Photooxidation of 2-(\textit{tert}-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one, an example of singlet oxygen \textit{ene} reaction.

A. Méndez\textsuperscript{1}, Jonathan R. Valdez-Camacho\textsuperscript{1}, and Jaime Escalante\textsuperscript{1,}*  

\textsuperscript{1} The Center for Chemical Research, Autonomous University of Morelos State, Avenida Universidad 1001, Chamilpa, Cuernavaca 62210, Mexico.  
\textsuperscript{*} Correspondence: jaime@uaem.mx (J.E.); Tel.: +52-77-7329-7997 (J.E.)

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1) General considerations for the synthesis and characterizations

Dichloromethane, ethyl acetate, and hexane were distilled before use. Toluene (Aldrich), acetonitrile (Merck), tert-butanol (Aldrich), Isatoic Anhydride (Aldrich), Methylamine (Aldrich), p-toluene sulfonic acid (Aldrich), pivalaldehyde (Aldrich), sodium bicarbonate (Aldrich), sodium sulfate (Aldrich), sodium (Aldrich), palladium/carbon (Aldrich), 4,4-dimethylamino pyridine (Aldrich), and acetyl chloride (Aldrich) were acquired from the commercial suppliers indicated in parenthesis and used without further purification. Reactions were monitored by TLC on Al plates coated with silica gel with fluorescent indicator (60 F254). Column chromatography (CC) was performed on silica gel (230-400 mesh Merck). NMR Spectra: Varian Gemini at 200 (1H) and 50 MHz (13C), Varian Inova at 400 (1H) and 100 MHz (13C), Bruker AVANCE III HD 500 MHz (1H) and 125 MHz (13C). Chemical shifts in the 1H NMR spectra are reported in parts per million (ppm, δ scale) downfield relative to tetramethylsilane (δ 0), which was used as an internal standard in CDCl3, or relative to the residual proton in the solvent (CDCl3: δ 7.26). Chemical shifts in the 13C NMR spectra are reported in parts per million (ppm, δ scale) downfield relative to tetramethylsilane, and are referenced to the 13C NMR resonance of the solvent (CDCl3: δ 77.23). A mass spectrometric analysis was performed using an Agilent 6530 Quadrupole Time of Flight (QTOF) LCMS with an electrospray ionization (ESI) source (Agilent Technologies, Santa Clara, CA, USA). A mass spectrometry analysis was conducted in positive ion mode, set for a detection of mass-to-charge ratio (m/z) of 100 to 1000. Intensity data for the X-ray crystallographic analyses were collected at 100 or 120 K on a Agilent Technologies Super Nova equipped with a CCD area detector (EosS2). Using Mo-Kα (λ = 0.7107 Å). The structures were solved with the OLEX2 [1] program package using SHELXLTL [2] and refined with SHELXL-2014 [3]. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The crystal structure data were deposited at the Cambridge Crystallographic Data Center.
2) Synthesis of 2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(IH)-one (8) [4]

Scheme 1. Synthesis of quinazolinone 8

Prepared according to a known procedure [4] from isatoic anhydride (6 g, 30.68 mmol), methylamine (18.24 mL, 122.72 mmol), and ethyl acetate (50 mL). The reaction was heated at 40 °C for 2h. The resulting material was filtered and concentrated in a rotavapor, producing 2.06g of reaction crude. A suspension of reaction crude (2.06 g), p-toluenesulfonic acid (0.103 g, 5% w/w), pivalaldehyde (1.86 mL, 1.2 equiv.), and dichloromethane (60 mL). The reaction was refluxed for 5 h. The resulting material was filtered and concentrated in a rotavapor, then purified by column chromatography on silica, eluting with hexane-ethyl acetate (9:1 to 6:4). Yield: 90%; white solid; mp: 145-146 °C; $^1$H NMR (CDCl$_3$, 200 MHz): δ 0.91 (s, 9H), 3.20 (s, 3H), 4.34(d, 1H), 4.71 (sa, 1H), 6.56 - 6.58 (d, 1H), 6.70 - 6.74 (t, 1H), 7.19 - 7.23 (t, 1H), 7.80 - 7.83 (d, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 26.3 (C10-12), 38.5 (C11), 41.9 (C9), 79.9 (C2), 113.1 (C8), 116.6 (C4a), 118.1 (C6), 128.1 (C5), 133.4 (C7), 146.5 (C8a), 163.8 (C4). HREIMS m/z 218.1440 (calculated for C$_{13}$H$_{18}$N$_2$O, 218.1419).

3) Synthesis of 2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(IH)-one (11).

Scheme 2. Synthesis of hexahydroquinazolinone 11.

Prepared from ammonia (50 mL), 2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(IH)-one 8 (1 g, 4.64 mmol), and sodium (0.64 g, 28 mmol). The reaction was cooled and stirred at -78 °C. After 30 minutes, tert-butanol (1.4 mL, 14 mmol) was added and was allowed react for 1 hour. Finally, the reaction is quenched adding ammonium chloride (0.64 g, 18.56 mmol). The ammonia is evaporated and reaction crude is dissolved in dichloromethane, dried with sodium sulfate and the excess solvent is concentrated in vacuo. A suspension of reaction crude (0.8 g), Pd/C (0.04g, 5% w/w), and methanol (60 mL) was placed in a 100 mL flask containing a stir bar, then the system was closed with a septum. Two balloons were placed with hydrogen and the reaction was stirred overnight. The reaction mixture was filtered and concentrated in a rotavapor rotavapor, then purified by column chromatography on silica, eluting with hexane-ethyl acetate (9:1 to 2:8). Yield: 28%; light-yellow solid; mp: 134-137 °C. $^1$H NMR (200 MHz, CDCl$_3$) δ 4.18 (d, 1H, J = 4.6 Hz, 1H), 3.88 (s, 1H), 3.06 (s, 3H),
2.27 – 2.04 (m, 4H), 1.77 – 1.36 (m, 4H), 0.91 (s, 9H). $^{13}$C NMR due to the high reactivity of 11, it was not possible to acquire a suitable spectrum for its assignment.

4) Synthesis of 2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12)

2-(tert-Butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one 11 (0.071g, 0.32 mmol) was dissolved in 2 mL dichloromethane inside a suitable test tube, then 8 mL of hexane was added carefully to form a biphasic, the system was closed with a cotton septum and left exposed to the environment for the evaporation of the solvents. After overnight, crystals of the expected compound were obtained. Yield: 81mg, quantitative yield; White crystal; mp: 152-154°C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.02 (s, 9H), 1.55-1.67 (m, 3H), 1.94-1.97 (m, 1H), 2.08-2.11 (m, 1H), 2.39-2.47 (m, 2H), 2.94-2.95 (m, 1H) 3.10 (s, 3H), 4.90 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.3, 168.6, 85.3, 76.3, 40.1, 37.0, 34.2, 33.7, 28.5, 27.2, 20.5. HREIMS m/z 254.1654 (calculated for C$_{13}$H$_{22}$N$_2$O$_3$, 254.1630). CCDC No. 2006916.

5) Synthesis of 1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13)

2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one 11 (0.8 g, 3.6 mmol), 4-dimethylaminopyridine (0.439 g, 3.6 mmol) and toluene/acetonitrile solution 9:1 (40 mL) was added to a 100 mL flask. It was placed in an ice bath and the system purged with nitrogen. Acetyl chloride (0.3 mL, 4.32 mmol) was added dropwise and the reaction was stirred overnight. After time the reaction crude was filtered and concentrated in a rotavapor then purified by column chromatography on silica, eluting with hexane-ethyl acetate (9:1 to 3:7). Yield: quantitative; white solid; mp: 146-148 °C; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 5.44 (s, 1H), 3.03 (s, 3H), 2.79 – 2.54 (m, 2H), 2.13 (s, 3H), 2.09 – 1.98 (m, 2H), 1.91 – 1.36 (m, 4H), 0.89 (s, 9H). $^{13}$C NMR (50 MHz CDCl$_3$) $\delta$ 170.8, 163.5, 122.3, 38.4, 37.1, 30.5, 27.17, 27.0, 24.1, 22.6, 22.5, 21.6. HREIMS m/z 264.1843 (calculated for C$_{15}$H$_{24}$N$_2$O$_2$, 264.1838). CCDC No. 2007030.
6) $^1$H and $^{13}$C NMR spectra for compounds 8.

Figure S1. $^1$H spectrum (200 MHz, CDCl$_3$) of 8

Figure S2. $^{13}$C spectrum (100 MHz, CDCl$_3$) of 8
7) $^1$H and $^{13}$C NMR spectra for compounds 11.

*Figure S3. $^1$H spectrum (200 MHz, CDCl$_3$) of 11*

*Figure S4. $^{13}$C spectrum (50 MHz, CDCl$_3$) of 11*
8) $^1$H and $^{13}$C NMR spectra for compounds 12.

Figure S5. $^1$H spectrum (500 MHz, CDCl$_3$) of 12

Figure S6. $^{13}$C spectrum (125 MHz, CDCl$_3$) of 12
9) $^1$H and $^{13}$C NMR spectra for compounds 13.

**Figure S7.** $^1$H spectrum (200 MHz, CDCl$_3$) of 13

**Figure S8.** $^{13}$C spectrum (50 MHz, CDCl$_3$) of 13
10) Crystallographic data and structure refinement for product 8.

Table S1. Crystal data and structure refinement for 135leo (2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(IH)-one (8)).

| Property                           | Value                      |
|-----------------------------------|----------------------------|
| Identification code               | 135leo                     |
| Empirical formula                 | C_{33}H_{45}N_{3}O_{7}      |
| Formula weight                    | 595.72                     |
| Temperature/K                     | 293(2)                     |
| Crystal system                    | monoclinic                 |
| Space group                       | P2_1                       |
| a/Å                               | 6.91475(15)                |
| b/Å                               | 11.68447(15)               |
| c/Å                               | 8.08083(14)                |
| α/°                               | 90                         |
| β/°                               | 113.833(2)                 |
| γ/°                               | 90                         |
| Volume/Å³                         | 597.22(2)                  |
| Z                                 | 1                          |
| ρ<sub>calc</sub>/g/cm³            | 1.656                      |
| μ/mm⁻¹                            | 0.945                      |
| F(000)                            | 320.0                      |
| Crystal size/mm³                  | 0.21 × 0.23 × 0.34         |
| Radiation                         | CuKα (λ = 1.54184)         |
| 2Θ range for data collection/°    | 11.974 to 144.606          |
| Index ranges                      | -8 ≤ h ≤ 8, -14 ≤ k ≤ 14, -9 ≤ l ≤ 9 |
| Reflections collected             | 7294                       |
| Independent reflections           | 2301 [R<sub>int</sub> = 0.0152, R<sub>sigma</sub> = 0.0121] |
| Data/restraints/parameters        | 2301/1/149                 |
| Goodness-of-fit on F²             | 1.094                      |
| Final R indexes [I>=2σ (I)]      | R₁ = 0.0338, wR₂ = 0.1120  |
| Final R indexes [all data]       | R₁ = 0.0339, wR₂ = 0.1122  |
| Largest diff. peak/hole / e Å⁻³   | 0.37/-0.30                 |
| Flack parameter                   | 0.52(7)                    |
Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for 135leo (2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(1H)-one (8)). $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | $x$   | $y$       | $z$       | $U_{eq}$ |
|------|-------|-----------|-----------|----------|
| O1   | -18(2)| 4586.0(15)| 7283.1(18)| 30.2(4)  |
| N1   | 5666(2)| 4418.1(12)| 7052.9(18)| 18.0(4)  |
| N3   | 2066(2)| 3862.8(12)| 5969.7(19)| 19.6(4)  |
| C2   | 3904(2)| 3974.0(13)| 5491(2)   | 17.2(4)  |
| C4   | 1632(3)| 4626.8(16)| 7025(2)   | 20.4(4)  |
| C4A  | 3293(3)| 5478.8(14)| 7963(2)   | 18.5(4)  |
| C5   | 2919(3)| 6394.6(15)| 8910(2)   | 22.8(4)  |
| C6   | 4517(3)| 7127.5(16)| 9931(3)   | 26.1(4)  |
| C7   | 6559(3)| 6926.3(15)| 10036(2)  | 27.4(4)  |
| C8   | 6974(3)| 6029.0(16)| 9108(2)   | 22.4(4)  |
| C8A  | 5322(3)| 5308.0(14)| 8020(2)   | 17.3(3)  |
| C9   | 3444(3)| 4641.7(14)| 3697(2)   | 20.2(4)  |
| C10  | 1528(3)| 4110.3(17)| 2162(2)   | 27.0(4)  |
| C11  | 5388(3)| 4510.0(17)| 3249(2)   | 26.8(4)  |
| C12  | 2992(4)| 5906.2(16)| 3857(3)   | 29.9(5)  |
| C13  | 679(3) | 2874.7(17)| 5302(3)   | 29.3(4)  |

Table S3 Anisotropic Displacement Parameters ($Å^2\times10^3$) for 135leo(2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(1H)-one (8)). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hkab^*U_{12}+...].$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| O1   | 16.7(6)  | 48.3(8)  | 28.8(7)  | -4.3(6)  | 12.4(5)  | -7.2(6)  |
| N1   | 12.5(7)  | 20.6(7)  | 22.0(7)  | 0.4(5)   | 8.2(6)   | 2.5(5)   |
| N3   | 17.6(7)  | 20.9(7)  | 20.5(6)  | 0.1(5)   | 8.0(5)   | -4.9(5)  |
| C2   | 17.8(7)  | 13.6(7)  | 21.5(8)  | 0.6(5)   | 9.4(6)   | 1.4(5)   |
| C4   | 16.0(8)  | 27.1(8)  | 19.8(8)  | 3.3(6)   | 9.1(6)   | 0.6(7)   |
| C4A  | 18.3(8)  | 21.7(8)  | 17.0(7)  | 2.3(6)   | 8.6(6)   | -0.3(6)  |
| C5   | 25.7(8)  | 24.8(9)  | 22.7(8)  | 3.1(6)   | 14.6(7)  | 3.9(7)   |
| C6   | 40.2(12)| 21.2(8)  | 22.9(8)  | -2.7(6)  | 19.0(8)  | -3.1(7)  |
| C7   | 34.3(10)| 26.4(9)  | 21.8(8)  | -2.8(7)  | 11.7(7)  | -10.7(7) |
| C8   | 20.3(8)  | 26.7(9)  | 22.4(9)  | 1.4(6)   | 10.7(6)  | -5.2(7)  |
| C8A  | 17.2(7)  | 18.9(7)  | 17.0(7)  | 4.3(6)   | 8.2(6)   | 0.9(6)   |
| C9   | 23.8(8)  | 19.9(8)  | 20.3(8)  | 0.4(6)   | 12.3(6)  | 2.6(6)   |
| C10  | 25.7(10)| 33.4(10)| 20.1(8)  | 1.5(7)   | 7.6(7)   | 5.0(7)   |
| C11  | 26.1(9)  | 34.3(10)| 24.8(8)  | 1.6(7)   | 15.3(7)  | 1.8(8)   |
| C12  | 47.9(11)| 21.3(9)  | 26.9(10)| 6.3(7)   | 21.8(9)  | 9.8(8)   |
| C13  | 26.1(9)  | 29.5(10)| 31.7(10)| -4.2(7)  | 11.1(7)  | -11.1(7)|
Table S4 Bond Lengths for 135leo (2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(1H)-one (8)).

| Atom | Atom | Length/Å |
|------|------|----------|
| O1   | C4   | 1.241(2) |
| N1   | C2   | 1.4508(19) |
| N1   | C8A  | 1.378(2) |
| N3   | C2   | 1.476(2) |
| N3   | C4   | 1.349(2) |
| N3   | C13  | 1.458(2) |
| C2   | C9   | 1.561(2) |
| C4   | C4A  | 1.477(2) |
| C4A  | C5   | 1.399(2) |
| C4A  | C8A  | 1.406(2) |
| C5   | C6   | 1.378(3) |
| C6   | C7   | 1.400(3) |
| C7   | C8   | 1.385(3) |
| C8   | C8A  | 1.406(2) |
| C9   | C10  | 1.534(2) |
| C9   | C11  | 1.535(2) |
| C9   | C12  | 1.526(2) |

Table S5 Bond Angles for 135leo (2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(1H)-one (8)).

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C8A  | N1   | C2   | 119.09(13) |
| C4   | N3   | C2   | 122.82(13) |
| C4   | N3   | C13  | 118.49(15) |
| C13  | N3   | C2   | 118.68(14) |
| N1   | C2   | N3   | 108.25(12) |
| N1   | C2   | C9   | 114.41(13) |
| N3   | C2   | C9   | 114.41(12) |
| O1   | C4   | N3   | 122.34(16) |
| O1   | C4   | C4A  | 121.11(16) |
| N3   | C4   | C4A  | 116.43(14) |
| C5   | C4A  | C4   | 121.27(16) |
| C5   | C4A  | C8A  | 119.71(16) |
| C8A  | C4A  | C4   | 118.82(15) |
| C6   | C5   | C4A  | 121.47(17) |
| C5   | C6   | C7   | 118.52(17) |
| C8   | C7   | C6   | 121.25(17) |
| C7   | C8   | C8A  | 119.91(16) |
| N1   | C8A  | C4A  | 119.33(15) |
| N1   | C8A  | C8   | 121.58(14) |
| C4A  | C8A  | C8   | 119.05(15) |
| C10  | C9   | C2   | 109.52(14) |
| C10  | C9   | C11  | 108.71(13) |
| C11  | C9   | C2   | 107.45(13) |
| C12  | C9   | C2   | 112.17(13) |
| C12  | C9   | C10  | 108.71(15) |
| C12  | C9   | C11  | 110.21(15) |
Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 135leo (2-(tert-butyl)-3-methyl-2,3-dihydroquinazolin-4(IH)-one (8)).

| Atom  | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| H1    | 6909 | 4130 | 7371 | 22    |
| H2    | 4294 | 3195 | 5298 | 21    |
| H5    | 1561 | 6511 | 8849 | 27    |
| H6    | 4245 | 7742 | 10536| 31    |
| H7    | 7658 | 7404 | 10743| 33    |
| H8    | 8344 | 5903 | 9205 | 27    |
| H10A  | 1700 | 3295 | 2167 | 40    |
| H10B  | 1418 | 4415 | 1024 | 40    |
| H10C  | 266  | 4289 | 2334 | 40    |
| H11A  | 6596 | 4847 | 4196 | 40    |
| H11B  | 5133 | 4889 | 2125 | 40    |
| H11C  | 5651 | 3712 | 3144 | 40    |
| H12A  | 1825 | 5977 | 4206 | 45    |
| H12B  | 2646 | 6275 | 2711 | 45    |
| H12C  | 4221 | 6261 | 4753 | 45    |
| H13A  | -397 | 3044 | 4129 | 44    |
| H13B  | 30   | 2701 | 6122 | 44    |
| H13C  | 1491 | 2228 | 5216 | 44    |
11) Crystallographic data and structure refinement for product 12.

Table S7. Crystal data and structure refinement for leo144a (2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12).

| Identification code       | leo144a                  |
|---------------------------|--------------------------|
| Empirical formula         | C_{13}H_{22}N_{2}O_{3}   |
| Formula weight            | 254.32                   |
| Temperature/K             | 100.01(11)               |
| Crystal system            | orthorhombic             |
| Space group               | Pna21                    |
| a/Å                       | 12.0759(8)               |
| b/Å                       | 9.9245(6)                |
| c/Å                       | 22.5539(16)              |
| α/°                       | 90                       |
| β/°                       | 90                       |
| γ/°                       | 90                       |
| Volume/Å³                 | 2703.0(3)                |
| Z                         | 8                        |
| ρcalcg/cm³                | 1.25                     |
| μ/mm-1                    | 0.089                    |
| F(000)                    | 1104                     |
| Crystal size/mm³          | 0.4 × 0.3 × 0.3          |
| Radiation                 | MoKα (λ = 0.71073)       |
| 2θ range for data collection/° | 5.312 to 58.264         |
| Index ranges              | -16 ≤ h ≤ 8, -13 ≤ k ≤ 13, -28 ≤ l ≤ 26 |
| Reflections collected     | 10662                    |
| Independent reflections   | 5466 [R_{int} = 0.0280, R_{sigma} = 0.0396] |
| Data/restraints/parameters| 5466/1/341               |
| Goodness-of-fit on F2     | 1.041                    |
| Final R indexes [I>=2σ (I)] | R1 = 0.0460, wR2 = 0.1095 |
| Final R indexes [all data]| R1 = 0.0532, wR2 = 0.1136 |
| Largest diff. peak/hole / e Å-3 | 0.30/-0.25               |
| Flack parameter           | -0.3(7)                  |
Table S8 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for leo144a (2-$(t$ert-$b$utyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3$H$)-one (12). $U_{eq}$ is defined as $1/3$ of of the trace of the orthogonalised $\mathbf{U}_{ij}$ tensor.

| Atom | $x$       | $y$       | $z$            | $U_{eq}$     |
|------|-----------|-----------|----------------|--------------|
| C2   | 9027(2)   | 2972(3)   | 3835.8(14)     | 15.6(6)      |
| C4   | 7266(2)   | 3998(3)   | 4178.9(14)     | 15.9(6)      |
| C4A  | 7826(2)   | 5374(3)   | 4180.2(14)     | 15.4(6)      |
| C5   | 7335(3)   | 6364(3)   | 3729.5(15)     | 18.5(7)      |
| C6   | 7911(3)   | 7736(4)   | 3773(2)        | 21.2(7)      |
| C7   | 9162(3)   | 7601(3)   | 3691(2)        | 23.0(9)      |
| C8   | 9655(3)   | 6610(3)   | 4143.5(15)     | 19.8(7)      |
| C8A  | 9072(2)   | 5285(3)   | 4092.9(14)     | 14.8(6)      |
| C9   | 9102(3)   | 2616(3)   | 3159.5(19)     | 15.3(7)      |
| C10  | 8502(3)   | 3680(4)   | 2784.7(16)     | 21.8(8)      |
| C11  | 8593(3)   | 1234(4)   | 3038.3(17)     | 25.2(8)      |
| C12  | 10335(3)  | 2581(4)   | 2995(2)        | 23.7(10)     |
| C13  | 7434(3)   | 1609(3)   | 4268.2(17)     | 21.4(7)      |
| N1   | 9591(2)   | 4235(3)   | 3933.5(12)     | 15.1(5)      |
| N3   | 7885(2)   | 2913(3)   | 4066.8(12)     | 14.9(5)      |
| O1   | 7573.1(19)| 6001(2)   | 4732.6(10)     | 20.0(5)      |
| O2   | 8021.2(19)| 5146(2)   | 5194.6(11)     | 22.4(5)      |
| O4   | 6276.4(17)| 3894(2)   | 4318.0(11)     | 21.8(5)      |
| C15  | 3571(2)   | 2991(3)   | 6158.4(14)     | 15.8(6)      |
| C17  | 5336(2)   | 4024(3)   | 5830.9(13)     | 15.1(6)      |
| C17A | 4769(2)   | 5393(3)   | 5823.1(14)     | 14.9(6)      |
| C18  | 5249(3)   | 6402(3)   | 6273.7(16)     | 19.8(7)      |
| C19  | 4660(3)   | 7761(4)   | 6235.0(19)     | 20.5(7)      |
| C20  | 3408(3)   | 7610(3)   | 6299(2)        | 19.4(8)      |
| C21  | 2934(2)   | 6619(3)   | 5842.0(15)     | 17.3(6)      |
| C21A | 3524(2)   | 5296(3)   | 5900.4(14)     | 15.0(6)      |
| C22  | 3496(3)   | 2652(4)   | 6832(2)        | 19.2(8)      |
| C23  | 4112(3)   | 3684(3)   | 7207.0(15)     | 18.8(7)      |
| C24  | 2268(3)   | 2635(4)   | 7012(2)        | 22.7(9)      |
| C25  | 3976(3)   | 1255(4)   | 6962.4(19)     | 28.3(9)      |
| C26  | 5180(3)   | 1631(3)   | 5745.1(17)     | 22.2(7)      |
| N14  | 3005(2)   | 4251(3)   | 6053.0(12)     | 15.0(5)      |
| N16  | 4717(2)   | 2938(3)   | 5928.5(12)     | 15.9(6)      |
| O5   | 5034.2(19)| 6030(2)   | 5271.1(10)     | 20.0(5)      |
| Atom | U_{11}   | U_{22}   | U_{33}   | U_{23}   | U_{13}   | U_{12}   |
|------|----------|----------|----------|----------|----------|----------|
| C2   | 11.9(14) | 16.9(16) | 17.9(16) | 1.7(12)  | 1.6(12)  | 2.2(12)  |
| C4   | 14.2(14) | 19.5(15) | 14.1(16) | -4.6(13) | 2.2(12)  | -2.5(13) |
| C4A  | 11.5(13) | 16.8(14) | 17.9(16) | -2.9(12) | -0.7(12) | 1.4(12)  |
| C5   | 13.8(14) | 19.9(15) | 21.7(17) | -0.5(13) | 0.4(13)  | 3.4(13)  |
| C6   | 21.2(17) | 17.3(14) | 25(2)    | -0.9(17) | -0.3(14) | 1.7(14)  |
| C7   | 19.2(17) | 18.9(18) | 31(3)    | 1.9(14)  | 2.9(17)  | -1.9(13) |
| C8   | 13.4(14) | 21.1(16) | 24.8(18) | -1.6(14) | 0.2(12)  | -3.5(13) |
| C8A  | 12.7(14) | 18.2(15) | 13.6(15) | 2.6(11)  | -3.3(11) | -2.5(13) |
| C9   | 14.5(15) | 17.2(16) | 14.3(19) | -1.0(12) | 1.5(13)  | 1.0(12)  |
| C10  | 18.9(16) | 27.0(19) | 20(2)    | 2.2(15)  | -1.3(14) | 3.6(14)  |
| C11  | 29.9(19) | 21.3(17) | 24(2)    | -5.2(14) | 4.5(15)  | -1.2(15) |
| C12  | 16.6(17) | 32(2)    | 23(3)    | -3.7(14) | 2.3(15)  | 4.8(14)  |
| C13  | 19.7(16) | 17.6(16) | 26.8(19) | 4.7(15)  | 1.3(15)  | -2.9(14) |
| N1   | 11.8(12) | 18.0(13) | 15.6(14) | 1.7(10)  | -1.3(10) | 0.1(10)  |
| N3   | 11.6(12) | 15.6(13) | 17.3(14) | 1.9(11)  | 1.4(10)  | 0.1(11)  |
| O1   | 22.1(12) | 19.7(11) | 18.4(13) | -2.0(9)  | 1.9(10)  | -0.5(10) |
| O2   | 21.5(12) | 28.9(12) | 16.6(12) | 2.1(10)  | -0.6(9)  | -4.2(10) |
| O4   | 12.9(11) | 26.3(12) | 26.1(13) | -10.5(10)| 5.5(9)   | -3.7(9)  |
| C15  | 11.0(14) | 15.4(16) | 21.0(17) | -1.9(12) | 0.2(12)  | -1.8(12) |
| C17  | 14.8(14) | 21.5(16) | 8.9(15)  | 3.0(12)  | -2.1(12) | 0.3(13)  |
| C17A | 12.3(13) | 18.5(15) | 14.0(15) | 4.9(12)  | 2.0(12)  | 1.9(12)  |
| C18  | 13.6(14) | 19.2(15) | 26.7(18) | 1.0(13)  | -0.5(13) | -1.6(13) |
| C19  | 20.3(17) | 16.1(14) | 25(2)    | -3.6(17) | -3.7(14) | -2.7(14) |
| C20  | 20.4(17) | 18.0(17) | 20(2)    | -1.3(13) | 0.8(15)  | 2.7(13)  |
| C21  | 12.3(14) | 20.8(16) | 18.8(16) | 1.1(13)  | -1.7(12) | 2.7(13)  |
| C21A | 14.0(14) | 20.5(15) | 10.3(15) | -1.4(11) | -2.1(11) | 1.4(13)  |
| C22  | 14.4(15) | 19.7(17) | 23(2)    | 2.0(14)  | 1.6(14)  | -0.2(13) |
| C23  | 16.2(15) | 24.4(17) | 15.8(18) | 1.9(13)  | 0.6(13)  | -0.1(13) |
| C24  | 15.8(15) | 31(2)    | 21(2)    | 0.4(14)  | 2.2(15)  | -6.2(15) |

Table S9 Anisotropic Displacement Parameters (Å²× 10³) for leo144a (2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12). The Anisotropic displacement factor exponent takes the form: \(-2\pi²[h²a²*U_{11}+2hk*b²*U_{12}+\ldots]\).
| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C2   | C9   | 1.568(5) | C15  | C22  | 1.559(6) |
| C2   | N1   | 1.444(4) | C15  | N14  | 1.445(4) |
| C2   | N3   | 1.475(4) | C15  | N16  | 1.479(4) |
| C4   | C4A  | 1.524(4) | C17  | C17A | 1.522(4) |
| C4   | N3   | 1.335(4) | C17  | N16  | 1.330(4) |
| C4   | O4   | 1.240(4) | C17  | O17  | 1.240(4) |
| C4A  | C5   | 1.533(4) | C17A | C18  | 1.540(4) |
| C4A  | C8A  | 1.520(4) | C17A | C21A | 1.516(4) |
| C4A  | O1   | 1.426(4) | C17A | O5   | 1.433(4) |
| C5   | C6   | 1.532(5) | C18  | C19  | 1.528(5) |
| C6   | C7   | 1.528(5) | C19  | C20  | 1.527(5) |
| C7   | C8   | 1.537(5) | C20  | C21  | 1.536(5) |
| C8   | C8A  | 1.495(4) | C21  | C21A | 1.500(4) |
| C8A  | N1   | 1.269(4) | C21A | N14  | 1.260(4) |
| C9   | C10  | 1.534(5) | C22  | C23  | 1.523(5) |
| C9   | C11  | 1.528(5) | C22  | C24  | 1.538(5) |
| C9   | C12  | 1.535(5) | C22  | C25  | 1.531(5) |
| C13  | N3   | 1.476(4) | C26  | N16  | 1.472(4) |
| O1   | O2   | 1.448(3) | O5   | O6   | 1.450(3) |

Table S10 Bond Lengths for leo144a (2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12).
Table S11 Bond Angles for leo144a (2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N1   | C2   | C9   | 108.5(3)| N14  | C15  | C22  | 108.7(3) |
| N1   | C2   | N3   | 114.9(3)| N14  | C15  | N16  | 114.6(3) |
| N3   | C2   | C9   | 112.9(3)| N16  | C15  | C22  | 112.9(3) |
| N3   | C4   | C4A  | 118.4(3)| N16  | C17  | C17A | 118.2(2) |
| O4   | C4   | C4A  | 120.1(3)| O17  | C17  | C17A | 120.2(3) |
| O4   | C4   | N3   | 121.4(3)| O17  | C17  | N16  | 121.4(3) |
| C4   | C4A  | C5   | 113.7(3)| C17  | C17A | C18  | 113.8(3) |
| C8A  | C4A  | C4   | 112.8(2)| C21A | C17A | C17  | 112.9(3) |
| C8A  | C4A  | C5   | 109.5(2)| C21A | C17A | C18  | 109.8(2) |
| O1   | C4A  | C4   | 107.3(2)| O5   | C17A | C17  | 107.7(2) |
| O1   | C4A  | C5   | 102.5(2)| O5   | C17A | C18  | 101.7(2) |
| O1   | C4A  | C8A  | 110.5(2)| O5   | C17A | C21A | 110.5(2) |
| C6   | C5   | C4A  | 110.6(3)| C19  | C18  | C17A | 111.2(3) |
| C7   | C6   | C5   | 111.3(3)| C20  | C19  | C18  | 111.6(3) |
| C6   | C7   | C8   | 111.1(3)| C19  | C20  | C21  | 111.6(3) |
| C8A  | C8   | C7   | 109.2(3)| C21A | C21  | C20  | 108.9(3) |
| C8   | C8A  | C4A  | 113.9(3)| C21  | C21A | C17A | 114.0(3) |
| N1   | C8A  | C4A  | 125.0(3)| N14  | C21A | C17A | 125.2(3) |
| N1   | C8A  | C8   | 120.7(3)| N14  | C21A | C21  | 120.5(3) |
| C10  | C9   | C2   | 110.7(3)| C23  | C22  | C15  | 111.6(3) |
| C10  | C9   | C12  | 109.9(3)| C23  | C22  | C24  | 109.4(3) |
| C11  | C9   | C2   | 110.7(3)| C23  | C22  | C25  | 108.5(3) |
| C11  | C9   | C10  | 109.2(3)| C24  | C22  | C15  | 108.4(3) |
| C11  | C9   | C12  | 109.1(3)| C25  | C22  | C15  | 111.2(3) |
| C12  | C9   | C2   | 107.2(3)| C25  | C22  | C24  | 107.7(3) |
| C8A  | N1   | C2   | 121.6(2)| C21A | N14  | C15  | 121.4(2) |
| C2   | N3   | C13  | 119.2(3)| C17  | N16  | C15  | 123.7(3) |
| C4   | N3   | C2   | 123.9(3)| C17  | N16  | C26  | 117.0(3) |
| C4   | N3   | C13  | 116.3(2)| C26  | N16  | C15  | 119.0(3) |
| C4A  | O1   | O2   | 107.0(2)| C17A | O5   | O6   | 106.9(2) |
| A  | B   | C   | D   | Angle° | A  | B   | C   | D   | Angle° |
|----|-----|-----|-----|--------|----|-----|-----|-----|--------|
| C4 | C4A | C5  | C6  | 178.0(3) | C17| C17A| C18 | C19 | 178.9(3) |
| C4 | C4A | C8A | C8  | -175.1(3) | C17| C17A| C21A| C21 | -175.0(3) |
| C4 | C4A | C8A | N1  | 11.7(4)  | C17| C17A| C21A| N14 | 11.3(4)  |
| C4 | C4A | O1  | O2  | 60.8(3)  | C17| C17A| O5  | O6  | 61.2(3)  |
| C4A| C4  | N3  | C2  | -11.8(4) | C17| C17A| N16 | C15 | -14.0(4) |
| C4A| C4  | N3  | C13 | 159.5(3) | C17A| C17 | N16 | C26 | 160.5(3) |
| C4A| C5  | C6  | C7  | 56.1(4)  | C17A| C18 | C19 | C20 | 54.2(4)  |
| C4A| C8A | N1  | C2  | -2.1(5)  | C17A| C21A| N14 | C15 | -1.6(5)  |
| C5A| C4A | C8A | C8  | 57.2(3)  | C18 | C17A| C21A| C21 | 56.9(3)  |
| C5 | C4A | O1  | O2  | -179.1(2) | C18| C17A| O5  | O6  | -179.0(2) |
| C5 | C6  | C7  | C8  | -56.4(5) | C18 | C19 | C20 | C21 | -55.5(5) |
| C6 | C7  | C8  | C8A | 55.6(4)  | C19 | C20 | C21 | C21A| 55.7(4)  |
| C7 | C8  | C8A | C4A | -57.1(4) | C20 | C21 | C21A| C17A| -57.5(4) |
| C7 | C8  | C8A | N1  | 116.4(3) | C20 | C21 | C21A| N14 | 116.6(3) |
| C8 | C8A | N1  | C2  | -174.9(3) | C21 | C21A| N14 | C15 | -174.9(3) |
| C8A| C4A | C5  | C6  | -54.9(3) | C21A| C17A| C18 | C19 | -53.5(4) |
| C8A| C4A | O1  | O2  | -62.5(3) | C21A| C17A| O5  | O6  | -62.4(3) |
| C9 | C2  | N1  | C8A | 113.6(3) | C22 | C15 | N14 | C21A| 112.3(3) |
| C9 | C2  | N3  | C4  | -103.7(3) | C22 | C15 | N16 | C17 | -101.6(3) |
| C9 | C2  | N3  | C13 | 85.3(3)  | C22 | C15 | N16 | C26 | 84.1(3)  |
| N1 | C2  | C9  | C10 | -63.0(3) | N14 | C15 | C22 | C23 | -64.7(3) |
| N1 | C2  | C9  | C11 | 175.7(3) | N14 | C15 | C22 | C24 | 55.8(3)  |
| N1 | C2  | C9  | C12 | 56.9(3)  | N14 | C15 | C22 | C25 | 174.1(3) |
| N1 | C2  | N3  | C4  | 21.4(4)  | N14 | C15 | N16 | C17 | 23.5(4)  |
| N1 | C2  | N3  | C13 | -149.6(3) | N14 | C15 | N16 | C26 | -150.9(3) |
| N3 | C2  | C9  | C10 | 65.5(3)  | N16 | C15 | C22 | C23 | 63.6(3)  |
| N3 | C2  | C9  | C11 | -55.7(4) | N16 | C15 | C22 | C24 | -175.9(3) |
| N3 | C2  | C9  | C12 | -174.6(3) | N16 | C15 | C22 | C25 | -57.7(4) |
| N3 | C2  | N1  | C8A | -13.8(4) | N16 | C15 | N14 | C21A| -15.0(4) |
| N3 | C4  | C4A | C5  | 121.2(3) | N16 | C17 | C17A| C18 | 123.0(3) |
| N3 | C4  | C4A | C8A | -4.3(4)  | N16 | C17 | C17A| C21A| -3.0(4)  |
| N3 | C4  | C4A | O1  | -126.2(3) | N16 | C17 | C17A| O5  | -125.2(3) |
| O1 | C4A | C5  | C6  | 62.4(3)  | O5  | C17A| C18 | C19 | 63.4(3)  |
| O1 | C4A | C8A | C8  | -55.0(3) | O5  | C17A| C21A| C21 | -54.4(3) |
Table S13 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å²×103) for leo144a (2-(tert-butyl)-4a-hydroperoxy-3-methyl-2,4a,5,6,7,8-hexahydroquinazolin-4(3H)-one (12)).

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H2   | 9450  | 2281  | 4048  | 19    |
| H5A  | 7425  | 6006  | 3332  | 22    |
| H5B  | 6549  | 6473  | 3804  | 22    |
| H6A  | 7617  | 8333  | 3471  | 25    |
| H6B  | 7758  | 8134  | 4157  | 25    |
| H7A  | 9507  | 8476  | 3739  | 28    |
| H7B  | 9318  | 7285  | 3293  | 28    |
| H8A  | 10440 | 6490  | 4067  | 24    |
| H8B  | 9568  | 6965  | 4541  | 24    |
| H10A | 7739  | 3726  | 2903  | 33    |
| H10B | 8546  | 3437  | 2373  | 33    |
| H10C | 8845  | 4542  | 2843  | 33    |
| H11A | 8961  | 567   | 3275  | 38    |
| H11B | 8678  | 1015  | 2626  | 38    |
| H11C | 7820  | 1251  | 3137  | 38    |
| H12A | 10643 | 3469  | 3034  | 35    |
| H12B | 10415 | 2279  | 2593  | 35    |
| H12C | 10717 | 1974  | 3256  | 35    |
| H13A | 7175  | 1693  | 4669  | 32    |
| H13B | 8003  | 935   | 4250  | 32    |
| H13C | 6830  | 1350  | 4016  | 32    |
| H2A  | 7320(40) | 4840(50) | 5330(20) | 65(16) |
| H15  | 3152  | 2293  | 5948  | 19    |
| H18A | 5169  | 6041  | 6671  | 24    |
| H18B | 6033  | 6525  | 6197  | 24    |
| H19A | 4936  | 8349  | 6545  | 25    |
|   |   |   |   |   |
|---|---|---|---|---|
| **H19B** | 4826 | 8177 | 5856 | 25 |
| **H20A** | 3059 | 8483 | 6249 | 23 |
| **H20B** | 3237 | 7291 | 6696 | 23 |
| **H21A** | 2147 | 6495 | 5910 | 21 |
| **H21B** | 3034 | 6975 | 5445 | 21 |
| **H23A** | 4877 | 3706 | 7091 | 28 |
| **H23B** | 4060 | 3439 | 7618 | 28 |
| **H23C** | 3789 | 4558 | 7149 | 28 |
| **H24A** | 1976 | 3534 | 6995 | 34 |
| **H24B** | 2199 | 2293 | 7409 | 34 |
| **H24C** | 1861 | 2067 | 6745 | 34 |
| **H25A** | 3659 | 609  | 6695 | 42 |
| **H25B** | 3804 | 1005 | 7363 | 42 |
| **H25C** | 4764 | 1275 | 6911 | 42 |
| **H26A** | 5393 | 1674 | 5335 | 33 |
| **H26B** | 4632 | 940  | 5797 | 33 |
| **H26C** | 5817 | 1427 | 5983 | 33 |
| **H6** | 5260(40) | 4800(40) | 4630(20) | 44(13) |
12) Crystallographic data and structure refinement for product 13.

Table S14. Crystal data and structure refinement for redn (1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13).

| Parameter                        | Value                           |
|----------------------------------|---------------------------------|
| Identification code              | redn                            |
| Empirical formula                | C15H24N2O2                      |
| Formula weight                   | 264.36                          |
| Temperature/K                    | 99.9(4)                         |
| Crystal system                   | orthorhombic                    |
| Space group                      | Pbca                            |
| a/Å                              | 14.0614(2)                      |
| b/Å                              | 7.94150(10)                     |
| c/Å                              | 25.2493(3)                      |
| α/°                              | 90                              |
| β/°                              | 90                              |
| γ/°                              | 90                              |
| Volume/Å³                        | 2819.55(6)                      |
| Z                                | 8                               |
| ρcalcg/cm³                       | 1.246                           |
| μ/mm⁻¹                           | 0.658                           |
| F(000)                           | 1152                            |
| Crystal size/mm³                 | 0.12 × 0.099 × 0.05             |
| Radiation                        | CuKα (λ = 1.54184)              |
| 2Θ range for data collec         | 9.414 to 145.654                |
| Index ranges                     | -17 ≤ h ≤ 16, -9 ≤ k ≤ 6, -31 ≤ l ≤ 31 |
| Reflections collected            | 18083                           |
| Independent reflections          | 2782 [Rint = 0.0248, Rsigma = 0.0140] |
| Data/restraints/paramet          | 2782/0/177                      |
| Goodness-of-fit on F2            | 1.072                           |
| Final R indexes [I>2σ (I)]       | R1 = 0.0373, wR2 = 0.0925       |
| Final R indexes [all data]       | R1 = 0.0391, wR2 = 0.0939       |
| Largest diff. peak/hole / e Å⁻³  | 0.24/-0.18                     |
Table S15 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å²× 103) for redn (1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13). Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

| Atom | x      | y      | z      | U(eq) |
|------|--------|--------|--------|-------|
| N1   | 5957.4(7) | 2747.8(12) | 4006.1(4) | 15.4(2) |
| C2   | 5098.2(8) | 3756.3(14) | 4091.2(4) | 15.3(2) |
| N3   | 5161.5(7) | 5282.0(12) | 3762.3(4) | 16.6(2) |
| C4   | 5654.3(8) | 5314.1(14) | 3300.1(4) | 15.7(2) |
| O4   | 5779.5(6) | 6632.1(10) | 3050.7(3) | 21.2(2) |
| C4A  | 6040.3(8) | 3675.4(14) | 3114.1(4) | 14.8(2) |
| C5   | 6207.1(8) | 3500.6(14) | 2527.9(5) | 17.9(2) |
| C6   | 6741.7(9) | 1891.1(15) | 2389.8(5) | 22.3(3) |
| C7   | 6356.7(9) | 429.1(15)  | 2710.2(5) | 20.7(3) |
| C8   | 6539.9(9) | 712.8(15)  | 3297.7(5) | 19.0(3) |
| C8A  | 6213.2(8) | 2446.0(14) | 3464.2(4) | 14.7(2) |
| C9   | 6551.9(9) | 2490.3(15) | 4433.0(5) | 19.1(3) |
| O9   | 6311.9(7) | 2866.4(12) | 4882.2(3) | 26.9(2) |
| C10  | 7519.9(9) | 1743.8(18) | 4329.3(5) | 26.7(3) |
| C11  | 4164.3(8) | 2726.4(15) | 4033.4(5) | 17.0(2) |
| C12  | 3315.9(9) | 3900.0(16) | 4134.0(5) | 23.8(3) |
| C13  | 4180.5(9) | 1358.9(16) | 4464.1(5) | 21.8(3) |
| C14  | 4039.0(9) | 1892.8(17) | 3491.1(5) | 22.1(3) |
| C15  | 4852.2(9) | 6897.5(15) | 3983.0(5) | 20.9(3) |

Table S16 Anisotropic Displacement Parameters (Å²×103) for redn (1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13). The Anisotropic displacement factor exponent takes the form: \(-2\pi^2|h2a^*2U11+2hka*b*U12+...|\).

| Atom | U11   | U22   | U33   | U23   | U13   | U12   |
|------|-------|-------|-------|-------|-------|-------|
| N1   | 14.8(5) | 14.9(5) | 16.4(5) | 0.2(4) | -0.5(4) | 0.4(4) |
| C2   | 15.9(5) | 14.4(5) | 15.6(5) | -0.2(4) | 1.0(4)  | 0.3(4) |
| N3   | 18.6(5) | 11.6(5) | 19.4(5) | -0.2(4) | 2.6(4)  | 0.8(4) |
| C4   | 13.2(5) | 15.0(5) | 18.7(5) | 0.4(4)  | -1.7(4) | -0.2(4) |
| O4   | 23.7(4) | 14.2(4) | 25.5(4) | 4.6(3)  | 3.5(3)  | 1.0(3) |
| C4A  | 11.9(5) | 14.0(5) | 18.4(5) | -0.9(4) | 0.3(4)  | -1.4(4) |
| C5   | 18.1(6) | 18.0(6) | 17.6(5) | 1.0(4)  | 1.5(4)  | 0.3(5) |
| C6   | 24.7(6) | 21.6(6) | 20.6(6) | -3.7(5) | 4.0(5)  | 0.8(5) |
| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| N1   | C2   | 1.4654(14)| C4A  | C8A  | 1.3393(16)|
| N1   | C8A  | 1.4348(14)| C5   | C6   | 1.5233(16)|
| N1   | C9   | 1.3794(15)| C6   | C7   | 1.5151(17)|
| C2   | N3   | 1.4716(14)| C7   | C8   | 1.5222(16)|
| C2   | C11  | 1.5539(15)| C8   | C8A  | 1.5107(16)|
| N3   | C4   | 1.3574(15)| C9   | O9   | 1.2202(15)|
| N3   | C15  | 1.4649(14)| C9   | C10  | 1.5075(18)|
| C4   | O4   | 1.2342(14)| C11  | C12  | 1.5351(16)|
| C4   | C4A  | 1.4862(15)| C11  | C13  | 1.5370(16)|
| C4A  | C5   | 1.5051(15)| C11  | C14  | 1.5310(16)|

Table S17 Bond Lengths for redn (1-acetyl-2-( tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(IH)-one (13).
Table S18 Bond Angles for redn (1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C8A  | N1   | C2   | 115.96(9)| C7   | C6   | C5   | 110.15(10) |
| C9   | N1   | C2   | 117.78(10)| C6   | C7   | C8   | 110.27(10) |
| C9   | N1   | C8A  | 124.65(10)| C8A  | C8   | C7   | 110.77(10) |
| N1   | C2   | N3   | 108.50(9) | N1   | C8A  | C8   | 119.59(10) |
| N1   | C2   | C11  | 113.29(9) | C4A  | C8A  | N1   | 117.52(10) |
| N3   | C2   | C11  | 115.57(9) | C4A  | C8A  | C8   | 122.39(10) |
| C4   | N3   | C2   | 122.10(9) | N1   | C9   | C10  | 118.01(10) |
| C4   | N3   | C15  | 117.53(9) | O9   | C9   | N1   | 121.50(11) |
| C15  | N3   | C2   | 119.24(9) | O9   | C9   | C10  | 120.49(11) |
| N3   | C4   | C4A  | 116.21(10)| C12  | C11  | C2   | 108.76(9)  |
| O4   | C4   | N3   | 121.83(10)| C12  | C11  | C13  | 108.87(10) |
| O4   | C4   | C4A  | 121.95(10)| C13  | C11  | C2   | 107.04(9)  |
| C4   | C4A  | C5   | 116.65(10)| C14  | C11  | C2   | 114.13(9)  |
| C8A  | C4A  | C4   | 119.74(10)| C14  | C11  | C12  | 108.72(10) |
| C8A  | C4A  | C5   | 123.61(10)| C14  | C11  | C13  | 109.20(10) |
| C4A  | C5   | C6   | 112.30(10)|      |      |      |         |
Table S19 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for redn (1-acetyl-2-(tert-butyl)-3-methyl-2,3,5,6,7,8-hexahydroquinazolin-4(1H)-one (13).

| Atom  | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| H2    | 5122 | 4137 | 4460 | 18    |
| H5A   | 6569 | 4462 | 2403 | 21    |
| H5B   | 5599 | 3503 | 2346 | 21    |
| H6A   | 6671 | 1654 | 2015 | 27    |
| H6B   | 7413 | 2037 | 2464 | 27    |
| H7A   | 6662 | -606 | 2598 | 25    |
| H7B   | 5679 | 318  | 2649 | 25    |
| H8A   | 6203 | -132 | 3502 | 23    |
| H8B   | 7214 | 594  | 3370 | 23    |
| H10A  | 7928 | 1963 | 4626 | 40    |
| H10B  | 7787 | 2243 | 4016 | 40    |
| H10C  | 7461 | 550  | 4279 | 40    |
| H12A  | 3401 | 4470 | 4466 | 36    |
| H12B  | 2741 | 3250 | 4145 | 36    |
| H12C  | 3275 | 4714 | 3854 | 36    |
| H13A  | 4699 | 600  | 4399 | 33    |
| H13B  | 3592 | 746  | 4458 | 33    |
| H13C  | 4260 | 1876 | 4805 | 33    |
| H14A  | 4077 | 2734 | 3219 | 33    |
| H14B  | 3430 | 1350 | 3476 | 33    |
| H14C  | 4531 | 1072 | 3439 | 33    |
| H15A  | 5397 | 7598 | 4046 | 31    |
| H15B  | 4523 | 6707 | 4311 | 31    |
| H15C  | 4434 | 7446 | 3737 | 31    |
13) Cartesian coordinates from optimized structures of 11.

**Figure S9.** Cartesian coordinates from optimized structure of 11 at the B3LYP/6-311++G** level of theory.

![Cartesian coordinates diagram](image)

E = -843.603591 Hartree

Negative eigenvalues = 0

|   |      |      |      |      |
|---|------|------|------|------|
| 6 | -3.383965000 | -1.351790000 | 0.093141000 |
| 1 | -3.797238000 | -0.612645000 | 0.785358000 |
| 1 | -4.047160000 | -2.221289000 | 0.108021000 |
| 6 | -3.305495000 | -0.746630000 | -1.312375000 |
| 1 | -4.306980000 | -0.507085000 | -1.680223000 |
| 1 | -2.885899000 | -1.486997000 | -2.005259000 |
| 6 | -1.989583000 | -1.766570000 | 0.579246000 |
| 1 | -1.685590000 | -2.705395000 | 0.096612000 |
| 1 | -1.997401000 | -1.957657000 | 1.658626000 |
| 6 | -2.439128000 | 0.518106000 | -1.315417000 |
| 1 | -2.989513000 | 1.357275000 | -0.871498000 |
|   |           |           |           |           |
|---|-----------|-----------|-----------|-----------|
| 1 | -2.201657 | 0.837153  | -2.334376 |          |
| 6 | -1.162433 | 0.350530  | -0.544534 |          |
| 6 | -0.941393 | -0.725825 | 0.285779  |          |
| 6 | -0.129707 | 1.398834  | -0.685448 |          |
| 7 | 1.044429  | 1.209641  | 0.014654  |          |
| 7 | 0.219352  | -0.808909 | 0.963617  |          |
| 1 | 0.296098  | -1.489220 | 1.702957  |          |
| 6 | 1.427083  | -0.063498 | 0.612968  |          |
| 1 | 1.936757  | 0.162124  | 1.554738  |          |
| 6 | 1.879442  | 2.392315  | 0.223576  |          |
| 1 | 1.239390  | 3.239611  | 0.471194  |          |
| 1 | 2.456556  | 2.655614  | -0.666520 |          |
| 1 | 2.564514  | 2.203297  | 1.049845  |          |
| 8 | -0.330667 | 2.424746  | -1.326120 |          |
| 6 | 2.421082  | -0.936230 | -0.244253 |          |
| 6 | 3.721866  | -0.145280 | -0.477308 |          |
| 1 | 3.558579  | 0.727431  | -1.110826 |          |
| 1 | 4.455519  | -0.782580 | -0.978615 |          |
| 1 | 4.167864  | 0.191357  | 0.463982  |          |
| 6 | 1.816411  | -1.326250 | -1.602172 |          |
| 1 | 1.555241  | -0.444572 | -2.191862 |          |
| 1 | 0.920642  | -1.941200 | -1.488329 |          |
| 1 | 2.542846  | -1.906911 | -2.178339 |          |
| 6 | 2.764444  | -2.208060 | 0.558105  |          |
| 1 | 3.155790  | -1.964216 | 1.552169  |          |
| 1 | 3.534447  | -2.782935 | 0.037156  |          |
| 1 | 1.899323  | -2.865313 | 0.679521  |          |
| 8 | -0.846917 | 1.019917  | 2.441588  |          |
| 8 | -1.733710 | 1.199230  | 1.568276  |          |
14) Cartesian coordinates from optimized structures of 12.

**Figure S10.** Cartesian coordinates from optimized structure of 12 at the B3LYP/6-311++G** level of theory.

![Figure S10](image)

E = -804.377436 Hartree

Negative eigenvalues = 0

| 6   | -2.201070000 | -2.399444000 | -0.248377000 |
|-----|--------------|--------------|--------------|
| 1   | -2.922574000 | -3.175300000 | 0.023628000  |
| 1   | -1.411408000 | -2.893278000 | -0.827688000 |
| 6   | -2.878188000 | -1.324618000 | -1.110181000 |
| 1   | -3.762677000 | -0.941350000 | -0.593732000 |
| 1   | 3.225597000  | -1.761229000 | -2.051693000 |
| 6   | -1.929307000 | -0.156814000 | -1.423070000 |
| 1   | -2.438742000 | 0.645829000  | -1.960610000 |
| 1   | -1.100841000 | -0.502177000 | -2.050983000 |
| 6   | -1.579722000 | -1.799480000 | 1.032073000  |
| 1   | -1.016104000 | -2.547638000 | 1.590796000  |
|   | x1       | y1       | z1       |
|---|----------|----------|----------|
| 1 | -2.377642000 | -1.414428000 | 1.675245000 |
| 6 | -0.653860000 | -0.666062000 | 0.669999000 |
| 6 | -1.320318000 | 0.447196000 | -0.137135000 |
| 8 | -2.459898000 | 0.965723000 | 0.564540000 |
| 8 | -2.001126000 | 1.708626000 | 1.722762000 |
| 1 | 2.038728000 | 2.613623000 | 1.372988000 |
| 7 | 0.580818000 | -0.729596000 | 0.961122000 |
| 6 | 1.513397000 | 0.302850000 | 0.598055000 |
| 1 | 1.839345000 | 0.759933000 | 1.543767000 |
| 7 | 0.939569000 | 1.373754000 | -0.235648000 |
| 1 | 1.529445000 | 2.174171000 | -0.426445000 |
| 6 | -0.374685000 | 1.606079000 | -0.467094000 |
| 6 | 2.794791000 | -0.314301000 | 0.058106000 |
| 6 | 3.446829000 | -1.267350000 | 0.960214000 |
| 1 | 3.728811000 | -0.735928000 | 1.875116000 |
| 1 | 4.355920000 | -1.702276000 | 0.535282000 |
| 1 | 2.769241000 | -2.075193000 | 1.236332000 |
| 6 | 3.793741000 | 0.811185000 | -0.390440000 |
| 1 | 4.004734000 | 1.434435000 | 0.485448000 |
| 1 | 3.442368000 | 1.456597000 | -1.200431000 |
| 1 | 4.742688000 | 0.379325000 | -0.718754000 |
| 6 | 2.432195000 | -1.080921000 | -1.339862000 |
| 1 | 1.938729000 | -0.430519000 | -2.067373000 |
| 1 | 1.769601000 | -1.921745000 | -1.121927000 |
| 1 | 3.336168000 | -1.479975000 | -1.808553000 |
| 8 | -0.797509000 | 2.657827000 | -0.925451000 |
15) Cartesian coordinates from optimized structures of R.

**Figure S11.** Cartesian coordinates from optimized structure of the R at the B3LYP/6-311++G** level of theory.

\[ E = -687.587349 \]

Negative eigenvalues = 0

|    |          |          |          |          |
|----|----------|----------|----------|----------|
| 7  | 0.130729 | -1.451624| -0.061054| 0.562675 |
| 6  | -0.562675| -0.253416| -0.543368| -0.253416|
| 7  | 0.277861 | 0.917533 | 0.300628 | 0.277861 |
| 6  | 1.189945 | 1.008707 | 0.737606 | 1.189945 |
| 6  | 1.512414 | -0.254859 | 1.414939 | 1.512414 |
| 6  | 0.969886 | -1.427424 | 0.991019 | 0.969886 |
| 1  | -0.160675 | -2.338455 | -0.437606 | -0.160675 |
|   |         |         |         |         |
|---|---------|---------|---------|---------|
| 8 | 2.945134 | -0.879311 | -0.554593 |
| 8 | 2.195573 | -1.181577 | -1.502413 |
| 1 | 1.274407 | -2.386365 | 1.392351  |
| 1 | 2.211754 | -0.215453 | 2.235831  |
| 8 | 1.748978 | 2.063862  | 1.007528  |
| 6 | 0.251526 | 2.033539  | -1.246021 |
| 1 | 1.274226 | 2.356455  | -1.442712 |
| 1 | -0.208018 | 1.701576  | -2.176966 |
| 1 | -0.303273 | 2.892469  | -0.859823 |
| 6 | -2.027893 | -0.161660 | 0.028218  |
| 6 | -2.041444 | 0.021307  | 1.554029  |
| 1 | -1.522002 | 0.934488  | 1.853522  |
| 1 | -3.073715 | 0.096831  | 1.907890  |
| 1 | -1.577000 | -0.820982 | 2.071652  |
| 6 | -2.751723 | 1.026757  | -0.632886 |
| 1 | -2.312633 | 1.982029  | -0.343377 |
| 1 | -2.733917 | 0.956415  | -1.725223 |
| 1 | -3.799667 | 1.038324  | -0.321326 |
| 6 | -2.779432 | -1.455060 | -0.348796 |
| 1 | -3.833340 | -1.368454 | -0.072537 |
| 1 | -2.739896 | -1.646128 | -1.427041 |
| 1 | -2.384051 | -2.330975 | 0.172704  |
| 1 | -0.653419 | -0.364280 | -1.628187 |
16) Cartesian coordinates from optimized structures of P.

Figure S12. Cartesian coordinates from optimized structure of the P at the B3LYP/6-311++G** level of theory.

\[ E = -687.652243 \]

Negative eigenvalues = 0

|   |    |    |   |    |
|---|----|----|---|----|
| 7 | -0.270639000 | -1.229657000 | -1.112563000 |
| 6 | -0.927317000 | 0.012062000  | -0.748702000 |
| 7 | -0.000457000 | 1.054337000  | -0.235452000 |
| 6 | 1.211994000  | 0.769684000  | 0.302443000  |
| 6 | 1.500956000  | -0.719986000 | 0.512377000  |
| 6 | 0.826687000  | -1.540062000 | -0.565064000 |
| 1 | 3.681421000  | 0.438666000  | -0.286780000 |
| 8 | 2.880751000  | -0.983825000 | 0.648879000  |
| 8 | 3.560445000  | -0.495673000 | -0.536340000 |
|   |        |        |        |        |
|---|--------|--------|--------|--------|
| 1 | 1.324338000 | -2.466730000 | -0.852754000 |        |
| 1 | 1.100183000 | -1.025843000 | 1.486674000  |        |
| 8 | 2.055374000 | 1.621322000 | 0.560907000  |        |
| 6 | -0.224527000 | 2.458513000 | -0.604987000 |        |
| 1 | 0.621711000 | 2.831061000 | -1.185857000 |        |
| 1 | -1.135089000 | 2.533783000 | -1.194588000 |        |
| 1 | -0.323240000 | 3.083145000 | 0.284635000  |        |
| 6 | -2.173441000 | -0.271195000 | 0.170079000  |        |
| 6 | -1.757575000 | -0.871574000 | 1.523051000  |        |
| 1 | -1.111059000 | -0.191166000 | 2.084258000  |        |
| 1 | -2.646121000 | -1.050925000 | 2.134413000  |        |
| 1 | -1.248566000 | -1.830662000 | 1.402008000  |        |
| 6 | -2.941646000 | 1.039305000 | 0.422300000  |        |
| 1 | -2.347295000 | 1.762905000 | 0.984023000  |        |
| 1 | -3.263641000 | 1.506673000 | -0.513399000 |        |
| 1 | -3.840741000 | 0.828235000 | 1.007594000  |        |
| 6 | -3.102874000 | -1.253346000 | -0.570223000 |        |
| 1 | -4.016290000 | -1.408285000 | 0.011069000  |        |
| 1 | -3.394198000 | -0.861102000 | -1.549596000 |        |
| 1 | -2.623923000 | -2.219863000 | -0.728747000 |        |
| 1 | -1.325934000 | 0.422341000 | -1.682126000 |        |
17) Cartesian coordinates from optimized structures of TS1z.

**Figure S13.** Cartesian coordinates from optimized structure of the TS1z at the B3LYP/6-311++G** level of theory.
|   | 2.758492000 | -0.935412000 | -0.403268000 |
|---|-------------|---------------|---------------|
| 8 | 2.134939000 | -0.760363000 | -1.547936000 |
| 1 | 1.213773000 | -2.599540000 | 1.062934000  |
| 1 | 2.536488000 | -0.546380000 | 1.781852000  |
| 8 | 1.940739000 | 1.872777000  | 1.026466000  |
| 6 | 0.104343000 | 2.211555000  | -0.922371000 |
| 1 | 1.093205000 | 2.581067000  | -1.193403000 |
| 1 | -0.475784000 | 2.035863000  | -1.827012000 |
| 1 | -0.390157000 | 2.975356000  | -0.317935000 |
| 6 | -2.037451000 | -0.149276000 | 0.071767000  |
| 6 | -1.974303000 | -0.080545000 | 1.605538000  |
| 1 | -1.461440000 | 0.822849000  | 1.943379000  |
| 1 | -2.986571000 | -0.063278000 | 2.019086000  |
| 1 | -1.459424000 | -0.944383000 | 2.033535000  |
| 6 | -2.814877000 | 1.069568000  | -0.461710000 |
| 1 | -2.395889000 | 2.011602000  | -0.109024000 |
| 1 | -2.839385000 | 1.089726000  | -1.555734000 |
| 1 | -3.849492000 | 1.021404000  | -0.111548000 |
| 6 | -2.796871000 | -1.420171000 | -0.366674000 |
| 1 | -3.845907000 | -1.346087000 | -0.070185000 |
| 1 | -2.776262000 | -1.550348000 | -1.454596000 |
| 1 | -2.400752000 | -2.326125000 | 0.100141000  |
| 1 | -0.702728000 | -0.173927000 | -1.650290000 |
18) Cartesian coordinates from optimized structures of TS1D.

Figure S14. Cartesian coordinates from optimized structure of the TS1D at the B3LYP/6-311++G** level of theory.

E = -687.562242

Negative eigenvalues = 1; Frequency = -699.8647

|   |     |     |     |     |
|---|-----|-----|-----|-----|
| 7 | -0.037849000 | -1.446400000 | -0.314805000 |     |
| 6 | -0.683812000 | -0.148251000 | -0.570267000 |     |
| 7 | 0.155188000  | 0.958062000  | -0.151069000 |     |
| 6 | 1.351516000  | 0.856437000  | 0.535939000  |     |
| 6 | 1.922060000  | -0.539583000 | 0.803839000  |     |
| 6 | 1.037154000  | -1.644254000 | 0.357474000  |     |
| 1 | -0.468781000 | -2.234273000 | -0.785036000 |     |
|   |    |    |    |    |    |    |
|---|----|----|----|----|----|----|
| 8 | 3.029881000 | -0.799701000 | -0.004437000 |    |    |    |
| 8 | 2.512816000 | -0.641302000 | -1.403433000 |    |    |    |
| 1 | 1.405647000 | -2.660742000 | 0.447181000  |    |    |    |
| 1 | 2.211511000 | -0.630667000 | 1.856686000  |    |    |    |
| 8 | 1.964563000 | 1.842360000  | 0.885344000  |    |    |    |
| 6 | -0.053487000 | 2.256724000  | -0.813089000 |    |    |    |
| 1 | 0.909366000 | 2.616038000  | -1.175995000 |    |    |    |
| 1 | -0.731899000 | 2.130772000  | -1.655196000 |    |    |    |
| 1 | -0.464277000 | 3.000700000  | -0.128015000 |    |    |    |
| 6 | -2.123500000 | -0.186740000 | 0.085174000  |    |    |    |
| 6 | -2.015320000 | 0.232267000  | 1.617318000  |    |    |    |
| 1 | -1.484439000 | 0.640873000  | 2.002442000  |    |    |    |
| 1 | -3.014278000 | -0.240320000 | 2.060975000  |    |    |    |
| 1 | -1.497756000 | -1.129546000 | 1.968339000  |    |    |    |
| 6 | -2.925529000 | 1.059100000  | -0.334660000 |    |    |    |
| 1 | -2.503452000 | 1.976961000  | 0.072664000  |    |    |    |
| 1 | -2.986063000 | 1.157300000  | -1.422619000 |    |    |    |
| 1 | -3.947040000 | 0.971989000  | 0.044154000  |    |    |    |
| 6 | -2.879756000 | -1.430488000 | -0.432554000 |    |    |    |
| 1 | -3.925743000 | -1.381079000 | -0.122192000 |    |    |    |
| 1 | -2.871196000 | -1.485935000 | -1.526945000 |    |    |    |
| 1 | -2.482245000 | -2.367271000 | -0.030589000 |    |    |    |
| 1 | -0.804767000 | -0.101372000 | -1.659584000 |    |    |    |
19) Cartesian coordinates from optimized structures of TS2₂.

**Figure S15.** Cartesian coordinates from optimized structure of the TS2₂ at the B3LYP/6-311++G** level of theory.

E = -687.571828

|   |                  |                  |                  |
|---|------------------|------------------|------------------|
| 7 | 0.083399000     | -1.438665000      | -0.324917000     |
| 6 | -0.589170000    | -0.156711000      | -0.577114000     |
| 7 | 0.222987000     | 1.016211000       | -0.198152000     |
| 6 | 1.354396000     | 0.943371000       | 0.554784000      |
| 6 | 1.830265000     | -0.447221000      | 0.903209000      |
| 6 | 0.898319000     | -1.562827000      | 0.730299000      |
| 1 | 0.597265000     | -1.764895000      | -1.195158000     |
| 8 | 2.665327000     | -1.026165000      | -0.222487000     |
|   | 2.158838000 | -0.846422000 | -1.471410000 |
|---|-------------|--------------|--------------|
| 1 | 1.199347000 | -2.556738000 | 1.041305000  |
| 1 | 2.487045000 | -0.453439000 | 1.766237000  |
| 8 | 2.012682000 | 1.918986000  | 0.880385000  |
| 6 | -0.017702000| 2.303141000  | -0.859244000 |
| 1 | 0.938387000 | 2.707893000  | -1.192833000 |
| 1 | -0.668350000| 2.150641000  | -1.718399000 |
| 1 | -0.476319000| 3.030190000  | -0.185713000 |
| 6 | -2.018959000| 0.087341000  | 0.087341000  |
| 6 | -1.921831000| 0.235185000  | 1.620895000  |
| 1 | -1.393540000| 0.637130000  | 2.014413000  |
| 1 | -2.925738000| -0.238294000 | 2.054807000  |
| 1 | -1.412484000| -1.134869000 | 1.975589000  |
| 6 | -2.839849000| 1.045120000  | -0.326461000 |
| 1 | -2.445843000| 1.969152000  | 0.097068000  |
| 1 | -2.889887000| 1.154788000  | -1.414088000 |
| 1 | -3.864856000| 0.933167000  | 0.036539000  |
| 6 | -2.759327000| -1.443454000 | -0.428591000 |
| 1 | -3.783384000| -1.450441000 | -0.045577000 |
| 1 | -2.816470000| -1.448868000 | -1.522237000 |
| 1 | -2.269766000| -2.365184000 | -0.113316000 |
| 1 | -0.731744000| -0.106340000 | -1.659783000 |
20) Cartesian coordinates from optimized structures of TS2_d.

**Figure S16.** Cartesian coordinates from optimized structure of the TS2_d at the B3LYP/6-311++G** level of theory.
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| 1 | -0.488944000 | -2.234312000 | -0.784695000 |       |
| 8 | 3.030061000  | -0.799567000  | -0.004562000 |       |
| 8 | 2.512758000  | -0.641206000  | -1.403564000 |       |
| 1 | 1.405457000  | -2.660860000  | 0.447646000  |       |
| 1 | 2.211650000  | -0.630739000  | 1.856583000  |       |
| 8 | 1.964827000  | 1.842296000   | 0.885088000  |       |
| 6 | -0.053825000 | 2.256767000   | -0.812683000 |       |
| 1 | 0.909130000  | 2.616886000   | -1.174485000 |       |
| 1 | -0.731282000 | 2.130569000   | -1.655533000 |       |
| 1 | -0.465858000 | 3.000244000   | -0.127808000 |       |
| 6 | -2.123540000 | -0.186727000  | 0.085147000  |       |
| 6 | -2.015521000 | -0.231160000  | 1.617329000  |       |
| 1 | -1.485414000 | 0.642654000   | 2.001965000  |       |
| 1 | -3.014530000 | -0.239810000  | 2.060861000  |       |
| 1 | -1.497219000 | -1.127774000  | 1.968982000  |       |
| 6 | -2.925878000 | 1.058579000   | -0.335732000 |       |
| 1 | -2.504488000 | 1.976808000   | 0.071469000  |       |
| 1 | -2.985757000 | 1.156299000   | -1.423769000 |       |
| 1 | -3.947596000 | 0.971178000   | 0.042460000  |       |
| 6 | -2.879416000 | -1.431057000  | -0.431770000 |       |
| 1 | -3.925535000 | -1.381508000  | -0.121886000 |       |
| 1 | -2.870432000 | -1.487499000  | -1.526113000 |       |
| 1 | -2.481930000 | -2.367408000  | -0.028786000 |       |
| 1 | -0.804609000 | -0.101459000  | -1.659495000 |       |
21) Cartesian coordinates from optimized structures of I₂.

**Figure S17.** Cartesian coordinates from optimized structure of the I₂ at the B3LYP/6-311++G** level of theory.

![Image of molecular structure]

\[ E = -687.578826 \]

Negative eigenvalues = 0

|    |          |          |          |
|----|----------|----------|----------|
| 7  | 0.067430000 | -1.429781000 | -0.202479000 |
| 6  | -0.586257000 | -0.157893000 | -0.532443000 |
| 7  | 0.237332000 | 0.976607000 | -0.118301000 |
| 6  | 1.426637000 | 0.879702000 | 0.560591000 |
| 6  | 1.950582000 | -0.517572000 | 0.817693000 |
| 6  | 0.964723000 | -1.592734000 | 0.749708000 |
| 1  | -0.358902000 | -2.243748000 | -0.621931000 |
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| 8 | 2.726368000 | -0.994856000 | -0.354029000 |       |
| 8 | 2.086056000 | -0.736401000 | -1.542248000 |       |
| 1 | 1.203093000 | -2.595536000 | 1.077063000  |       |
| 1 | 2.630681000 | -0.537445000 | 1.662918000  |       |
| 8 | 2.076168000 | 1.858754000  | 0.883211000  |       |
| 6 | -0.000891000 | 2.273587000  | -0.765733000 |       |
| 1 | 0.960102000 | 2.689338000  | -1.067094000 |       |
| 1 | -0.624293000 | 2.130066000  | -1.646349000 |       |
| 1 | -0.483454000 | 2.985395000  | -0.092449000 |       |
| 6 | -2.051281000 | -0.156705000 | 0.073009000  |       |
| 6 | -2.015405000 | -0.078504000 | 1.607199000  |       |
| 1 | -1.536516000 | 0.842363000  | 1.947126000  |       |
| 1 | -3.034288000 | -0.093231000 | 2.004191000  |       |
| 1 | -1.477908000 | -0.921962000 | 2.047985000  |       |
| 6 | -2.863335000 | 1.031371000  | -0.480064000 |       |
| 1 | -2.498243000 | 1.990671000  | -0.115926000 |       |
| 1 | -2.861360000 | 1.051908000  | -1.574224000 |       |
| 1 | -3.903271000 | 0.936371000  | -0.156485000 |       |
| 6 | -2.770153000 | -1.450451000 | -0.371279000 |       |
| 1 | -3.828590000 | -1.393400000 | -0.106941000 |       |
| 1 | -2.715638000 | -1.594105000 | -1.456382000 |       |
| 1 | -2.372653000 | -2.342696000 | 0.119867000  |       |
| 1 | -0.668552000 | -0.136549000 | -1.623465000 |       |
22) Cartesian coordinates from optimized structures of \(I_D\).

**Figure S18.** Cartesian coordinates from optimized structure of the \(I_D\) at the B3LYP/6-311++G** level of theory.

![Cartesian coordinates diagram](image)

\[E = -687.622762\]

Negative eigenvalues = 0

|   |            |            |            |
|---|------------|------------|------------|
| 7 | 0.043125465 | -1.380461731 | 0.329671458 |
| 6 | -0.598716680 | -0.286547555 | -0.398771752 |
| 7 | 0.169276000 | 0.957628000 | -0.183078000 |
| 6 | 1.384991000 | 1.045976000 | 0.448863000 |
| 6 | 2.181696000 | -0.234723000 | 0.642752000 |
| 6 | 1.436557000 | -1.509519000 | 0.331675000 |
| 1 | -0.438156000 | -2.255633000 | 0.190874000 |
| 8 | 3.019715000 | -0.441666000 | -0.531068000 |
| 8 | 2.127000000 | -1.545467000 | -0.982802000 |
23) Supplementary References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, **2009**, *42*, 339–341.

2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, **2015**, *71*, 3–8.

3. G. M. Sheldrick, *Acta Cryst. C*, **2015**, *71*, 3–8.

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