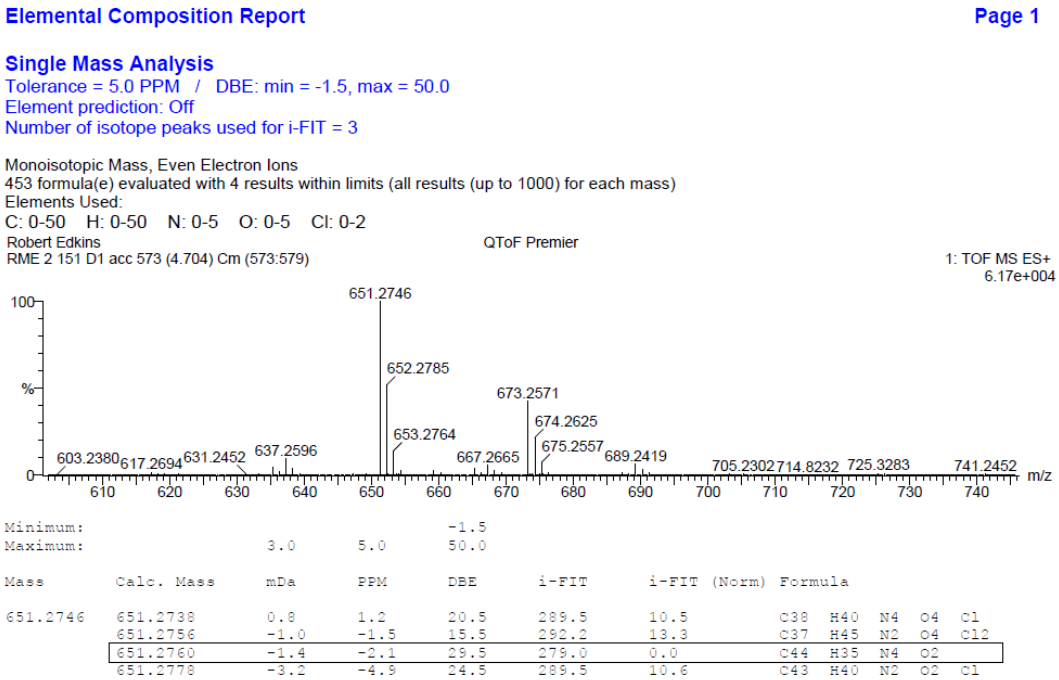


Fig. S14 Proposed peroxide of the 2-(4′-chlorophenyl)-4,5-diphenylimidazolyl radical (top). Accurate mass spectrum (ESI$^+$ MS) of the [peroxide+H]$^+$ (*m*/*z* = 691.1681) and [peroxide+Na]$^+$ (*m*/*z* = 713.1502) formed following irradiation of the radical’s 2C-1′N dimer under an oxygen atmosphere. The best fit between calculated and observed mass of [peroxide+H]$^+$ is highlighted in the list of possible formulae (middle). Calculated isotope pattern of [peroxide+H]$^+$ for comparison (bottom).





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
453 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5 Cl: 0-2
Robert Edkins QToF Premier
RME 2 151 D1 acc 573 (4.704) Cm (573:579) 1: TOF MS ES+
6.17e+004

```
Minimum:                                 -1.5
Maximum:                  3.0       5.0      50.0

Mass        Calc. Mass     mDa       PPM      DBE      i-FIT       i-FIT (Norm) Formula

651.2746    651.2738       0.8       1.2      20.5     289.5       10.5         C38  H40  N4  O4  Cl
            651.2756       -1.0      -1.5     15.5     292.2       13.3         C37  H45  N2  O4  Cl2
            651.2760       -1.4      -2.1     29.5     279.0       0.0          C44  H35  N4  O2
            651.2778       -3.2      -4.9     24.5     289.5       10.6         C43  H40  N2  O2  Cl
```

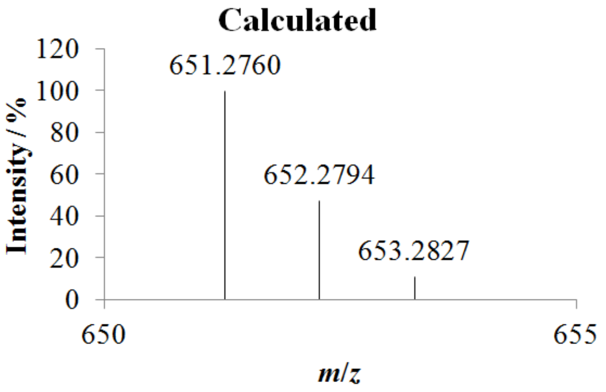
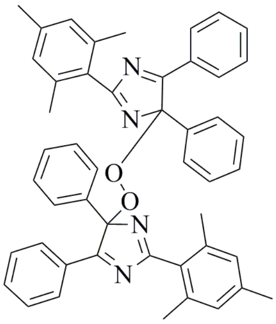
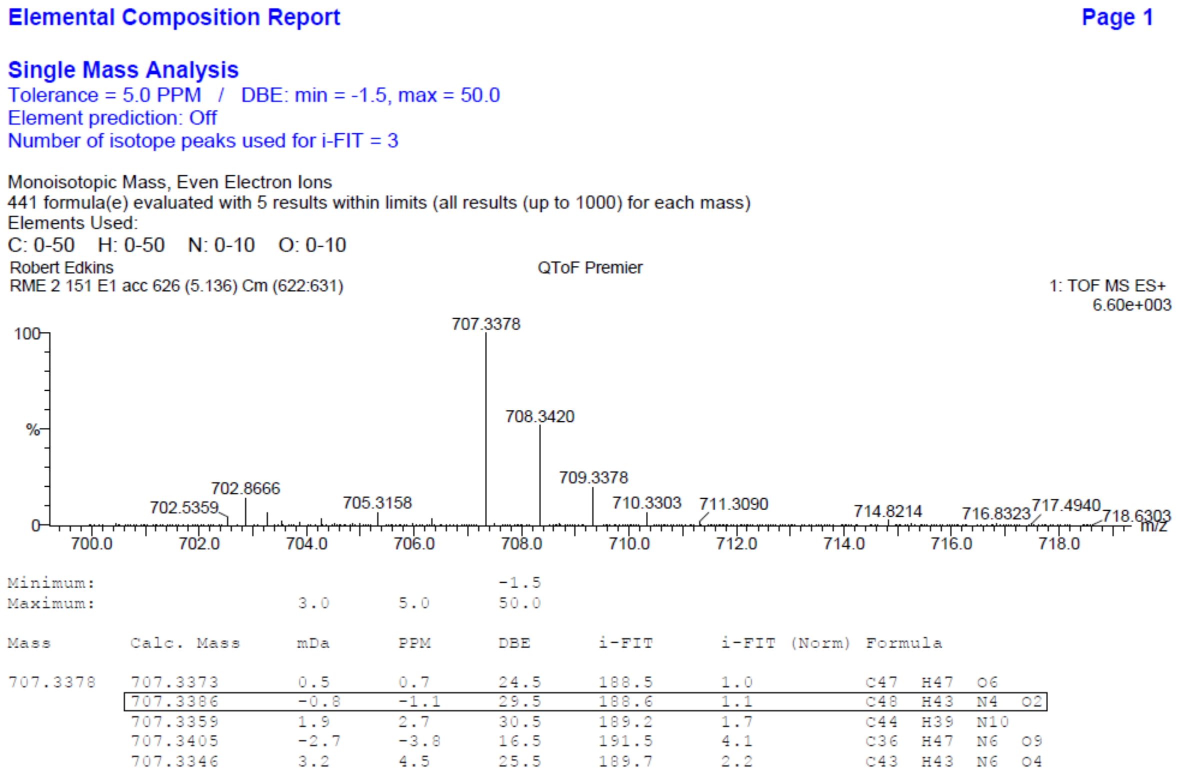


Fig. S15 Proposed peroxide of the 2-(2′-methylphenyl)-4,5-diphenylimidazolyl radical (top). Accurate mass spectrum (ESI^+ MS) of the $[peroxide+H]^+$ (*m*/*z* = 651.2746) and $[peroxide+Na]^+$ (*m*/*z* = 673.2571) formed following irradiation of the radical's 2C-1′N dimer under an oxygen atmosphere. The best fit between calculated and observed mass of $[peroxide+H]^+$ is highlighted in the list of possible formulae (middle). Calculated isotope pattern of $[peroxide+H]^+$ for comparison (bottom).





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
441 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-10 O: 0-10
Robert Edkins QToF Premier
RME 2 151 E1 acc 626 (5.136) Cm (622:631) 1: TOF MS ES+
6.60e+003

```
Minimum:                                -1.5
Maximum:                 3.0      5.0   50.0

Mass      Calc. Mass     mDa      PPM   DBE     i-FIT     i-FIT (Norm) Formula

707.3378  707.3373       0.5      0.7   24.5    188.5     1.0          C47  H47  O6
          707.3386       -0.8     -1.1  29.5    188.6     1.1          C48  H43  N4  O2
          707.3359       1.9      2.7   30.5    189.2     1.7          C44  H39  N10
          707.3405       -2.7     -3.8  16.5    191.5     4.1          C36  H47  N6  O9
          707.3346       3.2      4.5   25.5    189.7     2.2          C43  H43  N6  O4
```

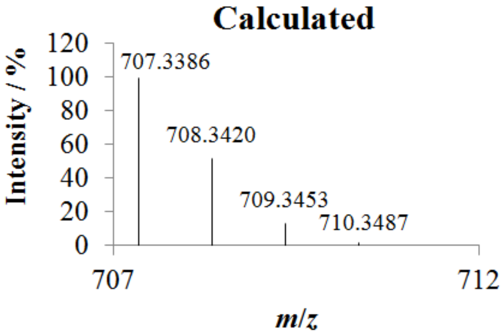


Fig. S16 Proposed peroxide of the 2-(2′,4′,6′-trimethylphenyl)-4,5-diphenylimidazolyl radical (top). Accurate mass spectrum (ESI$^+$ MS) of the [peroxide+H]$^+$ (*m*/*z* = 707.3378) formed following irradiation of the radical's 2C-1′N dimer under an oxygen atmosphere. The best fit between calculated and observed mass of [peroxide+H]$^+$ is highlighted in the list of possible formulae (middle). Calculated isotope pattern of [peroxide+H]$^+$ for comparison (bottom).

Table S1. Single crystal X-ray diffraction data.

	2-tBu-Im	**4-tBu-Im**	**4-tBu-Dimer (Form I)**	**4-tBu-Dimer (Form II)**	**2-tBu Peroxide**	**2-tBu Peroxide**	**4-tBu Peroxide (Form I)**	**4-tBu Peroxide (Form II)**
Compound number	**1**	**3**	**4-CN**	**4-CN**	**5**	**5′**	**6**	**6**
Empirical formula	$C_{25}H_{24}N_2$	$C_{25}H_{24}N_2$	$C_{50}H_{46}N_4$	$C_{50}H_{46}N_4$	$C_{50}H_{46}N_4O_2$	$C_{50}H_{46}N_4O_2$	$C_{50}H_{46}N_4O_2$	$C_{50}H_{46}N_4O_2$
M_r	352.46	352.46	702.91	702.91	734.91	734.91	734.91	734.91
Crystal colour	Colourless	Colourless	Light yellow	Light yellow	Colourless	Colourless	Colourless	Colourless
Crystal habit	Block	Lath	Block	Needle	Block	Block	Block	Block
Crystal size / mm^3	0.03 × 0.01 × 0.01	0.30 x 0.08 x 0.01	0.26 x 0.20 x 0.11	0.18 x 0.11 x 0.09	0.22 x 0.16 x 0.08	0.24 × 0.18 × 0.09	0.28 x 0.12 x 0.10	0.28 x 0.12 x 0.10
T / K	120(2)	120(2)	100(2)	100(2)	100(2)	100(2)	160(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$	C2/c	$I2/a$	$P2_1/c$
Unit cell dimensions								
a / Å	9.692(2)	36.809(6)	12.6166(2)	12.1735(2)	8.88770(10)	18.7885(5)	16.1305(10)	16.0313(4)
b / Å	19.705(5)	12.205(2)	12.1515(2)	12.2821(3)	23.4338(4)	10.0808(3)	15.4759(6)	30.9627(9)
c / Å	21.494(5)	8.9185(15)	26.5190(4)	15.1686(3)	10.4997(2)	21.5264(5)	16.6219(6)	16.5171(5)
α / deg.	90.00	90.00	90.00	111.6050(4)	90.00	90.00	90.00	90.00
β / deg.	100.178(3)	95.551(2)	98.3060(4)	101.1490(4)	114.4170(3)	102.4180(10)	94.2670(10)	93.7920(10)
γ / deg	90.00	90.00	90.00	98.8910(5)	90.00	90.00	90.00	90.00
V / Å^3	4040.3(16)	3987.9(11)	4023.00(11)	2004.46(7)	1991.21(6)	3981.78(18)	4137.9(3)	8180.7(4)
Z	8	8	4	2	2	4	4	8
D_{calc} / g cm^{-3}	1.159	1.174	1.161	1.165	1.226	1.226	1.180	1.193
μ / mm^{-1}	0.068	0.069	0.519	0.521	0.585	0.585	0.563	0.570
F(000)	1504	1504	1496	748	780	1560	1560	3120.0
λ / Å	0.68890	0.68890	1.54188	1.54188	1.54188	1.54188	1.54188	1.54188
No. of reflections	31649	39090	43177	25172	15174	16975	15378	62341
Independent reflections	6990	9628	7083	9796	3528	3282	3209	12830
Data / restraints / parameters	6990/0/501	9628/0/554	7083/0/493	/0/493	3528/0/256	3282/0/256	3209/0/264	12830/0/1032
Refinement method	Full-matrix least squares on $F^2\theta$ range for data collection							
Theta range / °	1.37 to 24.80	1.62 to 27.37	3.37 to 68.66	3.26 to 68.97	3.77 to 68.41	4.21 to 67.80	3.91 to 63.42	3.70 to 68.23
Index range	$-11 \leq h \leq 11$	$-49 \leq h \leq 49$	$-15 \leq h \leq 15$	$-14 \leq h \leq 13$	$-10 \leq h \leq 10$	$-21 \leq h \leq 20$	$-18 \leq h \leq 18$	$-18 \leq h \leq 18$
	$-23 \leq k \leq 23$	$-16 \leq k \leq 16$	$-14 \leq k \leq 14$	$-14 \leq k \leq 13$	$-28 \leq k \leq 28$	$-11 \leq k \leq 12$	$-17 \leq k \leq 17$	$-35 \leq k \leq 35$
	$-23 \leq l \leq 25$	$-8 \leq l \leq 11$	$-29 \leq l \leq 31$	$-18 \leq l \leq 18$	$-11 \leq l \leq 12$	$-25 \leq l \leq 24$	$-19 \leq l \leq 19$	$-18 \leq l \leq 19$
R_{int}	0.0859	0.0576	0.0291	0.0243	0.0248	0.0408	0.0405	0.0480
Final R [$I > 2\sigma(I)$]								
R_1	0.0559	0.0834	0.0353	0.0373	0.0350	0.0367	0.0498	0.0577
wR_2	0.1293	0.2142	0.0882	0.0937	0.0897	0.0963	0.1357	0.1604
R indices (all data)								
R_1	0.0971	0.0925	0.0380	0.0381	0.0363	0.0382	0.0520	0.0637
wR_2	0.1471	0.2205	0.0903	0.0943	0.0907	0.0976	0.1379	0.1659
Goodness of fit on F^2	1.001	1.035	1.031	1.036	1.030	1.017	1.022	1.076
Largest diff. peak / hole (e Å^3)	0.23/-0.21	1.28/-1.09	0.22/-0.23	0.181/-0.217	0.25/-0.21	0.24/-0.21	0.24 / -0.21	0.35/-0.23

References

1. N. Azizi, N. Dado and A. K. Amiri, *Can. J. Chem.*, 2011, **90**, 195-198.
2. G. R. Coraor, L. A. Cescon, R. Dessauer, E. F. Silversmith and E. J. Urban, *J. Org. Chem.*, 1971, **36**, 2262-2267.
3. S. E. Wolkenberg, D. D. Wisnoski, W. H. Leister, Y. Wang, Z. J. Zhao and C. W. Lindsley, *Org. Lett.*, 2004, **6**, 1453-1456.
4. N. Fey, J. A. S. Howell, J. D. Lovatt, P. C. Yates, D. Cunningham, P. McArdle, H. E. Gottlieb and S. J. Coles, *Dalton Trans.*, 2006, 5464-5475.
5. J. A. Varela, D. Peña, B. Goldfuss, D. Denisenko, J. Kulhanek, K. Polborn and P. Knochel, *Chem. Eur. J.*, 2004, **10**, 4252-4264.